

Design and Reactions of a Carbon Lewis Base / Boron Lewis Acid Frustrated Lewis Pair

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Supplementary material

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1. General Procedure

All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. NMR spectra were recorded on an Agilent DD2- 500 MHz (^1H : 500 MHz, ^{13}C : 126 MHz, ^{19}F : 470 MHz, ^{11}B : 160 MHz, ^{31}P : 202 MHz) and on an Agilent DD2- 600 MHz (^1H : 600 MHz, ^{13}C : 151 MHz, ^{19}F : 564 MHz, ^{11}B : 192 MHz, ^{31}P : 243 MHz). ^1H NMR and ^{13}C NMR: chemical shifts are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts are given relative to CFCl_3 ($\delta = 0$, external reference), ^{11}B NMR: chemical shifts are given relative to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ($\delta = 0$, external reference), ^{31}P NMR: chemical shifts are given relative to H_3PO_4 (85% in D_2O) ($\delta = 0$, external reference). NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on Vario EL III Element Analyzer. IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series). Melting points (M.p.) and decomposition points (D.p.) were obtained with a DSC 2010 (TA Instruments). All accurate mass spectra were recorded using a Thermo Scientific Orbitrap LTQ XL (ESI-spectra) machine.

2. X-Ray diffraction

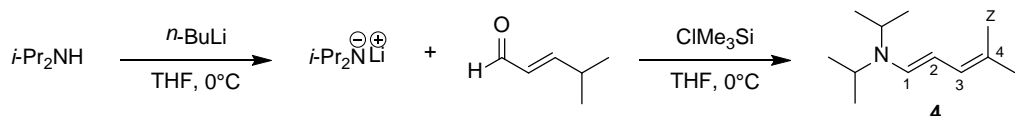
For compounds **6**, **8b** and **8c** data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, 276, 307-326); absorption correction, Denzo (Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, A59, 228-234); structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467-473); structure refinement SHELXL-97 (Sheldrick, G. M. *Acta Crystallogr.* **2008**, A64, 112-122) and graphics, XP (Bruker AXS, 2000). For compounds **5/5'** and **8a** data sets were collected with a Kappa CCD APEXII Bruker diffractometer. For compound **9** 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*: For compound **5/5'** one badly disordered toluene molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A. L. *J. Appl. Cryst.*, **2003**, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. CCDC deposition numbers are 1525271 to 1525275.

3. Materials

Diisopropylamine and (E)-4-methylpent-2-enal were purchased from ACROS Organics and used without further purification. $\text{HB}(\text{C}_6\text{F}_5)_2$ (a) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, 17, 5492-5503; b) Parks, D. J.; Spence R. E. v. H.; Piers, W. E. *Angew. Chem. Int. Ed.* **1995**, 34, 809-811) was prepared according to the literature. Compound **4** (Aznar, F.; Fañañas-Mastral, M.; Alonso, J.; Fañañas, F. J. *Chem. Eur. J* **2008**, 14, 325-332) was synthesized by a modified procedure.

4. Synthesis and Characterization

4.1 Preparation of (*E*)-*N,N*-diisopropyl-4-methyl-1,3-pentadien-1-amine (**4**)



Supplementary Scheme 1.

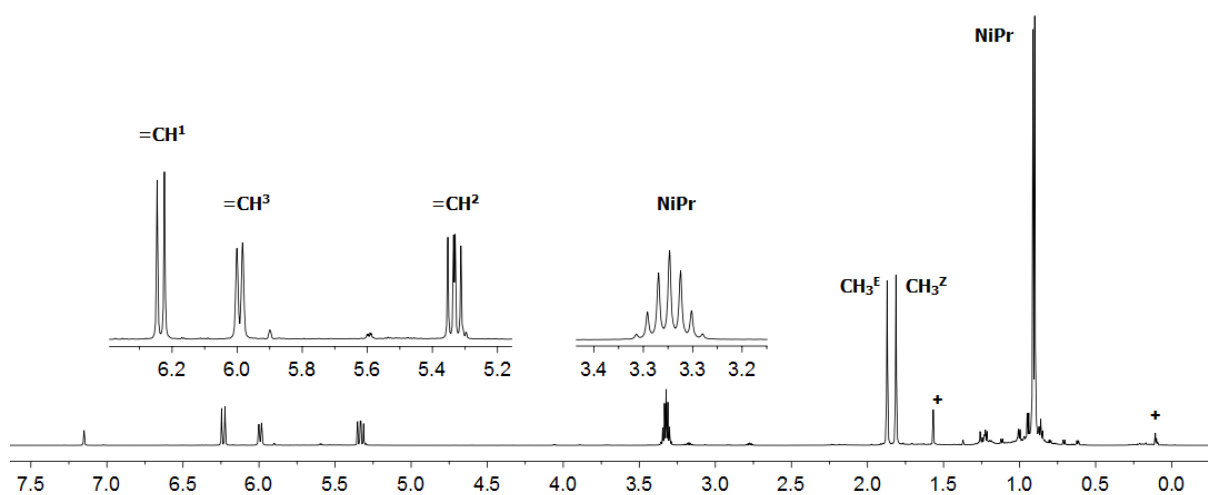
Diisopropylamine (3.5 mL, 25.0 mmol, 1.25 eq.) was added to THF (20 mL) and cooled to 0°C . n -Butyllithium 1.6 M in n -hexane (15.6 mL, 25.0 mmol, 1.25 eq.) was added via a syringe within 20 min and the mixture was stirred for 2 h at 0°C to generate lithium diisopropylamide. Afterwards, (*E*)-4-methylpent-2-enal (2.3 mL, 20.0 mmol, 1.00 eq.) was added slowly to the solution followed by trimethylsilyl chloride (3.8 mL, 30.0 mmol, 1.50 eq.). The mixture was stirred at room temperature overnight until the solution turned colorless and a white solid precipitated. The solvent was removed *in vacuo*, the residue was suspended in n -pentane (20 mL) and the suspension was filtered via cannula filtration and through alumina (N, act. I). Then the solvent of the filtrate was removed and the resulting residue dried *in vacuo*. Compound **4** was obtained as a yellow liquid (3.10 g, 17.1 mmol, 85%).¹

Exact mass: calcd. for $\text{C}_{12}\text{H}_{23}\text{NH}^+$: 182.1903 m/z; found: 182.1910 m/z.

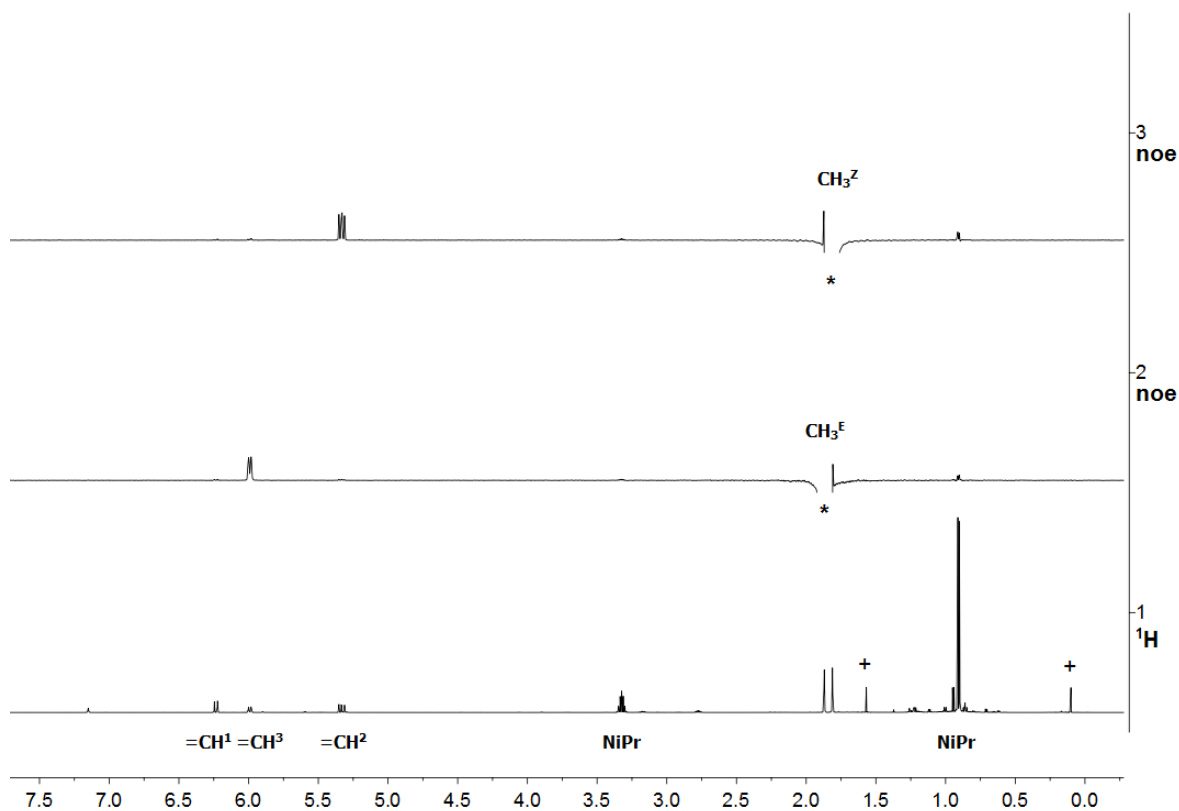
^1H NMR (600 MHz, 299 K, C_6D_6): δ = 6.23 (d, $^3J_{\text{HH}}$ = 13.5 Hz, 1H, =CH¹), 5.99 (dm, $^3J_{\text{HH}}$ = 10.5 Hz, 1H, =CH³), 5.33 (dd, $^3J_{\text{HH}}$ = 13.5, 10.5 Hz, 1H, =CH²), 3.32 (sept, $^3J_{\text{HH}}$ = 6.7 Hz, 2H, NiPr), 1.87 (s, 3H, CH₃^E), 1.81 (s, 3H, CH₃^Z), 0.91 (d, $^3J_{\text{HH}}$ = 6.7 Hz, 12H, NiPr).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6): δ = 134.1 (=CH¹), 126.7 (=CH³), 119.7 (=C⁴), 96.0 (=CH²), 46.1 (NiPr), 26.1 (CH₃^E), 21.5 (NiPr), 18.3 (CH₃^Z).

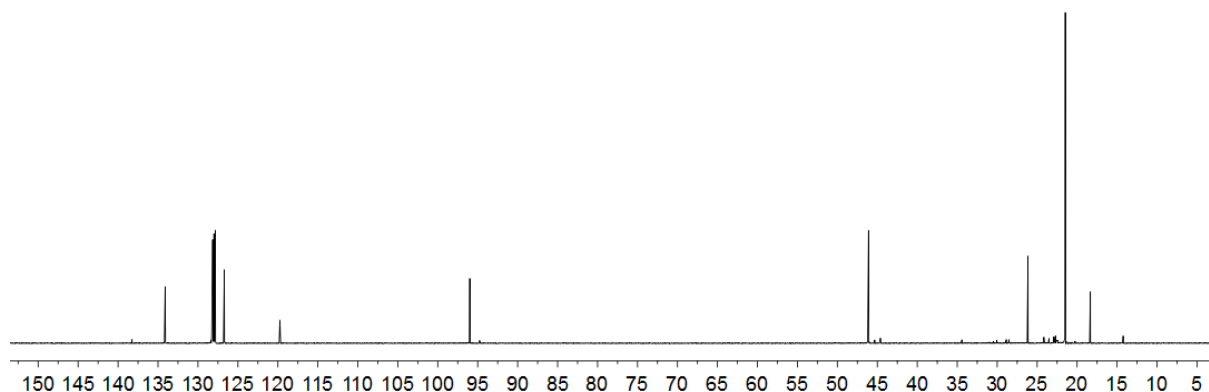
¹ Compound **4** was synthesized by a modified procedure [Aznar, F.; Fañañas-Mastral, M.; Alonso, J.; Fañañas, F. *J. Chem. Eur. J.* **2008**, *14*, 325-332].



Supplementary Figure 1: ¹H NMR (600 MHz, 299 K, C₆D₆) spectrum of compound 4 [+ impurities].

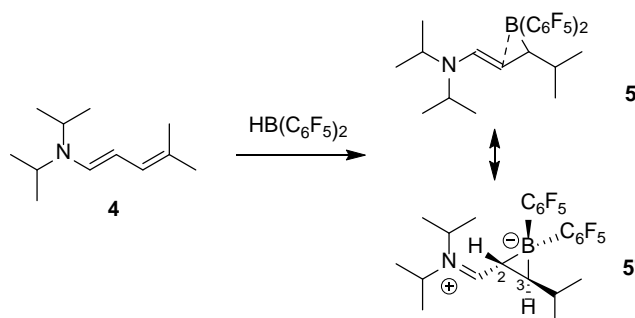


Supplementary Figure 2: (1) ¹H NMR (600 MHz, 299 K, C₆D₆), (2,3) ¹H{¹H} noe [* irradiation points: (2) δ¹H 1.87 (CH₃^E), (3) δ¹H 1.81 (CH₃^Z)] spectra of compound 4 [+ impurities].



Supplementary Figure 3: $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of compound **4**.

4.2 Preparation of compound 5/5'



Supplementary Scheme 2.

(*E*)-*N,N*-diisopropyl-4-methyl-1,3-pentadien-1-amine (**4**) (181 mg, 1.00 mmol, 1.00 eq.) was dissolved in *n*-pentane (2 mL) and added to a suspension of bis(pentafluorophenyl)borane (346 mg, 1.00 mmol, 1.00 eq.) in pentane (8 mL). The mixture was stirred for 30 min at room temperature, whereas a orange precipitate was formed. The solution was separated via cannula filtration, the solvent of the filtrate was removed under reduced pressure and the obtained residue was dried *in vacuo* to give a yellow solid (327 mg, 0.62 mmol, 62%).

Elemental analysis: calcd. (%) for $\text{C}_{24}\text{H}_{24}\text{BF}_{10}\text{N}$: C 54.67, H 4.59, N 2.66; found: C 54.79, H 4.56, N 2.77.

Melting point: 82 °C

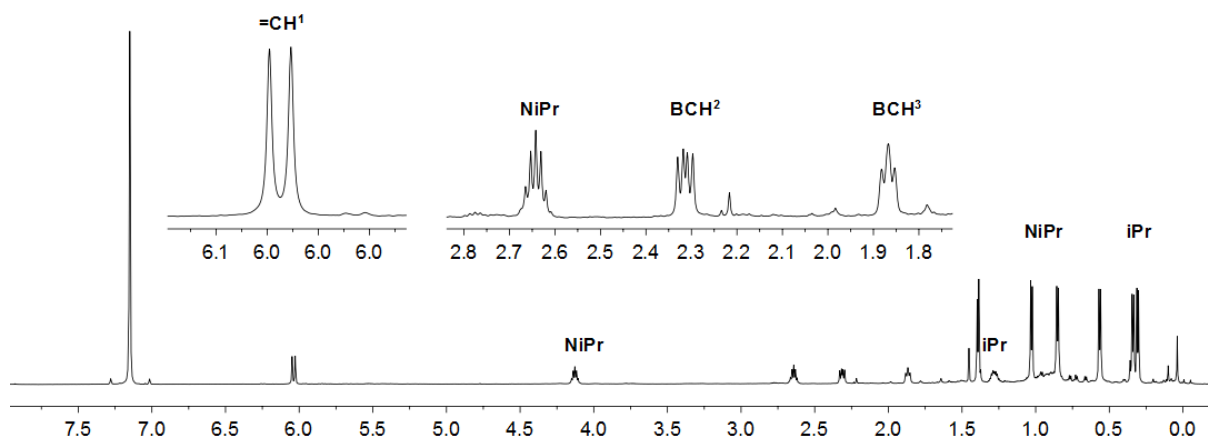
^1H NMR (600 MHz, 299 K, C_6D_6): δ = 6.04 (d, $^3J_{\text{HH}} = 12.5$ Hz, 1H, =CH), 4.13 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 1H), 0.85, 0.57 (each d, $^3J_{\text{HH}} = 6.7$ Hz, each 3H)(NiPr), 2.64 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 1H), 0.34, 0.31 (each d, $^3J_{\text{HH}} = 6.7$ Hz, each 3H)(NiPr), 2.31 (dd, $^3J_{\text{HH}} = 12.5, 7.2$ Hz, 1H, BCH²), 1.87 (m, 1H, BCH³), 1.28 (m, 1H), 1.39, 1.03 (each d, $^3J_{\text{HH}} = 6.5$ Hz, each 3H)(iPr).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6): δ = 170.3 (=CH), 50.0, 19.3, 18.7 (NiPr), 47.6 (br, BCH³), 47.5 (br, BCH²), 47.2, 23.2, 22.5 (NiPr), 31.8, 24.1, 23.1 (iPr), [C_6F_5 not listed].

