Electronic Supplementary Material (ESI) for Dalton Transactions.

Stabilized Borata-Alkene Formation: Structural Features, Reactions and the Special Role of the Counter Cation

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Supporting Information

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 and stored under an argon atmosphere. NMR spectra were recorded on the following instruments: Bruker AV 300 (^{1}H: 300 MHz), Agilent DD2 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 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). X-Ray diffraction: for compounds **9a**, **14** [LiHTMP] and **17a** data sets were collected with a Nonius KappaCCD 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 compounds **11a, 12**, **14** [PPh_3NPPh_3]**, 15a**, **17b** and **19** data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: 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*: One half disordered over two positions benzene molecule was found in the asymmetrical unit of **9a**. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. Compound **11a** was refined as a 2-component inversion twin. The CCDC deposition numbers are 1427492 to 1427500. All compounds described in this paper are racemic.

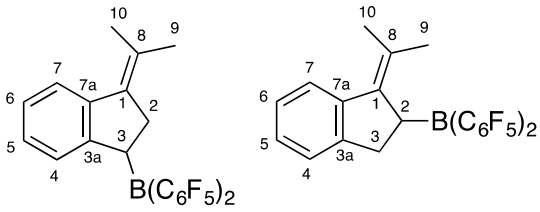
2. Materials

Bis(pentafluorophenyl)borane was prepared according to modified literature procedures [D. J. Parks, R. E. von H. Spence, W. E. Piers, *Angew. Chem. Int. Ed.* **1995**, *34*, 809-811; D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492-5503]. Benzofulvene **7** was prepared according to a modified literature procedure [J. Paradies, G. Kehr, R. Fröhlich, G. Erker, *PNAS* **2006**, *103*, 15333-15337]. Pyridine was purchased from Acros, distilled and stored over molecular sieves prior to use. ^{t}Butyl nitrile was purchased from Acros and distilled prior to use. 4-(Dimethylamino)-pyridine was

purchased from Sigma-Aldrich, dried *in vacuo* and stored under argon prior to use. Lithium 2,2,6,6-tetramethylpiperidide was purchased from Sigma-Aldrich and used without further purification. Triphenylphosphanylidene ammonium chloride was purchased from Sigma-Aldrich and used without further purification. 2,2,6,6-Tetramethylpiperidine (HTMP) was purchased from Sigma-Aldrich, distilled from KOH and stored over molecular sieves prior to use. (*E*)-Chalcone (**16a**) was purchased by TCI and used without further purification. (*E*)-Chalcone derivative **16b** was synthesized according to a literature procedure [A. Stroba, F. Schaeffer, V. Hindie, L. Lopez-Garcia, I. Adrian, W. Frohner, R. W. Hartmann, R. M. Biondi, M. Engel, *Med. Chem.* **2009**, *52*, 4683-4693]. Phenyl methyl ketene was synthesized according to modified literature procedures [B. L. Hodous, G. C. Fu, *J. Am. Chem. Soc.* **2002**, *124*, 1578-1579; N. Çelebi-Ölçüm, Y.-h. Lam, E. Richmond, K. B. Ling, A. D. Smith, K. N. Houk, *Angew. Chem. Int. Ed.* **2011**, *51*, 11478-11482].

3. Preparation and characterization

Compounds 8a,**b**



8a **8b**

Benzofulvene **7** (10.4 mg, 0.07 mmol, 1.0 equiv) was dissolved in CD_2Cl_2 (0.2 mL), cooled to -78 °C and added to a precooled suspension of $HB(C_6F_5)_2$ (23.0 mg, 0.07 mmol, 1.0 equiv) in CD_2Cl_2 (0.8 mL) within a NMR tube. The NMR tube was sealed and shaken until a clear yellow solution was obtained. The NMR tube was kept at -78 °C and the reaction mixture was characterized by NMR experiments at 195K. A mixture of a major and minor isomer (ratio ca. 1.3 : 1 (^{1}H)) and compound **7** (ca. 8 mol%) was obtained.

Major isomer assigned as compound 8a

^{1}H NMR (500 MHz, 195 K, CD_2Cl_2): δ [ppm] = 7.44 (d, $^3J_{HH}$ = 7.8 Hz, 1H, C7-H), 7.17 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C6-H), 7.00 (m, 1H, C5-H), 6.92 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4-H), 4.22 (dd, $^3J_{HH,trans}$ = 9.6 Hz, $^3J_{HH,cis}$ = 3.6, 1H, C3-H), 3.01 (br dd, $^2J_{HH}$ = 15.7 Hz, $^3J_{HH,trans}$ = 9.6, 1H, C2-H), 2.81 (br d, $^2J_{HH}$ = 15.7 Hz, 1H, C2-H), 1.82 (s, 3H, C10-H), 1.65 (s, 3H, C9-H).

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 195 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.44 / 7.17 (C7-H / C6-H), 7.17 / 7.00 (C6-H / C5-H), 7.00 / 6.92 (C5-H / C4-H), 4.22 / 3.01, 2.81 (C3-H / C2-H, C2-H), 3.01 / 2.81, 1.82, 1.65 (C2-H / C2-H, C10-H, C9-H), 2.81 / 1.82, 1.65 (C2-H / C10-H, C9-H), 1.82 / 1.65 (C10-H / C9-H).

^{1}H NOESY (600 MHz / 600 MHz, 195 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 4.22 / 6.92, 3.01, 2.81 (C3-H / C4-H, C2-H, C2-H), 1.82 / 7.44, 1.65 (C10-H / C7-H, C9-H), 1.65 / 3.01, 2.81, 1.82 (C9-H / C2-H, C2-H, C10-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 195 K, CD_2Cl_2): δ^1H [ppm] / δ^{13}C [ppm] = 7.44 / 124.6 (C7), 7.17 / 126.7 (C6), 7.00 / 125.7 (C5), 6.92 / 126.5 (C4), 4.22 / 42.9 (C3), 3.01 / 33.1 (C2), 2.81 / 33.1

(C2), 1.82 / 20.5 (C10), 1.65 / 23.27 (C9).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 195 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.44 / 141.4, 133.0, 125.7 (C7-H / C3a, C1, C5), 7.17 / 143.2, 126.5 (C6-H / C7a, C4), 7.00 / 141.4, 124.6 (C5-H / C3a, C7), 6.92 / 143.2, 126.7, 42.9 (C4-H / C7a, C6, C3), 4.22 / 143.2, 141.4, 133.0, 126.7, 111.8, 33.1 (C3/ C7a, C3a, C1, C8, $^{ipso}C_6F_5$, C2), 3.01 / 133.0, 126.7 (C2-H / C1, C8), 2.81 / 143.2, 141.1, 133.0, 126.7 (C2-H / C7a, C3a, C1, C8), 1.82 / 143.2, 133.0, 126.7, 23.27 (C10-H / C7a, C8, C1, C9), 1.64 / 143.2, 133.0, 126.5, 20.5 (C9-H / C7a, C8, C1, C10).

^{13}C{^{1}H} NMR (126 MHz, 195 K, CD_2Cl_2): δ^{13}C [ppm] = 143.2 (C7a), 141.4 (C3a), 133.0 (C1), 126.7 (C8), 126.7 (C6), 126.5 (C4), 125.7 (C5), 124.6 (C7), 42.9 (C3), 33.1 (C2), 23.27 (C9)^{t}, 20.5 (C10)^{t}, [C_6F_5 not listed; ^{t} tentative assignment].

^{11}B{^{1}H} NMR (160 MHz, 195 K, CD_2Cl_2): δ [ppm] = 60 ($\nu_{1/2} \approx 8500$ Hz).

^{19}F NMR (470 MHz, 195 K, CD_2Cl_2): δ [ppm] = -128.9 (m, 2F, *o*-C_6F_5), -148.1 (br, 1F, *p*-C_6F_5), -161.6 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 13.5].

Minor isomer assigned as compound 8b

^{1}H NMR (500 MHz, 195 K, CD_2Cl_2): δ [ppm] = 7.61 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, C7-H), 7.08 (m, 1H, C6-H), 6.99 (m, 1H, C5-H), 6.97 (m, 1H, C4-H), 4.02 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, C2-H), 3.33 (dd, $^{2}J_{HH}$ = 16.7 Hz, $^{3}J_{HH}$ = 8.0 Hz, 1H, C3-H), 3.02 (d, $^{2}J_{HH}$ = 16.7 Hz, 1H, C3-H), 2.19 (s, 3H, C10-H), 1.51 (s, 3H, C9-H).

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 195 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.61 / 7.08 (C7-H / C6-H), 7.08 / 6.99 (C6-H / C5-H), 4.02 / 3.33, 2.19, 1.51 (C2-H / C3-H, C9-H, C10-H), 3.33 / 3.02 (C3-H / C3-H), 2.19 / 1.51 (C9-H / C10-H).

^{1}H NOESY (600 MHz / 600 MHz, 195 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 3.33 / 6.97, 4.02, 3.02 (C3-H / C4-H, C2-H, C3-H), 2.19 / 7.61, 7.08, 1.51 (C10-H / C7-H, C6-H, C9-H), 1.51 / 4.02, 2.19 (C9-H / C2-H, C10-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 195 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.61 / 125.3 (C7), 7.08 / 125.4 (C6), 6.99 / 127.1 (C5), 6.97 / 124.1 (C4), 4.02 / 43.7 (C2), 3.33 / 31.1 (C3), 3.02 / 31.1 (C3), 2.19 / 23.25 (C10), 1.51 / 26.8 (C9).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 195 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.61 / 146.5, 127.1, 121.8 (C7-H / C3a, C5, C1), 7.08 / 139.4, 124.1 (C6-H / C7a, C4), 6.99 / 146.5, 125.3 (C5-H / C3a, C7), 6.97 / 139.4, 125.4, 31.1 (C4-H / C7a, C6, C3), 4.02 / 146.5, 145.6, 139.4, 121.8, 112.0 (C2-H/ C3a, C8, C7a, C1, $^{ipso}C_6F_5$), 3.33 / 146.5, 139.4, 43.7 (C3-H / C3a, C7a, C2), 3.02 / 146.5, 139.4, 121.8, 43.7 (C3-H / C3a, C7a, C1, C2), 2.19 / 145.6, 139.4, 121.8, 26.8 (C10-H / C8, C7a, C1, C9), 1.51 / 145.6, 139.4, 121.8, 23.25 (C9-H / C8, C7a, C1, C10).

^{13}C{^{1}H} NMR (126 MHz, 195 K, CD_2Cl_2): δ^{13}C [ppm] = 146.5 (C3a), 145.6 (C8), 139.4 (C7a), 127.1 (C5), 125.3 (C7), 125.4 (C6), 124.1 (C4), 121.8 (C1), 43.7 (C2), 31.1 (C3), 26.8 (C9), 23.25 (C10), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (160 MHz, 195 K, CD_2Cl_2): δ [ppm] = 60 ($\nu_{1/2} \approx 8500$ Hz).

^{19}F NMR (470 MHz, 195 K, CD_2Cl_2): δ [ppm] = -130.8 (br, 2F, *o*-C_6F_5), -151.7 (br, 1F, *p*-C_6F_5), -162.2 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 9.4].

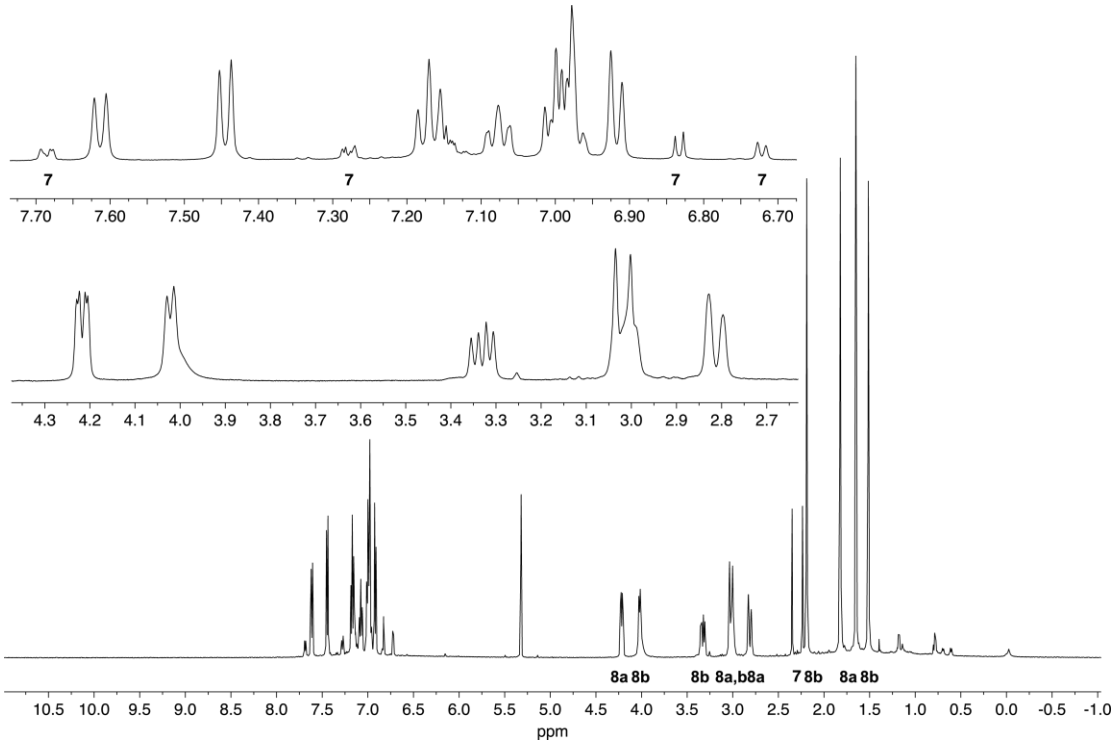


Figure S1 ^{1}H NMR (500 MHz, 193 K, CD_2Cl_2) of compounds **8a**,**b**.

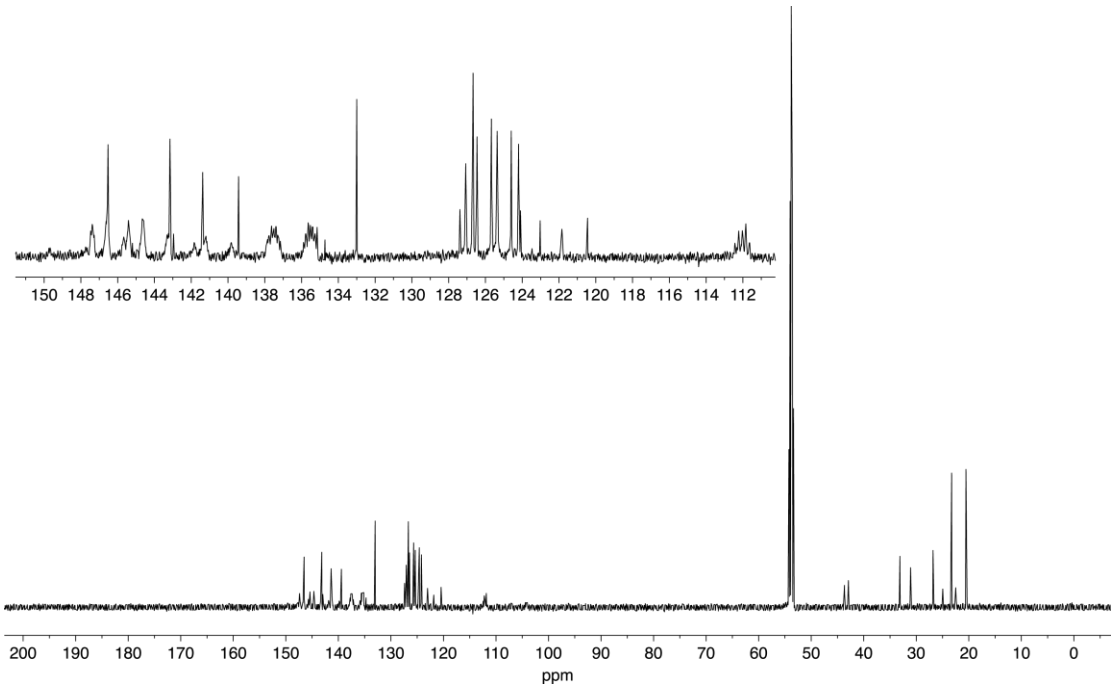


Figure S2 $^{13}C\{^{1}H\}$ NMR (126 MHz, 195 K, CD_2Cl_2) of compounds **8a**,**b**.

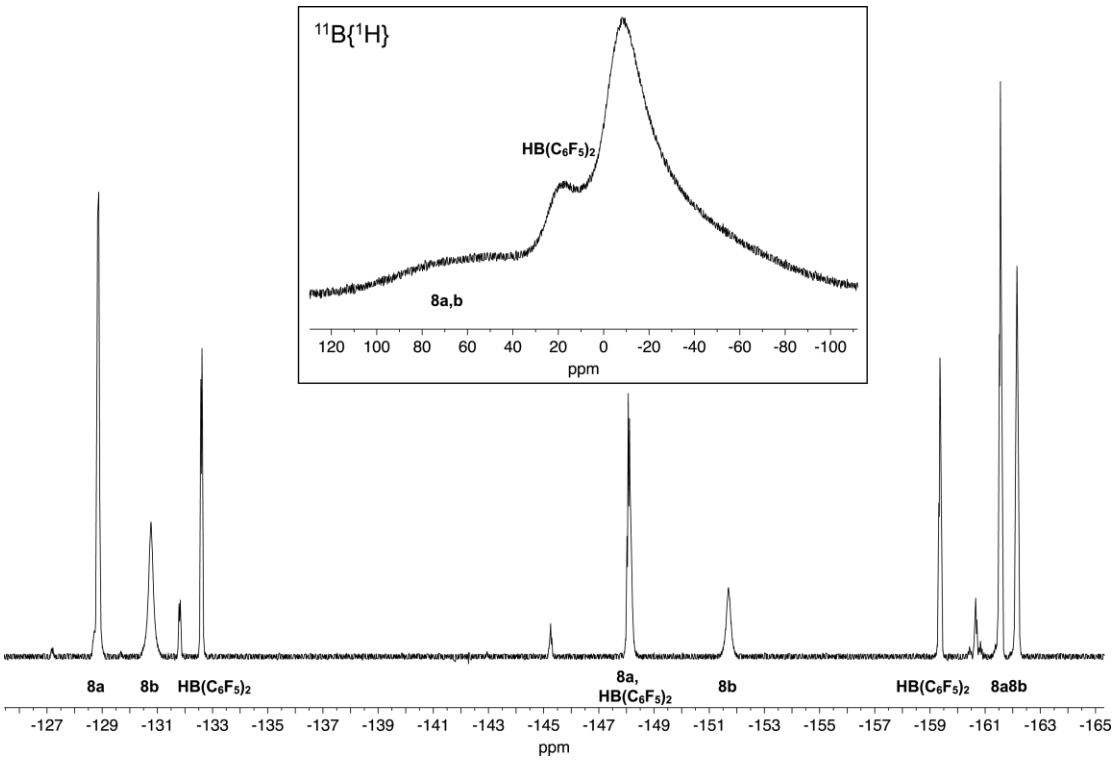
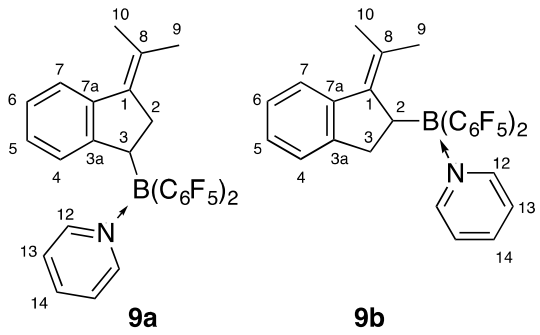


Figure S3 $^{11}B\{^{1}H\}$ NMR (160 MHz, 195 K, CD_2Cl_2) and ^{19}F NMR (470 MHz, 195 K, CD_2Cl_2) of compounds **8a**,**b**.

Compounds 9a,**b**



9a **9b**

Benzofulvene **7** (52.0 mg, 0.33 mmol, 1.0 equiv) was dissolved in toluene (1.5 mL), and added to a suspension of $HB(C_6F_5)_2$ (115.0 mg, 0.33 mmol, 1.0 equiv) in toluene (2.0 mL). After stirring for 15 minutes at ambient temperature pyridine (30.2 mg, 0.35 mmol, 1.15 equiv) was added affording a change in color from intense yellow to colorless. The reaction mixture was stirred for 15 minutes and concentrated *in vacuo* subsequently. The residue was triturated by stirring (15 min) in pentane (2.0 mL) giving a white precipitate. The suspension was filtrated. The residue was washed with pentane (2 × 1 mL) and dried *in vacuo* giving a colorless solid (92 mg, 0.16 mmol, 48%).

Elemental analysis: calc. for $C_{29}H_{18}BF_{10}N$ (580.26 g mol^{-1}): C, 59.92; H, 3.12; N, 2.41; Found: C, 60.16; H, 3.06 N (corr), 2.37.

The solution of the obtained solid in CD_2Cl_2 showed a mixture of isomers (ratio ≈ 1.9:1 (^{1}H)).

Major isomer assigned as compound 9a

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ [ppm] = 7.96 (br t, $^{3}J_{HH}$ = 7.7 Hz, 1H, C14-H), 7.88, 7.31 (each br, each 2H, C12,13-H), 7.22 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, C7-H), 7.04 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, C6-H), 6.95 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, C5-H), 6.79 (br d, $^{3}J_{HH}$ = 7.0 Hz, 1H, C4-H), 4.04 (d, $^{3}J_{HH}$ = 9.5 Hz, 1H, C3-H), 2.93 (br dd, $^{2}J_{HH}$ = 15.0 Hz, $^{3}J_{HH,trans}$ = 9.5 Hz, 1H, C2-H), 2.26 (br d, $^{2}J_{HH}$ = 15.0 Hz, 1H, C2-H), 1.58 (s, 3H, C10-H), 1.46 (s, 3H, C9-H).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.22 / 7.04 (C7-H / C6-H), 7.04 / 6.95 (C6-H / C5-H), 6.95 / 6.79 (C5-H / C4-H), 4.04 / 2.93 (C3-H / C2-H), 2.93 / 2.26, 1.58, 1.46 (C2-H / C2-H, C10-H, C9-H), 1.58 / 1.46 (C10-H / C9-H).

^{1}H NOESY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 7.22 / 1.58 (C7-H / C6-H, C8-H, C10-H), 2.93 / 4.04, 2.26 (C2-H / C3-H, C2-H), 1.46 / 2.26 (C9-H / C2-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.96 / 141.9 (C14), 7.22 / 124.4 (C7), 7.04 / 125.5 (C6), 6.95 / 126.6 (C5), 6.79 / 125.1 (C4), 4.04 / 36.1 (C3), 2.93 / 37.4 (C2), 2.26 / 37.4 (C2), 1.58 / 21.2 (C10), 1.46 / 23.5 (C9).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 228 K, CD_2Cl_2): [selective resonances] δ^{1}H [ppm] / δ^{13}C [ppm] = 8.21 / 143.3 (C12), 7.92 / 141.6 (C14), 7.10 / 146.7 (C13).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.22 / 152.4, 126.6 (C7-H / C3a, C5), 7.04 / 143.2, 125.1 (C6-H / C7a, C4), 6.95 / 152.4, 124.4 (C5-H / C3a, C7), 4.04 / 152.4, 143.2, 135.4 (C3-H / C3a, C7a, C1), 1.58 / 135.4, 123.3, 23.5 (C10-H / C1, C8, C9), 1.46 / 135.4, 123.3, 21.2 (C9-H / C1, C8, C10).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ^{13}C [ppm] = 152.4 (C3a), 145.9 (br), 141.9, 124.2 (br)(C12,13,14)^{t}, 143.2 (C7a), 135.4 (C1), 126.6 (C5), 125.5 (C6), 125.1 (C4), 124.4 (C7), 123.3 (C8), 37.4 (C2), 36.1 (br, C3), 23.5 (C9), 21.2 (C10) [C_6F_5 not listed; ^{t} tentative assignment].

^{11}B NMR (192 MHz, 299 K, CD_2Cl_2): δ [ppm] = 0.7 ($\nu_{1/2} \approx 130$ Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ [ppm] = -129.5 (br, 4F, *o*-C_6F_5), -157.7, -159.2 (each br, each 1F, *p*-C_6F_5), -163.7, -164.2 (each br, each 2F, *m*-C_6F_5).

Minor isomer assigned as compound 9b

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ [ppm] = 8.46 (m, 2H, C12-H), 7.75 (tt, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H, C14-H), 7.22 (m, 2H, C13-H), 7.07 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, C7-H), 6.83 (tm, $^{3}J_{HH}$ = 7.7 Hz, 1H, C6-H), 6.75 (td, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 1.0 Hz, 1H, C5-H), 6.71 (dm, $^{3}J_{HH}$ = 7.4 Hz, 1H, C4-H), 3.96 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, C2-H), 3.40 (dd, $^{2}J_{HH}$ = 16.6 Hz, $^{3}J_{HH,trans}$ = 8.9 Hz, 1H, C3-H), 2.61 (d, $^{2}J_{HH}$ = 16.6 Hz, 1H, C3-H), 1.95 (s, 3H, C10-H), 1.70 (s, 3H, C9-H).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 8.46 / 7.75, 7.22 (C12-H / C14-H, C13-H), 7.75 / 7.22 (C14-H / C13-H), 7.07 / 6.83 (C7-H / C6-H), 6.83 / 6.75 (C6-H / C5-H), 6.75 / 6.71 (C5-H / C4-H), 3.96 / 3.40, 2.61, 1.95, 1.70 (C2-H / C3-H, C3-H, C10, C9), 3.40 / 2.61, 1.95, 1.70 (C3-H / C3-H, C10, C9), 1.95 / 1.70 (C10-H / C9-H).

^{1}H NOESY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 7.22 / 8.46, 7.75 (C13-H / C12-H, C14-H), 3.40 / 3.96, 2.61 (C3-H / C2-H, C3-H), 1.95 / 7.07 (C10-H / C7-H),

1.70 / 3.96 (C9-H / C2-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 8.46 / 146.6 (C12), 7.75 / 141.5 (C14), 7.07 / 125.0 (C7), 6.83 / 125.1 (C6), 6.75 / 125.6 (C5), 6.71 / 124.1 (C4), 3.96 / 37.7 (C2), 3.40 / 37.1 (C3), 2.61 / 37.1 (C3), 1.95 / 22.8 (C10), 1.70 / 24.4 (C9).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 8.46 / 146.6, 141.5, 124.3 (C12-H/ C12, C14, C13), 7.75 / 146.6 (C14-H / C12), 7.22 / 146.6, 124.3 (C13-H / C12, C13), 7.07 / 146.7, 125.6 (C7-H / C3a, C5), 6.83 / 144.1, 124.1 (C6-H / C7a, C4), 6.75 / 146.7, 125.0 (C5-H / C3a, C7), 6.71 / 144.1, 125.1 (C4-H / C7a, C6), 3.96 / 146.7, 144.1, 140.9 (C2-H / C3a, C7a, C1), 3.40 / 146.7 (C3-H / C3a), 2.61 / 146.7, 144.1, 140.8 (C3-H / C3a, C7a, C1), 1.95 / 140.9, 125.8, 24.4 (C10-H / C1, C8, C9), 1.70 / 140.9, 125.8, 22.8 (C9-H / C1, C8, C10).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ^{13}C [ppm] = 146.7 (C3a), 146.6 (C12), 141.5 (C14), 144.1 (C7a), 140.9 (C1), 125.8 (C8), 125.6 (C5), 125.1 (C6), 125.0 (C7), 124.3 (C13), 124.1 (C4), 37.7 (br, C2), 37.1 (C3), 24.4 (C9), 22.8 (C10) [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ [ppm] = 0.7 ($\nu_{1/2} \approx 130$ Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ [ppm] = -128.3, -129.0 (each br, each 2F, *o*-C_6F_5), -158.8, -159.8 (each t, $^{3}J_{FF}$ = 20.3 Hz, each 1F, *p*-C_6F_5), -164.2, -164.8 (each m, each 2F, *m*-C_6F_5).

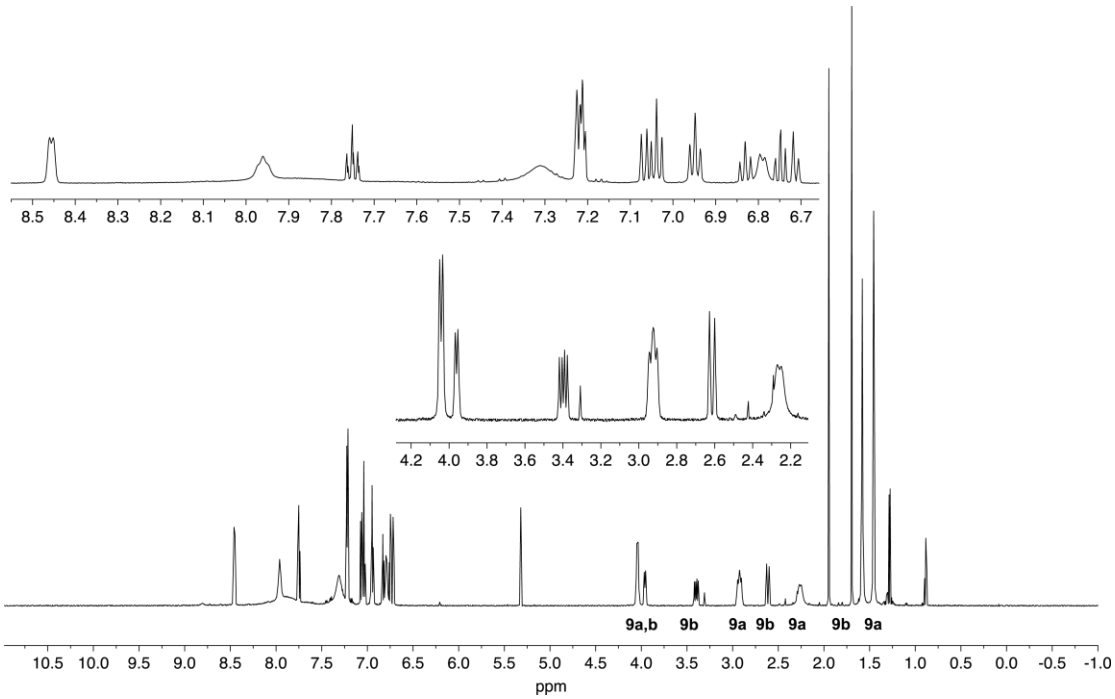


Figure S4 ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of compounds **9a**,**b**.

