Supporting Information

Borata-Wittig Olefination Reactions of Ketones, Carboxylic Esters and Amides with Bis(pentafluorophenyl)borata-alkene Reagents

Tongdao Wang,‡ Sonja Kohrt,‡ Constantin G. Daniliuc, Gerald Kehr, Gerhard Erker *

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany

‡These authors contributed equally to this paper.

Contents

1 General

All transformations involving air- and/or moisture-sensitive compounds were carried out using standard Schlenk-type glassware or within a glove box under an atmosphere of argon. Solvents were dried with the procedure according to Grubbs [A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518-20] or were distilled from appropriate drying agents and stored under an argon atmosphere. NMR spectra were recorded on the following instruments: Agilent DD2 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{7}Li: 195 MHz, ^{11}B: 160 MHz), Agilent DD2 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{7}Li: 233 MHz, ^{11}B: 192 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift is given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shift is given relative to $CFCl_3$ (external reference); ^{11}B NMR: chemical shift is given relative to $BF_3{\cdot}Et_2O$ (external reference); ^{7}Li NMR: chemical shift is given relative to LiCl (external reference). NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on an Elementar Vario El III. IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (TA Instruments). Mass spectroscopic measurements were performed on a MicroTof for exact mass by ESI (Bruker Daltronics, Bremen, ESI exact mass) and a Triplequad Quattro Micro GC by EI.

X-ray diffraction: For compounds **10**, **11b**, **11c**, **20a** and **29'** data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* 1997, **276**, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. 2003, **A59**, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. 1990, **A46**, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. 2008, **A64**, 112-122) and graphics, XP (BrukerAXS, 2000). For compound **12b·HCl**, **16a**, **16a-byproduct**, **18** and **19** data sets were collected with a Bruker APEX II CCD diffractometer. Data sets for the compounds **9**, **11a**, **12a·HCl**, **13** and **29** were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used for compounds **13**, **18**: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., 2016); cell refinement: SAINT V8.37A (Bruker AXS Inc., 2015); data reduction: SAINT V8.37A (Bruker AXS Inc., 2015); absorption correction, SADABS V2014/7 (Bruker AXS Inc., 2014); structure solution SHELXT-2015 (Sheldrick, 2015); structure refinement SHELXL-2015 (Sheldrick, 2015). Programs used for compounds **9**, **11a**, **12a·HCl**, **12b·HCl**, **16a**, **16a-byproduct**, **19** and **29**: data collection: APEX2 V2014.5-0 (Bruker AXS Inc., 2014); cell refinement: SAINT V8.34A (Bruker AXS Inc., 2013); data reduction: SAINT V8.34A (Bruker AXS Inc., 2013); absorption correction, SADABS V2014/2 (Bruker AXS Inc., 2014); structure solution SHELXT-2014 (Sheldrick, 2014); structure refinement SHELXL-2014 (Sheldrick, 2014) and graphics, XP (Bruker AXS Inc., 2014). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compounds **11b** and **18** one dichloromethane molecule and for compound **13** one TMP group were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For compound **10** and **11c** one disordered solvent molecule (probably one dichloromethane molecule)

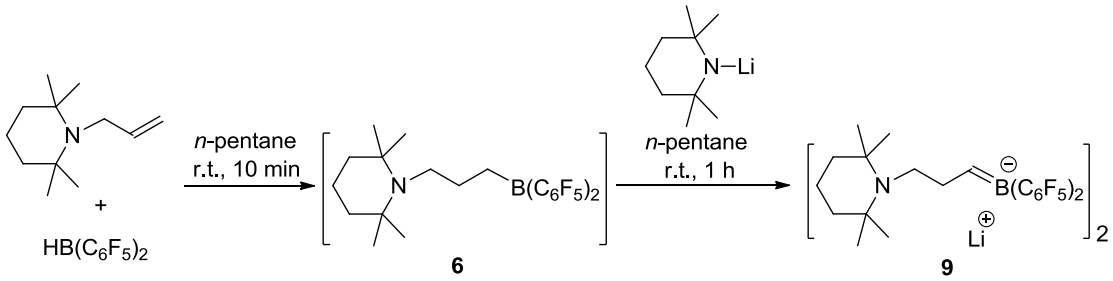
was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules. CCDC deposition numbers are 1549010 to 1549024.

2 Reported Materials

The trimethylene-bridged N/B FLP **6** was prepared according to the literature procedure [Wang, T.; Kehr, G.; Liu, L.; Grimme, S.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* 2016, **138**, 4302.]. Allylbenzene was purchased from TCI and used without further purification. 1-Hexene was purchased from Acros, dried over CaH_2 and distilled onto activated molecular sieves. 3,3-Dimethyl-1-butene was purchased from ABCR and distilled onto activated molecular sieves. Vinyl cyclohexane was purchased from Sigma-Aldrich, stored in a GloveBox and used without further purification. 4-Phenylbut-1-ene was purchased from TCI, stored in a GloveBox and used without further purification. Acetoe was purchased from Acros Organics, dried over anhydrous $CaSO_4$, subsequently distilled and stored in a gove-box prior to use. Acetophenone and benzophenone were purchased from Sigma-Aldrich and distilled from P_2O_5 prior to use. 9-Fluorenone was purchased from Alfa Aesar and used without further purification. 4-Chlorobenzaldehyde was purchased from Sigma-Aldrich and used without further purification. Methyl formate was purchased from Sigma-Aldrich. Free acid and/or alcohol was removed by washing with saturated Na_2CO_3, standing over solid Na_2CO_3 followed by distilling from P_2O_5. Ethyl formate was purchased from Sigma-Aldrich. Free acid and/or alcohol was removed by standing with anhydrous K_2CO_3 with occasional shaking, decanting and subsequently distilling from P_2O_5. Methyl acetate was purchased from Sigma-Aldrich, freed from free alcohol or acid by shaking with saturated Na_2CO_3 (3x), then with aqueous 50% $CaC1_2$ (3x), saturated aqueous NaCl (2x), followed by drying with K_2CO_3 and distillation from P_2O_5. Ethyl acetate (extra dry) was purchased from Acros Organics and used without further drying. γ-Butyrolactone was purchased from Sigma-Aldrich and used without further purification. *N,N*-Dimethyl formamide (extra dry) was purchased from Sigma-Aldrich and used without further purification.

3 Preparation and characterization

3.1 Compound 9



Scheme S1.

1-Allyl-2,2,6,6-tetramethylpiperidine (181.5 mg, 1.00 mmol) was added to a suspension of $HB(C_6F_5)_2$ (345.7 mg, 1.00 mmol) in *n*-pentane (25 mL), which was stirred at room temperature for 10 min to give a yellow solution. Then lithium tetramethylpiperidide (LiTMP) (147.6 mg, 1.00 mmol) was added to the solution. The mixture was stirred at room temperature for 1 h to give a suspension. All the volatiles were removed in vacuo, the obtained residue was washed with *n*-pentane (3×5 mL) and dried in vacuo to give a white solid. Yield: 442.5 mg, 83%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **9** in CH_2Cl_2 covered with *n*-pentane at -35 °C.

[**TMP**: 2,2,6,6-tetramethylpiperidino]

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 4.01 (t, $^{3}J_{HH}$ = 8.6 Hz, 1H, B=C*H*), 2.78 (m, 2H, NCH_2), 2.34 (br, 2H, CH_2), 1.76, 1.62 (each br, 6H, CH_2^{TMP}), 1.11 (br, 12H, CH_3^{TMP}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 104.6 (br, B=*C*H), 57.0 (N*C*^{TMP}), 47.3 (N*C*H_2), 42.9, 17.6 (*C*H_2^{TMP}), 34.0, 21.5 (each br, *C*H_3^{TMP}), 33.8 (*C*H_2) [C_6F_5 not listed].

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = 22.9 ($\nu_{1/2}$ ~ 150 Hz).

^{7}Li NMR (195 MHz, 299 K, CD_2Cl_2): δ = 1.9 ($\nu_{1/2}$ ~ 15 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = -134.5 (m, 2F, *o*-C_6F_5), -158.9 (t, $^{3}J_{FF}$ = 19.9 Hz, 1F, *p*-C_6F_5), -163.3 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.4], -137.0 (m, 2F, *o*-C_6F_5'), -159.9 (t, $^{3}J_{FF}$ = 19.9 Hz, 1F, *p*-C_6F_5'), -163.4 (m, 2F, *m*-C_6F_5')[$\Delta\delta^{19}F_{m,p}$ = 3.5].

Elemental analysis: calc. for $C_{48}H_{46}N_2B_2F_{20}Li_2$: C, 54.06; H, 4.35; N, 2.63. Found: C, 54.19; H, 5.61; N, 3.11.

Decomp. Point: 190 °C.

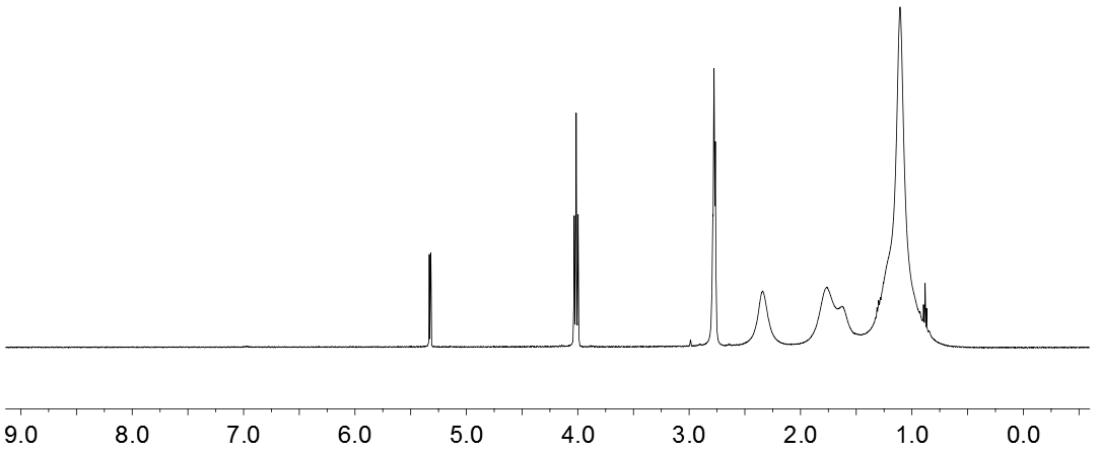


Figure S1. ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**.

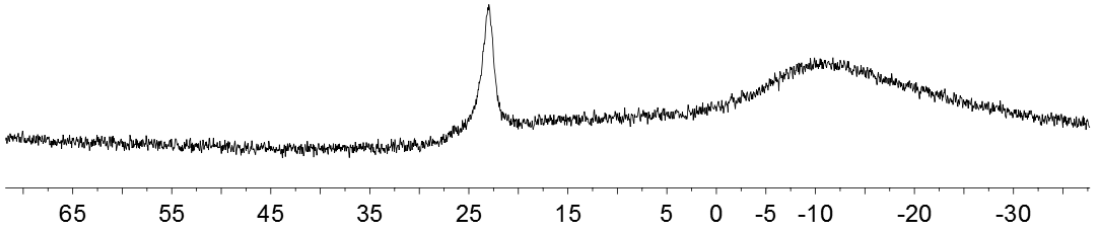


Figure S2. $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**.

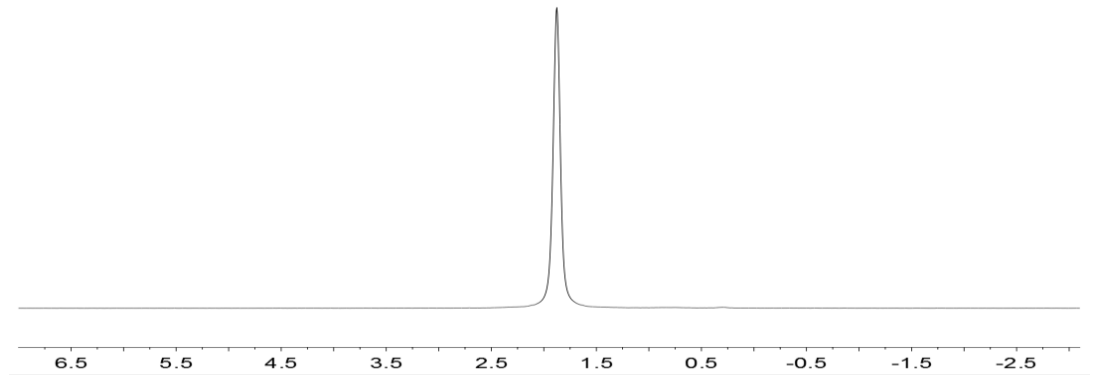


Figure S3. ^{7}Li NMR (195 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**.

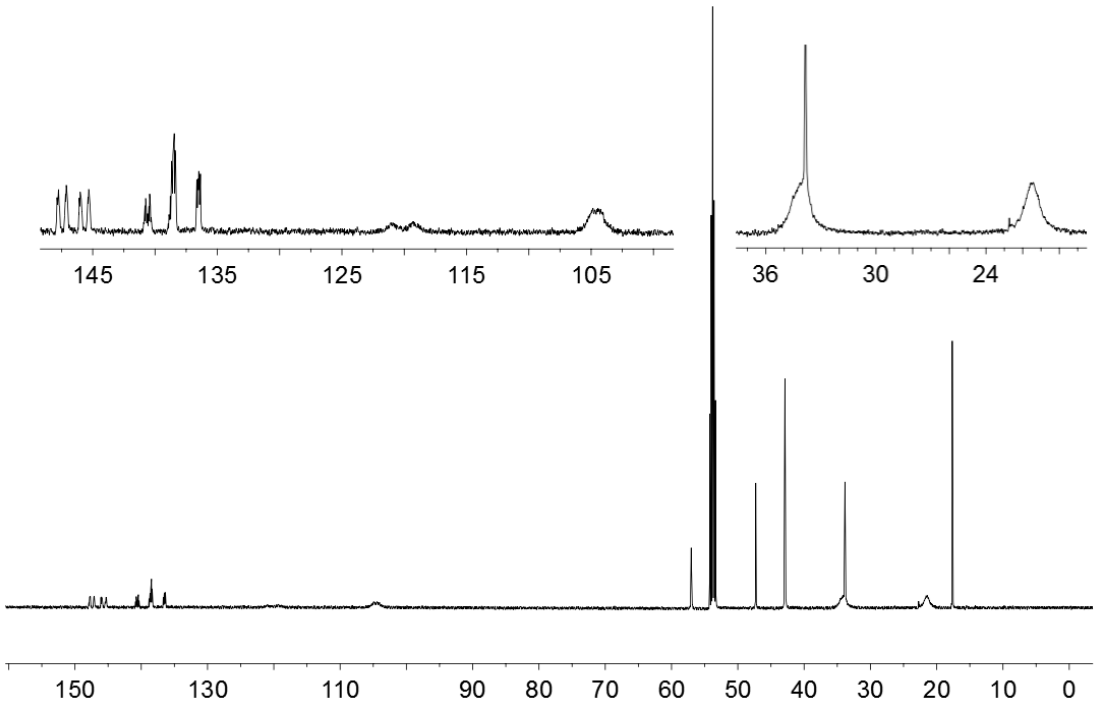


Figure S4. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**.

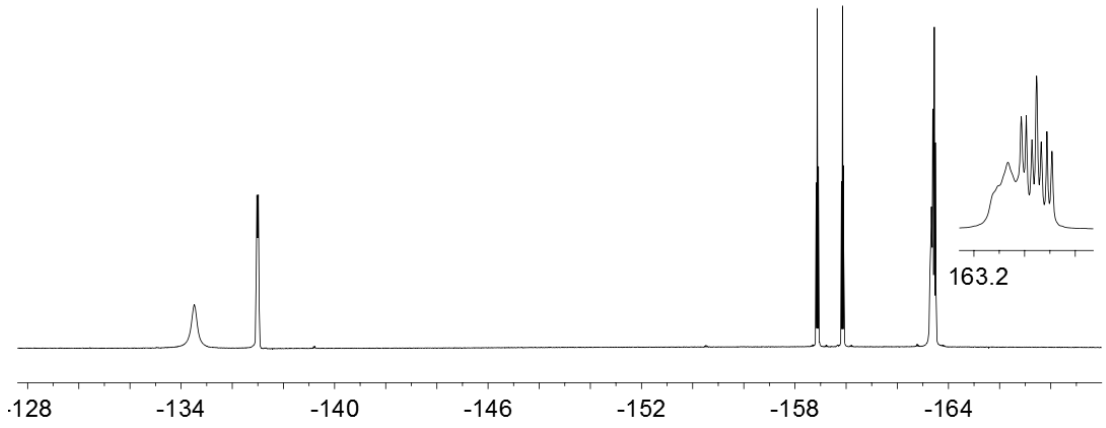


Figure S5. ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**.

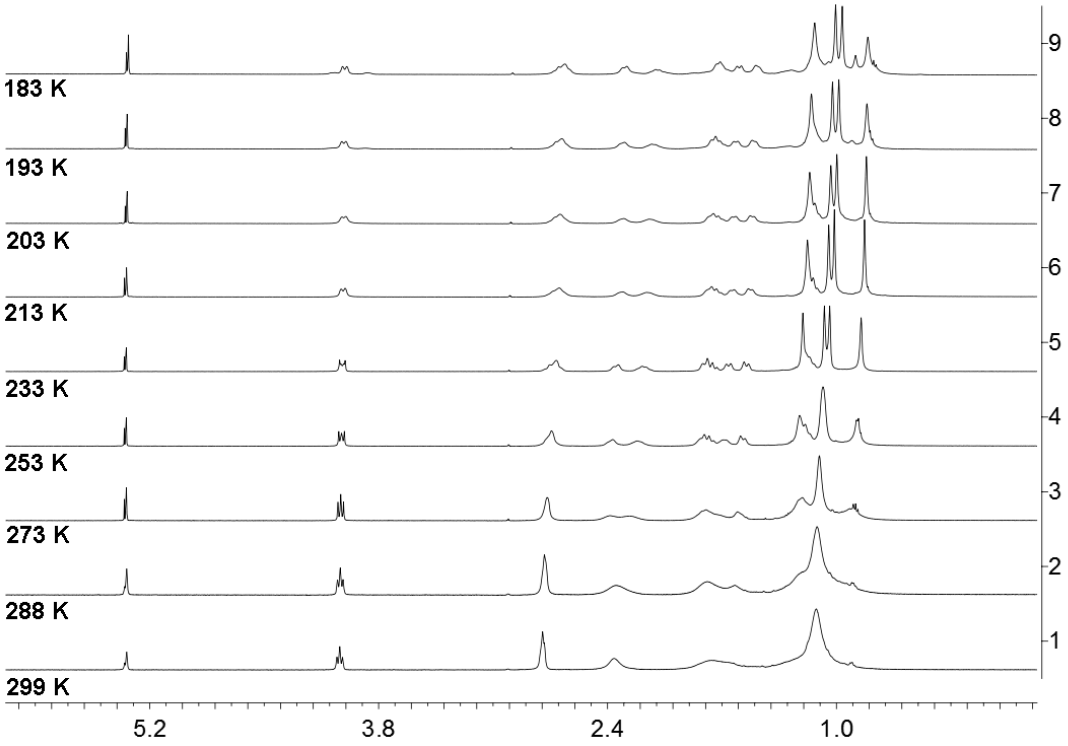


Figure S6. ^{1}H NMR (500 MHz, from 299 K to 183 K, CD_2Cl_2) spectra of compound **9**.

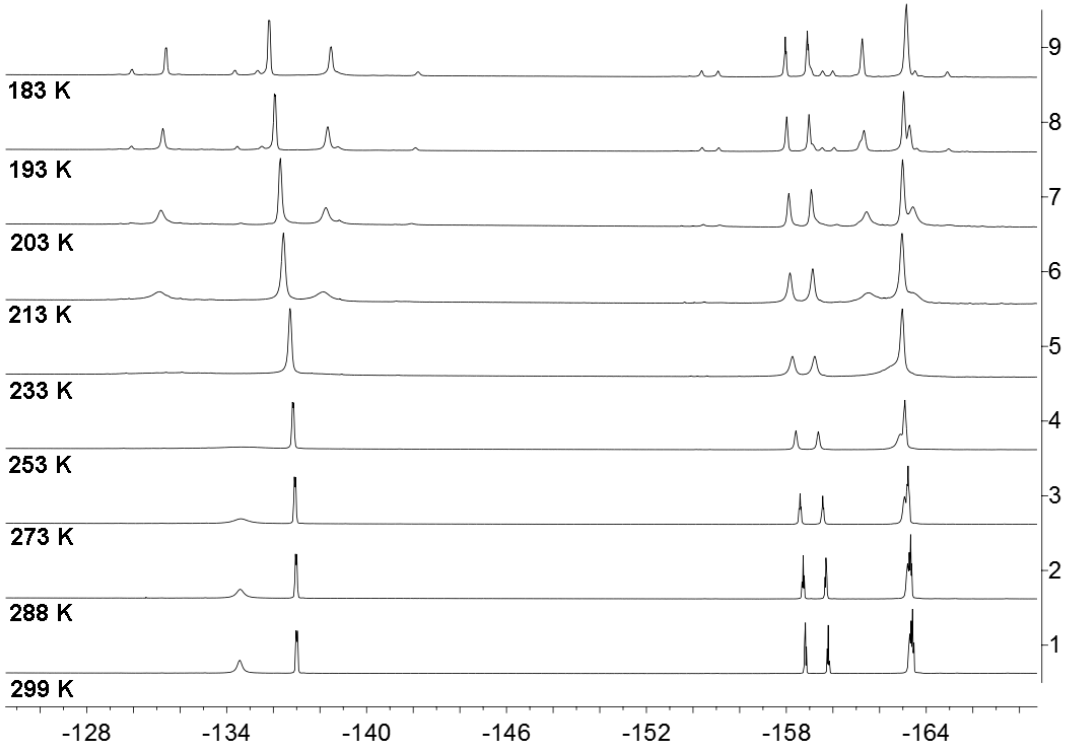


Figure S7. ^{19}F NMR (470 MHz, from 299 K to183 K, CD_2Cl_2) spectra of compound **9**.

X-ray crystal structure analysis of compound 9: A colorless prism-like specimen of $C_{48}H_{46}B_2F_{20}Li_2N_2$, approximate dimensions 0.080 mm x 0.151 mm x 0.272 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 464 frames were collected. The total exposure time was 3.87 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 21284 reflections to a maximum θ angle of 27.56° (0.77 Å resolution), of which 5187 were independent (average redundancy 4.103, completeness = 99.5%, R_{int} = 2.87%, R_{sig} = 2.27%) and 4452 (85.83%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.4978(3) Å, b = 10.8784(3) Å, c = 14.5077(5) Å, α = 83.4720(10)°, β = 89.7130(10)°, γ = 73.8890(10)°, volume = 1129.03(7) Å^3, are based upon the refinement of the XYZ-centroids of 9954 reflections above 20 σ(I) with 4.560° < 2θ < 55.06°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.969. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9610 and 0.9880. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 1 for the formula unit, $C_{48}H_{46}B_2F_{20}Li_2N_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 342 variables converged at R1 = 3.38%, for the observed data and wR2 = 8.83% for all data. The goodness-of-fit was 1.016. The largest peak in the final difference electron density synthesis was 0.371 e$^-$/Å^3 and the largest hole was -0.259 e$^-$/Å^3 with an RMS deviation of 0.051 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.568 g/cm^3 and F(000), 544 e$^-$.

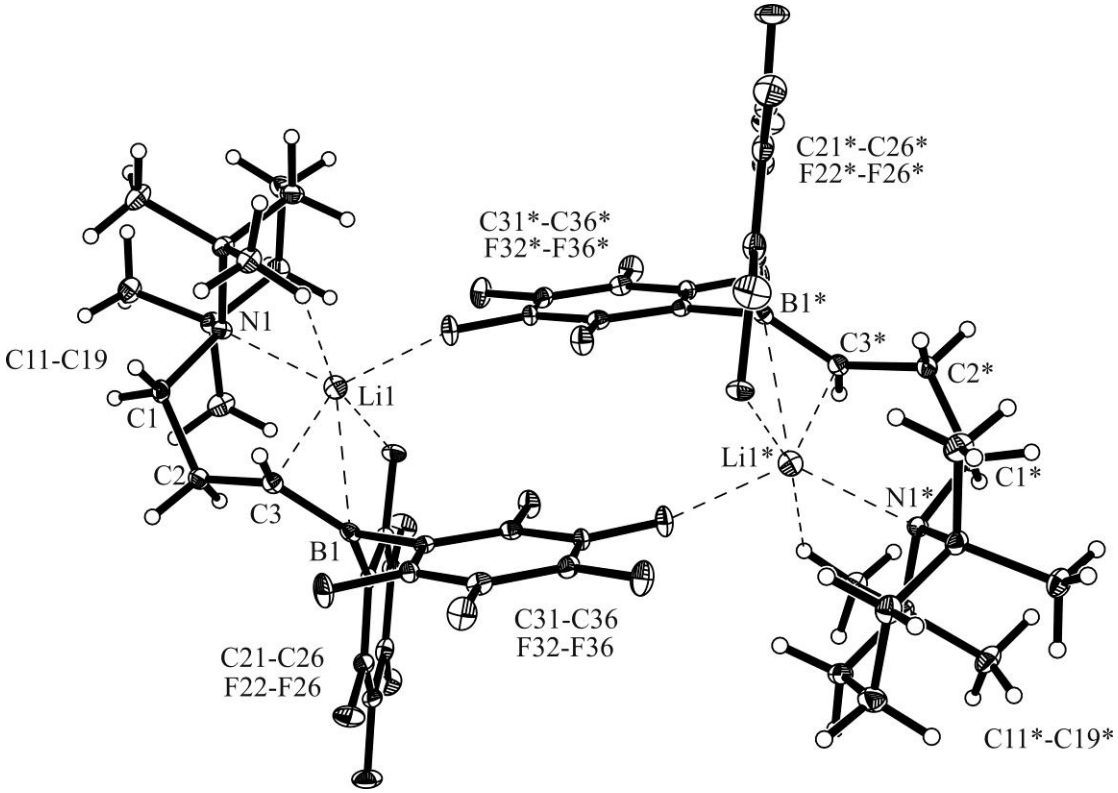
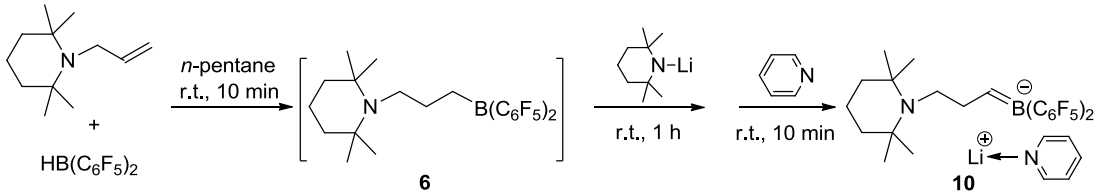


Figure S8. A view of the molecular structure of the borata-alkene dimer **9**:

3.2 Compound 10



Scheme S2.

1-Allyl-2,2,6,6-tetramethylpiperidine (90.7 mg, 0.50 mmol) was added to a suspension of $HB(C_6F_5)_2$ (172.9 mg, 0.50 mmol) in *n*-pentane (10 mL), which was stirred at room temperature for 10 min to give a yellow solution. Then lithium tetramethylpiperidide (LiTMP) (73.7 mg, 0.50 mmol) was added to the solution. The mixture was stirred at room temperature for 1 h to give a suspension. After that, a solution of pyridine (43.5mg, 0.55 mmol) in *n*-pentane (1 mL) was added to the mixture, which gave a colorless solution immediately. After 10 min, the solution was stored at -78 °C for 6 h to give a colorless crystalline solid, which were collected by filtration and dried in vacuo. Yield: 266.3 mg, 87%. Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **10** in CH_2Cl_2 covered with *n*-pentane at -35 °C.

[**TMP**: 2,2,6,6-tetramethylpiperidino, Py: pyridine]

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 8.39 (d, $^3J_{HH}$ = 4.6 Hz, 2H, *o*-Py), 7.84 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-Py), 7.38 (m, 2H, *m*-Py), 4.28 (t, $^3J_{HH}$ = 8.2 Hz, 1H, B=C*H*), 2.69 (t, $^3J_{HH}$ = 6.6 Hz, 2H, NCH_2), 2.33 (m, 2H, CH_2), 1.50 (m, 2H, CH_2^{TMP}), 1.37 (m, 4H, ^{C}CH_2^{TMP}), 1.09 (s, 12H, CH_3^{TMP}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 149.4 (*o*-Py), 138.8 (*p*-Py), 125.5 (*m*-Py), 102.5 (br, B=*C*H), 56.7 (N*C*^{TMP}), 48.3 (N*C*H$_2$), 41.6 (^{C}*C*H$_2^{TMP}$), 35.3 (*C*H$_2$), 27.4(br, *C*H$_3^{TMP}$), 18.2 (*C*H$_2^{TMP}$) [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 23.5 ($\nu_{1/2}$ ~ 290 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -133.0 (m, 2F, *o*-C_6F_5), -161.2 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), -165.1 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.9], -134.5 (m, 2F, *o*-C_6F_5), -161.9 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), -165.8 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.9].

Elemental analysis: calc. for $C_{29}H_{28}N_2BF_{10}Li$: C, 56.89; H, 4.61; N, 4.58. Found: C, 57.25; H, 4.74; N, 4.66.

Decomp. Point: 208 °C.

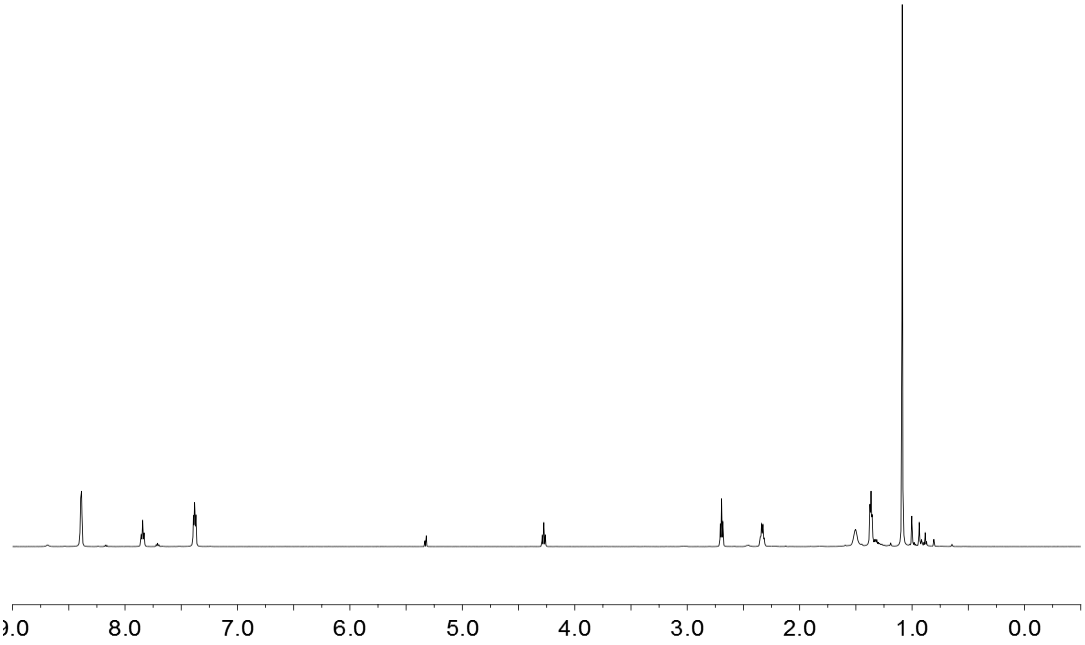


Figure S9. ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**.

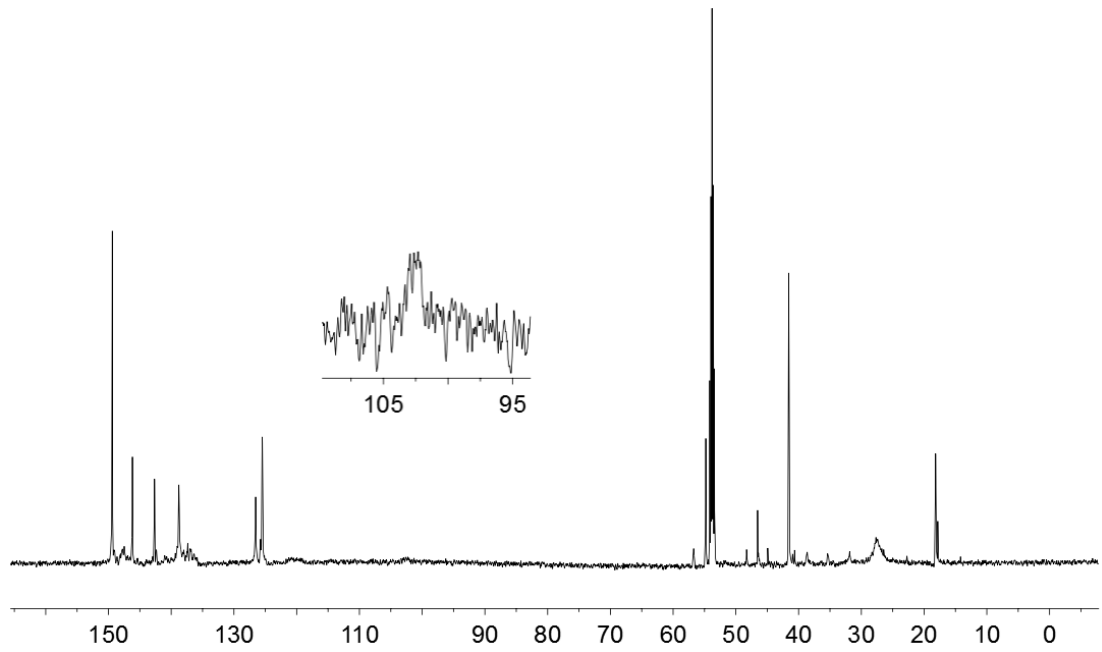


Figure S10. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**.

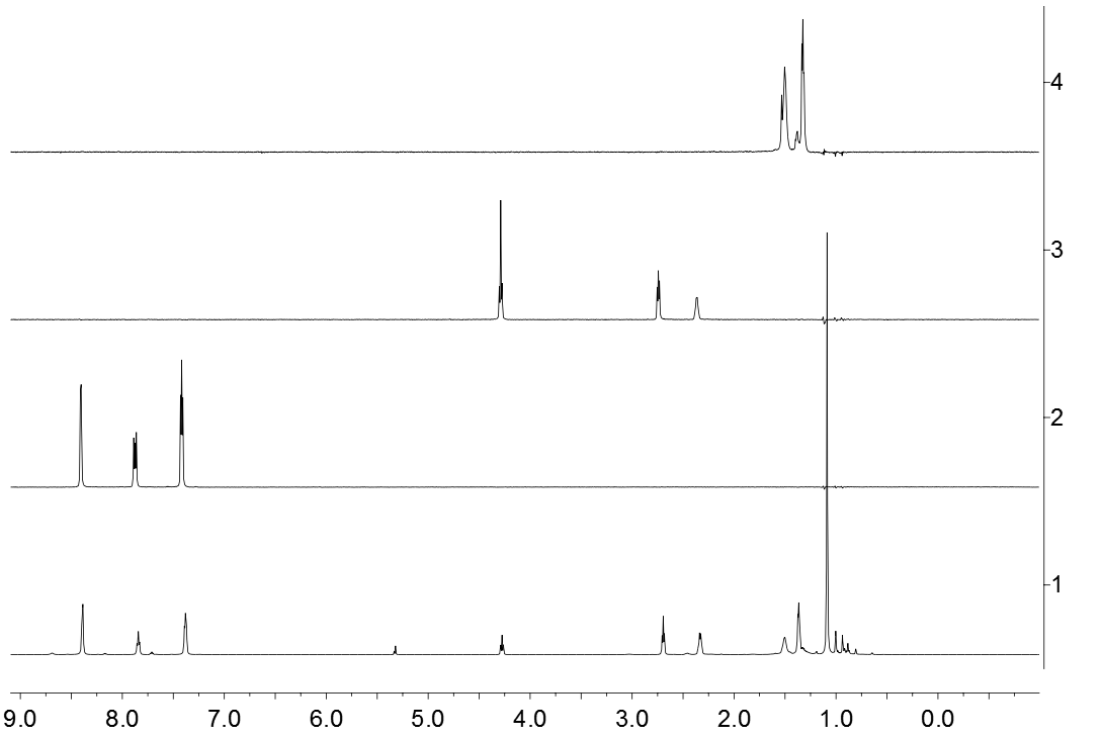


Figure S11. ^{1}H NMR (1) and ^{1}H{^{1}H} TOCSY (600 MHz, 299 K, CD_2Cl_2) spectra of compound **10**. * Irradiation points: $\delta^{1}H_{irr}$ = 8.39 (*o*-Py) (2), 4.28 (B=C*H*) (3), 1.50 (CH_2^{TMP}) (4).

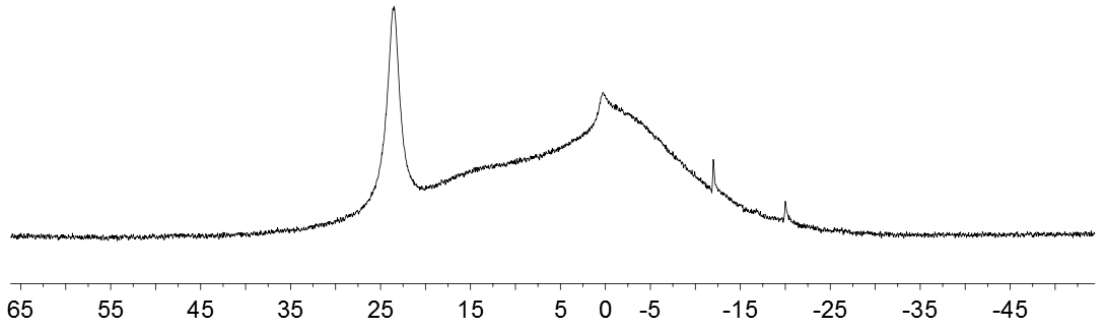


Figure S12. ^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**.

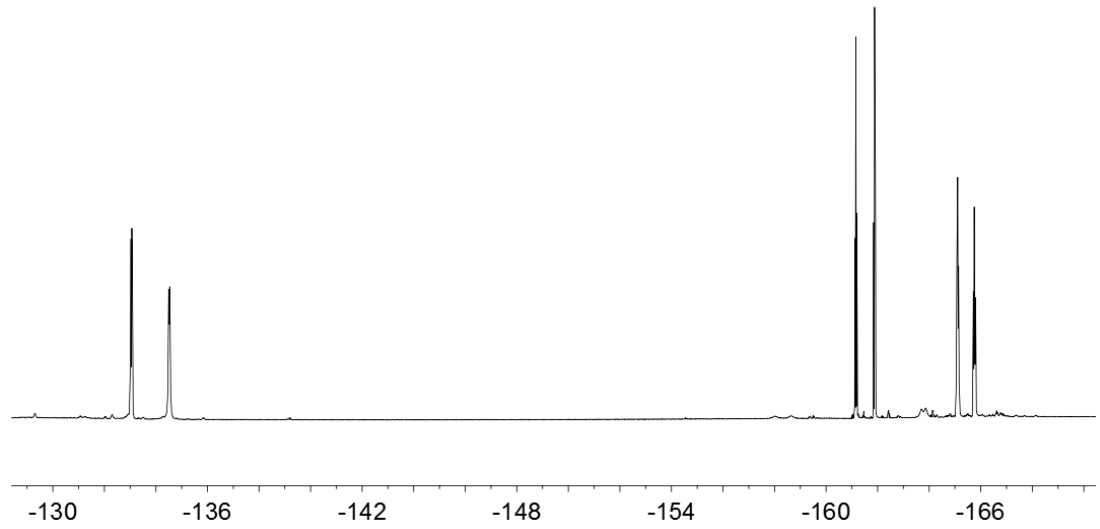


Figure S13. ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **10**.

X-ray crystal structure analysis of compound 10: formula $C_{29}H_{28}BF_{10}LiN_2$, M = 612.28, colourless crystal, 0.17 x 0.10 x 0.07 mm, a = 11.9795(2), b = 16.9234(3), c = 15.3648(3) Å, β = 96.686(1)°, V = 3093.8(1) Å^3, ρ_{calc} = 1.315 gcm^{-3}, μ = 0.118 mm^{-1}, empirical absorption correction (0.980 ≤ T ≤ 0.991), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 18116 reflections collected (±h, ±k, ±l), 5350 independent (R_{int} = 0.055) and 3818 observed reflections [I>2σ(I)], 392 refined parameters, R = 0.098, wR^2 = 0.154, max. (min.) residual electron density 0.43 (-0.24) e.Å^{-3}, the hydrogen atoms were calculated and refined as riding atoms.

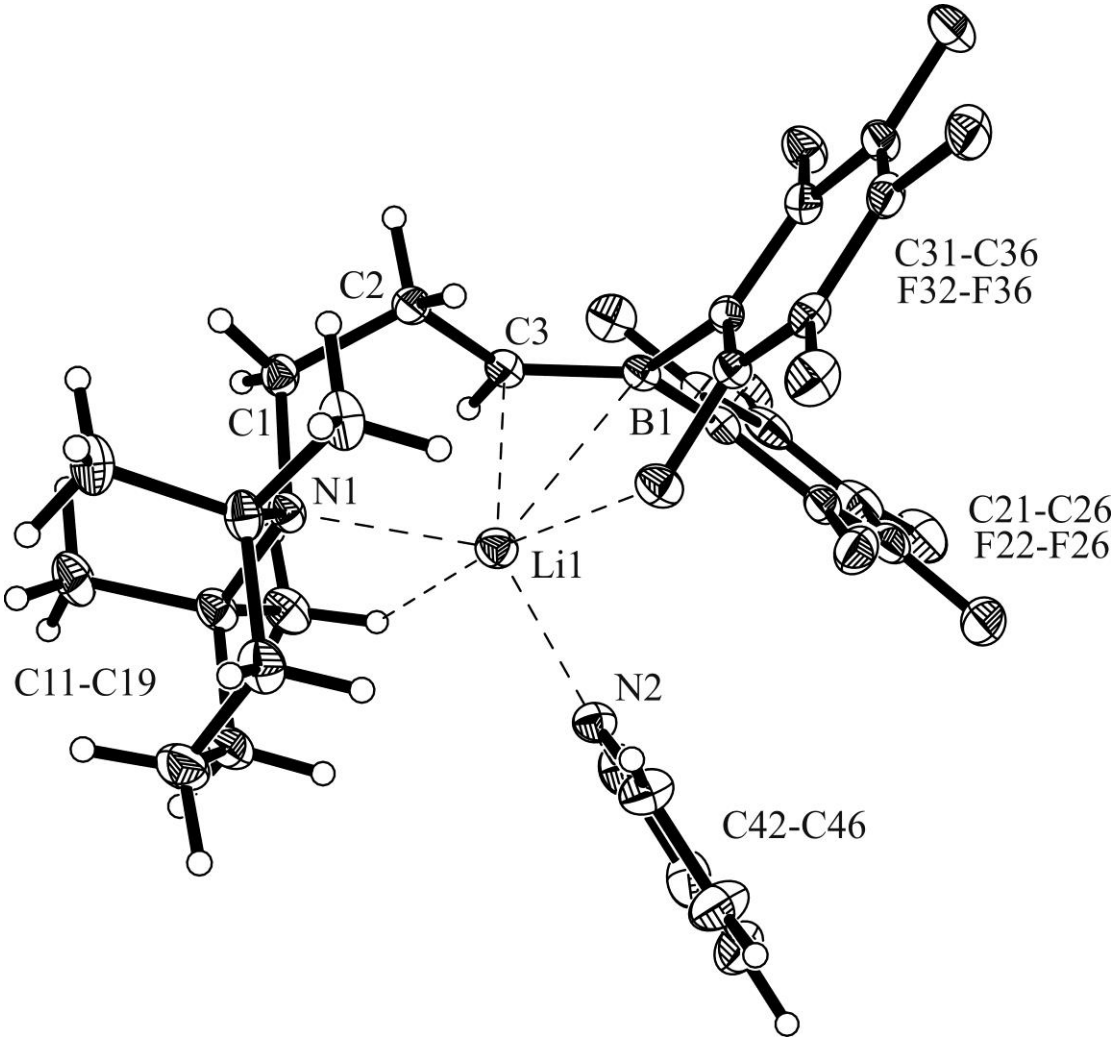
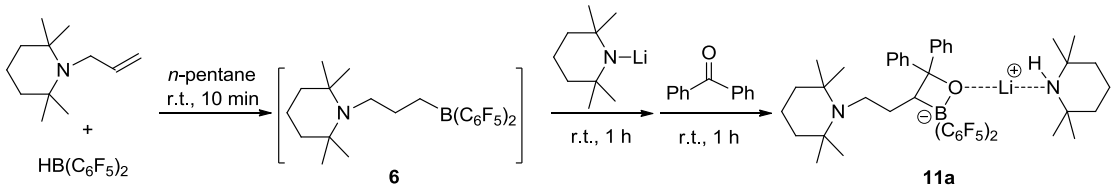


Figure S14. A view of the molecular structure of the borata-alkene monomer **10**.

3.3 Compounds 11

3.3.1 Compound 11a



Scheme S3.

1-Allyl-2,2,6,6-tetramethylpiperidine (181.5 mg, 1.00 mmol) was added to a suspension of $HB(C_6F_5)_2$ (346.1 mg, 1.00 mmol) in *n*-pentane (25 mL), which was stirred at room temperature for 10 min to give a yellow solution. Then lithium tetramethylpiperidide (LiTMP) (147.3 mg, 1.00 mmol) was added to the solution. The mixture was stirred at room temperature for 1 h to give a suspension. After that, benzophenone (182.5 mg, 1.00 mmol) was added to the mixture, which initially resulted in a pale yellow solution. The mixture was stirred at room temperature for another 1 h to give a white precipitate, the precipitate was collected by filtration, washed with *n*-pentane (3×5 mL), and dried in vacuo to give a white solid. Yield: 728.6 mg, 85%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **11a** in CH_2Cl_2 covered with *n*-pentane at -35 °C.

[**TMP**: 2,2,6,6-tetramethylpiperidino]

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.37 (m, 2H, *o*-Ph), 7.28 (m, 2H, *m*-Ph), 7.17 (m, 1H, *p*-Ph), 7.27 (m, 2H, *o*-Ph'), 7.20 (m, 2H, *m*-Ph'), 7.12 (m, 1H, *p*-Ph), 2.64 (m, 1H, BC*H*), 2.21, 2.01 (each m, each 1H, NCH_2), 1.64, 1.34 (each m, 4H, CH_2^{TMP}), 1.52, 1.44 (each m, each 1H, CH_2), 1.42, 1.23 (each m, 8H, ^{C}CH_2^{TMP}), 1.05, 0.85, 0.55 (each br, Σ24H, CH_3^{TMP}), 1.01 (s, 1H, N*H*).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 149.9 (*i*-Ph), 127.7 (*m*-Ph), 126.7 (*o*-Ph), 126.4 (*p*-Ph), 146.3 (*i*-Ph'), 128.3 (*o*-Ph'), 128.1 (*m*-Ph'), 127.1 (*p*-Ph'), 92.3 (*C*O), 54.4, 51.7 (NC^{TMP}), 46.7 (br, NCH_2), 41.5 (br), 38.9 (^{C}CH_2^{TMP}), 40.3 (br, BC*H*), 34.6 (CH_2), 33.4, 27.2 (each br, CH_3^{TMP}), 18.1, 17.8 (CH_2^{TMP}) [C_6F_5 not listed].

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = 2.4 ($\nu_{1/2}$ ~ 175 Hz).

^{7}Li NMR (195 MHz, 299 K, CD_2Cl_2): δ = 0.6 ($\nu_{1/2}$ ~ 17 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = -140.7 (br, 4F, *o*-C_6F_5, *o*-C_6F_5'), -160.2 (t, $^3J_{FF}$ = 19.9 Hz, 1F, *p*-C_6F_5), -163.0 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 2.8], -161.1(t, $^3J_{FF}$ = 19.9 Hz, 1F, *p*-C_6F_5'), -164.1 (m, 2F, *m*-C_6F_5')[$\Delta\delta^{19}F_{m,p}$ = 3.0].

Elemental analysis: calc. for $C_{46}H_{52}N_2BF_{10}OLi$: C, 64.49; H, 6.12; N, 3.27. Found: C, 65.02; H, 6.16; N, 3.23.

Decomp. Point: 162°C.

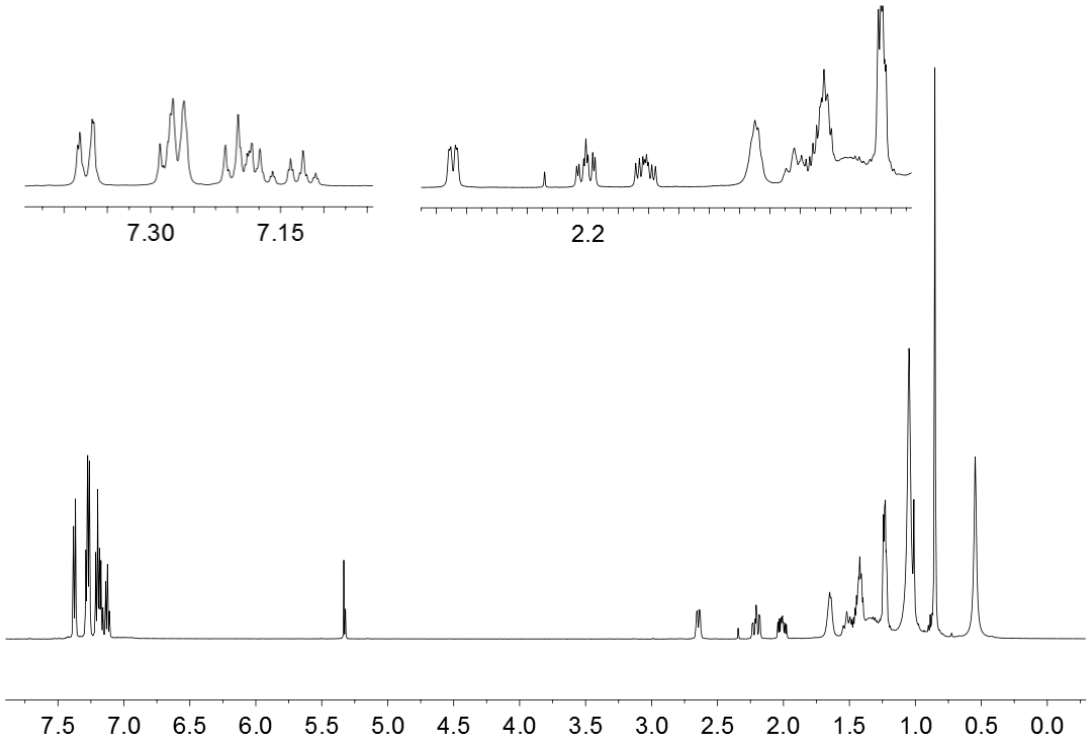


Figure S15. ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **11a**.

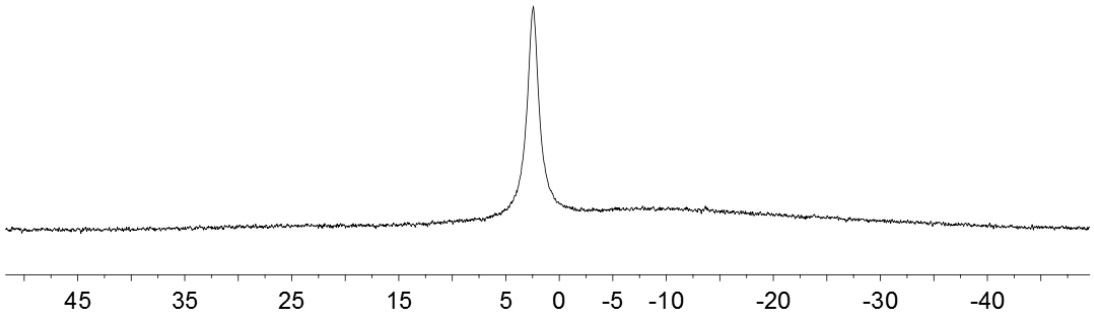


Figure S16. $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **11a**.

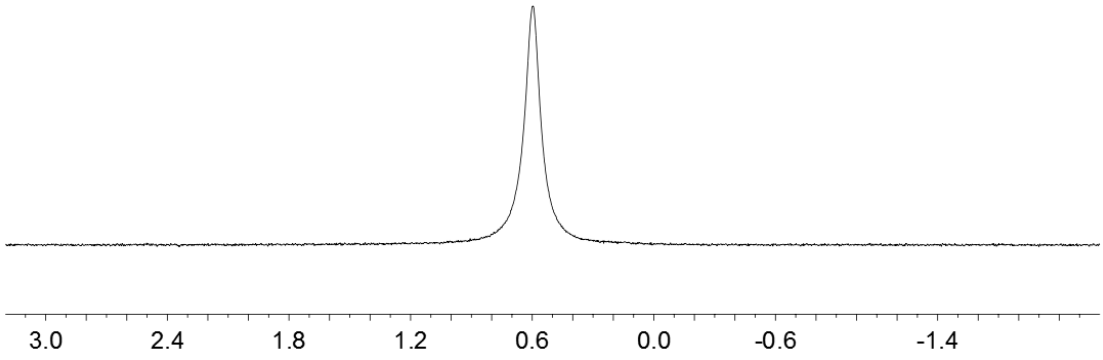


Figure S17. ^{7}Li NMR (195 MHz, 299 K, CD_2Cl_2) spectrum of compound **11a**.

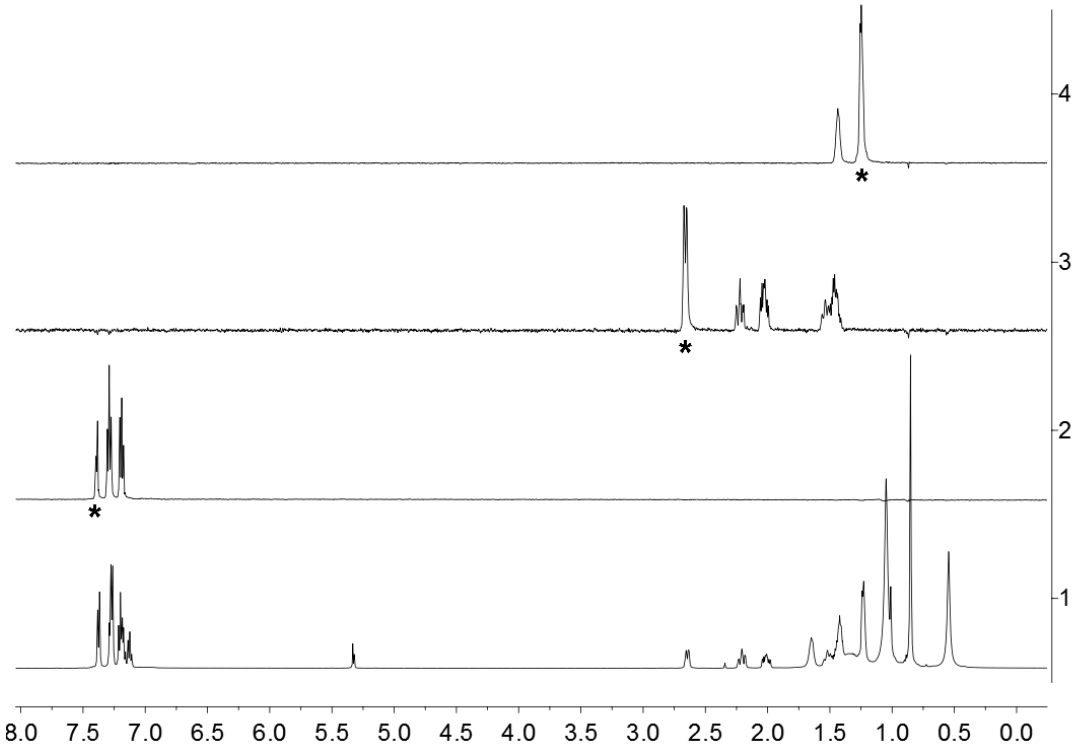


Figure S18. ^{1}H NMR (1) and ^{1}H{^{1}H} TOCSY (500 MHz, 299 K, CD_2Cl_2) spectra of compound **11a**. * Irradiation points: $^{1}H_{irr}$ = 7.37 (*o*-Ph) (2), 2.64 (BC*H*) (3), 1.23 ($^{C}CH_2^{TMP}$) (4).

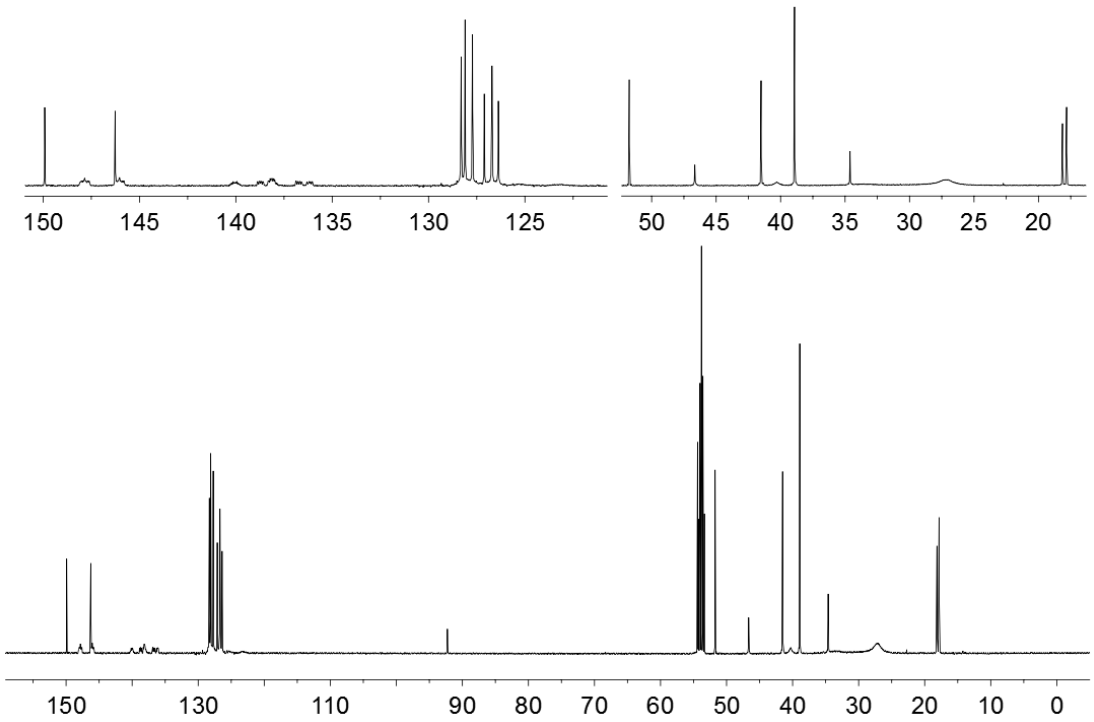


Figure S19. ^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **11a**.

