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

Phillip Pommerening[a] and Martin Oestreich*[a]

Abstract: The synthesis and characterization of chiral $[B(C_6F_5)_4]^-$ 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 counteranion-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 asymmetic 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 ($[BAr^F{}_4]^-$)[2] and tetrakis(pentafluorophenyl)borate ($[B(C_6F_5)_4]^-$).[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independently introduced chiral versions of $[B(C_6F_5)_4]^-$ where the fluorine atoms in the *para* positions have been replaced by 1,1'-binaphthalene-2-yl groups (Figure 1, left).[5,6] We showed that the trityl salt of [**1**]$^-$ promotes Diels–Alder reactions as well as a Mukaiyama aldol addition but did not obtained 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 in [**2**]$^-$, a Mukaiyama aldol reaction afforded 16% ee as proof of concept.[6]

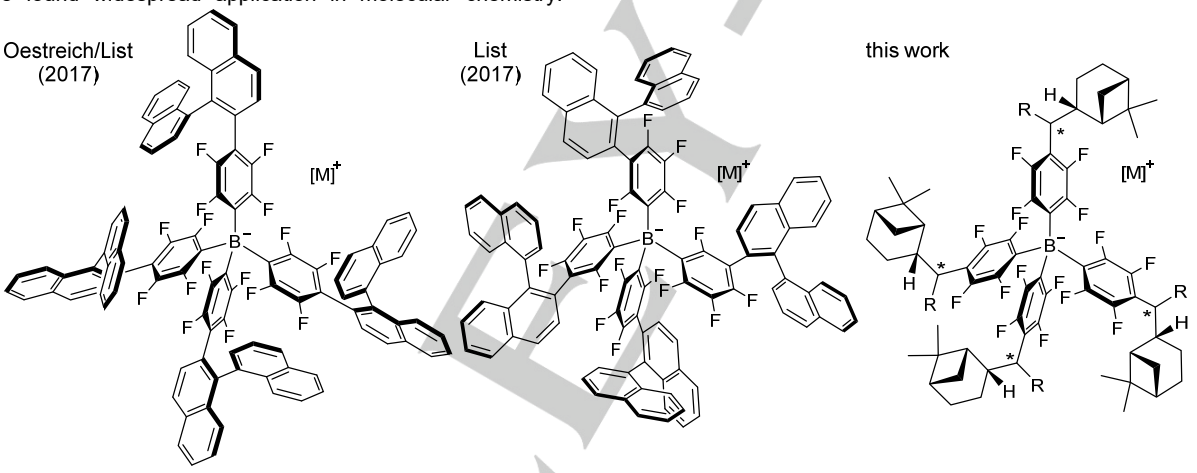

Figure 1. Chiral congeners of $[B(C_6F_5)_4]^-$ where one of the fluorine atoms at the aryl groups has been replaced by chiral moieties; $[Tr]^+$ = triphenylmethylium, $[^{Me}Tr]^+$ = diphenyl(4-tolyl)methylium.

Despite these modest prospects, we decided to further pursue the development of chiral, partially fluorinated tetraarylborates. Our initial goal had been to design chiral counteranions for silylium ions and silylium-ion-like Lewis acids to drive our silylium-ion-catalyzed Diels–Alder reactions of cyclohexa-1,3-diene enantioselectively.[5,6] Counteranion [**1**]$^-$ with its π-donating naphthyl groups is not chemically resistant against those strong electrophiles. We therefore considered more robust aliphatic rather than aromatic chiral units for the modification of the $[B(C_6F_5)_4]^-$ platform, and we report here the synthesis and characterization of the myrtanyl-substituted borates [**3**]$^-$ and [**4**]$^-$ with various countercations (Figure 1, right).

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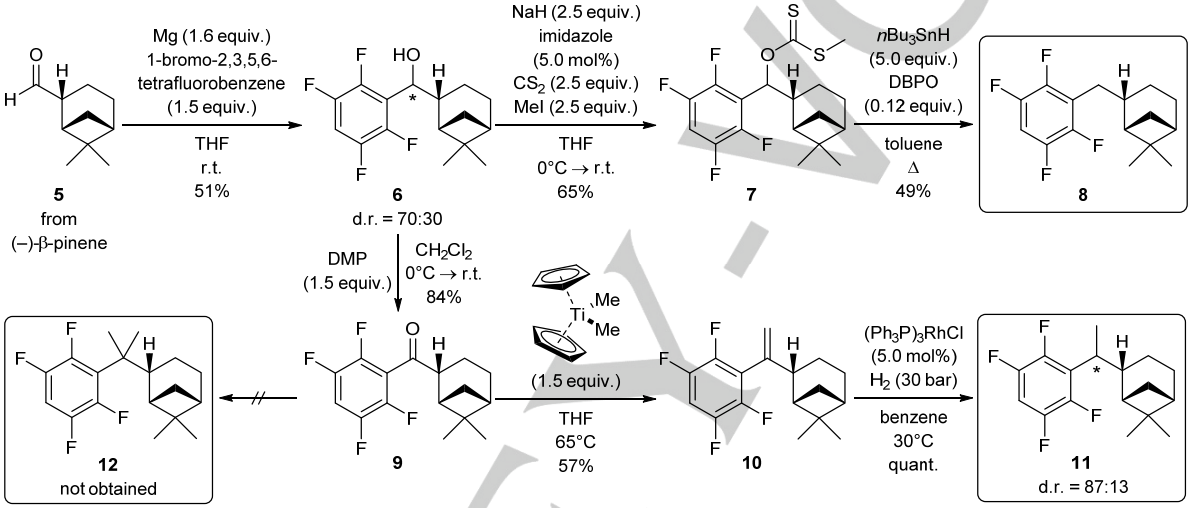
Results and Discussion

