bubbler. The reaction mixture was cooled to −22 °C and **6** precipitated as a microcrystalline solid, which was collected by filtration and dried in vacuo. Single crystals suitable for X-ray structure analysis were obtained by recrystallization from *n*-hexane/toluene (1/1) after 16 h at room temperature. Yield 1.20 g (65%). M.p. 150 °C (decomp): ^{1}H NMR (200 MHz, C_6D_6/[D_8]THF (1/10), TMS): $\delta = -0.30$ (q, 6H, $AlCH_2CH_3$), 0.18 (s, 9H, $Si(CH_3)_3$), 0.95 (m, 9H, $AlCH_2CH_3$), 1.05 (d, 12H, $CH(CH_3)_2$), 1.60 (m, 4H, THF), 3.45 (m, 4H, THF), 4.05 (sept., 2H, $CH(CH_3)_2$), 6.75 (m, 3H; H_{arom}); ^{29}Si NMR (50 MHz, C_6D_6/[D_8]THF, TMS): $\delta = -9.1$ ($Si(CH_3)_3$); IR (KBr, Nujol): $\tilde{\nu} = 1578$, 1423, 1362, 1260, 1099, 1041, 908, 838, 747 cm^{-1}; EI-MS: m/z (%): 162 (80, $C_{12}H_{18}$), 73 (100, $SiMe_3$); elemental analysis $C_{21}H_{41}AlSiNNa \cdot C_4H_8O$: calcd: C 65.67, H 10.71, Al 5.9, N 3.06, Si 6.14; found: C 67.5, H 11.0, Al 6.1, N 2.9, Si 6.4.

Received: August 22, 1996 [Z9482IE]
German version: *Angew. Chem.* **1997**, *109*, 644–647

Keywords: aluminum · amides · hydrido complexes · lithium · sodium

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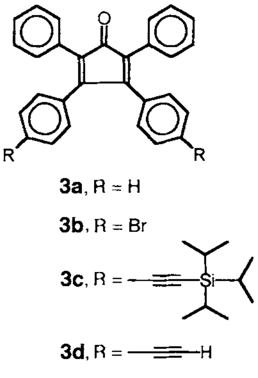
Polyphenylene Dendrimers: From Three-Dimensional to Two-Dimensional Structures[**]

Frank Morgenroth, Erik Reuther, and Klaus Müllen[*]

By making use of weak intermolecular forces and suitable reaction conditions, chemists have attempted to produce supramolecular structures from molecules of different shapes and sizes.[1] In addition to stiff rodlike and spherical molecules, disk-shaped molecules have attracted particular attention. This latter group includes polycyclic aromatic hydrocarbons (PAHs), which are characterized by their typical crystal packings and their stacking in discotic mesophases.[2–4] We have recently developed routes to extended PAHs which enable the systematic alteration of the shape and size of the disks.[5] The key step is the flattening of branched polyphenylene precursors to planar structures by means of cyclodehydrogenation. Here we describe the use of 3,4-bis[4-(triisopropylsilylethynyl)-phenyl]-2,5-diphenylcyclopentadienone (**3c** in Scheme 1) as a building block that can be used for the rapid construction of complex, highly branched polyphenylene structures and dendrimers by Diels–Alder cycloaddition.



Scheme 1. Tetraphenylcyclopentadienone derivatives.

Our synthetic strategy is based on the fact that Diels–Alder reactions of tetraphenylcyclopentadienone (**3a**) with di- (mono-)phenylacetylenes yield hexa- (penta-)phenylbenzenes.[6] The diethynyl derivative **3d** contains one diene as well as two dienophile functions. However, participation of the triple bonds in cycloaddi-

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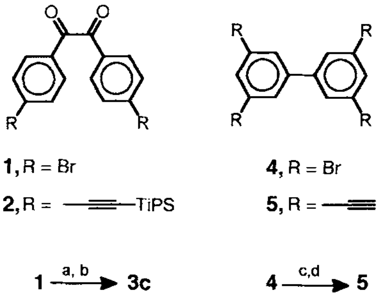
[**] We thank Dr. J. Räder and Dipl.-Chem K. Martin for recording the MALDI-TOF and LD-TOF mass spectra, and Dr. M. Wagner and Dipl.-Chem C. Kübel for the NMR spectra. F. M. thanks the Fonds der Chemischen Industrie for a Kekulé stipend. This work was supported by the Volkswagenstiftung and the Bundesministerium für Bildung und Forschung.

tion can be prevented by protecting them with triisopropylsilyl (TiPS) substituents (compound **3c**). After the Diels–Alder addition of **3c** with a suitable phenylacetylene derivative, the TiPS groups can be removed and the diethynyl functions activated for further Diels–Alder cycloadditions.