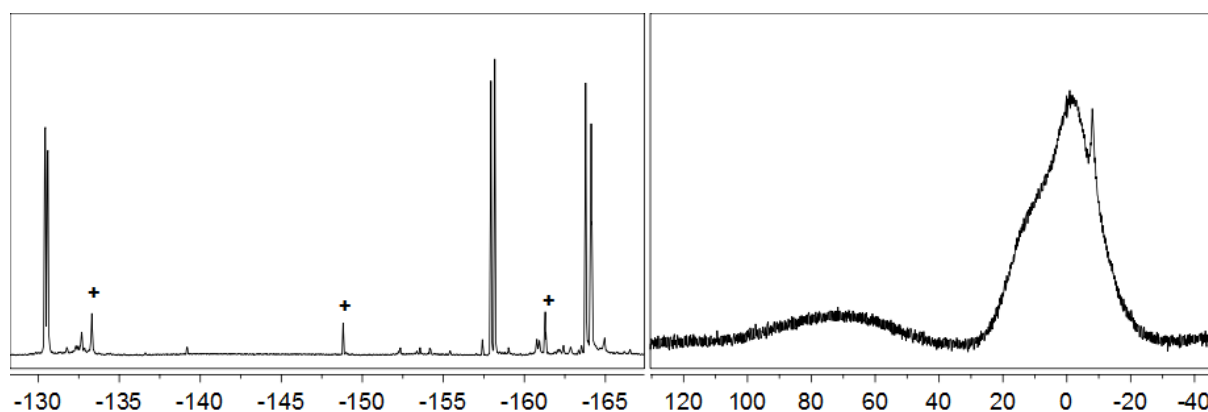
$^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6): δ = -8.1 ($\nu_{1/2} \approx 160$ Hz).

^{11}B NMR (192 MHz, 299 K, C_6D_6): δ = -8.1 ($\nu_{1/2} \approx 160$ Hz).

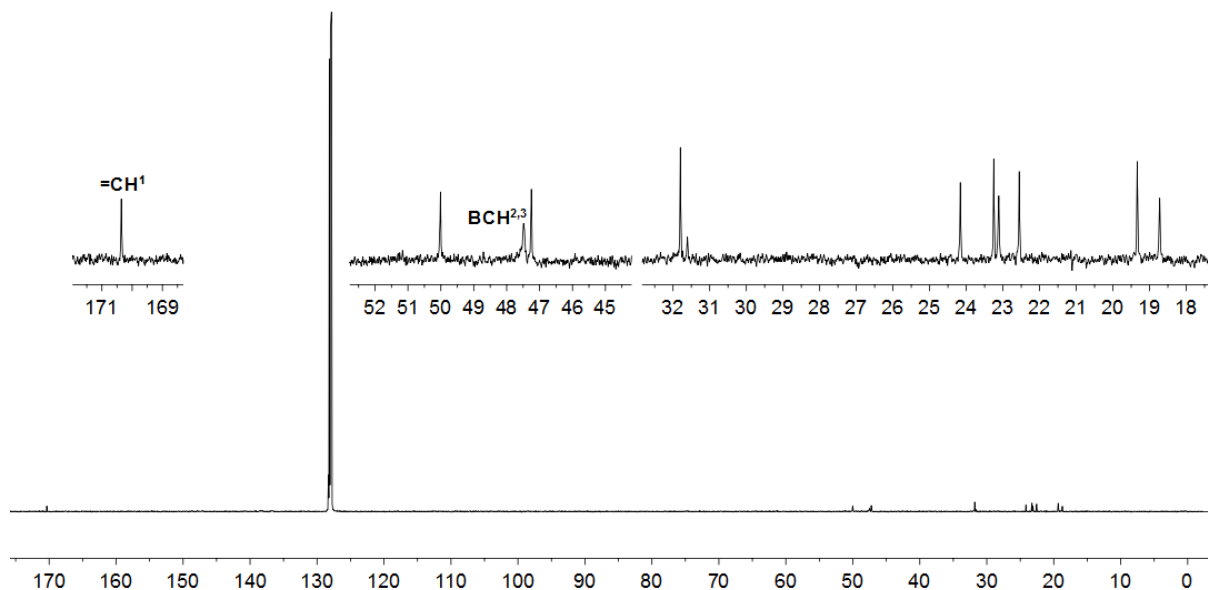
^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -130.4 (m, 2F, o), -157.9 (t, $^3J_{\text{FF}} = 20.9$ Hz, 1F, p), -164.1 (m, 2F, m), (C_6F_5) [$\Delta\delta^{19}\text{F}_{\text{pm}} = 5.6$], -130.6 (m, 2F, o), -158.2 (t, $^3J_{\text{FF}} = 20.4$ Hz, 1F, p), -163.8 (m, 2F, m), (C_6F_5) [$\Delta\delta^{19}\text{F}_{\text{pm}} = 6.4$].



Supplementary Figure 4: ^1H NMR (600 MHz, 299 K, C_6D_6) spectrum of compound 5/5'.



Supplementary Figure 5: ^{19}F NMR (564 MHz, 299 K, C_6D_6 , [+ impurities]) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, C_6D_6) spectra of compound 5/5'.

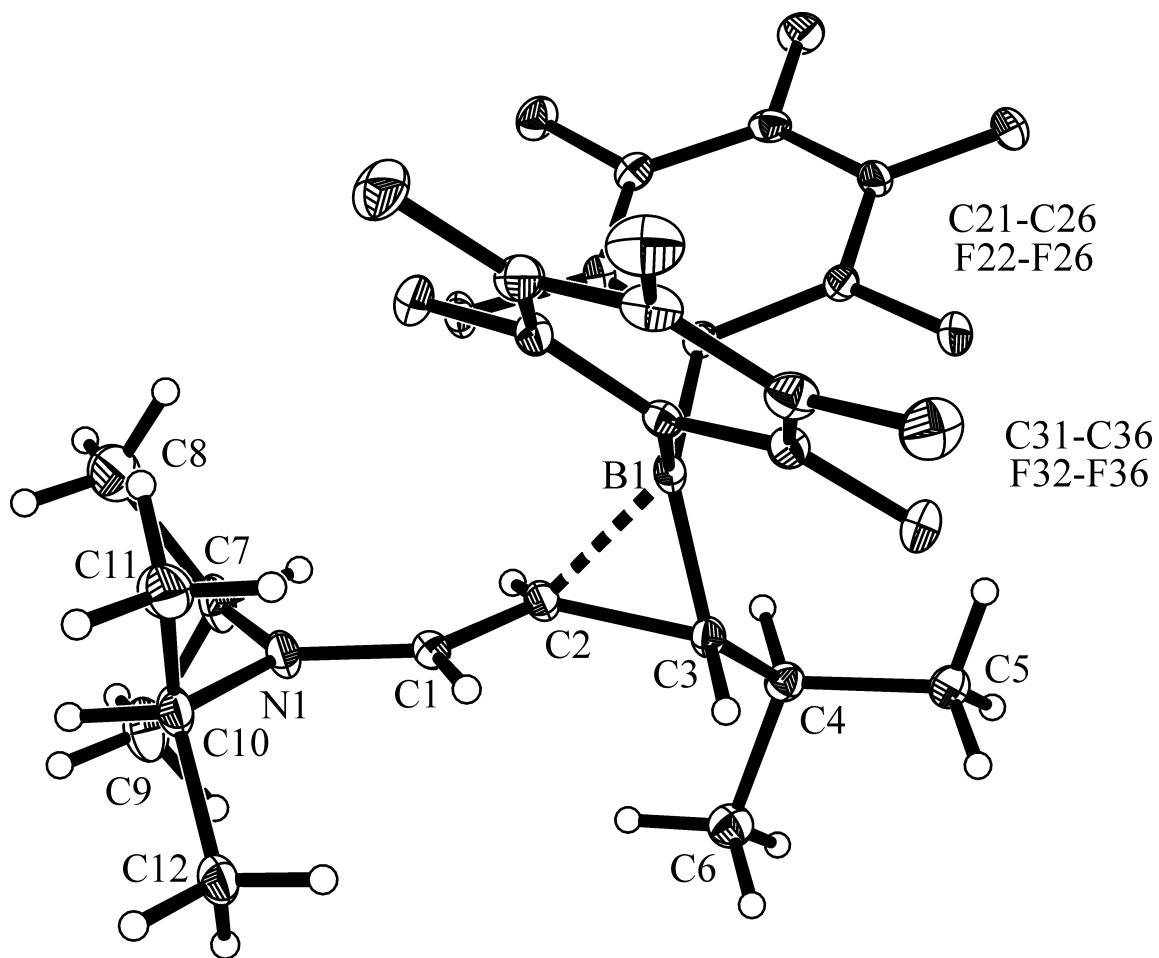


Supplementary Figure 6: $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, C_6D_6) spectrum of compound 5/5'.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of the isolated yellow solid in toluene layered with pentane at $-36\text{ }^\circ\text{C}$.

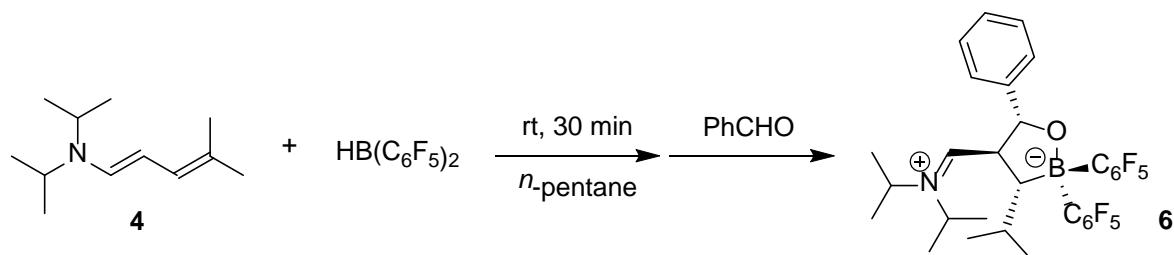
IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2957 (m), 2875 (w), 1604 (s), 1515 (s), 1470 (s), 1382 (m), 1324 (m), 1138 (m), 1090 (m), 971 (s), 915 (m), 860 (w), 771 (m), 738 (w), 654 (m), 618 (m), 553 (m), 476 (w), 422 (w).

X-ray crystal structure analysis of compound 5/5': A colorless plate-like specimen of $\text{C}_{24}\text{H}_{24}\text{BF}_{10}\text{N}$, approximate dimensions 0.040 mm x 0.120 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1547 frames were collected. The total exposure time was 18.18 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 4912 reflections to a maximum θ angle of 68.09° (0.83 \AA resolution), of which 4912 were independent (average redundancy 1.000, completeness = 99.0%, $R_{\text{int}} = 5.30\%$, $R_{\text{sig}} = 2.80\%$) and 4012 (81.68%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 10.6770(3)\text{ \AA}$, $b = 13.7158(3)\text{ \AA}$, $c = 19.0578(5)\text{ \AA}$, $\beta = 102.7960(10)^\circ$, volume = $2721.58(12)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9898 reflections above $20\sigma(I)$ with $8.011^\circ < 2\theta < 136.1^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.854. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8130 and 0.9580. 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, $\text{C}_{24}\text{H}_{24}\text{BF}_{10}\text{N}$. The final anisotropic full-matrix least-squares refinement on F^2 with 343 variables converged at $R1 = 3.37\%$, for the observed data and $wR2 = 8.47\%$ for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was $0.205\text{ e}/\text{\AA}^3$ and the largest hole was $-0.179\text{ e}/\text{\AA}^3$ with an RMS deviation of $0.039\text{ e}/\text{\AA}^3$. On the basis of the final model, the calculated density was $1.287\text{ g}/\text{cm}^3$ and $F(000)$, 1080 e $^-$.



Supplementary Figure 7.

4.3 Preparation of compound 6



Supplementary Scheme 3.

(E)-N,N-diisopropyl-4-methyl-1,3-pentadien-1-amine (**4**) (90.7 mg, 0.50 mmol, 1.00 eq.) was dissolved in *n*-pentane (1 mL) and added to a suspension of bis(pentafluorophenyl)borane (173 mg, 0.50 mmol, 1.00 eq.) in pentane (3 mL). After the yellow solution was stirred for 30 min at room temperature, benzaldehyde (63.7 mg, 0.50 mmol, 1.00 eq.) in *n*-pentane (1 mL) was added and the obtained reaction mixture was stirred overnight. The formed precipitate was separated via cannula filtration, washed with pentane (3 x 2 mL) and dried in *vacuo* to give an orange solid (208 mg, 0.33 mmol, 67%).

IR (KBr): $\bar{\nu}$ = 2964 (m), 2877 (m), 1639 (s), 1512 (s), 1452 (s), 1384 (m), 1078 (s), 963 (s), 794 (m), 763 (m), 706 (m), 614 (w), 571 (w).

Elemental analysis: calcd. (%) for C₃₁H₃₀BF₁₀NO: C 58.79, H 4.77, N 2.21; found: C 58.30, H 4.60, N 2.33.

Melting point: 158 °C

Decomposition point: 163 °C

The solution of the orange solid in THF-*d*₈ contains compound **6** and ca. 10% (¹H) of a second compound, probably a diastereoisomere.

