Functionalized 3,3′,5,5′-Tetraaryl-1,1′-Biphenyls: Novel Platforms for Molecular Receptors

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This paper describes the development of novel aromatic platforms for supramolecular construction. By the *Suzuki* cross-coupling protocol, a variety of functionalized *m*-terphenyl derivatives were prepared (*Schemes 1–4*). Macrolactamization of bis(ammonium salt) (*S,S*)-**6** with bis(acyl halide) **7** afforded the macrocyclic receptor (*S,S*)-**2** (*Scheme 1*), which was shown by ^{1}H-NMR titration studies to form 'nesting' complexes of moderate stability (K_a between 130 and 290 M^{-1}, 300 K) with octyl glucosides **13**–**15** (*Fig. 2*) in the noncompetitive solvent $CDCl_3$. *Suzuki* cross-coupling starting from 3,3′,5,5′-tetrabromo-1,1′-biphenyl provided access to a novel series of extended aromatic platforms (*Scheme 5*) for cleft-type (*Fig. 1*) and macrotricyclic receptors such as (*S,S,S,S*)-**1**. Although mass-spectral evidence for the formation of (*S,S,S,S*)-**1** by macrolactamization between the two functionalized 3,3′,5,5′-tetraaryl-1,1′-biphenyl derivatives (*S,S*)-**33** and **36** was obtained, the ^{1}H- and ^{13}C-NMR spectra of purified material remained rather inconclusive with respect to both purity and constitution. The versatile access to the novel, differentially functionalized 3,3′,5,5′-tetrabromo-1,1′-biphenyl platforms should ensure their wide use in future supramolecular construction.

1. Introduction. – The design of efficient cleft-type or macrocyclic receptors for host-guest complexation studies frequently relies on the use of rigid molecular platforms that can be decorated with multiple convergent functional groups. An incomplete list of examples for such platforms, recently used in the construction of artificial receptors, includes *meso*-tetraarylporphyrins [1][2], hexasubstituted benzene derivatives [3], cholic acid derivatives [4], and hexasubstituted triphenylenes [5]. During the course of our carbohydrate recognition studies with synthetic receptors [6], we identified functionalized 3,3′,5,5′-tetraarylated 1,1′-biphenyls as interesting new platforms for incorporation into molecular receptors (*Fig. 1*). A literature search, however, revealed that the preparation of such functionalized platforms had not been previously described; only access to the parent scaffold had been reported [7]. Here, we describe synthetic routes to 3,3′,5,5′-tetraaryl-1,1′-biphenyls, suitably functionalized for the targeted construction of macrotricycle (*S,S,S,S*)-**1**, which we had designed by molecular modeling for the inclusion complexation of disaccharides such as maltose (for a review on carbohydrate recognition with artificial receptors, see [8]). During the course of this work, *Davis* and *Wareham* reported a related macrotricyclic receptor featuring two 1,1′-biphenyl platforms linked by four amide bridges [9]. They observed efficient inclusion complexation of monosaccharides in $CDCl_3/CD_3OD$ mixtures through H-bonding of the guest to the amide bridges and C–H/π interactions between the saccharide and the two sandwiching 1,1′-biphenyl moieties of the receptor; noncovalent bonding interactions that are seen in the X-ray crystal structures of

protein–carbohydrate complexes [10][11]. We also hoped to see the beneficial effects of these interactions in complexes formed with the new receptor (*S,S,S,S*)-**1**.

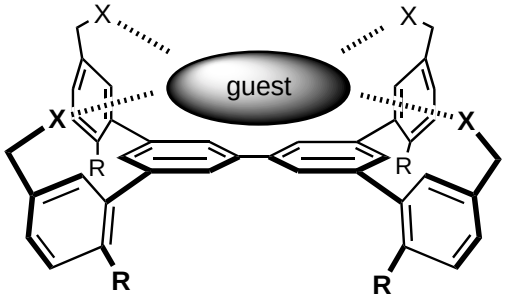
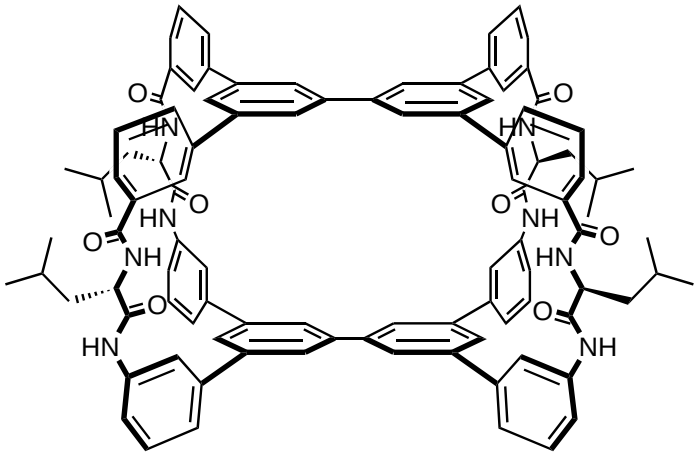


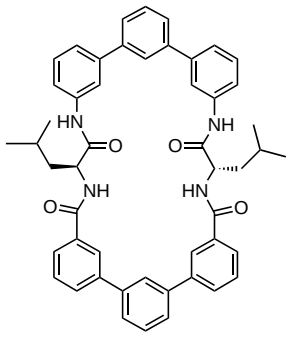
Fig. 1. *Schematic representation of guest recognition by functionalized 3,3′,5,5′-tetraaryl-1,1′-biphenyl platforms.* X = Recognition groups such as H-bonding donor and/or acceptor sites; R = solubilizing and conformationally enforcing residues.



(*S,S,S,S*)-**1**

2. Results and Discussion. – 2.1. *Synthesis and Complexation Behavior of a Model Receptor*. Macrocycle (*S,S*)-**2** was selected as a first target to work out protocols for linking *m*-terphenyl moieties (as in (*S,S,S,S*)-**1**) with peptidic bridges derived from L-leucine (L-Leu) [12].

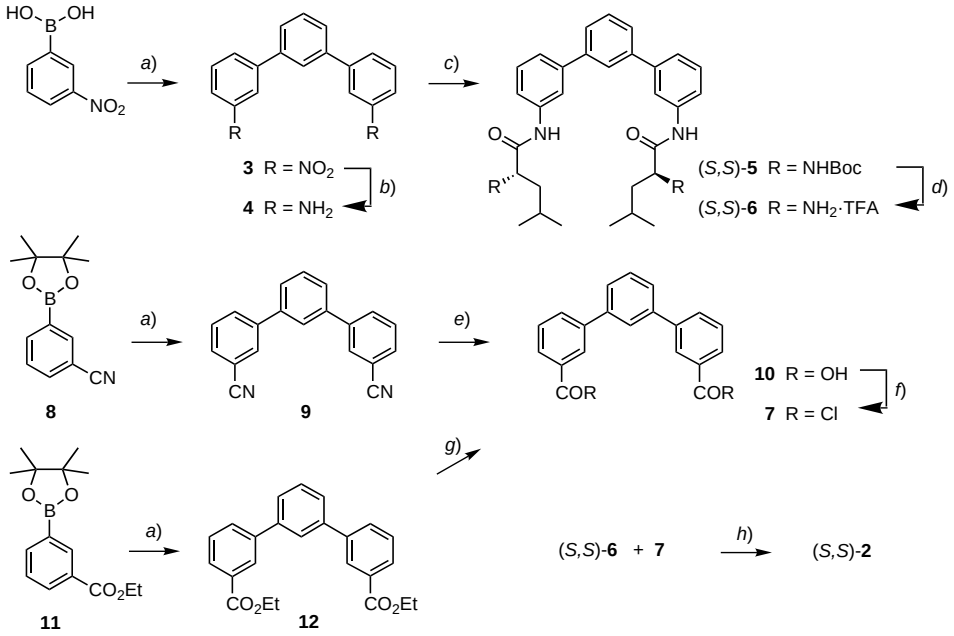
In the synthesis of (*S,S*)-**2**, *Suzuki* cross-coupling [13] between 3-nitrophenylboronic acid and 1,3-dibromobenzene afforded dinitro-*m*-terphenyl **3** [14], which was reduced (H_2, Pd/C) to diamine **4** [14] and subsequently transformed with *N*-Boc-L-Leu, EDC·HCl, and DMAP into diamide (*S,S*)-**5** (*Scheme 1*). Boc-Deprotection with CF_3COOH afforded the macrocyclization precursor (*S,S*)-**6**. The second component, **7**, for the macrocyclization to (*S,S*)-**2** was obtained starting from boronate **8** [15], which was transformed by *Suzuki* cross-coupling into dicarbonitrile **9** [16]. Hydrolysis under basic conditions afforded dicarboxylic acid **10**, which was converted into bis(acyl



(*S,S*)-**2**

halide) **7**. By a similar route, **7** was also prepared starting from boronate **11** [17] *via* **12** and **10**. Macrocyclization of (*S,S*)-**6** with **7** under high-dilution conditions ($c = 1$ mM) in the presence of Et_3N afforded the model system (*S,S*)-**2** in good yield (60%).

Scheme 1. *Synthesis of Macrocycle* (*S,S*)-**2**



a) 1,3-Dibromobenzene, $[Pd(dppf)Cl_2] \cdot CH_2Cl_2$, Na_2CO_3, PhH, EtOH, H_2O, 80°, 3 d; 85% (**3**), 60% (**9**), 62% (**12**). *b*) H_2 (4 bar), Pd/C, EtOH, r.t., 16 h; 98%. *c*) *N*-Boc-L-Leu, EDC · HCl, DMAP, r.t., 1 d; 35%. *d*) TFA, CH_2Cl_2, r.t., 4 h; 93%. *e*) NaOH, H_2O, diethyleneglycol, Δ, 3.5 d, then 1M HCl, r.t.; 83%. *f*) $SOCl_2$, Δ, 16 h. *g*) 2M aq. LiOH, THF, r.t., 12 h; 76%. *g*) Et_3N, THF, high dilution, Δ, 32 h, 60%. Dppf = 1,1′-bis(diphenylphosphino)-ferrocene; Boc = (*tert*-butoxy)carbonyl; EDC = 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide; DMAP = (4-dimethylamino)pyridine; TFA = trifluoroacetic acid.