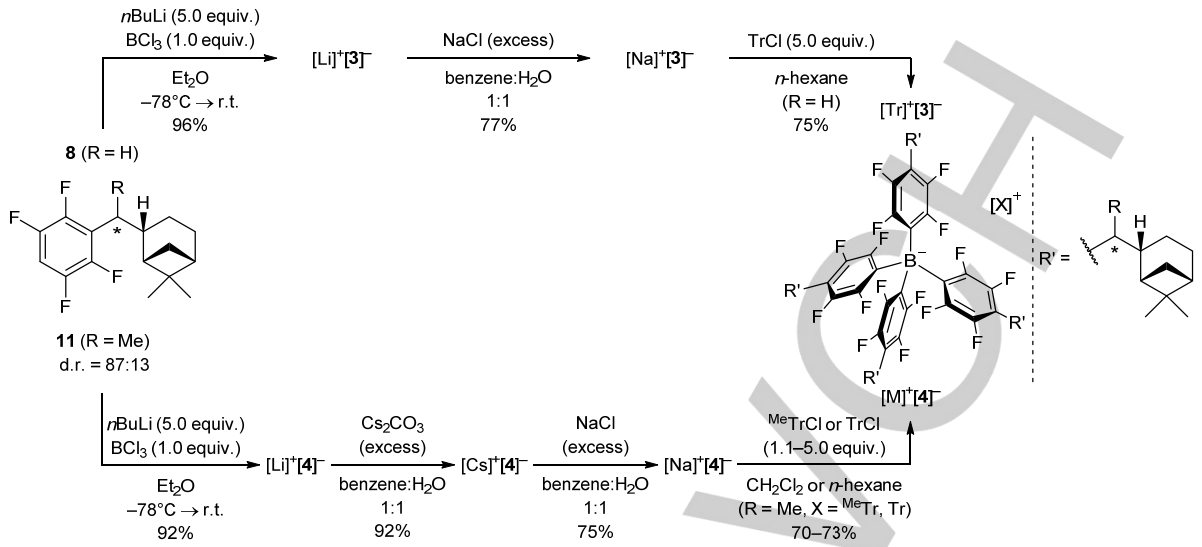
To replace the fluorine atom in the *para* position of the C_6F_5 group by myrtanyl groups, we targeted intermediate **6**. Its

synthesis began with literature-known myrtanal (**5**) derived from (–)-β-pinene[7] in two steps (Scheme 1, left).[8] The alcohol **6** was obtained by the addition[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 subequent to xanthate formation (**6** → **7** → **8**); alternative palladium-catalyzed methods using H_2 or Et_3SiH as reducing agents gave no conversion. Another building block with a methyl group at the benzylic center was obtained by Dess–Martin oxidation (**6** → **9**) followed by methenylation using the Petasis reagent[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[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[11] resulted in decomposition of the starting material. The detour involving cyclopropanation followed by hydrogenolysis was not feasible due to low conversion of the Simmons–Smith reaction under various reaction conditions.[12]



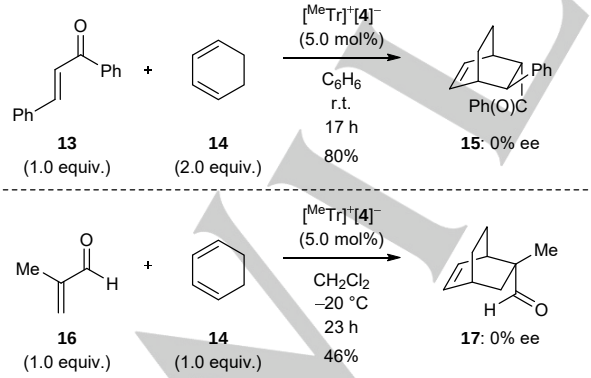
Scheme 1. Preparation of the borate precursors **8** and **11**.

The lithium borate [Li]$^+$[**3**]$^-$ was accessible by chemoselective deprotonation of **8** using *n*-butyllithium followed by the reaction with BCl_3 (Scheme 2, top). We used a salt metathesis reaction with excess of NaCl ([Li]$^+$[**3**]$^-$ → [Na]$^+$[**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 [Na]$^+$[**3**]$^-$ was then reacted with trityl chloride ([Na]$^+$[**3**]$^-$ → [Tr]$^+$[**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 [Li]$^+$[**4**]$^-$ was obtained in high yield. To fully remove coordinating solvents from the purification process, we started the salt metathesis with an excess of Cs_2CO_3 which allowed isolation of solvent- and LiCl-free [Cs]$^+$[**4**]$^-$. However, an exchange from cesium to sodium as countercation is crucial for the formation of trityl borates ([Cs]$^+$[**4**]$^-$ → [Na]$^+$[**4**]$^-$). Treatment of the sodium salt [Na]$^+$[**4**]$^-$ with trityl chloride resulted in formation of the desired trityl borate [Tr]$^+$[**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 **11**-d_2 and the corresponding borates [**4**-d_2]$^-$, see the Supporting Information). For [Na]$^+$[**4**-d_2]$^-$ to [Tr]$^+$[**4**-d_2]$^-$, 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 TrCl to diphenyl(4-tolyl)methyl chloride (^{Me}TrCl). Despite the reduced hydride affinity of [^{Me}Tr]$^+$[**4**]$^-$,[13] the formation of diphenyl(4-tolyl)methane was not fully prevented.