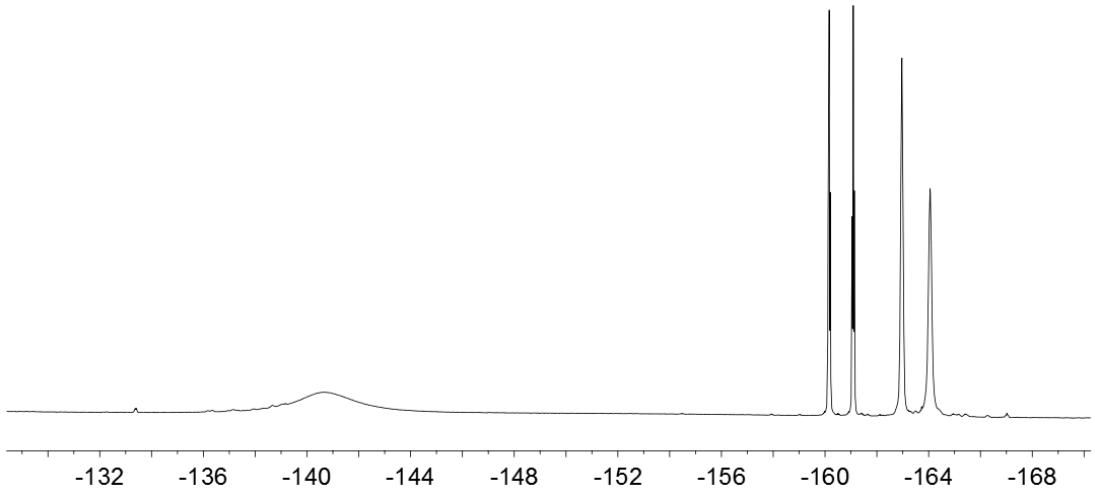


Figure S20. ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **11a**.

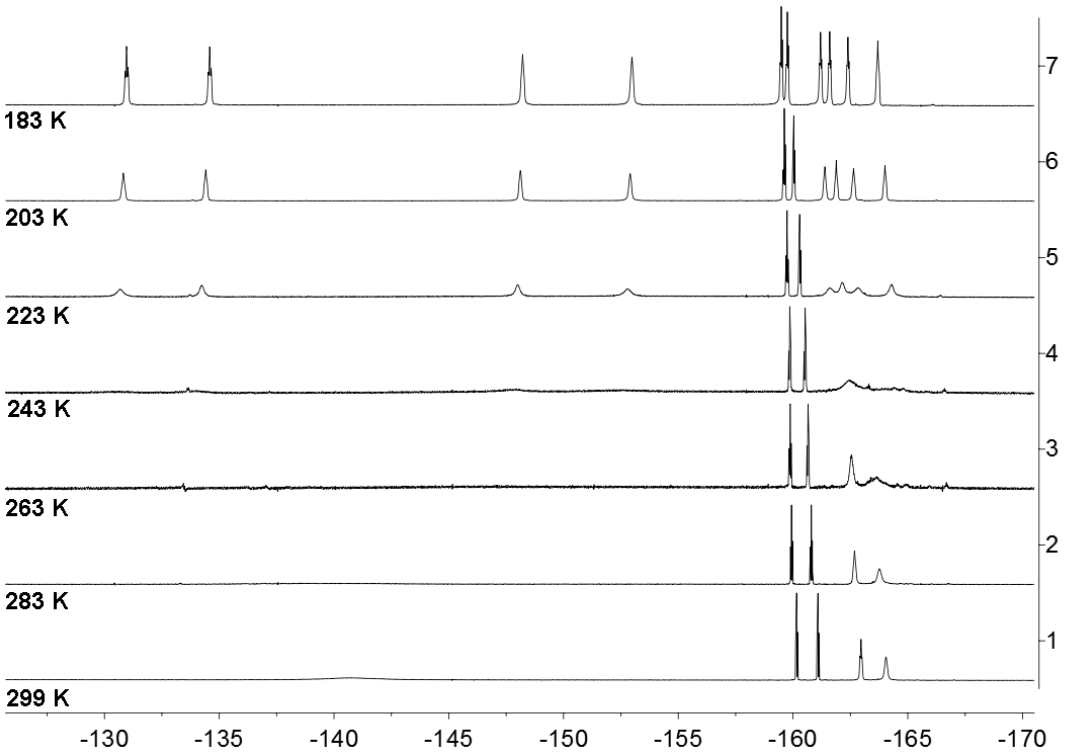


Figure S21. ^{19}F NMR (470 MHz, from 299 K to183 K, CD_2Cl_2) spectra of compound **11a**.

X-ray crystal structure analysis of compound 11a: A colorless prism-like specimen of $C_{46}H_{52}BF_{10}LiN_2O \cdot 1{,}5 \times CH_2Cl_2$, approximate dimensions 0.124 mm x 0.137 mm x 0.309 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 470 frames were collected. The total exposure time was 3.26 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 36440 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 8628 were independent (average redundancy 4.223, completeness = 99.9%, R_{int} = 4.24%, R_{sig} = 3.34%) and 6865 (79.57%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.5212(4) Å, b = 12.3482(4) Å, c = 17.2949(6) Å, α = 74.8320(10)°, β = 84.5700(10)°, γ = 84.5730(10)°, volume = 2357.86(14) $Å^3$, are based upon the refinement of the XYZ-centroids of 9984 reflections above 20 σ(I) with 4.691° < 2θ < 54.90°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.953. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9210 and 0.9670. The final anisotropic full-matrix least-squares refinement on F^2 with 616 variables converged at R1 = 3.96%, for the observed data and wR2 = 9.38% for all data. The goodness-of-fit was 1.040. The largest peak in the final difference electron density synthesis was 0.303 $e^-/Å^3$ and the largest hole was -0.386 $e^-/Å^3$ with an RMS deviation of 0.050 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.386 g/cm^3 and F(000), 1022 e^-.

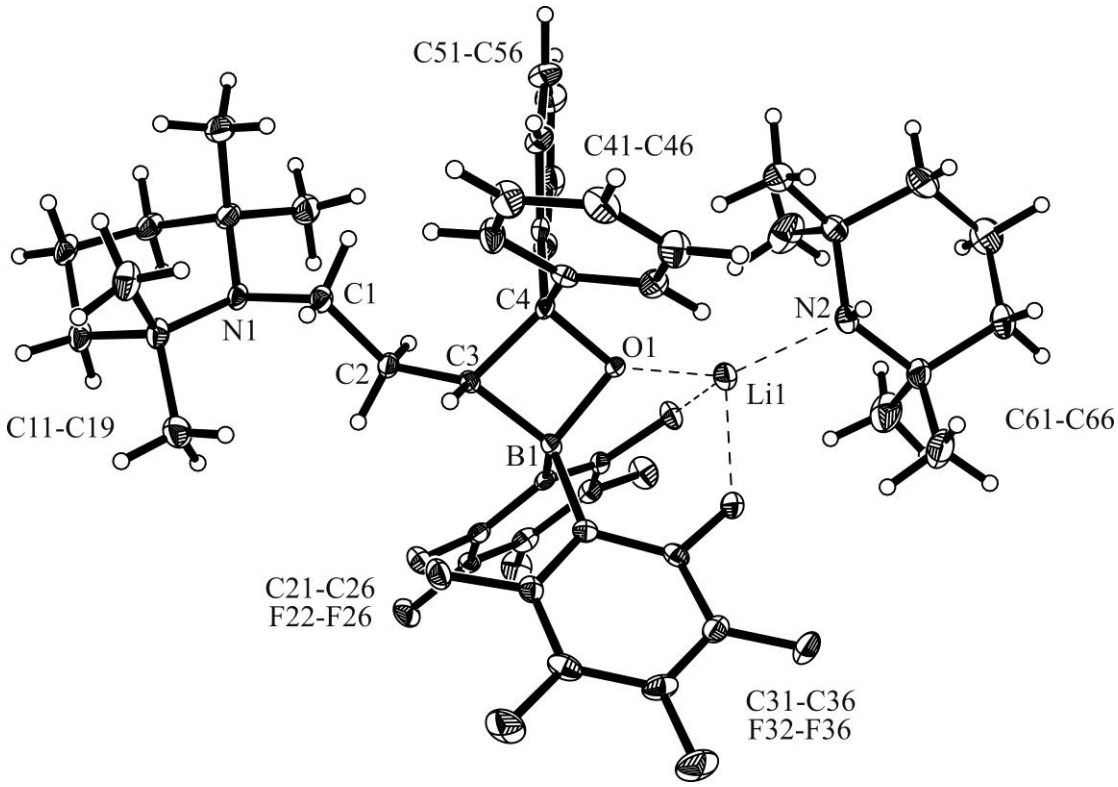
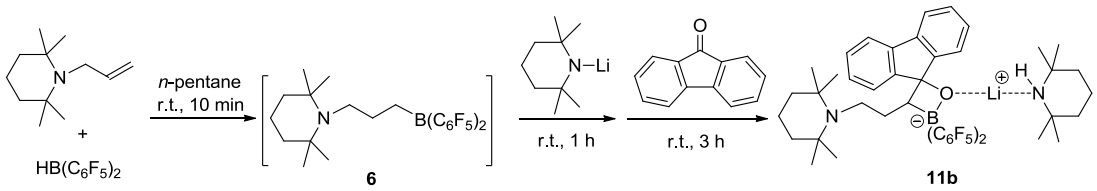


Figure S22. A view of the molecular structure of compound **11a**.

3.3.2 Compound 11b



Scheme S4.

1-Allyl-2,2,6,6-tetramethylpiperidine (181.6 mg, 1.00 mmol) was added to a suspension of $HB(C_6F_5)_2$ (346.0mg, 1.00 mmol) in *n*-pentane (25 mL), which was stirred at room temperature for 10 min to give a yellow solution. Then lithium tetramethylpiperidide (LiTMP) (147.3 mg, 1.00 mmol) was added to the solution. The mixture was stirred at room temperature for 1 h to give a suspension. After that, fluorenone (181.1 mg, 1.00 mmol) was added to the mixture, which initially resulted in a pale yellow solution. The mixture was stirred at room temperature for another 3 h to give a white precipitate, the precipitate was collected by filtration, washed with *n*-pentane (3×5 mL), and dried in vacuo to give a white solid. Yield: 676.0 mg, 79%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **11b** in CH_2Cl_2 covered with *n*-pentane at -35 °C.

[**TMP**: 2,2,6,6-tetramethylpiperidino]

^{1}H NMR (500 MHz, 203 K, CD_2Cl_2): δ = 7.55 (m, 1H, Ph), 7.51 (m, 1H, Ph), 7.21 (m, 4H, Ph), 7.12 (m, 1H, Ph), 7.07 (m, 1H, Ph), 2.53 (m, 1H, BC*H*), 1.60, 1.47 (each m, each 1H, CH_2), 1.49, 1.28 (each m, each 1H, NCH_2), 1.33, 1.06 (each m, Σ4H, CH_2^{TMP}), 1.30, 1.18, 0.98, 0.79 (each m, Σ8H, ^{C}CH_2^{TMP}), 0.87, 0.60, 0.58, 0.56, 0.46, 0.40, 0.30, -0.12 (each s, each 3H, CH_3^{TMP}), 0.69 (s, 1H, N*H*).

^{13}C{^{1}H} NMR (126 MHz, 203 K, CD_2Cl_2): δ = 151.8, 146.2, 139.3, 137.4, 128.0, 127.6, 127.2, 127.1, 125.9, 123.6, 119.3, 118.8 (two Ph), 93.2 (*C*O), 54.2, 53.8, 52.9, 50.1 (NC^{TMP}), 44.3 (N*C*H$_2$), 39.9, 39.8, 37.0, 36.90 (^{C}*C*H$_2^{TMP}$), 36.87 (br, B*C*H), 32.94 (*C*H$_2$), 32.87, 32.4 (br), 31.8, 25.0 (br), 19.5, 19.4 (*C*H$_3^{TMP}$), 17.1, 16.8 (*C*H$_2^{TMP}$) [C_6F_5 not listed].

^{11}B{^{1}H} NMR (160 MHz, 203 K, CD_2Cl_2): δ = 2.4 ($\nu_{1/2}$ ~ 600 Hz).

^{7}Li NMR (195 MHz, 203 K, CD_2Cl_2): δ = 0.1 ($\nu_{1/2}$ ~ 40 Hz).

^{19}F NMR (470 MHz, 203 K, CD_2Cl_2): δ = -129.8, -134.2, -148.6 (br), -152.8 (br) (each 1F, *o*-C_6F_5), -159.5, -160.1 (each t, each $^3J_{FF}$ = 20.7 Hz, each 1F, *p*-C_6F_5), -161.7, -162.8, -164.1 (4F, *m*-C_6F_5).

Elemental analysis: calc. for $C_{46}H_{50}N_2BF_{10}LiO$: C, 64.65; H, 5.90; N, 3.28. Found: C, 64.77; H, 6.07; N, 3.24.

Decomp. Point: 173 °C.

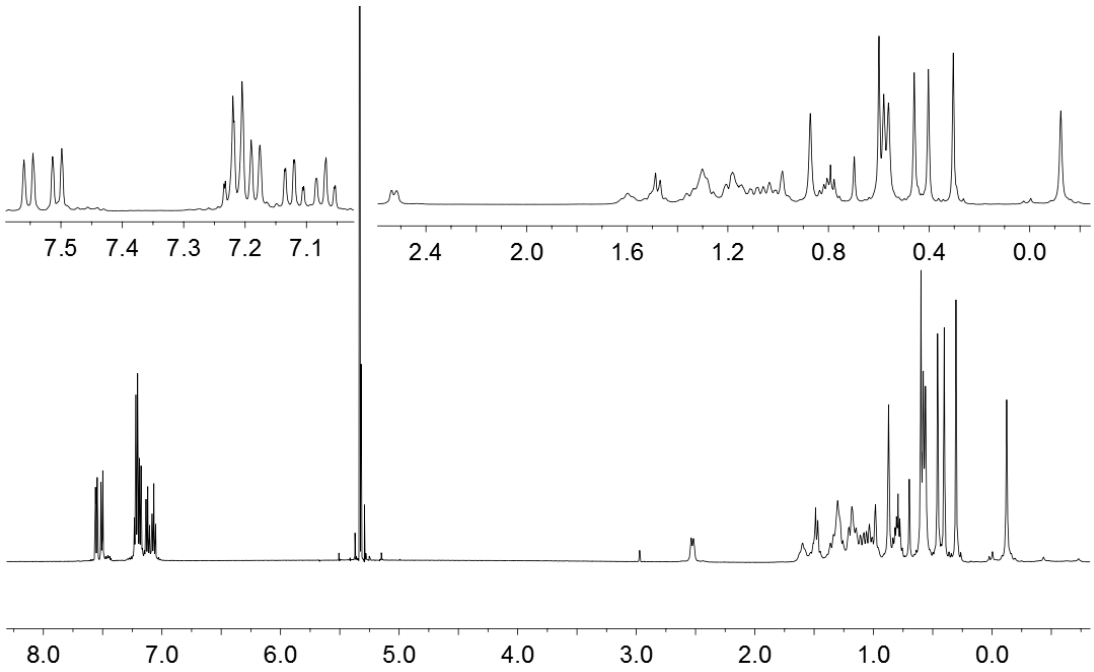


Figure 23. ^{1}H NMR (500 MHz, 203 K, CD_2Cl_2) spectrum of compound **11b**.

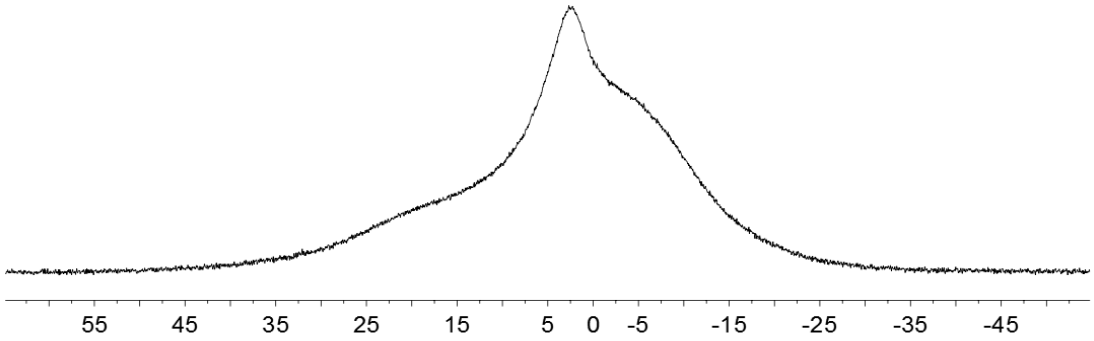


Figure 24. $^{11}B\{^{1}H\}$ NMR (160 MHz, 203 K, CD_2Cl_2) spectrum of compound **11b**.

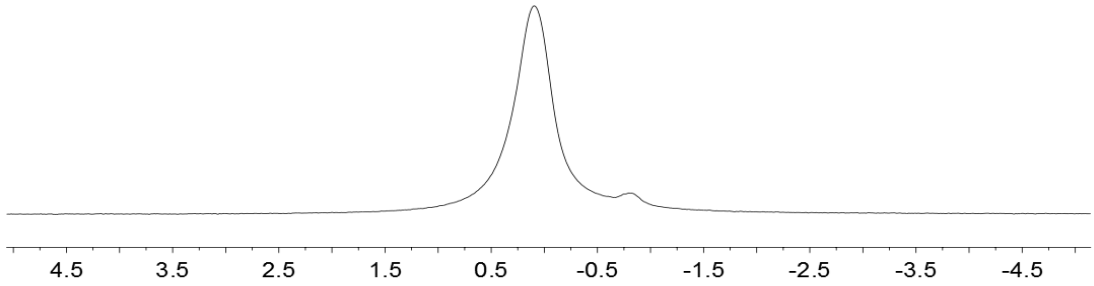


Figure 25. ^{7}Li NMR (195 MHz, 203 K, CD_2Cl_2) spectrum of compound **11b**.

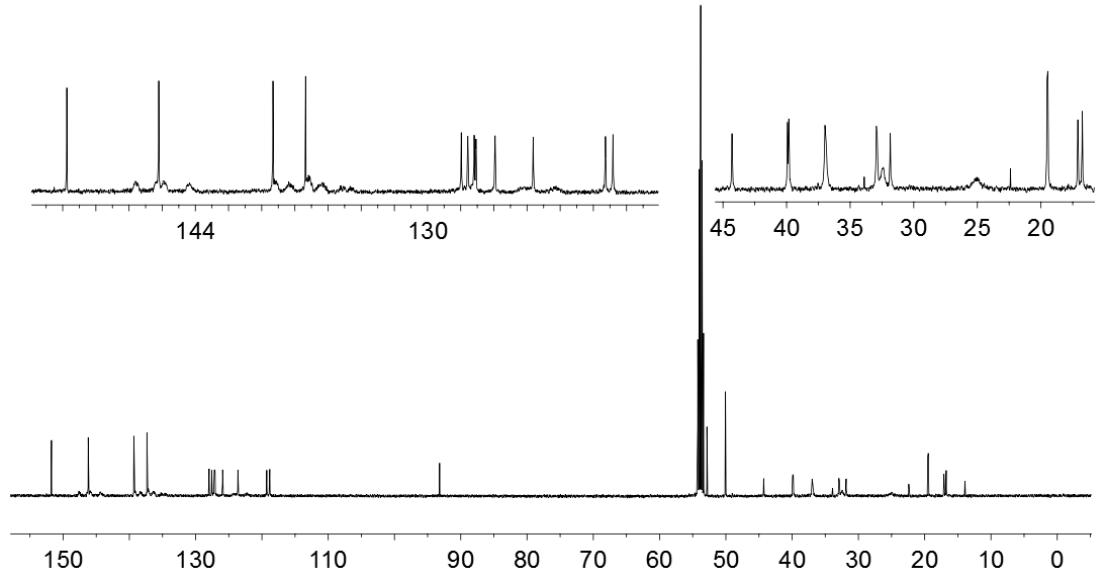


Figure 26. $^{13}C\{^{1}H\}$ NMR (126 MHz, 203 K, CD_2Cl_2) spectrum of compound **11b**.

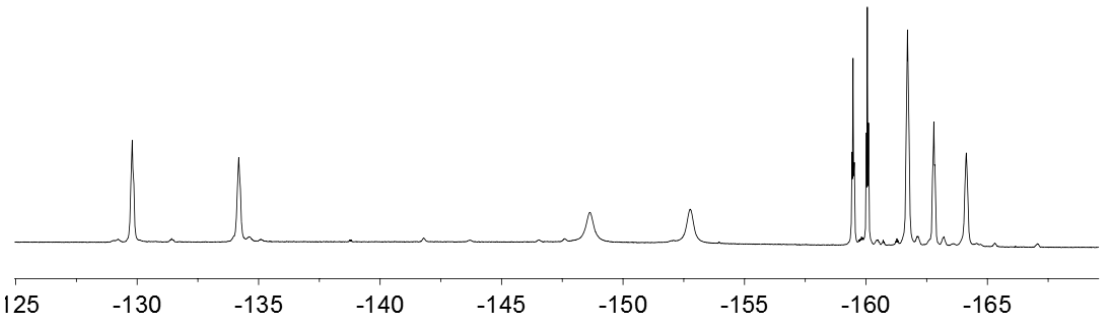


Figure 27. ^{19}F NMR (470 MHz, 203 K, CD_2Cl_2) spectrum of compound **11b**.

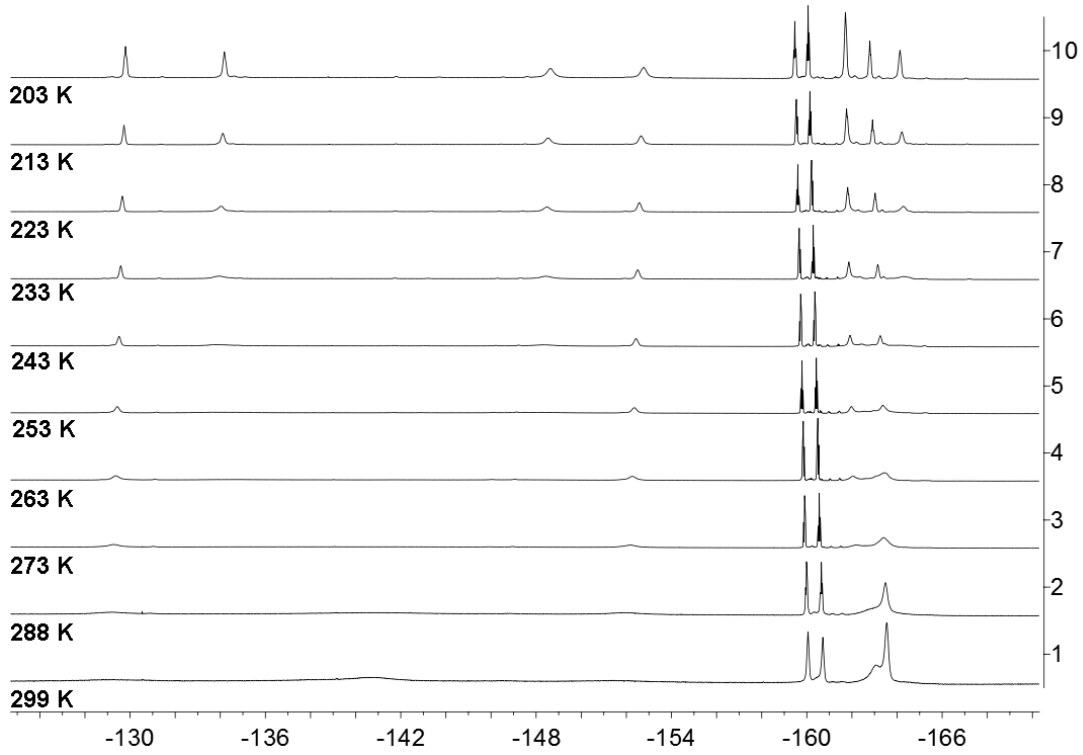


Figure 28. ^{19}F NMR (470 MHz, from 299 K to203 K, CD_2Cl_2) spectra of compound **11b**.

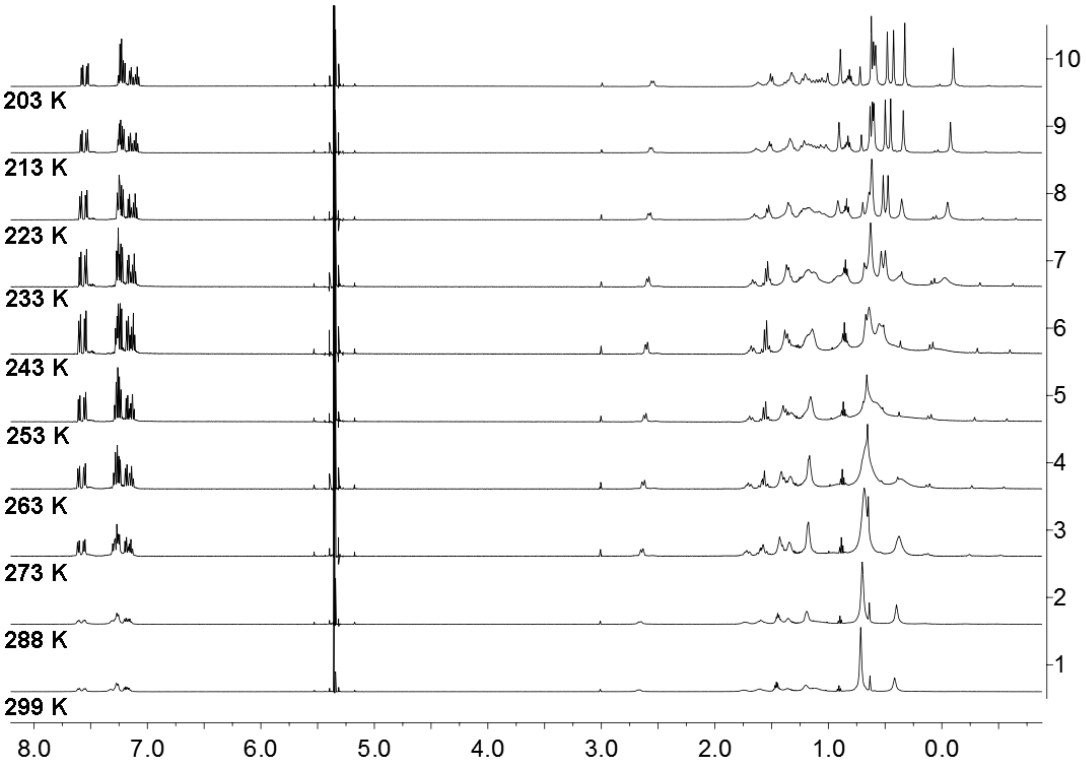


Figure 29. ^{19}F NMR (470 MHz, from 299 K to203 K, CD_2Cl_2) spectra of compound **11b**.

X-ray crystal structure analysis of compound 11b: formula $C_{46}H_{50}BF_{10}LiN_2O$, M = 939.56, colourless crystal, 0.26 x 0.10 x 0.05 mm, a = 11.5750(1), b = 21.5349(3), c = 18.6398(4) Å, β = 97.633(1)°, V = 4605.1(1) Å^3, ρ_{calc} = 1.355 gcm^{-3}, μ = 0.219 mm^{-1}, empirical absorption correction (0.945 ≤ T ≤ 0.989), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 30685 reflections collected ($\pm h$, $\pm k$, $\pm l$), 7980 independent (R_{int} = 0.070) and 5168 observed reflections [$I>2\sigma(I)$], 617 refined parameters, R = 0.074, wR^2 = 0.151, max. (min.) residual electron density 0.34 (-0.34) e.Å^{-3}, the position of the hydrogen atom at N2 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

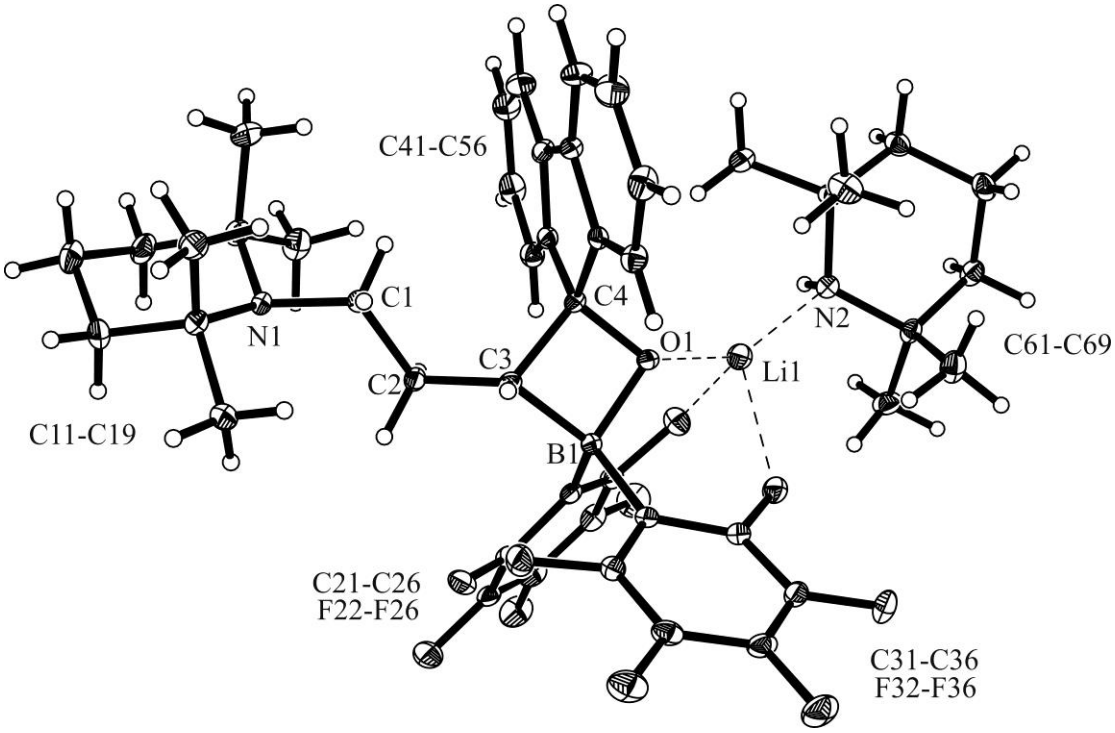
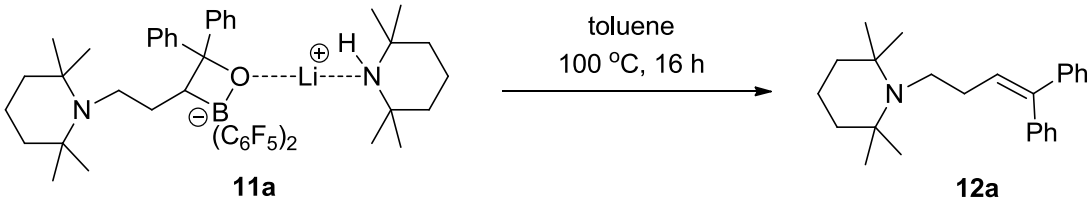


Figure 30. A view of the molecular structure of compound **11b**.

3.4 Compounds 12

3.4.1 1-(4',4'-Diphenylbut-3'-en-1'-yl)-2,2,6,6-tetramethylpiperidine (12a)



11a **12a**

Scheme S5.

The solution of compound **11a** in toluene (20 mL) was heated at 100 °C for 16 h to give a brown solution. Then all the volatiles were removed in vacuo, the obtained residue was extracted by *n*-pentane

(3×20 mL) for three times. The *n*-pentane solution was collected, concentrated to ca. 3 mL, and then purified by silica gel column chromatography (eluent: *n*-pentane: ethyl acetate: triethylamine = 100:5:1). The product was dried in vacuo and obtained as a sticky solid. Yield: 130.5 mg, 79%.

[**TMP**: 2,2,6,6-tetramethylpiperidino]

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.36 (m, 4H, *m*-Ph), 7.29 (m, 2H, *p*-Ph), 7.20 (m, 4H, *o*-Ph), 6.09 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, =C*H*), 2.48 (m, 2H, NCH_2), 2.21 (m, 2H, CH_2), 1.51 (m, 2H, CH_2^{TMP}), 1.36 (m, 4H, ^{C}CH_2^{TMP}), 0.96 (s, 12H, CH_3^{TMP}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 142.6 (=*C*), 142.2, 140.2 (*i*-Ph), 129.9, 127.0 (*o*-Ph), 128.1, 128.0 (*m*-Ph), 126.8, 126.7 (*p*-Ph), 127.6 (=*C*H), 54.4 (N*C*^{TMP}), 44.7 (N*C*H_2), 41.1 (^{C}*C*H_2^{TMP}), 36.9 (*C*H_2), 27.4 (br, *C*H_3^{TMP}), 17.7 (*C*H_2^{TMP}).

Elemental analysis: calc. for $C_{25}H_{33}N$: C, 86.40; H, 9.57; N, 4.03. Found: C, 86.32; H, 8.98; N, 4.15.

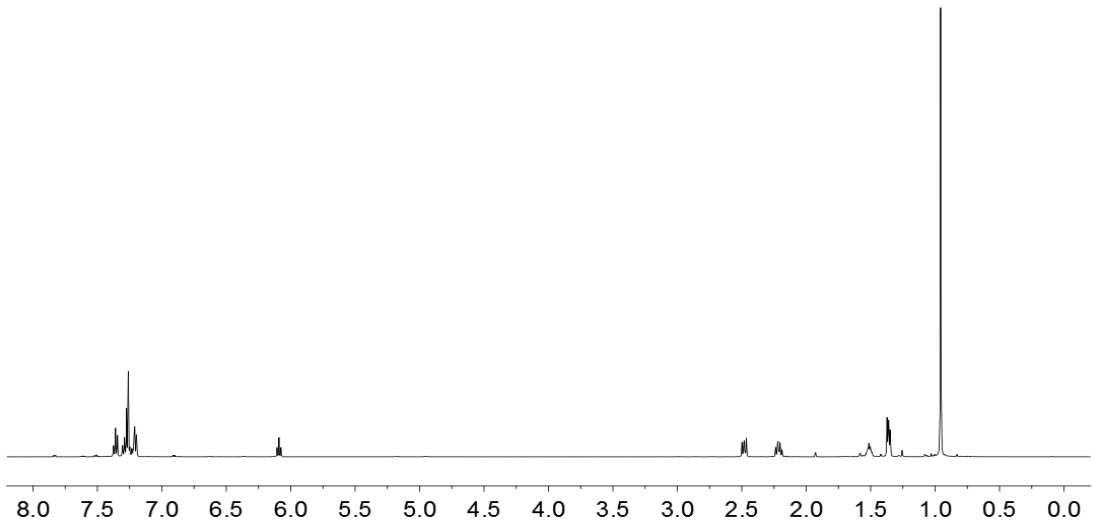


Figure S31. ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **12a**.

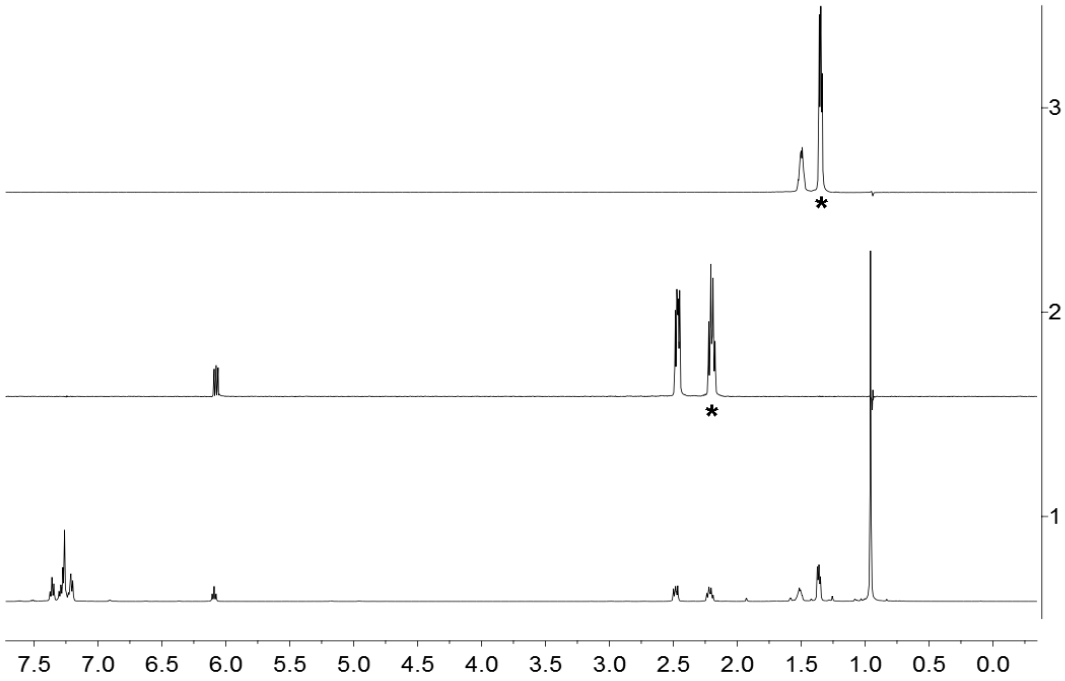


Figure S32. ^{1}H NMR (1) and ^{1}H{^{1}H} TOCSY (500 MHz, 299 K, CD_2Cl_2) spectra of compound **12a**. * Irradiation points: $\delta^{1}H_{irr}$ = 2.21 (CH_2) (2), 1.36 (^{C}CH_2^{TMP}) (3).

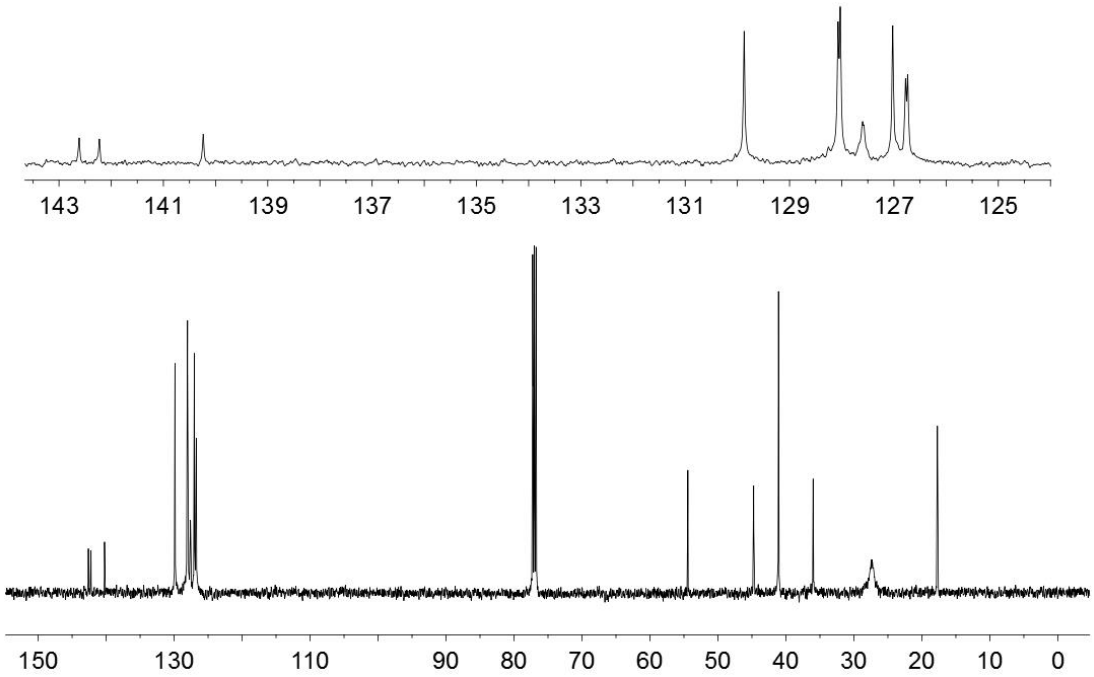
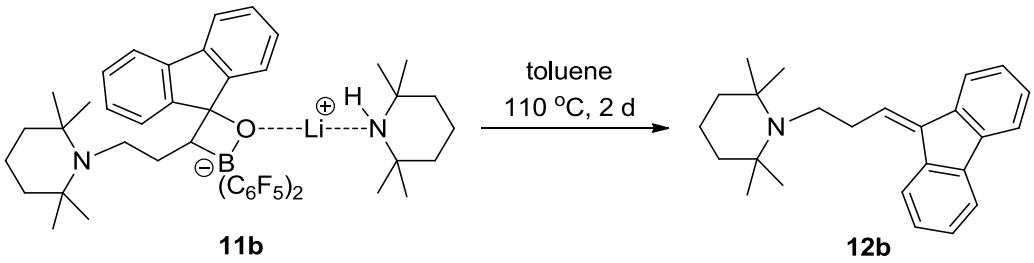


Figure S33. ^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **12a**.

*3.4.2 1-(3'-(9''***H***-Fluoren-9'-ylidene)propyl)-2,2,6,6-tetramethylpiperidine (12b)*



Scheme S6.

The solution of compound **11b** in toluene (30 mL) was heated at 110 °C for 2 d to give a brown solution. Then all the volatiles were removed in vacuo, the obtained residue was extracted by *n*-pentane (3×20 mL) for three times. The *n*-pentane solution was collected, concentrated to ca. 3 mL, and then purified by silica gel column chromatography (eluent: *n*-pentane: ethyl acetate: triethylamine = 100:5:1). The product was dried in vacuo and obtained as a sticky solid. Yield: 89.1 mg, 61%.

[**TMP**: 2,2,6,6-tetramethylpiperidino]

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.97, 7.76, 7.36, 7.32 (each m, each 1H, Ph), 7.71, 7.68, 7.33, 7.29 (each m, each 1H, Ph'), 6.67 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, =C*H*), 2.98 (m, 2H, CH_2), 2.77 (m, 2H, NCH_2), 1.58 (m, 2H, CH_2^{TMP}), 1.48 (m, 4H, ^{C}CH_2^{TMP}), 1.12 (s, 12H, CH_3^{TMP}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 140.8, 139.4, 138.6, 137.6, 127.6, 127.3, 126.9, 126.8, 124.9, 119.7, 119.6, 119.4(two Ph), 135.3 (=*C*), 128.6 (=*C*H), 54.8 (NC^{TMP}), 45.0 (NCH_2), 41.1 ($^{C}CH_2^{TMP}$), 35.8 (*C*H_2), 27.5 (br, *C*H_3^{TMP}), 17.7 (*C*H_2^{TMP}).

Elemental analysis: calc. for $C_{25}H_{31}N$: C, 86.90; H, 9.04; N, 4.05. Found: 86.55; 9.04; N, 4.09.

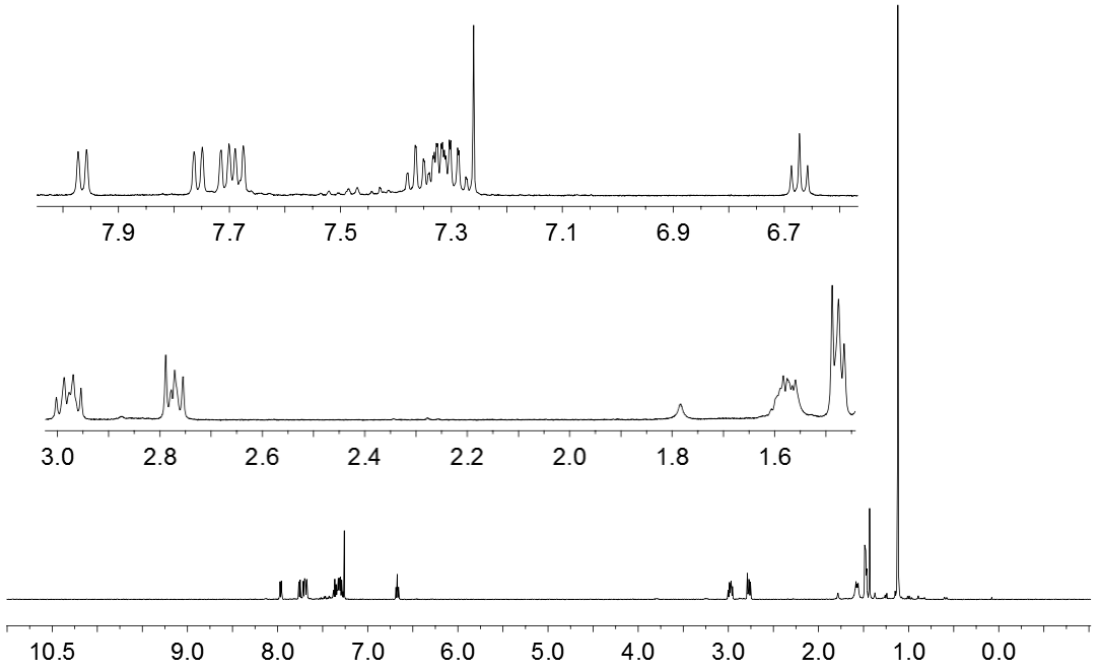


Figure S34. ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **12b**.

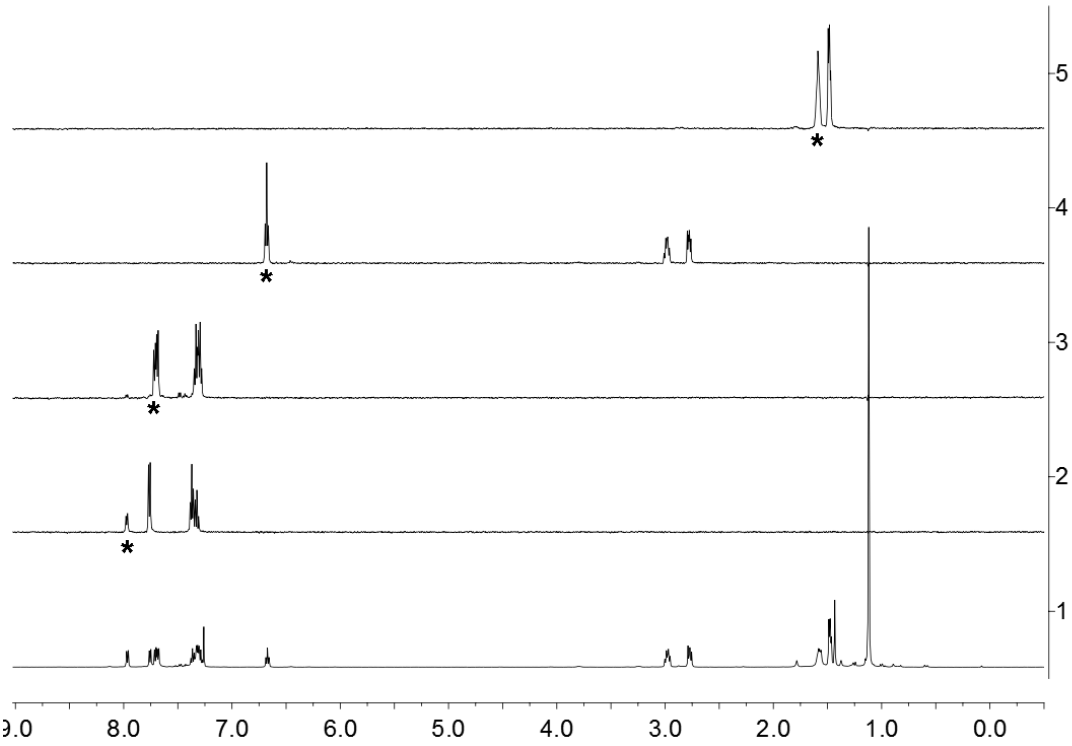


Figure S35. ^{1}H NMR (1) and ^{1}H{^{1}H} TOCSY (500 MHz, 299 K, CD_2Cl_2) spectra of compound **12b**. * Irradiation points: $^{1}H_{irr}$ = 7.97 (Ph) (2), 7.71 (Ph') (3) 6.67 (=C*H*) (4), 1.58 (CH_2^{TMP}) (5).

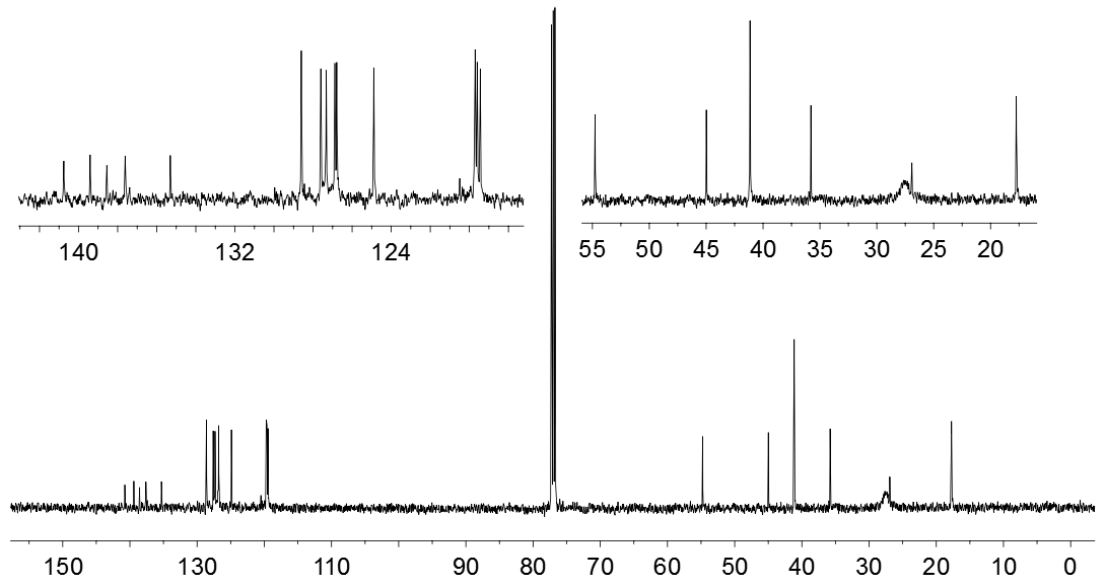
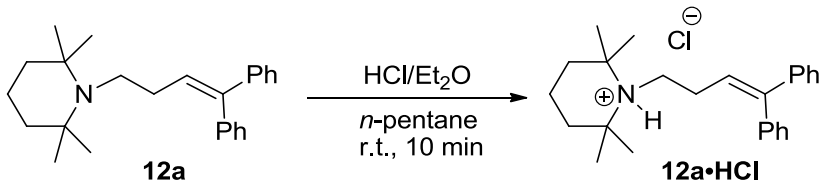


Figure S36. ^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **12b**.

3.5 Compounds 12·HCl

3.5.1 1-(4',4'-Diphenylbut-3'-en-1'-yl)-2,2,6,6-tetramethylpiperidin-1-ium chloride (12a·HCl)

Method A



Scheme S7.

Compound **12a** (42.5 mg, 0.12 mmol) was dissolved in *n*-pentane (3 mL), then HCl·Et_2O (0.15 mL, 1.0 M in Et_2O, 0.15 mmol) was added to the solution, which resulted in a white precipitate immediately. After stirring at room temperature for 10 min, the suspension was filtered, washed with *n*-pentane (1 mL), and dried in vacuo to give a white solid. Yield: 40.9 mg, 87%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **12a·HCl** in $CHCl_3$ covered with *n*-pentane at room temperature.

[**TMP**: 2,2,6,6-tetramethylpiperidino]

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 10.09 (br, 1H, N*H*), 7.35 (m, 2H, *m*-Ph), 7.27 (m, 1H, *p*-Ph), 7.15 (m, 2H, *o*-Ph), 7.22 (m, 2H, *p*-Ph'), 7.21 (m, 1H, *m*-Ph'), 7.17 (m, 2H, *o*-Ph'), 6.07 (t, $^3J_{HH}$ = 7.8 Hz, 1H, =C*H*), 2.91 (m, 2H, CH_2), 2.80 (m, 2H, NCH_2), 2.62, 1.42 (each m, each 2H, ^{C}CH_2^{TMP}), 1.61 (m, 2H, CH_2^{TMP}), 1.34, 1.19 (s, 12H, CH_3^{TMP}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 145.9 (=*C*), 141.1, 139.0 (*i*-Ph), 129.3, 126.8 (*o*-Ph), 128.6, 128.1 (*m*-Ph), 127.45, 127.43 (*p*-Ph), 122.4 (=*C*H), 65.0 (NC^{TMP}), 45.7 (NCH_2), 35.8, 35.6 (^{C}*C*H_2^{TMP}), 29.3 (*C*H_2), 28.2, 28.0, 21.4, 21.2 (*C*H_3^{TMP}), 15.8 (*C*H_2^{TMP}).

Elemental analysis: calc. for $C_{25}H_{34}NCl$: C, 78.20; H, 8.92; N, 3.65. Found: C, 77.36; H, 8.77; N, 3.78.

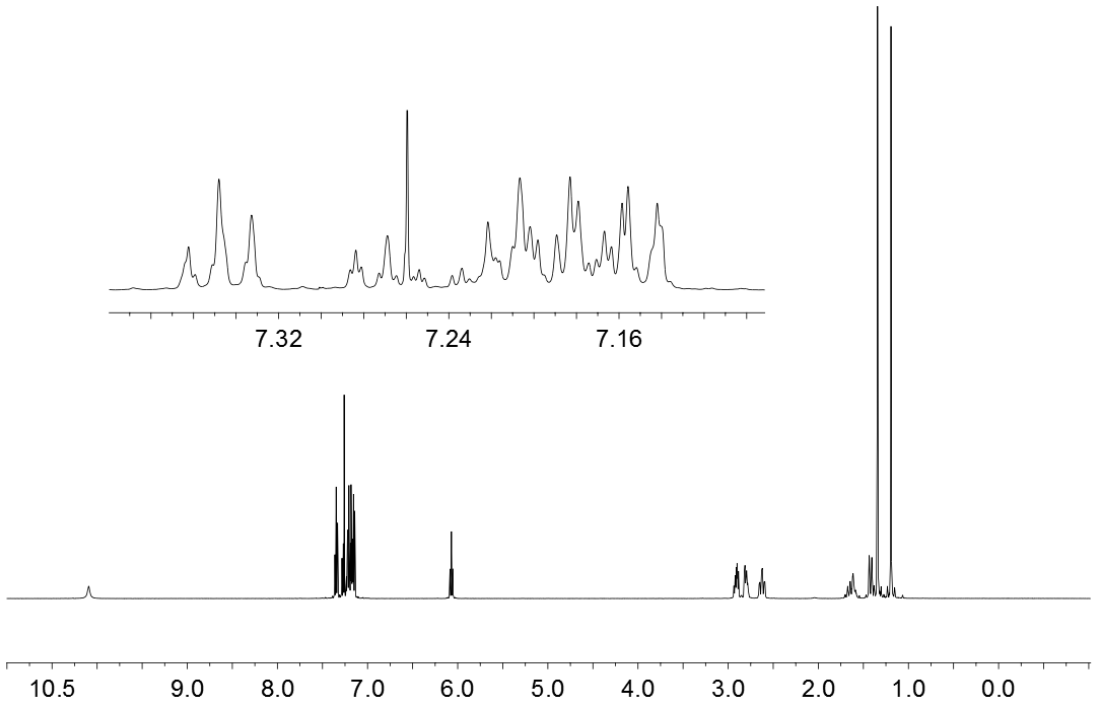


Figure S37. ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **12a·HCl**.

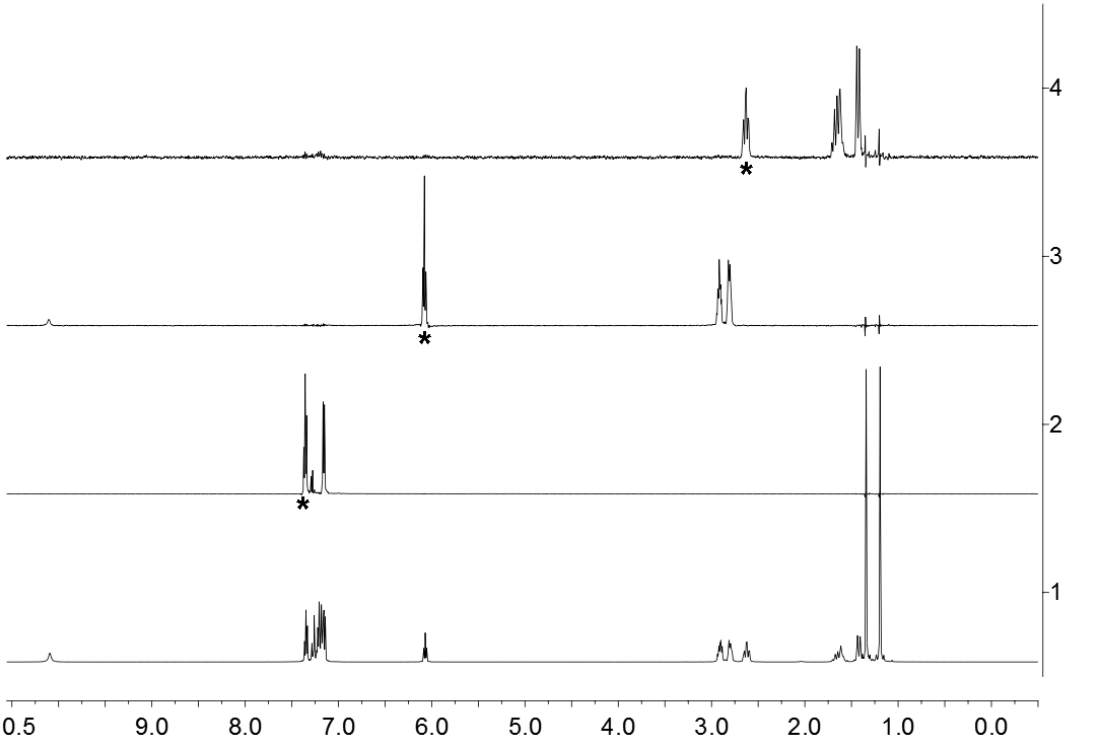


Figure S38. ^{1}H NMR (1) and ^{1}H{^{1}H} TOCSY (500 MHz, 299 K, CD_2Cl_2) spectra of compound **12a·HCl**. * Irradiation points: $^{1}H_{irr}$ = 7.35 (*m*-Ph) (2), 6.07 (=C*H*) (3), 2.62 ($^{C}CH_2^{TMP}$) (4).

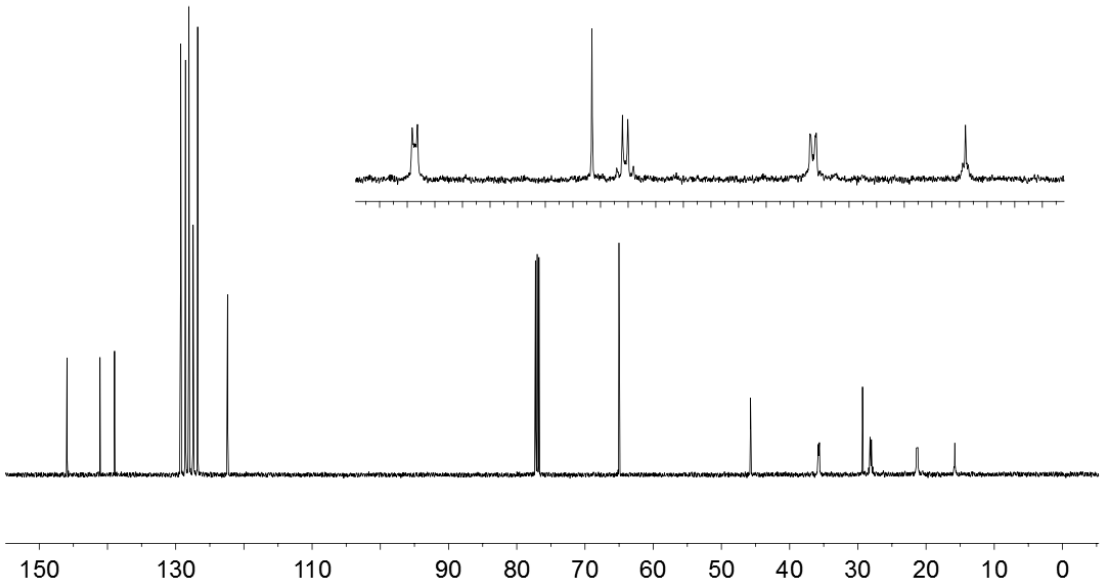


Figure S39. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **12a·HCl**.

