CONCAVE REAGENTS+. NEW 2′-SUBSTITUTED *m*-TERPHENYLS

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Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday.

New 2′-substituted 2,2″,6,6″-tetramethyl-1,1′:3′,1″-terphenyls have been synthesized. Solubility of concave acids **4b**–**6b** could be enhanced by substitution in 4 and 4″ position, allowing the study of hydrogen-bonded heterodimers. Concave acids show larger binding constants for 2-amidopyridines **7** than non-macrocyclic ones, probably due to the prevention of homodimer formation by the macrocyclic shielding. New 2,6-diarylbenzyl alcohols **1d**, **8d** and **9d** have been synthesized and tested in protonation reactions. New functional groups were introduced into the 2′ position: OH (phenols **1f** and **12f**) and NH_2 (aniline **1j**). The basicity of aniline **1j** in ethanol was determined by titration and was compared to other bases. Also sulfonic acids **1l** and **17l** were prepared, and the corresponding methyl esters **1m** and **17m** were tested as methylating agents.

Keywords: Arenes; Biaryls; Terphenyls; Phenols; Sulfonic acids; Receptors; Basicity; Hydrogen bonds; Macrocycles; Supramolecular chemistry.

The high selectivity of enzymatic reactions is largely caused by the concave shielding of the active site within the polypeptide environment (e.g. lit.[2]). In artificial compounds, concave structures play an increasingly important role[3–5], and concave reagents and catalysts have been developed[6,7]. Many of

+ Part 42 of the series. For part 41 see: ref.[1]

these compounds are macrocyclic or oligomacrocyclic, but also tweezer-, clip-, cleft- or pincer-like compounds[8–15] have been synthesized.

An important structure for concave molecules is the *m*-terphenyl moiety (Fig. 1). If a functional group is introduced into the 2′ position of a *m*-terphenyl, the outer benzene rings shield this functional group. The shielding is extremely efficient if the outer benzene rings carry further substituents in the *ortho* positions, i.e. in positions 2, 6, 2″ and 6″.

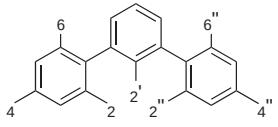
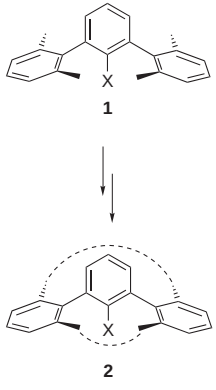


FIG. 1
Numbering of the 1,1′:3′,1″-terphenyl system

m-Terphenyls of this kind have been used by many research groups, and for many purposes, for instance for the stabilization of highly reactive functional groups bound in position 2′ [16]. A very convenient synthetic approach to these *m*-terphenyls has been developed by Hart[17,18] and has been exploited by us[19–23].

A key intermediate in the synthesis of such *m*-terphenyls is the 2′-iodo-2,2″,6,6″-tetramethyl-1,1′:3′,1″-terphenyl (**1a**)[19]. A variety of different functional groups has been introduced into the 2′ position[19–23] and the influence of the shielding by the *m*-terphenyl on the reactivity and selectivity of functional groups in position 2′ has been studied in several cases. The methyl groups have been also functionalized and bridged to finally give bimacrocylic concave *m*-terphenyl structures **2** [19–22] containing, for instance, acid functionalities inside. Thus, concave benzoic acids[19,20], concave thiols[21] and concave sulfinic acids[22] have been synthesized (Scheme 1).



	X
a	I
b	COOH
c	CHO
d	CH_2OH
e	Li
f	OH
g	COCl
h	CON_3
i	NCO
j	NH_2
k	SO_2Cl
l	SO_3H
m	SO_3Me

SCHEME 1

In this work, we present new *m*-terphenyls. The solubility of some *m*-terphenyls containing bimacrocycles has been enhanced by substitution in positions 4 and 4″. Furthermore, the outer aryl rings have been varied, and new functional groups have been introduced into the 2′ position.

RESULTS

All final compounds described below have been characterized by IR, MS, NMR and elemental analyses. In the case of one final product (**9d**), a correct elemental analysis could not be obtained. Instead, the compound has been characterized by high-resolution MS in combination with a purity check by GC. Some of the intermediates have been fully characterized, others not. However, subsequent reactions to the final products are additional structural proofs for the intermediates.

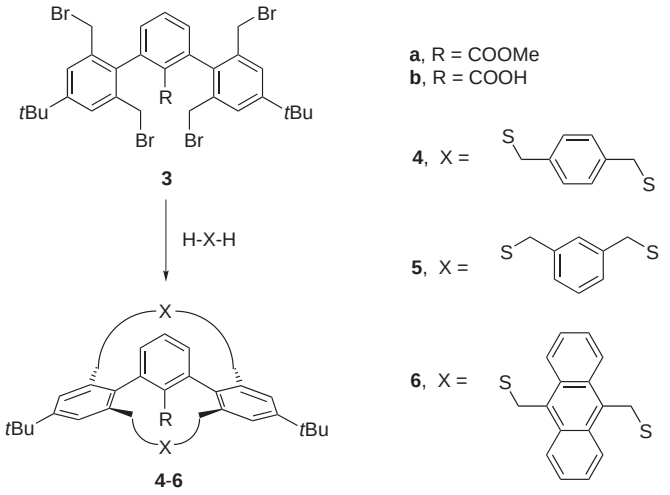
Concave Acids – Hydrogen Bond Formation

Concave benzoic acids and their methyl esters based on the *m*-terphenyl skeleton have already been synthesized starting from the 2,6-bis(2,6-dimethylphenyl)benzoic acid (**1b**)[19].

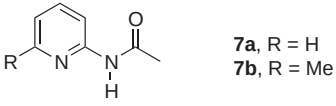
Monobromination of all four methyl groups was possible using NBS [19]. The resulting tetrabromide could then be bridged with dithiols to give bimacrocyclic esters, and the corresponding acids after hydrolysis[19]. In order to enhance the solubility, *tert*-butyl groups have already been introduced into the 4 and 4″ positions of an anthracene-containing concave acid **6b** [20]. Performing analogous tetrabromination with the *tert*-butylated methyl ester gave tetrabromide **3a** [20]. Bis-macrocyclization with dithiols gave the concave esters **4a** and **5a**, and hydrolysis led to the concave acids **4b** and **5b** in sufficient quantities to study their acid/base behavior[22] (Scheme 2). Furthermore, their potential to bind guest molecules by hydrogen bonds could be investigated, now that the solubility was large enough for NMR titrations.

Carboxylic acids can form two hydrogen bonds (an example: lit.[24]). The COOH group acts as a hydrogen bond donor D and as a hydrogen bond acceptor A. 2-Acetamidopyridines such as **7** [25–27] (Scheme 3) have been chosen as complementary partners, which also form two (DA) hydrogen bonds (an example of such interactions: lit.[28]).

These compounds have been investigated in NMR titrations (for investigation of the formation of hydrogen bonds to other *m*-terphenyl acid, see[29]) with three *m*-terphenylcarboxylic acids: with the parent *m*-terphenyl-



SCHEME 2



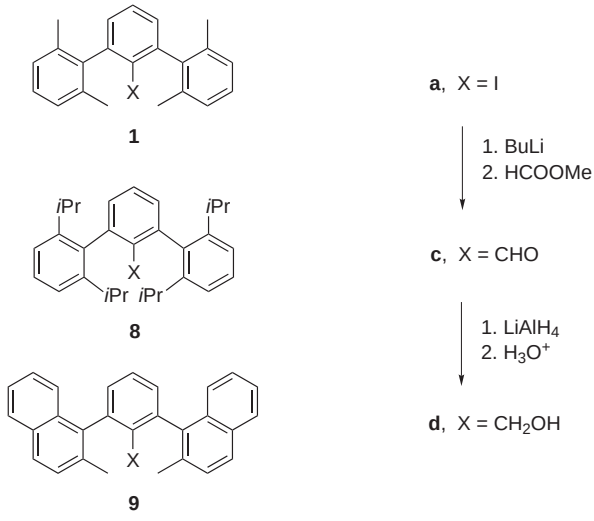
SCHEME 3

carboxylic acid **1b**, and with carboxylic acids **4b** and **6b** [20]. Remarkably, the concave acids **4b** and **6b** showed association constants of 10^3 while **1b** possessed constants of less than 100. A possible explanation may be the competing self-dimerization of carboxylic acids because the DA pattern is self-complementary. However, in a concave structure, self-dimerization is prohibited, thus leading to a larger degree of heterodimer formation with acetamidopyridines **7**.

