

# Combinatorial organic materials research (COMR): design, synthesis and screening of a 225-membered materials library of liquid crystalline fluorinated *p*-quaterphenyls†

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The rapid solution phase synthesis of novel liquid crystalline materials is demonstrated by utilising combinatorial and parallel methods for the preparation of a library of 225 differently fluorinated 4,4''-dipropyl-*p*-quaterphenyls. Chemical diversity was introduced into the growing oligomers *via* a convergent synthetic sequence of iodinations and Suzuki cross-couplings by using various fluorinated phenyl building blocks. A highly efficient rapid parallel purification method was developed that provided HPLC-pure library members in amounts sufficient for the characterization of bulk properties.

## Introduction

During the last decade, the concept of combinatorial chemistry emerged as a key technology in pharmaceutical research: numerous examples of lead structure identification and optimisation have been published.<sup>1</sup> A similar development was recently seen in the area of inorganic solid state materials,<sup>2</sup> catalysts<sup>3</sup> and polymers,<sup>4</sup> where combinatorial techniques have been successfully used to discover new materials. Due to rapidly advancing technologies in the area of organic materials, there is a strong need to accelerate the development process. The bottlenecks of conventional material research, namely the time consuming “one-at-a-time” synthesis, purification and subsequent evaluation of materials, could be overcome by implementing combinatorial methodologies that were developed for high-speed synthesis and high-throughput screening of pharmaceuticals. The first examples of *combinatorial organic materials research* (COMR) have been published only recently.<sup>5</sup> Single molecule libraries of fluorescence dyes as potential candidates for laser dyes or bio-labelling,<sup>5a</sup> and conjugated oligomers for organic electronic devices<sup>5b,c</sup> were generated by combinatorial strategies and their molecular properties investigated by automated screening methods.

In the case of solid state materials, where for applications the bulk-properties are crucial, the development of new materials is aggravated by the fact that the appropriate structure–property relationships are not readily predictable by current theories, because these bulk properties strongly depend on numerous interdependent parameters as well as on packing-effects and subtle intermolecular interactions in the solid state. In this context, the preparation of a library of liquid crystals (LCs) for display application seems to be particularly challenging, because the aforementioned lack of predictability of solid state materials renders LCs a prime target for a combinatorial optimisation strategy.

In a very recent publication, we already described the fabrication of a first small 16-membered library of liquid crystals by combinatorial approaches.<sup>6</sup> In this publication, we describe the first parts of a full combinatorial development process leading to a much bigger library of a novel class of liquid crystalline (LC) materials which includes: 1. design of the lead structure;

2. development of an effective synthetic route; 3. library generation; 4. purification. The final steps of the developmental loop, screening and data analysis, will be described in a forthcoming paper.<sup>7</sup>

## Results and discussion

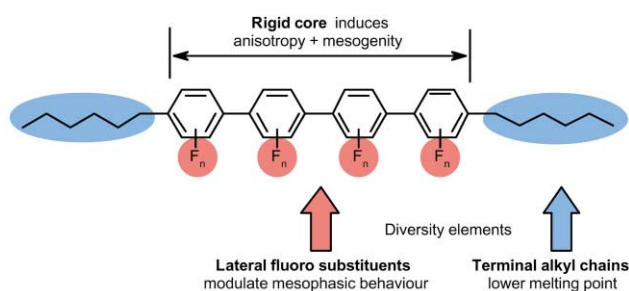
### Library design

Despite the fact that numerous liquid crystalline compounds are already known today, the steadily progressing technological advancement demands the provision of continuously new and better materials. For example, whereas most LC displays (LCD) so far were operated at room temperature, in automotive applications operating temperature ranges from –40 to 110 °C are desirable. Whereas biphenyl and terphenyl based LCs have been extensively studied in the past<sup>8</sup> and are part of commercial LC mixtures, quaterphenyl LCs are very rare and only published in recent patents.<sup>9</sup> This is mainly due to the very high melting point of the core structure and unfavourable phase behaviour of known quaterphenyls. The increased length-to-breadth ratio of the conjugated core of a quaterphenyl, however, should result in increased clearing temperatures ( $T_{\text{clear}}$ ) which would render them suitable candidates for LC mixtures with an extended temperature range. Therefore, we chose as the lead structure a *p*-quaterphenyl which is substituted with two terminal alkyl chains and lateral fluoro substituents. The rigid core should induce anisotropy and is a prerequisite for liquid crystallinity. The terminal alkyl side chains serve as flexible elements that should lower the melting point to an extent that liquid crystalline mesophases occur. Lateral fluoro substituents are known to have a distinct influence on the phase behaviour by altering the association of the molecules in the liquid crystalline phase.<sup>10</sup> Both the terminal alkyl and the lateral fluoro substituents serve as diversity elements in the combinatorial development process (Fig. 1). In addition to the expected improved values for  $T_{\text{clear}}$ , the quaterphenyl target molecules are expected to possess an intrinsic high chemical, thermal and photochemical stability that is also important for application in LCDs.

### Synthetic strategy

The oligomer elongation sequence that is based on an iterative synthesis that we developed recently, is outlined in Scheme 1.<sup>6</sup>

† Electronic supplementary information (ESI) available: tables of product yield and purity, and NMR spectra and HPLC traces. See <http://www.rsc.org/suppdata/ob/b2/b212107g/>



**Fig. 1** *p*-Quaterphenyl as the lead structure for novel liquid crystalline materials.

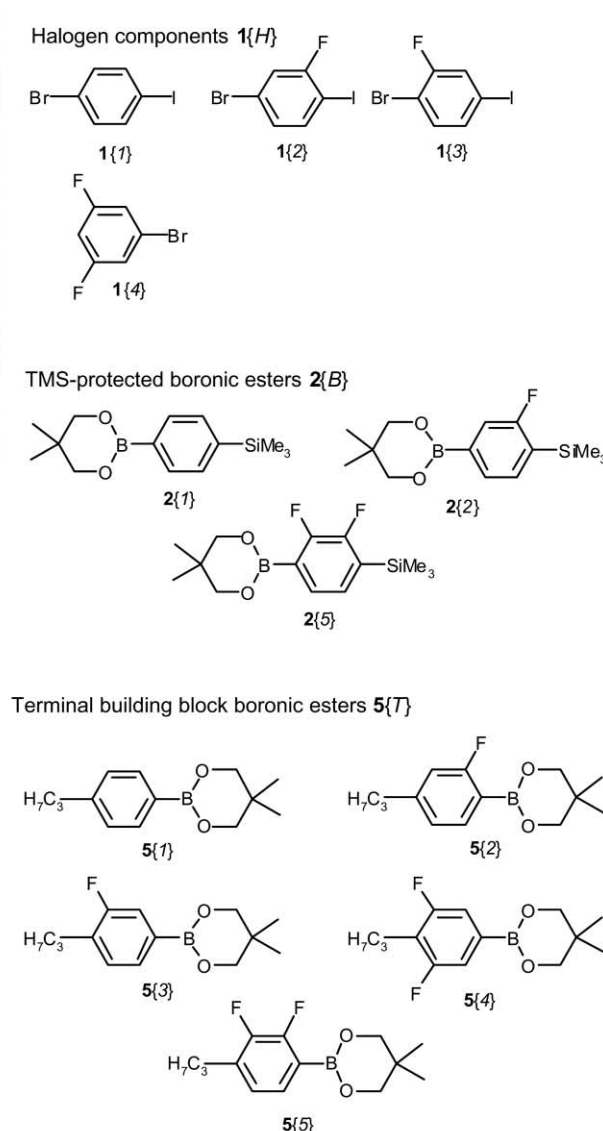
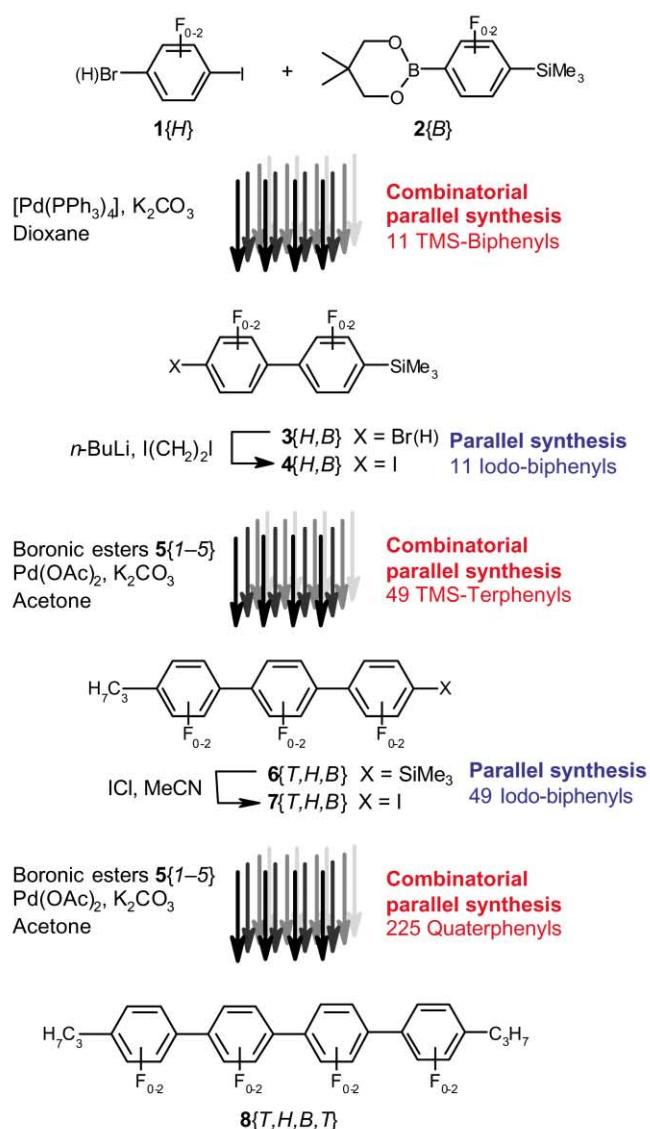
A convergent bi-directional stepwise addition approach seems to be well suited for the construction of a library of *p*-quaterphenyls, since the bi-directional growth-strategy minimises the number of reactions and intermediates, compared to a standard linear oligomer synthesis. Furthermore, iterative Suzuki-couplings can be easily translated into a combinatorial protocol by using different building blocks as diversity reagents.<sup>5</sup>

In a first Suzuki cross-coupling, a halogen component **1** and a trimethylsilyl (TMS) protected phenylboronic ester **2** react to give biphenyl **3**, which is subsequently transformed into iodo biphenyl **4** by treatment with *n*-butyllithium and 1,2-diiodoethane. Biphenyl **4** undergoes palladium-catalysed cross-coupling with boronic ester **5** to yield TMS-protected terphenyl

**6**. After conversion of the TMS-group into the iodo moiety by treatment with iodine chloride, the resulting iodoterphenyl **7** is cross-coupled with boronic ester **5** to yield quaterphenyl **8**.

### Building block selection and synthesis

In a recent study, we evaluated the influence of the terminal alkyl chains on the mesomorphic behaviour of quaterphenyls by synthesis and screening of a first 16-membered library of novel 4,4''-dialkyl-3',2'',3''-trifluoro-*p*-quaterphenyls. The data analysis clearly revealed that short linear alkyl terminal chains are favourable for large mesophase ranges.<sup>6b</sup> Therefore, in the synthesis of this second, more extended material library, the terminal alkyl chains were kept constant and the terminal building blocks **5{T}** were designed to bear exclusively short propyl chains (Scheme 1). Instead of a variation of the alkyl chains, in this library, the number and positions of the fluoro atoms at the quaterphenyl core were varied since the properties of LCs are strongly influenced by fluoro substituents.<sup>10</sup> The selection of building blocks was also based on the aim of maximizing the overall efficiency of the combinatorial synthesis: Terminal building blocks **5{T}** are used twice in the synthesis to introduce diversity and with utilizing a larger number of these building blocks, the diversity of the final library can be enhanced surpassingly. After careful selection of a set of suitable diversity reagents, that bear up to two fluoro substituents at various positions of the phenyl core (Scheme 1), the next step towards the

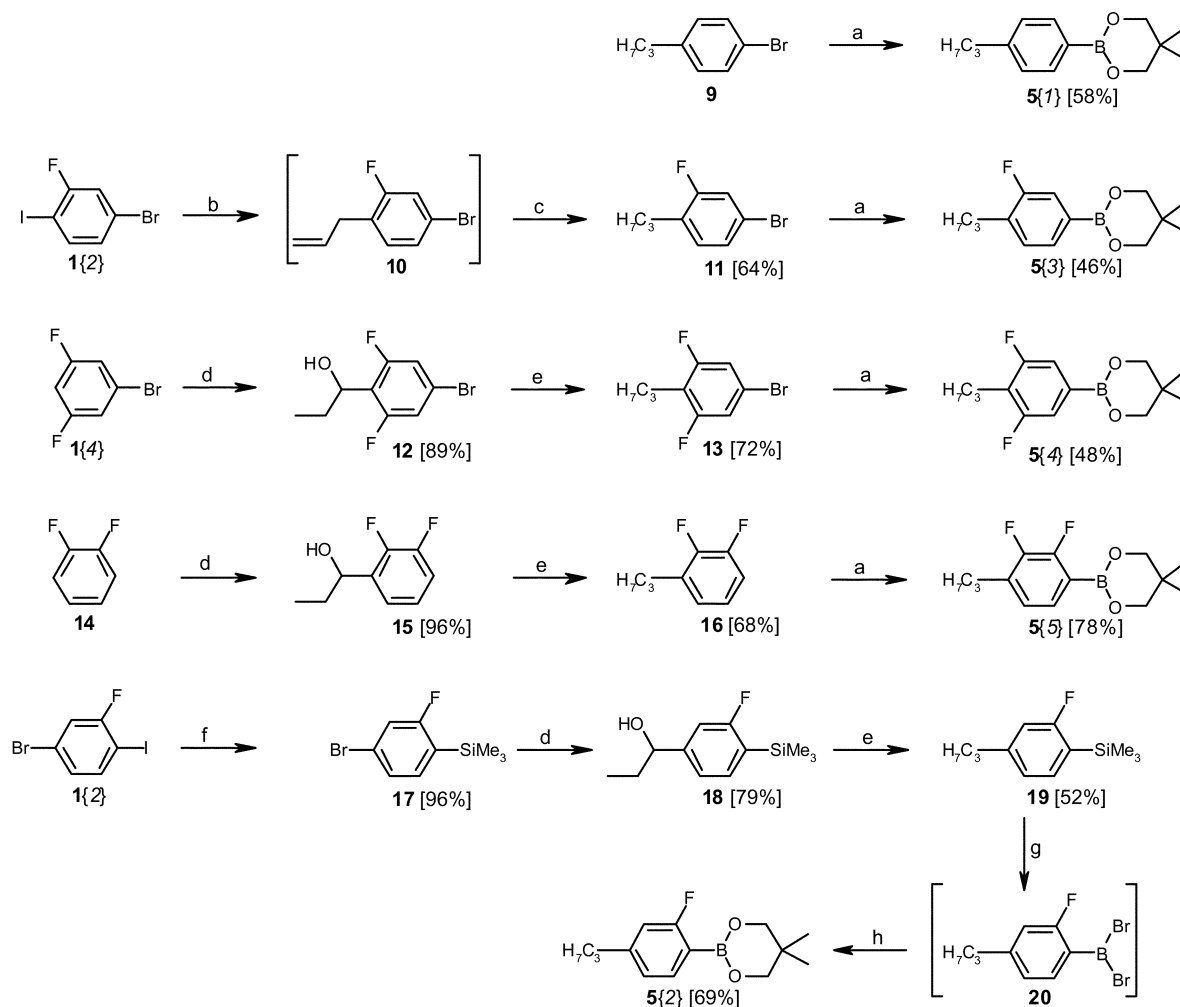


**Scheme 1** Combinatorial synthesis of quaterphenyls **8{T,H,B,T}** and utilised building blocks **1{H}**, **2{B}** and **5{T}**.

library construction was the synthesis of the building blocks, which are the halogen components **1{H}**, the TMS-protected boronic esters **2{B}** and the terminal boronic esters **5{T}**. It was envisaged to implement the boronic functionalities of building blocks **2{B}** and **5{T}** as boronic esters and not as boronic acids. Boronic acids show a tendency to form adducts with coordinating solvents, such as THF, and are usually obtained as waxy solids that are mixtures of free acid and the anhydride of unknown stoichiometric composition, which renders it impossible to dose them in exact amounts.<sup>11</sup> In contrast to that, boronic esters are molecularly well defined compounds, that can be exactly dosed, which is essential for our combinatorial synthetic strategy. Boronic esters derived from neopentyl glycol have the particular advantage of being crystalline solids that can easily be purified in large amounts by recrystallisation, whereas propanediol boronic esters and boronic acids have to be purified by chromatography in small batches. Moreover, especially fluorinated arylboronic esters are much more stable towards deboronation than the free acids. This improved robustness of building blocks **2{B}** and **5{T}** is a prerequisite for the parallelisation of the individual reaction under standard coupling conditions, which are not individually optimised for each reaction. The synthesis of the terminal alkylbenzene boronic esters **5** is shown in Scheme 2.

Commercially available *p*-bromopropylbenzene **9** was reacted with butyllithium (*n*-BuLi) and triisopropyl borate [B(O*i*Pr)<sub>3</sub>], to yield the corresponding boronic acid, which was not isolated, but esterified *in situ* with neopentyl glycol to give boronic ester **5{1}**. The fluorinated propylbenzenes that were needed for the other building blocks **5{2–5}** were synthesized by three differ-

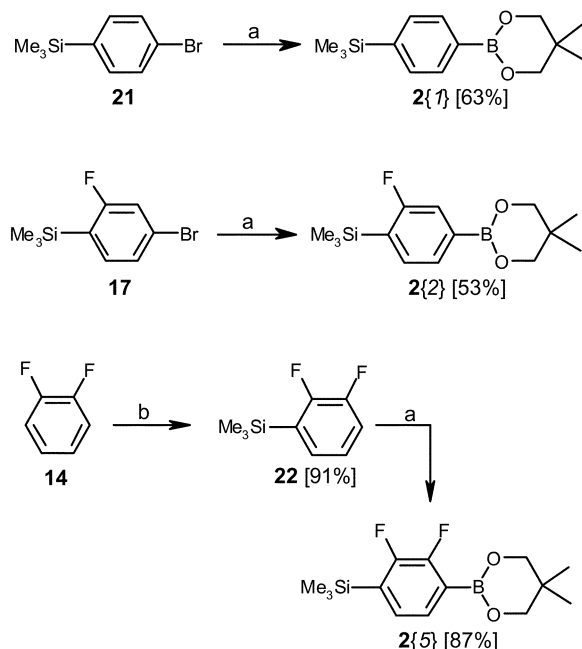
ent routes. In the first synthetic approach, commercially available 1-bromo-3-fluoro-4-iodobenzene **1{2}** was metallated with *n*-BuLi and then reacted with allyl bromide under copper catalysis to form allylbenzene **10** which without isolation was subsequently hydrogenated with PtO<sub>2</sub>/H<sub>2</sub> to yield alkylbenzene **11**. The latter was converted into boronic ester **5{3}** by the standard reaction sequence mentioned above. In a second approach, commercially available 5-bromo-1,3-difluorobenzene **1{4}** was converted into benzylic alcohol **12** by metallation with *n*-BuLi and quenching with propanal. By treatment with phosphorus pentaoxide, benzylic alcohol **12** was dehydrated to the corresponding styrene derivative, which was directly hydrogenated to propylbenzene **13**. The latter was converted to boronic ester **5{4}** by the standard reaction sequence. Analogously, boronic ester **5{5}** was prepared from 1,2-difluorobenzene **14** via benzylic alcohol **15** and 1,2-difluoro-3-propylbenzene **16**. Attempts to synthesize boronic ester **5{2}** from commercially available 3-bromo-2-fluoroiodobenzene **1{3}** failed, as both aforementioned routes resulted in a mixture of isomeric products, probably due to lithium migration in lithiated **1{3}**. Therefore, another synthesis was developed, using again 1-bromo-3-fluoro-4-iodobenzene **1{2}**, which was converted into silyl benzene **17** by lithiation with *n*-BuLi and subsequent quenching with trimethylsilyl chloride (TMSCl) in the presence of catalytic amounts of *N,N*-dimethylaminopyridine (DMAP), which activates the electrophile to be sufficiently reactive at –78 °C. Without the addition of DMAP, no reaction takes place at –78 °C and upon warming on room temperature, decomposition occurs, giving only a very poor yield of silyl benzene **17**. Compound **17** was then converted to propylsilylbenzene **19**.



**Scheme 2** Synthesis of building blocks **5{T}**: a) 1. *n*-BuLi, THF; 2. B(O*i*Pr)<sub>3</sub>; 3. neopentyl glycol. b) 1. *n*-BuLi, THF; 2. CuCN (5 mol%); 3. allyl bromide. c) PtO<sub>2</sub>, H<sub>2</sub>, methanol. d) 1. *n*-BuLi, THF; 2. propanal. e) 1. P<sub>2</sub>O<sub>5</sub>, pentane; 2. PtO<sub>2</sub>, H<sub>2</sub>. f) 1. *n*-BuLi, diethyl ether; 2. DMAP (5 mol%), TMSCl. g) BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>. h) neopentyl glycol.

via alcohol **18**, by the established synthetic protocol. Silylbenzene **19** was borodesilylated with  $\text{BBr}_3$  to yield dibromophenylborane **20**, which was directly converted to boronic ester **5{2}** by reaction with neopentyl glycol.

The synthesis of the TMS-protected boronic ester building blocks **2{1}**, **2{2}** and **2{5}** was straightforwardly effected from silylbenzenes **21**, **17** and **22** by the standard reaction sequence lithiation, quenching with  $\text{B(OiPr)}_3$  and esterification with neopentyl glycol (Scheme 3).



**Scheme 3** Synthesis of building blocks **2{1}**, **2{2}** and **2{5}**: a) 1.  $n\text{-BuLi}$ , THF; 2.  $\text{B(OiPr)}_3$ ; 3. neopentyl glycol. b) 1.  $n\text{-BuLi}$ , THF; 2. TMSCl.

### Optimisation

When carrying out first trial reactions, it became evident that careful optimisation of each synthetic step was necessary to translate the convergent bi-directional oligomer synthesis outlined in Scheme 1 into a combinatorial protocol. The propensity of *o*-fluoroboronic acids to undergo deboronation under Suzuki-coupling conditions could be overcome by using the corresponding boronic esters instead and utilizing potassium carbonate as a relatively weak base. When reacting halogenated benzene **1** with 1.0 eq. boronic ester **2**, the Suzuki-coupling exclusively occurred at the iodo-site of compound **1**, to yield bromo biphenyl **3**. Because the following parallel synthetic steps were to be carried out as a three step synthesis in solution without purification of the crude products, we put a lot of effort in optimising the reactions with respect to a complete turnover of the starting materials as well as minimum contamination of by-products. Unfortunately, the Suzuki reaction of bromo biphenyl **3** with boronic ester **5** proceeded in only about 80% conversion of starting material, and a mixture of biphenyl **3** and terphenyl **6** was obtained. These circumstances would spoil the synthesis, because in the following iododesilylation step, the leftover **3** would be converted into a diiodo biphenyl that would in turn give rise to a different than the desired quaterphenyl in the following Suzuki-coupling. The purification of the resulting mixture of two different quaterphenyls **8** would be rather difficult, if possible at all. Because all efforts to improve the yields of the reaction of biphenyl **3** with boronic ester **5** by variation of base [ $\text{K}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$ ,  $\text{Ba(OH)}_2$ ], catalyst [ $\text{Pd(PPh}_3)_4$ ,  $\text{Pd}_2\text{dba}_3/\text{P}^t\text{Bu}_3$ ,  $\text{PdCl}_2(\text{PPh}_3)_2/\text{P}(o\text{Tol})_3$ ], amount of catalyst (1–5 mol%), amount of boronic ester (1–2 equiv.), solvent (THF, dioxane, toluene) and conditions (aqueous, non-aqueous) failed, we had to elongate the

synthesis by an additional step, which is the conversion of bromo biphenyl **3** into the more reactive iodo biphenyl **4**. The Suzuki-coupling reaction of iodo compounds **4** and **7** with boronic esters **5** had also to be further optimised, because the crude Suzuki-coupling products were contaminated with Pd-black, when  $[\text{Pd(PPh}_3)_4]$  was used as catalyst. This could be completely avoided by the use of  $\text{Pd(OAc)}_2$  as catalyst precursor without the addition of additional ligands. However, the optimisation studies also revealed some restrictions with respect to the compatibility of the building blocks. It was found that the Suzuki-coupling did not tolerate more than two fluoro atoms *ortho* to the Ar–Ar bond formed in the cross-coupling reaction. For example, Suzuki-couplings of biphenyl **4{4,5}** and *ortho*-fluoro boronic esters **5{2}** and **5{5}** proceeded in only 16 and 0% yield, respectively, indicating that the formation of *o,o,o'*-trifluoro-substituted biaryl moieties is not tolerated under the chosen reaction conditions. This implies, that in the synthesis of the library, combinations of *ortho*-fluoro boronic esters **5{2}** and **5{5}** with biphenyls **4{4,1}**, **4{4,2}** and **4{4,5}**, which bear two fluorine atoms *ortho* to the iodo moiety, have to be omitted. Another issue that had to be addressed was the side chain chlorination that was observed when carrying out the iodo-desilylation of compounds **6** under standard conditions, *i.e.* using iodine chloride and chlorinated solvents. Treatment of TMS-protected terphenyl **6{1,1,1}** with ICl in dichloromethane gave iodo terphenyl **7{1,1,1}**, which was contaminated with 5% of a chlorinated iodo terphenyl, in which the chlorine is presumably located at the benzylic position of the propyl side chain. If the reaction mixture was exposed to sunlight, the amount of chlorinated by-product increased to 23%, indicating that the chlorination takes place *via* a radical process. By increasing solvent polarity and using acetonitrile instead of dichloromethane, the chlorination reaction could be completely suppressed even in the presence of sunlight. Moreover, the reaction rate of the iododesilylation was found to be increased by using acetonitrile as solvent.