^{1}H-NMR binding titrations with the octyl glucosides **13**–**15** (*Fig. 2*), executed in $CDCl_3$ at 300 K and at constant concentration of (*S,S*)-**2**, showed that the model system was able to complex a carbohydrate guest. Its cavity, however, is too small for monosaccharide incorporation, and, correspondingly, the association is of moderate strength only (K_a between 130 and 290 M^{-1}, *Table*). We propose a 'nesting' geometry for the 1:1 host-guest complexes that are most probably stabilized by H-bonding of sugar OH groups to the amide residues of the receptor and, possibly, by additional C–H/π interactions. The diastereoselectivity ($\Delta(\Delta G) = 0.5$ kcal mol^{-1}) observed in the association of the stronger binding β- and the weaker binding α-anomer, **13** and **14**, respectively, is in good agreement with the one measured in previous investigations [18]. It reflects the difference in energy of the intramolecular H-bonds in the two anomers that are lost upon complexation. As expected for a conformationally flexible receptor, no enantioselectivity was observed.

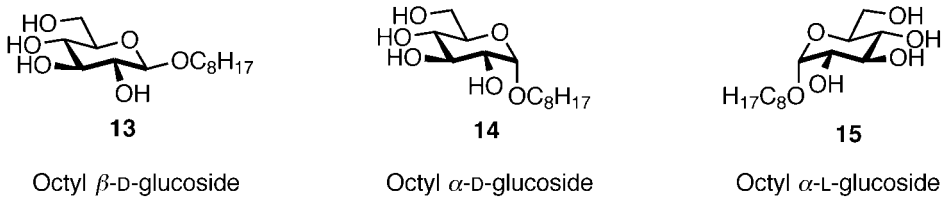


Fig. 2. *Monosaccharides investigated as guests in this study*

Table. *Association Constants* K_a [M^{-1}] *and Complexation Free Enthalpies* ΔG [kcal mol^{-1}] *Determined by* ^{1}*H-NMR Titrations for the Complexes of Receptor* (S,S)-**2** *with Monosaccharides* **13**–**15** *in* $CDCl_3$ (300 K)

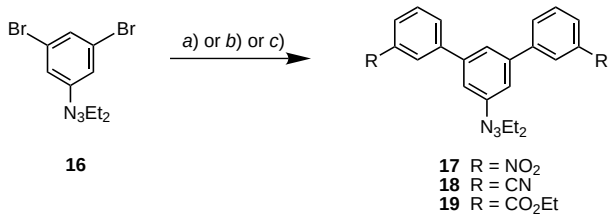
Guest[a])	K_a [M^{-1}]	ΔG [b]) [kcal mol^{-1}]	$\Delta\delta_{sat}$ [c]) [ppm]	Degree of saturation ($\Delta\delta_{max.\ obs}/\Delta\delta_{sat}$)
13	290	– 3.4	0.12	0.76
14	130	– 2.9	0.17	0.61
15	130	– 2.9	0.05	0.58

[a]) $[Host]_0 = 10^{-3}$ M. [b]) Uncertainty in ΔG: ± 0.1 kcal mol^{-1}. [c]) The downfield shift of the aromatic host resonance at 8.1 ppm was monitored. $\Delta\delta_{sat}$ = Shift at saturation binding; $\Delta\delta_{max.\ obs}$ = maximum shift reached in the titration.

2.2. Synthetic Approaches towards Macrotricyclic Receptor (S,S,S,S)-**1**. *2.2.1. Iodinated* m-*Terphenyls as Potential Precursors of 3,3′,5,5′-Tetraaryl-1,1′-biphenyls.* Retrosynthetic analysis suggested two approaches for the preparation of the targeted receptor. In route I, the macrotricyclic skeleton could be constructed in the final step by four-fold amide bond formation, thereby generating the four bridges between the two 3,3′,5,5′-tetraaryl-1,1′-biphenyl platforms (see below). In route II, two-fold aryl-aryl homocoupling (for biaryl formation *via* homocoupling, see [19]) between two molecules similar to (*S,S*)-**2**, but bearing iodo substituents in the *meso*-position of the central *m*-terphenyl rings, would generate the receptor. Since the functionalized platforms in route I could also be constructed by aryl-aryl coupling between iodinated *m*-terphenyls, we focused our initial efforts at the preparation of such derivatives.

For the construction of iodinated *m*-terphenyls by *Suzuki* cross-coupling as shown in *Scheme 1*, we employed the diethyltriazene group as a masked iodo synthon [20]. Thus, 1-(3,5-dibromophenyl)-3,3-diethyltriaz-1-ene (**16**) [21] was coupled with 3-nitrophenylboronic acid and the two boronates **8** and **11** to give triazenes **17**–**19**, respectively (*Scheme 2*). The X-ray crystal structure of dicarbonitrile **18** revealed the presence of two conformers in the crystal lattice. In both structures, the absolute values of the dihedral angles about the C(aryl)–C(aryl) bonds varied between 27.3° and 39.2° (*Fig. 3*).

Scheme 2. *Synthesis of* m-*Terphenyls* **17**–**19**



16

17 R = NO_2
18 R = CN
19 R = CO_2Et

a)–*c*) [Pd(dppf)Cl_2]·CH_2Cl_2, 3-nitrophenylboronic acid (*a*), or **8** (*b*), or **11** (*c*), Na_2CO_3, PhH, EtOH, H_2O, 80°, 24 h; 80% (**17**), 67% (**18**), 84% (**19**).

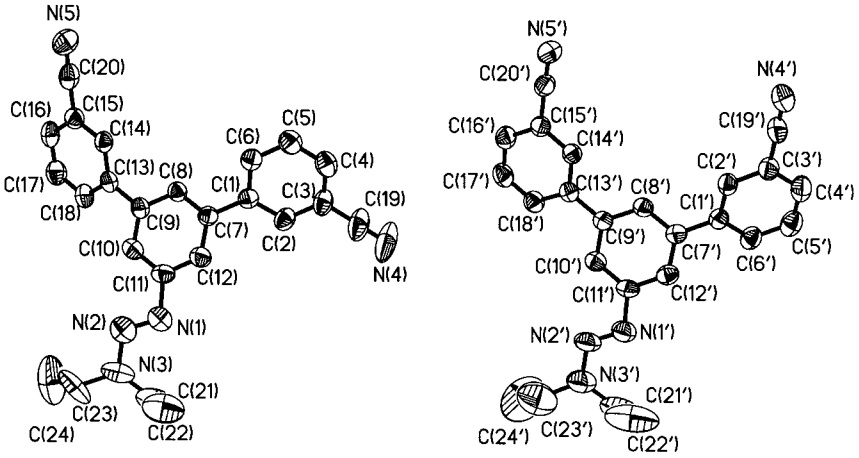
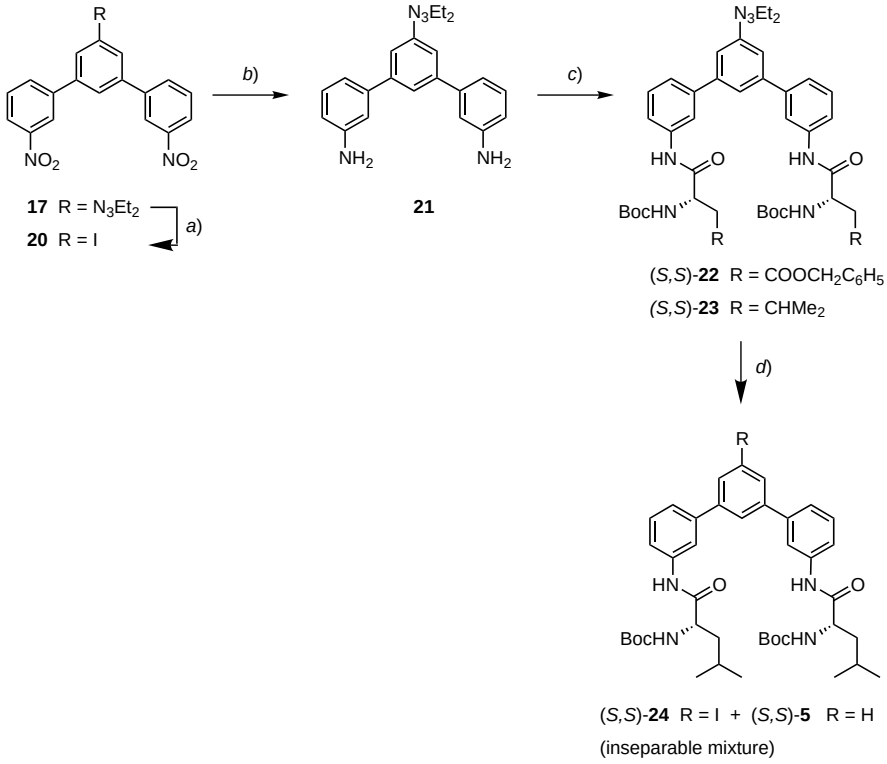


Fig. 3. *X-Ray crystal structure of* **18** *showing two conformers in the asymmetric unit.* Arbitrary numbering. Atomic displacement parameters obtained at 293 K are drawn at the 30% probability level. The absolute values of the dihedral angles about the C(aryl)–C(aryl) bonds are 33.8° for C(9)–C(13), 39.2° for C(7)–C(1), 27.3° for C(9′)–C(13′), and 36.6° for C(7′)–C(1′). The angles were calculated from the least-squares planes through the corresponding six-membered rings.

