Supplementary Information (SI) for Organic Chemistry Frontiers.

Supplementary Information

Bis(pentafluorophenyl)borane catalyzed atom-economic formation of alkenyl- and (homo)allyl boronates from dienes and boronic esters

Felix Wech[a], Niklas Koch[a], Tizian Müller[a], and Urs Gellrich*[,b]

[a]Institut für Organische Chemie, Justus-Liebig-Universität Gießen,

Heinrich-Buff-Ring 17, 35392 Gießen, Germany.

[b]Fachbereich Organische Chemie, Universität Hohenheim, Garbenstraße 30, 70599 Stuttgart, Germany.

E-mail: urs.gellrich@uni-hohenheim.de

Table of Contents

1 General specifications

All manipulations of air and moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk and glovebox techniques. Flash column chromatography was carried out with Silica 60 M (0.04–0.063 mm) from Macherey-Nagel GmbH&Co. KG. Thin-layer chromatography was carried out on Polygram®SIL G/UV254 from Macherey-Nagel GmbH&Co. KG. Solvents for column chromatography were distilled bulb to bulb prior to use. All dry, non-deuterated solvents were, if commercially available, purchased from Acros Organics or Sigma Aldrich in a sealed bottle with a septum. Pinacolborane was purchased from TCI and distilled under inert conditions and stored inside a glovebox at −35 °C. Deuterated solvents were subjected to three freeze/pump/thaw cycles and kept in a nitrogen glovebox over 4 Å molecular sieves. The dienes were purchased from either Sigma Aldrich, TCI, Fisher Scientific or BLDPharm, and distilled under inert conditions and stored over molecular sieves under an N_2 atmosphere. GC MS of the reaction solutions was measured on Agilent 5977B GC/MSD using DCM as solvent with a set EI voltage of 70 kV. The GC MS method uses 1.2 mL/min He flow and 10.42 psi pressure. The oven starts at 60 °C and 10 minutes hold time, which is then heating at 10 °C/min up to 200 °C, which is then held for 6 minutes. The total run time is 30 minutes. Exact masses were measured using ESI or APCI MS on a Bruker MicrOTOF mass spectrometer in positive ion mode with a capillary voltage set to 4.5 kV and endplate offset to -0.5kV. NMR spectra were recorded on a Bruker Avance II 200 MHz, Bruker Avance III HD 400 MHz, Bruker Avance II 400 MHz and Bruker Avance III HD 600 MHz spectrometers. ^{1}H and ^{13}C NMR chemical shifts are referenced to residual solvent resonance peaks. 1-(4-Methylphenyl)-1,4-butadiene, and 1-(4-chlorophenyl)-1,4-butadiene were synthesised from the aldehyde and diethoxyallyl phosphonate according to a literature procedure.[1] 4,4,6-Trimethyl-1,3,2-dioxaborinane and neopentylborane were synthesized according to literature procedures.[2] Tris(pentafluorophenyl)borane was synthesized according to a literature procedure.[3]

2 Synthetic procedures

2.1 Synthesis of Piers' borane 2

$H{-}B(C_6F_5)_2$

In a nitrogen filled glovebox, tris(pentafluorophenyl)borane (9.01 g, 17.6 mmol) was suspended in toluene (50 mL) in an 100 mL ace pressure tube. Triethylsilane (2930 µL, 1.03 equiv.) was added via Eppendorf pipette and the tube sealed. It was heated to 65 °C upon which all solid dissolved. After stirring at 65 °C for 8 days, a white precipitate was observed. The tube was allowed to cool to r.t. for 30 minutes upon which colorless crystals formed. The supernatant was removed, and the residue washed 8-10 times with benzene (3-5 mL). Afterwards, the residue was washed three times with pentane (3 mL) and dried in vacuo. The product **2** was obtained as a white solid (4.6 g, 75%). The purity was monitored by ^{19}F NMR.

The NMR data are in accordance with the literature.[4]

^{19}F NMR (377 MHz, Chloroform-*d*) δ −132.22 (dd-like, *J* ~ 23.0, 9.1 Hz), −146.83 – −147.53 (m), −158.80 (td-like, *J* ~ 20.8, 7.5 Hz).

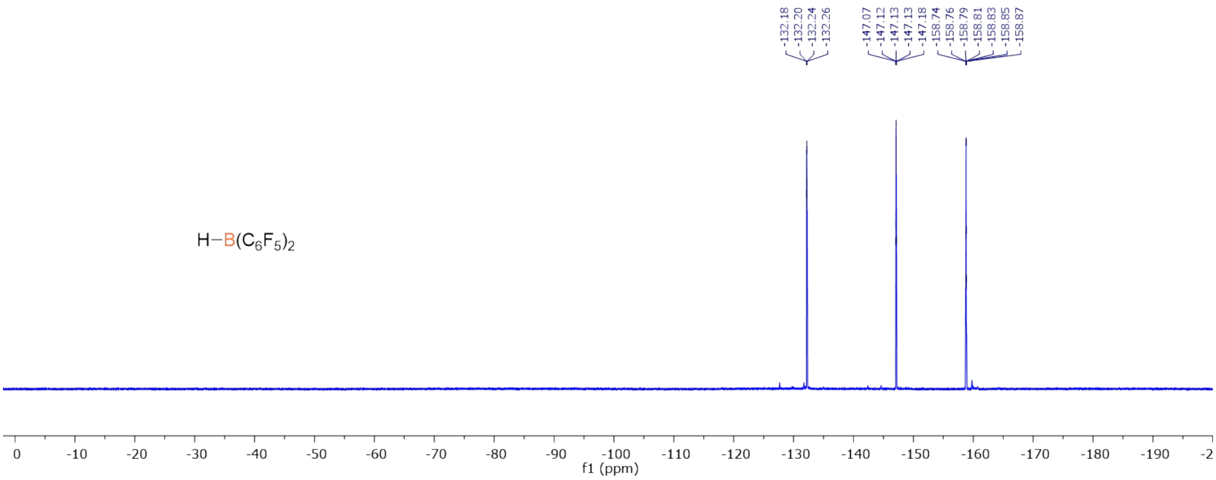
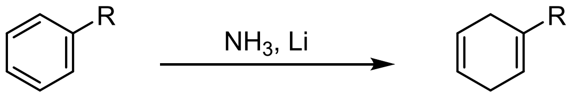


Figure SI 1: ^{19}F NMR spectrum of Piers' borane **2** (377 MHz, Chloroform-*d*).

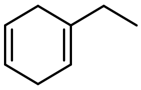
2.2 Substrate synthesis by Birch reduction

2.2.1 General procedure



Dry NH_3 (ca. 150 mL) was condensed into a three-neck, round-bottom flask equipped with a standpipe that was cooled with liquid N_2. The respective arene (100 mmol), *tert*-butanol (3.1 equiv., 29 mL), and dry diethylether (ca. 60 mL) was added. Then, Li metal (3.17 equiv., 2.2 g, Li ribbon) was added in small portions over 45 minutes. The mixture turned blue with a metallic appearing surface. The temperature was maintained at −45 °C and the mixture stirred until full conversion (check via crude NMR). Ether (150 mL) was added, and conc. NH_4Cl solution added slowly under cooling. The colorless mixture was then extracted with ether three times and the solvent carefully evaporated. The residue was distilled to give the diene product.

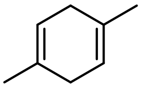
2.2.2 1-Ethyl-1,4-cyclohexadiene



The product was obtained as a colorless liquid (83%, 8.9 g). The analytical data are in accordance with the literature.[5]

^{1}H NMR (200 MHz, $CDCl_3$) δ5.72 (t, J = 1.1 Hz, 2H), 5.46 – 5.35 (m, 1H), 2.82 – 2.47 (m, 4H), 2.08 – 1.85 (m, 2H), 1.02 (t, J = 7.5 Hz, 3H).

2.2.3 1,4-Dimethyl-1,4-cyclohexadiene



The product was obtained as a colorless liquid (61%, 6.6 g). The analytical data are in accordance with the literature.[6]

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.41 (p, J = 1.8 Hz, 2H), 2.57 (s, 4H), 1.67 (p, J = 1.3 Hz, 6H).

2.2.4 Additional NMR spectra

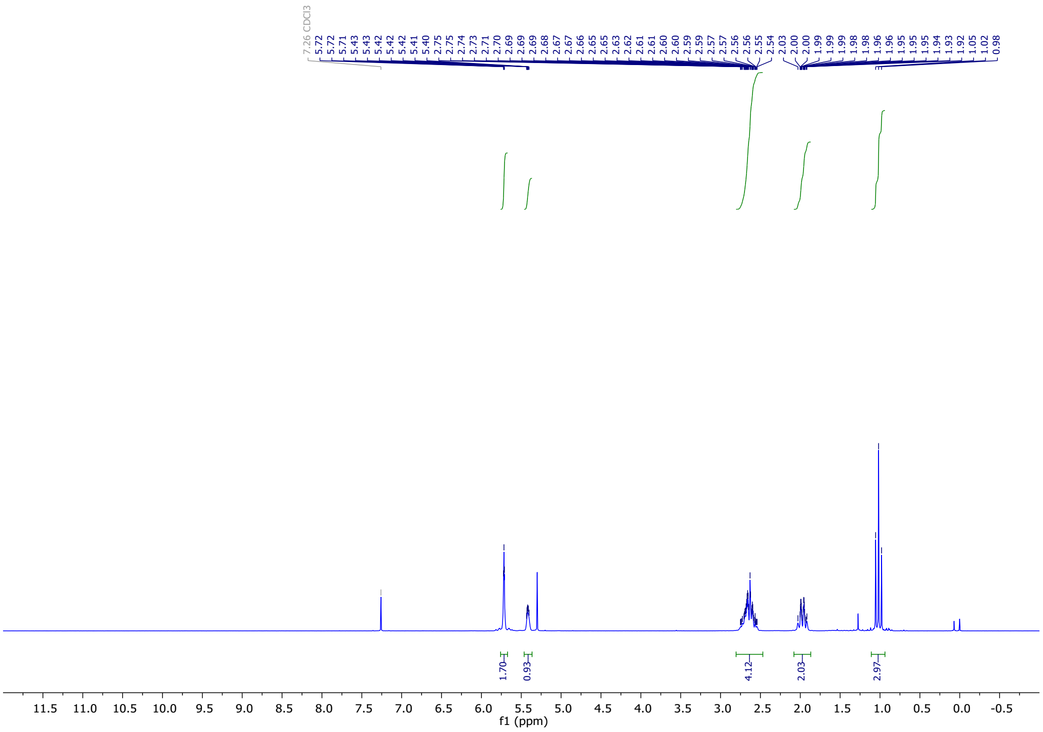


Figure SI 2: ^{1}H NMR spectrum of 1-ethyl-1,4-cyclohexadiene (200 MHz, $CDCl_3$).

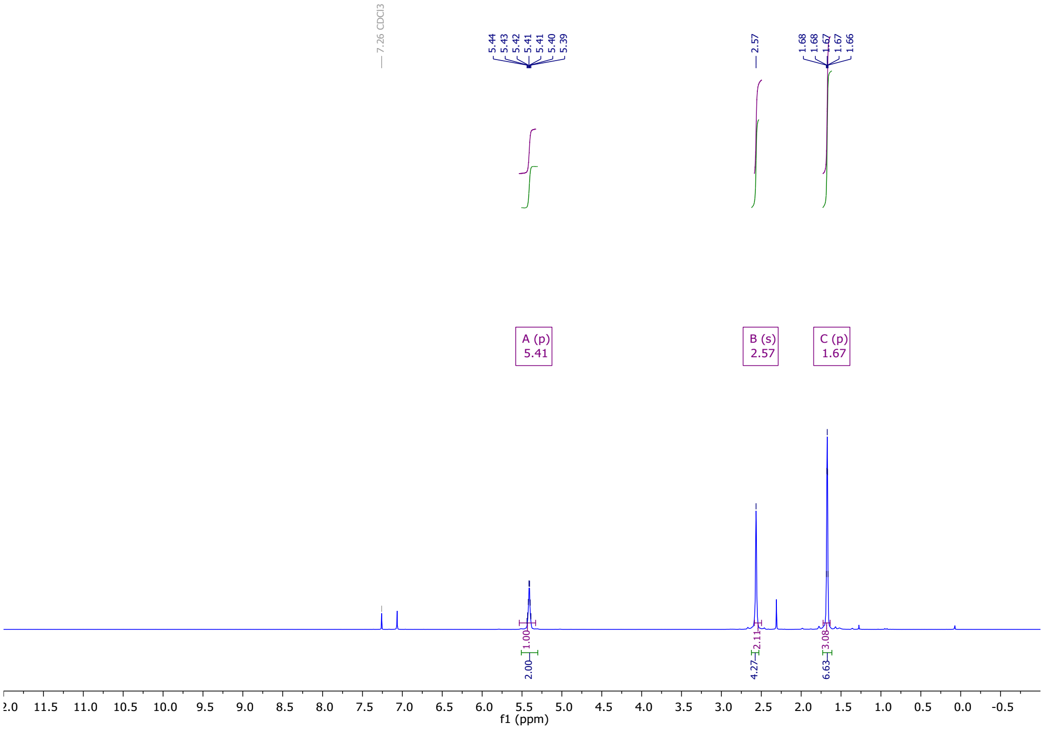
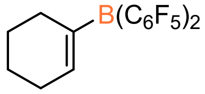


Figure SI 3: ^{1}H NMR spectrum of 1,4-dimethyl-1,4-cyclohexadiene (200 MHz, $CDCl_3$).

2.1 Synthesis of Bis(pentafluorophenyl)cyclohex-1-enylborane 5



Inside a nitrogen filled glovebox, bis(pentafluorphenyl)borane (0.5 mmol, 173 mg) was suspended in toluene (1 mL) in a vial. 1,4-Cyclohexadiene (0.5 mmol, 47.3 µL) was added via an Eppendorf pipette. The solid dissolved within 5 minutes. The solution was transferred to a Schlenk tube with J. Young valve and heated to 80 °C for 24 h. The solvent was removed in vacuo and the product was obtained as a white solid (187 mg, 88%). Single crystals were obtained via slow evaporation from pentane.

^{1}H NMR (400 MHz, benzene-*d*$_6$) δ 6.58 (tt, *J* = 3.7, 1.7 Hz, 1H), 1.93 (td, *J* = 5.7, 2.3 Hz, 2H), 1.76 (dtt, *J* = 8.5, 5.8, 2.4 Hz, 2H), 1.28 – 1.11 (m, 4H) ppm.

^{13}C NMR (101 MHz, benzene-*d*$_6$) δ 163.1 (CH), 28.6 (CH_2), 27.1 (CH_2), 22.0 (CH_2), 21.0 (CH_2) ppm.

^{11}B NMR (128 MHz, benzene-*d*$_6$) δ 62.4 ppm.

^{19}F NMR (377 MHz, benzene-*d*$_6$) δ−131.10 – −131.34 (m), −149.88 (t-like, *J* ~ 20.7 Hz), −160.98– −161.21 (m) ppm.

Note: The ^{13}C signals of the C_6F_5 groups appear as broad peaks in the area between 148 ppm and 136 ppm.

2.1.1 NMR spectra of 5

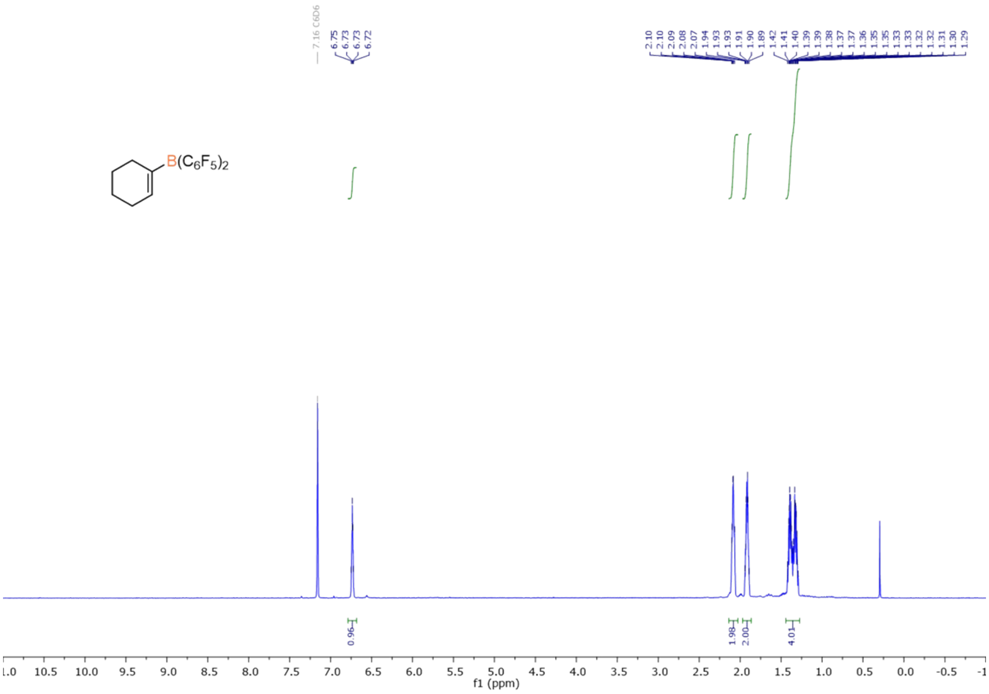


Figure SI 4: ^{1}H NMR spectrum of **5** (400 MHz, benzene-d_6).

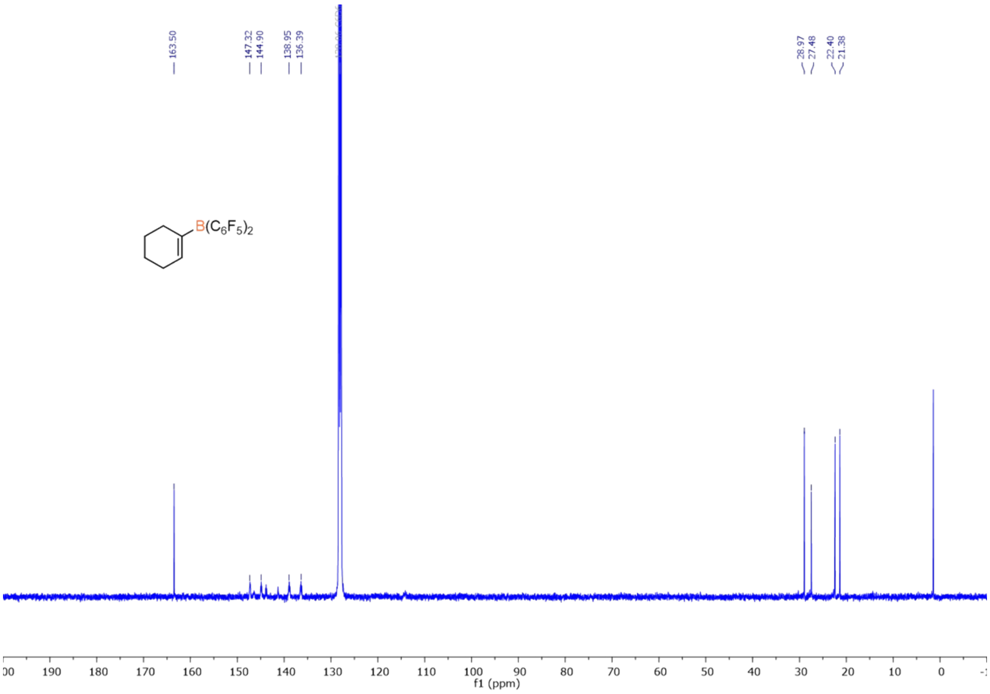


Figure SI 5: ^{13}C spectrum of **5** (101 MHz, benzene-d_6).

Note: The ^{13}C signals of the C_6F_5 Rings are broad.

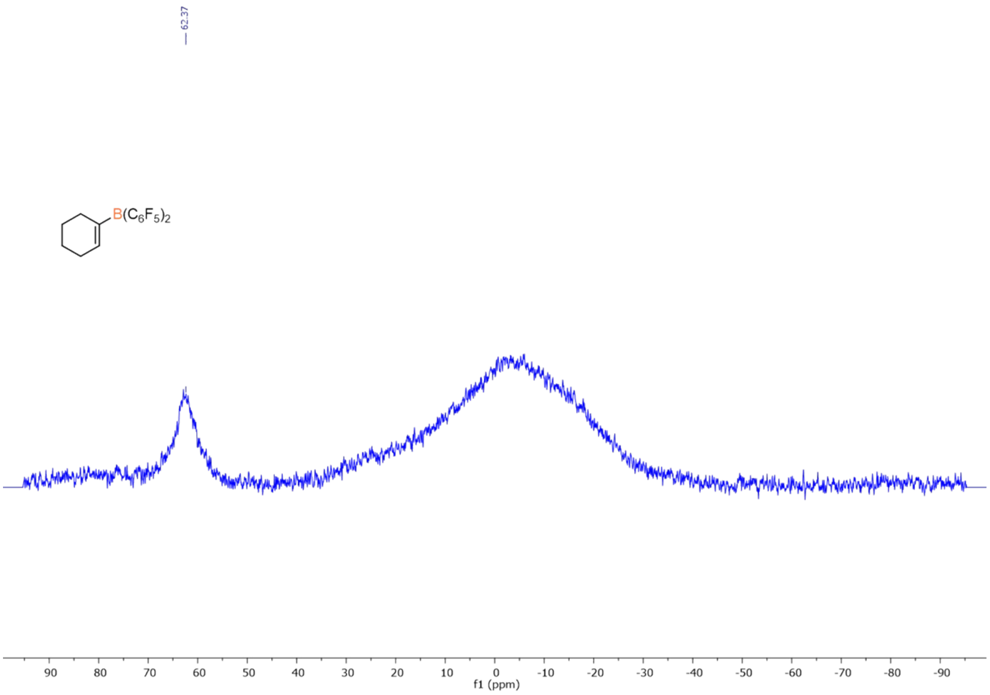


Figure SI 6: ^{11}B spectrum of **5** (128 MHz, benzene-d_6).

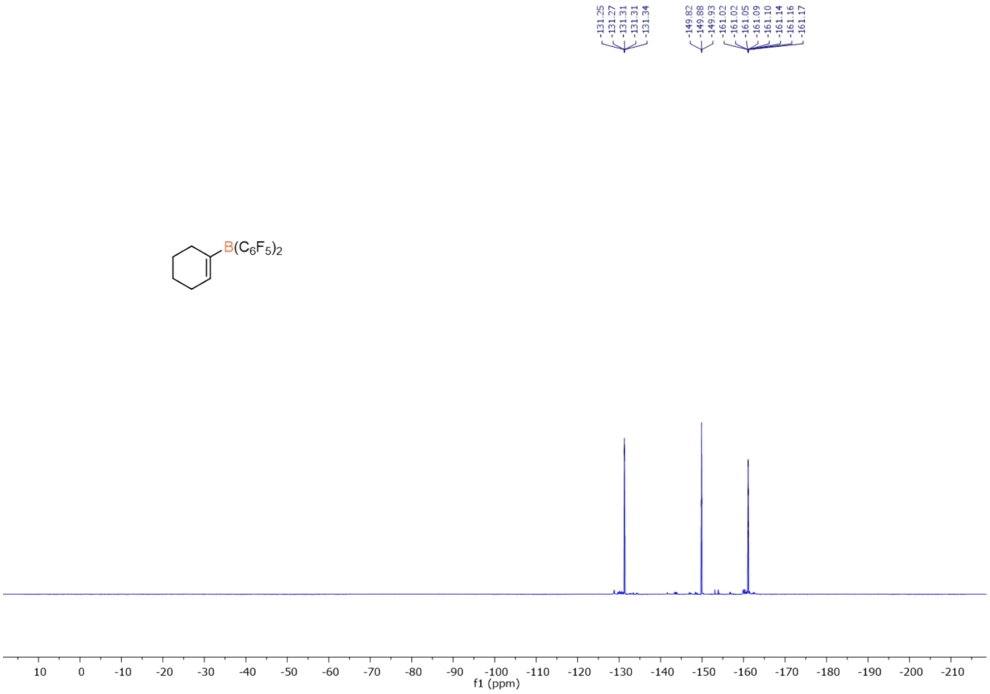


Figure SI 7: ^{19}F spectrum of **5** (377 MHz, benzene-d_6).

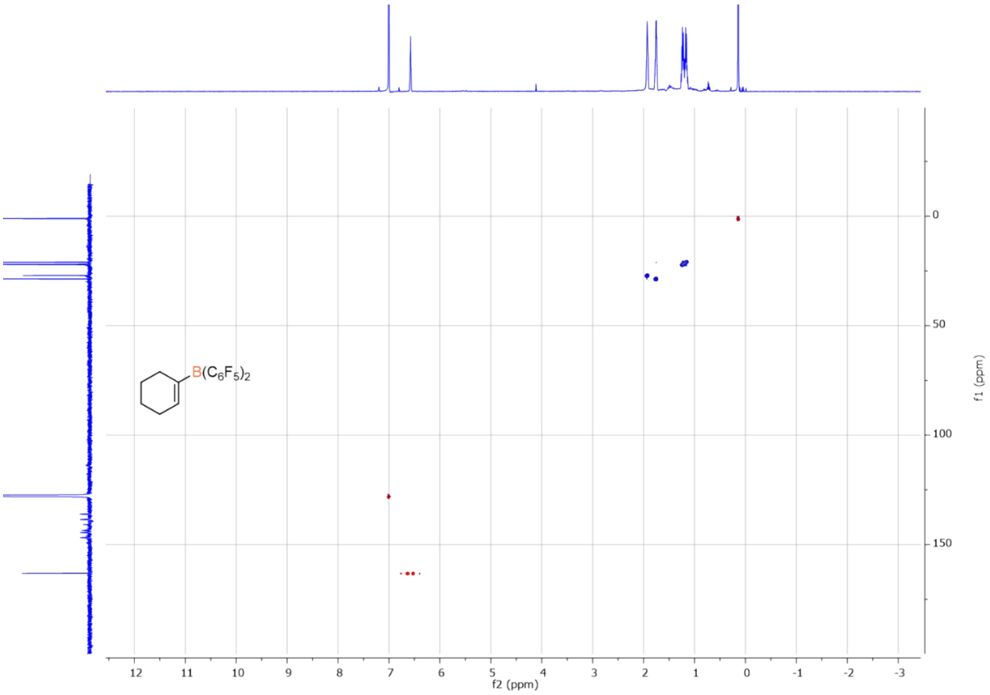


Figure SI 8: DEPT 135 edited ^{1}H-^{13}C HSQC spectrum of **5** (400, 101 MHz, benzene-d_6).

3 Catalytic experiments

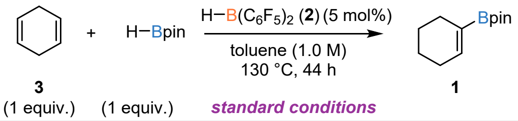
3.1 General procedure 1

Inside a N_2 glove box, Piers' borane (8.7 mg, 0.025 mmol, 5 mol%) was suspended in toluene-d_8 and 1,4-cyclohexadiene (0.5 mmol, 47.3 µL) was added via Eppendorf pipette. The solution cleared up within two minutes. Pinacolborane (72 µL, 1.0 equiv.) was added, and the solution transferred to an NMR tube with J. Young valve. The mixture was heated at 130 °C for 44 h. The reaction mixture was directly analyzed by NMR spectroscopy. The product can be isolated by silica gel column chromatography using pentane/Et_2O (3%) or pentane/DCM (5%).

3.2 Testing of reaction conditions and borane catalysts

The reactions were carried out according to the general procedure 1 given in 4.1 with the deviations given in table SI 1.

Table SI 1: Testing of reaction conditions and catalysts.



entry	Deviations from standard conditions	yield [%][a,b]
1	none	91 (88)
2	reaction at 80 °C (22 h)	0
3	0.1 M concentration	19
4	no $HB(C_6F_5)_2$	0
5	$HB(2,6\text{-}C_6F_2H_3)_2$ instead of $HB(C_6F_5)_2$	33
6	$HB(Cy)_2$ instead of $HB(C_6F_5)_2$	0
7	9-BBN instead of $HB(C_6F_5)_2$	0

[a]Yield determined by NMR using *p*-Xylene was used as internal standard. [b]Yield of isolated product after column chromatography in parenthesis.

3.2.1 Additional NMR spectra

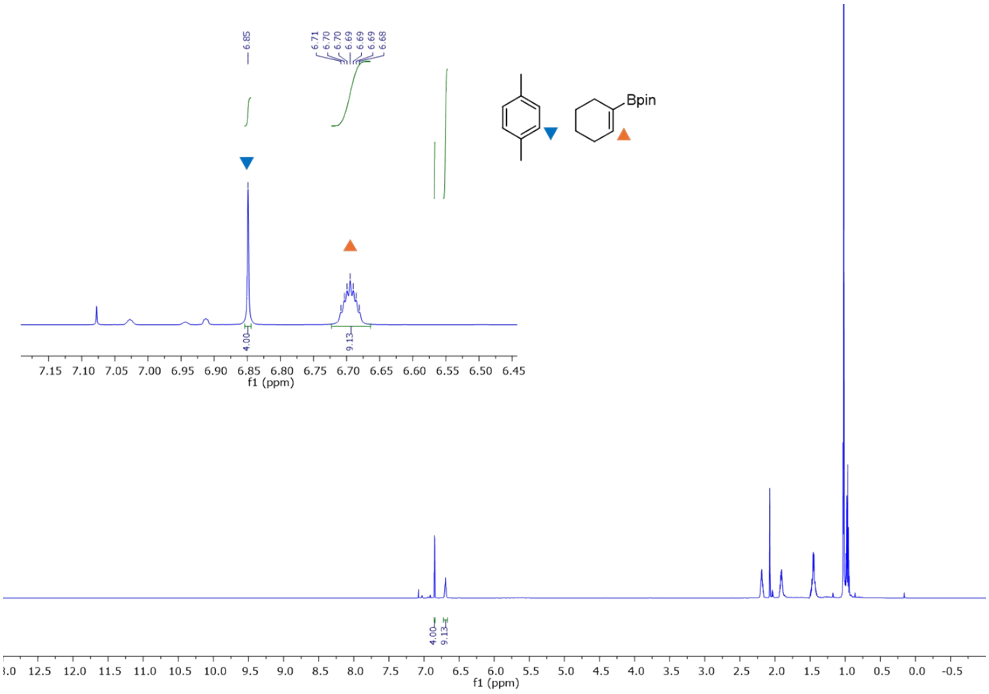


Figure SI 9: ^{1}H NMR spectrum of the reaction mixture using standard conditions as given in Table SI 1, entry 1. *p*-xylene (0.5 mmol) was used as an internal standard (Yield: 91%).

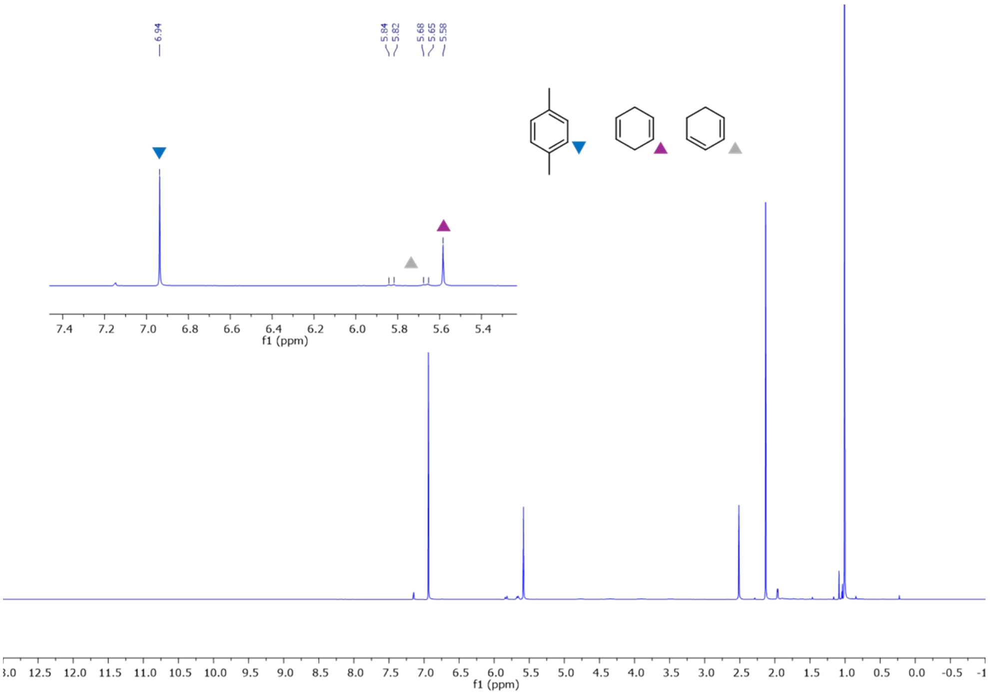


Figure SI 10: ^{1}H NMR spectrum of the reaction using standard conditions, but at 80 °C for 22 h (table SI1, entry 2). *p*-xylene (0.5 mmol) was used as an internal standard.

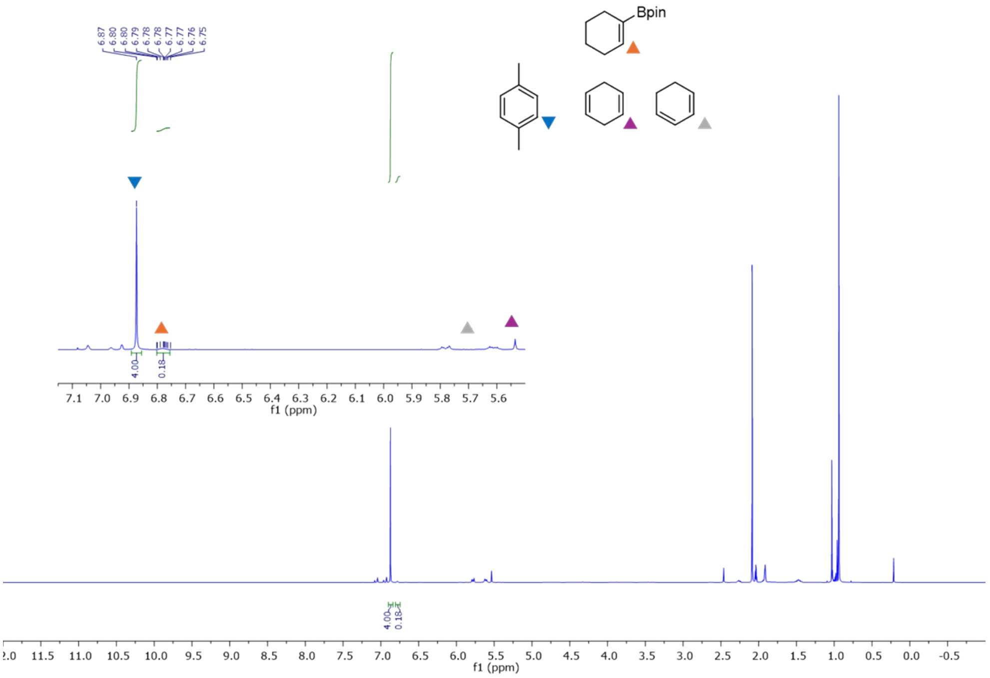


Figure SI 11: ^{1}H NMR spectrum of the reaction using standard conditions, but at 0.1 M concentration (table SI1, entry 3). *p*-xylene (0.05 mmol) was used as an internal standard (Yield: 19%).