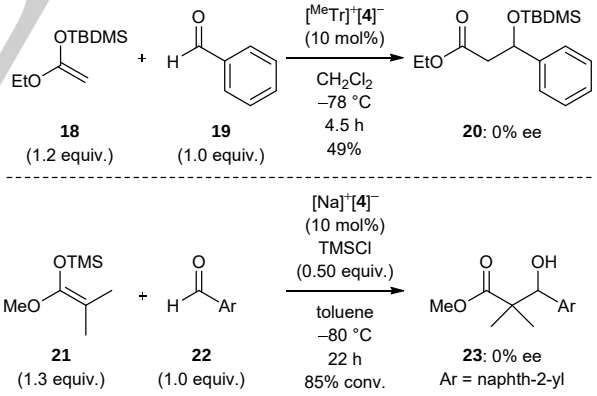
Scheme 2. Formation of the chiral borates [**3**]$^-$ and [**4**]$^-$ with various countercations.

With the modified trityl salt [^{Me}Tr]$^+$[**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 [^{Me}Tr]$^+$[**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.[15b] 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]



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

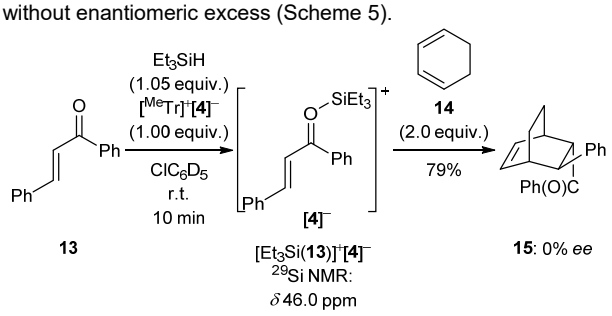
Enantioselective Mukaiyama aldol reactions either promoted by chiral carbocations[16] or performed in the presence of chiral counteranions[6,17] are known. We applied [^{Me}Tr]$^+$[**4**]$^-$ in the model aldol reaction of **18** with benzaldehyde (**19**). Although our trityl salt [^{Me}Tr]$^+$[**4**]$^-$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



Scheme 4. Representative Mukaiyama aldol reactions.

To assess the stability of borate [**4**]$^-$ towards silylium ions, we treated Et_3SiH with [^{Me}Tr]$^+$[**4**]$^-$ in ClC_6D_5 to achieve the established silicon-to-carbon hydride transfer.[19] The formation of the chlorobenzene-stabilized silylium ion $[Et_3Si(ClC_6D_5)]^+$·[**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, $[Et_3Si(\mathbf{13})]^+[\mathbf{4}]^-$ did form as major product with a chemical shift of ^{29}Si NMR = 46.0 ppm; this was confirmed by comparison with $[Et_3Si(\mathbf{13})]^+[B(C_6F_5)_4]^-$ prepared by a literature-known procedure.[20] However, the formation of hexamethyldisiloxane as a sideproduct was also observed in small amounts (^{29}Si NMR = 8.6 ppm). Cyclohexa-1,3-diene (**14**) was then added to verify the catalytic activity of $[Et_3Si(\mathbf{13})]^+[\mathbf{4}]^-$ 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 $[Et_3Si(\mathbf{13})]^+[\mathbf{4}]^-$ by Corey's hydride abstraction with subsequent Diels–Alder reaction, ^{29}Si NMR resonance signal determined by $^1H/^{29}Si$ HMQC (500/99 MHz, ClC_6D_5).

Conclusion

In summary, a new class of *para*-myrtanyl-substituted chiral borates based on the ubiquitous $[B(C_6F_5)_4]^-$ anion has been introduced. Their synthesis hinges on the easily accessible 2,3,5,6-tetrafluorophenyl-substituted benzyl alcohol **6** (three steps from (–)-β-pinene). To turn the derived chiral borates into counteranions suitable for strong Lewis acids such as trityl or silicon cations, a series of salt metathesis reactions had to be performed to obtain LiCl-free material ($[Li]^+$ to $[Na]^+$ or ($[Li]^+$ to $[Cs]^+$ to $[Na]^+$). To increase the chemical stability of the borate anion, the hydride affinity of the trityl salt was attenuated with the use of diphenyl(4-tolyl)methyl chloride as carbocation precursor (to form $[^{Me}Tr]^+[\mathbf{4}]^-$). Representative Diels–Alder and Mukaiyama-aldol reactions were feasible but with no enantioinduction. The generation of a silicon cation from Et_3SiH with $[\mathbf{4}]^-$ as counteranion was successful as its chalcone adduct. Its subsequent reaction with cyclohexa-1,3-diene (**14**) gave the cycloaddition product as a racemic mixture.

Experimental Section

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

((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)(2,3,5,6-tetrafluorophenyl)methanol (6)

