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Synthesis of Ether-Linked Oligoribo- and Xylonucleosides from 3,5′-Ether-Linked Pseudosaccharides

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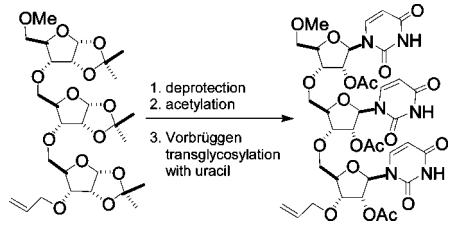
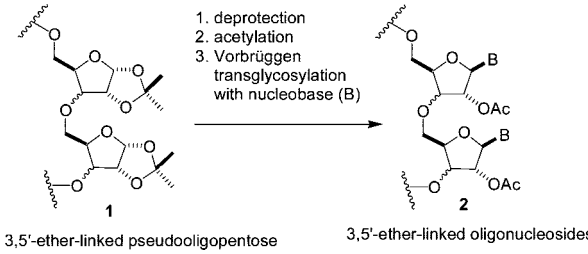


First examples of di- and trinucleosides with ribose and xylose stereochemistry having internucleoside ether linkage were synthesized from 3,5′-ether-linked pseudosaccharides. The synthetic protocol involved removal of 1,2-isopropylidene protecting groups from the pseudosaccharides followed by acetylation and a subsequent Vorbrüggen transglycosylation with uracil and *N*-benzoylaminopurine. The synthetic strategy is potentially important for the development of RNA analogues with internucleoside ether linkage.

Ether-linked pseudosaccharides constitute a relatively little known class of carbohydrate derivatives despite their biological and synthetic importance.[1] The primary feature of an ether-linked pseudosaccharide is that two sugar units are combined by a nonphosphate ether linkage. The sugar anomeric positions remain free in these molecules, and can be used for further structural modfication. The examples of ether-linked pseudooligosaccharides are scarce, and only a few 2,6′-, 3,6′-, and 6,6′-ether-linked dihexoses and a 5,5′-ether-linked dipentose are known.[1–3] Recently, we reported the synthesis of the first examples of 3,5′-ether-linked oligosaccharides from readily available carbohydrate derivatives.[4] The general structure of a 3,5′-ether-linked oligopentose is represented by **1** (Scheme 1). A special structural feature of **1** is the presence of the 1,2-isopropylidene-protected furanoside rings. The anomeric sites of these molecules or molecules derived from them are amenable to functionalization via deprotection and subsequent reactions such as diol cleavage and transglycosylation. We previously demonstrated the synthetic potential of these pseudosaccharides by their conversion to novel macrooxacycles[4] and nucleosides incorporating medium-ring oxacycles.[5] More importantly, the structure of **1** suggests that oligopentose derivatives with this general structure could be converted to oligonucleosides having internucleoside ether linkage. The particular significance of such a process lies in the future development of hitherto unknown ether-backbone RNA analogues. Modification of the backbone structure of DNA and RNA is a topic of paramount interest due to their potential application in antisense therapy.[6] As a first step toward the realization of this goal, we herein describe the synthesis of the first examples of 3,5′-ether-linked di- and trinucleosides **2** from the corresponding pseudosaccharides **1** (Scheme 1).

SCHEME 1. General Strategy for the Conversion of Ether-Linked Pseudosaccharides to Ether-Linked Oligonucleosides



The general strategy for the above synthetic exercise outlined in Scheme 1 consists of the removal of the isopropylidene groups in **1** followed by acetylation and subsequent Vorbrüggen transglycosylation[7] with a suitable nucleobase (B). The outcome would be an ether-linked oligonucleoside **2**. It should be mentioned at the outset that this strategy would furnish nucleosides carrying a single type of base. The implementation of the strategy is described in the following sequel.

