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SUPPORTING INFORMATION

Copper(II)-catalyzed Protoboration of Allenes in Aqueous Media and Open Air

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1. Materials and Methods

With the exception of the copper(II)-catalyzed allene borylation reactions, all reactions were performed under a nitrogen or argon atmosphere. Tetrahydrofuran, dichloromethane, dimethylformamide, and acetonitrile were obtained from an Innovative Technology Pure Solv-MD system. To ensure trace amounts of undesired transition metals were not present in the solvent for the allene borylation experiments, a Barnstead Easypure UV Compact Ultrapure Water System was used to obtain water for all borylation experiments and in preparation of the $CuSO_4$ solutions.

Commercially available reagents were used without further purification. Bis(pinacolato)diboron was purchased from Boron Molecular or donated by AllyChem.

Reactions were monitored through TLC analysis or GC analysis. TLC analyses were performed with EMD silica gel 60 F_{254} plates. Spots were visualized under UV light (254 nm or 365 nm) and with permanganate stain. NMR yields were taken in deuterated chloroform purchased with 0.05% v/v tetramethylsilane internal standard.

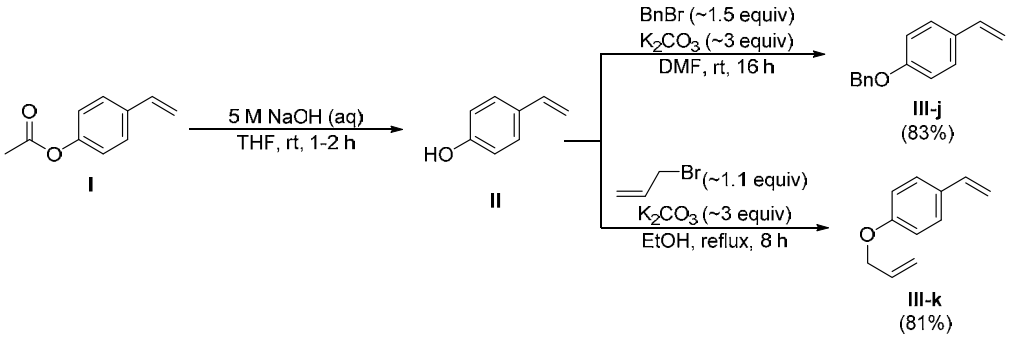
NMR spectra were obtained on Bruker 500 MHz spectrometer at 500 (^{1}H) and 125 (^{13}C) MHz or Unity-plus 400 at 400 (^{1}H) and 100 (^{13}C) MHz. Chemical shifts for proton and carbon spectra are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm for ^{1}H spectra and 77.16 ppm for ^{13}C spectra). The shift for boron-bound carbon atoms in the ^{13}C are typically not observed due to quadrupolar relaxation. Chemical shifts for ^{11}B spectra, which were taken in a quartz NMR tube, are reported in ppm with boron trifluoride diethyl etherate as an external standard (BF_3•Et_2O: 0 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, qt = quartet of triplets, tt = triplet of triplets, br = broad), coupling constants (Hz), and integration. High-resolution ESI mass spectra were obtained on an Agilent 6220 accurate mass TOF LC/MS, while low-resolution ESI mass

spectra were obtained on an Agilent 7890B GC System with an Agilent 5977A MSD. GC samples were injected with a 7963 Agilent autosampler system.

2. Substrate synthesis

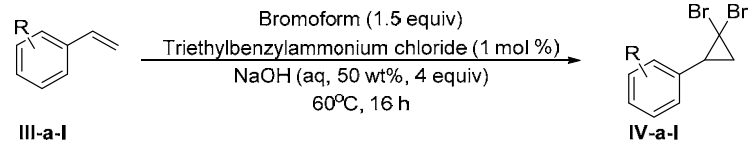
Cyclohexylallene (**1l**) was commercially available.

General procedure **1** for the non-commercially available styrenes **III-j** and **III-k**:



For styrenes **III-j** and **III-k**, the corresponding styrene was prepared through saponification of **I** followed by Williamson ether synthesis of **II** with either allyl bromide or benzyl bromide.[1]

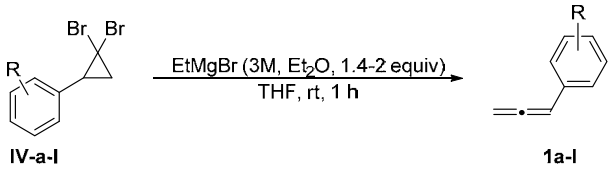
General Procedure **2** for the Synthesis of Dibromocyclopropane precursors **IV-a-l**:



Following the general procedure,[2] styrene (1.0 equiv), bromoform (1.5 equiv), and triethylbenzylammonium chloride (0.01 equiv) were added to a 25 mL round bottomed flask equipped with a stir bar. The flask was attached to a reflux condenser under nitrogen and heated to 60°C with stirring. An aqueous solution of NaOH (50 wt%, 4 equiv) was added semi-dropwise to the solution such that the temperature of the reaction was maintained. After addition of this solution, a dark purple and highly viscous reaction mixture was observed. The mixture was allowed to stir overnight (16 h).

The product mixture was quenched with water and extracted thrice with chloroform. The combined organic layers were dried over sodium sulfate and filtered. After removal of the solvent *in vacuo*, the remaining residue was purified by either flash chromatography (100% hexane) or Kugelrohr distillation to furnish the products as viscous oils.

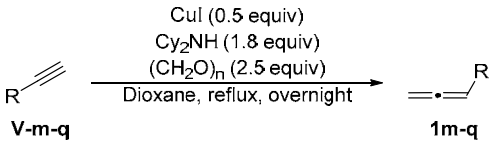
General Procedure **3A** for the Synthesis of Phenylallene Derivatives (**1a-l**):



Following the general procedure,[2] the dibromocylopropane precursor was dissolved in THF (0.5 M) and stirred under nitrogen. A solution of EtMgBr (3M in diethyl ether, 1.4-2 equiv) was added dropwise to the solution, which turned from clear to yellow. After completion of Grignard addition, the solution was allowed to stir until all dibromocyclopropane was consumed as monitored by TLC.

The reaction mixture was then quenched with water (added dropwise) and extracted with hexanes or petroleum ether thrice. The combined organic layers were dried over sodium sulfate, filtered, and removed *in vacuo* to furnish a yellow residue. This residue was then purified by a silica plug (eluting with hexanes) or flash column (again, eluting with hexanes) to furnish the pure allene.

General Procedure **3B** for the Synthesis of Allenes **1m-q** from Terminal Alkynes:

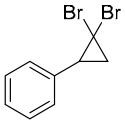


Following the general procedure,[3] paraformaldehyde (2.5 equiv), copper(I) iodide (0.5 equiv), dioxane, alkyne **V-m-q** (1.0 equiv), and dicyclohexylamine (1.8 equiv) were added to a round bottom flask equipped with a stirbar and attached to a reflux condenser under nitrogen.

The mixture was stirred overnight (16 h) at reflux during which time a dark solution formed. Deionized water was then added to the reaction mixture, and the mixture was extracted thrice with diethyl ether, dried over sodium sulfate, and filtered. The ether was removed *in vacuo* and the resulting residue was purified by flash chromatography (eluting with hexanes) to furnish the allene products as clear, viscous oils.

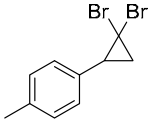
Characterization data of Dibromocyclopropane precursors **IV-a-k**:

(2,2-Dibromocyclopropyl)benzene (IV-a)



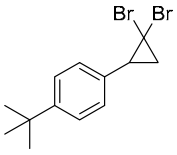
Synthesized by General Procedure **2** in 47% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[4]

1-(2,2-Dibromocyclopropyl)-4-methylbenzene (IV-b)



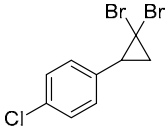
Synthesized by General Procedure **2** in 42% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[4]

1-(tert-Butyl)-4-(2,2-dibromocyclopropyl)benzene (IV-c)



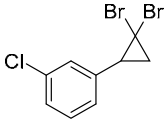
Synthesized by General Procedure **2** in 96% yield, isolated as a clear oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.22 – 7.14 (m, 2H), 2.93 (ddd, *J* = 10.5, 8.3, 0.8 Hz, 1H), 2.12 (dd, *J* = 10.6, 7.7 Hz, 1H), 1.99 (dd, *J* = 8.3, 7.7 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 133.1, 128.7, 125.3, 35.7, 34.7, 31.5, 29.0, 27.5.

1-Chloro-4-(2,2-dibromocyclopropyl)benzene (IV-d)



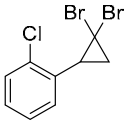
Synthesized by General Procedure **2** in 50% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[4]

1-Chloro-3-(2,2-dibromocyclopropyl)benzene (IV-e)



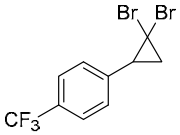
Synthesized by General Procedure **2** in 43% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[5]

1-Chloro-2-(2,2-dibromocyclopropyl)benzene (IV-f) Synthesized by General Procedure **2** in



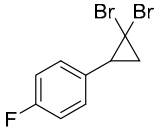
51% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[5]

1-(2,2-Dibromocyclopropyl)-4-(trifluoromethyl)benzene (IV-g)



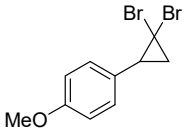
Synthesized by General Procedure **2** in 52% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[5]

1-(2,2-Dibromocyclopropyl)-4-fluorobenzene (IV-h)



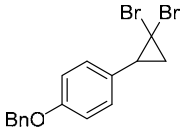
Synthesized by General Procedure **2** in 41% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[5]

1-(2,2-Dibromocyclopropyl)-4-methoxybenzene (IV-i)



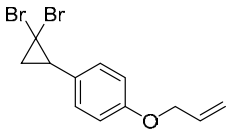
Synthesized by General Procedure **2** in 32% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[5]

1-(Benzyloxy)-4-(2,2-dibromocyclopropyl)benzene (IV-j)



Synthesized by General Procedure **2** in 84% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[6]

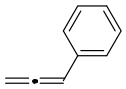
1-(Allyloxy)-4-(2,2-dibromocyclopropyl)benzene (IV-k):



Synthesized by General Procedure **2** in 15% yield, isolated as a clear liquid. Product contains ethyl acetate impurities as was taken forward crude in General Procedure **3A**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.12 – 5.94 (m, 1H), 5.40 (ddd, *J* = 17.2, 1.6, 0.5 Hz, 1H), 5.27 (dqd, *J* = 10.5, 1.4, 0.5 Hz, 1H), 4.52 (dt, *J* = 5.3, 1.5 Hz, 2H), 2.92 – 2.77 (m, 1H), 2.12 – 2.05 (m, 1H), 1.93 (dd, *J* = 8.3, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 133.3, 130.2, 130.1, 128.5, 117.9, 114.6, 69.00, 35.5, 29.4, 27.5.

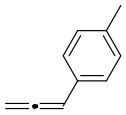
Characterization Data for Allenes **1a-q**:

Propa-1,2-dien-1-ylbenzene (1a):



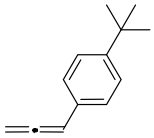
Synthesized by General Procedure **3A** in 40% yield as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[7]

1-Methyl-4-(propa-1,2-dien-1-yl)benzene (1b):



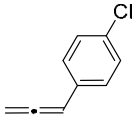
Synthesized by General Procedure **3A** in 82% yield as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[7]

1-(tert-Butyl)-4-(propa-1,2-dien-1-yl)benzene (1c):



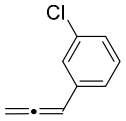
Synthesized by General Procedure **3A** in 95% yield. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[8]

1-Chloro-4-(propa-1,2-dien-1-yl)benzene (1d):



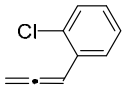
Synthesized by General Procedure **3A** in 97% yield as a clear oil in 82% yield as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[7]

1-Chloro-3-(propa-1,2-dien-1-yl)benzene (1e):



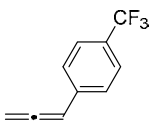
Synthesized by General Procedure **3A** in 69% yield, obtained as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[5]

1-Chloro-2-(propa-1,2-dien-1-yl)benzene (1f):



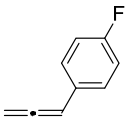
Synthesized by General Procedure **3A** in 95 % yield, obtained as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[5]

1-(Propa-1,2-dien-1-yl)-4-(trifluoromethyl)benzene (1g):



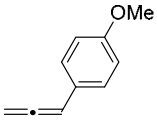
Synthesized by General Procedure **3A** in 57% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[5]

1-Fluoro-4-(propa-1,2-dien-1-yl)benzene (1h):



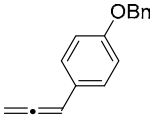
Synthesized by General Procedure **3A** in 60% yield, isolated as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[7]

1-Methoxy-4-(propa-1,2-dien-1-yl)benzene (1i):



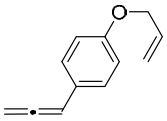
Synthesized by General Procedure **3A**, isolated in 56% yield as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[9]

1-(Benzyloxy)-4-(propa-1,2-dien-1-yl)benzene (1j):



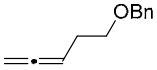
Synthesized by General Procedure **3A**, isolated as a clear oil in 83% yield. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[6]

1-(Allyloxy)-4-(propa-1,2-dien-1-yl)benzene (1k):



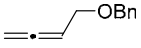
Synthesized by General Procedure **3A**, isolated in 74% yield as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 6.93 – 6.82 (m, 2H), 6.12 (t, *J* = 6.8 Hz, 1H), 6.05 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.41 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.29 (dq, *J* = 10.5, 1.4 Hz, 1H), 5.12 (dd, *J* = 6.8, 0.6 Hz, 2H), 4.53 (dt, *J* = 5.3, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 157.8, 133.4, 127.9, 126.4, 117.9, 115.1, 93.5, 78.9, 69.0.

((Penta-3,4-dien-1-yloxy)methyl)benzene (1m):



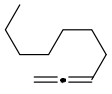
Synthesized by General Procedure **3B** in 94% yield, isolated as a yellow oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[10]

((Buta-2,3-dien-1-yloxy)methyl)benzene (1n):



Synthesized by General Procedure **3B**, isolated as a dark oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[11]

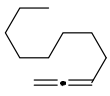
Deca-1,2-diene (1o):



Synthesized by General Procedure **3B** isolated in 15% yield as a clear oil. The terminal protons on the allene display a doublet of triplets due to both ^{4}J coupling and ^{5}J (homoallenic) coupling, the latter of which has been readily established in the literature

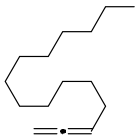
for allene ^{1}H spectra.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (p, *J* = 6.8 Hz, 1H), 4.65 (dt, *J* = 6.6, 3.2 Hz, 2H), 1.99 (ddt, *J* = 10.9, 6.7, 3.4 Hz, 2H), 1.47 – 1.18 (m, 10H), 0.98 – 0.81 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6, 90.27, 74.66, 32.00, 29.30, 29.27, 29.21, 28.43, 22.81, 14.26.

Undeca-1,2-diene (1p):



Synthesized by General Procedure **3B**, isolated in 35% yield as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[3b]

Pentadeca-1,2-diene (1q):

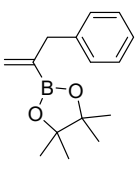


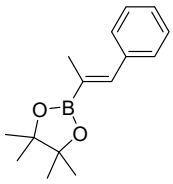
Synthesized by General Procedure **3B**, isolated in 89% yield as a clear oil. ^{1}H and ^{13}C NMR spectra are consistent with the literature.[13]

Characterization of Protoboration Products **2/3a-q**:

Isolated peaks in the ^{1}H and ^{13}C spectra corresponding solely to the minor isomer are labelled with an asterisk. In some instances, the highest quality spectrum was obtained after repurification of the borylation products. Because products **2a-q** degrade more rapidly than **3a-q**, the isomeric ratios in those spectra do not reflect the initial isomeric ratios, and a second ^{1}H spectrum is given in these cases to show the true ratios.