X-ray crystal structure analysis of compound 12a·HCl: A colorless plate-like specimen of $C_{25}H_{34}ClN$, approximate dimensions 0.088 mm x 0.168 mm x 0.213 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2011 frames were collected. The total exposure time was 19.55 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 71974 reflections to a maximum θ angle of 27.61° (0.77 Å resolution), of which 4993 were independent (average redundancy 14.415, completeness = 99.3%, R_{int} = 4.21%, R_{sig} = 1.79%) and 4261 (85.34%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.6815(3) Å, b = 15.5318(6) Å, c = 20.9543(8) Å, β = 95.2790(10)°, volume = 2165.32(15) $Å^3$, are based upon the refinement of the XYZ-centroids of 9795 reflections above 20 σ(I) with 4.703° < 2θ < 55.05°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.960. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9610 and 0.9840. The final anisotropic full-matrix least-squares refinement on F^2 with 252 variables converged at R1 = 3.39%, for the observed data and wR2 = 8.10% for all data. The goodness-of-fit was 1.061. The largest peak in the final difference electron density synthesis was 0.314 $e^-/Å^3$ and the largest hole was -0.277 $e^-/Å^3$ with an RMS deviation of 0.045 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.178 g/cm^3 and F(000), 832 e^-. The position of the hydrogen atom at N1 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

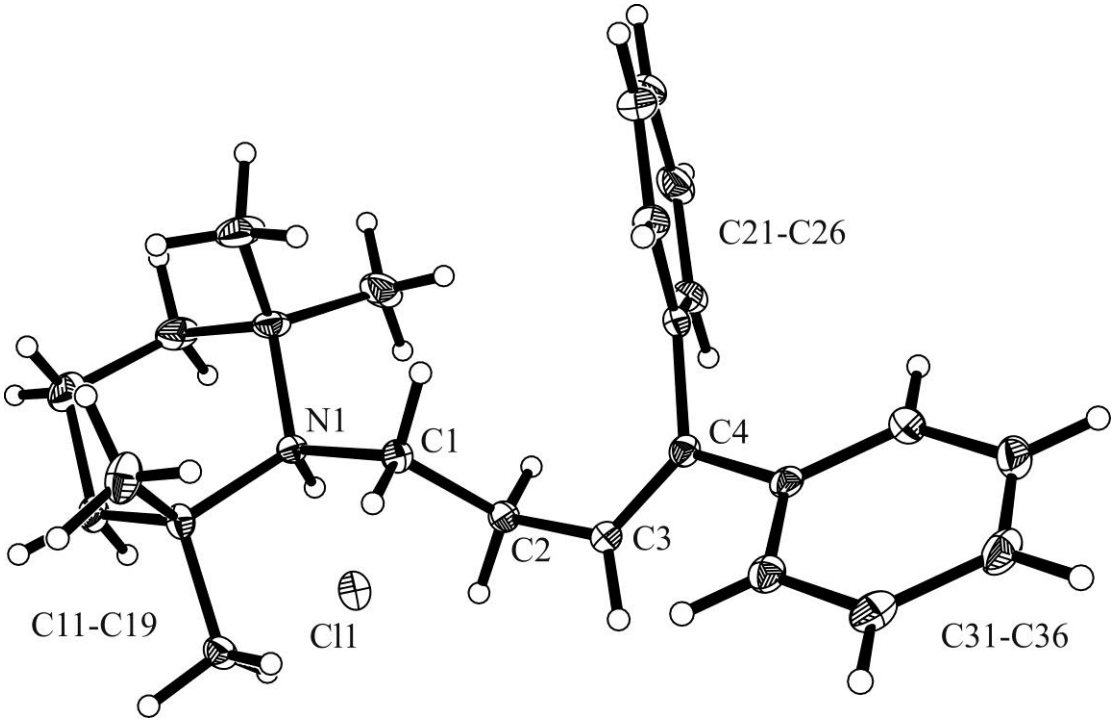
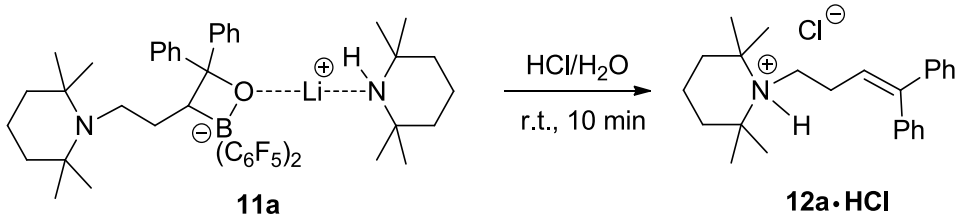


Figure S40. A view of the molecular structure of compound **12a·HCl**.

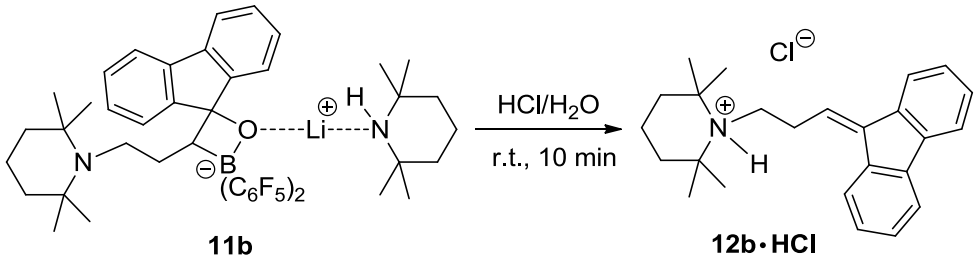
Method B



Scheme S8.

Compound **11a** (183.7 mg, 0.21 mmol) was dissolved in CH_2Cl_2 (10 mL), then hydrochloric acid (37wt%, 1 drop, ca. 0.60 mmol) was added to the solution. After stirring at room temperature for 10 min, water (3 mL) was added to give two phases and the CH_2Cl_2 layer was collected and washed with water (3×3 mL). Then the obtained CH_2Cl_2 solution was dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, CH_2Cl_2) to give a white solid. Yield: 61.9 mg, 75%.

3.5.2 1-(3'-(9''H-Fluoren-9'-ylidene)propyl)-2,2,6,6-tetramethylpiperidin-1-ium chloride (12b·HCl)



Scheme S9.

Compound **11b** (251.3 mg, 0.29 mmol) was dissolved in CH_2Cl_2 (10 mL), then hydrochloric acid (37wt%, 1 drop, ca. 0.60 mmol) was added to the solution. After stirring at room temperature for 10 min, water (3 mL) was added to give two phases and the CH_2Cl_2 layer was collected and washed with water (3×3 mL). Then the obtained CH_2Cl_2 solution was dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, CH_2Cl_2) to give a white solid. Yield: 93.5 mg, 83%.
Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **12b·HCl** in CH_2Cl_2 covered with *n*-pentane at room temperature.

[**TMP**: 2,2,6,6-tetramethylpiperidino]
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 10.83 (br, 1H, N*H*), 8.15, 7.75, 7.40, 7.39 (each m, each 1H, Ph), 7.71, 7.68, 7.35, 7.30 (each m, each 1H, Ph'), 6.53 (t, $^3J_{HH}$ = 6.9 Hz, 1H, =C*H*), 3.75 (m, 2H, CH_2), 3.28 (m, 2H, NCH_2), 2.72, 1.61 (each m, each 2H, $^{C}CH_2^{TMP}$), 1.82, 1.74 (each m, each 1H, CH_2^{TMP}), 1.73, 1.36 (each s, each 6H, CH_3^{TMP}).
^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 141.2, 139.3, 139.1, 137.0, 128.7, 128.4, 128.0, 127.4, 126.0, 120.1 (2×C), 119.9 (2×Ph), 137.9 (=*C*), 123.3 (=*C*H), 66.0 (NC^{TMP}), 46.7 (NCH_2), 36.4 ($^{C}CH_2^{TMP}$), 30.4 (*C*H_2), 28.8, 21.7 (each s, CH_3^{TMP}), 16.3 (CH_2^{TMP}).

Elemental analysis: calc. $C_{25}H_{32}NCl$: C, 78.61; H, 8.44; N, 3.67. Found: C, 77.72; H, 8.73; N, 3.92.

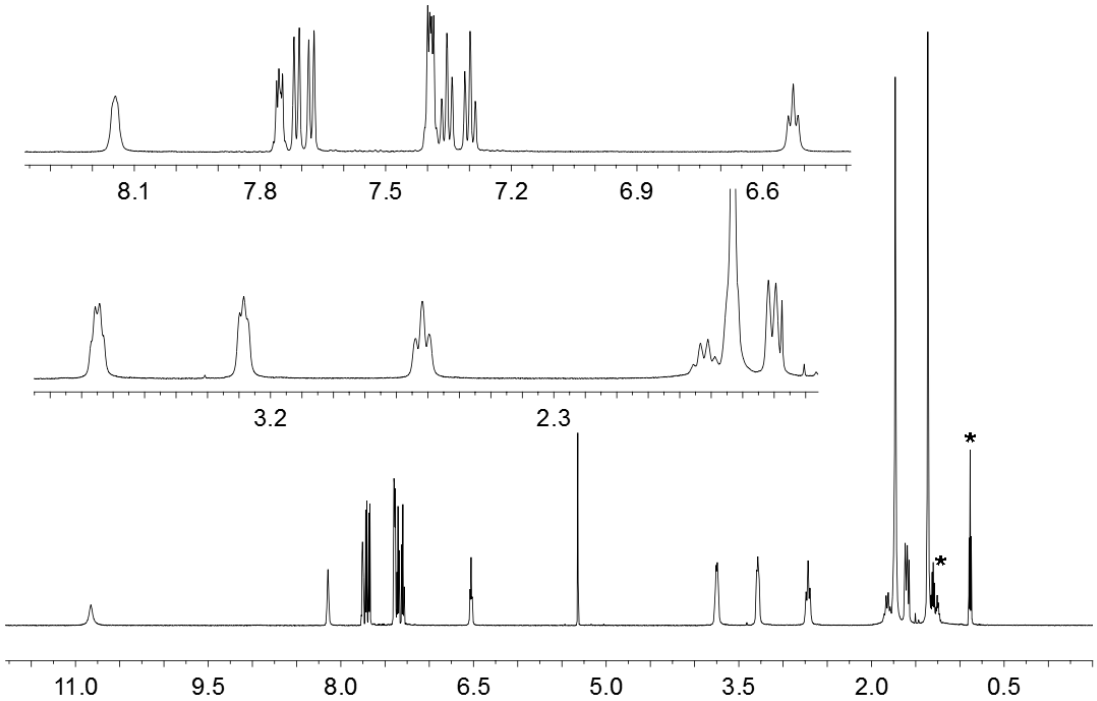


Figure S41. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **12b·HCl**. * pentane

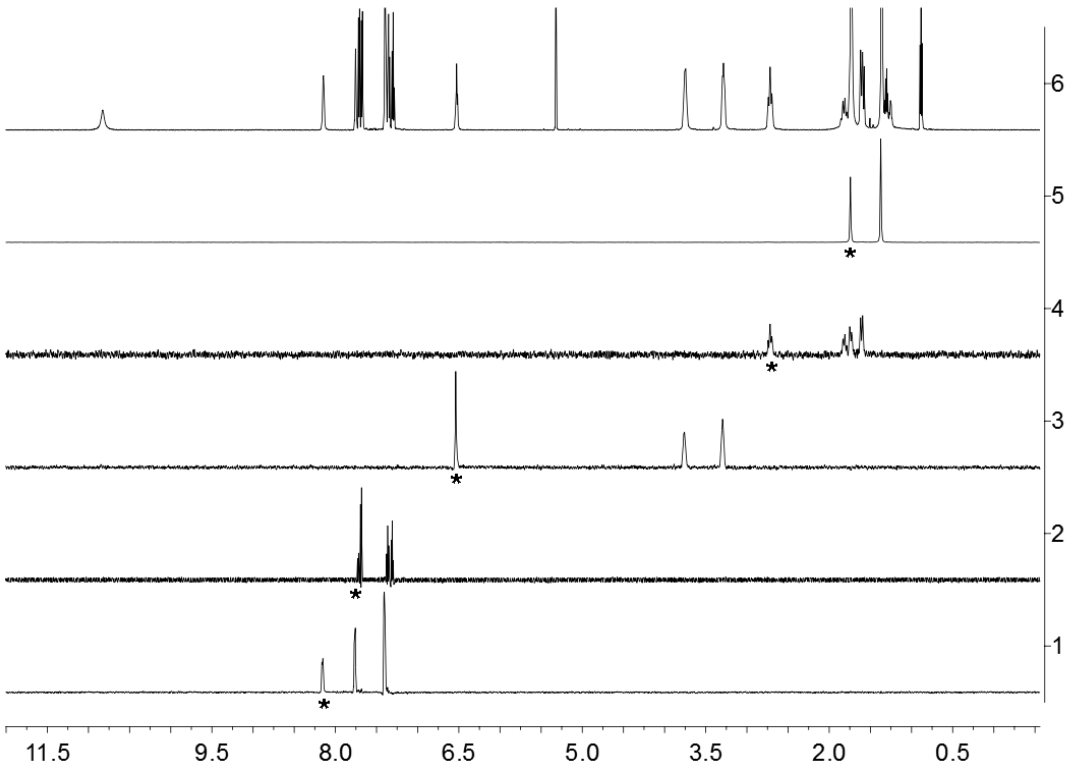


Figure S42. ^{1}H NMR (6) and ^{1}H{^{1}H} TOCSY (600 MHz, 299 K, CD_2Cl_2) spectra of compound **12b·HCl**. * Irradiation points: $\delta^{1}H_{irr}$ = 8.15 (Ph) (1), 7.71 (Ph') (2), 6.53 (=C*H*) (3), 2.72 ($^{C}CH_2^{TMP}$) (4), 1.73 (CH_2^{TMP}) (5).

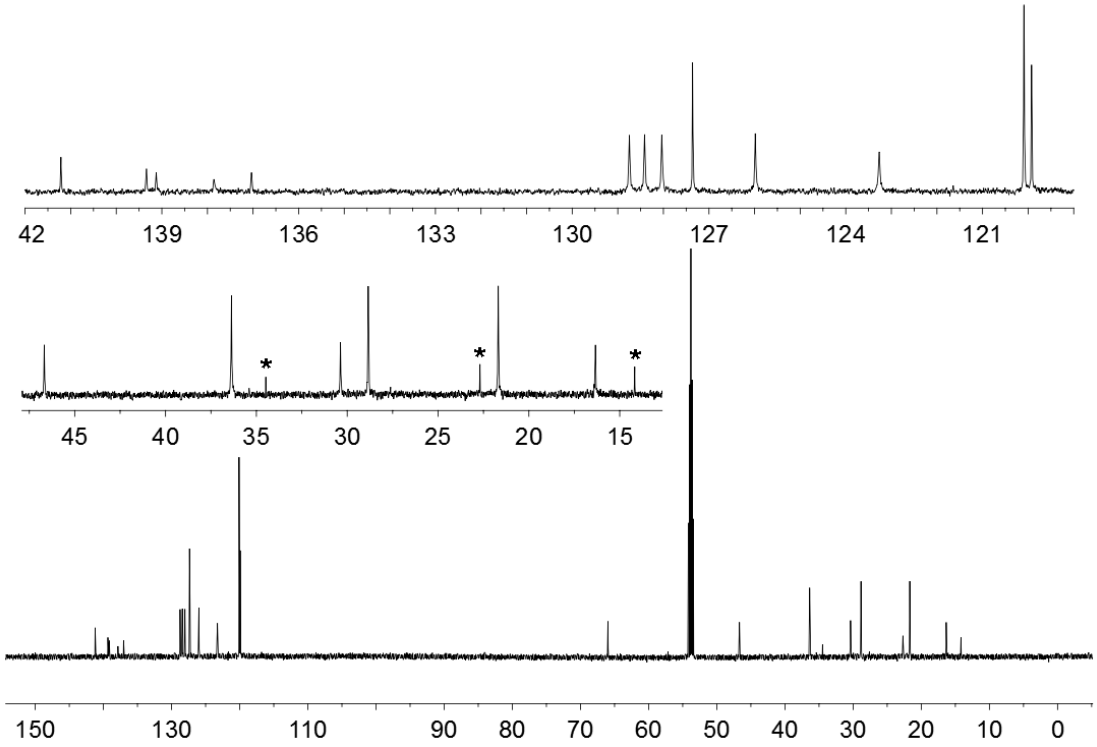


Figure S43. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **12b·HCl**. * pentane

X-ray crystal structure analysis of compound 12b·HCl: A colorless prism-like specimen of $C_{25}H_{32}NCl \cdot 0.26 \times H_2O$, approximate dimensions 0.160 mm x 0.180 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1197 frames were collected. The total exposure time was 23.91 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 46891 reflections to a maximum θ angle of 66.72° (0.84 Å resolution), of which 7730 were independent (average redundancy 6.066, completeness = 99.2%, R_{int} = 7.32%, R_{sig} = 4.94%) and 5891 (76.21%) were greater than $2\sigma(F^2)$. The final cell constants of a = 25.0211(8) Å, b = 13.2663(5) Å, c = 13.5992(4) Å, β = 103.116(2)°, volume = 4396.3(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 8009 reflections above 20 σ(I) with 7.255° < 2θ < 133.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.871. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7410 and 0.7840. The final anisotropic full-matrix least-squares refinement on F^2 with 528 variables converged at R1 = 4.83%, for the observed data and wR2 = 12.70% for all data. The goodness-of-fit was 1.075. The largest peak in the final difference electron density synthesis was 0.280 $e^-/Å^3$ and the largest hole was -0.240 $e^-/Å^3$ with an RMS deviation of 0.051 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.168 g/cm^3 and F(000), 1669 e^-. The positions of the hydrogen atoms at N1A and N1B were refined freely; others hydrogen atoms were calculated and refined as riding atoms.

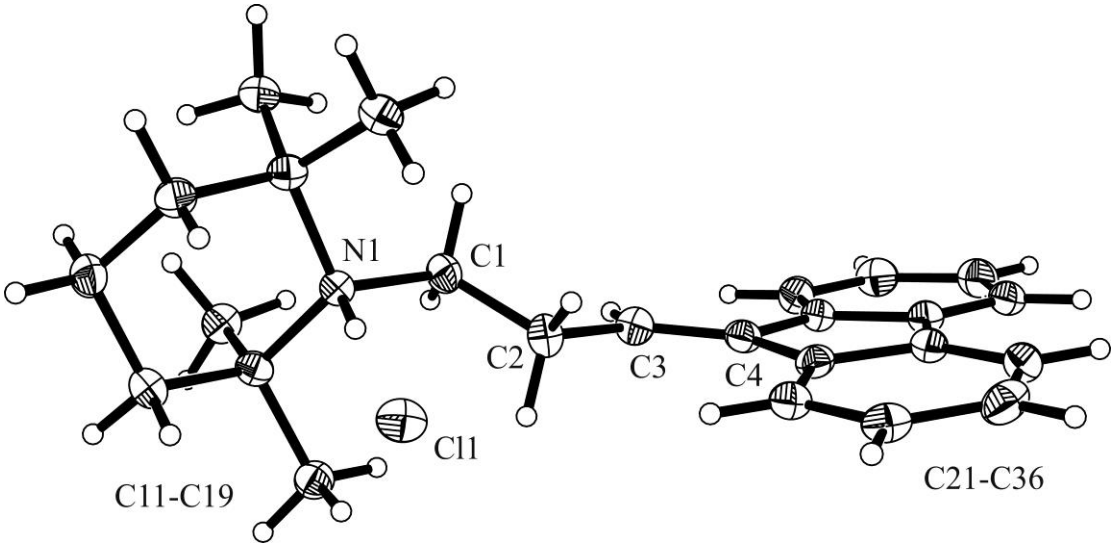
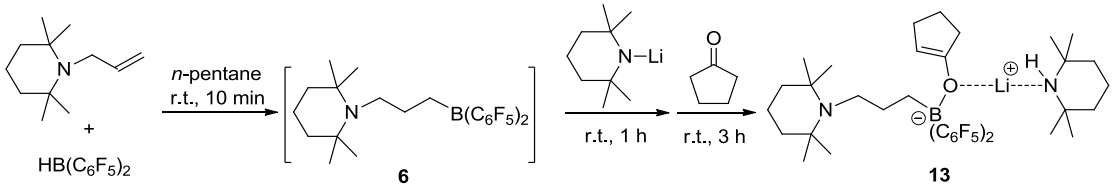


Figure S44. A view of the molecular structure of compound **12b·HCl**.

3.6 Compound 13



Scheme S10.

1-Allyl-2,2,6,6-tetramethylpiperidine (90.8 mg, 0.50 mmol) was added to a suspension of $HB(C_6F_5)_2$ (172.9mg, 0.50 mmol) in *n*-pentane (15 mL), which was stirred at room temperature for 10 min to give a yellow solution. Then lithium tetramethylpiperidide (LiTMP) (73.8 mg, 0.50 mmol) was added to the solution. The mixture was stirred at room temperature for 1 h to give a suspension. After that, cyclopentanone (42.3mg, 0.50 mmol) was added to the mixture. Then the mixture was stirred at room temperature for another 3 h to give a pale yellow solution, which was concentrated to ca. 5 mL and kept in the fridge (ca. -35 °C) for 2 d to give white crystalline solid. The solid was collected by filtration and dried in vacuo to give a white solid. Yield: 261.7 mg, 69%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of the obtained solid in CH_2Cl_2 covered with *n*-pentane at -35 °C.

Comment: the NH-hydrogen of compound **13** in solution (CD_2Cl_2) could not be located without doubt by NMR experiments.

[**TMP**: 2,2,6,6-tetramethylpiperidino, **HTMP**: 2,2,6,6-tetramethylpiperidine, **CP**: cyclopentanone]

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 4.74 (m, 1H, =C*H*), 2.28 (m, 2H, NCH_2), 2.15, 1.98, 1.79 (each m, each 2H, CH_2^{CP}), 1.69 (m, 2H, CH_2^{HTMP}), 1.49 (m, 2H, CH_2^{TMP}), 1.39 (m, 4H, ^{C}CH_2^{HTMP}),

1.30 (m, 4H, $^{C}CH_2^{TMP}$), 1.16 (s, 12H, CH_3^{HTMP}), 1.07 (m, 2H, CH_2), 0.92 (s, 12H, CH_3^{TMP}), 0.91 (m, 2H, BCH_2), 1.01 (s, 1H, N*H*).

$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2): δ = 157.2 (*C*O), 109.0 (=*C*H), 54.6 (NC^{TMP}), 51.4 (NC^{HTMP}), 49.3 (NCH_2), 41.6 ($^{C}CH_2^{TMP}$), 38.8 ($^{C}CH_2^{HTMP}$), 33.3, 27.7, 22.3 (CH_2^{CP}), 33.0 (CH_2), 32.7, 28.5 (each br, CH_3^{HTMP}), 27.5 (br, CH_3^{TMP}), 27.5 (br, CH_3^{TMP}), 19.2 (br, BCH_2), 18.2(CH_2^{TMP}), 18.0(CH_2^{HTMP}) [C_6F_5 not listed].

$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, CD_2Cl_2): δ = 0.9 ($\nu_{1/2}$ ~ 235 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = -140.5 (br, 2F, *o*-C_6F_5), -161.0 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), -164.1 (4F, *m*-C_6F_5).

Elemental analysis: calc. for $C_{38}H_{50}N_2BF_{10}LiO$: C, 60.17; H, 6.64; N, 3.69. Found: C, 59.38; H, 6.92; N, 4.06.

Decomposition point: 125 °C

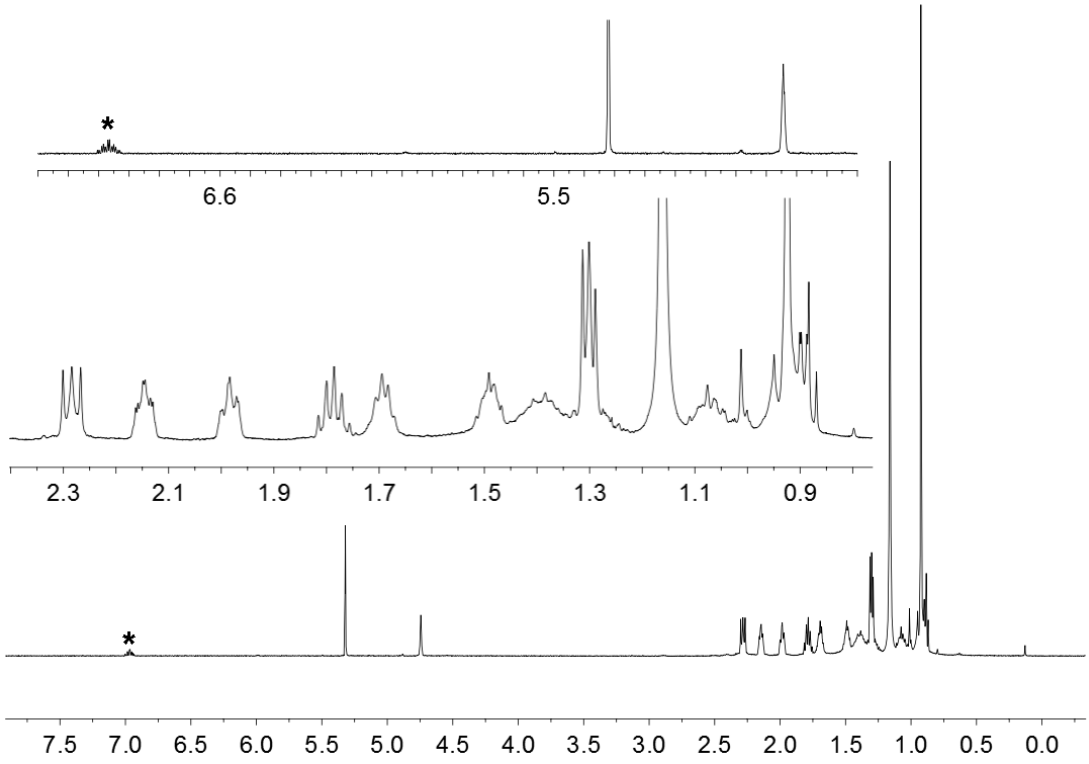


Figure S45. ^1H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **13**. * C_6F_5H

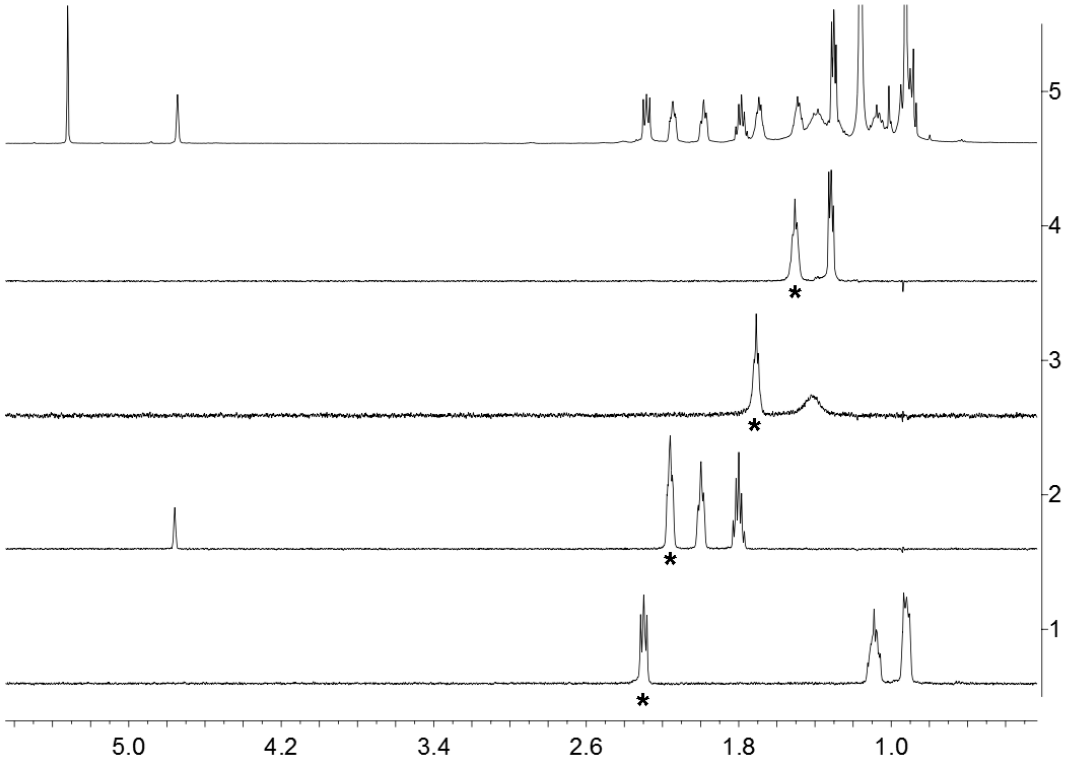


Figure S46. ^{1}H NMR (**5**) and ^{1}H{^{1}H} TOCSY (500 MHz, 299 K, CD_2Cl_2) spectra of compound **13**. * Irradiation points: $\delta^{1}H_{irr}$ = 2.28 (NCH_2) (**1**), 2.15 (CH_2^{CP}) (**2**), 1.69 (CH_2^{HTMP}) (**3**), 1.49 (CH_2^{TMP}) (**4**).

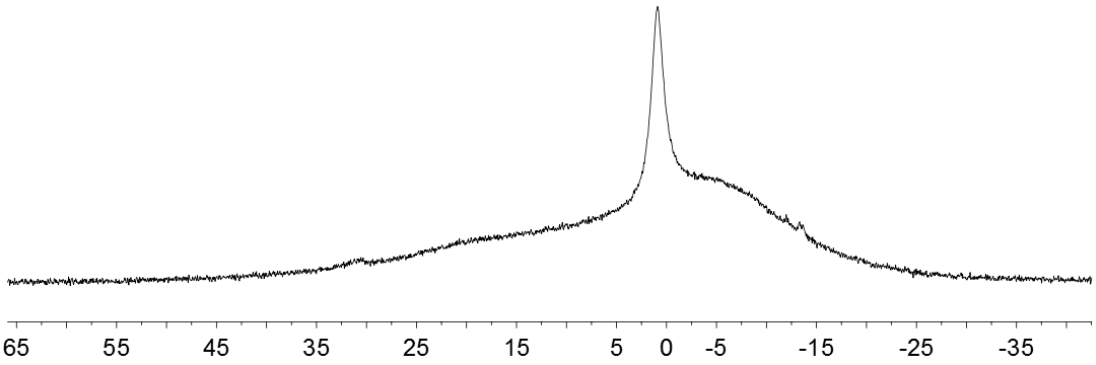


Figure S47. ^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2) spectrum of compound **13**.

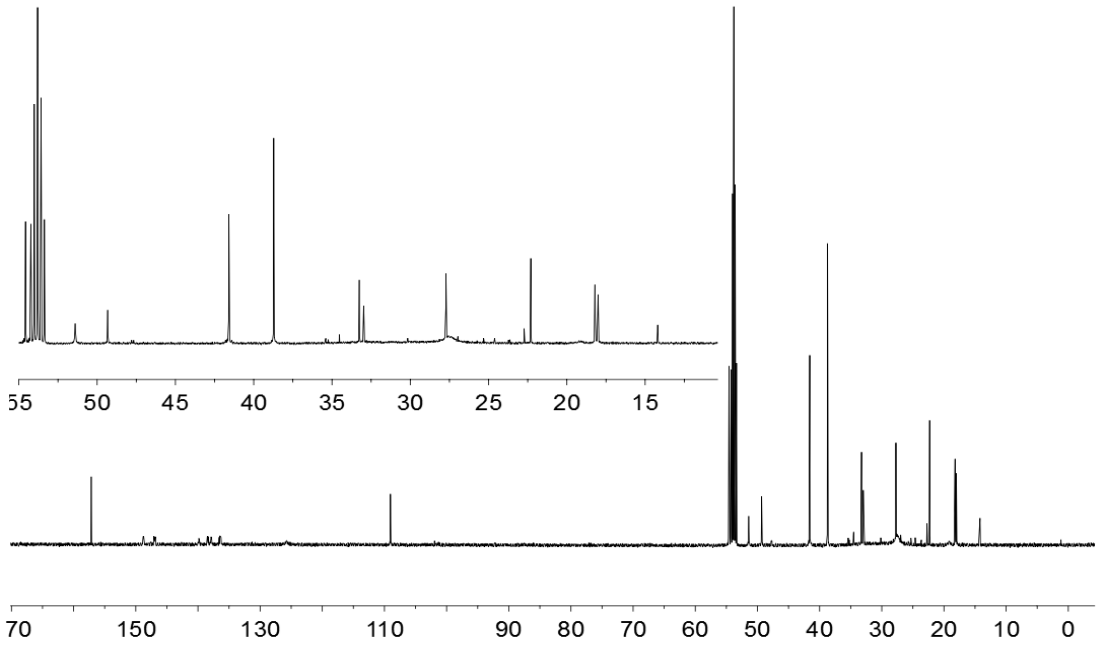


Figure S48. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **13**.

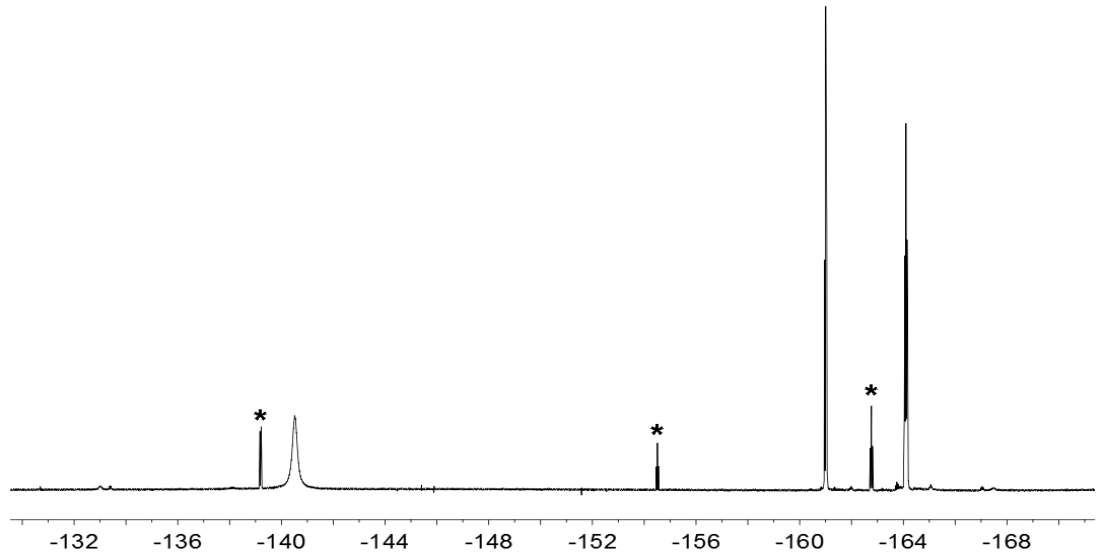


Figure S49. ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) spectrum of compound **13**. * C_6F_5H

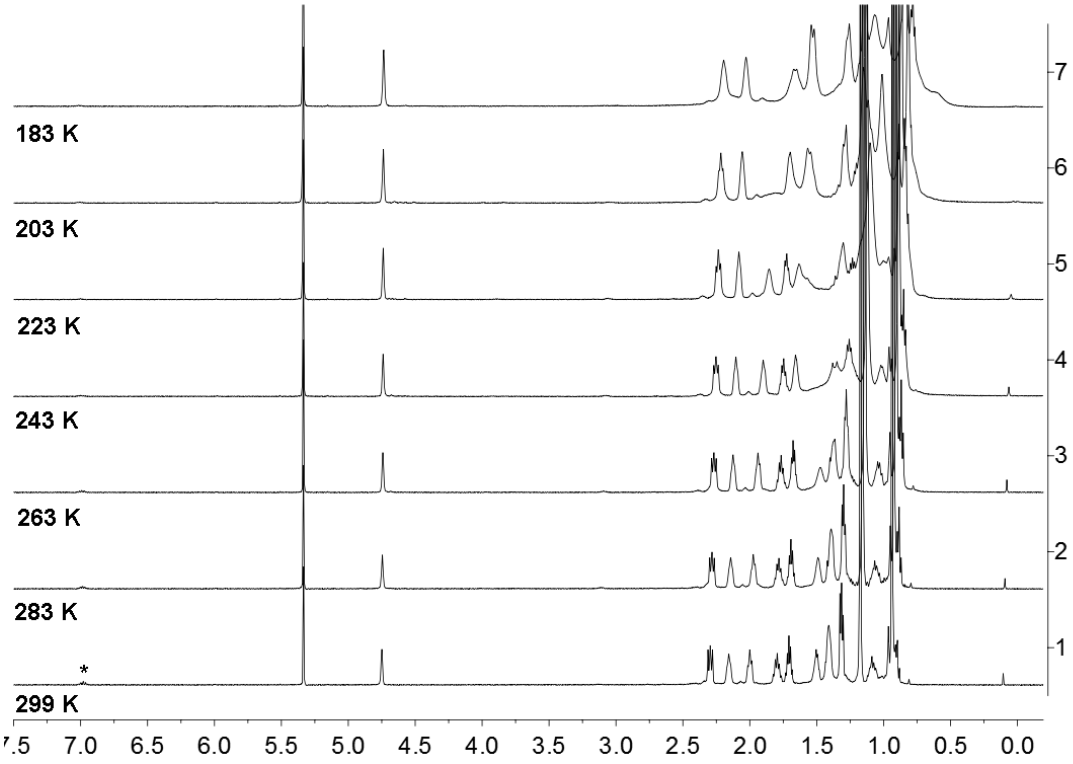


Figure S50. ^{1}H NMR (500 MHz, from 299 K to 183 K, CD_2Cl_2) spectra of compound **13**. * C_6F_5H

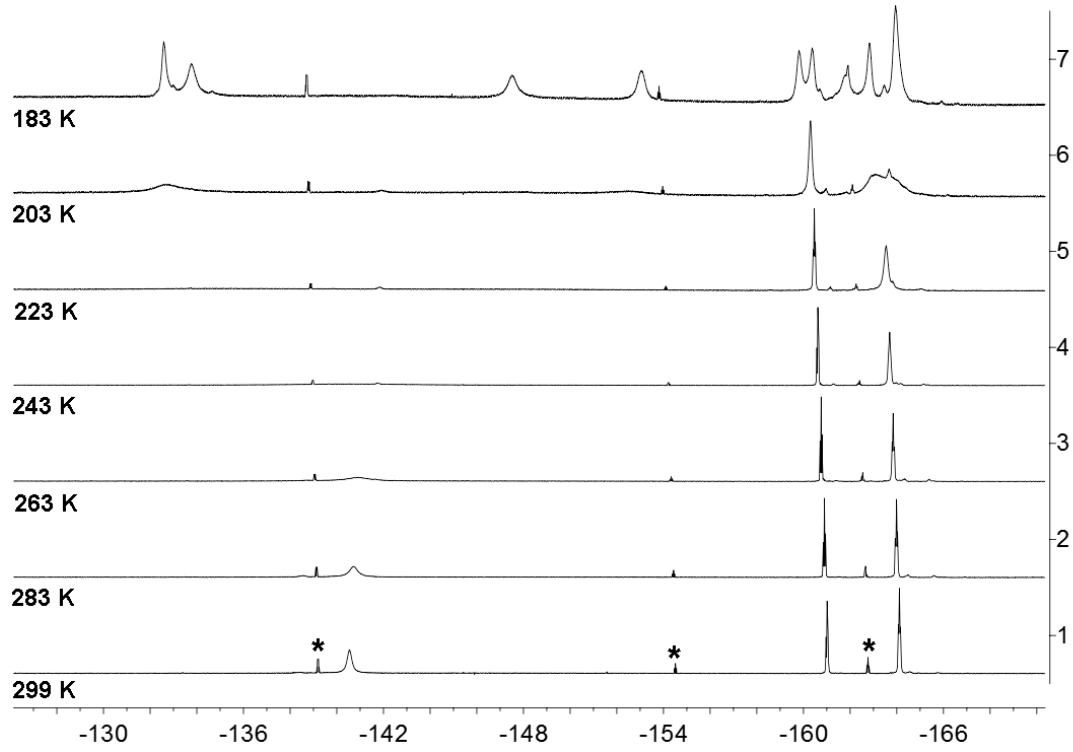


Figure S51. ^{19}F NMR (470 MHz, from 299 K to 183 K, CD_2Cl_2) spectra of compound **13**. * C_6F_5H

X-ray crystal structure analysis of compound 13: A colorless prism-like specimen of $C_{38}H_{50}BF_{10}LiN_2O$, approximate dimensions 0.136 mm x 0.253 mm x 0.295 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 667 frames were collected. The total exposure time was 11.12 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 87129 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 7178 were independent (average redundancy 12.138, completeness = 99.8%, R_{int} = 9.76%, R_{sig} = 3.89%) and 5470 (76.21%) were greater than $2\sigma(F^2)$. The final cell constants of a = 26.6576(19) Å, b = 17.0458(14) Å, c = 20.604(3) Å, β = 123.014(2)°, volume = 7850.8(14) $Å^3$, are based upon the refinement of the XYZ-centroids of 9955 reflections above 20 σ(I) with 4.68° < 2θ < 52.67°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.928. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9690 and 0.9850. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C* 2/*c*, with Z = 8 for the formula unit, $C_{38}H_{50}BF_{10}LiN_2O$. The final anisotropic full-matrix least-squares refinement on F^2 with 594 variables converged at R1 = 4.24%, for the observed data and wR2 = 10.96% for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was 0.320 $e^-/Å^3$ and the largest hole was -0.326 $e^-/Å^3$ with an RMS deviation of 0.048 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.284 g/cm^3 and F(000), 3184 e^-. The position of the hydrogen atom at N2 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

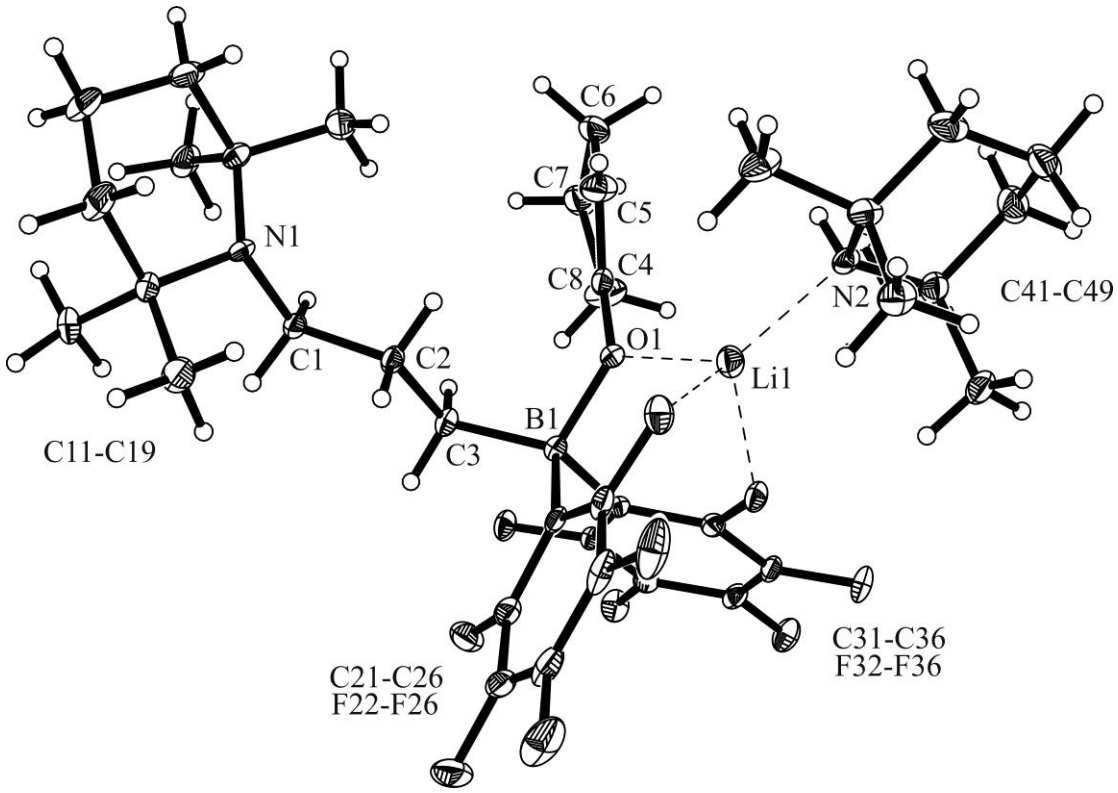
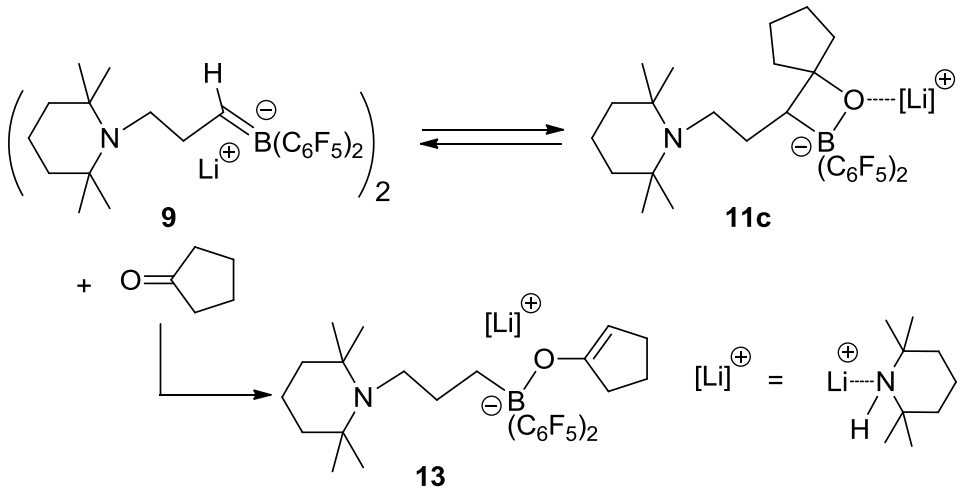


Figure S52. A view of the molecular structure of compound **13**.

We once got several single crystals from a CH_2Cl_2 solution of the above obtained solid covered with a pentane layer at -35 °C. The X-ray crystal structure analysis to our surprise revealed that we had obtained the oxaboretanide [2+2] adduct **11c** from the crystallization procedure. But our attempts to get more crystal material of compound **11** for the NMR from crystallization were not successful. We assume that in this case the boron enolate **13** is in a probably endergonic equilibrium situation with the oxaboretanide isomer **11c**. Since we never observed compound **11c** by NMR spectra, we do not have any direct evidence for this equilibrium of compound **11c** and **13**.



Scheme S11.

X-ray crystal structure analysis of compound 11c: formula $C_{38}H_{50}BF_{10}LiN_2O$, M = 758.55, colourless crystal, 0.18 x 0.10 x 0.06 mm, a = 11.3860(2), b = 12.1287(3), c = 15.1316(3) Å, α = 91.934(2), β = 94.577(1), γ = 99.948(1)°, V = 2049.3(1) Å^3, ρ_{calc} = 1.229 gcm^{-3}, μ = 0.104 mm^{-1}, empirical absorption correction (0.981 ≤ T ≤ 0.993), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 16840 reflections collected (±h, ±k, ±l), 7108 independent (R_{int} = 0.032) and 5706 observed reflections [I>2σ(I)], 490 refined parameters, R = 0.060, wR^2 = 0.142, max. (min.) residual electron density 0.39 (-0.18) e.Å^{-3}, the position of the hydrogen atom at N2 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

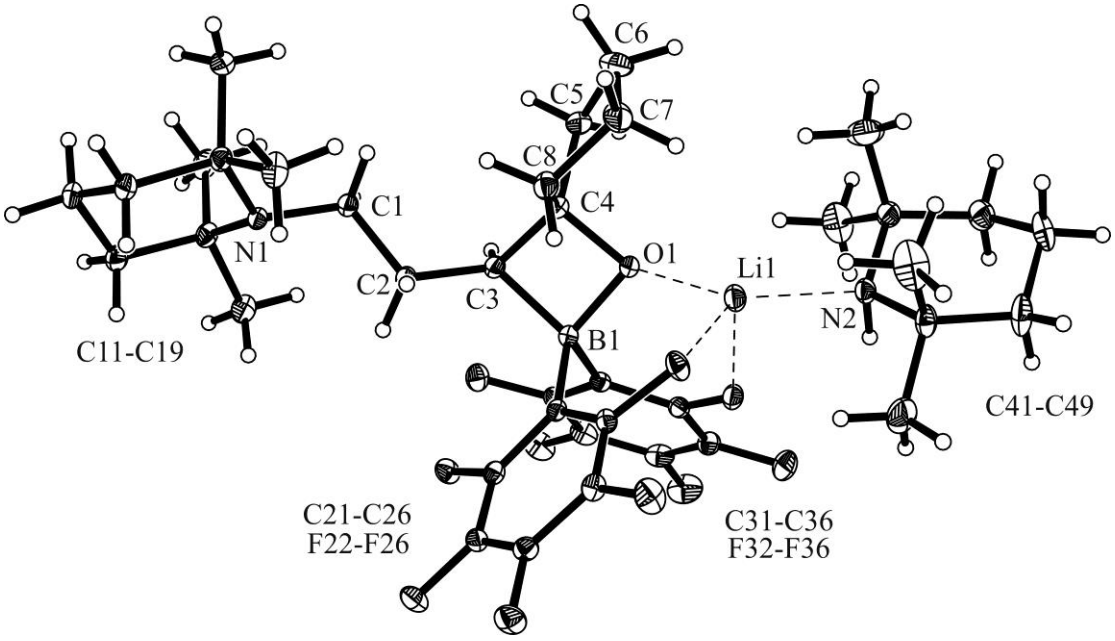
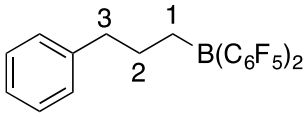


Figure S53. A view of the molecular structure of compound **11c**.

3.7 Compounds 15

3.7.1 (3-Phenylprop-1-yl)bis(pentafluorophenyl)borane (15a)

Diluted allylbenzene (11.8 mg, 0.1 mmol, 1.0 equiv, C_6D_6: 0.5 mL) was added to a suspension of Piers' borane $HB(C_6F_5)_2$ in C_6D_6 (0.3 mL). Reaction is complete usually during the course of several minutes. The hydroborated species was not isolated but characterized *in situ* by NMR experiments.



Scheme S12.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.10 (m, 2H, *m*-Ph), 7.03 (m, 1H, *p*-Ph), 7.00 (m, 2H, *o*-Ph), 2.51 (t, $^3J_{HH}$ = 7.2 Hz, 1H, C3-H), 1.85 (m, 2H, C1-H), 1.73 (m, 2H, C2-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 147.1 (dm, $^1J_{FC}$ ~ 247 Hz, C_6F_5), 143.2 (dm, $^1J_{FC}$ ~ 258 Hz, C_6F_5), 141.5 (*i*-Ph), 137.5 (dm, $^1J_{FC}$ ~ 253 Hz, C_6F_5), 128.8 (*m*-Ph), 128.7 (*o*-Ph), 126.5 (*p*-Ph), 114.1 (br s, *i*-C_6F_5), 38.7 (C3), 32.0 (br, C1), 27.2 (C2).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = 73.4 ($\nu_{1/2}$ ~ 680 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -130.3 (m, 2F, *o*-C_6F_5), -147.5 (tt, $^3J_{FF}$ = 20.8 Hz, *J* = 4.7 Hz, 1F, *p*-C_6F_5), -161.1 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 13.6].

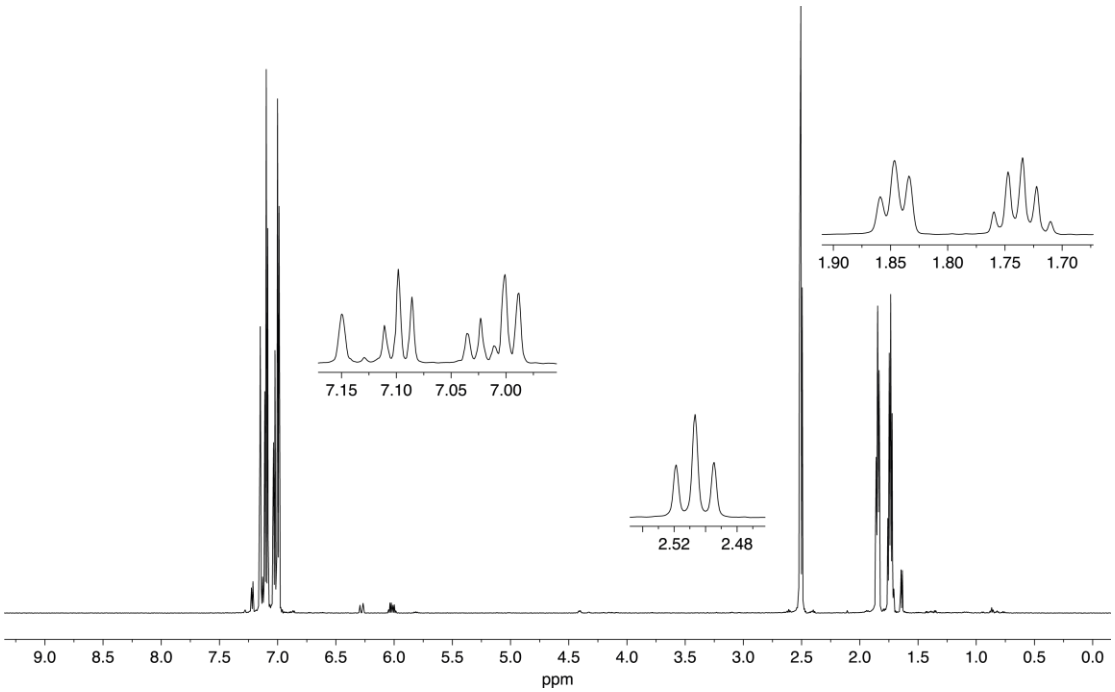


Figure S54. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15a**.

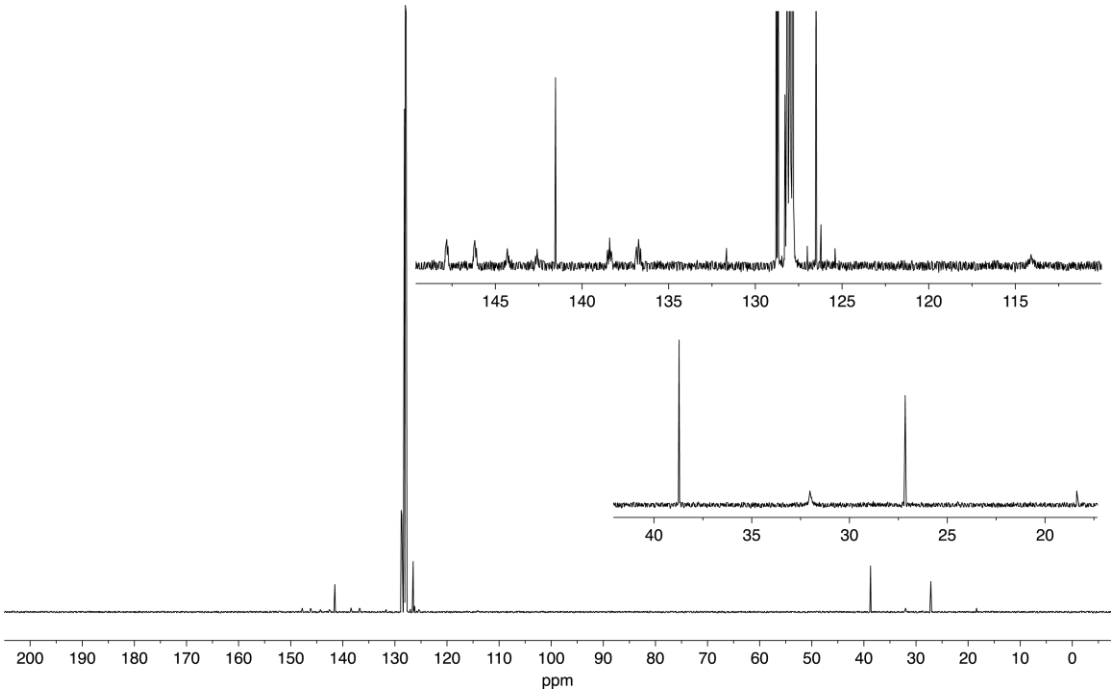


Figure S55. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15a**.

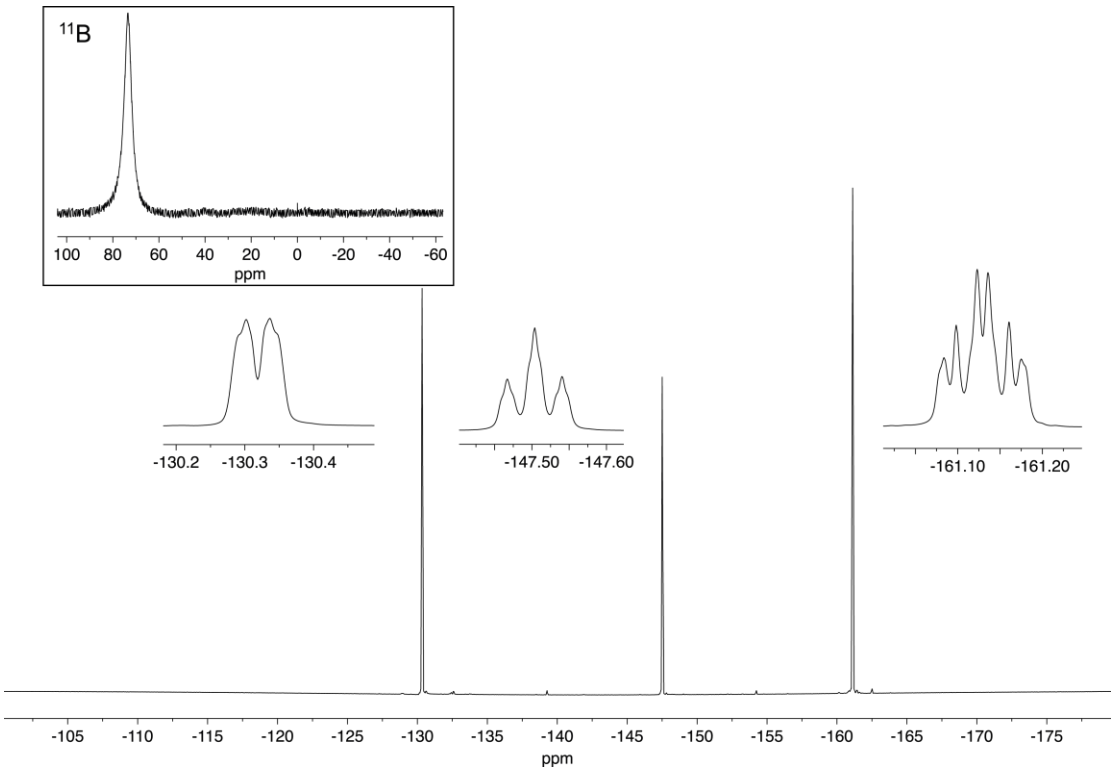
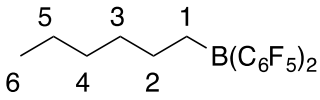


Figure S56. ^{19}F NMR (564 MHz, 299 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6) spectra of *in situ* generated compound **15a**.