m-Terphenylmethanols and Protonation Reactions

The use of *m*-terphenylmethanols in the protonation of carbanions has led to predominant formation of only one stereoisomer[23] (the special *cis* selectivity of *m*-terphenyl alcohols in protonation reactions is probably caused by a selective transesterification[30]). Two new *m*-terphenyls have been synthesized and investigated: the methyl groups in the *ortho* positions of the outer rings (**1d**) have been replaced by isopropyl groups (**8d**), and the dimethylphenyl rings have been enlarged to methylnaphthyl rings (**9d**) (Scheme 4). In both cases, the synthesis of the *m*-terphenylmethanols **8d**

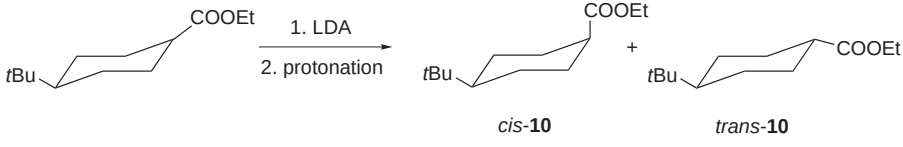
and **9d** was carried out analogously to the synthesis of the parent tetramethyl-*m*-terphenyl **1** [23].



SCHEME 4

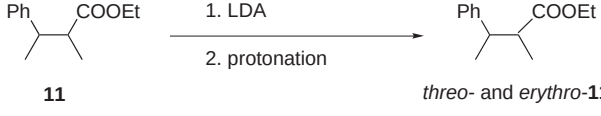
First, the enlarged *m*-terphenyl structure was built up using iodides **8a** and **9a**. Iodide–lithium exchange followed by reaction with methyl formate gave the new aldehydes **8c** and **9c**, which were reduced to methanols **8d** and **9d** by reaction with lithium aluminium hydride.

All three alcohols **1d**, **8d** and **9d** were investigated in the protonation of several substrates, for instance in the reprotonation of the α-deprotonated ethyl 4-*tert*-butylcyclohexane-1-carboxylate (**10**)[23,31] (Scheme 5) or ethyl



SCHEME 5

2-methyl-3-phenylbutanoate (**11**)[32,33] (Scheme 6). All protonation experiments were carried out as described for tetramethyl-*m*-terphenyl-2′-methanol **1d** and the ratio of the stereoisomers was determined by GC as de-



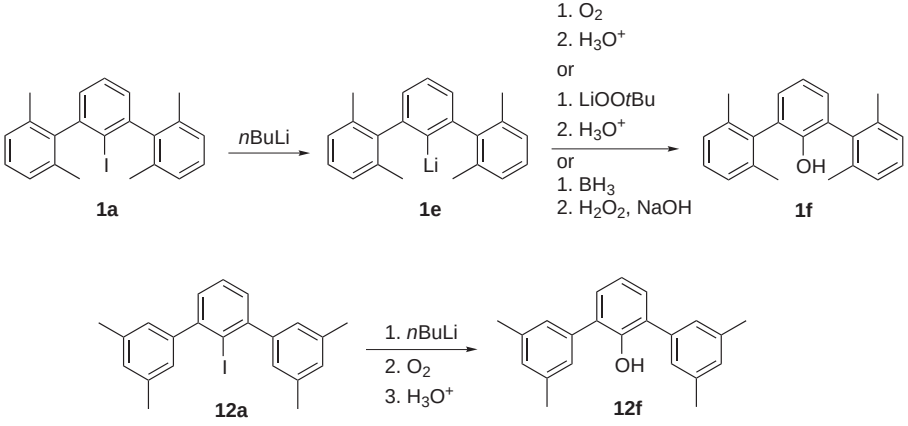
SCHEME 6

scribed in[23]. As with **1d** [23], the *cis* and *erythro* products were found in excess when the modified methanols **8d** and **9d** were used. With the cyclohexane ester **10** and the methylnaphthylated alcohol **9d**, also a very good *cis*/*trans* ratio of >97:3 was found. In contrast, the isopropylated methanol **8d** was less selective, and even less reproducible. Varying ratios were found for *cis*-**10**/*trans*-**10**, from 80:20 to >97:3. This finding is supported by the data obtained for acyclic butanoate **11**. The *threo*/*erythro* ratios obtained with **8d** (22:78) were smaller than those obtained with **1d** and **9d** (both 15:85).

Other Acids and Bases: m-Terphenyl Phenols and Aniline

With *m*-terphenylmethanols, and the respective carboxylic and sulfinic acids[19–22], only a small pK_a range of acids and bases was covered. Therefore, alternative reactions to introduce further functional groups into the 2′ position of the *m*-terphenyl have been investigated.

In the first reaction, the 2′-iodo-*m*-terphenyl **1a** [19] was lithiated, and the intermediate **1e** was oxidized to give the phenol **1f** (Scheme 7). Oxygen and lithium *tert*-butyl peroxide could be used as oxidants. Furthermore, the lithium compound **1e** was also quenched with borane and then oxidized with hydrogen peroxide. In all cases, the phenol **1f** could be obtained, but only in moderate yields (max. 25%).

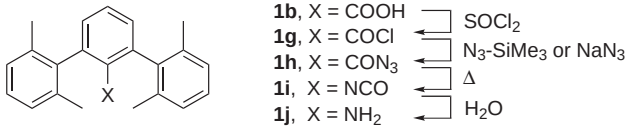


SCHEME 7

The same reaction was possible for the 3,5-dimethylated analog **12f** starting from iodide **12a** [19]. In protonation reactions, however, no special selectivity is expected for phenols **1f** and **12f** because phenols are more acidic than alcohols (Scheme 7). The competition between a general and specific

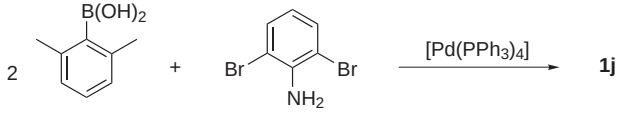
protonation – protonation by any acid or specifically by protonated solvent molecules – is determined by the concentration of protonated solvent molecules, thus by the acidity of the proton source[7,34] (for general and specific acid catalysis, see[35], for general and specific protonation, see[36]). Indeed, no special *cis* or *erythro* selectivity was found.

So far, *m*-terphenyls had only been synthesized as acids, no basic functionalities like an amino group were introduced. We have realized two ways to obtain *m*-terphenyl-2′-amine **1j**. The first approach exploits a rearrangement reaction. Starting from acid **1b**[19], acid chloride **1g** was synthesized and reacted with an azide source (trimethylsilyl azide or sodium azide). The resulting *m*-terphenyl azide **1h** was allowed to decompose at elevated temperature and rearranged to give isocyanate **1i**. Subsequent hydrolysis resulted in the formation of the aniline **1j** (Scheme 8).



SCHEME 8

Alternatively, the 2′-amino-*m*-terphenyl **1j** can also be built up starting from 2,6-dibromoaniline (**14**). A double Suzuki coupling of two equivalents of boronic acid[37] **13** with 2,6-dibromoaniline (**14**) resulted in the formation of the same aniline **1j** (Scheme 9).



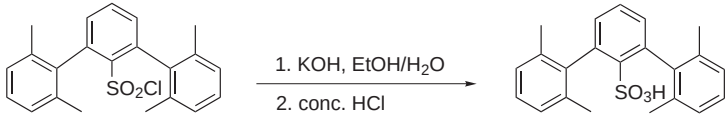
13 **14**

SCHEME 9

The basicity of the new aniline **1j** was investigated in ethanolic solution using a method which was established to determine relative basicities for a large number of other sterically hindered bases[38,39]. A dilute solution of Thymol Blue was slowly titrated with a base, and the UV spectrum was recorded. The resulting log *K* values are relative basicities. Table I compares different bases. The dimethylaryl rings *ortho* to the amino function lower the basicity of the new aniline **1j** by more than one order of magnitude.

m-Terphenylsulfonic Acids and Esters – Methylation Reactions

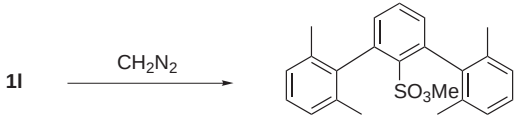
As observed in many cases, the reactivity of the functional group in position 2′ of a sterically shielded *m*-terphenyl is reduced, for instance the reactivity of sulfonyl chloride **1k** [21]. Only under harsh conditions this chloride[23] can be hydrolyzed to give sulfonic acid **1l** (Scheme 10). The use of ethanol to enhance the solubility was crucial.