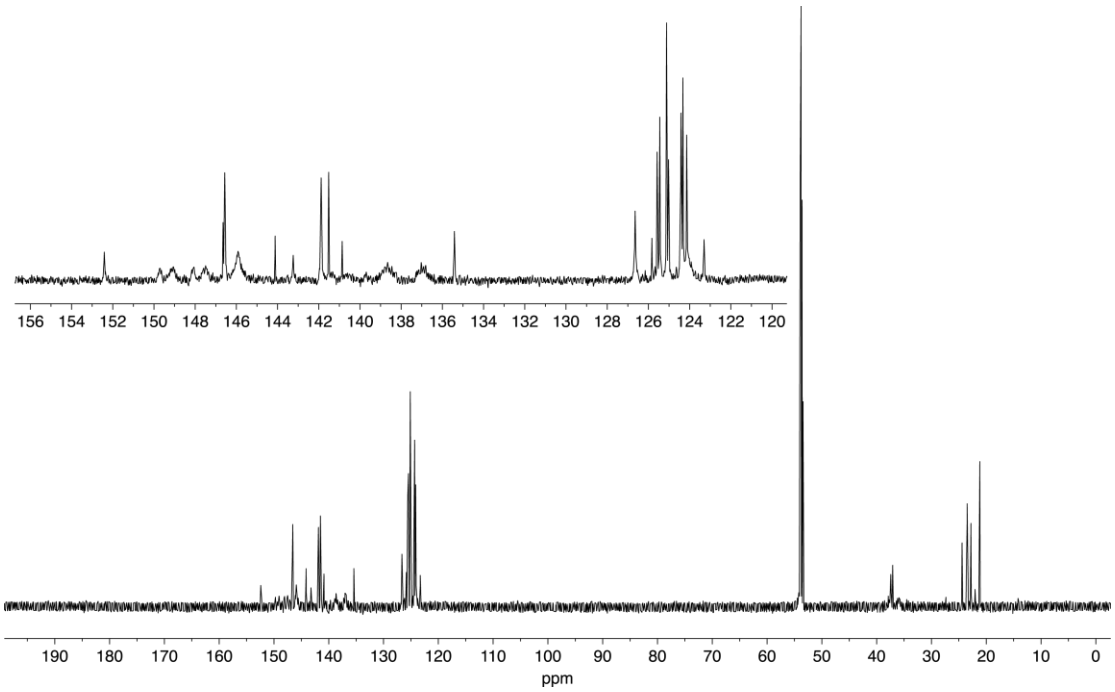


Figure S5 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) of compounds **9a**,**b**.

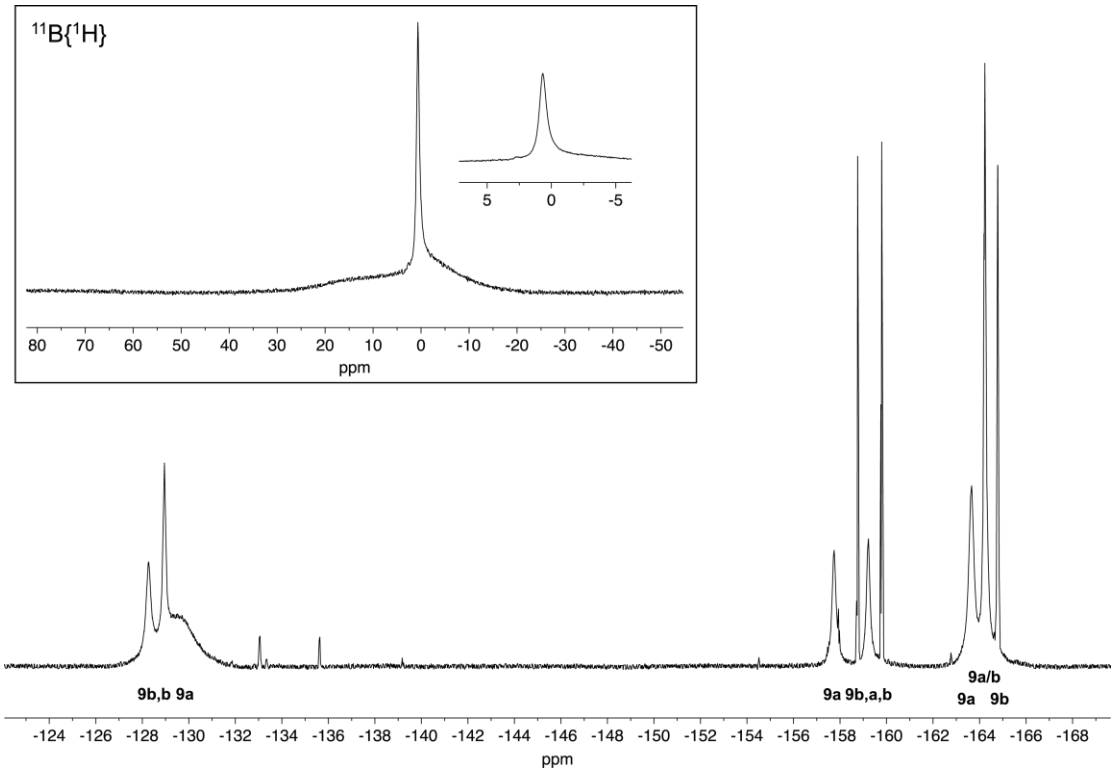
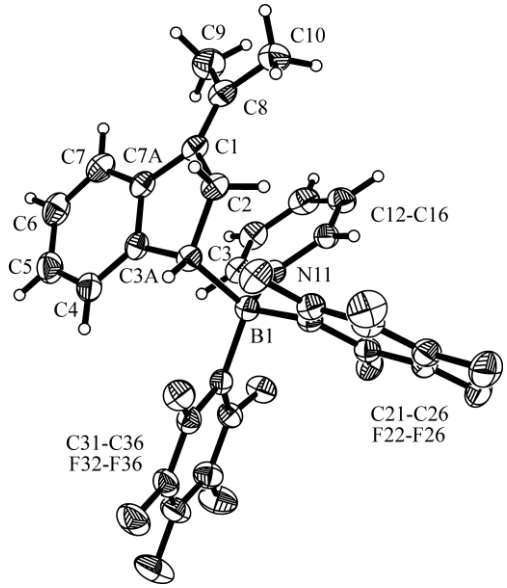


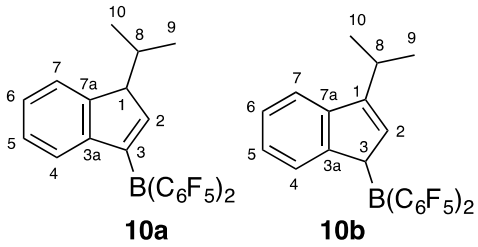
Figure S6 ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) and $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) of compounds **9a**,**b**.

Crystals of **9a** suitable for the X-ray crystal structure analysis were obtained from a saturated solution of the obtained solid in benzene.

X-ray crystal structure analysis of compound 9a: formula $C_{29}H_{18}BF_{10}N \cdot 0.5 \times C_6H_6$, M = 620.31, colourless crystal, 0.18 x 0.15 x 0.12 mm, a = 19.9204(3), b = 14.3820(2), c = 18.9519(2) Å, V = 5429.6(1) Å^3, ρ_{calc} = 1.518 gcm^{-3}, μ = 0.136 mm^{-1}, empirical absorption correction ($0.976 \leq T \leq 0.983$), Z = 8, orthorhombic, space group *P*bcn (No. 60), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 36449 reflections collected ($\pm h$, $\pm k$, $\pm l$), 5520 independent (R_{int} = 0.043) and 4202 observed reflections [$I > 2\sigma(I)$], 428 refined parameters, R = 0.046, wR^2 = 0.108, max. (min.) residual electron density 0.17 (-0.17) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



Compounds 10a,**b**



Benzofulvene **7** (10.4 mg, 0.07 mmol, 1.0 equiv) was dissolved in CD_2Cl_2 (0.2 mL), cooled to -78 °C and added to a precooled suspension of $HB(C_6F_5)_2$ (23.0 mg, 0.07 mmol, 1.0 equiv) in CD_2Cl_2 (0.8 mL) using a NMR tube. The NMR tube was sealed and shaken carefully until a clear yellow solution was obtained. After the reaction mixture was warmed to ambient temperature and kept for 3 hours at room temperature it was characterized by NMR experiments.

A mixture of isomers was observed (ratio ca. 4 : 1(^{1}H)).

Major isomer assigned as compound 10a

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ [ppm] = 7.51 (dm, $^3J_{HH}$ = 7.6 Hz, 1H, C7-H), 7.47 (d, $^3J_{HH}$ = 1.7 Hz, 1H, C2-H), 7.27 (t, $^3J_{HH}$ = 7.6 Hz, 1H, C6-H), 7.19 (tm, $^3J_{HH}$ = 7.6 Hz, 1H, C5-H), 7.05 (dm,

$^{3}J_{HH}$ = 7.6 Hz, 1H, C4-H), 3.74 (dm, $^{3}J_{HH}$ = 4.4 Hz, 1H, C1-H), 2.51 (septd, $^{3}J_{HH}$ = 6.9, 4.4 Hz, 1H, C8-H), 1.15 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, C10-H)^{t}, 0.68 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, C9-H)^{t} [^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.51 / 7.27 (C7-H / C6-H), 7.27 / 7.19 (C6-H / C5-H), 7.19 / 7.05 (C5-H / C4-H), 3.74 / 2.51 (C1-H / C8-H), 2.51 / 1.15, 0.68, (C8-H / C10-H, C9-H).

^{1}H NOESY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 7.22 / 8.46, 7.75 (C13-H / C12-H, C14-H), 3.40 / 3.96, 2.61 (C3-H / C2-H, C3-H), 1.95 / 7.07 (C10-H / C7-H), 1.70 / 3.96 (C9-H / C2-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.51 / 124.1 (C7), 7.47 / 166.7 (C2), 7.27 / 126.3 (C6), 7.19 / 127.2 (C5), 7.05 / 121.8 (C4), 3.74 / 59.9 (C1), 2.51 / 31.4 (C8), 1.15 / 21.5 (C10), 0.68 / 18.2 (C9).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.51 / 145.3, 127.2, 59.9 (C7-H / C3a, C5, C1), 7.47 / 151.0, 147.3, 145.3, 59.9, 31.4 (C2-H / C3, C7a, C3a, C1, C8), 7.27 / 147.3, 121.8 (C6-H / C7a, C4), 7.19 / 145.3, 124.1 (C5-H / C3a, C7), 7.05 / 147.3, 126.3 (C4-H/ C7a, C6), 3.74 / 166.7, 151.0, 147.3, 31.4, 21.5, 18.2 (C1-H / C2, C3, C7a, C8, C10, C9), 2.51 / 166.7, 59.9, 21.5, 18.2 (C8-H / C2, C1, C10, C9), 1.15 / 59.9, 31.4, 18.2 (C10-H / C1, C8, C9), 0.68 / 59.9, 31.4, 21.5 (C9-H / C1, C8, C10).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ^{13}C [ppm] = 166.7 (C2), 151.0 (br, C3), 147.3 (C7a), 145.3 (C3a), 127.2 (C5), 126.3 (C6), 124.1 (C7), 121.8 (C4), 59.9 (C1), 31.4 (C8), 21.5 (C10)^{t}, 18.2 (C9)^{t} [C_6F_5 not listed; ^{t} tentative assignment].

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ [ppm] = 58.6 ($\nu_{1/2}$ ≈ 900 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ [ppm] = -129.0 (m, 2F, *o*-C_6F_5), -149.0 (tm, $^{3}J_{FF}$ = 19.9 Hz, 1F, *p*-C_6F_5), -161.8 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 12.8].

Minor isomer assigned as compound 10b

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ [ppm] = 7.50 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, C4-H), 7.40 (dm, $^{3}J_{HH}$ = 7.5 Hz, 1H, C7-H), 7.29 (tm, $^{3}J_{HH}$ = 7.5 Hz, 1H, C6-H), 7.23 (tm, $^{3}J_{HH}$ = 7.5 Hz, 1H, C5-H), 6.13 (s, 1H, C2-H), 5.13 (s, 1H, C3-H), 3.01 (septm, $^{3}J_{HH}$ = 6.8 Hz, 1H, C8-H), 1.28 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, C10-H)^{t}, 1.17 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, C9-H)^{t} [^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.50 / 7.23 (C4-H / C5-H), 7.40 / 7.29 (C7-H / C6-H), 7.29 / 7.23 (C6-H / C5-H), 6.13 / 5.13 (C2-H / C3-H), 3.01 / 1.28, 1.17 (C8- H / C10-H, C9-H).

^{1}H NOESY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 7.40 / 3.01 (C7-H / C8-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.50 / 125.6 (C4), 7.40 / 120.8 (C7), 7.29 / 127.0 (C6), 7.23 / 126.1 (C5), 6.13 / 116.1 (C2), 5.13 / 55.9 (C3), 3.01 / 28.5 (C8), 1.28 / 21.9 (C10), 1.17 / 21.8 (C9).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.50 / 55.9 (C4-H / C3), 7.40 / 163.0, 144.6, 126.1 (C7-H / C1, C3a, C5), 7.29 / 145.5, 125.6 (C6-H / C7a, C4), 7.23 / 144.6, 120.8 (C5-H / C3a, C7), 6.13 / 163.0, 145.5, 144.6, 55.9, 28.5 (C2-H / C1, C7a, C3a, C3, C8),

5.13 / 163.0, 145.5, 116.1, 112.7 (C3-H / C1, C7a, C2, $^{ipso}C_6F_5$), 3.01 / 163.0, 145.5, 116.1, 21.9, 21.8 (C8-H / C1, C7a, C2, C10, C9), 1.28 / 163.0, 28.5, 21.8 (C10-H / C1, C8, C9), 1.17 / 163.0, 28.5, 21.9 (C9-H / C1, C8, C10).

$^{13}C\{^1H\}$ NMR (126 MHz, 299 K, CD_2Cl_2): $\delta^{13}C$ [ppm] = 163.0 (C1), 145.5 (C7a), 144.6 (C3a), 127.0 (C6), 126.1 (C5), 125.6 (C4), 120.8 (C7), 116.1 (C2), 55.9 (br, C3), 28.5 (C8), 21.9 (C10)^t, 21.8 (C9)^t [C_6F_5 not listed; ^{t} tentative assignment].

$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, CD_2Cl_2): δ [ppm] = 61.5 ($\nu_{1/2} \approx 600$ Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ [ppm] = -128.4 (m, 2F, *o*-C_6F_5), -150.2 (tm, $^3J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), -162.9 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 12.7].

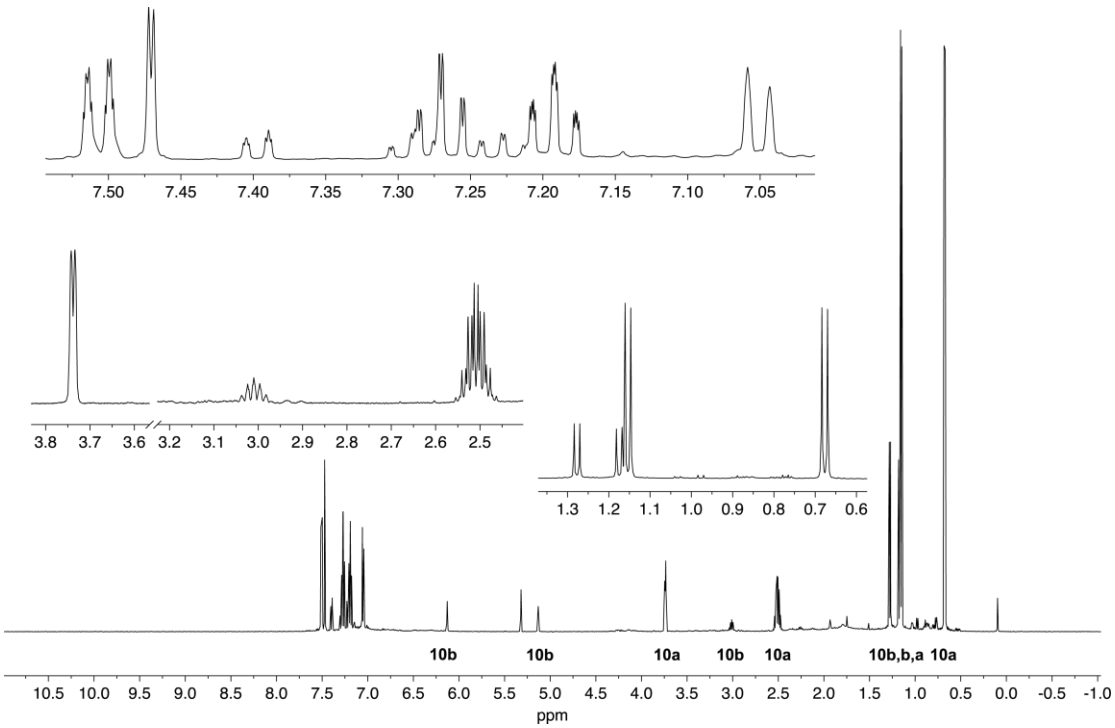


Figure S7 ^1H NMR (500 MHz, 299 K, CD_2Cl_2) of compounds **10a**,**b**.

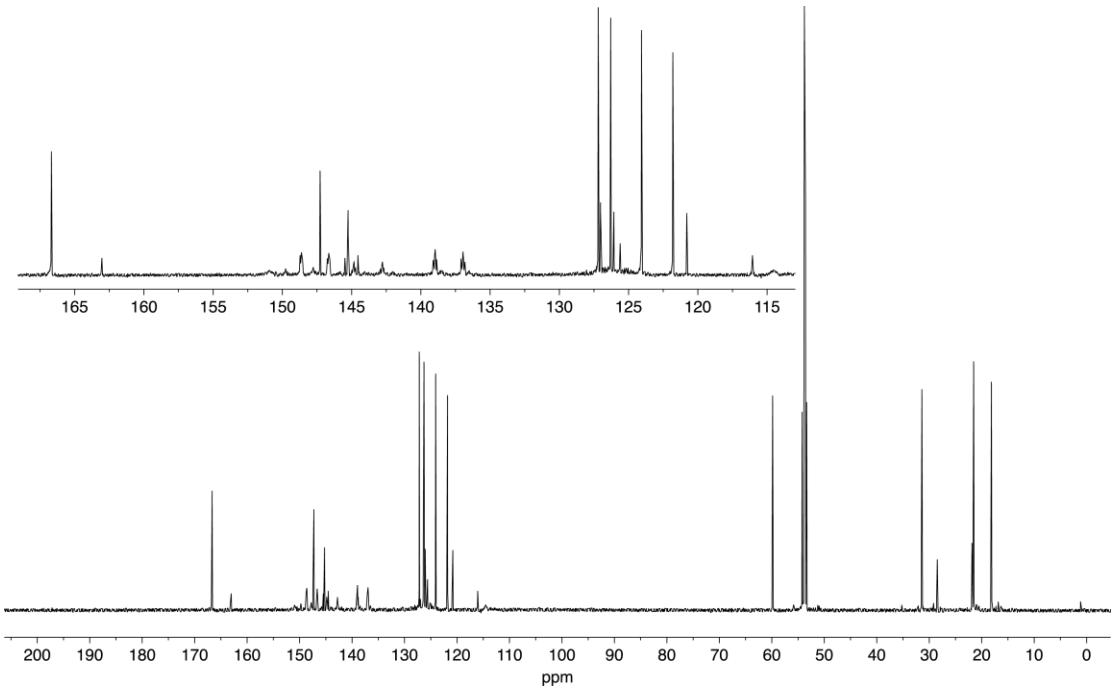


Figure S8 $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) of compounds **10a**,**b**.

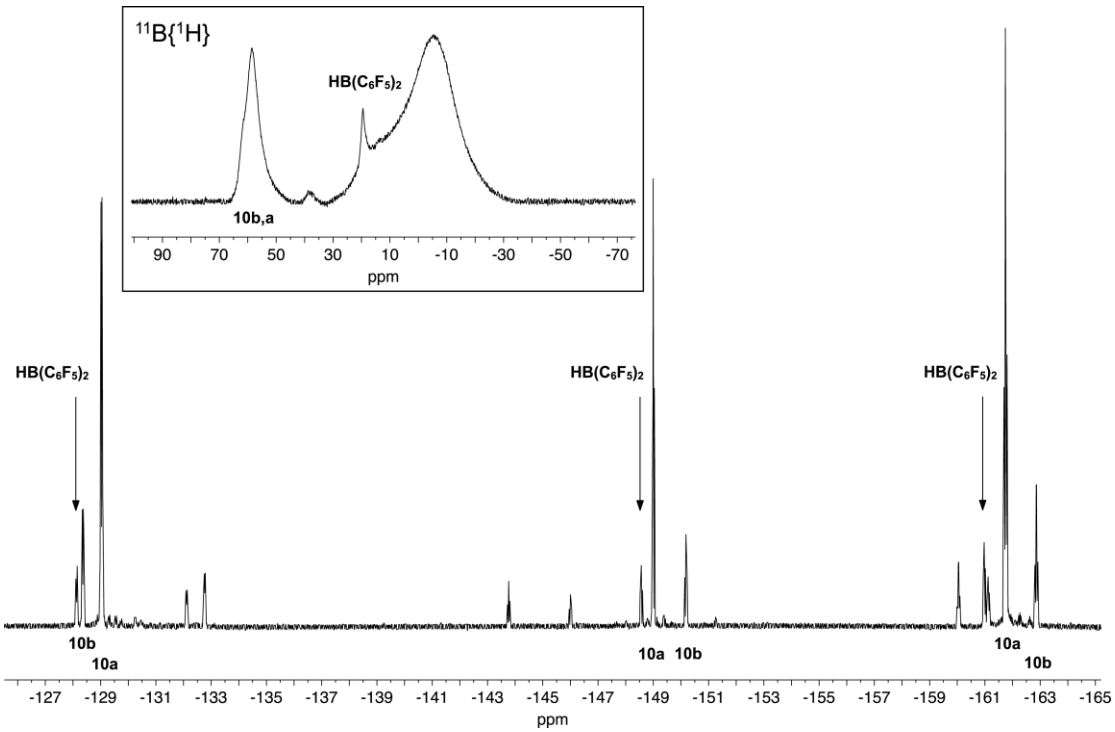
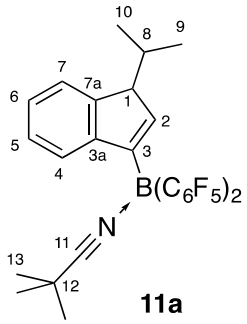


Figure S9 ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) and $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) of compounds **10a**,**b**.

Compound 11a



11a

Benzofulvene **7** (156.1 mg, 1.0 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (7.5 mL), cooled to -78 °C and added to a precooled (-78 °C) suspension of $HB(C_6F_5)_2$ (345.9 mg, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (7.5 mL). The reaction mixture was stirred for 20 minutes at -78 °C before warmed under rinsing water. The obtained yellow solution was stirred for 72 hours at ambient temperature. ^{t}BuCN (83.1 mg, 1.0 mmol, 1.0 equiv) was added affording a colorless solution. After stirring for additional 2 hours all volatiles were removed *in vacuo*. The residue was extracted with pentane (4 × 2 mL). The combined liquid phases were slowly evaporated over the course of several days to give compound **11a** as colorless crystals (110 mg, 0.19 mmol, 19%). The obtained crystals were suitable for the X-ray crystal structure analysis.

IR (KBr, selective wavenumbers): $\tilde{\nu}$ [cm^{-1}] = 2377 (s, C≡N).

Melting point (DSC): 154 °C.

Elemental analysis: calc. for $C_{29}H_{22}BF_{10}N$ (585.30 g mol^{-1}): C, 59.51; H, 3.79; N, 2.39; Found: C, 59.76; H, 3.63; N (corr), 2.34.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ [ppm] = 7.44 (m, 1H, C7-H), 7.14 (m, 2H, C6,5-H), 7.05 (m, 1H, C4-H), 6.05 (d, $^3J_{HH}$ = 1.8 Hz, 1H, C2-H), 3.39 (dd, $^3J_{HH}$ = 4.1, 1.8 Hz, 1H, C1-H), 2.35 (septd, $^3J_{HH}$ = 6.8, 4.1 Hz, 1H, C8-H), 1.42 (s, 9H, C13-H), 1.05 (d, $^3J_{HH}$ = 6.8 Hz, 1H, C9-H)^t, 0.61 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C10-H)^t [^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.44 / 7.14, 7.05 (C7-H / C6-H, C5-H), 7.14 / 7.05 (C5-H / C4-H), 6.05 / 3.39 (C2-H / C1-H), 3.39 / 2.35 (C1-H / C8-H), 2.35 / 1.05, 0.61 (C8-H / C9-H, C10-H).

^{1}H NOESY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 7.44 / 3.39, 2.35, 1.05, 0.61 (C7-H / C1-H, C8-H, C9-H, C10-H), 6.05 / 3.39, 2.35, 1.05, 0.61 (C2-H / C1-H, C8-H, C9-H, C10-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^1H [ppm] / δ^{13}C [ppm] = 7.44 / 123.5 (C7), 7.14 / 126.1, 124.2 (C5, C6), 7.05 / 120.5 (C4), 6.05 / 141.8 (C2), 3.39 / 57.3 (C1), 2.35 / 30.9 (C8), 1.42 / 26.8 (C13), 1.05 / 21.6 (C9), 0.61 / 17.7 (C10).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^1H [ppm] / δ^{13}C [ppm] = 7.44 / 148.8, 126.1 (C7-H / C3a, C5), 7.14 / 148.9, 148.8, 123.5, 120.5 (C6,5-H / C7a, C3a, C7, C4), 7.05 / 148.9, 124.2 (C4-H / C7a, C6), 6.05 / 148.8, 147.0, 57.3 (C2-H / C3a, C3, C1), 3.39 / 148.9, 147.0, 141.8, 30.9, 21.6, 17.7 (C1-H / C7a, C3, C2, C8, C9, C10), 2.35 / 148.9, 141.8, 57.3, 21.6, 17.7 (C8-H / C7a, C2, C1, C9, C10), 1.42 / 121.3, 29.7, 26.8 (C13-H / C11, C12, C13), 1.05 / 57.3, 30.9, 17.7 (C9-H / C1, C8, C10), 0.61 / 57.3, 30.9, 21.6 (C10-H / C1, C8, C9).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ^{13}C [ppm] = 148.9 (C7a), 148.8 (C3a), 148.3 (dm, $^1J_{CF}$ ~ 240 Hz, C_6F_5), 147.0 (br, C3), 141.8 (C2), 140.3 (dm, $^1J_{CF}$ ~ 250 Hz, C_6F_5), 137.6 (dm, $^1J_{CF}$ ~ 250 Hz, C_6F_5), 126.1 (C5), 124.2 (C6), 123.5 (C7), 121.3 (br, C11), 120.5 (C4), 117.5 (br, $^{ipso}C_6F_5$), 57.3 (C1), 30.9 (C8), 29.7 (C12), 26.8 (C13), 21.6 (C9)^t, 17.7 (C10)^t [^{t} tentative assignment].

$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2): δ [ppm] = -8.9 ($\nu_{1/2} \approx 350$ Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ [ppm] = -133.9 (br, 2F, *o*-C_6F_5), -158.7 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-C_6F_5), -164.7 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 6.0].

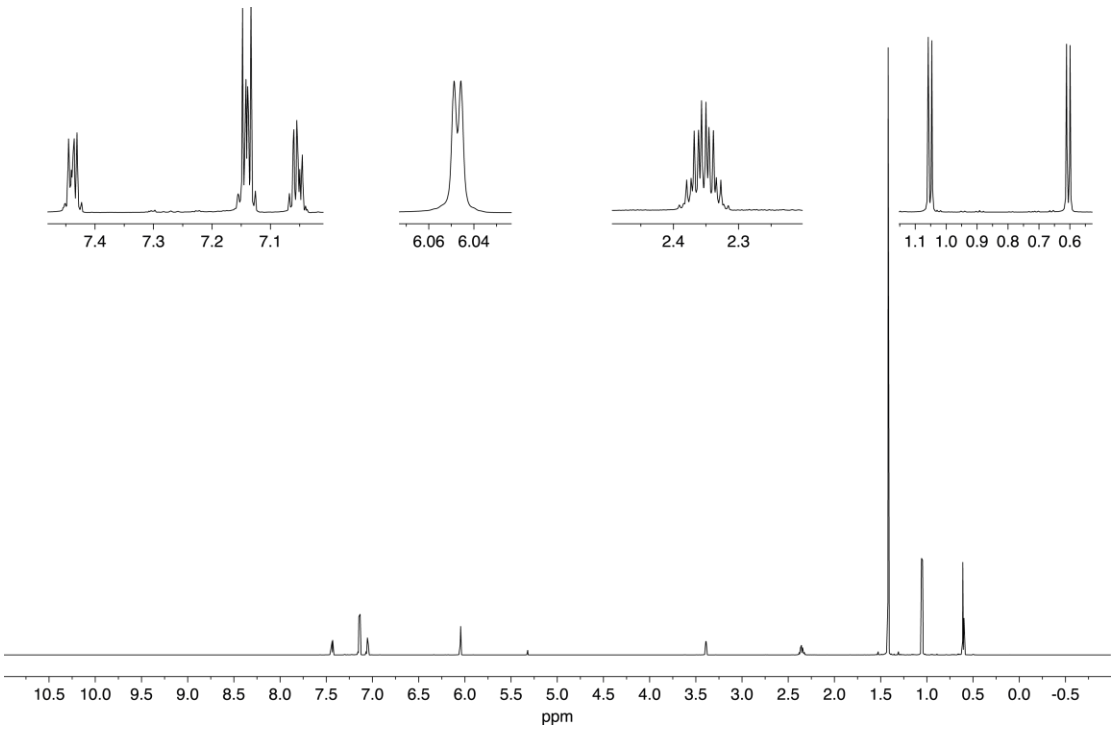


Figure S10 ^1H NMR (600 MHz, 299 K, CD_2Cl_2) of compound **11a**.

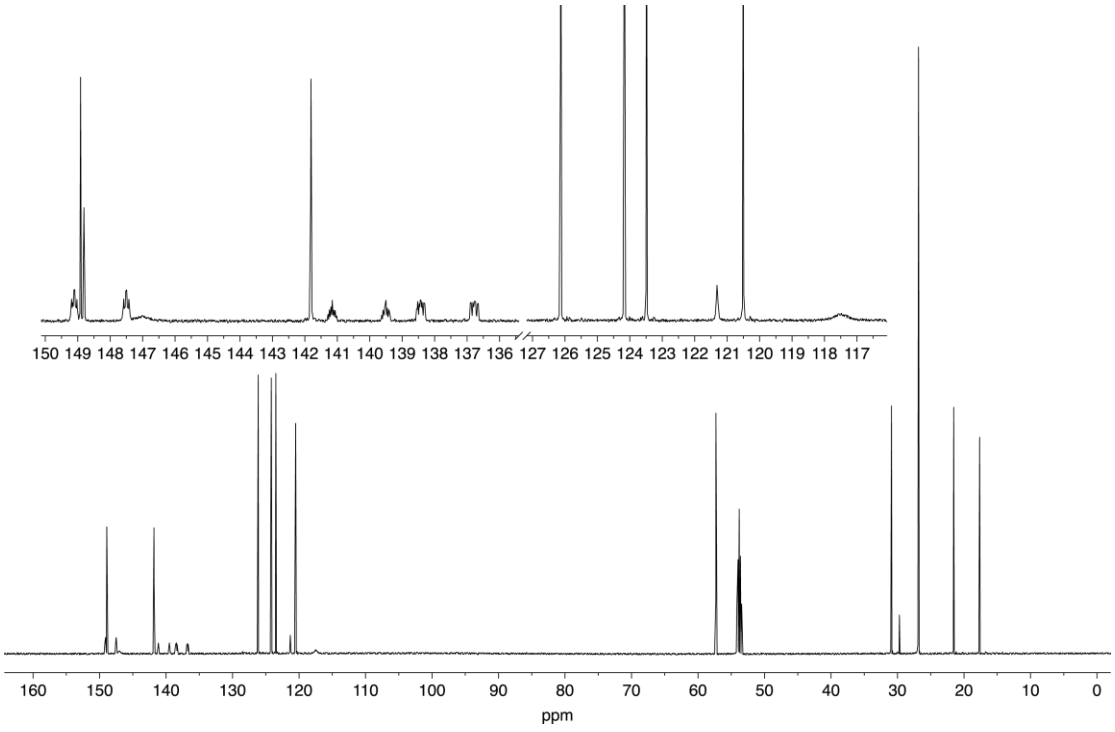


Figure S11 $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) of compound **11a**.