4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (2a) and (Z)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (3a):

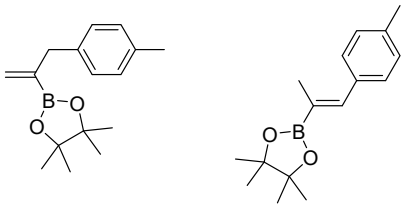




Synthesized by General Procedure **4**, isolated as an off yellow oil, 78% yield, 87:13 isomeric ratio **2a** to **3a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.04** (m, 5H), 5.76 (d, *J* = 2.8 Hz, 1H), 5.45 (s, 1H), 3.41 (s, 2H), 1.92* (d, *J* = 1.4 Hz, 3H), 1.23* (s, 12H), 1.13 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5*, 140.8, 129.9, 129.5*, 129.3, 129.3*, 128.2, 128.2*, 127.2*,

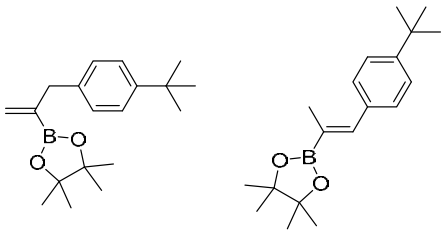
125.8, 83.6*, 83.6, 41.5, 25.0*, 24.8, 16.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.09. LRMS: (EI) $[M]^{+\cdot}$ Calcd for $C_{15}H_{21}BO_2$ 244.16, observed 244.1.

4,4,5,5-Tetramethyl-2-(3-(p-tolyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (2b) and (Z)-4,4,5,5-Tetramethyl-2-(1-(p-tolyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (3b):



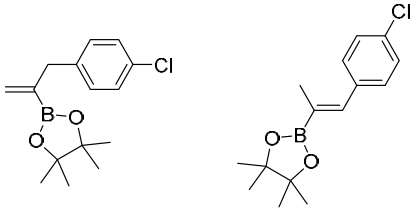
Synthesized by General Procedure **4**, isolated as an off yellow oil, 67% yield, 89:11 isomeric ratio of **2b** to **3b.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31* (d, *J* = 7.9 Hz, 2H), 7.23* (s, 1H), 7.17* (d, *J* = 7.8 Hz, 2H), 7.12 – 7.05 (m, 4H), 5.85 – 5.79 (m, 1H), 5.52 (s, 1H), 3.45 (s, 3H), 2.36* (s, 3H), 2.32 (s, 3H), 2.01* (s, 3H), 1.33* (s, 12H), 1.24 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5*, 137.7, 137.0*, 135.3*, 135.2, 129.8, 129.6*, 129.1, 128.9, 128.9*, 83.6, 83.6*, 41.00, 25.00*, 24.9, 21.4*, 21.1, 16.1*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.16. LRMS: (EI) $[M]^{+\cdot}$ Calcd for $C_{16}H_{23}BO_2$ 258.18, observed 258.3.

2-(3-(4-(tert-Butyl)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c) and (Z)-2-(1-(4-(tert-Butyl)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c):



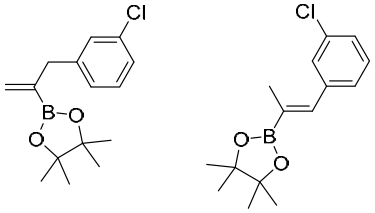
Synthesized by General Procedure **4**, isolated as off yellow oil, 47% yield, 90:10 isomeric ratio of **2c** to **3c**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33* (q, *J* = 8.6 Hz, 4H), 7.24 (d, *J* = 4.2 Hz, 2H), 7.18* (s, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 5.79 (s, 1H), 5.49 (s, 1H), 3.42 (s, 2H), 1.98* (s, 3H), 1.30* (s, 9H), 1.29* (s, 12H), 1.27 (s, 9H), 1.19 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2*, 148.6, 142.4*, 137.7, 129.8, 129.4*, 128.9, 125.1, 83.6, 40.9, 34.7*, 34.5, 31.6, 31.4*, 25.0*, 24.8, 16.2*.^{11}B NMR (128 MHz, $CDCl_3$) δ 30.07. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{19}H_{29}BO_2$ 300.23, observed 300.3.

2-(3-(4-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d) and (Z)-2-(1-(4-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d):



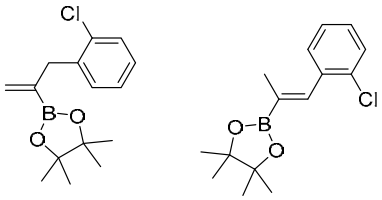
Synthesized by General Procedure **4**, isolated as yellow oil, 87% yield, 90:10 isomeric ratio **2d** to **3d**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31* (s, 4H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.17* (s, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 5.83 (s, 1H), 5.53 (s, 1H), 3.43 (s, 2H), 1.96* (s, 3H), 1.31 (s, 12H), 1.21 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1*, 139.4, 131.6, 130.8*, 130.6, 130.3, 128.4*, 128.3, 83.7, 41.00, 25.0*, 24.9, 16.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.92. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{15}H_{20}BClO_2$ 278.12, observed 278.1.

2-(3-(3-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e) and (Z)-2-(1-(4-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e):



Synthesized by General Procedure **4**, isolated as yellow oil, 62% yield, 89:11 isomeric ratio **2e** to **3e**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 6.96 (m, 4H), 5.77 (d, *J* = 2.3 Hz, 1H), 5.48 (s, 1H), 3.36 (s, 2H), 1.92 – 1.86* (m, 3H), 1.23* (s, 12H), 1.13 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 140.9*, 133.9, 130.5, 129.4, 129.4, 127.6*, 127.4, 127.2*, 126.0, 83.7, 41.4, 25.0*, 24.8, 16.0*. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{15}H_{20}BClO_2$ 278.12, observed 278.1.

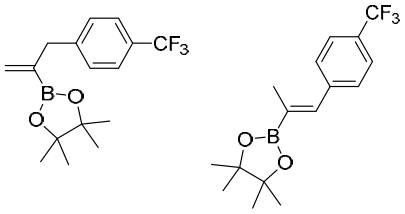
2-(3-(2-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f) and (Z)-2-(1-(2-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f):



Synthesized by General Procedure **4**, isolated as yellow oil, 87% yield, 90:10 isomeric ratio **2f** to **3f.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.12** (m, 4H), 5.92 (s, 1H), 5.47 (s, 1H), 3.62 (s, 2H), 1.89* (s, 3H), 1.35 (s, 12H), 1.27 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4*,

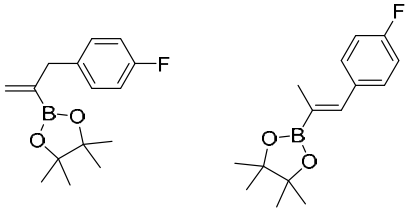
138.41, 136.2*, 134.5, 133.7*, 131.3, 130.8*, 130.7, 129.5*, 129.4, 128.4*, 127.4, 126.6, 126.1*, 83.7, 38.2, 25.00*, 24.9, 16.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.05. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{15}H_{20}BClO_2$ 278.12, observed 278.1.

4,4,5,5-Tetramethyl-2-(3-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (2g) and (Z)-4,4,5,5-Tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (3g)



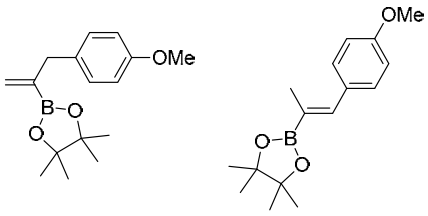
Synthesized by General Procedure **4**, isolated as a yellow oil, 19% yield, 93:7 isomeric ratio **2g** to **3g**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 5.80 (d, *J* = 3.0 Hz, 1H), 5.48 (d, *J* = 3.4 Hz, 1H), 3.45 (s, 2H), 1.90* (d, *J* = 1.9 Hz, 3H), 1.24* (s, 12H), 1.13 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 129.7, 128.3, 127.1 (q, *J* = 32.2 Hz), 124.5 (q, *J* = 271.7 Hz), 124.00 (q, *J* = 3.8 Hz), 82.6, 40.2, 28.7, 23.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.80. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{16}H_{20}BF_3O_2$ 312.15, observed 312.1.

2-(3-(4-Fluorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h) and (Z)-2-(1-(4-Fluorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h):



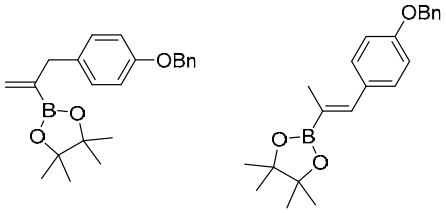
Synthesized by General Procedure **4**, isolated as a yellow oil, 19% isolated yield, 50% NMR yield, 83:17 isomeric ratio **2h** to **3h**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31* (m, 2H), 7.18* (s, 1H), 7.17 – 7.12 (m, 2H), 7.03* (t, *J* = 8.6 Hz, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 5.82 (s, 1H), 5.53 (s, 1H), 3.44 (s, 2H), 1.97* (s, 3H), 1.31* (s, 12H), 1.20 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5 (d, *J* = 243.0 Hz), 141.3, 136.5 (d, *J* = 3.0 Hz), 131.2* (d, *J* = 8.1 Hz), 130.6 (d, *J* = 7.7 Hz), 130.0, 114.9 (d, *J* = 20.9 Hz), 100.2*, 83.7, 40.8, 25.0*, 24.8, 15.9*.^{11}B NMR (128 MHz, $CDCl_3$) δ 29.98. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{15}H_{20}BFO_2$ 262.15, observed 262.3.

2-(3-(4-Methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i) and (Z)-2-(1-(4-Methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i):



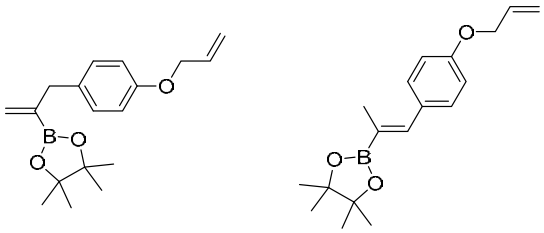
Synthesized by General Procedure **4**, isolated as an off yellow oil, 46% yield, 67:33 isomeric ratio **2i** to **3i**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32* (m, 2H), 7.18* (d, *J* = 1.8 Hz, 1H), 7.14 – 7.05 (m, 2H), 6.92 – 6.85* (m, 2H), 6.85 – 6.77 (m, 2H), 5.81 (dt, *J* = 3.3, 1.2 Hz, 1H), 5.51 (dt, *J* = 3.4, 1.6 Hz, 1H), 3.82* (s, 3H), 3.78 (s, 3H), 3.42 (d, *J* = 1.4 Hz, 2H), 2.00* (d, *J* = 1.7 Hz, 3H), 1.31* (s, 12H), 1.21 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8*, 157.9, 142.1*, 132. 9, 131.1*, 130.9, 130.2*, 129.6, 113.7, 113.6*, 83.6, 83.5*, 55.4, 55.4*, 40.6, 25.00*, 24.8, 16.1*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.21. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{16}H_{23}BO_3$ 274.17, observed 274.3.

2-(3-(4-(Benzyloxy)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j) and (Z)-2-(1-(3-(Benzyloxy)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j):



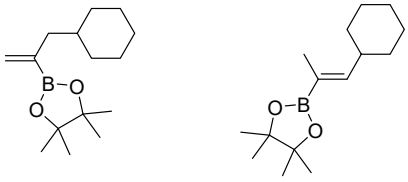
Synthesized by General Procedure **4**, isolated as white solid, 37%, 66:34 isomeric ratio **2j** to **3j**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.30** (m, 5H from **2j** and 7H from **3j**), 7.20* (s, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.97* (d, *J* = 8.1 Hz, 0H), 6.90 (d, *J* = 7.8 Hz, 2H), 5.82 (s, 1H), 5.53 (s, 1H), 5.08* (s, 2H), 5.05* (s, 2H), 3.44 (s, 2H), 2.02* (s, 3H), 1.32* (s, 12H), 1.22 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0*, 157.1, 142.0*, 137.4, 137.1*, 133.2, 131.1*, 131.1*, 130.2, 129.6, 128.7*, 128.7, 128.1*, 128.0, 127.7*, 127.6, 114.7, 114.5*, 83.6, 83.6*, 70.2, 70.1*, 40.7, 25.0*, 24.8, 16.1*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.13. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{22}H_{27}BO_3$ 350.21, observed 350.3.

2-(3-(4-(Allyloxy)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k) and (Z)-2-(1-(4-(Allyloxy)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k):



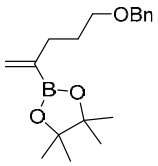
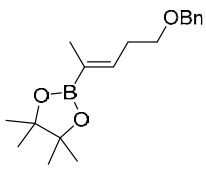
Synthesized by General Procedure **4**, isolated as an off yellow oil, 49% yield, 75:25 isomeric ratio. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35* (d, *J* = 8.6 Hz, 2H), 7.17* (s, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.89* (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.06** (ddq, *J* = 15.7, 10.3, 5.0 Hz, 1H), 5.81 – 5.79 (m, 1H), 5.51 (s, 1H), 5.41** (dd, *J* = 17.2, 10.3 Hz, 1H), 5.28** (t, *J* = 11.6 Hz, 1H), 4.55* (d, *J* = 5.2 Hz, 2H), 4.51 (d, *J* = 5.2 Hz, 2H), 3.41 (s, 2H), 1.99* (s, 3H), 1.31* (s, 12H), 1.21 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7*, 156.8, 141.9*, 133.6, 133.3, 133.0, 130.9*, 130.0, 129.4, 117.7*, 117.4, 114.4, 114.3*, 83.44, 83.4*, 68.9, 68.8*, 40.5, 24.8*, 24.7, 15.9*. ^{11}B NMR (128 MHz, cdcl$_3$) δ 30.02. HRMS: (ESI) $[M+H]^+$ Calcd for $C_{18}H_{25}BO_3$ 301.20, observed 301.1968.

2-(3-Cyclohexylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l) and (Z)-2-(1-Cyclohexylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l):



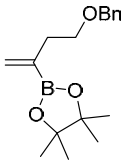
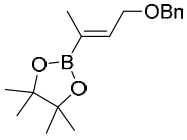
Synthesized by General Procedure **4**, isolated as a yellow oil, 84% yield, 78:22 isomeric ratio **2l** to **3l**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.11* (d, *J* = 8.7 Hz, 1H), 5.81 – 5.70 (m, 1H), 5.53 (s, 1H), 2.43 – 2.26* (m, 1H), 2.03 (d, *J* = 6.8 Hz, 2H), 1.74-1.58 (m, 6H), 1.25 (s, 12H), 1.22-1.05 (m, 3H), 0.84 (q, *J* = 11.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9*, 130.0, 83.4, 83.1*, 43.4, 37.8, 37.7*, 33.3, 32.4*, 26.8, 26.6, 26.3*, 26.1*, 25.0*, 24.8, 14.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.16. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{15}H_{27}BO_2$ 250.21, observed 250.3.

