Electronic Supporting Information (ESI)

Zinc Hydride Catalyzed Hydroboration of Esters

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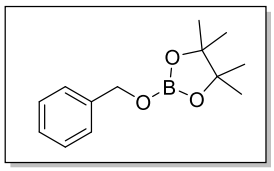
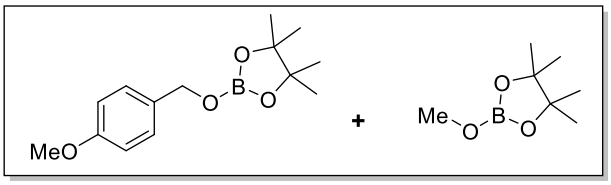
Contents

Analytical data for Hydroboration of Esters and other Carbonyls:

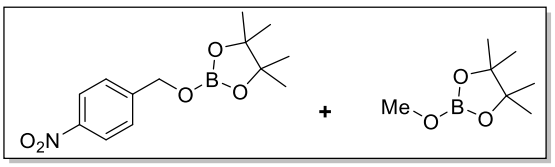
2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.03 (m, 5H), 4.83 (s, 2H), 1.15 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 139.2, 128.3, 127.4, 126.7, 82.9, 66.7, 24.6.



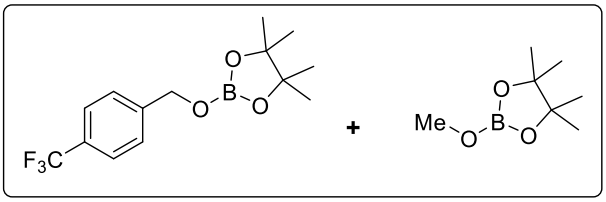
4,4,5,5-tetramethyl-2-((4-methoxybenzyl)oxy)-1,3,2-dioxaborolane (2b)[1], 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.29 (d, *J* = 8.7 Hz, 2H), 6.89 – 6.87 (d, *J* = 8.7 Hz, 2H), 4.87 (s, 2H), 3.82 (s, 3H), 3.62 (s, 3H), 1.29 (s, 12H), 1.28 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.0, 131.4, 128.5, 113.6, 82.8, 82.7, 66.4, 55.2, 52.6, 24.8, 24.6.



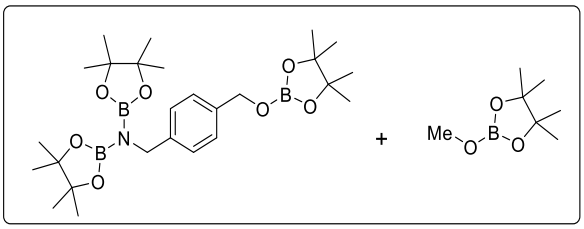
4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (2c)[1], 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.20 (d, *J* = 8.7 Hz, 2H), 7.53 – 7.51 (d, *J* = 8.9 Hz, 2H), 5.04 (s, 3H), 3.61 (s, 2H), 1.29 (s, 12H), 1.27 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 146.6, 126.8, 123.5, 83.3, 82.7, 65.5, 52.6, 24.6, 24.5.



4,4,5,5-tetramethyl-2-((4-(trifluoromethyl)benzyl)oxy)-1,3,2-dioxaborolane (2d)[1], 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 – 7.59 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.45 (d, *J* = 8.0 Hz, 2H), 4.99 (s, 2H), 3.61 (s, 3H), 1.27 (s, 12H), 1.26 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 143.2, 129.9, 129.3, 126.5, 125.2, 125.1, 122.8, 83.1, 82.7, 65.8, 52.5, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 22.29 ppm.

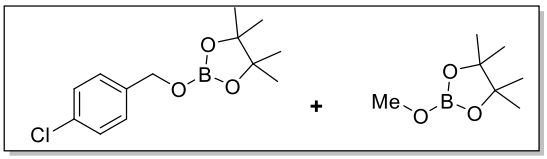


4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzyl)-1,3,2-dioxaborolan-2-amine

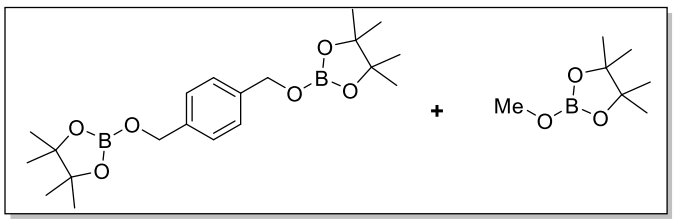


(2e)[2], 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.26 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.22 (d, *J* = 8.4 Hz, 2H), 4.88 (s, 2H), 4.22 (s, 2H), 3.61 (s, 3H), 1.28 (s, 12H), 1.26 (s, 12H), 1.20 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.2, 136.9, 127.3, 126.3, 83.2, 82.8, 82.2, 66.6, 52.5, 46.9, 24.8, 24.6, 24.4

2-((4-chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)[3], 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 4H), 4.90 (s, 2H), 3.62 (s, 3H), 1.28 (s, 12H), 1.27 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.7, 133.1, 128.4, 128.0, 83.2, 83.0, 65.9, 52.6, 24.8, 24.6.



1,4-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (2g)[1], 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 4H), 4.92 (s, 3H), 3.61 (s, 3H), 1.28 (s, 12H), 1.27 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.4, 126.7, 83.2, 82.8, 66.4, 52.5, 24.8, 24.5.

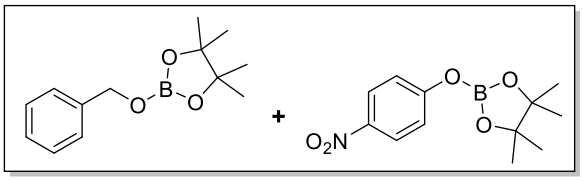


4,4,5,5-tetramethyl-2-((4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzyl)oxy)-1,3,2-dioxaborolane (2h)[4], 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (d, *J* = 5.9 Hz, 4H), 5.25 – 5.23 (m, 1H), 4.91 (s, 2H), 3.61 (s, 3H), 1.49 – 1.48 (d, *J* = 6.5 Hz, 3H), 1.28 (s, 12H), 1.27 (s, 12H), 1.25 – 1.22 (d, *J* = 5.9 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.8, 138.1, 126.6, 125.2, 83.2, 82.8, 82.6, 72.3, 66.5, 52.5, 25.3, 24.8, 24.5, 24.5.

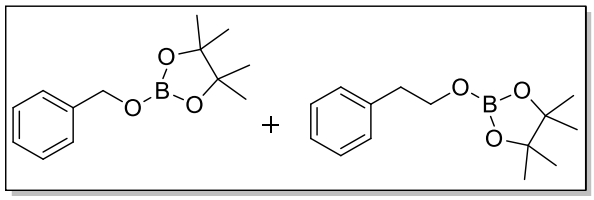
2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)[1], 4,4,5,5-tetramethyl-2-phenoxy-1,3,2-dioxaborolane (2i)[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 4H), 7.33 – 7.26 (m, 3H), 7.19 – 7.04 (m, 3H), 4.96 (s, 2H), 1.35 (s, 12H), 1.30 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.4, 139.2, 129.3, 128.2, 127.3, 126.7, 123.0, 119.5, 83.5, 82.9, 66.6, 24.6, 24.6.

2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)[1], 2-(benzyloxy)-4,4,5,5-tetramethyl-2-(*p*-tolyloxy)-1,3,2-dioxaborolane (2j)[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.24 (d, *J* = 6.5 Hz, 5H), 6.98 – 6.96 (d, *J* = 8.0 Hz, 2H), 6.89 – 6.87 (d, *J* = 7.9 Hz, 2H), 4.84 (s, 2H), 2.19 (s, 3H), 1.22 (s, 12H), 1.17 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.2, 139.2, 132.3, 129.7, 128.2, 127.3, 126.7, 119.2, 83.4, 82.9, 66.6, 24.8, 24.6, 20.6.

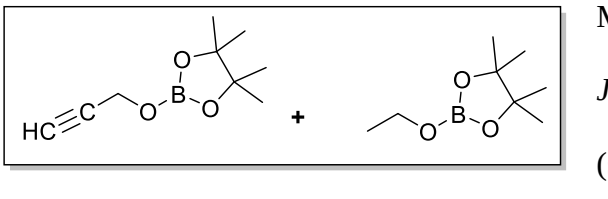
2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)[1], 4,4,5,5-tetramethyl-2-(4-nitrophenoxy)-1,3,2-dioxaborolane (2k)[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 – 8.20 (d, *J* = 9.2 Hz, 2H), 7.38 – 7.34 (d, *J* = 25.1 Hz, 4H), 7.30 – 7.25 (d, *J* = 32.6 Hz, 3H), 4.95 (s, 2H), 1.37 (s, 12H), 1.29 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.6, 139.2, 128.2, 127.3, 126.7, 125.4, 120.0, 84.2, 82.9, 66.6, 24.8, 24.6.



2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)[1], 4,4,5,5-tetramethyl-2-phenethoxy-1,3,2-dioxaborolane (2l)[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.38 (t, *J* = 8.0 Hz, 3H), 7.36 – 7.25 (m, 7H), 5.00 (s, 2H), 4.13 (t, *J* = 8.0 Hz, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 1.32 (s, 12H), 1.25 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 139.3, 138.5, 129.1, 128.3, 127.4, 126.7, 126.2, 82.9, 82.6, 66.7, 65.7, 38.1, 24.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.34 ppm.



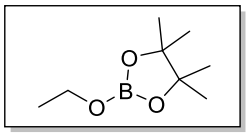
4,4,5,5-tetramethyl-2-(prop-2-yn-1-yloxy)-1,3,2-dioxaborolane (2m)[5], 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 – 4.12 (m, 2H), 3.84 (q, *J* = 8.0 Hz, 2H), 2.91 (s, 1H), 1.19 (s, 12H), 1.17 (s, 12H), 1.14 (t, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 85.1, 83.0, 82.5, 74.6, 62.2, 60.5, 24.5, 24.4, 17.1.



(E)-2-((3-methoxyallyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n), 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[1]: White solid, NMR Conv: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (d, *J* = 12.7 Hz, 1H), 5.17 – 5.14 (d, *J* = 12.6 Hz, 1H), 3.66 (s, 2H),

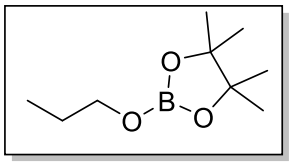
3.65 (s, 3H), 3.56 (s, 3H), 1.21 (s, 24H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.1, 95.5, 82.6, 57.1, 52.4, 50.9, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.17 ppm.

2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)[6]: White solid, NMR Conv.: >99%;



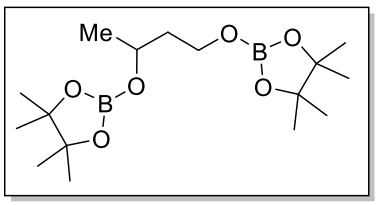
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 – 3.88 (m, 2H), 1.26 (s, 12H), 1.25 – 1.21 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 82.5, 60.6, 24.5, 17.1.

4,4,5,5-tetramethyl-2-propoxy-1,3,2-dioxaborolane (2p)[1]: White solid, NMR Conv.: >99%;



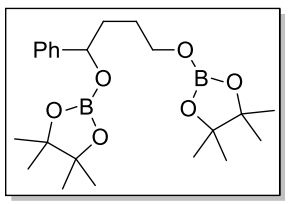
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (t, *J* = 6.5 Hz, 2H), 1.54 – 1.49 (dd, *J* = 14.1, 7.0 Hz, 2H), 1.18 (s, 12H), 0.84 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 82.5, 66.5, 24.6, 24.5, 10.0.

2,2'-(butane-1,4-diylbis(oxy))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2q)[7]: White

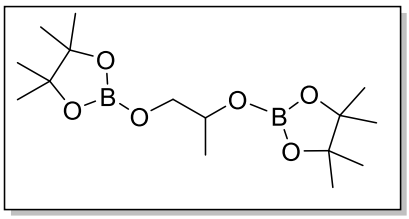


solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.29 – 4.24 (m, 1H), 3.85 (t, *J* = 8.0 Hz, 2H), 1.35 – 1.31 (m, 2H), 1.22 (s, 12H), 1.20 (s, 12H), 1.17 – 1.16 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 82.5, 82.4, 67.8, 61.6, 39.6, 24.5, 24.3, 22.5. ^{11}B NMR (128 MHz, $CDCl_3$): δ 21.91 ppm.

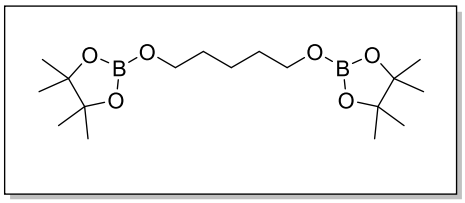
4,4,5,5-tetramethyl-2-(2-phenyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentyl)-1,3,2-dioxaborolane (2r)[8]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.34 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.22 (m, 1H), 5.08 (t, *J* = 6.4 Hz, 1H), 3.85 (t, *J* = 6.4 Hz, 2H), 1.88 – 1.78 (m, 2H), 1.70 – 1.56 (m, 2H), 1.29 (s, 12H), 1.25 (s, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 143.3, 128.0, 127.1, 125.8, 82.7, 82.6, 76.1, 64.6, 35.1, 27.4, 24.8, 24.5.



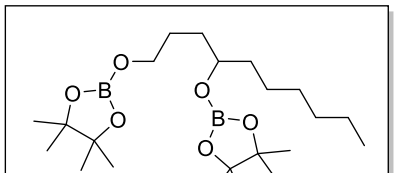
2,2'-(propane-1,2-diylbis(oxy))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2s)[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 – 5.15 (m, 1H), 3.92 – 3.72 (d, *J* = 8.7 Hz, 2H), 1.28 (s, 24H), 1.19 – 1.18 (d, *J* = 5.7 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 92.6, 83.2, 83.1, 71.6, 24.8, 24.5, 15.2.



1,5-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentane (2t)[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 – 3.82 (m, 4H), 1.63 – 1.57 (m, 4H), 1.47 – 1.34 (m, 2H), 1.25 (s, 24H,). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 82.5, 64.7, 31.0, 24.5, 21.6.

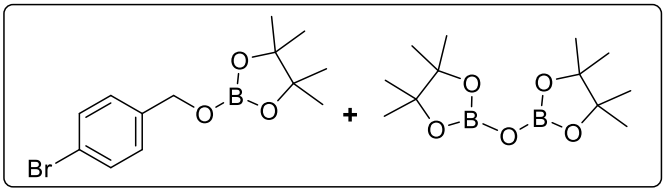


2,2'-(decane-1,4-diylbis(oxy))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2u)[1]: White solid, NMR Conv.: >99%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.76- 5.63 (d, *J* = 87.0 Hz, 1H), 4.11 – 3.90 (d, *J* = 146.4 Hz, 2H), 2.14 – 1.82 (m, 4H), 1.76 – 1.62 (m, 2H), 1.60 - 1.45 (m, 2H), 1.43 - 1.35 (m, 2H), 1.30 – 1.27 (m, 4H), 1.27 – 1.26 (m, 12H), 1.26 – 1.24 (m, 12H), 0.87 (t, *J* = 74.0 Hz 3H) . ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 99.0, 82.7, 81.5, 79.0, 37.3, 34.7, 31.8, 29.2, 28.6, 26.1, 24.8, 24.5, 22.5, 14.0.

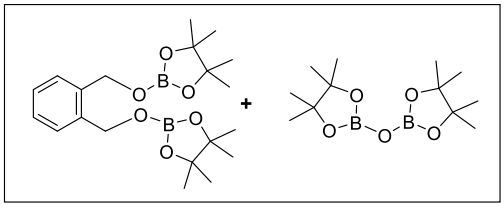


4,4,5,5-tetramethyl-2-(4-nitrophenoxy)-1,3,2-dioxaborolane (4a)[1], 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[1]: White solid, NMR Conv: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.08 (d, *J* = 8.7 Hz, 2H), 7.17 – 7.14 (d, *J* = 8.9 Hz, 2H),, 3.51 (s, 3H), 1.26 (s, 12H), 1.18 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.6, 143.3, 125.4, 120.0, 84.2, 83.0, 52.5, 24.5, 24.5.

2-(4-bromophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a)[1], 2,2'-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[1]: White solid, NMR Conv: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 -7.36 (d, *J* = 7.4 Hz, 2H), 7.15 – 7.13 (d, *J* = 7.6 Hz, 2H), 4.79 (s, 2H), 1.18 (s, 36H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.2, 131.3, 128.4, 121.1, 83.0, 81.9, 65.9, 24.5, 22.6.



1,2-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (8a)[9], 2,2'-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[1]: White solid, NMR Conv: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (d, *J* = 8.8 Hz, 2H), 7.21 – 7.17 (d, *J* = 8.8 Hz, 2H), 4.91 (s, 4H), 1.19 (s, 24H), 1.18 (s, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.3, 137.2, 130.6, 120.9, 83.1, 82.9, 34.1, 24.6, 24.5.



NMR Spectra (^{1}H, $^{13}C\{^{1}H\}$ and 11B NMR) of Stoichiometric Experiments

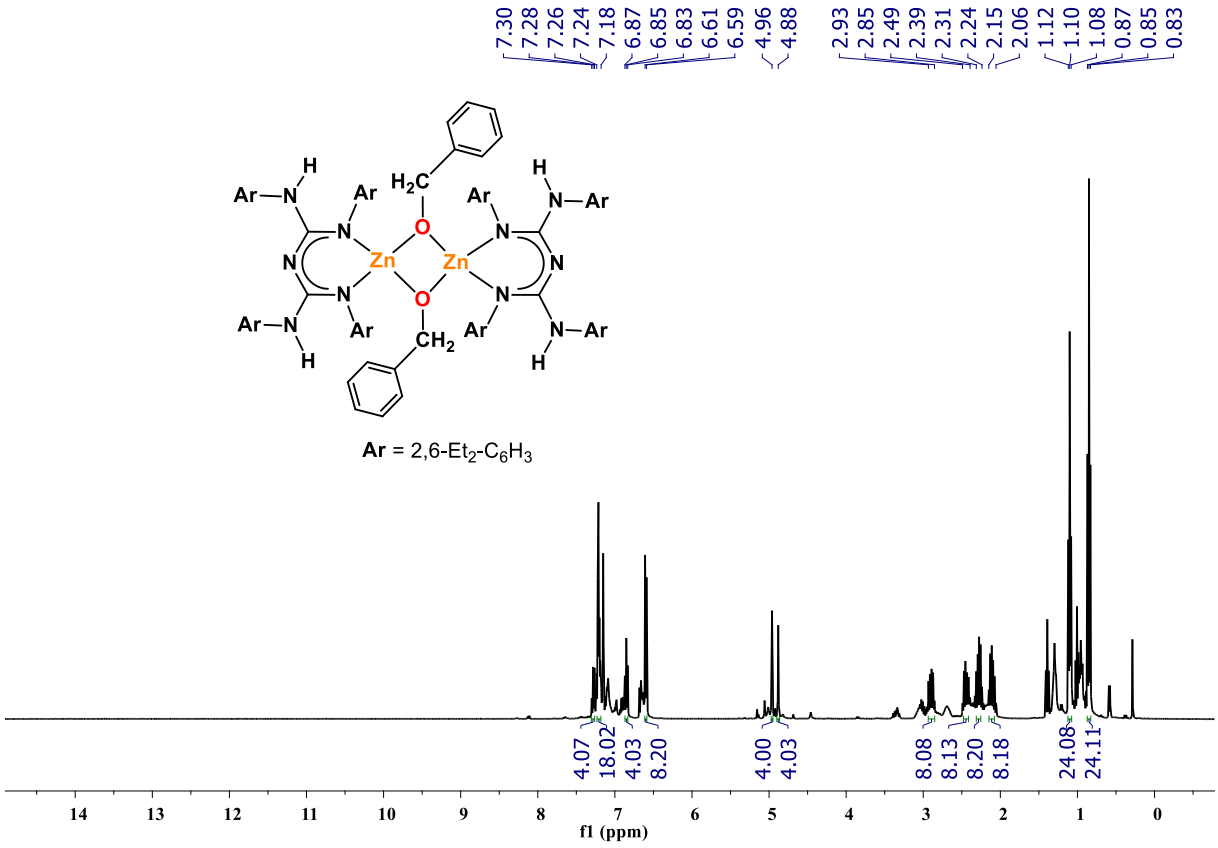


Figure S1: ^{1}H NMR of compound $[LZnOCH_2C_6H_5]_2$ (**Int A1**) (400 MHz, C_6D_6, 25 °C)

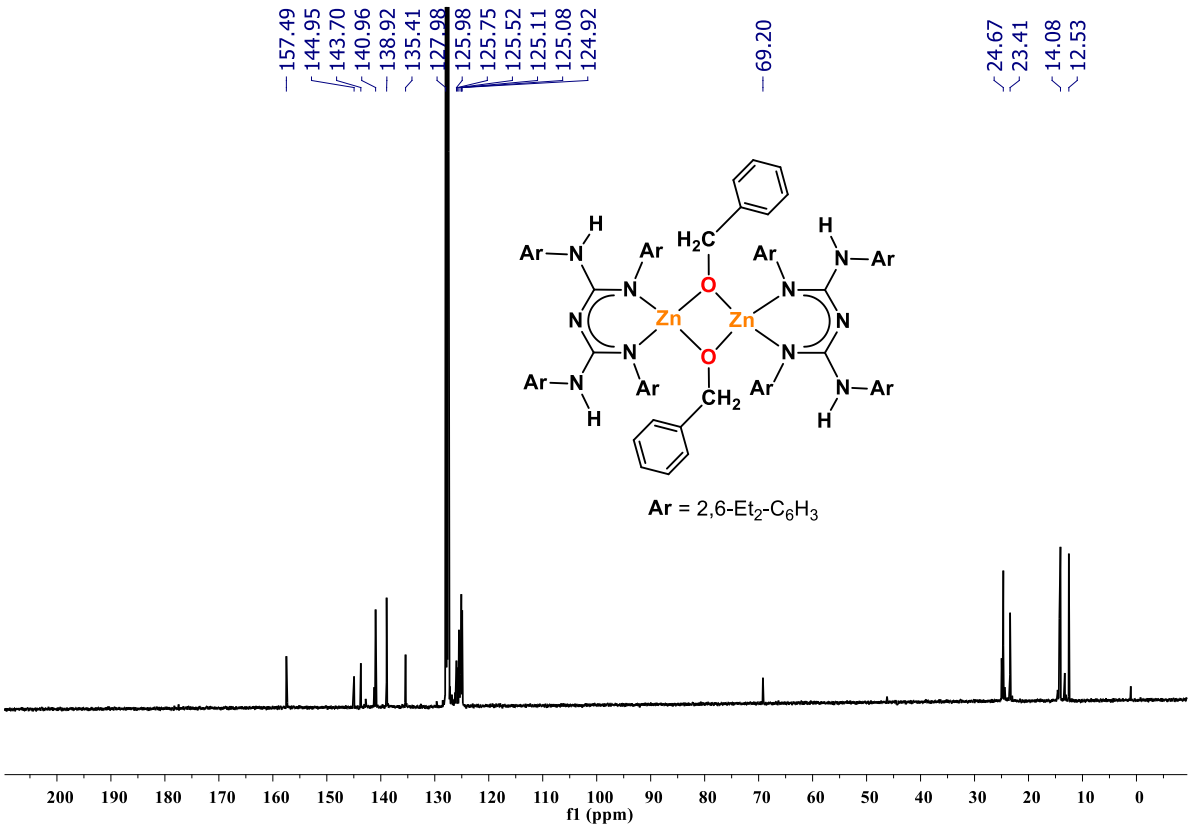


Figure S2: $^{13}C\{^{1}H\}$ NMR of compound $[LZnOCH_2C_6H_5]_2$ (**Int A1**) (100 MHz, C_6D_6, 25 °C)

Synthesis of [LZnH]$_2$ and 2a {NMR-Scale}: The addition of HBpin (6 µL, 0.042 mmol) to a J. Young valve NMR tube containing a solution of compounds **Int A1** (0.021 mmol) in C_6D_6 resulted in the formation of compounds **I** and **2a** at rt after 6h as observed by ^{1}H NMR spectroscopy. NMR Conversion >99%.