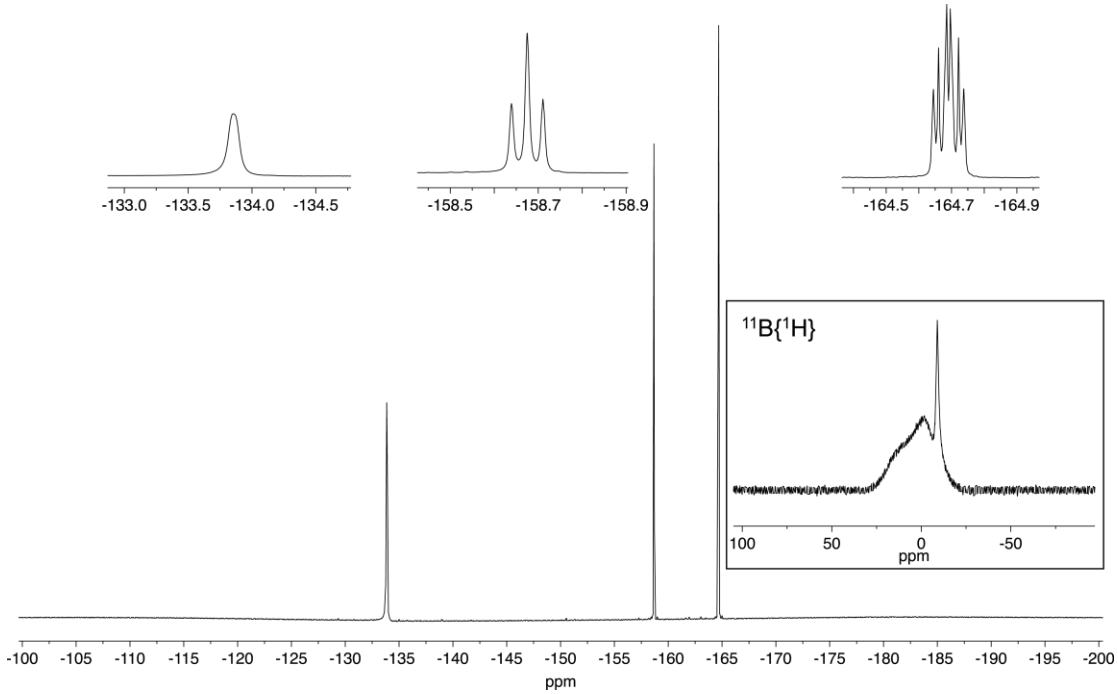
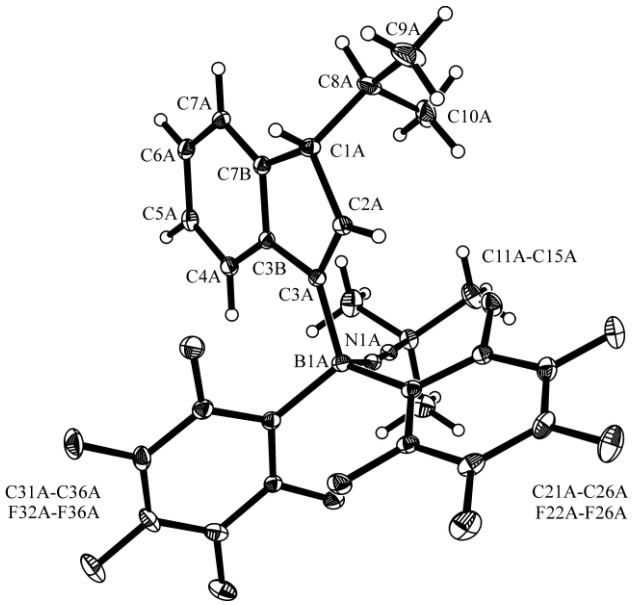
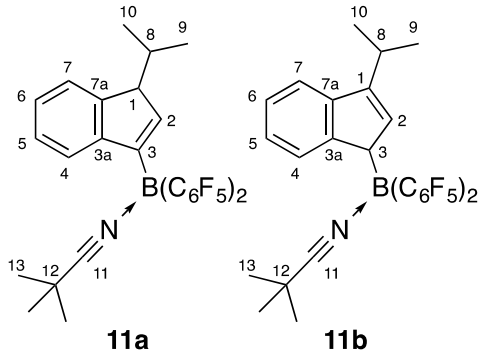


Figure S12 ^{19}F NMR (574 MHz, 299 K, CD_2Cl_2) and $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) of compound **11a**.

X-ray crystal structure analysis of compound 11a: A colorless prism-like specimen of $C_{29}H_{22}BF_{10}N$, approximate dimensions 0.110 mm x 0.137 mm x 0.155 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 838 frames were collected. The total exposure time was 19.27 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 26792 reflections to a maximum θ angle of 68.39° (0.83 Å resolution), of which 9453 were independent (average redundancy 2.834, completeness = 99.7%, R_{int} = 3.88%, R_{sig} = 4.25%) and 8351 (88.34%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.3766(2) Å, b = 17.8561(4) Å, c = 15.0102(4) Å, β = 106.5960(10)°, volume = 2665.32(11) $Å^3$, are based upon the refinement of the XYZ-centroids of 9988 reflections above 20 σ(I) with 7.892° < 2θ < 136.7°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.906. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8390 and 0.8820. The final anisotropic full-matrix least-squares refinement on F^2 with 750 variables converged at R1 = 3.19%, for the observed data and wR2 = 7.31% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 0.160 $e^-/Å^3$ and the largest hole was -0.158 $e^-/Å^3$ with an RMS deviation of 0.034 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.459 g/cm^3 and F(000), 1192 e^-.



Compounds 11a,b



11a **11b**

Benzofulvene **7** (15.6 mg, 0.1 mmol, 1.0 equiv) was dissolved in CD_2Cl_2 (0.4 mL), cooled to -78 °C and added to a precooled (-78 °C) suspension of $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol, 1.0 equiv) in CD_2Cl_2 (0.6 mL). The reaction mixture was warmed under rinsing water and kept at RT for 1.5 days. ^{t}BuCN (8.6 mg, 0.1 mmol, 1.0 equiv) was added to the obtained light yellow solution resulting in decolorification. The reaction mixture was subsequently characterized by NMR experiments.

A mixture of isomers was observed (ratio ca. 4 : 1(^{1}H)).

The NMR data of the major isomer are consistent to those listed for compound **11a** (see above).

Minor isomer assigned as compound 11b

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ [ppm] = 7.41 (dt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, C7-H), 7.22 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, C6-H), 7.03 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, C5-H), 6.81 (d, $^3J_{HH}$ = 7.6 Hz, 1H, C4-H), 6.23 (s, 1H, C2-H), 4.12 (br s, 1H, C3-H), 2.97 (septt, $^3J_{HH}$ = 6.8 Hz, J = 1.1 Hz, 1H, C8-H), 1.40 (s, 9H, C13-H)^t, 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C9-H)^t, 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C10-H)^t [^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.41 / 7.22 (C7-H / C6-H), 7.22 / 7.03 (C6-H / C5-H), 7.03 / 6.82 (C5-H / C4-H), 6.23 / 4.12 (C2-H / C3-H), 2.97 / 1.29, 1.26 (C8- H / C9-H, C10-H).

^{1}H NOESY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 2.97 / 7.41, 6.23, 1.29, 1.26 (C8-H / C7-H, C2-H, C9-H, C10-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.41 / 119.2 (C7), 7.22 / 125.3 (C6), 7.03 / 124.3 (C5), 6.81 / 123.5 (C4), 6.23 / 133.3 (C2), 4.12 / 45.2 (C3), 2.97 / 27.3 (C8), 1.40 / 27.5 (C13), 1.29 / 22.2 (C9), 1.26 / 22.9 (C10).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.41 / 150.1, 124.3 (C7-H / C3a, C5), 7.22 / 145.7, 123.5 (C6-H / C7a, C4), 7.03 / 150.1, 119.2 (C5-H / C3a, C7), 6.81 / 145.7, 125.3 (C4-H / C7a, C6), 6.23 / 150.1, 148.6, 145.7, 45.2, 27.3 (C2-H / C3a, C1, C7a, C3, C8), 4.12 / 150.1, 148.6, 133.3 (C3-H / C3a, C1, C2), 2.97 / 148.6, 145.7, 133.3, 22.9, 22.2 (C8-H / C1, C7a, C2, C10, C9), 1.40 / 29.2, 27.5 (C13-H / C12, C13), 1.29 / 148.6, 27.3, 22.9 (C9-H / C1, C8, C10), 1.26 / 148.6, 27.3, 22.2 (C10-H / C1, C8, C9).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ^{13}C [ppm] = 150.1 (C3a), 148.6 (C1), 145.7 (C7a), 133.3 (C2), 125.3 (C6), 124.3 (C5), 123.5 (C4), 119.2 (C7), 45.2 (br, C3), 29.2 (C12)^{t}, 27.5 (br, C13)^{t}, 27.3 (C8), 22.9 (C10)^{t}, 22.2 (C9)^{t} [C11, C_6F_5 not listed; ^{t} tentative assignment].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ [ppm] = -7.9 ($\nu_{1/2} \approx 150$ Hz).

^{19}F NMR (574 MHz, 299 K, CD_2Cl_2): δ [ppm] = -135.0 (m, 2F, *o*-C_6F_5), -157.3 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), -164.4 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 7.1].

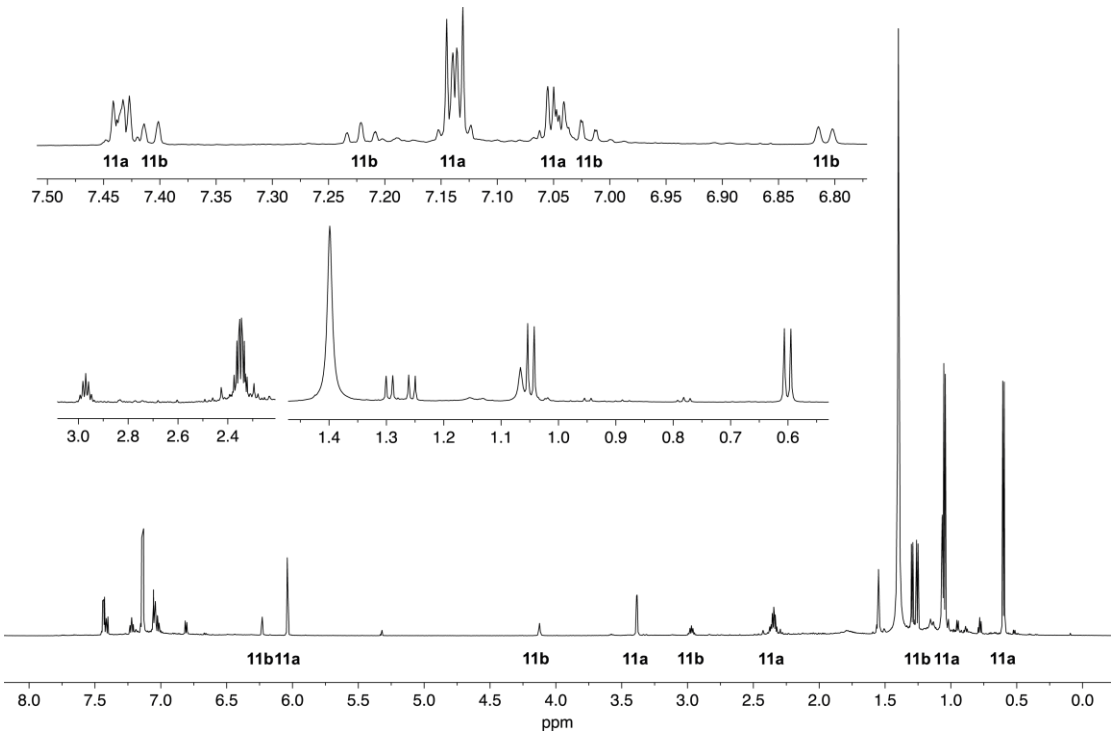


Figure S13 ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of compounds **11a,b**.

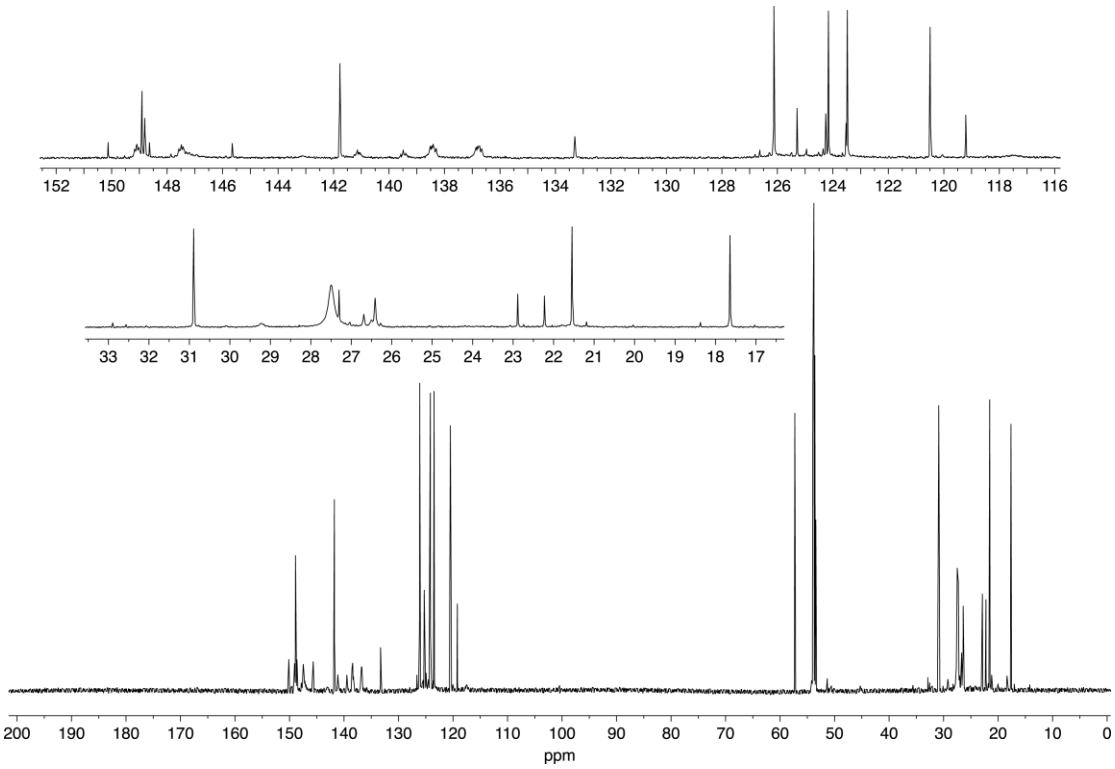


Figure S14 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) of compounds **11a,b**.

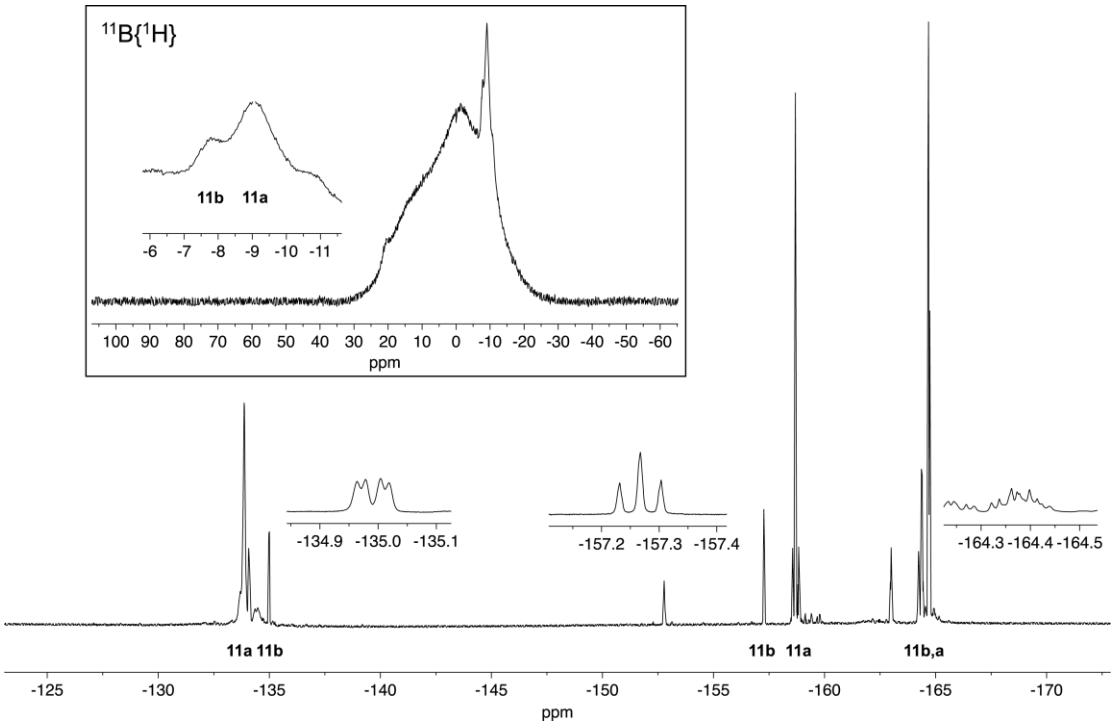
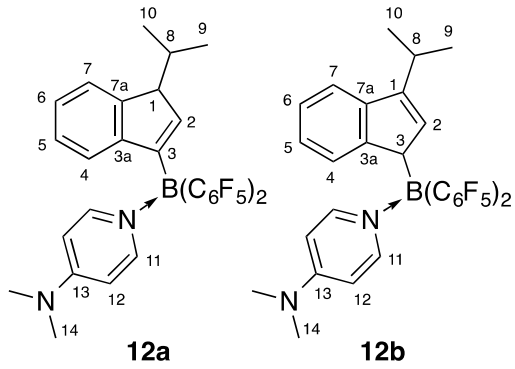


Figure S15 ^{19}F NMR (574 MHz, 299 K, CD_2Cl_2) and $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) of compounds **11a,b**.

Compounds 12a,b



Benzofulvene **7** (52.1 mg, 0.33 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (1.0 mL), cooled to -78 °C and added to a precooled (-78 °C) suspension of $HB(C_6F_5)_2$ (115.3 mg, 0.33 mmol, 1.0 equiv) in CH_2Cl_2 (4.0 mL). The reaction mixture was stirred for 20 minutes at -78 °C before warmed under rinsing water. The obtained yellow solution was stirred for 14 hours at ambient temperature. 4-Dimethylaminopyridine (40.7 mg, 0.33 mmol, 1.0 equiv) was added giving a colorless solution. After stirring for 1.5 hours at RT the reaction mixture was concentrated *in vacuo*. The obtained residue was dissolved in a small amount of toluene (0.3 mL) and triturated by stirring with pentane (5 mL) to give a white solid in 58% yield after drying *in vacuo* (120 mg, 0.19 mmol) in a ratio of approx. 4 : 1 for **12a** : **12b**.

Elemental analysis (solid): calc. for $C_{31}H_{23}BF_{10}N_2$ (624.33 g mol^{-1}): C, 59.64; H, 3.71; N, 4.49; Found: C, 58.57; H, 3.52; N, 4.55.

Major isomer assigned as compound 12a

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ [ppm] = 7.95 (d, $^3J_{HH}$ = 7.7 Hz, 2H, C11-H), 7.38 (dm, $^3J_{HH}$ = 7.5 Hz, 1H, C7-H), 7.34 (d, $^3J_{HH}$ = 7.2 Hz, 1H, C4-H), 7.18 (td, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, C5-H), 7.09 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, C6-H), 6.68 (br s, 1H, C2-H), 5.38 (d, $^3J_{HH}$ = 7.7 Hz, 2H, C12-H), 3.55 (dd, $^3J_{HH}$ = 4.1, *J* = 1.9 Hz, 1H, C1-H), 2.35 (septd, $^3J_{HH}$ = 6.8, 4.1 Hz, 1H, C8-H), 1.81 (s, 6H, C14-H), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 1H, C9-H)^t, 0.81 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C10-H)^t [^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, C_6D_6): δ [ppm] / δ [ppm] = 7.95 / 5.38 (C11-H / C12-H), 7.38 / 7.09, 3.55 (C7-H / C6-H, C1-H), 7.34 / 7.18 (C4-H / C5-H), 7.18 / 7.09 (C5-H / C6-H), 6.68 / 3.55 (C2-H / C1-H), 5.38 / 1.81 (C12-H / C14-H), 3.55 / 2.35 (C1-H / C8-H), 2.35 / 1.14, 0.81 (C8-H / C9-H, C10-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ^1H [ppm] / δ^{13}C [ppm] = 7.95 / 146.0 (C11), 7.38 / 123.4 (C7), 7.34 / 121.7 (C4), 7.18 / 126.5 (C5), 7.09 / 124.1 (C6), 6.68 / 141.2 (C2), 5.38 / 105.8 (C12), 3.55 / 57.5 (C1), 2.35 / 31.1 (C8), 1.81 / 38.1 (C14), 1.14 / 21.8 (C9), 0.81 / 17.8 (C10).

^{1}H,^{13}C GHMBC (500 MHz / 151 MHz, 299 K, C_6D_6): δ^1H [ppm] / δ^{13}C [ppm] = 7.95 / 155.0, 146.0 105.8 (C11-H / C13, C11, C12), 7.38 / 149.7, 126.5, 57.5 (C7-H / C3a, C5, C1), 7.34 / 148.9, 124.1 (C4-H / C7a, C6), 7.18 / 149.7, 123.4 (C5-H / C3a, C7), 7.09 / 148.9, 121.7 (C6-H / C7a, C4), 6.68 / 149.4, 57.5 (C2-H / C3, C1), 5.38 / 146.0, 105.8 (C12-H / C11, C12), 3.55 / 148.9, 31.1, 21.8, 17.8 (C1-H / C7a, C8, C10, C9), 2.35 / 148.9, 57.5, 21.8, 17.8 (C8-H / C7a, C1, C9, C10), 1.81 / 155.0, 38.1 (C14-H / C13, C14), 1.14 / 57.5, 31.1, 17.8 (C9-H / C1, C8, C10), 0.81 / 57.5, 31.1, 21.8 (C10-H / C1, C8, C9).

$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, C_6D_6): $\delta^{13}C$ [ppm] = 155.0 (C13), 149.7 (C3a), 149.4 (br, C3)^t, 148.9 (C7a), 146.0 (C11), 141.2 (C2), 126.5 (C5), 124.1 (C6), 123.4 (C7), 121.7 (C4), 105.8 (C12), 57.5 (C1), 38.1 (C13), 31.1 (C8), 21.8 (C9)^t, 17.8 (C10)^t [C_6F_5 not listed; ^{t} tentative assignment].

$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, C_6D_6): δ [ppm] = -3.7 ($\nu_{1/2} \approx 270$ Hz).

^{19}F NMR (574 MHz, 299 K, C_6D_6): δ [ppm] = -130.4 (br, 4F, *o*-C_6F_5), -158.3 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-$C_6F_5^a$), -158.5 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-$C_6F_5^b$), -164.1 (br, 2F, *m*-$C_6F_5^a$), -164.2 (m, 2F, *m*-$C_6F_5^b$) [$\Delta\delta^{19}F_{m,p}$ = 5.8^a, 5.7^b].

Minor isomer assigned as compound 12b

The quality of the obtained NMR data from the crystalline material was not sufficient for a complete assignment of the signals of the minor isomer. Therefore it was characterized by selected key resonances (see below).

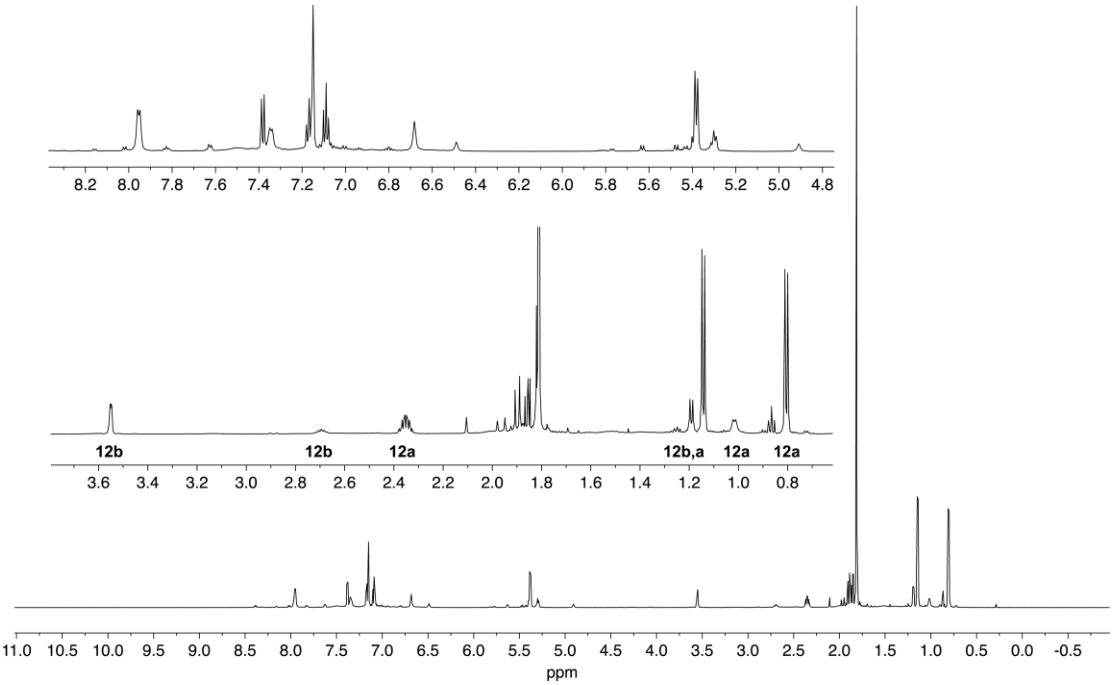


Figure S16 ^1H NMR (600 MHz, 299 K, C_6D_6) of compounds **12a**,**b** (white solid).

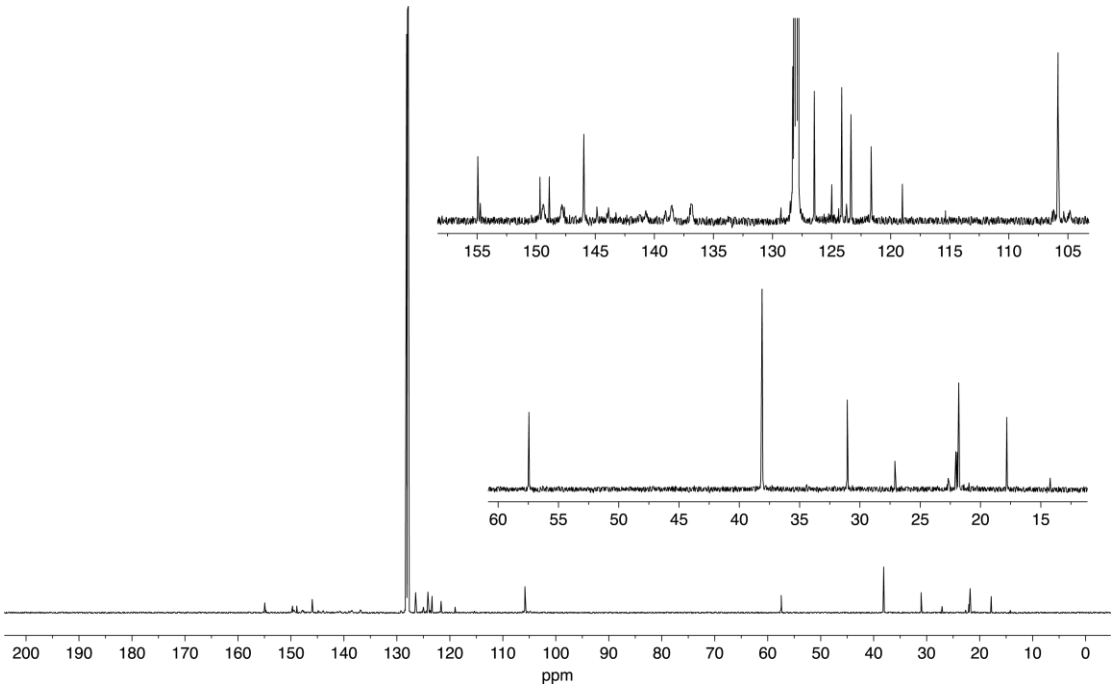


Figure S17 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) of compounds **12a**,**b** (white solid).

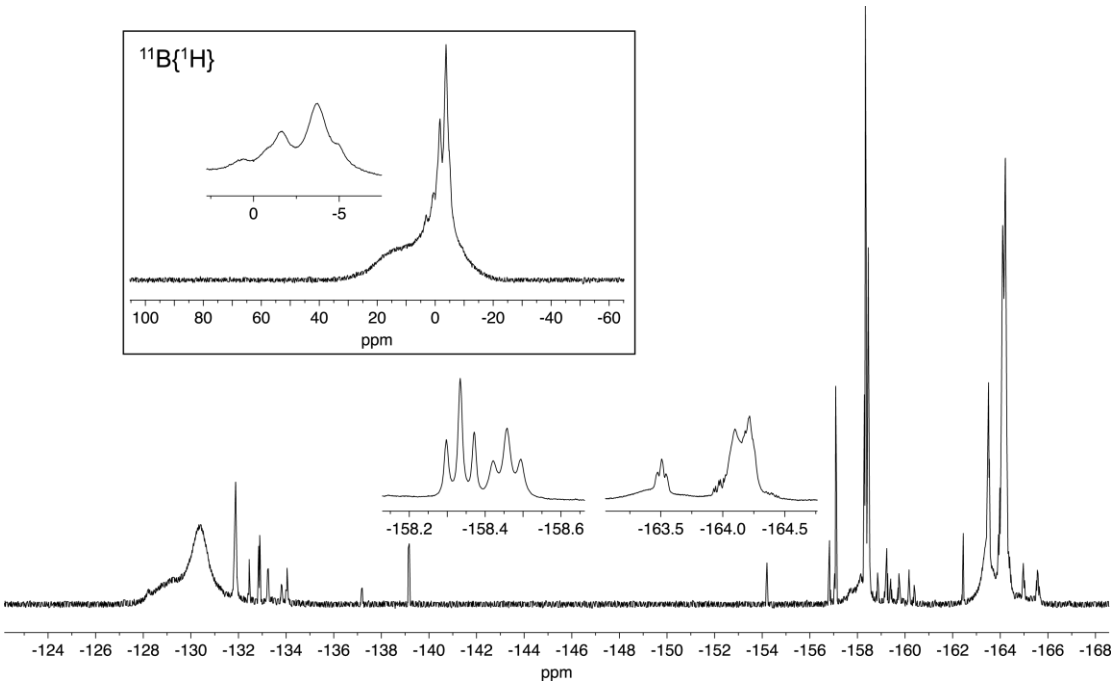


Figure S18 $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, C_6D_6) and ^{19}F NMR (574 MHz, 299 K, C_6D_6) of compounds **12a**,**b** (white solid).