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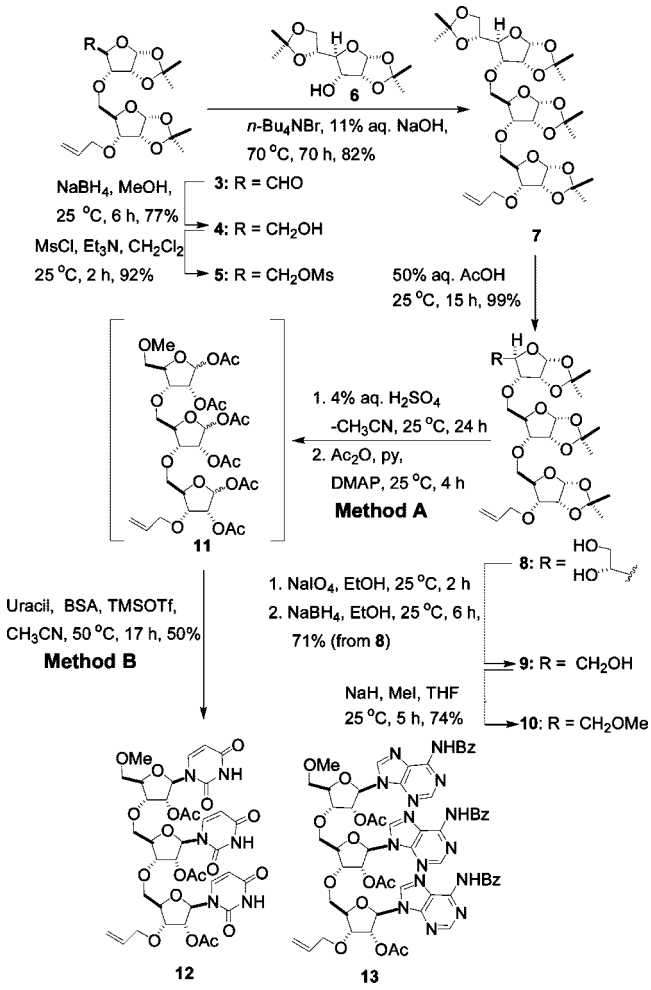
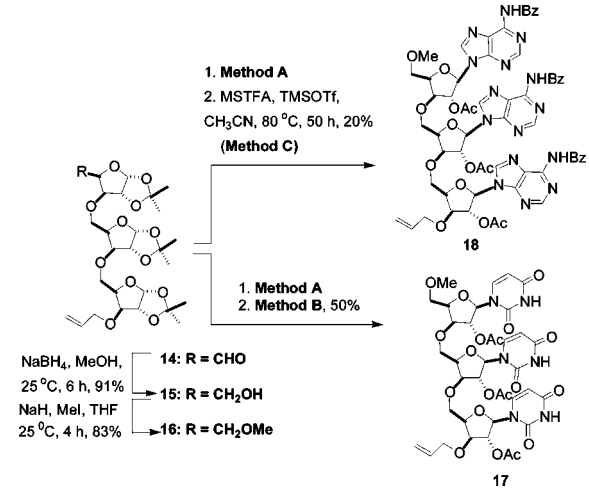
SCHEME 2. Synthesis of Pseudotrisaccharide 10 and Trinucleoside 12 with Ribose Stereochemistry



The 3,5′-ether-linked pseudosaccharide **7** was synthesized according to Scheme 2. The known[4] pseudodisaccharide aldehyde **3** was reduced to alcohol **4** and then to mesyl derivative **5**. Alkylation of 1,2:5,6-diisopropylidene−allofuranose (**6**) with **5** under the reported[4] condition for etherification in the presence of tetrabutylammonium bromide in aqueous NaOH led to the pseudotrisaccharide **7** in 82% yield (Scheme 2). The structure of **7** was consistent with the ^{1}H and ^{13}C NMR as well as mass spectral data. A sequence of reactions involving removal of the 5,6-isopropylidene group giving diol **8**, $NaIO_4$-mediated vicinal diol cleavage and reduction with $NaBH_4$ gave alcohol **9** in 71% overall yield from **8**. Methylation of **8** led to the 5′-capped pseudosaccharide **10** (Scheme 2), the OMe serving as a marker in the characterization of the subsequent compounds by ^{1}H NMR spectroscopy. The stereochemistry of the pseudosaccharide **10** at 3-C corresponds to that found in a typical ribonucleic acid. The next step was the application of the strategy outlined in Scheme 1 to **10**. The presence of the isopropylidene protected furanoside ring in **10** offered a unique opportunity for introducing nucleobases at the anomeric sites, and the Vorbrüggen method of transglycosylation was employed for this purpose as described below.