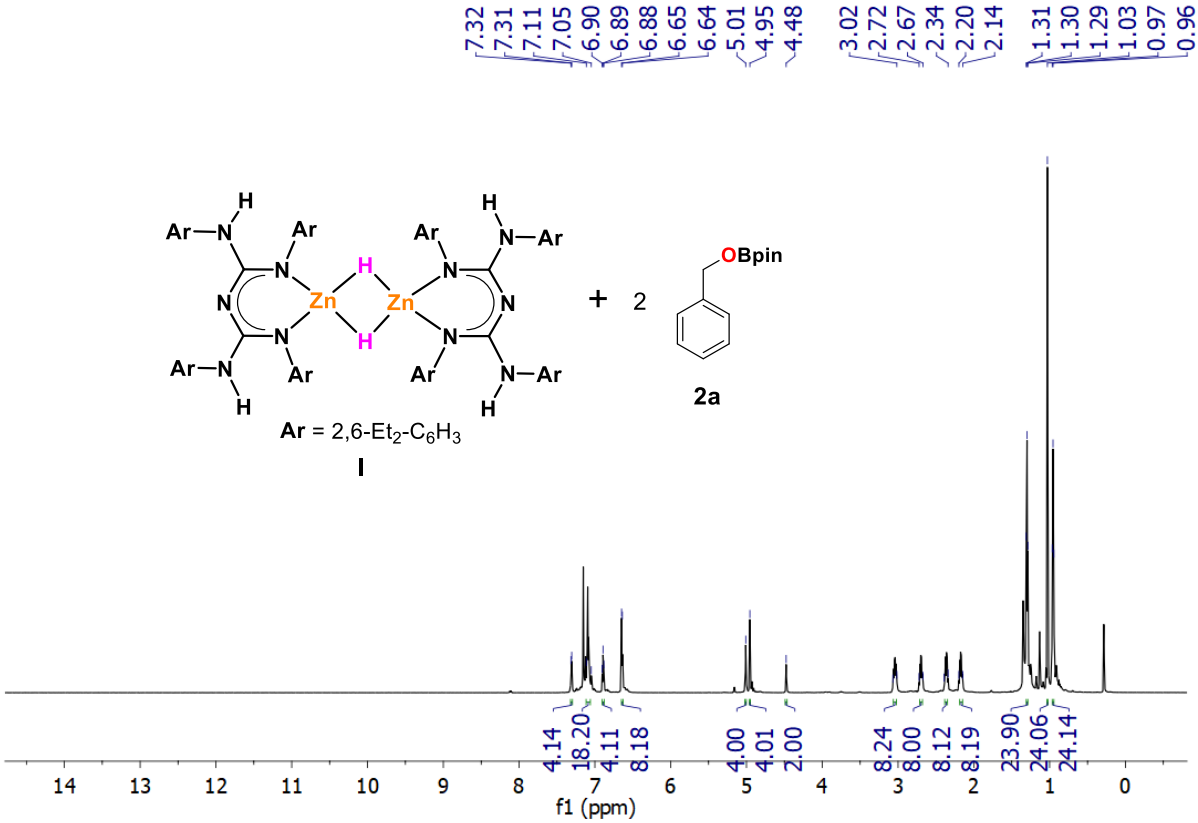


Figure S3: ^{1}H NMR of compounds **I** and **2a** (400 MHz, C_6D_6, 25 ^{o}C)

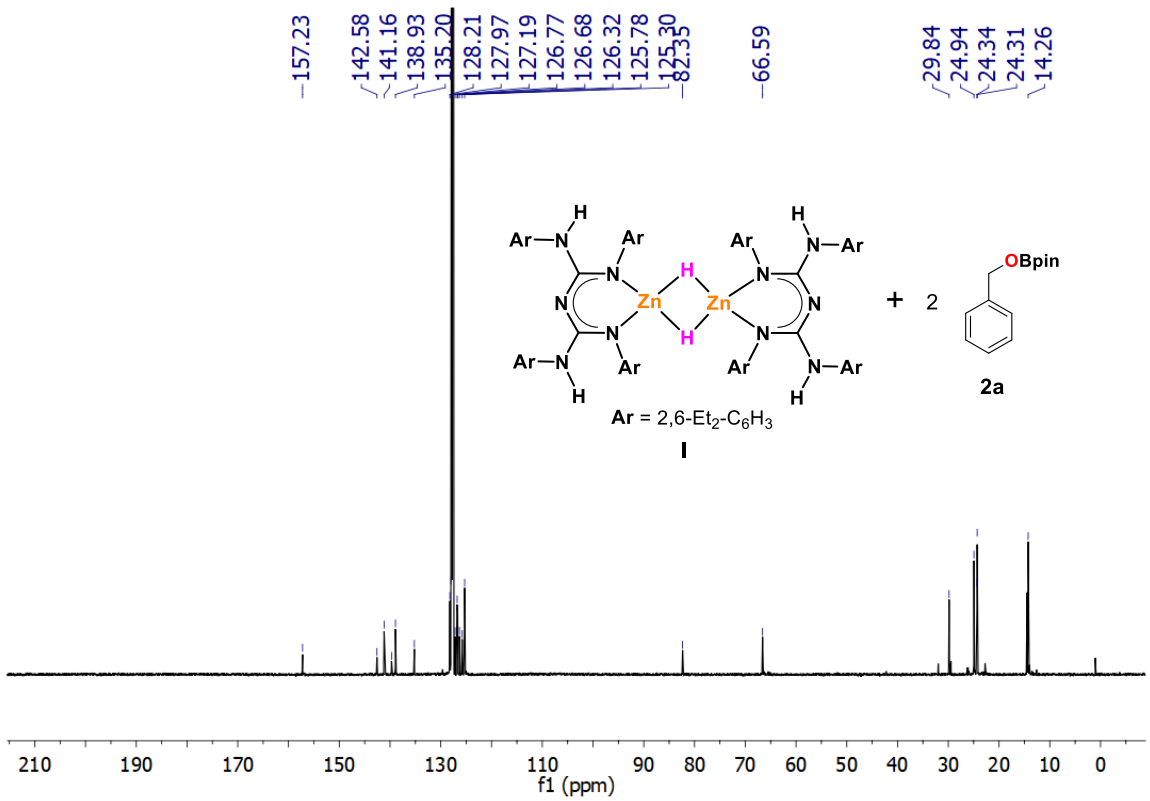


Figure S4: $^{13}C\{^{1}H\}$ NMR of compounds **I** and **2a** (100 MHz, C_6D_6, 25 °C)

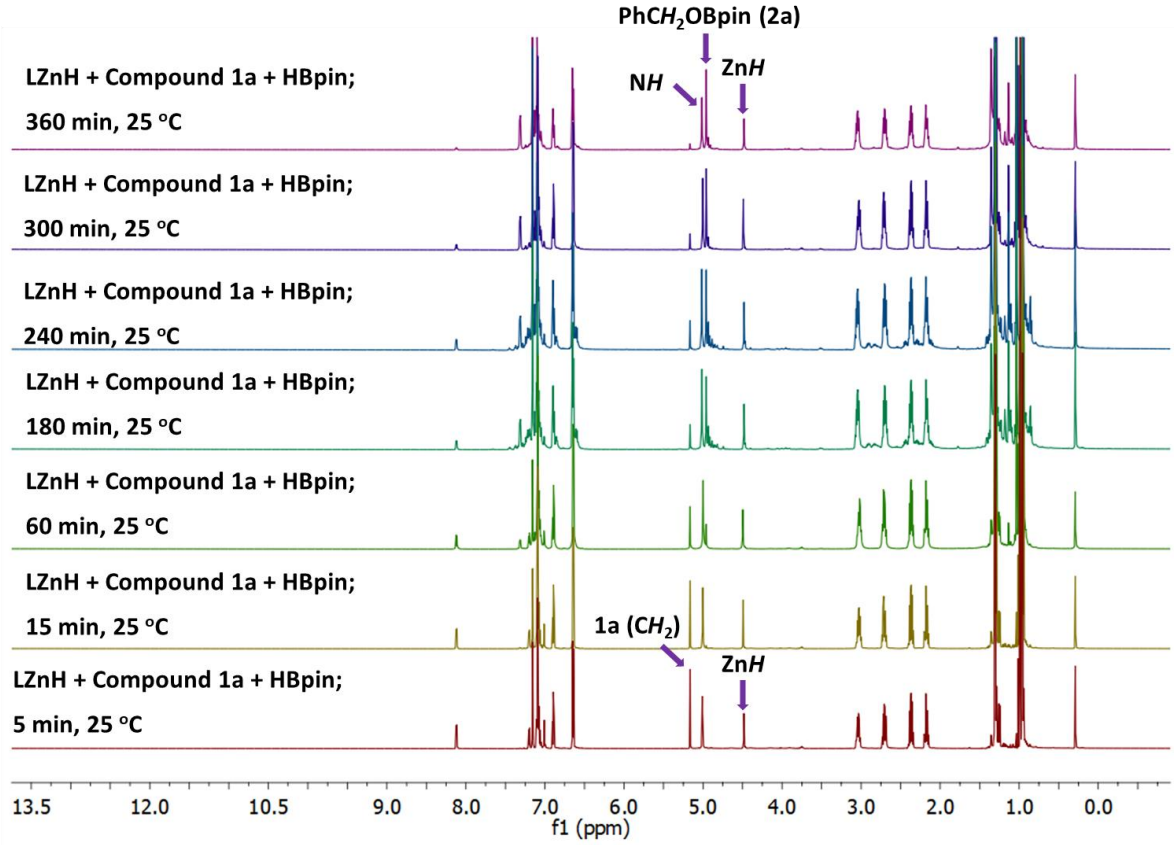


Figure S5: ^{1}H NMR monitoring: the stoichiometric reaction of benzoyl benzoate with HBpin and compound **I**.

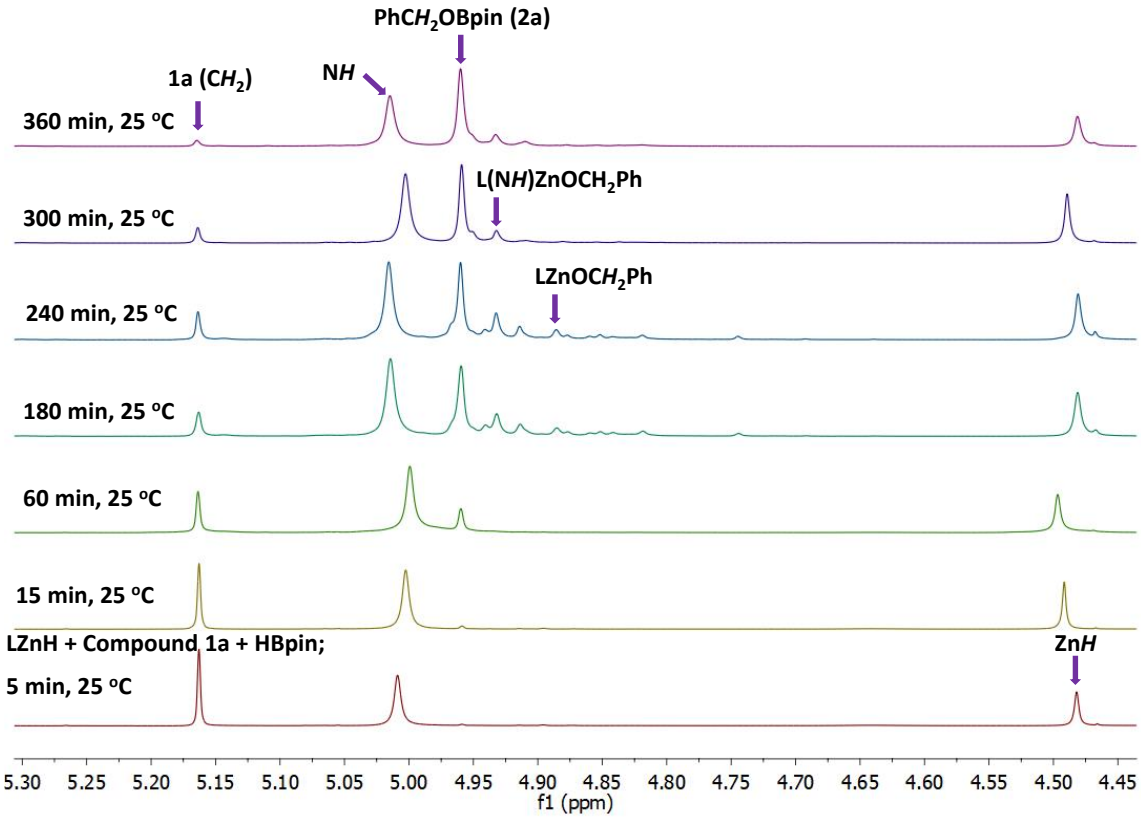


Figure S6: Zoom ^{1}H NMR monitoring: the stoichiometric reaction of benzoyl benzoate with HBpin and compound **I**.

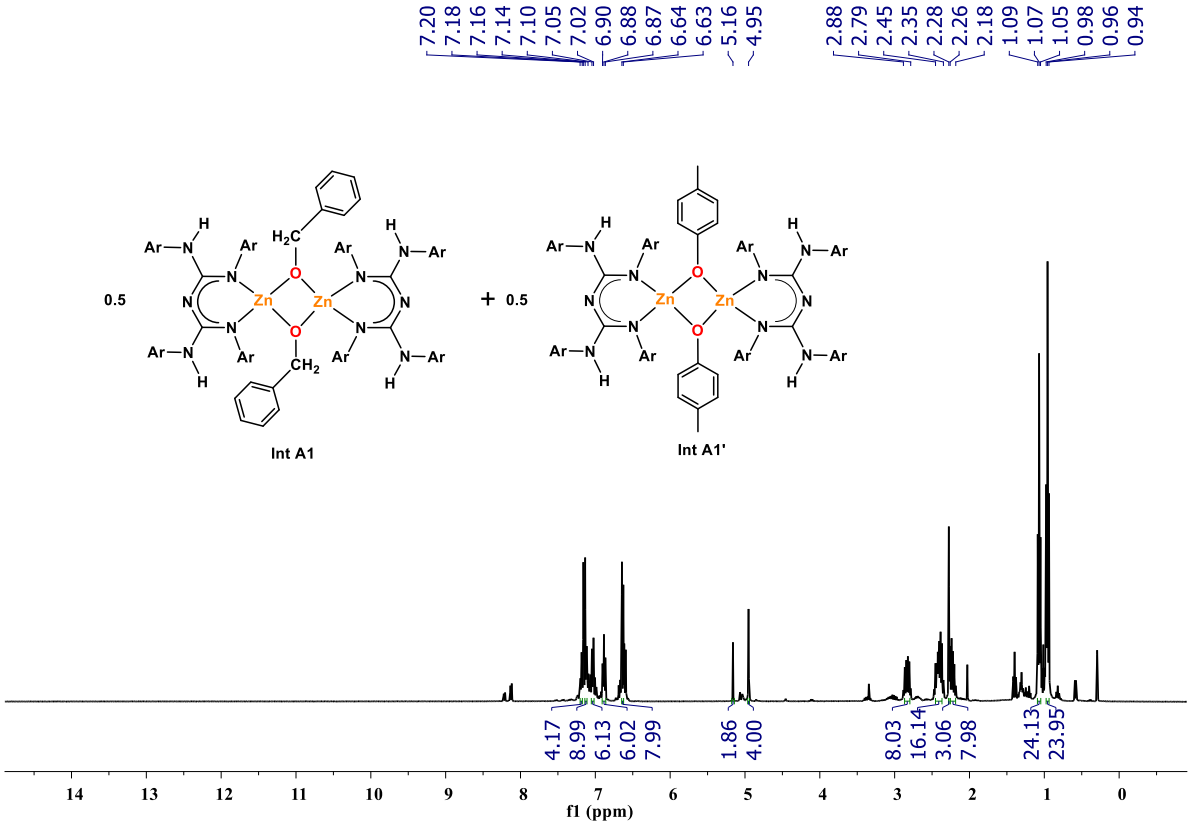


Figure S7: ^{1}H NMR of compounds **Int A1** and **Int A1'** (400 MHz, C_6D_6, 25 °C)

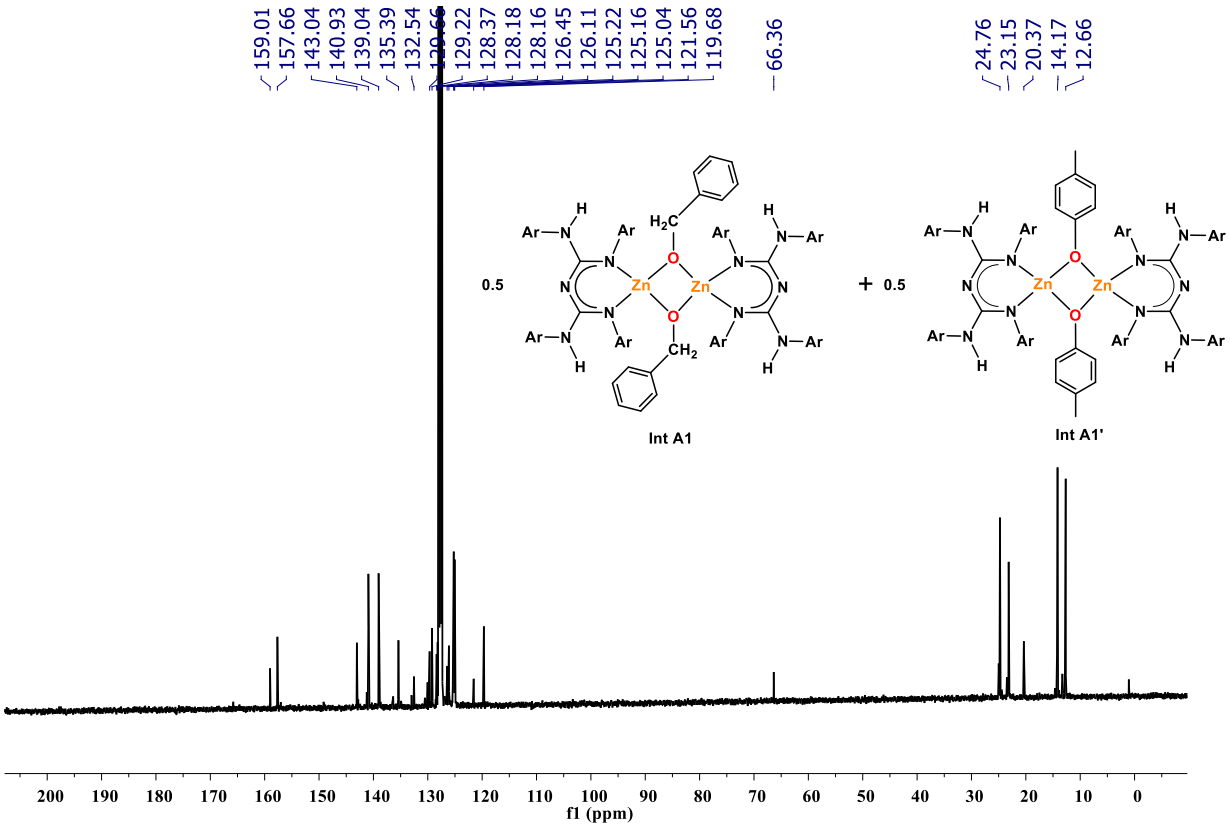


Figure S8: $^{13}C\{^{1}H\}$ NMR of compounds **Int A1** and **Int A1'** (100 MHz, C_6D_6, 25 ^{o}C)

Synthesis of [LZnH]$_2$, 2a and 2j {NMR-Scale}: The addition of HBpin (6 µL, 0.042 mmol) to a J. Young valve NMR tube containing a solution of compounds **Int A1** and **Int A1'** (0.021 mmol) in C_6D_6 resulted in the formation of compounds **I**, **2a**, and **2j** at rt after 6h as observed by ^{1}H NMR spectroscopy. NMR Conversion >99%.

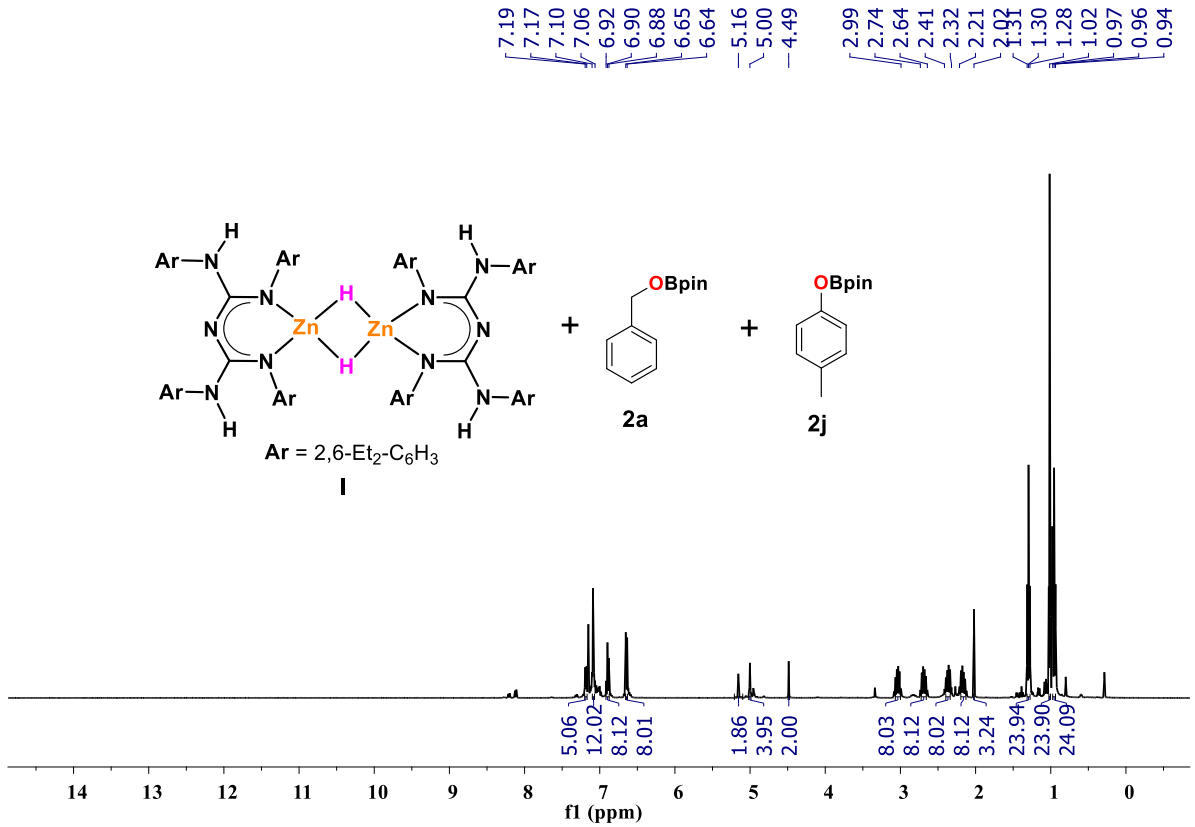


Figure S9: ^{1}H NMR of compounds **I**, **2a** and **2j** (400 MHz, C_6D_6, 25 ^{o}C)

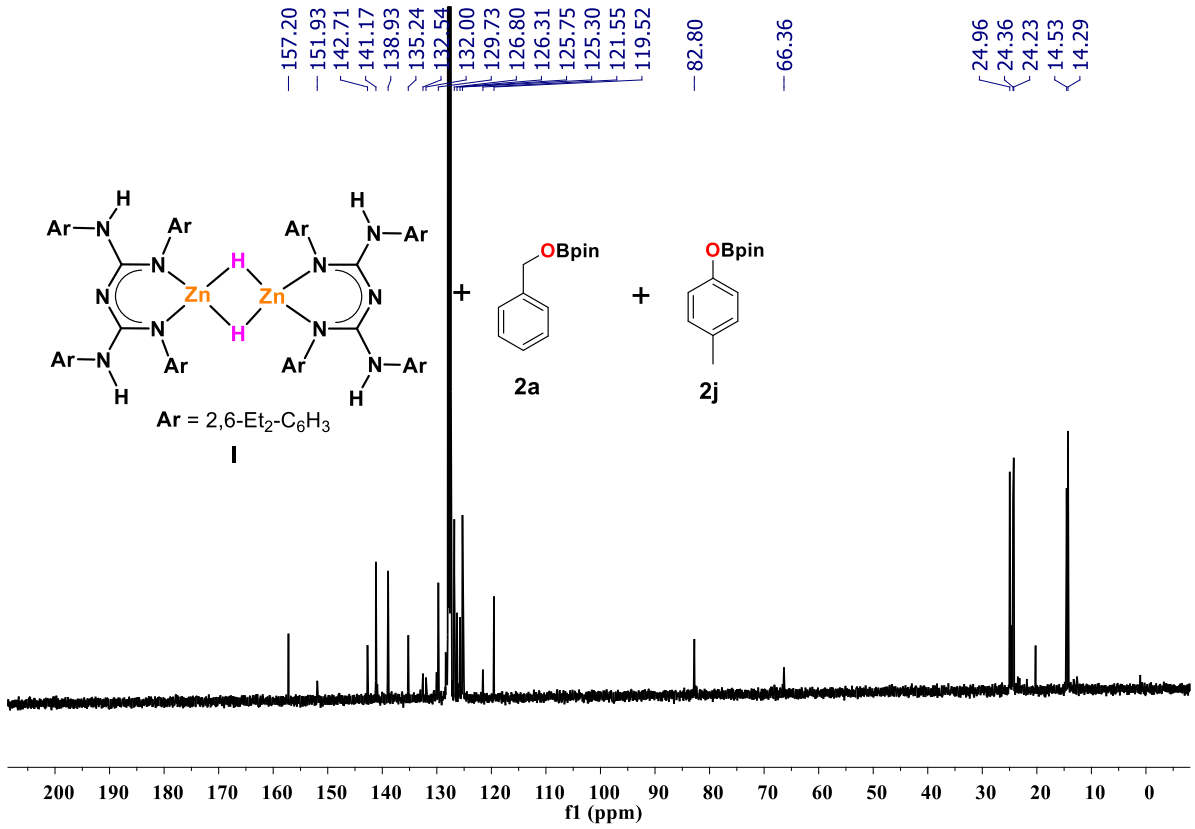


Figure S10: ^{13}C{^{1}H} NMR of compounds **I**, **2a** and **2j** (100 MHz, C_6D_6, 25 ^{o}C)

^{1}H, ^{13}C{^{1}H} and ^{11}B NMR Spectra of Hydroboration of Esters and Other Carbonyl Compounds

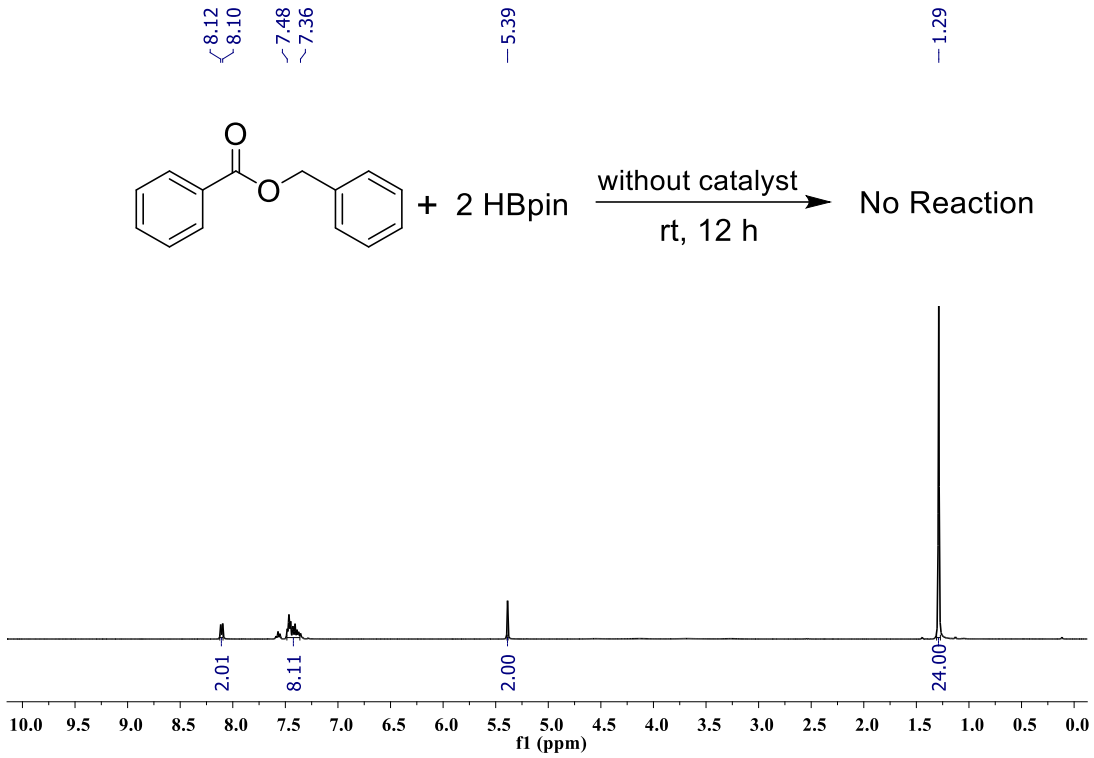


Figure S11: ^{1}H NMR spectrum of compound **1a+HBpin** (400 MHz, $CDCl_3$, 25 ^{o}C)

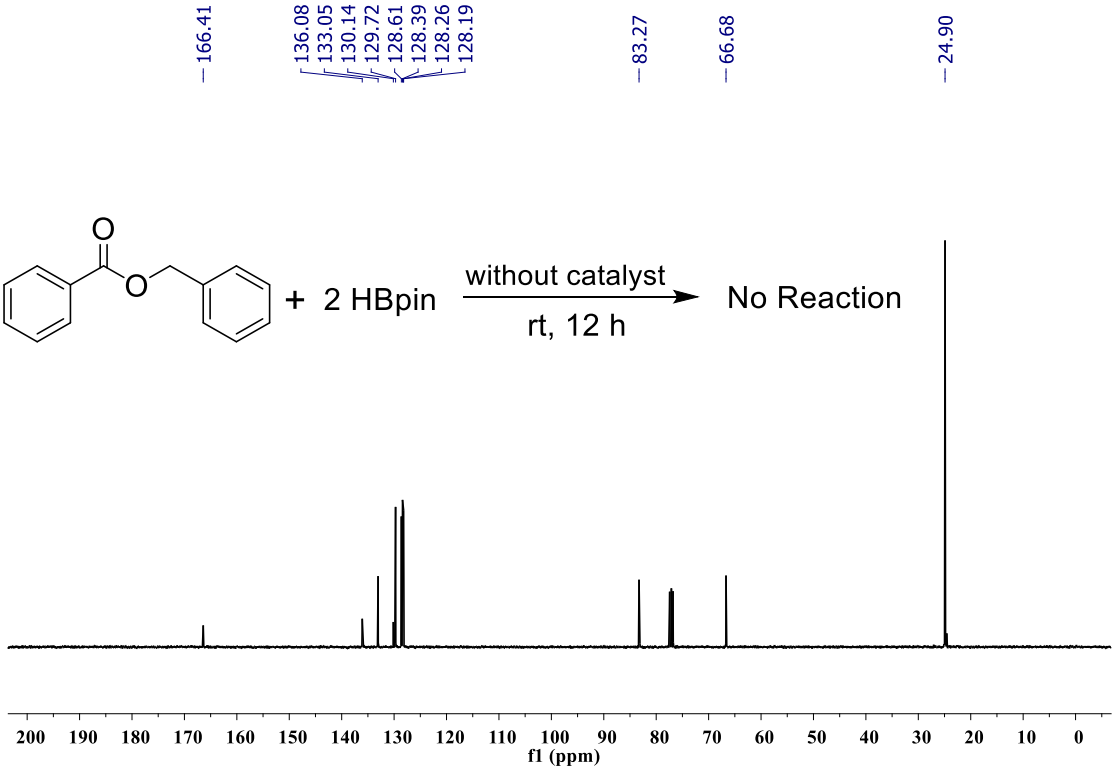


Figure S12: ^{13}C{^{1}H} NMR spectrum of compound **1a+HBpin** (100 MHz, $CDCl_3$, 25 ^{o}C)