### Library synthesis

With the optimised reaction conditions in hand, a library composed of 225 *p*-quaterphenyls was prepared according to Scheme 1. The library synthesis was initiated by building up the inner biphenyl core of the tetramer in a combinatorial parallel synthesis by palladium-catalysed Suzuki-coupling of components **1{H}** and TMS-protected phenylboronic esters **2{B}**, using the system  $[\text{Pd(PPh}_3)_4]$ –potassium carbonate in dioxane. From the 12 possible combinations of **1{H}** and **2{B}**, the coupling **1{3}** + **2{1}** was omitted, because the resulting biphenyl **3{3,1}** would finally lead to the identical *p*-quaterphenyls that are already obtained from biphenyl **3{1,2}**. The biphenyls **3{H,B}** were obtained in good yields of 68 to 95% (mean 82%). The biphenyls **3{H,B}** were then converted in parallel into the corresponding iodinated biphenyls **4{H,B}** by metallation with  $n\text{-BuLi}$  and subsequent reaction with 1,2-diiodoethane (49–95% yield, mean 85%). In order to further accelerate the synthesis, the following three parallel synthetic steps were carried out as a three step synthesis in solution without purification of the crude products, which was only possible because of the fact that the optimised reaction condition reliably ensured the complete turnover of all starting materials as well as minimum contamination of by-products. In the next step, in a combinatorial parallel synthesis 11 biphenyls **4{H,B}** were cross-coupled with five boronic esters **5{T}** under the optimised Suzuki reaction conditions to result in 49 TMS-protected terphenyls **6{T,H,B}** in a mean yield of 98% and a mean purity of 99%. The number of 55 possible combinations is reduced to 49 *p*-terphenyls **6{T,H,B}**, because the Suzuki-coupling did not tolerate more than two *ortho* fluoro atoms in the biphenyl moiety (*vide supra*). Therefore, the synthesis of the terphenyls **6{2,3,1}**, **6{2,3,2}**, **6{2,3,5}**, **6{5,4,1}**, **6{5,4,2}** and



6{5,4,5} was not attempted. In 49 parallel reactions, terphenyls 6{T,H,B} were iododesilylated using iodine chloride in acetonitrile. The resulting iodinated terphenyls 7{T,H,B} turned out to be poorly soluble in acetonitrile and therefore could easily be isolated by filtration in a mean yield of 89% and a mean purity of 98%. In the last step, by combinatorial parallel Suzuki reactions, 49 terphenyls 7{T,H,B} were cross-coupled with the five boronic esters 5{T} to finally yield a library of 225 crude *p*-quaterphenyls 8{T,H,B,T} comprising up to eight fluoro substituents at different positions. The number of 245 possible combinations of reactants is reduced to 225 *p*-quaterphenyls 8{T,H,B,T}, due to the symmetry of the inner biphenyl-cores of biphenyls 4{1,1} and 4{3,2}.

### Purification and analytical quality control

Special emphasis has been put on the purification of the final *p*-quaterphenyls 8{T,H,B,T}, because in contrast to libraries of drug-like molecules, where for biological screening in general purities of about 70–80% are satisfactory, in material libraries purities of 99% and higher are required for the reliable screening of their physical properties, as the accuracy of physical measurements crucially depends on purity.<sup>5a-c,6b</sup> For that reason, a method was needed that would allow the reliable and rapid purification of the individual library members. The usage of sequential automated semipreparative HPLC-MS, which we successfully applied in the purification of dye and conjugated oligomer libraries,<sup>5a,c</sup> would have been very tedious in this case, as the determination of the bulk-properties of liquid crystals requires the purification of larger (*i.e.* 40–50 mg) amounts of material. Therefore, we developed a method for a rapid parallel recrystallization (Fig. 2).

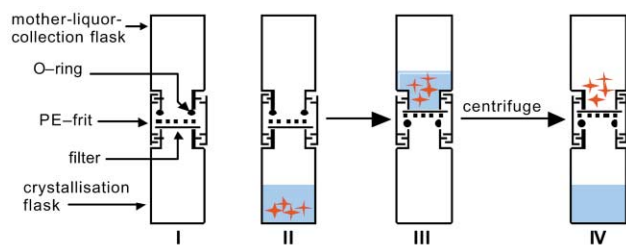


Fig. 2 Device used for the parallel recrystallization of quaterphenyls 8.

Custom-made apparatus I consists of a crystallization flask and a mother-liquor collection flask, that are held together *via* a double thread connector. The two flasks are separated by a filter paper which is supported by a PE frit and an O-ring for sealing. For the purification, the crude product is recrystallized in the crystallization flask (II). After complete crystallization, the setup is reversed (III) and put into a centrifuge. Upon centrifugation, the mother-liquor is transferred completely into the mother-liquor collection flask (IV). In contrast to other common means of purification like distillation or chromatography, this method can easily be parallelised, as the number of parallel purifications is only limited by the availability of the special recrystallization flasks and both, the recrystallization and crystal separation can be carried out in parallel fashion using standard equipment (Fig. 3).

Additionally, the recrystallization can be repeated several times without effort, until the desired purity is achieved. By recrystallizing up to 30 compounds at the same time, the purification of the whole library was performed in a matter of days. The overall yield of the last synthetic step ranged from 31 to 99% (mean 81%, Fig. 4) after purification, the absolute amount of purified product being in the range of 25–50 mg, which is sufficient for the screening of the mesophase properties.

The purity and identity of the library members was checked by sequential automated analytical HPLC-MS. Atmospheric-



Fig. 3 Parallel recrystallization of quaterphenyls 8.

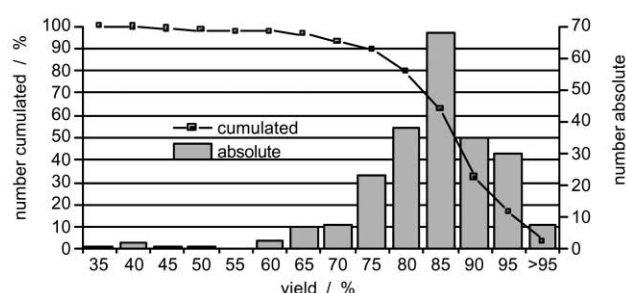


Fig. 4 Histogram representation of the isolated yields of quaterphenyls 8. Absolute (grey columns) = number of compounds within the specified yield range. Cumulated (black squares) = relative number of compounds with at least the specified yield.

pressure chemical ionisation (APCI) was employed as the ionisation technique, which allowed the detection of the  $[M + H]^+$  ions of the quaterphenyls as the base peaks of the mass spectra. A representative example (quaterphenyl 8{5,1,1,3}) of the HPLC-MS purity control after the purification is shown in Fig. 5 and 6. Both the UV-absorbance trace (Fig. 5a) and the total ion count (TIC) trace (Fig. 5b) show that no impurities are present in the final product.

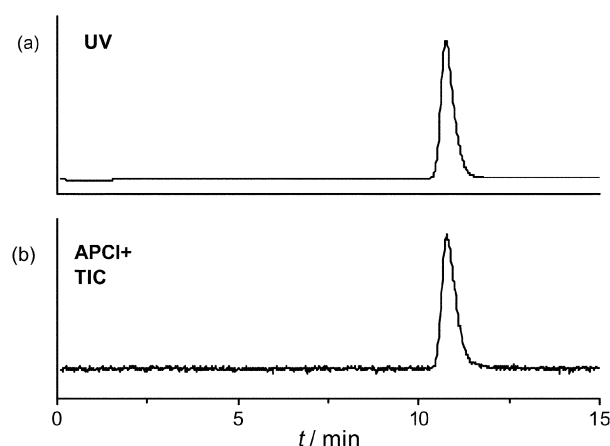
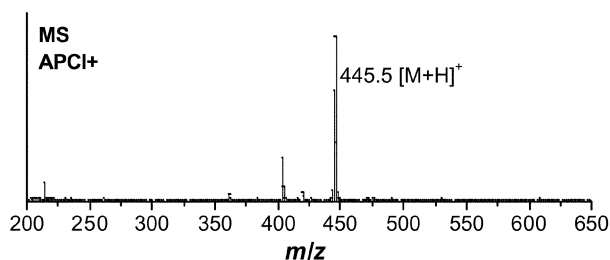


Fig. 5 HPLC-MS analysis of purified quaterphenyl 8{5,1,1,3}: a) UV absorbance trace (UV detection at  $\lambda = 230$  nm); b) total ion count (TIC) trace (APCI+). The mass spectrum under the peak is identical to the one displayed in Fig. 6.

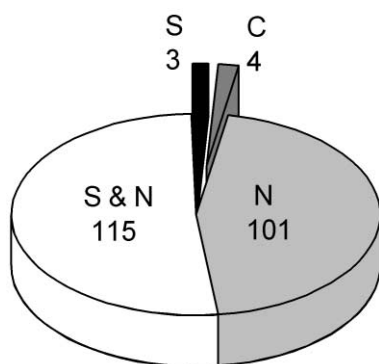
As displayed by the corresponding mass spectrum under the peak, the molecular ion  $[M + H]^+$  of quaterphenyl 8{5,1,1,3} showed the theoretical value of 445.5 amu (Fig. 6).



**Fig. 6** Mass spectrum of quaterphenyl **8**{5,1,1,3}. The molecular ion  $[M + H]^+$  of this compound is 445.5 amu, which corresponds to the theoretical value.

The purification of all 225 library members furnished 213 compounds (corresponding to 95% of all library members) that were pure by HPLC, 5 compounds in 99.0–99.9% purity, and 3 compounds in a purity of 98–99%, whereas 4 compounds were only 95–97% pure. According to that, a total of 221 compounds (corresponding to 98% of all library members) had a purity of >98%.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were taken for 19 randomly selected library members to provide additional structural characterisation. These NMR spectra along with the mass spectra and HPLC-chromatograms of all library members are given in the supporting information.

Screening of the individual library members by automated sequential DSC revealed that from 223 compounds investigated, 219 novel LC materials had been discovered and qualitative correlations of the molecular structure with the LC properties can be deduced (Fig. 7). 3 compounds showed a purely smectic phase, 115 compounds smectic followed by nematic phases, and 101 LC materials were purely nematogenic. Within the library, several “hits” with very broad mesophasic ranges up to 200 °C and melting points lower than 100 °C have been identified, which makes them very suitable candidates for LCD mixtures. Moreover, statistical analysis of the derived data sets revealed unique quantitative structure–property relationships (QSPR) for the LC materials that describe the influence of the various fluorine substituents on the physical properties of the molecules and finally allow the rational design of novel materials. In this respect, we found out that in order to obtain reliable QSPRs material libraries comprising at least 150 members are necessary. These two final steps of the combinatorial developmental cycle, screening and data analysis, will be described in detail in a forthcoming paper.<sup>7</sup>



**Fig. 7** Mesogeneity of the compounds of the material library. Number of compounds with: C, only crystalline phase; S, only smectic phase; N, only nematic mesophase; S & N, smectic and nematic mesophase.

## Conclusions

In summary, an efficient convergent synthesis of novel liquid crystalline *p*-quaterphenyls has been developed. Three types of building blocks were assembled by a sequence of iterative iodinations and Suzuki-couplings and by exploiting a bi-directional oligomer growth strategy, the number of synthetic steps was

minimised. This general synthetic scheme was applied to the synthesis of 225 *p*-quaterphenyls by combinatorial parallel synthesis. With the parallel recrystallization, a technique was developed that allowed the rapid purification of the individual library members in quantities needed for the determination of the bulk-properties of the materials. In this paper, we described the first four steps of a full combinatorial development process leading to a novel class of LC materials.

## Experimental

### General methods

Solvents and reagents were purified and dried by usual methods prior to use. Unless otherwise stated, reactions were carried out in flame-dried glassware under an atmosphere of argon. Diethyl ether and THF were continuously distilled from calcium hydride and potassium, respectively. Melting points were determined with a Büchi B-545 melting point apparatus and are uncorrected. Gas chromatograms were recorded on a Varian CP 3800 with a 30 m glass capillary column CP 5860, carrier gas helium 5.0, detection Varian-FID flame ionisation detector or Saturn 2000 mass detector operating in the electron-impact (EI)–mode.  $^1\text{H}$  NMR spectra were recorded on a Bruker AMX 400 (400 MHz) spectrometer. Chemical shifts are expressed in parts per million ( $\delta$ ) using residual solvent protons as internal standard.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX 400 (101 MHz) spectrometer. Infrared spectra were recorded on a Perkin-Elmer FTIR Spectrum 2000 spectrometer. Mass spectra were recorded on a Varian MAT 711. Ions were generated by electron impact at 70 eV or by chemical ionisation by using ethane as ionisation gas. Elemental analyses were performed on an Elementar vario EL (limit of experimental error:  $\pm 0.3\%$ ). HPLC analysis was accomplished using a Waters HPLC system (MassLynx, Version 3.4; Waters 600E Multisolute Delivery System; Waters 2700 Sample Manager; Waters Fraction Collector II; Waters Reagent Manager; Accurate Flow-stream Splitting Device ACM 10–50, LC Packings) equipped with a photodiode array detector (Waters 996 PDA Detector) coupled to a Platform-LC/detector (Micromass ZMD) operating with an APCI source. Conditions for LC analysis: Nucleosil nitrophenyl column (Macherey-Nagel, 250 mm  $\times$  4 mm, 5 mm/100 Å), eluent:  $\text{CH}_2\text{Cl}_2$ –*n*-hexane mixture 98 : 2 (isocratic), flow rate: 2.0 mL min<sup>−1</sup>, injection volume: 20  $\mu\text{L}$ , photodiode array detection: scan range 250–500 nm. Conditions: positive ion APCI, source block temperature 130 °C, APCI probe temperature: 600 °C, cone voltage: 27 V, corona voltage: 3.5 kV, extractor: 7 V, RF lens: 0.2 V, LM resolution: 15.0, HM resolution: 14.8; ion energy: 0.8, multiplier: 650, desolvation gas flow: 433 L h<sup>−1</sup>, cone gas flow: 95 L h<sup>−1</sup>.

### Parallel reactions

The combinatorial synthesis of terphenyls **6**{*T,H,B*}, **7**{*T,H,B*} and quaterphenyls **8**{*T,H,B,T*} was carried out in parallel fashion. Parallel heating of the closed vials equipped with magnetic stirring bars was achieved by inserting the reaction vessels into a custom made aluminium block that was put on top of a commercial temperature controlled magnetic stirring hotplate. The setup allows parallel heating and magnetic stirring of up to 35 vials. Parallel shaking was performed with an Advanced ChemTec PLS4  $\times$  6 shaker. Parallel filtration was performed with a IST VacMaster parallel vacuum manifold and Separtis SPE filter-syringes. Parallel evaporation of solvent was performed with a Labconco RAID VAP model 79 000 parallel evaporator under reduced pressure. The synthesis of biphenyls **3**{*H,B*} and **4**{*H,B*} was carried out in standard glassware in a fume hood according to the general procedures given below by using a large oil bath/cooling bath for parallel thermostating.

## Materials

Chemicals were purchased from commercial suppliers: 1,2-dibromoethane (Merck), 1,2-difluorobenzene **14** (Fluorochem), 1,2-diiodoethane (Merck), 1-bromo-3,5-difluorobenzene **14** (Fluorochem), 1-bromo-3-fluoro-4-iodobenzene **12** (Fluorochem), 4-bromo-3-fluoro-1-iodobenzene **13** (Fluorochem), *p*-bromiodobenzene **11** (ABCR), 4-bromopropylbenzene **9** (Aldrich), allyl bromide (Merck), boron tribromide (Merck), diisopropylamine (Merck), iodine chloride (Merck), potassium carbonate (Merck), diatomenic earth: Isolute MH (Separtis), copper(I) cyanide (Fluka), magnesium sulfate (Merck), *N,N*-dimethylaminopyridine (Merck), sodium dithiosulfate (Merck), *n*-butyllithium (1.6 M in *n*-hexane, Merck), neopentyl glycol (Merck), palladium(II) acetate (Merck), phosphorus pentaoxide (Merck), platinum dioxide (Merck), propanal (Merck), triisopropyl borate (Acros), trimethylsilyl chloride (Merck). Tetakis(triphenylphosphino)palladium(0)<sup>12</sup> and 4-bromotrimethylsilylbenzene **21**<sup>13</sup> were prepared according to literature procedures.

## General procedures (GPs)

**GP1: Synthesis of boronic esters 5{I}–5{5}, 2{I}, 2{2} and 2{5}.** To a solution of halogenated benzene **1{H}** in dry THF (1.5 ml per mmol) at  $-78^{\circ}\text{C}$  1.1 eq. 1.6 M *n*-BuLi were added. After 15 min. 1.3 eq. triisopropyl borate were added dropwise and allowed to reach room temperature over night. Water, diethyl ether and 1 eq. conc. HCl were added. The organic phase was washed with water and brine and the solvent was removed *in vacuo*. The oily residue was dissolved in THF (0.3 ml mmol<sup>-1</sup>) and 1 eq. neopentyl glycol and MgSO<sub>4</sub> (0.5 g mmol<sup>-1</sup>) were added. After stirring for 1 h the solvent was removed *in vacuo* and to the oily residue hexanes were added (0.30 ml mmol<sup>-1</sup>). Precipitated neopentyl glycol was removed by filtration. From the filtrate at  $-25^{\circ}\text{C}$  analytically pure boronic ester crystallised.

**GP2: Synthesis of biphenyls 3{H,B} by Suzuki coupling.** To a solution of 50.0 mmol halogenated benzene **1{H}**, 50.0 mmol boronic ester and 2.31 g (2.00 mmol) [Pd(PPh<sub>3</sub>)<sub>4</sub>] in 100 ml degassed dioxane, a solution of 16.6 g (120 mmol) K<sub>2</sub>CO<sub>3</sub> in 50 ml degassed water was added and refluxed under argon until reaction control by GC revealed complete reaction. The organic phase was washed with water and brine, dried over MgSO<sub>4</sub> and filtered over a silica plug. If necessary, the crude product was purified by Kugelrohr distillation. Solid products were recrystallised from hexanes at  $-25^{\circ}\text{C}$ .

**GP3: Synthesis of iodobiphenyls 4{H,B}.** To a solution of bromobiphenyl **3{H,B}** in dry THF (3 ml mmol<sup>-1</sup>) at  $-78^{\circ}\text{C}$  1.1 eq. 1.6 M *n*-BuLi were added. After 15 min. 1.3 eq. 1,2-diiodoethane were added as a solid and the mixture was allowed to reach room temperature within one hour. Water and diethyl ether were added and the organic phase was washed with water, satd. Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and brine, dried over MgSO<sub>4</sub> and filtered over a silica plug. If necessary, the crude product was purified by Kugelrohr distillation. All products were recrystallised from hexanes at  $-25^{\circ}\text{C}$ .

## Synthesis of boronic ester-building blocks 5{I}–5{5} and 2{I}, 2{2} and 2{5}

### 2-(4-Propylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 5{I}.

According to *GPI*, from 55.9 g (281 mmol) 4-bromopropylbenzene **9** was obtained 37.8 g (58%) boronic ester **5{I}**; mp  $86.3^{\circ}\text{C}$  (Found: C, 72.44; H, 9.12. C<sub>14</sub>H<sub>21</sub>BO<sub>2</sub> requires C, 72.42; H, 9.03%;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3078 (w), 3046 (w), 3026 (w), 2962 (s), 2934 (s), 2872 (m), 1611 (s), 1560 (w), 1482 (m), 1420 (m), 1381 (m), 1344 (m), 1317 (s), 1249 (m), 1218 (w), 1183 (w), 1130 (s), 1020 (m), 967 (w), 934 (w), 915 (w), 837 (m), 809 (m), 745

(m), 703 (m), 651 (s), 634 (m), 499 (m);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.98 (t,  $J = 7.4$  Hz, 3 H, CH<sub>2</sub>-CH<sub>3</sub>), 1.04 (s, 6 H, CMe<sub>2</sub>), 1.69 (sextet,  $J = 7.5$  Hz, 2 H, CH<sub>2</sub>-CH<sub>3</sub>), 2.63 (t,  $J = 7.7$  Hz, 2 H, Ar-CH<sub>2</sub>), 3.79 (s, 4 H, 2 × OCH<sub>2</sub>), 7.22 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 2 H, H3,5), 7.77 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 2 H, H2,6);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.8 (CH<sub>2</sub>-CH<sub>3</sub>), 21.9 (CMe<sub>2</sub>), 22.4 (CH<sub>2</sub>-CH<sub>3</sub>), 31.8 (CMe<sub>2</sub>), 38.2 (Ar-CH<sub>2</sub>), 72.2 (2 × OCH<sub>2</sub>), 127.8 (C3,5), 133.8 (C2,6), 145.4 (C4);  $m/z$  (CI): 233 [MH<sup>+</sup>], 203.

**1-Bromo-3-fluoro-4-propylbenzene 11.** To a solution of 151 g (500 mmol) 1-bromo-3-fluoro-4-iodobenzene **12** in 1 l dry diethyl ether at  $-78^{\circ}\text{C}$  313 ml (501 mmol) 1.6 M *n*-BuLi was added dropwise. After 1.5 h 2.24 g (25.0 mmol) CuCN were added and then 129 ml (151 g, 1.50 mol) allyl bromide was added at such a rate that the temperature never exceeded  $-70^{\circ}\text{C}$ . The mixture was allowed to reach room temperature over night and diethyl ether and water were added. The organic phase was washed with aq. ammonia, water and brine, dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The oily residue was dissolved in 500 ml methanol, 500 mg PtO<sub>2</sub> were added and the stirred mixture was hydrogenated at normal pressure for 12 h. The catalyst was filtered off and the solvent was removed under reduced pressure. Distillation (bp  $82^{\circ}\text{C}/11$  mbar) yielded 69.9 g (64%) alkylbenzene **11** (Found: C, 49.80; H, 4.64. C<sub>9</sub>H<sub>10</sub>BrF requires C, 49.51; H, 4.50%;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3070 (w), 2963 (s), 2933 (m), 2872 (m), 1605 (m), 1576 (m), 1485 (s), 1462 (m), 1403 (m), 1262 (m), 1220 (m), 1182 (w), 1129 (m), 1066 (w), 883 (m), 860 (m), 817 (m), 796 (w), 779 (w), 729 (w), 627 (w), 579 (w), 548 (w), 485 (w), 450 (w);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.95 (t,  $J = 7.3$  Hz, 3 H, CH<sub>2</sub>-CH<sub>3</sub>), 1.63 (sextet,  $J = 7.5$  Hz, 2 H, CH<sub>2</sub>-CH<sub>3</sub>), 2.57 (t,  $J = 7.6$  Hz, 2 H, Ar-CH<sub>2</sub>), 7.05 (t,  $J = 8.1$  Hz, 1 H, H2), 6.17–7.21 (m, 2 H, H5,6);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.7 (CH<sub>2</sub>-CH<sub>3</sub>), 23.1 (CH<sub>2</sub>-CH<sub>3</sub>), 30.6 (Ar-CH<sub>2</sub>), 118.7 (d,  $^2J_{\text{CF}} = 25.8$  Hz, C2), 119.3 (d,  $^3J_{\text{CF}} = 9.1$  Hz, C1), 127.0 (d,  $^4J_{\text{CF}} = 3.8$  Hz, C6), 128.5 (d,  $^2J_{\text{CF}} = 16.3$  Hz, C4), 131.7 (d,  $^3J_{\text{CF}} = 6.1$  Hz, C5), 161.0 (d,  $^1J_{\text{CF}} = 249.4$  Hz, C3);  $m/z$  (EI) 218, 216 [M<sup>+</sup>], 189, 187 [M<sup>+</sup>-C<sub>2</sub>H<sub>5</sub>], 108 [M<sup>+</sup>-C<sub>2</sub>H<sub>5</sub>-Br].

**2-(3-Fluoro-4-propylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 5{3}.** According to *GPI*, but using diethyl ether instead of THF as solvent, from 74.2 g (342 mmol) 1-bromo-3-fluoro-4-propylbenzene **11** was obtained 38.7 g (46%) boronic ester **5{3}** (Found: C, 67.23; H, 8.06. C<sub>14</sub>H<sub>20</sub>BFO<sub>2</sub> requires C, 67.36; H, 8.01%;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 2962 (m), 2934 (m), 2873 (m), 1621 (w), 1560 (w), 1505 (w), 1482 (m), 1424 (m), 1398 (m), 1377 (m), 1342 (m), 1318 (s), 1250 (w), 1222 (m), 1179 (w), 1134 (m), 1110 (m), 988 (w), 944 (w), 896 (w), 833 (w), 812 (w), 779 (w), 728 (w), 701 (m), 678 (m), 645 (w), 551 (w), 503 (w), 479 (w), 456 (w);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.97 (t,  $J = 7.4$  Hz, 3 H, CH<sub>2</sub>-CH<sub>3</sub>), 1.03 (s, 6 H, CMe<sub>2</sub>), 1.66 (sextet,  $J = 7.5$  Hz, 2 H, CH<sub>2</sub>-CH<sub>3</sub>), 2.65 (t,  $J = 7.7$  Hz, 2 H, Ar-CH<sub>2</sub>), 3.77 (s, 4 H, 2 × OCH<sub>2</sub>), 7.18 (t,  $^3J_{\text{HH}} \approx ^4J_{\text{FH}} \approx 7.4$  Hz, 1 H, H5), 7.43 (d,  $^3J_{\text{FH}} = 10.7$  Hz, 1 H, H2), 7.50 (d,  $^3J_{\text{HH}} = 7.5$  Hz, 1 H, H6);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.8 (CH<sub>2</sub>-CH<sub>3</sub>), 21.8 (CMe<sub>2</sub>), 23.2 (CH<sub>2</sub>-CH<sub>3</sub>), 31.1 (Ar-CH<sub>2</sub>), 31.8 (CMe<sub>2</sub>), 72.3 (2 × OCH<sub>2</sub>), 119.9 (d,  $^2J_{\text{CF}} = 20.5$  Hz, C2), 129.2 (d,  $^4J_{\text{CF}} = 3.0$  Hz, C6), 130.0 (d,  $^3J_{\text{CF}} = 4.6$  Hz, C5), 132.0 (d,  $^2J_{\text{CF}} = 16.3$  Hz, C4), 161.0 (d,  $^1J_{\text{CF}} = 244.8$  Hz, C3);  $m/z$  (CI) 251, 250, 249 [MH<sup>+</sup>], 231 [MH<sup>+</sup> - HF], 221, 207, 117.

**1-(4-Bromo-2,6-difluorophenyl)-propan-1-ol 12.** To a solution of 96.5 g (500 mmol) 1-bromo-3,5-difluorobenzene **14** in 500 ml dry THF at  $-78^{\circ}\text{C}$  501 mmol LDA (freshly prepared from 55.7 g (550 mmol) diisopropylamine and 313 ml (501 mmol) 1.6 M *n*-BuLi) was added dropwise. After 1.5 h 46.7 ml (37.8 g, 650 mmol) propanal was added at such a rate that the temperature never exceeded  $-70^{\circ}\text{C}$ . The mixture was allowed to reach room temperature and diethyl ether and water were added. The organic phase was washed with water and



brine, dried over  $\text{MgSO}_4$  and the solvent was removed under reduced pressure. Distillation (bp  $66^\circ\text{C}/10^{-3}$  mbar) yielded 112 g (89%) alcohol **12** (Found: C, 43.06; H, 3.61.  $\text{C}_9\text{H}_9\text{BrF}_2\text{O}$  requires C, 43.35; H, 3.88%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3373 (m), 3093 (w), 2969 (m), 2936 (m), 2879 (w), 1645 (s), 1579 (m), 1467 (m), 1417 (s), 1379 (w), 1331 (w), 1284 (w), 1241 (w), 1185 (m), 1094 (m), 1053 (m), 1008 (s), 974 (w), 906 (w), 859 (m), 842 (m), 743 (w), 607 (w), 584 (w), 538 (w), 516 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.88 (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{-CH}_3$ ), 1.72–1.82 (m, 1 H,  $\text{CH}_2\text{H}_b\text{-CH}_3$ ), 1.86–1.98 (m, 1 H,  $\text{CH}_2\text{H}_b\text{-CH}_3$ ), 2.84 (d,  $J = 7.7$  Hz, 1 H, OH), 4.85 (q,  $J = 7.5$ , 1 H, CH–OH), 7.02 (d, line distance 7.8 Hz, AA'-part of a AA'XX'-spectrum, 2 H, H3,5);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 10.1 ( $\text{CH}_2\text{-CH}_3$ ), 29.8 ( $\text{CH}_2\text{-CH}_3$ ), 67.6 (d,  $^3J_{\text{CF}} = 1.9$  Hz, CH–OH), 115.5 (d, line distance 30.4 Hz, AA'-part of a AA'XX'-spectrum, C3,5), 118.8 (t,  $^2J_{\text{CF}} = 16.9$  Hz, C1), 120.7 (t,  $^3J_{\text{CF}} = 12.9$  Hz, C4), 150.3 (dd,  $^1J_{\text{CF}} = 251.8$  Hz,  $^2J_{\text{CF}} = 10.1$  Hz, C2,6);  $m/z$  (CI) 251, 253 [ $\text{MH}^+$ ], 235, 233 [ $\text{MH}^+ - \text{H}_2\text{O}$ ], 223, 221, 207, 205.

**5-Bromo-1,3-difluoro-2-propylbenzene 13.** A suspension of 177 g (1.30 mol) phosphorus pentoxide in 500 ml pentane and 105 g (418 mmol) 1-(4-bromo-2,6-difluorophenyl)propan-1-ol **12** was stirred overnight. The solution was decanted from  $\text{P}_4\text{O}_{10}$ , filtered over basic alumina, 500 mg  $\text{PtO}_2$  were added and the stirred mixture was hydrogenated at normal pressure for 12 h. The catalyst was filtered off and the solvent was removed under reduced pressure. Distillation (bp  $75^\circ\text{C}/11$  mbar) yielded 70.5 g (72%) alkylbenzene **13** (Found: C, 45.99; H, 3.86.  $\text{C}_9\text{H}_9\text{BrF}_2$  requires C, 46.02; H, 3.90%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3096 (w), 2966 (s), 2936 (m), 2874 (m), 1618 (s), 1577 (m), 1505 (w), 1475 (s), 1416 (s), 1383 (w), 1344 (w), 1282 (w), 1226 (w), 1188 (w), 1113 (s), 1079 (w), 1038 (w), 994 (s), 866 (s), 842 (s), 771 (w), 694 (w), 580 (m), 512 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.94 (t,  $J = 7.4$  Hz, 3 H,  $\text{CH}_2\text{-CH}_3$ ), 1.59 (sextet,  $J = 7.4$  Hz, 2 H,  $\text{CH}_2\text{-CH}_3$ ), 2.60 (t,  $J = 7.5$  Hz, 2 H, Ar– $\text{CH}_2$ ), 7.02 (d, line distance 6.8 Hz, AA'-part of a AA'XX'-spectrum, 2 H, H4,6);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.6 ( $\text{CH}_2\text{-CH}_3$ ), 22.5 ( $\text{CH}_2\text{-CH}_3$ ), 24.0 (d,  $^3J_{\text{CF}} = 1.9$  Hz, Ar– $\text{CH}_2$ ), 114.9 (d, line distance 30.0 Hz, AA'-part of a AA'XX'-spectrum, C4,6), 117.4 (t,  $^2J_{\text{CF}} = 20.5$  Hz, C2), 118.7 (t,  $^3J_{\text{CF}} = 12.7$  Hz, C5), 161.5 (dd,  $^1J_{\text{CF}} = 249.9$  Hz,  $^2J_{\text{CF}} = 10.4$  Hz, C1,3);  $m/z$  (CI) 237, 235 [ $\text{MH}^+$ ], 207, 205 [ $\text{MH}^+ - \text{C}_2\text{H}_5$ ], 189, 136.

**2-(3,5-Difluoro-4-propylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 5{4}.** According to *GPI*, but using diethyl ether instead of THF as solvent, from 66.6 g (283 mmol) 5-bromo-1,3-difluoro-2-propylbenzene **13** was obtained 36.7 g (48%) boronic ester **5{4}**; mp  $40.0^\circ\text{C}$  (Found: C, 62.72; H, 7.14.  $\text{C}_{14}\text{H}_{19}\text{BF}_2\text{O}_2$  requires C, 62.61; H, 7.20%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  2966 (s), 2937 (m), 2899 (m), 2874 (m), 1628 (w), 1569 (m), 1483 (m), 1429 (m), 1381 (m), 1332 (s), 1253 (s), 1191 (w), 1109 (s), 1045 (w), 1000 (m), 984 (m), 912 (w), 868 (m), 811 (m), 709 (m), 689 (s), 583 (w), 550 (w), 493 (m), 443 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.94 (t,  $J = 7.4$  Hz, 3 H,  $\text{CH}_2\text{-CH}_3$ ), 1.00 (s, 6 H,  $\text{CMe}_2$ ), 1.61 (sextet,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2\text{-CH}_3$ ), 2.65 (t,  $J = 7.5$  Hz, 2 H, Ar– $\text{CH}_2$ ), 3.74 (s, 4 H,  $2 \times \text{OCH}_2$ ), 7.26 (d, line distance 8.3 Hz, AA'-part of a AA'XX'-spectrum, 2 H, H2,6);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.7 ( $\text{CH}_2\text{-CH}_3$ ), 21.8 ( $\text{CMe}_2$ ), 22.7 ( $\text{CH}_2\text{-CH}_3$ ), 24.4 (Ar– $\text{CH}_2$ ), 31.8 ( $\text{CMe}_2$ ), 72.3 ( $2 \times \text{OCH}_2$ ), 115.6 (d, line distance 24.3 Hz, AA'-part of a AA'XX'-spectrum, C2,6), 120.3 (t,  $^2J_{\text{CF}} = 20.7$  Hz, C4), 161.3 (dd,  $^1J_{\text{CF}} = 246.7$  Hz,  $^3J_{\text{CF}} = 8.4$  Hz, C3,5);  $m/z$  (CI)  $m/z = 269, 268, 267$  [ $\text{MH}^+$ ], 249 [ $\text{MH}^+ - \text{HF}$ ], 239.

**1-(2,3-Difluorophenyl)propan-1-ol 15.** The experimental procedure was as described for the preparation of compound **12**. Quantities: 54.8 g (480 mmol) 1,2-difluorobenzene **14**, 300 ml (480 mmol) 1.6 M *n*-BuLi, 47.7 ml (36.2 g, 624 mmol) propanal. Yield: 79.1 g (96%) alcohol **15**; bp  $68\text{--}70^\circ\text{C}/12$  mbar (Found: C, 62.78; H, 5.85.  $\text{C}_9\text{H}_{10}\text{F}_2\text{O}$  requires C, 62.66; H, 5.96%);  $\nu_{\text{max}}$

(KBr)/ $\text{cm}^{-1}$  3361 (s), 2971 (s), 2937 (m), 2881 (w), 1627 (w), 1596 (w), 1486 (s), 1383 (w), 1362 (w), 1329 (w), 1276 (m), 1202 (m), 1095 (w), 1064 (w), 1046 (w), 958 (m), 877 (w), 825 (w), 786 (w), 749 (m), 726 (m), 700 (w), 667 (w), 599 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.94 (t,  $J = 7.4$  Hz, 3 H,  $\text{CH}_2\text{-CH}_3$ ), 1.73–1.88 (m, 2 H,  $\text{CH}_2\text{-CH}_3$ ), 2.10 (d,  $J = 4.3$  Hz, 1 H, OH), 4.96 (dd,  $J = 11.1$  Hz,  $J = 6.4$  Hz, 1 H, CH–OH), 7.02–7.10 (m, 2 H, Ar–H), 7.19–7.23 (m, 1 H, Ar–H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 9.8 ( $\text{CH}_2\text{-CH}_3$ ), 30.8 ( $\text{CH}_2\text{-CH}_3$ ), 69.4 (CH–OH), 115.8 (d,  $^2J_{\text{CF}} = 17.1$  Hz, C4), 121.9 (t,  $J = 3.4$  Hz) and 124.1 (dd,  $J = 6.8$  Hz,  $J = 4.6$  Hz, C5,6), 134.0 (d,  $J = 10.2$  Hz, C1), 147.8 (dd,  $^1J_{\text{CF}} = 247.1$  Hz,  $^2J_{\text{CF}} = 12.9$  Hz) and 150.3 (dd,  $^1J_{\text{CF}} = 247.9$  Hz,  $^2J_{\text{CF}} = 12.9$  Hz, C2,3);  $m/z$  (EI) 172 [ $\text{M}^+$ ], 115, 95.

**1,2-Difluoro-3-propylbenzene 16.** The experimental procedure was as described for the preparation of compound **13**. Quantities: 184 g (1.30 mol) phosphorus pentoxide, 75.0 g (436 mmol) 1-(2,3-difluorophenyl)propan-1-ol **15**, 500 mg  $\text{PtO}_2$ . Yield: 46.3 g (68%) alkylbenzene **16**; bp  $40\text{--}43^\circ\text{C}/11$  mbar (Found: C, 69.22; H, 6.45.  $\text{C}_9\text{H}_{10}\text{F}_2$  requires C, 69.30; H, 6.39%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3051 (w), 2965 (m), 2935 (m), 2874 (m), 1627 (m), 1595 (m), 1489 (s), 1382 (w), 1342 (w), 1280 (m), 1203 (m), 1160 (w), 1102 (w), 1054 (w), 980 (w), 893 (w), 856 (w), 825 (w), 775 (m), 725 (m), 695 (w), 681 (w), 589 (w), 558 (w), 520 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.96 (t,  $J = 7.6$  Hz, 3 H,  $\text{CH}_2\text{-CH}_3$ ), 1.60–1.69 (m, 2 H,  $\text{CH}_2\text{-CH}_3$ ), 2.64 (t,  $J = 7.6$  Hz, 2 H, Ar– $\text{CH}_2$ ), 6.91–7.02 (m, 3 H, Ar–H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.7 ( $\text{CH}_2\text{-CH}_3$ ), 23.2 ( $\text{CH}_2\text{-CH}_3$ ), 30.8 (Ar– $\text{CH}_2$ ), 114.5 (d,  $^2J_{\text{CF}} = 17.1$  Hz, C6), 123.5 (dd,  $J = 6.8$  Hz,  $J = 4.6$  Hz) and 125.2 (t,  $J = 3.6$  Hz, C4,5), 131.9 (d,  $J = 12.9$  Hz, C3), 149.1 (dd,  $^1J_{\text{CF}} = 245.6$  Hz,  $^2J_{\text{CF}} = 12.1$  Hz) and 150.6 (dd,  $^1J_{\text{CF}} = 247.1$  Hz,  $^2J_{\text{CF}} = 13.3$  Hz, C1,2);  $m/z$  (EI) 156 [ $\text{M}^+$ ], 127 [ $\text{M}^+ - \text{C}_2\text{H}_5$ ].

**2-(2,3-Difluoro-4-propylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 5{5}.** According to *GPI* from 42.3 g (271 mmol) 1,2-difluoro-3-propylbenzene **16** was obtained 56.3 g (78%) boronic ester **5{5}**; mp  $26.7^\circ\text{C}$  (Found: C, 62.72; H, 7.14.  $\text{C}_{14}\text{H}_{19}\text{BF}_2\text{O}_2$  requires C, 62.61; H, 7.05%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  2963 (s), 2936 (s), 2874 (m), 1632 (w), 1481 (s), 1449 (s), 1377 (w), 1340 (m), 1319 (s), 1253 (m), 1191 (w), 1144 (m), 1097 (w), 1058 (w), 1011 (w), 971 (w), 869 (w), 818 (w), 693 (w), 669 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.94 (t,  $J = 7.3$  Hz, 3 H,  $\text{CH}_2\text{-CH}_3$ ), 1.03 (s, 6 H,  $\text{CMe}_2$ ), 1.64 (sextet,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2\text{-CH}_3$ ), 2.64 (t,  $J = 7.8$  Hz, 2 H, Ar– $\text{CH}_2$ ), 3.78 (s, 4 H,  $2 \times \text{OCH}_2$ ), 6.90 (ddd,  $^3J_{\text{HH}} = 7.5$  Hz,  $^4J_{\text{FH}} = 6.3$  Hz,  $^5J_{\text{FH}} = 1.1$  Hz, 1 H, H5), 7.34 (ddd,  $^3J_{\text{HH}} = 7.5$  Hz,  $^4J_{\text{FH}} = 5.6$  Hz,  $^5J_{\text{FH}} = 1.7$  Hz, 1 H, H5);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.6 ( $\text{CH}_2\text{-CH}_3$ ), 21.8 ( $\text{CMe}_2$ ), 23.1 ( $\text{CH}_2\text{-CH}_3$ ), 30.9 (Ar– $\text{CH}_2$ ), 31.8 ( $\text{CMe}_2$ ), 72.4 ( $2 \times \text{OCH}_2$ ), 125.6 (t,  $J_{\text{CF}} = 3.6$  Hz) and 129.5 (dd,  $^3J_{\text{CF}} = 7.4$  Hz,  $^4J_{\text{CF}} = 4.7$  Hz, C5,6), 134.2 (d,  $^2J_{\text{CF}} = 12.9$  Hz, C4), 149.0 (dd,  $^1J_{\text{CF}} = 245.8$  Hz,  $^2J_{\text{CF}} = 14.6$  Hz, C3), 154.6 (dd,  $^1J_{\text{CF}} = 251.3$  Hz,  $^2J_{\text{CF}} = 12.5$  Hz, C2);  $m/z$  (CI) 269, 268, 267 [ $\text{MH}^+$ ].

**1-Bromo-3-fluoro-4-trimethylsilylbenzene 17.** To a solution of 301 g (1.00 mol) 1-bromo-3-fluoro-4-iodobenzene **1{2}** in 1 l dry diethyl ether 625 ml (1.00 mol) 1.6 M *n*-BuLi were added at  $-78^\circ\text{C}$ . After 1 h 164 ml (141 g, 1.30 mol) TMSCl and 6.36 g (50.0 mmol) *N,N*-dimethylaminopyridine were added at  $-78^\circ\text{C}$ . The mixture was allowed to reach room temperature over night and diethyl ether and water were added. The organic phase was washed with water and brine, dried over  $\text{MgSO}_4$  and the solvent was removed under reduced pressure. Distillation (bp  $90\text{--}91^\circ\text{C}/11$  mbar) yielded 236 g (96%) silylbenzene **17** (Found: C, 43.73; H, 4.89.  $\text{C}_9\text{H}_{12}\text{BrFSi}$  requires C, 43.85; H, 4.93%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3059 (w), 2959 (m), 2900 (w), 1586 (s), 1552 (s), 1529 (w), 1468 (m), 1407 (m), 1380 (s), 1323 (w), 1252 (s), 1200 (s), 1154 (w), 1128 (m), 1089 (w), 1061 (m), 872 (s), 843 (s), 813 (m), 762 (m), 705 (w), 692 (w), 631 (w), 577 (w), 545 (w), 452 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.30 (s, 9 H,  $\text{SiMe}_3$ ), 7.16 (d,



$^3J_{\text{FH}} = 8.32$  Hz, 1 H, H2), 7.22–7.27 (m, 2 H, H5,6);  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.2 (SiMe<sub>3</sub>), 118.4 (d,  $^2J_{\text{CF}} = 29.6$  Hz, C2), 124.0 (d,  $^3J_{\text{CF}} = 9.9$  Hz, C1), 125.2 (d,  $^2J_{\text{CF}} = 30.7$  Hz, C4), 127.1 (d,  $^4J_{\text{CF}} = 3.4$  Hz, C6), 136.0 (d,  $^3J_{\text{CF}} = 12.5$  Hz, C5), 167.1 (d,  $^1J_{\text{CF}} = 245.2$  Hz, C3);  $m/z$  (EI) 248, 246 [ $\text{M}^+$ ], 233, 231, [ $\text{M}^+ - \text{CH}_3$ ], 151 [ $\text{M}^+ - \text{HBr}$ ], 105, 103, 77, 47.

**1-(3-Fluoro-4-trimethylsilylphenyl)propan-1-ol 18.** The experimental procedure was as described for the preparation of compound **12**. Quantities: 124 g (503 mmol) 1-bromo-3-fluoro-4-trimethylsilylbenzene **17**, 345 ml (552 mmol) 1.6 M *n*-BuLi, 50.0 ml (40.0 g, 689 mmol) propanal. Yield: 90.1 g (79%) alcohol **18**; bp 119 °C / 12 mbar (Found: C, 63.67; H, 8.46. C<sub>12</sub>H<sub>19</sub>FSi requires C, 63.53; H, 8.57%);  $\nu_{\text{max}}$  (KBr)/cm<sup>–1</sup> 3366 (br s), 2936 (s), 2900 (m), 2878 (m), 1613 (m), 1555 (m), 1484 (w), 1460 (w), 1402 (s), 1253 (s), 1223 (m), 1138 (w), 1094 (w), 1068 (m), 1044 (w), 1017 (w), 980 (w), 950 (w), 845 (s), 762 (m), 717 (w), 695 (w), 636 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.31 (s, 9 H, SiMe<sub>3</sub>), 0.93 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 3 H, CH<sub>2</sub>–CH<sub>3</sub>), 1.70–1.83 (m, 2 H, CH<sub>2</sub>–CH<sub>3</sub>), 1.99 (br. s, 1 H, OH), 4.59 (d,  $^3J_{\text{HH}} = 6.5$  Hz, 1 H, CH–OH), 6.99 (dd,  $^3J_{\text{FH}} = 9.6$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1 H, H2), 7.09 (dd,  $^3J_{\text{HH}} = 7.5$  Hz,  $^5J_{\text{FH}} = 0.7$  Hz, 1 H, H6), 7.36 (dd,  $^3J_{\text{HH}} = 7.5$  Hz,  $^4J_{\text{FH}} = 5.8$  Hz, 1 H, H5);  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.07 (SiMe<sub>3</sub>), 10.0 (CH<sub>2</sub>–CH<sub>3</sub>), 30.8 (CH<sub>2</sub>–CH<sub>3</sub>), 75.3 (CH–OH), 112.2 (d,  $^2J_{\text{CF}} = 26.1$  Hz, C2), 121.3 (d,  $^4J_{\text{CF}} = 2.3$  Hz, C6), 125.0 (d,  $^2J_{\text{CF}} = 30.7$  Hz, C4), 135.1 (d,  $^3J_{\text{CF}} = 11.8$  Hz, C5), 148.7 (d,  $^3J_{\text{CF}} = 7.6$  Hz, C1), 167.6 (d,  $^1J_{\text{CF}} = 241.0$  Hz, C3);  $m/z$  (EI) 226 [ $\text{M}^+$ ], 197 [ $\text{M}^+ - \text{C}_2\text{H}_5$ ], 73.

**2-Fluoro-4-propyl-1-trimethylsilylbenzene 19.** The experimental procedure was as described for the preparation of compound **13**. Quantities: 142 g (705 mmol) phosphorus pentoxide, 85.1 g (376 mmol) 1-(3-fluoro-4-trimethylsilylphenyl)propan-1-ol **18**, 1.00 g PtO<sub>2</sub>. Yield: 41.2 g (52%) alkylbenzene **19**; bp 90 °C/11 mbar (Found: C, 68.51; H, 9.10. C<sub>12</sub>H<sub>19</sub>FSi requires C, 68.61; H, 9.19%);  $\nu_{\text{max}}$  (KBr)/cm<sup>–1</sup> 3062 (w), 2960 (m), 2933 (m), 2901 (w), 2872 (w), 1614 (m), 1552 (w), 1486 (w), 1462 (w), 1403 (m), 1252 (m), 1227 (w), 1143 (w), 1073 (w), 950 (w), 844 (s), 762 (w), 714 (w), 694 (w), 663 (w), 628 (w), 546 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.31 (s, 9 H, SiMe<sub>3</sub>), 0.96 (t,  $J = 7.4$  Hz, 3 H, CH<sub>2</sub>–CH<sub>3</sub>), 1.65 (sextet,  $J = 7.5$  Hz, 2 H, CH<sub>2</sub>–CH<sub>3</sub>), 2.59 (t,  $J = 7.7$  Hz, 2 H, Ar–CH<sub>2</sub>), 6.83 (dd,  $^3J_{\text{FH}} = 9.7$  Hz,  $^4J_{\text{HH}} = 1.1$  Hz, 1 H, H3), 6.96 (d,  $^3J_{\text{HH}} = 7.4$  Hz, 1 H, H5), 7.30 (dd,  $^3J_{\text{HH}} = 7.4$  Hz,  $^4J_{\text{FH}} = 6.1$  Hz, 1 H, H6);  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –0.99 (SiMe<sub>3</sub>), 13.8 (CH<sub>2</sub>–CH<sub>3</sub>), 24.2 (CH<sub>2</sub>–CH<sub>3</sub>), 37.7 (Ar–CH<sub>2</sub>), 114.6 (d,  $^2J_{\text{CF}} = 25.4$  Hz, C3), 122.7 (d,  $^2J_{\text{CF}} = 30.4$  Hz, C1), 124.0 (d,  $^4J_{\text{CF}} = 2.7$  Hz, C5), 134.8 (d,  $^3J_{\text{CF}} = 11.8$  Hz, C6), 146.8 (d,  $^3J_{\text{CF}} = 8.0$  Hz, C4), 167.6 (dd,  $^1J_{\text{CF}} = 240.6$  Hz, C2);  $m/z$  (CI) 210 [ $\text{M}^+$ ], 195 [ $\text{M}^+ - \text{CH}_3$ ], 191 [ $\text{M}^+ - \text{F}$ ], 73.

**2-(2-Fluoro-4-propylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 5{2}.** To a solution of 31.8 g (151 mmol) 2-fluoro-4-propyl-1-trimethylsilylbenzene **19** in 200 ml dry dichloromethane 15.8 ml (41.6 g, 166 mmol) BBr<sub>3</sub> were added at room temperature. After 30 min a solution of 39.4 g (278 mmol) 2,2-dimethyl-1,3-propanediol in 100 ml dichloromethane was added. After 30 min satd. KHCO<sub>3</sub> was added until neutralization. The organic phase was washed with water and brine and dried over MgSO<sub>4</sub>, filtered and the solvent removed under reduced pressure. The oily residue was dissolved in 100 ml hexanes. Precipitated excess 2,2-dimethyl-1,3-propanediol was removed by filtration. From the filtrate the boronic ester **5{2}** crystallized at –25 °C. Yield: 26.1 g (69%); mp 71.8 °C (Found: C, 67.23; H, 8.06. C<sub>14</sub>H<sub>20</sub>BFO<sub>2</sub> requires C, 67.36; H, 8.01%);  $\nu_{\text{max}}$  (KBr)/cm<sup>–1</sup> 2962 (s), 2934 (s), 2874 (s), 1623 (m), 1560 (w), 1483 (s), 1422 (s), 1382 (m), 1340 (s), 1313 (s), 1254 (m), 1145 (m), 1106 (w), 1054 (w), 1034 (w), 999 (w), 946 (w), 866 (w), 819 (m), 738 (w), 707 (w), 663 (w), 632 (w), 555 (w), 505 (w), 488 (w), 456 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.93 (t,  $J = 7.4$  Hz, 3 H, CH<sub>2</sub>–CH<sub>3</sub>), 1.03

(s, 6 H, CMe<sub>2</sub>), 1.63 (sextet,  $J = 7.5$  Hz, 2 H, CH<sub>2</sub>–CH<sub>3</sub>), 2.58 (t,  $J = 7.7$  Hz, 2 H, Ar–CH<sub>2</sub>), 3.78 (s, 4 H, 2 × OCH<sub>2</sub>), 6.83 (dd,  $^3J_{\text{FH}} = 10.9$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1 H, H3), 6.94 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1 H, H5) 7.63 (t,  $^3J_{\text{HH}} \approx ^4J_{\text{FH}} \approx 7.1$  Hz, 1 H, H6);  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) 13.6 (CH<sub>2</sub>–CH<sub>3</sub>), 21.8 (CMe<sub>2</sub>), 24.0 (CH<sub>2</sub>–CH<sub>3</sub>), 31.7 (CMe<sub>2</sub>), 37.7 (Ar–CH<sub>2</sub>), 72.3 (2 × OCH<sub>2</sub>), 115.1 (d,  $^2J_{\text{CF}} = 24.3$  Hz, C3), 123.7 (d,  $^4J_{\text{CF}} = 2.7$  Hz, C5), 135.9 (d,  $^3J_{\text{CF}} = 8.7$  Hz, C6), 148.2 (d,  $^3J_{\text{CF}} = 8.4$  Hz, C4), 167.3 (d,  $^1J_{\text{CF}} = 249.4$  Hz, C2);  $m/z$  (CI) 251, 250, 249 [ $\text{MH}^+$ ], 231 [ $\text{MH}^+ - \text{HF}$ ].

**2-(4-Trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 2{1}.** According to *GPI* from 128 g (558 mmol) 4-bromo-1-trimethylsilylbenzene **21** was obtained 106 g (63%) boronic ester **2{1}**; mp 74.7 °C (Found: C, 64.12; H, 8.84. C<sub>14</sub>H<sub>23</sub>BO<sub>2</sub>Si requires C, 63.99; H, 8.79%);  $\nu_{\text{max}}$  (KBr)/cm<sup>–1</sup> 3063 (w), 3016 (w), 2957 (s), 2895 (m), 1685 (w), 1600 (m), 1535 (w), 1501 (m), 1482 (m), 1418 (s), 1382 (m), 1346 (s), 1319 (s), 1262 (m), 1245 (m), 1191 (w), 1140 (s), 1101 (s), 1020 (w), 966 (w), 837 (s), 816 (s), 757 (m), 729 (m), 687 (m), 667 (w), 648 (m), 625 (w), 560 (w), 498 (w), 476 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.32 (s, 9 H, SiMe<sub>3</sub>), 1.03 (s, 6 H, CMe<sub>2</sub>), 3.79 (s, 4 H, 2 × OCH<sub>2</sub>), 7.55 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 2 H, H3,5), 7.80 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 2 H, H2,6);  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.2 (SiMe<sub>3</sub>), 21.9 (CMe<sub>2</sub>), 31.9 (CMe<sub>2</sub>), 72.3 (2 × OCH<sub>2</sub>), 132.5 and 133.0 (C2,3,5,6) 143.3 (C4);  $m/z$  (EI) 262 [ $\text{M}^+$ ], 247 [ $\text{M}^+ - \text{CH}_3$ ], 177.

**2-(3-Fluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 2{2}.** According to *GPI*, but using diethyl ether instead of THF as solvent, from 156 g (632 mmol) 1-bromo-3-fluoro-4-trimethylsilylbenzene **17** was obtained 93.5 g (53%) boronic ester **2{2}**; mp 69.1 °C (Found: C, 60.01; H, 7.91. C<sub>14</sub>H<sub>22</sub>BFO<sub>2</sub>Si requires C, 59.98; H, 7.88%);  $\nu_{\text{max}}$  (KBr)/cm<sup>–1</sup> 2961 (s), 2903 (m), 2874 (m), 1612 (w), 1532 (m), 1483 (s), 1422 (s), 1384 (s), 1342 (s), 1316 (s), 1269 (m), 1249 (s), 1184 (m), 1120 (m), 1071 (s), 986 (m), 936 (w), 894 (m), 869 (m), 836 (s), 761 (m), 717 (m), 674 (s), 630 (w), 540 (w), 515 (w), 493 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.31 (s, 9 H, SiMe<sub>3</sub>), 0.99 (s, 6 H, CMe<sub>2</sub>), 3.74 (s, 4 H, 2 × OCH<sub>2</sub>), 7.36–7.40 (m, 2 H, H2,5), 7.54 (d,  $^3J_{\text{HH}} = 7.1$  Hz, 1 H, H6);  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.1 (SiMe<sub>3</sub>), 21.8 (CMe<sub>2</sub>), 31.8 (CMe<sub>2</sub>), 72.3 (2 × OCH<sub>2</sub>), 119.3 (d,  $^2J_{\text{CF}} = 23.9$  Hz, C2), 127.7 (d,  $^2J_{\text{CF}} = 30.4$  Hz, C4), 128.9 (d,  $^4J_{\text{CF}} = 2.7$  Hz, C6), 134.3 (d,  $^3J_{\text{CF}} = 10.6$  Hz, C5), 167.3 (d,  $^1J_{\text{CF}} = 241.0$  Hz, C3);  $m/z$  (CI) 281 [ $\text{MH}^+$ ], 280 [ $\text{M}^+$ ], 265 [ $\text{M}^+ - \text{CH}_3$ ], 261 [ $\text{M}^+ - \text{F}$ ], 223, 209, 195, 189.

**1,2-Difluoro-3-trimethylsilylbenzene 22.** To a solution of 114 g (1.00 mol) 1,2-difluorobenzene **14** in 1 l dry THF 625 ml (1.00 mol) 1.6 M *n*-BuLi were added at –78 °C. After 1 h 140 ml (120 g, 1.10 mol) TMSCl was added at –78 °C. The mixture was allowed to reach room temperature overnight and diethyl ether and water was added. The organic phase was washed with water and brine, dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. Distillation (bp 100–102 °C/70 mbar) yielded 170 g (91%) silylbenzene **22** (Found: C, 58.03; H, 6.49. C<sub>9</sub>H<sub>12</sub>SiF<sub>2</sub> requires C, 58.04; H, 6.57%);  $\nu_{\text{max}}$  (KBr)/cm<sup>–1</sup> 2959 (s), 2926 (m), 2874 (w), 1613 (w), 1582 (w), 1450 (s), 1412 (w), 1292 (w), 1266 (s), 1252 (s) 1219 (w), 1185 (m), 1146 (w), 1059 (w), 907 (w), 843 (s), 782 (w), 759 (m), 695 (w), 642 (w), 602 (w), 561 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.34 (s, 9 H, SiMe<sub>3</sub>), 7.03–7.18 (m, 3 H);  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.1 (SiMe<sub>3</sub>), 118.2 (d,  $^2J_{\text{CF}} = 17.8$  Hz, C6), 124.3 (dd,  $^3J_{\text{CF}} = 5.7$  Hz,  $^4J_{\text{CF}} = 3.8$  Hz, C5), 129.31 (d,  $^3J_{\text{CF}} = 5.7$  Hz, C4), 129.32 (d,  $^2J_{\text{CF}} = 14.0$  Hz, C3), 150.2 (dd,  $^1J_{\text{CF}} = 250.5$  Hz,  $^2J_{\text{CF}} = 15.6$  Hz, C1), 154.4 (dd,  $^1J_{\text{CF}} = 241.4$  Hz,  $^2J_{\text{CF}} = 10.7$  Hz, C2);  $m/z$  (EI) 186 [ $\text{M}^+$ ], 171 [ $\text{M}^+ - \text{CH}_3$ ], 143, 105, 103, 79, 77.

**2-(2,3-Difluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 2{2}.** According to *GPI* from 169 g (910 mmol) 1,2-difluoro-3-trimethylsilylbenzene **22** was obtained 251 g

(87%) boronic ester **2{5}**; mp 74.7 °C (Found: C, 56.39; H, 7.10.  $C_{14}H_{21}BF_2O_2Si$  requires C, 56.15; H, 6.91%);  $\nu_{max}$  (KBr)/ $cm^{-1}$  2964 (s), 2908 (m), 2875 (m), 1622 (m), 1481 (s), 1434 (s), 1407 (m), 1377 (m), 1340 (m), 1313 (s), 1251 (s), 1224 (m), 1172 (w), 1129 (m), 1059 (m), 1006 (m), 988 (w), 933 (w), 910 (m), 832 (s), 744 (m), 699 (m), 662 (m), 616 (w), 563 (w), 546 (w), 526 (w), 493 (w);  $\delta_H$ (400.1 MHz,  $CDCl_3$ ) 0.32 (s, 9 H,  $SiMe_3$ ), 1.03 (s, 6 H,  $CMe_2$ ), 3.79 (s, 4 H,  $2 \times OCH_2$ ), 7.07 (ddd,  $^3J_{HH} = 7.4$  Hz,  $^4J_{HF} = 4.1$  Hz,  $^5J_{HF} = 0.9$  Hz, 1 H, H5), 7.40 (ddd,  $^3J_{HH} = 7.3$  Hz,  $^4J_{HF} = 4.7$  Hz,  $^5J_{HF} = 0.8$  Hz, 1 H, H6);  $\delta_C$ (100.6 MHz,  $CDCl_3$ ) -1.2 ( $SiMe_3$ ), 21.7 ( $CMe_2$ ), 31.7 ( $CMe_2$ ), 72.4 ( $2 \times OCH_2$ ), 128.4 (dd,  $^3J_{CF} = 9.5$  Hz,  $^4J_{CF} = 4.3$  Hz, C5), 130.1 (dd,  $^3J_{CF} = 6.0$  Hz,  $^4J_{CF} = 3.6$  Hz, C6), 131.5 (d,  $^2J_{CF} = 27.2$  Hz, C4), 154.0 (dd,  $^1J_{CF} = 254.2$  Hz,  $^2J_{CF} = 15.3$  Hz, C3), 154.4 (dd,  $^1J_{CF} = 241.3$  Hz,  $^2J_{CF} = 13.4$  Hz, C2);  $m/z$  (CI) 299 [ $M^+$ ], 283 [ $M^+ - CH_3$ ], 279 [ $M^+ - F$ ], 241, 213, 197, 183, 69.

#### Parallel synthesis of biphenyls **3{H,B}** and **4{H,B}**

The reactions were carried out using standard glassware. Up to four reaction vessels were heated/cooled simultaneously in a large oil bath/dewar.

**4'-Bromo-4-trimethylsilylbiphenyl 3{I,I}**. According to *GP2* from *p*-bromiodobenzene **1{I}** and 2-(4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane **2{I}** was obtained bromo biphenyl **3{I,I}** 13.1 g (86%); mp 97–99 °C; lit.<sup>14</sup> mp 91–93 °C (Found: C, 59.01; H, 5.61.  $C_{15}H_{17}BrSi$  requires C, 59.09; H, 5.57%);  $\nu_{max}$  (KBr)/ $cm^{-1}$  3063 (w), 3019 (w), 2955 (m), 2894 (w), 1475 (w), 1379 (w), 1246 (m), 1112 (m), 1071 (m), 999 (m), 834 (s), 804 (s), 755 (s), 623 (m), 544 (m), 497 (s);  $\delta_H$ (400.1 MHz,  $CDCl_3$ ) 0.34 (s, 9 H,  $SiMe_3$ ), 7.46–7.50 (m, 2 H, H2',6'), 7.55–7.63 (m, 6 H, H2,3,3',5',5',6');  $\delta_C$ (100.6 MHz,  $CDCl_3$ ) -1.1 ( $SiMe_3$ ), 121.6 (C4'), 126.2 (C2,6), 128.7, (C2',6'), 131.9 (C3',5'), 133.9 (C3,5), 139.8 and 140.0 and 140.3 (C1,1',4);  $m/z$  (EI) 306, 304 [ $M^+$ ], 291, 289 [ $M^+ - CH_3$ ].

**4'-Iodo-4-trimethylsilylbiphenyl 4{I,I}**. According to *GP3* from 10.2 g (33.4 mmol) 4'-bromo-4-trimethylsilylbiphenyl **3{I,I}** was obtained 10.4 g (88%) iodo biphenyl **4{I,I}**; subl. 120 °C/10<sup>-3</sup> mbar; mp 111–112 °C (Found: C, 51.14; H, 4.86.  $C_{15}H_{17}ISi$  requires C, 51.26; H, 5.02%);  $\nu_{max}$  (KBr)/ $cm^{-1}$  3065(w), 3017 (w), 2953 (w), 2894 (w), 1596 (w), 1474 (m), 1377 (w), 1245 (m), 1112 (m), 997 (m), 843 (s), 803 (s), 756 (s), 621 (w), 494(m);  $\delta_H$ (400.1 MHz,  $CDCl_3$ ) 0.31 (s, 9 H,  $SiMe_3$ ), 7.34 (d, line distance 8.3 Hz, AA'-part of a AA'XX'-system, 2 H, H2,6), 7.49–7.61 (m, 4 H, H2',3',5',6'), 7.77 (d, line distance 8.4 Hz, XX'-part of a AA'XX'-system, 2 H, H3,5);  $\delta_C$ (100.6 MHz,  $CDCl_3$ ) -1.1 ( $SiMe_3$ ), 93.1 (C4'), 126.2 (C2,6), 129.0, (C2',6'), 133.9 (C3,5), 137.9 (C3',5'), 139.9 and 140.4 and 140.7 (C1,1',4);  $m/z$  (EI) 352 [ $M^+$ ], 337 [ $M^+ - CH_3$ ].

**4'-Bromo-3-fluoro-4-trimethylsilylbiphenyl 3{I,2}**. According to *GP2* from *p*-bromiodobenzene **1{I}** and 2-(3-fluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane **2{2}** was obtained bromo biphenyl **3{I,2}** 12.9 g (80%); bp 100 °C / 10<sup>-3</sup> mbar; mp 56.8 °C (Found: C, 55.73; H, 4.99.  $C_{15}H_{16}BrFSi$  requires C, 55.87; H, 5.08%);  $\nu_{max}$  (KBr)/ $cm^{-1}$  3062 (w), 2960 (w), 2900 (w), 1609 (m), 1569 (m), 1538 (m), 1498 (m), 1471 (m), 1405 (m), 1383 (m), 1299 (w), 1254 (m), 1179 (m), 1140 (w), 1106 (w), 1086 (m), 1072 (m), 1028 (w), 1009 (m), 950 (w), 893 (s), 877 (m), 844 (s), 813 (s), 764 (s), 712 (m), 696 (w), 630 (m), 550 (w), 500 (m), 461 (w), 447 (w);  $\delta_H$ (400.1 MHz,  $CDCl_3$ ) 0.37 (s, 9 H,  $SiMe_3$ ), 7.19 (dd,  $^3J_{FH} = 9.7$  Hz,  $^4J_{HH} = 1.3$  Hz, 1 H, H2), 7.33 (dd,  $^3J_{HH} = 7.6$  Hz,  $^4J_{HH} = 1.3$  Hz, 1 H, H6), 7.43–7.49 (m, 3 H), 7.56–7.60 (m, 2 H);  $\delta_C$ (100.6 MHz,  $CDCl_3$ ) -1.1 ( $SiMe_3$ ), 113.0 (d,  $^2J_{CF} = 26.9$  Hz, C2), 122.2 (C4'), 125.3 (d,  $^2J_{CF} = 30.7$  Hz, C4), 128.6 (C2',6'), 132.0 (C3',5'), 135.6 (d,  $^3J_{CF} = 12.1$  Hz, C5), 138.8 (d,  $^4J_{CF} = 2.7$  Hz, C1'), 143.3 (d,  $^3J_{CF} = 8.4$  Hz, C1), 167.8 (d,  $^1J_{CF} = 241.4$  Hz,

C3);  $m/z$  (EI) 324, 322 [ $M^+$ ], 309, 307 [ $M^+ - CH_3$ ], 247, 245 [ $M^+ - CH_3SiF$ ], 228 [ $M^+ - Br$ ], 213, 199, 165 [ $M^+ - CH_3 - CH_3SiF - HBr$ ], 77.

**3-Fluoro-4'-iodo-4-trimethylsilylbiphenyl 4{I,2}**. According to *GP3* from 12.5 g (38.8 mmol) 4'-bromo-3-fluoro-4-trimethylsilylbiphenyl **3{I,2}** was obtained 12.8 g (89%) iodo biphenyl **4{I,2}**; mp 74.0 °C (Found: C, 48.66; H, 4.36.  $C_{15}H_{16}FISi$  requires C, 48.61; H, 4.35%);  $\nu_{max}$  (KBr)/ $cm^{-1}$  2956 (w), 1607 (m), 1534 (m), 1496 (s), 1469 (m), 1402 (w), 1378 (m), 11299 (w), 1247 (m), 1179 (m), 1139 (w), 1084 (w), 1060 (w), 1002 (w), 893 (w), 844 (s), 808 (s), 760 (m), 710 (w), 623 (w), 544 (w), 494 (w), 457 (w), 434 (w);  $\delta_H$ (400.1 MHz,  $CDCl_3$ ) 0.36 (s, 9 H,  $SiMe_3$ ), 7.18 (dd,  $^3J_{FH} = 9.7$  Hz,  $^4J_{HH} = 1.5$  Hz, 1 H, H2), 7.30–7.33 (m, 3 H), 7.46 (dd,  $^3J_{HH} = 7.6$  Hz,  $^4J_{FH} = 5.9$  Hz, 1 H, H5), 7.78 (d, line distance 8.6 Hz, AA'-part of a AA'XX'-system, 2 H, H3',5');  $\delta_C$ (100.6 MHz,  $CDCl_3$ ) -1.1 ( $SiMe_3$ ), 93.7 (C4'), 113.0 (d,  $^2J_{CF} = 26.9$  Hz, C2), 122.1 (d,  $^4J_{CF} = 2.7$  Hz, C6), 125.4 (d,  $^2J_{CF} = 30.4$  Hz, C4), 128.8 (C2',6'), 135.7 (d,  $^3J_{CF} = 12.1$  Hz, C5), 138.0 (C3',5'), 139.4 (d,  $^4J_{CF} = 2.7$  Hz, C1'), 143.4 (d,  $^3J_{CF} = 8.4$  Hz, C1), 167.8 (d,  $^1J_{CF} = 241.4$  Hz, C3);  $m/z$  (EI) 370 [ $M^+$ ], 355 [ $M^+ - CH_3$ ], 293 [ $M^+ - (CH_3)_2SiF$ ], 228 [ $M^+ - CH_3 - I$ ], 228 [ $M^+ - 2CH_3 - I$ ], 165 [ $M^+ - (CH_3)_2SiF - HI$ ].

#### 4'-Bromo-2,3-difluoro-4-trimethylsilylbiphenyl 3{I,5}

According to *GP2* from *p*-bromiodobenzene **1{I}** and 2-(2,3-difluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane **2{5}** was obtained bromo biphenyl **3{I,5}** 15.0 g (88%); mp 64.0 °C (Found: C, 52.79; H, 4.43.  $C_{15}H_{15}BrF_2Si$  requires C, 52.91; H, 4.45%);  $\nu_{max}$  (KBr)/ $cm^{-1}$  3032 (w), 2958 (w), 2898 (w), 1614 (w), 1587 (w), 1539 (w), 1499 (w), 1470 (w), 1436 (s), 1388 (m), 1311 (w), 1279 (w), 1252 (m), 1223 (m), 1153 (m), 1098 (w), 1071 (w), 1008 (w), 914 (m), 891 (w), 838 (s), 806 (m), 763 (m), 740 (w), 715 (w), 696 (w), 652 (w), 630 (w), 607 (w), 555 (w), 527 (w), 485 (w), 432 (w);  $\delta_H$ (400.1 MHz,  $CDCl_3$ ) 0.37 (s, 9 H,  $SiMe_3$ ), 7.12–7.19 (m, 2 H, H5,6), 7.40–7.44 (m, 2 H, H2',6'), 7.57–7.60 (m, 2 H, H3',5');  $\delta_C$ (100.6 MHz,  $CDCl_3$ ) -1.1 ( $SiMe_3$ ), 122.5 (C4'), 124.8 (d,  $^3J_{CF} = 3.0$  Hz, C6), 128.4 (d,  $^2J_{CF} = 26.2$  Hz, C4), 129.0 (dd,  $^2J_{CF} = 11.4$  Hz,  $^3J_{CF} = 5.3$  Hz, C5), 130.5 (d,  $^4J_{CF} = 3.0$  Hz, C2',6'), 130.7 (d,  $^2J_{CF} = 10.2$  Hz, C1), 131.8 (C3',5'), 133.7 (d,  $^3J_{CF} = 2.2$  Hz, C1'), 147.4 (dd,  $^1J_{CF} = 252.2$  Hz,  $^2J_{CF} = 17.3$  Hz, C2), 155.0 (dd,  $^1J_{CF} = 241.8$  Hz,  $^2J_{CF} = 11.8$  Hz, C3);  $m/z$  (EI) 342, 340 [ $M^+$ ], 246, 165.

**2,3-Difluoro-4'-iodo-4-trimethylsilylbiphenyl 4{I,5}**. According to *GP3* from 15.0 g (44.0 mmol) 4'-bromo-2,3-difluoro-4-trimethylsilylbiphenyl **3{I,5}** was obtained 16.2 g (95%) iodo biphenyl **4{I,5}**; mp 89.1 °C (Found: C, 46.60; H, 3.89.  $C_{15}H_{15}F_2ISi$  requires C, 46.67; H, 3.91%);  $\nu_{max}$  (KBr)/ $cm^{-1}$  3029 (w), 2957 (w), 2896 (w), 1619 (w), 1584 (w), 1497 (w), 1468 (w), 1436 (s), 1385 (m), 1308 (w), 1278 (w), 1252 (m), 1221 (m), 1150 (w), 1195 (w), 1058 (w), 1004 (w), 913 (s), 842 (s), 810 (s), 764 (m), 740 (w), 708 (w), 654 (w), 634 (w), 608 (w), 527 (w);  $\delta_H$ (400.1 MHz,  $CDCl_3$ ) 0.37 (s, 9 H,  $SiMe_3$ ), 7.12–7.19 (m, 2 H, H5,6), 7.29 (d, line distance 7.1 Hz, AA'-part of a AA'XX'-spectrum, 2 H, H2',6'), 7.79 (d, line distance 9.0 Hz, XX'-part of a AA'XX'-spectrum, 2 H, H3',5');  $\delta_C$ (100.6 MHz,  $CDCl_3$ ) -1.1 ( $SiMe_3$ ), 94.2 (C4'), 124.7 (dd,  $^3J_{CF} = 2.8$  Hz,  $^4J_{CF} = 1.3$  Hz, C6), 128.4 (dd,  $^2J_{CF} = 27.3$  Hz,  $^3J_{CF} = 1.5$  Hz, C4), 129.0 (dd,  $^3J_{CF} = 11.4$  Hz,  $^4J_{CF} = 5.3$  Hz, C5), 130.6 (d,  $^4J_{CF} = 3.0$  Hz, C2',6'), 130.8 (d,  $^2J_{CF} = 10.6$  Hz, C1), 134.3 (d,  $^3J_{CF} = 3.0$  Hz, C1'), 137.7 (C3',5'), 147.4 (dd,  $^1J_{CF} = 252.8$  Hz,  $^2J_{CF} = 17.1$  Hz, C2), 155.0 (dd,  $^1J_{CF} = 241.8$  Hz,  $^2J_{CF} = 11.8$  Hz, C3);  $m/z$  (EI) 388 [ $M^+$ ], 373 [ $M^+ - CH_3$ ], 246 [ $M^+ - CH_3 - I$ ], 165, 77.

**4'-Bromo-2'-fluoro-4-trimethylsilylbiphenyl 3{2,I}**. According to *GP2* from 1-bromo-3-fluoro-4-iodobenzene **1{2}** and 2-(4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane **2{I}**

was obtained bromo biphenyl **3**{2,1} 11.6 g (72); bp 110 °C/10<sup>-3</sup> mbar; mp 43.7 °C (Found: C, 55.73; H, 4.99. C<sub>15</sub>H<sub>16</sub>BrFSi requires C, 55.85; H, 4.99%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 2958 (w), 1600 (w), 1564 (w), 1504 (w), 1474 (m), 1436 (w), 1405 (w), 1379 (m), 1314 (w), 1245 (m), 1207 (m), 1127 (w), 1108 (w), 1070 (w), 1002 (w), 870 (m), 834 (s), 805 (s), 755 (s), 725 (m), 694 (m), 624 (w), 570 (m), 539 (w), 508 (w), 464 (w), 433 (w);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.30 (s, 9 H), 7.31–7.35 (m, 3 H), 7.48–7.50 (m, 2 H), 7.59–7.61 (m, 2 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) –1.2 (SiMe<sub>3</sub>), 119.7 (d, <sup>2</sup>J<sub>CF</sub> = 26.2 Hz, C3'), 121.3 (d, <sup>3</sup>J<sub>CF</sub> = 9.5 Hz, C4'), 127.7 (d, <sup>4</sup>J<sub>CF</sub> = 3.8 Hz, C5'), 128.0 (C2,6), 131.7 (d, <sup>3</sup>J<sub>CF</sub> = 4.2 Hz, C6'), 133.6 (C3,5), 133.7 (d, <sup>2</sup>J<sub>CF</sub> = 19.7 Hz, C1'), 135.1 (d, <sup>3</sup>J<sub>CF</sub> = 1.1 Hz, C1), 140.4 (C4), 159.6 (d, <sup>1</sup>J<sub>CF</sub> = 252.8 Hz, C2'); *m/z* (EI) 324, 322 [M<sup>+</sup>], 309, 307 [M<sup>+</sup> – CH<sub>3</sub>].

**2'-Fluoro-4'-iodo-4-trimethylsilylbiphenyl 4**{2,1}. According to *GP3* from 11.0 g (34.2 mmol) 4'-bromo-2'-fluoro-4-trimethylsilylbiphenyl **3**{2,1} resulted 10.0 g (80%) iodo biphenyl **4**{2,1}; mp 39.8 °C (Found: C, 48.66; H, 4.36. C<sub>15</sub>H<sub>16</sub>FISi requires C, 48.45; H, 4.38%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 2955 (w), 1598 (m), 1561 (m), 1504 (w), 1472 (s), 1400 (m), 1379 (s), 1248 (s), 1206 (m), 1128 (w), 1108 (m), 1063 (w), 1002 (w), 949 (w), 859 (s), 833 (s), 805 (s), 754 (m), 725 (m), 663 (w), 622 (w), 572 (m), 533 (w), 505 (w), 461 (w), 423 (w);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.33 (s, 9 H), 7.18 (t, <sup>3</sup>J<sub>HH</sub> = <sup>4</sup>J<sub>FH</sub> = 8.1 Hz, 1 H, H6'), 7.51–7.58 (m, 4 H), 7.62–7.64 (m, 2 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) –1.2 (SiMe<sub>3</sub>), 92.0 (d, <sup>3</sup>J<sub>CF</sub> = 8.0 Hz, C4'), 125.4 (d, <sup>2</sup>J<sub>CF</sub> = 25.4 Hz, C3'), 128.0 (d, <sup>4</sup>J<sub>CF</sub> = 3.0 Hz, C2,6), 128.8 (d, <sup>2</sup>J<sub>CF</sub> = 13.3 Hz, C1'), 131.9 (d, <sup>3</sup>J<sub>CF</sub> = 3.8 Hz, C6'), 133.6 (C3,5), 133.7 (d, <sup>4</sup>J<sub>CF</sub> = 3.8 Hz, C5'), 135.2 (d, <sup>3</sup>J<sub>CF</sub> = 1.1 Hz, C1), 140.5 (C4), 159.3 (d, <sup>1</sup>J<sub>CF</sub> = 253.6 Hz, C2'); *m/z* (EI) 370 [M<sup>+</sup>], 355 [M<sup>+</sup> – CH<sub>3</sub>], 228 [M<sup>+</sup> – CH<sub>3</sub> – I].

#### 4'-Bromo-2',3-difluoro-4-trimethylsilylbiphenyl 3{2,2}.

According to *GP2* from 1-bromo-3-fluoro-4-iodobenzene **1**{2} and 2-(3-fluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]-dioxaborinane **2**{2} was obtained bromo biphenyl **3**{2,2} 12.5 g (73%); bp 100 °C/10<sup>-3</sup> mbar; mp 25.0 °C (Found: C, 52.79; H, 4.43. C<sub>15</sub>H<sub>15</sub>BrF<sub>2</sub>Si requires C, 53.01; H, 4.51%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3069 (w), 2958 (m), 2900 (w), 1612 (s), 1570 (m), 1538 (m), 1500 (m), 1472 (s), 1411 (m), 1384 (s), 1306 (m), 1251 (s), 1213 (m), 1178 (m), 1142 (m), 1125 (w), 1072 (m), 1130 (w), 902 (s), 845 (s), 812 (s), 763 (m), 713 (w), 696 (w), 632 (m), 583 (w), 547 (w), 451 (w);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.39 (s, 9 H, SiMe<sub>3</sub>), 7.19 (dt, <sup>3</sup>J<sub>FH</sub> = 9.6 Hz, <sup>4</sup>J<sub>HH</sub> = <sup>5</sup>J<sub>FH</sub> = 1.4 Hz, 1 H, H2), 7.30–7.40 (m, 4 H), 7.50 (dd, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>4</sup>J<sub>FH</sub> = 5.9 Hz, 1 H, H5);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) –1.1 (SiMe<sub>3</sub>), 115.0 (dd, <sup>2</sup>J<sub>CF</sub> = 27.3 Hz, <sup>4</sup>J<sub>CF</sub> = 3.4 Hz, C2), 119.9 (d, <sup>2</sup>J<sub>CF</sub> = 26.2 Hz, C3'), 121.9 (d, <sup>3</sup>J<sub>CF</sub> = 9.5 Hz, C4'), 124.1 (t, <sup>4</sup>J<sub>CF</sub> = <sup>4</sup>J<sub>CF'</sub> = 2.8 Hz, C6), 126.0 (d, <sup>2</sup>J<sub>CF</sub> = 30.7 Hz, C4), 127.8 (d, <sup>4</sup>J<sub>CF</sub> = 3.8 Hz, C5'), 131.4 (d, <sup>3</sup>J<sub>CF</sub> = 4.2 Hz, C6'), 133.7 (d, <sup>2</sup>J<sub>CF</sub> = 19.7 Hz, C1'), 135.3 (d, <sup>3</sup>J<sub>CF</sub> = 12.1 Hz, C5), 137.8 (dd, <sup>3</sup>J<sub>CF</sub> = 8.7 Hz, <sup>3</sup>J<sub>CF</sub> = 1.1 Hz, C1), 159.4 (d, <sup>1</sup>J<sub>CF</sub> = 253.2, C2'), 167.4 (d, <sup>1</sup>J<sub>CF</sub> = 241.0 Hz, C3); *m/z* (EI) 342, 340 [M<sup>+</sup>], 327, 325 [M<sup>+</sup> – CH<sub>3</sub>], 246 [M<sup>+</sup> – Br], 165.

**2',3-Difluoro-4'-iodo-4-trimethylsilylbiphenyl 4**{2,2}. According to *GP3* from 11.9 g (35.0 mmol) 4'-bromo-2',3-difluoro-4-trimethylsilyl-biphenyl **3**{2,2} was obtained 11.7 g (86%) iodo biphenyl **4**{2,2}; mp 53.2 °C (Found: C, 46.40; H, 3.89. C<sub>15</sub>H<sub>15</sub>F<sub>2</sub>ISi requires C, 46.61; H, 4.01%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3059 (w), 2957 (w), 2897 (w), 1611 (m), 1562 (m), 1535 (w), 1496 (w), 1468 (m), 1407 (m), 1380 (s), 1303 (w), 1250 (m), 1208 (m), 1178 (m), 1132 (w), 1082 (w), 1065 (w), 1028 (w), 898 (s), 842 (s), 809 (s), 762 (m), 711 (w), 662 (w), 630 (w), 578 (w), 542 (w), 517 (w), 447 (w);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.36 (s, 9 H, SiMe<sub>3</sub>), 7.14–7.18 (m, 2 H), 7.29 (dt, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>4</sup>J<sub>FH</sub> = <sup>5</sup>J<sub>FH</sub> = 1.6 Hz, 1 H, H6), 7.47 (dd, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>4</sup>J<sub>FH</sub> = 5.8 Hz, 1 H, H5), 7.54 (dd, <sup>3</sup>J<sub>FH</sub> = 10.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, 1 H, H2), 7.57 (dd, <sup>3</sup>J<sub>FH</sub> = 8.1 Hz, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1 H, H3');  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) –1.1 (SiMe<sub>3</sub>), 92.7

(d, <sup>3</sup>J<sub>CF</sub> = 8.4 Hz, C4'), 115.0 (dd, <sup>2</sup>J<sub>CF</sub> = 27.5 Hz, <sup>4</sup>J<sub>CF</sub> = 3.2 Hz, C2), 124.1 (t, <sup>4</sup>J<sub>CF</sub> = <sup>4</sup>J<sub>CF'</sub> = 3.0 Hz, C6), 125.6 (d, <sup>2</sup>J<sub>CF</sub> = 25.4 Hz, C3'), 126.0 (d, <sup>2</sup>J<sub>CF</sub> = 30.4 Hz, C4), 127.6 (dd, <sup>2</sup>J<sub>CF</sub> = 13.1 Hz, <sup>4</sup>J<sub>CF</sub> = 2.5 Hz, C1'), 131.7 (d, <sup>4</sup>J<sub>CF</sub> = 3.8 Hz, C5'), 133.8 (d, <sup>3</sup>J<sub>CF</sub> = 4.2 Hz, C6'), 135.3 (d, <sup>3</sup>J<sub>CF</sub> = 12.1 Hz, C5), 137.9 (dd, <sup>3</sup>J<sub>CF</sub> = 8.7 Hz, <sup>3</sup>J<sub>CF</sub> = 1.1 Hz, C1), 159.2 (d, <sup>1</sup>J<sub>CF</sub> = 254.3, C2'), 167.4 (d, <sup>1</sup>J<sub>CF</sub> = 241.0 Hz, C3); *m/z* (EI) 388 [M<sup>+</sup>], 373 [M<sup>+</sup> – CH<sub>3</sub>], 246 [M<sup>+</sup> – CH<sub>3</sub> – I], 246 [M<sup>+</sup> – Br], 183 [M<sup>+</sup> – CH<sub>3</sub> – CH<sub>3</sub>SiF – HBr], 165.

#### 4'-Bromo-2,3,2'-trifluoro-4-trimethylsilylbiphenyl 3{2,5}.

According to *GP2* from 1-bromo-3-fluoro-4-iodobenzene **1**{2} and 2-(2,3-difluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]-dioxaborinane **2**{5} was obtained bromo biphenyl **3**{2,5} 15.8 g (88%); mp 78.0 °C (Found: C, 50.15; H, 3.93. C<sub>15</sub>H<sub>14</sub>BrF<sub>3</sub>Si requires C, 50.20; H, 3.92%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3032 (w), 2958 (w), 2897 (w), 1498 (w), 1470 (w), 1436 (s), 1387 (m), 1311 (w), 1279 (w), 1252 (m), 1222 (m), 1153 (m), 1097 (w), 1070 (m), 1008 (m), 962 (w), 914 (m), 891 (w), 837 (s), 806 (s), 763 (m), 740 (w), 715 (w), 696 (w), 652 (w), 630 (w), 606 (w), 555 (w), 527 (w), 485 (w), 432 (w);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.36 (s, 9 H, SiMe<sub>3</sub>), 7.09 (ddt, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>4</sup>J<sub>FH</sub> = 5.6 Hz, <sup>5</sup>J<sub>FH</sub> = 0.9 Hz, 1 H, H6), 7.17 (ddd, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>4</sup>J<sub>FH</sub> = 4.5 Hz, <sup>5</sup>J<sub>FH</sub> = 1.4 Hz, 1 H, H5), 7.26 (td, <sup>3</sup>J<sub>HH</sub> = <sup>4</sup>J<sub>FH</sub> = 8.0 Hz, <sup>5</sup>J<sub>HH</sub> = 0.6 Hz, 1 H, H6'), 7.35–7.39 (m, 2 H, H3',5');  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) –1.1 (SiMe<sub>3</sub>), 119.7 (d, <sup>2</sup>J<sub>CF</sub> = 25.4 Hz, C3'), 121.7 (dd, <sup>2</sup>J<sub>CF</sub> = 15.6 Hz, <sup>3</sup>J<sub>CF</sub> = 3.0 Hz, C1'), 122.8 (d, <sup>3</sup>J<sub>CF</sub> = 9.5 Hz, C4'), 125.4 (d, <sup>2</sup>J<sub>CF</sub> = 12.1 Hz, C1), 125.7 (br. s, C6), 127.6 (d, <sup>4</sup>J<sub>CF</sub> = 3.8 Hz, C5'), 128.8 (dd, <sup>3</sup>J<sub>CF</sub> = 11.2 Hz, <sup>4</sup>J<sub>CF</sub> = 5.1 Hz, C5), 129.3 (d, <sup>2</sup>J<sub>CF</sub> = 26.9 Hz, C4), 132.4 (dd, <sup>3</sup>J<sub>CF</sub> = 3.4 Hz, <sup>4</sup>J<sub>CF</sub> = 1.9 Hz, C6'), 147.5 (dd, <sup>1</sup>J<sub>CF</sub> = 253.2 Hz, <sup>2</sup>J<sub>CF</sub> = 16.3 Hz, C2), 154.7 (dd, <sup>1</sup>J<sub>CF</sub> = 242.2 Hz, <sup>2</sup>J<sub>CF</sub> = 11.46 Hz, C3), 159.5 (d, <sup>1</sup>J<sub>CF</sub> = 253.6 Hz, C2'); *m/z* (EI) 360, 358 [M<sup>+</sup>], 345, 343 [M<sup>+</sup> – CH<sub>3</sub>], 264 [M<sup>+</sup> – CH<sub>3</sub> – Br], 183, 164, 77.

#### 2,3,2'-Trifluoro-4'-iodo-4-trimethylsilylbiphenyl 4{2,5}.

According to *GP3* from 15.8 g (44.0 mmol) 4'-bromo-2,3,2'-trifluoro-4-trimethylsilylbiphenyl **3**{2,5} was obtained 15.1 g (84%) iodo biphenyl **4**{2,5}; mp 76.0 °C (Found: C, 44.35; H, 3.47. C<sub>15</sub>H<sub>14</sub>F<sub>3</sub>ISi requires C, 44.34; H, 6.52%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3096 (w), 2957 (w), 2898 (w), 1623 (w), 1599 (w), 1567 (w), 1544 (w), 1500 (w), 1466 (m), 1433 (s), 1394 (m), 1313 (w), 1251 (m), 1220 (m), 1149 (w), 1086 (w), 1064 (w), 1027 (w), 916 (m), 895 (w), 841 (s), 812 (m), 761 (m), 740 (w), 699 (w), 646 (w), 610 (w), 568 (w), 532 (w), 485 (w), 452 (w);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.37 (s, 9 H, SiMe<sub>3</sub>), 7.08–7.13 (m, 2 H, H6,6'), 7.17 (ddd, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, <sup>4</sup>J<sub>FH</sub> = 4.5 Hz, <sup>5</sup>J<sub>FH</sub> = 1.4 Hz, 1 H, H5), 7.55–7.59 (m, 2 H, H3',5');  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) –1.1 (SiMe<sub>3</sub>), 93.6 (d, <sup>3</sup>J<sub>CF</sub> = 8.0 Hz, C4'), 122.3 (dd, <sup>2</sup>J<sub>CF</sub> = 15.6 Hz, <sup>3</sup>J<sub>CF</sub> = 3.0 Hz, C1'), 125.4 (d, <sup>2</sup>J<sub>CF</sub> = 25.0 Hz, C3'), 125.5 (d, <sup>2</sup>J<sub>CF</sub> = 12.1 Hz, C1), 125.7 (br. s, C6), 128.8 (dd, <sup>3</sup>J<sub>CF</sub> = 11.2 Hz, <sup>4</sup>J<sub>CF</sub> = 5.1 Hz, C5), 129.3 (d, <sup>2</sup>J<sub>CF</sub> = 27.3 Hz, C4), 132.6 (dd, <sup>3</sup>J<sub>CF</sub> = 3.2 Hz, <sup>4</sup>J<sub>CF</sub> = 2.1 Hz, C6'), 133.6 (d, <sup>4</sup>J<sub>CF</sub> = 3.8 Hz, C5'), 147.5 (dd, <sup>1</sup>J<sub>CF</sub> = 253.7 Hz, <sup>2</sup>J<sub>CF</sub> = 17.3 Hz, C2), 154.7 (dd, <sup>1</sup>J<sub>CF</sub> = 242.0 Hz, <sup>2</sup>J<sub>CF</sub> = 11.6 Hz, C3), 159.2 (d, <sup>1</sup>J<sub>CF</sub> = 255.1 Hz, C2'); *m/z* (CI) 407 [MH<sup>+</sup>], 406 [M<sup>+</sup>], 391 [M<sup>+</sup> – CH<sub>3</sub>], 387, 308, 280 [MH<sup>+</sup> – I].

#### 4'-Bromo-3,3'-difluoro-4-trimethylsilylbiphenyl 3{3,2}.

According to *GP2* from 4-bromo-3-fluoro-1-iodobenzene **1**{3} and 2-(3-fluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]-dioxaborinane **2**{2} was obtained bromo biphenyl **3**{3,2} 13.5 g (79%) bp 140 °C / 10<sup>-3</sup> mbar; mp 46.9 °C (Found: C, 52.79; H, 4.43. C<sub>15</sub>H<sub>15</sub>BrF<sub>2</sub>Si requires C, 52.88; H, 4.50%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3038 (w), 2960 (w), 2900 (w), 1608 (m), 1574 (w), 1538 (m), 1498 (w), 1469 (m), 1415 (w), 1385 (m), 1313 (w), 1248 (m), 1211 (m), 1138 (w), 1086 (w), 1049 (m), 1027 (w), 948 (m), 842 (s), 809 (s), 760 (s), 713 (m), 696 (m), 628 (m), 594 (w), 551 (w), 498 (w);  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 0.37 (s, 9 H, SiMe<sub>3</sub>), 7.18 (dd, <sup>3</sup>J<sub>FH</sub> = 9.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, 1 H, H2'), 7.24 (ddd, <sup>3</sup>J<sub>FH</sub> = 8.2 Hz,



$^4J_{\text{HH}} = 2.0$  Hz,  $^5J_{\text{HH}} = 0.5$  Hz, 1 H, H2), 7.31–7.35 (m, 2 H), 7.48 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{FH}} = 5.9$  Hz, 1 H, H5), 7.61 (dd,  $^3J_{\text{HH}} = 8.3$  Hz,  $^4J_{\text{FH}} = 7.1$  Hz, 1 H, H5');  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.1 ( $\text{SiMe}_3$ ), 108.5 (d,  $^2J_{\text{CF}} = 20.9$  Hz, C4'), 113.0 (d,  $^2J_{\text{CF}} = 27.3$  Hz, C2), 114.9 (d,  $^2J_{\text{CF}} = 23.2$  Hz, C2'), 122.2 (d,  $^4J_{\text{CF}} = 2.7$  Hz, C6), 123.7 (d,  $^4J_{\text{CF}} = 3.4$  Hz, C6'), 126.1 (d,  $^2J_{\text{CF}} = 30.7$  Hz, C4), 133.9 (C5'), 135.8 (d,  $^3J_{\text{CF}} = 12.1$  Hz, C5), 141.3 (dd,  $^3J_{\text{CF}} = 7.2$  Hz,  $^4J_{\text{CF}} = 2.3$  Hz, C1), 142.2 (dd,  $^3J_{\text{CF}} = 8.4$  Hz,  $^4J_{\text{CF}} = 1.9$  Hz, C1'), 159.4 (d,  $^1J_{\text{CF}} = 247.5$  Hz, C3'), 167.8 (d,  $^1J_{\text{CF}} = 241.4$  Hz, C3);  $m/z$  (EI) 342, 340 [ $\text{M}^+$ ], 327, 325 [ $\text{M}^+ - \text{CH}_3$ ], 265, 263 [ $\text{M}^+ - \text{CH}_3 - \text{CH}_3\text{SiF}$ ], 246 [ $\text{M}^+ - \text{Br}$ ], 183 [ $\text{M}^+ - \text{CH}_3 - \text{CH}_3\text{SiF} - \text{HBr}$ ], 165, 77.

