



Supporting Information

Selective Benzylic CH-Borylations by Tandem Cobalt Catalysis

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General

All experiments for air-sensitive compounds were performed under an atmosphere of dry argon, by using standard Schlenk and glovebox techniques.

Chemicals and Solvents: Commercially available liquid substrates were distilled under reduced pressure prior to use. Solvents (*n*-hexane, toluene) were distilled over sodium and benzophenone and stored over molecular sieves (4 Å). Crystalline LiN(SiMe₃)₂ (*Sigma-Aldrich*, 97%) was used as received. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (HBpin) was purchased from *Sigma-Aldrich* (97%) stored at -30 °C in an argon-filled Glovebox. Bis(pinacolato)diboron (B₂pin₂) was purchased from *Fluorochem* (98%). Anhydrous CoBr₂ (99%) was purchased from *Sigma Aldrich* and stored in an argon-filled Glovebox. Co(hmds)₂ was prepared according to literature procedure.^[1] Solvents used for GC were distilled under reduced pressure prior to use (ethyl acetate).

¹H-NMR, ¹³C-NMR, and ¹¹B-NMR Spectroscopy: Nuclear magnetic resonance spectra were recorded on a *Bruker Avance 400* (400 MHz), *Bruker Avance 500* (400 MHz) and *Bruker Avance 600* (600 MHz). ¹H-NMR: The following abbreviations are used to indicate multiplicities: s = singlet; d = doublet; t = triplet, q = quartet; m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of quartet. Chemical shift δ is given in ppm to the residual solvent peak.

Column Chromatography: Flash column chromatography with silica gel 60 from KMF (0.040-0.063mm). Mixtures of solvents used are noted in brackets.

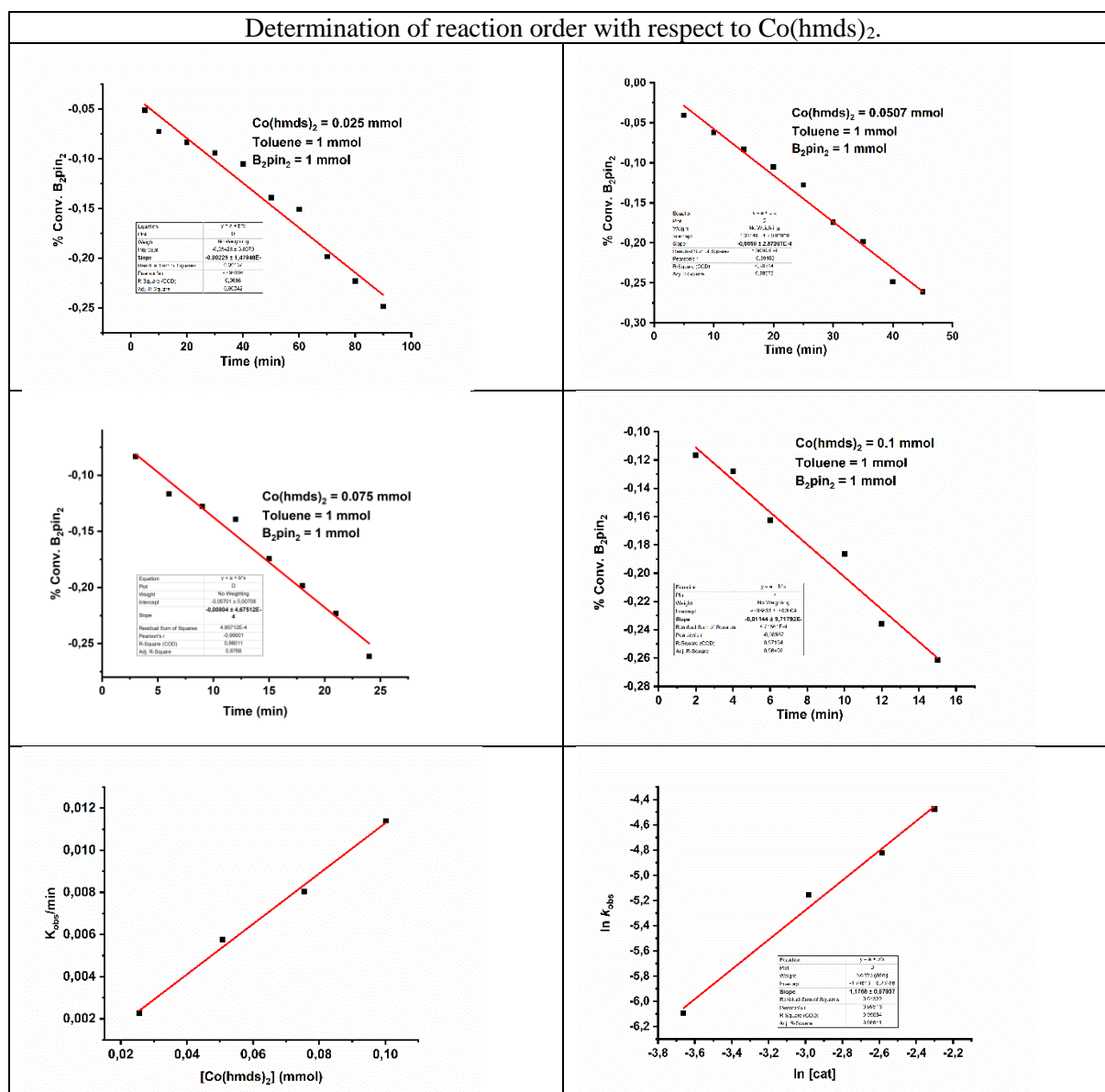
Gas chromatography with FID (GC-FID): HP6890 GC-System with injector 7683B and *Agilent 7820A* System. Column: HP-5, 19091J-413 (30 m × 0.32 mm × 0.25 μm), carrier gas: N₂. GC-FID was used for kinetic studies. Calibration with internal standard *n*-pentadecane and analytically pure samples.

Gas chromatography with mass-selective detector (GC-MS): *Agilent 6890N* Network GC-System, mass detector 5975 MS. Column: HP-5MS (30m × 0.25 mm × 0.25 μm, 5% phenylmethylsiloxane, carrier gas: H₂. Standard heating procedure: 50 °C (2 min), 25 °C/min -> 300 °C (5 min).

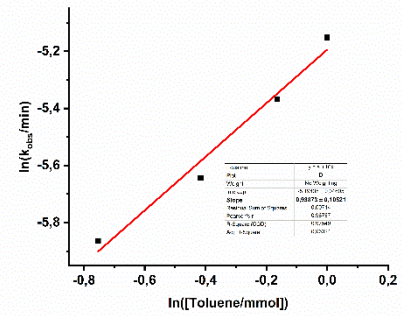
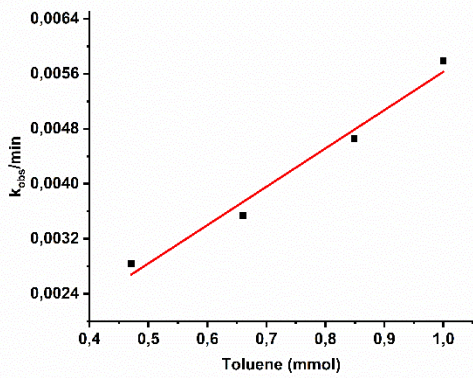
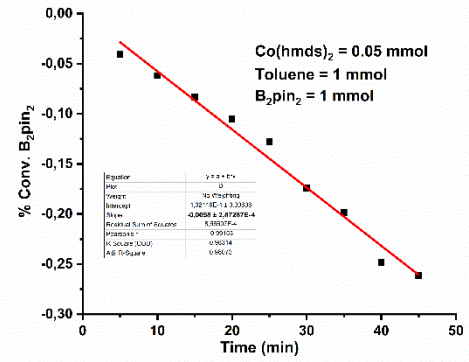
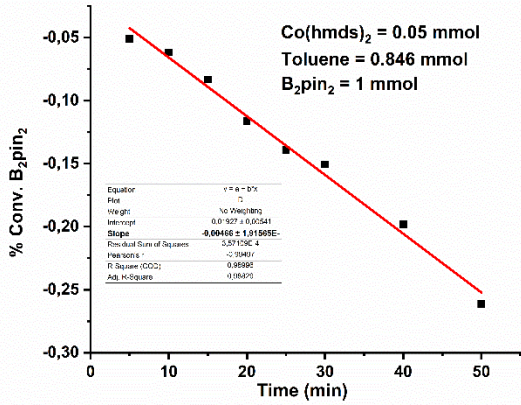
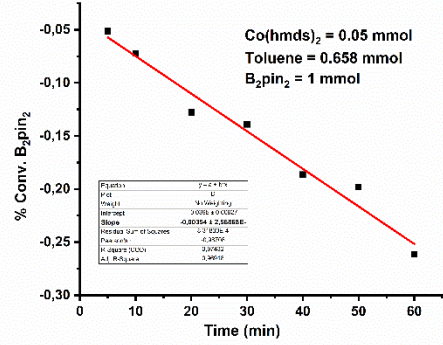
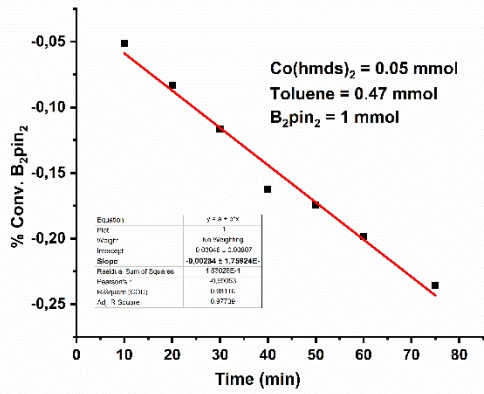
Kinetic experiments

In a glovebox desired amount of Co(hmds)₂ (0.0258 mmol, 0.051 mmol, 0.075, 0.1 mmol) was taken a Schleck flask (10 ml). Toluene (106 μl, 1 mmol), 50 μl pentadecane, and 254 mg (1.0 mmol) B₂pin₂ were added to the Schleck flask. To this solution, 3 ml hexane was added and capped with a septum. The reaction mixture was heated at 60 °C temperature. A certain amount of aliquot was taken at a regular time intervals. The aliquot was worked up with aq. NaHCO₃/EtOAc. The ethyl acetate part was dried over anhydrous Na₂SO₄ followed by conversion of B₂pin₂ was monitored by GC-FID. The data point is taken up to ca. 20 % conversion of B₂pin₂. To determine the order of reaction with respect to toluene and B₂pin₂, we have varied the concentration of respective reagents keeping the concentrations of other reagents constant.

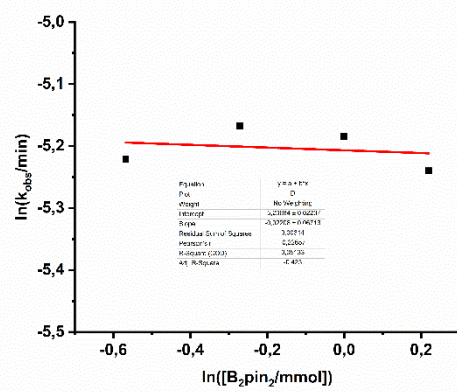
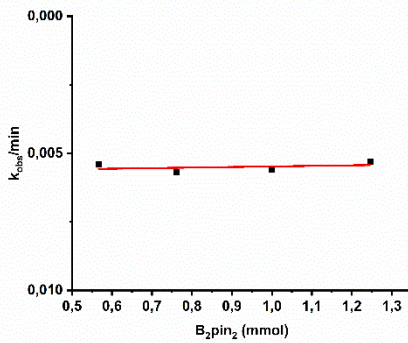
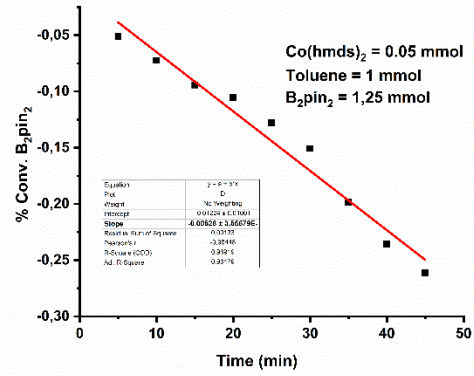
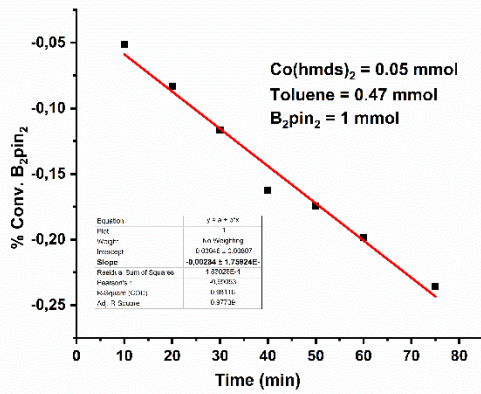
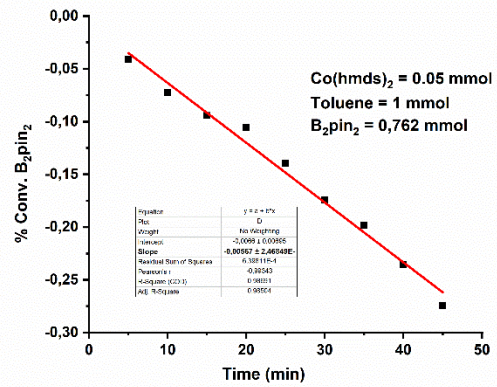
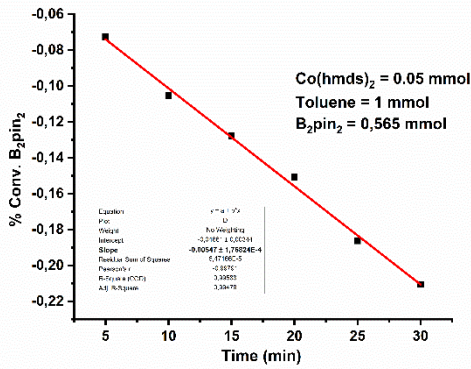
Table S1: Kinetic data for $\text{Co}(\text{hmds})_2$ catalysed benzylic borylation of toluene



Determination of reaction order with respect to toluene.



Determination of reaction order with respect to B_2pin_2 .



Comparison of react rates: Toluene -d₈/d₅/d₃/h₈

In a glovebox desired amount of Co(hmds)₂ (0.05 mmol) was taken in a Schleck flask (10 ml). 1 mmol toluene (d₈/d₅/d₃/h₈) (106 μl), 50 μl pentadecane and 254 mg (1.0 mmol) B₂pin₂ were added to the Schleck flask. 3 ml Hexane was added to this solution, and the reaction mixture was heated at 60 °C temperature. A certain amount of aliquot was taken at regular time intervals. The aliquot was worked up with aq. NaHCO₃/EtOAc. The ethyl acetate part was dried over anhydrous Na₂SO₄ followed by conversion of B₂pin₂ was monitored by GC-FID.

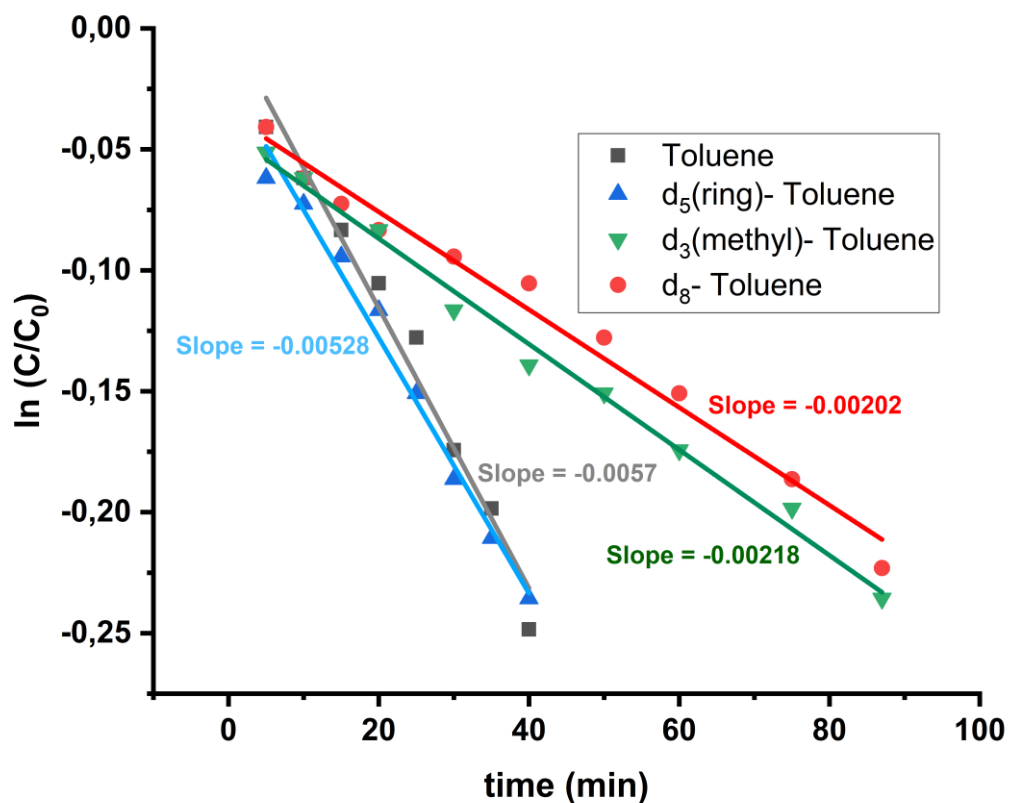


Figure S1: Reaction conditions: Co(hmds)₂ (0.05 mmol) + B₂pin₂ (1.0 mmol) + Toluene (d₈/d₅/d₃/h₈) (1.0 mmol) + pentadecane (50 μl) in hexane heated at 60 °C. Conversion of B₂pin₂ was monitored by GC-FID.

Detection of DBpin in the catalytic reaction mixture

In a glovebox $\text{Co}(\text{hmds})_2$ (3.8 mg) and 12.7 mg (0.1 mmol) B_2pin_2 were taken a J-Young NMR tube. 0.1 mmol d_8 -toluene (10.6 μl) and 0.6 ml hexane were added. The reaction mixture was heated at 60 $^\circ\text{C}$. The reaction was monitored by ^{11}B NMR where the formation of DBpin was detected in the reaction mixture.

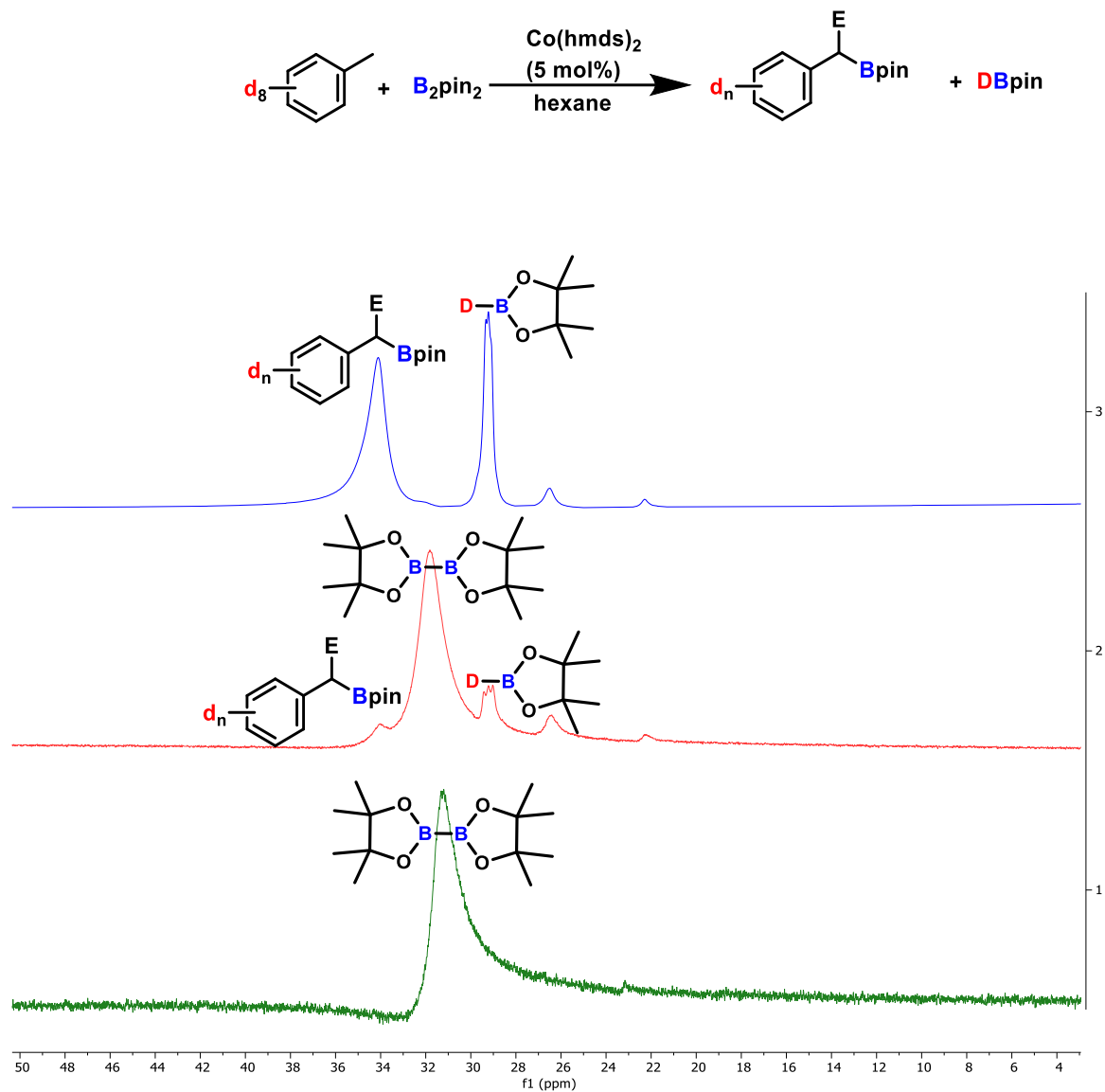


Figure S2: ^{11}B spectral changes of the reaction mixture of $\text{Co}(\text{hmds})_2$ (10 mol%) + B_2pin_2 and d_8 -toluene in hexane

Detection of D₂ gas evolution from dehydrocoupling

The reaction set up is shown in the figure. In an argon-filled glovebox, a Schlenk flask (10 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of Co(HMDS)₂, 106 μl (1.0 mmol) of *d*₈-toluene, and 280 mg (1.1 mmol) of B₂pin₂. n-Hexane (2 ml) was added, and the resulting mixture was connected to another round bottom flask charged with a magnetic stir bar, 1 mmol styrene, and Pd-C (10 mol%) in 2 ml hexane. The Schlenk flask was heated at 80 °C for 20 h while keeping the other reactions separated by closing the stopper. After cooling the reaction to room temperature, the stopper was turned on, allowing the mixing of gaseous reactant between two reactions vessel. The hydrogenation reaction was stirred overnight at room temperature. The hexane solution (hydrogenation) was diluted with EtOAc, and water was added. The EtOAc part was extracted and dried over anhydrous Na₂SO₄ and injected into GC-MS. GC-MS analysis indicates the formation of the PhCH(D)CH₂(D) compound with an *m/z* of 108.

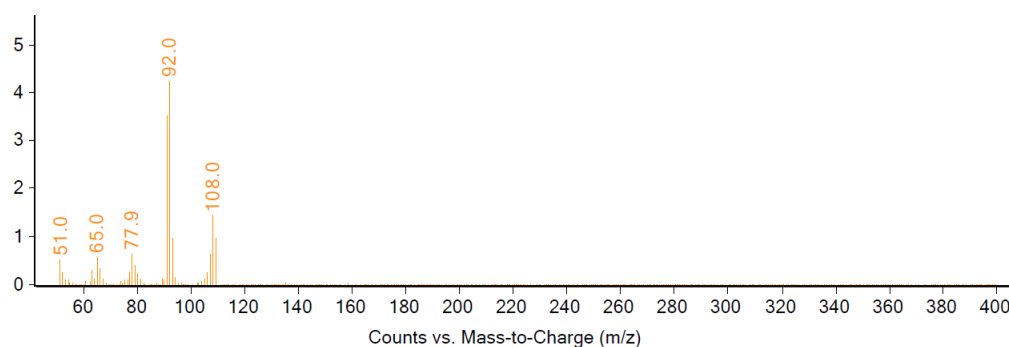


Figure S3: Reaction set up (top) and GC-MS data (bottom)

UV-vis spectral studies

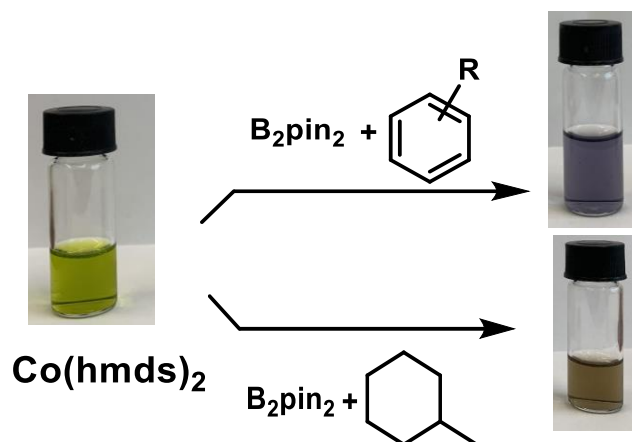


Figure S4: Colour of the reaction mixture $\text{Co}(\text{hmds})_2 + \text{B}_2\text{pin}_2 + \text{Toluene}$ (1:1:1) in hexane at room temperature (top); $\text{Co}(\text{hmds})_2 + \text{B}_2\text{pin}_2 + \text{methylcyclohexane}$ (1:1:1) in hexane (bottom)

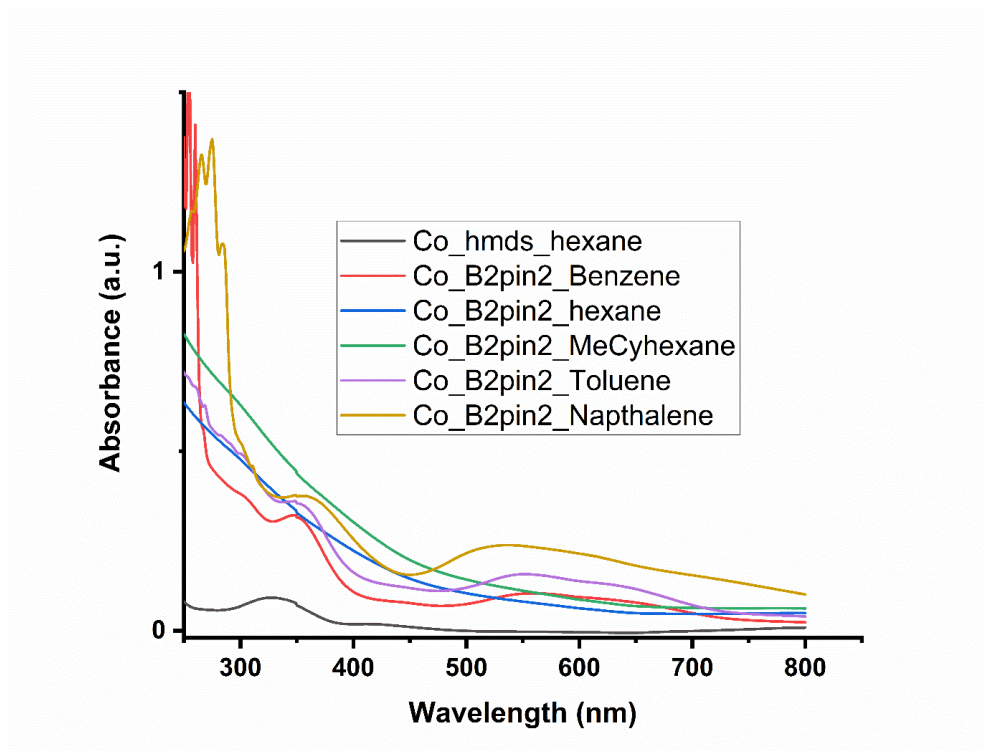


Figure S4b: UV-vis spectra of the complexes formed upon addition of different substrate to the $\text{Co}(\text{hmds})_2 + \text{B}_2\text{pin}_2$ mixture in hexane.

Poisoning experiments

Control experiment: In a glovebox desired amount of $\text{Co}(\text{hmds})_2$ (19 mg, 5 mol%) was taken in a Schleck flask (10 ml). Toluene (106 μl , 1 mmol), 50 μl pentadecane, and 254 mg (1.0 mmol) B_2pin_2 were added to the Schleck flask. To this solution 3 ml hexane was added and the reaction mixture was heated at 60 °C temperature. A certain amount of aliquot was taken at regular time intervals. The aliquot was worked up with aq. $\text{NaHCO}_3/\text{EtOAc}$. The ethyl acetate part was dried over anhydrous Na_2SO_4 followed by conversion of B_2pin_2 was monitored by GC-FID.

Addition of DCT: 4 Equiv. DCT w.r.t to Co was added after 50 min (ca. 20% conversion of B_2pin_2) in a separate reaction setup.

Addition of PMe_3 : 1/0.5/0.1 Equiv. PMe_3 w.r.t to Co was added after 50 min (ca. 20% conversion of B_2pin_2) in a separate reaction set up.

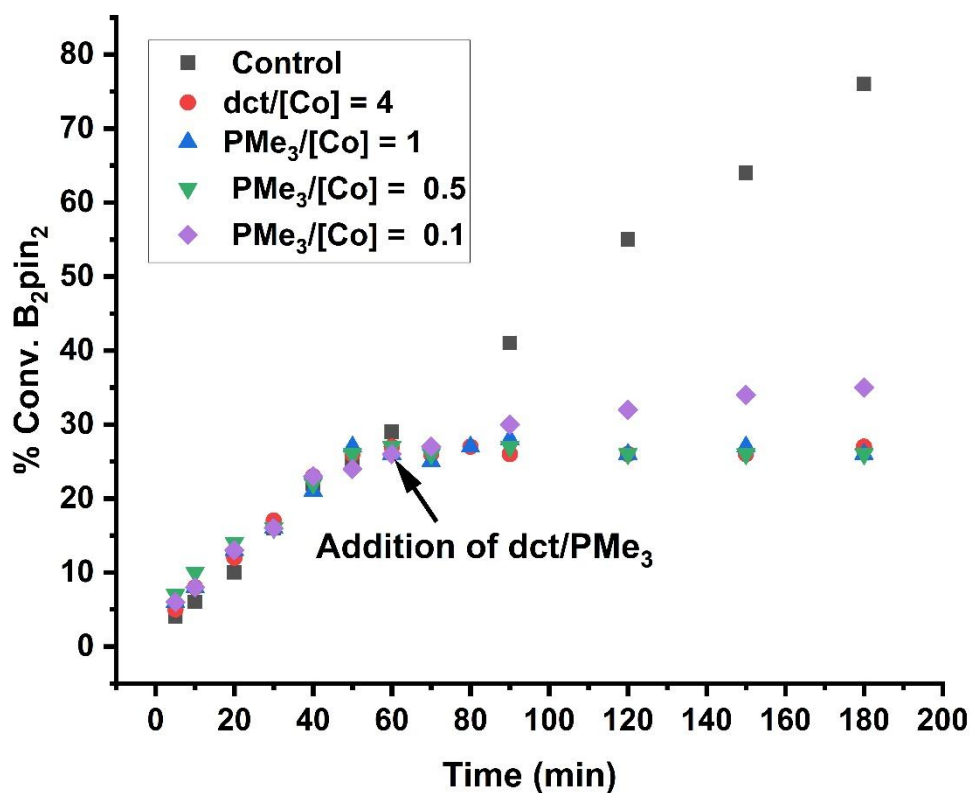


Figure S5. Poisoning experiments. Reaction conditions: $\text{Co}(\text{hmds})_2$ (0.05 mmol) + B_2pin_2 (1.0 mmol) + Toluene (1.0 mmol) + pentadecane (50 μl) in hexane heated at 60 °C. PMe_3 or dct was added after 50 min.

Poisoning experiments

Two parallel reactions were performed:

Control experiment: In a glovebox desired amount of $\text{Co}(\text{hmds})_2$ (38 mg, 10 mol%) was taken in a Schleck flask (10 ml). Toluene (106 μl , 1 mmol), 50 μl pentadecane and 254 mg (1.0 mmol) B_2pin_2 were added to the Schleck flask. To this solution, 3 ml hexane was added, and the reaction mixture was heated at 60 °C temperature. A certain amount of aliquot was taken at regular time intervals. The aliquot was worked up with aq. $\text{NaHCO}_3/\text{EtOAc}$. The ethyl acetate part was dried over anhydrous Na_2SO_4 followed by conversion of B_2pin_2 was monitored by GC-FID.

Addition of TEMPO: 10 mol% TEMPO (15.6 mg, 1 equiv. w.r.t. Co) was added after 15 min (ca. 20% conversion of B_2pin_2) in a separate reaction set up. We also did not observe the formation of TEMPO coupled product ($\text{PhCH}_2\text{-TEMPO}$) in the GC-MS.

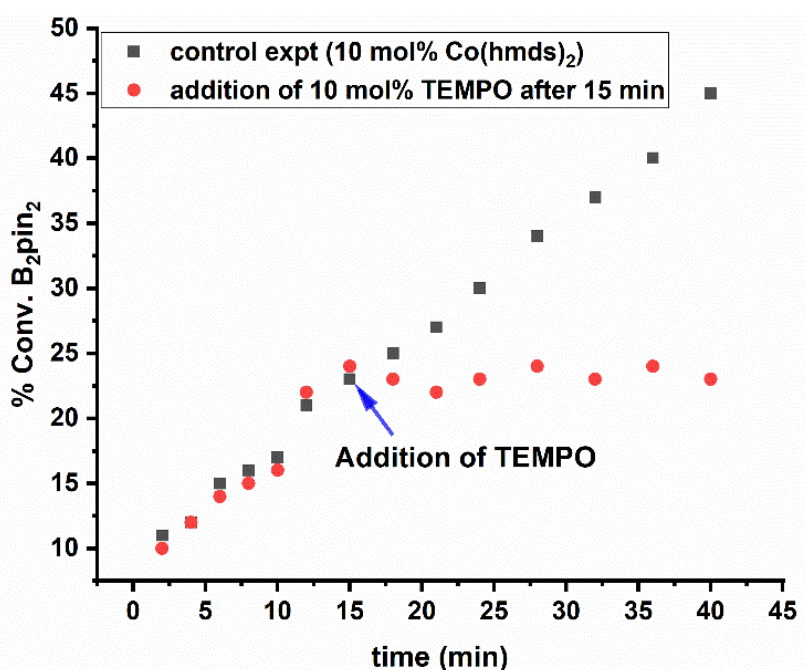


Figure S6: Reaction conditions: $\text{Co}(\text{hmds})_2$ (0.1 mmol) + B_2pin_2 (1.0 mmol) + Toluene (1.0 mmol) + pentadecane (50 μl) in hexane heated at 60 °C. TEMPO was added after 15 min.

Reaction between $\text{Co}(\text{hmds})_2$ and B_2pin_2 in hexane

In a glovebox $\text{Co}(\text{hmds})_2$ (19 mg, 0.05 mmol) and 12.7 mg (0.05 mmol) B_2pin_2 were taken in a reaction vial. Hexane (1 ml) was added and stirred for 18h at room temperature. The hexane was evaporated to dryness, and the resultant brown compound was dissolved in C_6D_6 . ^1H and ^{11}B NMR of the resultant solution were recorded. The conversion of B_2pin_2 was 95% determined by GC-FID using pentadecane as an internal standard.

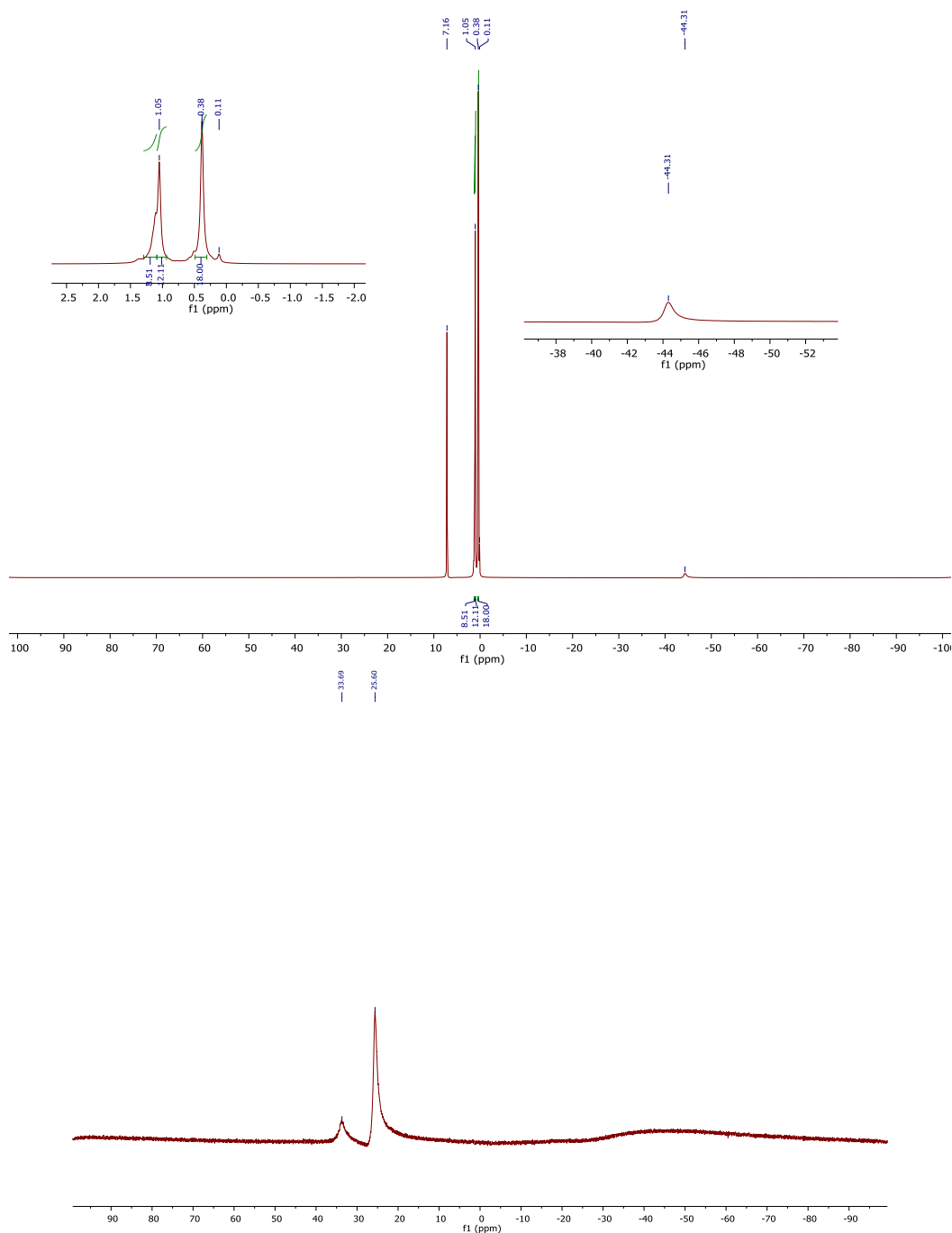
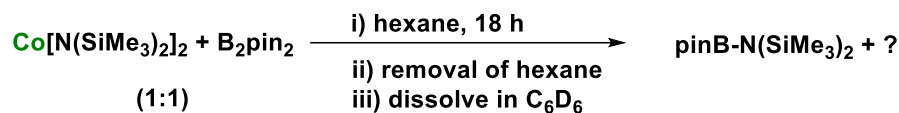


Figure S7: ^1H and ^{11}B spectra of the mixture of $\text{Co}(\text{hmds})_2 + \text{B}_2\text{pin}_2$ in hexane.

Quantification of hmnds-Bpin

In a glovebox $\text{Co}(\text{hmnds})_2$ (19 mg, 0.05 mmol) and 12.7 mg (0.05 mmol) B_2pin_2 were taken in a reaction vial. 0.7 ml C_6D_6 was added and stirred for 18h at room temperature. 25 μl C_6Me_6 from a 0.2 mmol stock solution in C_6D_6 was added to the reaction solution and the solution filtered through 0.2 μm syringe filter. Formation of hmnds-Bpin along with unreacted B_2pin_2 were identified from the ^1H and ^{11}B NMR spectra analysis. The conversion of B_2pin_2 was $\sim 60\%$, determined from an identical reaction using pentadecane as an internal standard.

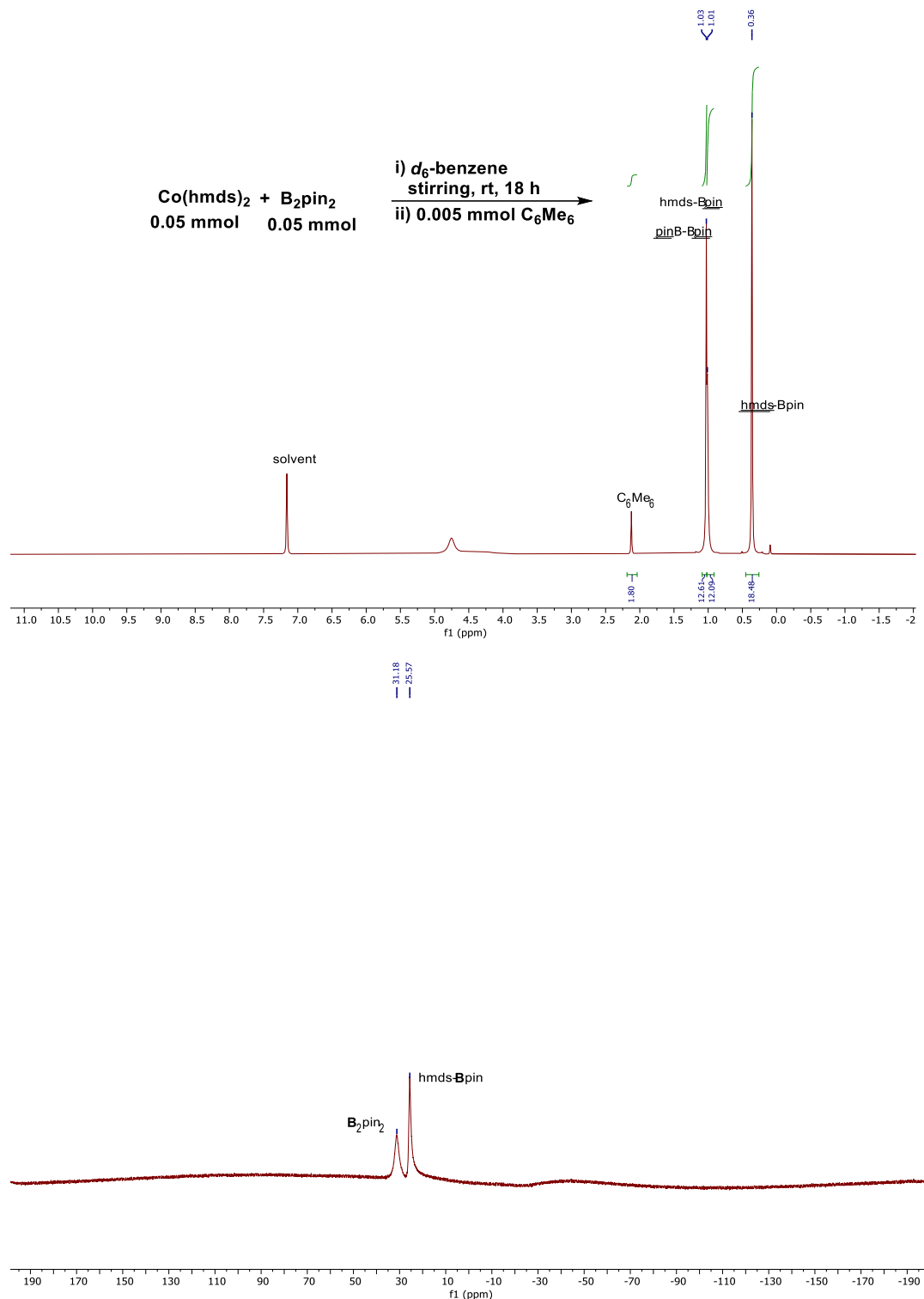


Figure S8: ^1H and ^{11}B spectra of the mixture of $\text{Co}(\text{hmnds})_2 + \text{B}_2\text{pin}_2$ in d_6 -benzene

Synthesis of catalyst derivatives: Trapping with phosphine ligands

In an argon-filled glovebox, a flame dried 4 mL reaction vial was charged with $\text{Co}(\text{hmds})_2$ (0.25 mmol), B_2pin_2 (0.125 mmol, 32 mg) and 1 ml benzene. The reaction was stirred overnight at room temperature. To this blue solution, 131 mg (0.5 mmol) PPh_3 was added, and the solution turned brown. The mixture was stirred for 1 h and evaporated to dryness. 2 ml Hexane was added and kept the solution in the freezer overnight. The solid brown compound was collected *via* filtration and washed with cold hexane (1 ml x 3). The compound was dried and analyzed by ^1H NMR in C_6D_6 .