Starting from triazenyl-substituted *m*-terphenyl **17**, the corresponding iodo derivative **20** was readily obtained by heating with MeI in a sealed tube [22] (*Scheme 3*). Reduction of **17** with H_2 and Pd/C in AcOEt provided diamine **21**, without affecting the triazene moiety. Under standard peptide-coupling conditions (DCC/BtOH), **21** reacted with 4-benzyl *N*-Boc-L-aspartate to give diamide (*S,S*)-**22** and with

N-Boc-L-Leu to afford (*S,S*)-**23**. However, the subsequent dialkyltriazene → iodide transformation proved to be problematic. Heating (*S,S*)-**23** to reflux with MeI gave a very polar product, possibly resulting from initial methylation of the amide N-atoms. An alternative method for this transformation consists in heating the triazene with I_2 in $ClCH_2CH_2Cl$ to 90° [23]. Although this reaction yielded the desired product (*S,S*)-**24**, it was not possible to separate it from the reduced I-free by-product (*S,S*)-**5**.

Scheme 3. *Conversions of Dinitro*-m-*terphenyl* **17**

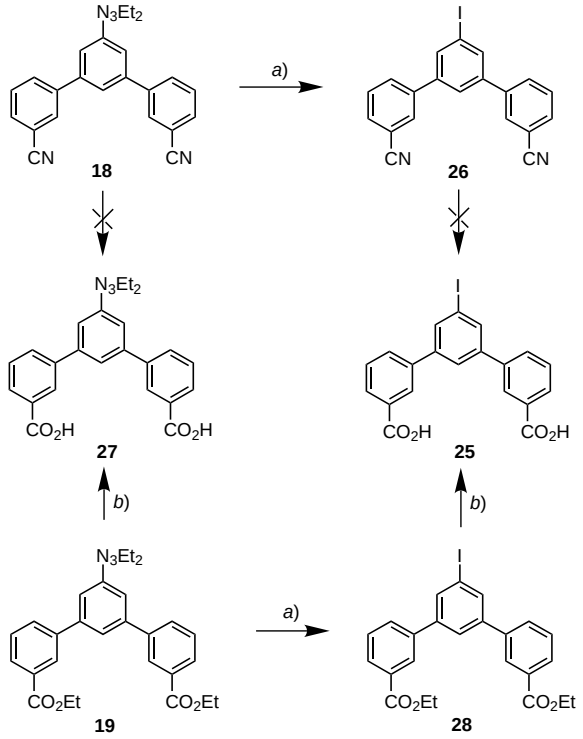


a) MeI, sealed tube, 130°, 16 h; 88%. *b*) H_2 (4 bar), Pd/C, AcOEt, r.t., 18 h; 83%. *c*) 4-Benzyl *N*-Boc-L-aspartate or *N*-Boc-L-leucine, DCC, BtOH, THF, 0°, 16–36 h; 51% (**22**), 61% (**23**). *d*) I_2, $ClCH_2CH_2Cl$, 90°, 7 h. DCC = dicyclohexylcarbodiimide; BtOH = 1-hydroxy-1*H*-benzotriazole.

The preparation of the iodinated dicarboxylic acid **25**, which we intended to cyclize with (*S,S*)-**24** (after removal of the Boc protecting groups), failed when starting from dicarbonitriles **18** or **26** (*Scheme 4*), since both acidic and basic hydrolysis of the two CN groups affected the dialkyltriazenyl (in **18**) and I (in **26**) substituents. However, the desired diacid **25** was obtained by starting from diester **19**. Ester hydrolysis did not affect the triazenyl substituent, which allowed preparation of diacid **27**. Also, after conversion of **19** into iodide **28**, hydrolysis readily afforded **25**.

Initial attempts to prepare suitably functionalized 3,3′,5,5′-tetraaryl-1,1′-biphenyl platforms by homocoupling of iodinated *m*-terphenyls such as those shown in *Scheme 4*

Scheme 4. *Synthesis of Iodinated* m-*Terphenyldicarboxylic acid* **25**

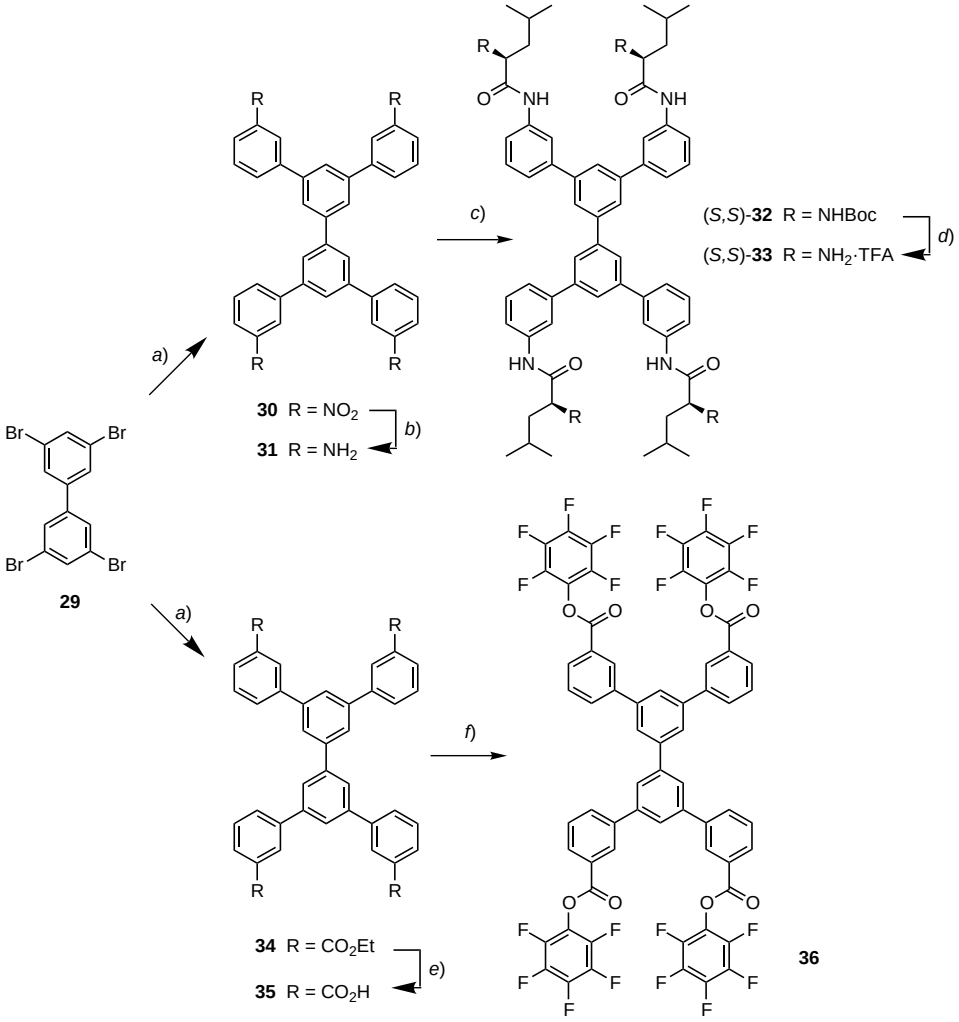


a) MeI, sealed tube, 130°, 14 – 16 h; 96% (**26**), 95% (**28**). *b*) LiOH, THF, EtOH, r.t., 14 h; 45% (**27**), 89% (**25**).

failed, mainly due to the poor solubility of the starting materials in the commonly used solvents. The *m*-terphenyl route was abandoned, when it proved to be more facile to obtain the desired platforms starting from 3,3′,5,5′-tetrabromo-1,1′-biphenyl (**29**).

2.2.2. *Functionalized 3,3′,5,5′-Tetraaryl-1,1′-biphenyls Starting from 3,3′,5,5′-Tetrabromo-1,1′-biphenyl.* When 3,3′,5,5′-tetrabromo-1,1′-biphenyl (**29**), conveniently prepared according to a literature procedure [24], was subjected to *Suzuki* cross-coupling with 3-nitrophenylboronic acid (*ca.* 6 equiv.), tetra-arylated biphenyl **30** formed as a precipitate and was isolated in 67% yield after recrystallization from 1,2-dichlorobenzene (*Scheme 5*). Compound **30** is poorly soluble in almost all solvents, but could be reduced with Sn in conc. HCl under heterogenous conditions. A reaction time of 2 weeks was required to obtain complete conversion to the more soluble tetramine **31**, which was isolated in 97% yield. Peptide coupling with *N*-Boc-L-Leu to (*S,S*)-**32**, followed by *N*-deprotection, provided the readily soluble tetrakis(ammonium salt) (*S,S*)-**33**, one of the two components for the macrocyclization to give (*S,S,S,S*)-**1** (Route I, see *Sect. 2.2.1*). ^{1}H-NMR spectra of (*S,S*)-**31** in $CDCl_3$ featured strongly broadened peaks, which we explain by the formation of H-bonding aggregates. In agreement with this proposal, highly resolved spectra were obtained in $(CD_3)_2SO$ in which H-bonding is weakened due to solvent competition.

Scheme 5. *Synthesis of Functionalized 3,3′,5,5′-Tetraaryl-1,1′-biphenyl Platforms*



a) 3-Nitrophenylboronic acid or **11**, $[Pd(dppf)Cl_2]\cdot CH_2Cl_2$, Na_2CO_3, PhH, EtOH, H_2O, 80°, 72 h; 67% (**29**), 73% (**33**). *b*) Sn, conc. HCl, 100°, 2 weeks; 97%. c) *N*-Boc-L-Leu, EDC·HCl, DMAP, 0°, 48 h; 67%. *d*) TFA, CH_2Cl_2, r.t., 4 h; 99%. *e*) LiOH, THF, H_2O, Δ, 17 h; 87%. *f*) Pentafluorophenol, DCC, DMF, 0°, 60 h; 51%.

Similarly, *Suzuki* cross-coupling of the tetrabromo derivative **29** with boronate **11** afforded the functionalized platform **34** (73% yield), which was soluble in THF (*Scheme 5*). Ester hydrolysis gave tetracarboxylic acid **35**, which was transformed into the activated tetrakis(pentafluorophenyl ester) **36**, the second cyclization component on the way to the targeted macrotricycle.

