Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Regio-divergent Hydroboration of Terminal Allenes Controlled by Nickel and Cobalt Catalysts

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Contents

1. General methods and materials

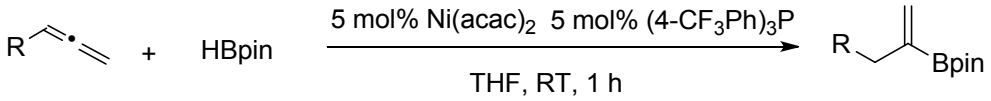
The liquid-state NMR was recorded on a 400 or 500 MHz spectrometer. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.28 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm). All ^{13}C NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. The solid-state ^{13}C CP/MAS NMR was performed on a VARIAN Infinity-plus spectrometer. Mass spectroscopy: We were grateful to the assistance of the Department of Chemistry, Xiamen University in obtaining the MS data.

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. The allenes[1,2,3] were prepared according to corresponding literature procedures.

References:

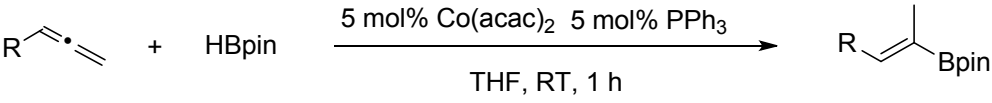
[1] J. Kuang and S. Ma, *J. Org. Chem*. **2009**, 74, 1763-1765.
[2] J. Kuang and S. Ma, *J. Am. Chem. Soc.* **2010**, 132, 1786-1787.
[3] X. Tang, Y. Han, and S. Ma, *Org. Lett*. **2015**, 17, 1176-1179.

2. General procedure for hydroboration of allenes



1 **2** **3**

In a nitrogen filled schlenk tube, $Ni(acac)_2$ (3.8 mg, 0.015 mmol), $(4\text{-}CF_3Ph)_3P$ (7 mg, 0.015 mmol) were added to THF (1 mL), followed by the addition of allenes (0.3 mmol) and HBpin (0.36 mmol) in THF (1 mL) under nitrogen. The reaction mixture was stirred at 25 ^{o}C. When the reaction was completed (1 h, monitored by TLC), the solvent was removed in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product.

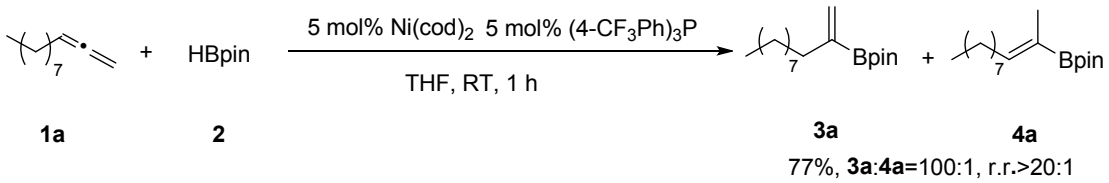


1 **2** **4**

In a nitrogen filled schlenk tube, $Co(acac)_2$ (3.8 mg, 0.015 mmol), PPh_3 (3.8 mg, 0.015 mmol) were added to THF (1 mL), followed by the addition of allenes (0.3 mmol) and HBpin (0.36 mmol) in THF (1 mL) under nitrogen. The reaction mixture was stirred at 25 ^{o}C. When the reaction was completed (1 h, monitored by TLC), the solvent was removed in vacuum. The crude product was

purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product.

3. Procedure for control experiment with $Ni(cod)_2$



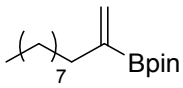
1a **2** **3a** **4a**

77%, **3a**:**4a**=100:1, r.r.>20:1

In a nitrogen filled schlenk tube, $Ni(cod)_2$ (4.2 mg, 0.015 mmol), $(4\text{-}CF_3Ph)_3P$ (7 mg, 0.015 mmol) were added to THF (1 mL), followed by the addition of allenes (0.3 mmol) and HBpin (0.36 mmol) in THF (1 mL) under nitrogen. The reaction mixture was stirred at 25 °C. When the reaction was completed (0.5-5 h, monitored by TLC), the solvent was removed in vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product with the yield of 77% and selectivity of >20:1.

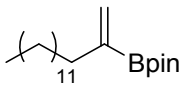
4. Analytical data for compounds

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



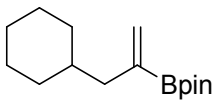
colorless liquid (80%, 67.2mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.76 (d, *J* = 3.54 Hz, 1H), 5.60 (d, apparent s, 1H), 2.15 (t, *J* = 7.53 Hz, 2H), 1.28-1.27 (m, 26H), 0.89 (t, *J* = 7.02 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 128.6, 83.3, 35.4, 31.9, 29.58, 29.57, 29.34, 29.28, 29.2, 24.7, 22.7, 14.1. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{17}H_{33}O_2BNa^+$ $[M+Na]^+$: 303.2471, found: 303.2479.

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



colorless liquid (70%, 70.6mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.76 (d, *J* = 3.53 Hz, 1H), 5.60 (d, apparent s, 1H), 2.15 (t, *J* = 7.44 Hz, 2H), 1.28-1.27 (m, 34H), 0.90 (t, *J* = 7.09 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 128.6, 83.3, 35.3, 31.9, 29.69, 29.65, 29.62, 29.56, 29.4, 29.3, 29.2, 24.7, 22.7, 14.1. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{21}H_{41}O_2BNa^+$ $[M+Na]^+$: 359.3097, found: 359.3090.

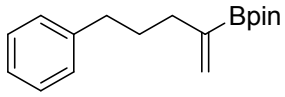
2-(3-cyclohexylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)



colorless liquid (72%, 54.1mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.79 (d, *J* = 3.71 Hz, 1H), 5.55 (d, *J* = 3.29 Hz, 1H), 2.05 (d, *J* = 7.03 Hz, 2H), 1.70-1.66 (m, 5H), 1.44-1.38 (m, 1H), 1.27 (s, 12H),

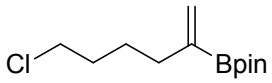
1.25-1.21 (m, 3H), 0.90-0.82 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 129.9, 83.3, 43.3, 37.7, 33.2, 26.7, 26.4, 24.7. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{15}H_{27}O_2BNa^+$ $[M+Na]^+$: 273.2002, found: 273.2008. Characterization data matched with those reported in the literature.[4]

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



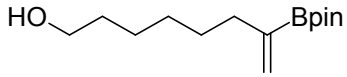
colorless liquid (79%, 64.5mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.22-7.18 (m, 3H), 5.82 (d, *J* = 3.43 Hz, 1H), 5.65 (d, apparent s, 1H), 2.64 (t, *J* = 7.79 Hz, 2H), 2.24 (t, *J* = 7.55 Hz, 2H), 1.82-1.76 (m, 2H), 1.29 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.8, 129.3, 128.4, 128.2, 125.5, 83.3, 35.5, 35.1, 30.9, 24.7. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{17}H_{25}O_2BNa^+$ $[M+Na]^+$: 295.1845, found: 295.1851. Characterization data matched with those reported in the literature.[4]

2-(6-chlorohex-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)



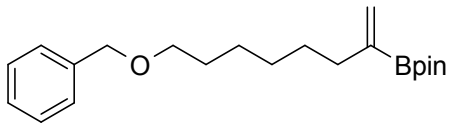
colorless liquid (74%, 54.2mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.80 (d, *J* = 3.33 Hz, 1H), 5.62 (d, apparent s, 1H), 3.55 (t, *J* = 6.78 Hz, 2H), 2.19 (t, *J* = 7.55 Hz, 2H), 1.80-1,77 (m, 2H), 1.61-1.57 (m, 2H), 1.28 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 129.4, 83.4, 45.0, 34.4, 32.2, 26.4, 24.7. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{12}H_{22}ClO_2BNa^+$ $[M+Na]^+$: 267.1299, found: 267.1292.

7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-ol (3f)



colorless liquid (70%, 53.4mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.77 (d, *J* = 3.55 Hz, 1H), 5.61 (d, apparent s, 1H), 3.65 (t, *J* = 6.65 Hz, 2H), 2.16 (t, *J* = 7.63 Hz, 2H), 1.60-1.55 (m, 2H), 1.46-1.41 (m, 2H), 1.37-1.33 (m, 4H), 1.28 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 128.8, 83.3, 63.1, 35.2, 32.7, 29.1, 29.0, 25.6, 24.7. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{17}H_{25}O_2BNa^+$ $[M+Na]^+$: 277.1951, found: 277.1956.

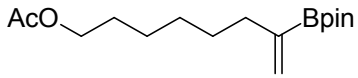
2-(8-(benzyloxy)oct-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)



colorless liquid (69%, 71.2mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 5H), 5.77 (d, *J* = 3.10 Hz, 1H), 5.60 (d, apparent s, 1H), 4.52 (s, 2H), 3.48 (t, *J* = 6.59 Hz, 2H), 2.15 (t, *J* = 7.49 Hz, 2H), 1.65-1.62 (m, 2H), 146-1.38 (m, 6H), 1.28 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 128.7, 128.3, 127.6, 127.44, 127.42, 83.3, 72.8, 70.5, 35.3, 29.7, 29.14, 29.10, 26.1, 24.7. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z

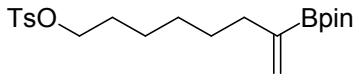
Calculated for $C_{21}H_{33}O_3BNa^+$ [M+Na]$^+$: 367.2420, found: 367.2427.

4,4,5,5-tetramethyl-2-(8-(prop-1-en-2-yloxy)oct-1-en-2-yl)-1,3,2-dioxaborolane (3h)



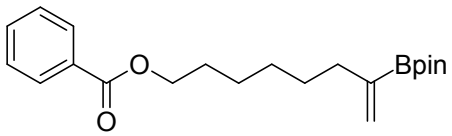
colorless liquid (72%, 63.9mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.77 (d, *J* = 3.31 Hz, 1H), 5.60 (d, apparent s, 1H), 4.06 (t, *J* = 6.75 Hz, 2H), 2.15 (t, *J* = 7.32 Hz, 2H), 2.05 (s, 3H), 1.65-1,61 (m, 2H), 1.45-1.40 (m, 2H), 1.37-1.32 (m, 4H), 1.28 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.2, 128.8, 83.3, 64.7, 35.2, 29.0, 28.8, 28.5, 25.8, 24.7, 21.0. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{16}H_{29}O_4BNa^+$ [M+Na]$^+$: 319.2057, found: 319.2051.

7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-yl 4-methylbenzenesulfonate (3i)



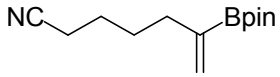
colorless liquid (77%, 94.3mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.24 Hz, 2H), 7.35 (d, *J* = 8.31 Hz, 2H)，5.76 (d, *J* = 3.49 Hz, 1H), 5.58 (d, apparent s, 1H), 4.03 (t, *J* = 6.56 Hz, 2H), 2.46 (s, 3H), 2.10 (t, *J* = 7.71 Hz, 2H), 1.67-1.61 (m, 4H), 1.39-1.34 (m, 4H), 1.27 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.6, 133.3, 129.8, 128.9, 127.9, 83.3, 70.7, 35.1, 28.9, 28.7, 28.5, 25.2, 24.7, 21.6. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{21}H_{33}O_5BSNa^+$ [M+Na]$^+$: 431.2039, found: 431.2033.

7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-yl benzoate (3j)



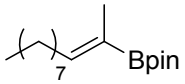
colorless liquid (68%, 75.9mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H), 7.59-7.54 (m, 1H), 7.47-7.43 (m, 2H), 5.78 (d, *J* = 3.46 Hz, 1H), 5.61 (d, apparent s, 1H), 4.33 (t, *J* = 6.65 Hz, 2H), 2.17 (t, *J* = 7.15 Hz, 2H), 1.82-1.75 (m, 2H), 1.51-1.41 (m, 6H), 1.28 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 132.7, 130.6, 129.5, 128.9, 128.3, 83.3, 65.1, 35.2, 29.0, 28.9, 28.7, 25.9, 24.7. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{22}H_{33}O_4BNa^+$ [M+Na]$^+$: 395.2370, found: 395.2377.

6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-enenitrile (3k)



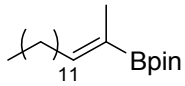
colorless liquid (73%, 51.5mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.80 (d, *J* = 3.12 Hz, 1H), 5.62 (d, apparent s, 1H), 2.35 (t, *J* = 7.05 Hz, 2H), 2.19 (t, *J* = 7.05 Hz, 2H), 1.69-1.58 (m, 4H), 1.28 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 129.9, 119.8, 83.5, 34.3, 28.1, 24.8, 24.7, 17.0. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{13}H_{22}NO_2BNa^+$ [M+Na]$^+$: 258.1641, found: 258.1632.

(Z)-4,4,5,5-tetramethyl-2-(undec-1-en-2-yl)-1,3,2-dioxaborolane (4a)



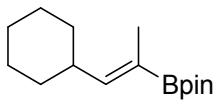
colorless liquid (78%, 65.5mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.33 (tq, apparent td, J_1 = 6.91 Hz, J_2 = 1.32 Hz, 1H), 2.15-2.10 (m, 2H), 1.69 (s, 3H), 1.28-1.27 (m, 24H), 0.89 (t, J = 7.19 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7, 83.0, 31.9, 29.53, 29.50, 29.3, 28.9, 28.7, 24.8, 22.7, 14.1, 13.8. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{17}H_{33}O_2BNa^+$ $[M+Na]^+$: 303.2471, found: 303.2465.

(Z)-4,4,5,5-tetramethyl-2-(pentadec-1-en-2-yl)-1,3,2-dioxaborolane (4b)



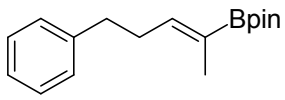
colorless liquid (68%, 68.5mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.33 ((tq, apparent td, J_1 = 6.99 Hz, J_2 = 1.65 Hz, 1H), 2.15-2.10 (m, 2H), 1.69 (s, 3H), 1.28-1.27 (m, 32H), 0.89 (t, J = 7.02 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 83.0, 31.9, 29.69, 29.65, 29.6, 29.5, 29.4, 28.9, 28.7, 24.8, 22.7, 14.1, 13.8. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{21}H_{41}O_2BNa^+$ $[M+Na]^+$: 359.3097, found: 359.3093.

(Z)-2-(1-cyclohexylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c)



colorless liquid (72%, 54.2mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.14 (dq, apparent dd, J_1 = 9.00 Hz, J_2 = 1.47 Hz, 1H), 2.42-2.33 (m, 1H), 1.70 (d, J = 1.60 Hz, 3H), 1.68-1.60 (m, 5H),1.32-1.07 (m, 17H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 83.0, 37.5, 32.2, 26.1, 26.0, 24.8, 13.9. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{15}H_{27}O_2BNa^+$ $[M+Na]^+$: 273.2002, found: 273.2008. Characterization data matched with those reported in the literature.[4]

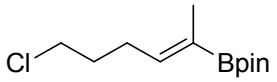
(Z)-4,4,5,5-tetramethyl-2-(5-phenylpent-2-en-2-yl)-1,3,2-dioxaborolane (4d)



colorless liquid (69%, 56.3mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 2H), 7.28-7.23 (m, 3H), 6.47 (tq, apparent td, J_1 = 6.85, J_2 = 1.59, 1H), 2.78 (t, J = 7.81 Hz, 2H), 2.55-2.49 (m, 2H), 1.74 (t, J = 0.80 Hz, 3H), 1.34 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.2, 142.1, 128.28, 128.27, 125.8, 83.1, 35.1, 30.7, 24.8, 13.8. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{17}H_{25}O_2BNa^+$

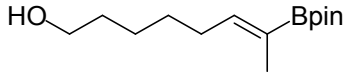
$[M+Na]^+$: 295.1845, found: 295.1838. Characterization data matched with those reported in the literature.[4]

(Z)-2-(6-chlorohex-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)



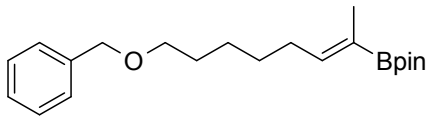
colorless liquid (81%, 59.3mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.32 (t, *J* = 6.30 Hz, 1H), 3.47 (t, *J* = 6.35 Hz, 2H), 2.24-2.20 (m, 2H), 1.84-1.80 (m, 2H), 1.63 (s, 3H), 1.20 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.9, 83.2, 44.7, 31.7, 25.8, 24.8, 13.9. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{12}H_{22}ClO_2BNa^+$ $[M+Na]^+$: 267.1299, found: 267.1293.