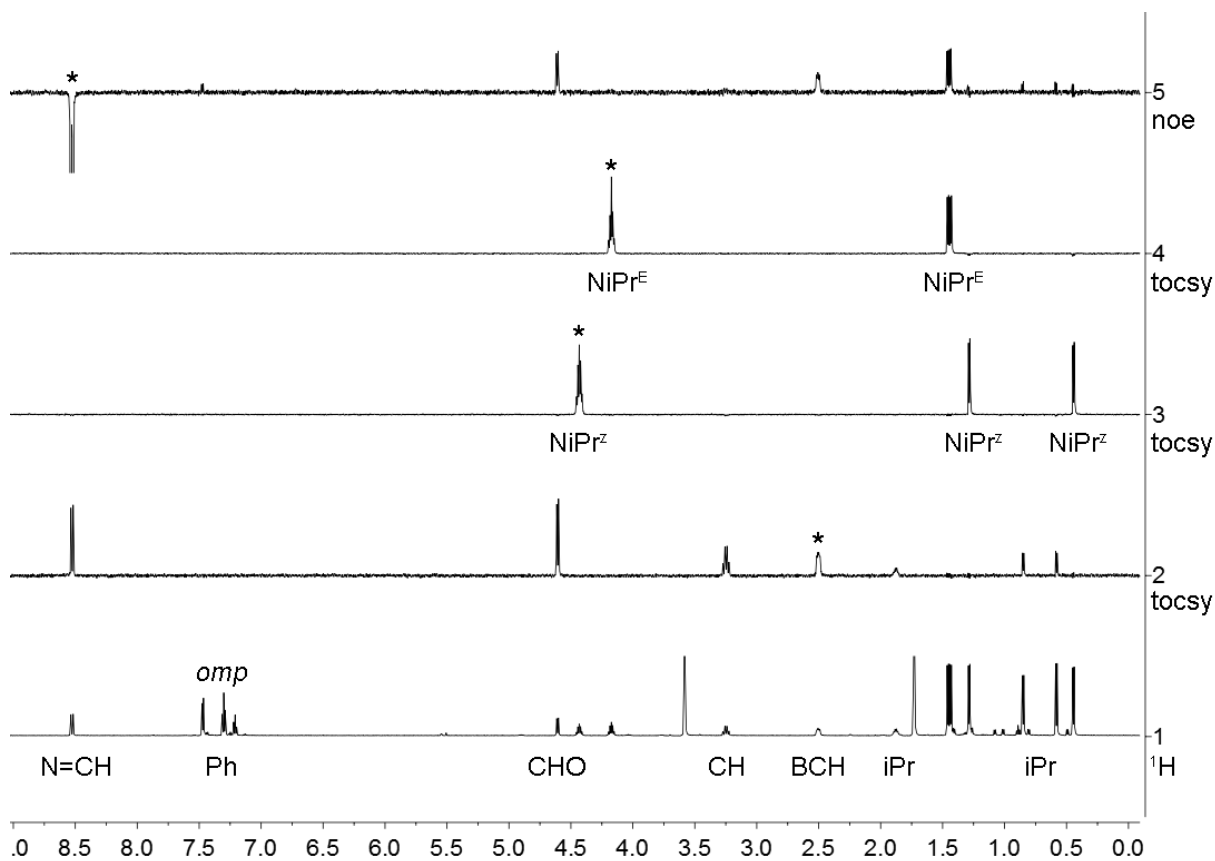
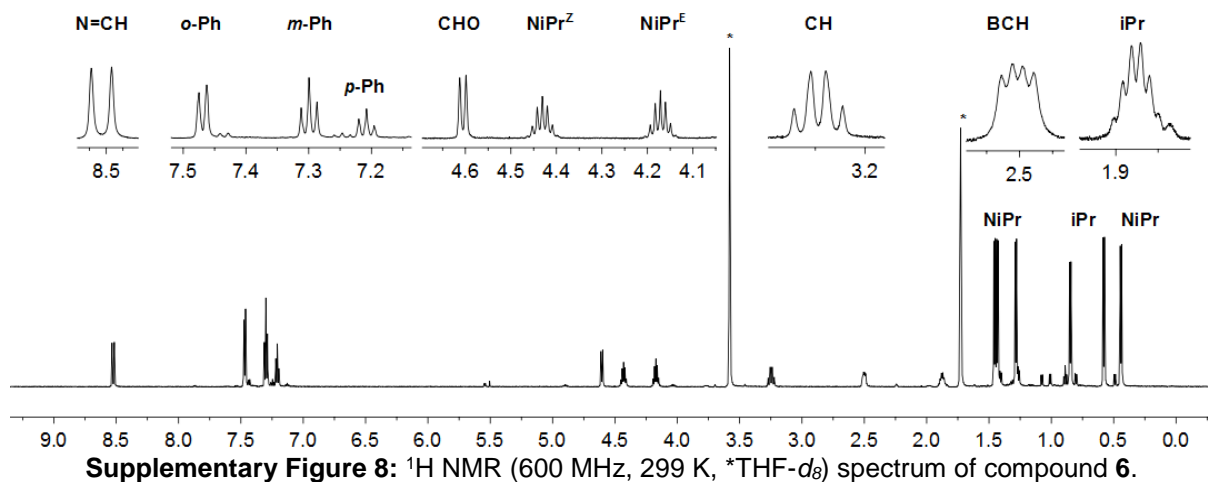
¹H NMR (600 MHz, 299 K, THF-*d*₈): δ = 8.52 (d, ³J_{HH} = 10.9 Hz, 1H, N=CH), 7.47 (m, 2H, *o*-Ph), 7.30 (m, 2H, *m*-Ph), 7.21 (m, 1H, *p*-Ph), 4.61 (d, ³J_{HH} = 8.3 Hz, 1H, CHO), 4.43 (sept, ³J_{HH} = 6.6 Hz, 1H), 1.28, 0.44 (each d, ³J_{HH} = 6.6 Hz, each 3H)(NiPr^Z), 4.17 (sept, ³J_{HH} = 6.7 Hz, 1H), 1.46, 1.43 (each d, ³J_{HH} = 6.7 Hz, each 3H)(NiPr^E), 3.25 (ddd, ³J_{HH} = 10.9, 9.7, 8.3 Hz, 1H, CH), 2.50 (dd, ³J_{HH} = 9.7, 5.1 Hz, 1H, BCH), 1.88 (m, 1H), 0.85, 0.58 (each d, ³J_{HH} = 6.8 Hz, each 3H)(iPr).

¹³C{¹H} NMR (151 MHz, 299 K, THF-*d*₈): δ = 184.2 (br, N=CH), 145.0 (*i*-Ph), 129.0 *p*-Ph), 128.5 (*m*-Ph), 127.6 (*p*-Ph), 84.7 (CHO), 59.4 (CH), 57.3, 18.7, 18.4 (NiPr^Z), 54.3, 24.1, 22.8 (NiPr^E), 54.3 (br, BCH), 30.0, 26.7, 22.5 (iPr), [C₆F₅ not listed].

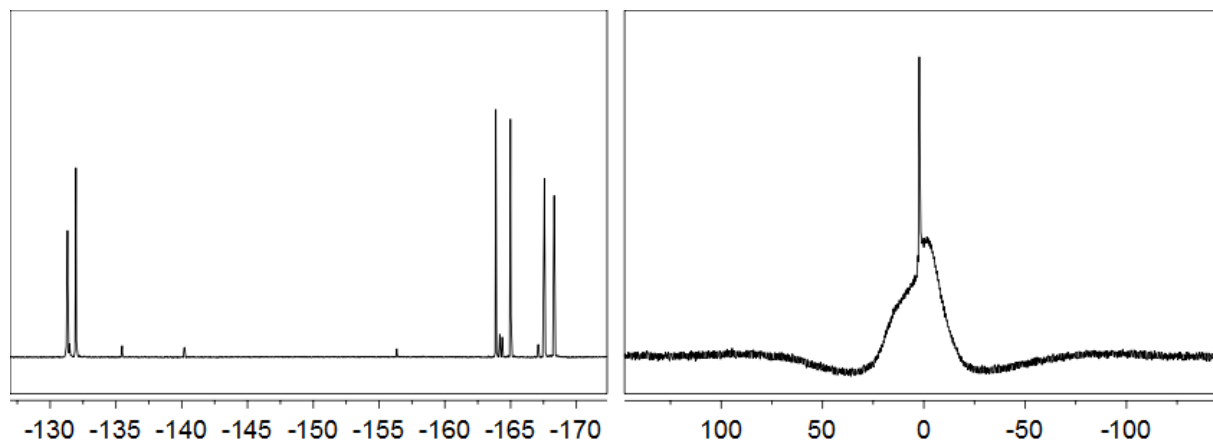
¹¹B{¹H} NMR (192 MHz, 299 K, THF-*d*₈): δ = 2.2 ($\nu_{1/2} \approx 60$ Hz).

¹¹B NMR (192 MHz, 299 K, THF-*d*₈): δ = 2.2 ($\nu_{1/2} \approx 60$ Hz).

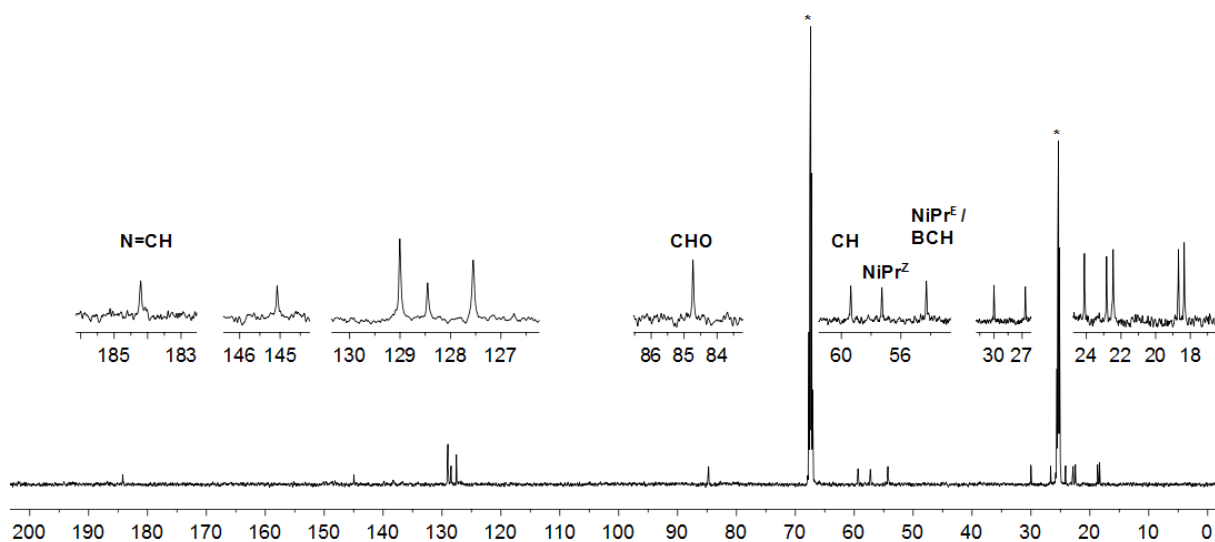
¹⁹F NMR (564 MHz, 299 K, THF-*d*₈): δ = -131.3 (m, 2F, *o*), -165.0 (t, ³J_{FF} = 20.2 Hz, 1F, *p*), -168.3 (m, 2F, *m*), (C₆F₅) [$\Delta\delta^{19}\text{F}_{pm}$ = 3.3], -131.9 (m, 2F, *o*), -163.9 (t, ³J_{FF} = 20.0 Hz, 1F, *p*), -167.6 (m, 2F, *m*), (C₆F₅) [$\Delta\delta^{19}\text{F}_{pm}$ = 3.7].



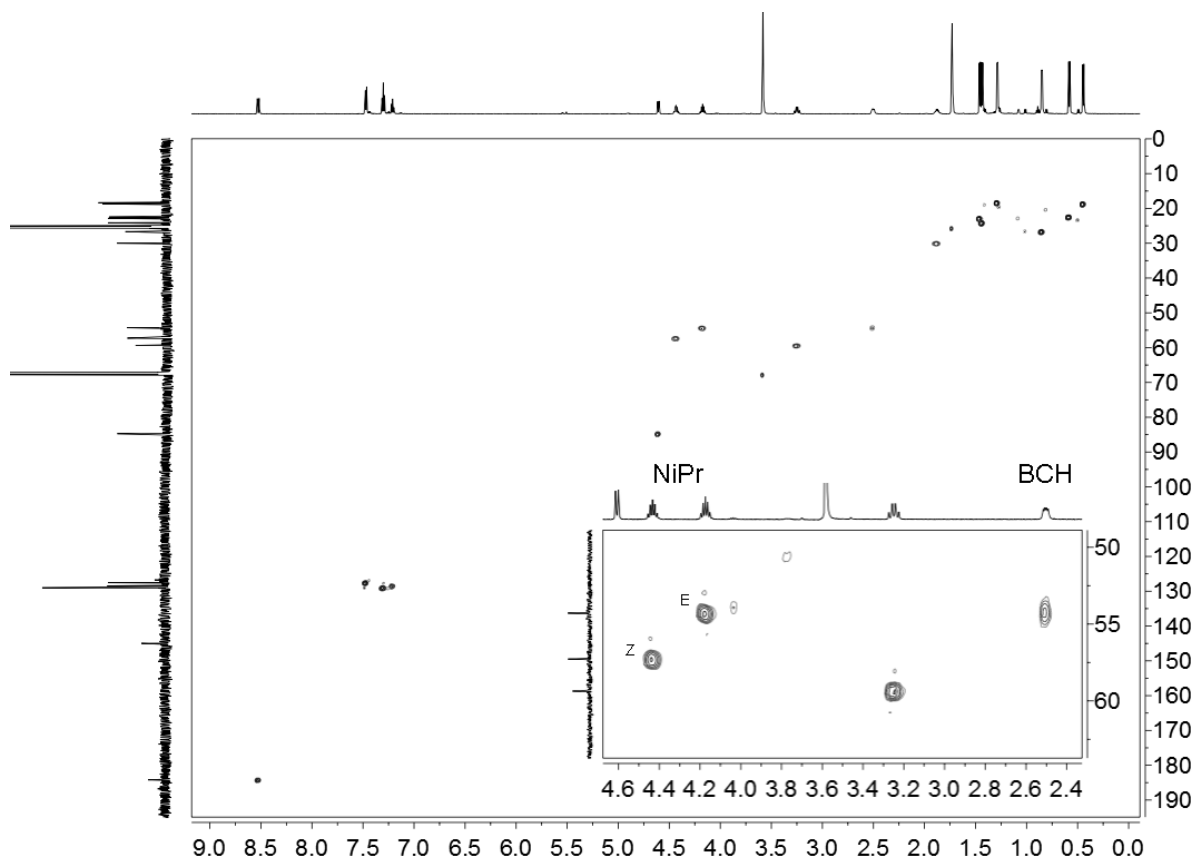
Supplementary Figure 9: (1) ^1H NMR (600 MHz, 299 K, $^*\text{THF-}d_8$), (2 to 4) $^1\text{H}\{^1\text{H}\}$ TOCSY [* irradiation points: (2) $\delta^1\text{H}$ 2.50 (BCH), (3) $\delta^1\text{H}$ 4.43 (NiPr^Z), (4) $\delta^1\text{H}$ 4.17 (NiPr^E)] and (5) $^1\text{H}\{^1\text{H}\}$ NOE [* irradiation point: (5) $\delta^1\text{H}$ 8.52 (N=CH)] spectra of compound **6**.



Supplementary Figure 10: ^{19}F NMR (564 MHz, 299 K, $\text{THF-}d_8$) and $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, 299 K, $\text{THF-}d_8$) spectra of compound **6**.



Supplementary Figure 11: $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 299 K, $^*\text{THF-}d_8$) spectrum of compound **6**.

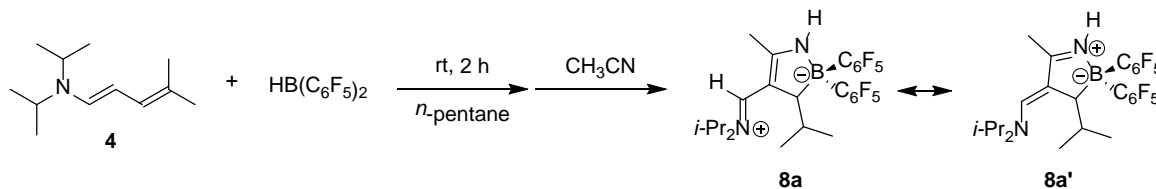


Supplementary Figure 12: ^1H , ^{13}C GHSQC (600 MHz / 151 MHz, 299 K, $\text{THF-}d_8$) spectrum of compound **6**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated solution of the isolated orange solid in pentane at $-36\text{ }^\circ\text{C}$.

X-ray crystal structure analysis of compound 6: formula $\text{C}_{31}\text{H}_{30}\text{BF}_{10}\text{NO}$, $M = 633.37$, colourless crystal, $0.12 \times 0.10 \times 0.03\text{ mm}$, $a = 12.1576(2)$, $b = 14.5361(3)$, $c = 17.2807(3)\text{ \AA}$, $\beta = 110.285(1)^\circ$, $V = 2864.5(1)\text{ \AA}^3$, $\rho_{\text{calc}} = 1.469\text{ g cm}^{-3}$, $\mu = 0.133\text{ mm}^{-1}$, empirical absorption correction ($0.984 \leq T \leq 0.996$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073\text{ \AA}$, $T = 223(2)\text{ K}$, ω and φ scans, 16995 reflections collected ($\pm h, \pm k, \pm l$), 5768 independent ($R_{\text{int}} = 0.038$) and 4354 observed reflections [$>2\sigma(I)$], 403 refined parameters, $R = 0.058$, $wR^2 = 0.113$, max. (min.) residual electron density 0.26 (-0.21) e.\AA^{-3} , hydrogen atoms were calculated and refined as riding atoms.