First attempts to obtain the macrotricyclic receptor (*S,S,S,S*)-**1** did not give conclusive results. Macrolactamization of (*S,S*)-**33** with activated ester **36** under high-dilution conditions ($c = 1$ mM, 18 h, 80°) in THF in the presence of $EtN(i\text{-}Pr)_2$ (8 equiv.)

as a base (to transform salt (*S,S*)-**33** into the free tetramine and to trap the pentafluorophenol leaving group) afforded, after usual extractive workup (H_2O/CH_2Cl_2), a crude product that, according to analytical gel-permeation chromatography (GPC, *BioBeads S-X1*, THF), contained a large amount of high-molecular weight by-products. Purification by repeated GPC (*BioBeads S-X1*) and subsequent preparative thin-layer chromatography (TLC, SiO_2; CH_2Cl_2/MeOH 98:2) provided 29 mg (13%) of a colorless powder, which was a homogenous product according to analytical GPC and TLC analysis. Its purity could not be further enhanced by HPLC. The analytical characterization of this product, however, remains incomplete. The fast-atom-bombardment mass spectrum (FAB-MS; matrix: 3-nitrobenzyl alcohol) clearly showed the molecular ion expected for (*S,S,S,S*)-**1** as the parent ion at *m/z* 1534.1 (MH^+, $C_{100}H_{93}N_8O_8^+$; calc. 1534.7). Besides a weak peak at *m/z* 1601.8, no major signals above *m/z* 400 were observed. In the IR spectrum (KBr), bands expected for free carboxylate and primary amine groups were absent. Nevertheless, the structure of the product remains uncertain, since the ^{1}H- and ^{13}C-NMR analysis in solvents of different polarity ($CDCl_3$, $(CD_3)_2SO$) was not conclusive. The peaks were broadened, and, although in the expected spectral regions, too many were observed. Since the spectra did not change substantially upon heating to 393 K, it is uncertain whether the large number of peaks is due to the presence of slowly exchanging conformational isomers. We also cannot exclude the formation of two constitutional isomers, namely the one shown with two parallel platforms and a second one, in which bridging occurs differently, leading to a crossed array of the two platforms. This inability of fully characterizing the product contrasts with our past success in purifying other complex macrotricyclic and macrobicyclic spherical receptors [12][25][26].

3. Conclusions. – A series of functionalized 3,3′,5,5′-tetraaryl-1,1′-biphenyls were prepared as aromatic 'floor' and 'ceiling' for incorporation into the targeted macrobicyclic disaccharide receptor (*S,S,S,S*)-**1**. These extended aromatic systems could also serve as versatile platforms in a diversity of novel cleft-type receptors (as schematically shown in *Fig. 1*). While approaches to these platforms involving the homocoupling of iodinated *m*-terphenyls proved rather tedious, a straightforward access was available by *Suzuki* cross-coupling to 3,3′,5,5′-tetrabromo-1,1′-biphenyl. Although mass-spectral evidence for formation of (*S,S,S,S*)-**1** by macrolactamization between (*S,S*)-**33** and **36** was obtained, the ^{1}H- and ^{13}C-NMR spectra of purified material remained rather inconclusive with respect to both purity and constitution. With (*S,S*)-**2**, a macrocyclic model receptor was prepared that forms 'nesting' complexes of moderate stability (K_a between 130 and 290 M^{-1}, 300 K) with octyl glucosides **13**–**15** in the noncompetitive solvent $CDCl_3$. H-Bonding interactions between the sugar OH groups and the amide residues of the receptor constitute the major driving force for the observed 1:1 host–guest complexation. Efforts are now underway to utilize other macrocyclization protocols for introducing the novel platforms into macrotricyclic receptors such as (*S,S,S,S*)-**1**.

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Experimental Part

General. Solvents and reagents were reagent-grade and commercially available, and used without further purification unless otherwise noted. CH_2Cl_2 was dried over CaH_2, and PhMe and THF over Na. All solns. for Pd-catalyzed cross-coupling reactions were carefully degassed and flushed with Ar. Evaporations and concentrations *in vacuo* were carried out at H_2O-aspirator pressure. Drying of anal. samples occurred at 10^{-2} Torr. Flash chromatography (FC): SiO_2 *60* (40–63 μm) from *Fluka* or *Merck*. Anal. TLC: *Polygram SIL G/UV$_{254}$* or *DURASIL-25 UV$_{254}$* from *Macherey-Nagel*. Prep. TLC: *PSC* plates (2 mm SiO_2 *60 F$_{254}$*) from *Merck*. M.p.: *Büchi Melting Point B-540*, uncorrected. Optical rotations: *Perkin-Elmer 241* polarimeter. IR Spectra [cm^{-1}]: *Perkin Elmer 1600-FTIR*; in $CHCl_3$ or in KBr pellets. ^{1}H- and ^{13}C-NMR-spectra [ppm]: *Bruker AMX-500*, *Varian Gemini-200* and *-300* at r.t. in $CDCl_3$ or $(CD_3)_2SO$. The ^{13}C-NMR resonances of the diethyltriazene moieties are often very broad due to hindered rotation about the N–N axis and could, therefore, not be detected. MS (*m/z* (%)): EI: *VG Tribrid* mass spectrometer at 70 eV ionization energy; ESI-MS: *Finnigan New Star FT/MS* with 7-T magnet; FAB-MS: *VG ZAB2-SEQ* spectrometer with 3-nitrobenzyl alcohol (3-NOBA) as matrix; FT-ICR-MALDI-MS: *Ion Spec Ultima FT-ICR-MS* (337-nm N_2-laser system, matrix: DHB (2,3-dihydroxybenzoic acid) or DCTB ({(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidenes} malononitrile). Elemental analyses were performed by the *Mikrolabor* at the *Laboratorium für organische Chemie, ETH-Zürich*.

^{1}H-NMR Binding Titrations. Quant. binding data (K_a, ΔG, $\Delta\delta_{sat}$) were determined by nonlinear least-squares curve-fitting of ^{1}H-NMR titration data (500 MHz, 300 K) with the program *Associate V.1.6* [27]. Octyl glucoside **15** was prepared according to published procedures [28]. Titration samples ($CDCl_3$ dried over 4-Å molecular sieves) were prepared by adding a soln. of guest in portions *via* microsyringe to the septum-capped NMR tube while keeping the host at constant concentration. Concentration ranges: $[host]_0 \approx 1$ mM, $[guest]_0 \approx$ 1–20 mM. After each addition, a ^{1}H-NMR spectrum was recorded.

*(–)-Di-(*tert*-butyl)* N,N′*-{1,1′:3′,1″-Terphenyl-3,3″-diylbis[(*S*)-iminocarbonyl)(2-methylpropyl)methyl]}dicarbamate* ((*S,S*)-**5**). Diamine **4** [14] (551 mg, 2.12 mmol), *N*-Boc-L-Leu (1.16 g, 4.65 mmol), and DMAP (79 mg, 0.65 mmol) were dissolved in dry THF (50 ml). After cooling to 0°, EDC · HCl (1.34 g, 4.65 mmol) was added, and the mixture was stirred for 1 d at r.t. The solvent was evaporated *in vacuo*, and the residue was taken up in CH_2Cl_2 and washed with sat. aq. $NaHCO_3$ soln. (2×), 1M HCl, and sat. aq. NaCl soln. The combined org. layers were dried ($MgSO_4$) and evaporated *in vacuo*. FC (SiO_2; CH_2Cl_2/AcOEt 5:1) gave (*S,S*)-**5** (509 mg, 35%). White powder. M.p. 200°. $[\alpha]_D^{23} = -56.2$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3309*w*, 3032*s*, 1668*s*, 1612*w*, 1498*m*, 1431*w*, 1046*m*, 928*m*. ^{1}H-NMR ($(CD_3)_2SO$, 300 MHz): 10.03 (*s*, 2 H); 7.92 (*s*, 2 H); 7.76 (*s*, 1 H); 7.68–7.63 (*m*, 2 H); 7.61–7.51 (*m*, 3 H); 7.46–7.34 (*m*, 4 H); 7.02-7.00 (*m*, 2 H); 4.14–4.08 (*m*, 2 H); 1.68–1.56 (*m*, 2 H); 1.55–1.38 (*m*, 4 H); 1.34 (*s*, 18 H); 0.87 (*d*, $J = 6.5$, 12 H). ^{13}C-NMR ($(CD_3)_2SO$, 75 MHz): 172.17; 155.66; 141.04; 140.75; 139.84; 129.81; 129.57; 126.07; 125.00; 121.90; 118.58; 117.69; 78.04; 53.60; 28.15; 24.31; 22.91; 21.48. FAB-MS: 685.4 (1, MH^+), 586.5 (23, $[MH - Boc]^+$), 487.4 (100, $[MH - 2\ Boc]^+$).

*(+)-*N,N′*-{1,1′:3′,1″-Terphenyl-3,3″-diylbis[(*S*)-iminocarbonyl)(2-methylpropyl)methyl]}diammonium Bis(trifluoroacetate)* ((*S,S*)-**6**). A soln. of (*S,S*)-**5** (1.248 g, 1.82 mmol) in CH_2Cl_2 (7.5 ml) and TFA (5 ml) was stirred for 4 h at r.t. After evaporation *in vacuo*, the residue was taken up in EtOH. Evaporation *in vacuo* afforded (*S,S*)-**6** (1.22 g, 93%), which was used without further purification. Slightly brownish powder. M.p. 136–138°. $[\alpha]_D^{23} = +4.3$ ($c = 1$, $CHCl_3$/EtOH 95:5). IR (KBr): 3416 (br.), 3125 (br.), 1675*m*, 1400*s*, 1203*m*, 1140*m*, 839*w*, 800*w*. ^{1}H-NMR ($(CD_3)_2SO$, 300 MHz): 10.77 (*s*, 2 H); 7.93 (*s*, 2 H); 7.79 (br. *s*, 1 H); 7.70–7.65 (*m*, 2 H); 7.62–7.58 (*m*, 3 H); 7.51–7.44 (*m*, 4 H); 3.96 (*m*, 2 H); 1.67 (*m*, 6 H); 0.91 (*d*, $J = 3.1$, 12 H). ^{13}C-NMR ($(CD_3)_2SO$, 75 MHz): 168.33; 140.91; 140.83; 138.92; 129.84; 129.60; 126.19; 125.12; 122.82; 118.94; 118.06; 51.80; 23.65; 22.57; 21.77. FAB-MS: 487.30 (100, $[MH - 2\ CF_3COOH]^+$).