Crystals suitable for the X-ray crystal structure analysis of compound **12b** were obtained from a solution of the white solid in benzene.

Minor isomer assigned as compound 12b

Melting point (crystals): 270 °C.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) [selected resonances]: δ [ppm] = 6.23 (s, 1H, C2-H), 4.49 (s, 1H, C3-H), 3.02 (s, 6H, C14-H), 2.66 (sept, $^{3}J_{HH}$ = 6.9 Hz, 1H, C8-H), 1.12 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H, C9-H)^{t}, 0.92 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, C10-H)^{t} [aromatic signals excluded; ^{t} tentative assignment].

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 6.23 / 4.49 (C2-H / C3-H), 2.66 / 1.12, 0.92 (C8-H / C9-H, C10-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2) [selected traces]: δ^{1}H [ppm] / δ^{13}C [ppm] = 3.02 / 39.7 (C14), 1.12 / 21.8 (C10), 0.92 / 22.0 (C9).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2) [selected traces]: δ^{1}H [ppm] / δ^{13}C [ppm] = 3.02 / 155.6, 39.7 (C14-H / C13, C14), 1.12 / 147.5, 27.0, 22.0 (C10-H / C1, C8, C9), 0.92 / 147.5, 27.0, 21.8 (C9-H / C1, C8, C10).

^{13}C NMR (151 MHz, 299 K, CD_2Cl_2) [selected resonances]: δ [ppm] = 155.6 (C13), 147.5 (C1), 39.7 (C14), 27.0 (C8), 22.0 (C9), 21.8 (C10).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ [ppm] = -1.9 ($\nu_{1/2} \approx 84$ Hz).

^{19}F NMR (574 MHz, 299 K, CD_2Cl_2): δ [ppm] = -130.0 (br, 2F, *o*-C_6F_5), -160.0 (br, 1F, *p*-C_6F_5), -164.5 (br, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{p,m}$ = 4.5].

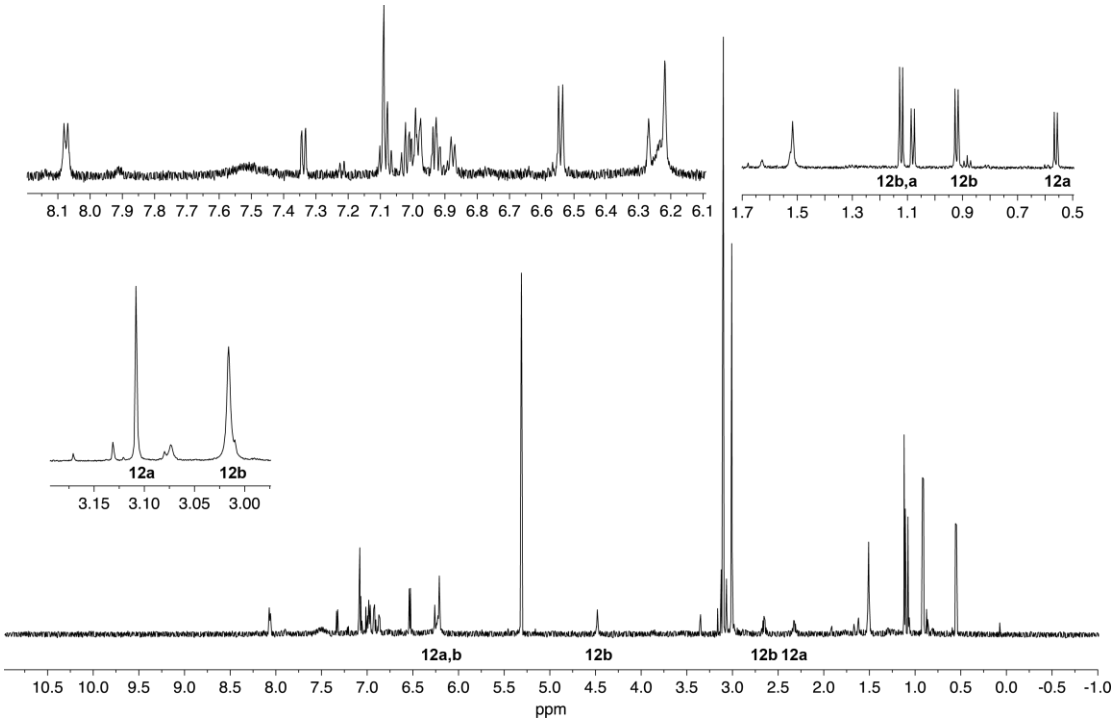


Figure S19 ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of compounds **12a**,**b** (crystalline material).

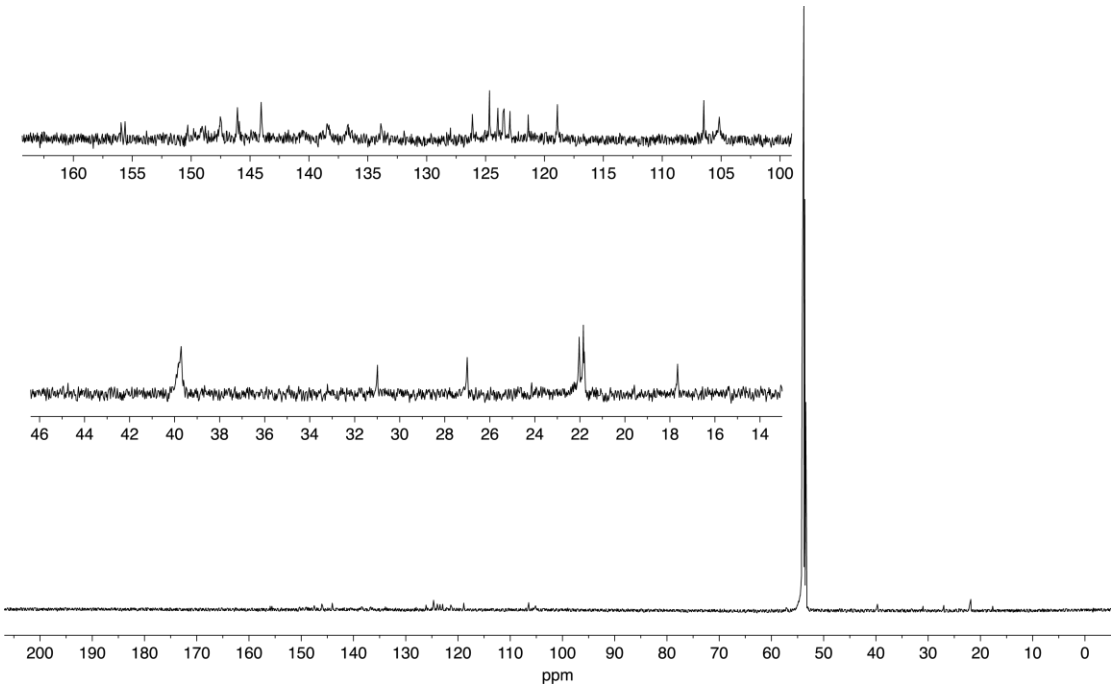


Figure S20 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) of compounds **12a**,**b** (crystalline material).

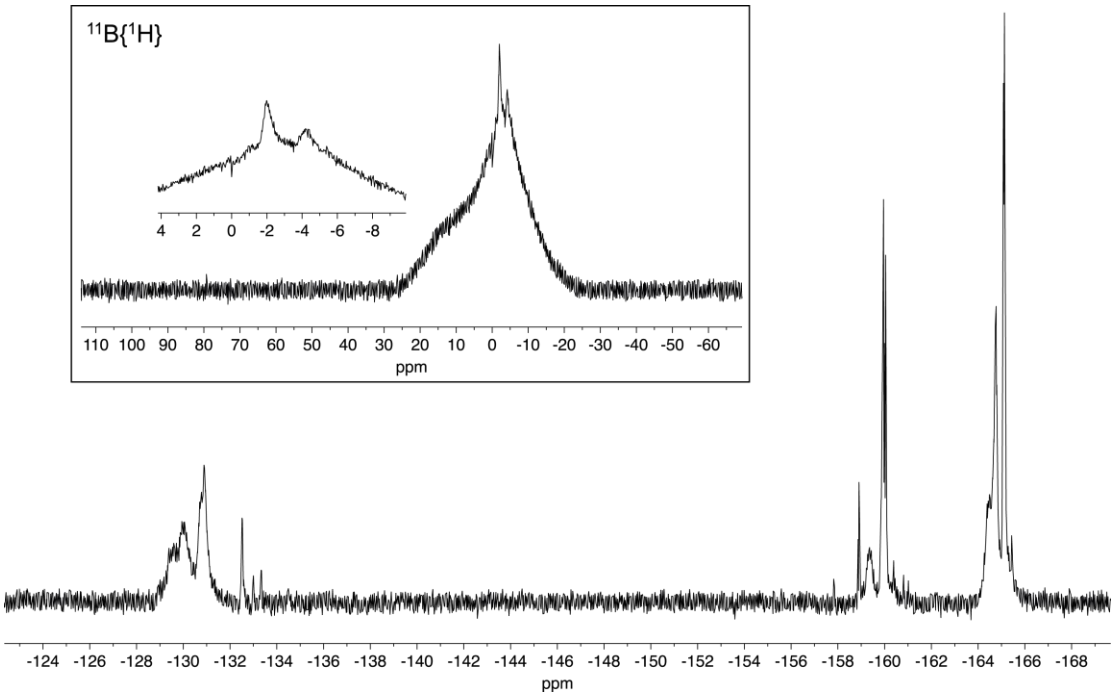
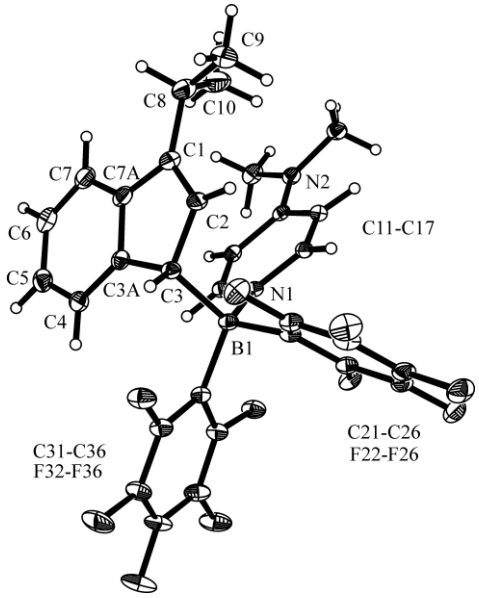


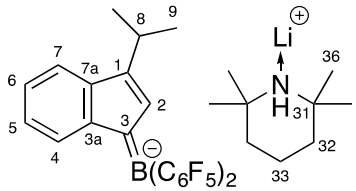
Figure S21 $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) and ^{19}F NMR (574 MHz, 299 K, CD_2Cl_2) of compounds **12a**,**b** (crystalline material).

X-ray crystal structure analysis of compound 12b: A colorless prism-like specimen of $C_{31}H_{23}BF_{10}N_2 \cdot C_6H_6$, approximate dimensions 0.133 mm x 0.172 mm x 0.250 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1390 frames were collected. The total exposure time was 19.77 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 48107 reflections to a maximum θ angle of 68.31° (0.83 Å resolution), of which 5954 were independent (average redundancy 8.080, completeness = 99.8%, R_{int} = 3.62%, R_{sig} = 2.01%) and 5280 (88.68%) were greater than $2\sigma(F^2)$. The final cell constants of a = 14.5937(4) Å, b = 15.5767(5) Å, c = 15.1672(4) Å, β = 109.2890(10)°, volume = 3254.29(16) $Å^3$, are based upon the refinement of the XYZ-centroids of 9780 reflections above 20 σ(I) with 8.388° < 2θ < 136.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.916. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7760 and 0.8710. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{37}H_{29}BF_{10}N_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 454 variables converged at R1 = 4.15%, for the observed data and wR2 = 11.11% for all data. The goodness-of-fit was 1.023. The largest peak in the final difference electron density synthesis was 0.626 $e^-/Å^3$ and the largest hole was -0.321 $e^-/Å^3$ with an RMS deviation of 0.043 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.434 g/cm^3 and F(000), 1440 e^-.



Compound 14 [LiHTMP]



14 [LiHTMP]

Benzofulvene **7** (312 mg, 2.0 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10.0 mL) and cooled to -78 °C. $HB(C_6F_5)_2$ (692 mg, 2.0 mmol, 1.0 equiv) was suspended in CH_2Cl_2 (20.0 mL) and cooled to -78 °C. Then the benzofulvene solution was added to the $HB(C_6F_5)_2$ suspension by using a canula. The reaction mixture was stirred for 20 minutes at -78 °C before warmed under rinsing water. The obtained yellow solution was stirred for 14 hours at ambient temperature. Toluene (70 mL) was added. Subsequently, the reaction volume was reduced to a total volume of 20 ml. Solid LiTMP **13** (294 mg, 2.0 mmol, 1.0 equiv) was

added. After two hours stirring at RT the lithium amide slowly dissolved. All volatiles were removed *in vacuo*. The obtained residue was suspended in pentane (10 mL). The suspension was filtrated. The filtrate was concentrated *in vacuo* and dissolved in a small amount of pentane (2.0 mL). Standing for an hour at ambient temperature resulted in precipitation. The yellow precipitate was filtrated, washed with pentane (2 × 1 mL) and dried *in vacuo* to give compound **14** [LiHTMP] in 67% yield (872 mg, 1.34 mmol).

IR (KBr, selective wavenumbers): $\tilde{\nu}$ [cm^{-1}] = 3266 (w, NH).

Melting point (DSC): 160 °C.

Elemental analysis: calc. for $C_{33}H_{31}BF_{10}LiN$ (649.35 g mol^{-1}): C, 61.04; H, 4.81; N, 2.16; Found: C, 60.52; H, 4.61; N, 2.61 N (corr.), 2.21.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ [ppm] = 7.61 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4-H), 7.47 (dt, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, C7-H), 7.12 (ddd, $^3J_{HH}$ = 8.0, 7.0, $^4J_{HH}$ = 1.1 Hz, 1H, C6-H), 7.07 (ddd, $^3J_{HH}$ = 8.0, 7.0, $^4J_{HH}$ = 1.0 Hz, 1H, C5-H), 6.92 (s, 1H, C2-H), 3.02 (septd, $^3J_{HH}$ = 6.8 Hz, J = 0.5 Hz, 1H, C8-H), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 6H, C9-H), 1.01 (br, 2H, C33-H), 0.65 (br, 4H, C32-H), 0.44 (br, 12H, C36-H), 0.05 (br, 1H, N-H).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, C_6D_6): δ [ppm] / δ [ppm] = 7.61 / 7.07 (C4-H / C5-H), 7.47 / 7.12 (C7-H / C6-H), 7.12 / 7.07 (C6-H / C5-H), 3.02 / 1.27 (C8-H / C9-H).

^{1}H NOESY (600 MHz / 600 MHz, 299 K, C_6D_6) [selected traces]: δ [ppm] / δ [ppm] = 1.27 / 7.47, 6.92, 3.02 (C9-H / C7-H, C2-H, C8-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ^1H [ppm] / δ^{13}C [ppm] = 7.61 / 123.0 (C4), 7.47 / 120.3 (C7), 7.12 / 123.2 (C6), 7.07 / 123.9 (C5), 6.92 / 124.6 (C2), 3.02 / 27.1 (C8), 1.27 / 22.9 (C9), 1.01 / 17.2 (C33), 0.65 / 37.1 (C32).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6): δ^1H [ppm] / δ^{13}C [ppm] = 7.61 / 136.1, 123.2 (C4-H / C7a, C6), 7.47 / 137.2, 123.9 (C7-H / C3a, C5), 7.12 / 136.1, 123.0 (C6-H / C7a, C4), 7.07 / 137.2, 120.3 (C5-H / C3a, C7), 6.92 / 137.2, 136.1, 115.6 (C2-H / C3a, C7a, C3), 3.02 / 136.2, 124.6, 22.9 (C8-H / C1, C2, C9), 1.27 / 136.2, 27.1, 22.9 (C9-H / C1, C8, C9).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ^{13}C [ppm] = 137.2 (C3a), 136.2 (C1), 136.1 (C7a), 124.6 (C2), 123.9 (C5), 123.2 (C6), 123.0 (C4), 120.3 (C7), 115.6 (br, C3), 50.4 (C31)^t, 37.1 (C32), 32.3 (br, C36)^t, 27.1 (C8), 22.9 (C9), 17.2 (C33) [C_6F_5 not listed; ^{t} tentative assignment].

^{7}Li NMR (233 MHz, 299 K, C_6D_6): δ [ppm] = -4.8 ($\nu_{1/2} \approx$ 80 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ [ppm] = 38.1 ($\nu_{1/2} \approx$ 1000 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ [ppm] = -132.3 (br, 4F, *o*-C_6F_5), -154.73, -154.74 (each t, $^3J_{FF}$ = 20.5 Hz, each 1F, *p*-C_6F_5), -162.4 (br, 4F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 7.7].

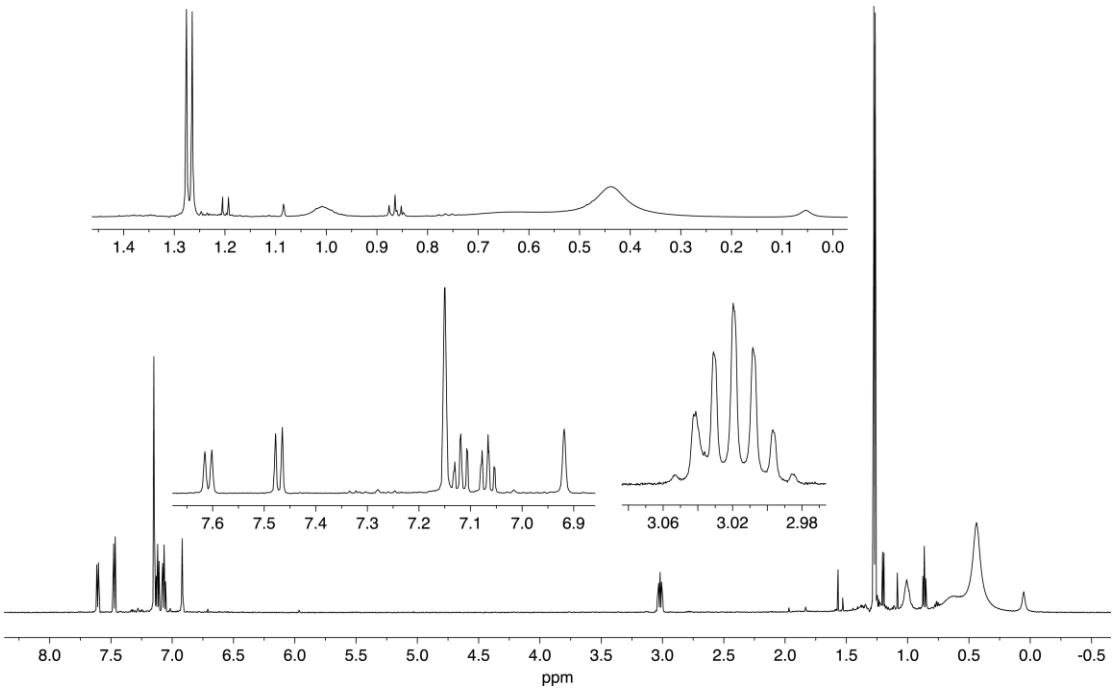


Figure S22 ^{1}H NMR (600 MHz, 299 K, C_6D_6) of compound **14** [LiHTMP].

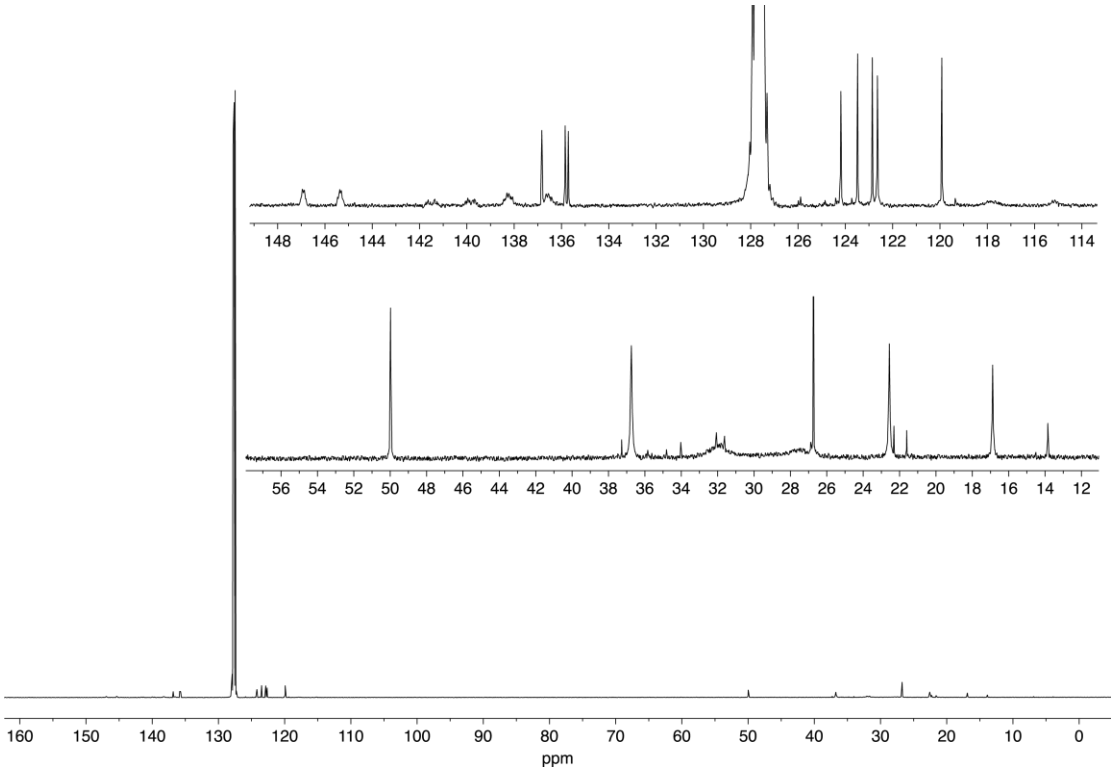


Figure S23 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) of compound **14** [LiHTMP].

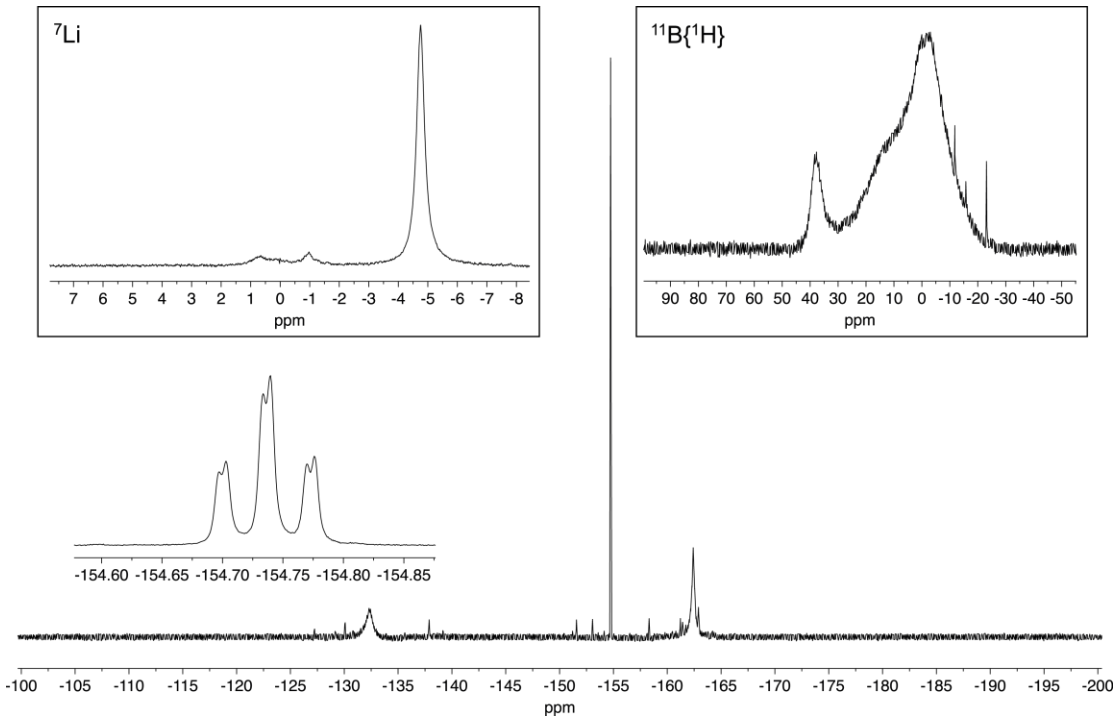


Figure S24 ^{7}Li NMR (233 MHz, 299 K, C_6D_6), ^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6) and ^{19}F NMR (574 MHz, 299 K, C_6D_6) of compound **14** [LiHTMP].

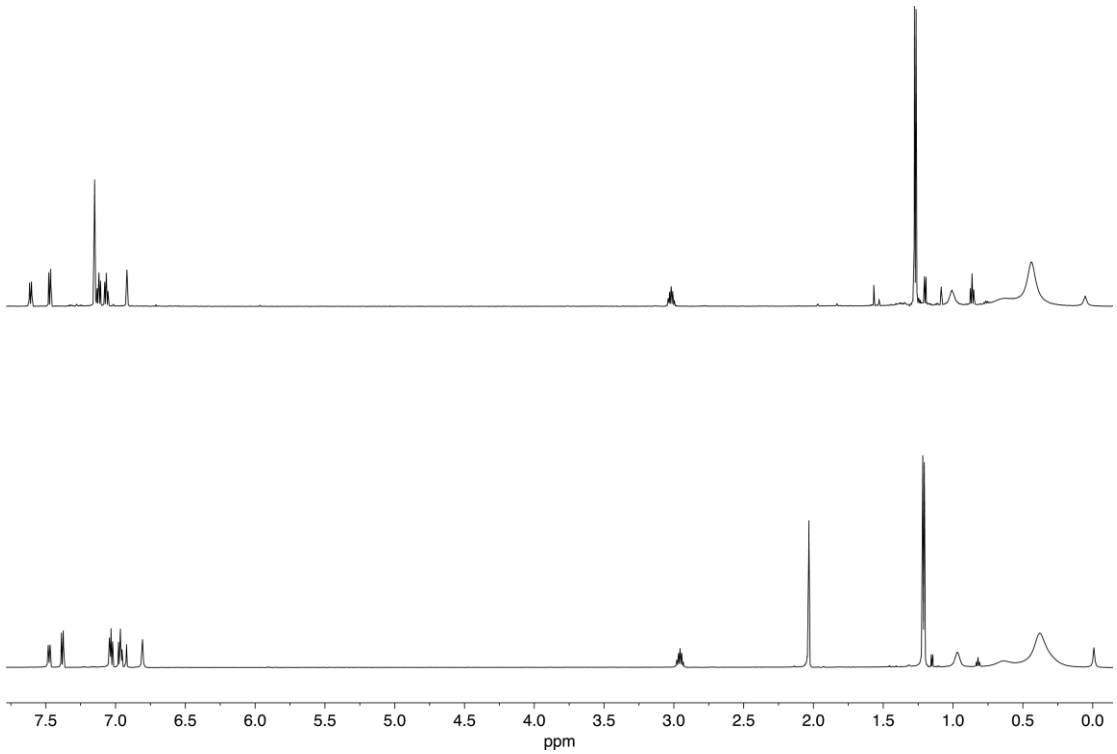


Figure S25 Stacked ^{1}H NMR (600 MHz, 299 K) of compound **14** [LiHTMP]: C_6D_6 (above), toluene-d_8 (below).

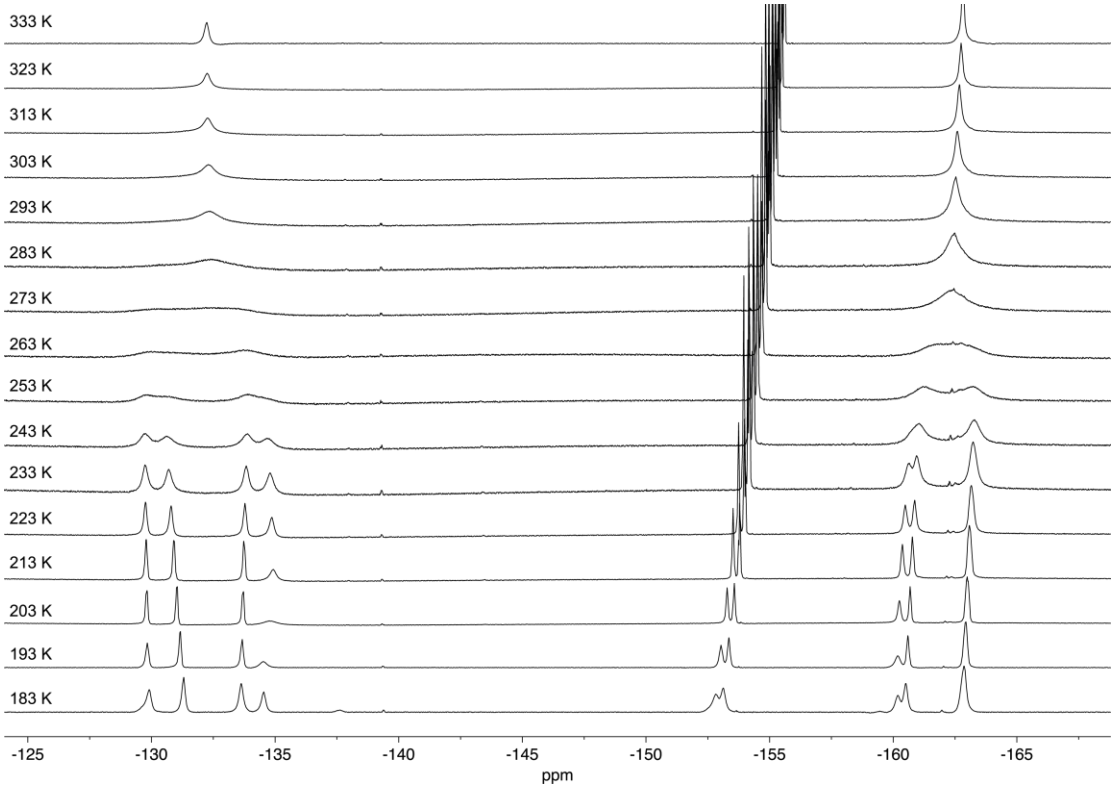


Figure S26 Variable temperature ^{19}F NMR (574 MHz, C_7D_8) of **14** [LiHTMP].