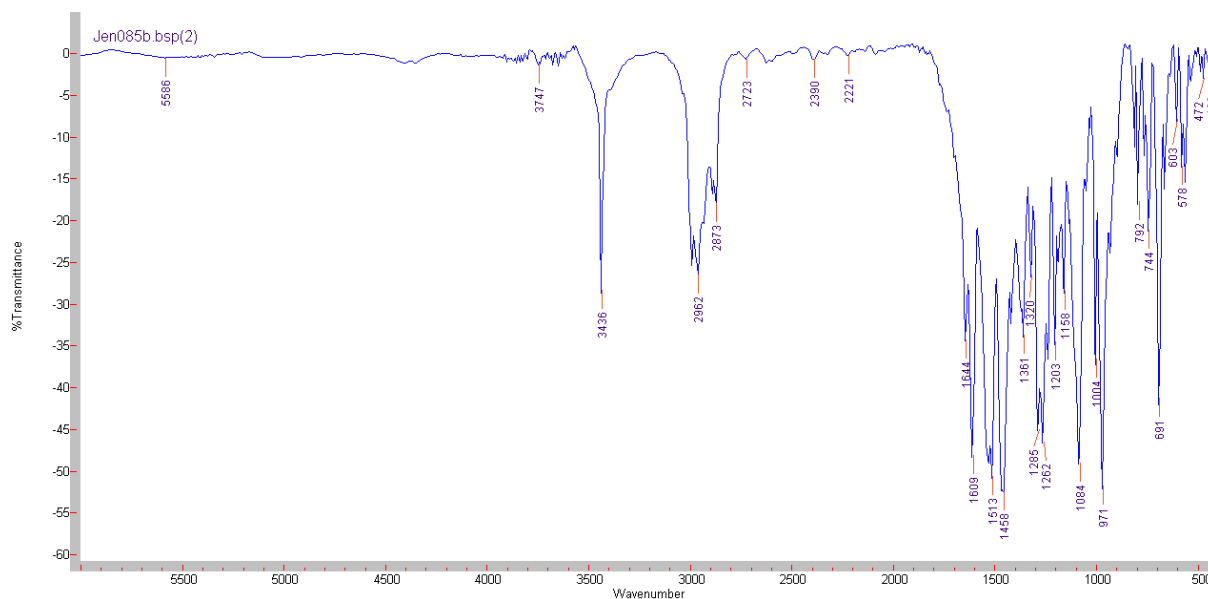
4.4 Preparation of compound 8a/8a'



Supplementary Scheme 4.

(*E*)-*N,N*-diisopropyl-4-methyl-1,3-pentadien-1-amine (**4**) (181 mg, 1.00 mmol, 1.00 eq.) was dissolved in *n*-pentane (2 mL) and added to a suspension of bis(pentafluorophenyl)borane (346 mg, 1.00 mmol, 1.00 eq.) in pentane (6 mL). The yellow solution was stirred for 2 h at room temperature, then acetonitrile (45.2 mg, 1.10 mmol, 1.10 eq.) in *n*-pentane (2 mL) was added and the reaction mixture was stirred overnight. The formed precipitate was separated via cannula filtration, washed with pentane (3 x 2 mL) and dried *in vacuo* to give compound **8a/8a'** as a yellow solid (325 mg, 0.57 mmol, 57%).

IR (KBr): $\tilde{\nu}$ = 3436 (m), 2962 (m), 2873 (w), 1644 (m), 1609 (s), 1531 (s), 1458 (s), 1361 (m), 1320 (m), 1285 (s), 1262 (s), 1203 (m), 1158 (w), 1084 (s), 971 (s), 792 (w), 744(w), 691 (s), 578 (w).



Supplementary Figure 14: IR spectrum of compound **8a/8a'**.

Elemental analysis: calcd. (%) for C₂₆H₂₇BF₁₀N₂: C 54.95, H 4.79, N 4.93; found: C 55.03, H 4.55, N 4.77.

Melting point: 203 °C

Decomposition point: 277 °C

¹H NMR (500 MHz, 253 K, C₇D₈): δ = 7.30 (br s, 1H, NH), 6.58 (br s, 1H, =CH), 4.83 (br sept, ³J_{HH} = 6.5 Hz, 1H), 0.89, 0.69 (each d, ³J_{HH} = 6.5 Hz, each 3H)(NiPr), 3.42 (s, 1H, BCH), 2.70 (br sept, ³J_{HH} =

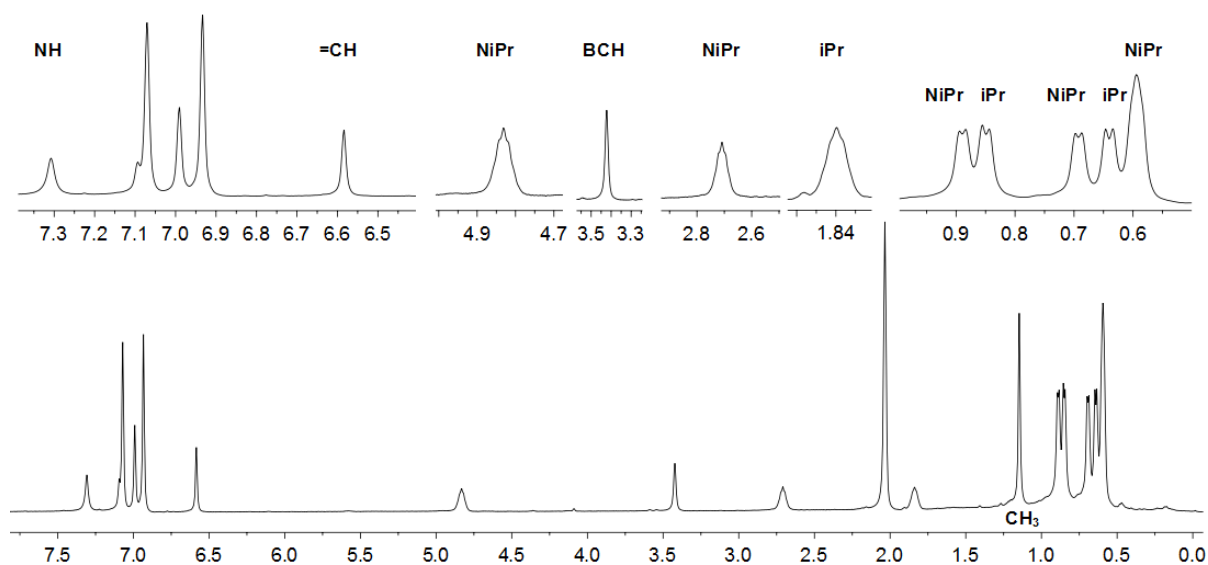
5.9 Hz, 1H), 0.58, 0.59 (each br d, $^3J_{\text{HH}} = 5.9$ Hz, each 3H)(NiPr), 1.83 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 1H), 0.85, 0.64 (each d, $^3J_{\text{HH}} = 6.7$ Hz, each 3H)(iPr), 1.14 (s, 3H, CH₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 253 K, C₇D₈): $\delta = 179.8$ (MeC=), 142.2 (=CH), 110.8 (=C), 48.8, 19.8, 19.1 (NiPr), 45.9, 23.8, 22.9 (NiPr), 37.9 (br, BCH), 32.8, 23.6, 19.3 (iPr), 15.2 (CH₃) [C₆F₅ not listed].

$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 253 K, C₇D₈): $\delta = -3.1$ ($\nu_{1/2} \approx 350$ Hz).

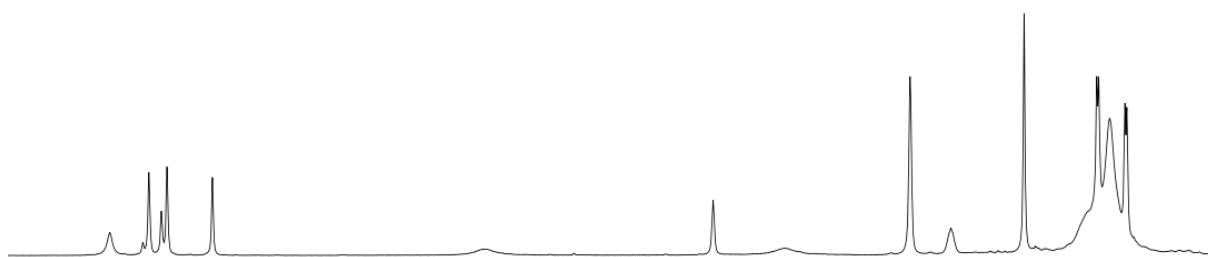
^{11}B NMR (160 MHz, 253 K, C₇D₈): $\delta = -3.1$ ($\nu_{1/2} \approx 350$ Hz).

^{19}F NMR (470 MHz, 253 K, C₇D₈): $\delta = -132.1$ (br, *o*), -137.5 (m, *o*), -159.2 (t, $^3J_{\text{FF}} = 20.7$ Hz, *p*), -163.7 (m, *m'*), -163.9 (m, *m*), (each 1F, C₆F₅) [$\Delta\delta^{19}\text{F}_{\text{pm}} = 4.5, 4.7$], -135.2 (m, 2F, *o*), -159.6 (t, $^3J_{\text{FF}} = 20.9$ Hz, 1F, *p*), -164.4 (m, 2F, *m*), (C₆F₅) [$\Delta\delta^{19}\text{F}_{\text{pm}} = 4.8$].

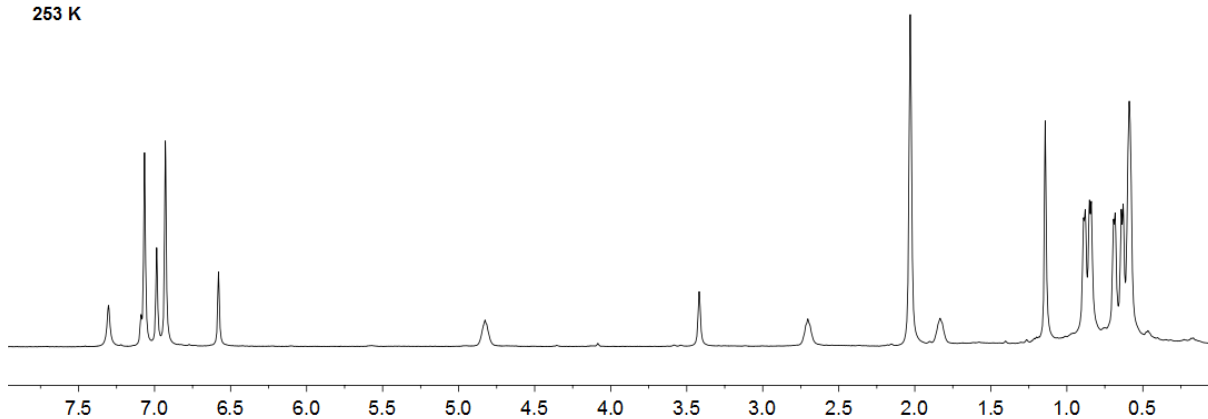


Supplementary Figure 15: ^1H NMR (500 MHz, 253 K, C₇D₈) spectrum of compound **8a/8a'**.

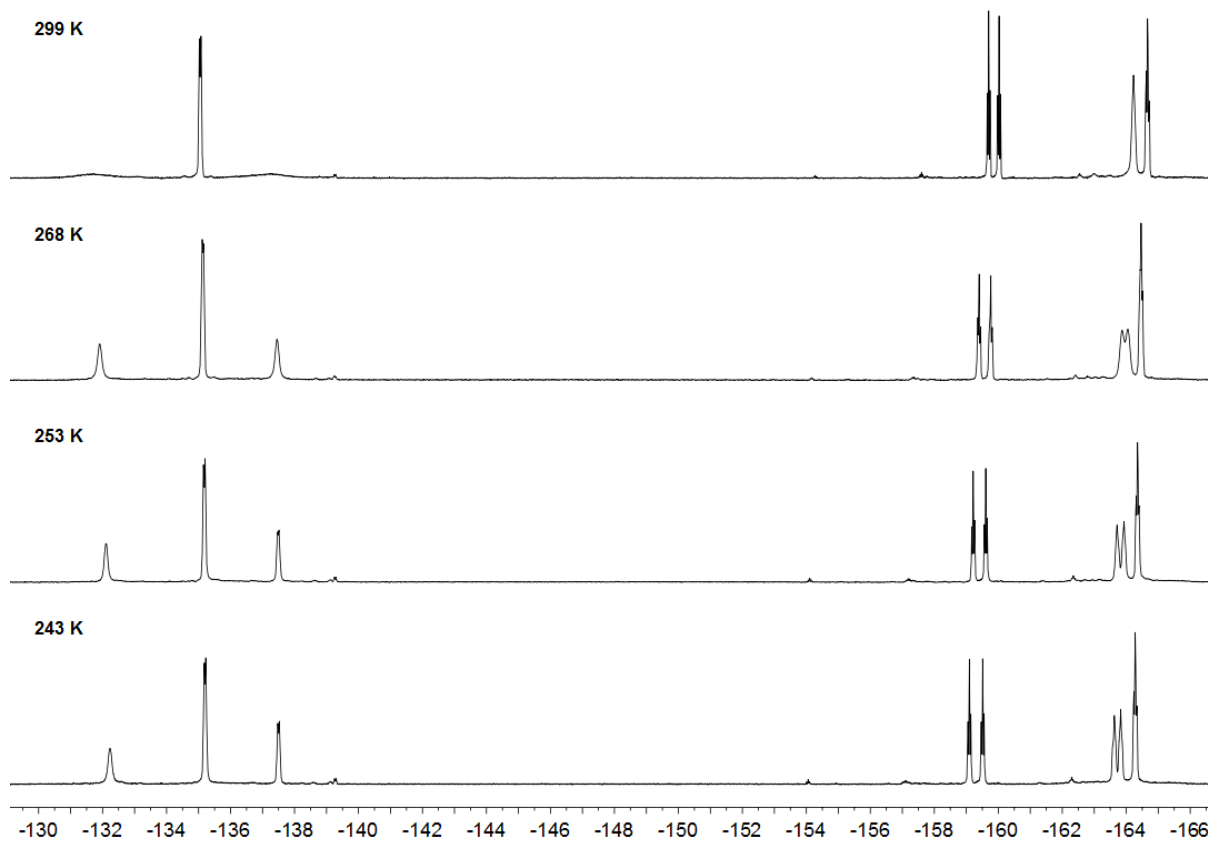
299 K



253 K



Supplementary Figure 16 ^1H NMR (500 MHz, C_7D_8) spectrum of compound **8a/8a'** at variable temperature



Supplementary Figure 17: ^{19}F NMR (470 MHz, C_7D_8) spectra of compound **8a/8a'** at variable temperature.