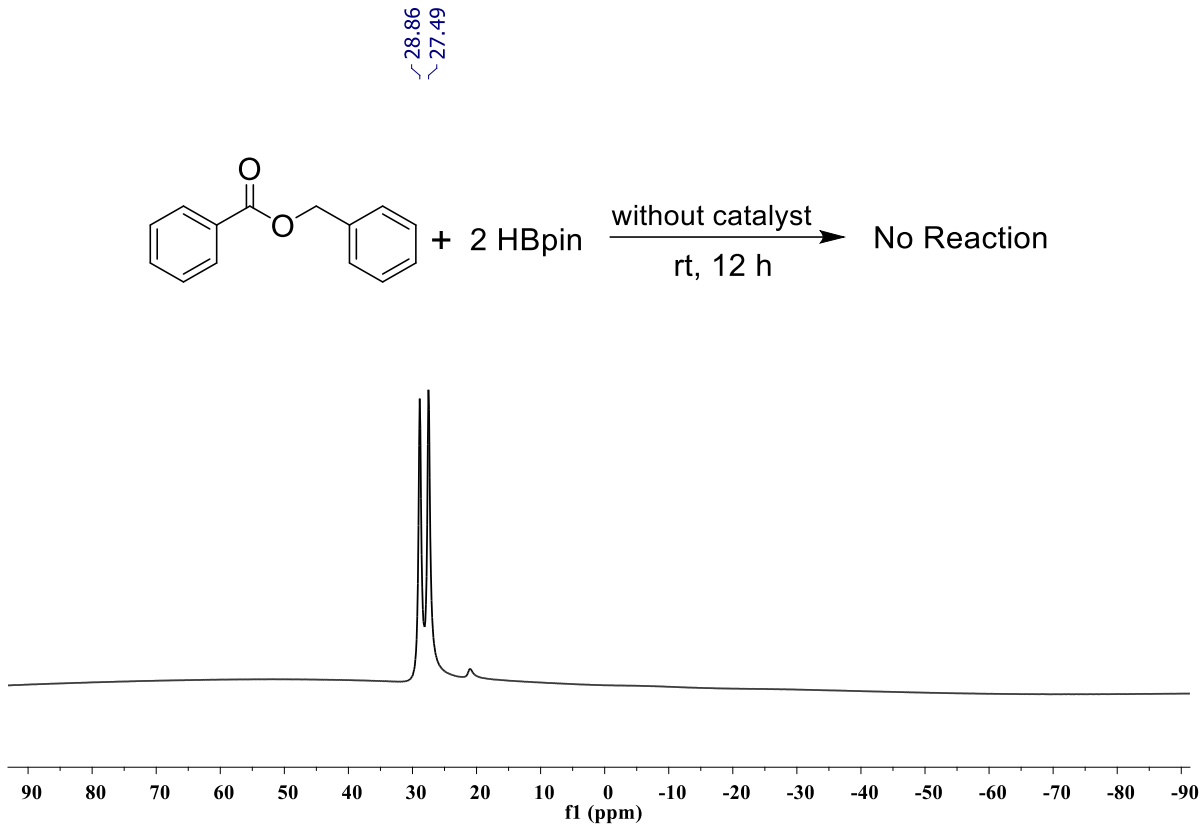


Figure S13: ^{11}B NMR spectrum of compound **1a+HBpin** (176 MHz, $CDCl_3$, 25 ^{o}C)

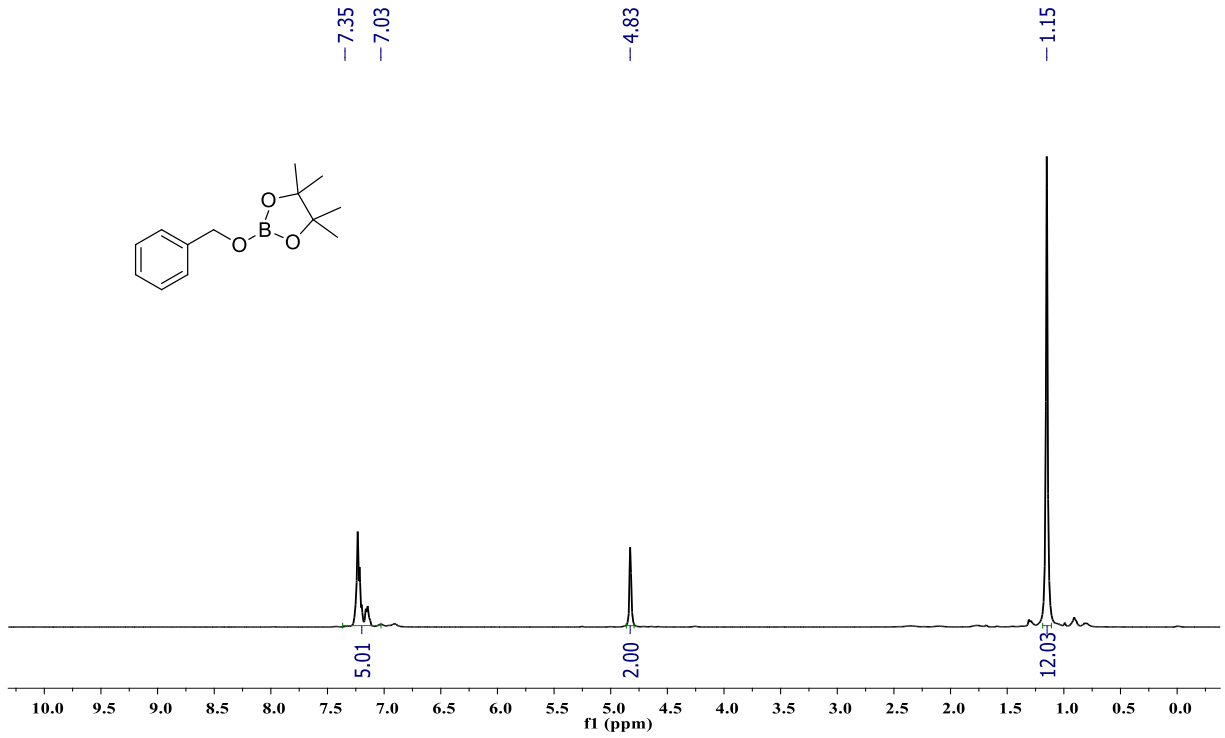


Figure S14: ^{1}H NMR spectrum of compound **2a** (400 MHz, $CDCl_3$, 25 ^{o}C)

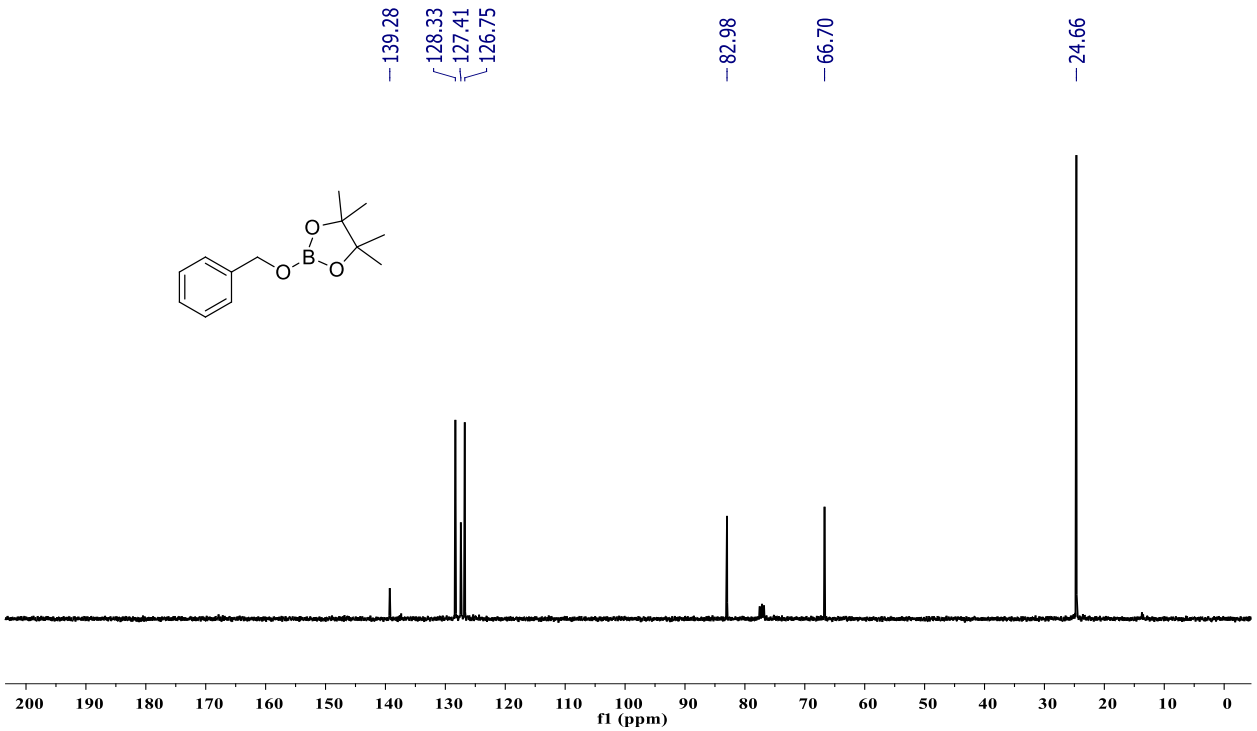


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2a** (101 MHz, $CDCl_3$, 25 °C)

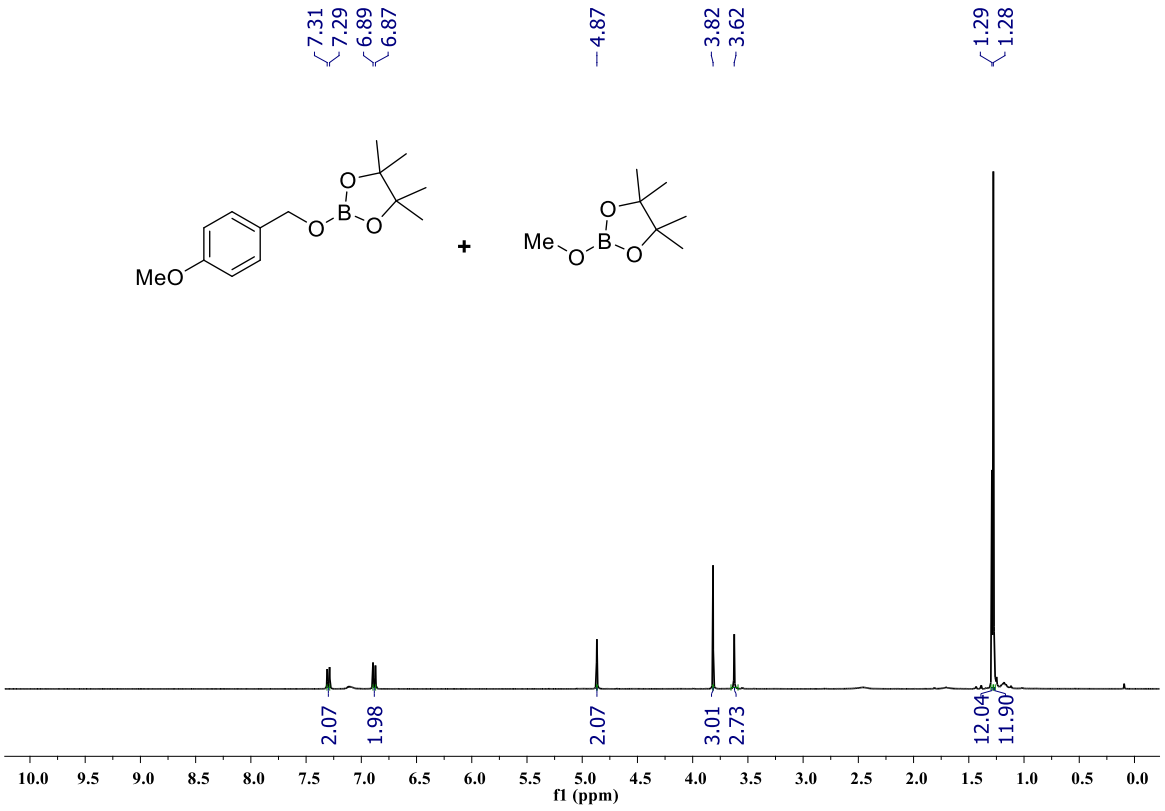


Figure S16: ^{1}H NMR spectrum of compounds **2b** and MeOBpin (400 MHz, $CDCl_3$, 25 °C)

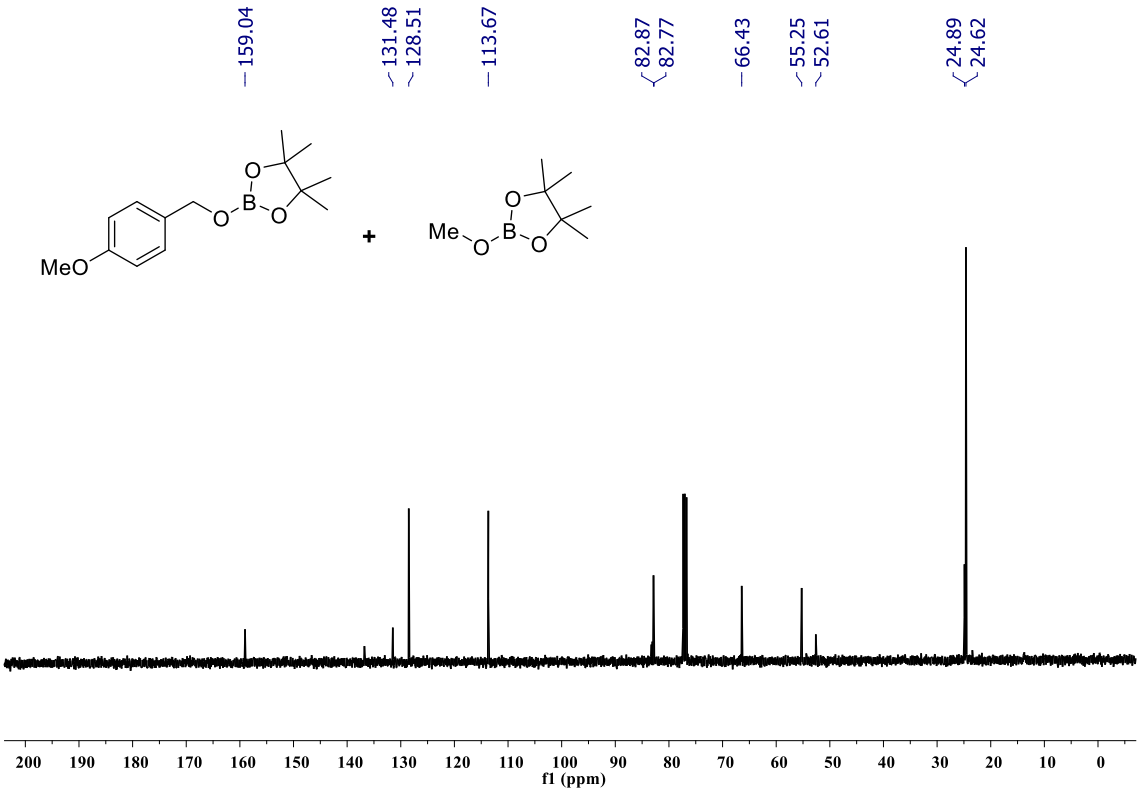


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2b** and MeOBpin (101 MHz, $CDCl_3$, 25 °C)

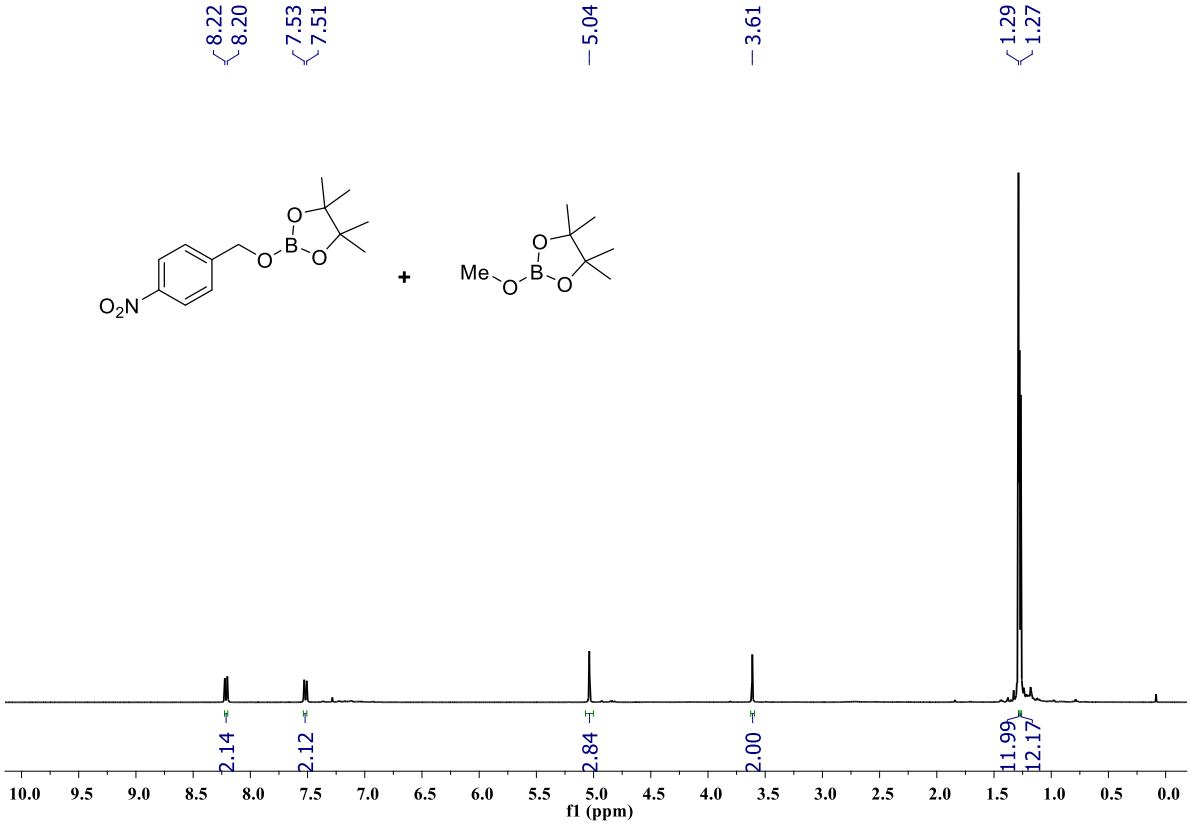


Figure S18: ^{1}H NMR spectrum of compounds **2c** and MeOBpin (400 MHz, $CDCl_3$, 25 °C).

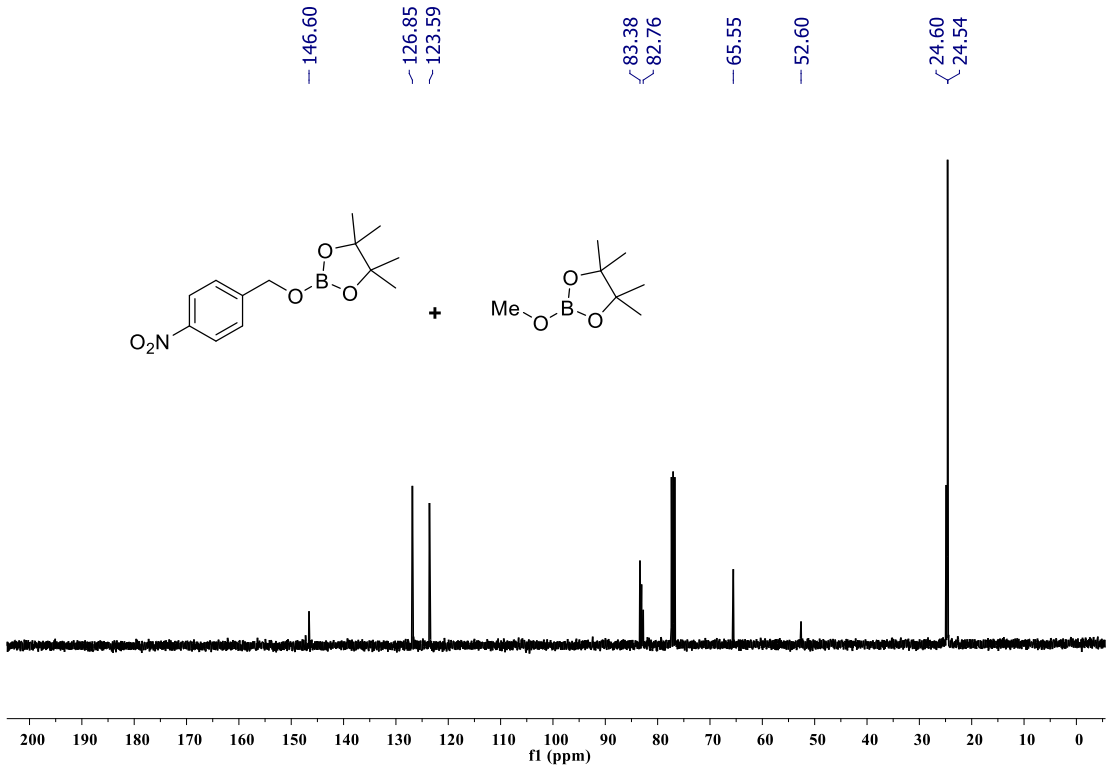


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2c and** MeOBpin (101 MHz, $CDCl_3$, 25 ^{o}C)

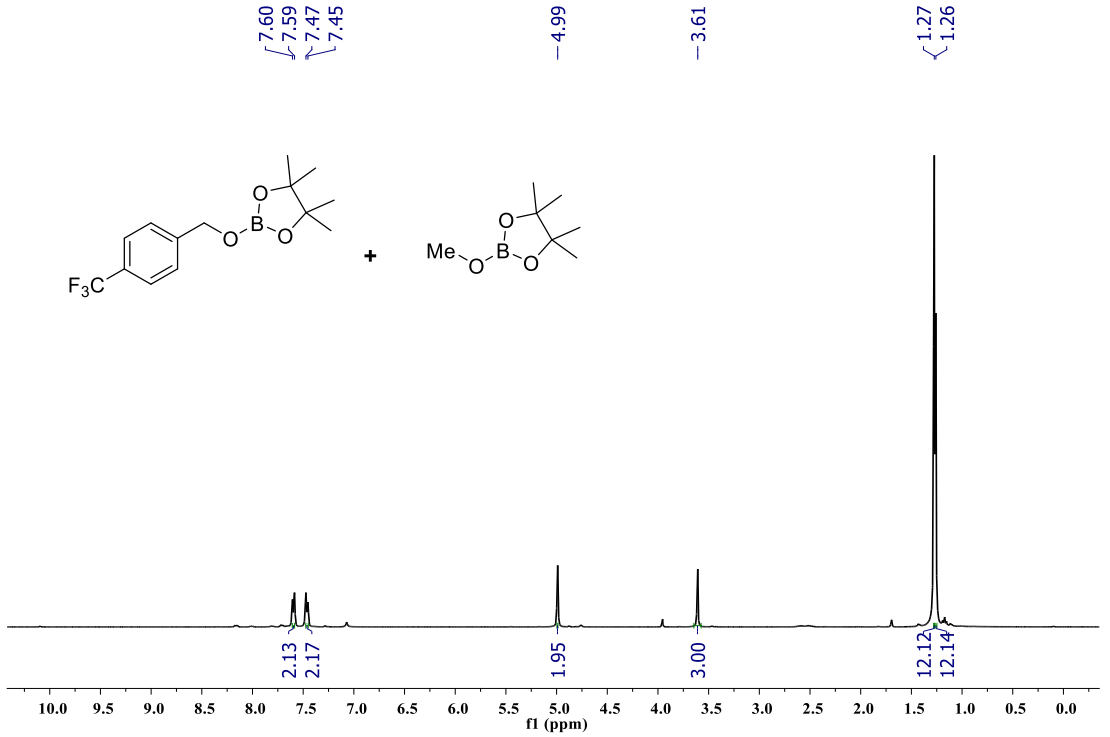


Figure S20: ^{1}H NMR spectrum of compounds **2d** and MeOBpin (400 MHz, $CDCl_3$, 25 ^{o}

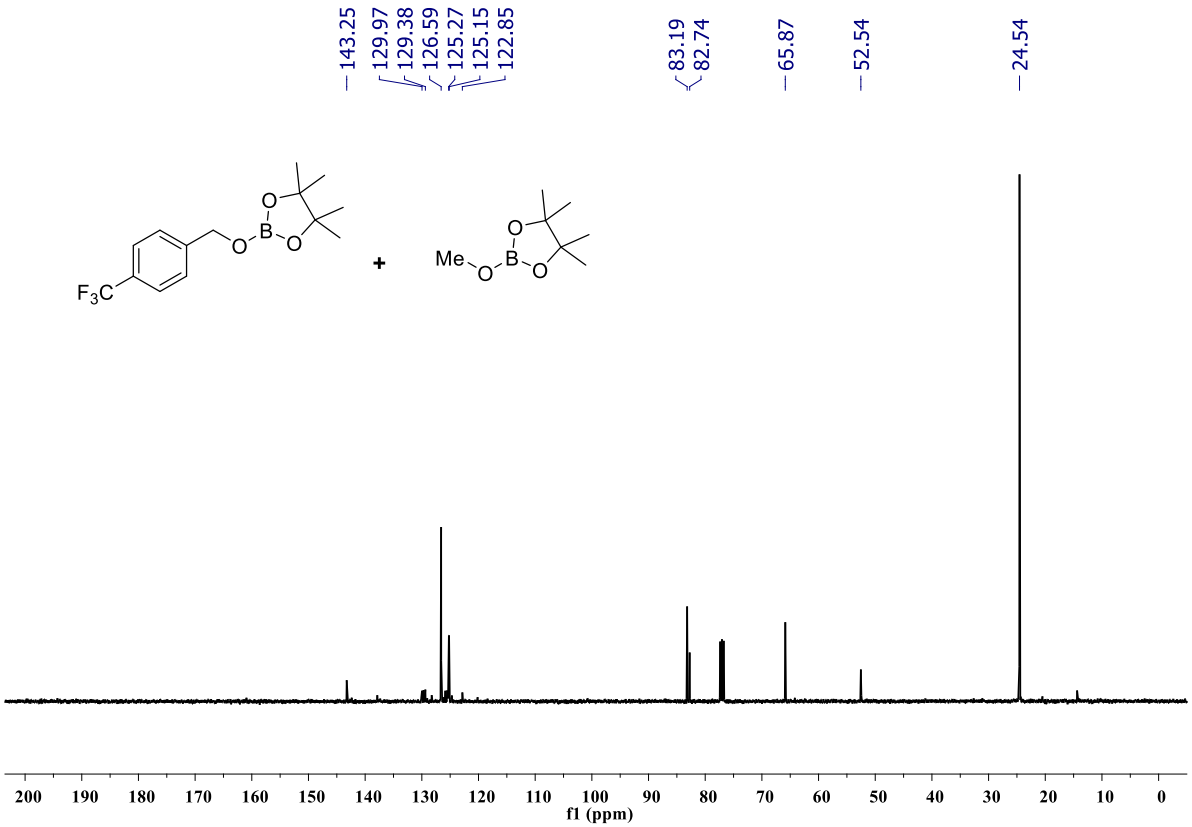


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2d** and MeOBpin (101 MHz, $CDCl_3$, 25 ^{o}C)