2-(5-(Benzyloxy)pent-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m) and (Z)-2-(5-(Benzyloxy)pent-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m):

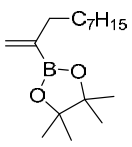
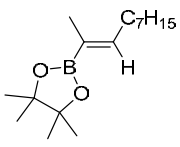
Synthesized by General Procedure **4**, isolated as a yellow oil, 34%, 93:7 isomeric ratio **2m** to **3m**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 5H), 6.38 – 6.28* (m, 1H), 5.79 (d, *J* = 3.3 Hz, 1H), 5.64 – 5.60 (m, 1H), 4.53* (s, 2H), 4.50 (s, 2H), 3.54 (t, *J* = 7.2 Hz, 2H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.48* (q, *J* = 7.0 Hz, 2H), 2.24 (t, *J* = 7.6 Hz, 2H), 1.77 (dt, *J* = 14.1, 6.8 Hz, 2H), 1.71* (s, 3H), 1.26 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9*, 138.8, 138.6*, 129.5, 128.5*, 128.4, 127.8, 127.6, 127.6*, 83.6, 83.3, 73.0*, 72.9, 70.2, 69.3*, 32.0, 29.5*, 29.3, 24.9*, 24.9, 14.2*. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{18}H_{27}BO_3$ 302.21, observed 302.3.

2-(4-(Benzyloxy)but-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n) and (Z)-2-(4-(Benzyloxy)but-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n):

Synthesized by General Procedure **4**, isolated as a yellow oil, 53%, 72:18 isomeric ratio **2n** to **3n**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 5H), 6.48* (tq, *J* = 5.8, 1.7 Hz, 1H), 5.85 (dt, *J* = 3.5, 0.9 Hz, 1H), 5.70 (dt, *J* = 3.3, 1.4 Hz, 1H), 4.53* (s, 2H), 4.52 (s, 2H), 4.17 (dq, *J* = 5.8, 1.1 Hz, 2H), 3.56 (t, *J* = 7.0 Hz, 2H), 2.49 (tt, *J* = 7.0, 1.1 Hz, 3H), 1.69* (dd, *J* = 1.8, 0.9 Hz, 3H), 1.26* (s, 12H), 1.24 (s, 12H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 141.9*, 138.8, 131.2, 128.5*, 128.4, 127.9*, 127.8, 127.7*, 127.5, 83.5, 72.8, 72.6*, 70.1, 67.1*, 35.9, 24.93*, 24.9, 14.5*. LRMS: (EI) $[M]^{+\cdot}$Calcd. for $C_{17}H_{25}BO_3$ 288.19, observed 288.3.

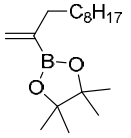
2-(Dec-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o) and (Z)-2-(Dec-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o):

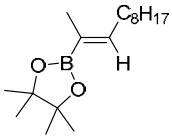



Synthesized by General Procedure **4**, isolated as a yellow oil, 48%. Isomeric ratio **2o** to **3o** is 74:26. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 6.31* (t, *J* = 5.9 Hz, 1H), 5.83 – 5.68 (m, 1H), 5.58 (s, 1H), 2.12 (q, *J* = 7.3 Hz, 2H), 1.66* (s, 3H), 1.26 (s, 24H), 0.87 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8*, 128.8, 83.4, 83.2*, 35.5, 32.1, 32.0*, 29.9*, 29.7, 29.6, 29.4, 29.4, 29.0*, 28.9*, 25.0*, 24.9, 22.8, 14.2, 14.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.16. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{16}H_{31}BO_2$ 266.24, observed 266.3.

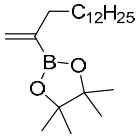
4,4,5,5-Tetramethyl-2-(undec-1-en-2-yl)-1,3,2-dioxaborolane (2p) and (Z)-4,4,5,5-Tetramethyl-2-(undec-2-en-2-yl)-1,3,2-dioxaborolane (3p):

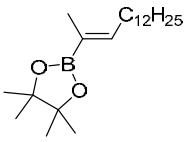




Synthesized by General Procedure **4**, isolated as a yellow oil, 50% yield, 84:16 isomeric ratio **2p** to **3p**. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.31* (t, *J* = 6.0 Hz, 1H), 5.74 (s, 1H), 5.57 (s, 1H), 2.12 (t, *J* = 7.4 Hz, 2H), 1.66* (s, 3H), 1.43-1.20 (m, 26H), 0.87 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8*, 128.8, 83.4, 83.2*, 35.5, 32.1, 29.9*, 29.7, 29.7, 29.7*, 29.7*, 29.5, 29.4, 29.4, 29.0*, 28.9*, 24.9*, 24.9, 22.8, 14.2, 14.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.13. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{17}H_{33}BO_2$ 280.26, observed 280.4.

4,4,5,5-Tetramethyl-2-(pentadec-1-en-2-yl)-1,3,2-dioxaborolane (2q) and (Z)-4,4,5,5-Tetramethyl-2-(pentadec-2-en-2-yl)-1,3,2-dioxaborolane (3q):





Synthesized by General Procedure 4, yellow oil, 75% yield, 83:17 isomeric ratio **2q** to **3q**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.32* (d, *J* = 6.4 Hz, 1H), 5.74 (s, 1H), 5.57 (s, 1H), 2.12 (t, *J* = 7.4 Hz, 2H), 1.66* (s, 3H), 1.44 – 1.16 (m, 34H), 0.87 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8*, 128.8, 83.4, 83.1*, 35.5, 32.1, 29.9, 29.8, 29.8, 29.7, 29.5, 29.4, 29.4, 29.0, 28.9, 24.9*, 24.9, 22.8, 14.2, 14.0 *. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.15. LRMS: (EI) $[M]^{+\cdot}$Calcd for $C_{21}H_{41}BO_2$ 336.32, observed 336.4.

3. References

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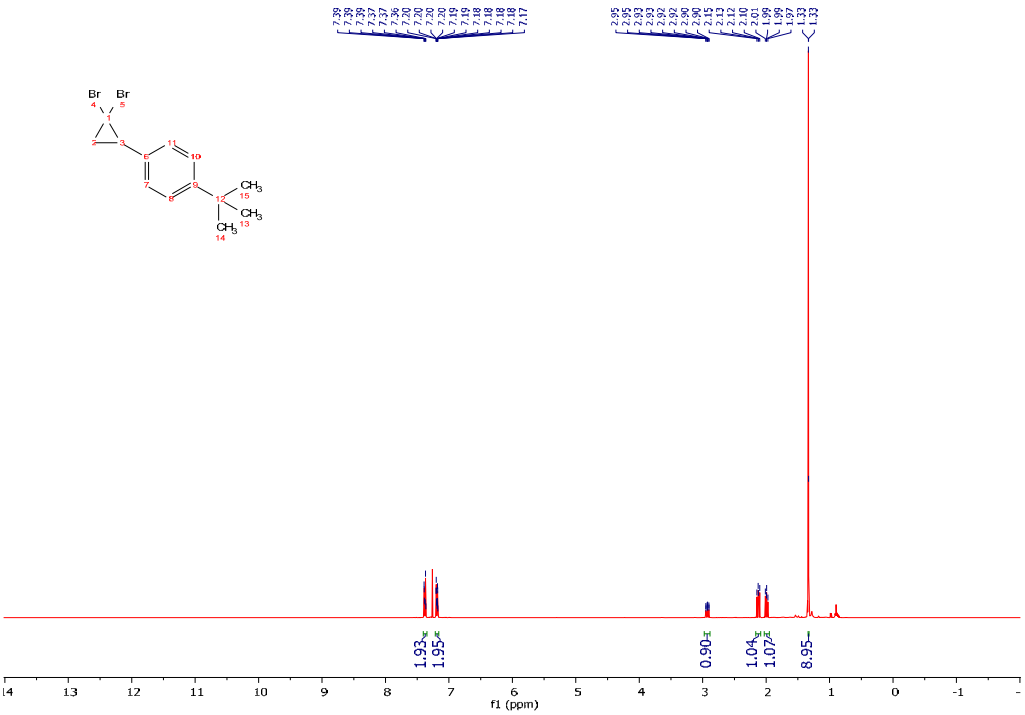
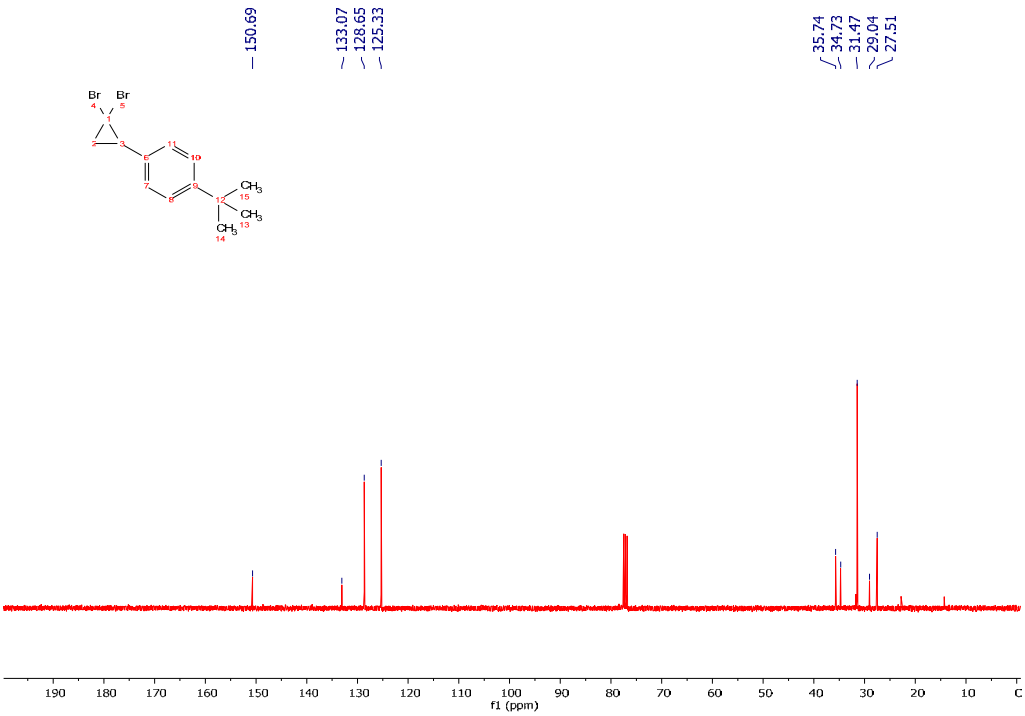
4. NMR Spectra

