Weakly Coordinating Anions

Chiral Modification of the Tetrakis(pentafluorophenyl)borate Anion with Myrtanyl Groups

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Abstract: The synthesis and characterization of chiral $[\text{B(C}_6\text{F}_5)_4]^{-}$ derivatives bearing a myrtanyl group instead of a fluoro substituent in the para position are described. These new chiral borates were isolated as their bench-stable lithium, sodium, and cesium salts. The corresponding trityl salts were prepared and tested as catalysts in representative counter-anion-directed Diels–Alder reactions and Mukaiyama aldol additions but no enantioselectivity was obtained. Preformation of a chalcone-derived silylcarboxonium ion with the chiral borate as counteranion did not lead to any asymmetric induction in a reaction with cyclohexa-1,3-diene.

Introduction

Boron- and aluminum-based weakly coordinating anions (WCAs) have found widespread application in molecular chemistry.[1] This is particularly true for borates containing highly fluorinated aryl groups such as tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($[\text{BAr}_F^4]$)[2] and tetrakis(pentafluorophenyl)borate $[\text{B(C}_6\text{F}_5)_4]^{-}$.[3] Chiral congeners of these anions are essentially unknown but their use as chiral counteranions in asymmetric catalysis[4] is attractive. Recently, we[5] and List and co-workers[6] independently introduced chiral versions of $[\text{B(C}_6\text{F}_5)_4]^{-}$ where the fluorine atoms in the para position have been replaced by 1,1′-binaphthalene-2-yl groups (Figure 1, left).[5,6] We showed that the trityl salt of $[\text{I}^-]$ promotes Diels–Alder reactions as well as a Mukaiyama aldol addition but we did not observe any enantioselectivity.[5] Similar observations were made by List and co-workers; however, when shifting the chiral unit from the para to the meta position as in $[\text{II}^-]$, a Mukaiyama aldol reaction afforded 16 % ee as proof of concept.[6]

![Figure 1. Chiral congeners of $[\text{B(C}_6\text{F}_5)_4]^{-}$ where one of the fluorine atoms at the aryl groups has been replaced by chiral moieties; $[\text{Tr}]^+ = \text{triphenylmethyl}$, $[\text{MeTr}]^+ = \text{diphenyl(4-tolyl)methyl}$.

Oestreich/List (2017)

List (2017)

this work
Despite these modest prospects, we decided to further pursue the development of chiral, partially fluorinated tetraarylborates. Our initial goal had been to design chiral analogues for silylum ions and silylum-ion-like Lewis acids to drive our silylum-ion-catalyzed Diels–Alder reactions of cyclohexa-1,3-diene enantioselectively.\textsuperscript{5,6} Counteranion \textsuperscript{[3]−} with its π-donating naphthyl units is not chemically resistant against these strong electrophiles. We, therefore, considered more robust aliphatic rather than aromatic chiral units for the modification of the \([\text{B(C}_6\text{F}_5)_4]\)− platform, and we report here the synthesis and characterization of the myrtanyl-substituted borates \([\text{Na}]^+\) and \([\text{Li}]^+\) with various countercations (Figure 1, right).

**Results and Discussion**

To replace the fluorine atom in the para position of the \(\text{C}_6\text{F}_5\) group by myrtanyl groups, we targeted intermediate 6. Its synthesis began with literature-known myrtanal (5) derived from (−)-β-pinene\textsuperscript{[15]} in two steps (Scheme 1, top left).\textsuperscript{[10]} The alcohol 6 was obtained by the addition\textsuperscript{[8b]} of the Grignard reagent prepared from 1-bromo-2,3,5,6-tetrafluorobenzene (5 → 6). The hydroxy group in 6 can be seen as a useful handle for further derivatization in the benzylic position. Defunctionalization was achieved by the Barton–McCombie deoxygenation subsequent to xanthate formation (6 → 7 → 8); alternative palladium-catalyzed methods using \(\text{H}_2\) or \(\text{Et}_3\text{SiH}\) as reducing agents gave no conversion.