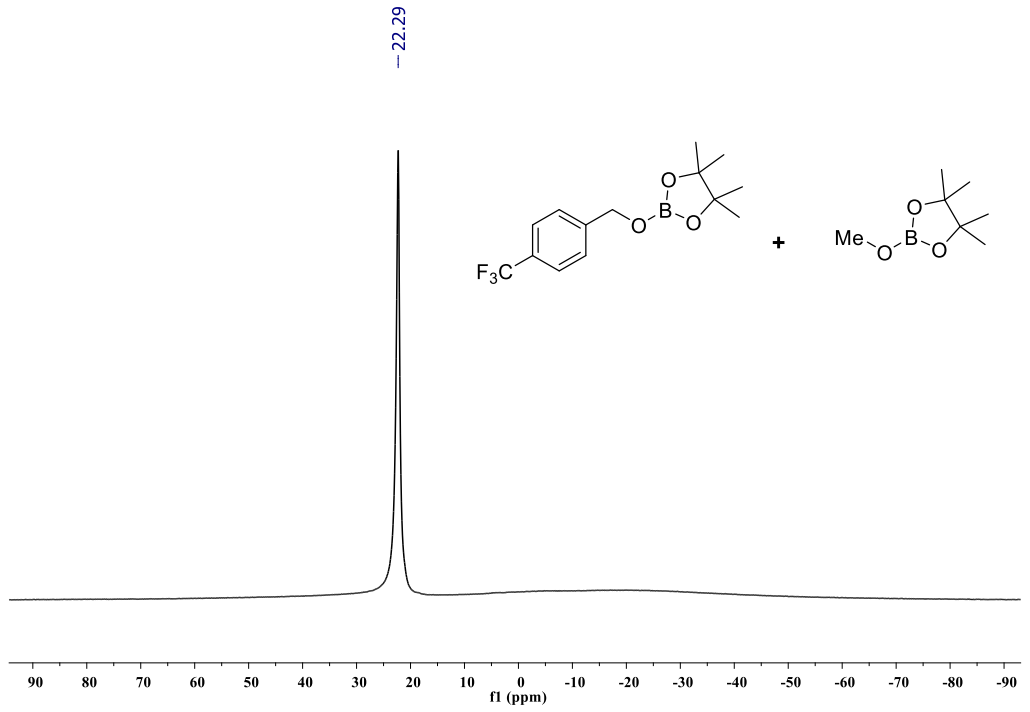


Figure S22: ^{11}B NMR spectrum of compounds **2d** and MeOBpin (128 MHz, $CDCl_3$, 25 ^{o}C)

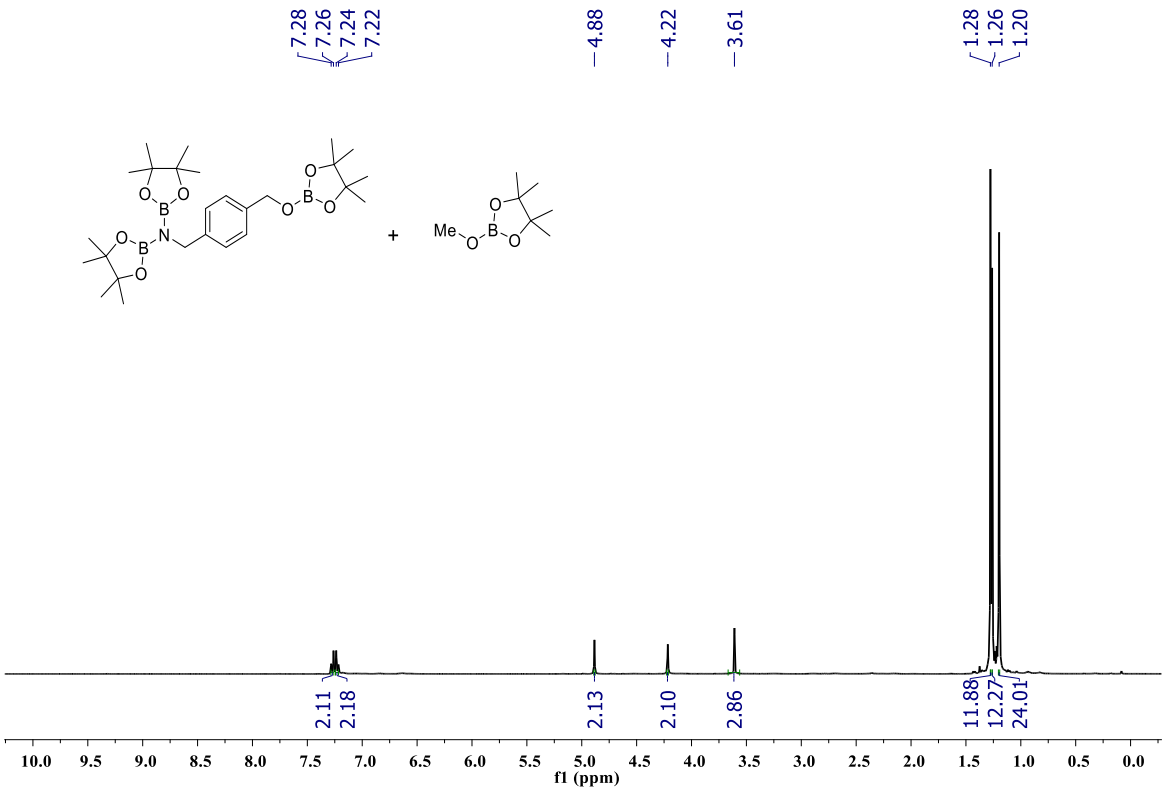


Figure S23: ^{1}H NMR spectrum of compounds **2e** and MeOBpin (400 MHz, $CDCl_3$, 25 ^{o}C)

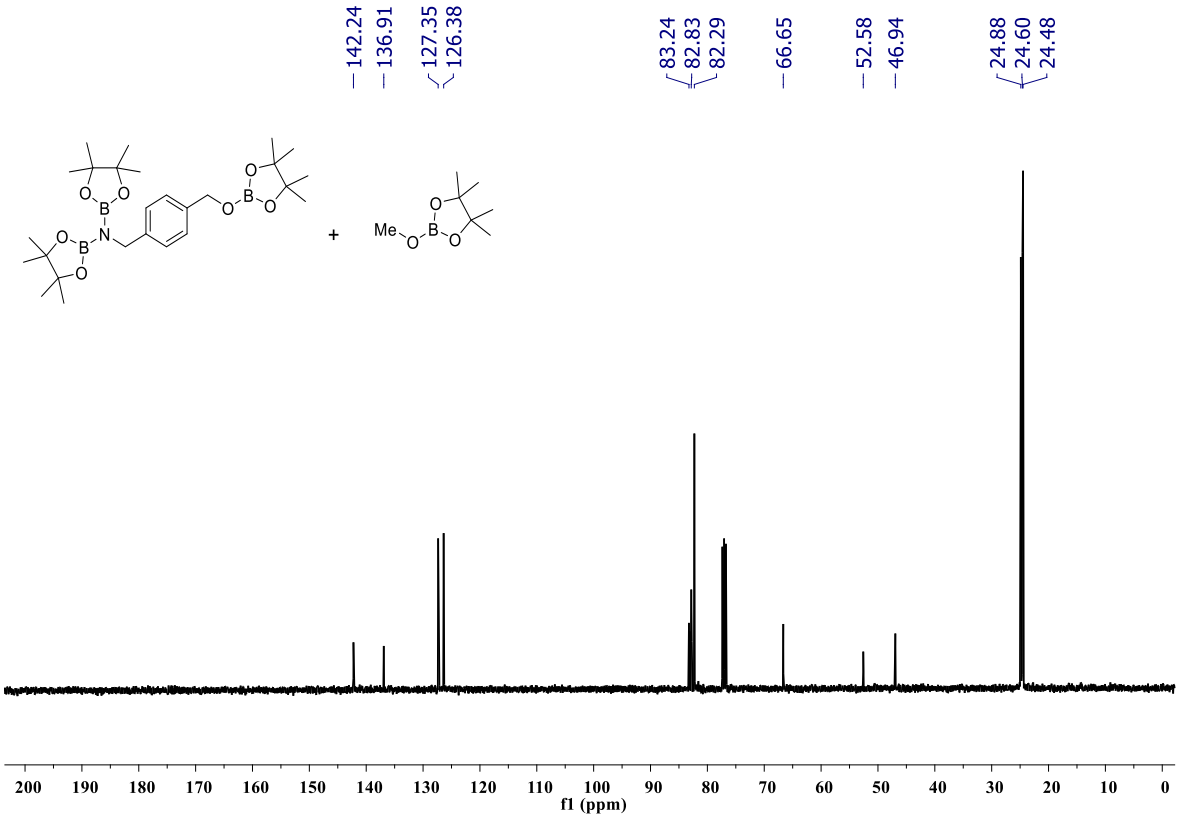


Figure S24: ^{13}C{^{1}H} NMR spectrum of compounds **2e** and MeOBpin (101 MHz, $CDCl_3$, 25 ^{o}C)

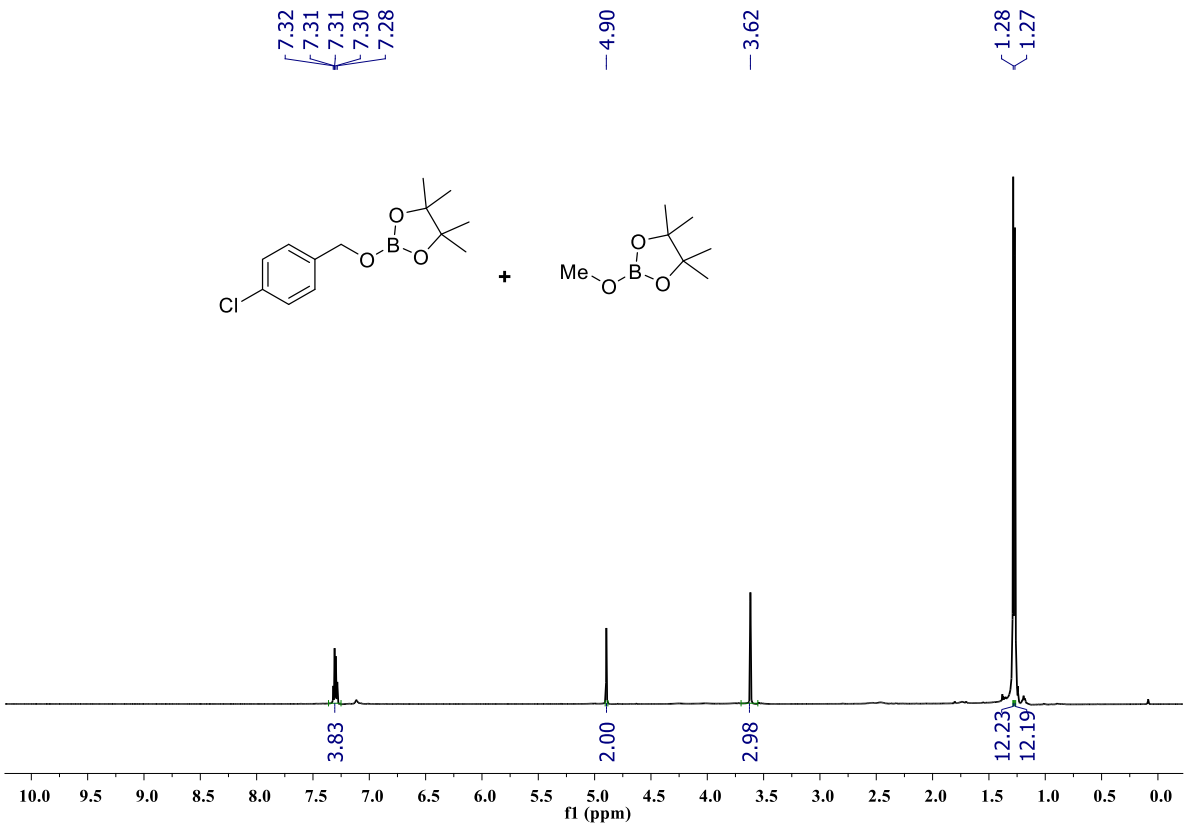


Figure S25: ^{1}H NMR spectrum of compounds **2f** and MeOBpin (400 MHz, $CDCl_3$, 25 ^{o}C)

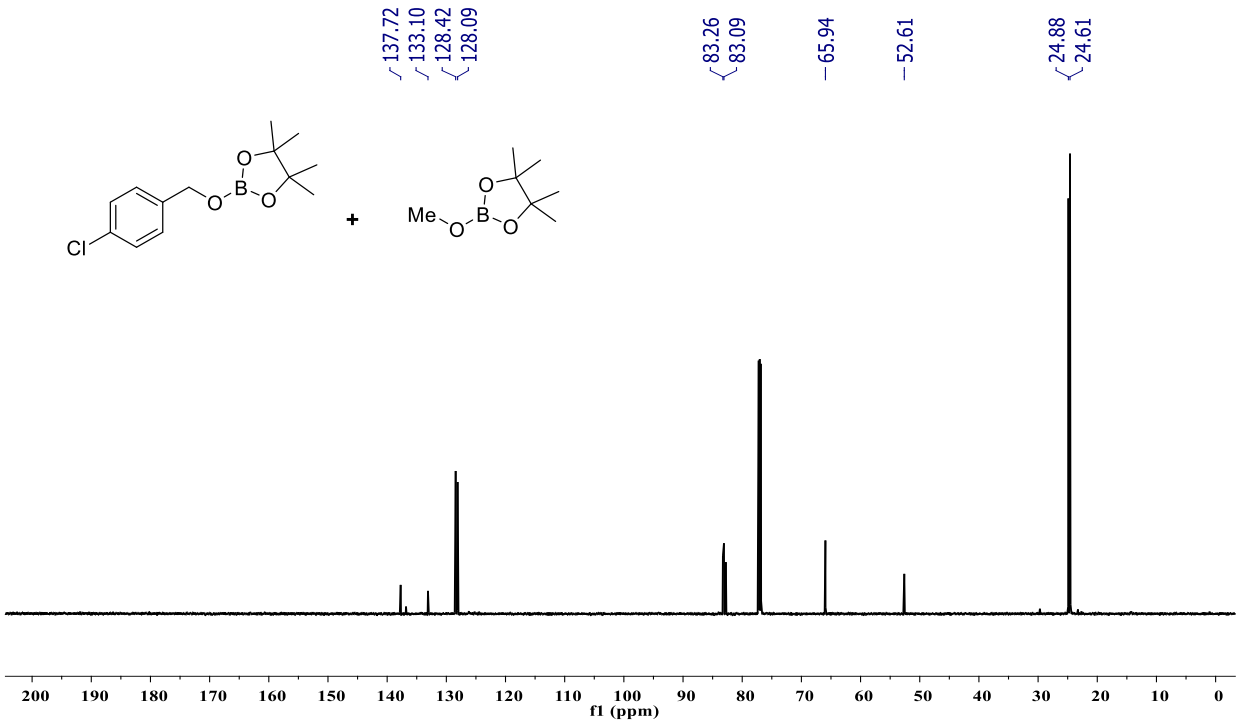


Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2f** and MeOBpin (101 MHz, $CDCl_3$, 25 ^{o}C)

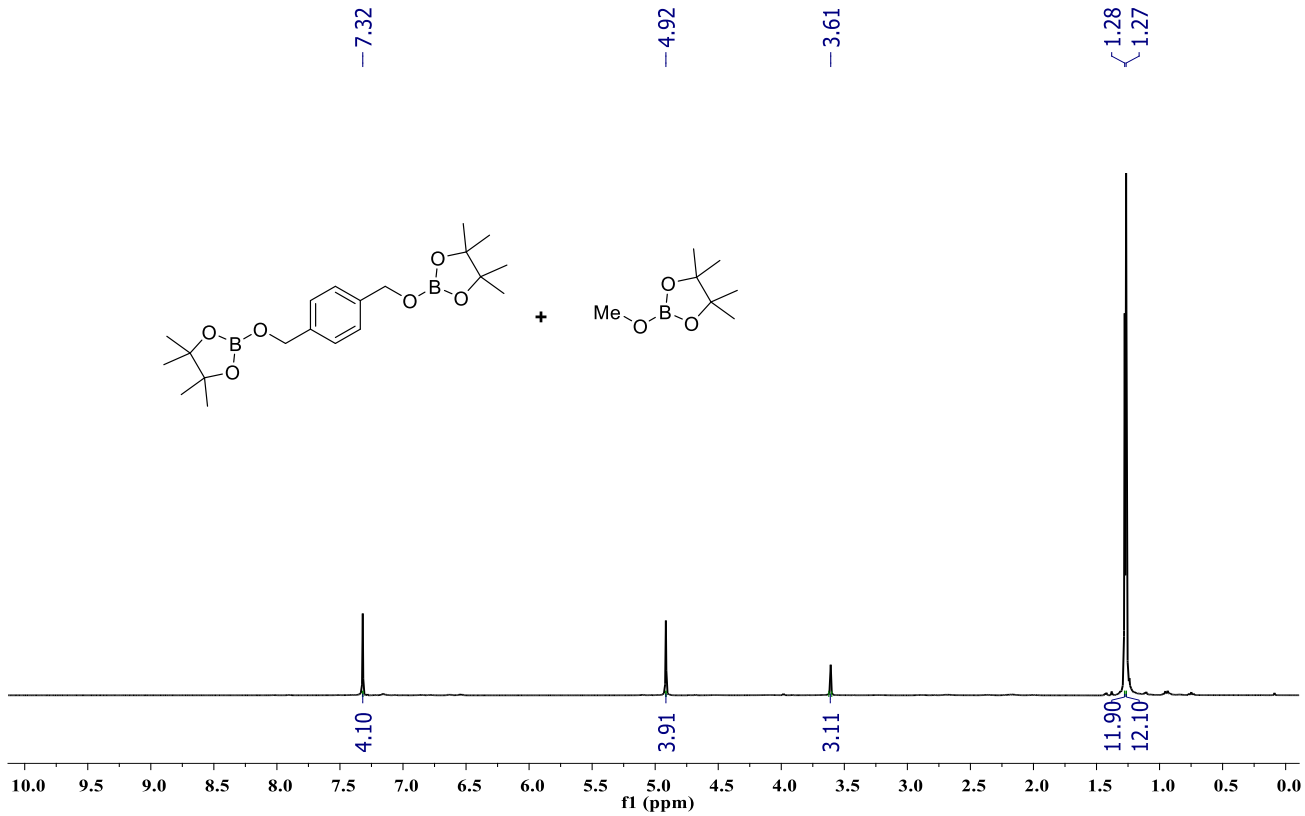


Figure S27: ^{1}H NMR spectrum of compounds **2g** and MeOBpin (400 MHz, $CDCl_3$, 25 ^{o}C)

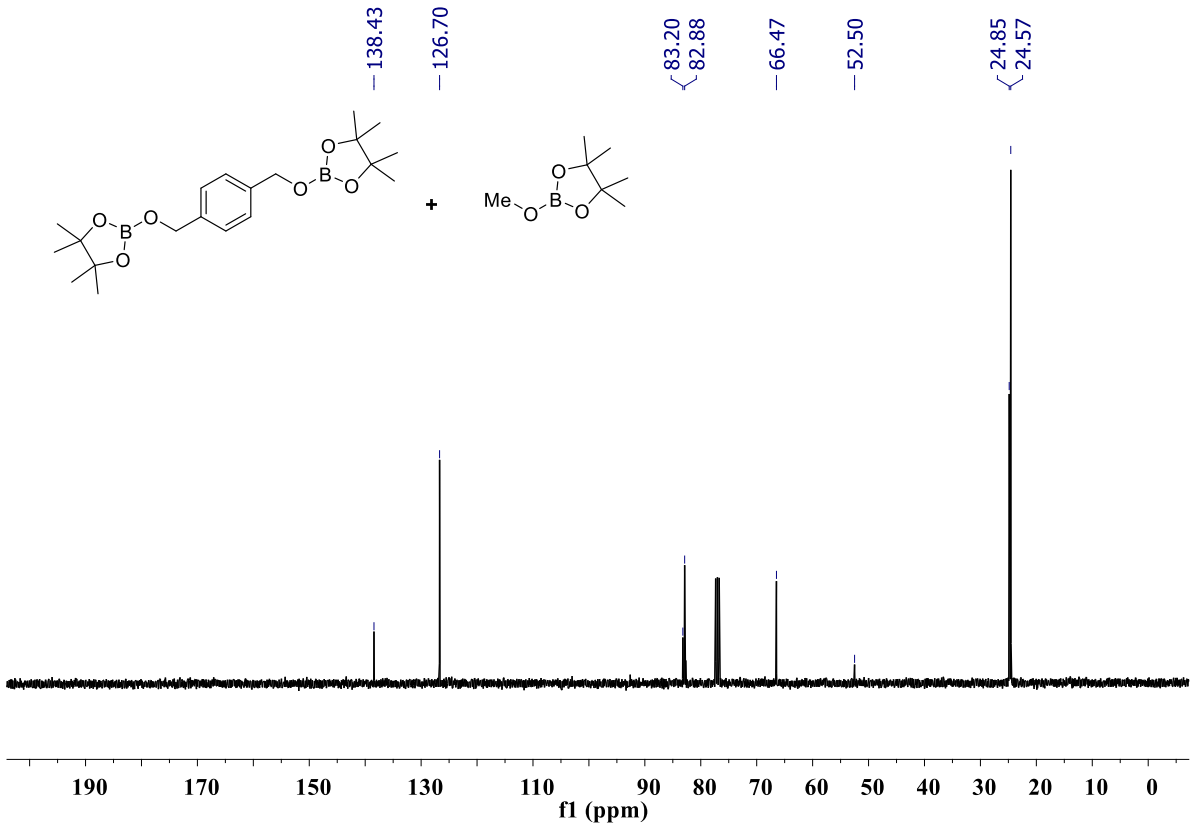


Figure S28: ^{13}C{^{1}H} NMR spectrum of compounds **2g** and MeOBpin (101 MHz, $CDCl_3$, 25 ^{o}C)

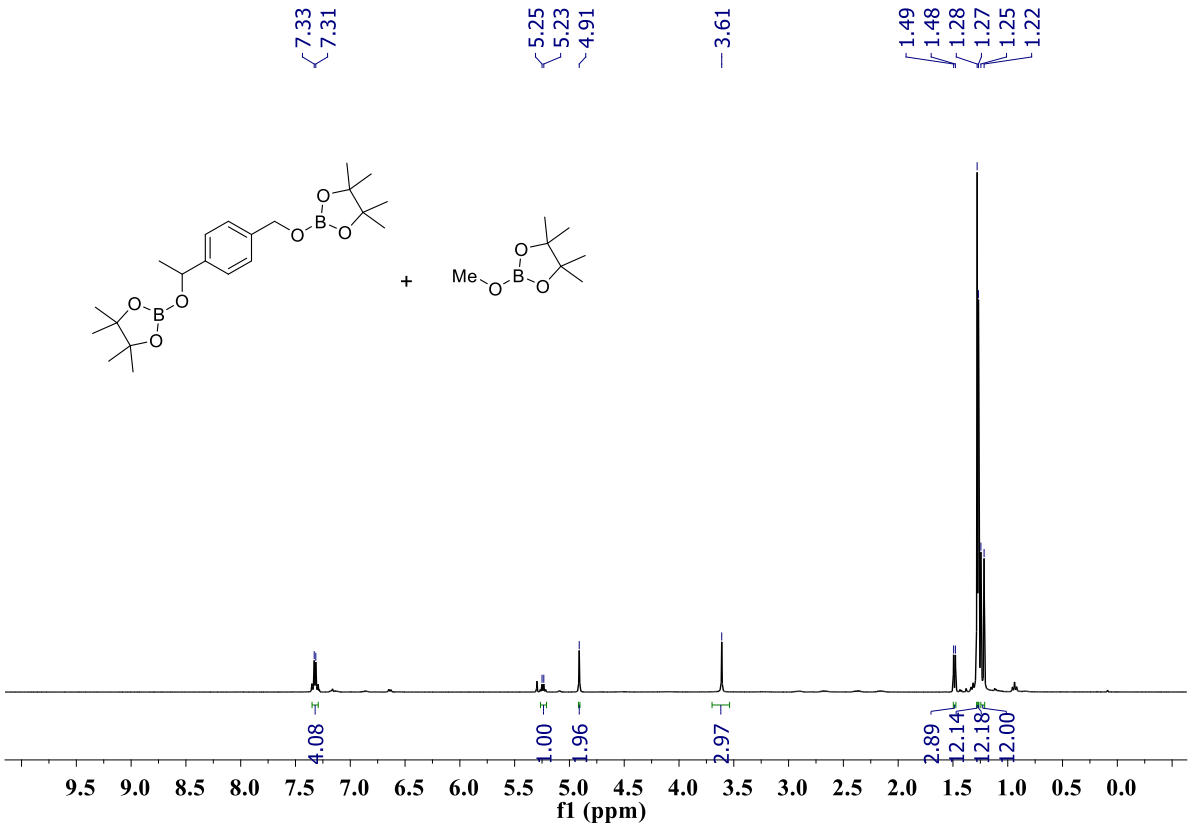


Figure S29: ^{1}H NMR spectrum of compounds **2h** and MeOBpin (400 MHz, $CDCl_3$, 25 ^{o}C)

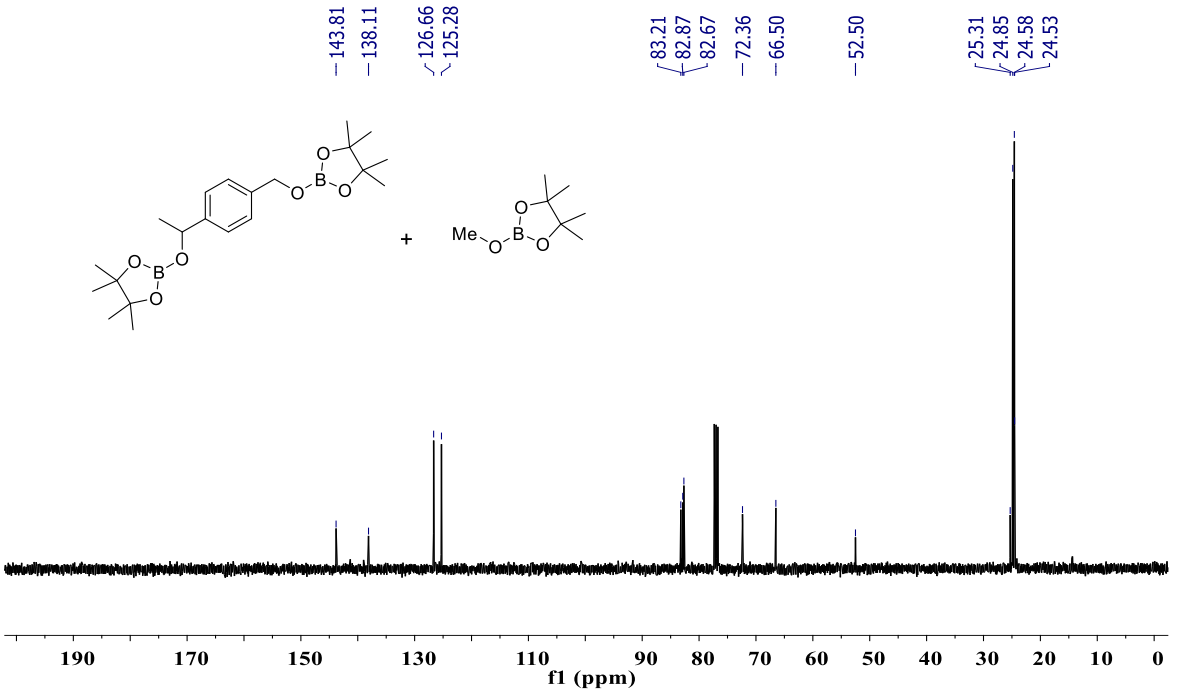


Figure S30: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2h** and MeOBpin (101 MHz, $CDCl_3$, 25 ^{o}C)