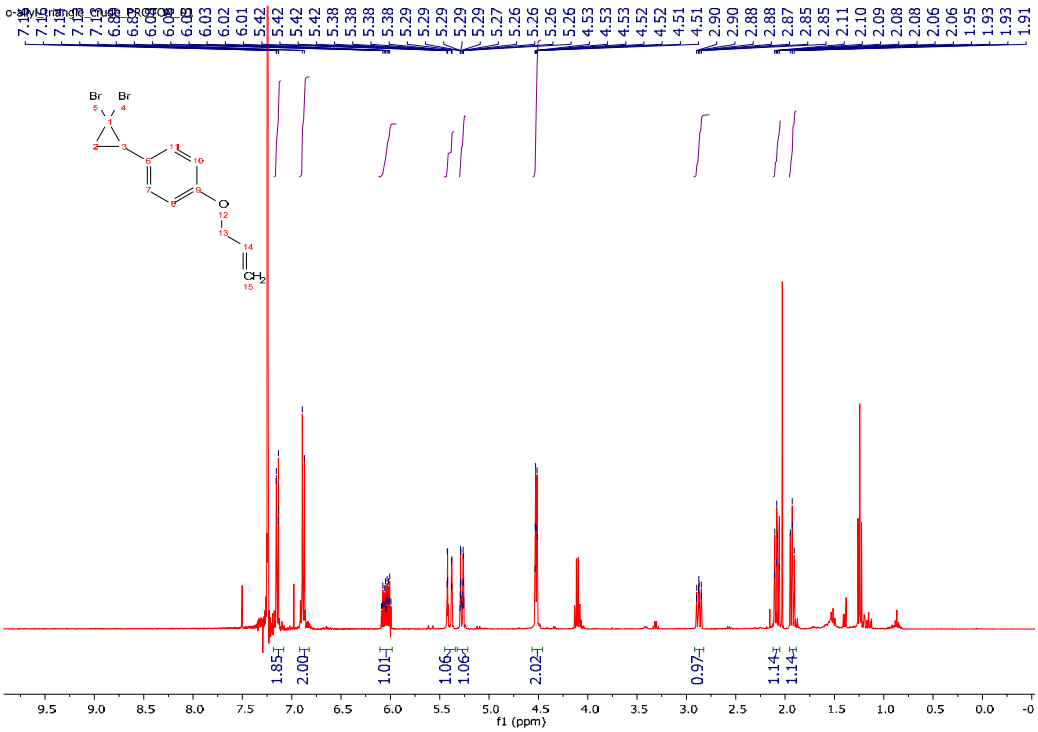
^{1}H NMR spectra of **IV-c**



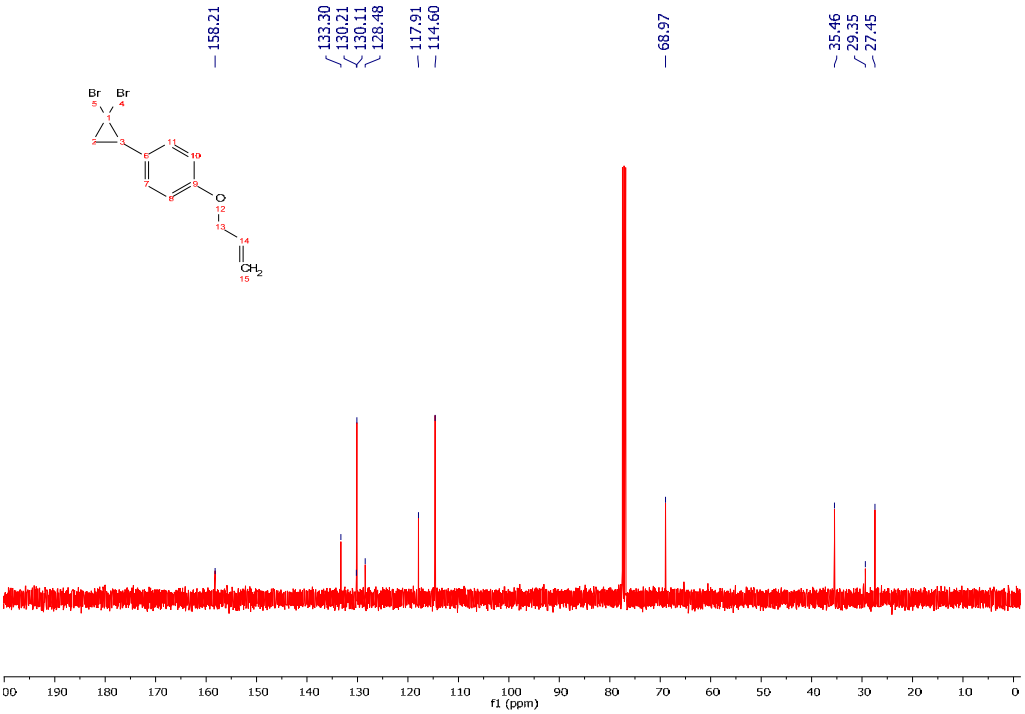
^{13}C NMR spectra of **IV-c**



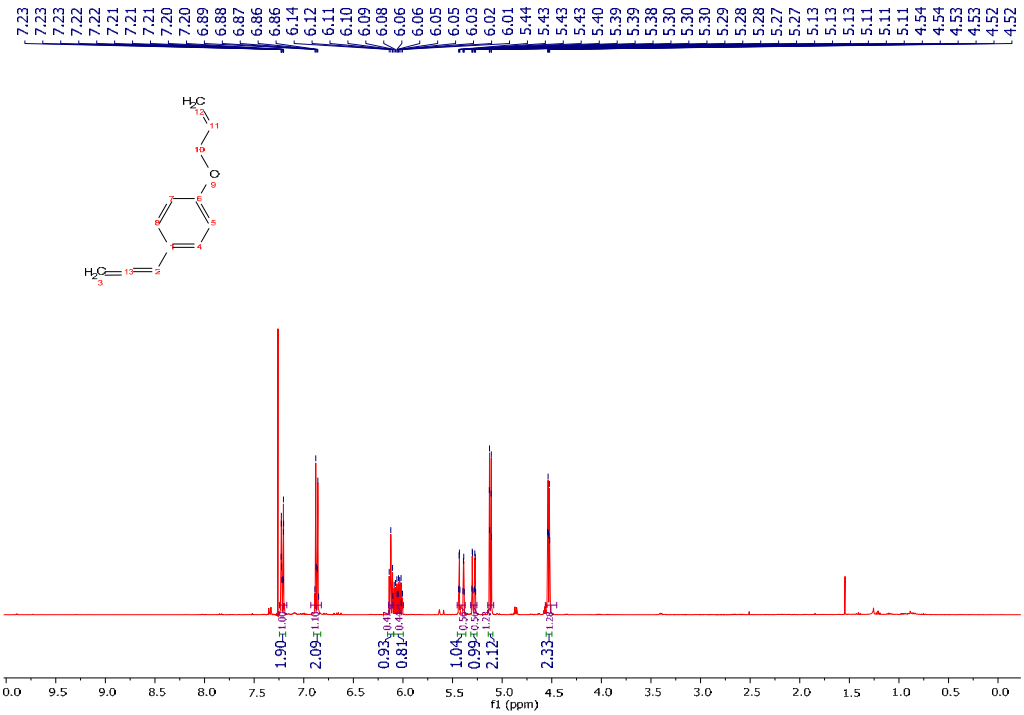
^{1}H NMR spectra of **IV-k**



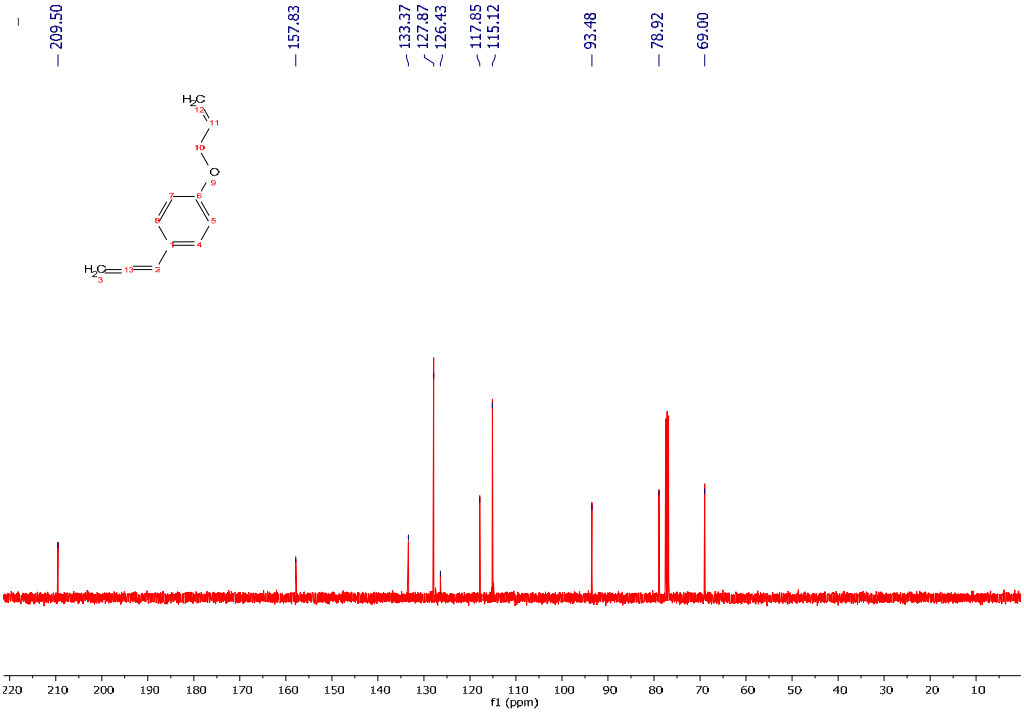
^{13}C NMR spectra of **IV-k**



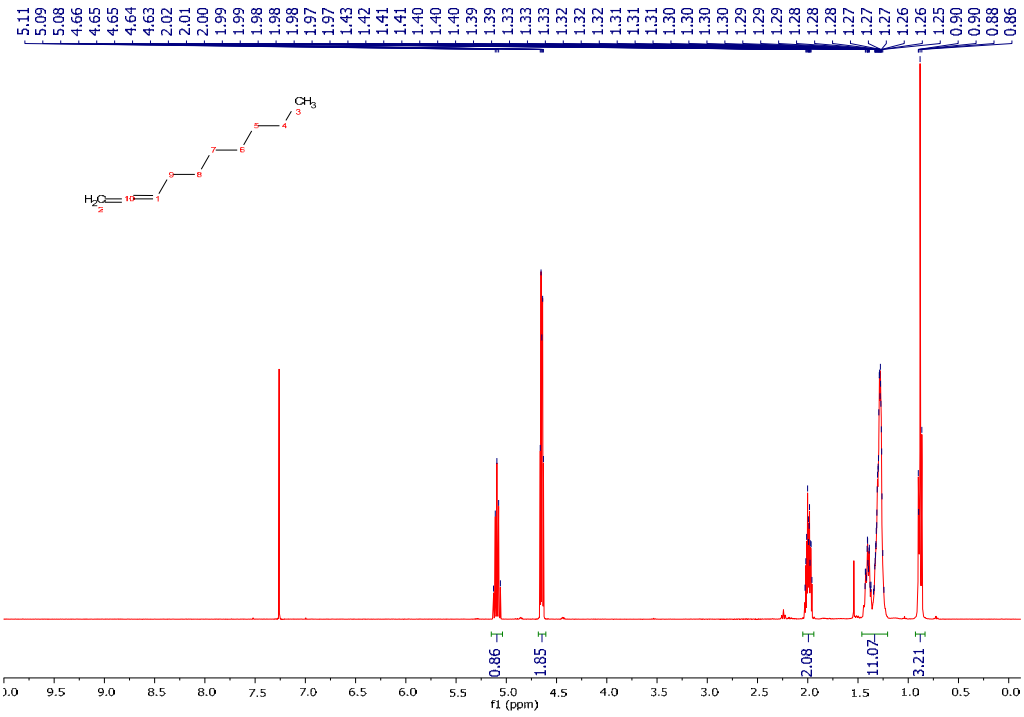
^{1}H NMR spectra of **1k**



^{13}C NMR spectra of **1k**



^{1}H NMR spectra of **1o**



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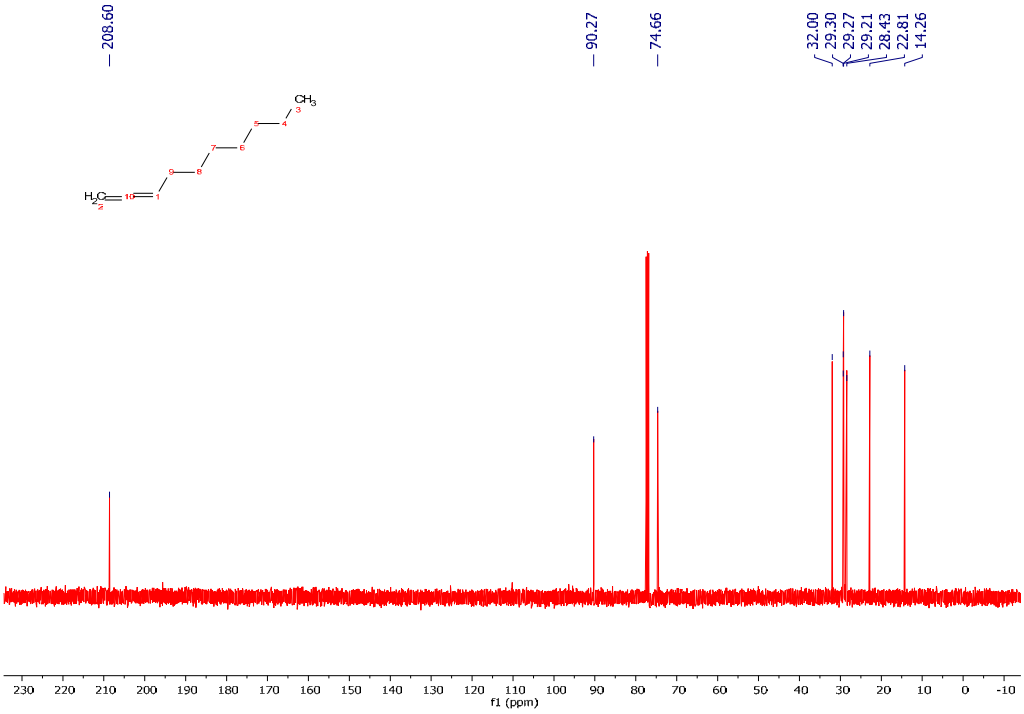
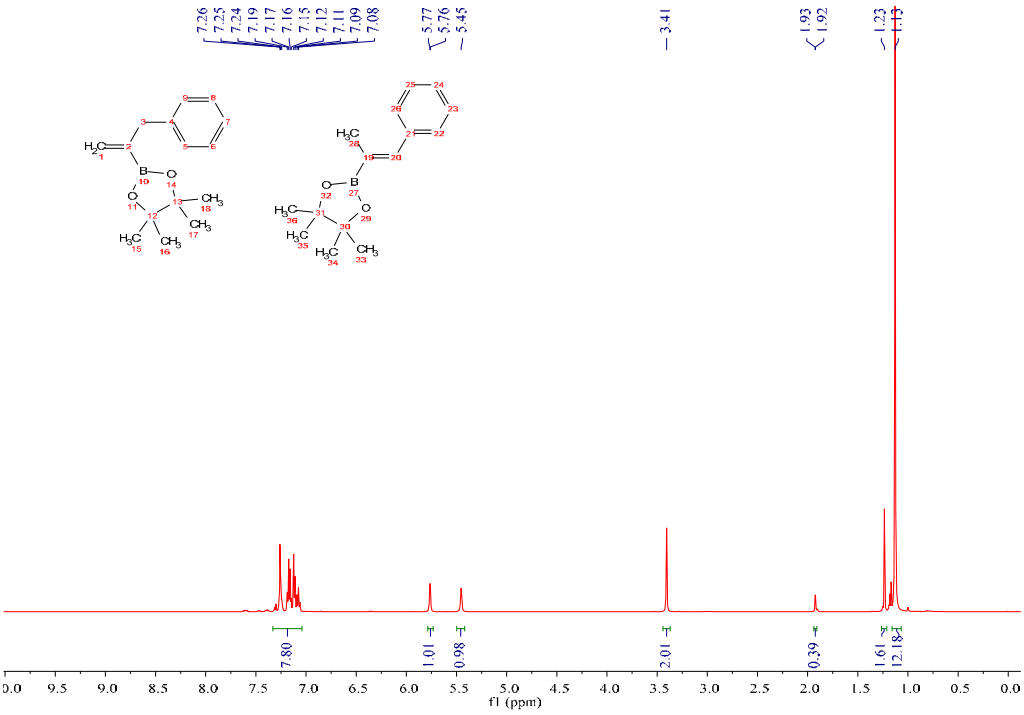


^{1}H NMR Spectra of **2/3a**



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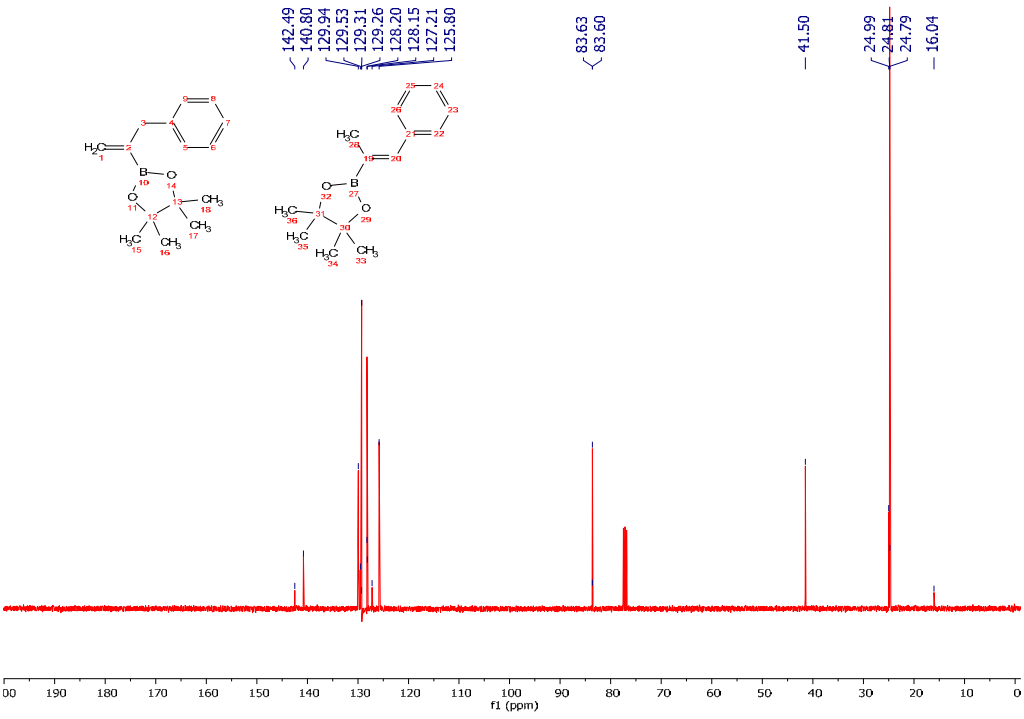
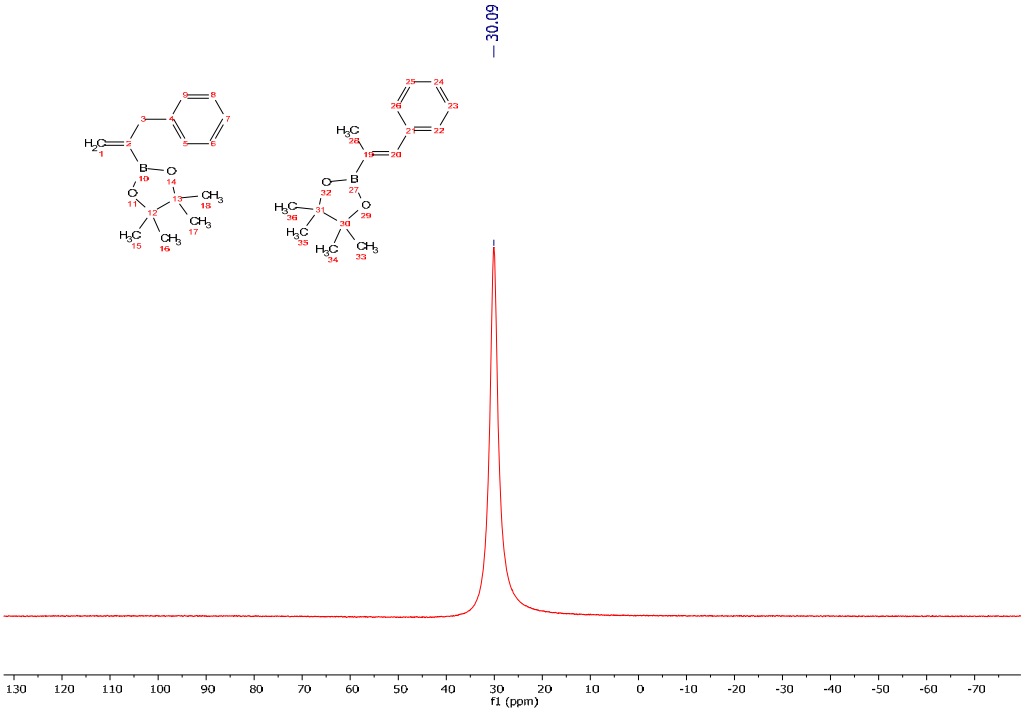
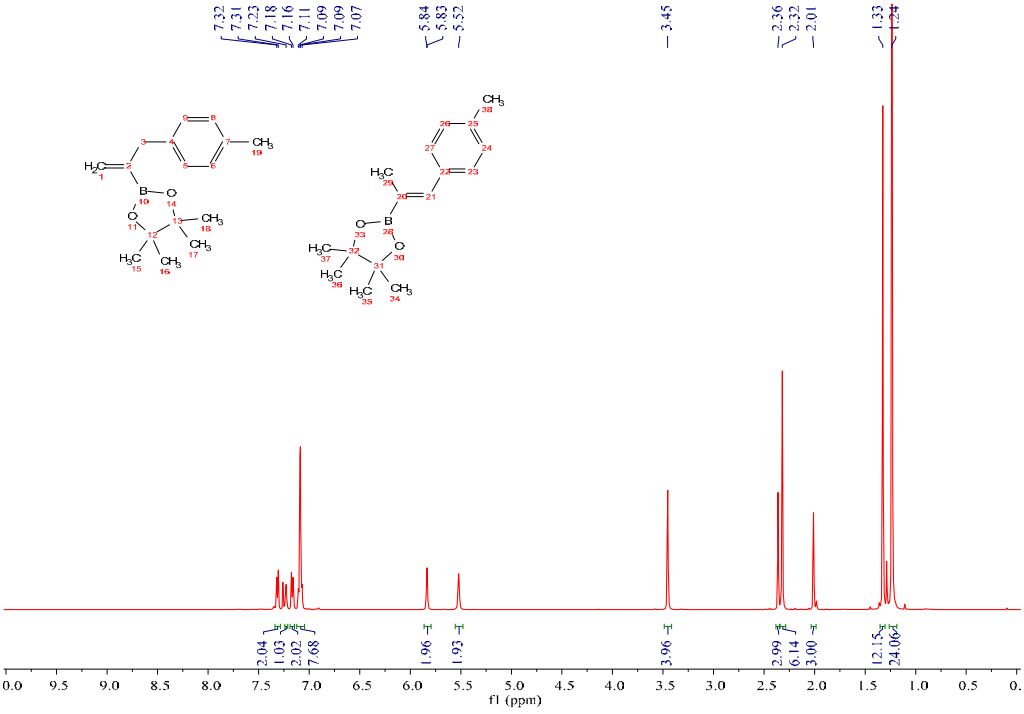