1k **1l**

SCHEME 10

Due to the strong acidity of sulfonic acids, the steric effect of the *m*-terphenyl moiety will probably have no large influence on the behaviour of this acid. However, the shielding should have an influence on the chemistry of the sulfonic acid derivatives, for instance esters. Methyl ester **1m** is a sterically shielded analog of dimethyl sulfate or methyl tosylate, well-known alkylating agents. It was synthesized by reaction of sulfonic acid **1l** with diazomethane (Scheme 11).



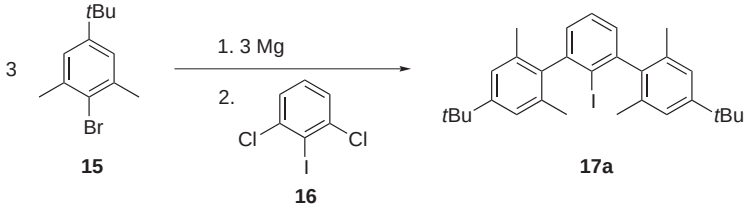
1m

SCHEME 11

TABLE I
log *K* values (relative basicities) for different bases obtained by UV titration of Thymol Blue (ca. 50 μmol/l) in ethanol (log *K*(Thymol Blue) ≡ 0)

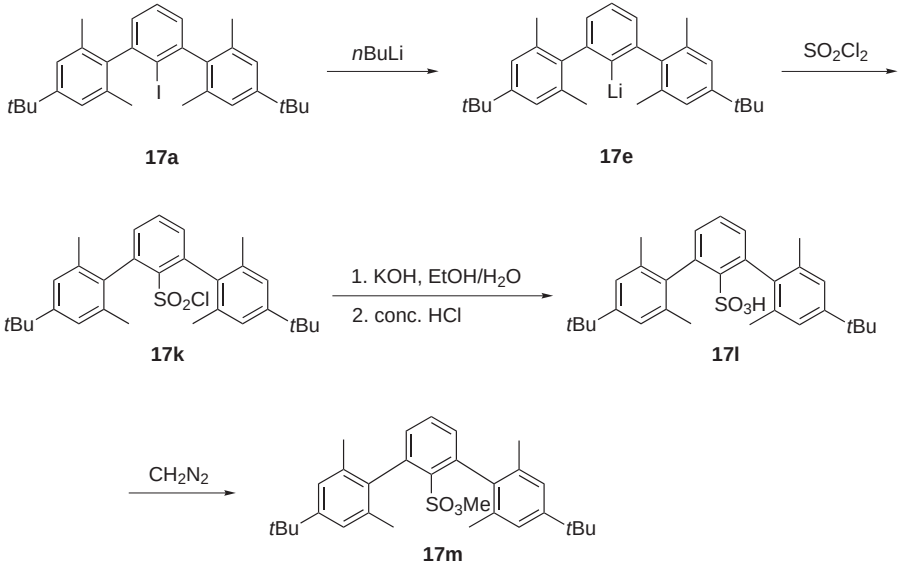
Base	log *K*
Pyridine	0 ... –0.2
2,6-Dimethylpyridine	1.2 ... 1.3
Aniline	0.6
2,6-Dimethylaniline	–0.3
Compound **1j**	–1.0

To enhance the solubility of acid **1l** and methyl ester **1m**, again, the outer benzene rings of the *m*-terphenyl moiety were substituted by *tert*-butyl groups in positions 4 and 4″. The *tert*-butyl-substituted *m*-terphenyl **17a** was built up by the Hart reaction[17] using *tert*-butylated aryl bromide **15** (Scheme 12) and 1,3-dichloro-2-iodobenzene (**16**).



SCHEME 12

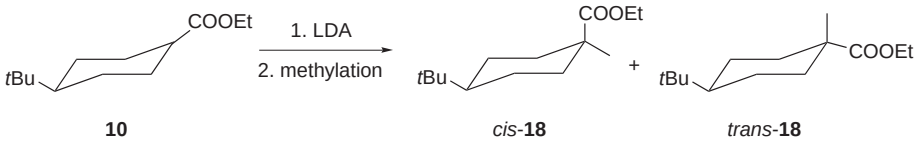
Starting from iodide **17a**, lithiation and following reaction of the lithiated compound **17e** with sulfuryl chloride gave sulfochloride **17k**. Hydrolysis to acid **17l** and reaction with diazomethane yielded methyl sulfonate **17m** (Scheme 13).



SCHEME 13

Then, esters **1m** and **17m** were investigated as alkylating reagents in a diastereoselective methylation of the ester enolate of **10** (Scheme 14). Both axial and equatorial attacks on the carbanion are possible, and two diastereo-

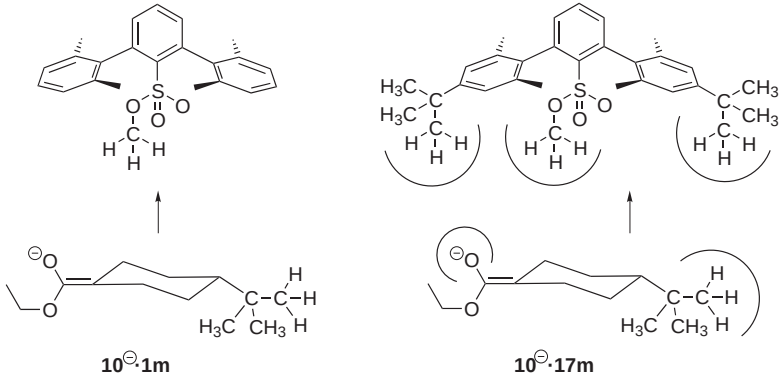
isomers of **18** are formed. The relative orientation of the *tert*-butyl and ester groups define *cis*-**18** and *trans*-**18**. The predominant equatorial attack leads to more *cis*- than *trans*-**18**.



10 *cis*-**18** *trans*-**18**

SCHEME 14

Indeed, the shielding of the methyl sulfonate group in *m*-terphenyl esters **1m** and **17m** had an influence on their alkylating ability. The smaller methyl *m*-terphenylsulfonate **1m** showed a *cis*/*trans* selectivity for the methylation of deprotonated cyclohexanecarboxylate **10** (87:13) which hardly differed from that found for methyl tosylate (90:10). However, the sterically more shielded methyl 4,4″-di-*tert*-butyl-*m*-terphenylsulfonate **17m** did not methylate the substrate at all. The change from the hydrogen atoms in 4 and 4″ positions to the *tert*-butyl groups had an unexpectedly dramatic influence on the methylating ability. Figure 2 shows the steric interactions that may be responsible for the inhibition of the methylation of enolate of **10** by *m*-terphenylsulfonate **17m**. In order to find a special selectivity, a fine-tuning of the steric shielding will be necessary.



10$^{\ominus}$**·1m** **10**$^{\ominus}$**·17m**

FIG. 2

Steric interactions in the methylation of deprotonated ethyl 4-*tert*-butylcyclohexane-1-carboxylate **10**$^{\ominus}$ by two different methyl *m*-terphenylsulfonates (left: **1m**, right: **17m**). The large *tert*-butyl groups in **17m** may repulse the enolate, thus prohibiting the alkylation

EXPERIMENTAL

General Remarks

Column chromatography was carried out on silica gel. Melting points are uncorrected. Elemental analyses were carried out with VarioEl, Elementaranalysensysteme GmbH. In some cases, the analyzed compounds contained solvent, which was also detected in the NMR. IR spectra were recorded on a Perkin–Elmer 1600 Series ($\tilde{\nu}$ is given in cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 or Bruker AM 300 (200–300 MHz for ^1H, 50–75 MHz for ^{13}C). Chemical shifts (δ) are given in ppm relative to tetramethylsilane, coupling constants (J) are given in Hz. MS spectra were recorded on a Finnegan MAT 8230. *Safety remark*: Azide **1h** was never isolated but decomposed in solution.