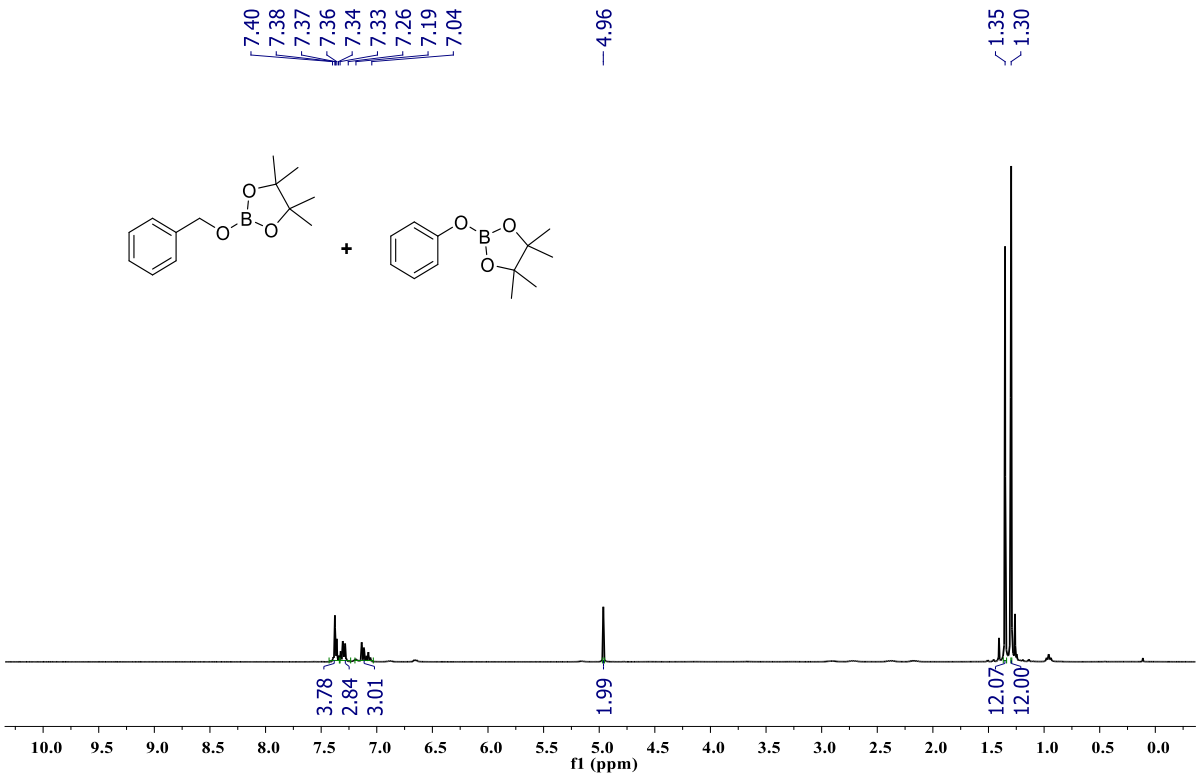


Figure S31: ^{1}H NMR spectrum of compounds **2a** and **2i** (400 MHz, $CDCl_3$, 25 ^{o}C)

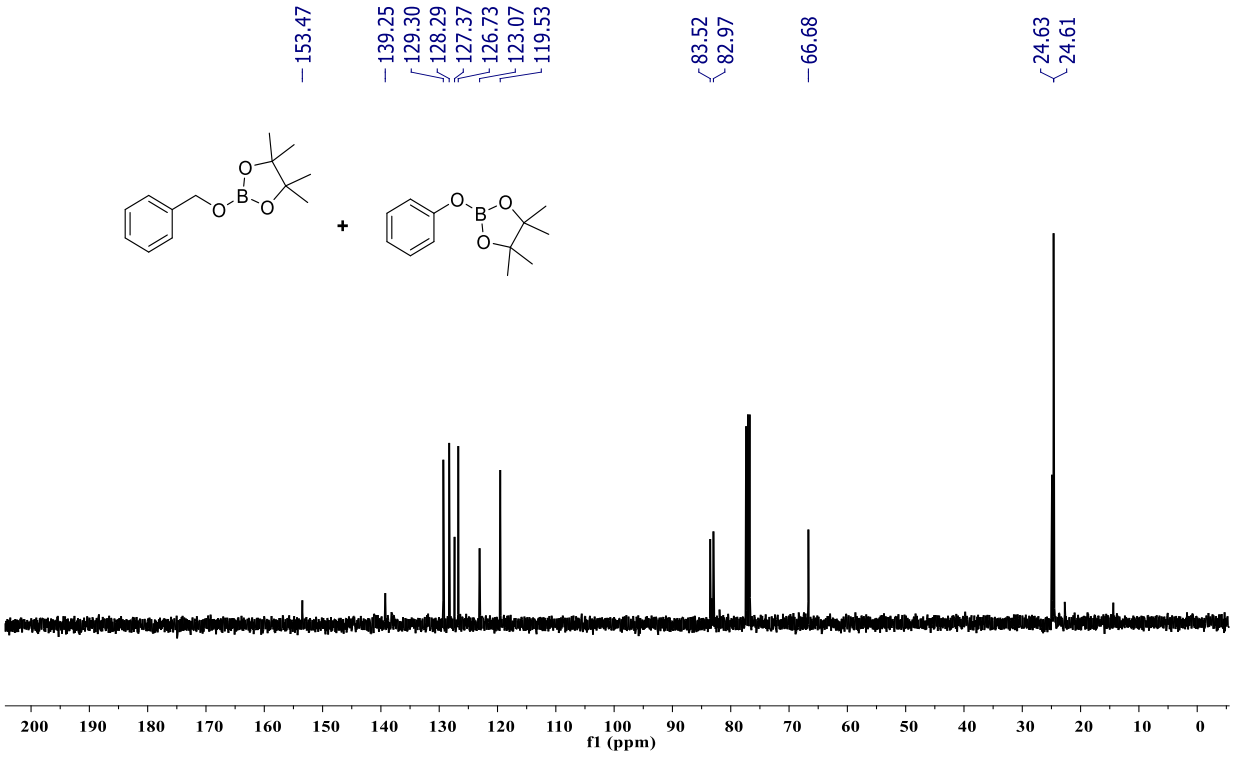


Figure S32: ^{13}C{^{1}H} NMR spectrum of compounds **2a** and **2i** (101 MHz, $CDCl_3$, 25 ^{o}C)

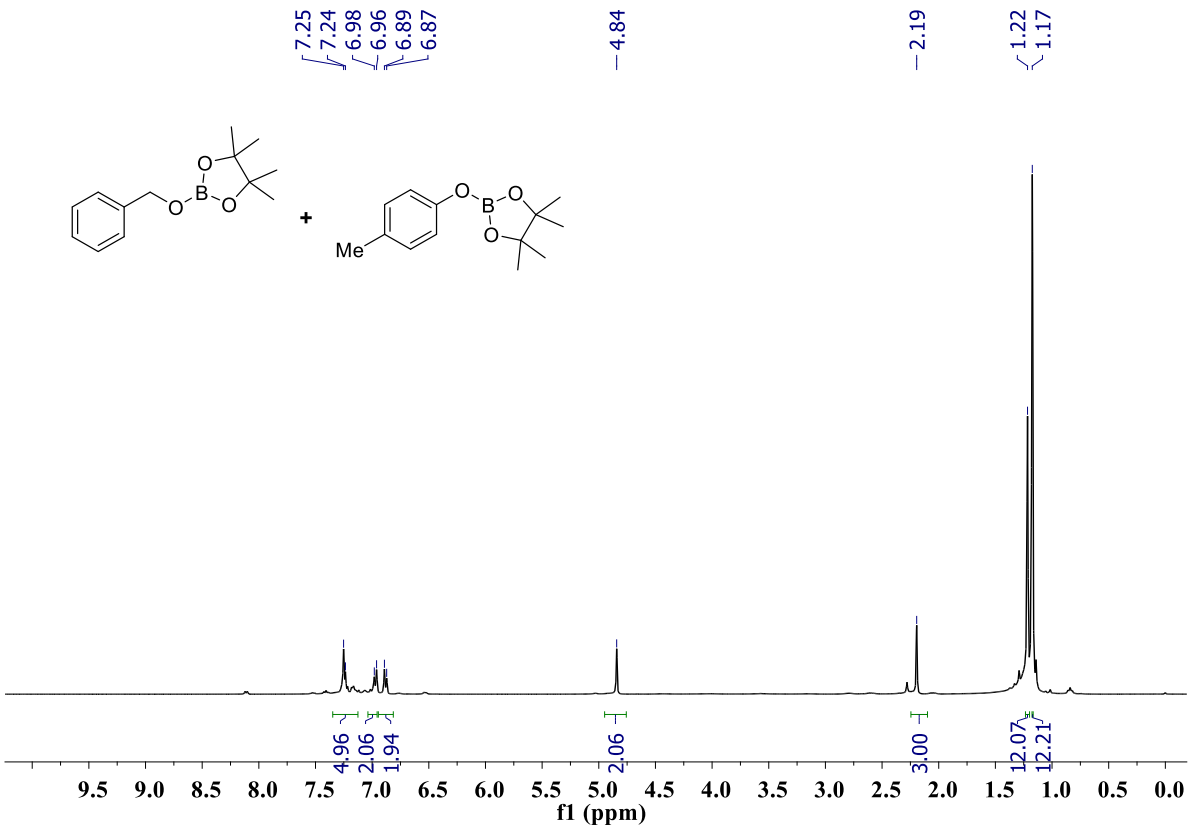


Figure S33: ^{1}H NMR spectrum of compounds **2a** and **2j** (400 MHz, $CDCl_3$, 25 ^{o}C)

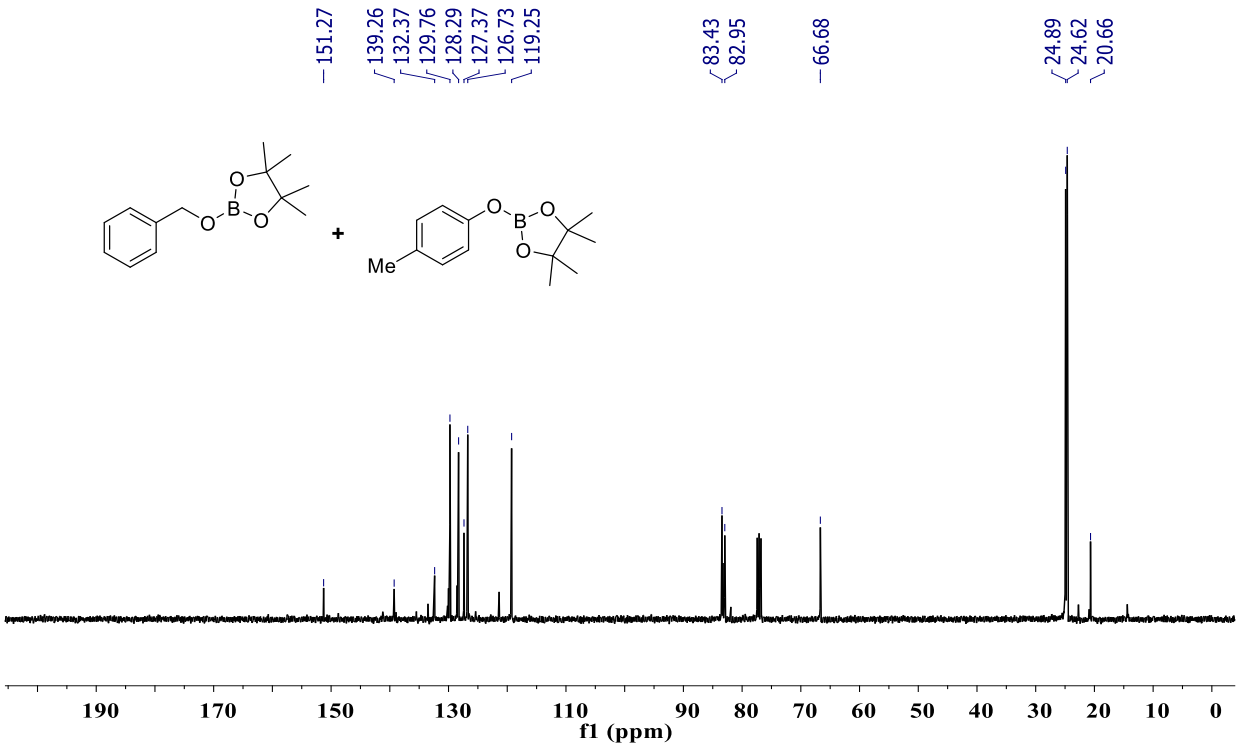


Figure S34: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2a** and **2j** (101 MHz, $CDCl_3$, 25 ^{o}C)

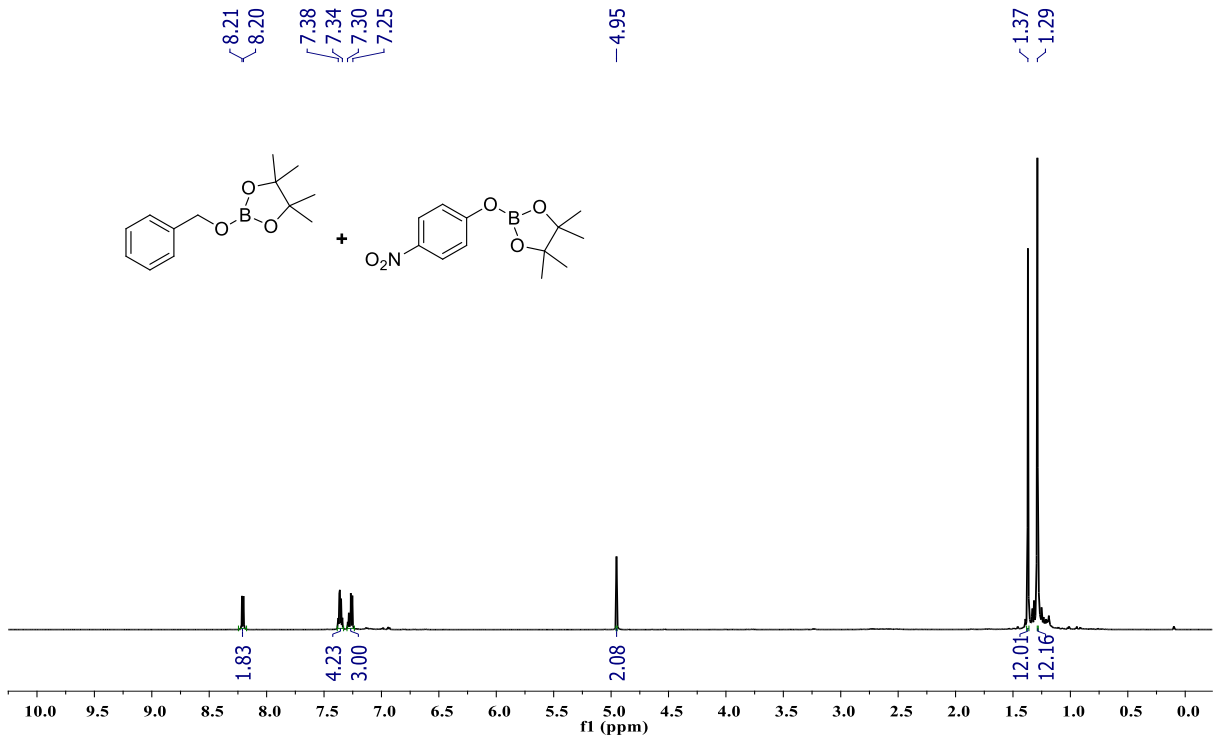


Figure S35: ^{1}H NMR spectrum of compounds **2a** and **2k** (400 MHz, $CDCl_3$, 25 °C)

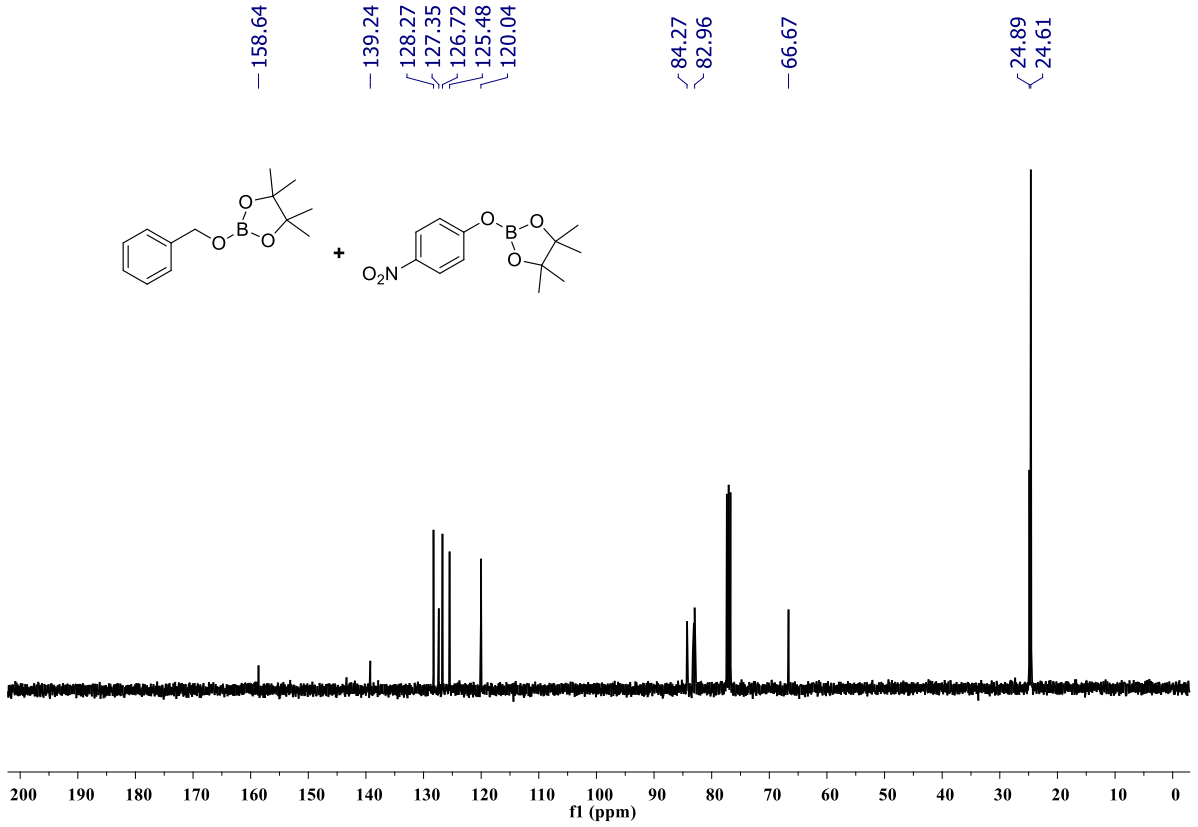


Figure S36: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2a** and **2k** (101 MHz, $CDCl_3$, 25 °C)

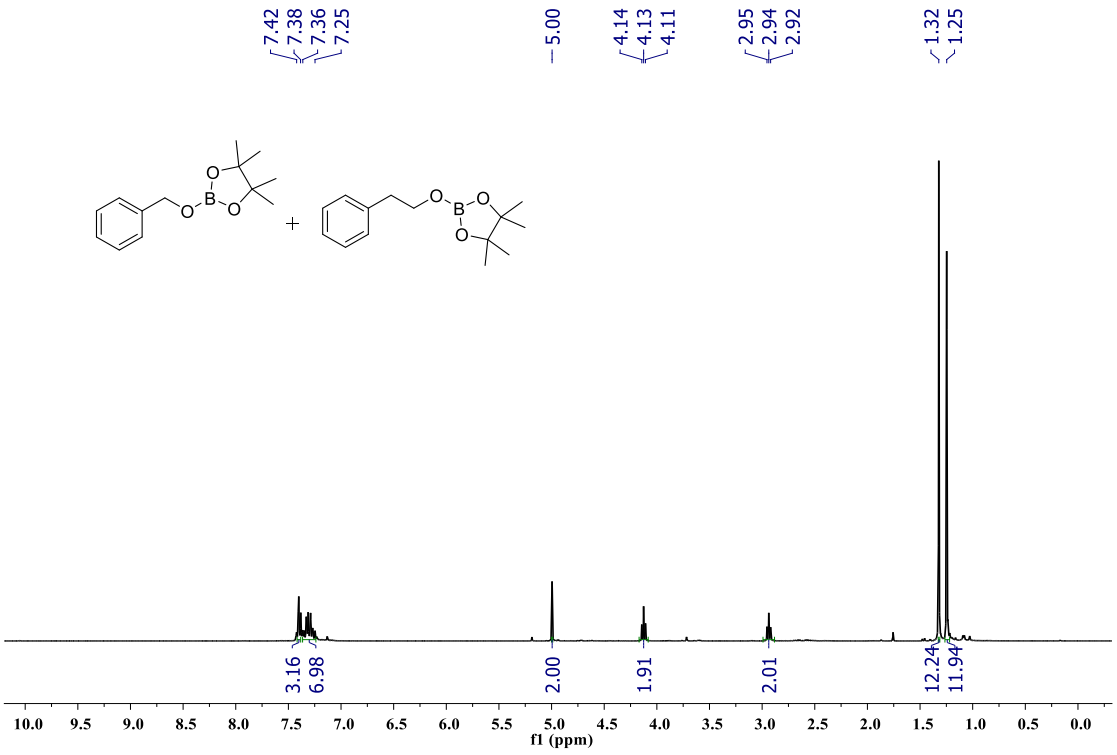


Figure S37: ^{1}H NMR spectrum of compounds **2a** and **2l** (400 MHz, $CDCl_3$, 25 ^{o}C)

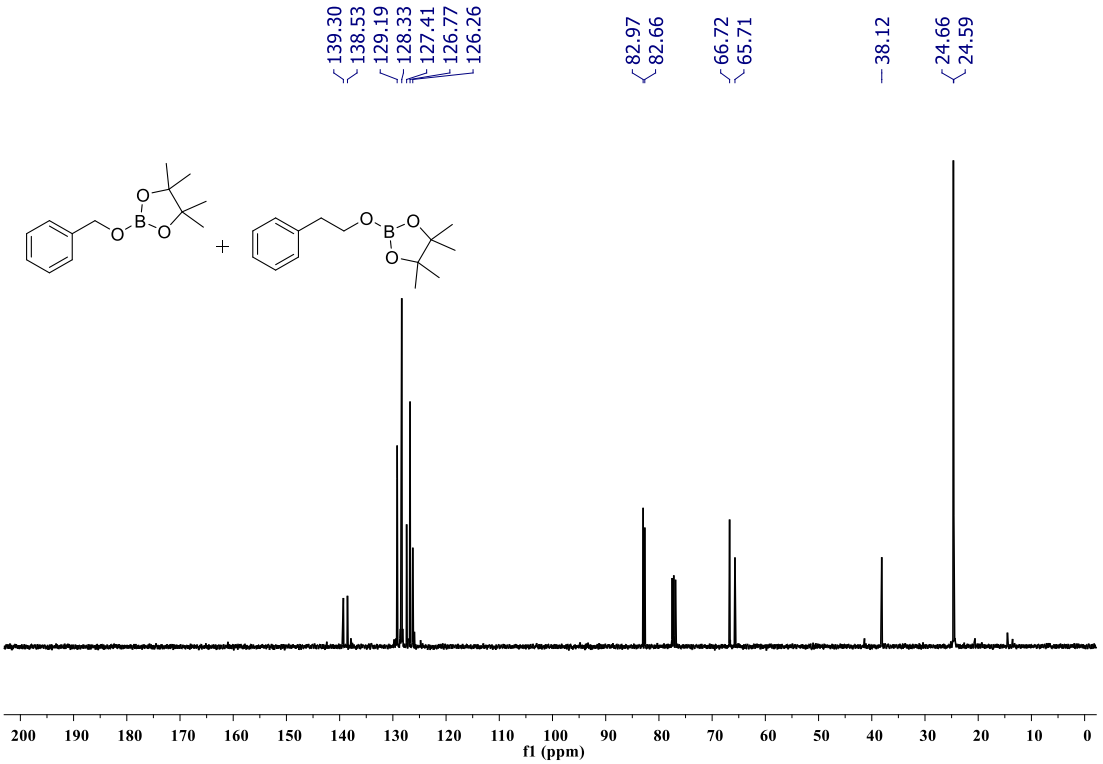


Figure S38: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2a** and **2l** (101 MHz, $CDCl_3$, 25 ^{o}C)

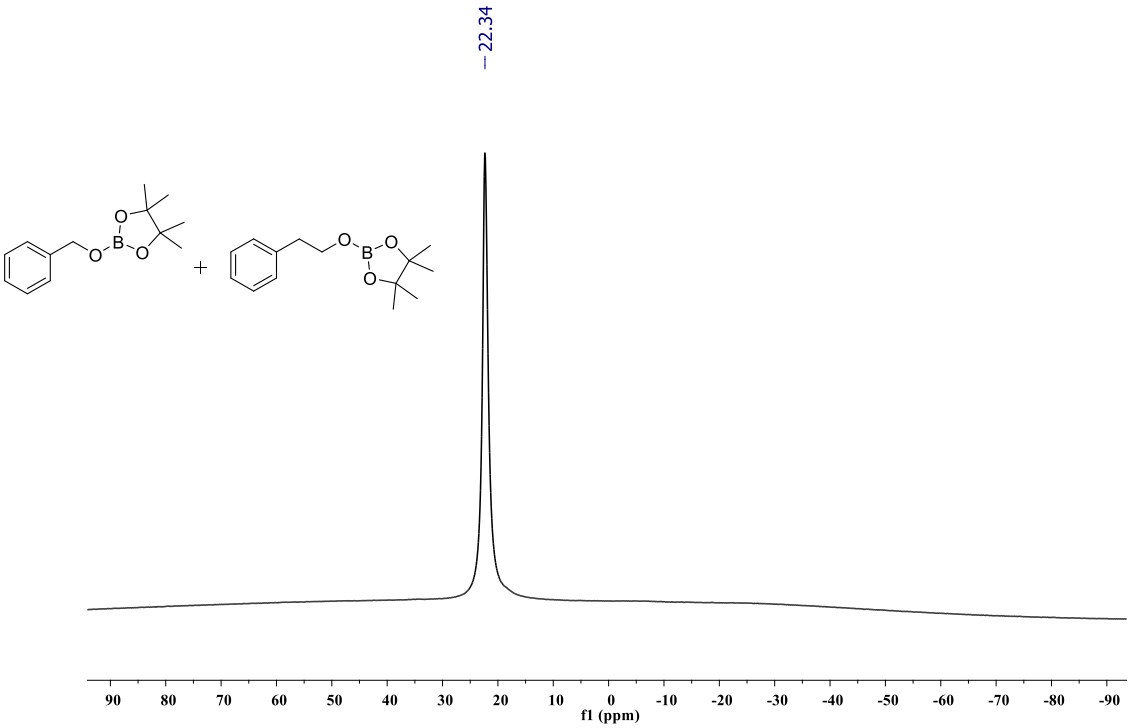


Figure S39: ^{11}B NMR spectrum of compounds **2a** and **2l** (128 MHz, $CDCl_3$, 25 ^{o}C)

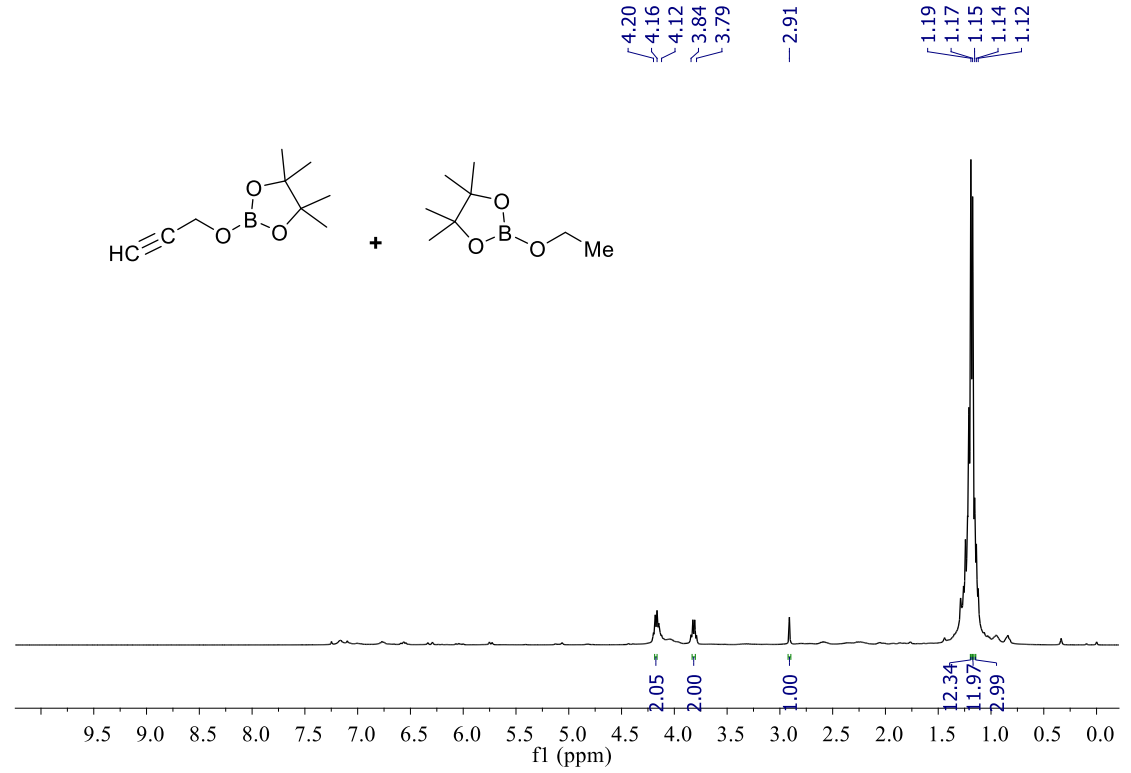


Figure S40: ^{1}H NMR spectrum of compounds **2m** and **2o** (400 MHz, $CDCl_3$, 25 ^{o}C)