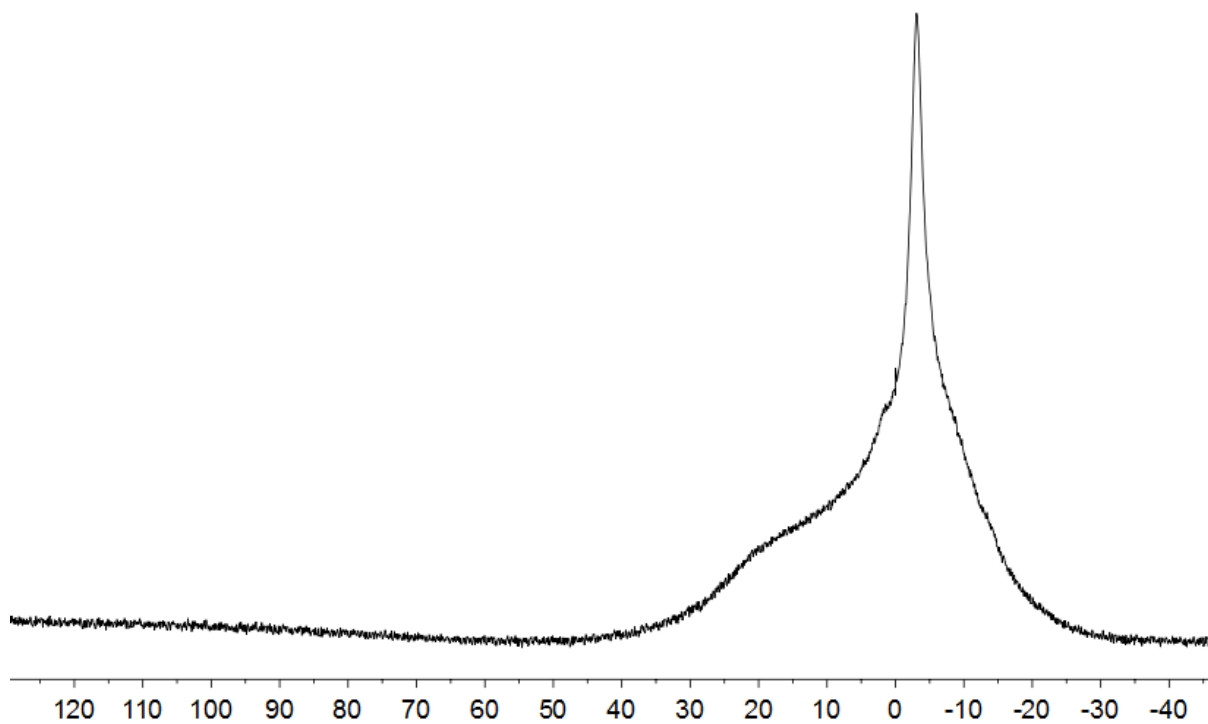
$$\Delta G^\ddagger[T_c, \Delta\nu(T)] = RT_c(22.96 + \ln(T_c/\Delta\nu)) \text{ [J/mol]}$$

T_c = coalescence temperature [K]: 284 K (^{19}F , m- BC_6F_5)

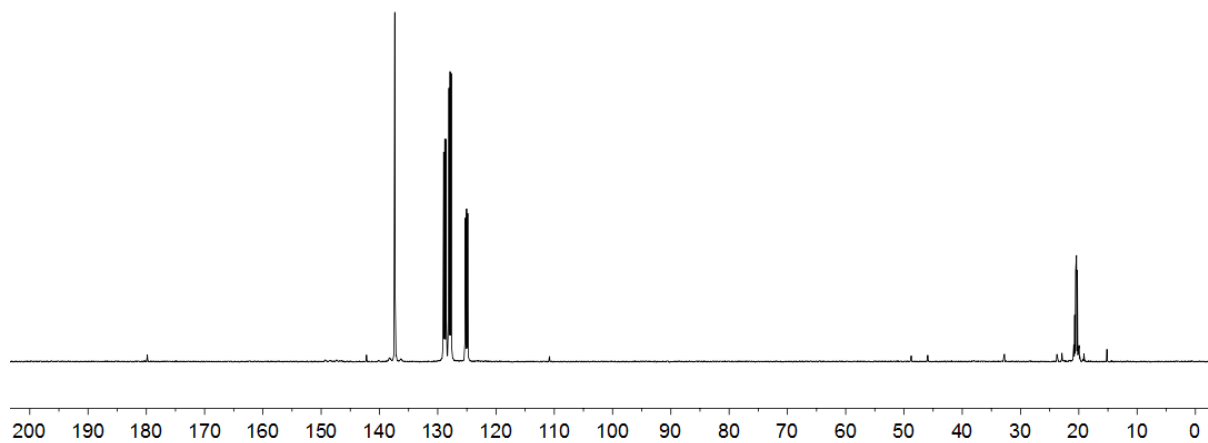
$\Delta\nu$ = chemical shift difference [Hz] (^{19}F , m- BC_6F_5 , 243 K): 94 Hz

$R = 8.134 \text{ J/(mol}\cdot\text{K)}$; $J = 0.239 \text{ cal}$

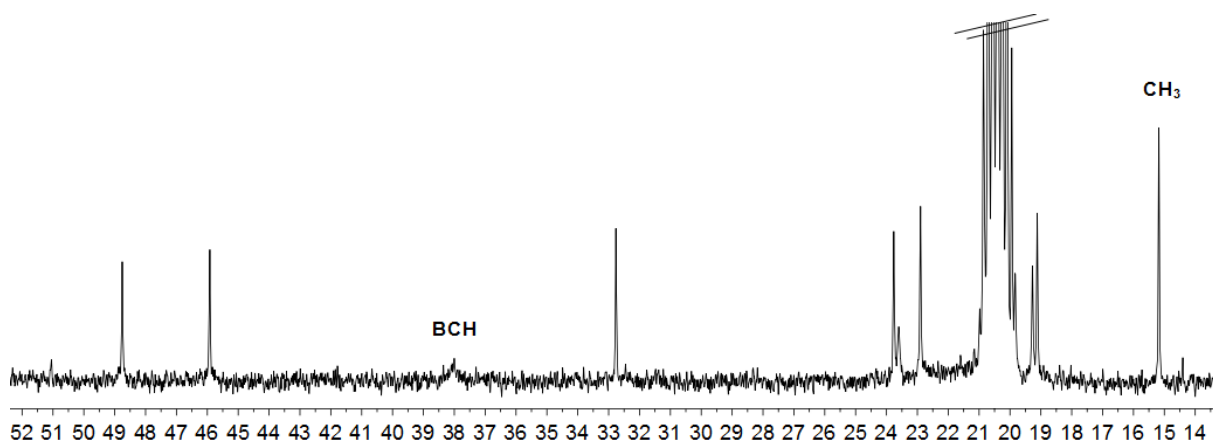
$$\Delta G^\ddagger[284 \text{ K}, \Delta\nu(243 \text{ K}) = 94 \text{ Hz}] = 56823 \text{ J/mol} = 13.6 \pm 0.7 \text{ kcal/mol}$$



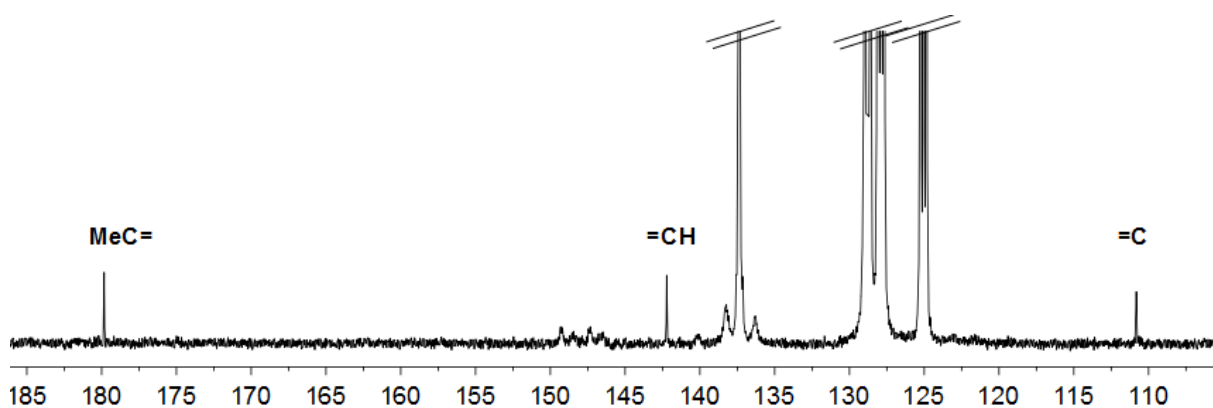
Supplementary Figure 18: $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 253 K, C_7D_8) spectrum of compound **8a/8a'**.



Supplementary Figure 19: $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 253 K, C_7D_8) spectrum of compound **8a/8a'**.



Supplementary Figure 20: $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 253 K, C_7D_8) spectrum of compound **8a/8a'**.

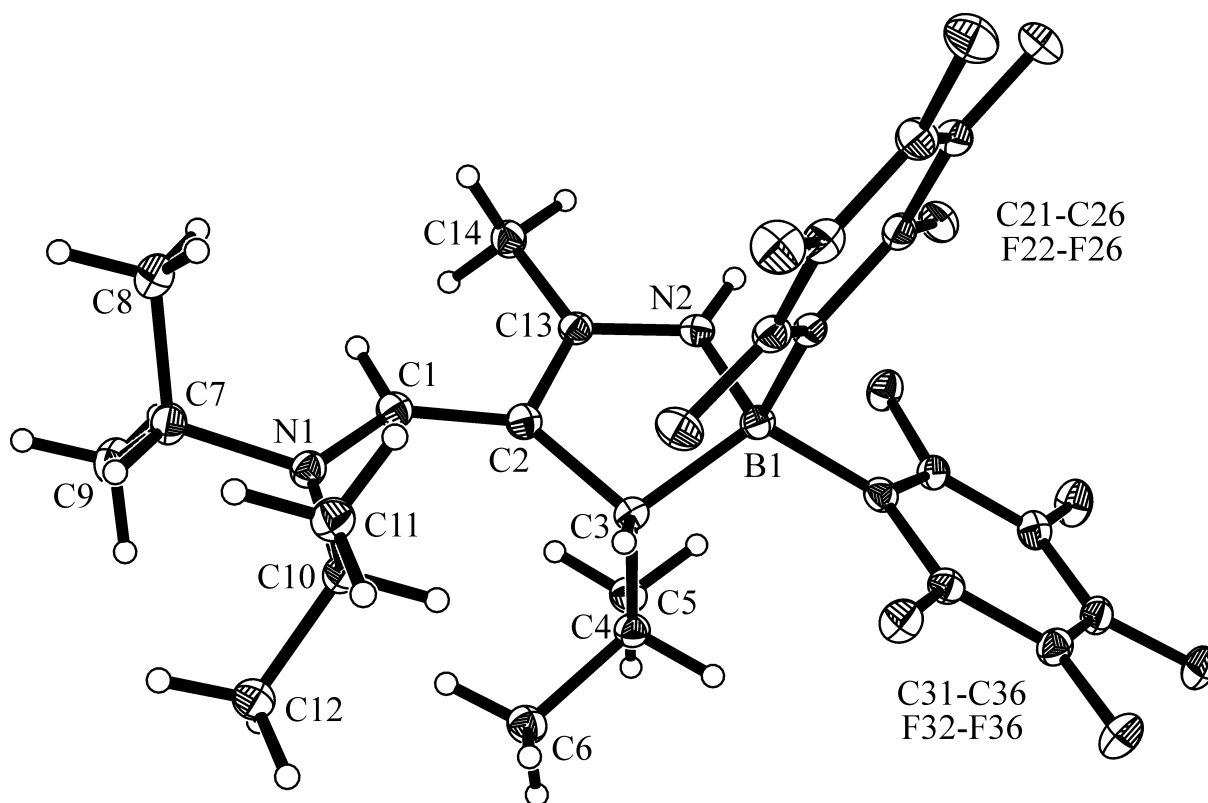


Supplementary Figure 21: $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 253 K, C_7D_8) spectrum of compound **8a/8a'**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated solution of compound **8a/8a'** in toluene at $-36\text{ }^\circ\text{C}$.

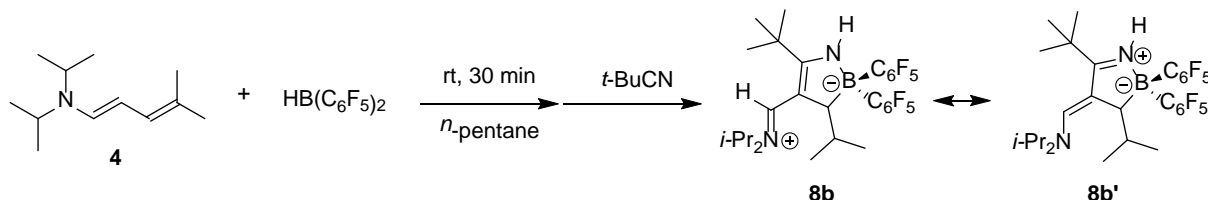
X-ray crystal structure analysis of compound 8a': A colorless prism-like specimen of $\text{C}_{26}\text{H}_{27}\text{BF}_{10}\text{N}_2$, approximate dimensions $0.090\text{ mm} \times 0.110\text{ mm} \times 0.180\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1741 frames were collected. The total exposure time was 37.94 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 56643 reflections to a maximum θ angle of 66.60° (0.84 \AA resolution), of which 4480 were independent (average redundancy 12.644, completeness = 99.9%, $R_{\text{int}} = 9.80\%$, $R_{\text{sig}} = 5.47\%$) and 3248 (72.50%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 13.7685(6)\text{ \AA}$, $b = 17.4146(7)\text{ \AA}$, $c = 21.1352(8)\text{ \AA}$, volume = $5067.6(4)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 7512 reflections above $20\sigma(I)$ with $8.367^\circ < 2\theta < 133.4^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.870. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8100 and 0.8980. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Pbca , with $Z = 8$ for the formula unit, $\text{C}_{26}\text{H}_{27}\text{BF}_{10}\text{N}_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 363 variables converged at $R_1 = 4.62\%$, for the observed data and $wR_2 = 12.59\%$ for all data. The goodness-of-fit was 1.042. The largest peak in the final difference electron density synthesis was $0.242\text{ e}^-/\text{\AA}^3$ and the

largest hole was $-0.289 \text{ e}/\text{\AA}^3$ with an RMS deviation of $0.059 \text{ e}/\text{\AA}^3$. On the basis of the final model, the calculated density was $1.490 \text{ g}/\text{cm}^3$ and $F(000)$, 2336 e.



Supplementary Figure 22.

4.5 Preparation of compound 8b/8b'



Supplementary Scheme 5.

(E)-N,N-diisopropyl-4-methyl-1,3-pentadien-1-amine (**4**) (181.4 mg, 1.00 mmol, 1.00 eq.) was dissolved in *n*-pentane (2 mL) and added to a suspension of bis(pentafluorophenyl)borane (346 mg, 1.00 mmol, 1.00 eq.) in pentane (6 mL). The yellow solution was stirred for 30 min at room temperature, pivalonitrile (91.4 mg, 1.00 mmol, 1.00 eq.) in *n*-pentane (2 mL) was added and the reaction mixture was stirred overnight. The formed precipitate was separated via cannula filtration and dried *in vacuo* to give compound **8b/8b'** as a white solid which was purified by crystallisation from pentane (253 mg, 0.41 mmol, 41%).

IR (KBr): $\bar{\nu}$ = 3459 (m), 2963 (m), 2872 (w), 1612 (s), 1537 (s), 1460 (s), 1405 (m), 1356 (m), 1280 (s), 1171 (m), 1099 (s), 970 (s), 760 (m), 681 (w), 610 (w), 530 (w), 419 (w).

Elemental analysis: calcd. (%) for $\text{C}_{26}\text{H}_{27}\text{BF}_{10}\text{N}_2$: C 57.06, H 5.45, N 4.59; found: C 57.21, H 5.54, N 4.44.