2,2″,6,6″-Tetramethyl-1,1′:3′,1″-terphenyl-2′ol (**1f**)

Method A) By lithiation and reaction with oxygen. Under nitrogen, iodide **1a** [19] (1.00 g, 2.42 mmol) in cyclohexane (15 ml) was reacted with butyllithium (2.5 M solution in hexane, 1.0 ml, 2.5 mmol). After a few minutes, the mixture turned turbid and was then stirred at room temperature for additional 15 h. Then oxygen gas was bubbled through the mixture for 2–3 h. After addition of 2 M hydrochloric acid (10 ml), the layers were separated and the aqueous layer was extracted twice with diethyl ether. The combined organic layer was dried with anhydrous magnesium sulfate, the solvents were evaporated in vacuo and the crude product was purified by chromatography (silica gel, dichloromethane/cyclohexane, 1:1), giving 148 mg (20%) of **1f**.

Method B) By lithiation and reaction with lithium tert-butyl peroxide. Lithium *tert*-butyl peroxide was prepared by reaction of 2.5–3 M hydrogen peroxide in nonane (420 µl, 2.1–2.5 mmol) with 2.5 M butyllithium in hexane (10.0 ml, 25.0 mmol) at –70 °C in THF (10 ml). Separately, iodo-*m*-terphenyl **1a** [19] (366 mg, 0.888 mmol) was reacted with 2.5 M butyllithium in hexane (360 µl, 0.900 mmol) in THF (10 ml). At –75 °C, this solution was added dropwise to the THF solution of lithium *tert*-butyl peroxide, the mixture was stirred at this temperature for additional 2 h, and stirring was continued at room temperature for 3 days. After work-up described above, GC analysis (SE 30, 25 m) determined a yield of ca. 10% of **1f**. An analogous reaction in cyclohexane at 0 °C gave ca. 11% of **1f**. The reaction of lithiated *m*-terphenyl **1e** (409 mg, 1.40 mmol) with a solution of lithium *tert*-butyl peroxide (prepared from a 75% solution of hydrogen peroxide in di-*tert*-butyl peroxide (0.33 ml, 2.5 mmol) with 2.5 M butyllithium in hexane (720 µl, 1.80 mmol)) in cyclohexane (25 ml) at room temperature gave ca. 25% of **1f** (GC analysis).

Method C) By reaction with borane and oxidation with hydrogen peroxide. In THF (15 ml), iodo-*m*-terphenyl **1a** [19] (412 mg, 1.00 mmol) was reacted with 2.5 M butyllithium in hexane (650 µl, 1.63 mmol). After 4 h of stirring at room temperature, this mixture was cooled to –78 °C, and 1 N borane in THF (5.0 ml, 5.0 mmol) was added. After stirring at room temperature for 15 h, the mixture was carefully hydrolyzed at 0 °C using a mixture of 30% hydrogen peroxide (4.5 ml) and 3 M sodium hydroxide (4.5 ml). After stirring the mixture at room temperature for 4 days, potassium carbonate (8.0 g) was added and the mixture was extracted three times with THF. The organic layer was dried with anhydrous magnesium sulfate, the solvent was evaporated and the yield was determined by GC: 17 and 25% in two batches.

For $C_{22}H_{22}O$ (302.4) calculated: 87.38% C, 7.33% H; found: 87.36% C, 7.35% H. IR (KBr): 3482, 3431 (OH); 3057 (CH arom.); 2945, 2917, 2854 (CH aliph.); 1582 (arom.); 1448, 1375, 1320, 1217, 1162, 1116, 1070, 830, 798, 770. ^{1}H NMR (300 MHz, $CDCl_3$): 2.10 s, 12 H (CH_3); 4.52 br s, 1 H (OH); 7.05 m_c, 3 H (Ar-H); 7.1–7.3 m, 6 H (Ar-H). MS (EI, 70 eV), *m/z* (%): 302 (100) [M^+], 287 (41) [$M^+ - CH_3$], 272 (8) [$M^+ - 2\ CH_3$]. MS (CI, isobutane), *m/z* (%): 303 (100) [$M^+ + H$].

2,2″,6,6″-Tetramethyl-1,1′:3′,1″-terphenyl-2′-amine (**1j**)

*Method A) From acid **1b** by rearrangement*. 2,2″,6,6″-Tetramethyl-1,1′:3′,1″-terphenyl-2′-carboxylic acid[19] (**1b**; 100 mg, 0.300 mmol) was mixed with freshly distilled thionyl chloride (53 mg, 0.450 mmol) and the mixture was heated to reflux for 1 h. Excess thionyl chloride was distilled off and its remaining traces were removed in vacuo (<0.1 mbar). IR check showed complete conversion of acid **1b** to acid chloride **1g**. IR (KBr): 1786 (COCl).

1. With trimethylsilyl azide. Under nitrogen, crude acid chloride **1g** was dissolved in dry toluene (5 ml), trimethylsilyl azide (0.5 ml, 4 mmol) was added, and after 3 h of stirring at room temperature, the mixture was heated to reflux for 10 h. After evaporation of the solvent in vacuo, IR check showed the production of isocyanate **1i** besides small amounts of acid chloride **1g**. IR (KBr): 2916 (CH_3); 2245 (N=C=O); 1786 (COCl). Hydrolysis of the crude isocyanate **1i** was achieved by adding a small amount of acetone (ca. 100 µl) and concentrated sodium hydroxide (2 ml). The mixture was heated to reflux for 2 h, the solvent was evaporated in vacuo and the yellowish residue was dissolved in diethyl ether and extracted four times with semi-concentrated hydrochloric acid. 30% Sodium hydroxide was added carefully until the mixture was strongly alkaline, and the mixture was extracted four times with diethyl ether. The combined ether layer was dried with anhydrous magnesium sulfate and evaporated in vacuo giving a slightly yellow residue. Recrystallization from cyclohexane gave **1j** (58 mg, 64% based on acid **1b**) as white crystals. M.p. 98 °C.

2. With sodium azide. Crude acid chloride **1g** was dissolved in dry DMF (5 ml). Under nitrogen, sodium azide (30 mg, 0.460 mmol) was added at 0 °C. After stirring at room temperature for 1 h, at reflux for 2 h and at room temperature for additional 15 h, the mixture was hydrolyzed with water (7.5 ml) (exothermic reaction), and a white precipitate formed. The mixture was cooled and extracted four times with diethyl ether (5 ml). The combined organic layer was dried with anhydrous magnesium sulfate, the solvent was evaporated and the remaining yellowish crystals were recrystallized from cyclohexane giving **1j** (67 mg, 73% based on acid **1b**). M.p. 98 °C.

Method B) By Suzuki coupling.

1. 2,6-Dimethylbenzeneboronic acid (**13**). Under nitrogen, 2-bromo-1,3-dimethylbenzene[40] (5.00 g, 27 mmol) in dry THF (5 ml) was added dropwise to magnesium (690 mg, 28 mmol) in dry THF (20 ml). The mixture was stirred at 50 °C for 12 h, before it was added dropwise to trimethyl borate (4.0 ml, d_{20} = 0.997 g/ml, 36 mmol, dried with lithium chloride) in diethyl ether (20 ml) at –50 °C. A white precipitate formed, additional diethyl ether (7 ml) was added and stirring was continued at –75 °C for 30 min. The mixture was allowed to warm to 0 °C during 1.5 h, first water (7 ml) and then 10% sulfuric acid (6 ml) was slowly added while keeping the temperature between 0 and 15 °C. After addition of water (8 ml), the organic layer was separated, and the aqueous layer was extracted three times with diethyl ether. The combined organic layer was dried with anhydrous magnesium sulfate and the sol-

vent was removed in vacuo. The slightly yellow residue was recrystallized several times from water and dried giving 916 mg (23%, lit.[37]: 50%). M.p. 121–124 °C, lit.[37]: 125 °C.