(Z)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-6-en-1-ol (4f)



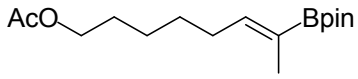
colorless liquid (77%, 58.7mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.32 (t, *J* = 6.49 Hz, 1H), 3.64 (t, *J* = 6.69 Hz, 2H), 2.17-2.12 (m, 2H), 1.68 (s, 3H), 1.60-1.55 (m, 2H), 1.45-1.37 (m, 4H), 1.26 (s, 12 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2, 83.1, 62.9, 32.7, 28.6, 28.5, 25.6, 24.8, 13.8. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{17}H_{25}O_2BNa^+$ $[M+Na]^+$: 277.1951, found: 277.1945.

(Z)-2-(8-(benzyloxy)oct-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4g)



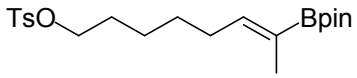
colorless liquid (80%, 82.6mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 6.34 (t, *J* = 6.22 Hz, 1H), 4.53 (s, 2H), 3.49 (t, *J* = 6.61 Hz, 2H), 2.15 (t, *J* = 6.69 Hz, 2H), 1.70 (s, 3H), 1.67-1.64 (m, 2H), 1.44-1.42 (m, 4H), 1.29 (s, 12 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3, 138.7, 128.3, 127.6, 127.4, 83.0, 72.8, 70.4, 29.7, 28.7, 28.6, 26.0, 24.8, 13.8. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{21}H_{33}O_3BNa^+$ $[M+Na]^+$: 367.2420, found: 367.2414.

(Z)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-6-en-1-yl acetate (4h)



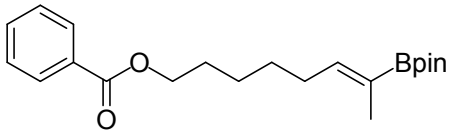
colorless liquid (86%, 76.4mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.30 (tq, apparent s, 1H), 4.05 (t, *J* = 6.67 Hz, 2H), 2.14-2.12 (m, 2H), 2.04 (s, 3H), 1.68 (s, 3H), 1.63 (t, *J* = 6.13 Hz, 2H) 1.44-1.36 (m, 4H), 1.26 (s, 12 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 146.0, 83.1, 64.5, 28.5, 28.4, 25.7, 24.8, 24.7, 21.0, 13.9. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{16}H_{29}O_4BNa^+$ $[M+Na]^+$: 319.2057, found: 319.2062.

(Z)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-6-en-1-yl-4-methylbenzenesulfonate (4i)



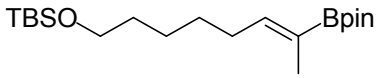
colorless liquid (73%, 89.4mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.25 Hz, 2H), 7.37 (d, *J* = 8.08 Hz, 2H), 6.25 (tq, apparent td, J_1 = 6.95 Hz, J_2 = 1.59 Hz, 1H), 4.03 (t, *J* = 6.63 Hz, 2H), 2.47 (s, 3H), 2.11-2.06 (m, 2H), 1.66 (s, 3H), 1.35-1.33 (m, 4H), 1.28 (s, 14H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.6, 133.3, 129.8, 128.9, 127.9, 83.1, 70.5, 28.7, 28.3, 28.1, 25.1, 24.8, 21.6, 13.8. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{21}H_{33}O_5BSNa^+$ $[M+Na]^+$: 431.2039, found: 431.2045.

(Z)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-6-en-1-yl benzoate (4j)



colorless liquid (77%, 85.9mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2H), 7.57-7.54 (m, 1H)，7.46-7.42 (m, 2H)，6.33 (tq, apparent td, J_1 = 7.07 Hz, J_2 = 1.39 Hz, 1H), 4.32 (t, *J* = 6.68 Hz, 2H), 2.18-2.15 (m, 2H), 1.80-1.76 (m, 2H), 1.69 (s, 3H), 1.49-1.48 (m, 4H), 1.27 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 146.0, 132.7, 130.5, 129.5, 128.2, 83.0, 65.0, 28.6, 28.44, 28.43, 25.8, 24.7, 13.8. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{22}H_{33}O_4BNa^+$ $[M+Na]^+$: 395.2370, found: 395.2377.

(Z)-tert-butyldimethyl((7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-6-en-1-yl)oxy)silane (4k)



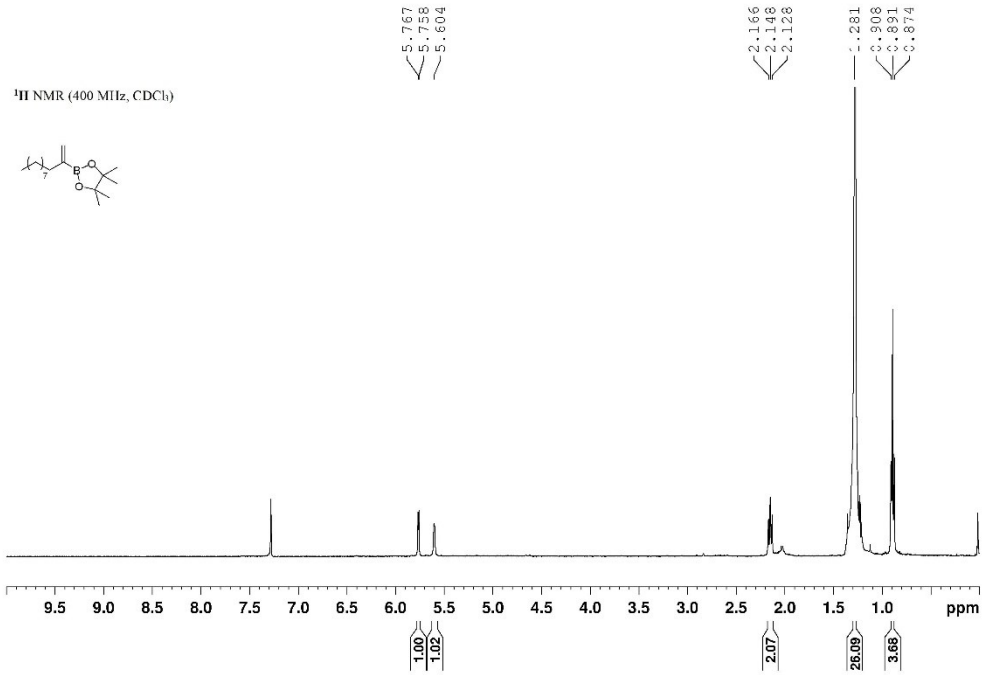
colorless liquid (71%, 78.4mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.31 (tq, apparent td, J_1 = 6.99 Hz, J_2 = 1.62 Hz, 1H), 3.59 (t, *J* = 6.61 Hz, 2H), 2.15-2.10 (m, 2H), 1.67 (d, *J* = 1.62 Hz, 3H), 1.55-1.48 (m, 2H), 1.40-1.30 (m, 4H), 1.25 (s, 12 H), 0.90 (s, 9H), 0.04 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 83.0, 63.1, 32.7, 28.6, 25.9, 25.6, 24.8, 24.7, 18.3, 13.8, -5.3. The carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus. **HRMS** (ESI) m/z Calculated for $C_{20}H_{41}O_3BSiNa^+$ $[M+Na]^+$: 391.2816, found: 391.2823.

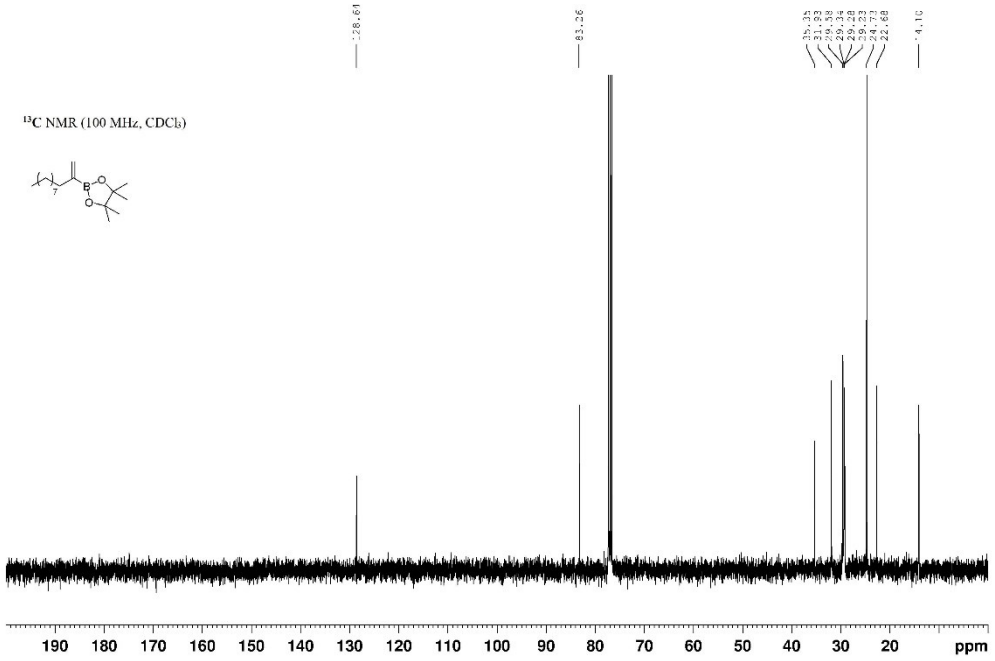
Reference:

[4] Semba, K.; Shinomiya, M.; Fujihara, T.; Terao, J.; Tsuji, Y. *Chem. Eur. J.* **2013**, *19*, 7125-7132