^{11}B NMR Spectra of **2/3a**



^{1}H NMR Spectra of **2/3b**



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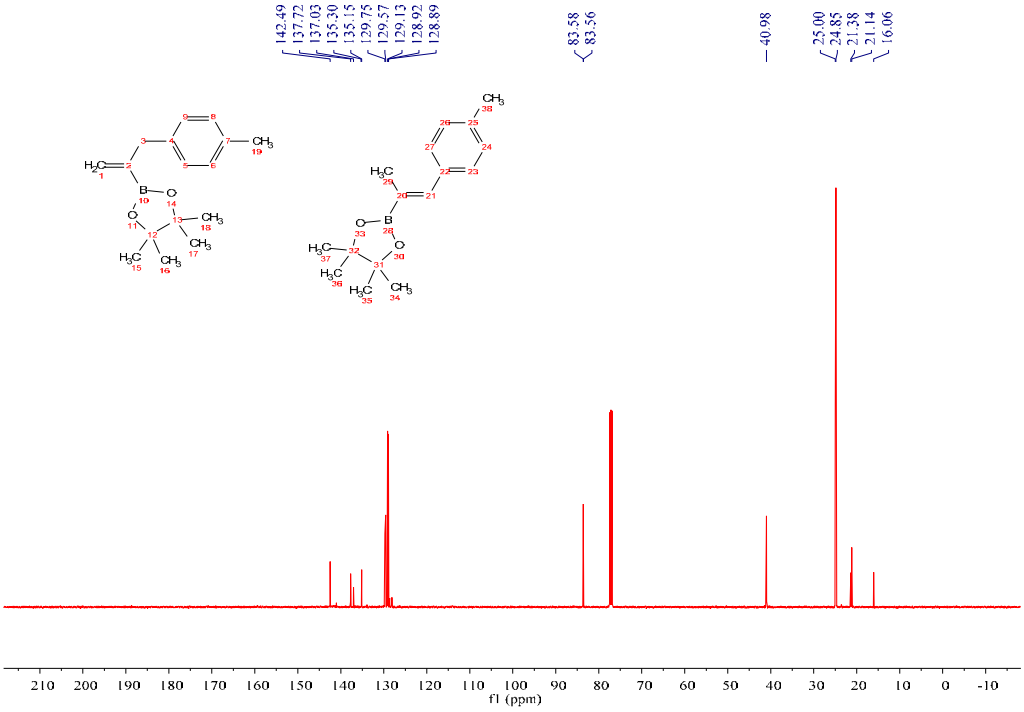

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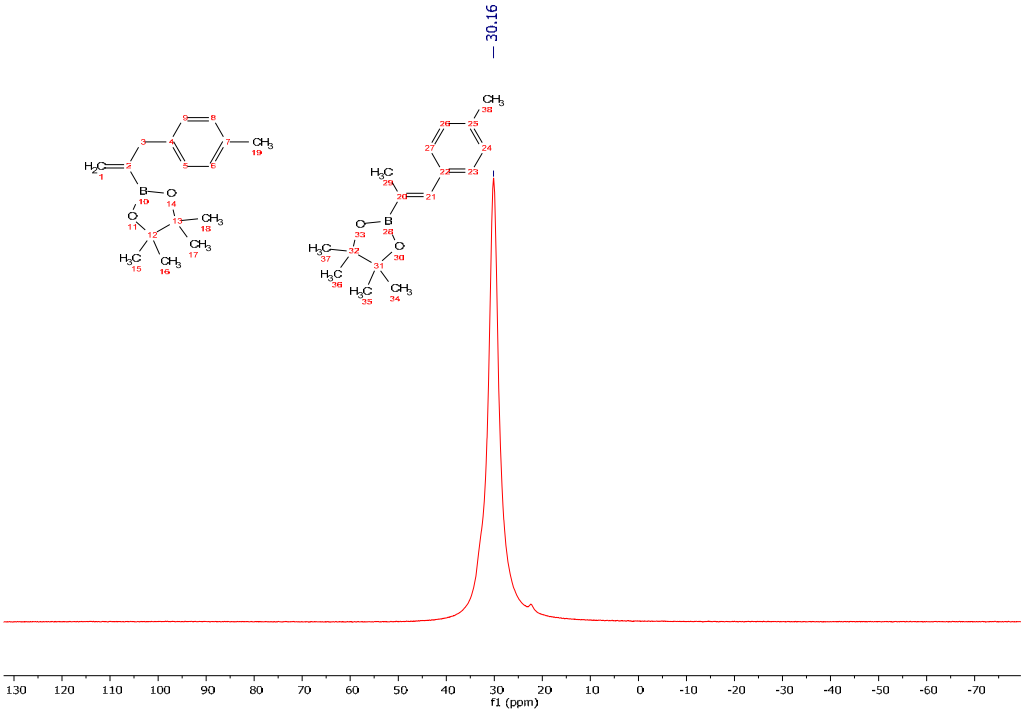

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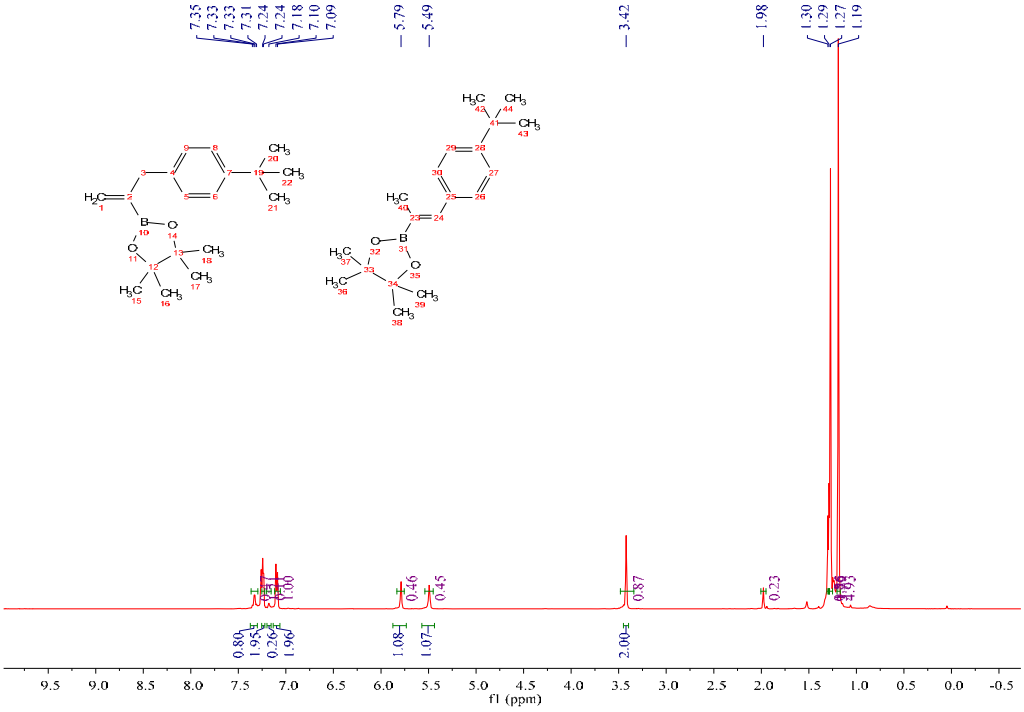

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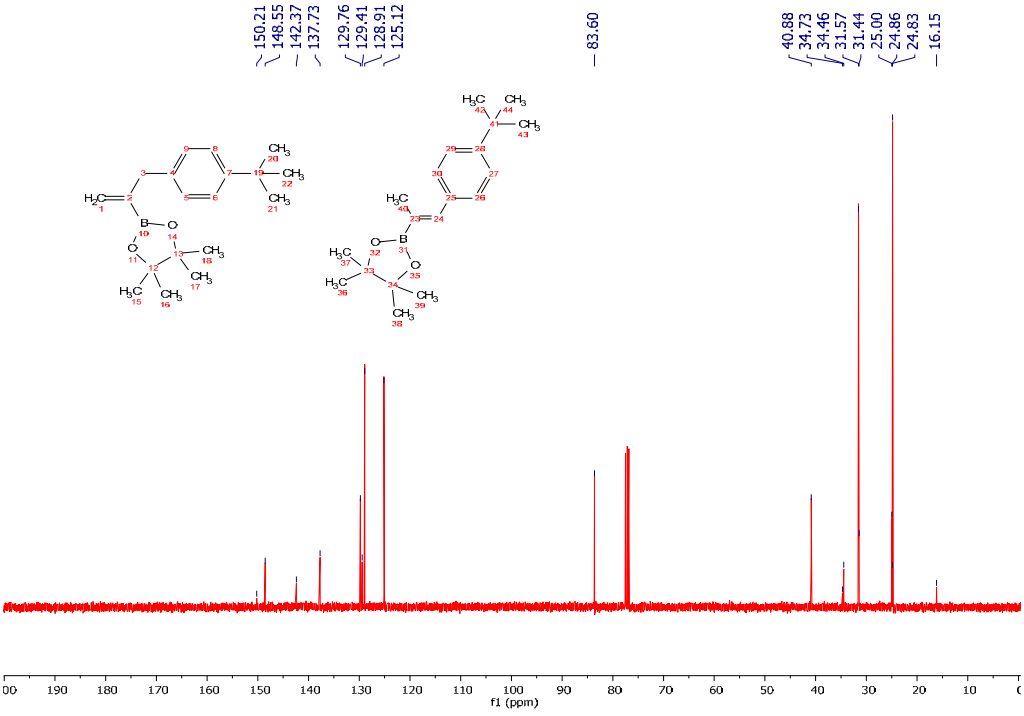

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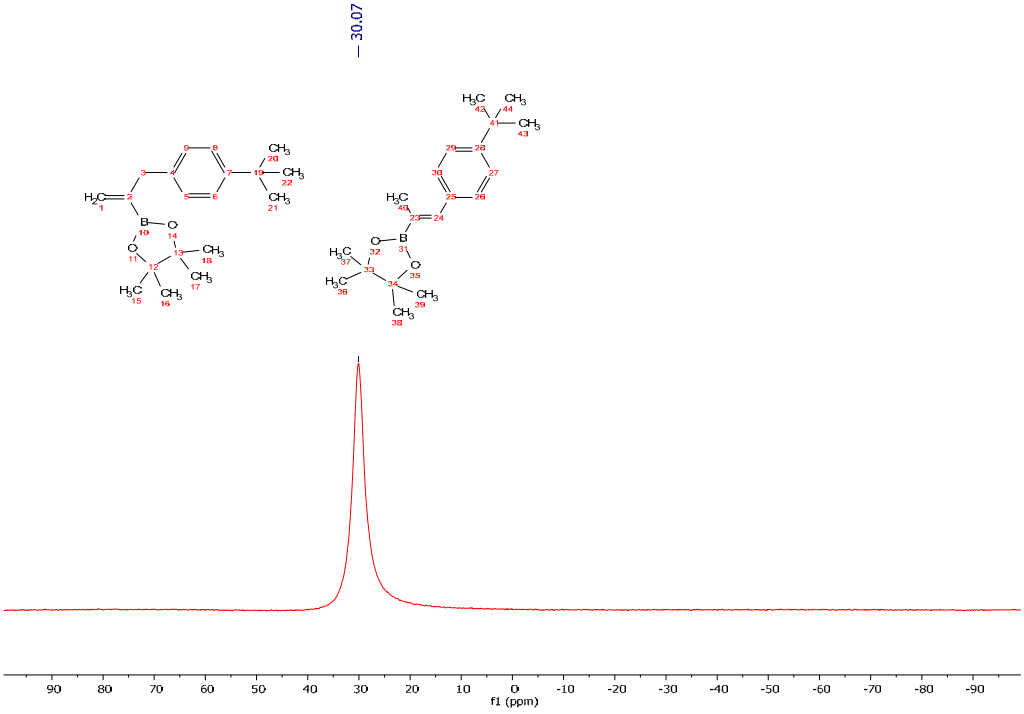