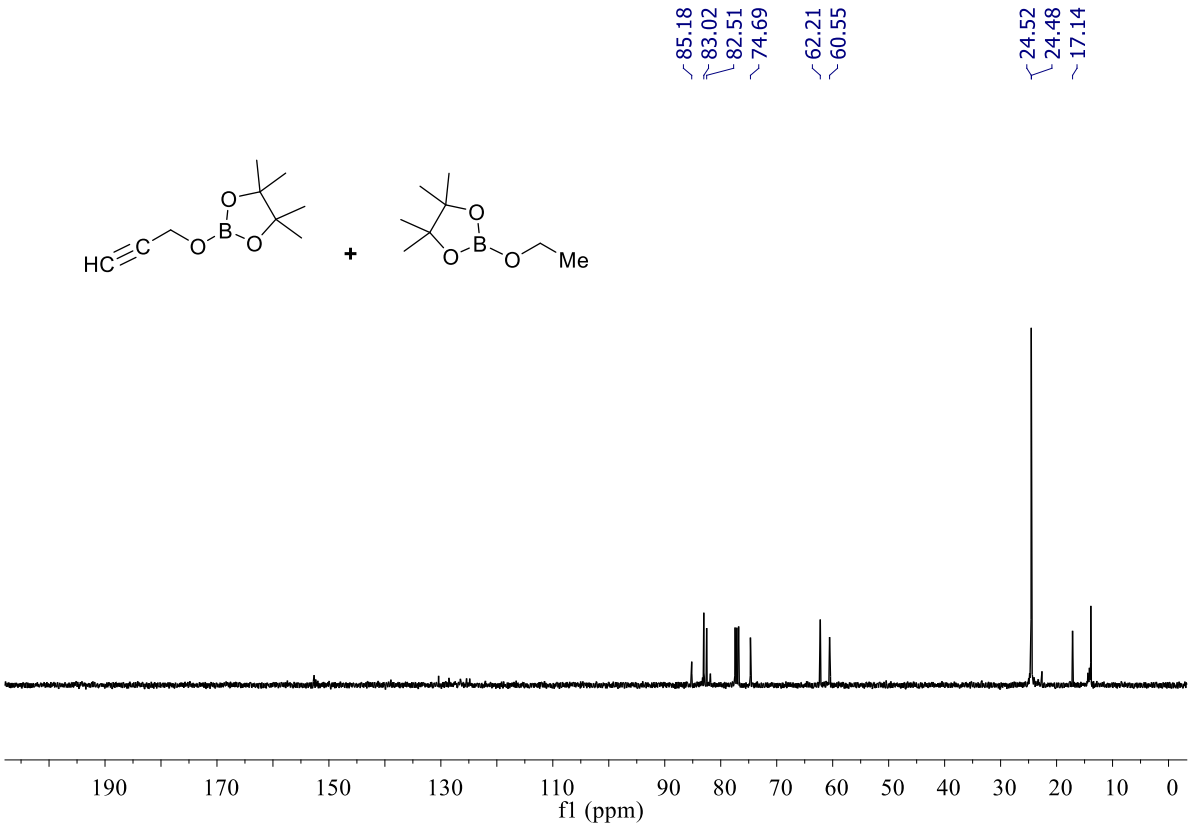


Figure S41: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2m** and **2o** (101 MHz, $CDCl_3$, 25 °C)

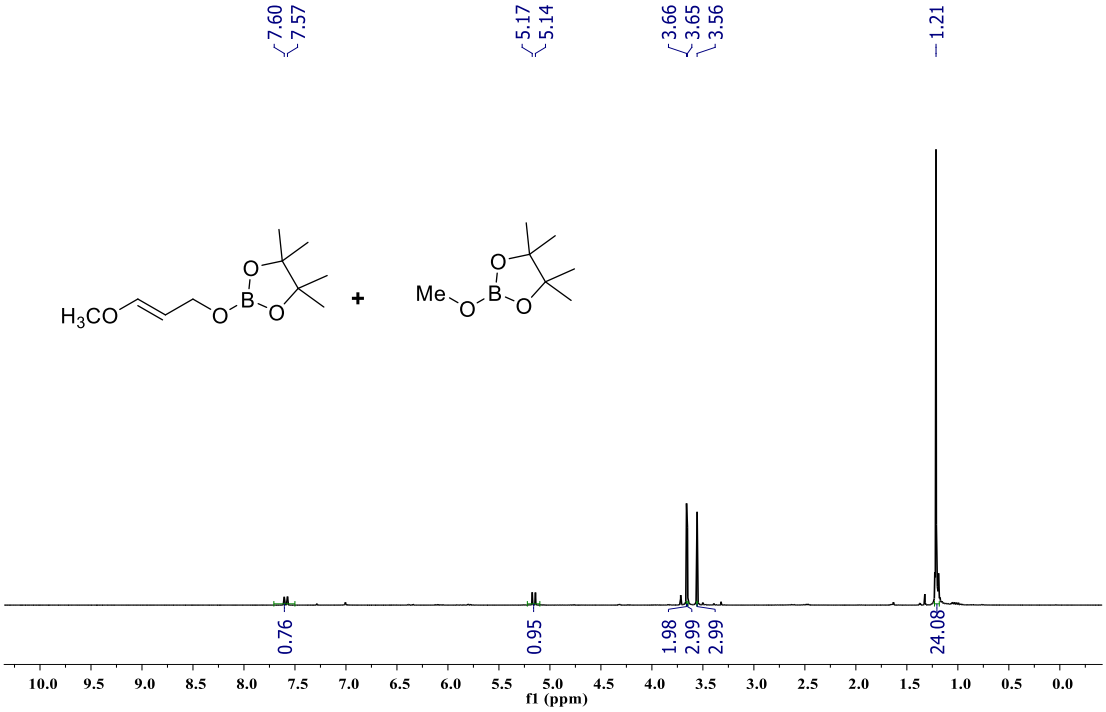


Figure S42: ^{1}H NMR spectrum of compounds **2n** and MeOBpin (400 MHz, $CDCl_3$, 25 °C)

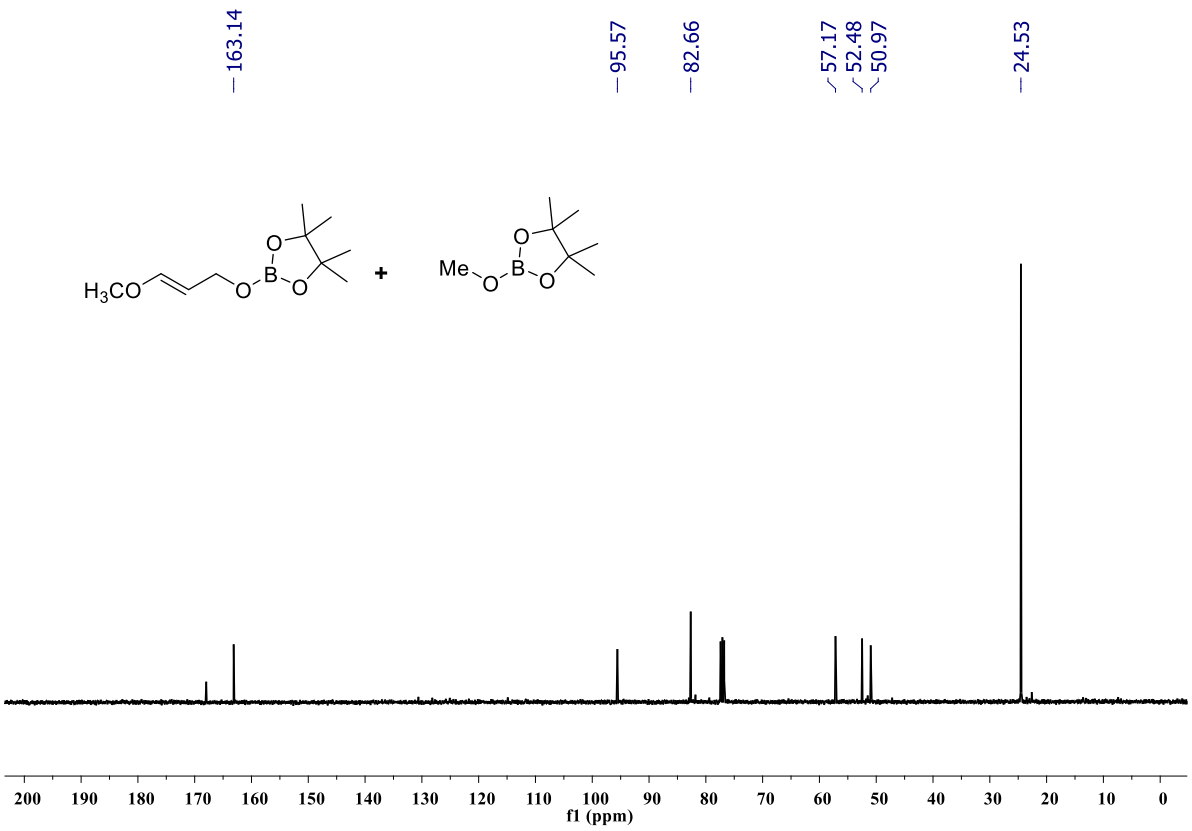


Figure S43: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **2n** and MeOBpin (101 MHz, $CDCl_3$, 25 ^{o}C)

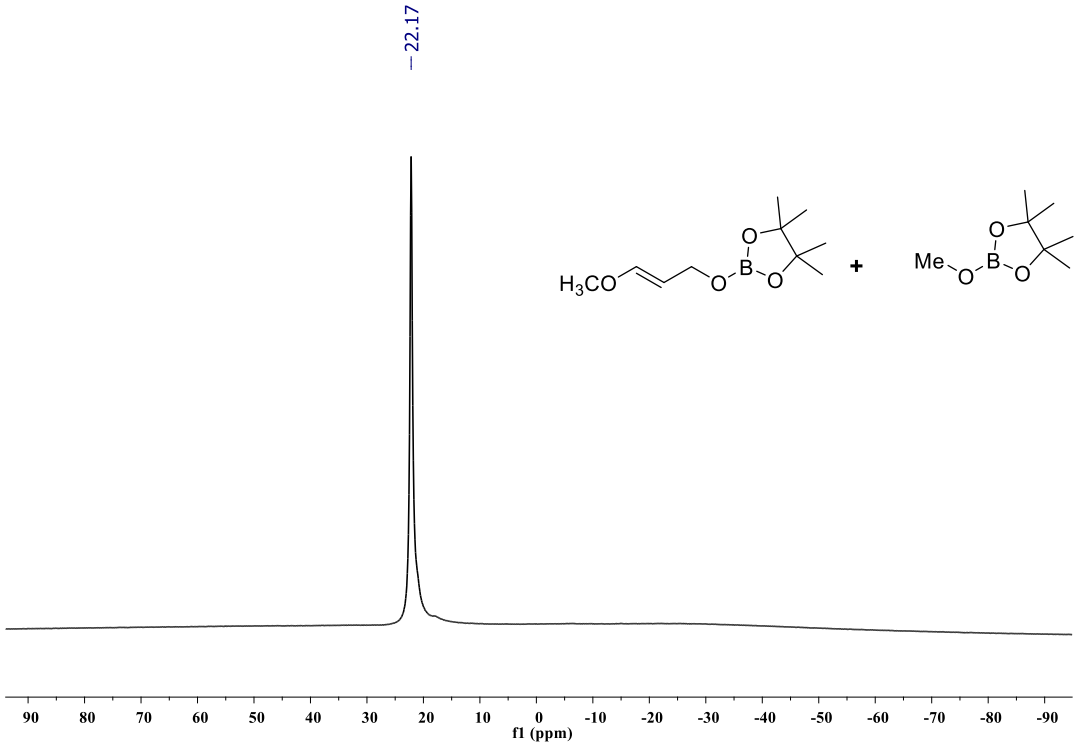


Figure S44: ^{11}B NMR spectrum of compounds **2n** and MeOBpin (128 MHz, $CDCl_3$, 25 ^{o}C)

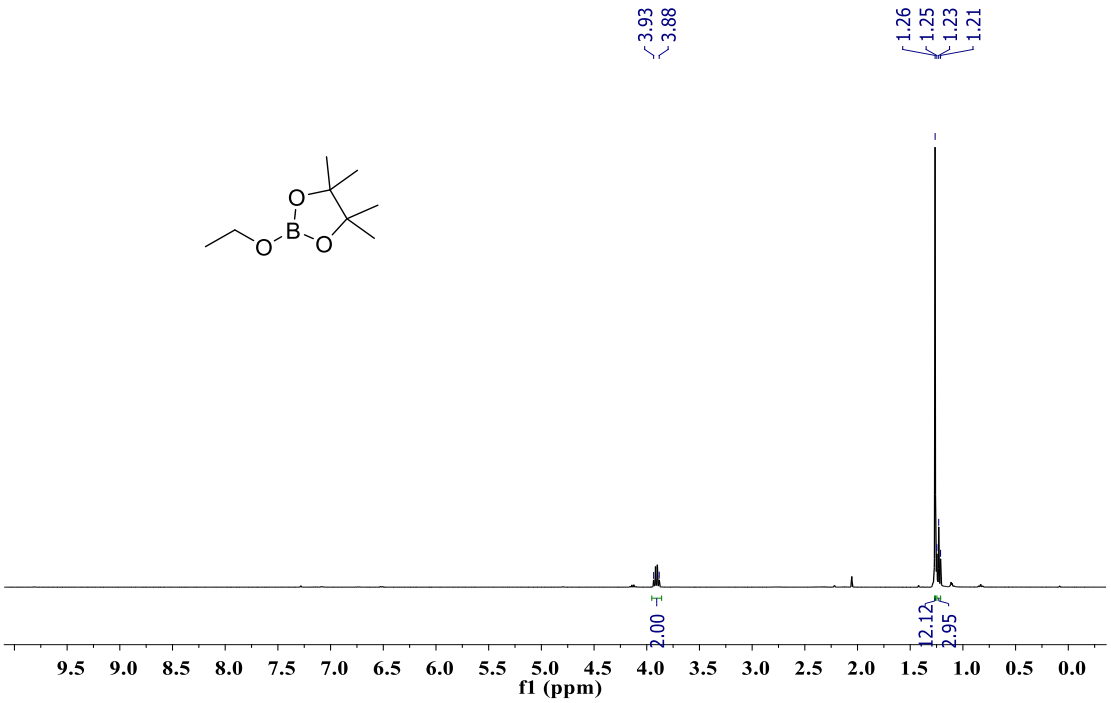


Figure S45: ^{1}H NMR spectrum of compound **2o** (400 MHz, $CDCl_3$, 25 ^{o}C)

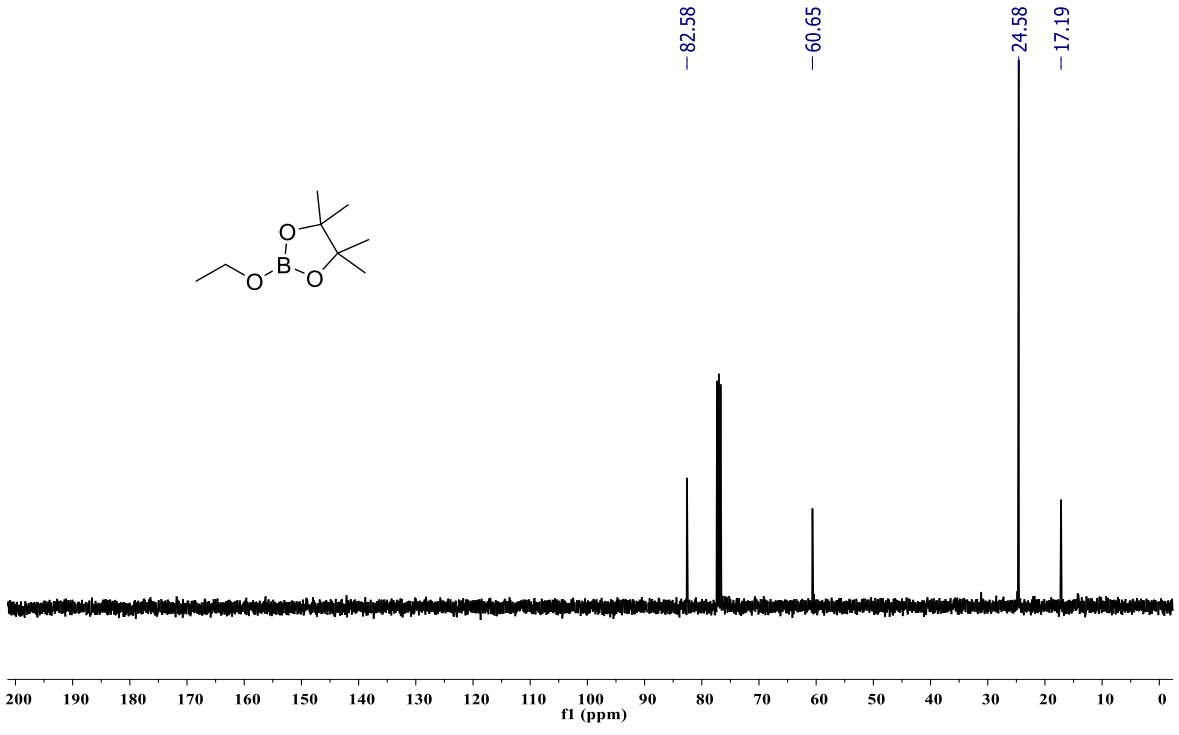


Figure S46: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2o** (101 MHz, $CDCl_3$, 25 ^{o}C)

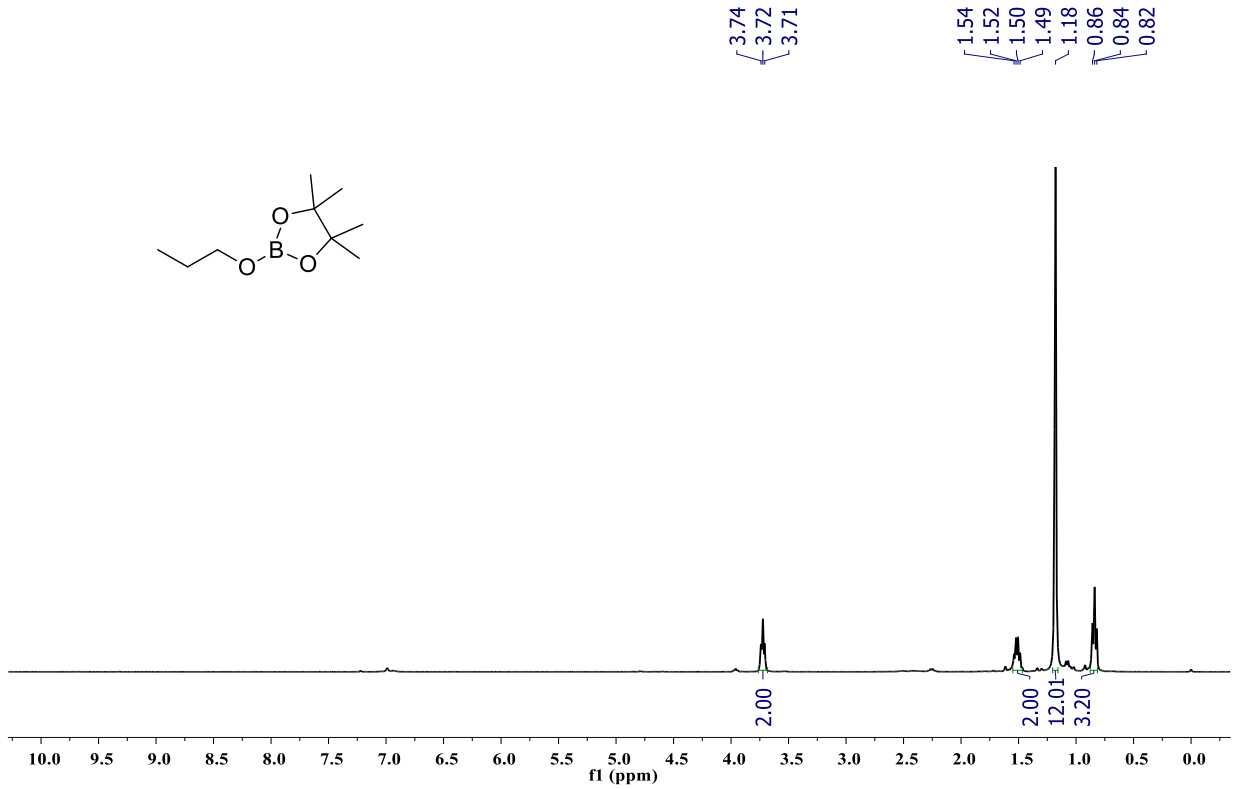


Figure S47: ^{1}H NMR spectrum of compound **2p** (400 MHz, $CDCl_3$, 25 ^{o}C)

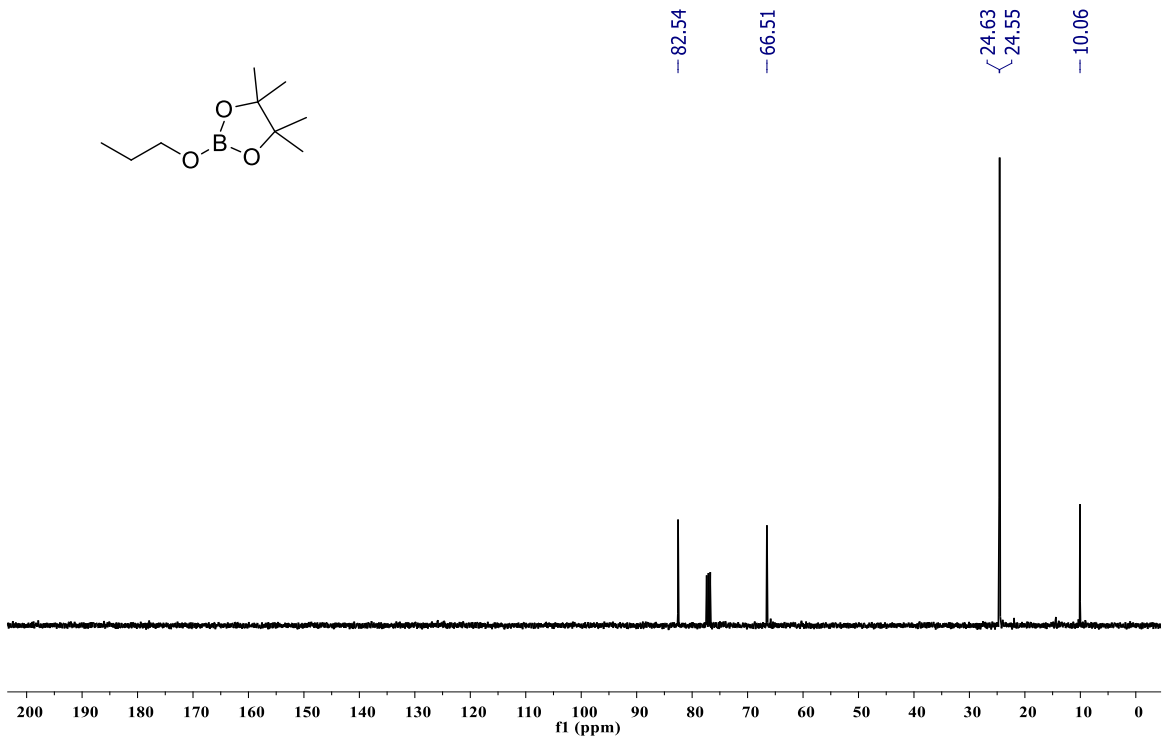


Figure S48: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2p** (101 MHz, $CDCl_3$, 25 ^{o}C)

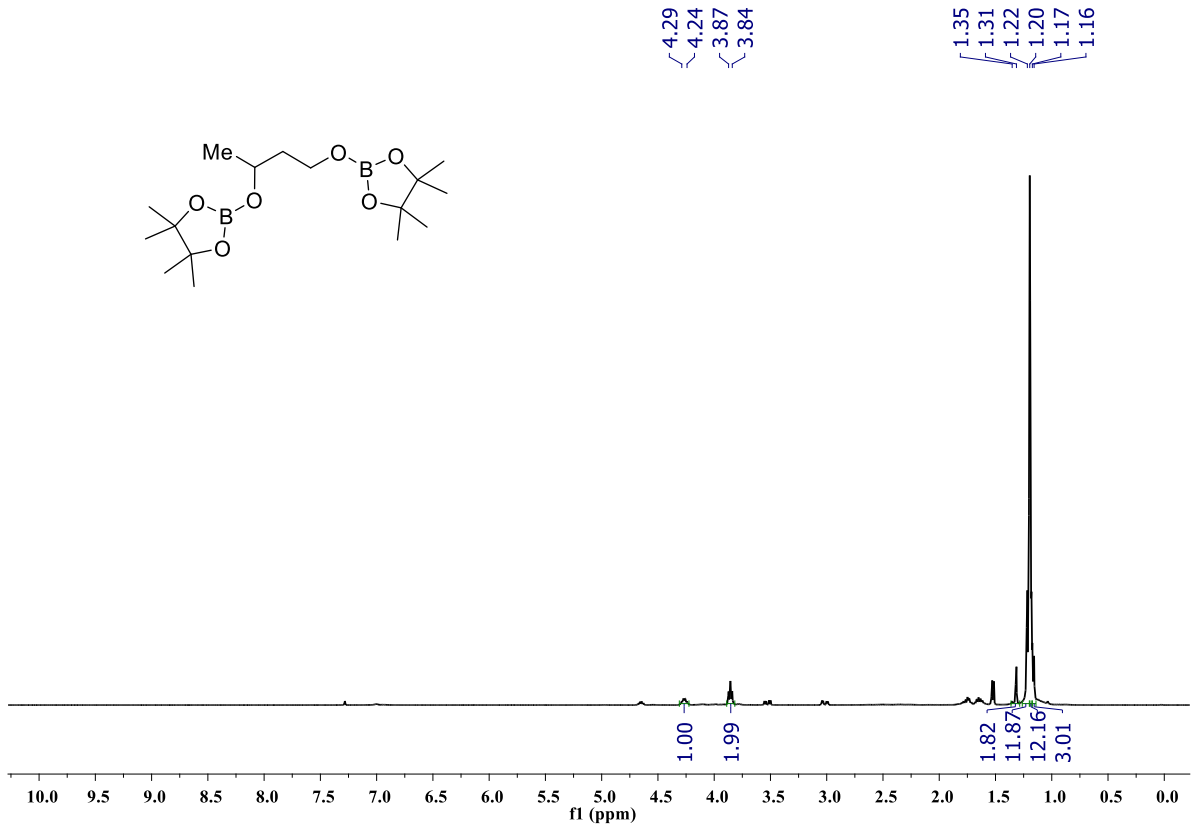


Figure S49: ^{1}H NMR spectrum of compound **2q** (400 MHz, $CDCl_3$, 25 °C)

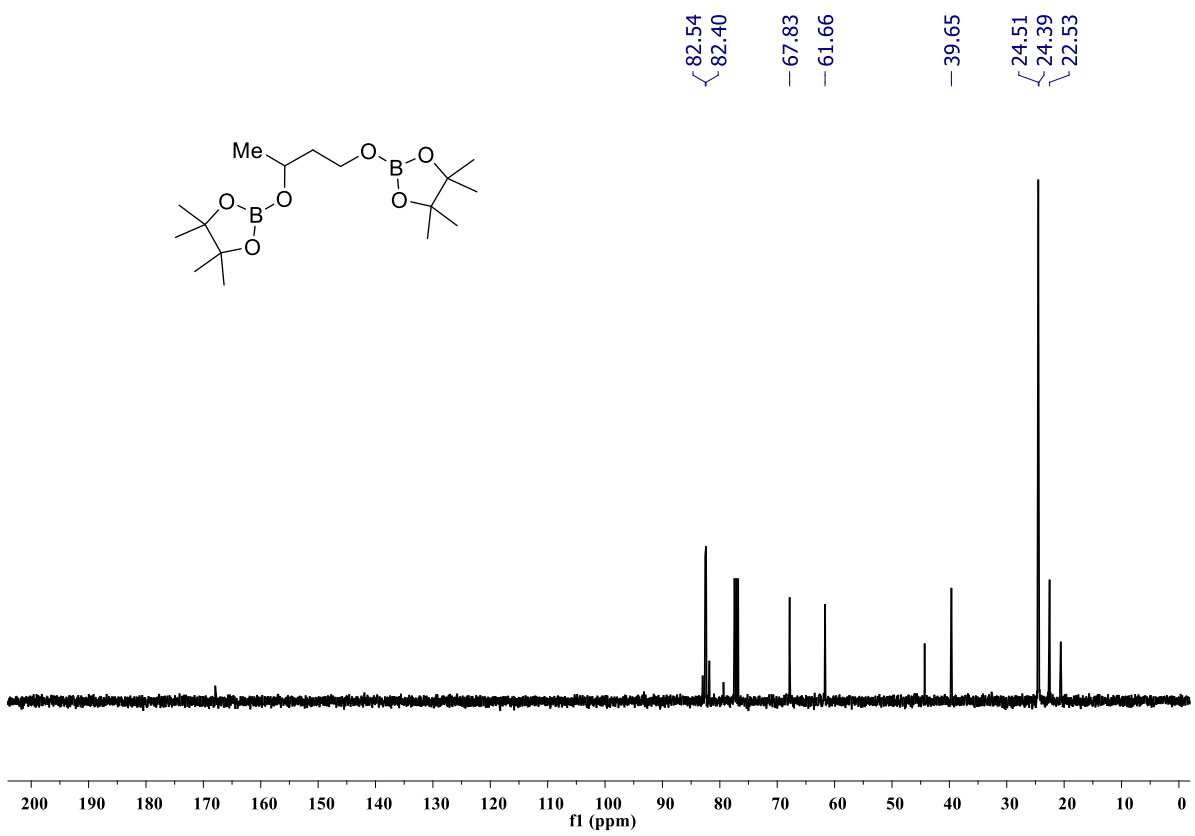


Figure S50: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2q** (101 MHz, $CDCl_3$, 25 °C)

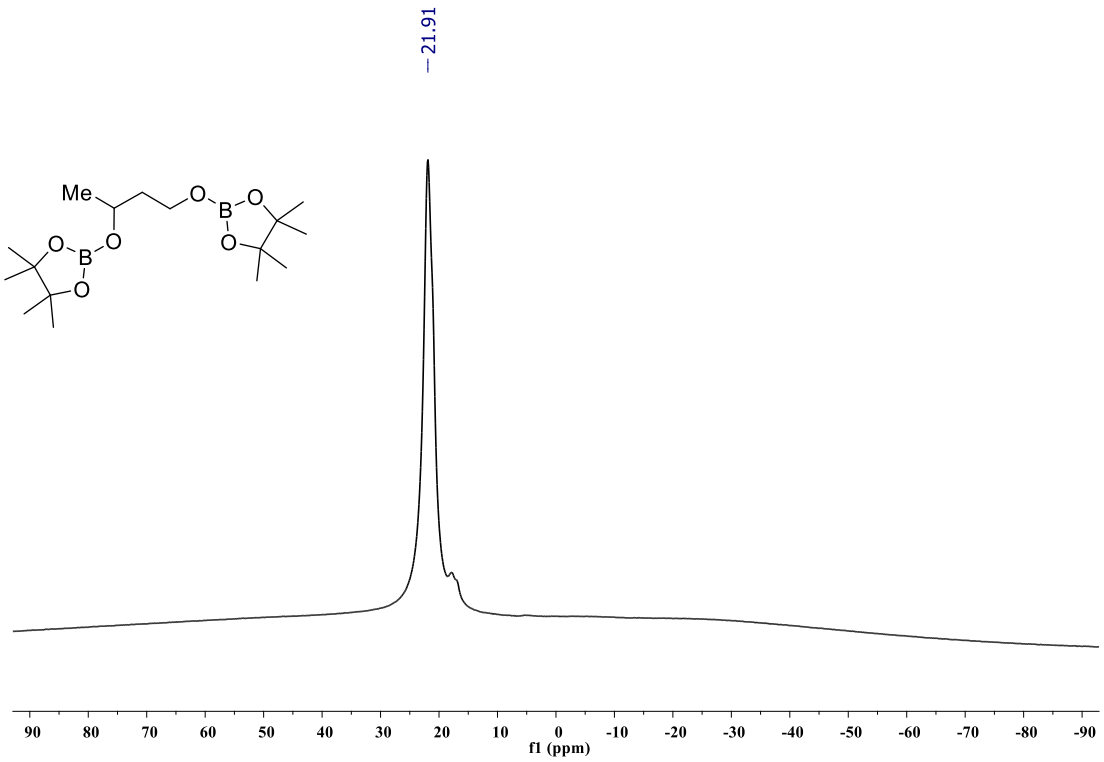


Figure S51: ^{11}B NMR spectrum of compound **2q** (128 MHz, $CDCl_3$, 25 ^{o}C)

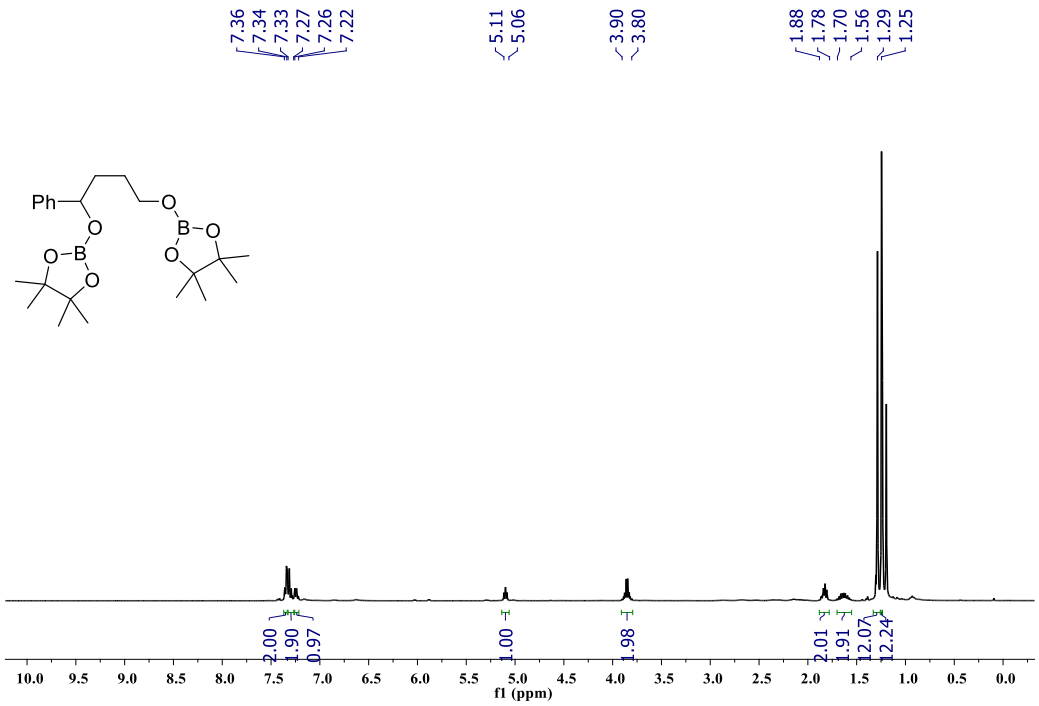


Figure S52: ^{1}H NMR spectrum of compound **2r** (400 MHz, $CDCl_3$, 25 ^{o}C)

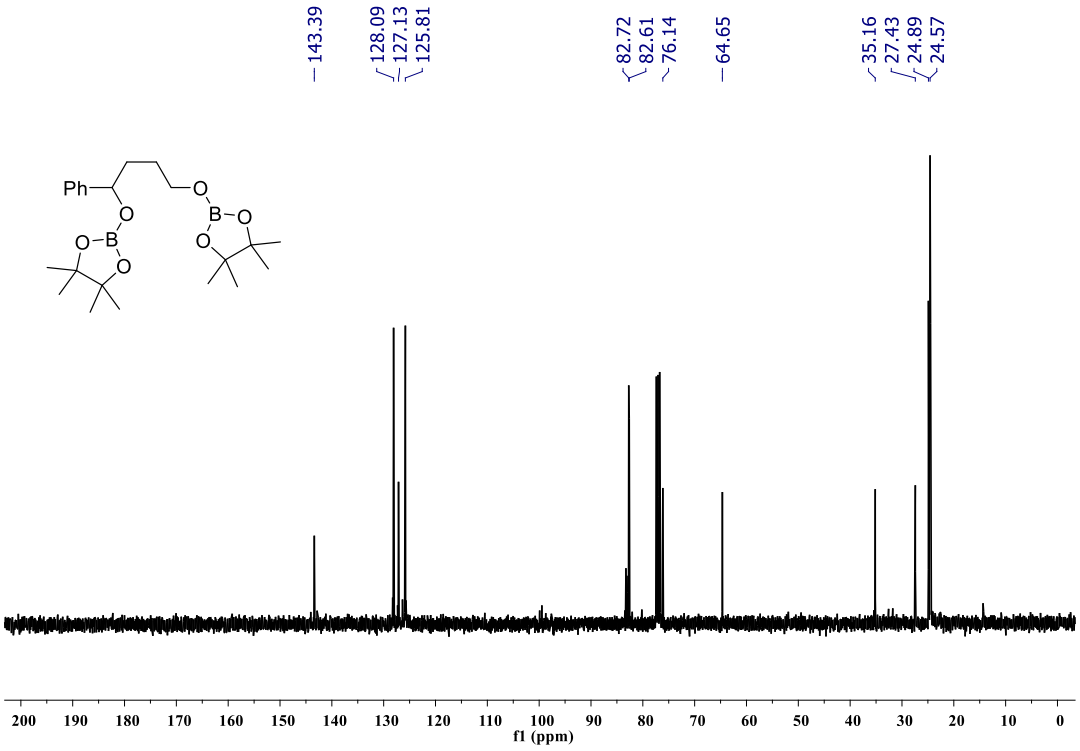


Figure S53: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2r** (101 MHz, $CDCl_3$, 25 °C)

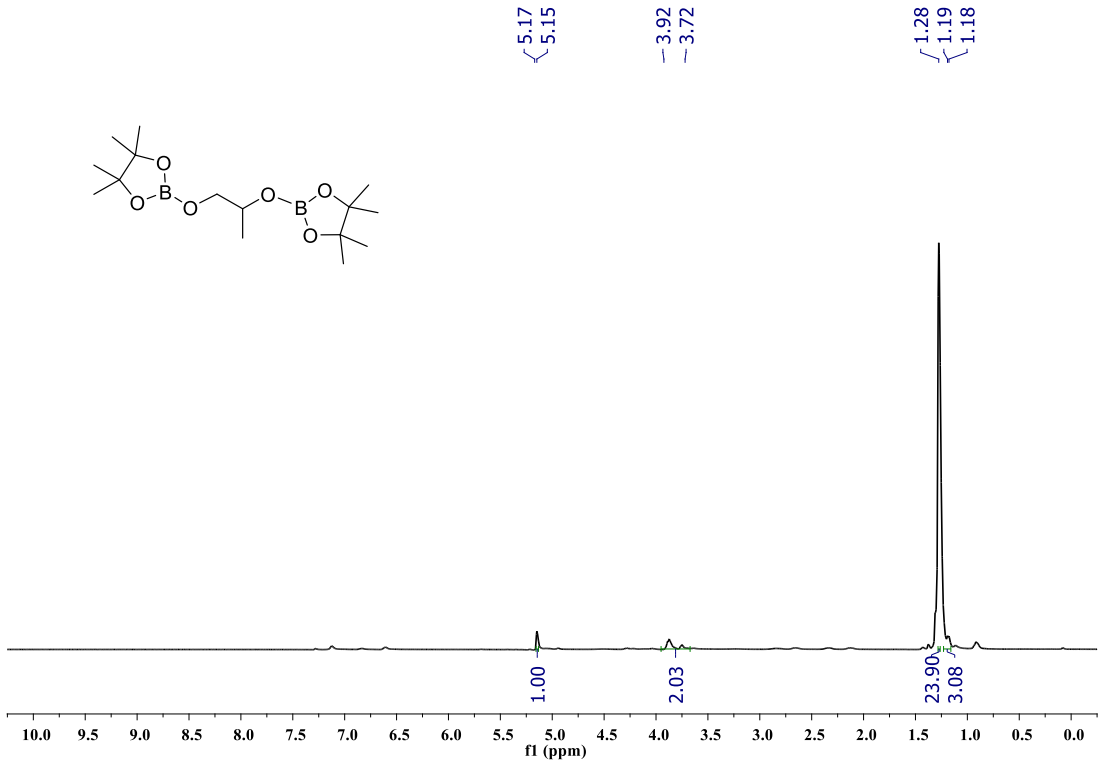


Figure S54: ^{1}H NMR spectrum of compound **2s** (400 MHz, $CDCl_3$, 25 °C)

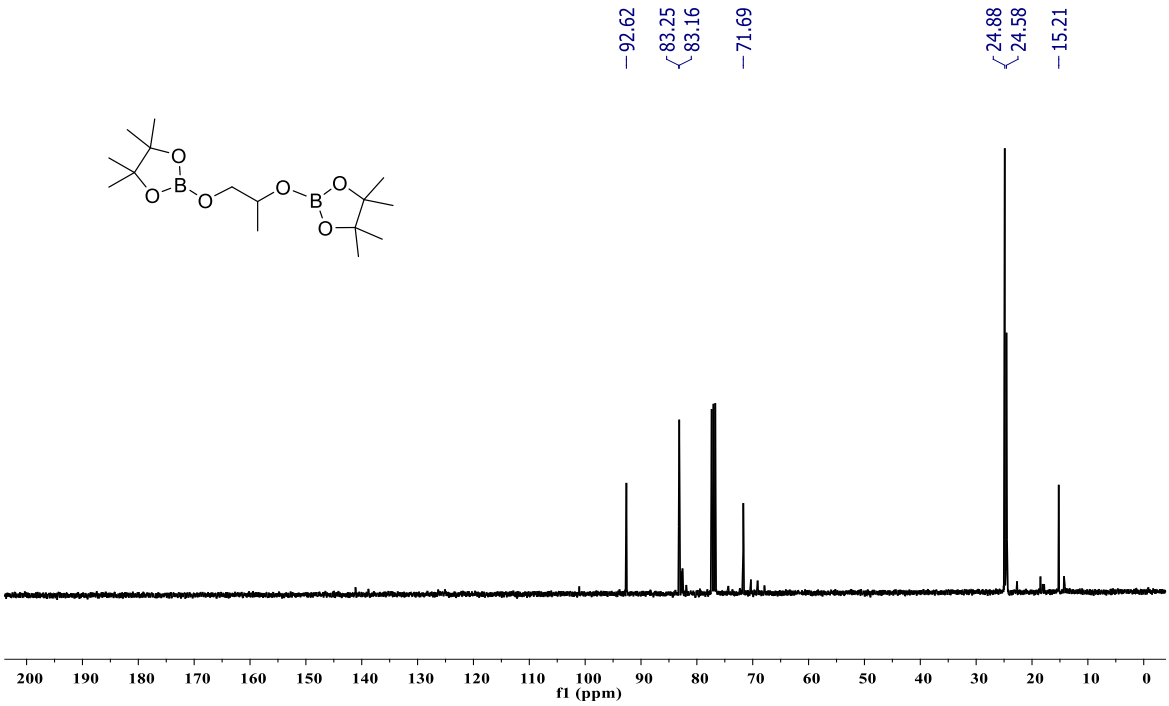


Figure S55: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2s** (101 MHz, $CDCl_3$, 25 °C)

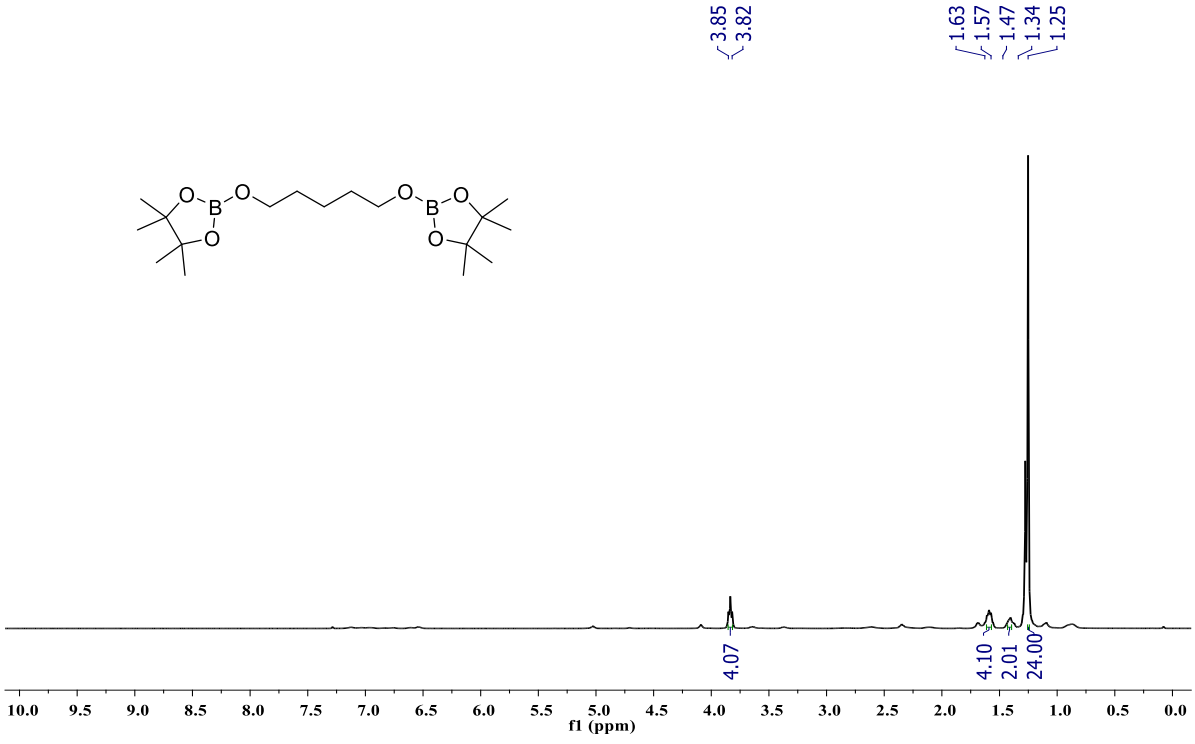


Figure S56: ^{1}H NMR spectrum of compound **2t** (400 MHz, $CDCl_3$, 25 °C)

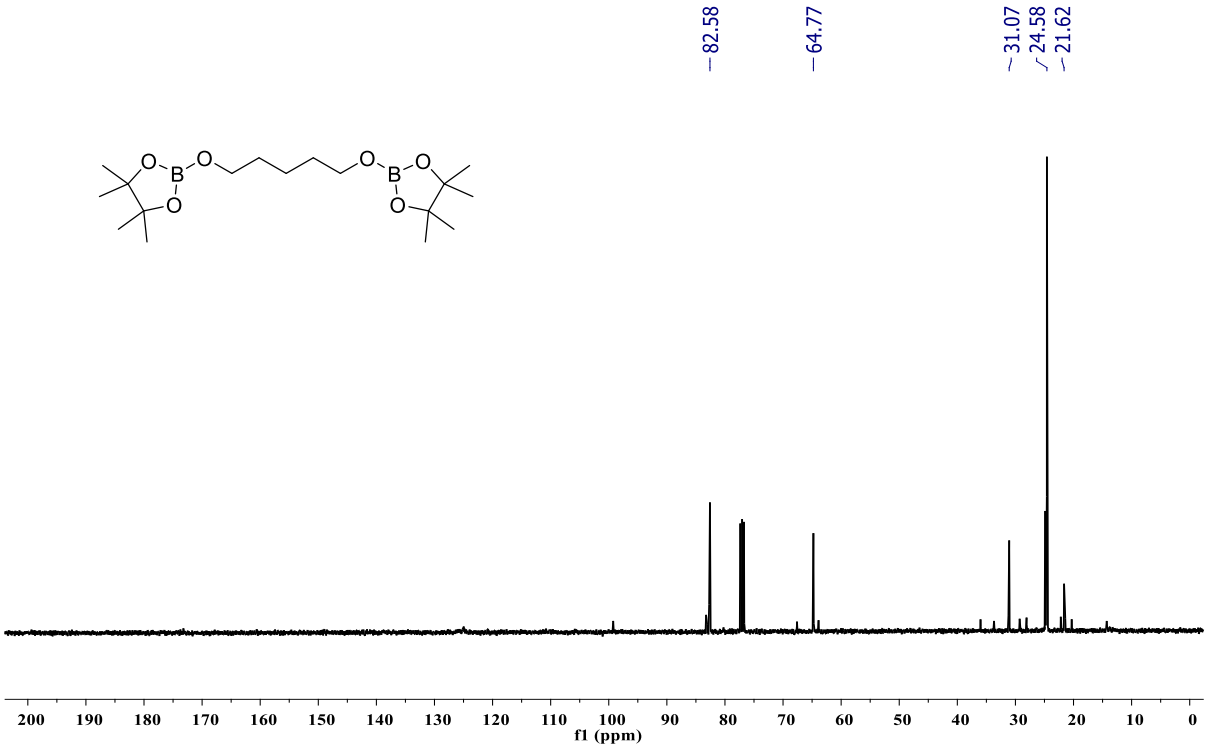


Figure S57: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2t** (101 MHz, $CDCl_3$, 25 °C)

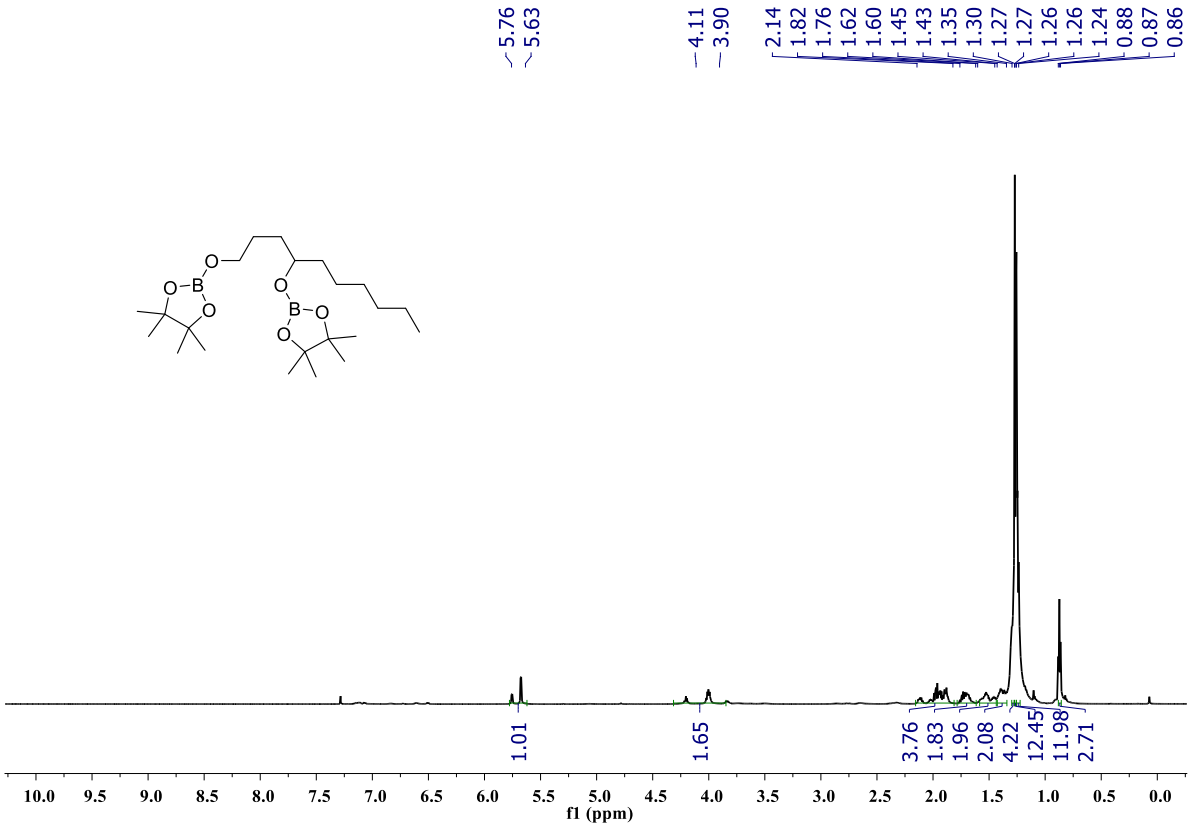


Figure S58: ^{1}H NMR spectrum of compound **2u** (400 MHz, $CDCl_3$, 25 °C)

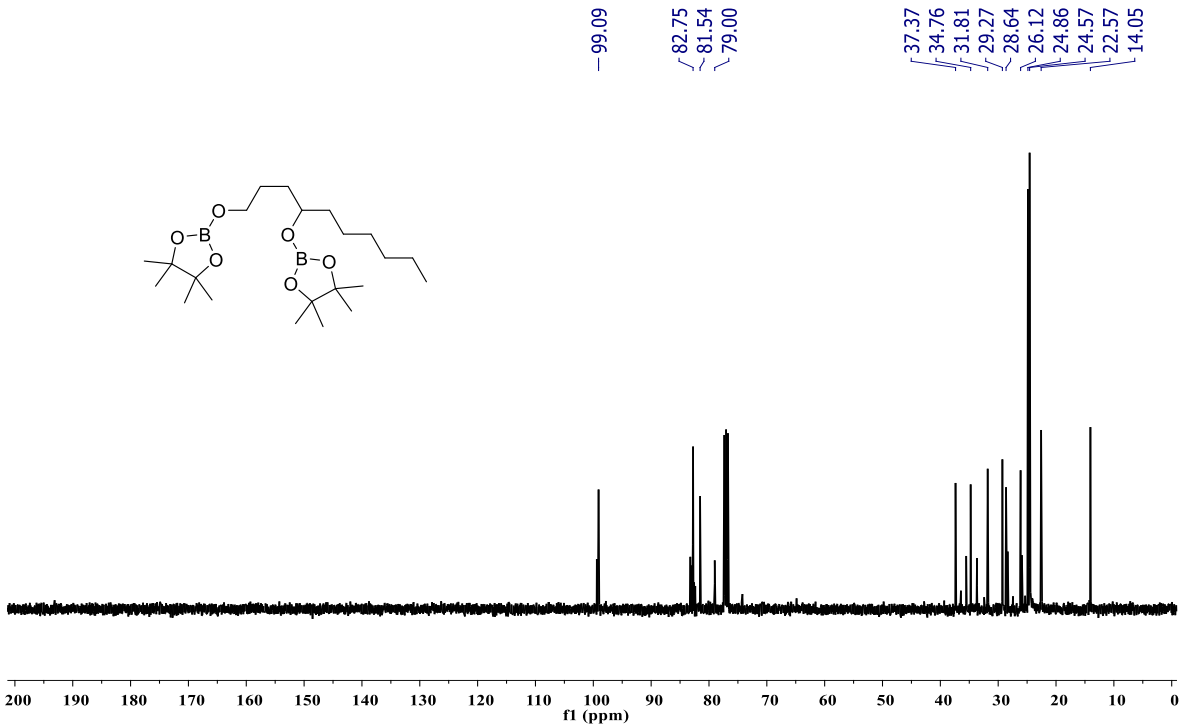


Figure S59: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2u** (101 MHz, $CDCl_3$, 25 °C)