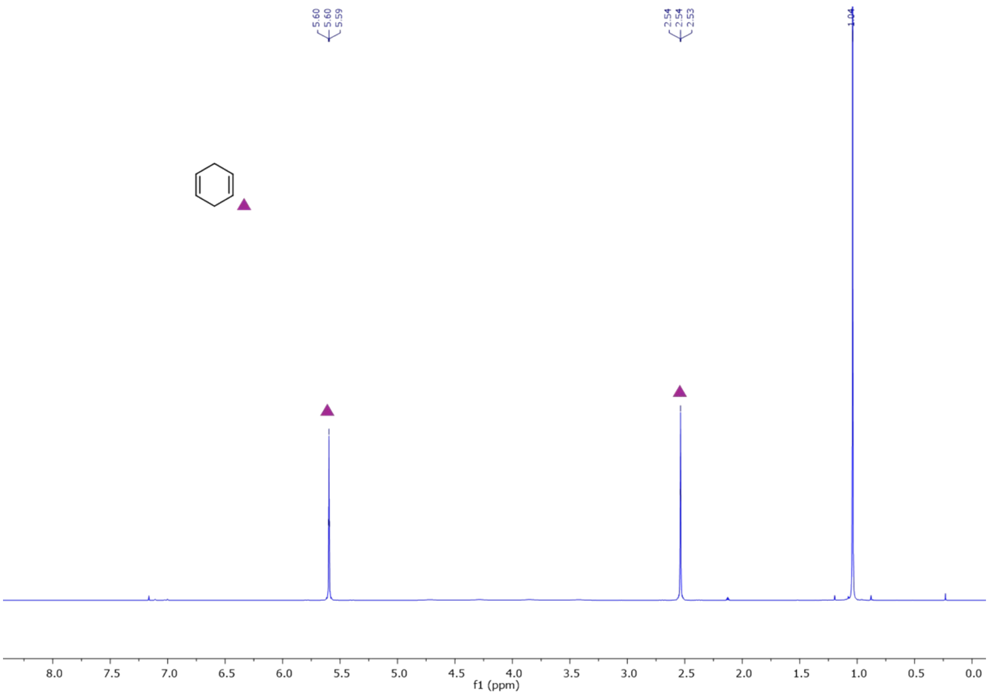


Figure SI 12: ^{1}H NMR spectrum of the reaction using standard conditions, but without $HB(C_6F_5)_2$ as a catalyst (table SI1, entry 4). Note that no internal standard was employed.

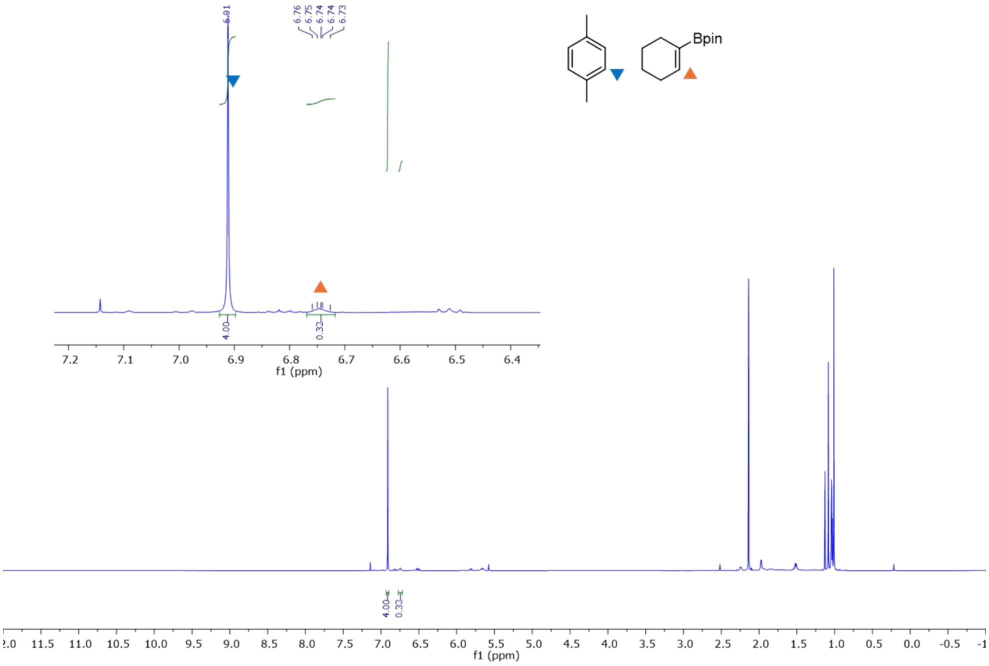


Figure SI 13: ^{1}H NMR spectrum of the reaction using standard conditions, but with $HB(2,6\text{-}C_6F_2H_3)_2$ instead of $HB(C_6F_5)_2$ (table SI1, entry 5). *p*-xylene (0.5 mmol) was used as an internal standard (Yield: 32%).

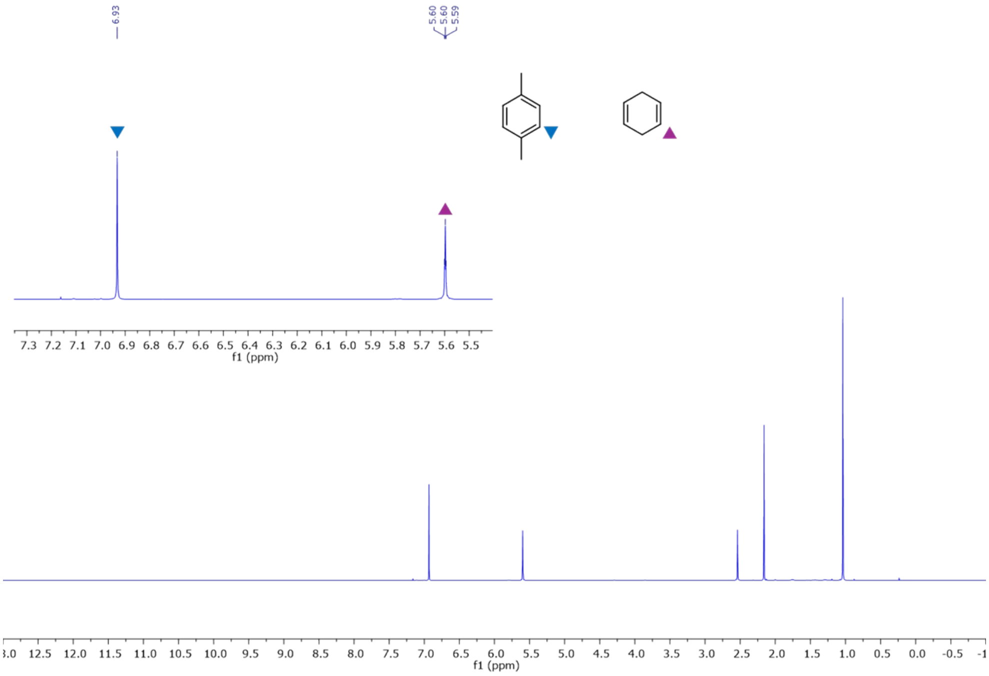


Figure SI 14: ^{1}H NMR spectrum of the reaction using standard conditions, but with $HBCy_2$ instead of $HB(C_6F_5)_2$ (table SI1, entry 5). *p*-xylene (0.5 mmol) was used as an internal standard.

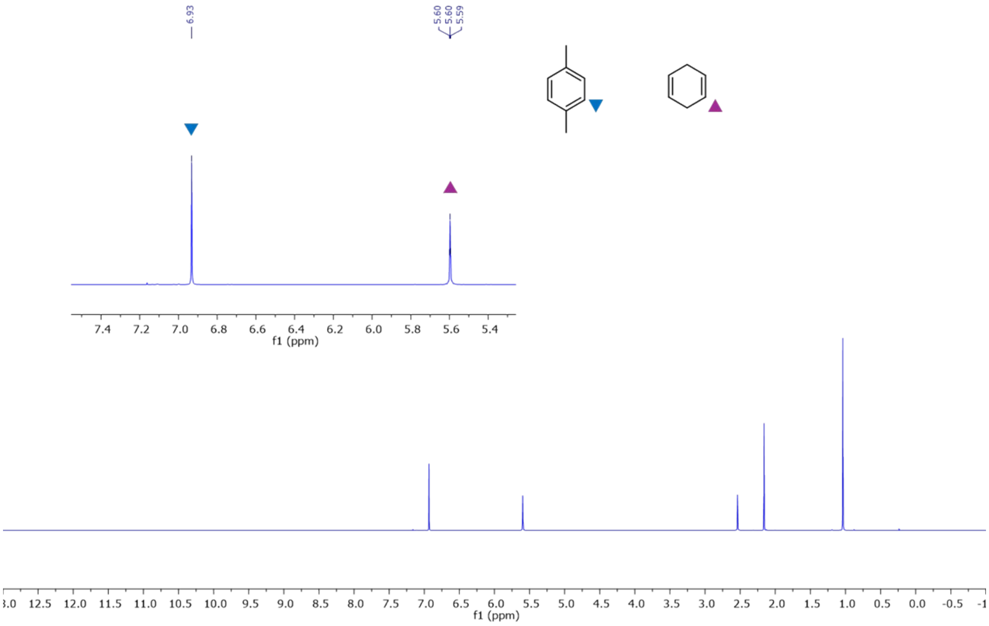


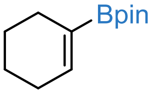
Figure SI 15: ^{1}H NMR spectrum of the reaction using standard conditions, but with 9-BBN instead of $HB(C_6F_5)_2$ (table SI1, entry 6). *p*-xylene (0.5 mmol) was used as an internal standard.

3.3 Substrate scope

3.3.1 General procedure 2

Inside a N_2 glove box, the diene (1.0 mmol) was dissolved in toluene (1 mL) in a vial. Piers' borane (17.3 mg, 0.05 mmol, 5 mol%) was added and the vial shaken until everything dissolved. Pinacolborane (144 µL, 1.0 equiv.) was added, and the solution transferred to a Schlenk tube with J. Young valve. The mixture was heated at 130 °C for 44 h. The reaction mixture was put directly on a flash silica column (ca. 10 g) and purified using pentane and then pentane/Et_2O (3%) or pentane/DCM (5% to 10%) as eluent.

3.3.2 2-(1-Cyclohexen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1



Starting from 1,4-cyclohexadiene: The reaction was carried out on 6.0 mmol scale according to general procedure 2. The product was obtained as a colorless oil after flash column chromatography (pentane/Et_2O 97:3) (88%, 1.1 g). The reaction was also carried out on NMR scale according to general procedure 1 to determine the *in situ* yield (91%).

Starting from 1,3-cyclohexadiene: The reaction was carried out at 1.0 mmol scale according to general procedure 2. The product was obtained as a colorless oil after flash column chromatography (pentane/Et_2O 97:3) (90%, 187 mg). The reaction was also carried out on NMR scale according to general procedure 1 to determine the *in situ* yield (93%).

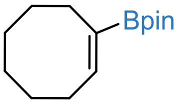
The spectral data are in accordance with the literature.[7]

^1H NMR (400 MHz, $CDCl_3$) δ 6.56 (t, J = 1.7 Hz, 1H), 2.09 (qt, J = 3.2, 1.7 Hz, 4H), 1.59 (tt, J = 3.0, 3.0 Hz, 4H), 1.25 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ143.1 (CH), 83.1 (C_q), 26.8 (CH_2), 26.3(CH_2), 25.0 (CH_3, Bpin), 24.7 (C_q), 22.7 (CH_2), 22.3 (CH_2).

HRMS (ESI) m/z [$M+Na^+$] calc. for $C_{12}H_{21}BNaO_2^+$ = 231.1527 m/z (found) = 231.1527.

3.3.3 2-(1-Cycloocten-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 6



Starting from 1,5-cyclooctadiene: The title compound was synthesized according to general procedure 2. The product was obtained as a colorless oil after flash column chromatography (145 mg, 61%). The *in situ* yield was determined following general procedure 1 (88%).

Starting from 1,3-cyclooctadiene: The title compound was synthesized according to general procedure 2. The product was obtained as a colorless oil after flash column chromatography (140 mg, 59%). The *in situ* yield was determined following general procedure 1 (84%).

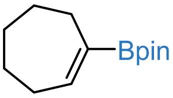
The spectroscopic data are in accordance with the literature.[8]

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.58 (t, J = 8.1 Hz, 1H), 2.33 – 2.12 (m, 4H), 1.54 – 1.40 (m, 9H), 1.25 (s, 12H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ146.2 (CH), 83.1 (C$_q$), 29.8 (CH$_2$), 29.0 (CH$_2$), 27.3 (CH$_2$), 26.6 (CH$_2$), 26.4 (CH$_2$), 26.1 (CH$_2$), 24.9 (CH$_3$, Bpin) ppm.

HRMS (ESI) m/z [M+Na$^+$] calc. for $C_{14}H_{25}BNaO_2^+$ = 259.1840 m/z (found) = 259.1837.

3.3.4 2-(1-Cyclohepten-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7



The title compound was synthesized according to general procedure 2 on a 1 mmol scale. The product was obtained as a colorless oil after column chromatography (148 mg, 67%).

The *in situ* yield was determined following general procedure 1 (74%).

The spectral data are in accordance with the literature.[9]

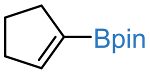
^{1}H NMR (400 MHz, CDCl$_3$) δ 6.77 (t, J = 6.3 Hz, 1H), 2.32 – 2.14 (m, 4H), 1.81 – 1.66 (m, 2H), 1.54 – 1.42 (m, 4H), 1.26 (s, 12H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ148.8 (CH), 83.3 (C$_q$), 32.9 (CH$_2$), 30.7 (CH$_2$), 29.7 (CH$_2$), 27.5 (CH$_2$), 26.6 (CH$_2$), 25.0 (CH$_3$, Bpin) ppm.

^{11}B NMR (128 MHz) δ 30.5 ppm.

GCMS (EI) *m*/*z* [M^+] = 222.1; RT = 20.472 min.

3.3.5 2-(1-Cyclopenten-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8



The title compound was synthesized according to general procedure 2, but at 110 °C for 22 h. The product was obtained as a colorless oil after column chromatography (66 mg, 35%). The reaction was also carried out on NMR scale according to general procedure 1 to determine the *in situ* yield (40%).

The spectral data are in accordance with the literature.[10]

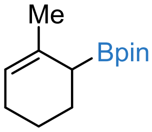
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (p, *J* = 2.2 Hz, 1H), 2.48 – 2.34 (m, 4H), 1.90 – 1.74 (m, 2H), 1.27 (s, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$)δ 146.5 (CH), 82.0 (C_q), 33.8 (CH_2), 33.5 (CH_2), 23.8 (CH_3), 22.9 (CH_2) ppm.

^{11}B NMR spectrum (128 MHz, $CDCl_3$) δ29.3 ppm.

GCMS (EI) *m*/*z* [M^+] = 194.1; RT = 14.841 min.

3.3.6 4,4,5,5-Tetramethyl-2-(6-methyl-1-cyclohexen-1-yl)-1,3,2-dioxaborolane 9



The title compound was synthesized according to general procedure 2 on 1 mmol scale but heated to 80 °C for 2 h. After careful solvent removal, the crude product was purified by Kugelrohr distillation (100 °C, 1 mbar) to give **9** in 50% yield (112 mg).

The spectral data are in accordance with the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (tt, *J* = 3.7, 1.6 Hz, 1H, CH), 2.02 – 1.94 (m, 2H, CH_2), 1.74 – 1.65 (m, 4H, CH_2), 1.68 (q, *J* = 1.9 Hz, 3H, CH_3), 1.27 – 1.24 (m, 1H, CH), 1.25 (s, 6H), 1.24 (s, 6H).

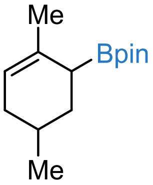
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5 (C_q), 120.4 (CH), 83.1 (C_q), 25.2 (CH_2), 24.9 (CH_2), 24.8 (CH_3, Bpin), 24.5 (CH_3, Bpin), 24.3 (CH_3), 21.7 (CH_2).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.4 ppm.

HRMS (ESI) *m/z* [$M+H^+$] calc. for $C_{13}H_{24}BO_2^+$ = 223.1864, *m/z* (found) = 223.1865.

Note: A ^{13}C NMR signal of the sp^3 carbon attached to boron is not visible due to quadrupolar relaxation.

3.3.7 4,4,5,5-Tetramethyl-2-(3,6-dimethyl-1-cyclohexen-1-yl)-1,3,2-dioxaborolane 10



The title compound was synthesized according to general procedure 1 on 0.5 mmol scale and the reaction mixture heated to 80 °C for 2 h. After careful solvent removal, the crude product was purified by flash column chromatography (pentane/DCM 5%) to give **10** in 45% yield (53 mg).

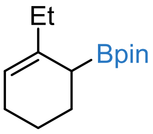
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 – 5.34 (m, 1H, CH), 2.11 – 2.01 (m, 1H, CH_2), 1.77 – 1.71 (m, 1H, CH_2), 1.69 (q, *J* = 1.8 Hz, 3H, CH_3), 1.66 – 1.49 (m, 2H, CH, CH_2), 1.43 – 1.32 (m, 1H, CH_2), 1.24 (d, *J* = 4.5 Hz, 12H, CH_3), 0.92 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6 (C_q), 119.9 (CH), 83.2 (C_q), 34.2 (CH_2), 33.4 (CH_2), 27.4 (CH), 25.0 (CH_3, Bpin), 24.6 (CH_3, Bpin), 24.2 (CH_3), 22.2 (CH_3). ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.6 ppm.

HRMS (ESI) *m/z* [$M+Na^+$] calc. for $C_{14}H_{25}BNaO_2^+$ = 259.1840, *m/z* (found) = 259.1843.

3.3.8 4,4,5,5-Tetramethyl-2-(6-ethyl-1-cyclohexen-1-yl)-1,3,2-dioxaborolane 11



The title compound was synthesized according to general procedure 1 on 0.5 mmol scale and the reaction mixture heated to 80 °C for 2 h. After careful solvent removal, the crude product was purified by flash column chromatography (pentane/DCM 5%) to give **11** in 45% yield (52 mg).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.41 (tq, *J* = 3.0, 1.5 Hz, 1H, CH), 2.10 – 1.86 (m, 4H, CH$_2$), 1.81 – 1.74 (m, 2H, CH$_2$), 1.73 – 1.66 (m, 2H, CH$_2$), 1.62 – 1.52 (m, 2H, CH$_2$), 1.27 – 1.24 (m, 1H, CH), 1.24 (s, 6H, CH$_3$), 1.23 (s, 6H, CH$_3$), 0.98 (t, *J* = 7.4 Hz, 3H, CH$_3$) ppm.

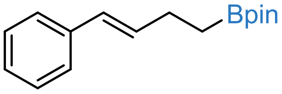
^{13}C NMR (101 MHz, CDCl$_3$)δ140.1 (C$_q$), 118.6 (CH), 83.2 (C$_q$), 30.6 (CH$_2$), 25.3 (CH$_2$), 25.2 (CH$_2$), 24.9 (CH$_3$, Bpin), 24.7 (CH$_3$, Bpin), 22.0 (CH$_2$), 12.4 (CH$_3$) ppm.

^{11}B NMR (128 MHz, CDCl$_3$) δ 33.6 ppm.

HRMS (ESI) *m/z* [M+Na$^+$] calc. for $C_{14}H_{25}BNaO_2^+$ = 259.1840, *m/z* (found) = 259.1841.

Note: A 13C NMR signal of the sp^3 carbon attached to boron is not visible due to quadrupolar relaxation.

3.3.9 4,4,5,5-Tetramethyl-2-(4-phenyl-3-buten-1-yl)-1,3,2-dioxaborolane 12



The reaction was carried out on 1 mmol scale according to general procedure 2, but the reaction mixture was heated at 80 °C for 22 h. The crude product was purified by flash column chromatography on silica using pentane/Et$_2$O (3%) (103 mg, 79%).

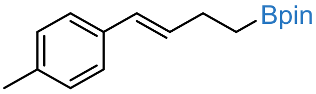
The analytical data are in accordance with the literature.[12]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.17 (m, 4H), 7.14 – 7.07 (m, 1H), 6.31 (dt, *J* = 15.9, 1.3 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.3 Hz, 1H), 2.26 (tdd, *J* = 7.6, 6.3, 1.3 Hz, 2H), 1.17 (s, 12H), 0.91 (t, *J* = 7.7 Hz, 2H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$)δ137.8, 132.6, 128.6, 128.2, 126.5, 125.8, 82.9, 27.2, 24.7 ppm.

HRMS (ESI) *m/z* [M+Na$^+$] calc. for $C_{16}H_{23}BO_2Na^+$ = 281.1683, *m/z* (found) = 281.1686.

3.3.10 4,4,5,5-Tetramethyl-2-[4-(4-methylphenyl)-3-buten-1-yl]-1,3,2-dioxaborolane 13



The reaction was carried out on 1 mmol scale according to general procedure 2, but the reaction mixture was heated at 80 °C for 22 h. The crude product was purified by flash column chromatography on silica using pentane/Et_2O (3%) (114 mg, 84%).

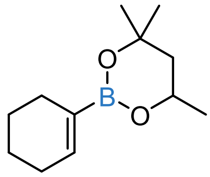
The analytical data are in accordance with the literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 7.11 – 7.05 (m, 2H), 6.38 – 6.31 (m, 1H), 6.22 (dt, J = 15.8, 6.4 Hz, 1H), 2.36 – 2.29 (m, 2H), 2.32 (s, 3H), 1.24 (s, 12H), 0.98 (t, J = 7.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ136.5, 135.4, 131.9, 129.3, 128.8, 126.0, 83.2, 27.4, 25.0, 21.3 ppm.

HRMS (ESI) m/z [M+H$^+$] calc. for $C_{17}H_{26}BO_2^+$ = 273.2021, m/z (found) = 273.2020.

3.3.11 2-(1-Cyclohexen-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane 14



The reaction was carried out on NMR scale according to general procedure 1 on 0.5 mmol scale. The in situ yield was determined using p-Xylene was used as internal standard (71%). The reaction mixture was purified by Kugelrohr distillation (1 mbar, 100 °C) to give a colorless oil (47 mg, 45%).

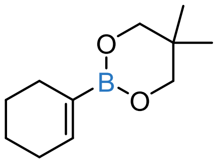
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (dt, J = 4.0, 2.0 Hz, 1H), 4.19 (ddh, J = 12.3, 6.1, 2.9 Hz, 1H), 2.10 – 2.01 (m, 4H), 1.76 (dd, J = 13.8, 2.9 Hz, 1H), 1.62 – 1.52 (m, 4H), 1.46 (dd, J = 13.8, 11.5 Hz, 1H), 1.27 (s, 6H), 1.25 (d, J = 6.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4 (CH), 70.5 (C_q), 64.6 (CH), 46.1 (CH_2), 31.5 (CH_3), 28.e (CH_3), 26.7 (CH_2), 25.9 (CH_2), 23.4 (CH_3), 22.9 (CH_2), 22.6 (CH_2) ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ 26.1 ppm.

HRMS (ESI) m/z [M+Na$^+$] calc. for $C_{12}H_{21}BNaO_2^+$ = 231.1527, m/z (found) = 231.1528.

3.3.12 2-(1-Cyclohexen-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane 15



The reaction was carried out on NMR scale according to general procedure 1, but the reaction mixture was heated to 130 °C for 22 h. The in situ yield was determined using *p*-Xylene was used as internal standard (61%).

The NMR data are in accordance with the literature.[13]

Note that the product decomposes on silica and is sensitive towards elevated temperatures.

3.4 Limitations of substrate scope

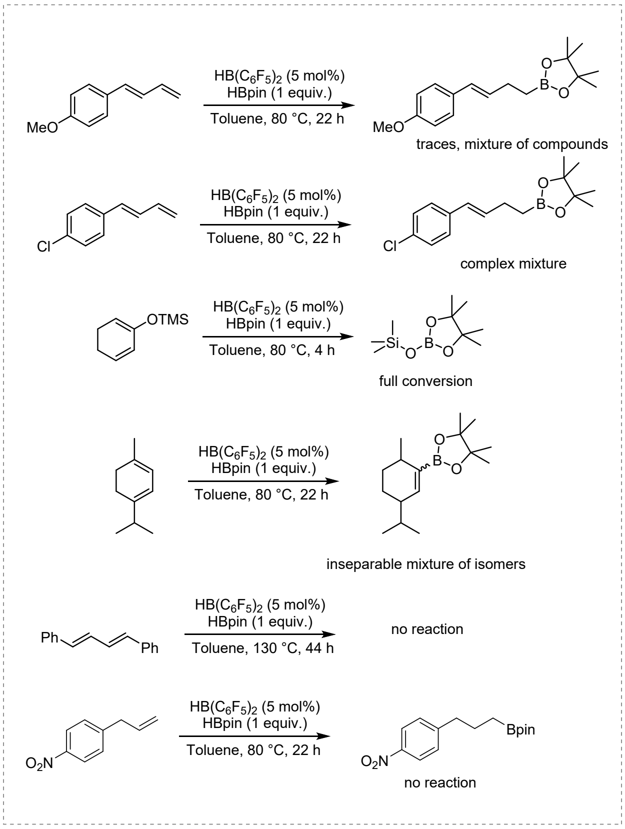
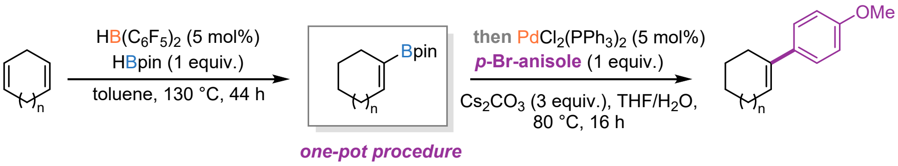


Figure SI 16: Selected unsuccessful substrates.

Note that the reaction is sensitive towards functional groups. The reaction with 1-(4-methoxyphenyl)-butadiene only shows traces of product and a large amount of unidentified side-product, the same was observed with 1-(4-chlorophenyl)-butadiene. Employing 2-

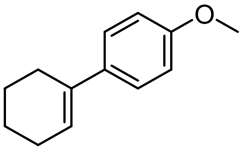
(Trimethylsiloxy)-1,3-cyclohexadiene as a substrate shows quantitative conversion to TMSOBpin after solvent removal. α-Terpinene is fully consumed after 22 h at 80 °C, however, a inseparable mixture of isomers is obtained. 1,4-Diphenyl-1,3-butadiene does not react at 130 °C for 44 h, as only starting material is recovered. We also tested 3-(4-nitrophenyl)-1-propene as a substrate, where we also observed no reaction.

3.5 One-pot procedure for the Suzuki-Miyaura coupling



In a Schlenk tube with J. Young valve, Piers' borane (17.3 mg, 0.05 mmol) was suspended in toluene (1 mL). The corresponding diene (1.0 mmol) was added, and the tube shaken until everything dissolved. Pinacolborane (1.0 mmol, 148 µL) was added, the tube sealed and heated to 130 °C for 44 h. Then, THF/H_2O (5:1, 1 mL) was added, and afterwards Cs_2CO_3 (3 equiv. 977 mg), $PdCl_2(PPh_3)_2$ (35.1 mg, 0.05 mmol) and 4-bromoanisole (1.05 equiv. 130 µL). The tube was sealed, and the mixture heated again to 80 °C for 16 h. Ether and water was added, and the mixture extracted 3 times. The mixture was filtered, dried over $MgSO_4$ and the solvent evaporated. Flash column chromatography over SiO_2 using *n*-hexane/EtOAc (200:1) gave the product.

3.5.1 1-(4-Methoxyphenyl)cyclohexene 16



The reaction was conducted following the general procedure starting from 1,4-cyclohexadiene. The product was obtained as a colorless oil (131 mg, 70%).

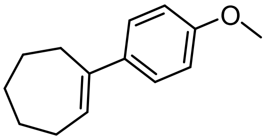
The analytical data are in accordance with the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 6.88 – 6.82 (m, 2H), 6.03 (tt, J = 4.0, 1.7 Hz, 1H), 3.81 (s, 3H), 2.45 – 2.32 (m, 2H), 2.24 – 2.15 (m, 2H), 1.82 – 1.73 (m, 2H), 1.69 – 1.60 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 126.0 (CH_{Ar}), 123.3 (CH), 113.7 (CH_{Ar}), 55.4 (CH_3), 27.6 (CH_2), 26.0 (CH_2), 23.3 (CH_2), 22.4 (CH_2) ppm.

GCMS (EI) *m*/*z* [M^+] = 188.1; RT = 7.685 min.

3.5.2 1-(4-Methoxyphenyl)cycloheptene 17



The reaction was conducted following the general procedure starting from 1,3-cycloheptadiene. The product was obtained as a colorless oil (98 mg, 48%).

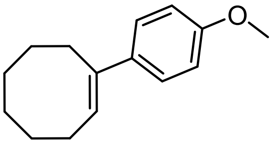
The spectroscopic data are in accordance with the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 6.86 – 6.81 (m, 2H), 6.02 (t, J = 6.8 Hz, 1H), 3.80 (s, 3H), 2.60 – 2.56 (m, 2H), 2.30 – 2.22 (m, 2H), 1.87 – 1.78 (m, 2H), 1.68 – 1.59 (m, 2H), 1.57 – 1.50 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.26 (C_q), 144.36 (C_q), 137.60 (C_q), 128.87 (CH), 126.69 (CH_{Ar}), 113.50 (CH_{Ar}), 55.31 (CH_3), 32.84 (CH_2), 32.78 (CH_2), 28.81(CH_2), 26.90 (2 CH_2) ppm.

HRMS (APCI) m/z [M+H$^+$] calc. for $C_{14}H_{19}O^+$ = 214.1431, m/z (found) = 214.1434.

3.5.3 1-(4-Methoxyphenyl)cyclooctene 18



The reaction was conducted following the general procedure starting from 1,4-cyclohexadiene. The product was obtained as a colorless oil (128 mg, 59%).

The spectral data are in accordance with the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 6.88 – 6.82 (m, 2H), 5.94 (t, J = 8.3 Hz, 1H), 3.81 (s, 3H), 2.67 – 2.58 (m, 2H), 2.28 (td, J = 8.2, 4.1 Hz, 2H), 1.70 – 1.49 (m, 8H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.39 (C_q), 139.54 (C_q), 135.71 (C_q), 126.78 (CH_{Ar}), 126.39 (CH), 113.59 (CH_{Ar}), 55.29 (CH_3), 30.14 (CH_2), 29.36 (CH_2), 28.39 (CH_2), 27.42 (CH_2), 26.97 (CH_2), 26.14 (CH_2) ppm.

HRMS (APCI) m/z [M+H$^+$] calc. for $C_{15}H_{21}O^+$ = 217.1587, m/z (found) = 217.1584.

3.6 Additional NMR spectra

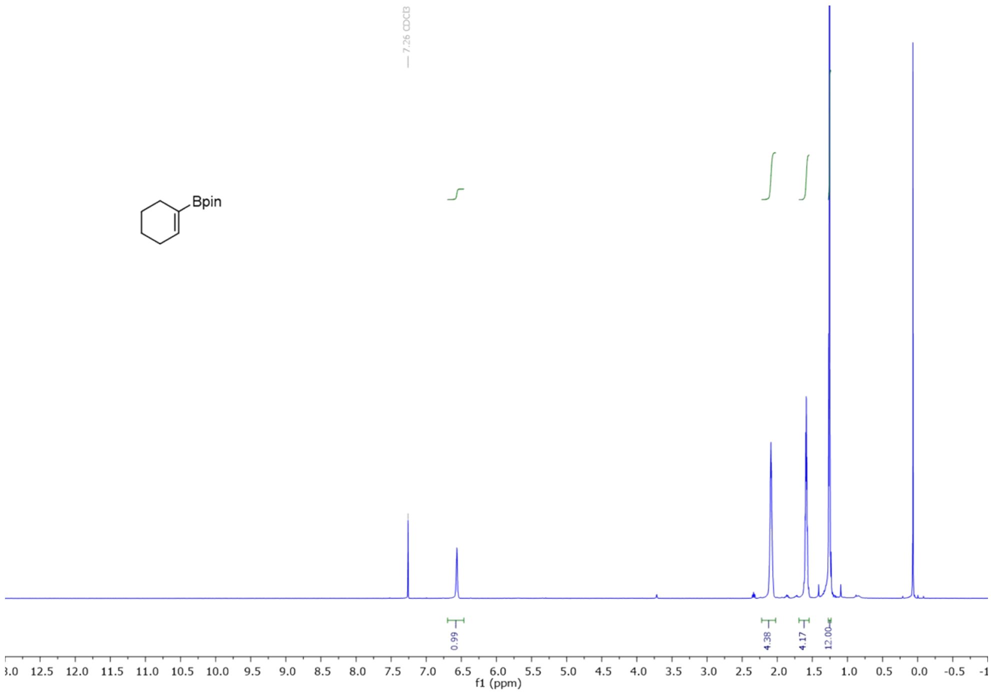


Figure SI 17: ^{1}H NMR spectrum of **1** ($CDCl_3$, 400 MHz).