Another building block with a methyl group at the benzylic center was obtained by Dess–Martin oxidation (9) followed by methenylation using the Petasis reagent\textsuperscript{[9]} (9 → 10). Substrate-controlled hydrogenation of the 1,1-disubstituted alkene employing Wilkinson’s catalyst proceeded quantitatively with good diastereoselectivity (10 → 11). We did not succeed improving the d.r. = 87:13 further. For example, iridium-catalyzed enantioselective hydrogenation\textsuperscript{[10]} of 10 did not override the substrate control, and yields were consistently lower (see the Supporting Information for details). The assignment of the relative configuration by nOe measurements was not conclusive. Attempts to transform ketone 9 into gem-dimethyl-substituted 12 by geminal dimethylation\textsuperscript{[11]} resulted in decomposition of the starting material. The detour involving cyclopropagation followed by hydrogenolysis was not feasible due to low conversion of the Simmons–Smith reaction under various reaction conditions.\textsuperscript{[12]}

The lithium borate \([\text{Li}]^+[\text{3}]−\) was accessible by chemoselective deprotonation of 8 using \(n\)-butyllithium followed by the reaction with \(\text{BCl}_3\) (Scheme 2, top). We used a salt metathesis reaction with an excess of \(\text{NaCl}\) \([\text{Li}]^+[\text{3}]− \rightarrow [\text{Na}]^+[\text{3}]−\) to ensure complete removal of the formed LiCl prior to the next step. The absence of LiCl was verified by \(^7\)Li NMR spectroscopy. The sodium borate \([\text{Na}]^+[\text{3}]−\) was then reacted with trityl chloride \([\text{Na}]^+[\text{3}]− \rightarrow \text{Tr}^+[\text{3}]−\). However, the steady formation of triphenylmethane was observed but we were unable to determine the origin of the hydride. For comparison, we subjected 11 with a more sterically hindered benzylic C–H to a similar reaction sequence (Scheme 2, bottom). The lithium borate \([\text{Li}]^+[\text{4}]−\) was obtained in high yield. To fully remove coordinating solvents from the purification process, we started the salt metathesis with an excess of \(\text{CS}_2\text{CO}_3\) which allowed isolation of solvent- and LiCl-free \([\text{Cs}]^+[\text{4}]−\). However, an exchange from cesium to sodium as countercation is crucial for the formation of trityl borates \([\text{Cs}]^+[\text{4}]− \rightarrow [\text{Na}]^+[\text{4}]−\). Treatment of the sodium salt \([\text{Na}]^+[\text{4}]−\) with trityl chloride resulted in the formation of the desired trityl borate \(\text{Tr}^+[\text{4}]−\); but again, the formation of triphenylmethane was observed. Hydride abstraction from the benzylic position was excluded by \(^2\)H-labeling of 11 (for the characterization of 11d3 and the corresponding borates \([\text{4}]^−\), see the Supporting Information). For \([\text{Na}]^+[\text{4}]d_3−\) to \(\text{Tr}^+[\text{4}]d_3−\), the formation of non-deuterated triphenylmethane persisted, and deuterated triphenylmethane was not detected. As a consequence, we turned towards reducing the hydride affinity of the trityl cation by moving from \(\text{TrCl}\) to diphenyl(4-tolyl)methyl chloride (MeTrCl). Despite the reduced hydride affinity of

\begin{align*}
\text{Mg (1.6 equiv.)} & \quad 1\text{-bromo-2,3,5,6-tetrafluorobenzene (1.5 equiv.)} \\
\text{THF} & \quad \text{r.t.} \\
\text{5} & \quad \text{71%}
\end{align*}

\begin{align*}
\text{NaH (2.5 equiv.)} & \quad \text{imidazole (5.0 mol%)} \\
\text{CS}_2 & \quad (2.5 \text{ equiv.)} \\
\text{MeI (2.5 equiv.)} & \quad 0^\circ \text{C} \rightarrow \text{r.t.} \\
\text{6} & \quad 65% \\
\text{THF} & \quad \text{r.t.} \\
\text{7} & \quad 49% \\
\text{0^°C} & \quad \text{toluene} \\
\text{CH}_2\text{Cl}_2 & \quad \Delta \\
\text{DMP (1.5 equiv.)} & \quad \text{r.t.} \\
\text{8} & \quad 84%
\end{align*}