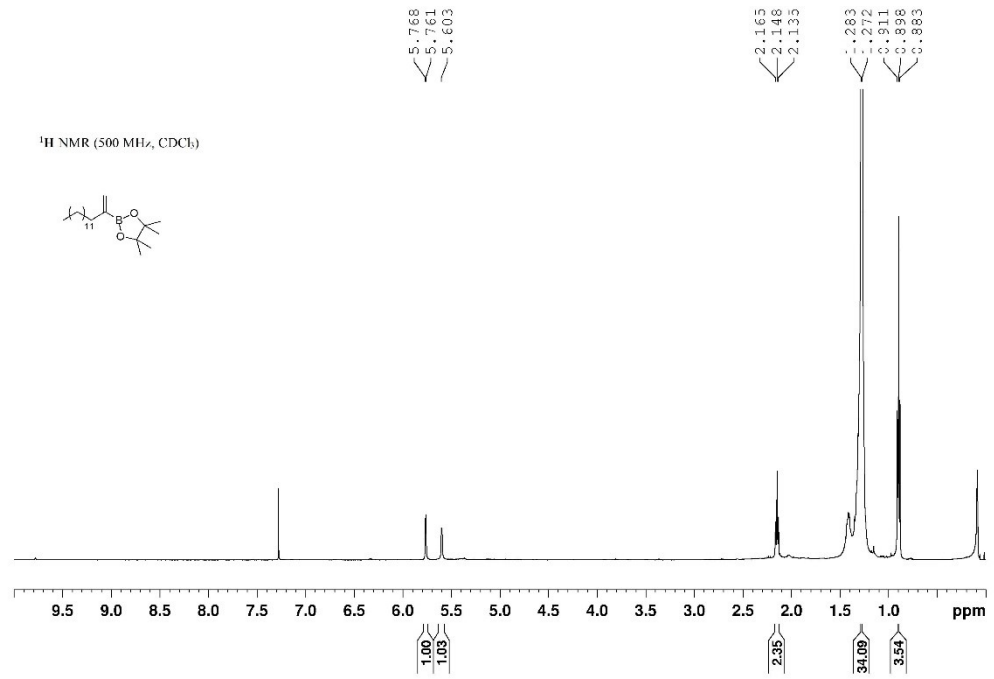
5. NMR spectra

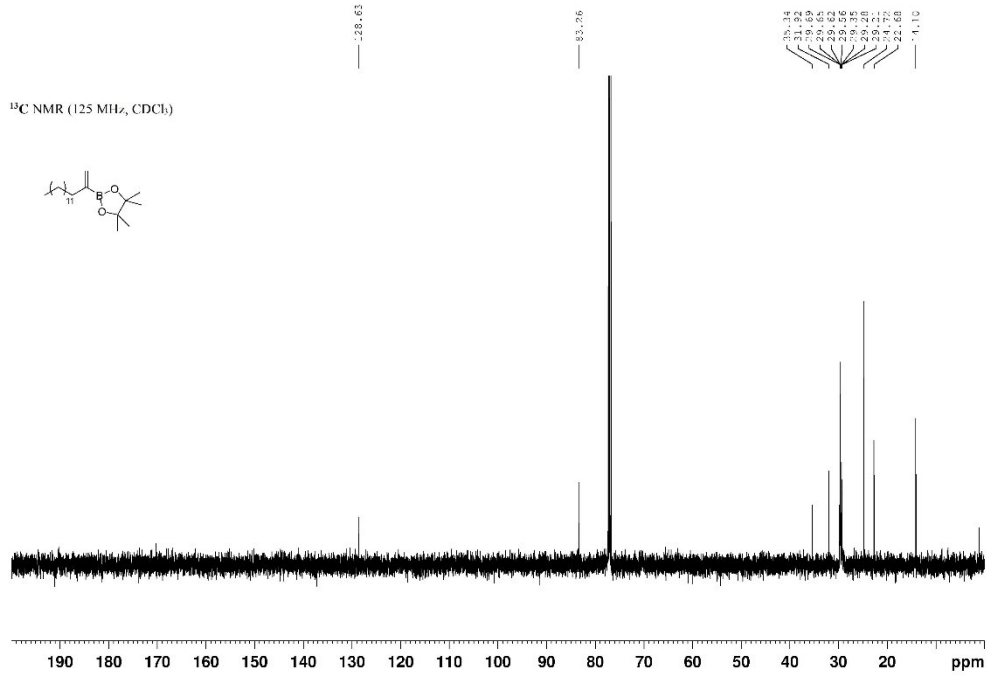
3a



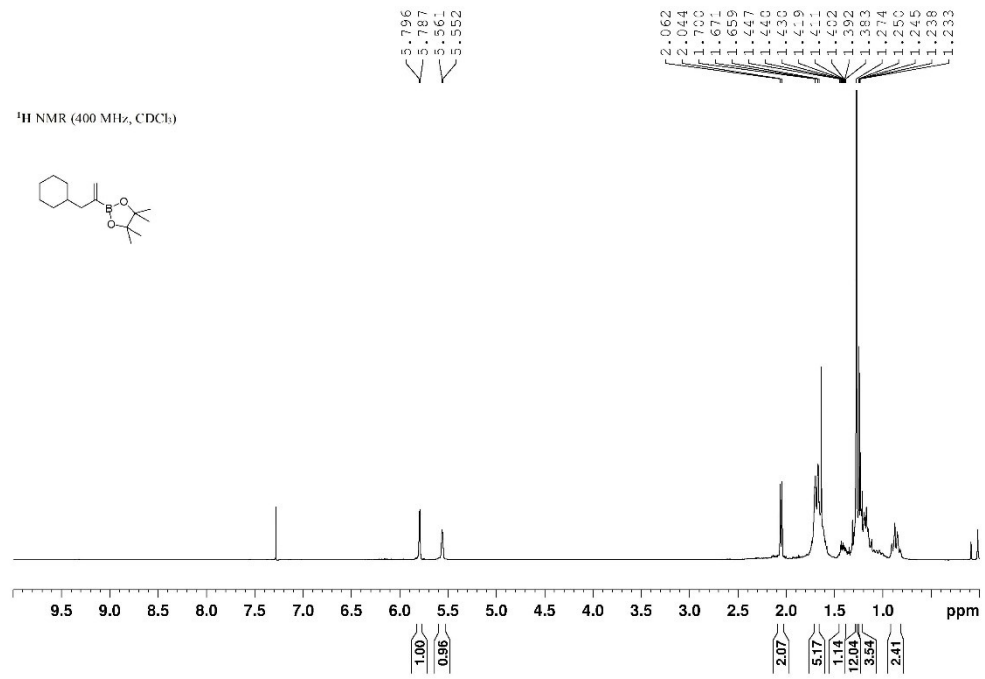


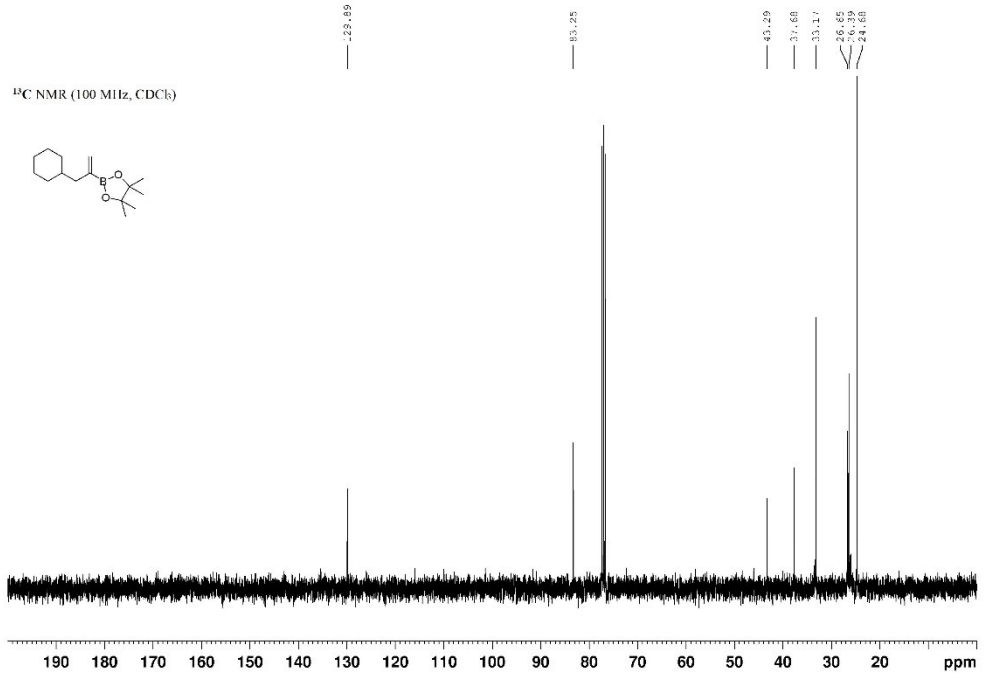
3b


5.768
5.761
5.603
2.165
2.148
2.135
1.283
1.272
0.911
0.898
0.883
^{1}H NMR (500 MHz, CDCl$_3$)
9.5 9.0 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 ppm
1.00
1.03
2.35
34.09
3.54

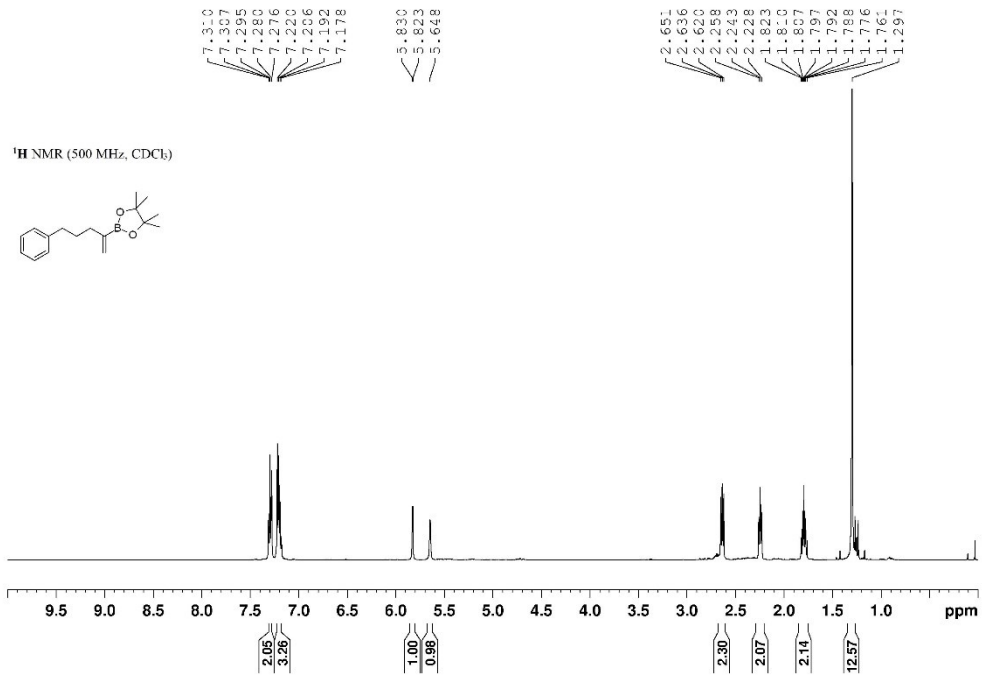

128.63
83.26
^{13}C NMR (125 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

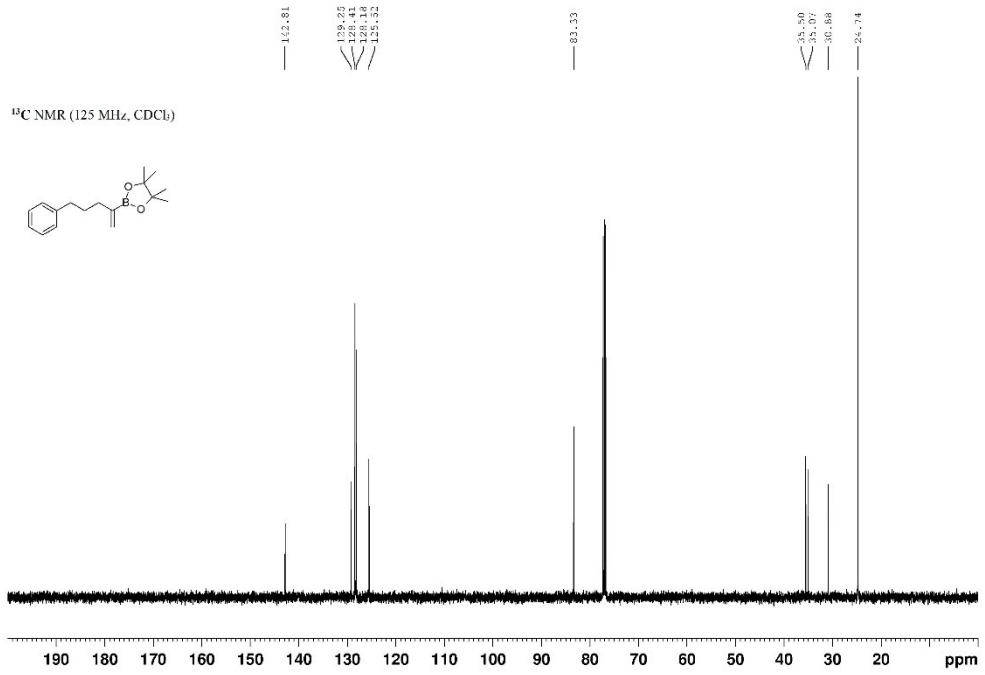
3c


5.796
5.787
5.561
5.552
2.062
2.044
1.659
1.447
1.392
1.383
1.274
1.250
1.245
1.238
1.233
¹H NMR (400 MHz, CDCl₃)
9.5 9.0 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 ppm
1.00
0.96
2.07
5.17
1.14
12.04
3.54
2.41

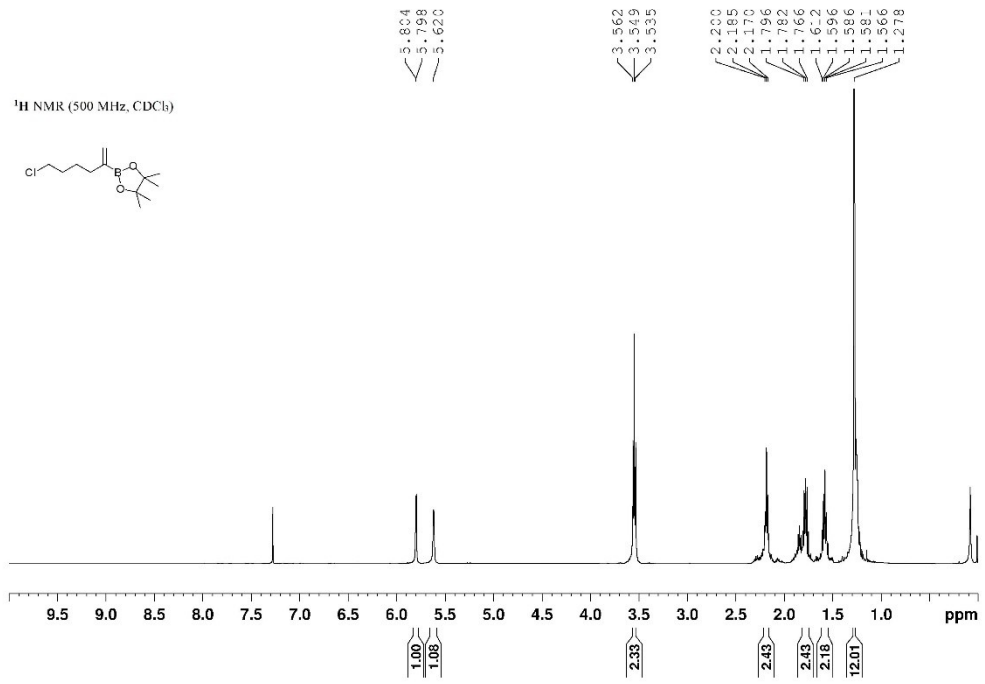

129.89
83.25
43.29
37.68
26.65
26.39
24.68
¹³C NMR (100 MHz, CDCl₃)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

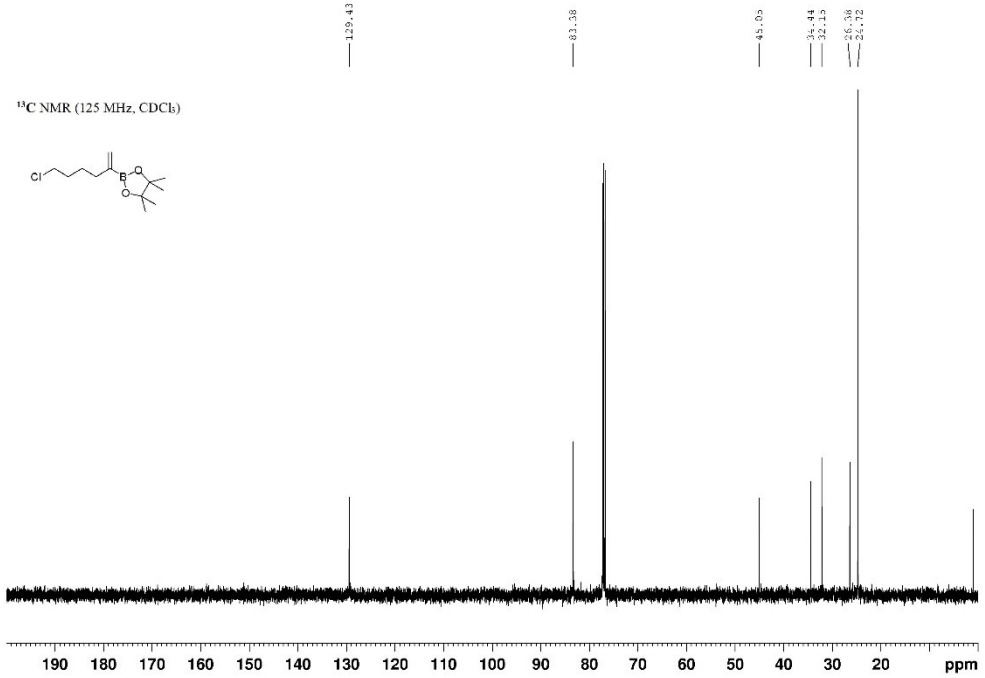
3d


7.310
7.307
7.295
7.280
7.276
7.220
7.206
7.192
7.178
5.830
5.823
5.648
2.651
2.636
2.620
2.258
2.243
2.228
1.823
1.807
1.797
1.792
1.788
1.776
1.761
1.297
^{1}H NMR (500 MHz, CDCl$_3$)
9.5 9.0 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 ppm
2.05
3.26
1.00
0.98
2.30
2.07
2.14
12.57

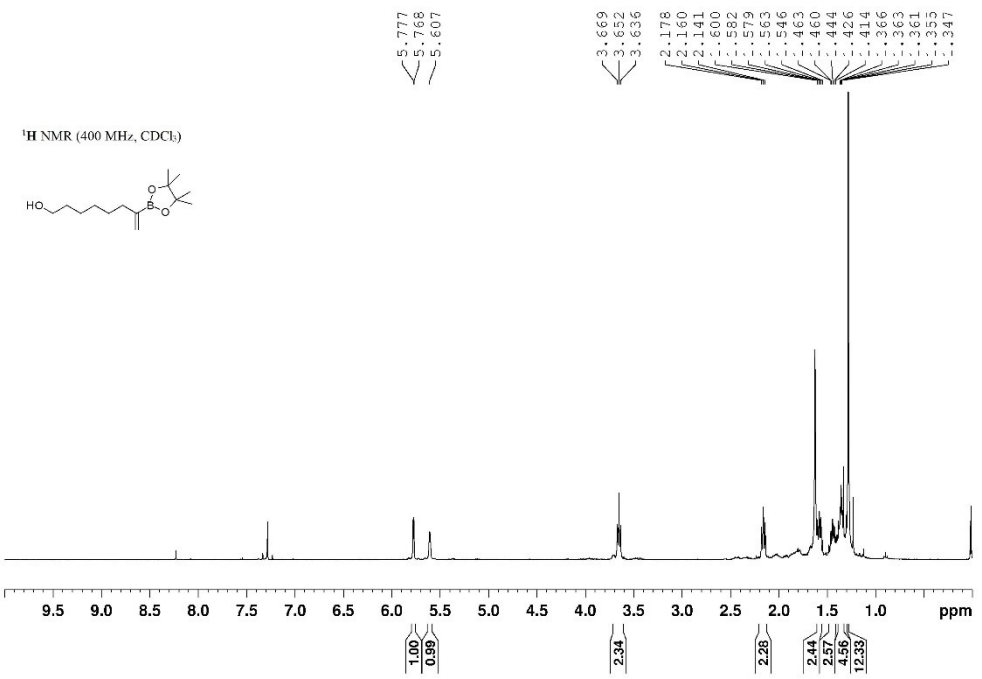

142.81
129.25
128.41
128.18
125.52
83.33
35.50
35.07
30.88
24.74
^{13}C NMR (125 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