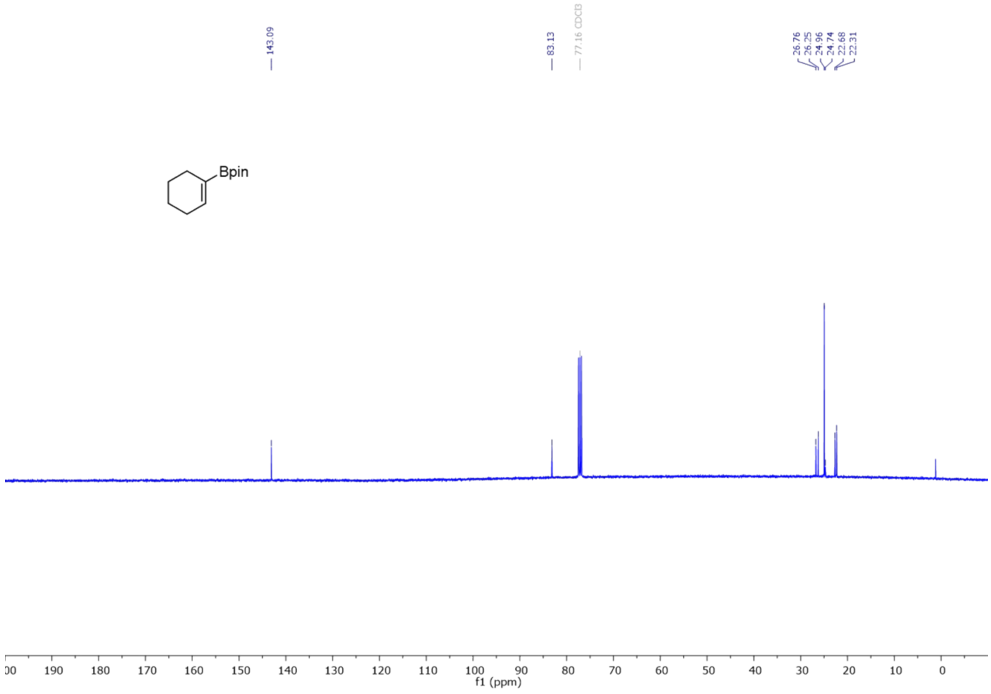


Figure SI 18: ^{13}C NMR spectrum of **1** ($CDCl_3$, 101 MHz).

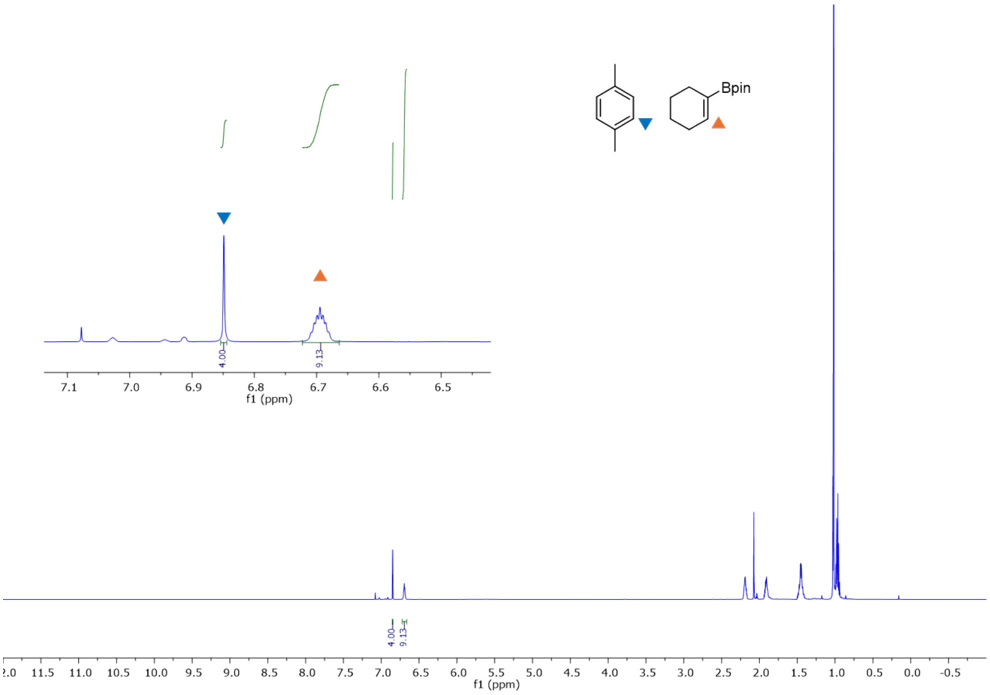


Figure SI 19: ^{1}H NMR spectrum for the determination of the in situ yield for the reaction of 1,4-cyclohexadiene. *p*-Xylene was used as internal standard (0.05 mmol) (400 MHz, toluene-d_8).

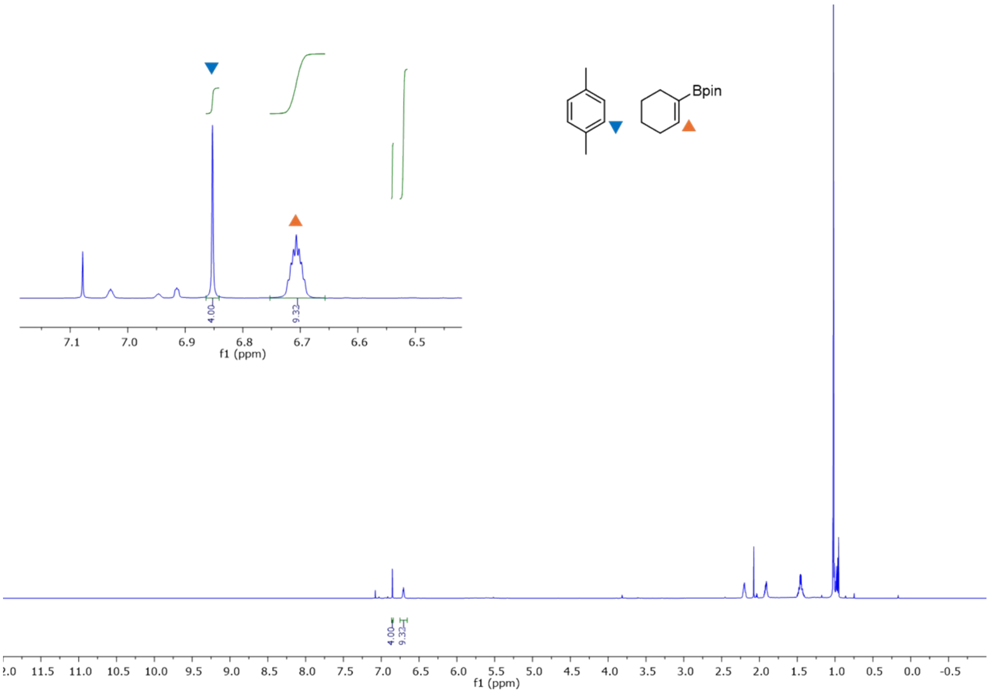


Figure SI 20: ^{1}H NMR spectrum for the determination of the in situ yield for the reaction of 1,3-cyclohexadiene. *p*-Xylene was used as internal standard (0.05 mmol) (400 MHz, toluene-d_8).

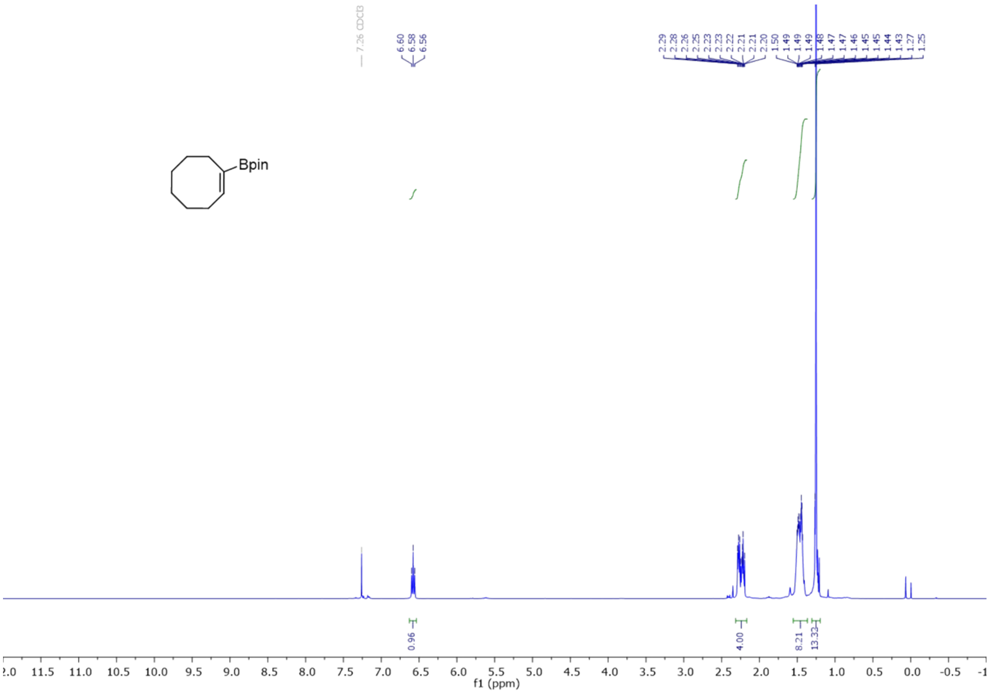


Figure SI 21: ^{1}H NMR spectrum of **6** ($CDCl_3$, 400 MHz).

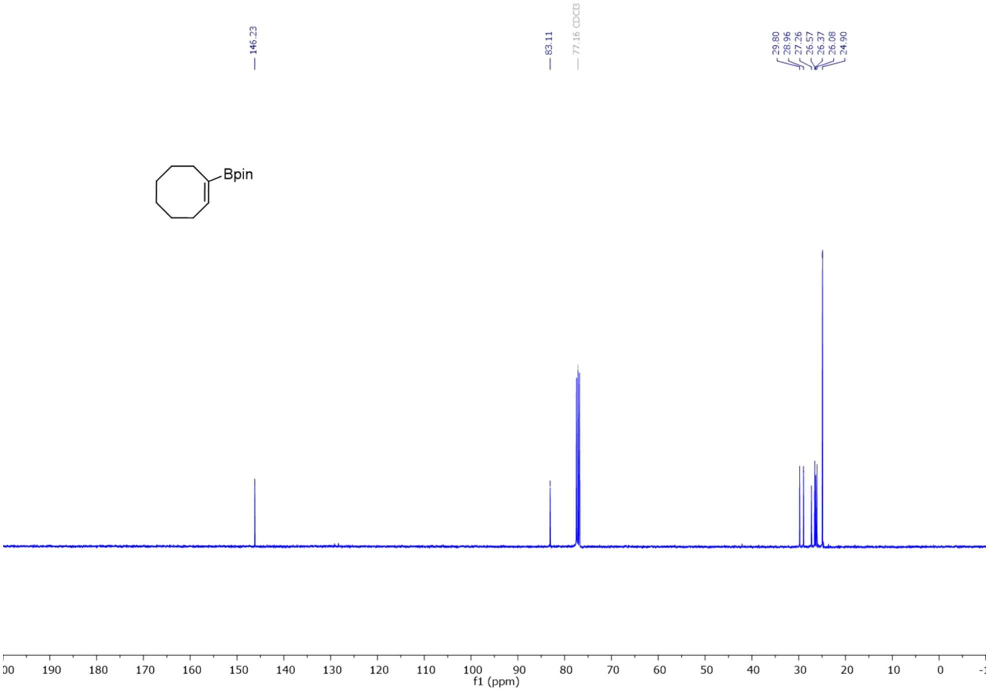


Figure SI 22: ^{13}C NMR spectrum of **6** ($CDCl_3$, 101 MHz).

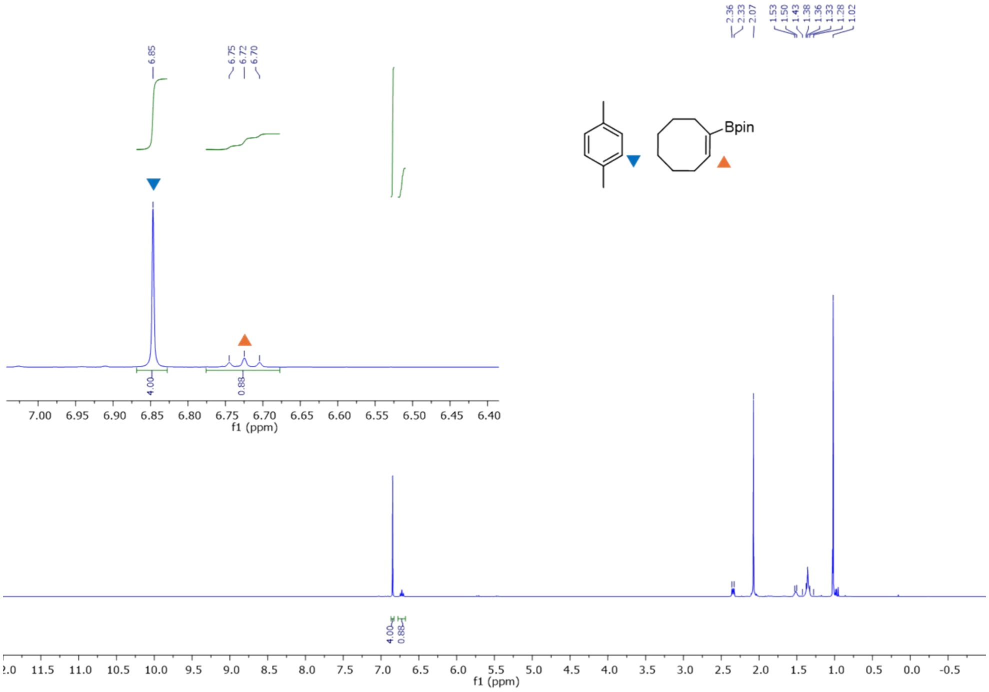


Figure SI 23: ^{1}H NMR spectrum for the determination of the in situ yield for the reaction of 1,5-cyclooctadiene. *p*-Xylene was used as internal standard (0.5 mmol) (400 MHz, toluene-d_8).

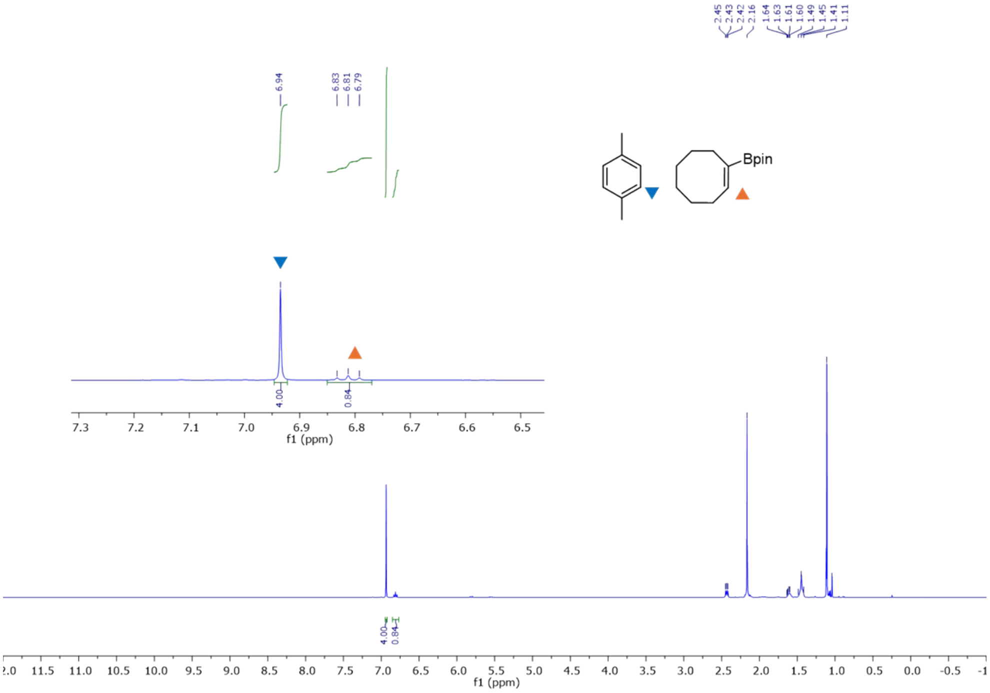


Figure SI 24: ^{1}H NMR spectrum for the determination of the in situ yield for the reaction of 1,3-cyclooctadiene. *p*-Xylene was used as internal standard (0. 5 mmol) (400 MHz, toluene-d_8).

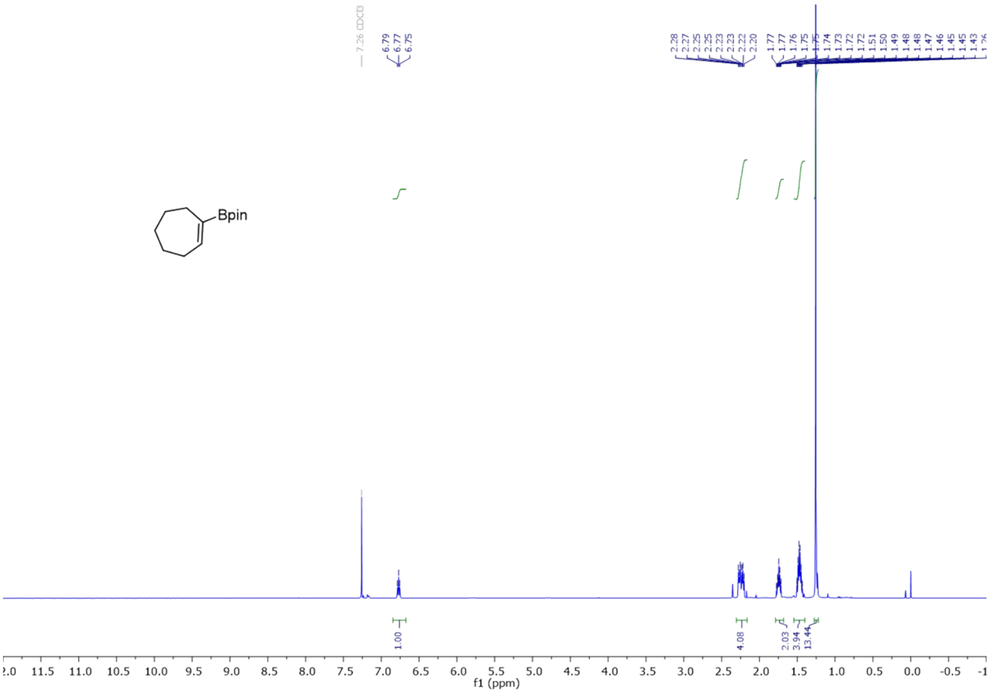


Figure SI 25: ^{1}H NMR spectrum of **7** ($CDCl_3$, 400 MHz).

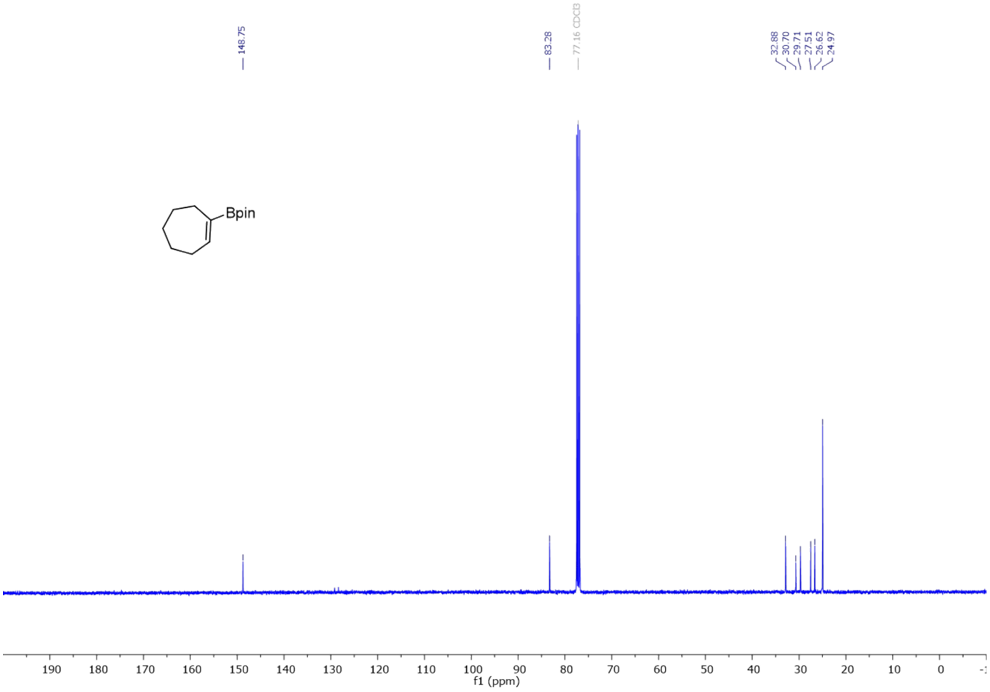


Figure SI 26: ^{13}C NMR spectrum of **7** ($CDCl_3$, 101 MHz).

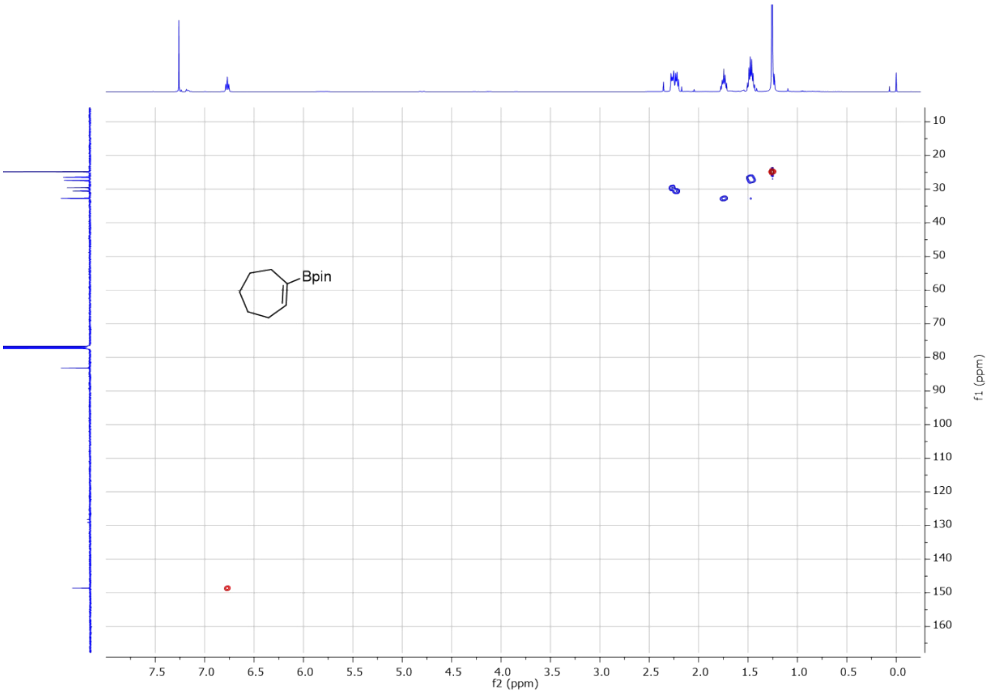


Figure SI 27: DEPT135 edited ^{1}H-^{13}C HSQC NMR spectrum of **7** ($CDCl_3$, 400 MHz, 101 MHz).

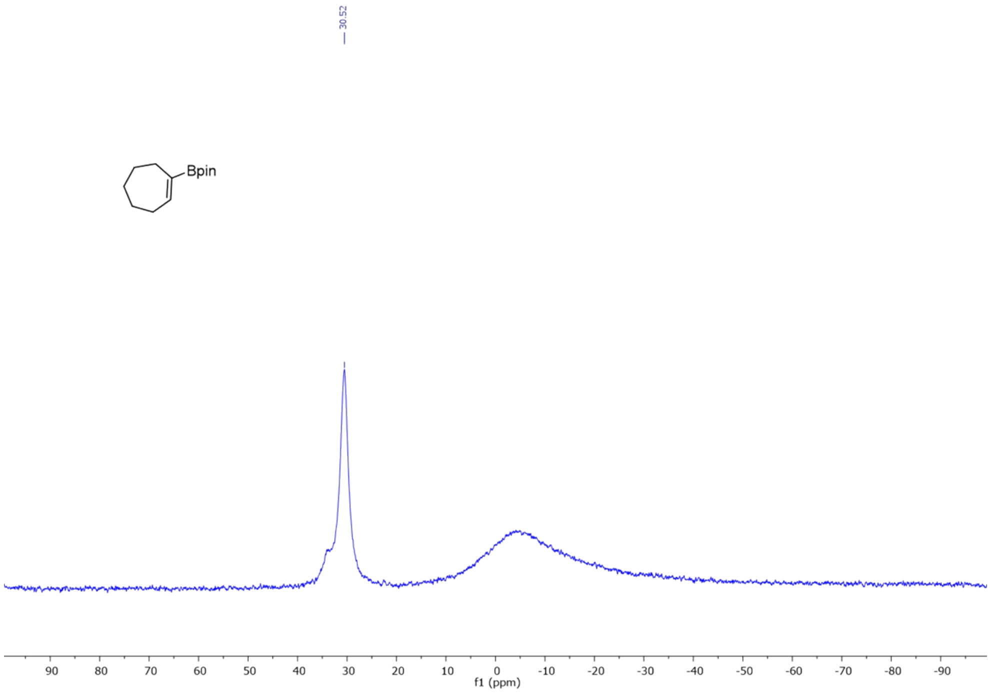


Figure SI 28: ^{11}B NMR spectrum of **7** ($CDCl_3$, 128 MHz).

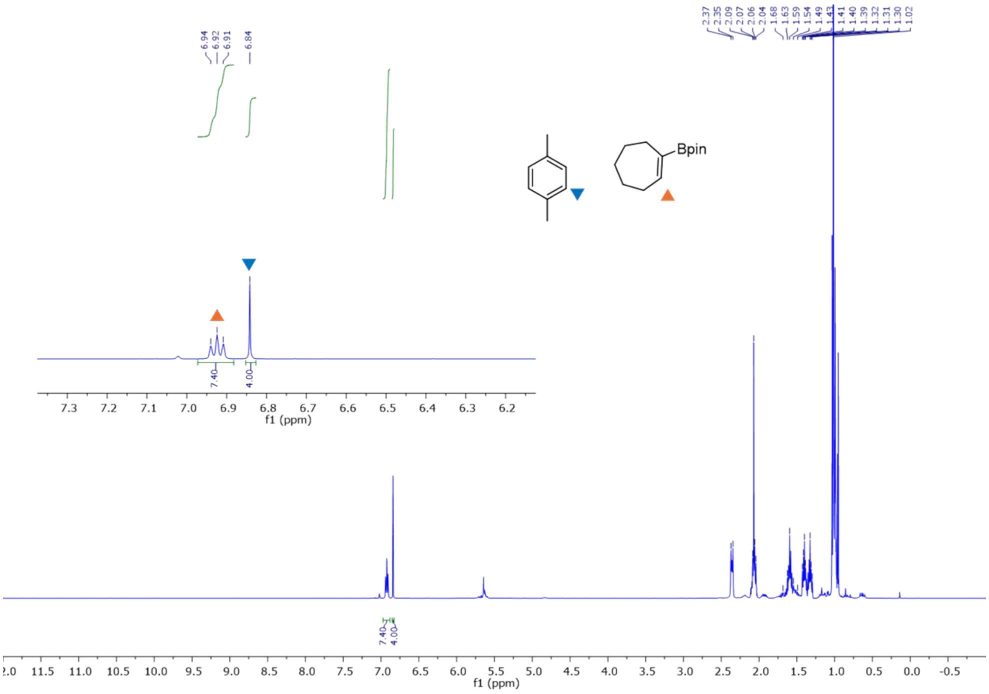


Figure SI 29: ^{1}H NMR spectrum for the determination of the in situ yield for the reaction of 1,3-cycloheptadiene (0.5 mmol). *p*-Xylene was used as internal standard (0.05 mmol) (400 MHz, toluene-d_8).

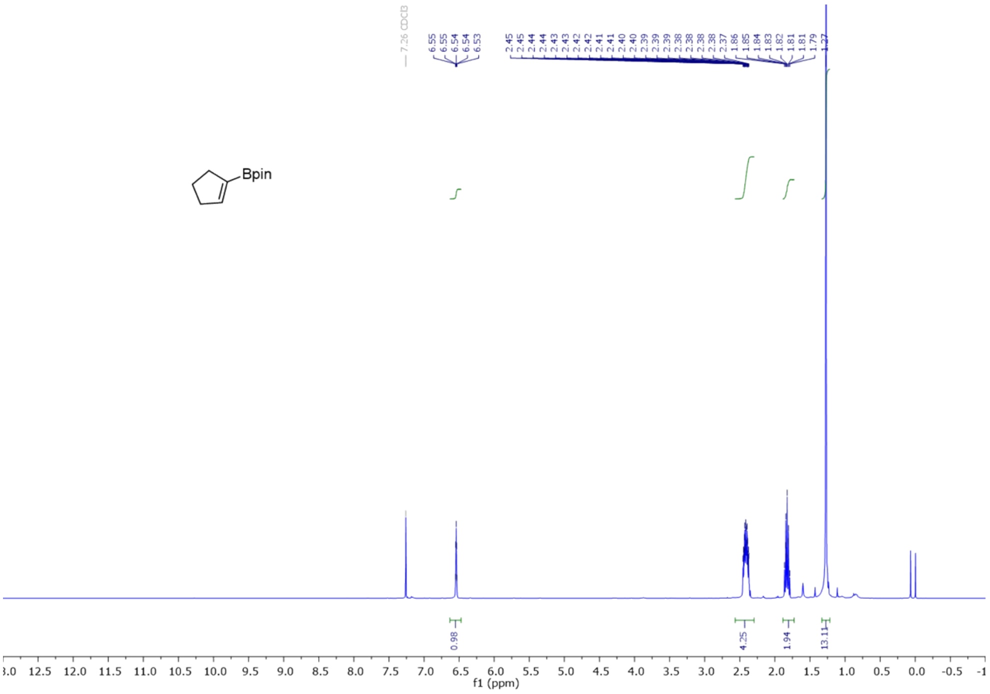


Figure SI 30: ^{1}H NMR spectrum of **8** (400 MHz, CDCl$_3$)

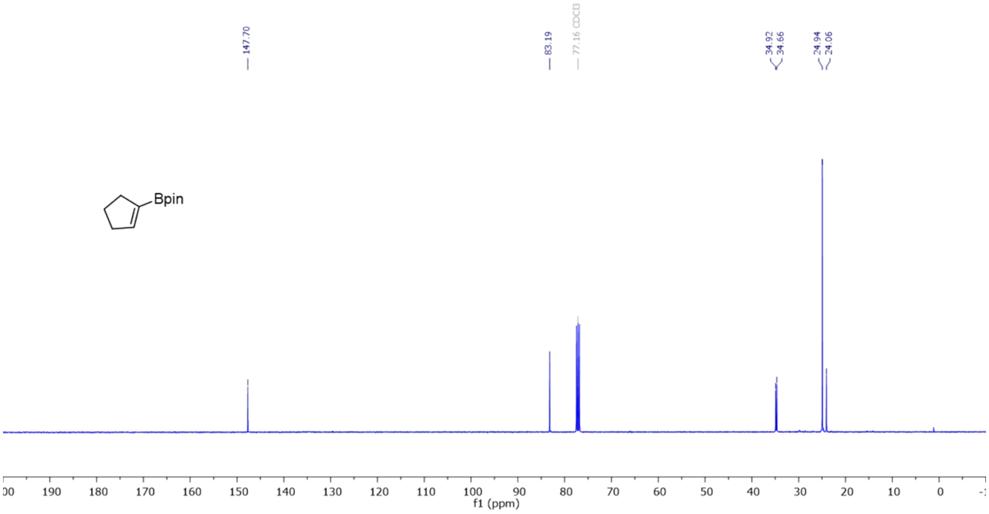


Figure SI 31: ^{13}C NMR spectrum of **8** (101 MHz, CDCl$_3$)

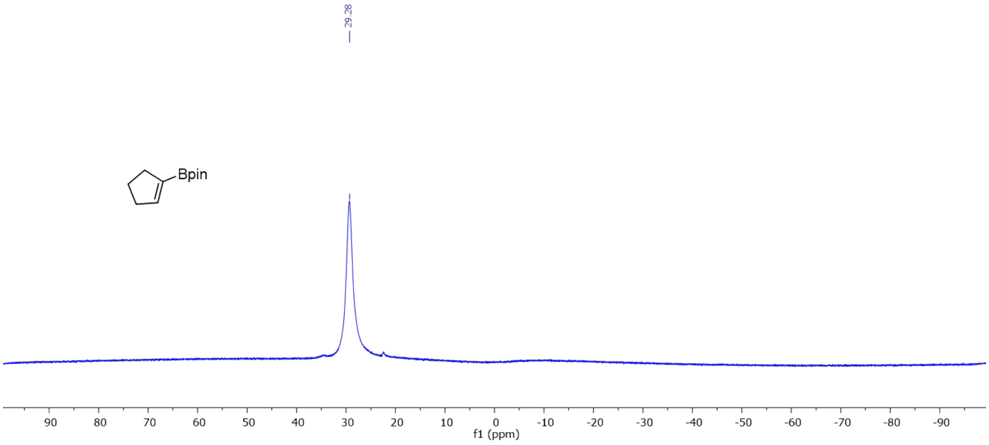


Figure SI 32: ^{11}B NMR spectrum of **8** (128 MHz, CDCl$_3$).

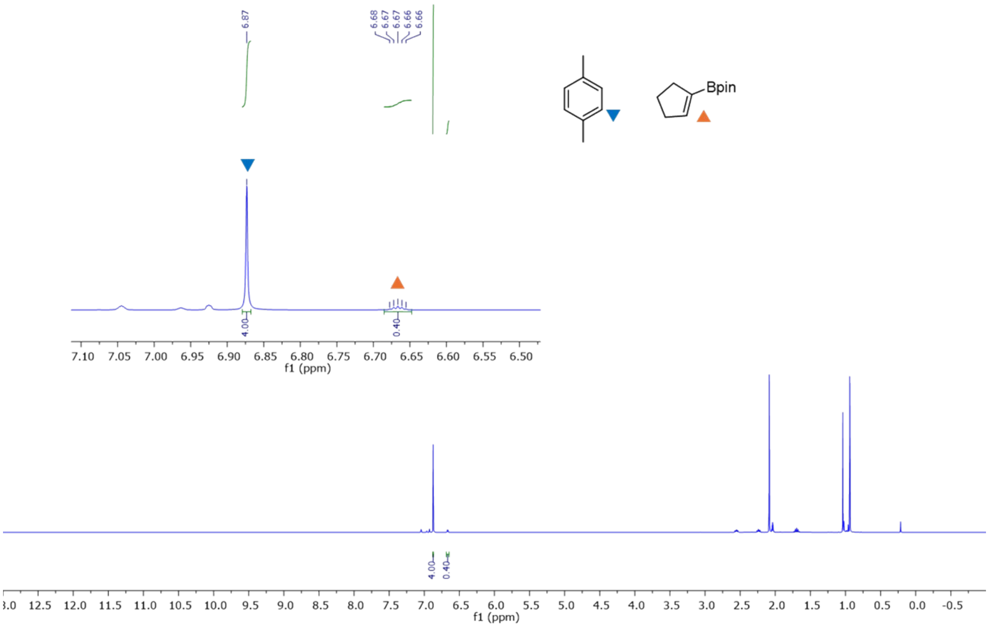


Figure SI 33: ^{1}H NMR spectrum for the determination of the in situ yield for the reaction of cyclopentadiene. *p*-Xylene was used as internal standard (0.05 mmol) (400 MHz, toluene-d_8).