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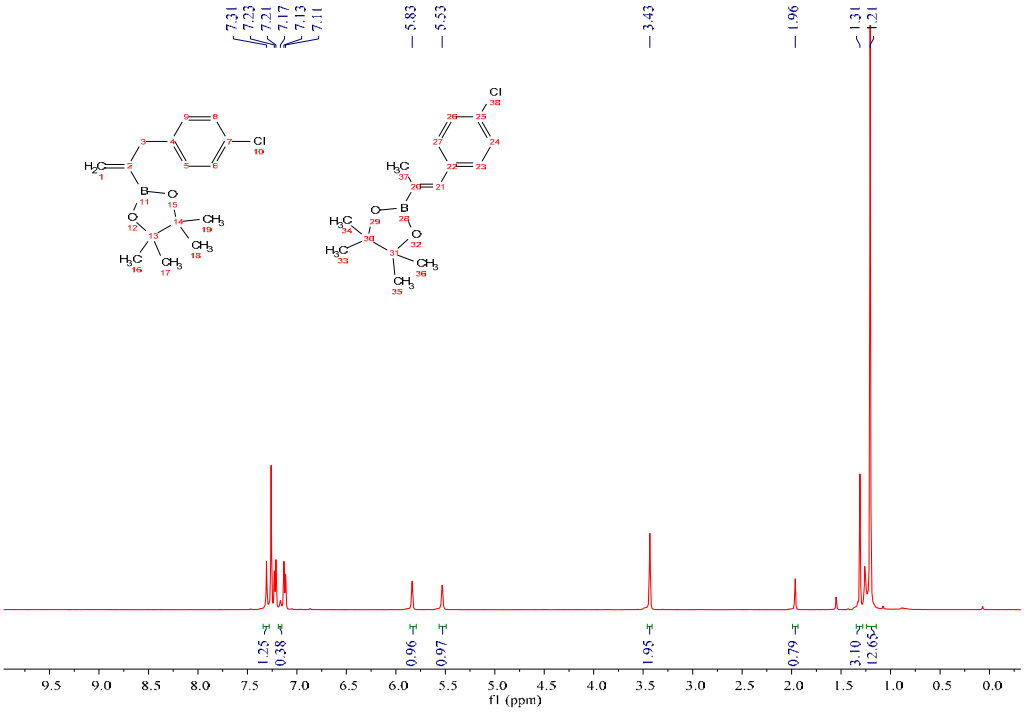

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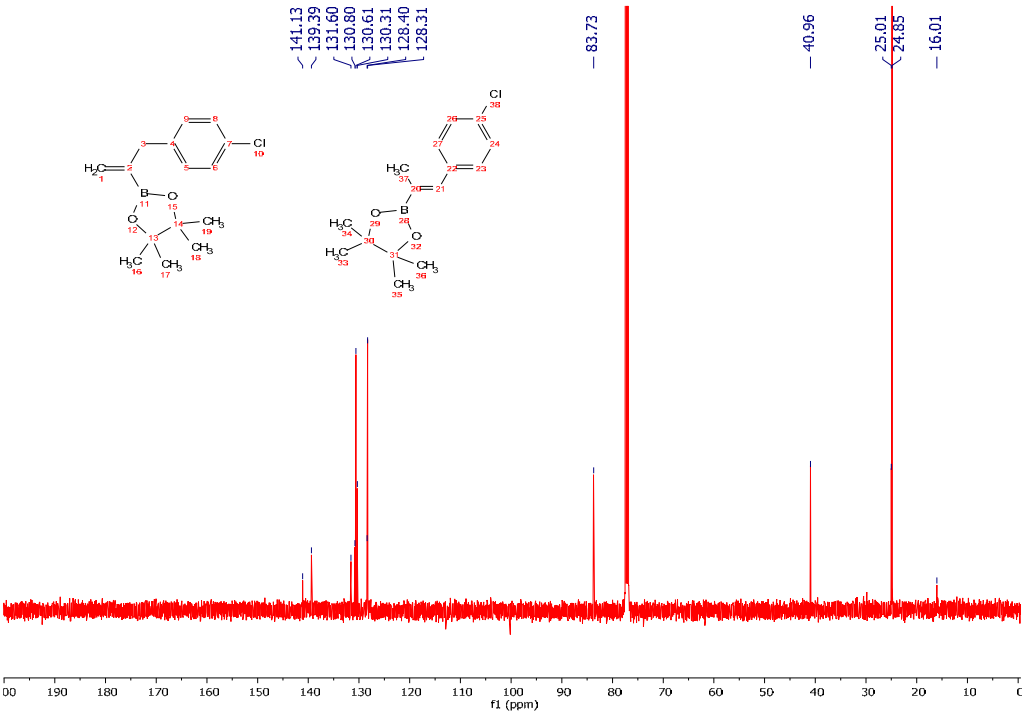

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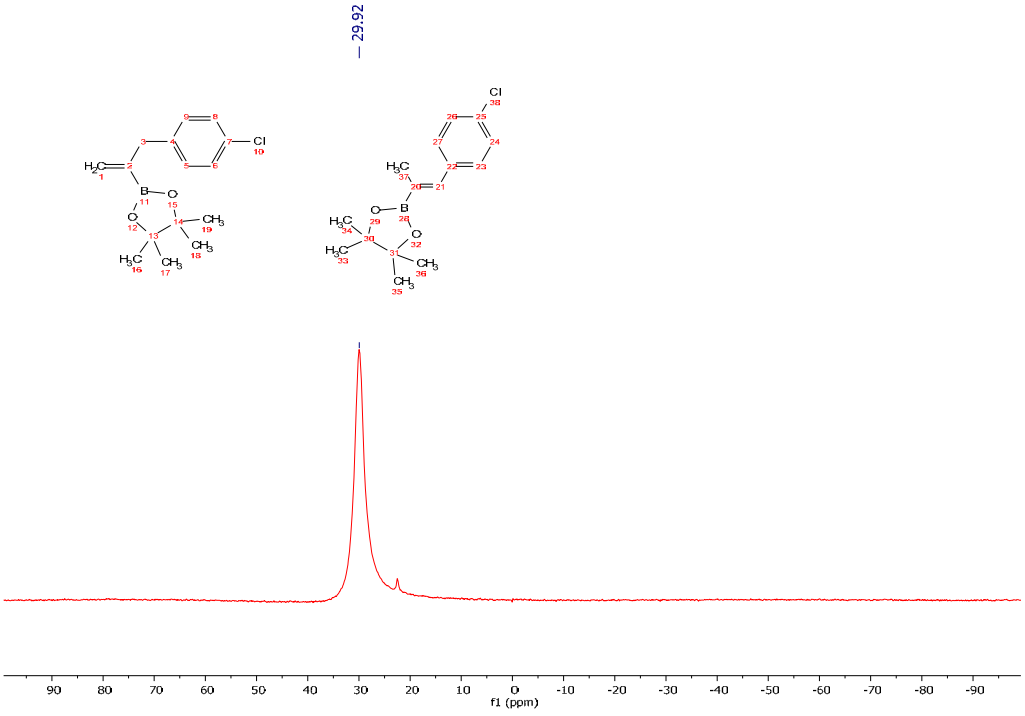

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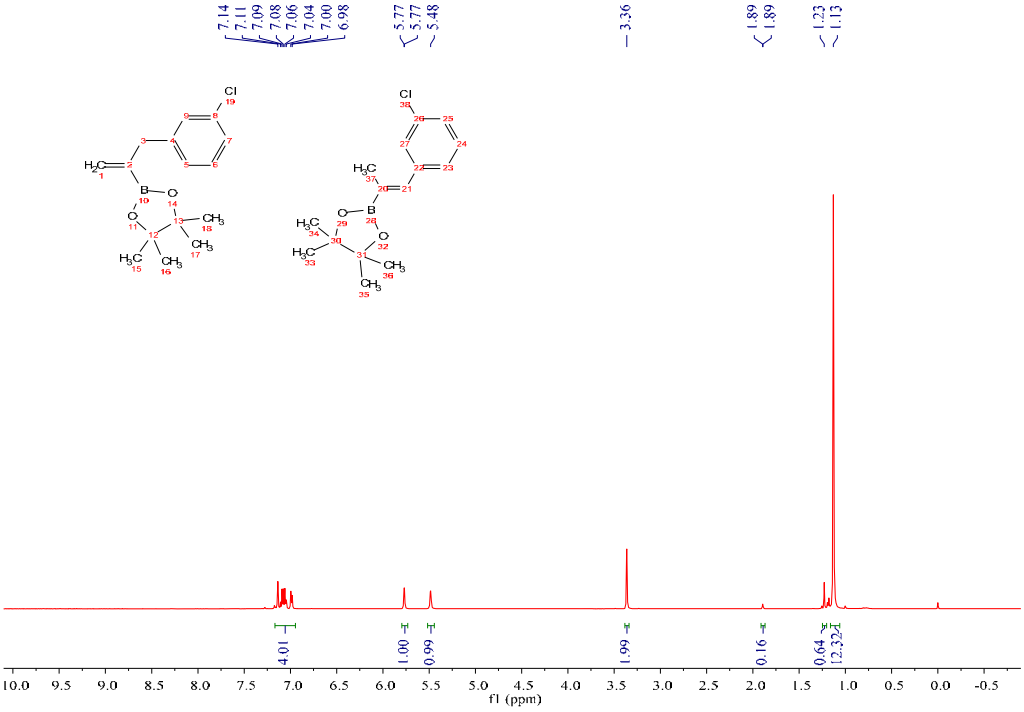

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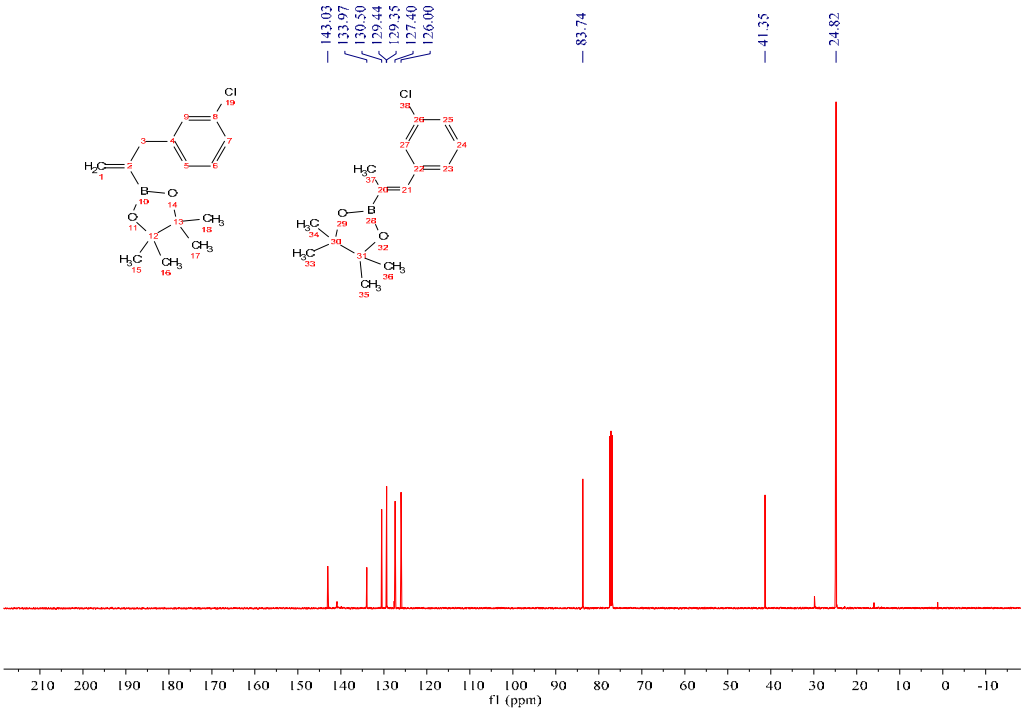

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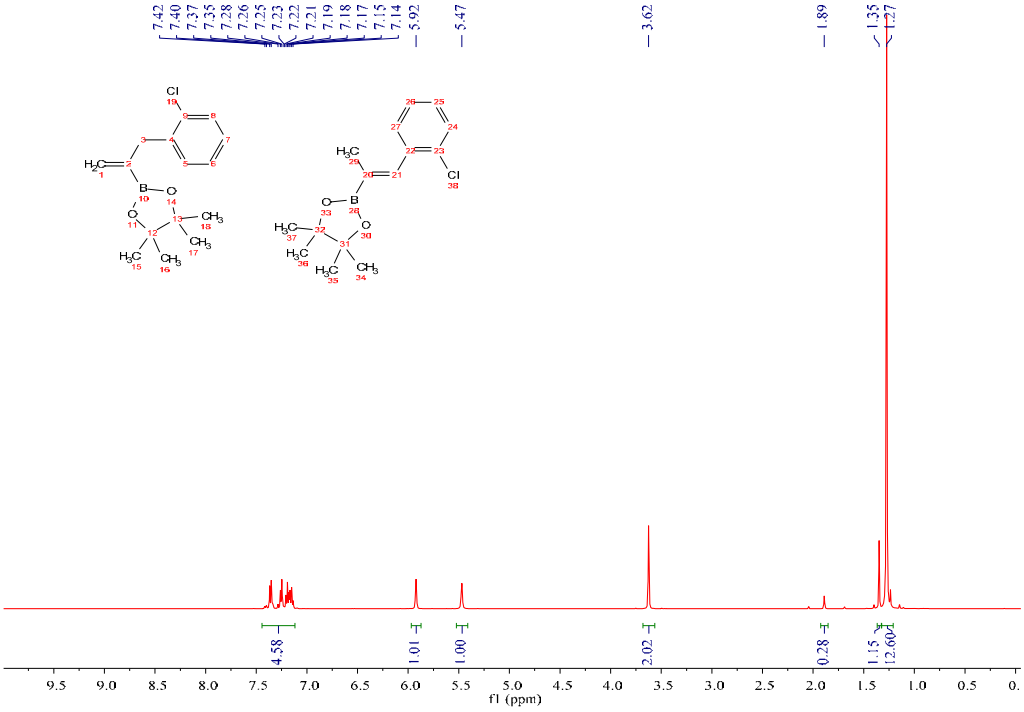

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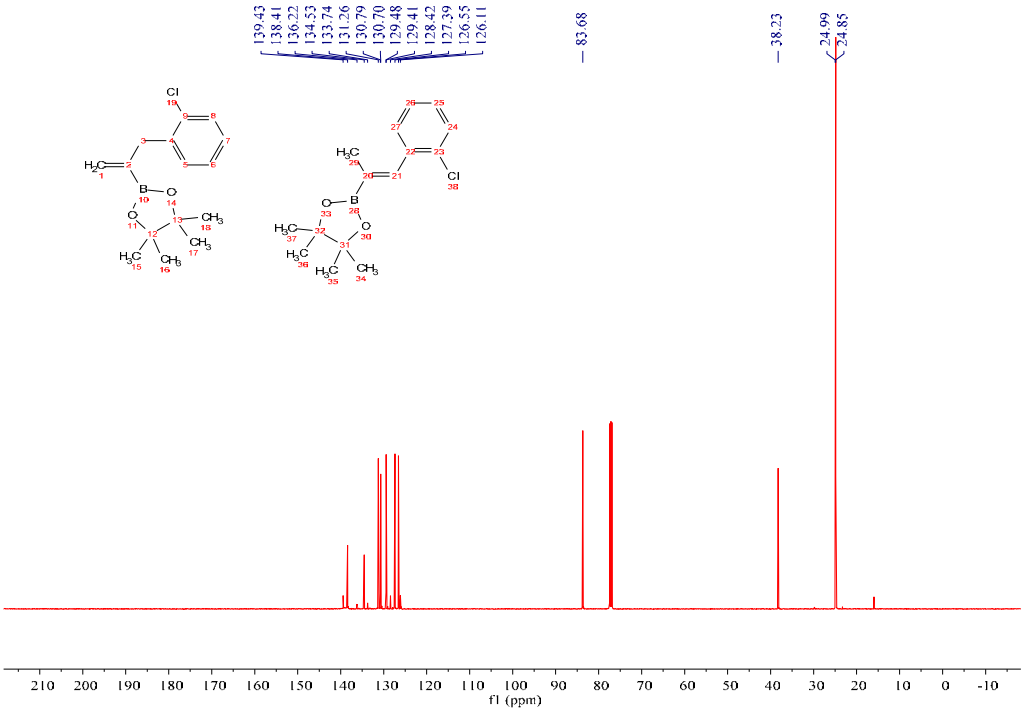