2. Coupling. 2,6-Dimethylbenzeneboronic acid (**13**; 920 mg, 7.5 mmol) in ethanol (6 ml) was added to a solution of 2,6-dibromoaniline (**14**; Fluka, 620 mg, 2.5 mmol) in benzene (30 ml). Aqueous 2 M sodium carbonate (10 ml) was added, the reaction vessel was flushed with nitrogen, degassed with ultrasound and flushed again with nitrogen. Then tetrakis-(triphenylphosphine)palladium(0) (ca. 0.42 g, 0.36 mmol) was added and the mixture was heated to reflux for 1.5 days and stirred at room temperature for 7 days. The layers were separated and the aqueous layer was extracted twice with diethyl ether (10 ml). The combined organic layer was dried with anhydrous magnesium sulfate and the solvent was evaporated in vacuo. The dark brown residue was dissolved in small amount of dichloromethane and purified by chromatography (silica gel, cyclohexane/dichloromethane, 1:1), giving 98 mg (13%) of **1j**. M.p. 104–106 °C. For $C_{22}H_{23}N$ (301.4) calculated: 87.66% C, 7.68% H, 4.55% N; found: 87.55% C, 7.60% H, 4.59% N. IR (KBr): 3460, 3368, 2916, 1603, 1446, 1376, 1260, 773, 551. Raman: 3040, 3021, 2951, 2913, 2860, 1599, 1448, 1378, 1293, 1247, 1167, 1074, 1006, 614, 554, 513, 347, 328, 213. ^{1}H NMR (200 MHz, $CDCI_3$): 2.1 s, 12 H (CH_3); 6.85–6.9 m, 3 H (4′-H, 5′-H, 6′-H); 7.1–7.2 m, 6 H (3-H, 3″-H, 4-H, 4″-H, 5-H, 5″-H). MS (EI, 70 eV), *m/z* (%): 301 (100) [M^+], 300 (10), 286 (35), 284 (13), 271 (13), 269 (14). MS (CI, isobutane), *m/z* (%): 302 (10) [$M^+ + H$], 190 (6), 75 (100).

2,2″,6,6″-Tetramethyl-1,1′:3′,1″-terphenyl-2′-sulfonic Acid (**1l**)

The sulfochloride **1k**[21] (105 mg, 0.285 mmol) and potassium hydroxide (140 mg, 2.50 mmol) were heated to reflux in an ethanol/water mixture (1:1, 4 ml) for 2 days. After evaporation of large part of the solvent, the residue was acidified with concentrated hydrochloric acid. The mixture was extracted three times diethyl ether (3 ml). The combined organic layer was dried with anhydrous magnesium sulfate. Evaporation of the solvent in vacuo gave **1l** (86 mg, 86%) as a slightly yellow solid. M.p. 220 °C (dec.). IR (KBr): 3440 (OH); 2916 (CH aliph.); 1581 (arom.); 1458, 1396, 1376, 1226 (S=O); 1130, 1069, 1023, 774, 756, 745. ^{1}H NMR (200 MHz, $CDCl_3$): 2.01 s, 12 H (CH_3); 2.97 br s, 3 H ($SO_3H + H_2O$); 6.9–7.0, 7.4–7.7 2 m, 9 H (Ar-H). ^{1}H NMR (200 MHz, DMSO-d_6): 1.98 s, 12 H (CH_3); 6.77 d, 2 H, J = 7.5 (3, 5-H); 6.8–7.0 m, 6 H (Ar-H); 7.36 t, 1 H, J = 7.5 (4-H). MS (EI, 70 eV), *m/z* (%): 366 (87) [M^+], 284 (63) [$M^+ - H_2SO_3$], 269 (100) [$M^+ - H_2SO_3 - CH_3$], 253 (69), 239 (27). MS (CI, isobutane), *m/z* (%): 367 (25) [$M^+ + H$], 287 (39) [$M^+ + H - SO_3$], 214 (16), 197 (15), 69 (100). HR-MS: $C_{22}H_{22}SO_3$ calculated: 366.12897; found: 366.12870; $C_{21}{}^{13}CH_{22}SO_3$ calculated: 367.13232; found: 367.13220.

Methyl 2,2″,6,6″-Tetramethyl-1,1′:3′,1″-terphenyl-2′-sulfonate (**1m**)

Under nitrogen, a solution of sulfonic acid **1l** (38 mg, 0.104 mmol) in THF (5 ml) was added to a 0.31 M solution of diazomethane in diethyl ether (500 µl, 0.155 mmol). After stirring for 5 h, the solvents were evaporated in vacuo. Spectroscopically, no impurities could be detected. For $C_{23}H_{24}O_3S$ calculated: 72.60% C, 6.36% H; for $C_{23}H_{24}O_3S{\cdot}0.1CH_2Cl_2$ calculated: 71.33% C, 6.27% H; found: 71.38% C, 6.29% H. ^{1}H NMR (200 MHz, $CDCl_3$): 2.07 s, 12 H (Ar-CH_3); 3.18 s, 3 H (SO_3CH_3); 7.0–7.3 m, 8 H (Ar-H); 7.69 t, 1 H, J = 7.8 (4-H). MS (EI, 70 eV), *m/z* (%): 380 (100) [M^+], 348 (10) [$M^+ - CH_4O$], 284 (80) [$M^+ - HSO_3CH_3$], 269 (74) [$M^+ - HSO_3CH_3 - CH_3$], 253 (33), 179 (13), 126 (18). HR-MS: $C_{23}H_{24}SO_3$ calculated: 380.14462; found: 380.14450; $C_{22}{}^{13}CH_{24}SO_3$ calculated: 381.14798; found: 381.14770.

Synthesis of Concave Esters **4a** and **5a**. General Procedure

Under nitrogen, tetrabromide **3**[20] and two equivalents of a phenylenedithiol dissolved in an ethanol/toluene mixture (1:1, 800 ml) were added dropwise to an intensively stirred, refluxing solution of potassium hydroxide (ca. 130 mmol) in dry ethanol (500 ml) during 10 h. After 15 h at room temperature, the solvents were evaporated in vacuo, the residue was dissolved in water (200 ml) and dichloromethane (200 ml), and the aqueous layer was extracted four times with dichloromethane (50 ml). The combined organic layer was dried with anhydrous magnesium sulfate and the solvent was evaporated in vacuo, the residue was dissolved in dichloromethane, and the solution was filtered through basic aluminium oxide (4 × 10 cm). Washing with dichloromethane was continued until TLC (silica gel, dichloromethane) showed no more product. After evaporation of the solvent in vacuo, the residue was purified twice by chromatography (silica gel, dichloromethane; dichloromethane/cyclohexane, 3:1) and recrystallized from diethyl ether.

Methyl $1^5,7^5$-di-tert-butyl-2,6,8,12-tetrathia-1(1,3,2),4(1,4),7(1,3,2),10(1,4),13(1,3)-pentabenzenabicyclo[5.5.1]tridecaphane-13^2-carboxylate (**4a**). Tetrabromide **3**[20] (2.40 g, 3.11 mmol) and 1,4-phenylenedithiol[41] (1.06 g, 6.22 mmol) with potassium hydroxide (7.00 g, 125 mmol). Yield 418 mg (17%) of a white solid. M.p. > 250 °C (dec.). For $C_{48}H_{52}O_2S_4$ (788.9) calculated: 73.05% C, 6.64% H; found: 72.52% C, 6.76% H. IR (KBr): 2961 (CH aliph.); 1736 (C=O); 1607 (arom.); 1439 (CH aliph.); 1265, 1117 (C–O). ^{1}H NMR (300 MHz, $CDCl_3$): 1.29 s, 18 H ($C(CH_3)_3$); 2.29 d, 4 H, *J* = 10.0 (ArC**H**$_a$H$_b$); 2.70 s, 3 H (OCH_3); 3.09 d, 4 H, *J* = 10.0 (ArCH$_a$**H**$_b$); 3.67 d, 4 H, *J* = 13.5 (Ar′C**H**$_a$H$_b$); 3.74 d, 4 H, *J* = 13.5 (Ar′CH$_a$**H**$_b$); 6.89 s, 4 H (Ar-H); 7.26 m$_c$, 8 H (Ar-H); 7.4–7.5 m, 3 H (Ar-H). MS (EI, 70 eV), *m/z* (%): 789 (56), 788 (100), 756 (67), 620 (35), 588 (24), 483 (17), 451 (24).