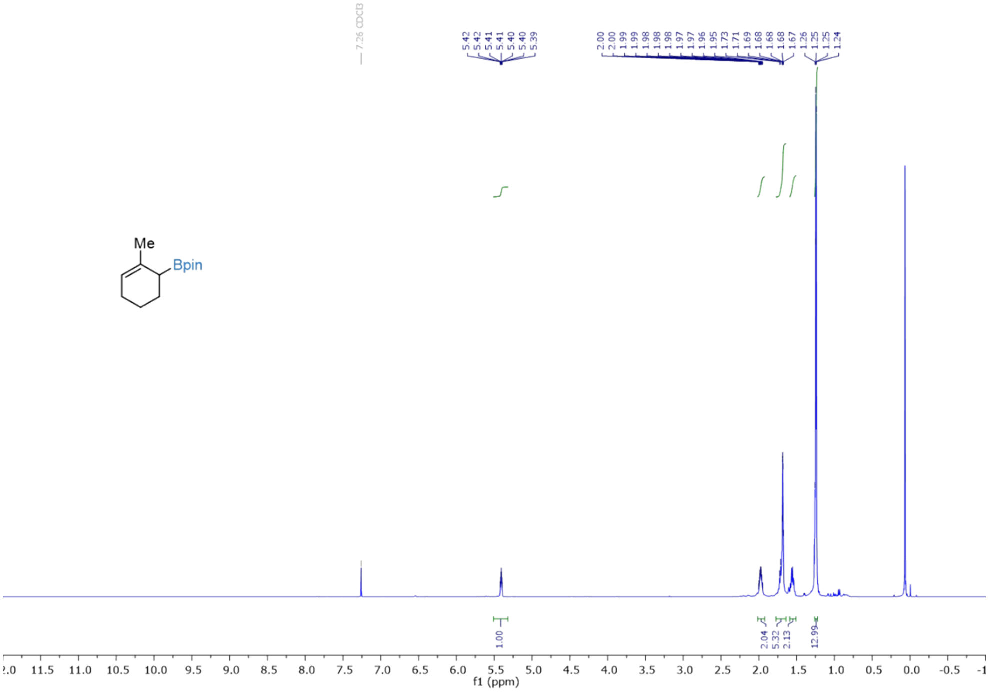


Figure SI 34: ^{1}H NMR spectrum of **9** (400 MHz, CDCl$_3$).

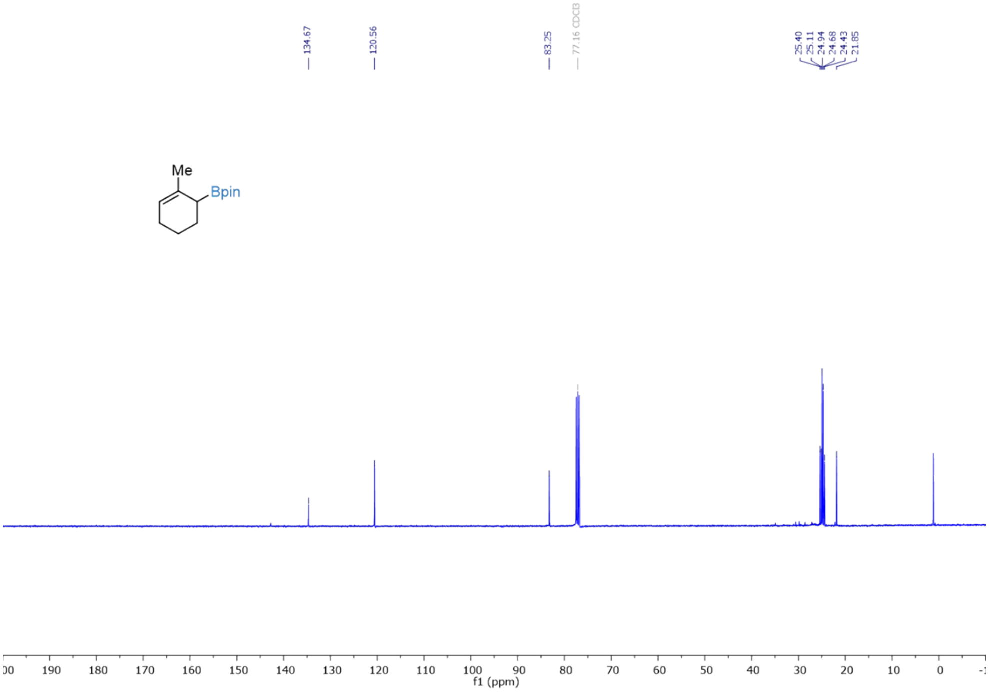


Figure SI 35: ^{13}C NMR spectrum of **9** (101 MHz, CDCl$_3$).

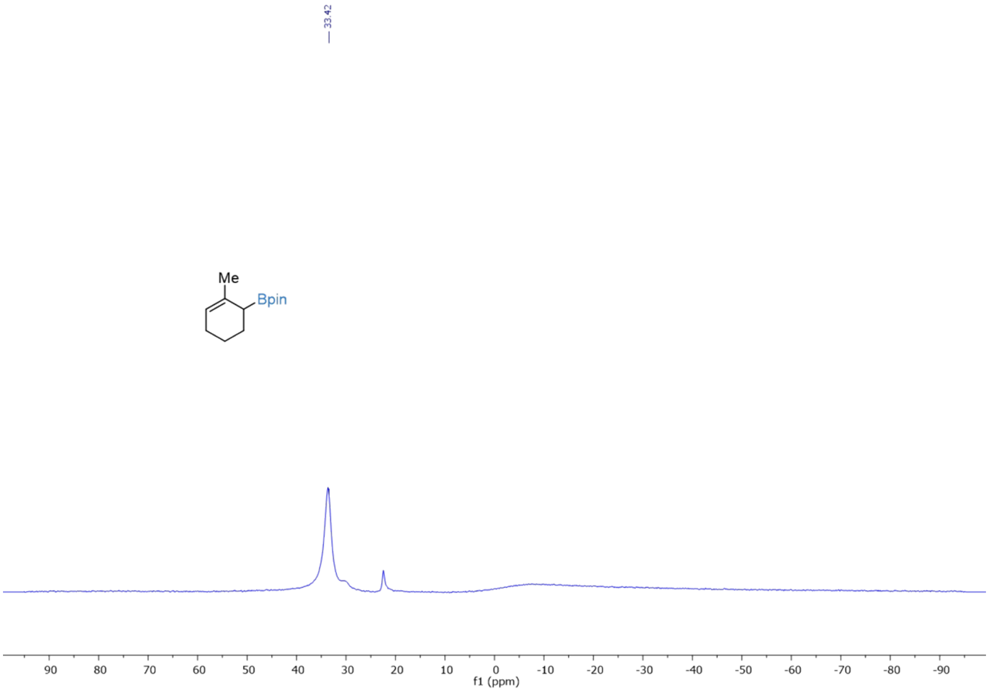


Figure SI 36: ^{11}B NMR spectrum of **9** (128 MHz, CDCl$_3$).

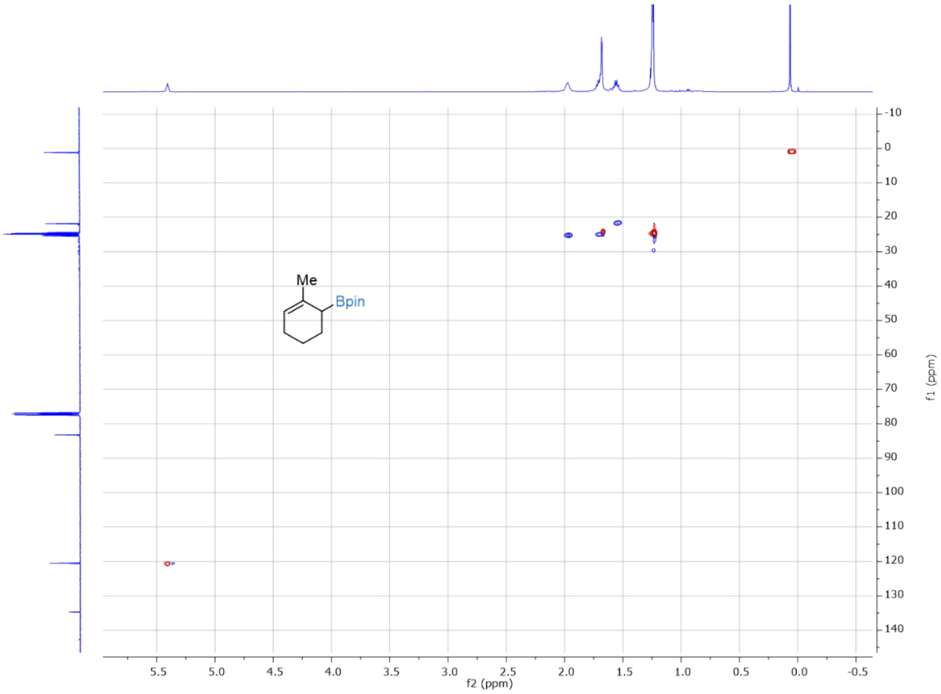


Figure SI 37: DEPT135 edited ^{1}H-^{13}C-HSQC NMR spectrum of **9** (400 MHz, 101 MHz, CDCl$_3$).

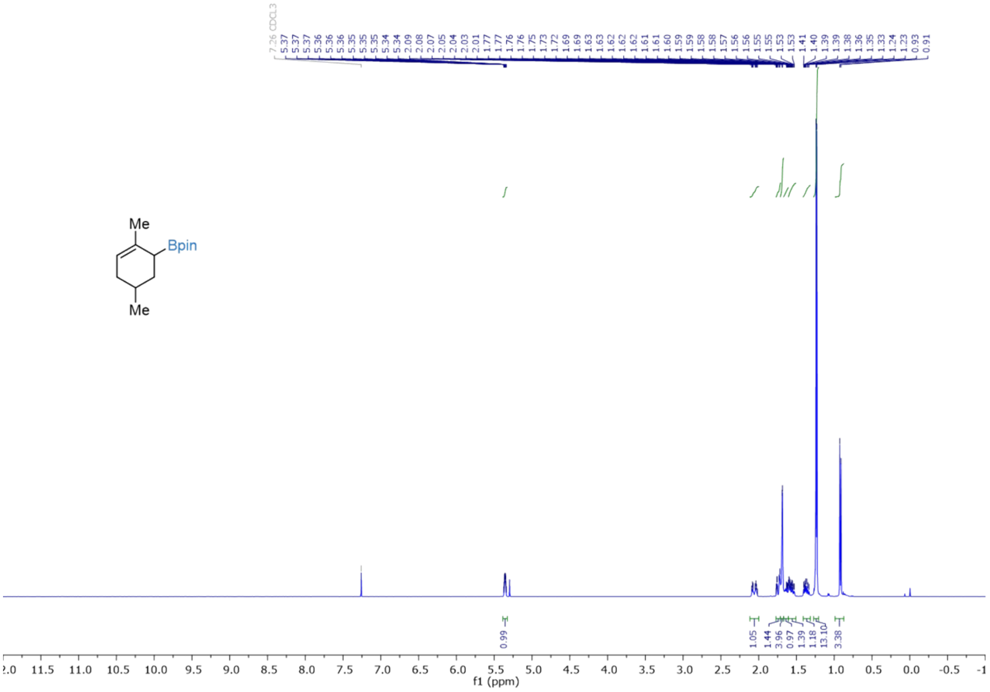


Figure SI 38: ^{1}H NMR spectrum of **10** (400 MHz, CDCl$_3$).

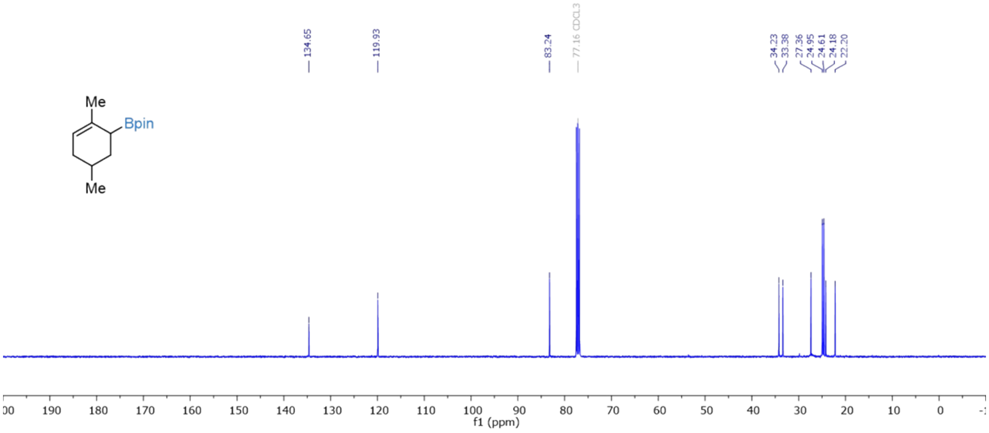


Figure SI 39: ^{13}C NMR spectrum of **10** (101 MHz, CDCl$_3$).

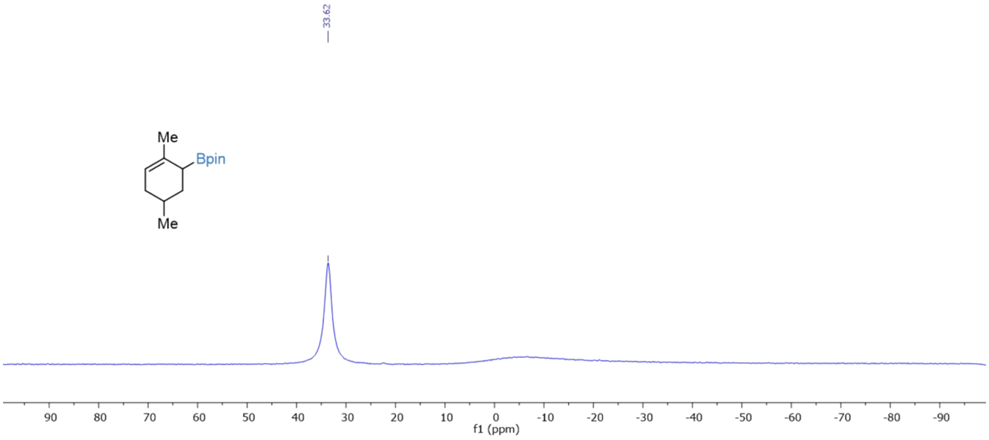


Figure SI 40: ^{11}B NMR spectrum of **10** (128 MHz, CDCl$_3$).

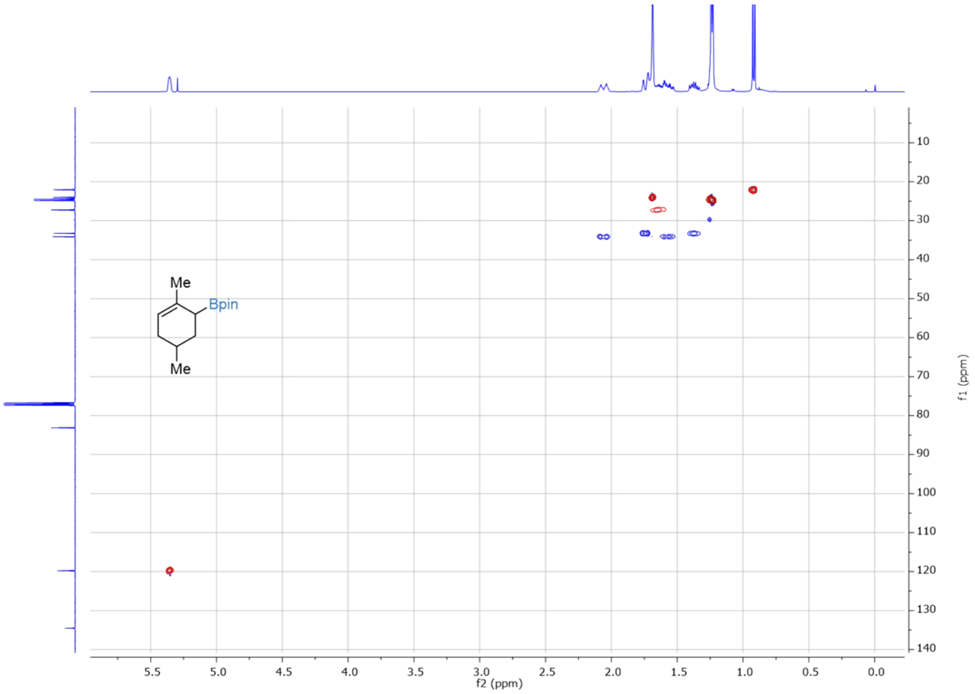


Figure SI 41: DEPT135 edited ^{1}H-^{13}C-HSQC NMR spectrum of **10** (400 MHz,101 MHz, CDCl$_3$).

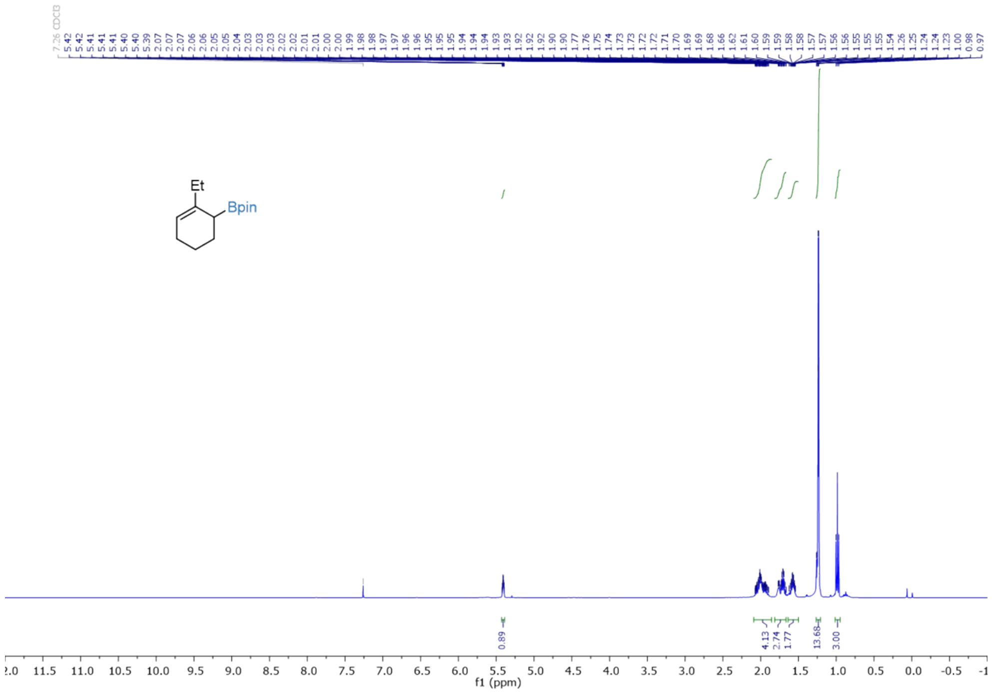


Figure SI 42: ^{1}H NMR spectrum of **11** (400 MHz, CDCl$_3$).

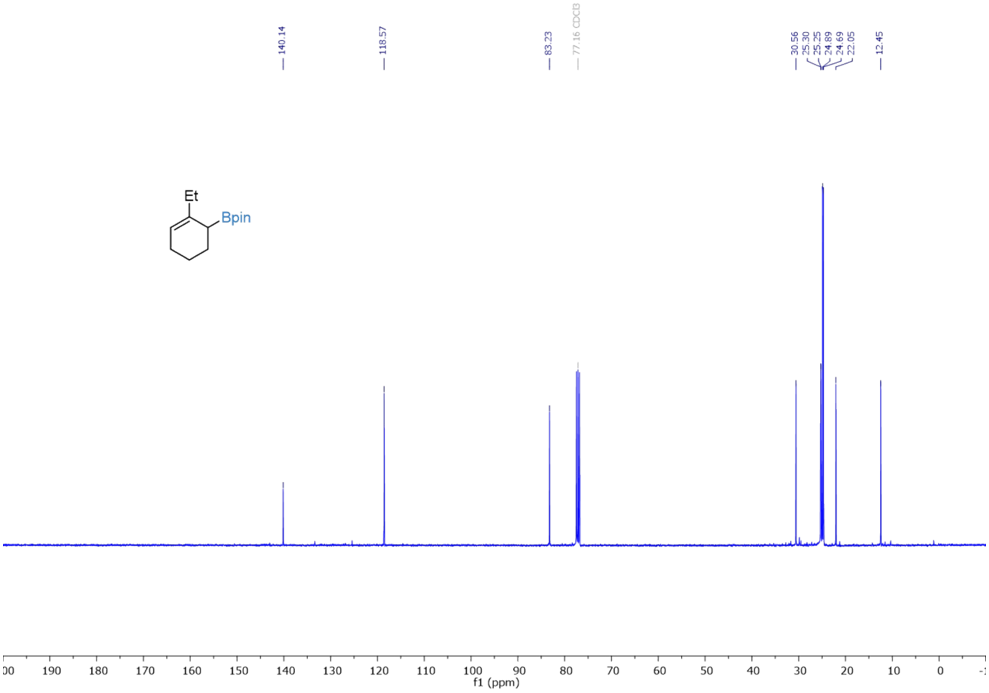


Figure SI 43: ^{11}C NMR spectrum of **11** (101 MHz, CDCl$_3$).

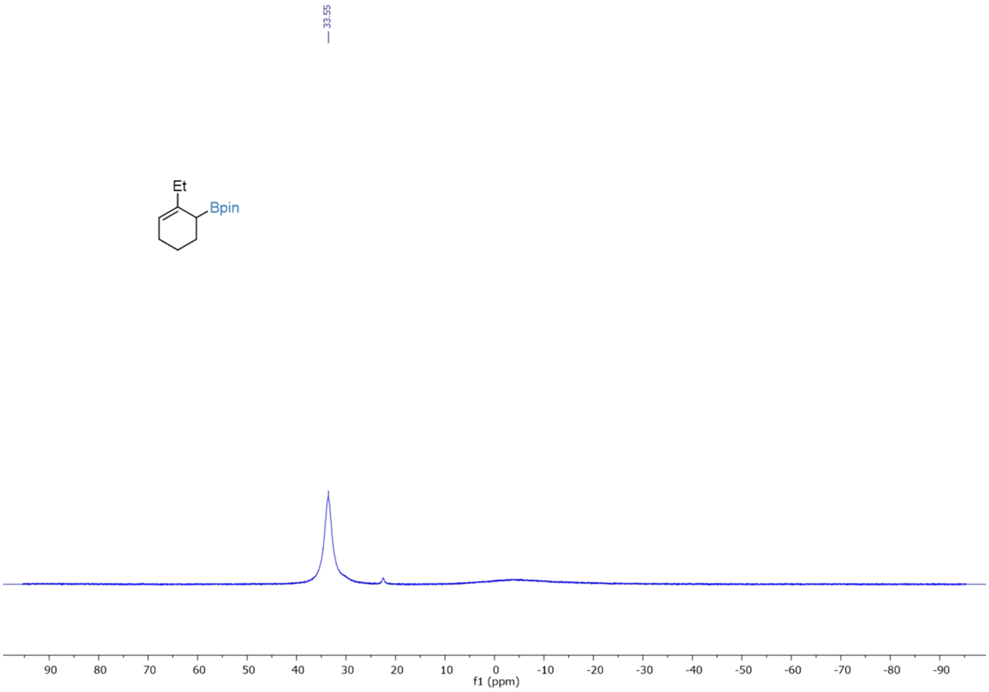


Figure SI 44: ^{11}B NMR spectrum of **11** (128 MHz, CDCl$_3$).

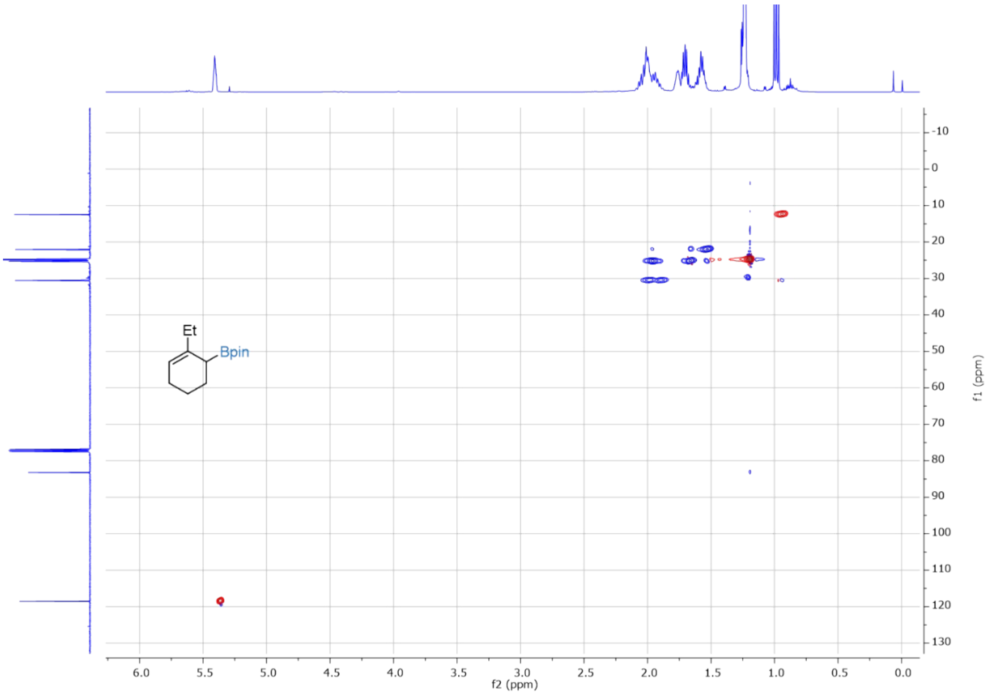


Figure SI 45: DEPT135 edited ^{1}H-^{13}C HSQC NMR spectrum of **11** (400 MHz, 101 MHz, $CDCl_3$).

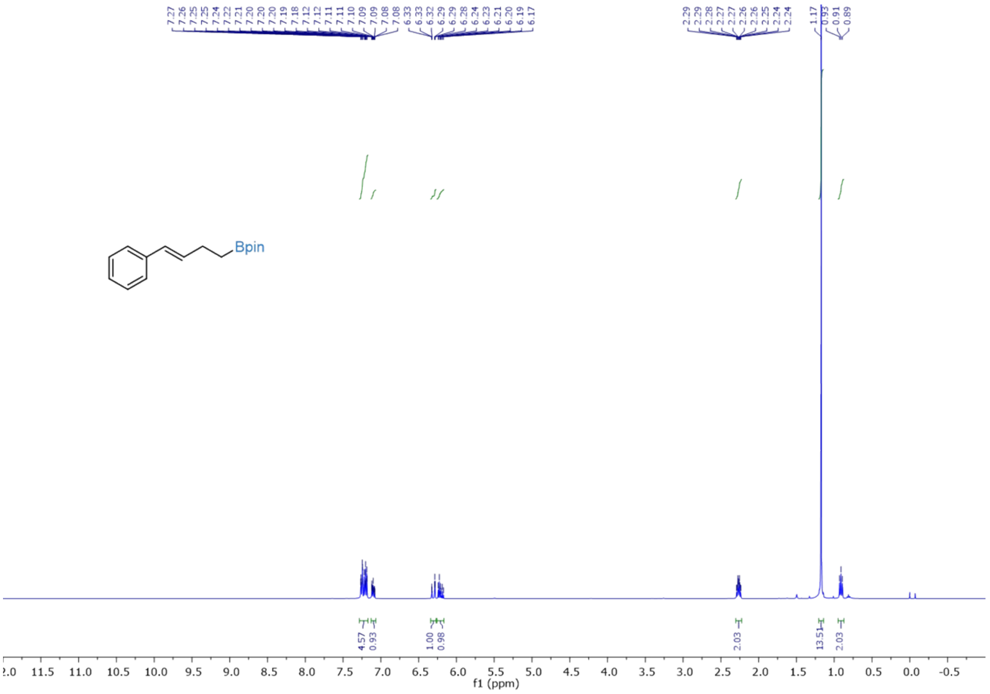


Figure SI 46: ^{1}H NMR spectrum of **12** ($CDCl_3$, 400 MHz).

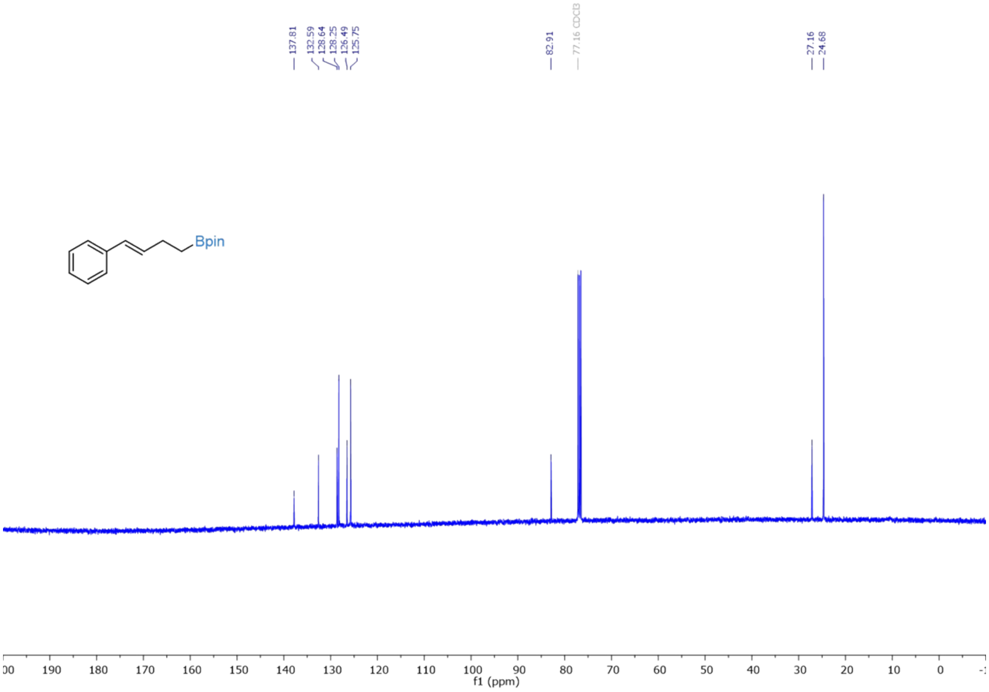


Figure SI 47: ^{13}C NMR spectrum of **12** (CDCl$_3$, 101 MHz).

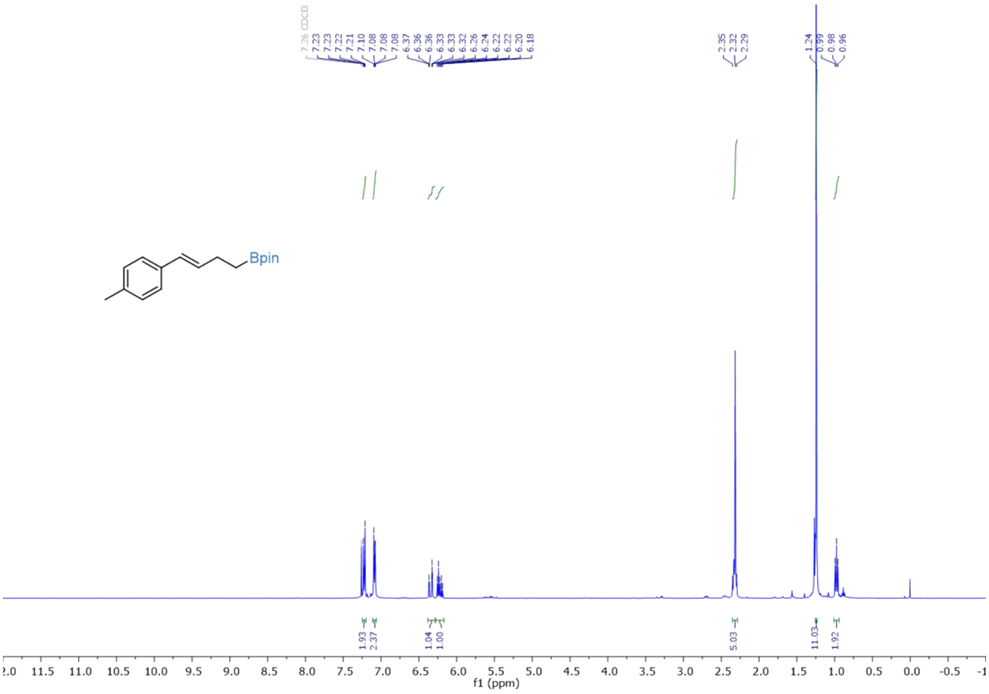


Figure SI 48: ^{1}H NMR spectrum of **13** ($CDCl_3$, 101 MHz).