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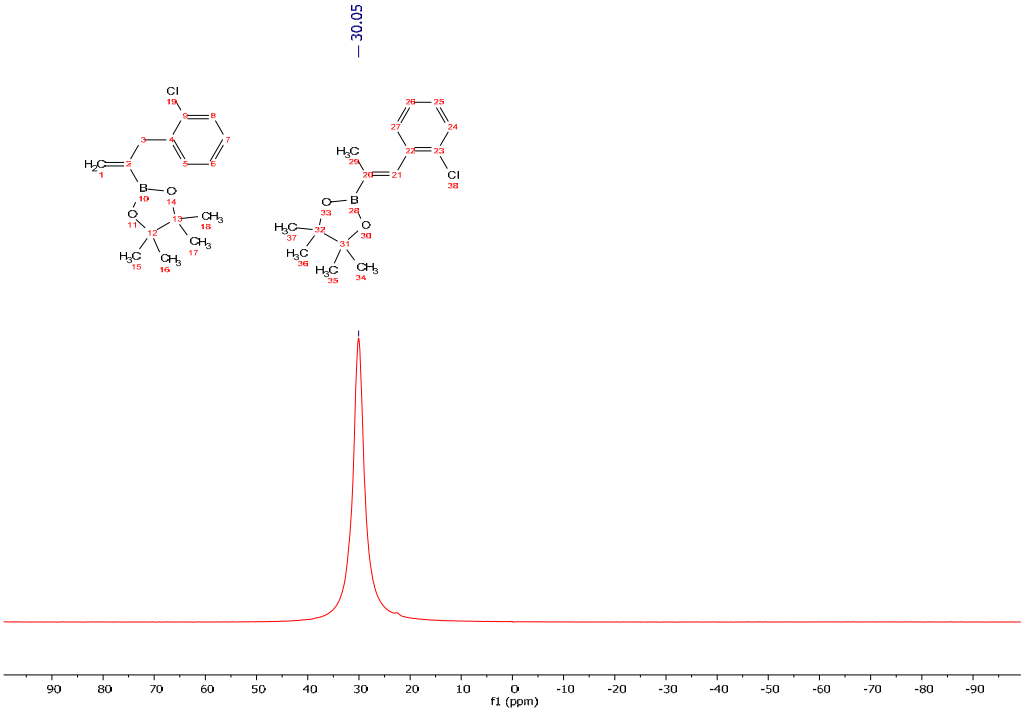

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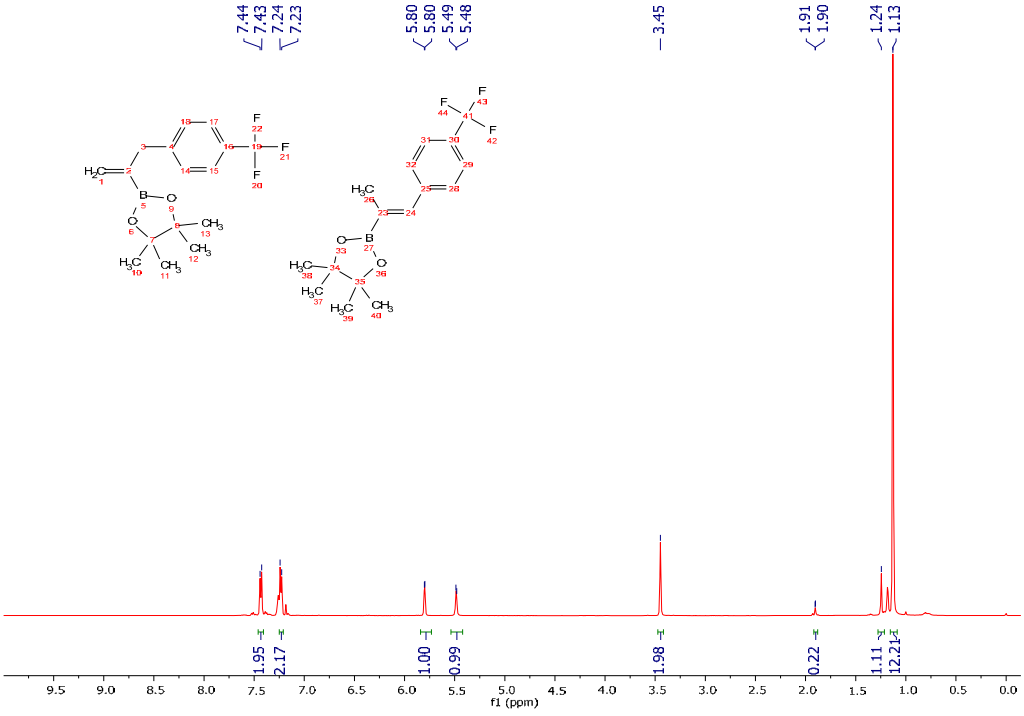

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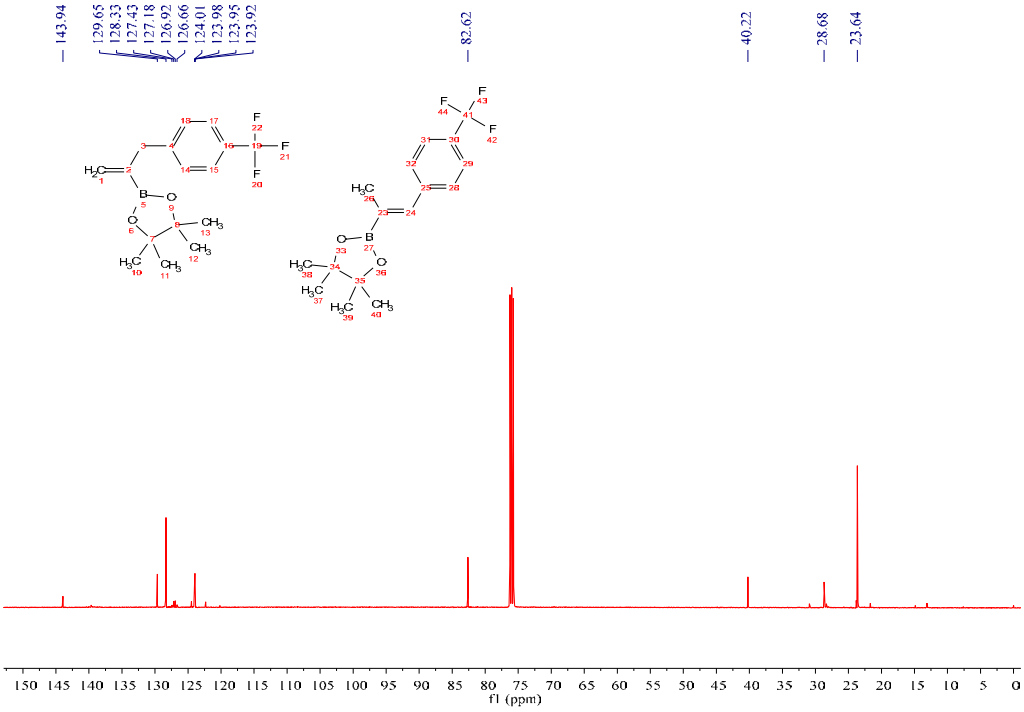

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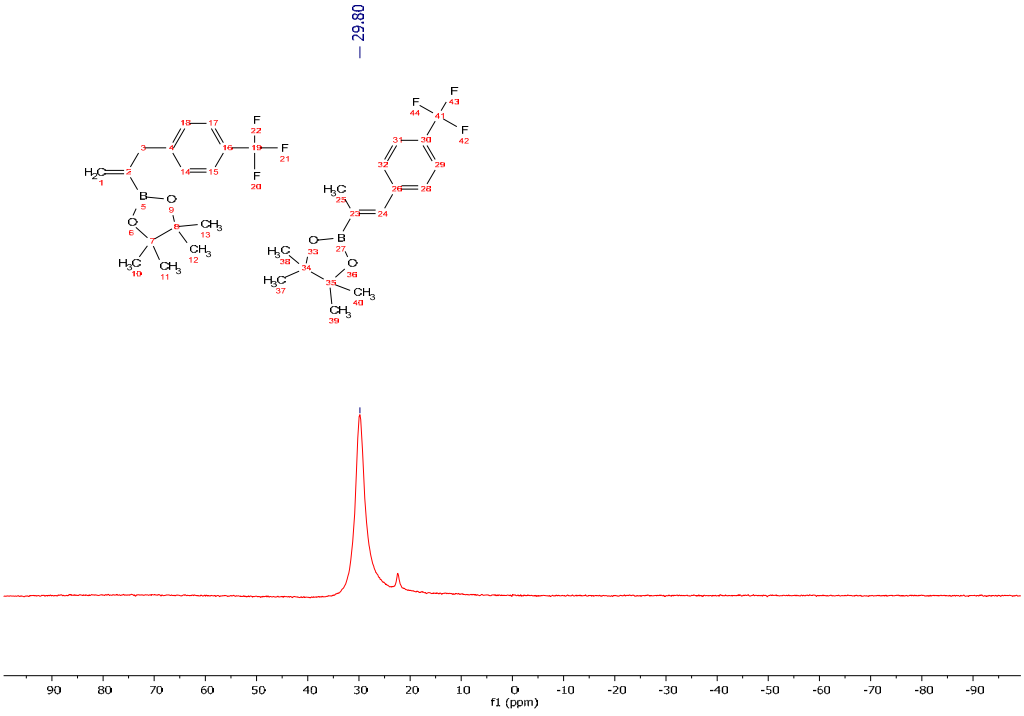

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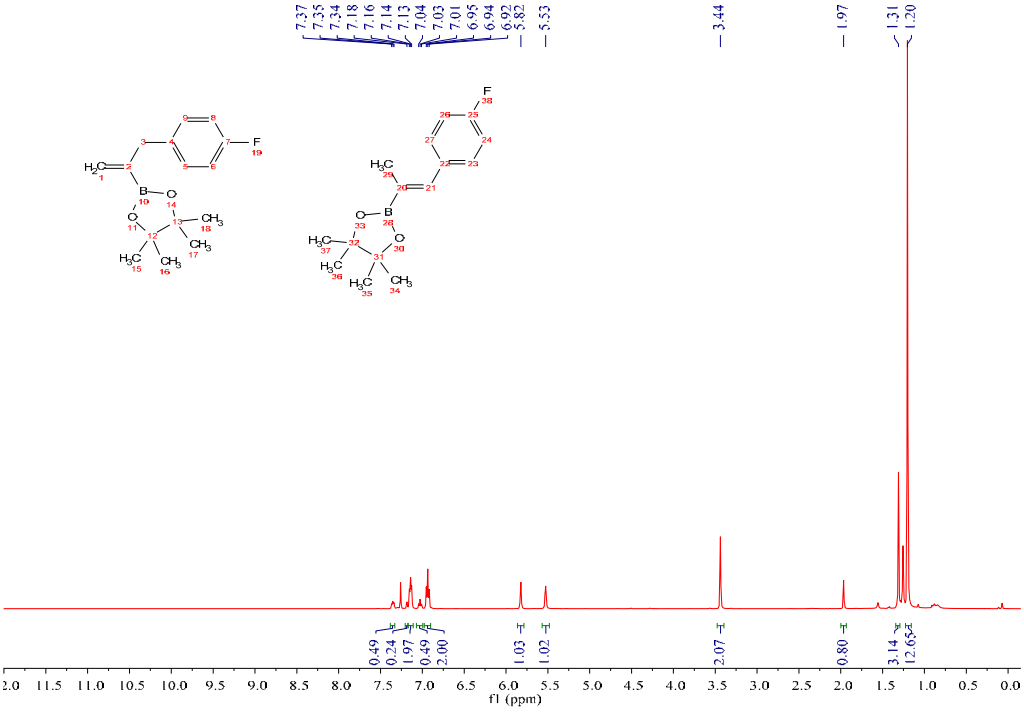