Based on a literature-known procedure[8b] 1,2-dibromoethane (3 drops) was added to a suspension of magnesium turning (1.0 g, 41 mmol, 1.6 equiv.) in THF (7.0 mL). After stirring for 5 min a solution of 1-bromo-2,3,5,6-tetrafluorobenzene (4.7 mL, 39 mmol, 1.5 equiv.) in THF (35 mL) was added slowly. The resulting dark brown solution was stirred for 1.5 h at room temperature and then 1 h at 60°C. The mixture was cooled to room temperature, and a solution of aldehyde **5** (3.9 g, 26 mmol, 1.0 equiv.) in THF (8.0 mL) was added quickly. After stirring for 5 h at room temperature, the reaction was quenched by slow addition of EtOH (10 mL). The brown suspension was extracted with *tert*-butylmethyl ether (3 x 100 mL), the combined organic phases washed with H_2O (100 mL) and dried over Na_2SO_4. After removal of all volatiles under reduced pressure, the residue was purified by flash column chromatography on silica gel using cyclohexane/*tert*-butylmethyl ether = 10/1 as eluent to afford the title compound **6** (d.r. = 70:30, 4.0 g, 51%) as a brown oil. The diastereomeric ratio was determined in ^1H NMR analysis by integration of the baseline-separated signals at δ 4.91 ppm and δ 4.96 ppm. HRMS (APCI) for $C_{16}H_{17}F_4^+$ $[M–OH]^+$: calculated 285.1261, found 285.1258. Minor diastereomer: ^1H NMR (500 MHz, C_6D_6): δ/ppm = 0.72 (d, *J* = 9.7 Hz, 1H), 1.01 (s, 3H), 1.02 (s, 3H), 1.37–1.41 (m, 1H), 1.66 (d, *J* = 7.2 Hz, 1H), 1.72–1.98 (m, 5H), 2.10–2.17 (m, 1H), 2.51–2.60 (m, 1H), 4.91 (dd, *J* = 7.3 Hz, *J* = 11.4 Hz, 1H), 6.17 (m_c, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ/ppm = 19.9, 23.0, 26.4, 27.9, 33.6, 38.6, 41.4, 43.8, 46.8, 71.0, 104.9 (t, *J* = 23 Hz), 123.7 (t, *J* = 15 Hz), 144.8 (dm), 146.3 (dm). $^{19}F\{^1H\}$ NMR (471 MHz, C_6D_6): δ/ppm = –143.5 (dd, *J* = 22 Hz, *J* = 13 Hz, 2F), –139.3 (dd, *J* = 23 Hz, *J* = 13 Hz, 2F). Major diastereomer: ^1H NMR (500 MHz, C_6D_6): δ/ppm = 0.75 (d, *J* = 9.7 Hz, 1H), 1.01 (s, 3H), 1.03–1.11 (m, 1H),1.11–1.22 (m, 1H), 1.18 (s, 3H), 1.53–1.64 (m, 2H), 1.73 (m_c, 1H), 1.79 (m_c, 1H), 2.29–2.36 (m, 1H), 2.39–2.44 (m, 1H), 2.52 (m_c, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 6.23 (m_c, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ/ppm = 18.2, 22.9, 26.3, 27.1, 27.2, 28.2, 33.4, 38.7, 41.5, 42.4, 46.6, 69.4, 104.9 (t, *J* = 22 Hz), 123.5, (t, *J* = 15 Hz), 144.4 (dm), 146.1 (dm). $^{19}F\{^1H\}$ NMR (471 MHz, C_6D_6): δ/ppm = –143.5 (dd, *J* = 23 Hz, *J* = 13 Hz, 2F), –139.4 (dd, *J* = 23 Hz, *J* = 13 Hz, 2F).

***O*-(((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)(2,3,5,6-tetrafluorophenyl)-methyl) *S*-methyl carbonodithioate (7)**

To a suspension of NaH (60% in mineral oil, 47 mg, 1.2 mmol, 2.5 equiv.) and imidazole (1.6 mg, 24 µmol, 5.0 mol%) in THF (4.0 mL) was added a solution of the alcohol **6** (0.14 g, 0.47 mmol, 1.0 equiv.) in THF (3.0 mL) at 0°C. The resulting suspension was stirred for 0.5 h at room temperature before CS_2 (70 µL, 90 mg, 1.2 mmol, 2.5 equiv.) was added dropwise. The mixture was stirred for an additional 0.5 h, then MeI (0.17 g, 1.2 mmol, 2.5 equiv.) was added dropwise, and the solution was stirred 1.5 h at room temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (5.0 mL) at 0°C. The phases were separated, the aqueous phase extracted with *tert*-butylmethyl ether (3 x 5.0 mL), and the combined organic phases dried over Na_2SO_4. After removal of all volatiles under reduced pressure, the residue was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford the title compound **7** (0.12 g, 65%) as a brown oil. HRMS (APCI) for $C_{18}H_{21}F_4OS_2^+$ $[M+H]^+$: calculated 393.0964, found 393.0966. ^1H NMR (500 MHz, C_6D_6): δ/ppm = 0.74 (d, *J* = 9.9 Hz, 1H), 1.11 (s, 3H), 1.13–1.21 (m, 2H), 1.18 (s, 3H), 1.53–1.63 (m, 1H), 1.70–1.80 (m, 2H), 2.03 (s, 3H), 2.25–2.32 (m, 1H), 2.32–2.38 (m, 1H), 3.07 (m_c, 1H), 6.16 (m_c, 1H), 7.17 (d, *J* = 8.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ/ppm = 17.4, 18.9, 22.8, 26.1, 27.9, 33.1, 38.5, 41.3, 42.5, 43.3, 78.7, 106.3 (t, *J* = 23 Hz), 118.5 (t, *J* = 15 Hz), 145.3 (dm, *J* = 249 Hz), 146.1 (dm, *J* = 248 Hz), 215.9. $^{19}F\{^1H\}$ NMR (471 MHz, C_6D_6): δ/ppm = –141.0–[–140.6] (br m, 2F), –138.6 (dd, *J* = 23 Hz, *J* = 13 Hz, 2F).