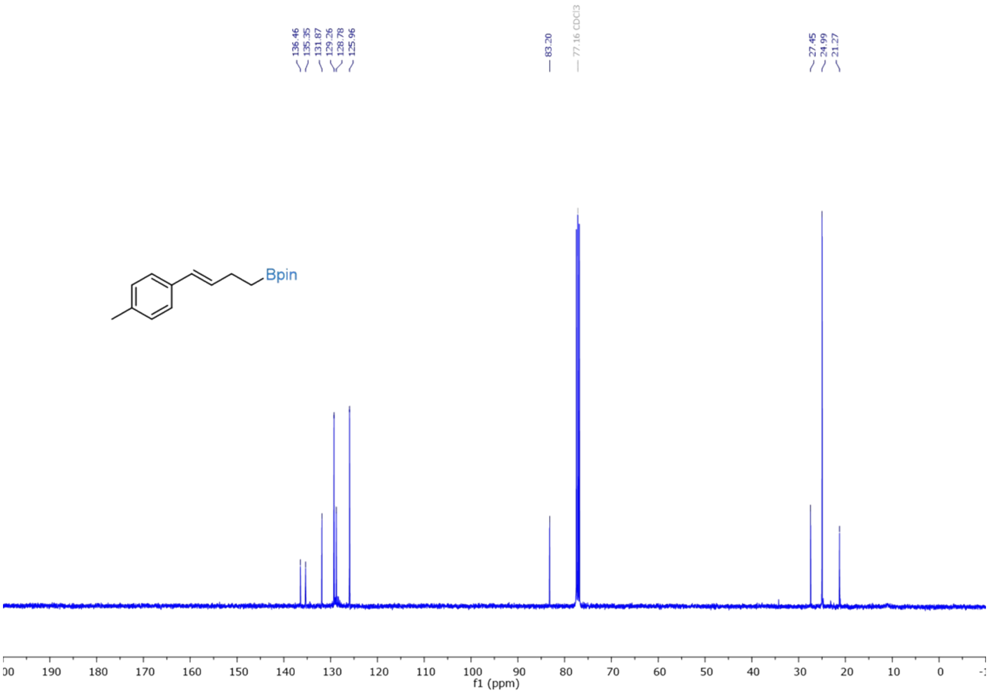


Figure SI 49: ^{13}C NMR spectrum of **13** ($CDCl_3$, 101 MHz).

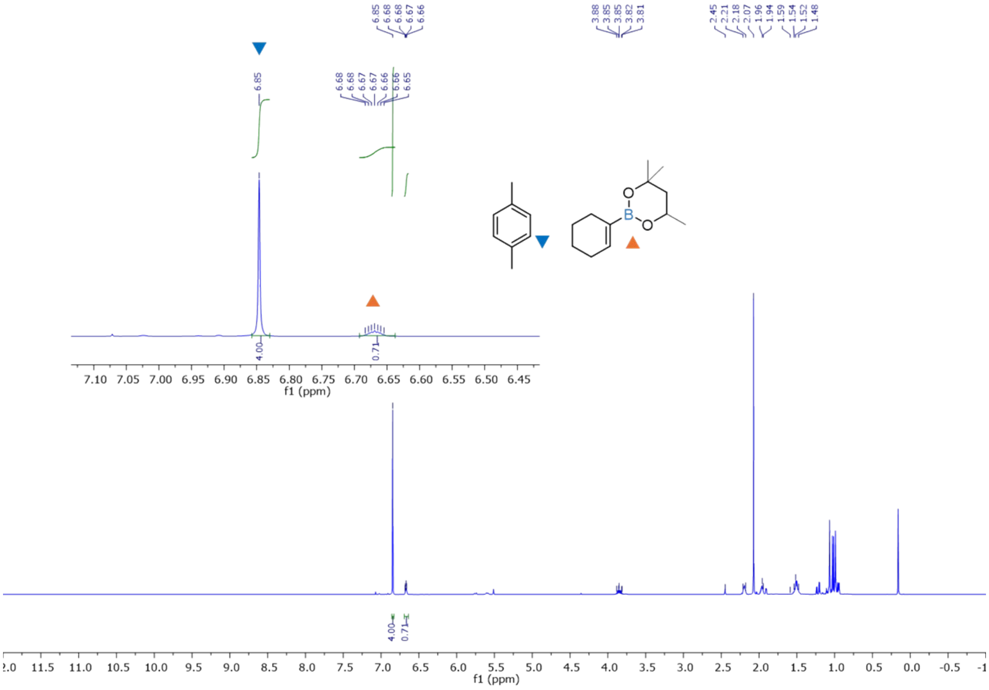


Figure SI 50: ^{1}H NMR spectrum for the determination of the in situ yield of **14**. *p*-Xylene was used as internal standard (0.05 mmol) (400 MHz, toluene-d_8).

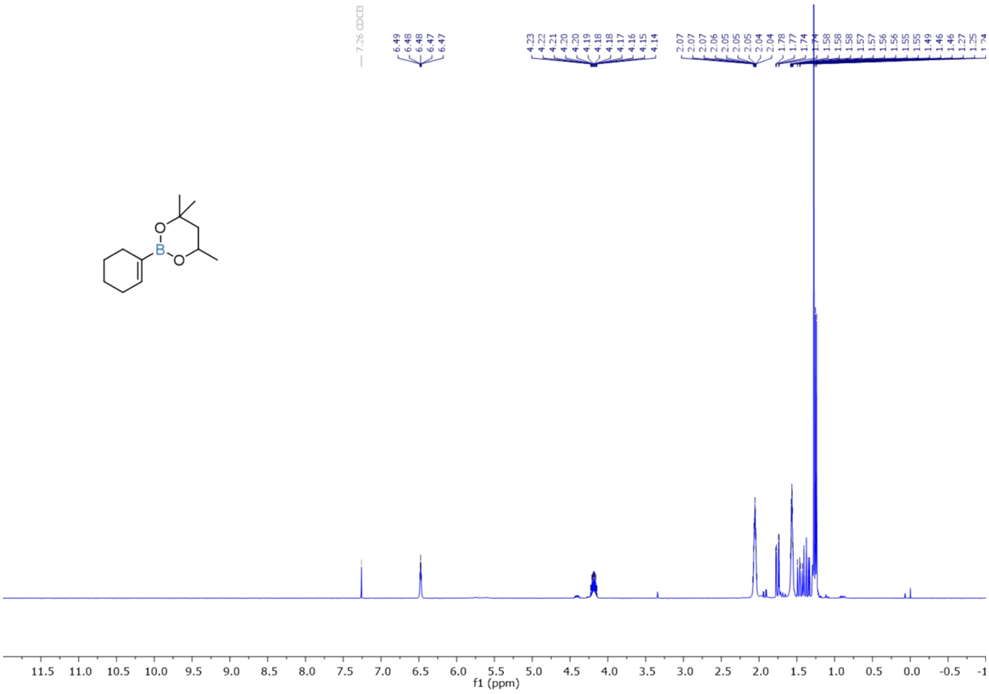


Figure SI 51: ^{1}H NMR spectrum of **14** (400 MHz, CDCl$_3$).

Note: The minor impurities in the aliphatic area most likely originate from $B_2(OR)_4$.

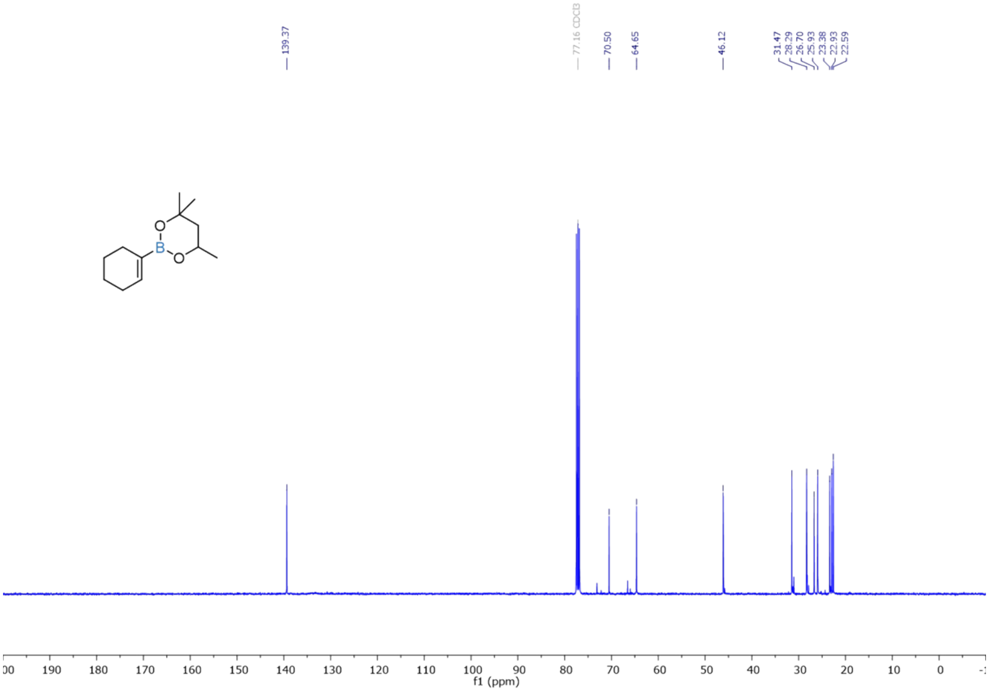


Figure SI 52: ^{13}C NMR spectrum of **14** (101 MHz, CDCl$_3$).

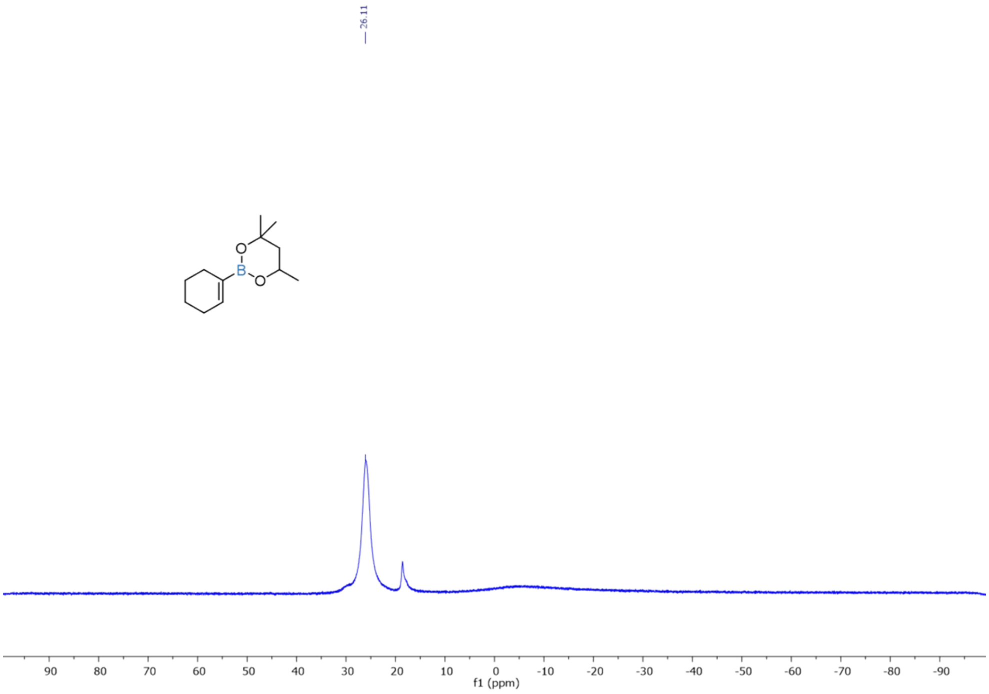


Figure SI 53: ^{11}B NMR spectrum of **14** (128 MHz, CDCl$_3$).

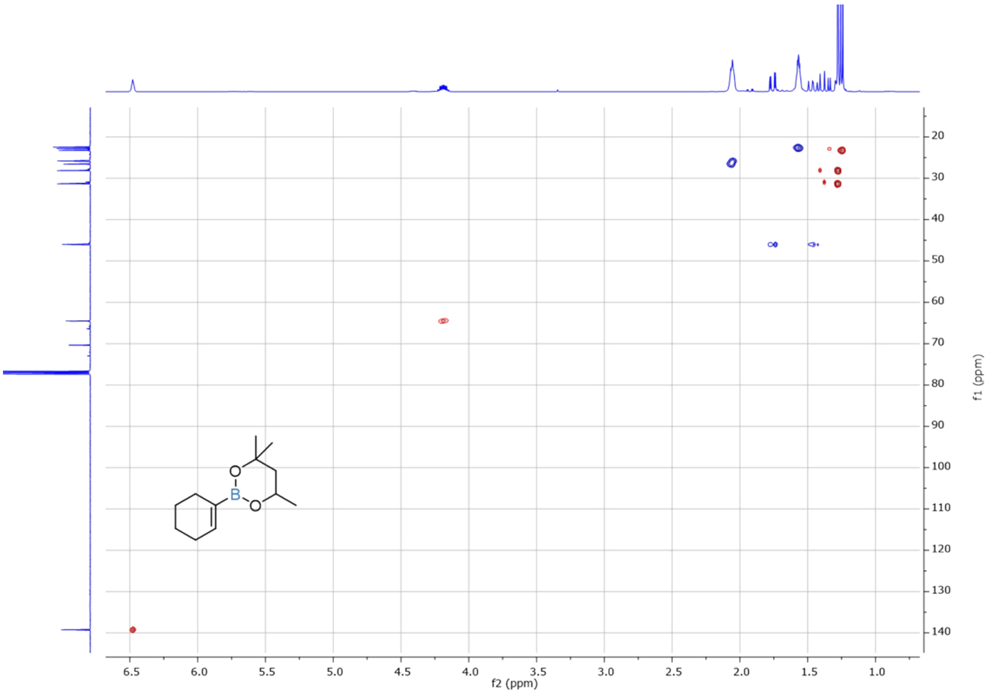


Figure SI 54: DEPT135 edited 1H-13C HSQC spectrum of **14** (400 MHz, 101 MHz, $CDCl_3$)

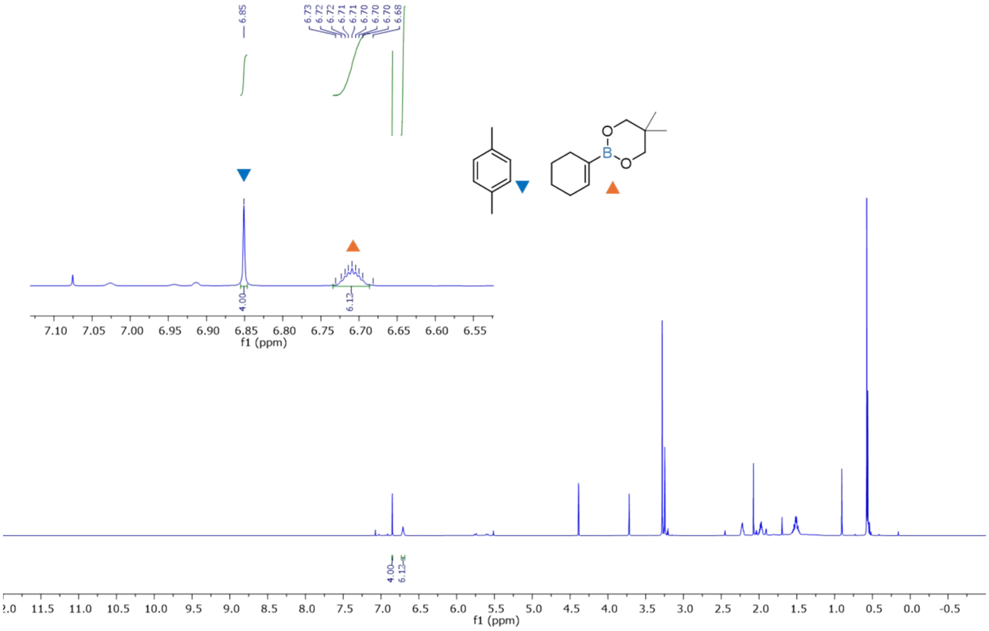


Figure SI 55: ^{1}H NMR spectrum for the determination of the in situ yield of 2-(1-Cyclohexen-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane **15**. *p*-Xylene was used as internal standard (0.05 mmol) (400 MHz, toluene-d_8).

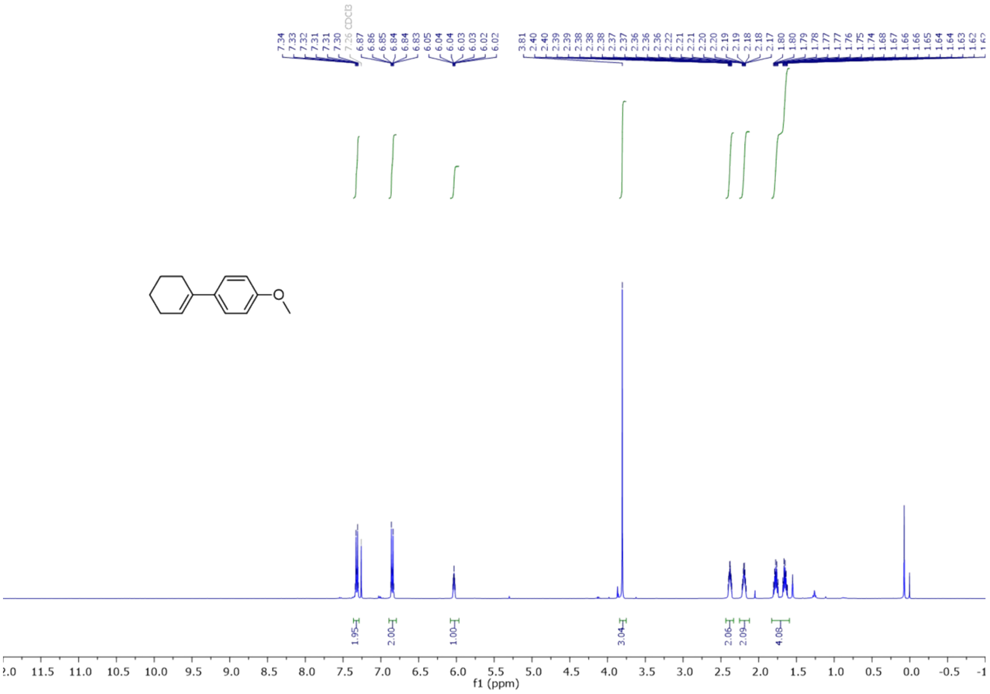


Figure SI 56: ^{1}H NMR spectrum of 1-(1-Cyclohexen-1-yl)-4-methoxybenzene **16** (400 MHz, CDCl$_3$).

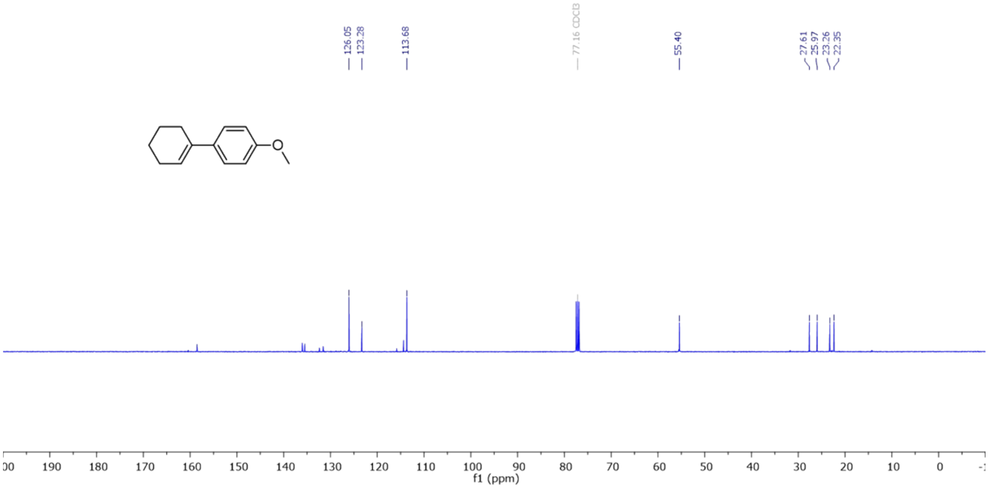


Figure SI 57: ^{13}C NMR spectrum of 1-(1-Cyclohexen-1-yl)-4-methoxybenzene **16** (101 MHz, CDCl$_3$)

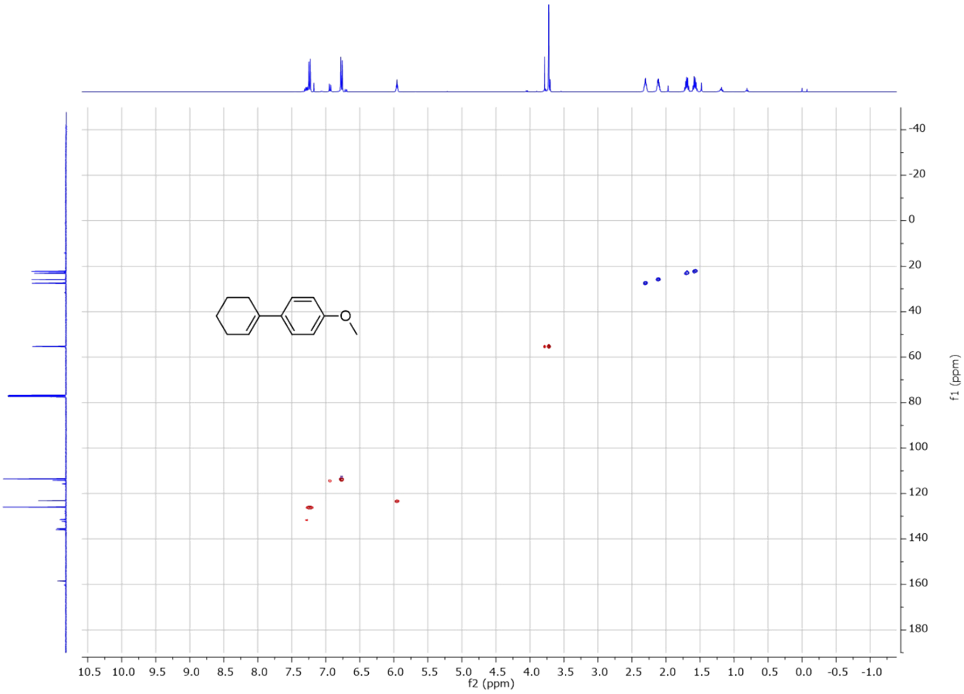


Figure SI 58: DEPT135 edited ^{1}H-^{13}C-HSQC NMR spectrum of 1-(1-Cyclohexen-1-yl)-4-methoxybenzene **16** (400 MHz ,101 MHz, $CDCl_3$).

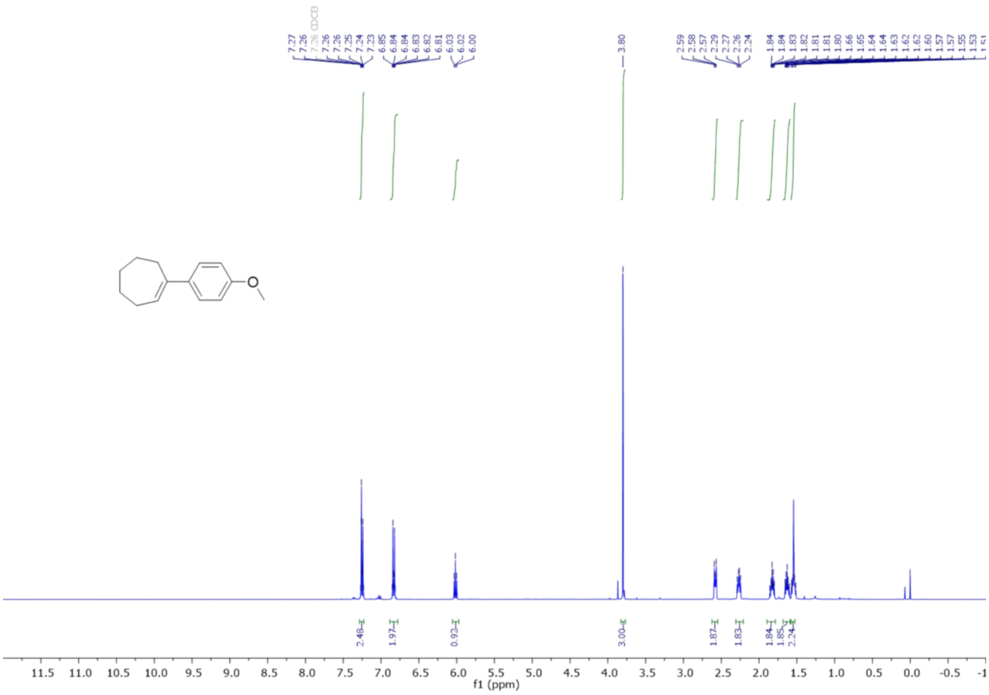


Figure SI 59: ^{1}H NMR spectrum of **17** (400 MHz, $CDCl_3$).

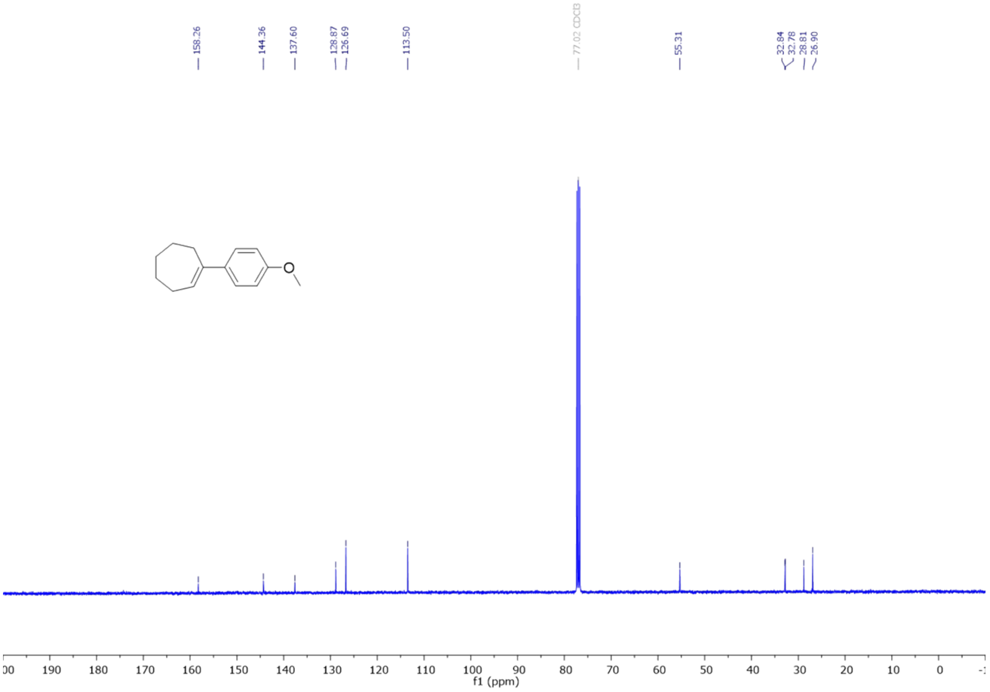


Figure SI 60: ^{13}C NMR spectrum of **17** (101 MHz, $CDCl_3$).

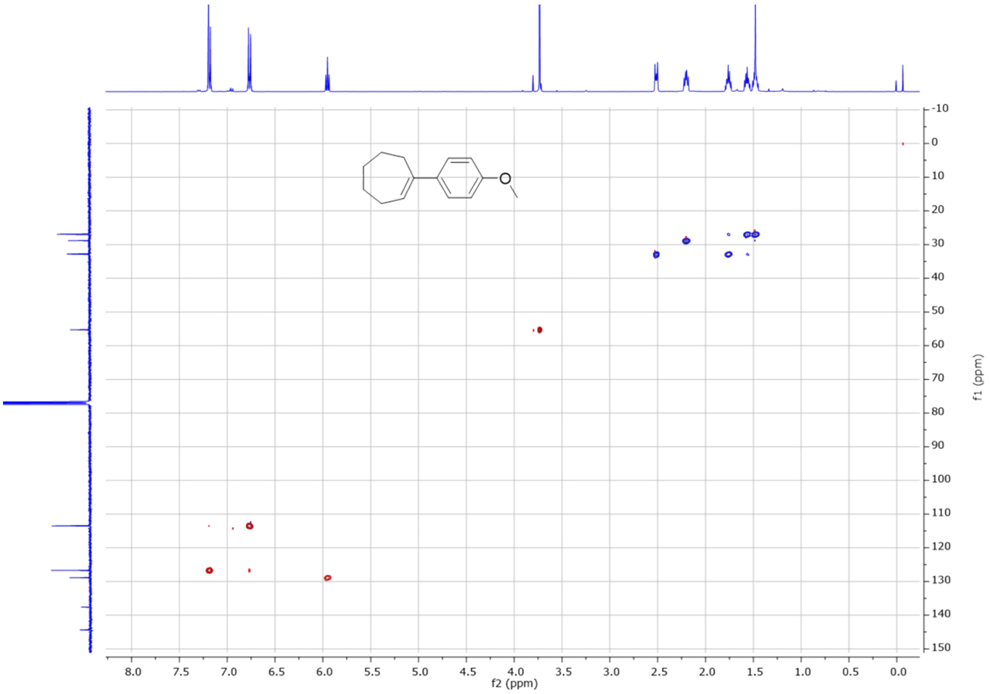


Figure SI 61: DEPT135 edited ^{1}H-^{13}C-HSQC NMR spectrum of 1-(1-Cyclohepten-1-yl)-4-methoxybenzene **17**. (400 MHz ,101 MHz, $CDCl_3$).

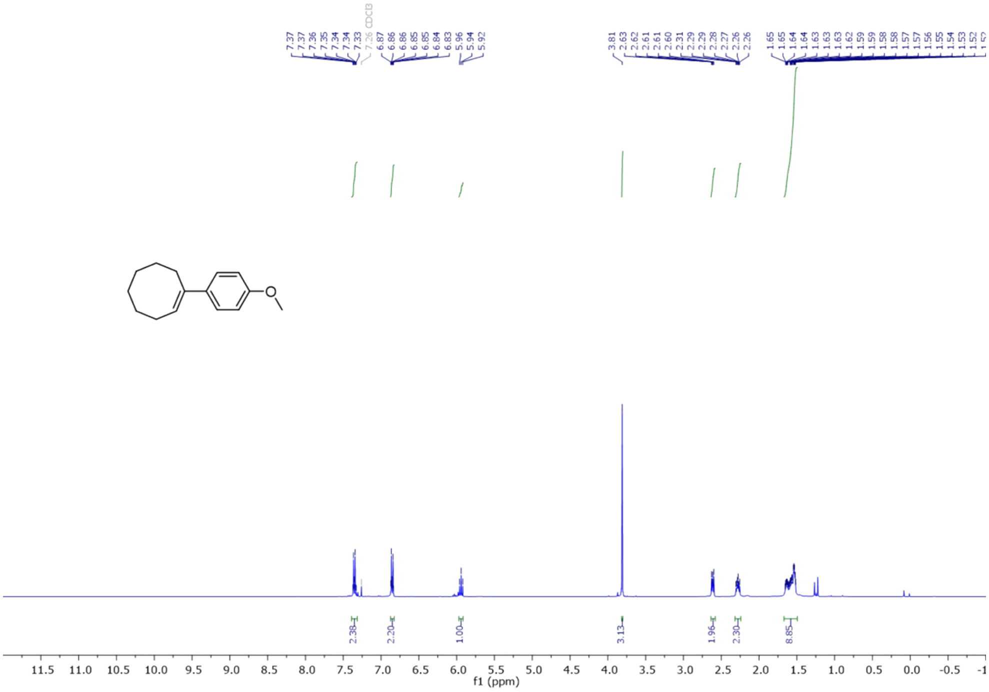


Figure SI 62: ^{1}H NMR spectrum of 1-(1-Cycloocten-1-yl)-4-methoxybenzene **18** (400 MHz, $CDCl_3$).

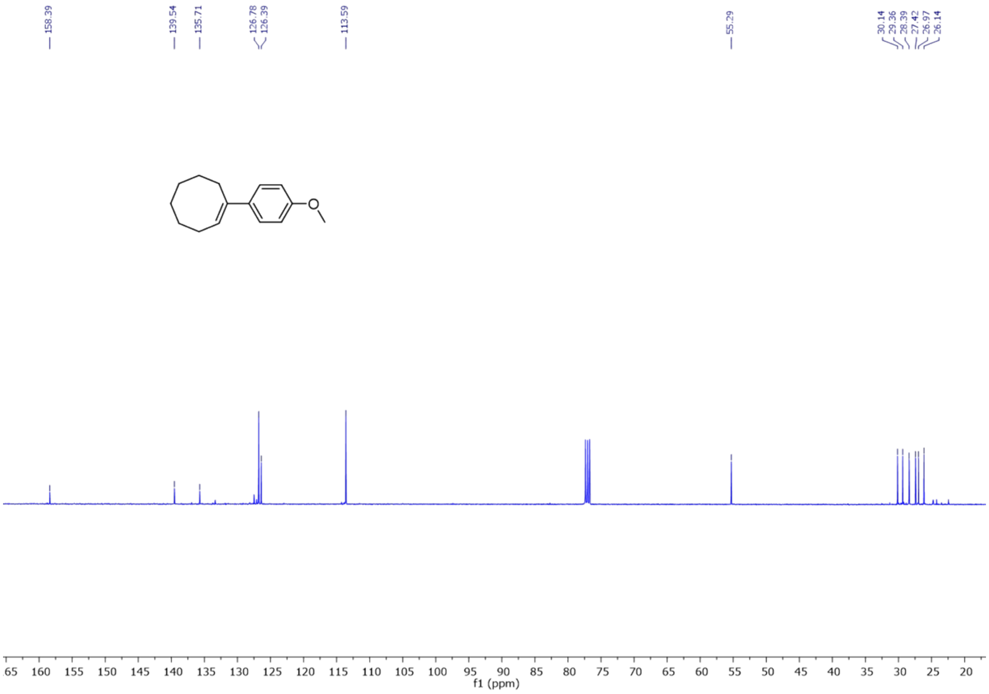


Figure SI 63: ^{13}C NMR spectrum of 1-(1-Cycloocten-1-yl)-4-methoxybenzene **18** (101 MHz, $CDCl_3$).

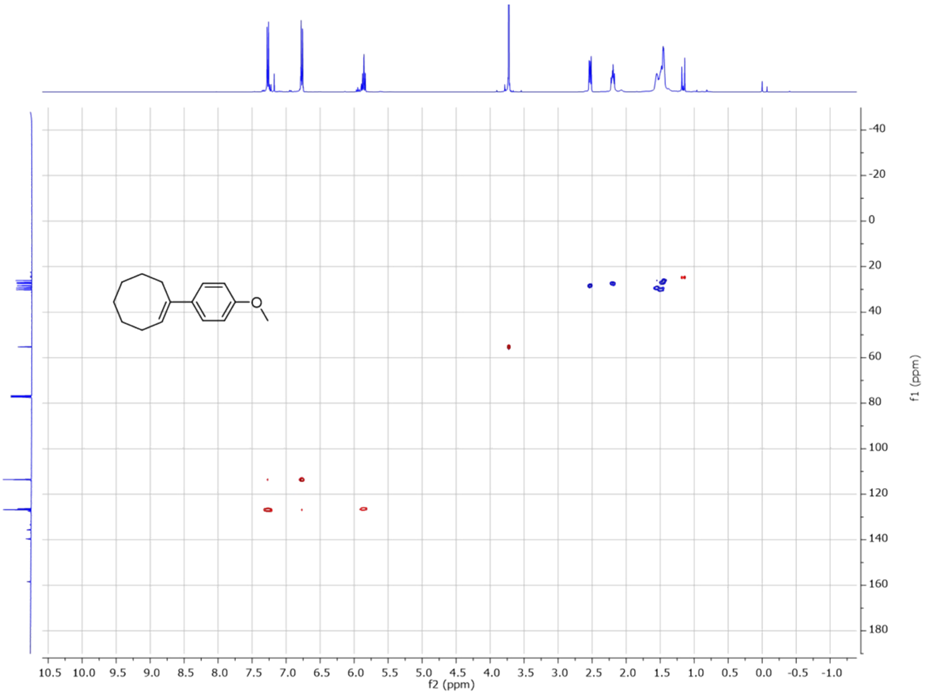


Figure SI 64: DEPT135 edited ^{1}H-^{13}C-HSQC NMR spectrum of 1-(1-Cyclohexen-1-yl)-4-methoxybenzene **18**. (400 MHz ,101 MHz, $CDCl_3$).