Methyl $1^5,7^5$-di-tert-butyl-2,6,8,12-tetrathia-1(1,3,2),4(1,3),7(1,3,2),10(1,3),13(1,3)-pentabenzenabicyclo[5.5.1]tridecaphane-13^2-carboxylate (**5a**). Tetrabromide **3**[20] (2.50 g, 3.24 mmol) and 1,3-phenylenedithiol[19] (1.10 g, 6.48 mmol) with potassium hydroxide (7.30 g, 130 mmol). Yield 560 mg (22%) of a white solid. M.p. > 250 °C (dec.). IR (KBr): 2960 (CH aliph.); 1730 (C=O); 1604 (arom.), 1443 (C-H aliph.); 1266, 1118 (C–O). ^{1}H NMR (300 MHz, $CDCl_3$): 1.32 s, 18 H ($C(CH_3)_3$); 2.87 s, 3 H (OCH_3); 2.88 d, 4 H, *J* = 10.5 (ArC**H**$_a$H$_b$); 3.44 d, 4 H, *J* = 10.5 (ArCH$_a$**H**$_b$); 3.48 d, 4 H, *J* = 14.0 (Ar′C**H**$_a$H$_b$); 3.59 d, 4 H, *J* = 14.0 (Ar′CH$_a$**H**$_b$); 6.64 br s, 2 H (Ar-H); 6.73 m$_c$, 1 H (Ar-H); 6.91 d, 2 H, *J* = 7.5 (Ar-H); 7.13 d, 4 H, *J* = 8.0 (Ar-H); 7.2–7.3 m, 6 H (Ar-H). MS (EI, 70 eV), *m/z* (%): 789 (8), 788 (15), 756 (100), 620 (16), 588 (18), 483 (9), 451 (17).

Synthesis of Concave Acids **4b** and **5b**. General Procedure

Under nitrogen, ester **4a** or **5a**, lithium iodide and 12-crown-4 were dissolved in dry pyridine (70 ml). The mixture was heated to reflux until two-dimensional TLC (silica gel, 1. dichloromethane, 2. diethyl ether) showed almost total conversion (264–329 h). Then, concentrated hydrochloric acid/ice (ca. 250 ml, 1:1) was added and the mixture was extracted four times with dichloromethane (50 ml). The combined organic layer was extracted twice with 6 M hydrochloric acid (50 ml) and once with water (50 ml). After drying with anhydrous magnesium sulfate, the solvent was evaporated in vacuo, the residue was purified by chromatography (silica gel, dichloromethane/diethyl ether, 40:1) and recrystallized from toluene.

$1^5,7^5$-Di-tert-butyl-2,6,8,12-tetrathia-1(1,3,2),4(1,4),7(1,3,2),10(1,4),13(1,3)-pentabenzenabicyclo[5.5.1]tridecaphane-13^2-carboxylic acid (**4b**). Ester **4a** (363 mg, 0.460 mmol), lithium iodide (1.23 g, 9.2 mmol) and 12-crown-4 (ca. 460 µl) were reacted as described for ca. 329 h.

Yield 184 mg (52%) of a white solid. M.p. > 310 °C (dec.). For $C_{47}H_{50}O_2S_4 \cdot C_7H_8$ (774.9 + 92.1) calculated: 74.78% C, 6.74% H; found: 74.44% C, 6.83% H. IR (KBr): 3050–2800 (OH); 2961 (CH aliph.); 1701 (C=O); 1605, 1508 (arom.); 1442 (CH aliph.). ^{1}H NMR (200 MHz, $CDCl_3$): 1.31 s, 18 H ($C(CH_3)_3$); 2.29 d, 4 H, *J* = 10.1 (ArC**H**$_a$H$_b$); 2.36 s, 3 H ($ArCH_3$, toluene); 3.11 d, 4 H, *J* = 10.1 (ArCH$_a$**H**$_b$); 3.65 d, 4 H, *J* = 13.4 (Ar′C**H**$_a$H$_b$); 3.74 d, 4 H, *J* = 13.4 (Ar′CH$_a$**H**$_b$); 6.86 s, 4 H (Ar-H); 7.1–7.3 m, 8 H (Ar-H) + 5 H (toluene); 7.4–7.6 m, 3 H (Ar-H). MS (EI, 70 eV), *m/z* (%): 775 (37), 774 (67), 756 (37), 637 (47), 606 (32), 573 (27), 469 (25), 423 (100).

1^5,7^5-Di-tert-butyl-2,6,8,12-tetrathia-1(1,3,2),4(1,3),7(1,3,2),10(1,3),13(1,3)-pentabenzenabicyclo[5.5.1]tridecaphane-13^2-carboxylic acid (**5b**). Ester **5a** (556 mg, 0.705 mmol), lithium iodide (1.88 g, 14.1 mmol) and 12-crown-4 (ca. 700 μl) were reacted as described for ca. 264 h. Yield 228 mg (42%) of a white solid. M.p. > 320 °C (dec.). For $C_{47}H_{50}O_2S_4$ (774.9) calculated: 72.83% C, 6.50% H; found: 72.78% C, 6.48% H. IR (KBr): 3055–2900 (OH); 2962 (CH aliph.); 1751 (C=O); 1604 (arom.); 1444 (CH aliph.). ^{1}H NMR (200 MHz, $CDCl_3$): 1.33 s, 18 H ($C(CH_3)_3$); 2.90 d, 4 H, *J* = 10.9 (ArC**H**$_a$H$_b$); 3.48 d, 4 H, *J* = 14.2 (Ar′C**H**$_a$H$_b$); 3.49 d, 4 H, *J* = 10.9 (ArCH$_a$**H**$_b$); 3.59 d, 4 H, *J* = 14.2 (Ar′CH$_a$**H**$_b$); 6.69 br s, 2 H (Ar-H); 6.76 m$_c$, 1 H (Ar-H); 6.90 d, 2 H, *J* = 6.9 (Ar-H); 7.11 brs, 4 H (Ar-H); 7.2–7.4 m, 6 H (Ar-H). MS (EI, 70 eV), *m/z* (%): 775 (5), 774 (8), 756 (100), 637 (30), 606 (13), 573 (11), 469 (15), 436 (18), 423 (93).

Synthesis of Iodo-*m*-terphenyls **8a** and **9a**. General Procedure

To obtain 300 mmol of an aryl Grignard reagent, 302 mmol of an aryl bromide in dry THF (220 ml) was slowly added to magnesium (7.35 g, 302 mmol) in dry THF (80 ml). At room temperature and under nitrogen, 1,3-dichloro-2-iodobenzene (**16**; 20.5 g, 75.0 mmol) in THF (300 ml) was added to this solution during 2 h and the mixture was stirred for 6 h. While cooling with ice, iodine (88.8 g, 0.35 mol) in THF (300 ml) was added slowly and the mixture was stirred for 15 h. Excess iodine was destroyed with aqueous sodium dithionite and most of the solvent was evaporated in vacuo. The aqueous residue was extracted four times with diethyl ether (1 l total). After drying of the combined organic layer with anhydrous magnesium sulfate, the solvents were evaporated in vacuo and volatile by-products were distilled off at 100 °C and 0.1 mbar.

2′-Iodo-2,2″,6,6″-tetraisopropyl-1,1′:3′,1″-terphenyl (**8a**)

2-Bromo-1,3-diisopropylbenzene[42] (2.88 g, 11.9 mmol), 1,3-dichloro-2-iodobenzene[43] (**16**; 680 mg, 2.49 mmol), magnesium (252 mg, 10.4 mmol), iodine (2.84 g, 11.2 mmol) and THF (30 ml total) were reacted according to the general procedure. The brown residue was dissolved in cyclohexane and filtered through silica gel. The solvent was evaporated and the residue was recrystallized from ethanol. Yield 750 mg (59%). M.p. 151–153 °C. GC purity (SE 30, 25 m): 95%. IR (KBr): 3065 (CH arom.); 2957, 2865 (CH aliph.); 1578 (arom.); 1461, 1382, 1360, 1057, 1002, 802, 791, 756. ^{1}H NMR (200 MHz, $CDCl_3$): 1.24 d, 12 H, *J* = 6.8 (CH_3); 3.49 sept, 4 H, *J* = 6.8 (C**H**$(CH_3)_2$); 7.0–7.3 m, 9 H (Ar-H). MS (EI, 70 eV), *m/z* (%): 524 (100) [M^+], 481 (11) [$M^+ - C_3H_7$], 381 (18), 339 (32). MS (CI, isobutane), *m/z* (%): 525 (100) [$M^+ + H$], 397 (16) [$M^+ - I$].

2-Iodo-1,3-bis(2-methyl-1-naphthyl)benzene (**9a**)

1-Bromo-2-methylnaphthalene (Janssen, 3.67 g, 15.8 mmol), 1,3-dichloro-2-iodobenzene[43] (**16**; 1.08 g, 3.96 mmol), magnesium (385 mg, 15.8 mmol), iodine (4.39 g, 17.3 mmol) and THF (60 ml total) were reacted according to the general procedure. The residue was recrystallized from toluene/methanol. Yield 921 mg (48%). M.p. > 210–215 °C. IR (KBr): 3047 (CH arom.); 1617, 1594, 1564, 1506 (arom.); 1372, 1261, 1009, 811, 798, 743. ^{1}H NMR (200 MHz, $CDCl_3$): 2.30 s, 6 H (CH_3); 7.3–7.5 m, 10 H (Ar-H); 7.62 m_c (AB_2), 1 H, $J \approx 7.6$ (4-H); 7.8–7.9 m, 4 H (Ar-H). MS (EI, 70 eV), *m/z* (%): 484 (100) [M^+], 357 (18) [$M^+ - I$], 342 (20) [$M^+ - I - CH_3$], 242 (14). MS (CI, isobutane), *m/z* (%): 485 (100) [$M^+ + H$].