Treatment of **10** with aqueous H_2SO_4 followed by acetylation gave **11** (Scheme 2), which represents a mixture of eight diastereomers due to the presence of α and β anomers of each of the furanose rings. This configurational scramble was of no serious consequence, because the next transglycosylation step was expected to furnish only the β nucleoside. This is why **11** was subjected to transglycosylation reaction without further purification and characterization. Treatment of **11** with uracil in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and trimethylsilyl trflate (TMSOTf) led to the ether-backbone uracil ribotrinucleoside **12** in 50% yield (Scheme 2). The structure of **12** was secured by ^{1}H and ^{13}C NMR and mass spectral analyses. The introduction of three uracil moieties was evident from the comparison of the ^{1}H NMR integrations of the three doublets due to uracil 5′-H's at δ 7.50−7.67 and the OMe protons. The β-anomeric stereochemistry of **12** and other nucleosides synthesized in this work was established by the observed chemical shift (∼δ 6 ppm) and $J_{1,2}$ (1.0 to 4.8 Hz) similar to those for β-nucleosides reported in the literature.[6m,7a,b] The exclusive formation of the β-anomer was due to the anchimeric assistance of the 2-*O*-acetyl group in Vorbrüggen type coupling.[7] The nucleoside **12** represents the first example of an oligonucleoside containing an internucleoside ether linkage.[8]

SCHEME 3. Synthesis of Ether-Linked Trinucleosides with Xylose Stereochemistry



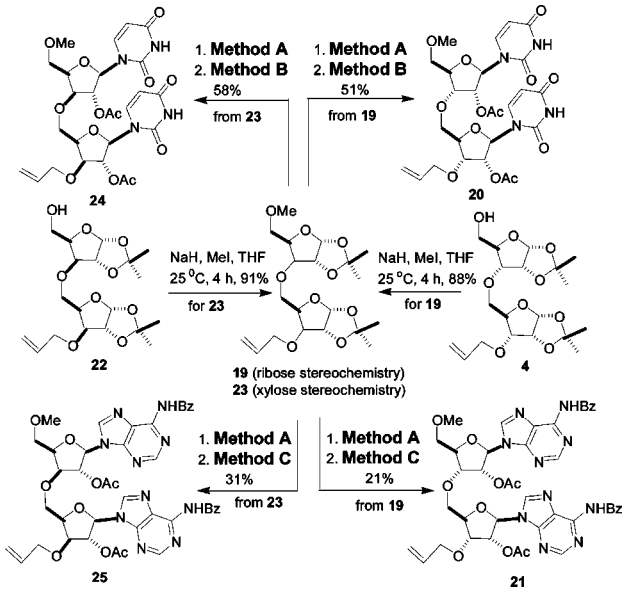
The above strategy could also be applied to the synthesis of trixylonucleosides.[9] The known[4] aldehyde **14** was converted to methyl ether **16** via alcohol **15** as outlined in Scheme 3. The application of the previously mentioned transglycosylation method to **16** gave rise to the uracil trinucleoside **17** in 50% yield. The corresponding *N*-benzoyladenine nucleoside **18** was prepared in 20% yield by using *N*-benzoylaminopurine in the presence of *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) and TMSOTf. The ^{1}H and ^{13}C NMR and mass spectral data of **17** and **18** were in good agreement with the assigned structures.

Ether-linked dinucleosides were also prepared by employing the strategy described above. Methyl ether **19** obtained from

(8) Unlike **12**, the application of the Vorbrüggen method using *N*-benzoylaminopurine led to a product, which was found to be extremely sensitive to purification by column chromatography or HPLC. However, the ESI mass spectrum of the product obtained immediately after isolation exhibited a strong peak at *m*/*z* 1280 (M + Na) corresponding to the molecular weight of the adenine nucleoside **13** (Scheme 2).

(9) Oligoxylonucleotides are important candidates in antisense therapy and have been found to bind to natural nucleic acids leading to the formation of triple helices: (a) Schoppe, A.; Hinz, H. J.; Rosenmeyer, H.; Seela, F. *Eur. J. Biochem.* **1996**, *239*, 33. (b) Sokolova, N. I.; Dolinnaya, N. G.; Krynetskaya, N. F.; Shabarova, Z. A. *Nucleosides, Nucleotides Nucleic Acids* **1990**, *9*, 515. (c) Ivanov, S.; Alekseev, Y.; Bertrand, J.-R.; Malvy, C.; Gottikh, M. B. *Nucleic Acids Res.* **2003**, *31*, 4256.