\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{12} & \quad \text{not obtained}
\end{align*}

\begin{align*}
\text{THF} & \quad 65^°\text{C} \\
\text{67%} & \quad \text{quant.}
\end{align*}

\begin{align*}
\text{Et}_3\text{SiH} & \quad (5.0 \text{ mol%}) \\
\text{H}_2 & \quad (30 \text{ bar}) \\
\text{benzene} & \quad 30^°\text{C}
\end{align*}

\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{11} & \quad \text{d.r.} = 87:13
\end{align*}

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Scheme 1. Preparation of the borate precursors 8 and 11.
the formation of diphenyl(4-tolyl)methane was not fully prevented.

With the modified trityl salt \([\text{MeTr}]^+\)[4]– in hand, we tested its catalytic activity in two representative Diels–Alder reactions[15] and two Mukaiyama aldol additions.[6] Franzén and co-workers demonstrated that trityl cations are able to catalyze difficult Diels–Alder reactions involving cyclohexa-1,3-diene (14) as enophile in good yields.[14] We applied trityl salt \([\text{MeTr}]^+\)[4]– to the cycloaddition of chalcone (13) with diene 14 (Scheme 3, top). The cycloadduct 15 was isolated in good yield but without enantiomeric excess. Franzén had also tested an enantioselective counteranion-directed Diels–Alder reaction of 14 with methacrolein (16) but could only observe cycloadduct 17 in trace amounts.[15a] Even though our catalyst enabled the desired reaction of 16 and 14 in moderate yield, there was no enantioinduction (Scheme 3, bottom). Diels–Alder reactions with anthracene as the enophile did not show any conversion.[15c]

Enantioselective Mukaiyama aldol reactions either promoted by chiral carboxations[16] or performed in the presence of chiral counteranions[6,17] are known. We applied \([\text{MeTr}]^+\)[4]– in the model aldol reaction of 18 with benzaldehyde (19). Although our trityl salt \([\text{MeTr}]^+\)[4]– is potent enough to catalyze the reaction, we could only isolate the adduct 20 as a racemic mixture (Scheme 4, top).[18] Examination of \([\text{Na}]^+\)[4]– in List’s model reaction of silyketene acetal 21 and 2-naphthaldehyde (22)[6] gave only racemic aldol adduct 23 (Scheme 4, bottom).

To assess the stability of borate [4]– towards silylium ions, we treated Et₃SiH with \([\text{MeTr}]^+\)[4]– in CIC₆D₅ to achieve the established silicon-to-carbon hydride transfer.[19] The formation of the chlorobenzene-stabilized silylium ion \([\text{Et₃Si(ClC₆D₅)]}^+\)[4]– was not observed. However, the same reaction in the presence of a carbonyl group as a Lewis base did result in the formation of the corresponding silylcarboxonium ion. With chalcone (13) in chlorobenzene, \([\text{Et₃Si(13)]}^+\)[4]– did form as major product with a chemical shift of $^{29}$Si NMR = 46.0 ppm; this was con-

Scheme 2. Formation of the chiral borates [3]– and [4]– with various counterions.

Scheme 3. Representative trityl-cation-catalyzed Diels–Alder reactions of cyclohexa-1,3-diene (14) with different enophiles.

Scheme 4. Representative Mukaiyama aldol reactions.
firmed by comparison with \( [\text{Et}_3\text{Si}(13)]^{1+} [\text{B}(\text{C}_6\text{F}_5)_3]\text{A}^- \) prepared by a literature-known procedure. However, the formation of hexamethyldisiloxane as a sideproduct was also observed in small amounts \((29\text{Si} \text{NMR} = 8.6 \text{ ppm})\). Cyclohexa-1,3-diene \((14)\) was then added to verify the reactivity of \( [\text{Et}_3\text{Si}(13)]^{1+} [\text{B}(\text{C}_6\text{F}_5)_3]\text{A}^- \) and the Diels–Alder adduct \(15\) was isolated in good yield but without enantiomeric excess (Scheme 5).