Syntheses of 2,6-Diarylbenzaldehydes **8c** and **9c**. General Procedure

Under nitrogen, the 2,6-diaryl-1-iodobenzene **8a** or **9a** in cyclohexane was reacted with butyllithium. After several minutes a white precipitate was formed. The mixture was stirred at room temperature for 15 h before excess methyl formate was added. The mixture turned viscous and the precipitate began to dissolve. After stirring for 3 h, water (20 ml) was added and the mixture was extracted three times with diethyl ether (100 ml total). The combined organic layer was washed with water and dried, the solvent was evaporated and the yellowish residue was recrystallized from hexane.

2,6-Bis(2,6-diisopropylphenyl)benzaldehyde (**8c**). **8a** (described in[44], but synthesized according to[17,18]) (112 mg, 214 μmol), butyllithium (300 μmol), methyl formate (120 μl, 1.94 mmol) in cyclohexane (1.2 ml). Yield 28 mg (31%) of **8c**. IR (KBr): 2958, 2864 (CH aliph.); 1698 (C=O); 1577 (arom.); 1459, 1381, 1361, 1326, 1250, 1191, 1055, 804, 792, 757. ^{1}H NMR (300 MHz, $CDCl_3$): 1.02, 1.12 2 d, 24 H, J = 6.9 ($CH(C\mathbf{H}_3)_2$); 2.52 sept, 4 H, J = 6.9 ($C\mathbf{H}(CH_3)_2$); 7.2–7.3 m, 6 H (Ar-H); 7.38 m_c, 2 H (3, 5-H); 7.64 t, 1 H, J = 7.6 (4-H); 9.70 s, 1 H (CHO). MS (Cl, isobutane), *m/z* (%): 427 (100) [$M^+ + H$], 415 (11), 399 (51) [$M^+ + H - CO$].

2,6-Bis(2-methyl-1-naphthyl)benzaldehyde (**9c**). **9a** (550 mg, 1.14 mmol), butyllithium (1.5 mmol), methyl formate (500 μl, 8.08 mmol) in cyclohexane (5 ml). Crude yield of **9c**: 440 mg. GC purity (SE 30, 25 m): 75%. IR (KBr): 2920 (CH arom.); 1697 (C=O); 1567, 1507 (arom.); 1375, 1262, 1028, 811.

Syntheses of 2,6-Diarylbenzyl Alcohols **8d** and **9d**. General Procedure

A solution of 2,6-diarylbenzaldehyde **8c** or **9c** in THF was added dropwise to a mixture of lithium aluminium hydride in dry THF (10 ml). The mixture was heated to reflux for 2–4 h, and then hydrolyzed carefully with water. After acidification with 1 M sulfuric acid, the mixture was extracted twice with diethyl ether (150 ml total). After drying of the organic layer with anhydrous magnesium sulfate and evaporation of the solvent, the remaining yellowish oil was recrystallized from hexane. For no benzylic alcohol **8d** and **9d** could an OH proton be observed in the ^{1}H NMR.

2,6-Bis(2,6-diisopropylphenyl)benzyl alcohol (**8d**). Benzaldehyde **8c** (85 mg, 0.20 mmol), lithium aluminium hydride (35 mg, 0.92 mmol), THF (8 and 10 ml). Yield 54 mg (63%). M.p. 193–196 °C. For $C_{31}H_{40}O$ (428.7) calculated: 86.86% C, 9.41% H; found: 86.79% C, 9.48% H. IR (KBr): 3569 (OH); 3060 (CH arom.); 2960, 2865 (CH aliph.); 1577 (arom.); 1459, 1381, 1360, 1326, 1261, 1055, 1013, 805, 792, 759. ^{1}H NMR (200 MHz, $CDCl_3$): 1.09 d, 6 H, J = 6.8 (CH_3); 1.13 d, 6 H, J = 6.9 (CH_3); 2.59 sept, 4 H, J = 6.9 ($C\mathbf{H}(CH_3)_2$); 4.05, 4.08 2 s,

2 H (C**H**$_2$OH); 7.1–7.4 m, 9 H (Ar-H). MS (EI, 70 eV), *m/z* (%): 428 (2) [M^+], 410 (100) [$M^+ - H_2O$], 353 (28) [$M^+ - H_2O - C_4H_9$], 311 (37), 283 (24), 269 (26).

2,6-Bis(2-methyl-1-naphthyl)benzyl alcohol (**9d**). Crude **9c** (300 mg, max. 776 μmol), lithium aluminium hydride (150 mg, 3.95 mmol), THF (10 ml). Yield 99 mg (33%, based on **9a**). M.p. 210–215 °C. GC purity (SE 30, 25 m): 98%. IR (KBr): 3582 (OH); 3048 (CH arom.); 2929 (CH aliph.); 1618, 1506 (arom.); 1376, 1189, 998, 811, 783, 743. ^{1}H NMR (200 MHz, $CDCl_3$): 2.29, 2.35 2 s, 6 H (CH_3); 3.9–4.0 m, 2 H (C**H**$_2$OH); 7.2–7.6, 7.8–7.9 2 m, 15 H (Ar-H). MS (EI, 70 eV), *m/z* (%): 388 (45) [M^+], 370 (100) [$M^+ - H_2O$], 355 (36) [$M^+ - H_2O - CH_3$], 339 (25), 228 (14), 170 (19). MS (CI, isobutane), *m/z* (%): 389 (8) [$M^+ + H$], 388 (22) [M^+], 371 (100) [$M^+ + H - H_2O$]. HR-MS: $C_{29}H_{24}O$ calculated: 388.18271; found: 388.18250; $C_{28}{}^{13}CH_{24}O$ calculated: 389.18607; found: 389.18600.

3,3″,5,5″-Tetramethyl-1,1′:3′,1″-terphenyl-2′-ol (**12f**)

By lithiation and reaction with oxygen: the synthesis was carried out in analogy to the synthesis of **1f**. An amount of 500 mg (1.21 mmol) of **12a** [19] gave 102 mg (28%) of **12f**. GC purity (SE 30, 25 m): >99%. For $C_{22}H_{22}O$ (302.4) calculated: 87.67% C, 7.02% H; found: 87.70% C, 7.26% H. IR (KBr): 3533 (OH); 3023 (CH arom.); 2918, 2857 (CH aliph.); 1598 (arom.); 1462, 1454, 1205, 849, 793, 700. ^{1}H NMR (300 MHz, $CDCl_3$): 2.37 s, 12 H (CH_3); 5.51 s, 1 H (OH); 7.01 t, 1 H, J = 7.8 (4-H); 7.02 m_c, 2 H (4′-H); 7.12 br s, 4 H (2′, 6′-H); 7.24 d, 2 H, J = 7.8 (3, 5-H). MS (EI, 70 eV), *m/z* (%): 302 (100) [M^+], 287 (24) [$M^+ - CH_3$], 272 (8) [$M^+ - 2\ CH_3$], 151 (10), 129 (11), 83 (42). MS (CI, isobutane), *m/z* (%): 303 (100) [$M^+ + H$], 163 (13), 157 (29), 117 (60), 99 (78).