$\Delta G^{\neq} = RT_c(22.96 + \ln(T_c/\Delta\nu)$ [J mol^{-1}]; R = 8.314 J (mol K)$^{-1}$; 1 cal = 4.187 J.

^{19}F NMR (574 MHz, C_6D_6): δ^{19}F(*o*-C_6F_5, 333K): -132.3 (br, 2F); δ^{19}F(*o*-C_6F_5, 273K): -130.1, -133.9 (each br, each 1F): $\Delta G^{\neq}$(ortho, T_c = 273 K; $\Delta\nu$(273K) = 2100 Hz) = 11.0 kcal/mol.

^{19}F NMR (574 MHz, C_6D_6): δ^{19}F(*m*-C_6F_5, 333K): -162.8 (br, 2F); δ^{19}F(*m*-C_6F_5, 253K): -161.2, -163.3 (each br, each 1F): $\Delta G^{\neq}$(meta, T_c = 263 K; $\Delta\nu$(253K) = 1270 Hz) = 11.2 kcal/mol.

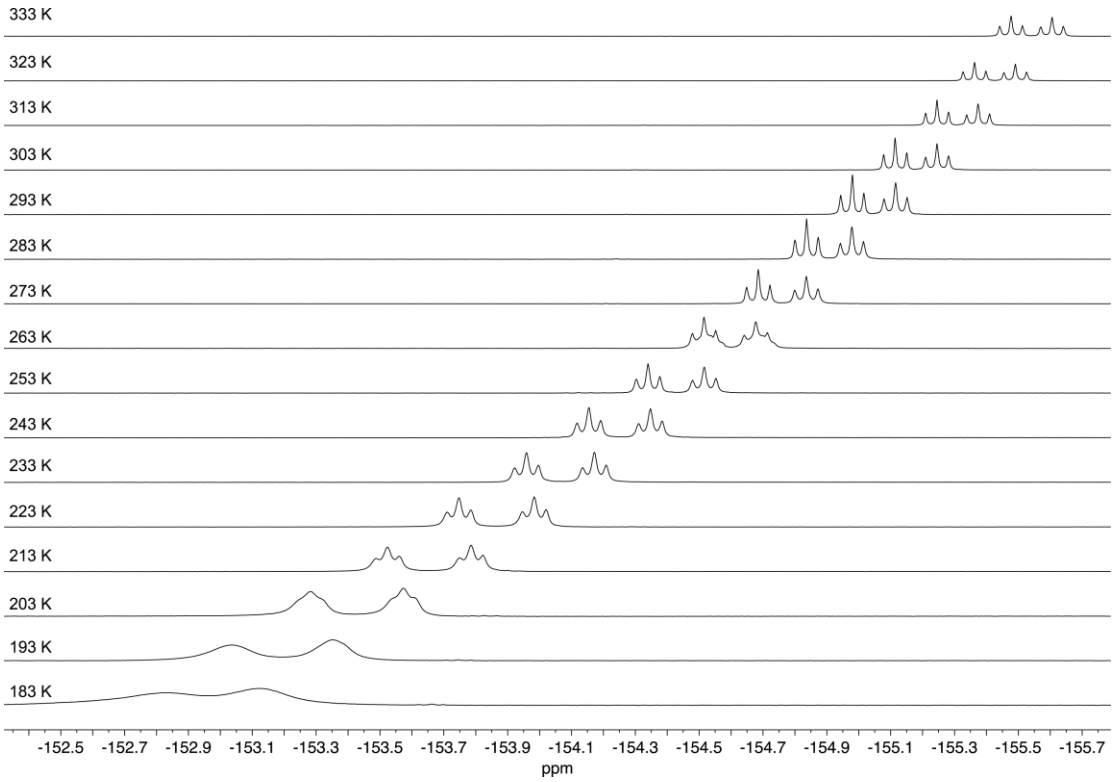
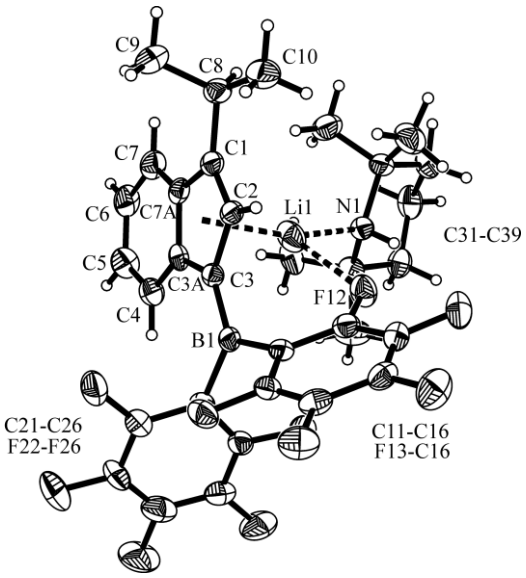


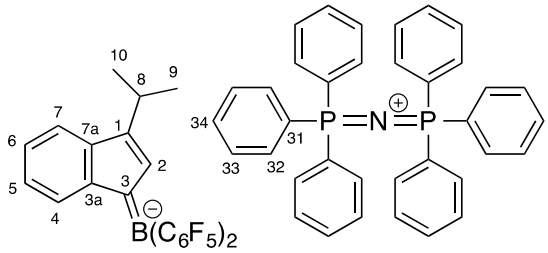
Figure S27 Variable temperature ^{19}F NMR (574 MHz, C_7D_8) [selected area: *para*-F] of compound **14** [LiHTMP].

Crystals suitable for the X-ray crystal structure analysis could be grown from a saturated solution of **14**[LiHTMP] in pentane at -32 °C.

X-ray crystal structure analysis of compound 14 [LiHTMP]: formula $C_{33}H_{31}BF_{10}LiN$, M = 649.34, colourless crystal, 0.20 x 0.18 x 0.05 mm, a = 10.6418(3), b = 17.7550(4), c = 16.8933(4) Å, β = 93.934(1)°, V = 3184.4(1) Å^3, ρ_{calc} = 1.354 gcm^{-3}, μ = 0.118 mm^{-1}, empirical absorption correction ($0.976 \leq T \leq 0.994$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073Å, T = 223(2) K, ω and φ scans, 17877 reflections collected ($\pm h$, $\pm k$, $\pm l$), 5530 independent (R_{int} = 0.065) and 3260 observed reflections [$I>2\sigma(I)$], 425 refined parameters, R = 0.087, wR^2 = 0.173, max. (min.) residual electron density 0.23 (-0.19) e.Å^{-3}, the hydrogen at N1 atom was refined freely; others were calculated and refined as riding atoms.



Compound 14 [Ph_3PNPPh_3]



Borata-alkene **14** [LiHTMP] (129.9 mg, 0.2 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.0 mL) and added to a solution of triphenylphosphanylidene ammonium chloride (114.8 mg, 0.2 mmol, 1.0 equiv) in CH_2Cl_2 (1.0 mL). The yellow reaction mixture was stirred for 3.5 hours before concentrated *in vacuo*. The residue was coevaporated from pentane (5.0 mL) and extracted with toluene (10 x 3.0 mL). The combined liquid layers were concentrated *in vacuo* to a total volume of ca. 2 mL resulting in a liquid-liquid layer separation after storage at -32 °C overnight. The upper layer was dried *in vacuo* and the sticky residue was suspended in pentane (2.0 mL) resulting in precipitation of a yellow solid. The solution of the suspension was decanted, the residue was washed with pentane (2 x 1.0 mL) and dried *in vacuo* to give compound **14** [Ph_3PNPPh_3] as a yellow solid (48%, 100 mg, 0.10 mmol).

Melting point: 134 °C.

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ [ppm] = 7.63 (t, $^3J_{HH}$ = 7.0 Hz, 6H, C34-H), 7.49 (m, 12H, C32-H), 7.45 (m, 12H, C33-H), 7.28 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C7-H), 7.05 (d, $^3J_{HH}$ = 7.6 Hz, 1H, C4-H), 6.81 (dd, $^3J_{HH}$ = 7.5, 7.2 Hz, 1H, C6-H), 6.67 (dd, $^3J_{HH}$ = 7.6, 7.2 Hz, 1H, C5-H), 6.55 (s, 1H, C2-H), 3.07 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C8-H), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C9-H)^t, 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C10-H)^t [^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.63 / 7.45 (C34-H / C33-H), 7.49 / 7.45 (C32-H / C33-H), 7.28 / 6.81 (C7-H / C6-H), 7.05 / 6.67 (C4-H / C5-H), 6.81 / 6.67 (C6-H / C5-H), 3.07 / 1.28, 1.27 (C8-H / C9-H, C10-H).

^{1}H NOESY (500 MHz / 500 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 7.28 / 6.81, 3.07, 1.27 (C7-H / C6-H, C8-H, C10-H), 7.05 / 6.67 (C4-H / C5-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.63 / 134.1 (C34), 7.49 / 132.5 (C32), 7.45 / 129.8 (C33), 7.28 / 117.3 (C7), 7.05 / 120.4 (C4), 6.81 / 118.9 (C6), 6.67 / 119.3 (C5), 6.55 / 128.6 (C2), 3.07 / 27.3 (C8), 1.28, 1.27 / 23.5 (C9,10).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.63 / 132.5 (C34-H / C32), 7.49 / 134.1, 132.5 (C32-H / C34, C32), 7.45 / 129.8, 127.4 (C33-H / C33, C31), 7.28 / 143.0, 119.3 (C7-H / C3a, C5), 7.05 / 139.8, 118.9 (C4-H / C7a, C6), 6.81 / 139.8, 120.4 (C6-H / C7a, C4), 6.67 / 143.0, 117.3 (C5-H / C3a, C7), 6.55 / 143.0, 139.8, 133.8, 124.3 (C2-H / C3a, C7a, C1, C3), 3.07 / 133.8, 128.6, 23.5 (C8-H / C1, C2, C9,10), 1.28, 1.27 / 133.8, 27.3, 23.5 (C9-H, C10-H / C1, C8, C9/10).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ [ppm] = 143.0 (C3a), 139.8 (C7a), 134.1 (AA'X, C34), 133.8 (C1), 132.5 (AA'X, C32), 129.8 (AA'X, C33), 128.6 (C2), 127.4 (dd, $^{1}J_{PC}$ = 108 Hz, J = 1.9 Hz, C31), 124.3 (br, C3), 120.4 (C4), 119.3 (C5), 118.9 (C6), 117.3 (C7), 27.3 (C8), 23.5 (C9,10) [C_6F_5 not listed; ^{t} tentative assignment].

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ [ppm] = 30.3 ($\nu_{1/2} \approx 580$ Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ [ppm] = 21.0 ($\nu_{1/2} \approx 2$ Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ [ppm] = -131.5 (m, 2F, *o*-$C_6F_5^{b}$), -140.0 (m, 2F, *o*-$C_6F_5^{a}$), -161.1 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-$C_6F_5^{a}$), -161.2 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-$C_6F_5^{b}$), -165.5 (m, 2F, *m*-$C_6F_5^{a}$), -165.9 (m, 2F, *m*-$C_6F_5^{b}$) [$\Delta\delta^{19}F_{m,p}$ = 4.4^{a}, 4.7^{b}].

^{19}F, ^{19}F GCOSY (470 MHz / 470 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = -131.5 / -165.9 (*o*-$C_6F_5^{b}$ / *m*-$C_6F_5^{b}$), -140.0 / -165.5 (*o*-$C_6F_5^{a}$ / *m*-$C_6F_5^{a}$), -161.1 / -165.5 (*p*-$C_6F_5^{a}$ / *m*-$C_6F_5^{a}$), -161.2 / -165.9 (*p*-$C_6F_5^{b}$ / *m*-$C_6F_5^{b}$).

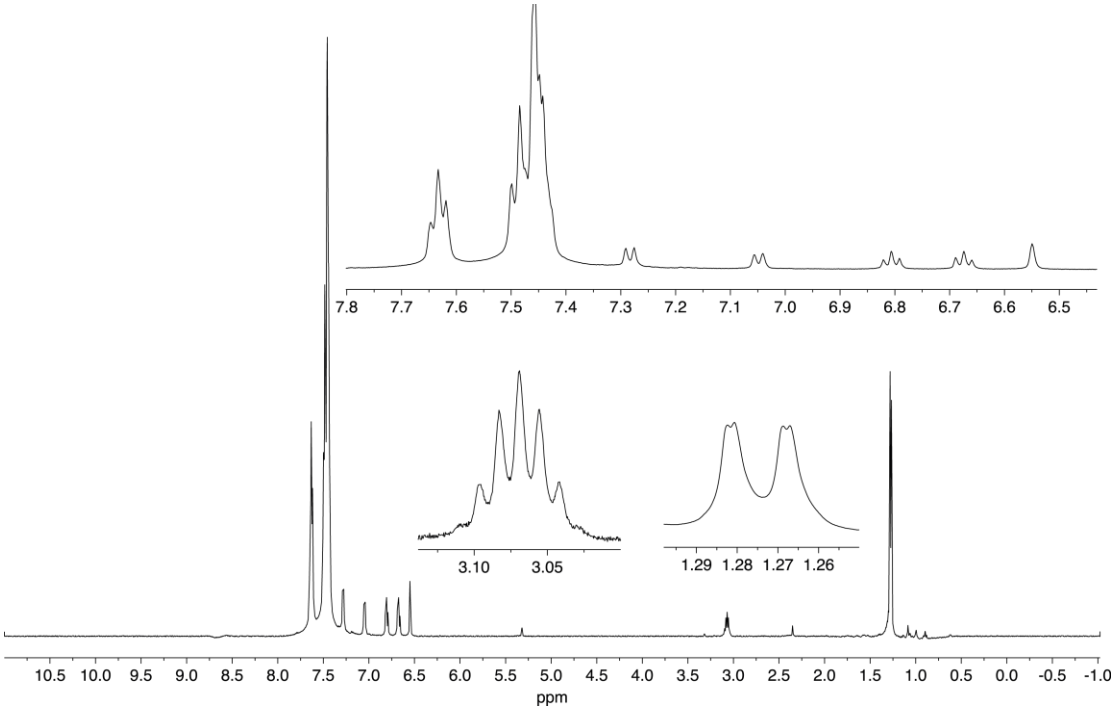


Figure S28 ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) of compound **14** [Ph_3PNPPh_3].

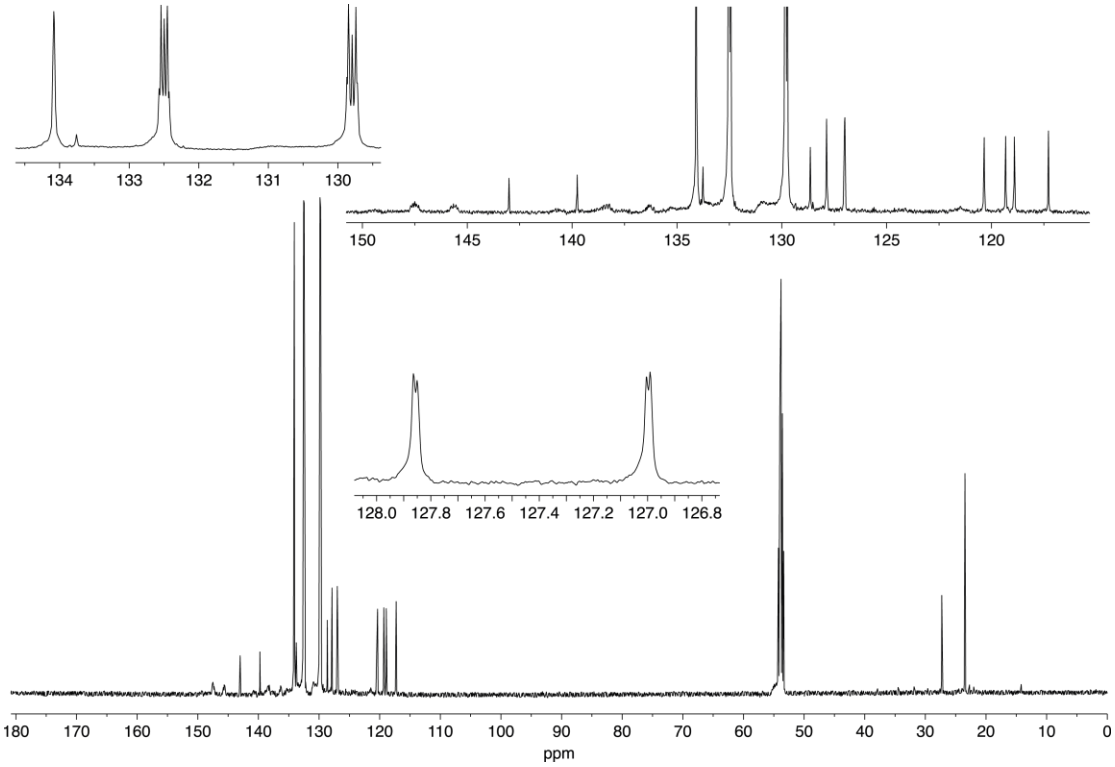


Figure S29 $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) of compound **14** [Ph_3PNPPh_3].

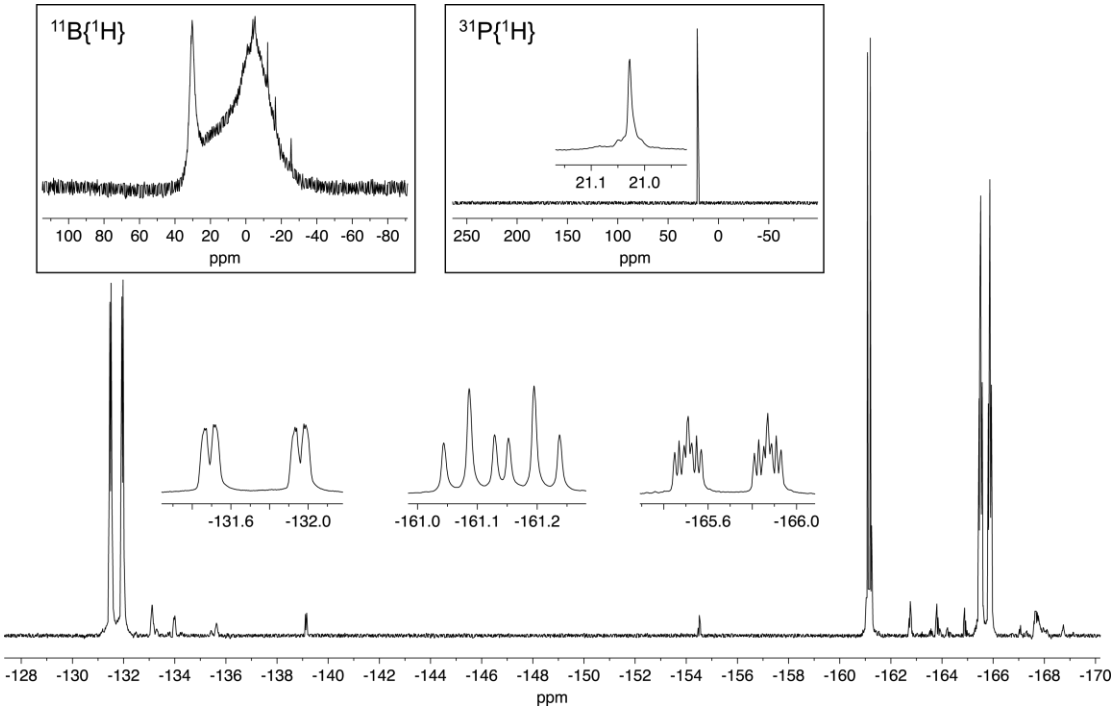
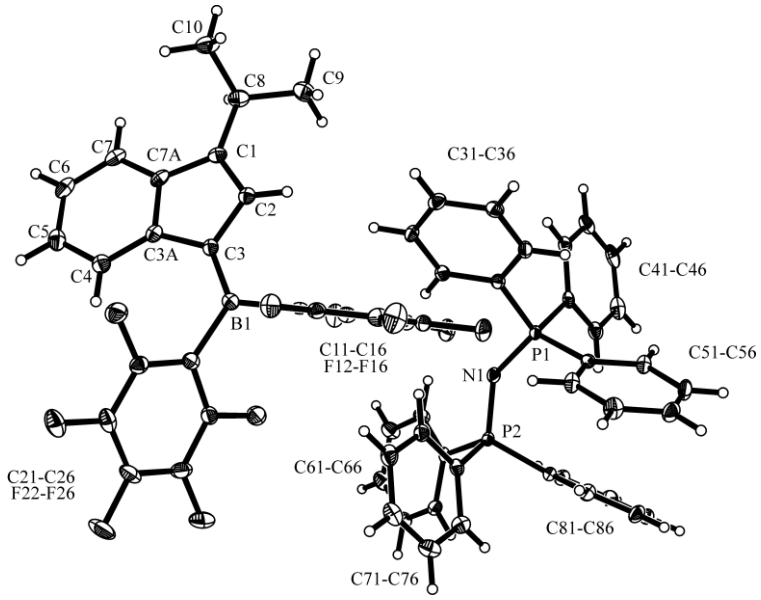


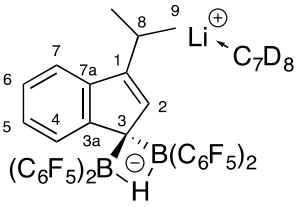
Figure S30 $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2), $^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2) and ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of compound **14** [Ph_3PNPPh_3].

Crystals suitable for the X-ray crystal structure analysis were obtained by diffusion of pentane into of a saturated solution of compound **14** [Ph_3PNPPh_3] in toluene at RT.

X-ray crystal structure analysis of compound 14 [Ph_3PNPPh_3]: A yellow plate-like specimen of $C_{60}H_{42}BF_{10}NP_2$, approximate dimensions 0.057 mm x 0.110 mm x 0.173 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1732 frames were collected. The total exposure time was 21.65 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 109452 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 10126 were independent (average redundancy 10.809, completeness = 99.9%, R_{int} = 6.63%, R_{sig} = 2.99%) and 8374 (82.70%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.8291(3) Å, b = 27.4015(7) Å, c = 18.7176(6) Å, β = 100.5170(10)°, volume = 4956.6(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9921 reflections above 20 σ(I) with 5.106° < 2θ < 55.07°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.950. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9720 and 0.9910. The final anisotropic full-matrix least-squares refinement on F^2 with 669 variables converged at R1 = 4.10%, for the observed data and wR2 = 9.01% for all data. The goodness-of-fit was 1.077. The largest peak in the final difference electron density synthesis was 0.368 $e^-/Å^3$ and the largest hole was -0.366 $e^-/Å^3$ with an RMS deviation of 0.053 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.393 g/cm^3 and F(000), 2136 e^-.



Compound 15a [LiC_7D_8]



15a [LiC_7D_8]

Compound **14** [LiHTMP] (32.5 mg, 0.05 mmol, 1.0 equiv) was dissolved in toluene-d_8 (0.8 mL) and added to a suspension of $HB(C_6F_5)_2$ (17.3 mg, 0.05 mmol, 1.0 equiv) in toluene-d_8 (0.2 mL) at RT. Within 5 minutes a clear yellow solution was obtained. *In situ* NMR studies revealed the formation of two species in a ratio of approximately 2 : 3. Upon standing for 1 day at RT colorless crystals were obtained to give compound **15a** [LiC_7D_8] in 34% yield (16.1 mg, 0.02 mmol). The crystals were suitable for the X-ray crystal structure analysis and used in the following characterization of compound **15a** [LiC_7D_8].

Melting point: 94 °C.

Elemental analysis: calc. for $C_{43}H_{21}B_2F_{20}Li$ (954.22g mol^{-1}): C, 54.59; H, 2.24; Found: C, 54.48; H, 2.58.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ [ppm] = 7.75 (dt, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, C7-H), 7.38 (ddd, $^3J_{HH}$ = 8.0, 7.1 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, C6-H), 6.95 (ddd, $^3J_{HH}$ = 8.1, 7.1 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, C5-H), 6.52 (s, 1H, C2-H), 6.04 (dt, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, C4-H), 3.92 (br, 1H, B1-H-B2), 3.22 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, C8-H), 1.36 (d, $^3J_{HH}$ = 6.8 Hz, 6H, C9-H).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.75 / 7.38 (C7-H / C6-H), 7.38 / 6.95 (C6-H / C5-H), 6.95 / 6.04 (C5-H / C4-H), 3.22 / 1.36 (C8-H / C9-H).

^{1}H NOESY (600 MHz / 600 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 1.36 / 7.75, 6.52, 3.22 (C9-H / C7-H, C2-H, C8-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^1H [ppm] / δ^{13}C [ppm] = 7.75 / 121.9 (C7), 7.38 / 125.8 (C6), 6.95 / 125.2 (C5), 6.52 / 140.4 (C2), 6.04 / 123.8 (C4), 3.22 / 27.2 (C8), 1.36 / 22.5 (C9).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^1H [ppm] / δ^{13}C [ppm] = 7.75 / 148.1, 125.2 (C7-H / C3a, C5), 7.38 / 138.4, 123.8 (C6-H / C7a, C4), 6.95 / 148.1, 121.9 (C5-H / C3a, C7), 6.52 / 148.1, 141.6, 138.4, 40.8 (C2-H / C3a, C1, C7a, C3), 6.04 / 138.4, 125.8 (C4-H / C7a, C6), 3.22 / 141.6, 140.4, 22.5 (C8-H / C1, C2, C9), 1.36 / 141.6, 27.2, 22.5 (C9-H / C1, C8, C9).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ^{13}C [ppm] = 148.1 (C3a), 141.6 (C1), 140.4 (C2), 138.4 (C7a), 125.8 (C6), 125.2 (C5), 123.8 (C4), 121.9 (C7), 40.8 (br, C3), 27.2 (C8), 22.5 (br, C9) [C_6F_5 not listed].

^{7}Li NMR (233 MHz, 299 K, CD_2Cl_2): δ [ppm] = -4.0 ($\nu_{1/2} \approx 30$ Hz).

^{7}Li NMR (233 MHz, 195 K, CD_2Cl_2): δ [ppm] = -4.2 (dd, $^1J_{LiF}$ = 41.4, 35.7 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ [ppm] = -15.8, -17.1 ($\nu_{1/2} \approx 300$ Hz).

^{19}F NMR (564 MHz, 195 K, CD_2Cl_2): δ [ppm] = -126.0 (1F), -127.3 (2F), -128.1 (1F), -130.2 (2F), -146.6 (2F)(each br m, *o*-C_6F_5), -153.6 (t, $^3J_{FF}$ = 20.4 Hz), -154.1 (t, $^3J_{FF}$ = 18.3 Hz), -156.5 (t, $^3J_{FF}$ = 21.4 Hz), -156.7 (t, $^3J_{FF}$ = 21.2 Hz)(each 1F, *p*-C_6F_5), -158.6 (1F), -158.9 (1F), -161.4 (2F), -163.4 (1F), -163.9 (2F), -164.1 (1F)(each br m, *m*-C_6F_5).

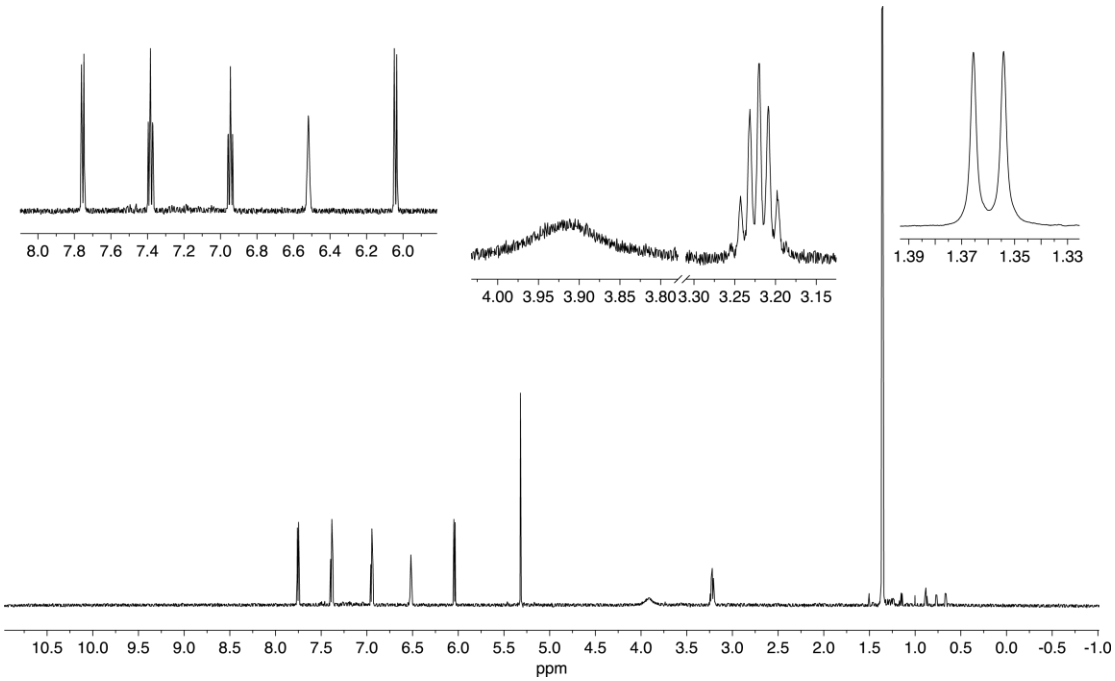


Figure S31 ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of crystalline compound **15a** [LiC_7D_8].