**Scheme 5. Preparation of chalcone-stabilized silicon cation \([\text{Et}_3\text{Si}(13)]^{1+} [\text{B}(\text{C}_6\text{F}_5)_3]\text{A}^- \) by Corey’s hydride abstraction with subsequent Diels–Alder reaction.**

29Si NMR = 8.6 ppm. Cyclohexa-1,3-diene \((14)\) was then added to verify the reactivity of \( [\text{Et}_3\text{Si}(13)]^{1+} [\text{B}(\text{C}_6\text{F}_5)_3]\text{A}^- \) and the Diels–Alder adduct \(15\) was isolated in good yield but without enantiomeric excess (Scheme 5).

**Conclusion**

In summary, a new class of para-mytanyl-substituted chiral borates based on the ubiquitous \([\text{B}(\text{C}_6\text{F}_5)_3]\text{A}^-\) anion has been introduced. Their synthesis hinges on the easily accessible 2,3,5,6-tetrafluorophenyl-substituted benzyl alcohol \(6\) [three steps from \((-\)-)\-pinene]. To turn the derived chiral borates into counteranions suitable for strong Lewis acids such as trityl or silicon tetrafluorophenyl-Methyl Chloride as Carbocation Pre- sided product was also observed in small amounts \((29\text{Si} \text{NMR} = 8.6 \text{ ppm})\). Cyclohexa-1,3-diene \((14)\) was then added to verify the reactivity of \( [\text{Et}_3\text{Si}(13)]^{1+} [\text{B}(\text{C}_6\text{F}_5)_3]\text{A}^- \) and the Diels–Alder adduct \(15\) was isolated in good yield but without enantiomeric excess (Scheme 5).

**Experimental Section**

For general remarks as well as experimental procedures and spectroscopic data for literature-known compounds see the Supporting Information.

\([15,28,55]-6,6\text{-Dimethylbicyclo[3.1.1]heptan-2-yl}(2,3,5,6\text{-tetrafluorophenyl})\text{-methyl} \) \(6\): Based on a literature-known procedure \((\text{dm}, 3.9 \text{ g}, 26 \text{ mmol}, 1.0 \text{ equiv.})\) in THF \((8.0 \text{ mL})\) was added quickly. After stirring for 5 h at room temperature, the reaction was quenched by slow addition of ETOH \((10 \text{ mL})\). The brown suspension was extracted with tert-butylmethyl ether \((3 \times 100 \text{ mL})\), the combined organic phases washed with \(\text{H}_2\text{O} \text{ (100 mL)}\) and dried with \(\text{Na}_2\text{SO}_4\). After removal of all volatiles under reduced pressure, the residue was purified by flash column chromatography on silica gel using cyclohexane/tert-

at room temperature, the reaction was quenched by slow addition of ETOH \((10 \text{ mL})\). The brown suspension was extracted with tert-butylmethyl ether \((3 \times 100 \text{ mL})\), the combined organic phases washed with \(\text{H}_2\text{O} \text{ (100 mL)}\) and dried with \(\text{Na}_2\text{SO}_4\). After removal of all volatiles under reduced pressure, the residue was purified by flash column chromatography on silica gel using cyclohexane/tert-

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**Full Paper**

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**Supporting Information**

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as eluent gave the title compound 8 (0.24 g, 49 %) as colorless oil. HRMS (APCI) for C16H15F4O+ [M – H]+: calculated 299.1054, found 299.1051. 1H NMR (500 MHz, CD3OD): δ/ppm = 0.86 (d, J = 9.5 Hz, 1H), 1.01 (s, 3H), 1.03 (s, 3H), 1.13 (s, 3H), 1.33–1.44 (m, 1H), 1.51 (m, 1H), 1.68–1.90 (m, 4H), 2.17 (m, 1H), 2.34–2.46 (m, 1H), 3.21 (m, 1H), 6.18 (m, 1H). 13C{1H} NMR (126 MHz, CD3OD): δ/ppm = 17.4, 21.9, 22.9, 26.8, 28.3, 34.2, 37.3, 38.6, 41.4, 45.06, 45.11, 103.6 (t, J = 23 Hz), 125.9 (t, J = 17 Hz). The ortho- and meta carbon atoms of the aromatic ring could not be detected. 19F NMR (471 MHz, CD3OD): δ/ppm = –146.6–141.0 (br, 2F, 1H), –140–139.2 (br, 2F, 1H). Optical rotation: [c]D0 +2.5 (c = 1.4, CHCl3).