3.7.2 Hex-1-ylbis(pentafluorophenyl)borane (15b)

Diluted 1-hexene (8.4 mg, 0.1 mmol, 1.0 equiv, C_6D_6: 0.5 mL) was added to a suspension of PIERS' borane $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol, 1.0 equiv) in C_6D_6 (0.3 mL). Reaction is complete usually during the course of several minutes. The hydroborated species was characterized *in situ* by NMR experiments. The obtained NMR data were consistent to those reported in the literature (Peuser, I.; Neu, R. C.; Zhao, X.; Ulrich, M.; Schirmer, B.; Tannert, J. A.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G.; Stephan, D. W. *Chem. Eur. J.* 2011, **17**, 9640.).



Scheme S13.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 1.89 (t, $^3J_{HH}$ = 7.6 Hz, 2H, C1-H), 1.45 (m, 2H, C2-H), 1.31 (m, 2H, C3-H), 1.24 (m, 2H, C5-H), 1.18 (m, 2H, C4-H), 0.87 (t, $^3J_{HH}$ = 7.2 Hz, 2H, C6-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 147.1 (dm, $^1J_{FC}$ ~ 247 Hz, C_6F_5), 143.5 (dm, $^1J_{FC}$ ~ 258 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 114.3 (br s, *i*-C_6F_5), 32.7 (C3), 32.4 (br, C1), 31.9 (C4), 25.2 (C2), 22.9 (C5), 14.2 (C6).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = 73.8 ($\nu_{1/2}$ ~ 620 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -130.7 (m, 2F, *o*-C_6F_5), -147.5 (tt, $^3J_{FF}$ = 20.7 Hz, *J* = 4.7 Hz, 1F, *p*-C_6F_5), -161.1 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 13.6].

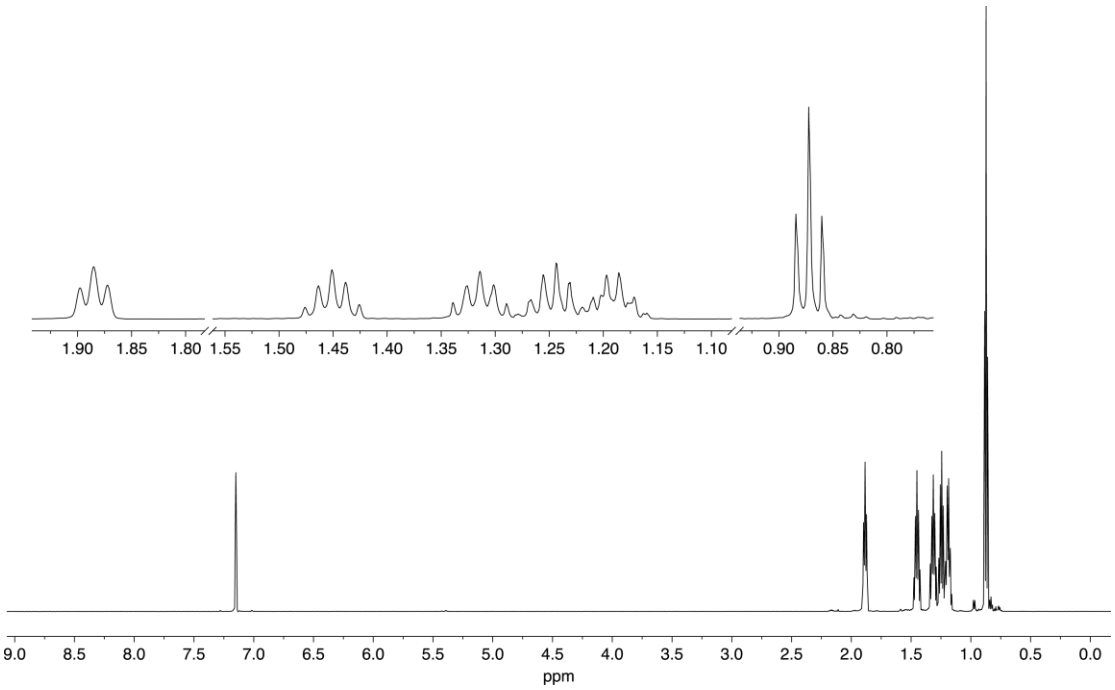


Figure S57. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15b**.

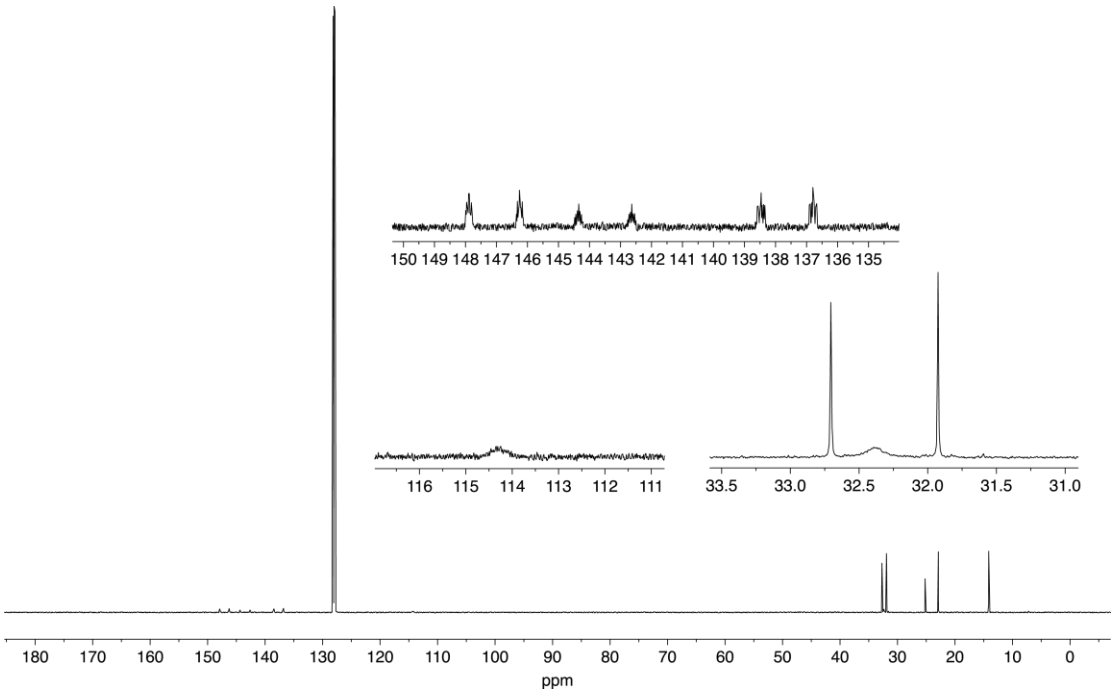


Figure S58. ^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15b**.

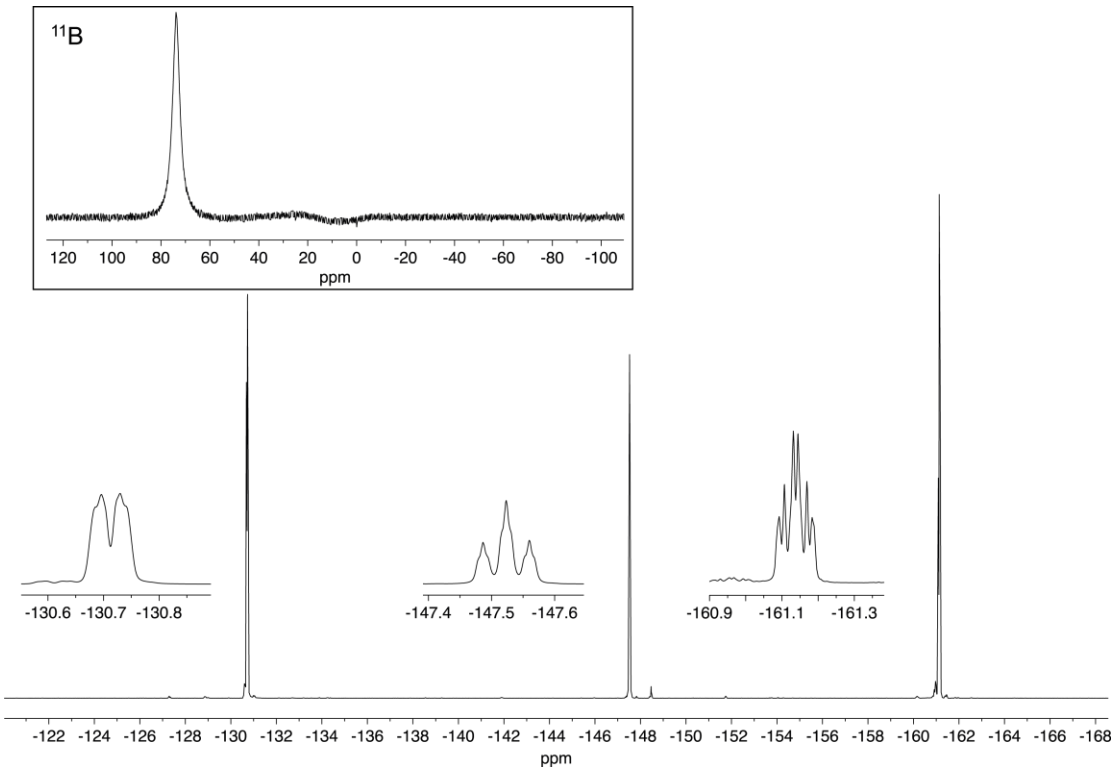
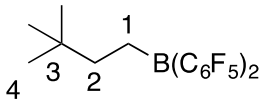


Figure S59. ^{19}F NMR (564 MHz, 299 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6) spectra of *in situ* generated compound **15b**.

3.7.3 (3,3-Dimethylbut-1-yl)bis(pentafluorophenyl)borane (15c)



Scheme S14.

Diluted 3,3-dimethylbut-1-ene (8.4 mg, 0.1 mmol, 1.0 equiv, C_6D_6: 0.5 mL) was added to a suspension of PIERS' borane $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol, 1.0 equiv) in C_6D_6 (0.3 mL). Reaction is complete usually during the course of several minutes. The hydroborated species was characterized *in situ* by NMR experiments. The obtained NMR data were consistent to those reported in the literature (Krupski, S.; Kehr, G.; Daniliuc, C. D.; Erker, G. *Dalton Trans.* 2016, **45**, 6111.).

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 1.86 (m, 2H, C1-H), 1.39 (m, 2H, C2-H), 0.87 (s, 9H, C4-H).
$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, C_6D_6): δ = 147.2 (dm, $^1J_{FC}$ ~ 244 Hz, C_6F_5), 143.5 (dm, $^1J_{FC}$ ~ 258 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 114.3 (br s, *i*-C_6F_5), 38.7 (C2), 31.1 (C3), 28.8 (C4), 27.3 (br, C1).
$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6): δ = 73.7 ($\nu_{1/2}$ ~ 600 Hz).
^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -130.6 (m, 2F, *o*-C_6F_5), -147.2 (tt, $^3J_{FF}$ = 20.8 Hz, J = 4.6 Hz, 1F, *p*-C_6F_5), -161.0 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 13.8].

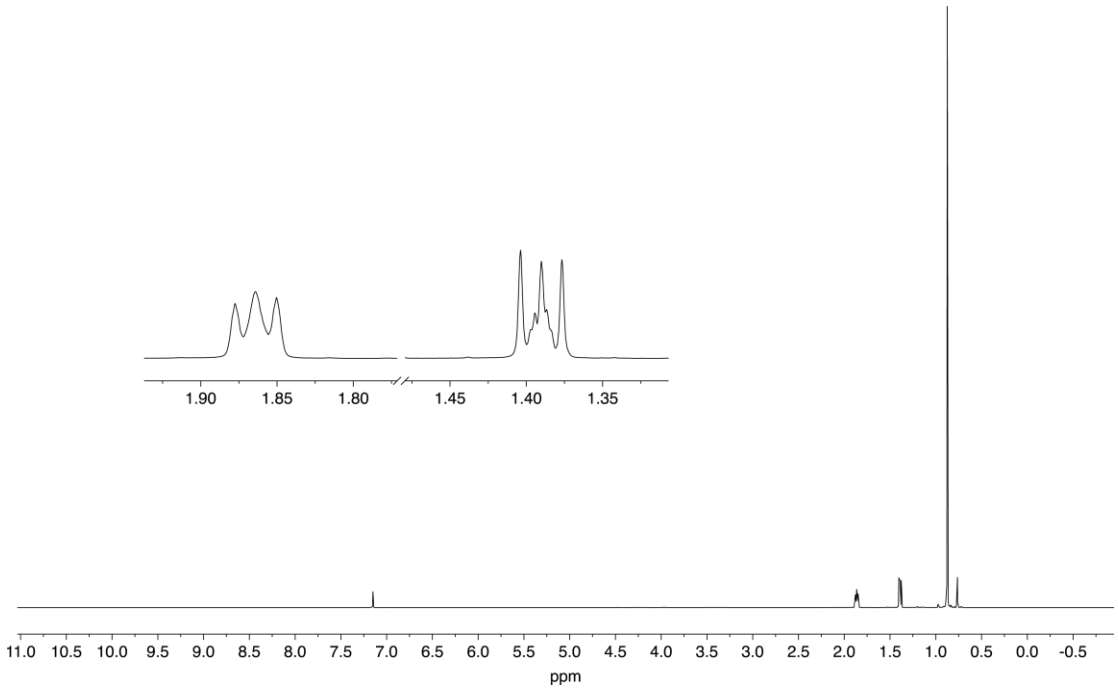


Figure S60. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15c**.

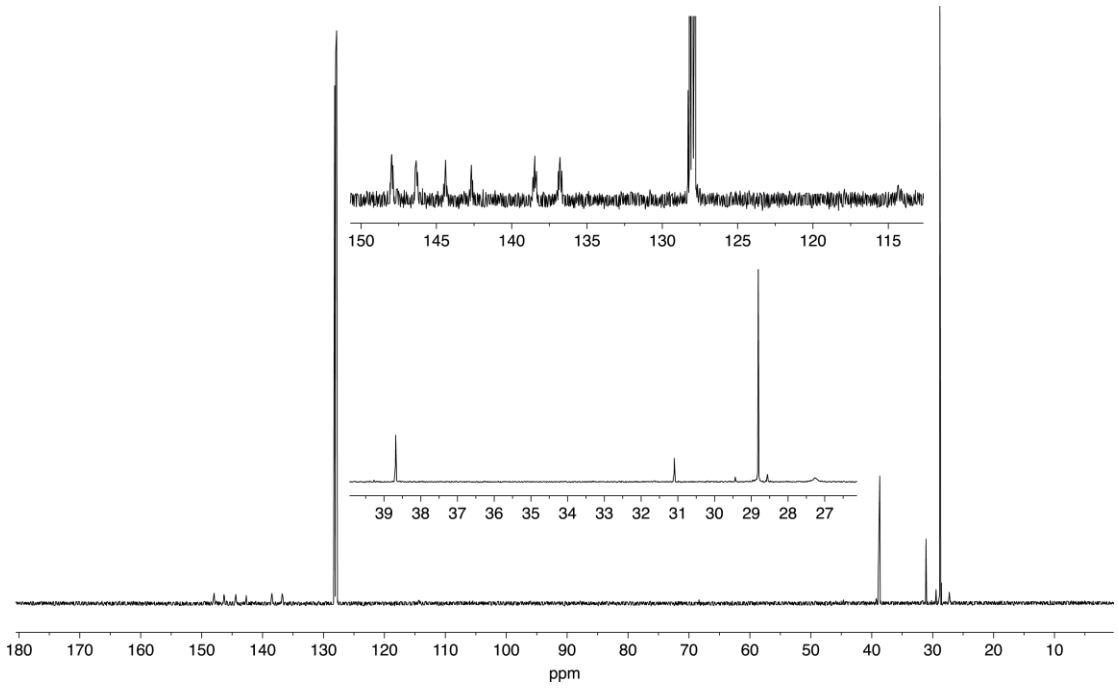


Figure S61. ^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15c**.

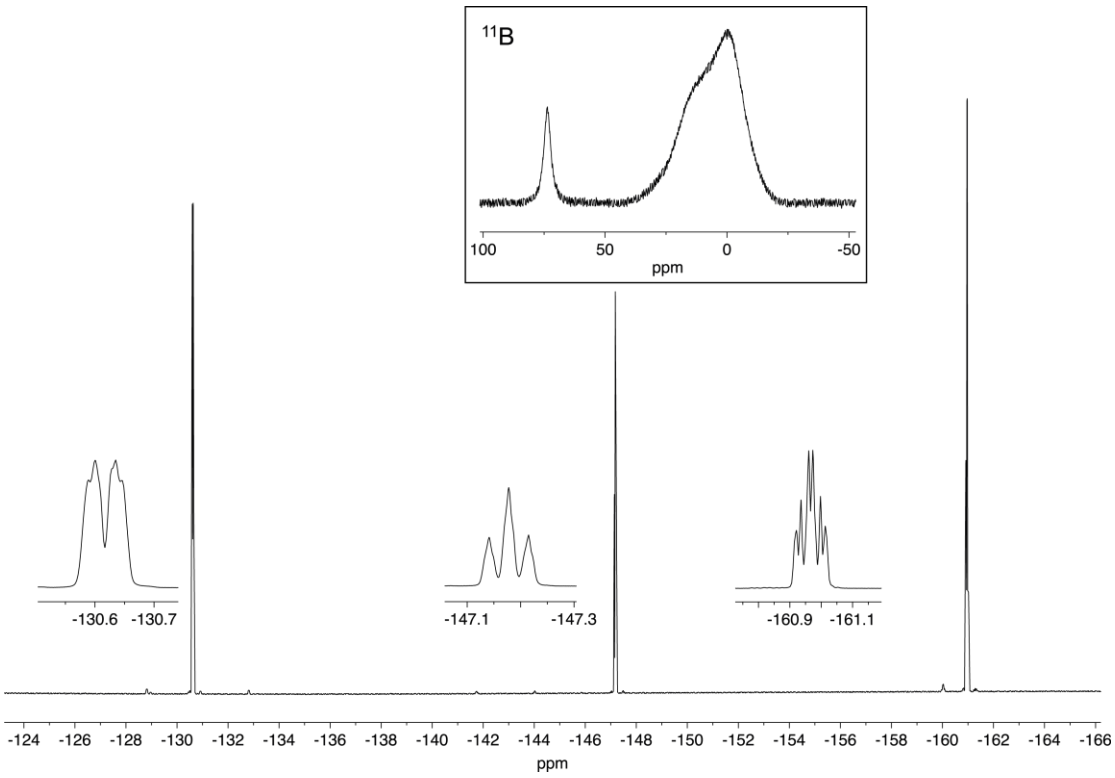
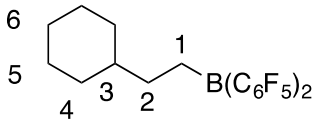


Figure S62. ^{19}F NMR (564 MHz, 299 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6) spectra of *in situ* generated compound **15c**.

3.7.4 (2-Cyclohexylethyl)bis(pentafluorophenyl)borane (15d)

Diluted vinyl cyclohexane (11.0 mg, 0.1 mmol, 1.0 equiv, C_6D_6: 0.5 mL) was added to a suspension of PIERS' borane $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol, 1.0 equiv) in C_6D_6 (0.3 mL). Reaction is complete usually during the course of several minutes. The hydroborated species was characterized *in situ* by NMR experiments.



Scheme S15.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 1.89 (t, $^3J_{HH}$ = 7.5 Hz, J = 1.3 Hz, 2H, C1-H), 1.68 (m, 2H, C5-H^{eq}), 1.66 (m, 2H, C4-H^{eq}), 1.61 (m, 1H, C6-H^{eq}), 1.39 (m, 2H, C2-H), 1.19 (m, 2H, C5-H^{ax}), 1.14 (m, 1H, C3-H^{ax}), 1.09 (m, 2H, C6-H^{ax}), 0.81 (m, 2H, C4-H^{ax}).

$^{13}C\{^1H\}$ NMR (126 MHz, 299 K, C_6D_6): δ = 147.1 (dm, $^1J_{FC}$ ~ 248 Hz, C_6F_5), 143.5 (dm, $^1J_{FC}$ ~ 258 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 114.2 (br s, *i*-C_6F_5), 40.3 (C3), 33.4 (C4), 32.8 (C2), 29.2 (br, C1), 26.9 (C6), 26.7 (C5).

$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, C_6D_6): δ = 73.0 ($\nu_{1/2}$ ~ 740 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = -130.6 (m, 2F, *o*-C_6F_5), -147.3 (tt, $^3J_{FF}$ = 21.0 Hz, J = 4.8 Hz, 1F, *p*-C_6F_5), -161.0 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 13.7].

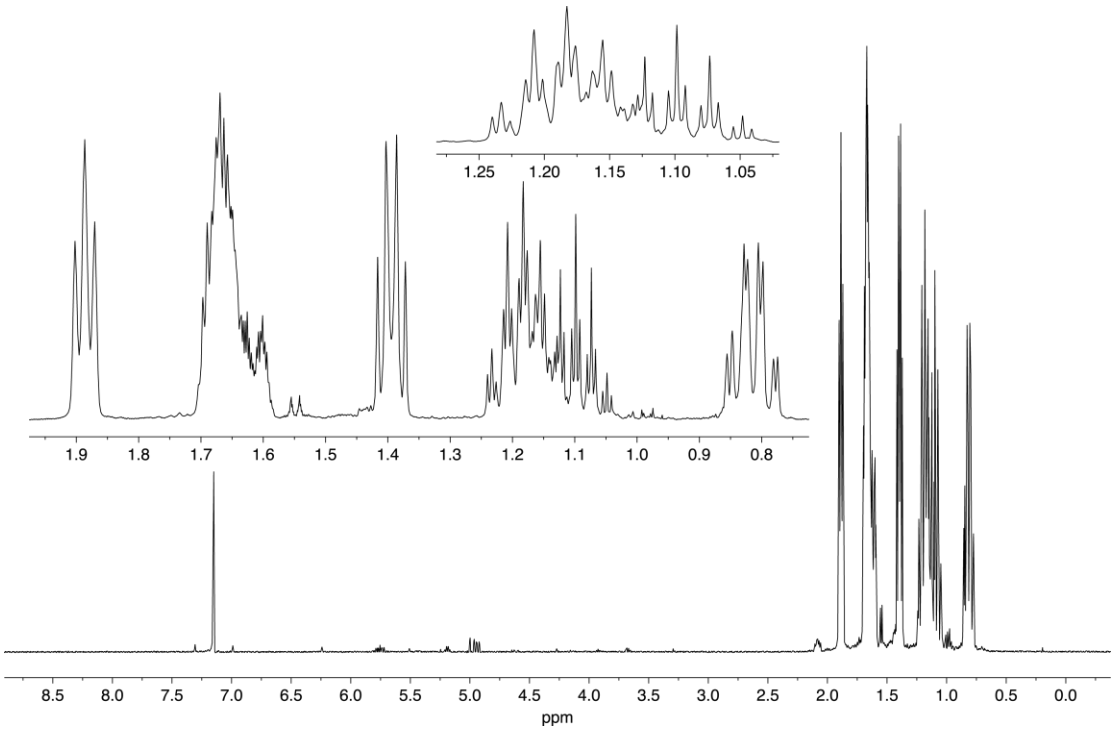


Figure S63. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15d**.

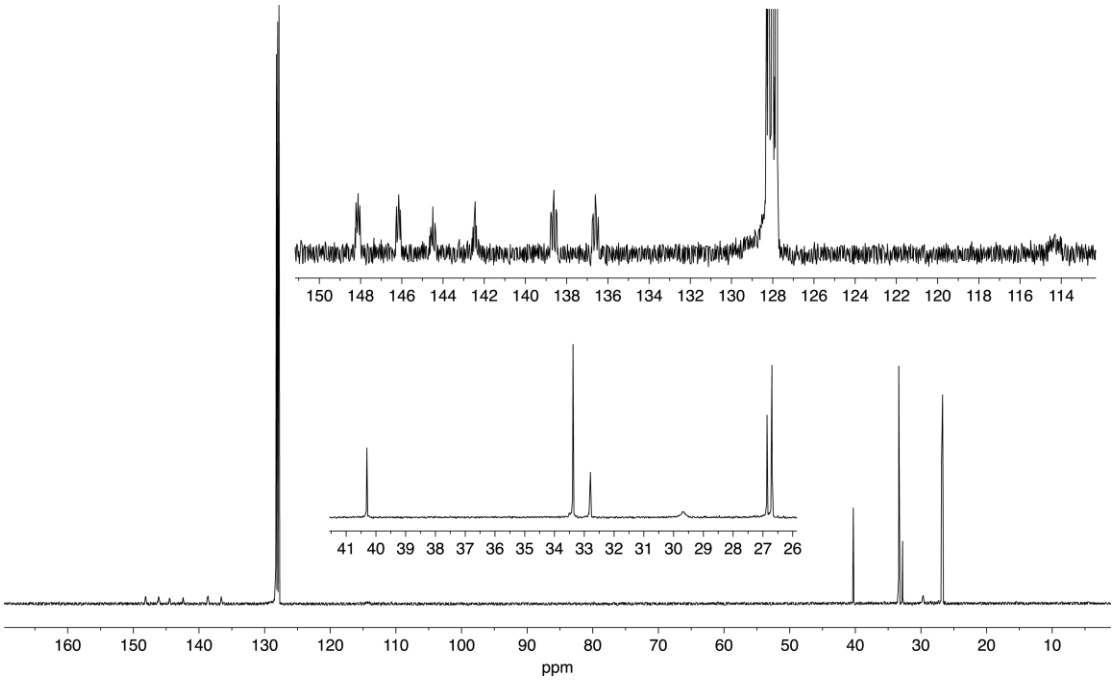


Figure S64. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15d**.

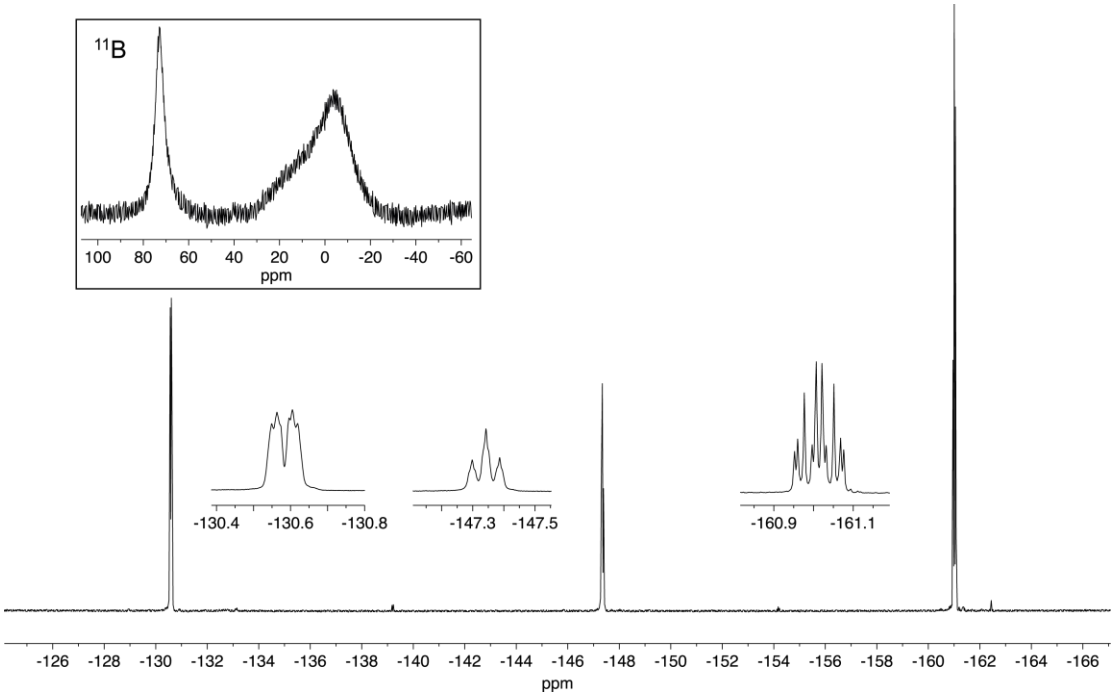
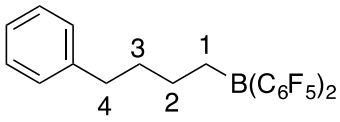


Figure S65. ^{19}F NMR (564 MHz, 299 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6) spectra of *in situ* generated compound **15d**.

3.7.5 (4-Phenylbut-1-yl)bis(pentafluorophenyl)borane (15e)

Diluted 4-phenylbut-1-ene (13.2 mg, 0.1 mmol, 1.0 equiv, C_6D_6: 0.5 mL) was added to a suspension of PIERS' borane $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol, 1.0 equiv) in C_6D_6 (0.3 mL). Reaction is complete usually during the course of several minutes. The hydroborated species was not isolated but characterized by NMR experiments.



Scheme S16.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 7.23 (m, 2H, *m*-Ph), 7.14 (m, 1H, *p*-Ph), 7.08 (m, 2H, *o*-Ph), 2.51 (t, $^3J_{HH}$ = 7.3 Hz, 2H, C4-H), 1.94 (m, 2H, C1-H), 1.63 (m, 2H, C3-H), 1.45 (m, 2H, C2-H).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 146.9 (dm, $^1J_{FC}$ ~ 247 Hz, C_6F_5), 143.5 (dm, $^1J_{FC}$ ~ 258 Hz, C_6F_5), 142.0 (*i*-Ph), 137.6 (dm, $^1J_{FC}$ ~ 252 Hz, C_6F_5), 128.59 (*m*-Ph), 128.58 (*o*-Ph), 126.2 (*p*-Ph), 114.1 (br s, *i*-C_6F_5), 35.8 (C4), 34.7 (C3), 32.1 (br, C1), 24.6 (C2).

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ = 73.9 ($\nu_{1/2}$ ~ 770 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = -132.5 (m, 2F, *o*-C_6F_5), -149.2 (tt, $^3J_{FF}$ = 20.8 Hz, *J* = 4.7 Hz, 1F, *p*-C_6F_5), -162.8 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 13.6].

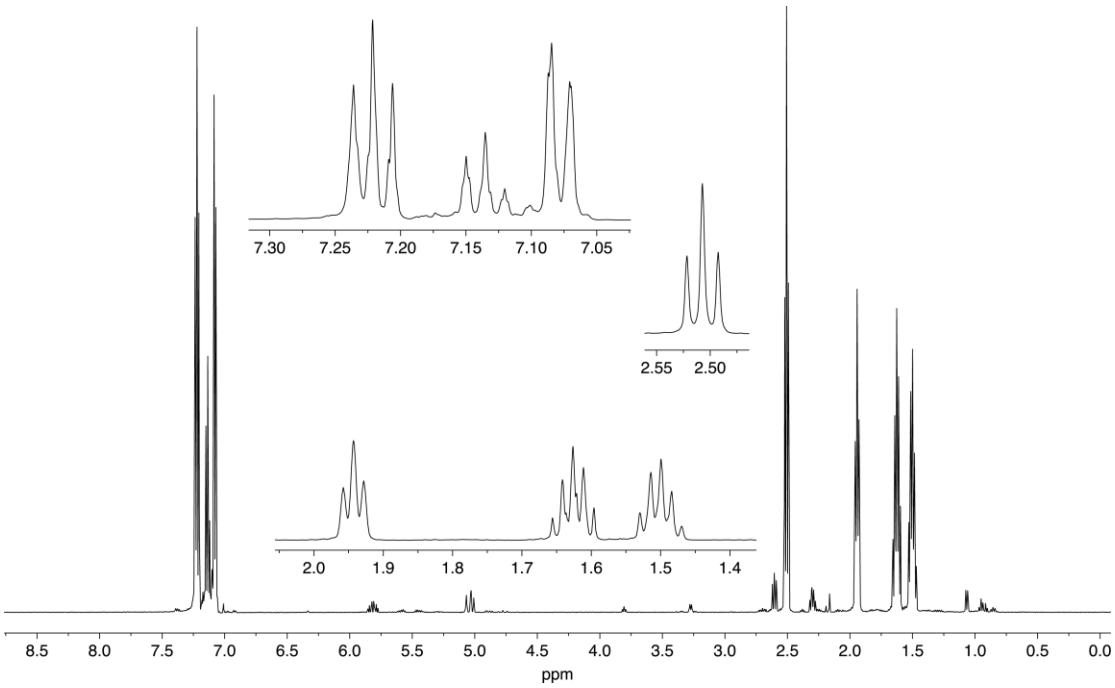


Figure S66. ^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15e**.

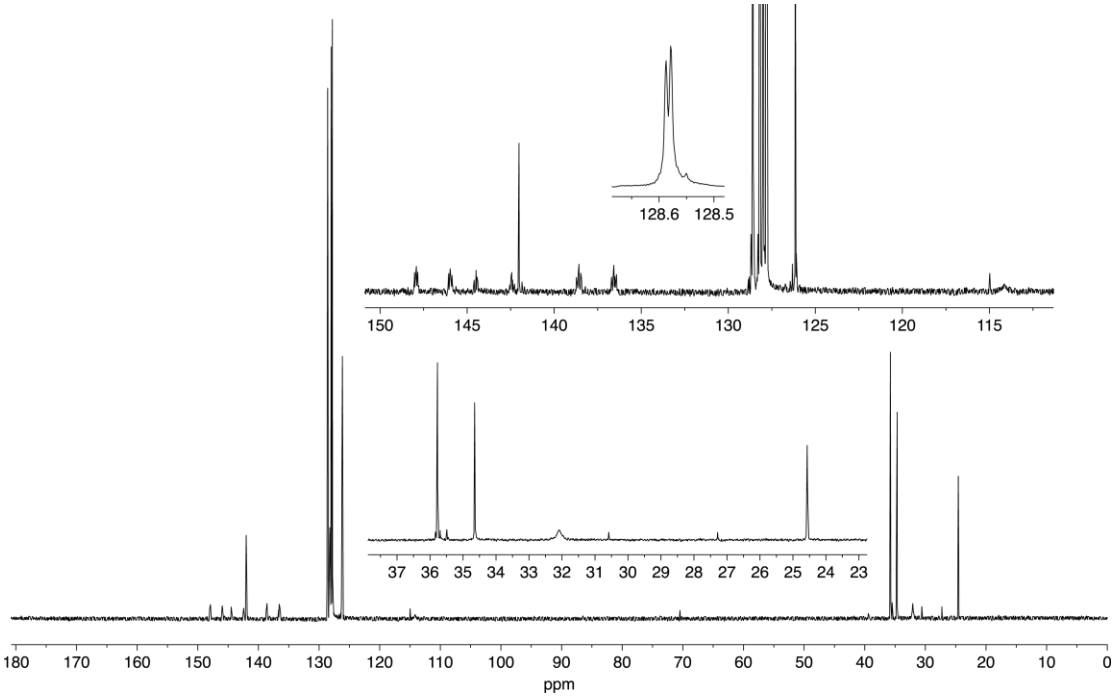


Figure S67. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **15e**.

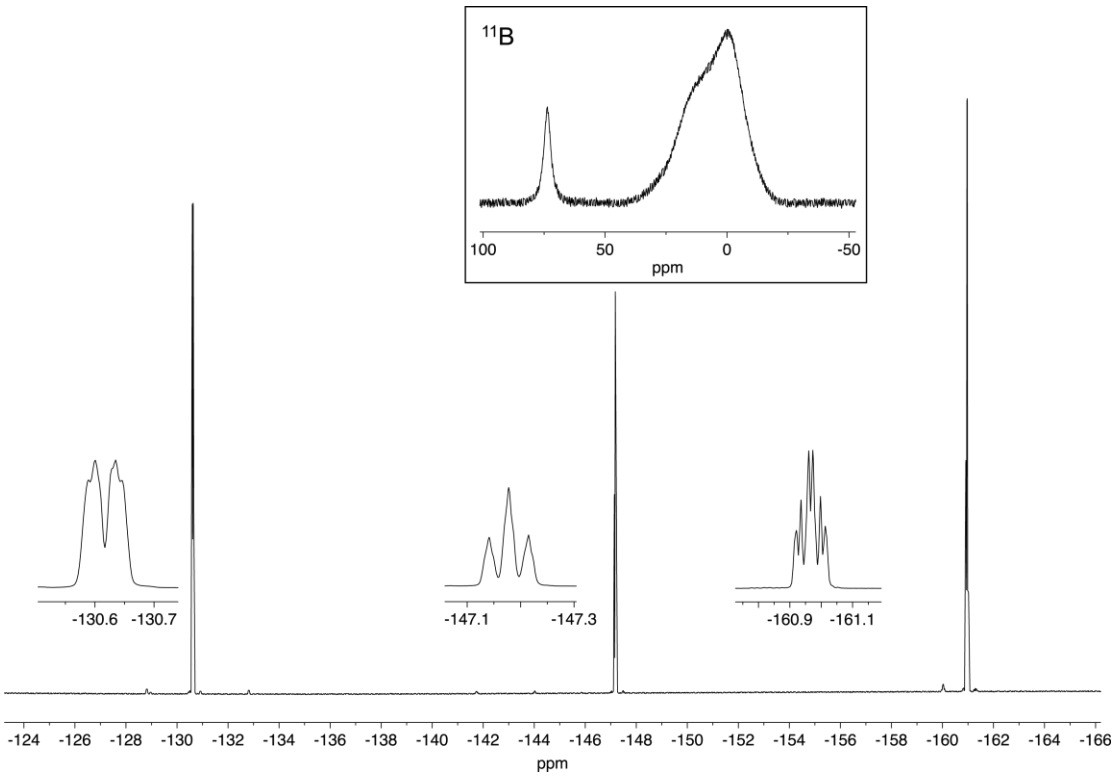
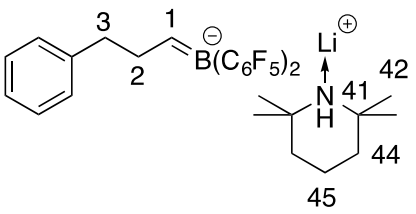


Figure S68. ^{19}F NMR (470 MHz, 299 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, C_6D_6) spectra of *in situ* generated compound **15e**.

3.8 Compounds 16

3.8.1 Lithium(HTMP) (3-phenylpropylidene)bis(pentafluorophenyl)borate (16a)



Scheme S17.

Isolation: Allylbenzene (118 mg, 1.0 mmol, 1.0 equiv) was diluted with pentane (2.0 mL) and added to a suspension of $HB(C_6F_5)_2$ (346 mg, 1.0 mmol, 1.0 equiv) in pentane (8.0 mL). The reaction mixture was stirred for 2 h before solid LiTMP (147 mg, 1.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred overnight and decanted. The liquid layer was stored at -32 °C causing a phase separation. The lower layer was dried *in vacuo* to afford a yellowish foam in 58% yield (353 mg, 0.6 mmol). The upper layer eventually furnished some crystals suitable for the X-ray crystal structure analysis by slow evaporation of the solvent at -32 °C. Some geminal hydride-bridged bisborane was obtained as by-product ($\delta^{11}B$ [ppm] = 24.8 (**16a**), -17.6 (**16a**-byproduct, see below *3.8.1.2*)).

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.23 (m, 2H, *o*-Ph), 7.15 (m, 2H, *m*-Ph), 7.02 (m, 1H, *p*-Ph), 4.24 (t, $^{3}J_{HH}$ = 8.1 Hz, 1H, C1-H), 2.89 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, C3-H), 2.41 (m, 2H, C2-H), 1.15 (m, 2H, C45-H), 0.80 (br, 4H, C44-H), 0.71 (br, 12H, C42-H), 0.29 (br, 1H, N-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 146.9 (dm, $^{1}J_{FC}$ ~ 234 Hz, C_6F_5), 146.4 (dm, $^{1}J_{FC}$ ~ 223 Hz, C_6F_5), 143.4 (*i*-Ph), 139.7 (dm, $^{1}J_{FC}$ ~ 251 Hz, C_6F_5), 139.5 (dm, $^{1}J_{FC}$ ≈ 249 Hz, C_6F_5), 137.6 (dm, $^{1}J_{FC}$ ~ 250 Hz, $2C_6F_5$), 129.0 (*o*-Ph), 128.5 (*m*-Ph), 125.9 (*p*-Ph), 120.6, 119.2 (each br, *i*-C_6F_5), 103.4 (br, C1), 50.9 (C41), 41.6 (C3), 37.7 (C44), 34.7 (C2), 30.4 (C42), 17.4 (C45).

^{7}Li NMR (233 MHz, 299 K, C_6D_6): δ = 1.0 ($\nu_{1/2}$ ≈ 20 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = 24.8 ($\nu_{1/2}$ ~ 400 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -135.3 (m, 2F, *o*-$C_6F_5^{A}$), -135.4 (br, 2F, *o*-$C_6F_5^{B}$), -157.7 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^{B}$), -158.7 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^{A}$), -162.5 (m, 2F, *m*-$C_6F_5^{B}$), -163.0 (m, 2F, *m*-$C_6F_5^{A}$) [$\Delta\delta^{19}F_{m,p}$ = 4.3^{A}, 4.8^{B}].

Elemental analysis: calc. for $C_{30}H_{29}BF_{10}LiN$ (611.30 g mol^{-1}): C, 58.94; H, 4.78; N, 2.29; Found: C, 58.17; H, 4.50; N 2.20.

Melting Point: 75 °C.

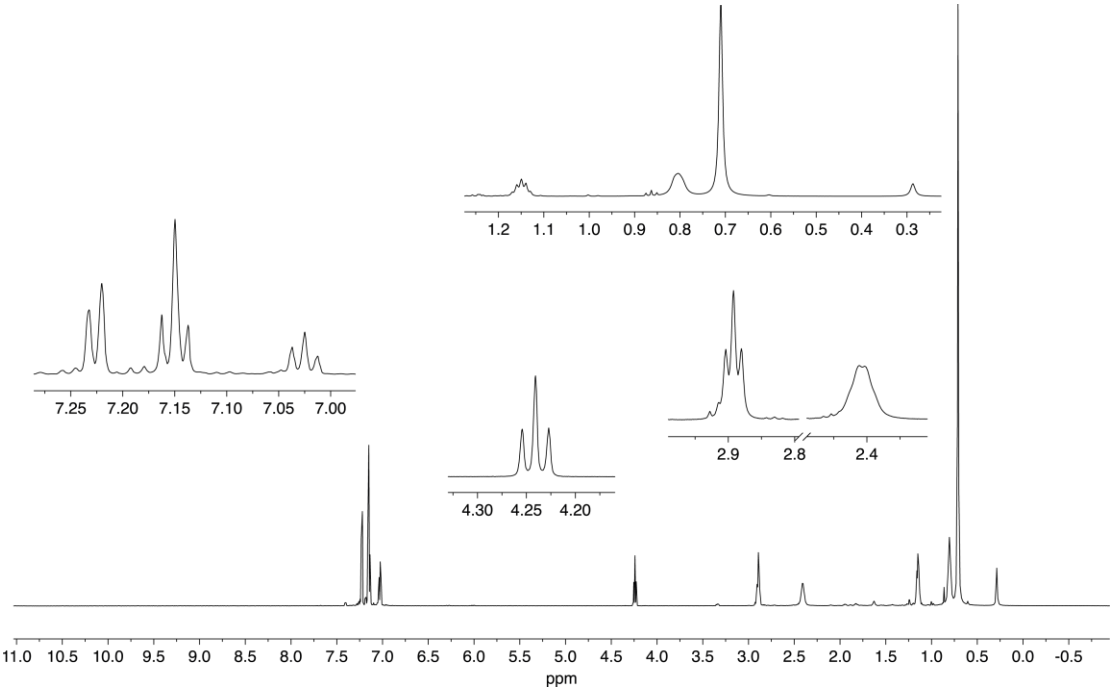


Figure S69. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of isolated compound **16a**.

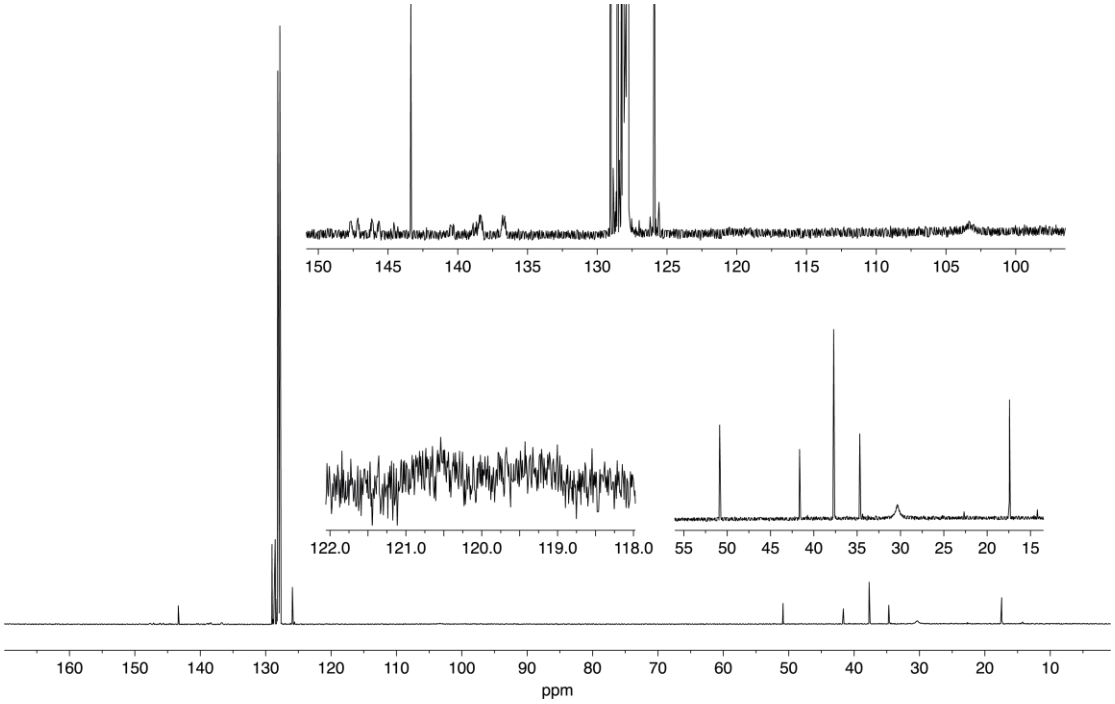


Figure S70. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of isolated compound **16a**.

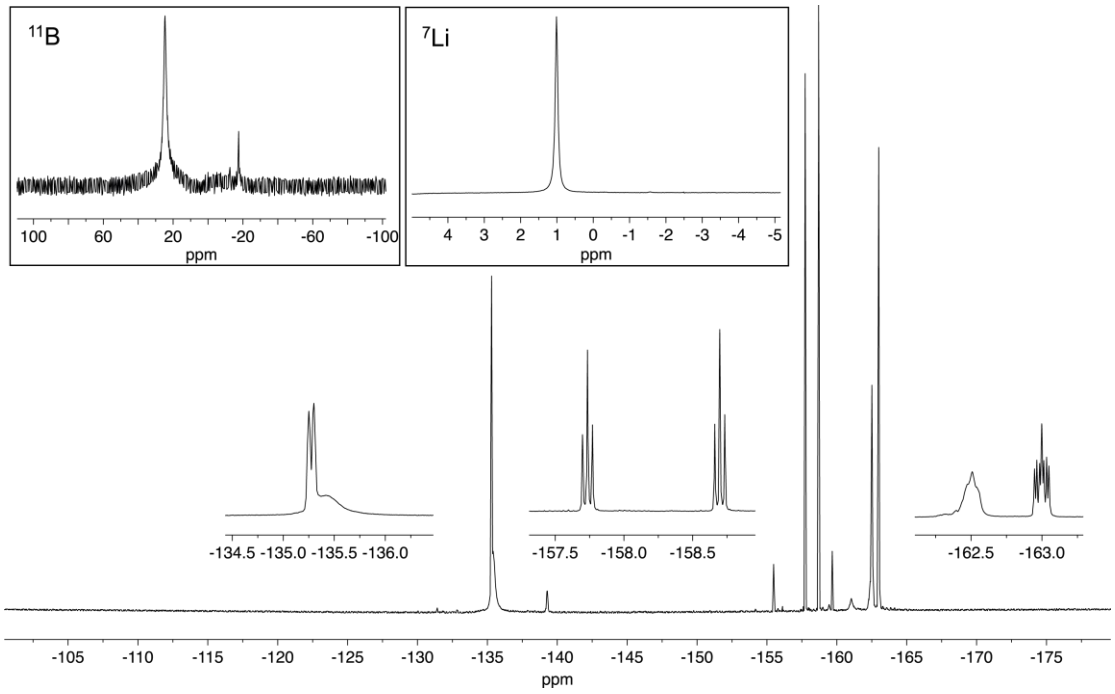


Figure S71. ^{19}F NMR (564 MHz, 299 K, C_6D_6), $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, C_6D_6) and ^{7}Li NMR (233 MHz, 299 K, C_6D_6) spectra of isolated compound **16a**.

X-ray crystal structure analysis of compound 16a: A colorless prism-like specimen of $C_{30}H_{29}BF_{10}LiN$, approximate dimensions 0.100 mm x 0.120 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1412 frames were collected. The total exposure time was 25.73 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 35307 reflections to a maximum θ angle of 66.78° (0.84 Å resolution), of which 9950 were independent (average redundancy 3.548, completeness = 95.7%, R_{int} = 7.80%, R_{sig} = 9.27%) and 6188 (62.19%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.3926(9) Å, b = 14.9007(13) Å, c = 16.7950(14) Å, α = 72.685(5)°, β = 82.243(5)°, γ = 84.547(5)°, volume = 2928.8(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 5427 reflections above 20 σ(I) with 5.546° < 2θ < 131.5°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.806. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8810 and 0.9000. The final anisotropic full-matrix least-squares refinement on F^2 with 792 variables converged at R1 = 6.21%, for the observed data and wR2 = 18.16% for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 0.361 $e^-/Å^3$ and the largest hole was -0.303 $e^-/Å^3$ with an RMS deviation of 0.063 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.386 g/cm^3 and F(000), 1256 e^-. The positions of the hydrogen atoms at N1A and N1B were refined freely; others hydrogen atoms were calculated and refined as riding atoms.

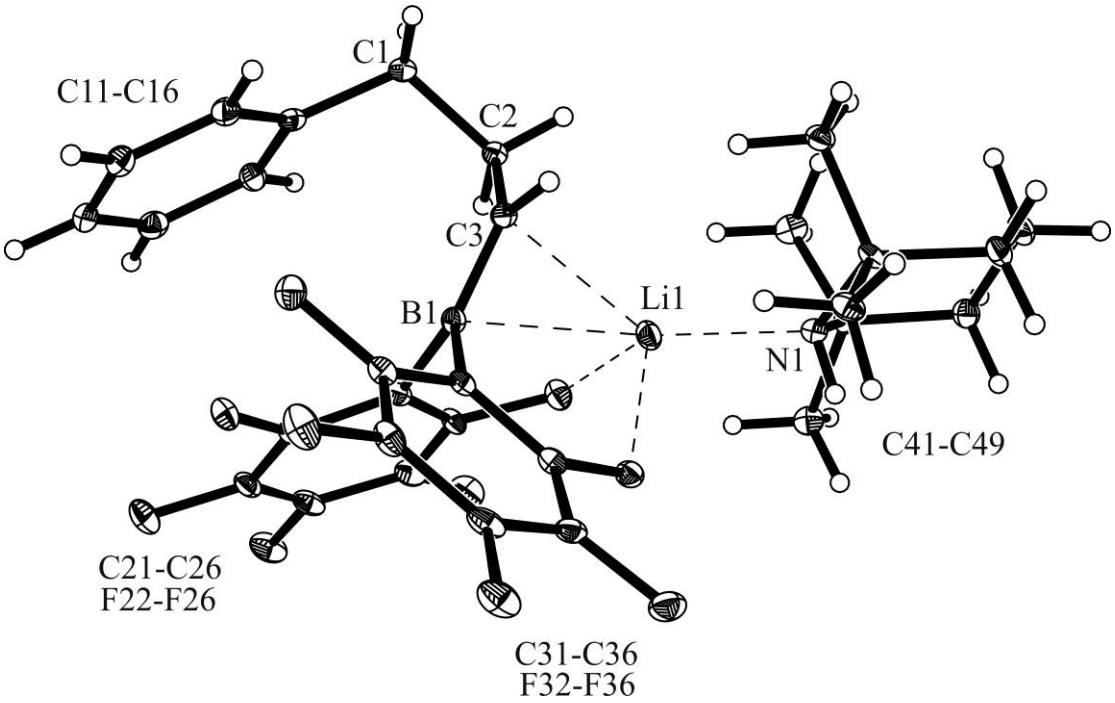
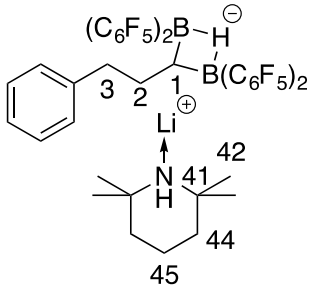


Figure S72. A view on the molecular structure of compound **16a**.

3.8.1.1 General Procedure: Preparation of Compound 16a

Allylbenzene (118 mg, 1.0 mmol, 1.0 equiv) was diluted with toluene (2.0 mL) and added to a suspension of $HB(C_6F_5)_2$ (346 mg, 1.0 mmol, 1.0 equiv) in toluene (2.0 mL). The reaction mixture was stirred for 5 min before solid LiTMP (147 mg, 1.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred until the base was dissolved (reaction complete, ca. 3 h). The obtained reaction mixture was diluted to a total volume of 20 mL in these cases when carboxylic acid derivatives were used as substrates (sensitive to concentration).

3.8.1.2 Lithium(HTMP) μ-hydrido-(3-phenylpropane-1,1-diyl)bis(bis(pentafluoro-phenyl)borate)



Scheme S18.

In pentane: Diluted allylbenzene (118.2, 1.0 mmol, 1.0 equiv) in pentane (2.0 mL) was added to a suspension of $HB(C_6F_5)_2$ (345.9 mg, 1.0 mmol, 1.0 equiv) in pentane (18 mL). After stirring for 40 min solid LiTMP (147.2 mg, 1.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred overnight before the second equivalent of $HB(C_6F_5)_2$ (345.9 mg, 1.0 mmol, 1.0 equiv) was added. The yellow reaction mixture was stirred for another 15 h during which a white precipitate was formed. From the remaining liquid layer a second solid fraction was isolated after concentration *in vacuo* to a total volume of 2 mL. The white solid fractions were isolated in a combined yield of 59% (566 mg, 0.59 mmol).

In toluene: Allylbenzene (59.1 mg, 0.5 mmol, 1.0 equiv) was diluted with toluene (1.0 mL) and added to a suspension of $HB(C_6F_5)_2$ (173.0 mg, 1.0 mmol, 1.0 equiv) in toluene (2.0 mL). The reaction mixture was stirred for 5 min before solid LiTMP (73.6 mg, 1.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred overnight before a second equivalent of $HB(C_6F_5)_2$ (173.0 mg, 1.0 mmol, 1.0 equiv) was added. After stirring for 16 h the reaction mixture was concentrated *in vacuo*. The residue was suspended in pentane (3 mL). The suspension was decanted and the residue was washed with additional pentane (3 x 1.5 mL) to afford a white solid after drying *in vacuo* in 49% yield (233 mg, 0.24 mmol). Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a saturated solution of the obtained solid in pentane at -32 °C.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.37 (m, 2H, *o*-Ph), 7.17 (m, 2H, *m*-Ph), 7.01 (m, 1H, *p*-Ph), 3.29 (t, $^3J_{HH}$ = 8.0 Hz, 2H, C3-H), 2.02 (br, 1H, B-H-B), 1.87 (m, 2H, C2-H), 1.81 (m, 1H, C1-H), 1.23 (m, 2H, C45-H), 0.87 (br, 16H, C42,44-H), 0.61 (br, 1H, N-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 148.3 (dm, $^1J_{FC}$ ~ 229 Hz, C_6F_5), 144.3 (*i*-Ph), 140.0 (dm, $^1J_{FC}$ ~ 253 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 256 Hz, C_6F_5), 128.9 (*o*-Ph), 128.7 (*m*-Ph), 125.9 (*p*-Ph), 117.2 (each br, *i*-C_6F_5), 51.5 (C41), 39.6 (C3), 38.0 (C44), 33.7 (C2), 17.3 (C45), 11.4 (br, C1) [C42 not observed].

^{7}Li NMR (233 MHz, 299 K, C_6D_6): δ = -1.0 ($\nu_{1/2}$ ~ 210 Hz).

^{11}B NMR (192 MHz, 299 K, C_6D_6): δ = -17.4 ($\nu_{1/2}$ ~ 720 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ [ppm] = -17.4 ($\nu_{1/2}$ ~ 680 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -134.8 (br, 1F, *o*-$C_6F_5^A$), -136.8 (br, 1F, *o*-$C_6F_5^B$), -155.6 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), -161.2 (br, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.6].

Elemental analysis: calc. for $C_{42}H_{30}B_2F_{20}LiN$ (957.23 g mol^{-1}): C, 52.70; H, 3.16; N, 1.46; Found: C, 52.87; H, 3.34; N, 1.76.

Melting Point: 124 °C.

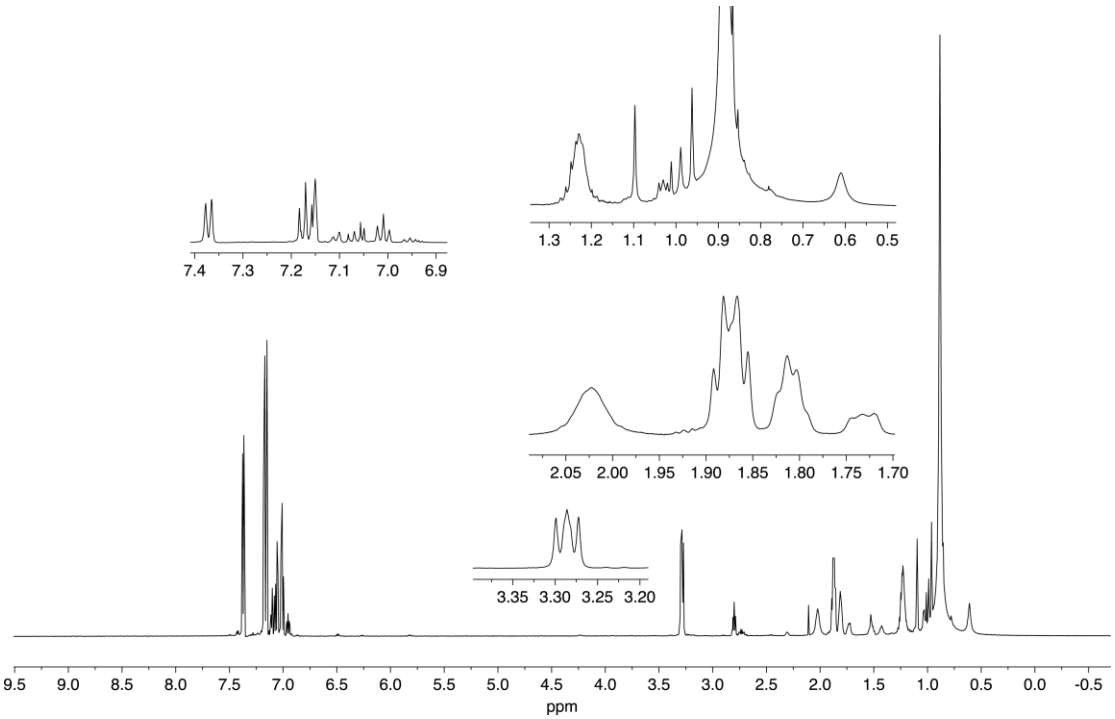


Figure S73. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of the **16a**-byproduct.