(1*S*,2*S*,5*S*)-6,6-Dimethyl-2-(2,3,5,6-tetrafluorobenzyl)bicyclo[3.1.1]heptane (8)

A solution of *n*Bu_3SnH (2.2 mL, 8.4 mmol, 5.0 equiv.), DBPO (49 mg, 0.20 mmol, 0.12 equiv.) and the xanthate **7** (0.66 g, 1.7 mmol, 1.0 equiv.) in toluene (22 mL) was degassed (3 x) and maintained at 105°C for 15 h. The reaction was then cooled to room temperature, diluted with cyclohexane (5.0 mL), and all volatiles were removed under reduced pressure. Purification of the residue by flash column chromatography using cyclohexane as eluent gave the title compound **8** (0.24 g, 49%) as colorless oil. HRMS (APCI) for $C_{16}H_{17}F_4^+$ $[M–H]^+$: calculated 285.1261, found 285.1265. ^1H NMR (500 MHz, C_6D_6): δ/ppm = 0.69 (d, *J* = 9.7 Hz, 1H), 1.07 (s, 3H), 1.14 (s, 3H), 1.34–1.46 (m, 1H), 1.60–1.73 (m, 3H),

1.77–1.88 (2H), 2.16–2.25 (m, 2H), 2.53–2.64 (m, 2H), 6.21 (m_c, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ/ppm = 22.0, 22.9, 26.6, 28.2, 30.0, 33.9, 38.9, 41.4, 41.6, 45.3, 103.6 (t, *J* = 23 Hz), 121.1 (t, *J* = 19 Hz), 145.3 (dm), 146.0 (dm). Optical rotation: $[\alpha]^{20}_D$ = +9.08 (c = 1.00, $CHCl_3$).

((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)(2,3,5,6-tetrafluorophenyl)methanone (9)

A solution of the alcohol **6** (1.7 g, 5.6 mmol, 1.0 equiv.) in CH_2Cl_2 (60 mL) was cooled to 0°C. Dess–Martin periodinane (3.6 g, 8.4 mmol, 1.5 equiv.) was added in one portion, and the resulting mixture stirred 4 h at room temperature. The reaction was quenched by addition of H_2O (100 mL). The phases were separated, the organic phase washed with H_2O (5 x 100 mL) and dried over $MgSO_4$. After removal of all volatiles, the resulting white solid was removed by filtration through a pad of cotton to afford the ketone **9** (d.r. = 95:5, 1.4 g, 84%) as an orange brown oil; it was used without further purification. The diastereomeric ratio was determined by GLC analysis. HRMS (APCI) for $C_{16}H_{15}F_4O^+$ $[M–H]^+$: calculated 299.1054, found 299.1051. ^1H NMR (700 MHz, C_6D_6): δ/ppm = 0.85 (d, *J* = 9.9 Hz, 1H), 0.88 (s, 3H), 1.06 (s, 3H), 1.55–1.65 (m, 2H), 1.67–1.71 (m, 1H), 1.76–1.83 (m, 1H), 2.12–2.19 (m, 1H), 2.25–2.31 (m, 1H), 2.34–2.39 (m, 1H), 3.13–3.20 (m_c, 1H), 6.08 (m_c, 1H). $^{13}C\{^1H\}$ NMR (176 MHz, C_6D_6): δ/ppm = 14.4, 22.7, 25.1, 27.1, 30.8, 39.0, 40.8, 43.0, 54.3, 107.2 (t, *J* = 23 Hz), 121.3 (t, *J* = 21 Hz), 142.9 (dm), 146.0 (dm), 196.9. ^{19}F NMR (659 MHz, C_6D_6): δ/ppm = –142.4 (m_c, 2F), –137.6 (m_c, 2F).

(1*S*,2*R*,5*S*)-6,6-Dimethyl-2-(1-(2,3,5,6-tetrafluorophenyl)vinyl)bicyclo[3.1.1]heptane (10)

Dimethyltitanocene (0.43M in THF, 5.9 mL, 2.5 mmol, 1.5 equiv.) was added to a solution of the ketone **9** (0.50 g, 1.7 mmol, 1.0 equiv.) in THF (10 mL) and heated at 65°C until full conversion monitored by GLC (18–48 h). The reaction was cooled to room temperature, quenched by addition of H_2O (5.0 mL) and extracted with *tert*-butylmethyl ether (2 x 10 mL). The combined organic phases were dried over $MgSO_4$. After removal of all volatiles, the residue was purified by flash column chromatography on silica gel using *n*-pentane as eluent to afford the alkene **10** (d.r. = 96:4, 0.28 g, 57%) as a colorless liquid. The diastereomeric ratio was determined by GLC analysis. HRMS (APCI) for $C_{17}H_{17}F_4^+$ $[M–H]^+$: calculated 297.1261, found 297.1265. ^1H NMR (500 MHz, C_6D_6): δ/ppm = 0.81 (d, *J* = 9.8 Hz, 1H), 1.00 (s, 3H), 1.15 (s, 3H), 1.48–1.70 (m, 3H), 1.75–1.88 (m, 2H), 2.18 (m_c, 1H), 2.27 (m_c, 1H), 3.07 (m_c, 1H), 4.95 (d, *J* = 2.0 Hz, 1H), 5.21 (d, *J* = 2.2 Hz, 1H), 6.24 (m_c, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ/ppm = 19.6, 23.6, 26.2, 28.1, 33.5, 38.7, 41.6, 44.0, 44.6, 104.5 (t, *J* = 23 Hz), 117.2, 141.7. The *ortho*- and *meta* carbon atoms of the aromatic ring could not be detected. $^{19}F\{^1H\}$ NMR (471 MHz, C_6D_6): δ/ppm = –142.3 (dd, *J* = 13 Hz, *J* = 24 Hz, 2F), –139.4 (dd, *J* = 13 Hz, *J* = 23 Hz, 2F).

(1*S*,2*S*,5*S*)-6,6-Dimethyl-2-(1-(2,3,5,6-tetrafluorophenyl)ethyl)bicyclo[3.1.1]heptane (11)

In a glass vial, the alkene **10** (45 mg, 0.15 mmol, 1.0 equiv.) and $(Ph_3P)_3RhCl$ (6.9 mg, 7.5 µmol, 5.0 mol%) were placed under a nitrogen atmosphere and dissolved in degassed benzene (2.0 mL). The reaction vessel was transferred to an autoclave pressurized with H_2 (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 alkane **11** (d.r. = 87:13, 44 mg, quant.) as a colorless liquid. The diastereomeric ratio was determined in ^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, C_6D_6): δ/ppm = 0.72 (d, *J* = 9.7 Hz, 1H), 1.01 (s, 3H), 1.03 (s, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.33–1.44 (m, 1H), 1.51 (m_c, 1H), 1.68–1.90 (m, 4H), 2.17 (m_c, 1H), 2.34–2.46 (m, 1H), 3.21 (m_c, 1H), 6.18 (m_c, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): 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. ^{19}F NMR (471 MHz, C_6D_6): δ/ppm = –144.6–[–141.0] (br m, 2F), –140–[–139.2] (br m, 2F). Minor diastereomer (selected signals): ^1H NMR (500 MHz, C_6D_6): δ/ppm = 0.77 (d, *J* = 9.7 Hz, 1H), 2.10 (m_c, 1H), 2.30 (m_c, 1H), 3.34 (m_c, 1H), 6.24 (m_c, 1H). Optical rotation: $[\alpha]^{20}_D$ = +2.5 (c = 1.4, $CHCl_3$).

Lithium tetrakis(4-(((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-2,3,5,6-tetrafluorophenyl)borate ([Li]$^+$[3**]$^–$)**

To a solution of alkane **8** (0.40 g, 1.4 mmol, 5.5 equiv.) in Et_2O (20 mL) was added dropwise *n*BuLi (2.7M in hexane, 0.48 mL, 1.3 mmol, 5.0 equiv.) at –78°C, and the resulting mixture stirred for 3 h. Afterwards BCl_3 (1M 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 H_2O (20 mL) and extracted with *tert*-butylmethyl ether (3 x 10 mL). After removal of all volatiles, the residue was purified by flash column chromatography on silica gel using subsequent cyclohexane (200 mL) and ethyl acetate (800 mL) as eluent. The lithium borate [Li]$^+$[**3**]$^–$ (0.25 g, 96%) was obtained as a white solid. HRMS (APCI) for $C_{64}H_{68}BF_{16}^–$ $[M]^–$: calculated 1151.5164, found 1151.5165. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ/ppm = 0.86 (d, *J* = 9.5 Hz, 4H), 1.14 (s, 12H), 1.19 (s, 12H), 1.57–1.67 (m, 4H), 1.80–1.94 (m, 16H), 1.95–2.02 (m, 4H), 2.24–2.37 (m, 8H), 2.65–2.76 (m, 8H), $^{11}B\{^1H\}$ NMR (160 MHz, $(CD_3)_2CO$): δ/ppm = –16.3. $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$): δ/ppm = 22.5, 23.3, 27.0, 28.5, 30.3 (determined by $^1H/^{13}C$ HSQC NMR experiment), 34.3, 39.4, 42.2, 42.3, 46.0, 114.7 (t, *J* = 19 Hz), 144.9 (dm, *J* = 240 Hz), 149.2 (dm, *J* = 243 Hz). The carbon atoms of the C–B bonds could not be detected. ^{19}F NMR (471 MHz, $(CD_3)_2CO$): δ/ppm = –150.5 (m_c, 8F), –133.4 (br s, 8F).

Lithium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)borate ([Li]$^+$[4**]$^–$)**

To a solution of alkane **11** (d.r. = 87:13, 1.1 g, 3.8 mmol, 4.5 equiv.) in Et_2O (60 mL) was added dropwise *n*BuLi (2.7M in hexane, 1.4 mL, 3.7 mmol, 4.4 equiv.) at –78°C and the resulting mixture stirred for 3 h. Afterwards BCl_3 (1M in heptane, 0.84 mL, 0.84 mmol, 1.0 equiv.) was added dropwise and the solution was allowed to warm up to room temperature overnight slowly. The reaction was quenched by addition of H_2O (10 mL) and extracted with *n*-pentane (3 x 30 mL). After removal of all volatiles the residue was purified by flash column chromatography on neutral aluminum oxide using subsequent *n*-pentane (500 mL), *tert*-butylmethyl ether (500 mL), *n*-pentane (500 mL) and acetonitrile (2 L) as eluent. The lithium borate [Li]$^+$[**4**]$^–$ (0.94 g, 92%) was obtained as a white solid. HRMS (APCI) for $C_{68}H_{76}BF_{16}^–$ $[M]^–$: calculated 1207.5790, found 1207.5754. ^1H NMR (500 MHz, C_6D_6): δ/ppm = 0.72–0.82 (br m, 4H), 1.05–1.14 (br m, 24H), 1.14–1.30 (br m, 12H), 1.44–1.55 (br m, 4H), 1.61–1.75 (br m, 4H), 1.76–1.88 (br m, 8H), 1.88–1.99 (br m, 8H), 2.13–2.26 (br m, 4H), 2.41–2.57 (br m, 4H), 3.22–3.35 (br m, 4H). ^7Li NMR (194 MHz, C_6D_6): δ/ppm = 0.0. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6): δ/ppm = –15.8. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ/ppm = 18.0, 22.2, 23.0, 27.0, 28.3, 34.2, 37.2, 38.6, 41.5, 45.2, 45.5, 120.1, (t, *J* = 17 Hz), 144.7 (dm, *J* = 242 Hz), 149.4 (dm, *J* = 238 Hz). The carbon atoms of the C–B bonds could not be detected. ^{19}F NMR (471 MHz, C_6D_6): δ/ppm = –150.5–[–143.7] (br m, 8F), –138.2–[–131.7] (br m, 8F).