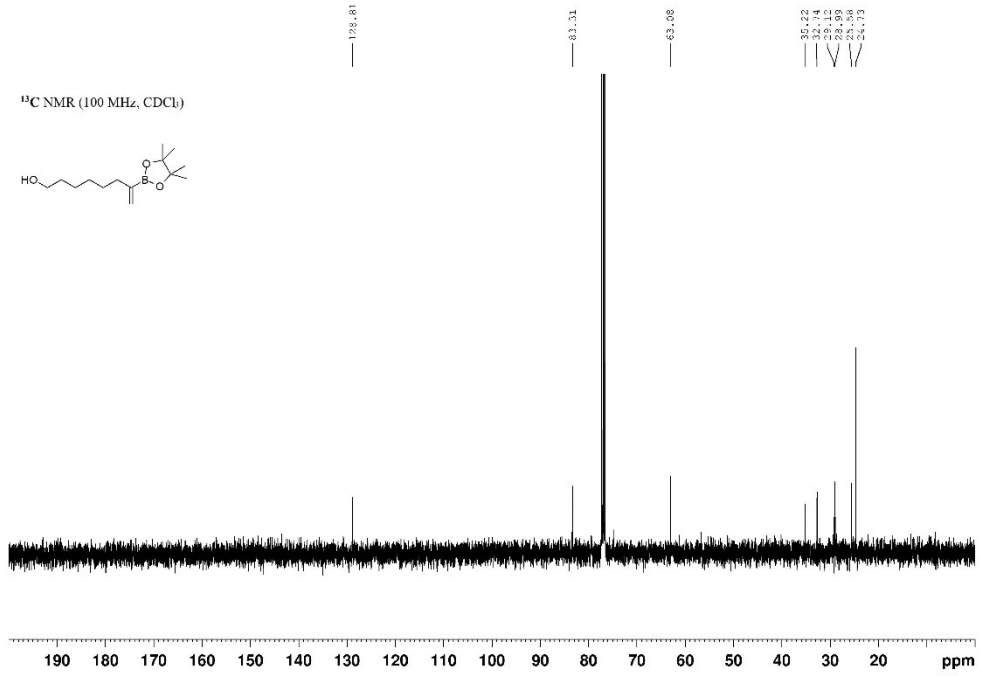
3e


5.804
5.798
5.620
3.562
3.549
3.535
2.200
2.185
2.170
1.796
1.782
1.766
1.596
1.586
1.566
1.278
1H NMR (500 MHz, CDCl3)
Cl
B
O
O
9.5 9.0 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 ppm
1.00
1.08
2.33
2.43
2.43
2.18
12.01

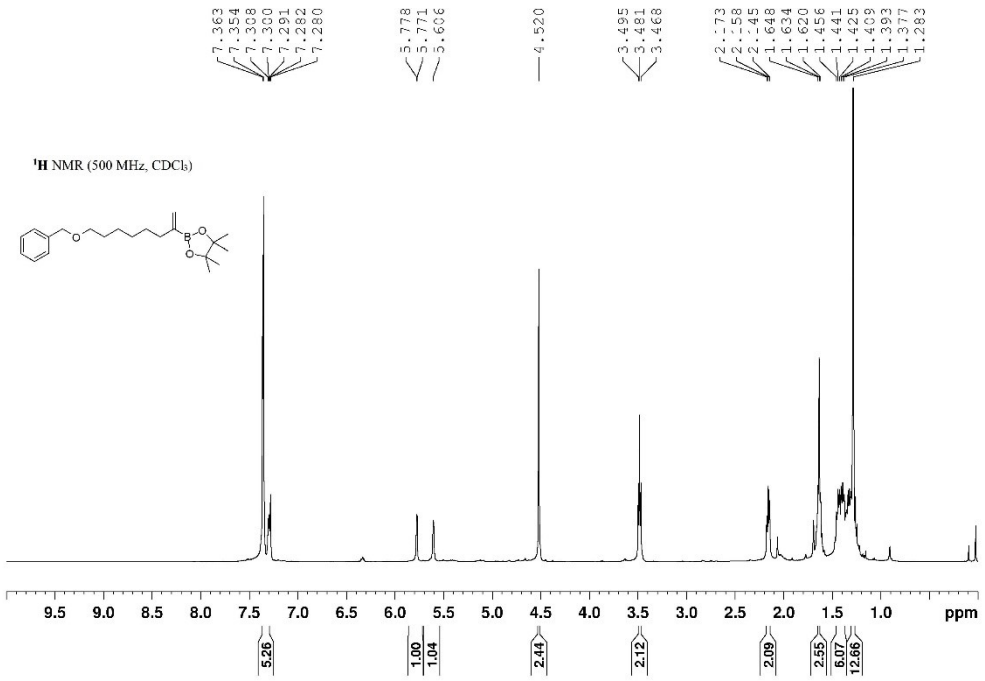

129.43
83.38
45.05
34.44
32.15
26.38
24.72
13C NMR (125 MHz, CDCl3)
Cl
B
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

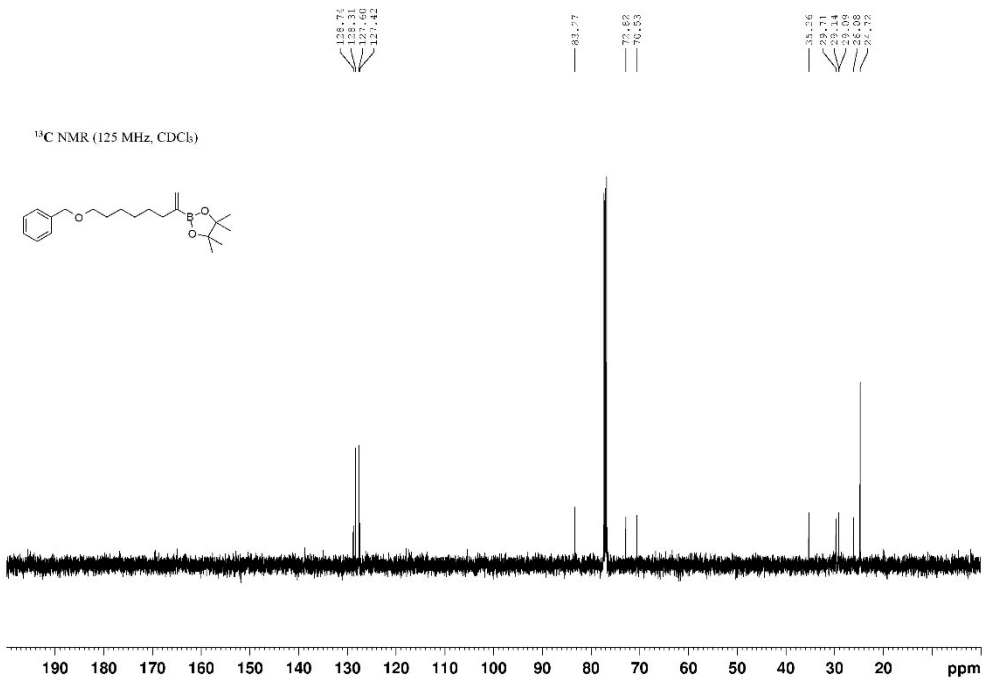
3f


5.777
5.768
5.607
3.669
3.652
3.636
2.178
2.160
2.141
1.600
1.582
1.579
1.563
1.546
1.463
1.460
1.444
1.426
1.414
1.366
1.363
1.361
1.355
1.347
^{1}H NMR (400 MHz, CDCl$_3$)
HO
9.5 9.0 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 ppm
1.00
0.99
2.34
2.28
2.44
2.57
4.56
12.33

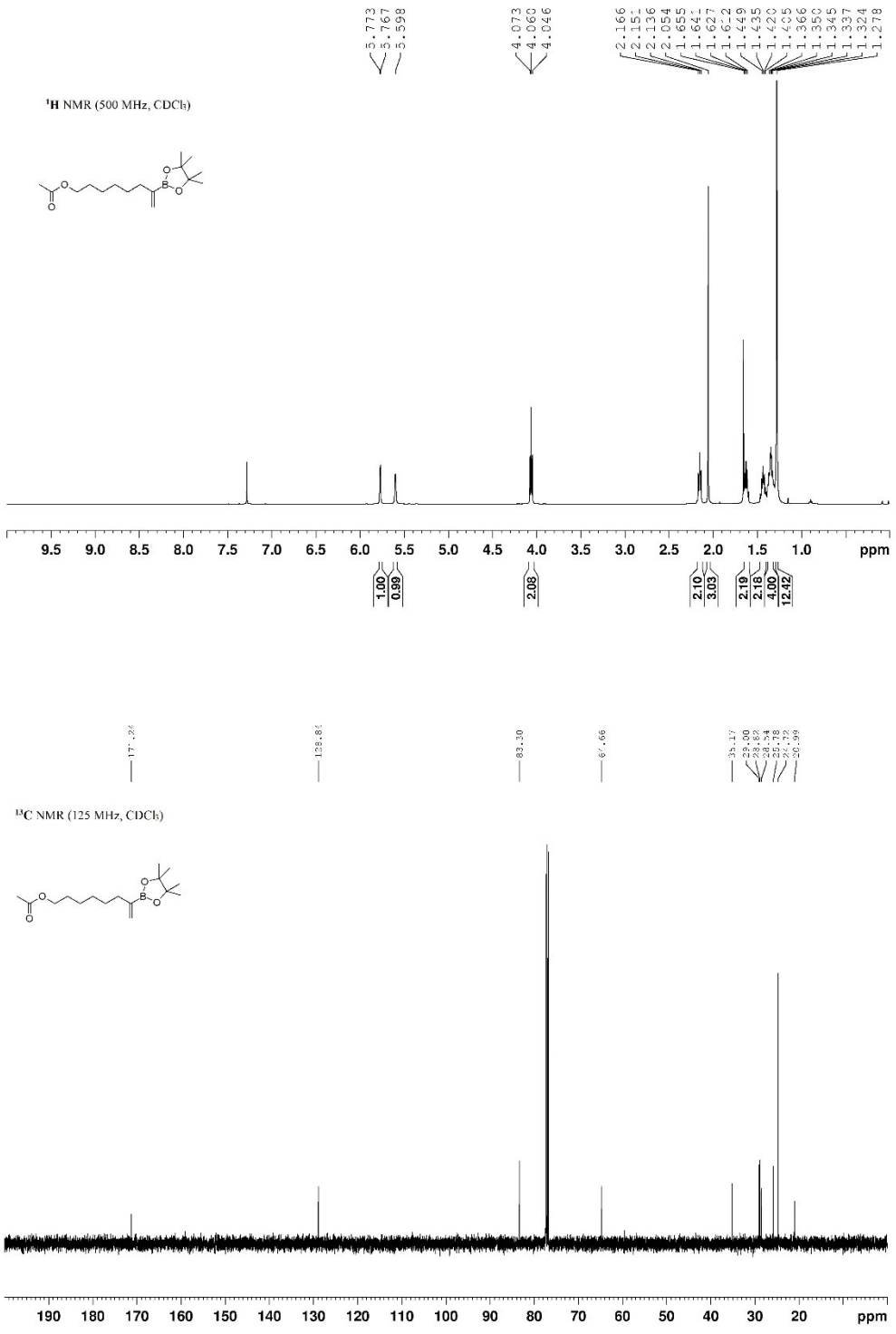

128.81
83.31
63.08
35.22
32.14
29.12
23.99
25.58
24.73
^{13}C NMR (100 MHz, CDCl$_3$)
HO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

3g

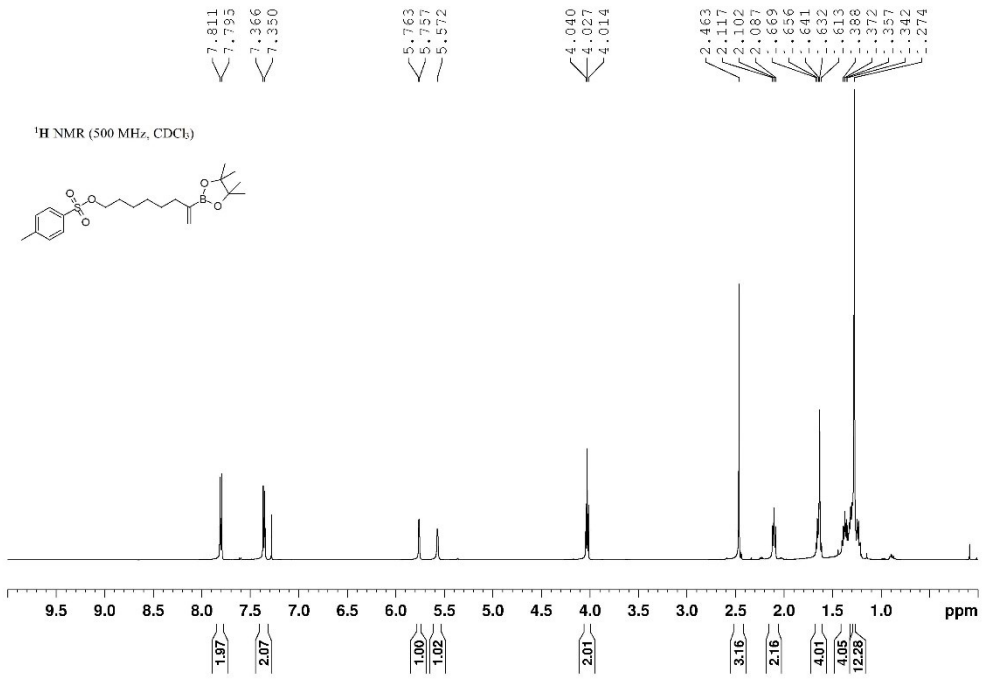

7.363
7.354
7.308
7.300
7.291
7.282
7.280
5.778
5.771
5.606
4.520
3.485
3.481
3.468
2.273
2.258
2.245
1.648
1.634
1.620
1.456
1.441
1.425
1.409
1.393
1.377
1.283
¹H NMR (500 MHz, CDCl₃)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
5.26
1.00
1.04
2.44
2.12
2.09
2.55
6.07
12.66

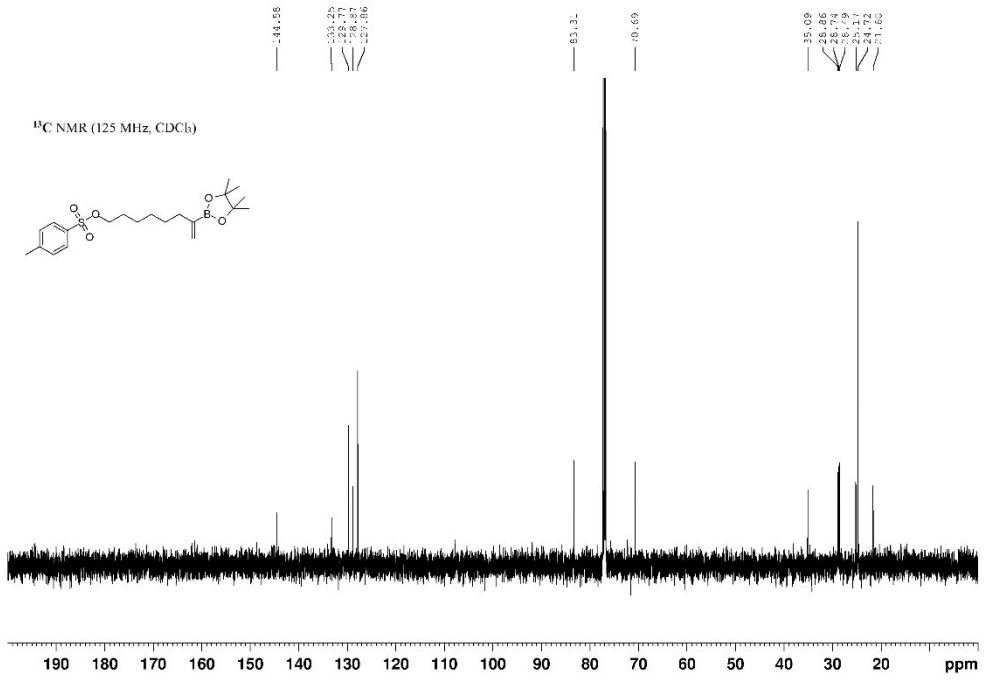

138.76
138.31
127.60
127.42
83.77
70.82
70.53
35.26
29.71
29.14
28.98
26.08
22.72
¹³C NMR (125 MHz, CDCl₃)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