SCHEME 4. Synthesis of Ether-Linked Dinucleosides with Ribose and Xylose Stereochemistry



alcohol **4** in 88% yield by methylation was converted to the uracil dinucleoside **20** (51%) and the protected adenine dincleoside **21** (21%) (Scheme 4). Similarly, the known[4] pseudosaccharide alcohol **22** afforded the uracil dinucleoside **24** (58%) and the adenine dinucleoside **25** (31%) via the methyl-capped pseudosaccharide **23** (Scheme 4). The sets of nucleosides **20/21** and **24/25** have the ribose and xylose stereochemistry, respectively.

In conclusion, the synthetic exercise described above revealed a novel strategy for the synthesis of oligonucleosides having internucleoside ether linkage as well as furanose rings with varied stereochemistry. Future development in this strategy will target the synthesis of oligonucleosides carrying different types of bases in the same molecule by changing the precursors of the starting pseudosaccharides. Another important modification will involve the incorporation of a four-atom internucleoside ether linkage, as opposed to two-atom in the present case, which would result in closer RNA analogues consisting of an ether backbone. The study of the complementary base pairing interactions in these molecules will be another important topic of the future research.[10]

Experimental Section

Pseudotrisaccharide 7. To a solution of the alcohol **4** (Supporting Information) (0.85 g, 2.11 mmol) and triethylamine (0.59 mL) in CH_2Cl_2 (30 mL) was added dropwise a solution of CH_3SO_2Cl (0.21 mL, 2.71 mmol) in CH_2Cl_2 (5.0 mL) at 0 °C, and the mixture was stirred at 25 °C for 1 h. The mixture was poured into crushed ice and stirred for 0.5 h. It was then extracted with CH_2Cl_2, and the organic layer was washed with saturated aq $NaHCO_3$ solution. Removal of solvent from the organic extract gave mesyl derivative **5** (0.93 g, 92%) as a pale yellow syrupy liquid, which was used without further purification for the next step: ^{1}H NMR δ 1.36 (s, 6H), 1.57 (s, 6H), 3.05 (s, 3H), 3.80−3.96 (m, 4H), 4.08−4.28 (m, 4H), 4.33 (dd, J = 3.9, 11.6 Hz, 1H), 4.49 (d, J = 10.5 Hz, 1H), 4.63 (t, J = 3.7 Hz, 1H), 4.72 (t, J = 3.6 Hz, 1H), 5.23 (d, J = 10.2 Hz, 1H), 5.33 (d, J = 17.2 Hz, 1H), 5.76−5.77 (m, 2H), 5.89−6.02 (m, 1H). A mixture of **6**[4] (0.27 g, 1.03 mmol), **5** (1 g, 2.08 mmol), tetrabutylammonium bromide (0.067 g, 0.20 mmol), and NaOH (0.66 g, 16.5 mmol) in water (5.0 mL) was heated with stirring at 70 °C for 70 h. The mixture was then extracted with CH_2Cl_2, and the organic layer was washed with water and dried. Removal of solvent afforded a syrupy residue, which was chromatographed (EtOAc−petroleum ether, 3:17) giving **7** (0.45 g, 82%) as a colorless sticky liquid: $[\alpha]^{25}_D$ +119.0 (*c* 0.44, $CHCl_3$); IR (neat) 1375, 1654 cm^{-1}; MS (FAB) *m*/*z* 667 (M + Na), 629 (M − CH_3); ^{1}H NMR δ 1.35 (s, 6H), 1.36 (s, 3H), 1.37 (s, 3H), 1.45 (s, 3H), 1.55 (s, 3H), 1.59 (s, 3H), 1.60 (s, 3H), 3.77−3.95 (m, 6H), 3.97−4.06 (m, 3H), 4.08−4.13 (m, 5H), 4.34−4.35 (m, 1H), 4.59 (t, J = 4.0 Hz, 1H), 4.66 (t, J = 3.9 Hz, 1H), 4.71 (t, J = 3.7 Hz, 1H), 5.22 (d, J = 9.6 Hz, 1H), 5.32 (d, J = 17.2 Hz, 1H), 5.73−5.76 (m, 3H), 5.90−6.03 (m, 1H); ^{13}C NMR δ 25.1 (CH_3), 26.1 (CH_3), 26.4 (CH_3), 26.7 (CH_3), 65.0 (CH_2), 67.7 (CH_2), 68.2 (CH_2), 71.5 (CH_2), 74.8 (CH), 77.0 (CH), 77.1 (CH), 77.4 (CH), 77.7 (CH), 77.8 (CH), 78.0 (CH), 78.4 (CH), 78.5 (CH), 79.3 (CH), 103.7 (CH), 103.71 (CH), 103.9 (CH), 109.5 (q), 112.6 (q), 112.64 (q), 112.7 (q), 117.6 (CH_2), 134.5 (CH). Anal. Calcd for $C_{31}H_{48}O_{14}$, C, 57.75; H, 7.50. Found: C, 57.51; H, 7.63.