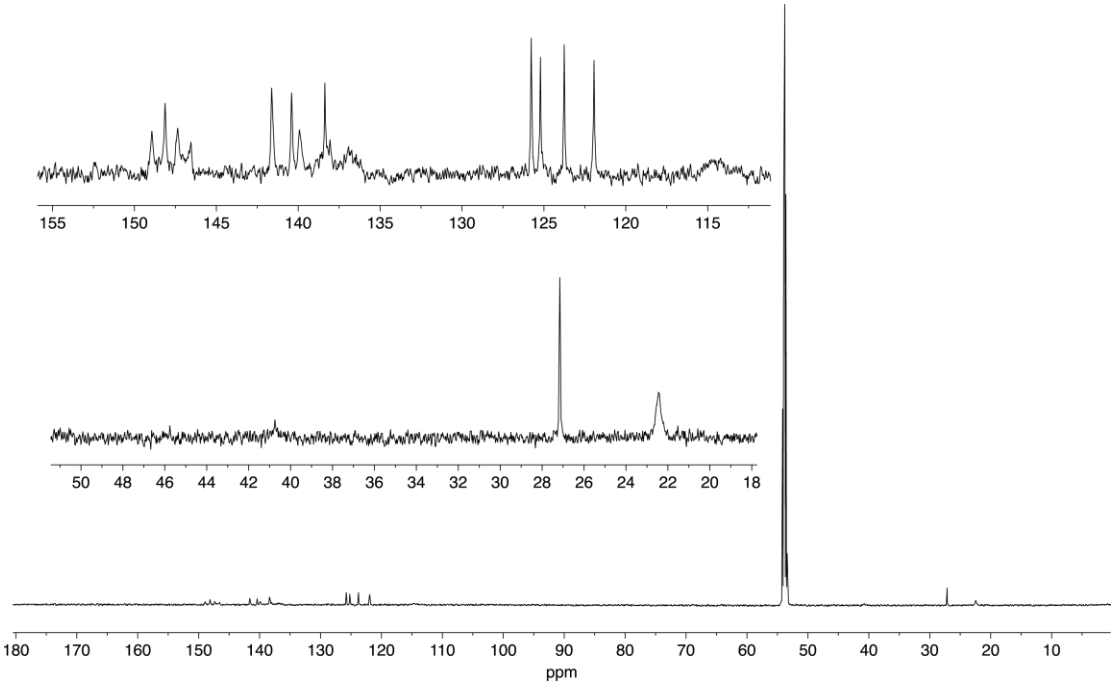


Figure S32 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) of crystalline compound **15a** [LiC_7D_8].

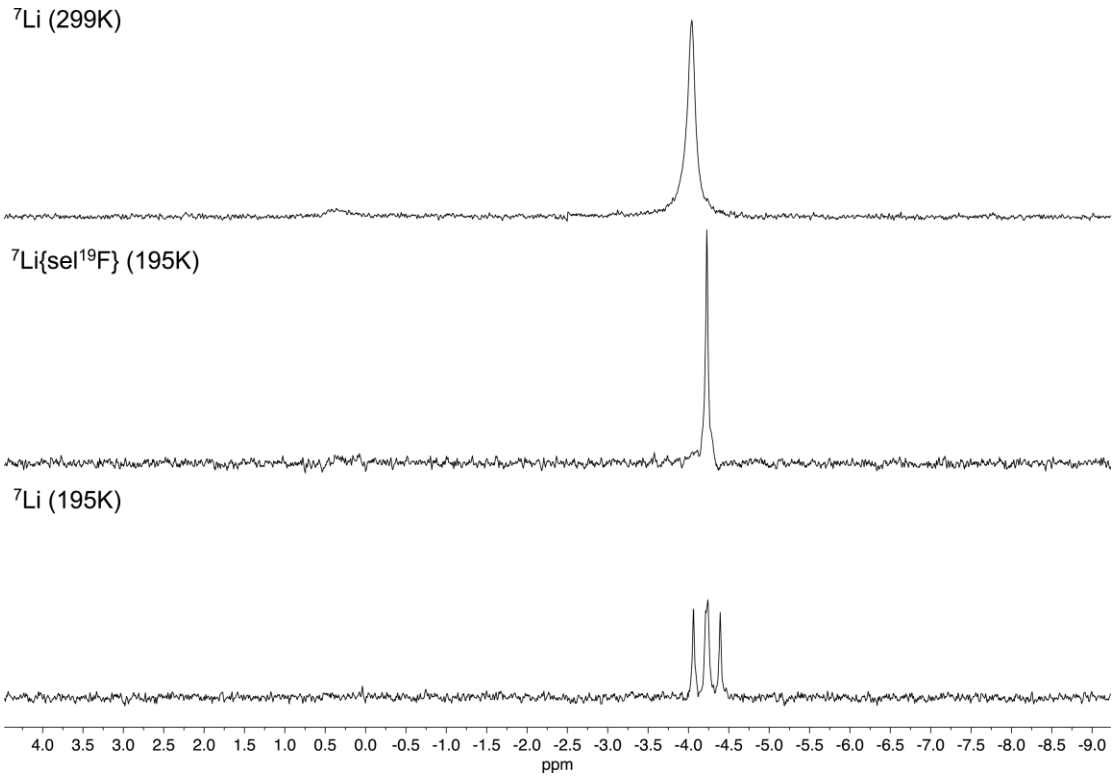


Figure S33 ^{7}Li NMR (233 MHz, CD_2Cl_2): 299 K (above), 195 K (below) and ^{7}Li{sel^{19}F: δ [ppm] = -146.6} NMR (233 MHz, 195 K, CD_2Cl_2) (middle) of crystalline compound **15a** [LiC_7D_8].

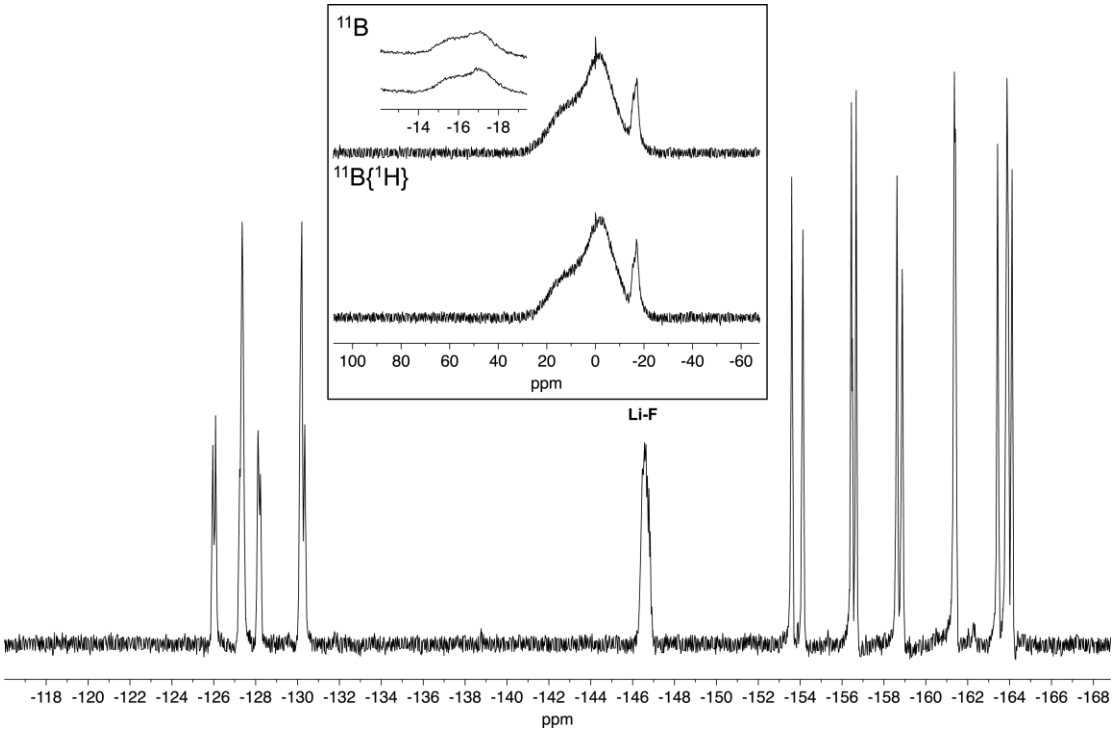
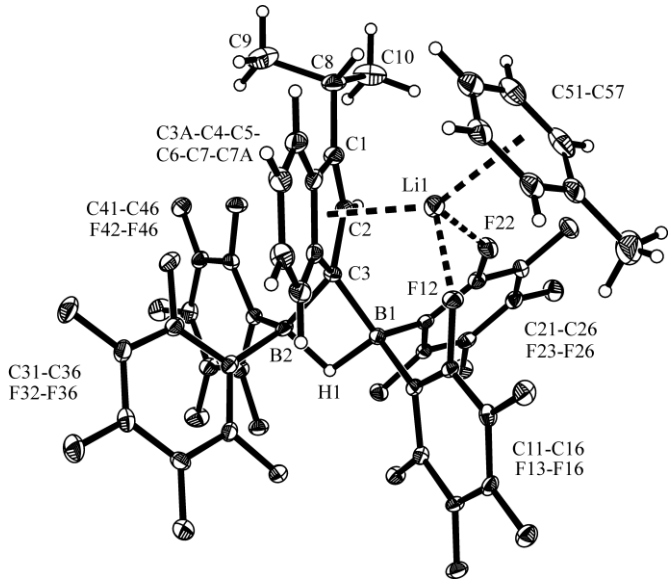
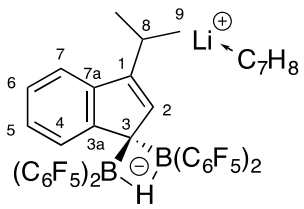


Figure S34 ^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2) and ^{19}F NMR (574 MHz, 195 K, CD_2Cl_2) of crystalline compound **15a** [LiC_7D_8].

X-ray crystal structure analysis of compound 15a: A colorless prism-like specimen of $C_{43}H_{21}B_2F_{20}Li$, approximate dimensions 0.100 mm x 0.160 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2128 frames were collected. The total exposure time was 14.27 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 29810 reflections to a maximum θ angle of 62.58° (0.87 Å resolution), of which 6061 were independent (average redundancy 4.918, completeness = 97.3%, R_{int} = 7.72%, R_{sig} = 5.47%) and 4420 (72.93%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.4396(4) Å, b = 10.5005(4) Å, c = 19.6063(7) Å, α = 91.665(2)°, β = 101.678(2)°, γ = 111.232(2)°, volume = 1949.53(13) $Å^3$, are based upon the refinement of the XYZ-centroids of 4534 reflections above 20 σ(I) with 9.092° < 2θ < 124.7°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.831. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7830 and 0.8700. The final anisotropic full-matrix least-squares refinement on F^2 with 602 variables converged at R1 = 4.71%, for the observed data and wR2 = 12.74% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.557 $e^-/Å^3$ and the largest hole was -0.307 $e^-/Å^3$ with an RMS deviation of 0.060 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.612 g/cm^3 and F(000), 944 e^-. The hydrogen at N1 atom was refined freely; others were calculated and refined as riding atoms.



1st Step: **Compound 15a** [LiC_7H_8]



15a [LiC_7H_8]

Compound **14** [LiHTMP] (64.9 mg, 0.10 mmol, 1.0 equiv) was dissolved in toluene (1.8 mL) and added to a suspension of $HB(C_6F_5)_2$ (34.6 mg, 0.10 mmol, 1.0 equiv) in toluene (0.2 mL) at RT. Within 5 minutes a clear yellow solution was obtained. A white powder precipitated from the reaction mixture upon standing for 1 day at RT. The white solid was washed with pentane (2 x 0.5 mL) and dried *in vacuo* to give compound **15a** in 44% yield (41.2 mg, 0.04 mmol).

The obtained filtrate was used for further workup (see 2nd Step below).

The NMR data of the obtained white powder in CD_2Cl_2 are consistent to those listed for compound **15a** [LiC_7D_8] (see above). Comment: ratio **15a** : toluene ca. 3 : 2.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ [ppm] = 7.24 (t, $^3J_{HH}$ = 7.2 Hz, 2H, *m*-tol), 7.18 (d, $^3J_{HH}$ = 7.2 Hz, 2H, *o*-tol), 7.14 (t, 7.3 Hz, 1H, *p*-tol), 2.34 (s, 3H, Me-tol).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.24 / 7.14 (*m*-tol-H / *p*-tol-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.24 / 128.5 (*m*-tol), 7.18 / 129.4 (*o*-tol), 7.14 / 125.6 (*p*-tol), 2.34 / 21.5 (Me-tol).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 2.34 / 138.4, 129.4, (tol-Me-H / ^{ipso}C-tol, *o*-tol).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ^{13}C [ppm] = 138.4 (C7a, ^{ipso}C-tol), 129.4 (*o*-tol), 128.5 (*m*-tol), 125.6 (*p*-tol), 21.5 (Me-tol).

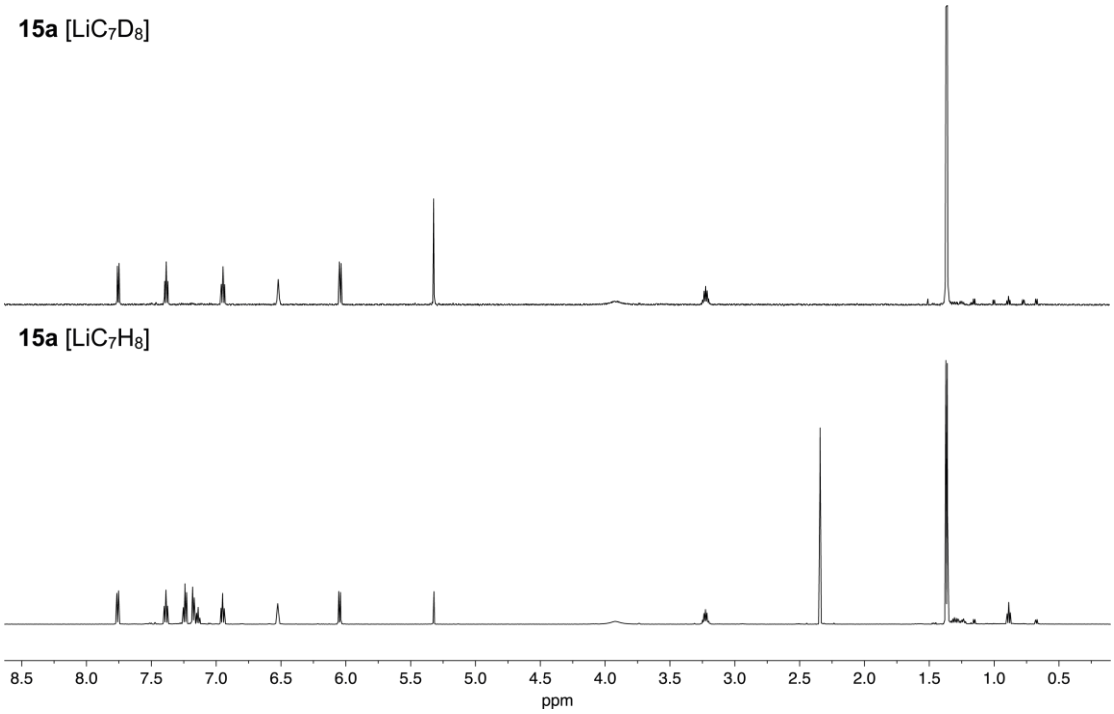


Figure S35 Stacked ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of compounds **15a** [LiC_7D_8] (above) and **15a** [LiC_7H_8] (below).

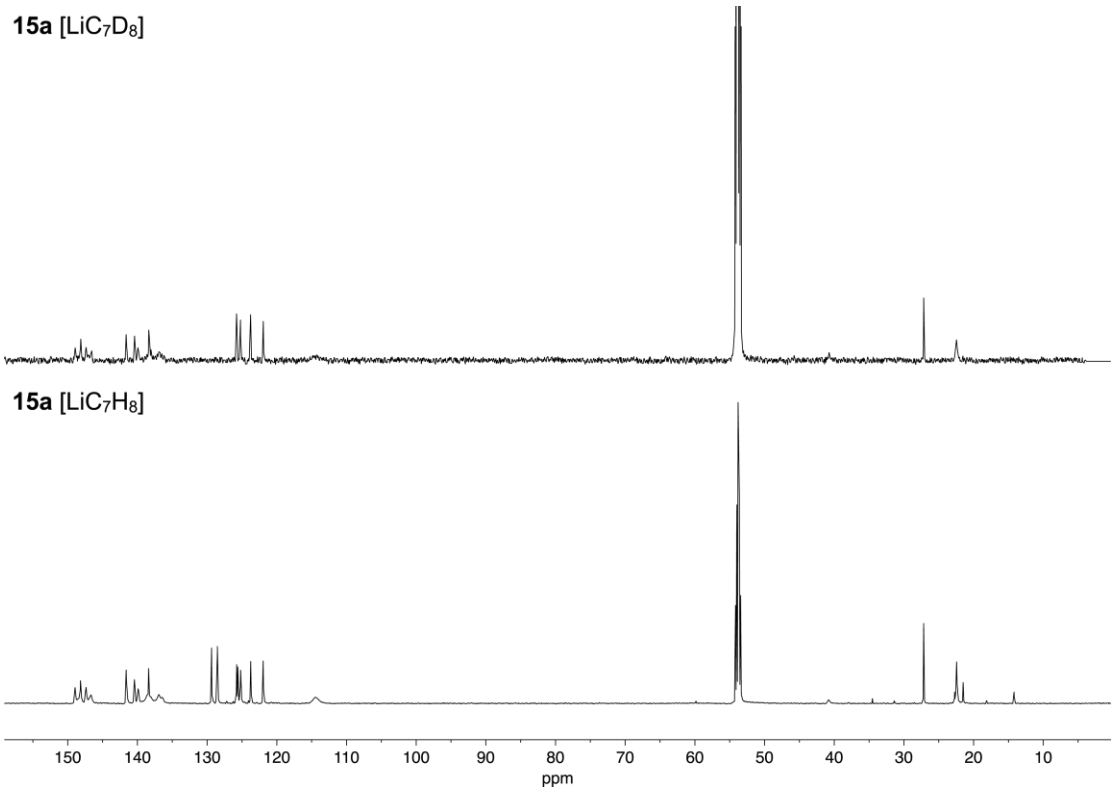
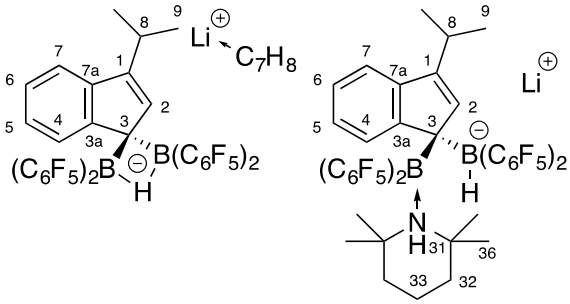


Figure S36 Stacked $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) compounds **15a** [LiC_7D_8] (above) and **15a** [LiC_7H_8] (below).

2nd Step: **Compounds 15a** [LiC_7H_8], **15b** [LiHTMP]



15a [LiC_7H_8] **15b** [LiHTMP]

All volatiles of the filtrate were removed in vacuo to give a yellow solid which was washed with pentane (2 x 0.5 mL) and dried in vacuo (11.7 mg, 0.02 mmol, 33%). The solution of the yellow solid in CD_2Cl_2 showed a ca. 1:1 mixture of **15a** [LiC_7H_8] and **15b** [LiHTMP].

The NMR data of compound **15a** [LiC_7H_8] of the mixture in CD_2Cl_2 are consistent to those given in the 1st Step (see above).

The NMR data of compound **15b** [LiHTMP] of the mixture in CD_2Cl_2 are consistent to those listed after reaction of compound **14** [LiHTMP] with $HB(C_6F_5)_2$ in the presence of an additional equivalent of HTMP (see below).

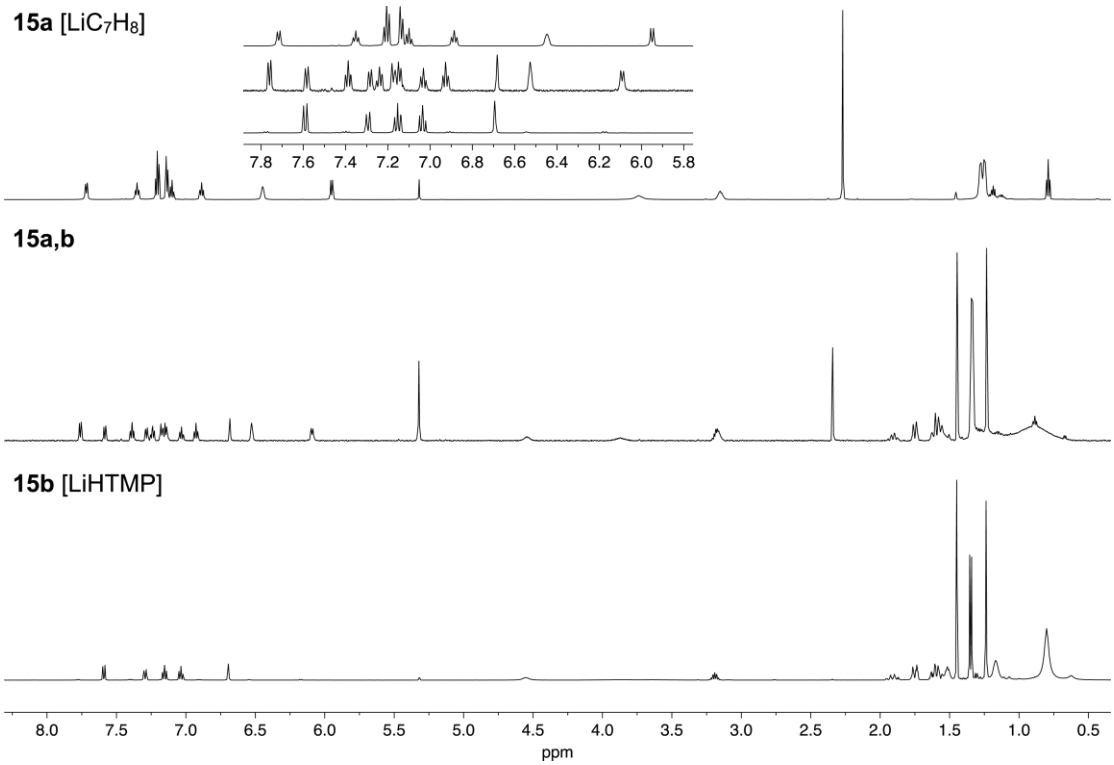
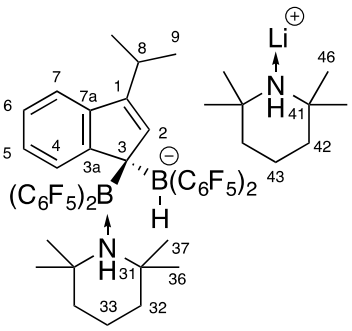


Figure S37 Stacked ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of compounds **15**: compound **15a** [LiC_7H_8] (above, 1st Step), compounds **15a** [LiC_7H_8], **15b** [LiHTMP] (middle, 2nd Step) and compound **15b** [LiHTMP] (below, additional equivalent of HTMP added).

Compound 15b [LiHTMP]



15b [LiHTMP]

Compound **14** [LiHTMP] (32.5 mg, 0.05 mmol, 1.0 equiv) was dissolved in CD_2Cl_2 (0.7 mL) and added to a suspension of $HB(C_6F_5)_2$ (17.3 mg, 0.05 mmol, 1.0 equiv) in CD_2Cl_2 (0.3 mL) at RT. The yellow solution was added to HTMP (14.1 mg, 0.05 mmol, 1.0 equiv) after standing for additional 30 minutes. The yellow solution was characterized by NMR experiments showing compound **15b** [LiHTMP].

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ [ppm] = 7.59 (dt, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.0 Hz, 1H, C7-H), 7.29 (dt, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.0 Hz, 1H, C4-H), 7.15 (ddd, $^{3}J_{HH}$ = 8.0, 7.0 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, C6-H), 7.04 (ddd, $^{3}J_{HH}$ = 8.1, 7.0 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, C5-H), 6.69 (d, $^{4}J_{HH}$ = 1.2 Hz, 1H, C2-H), 4.55 (br, 1H, B-H)^{t}, 3.75 (br m, 1H, N^{B}-H)^{t}, 3.19 (septd, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, C8-H), 1.91, 1.61 (each m, each 1H, C33-H), 1.75, 1.58 (each m, each 2H, C32-H), 1.51 (br t, $^{3}J_{HH}$ = 5.9 Hz, 2H, C43-H), 1.45, 1.24 (each s, each 6H, C36,37-H), 1.35 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, C9-H), 1.17 (br s, 4H, C42-H)^{t}, 0.80 (br s, 12H, C46-H)^{t}, 0.62 (br s, 1H, N^{Li}-H)^{t}. [^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, CD_2Cl_2): δ [ppm] / δ [ppm] = 7.59 / 7.15 (C7-H / C6-H), 7.29 / 7.04 (C4-H / C5-H), 7.15 / 7.04 (C6-H / C5-H), 3.19 / 1.35 (C8-H / C9-H), 1.91 / 1.75, 1.61 (C33-H / C32-H, C33-H), 1.75 / 1.58 (C32-H / C32-H), 1.58 / 1.45 (C32-H / C36-H), 1.51 / 1.17 (C43-H / C42-H), 1.45 / 1.24 (C36-H / C37-H).

^{1}H NOESY (500 MHz / 500 MHz, 299 K, CD_2Cl_2) [selected traces]: δ [ppm] / δ [ppm] = 3.19 / 7.59 (C8-H / C7-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.59 / 120.5 (C7), 7.29 / 122.9 (C4), 7.15 / 123.3 (C6), 7.04 / 123.8 (C4), 6.69 / 124.4 (C2), 3.19 / 27.2 (C8), 1.91 / 16.8 (C33), 1.75 / 42.7 (C32), 1.61 / 16.7 (C33), 1.58 / 42.7 (C32), 1.51 / 17.7 (C43), 1.45 / 21.6 (C36), 1.35 / 23.0 (C9), 1.24 / 33.0 (C37), 1.17 / 37.9 (C42).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.59 / 136.8, 123.8 (C7-H / C3a, C5), 7.29 / 136.1, 123.3 (C4-H / C7a, C6), 7.15 / 136.1, 122.9 (C6-H / C7a, C4), 7.04 / 136.8, 120.5 (C5-H / C3a, C7), 6.69 / 136.8, 136.0, 115.3, 27.2 (C2-H / C1/3a, C7a, C^{ipso}, C8), 3.19 / 136.8, 124.4, 23.0 (C8-H / C1, C2, C9), 1.91 / 42.7 (C33-H / C32), 1.75 / 16.8 (C32-H / C33), 1.58 / 62.8, 21.6 (C32-H / C31, C36), 1.51 / 51.0, 37.9 (C43-H / C41, C42), 1.45 / 62.8, 42.7, 33.0 (C36-H / C31, C32, C37), 1.35 / 136.8, 27.2, 23.0 (C9-H / C1, C8, C9), 1.24 / 62.8, 42.7, 21.6 (C37-H / C31, C32, C36).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ^{13}C [ppm] = 136.8 (C1), 136.8 (C3a), 136.1 (C7a), 124.4 (C2), 123.8 (C5), 123.3 (C6), 122.9 (C4), 120.5 (C7), 115.3 (br, C3), 62.8 (C31), 51.0 (C41), 42.7 (C32), 37.9 (C42), 33.0 (C37), 31.0 (br, C46)^{t}, 27.2 (C8), 23.0 (C9), 21.6 (C36), 17.7 (C43), 16.8 (C33) [C_6F_5 not listed, ^{t} tentative assignment].

^{7}Li NMR (194 MHz, 299 K, CD_2Cl_2): δ [ppm] = -4.5 ($\nu_{1/2} \approx 50$ Hz).

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ [ppm] = 37.9 ($\nu_{1/2} \approx 90$ Hz, B^N), -13.4 ($\nu_{1/2} \approx 90$ Hz, B^H).

^{11}B NMR (160 MHz, 299 K, CD_2Cl_2): δ [ppm] = 37.9 ($\nu_{1/2} \approx 90$ Hz, 1B, B^N), -13.4 (d, $^{1}J_{BH} \sim 100$ Hz, 1B, B^H).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ [ppm] = -130.1 (br, 2F, *o*-$C_6F_5^{c}$), -132.7 (br, 2F, *o*-$C_6F_5^{d}$)^{t}, -132.9 (br, 4F, *o*-$C_6F_5^{a,b}$), -156.6 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*-$C_6F_5^{a}$), -156.6 (t, $^{3}J_{FF}$ = 19.9 Hz, 1F, *p*-$C_6F_5^{b}$), -159.4 (t, $^{3}J_{FF}$ = 20.2 Hz, 2F, *p*-$C_6F_5^{c,d}$), -163.4 (m, 4F, *m*-$C_6F_5^{a,b}$), -164.3 (br, 2F, *m*-$C_6F_5^{c}$), -165.3 (br, 2F, *m*-$C_6F_5^{d}$) [$\Delta\delta^{19}F_{m,p}$ = 6.8^{a}, 6.7^{b}, 4.8^{c}, 5.9^{d}].

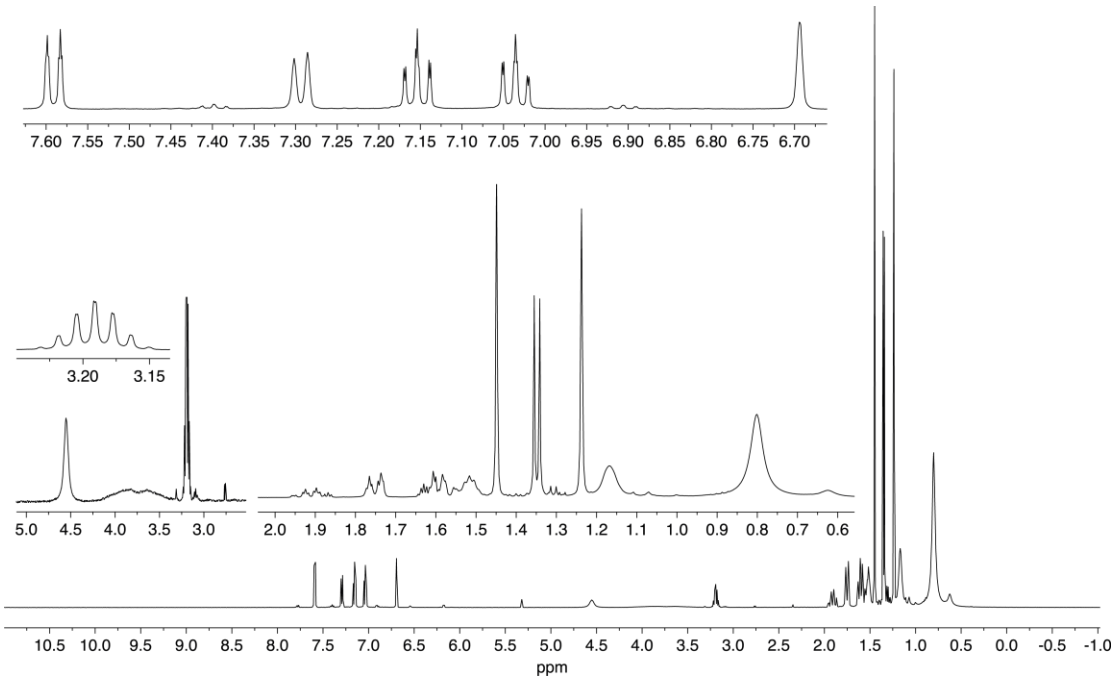


Figure S38 ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) of compound **15b** [LiHTMP].