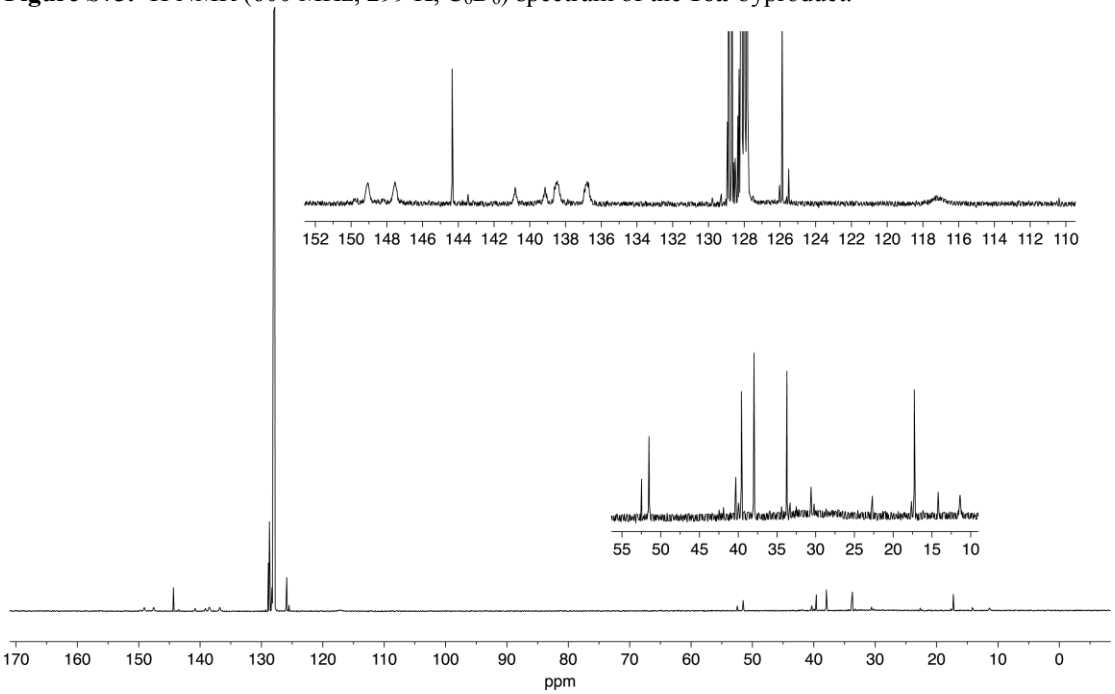


Figure S74. ^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) spectrum of the **16a**-byproduct.

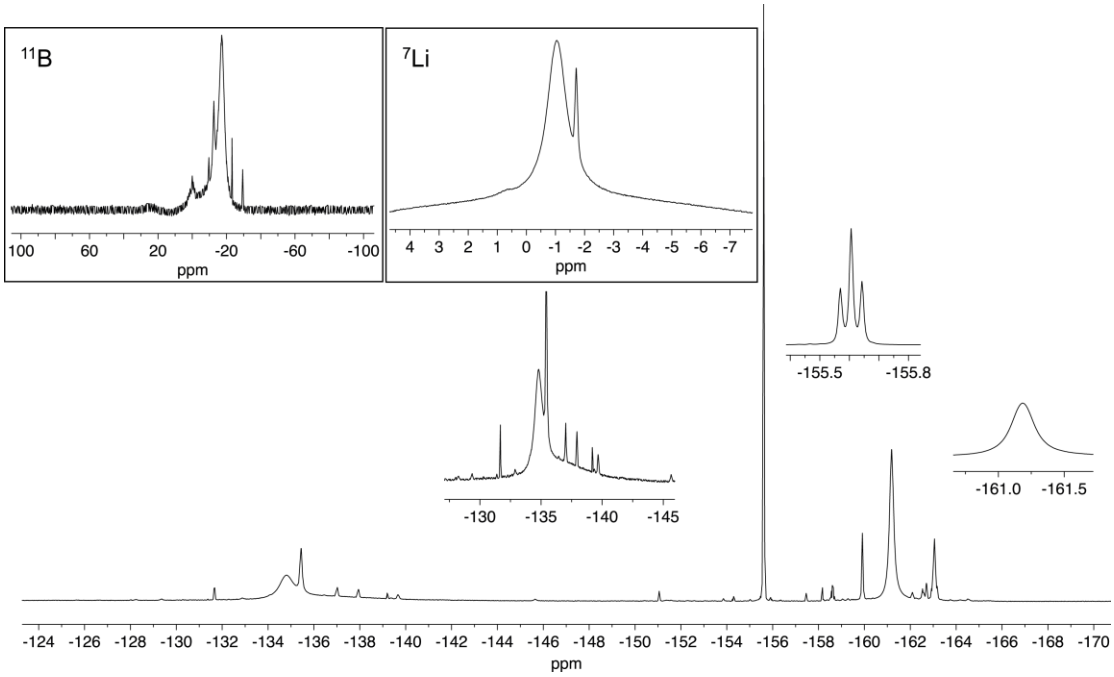


Figure S75. ^{19}F NMR (564 MHz, 299 K, C_6D_6), $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6) and ^7Li NMR (233 MHz, 299 K, C_6D_6) spectra of the **16a**-byproduct.

X-ray crystal structure analysis of compound 16a-byproduct: A colorless plate-like specimen of $C_{42}H_{30}B_2F_{20}LiN$, approximate dimensions 0.050 mm x 0.140 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1834 frames were collected. The total exposure time was 17.87 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 30146 reflections to a maximum θ angle of 66.56° (0.84 Å resolution), of which 6972 were independent (average redundancy 4.324, completeness = 99.8%, R_{int} = 6.53%, R_{sig} = 5.43%) and 5897 (84.58%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.1438(8) Å, b = 19.1936(16) Å, c = 10.2323(8) Å, β = 91.835(9)°, volume = 1991.2(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 8489 reflections above 20 σ(I) with 8.646° < 2θ < 132.6°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.816. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7860 and 0.9330. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1$, with Z = 2 for the formula unit, $C_{42}H_{30}B_2F_{20}LiN$. The final anisotropic full-matrix least-squares refinement on F^2 with 611 variables converged at R1 = 3.80%, for the observed data and wR2 = 8.69% for all data. The goodness-of-fit was 1.029. The largest peak in the final difference electron density synthesis was 0.193 $e^-/Å^3$ and the largest hole was -0.191 $e^-/Å^3$ with an RMS deviation of 0.043 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.597 g/cm^3 and F(000), 964 e^-.

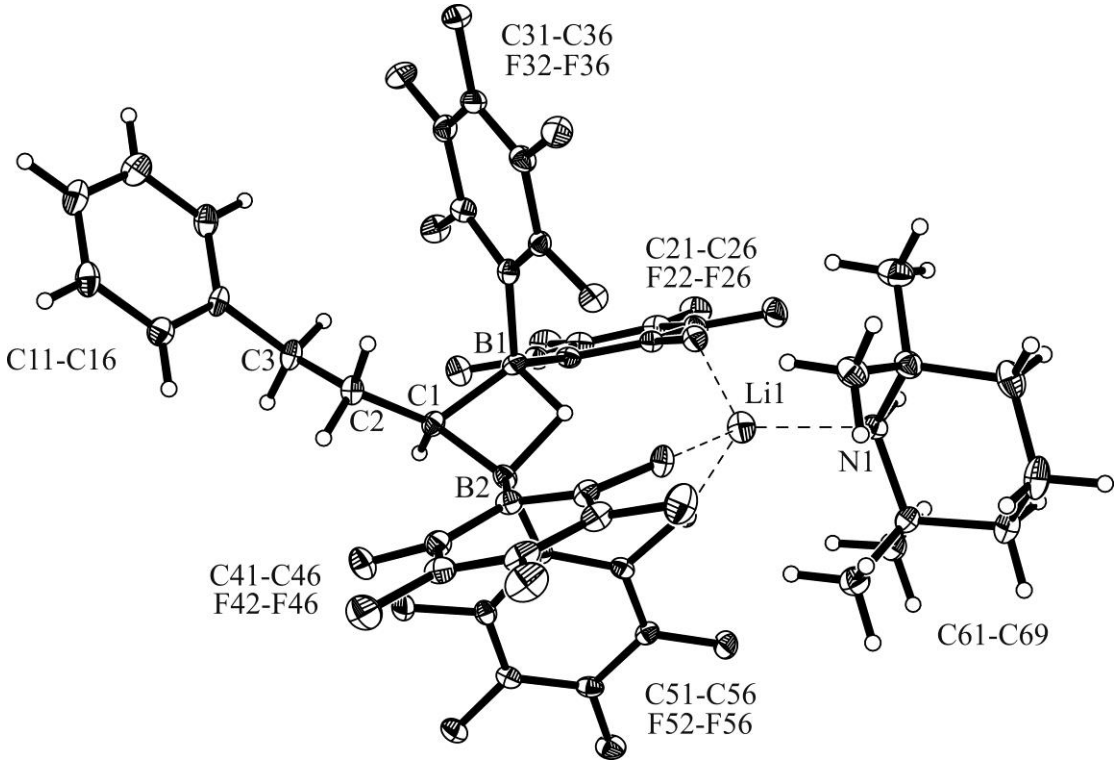
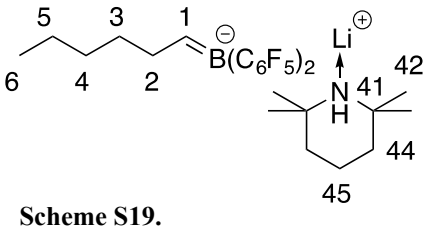


Figure S76. A view on the molecular structure of the **16a**-byproduct.

3.8.2 Lithium(HTMP) hex-1-ylidenebis(pentafluorophenyl)borate (16b)

Diluted 1-hexene (8.4 mg, 0.1 mmol, 1.0 equiv, C_6D_6: 0.5 mL) was added to a suspension of PIERS' borane $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol, 1.0 equiv) in C_6D_6 (0.3 mL). After 5 min solid LiTMP (14.7 mg, 0.1 mmol, 1.0 equiv) was added. The mixture was shaken for 3 h in the J. Young-NMR tube before being analyzed by NMR spectroscopic means. Borata-alkene alongside to some tetracoordinate borate species obtained.



Scheme S19.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 4.29 (t, $^3J_{HH}$ = 8.2 Hz, 1H, C1-H), 2.16 (m, 2H, C2-H), 1.65 (m, 2H, C3-H), 1.50 (m, 2H, C4-H), 1.36 (m, 2H, C5-H), 1.17 (m, 2H, C45-H), 0.94 (t, $^3J_{HH}$ = 7.3 Hz, 3H, C6-H), 0.83 (br, 4H, C44-H), 0.76 (br, 12H, C42-H), 0.40 (br, 1H, N-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 149.2 (dm, $^1J_{FC}$ ~ 232 Hz, C_6F_5), 147.1 (dm, $^1J_{FC}$ ~ 233 Hz, C_6F_5), 146.2 (dm, $^1J_{FC}$ ~ 225 Hz, C_6F_5), 139.7 (dm, $^1J_{FC}$ ~ 233 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 253 Hz, C_6F_5), 120.8, 119.9 (each br, *i*-C_6F_5), 104.5 (br, C1), 51.1 (C41), 37.7 (C44), 34.8 (C3), 31.9 (C2), 31.7 (C4), 30.4 (br, C42), 23.1 (C5), 17.4 (C45), 14.3 (C6).

^{7}Li NMR (233 MHz, 299 K, C_6D_6): δ = 1.1 ($\nu_{1/2}$ ~ 22 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = 24.2 ($\nu_{1/2}$ ~ 350 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -134.5 (m, 2F, *o*-$C_6F_5^B$), -135.9 (br, 2F, *o*-$C_6F_5^A$), -158.2 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-$C_6F_5^A$), -159.2 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-$C_6F_5^B$), -162.7 (m, 2F, *m*-$C_6F_5^A$), -163.5 (m, 2F, *m*-$C_6F_5^B$) [$\Delta\delta^{19}F_{m,p}$ = 4.5^A, 4.3^B].

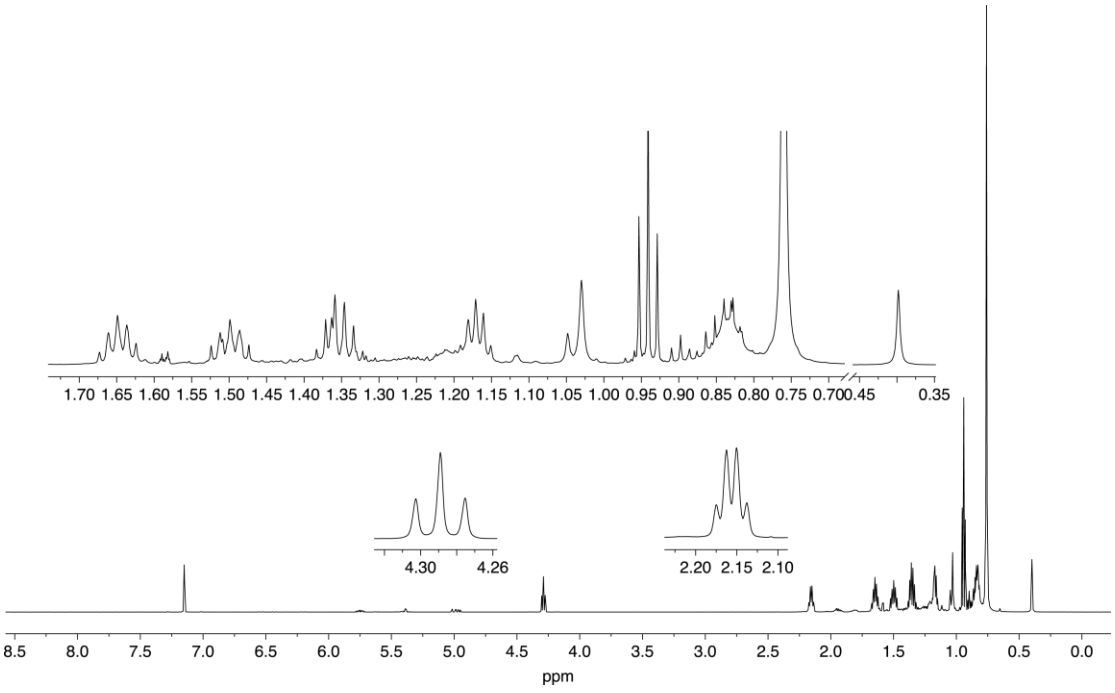


Figure S77. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **16b**.

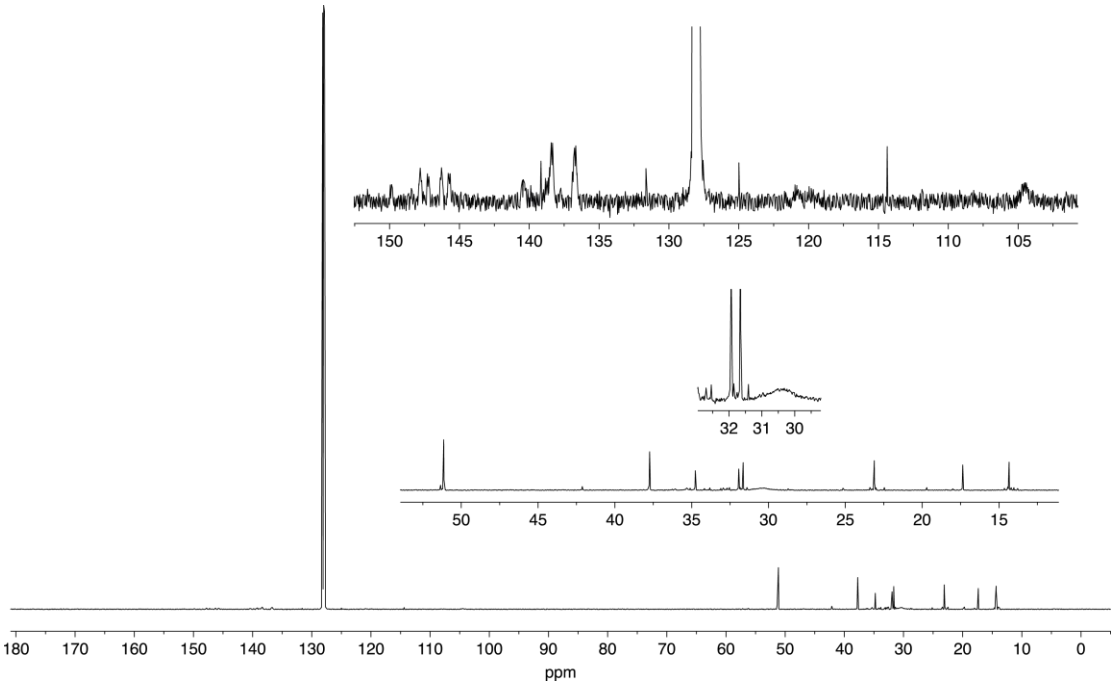


Figure S78. $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **16b**.

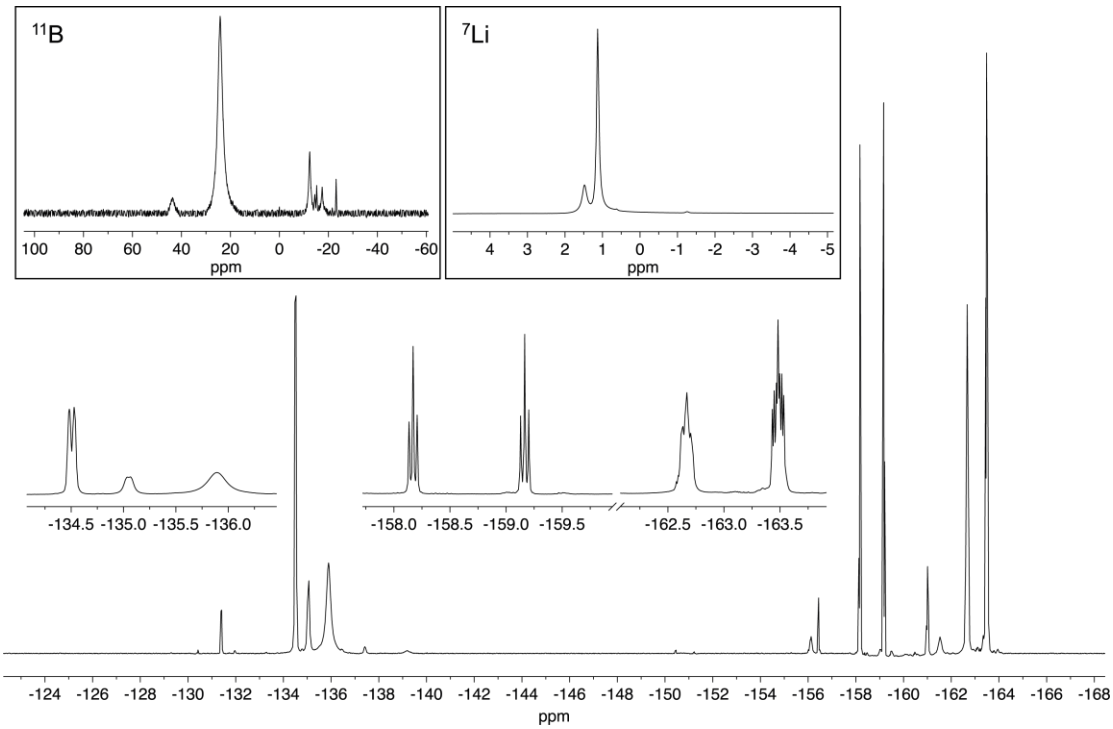
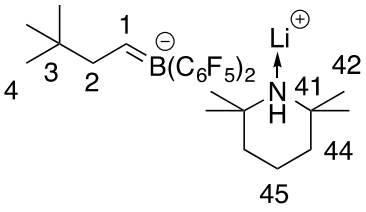


Figure S79. ^{19}F NMR (564 MHz, 299 K, C_6D_6), ^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6) and ^{7}Li NMR (233 MHz, 299 K, C_6D_6) spectra of *in situ* generated compound **16b**.

3.8.3 Lithium(HTMP) (3,3-dimethylbutylidene)bis(pentafluorophenyl)-borate (16c)

Diluted 3,3-dimethylbut-1-ene (8.4 mg, 0.1 mmol, 1.0 equiv, C_6D_6: 0.5 mL) was added to a suspension of PIERS' borane $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol, 1.0 equiv) in C_6D_6 (0.3 mL). After 10 min solid LiTMP (14.7 mg, 0.1 mmol, 1.0 equiv) was added. The mixture was shaken for 3 h in the J. Young-NMR tube before being analyzed by NMR spectroscopic means. Borata-alkene alongside to some tetracoordinate borate species obtained.



Scheme S20.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 4.24 (t, $^3J_{HH}$ = 8.7 Hz, 1H, C1-H), 1.97 (d, $^3J_{HH}$ = 8.7 Hz, 2H, C2-H), 1.12 (m, 2H, C45-H), 1.09 (s, 9H, C4-H), 0.77 (br, 4H, C44-H), 0.71 (br, 12H, C42-H), 0.32 (br, 1H, N-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 149.1 (dm, $^1J_{FC}$ ~ 233 Hz, C_6F_5), 147.0 (dm, $^1J_{FC}$ ~ 233 Hz, C_6F_5), 146.4 (dm, $^1J_{FC}$ ~ 230 Hz, C_6F_5), 139.6 (dm, $^1J_{FC}$ ~ 249 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 120.6, 119.9 (each br, *i*-C_6F_5), 99.5 (br, C1), 51.1 (C41), 46.1 (C2), 37.7 (C44), 32.8 (C3), 29.23 (C4), 29.20 (C42), 17.3 (C45).

^{7}Li NMR (233 MHz, 299 K, C_6D_6): δ = 0.7 ($\nu_{1/2}$ ~ 43 Hz).

$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6): δ = 24.9 ($\nu_{1/2}$ ~ 330 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -133.6 (m, 2F, *o*-$C_6F_5^B$), -135.9 (br, 2F, *o*-$C_6F_5^A$), -157.7 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^A$), -159.0 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-$C_6F_5^B$), -162.3 (m, 2F, *m*-$C_6F_5^A$), -163.6 (m, 2F, *m*-$C_6F_5^B$) [$\Delta\delta^{19}F_{m,p}$ = 4.6^A, 4.6^B].

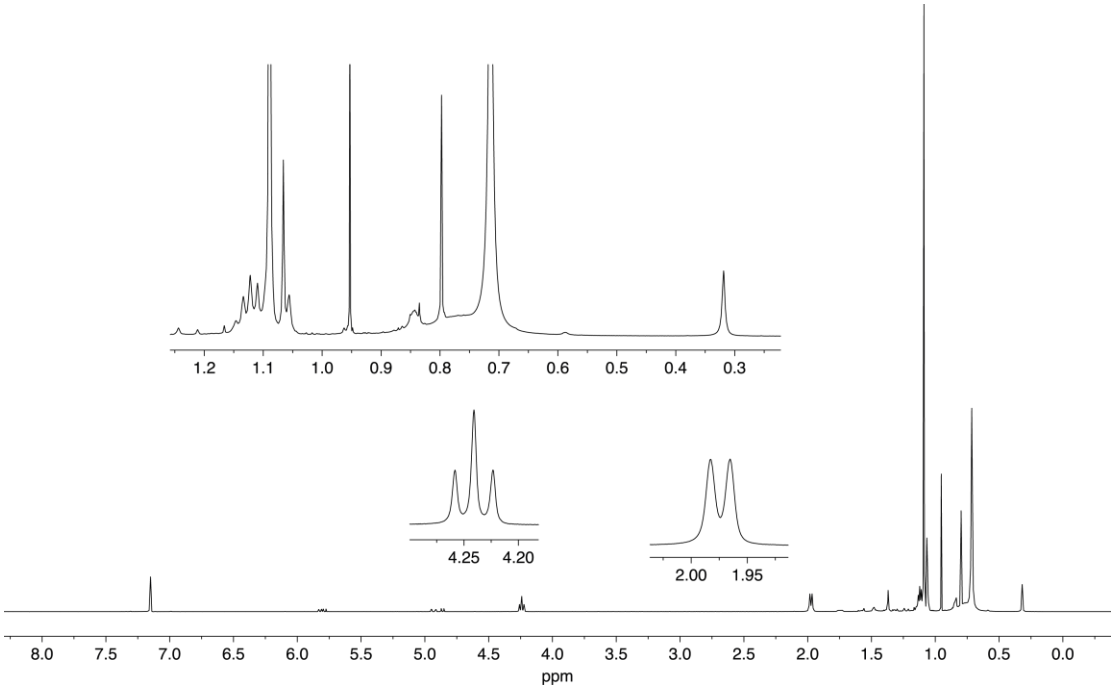


Figure S80. ^1H NMR (600 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **16c**.

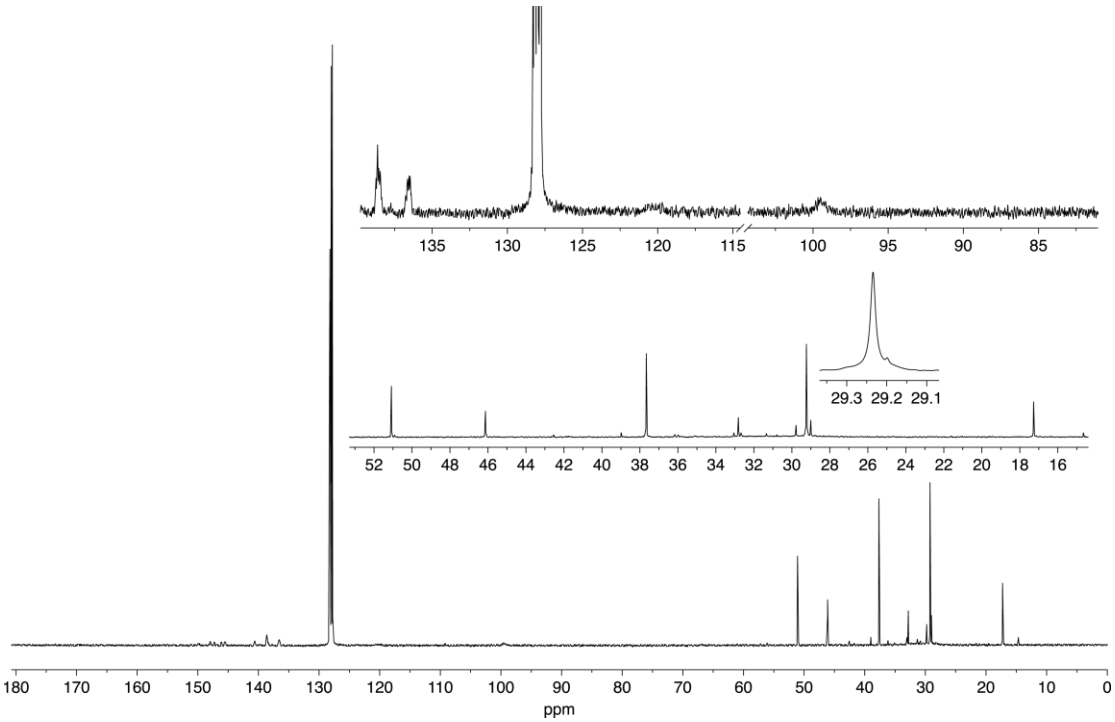


Figure S81. $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **16c**.

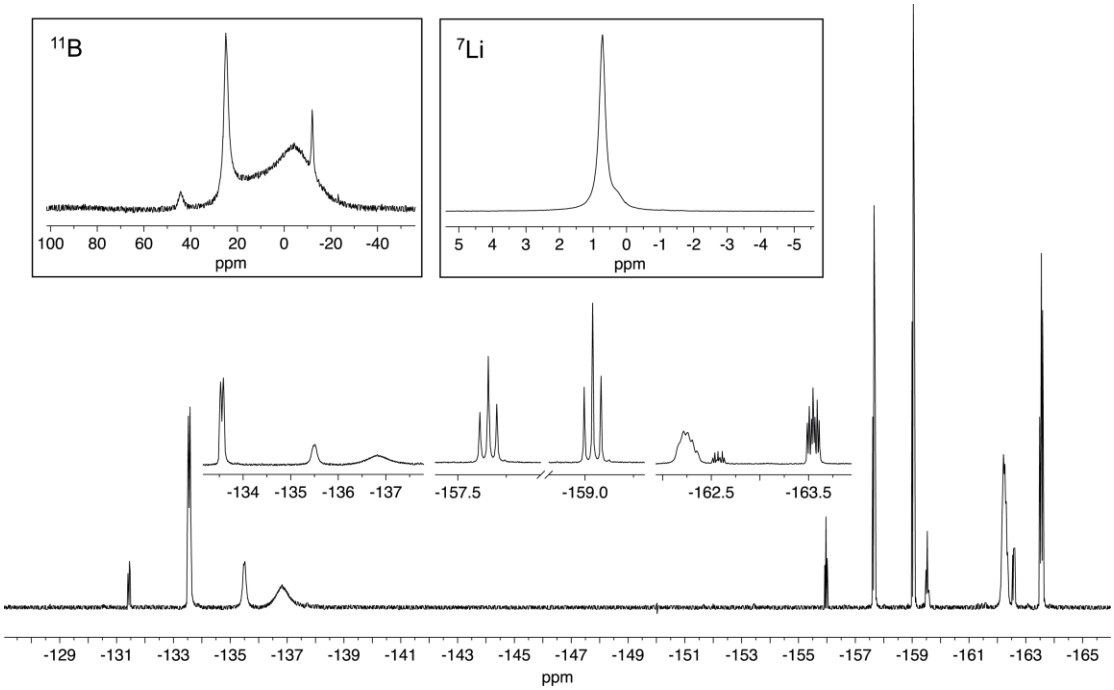
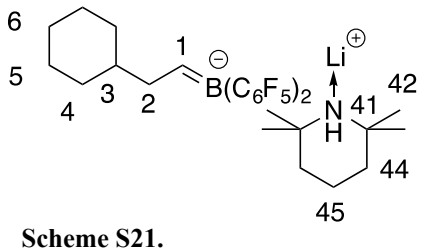


Figure S82. ^{19}F NMR (564 MHz, 299 K, C_6D_6), ^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6) and ^{7}Li NMR (233 MHz, 299 K, C_6D_6) spectra of *in situ* generated compound **16c**.

3.8.4 Lithium(HTMP) (2-cyclohexylethylidene)bis(pentafluorophenyl)-borate (16d)

LiTMP (14.7 mg, 0.1 mmol, 1.0 equiv) was added to the *in situ* prepared mixture of **15d**. The mixture was shaken for 3 h in the J. Young-NMR tube before being analyzed by NMR spectroscopic means. Borata-alkene alongside to some tetracoordinate borate species obtained.



Scheme S21.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 4.33 (t, $^3J_{HH}$ = 8.3 Hz, 1H, C1-H), 2.11 (m, 2H, C2-H), 2.09 (m, 2H, C4-H^{eq}), 1.77 (m, 2H, C5-H^{eq}), 1.66 (m, 1H, C6-H^{eq}), 1.49 (m, 1H, C3-H^{ax}), 1.32 (m, 2H, C5-H^{ax}), 1.19 (m, 2H, C6-H^{ax}), 1.15 (m, 2H, C45-H), 1.09 (m, 2H, C4-H^{ax}), 0.81 (br, 4H, C44-H), 0.75 (br, 12H, C42-H), 0.38 (br, 1H, N-H).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 149.1 (dm, $^1J_{FC}$ ~ 223 Hz, C_6F_5), 147.1 (dm, $^1J_{FC}$ ~ 226 Hz, C_6F_5), 146.5 (dm, $^1J_{FC}$ ~ 229 Hz, C_6F_5), 139.6 (dm, $^1J_{FC}$ ~ 249 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 255 Hz, C_6F_5), 120.8, 120.2 (each br, *i*-C_6F_5), 102.3 (br, C1), 51.1 (C41), 42.4 (C3), 40.0 (C2), 37.7 (C44), 33.6 (C4), 30.4 (C42), 27.3 (C6), 27.1 (C5), 17.3 (C45).

^{7}Li NMR (194 MHz, 299 K, C_6D_6): δ = 1.2 ($\nu_{1/2}$ ~ 18 Hz).

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ = 24.1 ($\nu_{1/2}$ ~ 490 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = -133.6 (br, 2F, *o*-$C_6F_5^B$), -135.9 (br, 2F, *o*-$C_6F_5^A$), -158.2 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-$C_6F_5^A$), -159.3 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^B$), -162.6 (m, 2F, *m*-$C_6F_5^A$), -163.7 (m, 2F, *m*-$C_6F_5^B$) [$\Delta\delta^{19}F_{m,p}$ = 4.4^A, 4.4^B].

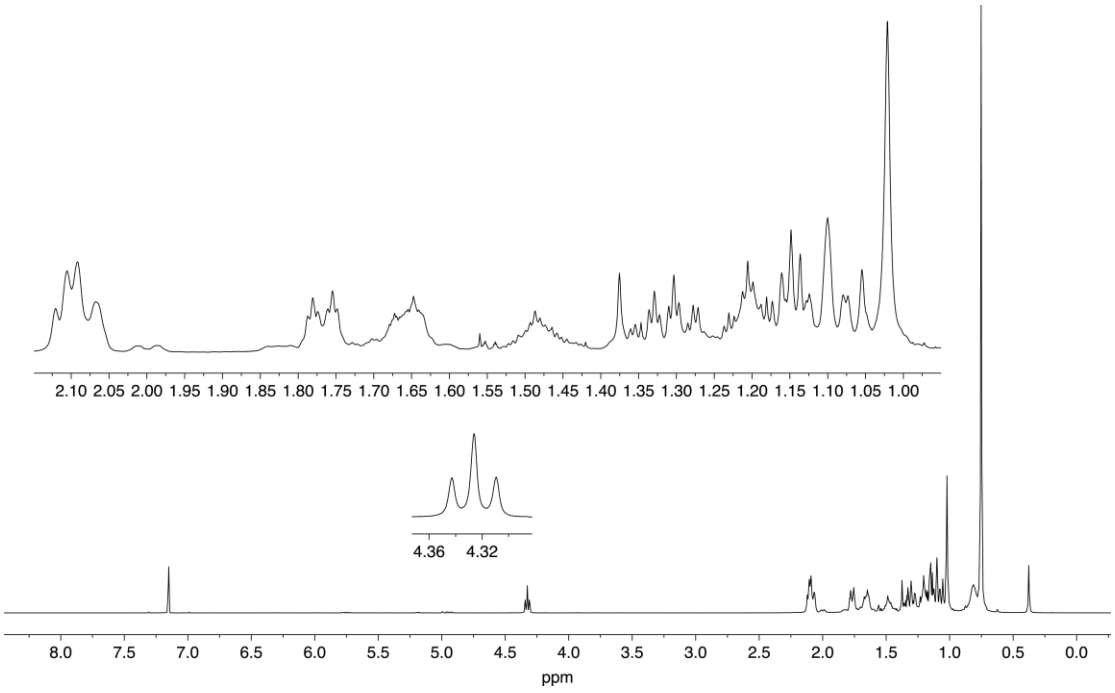


Figure S83. ^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **16d**.

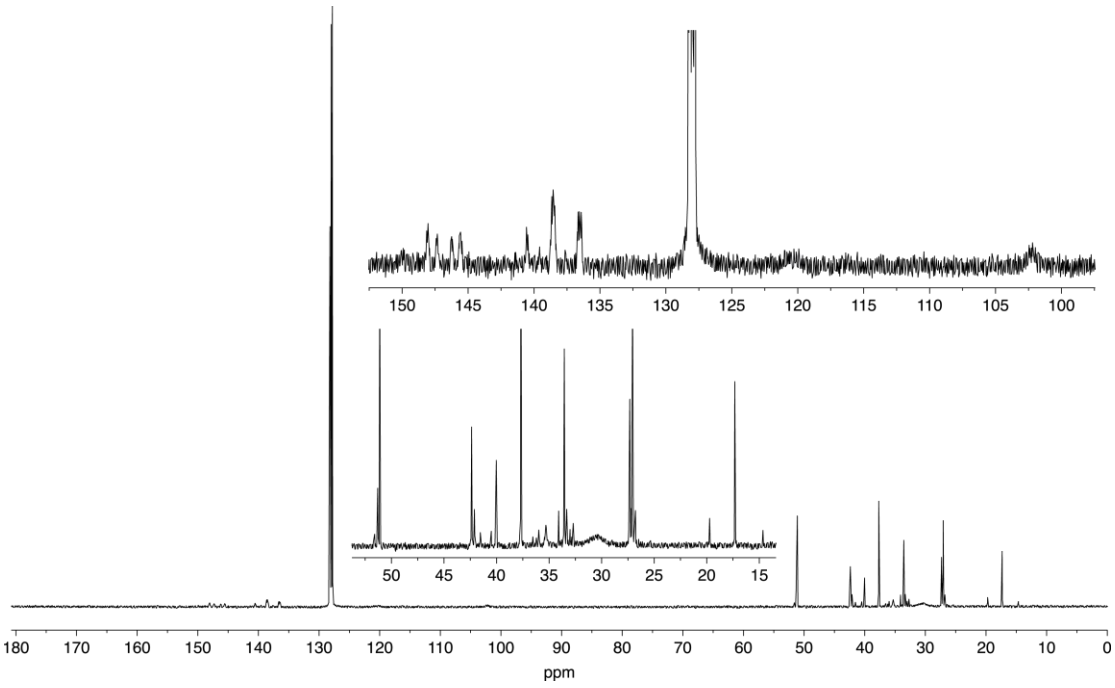


Figure S84. $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **16d**.

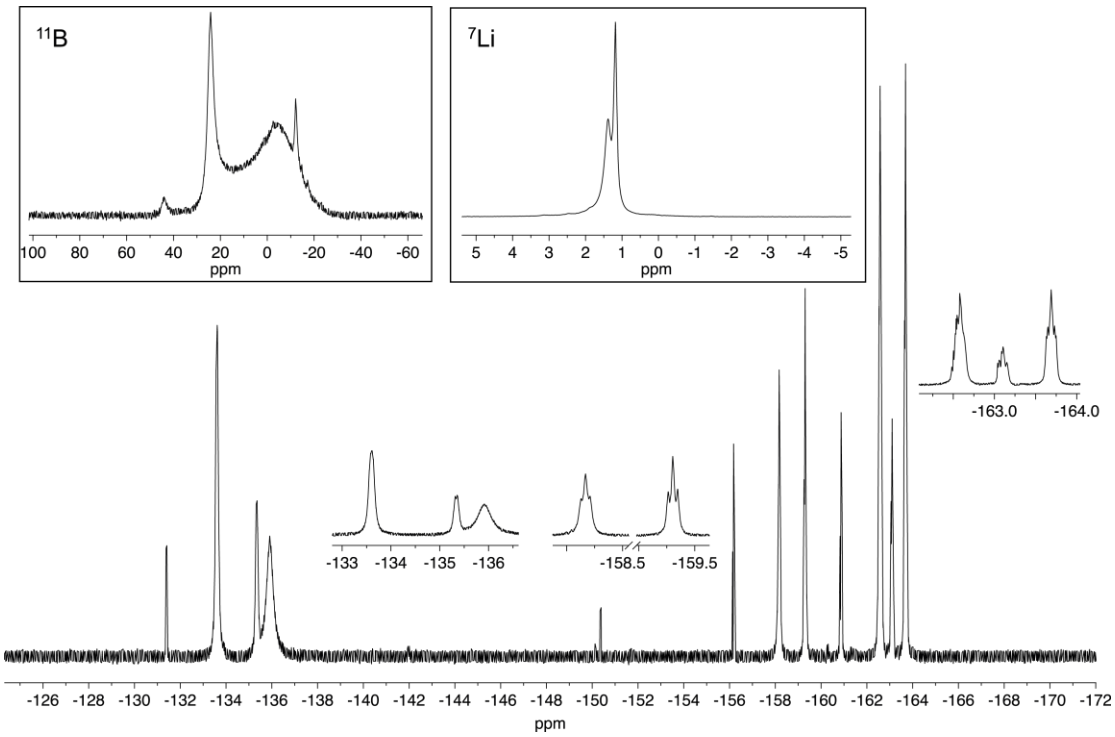
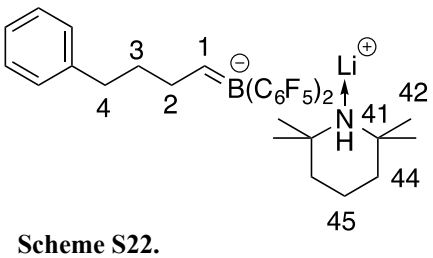


Figure S85. ^{19}F NMR (470 MHz, 299 K, C_6D_6), $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, C_6D_6) and ^{7}Li NMR (192 MHz, 299 K, C_6D_6) spectra of *in situ* generated compound **16d**.

3.8.5 Lithium(HTMP) (4-phenylbutylidene)bis(pentafluorophenyl)borate (16e)



Scheme S22.

Diluted 4-phenylbut-1-ene (13.2 mg, 0.1 mmol, 1.0 equiv, C_6D_6: 0.5 mL) was added to a suspension of PIERS' borane $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol, 1.0 equiv) in C_6D_6 (0.3 mL). After 10 min solid LiTMP (14.7 mg, 0.1 mmol, 1.0 equiv) was added. The mixture was shaken for 1.5 h in a J. Young-NMR tube before analyzed by NMR spectroscopic means. Borata-alkene alongside to some tetracoordinate borate species obtained.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.14 (m, 2H, *o*-Ph), 7.14 (m, 2H, *m*-Ph), 7.04 (m, 1H, *p*-Ph), 4.36 (t, $^3J_{HH}$ = 8.2 Hz, 1H, C1-H), 2.78 (t, $^3J_{HH}$ = 7.2 Hz, 2H, C4-H), 2.16 (dt, $^3J_{HH}$ = 8.2, 7.2 Hz, 2H, C2-H), 1.94 (p, $^3J_{HH}$ = 7.2 Hz, 2H, C3-H), 1.17 (p, $^3J_{HH}$ = 6.2 Hz, 2H, C45-H), 0.83 (br, 4H, C44-H), 0.75 (br s, 12H, C42-H), 0.35 (br, 1H, N-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 147.2 (dm, $^1J_{FC}$ ~ 224 Hz, C_6F_5), 146.4 (dm, $^1J_{FC}$ ~ 232 Hz, C_6F_5), 143.3 (*i*-Ph), 139.5 (dm, $^1J_{FC}$ ~ 237 Hz, C_6F_5), 137.5 (dm, $^1J_{FC}$ ~ 241 Hz, C_6F_5), 128.9 (*o*-Ph), 128.4 (*m*-Ph), 125.7 (*p*-Ph), 120.8, 120.1 (each br, *i*-C_6F_5), 104.2 (br, C1), 51.0 (C41), 37.8 (C44), 36.5 (C3), 35.2 (C4), 31.0 (C2), 30.7 (C42), 17.5 (C45).

^{7}Li NMR (233 MHz, 299 K, C_6D_6): δ = 1.2 ($\nu_{1/2}$ ~ 30 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = 24.2 ($\nu_{1/2}$ ~ 430 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -133.7 (br, 2F, *o*-$C_6F_5^B$), -135.4 (br, 2F, *o*-$C_6F_5^A$), -158.5 (br, 1F, *p*-$C_6F_5^A$), -159.4 (br, 1F, *p*-$C_6F_5^B$), -162.8 (br, 2F, *m*-$C_6F_5^A$), -163.7 (br, 2F, *m*-$C_6F_5^B$) [$\Delta\delta^{19}F_{m,p}$ = 4.3^A, 4.3^B].

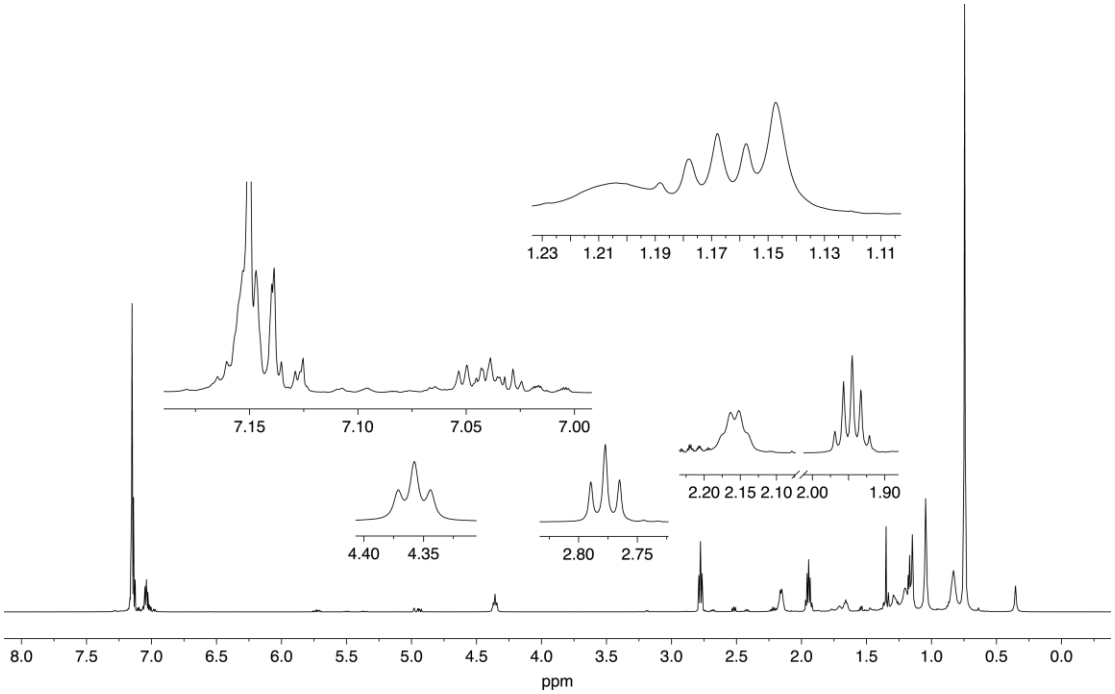


Figure S86. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **16e**.

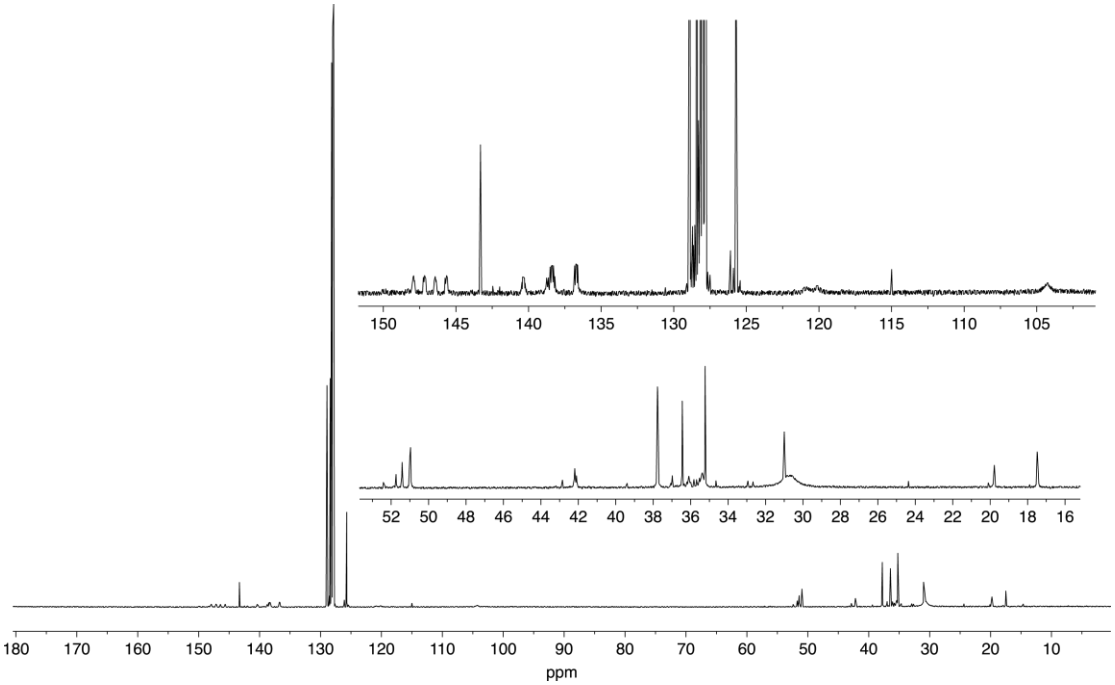


Figure S87. ^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) spectrum of *in situ* generated compound **16e**.

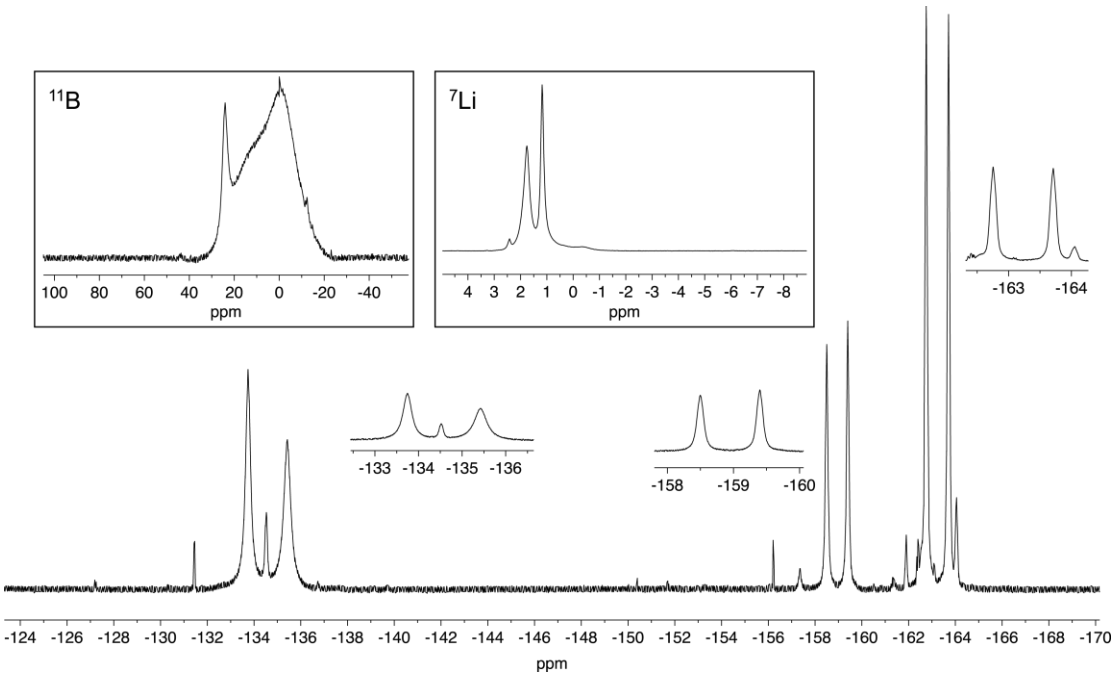
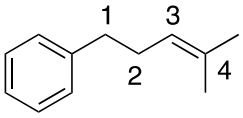


Figure S88. ^{19}F NMR (564 MHz, 299 K, C_6D_6), $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6) and ^{7}Li NMR (233 MHz, 299 K, C_6D_6) spectra of *in situ* generated compound **16e**.

3.9 Compounds 17

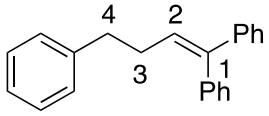
3.9.1 4-Methylpent-3-en-1-ylbenzene (17a)



Scheme S23.

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Acetone (58.1 mg, 1.0 mmol, 1.0 equiv) was added. The yellow color slowly faded during the course of 2 h. The reaction mixture was stirred overnight, before quenched with hydrochloric acid (37wt%, 7 drops) and water (2 mL). The phases were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 2 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane, R_f 0.60) to give a colorless oil in 77% yield (124 mg, 0.8 mmol). The obtained NMR data were consistent to those reported in the literature (Nakagiri, T.; Murai, M.; Takai, K. *Org. Lett.* 2015, **17**, 3346.).

3.9.2 1,1,4-Triphenylbut-1-ene (17b)



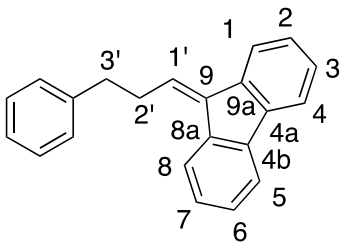
Scheme S24.

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Benzophenone (182.2 mg, 1.0 mmol, 1.0 equiv) was added causing a decolorification during the course of 4 h. The reaction mixture was stirred overnight, before quenched with

hydrochloric acid (37wt%, 7 drops) and water (2 mL). The phases were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 2 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane, R_f 0.19) to give a colorless oil in 82% yield (245 mg, 0.8 mmol). The obtained NMR data were consistent to those reported in the literature (Liwosz, T. W.; Chemler, S. R. *Org. Lett.* 2013, **15**, 3034.).

3.9.3 9-(3'-Phenylpropylidene)-9H-fluorene (17c)

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Fluorenone (180.2 mg, 1.0 mmol, 1.0 equiv) was added causing a decolorification during the course of 4 h. The reaction mixture was stirred overnight, before quenched with hydrochloric acid (37wt%, 7 drops) and water (2 mL). The phases were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 2 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane, R_f 0.13) to give a yellowish solid in 71% yield (203 mg, 0.7 mmol).



Scheme S25.

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 7.93 (m, 1H, C8-H), 7.83 (m, 1H, C5-H), 7.78 (m, 1H, C4-H), 7.71 (m, 1H, C1-H), 7.44 (m, 1H, C6-H), 7.42 (m, 2H, *m*-Ph), 7.41 (m, 1H, C3-H), 7.39 (m, 1H, C7-H), 7.38 (m, 2H, *o*-Ph), 7.36 (m, 1H, C2-H), 7.33 (m, 1H, *p*-Ph), 6.83 (t, $^3J_{HH}$ = 7.2 Hz, 1H, C1'-H), 3.23 (m, 2H, C2'-H), 3.07 (m, 2H, C3'-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$): δ = 141.3 (*i*-Ph), 140.8 (C4b), 139.2 (C9a), 138.6 (C4a), 137.3 (C8a), 135.8 (C9), 129.5 (C1'), 128.5 (*m*-Ph), 128.4 (*o*-Ph), 127.7 (C6), 127.4 (C3), 126.9 (C7), 126.8 (C2), 126.1 (*p*-Ph), 124.9 (C8), 119.8 (C5), 119.7 (C1), 119.4 (C4), 35.5 (C3'), 31.0 (C2').

Elemental analysis: calc. for $C_{22}H_{18}$ (282.39 g mol^{-1}): C, 93.57; H, 6.43; Found: C, 93.06; H, 6.22.
Mass (EI): calc. for $C_{22}H_{18}$ [M^+]: 282.1; Found: 282.3.
Melting Point: 84.8 °C.

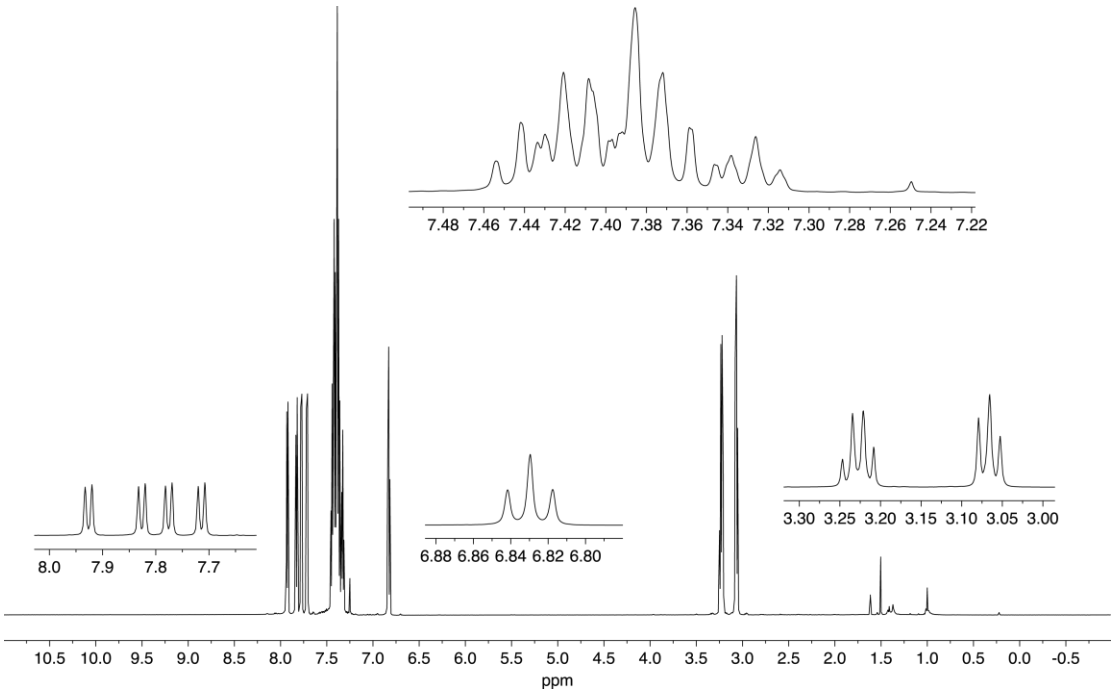


Figure S89. ^{1}H NMR (600 MHz, 299 K, $CDCl_3$) spectrum of compound **17c**.

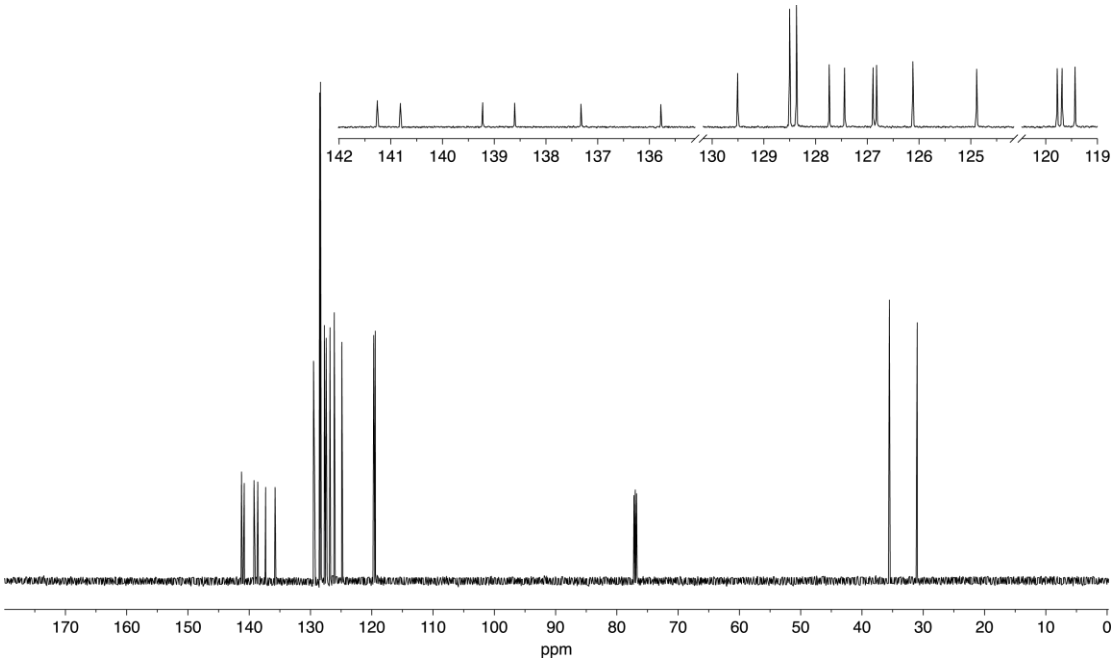
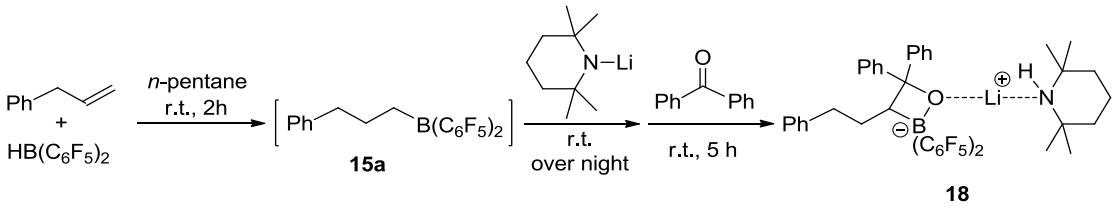


Figure S90. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$) spectrum of compound **17c**.