4 Control experiments

4.1 Reaction of 1,4-Cyclohexadiene 3 and Piers' borane 2 at rt

Inside a glovebox, 1,4-cyclohexadiene (0.05 mmol, 4.73 µL) was dissolved in benzene-*d*$_6$ inside a vial. Piers' borane (17.6 mg, 1.01 equiv.) was added, and the vial was shaken until the solid dissolved. The solution was transferred to an NMR tube with J. Young valve and NMR spectra directly recorded.

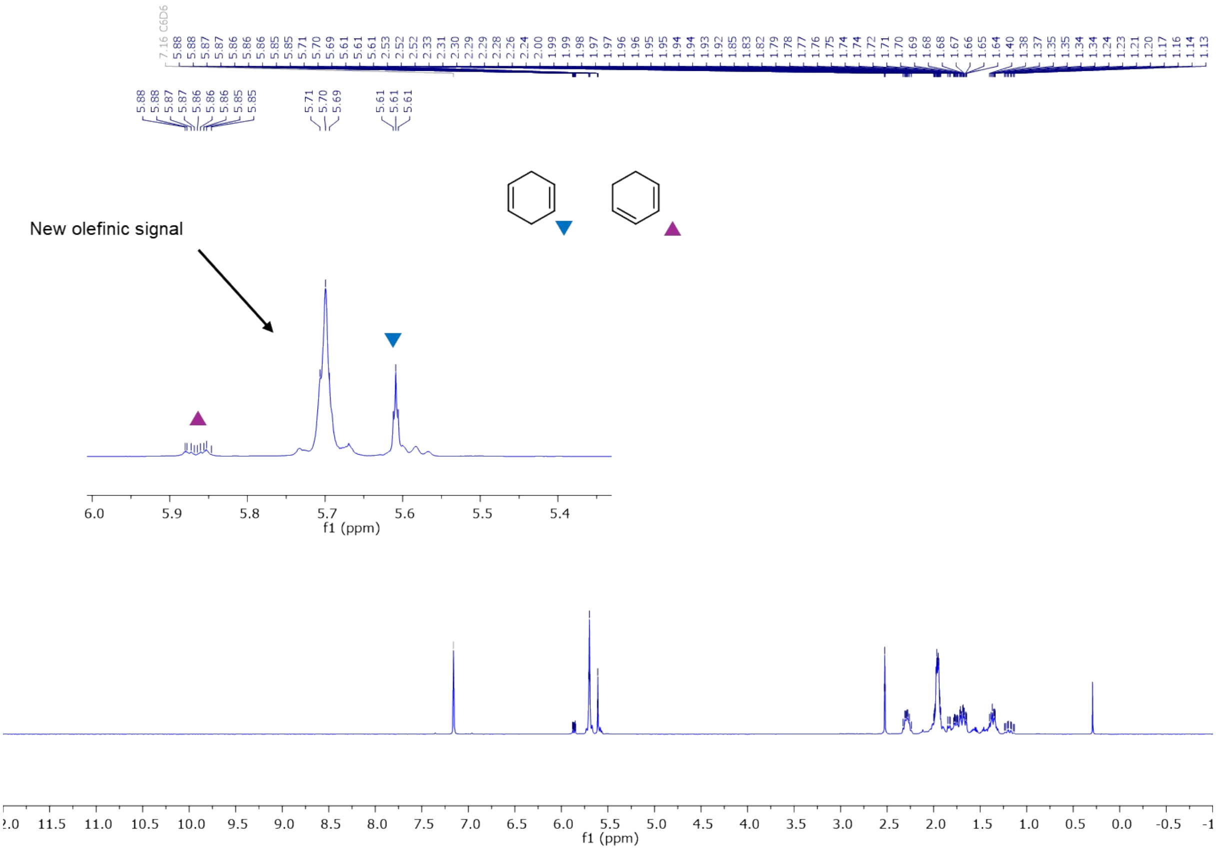


Figure SI 65: ^{1}H NMR spectrum of the reaction of 1,4-cyclohexadiene and Piers' borane at room temperature (400 MHz, benzene-*d*$_6$).

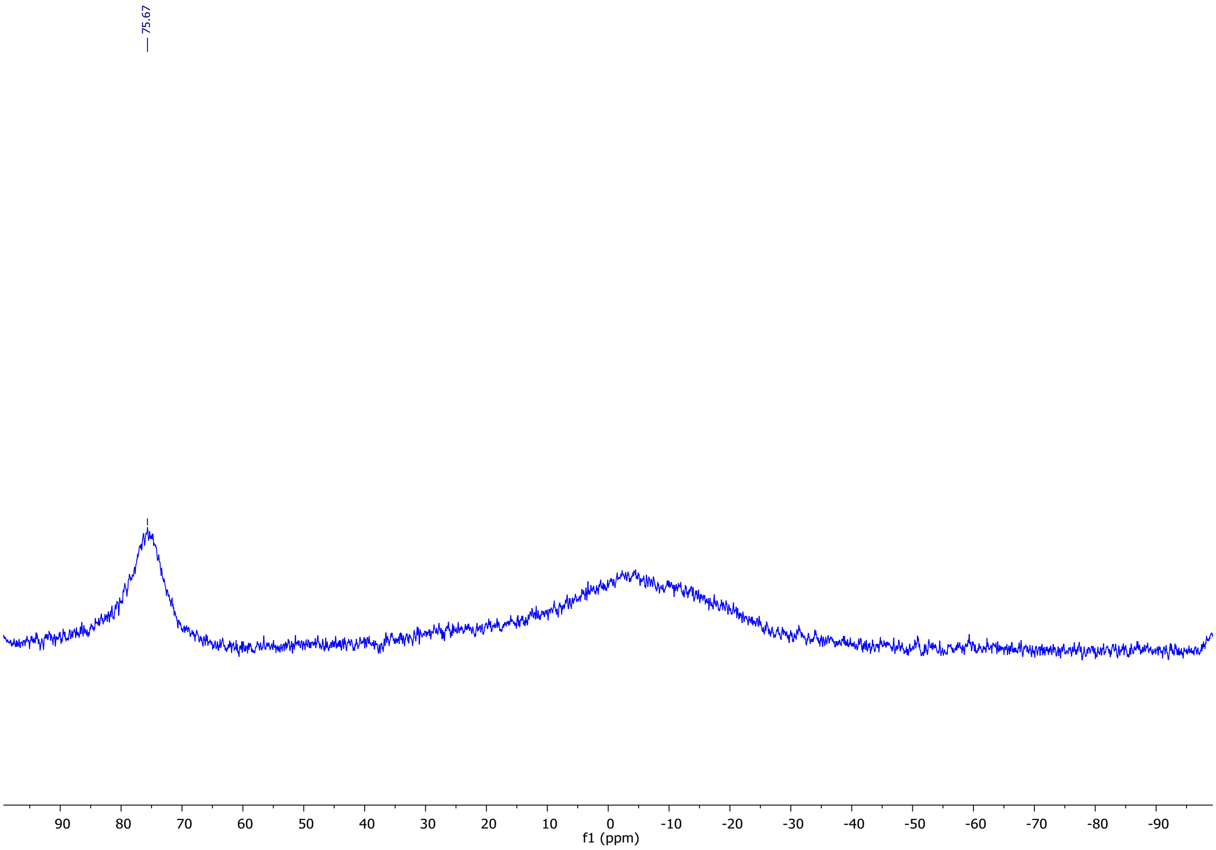


Figure SI 66: ^{11}B NMR spectrum of the reaction of 1,4-cyclohexadiene and Piers' borane at room temperature (128 MHz, benzene-d_6).

The NMR spectra indicate that Piers' borane is already fully consumed after a short time at room temperature. Besides 1,4-cyclohexadiene and 1,3-cyclohexadiene there is a new olefinic signal in the ^{1}H NMR. Because of the small amounts of diene left in the mixture, we assume that the mixture contains mono- and diborylated species. Upon heating the reaction mixture to 80 °C, slow formation of **5** is observed. The reaction is complete after 18 h at 80 °C (Figure SI 65).

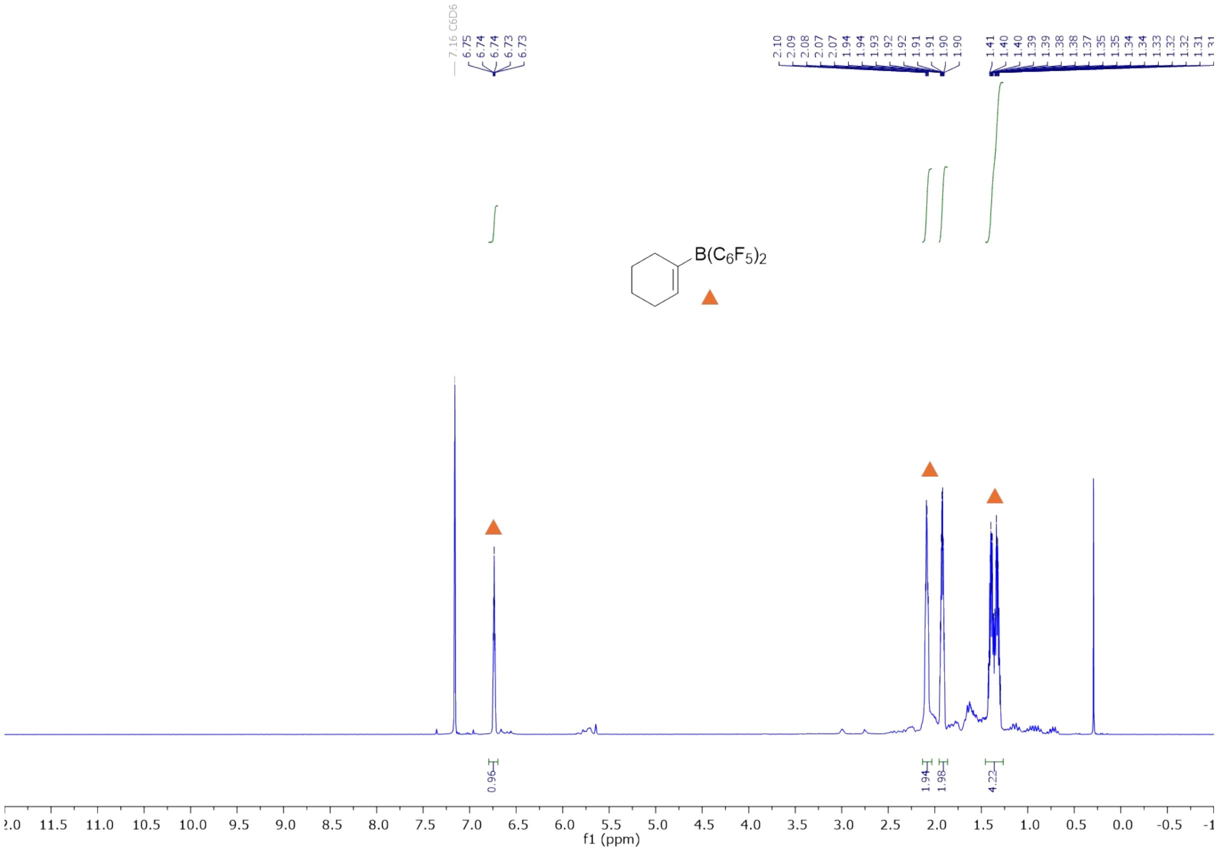
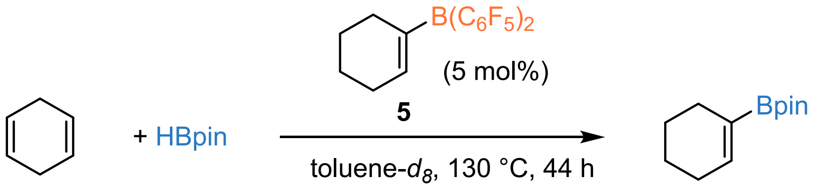


Figure SI 67: ^{1}H NMR spectrum of the reaction mixture of Piers' borane and 1,4-cyclohexadiene after heating to 80 °C for 18 h (400 MHz, benzene-d_6).

4.2 Using Bis(pentafluorophenyl)cyclohexen-1-ylborane 5 as a catalyst in the reaction of 1,4-cyclohexadiene and HBpin



Inside a glovebox, alkenyl borane **5** (10.7 mg, 0.025 mmol, 5 mol%) was added to an NMR tube with J. Young valve and dissolved in 0.5 mL toluene-d_8. 1,4-Cyclohexadiene (47.3 µL, 0.5 mmol), and Pinacolborane (74.2 µL, 0.5 mmol) were added, and the reaction heated to 130 °C for 44 h. *p*-xylene (0.5 mmol, 61.7 µL) was added as an internal standard and the yield determined by ^{1}H NMR (83%).

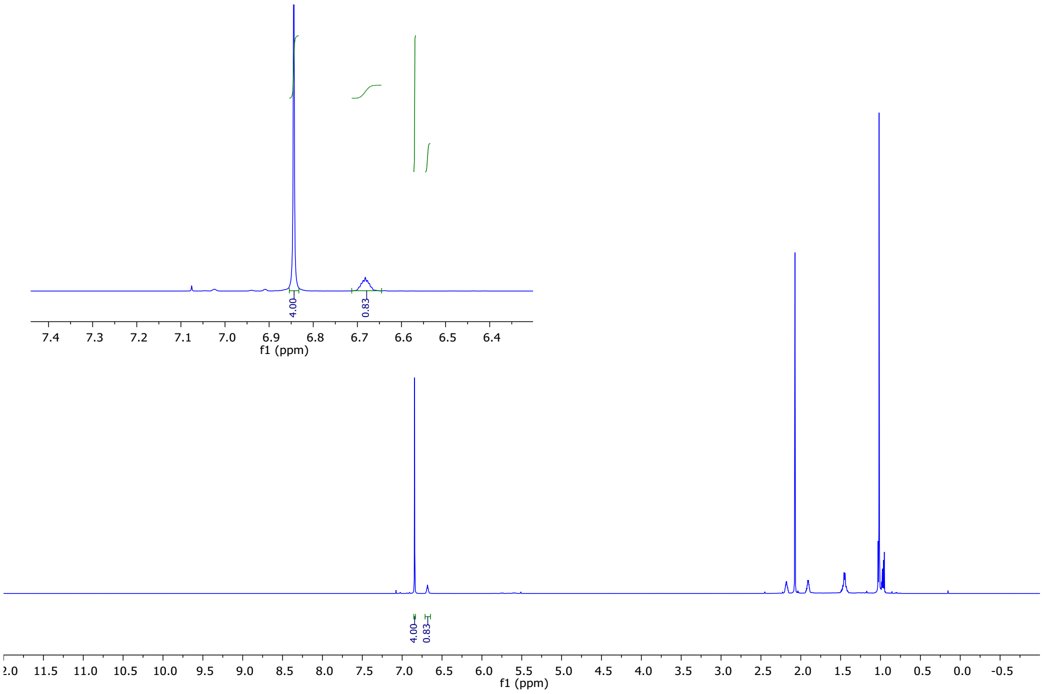
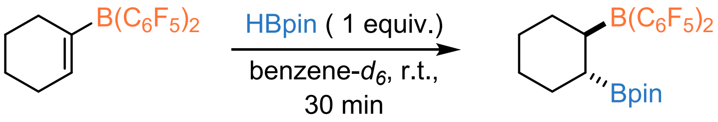


Figure SI 68: ^{1}H NMR of the reaction after 44 h at 130 °C (toluene-d_8, 400 MHz, p-Xylene was used as internal standard (0.5 mmol).

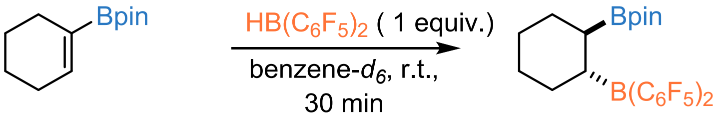
4.3 Synthesis of vic-diborylated compound 19 and its pyridine adduct

*Synthesis of **19** from bis(pentafluorophenyl)cyclohexenyl borane **5***



In an NMR tube with J. Young valve, bis(pentafluorophenyl)cyclohexenylborane **5** (21.3 mg, 0.05 mmol) was dissolved in benzene-d_6 (0.5 mL). Pinacolborane (7.2 µL, 1.0 equiv.) was added, and the solution kept at r.t. for 30 minutes. *p*-Xylene (6.17 µL, 0.05 mmol) was added as internal standard. It was then analyzed by NMR (93% in situ yield). A second reaction was attempted without internal standard to record ^{13}C and 2D NMR spectra.

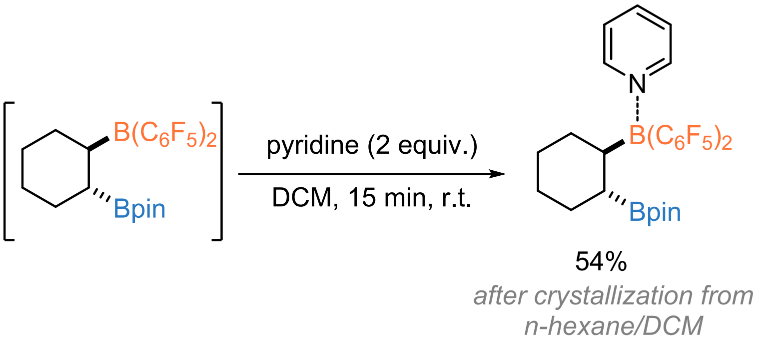
*Synthesis of **19** from 2-(1-Cyclohexen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **1***



Vic diborylated compound **19** can be alternatively synthesized from the cyclohexenyl boronate **1**. In an NMR tube with J. Young valve, 2-(1-cyclohexen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **1** (10.4 mg, 0.05 mmol) was dissolved in benzene-d_6 (0.5 mL). Piers' borane (17.3 mg, 0.05 mmol, 1 equiv.) was added, and the solution kept at r.t. for 30 minutes (100% conversion).

Note that the NMR spectra are almost identical to the spectra obtained from the procedure starting from **5**.

*Synthesis of the pyridine adduct of **19·pyr***



Vic diborylated compound **19** was synthesized in situ. 2-(1-cyclohexen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **1** (20.8 mg, 0.1 mmol) was dissolved in DCM (0.5 mL). Piers' borane **2** (34.6 mg, 0.1 mmol) was carefully added in portions (exothermic!). After 30 minutes, pyridine (2 equiv., 16.2 µL) was added, and the solution kept at r.t. for 15 minutes. The solution was then overlayed with *n*-hexane (10 mL) and the product allowed to crystallize overnight at r.t. The product was obtained as colorless crystals that were suitable for SCXRD (34 mg, 54%).

^{1}H NMR (400 MHz, DCM-d_2) δ 8.70 (s, 1H), 8.07 (t, J = 7.7 Hz, 2H), 7.64 – 7.56 (m, 2H), 2.22 – 2.07 (m, 1H), 1.73 – 1.56 (m, 4H), 1.50 – 1.37 (m, 1H), 1.37 – 1.23 (m, 2H), 1.11 – 0.96 (m, 1H), 0.97 (s, 6H), 0.89 (s, 6H), 0.92 – 0.84 (m, 1H) ppm.

^{13}C NMR (101 MHz, DCM-d_2) δ 147.3, 141.9, 125.6, 82.8, 32.5, 32.0, 28.9, 28.6, 25.5, 24.1, 14.4 ppm.

^{11}B NMR (128 MHz, DCM-d_2) δ33.57 (Bpin), 1.69 ($B(C_6F_5)_2$) ppm.

HRMS (ESI) *m*/*z* [M+Na$^+$] calc. for $C_{29}H_{27}B_2F_{10}NNaO_2^+$ = 656.1961, *m*/*z* (found) = 656.1963.

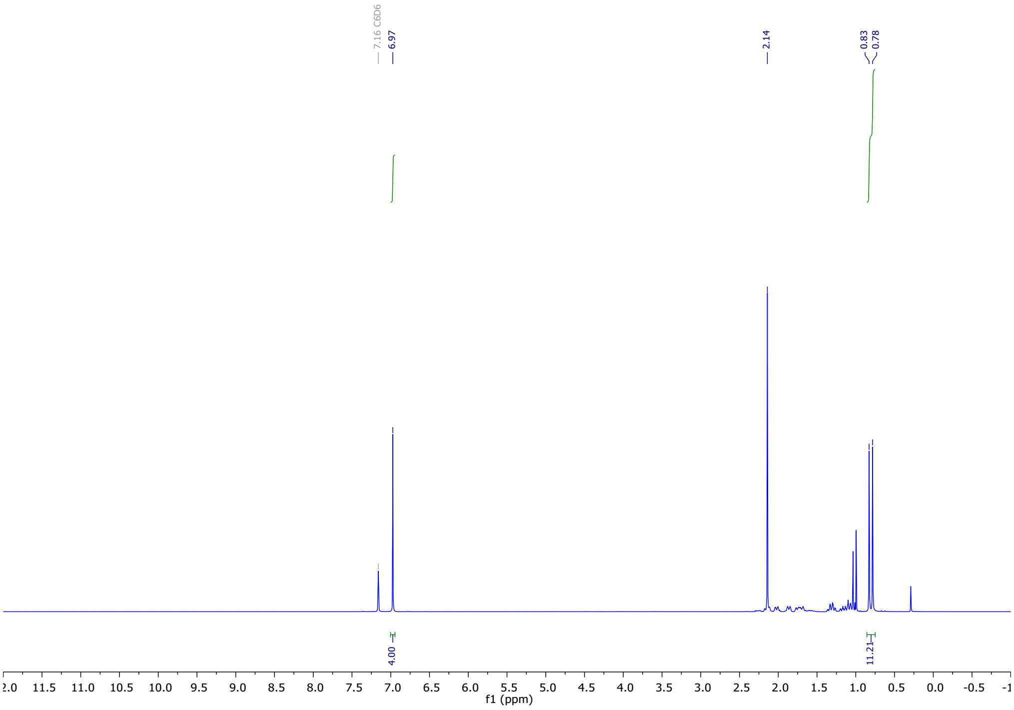


Figure SI 69: ^{1}H NMR spectrum of the reaction between **5** and pinacolborane. Note that the CH_3 groups of the pinacol moiety show diastereotopic splitting. *p*-Xylene was used as internal standard (0.05 mmol, 96% in situ yield) (400 MHz, C_6D_6).

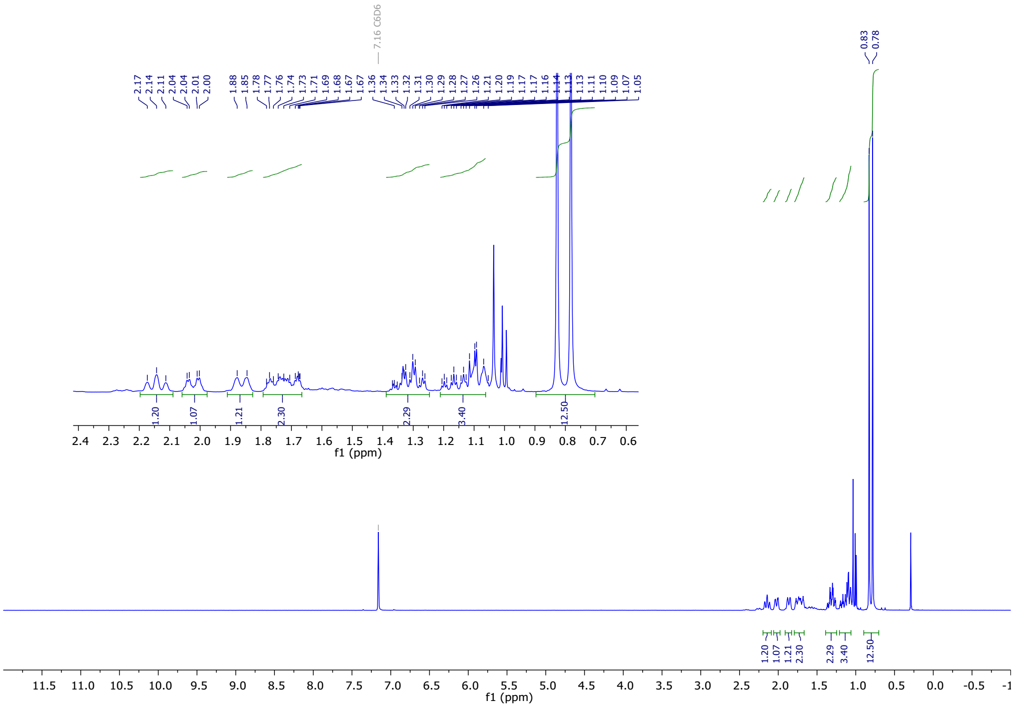


Figure SI 70: ^{1}H NMR spectrum of the reaction between **5** and pinacolborane without internal standard (400 MHz, C_6D_6).

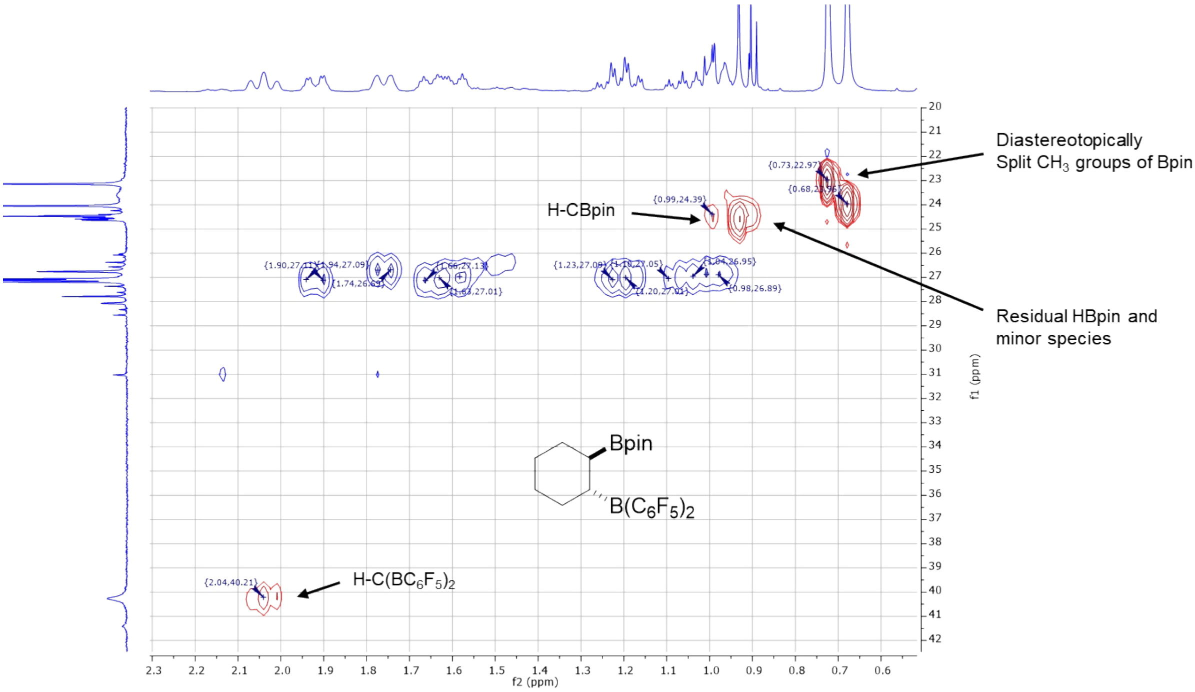


Figure SI 71: Dept135 edited ^1H-^{13}C HSQC spectrum of the reaction of **5** and pinacolborane (400 MHz, 101 MHz, C_6D_6, positive phase blue, negative phase in red).

Note that the broad pseudo triplet in the ^1H spectrum at 2.04 ppm shows a correlation peak to the broad ^{13}C peak at 40.21 ppm, with a negative phase indicating a CH group. We assigned this to the CH connected to the $B(C_6F_5)_2$ fragment, since the CH shift of 2.04 ppm is comparable to the parent Cy-$B(C_6F_5)_2$ (2.23-2.12 ppm).[16] The HC-Bpin moiety is high-field shifted in both the ^1H and ^{13}C spectra and overlaps with CH_2 groups in the ^1H NMR. The corresponding correlation peak with red phase is located at (0.99, 24.39) ppm, which is also in accordance with Cy-Bpin literature values.[17]

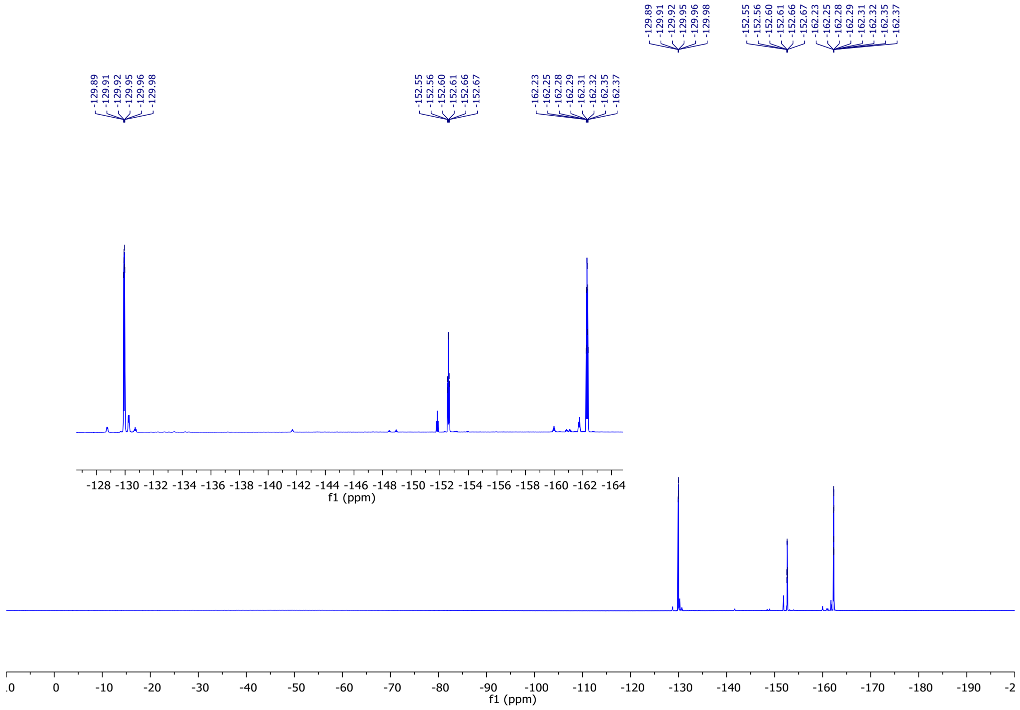


Figure SI 72: ^{19}F NMR spectrum of the reaction between **5** and pinacolborane (377 MHz, benzene-d_6).

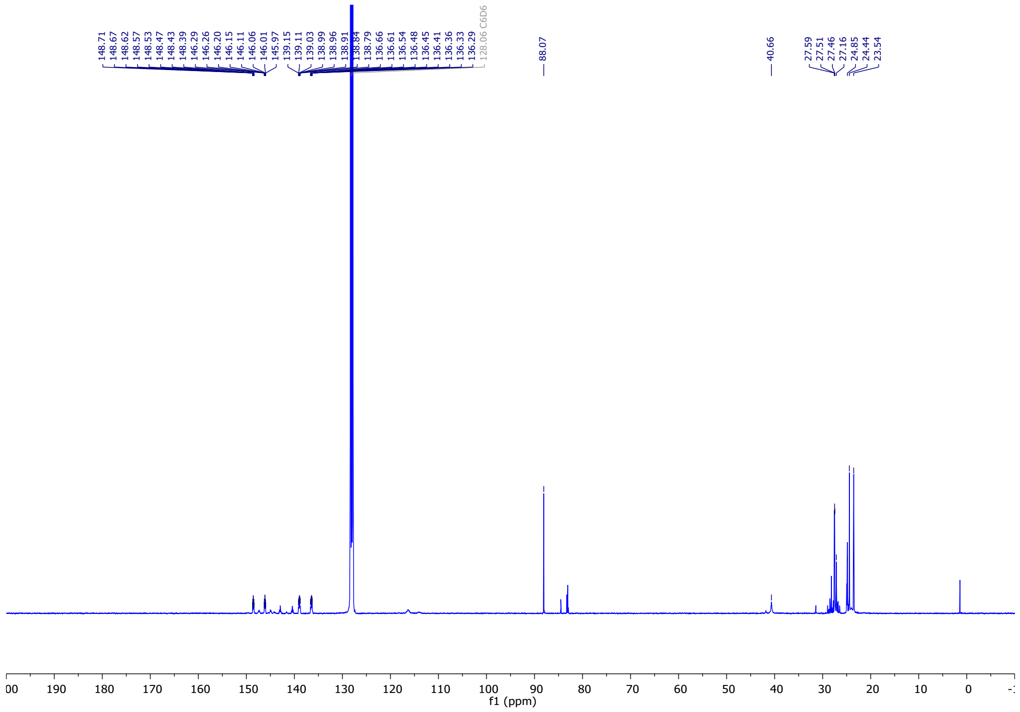


Figure SI 73: ^{13}C NMR spectrum of the reaction between **5** and pinacolborane (101 MHz, benzene-d_6).