Melting point: 166 °C

Decomposition point: 299 °C

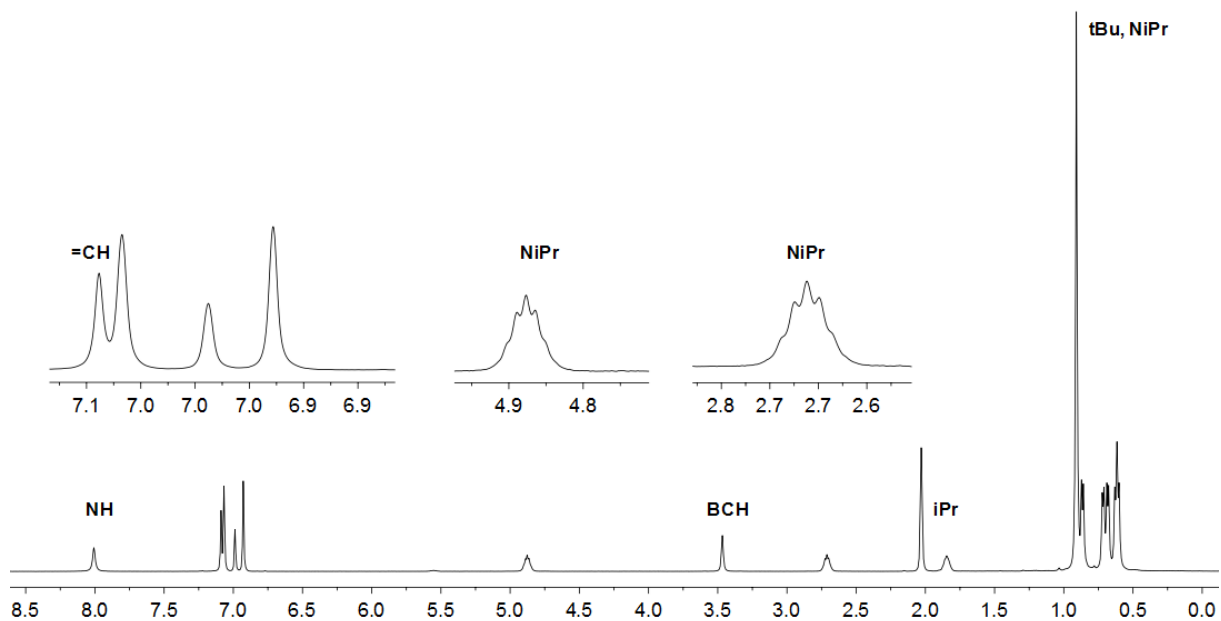
^1H NMR (500 MHz, 248 K, C_7D_8): δ = 8.01 (br s, 1H, NH), 7.09 (s, 1H, =CH), 4.88 (br sept, $^3J_{\text{HH}} = 6.6$ Hz, 1H), 0.91, 0.72 (each br d, $^3J_{\text{HH}} = 6.6$ Hz, each 3H)(NiPr), 3.47 (s, 1H, BCH), 2.71 (br sept, $^3J_{\text{HH}} = 6.6$ Hz, 1H), 0.62, 0.61 (each br d, $^3J_{\text{HH}} = 6.6$ Hz, each 3H)(NiPr), 1.85 (br sept, $^3J_{\text{HH}} = 6.7$ Hz, 1H), 0.87, 0.68 (each br d, $^3J_{\text{HH}} = 6.8$ Hz, each 3H)(iPr), 0.91 (s, 9H, tBu).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 248 K, C_7D_8): δ = 189.5 (tBuC=), 143.1 (=CH), 108.7 (=C), 48.5, 19.8 (br), 19.3 (NiPr), 46.0, 24.0, 23.1 (NiPr), 38.9 (br, BCH), 35.6, 29.6 (tBu), 32.8, 23.0 (br), 20.0 (iPr), [C_6F_5 not listed].

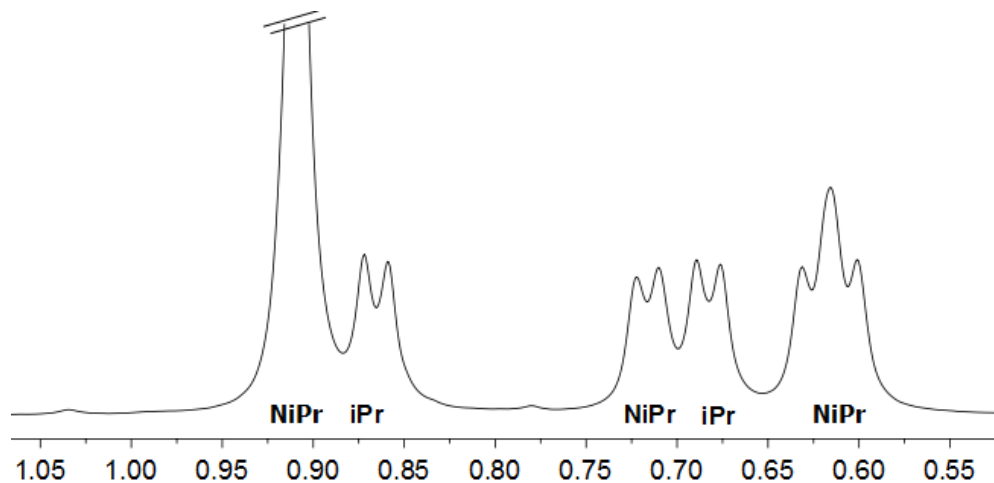
$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 248 K, C_7D_8): δ = -3.6 ($\nu_{1/2} \approx 350$ Hz).

^{11}B NMR (160 MHz, 248 K, C_7D_8): δ = -3.6 ($\nu_{1/2} \approx 350$ Hz).

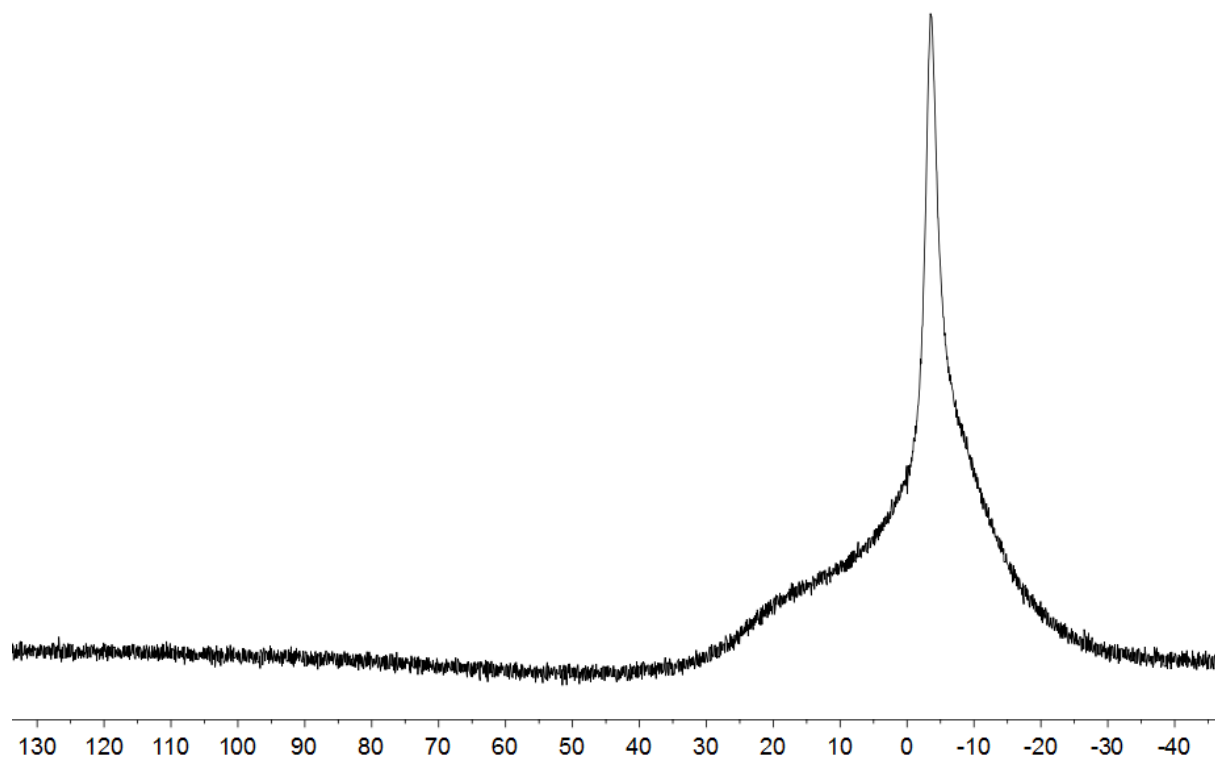
^{19}F NMR (470 MHz, 248 K, C_7D_8): δ = -131.4 (br, o), -138.0 (m, o), -159.0 (t, $^3J_{\text{FF}} = 20.1$ Hz, p), -163.6 (br m, m'), -163.8 (br m, m), (each 1F, C_6F_5) [$\Delta\delta^{19}\text{F}_{\text{pm}} = 4.6, 4.8$], -135.4 (m, 2F, o), -159.4 (t, $^3J_{\text{FF}} = 21.1$ Hz, 1F, p), -164.2 (m, 2F, m), (C_6F_5) [$\Delta\delta^{19}\text{F}_{\text{pm}} = 4.8$].



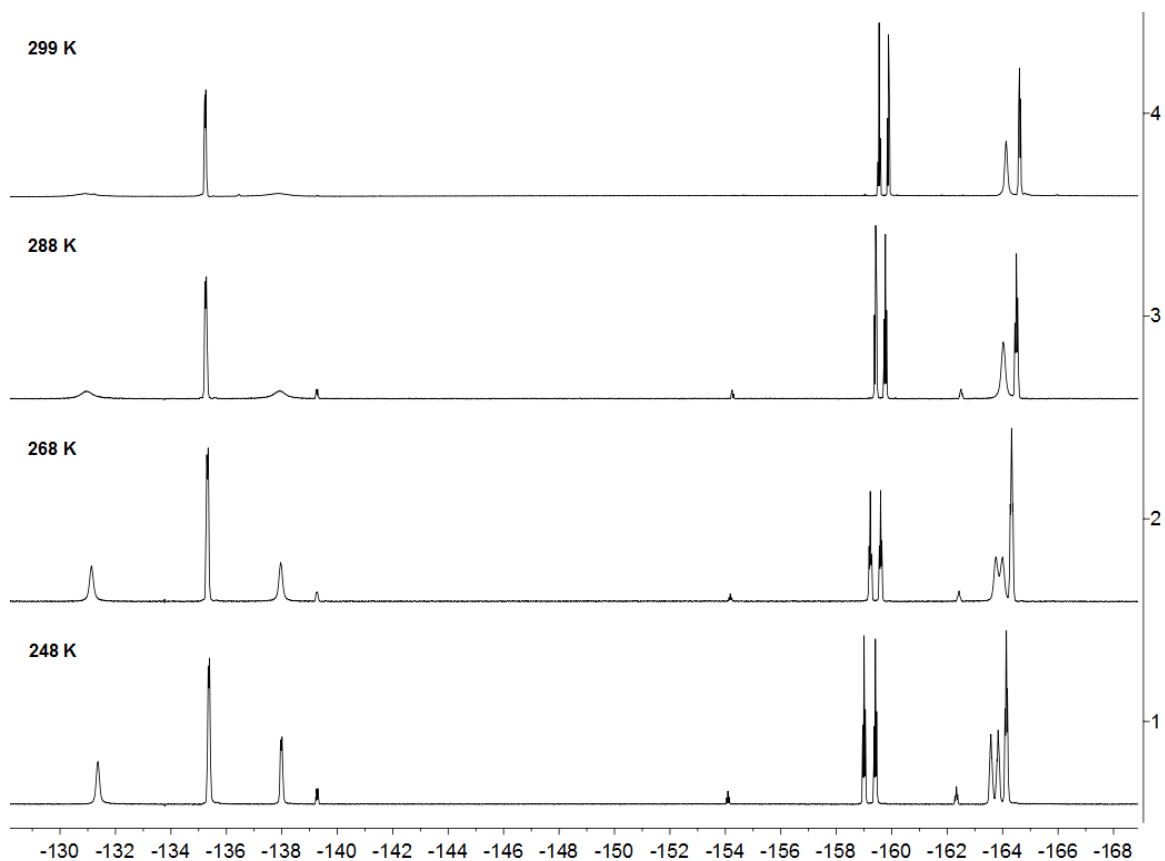
Supplementary Figure 23: ^1H NMR (500 MHz, 248 K, C_7D_8) spectrum of compound **8b/8b'**.



Supplementary Figure 24: ^1H NMR (500 MHz, 248 K, C_7D_8) spectrum of compound **8b/8b'**.



Supplementary Figure 25: $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 248 K, C_7D_8) spectrum of compound **8b/8b'**.



Supplementary Figure 26: ^{19}F NMR (470 MHz, C_7D_8) spectrum of compound **8b/8b'** at variable temperature.

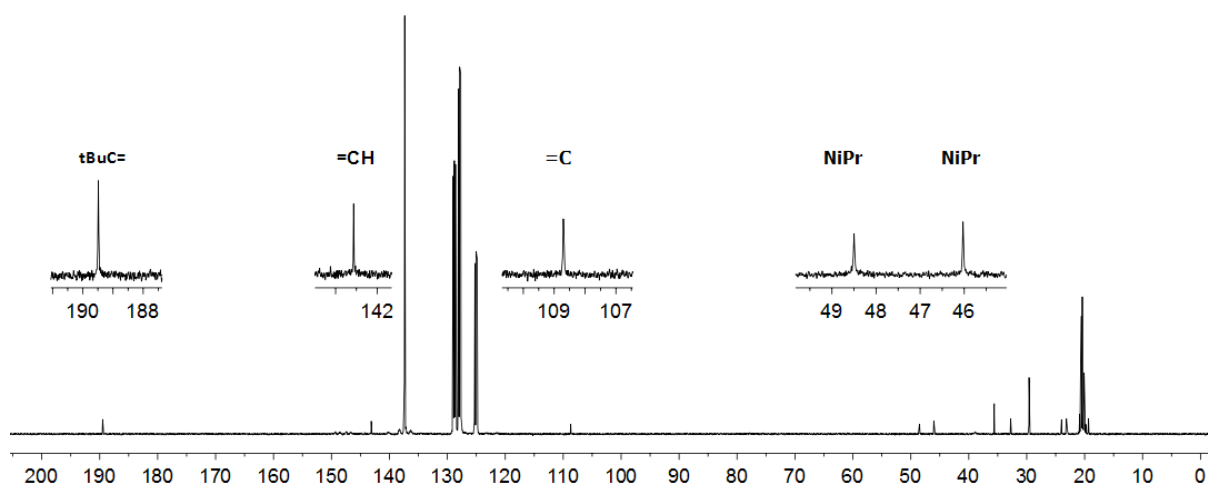
$$\Delta G^\ddagger[T_c, \Delta v(T)] = RT_c(22.96 + \ln(T_c / \Delta v)) \text{ [J/mol]}$$

T_c = coalescence temperature [K]: 278 K (^{19}F , m- BC_6F_5)

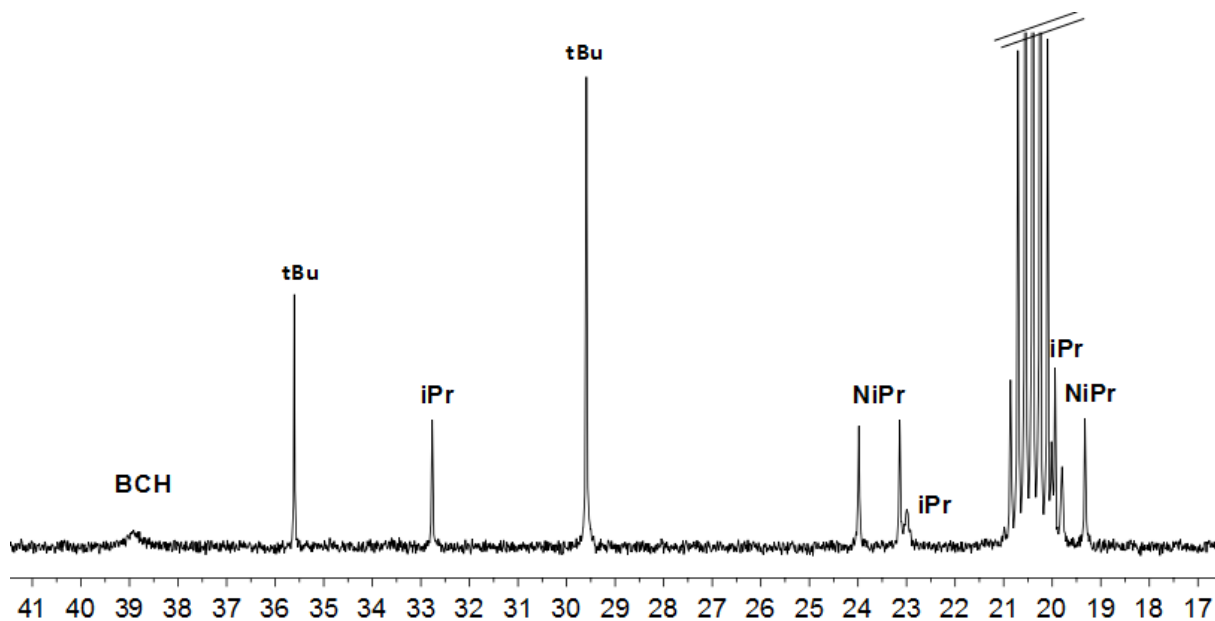
Δv = chemical shift difference [Hz] (^{19}F , m- BC_6F_5 , 248 K): 118 Hz