3h

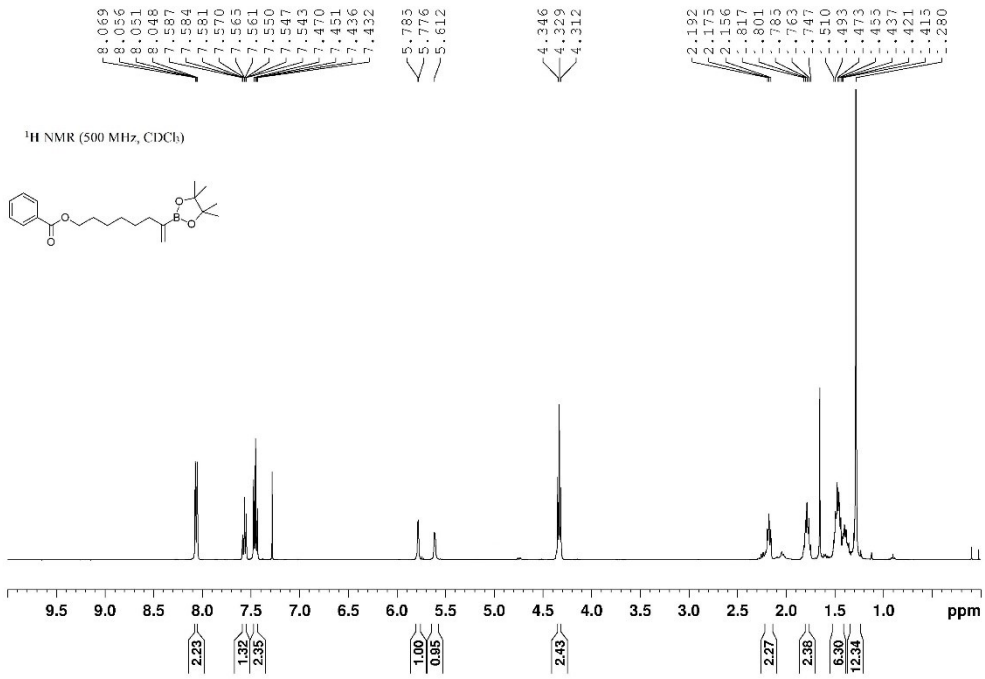

5.773
5.767
5.598
4.073
4.060
4.046
2.166
2.151
2.136
2.054
1.655
1.641
1.627
1.622
1.449
1.435
1.420
1.405
1.366
1.350
1.345
1.337
1.324
1.278
¹H NMR (500 MHz, CDCl₃)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
0.99
2.08
2.10
3.03
2.19
2.18
4.00
12.42
171.24
138.86
83.30
67.66
35.17
29.00
28.69
28.34
25.78
24.72
20.99
¹³C NMR (125 MHz, CDCl₃)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

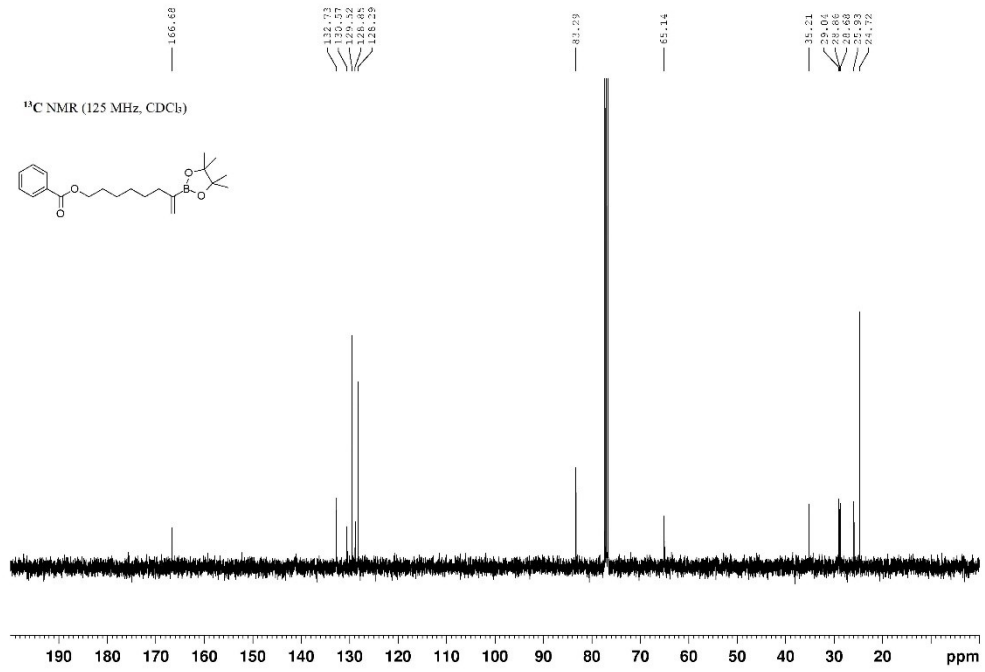
3i


7.811
7.795
7.366
7.350
5.763
5.757
5.572
4.040
4.027
4.014
2.463
2.117
2.102
2.087
1.669
1.656
1.641
1.632
1.613
1.388
1.372
1.357
1.342
1.274
^{1}H NMR (500 MHz, CDCl$_3$)
9.5 9.0 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 ppm
1.97
2.07
1.00
1.02
2.01
3.16
2.16
4.01
4.05
12.28

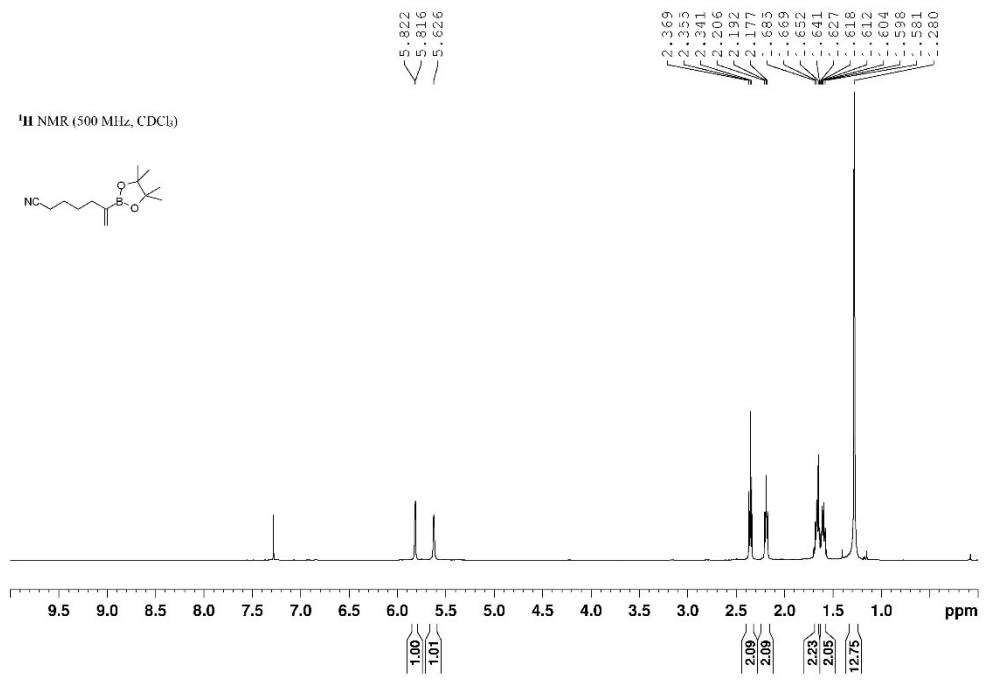

144.98
133.25
129.77
128.87
127.86
83.31
70.69
35.09
28.86
28.74
25.17
24.72
21.60
^{13}C NMR (125 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

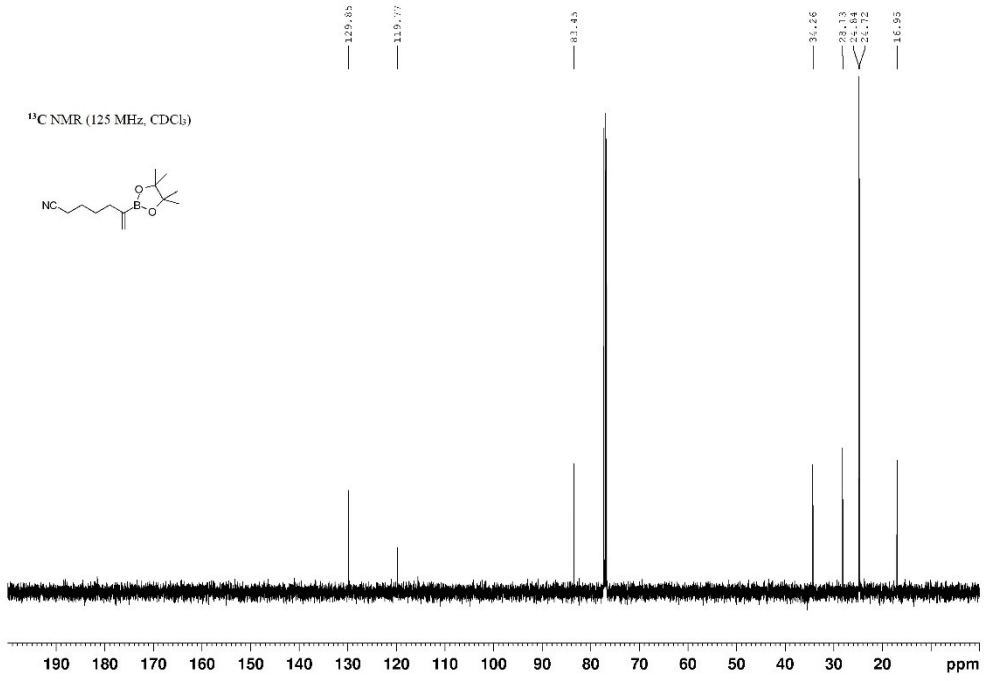
3j


8.069
8.056
8.051
8.048
7.587
7.584
7.581
7.570
7.565
7.561
7.550
7.547
7.543
7.470
7.451
7.436
7.432
5.785
5.776
5.612
4.346
4.329
4.312
2.192
2.175
2.156
1.817
1.801
1.785
1.763
1.747
1.510
1.493
1.473
1.455
1.437
1.421
1.415
1.280
¹H NMR (500 MHz, CDCl₃)
9.5 9.0 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 ppm
2.23
1.32
2.35
1.00
0.95
2.43
2.27
2.38
6.30
12.34

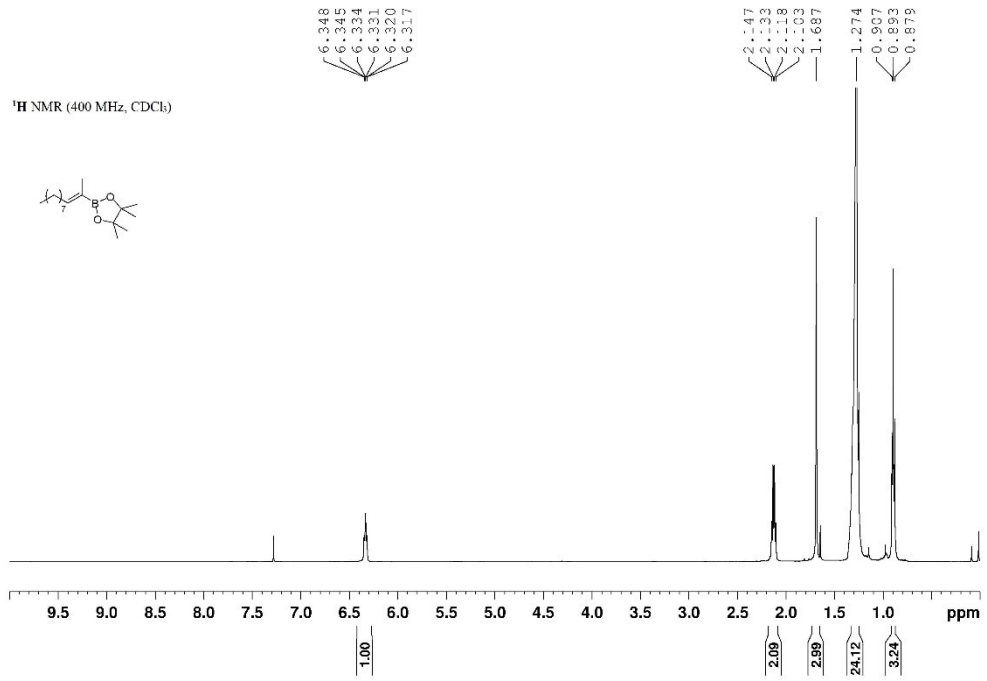

166.68
132.73
130.57
129.52
128.45
128.29
83.29
65.14
35.21
29.04
28.86
28.68
25.93
24.72
¹³C NMR (125 MHz, CDCl₃)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

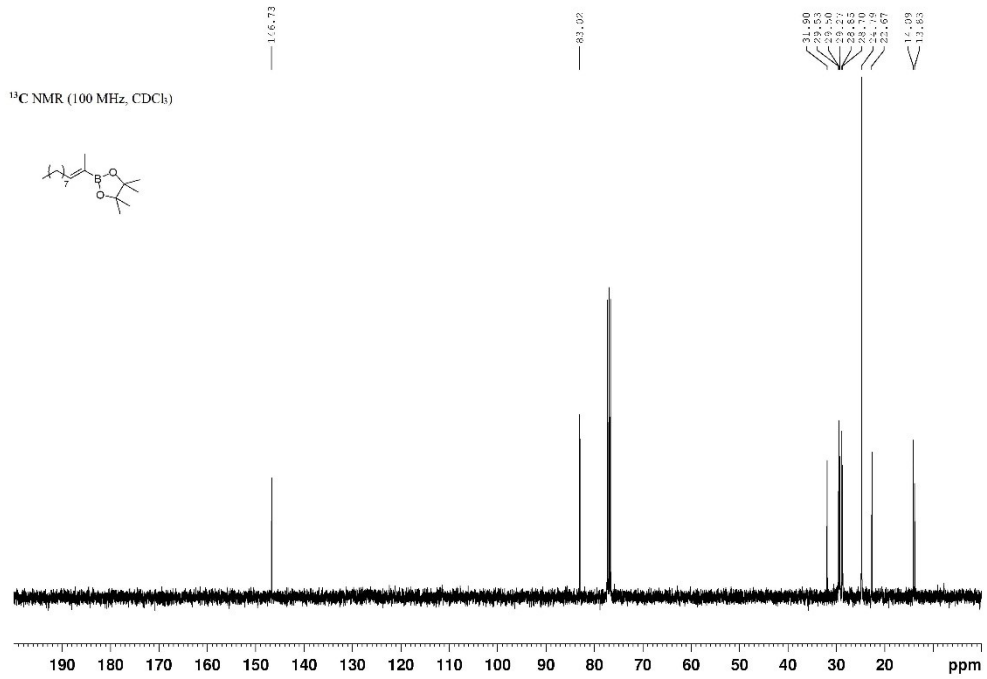
3k


5.822
5.816
5.626
2.369
2.355
2.341
2.206
2.192
2.177
1.685
1.669
1.652
1.641
1.627
1.618
1.612
1.604
1.598
1.581
1.280
^{1}H NMR (500 MHz, CDCl$_3$)
NC
9.5 9.0 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 ppm
1.00
1.01
2.09
2.09
2.23
2.05
12.75

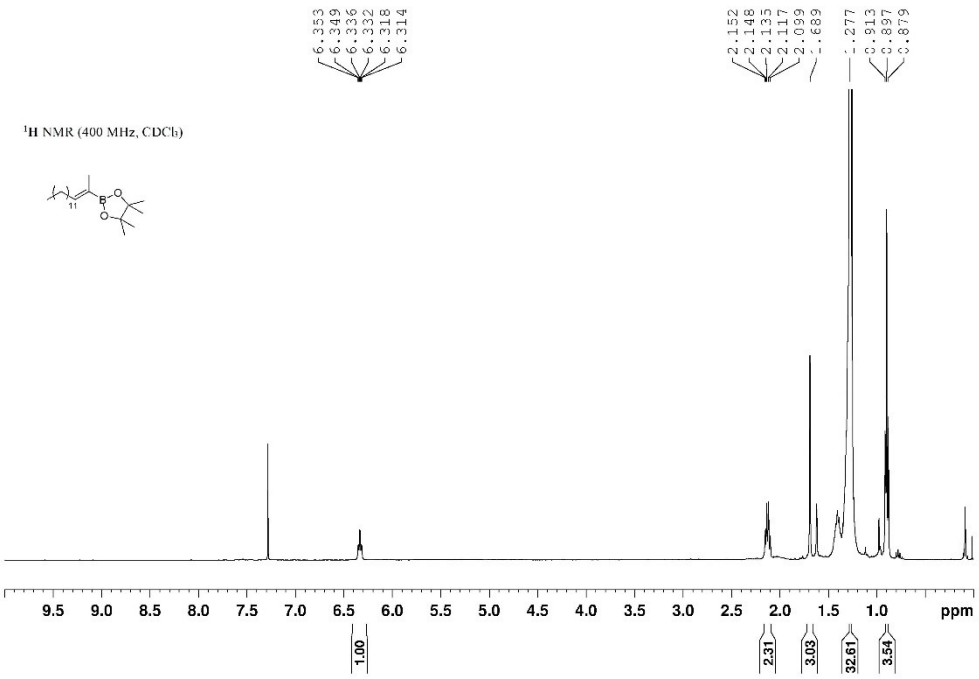

129.85
119.77
83.43
36.26
23.13
24.84
24.72
16.95
^{13}C NMR (125 MHz, CDCl$_3$)
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