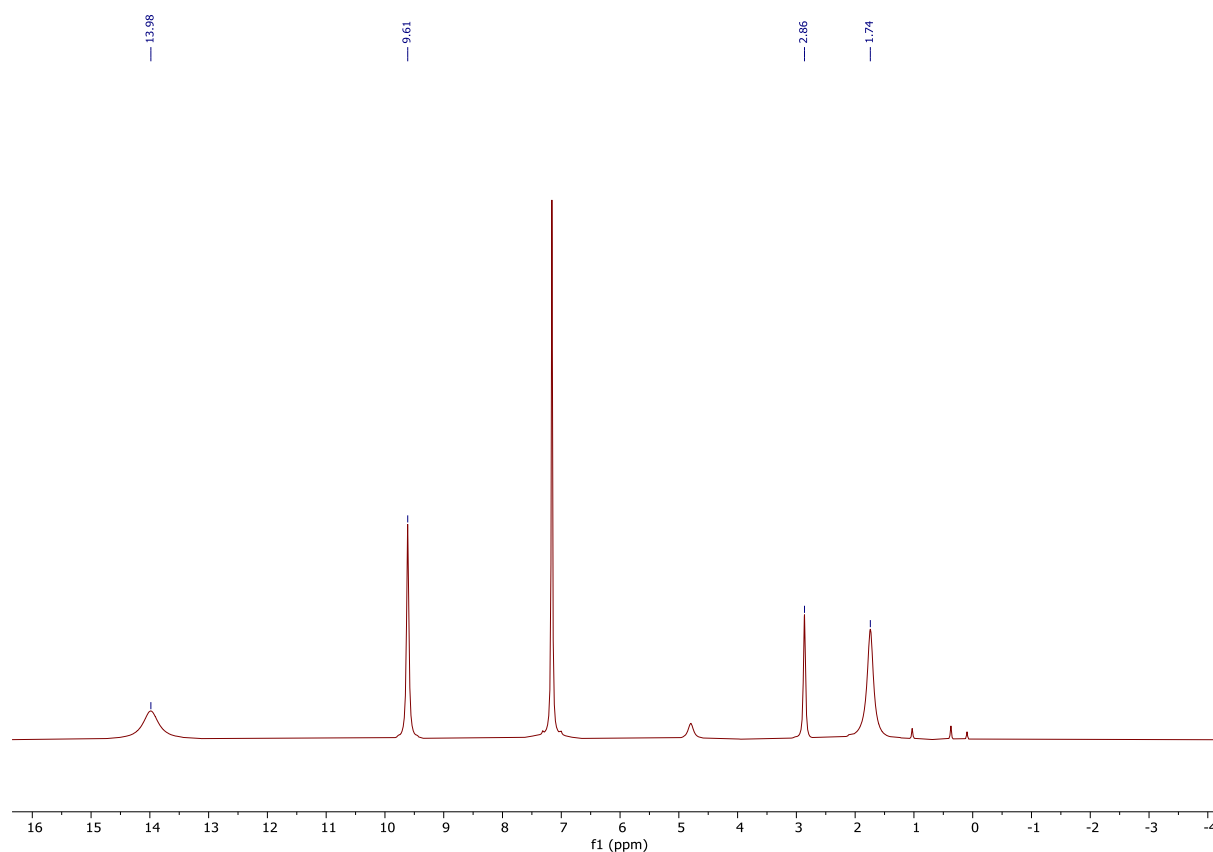
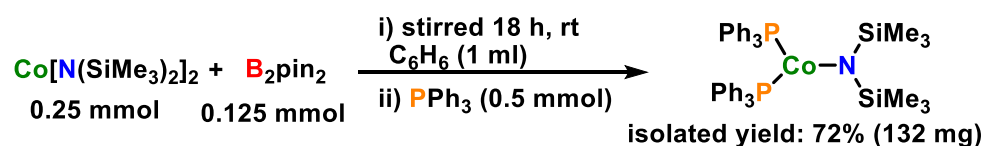


Figure S9. ^1H –NMR of $\text{Co}(\text{PPh}_3)_2(\text{hmds})$ in C_6D_6 . The spectrum matched with reported compound (Fout *et al.*; *Chem. Sci.* **2014**, *5*, 4831-4839).

Synthesis of catalyst derivatives: Trapping with phosphine ligands

In an argon-filled glovebox, a flame dried 4 mL reaction vial was charged with $\text{Co}(\text{hmds})_2$ (0.25 mmol), B_2pin_2 (0.125 mmol, 32 mg) and 1 ml benzene. The reaction was stirred overnight. To this blue, 106 mg (0.25 mmol) bis(dicyclohexylphosphino)ethane was added, and the solution turned green. The mixture was stirred for 1 h and evaporated to dryness. Diethyl ether (2 ml) was added, and the solution was filtered. A few red crystals were grown from the ether solution. The molecular view is shown below.

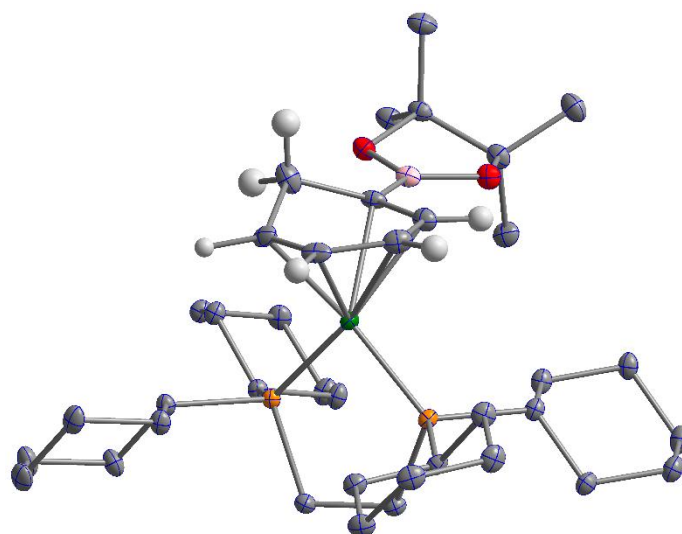


Figure S10: Molecular structure of $(\text{dcpe})\text{Co}(\eta^5\text{-C}_6\text{H}_6\text{-Bpin})$. CCDC 2097237 contains crystallographic data of this compound.

X-ray absorption spectroscopy

We performed X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis for solutions of $\text{Co}(\text{hmds})_2$ and the system $\{\text{Co}(\text{hmds})_2 + \text{B}_2\text{pin}_2\}$ in hexane. In addition, the reaction itself $\{\text{Co}(\text{hmds})_2 + \text{B}_2\text{pin}_2 + \text{toluene}\}$ was followed both, under stoichiometric conditions ($n(\text{Co}(\text{hmds})_2):\text{B}_2\text{pin}_2:\text{toluene}=1:1:1$) and under excess of B_2pin_2 and toluene ($n(\text{Co}(\text{hmds})_2):\text{B}_2\text{pin}_2:\text{toluene}=1:11:10$) by application of fast (60 s) XANES spectra (figure S11) and by EXAFS spectra of the formed initial and final states of the catalyst.

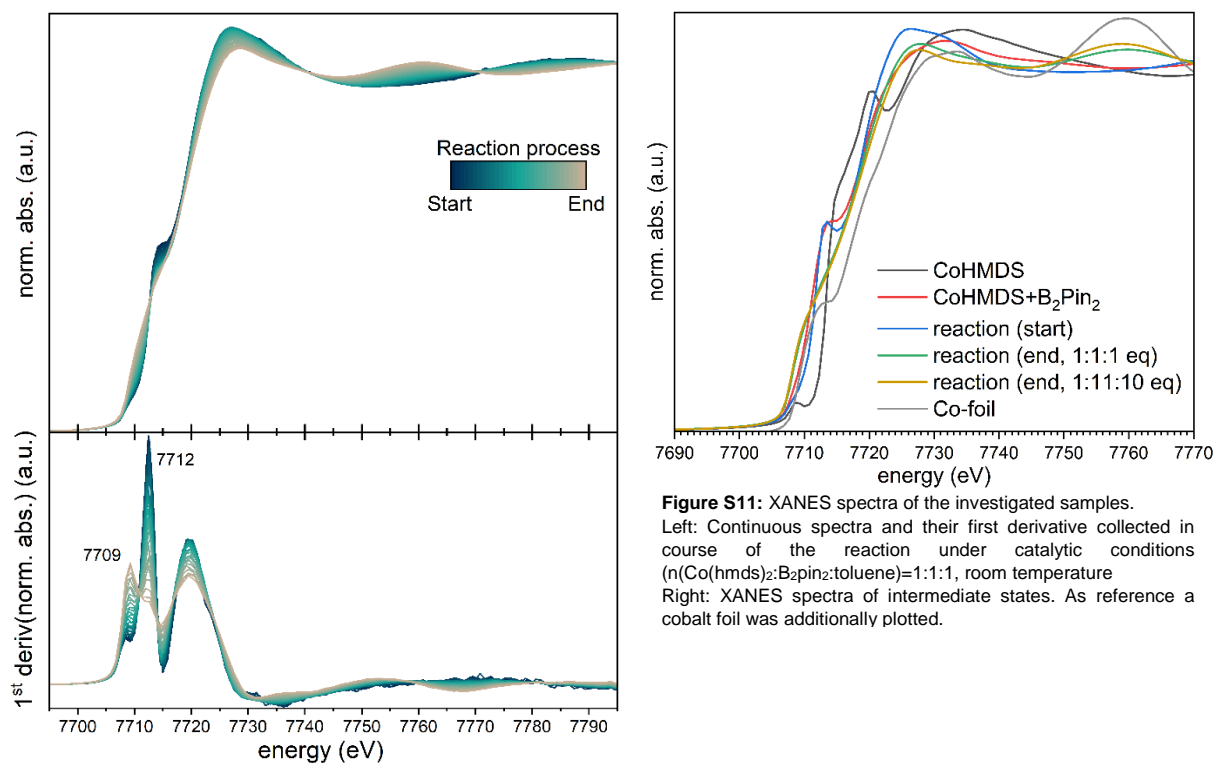


Figure S11: XANES spectra of the investigated samples. Left: Continuous spectra and their first derivative collected in course of the reaction under catalytic conditions ($n(\text{Co}(\text{hmds})_2:\text{B}_2\text{pin}_2:\text{toluene})=1:1:1$, room temperature). Right: XANES spectra of intermediate states. As reference a cobalt foil was additionally plotted.

XANES spectra of the investigated reaction steps are shown in figure S12 (right). Surprisingly, the edge energies for all measured samples differ not very much, as listed in table S1, which could be due to the electron donor properties of hmds. The $\text{Co}(\text{hmds})_2$ precursor exhibits an oxidation state of +II. The addition of B_2pin_2 leads to a slight shift of the absorption edge energy to lower values and a modification of the edge fine structure, indicating a reduced electron density at the Co center induced by structural modification such as ligand exchange. This XANES spectrum experiences a further slight change after addition of the reactant toluene (reaction start). In course of the reaction, the catalyst alters notably (see figure S12), forming finally a further reduced species with an edge energy comparable to metallic Co (7709 eV). This behaviour is identical for both investigated reactant ratios $\text{Co}(\text{hmds})_2:\text{B}_2\text{pin}_2:\text{toluene} = 1:1:1$ and $1:11:10$, only the time needed to reach the final state is different. This is further elucidated by linear combination (LC-) XANES fits (see figure S13 and figures S14 resp. S15), showing the XANES kinetics for both reactant ratios.

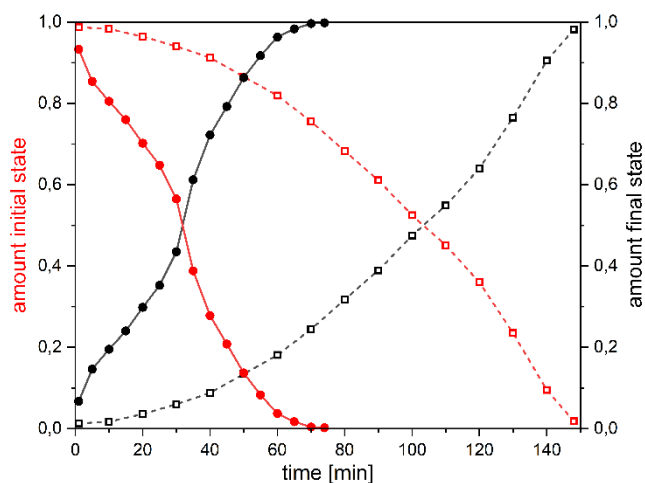


Figure S12: Ratios of initial state and final state depending on time obtained by LC-XANES fits of both investigated reactant ratios. Dotted line: $n(\text{Co}(\text{hmds})_2:\text{B}_2\text{pin}_2:\text{toluene})=1:1:1$; straight line: $n(\text{Co}(\text{hmds})_2:\text{B}_2\text{pin}_2:\text{toluene})=1:11:10$

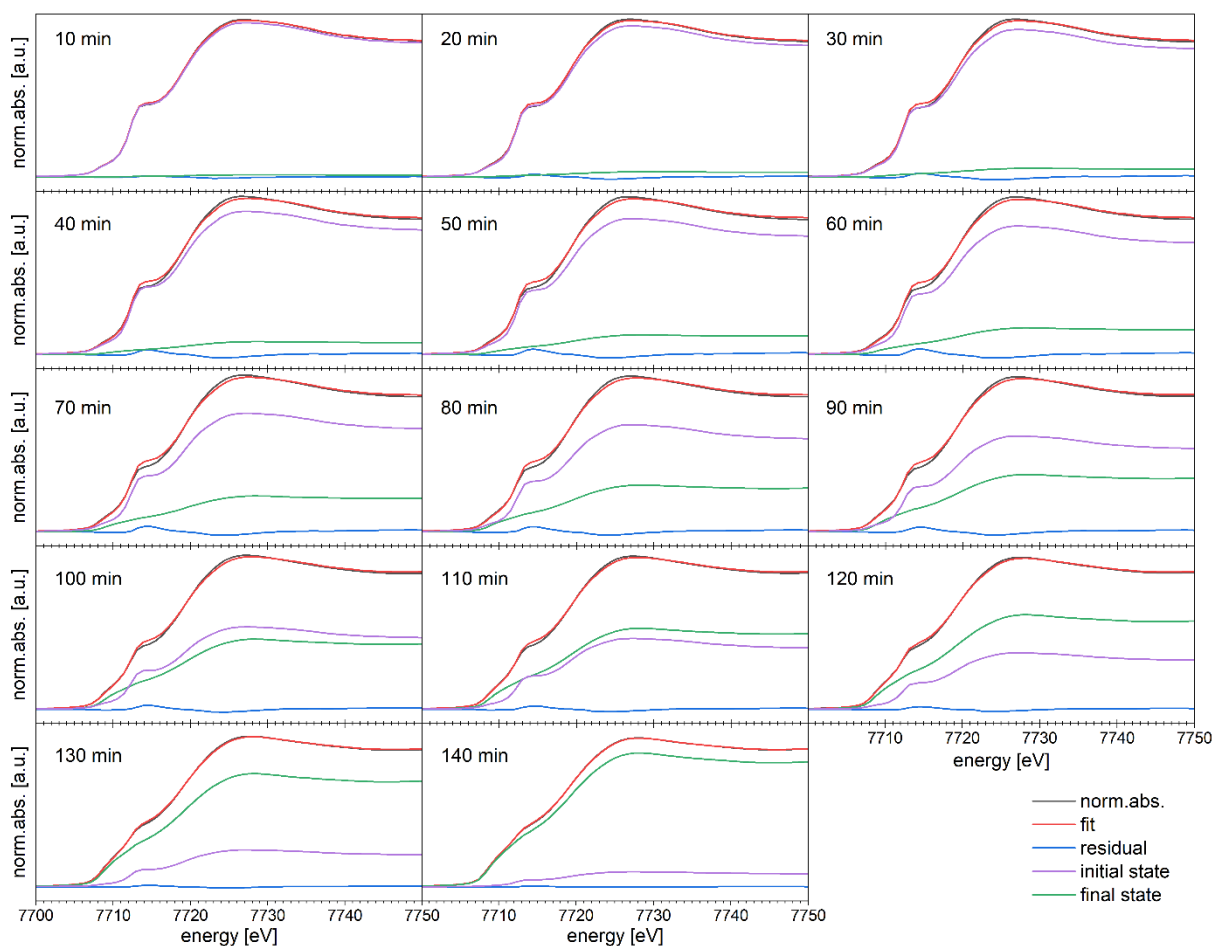


Figure S13: LC-XANES fits of selected XANES spectra recorded during the reaction with the reactants ratio: $n(\text{Co}(\text{hmds})_2:\text{B}_2\text{pin}_2:\text{toluene})=1:1:1$. As references for the fits, the first and the last recorded XANES spectrum was used.

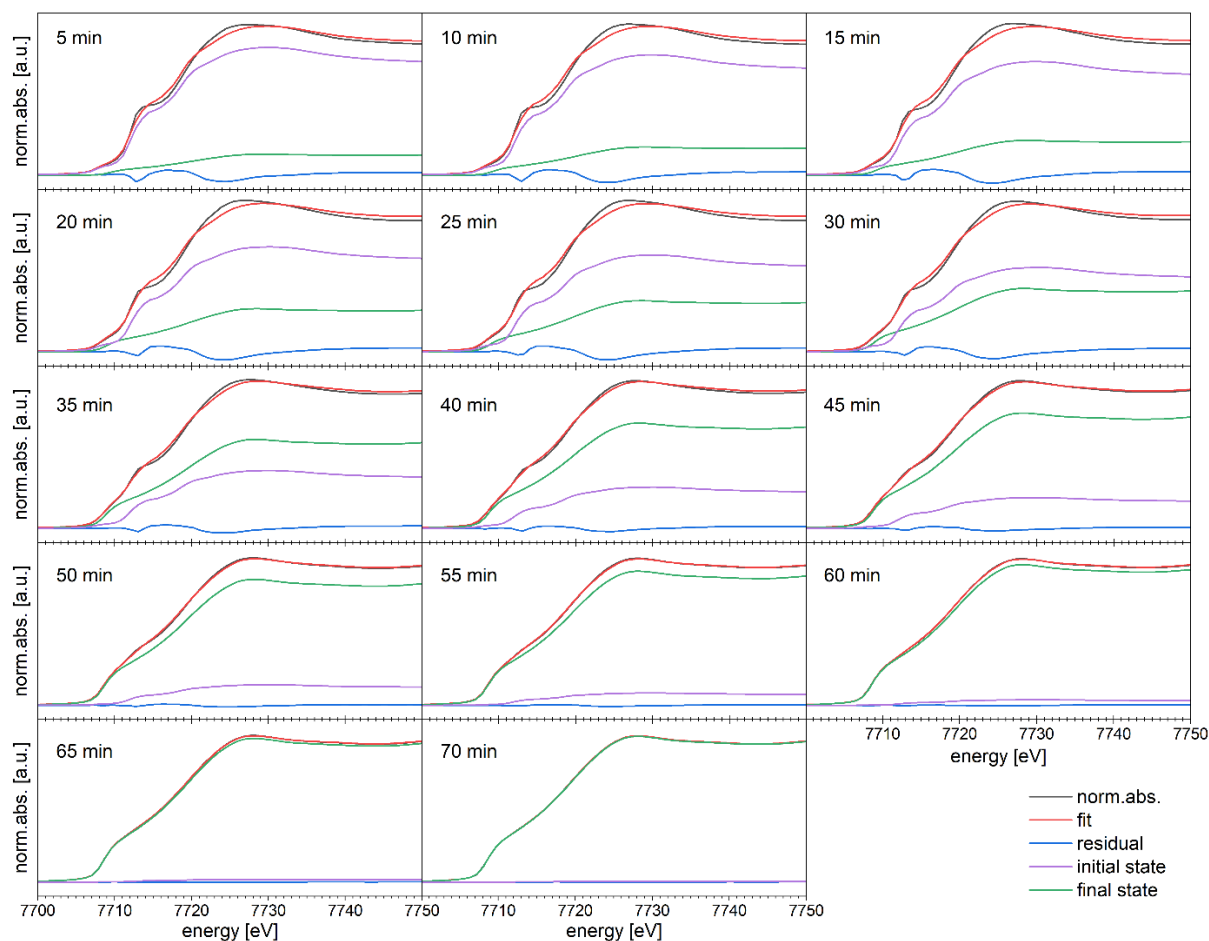
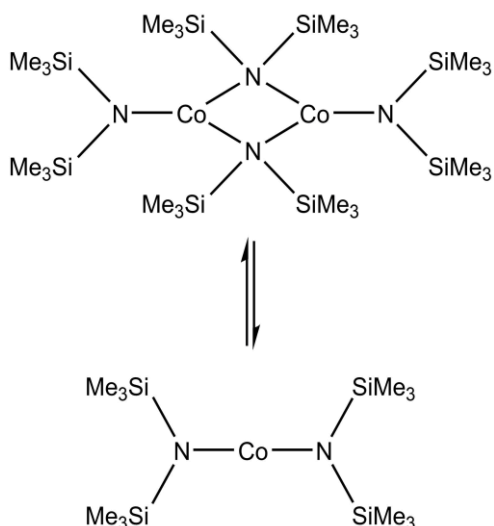


Figure S14: LC-XANES fits of selected XANES spectra recorded during the reaction with the reactants ratio: $n(\text{Co}(\text{hmnds})_2:\text{B}_2\text{pin}_2:\text{toluene})=1:11:10$. As references for the fits, the first and the last recorded XANES spectrum was used.

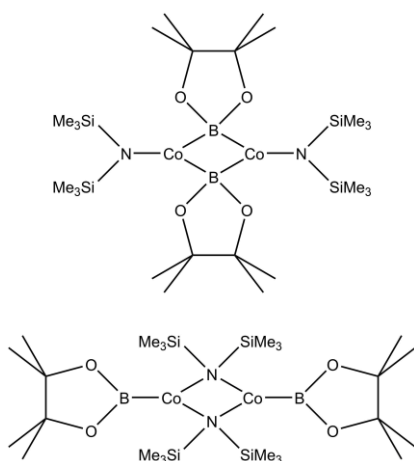
The initial and final species spectral contributions show a behaviour, and accordingly an abrupt formation of the final state can be excluded. Furthermore, the formation of the final state was significantly faster for $n(\text{Co}(\text{hmnds})_2:\text{B}_2\text{pin}_2:\text{toluene})=1:11:10$ than for the ratio 1:1:1 (75 min vs. 150 min). Still the final states of both reactions are identical (see figure S11).

As a starting point for EXAFS analysis, the catalyst precursor $\text{Co}(\text{hmnds})_2$ was measured, the resulting fitting parameters are displayed in table S2 and the Fourier transformed spectra are shown in figure S15. Since the formation of a dimer is known from crystal structure for this complex,^[1b] it is noteworthy, that only 0.3 Co backscatterers are found at a distance of 2.61 Å, which indicates an equilibrium between roughly 30% dimeric and 70% monomeric complex (see scheme S1) in hexane solution. In addition, two coordinating hmnds ligands could be fitted, including two nitrogen atoms at 1.84 Å, four silicon atoms at 3.02 Å and 3.45 Å and a fraction of the carbon atoms of the methyl groups at 3.90 Å.



Scheme S1: Structure suggestion of $\text{Co}(\text{hmds})_2$ in hexane obtained by EXAFS analysis – an equilibrium of monomer and dimer.

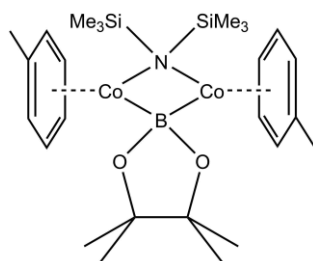
After addition of B_2pin_2 , the fine structure of the EXAFS spectrum changes significantly, as visible in figure S16, and the best fitting model including reasonable atomic distances^[2a] is displayed in table S1. Although a discrimination between nitrogen and boron in the first coordination shell is not possible, the observed changes in the XANES spectrum (figure S12) indicate a ligand exchange. The spectrum allowed the fit of a dimeric species (see scheme S2), whereby it was essential to fit an additional carbon shell at 2.40 Å to obtain a reasonable fit quality. Since no light atoms are available from the present reactants, the most obvious explanation could be a weak interaction with the solvent hexane.



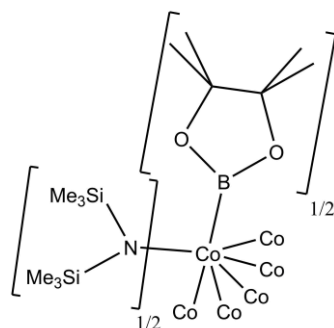
Scheme S2: Two possible structure suggestions of $\text{Co}(\text{hmds})_2 + \text{B}_2\text{pin}_2$ in hexane obtained by EXAFS analysis.

The presence of toluene as the second reactant triggers the start of the reaction and the formation of the catalytically active species. EXAFS analysis of the beginning of the reaction shows a dimeric species, which was formed after addition of B_2pin_2 and additional carbon backscatterer at a distance of 2.102 Å.

These carbon atoms can be assigned to the coordination of toluene to the Co centre,^[3] as proposed in scheme S3. However, the number of carbon backscatterers is smaller than expected, which could be related either to a η^3 -coordination of the toluene or to the dynamics of this coordination.



Scheme S3: Structure suggestion for the active catalyst at the beginning of the reaction obtained by EXAFS analysis.



Scheme S4: Structure suggestion for the final state of the catalyst obtained by EXAFS analysis.

After the reaction, the final state of the catalyst looks significantly different compared to the initial compound (see figure S16). The number of Co backscatterer at 2.412 Å increased significantly to 5 and even a second shell at a distance of 3.325 Å becomes visible. In contrast, the number of lighter backscatterers decreased. Combined with the XANES shape (figure S12) being very similar to that of bulk Co, the formation of small clusters or particles is concluded. The net structure is summarized in scheme S4. Assuming a spherical cluster size and using the first coordination number of Co, this allows the estimation of a cluster containing 12 Co atoms.^[4] This also explains the Co-Co distance of 2.412 Å, which is shorter than the Co-Co distance in the metal (2.506 Å), since for small clusters this distance is reduced due to the high ratio of surface atoms to bulk atoms.^[5] Since light backscatterer are still visible – on average half a hmds molecule and half a Bpin molecule are coordinating to a Co centre – also the presence of a mixture of cobalt nanoparticles and molecular complexes cannot be excluded based on the EXAFS results.

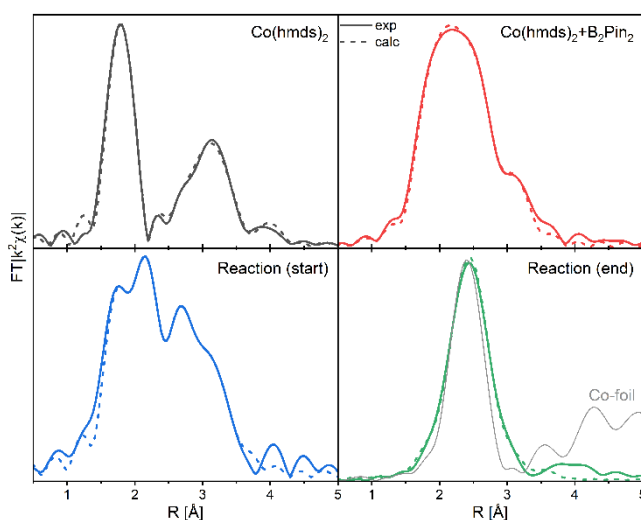


Figure S15: Fourier transformed EXAFS spectra of the investigated samples (solid line: experiment, dashed line: fit).

Table S2: Absorption edge energies (Co K-edge) and EXAFS analysis fitting parameters, results and fitting errors of the investigated samples

Sample	Abs-Bs ^[a]	N(Bs) ^[b]	R(Abs-Bs) [Å] ^[c]	σ [Å ⁻¹] ^[d]	R [%] ^[e]
<i>Edge-energy</i>					χ^2_{red} ^[f]
					E_f ^[g]
					Afac ^[h]
Co(hmds) ₂	N	1.5(1)	1.843(18)	0.050(5)	16.06
7713.5 eV	Co	0.3(1)	2.609(26)	0.112(11)	3.31E-6
	Si	2.8(3)	3.022(30)	0.112(11)	1.240
	Si	1.0(1)	3.452(34)	0.077(7)	0.800
	C	3.6(4)	3.902(39)	0.112(11)	
Co(hmds) ₂ + B ₂ pin ₂	N/B	2.3(2)	1.959(19)	0.081(8)	12.27
7711.3 eV	C	2.3(2)	2.403(24)	0.032(3)	1.85E-6
	Co	1.0(1)	2.793(27)	0.077(7)	-8.251
	O	1.1(1)	2.911(29)	0.032(3)	0.800
	Si	1.6(2)	3.150(31)	0.089(8)	
Reaction (start)	N/B	1.8(1)	1.919(19)	0.055(5)	20.01
7711.8 eV	C	2.1(2)	2.102(21)	0.032(3)	6.64E-06
	C	1.0(1)	2.417(24)	0.032(3)	-4.997
	Co	1.0(1)	2.806(28)	0.087(8)	0.5547
	O	4.6(5)	3.078(30)	0.112(11)	
	Si	3.6(4)	3.129(31)	0.095(9)	
Reaction (End)	N/B	1.0(1)	1.934(19)	0.105(10)	14.20
7708.3 eV	Co	5.1(5)	2.412(24)	0.112(11)	2.05E-6
	O	0.4(1)	3.002(30)	0.112(11)	-1.215
	Si	0.4(1)	3.122(31)	0.110(11)	0.8
	Co	0.6(1)	3.325(33)	0.112(11)	

[a] Abs: X-ray absorbing atom, Bs: backscattering atom; [b] Number of backscattering atoms; [c] Distance of absorbing atom to backscattering atom; [d] Debye-Waller like factor; [e] Fit index; [f] Reduced χ^2 ; [g] Fermi energy, which accounts for the shift between theory and experiment; [h] Amplitude reducing factor.

In an argon-filled glovebox, a flame dried 4 mL reaction vial was charged with $\text{Co}(\text{hmds})_2$ (0.1 mmol), B_2pin_2 (0.1 mmol, 25.4 mg), 19 μl (0.1 mmol) *p*-tolyltrimethylsilane and 2 ml (~15 mmol) hexane. The reaction was stirred overnight. D_2O was added and stirred for 30 min. The hexane solution was dried over anhydrous Na_2SO_4 . The solution was filtered through a 0.2 μm PTFE syringe filter. A reference sealed capillary was inserted in the NMR tube. The resultant solution was analysed by deuterium NMR. The NMR resonances indicated D-incorporation in benzylic position (2.15 ppm) of *p*-tolyltrimethylsilane along in the hexane (1.17 and 0.87 ppm) molecule.

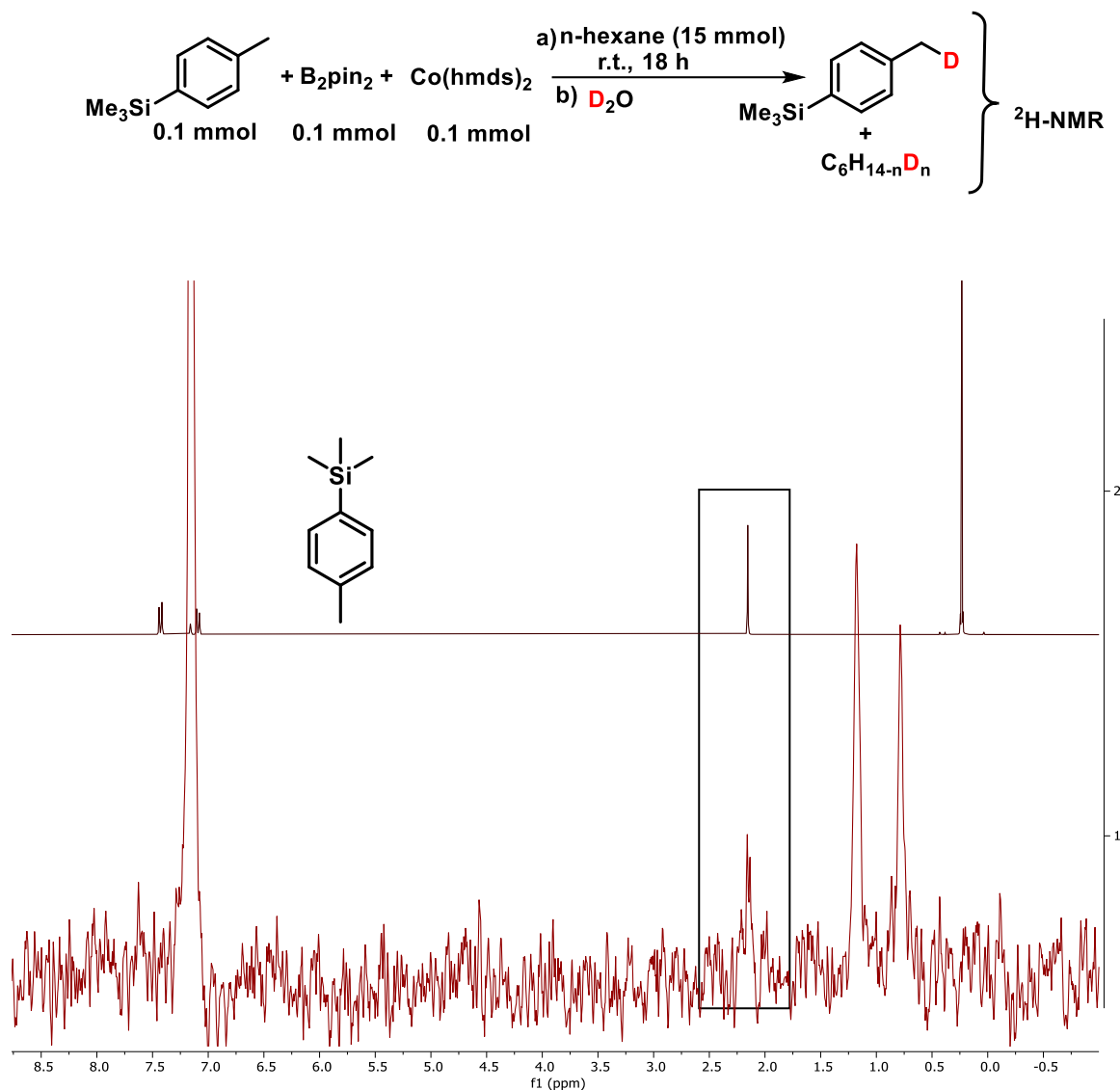


Figure S16. Top: ^1H -NMR of *p*-tolyltrimethylsilane in d_6 -benzene; **bottom:** ^2H -NMR of the D_2O quenched reaction of $\text{Co}(\text{hmds})_2 + \text{B}_2\text{pin}_2 + p$ -tolyltrimethylsilane (1:1:1) in hexane (d_6 -benzene in hexane used as internal standard)

Chemoselectivity of borylation at benzyl, aryl, alkyl positions. Competition with H/D exchange

In an argon-filled glovebox, a flame-dried 4 mL reaction vial was charged with $\text{Co}(\text{hmds})_2$ (0.05 mmol), HBpin (1 mmol, 145 μl), 106 μl d_8 -toluene, and 3 ml hexane. The reaction was stirred for 1 h at room temperature. 0.8 ml Reaction mixture was filtered through a 0.2 μm PTFE syringe filter into the nmr tube and submitted for ^{11}B -NMR. An identical reaction was performed using d_6 -benzene (90 μl) instead of d_8 -toluene. The crude ratio of DBpin and HBPin in the reaction mixture was determined from ^{11}B -NMR spectra.

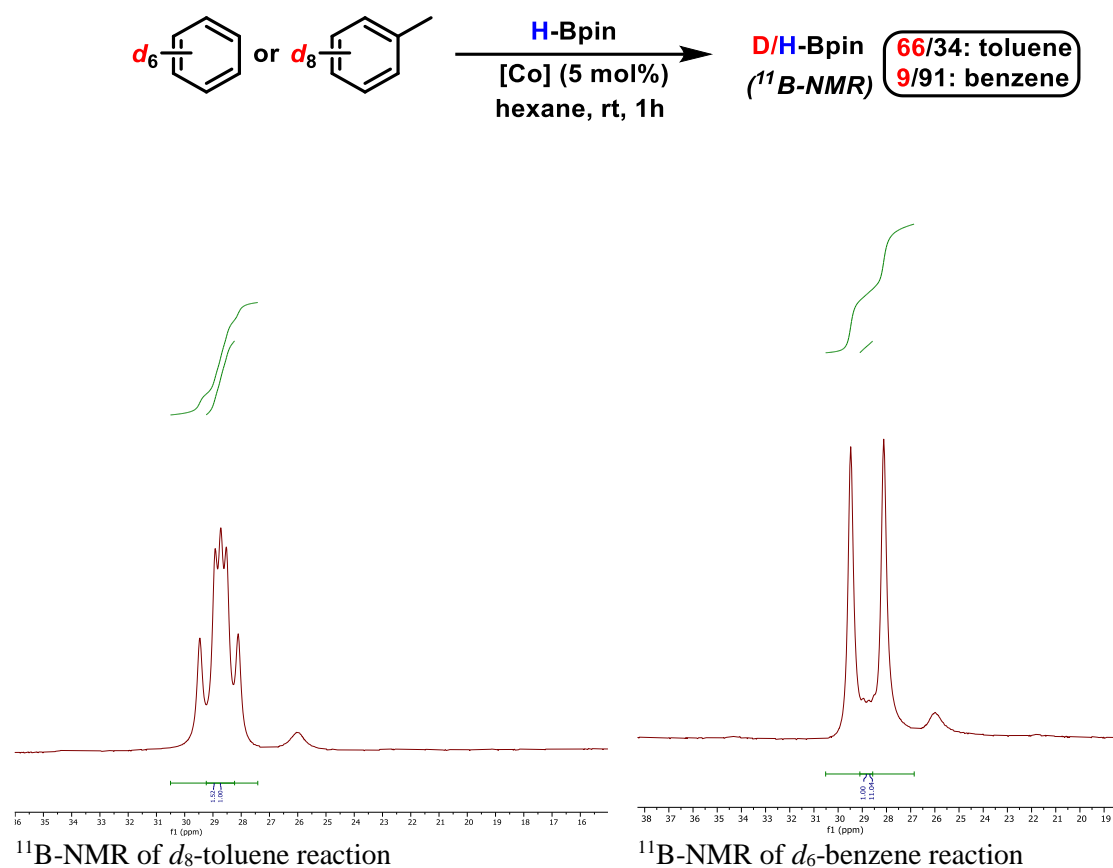


Figure S17. ^{11}B -NMR spectra for the H/D exchange reaction between d_8 -toluene/ d_6 -benzene with HBpin.

Comparison of reactivity between B₂pin₂ and HBpin

Reaction set up 1: In a glovebox desired amount of Co(hmnds)₂ (19 mg) was taken a Schleck flask (10 ml). 0.5 mmol *p*-Xylene (62 μl), 50 μl pentadecane, and 127 mg (0.5 mmol) B₂pin₂ were added to the Schlenk flask. To this solution, 3 ml hexane was added and the reaction mixture was heated at 60 °C temperature. A certain amount of aliquot was taken at regular time intervals. The aliquot was worked up with aq. NaHCO₃/EtOAc. The ethyl acetate part was dried over anhydrous Na₂SO₄ followed by conversion of *p*-xylene was monitored by GC-FID.

Reaction set up 2: In a glovebox desired amount of Co(hmnds)₂ (19 mg) was taken a Schleck flask (10 ml). 0.5 mmol *p*-Xylene (62 μl), 50 μl pentadecane, and 145 μl (1.0 mmol) HBpin were added to the Schlenk flask. To this solution, 3 ml hexane was added, and the reaction mixture was heated at 60 °C temperature. A certain amount of aliquot was taken at regular time intervals. The aliquot was worked up with aq. NaHCO₃/EtOAc. The ethyl acetate part was dried over anhydrous Na₂SO₄ followed by conversion of *p*-xylene was monitored by GC-FID.

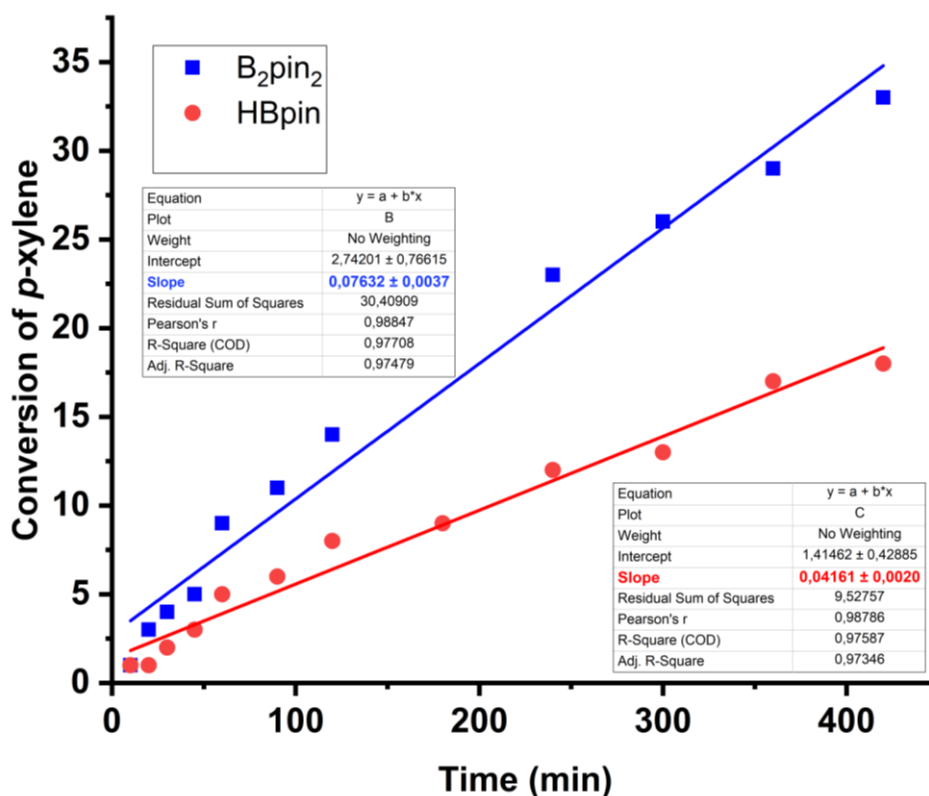


Figure S18: Plot of conversion of *p*-xylene in presence of B₂pin₂ (blue) and HBpin (red)

Experimental Details of XAS studies.

XAS experiments were carried out at the PETRA III beamline P65 at Deutsches Elektronensynchrotron (DESY) in Hamburg, Germany. The measurements at the cobalt K-edge (7709 eV) were performed using a Si(111) double-crystal monochromator and a maximum synchrotron beam current of 100 mA. Spectra were recorded in fluorescence mode with a PIPS (passivated implanted planar silicon) detector in solution using a special designed liquid cell enabling inert atmosphere and stirring during the measurement. For energy calibration, a cobalt foil was used, which was measured in advance and after the sample measurements.

XAS sample preparation

The preparation of the sample was carried out under inert atmosphere in a glove box directly in the liquid cell in 2 ml hexane. For the measurements of {Co(hm₂)₂} and {Co(hm₂)₂ + B₂pin₂}, 0.1 mmol Co(hm₂)₂ and 0.1 mmol B₂pin₂ were used. The reaction with toluene was investigated using two different reaction mixtures: 0.1 mmol Co(hm₂)₂ + 0.1 mmol B₂pin₂ + 0.1 mmol toluene (1:1:1 eq) and 0.05 mmol Co(hm₂)₂ + 0.55 mmol B₂pin₂ + 0.5 mmol toluene (1:11:10 eq).

Data analysis

In the first step of data analysis the background of the spectrum was removed by subtracting a Victoreen-type polynomial [6]. Due to the very differing shapes of the absorption edges of the samples and the used references, the first inflection point of the first derivative of the corresponding spectrum was defined as energy E₀. Afterwards a piecewise polynomial was used to determine the smooth part of the spectrum and was adjusted in a way that the low-R components of the resulting Fourier transform were minimal. The background subtracted spectrum was divided by its smoothed part and the photon energy was converted to photoelectron wave number *k*. For evaluation of the EXAFS spectra the resulting functions were weighted with *k*³ and calculated with EXCURVE98, which works based on the EXAFS function and according to a formulation in terms of radial distribution functions^[7,8]:

$$\chi(k) = \sum_j S_0^2(k) F_j(k) \int P_j(r_j) \frac{e^{-\frac{2r_j}{\lambda}}}{kr_j^2} \sin[2kr_j + \delta_j(k)] dr_j$$

The number of independent points *N*_{ind} was calculated according to information theory to determine the degree of overdeterminacy^[7]:

$$N_{ind} = \frac{2\Delta k \Delta R}{\pi}$$

Here, Δk describes the range in *k*-space used for data analysis and ΔR corresponds to the distance range in the Fourier filtering process. For the analysis a Δk -range of 10 and a ΔR -range of 4 was used, which yielded a number of independent points of 25. The quality of a fit was determined using two methods. The reduced χ_{red}^2 considers the degree of overdeterminacy of the system and the number of fitted parameters *p*. It therefore allows a direct comparison of different models^[9]:

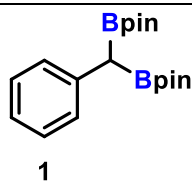
$$\chi_{red}^2 = \frac{(N_{ind}/N)}{N_{ind} - p} \sum_i \left(\frac{k_i^n}{\sum_j k_j^n |\chi_j^{exp}(k_j)|} \right)^2 (\chi^{exp}(k_i) - \chi^{theo}(k_i))^2$$

The R-factor, which represents the percental disagreement between experiment and adjusted function and takes into account both systematic and random errors according to the equation^[10]:

$$R = \sum_i \frac{k_i^n}{\sum_j k_j^n |\chi_j^{exp}(k_j)|} |\chi^{exp}(k_i) - \chi^{theo}(k_i)| \cdot 100\%$$

The accuracy of the determined distances is 1 %, of the Debye-Waller-like factor 10 %^[5] and of the coordination numbers depending of the distance 5-15 %. Initial values for coordination numbers and distances were adopted from Rietveld-analysis and afterwards iterated free in every fit as well as the Debye-Waller-like factor and the amplitude reducing factor.

Experimental details of catalytic reactions and spectral data of isolated complexes



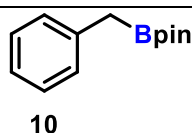
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 9.5 mg (0.025 mmol) of $\text{Co}(\text{HMDS})_2$, 53 μl (0.5 mmol) of toluene, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 18 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel, packed with pentane, gradient: 0→5→10% ethyl acetate in pentane. Yield: 148 mg (86%) as a white solid compound (mp: 78-80 °C).

^1H NMR (CDCl_3 , 400 MHz): 7.30-7.28 (m, 2H), 7.24 (t, 2H, $J = 7.6$ Hz), 7.10 (t, 1H, $J = 7.2$ Hz), 2.33 (s, 1H), 1.26 (s, 12H), 1.24 (s, 12H) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 139.61, 129.25, 128.03, 124.27, 83.46, 24.80, 24.71 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.7 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



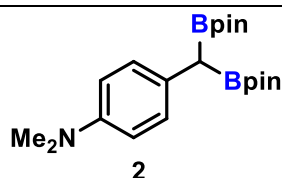
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 9.5 mg (0.025 mmol) of $\text{Co}(\text{HMDS})_2$, 53 μl (0.5 mmol) of toluene, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml n-hexane was added, and the resulting mixture was stirred at 80 °C for 18 hours outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0→5→10% ethyl acetate in pentane. Yield: 101 mg (92%) as colourless liquid.

^1H NMR (CDCl_3 , 400 MHz): 7.25-7.22 (m, 2H), 7.19-7.17 (m, 2H), 7.13-7.10 (m, 1H), 2.29 (s, 2H), 1.23 (s, 12H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ 138.76, 129.11, 128.37, 124.94, 83.54, 24.85 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



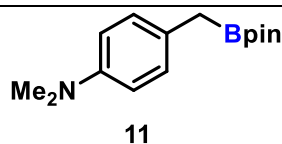
All the manipulation for this compound should be done anaerobic condition as it decomposed in air. Purification by flash chromatography is unsuccessful as the compound decomposed to (dimethylamino)benzaldehyde and protodeborylated product **11**. In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 72 μl (0.5 mmol) of 4-dimethylaminotoluene, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours at outside. During the reaction the compound was precipitated out from the solution. The reaction mixture was kept in freezer at -30 °C for overnight and put back to glove box. The solid compound was isolated by filtration and washed

with cold hexane (-30 °C). The compound is isolated as a white solid (mp: 138-140 °C). Yield: 105 mg (54%).

¹H NMR (CDCl₃, 400 MHz): 7.14 (d, 2H, *J* = 8.6 Hz), 6.69 (d, 2H, *J* = 8.4 Hz), 2.88 (s, 6H), 2.19 (s, 1H), 1.22 (s, 12H), 1.21 (s, 12H) ppm.
¹³C NMR (151 MHz, CDCl₃) δ 147.86, 129.76, 128.24, 113.77, 83.30, 41.29, 24.83, 24.77 ppm (benzylic carbon resonance was not observed).

¹¹B (CDCl₃, 128.38 MHz): 33.2 ppm

¹H and ¹³C NMR data agree with previously reported data.^[2]



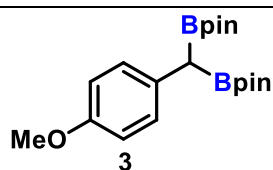
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 19 mg (0.05 mmol) of Co(HMDS)₂, 72 μl (0.5 mmol) of 4-dimethylaminotoluene, and 152 mg (0.6 mmol) of B₂pin₂. 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0→5→10→20% ethyl acetate in pentane with 1% trimethylamine). Yield: 108 mg (82%) as a colourless oil.

¹H NMR (CDCl₃, 400 MHz): 7.06 (d, 2H, *J* = 8.6 Hz), 6.67 (d, 2H, *J* = 8.4 Hz), 2.88 (s, 6H), 2.18 (s, 2H), 1.23 (s, 12H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 148.45, 129.51, 126.67, 113.34, 83.21, 41.04, 24.74 ppm (benzylic carbon resonance was not observed).

¹¹B (CDCl₃, 128.38 MHz): 33.2 ppm

¹H and ¹³C NMR data agree with previously reported data.^[2]



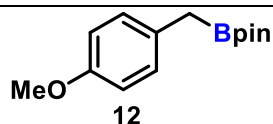
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of Co(HMDS)₂, 63 μl (0.5 mmol) of 4-methylanisole, and 152 mg (0.6 mmol) of B₂pin₂. 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel, packed with pentane, gradient: 0→5→10% ethyl acetate in pentane). Yield: 86 mg (46%) as white solid compound (mp: 85-87 °C).

¹H NMR (CDCl₃, 400 MHz): 7.18 (d, 2H, *J* = 8.3 Hz), 6.77 (d, 2H, *J* = 8.6 Hz), 3.76 (s, 3H), 2.23 (s, 1H), 1.22 (s, 12H), 1.21 (s, 12H) ppm

¹³C NMR (101 MHz, CDCl₃) δ 156.75, 131.48, 130.04, 113.61, 83.44, 55.27, 24.84, 24.76 ppm (benzylic carbon resonance was not observed).

¹¹B (CDCl₃, 128.38 MHz): 33.1 ppm

¹H and ¹³C NMR data agree with previously reported data.^[2]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 19 mg (0.05 mmol) of Co(HMDS)₂, 63 μl (0.5 mmol) of 4-methylanisole, and 152 mg (0.6 mmol) of B₂pin₂. 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0→2.5→5→10% ethyl acetate in pentane). Yield: 115 mg as colourless liquid. The ¹H and ¹³C NMR analysis indicates the formation of 27% complex **10** from arene C-O

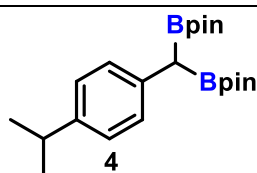
bond cleavage during catalysis. The overall yield of the desired compound is 63%.

^1H NMR (CDCl_3 , 400 MHz): 7.10 (d, 2H, $J = 8.5$ Hz), 6.79 (d, 2H, $J = 8.8$ Hz), 3.77 (s, 3H), 2.23 (s, 2H), 1.23 (s, 12H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ 157.25, 130.62, 129.95, 113.90, 83.49, 55.35, 24.88 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 33.1 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



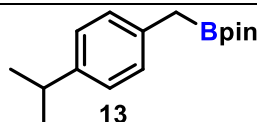
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 78 μl (0.5 mmol) of *p*-cymene and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel, packed with pentane, gradient: 0→2→5→10% ethyl acetate in pentane. Yield: 86 mg (44%) as white solid compound (mp: 80-82 °C)..

^1H NMR (CDCl_3 , 400 MHz): 7.17 (d, 2H, $J = 8$ Hz), 7.06 (d, 2H, $J = 8$ Hz), 2.84 (sep, 1H, $J = 6.8$ Hz), 2.28 (s, 1H), 1.23 (s, 12H), 1.22 (s, 12H), 1.22 (obscured d, 6H) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 144.50, 136.66, 129.21, 126.28, 83.52, 33.74, 24.93, 24.89, 24.29 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



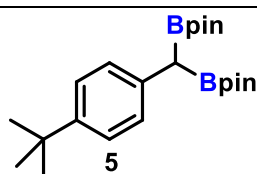
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 78 μl (0.5 mmol) of *p*-cymene, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 72 hours at preheated oil bath. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0→5→10% ethyl acetate in pentane. Yield: 93 mg (72%) as a colourless oil.

^1H NMR (CDCl_3 , 400 MHz): 7.12-7.06 (m, 4H), 2.84 (sept, 1H, $J = 6.8$ Hz), 2.25 (s, 2H), 1.23 (s, 12H), 1.21 (obscured d, 6H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 145.31, 135.85, 129.05, 126.45, 83.48, 33.75, 24.89, 24.22 ppm (benzylic carbon attached to boron was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.9 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 86 μl (0.5 mmol) of 4-tert-butyltoluene, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 120 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0→5→10% ethyl acetate in pentane. ^1H analysis indicated that *ca.*

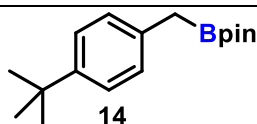
9% protodeborylated compound present with the desired diborylated compound. Yield: 59 mg (30%) as white solid.

^1H NMR (CDCl_3 , 400 MHz): 7.23-7.16 (m, 4H), 2.28 (s, 1H), 1.29 (s, 9H), 1.23 (s, 12H), 1.22 (s, 12H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 146.66, 136.20, 128.88, 125.04, 83.41, 34.32, 31.61, 24.85, 24.82 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.9 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



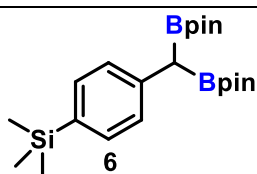
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 86 μl (0.5 mmol) of 4-tert-butyltoluene and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 120 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0→5→10% ethyl acetate in pentane). Yield: 85 mg (62%) as colourless oil.

^1H NMR (CDCl_3 , 400 MHz): 7.26 (d, 2H, J = 8.4 Hz), 7.12 (d, 2H, J = 8.4 Hz), 2.27 (s, 2H), 1.30 (s, 9H), 1.20 (s, 12H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 147.58, 135.48, 128.81, 125.31, 83.49, 34.38, 31.57, 24.90 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 33.1 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



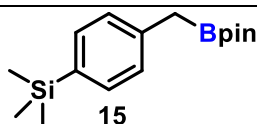
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 95 μl (0.5 mmol) of p-tolyltrimethylsilane, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 120 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0→2→5 ethyl acetate in pentane). Yield: 121 mg (58%) as white solid compound (mp: 123-127 °C).

^1H NMR (CDCl_3 , 400 MHz): 7.36 (d, 2H, J = 8.1 Hz), 7.24 (d, 2H, J = 8.2 Hz), 2.30 (s, 1H), 1.23 (s, 12H), 1.22 (s, 12H), 0.23 (s, 9H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ 140.31, 134.99, 133.26, 128.74, 83.49, 24.82, 24.79, -0.82 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.9 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



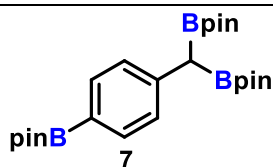
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 95 μl (0.5 mmol) of p-tolyltrimethylsilane, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 120 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0→5→10% ethyl acetate in pentane). Yield: 105 mg (73%) as colourless oil compound.

^1H NMR (CDCl_3 , 400 MHz): 7.40 (d, 2H, $J = 7.7$ Hz), 7.18 (d, 2H, $J = 8.1$ Hz), 2.29 (s, 2H), 1.24 (s, 12H), 0.24 (s, 9H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ 139.45, 136.12, 133.52, 128.64, 83.56, 24.88, -0.89 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.9 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



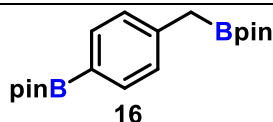
This compound prone to protodeborylation on silica gel. Isolation *via* column chromatography yielded compound **7** and **16**. In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 109 (0.5 mmol) of 4-tolylboronic acid pinacol ester, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml n-hexane was added, and the resulting mixture was stirred at 80 °C for 96 hours at outside. During the reaction white precipitate was observed. The reaction mixture was kept at -30 °C for overnight and solid compound was collected via filtration over frit. The solid compound was washed with chilled hexane. Yield: 148 mg (61%) as a white solid compound (mp: 204-206 °C).

^1H NMR (CDCl_3 , 400 MHz): 7.66 (d, 2H, $J = 7.8$ Hz), 7.26 (d, 2H, $J = 7.7$ Hz), 2.31 (s, 1H), 1.32 (s, 12H), 1.21 (s, 12H), 1.20 (s, 12H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 143.48, 134.64, 128.76, 83.52, 25.02, 24.83, 24.70 ppm (benzylic carbon and p-arene carbon attached to boron resonances were not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.9, 30.8 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



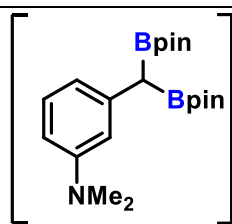
In a argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.05 mmol) of $\text{Co}(\text{HMDS})_2$, 109 mg (0.5 mmol) of 4-tolylboronic acid pinacol ester, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0→5→10→20% ethyl acetate in pentane). Yield: 154 mg (89%) as a white solid.

^1H NMR (CDCl_3 , 400 MHz): 7.68 (d, 2H, $J = 8$ Hz), 7.19 (d, 2H, $J = 8$ Hz), 2.30 (s, 2H), 1.33 (s, 12H), 1.21 (s, 12H) ppm.

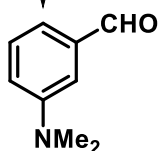
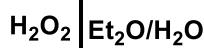
^{13}C NMR (101 MHz, CDCl_3) δ 142.47, 134.96, 128.57, 83.67, 83.58, 25.01, 24.84 ppm (benzylic carbon and p-arene carbon attached to boron resonances were not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8, 30.8 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



8

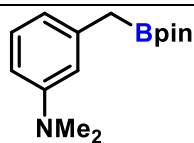


This compound is unstable under aerobic condition and purification *via* column chromatography was unsuccessful. The yield of the compound is determined after oxidation with H₂O₂. In a argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of Co(HMDS)₂, 72 μl (0.5 mmol) of 3-dimethylaminotoluene, and 152 mg (0.6 mmol) of B₂pin₂. 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 120 hours at outside. The oxidation of the intermediate diborylated compound to the corresponding aldehyde was performed following a literature procedure.^{2a} The reaction mixture was diluted with Et₂O and H₂O. Subsequently 1.70 g H₂O₂ (30% by wt. in water, 15 mmol) was added. Strong effervesce of gas was noted. The mixture was stirred for 2 h. The mixture was diluted with Et₂O and H₂O followed by extracted with Et₂O (3 times with 30 ml). The combine Et₂O part dried over anhydrous Na₂SO₄ followed concentrated in vacuum. The brown oil was purified by flash chromatography: silica gel packed with pentane, gradient pentane to dichloromethane to 1% trimethylamine in dichloromethane. Yield: 37 mg (49%) as yellow oil.

¹H NMR (CDCl₃, 400 MHz): 9.96 (s, 1H), 7.40 (t, 1H, *J* = 7.8 Hz), 7.24-7.22 (m, 2H), 7.06-7.03 (m, 1H), 3.02 (s, 6H) ppm.

¹³C NMR (75 MHz, CDCl₃) δ 193.21, 150.55, 137.42, 129.85, 119.74, 118.94, 112.14, 40.90 ppm (benzylic carbon resonance was not observed).

¹H and ¹³C NMR data agree with previously reported data.^[2]



17

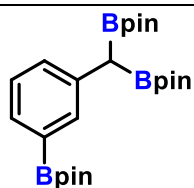
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 19 mg (0.05 mmol) of Co(HMDS)₂, 72 μl (0.5 mmol) of 3-dimethylaminotoluene, and 152 mg (0.6 mmol) of B₂pin₂. 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 120 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0→10→20→40% ethyl acetate in pentane with 1% triethylamine. Yield: 88 mg (67%) as colourless oil.

¹H NMR (CDCl₃, 400 MHz): 7.11 (t, 1H, *J* = 7.8 Hz), 6.59-6.52 (m, 3H), 2.92 (s, 6H), 2.26 (s, 2H), 1.24 (s, 12H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 150.85, 139.42, 128.98, 117.88, 113.69, 109.68, 83.42, 40.82, 24.85 ppm (benzylic carbon resonance not observed).

¹¹B (CDCl₃, 128.38 MHz): 33.01 ppm

¹H and ¹³C NMR data agree with previously reported data.^[2]



9

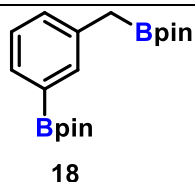
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of Co(HMDS)₂, 109 mg (0.5 mmol) of 3-tolylboronic acid pinacol ester, and 152 mg (0.6 mmol) of B₂pin₂. 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel, packed with pentane, gradient: 0→5→10→20% ethyl acetate in pentane. Yield: 191 mg (81%) as white solid compound.

^1H NMR (CDCl_3 , 400 MHz): 7.54-7.47 (m, 3H), 7.27-7.22 (m, 1H), 2.33 (s, 1H), 1.32 (s, 12H), 1.21 (s, 12H), 1.20 (s, 12H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 138.98, 135.63, 132.50, 130.85, 127.50, 83.64, 83.48, 25.02, 24.83, 24.74 ppm (benzylic carbon and m-arene carbon resonances were not observed).

^{11}B (CDCl_3 , 128.38 MHz): 30.7, 32.6 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



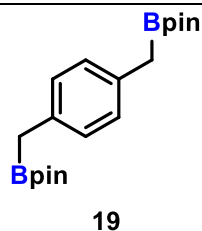
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 19 mg (0.05 mmol) of $\text{Co}(\text{HMDS})_2$, 109 mg (0.5 mmol) of 3-tolylboronic acid pinacol ester, and 152 mg (0.6 mmol) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours at outside. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0→5→10→20% ethyl acetate in pentane). Yield: 144 mg (84%) as white solid.

^1H NMR (CDCl_3 , 400 MHz): 7.61 (s, 1H), 7.57 (d, 1H, $J = 6.9$ Hz), 7.31-7.29 (m, 1H), 7.27-7.22 (m, 1H), 2.30 (s, 2H), 1.33 (s, 12H), 1.22 (s, 12H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 138.08, 135.59, 132.07, 131.45, 127.79, 83.75, 83.52, 25.02, 24.87 ppm (benzylic carbon and m-arene carbon attached to boron resonances were not observed).

^{11}B (CDCl_3 , 128.38 MHz): 30.9, 32.9 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



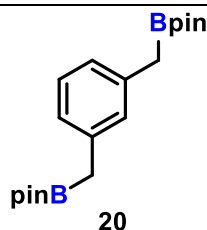
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 62 μl (0.5 mmol) of *p*-xylene and 267 mg (1.05 mmol, 2.1 equiv.) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 72 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel, packed with 5% trimethylamine in pentane, gradient: 0→5→10→20% ethyl acetate in pentane). Yield: 87 mg (48%) as white solid compound (mp: 130-132 °C).

^1H NMR (CDCl_3 , 400 MHz): 7.05 (s, 4H), 2.23 (s, 4H), 1.22 (s, 24H) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 134.87, 129.07, 83.45, 24.87 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.9 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



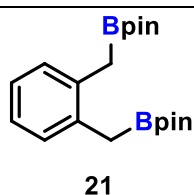
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 62 μl (0.5 mmol) of *m*-xylene and 267 mg (1.05 mmol, 2.1 equiv.) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel, packed with 5% trimethylamine in pentane, gradient: 0→5→10→20% ethyl acetate in pentane). Yield: 83 mg (46%) as semi-solid compound.

^1H NMR (CDCl_3 , 400 MHz): 7.10 (t, 1H, $J = 7.4$ Hz), 6.98 (s, 1H), 6.94 (d, 1H, $J = 7.5$ Hz), 2.24 (s, 4H), 1.22 (s, 24H) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 138.50, 129.96, 128.28, 125.68, 83.45, 24.87 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



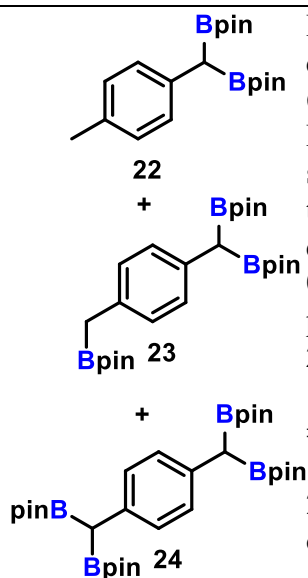
In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 60 μl (0.5 mmol) of *o*-xylene and 267 mg (1.05 mmol, 2.1 equiv.) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 120 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel, packed with 5% trimethylamine in pentane, gradient: 0→5→10→20% ethyl acetate in pentane). Yield: 51 mg (28%) as colourless oil.

^1H NMR (CDCl_3 , 400 MHz): 7.14-7.09 (m, 2H), 7.05-6.99 (m, 2H), 2.27 (s, 4H), 1.22 (s, 24H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 137.1, 129.8, 125.3, 83.4, 24.9 (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 62 μl (0.5 mmol) of *p*-xylene and 267 mg (1.05 mmol, 2.1 equiv.) of B_2pin_2 . 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 72 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0→5→10→20% ethyl acetate in pentane) to yield **22**, **23** and **24** products.

22—Isolated as white solid. Yield: 56 mg (31%)

^1H NMR (CDCl_3 , 400 MHz): 7.15 (d, 2H, $J = 7.8$ Hz), 7.02 (d, 2H, $J = 7.8$ Hz), 2.28 (s, 3H), 2.26 (s, 1H), 1.23 (s, 12H), 1.21 (s, 12H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 136.32, 133.41, 129.07, 128.81, 83.40, 24.80, 24.73, 21.09 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.7 ppm

23—Isolated as white solid (mp: 82-84 °C). Yield: 68 mg (28%)

^1H NMR (CDCl_3 , 400 MHz): 7.12 (d, 2H, $J = 7.8$ Hz), 7.02 (d, 2H, $J = 7.8$ Hz), 2.24 (s, 1H), 2.22 (s, 2H), 1.22 (s, 12H), 1.22 (s, 12H), 1.20 (s, 12H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 135.66, 133.97, 129.19, 128.86, 83.37, 24.85, 24.81, 24.74 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8 ppm

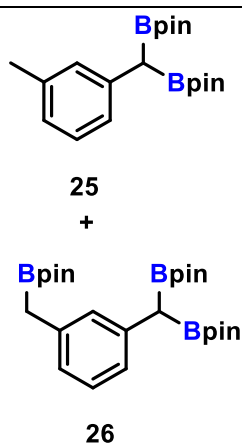
24—Isolated as white solid. Yield: 53 mg (18%)

^1H NMR (CDCl_3 , 400 MHz): 7.10 (s, 4H), 2.24 (s, 2H), 1.21 (s, 24H), 1.20 (s, 24H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 134.73, 129.01, 83.28, 24.77, 24.70 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.7 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 62 μl (0.5 mmol) of *m*-xylene and 267 mg (1.05 mmol, 2.1 equiv.) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0→5→10→20% ethyl acetate in pentane) to yield **25** and **26** products.

25—Isolated as white solid compound. Yield: 60 mg (33%)

^1H NMR (CDCl_3 , 400 MHz): 7.12-7.08 (m, 2H), 7.03 (s, 1H), 6.88-6.87 (m, 1H), 2.28 (s, 3H), 2.25 (s, 1H), 1.21 (s, 12H), 1.20 (s, 12H) ppm

^{11}B (CDCl_3 , 128.38 MHz): 32.7 ppm

^{13}C NMR (101 MHz, CDCl_3) δ 139.38, 137.36, 130.06, 127.89, 126.34, 125.12, 83.43, 24.81, 24.72, 21.61 ppm (benzylic carbon resonance was not observed).

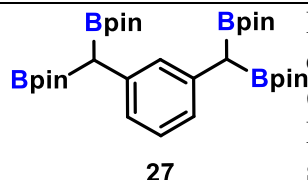
26—Isolated as semi-solid. Yield: 62 mg (26%)

^1H NMR (CDCl_3 , 400 MHz): 7.11-7.06 (m, 2H), 7.01 (s, 1H), 6.90 (d, 1H, $J = 6.5$ Hz) 2.25 (s, 1H), 2.23 (s, 2H), 1.22 (s, 12H), 1.22 (s, 12H), 1.20 (s, 12H) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 139.26, 137.96, 130.09, 128.00, 125.90, 125.11, 83.36, 83.34, 24.86, 24.82, 24.73 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.7 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 62 μl (0.5 mmol) of *m*-xylene and 267 mg (1.05 mmol, 2.1 equiv.) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, flashed with 100% dichloromethane followed by 0→5→10→20% ethyl acetate in pentane).

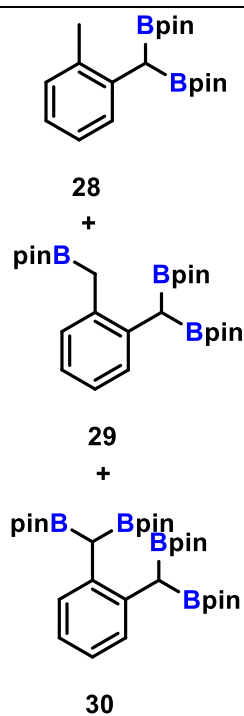
Di and tri -borylated products were not isolated. **27** Isolated as colourless oil. Yield: 48 mg (16%)

^1H NMR (CDCl_3 , 400 MHz): 7.10-6.99 (overlapping peaks, m, 4H), 2.24 (s, 2H), 1.21 (s, 24H), 1.20 (s, 24H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 138.71, 130.31, 127.82, 125.33, 83.28, 77.58, 77.16, 76.74, 24.83, 24.74 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 62 μl (0.5 mmol) of *o*-xylene and 267 mg (1.05 mmol, 2.1 equiv.) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 120 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0→5→10→20% ethyl acetate in pentane) to yield **28**, **29** and **30** products.

28 –Isolated as colourless oil. Yield: 58 mg (32%)

^1H NMR (CDCl_3 , 400 MHz): 7.45 (d, 2H, $J = 7.8$ Hz), 7.12-7.07 (m, 2H), 7.00 (t, 1H, $J = 7.2$ Hz), 2.40 (s, 1H), 2.22 (s, 3H), 1.24 (s, 12H), 1.23 (s, 12H) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 138.26, 135.82, 129.80, 129.27, 125.80, 124.48, 83.42, 24.87, 24.73, 20.74 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.7 ppm

29 –Isolated as colourless oil. Yield: 67 mg (27%)

^1H NMR (CDCl_3 , 400 MHz): 7.43 (dd, 1H, $J = 7.7, 1.4$ Hz), 7.09-7.02 (m, 2H), 6.97 (td, 1H, $J = 7.2, 1.5$ Hz) 2.45 (s, 1H), 2.22 (s, 2H), 1.22 (s, 24H), 1.20 (s, 12H) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 137.71, 136.49, 129.73, 129.45, 124.98, 124.36, 83.31, 83.27, 24.90, 24.86, 24.75 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8 ppm

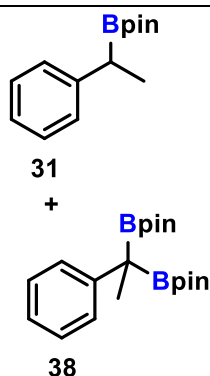
30 – Isolated as white solid compound. Yield: 17 mg (6%)

^1H NMR (CDCl_3 , 400 MHz): 7.43-7.41 (overlapping peaks, m, 2H), 7.00-6.98 (overlapping peaks, m, 2H) 2.40 (s, 2H), 1.21 (s, 24H), 1.20 (s, 24H) ppm

^{13}C NMR (101 MHz, CDCl_3) δ 137.18, 129.38, 124.12, 83.19, 24.83, 24.75 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 9.5 mg (0.025 mmol) of $\text{Co}(\text{HMDS})_2$, 61 μl (0.5 mmol) of ethylbenzene and 152 mg (0.6 mmol, 1.2 equiv.) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 20 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0→1→2→3→4→5% ethyl acetate in pentane) to yield mono and di-borylated products.

38 –Isolated as white solid (mp: 71-74 °C). Yield: 35 mg (20%)

^1H NMR (CDCl_3 , 300 MHz): 7.35-7.32 (m, 2H), 7.26-7.21 (m, 2H), 7.11-7.06 (m, 1H), 1.45 (s, 3H), 1.23 (s, 12H), 1.23 (s, 12H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 145.2, 128.3, 128.0, 124.5, 83.4, 24.8, 18.7 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.9 ppm

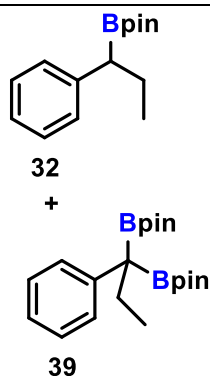
31 –Isolated as colourless oil. Yield: 45 mg (39%)

^1H NMR (CDCl_3 , 300 MHz): 7.29-7.20 (m, 4H), 7.16-7.11 (m, 1H), 2.43 (q, 1H, $J = 7.4$ Hz), 1.33 (d, 3H, $J = 7.8$ Hz), 1.21 (s, 6H), 1.20 (s, 6H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 145.1, 128.4, 127.9, 125.2, 83.4, 24.7, 17.2 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.9 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2,11]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.05 mmol) of $\text{Co}(\text{HMDS})_2$, 70 μl (0.5 mmol) of *n*-propylbenzene and 152 mg (0.6 mmol, 1.2 equiv.) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 $^\circ\text{C}$ for 48 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0 \rightarrow 2.5 \rightarrow 5 \rightarrow 10% ethyl acetate in pentane) to yield mono and diborylated products.

39 –Isolated as white solid (mp = 76-79 $^\circ\text{C}$). Yield: 26 mg (14%)

^1H NMR (CDCl_3 , 300 MHz): 7.37-7.34 (m, 2H), 7.22 (t, 2H, $J = 7.3$ Hz), 7.09 (t, 1H, $J = 7.2$ Hz), 1.97 (q, 2H, $J = 7.3$ Hz), 1.25 (s, 12H), 1.25 (s, 12H), 0.76 (t, 3H, $J = 7.2$ Hz) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 143.15, 130.26, 127.98, 124.77, 83.41, 27.32, 24.85, 24.80, 12.32 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.8 ppm

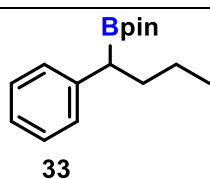
32 –Isolated as colourless oil. Yield: 75 mg (61%)

^1H NMR (CDCl_3 , 300 MHz): 7.25-7.18 (m, 4H), 7.14-7.09 (m, 1H), 2.21 (t, 1H, $J = 7.8$ Hz), 1.92-1.82 (m, 1H), 1.73-1.60 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H), 0.90 (t, 3H, $J = 7.2$ Hz) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 143.5, 128.5, 128.3, 125.2, 83.4, 25.9, 24.8, 24.7, 14.1 (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 32.9 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[2,11]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.05 mmol) of $\text{Co}(\text{HMDS})_2$, 78 μl (0.5 mmol) of *n*-butylbenzene and 152 mg (0.6 mmol, 1.2 equiv.) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 $^\circ\text{C}$ for 72 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with 5% triethylamine in pentane, gradient: 0 \rightarrow 5 \rightarrow 10 \rightarrow 15% ethyl acetate in pentane) to yield monoborylated product as colourless oil.

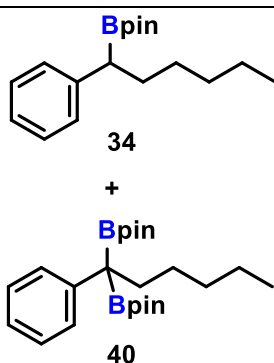
Isolated Yield: 93 mg (72%)

^1H NMR (CDCl_3 , 300 MHz): 7.25-7.17 (m, 4H), 7.13-7.07 (m, 1H), 2.30 (t, 1H, $J = 7.8$ Hz), 1.87-1.75 (m, 1H), 1.65-1.56 (m, 1H), 1.28-1.23 (m, 2H), 1.19 (s, 6H), 1.17 (s, 6H), 0.87 (t, 3H, $J = 7.2$ Hz) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 143.50, 128.41, 128.25, 125.10, 83.26, 34.87, 24.68, 24.64, 22.41, 14.18 (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 33.1 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[12]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.05 mmol) of $\text{Co}(\text{HMDS})_2$, 94 μl (0.5 mmol) of *n*-hexylbenzene and 152 mg (0.6 mmol, 1.2 equiv.) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 72 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0→2.5→5% ethyl acetate in pentane) to yield mono and di-borylated products.

40—isolated as colourless oil. Yield: 22 mg (11%)

^1H NMR (CDCl_3 , 300 MHz): 7.39-7.36 (m, 2H), 7.22 (t, 2H, $J = 7.4$ Hz), 7.08 (t, 1H, $J = 7.3$ Hz), 1.95-1.89 (m, 2H), 1.25 (s, 12H), 1.25 (s, 12H), 1.20-1.11 (m, 6H), 0.80 (t, 3H, $J = 6.7$ Hz) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 143.27, 129.92, 127.81, 124.53, 83.23, 33.96, 32.43, 27.52, 24.67, 22.52, 14.06 ppm (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 33.1 ppm

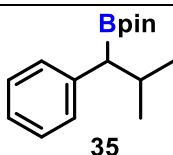
34—isolated as colourless oil. Yield: 68 mg (47%)

^1H NMR (CDCl_3 , 300 MHz): 7.27-7.19 (m, 4H), 7.14-7.09 (m, 1H), 2.29 (t, 1H, $J = 7.2$ Hz), 1.86-1.79 (m, 1H), 1.67-1.60 (m, 1H), 1.29-1.24 (m, 6H), 1.20 (s, 6H), 1.18 (s, 6H), 0.87-0.83 (m, 3H) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 143.65, 128.47, 128.34, 125.17, 83.34, 32.71, 31.98, 29.11, 24.78, 24.72, 22.69, 14.20 (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 33.2 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[13]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 19 mg (0.1 mmol) of $\text{Co}(\text{HMDS})_2$, 79 μl (0.5 mmol) of isopentylbenzene and 152 mg (0.6 mmol, 1.2 equiv.) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0→2.5→5% ethyl acetate in pentane) to yield mono borylated product. Traces of diborylated product was detected but not isolated.

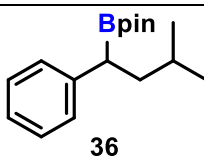
35—isolated as colourless oil. Yield: 84 mg (65%)

^1H NMR (CDCl_3 , 300 MHz): 7.30-7.23 (m, 4H), 7.19-7.14 (m, 1H), 2.22-2.10 (m, 1H), 2.01 (d, 1H, $J = 10$ Hz), 1.24 (s, 6H), 1.22 (s, 6H), 1.07 (d, 3H, $J = 6.5$ Hz), 0.77 (t, 3H, $J = 6.5$ Hz) ppm

^{13}C NMR (75 MHz, CDCl_3) δ 142.41, 129.24, 128.21, 125.27, 83.29, 31.11, 24.76, 24.71, 23.27, 22.11 (benzylic carbon resonance was not observed).

^{11}B (CDCl_3 , 128.38 MHz): 33.1 ppm

^1H and ^{13}C NMR data agree with previously reported data.^[11]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 19 mg (0.05 mmol) of $\text{Co}(\text{HMDS})_2$, 87 μl (0.5 mmol) of isopentylbenzene and 152 mg (0.6 mmol, 1.2 equiv.) of B_2pin_2 . 1 ml *n*-hexane was added and the resulting mixture was stirred at 80 °C for 48 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient:

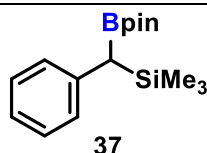
0→2.5→5% ethyl acetate in pentane) to yield mono borylated product. Traces of diborylated product was detected but not isolated. Mono –Isolated as colourless oil. Yield: 86 mg (63%)

¹H NMR (CDCl₃, 300 MHz): 7.31-7.23 (m, 4H), 7.18-7.13 (m, 1H), 2.46 (t, 1H, *J* = 7.8 Hz), 1.78-1.59 (m, 2H), 1.55-1.47 (m, 1H), 1.23 (s, 6H), 1.21 (s, 6H), 0.92 (t, 6H, *J* = 6.2 Hz) ppm

¹³C NMR (75 MHz, CDCl₃) δ 143.59, 128.47, 128.34, 125.15, 83.33, 41.60, 27.01, 24.71, 23.13, 22.31 (benzylic carbon resonance was not observed).

¹¹B (CDCl₃, 128.38 MHz): 33 ppm

¹H and ¹³C NMR data agree with previously reported data.^[11]



In an argon-filled glovebox, a thick-walled glass vessel (20 ml) was charged with a magnetic stir bar, 38 mg (0.1 mmol) of Co(HMDS)₂, 91 μl (0.5 mmol) of benzyltrimethylsilane and 152 mg (0.6 mmol, 1.2 equiv.) of B₂pin₂. 1 ml n-hexane was added and the resulting mixture was stirred at 80 °C for 96 hours. The reaction mixture was exposed to air to decompose the catalyst and subsequently purified by flash column chromatography (silica gel packed with pentane, gradient: 0→2.5→5% ethyl acetate in pentane) to yield mono borylated product. Traces of diborylated product was detected but not isolated.

37 –Isolated as colourless oil. Yield: 97 mg (67%)

¹H NMR (CDCl₃, 300 MHz): 7.18-7.10 (m, 4H), 7.02-6.96 (m, 1H), 1.92 (s, 1H), 1.21 (s, 6H), 1.19 (s, 6H), -0.04 (s, 9H) ppm

¹³C NMR (75 MHz, CDCl₃) δ 140.96, 128.77, 127.94, 123.53, 83.19, 25.28, 25.07, -1.35 (benzylic carbon resonance was not observed).

¹¹B (CDCl₃, 128.38 MHz): 33.1 ppm

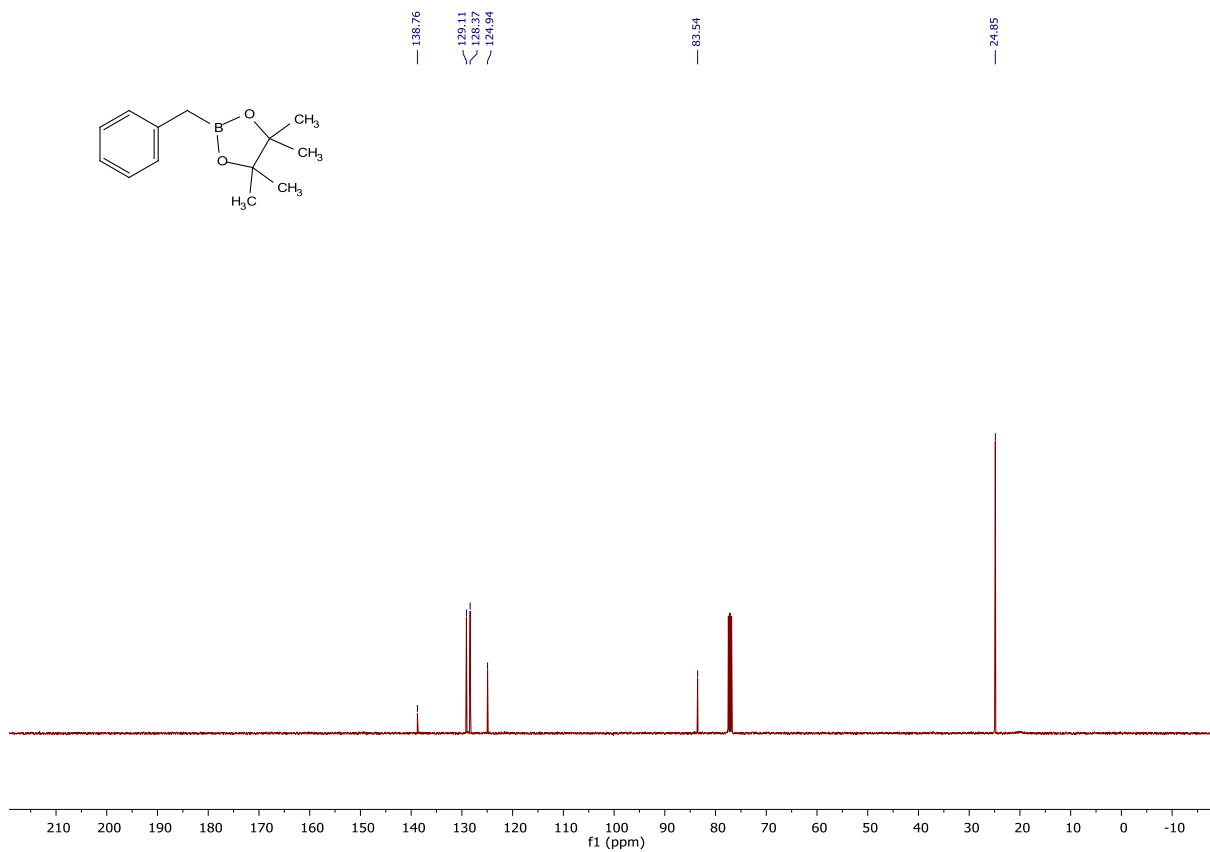
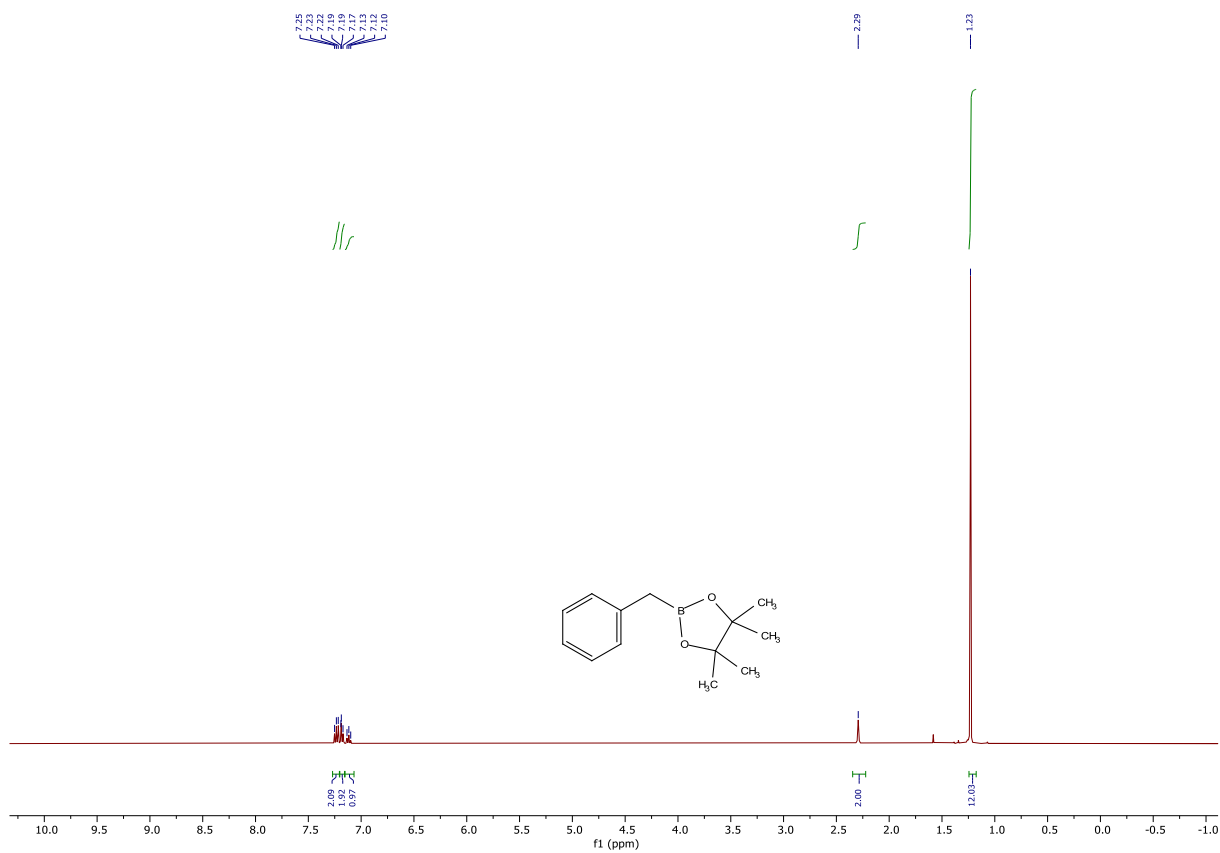
¹H and ¹³C NMR data agree with previously reported data.^[14]

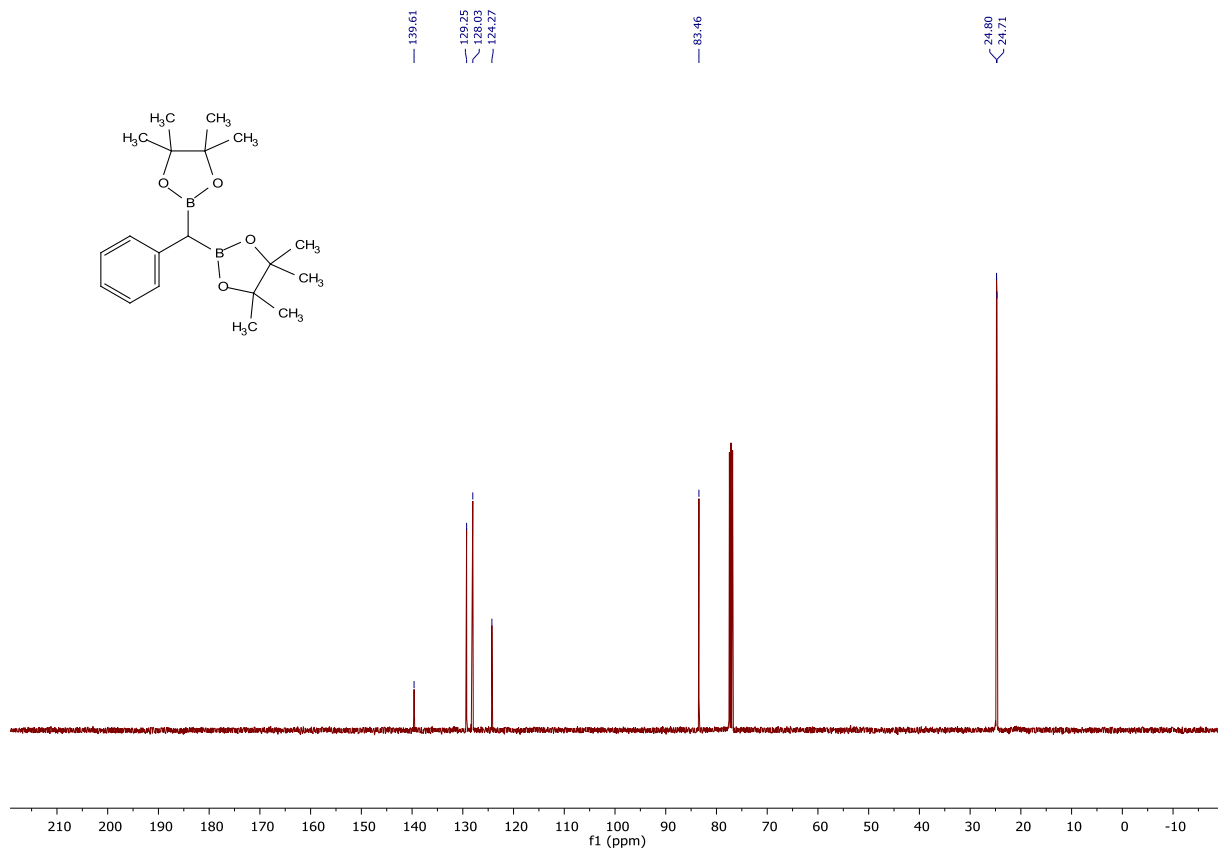
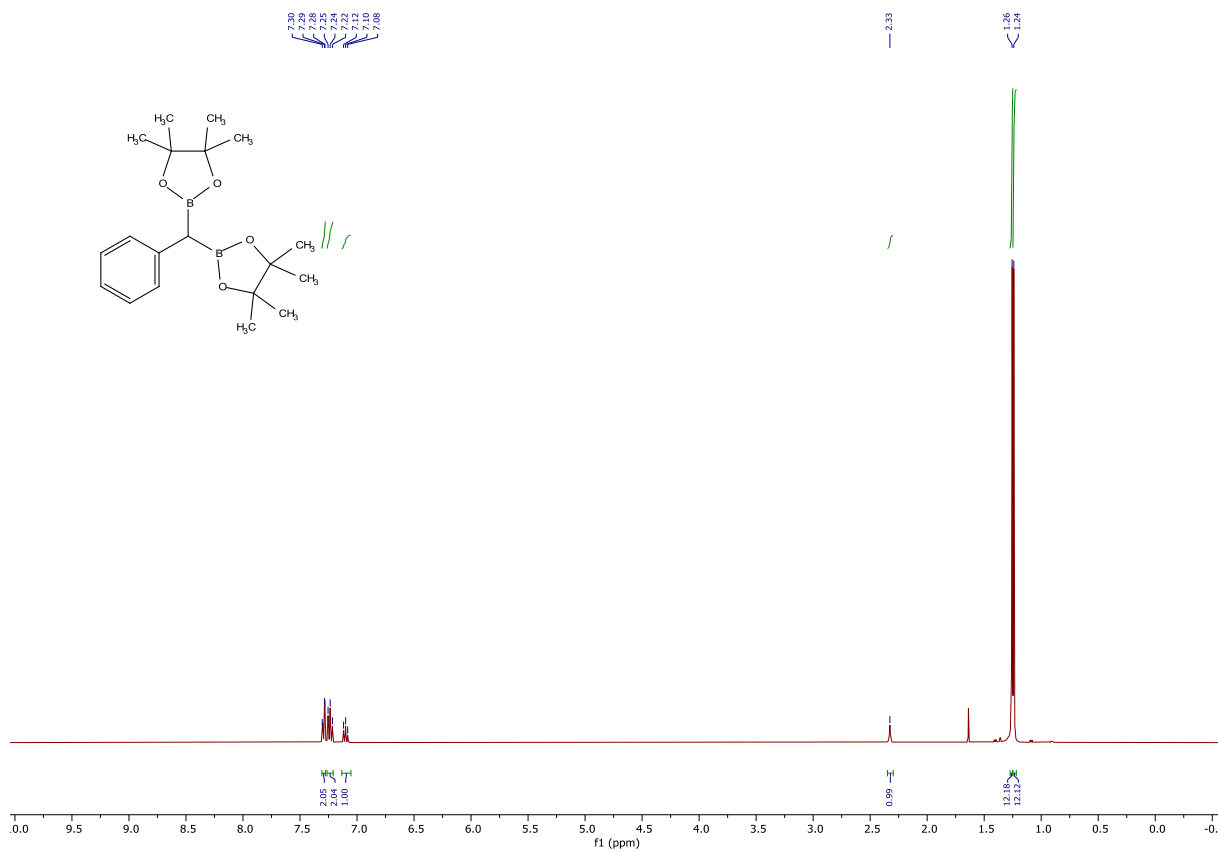
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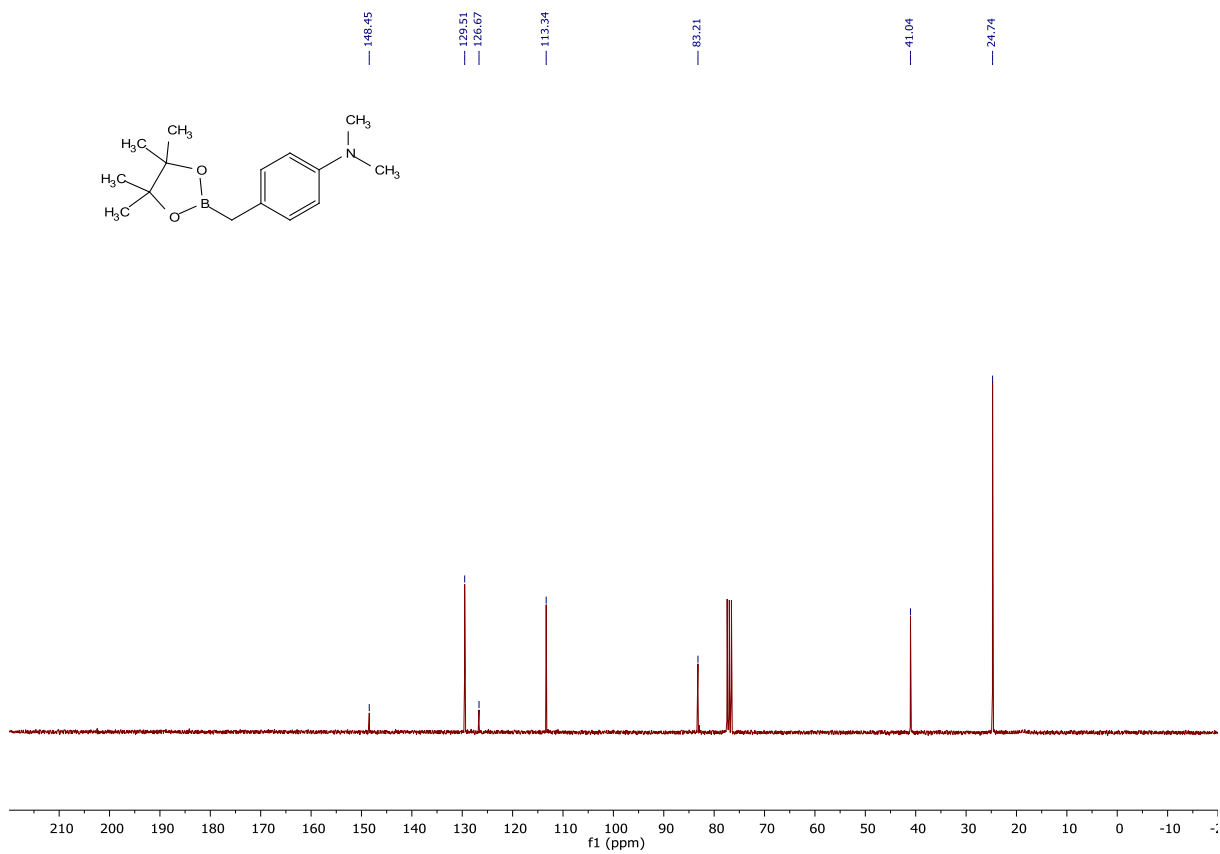
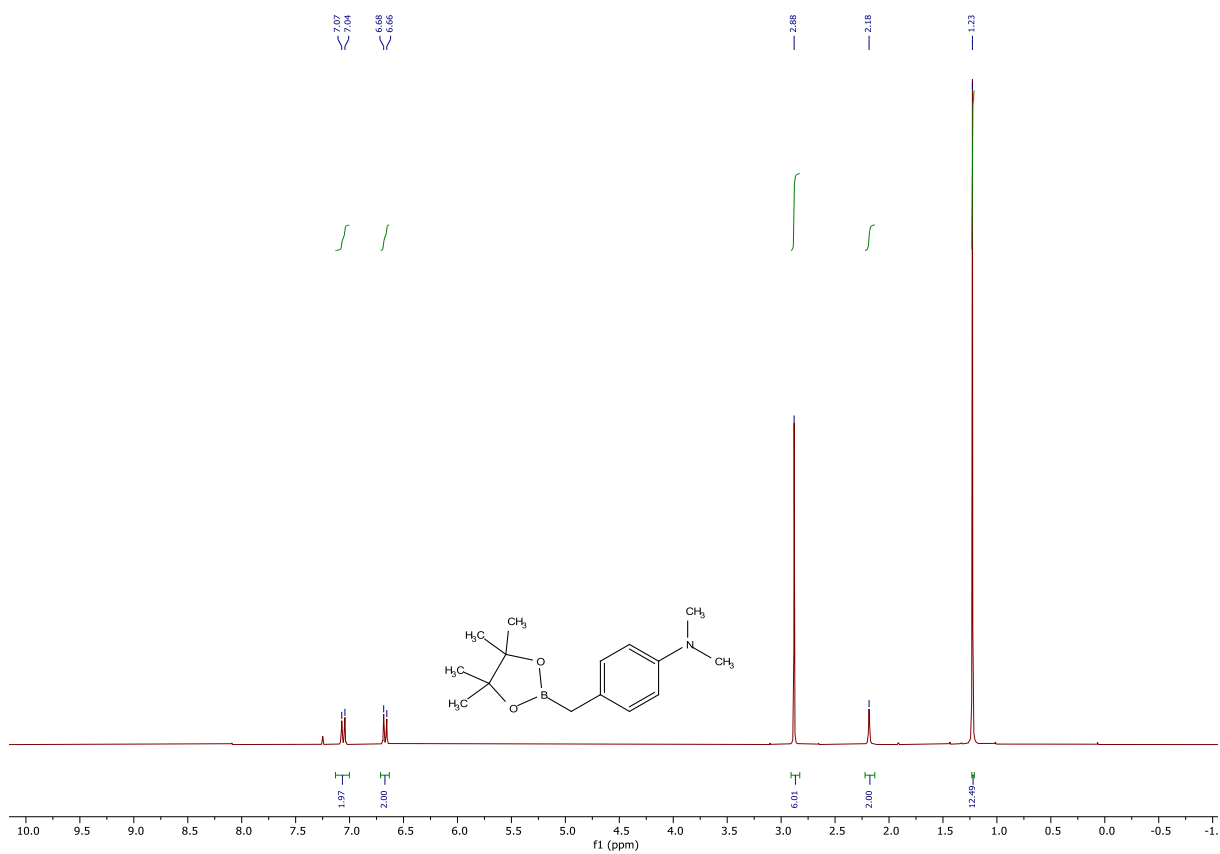
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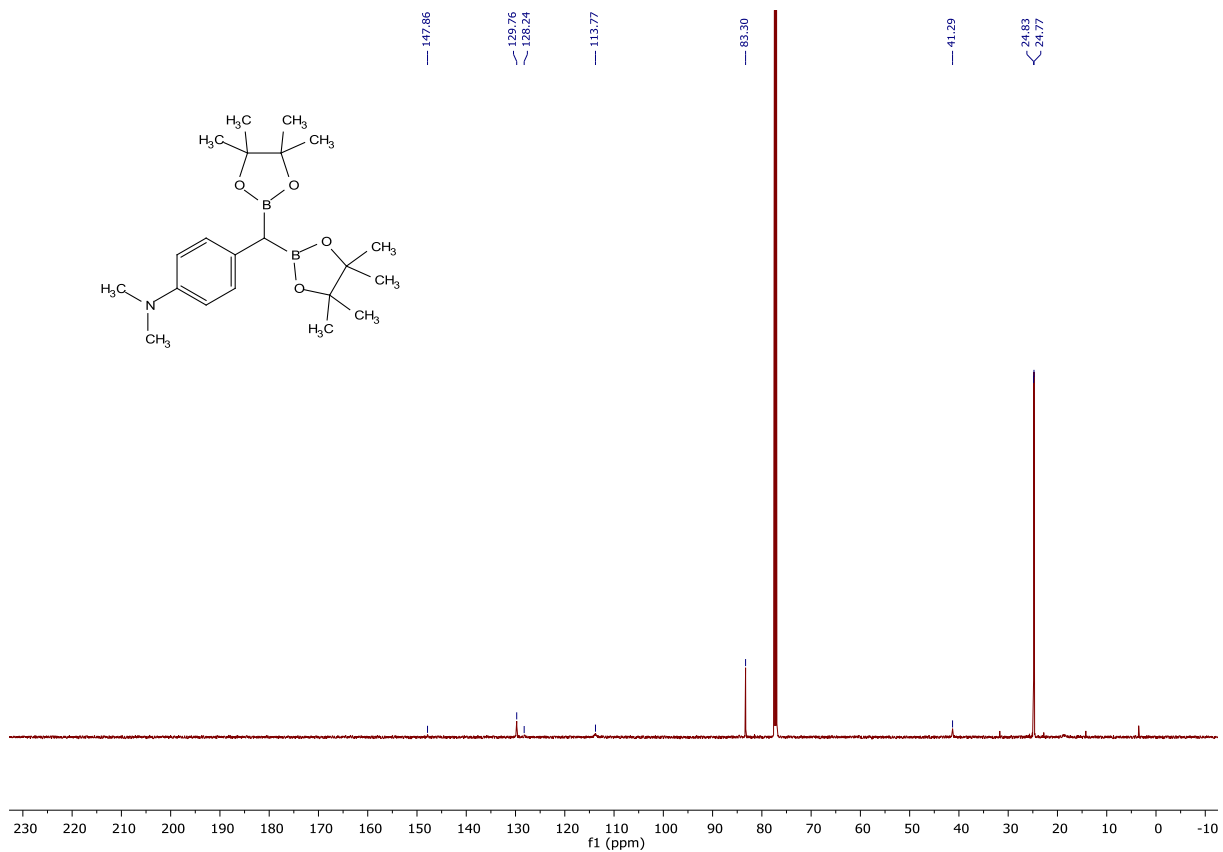
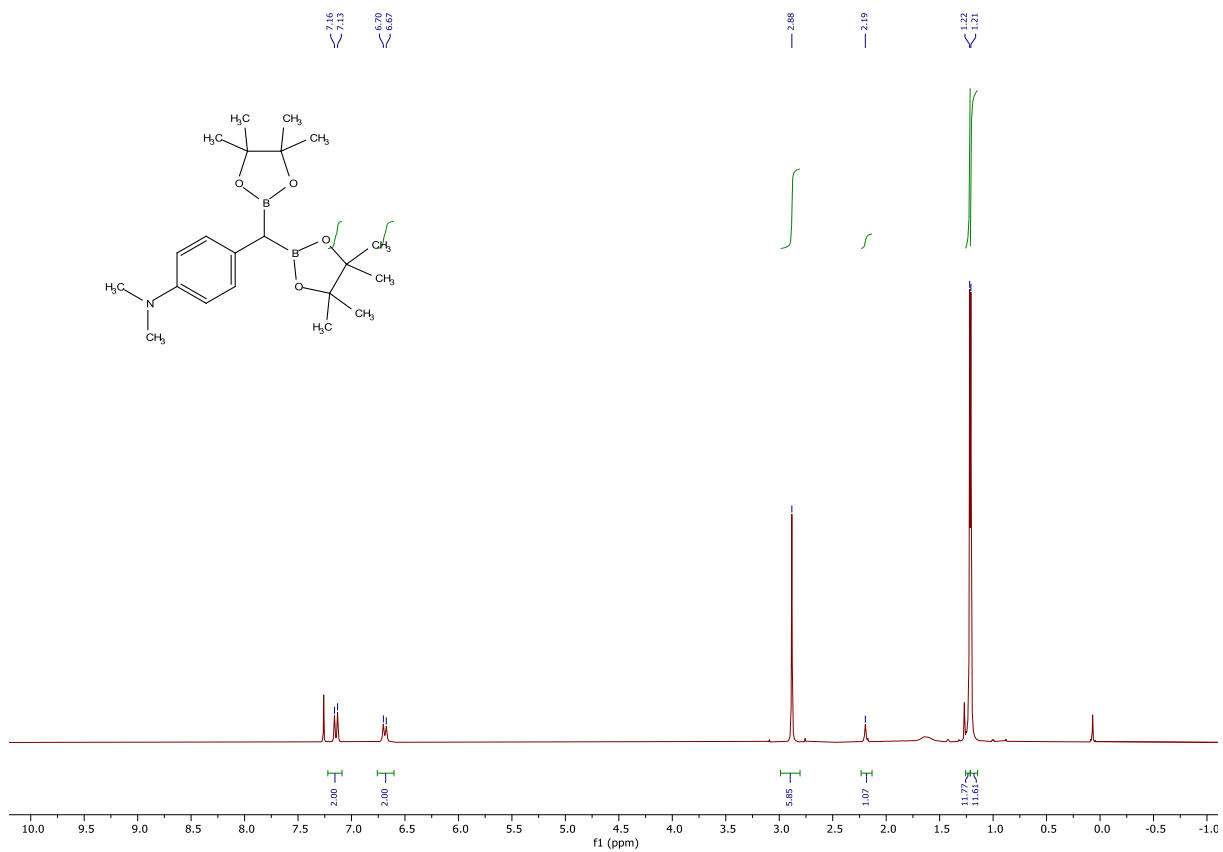
¹H and ¹³C NMR Spectra

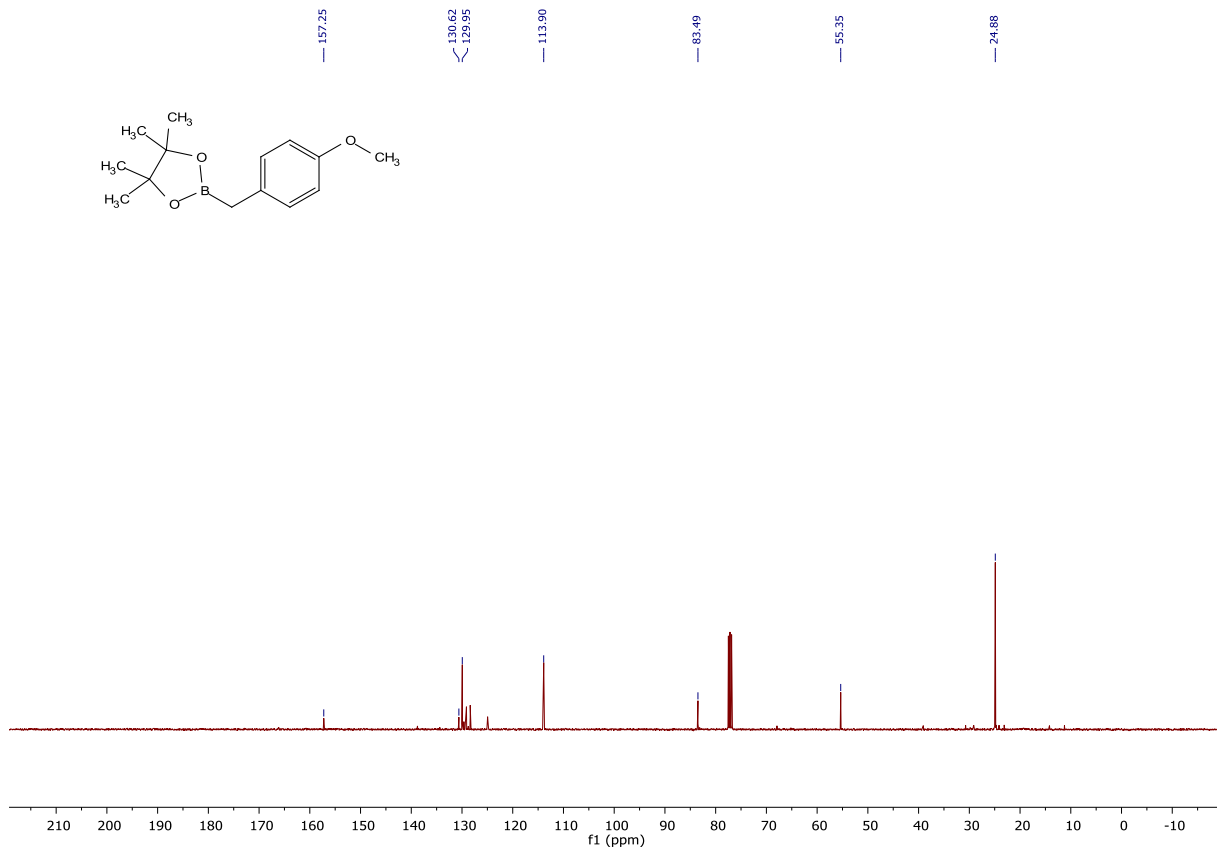
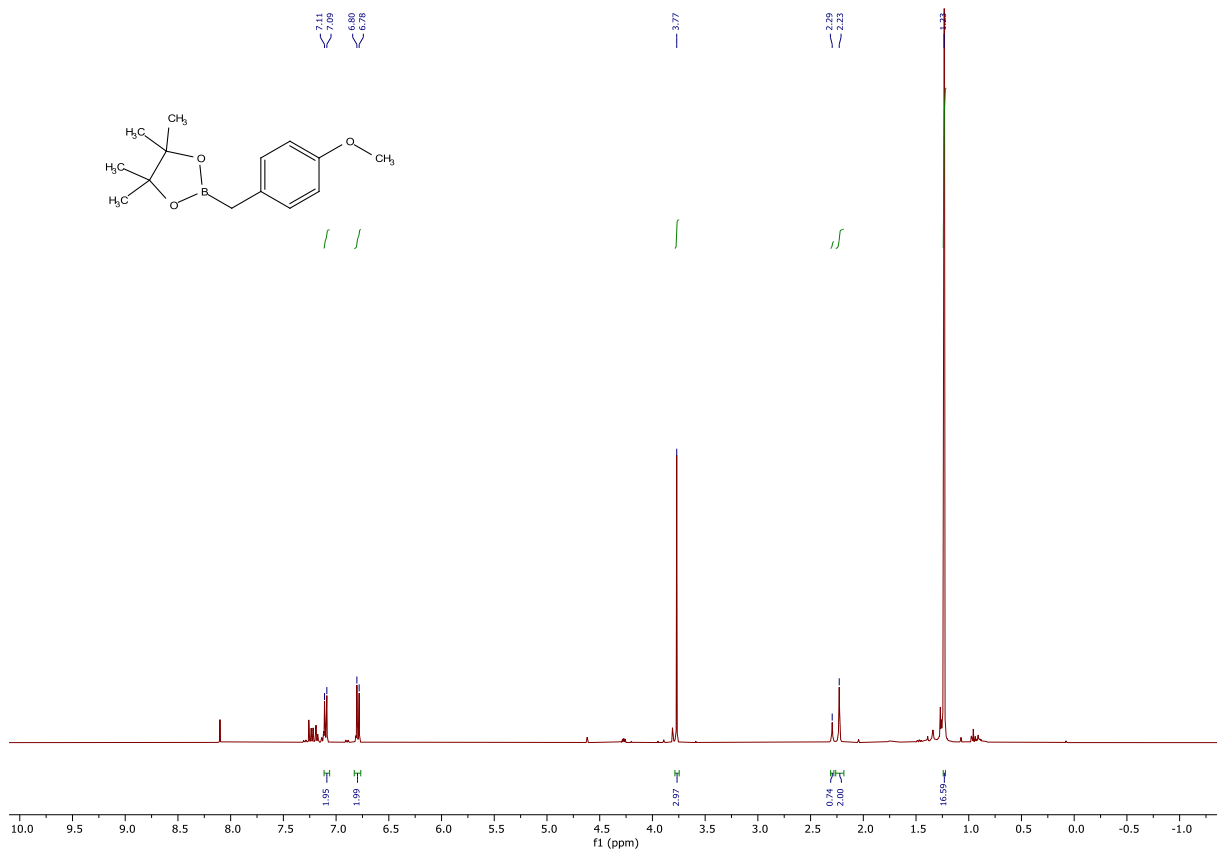
(x = impurity from pentane)

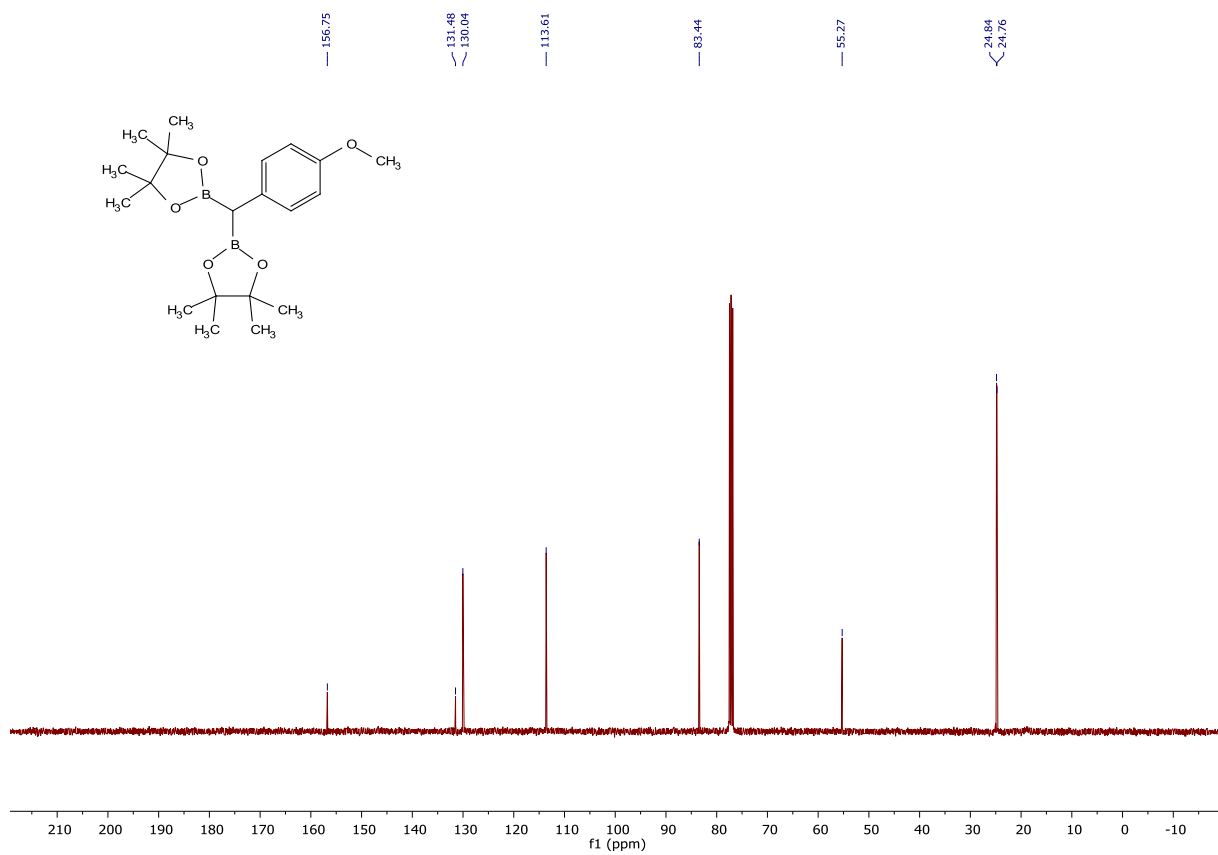
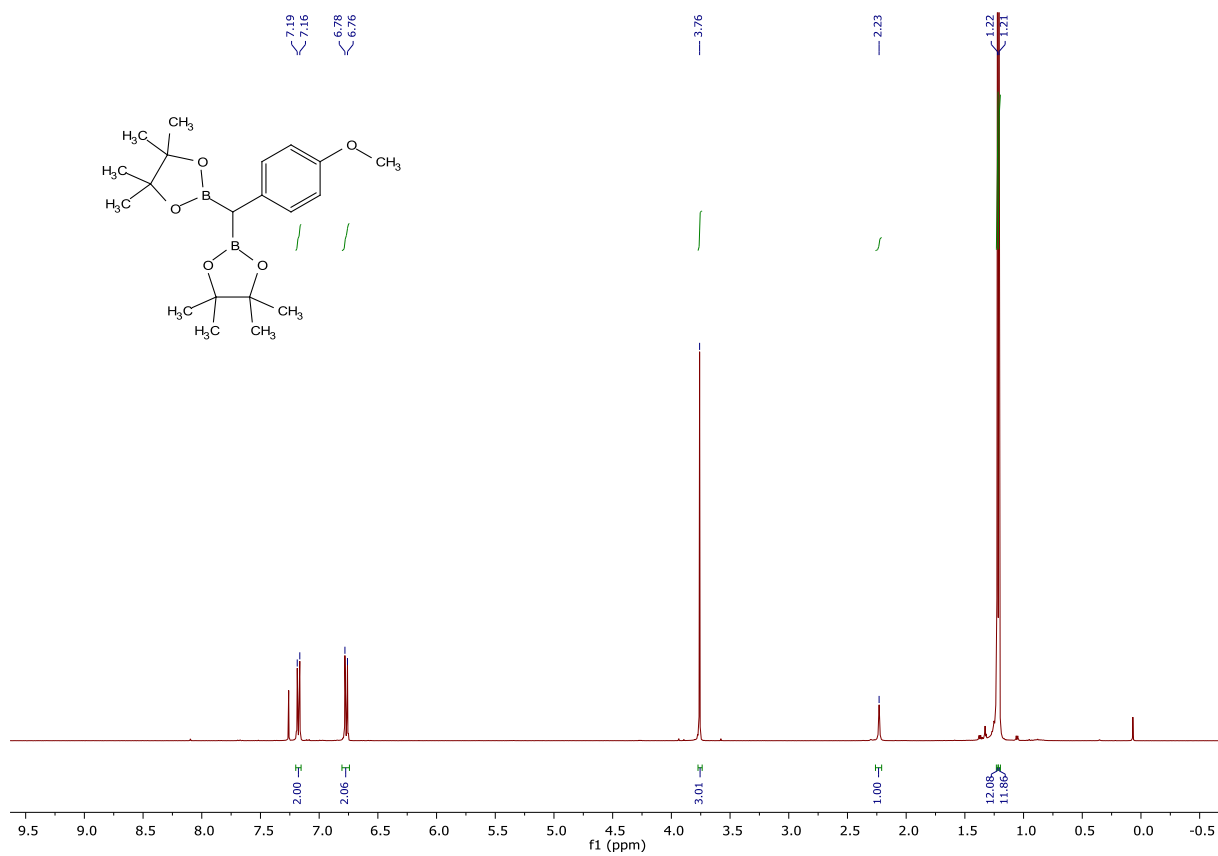


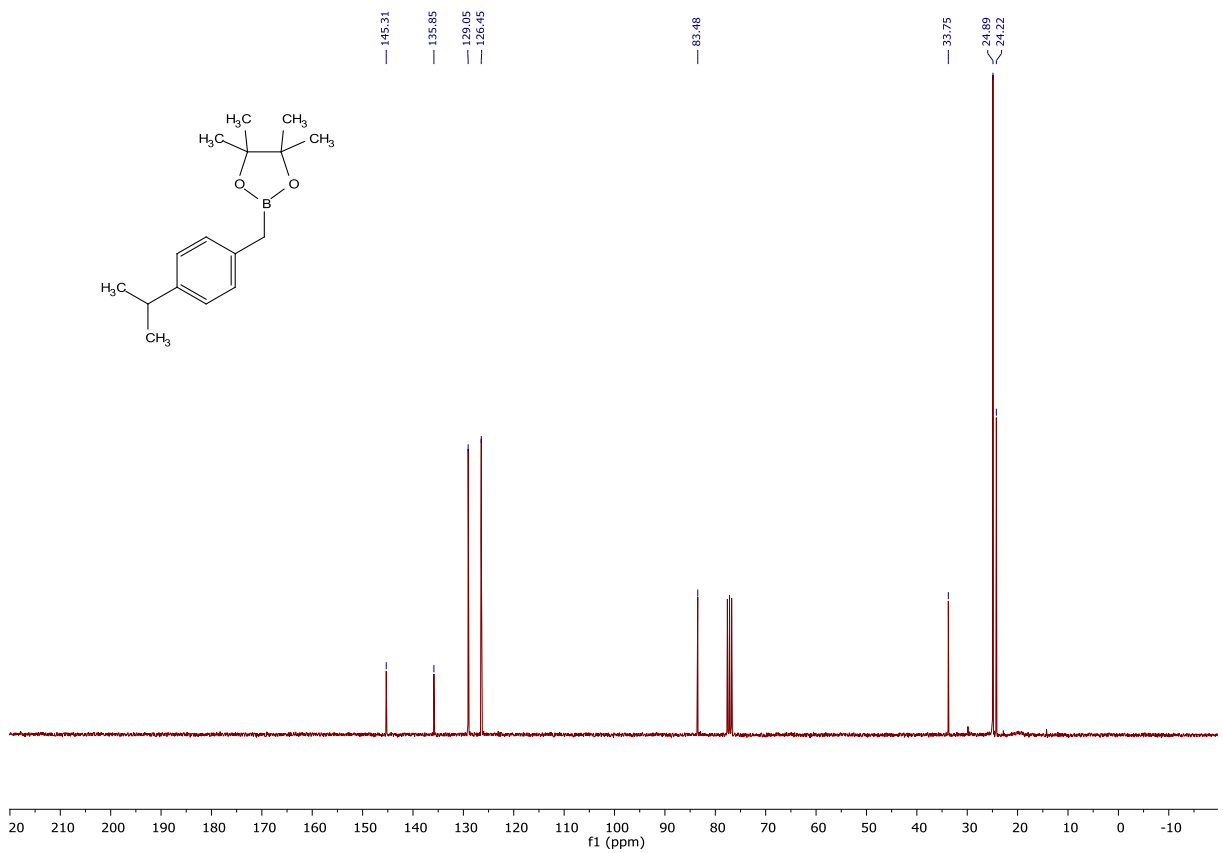
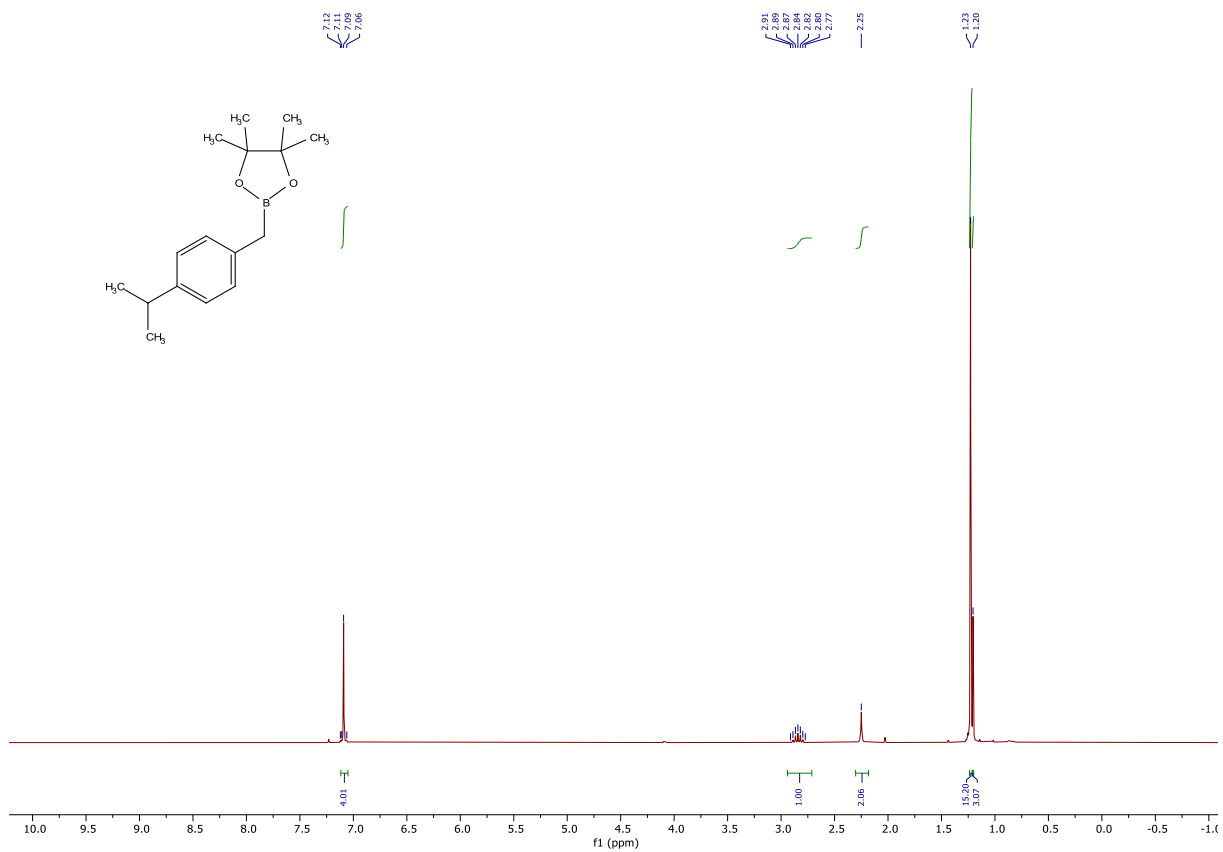


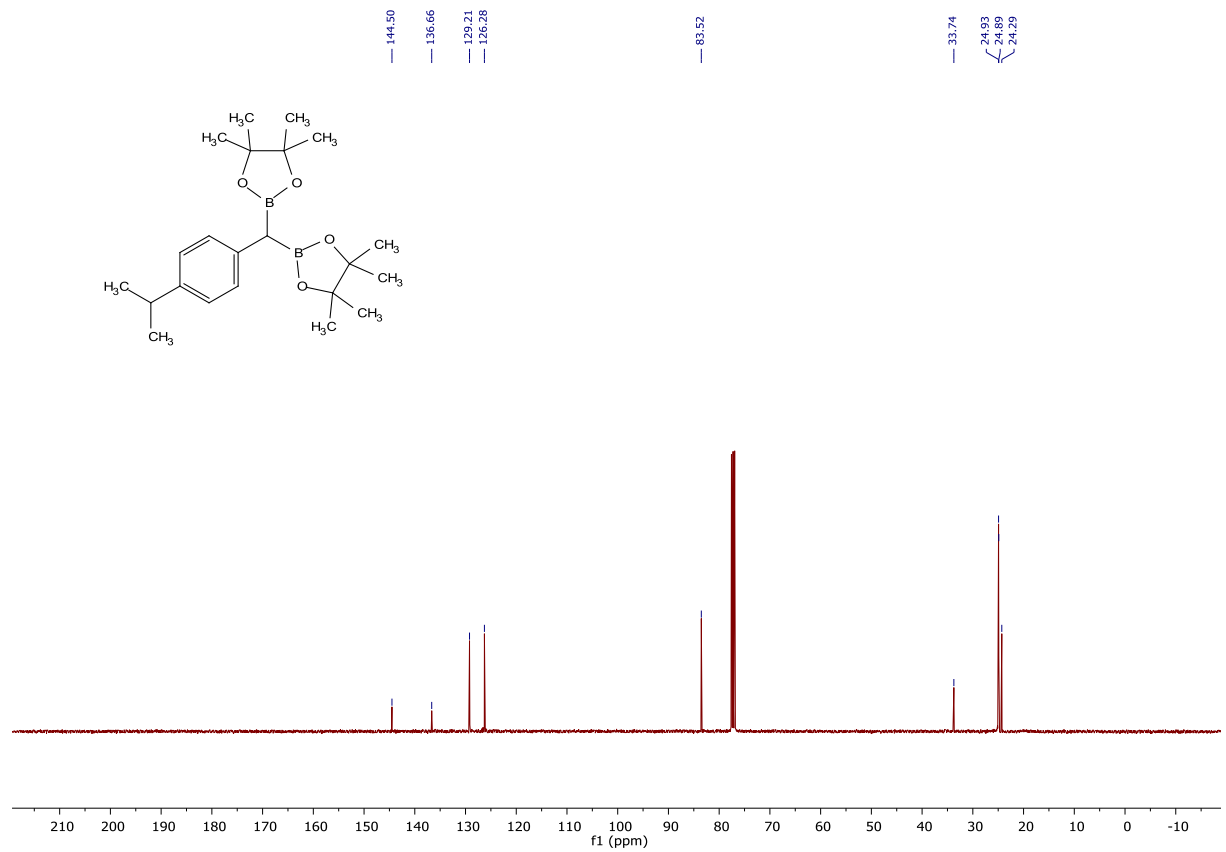
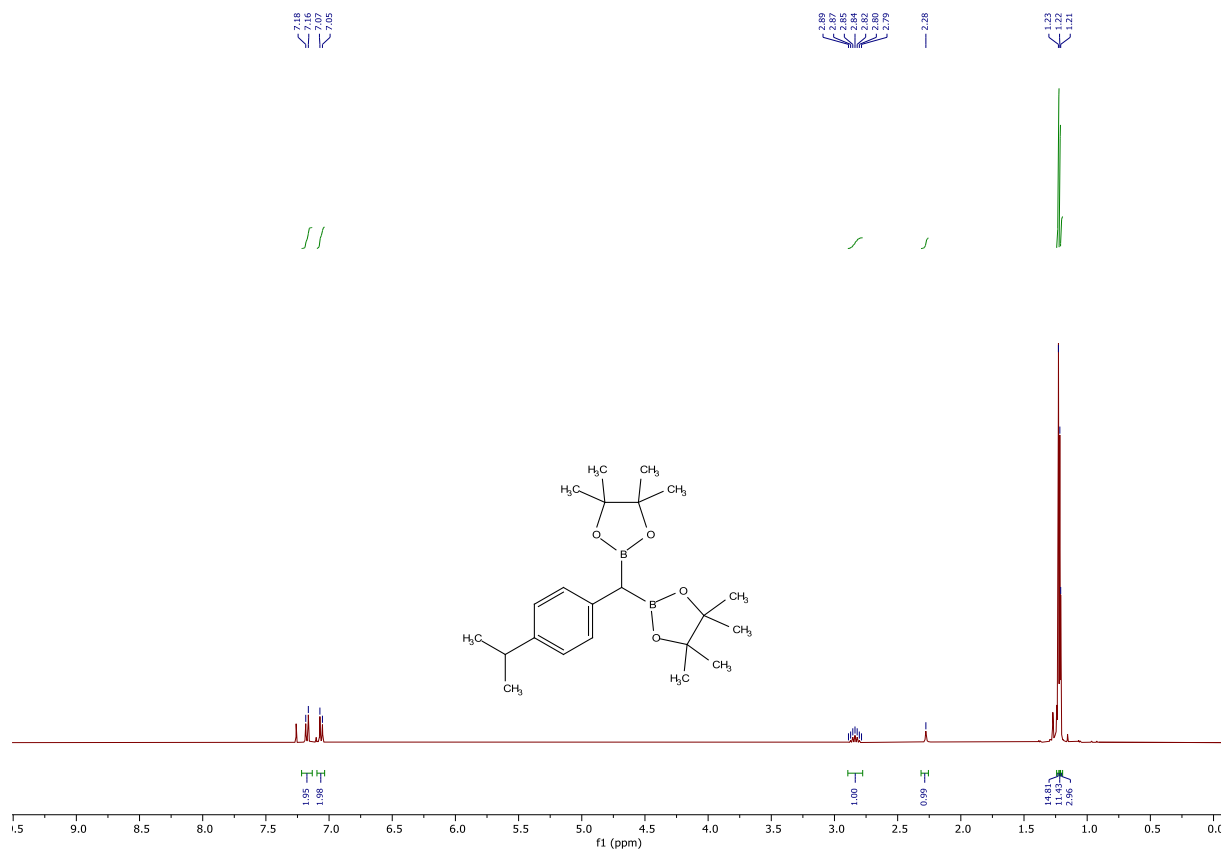


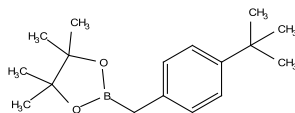
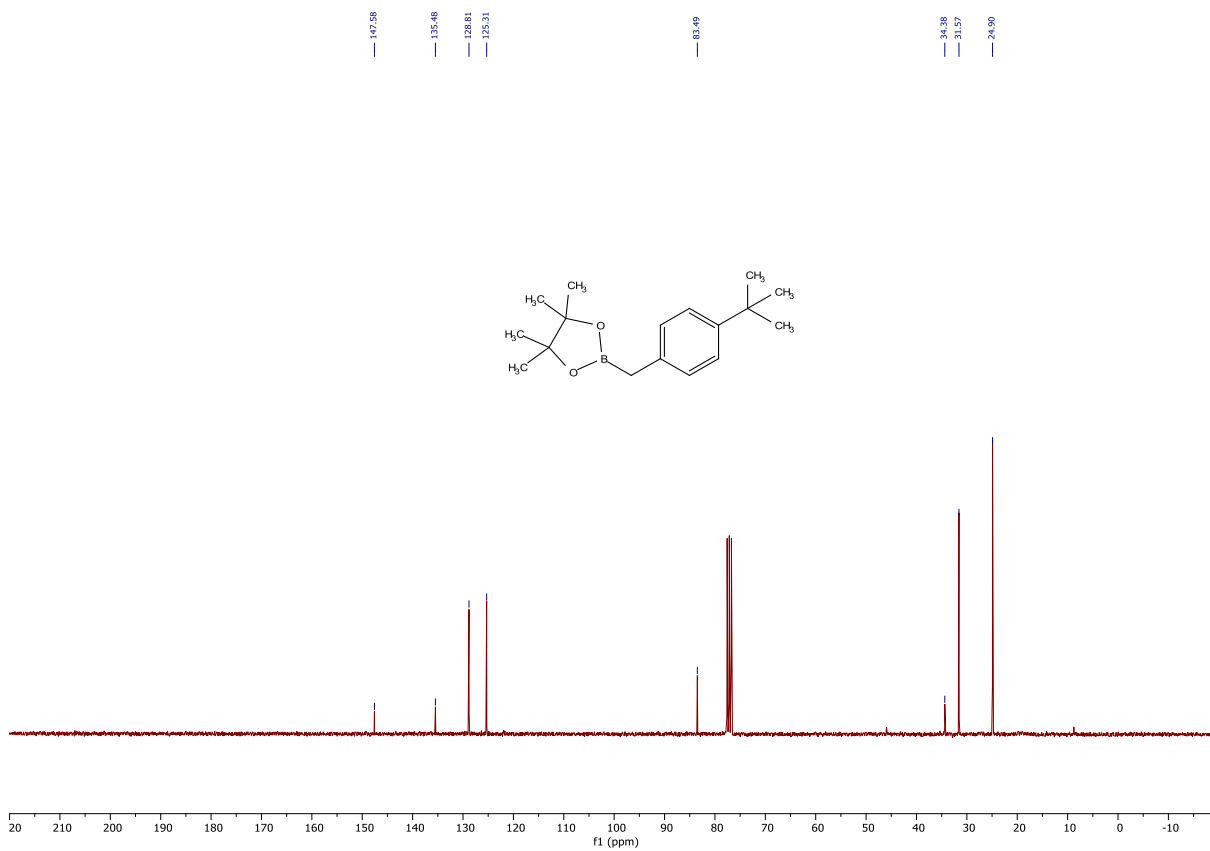
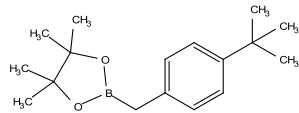
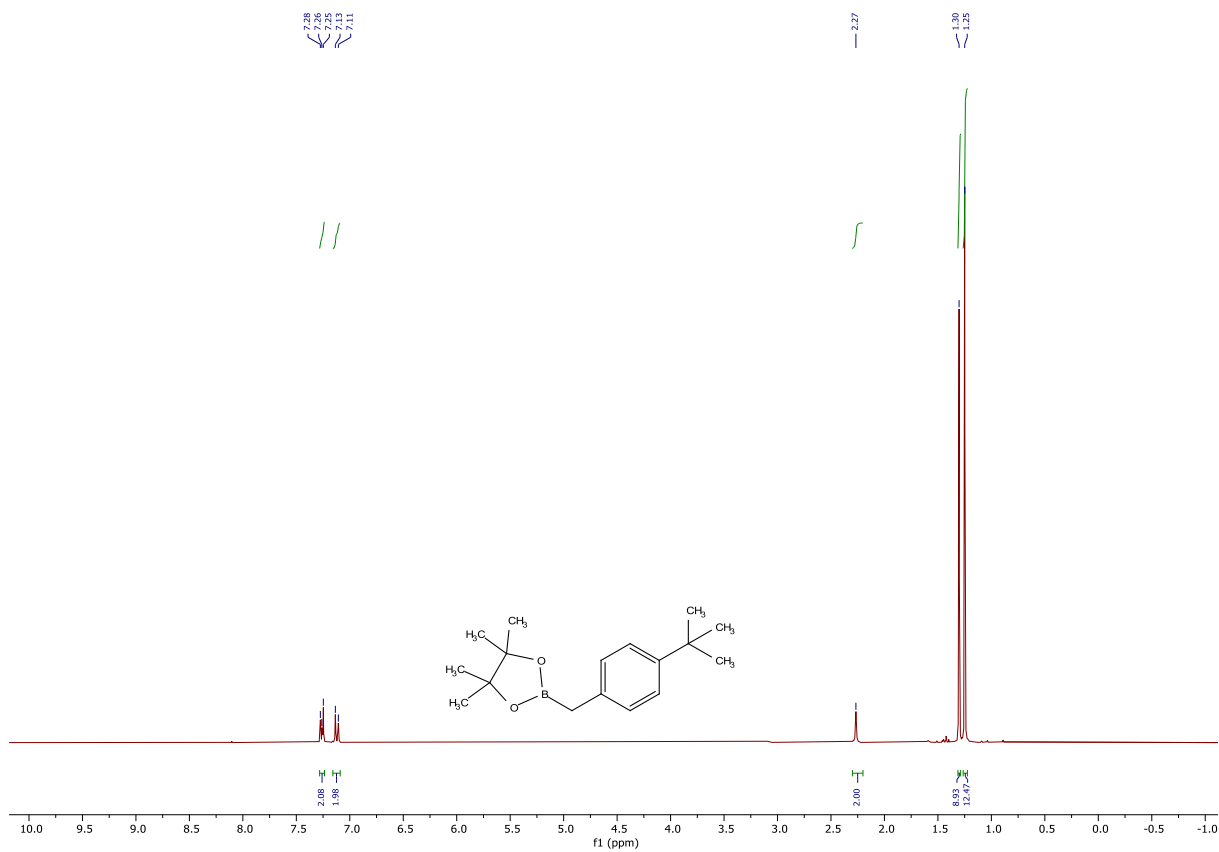


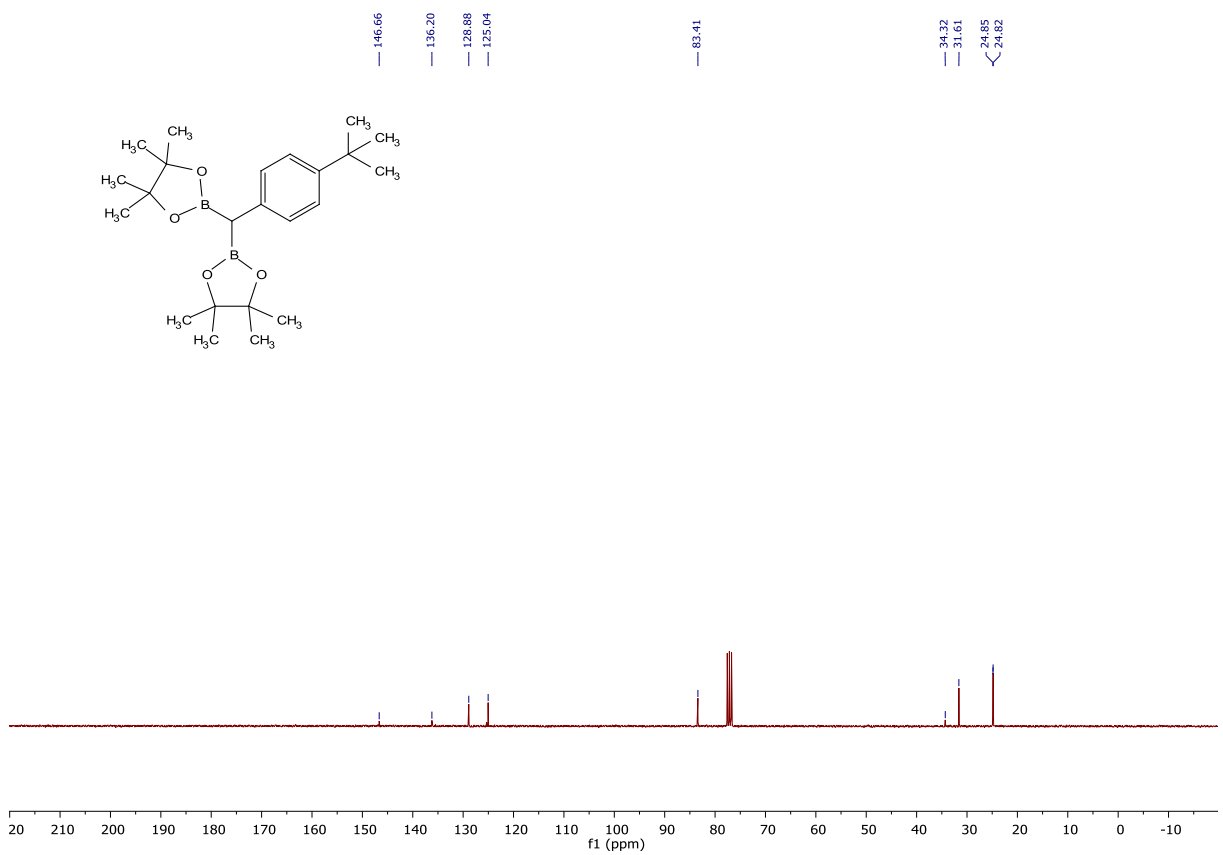
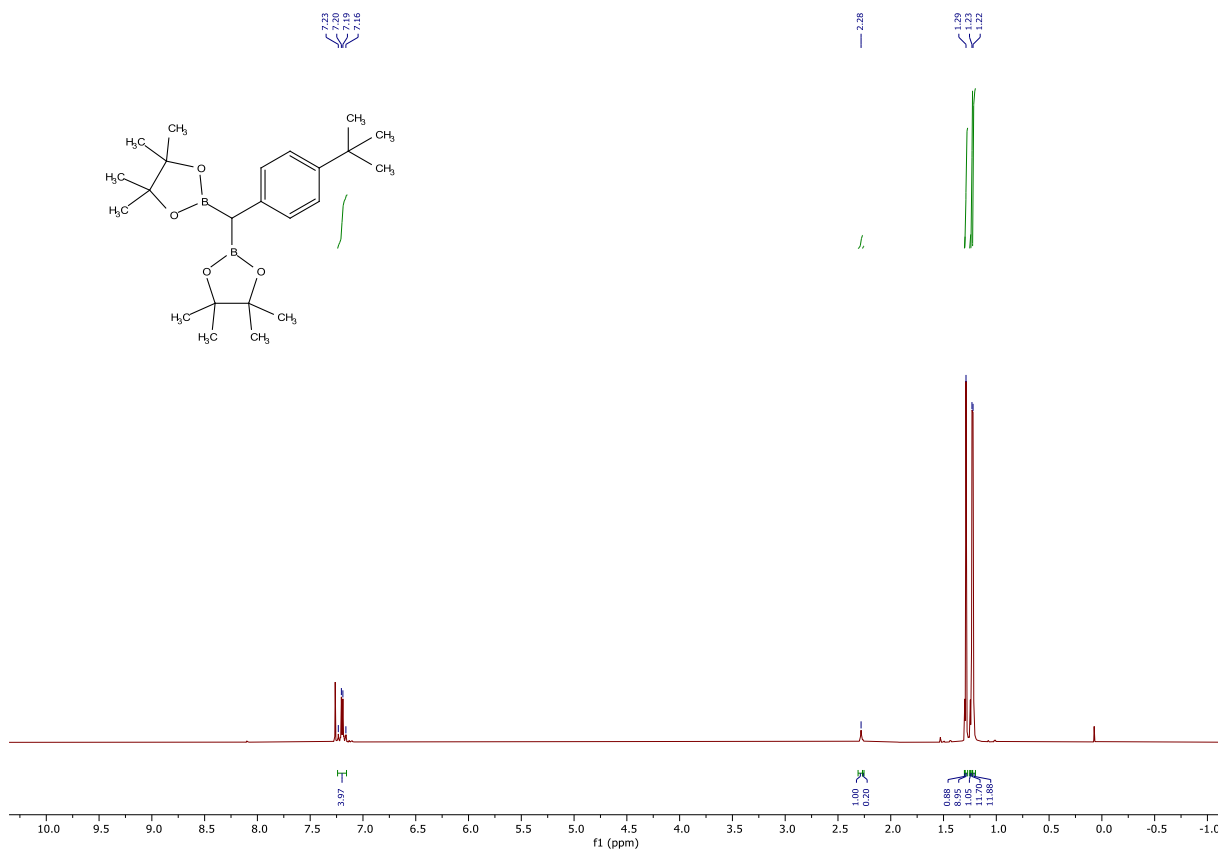


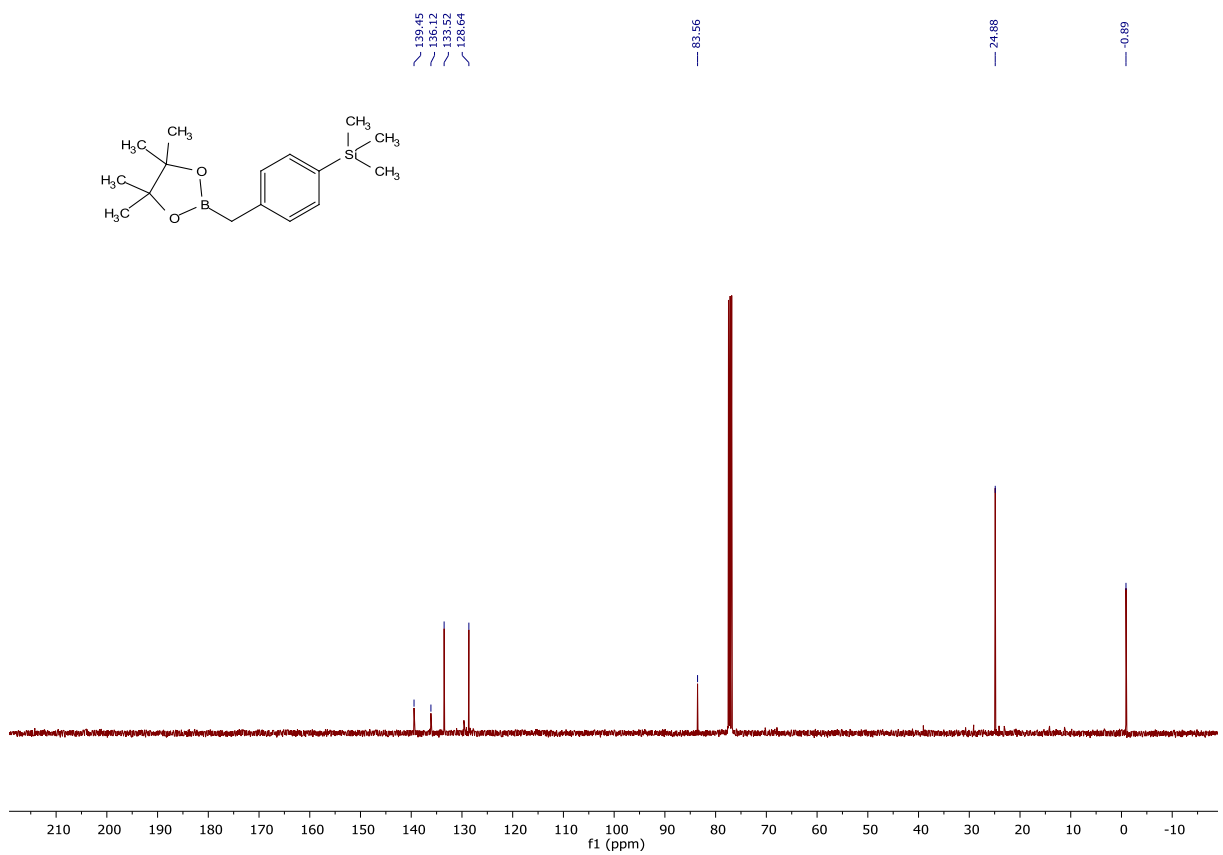
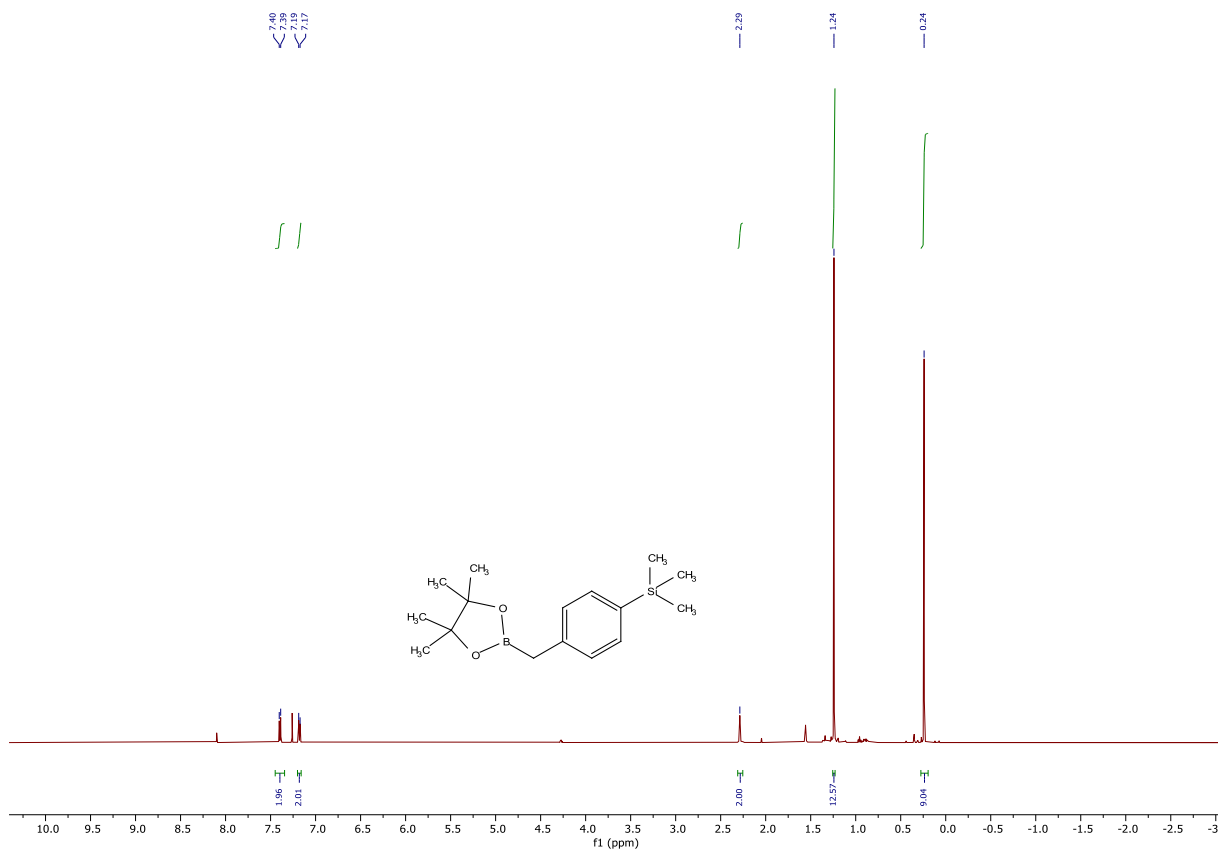


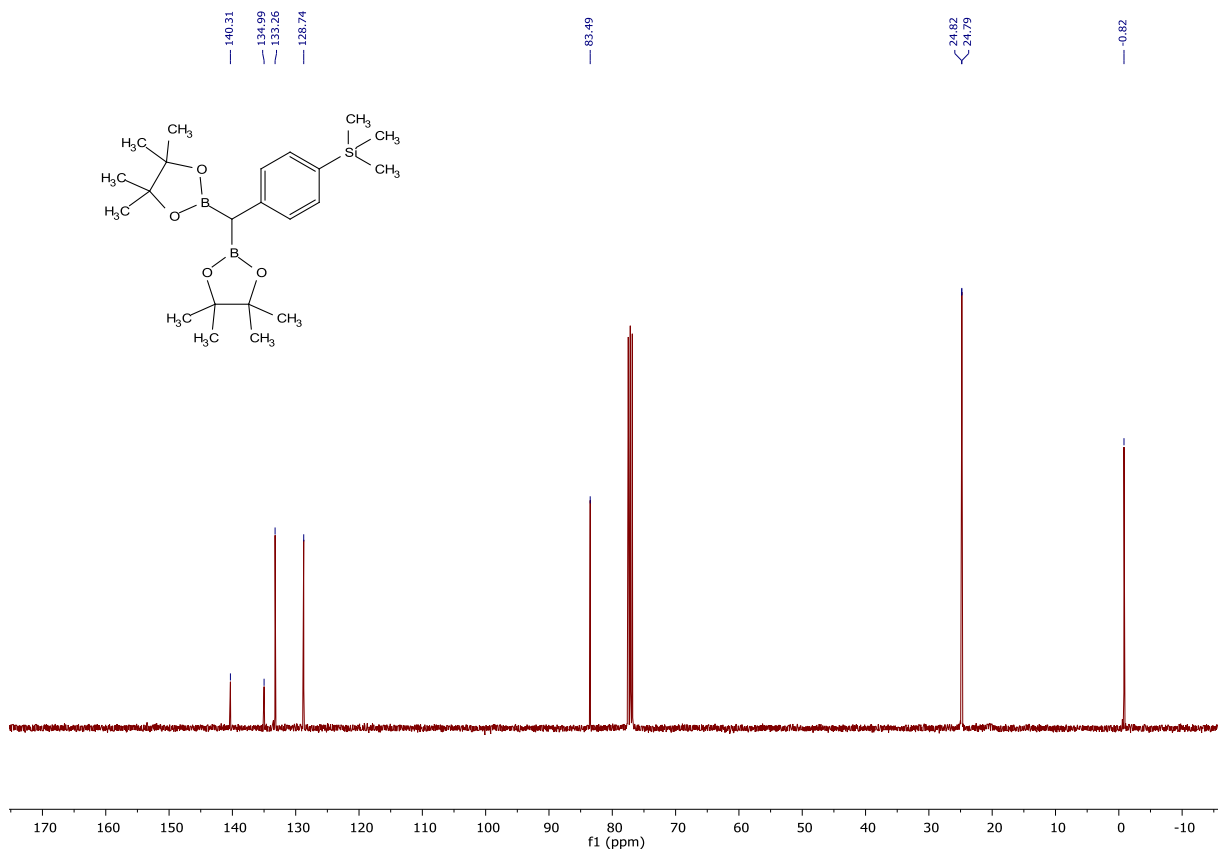
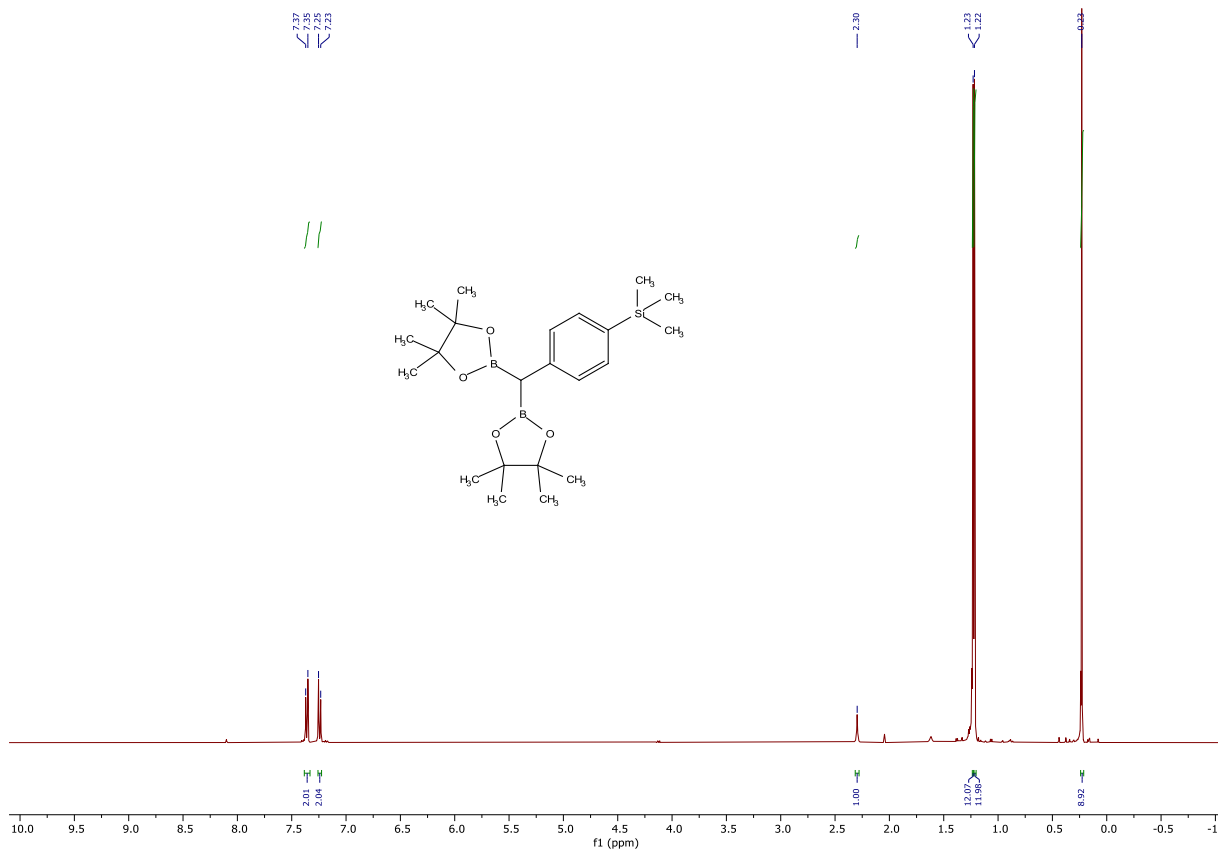


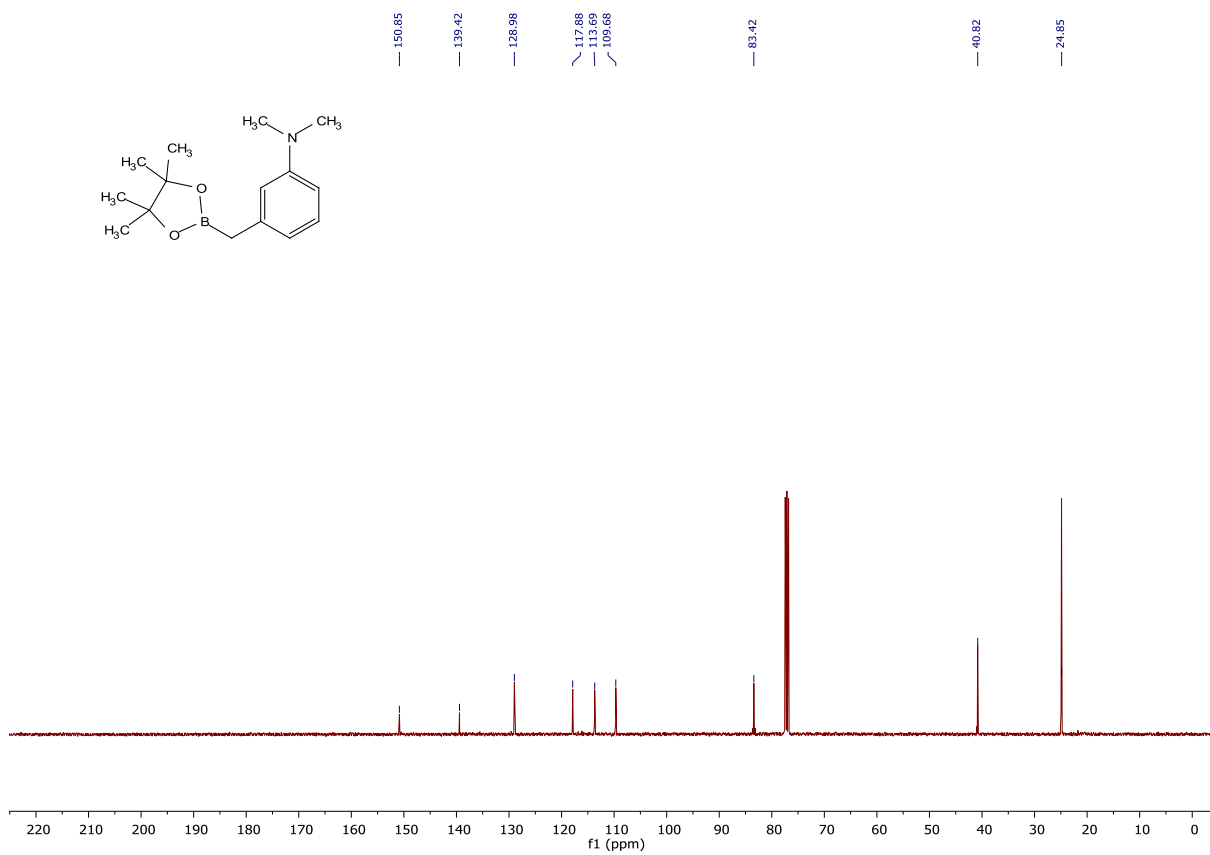
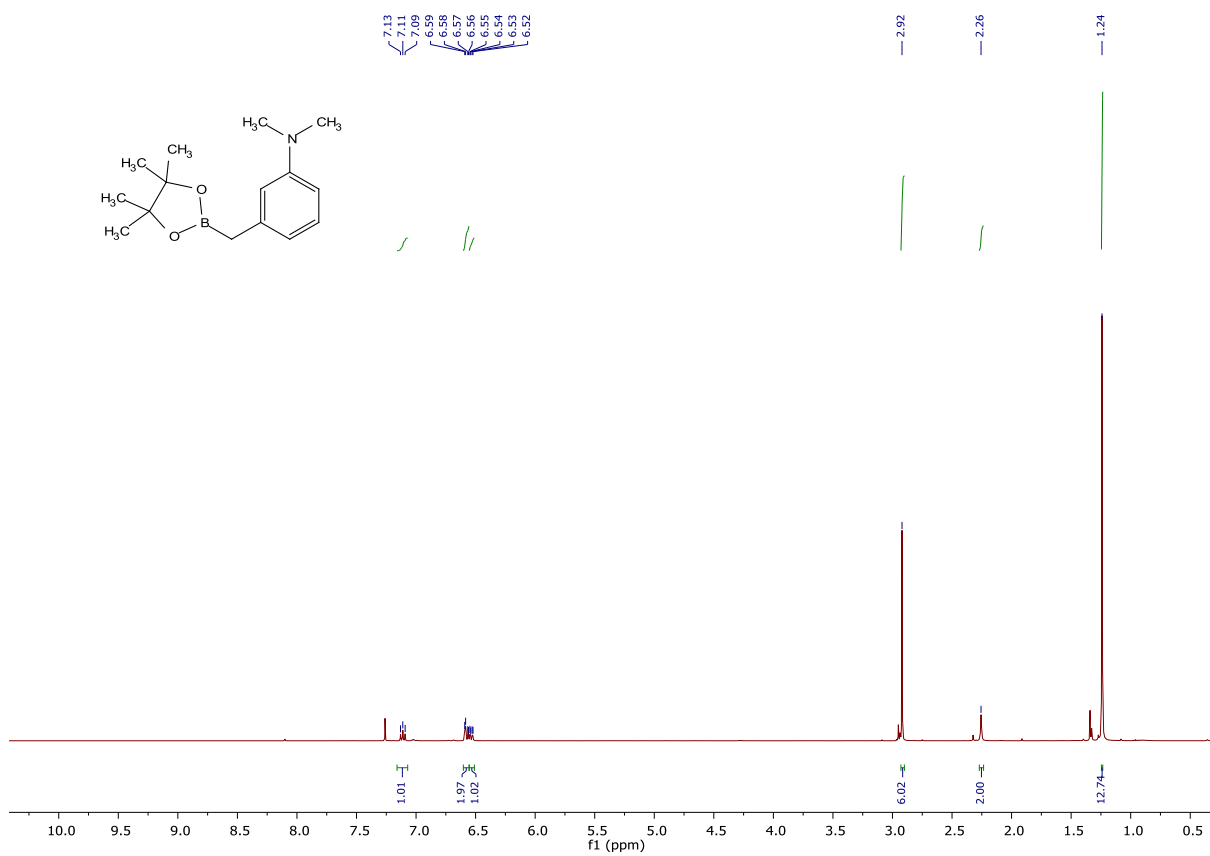


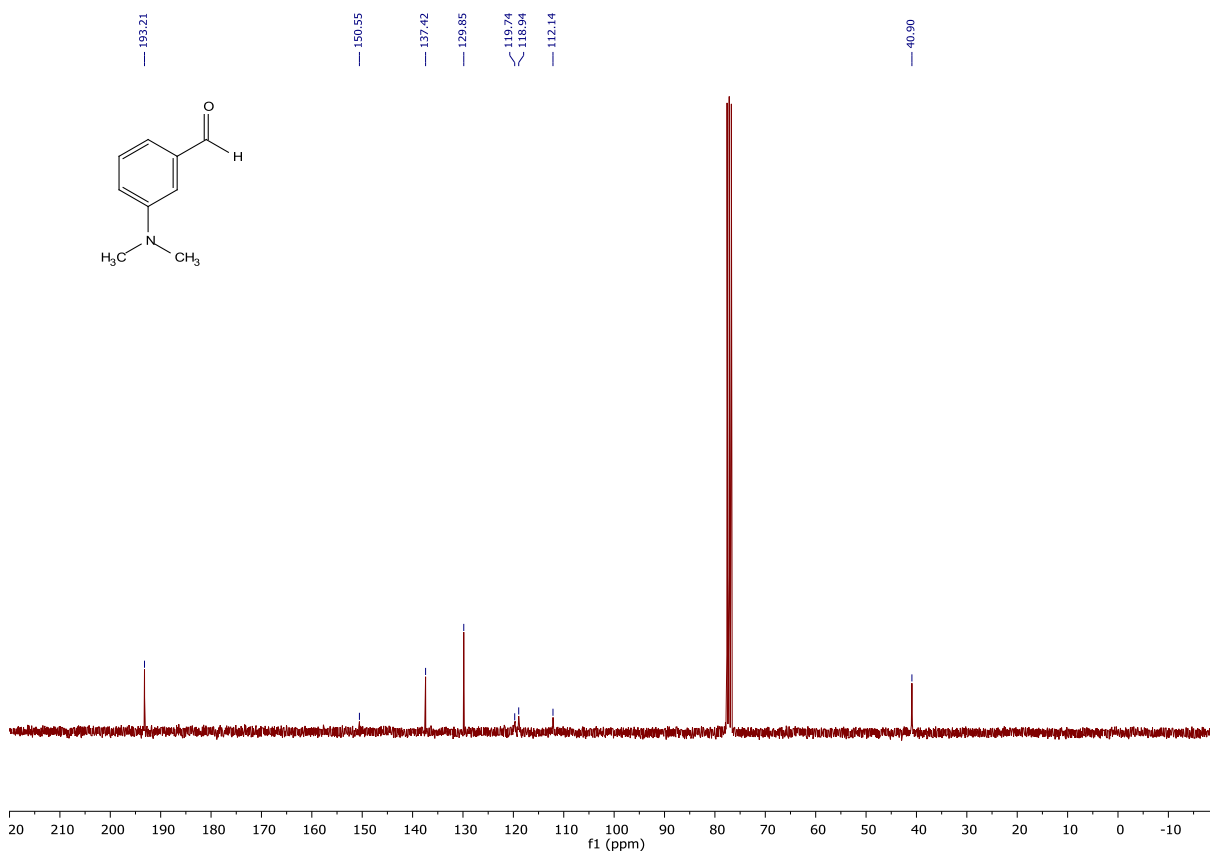
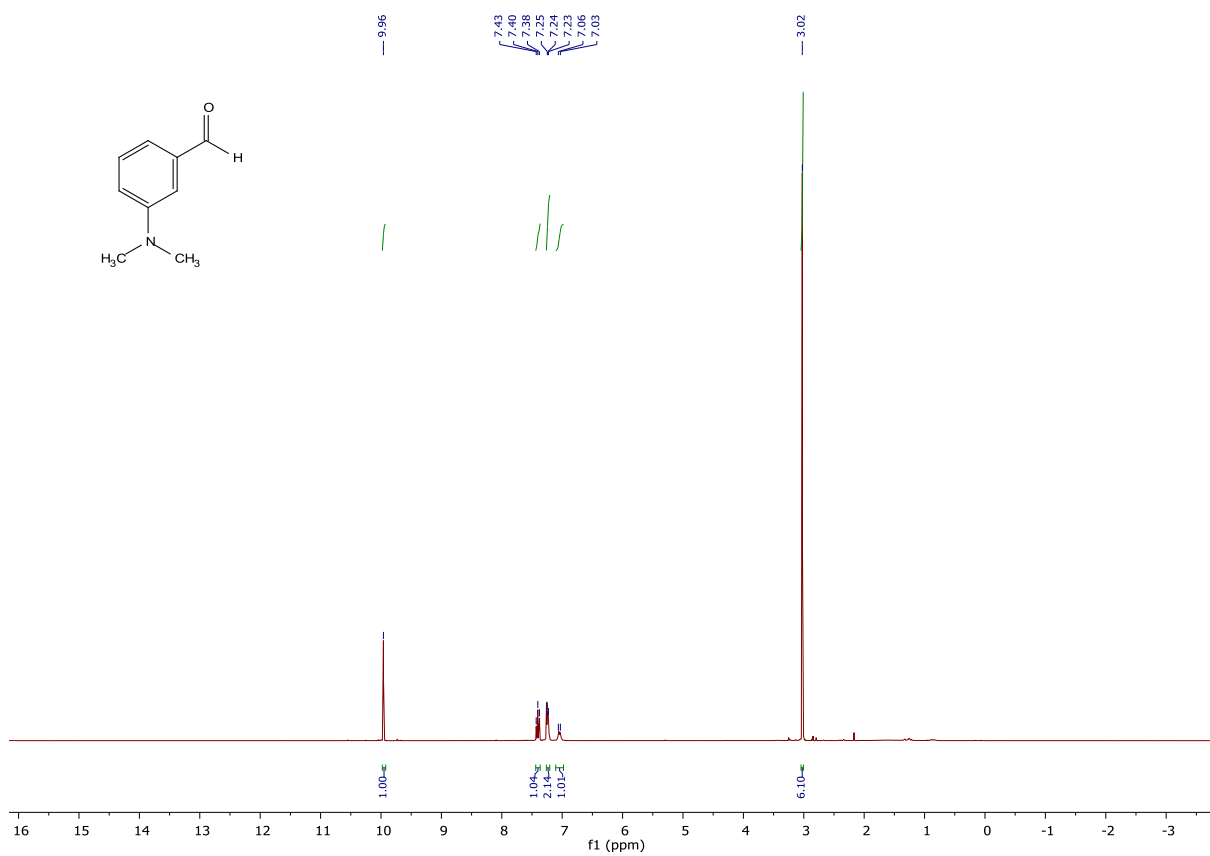


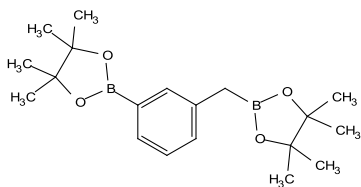
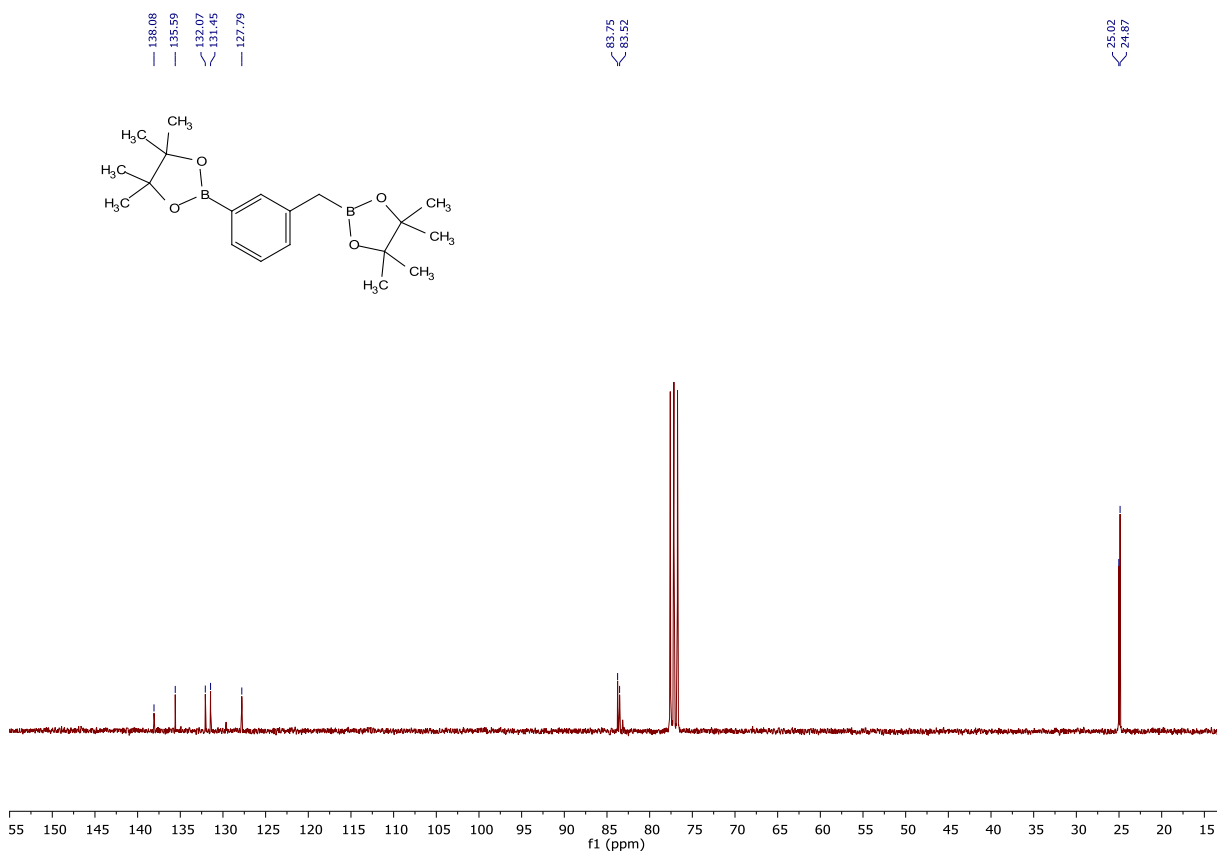
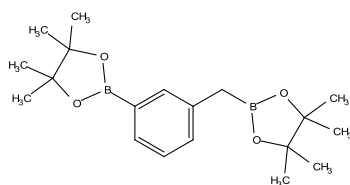
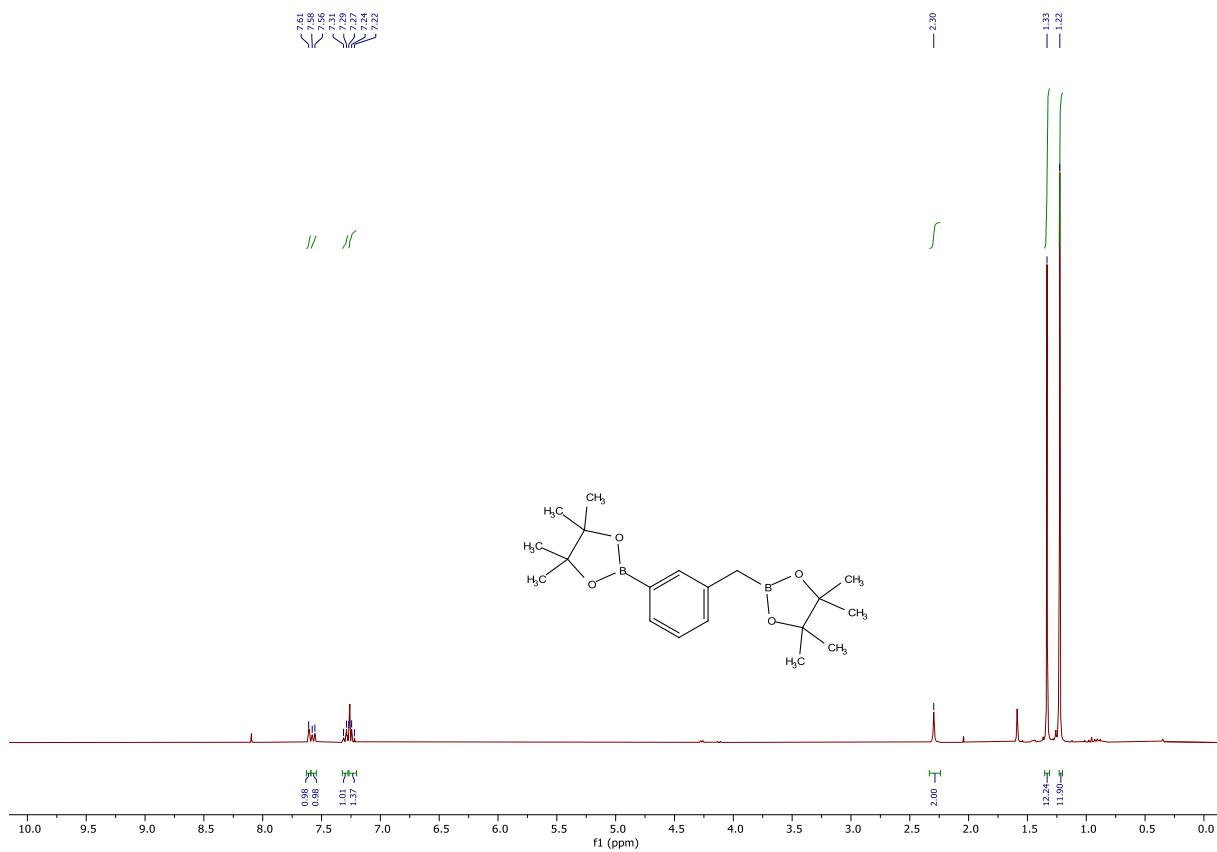


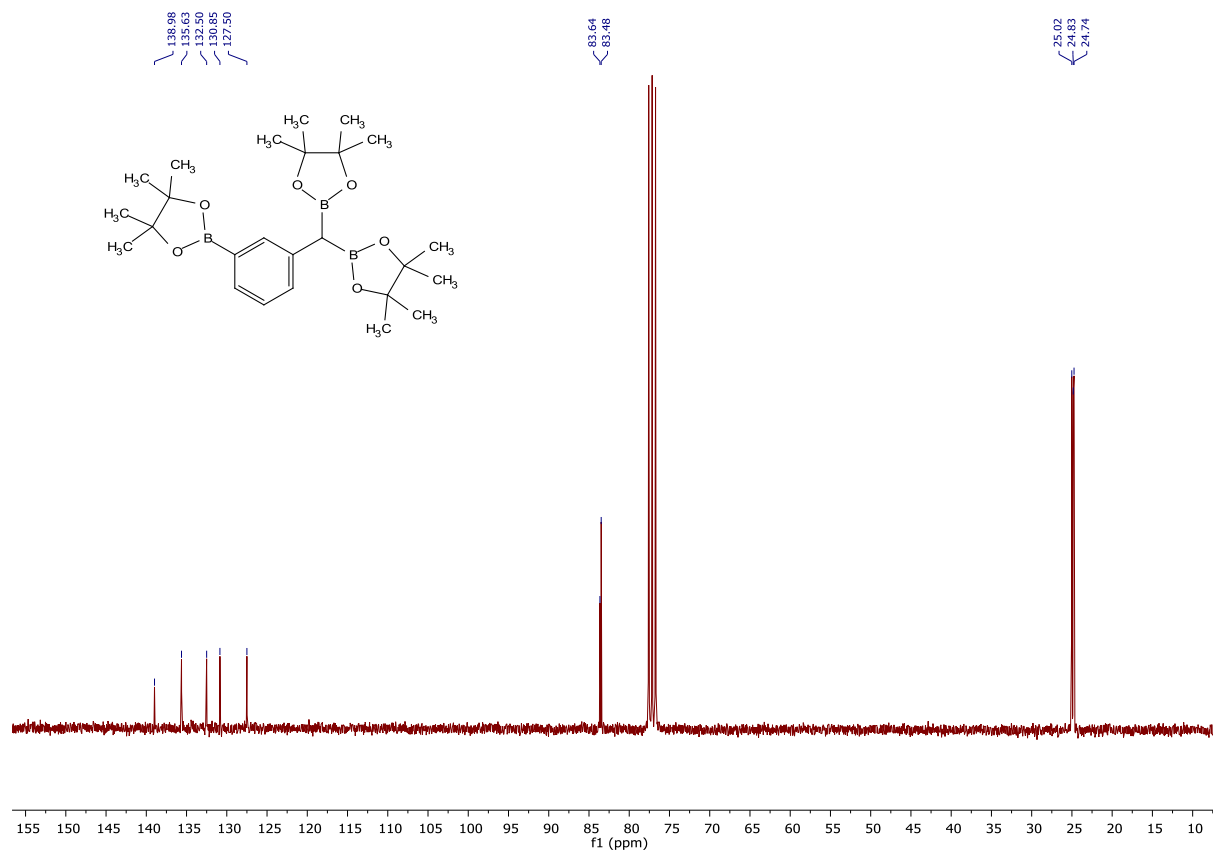
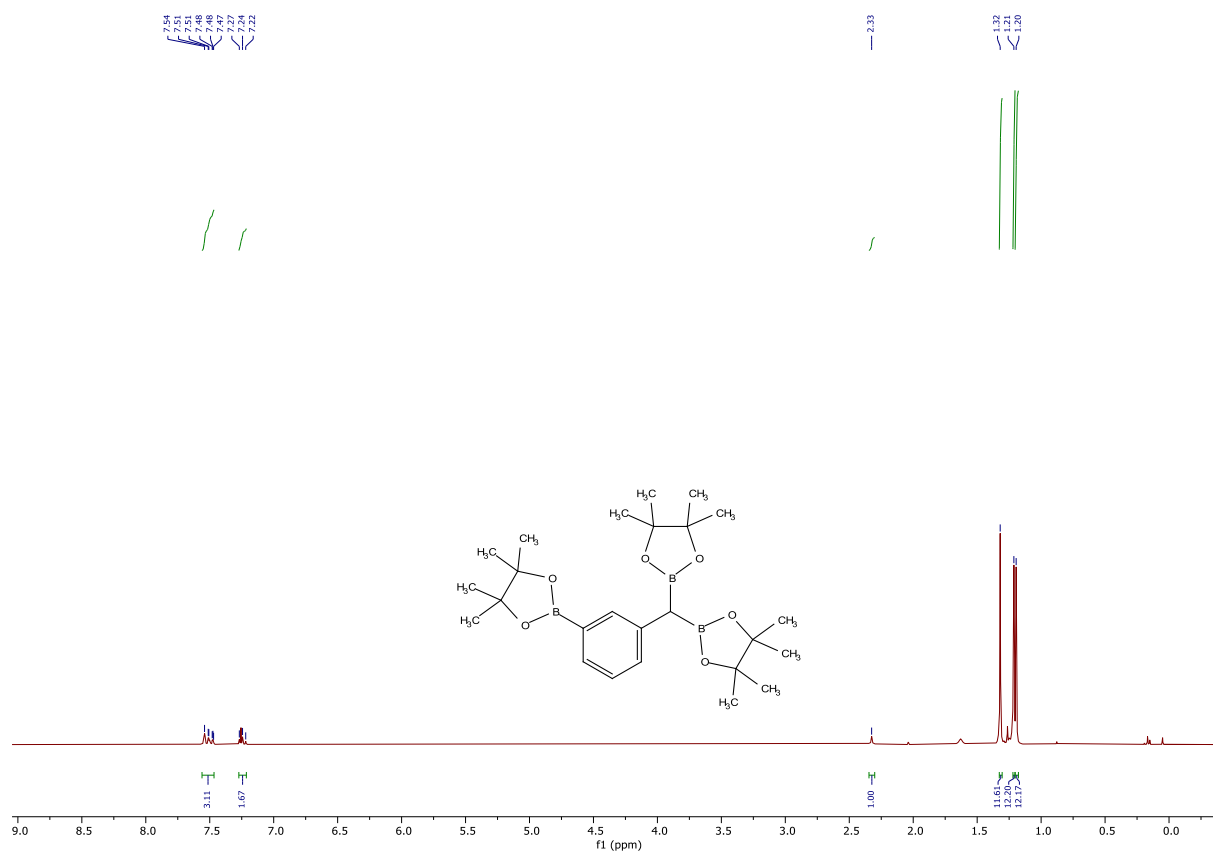


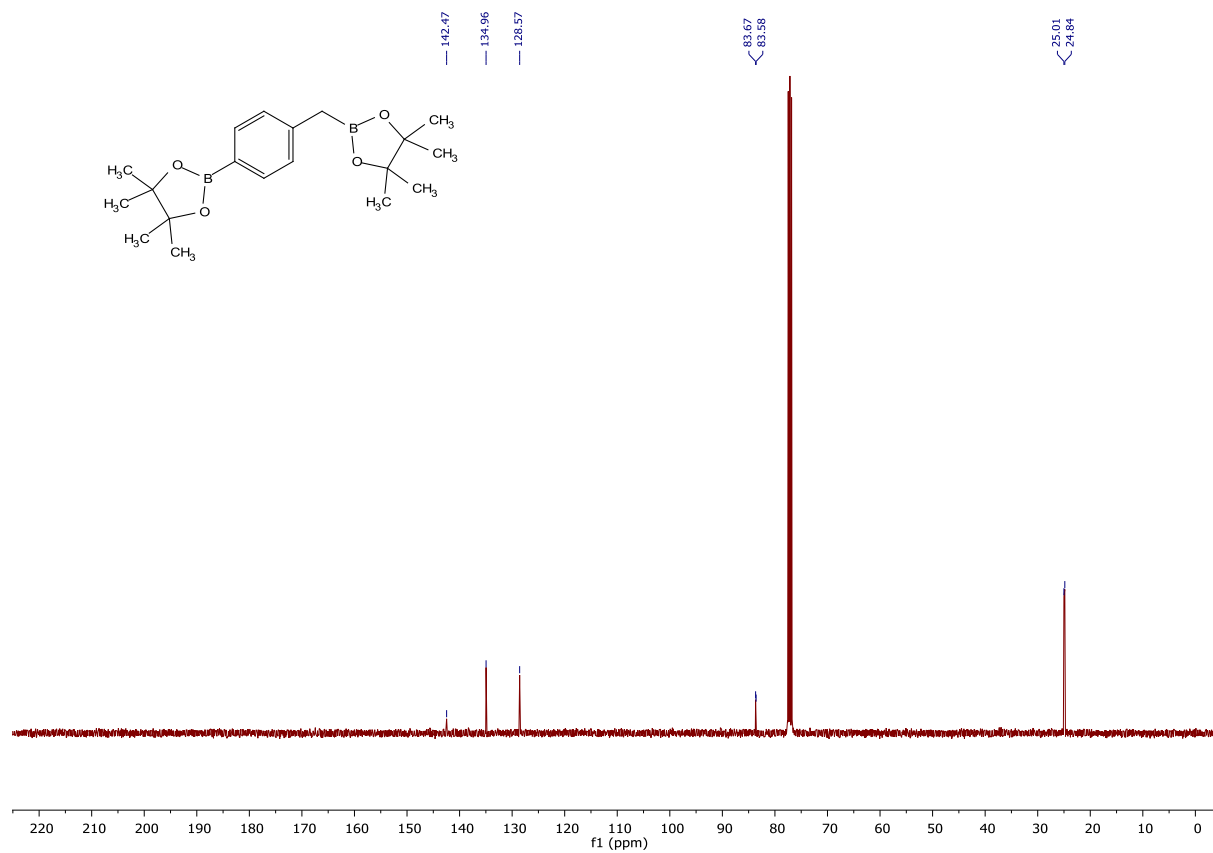
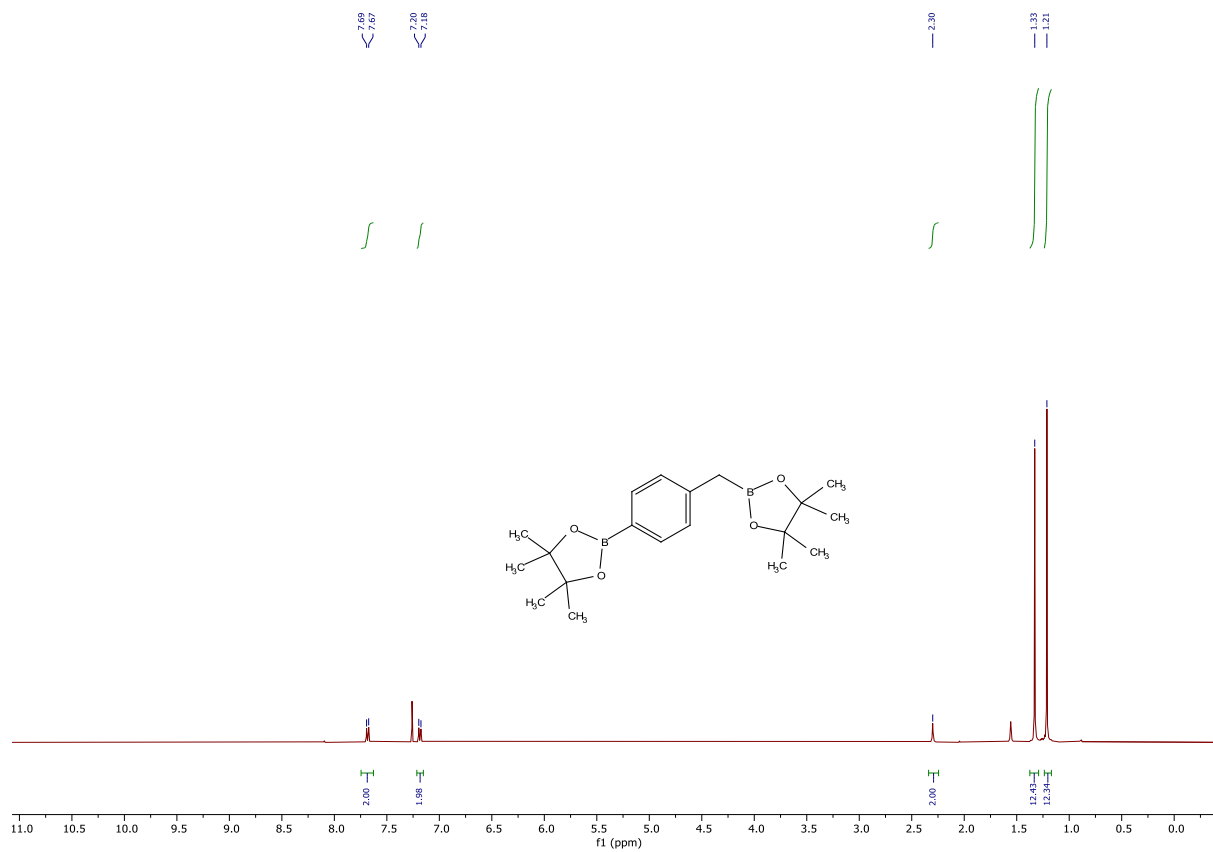


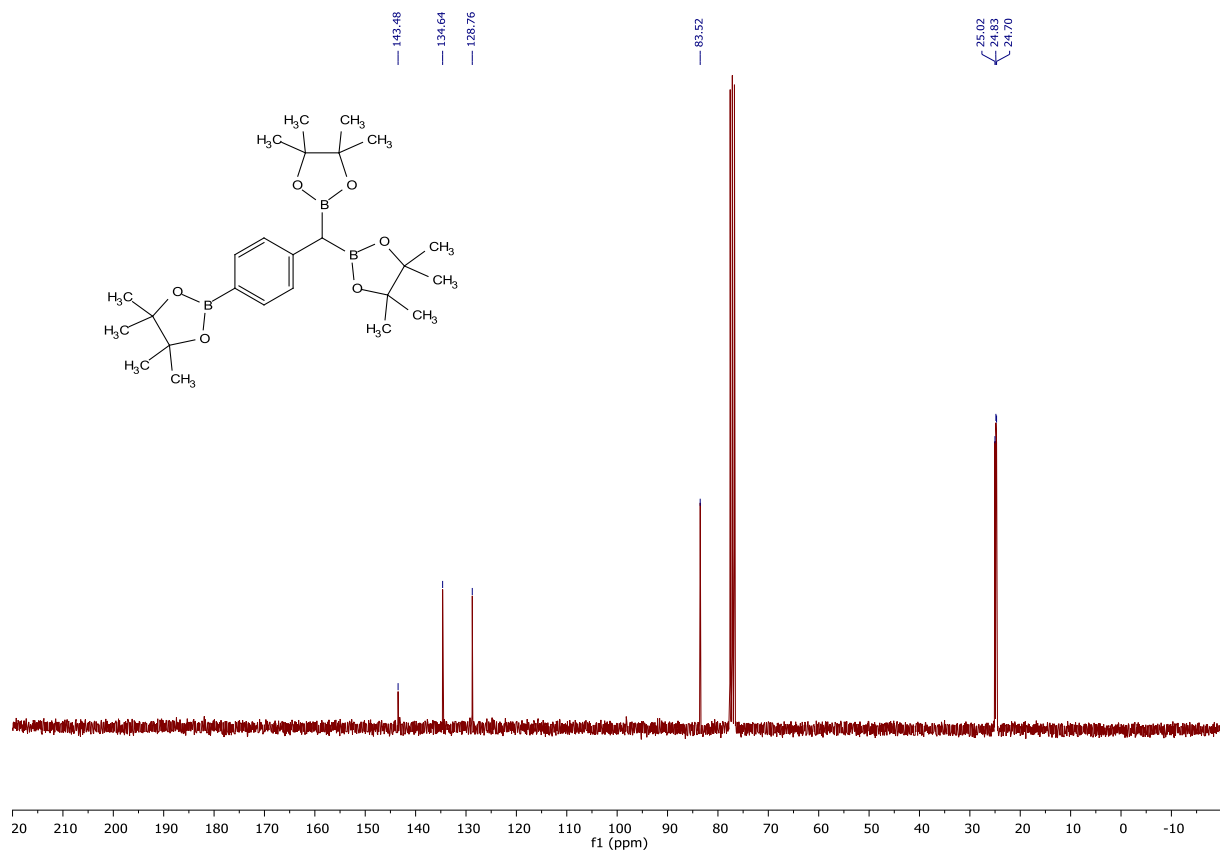
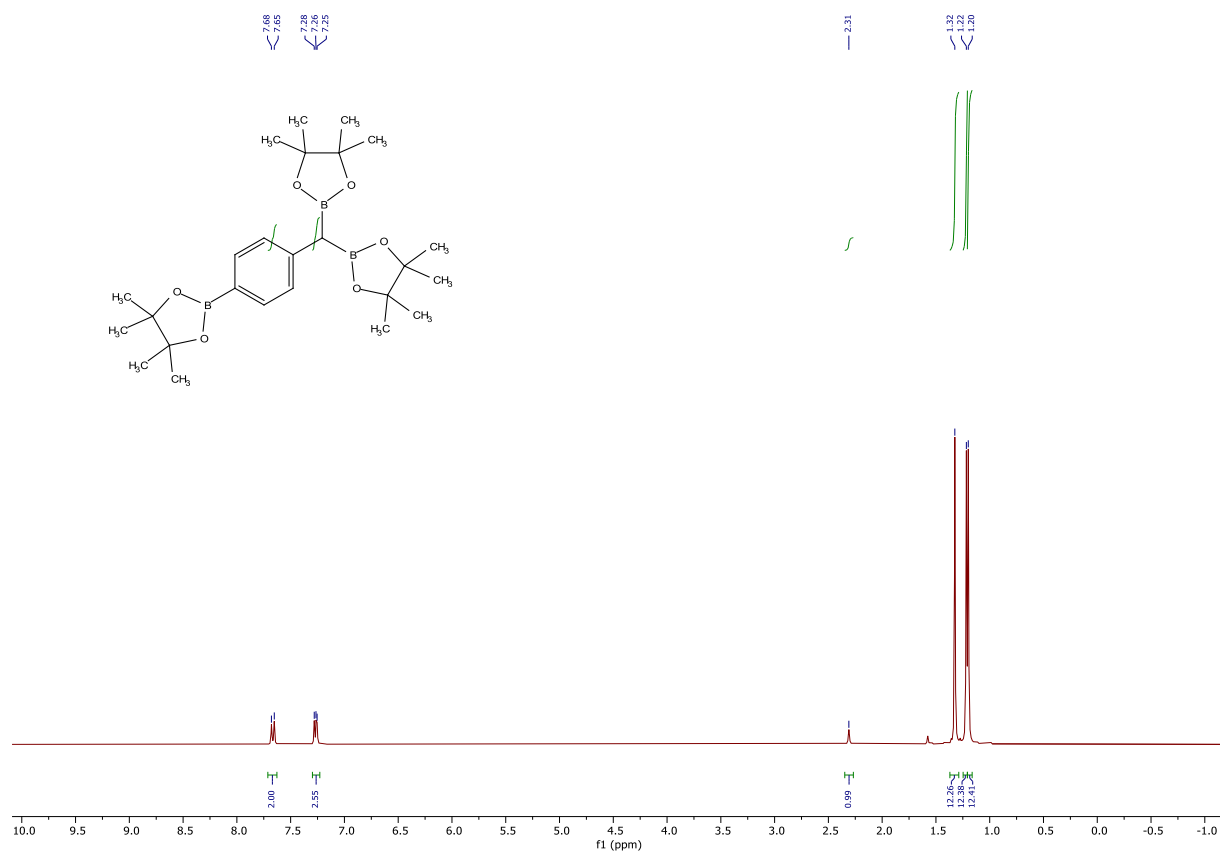


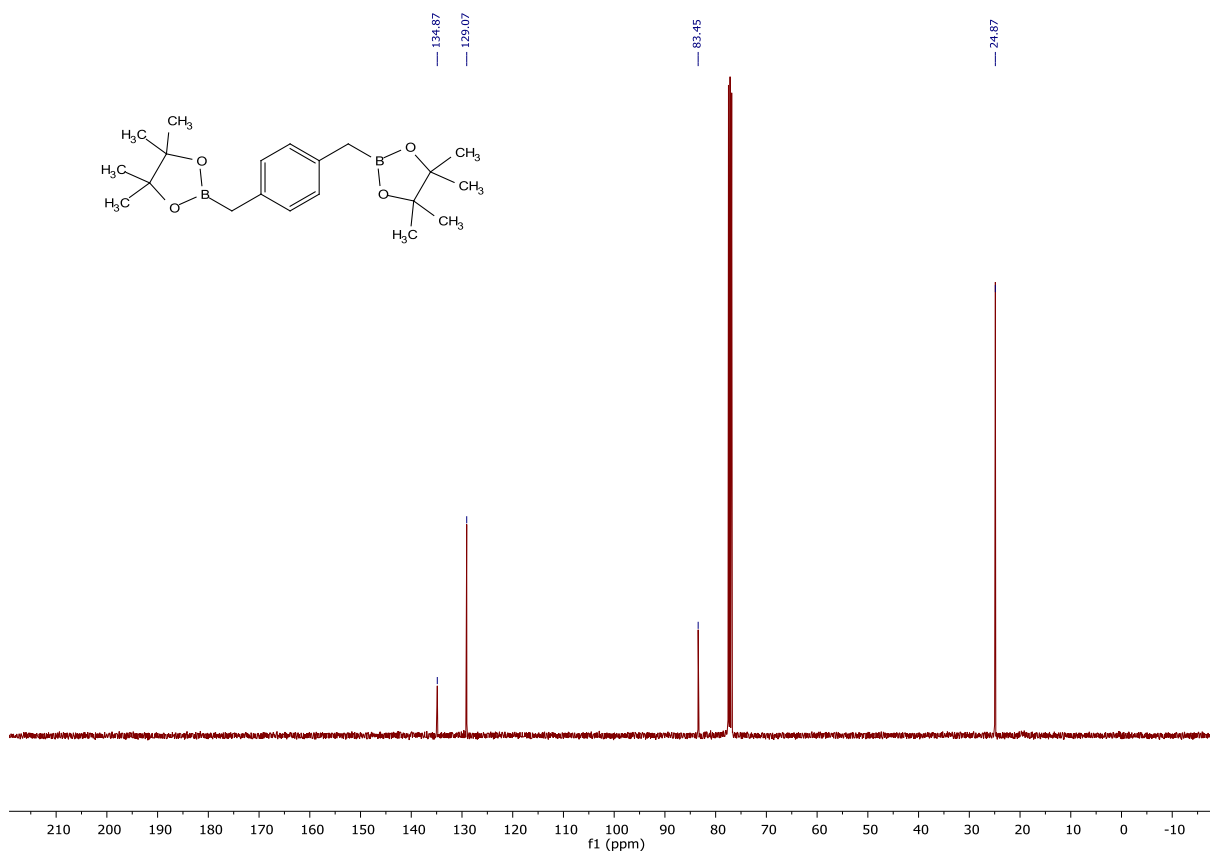
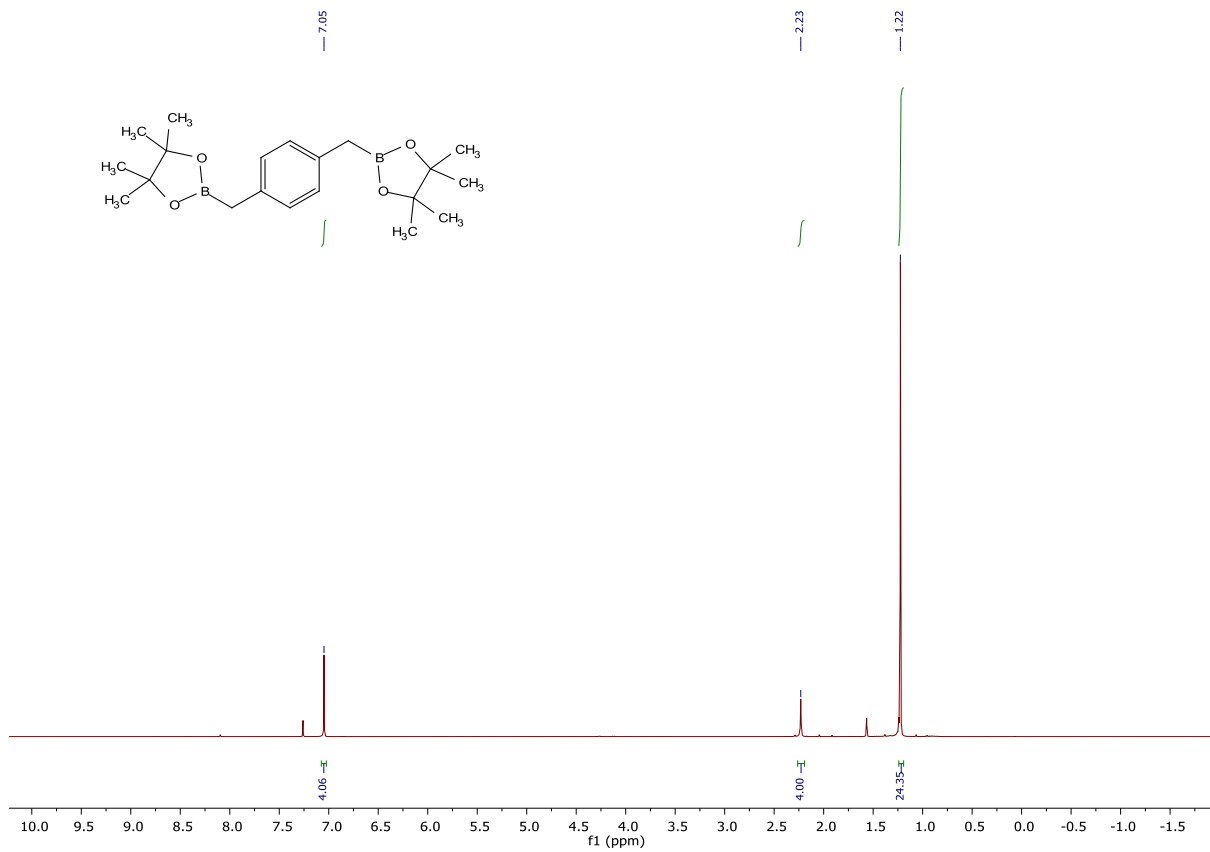


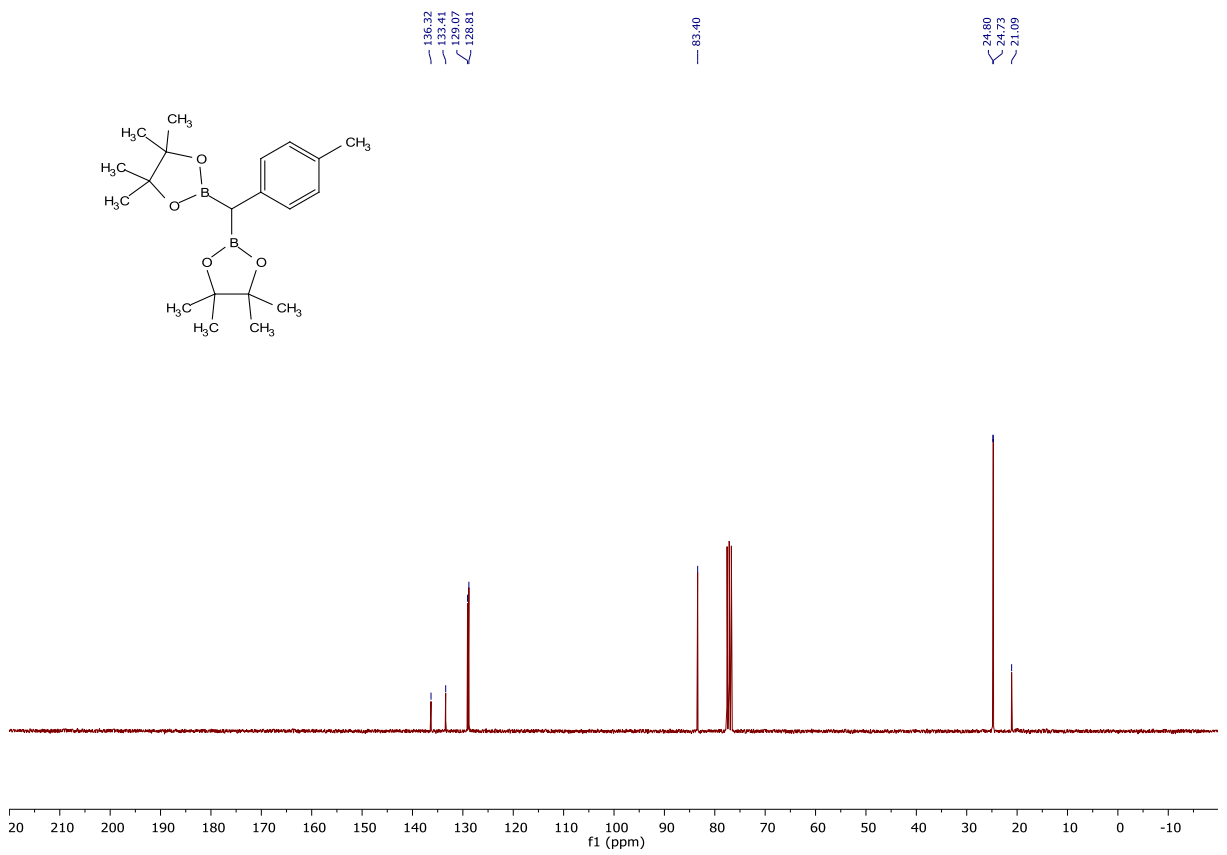
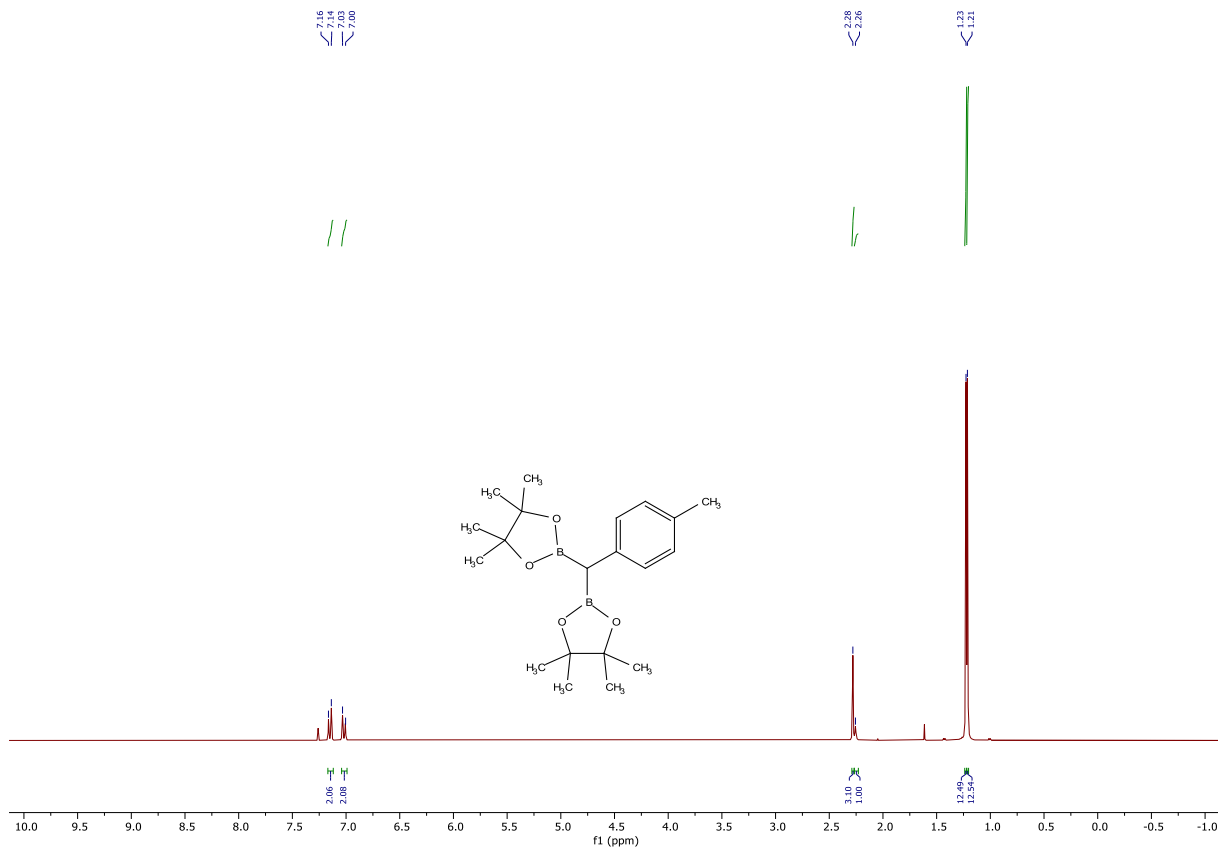


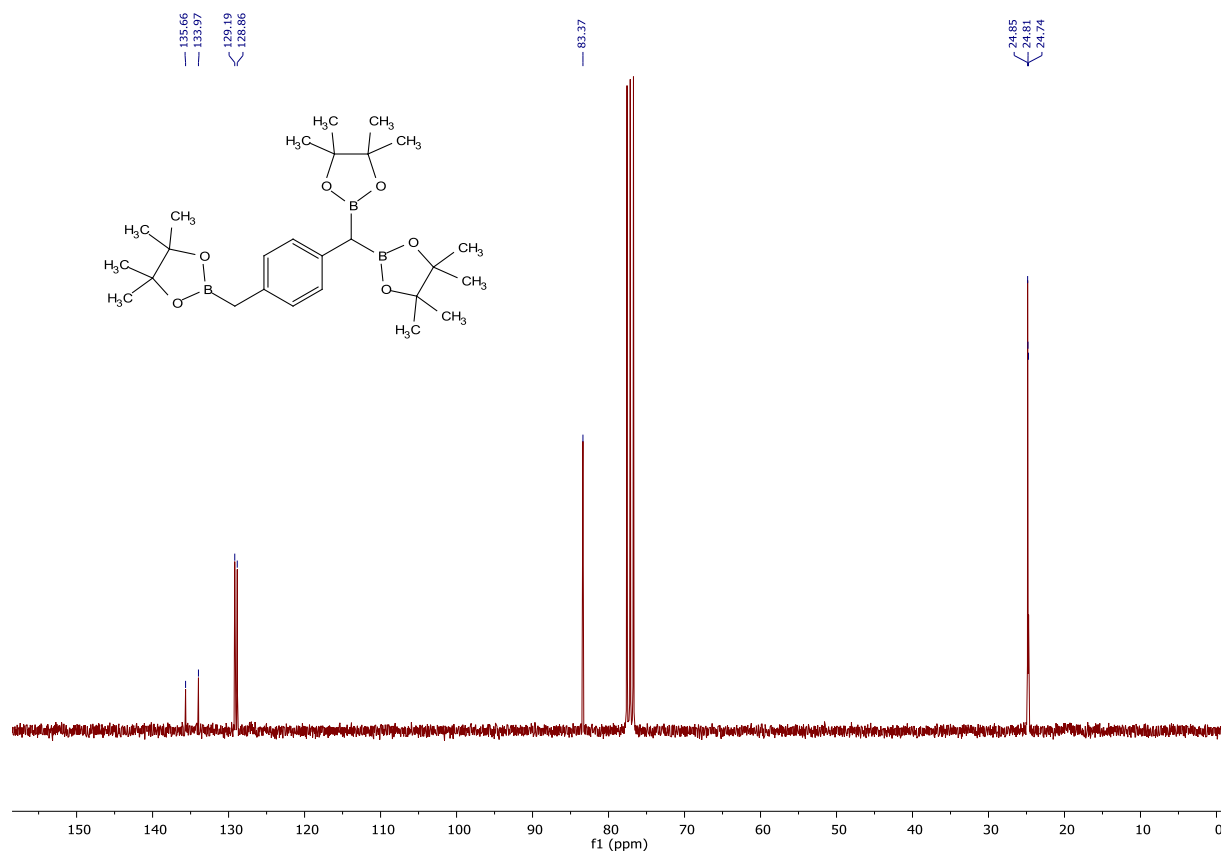
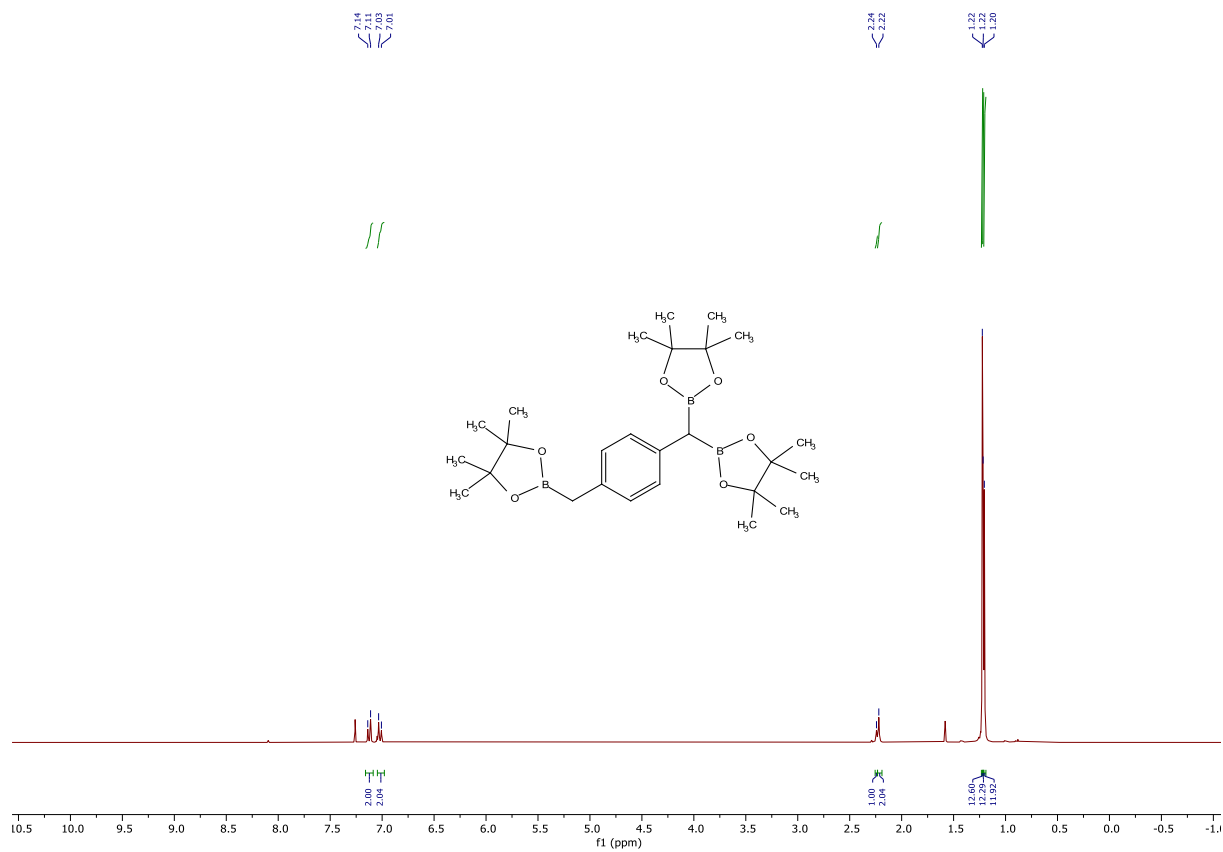


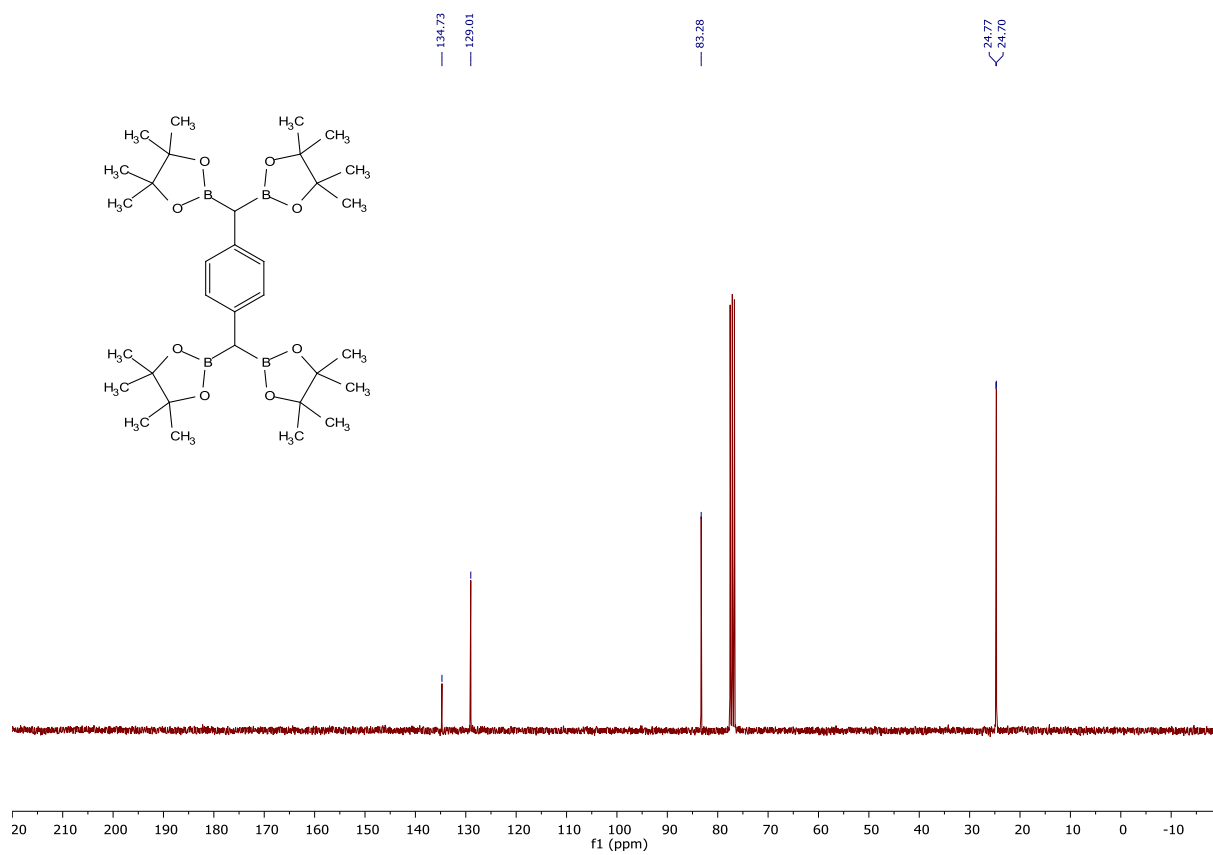
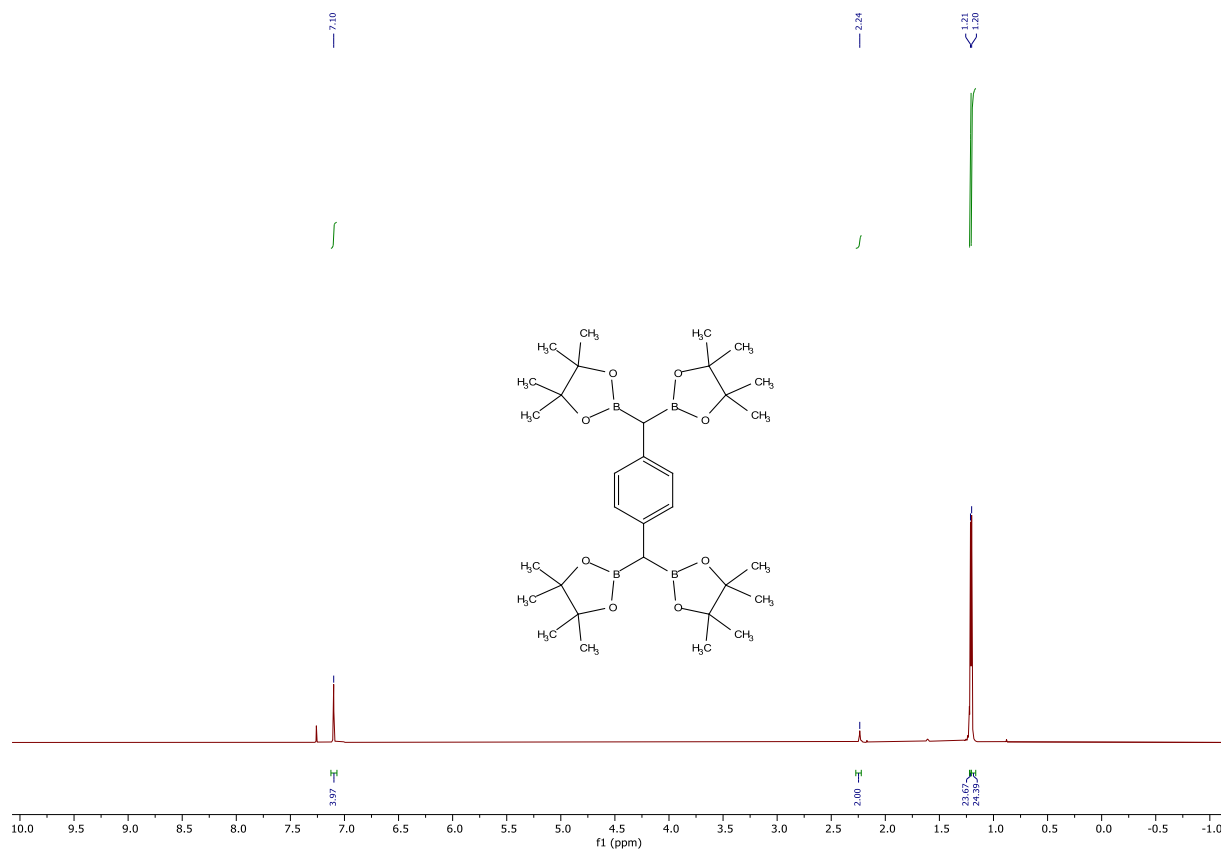


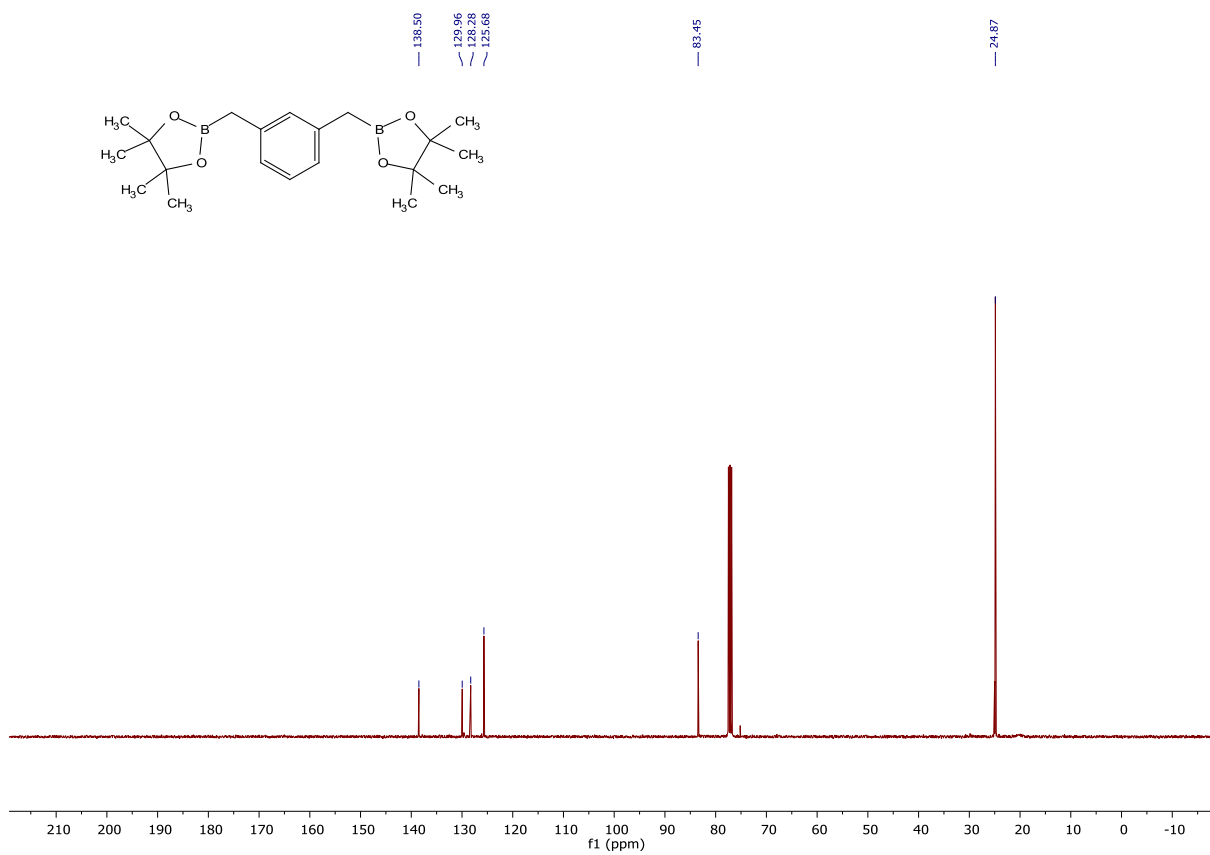
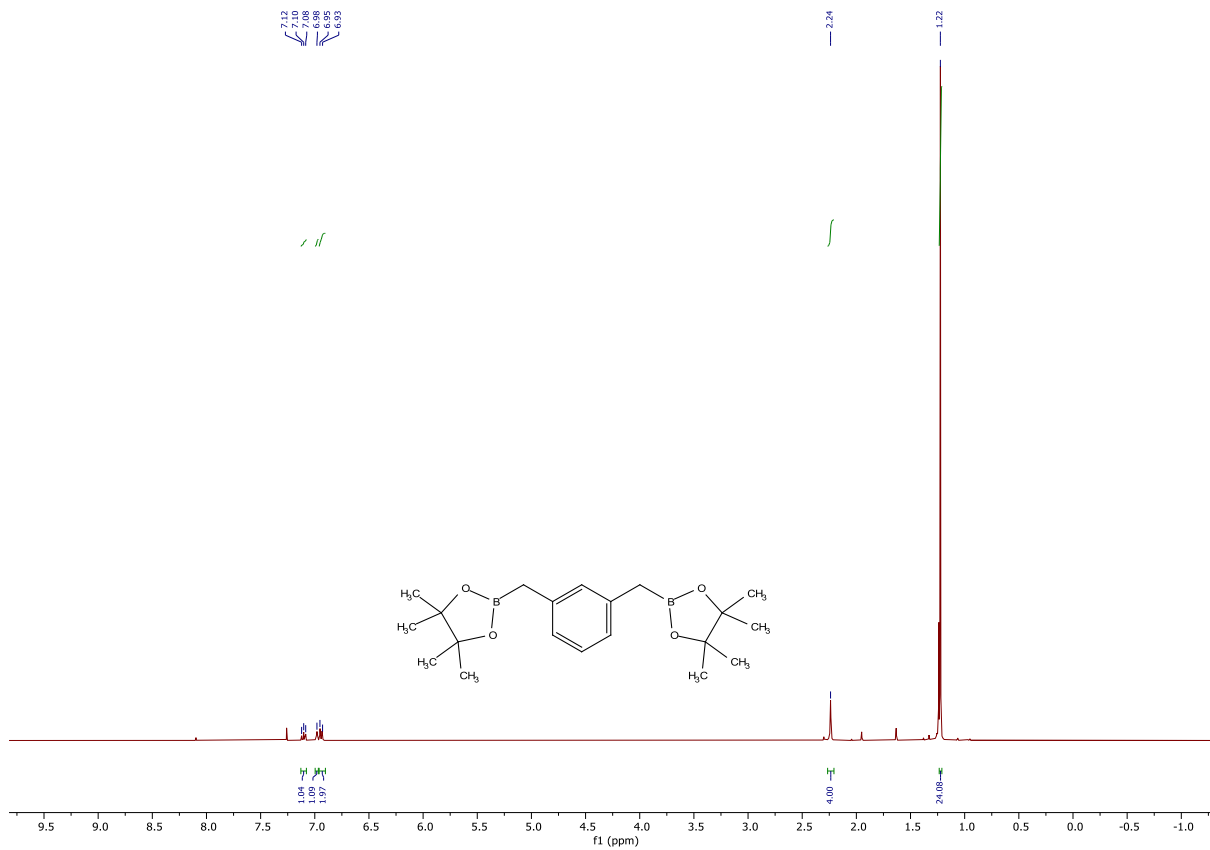


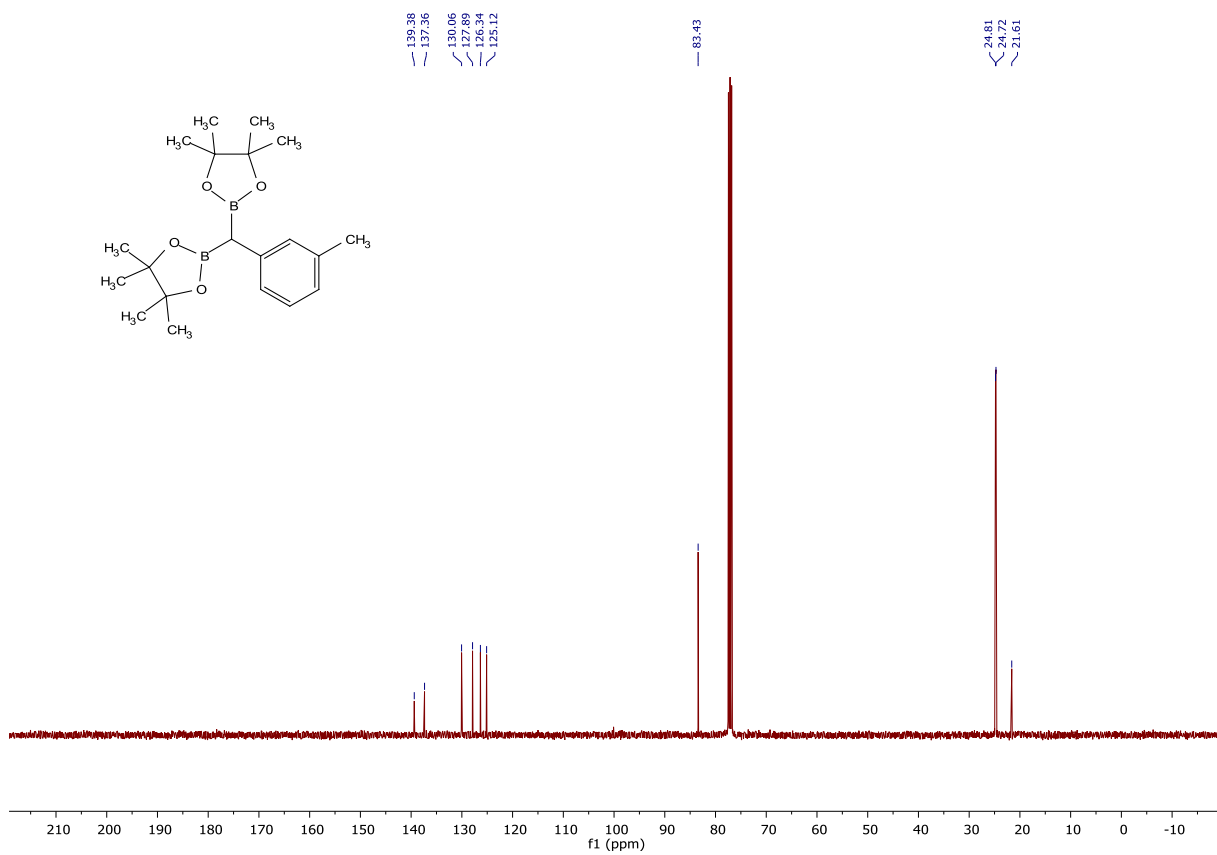
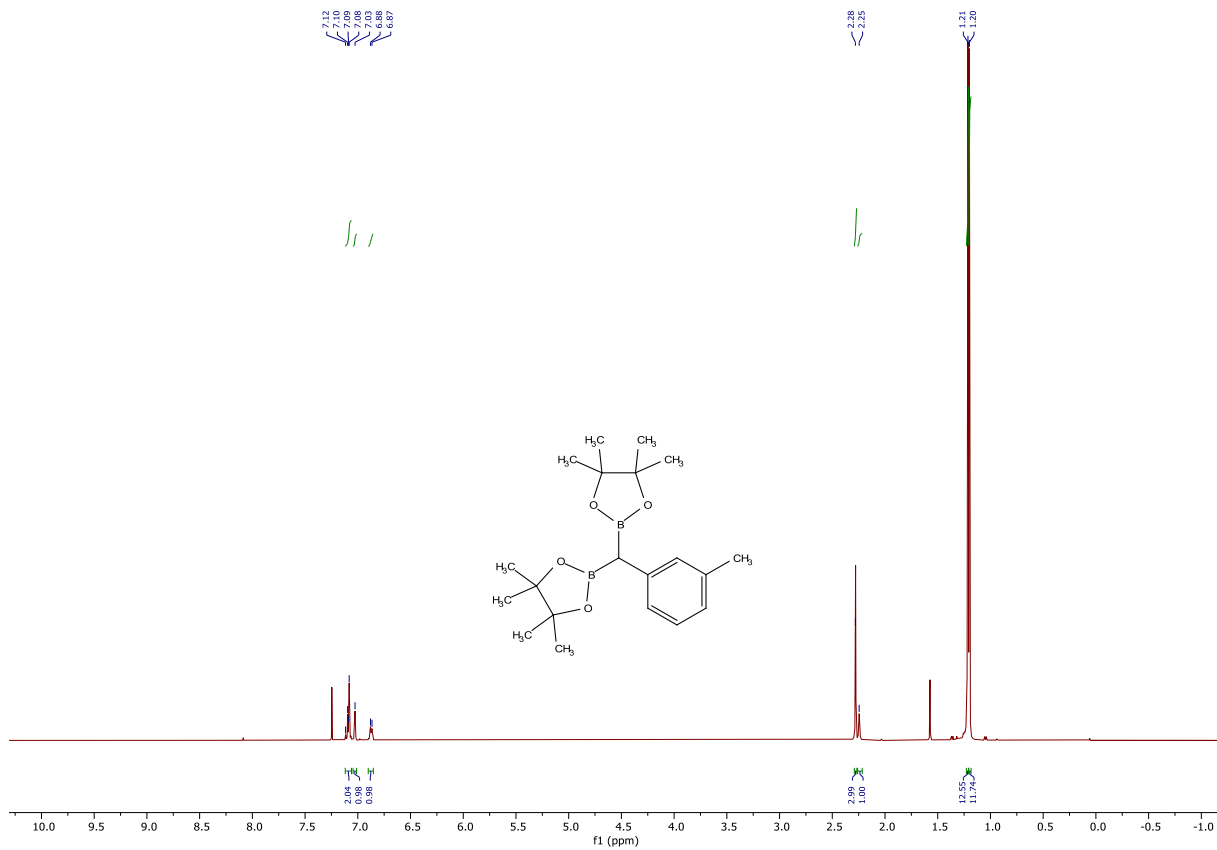


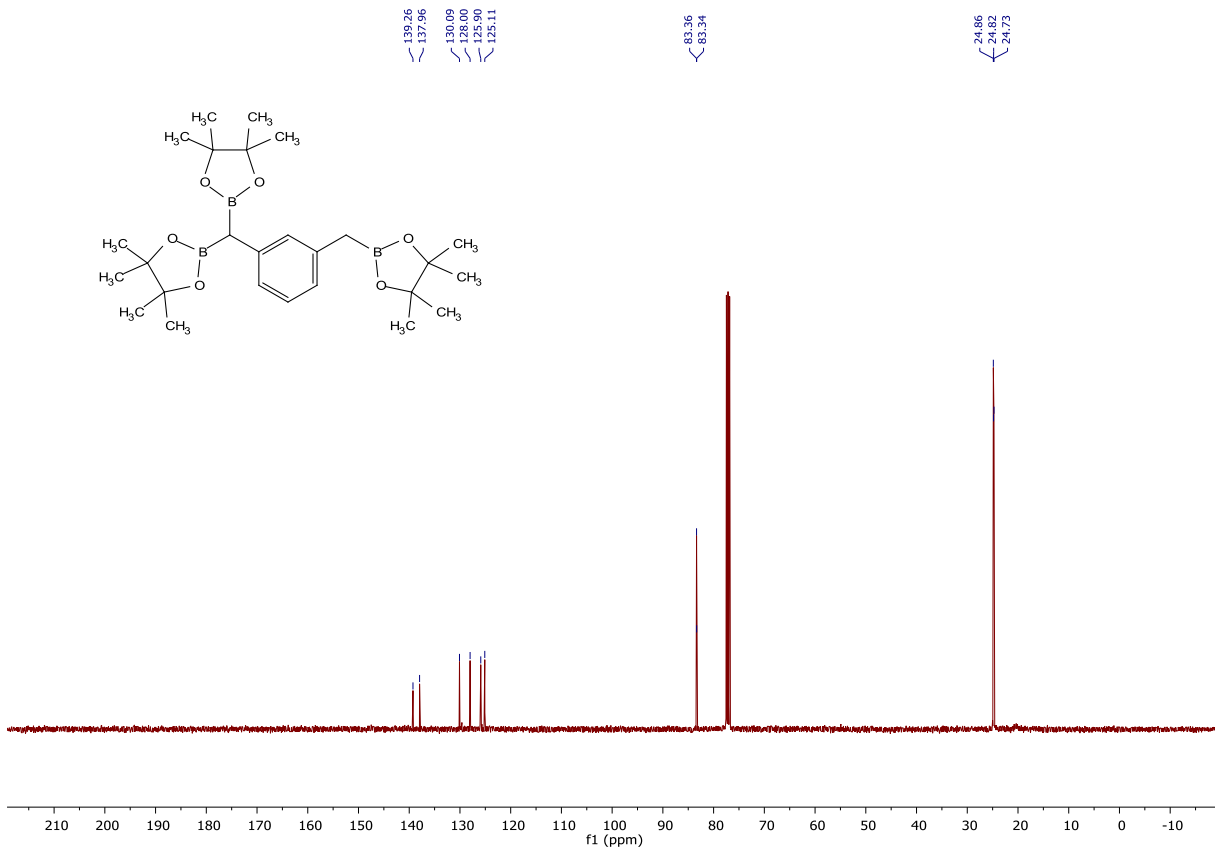
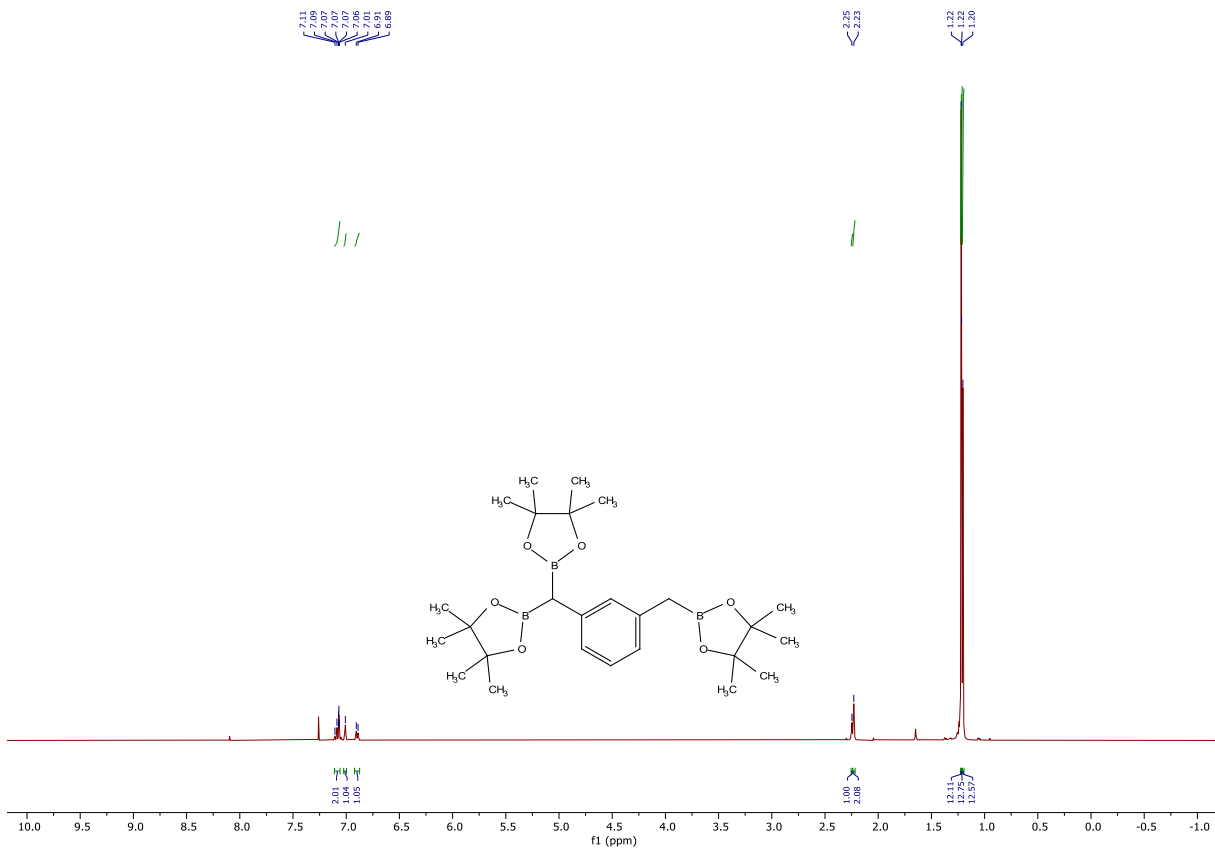


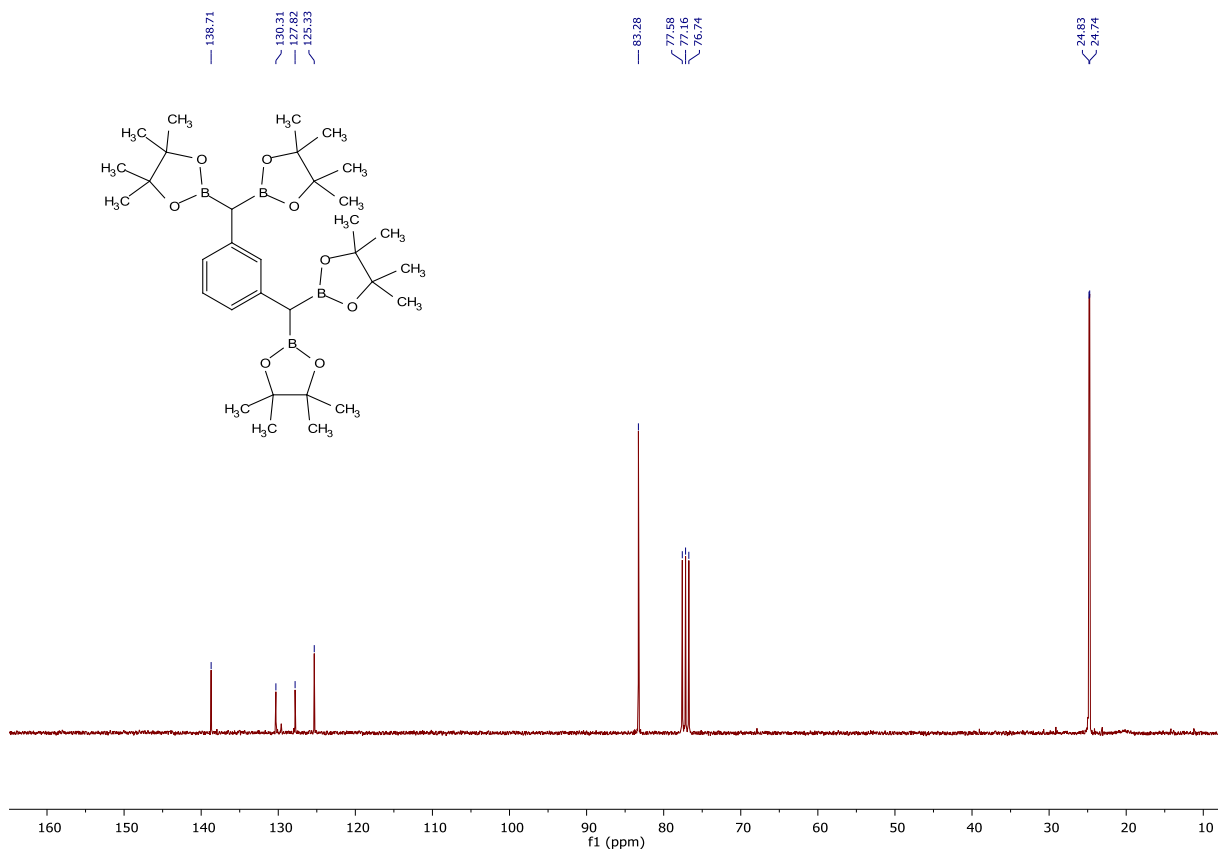
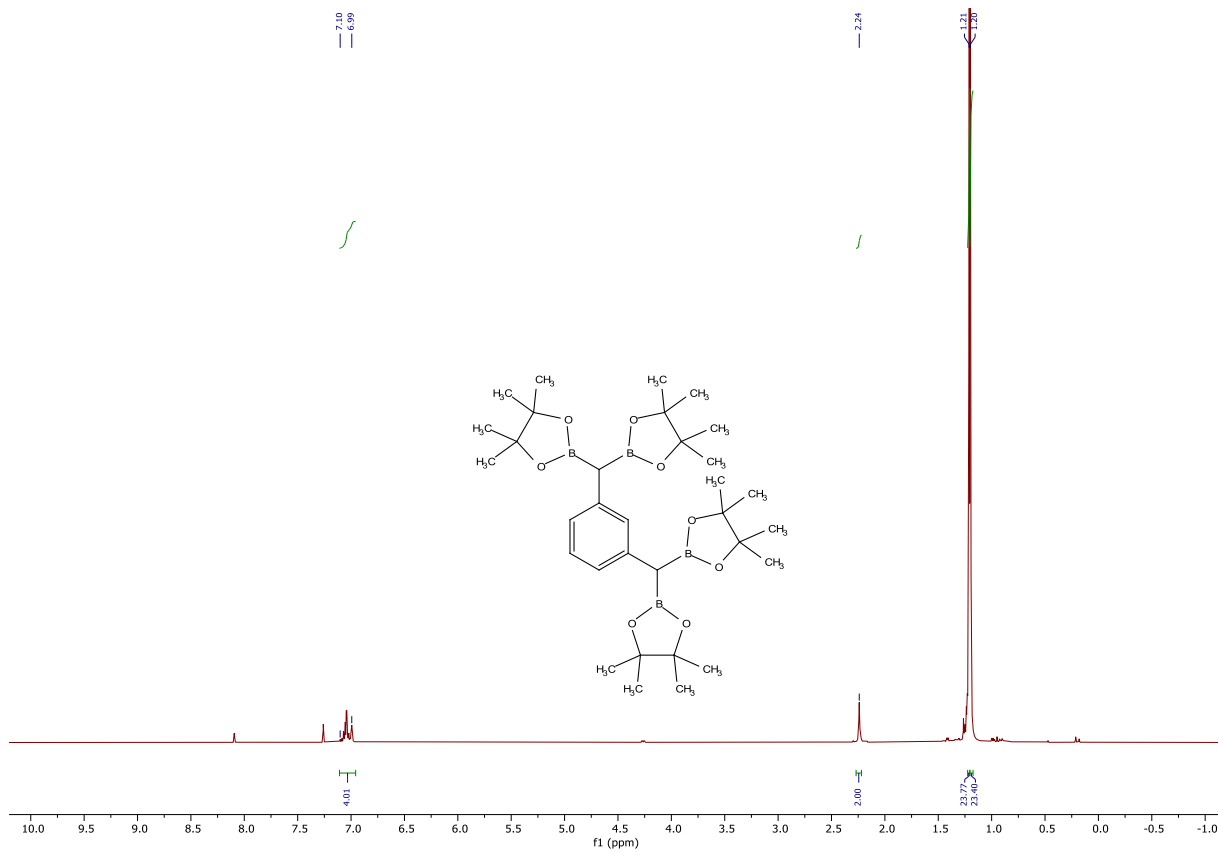


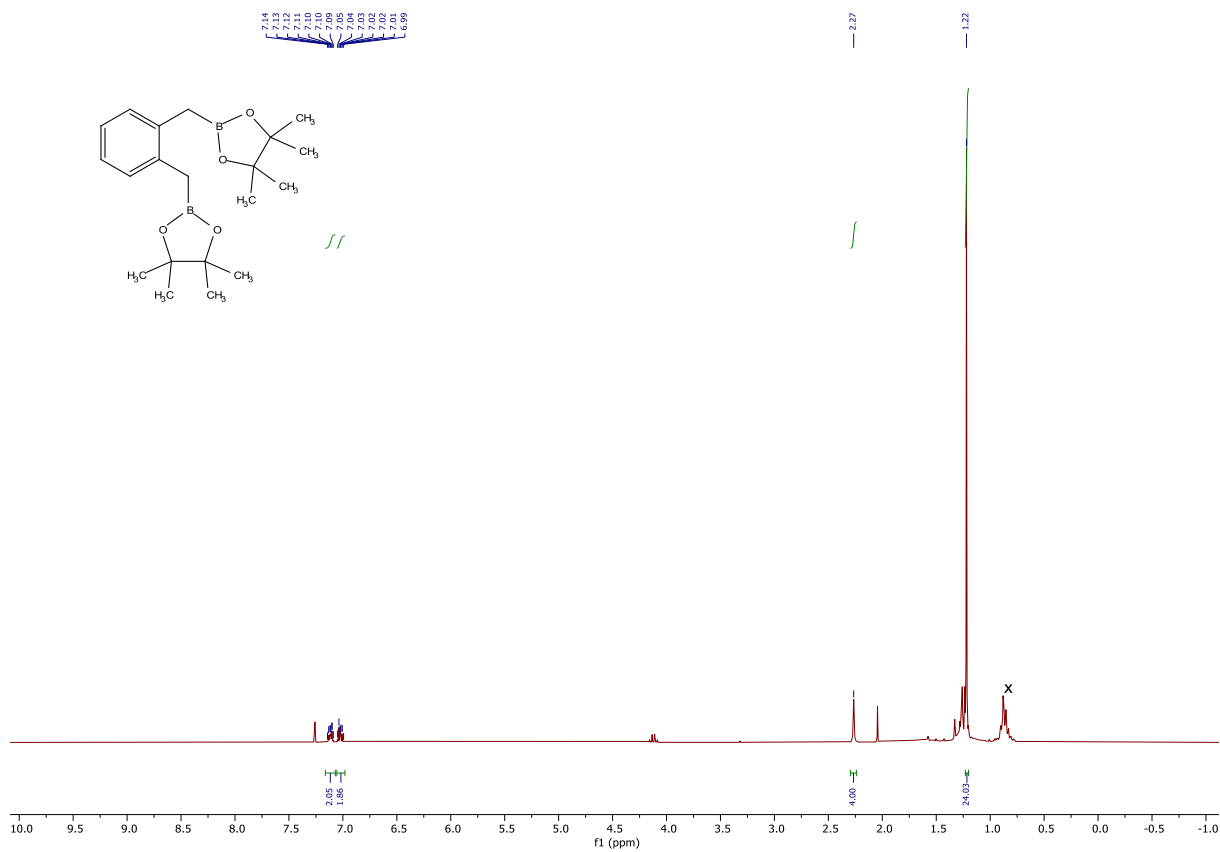




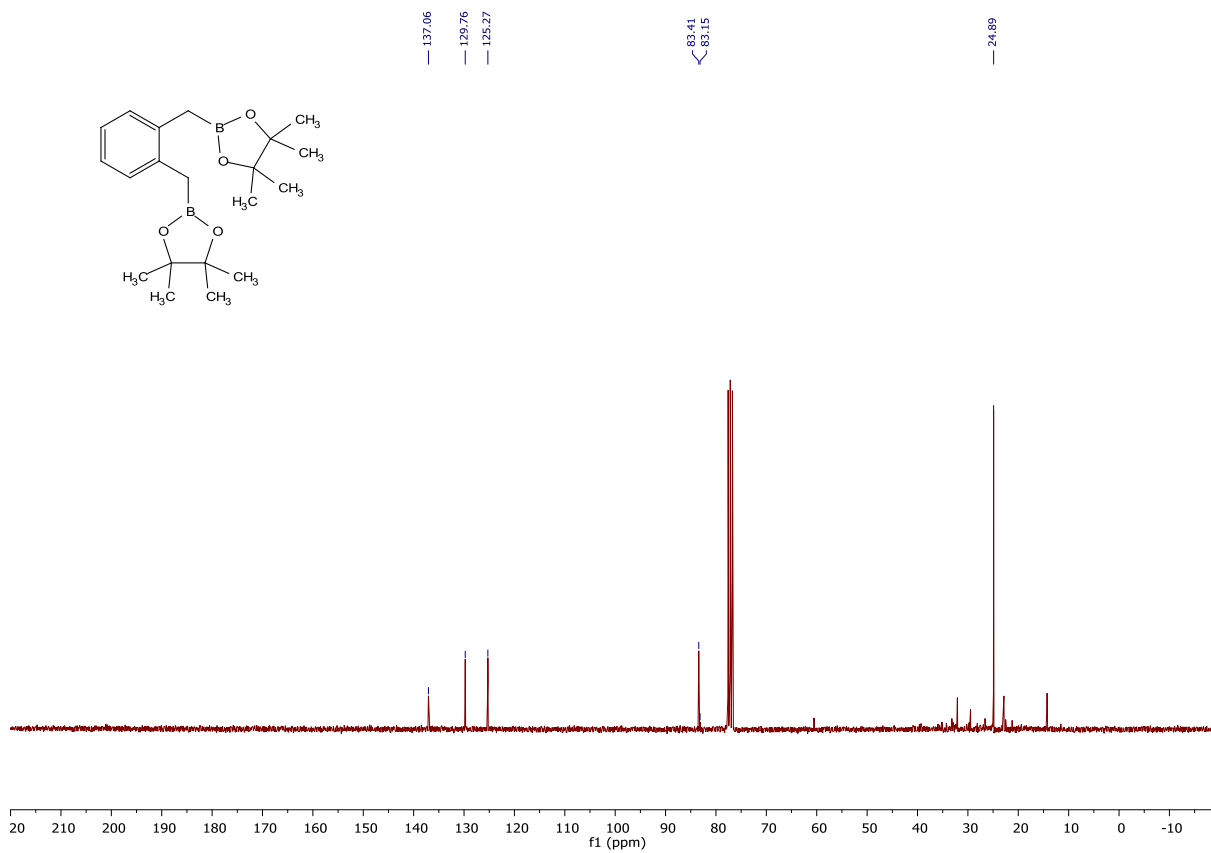


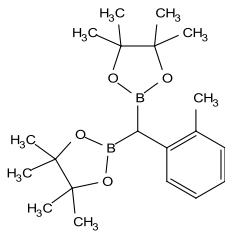
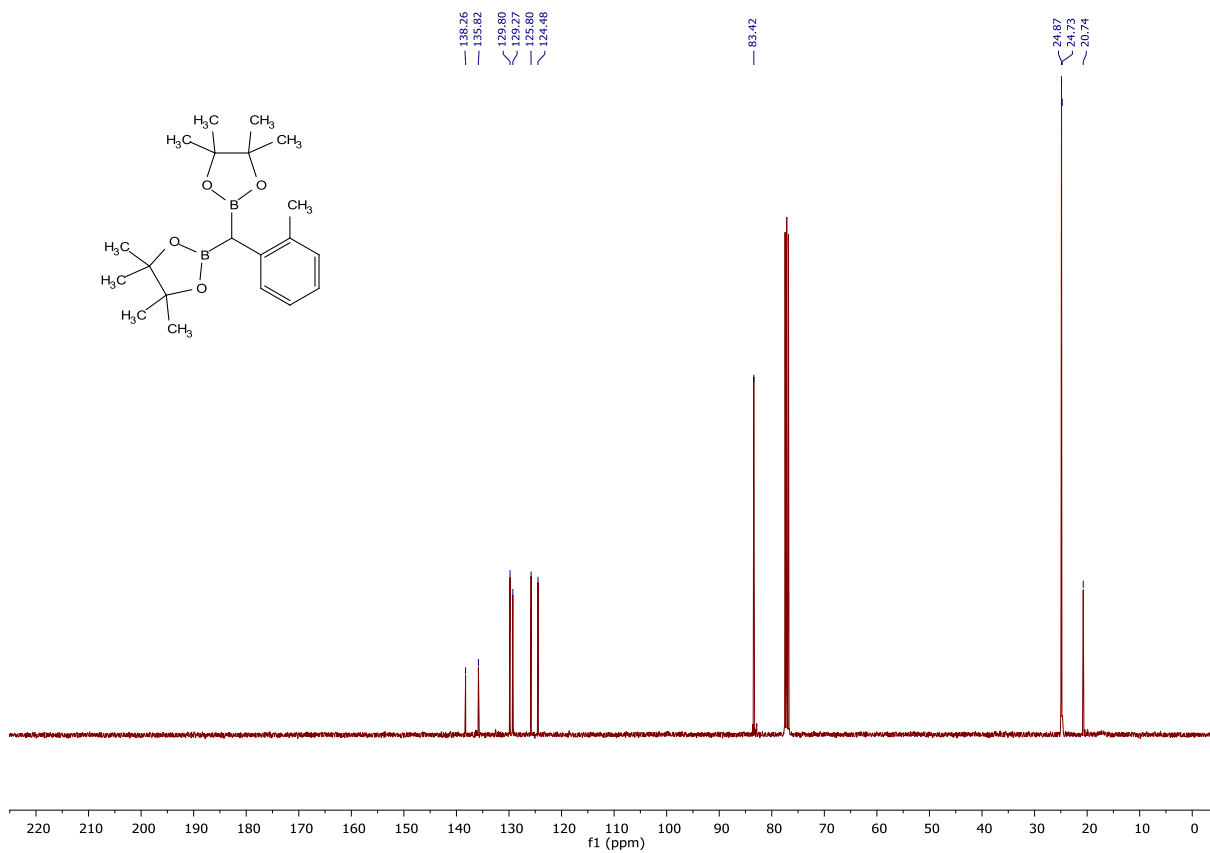
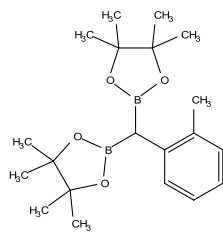
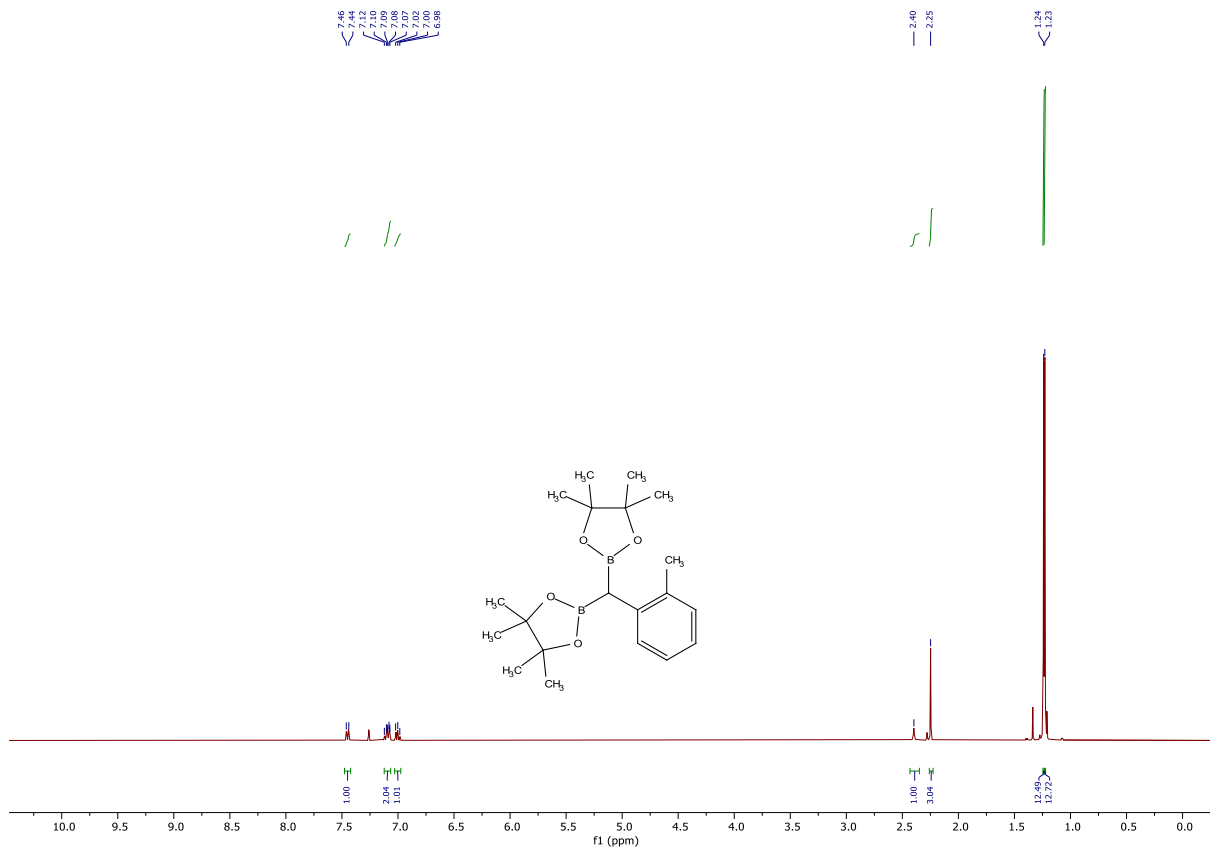


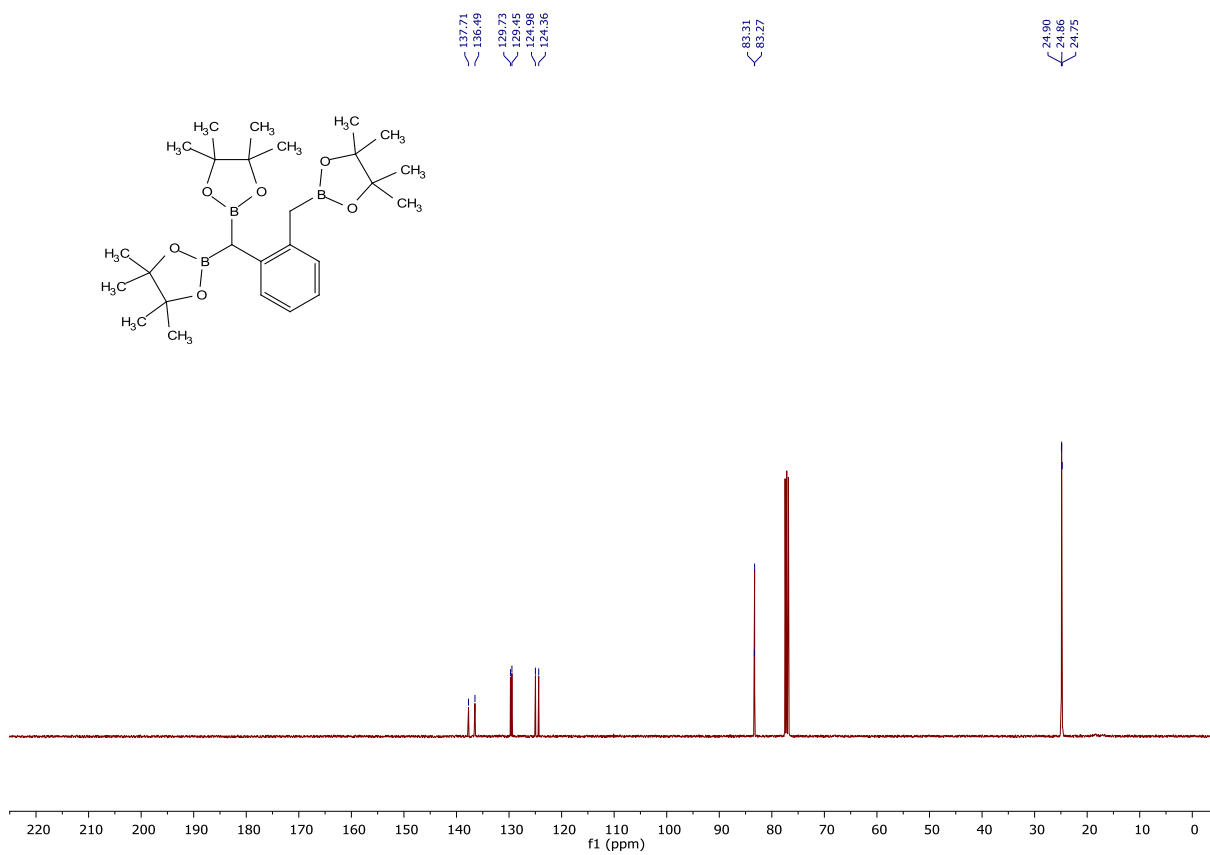
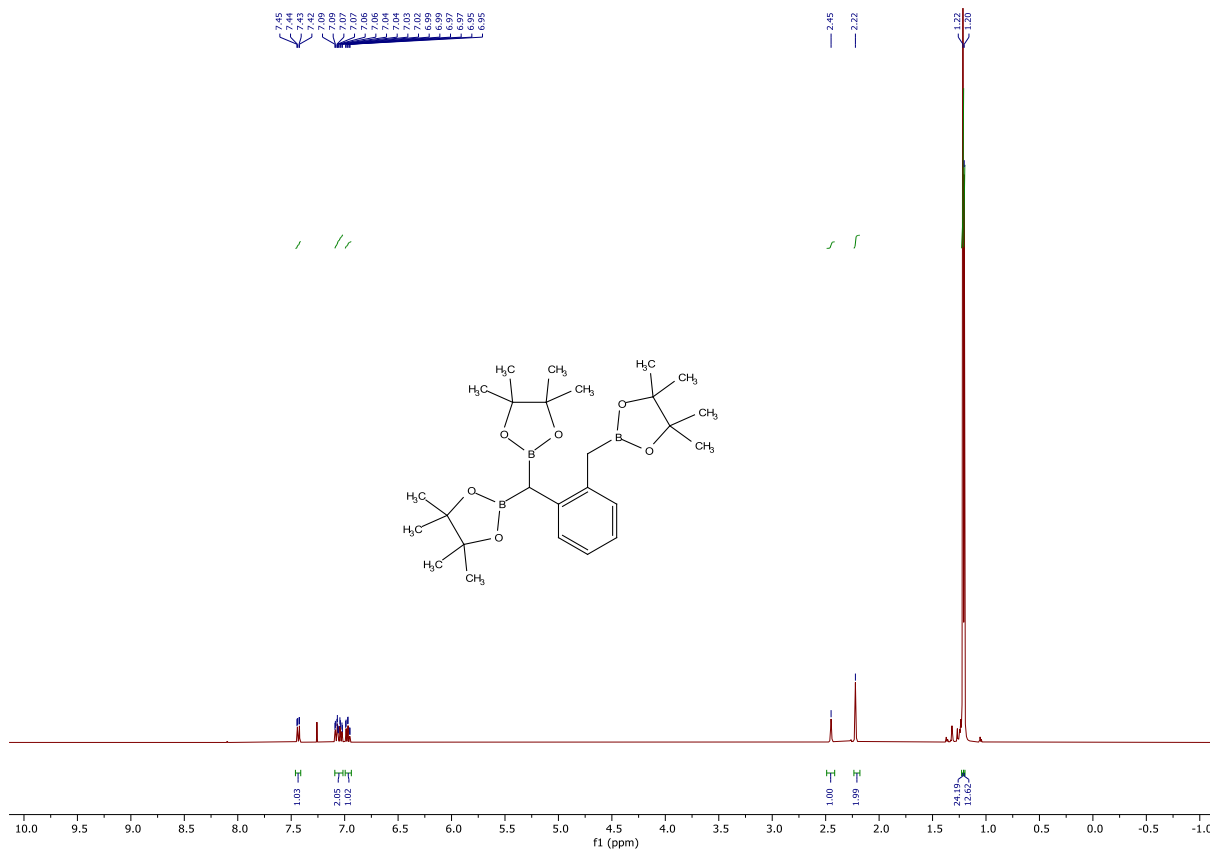


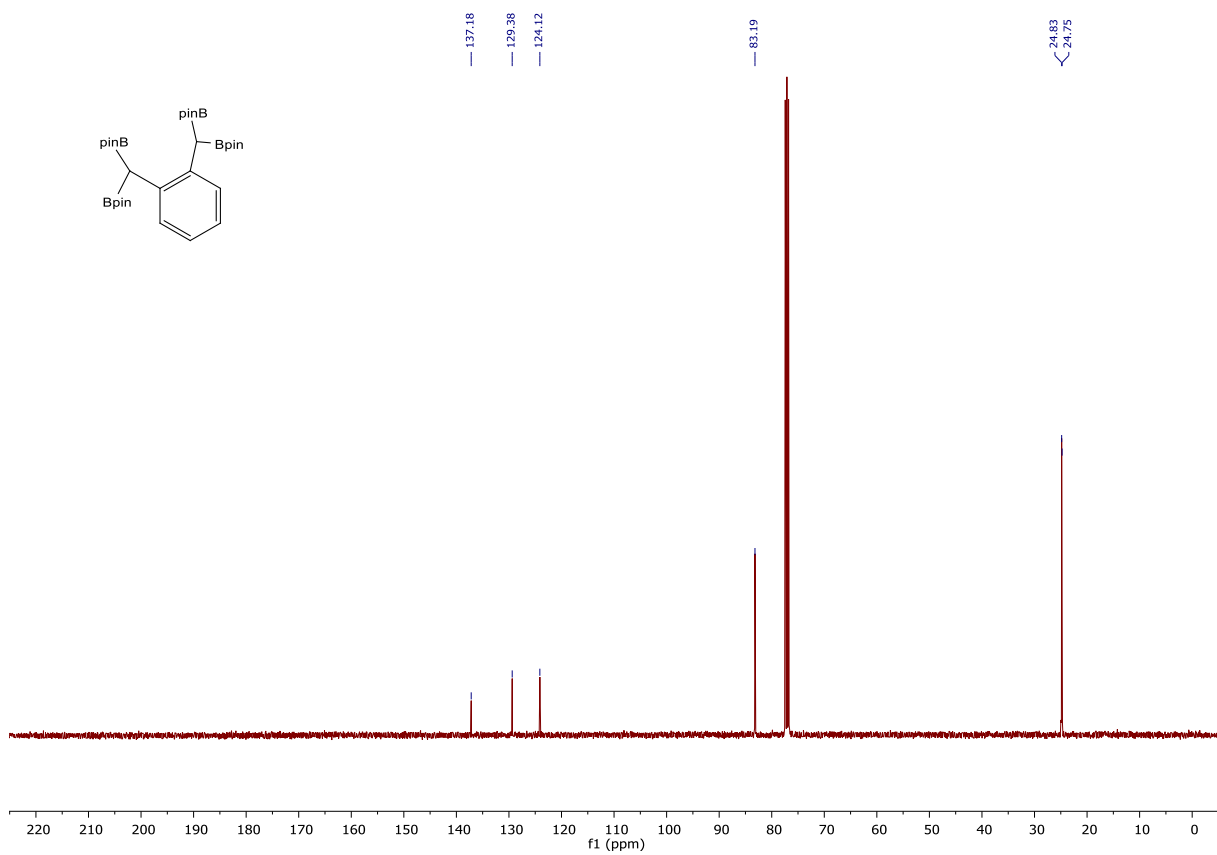
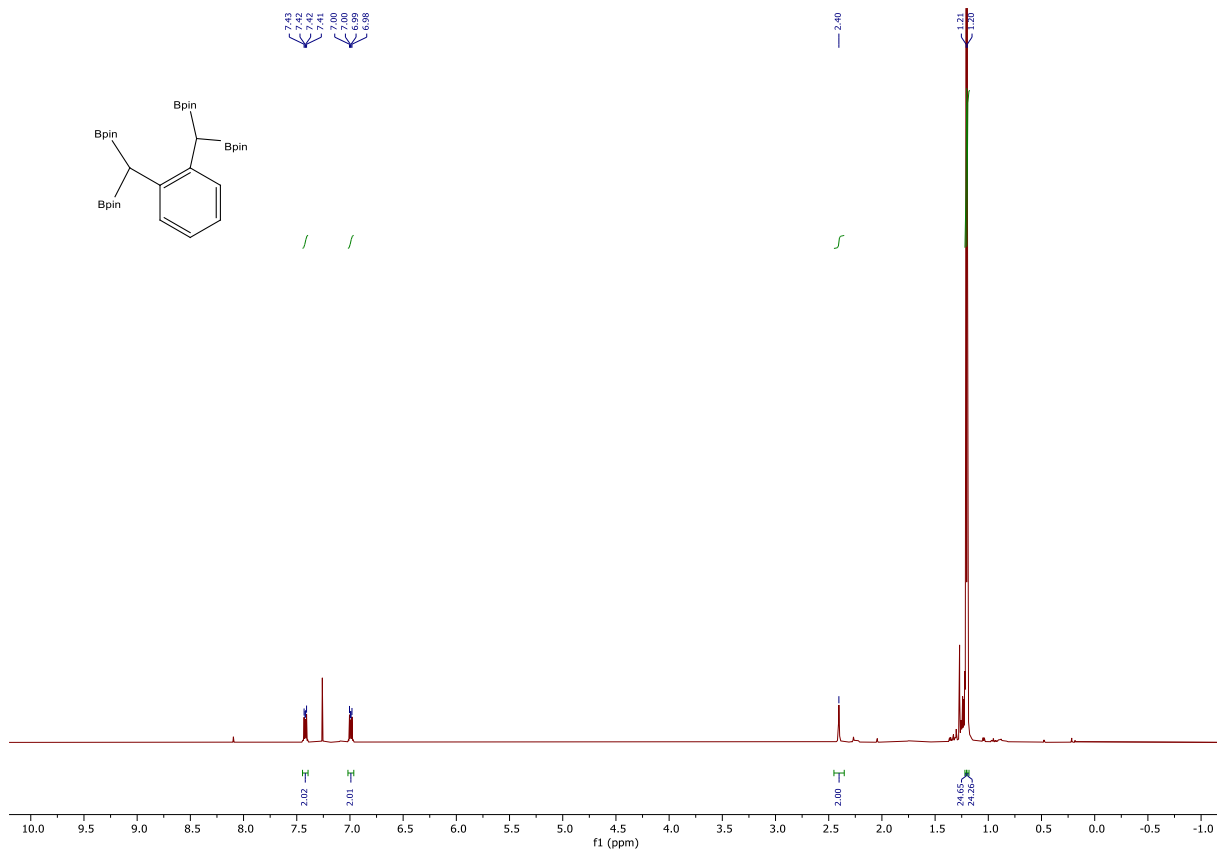


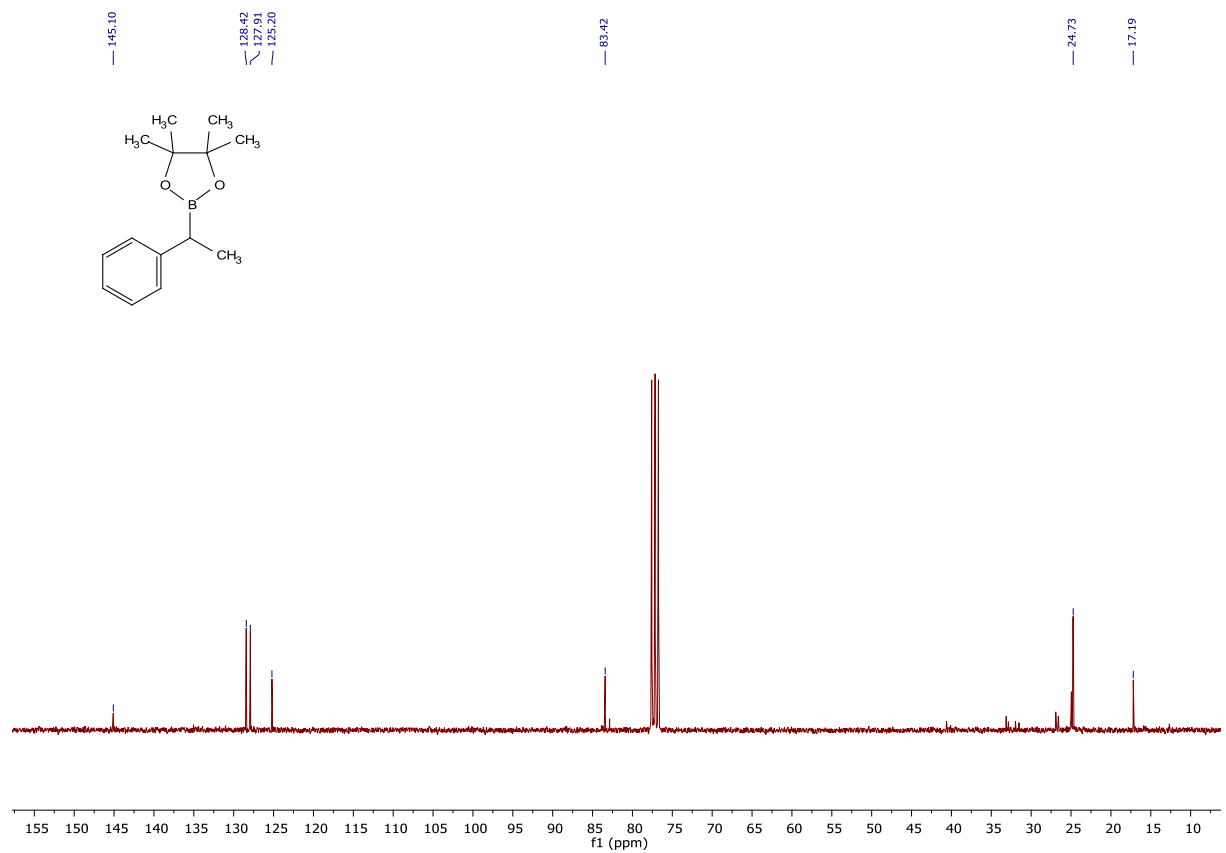
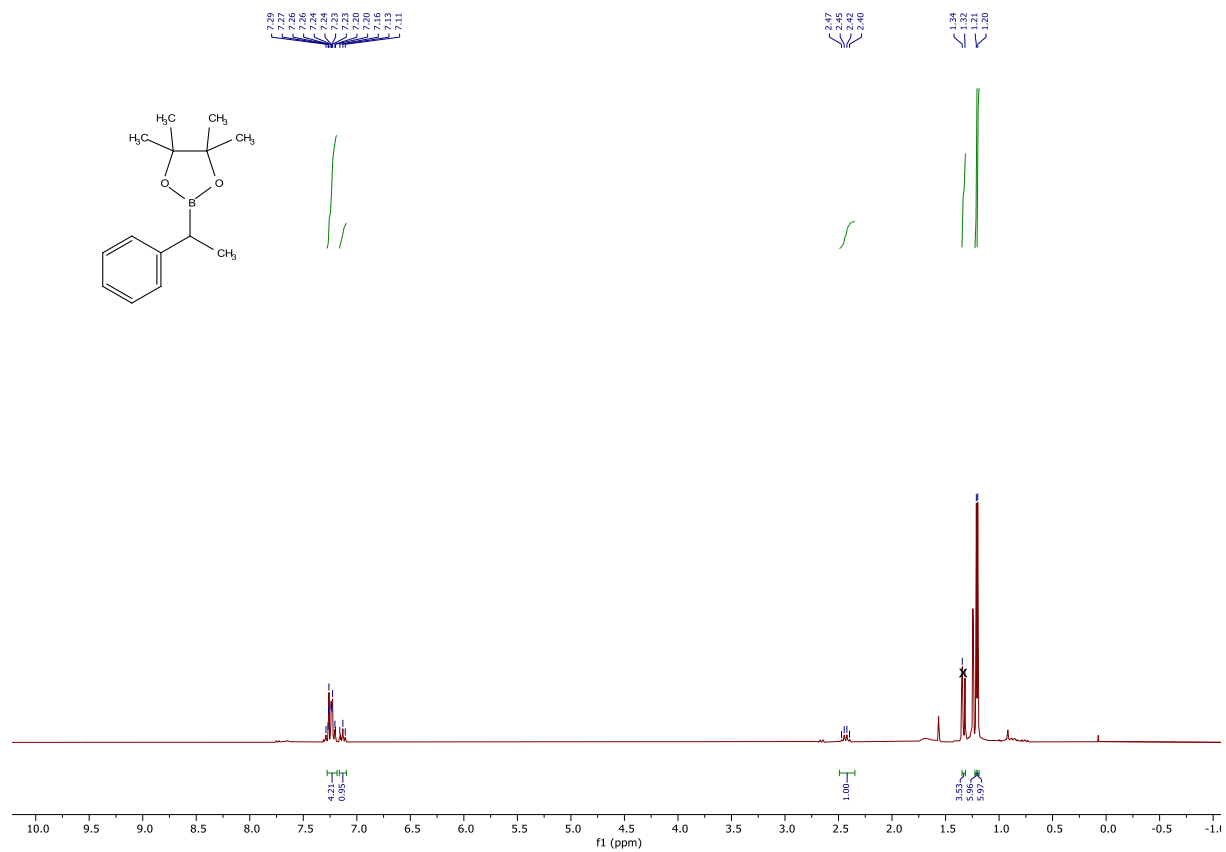
(x = impurity from pentane)

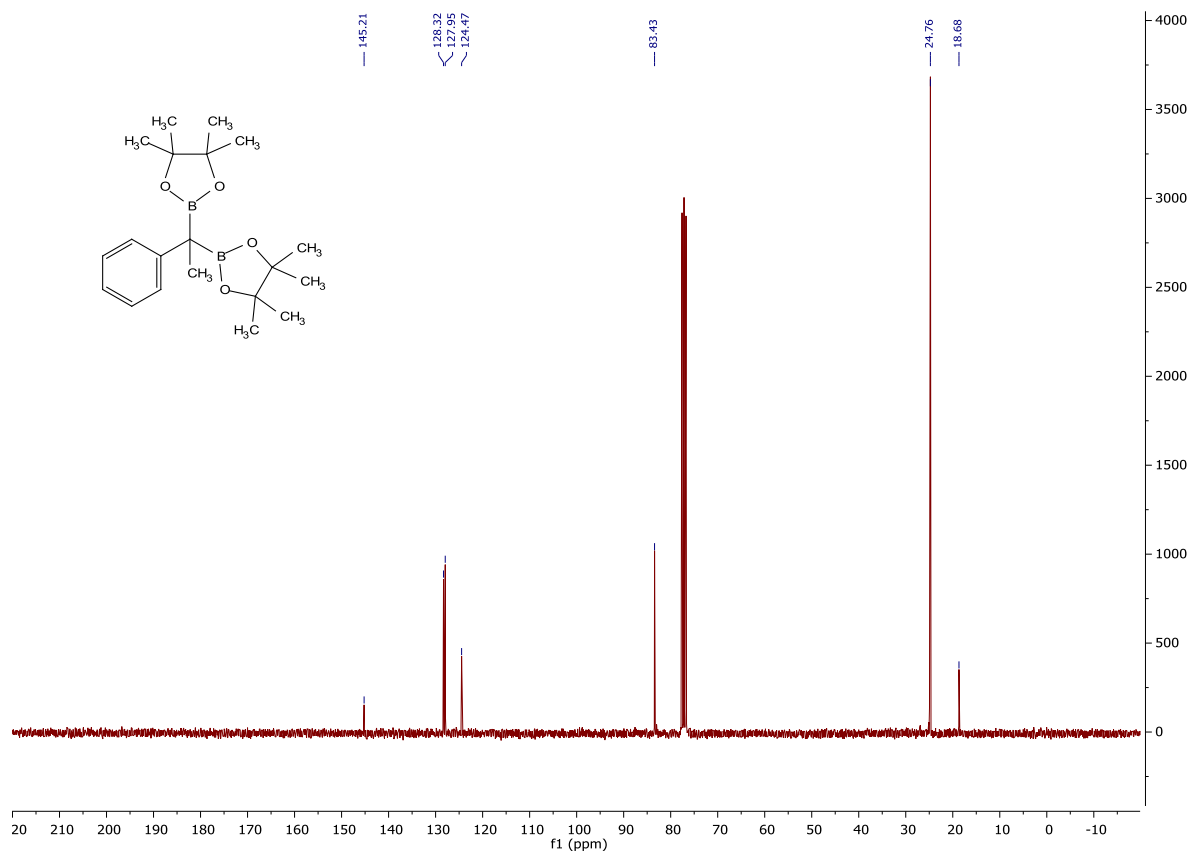
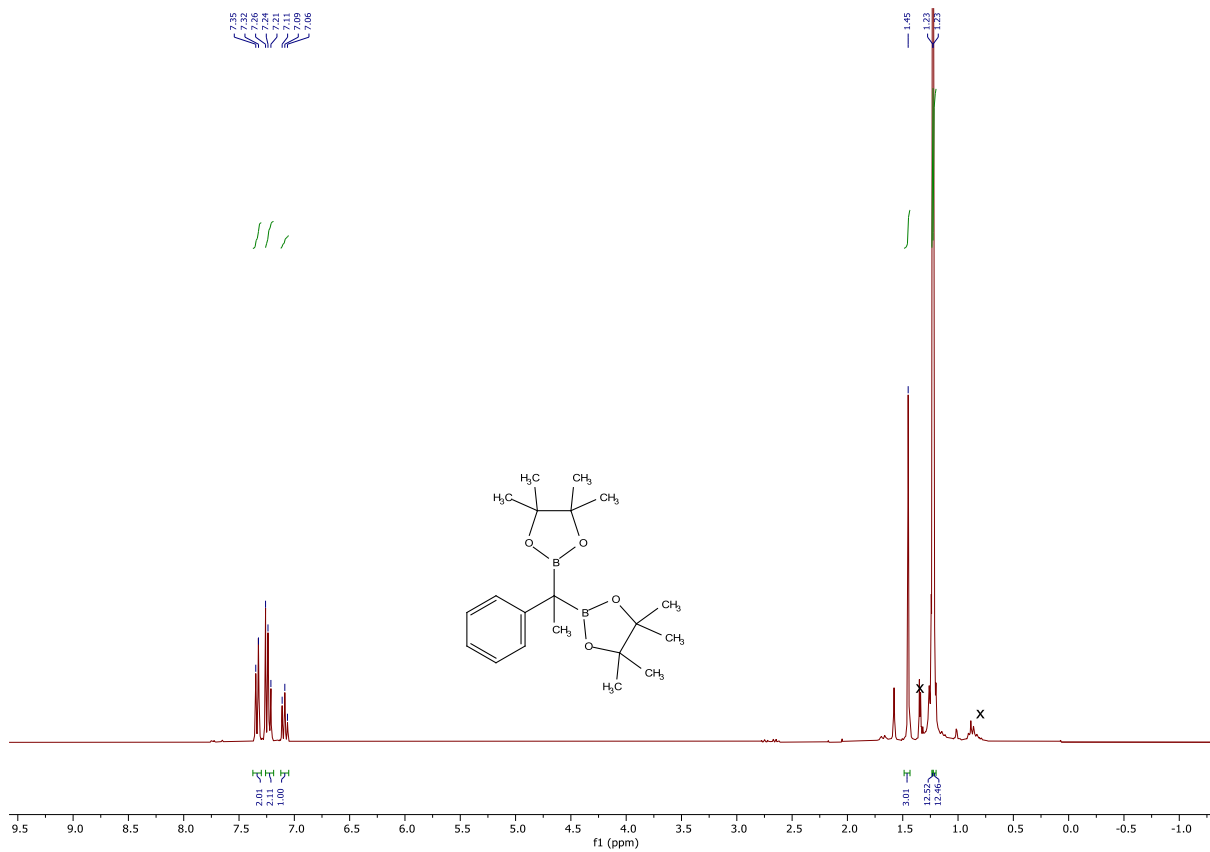


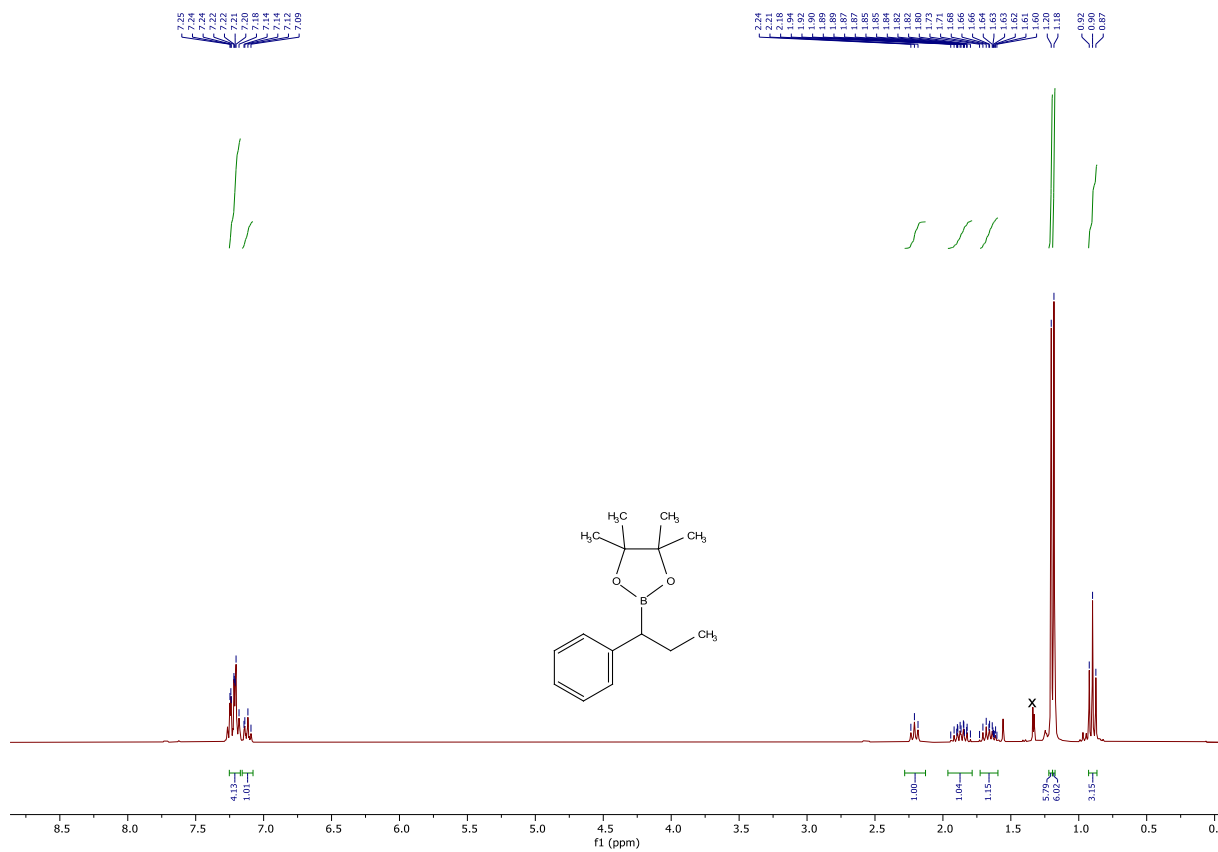












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