4,4″-Di-*tert*-butyl-2′-iodo-2,2″,6,6″-tetramethyl-1,1′:3′,1″-terphenyl (**17a**)

Under nitrogen, a solution of 2-bromo-5-*tert*-butyl-1,3-dimethylbenzene[45,46] (12 g, 50 mmol) in dry THF (30 ml) was added to magnesium (1.2 g, 50 mmol) previously warmed to ca. 70 °C. The resulting mixture was heated to reflux for 2 h and, during 2 h, a solution of 1,3-dichloro-2-iodobenzene (3.4 g, 13 mmol) in dry THF (50 ml) was added dropwise at room temperature. After 8 h of reflux, the mixture was cooled with an ice bath and iodine (15 g, 60 mmol) dissolved in dry THF (50 ml) was added dropwise. Stirring was continued at room temperature for 2 days and aqueous sodium disulfite was added until the color of the solution turned to orange. A major part of the solvent was evaporated in vacuo, and the aqueous layer was extracted three times with diethyl ether (80 ml). After drying with anhydrous magnesium sulfate, the solvent was evaporated in vacuo, and volatile by-products were distilled off at ca. 100 °C and ca. 0.5 mbar. The brown residue was dissolved in cyclohexane and purified by filtration through silica gel. Yield 5.0 g (76%). M.p. 158 °C. GC purity: 98.5%. IR (KBr): 2962 (CH aliph.); 1606 (arom.); 1573 (arom.); 1453 (CH_3). ^{1}H NMR (200 MHz, $CDCl_3$): 1.35 s, 18 H ($C(CH_3)_3$); 2.01 s, 12 H (Ar-CH_3); 7.07–7.12 m, 6 H (Ar-H); 7.44 t, 1 H, J = 7.5 (5′-H). MS (EI, 70 eV), *m/z* (%): 524 (86) [M^+], 509 (100) [$M^+ - CH_3$]. HR-MS: $C_{30}H_{37}I$ calculated: 524.19403; found: 524.19370; $C_{29}{}^{13}CH_{37}I$ calculated: 525.19739; found: 525.19710.

4,4″-Di-*tert*-butyl-2,2″,6,6″-tetramethyl-1,1′:3′,1″-terphenyl-2′-sulfonyl Chloride (**17k**)

Under nitrogen, 2.5 M butyllithium in hexane (2.0 ml, 5.0 mmol) was added to a solution of iodo-*m*-terphenyl **17a** (2.6 g, 5.0 mmol) in dry cyclohexane (30 ml). The mixture turned yel-

low and a fine, colorless solid precipitated after ca. 30 min. After stirring for 20 h, the solvent was evaporated in vacuo. The remaining lithium compound **17e** was dissolved in dry THF (30 ml) at –78 °C and stirred for 10 min. Within 1 min, freshly distilled sulfuryl chloride (0.47 ml, 5.8 mmol) was added. The mixture turned red and then yellow, and was stirred at 60 °C for 1 h and at room temperature for 2 days. Then, the mixture was poured onto saturated aqueous sodium hydrogensulfate (30 ml) and extracted three times with diethyl ether (25 ml). Iodine was removed by washing with a sodium thiosulfate solution, the organic layer was washed with water (50 ml) and then dried with anhydrous magnesium sulfate. After evaporation of the solvent in vacuo, the crude product was purified by chromatography to remove the side product, a 2′-chloro-*m*-terphenyl (silica gel, dichloromethane/cyclohexane, 1:2) giving 379 mg (15%) of **17k**. M.p. 110 °C. GC purity: 95.2%. IR (KBr): 2962 (CH aliph.); 1606 (arom.); 1572 (arom.); 1452 (CH_3); 1385 (S=O); 1190 (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): 1.34 s, 18 H ($C(CH_3)_3$); 2.07 s, 12 H (Ar-CH_3); 7.10–7.30 m, 6 H (Ar-H); 7.73 t, 1 H, *J* = 7.5 (5′-H). MS (EI, 70 eV), *m/z* (%): 498, 496 (22, 49) [M^+], 483, 481 (41, 100) [$M^+ - CH_3$], 414 (31) [M^+ – SOCl], 399 (44) [M^+ – SOCl – CH_3]. HR-MS: $C_{30}H_{37}{}^{35}ClO_2S$ calculated: 496.22028; found: 496.22020; $C_{29}{}^{13}CH_{37}{}^{35}ClO_2S$ calculated: 497.22363; found: 497.22340; $C_{30}H_{37}{}^{37}ClO_2S$ calculated: 498.21732; found: 497.21720.

4,4″-Di-*tert*-butyl-2,2″,6,6″-tetramethyl-1,1′:3′,1″-terphenyl-2′-sulfonic Acid (**17l**)

Sulfonyl chloride **17k** (248 mg, 0.500 mmol) and potassium hydroxide (280 mg, 5.00 mmol) in ethanol/water (1:1, 8 ml) were heated to reflux for 1 day. After evaporation of a major part of the solvents, the residue was acidified with concentrated hydrochloric acid. After three extractions with diethyl ether (3 ml), the combined organic layer was dried with anhydrous calcium chloride, and the solvent was evaporated in vacuo giving 242 mg (100%) of a slightly yellow solid. M.p. 72 °C. IR (KBr): 3438 (OH); 2963 (CH aliph.); 1636 (arom.); 1452 (CH_3); 1361 (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): 1.32 s, 18 H ($C(CH_3)_3$); 2.02 s, 12 H (Ar-CH_3); 6.32 s, 1 H (SO_3H); 7.06–7.13 m, 6 H (Ar-H); 7.55 t, 1 H, *J* = 7.5 (5′-H). MS (EI, 70 eV), *m/z* (%): 478 (16) [M^+], 463 (38) [$M^+ - CH_3$], 414 (56) [$M^+ - SO_2$], 399 (100) [$M^+ - SO_2 - CH_3$].

Methyl 4,4″-Di-*tert*-butyl-2,2″,6,6″-tetramethyl-1,1′:3′,1″-terphenyl-2′-sulfonate (**17m**)

Under nitrogen, 0.3 M diazomethane in diethyl ether (2.5 ml, 0.75 mmol) was added to a solution of the sulfonic acid **17l** (236 mg, 0.49 mmol) in dry THF (25 ml). After stirring at room temperature for 15 h, the solvents were evaporated in vacuo giving 235 mg (98%) of crude **17m**. Chromatography (silica gel, dichloromethane) gave 137 mg (57%) of **17m**. M.p. 166 °C. GC purity: 99.9%. For $C_{31}H_{40}O_3S$ calculated: 75.57% C, 8.18% H; for $C_{31}H_{40}O_3S{\cdot}0.1CH_2Cl_2$ calculated: 74.53% C, 8.08% H; found: 74.32% C, 8.17% H. IR (KBr): 2959 (CH aliph.); 1606 (arom.); 1574 (arom.); 1454 (CH_3); 1351 (S=O); 1178 (S=O). ^{1}H NMR (200 MHz, $CDCl_3$): 1.33 s, 18 H ($C(CH_3)_3$); 2.06 s, 12 H (Ar-CH_3); 3.07 s, 3 H (SO_3CH_3); 7.11–7.21 m, 6 H (Ar-H); 7.63 t, 1 H, *J* = 7.5 (5′-H). ^{13}C NMR (50 MHz, $CDCl_3$): 21.0 q (Ar-CH_3); 31.4 q ($C(CH_3)_3$); 34.3 s ($C(CH_3)_3$); 53.8 q (SO_3CH_3); 123.9 d (C arom.); 131.2 d (C arom.); 133.0 d (C arom.); 135.2 s (C arom.); 135.6 s (C arom.); 137.1 s (C arom.); 142.6 s (C arom.); 150.1 (s, C arom.). MS (EI, 70 eV), *m/z* (%): 492 (56) [M^+], 477 (100) [$M^+ - CH_3$], 445 (5) [$M^+ - CH_3 - CH_3OH$]. HR-MS: $C_{31}H_{40}O_3S$ calculated: 492.26981; found: 492.26940; $C_{30}{}^{13}CH_{40}O_3S$ calculated: 493.27316; found: 493.27280.

Methylation of the Enolate of Ethyl 4-*tert*-Butylcyclohexane-1-carboxylate (**10**)

Ethyl 4-*tert*-butylcyclohexane-1-carboxylate (**10**; 212 mg, 1.00 mmol) was dissolved in dry THF (2 ml). At –78 °C, this solution was added dropwise to a solution of 2 M LDA (1 ml) in dry THF (10 ml). After stirring for 2 h, methylating agent (3 mmol) was added and stirring was continued at –78 °C for 1 h. After stirring at room temperature for 10 h, water (5 ml) and 2 M hydrochloric acid (2 ml) was added, and the layers were separated. The aqueous layer was extracted three times with diethyl ether (20 ml), and the combined organic layer was dried with anhydrous magnesium sulfate. Analysis by GC (SE 30, 25 m, 10 min at 80 °C, heating with 5 °C/min until 200 °C): 18.19 (*cis*-**10** and *cis*-**18**), 20.11 min (*trans*-**10**), 20.88 min (*trans*-**18**).

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