3.10 Compound 18

3.10.1 Synthesis of compound 18



Scheme S26.

Allylbenzene (120.1 mg, 1.0 mmol) was added to a suspension of $HB(C_6F_5)_2$ (345.5 mg, 1.0 mmol) in pentane (30 mL). The mixture was stirred at r.t. for 2 h before solid LiTMP (147.5 mg, 1.0 mmol, 1.0 equiv) was added. Then the mixture was stirred at r.t. overnight and benzophenone (182.6 mg, 1.0 mmol) was added. After that, the mixture was stirred at r.t. for another 5 h. The pentane solution was filtered and the solvent was removed in vacuo. The obtained residue was washed with precooled pentane (3×5 mL) at -30 °C and dried in vacuo to give a white solid. Yield: 626.1 mg, 79%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of compound **18** in CH_2Cl_2 covered with *n*-pentane at -35 °C.

[**TMP**: 2,2,6,6-tetramethylpiperidino]

^{1}H NMR (500 MHz, 213 K, CD_2Cl_2): δ = 7.35 (2H, *o*), 7.30 (2H, *m*), 7.20 (1H, *p*)(each m, Ph), 7.25 (5H, m, Ph), 7.04 (2H, *m*), 6.99 (1H, *p*), 6.45 (2H, *o*)(each m, Ph), 2.69 (m, 1H, C*H*), 2.33, 1.97 (each m, each 1H, CH_2^{Ph}), 1.72, 1.44 (each m, each 1H, CH_2), 1.64, 1.49 (each m, each 1H, CH_2^{TMP}), 1.51, 1.04 (each m, each 2H, $^{C}CH_2^{TMP}$), 1.14, 1.01, 0.99, 0.81 (each s, each 3H, CH_3^{TMP}), 1.10 (s, 1H, N*H*).

^{13}C{^{1}H} NMR (126 MHz, 213 K, CD_2Cl_2): δ = 148.6, 144.4, 143.5, 127.9, 127.8, 127.7, 127.3, 127.2, 126.7, 125.9, 125.8, 124.9 (3Ph), 90.9 (*C*O), 51.0 (NC^{TMP}), 39.8 (br, *C*H), 37.84, 37.77 ($^{C}CH_2^{TMP}$), 36.1 (CH_2^{Ph}), 33.7, 33.4, 26.0, 25.6 (each br, CH_3^{TMP}), 32.2 (CH_2), 17.1 (CH_2^{TMP}).

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = 2.6 ($\nu_{1/2}$ ~ 150 Hz).

^{7}Li NMR (195 MHz, 299 K, CD_2Cl_2): δ = 0.6 ($\nu_{1/2}$ ~ 30 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = -131.1, -153.0 (each m, each 1F, *o*-C_6F_5), -159.2 (m, 1F, *p*-C_6F_5), -161.29, -162.3 (each m, each 1F, *m*-C_6F_5), -134.4, -148.2 (each m, each 1F, *o*-C_6F_5'), -159.4 (m, 1F, *p*-C_6F_5'), -161.34, -163.5 (each m, each 1F, *m*-C_6F_5').

Elemental analysis: calc. for $C_{43}H_{39}NBF_{10}OLi$: C, 65.09; H, 4.95; N, 1.77. Found: C, 66.18; H, 4.88; N, 1.67.

Decomp. Point: 163 °C.

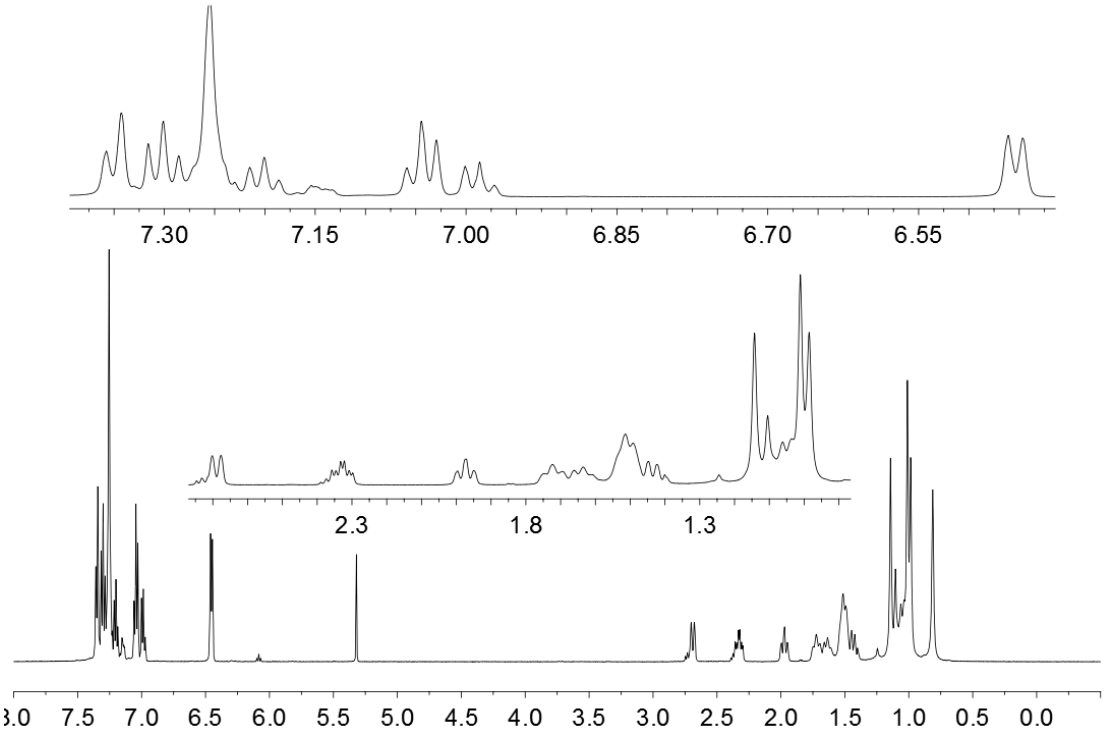


Figure S91. ^{1}H NMR (500 MHz, 213 K, CD_2Cl_2) spectrum of compound **18**.

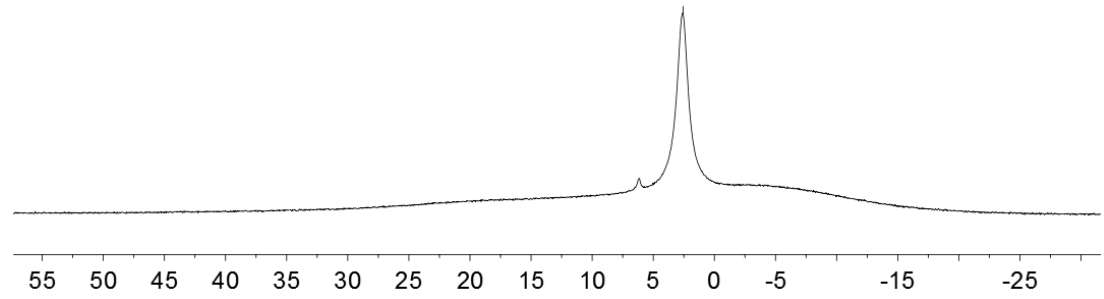


Figure S92. $^{11}B\{^{1}H\}$ NMR (160 MHz, 299K, CD_2Cl_2) spectrum of compound **18**.

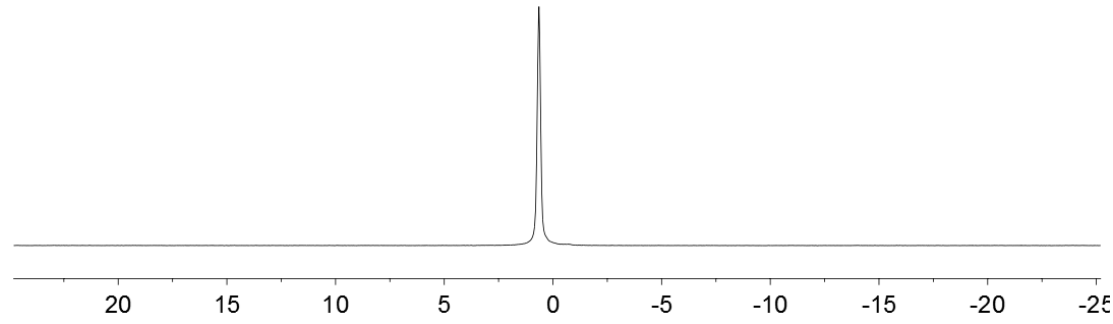


Figure S93. ^{7}Li NMR (195 MHz, 299 K, CD_2Cl_2) spectrum of compound **18**.

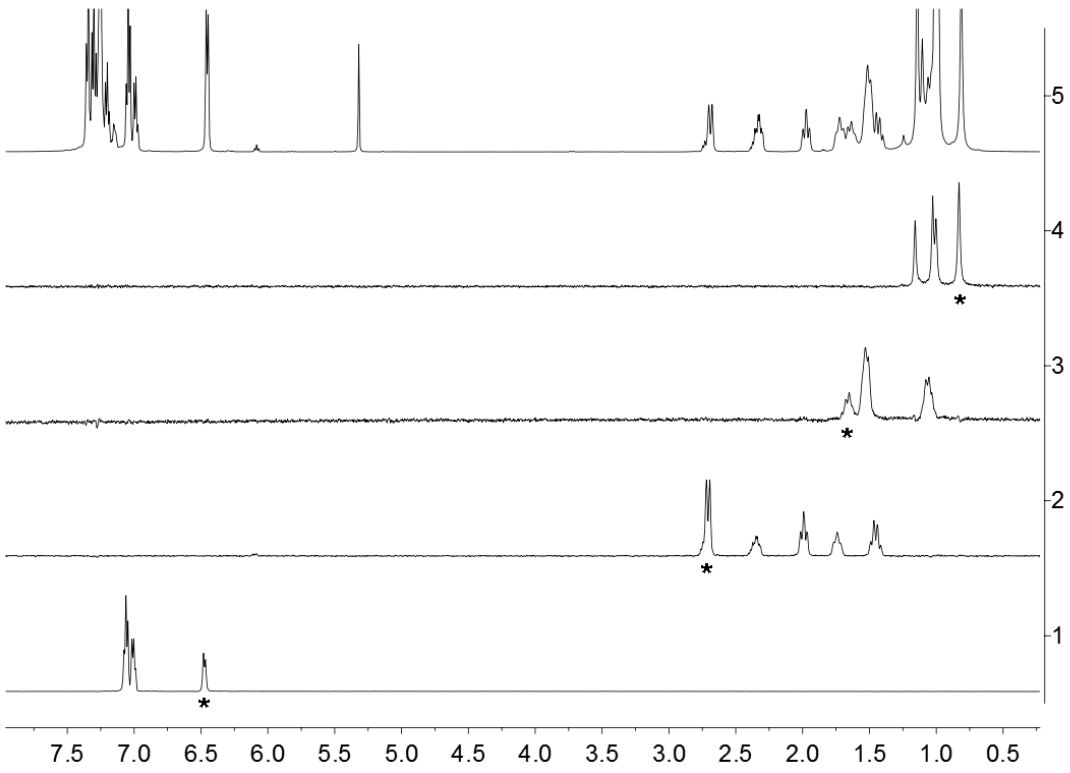


Figure S94. ^{1}H NMR (5) and ^{1}H{^{1}H} TOCSY (500 MHz, 213 K, CD_2Cl_2) spectra of compound **18**. * Irradiation points: $^{1}H_{irr}$ = 6.45 (*o*-Ph) (1), 2.69 (C*H*) (2), 1.64 (CH_2^{TMP}) (3), 0.81 (CH_3^{TMP}) (4).

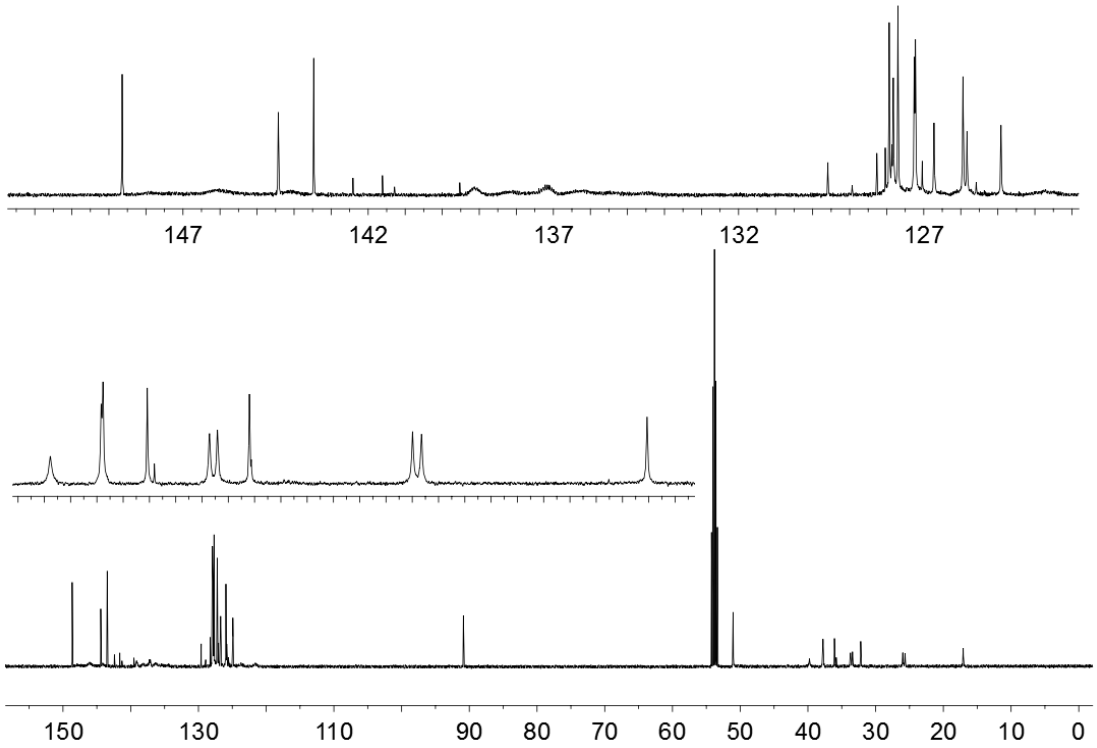


Figure S95. ^{13}C{^{1}H} NMR (126 MHz, 213 K, CD_2Cl_2) spectrum of compound **18**.

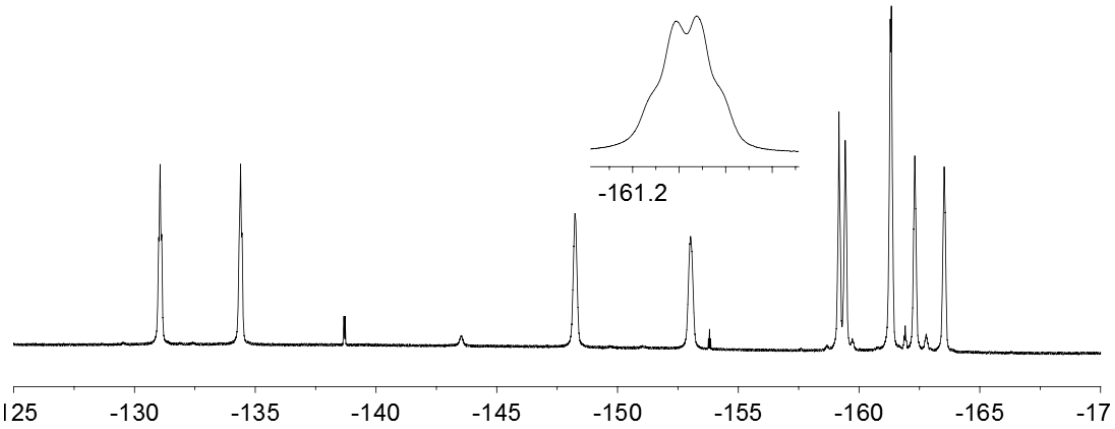


Figure S96. ^{19}F NMR (470 MHz, 183 K, CD_2Cl_2) spectrum of compound **18**.

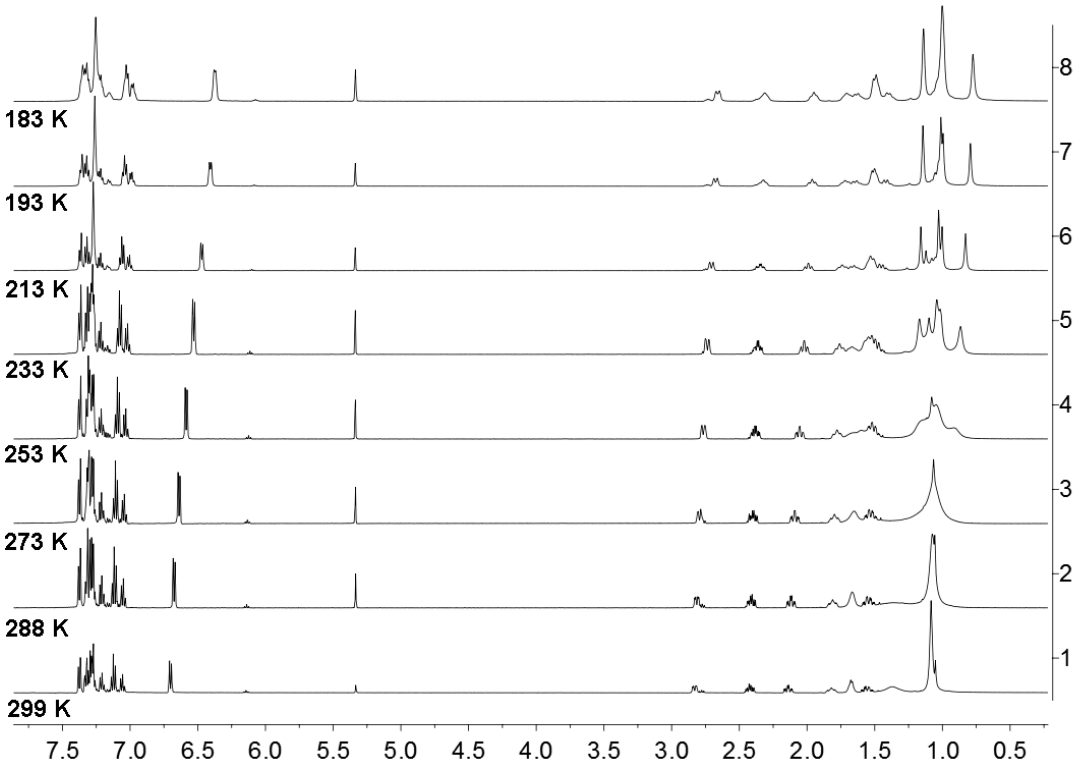


Figure S97. ^{1}H NMR (500 MHz, from 299 K to183 K, CD_2Cl_2) spectra of compound **18**.

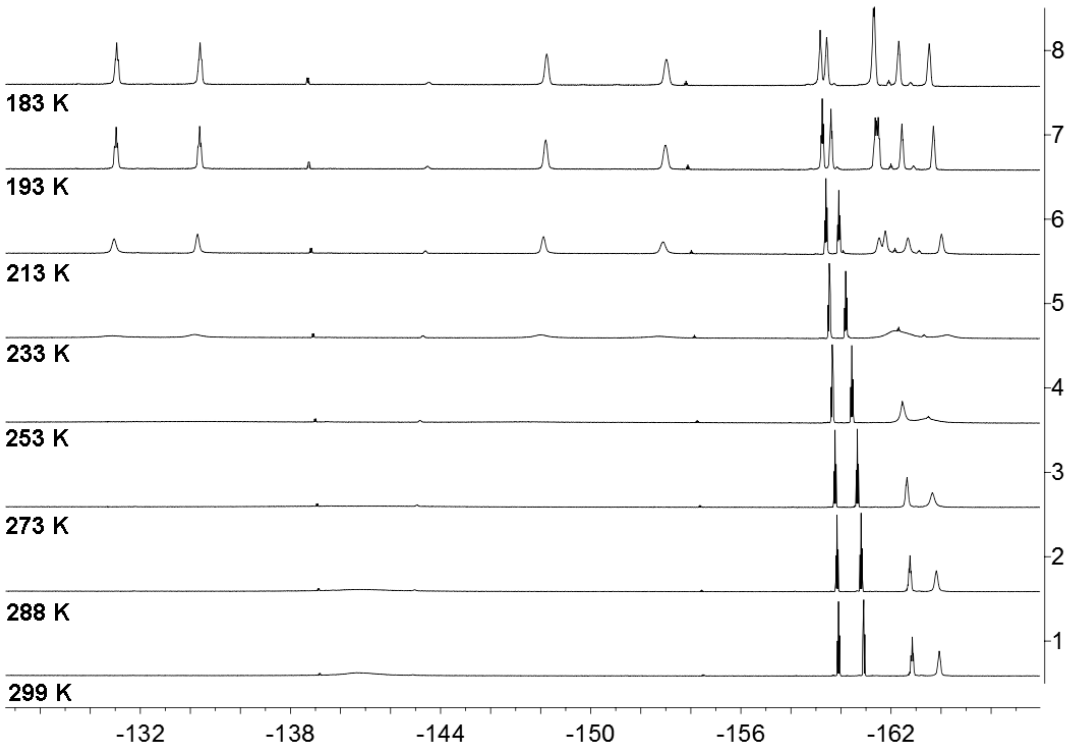


Figure S98. ^{19}F NMR (470 MHz, from 299 K to183 K, CD_2Cl_2) spectra of compound **18**.

X-ray crystal structure analysis of compound 18: A colorless plate-like specimen of $C_{43}H_{39}BF_{10}LiNO \cdot CH_2Cl_2$, approximate dimensions 0.030 mm x 0.140 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1586 frames were collected. The total exposure time was 23.26 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 34707 reflections to a maximum θ angle of 66.78° (0.84 Å resolution), of which 7169 were independent (average redundancy 4.841, completeness = 99.3%, R_{int} = 3.99%, R_{sig} = 3.00%) and 6204 (86.54%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.2492(3) Å, b = 11.9411(3) Å, c = 18.0278(5) Å, α = 80.1520(10)°, β = 74.0120(10)°, γ = 74.3990(10)°, volume = 2031.64(10) $Å^3$, are based upon the refinement of the XYZ-centroids of 9986 reflections above 20 σ(I) with 8.819° < 2θ < 133.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.866. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6970 and 0.9380. The final anisotropic full-matrix least-squares refinement on F^2 with 577 variables converged at R1 = 3.65%, for the observed data and wR2 = 9.31% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.502 $e^-/Å^3$ and the largest hole was -0.566 $e^-/Å^3$ with an RMS deviation of 0.046 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.436 g/cm^3 and F(000), 904 e^-. The position of the hydrogen atom at N1 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

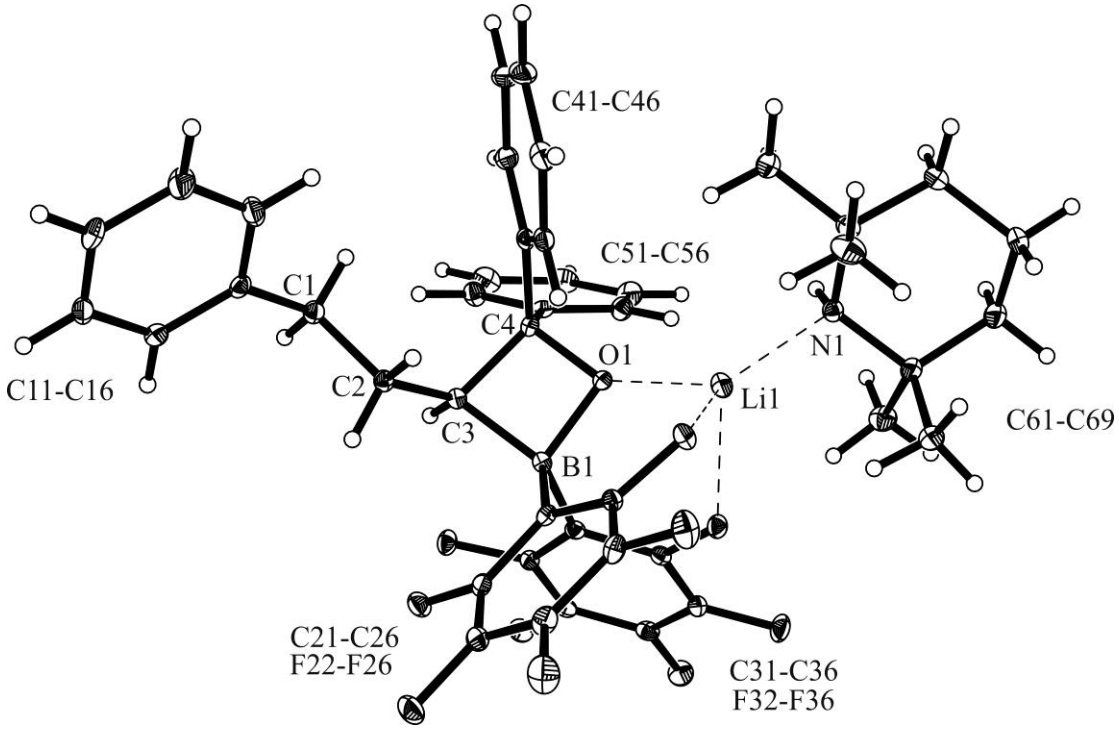
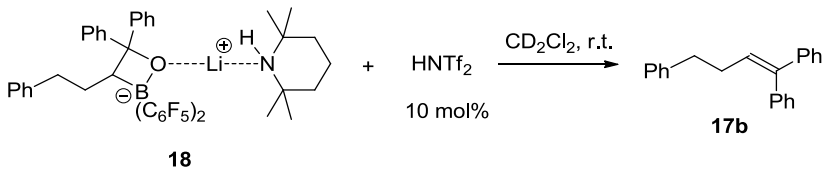


Figure S99. A view of the molecular structure of compound **18**.

3.10.2 In-situ reaction of compound 18 with catalytic $HNTf_2$ (10 mol%)



Scheme S27.

In a NMR tube, compound **18** (36.3 mg, 0.046 mmol) and $HNTf_2$ (1.3 mg, 0.0046 mmol) were weighed together and dissolved in CD_2Cl_2 (0.6 mL). Then the NMR data was collected at r.t..

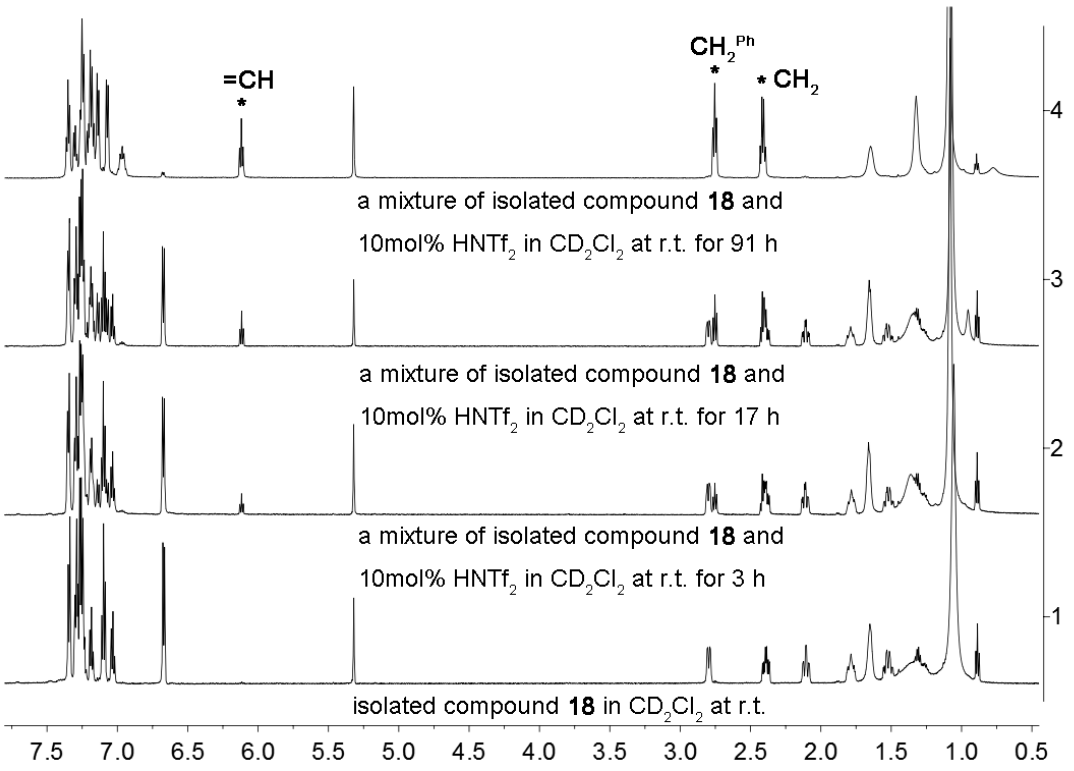
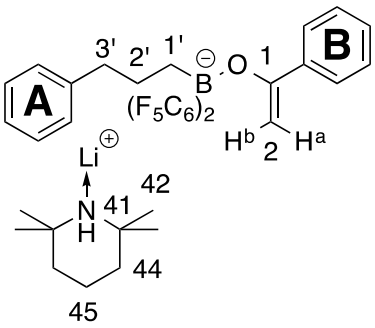


Figure S100. In-situ ^{1}H NMR (600 MHz, 299 K) spectra of (1) isolated compound **18** in CD_2Cl_2 ar r.t., (2) a mixture of isolated compound **18** and catalytic $HNTf_2$ (10 mol%) in CD_2Cl_2 ar r.t. for 3 h, (3) a mixture of isolated compound **18** and catalytic $HNTf_2$ (10 mol%) in CD_2Cl_2 ar r.t. for 17 h, and (4) a mixture of isolated compound **18** and catalytic $HNTf_2$ (10 mol%) in CD_2Cl_2 ar r.t. for 91 h,. * key signals of compound **17b**

3.11 Compound 19

In situ (r.t.): Borata-alkene **16a** was prepared according to the general procedure (see 3.8.1.1) and added to acetophenone at ambient temperature. The reaction was monitored by ^{1}H NMR spectroscopy. Formation of compound **19** alongside the corresponding oxa-boretinide compounds observed in a ratio of ca. 1 : 1.4 : 1 for **19** : *cis*-oxa-boretinide: *trans*-oxa-boretinide. *Cis*- and *trans*- were tentatively assigned.



Scheme S28.

^{1}H NMR (600 MHz, 299 K, toluene-d_8) [selected resonances]: δ = 4.77 (d, $^{2}J_{HH}$ = 1.8 Hz, 1H, C2-H^{a}), 4.36 (d, $^{2}J_{HH}$ = 1.8 Hz, 1H, C2-H^{b}), 1.73 (s, 3H, *cis*-oxa-boretinide,^{t} CH_3), 1.70 (s, 3H, *trans*-oxa-boretinide,^{t} CH_3) [^{t} tentative assignment].

Isolation (-78 °C): Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1) and cooled to -78 °C. A precooled solution of acetophenone (120.1 mg, 1.0 mmol, 1.0 equiv) in toluene (2 mL) was added slowly using a canula at -78 °C. The reaction mixture was allowed to reach ambient temperature while stirring overnight. The reaction mixture was concentrated *in vacuo*. The obtained residue was suspended in pentane (2 mL). The suspension was decanted and the residue was washed with additional pentane to afford an off-white solid (296 mg, 0.7 mmol) in 75% yield contaminated by a borate by-product in a ratio of 4 : 1. Separation is possible by crystallization by slow diffusion of pentane into a saturated solution in toluene.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.53 (m, 2H, *o*-Ph^B), 7.06 (m, 2H, *m*-Ph^A), 7.02 (m, 1H, *p*-Ph^B), 7.01 (m, 2H, *m*-Ph^B), 6.99 (m, 1H, *p*-Ph^A), 6.98 (m, 2H, *o*-Ph^A), 4.85 (d, $^{2}J_{HH}$ = 1.8 Hz, 1H, C2-H^a), 4.45 (d, $^{2}J_{HH}$ = 1.8 Hz, 1H, C2-H^b), 2.67 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, C3'-H), 1.90 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H, C1'-H), 1.63 (p, $^{3}J_{HH}$ = 7.8 Hz, 2H, C2'-H), 1.15 (p, $^{3}J_{HH}$ = 6.0 Hz, 2H, C45-H), 0.77 (br, 4H, C44-H), 0.71 (br s, 12H, C42-H), 0.13 (br, 1H, N-H).
^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 156.5 (C1), 148.1 (dm, $^{1}J_{FC}$ ~ 227 Hz, C_6F_5), 144.2 (*i*-Ph^A), 139.2 (dm, $^{1}J_{FC}$ ~ 241 Hz, C_6F_5), 139.1 (*i*-Ph^B), 136.7 (dm, $^{1}J_{FC}$ ~ 251 Hz, C_6F_5), 129.1 (*m*-Ph^B), 128.9 (*p*-Ph^B) 128.8 (*o*-Ph^A), 128.3 (*m*-Ph^A), 126.2 (*o*-Ph^B), 125.6 (*i*-C_6F_5), 125.4 (*p*-Ph^A), 94.8 (C2), 51.0 (C41), 40.5 (C3'), 38.0 (C44), 30.3 (C42), 29.7 (C2'), 19.8 (br s, C1'), 17.4 (C45).
^{7}Li NMR (233 MHz, 299 K, C_6D_6): δ = 0.2 ($\nu_{1/2}$ ~ 39 Hz).
^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = 2.3 ($\nu_{1/2}$ ~ 380 Hz).
^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -139.8 (br, 2F, *o*-C_6F_5), -158.7 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), -162.4 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.7].

Elemental Analysis: calc. for $C_{38}H_{37}BF_{10}LiNO$ [731.45 g mol^{-1}]: C, 62.40; H, 5.10; N, 1.91; Found: C, 62.64; H, 4.84; N, 1.71.
Decomp.: 122.8 °C.

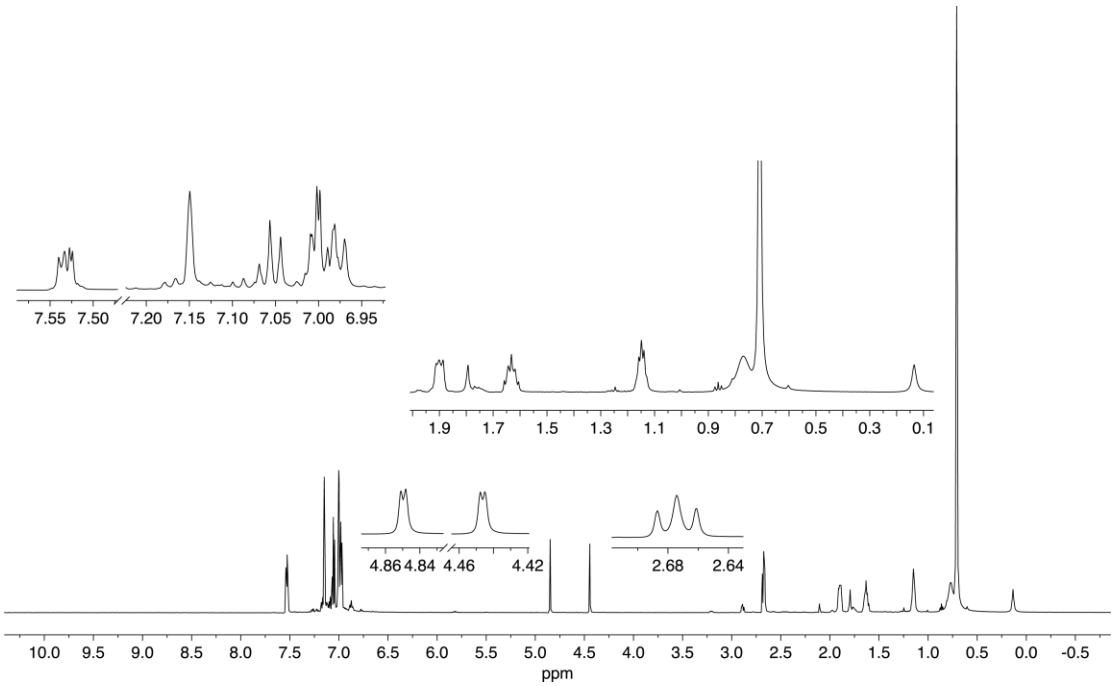


Figure S101. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of compound **19**.

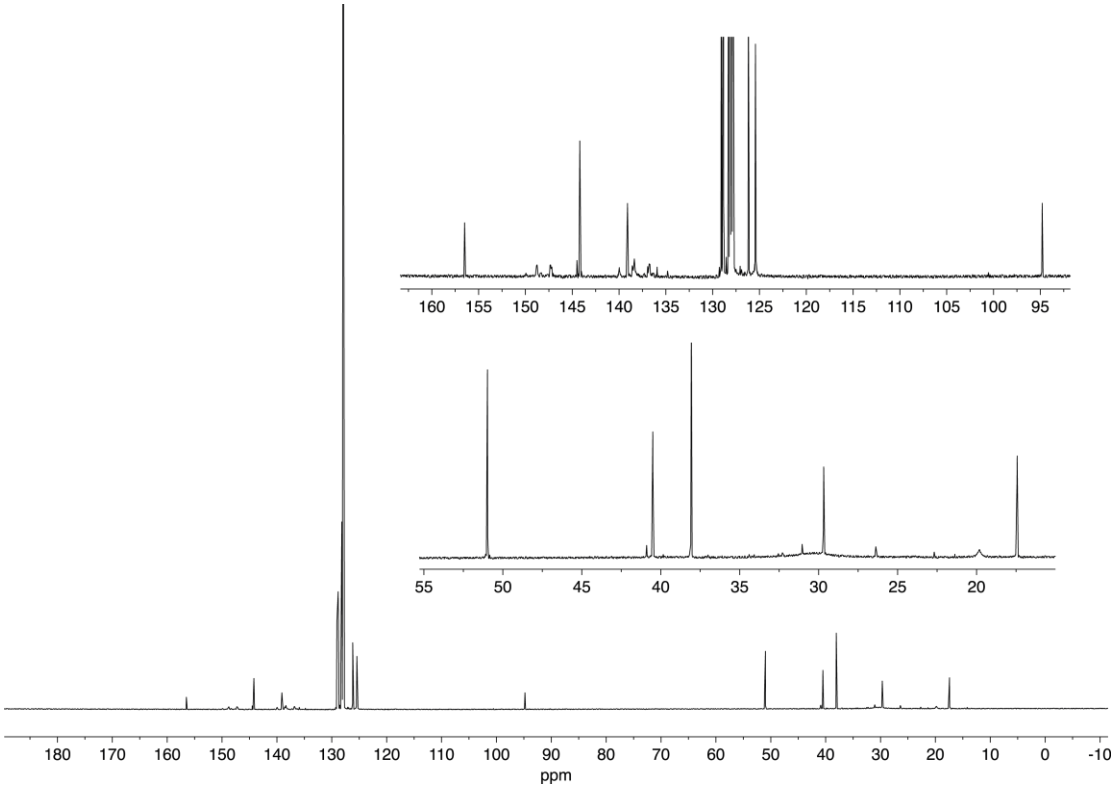


Figure S102. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of compound **19**.

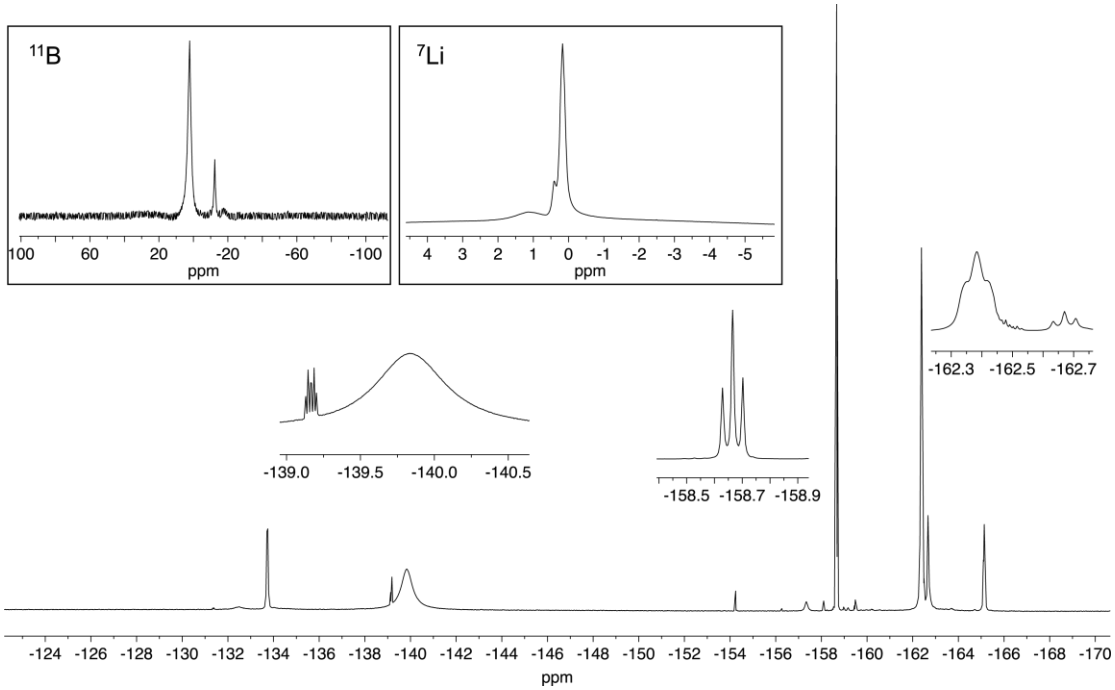


Figure S103. ^{19}F NMR (564 MHz, 299 K, C_6D_6), $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6) and ^7Li NMR (233 MHz, 299 K, C_6D_6) spectra of compound **19**.

X-ray crystal structure analysis of compound 19: A colorless plate-like specimen of $C_{38}H_{37}BF_{10}LiNO$, approximate dimensions 0.040 mm x 0.180 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1644 frames were collected. The total exposure time was 31.12 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 49367 reflections to a maximum θ angle of 68.33° (0.83 Å resolution), of which 6418 were independent (average redundancy 7.692, completeness = 99.4%, R_{int} = 3.66%, R_{sig} = 1.94%) and 5758 (89.72%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.4348(3) Å, b = 31.1087(8) Å, c = 11.4021(3) Å, β = 108.3640(10)°, volume = 3512.78(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9908 reflections above 20 σ(I) with 5.681° < 2θ < 136.6°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.908. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8070 and 0.9600. The final anisotropic full-matrix least-squares refinement on F^2 with 477 variables converged at R1 = 3.56%, for the observed data and wR2 = 9.14% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 0.229 $e^-/Å^3$ and the largest hole was -0.206 $e^-/Å^3$ with an RMS deviation of 0.039 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.383 g/cm^3 and F(000), 1512 e^-. The position of the hydrogen atom at N1 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

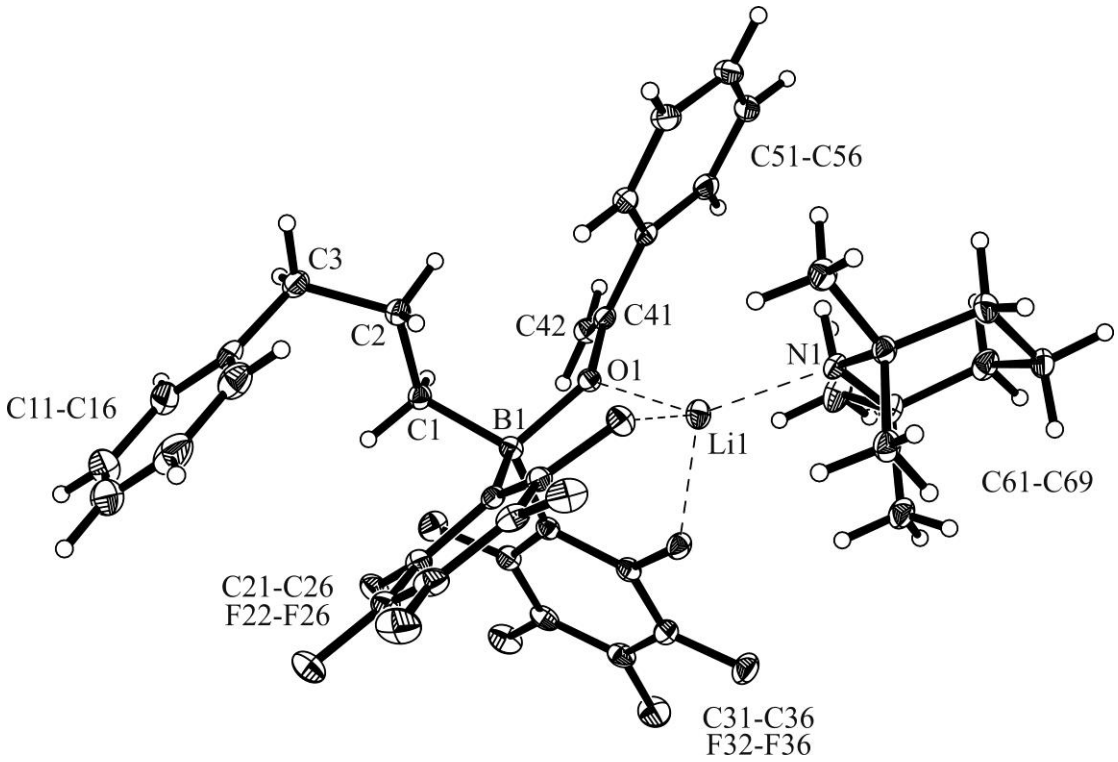
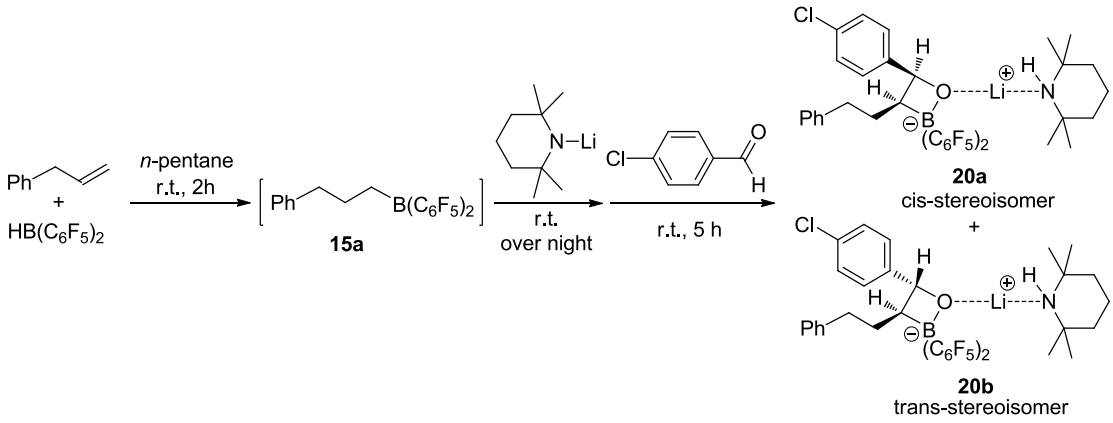


Figure S104. A view on the molecular structure of compound **19**.

3.12 Compound 20



Scheme 29.

Allylbenzene (120.3 mg, 1.0 mmol) was added to a suspen)sion of $HB(C_6F_5)_2$ (345.9 mg, 1.0 mmol) in pentane (30 mL). The mixture was stirred at r.t. for 2 h before solid LiTMP (147.7 mg, 1.0 mmol, 1.0 equiv) was added. Then the mixture was stirred at r.t. overnight and 4-chlorobenzaldehyde (141.1 mg, 1.0 mmol) was added. After that, the mixture was stirred at r.t. for another 5 h. The pentane solution was collected by filtration and the solvent was removed in vacuo. The obtained residue was washed with precooled pentane (3×5 mL) at -30 °C and dried in vacuo to give a white solid, which was identified as a mixture of compound **20a** and **20b** in a ratio of ca. 94 : 6 (ratio was detected by ^{1}H NMR;

cis-stereoisomer as the major product was indicated by $^{1}H\{^{1}H\}$ NOESY experiments). Yield: 473.6 mg, 63%.

Crystals suitable for the X-ray crystal structure analysis were obtained from a two-layer procedure using a solution of the obtained solid in CH_2Cl_2 covered with *n*-pentane at -35 °C.

cis-isomer 20a (major):

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.33 (m, 4H, *o*/*m*-Ph^{Cl}), 7.11 (m, 2H, *m*-Ph), 7.03 (m, 1H, *p*-Ph), 6.69 (m, 2H, *o*-Ph), 5.89 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, OC*H*), 2.46 (m, 1H, BC*H*), 2.15, 1.89 (each m, each 1H, CH_2^{Ph}), 1.67, 1.36 (each m, each 1H, CH_2), 1.60 (m, 2H, CH_2^{TMP}), 1.31 (m, 4H, $^{C}CH_2^{TMP}$), 1.07 (br, 1H, N*H*), 1.02 (s, 12H, CH_3^{TMP}).

^{13}C{^{1}H} NMR (1151 MHz, 299 K, CD_2Cl_2): δ = 144.1 (*i*-Ph), 142.3 (*i*-Ph^{Cl}), 133.0 (*p*-Ph^{Cl}), 129.1, 128.48 (each br, *o*/*m*-Ph^{Cl}), 128.54 (*o*-Ph), 128.3 (*m*-Ph), 125.5 (*p*-Ph), 84.5 (O*C*H), 51.6 (NC^{TMP}), 38.4 ($^{C}CH_2^{TMP}$), 36.5 (CH_2^{Ph}), 33.3 (br, B*C*H), 31.1 (*C*H_2), 30.6 (br, CH_3^{TMP}), 17.8 (CH_2^{TMP}) [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 3.2 ($\nu_{1/2}$ ~ 130 Hz).

^{7}Li{^{1}H} NMR (195 MHz, 299 K, CD_2Cl_2): δ = 0.5 ($\nu_{1/2}$ ~ 35 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -140.6 (br, 2F, *o*-C_6F_5), -160.0 (t, $^{3}J_{FF}$ = 19.4 Hz, 1F, *p*-C_6F_5), -163.1 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.1], -141.0 (m, 2F, *o*-C_6F_5'), -160.4 (t, $^{3}J_{FF}$ = 19.4 Hz, 1F, *p*-C_6F_5'), -163.6 (m, 2F, *m*-C_6F_5') [$\Delta\delta^{19}F_{m,p}$ = 3.2].

trans-isomer 20B (minor):

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2)[selected signals]: δ = 5.31 (m, 1H, OC*H*), 2.05 (br, 1H, BC*H*), 2.54/2.37, 2.03/1.67 (each m, each 1H, CH_2)

^{13}C{^{1}H} NMR (1151 MHz, 299 K, CD_2Cl_2)[selected signals]: δ = 88.6 (O*C*H), 39.4 (br, B*C*H), 36.6, 34.6 (*C*H_2).

Elemental analysis: calc. for $C_{37}H_{34}NBF_{10}OLiCl$: C, 59.11; H, 4.56; N, 1.86. Found: C, 58.88; H, 4.54; N, 1.80.

Decomp. Point: 160°C.

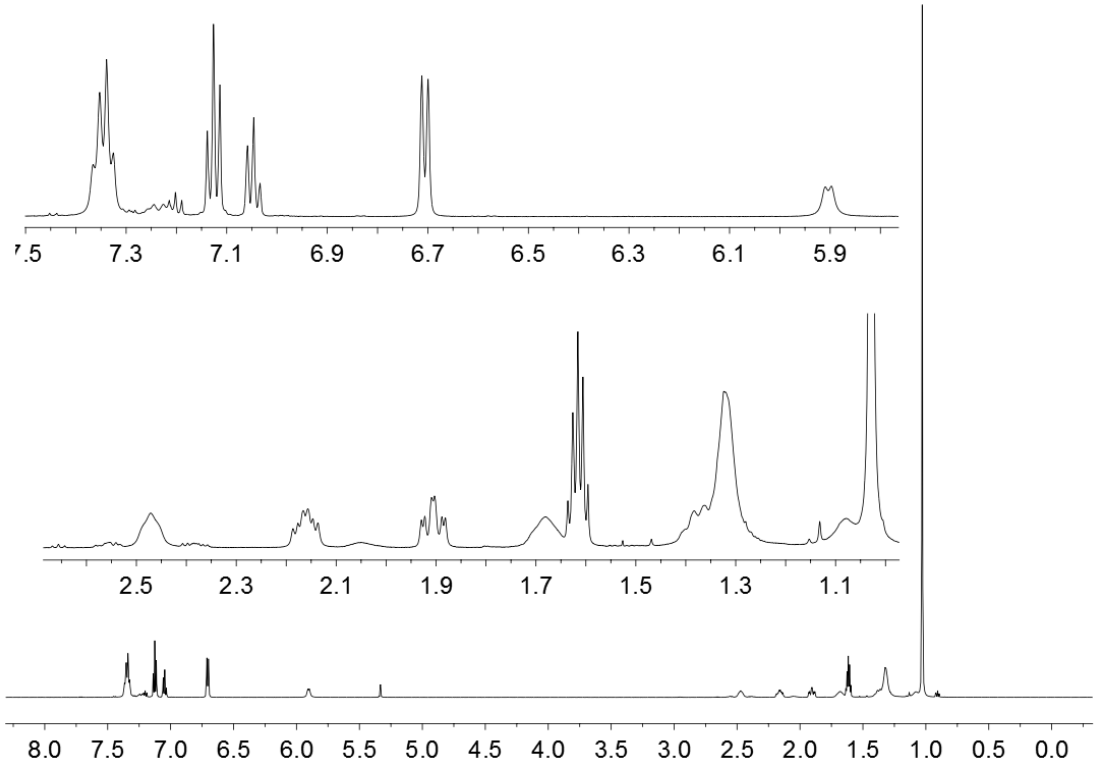


Figure S105. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **20a** and **20b**.

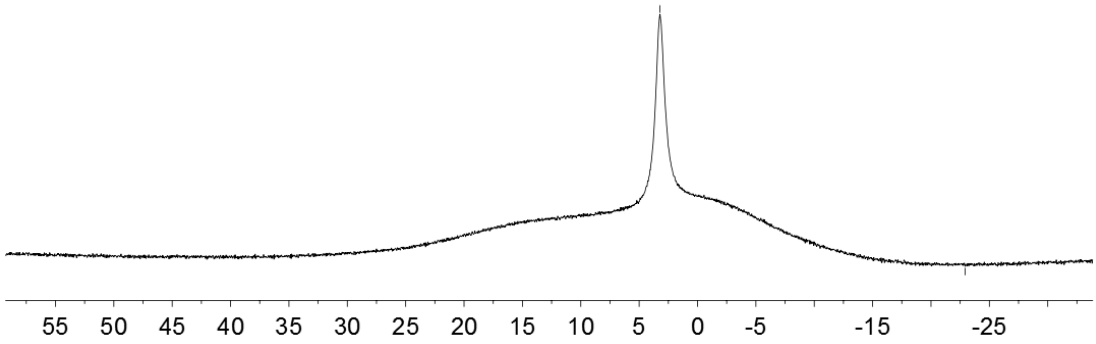


Figure S106. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299K, CD_2Cl_2) spectrum of compound **20a** and **20b**.

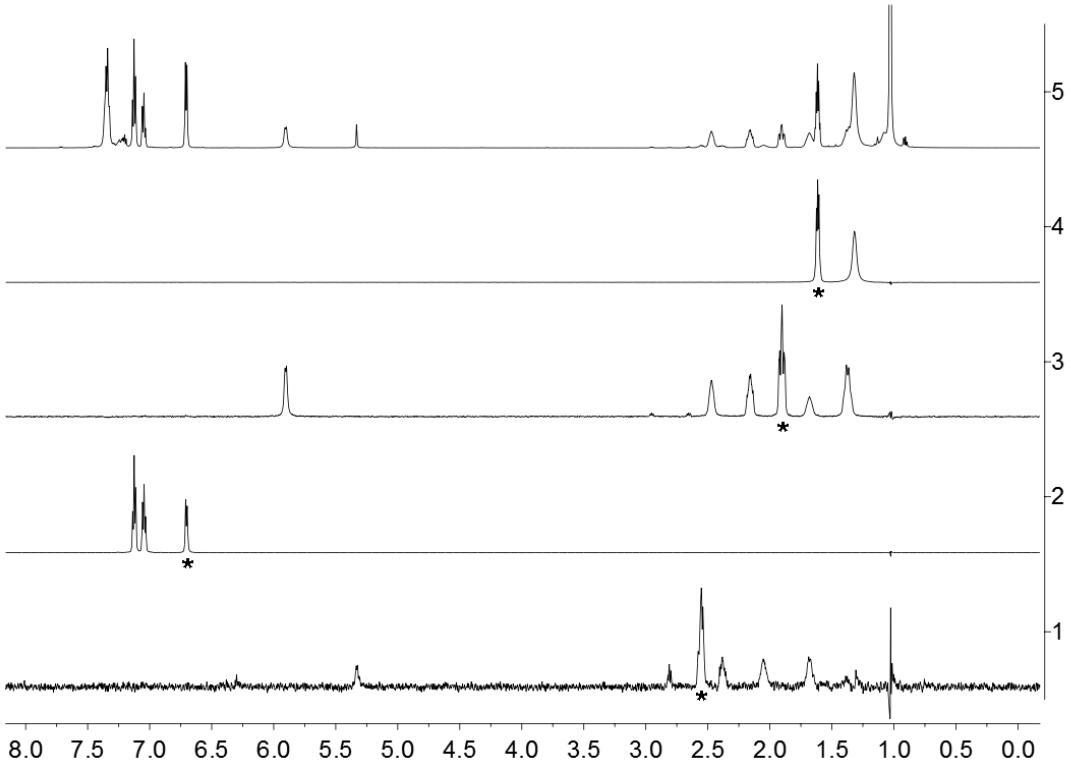


Figure S107. ^{1}H NMR (5) and ^{1}H{^{1}H} TOCSY (600 MHz, 299 K, CD_2Cl_2) spectra of compound **20a** and **20b**. * Irradiation points: δ $^{1}H_{irr}$ = 2.54 (C*H*$_2$C*H*$_2$C*H*, **20b**) (1), 6.69 (*o*-Ph, **20a**) (2), 1.89 (C*H*$_2^{Ph}$, **20a**) (3), 1.60 (C*H*$_2^{TMP}$, **20a**) (4).