Lithium Tetrakis(4-[[[(1S,2S,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl]ethyl]-2,3,5,6-tetrafluorophenyl]borate ([Li]1[3]–): To a solution of alkane 8 (0.40 g, 1.4 mmol, 5.5 equiv.) in Et2O (20 mL) was added dropwise nBuLi (2.7 mL in hexane, 0.48 mL, 1.3 mmol, 5.0 equiv.) at –78 °C, and the resulting mixture stirred for 3 h. Afterwards BCl3 (1 in heptane, 0.26 mL, 0.26 mmol, 1.0 equiv.) was added dropwise, and the solution was allowed to slowly warm to room temperature overnight. The reaction was quenched by addition of H2O (20 mL) and extracted with tert-butylmethyl ether (3 × 10 mL). After removal of all volatiles, the residue was purified by flash column chromatography on neutral alumina oxide using hexane/toluene (90:10) as eluent. The chromatography on neutral alumina oxide using hexane/toluene (90:10) as eluent. The lithium tetrakis(4-[[[(1S,2S,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl]ethyl]-2,3,5,6-tetrafluorophenyl]borate ([Li][4]–): To a solution of alkane 8 (0.84 g, 3.7 mmol, 4.4 equiv.) in Et2O (60 mL) was added dropwise nBuLi (2.7 mL in hexane, 1.4 mL, 3.7 mmol, 4.4 equiv.) at –78 °C and the resulting mixture stirred for 3 h. Afterwards BCl3 (1 in heptane, 0.84 mL, 0.84 mmol, 1.0 equiv.) was added dropwise and the solution was warmed up to room temperature overnight slowly. The reaction was quenched by addition of H2O (10 mL) and extracted with n-pentane (3 × 30 mL). After removal of all volatiles the residue was purified by flash column chromatography on neutral alumina oxide using hexane/pentane (95:5) and tert-butylmethyl ether (500 mL), n-pentane (500 mL) and acetonitrile (2 L) as eluent. The chromatography on neutral alumina oxide using hexane/pentane (95:5) and tert-butylmethyl ether (500 mL), n-pentane (500 mL) and acetonitrile (2 L) as eluent. The chromatography on neutral alumina oxide using hexane/pentane (95:5) and tert-butylmethyl ether (500 mL), n-pentane (500 mL) and acetonitrile (2 L) as eluent. The lithium tetrakis(4-[[[(1S,2S,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl]ethyl]-2,3,5,6-tetrafluorophenyl]borate ([Li][4]–): To a solution of alkane 8 (0.84 g, 3.7 mmol, 4.4 equiv.) in Et2O (60 mL) was added dropwise nBuLi (2.7 mL in hexane, 1.4 mL, 3.7 mmol, 4.4 equiv.) at –78 °C and the resulting mixture stirred for 3 h. Afterwards BCl3 (1 in heptane, 0.84 mL, 0.84 mmol, 1.0 equiv.) was added dropwise and the solution was warmed up to room temperature overnight slowly. The reaction was quenched by addition of H2O (10 mL) and extracted with n-pentane (3 × 30 mL). After removal of all volatiles the residue was purified by flash column chromatography on neutral alumina oxide using hexane/pentane (95:5) and tert-butylmethyl ether (500 mL), n-pentane (500 mL) and acetonitrile (2 L) as eluent. The lithium tetrakis(4-[[[(1S,2S,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl]ethyl]-2,3,5,6-tetrafluorophenyl]borate ([Li][4]–): To a solution of alkane 8 (0.84 g, 3.7 mmol, 4.4 equiv.) in Et2O (60 mL) was added dropwise nBuLi (2.7 mL in hexane, 1.4 mL, 3.7 mmol, 4.4 equiv.) at –78 °C and the resulting mixture stirred for 3 h. Afterwards BCl3 (1 in heptane, 0.84 mL, 0.84 mmol, 1.0 equiv.) was added dropwise and the solution was warmed up to room temperature overnight slowly. The reaction was quenched by addition of H2O (10 mL) and extracted with n-pentane (3 × 30 mL). After removal of all volatiles the residue was purified by flash column chromatography on neutral alumina oxide using hexane/pentane (95:5) and tert-butylmethyl ether (500 mL), n-pentane (500 mL) and acetonitrile (2 L) as eluent. The lithium tetrakis(4-[[[(1S,2S,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl]ethyl]-2,3,5,6-tetrafluorophenyl]borate ([Li][4]–): To a solution of alkane 8 (0.84 g, 3.7 mmol, 4.4 equiv.) in Et2O (60 mL) was added dropwise nBuLi (2.7 mL in hexane, 1.4 mL, 3.7 mmol, 4.4 equiv.) at –78 °C. The reaction vessel was transferred to an autoclave pressurized with H2 (30 bar) and stirred for 18 h at 30 °C. The vial was then removed from the autoclave and the crude material filtered through a plug of silica. Removal of all volatiles under reduced pressure gave the alkenne 11 (d2 = 87.13, 44 mg, quant.) as a colorless liquid. The diastereometric ratio was determined by 1H NMR analysis by integration of the baseline-separated signals at δ = 3.21 ppm and δ = 3.34 ppm and by GLC analysis. Major diastereomer: 1H NMR (500 MHz, CD2Cl2): δ/ppm = 0.72 (d, J = 9.7 Hz, 1H), 1.01 (s, 3H), 1.03 (s, 3H), 1.13 (s, 3H), 1.33–1.44 (m, 1H), 1.51 (m, 1H), 1.68–1.90 (m, 4H), 2.17 (m, 1H), 2.34–2.46 (m, 1H), 3.21 (m, 1H), 6.18 (m, 1H). 13C{1H} NMR (126 MHz, CD2Cl2): δ/ppm = 17.4, 21.9, 22.9, 26.8, 28.3, 34.2, 37.3, 38.6, 41.4, 45.06, 45.11, 103.6 (t, J = 23 Hz), 125.9 (t, J = 17 Hz). The ortho- and meta carbon atoms of the aromatic ring could not be detected. 19F NMR (471 MHz, CD2Cl2): δ/ppm = –146.6–141.0 (br, 2F, 1H), –140–139.2 (br, 2F, 1H). Optical rotation: [c]D0 +2.5 (c = 1.4, CHCl3).
Sodium Tetrakis(4-[(1S,3S,5S,6R)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-methyl)-2,3,5,6-tetrafluorophenylborate ([Na] +[4]–): To a solution of the lithium borate [Li]+[3]– (0.30 g, 0.26 mmol) in CH2Cl2 (2.0 mL) was added a saturated aqueous solution of NaCl (2.0 mL), and the two-phase mixture was vigorously stirred overnight at room temperature. The phases were then separated, the organic phase was dried with Na2SO4, and all volatiles were removed under reduced pressure. The residue was dried under high vacuum (130 °C/10–3 mbar) for 10 h giving the sodium borate ([Na] +[3]–) (0.24 mg, 77 %) as a white solid. 1H NMR (500 MHz, CD2Cl2): δ/ppm = 0.63 (d, J = 9.7 Hz, 4H), 1.05 (s, 12H), 1.38–1.51 (m, 4H), 1.56–1.67 (m, 8H), 1.74–1.83 (m, 12H), 2.08–2.15 (m, 4H), 2.18–2.28 (m, 4H), 2.59 (m, 8H). 11B{1H} NMR (160 MHz, CD2Cl2): δ/ppm = –15.5. 13C{1H} NMR (126 MHz, CD2Cl2): δ/ppm = –23.1, 21.3, 26.7, 28.2, 30.2, 34.0, 38.8, 41.5, 46.0, 46.0, 115.6 (determined by 1H/13C HMBC NMR). The meta carbon atoms of the aromatic rings as well as the carbon atoms of the C–B bonds could not be detected. 19F NMR (471 MHz, CD2Cl2): δ/ppm = –149.8 (m, 8F), –143.4 (s, 8F).