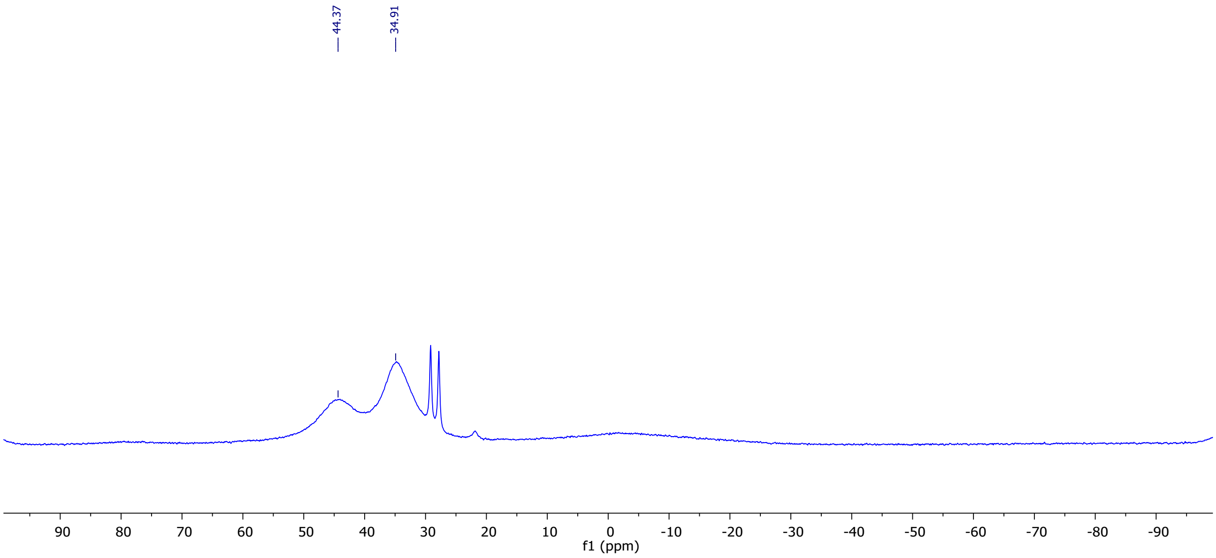


Figure SI 74: ^{11}B NMR spectrum of the reaction between **5** and pinacolborane after 30 min at r.t. The doublet at 29 ppm is residual pinacolborane (128 MHz, benzene-d_6).

We assigned the ^{11}B peak at 34.91 ppm to the Bpin moiety and the peak at 44.37 ppm to the $B(C_6F_5)_2$.

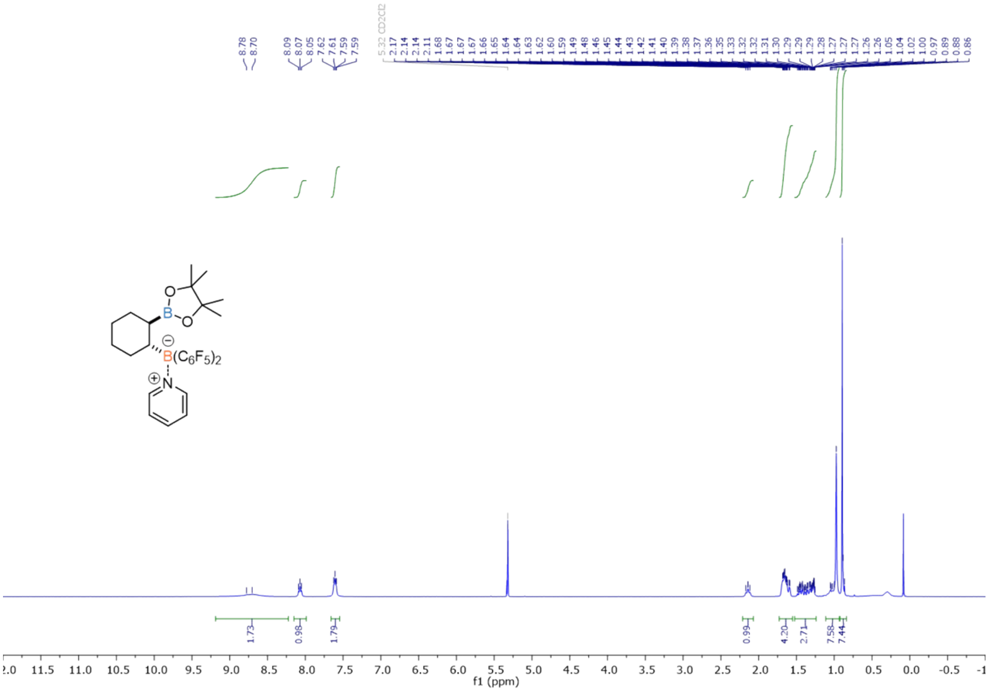


Figure SI 75: ^{1}H NMR spectrum of pyridine adduct **19·pyr** (400 MHz, DCM-d_2).

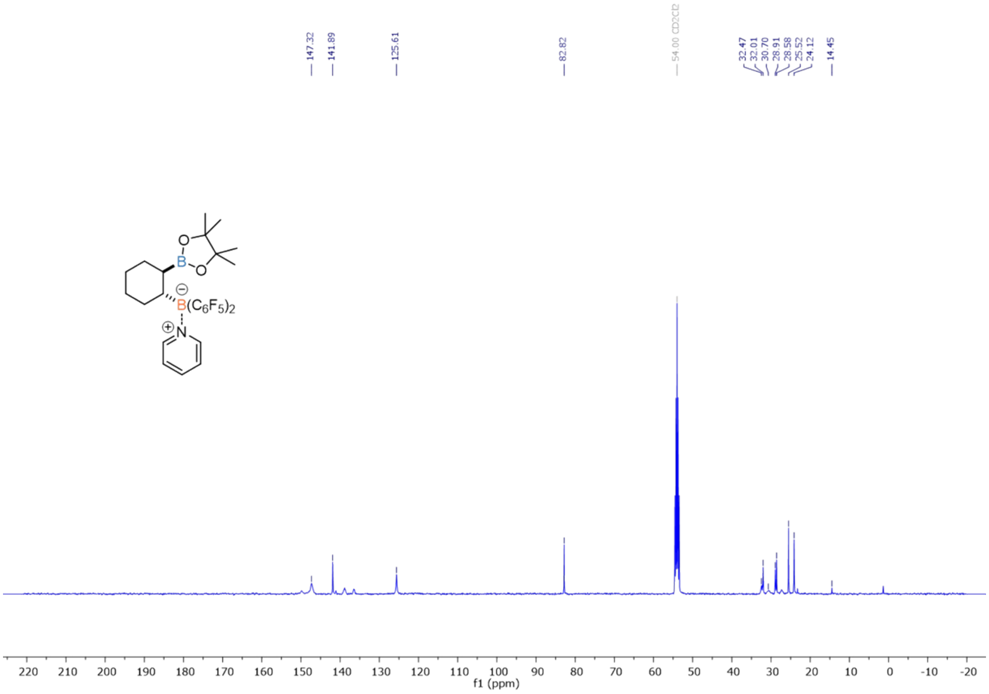


Figure SI 76: ^{13}C NMR spectrum of the pyridine adduct **19·pyr** (101 MHz, DCM-d_2).

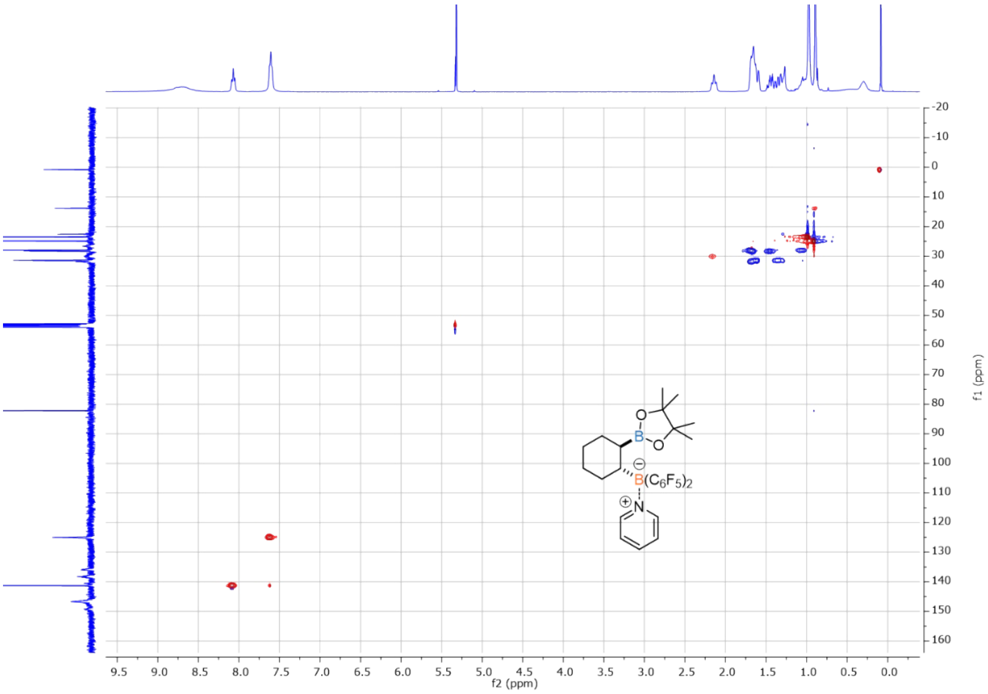


Figure SI 77: DEPT135 edited ^{1}H ^{13}C HSQC NMR spectrum of **19·pyr** (400, 101 MHz, DCM-d_2).

Note that some of the signals are very broad in the ^{1}H and ^{13}C spectra.

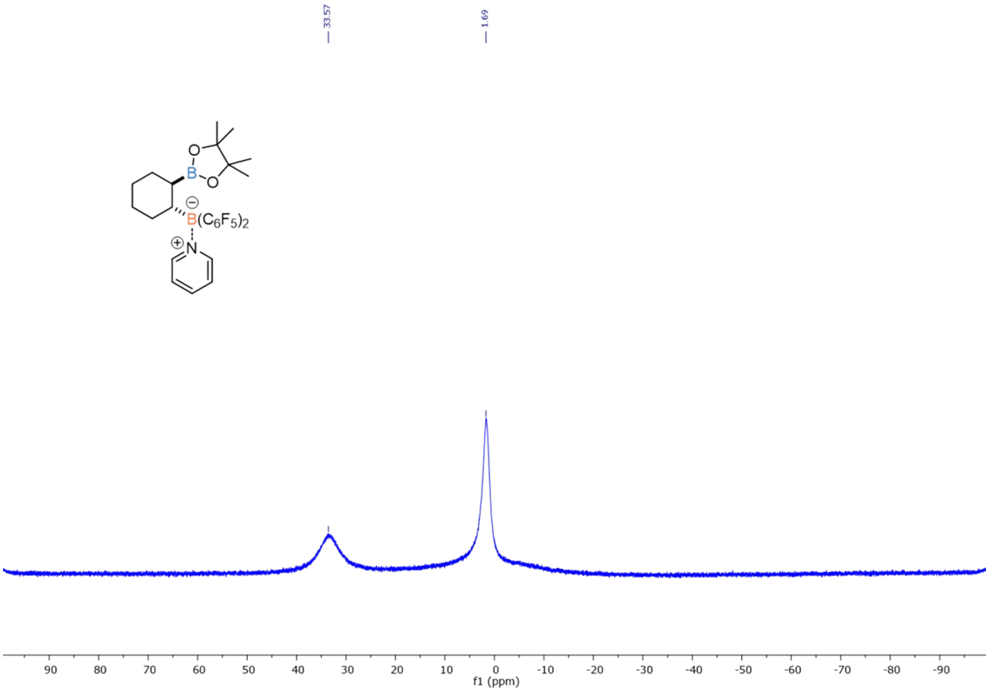


Figure SI 78: ^{11}B NMR spectrum of pyridine adduct **19·pyr** (128 MHz, DCM-d_2).

4.4 Using *vic*-diborylated species 19 as a catalyst

Inside a glovebox, alkenylborane **5** (21.3 mg, 0.05 mmol) was added to an NMR tube with J. Young valve and dissolved in 0.5 mL toluene-d_8. Then, HBpin (7.42 µL, 0.05 mmol) was added and the solution kept at r.t. for 30 minutes. Afterwards, 1,4-cyclohexadiene (47.3 µL, 0.5 mmol, 10 equiv.) and HBpin (72.4 µL, 0.5 mmol, 10 equiv.) were added and the solution heated to 130 °C for 22 h. *p*-Xylene (0.05 mmol, 6.17 µL) was added as internal standard and a ^{1}H NMR was recorded to determine the in situ yield (78%).

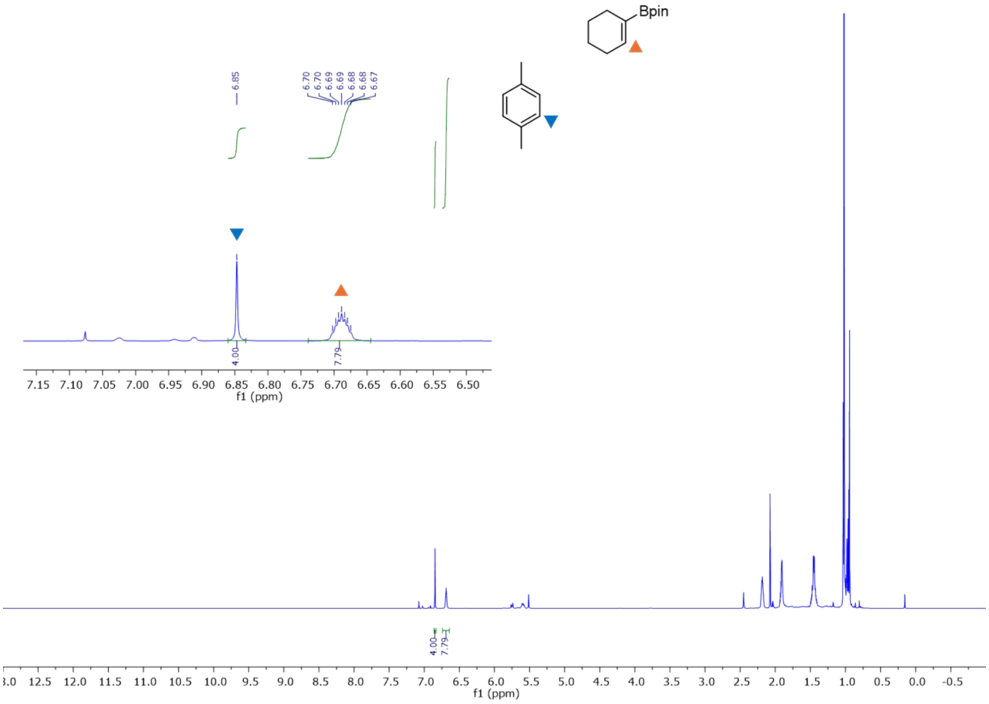


Figure SI 79: ^{1}H NMR spectrum of the reaction between 1,4-cyclohexadiene and HBpin using **19** as a catalyst. *p*-Xylene was used as an internal standard (0.05 mmol) (Yield: 78%).

4.5 Using cyclohexene and allyl benzene as substrates

4.5.1 Cyclohexene with HB(C_6F_5)$_2$ as a catalyst

The reaction was set up following general procedure 1 in an NMR tube with J. Young valve. The in situ yield of **21** was determined with *p*-xylene as internal standard (88%).

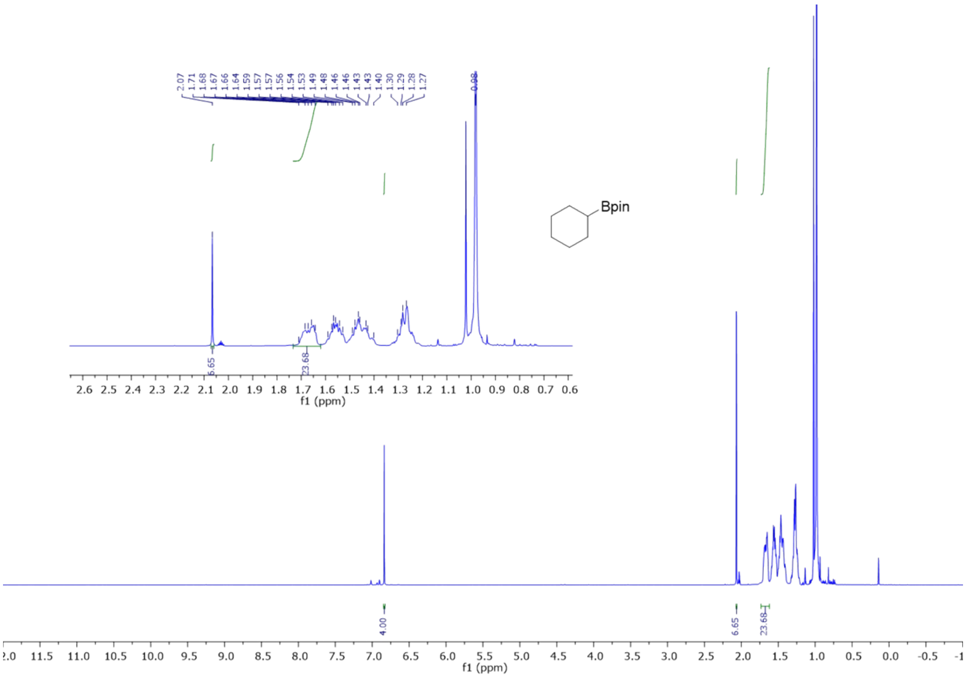


Figure SI 80: ^{1}H NMR spectrum of the reaction of cyclohexene and HBpin with Piers' borane (5 mol%) as a catalyst. *p*-Xylene (0.05 mmol) was used as internal standard (400 MHz, toluene-d_8).

4.5.2 Cyclohexene with HBCy$_2$ as a catalyst

The reaction was set up following general procedure 1 in an NMR tube with J. Young valve. The in situ yield of **21** was determined with *p*-xylene as internal standard (12%).

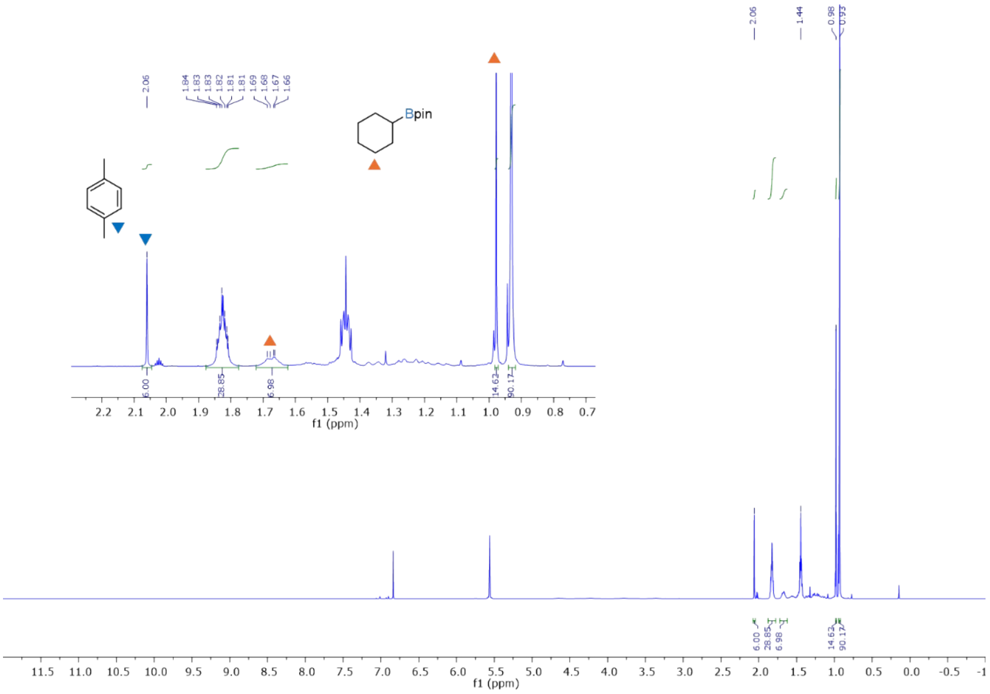


Figure SI 81: ^1H NMR spectrum of the reaction of cyclohexene and HBpin with $HBCy_2$ (5 mol%) as a catalyst. *p*-Xylene (0.05 mmol) was used as internal standard (400 MHz, toluene-d_8).

4.5.3 Allyl benzene with $HB(C_6F_5)_2$ as catalyst

The reaction was set up following general procedure 1 in an NMR tube with J. Young valve. The in situ yield of product was determined with *p*-xylene as internal standard (84%).

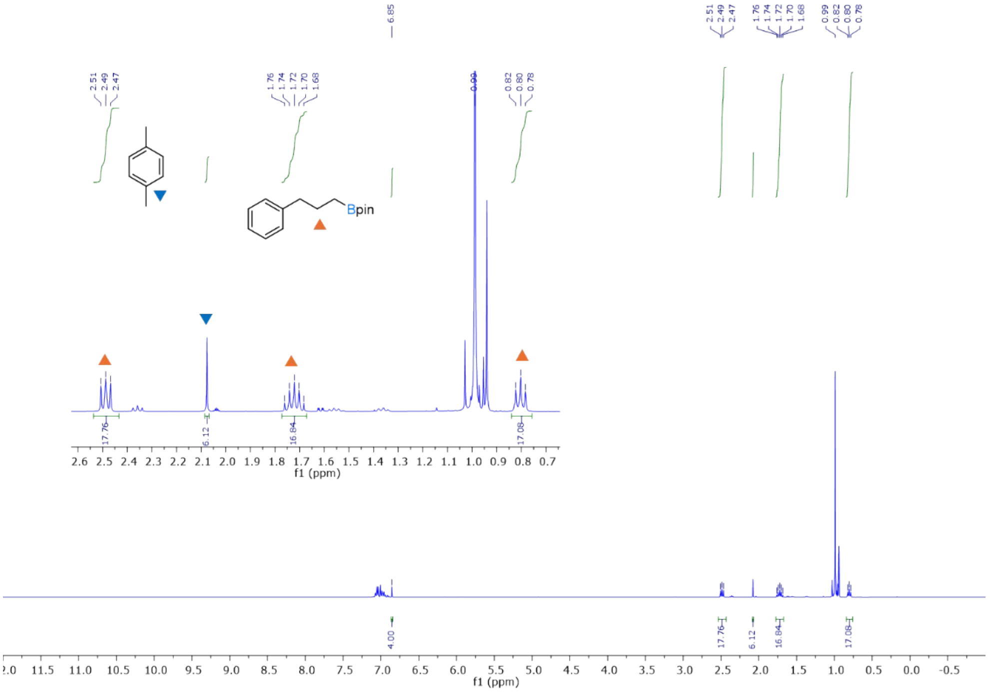
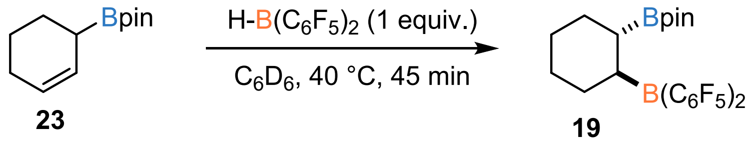


Figure SI 82: ^1H NMR spectrum of the reaction of allyl benzene and HBpin with $HB(C_6F_5)_2$ (5 mol%) as a catalyst at 80 °C for 22 h. *p*-Xylene (0.05 mmol) was used as internal standard (400 MHz, toluene-d_8).

4.6 Reaction of cyclic allyl boronate 23 with $HB(C_6F_5)_2$



In a vial, 23 (10.4 mg, 0.05 mmol) was dissolved in 0.5 mL C_6D_6. $HB(C_6F_5)_2$ (0.05 mmol, 17.3 mg) was added and shaken until dissolved. It was transferred to an NMR tube with J. Young valve and heated to 40 °C for 45 min. A ^1H NMR was recorded showing full conversion of **23**. A mixture of compounds is obtained, with **19** as a major product, as indicated by ^{19}F NMR.

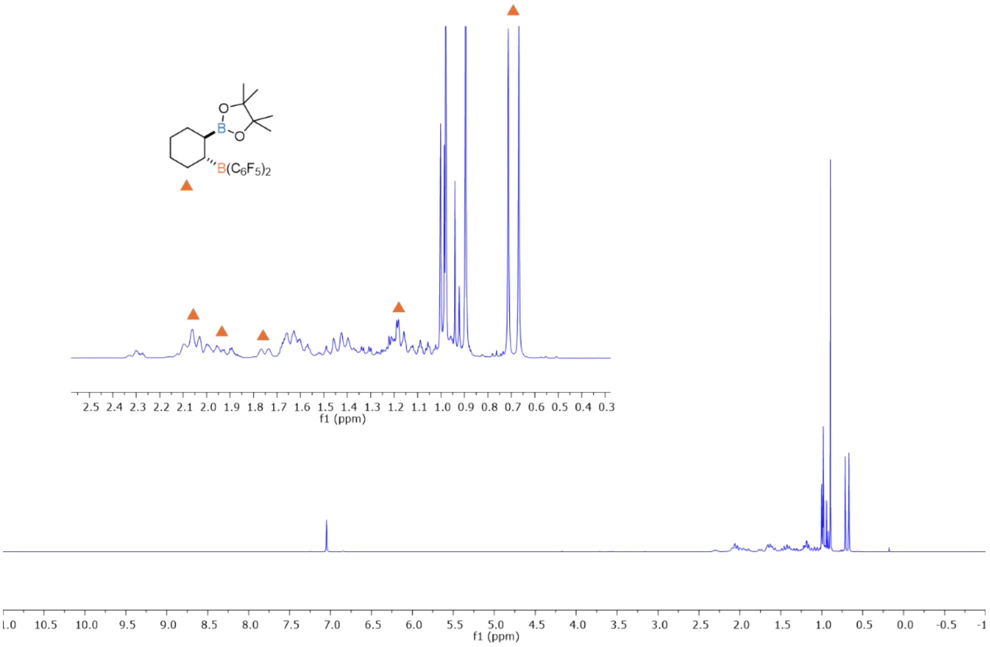


Figure SI 83: ^1H NMR of the reaction between **23** and **2** after 45 min at 40 °C, formation of **19** is observed (benzene-d_6, 400 MHz).

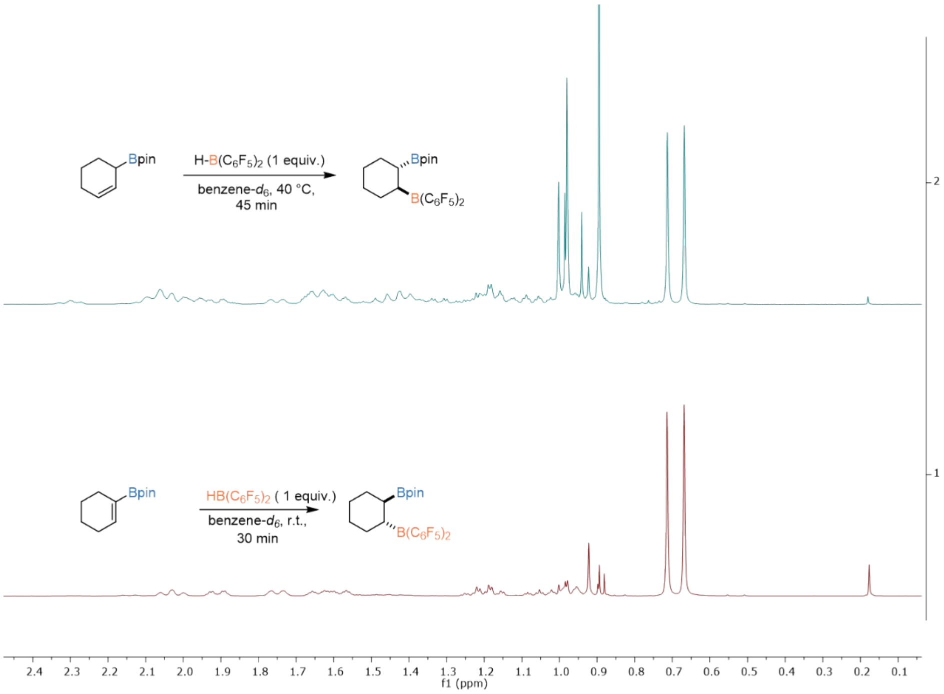


Figure SI 84: ^{1}H NMR overlay of the reaction between **23** and $HB(C_6F_5)_2$ (top) and **1** and $HB(C_6F_5)_2$ (bottom) (400 MHz, benzene-d_6).

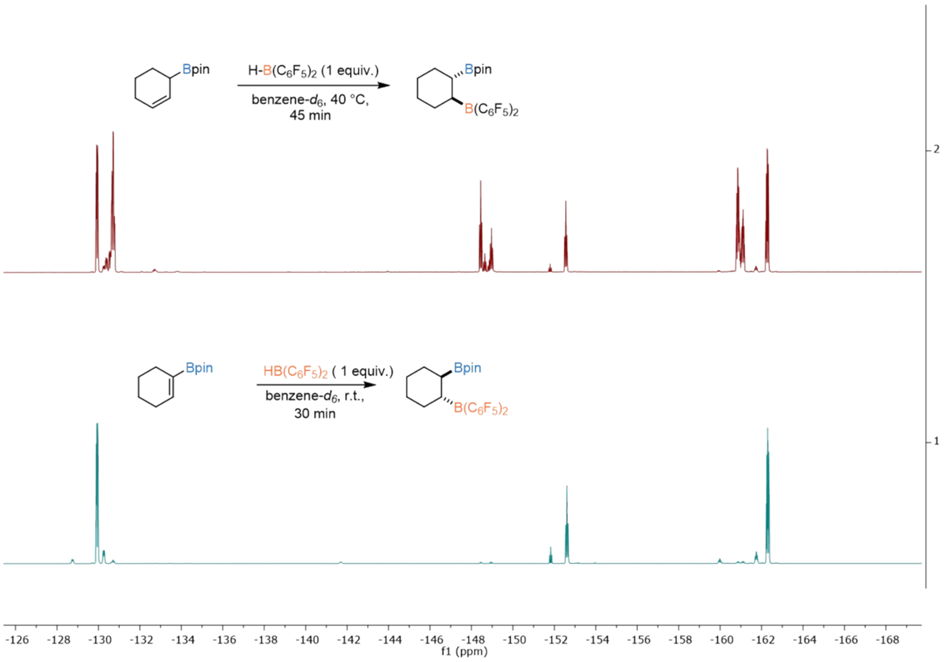


Figure SI 85: ^{19}F NMR overlay of the reaction between **23** and $HB(C_6F_5)_2$ (top) and **1** and $HB(C_6F_5)_2$ (bottom). (377 MHz, benzene-d_6). **19** forms as a major species.

5 Single crystal X-ray diffraction

Suitable single crystals for X-ray structure determination were selected from the mother liquor and transferred in protective perfluoro polyether oil on a microscope slide. The selected and mounted crystals were transferred to the cold gas stream on the diffractometer. The diffraction data were obtained at low temperatures from a Bruker D8 three-circle diffractometer, equipped with a PHOTON III-C14 CMOS detector and an INCOATEC microfocus source with Quazar mirror optics (Mo-Kα radiation, λ= 0.71073 Å). The data obtained were integrated with SAINT and a semi-empirical absorption correction from equivalents with SADABS was applied. The structures were solved and refined using the Bruker SHELX 2018 software package.[18] All non-hydrogen atoms were refined with anisotropic displacement parameters.

The structures have been deposited with Cambridge Crystallographic Data Centre as CCDC 2364438 and CCDC 2364453 and can be obtained free of charge.

5.1 Single-crystal X-ray diffraction analysis of 5

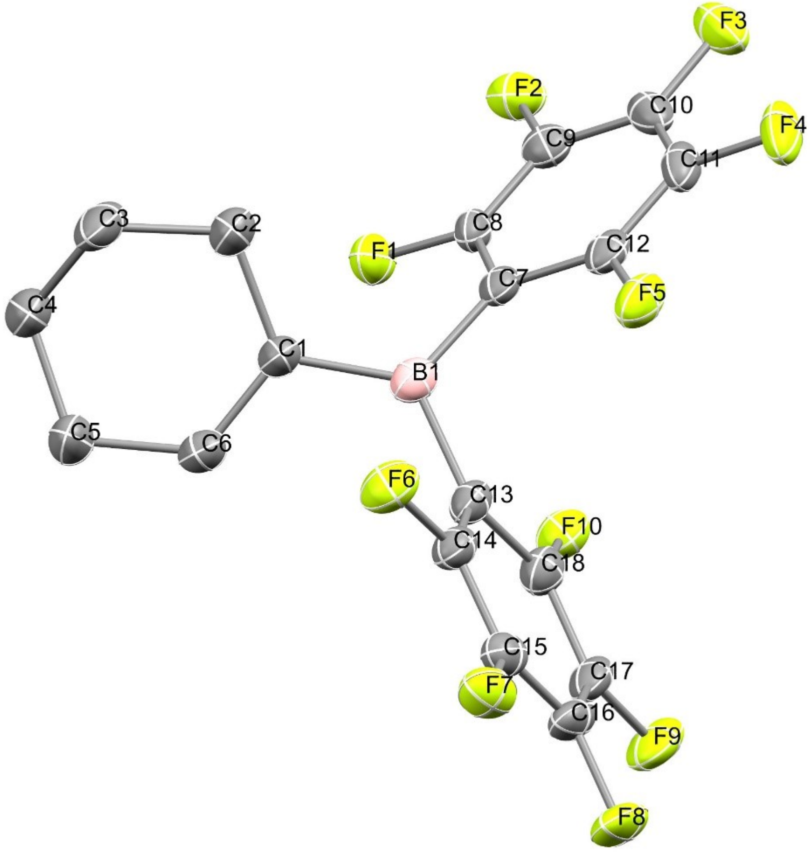


Figure SI 86: Thermal ellipsoid plot of **5** with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains one molecule. CCDC 2364438.

Table SI 2: Crystal data and structure refinement of **5**.