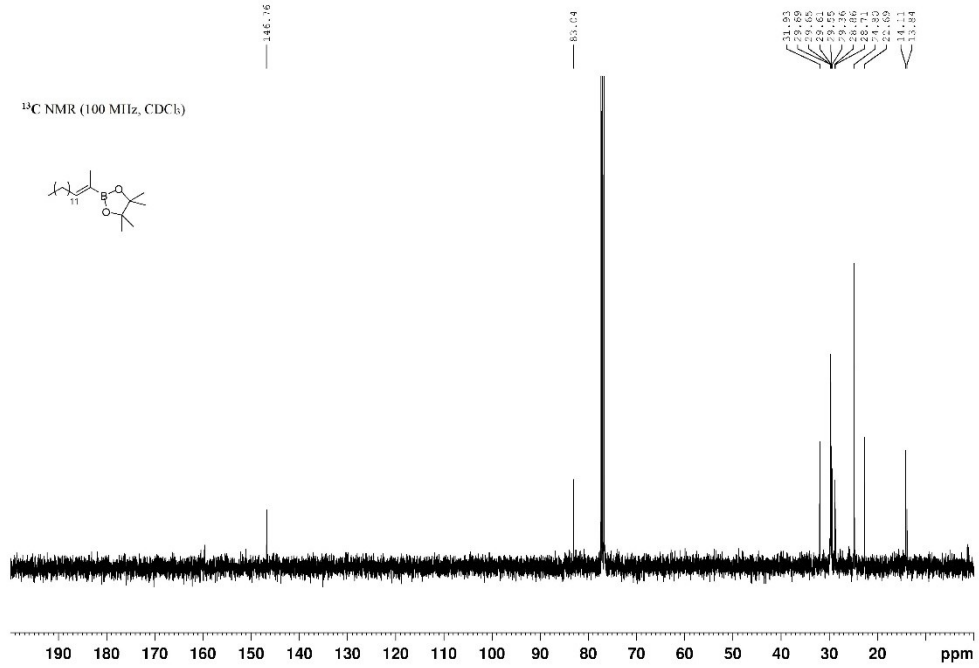
4a


6.348
6.345
6.334
6.331
6.320
6.317
2.147
2.133
2.118
2.103
1.687
1.274
0.907
0.893
0.879
¹H NMR (400 MHz, CDCl₃)
9.5 9.0 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 ppm
1.00
2.09
2.99
24.12
3.24

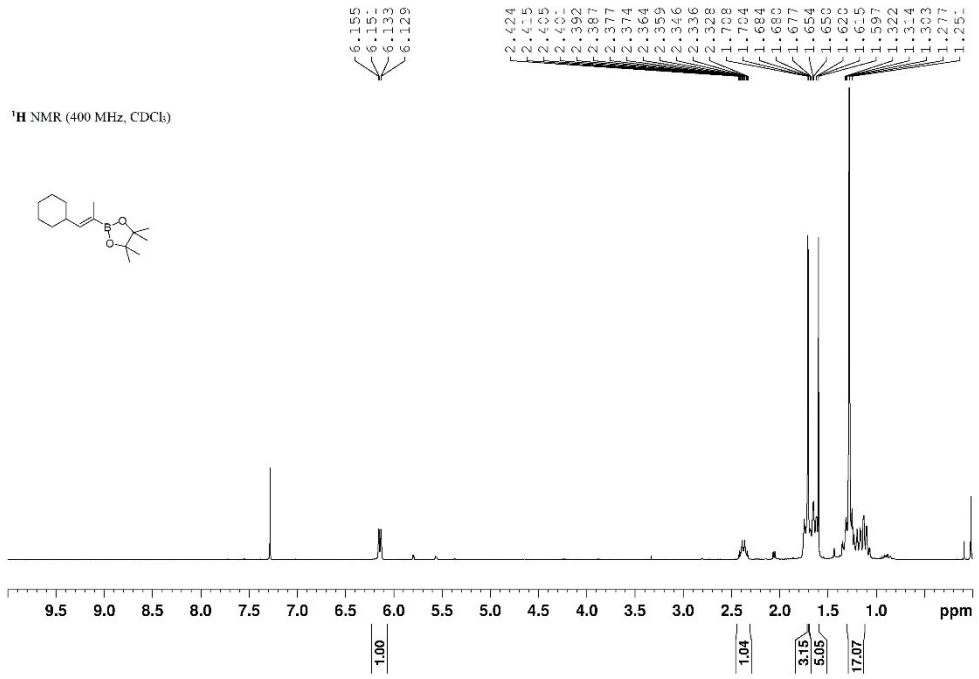

176.73
83.02
31.90
29.53
29.50
29.27
28.55
28.40
24.79
22.67
14.09
13.83
¹³C NMR (100 MHz, CDCl₃)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

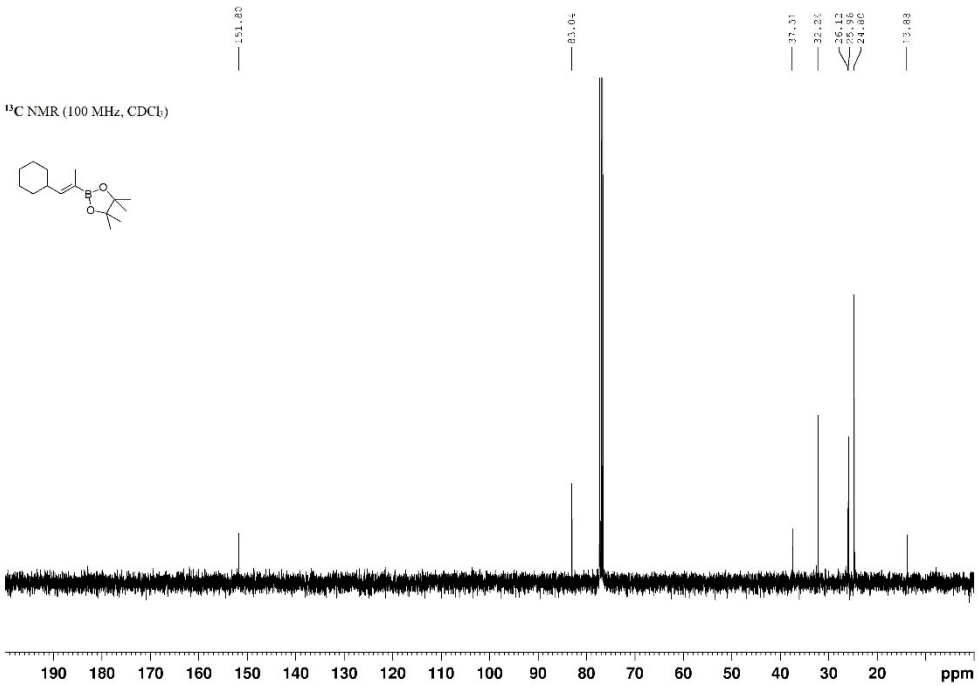
4b


6.353
6.349
6.336
6.332
6.318
6.314
2.152
2.148
2.135
2.117
2.099
1.689
1.277
0.913
0.897
0.879
^{1}H NMR (400 MHz, CDCl$_3$)
9.5 9.0 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 ppm
1.00
2.31
3.03
32.61
3.54

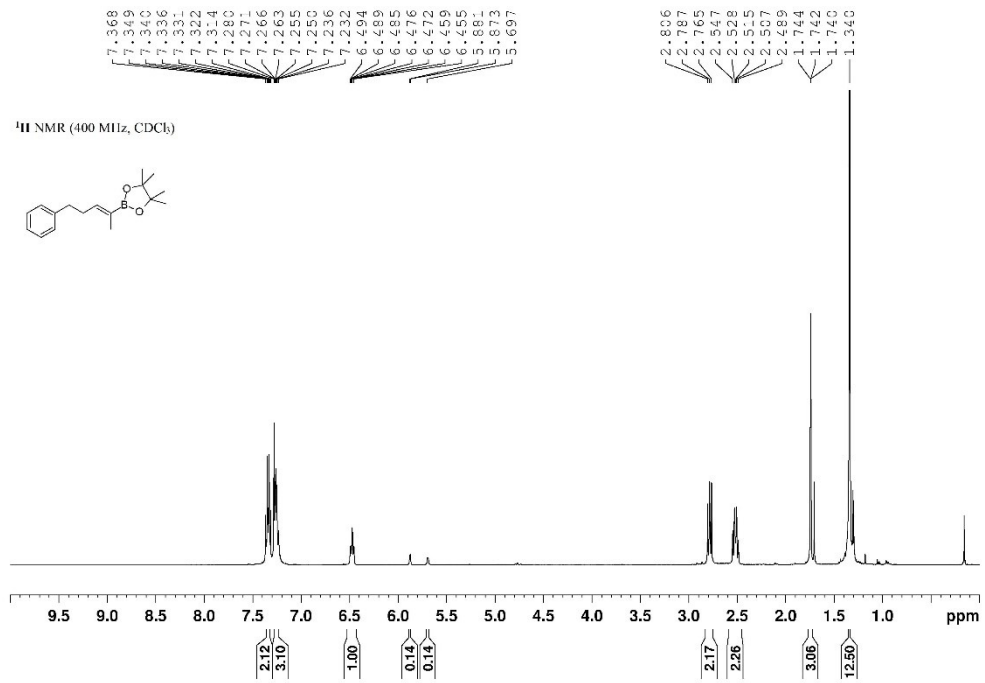

146.76
83.04
31.93
29.69
29.65
29.61
29.55
29.36
28.86
28.71
24.80
22.69
14.11
13.84
^{13}C NMR (100 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

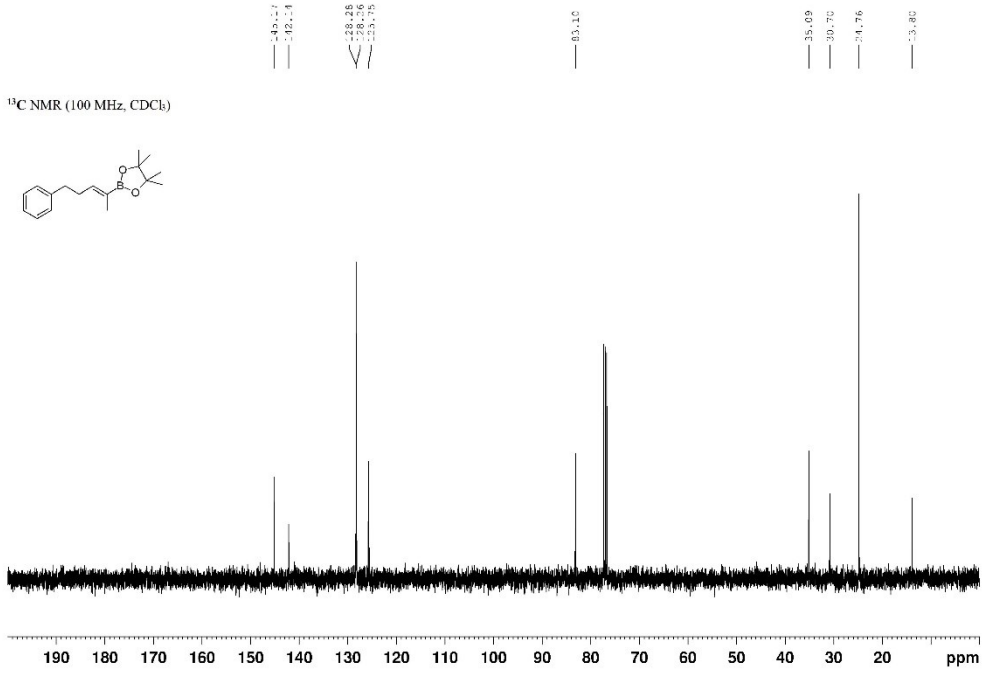
4c


6.155
6.151
6.133
6.129
2.424
2.415
2.405
2.392
2.387
2.377
2.374
2.364
2.359
2.346
2.336
2.328
1.708
1.704
1.684
1.680
1.677
1.654
1.650
1.623
1.615
1.597
1.322
1.314
1.303
1.277
1.251
^{1}H NMR (400 MHz, CDCl$_3$)
9.5 9.0 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 ppm
1.00
1.04
3.15
5.05
17.07

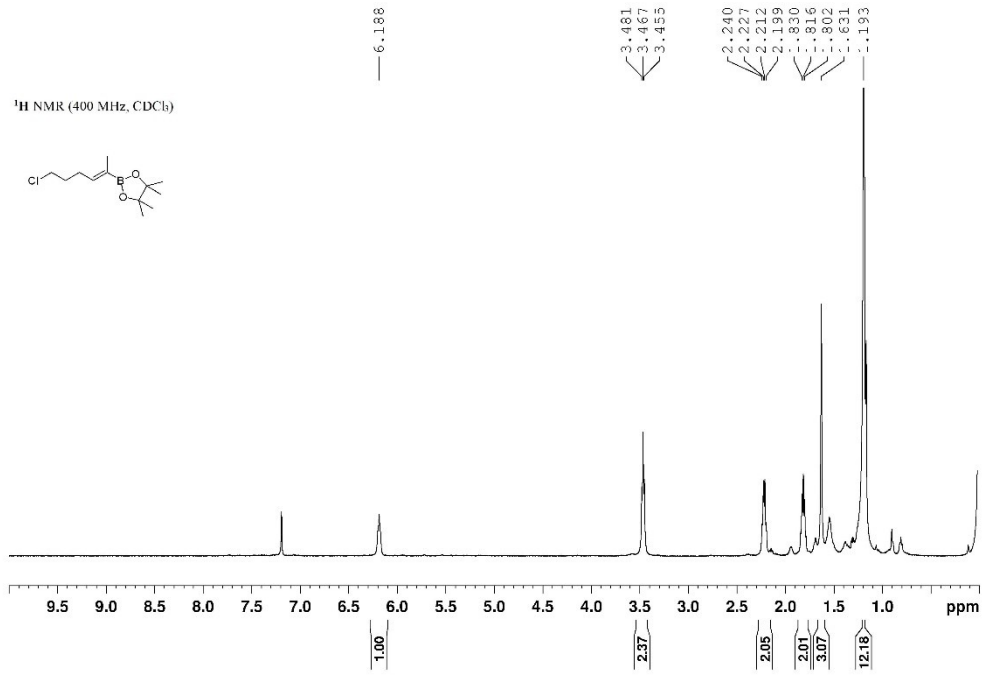

151.80
83.04
37.31
32.24
26.12
25.96
24.80
13.83
^{13}C NMR (100 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