Triphenylmethyl Tetrakis(4-[(1S,3S,5S,6R)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]-methyl)-2,3,5,6-tetrafluorophenylborate ([Tr] +[4]–): To a solution of the lithium borate [Li]+[3]– (0.30 g, 0.26 mmol) in CH2Cl2 (2.0 mL) and the two-phase mixture was stirred overnight at room temperature. The phases were then separated, the organic phase was washed with H2O (5.0 mL). The volatiles were removed under reduced pressure, and the resulting residue dried under high vacuum (130 °C/10–3 mbar) giving the cesium borate [Cs]+[4]– (0.30 g, 0.26 mmol) as a white solid; it was used without further purification. 1H NMR (500 MHz, CD2Cl2): δ/ppm = 0.71–0.84 (br m, 4H), 1.10–1.16 (br m, 24H), 1.22–1.37 (br m, 12H), 1.45–1.58 (br m, 4H), 1.64–1.75 (br m, 4H), 1.75–1.88 (br m, 8H), 1.88–2.01 (br m, 8H), 2.11–2.28 (br m, 4H), 2.46–2.64 (br m, 4H), 2.80–3.01 (br m, 24H). 11B{1H} NMR (160 MHz, CD2Cl2): δ/ppm = –15.8. 13C{1H} NMR (126 MHz, CD2Cl2): δ/ppm = 26.7, 28.2, 30.2, 34.0, 38.8, 41.5, 45.3, 45.6. The aromatic carbon atoms could not be detected. 19F NMR (471 MHz, CD2Cl2): δ/ppm = –150.2–[–142.2] (br m, 8F), –132.2 (s, 8F).