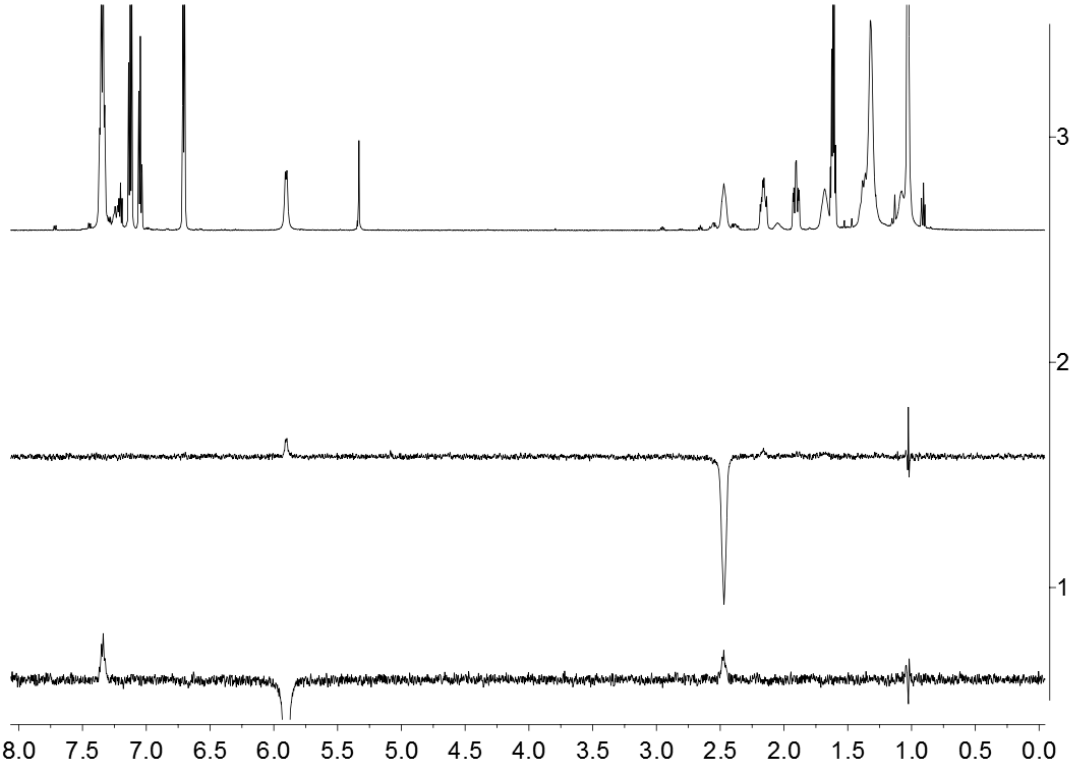


Figure S108. ^{1}H NMR (3) and ^{1}H{^{1}H} NOESY (600 MHz/600 MHz, 299 K, CD_2Cl_2) spectra of compound **20a** and **20b**. * Irradiation points: δ $^{1}H_{irr}$ =5.89 (OC*H*, **20a**) (1), 2.46 (BC*H*, **20a**) (2)).

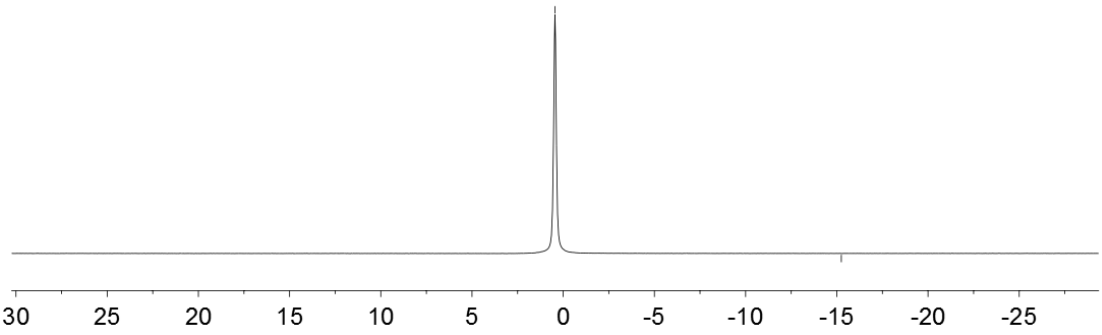


Figure S109. ^{7}Li NMR (195 MHz, 299 K, CD_2Cl_2) spectrum of compound **20a** and **20b**.

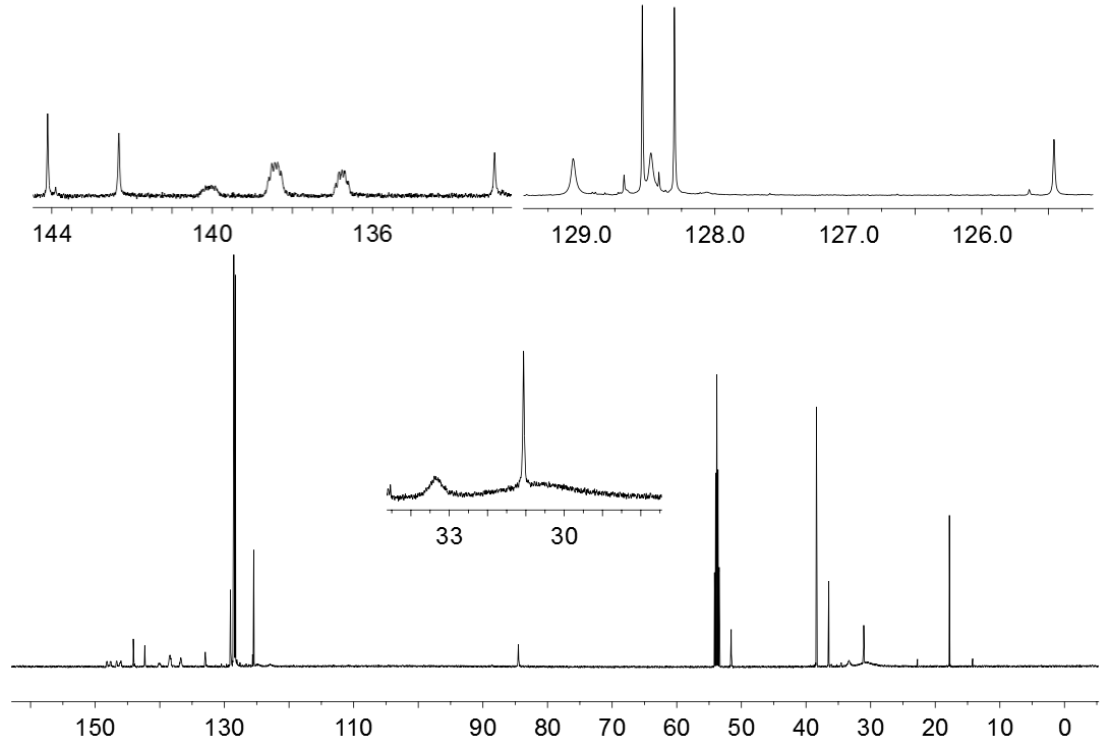


Figure S110. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **20a** and **20b**.

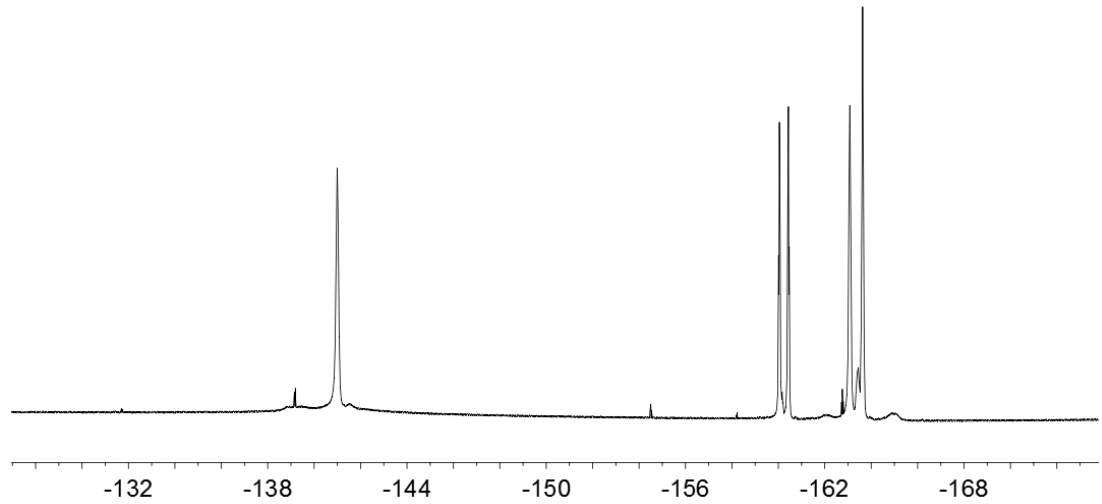


Figure S111. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **20a** and **20b**.

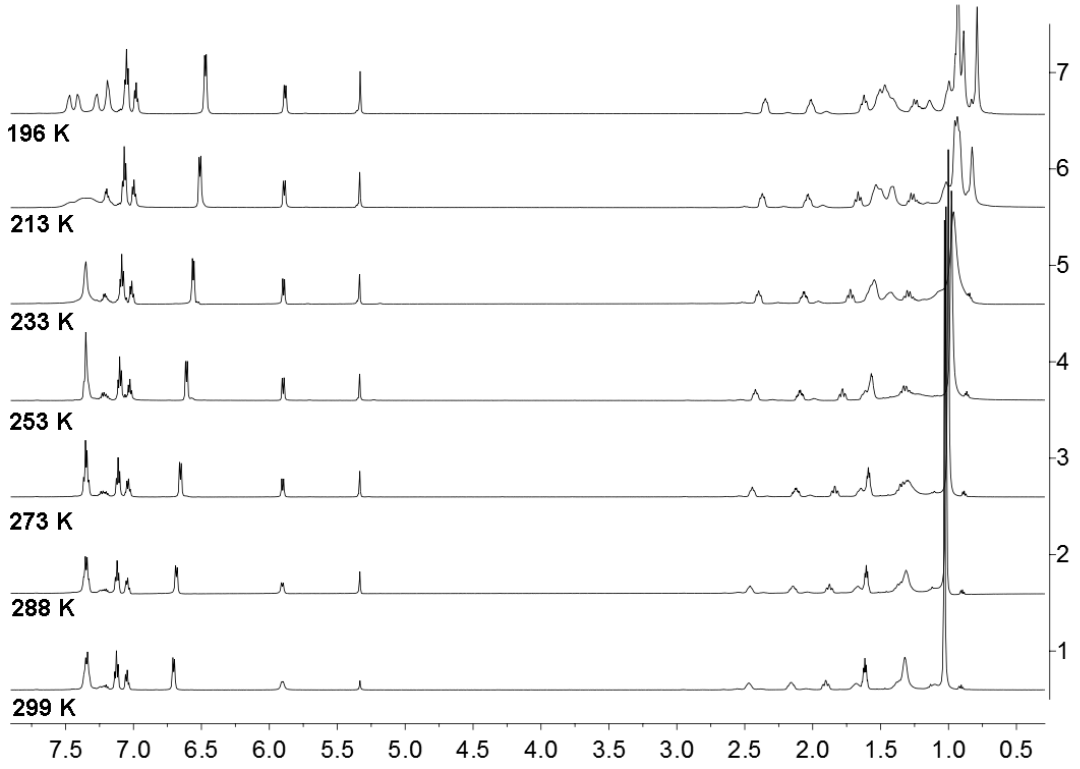


Figure S112. ^{1}H NMR (600 MHz, from 299 K to196 K, CD_2Cl_2) spectra of compound **20a** and **20b**.

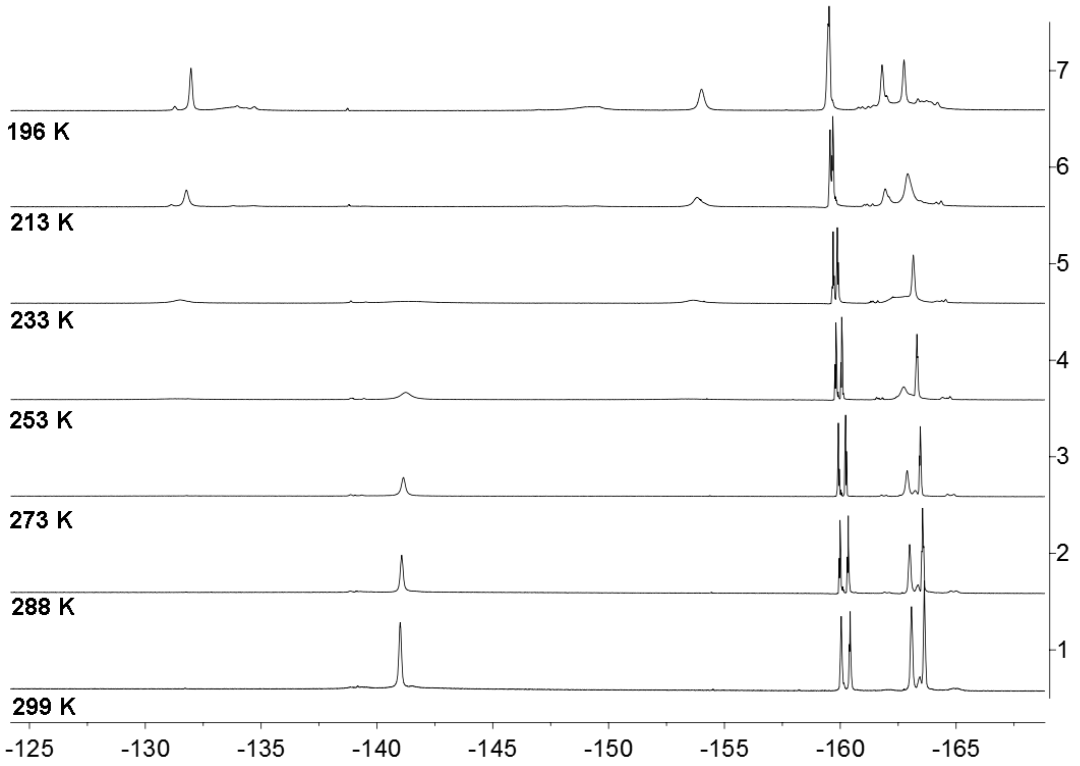


Figure S113. ^{19}F NMR (564 MHz, from 299 K to196 K, CD_2Cl_2) spectra of compound **20a** and **20b**.

X-ray crystal structure analysis of compound 20a: formula $C_{37}H_{34}BClF_{10}LiNO$, M = 751.85, colourless crystal, 0.08 x 0.05 x 0.03 mm, a = 10.1977(3), b = 13.1232(5), c = 13.9306(5) Å, α = 95.042(2), β = 90.491(2), γ = 109.468(2)°, V = 1749.5(1) Å^3, ρ_{calc} = 1.427 gcm^{-3}, μ = 0.194 mm^{-1}, empirical absorption correction (0.984 ≤ T ≤ 0.994), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 17082 reflections collected (±h, ±k, ±l), 6015 independent (R_{int} = 0.056) and 4299 observed reflections [I>2σ(I)], 477 refined parameters, R = 0.074, wR^2 = 0.151, max. (min.) residual electron density 0.35 (-0.41) e.Å^{-3}, the position of the hydrogen atom at N1 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

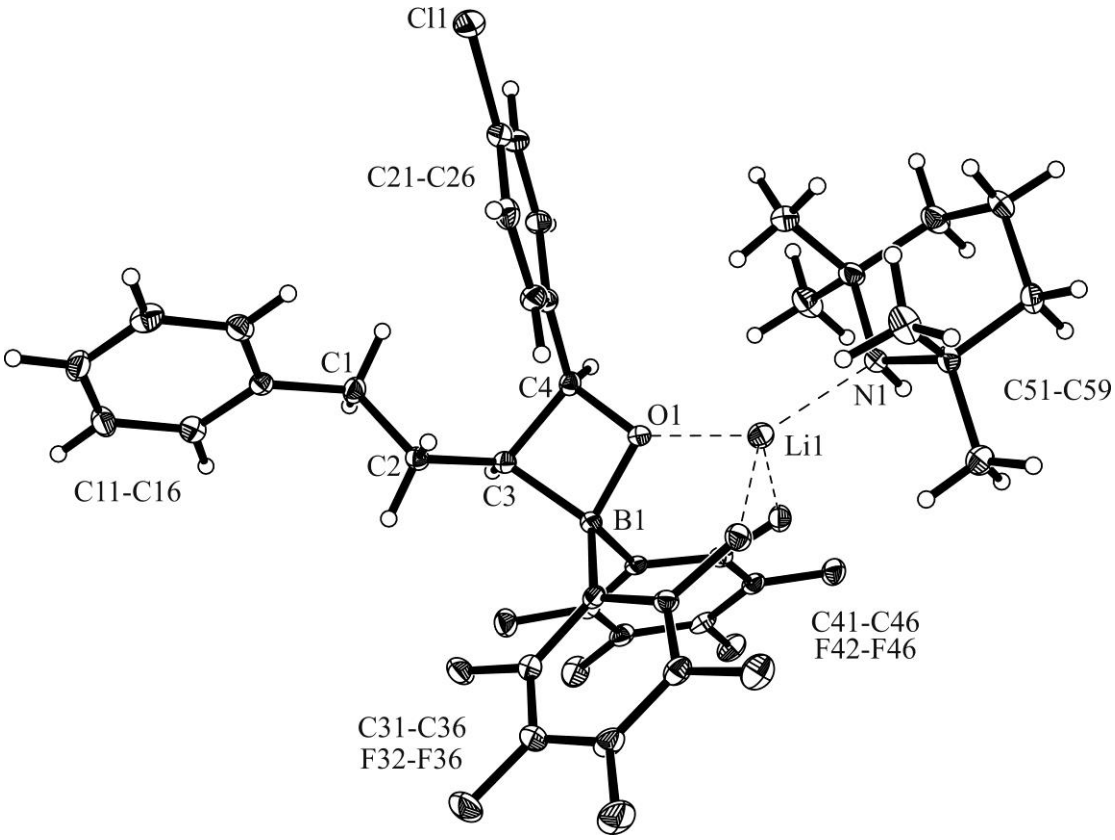
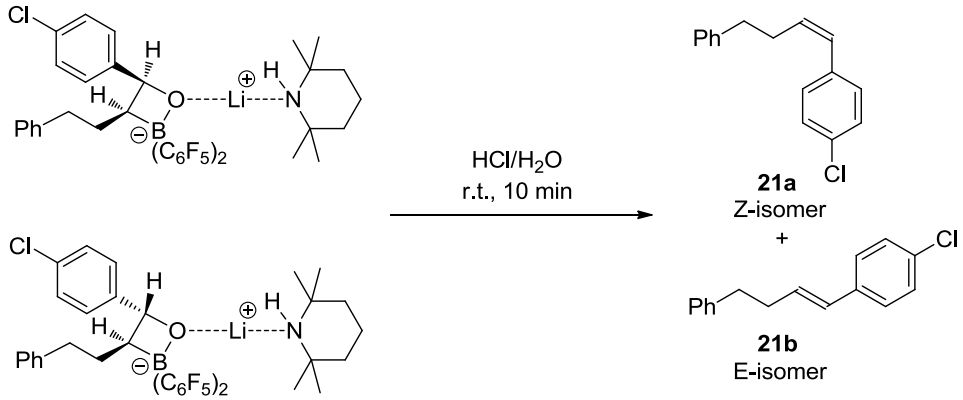


Figure S114. A view of the molecular structure of compound **20a**.

3.13 1-(4-Chlorophenyl)-4-phenylbut-1-ene (21a and 21b)



Scheme S30.

Compound **20** (238.1 mg, 0.32 mmol, the mixture of compound **20a** and **20b** in a ration of ca. 94:6 was dissolved in CH_2Cl_2 (10 mL), then hydrochloric acid (37wt%, 1 drop, ca. 0.60 mmol) was added to the solution. After stirring at room temperature for 10 min, water (3 mL) was added to give two phases and the CH_2Cl_2 layer was collected and washed with water (3×3 mL). Then the obtained CH_2Cl_2 solution was dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane) to give a colorless oil, which was identified as compound **21a** and **21b** in a ratio of 80:20 (detected by ^{1}H NMR, Z-isomer : E-isomer). Yield: 66.2 mg, 86%.

Z-isomer 21a (major):

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.17-7.31 (m, 9H, Ph, Ph^{Cl}), 6.41 (dm, $^3J_{HH}$ = 11.6 Hz, 1H, =C*H*), 5.75 (dt, $^3J_{HH}$ = 11.6, 7.2 Hz, 1H, =C*H*^{CH2}), 2.78 (m, 2H, CH_2^{Ph}), 2.63 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 142.0, 136.5, 130.4, 128.8, 128.7, 128.5 amd 126.3 (Ph, Ph^{Cl}), 133.0 (=*C*H^{CH2}), 128.6 (=*C*H), 36.2 (*C*H_2^{Ph}), 30.8 (*C*H_2).

E-isomer 21b (minor):

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.17-7.32 (m, 9H, Ph, Ph^{Cl}), 6.39 (dm, $^3J_{HH}$ = 15.8 Hz, 1H, =C*H*), 6.28 (dt, $^3J_{HH}$ = 15.8, 6.8 Hz, 1H, =C*H*^{CH2}), 2.81 (m, 2H, CH_2^{Ph}), 2.54 (m, 2H, CH_2).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 142.2, 136.8, 132.5, 128.9, 128.7, 127.6 amd 126.2 (Ph, Ph^{Cl}), 131.3 (=*C*H^{CH2}), 129.4 (=*C*H), 36.0 (*C*H_2^{Ph}), 35.2 (*C*H_2).

Mass (EI): Calc. for $[M]^+$: 242.1; Found: 242.1.

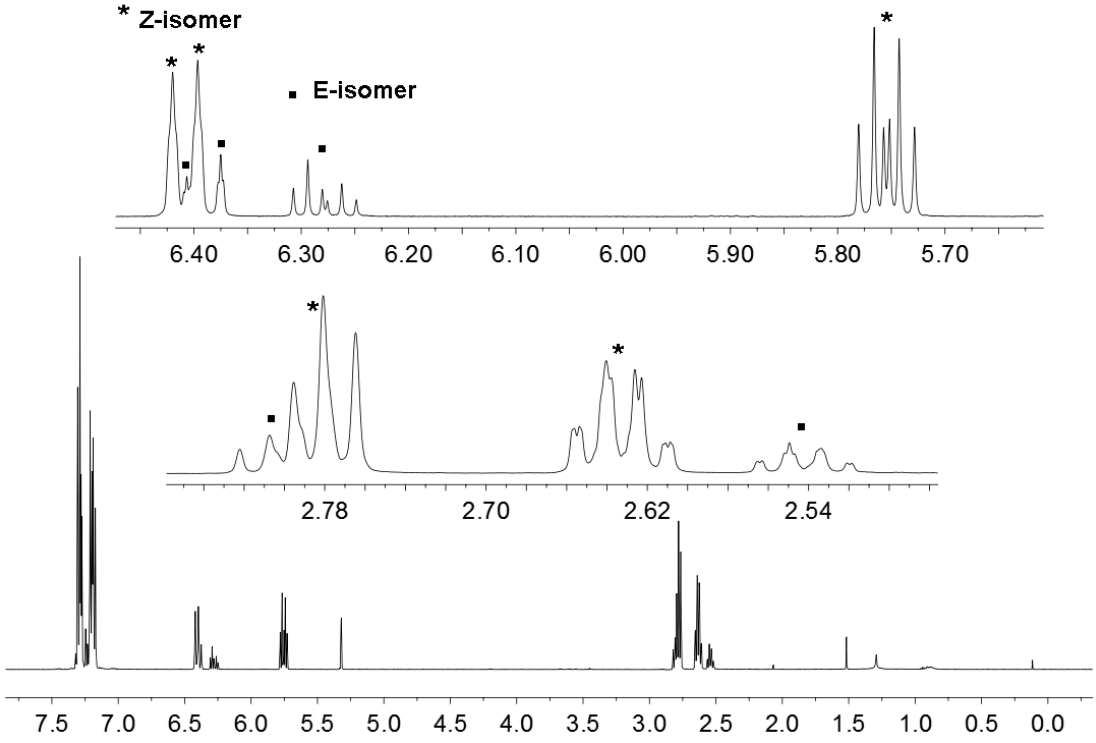


Figure S115. ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) spectrum of compound **21a** (* major, **Z-isomer**) and **21b** (• minor, **E-isomer**).

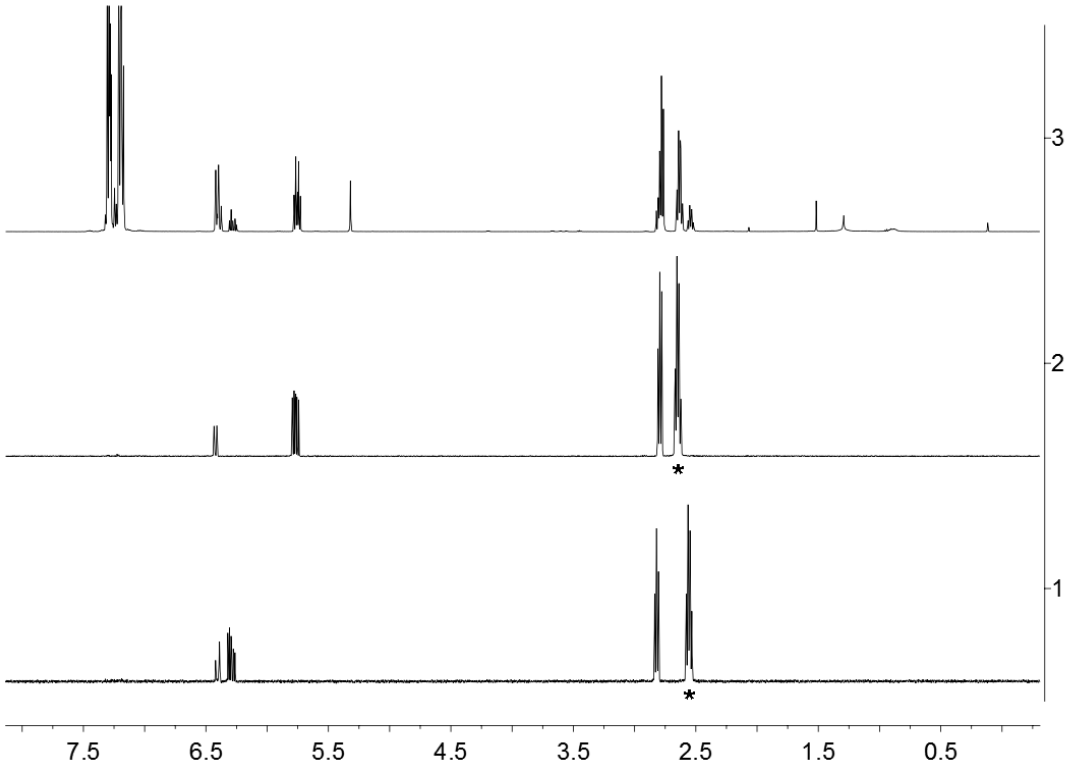


Figure S116. ^{1}H NMR (3) and ^{1}H{^{1}H} TOCSY (500 MHz, 299 K, CD_2Cl_2) spectra of compound **21a** and **21b**. * Irradiation points: $^{1}H_{irr}$ = 2.54 (C*H*$_2$, **21b**) (1), 2.63 (C*H*$_2$, **21a**) (2).

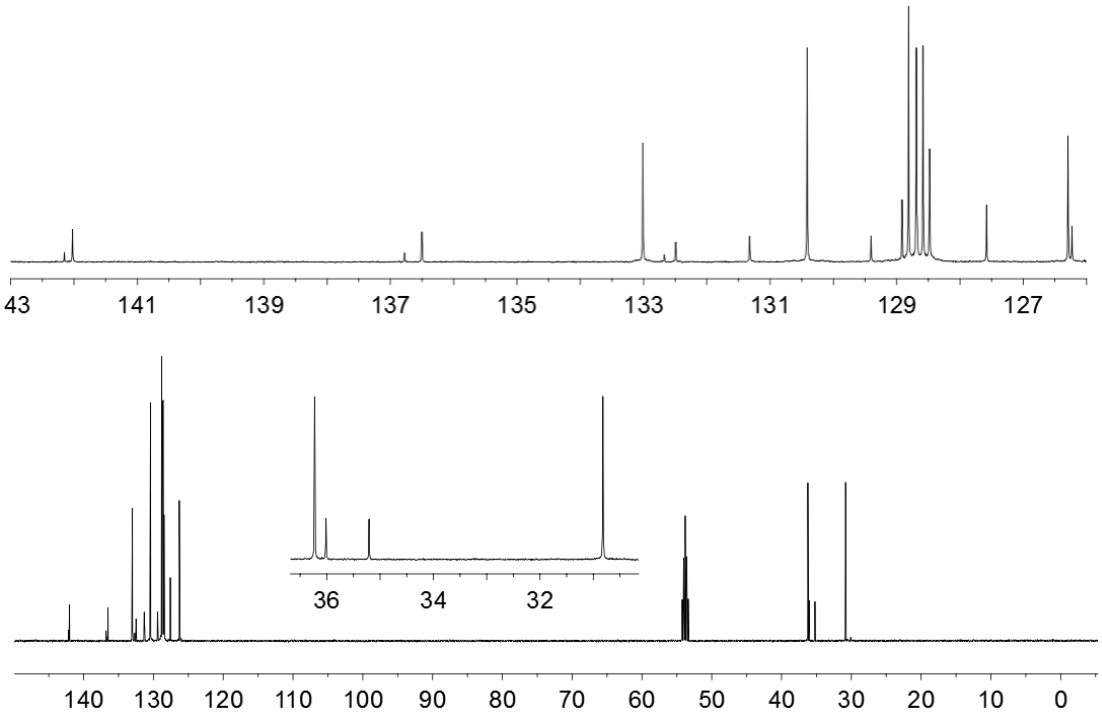
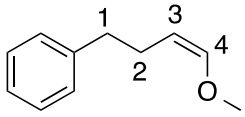


Figure S117. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) spectrum of compound **21a** and **21b**.

3.14 (Z)-(4-Methoxybut-3-en-1-yl)benzene (22a)



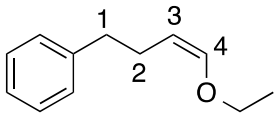
Scheme S31.

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Methyl formate (60.1 mg, 1.0 mmol, 1.0 equiv) was added causing an instantaneous color change from yellow to colorless. The reaction mixture was stirred for additional 20 min, concentrated *in vacuo* and purified by column chromatography (Alox B II, pentane, R_f (SiO_2, pentane) 0.08) to give a colorless oil in 60% yield (97 mg, 0.6 mmol). Alongside the corresponding aldehyde (**24**) was isolated in 26% yield (39 mg, 0.3 mmol). The obtained NMR data were consistent to those reported in the literature (Miura, T.; Kim, S.; Kitano, Y.; Tada, M.; Chiba, K. *Angew. Chem. Int. Ed.* 2006, **45**, 1461.).

3.15 Compound 23

3.15.1 (Z)-(4-Ethoxybut-3-en-1-yl)benzene (23a)

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Ethyl formate (74.1 mg, 1.0 mmol, 1.0 equiv) was added causing an instantaneous color change from yellow to colorless. The reaction mixture was stirred for additional 20 min and concentrated *in vacuo*. The crude product was purified by column chromatography (Alox B II, pentane, R_f (SiO_2, pentane:Et_2O = 95:5) 0.68) to give a colorless oil in 80% yield (140 mg, 0.8 mmol) as a single isomer.



Scheme S32.

(*Z*)-23a

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 7.27 (m, 2H, *m*-Ph), 7.20 (m, 2H, *o*-Ph), 7.16 (m, 1H, *p*-Ph), 5.93 (dt, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, C4-H), 4.36 (m, 1H, C3-H), 3.74 (q, $^3J_{HH}$ = 7.0 Hz, 2H, OCH_2), 2.67 (m, 2H, C1-H), 2.40 (m, 2H, C2-H), 1.22 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$): δ = 145.1 (C4), 142.4 (*i*-Ph), 128.6 (*o*-Ph), 128.2 (*m*-Ph), 125.7 (*p*-Ph), 106.0 (C3), 67.6 (OCH_2), 36.1 (C1), 25.7 (C2), 15.4 (CH_3).

Exact Mass (ESI): Calcd. for $[M+Na]^+$: 199.1093; Found: 199.1102.

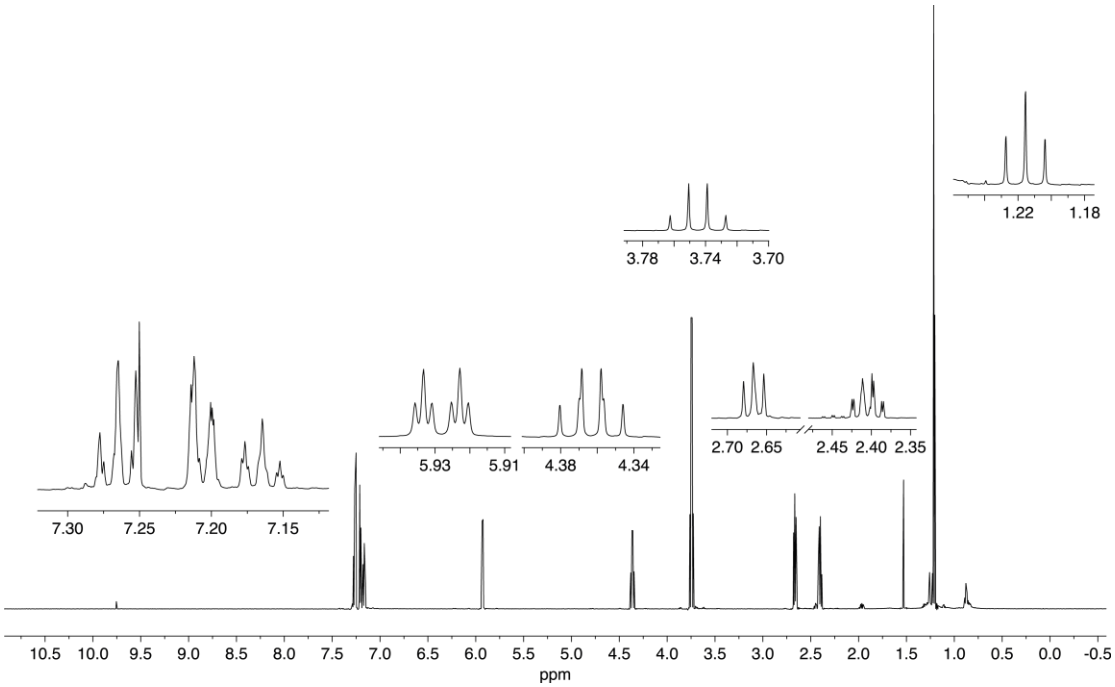


Figure S118. ^{1}H NMR (600 MHz, 299 K, $CDCl_3$) spectrum of compound **(*Z*)-23a**.

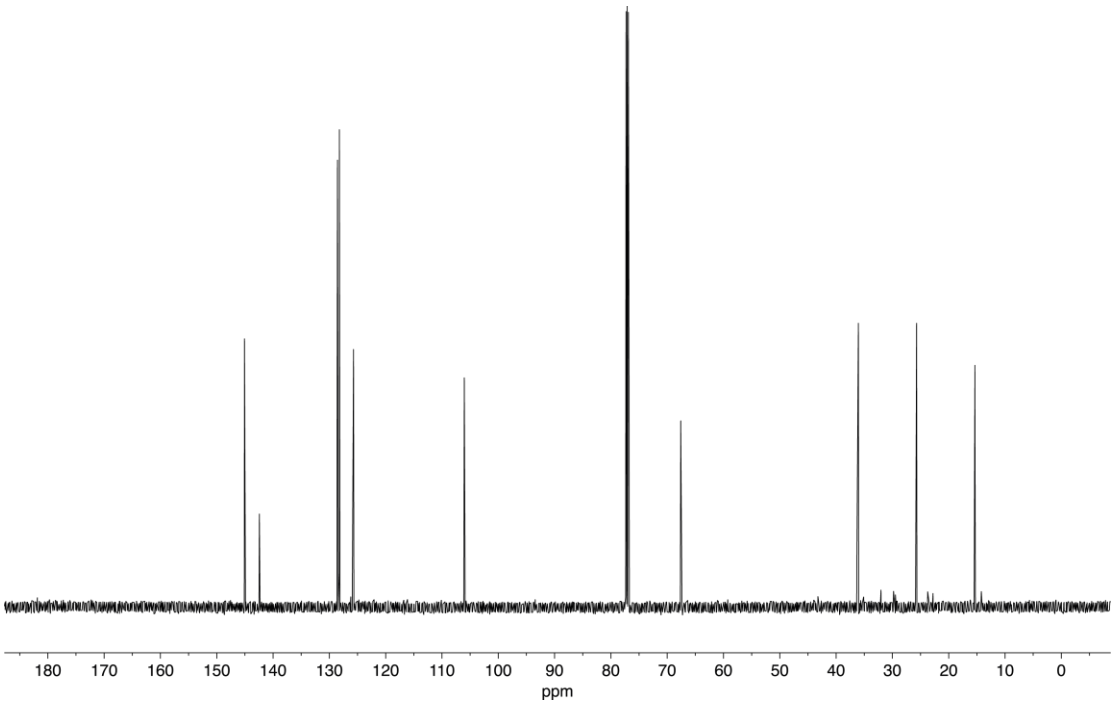


Figure S119 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$) spectrum of compound **(*Z*)-23a**.

Purification by column chromatography using SiO_2 as stationary phase allowed for isolation of a mixture of both isomers in a combined yield of 77% (136 mg, 0.8 mmol) with (*E*) : (*Z*) = 18 : 82 (δ^1H, as observed in the *in situ* reaction). The obtained material contained a considerable amount of pentane, which was considered in the yield and is not listed.

(*E*)-23a

^{1}H NMR (500 MHz, 299 K, $CDCl_3$): δ = 6.23 (d, $^3J_{HH}$ = 12.6 Hz, 1H, C4-H), 4.80 (dt, $^3J_{HH}$ = 12.4, 7.3 Hz, 1H, C3-H), 3.48 (q, $^3J_{HH}$ = 7.0 Hz, 2H, OCH_2), 2.65 (t, $^3J_{HH}$ = 7.7 Hz, 2H, C1-H), 2.23 (td, $^3J_{HH}$ = 7.7, 7.3 Hz, 2H, C2-H), 1.22 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3) [aromatic signals not listed].

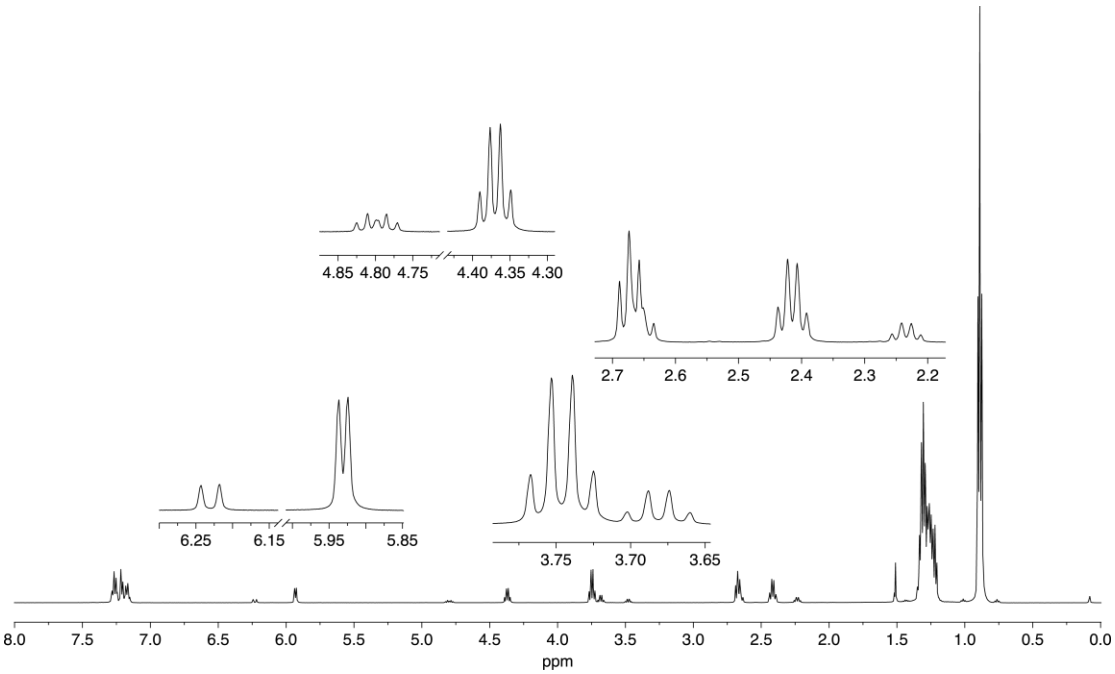
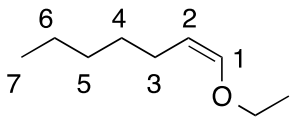


Figure S120. ^{1}H NMR (500 MHz, 299 K, $CDCl_3$) spectrum of compounds **(*Z*)-23a** and **(*E*)-23a**.

3.15.2 (Z)-1-Ethoxyhept-1-ene (23b)

Diluted 1-hexene (118.2 mg, 1.0 mmol, 1.0 equiv, pentane: 2.0 mL) was added to a suspension of $HB(C_6F_5)_2$ (345.9 mg, 1.0 mmol, 1.0 equiv) in pentane 13.0 mL). During the course of 1 h the reaction mixture became a clear solution. LiTMP (147.2 mg, 1.0 mmol, 1.0 equiv) was added and the reaction mixture was stirred for additional 2 h before ethyl formate (74.1 mg, 1.0 mmol, 1.0 equiv) was added (Careful: Add slowly since the reaction is strongly exothermic!) resulting in immediate decolorification. The reaction mixture was stirred for additional 1 h before concentrated *in vacuo* to a total volume of 1 mL. The crude product was purified by column chromatography (Alox B V, pentane, R_f = 0.85) to afford an colorless oil in 74% yield (105 mg, 0.7 mmol) as a mixture of both isomers in a ratio of (*Z*) : (*E*) = 73 : 27 (δ^1H). The obtained NMR data were consistent to those reported in the literature (Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* 1980, **21**, 4105.).



Scheme S33.

Major: (*Z*)-23b

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 5.91 (dt, $^{3}J_{HH}$ = 6.3 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, C1-H), 4.33 (td, $^{3}J_{HH}$ = 7.3, 6.3 Hz, 1H, C2-H), 3.76 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H, OCH_2), 2.06 (qd, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H, C3-H), 1.34 (m, 2H, C4-H), 1.30 (m, 2H, C6-H), 1.29 (m, 2H, C5-H), 1.23 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 0.87 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, C7-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$): δ = 144.5 (C1), 107.3 (C2), 67.5 ($O\mathbf{C}H_2$), 31.6 (C5), 29.6 (C4), 24.0 (C3), 22.63 (C6), 15.4 ($OCH_2\mathbf{C}H_3$), 14.17 (C7).

Minor: (*E*)-23b

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 6.20 (dt, $^{3}J_{HH}$ = 12.6 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, C1-H), 4.76 (dt, $^{3}J_{HH}$ = 12.6, 7.3 Hz, 1H, C2-H), 3.69 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H, OCH_2), 1.89 (qd, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, C3-H), 1.32 (m, 2H, C4-H), 1.30 (m, 2H, C6-H), 1.27 (m, 2H, C5-H), 1.25 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 0.87 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, C7-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$): δ = 145.9 (C1), 104.5 (C2), 64.7 (OCH_2), 31.3 (C5), 30.5 (C4), 27.8 (C3), 22.62 (C6), 14.9 (OCH_2CH_3), 14.20 (C7).

Mass (EI): Calc. for $[M]^+$: 142.1; Found: 142.1.

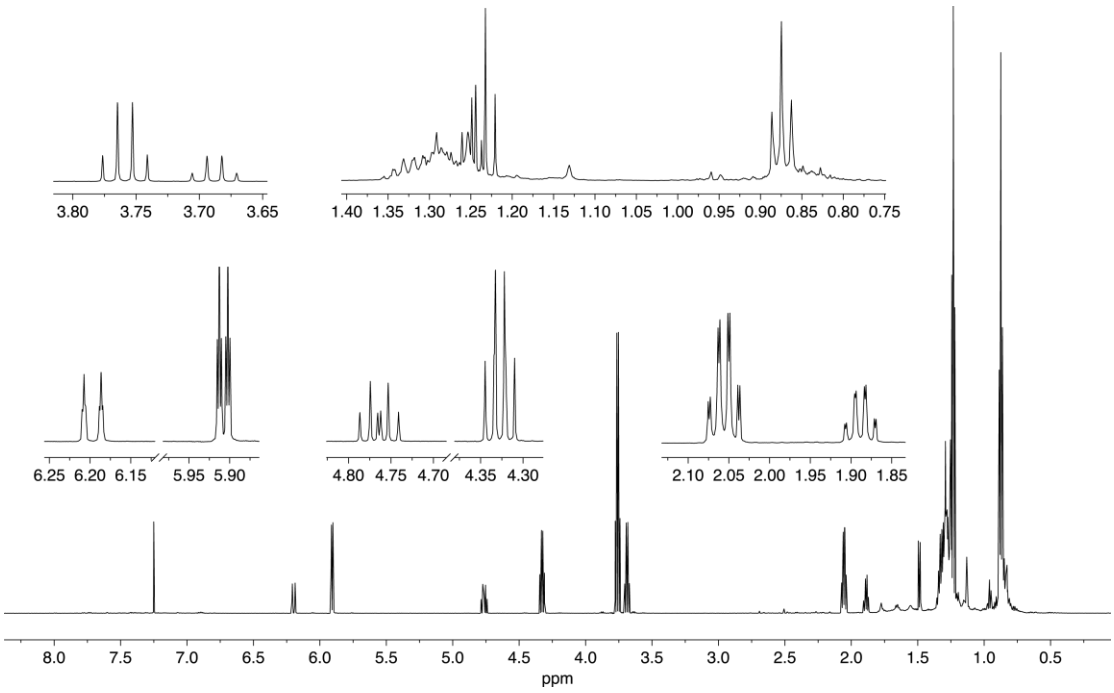


Figure S121. ^{1}H NMR (600 MHz, 299 K, $CDCl_3$) spectrum of compound **23b**.

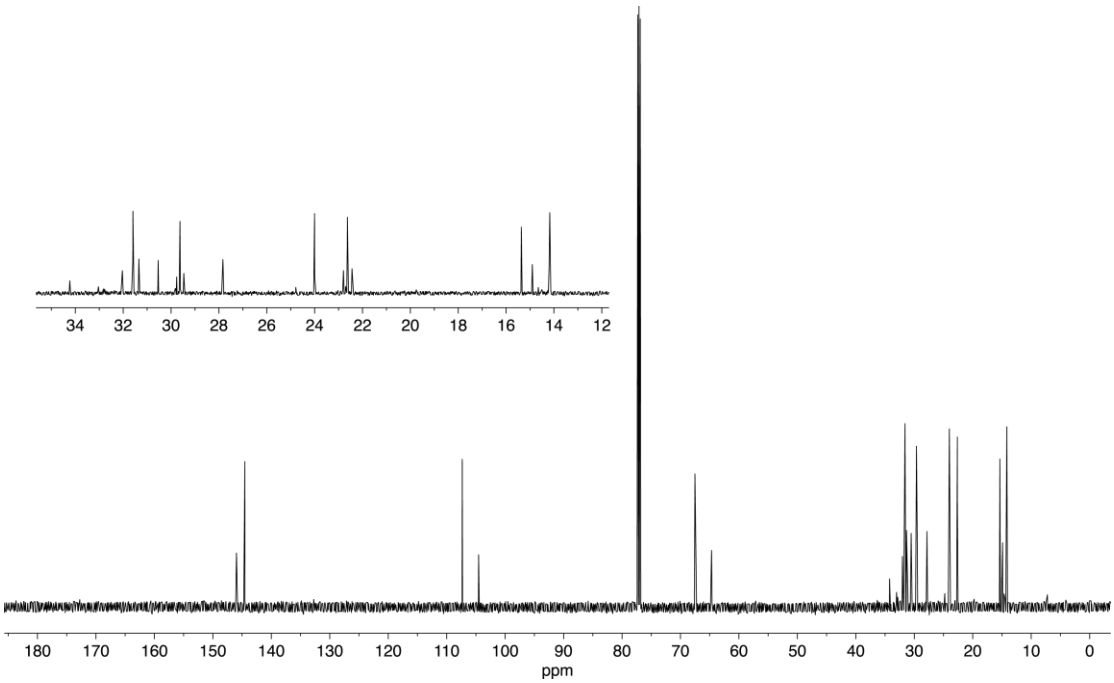
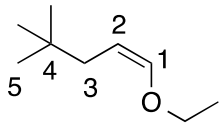


Figure S122. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$) spectrum of compound **23b**.

3.15.3 (Z)-1-Ethoxy-4,4-dimethylpent-1-ene (23c)



Scheme S34.

Diluted 3,3-dimethylbut-1-ene (84.1 mg, 1.0 mmol, 1.0 equiv, pentane: 2.0 mL) was added to a suspension of $HB(C_6F_5)_2$ (345.9 mg, 1.0 mmol, 1.0 equiv) in pentane 13.0 mL. During the course of 1 h the reaction mixture became a clear solution. LiTMP (147.2 mg, 1.0 mmol, 1.0 equiv) was added and the reaction mixture was stirred for additional 2 h before ethyl formate (74.1 mg, 1.0 mmol, 1.0 equiv) was added (Careful: Add slowly as reaction is strongly exothermic!) resulting in immediate decolorification. The reaction mixture was stirred for additional 1 h before concentrated *in vacuo* to a total volume of 1 mL. The crude product was purified by column chromatography (Alox B V, pentane, $R_f = 0.71$) to afford an colorless oil in 70% yield (99 mg, 0.7 mmol) as a mixture of both isomers in a ratio of (*Z*) : (*E*) = 83 : 17.

Major: (*Z*)-23c

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 5.98 (dt, $^{3}J_{HH}$ = 6.4 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, C11-H), 4.37 (td, $^{3}J_{HH}$ = 7.7, 6.4 Hz, 1H, C2-H), 3.75 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H, OCH_2), 1.95 (dd, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.4 Hz, 2H, C3-H), 1.22 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 0.87 (s, 9H, C5-H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$): δ = 145.6 (C1), 104.1 (C2), 67.5 (OCH_2), 38.0 (C3), 31.1 (C4), 29.21 (C5), 15.4 (OCH_2CH_3).

Minor: (*E*)-23c

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 6.14 (dt, $^{3}J_{HH}$ = 12.6 Hz, $^{4}J_{HH}$ = 1.2 Hz, 1H, C1-H), 4.79 (dt, $^{3}J_{HH}$ = 12.6, 7.9 Hz, 1H, C2-H), 3.71 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H, OCH_2), 1.75 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H, C3-H), 1.26 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 0.84 (s, 9H, C5-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$): δ = 147.1 (C1), 101.2 (C2), 64.8 (OCH_2), 42.2 (C3), 30.9 (C4), 29.15 (C5), 14.9 (OCH_2CH_3).

Mass (EI): Calc. for [M]+: 142.1; Found: 142.1.

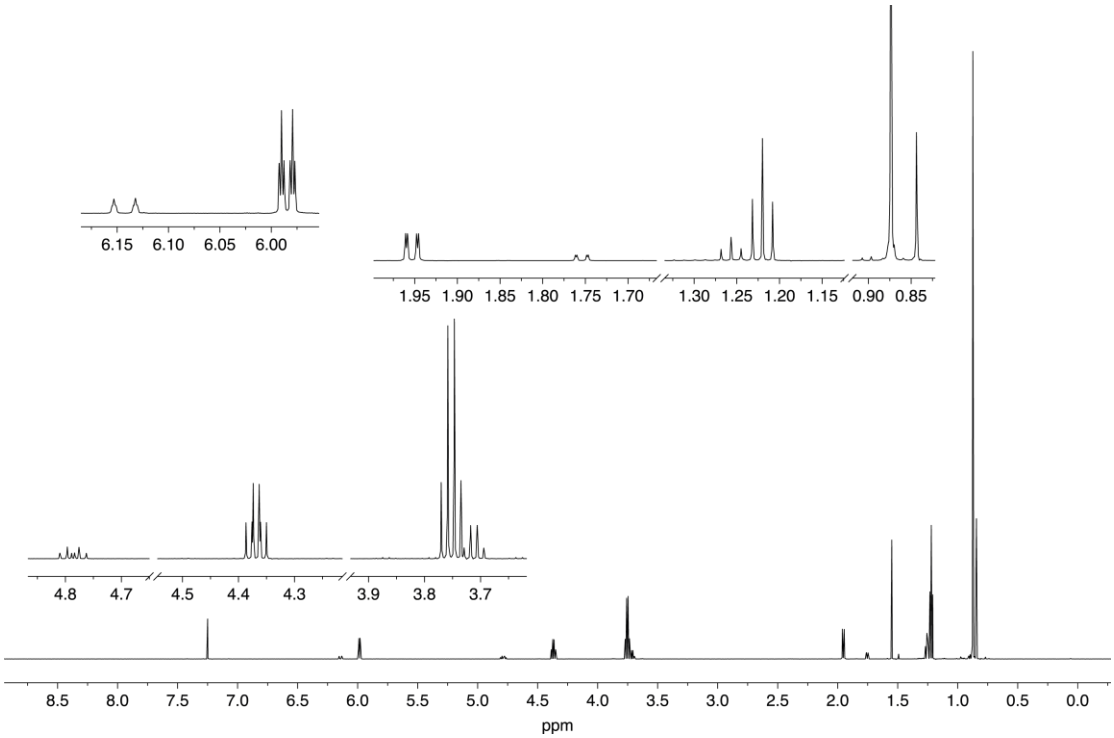


Figure S123. ^{1}H NMR (600 MHz, 299 K, $CDCl_3$) spectrum of compound **23c**.

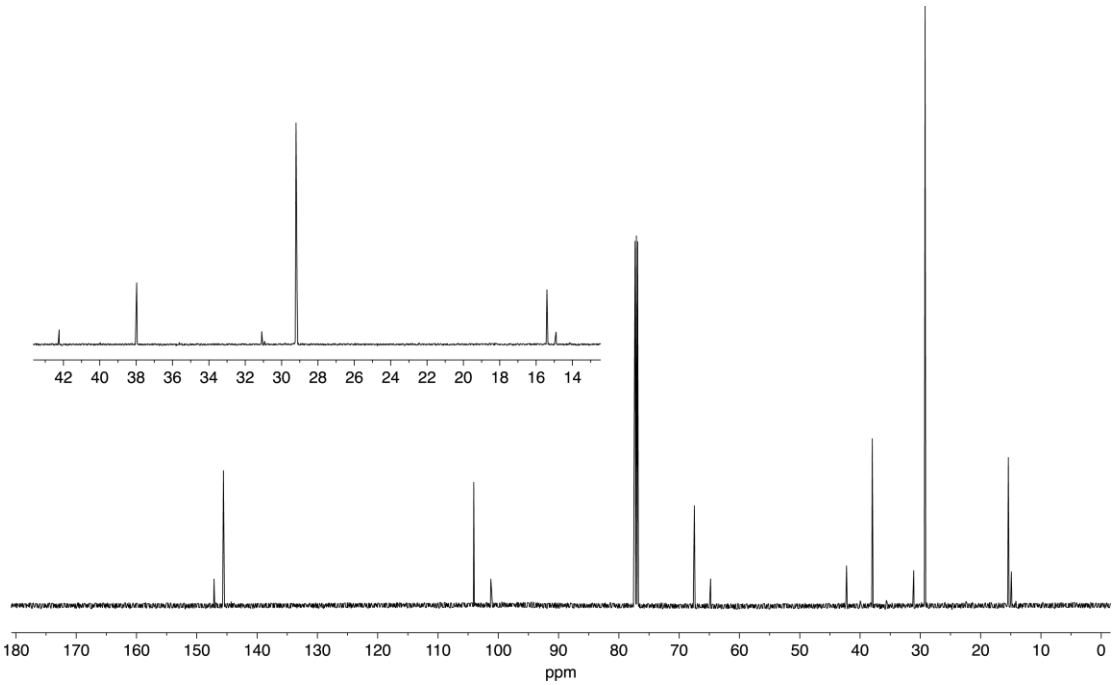
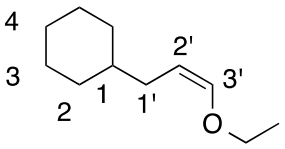


Figure S124. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$) spectrum of compound **23c**.

3.15.4 (Z)-(3'-Ethoxyallyl)cyclohexane (23d)



Scheme S35.

Diluted vinyl cyclohexane (110.2 mg, 1.0 mmol, 1.0 equiv, pentane: 2.0 mL) was added to a suspension of $HB(C_6F_5)_2$ (345.9 mg, 1.0 mmol, 1.0 equiv) in pentane (13.0 mL). During the course of 1h the reaction mixture became a clear solution. LiTMP (147.2 mg, 1.0 mmol, 1.0 equiv) was added and the reaction mixture was stirred for additional 2 h before ethyl formate (74.1 mg, 1.0 mmol, 1.0 equiv) was added (careful: slowly as reaction is exothermic), resulting in immediate decolorification. The reaction mixture was stirred for additional 1h before concentrated *in vacuo* to a total volume of 1 mL. The crude product was purified by column chromatography (Alox B V, pentane, R_f = 0.75) to afford an colorless oil in 57% yield (96 mg, 0.6 mmol) as a mixture of both isomers in a ratio of (*Z)* : (*E)* = 79 : 21.

Major: (*Z*)-23d

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 5.94 (dt, $^{3}J_{HH}$ = 6.3 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, C3'-H), 4.34 (td, $^{3}J_{HH}$ = 7.5, 6.3 Hz, 1H, C2'-H), 3.75 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H, OCH_2), 1.96 (ddd, $^{3}J_{HH}$ = 7.5, 6.9 Hz, $^{4}J_{HH}$ = 1.4 Hz, 2H, C1'-H), 1.71 (m, 2H, C2-H^{eq}), 1.67 (dt, $^{2}J_{HH}$ = 12.7 Hz, $^{3}J_{HH}$ = 3.2 Hz, 2H, C3-H^{eq}), 1.62 (dtt, $^{2}J_{HH}$ = 12.1 Hz, $^{3}J_{HH}$ = 3.2, 1.6 Hz, 1H, C4-H^{eq}), 1.23 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 1.22 (m, 1H, C1-H), 1.20 (qt, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 13.0 Hz, $^{3}J_{HH}$ = 3.2 Hz, 2H, C3-H^{ax}), 1.14 (m, 1H, C4-H^{ax}), 0.90 (dtd, $^{3}J_{HH}$ = 12.4 Hz, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 11.6 Hz, $^{3}J_{HH}$ = 2.9 Hz, 2H, C2-H^{ax}).

$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, $CDCl_3$): δ = 145.0 (C3'), 105.7 (C2'), 67.5 (OCH_2), 38.4 (C1), 33.2 (C2), 31.7 (C1'), 26.76 (C4), 26.49 (C3), 15.4 (OCH_2CH_3).

Minor: (*E*)-23d

^1H NMR (600 MHz, 299 K, $CDCl_3$): δ = 6.16 (dt, $^3J_{HH}$ = 12.6 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, C3'-H), 4.75 (dt, $^3J_{HH}$ = 12.6, 7.7 Hz, 1H, C2'-H), 3.69 (q, $^3J_{HH}$ = 7.0 Hz, 2H, OCH_2), 1.77 (ddd, $^3J_{HH}$ = 7.7, 6.6 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, C1'-H), 1.71 (m, 2H, C2-H^{eq}), 1.67 (m, 2H, C3-H^{eq}), 1.62 (m, 1H, C4-H^{eq}), 1.25 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 1.20 (m, 2H, C3-H^{ax}), 1.18 (m, 1H, C1-H), 1.14 (m, 1H, C4-H^{ax}), 0.86 (m, 2H, C2-H^{ax}).