$R = 8.134 \text{ J}/(\text{mol}\cdot\text{K})$; $J = 0.239 \text{ cal}$

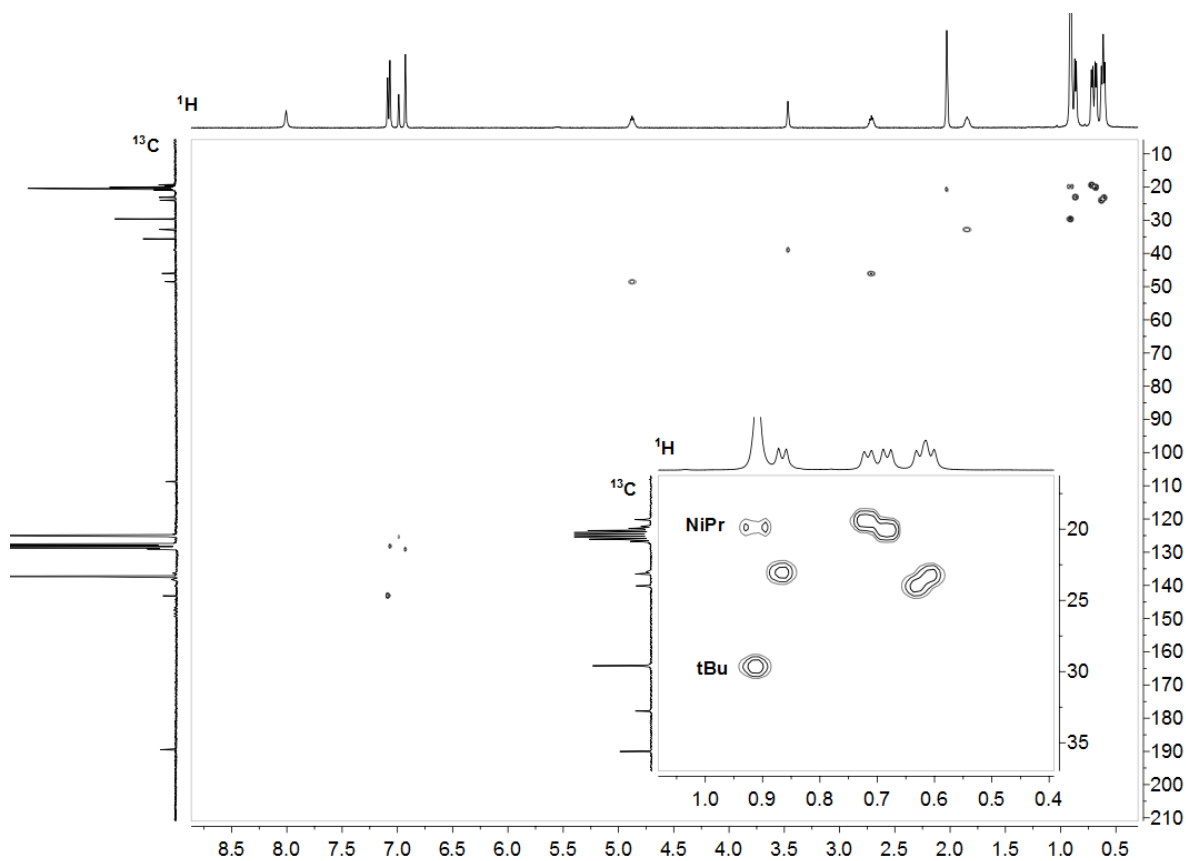
$$\Delta G^\ddagger[278 \text{ K}, \Delta v(248 \text{ K}) = 118 \text{ Hz}] = 53856 \text{ J/mol} = 12.9 \pm 0.4 \text{ kcal/mol}$$



Supplementary Figure 27: $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz, 248 K, C_7D_8) spectrum of compound **8b/8b'**.



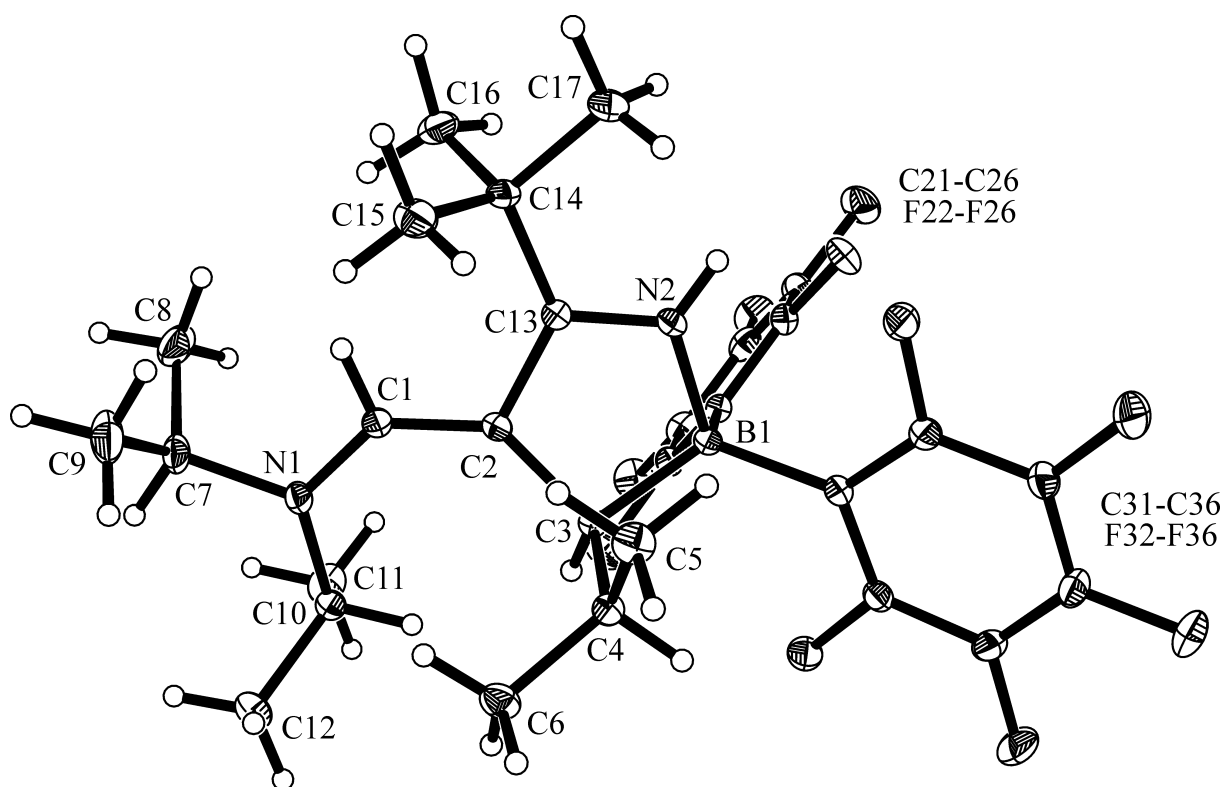
Supplementary Figure 28: $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 248 K, C_7D_8) spectrum of compound 8b/8b'.



Supplementary Figure 29: ^1H , ^{13}C GHSQC (500 MHz / 126 MHz, 248 K, C_7D_8) spectrum of compound 8b/8b'.

Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated solution of compound **8b/8b'** in pentane at -36 °C.

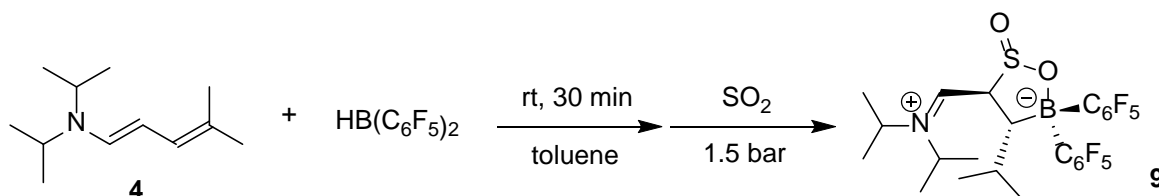
X-ray crystal structure analysis of compound 8b/8b': formula $C_{29}H_{33}BF_{10}N_2$, $M = 610.38$, colourless crystal, $0.19 \times 0.12 \times 0.04$ mm, $a = 9.3529(2)$, $b = 11.3606(3)$, $c = 14.1891(5)$ Å, $\alpha = 89.262(1)$, $\beta = 87.765(1)$, $\gamma = 79.985(2)^\circ$, $V = 1483.5(1)$ Å³, $\rho_{\text{calc}} = 1.366$ gcm⁻³, $\mu = 0.123$ mm⁻¹, empirical absorption correction ($0.976 \leq T \leq 0.995$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 13544 reflections collected ($\pm h, \pm k, \pm l$), 5116 independent ($R_{\text{int}} = 0.047$) and 3833 observed reflections [$>2\sigma(I)$], 392 refined parameters, $R = 0.068$, $wR^2 = 0.138$, max. (min.) residual electron density 0.23 (-0.24) e.Å⁻³, the hydrogen at N2 atom was refined freely; others were calculated and refined as riding atoms.



Supplementary Figure 30.

4.6 Preparation of compound 9 (*in situ* + crystals)

4.6.1 Reaction of compound 5/5' with SO₂: X-ray crystal structure analysis



Supplementary Scheme 6.

(*E*)-N,N-diisopropyl-4-methyl-1,3-pentadien-1-amine (**4**) (90.7 mg, 0.50 mmol, 1.00 eq.) was dissolved in toluene (2 mL) and added to a suspension of bis(pentafluorophenyl)borane (173 mg, 0.50 mmol, 1.00 eq.) in toluene (3 mL). The yellow solution was stirred for 30 min at room temperature, then the mixture was exposed to a SO₂ atmosphere (1.5 bar) and stirred overnight. The volume of the obtained red solution was reduced to one half in *vacuo*, then it was layered with pentane (2 mL) and stored at room temperature to finally give crystals suitable for the X-ray crystal structure analysis.

X-ray crystal structure analysis of compound 9: A colorless prism-like specimen of C₂₄H₂₄BF₁₀NO₂S, approximate dimensions 0.173 mm x 0.185 mm x 0.281 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 241 frames were collected. The total exposure time was 2.01 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 19934 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 4664 were independent (average redundancy 4.274, completeness = 99.8%, R_{int} = 5.15%, R_{sig} = 4.27%) and 4088 (87.65%) were greater than 2 σ (F²). The final cell constants of $a = 8.8586(4)$ Å, $b = 16.1993(6)$ Å, $c = 17.7505(7)$ Å, volume = 2547.25(18) Å³, are based upon the refinement of the XYZ-centroids of 7134 reflections above 20 σ (I) with 4.589° < 2 θ < 54.79°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.938. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9400 and 0.9620. The final anisotropic full-matrix least-squares refinement on F² with 358 variables converged at R1 = 3.31%, for the observed data and wR2 = 6.82% for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 0.213 e/Å³ and the largest hole was -0.252 e/Å³ with an RMS deviation of 0.047 e/Å³. On the basis of the final model, the calculated density was 1.542 g/cm³ and F(000), 1208 e⁻.

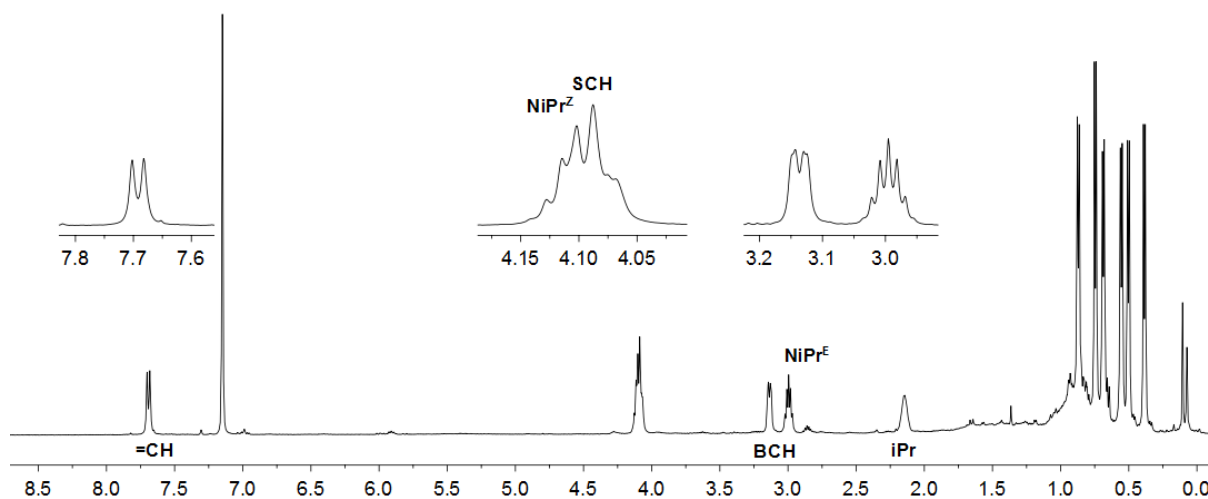
¹H NMR (500 MHz, 299 K, C₆D₆): δ = 7.69 (d, ³J_{HH} = 10.9 Hz, 1H, =CH), 4.10 (m, 1H), 0.69, 0.50 (each d, ³J_{HH} = 6.6 Hz, each 3H)(NiPr^Z), 4.09 (m, 1H, SCH), 3.14 (dd, ³J_{HH} = 9.8, 2.7 Hz, 1H, BCH), 2.99 (sept, ³J_{HH} = 6.6 Hz, 1H), 0.75, 0.55 (each d, ³J_{HH} = 6.6 Hz, each 3H)(NiPr^E), 2.15 (br m, 1H), 0.87, 0.39 (each d, ³J_{HH} = 6.6 Hz, each 3H)(iPr).

¹³C{¹H} NMR (126 MHz, 299 K, C₆D₆): δ = 182.1 (=CH), 71.6 (br, SCH), 57.1, 19.5, 17.9 (NiPr^Z), 54.6, 23.7, 22.0 (NiPr^E), 44.6 (BCH), 28.0, 26.4, 20.7 (iPr), [C₆F₅: not listed].