Ethyl 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**11**). A soln of ethyl 3-iodobenzoate (1.000 g, 3.6 mmol), AcOK (1.066 mg, 10.8 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [29] (1.015 g, 4.0 mmol), and $[Pd(dppf)Cl_2] \cdot CH_2Cl_2$ (50 mg, 68 μmol) was flushed with Ar, then Me_2SO (12 ml) was added, and the mixture was heated to 80–90° for 4.5 h. After cooling to r.t., the soln. was diluted with PhMe (30 ml), and the org. layer was washed with H_2O (3×), dried ($MgSO_4$), and evaporated *in vacuo*. The remaining brown oil was purified by bulb-to-bulb distillation (< 0.5 Torr 110–120°) to yield **11** (646 mg, 85%). Colorless oil. IR ($CHCl_3$): 2979*s*, 2928*m*, 2873*w*, 1721*s*, 1606*m*, 1358*s*, 1320*m*, 1274*m*, 1254*s*, 1144*m*, 1092*m*, 1023*m*, 964*m*, 853*m*, 757*m*, 702*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.47 (*m*, 1 H); 8.18–8.09 (*m*, 1 H); 8.03–7.94 (*m*, 1 H); 7.45 (*dd*, $J = 7.5$, 7.5, 1 H); 4.39 (*q*, $J = 7.0$, 2 H); 1.41 (*t*, $J = 7.0$, 3 H); 1.37 (*s*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.0; 139.3; 135.9; 132.6; 132.5; 127.9; 84.2; 61.0; 24.9; 14.4. EI-MS: 276 (23, M^+), 261 (41, $[M - Me]^+$), 233 (100). Anal. calc. for $C_{15}H_{21}BO_4$ (276.14): C 65.24, H 7.66; found: C 65.32 H 7.70.

Diethyl 1,1′:3′,1″-Terphenyl-3,3″-dicarboxylate (**12**). A soln. of **11** (1.200 g, 4.34 mmol), 1,3-dibromobenzene (0.237 g, 1.97 mmol), and Na_2CO_3 (951 mg, 8.69 mmol) in PhH/EtOH (11:3, 20 ml) and H_2O (13 ml) was flushed with Ar for 1 h, then heated to 80°. A spatula tip of $[Pd(dppf)Cl_2]\cdot CH_2Cl_2$ was added, and the mixture was heated to reflux for 3 d. After cooling to r.t., the org. solvents were evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2. Drying ($MgSO_4$) and evaporation *in vacuo* left a residue, which was purified by FC (SiO_2; hexane/CH_2Cl_2 2:1) to give **12** (463 mg, 62%). Colorless solid. M.p. 68–70°. IR (KBr): 2977*m*, 2366*w*, 2333*w*, 1718*s*, 1588*w*, 1472*m*, 1299*s*, 1251*s*, 1230*m*, 1109*m*, 1077*m*, 1016*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.35–8.32 (*m*, 2 H); 8.07 (*dd*, *J* = 7.8, 0.6, 2 H); 7.86–7.80 (*m*, 3 H); 7.65–7.61 (*m*, 2 H); 7.58–7.50 (*m*, 3 H); 4.41 (*q*, *J* = 7.2, 4 H); 1.42 (*t*, *J* = 7.2, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.8; 141.5; 141.2; 131.8; 129.7; 129.1; 128.8; 128.5; 126.8; 126.3; 61.2; 14.4. HR-MALDI-MS: 397.1412 (100, M^+, $C_{24}H_{22}O_4Na^+$; calc. 397.1415).

1,1′:3′,1″-Terphenyl-3,3″-dicarboxylic Acid (**10**). *Method A:* A mixture of **9** (1.38 g, 4.93 mmol) and finely powdered NaOH (1.6 g, 39.43 mmol) in diethyleneglycol (30 ml) and H_2O (0.5 ml) was heated to reflux for 3.5 d. After cooling to r.t., 1M HCl was added, and the formed precipitate was isolated by filtration and washed with H_2O (2×). The solid was heated to reflux in EtOH (40 ml), and the precipitate formed upon cooling was filtered off, washed with ice-cold EtOH (2×), and dried to give **10** (1.3 g, 83%). Grey solid.

Method B: To a soln. of **12** (470 mg, 1.25 mmol) in THF (11 ml), LiOH (120 mg, 5.02 mmol) in H_2O (2.5 ml) was added, and the mixture was heated to reflux for 4 h. After cooling to r.t. and evaporation of the solvent *in vacuo*, the residue was dissolved in sat. aq. Na_2CO_3 soln., which was washed with CH_2Cl_2. The aq. phase was acidified (pH 1) by addition of conc. HCl, and the formed precipitate was isolated by filtration and dried to give **10** (312 mg, 76%). Colorless powder. M.p. > 250° (dec.). IR (KBr): 3000–2533 (br.), 1690*s*, 1601*w*, 1579*w*, 1440*m*, 1412*m*, 1384*w*, 1307*s*, 1262*m*, 1240*m*, 923*m*, 745*s*, 684*m*. ^{1}H-NMR (200 MHz, $(CD_3)_2SO$): 13.08 (br. *s*, 2 H); 8.25 (*m*, 2 H); 8.11–7.88, 7.81–7.51 (2*m*, 10 H). ^{13}C-NMR (75 MHz, $(CD_3)_2SO$): 167.5; 140.5; 140.4; 131.7; 131.6; 130.0; 129.5; 128.6; 127.7; 126.6; 125.5. ESI-MS: 349 (22, $[M-H+MeOH]^-$), 339 (11, $[M-H+Na]^-$), 317 (100, $[M-H]^-$), 174 (8, $[M-2\,H+MeOH]^{2-}$), 158 (68, $[M-2\,H]^{2-}$). HR-EI-MS: 318.0898 (100, M^+, $C_{20}H_{14}O^+$, calc. 318.0898). Anal. calc. for $C_{20}H_{14}O_4$ (318.33): C 75.46, H 4.43; found: C 73.77, H 4.71.

(6S,14S)-6,14-Bis(2-methylpropyl)-4,7,13,16-tetraaza-1,2,3,9,10,11(1,3)-hexabenzenacyclohexadecaphane-5,8,12,15-tetraone ((*S,S*)-**2**). A soln. of **10** (310 mg, 0.97 mmol) in $SOCl_2$ (10 ml) was heated to reflux for 16 h. The excess of $SOCl_2$ was removed by distillation, and the residue was dried at 10^{-2} Torr to yield crude **7**. To a soln. of (*S,S*)-**6** (673 mg, 0.97 mmol) in dry THF (900 ml), Et_3N (2 ml) was added, followed by crude **7** in dry THF (60 ml). The mixture was stirred at r.t. for 24 h and at 80° for 8 h. Evaporation *in vacuo* left a residue, which was purified by FC (SiO_2; CH_2Cl_2/MeOH 20:1) to give (*S,S*)-**2** (458 mg, 60%). White powder. M.p. 302–304° (dec.). $[\alpha]_D^{23} = +1.4$ (*c* = 1, THF). IR (KBr): 3427*m*, 3306*m*, 3032*w*, 2956*m*, 2925*m*, 2879*m*, 2466*w*, 1669*s*, 1629*s*, 1534*s*, 1497*m*, 1437*m*, 1384*m*, 1384*m*, 1096*m*, 881*w*, 785*m*, 695*m*. ^{1}H-NMR ($(CD_3)_2SO$, 500 MHz): 10.29 (*s*, 2 H); 8.88 (*d*, *J* = 7.7, 2 H); 8.45 (*s*, 2 H); 8.26 (*s*, 2 H); 8.18 (*s*, 1 H); 7.99 (*d*, *J* = 7.8, 2 H); 7.85 (*d*, *J* = 7.8, 2 H); 7.68 (*d*, *J* = 7.32, 2 H); 7.64 (*s*, 2 H); 7.64–7.52 (*m*, 5 H); 7.43–7.38 (*m*, 4 H); 7.34–7.32 (*d*, *J* = 7.3, 2 H); 4.81–4.78 (*m*, 2 H); 1.87–1.78 (*m*, 2 H); 1.71–1.58 (*m*, 4 H); 0.90 (*d*, *J* = 6.4, 6 H); 0.87 (*d*, *J* = 6.4, 6 H). ^{13}C-NMR ($(CD_3)_2SO$, 125 MHz): 171.44; 165.75; 141.20; 140.87; 140.71; 140.48; 139.64; 134.19; 130.10; 129.55; 129.48; 129.31; 128.94; 127.29; 126.53; 126.45; 126.37; 125.89; 124.15; 122.29; 118.54; 117.20; 52.77; 24.52; 22.83; 21.59. FAB-MS: 769.2 (MH^+). Anal. calc. for $C_{50}H_{48}N_4O_4$ (768.95): C 78.10, H 6.29; found: C 76.68, H 7.06.