**3,3'-Difluoro-4'-iodo-4-trimethylsilylbiphenyl 4{3,2}.** According to GP3 from 10.3 g (30.3 mmol) 4'-bromo-3,3'-difluoro-4-trimethylsilylbiphenyl 3{3,2} was obtained 10.9 g (93%) iodo biphenyl 4{3,2}; mp 50.1 °C (Found: C, 46.40; H, 3.89.  $\text{C}_{15}\text{H}_{15}\text{F}_2\text{Si}$  requires C, 46.64; H, 3.98%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3064 (w), 2956 (w), 2899 (w), 1608 (m), 1568 (w), 1536 (m), 1496 (w), 1463 (m), 1412 (w), 1385 (m), 1312 (w), 1249 (m), 1207 (m), 1168 (w), 1135 (w), 1083 (w), 1042 (w), 1019 (w), 948 (m), 844 (s), 807 (s), 761 (s), 711 (m), 662 (w), 626 (w), 591 (w), 550 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.36 (s, 9 H,  $\text{SiMe}_3$ ), 7.13 (dd,  $^3J_{\text{HH}} = 8.2$  Hz,  $^4J_{\text{HH}} = 2.1$  Hz, 1 H, H6'), 7.18 (dd,  $^3J_{\text{FH}} = 9.7$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1 H, H2), 7.27 (dd,  $^3J_{\text{FH}} = 9.3$  Hz,  $^4J_{\text{HH}} = 2.1$  Hz, 1 H, H2'), 7.32 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1 H, H6), 7.47 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{FH}} = 5.9$  Hz, 1 H, H5), 7.80 (dd,  $^3J_{\text{HH}} = 8.2$  Hz,  $^4J_{\text{FH}} = 6.6$  Hz, 1 H, H5');  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.1 ( $\text{SiMe}_3$ ), 80.4 (d,  $^2J_{\text{CF}} = 25.8$  Hz, C4'), 113.0 (d,  $^2J_{\text{CF}} = 27.3$  Hz, C2), 114.1 (d,  $^2J_{\text{CF}} = 24.7$  Hz, C2'), 122.1 (d,  $^4J_{\text{CF}} = 2.7$  Hz, C6), 124.2 (d,  $^4J_{\text{CF}} = 3.0$  Hz, C6'), 126.1 (d,  $^2J_{\text{CF}} = 31.1$  Hz, C4), 135.8 (d,  $^3J_{\text{CF}} = 12.1$  Hz, C5), 139.7 (d,  $^3J_{\text{CF}} = 1.9$  Hz, C5'), 142.2 (dd,  $^3J_{\text{CF}} = 8.4$  Hz,  $^4J_{\text{CF}} = 1.9$  Hz, C1), 142.4 (dd,  $^3J_{\text{CF}} = 7.2$  Hz,  $^4J_{\text{CF}} = 2.3$  Hz, C1'), 162.1 (d,  $^1J_{\text{CF}} = 245.6$  Hz, C3), 167.8 (d,  $^1J_{\text{CF}} = 241.4$  Hz, C3');  $m/z$  (EI) 388 [ $\text{M}^+$ ], 373 [ $\text{M}^+ - \text{CH}_3$ ], 246 [ $\text{M}^+ - \text{CH}_3 - \text{I}$ ], 246 [ $\text{M}^+ - \text{Br}$ ], 183 [ $\text{M}^+ - \text{CH}_3 - \text{CH}_3\text{SiF} - \text{HBr}$ ], 165, 77.

#### 4'-Bromo-2,3,3'-trifluoro-4-trimethylsilylbiphenyl 3{3,5}.

According to GP2 from 4-bromo-3-fluoro-1-iodobenzene 1{3} and 2-(2,3-difluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]-dioxaborinane 2{5} was obtained bromo biphenyl 3{3,5} 12.2 g (68%); bp 125 °C/10<sup>–3</sup> mbar; mp 67.7 °C (Found: C, 50.15; H, 3.93.  $\text{C}_{15}\text{H}_{14}\text{BrF}_3\text{Si}$  requires C, 50.09; H, 3.96%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  2959 (m), 2900 (w), 1620 (w), 1574 (w), 1544 (w), 1498 (w), 1470 (w), 1435 (m), 1388 (m), 1320 (w), 1287 (w), 1248 (w), 1223 (w), 1201 (w), 1146 (w), 1094 (w), 1036 (m), 968 (w), 898 (w), 841 (s), 809 (s), 760 (m), 734 (w), 694 (w), 650 (w), 566 (w), 548 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.37 (s, 9 H,  $\text{SiMe}_3$ ), 7.13–7.24 (m, 3 H), 7.33 (ddd,  $^3J_{\text{FH}} = 9.7$  Hz,  $^4J_{\text{HH}} = 1.7$  Hz,  $^5J_{\text{FH}} = 1.5$  Hz, 1 H, H2'), 7.63 (dd,  $^3J_{\text{HH}} = 8.3$  Hz,  $^4J_{\text{FH}} = 7.3$  Hz, 1 H, H5');  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.2 ( $\text{SiMe}_3$ ), 109.0 (d,  $^2J_{\text{CF}} = 20.9$  Hz, C4'), 116.9 (dd,  $^2J_{\text{CF}} = 23.5$  Hz,  $^4J_{\text{CF}} = 3.4$  Hz, C2'), 124.6 (dd,  $^3J_{\text{CF}} = 3.0$  Hz,  $^4J_{\text{CF}} = 0.8$  Hz, C6), 125.7 (t,  $^4J_{\text{CF}} \approx ^4J_{\text{CF}} \approx 3.4$  Hz, C6'), 129.1 (dd,  $^2J_{\text{CF}} = 27.3$  Hz,  $^3J_{\text{CF}} = 1.1$  Hz, C4), 129.1 (dd,  $^3J_{\text{CF}} = 11.4$  Hz,  $^4J_{\text{CF}} = 5.3$  Hz, C5), 129.6 (dd,  $^2J_{\text{CF}} = 9.9$  Hz,  $^3J_{\text{CF}} = 1.1$  Hz, C1), 133.6 (C5'), 136.0 (dd,  $^3J_{\text{CF}} = 7.6$  Hz,  $^3J_{\text{CF}} = 2.7$  Hz, C1'), 147.4 (dd,  $^1J_{\text{CF}} = 253.4$  Hz,  $^2J_{\text{CF}} = 17.3$  Hz, C2), 155.0 (dd,  $^1J_{\text{CF}} = 242.4$  Hz,  $^2J_{\text{CF}} = 11.6$  Hz, C3), 159.0 (d,  $^1J_{\text{CF}} = 247.5$  Hz, C3');  $m/z$  (EI) 360, 358 [ $\text{M}^+$ ], 345, 343 [ $\text{M}^+ - \text{CH}_3$ ], 264 [ $\text{M}^+ - \text{CH}_3 - \text{Br}$ ], 198, 183, 164.

#### 4'-Iodo-2,3,3'-trifluoro-4-trimethylsilylbiphenyl 4{3,5}.

According to GP3 from 11.6 g (32.3 mmol) 4'-bromo-2,3,3'-trifluoro-4-trimethylsilylbiphenyl 3{3,5} was obtained 11.7 g (89%) iodo biphenyl 4{3,5}; bp 170 °C/10<sup>–3</sup> mbar; mp 46.8 °C (Found: C, 44.35; H, 3.47.  $\text{C}_{15}\text{H}_{14}\text{F}_3\text{Si}$  requires C, 44.29; H, 3.54%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3069 (w), 3031 (w), 2958 (m), 2898 (w), 1617 (w), 1595 (w), 1567 (m), 1540 (m), 1493 (m), 1465 (m), 1437 (s), 1390 (s), 1319 (w), 1285 (m), 1250 (s), 1221 (s), 1204

(s), 1143 (m), 1096 (w), 1024 (m), 969 (w), 901 (w), 877 (m), 841 (m), 805 (m), 763 (w), 737 (w), 698 (w), 651 (w), 617 (w), 601 (w), 567 (w), 495 (w), 456 (w), 416 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.37 (s, 9 H,  $\text{SiMe}_3$ ), 7.10 (dt,  $^3J_{\text{FH}} = 8.2$  Hz,  $^4J_{\text{HH}} = ^5J_{\text{FH}} = 1.6$  Hz, 1 H, H2'), 7.13–7.20 (m, 2 H), 7.27 (dt,  $^3J_{\text{HH}} = 8.5$  Hz,  $^4J_{\text{HH}} = ^5J_{\text{FH}} = 1.5$  Hz, 1 H, H6'), 7.82 (dd,  $^3J_{\text{HH}} = 8.5$  Hz,  $^4J_{\text{FH}} = 6.6$  Hz, 1 H, H5');  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.1 ( $\text{SiMe}_3$ ), 81.0 (d,  $^2J_{\text{CF}} = 25.8$  Hz, C4'), 116.1 (dd,  $^2J_{\text{CF}} = 25.1$  Hz,  $^4J_{\text{CF}} = 3.4$  Hz, C2'), 124.6 (dd,  $^3J_{\text{CF}} = 3.0$  Hz,  $^4J_{\text{CF}} = 0.8$  Hz, C6), 126.2 (t,  $^4J_{\text{CF}} = ^4J_{\text{CF}} = 3.2$  Hz, C6'), 129.1 (dd,  $^2J_{\text{CF}} = 27.3$  Hz,  $^3J_{\text{CF}} = 1.1$  Hz, C4), 129.1 (dd,  $^3J_{\text{CF}} = 11.0$  Hz,  $^4J_{\text{CF}} = 5.3$  Hz, C5), 129.7 (br. d,  $^2J_{\text{CF}} = 10.6$  Hz, C1), 137.1 (dd,  $^3J_{\text{CF}} = 7.4$  Hz,  $^3J_{\text{CF}} = 2.5$  Hz, C1'), 139.5 (d,  $^3J_{\text{CF}} = 1.9$  Hz, C5'), 147.4 (dd,  $^1J_{\text{CF}} = 253.4$  Hz,  $^2J_{\text{CF}} = 17.3$  Hz, C2), 155.0 (dd,  $^1J_{\text{CF}} = 242.2$  Hz,  $^2J_{\text{CF}} = 11.8$  Hz, C3), 161.8 (d,  $^1J_{\text{CF}} = 245.6$  Hz, C3');  $m/z$  (EI) 406 [ $\text{M}^+$ ], 391 [ $\text{M}^+ - \text{CH}_3$ ], 264 [ $\text{M}^+ - \text{CH}_3 - \text{I}$ ], 198, 183, 164, 77.

**3',5'-Difluoro-4-trimethylsilylbiphenyl 3{4,I}.** According to GP2 from 1-bromo-3,5-difluorobenzene 1{4} and 2-(4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 2{I} was obtained biphenyl 3{4,I} 11.4 g (87%); bp 165 °C / 14 mbar (Found: C, 68.67; H, 6.15.  $\text{C}_{15}\text{H}_{16}\text{F}_2\text{Si}$  requires C, 68.93; H, 6.19%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3069 (w), 3022 (w), 2957 (m), 2898 (w), 1622 (s), 1597 (s), 1548 (w), 1460 (w), 1441 (w), 1386 (w), 1340 (m), 1205 (w), 1116 (s), 989 (m), 841 (s), 817 (s), 758 (m), 722 (w), 703 (w), 985 (w), 624 (w), 605 (w), 567 (w), 534 (w), 510 (w), 488 (w), 434 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.36 (s, 9 H,  $\text{SiMe}_3$ ), 6.81 (tt,  $^3J_{\text{FH}} = 8.8$  Hz,  $^4J_{\text{HH}} = 2.1$  Hz, 1 H, H4'), 7.14 (d, line distance 6.6 Hz, AA'-part of a AA'XX'-system, 2 H, H2',6'), 7.57 (d, line distance 8.1 Hz, AA'-part of a AA'XX'-system, 2 H, H2,6) 7.65 (d, line distance 8.1 Hz, XX'-part of a AA'XX'-system, 2 H, H3,5);  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.2 ( $\text{SiMe}_3$ ), 102.5 (t,  $^2J_{\text{CF}} = 25.4$  Hz, C4'), 109.9 (d, line distance 25.4 Hz, AA'-part of a AA'XX'-system, C2',6'), 126.3 (C2,6), 134.0 (C3,5), 139.2 (t,  $^4J_{\text{CF}} = 2.5$  Hz, C1), 141.0 (C4), 144.5 (t,  $^3J_{\text{CF}} = 9.5$  Hz, C1'), 163.3 (dd,  $^1J_{\text{CF}} = 248.1$  Hz,  $^3J_{\text{CF}} = 13.0$  Hz, C3',5');  $m/z$  (EI) 262 [ $\text{M}^+$ ], 249 [ $\text{M}^+ - \text{CH}_3$ ], 168.

#### 3',5'-Difluoro-4'-iodo-4-trimethylsilylbiphenyl 4{4,I}.

According to GP3 from 9.41 g (35.9 mmol) 3',5'-difluoro-4-trimethylsilylbiphenyl 3{4,I} was obtained 12.3 g (88%) iodo biphenyl 4{4,I}; bp 156 °C/10<sup>–3</sup> mbar; mp 57.3 °C (Found: C, 46.40; H, 3.89.  $\text{C}_{15}\text{H}_{15}\text{F}_2\text{Si}$  requires C, 46.42; H, 3.98%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3062 (w), 3018 (w), 2954 (m), 2896 (w), 1603 (m), 1576 (m), 1538 (m), 1460 (w), 1443 (w), 1418 (m), 1383 (m), 1340 (w), 1249 (m), 1202 (w), 1109 (w), 1072 (w), 1022 (s), 841 (s), 845 (s), 757 (s), 721 (m), 692 (m), 623 (m), 595 (w), 561 (w), 530 (w), 492 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.33 (s, 9 H,  $\text{SiMe}_3$ ), 7.14 (d, line distance 7.3 Hz, AA'-part of a AA'XX'-system, 2 H, H2',6'), 7.54 (d, line distance 8.3 Hz, AA'-part of a AA'XX'-system, 2 H, H2,6) 7.63 (d, line distance 8.2 Hz, XX'-part of a AA'XX'-system, 2 H, H3,5);  $\delta_{\text{C}}(100.6$  MHz,  $\text{CDCl}_3$ ) –1.2 ( $\text{SiMe}_3$ ), 69.2 (t,  $^2J_{\text{CF}} = 29.6$  Hz, C4'), 109.8 (d, line distance 28.1 Hz, AA'-part of a AA'XX'-system, C2',6'), 126.0 (C2,6), 134.1 (C3,5), 139.4 (t,  $^4J_{\text{CF}} = 2.3$  Hz, C1), 141.4 (C4), 144.5 (t,  $^3J_{\text{CF}} = 9.1$  Hz, C1'), 163.0 (dd,  $^1J_{\text{CF}} = 246.3$  Hz,  $^3J_{\text{CF}} = 6.8$  Hz, C3',5');  $m/z$  (EI) 388 [ $\text{M}^+$ ], 373 [ $\text{M}^+ - \text{CH}_3$ ], 246 [ $\text{M}^+ - \text{CH}_3 - \text{I}$ ], 186.

**3,3',5'-Trifluoro-4-trimethylsilylbiphenyl 3{4,2}.** According to GP2 from 1-bromo-3,5-difluorobenzene 1{4} and 2-(3-fluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 2{2} was obtained biphenyl 3{4,2} 13.3 g (95%); bp 152 °C/14 mbar; mp 56.5 °C (Found: C, 64.26; H, 5.39.  $\text{C}_{15}\text{H}_{15}\text{F}_3\text{Si}$  requires C, 64.45; H, 5.39%);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3094 (w), 2954 (m), 2898 (w), 1614 (s), 1595 (s), 1546 (m), 1498 (w), 1458 (m), 1391 (m), 1337 (w), 1253 (s), 1221 (m), 1162 (m), 1141 (w), 1114 (s), 1085 (m), 1053 (w), 986 (s), 958 (w), 844 (s), 794 (m), 752 (w), 713 (w), 692 (w), 641 (w), 625 (w), 593 (w), 505 (w);  $\delta_{\text{H}}(400.1$  MHz,  $\text{CDCl}_3$ ) 0.37 (s, 9 H,  $\text{SiMe}_3$ ), 6.81 (tt,  $^3J_{\text{FH}} = 8.8$  Hz,  $^4J_{\text{HH}} = 2.3$  Hz, 1 H,

H4'), 7.10 (d, line distance 6.3 Hz, AA'-part of a AA'XX'-system, 2 H, H2',6'), 7.18 (dd,  $^3J_{\text{FH}} = 9.6$  Hz,  $^4J_{\text{HH}} = 1.5$  Hz, 1 H, H2), 7.32 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.5$  Hz, 1 H, H6), 7.49 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{FH}} = 6.0$  Hz, 1 H, H5);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) -1.1 (SiMe<sub>3</sub>), 103.1 (t,  $^2J_{\text{CF}} = 25.4$  Hz, C4'), 109.9 (d, line distance 26.2 Hz, AA'-part of a AA'XX'-system, C2',6'), 113.2 (d,  $^2J_{\text{CF}} = 27.3$  Hz, C2), 122.3 (d,  $^4J_{\text{CF}} = 2.7$  Hz, C6), 126.4 (d,  $^2J_{\text{CF}} = 30.7$  Hz, C4), 135.8 (d,  $^3J_{\text{CF}} = 12.1$  Hz, C5), 142.1 (dt,  $^3J_{\text{CF}} = 8.4$  Hz,  $^4J_{\text{CF}} = 2.5$  Hz, C1), 143.2 (td,  $^3J_{\text{CF}} = 9.6$  Hz,  $^4J_{\text{CF}} = 2.5$  Hz, C1'), 163.4 (dd,  $^1J_{\text{CF}} = 248.2$  Hz,  $^3J_{\text{CF}} = 12.9$  Hz, C3',5'), 167.8 (d,  $^1J_{\text{CF}} = 241.4$  Hz, C3); *m/z* (EI) 280 [M<sup>+</sup>], 265 [M<sup>+</sup> - CH<sub>3</sub>], 203 [M<sup>+</sup> - CH<sub>3</sub> - CH<sub>3</sub>SiF], 183, 165, 138, 77.

### 3,3',5'-Trifluoro-4'-iodo-4-trimethylsilylbiphenyl 4{4,2}.

According to GP3 from 9.71 g (34.6 mmol) 3,3,5'-trifluoro-4-trimethylsilylbiphenyl 3{4,2} 12.7 g (90%) was obtained iodo biphenyl 4{4,2}; bp 119 °C/10<sup>-3</sup> mbar; mp 76.1 °C (Found: C, 44.35; H, 3.47. C<sub>15</sub>H<sub>14</sub>F<sub>3</sub>Si requires C, 44.30; H, 3.54%);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3065 (w), 2950 (m), 2896 (w), 1610 (m), 1578 (m), 1499 (w), 1458 (w), 1426 (w), 1386 (m), 1266 (w), 1246 (m), 1224 (w), 1208 (w), 1167 (w), 1137 (w), 1090 (w), 1059 (m), 1021 (s), 961 (m), 880 (m), 859 (s), 843 (s), 825 (s), 805 (m), 759 (m), 712 (w), 694 (w), 615 (w), 561 (m), 545 (w), 529 (w), 511 (w), 450 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.37 (s, 9 H, SiMe<sub>3</sub>), 7.11 (d, line distance 7.1 Hz, AA'-part of a AA'XX'-system, 2 H, H2',6'), 7.17 (dd,  $^3J_{\text{FH}} = 9.5$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1 H, H2), 7.32 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1 H, H6), 7.49 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{FH}} = 5.8$  Hz, 1 H, H5);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) -1.1 (SiMe<sub>3</sub>), 70.0 (t,  $^2J_{\text{CF}} = 29.4$  Hz, C4'), 109.8 (d, line distance 28.5 Hz, AA'-part of a AA'XX'-system, C2',6'), 113.0 (d,  $^2J_{\text{CF}} = 27.7$  Hz, C2), 122.1 (d,  $^4J_{\text{CF}} = 3.0$  Hz, C6), 126.9 (d,  $^2J_{\text{CF}} = 30.7$  Hz, C4), 135.9 (d,  $^3J_{\text{CF}} = 12.1$  Hz, C5), 141.3 (dt,  $^3J_{\text{CF}} = 8.4$  Hz,  $^4J_{\text{CF}} = 2.5$  Hz, C1), 143.1 (td,  $^3J_{\text{CF}} = 9.2$  Hz,  $^4J_{\text{CF}} = 2.4$  Hz, C1'), 163.0 (dd,  $^1J_{\text{CF}} = 246.7$  Hz,  $^3J_{\text{CF}} = 6.5$  Hz, C3',5'), 167.8 (d,  $^1J_{\text{CF}} = 241.8$  Hz, C3); *m/z* (EI) 406 [M<sup>+</sup>], 391 [M<sup>+</sup> - CH<sub>3</sub>], 329, 264 [M<sup>+</sup> - CH<sub>3</sub> - I], 201, 183, 164, 77.

**2,3,3',5'-Tetrafluoro-4-trimethylsilylbiphenyl 3{4,5}.** According to GP2 from 1-bromo-3,5-difluorobenzene 1{4} and 2-(2,3-difluoro-4-trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane 2{5} was obtained biphenyl 3{4,5} 12.2 g (82%); bp 150 °C/13 mbar (Found: C, 60.39; H, 4.73. C<sub>15</sub>H<sub>14</sub>F<sub>4</sub>Si requires C, 60.46; H, 4.77%);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3092 (w), 2960 (m), 2902 (w), 1623 (m), 1596 (m), 1551 (w), 1497 (w), 1457 (m), 1482 (s), 1347 (m), 1284 (w), 1254 (m), 1217 (m), 1142 (w), 1121 (s), 986 (m), 903 (w), 842 (s), 796 (m), 766 (m), 742 (w), 690 (w), 653 (w), 627 (w), 605 (w), 561 (w), 509 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.38 (s, 9 H, SiMe<sub>3</sub>), 6.84 (tt,  $^3J_{\text{FH}} = 8.9$  Hz,  $^4J_{\text{HH}} = 2.3$  Hz, 1 H, H4'), 7.06–7.11 (m, 2 H), 7.13–7.21 (m, 2 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) -1.2 (SiMe<sub>3</sub>), 103.5 (t,  $^2J_{\text{CF}} = 25.2$  Hz, C4'), 111.9 (d, line distance 22.8 Hz, AA'-part of a AA'XX'-system, C2',6'), 124.6 (d,  $^3J_{\text{CF}} = 2.7$  Hz, C6), 128.5 (d,  $^3J_{\text{CF}} = 6.8$  Hz, C5), 129.1 (dd,  $^2J_{\text{CF}} = 11.0$  Hz,  $^3J_{\text{CF}} = 5.3$  Hz, C1), 133.8 (d,  $^2J_{\text{CF}} = 19.4$  Hz, C4), 137.8 (td,  $^3J_{\text{CF}} = 10.2$  Hz,  $^3J_{\text{CF}} = 3.3$  Hz, C1'), 147.5 (dd,  $^1J_{\text{CF}} = 253.9$  Hz,  $^2J_{\text{CF}} = 17.5$  Hz, C2), 155.0 (dd,  $^1J_{\text{CF}} = 242.5$  Hz,  $^2J_{\text{CF}} = 11.8$  Hz, C3), 163.0 (dd,  $^1J_{\text{CF}} = 248.2$  Hz,  $^3J_{\text{CF}} = 12.9$  Hz, C3',5'); *m/z* (EI) 298 [M<sup>+</sup>], 283 [M<sup>+</sup> - CH<sub>3</sub>], 201, [M<sup>+</sup> - CH<sub>3</sub> - HF - CH<sub>3</sub>SiF], 81, 77.

### 2,3,3',5'-Tetrafluoro-4'-iodo-4-trimethylsilylbiphenyl 4{4,5}.

According to GP3 from 3.51 g (11.8 mmol) 2,3,3',5'-tetrafluoro-4-trimethylsilylbiphenyl 3{4,5} was obtained 2.45 g (49%) iodo biphenyl 4{4,5}; mp 66.9 °C (Found: C, 42.47; H, 3.09. C<sub>15</sub>H<sub>14</sub>F<sub>4</sub>Si requires C, 42.61; H, 3.23%);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3040 (w), 2960 (w), 2901 (w), 1611 (m), 1576 (s), 1543 (m), 1495 (w), 1438 (s), 1404 (s), 1281 (w), 1252 (m), 1205 (m), 1140 (m), 1106 (w), 1037 (w), 1019 (s), 989 (m), 953 (w), 903 (w), 840 (s), 819 (s), 761 (m), 693 (w), 662 (w), 626 (w), 605 (w), 556 (m), 518 (w);  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 0.37 (s, 9 H, SiMe<sub>3</sub>), 7.10 (d, line

distance 8.1 Hz, AA'-part of a AA'XX'-system, 2 H, H2',6'), 7.13–7.21 (m, 2 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) -1.2 (SiMe<sub>3</sub>), 70.7 (t,  $^2J_{\text{CF}} = 29.4$  Hz, C4'), 111.8 (d, line distance 25.7 Hz, AA'-part of a AA'XX'-system, C2',6'), 124.4 (d,  $^3J_{\text{CF}} = 3.0$  Hz, C6), 128.8 (br. d,  $^2J_{\text{CF}} = 9.9$  Hz, C1), 129.3 (dd,  $^3J_{\text{CF}} = 11.4$  Hz,  $^4J_{\text{CF}} = 5.3$  Hz, C5), 129.8 (dd,  $^2J_{\text{CF}} = 27.3$  Hz,  $^3J_{\text{CF}} = 1.1$  Hz, C4), 137.8 (t,  $^3J_{\text{CF}} = 10.1$  Hz, C1'), 147.4 (dd,  $^1J_{\text{CF}} = 254.3$  Hz,  $^2J_{\text{CF}} = 17.5$  Hz, C2), 155.0 (dd,  $^1J_{\text{CF}} = 242.5$  Hz,  $^2J_{\text{CF}} = 11.8$  Hz, C3), 162.7 (dd,  $^1J_{\text{CF}} = 246.7$  Hz,  $^3J_{\text{CF}} = 6.5$  Hz, C3',5'); *m/z* (EI) 424 [M<sup>+</sup>], 409 [M<sup>+</sup> - CH<sub>3</sub>], 282, [M<sup>+</sup> - CH<sub>3</sub> - I], 201, 182, 77.