Cesium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)borate ([Cs]$^+$[4**]$^–$)**

To a solution of borate [Li]$^+$[**4**]$^–$ (0.11 g, 0.091 mmol) in benzene (1.0 mL) was added a saturated aqueous solution of Cs_2CO_3 (1.0 mL), and the two-phase mixture was vigorously stirred for 5 h at room temperature. The phases were then separated, extracted with benzene (2 x 5.0 mL), and the combined organic phases were washed with H_2O (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**]$^–$ (0.11 g, 92%) as a white solid; it was used without further

purification. ^{1}H NMR (500 MHz, C_6D_6): δ/ppm = 0.71–0.84 (br m, 4H), 1.03–1.16 (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), 3.26–3.41 (br m, 4H). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ/ppm = –15.8. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ/ppm = 18.2, 22.2, 23.1, 27.0, 28.3, 34.3, 37.3, 38.6, 41.5, 45.3, 45.6. The aromatic carbon atoms could not be detected. ^{19}F NMR (471 MHz, C_6D_6): δ/ppm = –150.2–[–142.2] (br m, 8F), –132.2 (br s, 8F).

Sodium tetrakis(4-(((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-2,3,5,6-tetrafluorophenyl)borate ([Na]$^+$[3**]$^-$)**

To a solution of the lithium borate [Li]$^+$[**3**]$^-$ (0.30 g, 0.26 mmol) in CH_2Cl_2 (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 dried over Na_2SO_4, all volatiles removed under reduced pressure, and 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. ^{1}H NMR (500 MHz, C_6D_6): δ/ppm = 0.63 (d, *J* = 9.7 Hz, 4H), 1.05 (s, 12H), 1.09 (s, 12H), 1.38–1.51 (m, 4H), 1.56–1.67 (m, 8H), 1.73–1.84 (m, 12H), 2.08–2.15 (m, 4H), 2.18–2.28 (m, 4H), 2.59 (m_c, 8H). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ/ppm = –15.5. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ/ppm = 21.8, 23.1, 26.7, 28.2, 30.2, 34.0, 38.8, 41.5, 41.6, 46.0, 115.6 (determined by ^{1}H/^{13}C HMBC NMR), 145.1 (determined by ^{1}H/^{13}C 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. ^{19}F{^{1}H} NMR (471 MHz, C_6D_6): δ/ppm = –147.7 (s, 8F), –134.7 (s, 8F). Optical rotation: $[\alpha]^{20}_D$ = +23.4 (c = 1.07, $CHCl_3$).

Sodium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)borate ([Na]$^+$[4**]$^-$)**

To a solution of the cesium borate [Cs]$^+$[**4**]$^-$ (0.11 g, 0.084 mmol) in benzene (1.5 mL) was added a saturated aqueous solution of NaCl (1.5 mL), and the two-phase mixture was vigorously stirred for 3 h at room temperature. The phases were then separated, the organic phase dried over Na_2SO_4, and all volatiles were removed under reduced pressure. The resulting residue was transferred to a glove box, resuspended in benzene (3 mL), and the solution stirred overnight over molecular sieves (4 Å). The molecular sieves was filtered off, and the resulting solution dried under high vacuum (130°C/10^{-3} mbar) for 10 h to afford the sodium borate [Na]$^+$[**4**]$^-$ (78 mg, 75%) as a white solid. HRMS (APCI) for $C_{68}H_{76}BF_{16}^-$ [M]$^-$: calculated 1207.5790, found 1207.5797. ^{1}H NMR (500 MHz, C_6D_6): δ/ppm = 0.72–0.82 (br m, 4H), 1.05–1.14 (br m, 24H), 1.14–1.30 (br m, 12H), 1.44–1.55 (br m, 4H), 1.61–1.75 (br m, 4H), 1.76–1.88 (br m, 8H), 1.88–1.99 (br m, 8H), 2.13–2.26 (br m, 4H), 2.41–2.57 (br m, 4H), 3.22–3.35 (br m, 4H). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ/ppm = –15.8. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ/ppm = 18.0, 22.2, 23.0, 27.0, 28.3, 34.2, 37.2, 38.6, 41.5, 45.2, 45.5, 120.3, (t, *J* = 17 Hz), 144.8 (dm, *J* = 248 Hz), 149.3 (dm, *J* = 236 Hz). The carbon atoms of the C–B bonds could not be detected. ^{19}F NMR (471 MHz, C_6D_6): δ/ppm = –151.5–[–143.6] (br m, 8F), –139.6–[–131.1] (br m, 8F). Optical rotation: $[\alpha]^{20}_D$ = +18.1 (c = 1.22, $CHCl_3$).