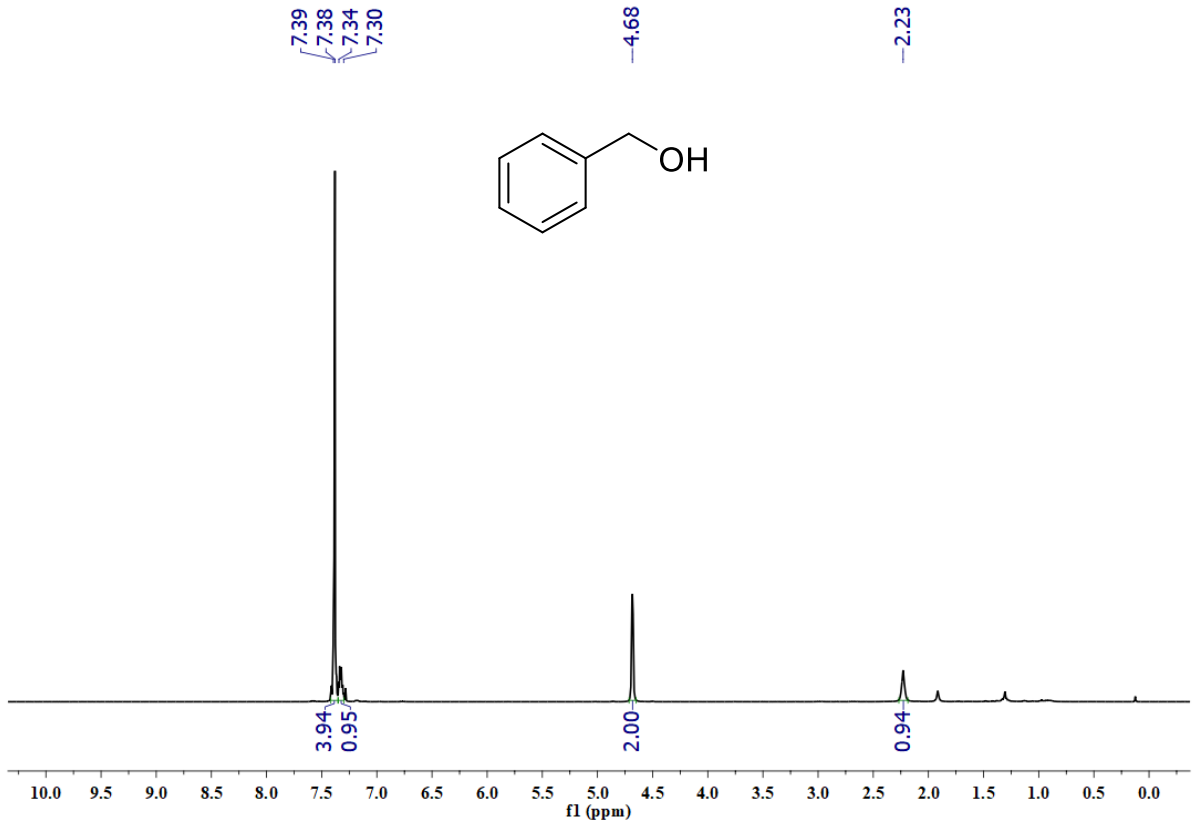


Figure S60: ^{1}H NMR spectrum of compound **2a'** (400 MHz, $CDCl_3$, 25 °C)

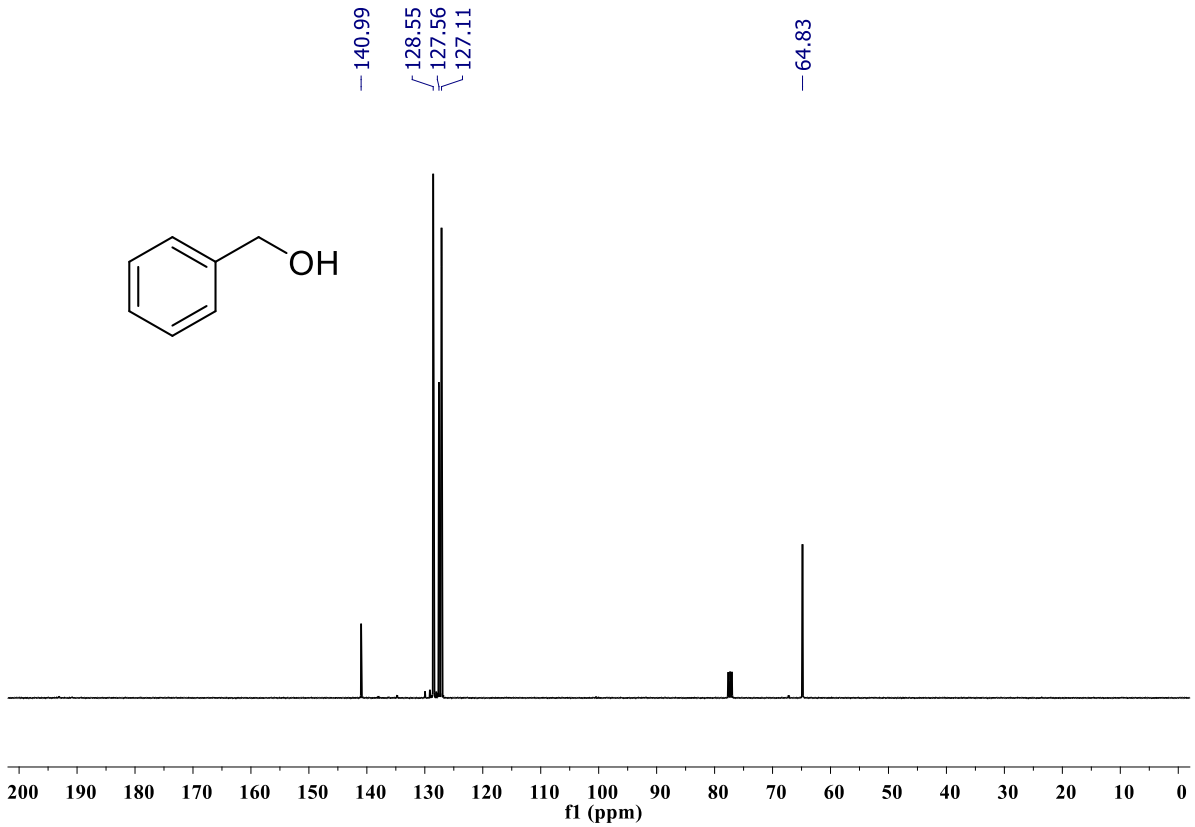


Figure S61: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2a'** (101 MHz, $CDCl_3$, 25 °C)

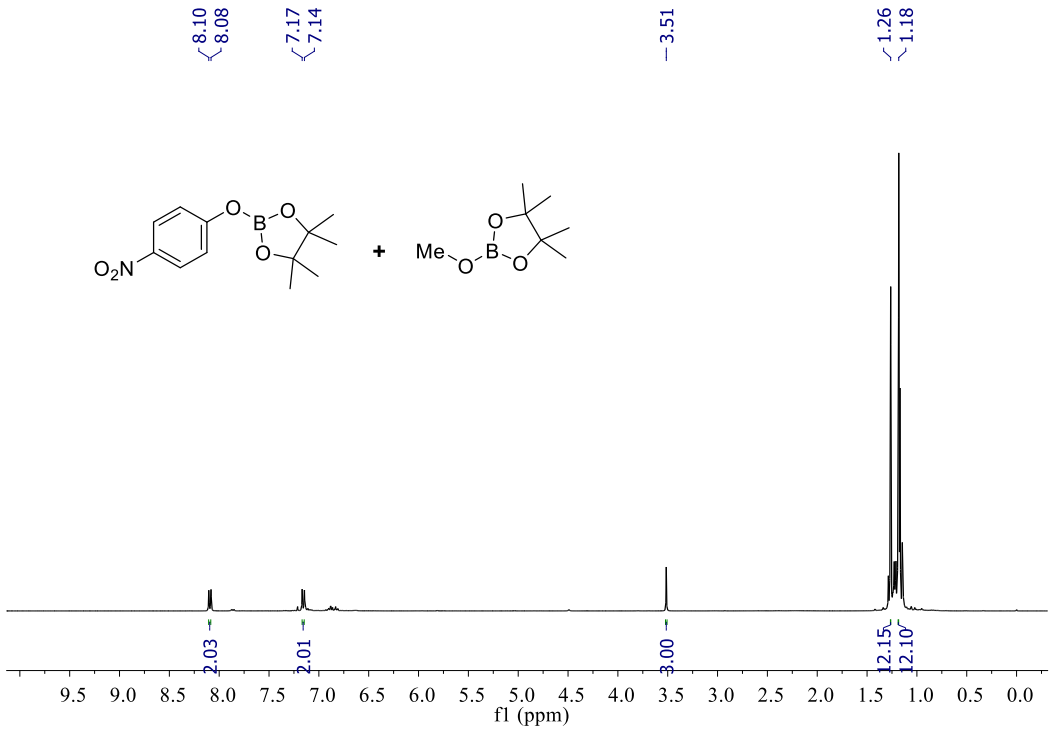


Figure S62: ^{1}H NMR spectrum of compounds **4a** and MeOBpin (400 MHz, $CDCl_3$, 25 °C)

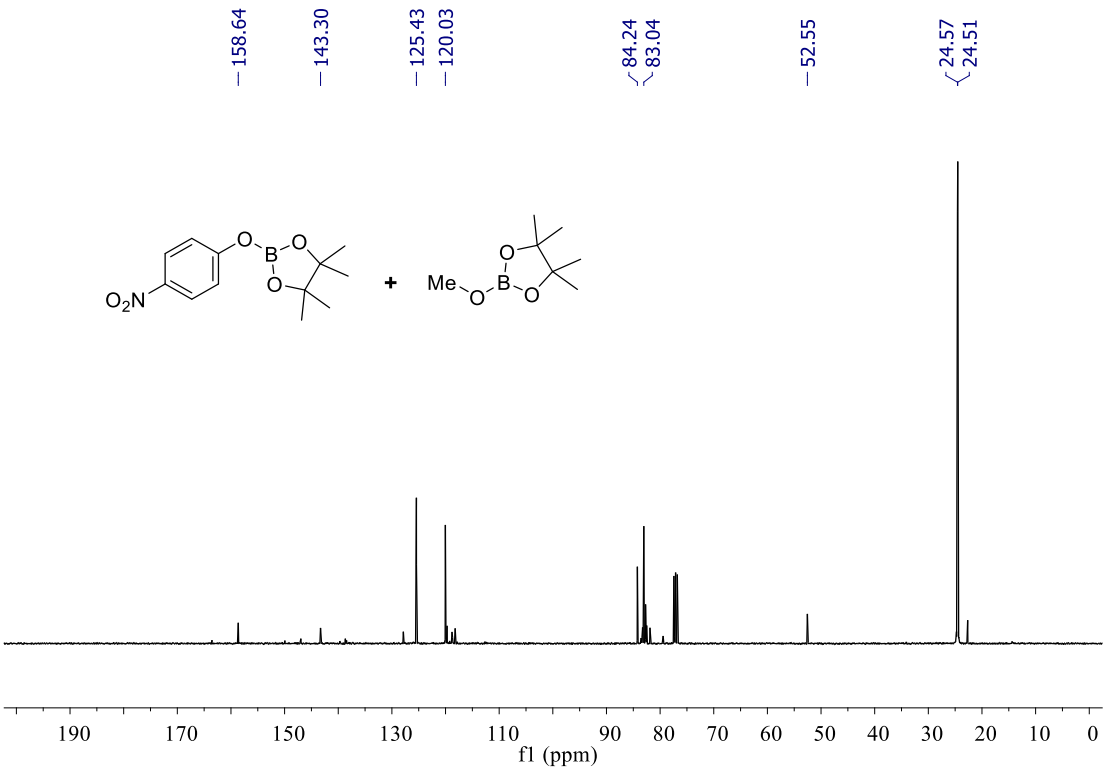


Figure S63: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **4a** and MeOBpin (101 MHz, $CDCl_3$, 25 ^{o}C)

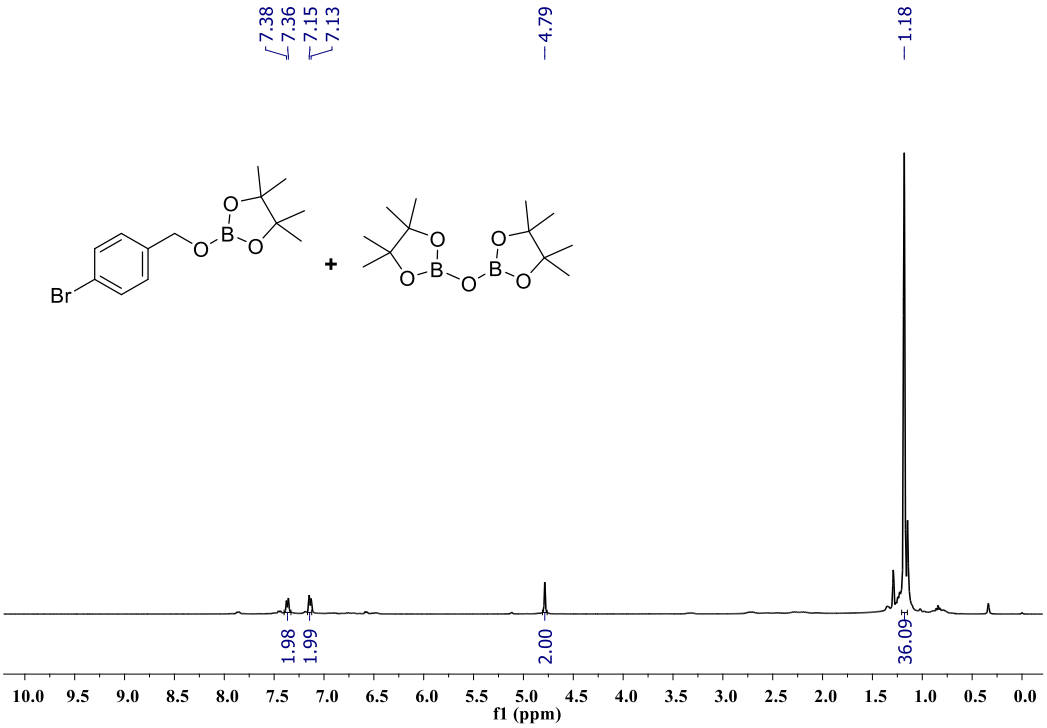


Figure S64: ^{1}H NMR spectrum of compounds **6a** and $(Bpin)_2O$ (400 MHz, $CDCl_3$, 25 ^{o}C)

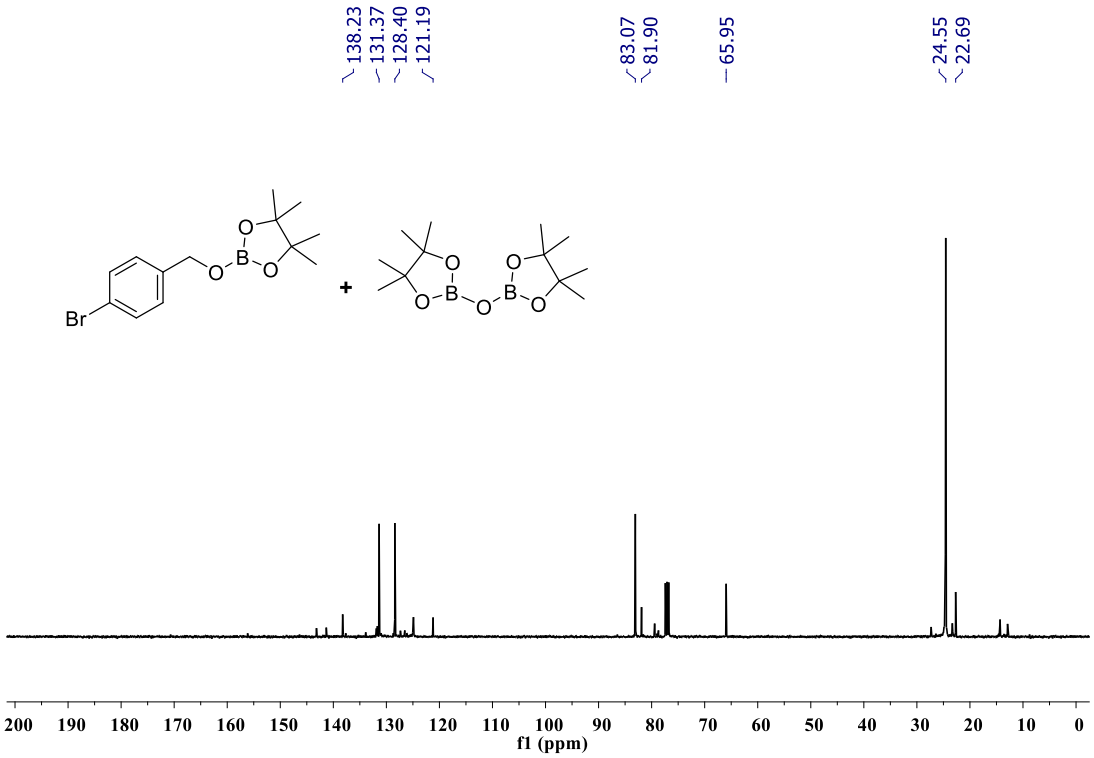


Figure S65: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **6a** and $(Bpin)_2O$ (101 MHz, $CDCl_3$, 25 ^{o}C)

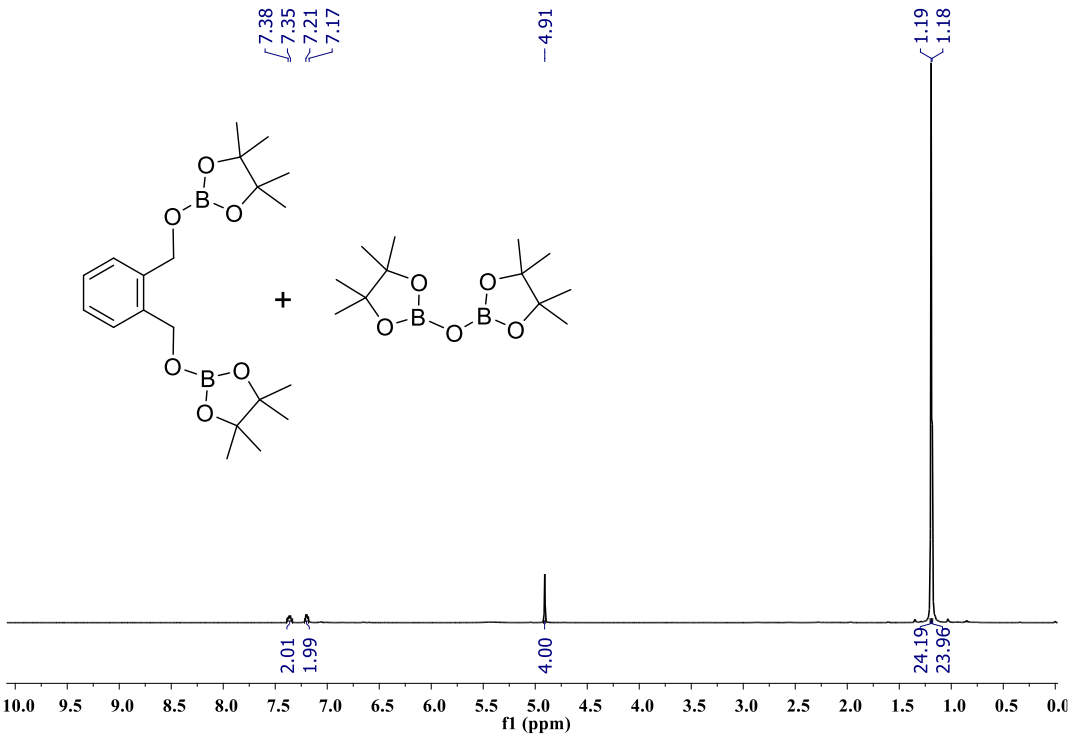


Figure S66: ^{1}H NMR spectrum of compounds **8a** and $(Bpin)_2O$ (400 MHz, $CDCl_3$, 25 ^{o}C)

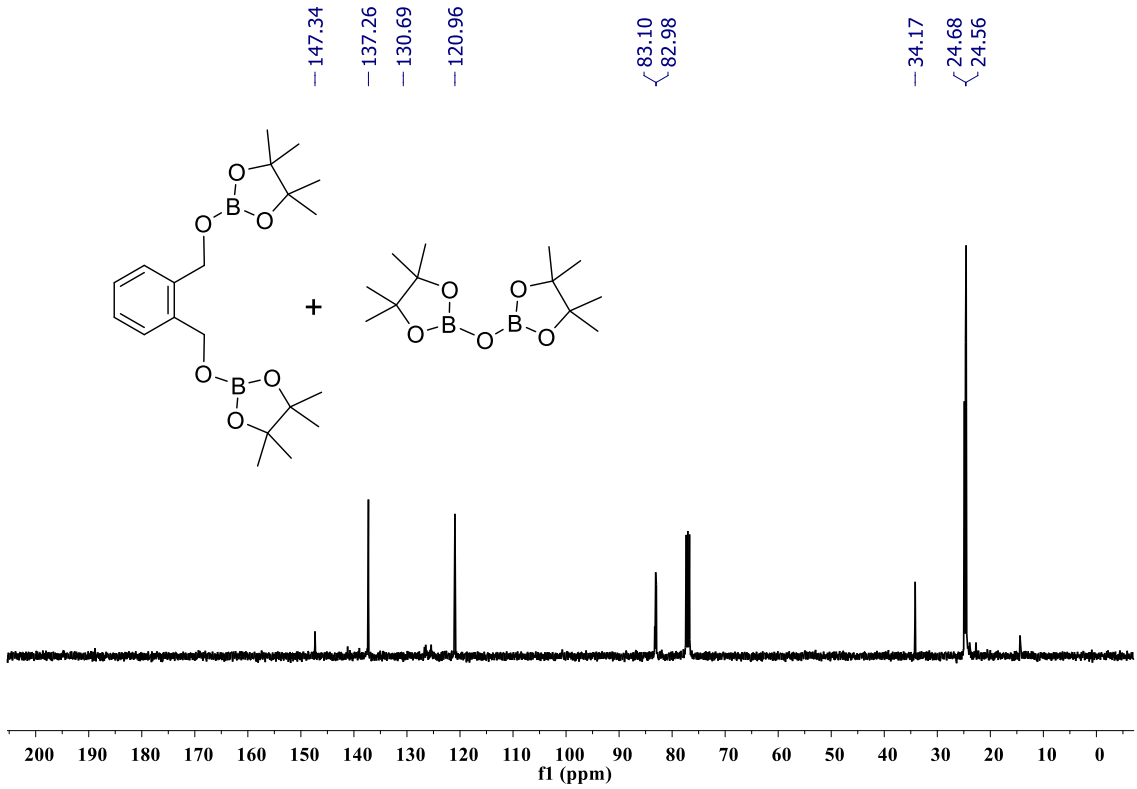


Figure S67: $^{13}C\{^{1}H\}$ NMR spectrum of compounds **8a** and $(Bpin)_2O$ (101 MHz, $CDCl_3$, 25 ^{o}C)

X-ray Crystallographic Data of Int A1'

The compound Int A1' single crystals were crystallized from benzene at rt as colorless blocks after 1 d. Compound Int A1' crystal data was collected on a Rigaku Oxford diffractometer at 100 K. The crystal data of compounds **Int A1'** is collected on a Rigaku Oxford diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å) at 100 K. Selected data collection parameters and other crystallographic results are summarized in Table S1. The structure was determined using direct methods employed in *ShelXT,*[10] *OleX*,[11,] and refinement was carried out using least-square minimization implemented in *ShelXL*.[12] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were fixed geometrically in idealized positions and were refined using a riding model.

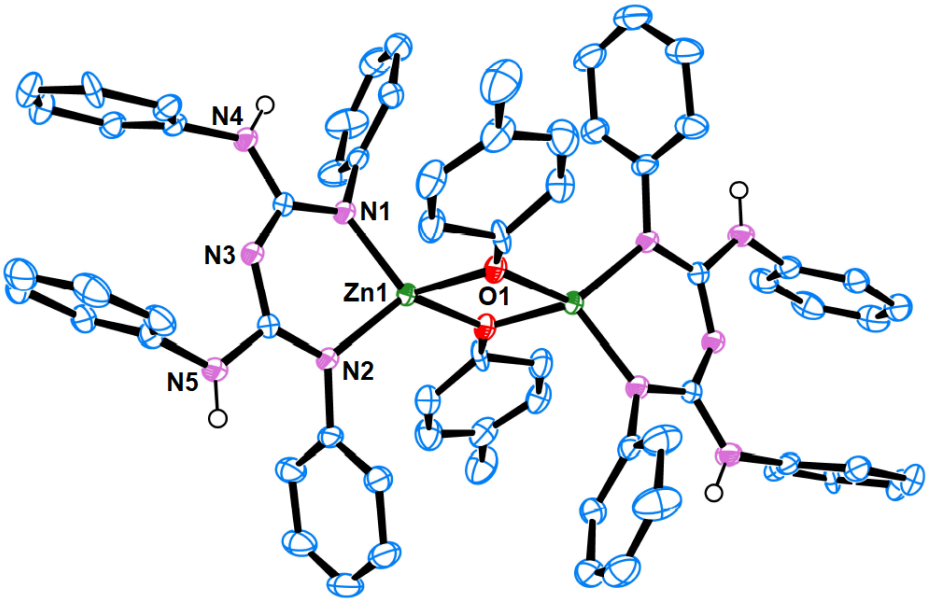


Figure 68. Molecular structure of **Int A1'**. The thermal ellipsoids are shown at 50% probability, and all the hydrogen atoms except those bound to nitrogen atoms and ethyl groups have been removed for clarity. Selected bond lengths (Å) and angles (deg), For **Int A1'**: Zn1-Zn1' 3.0844(7), Zn1-N1 1.974(2), Zn1-N2 1.965(2), Zn1-O1 1.972(2), Zn1-O1' 2.040(2); N1-Zn1-N2 94.84(10), N1-Zn1-O1 124.04(10), N2-Zn1-O1 126.95(10), O1-Zn1-O1' 79.49(10), Zn1-O1-Zn1' 100.51(10).

Table S1. Crystallographic Data and Refinement Parameters for Compound **Int A1'**.

Compound	**Int A1'**
Empirical Formula	$C_{98}H_{122}N_{10}O_2Zn_2$
CCDC	2245811
Molecular mass	1602.79
Temperature (K)	100.00(10)
Wavelength (Å)	1.54184
Size(mm)	0.2×0.18×0.17
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	15.62480(10)
b (Å)	14.65430(10)
c (Å)	19.2404(2)
α (deg)°	90
β (deg)°	99.8730(10)
γ (deg)°	90
Volume ($Å^3$)	4340.24(6)
Z	2
Calculated density (g/cm^3)	1.226
Absorption coefficient (mm^{-1})	1.097
F(000)	1712.0
Theta range for data collection (deg)°	6.748 to 151.398
Limiting indices	$-18 \le h \le 19$, $-17 \le k \le 18$, $-24 \le l \le 17$
Reflections collected	38610
Independent reflections	8828 [R_{int} = 0.0455, R_{sigma} = 0.0532]
Completeness to theta	99 %
Absorption correction	Empirical
Data/restraints/parameters	8828 / 2 / 508
Goodness – of–fit on F ^ 2	1.071
Final R indices [I>2 sigma(I)]	R_1 = 0.0688, wR_2 = 0.1647

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