## Library synthesis

**1. Suzuki-coupling yielding terphenyls 6{T,H,B}.** The combinatorial synthesis was carried out by reaction of each of the terminal boronic esters 5{I}–5{5} with each of the biphenyls 4{I,I}, 4{I,2}, 4{I,5}, 4{2,I}, 4{2,2}, 4{2,5}, 4{3,2}, and 4{3,5} and by reaction of the boronic esters 5{I}, 5{3} and 5{4} with the biphenyls 4{4,I}, 4{4,2} and 4{4,5}.

In each of 49 closed vials under argon 2.50 mmol biphenyl 4{H,B} was reacted with 3.75 mmol boronic ester 5{T}, 4.50 ml (9.00 mmol) of a 2 M K<sub>2</sub>CO<sub>3</sub>-solution, 0.500 ml (0.038 mmol, 1 mol%) of a 76 mM Pd(OAc)<sub>2</sub> solution in acetone with 20 ml degassed acetone as solvent with magnetic stirring for 12 h at 80 °C. Subsequently the solvent was removed under reduced pressure. To the residue 10 ml H<sub>2</sub>O were added and the mixture was extracted with dichloromethane (5 ml). The organic phase was filtered over diatomenic earth, 2 ml 30% H<sub>2</sub>O<sub>2</sub> and some *i*PrOH were added, until the mixture became a homogeneous solution (*ca.* 10 ml *i*PrOH). After 6 h stirring at rt excess H<sub>2</sub>O<sub>2</sub> was destroyed by addition of 3 ml 5 M NaOH. After stirring for another 12 h, the solvent was removed under reduced pressure. To the residue 10 ml H<sub>2</sub>O were added and the mixture was extracted with dichloromethane (3 × 5 ml). The organic phases were purified by solid phase extraction (SPE). The custom-made SPE cartridges consisted of a 10 ml SPE syringe with a PE frit, a glass-fibre filter, *ca.* 2 ml SiO<sub>2</sub>, and *ca.* 1 ml diatomenic earth. GC control showed that the turnover of biphenyl was 100% in all cases. The main impurity appeared to be the homo-coupling product of the boronic esters.

**2. Iododesilylation yielding terphenyls 7{T,H,B}.** In 49 vials 2.00 mmol of each of the terphenyls 6{T,H,B} was dissolved in 4 ml abs. acetonitrile, 1.20 ml (6.00 mmol) of a 5 M solution of ICl in MeCN was added and the mixture shaken vigorously for 1 h at rt. Subsequently, the product was precipitated by addition of water (10 ml) and 2 M Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (10 ml). The product 7{T,H,B} was removed by filtration, washed with water and dried under vacuum.

**3. Suzuki-coupling yielding quaterphenyls 8{T,H,B,T}.** The combinatorial synthesis was carried out by reaction of 5{I} with 7{I,I,I}, 7{I,3,2}, 7{2,3,2}, 7{3,I,I}, 7{3,3,2}, 7{5,I,I} and 7{5,3,2}; of 5{2} with 7{I,I,I}, 7{I,3,2}, 7{2,3,2}, 7{2,I,I}, 7{4,I,I} and 7{4,3,2}; of 5{3} with 7{2,I,I}, 7{3,I,I}, 7{3,3,2}, 7{5,I,I} and 7{5,3,2}; of 5{4} with 7{I,I,I}, 7{I,3,2}, 7{2,3,2}, 7{3,I,I}, 7{3,3,2}, 7{4,I,I} and 7{4,3,2}; of 5{5} with 7{2,I,I}, 7{4,I,I}, 7{4,3,2}, 7{5,I,I} and 7{5,3,2}. The remaining 39 terphenyls were reacted in all possible combinations with the boronic 5{I}–5{5}.

In each of 225 closed vials under argon 0.100 mmol terphenyl 7{T,H,B} was reacted with 0.150 mmol boronic ester 5{T}, 0.200 ml (0.400 mmol) of a 2 M K<sub>2</sub>CO<sub>3</sub> solution, 20  $\mu$ l (1.52  $\mu$ mol, 1 mol%) of a 76 mM Pd(OAc)<sub>2</sub> solution in acetone with 2 ml degassed acetone as solvent with magnetic stirring for 12 h at 80 °C. Subsequently, the solvent was removed under reduced pressure. To the residue 2 ml H<sub>2</sub>O were added and the mixture was extracted with dichloromethane (3 × 2 ml). The organic phases were purified by SPE filtration. The custom-made SPE

cartridges consisted of a 5 ml SPE syringe with a PE frit, a glass-fibre filter, *ca.* 1 ml SiO<sub>2</sub>, and *ca.* 0.5 ml diatomenic earth. The crude products were recrystallised twice from nonane. The purity and identity of the quaterphenyls **8**{*T,H,B,T*} was verified by HPLC-MS.

#### NMR and mass-spectrometric characterization of selected library members

**2,3,2',3',2'',3'''-Hexafluoro-4,4'''-dipropyl[1,4':1',1'':4'',1''']-quaterphenyl **8**{3,2,3,5}.**  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 1.00 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.02 (t,  $J_{\text{HH}} = 7.1$  Hz, 3 H), 1.70 (sextet,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 1.71 (sextet,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 2.68 (t,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 2.72 (t,  $J_{\text{HH}} = 7.4$  Hz, 2 H), 7.03–7.13 (m, 2 H), 7.21–7.36 (m, 5 H), 7.40–7.52 (m, 3 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.78, 13.81, 23.1, 23.3, 30.81, 30.84, 113.7 (d,  $J_{\text{CF}} = 23.5$  Hz), 114.3 (d,  $J_{\text{CF}} = 23.2$  Hz), 121.1 (dd,  $J_{\text{CF}} = 15.4$  Hz,  $J_{\text{CF}} = 2.5$  Hz), 121.5 (dd,  $J_{\text{CF}} = 12.5$  Hz,  $J_{\text{CF}} = 2.3$  Hz), 122.3 (d,  $J = 3.0$  Hz), 122.6 (d,  $J_{\text{CF}} = 3.0$  Hz), 124.4 (dd,  $J_{\text{CF}} = 11.8$  Hz,  $J_{\text{CF}} = 1.9$  Hz), 124.9 (t,  $J_{\text{CF}} = 4.4$  Hz), 125.0 (br. s), 125.1 (br. s), 125.5 (br. s), 125.6 (br. s), 129.4 (d,  $J_{\text{CF}} = 16.7$  Hz), 131.2 (d,  $J_{\text{CF}} = 6.1$  Hz), 131.7, 132.3 (d,  $J_{\text{CF}} = 13.3$  Hz), 138.8 (dd,  $J_{\text{CF}} = 8.0$  Hz,  $J_{\text{CF}} = 1.9$  Hz), 142.6 (dd,  $J_{\text{CF}} = 8.0$  Hz,  $J_{\text{CF}} = 1.9$  Hz), 148.1 (dd,  $J_{\text{CF}} = 250.9$  Hz,  $J_{\text{CF}} = 14.0$  Hz), 148.41 (dd,  $J_{\text{CF}} = 253.6$  Hz,  $J_{\text{CF}} = 16.3$  Hz), 148.45 (dd,  $J_{\text{CF}} = 253.2$  Hz,  $J_{\text{CF}} = 15.6$  Hz), 149.4 (dd,  $J_{\text{CF}} = 246.3$  Hz,  $J_{\text{CF}} = 12.9$  Hz), 160.0 (d,  $J_{\text{CF}} = 249.4$  Hz), 161.5 (d,  $J_{\text{CF}} = 245.2$  Hz); *m/z* (APCI+, CH<sub>2</sub>Cl<sub>2</sub>, hexane) 499.5 [M + H]<sup>+</sup>.

**2',3',2''-Trifluoro-4,4'''-dipropyl[1,4':1',1'':4'',1''']quaterphenyl **8**{1,2,3,1}.**  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 1.007 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.013 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.72 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.73 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.67 (t,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 2.68 (t,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 7.23–7.32 (m, 6 H), 7.43–7.58 (m, 7 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.84, 13.87, 24.4, 24.5, 37.7, 37.8, 114.2 (d,  $J_{\text{CF}} = 23.2$  Hz), 120.8 (dd,  $J_{\text{CF}} = 15.2$  Hz,  $J_{\text{CF}} = 2.3$  Hz), 122.6 (d,  $J_{\text{CF}} = 3.4$  Hz), 123.8 (d,  $J_{\text{CF}} = 12.5$  Hz), 124.5 (t,  $J_{\text{CF}} = 3.4$  Hz), 125.6 (br. s), 126.9, 128.74, 128.76, 129.1, 130.7 (d,  $J_{\text{CF}} = 10.6$  Hz), 131.6 (br. s), 131.9, 136.7 (d,  $J_{\text{CF}} = 1.9$  Hz), 142.9 (d,  $J_{\text{CF}} = 12.9$  Hz), 143.6 (d,  $J_{\text{CF}} = 8.4$  Hz), 148.3 (dd,  $J_{\text{CF}} = 249.6$  Hz,  $J_{\text{CF}} = 13.9$  Hz), 148.7 (dd,  $J_{\text{CF}} = 250.1$  Hz,  $J_{\text{CF}} = 14.4$  Hz), 160.0 (d,  $J_{\text{CF}} = 249.4$  Hz), the increased intensity of the signal at  $\delta = 128.76$  indicates, that two carbon resonances coincide here; *m/z* (APCI+, CH<sub>2</sub>Cl<sub>2</sub>, hexane) 445.5 [M + H]<sup>+</sup>.

**3,5,2',2'',3'',3'''-Hexafluoro-4,4'''-dipropyl[1,4':1',1'':4'',1''']-quaterphenyl **8**{4,2,3,3}.**  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 1.00 (t,  $J_{\text{HH}} = 7.4$  Hz, 3 H), 1.01 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.67 (sextet,  $J_{\text{HH}} = 7.4$  Hz, 2 H), 1.71 (sextet,  $J_{\text{HH}} = 7.3$  Hz, 2 H), 2.69 (t,  $J_{\text{HH}} = 6.6$  Hz, 2 H), 2.71 (t,  $J_{\text{HH}} = 6.3$  Hz, 2 H), 7.10–7.16 (m, 2 H), 7.22–7.33 (m, 5 H), 7.37–7.45 (m, 2 H), 7.49–7.52 (m, 1 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.7, 13.8, 22.7, 23.2, 24.2, 30.9, 109.5 (d, line distance 28.1 Hz, AA'–part of a AA'XX'–spectrum), 114.3 (d,  $J_{\text{CF}} = 23.5$  Hz), 115.6 (dd,  $J_{\text{CF}} = 24.1$  Hz,  $J_{\text{CF}} = 3.2$  Hz), 117.8 (t,  $J_{\text{CF}} = 20.9$  Hz), 121.8 (dd,  $J_{\text{CF}} = 15.6$  Hz,  $J_{\text{CF}} = 2.3$  Hz), 122.5 (d,  $J_{\text{CF}} = 3.4$  Hz), 124.0 (d,  $J_{\text{CF}} = 12.5$  Hz), 124.3 (t,  $J_{\text{CF}} = 3.2$  Hz), 124.4 (t,  $J_{\text{CF}} = 3.2$  Hz), 125.7 (br. s), 129.6 (br. s), 129.8 (br. s), 130.9 (d,  $J_{\text{CF}} = 5.7$  Hz), 131.9 (dd,  $J_{\text{CF}} = 3.4$  Hz,  $J_{\text{CF}} = 2.3$  Hz), 133.7 (d,  $J_{\text{CF}} = 8.4$  Hz), 138.9 (dd,  $J_{\text{CF}} = 10.1$  Hz,  $J_{\text{CF}} = 2.0$  Hz), 141.4 (dd,  $J_{\text{CF}} = 8.1$  Hz,  $J_{\text{CF}} = 2.4$  Hz), 148.3 (dd,  $J_{\text{CF}} = 250.5$  Hz,  $J_{\text{CF}} = 14.0$  Hz), 148.6 (dd,  $J_{\text{CF}} = 250.9$  Hz,  $J_{\text{CF}} = 14.0$  Hz), 160.1 (d,  $J_{\text{CF}} = 250.1$  Hz), 161.1 (d,  $J_{\text{CF}} = 245.2$  Hz), 161.9 (dd,  $J_{\text{CF}} = 246.5$  Hz,  $J_{\text{CF}} = 10.4$  Hz); *m/z* (APCI+, CH<sub>2</sub>Cl<sub>2</sub>, hexane) 499.5 [M + H]<sup>+</sup>.

**3,2',3'',3'''-Pentafluoro-4,4'''-dipropyl[1,1':4',1'':4'',1''']quaterphenyl **8**{3,1,3,4}.**  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 1.010 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.012 (t,  $J_{\text{HH}} = 7.4$  Hz, 3 H), 1.68 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.70 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.68 (t,  $J_{\text{HH}} = 7.8$  Hz, 2 H), 2.72 (t,  $J_{\text{HH}} = 7.4$  Hz, 2 H), 7.10–7.16 (m,

2 H), 7.23–7.37 (m, 5 H), 7.65–7.71 (m, 4 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.78, 13.82, 22.7, 23.3, 24.2, 30.8, 111.1 (d, line distance 25.1 Hz, AA'–part of a AA'XX'–spectrum), 113.6 (d,  $J_{\text{CF}} = 23.5$  Hz), 118.0 (t,  $J_{\text{CF}} = 20.7$  Hz), 122.3 (d,  $J_{\text{CF}} = 3.0$  Hz), 124.3 (t,  $J_{\text{CF}} = 3.4$  Hz), 124.8 (t,  $J_{\text{CF}} = 3.6$  Hz), 127.1, 127.7 (d,  $J_{\text{CF}} = 9.5$  Hz), 128.8 (d,  $J_{\text{CF}} = 16.3$  Hz), 129.3 (d,  $J_{\text{CF}} = 2.7$  Hz), 130.1 (dd,  $J_{\text{CF}} = 8.7$  Hz,  $J_{\text{CF}} = 1.9$  Hz), 131.1 (d,  $J_{\text{CF}} = 5.7$  Hz), 133.5, 133.9 (td,  $J_{\text{CF}} = 10.3$  Hz,  $J_{\text{CF}} = 2.0$  Hz), 139.9 (d,  $J_{\text{CF}} = 8.0$  Hz), 140.0 (d,  $J_{\text{CF}} = 2.3$  Hz), 148.5 (dd,  $J_{\text{CF}} = 252.6$  Hz,  $J_{\text{CF}} = 16.1$  Hz), 148.6 (dd,  $J_{\text{CF}} = 251.8$  Hz,  $J_{\text{CF}} = 15.4$  Hz), 161.5 (d,  $J_{\text{CF}} = 246.0$  Hz), 161.6 (dd,  $J_{\text{CF}} = 245.6$  Hz,  $J_{\text{CF}} = 9.5$  Hz); *m/z* (APCI+, CH<sub>2</sub>Cl<sub>2</sub>, hexane) 481.5 [M + H]<sup>+</sup>.

**3,5,2',3'',3'''-Hexafluoro-4,4'''-dipropyl[1,1':4',1'':4'',1''']quaterphenyl **8**{4,1,3,5}.**  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 1.00 (t,  $J_{\text{HH}} = 7.0$  Hz, 3 H), 1.02 (t,  $J_{\text{HH}} = 7.1$  Hz, 3 H), 1.67 (sextet,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 1.72 (sextet,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 2.70 (t,  $J_{\text{HH}} = 7.1$  Hz, 2 H), 2.72 (t,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 7.03–7.33 (m, 6 H), 7.64–7.69 (m, 4 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.76, 13.77, 22.8, 23.16, 24.2, 30.8, 109.5 (d,  $J_{\text{CF}} = 27.3$  Hz), 117.1 (t,  $J_{\text{CF}} = 20.9$  Hz), 121.6 (dd,  $J_{\text{CF}} = 12.0$  Hz,  $J_{\text{CF}} = 2.5$  Hz), 123.7 (dd,  $J_{\text{CF}} = 12.3$  Hz,  $J_{\text{CF}} = 2.5$  Hz), 124.5 (t,  $J_{\text{CF}} = 3.2$  Hz), 124.9 (t,  $J_{\text{CF}} = 4.4$  Hz), 125.0 (br. s), 125.7 (br. s), 127.0, 129.5 (d,  $J_{\text{CF}} = 3.0$  Hz), 130.2 (d,  $J_{\text{CF}} = 10.6$  Hz), 132.2 (d,  $J_{\text{CF}} = 13.3$  Hz), 134.2, 138.9 (t,  $J_{\text{CF}} = 2.5$  Hz), 140.0 (t,  $J_{\text{CF}} = 9.9$  Hz), 148.1 (dd,  $J_{\text{CF}} = 250.7$  Hz,  $J_{\text{CF}} = 14.2$  Hz), 148.4 (dd,  $J_{\text{CF}} = 250.5$  Hz,  $J_{\text{CF}} = 14.0$  Hz), 148.6 (dd,  $J_{\text{CF}} = 251.3$  Hz,  $J_{\text{CF}} = 14.0$  Hz), 149.4 (dd,  $J_{\text{CF}} = 246.7$  Hz,  $J_{\text{CF}} = 12.9$  Hz), 161.9 (dd,  $J_{\text{CF}} = 246.0$  Hz,  $J_{\text{CF}} = 10.2$  Hz); *m/z* (APCI+, CH<sub>2</sub>Cl<sub>2</sub>, hexane) 499.5 [M + H]<sup>+</sup>.

**2,3,2',3''-Tetrafluoro-4,4'''-dipropyl[1,1':4',1'':4'',1''']quaterphenyl **8**{5,1,3,1}.**  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 1.01 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.02 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.721 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.724 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.68 (t,  $J_{\text{HH}} = 7.8$  Hz, 2 H), 2.71 (t,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 7.03 (ddd,  $J = 7.8$  Hz,  $J = 6.7$  Hz,  $J = 1.1$  Hz, 1 H), 7.18 (ddd,  $J = 8.2$  Hz,  $J = 6.8$  Hz,  $J = 1.5$  Hz, 1 H), 7.30–7.32 (m, 4 H), 7.54 (d,  $J = 8.0$  Hz, 2 H), 7.67–7.71 (m, 4 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.8, 13.9, 23.2, 24.4, 30.8, 37.8, 124.2 (dd,  $J_{\text{CF}} = 3.8$  Hz,  $J_{\text{CF}} = 2.7$  Hz), 124.5 (t,  $J_{\text{CF}} = 3.4$  Hz), 124.7 (t,  $J_{\text{CF}} = 3.4$  Hz), 124.9 (t,  $J_{\text{CF}} = 4.3$  Hz), 127.8 (d,  $J_{\text{CF}} = 10.2$  Hz), 128.7 (br. s), 128.8, 128.99 (br. s), 129.04 (d,  $J_{\text{CF}} = 3.0$  Hz), 130.1 (dd,  $J_{\text{CF}} = 7.2$  Hz,  $J_{\text{CF}} = 3.8$  Hz), 131.0 (d,  $J_{\text{CF}} = 13.7$  Hz), 131.9, 134.2, 134.8 (br. s), 142.9, 148.1 (dd,  $J_{\text{CF}} = 248.6$  Hz,  $J_{\text{CF}} = 13.3$  Hz), 148.5 (dd,  $J_{\text{CF}} = 250.9$  Hz,  $J_{\text{CF}} = 15.6$  Hz), 148.6 (dd,  $J_{\text{CF}} = 251.3$  Hz,  $J_{\text{CF}} = 15.6$  Hz), 149.6 (dd,  $J_{\text{CF}} = 244.3$  Hz,  $J_{\text{CF}} = 11.6$  Hz), the increased intensity of the signal at  $\delta = 128.8$  indicates that two carbon resonances coincide here; *m/z* (APCI+, CH<sub>2</sub>Cl<sub>2</sub>, hexane) 463.5 [M + H]<sup>+</sup>.

**3,5,3'',5'''-Tetrafluoro-4,4'''-dipropyl[1,1':4',1'':4'',1''']quaterphenyl **8**{5,1,5,5}.**  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 1.00 (t,  $J_{\text{HH}} = 7.4$  Hz, 6 H), 1.67 (sextet,  $J_{\text{HH}} = 7.4$  Hz, 4 H), 2.70 (t,  $J_{\text{HH}} = 7.5$  Hz, 4 H), 7.11–7.17 (m, 4 H), 7.63–7.73 (m, 8 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.8, 22.8, 24.2, 109.3 (d, line distance 27.7 Hz, AA'–part of a AA'XX'–spectrum), 116.9 (t,  $J_{\text{CF}} = 20.9$  Hz), 127.2, 127.5, 138.2 (d,  $J_{\text{CF}} = 2.5$  Hz), 140.1, 140.2 (t,  $J_{\text{CF}} = 9.9$  Hz), 161.9 (dd,  $J_{\text{CF}} = 245.8$  Hz,  $J_{\text{CF}} = 10.4$  Hz); (APCI+, CH<sub>2</sub>Cl<sub>2</sub>, hexane): *m/z* = 463.5 [M + H]<sup>+</sup>.

**3,5,2',2'',3'',5'''-Hexafluoro-4,4'''-dipropyl[1,1':4',1'':4'',1''']quaterphenyl **8**{4,3,2,4}.**  $\delta_{\text{H}}$ (400.1 MHz, CDCl<sub>3</sub>) 1.00 (t,  $J_{\text{HH}} = 7.4$  Hz, 6 H), 1.67 (sextet,  $J_{\text{HH}} = 7.4$  Hz, 4 H), 2.71 (d,  $J_{\text{HH}} = 7.5$  Hz, 4 H), 7.09–7.15 (m, 4 H), 7.40–7.53 (m, 6 H);  $\delta_{\text{C}}$ (100.6 MHz, CDCl<sub>3</sub>) 13.8, 22.8, 24.2, 111.5 (d, line distance 31.5 Hz, AA'–part of a AA'XX'–spectrum), 114.7 (d,  $J_{\text{CF}} = 24.3$  Hz), 117.6 (t,  $J_{\text{CF}} = 20.9$  Hz), 122.9 (d,  $J_{\text{CF}} = 3.4$  Hz), 126.5 (dt,  $J_{\text{CF}} = 13.0$  Hz,  $J_{\text{CF}} = 2.6$  Hz), 130.7 (d,  $J_{\text{CF}} = 3.8$  Hz), 134.5 (t,  $J_{\text{CF}} = 10.4$  Hz), 140.9 (dd,  $J_{\text{CF}} = 8.2$  Hz,  $J_{\text{CF}} = 1.7$  Hz), 160.0 (d,  $J_{\text{CF}} = 249.8$  Hz), 161.5 (dd,  $J_{\text{CF}} = 245.6$  Hz,  $J_{\text{CF}} = 10.2$  Hz); *m/z* (APCI+, CH<sub>2</sub>Cl<sub>2</sub>, hexane) 499.5 [M + H]<sup>+</sup>.



**2'-Fluoro-4,4''-dipropyl[1,4':1',1'':4'',1''']quaterphenyl**

**8{I,2,I,I}**.  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 1.013 (t,  $J_{\text{HH}} = 7.4$  Hz, 3 H), 1.016 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.72 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.73 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.67 (br. t,  $J_{\text{HH}} = 7.8$  Hz, 4 H), 7.30 (br. d,  $J = 8.0$  Hz, 4 H), 7.43 (dd,  $J = 12.2$  Hz,  $J = 1.7$  Hz, 1 H), 7.48 (dd,  $J = 8.0$  Hz,  $J = 1.8$  Hz, 1 H), 7.54–7.60 (m, 5 H), 7.67–7.72 (m, 4 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.85, 13.88, 24.50, 24.53, 37.71, 37.72, 114.4 (d,  $J_{\text{CF}} = 23.5$  Hz), 122.7 (d,  $J_{\text{CF}} = 3.0$  Hz), 126.8, 126.9, 127.01, 127.02 (d,  $J_{\text{CF}} = 13.3$  Hz), 128.9, 129.1, 129.3 (d,  $J_{\text{CF}} = 3.0$  Hz), 130.8 (d,  $J_{\text{CF}} = 4.2$  Hz), 134.2 (d,  $J_{\text{CF}} = 1.1$  Hz), 136.9 (d,  $J_{\text{CF}} = 1.9$  Hz), 138.0, 140.4, 142.0, 142.3 (d,  $J_{\text{CF}} = 8.0$  Hz), 142.6, 160.1 (d,  $J_{\text{CF}} = 247.9$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 409.5  $[\text{M} + \text{H}]^+$ .