Triphenylmethylium tetrakis(4-(((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-2,3,5,6-tetrafluorophenyl)borate ([Tr]$^+$[3**]$^-$)**

The borate [Na]$^+$[**3**]$^-$ (0.10 g, 0.085 mmol, 1.0 equiv.) and triphenylmethyl chloride (0.12 g, 0.43 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 CH_2Cl_2 (2.0 mL) and then dried under high vacuum (50°C/10^{-3} mbar). The trityl salt [Tr]$^+$[**3**]$^-$ (87 mg, 0.063 mmol, 75%) was obtained as an orange solid with triphenylmethane (2.7 mg, 0.011 mmol, 13%) as byproduct. The amount of triphenylmethane was determined by ^{1}H NMR analysis by integration of the baseline-separated signals at δ 7.58–7.70 ppm and δ 7.13 ppm. HRMS (APCI) for $C_{64}H_{68}BF_{16}^-$ [M]$^-$: calculated 1151.5164, found 1151.5144. HRMS (APCI) for $C_{19}H_{15}^+$ [M]$^+$: calculated 243.1168, found 243.1163. ^{1}H NMR (500 MHz, CD_2Cl_2): 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). ^{11}B{^{1}H} NMR (161 MHz, CD_2Cl_2): δ/ppm = –16.4. ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2): 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, 143.1, 144.0, 211.1 (determined by ^{1}H/^{13}C 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. ^{19}F NMR (471 MHz, CD_2Cl_2): δ/ppm = –149.8 (m_c, 8F), –134.1 (br s, 8F).

Triphenylmethylium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)borate ([Tr]$^+$[4**]$^-$)**

The borate [Na]$^+$[**4**]$^-$ (0.10 g, 0.081 mmol, 1.0 equiv.) and triphenylmethyl 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 (6 x 3.0 mL). The red orange residue was redissolved in CH_2Cl_2 (2.0 mL) and then dried under high vacuum (50°C/10^{-3} mbar). The trityl salt [Tr]$^+$[**4**] (86 mg, 0.059 mmol, 73%) was obtained as an orange solid with triphenylmethane (2.0 mg, 0.010 mmol, 12%) as byproduct. The amount of triphenylmethane was determined by ^{1}H NMR analysis by integration of the baseline-separated signals at δ 7.64 ppm and δ 7.13 ppm. ^{1}H NMR (400 MHz, CD_2Cl_2): 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, 4H), 1.55–1.70 (br m, 4H), 1.76–1.92 (br m, 8H), 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), 7.64 (d, *J* = 7.9 Hz, 6H), 7.85 (t, *J* = 7.6 Hz, 6H), 8.25 (t, *J* = 7.6 Hz, 3H). ^{11}B{^{1}H} NMR (161 MHz, CD_2Cl_2): δ/ppm = –16.5. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): 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. ^{19}F NMR (471 MHz, CD_2Cl_2): δ/ppm = –151.8–[–145.7] (br m, 8F), –134.1 (br s, 8F).

Diphenyl(4-tolyl)methylium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)borate ([^{Me}Tr]$^+$[4**]$^-$)**

The borate [Na]$^+$[**4**]$^-$ (0.10 g, 0.081 mmol, 1.0 equiv.) and diphenyl(4-tolyl)methyl chloride (25 mg, 85 μmol, 1.1 equiv.) were dissolved in CH_2Cl_2 (2.5 mL) and stirred overnight at room temperature. The supernatant was transferred into a Schlenk tube, and the remaining solid was washed with CH_2Cl_2 (2 x 2.0 mL). The red orange solution was transferred out of the glovebox and connected to a vacuum-nitrogen manifold to remove all volatiles under high vacuum (50°C/10^{-3} mbar). The trityl salt [^{Me}Tr]$^+$[**4**] (83 mg, 0.056 mmol, 70%) was obtained as an orange solid with diphenyl(4-tolyl)methane (1.0 mg, 0.006 mmol, 7%) as byproduct. The amount of diphenyl(4-tolyl)methane was determined by ^{1}H NMR analysis by integration of the baseline-separated signals at δ 7.67 ppm and δ 7.01 ppm. HRMS (APCI) for $C_{68}H_{76}BF_{16}^-$ [M]$^-$: calculated 1207.5790, found 1207.5792. HRMS (APCI) for $C_{20}H_{17}^+$ [M]$^+$: calculated 257.1325, found 257.1329. ^{1}H NMR (500 MHz, CD_2Cl_2): δ/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, 3H), 3.08–3.18 (br m, 4H), 7.54–7.62 (m, 6H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.81 (t, *J* = 7.7 Hz, 4H), 8.18 (t, *J* = 7.5 Hz, 2H). ^{11}B{^{1}H} NMR (161 MHz, CD_2Cl_2): δ/ppm = –16.5. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ/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_2Cl_2): δ/ppm = –151.5–[–145.1] (br m, 8F), –134.1 (br s, 8F).

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Keywords: Cations • Chirality • Diels–Alder reaction • Lewis acids • Trityl group

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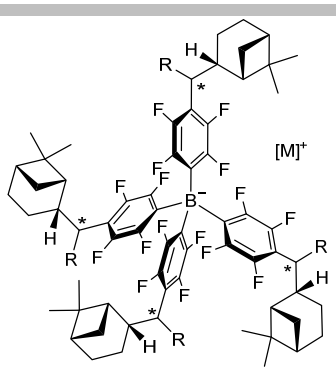
Suggestion for the Entry for the Table of Contents

FULL PAPER

New chiral versions of the ubiquitous $[B(C_6F_5)_4]^-$ anion decorated with myrtanyl backbones and paired with various countercations are presented (Tr = Ph_3C). Their use as catalysts in Diels–Alder reactions and Mukaiyama aldol additions is demonstrated, and their stability against highly electrophilic silylium-ion-like species is investigated.



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