Diphenyl(4-tolyl)methylium Tetrakis(4-[(1S,3S,5S,6R)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]-methyl)-2,3,5,6-tetrafluorophenylborate ([Tr]+[4]–): To a solution of the solution of the cesium borate [Cs]+[4]– (0.11 g, 92 %) in CH2Cl2 (1.0 mL) was added a saturated aqueous solution of Cs2CO3 (1.0 mL), and the two-phase mixture was vigorously stirred for 5 h at room temperature. The phases were then separated, the organic phase was washed with H2O (5.0 mL). The volatiles were removed under reduced pressure, and the resulting residue dried under high vacuum (130 °C/10–3 mbar) giving the cesium borate [Cs]+[4]– (0.24 mg, 77 %) as a white solid. 1H NMR (500 MHz, CD2Cl2): δ/ppm = 0.81 (d, J = 9.4 Hz, 4H), 1.11 (s, 12H), 1.18 (s, 12H), 1.51–1.62 (m, 4H), 1.76–1.91 (m, 16H), 1.91–2.00 (m, 4H), 2.22–2.34 (m, 8H), 2.60–2.71 (m, 8H), 7.58–7.70 (m, 6H), 7.84 (t, J = 7.5 Hz, 6H), 8.18–8.29 (m, 3H). 11B{1H} NMR (161 MHz, CD2Cl2): δ/ppm = –16.4. 13C{1H} NMR (176 MHz, CD2Cl2): δ/ppm = 22.3, 23.1, 26.8, 28.3, 30.2, 34.1, 39.1, 41.8, 41.9, 45.7, 114.5, 131.0, 140.3, 143.0, 144.0, 211.1 (determined by 1H/13C HMBC NMR experiment). The ortho- and meta carbon atoms of the aromatic rings as well as the carbon atoms of the C–B bonds could not be detected. 19F NMR (471 MHz, CD2Cl2): δ/ppm = –149.8 (m, 8F), –134.1 (s, 8F).