**3,5,2'-Trifluoro-4,4''-dipropyl[1,4':1',1'':4'',1''']quaterphenyl**

**8{4,2,I,I}**.  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 1.007 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.011 (t,  $J_{\text{HH}} = 7.4$  Hz, 3 H), 1.68 (sextet,  $J_{\text{HH}} = 7.1$  Hz, 2 H), 1.72 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.66 (t,  $J_{\text{HH}} = 7.8$  Hz, 2 H), 2.71 (t,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 7.10–7.17 (m, 2 H), 7.29 (br. d,  $J = 8.2$  Hz, 2 H), 7.37 (dd,  $J = 11.8$  Hz,  $J = 1.7$  Hz, 1 H), 7.42 (dd,  $J = 8.0$  Hz,  $J = 1.8$  Hz, 1 H), 7.55–7.59 (m, 3 H), 7.66–7.71 (m, 4 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.8, 13.9, 22.8, 24.2, 24.5, 37.7, 109.4 (d,  $J_{\text{CF}} = 27.7$  Hz), 114.4 (d,  $J_{\text{CF}} = 24.3$  Hz), 117.4 (t,  $J_{\text{CF}} = 21.1$  Hz), 122.6 (d,  $J_{\text{CF}} = 3.4$  Hz), 126.9, 127.1, 128.3 (d,  $J_{\text{CF}} = 13.7$  Hz), 129.0, 129.3 (d,  $J_{\text{CF}} = 3.4$  Hz), 131.0 (d,  $J_{\text{CF}} = 4.2$  Hz), 133.8 (d,  $J_{\text{CF}} = 1.1$  Hz), 137.9, 139.1 (td,  $J_{\text{CF}} = 10.0$  Hz,  $J_{\text{CF}} = 2.0$  Hz), 140.0 (dt,  $J_{\text{CF}} = 8.0$  Hz,  $J_{\text{CF}} = 2.5$  Hz), 140.7, 142.1, 160.1 (d,  $J = 248.2$  Hz), 161.9 (dd,  $J_{\text{CF}} = 246.3$  Hz,  $J_{\text{CF}} = 10.2$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 445.5  $[\text{M} + \text{H}]^+$ .

**3,5,2',2''-Tetrafluoro-4,4''-dipropyl[1,1':4',1'':4'',1''']quaterphenyl 8{I,2,2,4}**.  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 1.00 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.02 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.69 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.71 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.66 (t,  $J_{\text{HH}} = 7.7$  Hz, 2 H), 2.71 (t,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 7.11–7.16 (m, 2 H), 7.30 (br. d,  $J = 8.2$  Hz, 2 H), 7.40–7.57 (m, 8 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.79, 13.84, 22.8, 24.2, 24.5, 37.7, 111.5 (d,  $J_{\text{CF}} = 27.7$  Hz), 114.6 (d,  $J_{\text{CF}} = 23.5$  Hz), 116.7 (dd,  $J_{\text{CF}} = 24.1$  Hz,  $J_{\text{CF}} = 3.6$  Hz), 117.4 (t,  $J_{\text{CF}} = 20.9$  Hz), 122.9 (d,  $J_{\text{CF}} = 3.4$  Hz), 125.0 (t,  $J_{\text{CF}} = 3.2$  Hz), 125.5 (dd,  $J_{\text{CF}} = 13.1$  Hz,  $J_{\text{CF}} = 1.7$  Hz), 126.0 (d,  $J_{\text{CF}} = 12.9$  Hz), 126.8, 129.1, 130.2 (d,  $J_{\text{CF}} = 3.4$  Hz), 130.5 (d,  $J_{\text{CF}} = 3.4$  Hz), 134.8 (t,  $J_{\text{CF}} = 10.1$  Hz), 136.6 (d,  $J_{\text{CF}} = 1.9$  Hz), 137.4 (d,  $J_{\text{CF}} = 8.7$  Hz), 142.9, 143.2 (d,  $J_{\text{CF}} = 8.0$  Hz), 159.5 (d,  $J_{\text{CF}} = 249.0$  Hz), 160.0 (d,  $J_{\text{CF}} = 248.6$  Hz), 161.5 (dd,  $J_{\text{CF}} = 245.6$  Hz,  $J_{\text{CF}} = 10.6$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 463.5  $[\text{M} + \text{H}]^+$ .

**3,2',2'',2'''-Tetrafluoro-4,4''-dipropyl[1,1':4',1'':4'',1''']quaterphenyl 8{2,2,2,3}**.  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 1.00 (t,  $J_{\text{HH}} = 7.2$  Hz, 3 H), 1.02 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.71 (br. sextet,  $J_{\text{HH}} = 7.5$  Hz, 4 H), 2.65 (t,  $J_{\text{HH}} = 7.8$  Hz, 2 H), 2.69 (t,  $J_{\text{HH}} = 7.7$  Hz, 2 H), 7.02 (dd,  $J = 11.9$  Hz,  $J = 1.5$  Hz, 1 H), 7.07 (dd,  $J = 7.9$  Hz,  $J = 1.6$  Hz, 1 H), 7.28–7.34 (m, 3 H), 7.38–7.48 (m, 5 H), 7.51–7.56 (m, 2 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.7, 13.9, 23.3, 24.2, 30.9, 37.5, 115.7 (dd,  $J_{\text{CF}} = 23.9$  Hz,  $J_{\text{CF}} = 3.4$  Hz), 116.2 (d,  $J_{\text{CF}} = 22.4$  Hz), 116.7 (ddd,  $J_{\text{CF}} = 23.9$  Hz,  $J_{\text{CF}} = 3.4$  Hz,  $J_{\text{CF}} = 1.9$  Hz), 124.341 (d,  $J_{\text{CF}} = 6.5$  Hz), 124.342, 124.5 (d,  $J_{\text{CF}} = 1.9$  Hz), 124.7 (d,  $J_{\text{CF}} = 3.0$  Hz), 124.9 (t,  $J_{\text{CF}} = 3.2$  Hz), 125.0 (t,  $J_{\text{CF}} = 3.2$  Hz), 126.2 (dd,  $J_{\text{CF}} = 12.9$  Hz,  $J_{\text{CF}} = 1.9$  Hz), 127.1 (dd,  $J_{\text{CF}} = 13.3$  Hz,  $J_{\text{CF}} = 1.9$  Hz), 129.0 (d,  $J_{\text{CF}} = 16.3$  Hz), 130.0 (d,  $J_{\text{CF}} = 3.4$  Hz), 130.2 (d,  $J_{\text{CF}} = 3.4$  Hz), 130.4 (d,  $J_{\text{CF}} = 3.8$  Hz), 130.7 (d,  $J_{\text{CF}} = 5.7$  Hz), 134.7 (dd,  $J_{\text{CF}} = 8.4$  Hz,  $J_{\text{CF}} = 1.1$  Hz), 136.7 (dd,  $J_{\text{CF}} = 8.5$  Hz,  $J_{\text{CF}} = 0.9$  Hz), 137.6 (dd,  $J_{\text{CF}} = 8.5$  Hz,  $J_{\text{CF}} = 0.9$  Hz), 145.3 (d,  $J_{\text{CF}} = 7.6$  Hz), 159.60 (d,  $J_{\text{CF}} = 248.2$  Hz), 159.61 (d,  $J_{\text{CF}} = 248.6$  Hz), 159.7 (d,  $J_{\text{CF}} = 248.2$  Hz), 161.1 (d,  $J_{\text{CF}} = 244.4$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 463.5  $[\text{M} + \text{H}]^+$ .

**2'-Fluoro-4,4''-dipropyl[1,1':4',4'':1'',1''']quaterphenyl 8{I,1,2,I}**.  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 1.016 (t,  $J_{\text{HH}} = 7.4$  Hz, 3 H),

1.020 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.73 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.73 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.67 (br. t,  $J_{\text{HH}} = 7.6$  Hz, 4 H), 7.29–7.31 (m, 4 H), 7.44–7.60 (m, 7 H), 7.70 (s, 4 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.88, 13.90, 24.49, 24.53, 37.7, 37.8, 114.4 (d,  $J_{\text{CF}} = 23.9$  Hz), 122.7 (d,  $J_{\text{CF}} = 3.0$  Hz), 126.8, 127.2, 127.4, 127.7 (d,  $J_{\text{CF}} = 13.7$  Hz), 128.6, 128.77, 128.80, 129.0, 130.9 (d,  $J_{\text{CF}} = 4.2$  Hz), 132.8 (d,  $J_{\text{CF}} = 1.5$  Hz), 137.8, 138.1 (d,  $J_{\text{CF}} = 1.9$  Hz), 140.7, 141.5 (d,  $J_{\text{CF}} = 7.6$  Hz), 142.2 (d,  $J_{\text{CF}} = 20.9$  Hz), 160.1 (d,  $J_{\text{CF}} = 247.5$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 409.5  $[\text{M} + \text{H}]^+$ .

**2,3,2',3''-Tetrafluoro-4,4''-dipropyl[1,1':4',4'':1'',1''']quaterphenyl 8{5,I,2,2}**.  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 1.02 (br. t,  $J_{\text{HH}} = 7.4$  Hz, 6 H), 1.712 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.715 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.69 (t,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.71 (t,  $J_{\text{HH}} = 7.2$  Hz, 2 H), 7.02 (ddd,  $J = 8.1$  Hz,  $J = 6.7$  Hz,  $J = 1.4$  Hz, 1 H), 7.17 (ddd,  $J = 8.2$  Hz,  $J = 6.9$  Hz,  $J = 1.5$  Hz, 1 H), 7.28–7.34 (m, 3 H), 7.43–7.55 (m, 3 H), 7.64–7.72 (m, 4 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.76, 13.85, 23.2, 23.3, 30.8, 30.9, 114.6 (d,  $J_{\text{CF}} = 23.9$  Hz), 115.6 (dd,  $J_{\text{CF}} = 23.7$  Hz,  $J_{\text{CF}} = 3.6$  Hz), 122.9 (d,  $J_{\text{CF}} = 3.0$  Hz), 124.1 (dd,  $J_{\text{CF}} = 3.6$  Hz,  $J_{\text{CF}} = 2.8$  Hz), 124.3 (t,  $J_{\text{CF}} = 3.2$  Hz), 124.9 (t,  $J_{\text{CF}} = 4.4$  Hz), 126.8 (dd,  $J_{\text{CF}} = 13.3$  Hz,  $J_{\text{CF}} = 1.9$  Hz), 127.0, 127.7 (d,  $J_{\text{CF}} = 10.2$  Hz), 129.0 (d,  $J_{\text{CF}} = 16.3$  Hz), 129.4 (d,  $J_{\text{CF}} = 3.4$  Hz), 130.7 (d,  $J_{\text{CF}} = 6.1$  Hz), 130.8 (d,  $J_{\text{CF}} = 4.2$  Hz), 131.0 (d,  $J_{\text{CF}} = 13.7$  Hz), 134.7 (br. s), 134.8 (d,  $J_{\text{CF}} = 1.1$  Hz), 138.8 (d,  $J_{\text{CF}} = 1.9$  Hz), 141.8 (d,  $J_{\text{CF}} = 8.4$  Hz), 148.1 (dd,  $J_{\text{CF}} = 248.6$  Hz,  $J_{\text{CF}} = 13.3$  Hz), 149.6 (dd,  $J_{\text{CF}} = 244.3$  Hz,  $J_{\text{CF}} = 11.6$  Hz), 160.0 (d,  $J_{\text{CF}} = 248.2$  Hz), 161.1 (d,  $J_{\text{CF}} = 244.4$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 463.5  $[\text{M} + \text{H}]^+$ .

**3,2',2'',3''-Tetrafluoro-4,4''-dipropyl[1,1':4',4'':1'',1''']quaterphenyl 8{3,3,3,I}**.  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 1.01 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.02 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.71 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.72 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.67 (t,  $J_{\text{HH}} = 7.9$  Hz, 2 H), 2.69 (t,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 7.29–7.34 (m, 7 H), 7.41–7.47 (m, 2 H), 7.52–7.56 (m, 3 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.86, 13.87, 23.3, 24.5, 30.9, 37.8, 115.7 (dd,  $J_{\text{CF}} = 23.9$  Hz,  $J_{\text{CF}} = 3.4$  Hz), 116.6 (d,  $J_{\text{CF}} = 24.3$  Hz), 124.3 (q,  $J_{\text{CF}} = 3.3$  Hz), 124.8 (d,  $J_{\text{CF}} = 3.8$  Hz), 124.9 (d,  $J_{\text{CF}} = 3.4$  Hz), 127.5 (d,  $J_{\text{CF}} = 1.9$  Hz), 127.6 (d,  $J_{\text{CF}} = 2.3$  Hz), 127.7 (d,  $J_{\text{CF}} = 5.3$  Hz), 127.8 (d,  $J_{\text{CF}} = 1.9$  Hz), 128.7, 128.8, 129.2 (d,  $J_{\text{CF}} = 16.3$  Hz), 130.6 (d,  $J_{\text{CF}} = 3.8$  Hz), 130.7 (d,  $J_{\text{CF}} = 5.7$  Hz), 131.7 (d,  $J_{\text{CF}} = 0.8$  Hz), 134.6 (d,  $J_{\text{CF}} = 8.4$  Hz), 135.8 (d,  $J_{\text{CF}} = 8.7$  Hz), 143.1, 148.55 (dd,  $J_{\text{CF}} = 251.3$  Hz,  $J_{\text{CF}} = 15.6$  Hz), 148.60 (dd,  $J_{\text{CF}} = 252.0$  Hz,  $J_{\text{CF}} = 15.9$  Hz), 159.6 (d,  $J_{\text{CF}} = 248.6$  Hz), 161.1 (d,  $J_{\text{CF}} = 244.8$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 463.5  $[\text{M} + \text{H}]^+$ .

**2',2'',3'',2'''-Pentafluoro-4,4''-dipropyl[1,1':4',4'':1'',1''']quaterphenyl 8{I,3,3,5}**.  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 1.00 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.02 (t,  $J_{\text{HH}} = 7.2$  Hz, 3 H), 1.716 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.719 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.67 (t,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 2.72 (t,  $J_{\text{HH}} = 7.4$  Hz, 2 H), 7.03–7.13 (m, 2 H), 7.23 (br. t,  $J = 7.6$  Hz, 1 H), 7.29–7.34 (m, 3 H), 7.41–7.46 (m, 2 H), 7.53–7.58 (m, 3 H);  $\delta_{\text{C}}$ (100.6 MHz,  $\text{CDCl}_3$ ) 13.8, 13.9, 23.2, 24.5, 30.9, 37.8, 116.6 (dd,  $J_{\text{CF}} = 24.7$  Hz,  $J_{\text{CF}} = 3.4$  Hz), 121.5, (d,  $J_{\text{CF}} = 14.4$  Hz), 124.0 (dd,  $J_{\text{CF}} = 12.3$  Hz,  $J_{\text{CF}} = 2.5$  Hz), 124.4 (dd,  $J_{\text{CF}} = 3.4$  Hz,  $J_{\text{CF}} = 3.0$  Hz), 124.8 (t,  $J_{\text{CF}} = 3.2$  Hz), 124.9 (t,  $J_{\text{CF}} = 4.4$  Hz), 125.0 (t,  $J_{\text{CF}} = 1.9$  Hz), 125.8 (t,  $J_{\text{CF}} = 1.9$  Hz), 128.7, 128.8 (d,  $J_{\text{CF}} = 3.0$  Hz), 129.0 (d,  $J_{\text{CF}} = 13.7$  Hz), 129.3 (dd,  $J_{\text{CF}} = 10.4$  Hz,  $J_{\text{CF}} = 1.7$  Hz), 130.8 (d,  $J_{\text{CF}} = 4.2$  Hz), 132.3 (d,  $J_{\text{CF}} = 13.3$  Hz), 132.5 (d,  $J_{\text{CF}} = 1.5$  Hz), 134.9 (dd,  $J_{\text{CF}} = 8.9$  Hz,  $J_{\text{CF}} = 1.7$  Hz), 142.6, 148.1 (dd,  $J_{\text{CF}} = 250.7$  Hz,  $J_{\text{CF}} = 14.2$  Hz), 148.4 (dd,  $J_{\text{CF}} = 250.9$  Hz,  $J_{\text{CF}} = 14.0$  Hz), 148.6 (dd,  $J_{\text{CF}} = 251.7$  Hz,  $J_{\text{CF}} = 14.0$  Hz), 149.4 (dd,  $J_{\text{CF}} = 246.5$  Hz,  $J_{\text{CF}} = 12.7$  Hz), 159.7 (d,  $J_{\text{CF}} = 247.9$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 481.5  $[\text{M} + \text{H}]^+$ .

**2',6',2'',3'',2'''-Pentafluoro-4,4''-dipropyl[1,1':4',4'':1'',1''']quaterphenyl 8{I,4,3,2}**.  $\delta_{\text{H}}$ (400.1 MHz,  $\text{CDCl}_3$ ) 1.003 (t,  $J_{\text{HH}} =$

7.3 Hz, 3 H), 1.004 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.71 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 1.72 (sextet,  $J_{\text{HH}} = 7.5$  Hz, 2 H), 2.66 (br. t,  $J_{\text{HH}} = 7.6$  Hz, 4 H), 7.04 (dd,  $J = 11.2$ ,  $J = 1.3$  Hz, 1 H), 7.08 (dd,  $J = 7.8$  Hz,  $J = 1.6$  Hz, 1 H), 7.23–7.27 (m, 3 H), 7.29–7.36 (m, 4 H), 7.44–7.46 (m, 2 H);  $\delta_{\text{C}}$  (100.6 MHz,  $\text{CDCl}_3$ ) 13.8, 13.9, 24.2, 24.4, 37.6, 37.9, 112.2 (d, line distance 28.5 Hz, AA'–part of a AA'XX'–spectrum), 115.9 (d,  $J_{\text{CF}} = 21.6$  Hz), 118.3 (t,  $J_{\text{CF}} = 18.8$  Hz), 119.1 (dd,  $J_{\text{CF}} = 15.4$  Hz,  $J_{\text{CF}} = 2.5$  Hz), 124.0 (dd,  $J_{\text{CF}} = 3.6$  Hz,  $J_{\text{CF}} = 2.5$  Hz), 124.4 (d,  $J_{\text{CF}} = 3.0$  Hz), 125.7 (d,  $J_{\text{CF}} = 12.9$  Hz), 125.9, 126.1 (br. s), 127.9 (d,  $J_{\text{CF}} = 9.9$  Hz), 128.5, 130.1, 130.9 (dd,  $J_{\text{CF}} = 3.2$  Hz,  $J_{\text{CF}} = 2.1$  Hz), 135.1 (dd,  $J_{\text{CF}} = 11.0$  Hz,  $J_{\text{CF}} = 2.7$  Hz), 143.1, 146.2 (d,  $J_{\text{CF}} = 7.6$  Hz), 148.3 (dd,  $J_{\text{CF}} = 251.5$  Hz,  $J_{\text{CF}} = 14.2$  Hz), 148.7 (dd,  $J_{\text{CF}} = 251.3$  Hz,  $J_{\text{CF}} = 14.0$  Hz), 159.7 (d,  $J_{\text{CF}} = 249.0$  Hz), 160.1 (dd,  $J_{\text{CF}} = 248.2$  Hz,  $J_{\text{CF}} = 8.4$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 481.5  $[\text{M} + \text{H}]^+$ .

**3,2',6',2"-Tetrafluoro-4,4"-dipropyl[1,1':4',4'':1'',1''']quaterphenyl 8{3,4,2,I}.**  $\delta_{\text{H}}$  (400.1 MHz,  $\text{CDCl}_3$ ) 1.01 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.02 (t,  $J_{\text{HH}} = 7.3$  Hz, 3 H), 1.72 (br. sextet,  $J_{\text{HH}} = 7.5$  Hz, 4 H), 2.67 (t,  $J_{\text{HH}} = 7.8$  Hz, 2 H), 2.70 (t,  $J_{\text{HH}} = 7.8$  Hz, 2 H), 7.20–7.31 (m, 7 H), 7.39 (dd,  $J = 11.7$  Hz,  $J = 1.8$  Hz, 1 H), 7.44 (dd,  $J = 8.0$  Hz,  $J = 1.8$  Hz, 1 H), 7.52–7.57 (m, 3 H);  $\delta_{\text{C}}$  (100.6 MHz,  $\text{CDCl}_3$ ) 13.9, 23.2, 24.5, 30.9, 37.8, 110.1 (d,  $J_{\text{CF}} = 27.7$  Hz), 114.4 (d,  $J_{\text{CF}} = 24.7$  Hz), 116.5 (t,  $J_{\text{CF}} = 18.4$  Hz), 117.1 (d,  $J_{\text{CF}} = 23.9$  Hz), 122.6 (d,  $J_{\text{CF}} = 3.4$  Hz), 125.8 (br. s), 128.0 (d,  $J_{\text{CF}} = 8.7$  Hz), 128.7, 128.8 (d,  $J_{\text{CF}} = 3.0$  Hz), 129.1 (d,  $J_{\text{CF}} = 13.7$  Hz), 129.7 (d,  $J_{\text{CF}} = 16.3$  Hz), 130.5 (d,  $J_{\text{CF}} = 5.7$  Hz), 131.2 (d,  $J_{\text{CF}} = 4.2$  Hz), 132.4 (d,  $J_{\text{CF}} = 1.1$  Hz), 139.1 (dt,  $J_{\text{CF}} = 8.2$  Hz,  $J_{\text{CF}} = 2.1$  Hz), 141.0 (td,  $J_{\text{CF}} = 10.0$  Hz,  $J_{\text{CF}} = 2.0$  Hz), 142.7, 160.1 (d,  $J_{\text{CF}} = 248.6$  Hz), 160.3 (dd,  $J_{\text{CF}} = 248.8$  Hz,  $J_{\text{CF}} = 7.8$  Hz), 160.8 (d,  $J_{\text{CF}} = 244.4$  Hz), the increased intensity of the signal at  $\delta = 13.9$  indicates that two carbon resonances coincide here;  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 463.5  $[\text{M} + \text{H}]^+$ .

**2',6',3'',5''-Tetrafluoro-4,4"-dipropyl[1,1':4',4'':1'',1''']quaterphenyl 8{I,4,I,4}.**  $\delta_{\text{H}}$  (400.1 MHz,  $\text{CDCl}_3$ ) 0.99 (br. t,  $J_{\text{HH}} = 7.4$  Hz, 6 H), 1.67 (sextet,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 1.69 (sextet,  $J_{\text{HH}} = 7.7$  Hz, 2 H), 2.65 (t,  $J_{\text{HH}} = 7.7$  Hz, 2 H), 2.69 (t,  $J_{\text{HH}} = 7.6$  Hz, 2 H), 7.12 (d, line distance 8.5 Hz, AA'–part of a AA'XX'–spectrum, 2 H), 7.24–7.30 (m, 4 H), 7.43 (d, line distance 8.1 Hz, AA'–part of a AA'XX'–spectrum, 2 H), 7.61–7.67 (m, 4 H);  $\delta_{\text{C}}$  (100.6 MHz,  $\text{CDCl}_3$ ) 13.8, 13.9, 22.8, 24.2, 24.4, 37.9, 109.4 (d, line distance 27.7 Hz, AA'–part of a AA'XX'–spectrum), 110.0 (d, line distance 27.7 Hz, AA'–part of a AA'XX'–spectrum), 117.1 (t,  $J_{\text{CF}} = 21.1$  Hz), 117.4 (t,  $J_{\text{CF}} = 18.8$  Hz), 126.2, 127.3, 127.4, 128.4, 130.1, 138.3 (t,  $J_{\text{CF}} = 2.5$  Hz), 139.0 (t,  $J_{\text{CF}} = 2.5$  Hz), 139.9 (t,  $J_{\text{CF}} = 9.9$  Hz), 141.2 (t,  $J_{\text{CF}} = 10.1$  Hz), 142.9, 160.4 (dd,  $J_{\text{CF}} = 247.9$  Hz,  $J_{\text{CF}} = 8.4$  Hz), 161.9 (dd,  $J_{\text{CF}} = 246.3$ ,  $J_{\text{CF}} = 10.2$  Hz);  $m/z$  (APCI+,  $\text{CH}_2\text{Cl}_2$ , hexane) 463.5  $[\text{M} + \text{H}]^+$ .

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