$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, $CDCl_3$): δ = 146.5 (C3'), 102.7 (C2'), 64.7 (OCH_2), 38.9 (C1), 35.7 (C1'), 33.1 (C2), 26.74 (C4), 26.46 (C3), 14.9 (OCH_2CH_3).

Mass (EI): Calc. for $[M]^+$: 168.2; Found: 168.2.

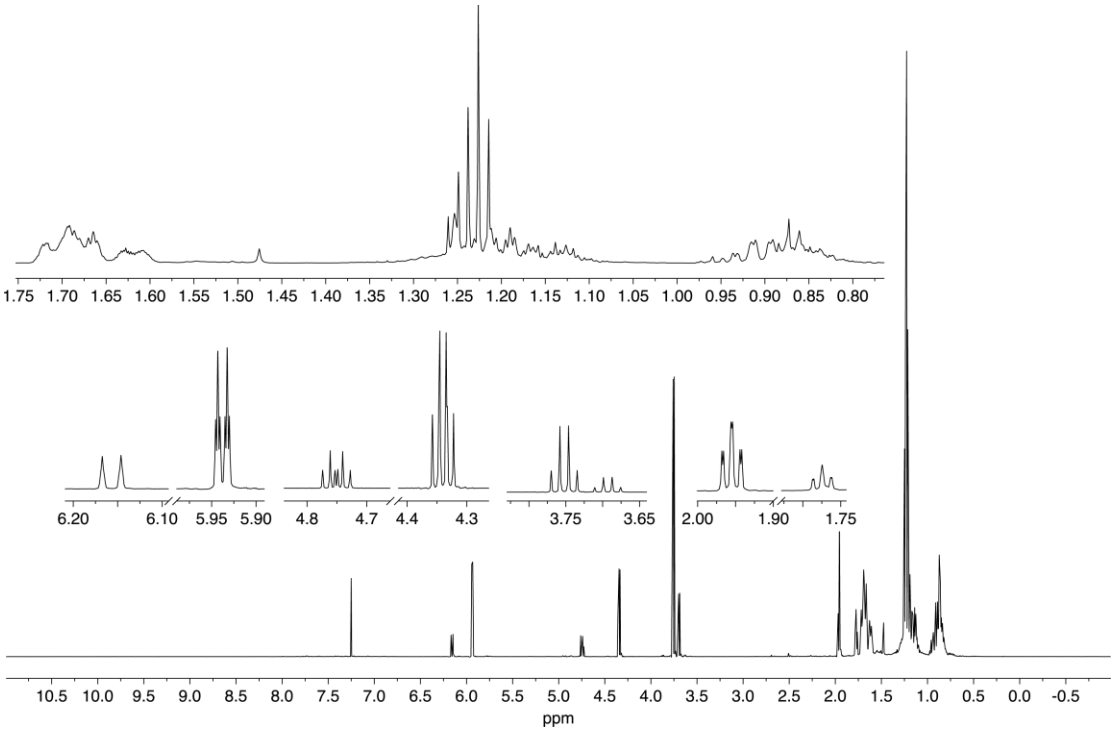


Figure S125. ^1H NMR (600 MHz, 299 K, $CDCl_3$) spectrum of compound **23d**.

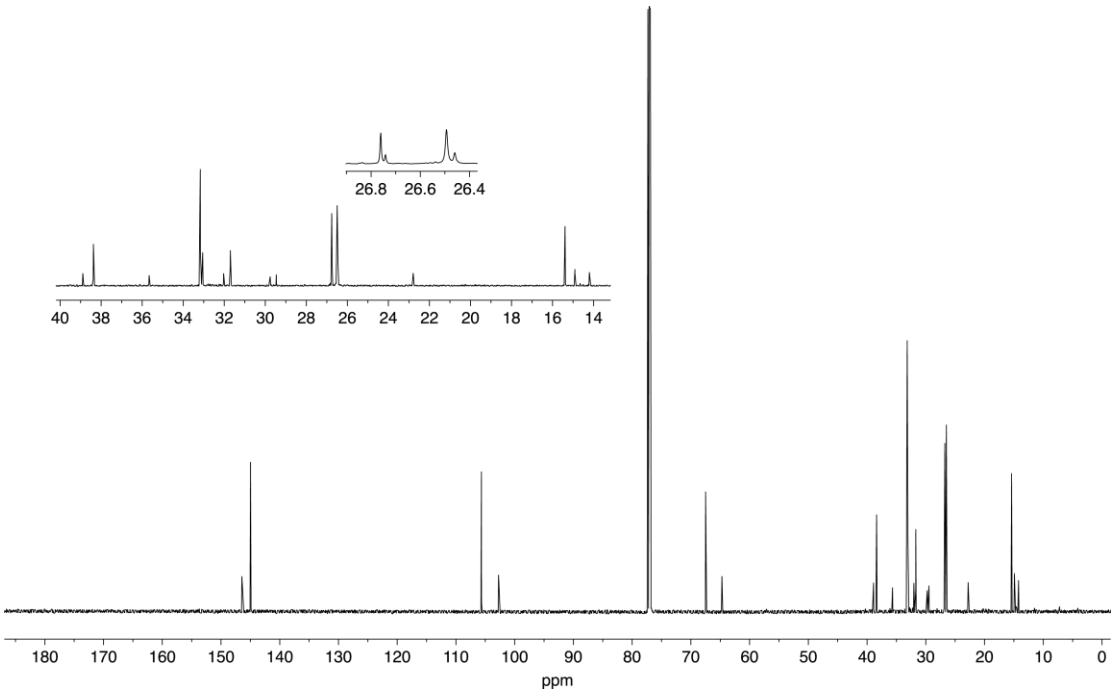
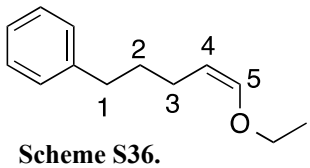


Figure S126. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$) spectrum of compound **23d**.

3.15.5 (Z)-(5-Ethoxypent-4-en-1-yl)benzene (23e)



Scheme S36.

Diluted 4-phenylbut-1-ene (132.2 mg, 1.0 mmol, 1.0 equiv, toluene: 2.0 mL) was added to a suspension of $HB(C_6F_5)_2$ (345.9 mg, 1.0 mmol, 1.0 equiv) in toluene (8.0 mL). During the course of 10 min the reaction mixture became a clear solution. LiTMP (147.2 mg, 1.0 mmol, 1.0 equiv) was added and the reaction mixture was stirred for additional 2 h before ethyl formate (74.1 mg, 1.0 mmol, 1.0 equiv) was added resulting in immediate decolorification. The reaction mixture was stirred for additional 1 h before concentrated *in vacuo*. The crude product was purified by column chromatography (Alox B V, pentane, R_f = 0.43) to afford an colorless oil in 81% yield (154 mg, 0.8 mmol) as a mixture of both isomers in a ratio of (*Z*):(*E*) = 88:12.

Major: (*Z*)-23e

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 7.26 (m, 2H, *m*-Ph), 7.18 (m, 2H, *o*-Ph), 7.16 (m, 1H, *p*-Ph), 5.95 (dt, $^{3}J_{HH}$ = 6.3 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, C5-H), 4.35 (td, $^{3}J_{HH}$ = 7.2, 6.3 Hz, 1H, C4-H), 3.77 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H, OCH_2), 2.62 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H, C1-H), 2.12 (m, 2H, C3-H), 1.66 (m, 2H, C2-H), 1.24 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3).

$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$): δ = 145.0 (C5), 142.9 (*i*-Ph), 128.6 (*o*-Ph), 128.3 (*m*-Ph), 125.6 (*p*-Ph), 106.6 (C4), 67.6 (OCH_2), 35.6 (C1), 31.8 (C2), 23.8 (C3), 15.4 (OCH_2CH_3).

Minor: (*E*)-23e

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 6.21 (d m, $^{3}J_{HH}$ = 12.6 Hz, 1H, C5-H), 4.78 (dt, $^{3}J_{HH}$ = 12.6, 7.3 Hz, 1H, C4-H), 3.70 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H, OCH_2), 2.59 (t, $^{3}J_{HH}$ = 6.9 Hz, 2H, C1-H), 1.95 (m, 2H, C3-H), 1.66 (m, 2H, C2-H), 1.26 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3) [aromatic signals excluded].

^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$): δ = 146.4 (C5), 142.7 (*i*-Ph), 128.5 (*o*-Ph), 128.33 (*m*-Ph), 125.7 (*p*-Ph), 103.9 (C4), 64.8 (OCH_2), 35.3 (C1), 32.5 (C2), 27.5 (C3), 14.9 (OCH_2CH_3).

Mass (EI): Calc. for $[M]^+$: 190.1; Found: 190.2.

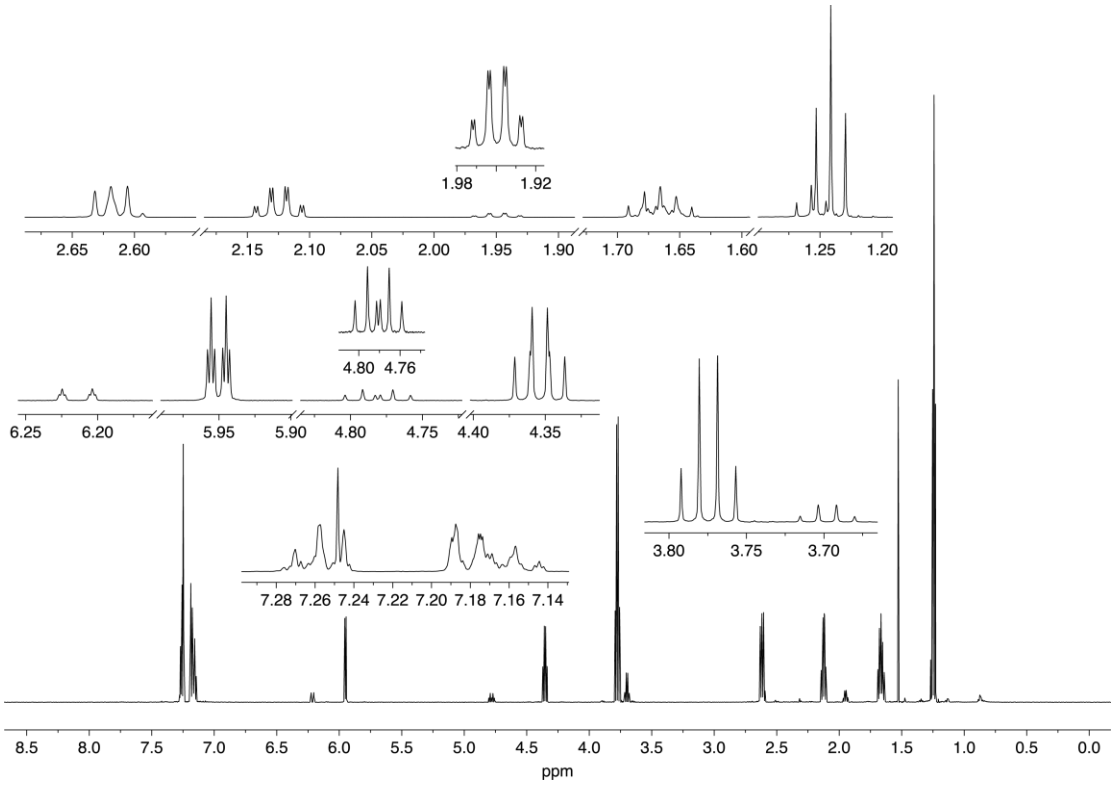


Figure S127. ^{1}H NMR (600 MHz, 299 K, $CDCl_3$) spectrum of compound **23e**.

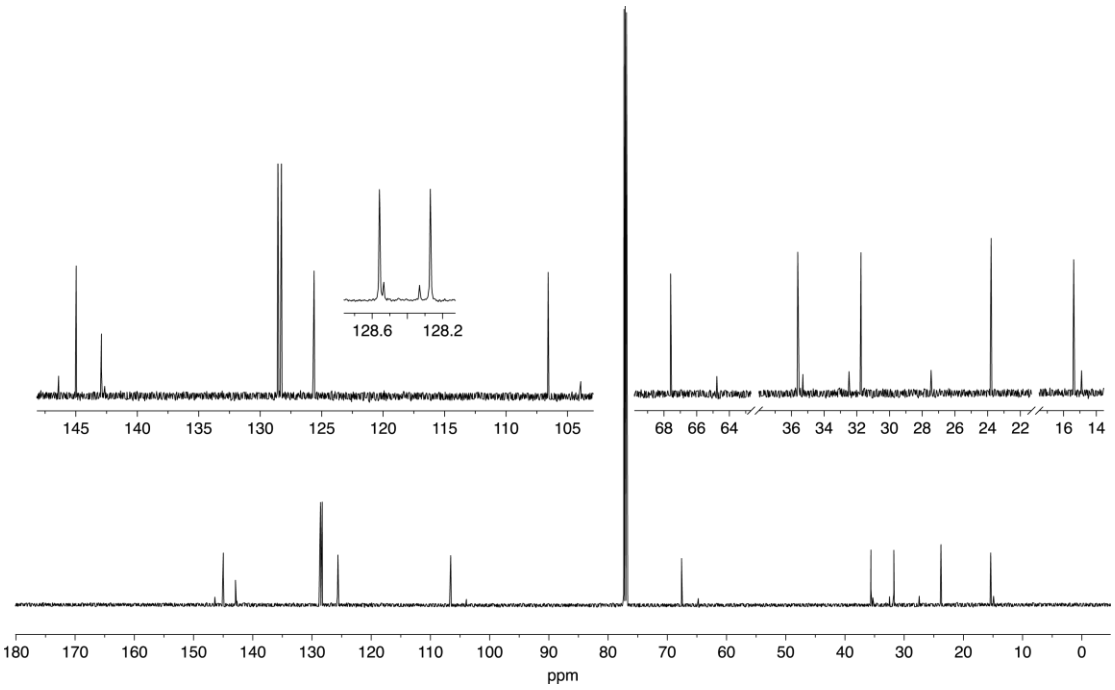
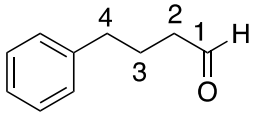


Figure S128. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$) spectrum of compound **23e**.

3.16 4-Phenylbutanal (24)



Scheme S37.

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Ethyl formate (74.1 mg, 1.0 mmol, 1.0 equiv) was added causing an instantaneous color change from yellow to colorless. The reaction mixture was stirred for additional 2 h. Hydrochloric acid (37wt%, 5 droplets), followed by distilled water (1 mL) was added at 0 °C. The two-phase system was allowed to warm to room temperature overnight and stirred for 1 additional day. The reaction mixture was concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane to pentane : Et_2O = 3 : 1, R_f (SiO_2, pentane) 0.25) to give a colorless oil in 69% yield (103 mg, 0.7 mmol). The obtained NMR data were consistent to those reported in the literature (Karimi, B.; Elhamifar, D.; Clark, J. H.; Hunt, A. J. *Org. Biomol. Chem.* 2011, **9**, 7420.).

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 9.75 (t, $^{4}J_{HH}$ = 1.6 Hz, 2H, C1-H), 7.28 (m, 2H, *m*-Ph), 7.19 (m, 1H, *p*-Ph), 7.17 (m, 2H, *o*-Ph), 2.65 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, C4-H), 2.45 (m, 2H, C2-H), 1.96 (m, 2H, C3-H).

^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$): δ = 202.4 (C1), 141.3 (*i*-Ph), 128.5 (*o,m*-Ph), 126.2 (*p*-Ph), 43.2 (C2), 35.1 (C4), 23.7 (C3).

Mass (EI): Calcd. for [M]+: 148.1; Found: 148.2.

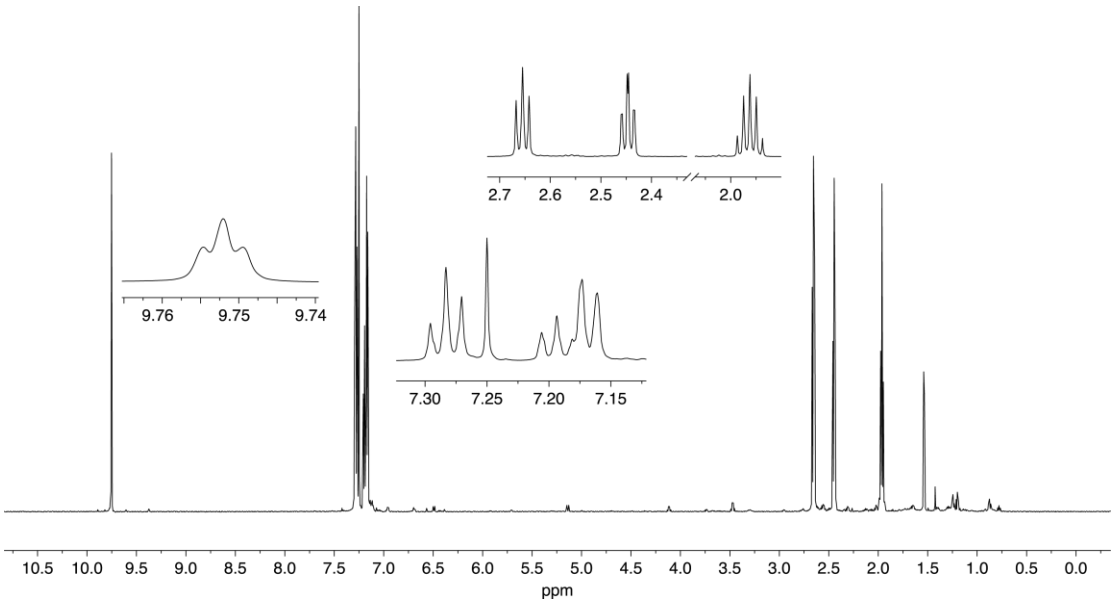


Figure S129. ^{1}H NMR (600 MHz, 299 K, $CDCl_3$) spectrum of compound **24**.

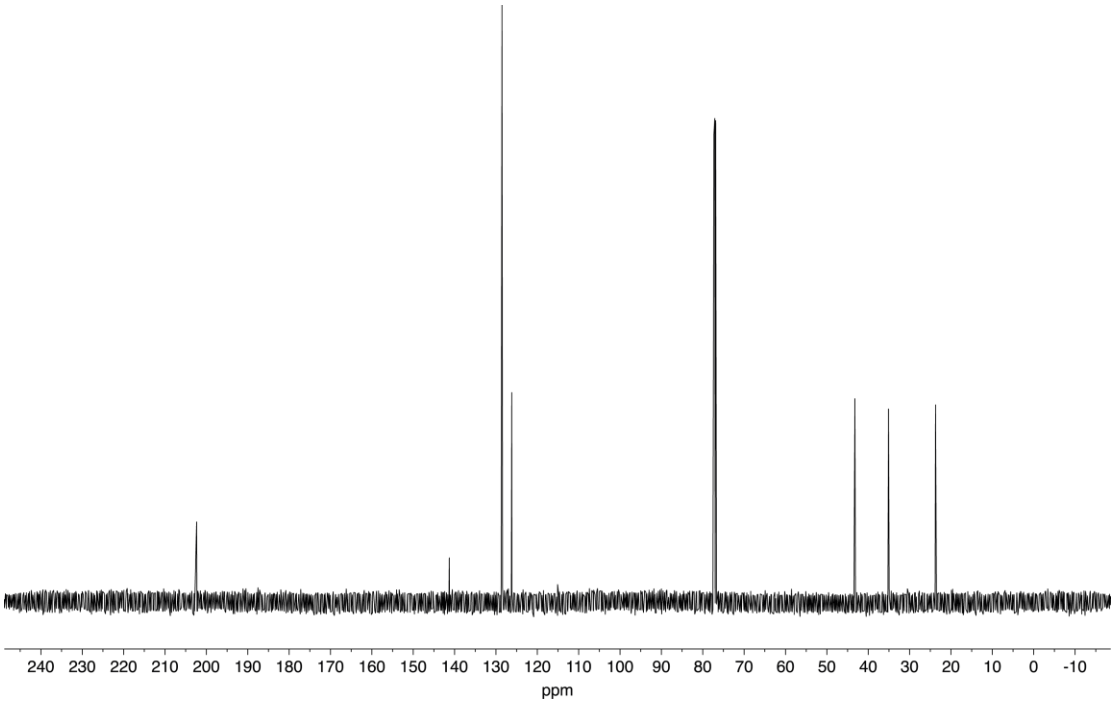


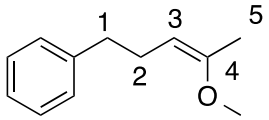
Figure S130. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$) spectrum of compound **24**.

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). The reaction mixture was concentrated *in vacuo* (3 h after LiTMP addition). *N*,*N*-Dimethylformamide (1 mL, 13 mmol, 13 equiv) was added. The reaction mixture was stirred for 3 d and directly purified by column chromatography (Alox B V, pentane to pentane : Et_2O = 1 : 1) to give a colorless liquid in 49% yield (73 mg, 0.5 mmol). The NMR spectroscopic data are in agreement with those listed above.

3.17 Compound 25

3.17.1 (Z)-(4-Methoxypent-3-en-1-yl)benzene (25a)

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Methyl acetate (74.1 mg, 1.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 2 d, concentrated *in vacuo* and purified by column chromatography (Alox N V, pentane, R_f (SiO_2, pentane : Et_2O = 95 : 5) 0.67) to give a colorless oil in 42% yield (75 mg, 0.4 mmol).



Scheme S38.

^{1}H NMR (500 MHz, 299 K, $CDCl_3$): δ = 7.27 (m, 2H, *m*-Ph), 7.20 (m, 2H, *o*-Ph), 7.17 (m, 1H, *p*-Ph), 4.45 (tq, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, C3-H), 3.49 (s, 3H, OCH_3), 2.62 (dd, $^3J_{HH}$ = 8.5, 6.8 Hz, 2H, C1-H), 2.36 (m, 2H, C2-H), 1.80 (m, 3H, C5-H).
^{13}C{^{1}H} NMR (126 MHz, 299 K, $CDCl_3$): δ = 151.4 (C4), 142.6 (*i*-Ph), 128.6 (*o*-Ph), 128.2 (*m*-Ph), 125.7 (*p*-Ph), 107.7 (C3), 55.7 (OCH_3), 36.3 (C1), 26.5 (C2), 17.4 (C5).

Exact Mass (ESI): Calcd. for $[M+Na]^+$: 199.1093; Found: 199.1097.

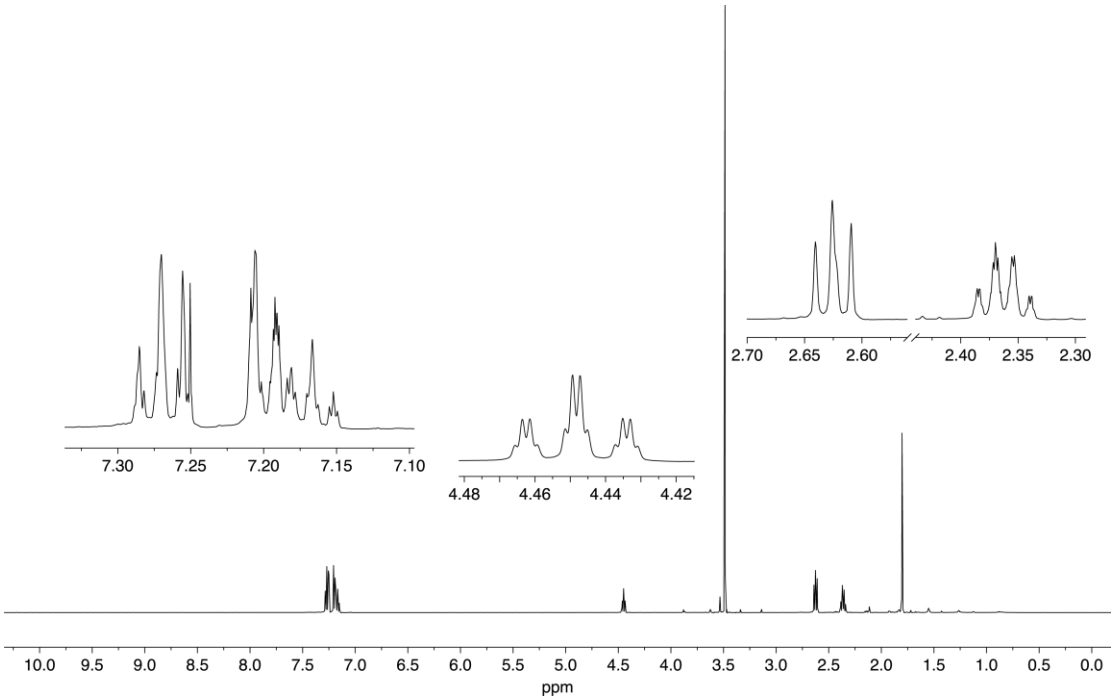


Figure S131. ^{1}H NMR (500 MHz, 299 K, $CDCl_3$) spectrum of compound **25a**.

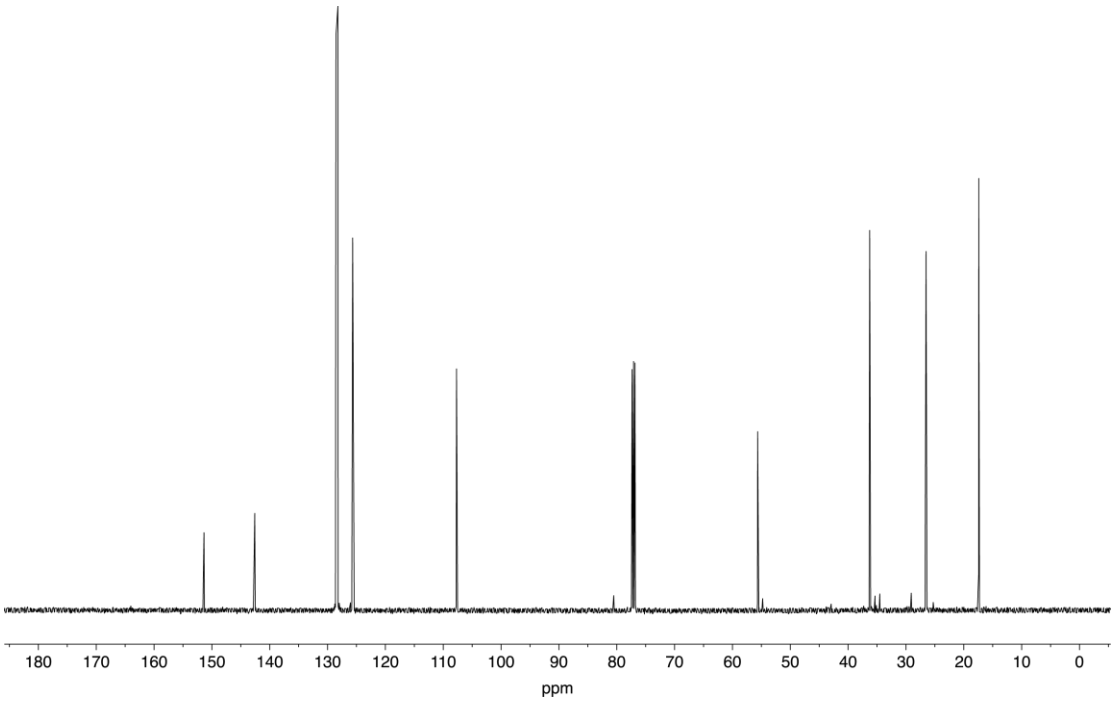
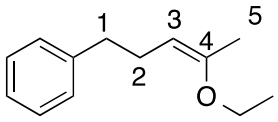


Figure S132. $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, $CDCl_3$) spectrum of compound **25a**.

3.17.2 (Z)-(4-Ethoxypent-3-en-1-yl)benzene (25b)



Scheme S39.

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Ethyl acetate (88.1 mg, 1.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 2 d, concentrated *in vacuo* and purified by column chromatography (Alox N V, pentane, R_f (SiO_2, pentane : Et_2O = 95 : 5) 0.12) to give a colorless oil in 52% yield (98 mg, 0.5 mmol).

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 7.26 (m, 2H, *m*-Ph), 7.20 (m, 2H, *o*-Ph), 7.15 (m, 1H, *p*-Ph), 4.48 (dt, $^{3}J_{HH}$ = 7.1 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, C3-H), 3.70 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H, OCH_2), 2.61 (dd, $^{3}J_{HH}$ = 8.5, 6.8 Hz, 2H, C1-H), 2.37 (m, 2H, C2-H), 1.78 (m, 3H, C5-H), 1.20 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, CH_3).
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$): δ = 150.5 (C4), 142.7 (*i*-Ph), 128.6 (*o*-Ph), 128.3 (*m*-Ph), 125.7 (*p*-Ph), 108.8 (C3), 63.4 (OCH_2), 36.4 (C1), 26.8 (C2), 18.1 (C5), 15.6 (CH_3).

Exact Mass (ESI): Calcd. for $[M+Na]^+$: 213.1250; Found: 213.1251.

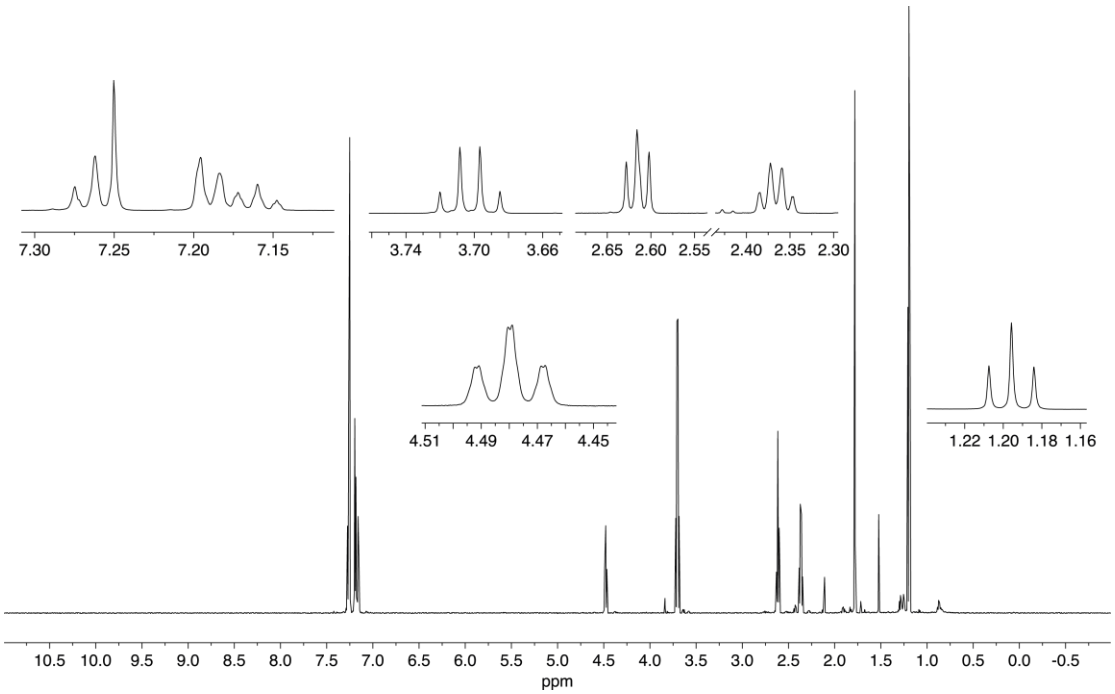


Figure S133. ^{1}H NMR (600 MHz, 299 K, $CDCl_3$) spectrum of compound **25b**.

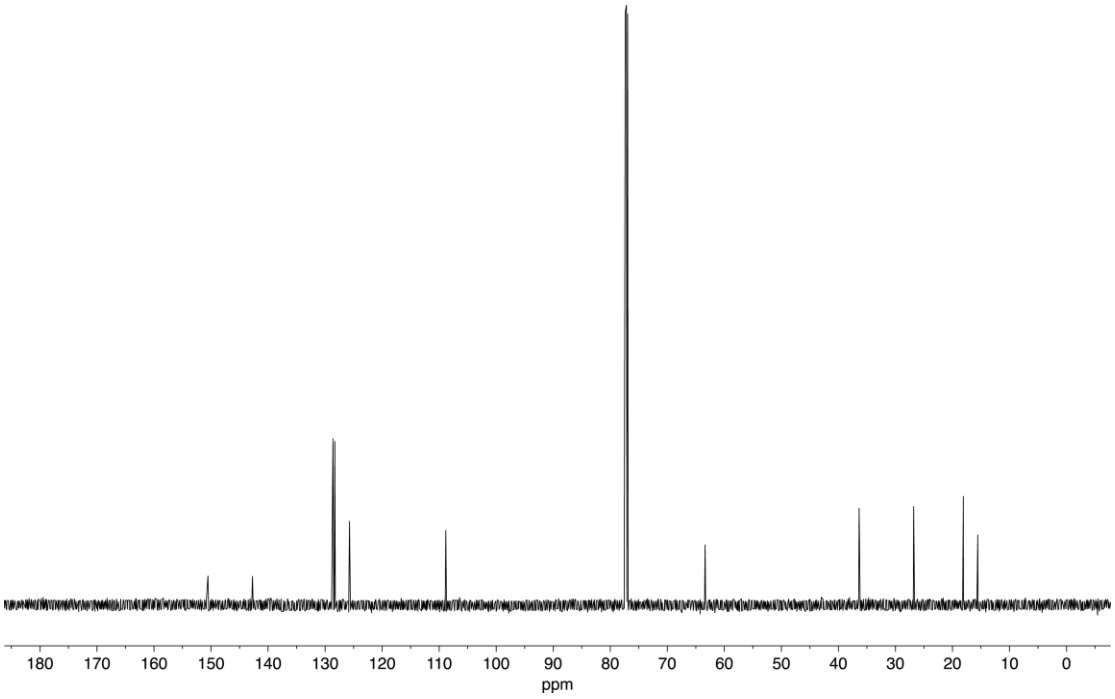
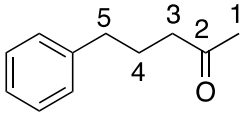


Figure S134. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$) spectrum of compound **25b**.

3.18 5-Phenylpentan-2-one (26)



Scheme S40.

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Ethyl acetate (88.1 mg, 1.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred for additional 2.5 d. Hydrochloric acid (37wt%, 12 droplets), followed by distilled water (2.5 mL) was added at 0 °C. The two-phase system was allowed to warm to room temperature overnight and stirred for an additional 1 d. The phases were separated, the aqueous layer extracted with toluene (2 x 3 mL). The combined organic layers were concentrated *in vacuo* and purified by column chromatography (SiO_2, pentane to Et_2O, R_f (SiO_2, pentane : Et_2O = 3 : 1) 0.11) to give a colorless oil in 78% yield (127 mg, 0.8 mmol). The obtained NMR data were consistent to those reported in the literature (Mori, N.; Togo, H. *Tetrahedron* 2005, **61**, 5915.).

^{1}H NMR (600 MHz, 299 K, $CDCl_3$): δ = 7.28 (m, 2H, *m*-Ph), 7.18 (m, 1H, *p*-Ph), 7.16 (m, 2H, *o*-Ph), 2.62 (t, $^3J_{HH}$ = 7.6 Hz, 2H, C5-H), 2.43 (t, $^3J_{HH}$ = 7.4 Hz, 2H, C3-H), 2.11 (s, 3H, C1-H), 1.96 (tt, $^3J_{HH}$ = 7.6, 7.4 Hz, 2H, C4-H).
^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$): δ = 208.7 (C2), 141.5 (*i*-Ph), 128.4 (*o*-Ph), 128.3 (*m*-Ph), 125.9 (*p*-Ph), 42.8 (C3), 35.0 (C5), 29.9 (C1), 25.2 (C4).

Exact Mass (ESI): Calcd. for $[M+Na]^+$: 185.0937; Found: 185.0940.

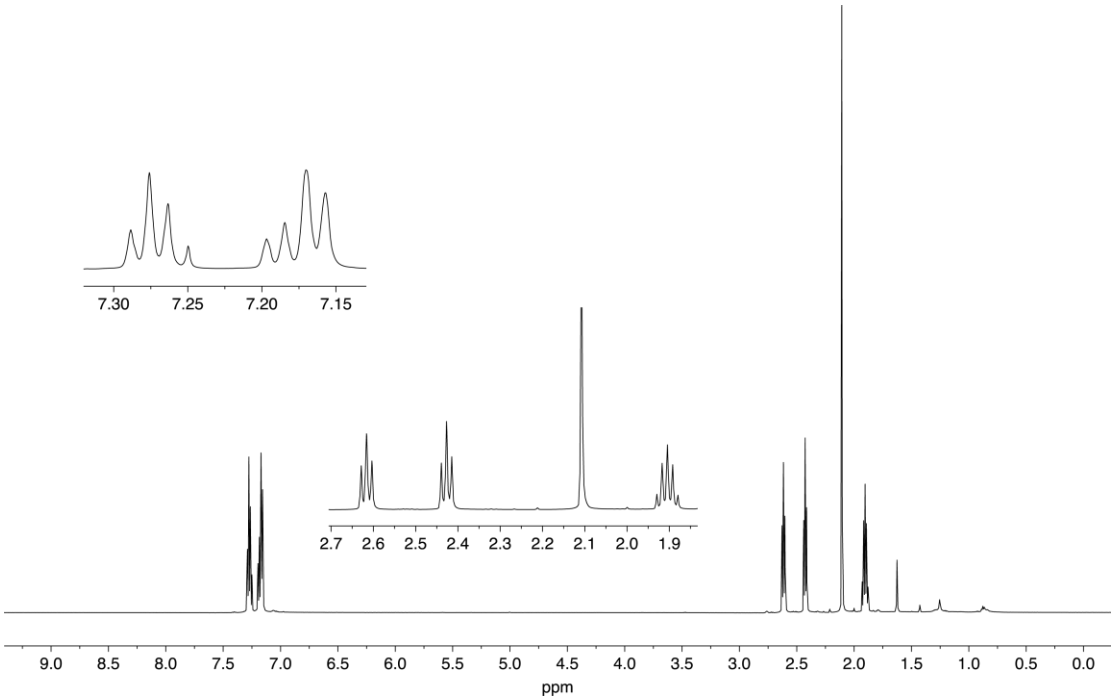


Figure S135. ^{1}H NMR (600 MHz, 299 K, $CDCl_3$) spectrum of compound **26**.

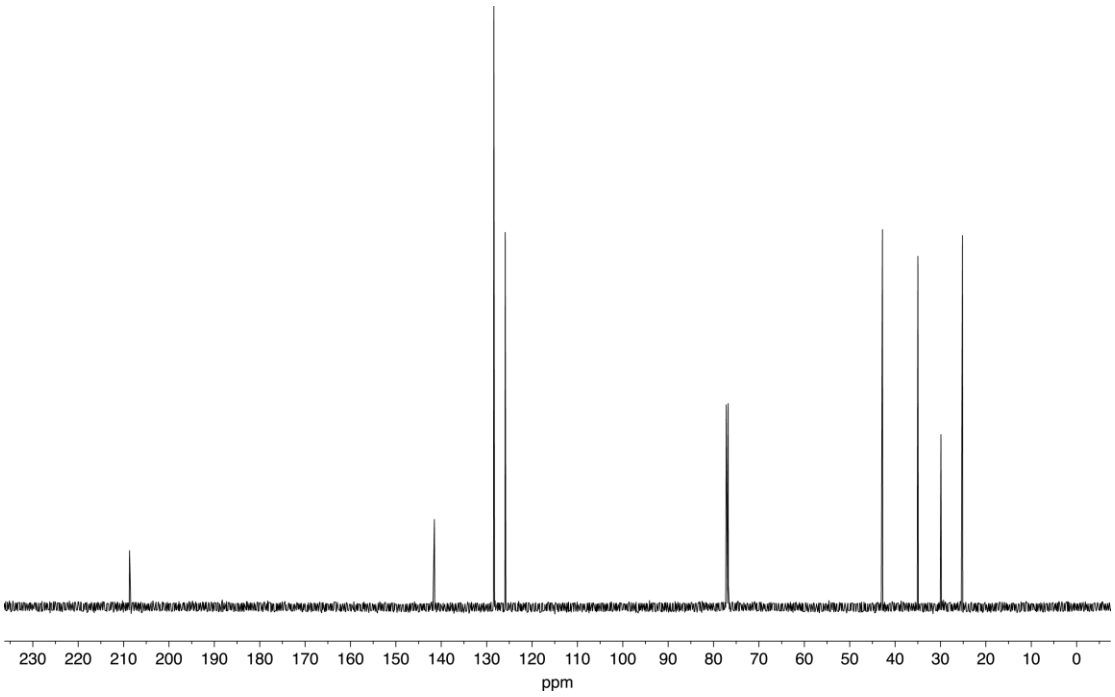
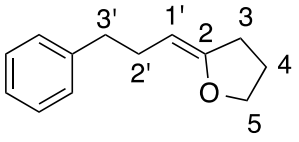


Figure S136. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $CDCl_3$) spectrum of compound **26**.

3.19 (Z)-2-(3'-Phenylpropylidene)tetrahydrofurane (27)

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). γ-Butyrolactone (86.1 mg, 1.0 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 30 min, concentrated *in vacuo* and purified by column chromatography (Alox N V, pentane to pentane : Et_2O = 1 : 1, R_f (SiO_2, pentane) 0.41) to give a colorless oil in 31% yield (58 mg, 0.3 mmol). Alongside some hydrolysis product **28** was isolated. The enolether product **27** decomposes in $CDCl_3$.



Scheme S41.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.18 (m, 2H, *o*-Ph), 7.15 (m, 2H, *m*-Ph), 7.06 (m, 1H, *p*-Ph), 4.27 (tt, $^{3}J_{HH}$ = 6.9 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H, C1'-H), 3.65 (t, $^{3}J_{HH}$ = 6.6 Hz, 2H, C5-H), 2.75 (m, 2H, C3'-H), 2.67 (m, 2H, C2'-H), 2.08 (m, 2H, C3-H), 1.32 (m, 2H, C4-H).
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6): δ = 155.6 (C2), 143.0 (*i*-Ph), 128.9 (*o*-Ph), 128.5 (*m*-Ph), 125.9 (*p*-Ph), 94.8 (C1'), 70.0 (C5), 37.0 (C3'), 28.9 (C3), 27.8 (C2'), 25.1 (C4).

Exact Mass (ESI): Calcd. for $[M+Na]^+$: 211.1111; Found: 211.1093.

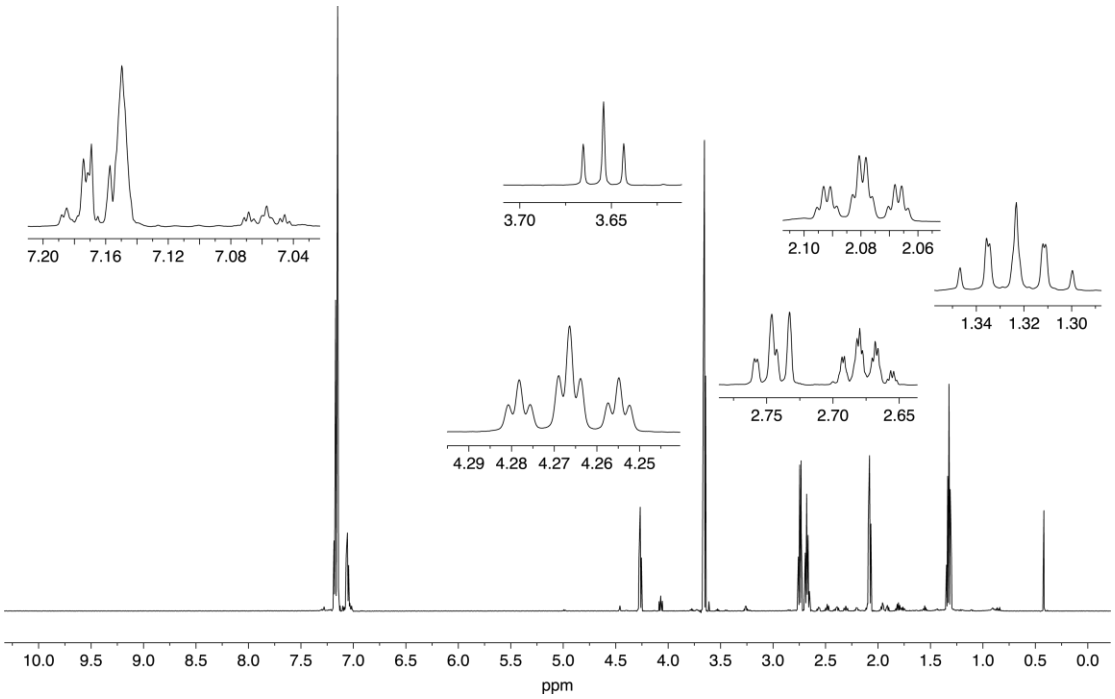


Figure S137. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of compound **27**.

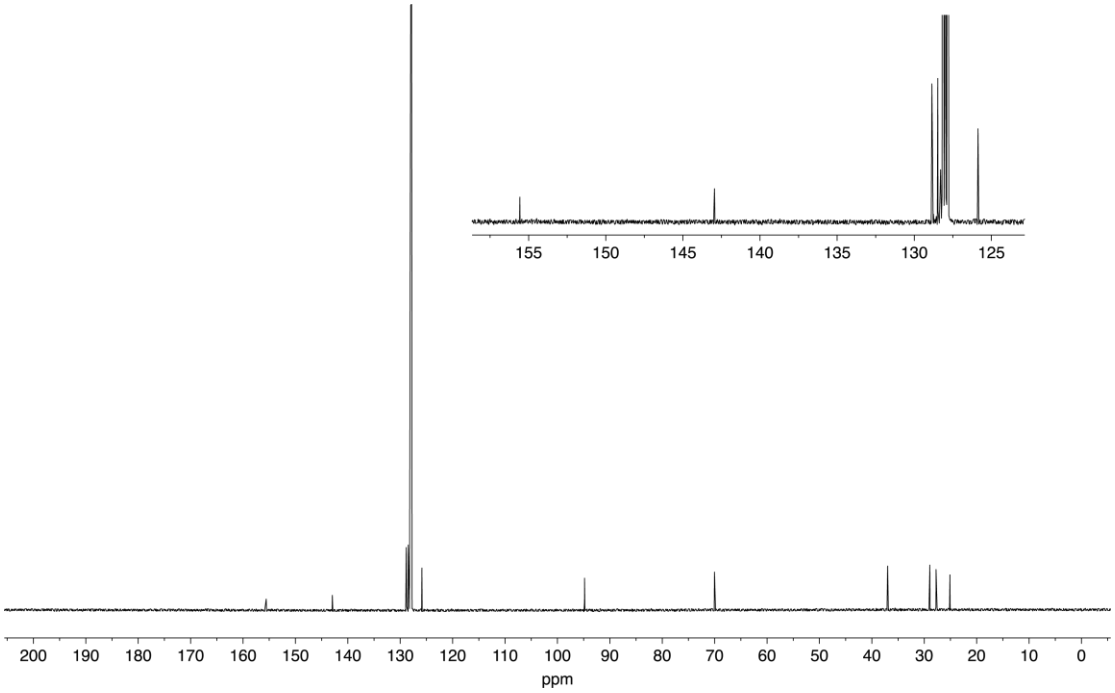
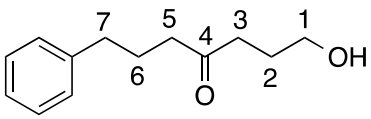


Figure S138. ^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) spectrum of compound **27**.

3.20 1-Hydroxy-7-phenyl-heptan-4-one (28)

Procedure see 3.19. Purification from the same crude mixture by column chromatography using a gradient (pentane to pentane : Et_2O = 1 : 1; R_f (pentane : Et_2O = 1 : 1) 0.14) allowed for the isolation of 1-hydroxy-7-phenylheptan-4-one (**28**) in 17% yield (35 mg, 0.2 mmol).



Scheme S42.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.15 (m, 2H, *m*-Ph), 7.06 (m, *p*-Ph), 7.03 (m, 2H, *o*-Ph), 3.29 (t, $^3J_{HH}$ = 6.1 Hz, 2H, C2-H), 2.39 (t, $^3J_{HH}$ = 7.5, 2H, C7-H), 1.97 (t, $^3J_{HH}$ = 7.0 Hz, 2H, C3-H), 1.92 (t, $^3J_{HH}$ = 7.3 Hz, 2H, C5-H), 1.76 (m, 2H, C6-H), 1.57 (m, 2H, C1-H) [OH not observed].

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 209.3 (C4), 142.1 (*i*-Ph), 128.8 (*o*-Ph), 128.7 (*m*-Ph), 126.2 (*p*-Ph), 62.0 (C2), 41.7 (C5), 39.2 (C3), 35.3 (C7), 26.8 (C1), 25.5 (C6).

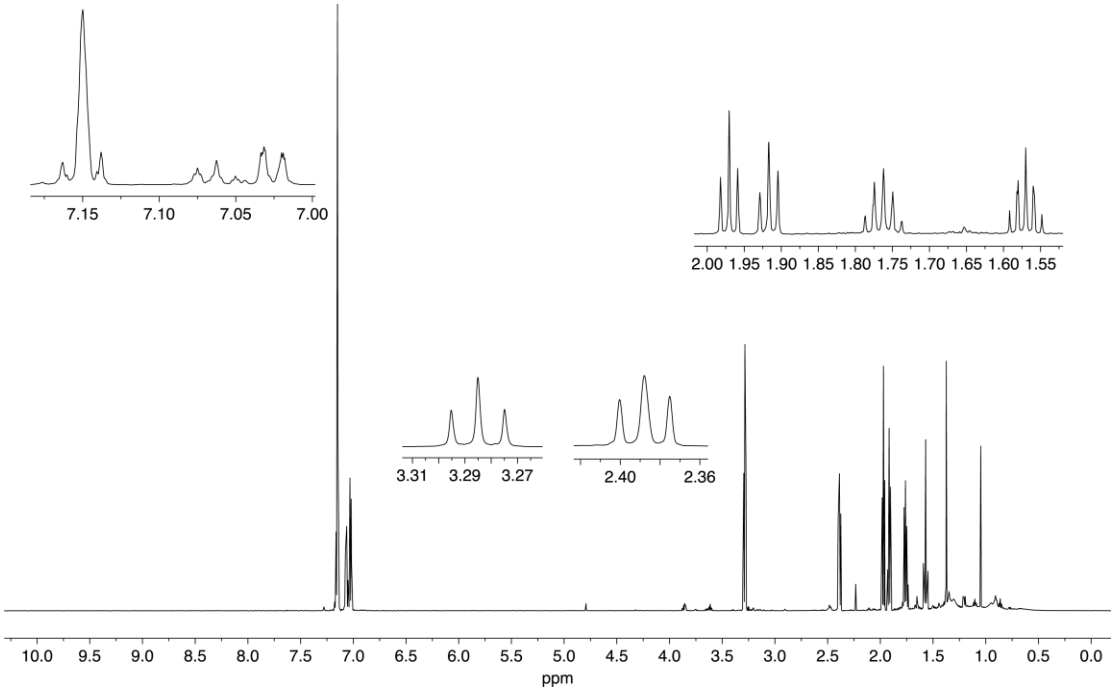


Figure S139. ^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of compound **28**.

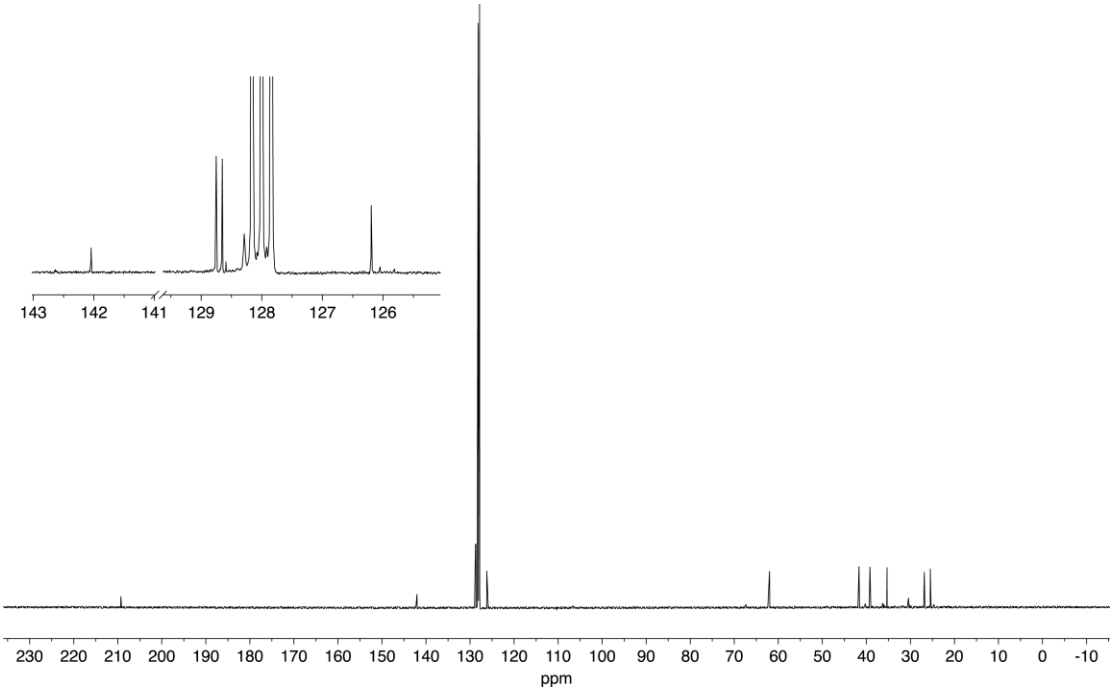
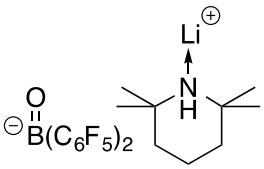


Figure S140. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of compound **28**.

3.21 Compound 29

Borata-alkene **16a** (1.0 mmol, 1.0 equiv) was prepared according to the general procedure (see 3.8.1.1). Ethyl formate (74.1 mg, 1.0 mmol, 1.0 equiv) was added causing an instantaneous color change from yellow to colorless. The reaction mixture was stirred for additional 20 min and concentrated *in vacuo*. The residue was extracted with pentane. Slow evaporation of the solvent eventually furnished some colorless crystals of the borinate by-product **29**.



Scheme S43.

X-ray crystal structure analysis of compound 29: A pale yellow prism-like specimen of $C_{42}H_{38}B_2F_{20}Li_2N_2O_2$, approximate dimensions 0.060 mm x 0.120 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 466 frames were collected. The total exposure time was 4.53 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 18511 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 4484 were independent (average redundancy 4.128, completeness = 99.8%, R_{int} = 3.44%, R_{sig} = 2.78%) and 3589 (80.04%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.8919(3) Å, b = 11.1034(4) Å, c = 11.1528(4) Å, α = 105.3350(10)°, β = 98.6630(10)°, γ = 106.3030(10)°, volume = 1099.87(7) Å^3, are based upon the refinement of the XYZ-centroids of 8232 reflections above 20 σ(I) with 4.885° < 2θ < 54.97°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio

of minimum to maximum apparent transmission was 0.971. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9780 and 0.9910. The final anisotropic full-matrix least-squares refinement on F^2 with 324 variables converged at R1 = 3.52%, for the observed data and wR2 = 8.87% for all data. The goodness-of-fit was 1.032. The largest peak in the final difference electron density synthesis was 0.309 $e^-/Å^3$ and the largest hole was -0.240 $e^-/Å^3$ with an RMS deviation of 0.046 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.537 g/cm^3 and F(000), 516 e^-. The position of the hydrogen atom at N1 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.

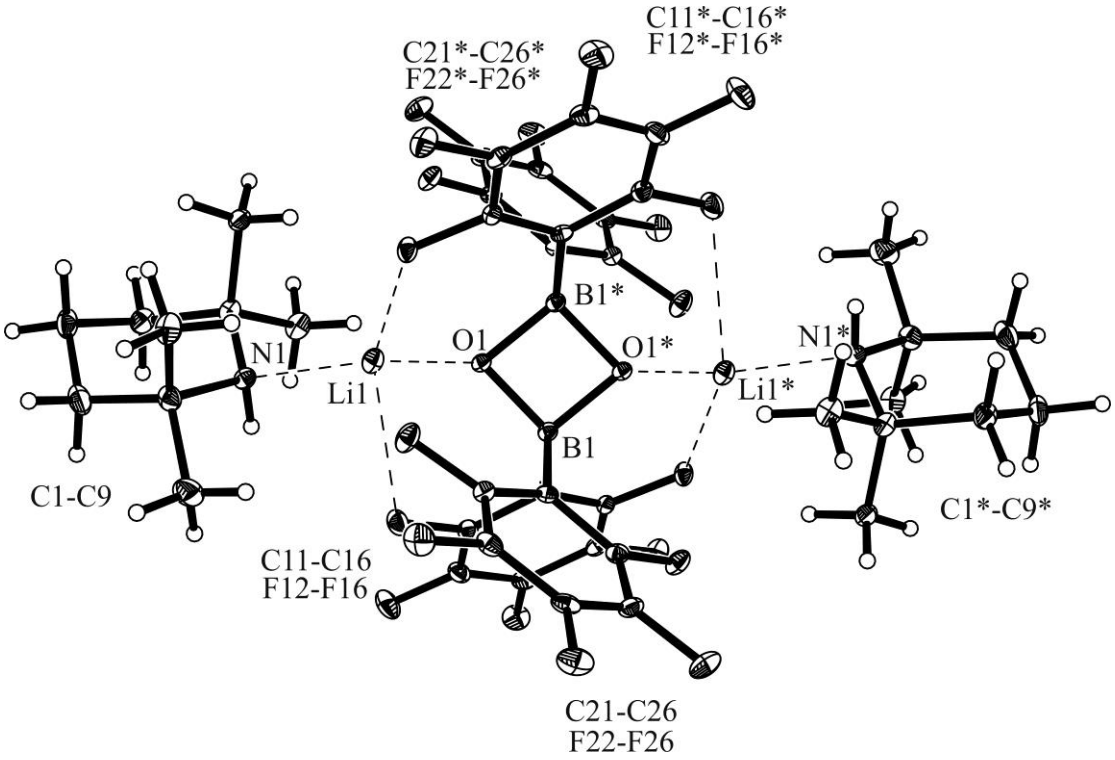


Figure S141. A view on the molecular structure of compound **29**.

Comment: Compound **29** was obtained as polymorphic crystals.

X-ray crystal structure analysis of compound 29': formula $C_{42}H_{38}B_2F_{20}Li_2N_2O_2$, M = 1018.24, colourless crystal, 0.26 x 0.20 x 0.10 mm, a = 9.4685(2), b = 11.0334(2), c = 21.6455(4) Å, β = 93.492(1)°, V = 2257.1(1) $Å^3$, ρ_{calc} = 1.498 gcm^{-3}, μ = 0.147 mm^{-1}, empirical absorption correction ($0.962 \leq T \leq 0.985$), Z = 2, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 20908 reflections collected ($\pm h$, $\pm k$, $\pm l$), 3932 independent (R_{int} = 0.050) and 2993 observed reflections [$I>2\sigma(I)$], 323 refined parameters, R = 0.058, wR^2 = 0.159, max. (min.) residual electron density 0.40 (-0.23) $e.Å^{-3}$, the position of the hydrogen atom at N1 was refined freely; others hydrogen atoms were calculated and refined as riding atoms.