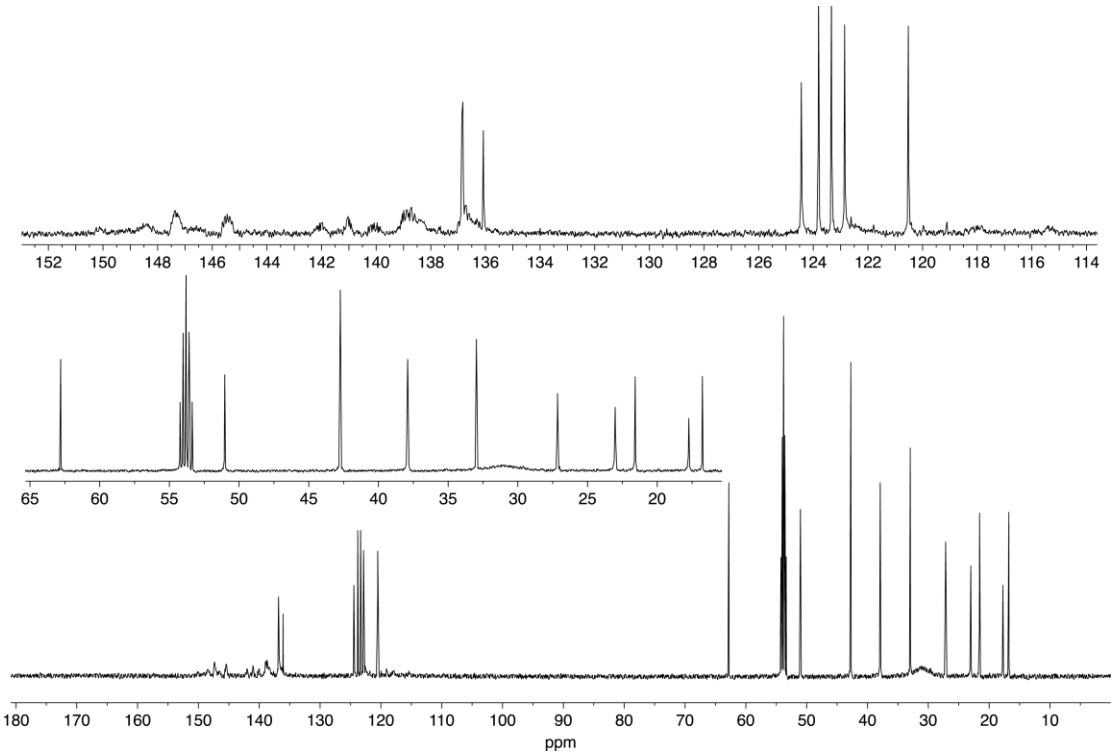


Figure S39 $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) of compound **15b** [LiHTMP].

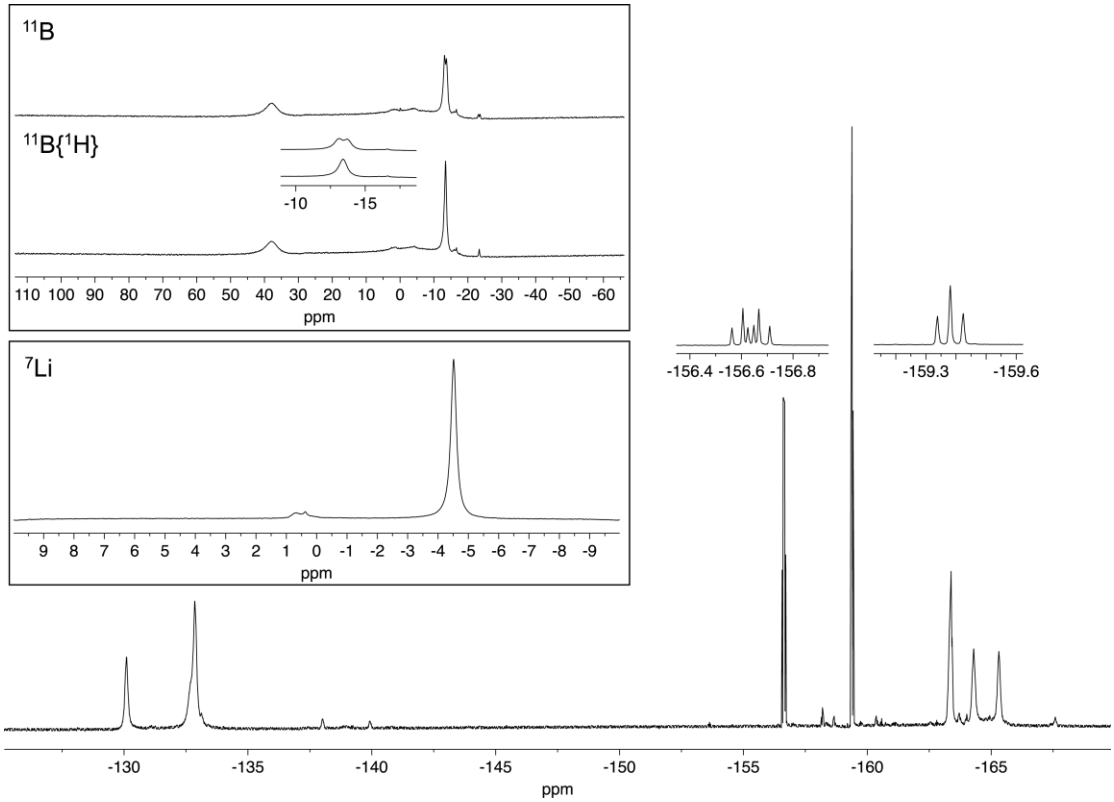
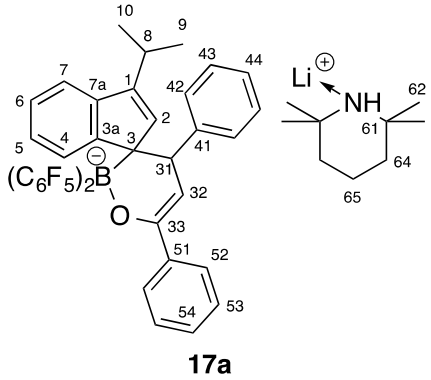


Figure S40 ^{11}B NMR (160 MHz, 299 K, CD_2Cl_2), $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, CD_2Cl_2), ^{7}Li NMR (194 MHz, 299 K, CD_2Cl_2) and ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of compound **15b** [LiHTMP].

Compound 17a



17a

Compound **14** [LiHTMP] (32.5 mg, 0.05 mmol, 1.0 equiv) was dissolved in toluene-d_8 (0.8 mL) and added to a solution of (*E*)-chalcone (**16a**) (10.4 mg, 0.05 mmol, 1.0 equiv) in toluene-d_8 (0.2 mL). An instantaneous colour change towards dark red was observed. The red colour faded during the course of 30 minutes. All volatiles were removed by slow evaporation at normal pressure to give compound **17a** as a white solid (37.3 mg, 0.04 mmol, 87%). Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated solution of compound **17a** in pentane.

IR (KBr, selective wavenumbers): $\tilde{\nu}$ [cm^{-1}] = 3254 (w, NH).

Decomp.: 173 °C.

Elemental analysis: calc. for $C_{48}H_{43}BF_{10}LiNO$ (857.61 g mol^{-1}): C, 67.22; H, 5.05; N, 1.63; Found: C, 67.22; H, 4.59; N (corr), 1.54.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ [ppm] = 7.86 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, C4-H), 7.44 (m, 2H, C52-H), 7.31 (m, 2H, C42-H), 7.30 (s, 1H, C2-H), 7.08 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, C5-H), 7.00 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, C6-H), 6.99 (m, 2H, C53-H), 6.96 (m, 2H, C43-H), 6.92 (m, 1H, C54-H), 6.83 (m, 1H, C44-H), 6.79 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, C7-H), 5.69 (d, $^{3}J_{HH}$ = 2.6 Hz, 1H, C32-H), 5.23 (s, 1H, C31-H), 2.59 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, C8-H), 1.25 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, C10-H)^{t}, 1.23 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, C9-H)^{t}, 1.15 (br, 2H, C65-H), 0.86 (br, 4H, C64-H), 0.74 (br, 12H, C62-H), 0.01 (br, 1H, NH) [^{t} tentative assignment]

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, C_6D_6): δ [ppm] / δ [ppm] = 7.86 / 7.08 (C4-H / C5-H), 7.44 / 6.99 (C52-H / C53-H), 7.30 / 6.96 (C42-H / C43-H), 7.08 / 7.00 (C5-H / C6-H), 7.00 / 6.79 (C6-H / C7-H), 5.69 / 5.23 (C32-H / C31-H), 2.59 / 1.23 (C8-H / C10,9-H).

^{1}H NOESY (500 MHz / 500 MHz, 299 K, C_6D_6) [selected traces]: δ [ppm] / δ [ppm] = 6.79 / 2.59, 1.25 (C7-H / C8-H, C10-H), 5.69 / 7.44, 7.31 (C32-H / C52-H, C42-H), 5.23 / 7.31 (C31-H / C42-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.86 / 125.0 (C4), 7.44 / 126.7 (C52), 7.31 / 129.1 (C42), 7.30 / 138.1 (C2), 7.08 / 122.0 (C5), 7.00 / 124.8 (C6), 6.99 / 129.8 (C53), 6.96 / 126.6 (C43), 6.92 / 128.7 (C54), 6.83 / 125.9 (C44), 6.79 / 118.5 (C7), 5.69 / 112.3 (C32), 5.23 / 44.2 (C31), 2.59 / 26.8 (C8), 1.25 / 21.9 (C10), 1.23 / 22.3 (C9), 1.15 / 17.7 (C65), 0.86 / 37.8 (C64), 0.74 / 31.0 (C62).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_6D_6): δ^{1}H [ppm] / δ^{13}C [ppm] = 7.86 / 145.7, 124.8 (C4-H / C7a, C6), 7.44 / 128.7 (C52-H / C54), 7.31 / 129.1, 125.9 (C42-H / C42, C44), 7.30 / 152.3, 145.7, 54.3, 44.2 (C2-H / C3a, C7a, C3, C31), 7.08 / 152.3, 118.5 (C5-H / C3a, C7), 7.00 / 145.7, 125.0 (C6-H / C7a, C4), 6.99 / 140.7, 129.8 (C53-H / C51, C53), 6.96 / 142.3, 126.6 (C43-H / C41, C43), 6.92 / 126.7 (C54-H / C52), 6.83 / 129.1 (C44-H / C42), 6.79 / 152.3, 122.0 (C7-H / C3a, C5), 5.69 / 151.2 (C32-H / C33), 5.23 / 152.3, 151.2, 142.3, 129.1, 112.3 (C31-H / C3a, C33, C41, C42, C32), 2.59 / 146.4, 138.1, 22.3, 21.9 (C8-H / C1, C2, C9, C10), 1.25 / 146.4, 26.8, 22.3 (C10-H / C1, C8, C9), 1.23 / 146.4, 26.8, 21.9 (C9-H / C1, C8, C10).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ^{13}C [ppm] = 152.3 (C3a), 151.2 (C33), 146.4 (C1), 145.7 (C7a), 142.3 (C41), 140.7 (C51), 138.1 (C2), 129.8 (C53), 129.1 (C42), 128.7 (C54), 126.7 (C52), 126.6 (C43), 125.9 (C44), 125.0 (C4), 124.8 (C6), 122.0 (C5), 118.5 (C7), 112.3 (br, C32), 54.3 (br, C3)^{t}, 50.9 (br, C61)^{t}, 44.2 (C31), 37.8 (C64), 31.0 (br, C62), 26.8 (C8), 22.3 (C9), 21.9 (C10), 17.7 (br, C65) [C_6F_5 not listed; ^{t} tentative assignment].

^{7}Li NMR (194 MHz, 299 K, C_6D_6): δ [ppm] = 0.3 (d, $^{1}J_{LiF}$ = 30.9 Hz)

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ [ppm] = 1.9 ($\nu_{1/2} \approx 200$ Hz).

^{19}F NMR (470 MHz, 223 K, CD_2Cl_2): δ [ppm] = -126.1, -126.4 (each m), -134.3, -150.0 (each br)(each 1F, *o*-C_6F_5), -159.8, -159.9 (each t, $^{3}J_{FF}$ = 21.0 Hz, each 1F, *p*-C_6F_5), -162.2, -164.1, -164.3, -165.9 (each br m, each 1F, *m*-C_6F_5).

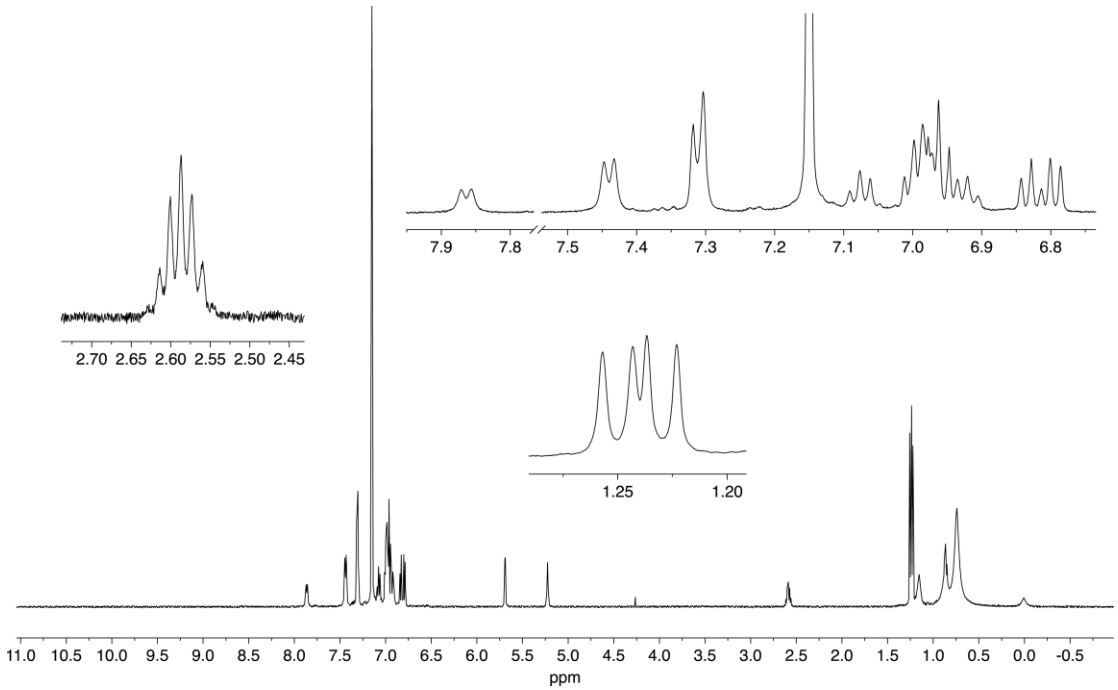


Figure S41 ^{1}H NMR (500 MHz, 299 K, C_6D_6) of crystalline compound **17a**.

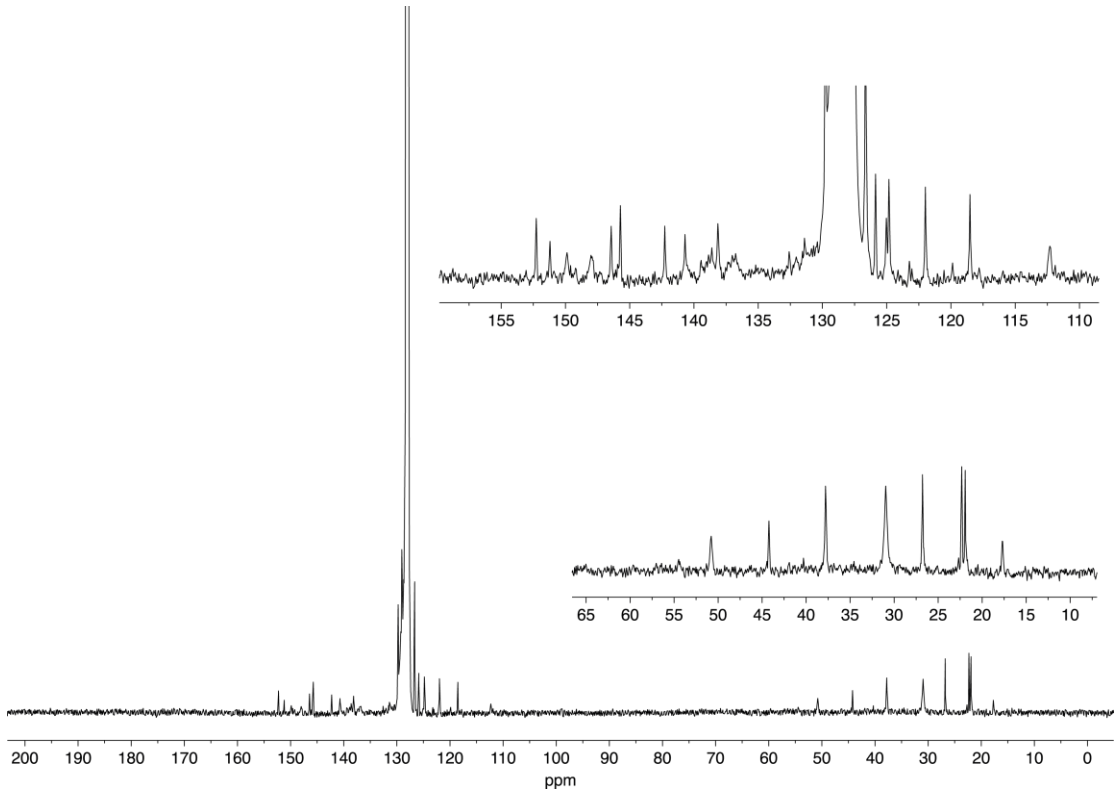


Figure S42 $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6) of crystalline compound **17a**.

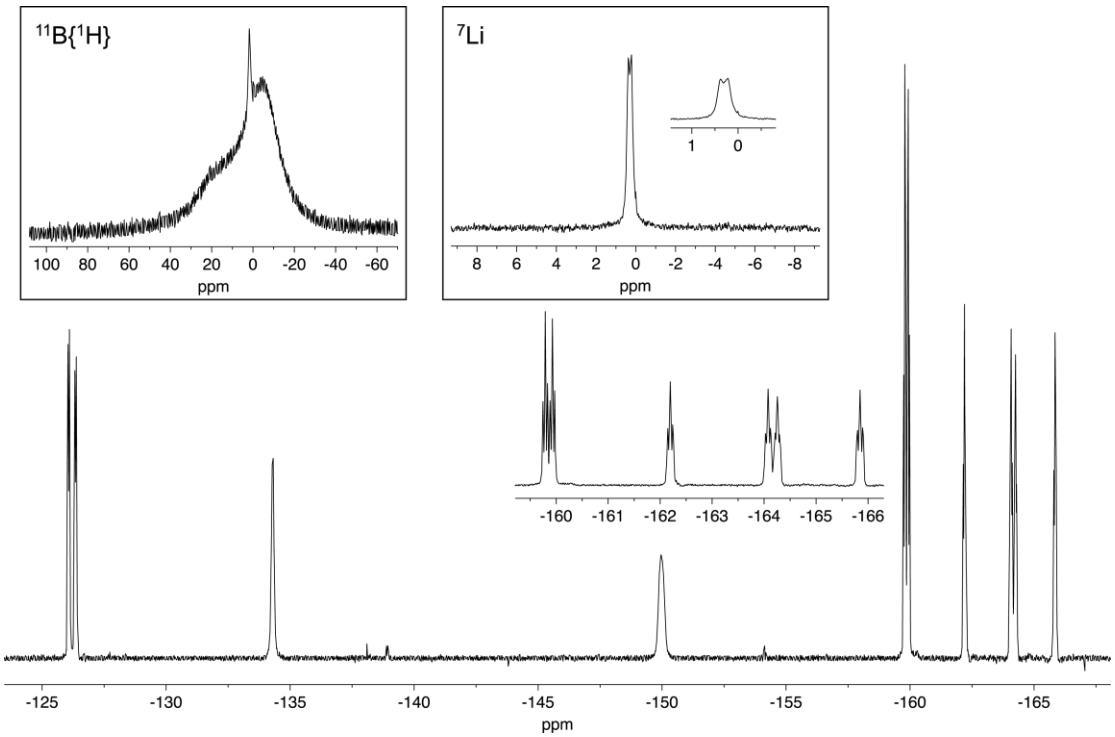
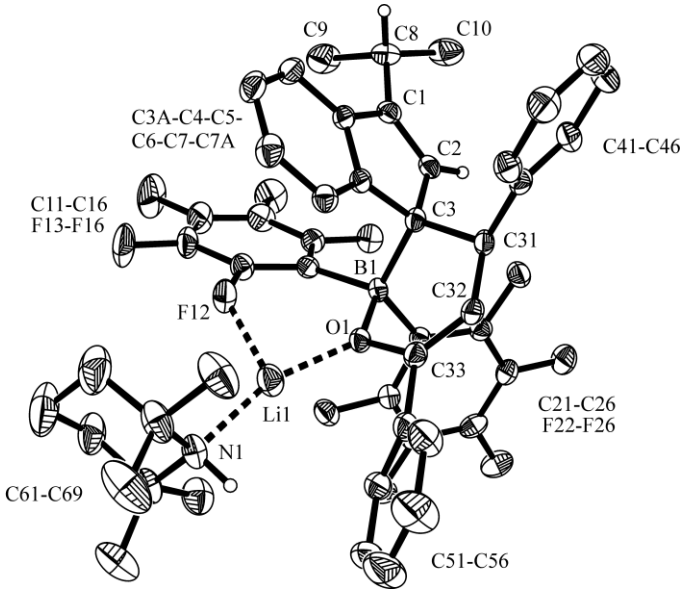


Figure S43 ^{7}Li NMR (194 MHz, 299 K, C_6D_6), $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6) and ^{19}F NMR (470 MHz, 223 K, CD_2Cl_2) of crystalline compound **17a**.

X-ray crystal structure analysis of compound 17a: formula $C_{48}H_{43}BF_{10}LiNO$, M = 857.58, colourless crystal, 0.15 x 0.12 x 0.05 mm, a = 12.1842(2), b = 13.8403(2), c = 14.1877(3) Å, α = 95.871(1)°, β = 108.906(1)°, γ = 105.653(2)°, V = 2131.7(1) Å^3, ρ_{calc} = 1.336 gcm^{-3}, μ = 0.108 mm^{-1}, empirical absorption correction (0.983 ≤ T ≤ 0.994), Z = 2, triclinic, space group P-1 (No. 2), λ = 0.71073Å, T = 223(2) K, ω and φ scans, 19288 reflections collected (±h, ±k, ±l), 7318 independent (R_{int} = 0.048) and 5403 observed reflections [I>2σ(I)], 569 refined parameters, R = 0.072, wR^2 = 0.158, max. (min.) residual electron density 0.26 (-0.25) e.Å^{-3}, the hydrogen at N1 atom was refined freely; others were calculated and refined as riding atoms.



Compound 17a (in situ reaction)

Compound **14[LiHTMP]** (32.5 mg, 0.05 mmol, 1.0 equiv) was dissolved in C_6D_6 (1.0 mL) and added to chalcone **16a** (10.4 mg, 0.05 mmol, 1.0 equiv). The reaction mixture turned instantaneously red. The colour faded during the course of 30 minutes. The reaction mixture was characterized by NMR experiments. [Comment: the ^1H resonance at δ^1H = 5.68 was tentatively assigned as the diastereoisomer of **17a**].

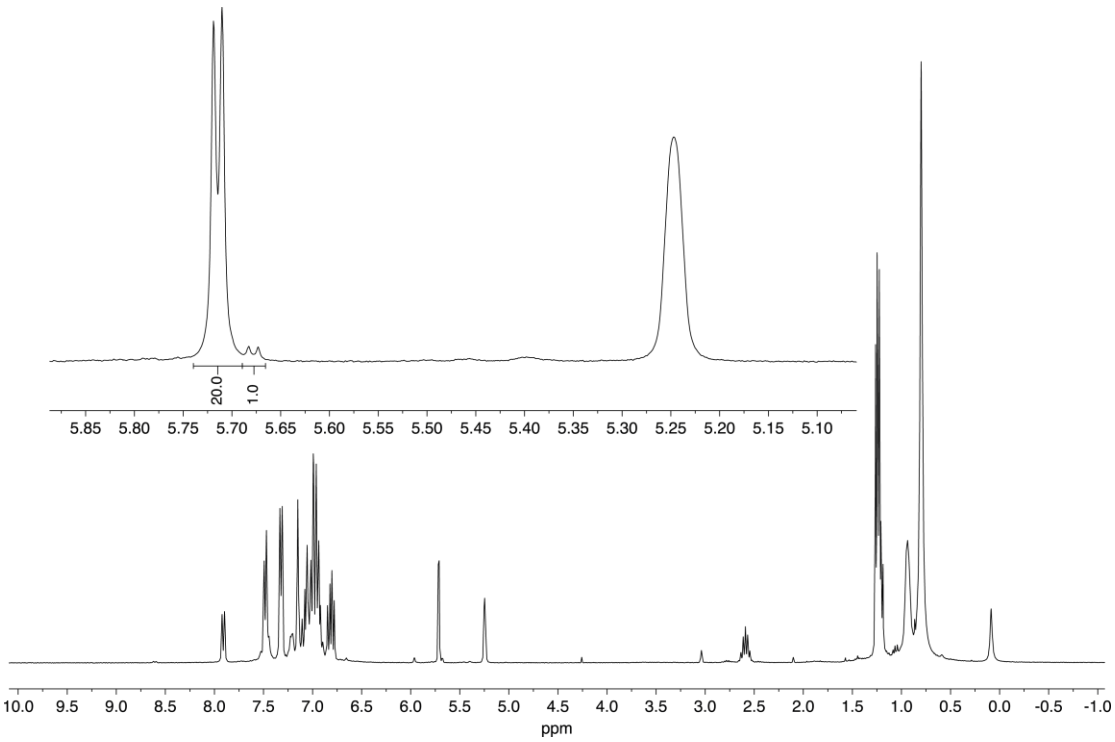
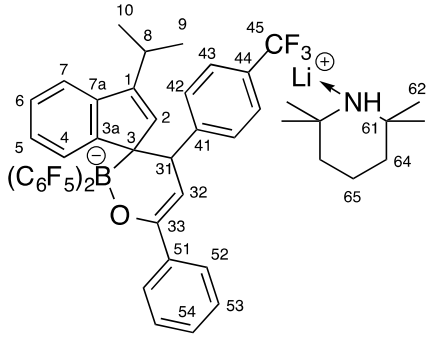


Figure S44 ^1H NMR (300 MHz, 295 K, C_6D_6) of compound **17a** (in situ reaction mixture).

Compound 17b



17b

Compound **14** [LiHTMP] (130.0 mg, 0.2 mmol, 1.0 equiv) was dissolved in toluene (0.3 mL) and added to a solution of (*E*)-4-(trifluoromethyl)chalcone (55.3 mg, 0.2 mmol, 1.0 equiv) in toluene (0.3 mL). Gas diffusion of pentane into the toluene solution at -32 °C gave colorless crystals of **17b***toluene (102.8 mg, 0.10 mmol, 50%), which were collected and dried in vacuo. The obtained crystals were suitable for the X-ray crystal structure analysis.

IR (KBr, selective wavenumbers): $\tilde{\nu}$ [cm^{-1}] = 3249 (w, NH).

Melting point (DSC): 114 °C.

Elemental analysis: calc. for $C_{49}H_{42}BF_{13}LiNO*C_7H_8$ (1017.75 g mol^{-1}): C, 66.09; H, 4.95; N, 1.38; Found: C, 65.72; H, 4.82; N, 1.56.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ [ppm] = 7.80 (d, $^3J_{HH}$ = 7.3 Hz, 1H, C4-H), 7.44 (m, 2H, C52-H), 7.21 (s, 4H, C42,43-H), 7.20 (br, 1H, C2-H), 7.05 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5-H), 7.00 (m, 2H, C53-H), 6.95 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C6-H), 6.94 (m, 1H, C54-H), 6.73 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C7-H), 5.51 (d, $^3J_{HH}$ = 2.6 Hz, 1H, C32-H), 5.13 (s, 1H, C31-H), 2.52 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C8-H), 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C9-H)^t, 1.17 (br, 2H, C65-H), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C10-H)^t, 0.88 (br, 4H, C64-H), 0.75 (br, 12H, C62-H), 0.02 (br, 1H, N-H) [^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, C_6D_6): δ [ppm] / δ [ppm] = 7.80 / 7.05 (C4-H / C5-H), 7.44 / 7.00 (C52-H / C53-H), 7.05 / 6.95 (C5-H / C6-H), 7.00 / 6.94 (C53-H / C54-H), 6.95 / 6.73 (C6-H / C7-H), 5.51 / 5.13 (C32-H / C31-H), 2.52 / 1.21, 1.16 (C8-H / C9-H, C10-H).

^{1}H NOESY (600 MHz / 600 MHz, 299 K, C_6D_6) [selected traces]: δ [ppm] / δ [ppm] = 7.21 / 5.13 (C42-H / C31-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H [ppm] / δ ^{13}C [ppm] = 7.80 / 124.9 (C4), 7.44 / 126.7 (C52), 7.21 / 129.3, 123.5 (C42, C43), 7.20 / 137.3 (C2), 7.05 / 122.1 (C5), 7.00 / 129.9 (C53), 6.95 / 125.2 (C6), 6.94 / 129.1 (C54), 6.73 / 118.8 (C7), 5.51 / 111.1 (C32), 5.13 / 44.0 (C31), 2.52 / 26.7 (C8), 1.21 / 21.8 (C9), 1.17 / 17.4 (C65), 1.16 / 22.2 (C10), 0.88 / 37.6 (C64).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H [ppm] / δ ^{13}C [ppm] = 7.44 / 151.7, 129.1 (C52-H / C33, C54), 7.21 / 146.5, 129.3, 128.0, 126.1, 124.2, 123.5, 44.1, (C42,43-H / C41, C44^t, C45, C45, C42, C43, C31), 7.20 / 151.5, 145.5, 53.9 (C2-H / C3a, C7a, C3), 7.05 / 151.5, 118.8 (C5-H / C3a, C7), 7.00 / 140.4, 129.9 (C53-H / C51, C53), 6.95 / 145.5, 124.9 (C6-H / C7a, C4), 6.94 / 126.7 (C54-H / C52), 6.73 / 151.5, 122.1 (C7-H / C3a, C5), 5.51 / 151.7 (C32-H / C33), 5.13 / 151.7, 151.5, 146.4, 129.3, 111.1, 53.9 (C31-H / C33, C3a, C41, C42, C32, C3), 2.52 / 147.1, 145.5, 137.3, 22.2, 21.8 (C8-H / C1, C7a, C2, C10, C9), 1.21 / 147.1, 26.7, 22.2 (C9-H / C1, C8, C10), 1.16 / 147.1, 26.7, 21.8 (C10-H / C1, C8, C9).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ [ppm] = 151.7 (C33), 151.5 (C3a), 147.1 (C1), 146.4 (C41), 145.5 (C7a), 140.4 (C51), 137.3 (C2), 129.9 (C53), 129.3 (C42), 129.2 (q, $^2J_{FC}$ ~ 5 Hz, C44), 129.1

(C54), 126.7 (C52), 125.2 (C6), 125.1 (q, $^{1}J_{FC}$ ~ 272 Hz, C45), 124.9 (C4), 123.5 (q, $^{3}J_{FC}$ = 4.0 Hz, C43), 122.1 (C5), 118.8 (C7), 111.1 (C32), 53.9 (br, C3), 51.0 (br, C61)^{t}, 44.0 (C31), 37.6 (br, C64), 30.9, 30.2 (each br, C62), 26.7 (C8), 22.2 (C10)^{t}, 21.8 (C9)^{t}, 17.4 (br, C65) [C_6F_5 not listed; ^{t} tentative assignment].