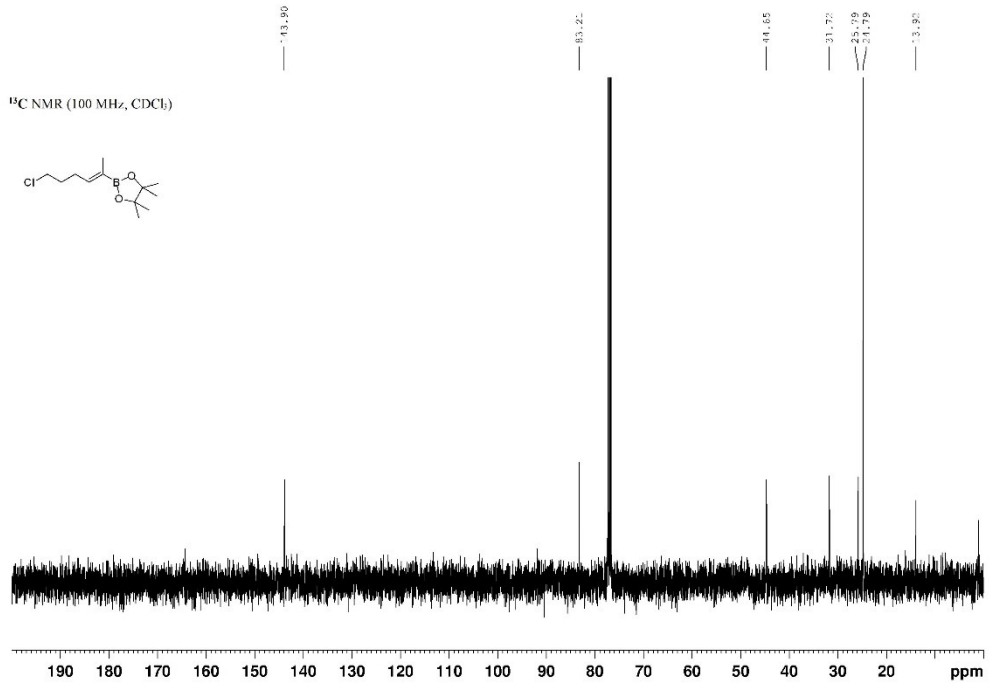
4d


^{1}H NMR (400 MHz, CDCl$_3$)
7.368
7.349
7.340
7.336
7.332
7.322
7.314
7.280
7.271
7.266
7.263
7.255
7.250
7.236
7.232
6.494
6.489
6.485
6.476
6.472
6.459
6.455
5.881
5.873
5.697
2.806
2.787
2.765
2.547
2.528
2.515
2.507
2.489
1.744
1.742
1.740
1.340
9.5 9.0 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 ppm
2.12
3.10
1.00
0.14
0.14
2.17
2.26
3.06
12.50

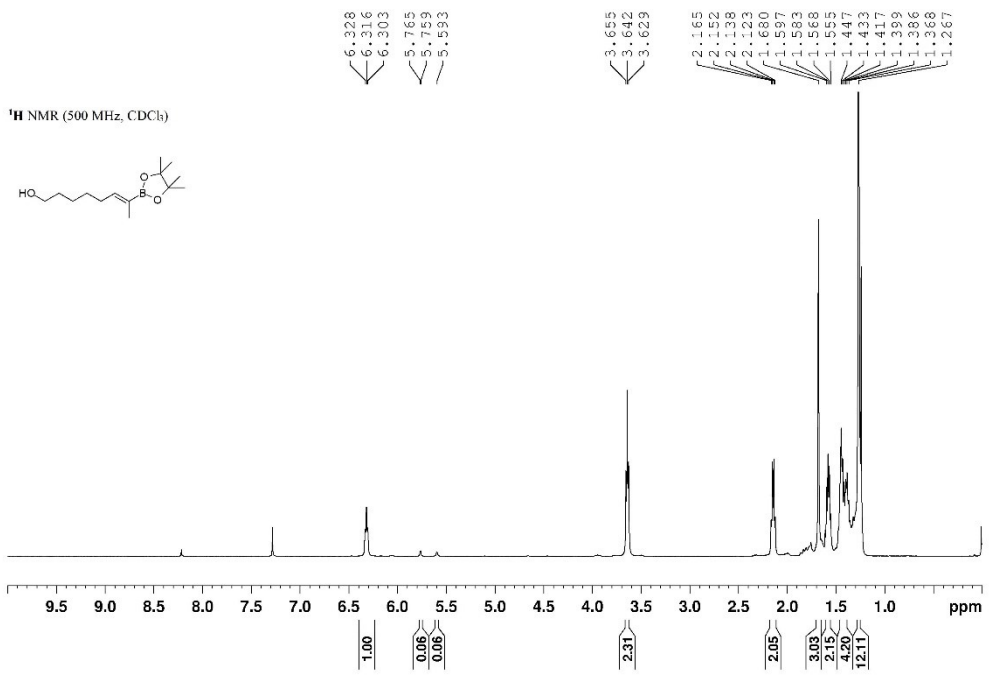

^{13}C NMR (100 MHz, CDCl$_3$)
128.26
128.16
125.75
83.10
35.09
30.70
24.76
13.80
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

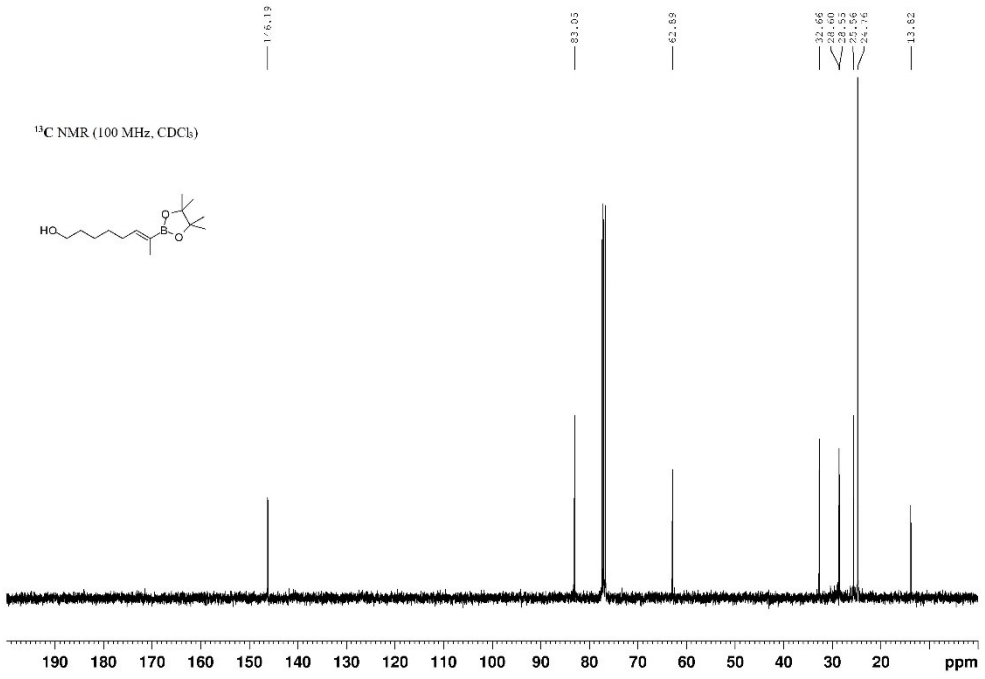
4e


6.188
3.481
3.467
3.455
2.240
2.227
2.212
2.199
1.830
1.816
1.802
1.631
1.193
^{1}H NMR (400 MHz, CDCl$_3$)
Cl
B
O
O
9.5 9.0 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 ppm
1.00
2.37
2.05
2.01
3.07
12.18

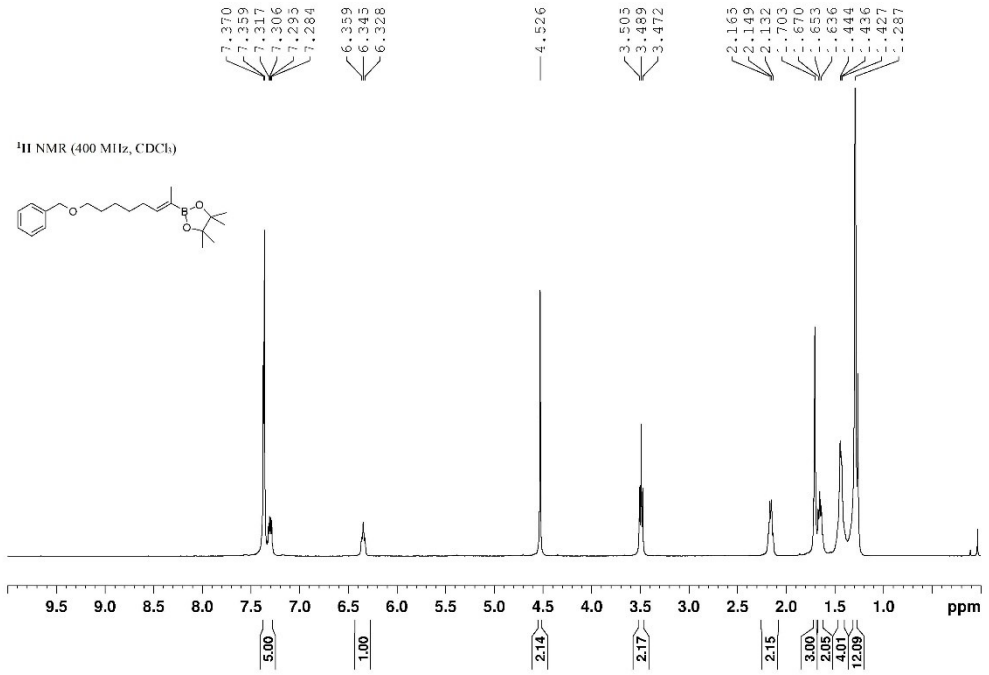

143.90
83.22
44.65
31.72
25.79
24.79
13.93
^{13}C NMR (100 MHz, CDCl$_3$)
Cl
B
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

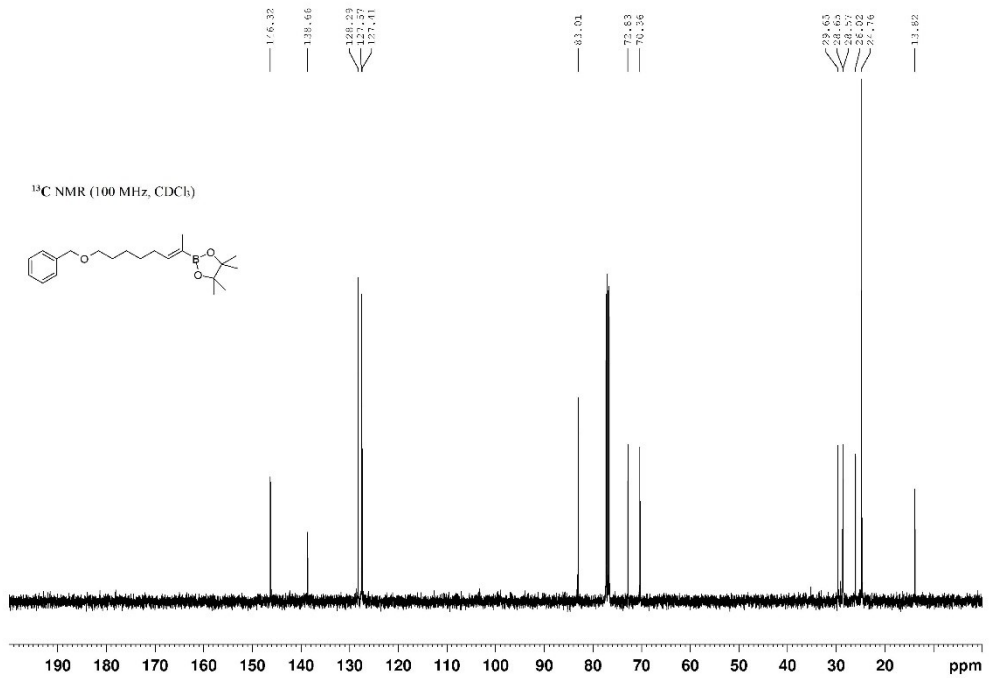
4f


6.328
6.316
6.303
5.765
5.753
5.593
3.655
3.642
3.629
2.165
2.152
2.138
2.123
1.680
1.597
1.583
1.568
1.555
1.447
1.433
1.417
1.399
1.386
1.368
1.267
¹H NMR (500 MHz, CDCl₃)
HO
B
O
9.5 9.0 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 ppm
1.00
0.06
0.06
2.31
2.05
3.03
2.15
4.20
12.11

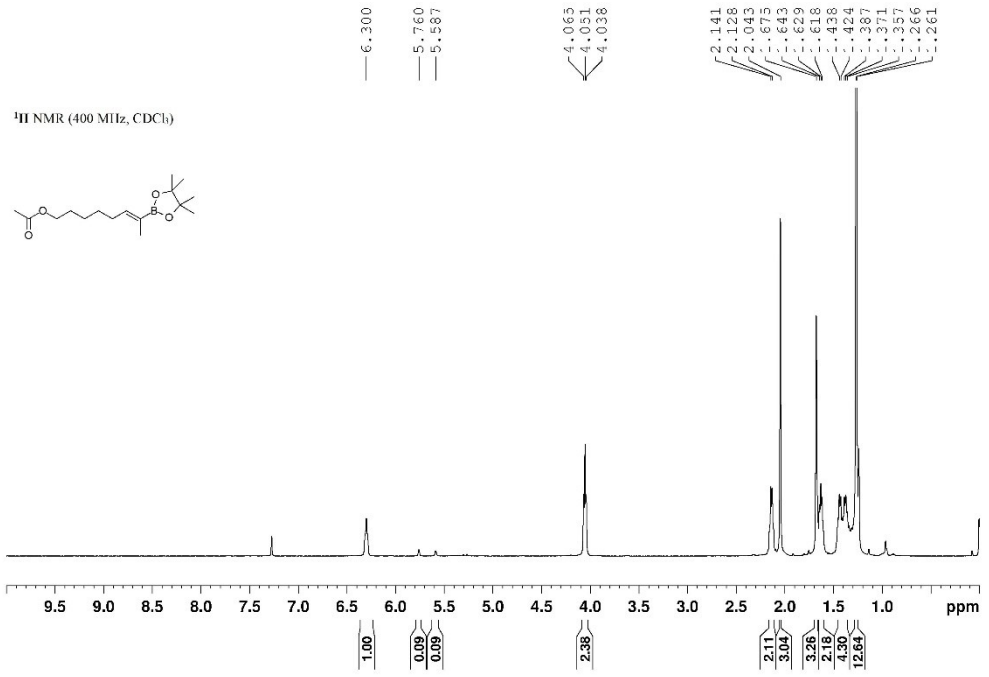

176.19
83.05
62.89
32.66
28.60
28.53
25.56
24.76
13.62
¹³C NMR (100 MHz, CDCl₃)
HO
B
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

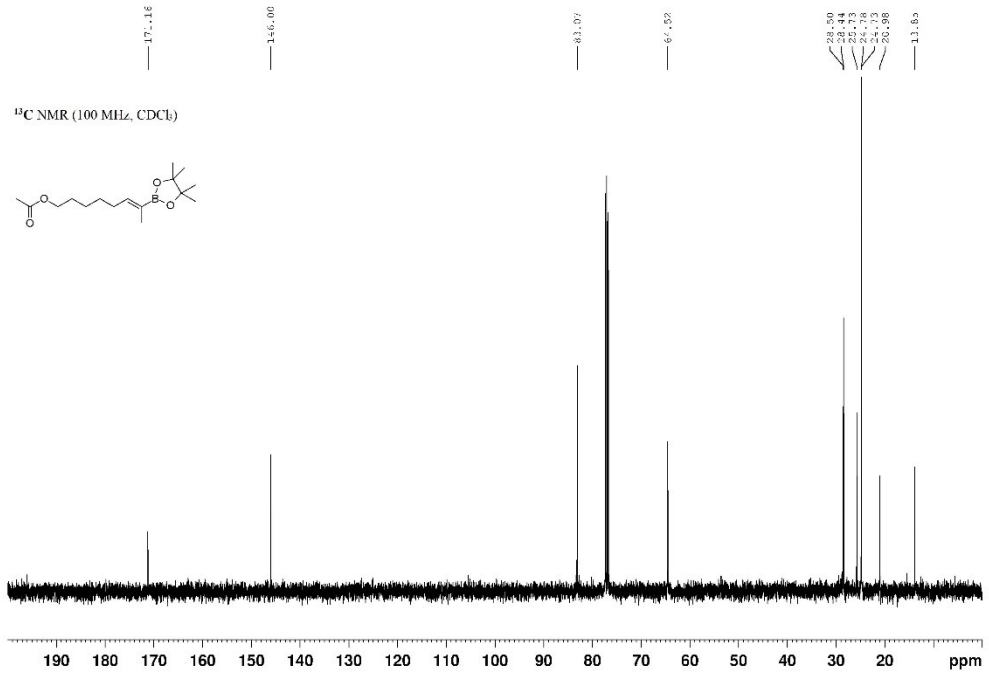
4g


7.370
7.359
7.317
7.306
7.295
7.284
6.359
6.345
6.328
4.526
3.505
3.489
3.472
2.165
2.149
2.132
1.703
1.670
1.653
1.636
1.444
1.436
1.427
1.287
^{1}H NMR (400 MHz, CDCl$_3$)
9.5 9.0 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 ppm
5.00
1.00
2.14
2.17
2.15
3.00
2.05
4.01
12.09