3,3-Diethyl-1-(3,3″-dinitro-1,1′:3′,1″-terphenyl-5′-yl)triaz-1-ene (**17**). A degassed soln. of 3-nitrophenylboronic acid (1.00 g, 5.99 mmol), **16** (0.912 g, 2.72 mmol), and Na_2CO_3 (1.15 g, 10.88 mmol) in PhH (39 ml), EtOH (11 ml), and H_2O (50 ml) was heated to 80°, then treated with a few mg of $[Pd(dppf)Cl_2]\cdot CH_2Cl_2$. The mixture was heated to reflux for 24 h, then the solvents were removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 and washed with 1M NH_4Cl. The org. layer was dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. FC (SiO_2; hexane/CH_2Cl_2 1:1) gave **17** (860 mg, 80%). Pale-red solid. M. p. 146.8–147.5°. IR (KBr): 2974*m*, 2931*m*, 1586*m*, 1524*s*, 1449*m*, 1404*m*, 1351*s*, 1232*m*, 1113*m*, 900*s*, 878*s*, 819*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.58–8.56 (*m*, 2 H); 8.28–8.23 (*m*, 2 H); 8.08–8.03 (*m*, 2 H); 7.75 (*d*, *J* = 1.7, 2 H); 7.71–7.63 (*m*, 2 H); 7.61 (*t*, *J* = 1.7, 1 H); 3.87 (*q*, *J* = 7.1, 4 H); 1.35 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 153.06; 149.03; 142.95; 140.54; 133.50; 130.02; 122.58; 122.35; 119.59. FAB-MS: 420.11 (100, MH^+). Anal. calc. for $C_{22}H_{21}N_5O_4$: C 63.00, H 5.05, N 16.70; found: C 63.01, H 5.10, N 16.87.

5′-(3,3-Diethyltriaz-1-enyl)-1,1′:3′,1″-terphenyl-3,3″-dicarbonitrile (**18**). According to the protocol for **17**, **8** (2.439 g, 10.6 mmol) and **16** (1.62 g, 4.8 mmol) in the presence of a few mg of $[Pd(dppf)Cl_2]\cdot CH_2Cl_2$ reacted to give, after FC (SiO_2; hexane/AcOEt 9:1), **18** (2.69 g, 67%). White solid. M.p. 110–113°. IR (KBr): 3067*w*, 2967*m*, 2922*m*, 2866*w*, 2222*s*, 1572*m*, 1461*m*, 1400*s*, 1333*s*, 1250*m*, 1233*s*, 1105*m*, 867*m*, 789*s*, 683*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.98–7.95 (*m*, 2 H); 7.94–7.88 (*m*, 2 H); 7.69–7.63 (*m*, 4 H); 7.61–7.53 (*m*, 2 H); 7.47 (*t*, *J* = 1.7, 1 H); 3.84 (*q*, *J* = 7.1, 4 H); 1.32 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 152.98; 142.53; 140.65; 131.85;

131.21; 131.11; 129.88; 122.44; 119.36; 119.04; 113.23. FAB-MS: 380.11 (MH^+). Anal. calc. for $C_{24}H_{21}N_5$ (379.46): C 75.97, H 5.58, N 18.46; found: C 75.96, H 5.69, N 18.28. X-Ray: see *Fig. 3*.

Diethyl 5′-(3,3-Diethyltriaz-1-enyl)-1,1′:3′,1″-terphenyl-3,3″-dicarboxylate (**19**). According to the protocol for **17**, **11** (825 mg, 2.9 mmol) and **16** (334 mg, 996 μmol) in the presence of a few mg of $[Pd(dppf)Cl_2]\cdot CH_2Cl_2$ (44 mg, 60 μmol) reacted to give, after FC (SiO_2; CH_2Cl_2/hexane 4:1), **19** (396.8 mg, 84%). Yellow oil. IR (NaCl): 2978*w*, 2929*w*, 1719*s*, 1578*w*, 1466*w*, 1449*w*, 1337*m*, 1283*m*, 1254*m*, 1221*m*, 1171*w*, 1110*m*, 1083*w*, 1020*w*, 870*w*, 753*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.35 (*t*, *J* = 1.7, 2 H); 8.12–8.02, 7.95–7.86 (2*m*, 4 H); 7.72 (*d*, *J* = 1.7, 2 H); 7.63 (*t*, *J* = 1.7, 1 H); 7.56 (*t*, *J* = 7.7, 2 H); 4.45 (*q*, *J* = 7.0, 4 H); 3.85 (*q*, *J* = 7.0, 4 H); 1.45 (*t*, *J* = 7.0, 6 H); 1.34 (*t*, *J* = 7.0, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.9; 152.6; 141.85; 141.80; 131.9; 131.3; 129.0; 128.7; 128.6; 123.0; 119.0; 61.2; 14.4. EI-MS: 473 (9, M^+), 428 (7, $[M - C_2H_5O]^+$), 373 (100, $[M - N_3(C_2H_5)_2]^+$), 300 (37), 272 (13, $[M - N_3(C_2H_5)_2 - CO]^+$), 226 (24). HR-EI-MS: 473.2320 (M^+, $C_{28}H_{31}N_3O_4^+$; calc. 473.2314).

5′-Iodo-3,3″-dinitro-1,1′:3′,1″-terphenyl (**20**). A degassed soln. of **17** (100 mg, 0.23 mmol) in MeI (4 ml) in a sealed tube was heated to 130° for 16 h. The excess of MeI was removed by distillation, and FC (SiO_2; CH_2Cl_2) of the residue gave **20** (95 mg, 88%). White powder. M. p. 215.5–216.6°. IR (KBr): 3077*w*, 2922*m*, 2855*m*, 1521*s*, 1355*m*, 1085*s*, 876*m*, 1495*s*, 798*m*, 734*s*, 677*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.50–8.48 (*m*, 2 H); 8.28–8.33 (*m*, 2 H); 8.04 (*d*, *J* = 1.7, 2 H); 7.99–7.94 (*m*, 2 H); 7.81 (*t*, *J* = 1.7, 1 H); 7.74–7.66 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.09; 141.86; 141.06; 136.40; 133.39; 130.36; 125.77; 123.26; 122.34; 95.85. FAB-MS: 445.86 (100, M^+). Anal. calc. for $C_{18}H_{11}IN_2O_4$ (446.2): C 48.45, H 2.48, N 6.28; found: C 48.43, H 2.58, N 6.15.

5′-(3,3-Diethyltriaz-1-enyl)-1,1′:3′,1″-terphenyl-3,3″-diamine (**21**). To **17** (300 mg, 0.715 mmol) in AcOEt (20 ml) under Ar, Pd/C (10%, 300 mg) was added, and the mixture was stirred under H_2 (4 bar) for 18 h at r.t. Filtration over *Celite* and concentration of the filtrate *in vacuo*, followed by recrystallization (CH_2Cl_2/hexane), gave **21** (204 mg, 83%). Pale-yellow powder. M. p. 116–118°. IR (KBr): 3444*m*, 3355*m*, 3222*w*, 2978*w*, 2933*m*, 1622*s*, 1597*s*, 1578*s*, 1494*m*, 1466*m*, 1444*m*, 1400*s*, 1333*s*, 1311*m*, 1233*m*, 1161*w*, 1105*m*, 1077*m*, 989*w*, 856*m*, 783*s*, 694*s*. ^{1}H-NMR (500 MHz, $(CD_3)_2SO$): 7.47 (*t*, *J* = 1.7, 1 H); 7.45 (*d*, *J* = 1.7, 2 H); 7.11 (*t*, *J* = 7.8, 2 H); 6.93 (*t*, *J* = 1.9, 2 H); 6.85 (*ddd*, *J* = 7.6, 1.7, 1.0, 2 H); 6.58 (*ddd*, *J* = 8.0, 2.2, 0.9, 2 H); 5.16 (br. *s*, 4 H); 3.78 (*q*, *J* = 7.1, 4 H); 1.24 (br. *s*, 6 H). ^{13}C-NMR (75 MHz, $(CD_3)_2SO$): 151.77; 149.32; 142.35; 141.14; 129.57; 121.49; 117.06; 114.51; 113.44; 112.35. EI-MS: 359 (12, M^+), 260 (100), 259 (90, $[M - N_3(C_2H_5)_2]^+$). Anal. calc. for $C_{22}H_{25}N_5$ (359.48): C 73.51, H 7.01, N 19.48; found: C 73.39, H 7.08, N 19.56.

*Dibenzyl (3S,3′S)-3,3′-([[(*tert*-Butyl)oxy]carbonyl]amino)-3,3′-[5′-(3,3-diethyltriaz-1-enyl)-1,1′:3′,1″-terphenyl-3,3″-diylbis(iminocarbonyl)]dipropanoate* ((*S,S*)-**22**). 4-Benzyl *N*-Boc-L-aspartate (440 mg, 1.36 mmol), DCC (766 mg, 3.71 mmol), and BtOH (250 mg, 1.85 mmol) were dissolved in THF (1.5 ml) at 0°. After the soln. turned turbid, **21** (204 mg, 0.619 mmol) was added, and the mixture was stirred at r.t. for 16 h. Filtration, concentration of the filtrate *in vacuo*, and FC (SiO_2, CH_2Cl_2/AcOEt 4:1) afforded (*S,S*)-**22** (308 mg, 51%). Colorless oil. IR ($CHCl_3$): 3316 (br.), 2976*m*, 2932*m*, 1733*s*, 1673*s*, 1611*w*, 1495*m*, 1163*s*, 867*m*, 787*s*, 697*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.02–7.92 (*m*, 2 H); 7.58 (*m*, 4 H); 7.36–7.25 (*m*, 17 H); 6.34 (*m*, 2 H); 5.15 (*s*, 4 H); 5.03–4.85 (*m*, 2 H); 3.82 (*q*, *J* = 7.2, 4 H); 3.11–2.85 (*m*, 4 H); 1.42 (*s*, 18 H); 1.31 (*t*, *J* = 7.2, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 171.45; 170.24; 156.52; 152.23; 141.78; 141.31; 138.45; 135.83; 129.42; 128.76; 128.44; 123.10; 118.92; 118.78; 118.29; 80.71; 66.92; 52.33; 36.77; 26.05; 25.53; 24.69. ESI-MS: 1008.6 (20, $[M + K]^+$, 992.6 (85, $[M + Na]^+$, 871.6 (20, $[M - N_3Et_2]^+$), 552.4 (100).

*(+)-Di(*tert*-butyl) N,N′-{5′-(3,3-Diethyltriaz-1-enyl)-1,1′:3′,1″-terphenyl-3,3″-diylbis[(S)-(iminocarbonyl)-(2-methylpropyl)methyl]}dicarbamate* ((*S,S*)-**23**). A soln. of **21** (238 mg, 663 μmol), EDC·HCl (445 mg, 2.32 mmol), *N*-Boc-L-leucine (330 mg, 1.32 mmol), and DMAP (20.2 mg, 166 μmol) in dry THF (40 ml) was stirred at r.t. for 1.5 d. After evaporation *in vacuo*, the residue was dissolved in CH_2Cl_2, and washed with 1M HCl, sat. aq. $NaHCO_3$ soln., and sat. aq. NaCl soln. The combined org. layers were dried ($MgSO_4$), the solvent was evaporated *in vacuo*, and the remaining oil was purified by FC (SiO_2; CH_2Cl_2/AcOEt 6:1). The pale-yellow product foam was recrystallized from CH_2Cl_2/hexane to give (*S,S*)-**23** (318 mg, 61%). Colorless needles. M.p. 156–158° (CH_2Cl_2/hexane). $[\alpha]_D^{25} = +44.6$ (*c* = 1, $CHCl_3$). IR (KBr): 3312*m*, 2958*m*, 2867*w*, 1669*s*, 1611*m*, 1561*m*, 1528*m*, 1496*m*, 1361*m*, 1232*m*, 1164*m*, 1105*w*, 1049*w*, 870*w*, 785*w*, 697*w*. ^{1}H-NMR (500 MHz, $(CD_3)_2SO$): 10.05 (br. *s*, 2 H), 7.95 (*m*, 2 H); 7.73–7.71 (*m*, 2 H), 7.57 (*m*, 1 H), 7.54 (*m*, 2 H); 7.45–7.41 (*m*, 4 H); 7.04 (*d*, *J* = 6.0, 2 H); 4.17–4.13 (*m*, 2 H); 3.80 (*q*, *J* = 6.9, 4 H); 1.68–1.64 (*m*, 2 H); 1.59–1.51 (*m*, 4 H); 1.39 (*s*, 18 H); 1.26 (*m*, 6 H); 0.92–0.90 (*m*, 12 H). ^{13}C-NMR (75 MHz, $(CD_3)_2SO$): 172.2; 155.7; 152.1; 141.7; 140.8; 139.8; 129.6; 121.8; 121.6; 118.6; 117.6; 78.1; 53.7; 28.1; 24.3; 22.9; 21.5. ESI-MS: 825 (35, $[MH + K]^+$), 809 (100, $[MH + Na]^+$). HR-FAB-MS: 784.4752 (MH^+, $C_{44}H_{63}N_7O_6^+$; calc. 784.4761). Anal. calc. for $C_{44}H_{63}N_7O_6$ (786.03): C 67.24, H 8.08, N 12.21; found: C 67.33, H 7.86, N 12.35.

5′-Iodo-1,1′:3′,1″-terphenyl-3,3″-dicarbonitrile (**26**). A degassed soln. of **18** (100 mg, 0.26 mmol) in MeI (4 ml) was heated to 130° in a sealed tube for 16 h. The excess of MeI was removed by distillation, and FC (SiO_2;

CH_2Cl_2) of the residue gave **26** (103 mg, 96%). White powder. M.p. 266°. IR (KBr): 3056*m*, 2222*s*, 1594*m*, 1572*m*, 1550*s*, 1478*m*, 1495*s*, 1317*m*, 867*m*, 783*s*, 722*s*, 686*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.67–7.58 (*m*, 2 H); 7.69 (*t*, *J* = 1.7, 1 H); 7.77–7.70 (*m*, 2 H); 7.88–7.82 (*m*, 2 H); 7.91–7.89 (*m*, 2 H); 7.97 (*d*, *J* = 1.7, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 142.01; 140.70; 136.17; 131.90; 131.77; 130.99; 130.17; 125.64; 118.63; 113.59; 95.77. EI-MS: 406.0 (100, M^+).

Diethyl 5′-Iodo-1,1′:3′,1″-terphenyl-3,3″-dicarboxylate (**28**). A soln. of **19** (63 mg, 133 μmol) and MeI (3 ml) in a sealed tube was flushed with Ar and then stirred at 130° for 16 h. After cooling and evaporation *in vacuo*, the residue was purified by FC (SiO_2; CH_2Cl_2/hexane 5:1) to give **28** (63.5 mg, 95%). Colorless oil. IR (NaCl): 2978*w*, 1717*s*, 1583*w*, 1550*w*, 1444*w*, 1389*w*, 1367*w*, 1283*m*, 1250*m*, 1222*m*, 1172*w*, 1111*m*, 1083*w*, 1050*w*, 1022*w*, 867*w*, 816*w*, 750*m*, 689*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.29 (*m*, 2 H); 8.15–8.06 (*m*, 2 H); 7.99 (*d*, *J* = 1.7, 2 H); 7.85–7.77 (*m*, 3 H); 7.57 (*t*, *J* = 7.8, 2 H); 4.45 (*q*, *J* = 7.0, 4 H); 1.45 (*t*, *J* = 7.0, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.7; 143.2; 140.0; 135.6; 131.8; 131.6; 129.4; 129.3; 128.5; 125.9; 95.5; 61.4; 14.4. EI-MS: 500 (100, M^+), 455 (48, $[M-C_2H_5O]^+$); 427 (8, $[M-C_2H_5O-CO]^+$); 300 (21, $[M-C_2H_5O-I]^+$); 272 (36, $[M-C_2H_5O-CO]^+$); 226 (45). HR-EI-MS: 500.0487 (M^+, $C_{24}H_{21}IO_4^+$; calc. 500.0486).

5′-Iodo-1,1′:3′,1″-terphenyl-3,3″-dicarboxylic Acid (**25**). A soln. of **28** (59.6 mg, 119 μmol) and LiOH (14.3 mg, 596 μmol) in EtOH (3 ml), H_2O (2 ml), and THF (1 ml) was stirred at r.t. for 16 h, after which 1M HCl was added. The mixture was extracted with AcOEt (2×), the combined org. layers were dried ($MgSO_4$), and the solvent was evaporated *in vacuo* to yield **25** (47 mg, 89%). Colorless solid. M.p. 300°. ^{1}H-NMR (200 MHz, $(CD_3)_2SO$): 13.13 (br. *s*, 2 H); 8.26 (*m*, 2 H); 8.11–7.97 (*m*, 7 H); 7.64 (*t*, *J* = 7.7, 2 H). EI-MS: 444 (100, M^+).

5′,5″-Bis(3-nitrophenyl)-1,1′:3′,1″:3″,1‴-quaterphenyl (**30**). A soln. of **29** [24] (770 mg, 1.63 mmol), 3-nitrophenylboronic acid (1.641 g, 9.83 mmol), and Na_2CO_3 (2.084 g, 19.66 mmol) in PhH/EtOH 11:3 (115 ml) and H_2O (77 ml) was flushed with Ar and heated to 80°. Subsequently, [Pd(dppf)Cl_2] (10 mg, 0.01 mmol) was added, and the mixture was heated to reflux for 3 d. The precipitate was filtered off and recrystallized from 1,2-dichlorobenzene to give **30** (703 mg, 67%). Pale-gray powder. M.p. > 350° (dec.). IR (KBr): 3109*m*, 2923*m*, 2369*s*, 2339*s*, 1843*m*, 1771*m*, 1717*m*, 1689*m*, 1652*m*, 1538*s*, 1526*s*, 1346*m*, 867*w*, 802*w*, 736*m*, 665*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.60–8.59 (*m*, 4 H); 8.34–8.24 (*m*, 4 H); 8.12–8.04 (*m*, 4 H); 7.96 (*d*, *J* = 2.1, 4 H); 7.93–7.91 (*m*, 2 H); 7.78–7.68 (*m*, 4 H). Due to the poor solubility of **30** in commonly used solvents, no ^{13}C-NMR spectra could be obtained. DEI-MS: 638.58 (M^+).

3,3′,3″,3‴-(1,1′-Biphenyl-3,3′,5,5′-tetrayl)tetrakis(benzenamine) (**31**). A dispersion of **30** (800 mg, 1.25 mmol) and Sn (1.78 g, 15 mmol) in conc. HCl (40 ml) was heated to reflux for 2 weeks. After cooling to r.t., the mixture was made basic (pH 14) with NaOH tablets. The soln. was diluted with H_2O and extracted with CH_2Cl_2 (4 × 150 ml). The combined org. layers were dried ($MgSO_4$), and the solvent was evaporated *in vacuo* to give **31** (632 mg, 97%). Pale-yellow powder. M.p. 284° (dec.). IR (KBr): 3336*m*, 3022*m*, 1927*w*, 1605*s*, 1580*s*, 1491*m*, 1401*m*, 1303*w*, 1204*w*, 1167*w*, 992*m*, 863*m*, 782*m*, 701*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.86 (*d*, *J* = 1.7, 4 H); 7.79 (*t*, *J* = 1.7, 2 H); 7.34–7.24 (*m*, 4 H); 7.11–7.10 (*m*, 4 H); 7.08–7.03 (*m*, 4 H); 6.77–6.72 (*m*, 4 H). ^{13}C-NMR (75 MHz, $(CD_3)_2SO$): 149.39; 142.48; 141.70; 140.96; 129.63; 124.20; 114.78; 113.5; 112.53. DEI-MS: 518.4 (100, M^+).

Tetra(tert-*butyl*) N,N′,N″,N‴-*(1,1′-Biphenyl-3,3′,5,5′-tetrayltetrakis{(*S*)-[(1,3-phenylene)iminocarbonyl](2-methylpropyl)methyl})tetracarbamate* ((*S,S*)-**32**). To a soln. of **31** (200 mg, 0.385 mmol), *N*-Boc-L-leucine (504 mg, 2.02 mmol), and DMAP (20 mg, 0.16 mmol) in DMF (40 ml) and dioxane (10 ml) at 0°, EDC·HCl (512 mg, 2.67 mmol) was added, and the mixture was stirred at r.t. over 2 d. More *N*-Boc-L-leucine (504 mg, 2.02 mmol) and additional EDC·HCl (512 mg, 2.67 mmol) were added at 0°. After stirring at r.t. for 3 d, the solvent was evaporated *in vacuo* and the residue taken up in CH_2Cl_2. The org. layers were washed with 1M HCl (2×) and sat. aq. $NaHCO_3$ soln. (3×). The combined org. layers were dried ($MgSO_4$), and FC (SiO_2; CH_2Cl_2/AcOEt 20:1) afforded (*S,S*)-**32** (342 mg, 67%). White solid. M.p. 266°. $[\alpha]_D^{23} = +167$ (*c* = 1, $CHCl_3$). IR (KBr): 3422*w*, 3314*m*, 2958*m*, 1670*s*, 1558*m*, 1550*m*, 1495*m*, 1367*m*, 1235*w*, 1164*m*, 1048*w*, 868*w*, 786*w*, 698*w*. ^{1}H-NMR (500 MHz, $(CD_3)_2SO$): 10.04 (br. *s*, 4 H); 7.97 (br. *s*, 8 H); 7.83 (br. *s*, 2 H); 7.77–7.75 (*m*, 4 H); 7.57–7.56 (*m*, 4 H); 7.46–7.43 (*m*, 4 H); 7.01 (*d*, *J* = 8.1, 4 H); 4.14–4.10 (*m*, 4 H); 1.65–1.63 (*m*, 4 H); 1.52–1.50 (*m*, 4 H); 1.46–1.41 (*m*, 4 H); 1.35 (*s*, 36 H,); 0.88 (*s*, 24 H). ^{13}C-NMR (125 MHz, $(CD_3)_2SO$): 171.89; 155.42; 141.80; 141.60; 140.39; 139.63; 129.40; 124.86; 124.36; 122.09; 118.60; 117.75; 77.96; 53.57; 28.14; 24.30; 22.92; 21.48. ESI-MS: 1395.1 (100, $[M + Na]^+$).

N,N′,N″,N‴-*(1,1′-Biphenyl-3,3′,5,5′-tetrayltetrakis{(*S*)-[(1,3-phenylene)iminocarbonyl](2-methylpropyl)methyl})tetraammonium Tetrakis(trifluoroacetate)* ((*S,S*-**33**). A soln. of (*S,S*)-**32** (342 mg, 0.259 mmol) in CH_2Cl_2/TFA 1:1 (40 ml) was stirred at r.t for 4 h under Ar. The mixture was evaporated *in vacuo*, EtOH was added, and the solvent was again evaporated *in vacuo* to yield (*S,S*)-**33** (364 mg, 99%). White powder. M.p. 234°. $[\alpha]_D^{23} = -18.4$ (*c* = 0.5, THF). IR (KBr): 3233*m*, 1964*m*, 1670*s*, 1488*m*, 1436*m*, 1391*m*, 1303*w*, 1202*s*, 1138*s*, 865*m*,

840*m*, 799*m*, 732*m*, 697*m*. ^{1}H-NMR (500 MHz, $(CD_3)_2SO$): 10.76 (br. *s*, 4 H), 7.99 (br. *s*, 8 H); 7.85 (br. *s*, 2 H); 7.75–7.73 (*m*, 4 H); 7.66–7.64 (*m*, 4 H); 7.53–7.49 (*m*, 4 H); 3.74 (br. *s*, 12 H); 3.9 (*m*, 4 H); 1.68 (*m*, 12 H); 0.92 (*s*, 24 H). ^{13}C-NMR (125 MHz, $(CD_3)_2SO$): 168.08; 141.83; 141.46; 140.57; 138.70; 129.69; 125.02; 123.05; 119.05; 118.18; 51.78; 23.65; 22.63; 21.77. FAB-MS: 1200.45 (5, $[M-2\ CF_3COOH]^+$); 1086.27 (5, $[M-3\ CF_3COOH]^+$); 971.49 (100, $[M-4\ CF_3COOH]^+$).

Tetraethyl 3,3′,3″,3‴-(1,1′-Biphenyl-3,3′,5,5′-tetrayl)tetrakis(benzenecarboxylate) (**34**). A degassed soln. of **11** (700 mg, 2.53 mmol), **29** (198 mg, 0.42 mmol), and Na_2CO_3 (535 mg, 5.05 mmol) in PhH (24 ml), EtOH (6 ml), and H_2O (20 ml) was heated to 80°. Subsequently, $[Pd(dppf)Cl_2]\cdot CH_2Cl_2$ (20 mg) was added, and the mixture was heated to reflux for 3 d. After evaporation *in vacuo*, the residue was taken up in CH_2Cl_2, and the soln. was washed with 1M NH_4Cl. The org. layer was dried ($MgSO_4$) and evaporated *in vacuo*. FC (SiO_2; CH_2Cl_2) gave **34** (251 mg, 73%). Slightly yellow solid. M.p. 163°. IR (KBr): 2978*m*, 1716*s*, 1581*m*, 1450*w*, 1366*m*, 1285*s*, 1224*s*, 1110*m*, 869*w*, 753*s*, 693*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.41–8.40 (*m*, 4 H); 8.12–8.08 (*m*, 4 H); 7.95–7.91 (*m*, 8 H); 7.88 (*t*, *J* = 1.6, 2 H); 7.61–7.55 (*m*, 4 H); 4.43 (*q*, *J* = 7.2, 8 H); 1.42 (*t*, *J* = 7.2, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.50; 142.41; 141.86; 141.12; 131.80; 131.28; 129.03; 128.85; 128.48; 125.86; 125.70; 61.19; 14.39. DEI-MS: 746.2 (M^+).

3,3′,3″,3‴-(1,1′-Biphenyl-3,3′,5,5′-tetrayl)tetrakis(benzenecarboxylic Acid) (**35**). To **34** (251 mg, 0.336 mmol) in THF (25 ml), LiOH (100 mg, 4.18 mmol) in H_2O (2.0 ml) was added, and the mixture was heated to reflux for 17 h. The mixture was partitioned between sat. aq. K_2CO_3 soln. and CH_2Cl_2. The aq. soln. was acidified with 1M HCl to pH 1, and the formed precipitate was filtered off and dried to yield **35** (175 mg, 87%). Pale-green solid. M.p. > 400°. IR (KBr): 3426*m*, 3032 (br.), 2655*w*, 2544*w*, 1700*s*, 1582*m*, 1450*m*, 1426*m*, 1388*w*, 1270*m*, 858*w*, 752*m*, 686*m*. ^{1}H-NMR (300 MHz, $(CD_3)_2SO$): 13.03 (br. *s*, 4 H); 8.34 (*m*, 4 H); 8.20–8.11 (*m*, 8 H); 8.00–7.91 (*m*, 6 H); 7.66–7.57 (*m*, 4 H). ^{13}C-NMR (125 MHz, $(CD_3)_2SO$): 167.26; 141.78; 141.2; 140.39; 131.88; 131.59; 129.23; 128.53; 127.89; 125.61; 124.97. ESI-MS: 634 (22, M^-).

Tetrakis(pentafluorophenyl) 3,3′,3″,3‴-(1,1′-Biphenyl-3,3′,5,5′-tetrayl)tetrakis(benzenecarboxylate) (**36**). To **35** (170 mg, 0.267 mmol) in dry DMF (7 ml) under Ar, pentafluorophenol (246 mg, 1.340 mmol) was added, and the soln. was cooled to 0°. After addition of DCC (332 mg, 1.608 mmol), the mixture was stirred at 0° for 60 h. Filtration over *Celite* and evaporation *in vacuo* provided a residue that was dissolved in PhMe and filtered over *Celite* again. Evaporation *in vacuo* and FC (SiO_2; CH_2Cl_2) gave **36** (178 mg, 51%). White solid. M.p. 254°. IR (KBr): 3445 (br.), 2922*w*, 2666*w*, 2455*w*, 2360*m*, 1771*s*, 1593*w*, 1521*s*, 1271*m*, 1210*m*, 1146*w*, 1040*m*, 997*m*, 735*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.55–8.54 (*m*, 4 H); 8.28–8.25 (*m*, 4 H); 8.11–8.07 (*m*, 4 H); 7.99 (*d*, *J* = 1.6, 4 H); 7.93 (*t*, *J* = 1.6, 2 H); 7.94–7.68 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 162.78; 143.25; 142.80; 141.86; 141.72; 139.86; 138.22; 136.57; 133.87; 130.25; 129.91; 129.78; 128.02; 126.43; 126.03. HR-MALDI-MS: 1321.0864 (100, $[M + Na]^+$, $C_{64}H_{22}F_{20}O_8Na^+$; calc. 1321.0893).

X-Ray Crystal Structure of **18**. Data for $C_{24}H_{21}N_5$, M_r = 379.46, at *T* = 293 K: triclinic, space group $P\bar{1}$ (No. 2), D_c = 1.173 g cm^{-3}, *Z* = 4, *a* = 8.343(6), *b* = 14.306(11), *c* = 18.797(12) Å, α = 80.66(6), β = 87.54(6), γ = 76.01(6)°, *V* = 2148.1(3) Å^3. Syntex diffractometer, MoK_α radiation, λ = 0.7107 Å. A single crystal with linear dimensions of ca. 0.5 × 0.3 × 0.3 mm was used. The structure was solved by direct methods and refined by full-matrix least-squares analysis (SHELXTL). All heavy atoms were refined anisotropically, H-atoms fixed isotropically with atomic positions based on stereochemical considerations. Final $R(F) = 0.049$, $wR(F^2) = 0.137$ for 528 parameters and 2489 reflections with $I > 2\sigma(I)$ and $2.2 < \theta < 20.0°$ (corresponding *R* values based on all 4002 reflections are 0.072 and 0.145, resp.). Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-197055. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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