^{7}Li NMR (233 MHz, 299 K, C_6D_6): δ [ppm]= 0.3 (d, $^{1}J_{FLi}$ = 25.6 Hz).

^{11}B NMR (192 MHz, 299 K, C_6D_6): δ [ppm] = 1.7 ($\nu_{1/2} \approx 250$ Hz).

^{19}F NMR (470 MHz, 223 K, CD_2Cl_2): δ (ppm) = -62.0 (s, 3F, CF_3), -126.1, -126.5 (each m), -134.4, -150.2 (each br)(each 1F, *o*-C_6F_5), -159.5, -159.6 (each br t, $^{3}J_{FF}$ = 21.0 Hz, each 1F, *p*-C_6F_5), -162.0, -165.6 (each m, each 1F), -163.9 (br, 2F)(*m*-C_6F_5).

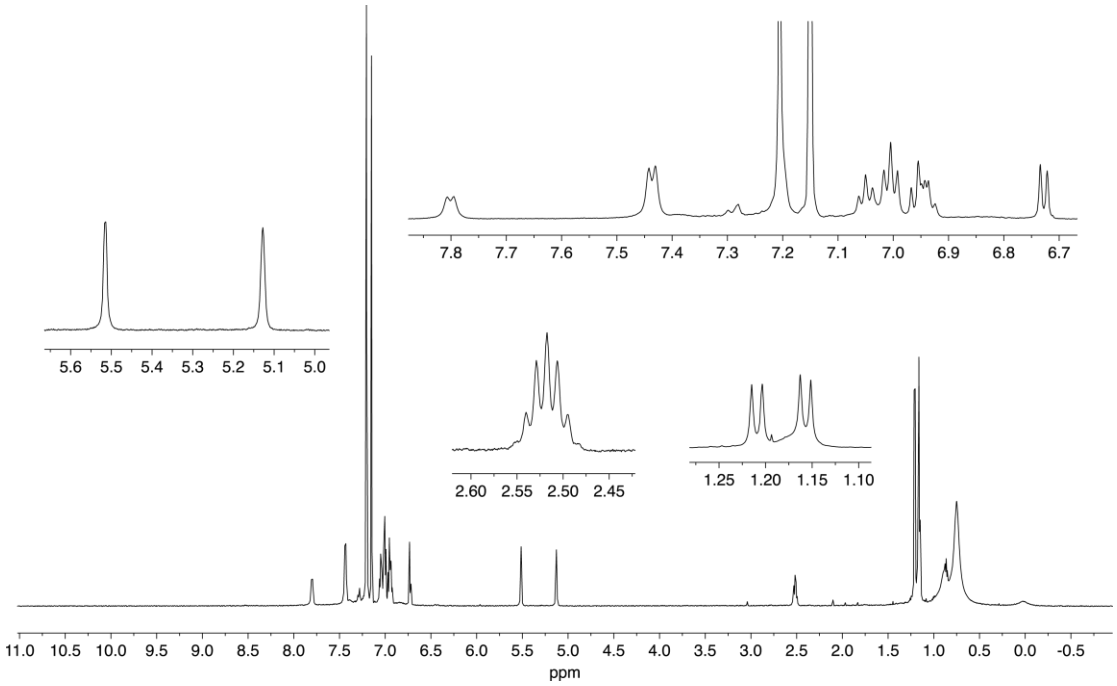


Figure S45 ^{1}H NMR (600 MHz, 299 K, C_6D_6) of crystalline compound **17b**.

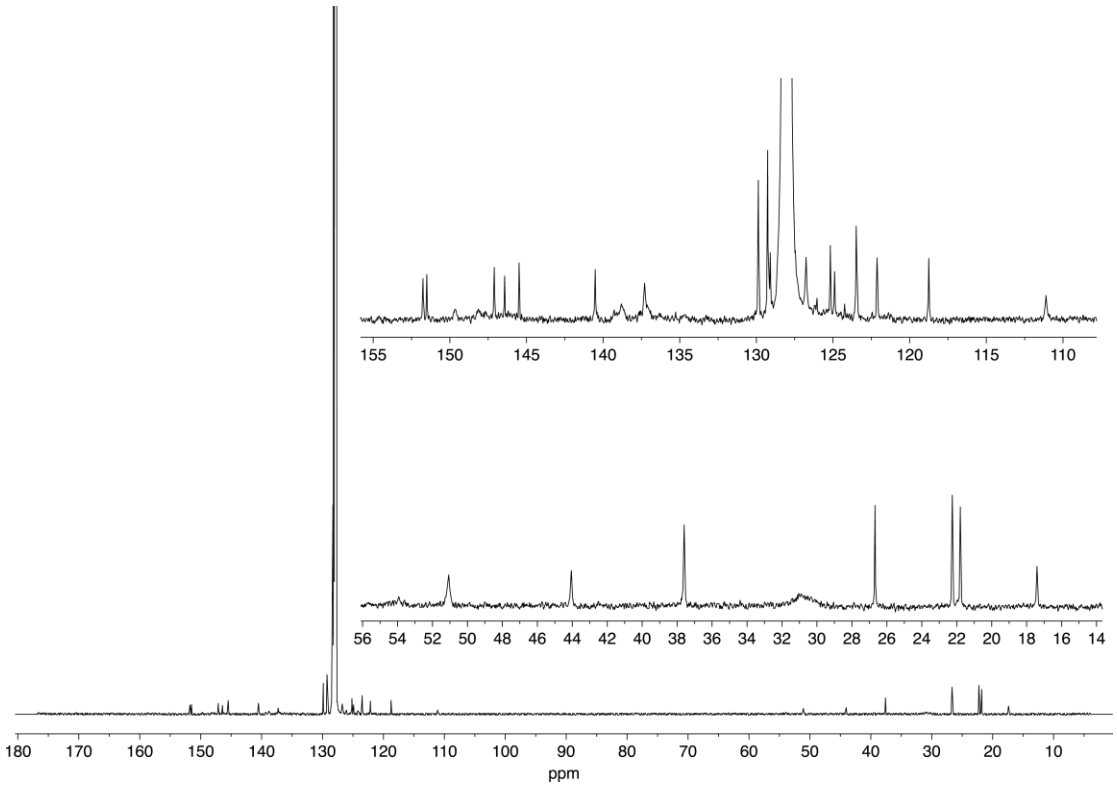


Figure S46 $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) of crystalline compound **17b**.

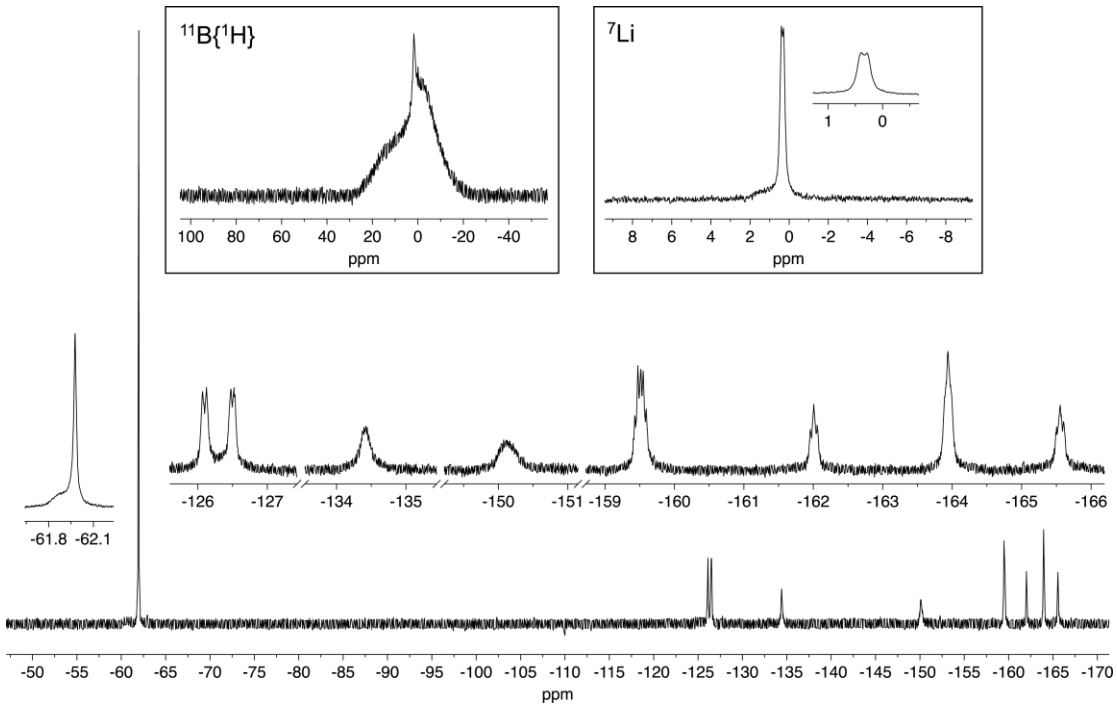


Figure S47 ^{7}Li NMR (233 MHz, 299 K, C_6D_6), ^{11}B NMR (192 MHz, 299 K, C_6D_6) and ^{19}F NMR (470 MHz, 223 K, CD_2Cl_2) of crystalline compound **17b**.

X-ray crystal structure analysis of compound 17b: A colorless prism-like specimen of $C_{49}H_{42}BF_{13}NLiO \cdot C_7H_8$, approximate dimensions 0.097 mm x 0.098 mm x 0.180 mm, was used for

the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 511 frames were collected. The total exposure time was 7.81 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 40956 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 8919 were independent (average redundancy 4.592, completeness = 99.8%, R_{int} = 6.38%, R_{sig} = 4.67%) and 6651 (74.57%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.8630(6) Å, b = 14.0401(6) Å, c = 15.2449(5) Å, α = 90.6950(10)°, β = 110.3370(10)°, γ = 116.5010(10)°, volume = 2440.00(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9996 reflections above 20 σ(I) with 4.820° < 2θ < 52.78°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.951. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9800 and 0.9890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{49}H_{42}BF_{13}NLiO \cdot C_7H_8$. The final anisotropic full-matrix least-squares refinement on F^2 with 669 variables converged at R1 = 4.90%, for the observed data and wR2 = 11.65% for all data. The goodness-of-fit was 1.040. The largest peak in the final difference electron density synthesis was 0.308 $e^-/Å^3$ and the largest hole was -0.370 $e^-/Å^3$ with an RMS deviation of 0.055 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.385 g/cm^3 and F(000), 1052 e^-. The hydrogen at N1 atom was refined freely; others were calculated and refined as riding atoms.

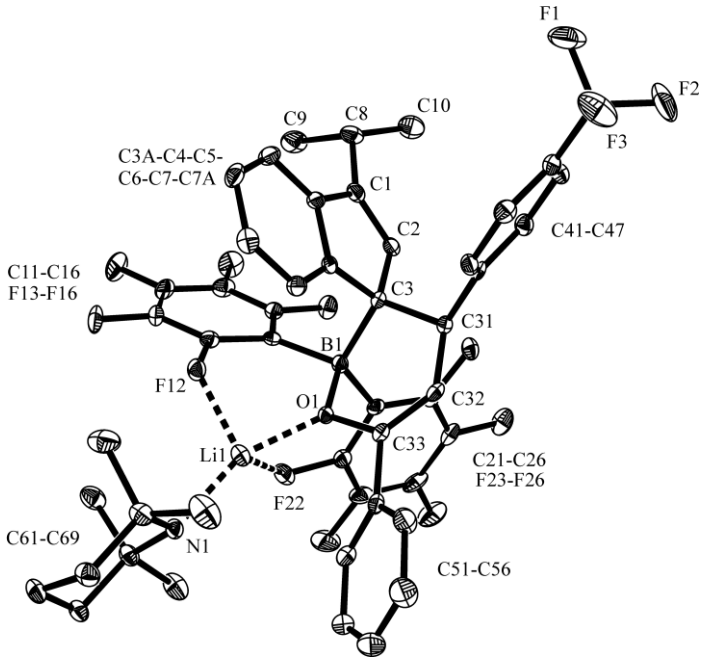


Figure 48 A view of the molecular structure of compound **17b** (thermal ellipsoids are shown with 50% probability, hydrogen atoms are omitted for reasons of clarity).

Compound 17b (in situ reaction)

Compound **14[LiTMP]** (32.5 mg, 0.05 mmol, 1.0 equiv) was dissolved in C_6D_6 (0.5 mL) and added to chalcone derivative **16b** (13.8 mg, 0.05 mmol, 1.0 equiv) in C_6D_6 (0.5 mL). The reaction mixture turned instantaneously red. The colour faded during the course of 30 minutes. The reaction mixture was subsequently characterized by NMR experiments.

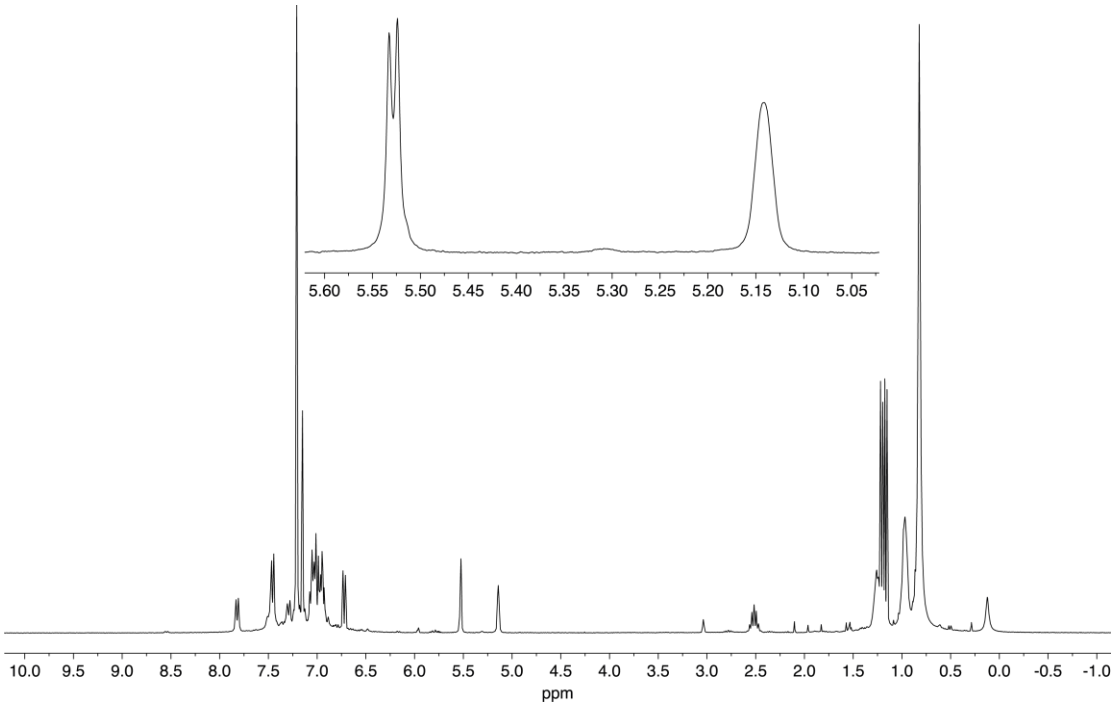
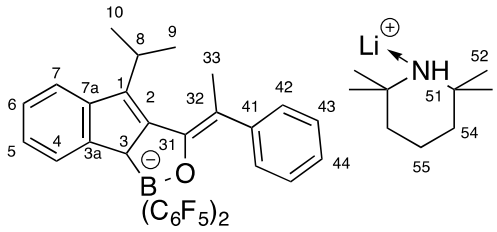


Figure S49 ^{1}H NMR (300 MHz, 295 K, C_6D_6) of compound **17b** (reaction mixture).

Compound 19



19

Compound **14** [LiHTMP] (32.5 mg, 0.05 mmol, 1.0 equiv) was dissolved in C_6D_6 (0.8 mL) and added to a solution of phenyl methyl ketene (**18**) (13.2 mg, 0.10 mmol, 2.0 equiv) in C_6D_6 (0.2 mL). An instantaneous colour change towards red was observed. The formation of a major product along with some polymer was observed by NMR experiments. Isolation of a product in satisfactory purity failed despite great effort, therefore the obtained reaction mixture was used to characterize compound **19** by NMR experiments.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ [ppm] = 8.21 (d, $^3J_{HH}$ = 7.7 Hz, 1H, C4-H), 7.55 (m, 2H, C42-H), 7.45 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, C7-H), 7.24 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, C5-H), 7.11 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, C6-H), 7.01 (m, 2H, C43-H), 6.80 (m, 1H, C44-H), 4.59 (s, 1H, C3-H), 3.32 (sept, $^3J_{HH}$ = 7.1 Hz, 1H, C8-H), 2.17 (s, 3H, C33-H), 1.50 (d, $^3J_{HH}$ = 7.1 Hz, 3H, C9-

H)^{t}, 1.38 (d, $^{3}J_{HH}$ = 7.1 Hz, 3H, C10-H)^{t}, 1.32 (br m, 4H^{a}, C55-H), 1.02 (br m, 8H^{a}, C54-H), 0.86 (br, 24H^{a}, C52-H), 0.00 (br, 2H^{a}, NH) [^{a} in relation to C8-H; ^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, C_6D_6): δ [ppm] / δ [ppm] = 8.21 / 7.24 (C4-H / C5-H), 7.55 / 7.01 (C42-H / C43-H), 7.45 / 7.11 (C7-H / C6-H), 7.24 / 7.11 (C5-H / C6-H), 7.01 / 6.80 (C43-H / C44-H), 3.32 / 1.50, 1.38 (C8-H / C9-H, C10-H), 1.32 / 1.02 (C55-H / C54-H).

^{1}H NOESY (500 MHz / 500 MHz, 299 K, C_6D_6) [selected traces]: δ [ppm] / δ [ppm] = 8.21 / 7.24, 4.59 (C4-H / C5-H, C3-H), 7.45 / 7.11, 1.50, 1.38 (C7-H / C6-H, C9-H, C10-H), 2.17 / 7.55, 3.32, 1.50 (C33-H / C42-H, C8-H, C9-H).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6): δ^{1}H [ppm] / δ^{13}C [ppm] = 8.21 / 125.7 (C4), 7.55 / 128.0 (C42), 7.45 / 122.0 (C7), 7.24 / 124.7 (C5), 7.11 / 125.0 (C6), 7.01 / 130.1 (C43), 6.80 / 126.5 (C44), 4.59 / 53.9 (C3), 3.32 / 29.4 (C8), 2.17 / 20.0 (C33), 1.50 / 20.8 (C9), 1.38 / 21.6 (C10), 1.32 / 18.0 (C55), 1.02 / 38.2 (C54), 0.86 / 31.2 (C52).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_6D_6): δ^{1}H [ppm] / δ^{13}C [ppm] = 8.21 / 145.2, 125.0 (C4-H / C7a, C6), 7.55 / 128.0, 126.5, 103.8 (C42-H / C42, C44, C31), 7.45 / 149.3, 124.7 (C7-H / C3a, C5), 7.24 / 149.3, 122.0 (C5-H / C3a, C7), 7.11 / 145.2, 125.7 (C6-H / C7a, C4), 7.01 / 142.2, 130.1 (C43-H / C41, C43), 6.80 / 128.0 (C44-H / C42), 4.59 / 144.0, 142.1 (C3-H / C2, C1), 3.32 / 145.2, 144.0, 142.1, 20.8 (C8-H / C7a, C2, C1, C9), 2.17 / 148.8, 142.2, 103.8 (C33-H / C31, C41, C32), 1.50 / 142.1, 29.4, 21.6 (C9-H / C1, C8, C10), 1.38 / 142.1, 29.4, 20.8 (C10-H / C1, C8, C9), 1.32 / 50.4, 38.2 (C55-H / C51, C54), 1.02 / 50.4, 38.2, 31.2, 18.0 (C54-H / C51, C54, C52, C55), 0.86 / 50.4, 38.2, 31.2 (C52-H / C51, C54, C52).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ^{13}C [ppm] = 149.3 (C3a), 148.8 (C31), 145.2 (C7a), 144.0 (C2), 142.2 (C41), 142.1 (C1), 130.1 (C43), 128.0 (C42), 126.5 (C44), 125.7 (br, C4), 125.0 (C6), 124.7 (C5), 122.0 (C7), 103.8 (C32), 53.9 (br, C3), 50.4 (C51), 38.2 (C54), 31.2 (C52), 29.4 (C8), 21.6 (C10)^{t}, 20.8 (C9)^{t}, 20.0 (C33), 18.0 (C55) [C_6F_5 not listed; ^{t} tentative assignment].

^{7}Li NMR (194 MHz, 299 K, C_6D_6): δ [ppm] = -0.4 ($\nu_{1/2} \approx 30$ Hz)

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ [ppm] = 1.2 ($\nu_{1/2} \approx 300$ Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ [ppm] = -136.9, -137.6 (br, each 2F, *o*-C_6F_5), -158.2 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^{a}$), -158.4 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-$C_6F_5^{b}$), -162.4 (m, 2F, *m*-$C_6F_5^{a}$), -164.1 (m, 2F, *m*-$C_6F_5^{b}$) [$\Delta\delta^{19}F_{m,p}$ = 4.2^{a}, 5.7^{b}].

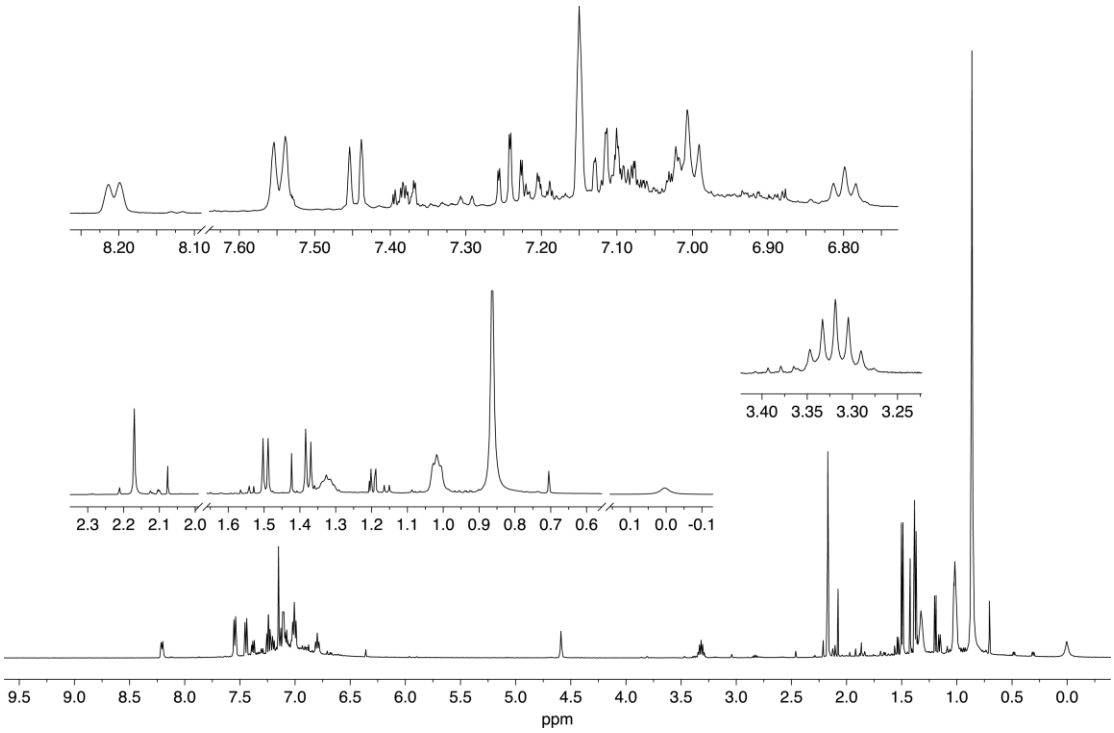


Figure S50 ^{1}H NMR (500 MHz, 299 K, C_6D_6) of compound **19** (reaction mixture).

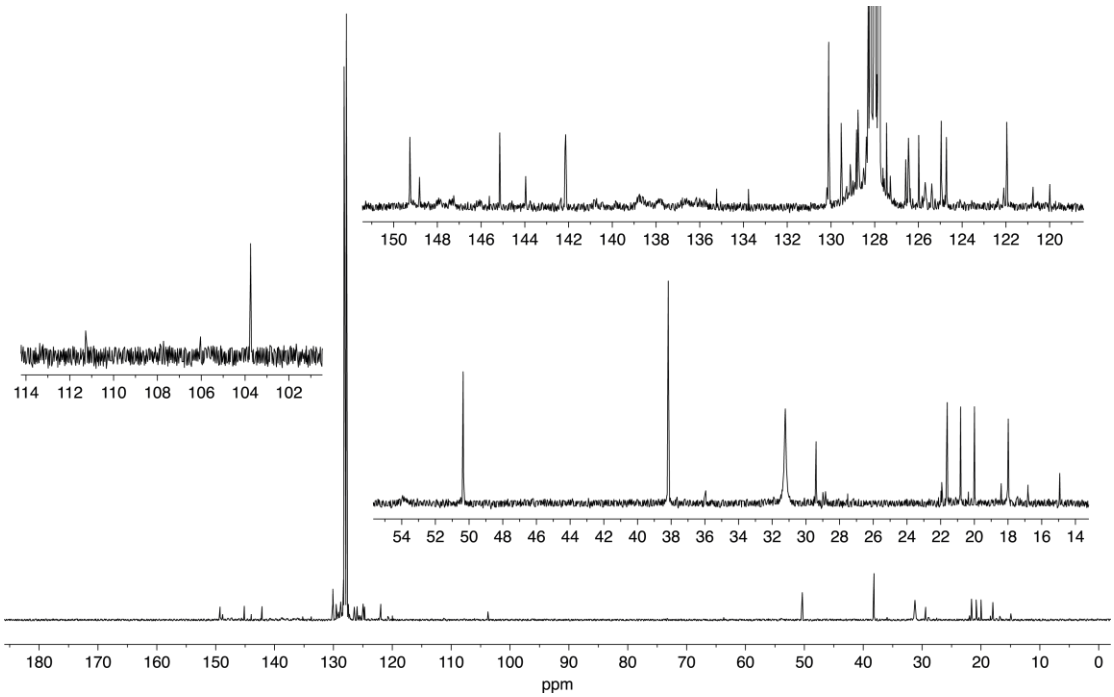


Figure S51 $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6) of compound **19** (reaction mixture).

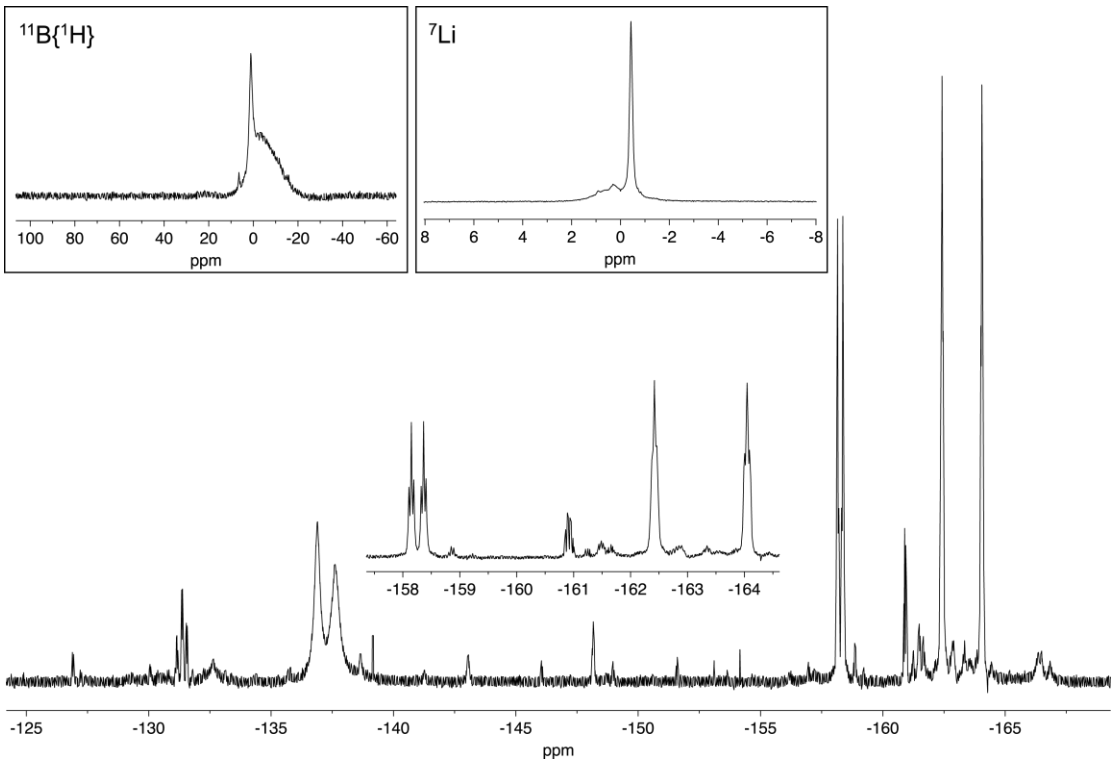


Figure S52 ^{7}Li NMR (194 MHz, 299 K, C_6D_6), $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6) and ^{19}F NMR (470 MHz, 299 K, C_6D_6) of compound **19** (reaction mixture).

Single crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **19** in pentane at RT. However, the crystalline material decomposed within two days of storage inside a glovebox at RT.

X-ray crystal structure analysis of compound 19: A colorless prism-like specimen of $C_{42}H_{39}BF_{10}LiNO$, approximate dimensions 0.060 mm x 0.080 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 520 frames were collected. The total exposure time was 4.77 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 39852 reflections to a maximum θ angle of 25.02° (0.84 Å resolution), of which 6550 were independent (average redundancy 6.084, completeness = 99.7%, R_{int} = 5.33%, R_{sig} = 3.28%) and 5842 (89.19%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 12.0328(4) Å, $\underline{b}$ = 14.7766(5) Å, $\underline{c}$ = 20.8614(8) Å, volume = 3709.2(2) Å^3, are based upon the refinement of the XYZ-centroids of 9867 reflections above 20 σ(I) with 4.78° < 2θ < 50.63°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.955. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9860 and 0.9930. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{42}H_{39}BF_{10}LiNO$. The final anisotropic full-matrix least-squares refinement on F^2 with 516 variables converged at R1 = 3.51%, for the observed data and wR2 = 8.32% for all data. The goodness-of-fit was 1.077. The largest peak in the final difference electron density synthesis was 0.261 e^-/Å^3 and the largest

hole was -0.211 $e^-/Å^3$ with an RMS deviation of 0.047 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.399 g/cm^3 and F(000), 1616 e^-. The hydrogen at N1 atom was refined freely; others were calculated and refined as riding atoms.