General Method of Preparation of Uracil Nucleosides. The general method of the preparation of uracil nucleosides is illustrated by that of **12** via the combination of method A and method B.

Method A: Deprotection of Pseudosaccharide Methyl Ethers and Subsequent Acetylation. A stock solution was prepared by mixing CH_3CN, water, and concd H_2SO_4 in a volumetric ratio 18:6:1. A mixture of **10** (0.4 g, 0.68 mmol) in this solution (15 mL) was stirred at 25 °C for 24 h. The solution was neutralized by adding solid $CaCO_3$, and the mixture was filtered. The residue was washed with acetonitrile and the combined washings were concentrated under reduced pressure. To a solution of the resulting deprotected compound in pyridine (10 mL) were added acetic anhydride (0.52 mL, 5.77 mmol) and a catalytic amount of DMAP at 0 °C. The mixture was stirred at 25 °C for 4 h. Excess Ac_2O was destroyed by adding water, and the resulting AcOH was removed by azeotropic distillation with toluene. The residue was chromatographed (EtOAc−petroleum ether, 9:1) to give **11** as a syrupy liquid, which was transglycosylated as described below.

Method B: Transglycosylation with Uracil. To a solution of this material (0.35 g, 0.49 mmol) in CH_3CN (15 mL) containing uracil (0.33 g, 2.92 mmol) was added with stirring BSA (1.8 mL, 7.29 mmol), and the mixture was heated at reflux for 1 h. Then TMSOTf (0.5 mL, 2.48 mmol) was added at 0 °C, and the mixture was heated at 50 °C for 15 h. The reaction was quenched with cold saturated $NaHCO_3$ solution. After removal of solvent, the residue was extracted with ethyl acetate, washed with brine, dried, and concentrated to afford a sticky liquid, which was chromatographed ($CHCl_3$−MeOH, 24:1) to give **12** (0.3 g, 50%) as a white solid: mp 138−140 °C; $[\alpha]^{25}_D$ −8.4 (*c* 0.21, $CHCl_3$); IR (neat) 1380, 1695, 1738, 3209, 3509 cm^{-1}; MS (FAB) *m*/*z* 899 (M + Na), 877 (M + H); ^{1}H NMR δ 2.11 (s, 3H), 2.13 (s, 3H), 2.15 (s, 3H), 3.46 (s, 3H), 3.51−3.57 (m, 2H), 3.73−4.08 (m, 7H), 4.16−4.27 (m, 6H), 5.18−5.39 (m, 5H), 5.76−6.04 (m, 7H), 7.50 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.2 Hz, 1H), 9.36 (bs, 1H), 9.42 (bs, 2H); ^{13}C NMR δ 20.7 (CH_3), 59.4 (CH_3), 69.8 (CH_2), 71.9 (CH_2), 72.1 (CH_2), 74.0 (CH), 75.6 (CH), 77.2 (CH), 78.0 (CH), 80.9 (CH), 81.2 (CH), 81.4 (CH), 87.6 (CH), 88.1 (CH), 90.9 (CH), 102.8 (CH), 103.0 (CH), 103.2 (CH), 117.8 (CH_2), 133.7 (CH), 139.8 (CH), 140.0 (CH), 140.6 (CH), 150.4 (q), 150.6 (q), 150.7 (q), 163.5 (q), 169.9 (q), 169.94 (q), 170.2 (q); HRMS (ESI, positive ion) calcd for $C_{37}H_{44}N_6O_{19}Na$ *m*/*z* 899.2559, found 899.2498.

General Method of Preparation of *N*-Benzoyladenine Nucleosides. The general method is illustrated by the synthesis of **25** via the combination of method A and method C.

(10) Although no detailed study has been made regarding the complementary interaction between the uracil and adenine nucleosides, the ^{1}H NMR spectrum of a mixture of **17** and **25** indicated downfield shifts of 0.338−0.387 ppm for the uracil NH protons suggesting H-bonding interaction, albeit small, between the uracil and the adenine moieties (Supporting Information). A similar interaction was observed in the CD spectra of **12/21** and **17/25** (Supporting Information).