Diphenyl(4-tolyl)methyl Tetrakis(4-[(1S,3S,5S,6R)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]-methyl)-2,3,5,6-tetrafluorophenylborate ([Me Tr]+[4]–): To a solution of the trityl salt [Me Tr]+[4]– (86 mg, 0.059 mmol, 73 %) was obtained as an orange solid with triphenylmethane (2.0 mg, 0.010 mmol, 12 %) as by-product. The amount of triphenylmethane was determined by 1H NMR analysis by integration of the baseline-separated signals at δ = 7.64 ppm and δ = 7.13 ppm. 1H NMR (400 MHz, CD2Cl2): δ/ppm = 0.77 (br d, J = 9.2 Hz, 4H), 1.02 (br s, 24H), 1.21 (br s, 12H), 1.40–1.55 (br m, 101 Hz, 4H), 1.55–1.70 (br m, 4H), 1.76–1.92 (br m, 4H), 1.92–2.11 (br m, 8H), 2.16–2.28 (br m, 4H), 2.28–2.42 (br m, 4H), 3.06–3.19 (br m, 4H), 6.74 (d, J = 7.9 Hz, 6H), 7.85 (t, J = 7.6 Hz, 6H), 8.25 (t, J = 7.6 Hz, 6H). 11B{1H} NMR (161 MHz, CD2Cl2): δ/ppm = –16.5. 13C{1H} NMR (110 MHz, CD2Cl2): δ/ppm = 18.0, 22.2, 22.9, 27.1, 28.3, 34.3, 36.8, 38.7, 41.7, 45.1, 45.5, 131.0, 140.3, 143.0, 144.0, 211.1. The ortho- and meta carbon atoms of the aromatic rings as well as the carbon atoms of the C–B bonds could not be detected. 19F NMR (471 MHz, CD2Cl2): δ/ppm = –151.8–[–145.7] (br m, 8F), –134.1 (s, 8F).

Triphenylmethyl Tetrakis(4-[(1S,3S,5S,6R)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]-methyl)-2,3,5,6-tetrafluorophenylborate ([Me Tr]+[4]–): To a solution of the solution of the lithium borate [Li]+[3]– (0.10 g, 0.081 mmol, 1.0 equiv.) and diphenyl(4-tolyl)methyl chloride (0.11 g, 0.41 mmol, 5.0 equiv.) were suspended in n-hexane (6.0 mL) and stirred overnight at room temperature. The suspension was filtered under nitrogen atmosphere, and the remaining solid was washed with n-hexane (2 x 3.0 mL). The red orange residue was redissolved in CH2Cl2 (2.0 mL) and then dried under high vacuum (50 °C/10–3 mbar). The trityl salt [Tr]+[4]– (83 mg, 0.056 mmol, 7 %) was obtained as an orange solid with triphenylmethane (2.7 mg, 0.011 mmol, 13 %) as by-product. The amount of triphenylmethane was determined by 1H NMR analysis by integration of the baseline-separated signals at δ = 7.67 ppm and δ = 7.01 ppm. HRMS (APCI)
for C_{20}H_{17}BF_{16} \cdot [M]\cdot calculated 1207.5790, found 1207.5792. HRMS (APCI) for C_{20}H_{17}^{+}\cdot [M]\cdot calculated 257.1325, found 257.1329. ^{1}H NMR (500 MHz, CD_{2}Cl_{2}); \delta/ppm = 0.77 (br, d, J = 9.3 Hz, 4H), 1.03 (br, s, 24H), 1.22 (br, s, 12H), 1.39–1.56 (br m, 4H), 1.56–1.68 (br m, 4H), 1.78–1.92 (br m, 8H), 1.92–2.09 (br m, 8H), 2.15–2.27 (br m, 4H), 2.28–2.41 (br m, 4H), 2.70 (br s, 24H), 3.08–3.18 (br m, 4H), 3.50–3.74 (m, 6H), 6.17 (d, J = 7.9 Hz, 2H), 7.21 (t, J = 7.7 Hz, 4H), 8.18 (t, J = 7.5 Hz, 2H). ^{11}B{^{1}H} NMR (161 MHz, CD_{2}Cl_{2}); \delta/ppm = -16.5. ^{13}C{^{1}H} NMR (126 MHz, CD_{2}Cl_{2}); \delta/ppm = 18.1, 22.3, 22.9, 23.7, 27.1, 28.4, 34.4, 36.9, 38.7, 41.7, 45.1, 45.5, 119.0 (t, J = 17 Hz), 130.7, 132.5, 138.2, 140.1, 142.0, 142.7, 143.7, 160.8, 208.4. ^{19}F NMR (471 MHz, CD_{2}Cl_{2}); \delta/ppm = 18.1, 22.3, 22.9, 23.7, 27.1, 28.4, 34.4, 36.9, 38.7, 41.7, 45.1, 45.5, 119.0 (t, J = 17 Hz), 130.7, 132.5, 138.2, 140.1, 142.0, 142.7, 143.7, 160.8, 208.4.  

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