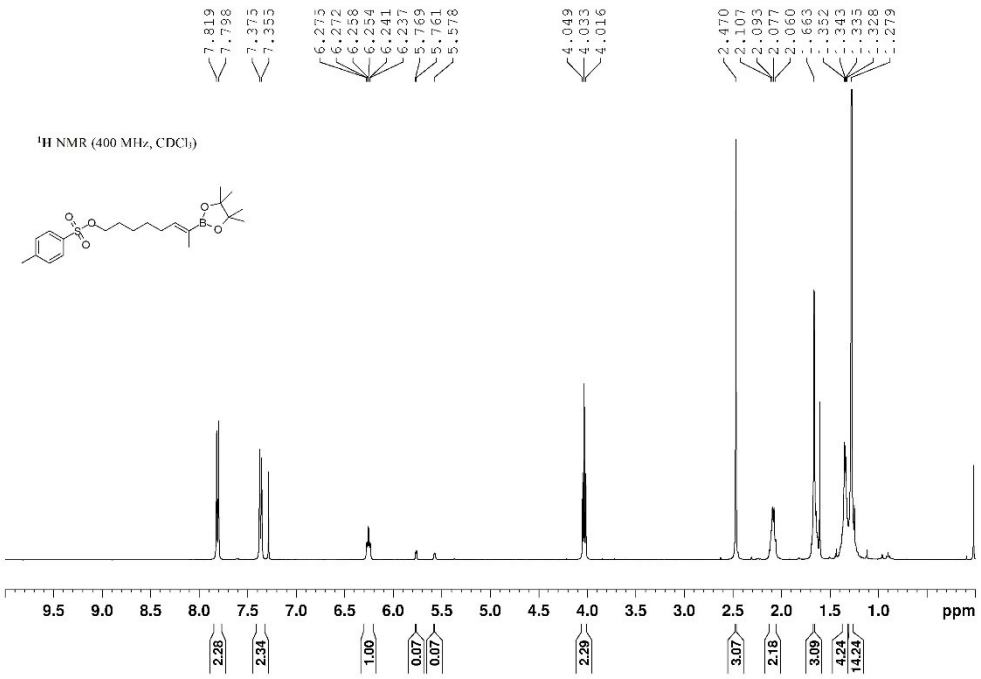

176.32
138.66
128.29
127.37
127.11
83.01
73.83
70.36
29.63
28.63
28.37
26.02
24.76
13.82
^{13}C NMR (100 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

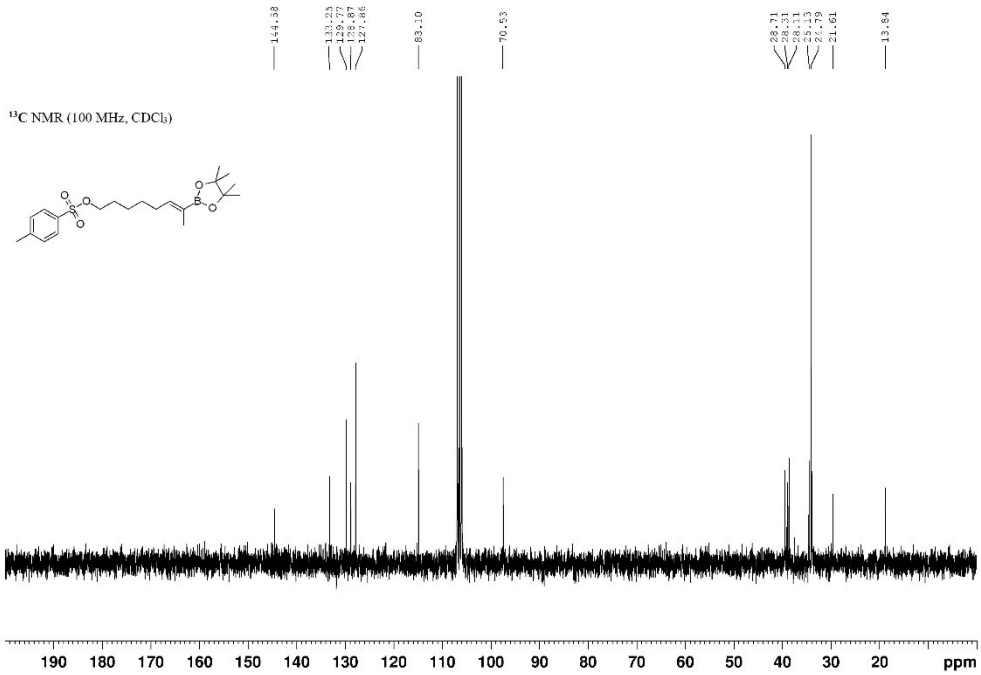
4h


6.300
5.760
5.587
4.065
4.051
4.038
2.141
2.128
2.043
1.675
1.643
1.629
1.618
1.438
1.424
1.387
1.371
1.357
1.266
1.261
¹H NMR (400 MHz, CDCl₃)
9.5 9.0 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 ppm
1.00
0.09
0.09
2.38
2.11
3.04
3.26
2.18
4.30
12.64

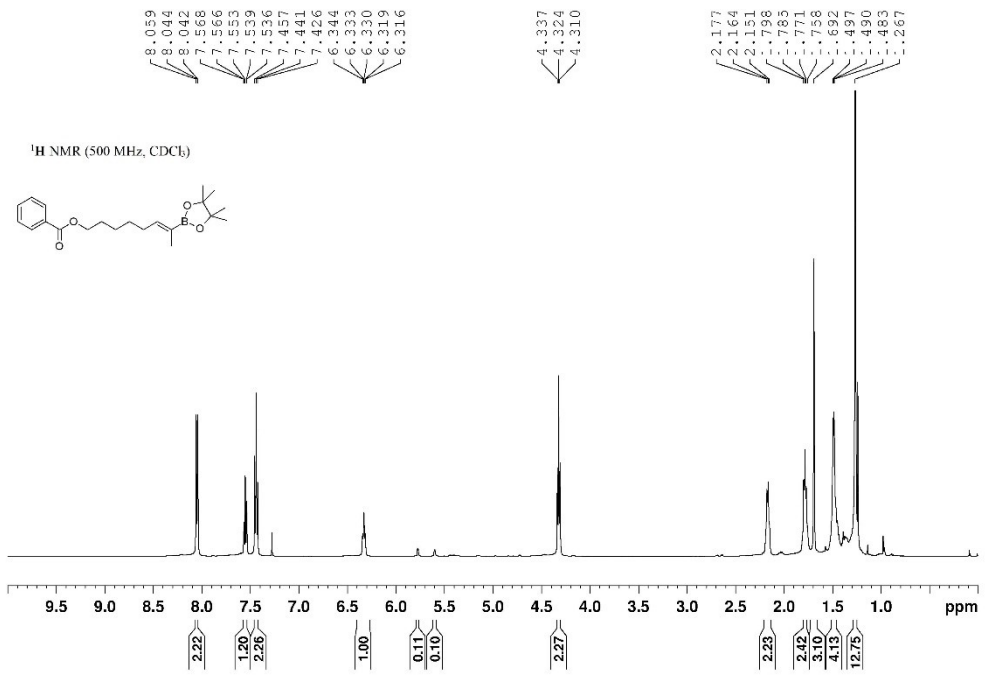

170.16
146.00
83.07
64.53
28.50
28.44
25.73
24.78
24.33
20.98
13.85
¹³C NMR (100 MHz, CDCl₃)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

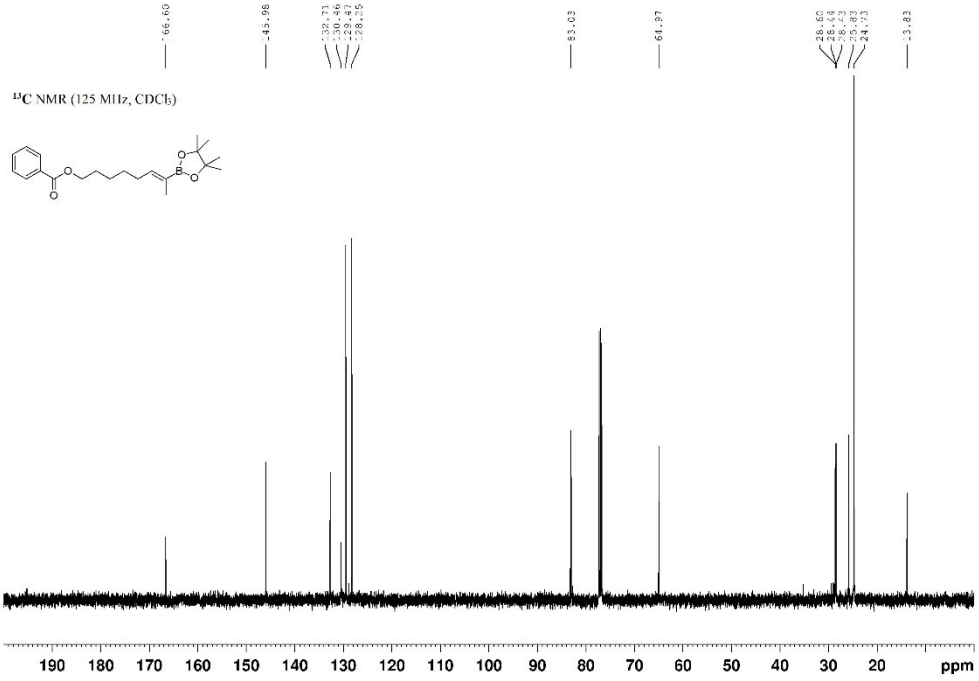
4i


7.819
7.798
7.375
7.355
6.275
6.272
6.258
6.254
6.241
6.237
5.769
5.761
5.578
4.049
4.033
4.016
2.470
2.107
2.093
2.077
2.060
1.663
1.352
1.343
1.335
1.328
1.279
¹H NMR (400 MHz, CDCl₃)
9.5 9.0 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 ppm
2.28
2.34
1.00
0.07
0.07
2.29
3.07
2.18
3.09
4.24
14.24

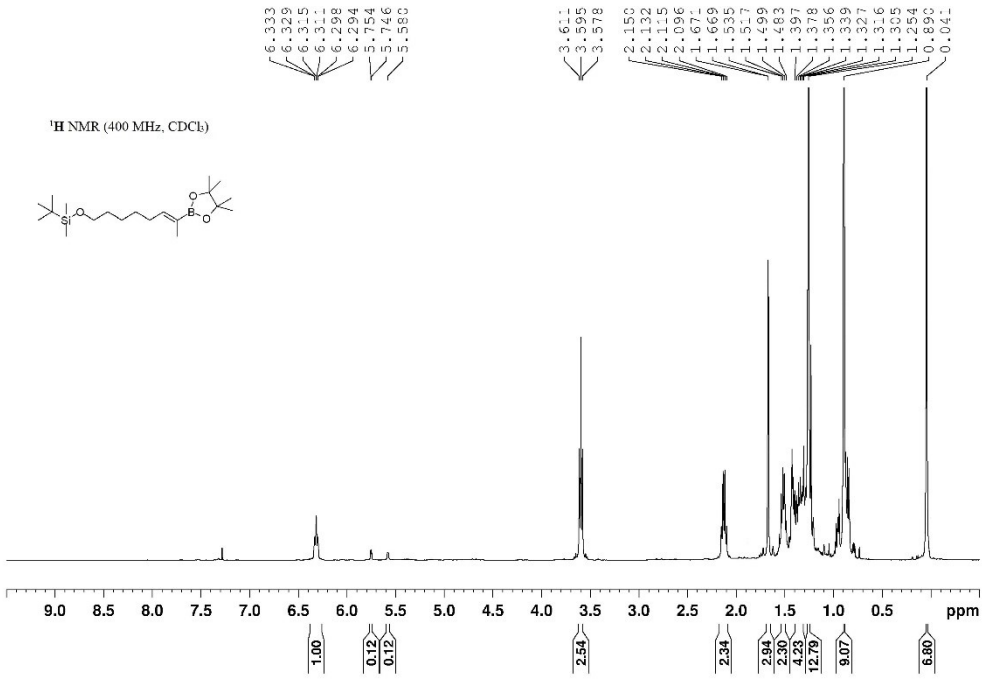

144.38
133.23
129.77
128.87
127.86
83.10
70.53
28.71
28.31
28.11
25.13
24.79
21.61
13.84
¹³C NMR (100 MHz, CDCl₃)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

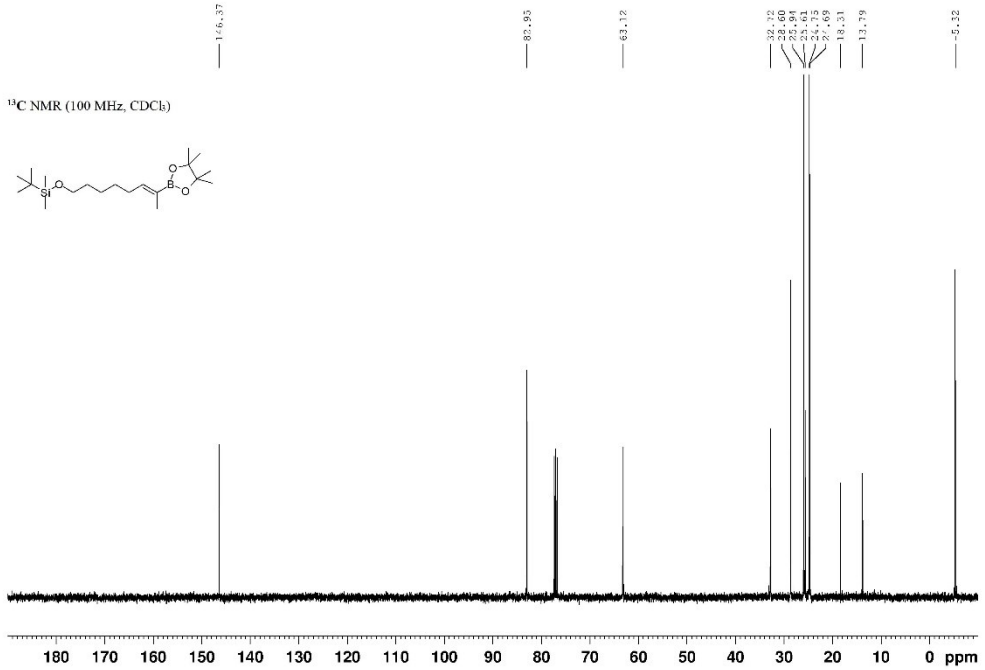
4j


8.059
8.044
8.042
7.568
7.566
7.553
7.539
7.536
7.457
7.441
7.426
6.344
6.333
6.330
6.319
6.316
4.337
4.324
4.310
2.177
2.164
2.151
1.798
1.785
1.771
1.758
1.692
1.497
1.490
1.483
1.267
¹H NMR (500 MHz, CDCl₃)
9.5 9.0 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 ppm
2.22
1.20
2.26
1.00
0.11
0.10
2.27
2.23
2.42
3.10
4.13
12.75


166.60
145.98
132.71
130.46
129.47
128.25
83.03
64.97
28.60
28.44
25.83
24.73
13.83
¹³C NMR (125 MHz, CDCl₃)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

4k


6.333
6.329
6.315
6.311
6.298
6.294
5.754
5.746
5.580
3.611
3.595
3.578
2.153
2.132
2.115
2.096
1.671
1.669
1.535
1.517
1.499
1.483
1.397
1.378
1.356
1.339
1.327
1.316
1.305
1.254
0.890
0.041
¹H NMR (400 MHz, CDCl₃)
9.0 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 ppm
1.00
0.12
0.12
2.54
2.34
2.94
2.30
4.23
12.79
9.07
6.80


146.37
82.95
63.12
32.72
28.60
25.94
25.81
24.75
24.69
18.31
13.79
-5.32
¹³C NMR (100 MHz, CDCl₃)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm