Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Transition-metal-free synthesis of vicinal triborated compounds and selective functionalisation of the internal C-B bond

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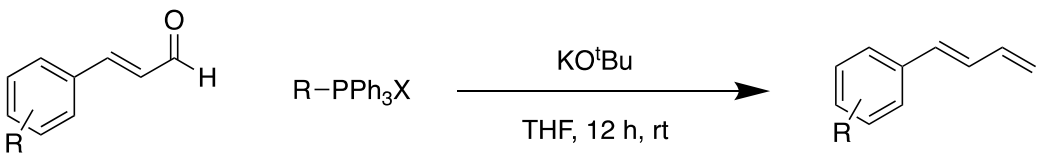
Content:

General Information

NMR spectra were recorded at 300K using a Varian Goku 400 (400 MHz) spectrometer or a Varian Mercury 400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: 7.26 ppm (^1H)) and ($CDCl_3$: 77.16 ppm (^{13}C)). $^{11}B\{^1H\}$ NMR chemical shifts (δ) are reported in ppm relative to $(CH_3CH_2)_2O$---BF_3. Data are reported as follows: chemical shift, multiplicity (d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. *High resolution mass spectra (HRMS)* were recorded using a 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies (Waldbronn, Germany) with an ESI interface and it was performed at the Servei de Recursos Científics i Tècnics (Universitat Rovira I Virgili, Tarragona) or using a BIOTOF II Time of Flight (TOF) mass spectrometer from Bruker with an APCI interface or an EI interface and it was performed at the Unidade de Espectrometria de Masas e Proteómica (Universidade de Santiago de Compostela, Santiago de Compostela). Solvents and reagents were obtained from commercial suppliers such as Sigma Aldrich or Alfa Aesar and used as received. All reactions were conducted in oven and flame-dried glassware under an inert atmosphere of argon, using Schlenk-type techniques. Flash chromatography was performed on standard silica gel (Merck Kieselgel 60 F_{254} 400-630 mesh) using standard visulaising agents: UV fluorescence (254 nm) and potassium permanganate/Δ. GC-MS analysis was performed on an HP6890 gas chromatograph with an Agilent Technologies 5973 Mass selective detector (Waldbronn, Germany) equipped with an achiral capillary column HP-5 (30 m, 0.25 mm, i.d., 0.25 μm thickness) using He as the carrier gas.

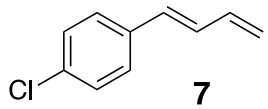
General procedure for the preparation of 1,3-dienes via Wittig olefination[1]



To a dry reaction vessel equipped with a magnetic stirrer bar, alkyl phosphonium bromide (3.75 mmol, 1.25 equiv) and potassium tert-butoxide (3.9 mmol, 1.3 equiv) were added. The flask was flushed with argon 3 times and dry THF (8 mL) was added slowly with stirring at room temperature. The mixture was left for 30 minutes before the corresponding aldehyde, dissolved in dry THF (4 mL), was added dropwise over 10 minutes at room temperature. The mixture was then left to stir for 16 hours. The reaction was quenched with aqueous saturated ammonium chloride solution (25 mL). The aqueous layer was then extracted three times with diethyl ether before the combined organic extracts were washed with brine and dried over sodium sulphate. After filtration, the volatile components were removed under reduced pressure. The crude residue was purified by silica gel flash chromatography to afford the diene product.

<u>Spectral data of 1,3-dienes:</u>

(*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (7)



7

The product was synthesised according to the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol) and *trans*-4-chlorocinnamaldehyde (499.8 mg, 3 mmol). The product was purified by flash column chromatography using pentane:ethyl acetate (40:1) as eluent. The product **7** was obtained as an orange oil (2.44 mmol, 81.4%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.15 (m, 4H), 6.74 – 6.60 (m, 1H), 6.49 – 6.34 (m, 2H), 5.31 – 5.22 (d, *J* = 16.2 Hz, 1H), 5.12 (d, *J* = 9.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.9, 135.7, 133.2, 131.5, 130.2, 128.8, 127.6, 118.2.

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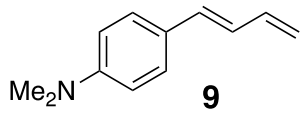
1. S. R. Sardini, M. K. Brown, *J. Am. Chem. Soc.*, 2017, **139**, 9823.

(*E*)-4-(buta-1,3-dien-1-yl)-*N*,*N*-dimethylaniline (9)



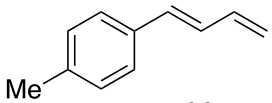
9

The product was synthesised according to the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol) and *trans*-4-(dimethylamino)cinnamaldehyde (525.7 mg, 3 mmol). The product was purified by flash column chromatography using pentane:ethyl acetate (10:1) as eluent. The product **9** was obtained as a yellow solid (2.80 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.28 (m, 2H), 6.73 – 6.58 (m, 1H), 6.56 – 6.43 (m, 2H), 5.24 (d, *J* = 17.4 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 2.97 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.1, 137.8, 133.1, 127.5, 125.6, 125.6, 115.0, 112.4, 40.5.

(*E*)-1-(buta-1,3-dien-1-yl)-4-methylbenzene (11)



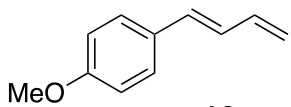
11

The product was synthesised according to the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol) and *trans*-4-methylcinnamaldehyde (438.57 mg, 3 mmol). The product was purified by flash column chromatography using pentane as eluent. The product **11** was obtained as a yellow liquid (2.06 mmol, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.68 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.52 – 6.36 (m, 2H), 5.23 (d, *J* = 16.5 Hz, 1H), 5.07 (d, *J* = 9.7 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.6, 137.3, 134.3, 132.8, 129.4, 128.7, 126.4, 117.1, 21.3.

(*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (13)



13

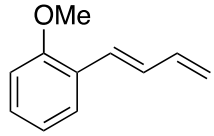
The product was synthesised according to the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol) and trans-*p*-methoxycinnamaldehyde

(486.57 mg, 3 mmol). The product was purified by flash column chromatography using pentane:ethyl acetate (4:1) as eluent. The product **13** was obtained as a colourless oil (2.82 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.60 (dd, *J* = 15.4, 10.6 Hz, 1H), 6.49 – 6.34 (m, 2H), 5.21 (d, *J* = 15.4 Hz, 1H), 5.05 (d, *J* = 9.2 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.3, 137.4, 132.4, 129.9, 127.7, 116.5, 114.1, 55.3.

(*E*)-1-(buta-1,3-dien-1-yl)-2-methoxybenzene (15)



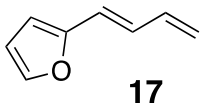
15

The product was synthesised according to the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol) and 2-methoxycinnamaldehyde (486.6 mg, 3 mmol). The product was purified by flash column chromatography using pentane:ethyl acetate (30:1) as eluent. The product **15** was obtained as a yellow liquid (2.68 mmol, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.22 – 7.08 (m, 1H), 6.93 – 6.64 (m, 4H), 6.56 – 6.36 (m, 1H), 5.24 (ddd, *J* = 17.0, 1.7, 0.8 Hz, 1H), 5.07 (ddd, *J* = 10.0, 1.7, 0.8 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.8, 138.0, 130.3, 128.7, 127.6, 126.5, 126.1, 120.7, 117.0, 110.9, 55.5.

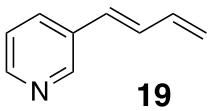
(*E*)-2-(buta-1,3-dien-1-yl)furan (17)



17

The product was synthesised according to the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol) and 3-(2-furyl)acrolein (366.36 mg, 3 mmol). The product was purified by flash column chromatography using pentane as eluent. The product **17** was obtained as a yellow oil (1.59 mmol, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 1.8 Hz, 1H), 6.63 (dd, *J* = 15.6, 10.8 Hz, 1H), 6.44 – 6.24 (m, 3H), 6.20 (d, *J* = 3.3 Hz, 1H), 5.25 (d, *J* = 17.7 Hz, 1H), 5.08 (d, *J* = 10.0 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.0, 142.2, 136.7, 128.2, 120.4, 117.8, 111.6, 108.6.

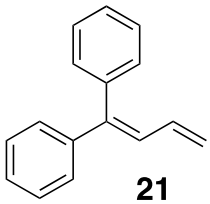


19

(*E*)-3-(buta-1,3-dien-1-yl)pyridine (19)

The product was synthesised according to the general procedure using methyl phosphonium bromide (835 mg, 3.75 mmol) and 3-(3-pyridyl)acrolein (250 mg, 1.87 mmol). The product was purified by flash column chromatography using pentane:ethyl acetate (10:1) as eluent. The product **19** was obtained as a yellow oil (1.4 mmol, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (s, 1H), 8.39 (d, *J* = 4.9 Hz, 1H), 7.73 – 7.57 (m, 1H), 7.19 (m, 1H), 6.77 (dd, *J* = 16.4, 10.7, 1H), 6.54 – 6.36 (m, 2H), 5.33 (d, *J* = 16.4 Hz, 1H), 5.19 (d, *J* = 10.1 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.3, 148.2, 136.6, 132.9, 132.8, 131.7, 128.9, 123.6, 119.3.



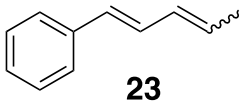
21

buta-1,3-diene-1,1-diyldibenzene (21)

The product was synthesised according to the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol) and β-phenylcinnamaldehyde (624.78 mg, 3 mmol). The product was purified by flash column chromatography using pentane:ethyl acetate (30:1) as eluent. The product **21** was obtained as a yellow liquid (2.85 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (m, 3H), 7.20 – 7.09 (m, 7H), 6.63 (d, *J* = 11.0 Hz, 1H), 6.35 (ddd, *J* = 16.8, 11.0, 10.1 Hz, 1H), 5.34 – 5.25 (dd, *J* = 16.9, 1.5 Hz, 1H), 5.03 (dd, *J* = 10.1, 1.9 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.2, 142.1, 139.7, 135.0, 130.4, 128.5, 128.2, 127.6, 127.5, 127.4, 118.6.

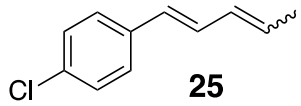
((1*E*)-penta-1,3-dien-1-yl)benzene (23)



23

The product was synthesised according to the general procedure using ethyl phosphonium bromide (1.39 g, 3.75 mmol) and *trans*-cinnamaldehyde (396.48 mg, 3 mmol). The product was purified by flash column chromatography using pentane as eluent. The product **23** was obtained as a yellow oil (2.2 mmol, 72%) (*E:Z* = 78:22).
^{1}H NMR (400 MHz, $CDCl_3$) δ = (*E)*: 7.38 – 7.29 (m, 2H), 7.25 – 7.16 (m, 2H), 7.15 – 7.05 (m, 1H), 6.99 (dd, *J* = 15.6, 11.1 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.19 – 6.02 (m, 1H), 5.58 – 5.45 (m, 1H), 1.77 (dd, *J* = 7.2, 1.8 Hz, 3H). (*Z)*: 7.29 – 7.25 (m, 2H), 7.25 – 7.16 (m, 2H), 7.15 – 7.05 (m, 1H), 6.65 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.33 (d, *J* = 15.7 Hz, 1H), 6.19 – 6.02 (m, 1H), 5.74 (dq, *J* = 14.0, 6.8 Hz, 1H), 1.73 (dd, *J* = 6.8, 1.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = (*E:Z* = 78:22) 137.7, 131.9, 130.3, 129.8, 129.7, 129.4, 128.6, 128.5, 127.3, 127.1, 127.1, 126.3, 126.1, 124.2, 18.3, 13.6.

1-chloro-4-((1*E*)-penta-1,3-dien-1-yl)benzene (25)



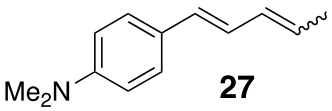
25

The product was synthesised according to the general procedure using ethyl phosphonium bromide (1.39 g, 3.75 mmol) and *trans*-4-chlorocinnamaldehyde (499.8 mg, 3 mmol). The product was purified by flash column chromatography using pentane as eluent. The product **25** was obtained as a yellow solid (2.6 mmol, 87%) (*E:Z* = 56:44).

^{1}H NMR (400 MHz, $CDCl_3$) δ = (*E)*: 7.29 – 7.15 (m, 4H), 6.63 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.28 (d, *J* = 15.7 Hz, 1H), 6.19 – 6.03 (m, 1H), 5.83 – 5.70 (m, 1H), 1.74 (dd, *J* = 6.8, 1.6 Hz, 3H). (*Z)*: 7.29 – 7.15 (m, 4H), 6.98 (ddd, *J* = 15.6, 11.1, 1.2 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.19 – 6.03 (m, 1H), 5.61 – 5.48 (m, 1H), 1.78 (dd, *J* = 7.2, 1.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = (*E:Z* = 56:44) 136.2, 132.8, 132.5, 131.6, 131.1, 130.5, 130.0, 129.4, 128.8, 128.7, 128.4, 127.9, 127.5, 127.3, 124.7, 18.5, 13.7.

_N_,_N_-dimethyl-4-((1_E_)-penta-1,3-dien-1-yl)aniline (27)



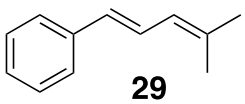
27

The product was synthesised according to the general procedure using ethyl phosphonium bromide (1.39 g, 3.75 mmol) and 4-(dimethylamino)cinnamaldehyde (512 mg, 3 mmol). The product was purified by flash column chromatography using pentane as eluent. The product **27** was obtained as a yellow solid (2.6 mmol, 85%) (*E:Z* = 56:44).

^{1}H NMR (400 MHz, $CDCl_3$) δ = (*E)*: 7.29 – 7.15 (m, 4H), 6.63 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.28 (d, *J* = 15.7 Hz, 1H), 6.19 – 6.03 (m, 1H), 5.83 – 5.70 (m, 1H), 1.74 (dd, *J* = 6.8, 1.6 Hz, 3H). (*Z)*: 7.29 – 7.15 (m, 4H), 6.98 (ddd, *J* = 15.6, 11.1, 1.2 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.19 – 6.03 (m, 1H), 5.61 – 5.48 (m, 1H), 1.78 (dd, *J* = 7.2, 1.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = (*E:Z* = 56:44) 150.0, 133.3, 131.1, 129.8, 129.7, 127.3, 126.9, 125.1, 121.2, 111.3, 40.2, 19.1, 13.7.

(_E_)-(4-methylpenta-1,3-dien-1-yl)benzene (29)

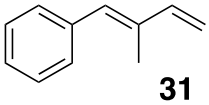


29

The product was synthesised according to the general procedure using isopropyl phosphonium iodide (1.62 g, 3.75 mmol) and *trans*-cinnamaldehyde (396.5 mg, 3 mmol). The product was purified by flash column chromatography using pentane as eluent. The product **29** was obtained as a clear liquid (1.95 mmol, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.92 (dd, *J* = 15.5, 10.9 Hz, 1H), 6.35 (d, *J* = 15.5 Hz, 1H), 5.94 (d, *J* = 11.0 Hz, 1H), 1.79 (s, 3H), 1.75 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.1, 136.7, 129.5, 128.6, 126.9, 126.1, 125.7, 125.5, 26.3, 18.6.

(*E*)-(2-methylbuta-1,3-dien-1-yl)benzene (31)

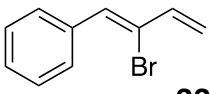


31

The product was synthesised according to the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol) and α-methyl-*trans*-cinnamaldehyde (438.5 mg, 3 mmol). The product was purified by flash column chromatography using pentane as eluent. The product **31** was obtained as a colourless oil (2.64 mmol, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.17 (m, 4H), 7.17 – 7.10 (m, 1H), 6.47 (dd, *J* = 17.2, 10.6, 1H), 6.43 (s, 1H), 5.21 (d, *J* = 17.5 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H), 1.91 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.9, 137.7, 136.0, 131.7, 129.2, 128.2, 126.6, 113.0, 13.2.

(*Z*)-(2-bromobuta-1,3-dien-1-yl)benzene (33)

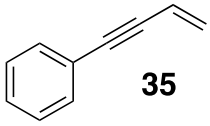


33

The product was synthesised according to an adapted version of the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol), α-bromocinnamaldehyde (633 mg, 3 mmol) and potassium tertbutoxide (201 mg, 0.6 equiv). The product was purified by flash column chromatography using pentane as eluent. The product **33** was obtained as a yellow oil (1.59 mmol, 53%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 7.5 Hz, 2H), 7.37 – 7.19 (m, 3H), 6.92 (s, 1H), 6.44 (dd, *J* = 16.2, 10.4 Hz, 1H), 5.66 (d, *J* = 16.2 Hz, 1H), 5.27 (d, *J* = 10.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.1, 135.6, 132.3, 129.6, 128.3, 128.1, 125.5, 123.9, 119.0.

But-3-en-1-yn-1-ylbenzene (35)



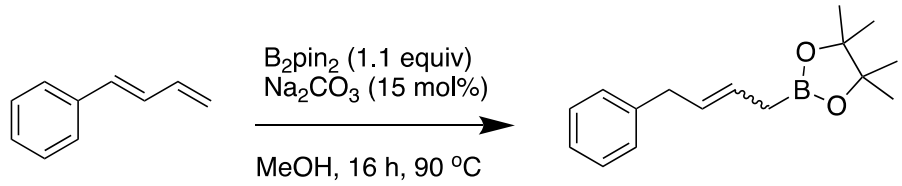
35

The product was synthesised according to an adapted version of the general procedure using methyl phosphonium bromide (1.34 g, 3.75 mmol), α-bromocinnamaldehyde (633 mg, 3 mmol) and potassium tertbutoxide (840 mg, 2.5 equiv). The product was purified by flash column chromatography using pentane as eluent. The product **35** was obtained as a yellow oil (2.2 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.33 (m, 2H), 7.28 – 7.19 (m, 3H), 5.95 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.66 (dd, *J* = 17.5, 2.1 Hz, 1H), 5.47 (dd, *J* = 11.1, 2.1 Hz, 1H).

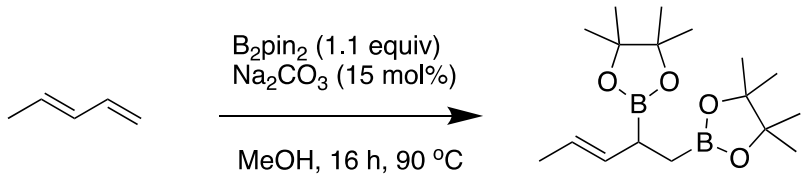
^{13}C NMR (100 MHz, $CDCl_3$) δ = 131.6, 131.5, 128.3, 128.3, 126.8, 123.2, 117.2, 90.0, 88.1.

General Procedure for the transition metal-free 1,4-hydroboration reaction

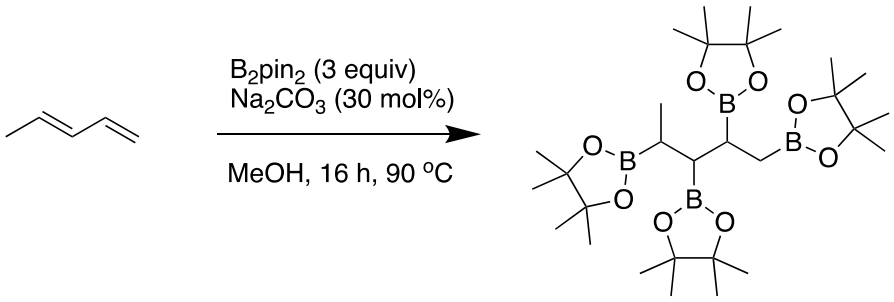


To an oven-dried Schlenk-flask equipped with a magnetic stir bar, B_2pin_2 (0.55 mmol, 1.1 equiv), sodium carbonate (0.075 mmol, 0.15 equiv), dry MeOH as solvent (1 mL), and substrate **2** (0.5 mmol, 1 equiv) were added. The vial was sealed with a plastic cap and heated to 90ºC in an oil bath for 16 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and a known amount of naphthalene (ca. 10 mg) as internal standard was added. An aliquot was taken to determine the conversion and selectivity by ^{1}H NMR and GC-MS analysis. The crude residue was purified by silica gel flash chromatography to afford the hydroborated product.

General procedure for the transition metal free 1,2-diboration reaction



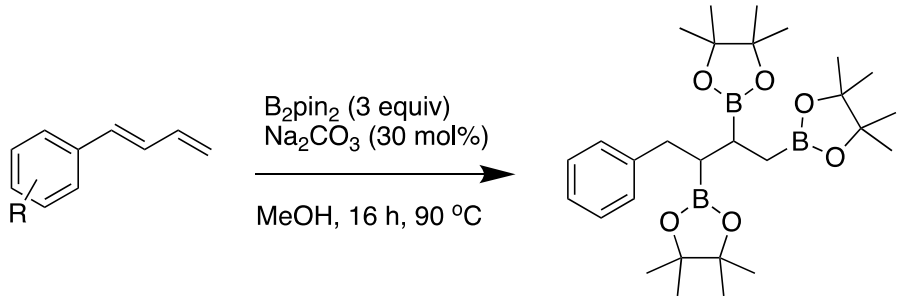
To an oven-dried Schlenk-flask equipped with a magnetic stir bar, B_2pin_2 (0.55 mmol, 1.1 equiv), sodium carbonate (0.075 mmol, 0.15 equiv), dry MeOH as solvent (1 mL), and substrate **4** (0.5 mmol, 1 equiv) were added. The vial was sealed with a plastic cap and heated to 90ºC in an oil bath for 16 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and a known amount of naphthalene (ca. 10 mg) as internal standard was added. An aliquot was taken to determine the conversion and selectivity by ^{1}H NMR and GC-MS analysis. The crude residue was purified by silica gel flash chromatography to afford the diborated product.



General procedure for the transition metal-free 1,2,3,4-tetraboration reaction

To an oven-dried Schlenk-flask equipped with a magnetic stir bar, B_2pin_2 (1.50 mmol, 3 equiv), sodium carbonate (0.15 mmol, 0.3 equiv), dry MeOH as solvent (1 mL), and substrate **4** (0.5 mmol, 1 equiv) were added. The vial was sealed with a plastic cap and heated to 90ºC in an oil bath for 16 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and a known amount of naphthalene (ca. 10 mg) as internal standard was added. An aliquot was taken to determine the conversion and selectivity by ^{1}H NMR and GC-MS analysis. The crude residue was purified by silica gel flash chromatography to afford the polyborylated product.

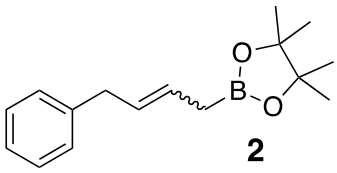
General procedure for the transition metal-free 1,2,3-triboration



To an oven-dried Schlenk-flask equipped with a magnetic stir bar, B_2pin_2 (1.50 mmol, 3 equiv), sodium carbonate (0.15 mmol, 0.3 equiv), dry MeOH as solvent (1 mL), and the substrate (0.5 mmol, 1 equiv) were added. The vial was sealed with a plastic cap and heated to 90ºC in an oil bath for 16 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and a known amount of naphthalene (ca. 10 mg) as internal standard was added. An aliquot was taken to determine the conversion and selectivity by ^{1}H NMR and GC-MS analysis. The crude residue was purified by silica gel flash chromatography to afford the triborated product.

Spectral data of organoboron compounds:

4,4,5,5-tetramethyl-2-(4-phenylbut-2-en-1-yl)-1,3,2-dioxaborolane (2)

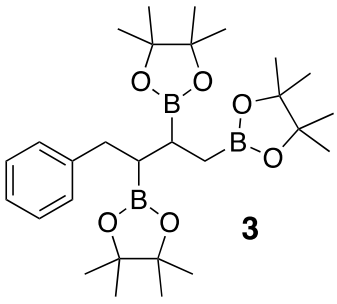


2

The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **2** was obtained as a colourless liquid (52 mg, 40%) (*E:Z* = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = (*E*) 7.35 – 7.13 (m, 5H), 5.70 – 5.51 (m, 2H), 3.44 – 3.36 (d, *J* = 6.5 Hz, 2H), 1.80 (d, *J* = 7.6 Hz, 2H). (*Z*) 7.35 – 7.13 (m, 5H), 5.70 – 5.51 (m, 2H), 3.33 (d, *J* = 5.5 Hz, 2H), 1.69 (d, *J* = 5.8 Hz, 2H), 1.25 (s, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.3, 132.8, 128.5, 128.3, 128.3, 128.1, 126.7, 125.9, 125.8, 125.3, 83.3, 83.1, 39.2, 33.3, 27.4, 24.9, 24.8, 24.6.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.01.
HRMS-(ESI+) for $C_{16}H_{23}BO_2$ $[M]^+$: calculated: 258.1791, found: 258.1786.

2,3',2''-(4-phenylbutane-1,2,3-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3)

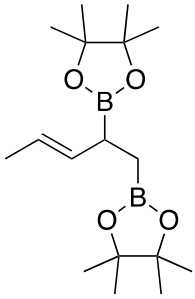


3

The product was purified by flash column chromatography using pentane:ethyl acetate (10:1) as eluent. The product **3** was obtained as a colourless liquid (182 mg, 71%)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (m, 4H), 7.08 (m, 1H), 2.72 (m, 2H), 1.50 (m, 1H), 1.31 (m, 1H), 1.21-1.19 (m, 24H), 1.10 (s, 6H), 1.08 (s, 6H), 0.91-0.78 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.0, 129.1, 129.1, 127.8, 127.8, 125.2, 82.8, 82.8, 82.7, 36.3, 24.9.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.15 (br s).
HRMS-(ESI+) for $NaC_{28}H_{47}B_3O_6$ $[M+Na]^+$: calculated: 535.3549, found: 535.3549.

(E)-2,2'-(pent-3-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5)

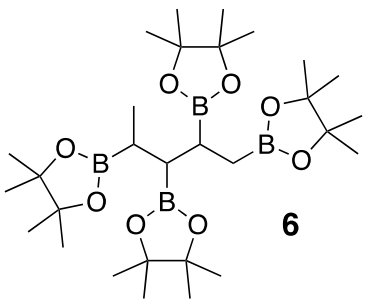


5

The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **5** was obtained as a colourless oil (41.2 mg, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.49 (ddd, *J* = 15.3, 7.6, 1.5 Hz, 1H), 5.41 – 5.30 (m, 1H), 1.90 (m, 1H), 1.61 (d, *J* = 6.2 Hz, 3H), 1.20 (s, 24H), 0.98 (dd, *J* = 15.9, 9.2 Hz, 1H), 0.87 (dd, *J* = 15.9, 6.3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 133.6, 122.7, 83.0, 82.9, 82.8, 28.6, 25.7, 24.9, 24.8, 24.7, 18.2.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.41 (br s)
HRMS-(ESI+) for $C_{17}H_{33}B_2O_4$ $[M+H^+]^+$: calculated: 323.2565, found: 323.2562.

2,2',2'',2'''-(pentane-1,2,3,4-tetrayl)tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6)



6

The product was purified by flash column chromatography using pentane:ethyl acetate (10:1) as eluent. The product **6** was obtained as a colourless oil (68.7 mg, 52%).

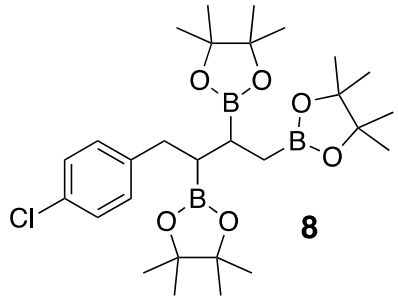
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.39 (m, 1H),), 1.16 – 1.13 (m, 24H), 1.12 (s, 12H), 1.10 (s, 12H), 0.89 (d, *J* = 7.2 Hz, 2H), 0.82 (d, *J* = 7.2 Hz, 3H), 0.59 – 0.54 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 8289, 82.6,, 82.5, 82.4, 25.2, 25.1, 25.0, 24.9, 24.8, 24.7, 24.6, 15.0, 13.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.02 (br s).

HRMS-(ESI+) for $C_{29}H_{57}B_4O_8$ $[M+H^+]^+$: calculated: 577.4426, found: 577.4432.

2,2',2''-(4-(4-chlorophenyl)butane-1,2,3-triyl)tris(4,4,5,5-tetramethyl-1,3,2-



8

dioxaborolane) (8)

The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **8** was obtained as a white solid (108.6 mg, 50%).

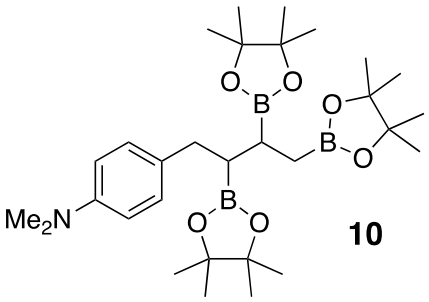
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 – 7.03 (m, 4H), 2.73 – 2.53 (m, 2H), 1.44 – 1.33 (m, 1H), 1.23 – 1.12 (m, 24H), 1.05 (s, 6H), 1.03 (s,6H), 0.96 – 0.72 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 130.9, 130.5, 127.9, 82.9, 82.9, 35.8, 35.5, 25.0, 24.9, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.48 (br s).

HRMS-(ESI+) for $C_{28}H_{47}B_3ClO_6$ $[M+H^+]^+$: calculated: 547.3340, found: 547.3335.

***N*,*N*-dimethyl-4-(2,3,4-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-**



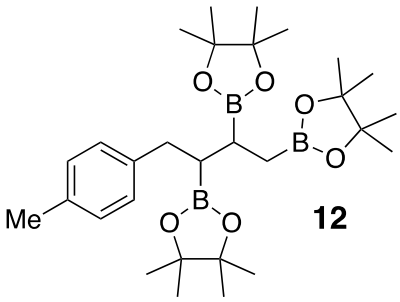
10

yl)butyl)aniline (10)

The product was purified by flash column chromatography using pentane:ethyl acetate (10:1) as eluent. The product **10** was obtained as a yellow liquid (162 mg, 60%)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 – 7.05 (m, 2H), 6.64 (dd, *J* = 8.8, 2.4 Hz, 2H), 2.85 (s, 6H), 2.73 – 2.56 (m, 2H), 1.45 (dd, *J* = 9.8, 6.1 Hz, 1H), 1.37-1.27 (m, 1H) 1.29 – 1.17 (m, 24H), 1.15 (s, 6H), 1.04 (s, 6H), 0.99 – 0.78 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.0, 132.0, 129.7, 129.6, 110.1, 82.7, 82.6, 41.2, 35.3, 25.0, 24.9, 24.8, 24.7.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.27 (br s).
HRMS-(APCI+) for $C_{30}H_{53}B_3NO_6$ $[M+H^+]^+$: calculated: 556.4152, found: 556.4151.

2,2',2''-(4-(*p*-tolyl)butane-1,2,3-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



12

(12)

The product was synthesized according to the general procedure. The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **12** was obtained as a colourless liquid (168 mg, 65%)

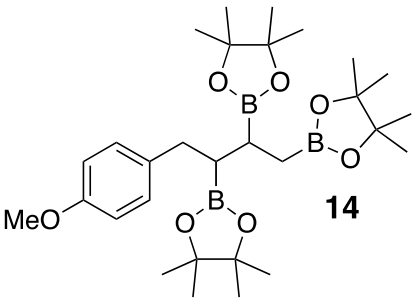
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.04 (dd, *J* = 7.8, 5.3 Hz, 2H), 6.94 (d, *J* = 7.7 Hz, 2H), 2.73 – 2.53 (m, 2H), 2.20 (s, 3H), 1.48 – 1.34 (m, 1H), 1.18 – 1.10 (m, 24H), 1.09 (s, 6H), 0.97 (s, 6H), 0.97 – 0.71 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.0, 139.9, 134.5, 129.0, 128.5, 83.5, 82.8, 82.7, 36.0, 35.7, 25.1, 25.0, 24.9, 24.8, 24.7, 21.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 35.53 (br s).

HRMS-(ESI+) for $C_{29}H_{49}NaB_3O_6$ $[M+Na^+]^+$: calculated: 549.3706, found:549.3717.

2,2',2''-(4-(4-methoxyphenyl)butane-1,2,3-triyl)tris(4,4,5,5-tetramethyl-1,3,2-



14

dioxaborolane) (14)

The product was synthesized according to the general procedure. The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **14** was obtained as a colourless liquid (162 mg, 60%)

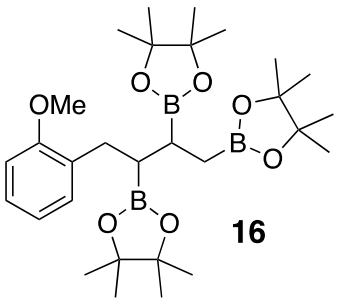
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 (dd, *J* = 8.4, 4.9 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 3.69 (s, 3H), 2.71 – 2.52 (m, 2H), 1.39 (m, 1H), 1.33 – 1.21 (m, 1H), 1.19 – 1.10 (m, 24H), 1.09 (s, 6H), 0.97 (s, 6H), 0.96 – 0.75 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.4, 135.3, 135.2, 130.0, 113.3, 82.7, 55.3, 35.5, 29.7, 25.0, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.00 (br s).

HRMS-(ESI+) for $C_{29}H_{49}NaB_3O_7$ $[M+Na^+]^+$: calculated: 565.3655, found: 565.3666.

2,2',2''-(4-(2-methoxyphenyl)butane-1,2,3-triyl)tris(4,4,5,5-tetramethyl-1,3,2-



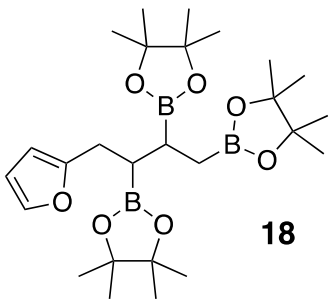
16

dioxaborolane) (16)

The product was synthesized according to the general procedure. The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **16** was obtained as a colourless liquid (177 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14 (m, 1H), 7.02 (m, 1H), 6.78 – 6.65 (m, 2H), 3.70 (s, 3H), 2.80 – 2.58 (m, 2H), 1.58 – 1.45 (m, 1H), 1.19 (m, 1H), 1.19 – 1.12 (m, 24H), 1.05 (m, 6H), 1.01 (m, 6H), 0.97 – 0.83 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 131.3, 130.7, 126.4, 119.8, 109.9, 82.8, 55.1, 30.0, 25.0, 24.9.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.17 (br s).
HRMS-(ESI+) for $C_{29}H_{49}NaB_3O_7$ $[M+Na^+]^+$: calculated: 565.3662, found: 565.3655.

2,2',2''-(4-(furan-2-yl)butane-1,2,3-triyl)tris(4,4,5,5-tetramethyl-1,3,2-



18

dioxaborolane) (18)

The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **18** was obtained as a white solid (160.6 mg, 64%).

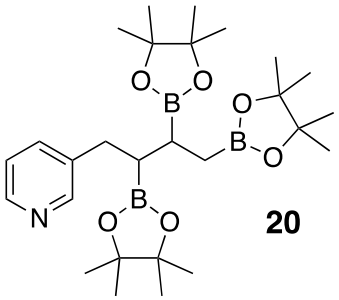
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19 – 7.13 (s, 1H), 6.17 – 6.10 (m, 1H), 5.93 – 5.85 (m, 1H), 2.76 (dd, *J* = 15.0, 10.2 Hz, 1H), 2.62 (dd, *J* = 15.1, 5.9 Hz, 1H), 1.57 – 1.45 (m, 1H), 1.25 (dt, *J* = 11.8, 4.8 Hz, 1H), 1.15 (m, 24H), 1.09 (m, 12H), 0.93 – 0.70 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.0, 140.2, 109.9, 104.9, 83.5, 83.0, 82.9, 28.5, 25.0, 24.9, 24.8, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.74 (br s), 30.45 (s)

HRMS-(APCI+) for $C_{26}H_{46}B_3O_7$ $[M+H^+]^+$: calculated: 503.3523, found: 503.3517.

3-(2,3,4-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)pyridine (20)



20

The product was synthesized according to the general procedure. The product was purified by flash column chromatography using pentane:ethyl acetate (1:1) as eluent. The product **20** was obtained as a colourless liquid (20 mg, 10%)

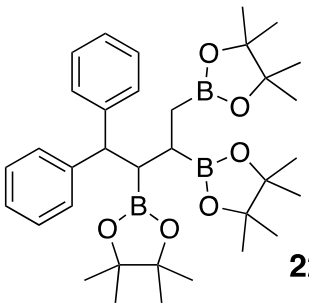
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45 (m, 1H), 8.35 (m, 1H), 7.52 – 7.45 (m, 1H), 7.08 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.71 (dd, *J* = 13.6, 10.1 Hz, 1H), 2.61 (dd, *J* = 13.6, 6.1 Hz, 1H), 1.42 (dt, *J* = 10.2, 5.6 Hz, 1H), 1.29 – 1.22 (m, 1H), 1.16 (m, 24H), 1.04 (s, 6H), 1.03 (s, 6H), 0.96 – 0.73 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.3, 145.4, 130.7, 86.8, 85.7, 35.9, 28.7, 23.9, 23.7, 23.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.23 (br s), 22.49 (s)

HRMS-(APCI+) for $C_{27}H_{47}B_3NO_6$ $[M+H^+]^+$: calculated: 514.3683, found: 514.3677 .

2,2',2''-(4,4-diphenylbutane-1,2,3-triyl)tris(4,4,5,5-tetramethyl-1,3,2-



22

dioxaborolane) (22)

The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **22** was obtained as a colourless oil (138.2 mg, 47%).

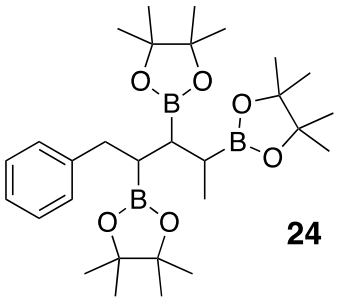
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.30 (m, 2H), 7.28 – 7.17 (m, 2H), 7.17 – 7.03 (m, 4H), 7.03 – 6.90 (m, 2H), 4.33 (d, *J* = 12.6 Hz, 1H), 2.06 (dd, *J* = 12.7, 5.0 Hz, 1H), 1.25 (s, 6H), 1.15 (s, 6H), 1.12 (s, 12H), 1.07 (d, *J* = 7.9 Hz, 2H), 0.84 (s, 6H), 0.81 (s, 6H), 0.63 (dd, *J* = 16.2, 5.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.7, 128.4, 128.3, 128.1, 125.7, 125.5, 82.8, 82.7, 82.6, 51.8, 29.7, 25.5, 25.1, 24.8, 24.7, 24.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 38.86 (br s).

HRMS-(APCI+) for $C_{34}H_{52}B_3O_6$ $[M+H^+]^+$: calculated: 589.4043, found: 589.4038.

2,2',2''-(1-phenylpentane-2,3,4-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



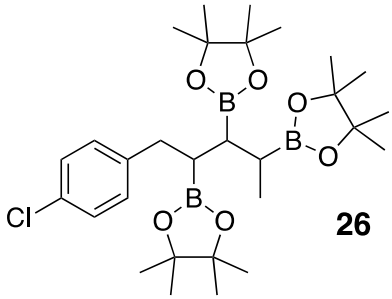
24

(24)

The product was purified by flash column chromatography using pentane:ethyl acetate (10:1) as eluent. The product **24** was obtained as a colourless oil (79 mg, 30%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 – 7.09 (m, 4H), 7.07 – 6.99 (m, 1H), 2.83 (ddd, *J* = 13.5, 5.9, 2.7 Hz, 1H), 2.49 (ddd, *J* = 47.0, 13.3, 10.8 Hz, 1H), 1.60 (m, 1H), 1.44 – 1.24 (m, 2H), 1.16 (m, 24H), 1.09 (s, 6H), 0.98 (s, 6H), 0.83 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.3, 142.7, 129.2, 127.8, 125.3, 125.3, 83.0, 82.6, 36.7, 36.5, 25.1, 25.0, 24.8, 24.7, 15.1, 12.9.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.64 (br s).
HRMS-(ESI+) for $C_{29}H_{49}B_3NaO_6$ $[M+Na^+]^+$: calculated: 549.3711, found: 549.3706.

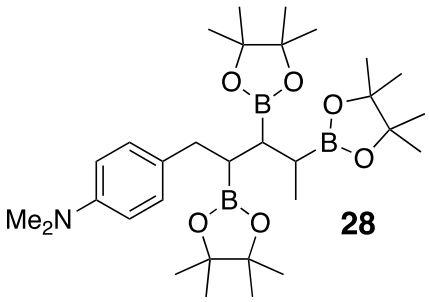
2,2',2''-(1-(4-chlorophenyl)pentane-2,3,4-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (26)



26

The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **26** was obtained as a colourless oil (56 mg, 20%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (m, 4H), 2.74 (dd, *J* = 13.4, 6.1 Hz, 1H), 2.45 (dd, *J* = 13.6, 10.3 Hz, 1H), 1.49 (m, 1H), 1.31 (m, 1H), 1.16 (d, *J* = 4.9 Hz, 24H), 1.05 (s, 6H), 0.97 (s, 6H), 0.87 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.9, 141.3, 130.9, 130.5, 127.9, 83.0, 82.7, 53.5, 35.9, 29.7, 25.2, 24.8, 15.1, 13.2.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.00 (br s).
HRMS-(ESI+) for $C_{29}H_{48}B_3ClNaO_6$ $[M+Na^+]^+$: calculated: 583.3316, found: 583.3339.

***N*,*N*-dimethyl-4-(2,3,4-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-**



28

yl)pentyl)aniline (28)

The product was purified by flash column chromatography using pentane:ethyl acetate (10:1) as eluent. The product **28** was obtained as a colourless oil (81.4 mg, 30%).

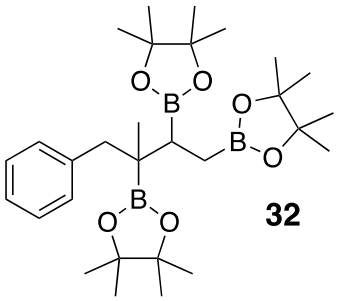
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.04 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 7.9 Hz, 2H), 2.80 (s, 6H), 2.74 (dd, *J* = 13.5, 5.9 Hz, 1H), 2.37 (dd, *J* = 13.6, 10.5 Hz, 1H), 1.49 (m, 1H), 1.41 – 1.30 (m, 2H), 1.19 (s, 12H), 1.11 (s, 12H), 1.04 (s, 6H), 0.94 (s, 6H), 0.88 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 129.7, 113.6, 113.6, 82.9, 82.5, 41.6, 35.4, 29.7, 25.0, 24.8, 12.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.98 (br s).

HRMS-(ESI+) for $C_{31}H_{55}B_3NO_6$ $[M+H^+]^+$: calculated: 570.4309, found: 570.4311.

2,2',2''-(3-methyl-4-phenylbutane-1,2,3-triyl)tris(4,4,5,5-tetramethyl-1,3,2-



32

dioxaborolane) (32)

The product was purified by flash column chromatography using pentane:ethyl acetate (10:1) as eluent. The product **32** was obtained as a colourless oil (126.7 mg, 48%).

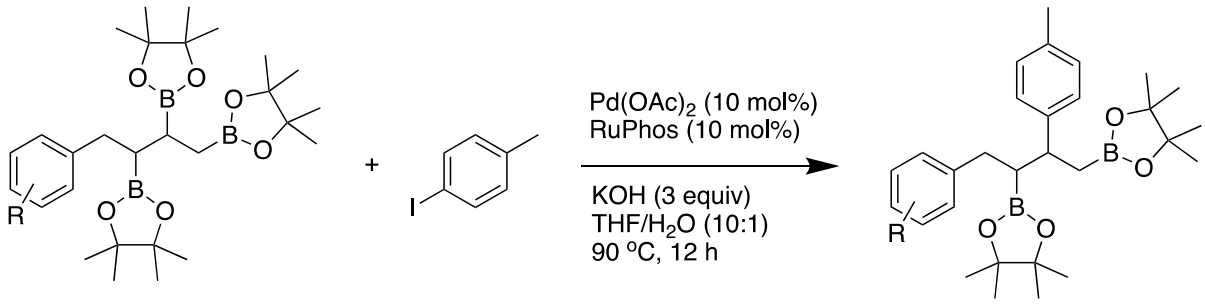
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.15 – 7.08 (m, 2H), 7.08 – 7.01 (m, 1H), 2.88 (d, *J* = 12.9 Hz, 1H), 2.45 (d, *J* = 12.9 Hz, 1H), 1.26 (dd, *J* = 12.4, 3.5 Hz, 1H), 1.21 – 1.14 (m, 24H), 1.12 (s, 6H), 1.03 (s, 6H), 0.95 (m, 2H), 0.85 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.3, 130.7, 127.4, 125.4, 83.0, 82.9, 82.7, 43.5, 25.3, 25.1, 25.0, 24.9, 24.7, 20.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.09 (br s).

HRMS-(ESI+) for $C_{29}H_{49}NaB_3O_6$ $[M+Na^+]^+$: calculated: 549.3706, found: 549.3716.

General Procedure for the Suzuki-Miyaura Cross-Coupling Reaction:[2]

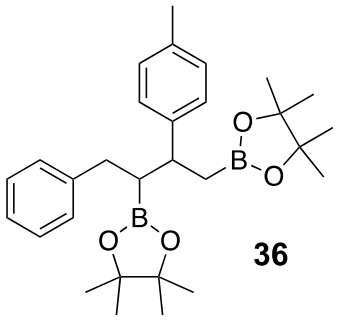


To a Schlenk flask equipped with a stirrer bar was added the substrate (1 equiv, 0.3 mmol), 4-iodotoluene (1.5 equiv, 0.45 mmol) and solid potassium hydroxide (3 equiv, 0.9 mmol). The flask was then sealed and flushed three times with argon before being taken to the glovebox where palladium acetate (10 mol%) and Ruphos (10 mol%) were added. The flask was once again sealed. The sealed flask was taken from the glovebox and dry THF (3.5 mL) and water, sparged for thirty minutes with argon (0.35 mL), were added. The reaction was heated to 90 °C and left to stir for 12 hours.

2. S. N. Mlynarski, C. H. Schuster, J. P. Morken, *Nature*, 2014, **505**, 386.

Spectral Data for Suzuki-Miyaura Cross-Coupling Products:

2,2'-(4-phenyl-2-(*p*-tolyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (36)



36

The product was synthesised according to the general procedure. The product was purified by flash column chromatography using pentane:ethyl acetate (30:1) as eluent. The product **36** was obtained as a colourless oil (11 mg, 11% (22% by NMR)).

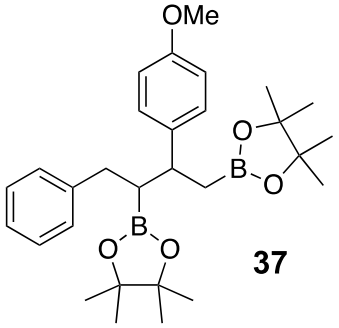
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.08 (dt, *J* = 7.4, 3.3 Hz, 4H), 7.05 – 6.95 (m, 5H), 2.87 (ddd, *J* = 11.8, 10.3, 4.6 Hz, 1H), 2.46 – 2.29 (m, 2H), 2.21 (s, 3H), 1.63 (ddd, *J* = 11.5, 10.3, 5.7 Hz, 1H), 1.23 – 1.14 (m, 2H), 1.02 (s, 6H), 0.93 (s, 6H), 0.91 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5, 142.3, 135.1, 128.8, 128.7, 127.9, 127.8, 125.4, 83.0, 82.8, 43.2, 36.6, 29.7, 25.0, 24.9, 24.7, 24.6, 24.5, 21.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 34.37 (br s).

HRMS-(ESI+) for $C_{29}H_{42}B_2O_4Na$ $[M+Na^+]^+$: calculated: 499.3174, found: 499.3166.

2,2'-(2-(4-methoxyphenyl)-4-phenylbutane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (37)

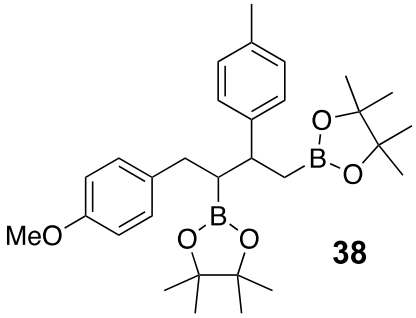


37

The product was synthesised according to an adapted version of the general procedure using 4-iodoanisole. The product was purified by flash column chromatography using pentane:ethyl acetate (25:1) as eluent. The product **37** was obtained as a colourless oil (20 mg, 10% (40% by NMR)).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19 – 7.05 (m, 4H), 7.05 – 6.96 (m, 3H), 6.79 – 6.71 (m, 2H), 3.70 (s, 3H), 2.86 (ddd, J = 11.8, 10.3, 4.7 Hz, 1H), 2.46 – 2.28 (m, 2H), 1.59 (td, J = 10.9, 5.8 Hz, 1H), 1.18 – 1.08 (m, 2H), 1.02 (s, 6H), 0.94 (s, 6H), 0.92 (s, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 142.2, 138.9, 128.8, 127.9, 125.4, 113.4, 83.0, 82.8, 55.3, 42.8, 36.6, 29.7, 25.0, 24.7, 24.5.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 39.26 (br s).
HRMS-(ESI+) for $C_{29}H_{42}B_2O_5Na$ $[M+Na^+]^+$: calculated: 515.3118, found: 515.3166.

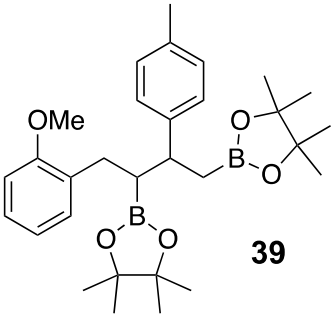
2,2'-(4-(4-methoxyphenyl)-2-(*p*-tolyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (38)



38

The product was synthesised according to the general procedure. The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **38** was obtained as a colourless oil (20 mg, 20%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 3.66 (s, 3H), 2.85 (ddd, *J* = 11.7, 10.3, 4.6 Hz, 1H), 2.35 – 2.27 (m, 2H), 2.21 (s, 3H), 1.59 (dt, *J* = 10.6, 5.3 Hz, 1H), 1.19 (m, 2H), 1.03 (s, 6H), 0.95 (s, 6H), 0.91 (s, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.5, 143.5, 135.1, 134.4, 129.7, 128.6, 127.8, 113.3, 83.0, 82.7, 55.3, 43.1, 35.7, 25.0, 24.8, 24.6, 24.5, 21.1.
^{11}B NMR (128 MHz, $CDCl_3$) δ = 32.56 (br s).
HRMS-(ESI+) for $C_{30}H_{44}B_2O_5Na$ $[M+Na^+]^+$: calculated: 529.3275, found: 529.3272.

2,2'-(4-(2-methoxyphenyl)-2-(*p*-tolyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (39)



39

The product was synthesised according to the general procedure. The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **39** was obtained as a colourless oil (11 mg, 11% (40% by NMR)).

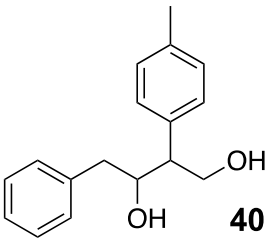
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, *J* = 7.3, 1.9 Hz, 1H), 6.99 – 6.94 (m, 3H), 6.72 – 6.60 (m, 2H), 3.64 (s, 3H), 2.94 – 2.82 (m, 1H), 2.43 – 2.35 (m, 2H), 2.21 (s, 3H), 1.75 (td, *J* = 9.8, 7.2 Hz, 1H), 1.13 – 1.08 (m, 2H), 1.04 (s, 6H), 0.95 (s, 6H), 0.92 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.6, 143.7, 134.9, 130.8, 130.3, 129.4, 128.4, 128.0, 126.8, 126.6, 119.8, 110.0, 82.8, 82.7, 55.1, 43.3, 31.0, 29.7, 25.1, 24.8, 24.7, 24.6, 21.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ = 30.48 (br s).

HRMS-(ESI+) for $C_{30}H_{44}B_2O_5Na$ $[M+Na^+]^+$: calculated: 529.3273, found: 529.3272.

4-phenyl-2-(*p*-tolyl)butane-1,3-diol (40)



40

The product was synthesised according to an adapted version of the general procedure using an oxidative workup (H_2O_2/NaOH) upon completion of the reaction. The product was purified by flash column chromatography using pentane:ethyl acetate

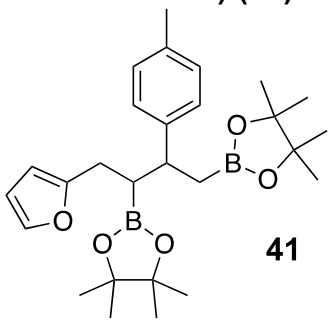
(2:1) as eluent. The product **40** was obtained as a colourless oil (12 mg, 15% (20% by NMR)).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.13 (m, 4H), 7.13 – 6.99 (m, 5H), 4.14 (td, *J* = 9.5, 2.7 Hz, 1H), 4.00 (dd, *J* = 11.1, 7.9 Hz, 1H), 3.77 (dd, *J* = 11.1, 4.4 Hz, 1H), 2.93 (br s, 1H), 2.81 (ddd, *J* = 9.4, 7.9, 4.5 Hz, 1H), 2.64 (dd, *J* = 13.8, 2.7 Hz, 1H), 2.41 (dd, *J* = 13.8, 9.6 Hz, 1H), 2.28 (s, 3H), 1.55 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.0, 136.8, 136.8, 129.7, 129.4, 128.7, 128.1, 126.7, 67.3, 53.1, 42.5, 24.9, 21.1.

HRMS-(ESI+) for $C_{17}H_{20}O_2$ $[M]^+$: calculated: 256.1463, found: 256.1465.

2,2'-(4-(furan-2-yl)-2-(*p*-tolyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (41)



41

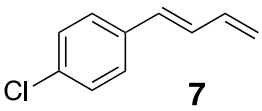
The product was synthesised according to the general procedure. The product was purified by flash column chromatography using pentane:ethyl acetate (20:1) as eluent. The product **41** was obtained as a colourless oil (40 mg, 29% (50% by NMR)).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, *J* = 1.8 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.10 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.83 (d, *J* = 3.1 Hz, 1H), 2.85 (td, *J* = 10.2, 6.4 Hz, 1H), 2.45 (dd, *J* = 15.1, 11.6 Hz, 1H), 2.32 (dd, *J* = 15.2, 4.6 Hz, 1H), 2.20 (s, 3H), 1.67 – 1.54 (m, 1H), 1.19 (m, 2H), 1.10 (s, 12H), 0.90 (s, 12H).

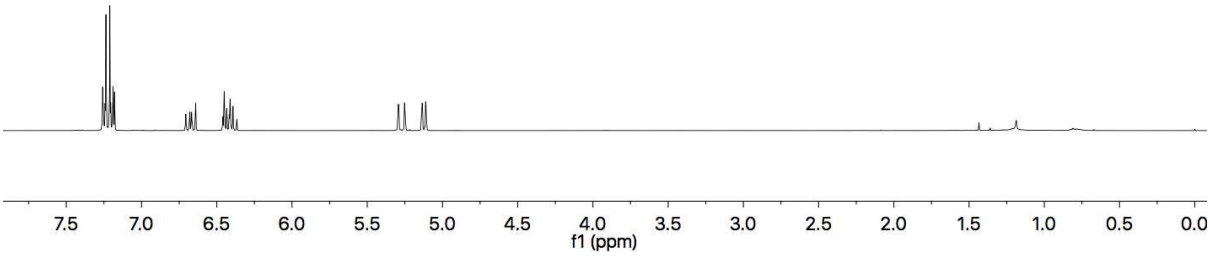
^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.1, 140.4, 135.2, 128.6, 127.8, 109.8, 105.0, 83.1, 82.8, 42.5, 28.7, 24.9, 24.6, 21.0.

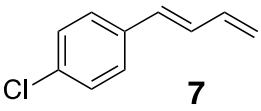
^{11}B NMR (128 MHz, $CDCl_3$) δ = 33.03 (br s).

HRMS-(ESI+) for $C_{27}H_{40}B_2O_5Na$ $[M+Na^+]^+$: calculated: 489.2953, found: 489.2959



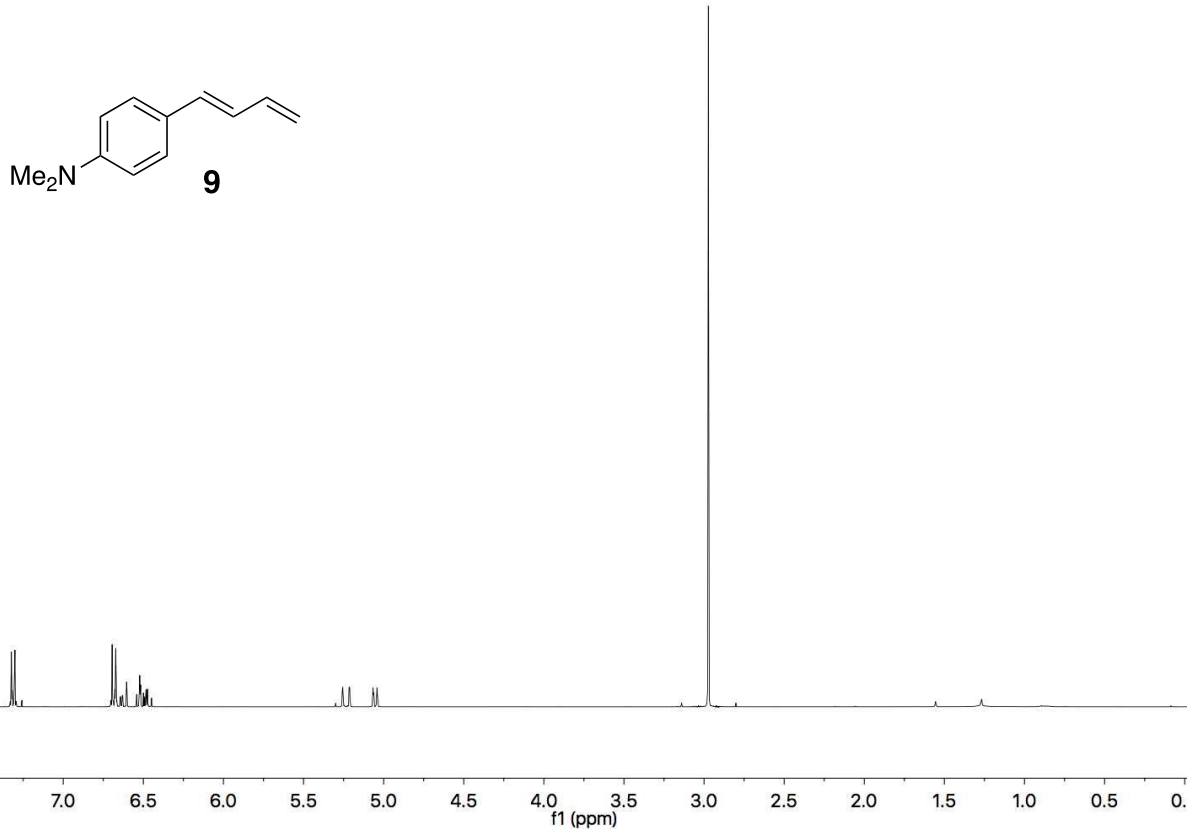
7

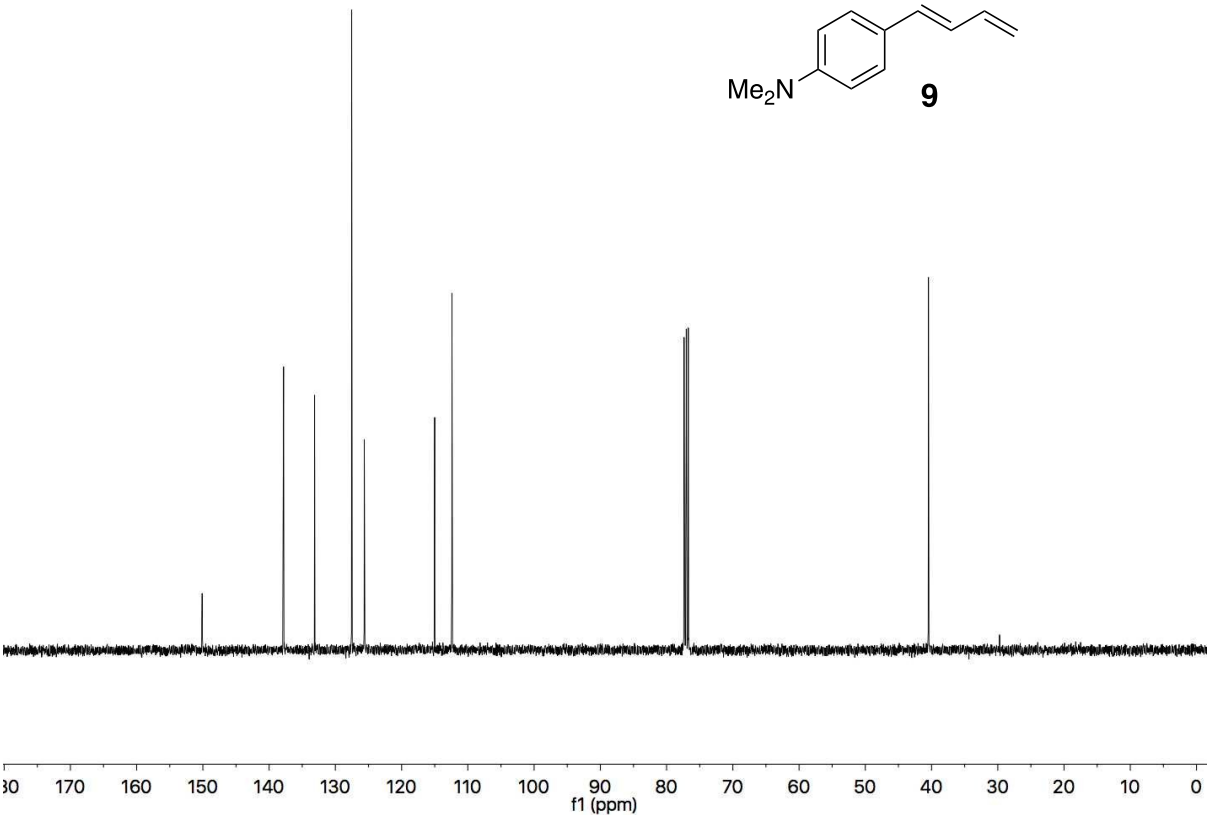


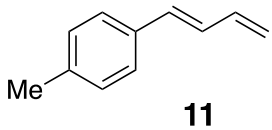


7

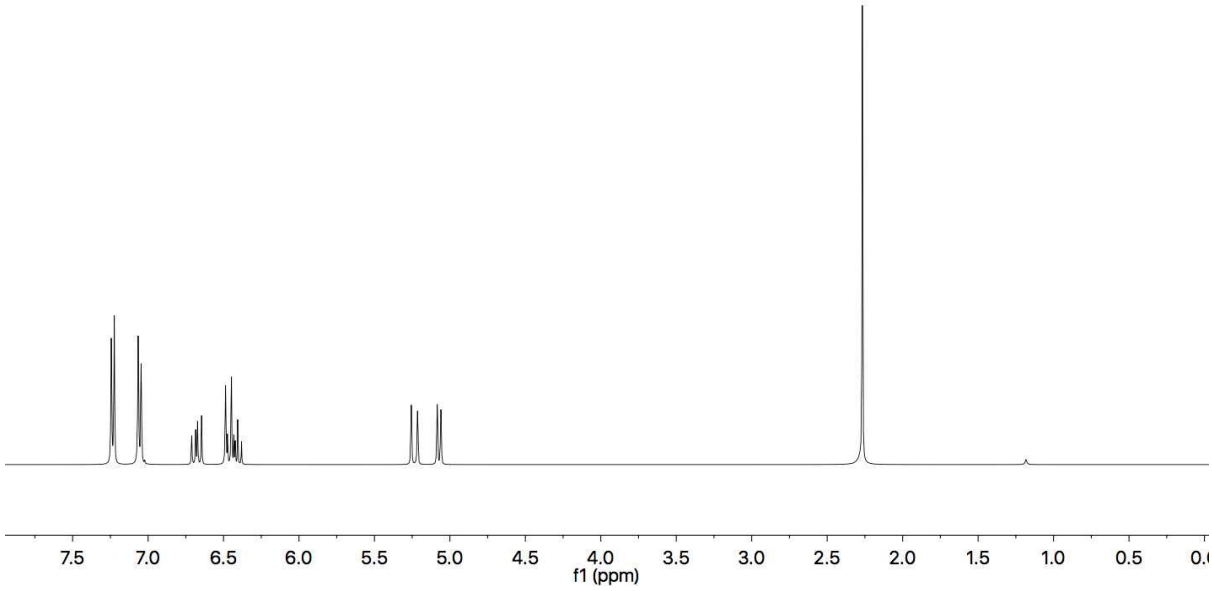
Spectra for 1,3-dienes:

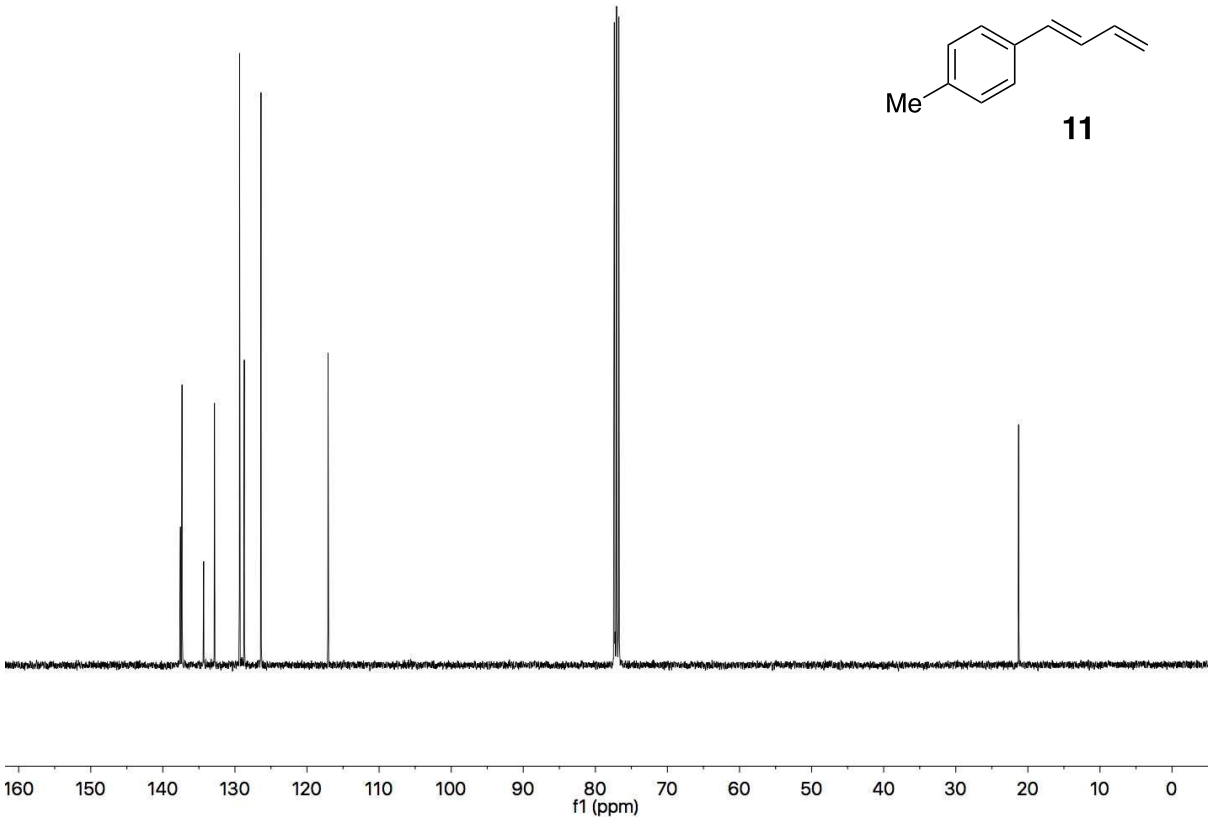

Me2N
9
5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

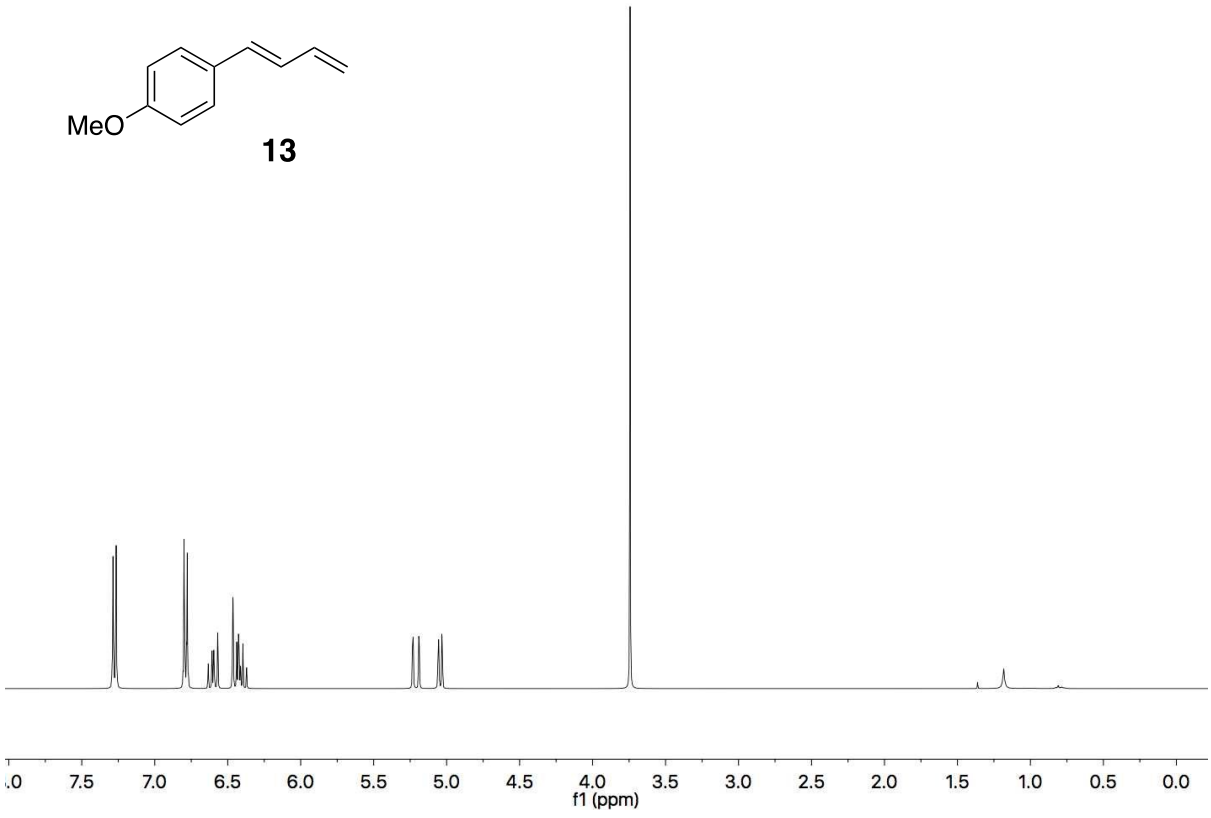

Me2N
9
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

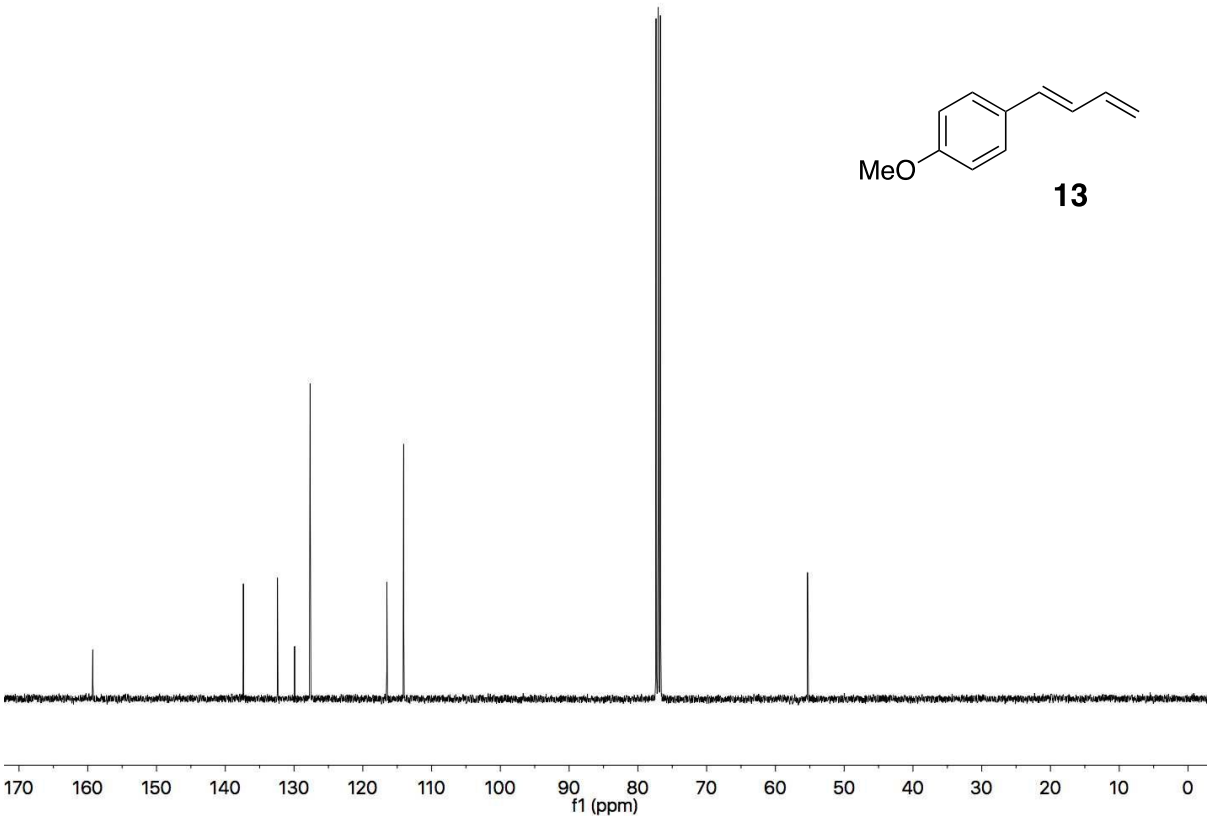


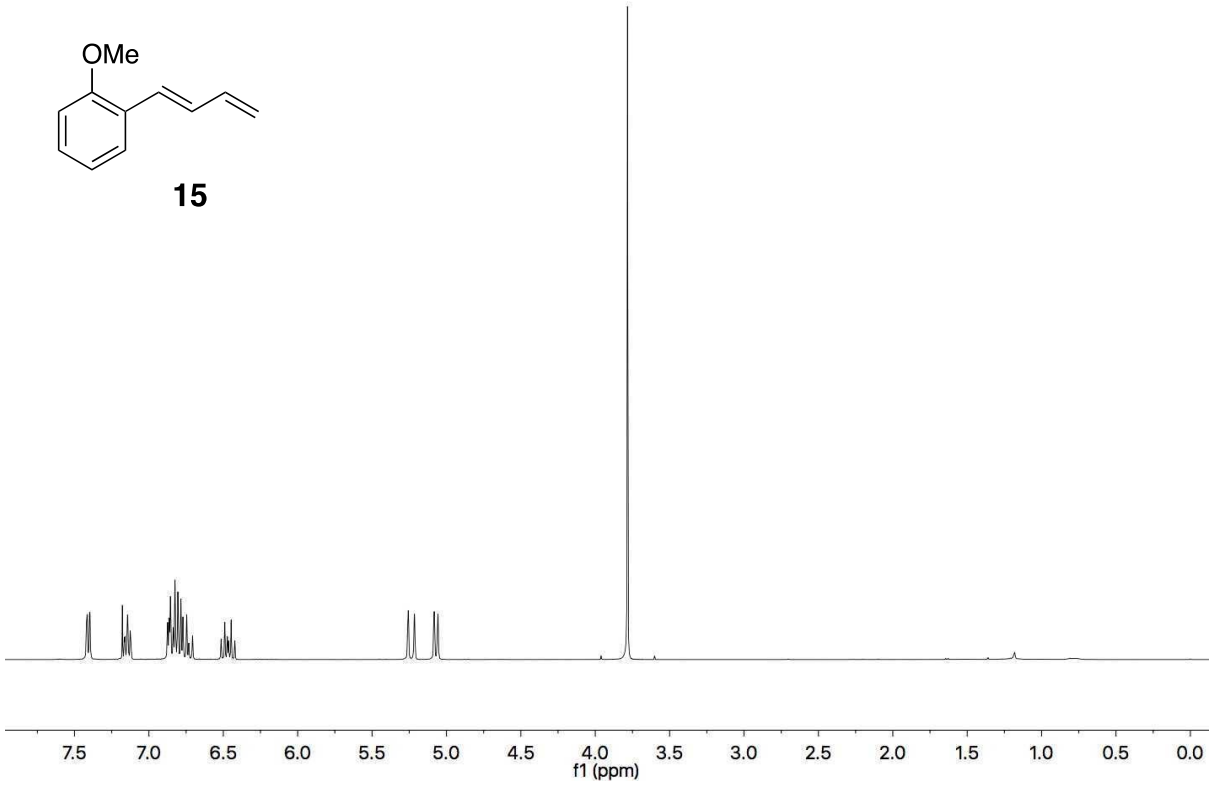
11

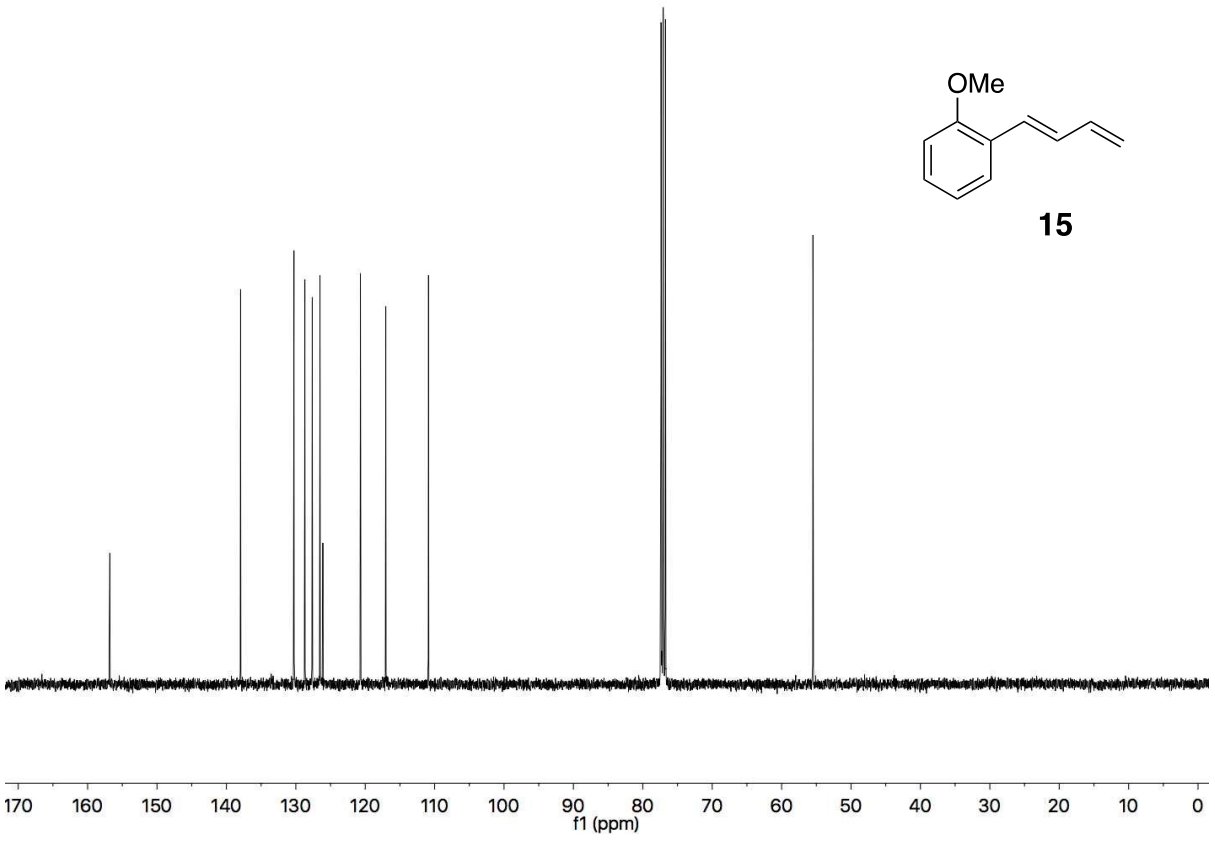


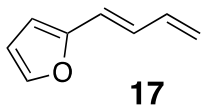

Me
11
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO
13
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

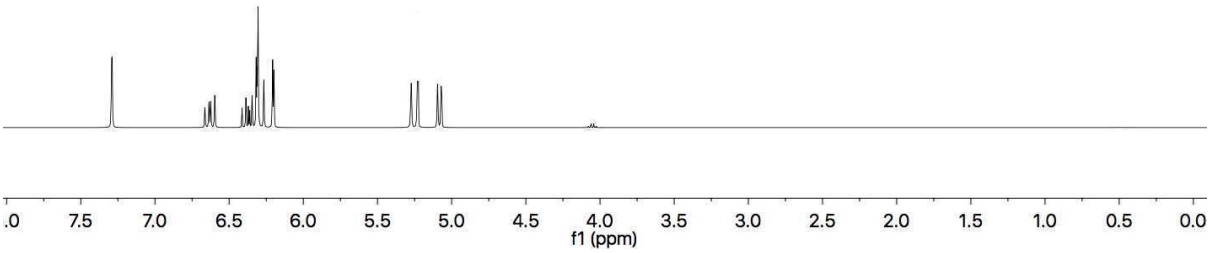

MeO
13
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
15
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OMe
15
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



17


7.5
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6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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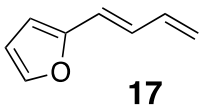
0.0
f1 (ppm)



17

170
160
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130
120
110
100
90
80
70
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50
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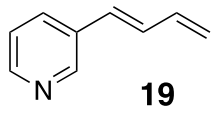
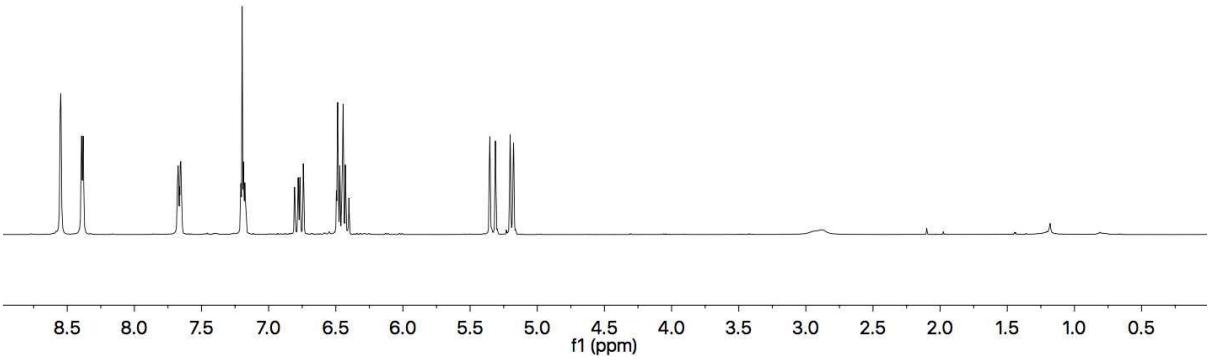
10
0
f1 (ppm)



19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5.0
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3.5
3.0
2.5
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1.5
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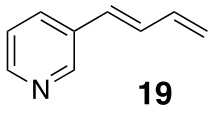
0.5
f1 (ppm)



19

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30
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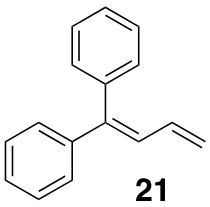
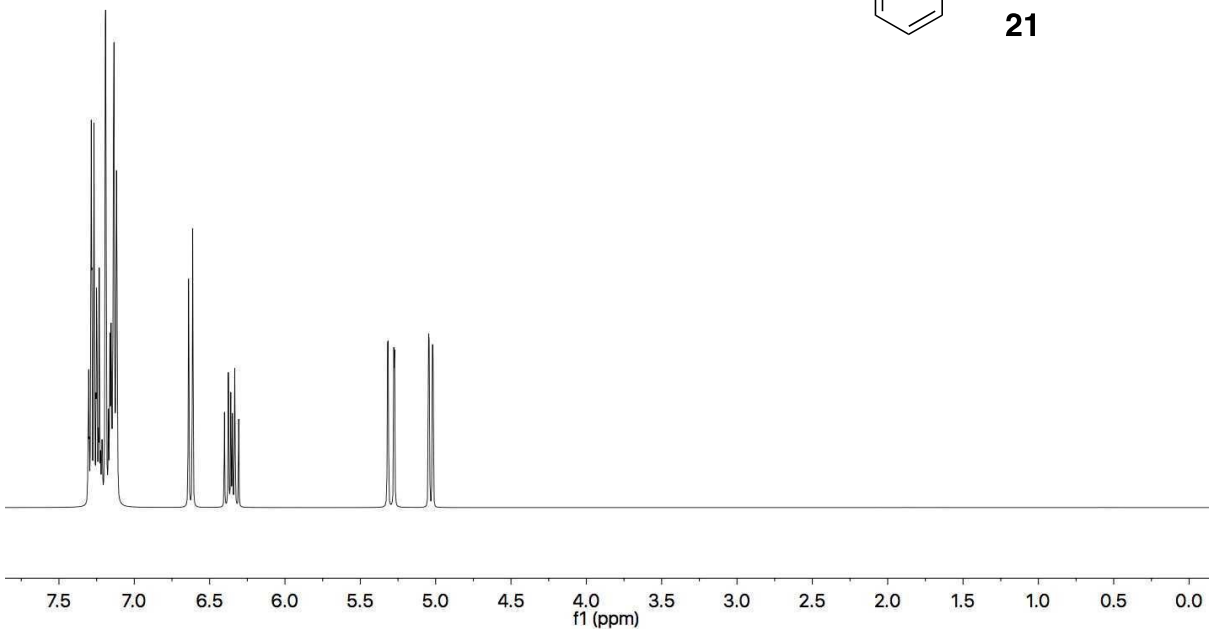
10
0
f1 (ppm)



21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5.5
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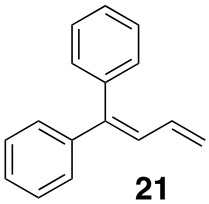
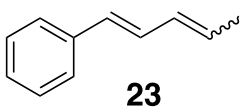
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

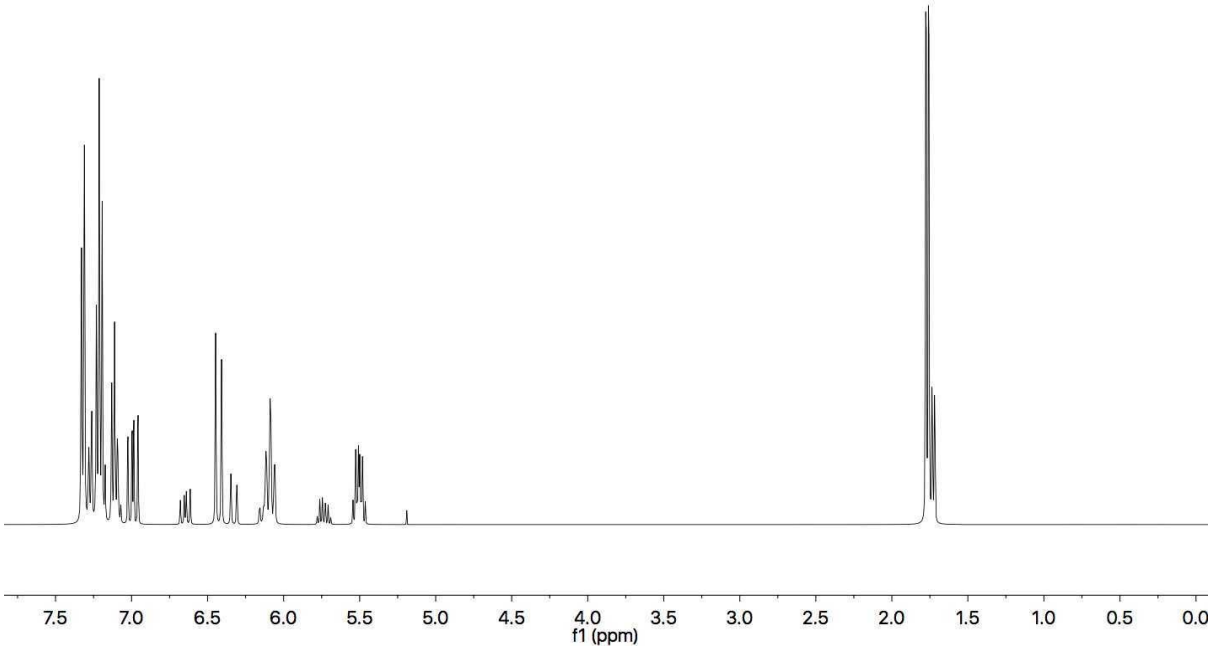


21

150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)



23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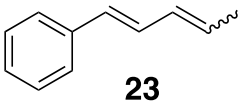
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



23

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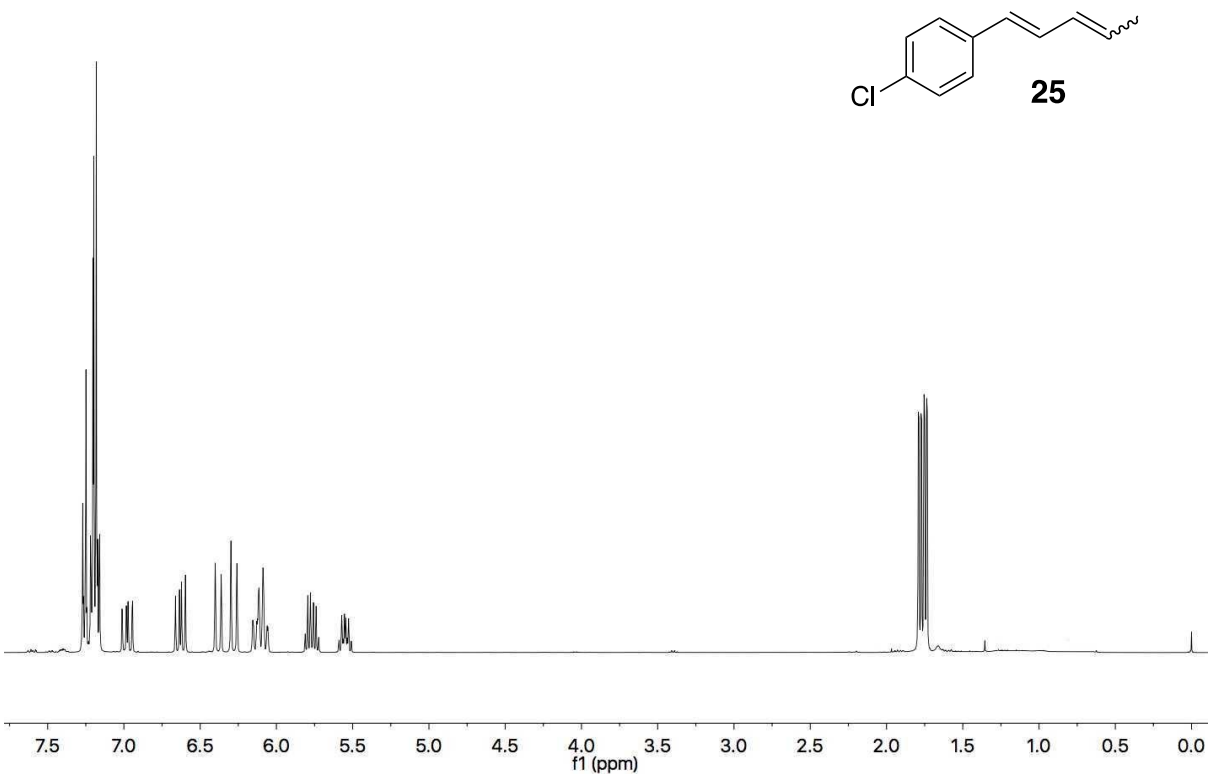
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
25
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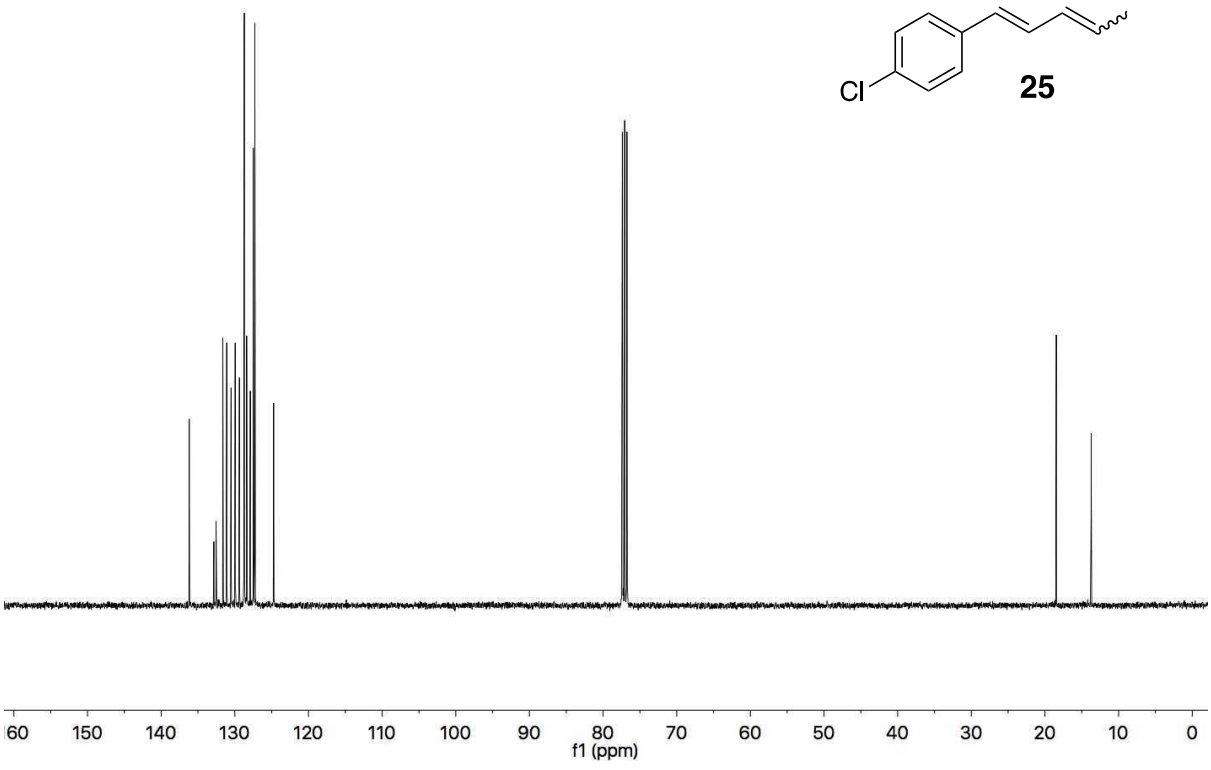
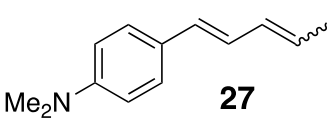
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Cl
25
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me2N

27

7.5
7.0
6.5
6.0
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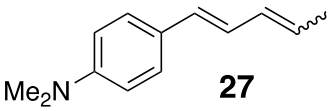
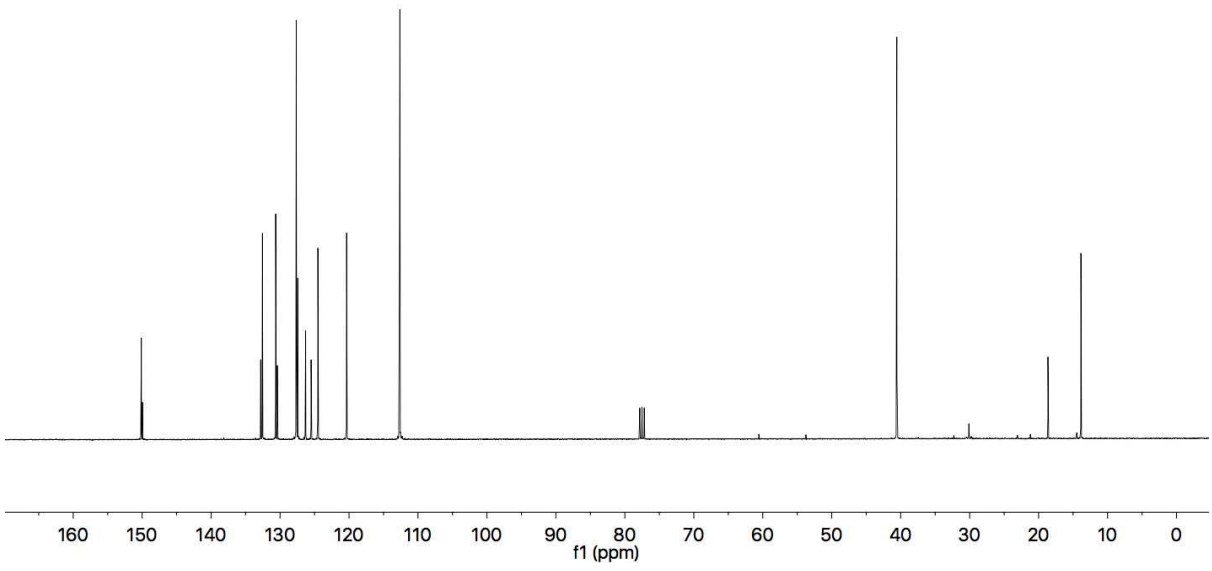
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Me2N

27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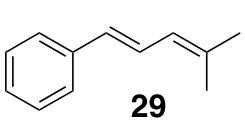
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



29

7.5
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6.5
6.0
5.5
5.0
4.5
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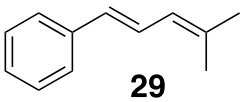
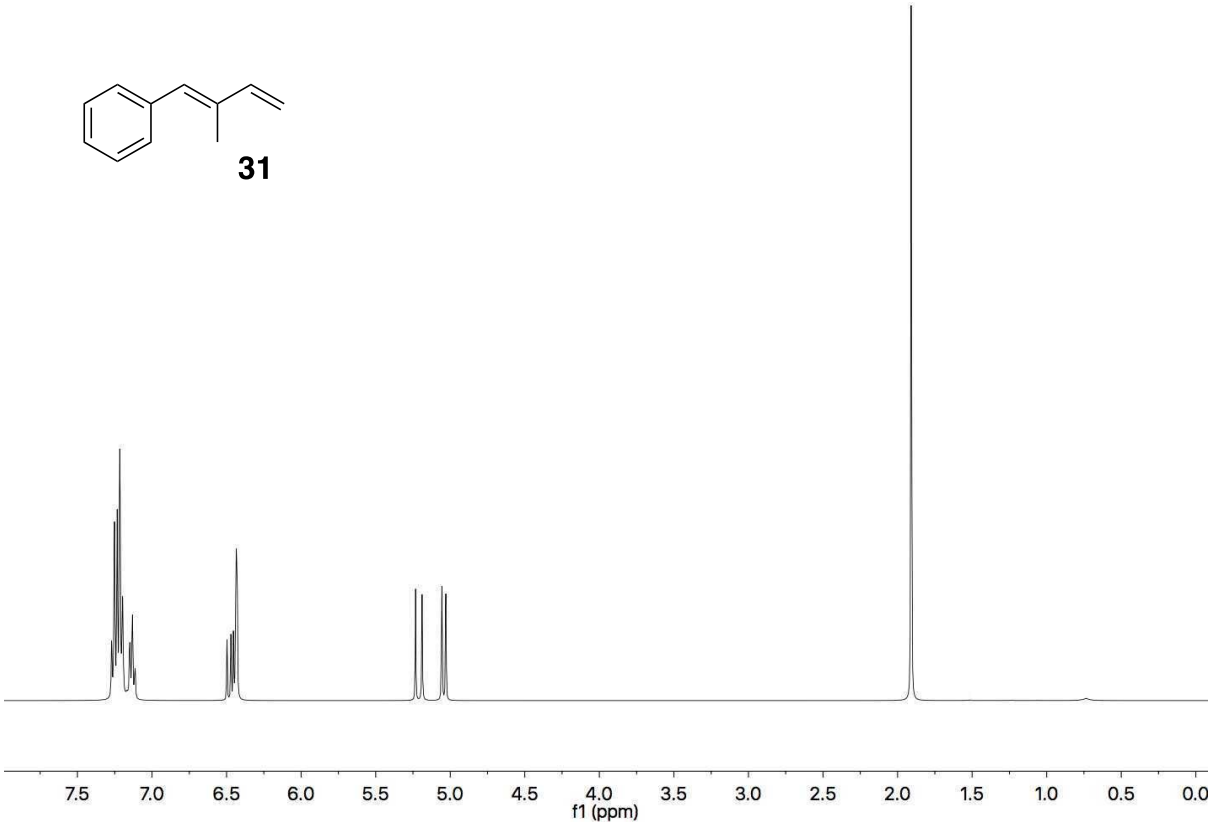
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



29

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


31
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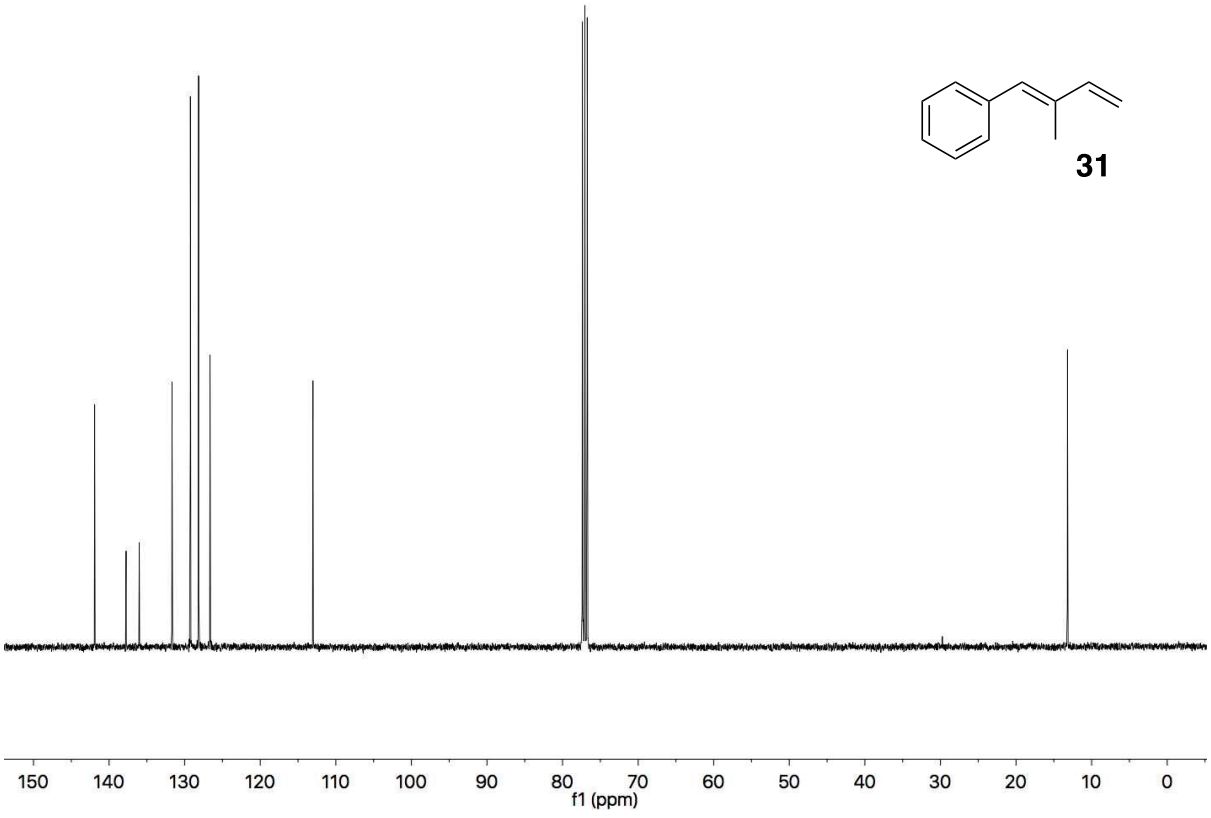
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


31
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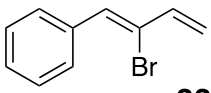
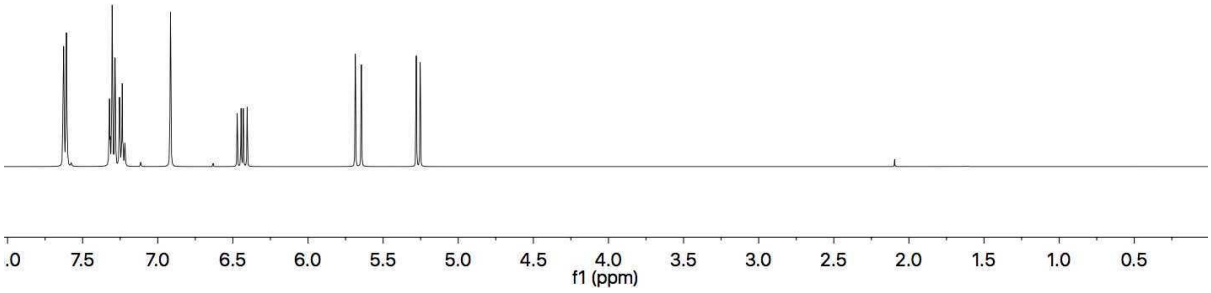
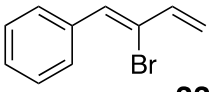
10
0
f1 (ppm)


Br

33


.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Br

33

160
150
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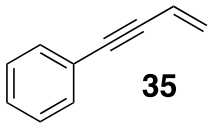
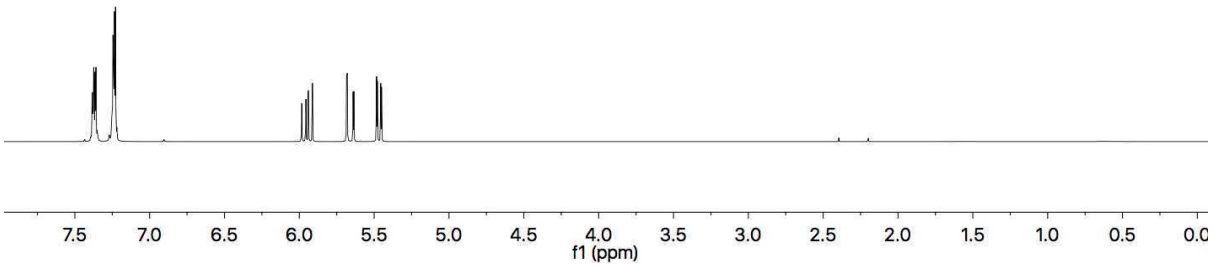
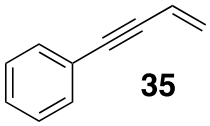
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

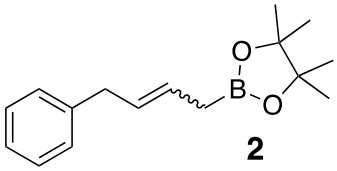


35



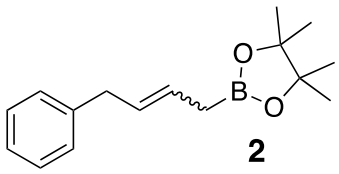


35

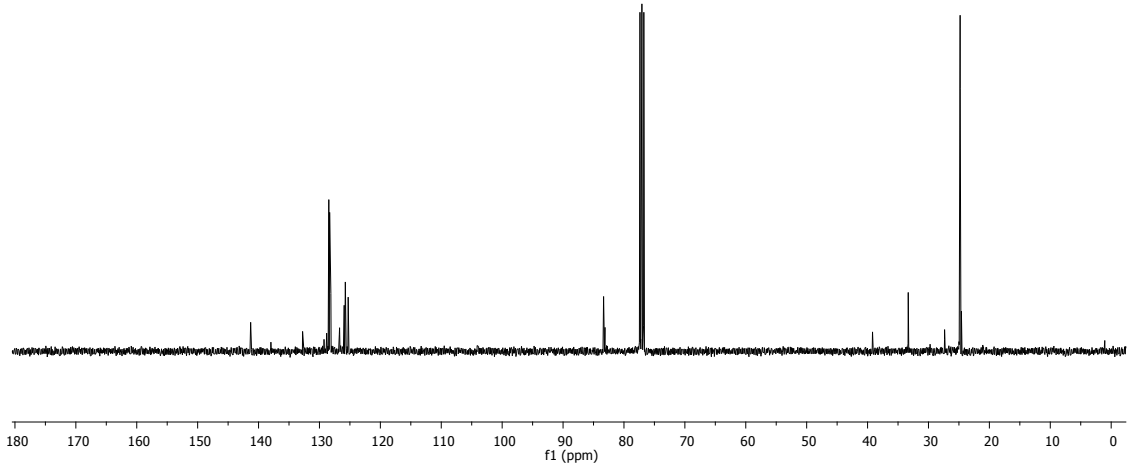


2

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



2


180
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160
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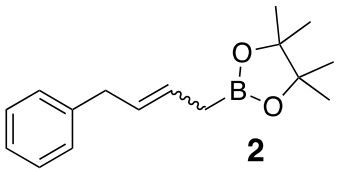
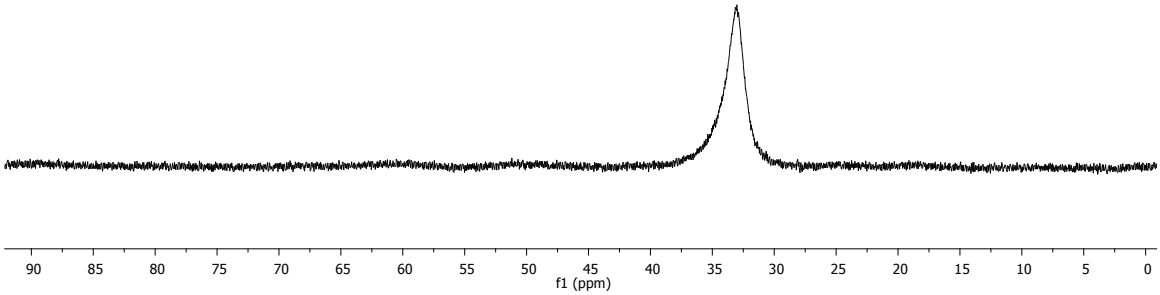
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



2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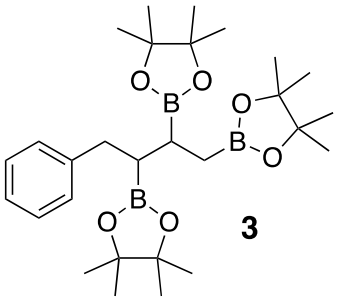
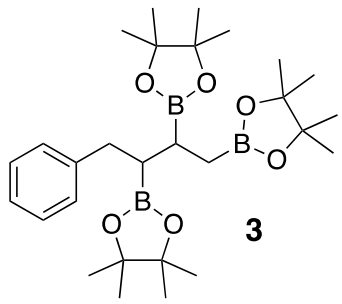
f1 (ppm)



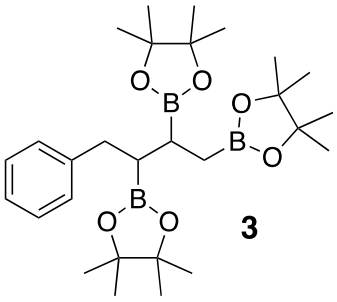
3

3.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

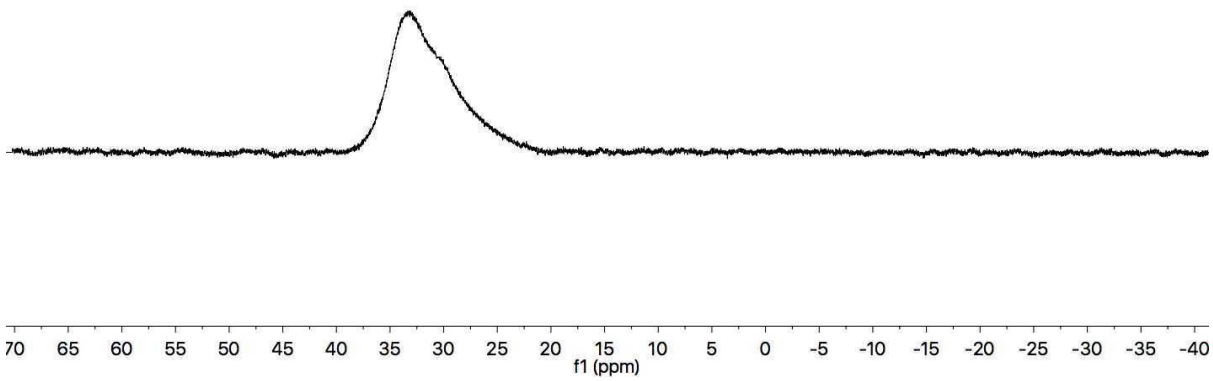


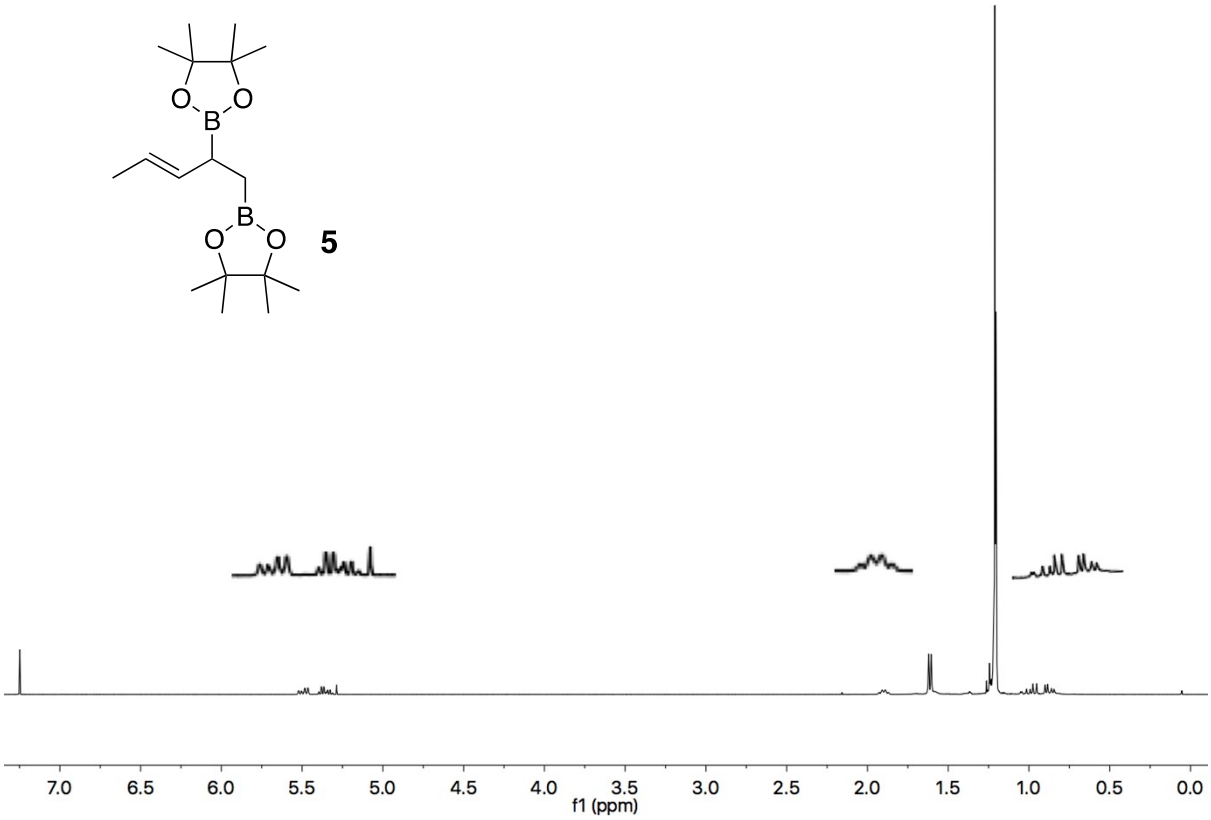
3

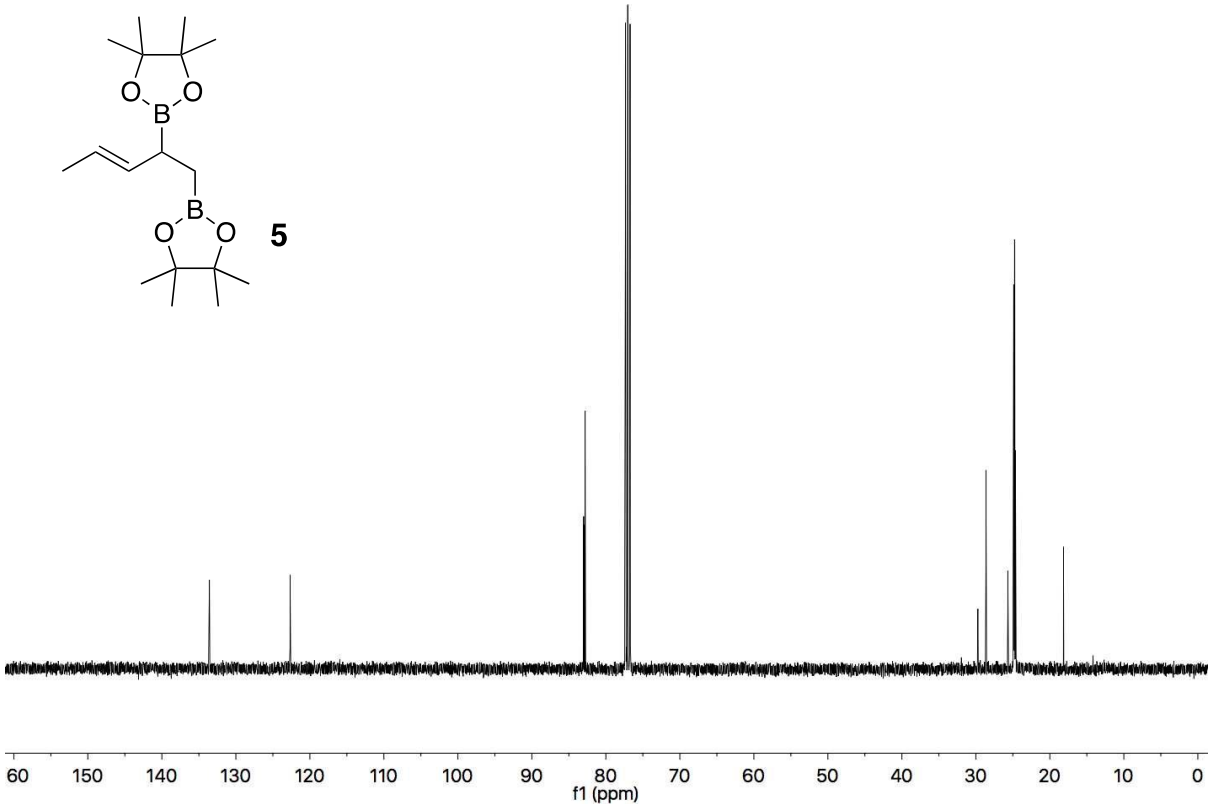
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3


70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)


5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


5
60
150
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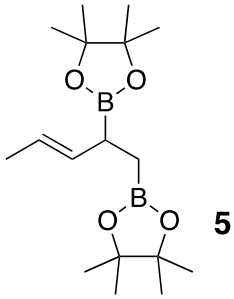
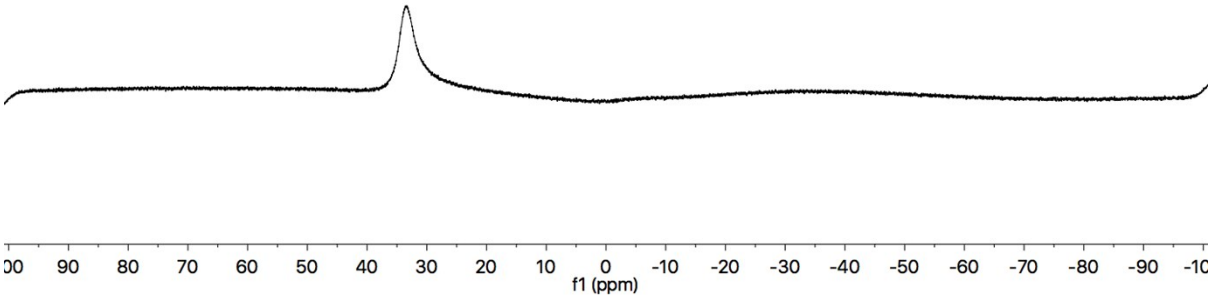
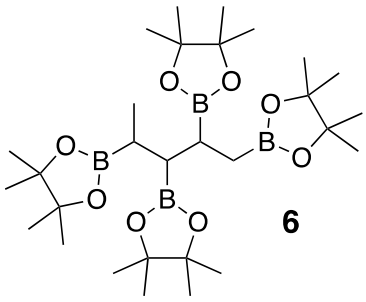
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

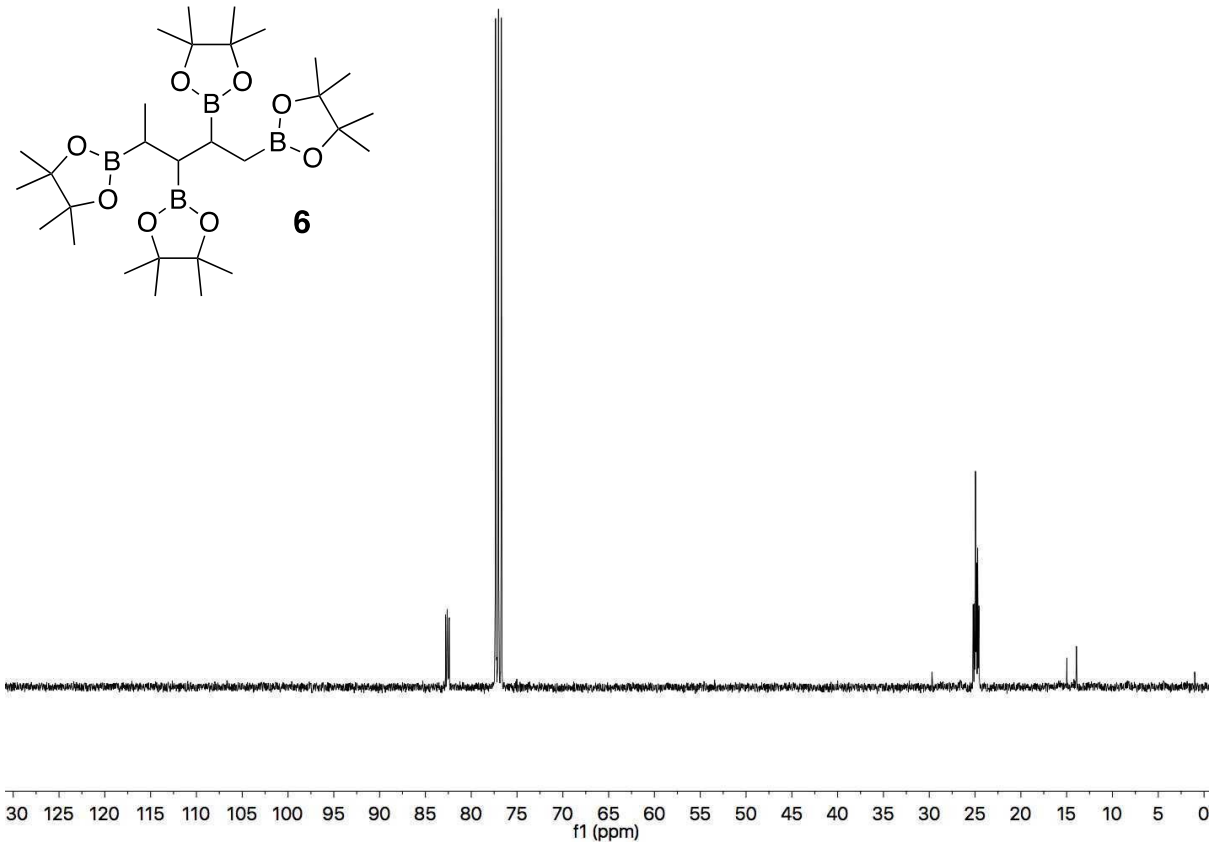


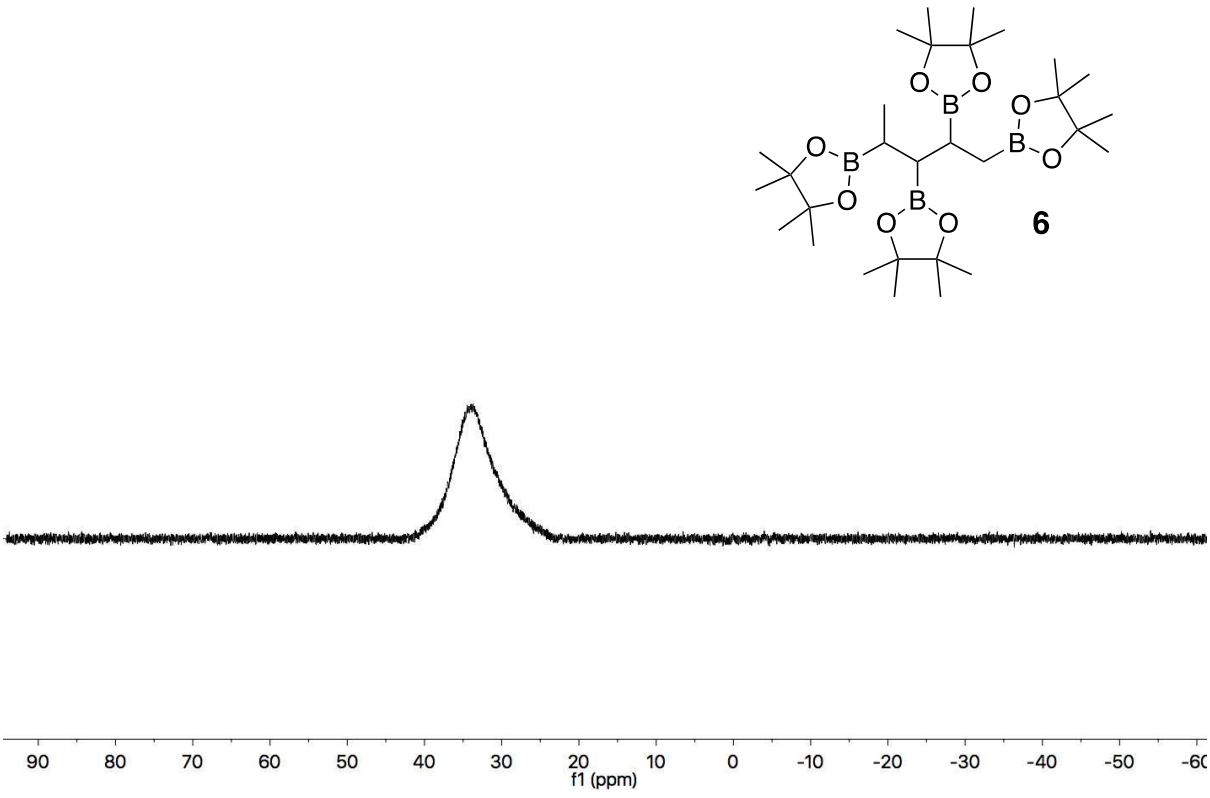
5

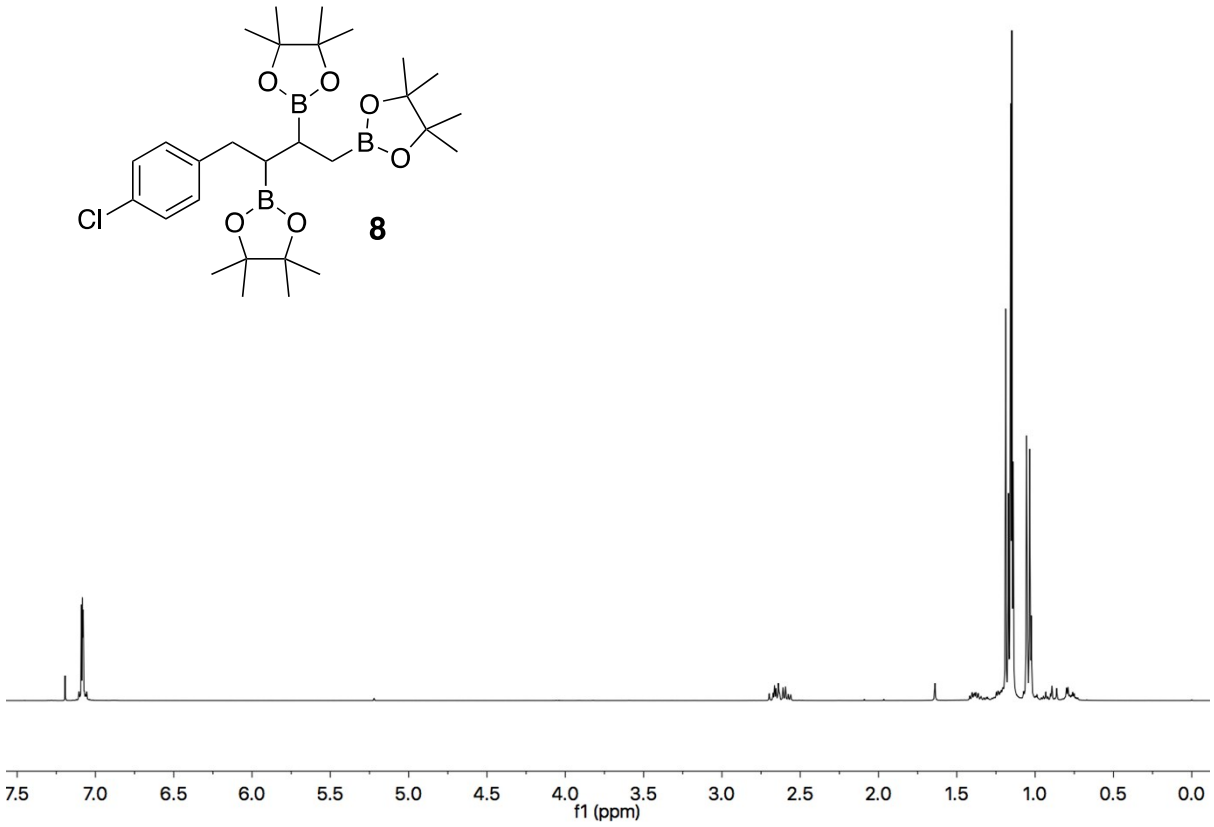




6


6
30 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


6
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)


Cl
8
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4.5
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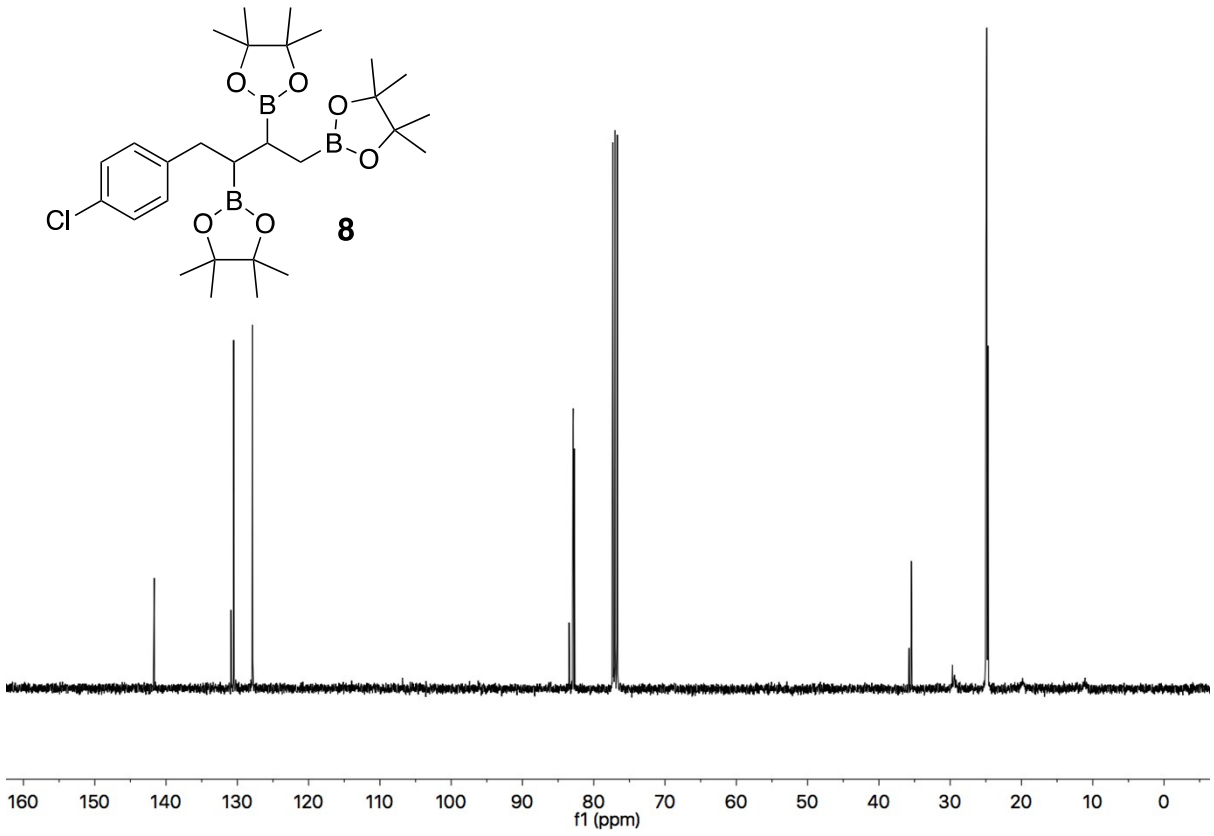
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Cl
8
160
150
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130
120
110
100
90
80
70
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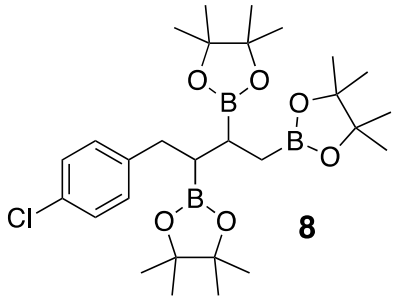
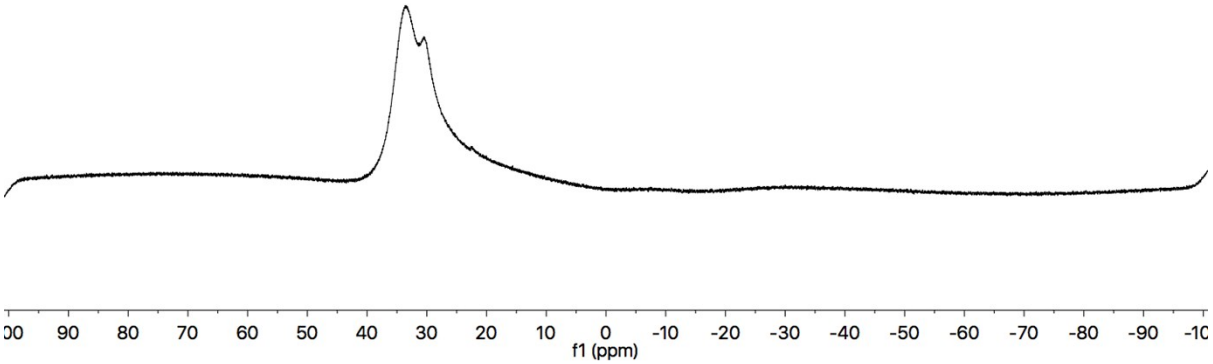
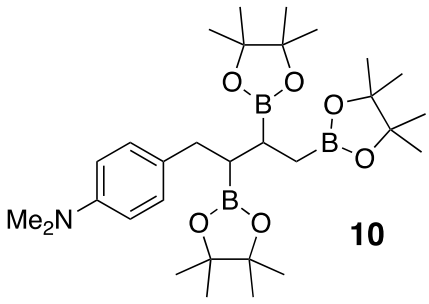
50
40
30
20
10
0
f1 (ppm)


Cl
B
O

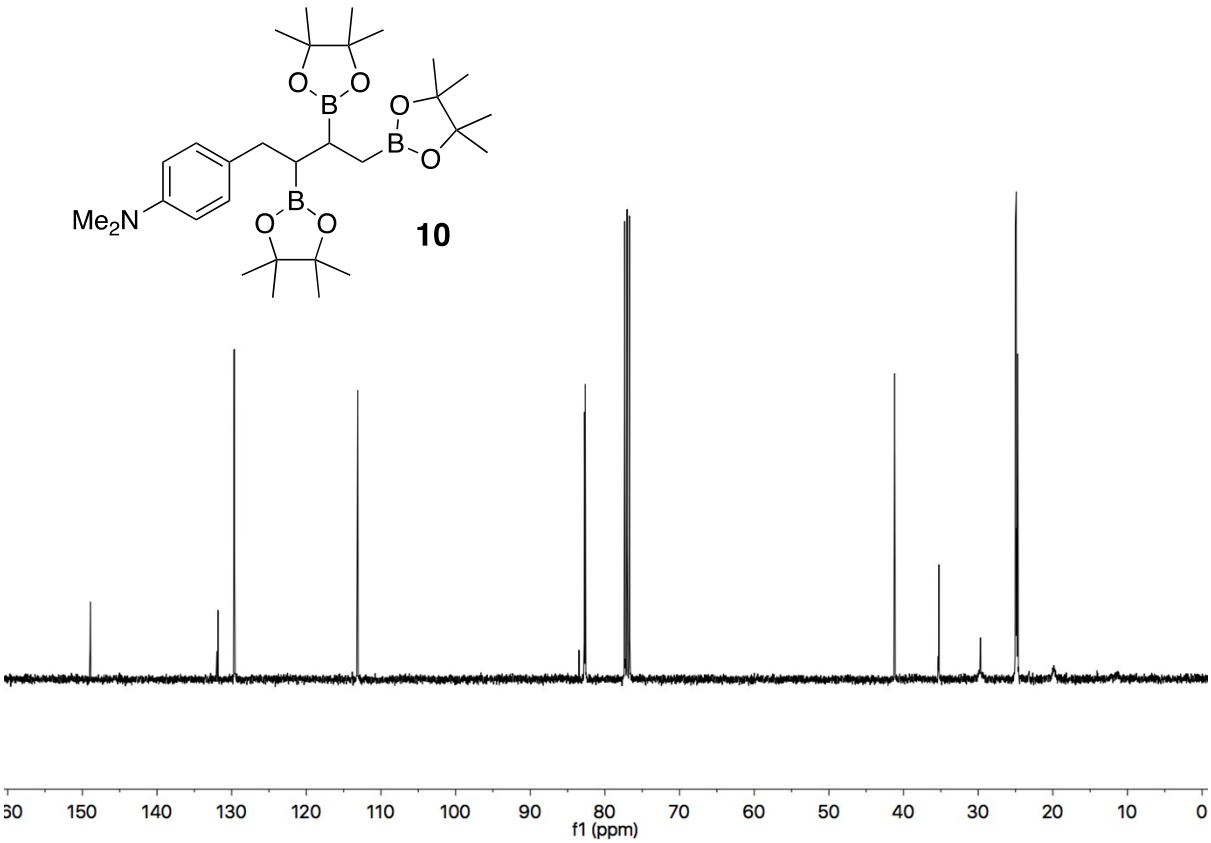
8

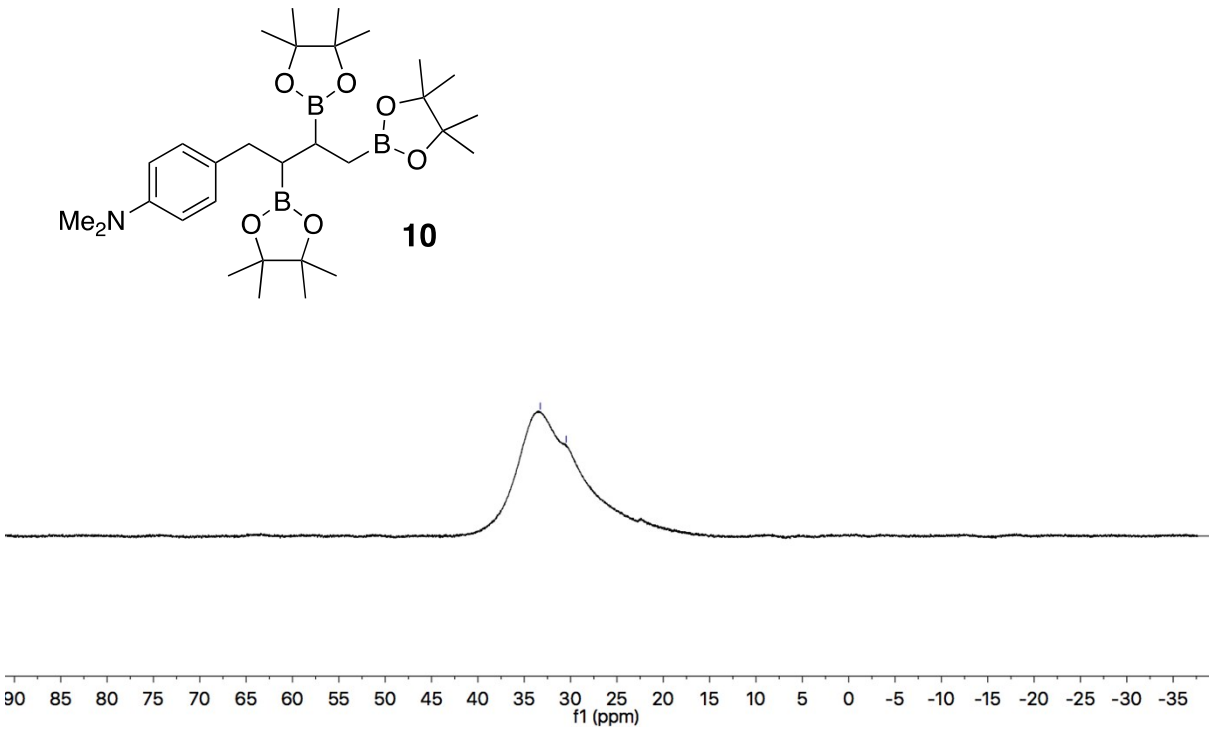

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

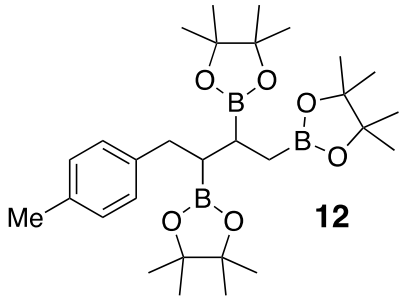

Me2N
B
O

10

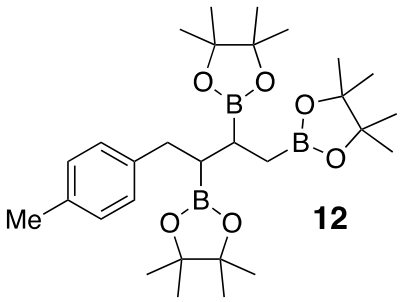
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Me2N
10
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

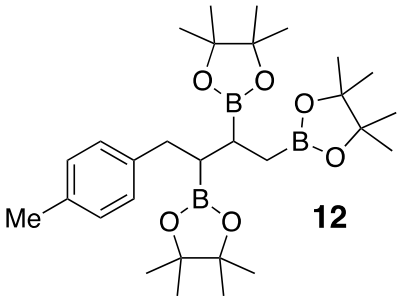

Me2N
10
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
f1 (ppm)


Me
12

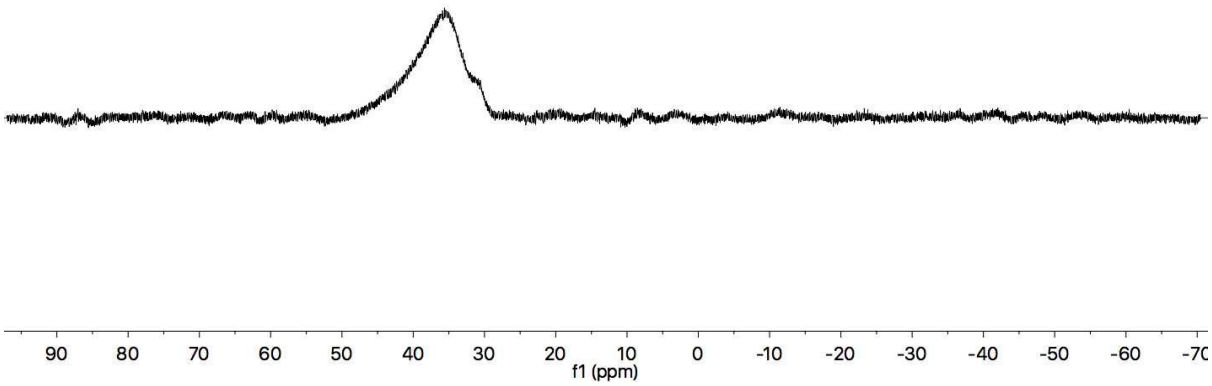
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

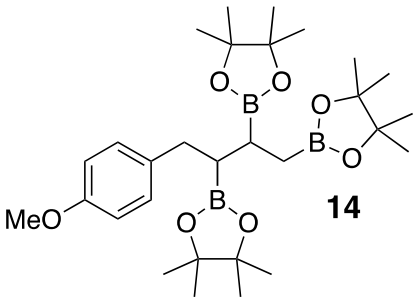

Me
12

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me

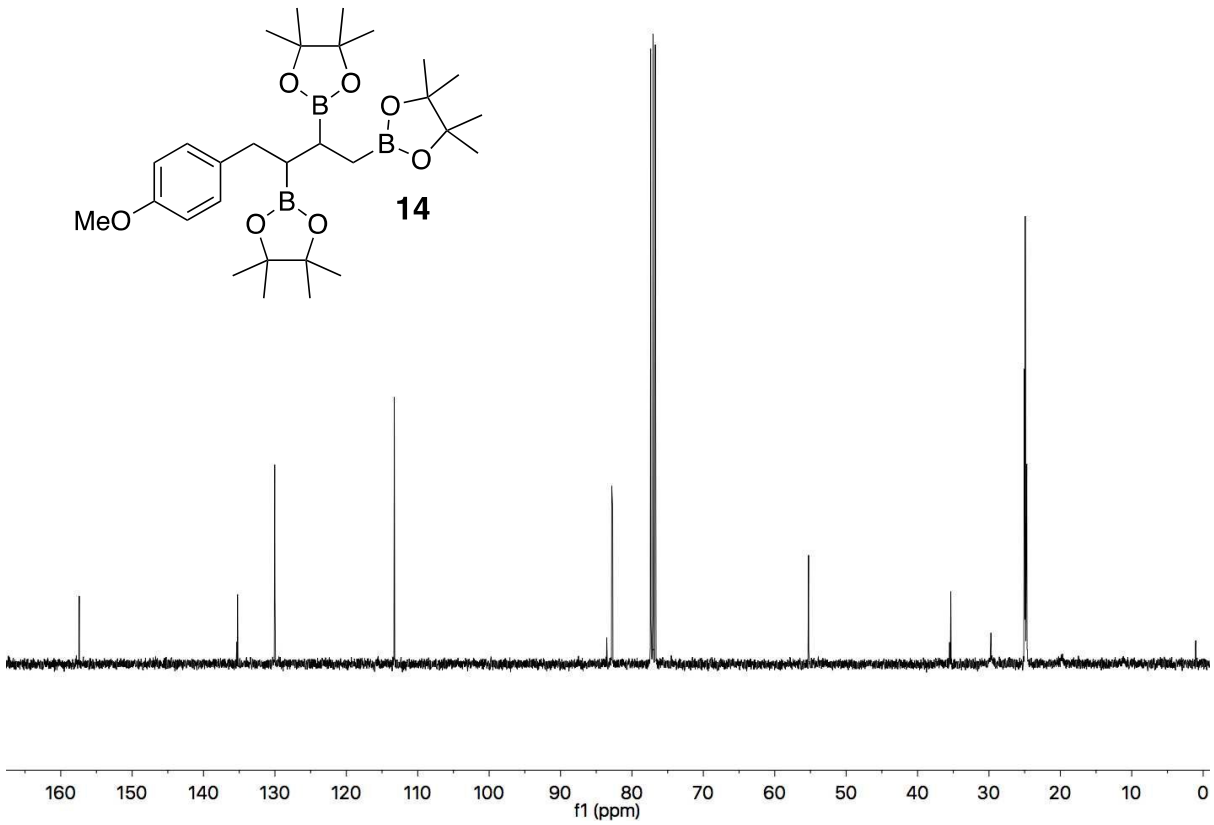
12

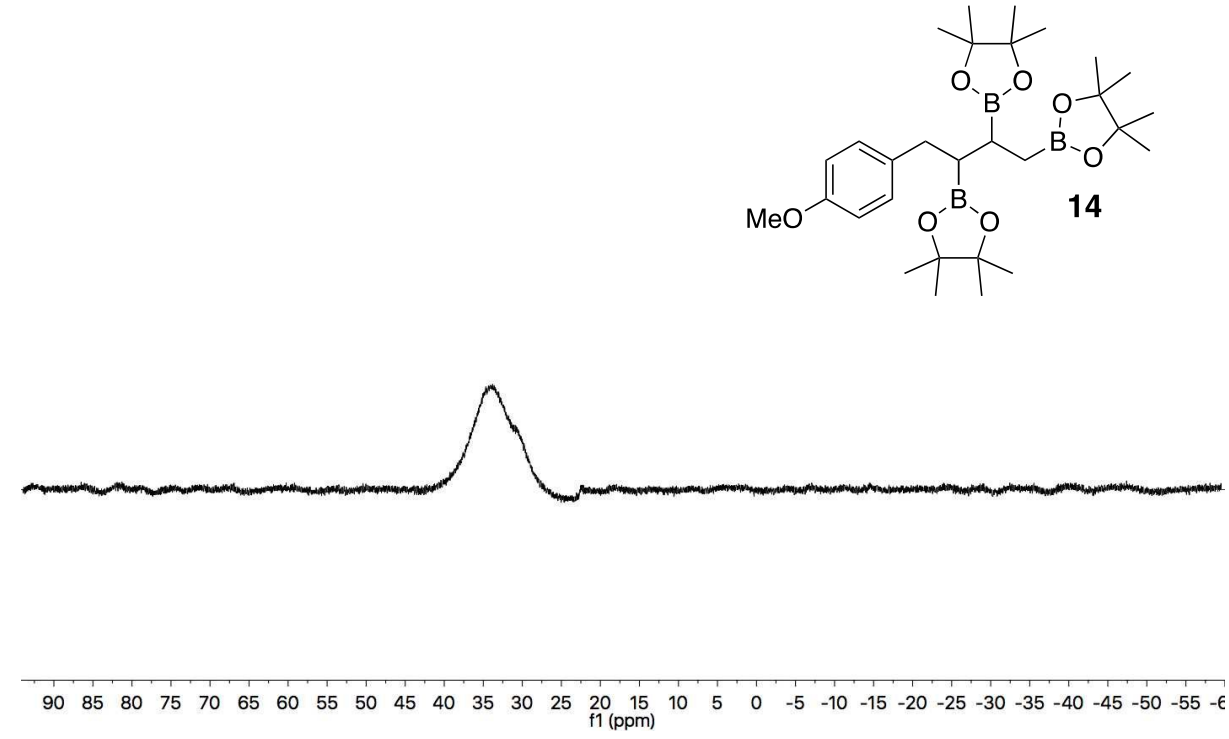

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

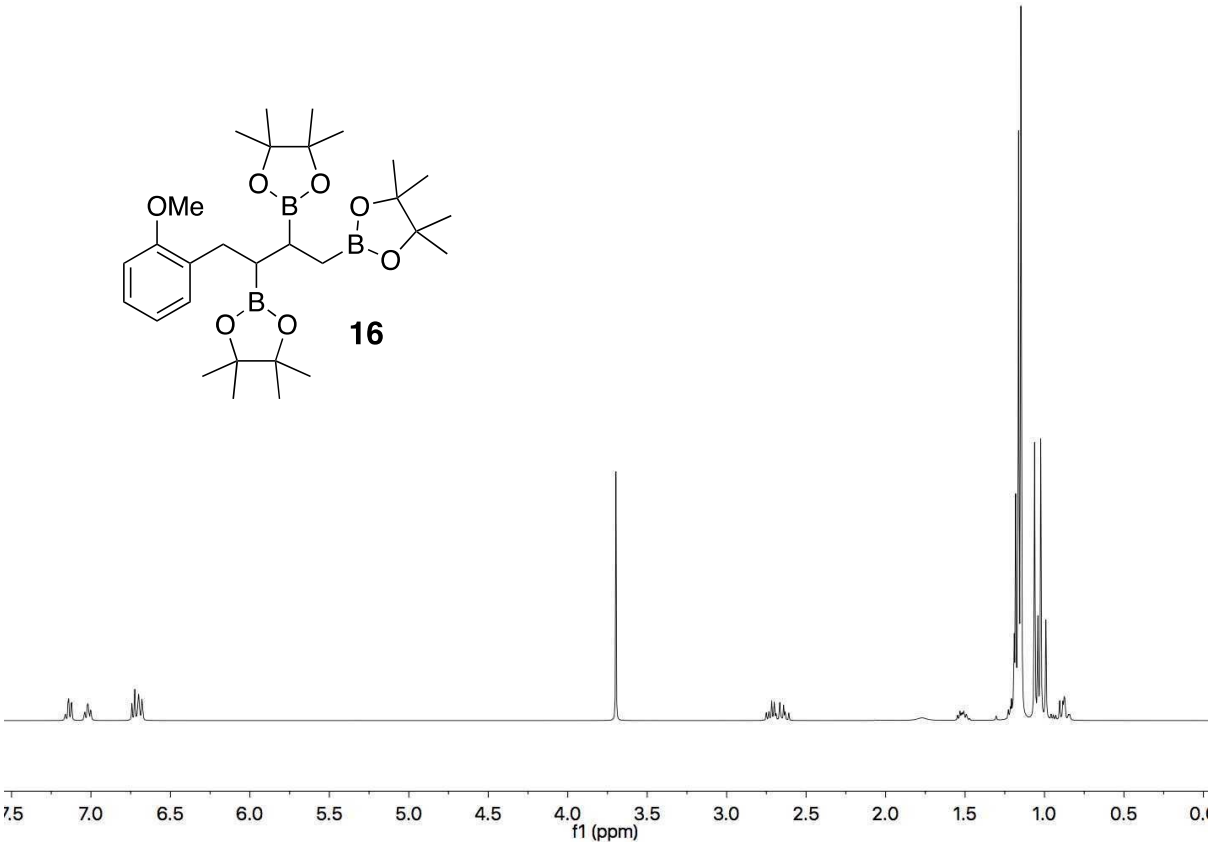

MeO

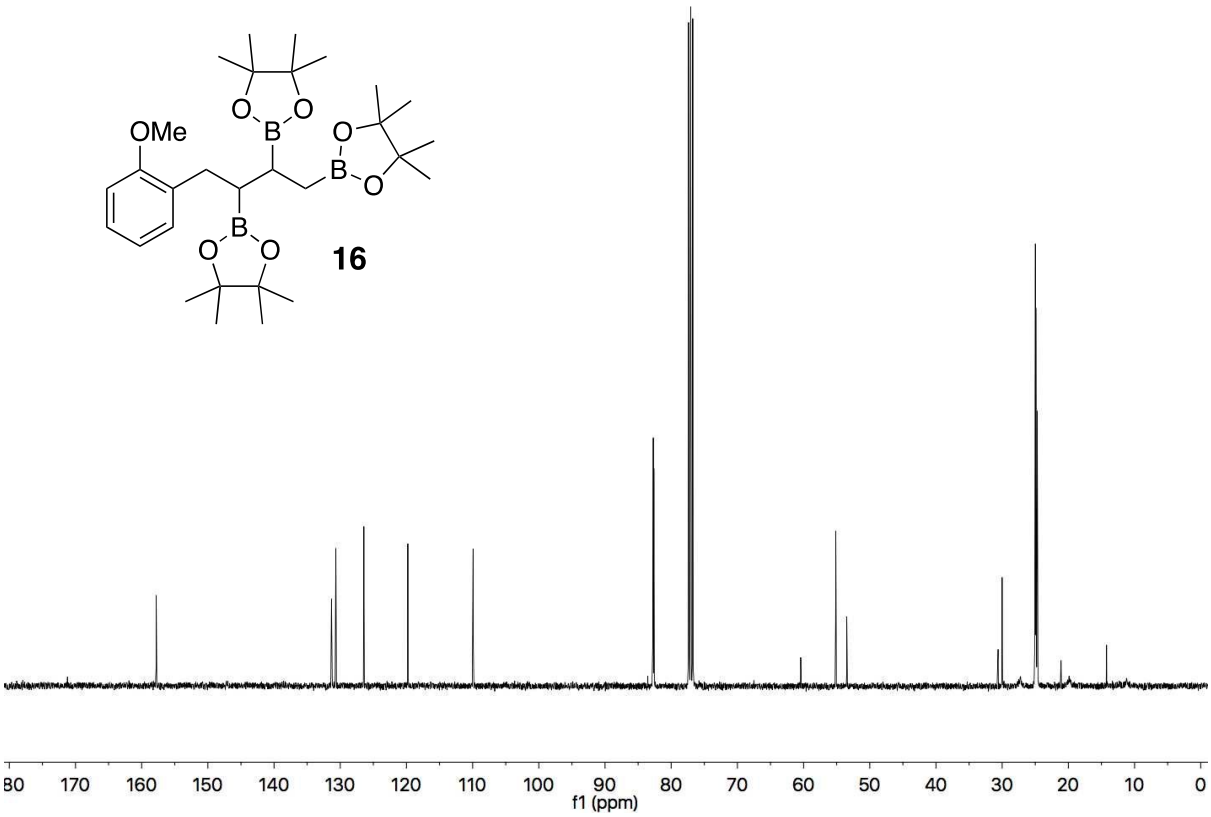
14

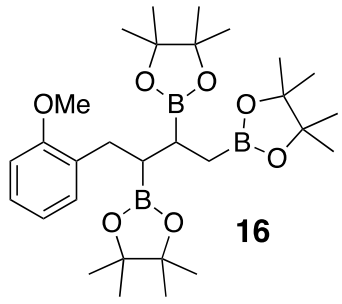
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


MeO
14
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

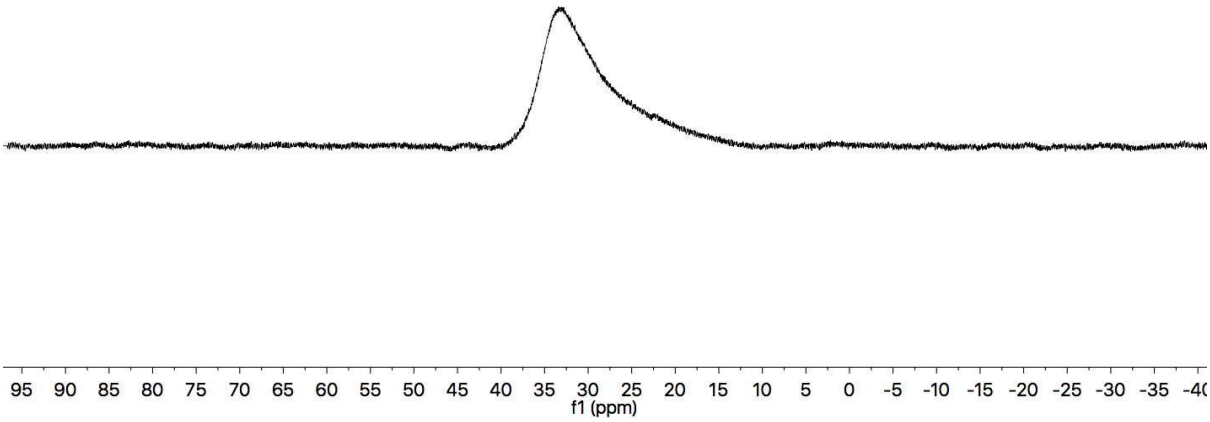

MeO
14
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
f1 (ppm)

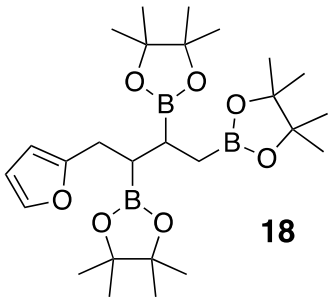

OMe
B
O
B
O
B
O
O
O
O
16
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


OMe
B
O
B
O
B
O
O
O
O
16
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
B
O
B
O
B
O
O

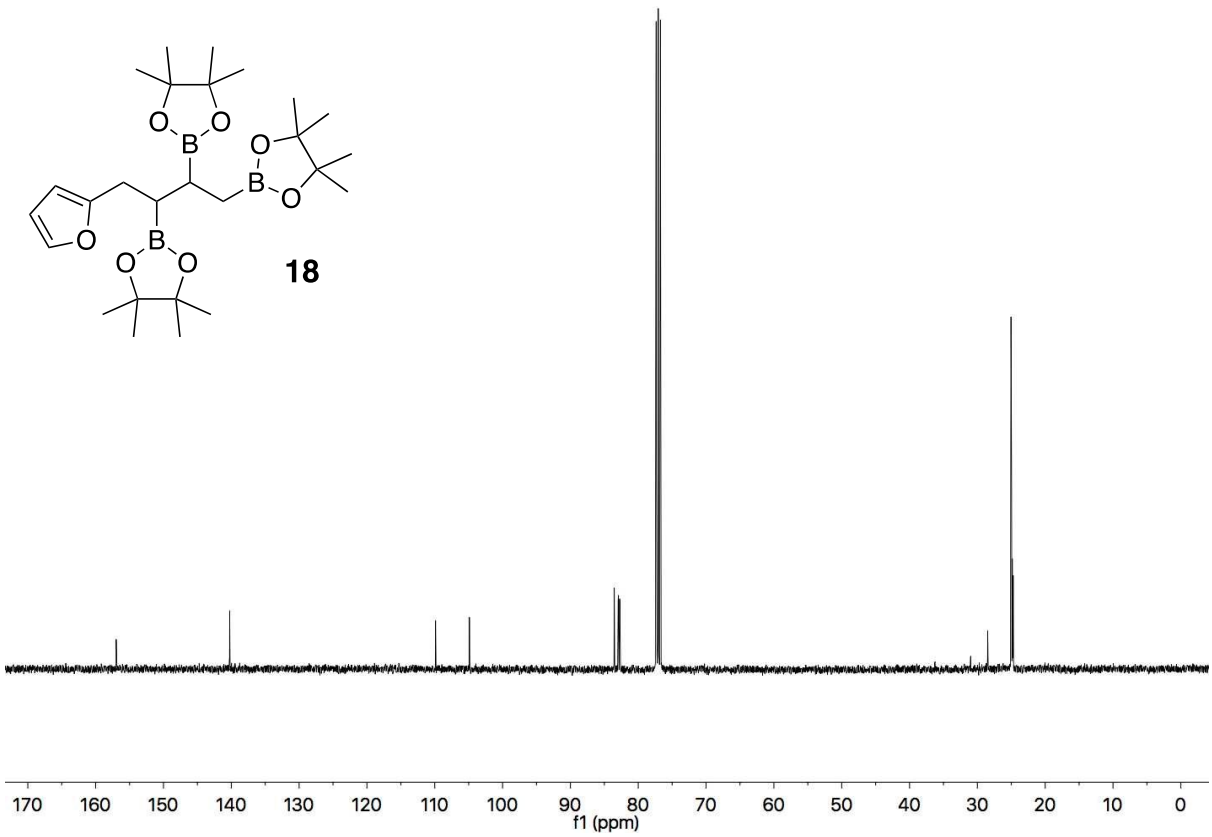
16

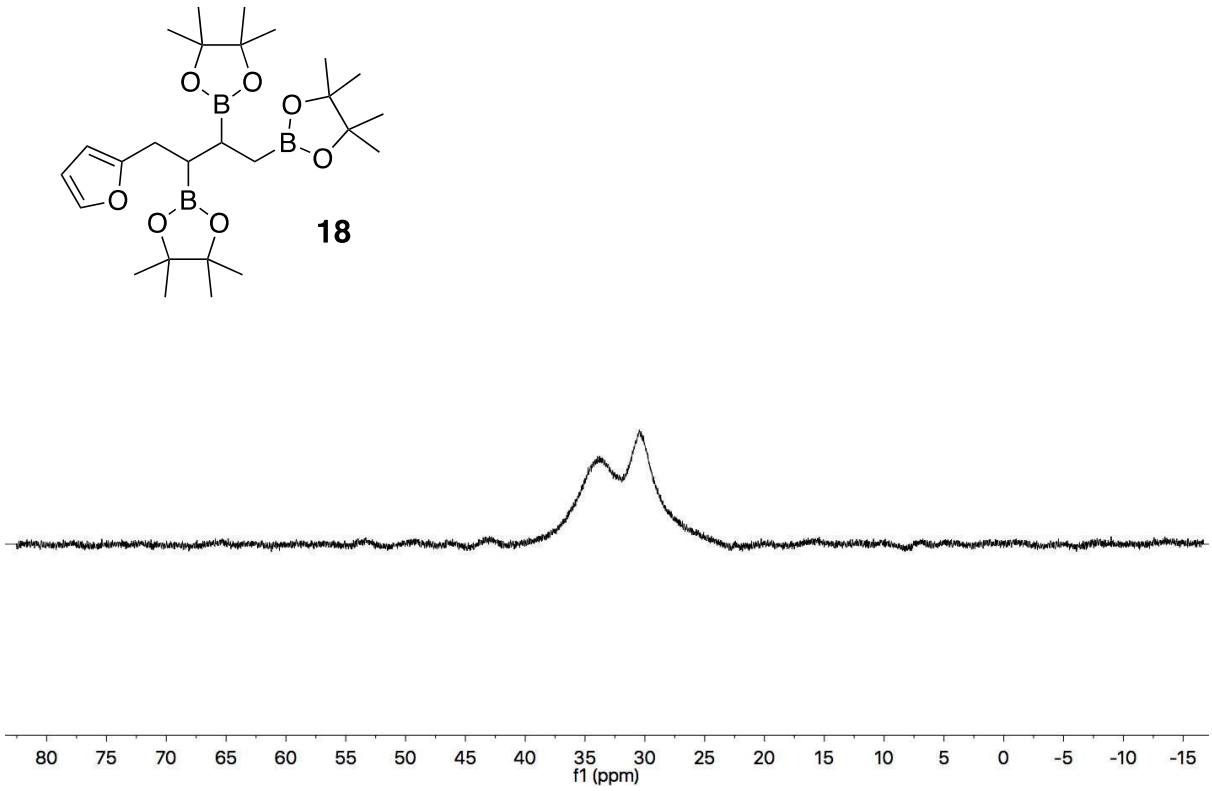

95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

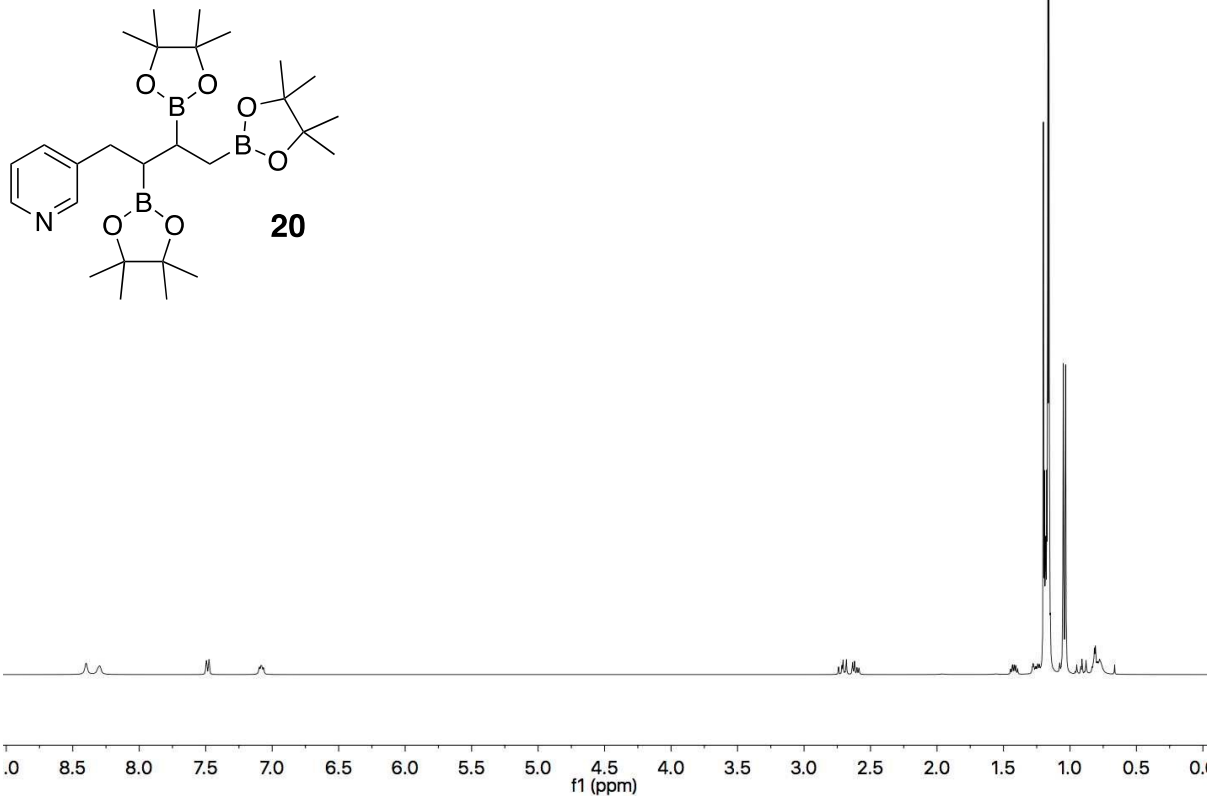

O
B
O
B
O
O
B
O
O

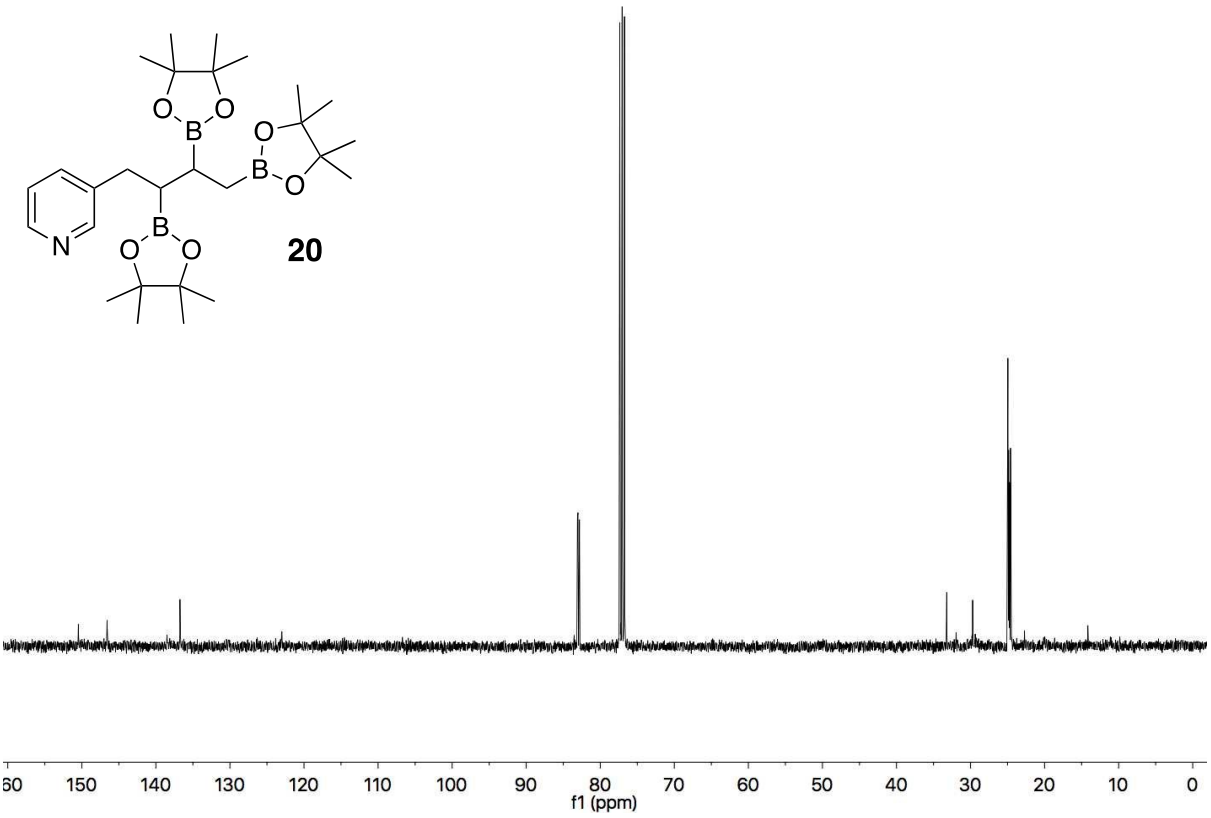
18

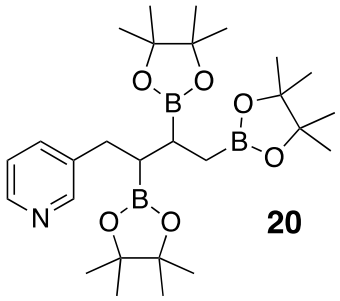
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


18
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

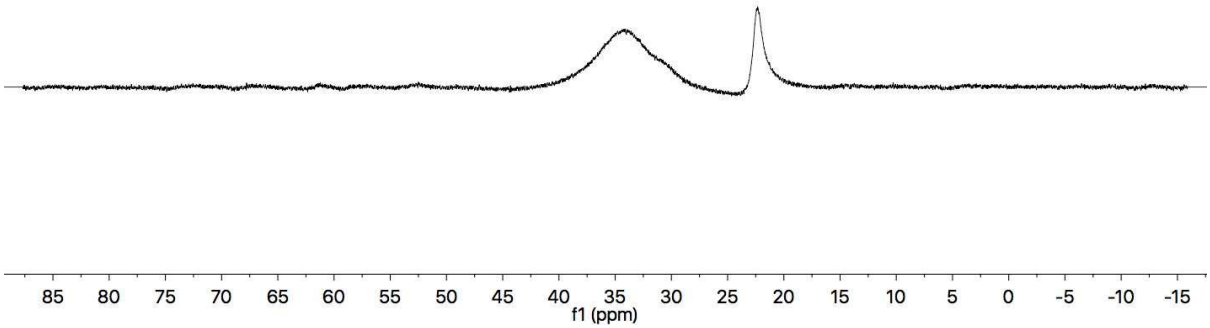

18
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

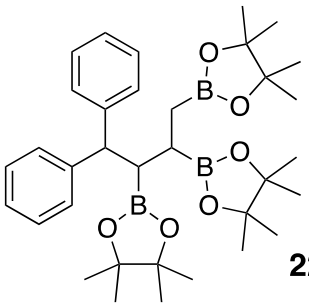

20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


20
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



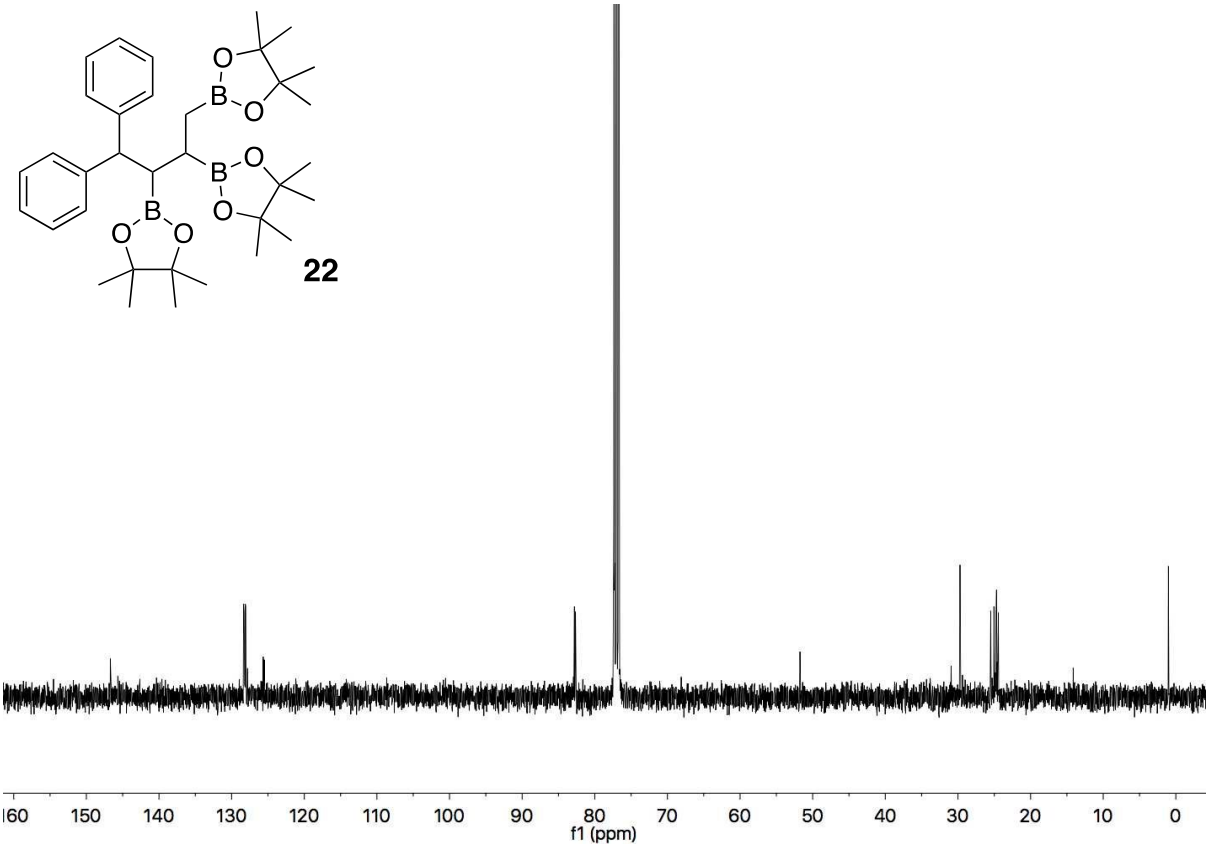
20

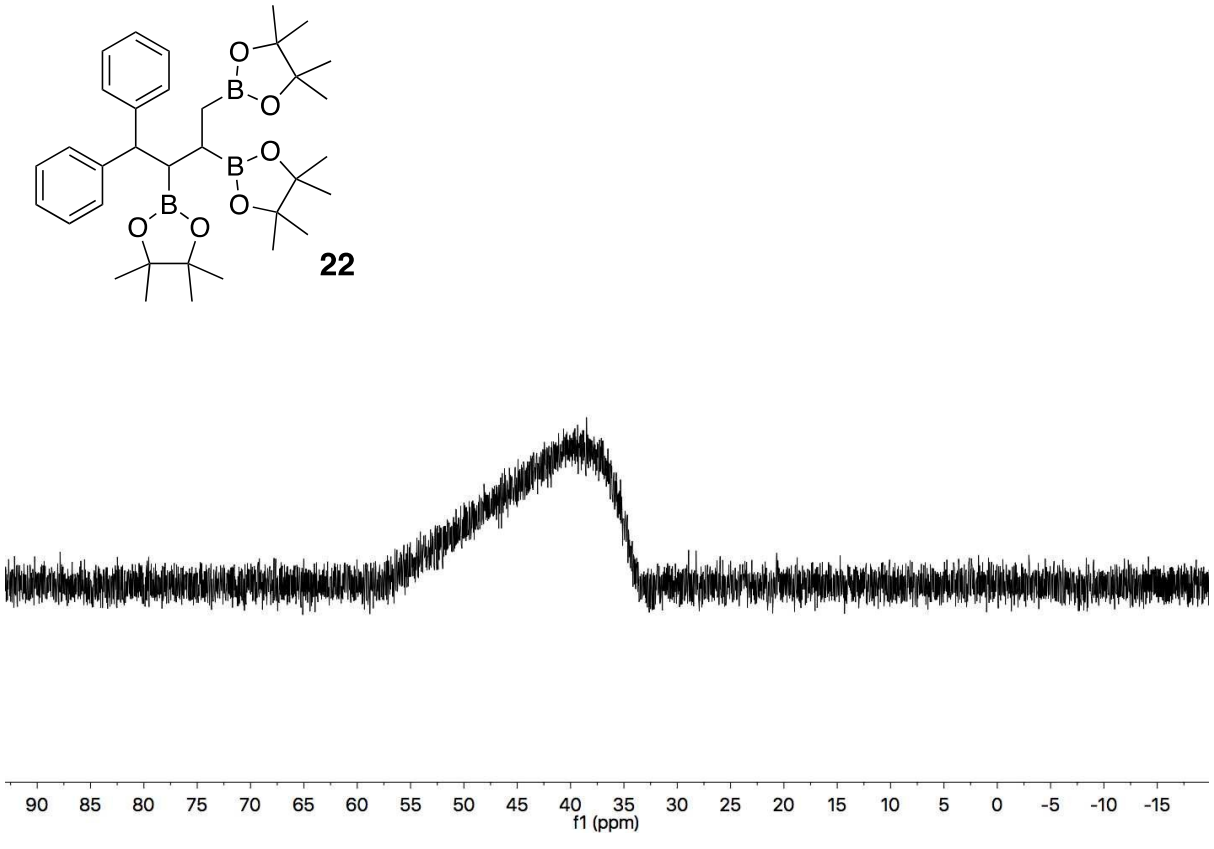

85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

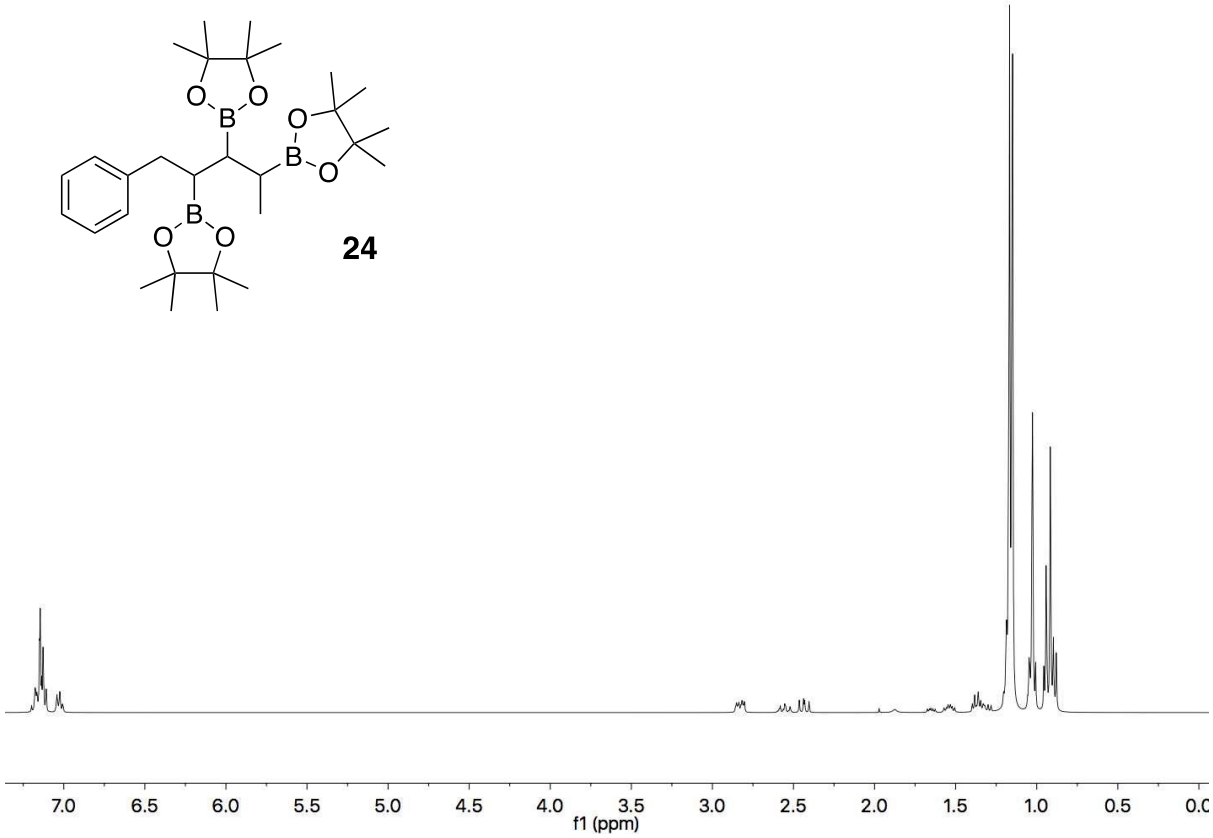


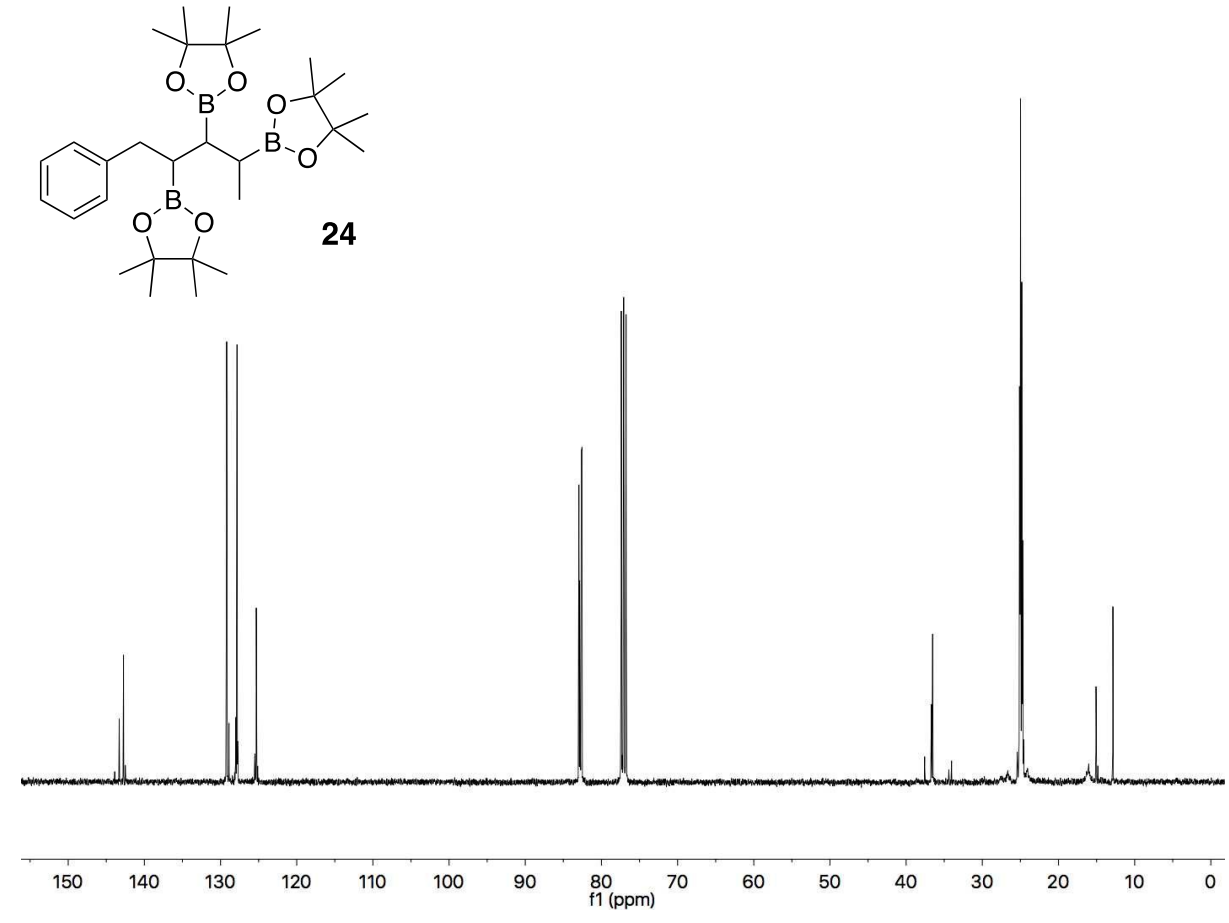
22

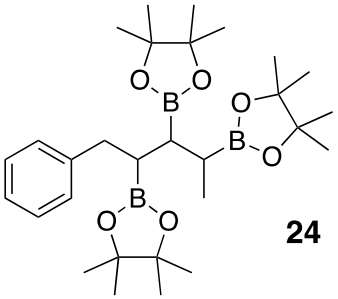
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


22
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

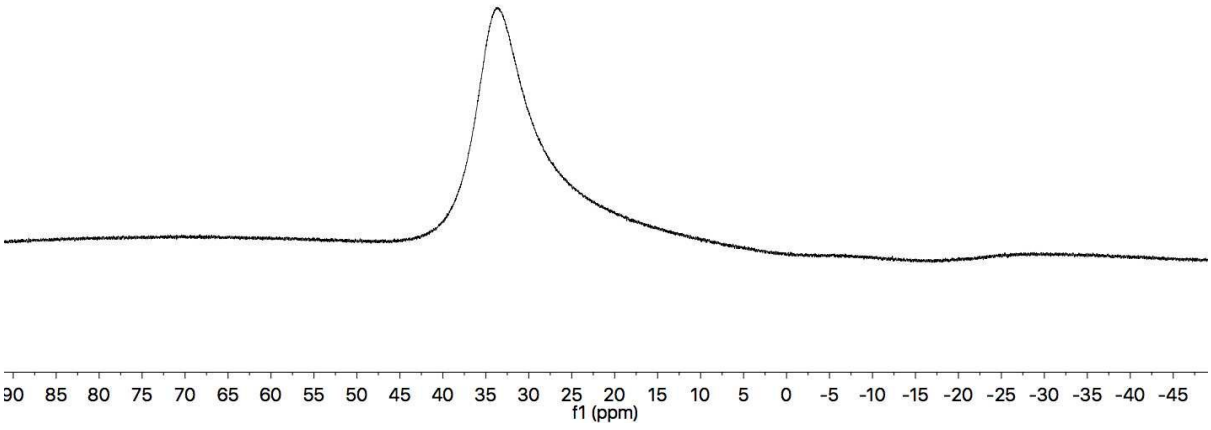

22
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
f1 (ppm)

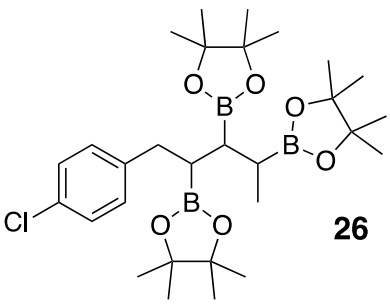

24
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


24
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



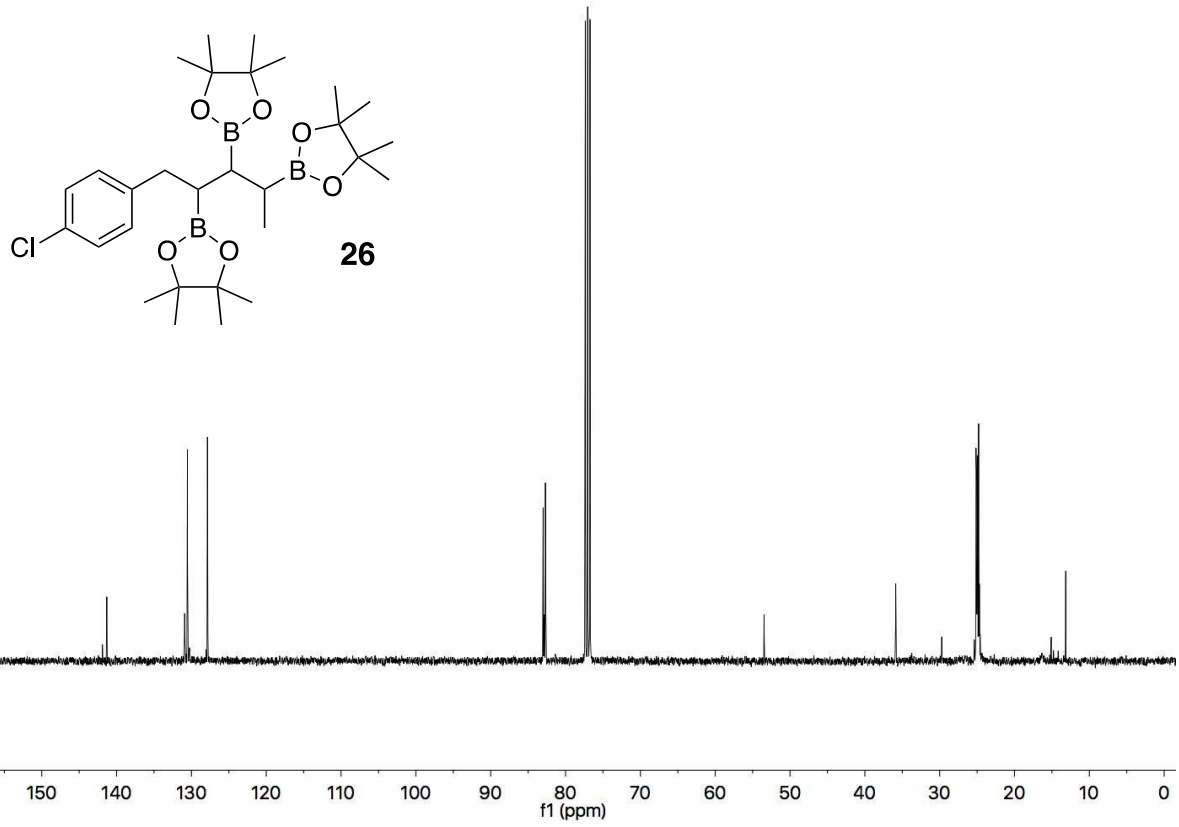
24

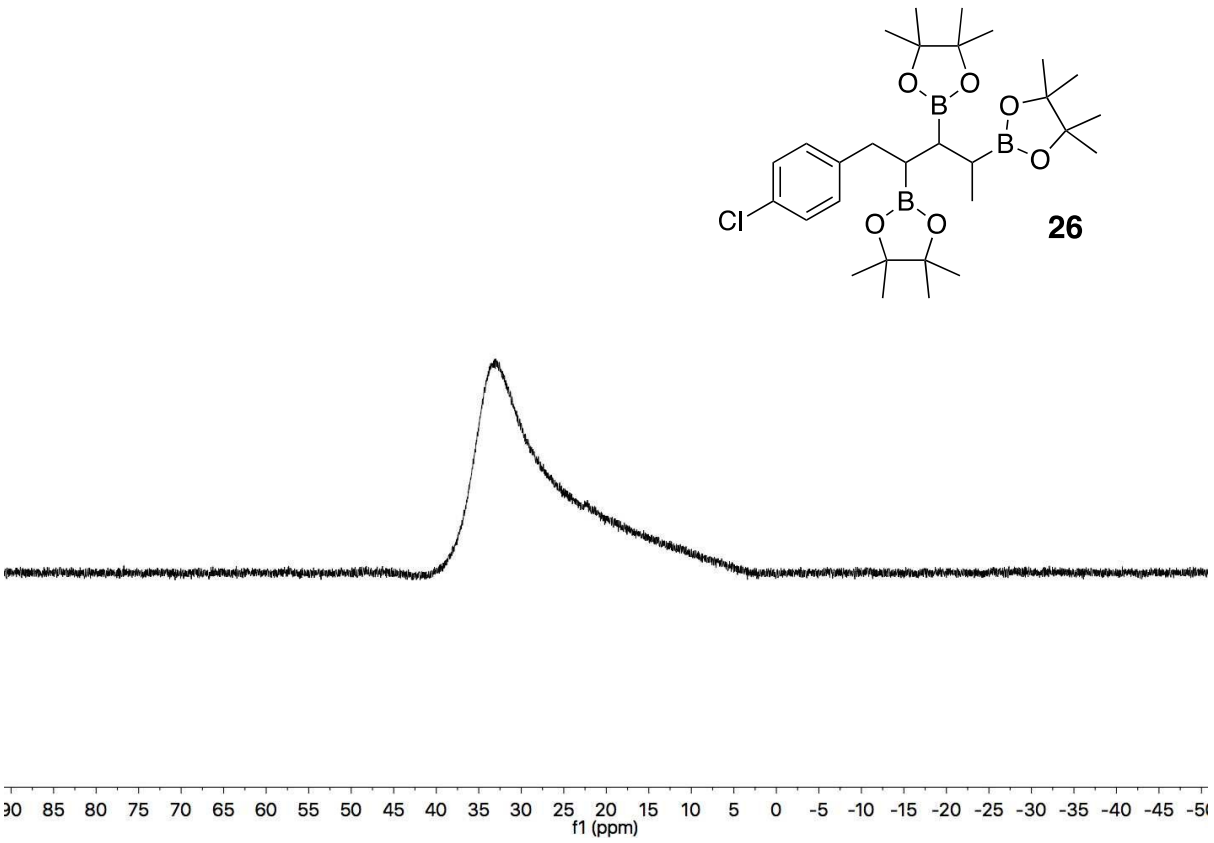

90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

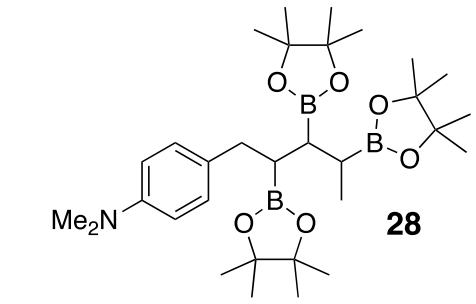


26

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

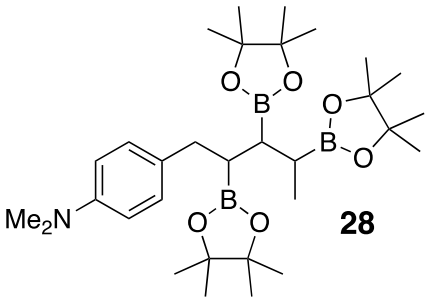

Cl
26
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
26
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -5
f1 (ppm)


Me2N
B
O
O
B
O
O
B
O
O

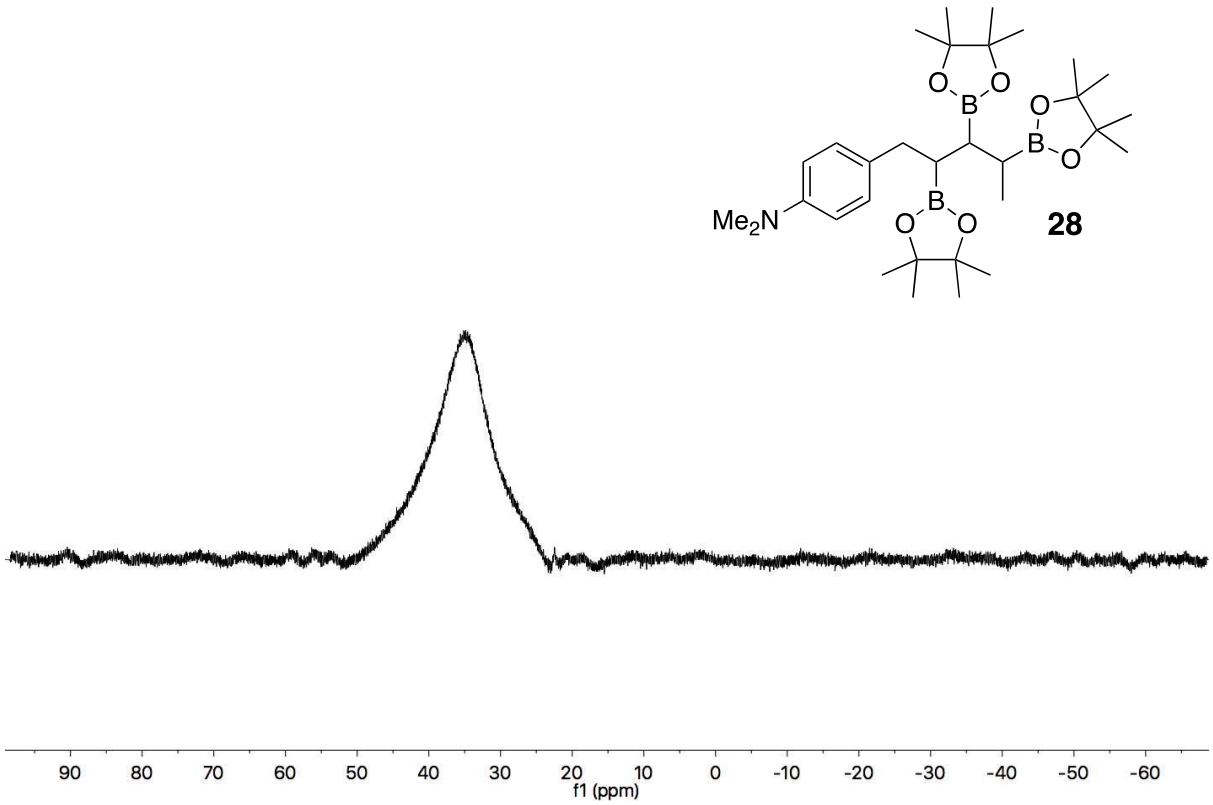
28

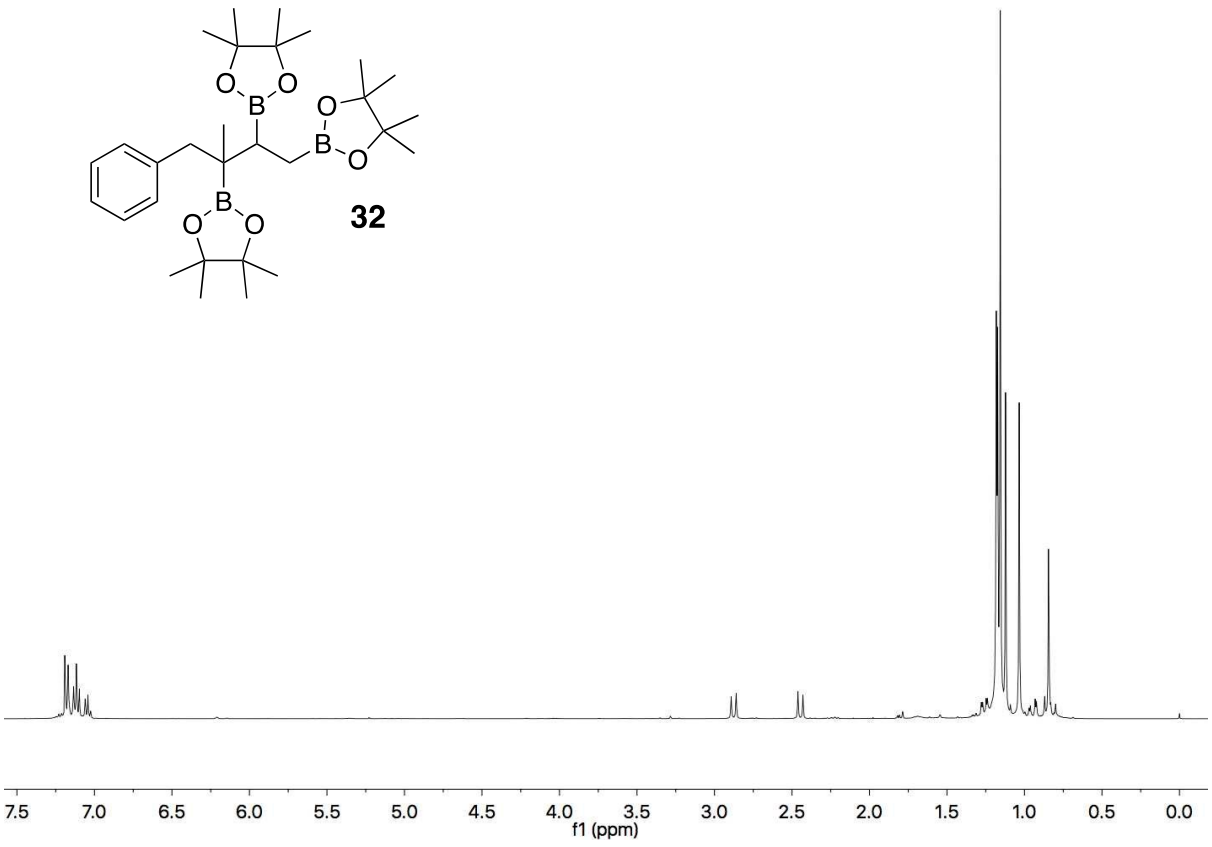
.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

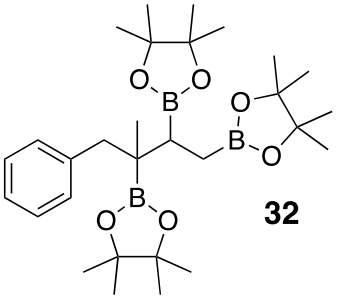

Me2N
B
O
O
B
O
O
B
O
O

28

50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

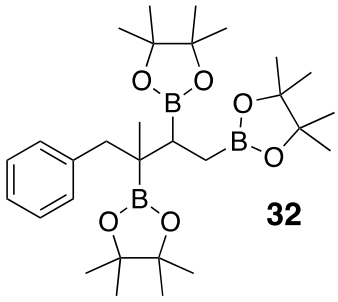

Me2N
28
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)


32
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

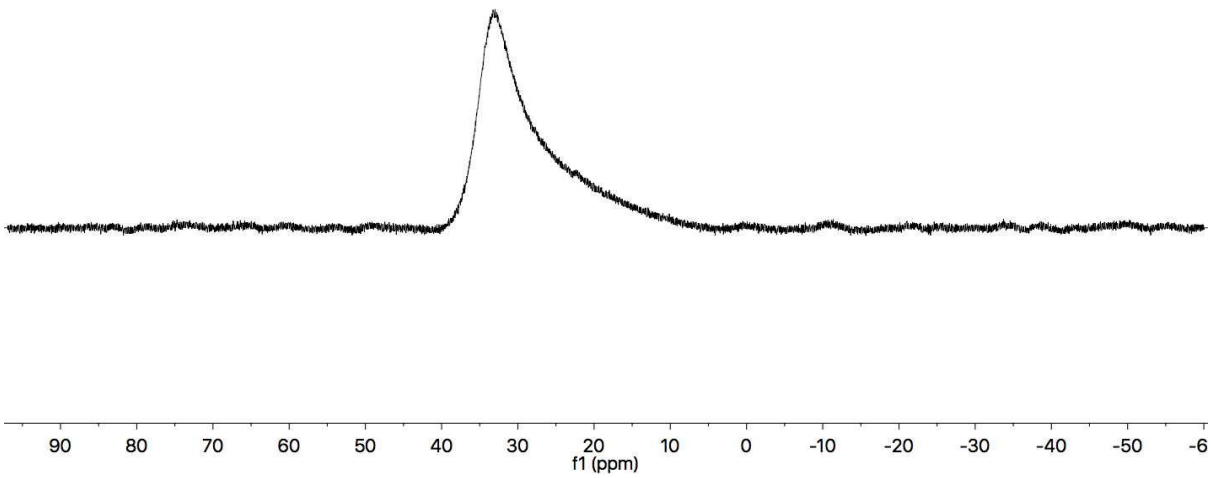


32

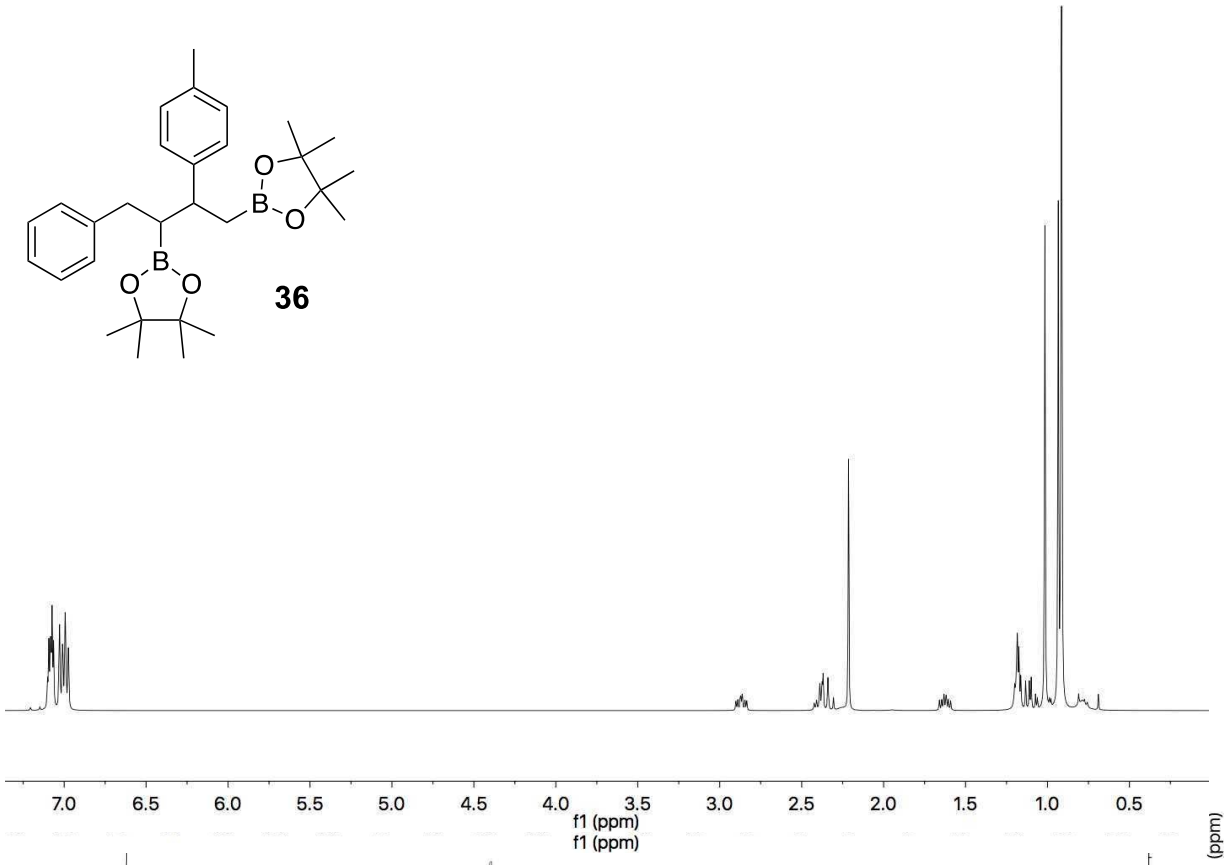
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

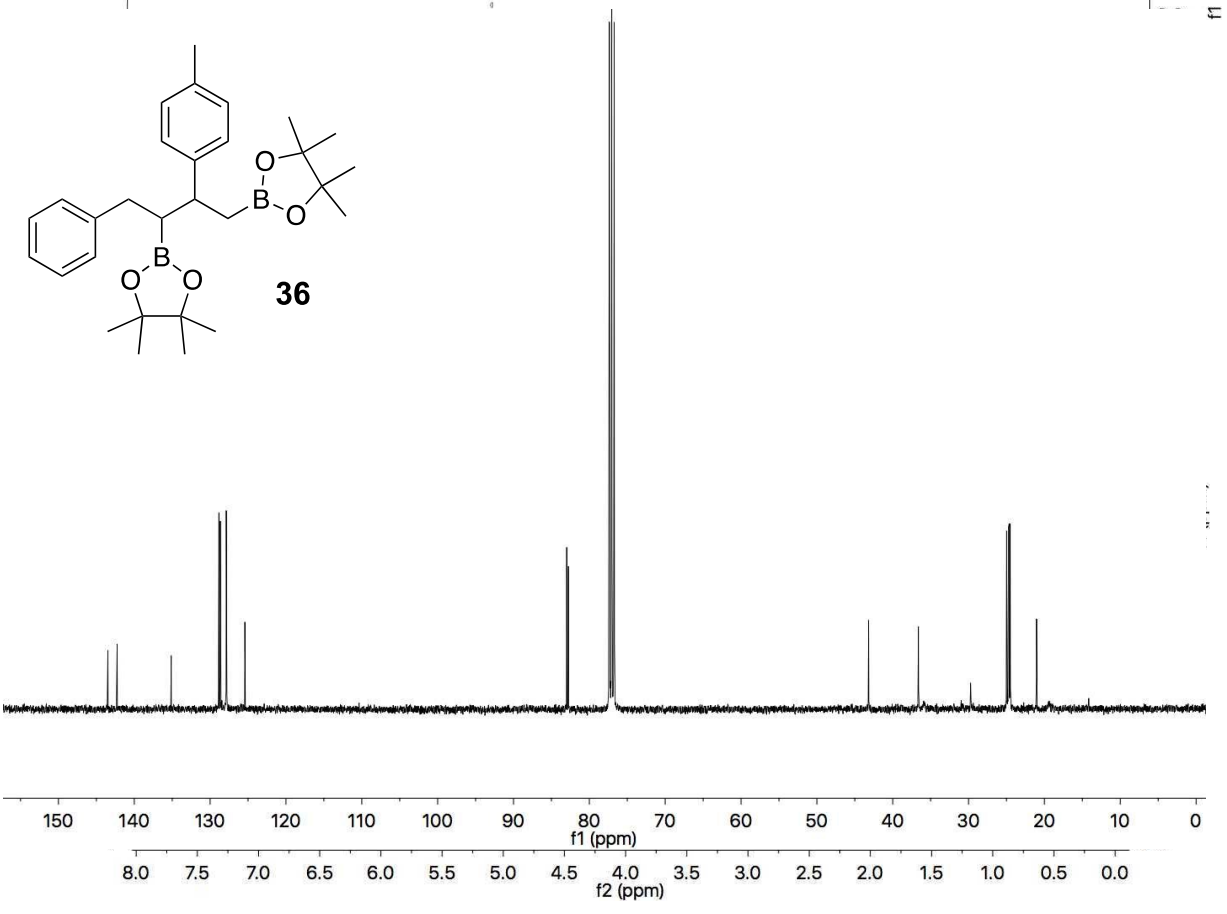


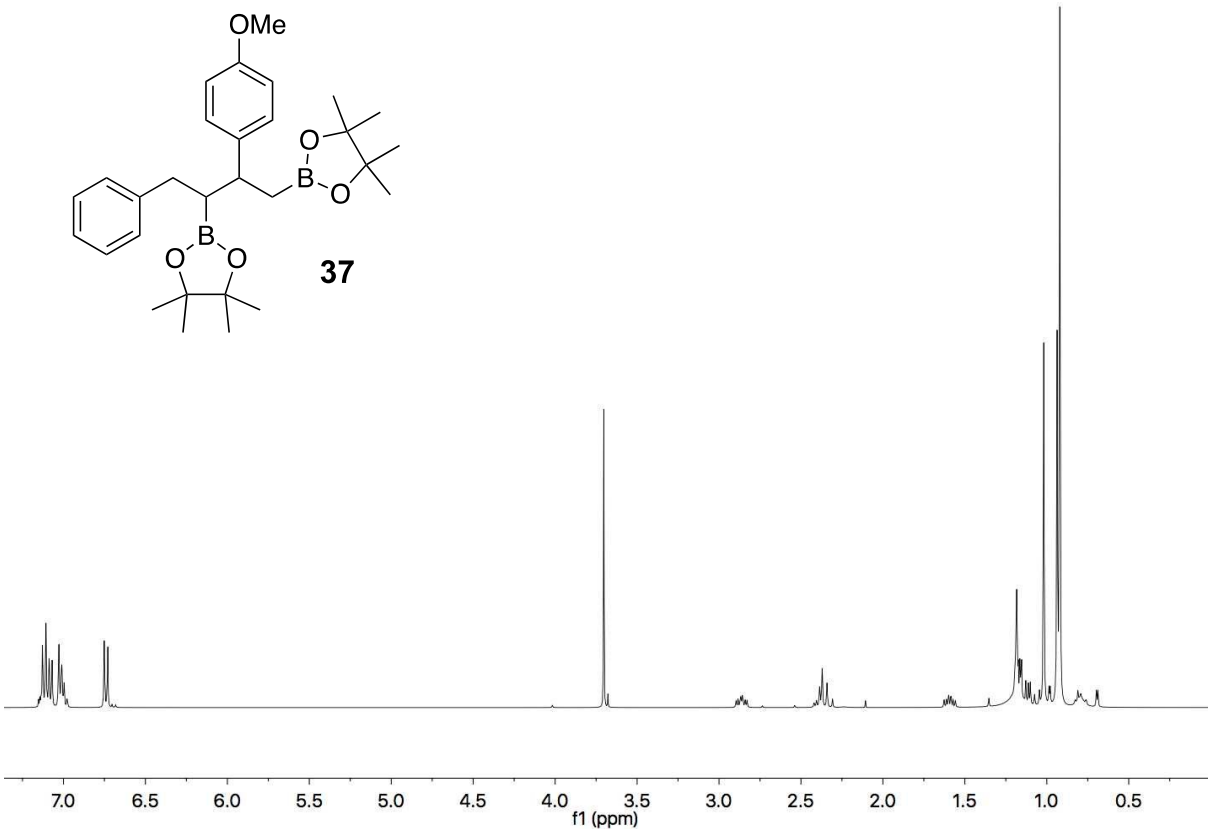
32

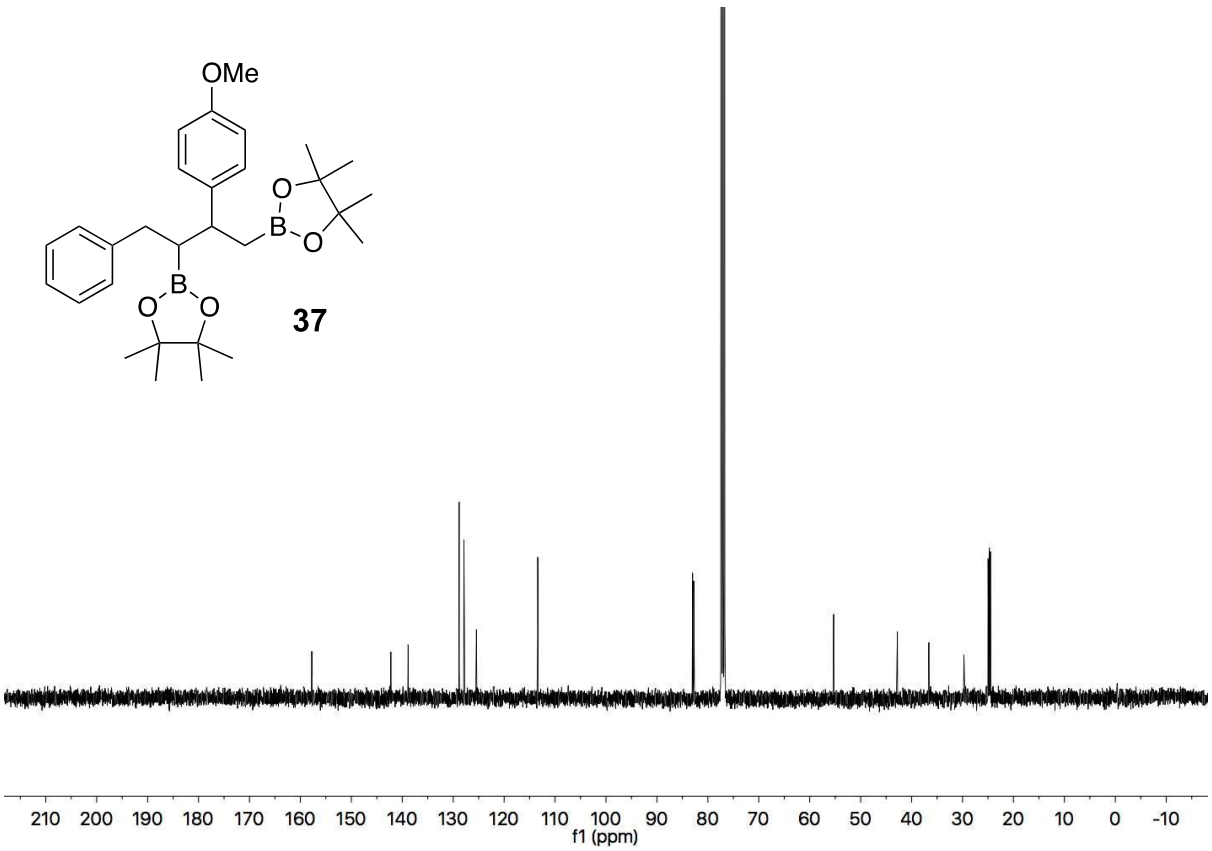

90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-6
f1 (ppm)

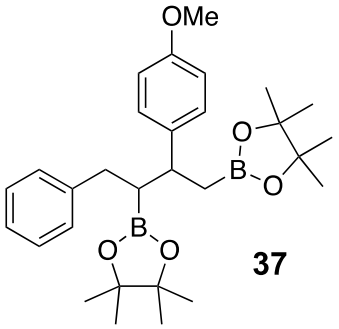
Spectra for Suzuki-Miyaura Cross-Coupling Products:



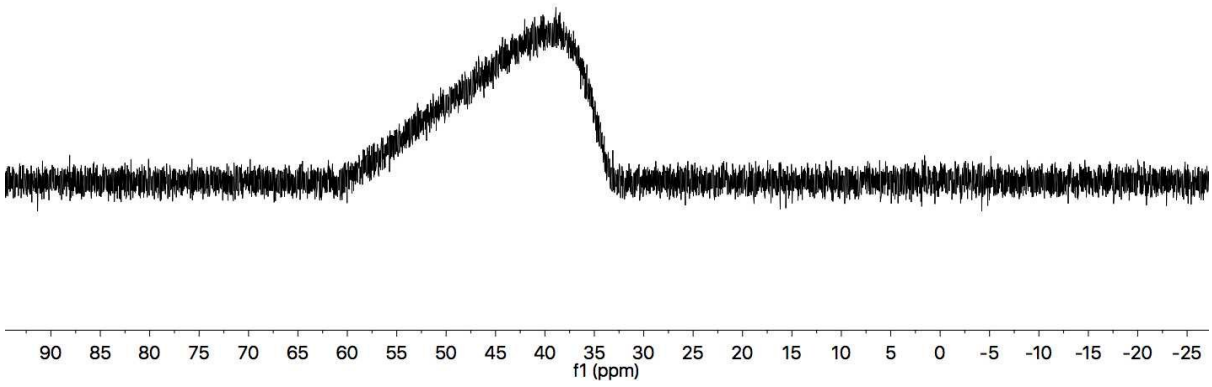


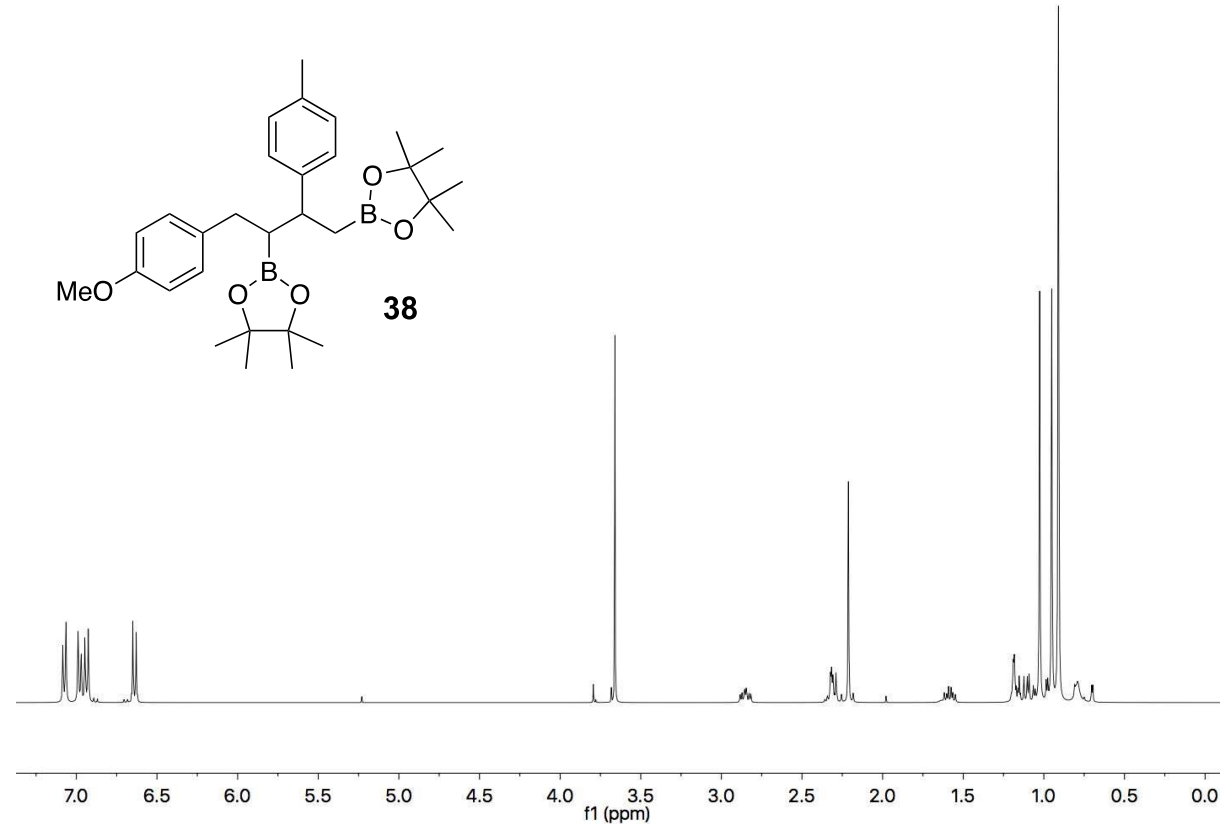

OMe
O
B
O
B
O
O
37
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

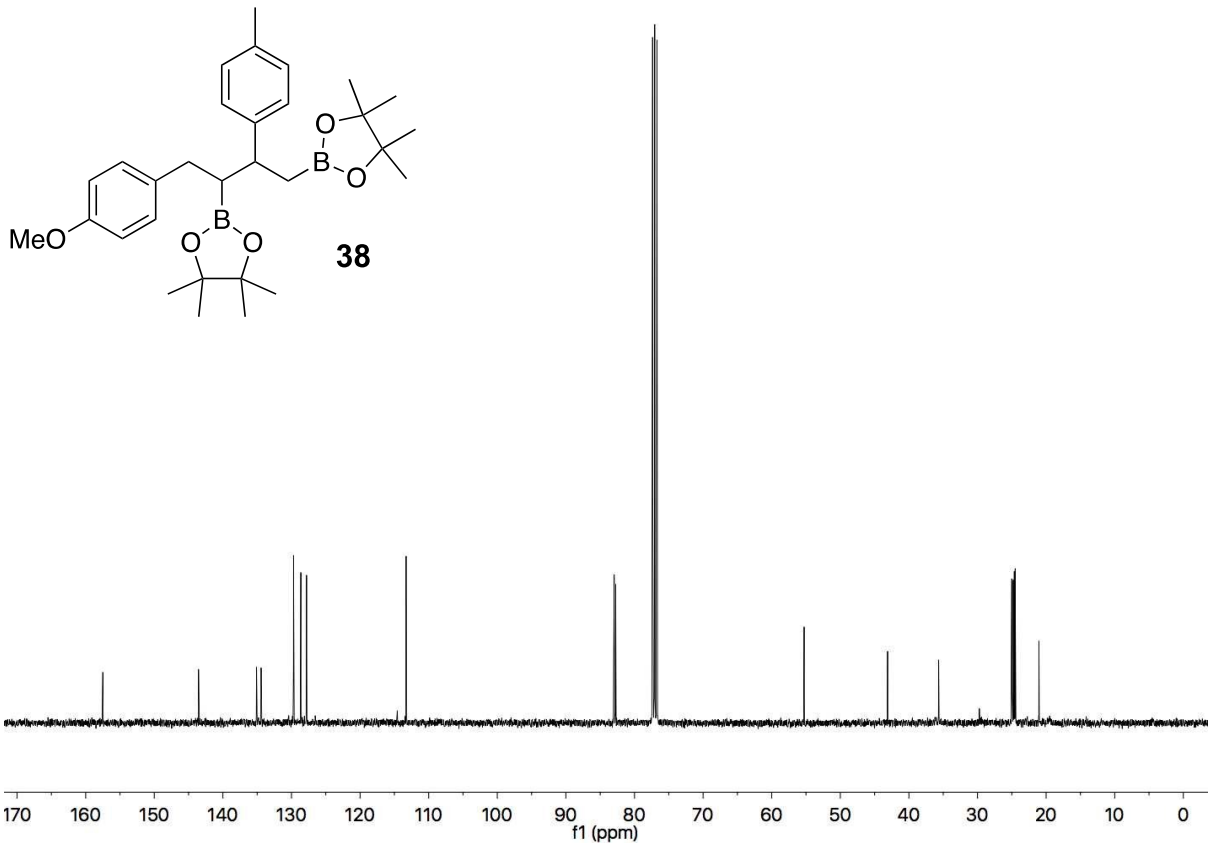

OMe
O
B
O
B
O
O
37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

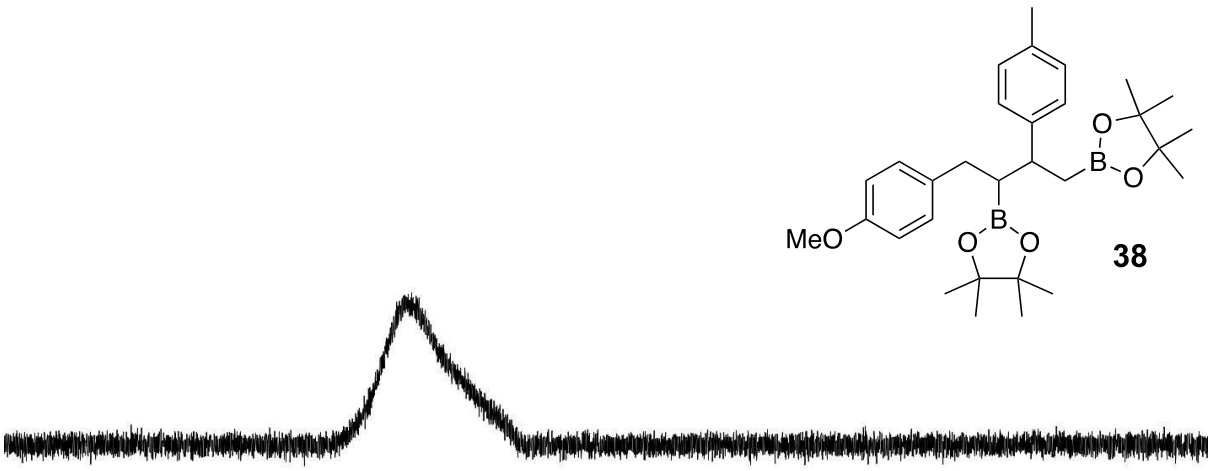

OMe
O
B
O
B
O
O

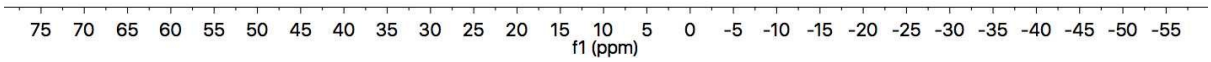
37

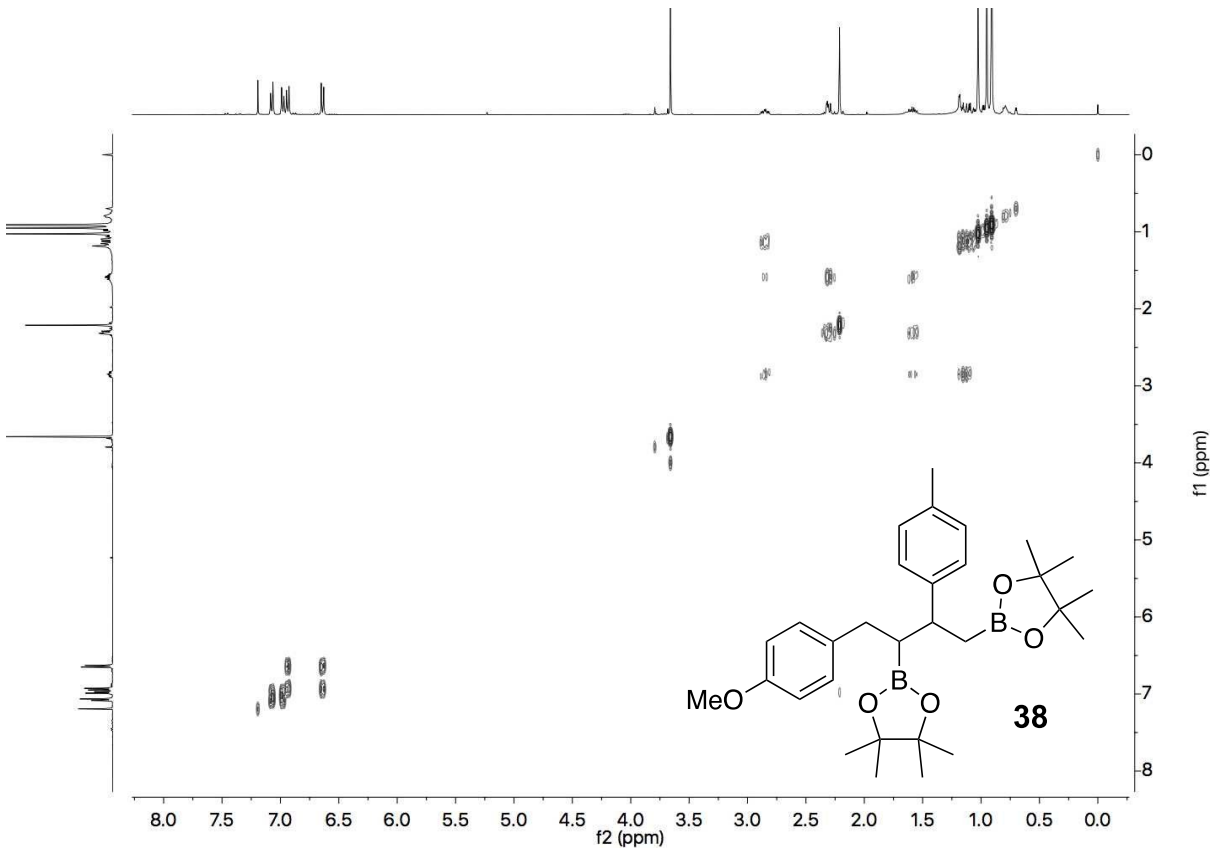

90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

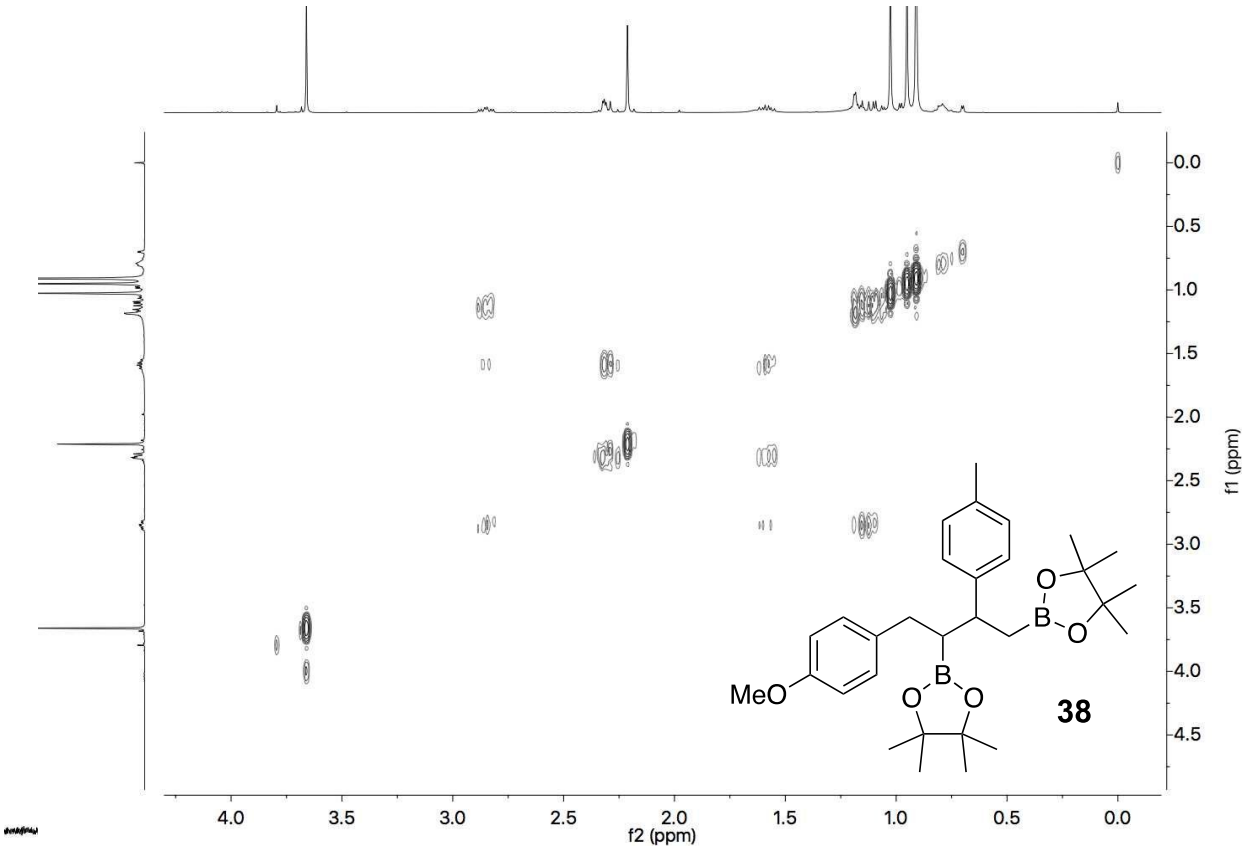

MeO
B
O
O
B
O
O
38
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

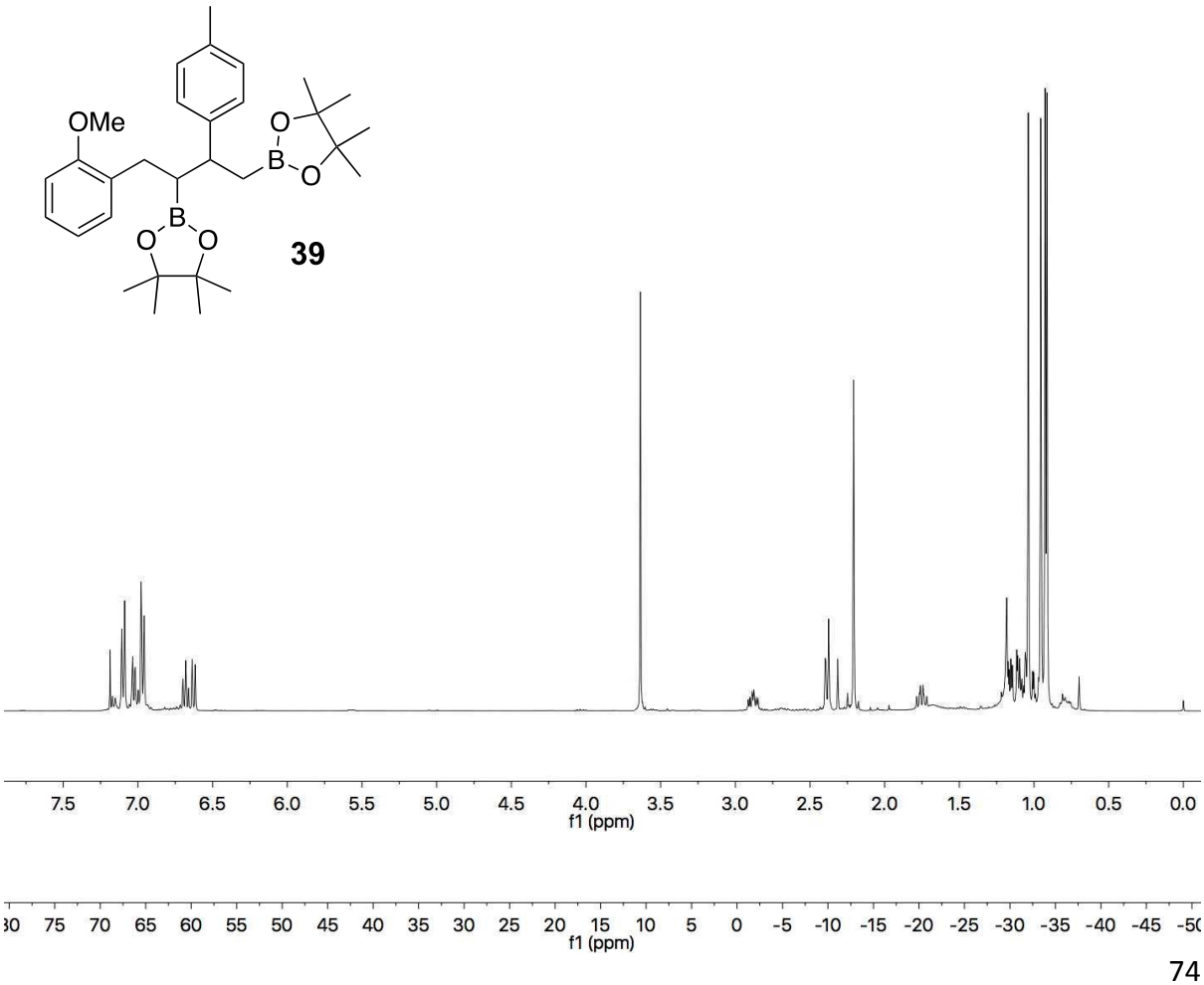

MeO
B
O
O
B
O
O
38
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

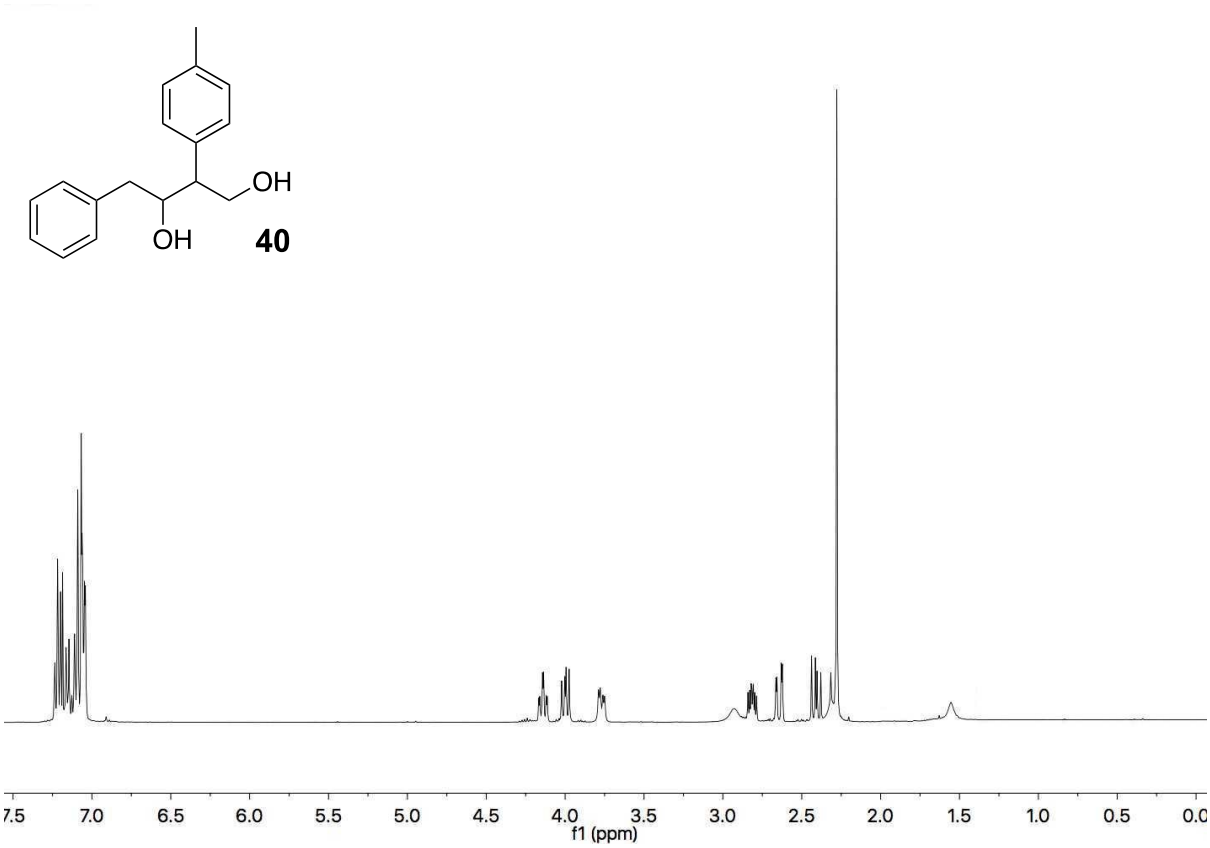

MeO
B
O
O
B
O
O
38

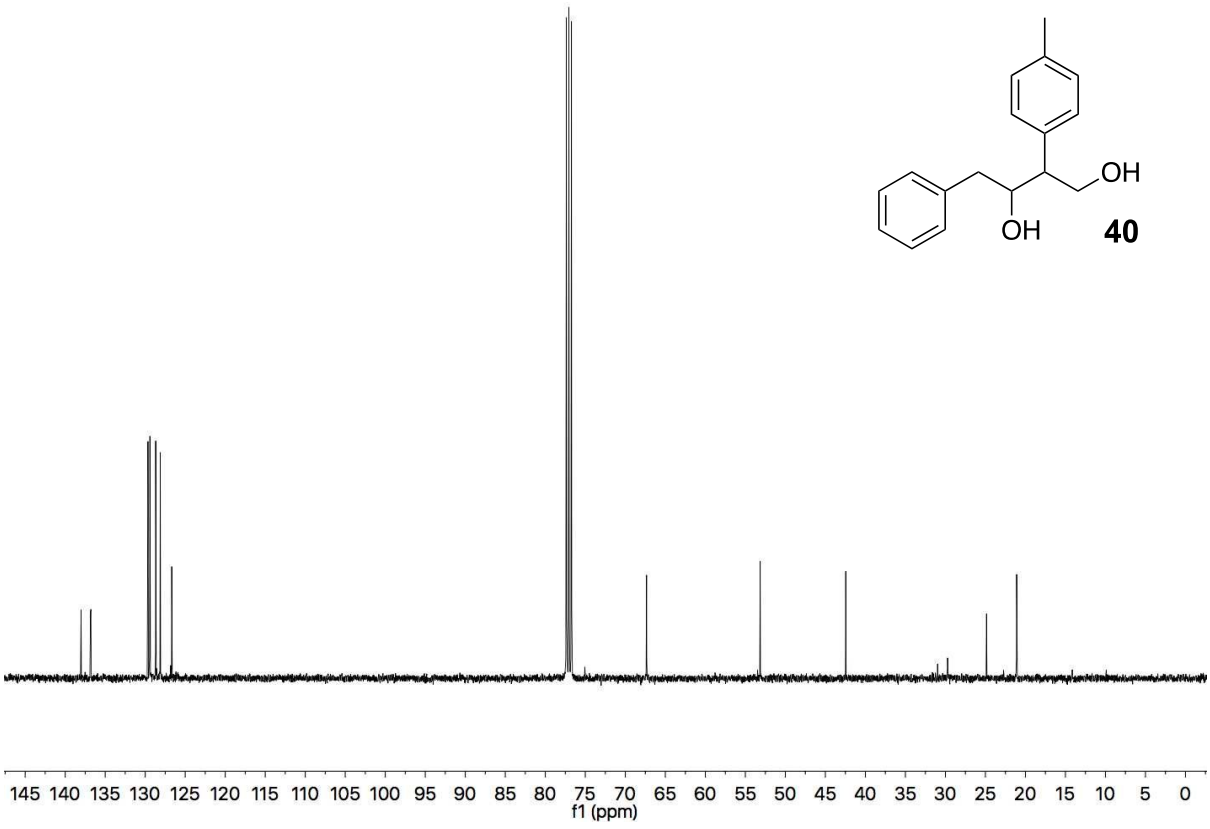

75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
f1 (ppm)

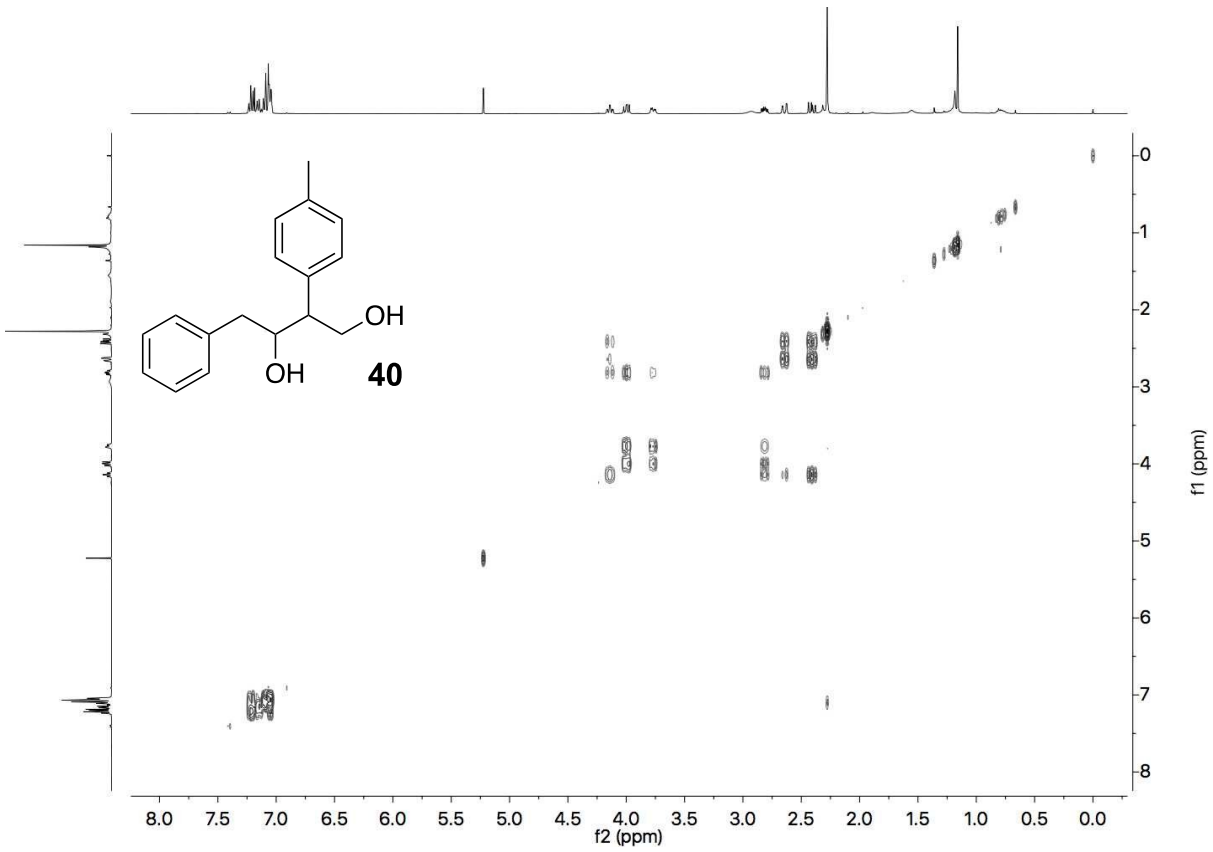

0
1
2
3
4
5
6
7
8
f1 (ppm)
MeO
B
O
O
B
O
O
38
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)

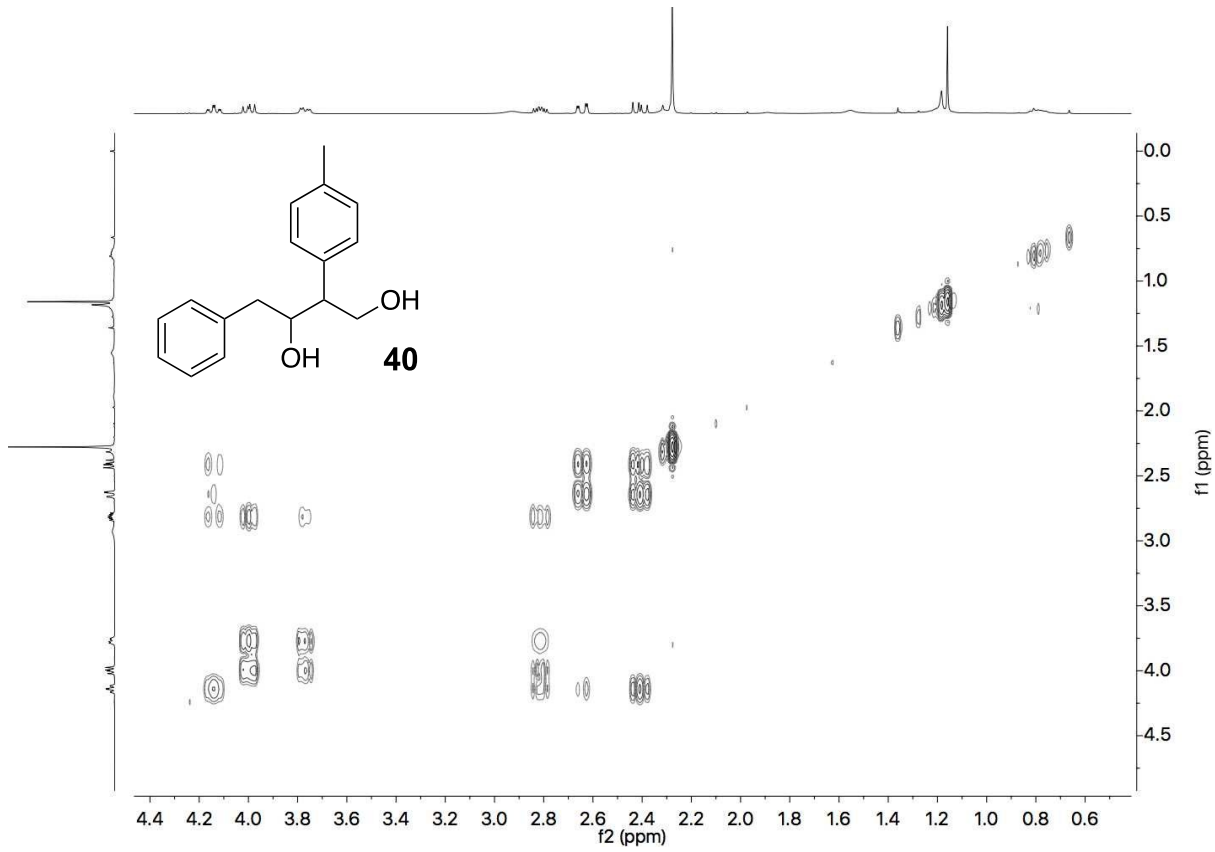

MeO
B
O
38
f2 (ppm)
f1 (ppm)

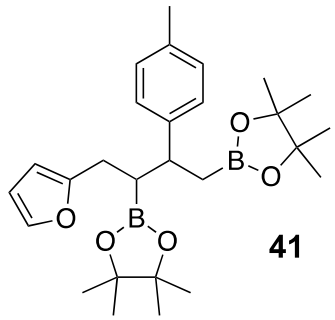

OMe
B
O
39
f1 (ppm)


OH
OH
40
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

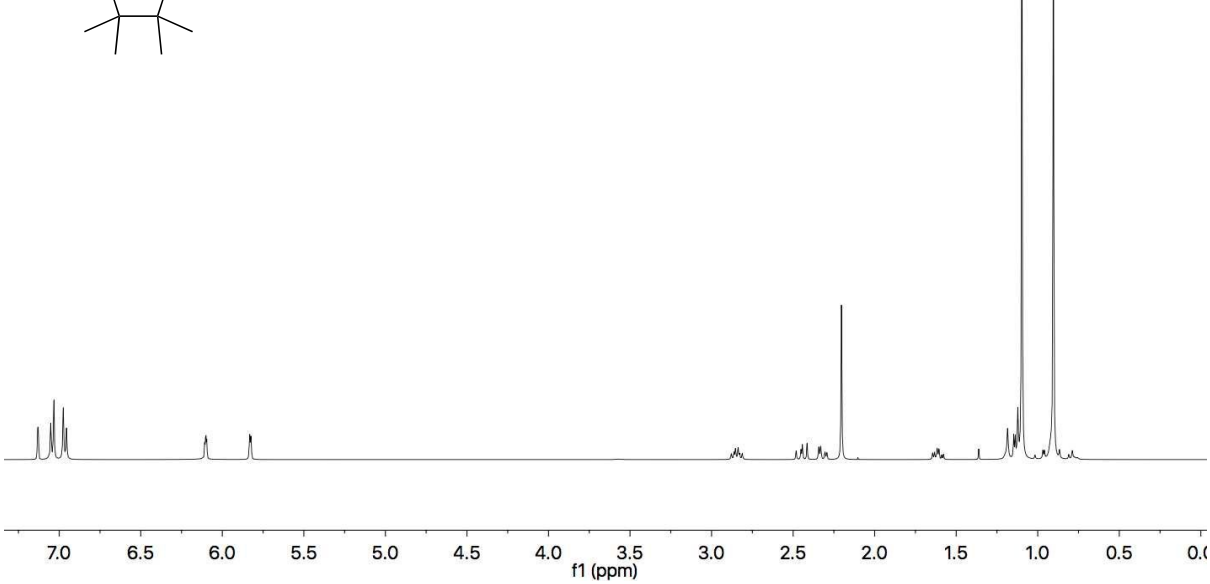

OH
OH
40
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

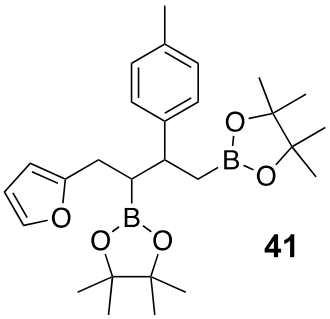

OH
OH
40
f1 (ppm)
f2 (ppm)


OH
OH
40
f1 (ppm)
f2 (ppm)



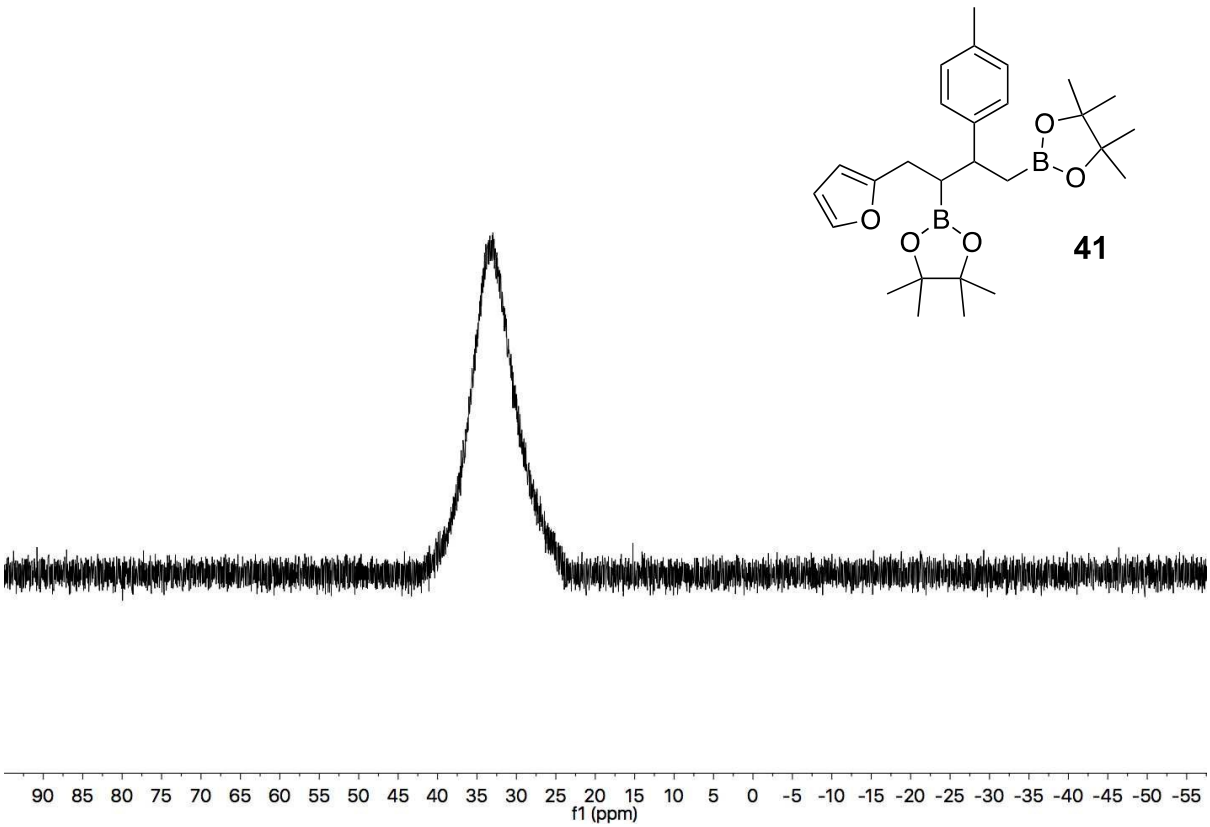
41


7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



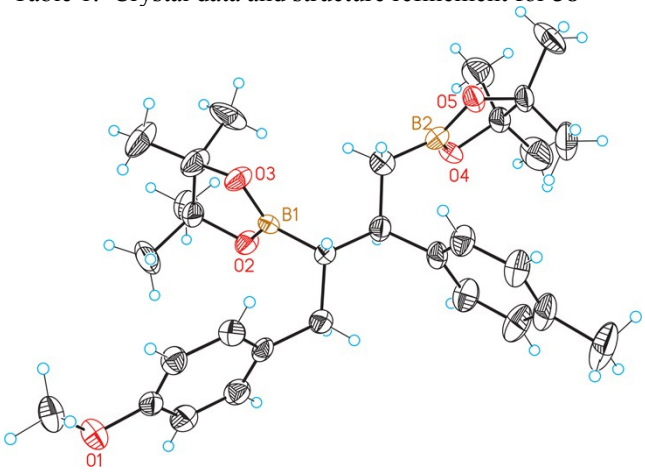
41

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



X-Ray Crystal Data for **38**

Table 1. Crystal data and structure refinement for **38**



Identification code	mo_ED134_0m
Empirical formula	C30 H44 B2 O5
Formula weight	506.27
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P2(1)/c	
Unit cell dimensions	a = 13.0983(18)Å	α= 90°.
	b = 12.425(3)Å	β = 95.349(5)°.
	c = 18.235(4)Å	γ = 90°.
Volume	2954.8(10) $Å^3$	
Z	4	
Density (calculated)	1.138 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	1096	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.986 to 26.425°.	
Index ranges	-16<=h<=16,-15<=k<=15,-17<=l<=22	
Reflections collected	25716	
Independent reflections	5972[R(int) = 0.0479]	
Completeness to theta =26.425°	98.2%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.996 and 0.91	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5972/ 476/ 497	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0769, wR2 = 0.1844	
R indices (all data)	R1 = 0.1121, wR2 = 0.2055	
Largest diff. peak and hole	0.664 and -0.377 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **38**

Bond lengths----	
O1-C7	1.384(3)
O1-C1	1.429(4)
C2-C7	1.376(4)
C2-C3	1.406(4)
C3-C4	1.408(4)
C4-C5	1.382(4)
C4-C8	1.524(4)
C5-C6	1.364(4)
C6-C7	1.392(4)
C8-C9	1.543(4)

C9-C16	1.541(4)
C9-B1	1.581(4)
B1-O2'	1.292(11)
B1-O3	1.338(6)
B1-O2	1.409(6)
B1-O3'	1.417(10)
O2-C10	1.461(5)
O3-C13	1.460(5)
C10-C12	1.444(7)
C10-C13	1.528(6)
C10-C11	1.596(8)
C13-C14	1.472(9)
C13-C15	1.620(9)
O2'-C10'	1.464(7)
O3'-C13'	1.470(7)
C10'-C12'	1.427(10)
C10'-C13'	1.526(8)
C10'-C11'	1.621(11)
C13'-C14'	1.467(10)
C13'-C15'	1.606(11)
C16-C24	1.520(4)
C16-C17	1.526(4)
C17-C22	1.377(4)
C17-C18	1.394(4)
C18-C19	1.387(4)
C19-C20	1.393(5)
C20-C21	1.378(5)
C20-C23	1.521(4)
C21-C22	1.389(4)
C24-B2	1.577(4)
B2-O4	1.292(9)
B2-O5'	1.302(8)
B2-O5	1.370(6)
B2-O4'	1.460(10)
O4-C25	1.482(6)
O5-C28	1.456(6)
C25-C27	1.494(8)
C25-C28	1.534(7)

C25-C26	1.539(7)
C28-C29	1.514(7)
C28-C30	1.527(8)
O4'-C25'	1.475(7)
O5'-C28'	1.459(6)
C25'-C27'	1.497(8)
C25'-C28'	1.541(8)
C25'-C26'	1.544(8)
C28'-C30'	1.514(9)
C28'-C29'	1.521(8)

Angles----------

C7-O1-C1	116.7(2)
C7-C2-C3	119.0(3)
C2-C3-C4	120.6(3)
C5-C4-C3	118.0(3)
C5-C4-C8	120.0(3)
C3-C4-C8	122.0(3)
C6-C5-C4	121.9(3)
C5-C6-C7	120.0(3)
C2-C7-O1	124.3(3)
C2-C7-C6	120.5(3)
O1-C7-C6	115.2(3)
C4-C8-C9	115.3(2)
C16-C9-C8	113.4(2)
C16-C9-B1	111.0(2)
C8-C9-B1	110.5(2)
O3-B1-O2	112.0(3)
O2'-B1-O3'	114.0(5)
O2'-B1-C9	124.8(4)
O3-B1-C9	126.3(3)
O2-B1-C9	121.7(3)
O3'-B1-C9	121.2(4)
B1-O2-C10	106.6(4)
B1-O3-C13	109.2(4)
C12-C10-O2	109.8(4)
C12-C10-C13	118.9(5)
O2-C10-C13	103.6(4)

C12-C10-C11	113.7(5)
O2-C10-C11	103.2(4)
C13-C10-C11	106.2(5)
O3-C13-C14	111.2(6)
O3-C13-C10	103.4(4)
C14-C13-C10	119.9(6)
O3-C13-C15	103.2(4)
C14-C13-C15	113.1(5)
C10-C13-C15	104.3(5)
B1-O2'-C10'	109.0(6)
B1-O3'-C13'	104.2(6)
C12'-C10'-O2'	107.4(8)
C12'-C10'-C13'	121.9(9)
O2'-C10'-C13'	102.4(6)
C12'-C10'-C11'	111.8(9)
O2'-C10'-C11'	108.1(8)
C13'-C10'-C11'	104.3(8)
C14'-C13'-O3'	104.1(7)
C14'-C13'-C10'	119.4(9)
O3'-C13'-C10'	103.3(6)
C14'-C13'-C15'	114.2(9)
O3'-C13'-C15'	108.2(9)
C10'-C13'-C15'	106.5(8)
C24-C16-C17	111.0(2)
C24-C16-C9	112.8(2)
C17-C16-C9	112.5(2)
C22-C17-C18	117.5(3)
C22-C17-C16	120.7(3)
C18-C17-C16	121.8(2)
C19-C18-C17	121.6(3)
C18-C19-C20	120.4(3)
C21-C20-C19	117.9(3)
C21-C20-C23	121.5(3)
C19-C20-C23	120.6(3)
C20-C21-C22	121.5(3)
C17-C22-C21	121.1(3)
C16-C24-B2	113.5(2)
O4-B2-O5	115.3(4)

O5'-B2-O4'	108.8(5)
O4-B2-C24	124.2(4)
O5'-B2-C24	126.7(4)
O5-B2-C24	120.5(3)
O4'-B2-C24	124.1(4)
B2-O4-C25	107.6(5)
B2-O5-C28	105.6(4)
O4-C25-C27	110.3(6)
O4-C25-C28	102.0(5)
C27-C25-C28	115.9(6)
O4-C25-C26	106.6(5)
C27-C25-C26	109.6(7)
C28-C25-C26	111.9(6)
O5-C28-C29	107.9(5)
O5-C28-C30	104.0(5)
C29-C28-C30	110.1(6)
O5-C28-C25	102.7(4)
C29-C28-C25	117.4(6)
C30-C28-C25	113.4(5)
B2-O4'-C25'	108.3(6)
B2-O5'-C28'	112.1(5)
O4'-C25'-C27'	113.2(8)
O4'-C25'-C28'	101.9(6)
C27'-C25'-C28'	114.6(8)
O4'-C25'-C26'	105.0(7)
C27'-C25'-C26'	109.9(7)
C28'-C25'-C26'	111.7(8)
O5'-C28'-C30'	107.5(6)
O5'-C28'-C29'	106.8(5)
C30'-C28'-C29'	110.9(7)
O5'-C28'-C25'	103.3(6)
C30'-C28'-C25'	113.1(6)
C29'-C28'-C25'	114.5(7)

Table 3. Torsion angles [°] for **38**.

C7-C2-C3-C4	0.3(4)
C2-C3-C4-C5	-0.7(4)
C2-C3-C4-C8	178.9(2)
C3-C4-C5-C6	0.7(4)
C8-C4-C5-C6	-178.9(3)
C4-C5-C6-C7	-0.3(4)
C3-C2-C7-O1	-179.8(2)
C3-C2-C7-C6	0.2(4)
C1-O1-C7-C2	8.0(4)
C1-O1-C7-C6	-172.0(3)
C5-C6-C7-C2	-0.2(4)
C5-C6-C7-O1	179.8(3)
C5-C4-C8-C9	137.3(3)
C3-C4-C8-C9	-42.4(4)
C4-C8-C9-C16	-173.9(2)
C4-C8-C9-B1	-48.5(3)
C16-C9-B1-O2'	58.1(6)
C8-C9-B1-O2'	-68.6(6)
C16-C9-B1-O3	-96.9(4)
C8-C9-B1-O3	136.4(4)
C16-C9-B1-O2	81.8(4)
C8-C9-B1-O2	-44.9(4)
C16-C9-B1-O3'	-121.8(5)
C8-C9-B1-O3'	111.5(5)
O3-B1-O2-C10	-10.6(5)
C9-B1-O2-C10	170.5(3)
O2-B1-O3-C13	-4.6(5)
C9-B1-O3-C13	174.2(4)
B1-O2-C10-C12	148.2(4)
B1-O2-C10-C13	20.3(6)
B1-O2-C10-C11	-90.3(5)
B1-O3-C13-C14	147.0(5)
B1-O3-C13-C10	17.0(6)
B1-O3-C13-C15	-91.4(5)
C12-C10-C13-O3	-144.5(5)
O2-C10-C13-O3	-22.4(6)
C11-C10-C13-O3	85.9(5)
C12-C10-C13-C14	91.0(8)

O2-C10-C13-C14	-146.9(6)
C11-C10-C13-C14	-38.6(7)
C12-C10-C13-C15	-36.8(6)
O2-C10-C13-C15	85.3(5)
C11-C10-C13-C15	-166.4(4)
O3'-B1-O2'-C10'	6.4(10)
C9-B1-O2'-C10'	-173.5(5)
O2'-B1-O3'-C13'	11.3(9)
C9-B1-O3'-C13'	-168.7(5)
B1-O2'-C10'-C12'	108.9(10)
B1-O2'-C10'-C13'	-20.5(10)
B1-O2'-C10'-C11'	-130.3(9)
B1-O3'-C13'-C14'	102.6(9)
B1-O3'-C13'-C10'	-22.9(9)
B1-O3'-C13'-C15'	-135.6(8)
C12'-C10'-C13'-C14'	151.4(11)
O2'-C10'-C13'-C14'	-88.8(9)
C11'-C10'-C13'-C14'	23.7(10)
C12'-C10'-C13'-O3'	-93.7(11)
O2'-C10'-C13'-O3'	26.1(9)
C11'-C10'-C13'-O3'	138.7(8)
C12'-C10'-C13'-C15'	20.3(13)
O2'-C10'-C13'-C15'	140.1(9)
C11'-C10'-C13'-C15'	-107.4(10)
C8-C9-C16-C24	177.5(2)
B1-C9-C16-C24	52.4(3)
C8-C9-C16-C17	-56.0(3)
B1-C9-C16-C17	178.9(2)
C24-C16-C17-C22	-127.6(3)
C9-C16-C17-C22	104.9(3)
C24-C16-C17-C18	54.1(3)
C9-C16-C17-C18	-73.4(3)
C22-C17-C18-C19	-1.1(4)
C16-C17-C18-C19	177.3(3)
C17-C18-C19-C20	-0.9(5)
C18-C19-C20-C21	1.7(5)
C18-C19-C20-C23	-176.2(3)
C19-C20-C21-C22	-0.6(5)

C23-C20-C21-C22	177.3(3)
C18-C17-C22-C21	2.2(5)
C16-C17-C22-C21	-176.2(3)
C20-C21-C22-C17	-1.4(5)
C17-C16-C24-B2	51.5(3)
C9-C16-C24-B2	178.8(3)
C16-C24-B2-O4	53.2(5)
C16-C24-B2-O5'	-155.7(4)
C16-C24-B2-O5	-125.3(4)
C16-C24-B2-O4'	31.9(6)
O5-B2-O4-C25	-4.1(6)
C24-B2-O4-C25	177.3(4)
O4-B2-O5-C28	-13.2(6)
C24-B2-O5-C28	165.4(4)
B2-O4-C25-C27	142.1(7)
B2-O4-C25-C28	18.5(6)
B2-O4-C25-C26	-98.9(6)
B2-O5-C28-C29	148.1(5)
B2-O5-C28-C30	-94.9(5)
B2-O5-C28-C25	23.5(6)
O4-C25-C28-O5	-25.1(6)
C27-C25-C28-O5	-144.9(6)
C26-C25-C28-O5	88.5(6)
O4-C25-C28-C29	-143.2(5)
C27-C25-C28-C29	96.9(8)
C26-C25-C28-C29	-29.7(8)
O4-C25-C28-C30	86.5(6)
C27-C25-C28-C30	-33.4(8)
C26-C25-C28-C30	-160.0(6)
O5'-B2-O4'-C25'	-3.7(8)
C24-B2-O4'-C25'	169.9(5)
O4'-B2-O5'-C28'	-12.3(7)
C24-B2-O5'-C28'	174.3(5)
B2-O4'-C25'-C27'	140.0(8)
B2-O4'-C25'-C28'	16.5(8)
B2-O4'-C25'-C26'	-100.1(8)
B2-O5'-C28'-C30'	-97.4(7)
B2-O5'-C28'-C29'	143.6(7)

B2-O5'-C28'-C25'	22.5(7)
O4'-C25'-C28'-O5'	-22.4(7)
C27'-C25'-C28'-O5'	-144.9(8)
C26'-C25'-C28'-O5'	89.3(8)
O4'-C25'-C28'-C30'	93.5(8)
C27'-C25'-C28'-C30'	-29.0(10)
C26'-C25'-C28'-C30'	-154.8(8)
O4'-C25'-C28'-C29'	-138.0(7)
C27'-C25'-C28'-C29'	99.4(9)
C26'-C25'-C28'-C29'	-26.4(10)