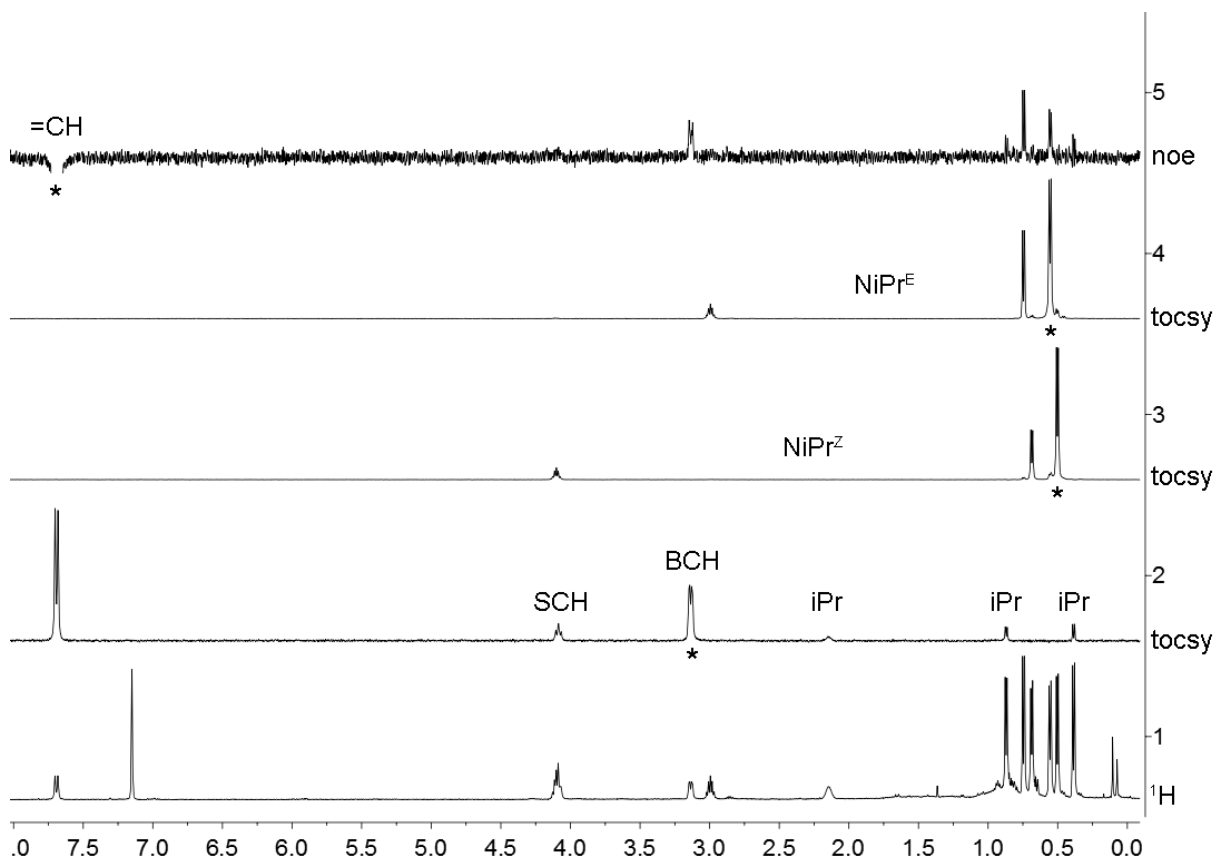
¹¹B{¹H} NMR (160 MHz, 299 K, C₆D₆): δ = 9.3 (ν_{1/2} ≈ 400 Hz).

¹¹B NMR (160 MHz, 299 K, C₆D₆): δ = 9.3 (ν_{1/2} ≈ 400 Hz).

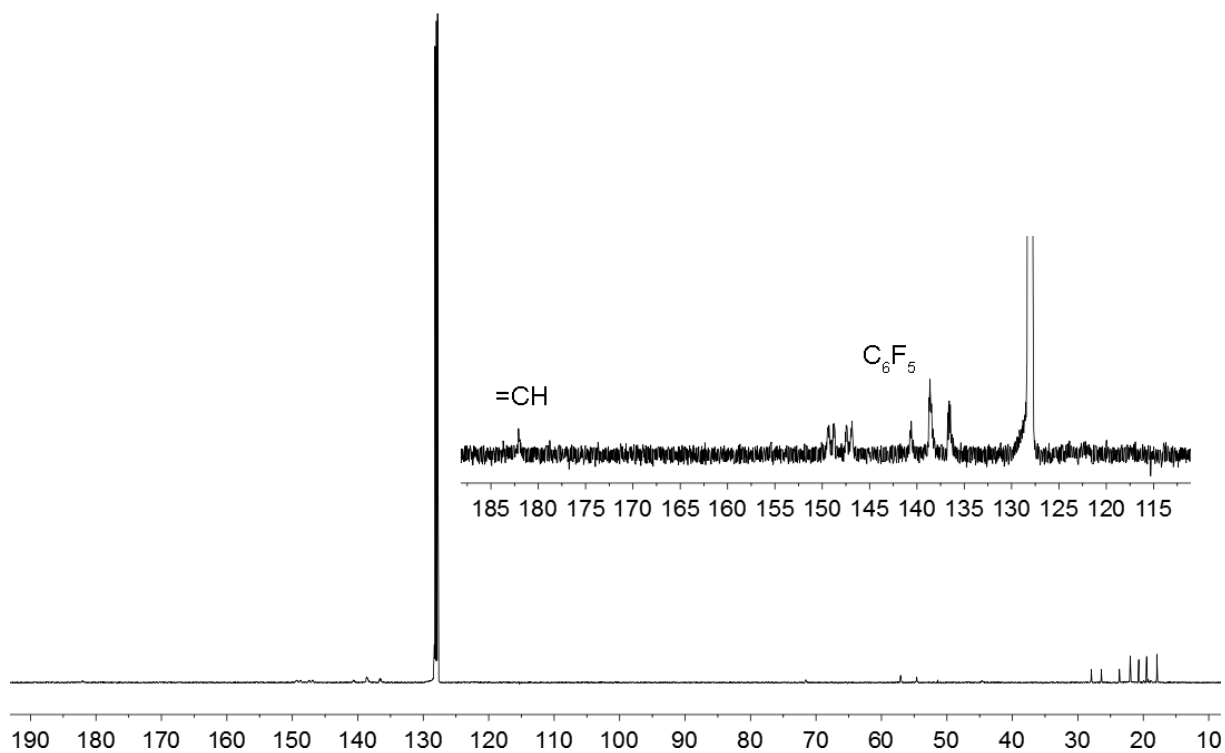
¹⁹F NMR (470 MHz, 299 K, C₆D₆): δ = -132.4 (m, 2F, o), -160.1 (br, 1F, p), -165.1 (br m, 2F, m), (C₆F₅) [Δδ¹⁹F_{pm} = 5.0], -133.6 (m, 2F, o), -158.8 (br, 1F, p), -164.2 (br m, 2F, m), (C₆F₅) [Δδ¹⁹F_{pm} = 5.4].



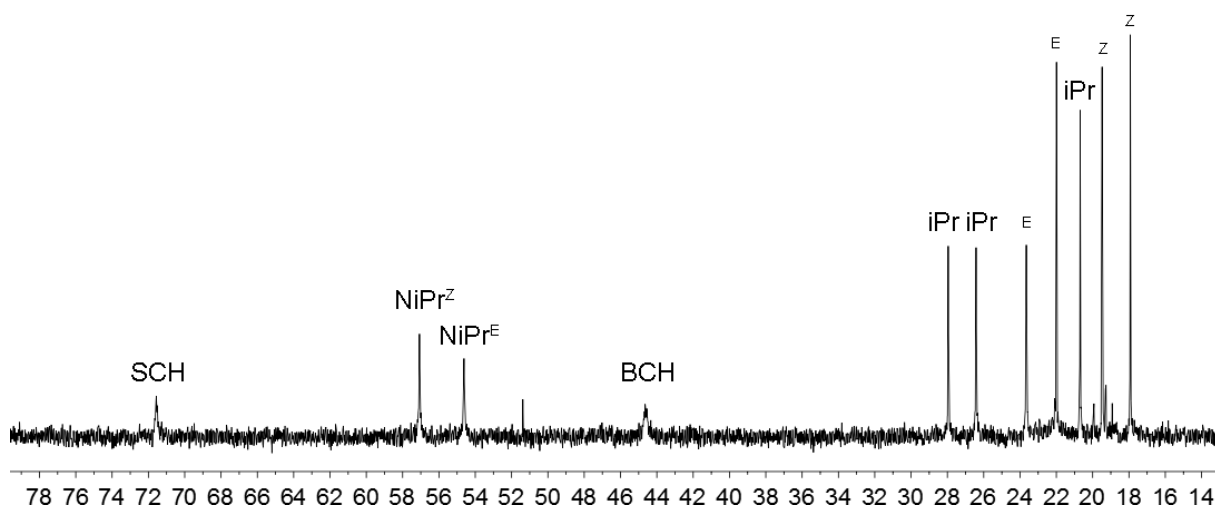
Supplementary Figure 32: ¹H NMR (500 MHz, 299 K, C₆D₆) spectrum of the reaction mixture.



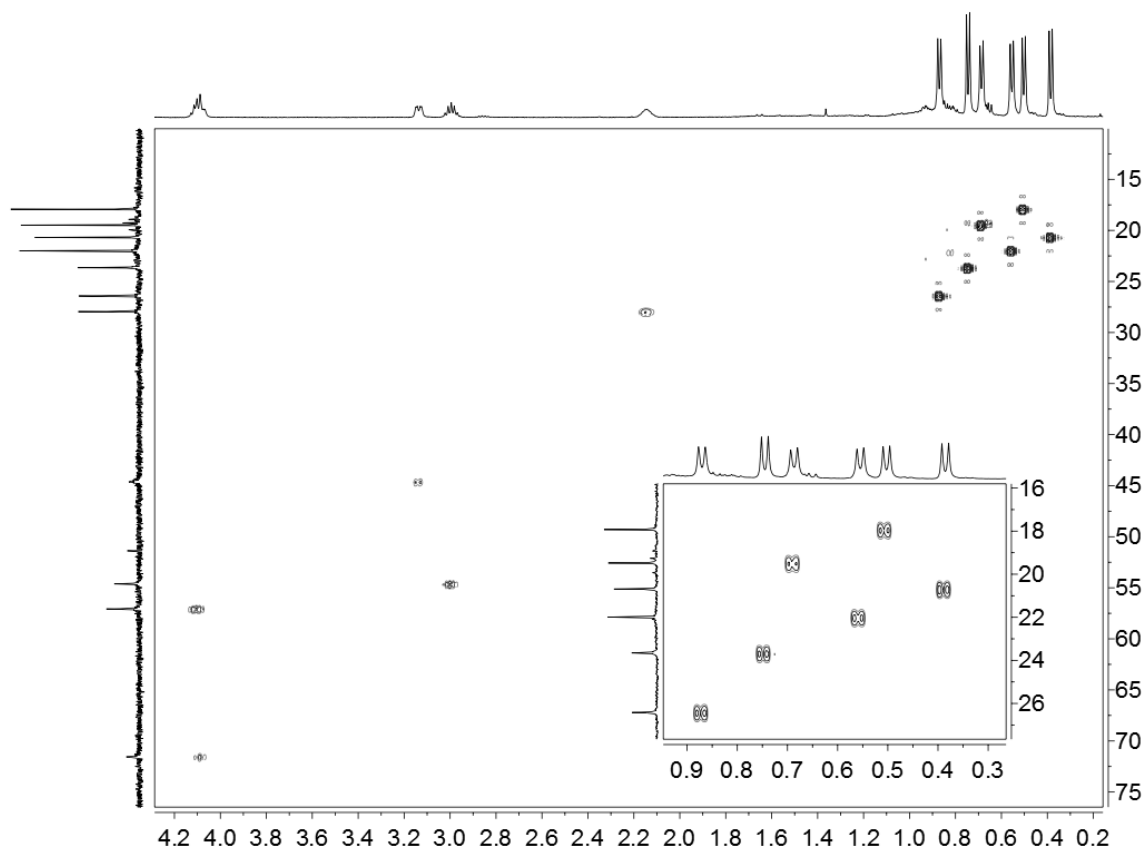
Supplementary Figure 33: (1) ¹H NMR (500 MHz, 299 K, C₆D₆), (2 to 4) ¹H{¹H} TOCSY [* irradiation points: (2) δ¹H 3.14 (BCH), (3) δ¹H 0.50 (NiPr^Z), (4) δ¹H 0.55 (NiPr^E)] and (5) ¹H{¹H} NOE [* irradiation point: (5) δ¹H 7.69 (=CH)] spectra of the reaction mixture.



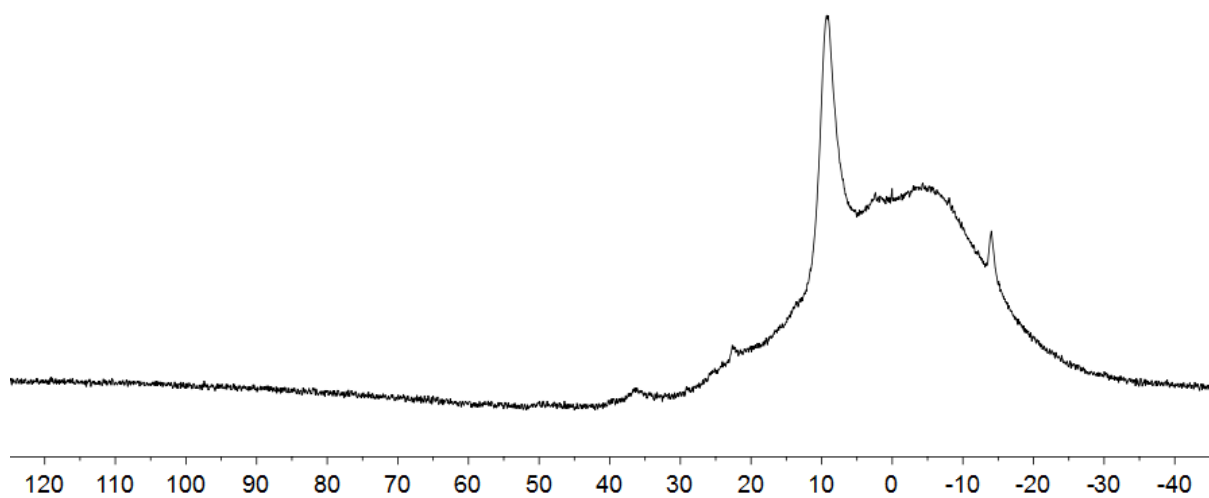
Supplementary Figure 34: ¹³C{¹H} NMR (126 MHz, 299 K, C₆D₆) spectrum of the reaction mixture.



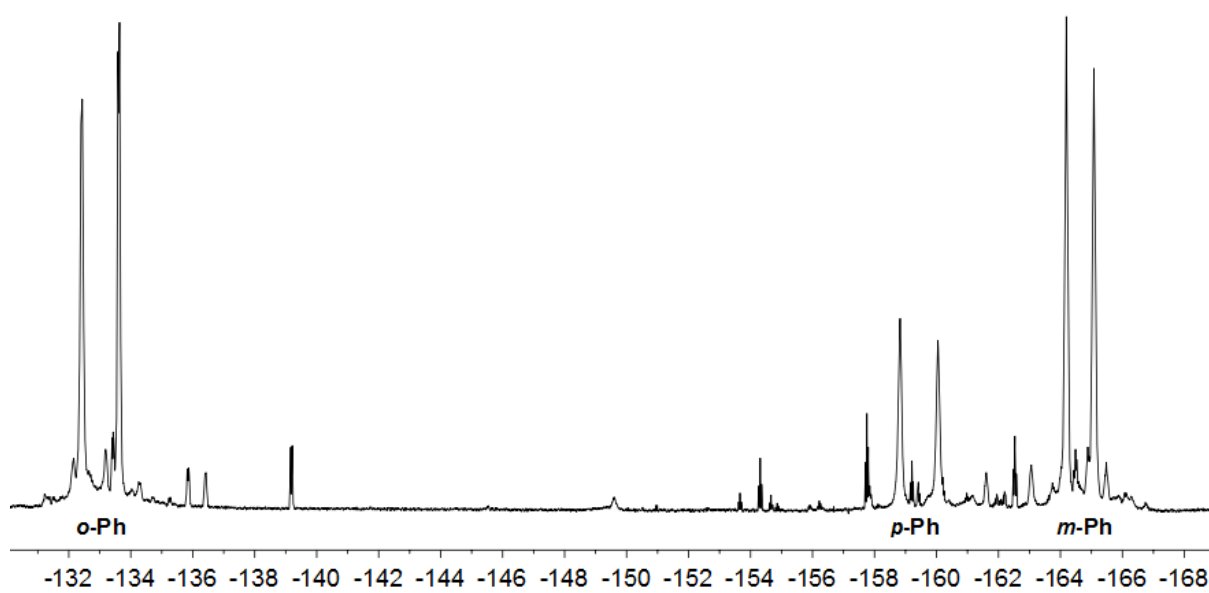
Supplementary Figure 35: $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



Supplementary Figure 36: ^1H , ^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



Supplementary Figure 37: $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.



Supplementary Figure 38: ^{19}F NMR (470 MHz, 299 K, C_6D_6) spectrum of the reaction mixture.