Identification code	D8K23082_a	
Empirical formula	C18 H9 B F10	
Formula weight	426.06	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.5324(13) Å	α= 81.510(11)°.
	b = 9.570(2) Å	β= 84.630(11)°.
	c = 16.636(4) Å	γ = 74.299(10)°.
Volume	837.3(4) Å^3	
Z	2	
Density (calculated)	1.690 Mg/m^3	
Absorption coefficient	0.175 mm^{-1}	
F(000)	424	

Crystal size	0.238 x 0.045 x 0.021 mm^3
Theta range for data collection	2.229 to 26.022°.
Index ranges	-6<=h<=6, -11<=k<=11, -20<=l<=20
Reflections collected	35773
Independent reflections	3293 [R(int) = 0.1193]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3293 / 0 / 263
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0661, wR2 = 0.1425
R indices (all data)	R1 = 0.0993, wR2 = 0.1634
Extinction coefficient	0.021(3)
Largest diff. peak and hole	0.412 and -0.329 e.$Å^{-3}$

Table SI 3: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	10943(4)	5208(2)	3515(1)	34(1)
C(1)	6468(7)	6559(4)	2426(2)	28(1)
B(1)	7091(8)	4879(5)	2529(3)	26(1)
F(2)	12228(4)	3645(3)	4945(1)	38(1)
C(2)	5532(9)	7386(4)	3138(2)	37(1)
F(3)	9933(5)	1529(3)	5610(2)	48(1)
C(3)	4599(9)	9040(5)	2892(3)	45(1)
F(4)	6333(5)	977(2)	4784(2)	49(1)
C(4)	6430(8)	9593(4)	2295(2)	37(1)
F(5)	5073(4)	2504(2)	3329(2)	39(1)
C(5)	6823(9)	8858(4)	1528(3)	41(1)
F(6)	2838(4)	5376(3)	1505(2)	39(1)
C(6)	6984(7)	7275(4)	1682(2)	30(1)
F(7)	2745(4)	3918(3)	266(1)	39(1)
C(7)	7923(7)	3936(4)	3364(2)	25(1)
F(8)	6840(5)	1798(3)	-158(1)	45(1)
C(8)	9737(7)	4169(4)	3808(2)	27(1)
F(9)	11038(5)	1129(3)	702(2)	46(1)
C(9)	10454(7)	3368(4)	4547(2)	30(1)
F(10)	11107(4)	2530(2)	1977(1)	37(1)
C(10)	9305(8)	2291(4)	4878(2)	34(1)
C(11)	7505(8)	2005(4)	4457(3)	34(1)
C(12)	6876(7)	2810(4)	3715(2)	30(1)
C(13)	7001(7)	4029(4)	1789(2)	27(1)
C(14)	4919(7)	4334(4)	1326(2)	29(1)
C(15)	4825(7)	3591(4)	680(2)	31(1)
C(16)	6898(8)	2511(4)	474(2)	33(1)
C(17)	9001(7)	2163(4)	913(2)	33(1)
C(18)	9010(7)	2903(4)	1566(2)	30(1)

Table SI 4: Bond lengths [Å] and angles [°] **5**.

F(1)-C(8)	1.352(4)
C(1)-C(6)	1.368(5)
C(1)-C(2)	1.495(5)
C(1)-B(1)	1.537(5)
B(1)-C(7)	1.575(6)
B(1)-C(13)	1.584(5)
F(2)-C(9)	1.336(4)
C(2)-C(3)	1.531(6)
F(3)-C(10)	1.347(4)
C(3)-C(4)	1.497(6)
F(4)-C(11)	1.344(4)
C(4)-C(5)	1.517(6)
F(5)-C(12)	1.351(4)
C(5)-C(6)	1.478(5)
F(6)-C(14)	1.346(4)
F(7)-C(15)	1.336(5)
C(7)-C(8)	1.383(5)
C(7)-C(12)	1.388(5)
F(8)-C(16)	1.343(4)
C(8)-C(9)	1.380(5)
F(9)-C(17)	1.341(4)
C(9)-C(10)	1.375(6)
F(10)-C(18)	1.339(4)
C(10)-C(11)	1.375(6)
C(11)-C(12)	1.377(6)
C(13)-C(14)	1.387(5)
C(13)-C(18)	1.388(5)
C(14)-C(15)	1.385(5)
C(15)-C(16)	1.375(6)
C(16)-C(17)	1.370(6)
C(17)-C(18)	1.382(5)

C(6)-C(1)-C(2)	120.5(3)
C(6)-C(1)-B(1)	118.4(3)
C(2)-C(1)-B(1)	120.9(3)
C(1)-B(1)-C(7)	121.4(3)
C(1)-B(1)-C(13)	121.1(3)

C(7)-B(1)-C(13)	117.5(3)
C(1)-C(2)-C(3)	113.1(3)
C(4)-C(3)-C(2)	111.1(4)
C(3)-C(4)-C(5)	111.1(3)
C(6)-C(5)-C(4)	113.8(3)
C(1)-C(6)-C(5)	124.0(3)
C(8)-C(7)-C(12)	114.7(3)
C(8)-C(7)-B(1)	122.8(3)
C(12)-C(7)-B(1)	122.5(3)
F(1)-C(8)-C(9)	116.6(3)
F(1)-C(8)-C(7)	120.0(3)
C(9)-C(8)-C(7)	123.4(3)
F(2)-C(9)-C(10)	120.0(4)
F(2)-C(9)-C(8)	120.5(3)
C(10)-C(9)-C(8)	119.5(4)
F(3)-C(10)-C(9)	120.2(4)
F(3)-C(10)-C(11)	120.4(4)
C(9)-C(10)-C(11)	119.4(4)
F(4)-C(11)-C(10)	119.8(4)
F(4)-C(11)-C(12)	120.8(4)
C(10)-C(11)-C(12)	119.3(3)
F(5)-C(12)-C(11)	117.2(3)
F(5)-C(12)-C(7)	119.1(4)
C(11)-C(12)-C(7)	123.6(4)
C(14)-C(13)-C(18)	115.2(3)
C(14)-C(13)-B(1)	122.9(3)
C(18)-C(13)-B(1)	121.9(3)
F(6)-C(14)-C(15)	116.7(3)
F(6)-C(14)-C(13)	120.1(3)
C(15)-C(14)-C(13)	123.2(3)
F(7)-C(15)-C(16)	120.6(3)
F(7)-C(15)-C(14)	120.4(4)
C(16)-C(15)-C(14)	119.0(4)
F(8)-C(16)-C(17)	120.4(4)
F(8)-C(16)-C(15)	119.5(4)
C(17)-C(16)-C(15)	120.1(3)
F(9)-C(17)-C(16)	120.1(3)
F(9)-C(17)-C(18)	120.6(4)
C(16)-C(17)-C(18)	119.4(3)

F(10)-C(18)-C(17)	117.3(3)
F(10)-C(18)-C(13)	119.5(3)
C(17)-C(18)-C(13)	123.1(4)

Table SI 5: Anisotropic displacement parameters (Å^{2}x 10^3) for **5**. The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	40(1)	32(1)	34(1)	-4(1)	0(1)	-17(1)
C(1)	35(2)	24(2)	25(2)	-7(2)	0(2)	-7(2)
B(1)	20(2)	29(2)	32(2)	-9(2)	3(2)	-7(2)
F(2)	36(1)	44(1)	31(1)	-7(1)	-3(1)	-2(1)
C(2)	49(3)	28(2)	34(2)	-9(2)	0(2)	-10(2)
F(3)	54(2)	39(1)	34(1)	7(1)	9(1)	4(1)
C(3)	59(3)	35(2)	46(3)	-21(2)	18(2)	-18(2)
F(4)	56(2)	26(1)	62(2)	0(1)	24(1)	-15(1)
C(4)	47(2)	28(2)	35(2)	-7(2)	1(2)	-9(2)
F(5)	39(1)	35(1)	50(2)	-17(1)	10(1)	-18(1)
C(5)	60(3)	30(2)	34(2)	-5(2)	-1(2)	-17(2)
F(6)	32(1)	41(1)	44(1)	-17(1)	0(1)	-3(1)
C(6)	33(2)	31(2)	28(2)	-10(2)	-1(2)	-7(2)
F(7)	44(1)	47(1)	33(1)	-7(1)	-7(1)	-20(1)
C(7)	27(2)	20(2)	27(2)	-9(1)	7(2)	-5(2)
F(8)	65(2)	44(1)	34(1)	-23(1)	5(1)	-23(1)
C(8)	33(2)	20(2)	28(2)	-5(2)	8(2)	-12(2)
F(9)	47(2)	37(1)	53(2)	-25(1)	13(1)	-4(1)
C(9)	25(2)	30(2)	31(2)	-9(2)	3(2)	-2(2)
F(10)	33(1)	36(1)	41(1)	-13(1)	1(1)	-5(1)
C(10)	37(2)	27(2)	27(2)	-1(2)	10(2)	2(2)
C(11)	37(2)	22(2)	41(2)	-4(2)	17(2)	-10(2)
C(12)	28(2)	24(2)	36(2)	-13(2)	10(2)	-7(2)
C(13)	26(2)	24(2)	32(2)	-10(2)	5(2)	-9(2)
C(14)	31(2)	26(2)	31(2)	-10(2)	6(2)	-8(2)
C(15)	37(2)	33(2)	27(2)	-5(2)	2(2)	-18(2)
C(16)	47(2)	33(2)	28(2)	-15(2)	7(2)	-22(2)
C(17)	35(2)	24(2)	38(2)	-14(2)	13(2)	-8(2)
C(18)	28(2)	27(2)	35(2)	-7(2)	2(2)	-9(2)

Table SI 6: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for **5**.

	x	y	z	U(eq)
H(2A)	6906	7191	3513	44
H(2B)	4141	7024	3435	44
H(3A)	2952	9265	2648	54
H(3B)	4362	9545	3383	54
H(4A)	8059	9400	2547	44
H(4B)	5791	10665	2152	44
H(5A)	5414	9346	1174	49
H(5B)	8392	8997	1230	49
H(6)	7475	6721	1238	36

5.2 Single-crystal X-ray diffraction analysis of 19·pyr

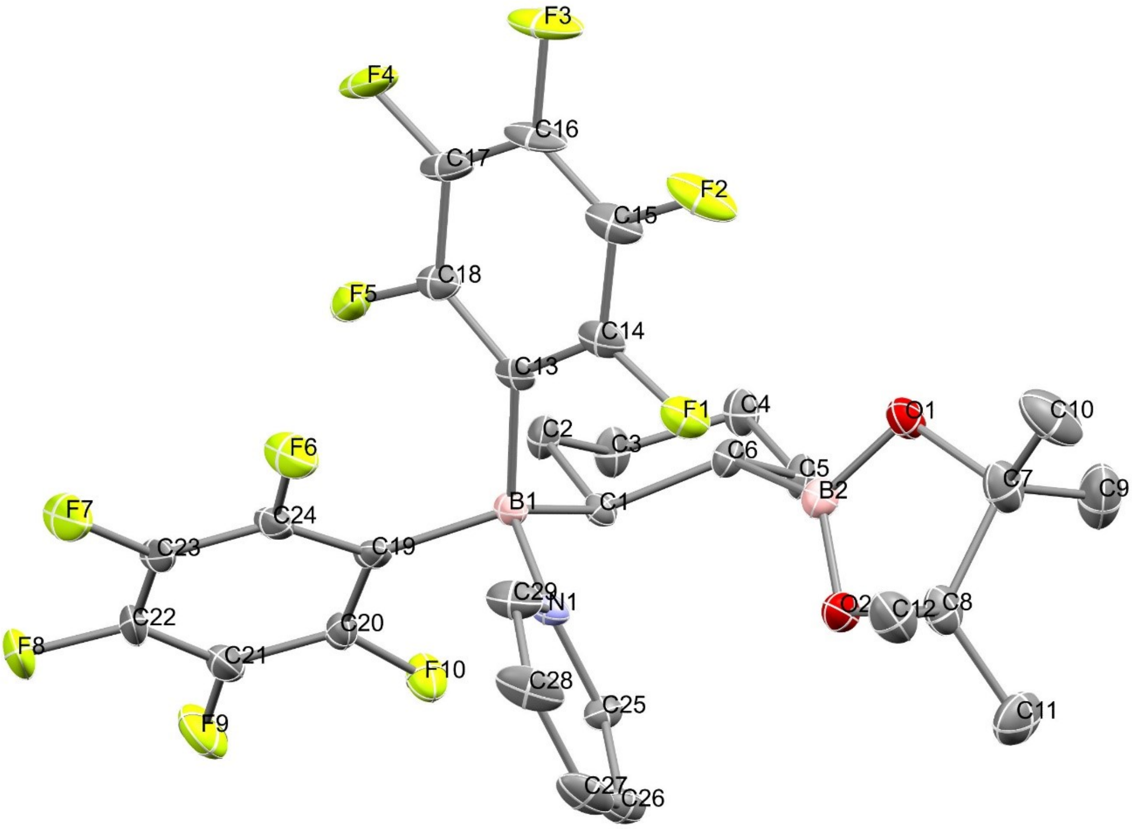


Figure SI 87: Thermal ellipsoid plot of **19·pyr** with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains one molecule CCDC 2364453.

Table SI 7: Crystal data and structure refinement of **19·pyr**.

Identification code	mo_D8K_24005_twin	
Empirical formula	C29 H27 B2 F10 N O2	
Formula weight	633.13	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.872(4) Å	α= 74.725(11)°.
	b = 10.170(5) Å	β= 86.892(11)°.
	c = 15.735(7) Å	γ = 65.383(10)°.
Volume	1382.6(11) Å^3	
Z	2	
Density (calculated)	1.521 Mg/m^3	
Absorption coefficient	0.139 mm^{-1}	

F(000)	648
Crystal size	0.208 x 0.056 x 0.029 mm^3
Theta range for data collection	2.274 to 27.599°.
Index ranges	-12<=h<=12, -12<=k<=13, 0<=l<=20
Reflections collected	6506
Independent reflections	6506 [R(int) = ?]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6506 / 0 / 402
Goodness-of-fit on F^2	1.137
Final R indices [I>2sigma(I)]	R1 = 0.0995, wR2 = 0.1917
R indices (all data)	R1 = 0.1472, wR2 = 0.2142
Extinction coefficient	n/a
Largest diff. peak and hole	0.763 and -0.628 e.Å^{-3}

Table SI 8: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)for **19·pyr**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5386(4)	2125(4)	7946(2)	22(1)
N(1)	5681(4)	6642(4)	7300(3)	16(1)
C(1)	3520(5)	6177(5)	8330(3)	13(1)
B(1)	3875(6)	7158(6)	7406(3)	16(1)
F(2)	3965(4)	4215(4)	5278(2)	38(1)
O(2)	6760(4)	3100(4)	8475(2)	22(1)
C(2)	1843(5)	6944(5)	8505(3)	20(1)
B(2)	5366(6)	3303(6)	8232(4)	17(1)
F(3)	1110(5)	6090(5)	4631(2)	45(1)
C(3)	1503(5)	6236(5)	9428(3)	21(1)
F(4)	-414(4)	8521(4)	5280(2)	41(1)
C(4)	1933(5)	4577(5)	9549(3)	22(1)
F(5)	819(3)	9028(3)	6531(2)	28(1)
C(5)	3538(5)	3787(5)	9343(3)	18(1)
F(6)	3250(4)	9676(4)	5798(2)	38(1)
C(6)	3844(5)	4524(5)	8395(3)	15(1)
F(7)	2262(5)	12569(4)	5717(3)	60(1)
C(7)	6868(6)	909(6)	8160(4)	28(1)
F(8)	1847(4)	13513(3)	7202(3)	54(1)
C(8)	7854(6)	1733(5)	8273(4)	25(1)
F(9)	2499(4)	11459(4)	8796(3)	41(1)
C(9)	6767(7)	-165(7)	9018(5)	43(2)
F(10)	3546(4)	8575(3)	8916(2)	26(1)
C(10)	7250(7)	142(7)	7428(5)	44(2)
C(11)	9017(6)	933(6)	9020(4)	37(1)
C(12)	8552(6)	2216(6)	7426(4)	32(1)
C(13)	3125(5)	6916(5)	6585(3)	17(1)
C(14)	3831(6)	5716(6)	6230(3)	21(1)
C(15)	3192(6)	5413(7)	5581(3)	27(1)
F(1)	5241(3)	4709(3)	6510(2)	25(1)
C(16)	1768(7)	6358(7)	5257(3)	31(1)
C(17)	999(6)	7573(7)	5581(4)	29(1)
C(18)	1672(6)	7831(6)	6235(3)	22(1)
C(19)	3349(5)	8947(5)	7362(3)	17(1)

C(20)	3211(5)	9509(5)	8087(3)	17(1)
C(21)	2689(6)	11010(5)	8056(4)	24(1)
C(22)	2373(6)	12040(5)	7257(4)	32(1)
C(23)	2570(7)	11564(6)	6510(4)	32(1)
C(24)	3059(6)	10063(5)	6572(3)	22(1)
C(25)	6631(5)	6105(5)	8013(3)	16(1)
C(26)	8124(5)	5859(6)	7942(4)	22(1)
C(27)	8643(6)	6173(6)	7122(4)	29(1)
C(28)	7677(7)	6725(7)	6386(4)	33(1)
C(29)	6216(6)	6941(6)	6503(4)	27(1)

Table SI 9: Bond lengths [Å] and angles [°] for **19·pyr**.

O(1)-B(2)	1.379(6)
O(1)-C(7)	1.453(6)
N(1)-C(25)	1.343(6)
N(1)-C(29)	1.344(7)
N(1)-B(1)	1.648(7)
C(1)-C(6)	1.550(6)
C(1)-C(2)	1.553(6)
C(1)-B(1)	1.644(7)
C(1)-H(1)	0.9800
B(1)-C(13)	1.644(7)
B(1)-C(19)	1.653(7)
F(2)-C(15)	1.336(7)
O(2)-B(2)	1.364(6)
O(2)-C(8)	1.464(6)
C(2)-C(3)	1.528(7)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
B(2)-C(6)	1.561(6)
F(3)-C(16)	1.351(6)
C(3)-C(4)	1.518(6)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
F(4)-C(17)	1.345(6)
C(4)-C(5)	1.511(7)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
F(5)-C(18)	1.346(6)
C(5)-C(6)	1.559(6)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
F(6)-C(24)	1.357(7)
C(6)-H(6)	0.9800
F(7)-C(23)	1.343(6)
C(7)-C(10)	1.502(8)
C(7)-C(9)	1.524(8)
C(7)-C(8)	1.568(8)
F(8)-C(22)	1.345(6)

C(8)-C(11)	1.492(8)
C(8)-C(12)	1.526(8)
F(9)-C(21)	1.335(7)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
F(10)-C(20)	1.359(5)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(14)	1.377(7)
C(13)-C(18)	1.390(7)
C(14)-F(1)	1.350(6)
C(14)-C(15)	1.391(7)
C(15)-C(16)	1.361(9)
C(16)-C(17)	1.367(9)
C(17)-C(18)	1.390(7)
C(19)-C(20)	1.382(7)
C(19)-C(24)	1.392(7)
C(20)-C(21)	1.381(6)
C(21)-C(22)	1.361(8)
C(22)-C(23)	1.362(9)
C(23)-C(24)	1.372(7)
C(25)-C(26)	1.391(6)
C(25)-H(25)	0.9300
C(26)-C(27)	1.370(8)
C(26)-H(26)	0.9300
C(27)-C(28)	1.378(8)
C(27)-H(27)	0.9300
C(28)-C(29)	1.375(8)
C(28)-H(28)	0.9300
C(29)-H(29)	0.9300

B(2)-O(1)-C(7)	108.2(4)
C(25)-N(1)-C(29)	117.8(4)
C(25)-N(1)-B(1)	120.7(4)
C(29)-N(1)-B(1)	120.9(4)
C(6)-C(1)-C(2)	105.8(4)
C(6)-C(1)-B(1)	117.6(4)
C(2)-C(1)-B(1)	109.8(4)
C(6)-C(1)-H(1)	107.8
C(2)-C(1)-H(1)	107.8
B(1)-C(1)-H(1)	107.8
C(13)-B(1)-C(1)	107.6(4)
C(13)-B(1)-N(1)	109.9(4)
C(1)-B(1)-N(1)	112.2(4)
C(13)-B(1)-C(19)	112.9(4)
C(1)-B(1)-C(19)	114.1(4)
N(1)-B(1)-C(19)	100.1(3)
B(2)-O(2)-C(8)	108.6(4)
C(3)-C(2)-C(1)	112.1(4)
C(3)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2A)	109.2
C(3)-C(2)-H(2B)	109.2
C(1)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
O(2)-B(2)-O(1)	112.4(4)
O(2)-B(2)-C(6)	127.2(5)
O(1)-B(2)-C(6)	119.6(4)
C(4)-C(3)-C(2)	110.4(4)
C(4)-C(3)-H(3A)	109.6
C(2)-C(3)-H(3A)	109.6
C(4)-C(3)-H(3B)	109.6
C(2)-C(3)-H(3B)	109.6
H(3A)-C(3)-H(3B)	108.1
C(5)-C(4)-C(3)	111.1(4)
C(5)-C(4)-H(4A)	109.4
C(3)-C(4)-H(4A)	109.4
C(5)-C(4)-H(4B)	109.4
C(3)-C(4)-H(4B)	109.4
H(4A)-C(4)-H(4B)	108.0
C(4)-C(5)-C(6)	111.8(4)

C(4)-C(5)-H(5A)	109.3
C(6)-C(5)-H(5A)	109.3
C(4)-C(5)-H(5B)	109.3
C(6)-C(5)-H(5B)	109.3
H(5A)-C(5)-H(5B)	107.9
C(1)-C(6)-C(5)	108.6(4)
C(1)-C(6)-B(2)	125.6(4)
C(5)-C(6)-B(2)	102.6(4)
C(1)-C(6)-H(6)	106.2
C(5)-C(6)-H(6)	106.2
B(2)-C(6)-H(6)	106.2
O(1)-C(7)-C(10)	108.2(5)
O(1)-C(7)-C(9)	106.1(4)
C(10)-C(7)-C(9)	110.3(5)
O(1)-C(7)-C(8)	102.8(4)
C(10)-C(7)-C(8)	115.8(5)
C(9)-C(7)-C(8)	112.9(5)
O(2)-C(8)-C(11)	107.4(4)
O(2)-C(8)-C(12)	107.3(4)
C(11)-C(8)-C(12)	109.9(5)
O(2)-C(8)-C(7)	102.5(4)
C(11)-C(8)-C(7)	115.6(5)
C(12)-C(8)-C(7)	113.3(5)
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5

H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(18)	113.6(4)
C(14)-C(13)-B(1)	123.1(4)
C(18)-C(13)-B(1)	123.1(4)
F(1)-C(14)-C(13)	120.8(4)
F(1)-C(14)-C(15)	114.4(5)
C(13)-C(14)-C(15)	124.8(5)
F(2)-C(15)-C(16)	120.6(5)
F(2)-C(15)-C(14)	120.5(5)
C(16)-C(15)-C(14)	118.9(5)
F(3)-C(16)-C(15)	120.4(6)
F(3)-C(16)-C(17)	120.2(6)
C(15)-C(16)-C(17)	119.4(4)
F(4)-C(17)-C(16)	120.8(5)
F(4)-C(17)-C(18)	119.2(6)
C(16)-C(17)-C(18)	119.9(5)
F(5)-C(18)-C(17)	115.9(5)
F(5)-C(18)-C(13)	120.7(4)
C(17)-C(18)-C(13)	123.3(5)
C(20)-C(19)-C(24)	111.9(4)
C(20)-C(19)-B(1)	124.9(4)
C(24)-C(19)-B(1)	123.1(4)
F(10)-C(20)-C(21)	114.2(4)
F(10)-C(20)-C(19)	120.6(4)
C(21)-C(20)-C(19)	125.1(5)
F(9)-C(21)-C(22)	119.8(5)
F(9)-C(21)-C(20)	121.0(5)
C(22)-C(21)-C(20)	119.1(5)
F(8)-C(22)-C(21)	120.8(6)
F(8)-C(22)-C(23)	120.1(5)
C(21)-C(22)-C(23)	119.1(5)
F(7)-C(23)-C(22)	119.7(5)

F(7)-C(23)-C(24)	120.6(6)
C(22)-C(23)-C(24)	119.7(5)
F(6)-C(24)-C(23)	116.2(5)
F(6)-C(24)-C(19)	119.1(4)
C(23)-C(24)-C(19)	124.7(5)
N(1)-C(25)-C(26)	121.9(5)
N(1)-C(25)-H(25)	119.1
C(26)-C(25)-H(25)	119.1
C(27)-C(26)-C(25)	119.3(5)
C(27)-C(26)-H(26)	120.4
C(25)-C(26)-H(26)	120.4
C(26)-C(27)-C(28)	119.3(5)
C(26)-C(27)-H(27)	120.3
C(28)-C(27)-H(27)	120.3
C(29)-C(28)-C(27)	118.4(5)
C(29)-C(28)-H(28)	120.8
C(27)-C(28)-H(28)	120.8
N(1)-C(29)-C(28)	123.3(5)
N(1)-C(29)-H(29)	118.3
C(28)-C(29)-H(29)	118.3

Table SI 10: Anisotropic displacement parameters (Å^2x 10^3) for **19·pyr**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	21(2)	18(2)	30(2)	-11(1)	4(2)	-8(1)
N(1)	18(2)	21(2)	13(2)	-7(2)	3(2)	-12(2)
C(1)	16(2)	14(2)	13(2)	-5(2)	3(2)	-8(2)
B(1)	20(3)	16(2)	13(2)	-1(2)	-1(2)	-11(2)
F(2)	56(2)	63(2)	27(2)	-31(2)	24(2)	-48(2)
O(2)	14(2)	18(2)	33(2)	-11(2)	2(1)	-3(1)
C(2)	17(2)	14(2)	23(3)	-1(2)	3(2)	-4(2)
B(2)	18(2)	19(2)	13(3)	-5(2)	4(2)	-6(2)
F(3)	62(2)	80(3)	22(2)	-11(2)	-6(2)	-56(2)
C(3)	15(2)	17(2)	26(3)	-6(2)	12(2)	-3(2)
F(4)	36(2)	52(2)	37(2)	10(2)	-22(2)	-29(2)
C(4)	23(2)	18(2)	21(2)	-2(2)	6(2)	-8(2)
F(5)	24(2)	24(2)	31(2)	1(1)	-9(1)	-10(1)
C(5)	20(2)	13(2)	15(2)	-1(2)	4(2)	-4(2)
F(6)	62(2)	43(2)	19(2)	5(1)	-8(2)	-38(2)
C(6)	14(2)	15(2)	13(2)	-3(2)	3(2)	-3(2)
F(7)	94(3)	40(2)	49(2)	27(2)	-45(2)	-47(2)
C(7)	24(3)	21(2)	39(3)	-13(2)	10(2)	-7(2)
F(8)	55(2)	13(2)	89(3)	-2(2)	-31(2)	-13(2)
C(8)	24(3)	19(2)	32(3)	-13(2)	8(2)	-5(2)
F(9)	48(2)	28(2)	58(2)	-25(2)	6(2)	-18(2)
C(9)	37(3)	26(3)	54(4)	1(3)	5(3)	-10(3)
F(10)	39(2)	22(1)	19(2)	-7(1)	2(1)	-14(1)
C(10)	41(3)	45(4)	65(5)	-41(3)	22(3)	-24(3)
C(11)	25(3)	30(3)	44(4)	-14(3)	-3(3)	2(2)
C(12)	26(3)	29(3)	44(3)	-16(2)	13(2)	-13(2)
C(13)	22(2)	23(2)	12(2)	2(2)	2(2)	-20(2)
C(14)	28(3)	31(3)	15(2)	-4(2)	6(2)	-23(2)
C(15)	38(3)	45(3)	16(3)	-13(2)	12(2)	-32(3)
F(1)	26(2)	31(2)	24(2)	-13(1)	8(1)	-16(1)
C(16)	50(3)	56(4)	7(2)	-3(2)	-1(2)	-45(3)
C(17)	34(3)	44(3)	15(3)	8(2)	-10(2)	-30(3)
C(18)	28(3)	28(3)	13(2)	1(2)	-2(2)	-19(2)
C(19)	14(2)	19(2)	18(2)	-1(2)	-2(2)	-10(2)

C(20)	17(2)	14(2)	19(2)	0(2)	0(2)	-7(2)
C(21)	21(2)	19(2)	34(3)	-9(2)	-1(2)	-10(2)
C(22)	30(3)	10(2)	54(4)	0(2)	-16(3)	-8(2)
C(23)	42(3)	22(2)	33(3)	15(2)	-22(3)	-25(2)
C(24)	29(3)	23(2)	20(3)	1(2)	-5(2)	-19(2)
C(25)	14(2)	20(2)	14(2)	-7(2)	2(2)	-6(2)
C(26)	14(2)	26(2)	31(3)	-15(2)	4(2)	-9(2)
C(27)	20(2)	38(3)	44(4)	-24(3)	15(2)	-20(2)
C(28)	38(3)	60(4)	25(3)	-20(3)	21(2)	-40(3)
C(29)	29(3)	42(3)	20(3)	-10(2)	5(2)	-23(2)

Table SI 11: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **19·pyr.**

	x	y	z	U(eq)
H(1)	4107	6178	8813	16
H(2A)	1566	8001	8440	24
H(2B)	1244	6866	8068	24
H(3A)	2056	6363	9868	25
H(3B)	447	6737	9509	25
H(4A)	1798	4124	10154	26
H(4B)	1284	4457	9163	26
H(5A)	3766	2743	9396	21
H(5B)	4191	3817	9769	21
H(6)	3095	4560	7995	18
H(9A)	7732	-979	9200	65
H(9B)	6067	-552	8927	65
H(9C)	6441	361	9468	65
H(10A)	8243	-641	7545	66
H(10B)	7195	859	6879	66
H(10C)	6555	-281	7393	66
H(11A)	9710	-10	8930	55
H(11B)	8550	759	9564	55
H(11C)	9540	1535	9047	55
H(12A)	9306	1345	7287	48
H(12B)	8994	2859	7507	48
H(12C)	7794	2748	6951	48
H(25)	6282	5891	8571	19
H(26)	8762	5486	8446	27
H(27)	9638	6014	7064	35
H(28)	8005	6947	5823	39
H(29)	5565	7313	6005	33

6 References

1. R. A. Fernandes, P. Kumar, A. Bhowmik and D. A. Gorve, Regioselective Disulfide-Catalyzed Photocatalytic Oxidative Cleavage of 1-Arylbutadienes to Cinnamaldehydes, *Org. Lett.*, 2022, **24**, 3435–3439.

2. (a) N. PraveenGanesh and P. Y. Chavant, Improved Preparation of 4,6,6-Trimethyl-1,3,2-dioxaborinane and Its Use in a Simple [$PdCl_2(TPP)_2$]-Catalyzed Borylation of Aryl Bromides and Iodides, *Eur. J. Org. Chem.*, 2008, **2008**, 4690–4696; (b) B. M. Rosen, C. Huang and V. Percec, Sequential Ni-catalyzed borylation and cross-coupling of aryl halides via in situ prepared neopentylglycolborane, *Org. Lett.*, 2008, **10**, 2597–2600.

3. T. A. Gazis, B. A. J. Mohajeri Thaker, D. Willcox, D. M. C. Ould, J. Wenz, J. M. Rawson, M. S. Hill, T. Wirth and R. L. Melen, 1,3-Carboboration of iodonium ylides, *Chem. Commun.*, 2020, **56**, 3345–3348.

4. D. J. Parks, W. E. Piers and G. P. A. Yap, Synthesis, Properties, and Hydroboration Activity of the Highly Electrophilic Borane Bis(pentafluorophenyl)borane, $HB(C_6F_5)_2$, *Organometallics*, 1998, **17**, 5492–5503.

5. M. J. O'Mahony, R. A. More O'Ferrall, D. R. Boyd, C. M. Lam and A. C. O'Donoghue, Substituent effects on the dehydration of arene hydrates in aqueous solution, *J. Phys. Org. Chem.*, 2013, **26**, 989–996.

6. M. Yang, J. Sun and C. Zhu, Synthesis of Novel 1,4-Bissulfonamide Ligands for Enantioselective Addition of Diethylzinc to Aldehydes, *Chin. J. Chem.*, 2011, **29**, 1697–1702.

7. J. Takagi, K. Takahashi, T. Ishiyama and N. Miyaura, Palladium-catalyzed cross-coupling reaction of bis(pinacolato)diboron with 1-alkenyl halides or triflates: convenient synthesis of unsymmetrical 1,3-dienes via the borylation-coupling sequence, *J. Am. Chem. Soc.*, 2002, **124**, 8001–8006.

8. S. Geng, J. Zhang, S. Chen, Z. Liu, X. Zeng, Y. He and Z. Feng, Development and Mechanistic Studies of Iron-Catalyzed Construction of Csp2-B Bonds via C-O Bond Activation, *Org. Lett.*, 2020, **22**, 5582–5588.

9. Y. Hu, W. Sun, T. Zhang, N. Xu, J. Xu, Y. Lan and C. Liu, Stereoselective Synthesis of Trisubstituted Vinylboronates from Ketone Enolates Triggered by 1,3-Metalate Rearrangement of Lithium Enolates, *Angew. Chem., Int. Ed.*, 2019, **58**, 15813–15818.

10. V. Rauniyar, H. Zhai and D. G. Hall, Catalytic enantioselective allyl- and crotylboration of aldehydes using chiral diol x SnCl4 complexes. Optimization, substrate scope and mechanistic investigations, *J. Am. Chem. Soc.*, 2008, **130**, 8481–8490.

11. A. S. Patil, D.-L. Mo, H.-Y. Wang, D. S. Mueller and L. L. Anderson, Preparation of α-oxygenated ketones by the dioxygenation of alkenyl boronic acids, *Angew. Chem., Int. Ed.*, 2012, **51**, 7799–7803.

12. K. Endo, T. Ohkubo, T. Ishioka and T. Shibata, Cross coupling between sp3-carbon and sp3-carbon using a diborylmethane derivative at room temperature, *J. Org. Chem.*, **2012**, 77, 4826–4831.

13. J. Kenyon and I. Larrosa, Electrochemical Ruthenium-Catalysed Directed C−H Functionalization of Arenes with Boron Reagents, *Adv. Synth. Catal.*, 2024, **366**, 830–837.

14. X. Wu and J. S. Zhou, Selective arylation at the vinylic site of cyclic olefins, *Chem. Commun.*, 2013, **49**, 4794–4796.

15. X. Wu, Y. Lu, H. Hirao and J. S. Zhou, Achieving Vinylic Velectivity in Mizoroki-Heck Reaction of Cyclic Olefins, *Chem. Eur. J.*, 2013, **19**, 6014–6020.

16. U. Yolsal, T. A. R. Horton, M. Wang and M. P. Shaver, Cyclic Ether Triggers for Polymeric Frustrated Lewis Pair Gels, *J. Am. Chem. Soc.*, 2021, **143**, 12980–12984.

17. Y. Yamamoto, R. Fujikawa, T. Umemoto and N. Miyaura, Iridium-catalyzed hydroboration of alkenes with pinacolborane, *Tetrahedron*, 2004, **60**, 10695–10700.

18. (a) L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination, *J. Appl. Cryst.*, 2015, **48**, 3–10; (b) G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3–8; (c) G. M. Sheldrick, A short history of SHELX, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.