Method A: Deprotection and Subsequent Acetylation. A stock solution was prepared by mixing CH_3CN, water, and concd H_2SO_4 in a volumetric ratio 18:6:1. A mixture of **23** (0.11 g, 0.26 mmol) in this solution (10 mL) was stirred at 25 °C for 24 h. The solution was neutralized by adding solid $CaCO_3$, and the mixture was filtered. The residue was washed with acetonitrile, and the combined washings were concentrated under reduced pressure. To a solution of the resulting deprotected compound in pyridine (5 mL) were added acetic anhydride (0.12 mL, 1.29 mmol) and a pinch of DMAP at 0 °C. The mixture was stirred at 25 °C for 4 h. Excess Ac_2O was destroyed by addition of water, and the resulting AcOH was removed by azeotropic distillation with toluene The residue was chromatographed (EtOAc−petroleum ether, 3:2) to give the corresponding acetate as a viscous liquid, which was transglycosylated as described below.

Method C: Transglycosylation with *N*-Benzoyladenine. To a solution of *N*-benzoylaminopurine (0.15 g, 0.63 mmol) in CH_3CN (10 mL) was added with stirring MSTFA (0.28 mL, 1.51 mmol), and the mixture was stirred at 25 °C for 1 h. A solution of the above acetate (0.1 g, 0.2 mmol) in CH_3CN (5 mL) and TMSOTf (0.05 mL, 0.24 mmol) was added to the above mixture at 0 °C, and the mixture was heated at 80 °C for 50 h. The reaction was quenched with cold saturated $NaHCO_3$ solution. After removal of solvent, the residue was extracted with ethyl acetate, and the organic layer was washed with brine, dried, and concentrated to afford an oily liquid, which was chromatographed (EtOAc−MeOH, 49:1) to give **25** (0.07 g, 31%) as a sticky pale yellow material: $[\alpha]^{25}_D$ −45.3 (*c* 0.10, $CHCl_3$); IR (neat) 1378, 1651, 1699, 1749, 3322 cm^{-1}; MS (ESI) *m*/*z* 885 (M + Na), 863 (M + H); ^1H NMR (600 MHz, $CDCl_3$) δ 2.19 (s, 3H), 2.22 (s, 3H), 3.40 (s, 3H), 3.63−3.65 (m, 1H), 3.76−3.79 (m, 1H), 3.84 (dd, J = 5.4, 10.2 Hz, 1H), 3.89 (dd, J = 5.4, 12.6 Hz, 1H), 3.95 (d, J = 4.2 Hz, 1H), 4.01 (dd, J = 7.2, 10.8 Hz, 1H), 4.07 (dd, J = 4.2, 12.0 Hz, 1H), 4.11−4.15 (m, 1H), 4.44−4.49 (m, 2H), 5.17 (dd, J = 1.2, 10.8 Hz, 1H), 5.22 (dd, J = 1.2, 16.8 Hz, 1H), 5.37 (s, 1H), 5.42 (s, 1H), 5.70−5.76 (m, 1H), 6.40−6.42 (m, 2H), 7.52−7.54 (m, 4H), 7.60−7.63 (m, 2H), 8.03 (d, J = 7.2 Hz, 2H), 8.05 (d, J = 7.2 Hz, 2H), 8.37 (s, 1H), 8.40 (s, 1H), 8.79 (s, 1H), 8.81 (s, 1H), 9.04 (bs, 1H), 9.08 (bs, 1H); ^{13}C NMR δ 20.80 (CH_3), 20.83 (CH_3), 59.4 (CH_3), 69.1 (CH_2), 69.6 (CH_2), 71.0 (CH_2), 79.4 (CH), 80.0 (CH), 80.2 (CH), 81.8 (CH), 82.2 (CH), 87.4 (CH), 87.5 (CH), 119.0 (CH_2), 123.0 (q), 127.90 (CH), 127.93 (CH), 128.9 (CH), 132.6 (CH), 132.8 (CH), 133.6 (q), 141.8 (CH), 149.4 (q), 151.7 (q), 152.7 (CH), 164.7 (q), 169.6 (q); HRMS (ESI, positive ion) calcd for $C_{42}H_{42}N_{10}O_{11}Na$ *m*/*z* 885.2932, found 885.2961.

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Supporting Information Available: Experimental procedure, ^1H and ^{13}C NMR spectra, EIMS of **13**, and CD spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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