Ultimately, we intend to flatten the polyphenylene precursors prepared by this method through intramolecular cyclodehydrogenation to obtain planar PAHs. In this way three-dimensional hydrocarbon structures would be converted into two-dimensional analogues. We therefore chose tetraethynylbiphenyl **5** as the nucleus for the synthesis of a dendrimer and diethynylhexaphenylbenzene **6** as the nucleus for the generation of dendrimer sections (dendrons). Both of the starting compounds may be reduced to the topology of a 3,3'-disubstituted biphenyl.



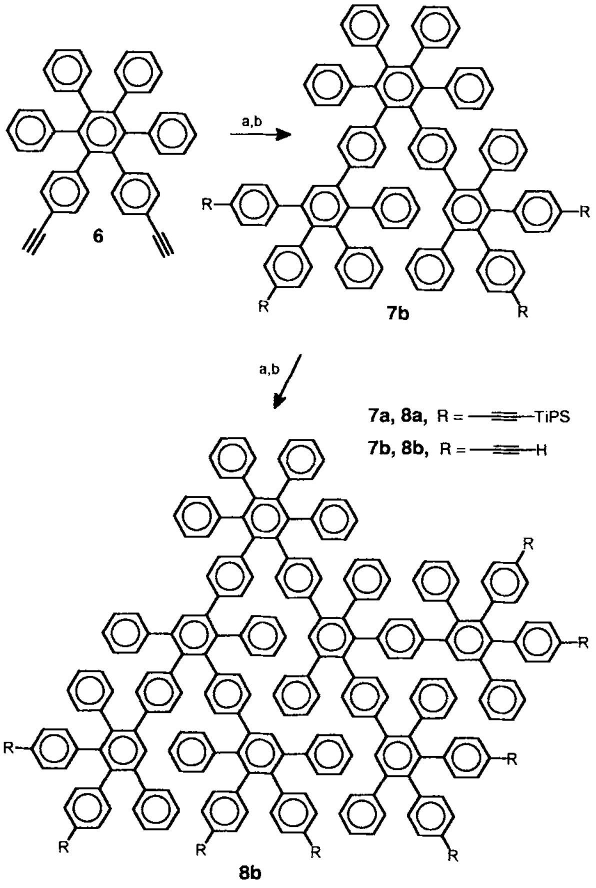
Scheme 2. a) TiPSA, $[Pd(PPh_3)_2Cl_2]$, CuI, PPh_3, Et_3N/toluene 2/1, 90 °C, 4 h (86%); b) 1,3-diphenylacetone, EtOH, KOH, reflux, 15 min (21%); c) TMSA, $[Pd(PPh_3)_2Cl_2]$, CuI, PPh_3, Et_3N/toluene 2/1, 80 °C, 4 h (61%); d) Bu_4NF, THF, room temperature (RT), 2 h (98%).

For the synthesis of **3c** we started with 4,4'-dibromobenzil (**1**), which was coupled with triisopropylsilylacetylene (TiPSA) by the method of Sonogashira et al.[7] to give benzil **2** in 86% yield (Scheme 2). Compound **2** was condensed with 1,3-diphenylacetone in the presence of potassium hydroxide to afford **3c**.[8] Attempts to couple TiPSA directly with **3b**[8] always led to hydrogenation of a double bond in the cyclopentadienone.

Several paths are available for the preparation of the acetylenic unit **6**; the simplest is [2+4]cycloaddition of cyclopentadienone **3c** with diphenylacetylene and subsequent removal of the TiPS groups with tetrabutylammonium fluoride.[9] Tetraethynylbiphenyl **5** was prepared by means of the Sonogashira coupling of the known tetrabromobiphenyl **4**[10] with trimethylsilylacetylene (TMSA) and subsequent removal of the trimethylsilyl groups (Scheme 2, 61% yield).

The synthesis of dendrons from **3c** is shown in Scheme 3. The addition of **3c** to **6** provided **7a**, which was converted to **7b**. Analogously, the related dienophile **3b** led to the corresponding bromo-substituted dendron. The bromo substituents serve as "handles" for further functionalization. Compound **7** is a first-generation (G_1) dendron constructed exclusively by the coupling of benzene rings. The C_{146} dendrimer unit **7a** contains 17 benzene rings and has a molecular mass of 2017 g mol^{-1}. The addition of **3c** to **7b** yields compound **8a**, a second-generation dendron. This step increases the number of benzenoid units to 37. Despite its large molecular mass of 4261 g mol^{-1}, the C_{310} building block **8a** is readily soluble in organic solvents such as tetrahydrofuran, chloroform, and dichloromethane, and can be characterized by NMR spectroscopy (Table 1). The high solubility is retained even after the protecting groups have been removed (**8b**).

In the synthesis of **8a** the reaction conditions for the [2+4]cycloaddition proved to be critical. Simply heating a mixture of the two components in diphenyl ether led to a mixture of di-, tri-, and tetracycloaddition products. However, when a solution of **7b** in methylnaphthalene was added under argon to two equivalents of **3c** at 180–200 °C in diphenyl ether, the TiPS-protected dendron **8a** was the sole product. Unreacted **3c** could



Scheme 3. a) **3c**, diphenyl ether/α-methylnaphthalene 1/1, 180–200 °C, 4 h (>85%); b) Bu_4NF, THF, RT, 5 h (>97%).

Table 1. Selected spectroscopic data for compounds **7b**, **8a**, **10**, **11b**, **12a**, and **14** [a].

7b: FD-MS: *m/z*: 1393, calcd for $C_{110}H_{70}$ 1392; ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K): δ = 7.39 (s, 2H), 7.17–6.57 (br., 64H), 3.03–3.01 (br., 4H); ^{13}C NMR (125 MHz, CD_2Cl_2, 303 K): δ = 142.26, 142.23, 141.79, 141.77, 141.70, 141.64, 141.61, 141.30, 141.22, 140.74, 140.43, 139.95, 139.64, 139.06, 138.91, 132.43, 132.39, 132.35, 132.31, 131.84, 131.67, 131.37, 130.75, 129.14, 128.60, 127.93, 127.45, 127.39, 126.71, 126.14, 126.04, 120.28, 119.97; m.p. >300 °C

8a: MALDI-TOF-MS (in the presence of silver): *m/z*: 4366, calcd for $C_{310}H_{310}Si_8,Ag^+$ 4368; ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K): δ = 7.42–6.40 (br., 142H), 1.24–1.00 (br., 168H); ^{13}C NMR (125 MHz, CD_2Cl_2, 303 K): δ = 142.20, 141.90, 141.50, 141.21, 141.13, 141.08, 140.76, 140.31, 140.04, 139.37, 139.55, 139.75, 138.92, 138.78, 138.65, 138.51, 131.97, 131.78, 131.38, 131.25, 131.02, 130.74, 130.27, 130.20, 128.86, 128.57, 128.06, 127.90, 127.37, 127.22, 126.89, 126.82, 126.50, 125.95, 125.80, 125.70, 121.19, 120.90, 107.33, 90.93, 90.83; m.p. 300 °C (decomp)

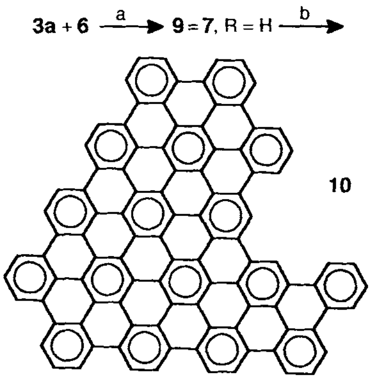
10: LD-TOF-MS: *m/z*: 1258, calcd for $C_{102}H_{32}$ 1257; m.p. >300 °C

11b: FD-MS: *m/z*: 1869, calcd for $C_{148}H_{90}$ 1868; ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K): δ = 7.25–7.21 (br., 12H), 7.14–6.97 (br., 28H), 6.88–6.68 (br., 38H), 6.45–6.38 (br., 4H), 3.03–3.00 (br., 8H); ^{13}C NMR (125 MHz, CD_2Cl_2, 303 K): δ = 141.54, 141.49, 141.27, 141.11, 141.00, 140.67, 140.04, 139.31, 138.66, 132.11, 131.87, 131.84, 131.79, 131.18, 130.88, 130.31, 128.12, 127.64, 127.01, 126.93, 126.50, 119.80, 119.50, 83.78, 77.43, 77.33; m.p. >300 °C

12a: MALDI-TOF-MS (in the presence of potassium): *m/z*: 7645, calcd for $C_{548}H_{570}Si_{16},K^+$ 7645; (in the presence of lithium): *m/z*: 7612, calcd for $C_{548}H_{570}Si_{16},Li^+$ 7613; ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K): δ = 7.40 (br., 3H), 7.34 (br., 3H), 7.24–6.30 (br., 228H), 1.09–1.08 (br., 336H); ^{13}C NMR (125 MHz, CD_2Cl_2, 303 K): δ = 142.32, 141.82, 141.65, 141.60, 141.53, 141.18, 140.46, 139.96, 139.87, 139.08, 132.40, 132.23, 132.19, 131.82, 131.69, 131.45, 131.17, 130.85, 130.62, 130.59, 129.30, 128.98, 128.49, 128.38, 127.78, 127.27, 126.64, 121.60, 121.31, 107.73, 91.35, 91.27, 19.19, 12.35, 12.13, 11.99, 11.90; m.p. >300 °C

14: LD-TOF-MS: *m/z*: 1621, calcd for $C_{132}H_{34}$ 1620; m.p. >300 °C

[a] 1,8,9-Trihydroxyanthracene served as the matrix for recording the MALDI-TOF mass spectra. The chemical shifts in the NMR spectra were calibrated from the residual protons of the deuteriated solvent [17].



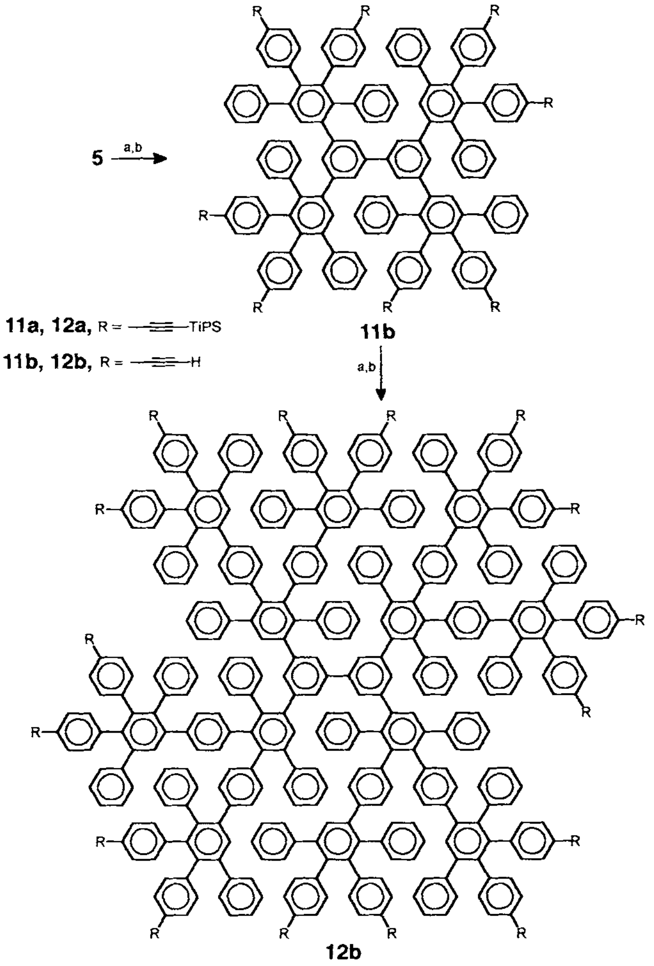
10

Scheme 4. a) Diphenyl ether/α-methylnaphthalene 1/1, 250 °C, 12 h (89%); b) $CuCl_2$, $AlCl_3$, CS_2, RT, 100 h (15%).

be separated subsequently by column chromatography or, more simply, by precipitation from an acetone solution on addition of methanol .

Compound **9**, which can be prepared from commercially available **3a** and **6** (Scheme 4), is an important model system for studying the flattening of dendrons. Cyclodehydrogenation of **9** under Kovacic conditions[11] afforded the planar hydrocarbon **10** (15% yield) together with partially cyclodehydrogenated compounds. Compound **10** was identified by mass spectrometry since its M^+ peak is 38 (2 × 19 hydrogen atoms) mass units less than that of **9** (Table 1).

The Diels–Alder reaction of nucleus **5** with **3c** yielded the first-generation dendrimer **11a** with 22 benzenoid rings, which was deprotected to give **11b**. Reaction of the latter with **3c** yielded the second-generation analogue **12a** (Scheme 5). Thus, in two steps we selectively converted the C_{220} building block **11a** with a molecular mass of 3119 g mol^{-1} to a C_{548} unit **12a** with a molecular mass of 7606 g mol^{-1}—2.4 times that of **11a**.

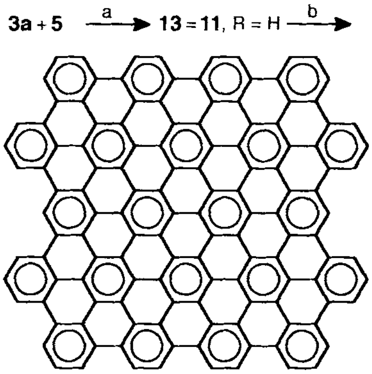


12b

Scheme 5. a) **3c**, Diphenyl ether/α-methylnaphthalene 1/1, 180–200 °C, 4 h (>85%); b) Bu_4NF, THF, RT, 5 h (>98%).

In spite of their high molecular masses both **11a,b** and **12a,b** are readily soluble in organic solvents and could be characterized by both mass spectrometry and NMR spectroscopy (Table 1). In the syntheses of **11a** and **12a** it again proved necessary to add the dienophile in portionwise to an excess of the diene.

For the synthesis of planar, extended PAHs it was logical to employ the reaction of tetraethynylbiphenyl **5** with tetraphenylcyclopentadienone (**3a**) to form the polyphenyl precursor **13** (Scheme 6). Under cyclodehydrogenation conditions **13** formed 28 new bonds to yield **14**, the planarized version of **11**, in 83% yield as a first-generation dendrimer unit. As in the case of **10** the spectroscopic characterization of **14** was difficult because of its extremely low solubility in all standard solvents. It was characterized by mass spectrometry based on its M^+ peak, which is 56 mass units (2 × 28 hydrogen atoms) less than that of **13** (Table 1).



14

Scheme 6. a) Diphenyl ether/α-methylnaphthalene 1/1, 250 °C, 2 h (91%); b) $CuCl_2$, $AlCl_3$, $C_2H_2Cl_4$, 100 °C, 9 h (83%).

Polyphenylene dendrimers formed by the direct C–C coupling[12–16] of 1,2-diphenyl-substituted arene units are available by means of the path described here. In each case the appropriate G_1 polyphenylenes **9** and **13** can be fused to form the discoidal polycyclic arenes **10** and **14**. At present we are investigating how the increasing degree of branching in the polyphenylenes leading to higher generation dendrimers affects their conformational mobility and the possibility of flattening them to form extended PAHs.

Received: October 7, 1996 [Z9619IE]
German version: *Angew. Chem.* **1997**, *109*, 647–649

Keywords: arenes · cyclizations · dendrimers · Diels–Alder reactions · polycycles

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Asymmetric Cyclopentannulation of Cyclic Enones with a Chiral 1,3-Dipole Equivalent**

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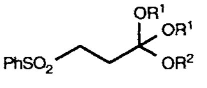
In memory of Jean-François Cordier

Interest in the stereocontrolled synthesis of five-membered carbocycles continues to generate many exciting strategies.[1] Among these, condensations of C_3 reagents with olefins bearing a chiral substituent have received much attention.[2] Reports on asymmetric cyclopentannulations with an olefinic substrate and a chiral C_3 reagent are less common.[3]

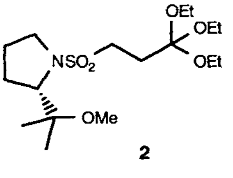
We have already described a very efficient method for cyclopentannulation of cyclic enones with readily available **1**.[4] The simplicity of this procedure and its generality could make it as useful as the much used Robinson annulation. We now report an equally simple asymmetric version of this cyclopentannulation with chiral sulfonamide orthoester **2** as 1,3 dipole reagent.



1

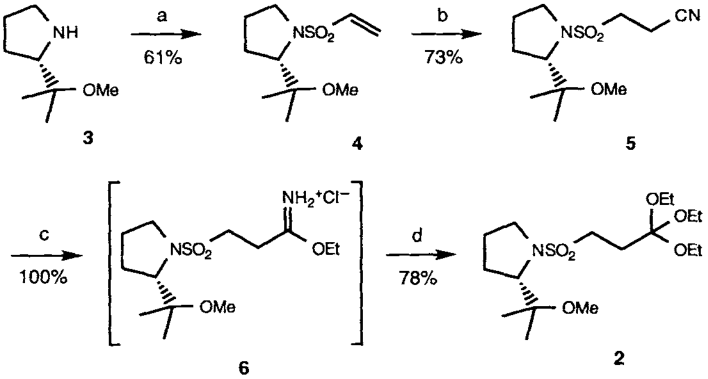
$R^1 = R^2 =$ Me, Et

$R^1 = -CH_2CH_2-$, $R^2 =$ Et



2

Compound **2** (pale yellow oil; $[\alpha]_D^{20} = -6.7$, $c = 1.6$ in chloroform) was readily prepared as depicted in Scheme 1 from the enantiomerically pure pyrrolidine **3** described by Enders et al.[5]



Scheme 1. Synthesis of enantiomerically pure **2**. a) $ClSO_2CH_2CH_2Cl$ (1 equiv), Et_3N (2 equiv) in CH_2Cl_2, 0 °C, 1 h. b) KCN (2 equiv), NH_4Cl (1.5 equiv) in water, **4** in DMF, 20 °C, 14 h. c) 1. **5** and EtOH (1.5 equiv) in CH_2Cl_2 at −60 °C, saturation with HCl(g). 2. 21 h at 5 °C, evaporation until a colorless solid remains. d) 1. Crude **6** in EtOH/CH_2Cl_2 (1/3), 20 °C, 60 h. 2. Filtration. 3. Treatment of the residue with 2 N NaOH(aq), 20 °C, until disappearance of ester carbonyl band at $\tilde{\nu} = 1740$ cm^{-1}

The cyclopentannulation sequence and subsequent transformation of the cyclocondensation products **9** into bicyclic cyclopentenones **11** are shown in Scheme 2. Sulfonamide **2** was deprotonated with *n*BuLi to give carbanion **7**, which underwent a kinetic 1,4-addition reaction with cyclic enones in the presence of hexamethyl phosphoramide (HMPA). The resulting enolates were quenched with TMSCl (TMS = trimethylsilyl) to give a crude organic extract, which mainly contained silylenol ethers **8** as shown by ^{1}H and ^{13}C NMR spectroscopy. Without further purification, the extract was allowed to react with TMSOTf (Tf = F_3CSO_2) in the cyclization step.[6] The cyclized products **9a** and **9d** were obtained as oils (77 and ≈60%, respectively; **9d** was contaminated by some ester), and **9b** and **9c** as colorless, crystalline solids (63 and 67%, respectively). Compounds **9a–c** gave correct elemental analyses. The ^{1}H NMR spectra of **9a** and **9c** confirmed the expected *cis*-fusion of the newly formed cyclopentane ring (^3J(H,H) = 7.3–10.5 Hz for the protons of the ring fusion), but did not allow an accurate determination of the facial selectivity of the reaction. However, in the case of **9c**, we were able to show that the mixture mainly consisted of two diastereoisomers that differ by the configuration of the carbon atom bearing the sulfonamide group (*exo*:*endo* = 9:1).

The structure and absolute configuration of **9b** was further confirmed by an X-ray diffraction analysis.[7] The absolute configurations of **9a**, **9c**, and **9d** were assigned accordingly on the basis that all reactions are expected to proceed with the same facial selectivity.

Ketones **9** were transformed into bicyclic cyclopentenones **11** in a sequence of three reactions; none of the intermediates required purification (Scheme 2, Tables 1 and 2). The first step was the stereoselective reduction of cup-shaped **9**, which occurred, as expected, from the convex face. The enantiomeric excesses of **11a–d** were determined by HPLC. Mosher's esters of crude **11a** and **11b** were prepared and analyzed by ^{1}H NMR spectroscopy. Both gave consistent results.

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[**] This work was supported by the Université catholique de Louvain, IRSIA, FNRS (fellowship for C. H.), the Ministère de l'Education et de la Recherche scientifique (Action concertée no. 91/96-145), and the Fonds de la Recherche fondamentale collective.