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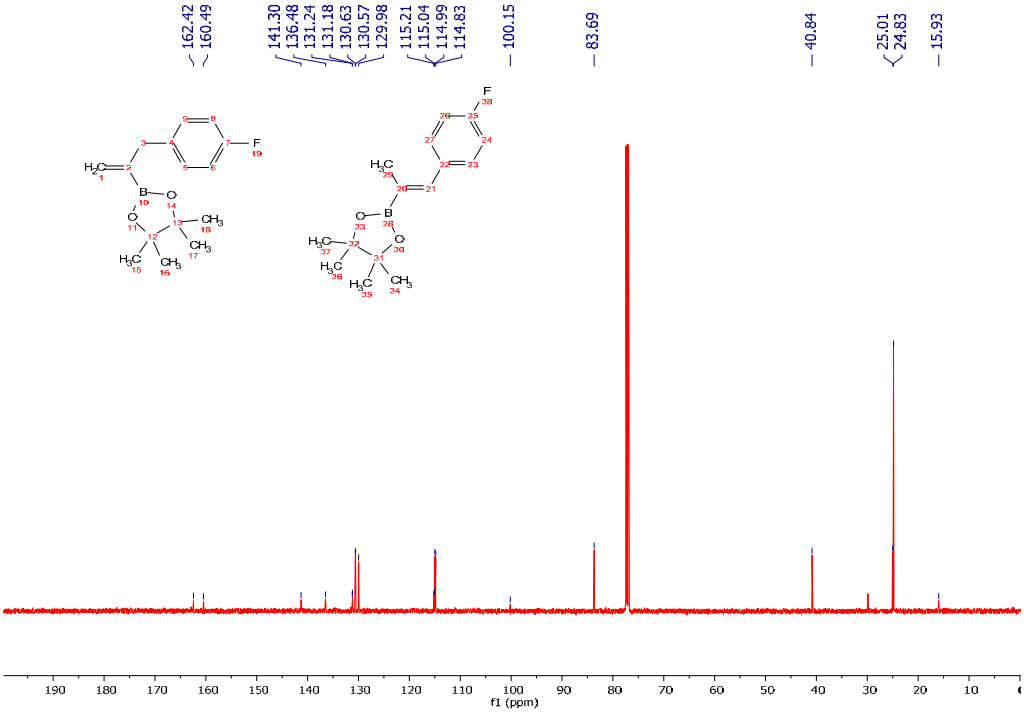
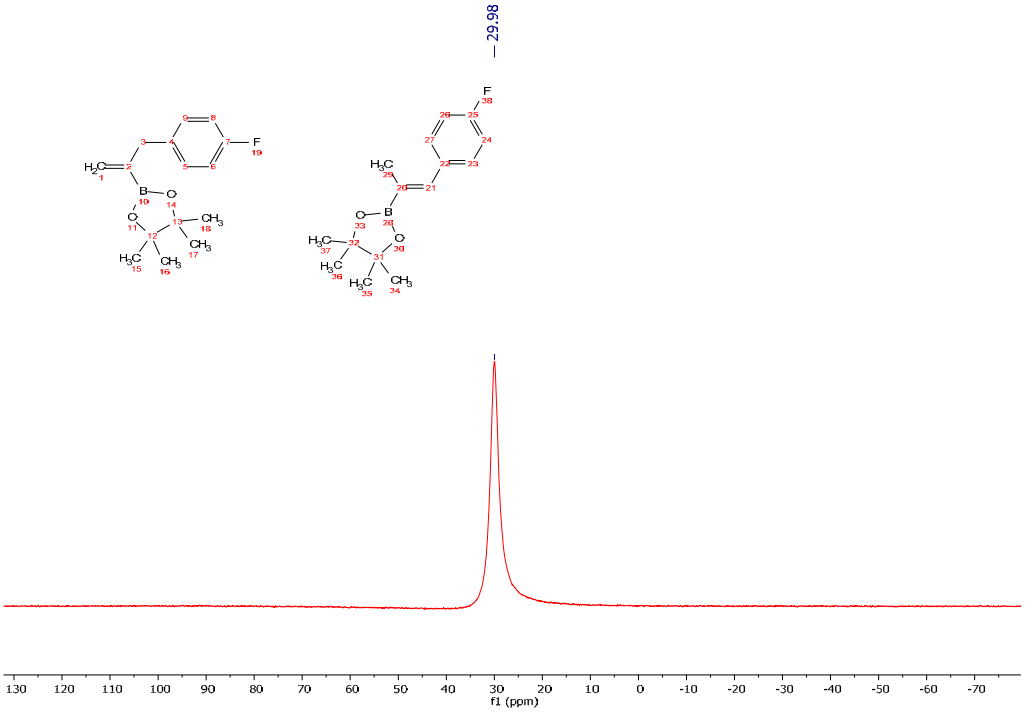
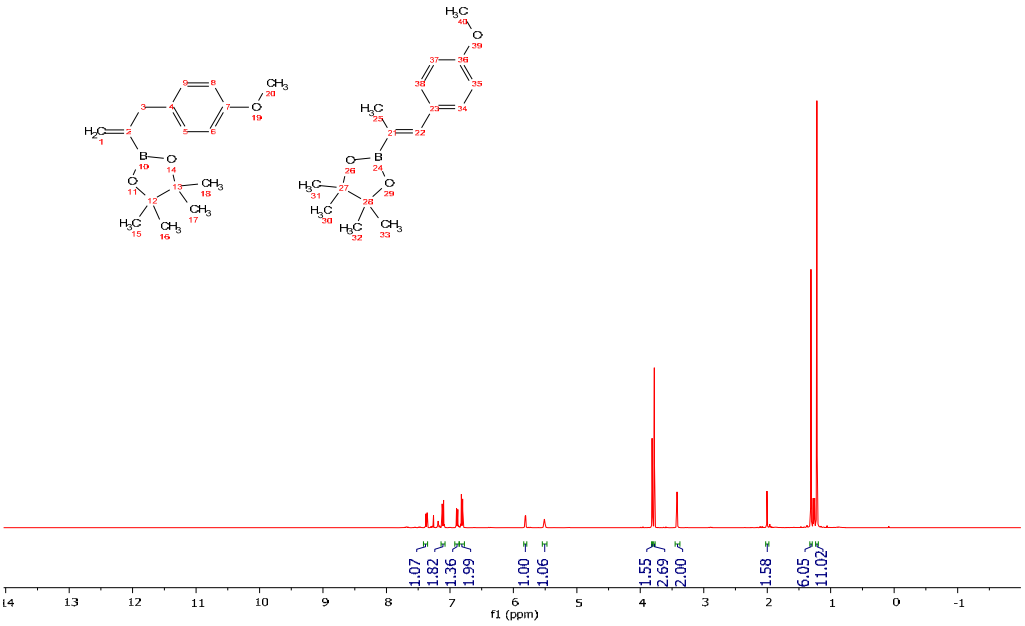


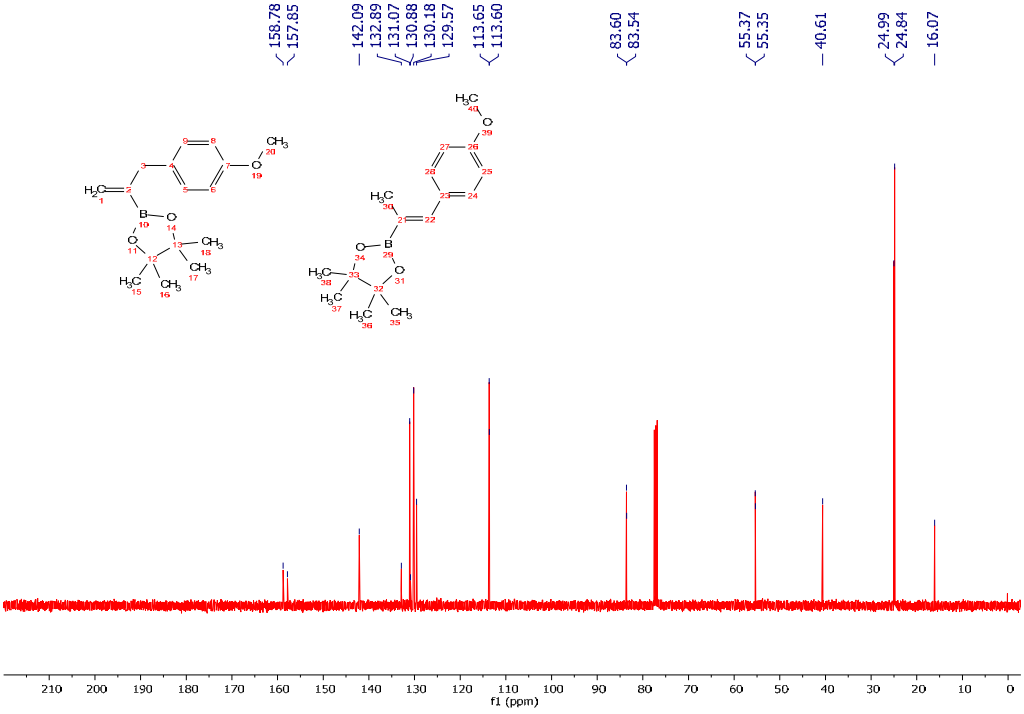
^{11}B NMR Spectra of **2/3h**



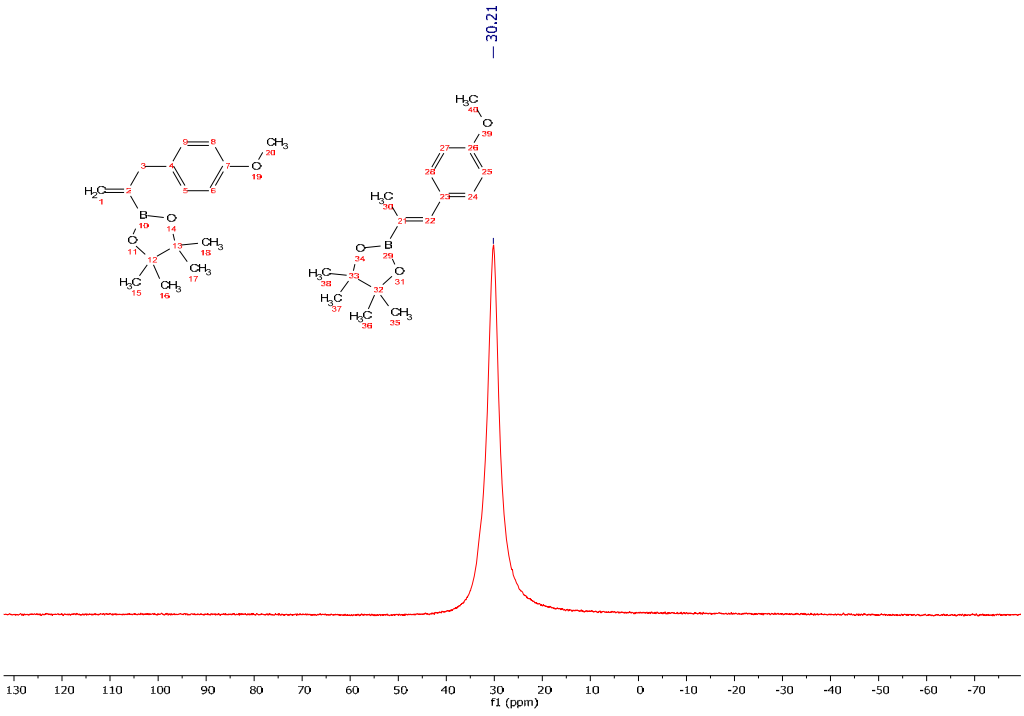
^{1}H NMR Spectra of **2/3i**



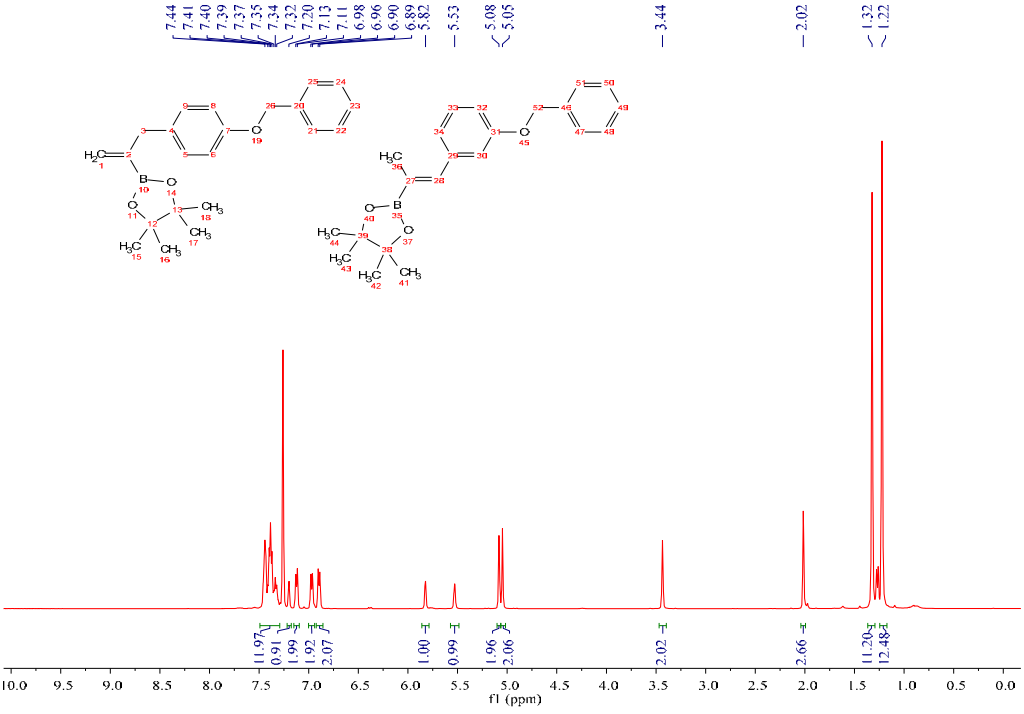
^{13}C NMR Spectra of **2/3i**



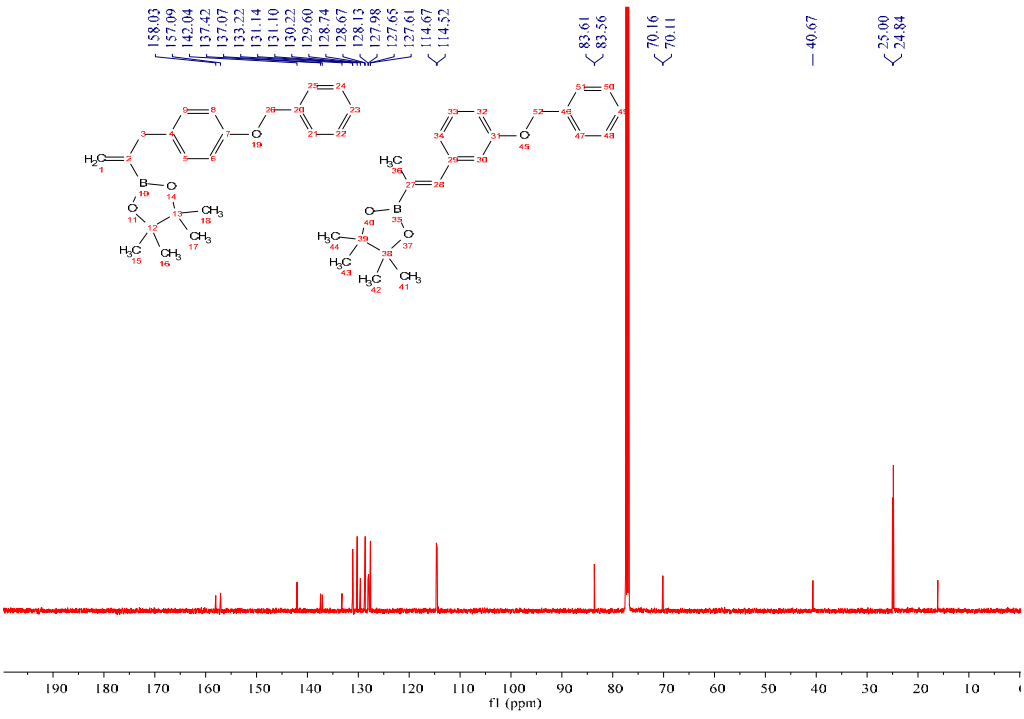
^{11}B NMR Spectra of **2/3i**



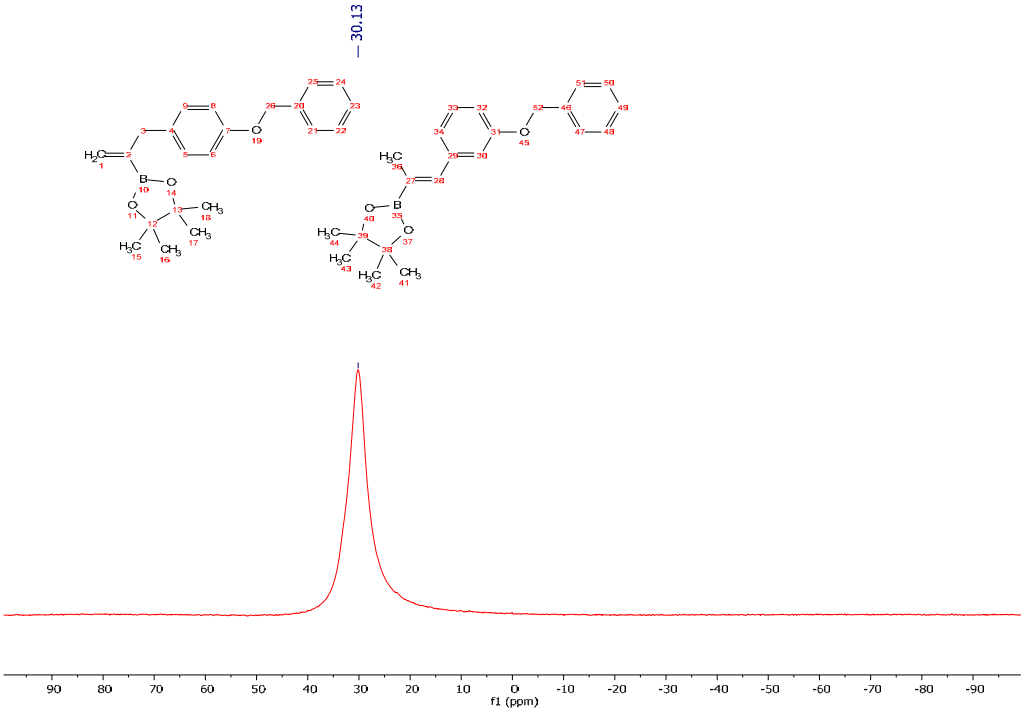
^{1}H NMR Spectra of **2/3j**



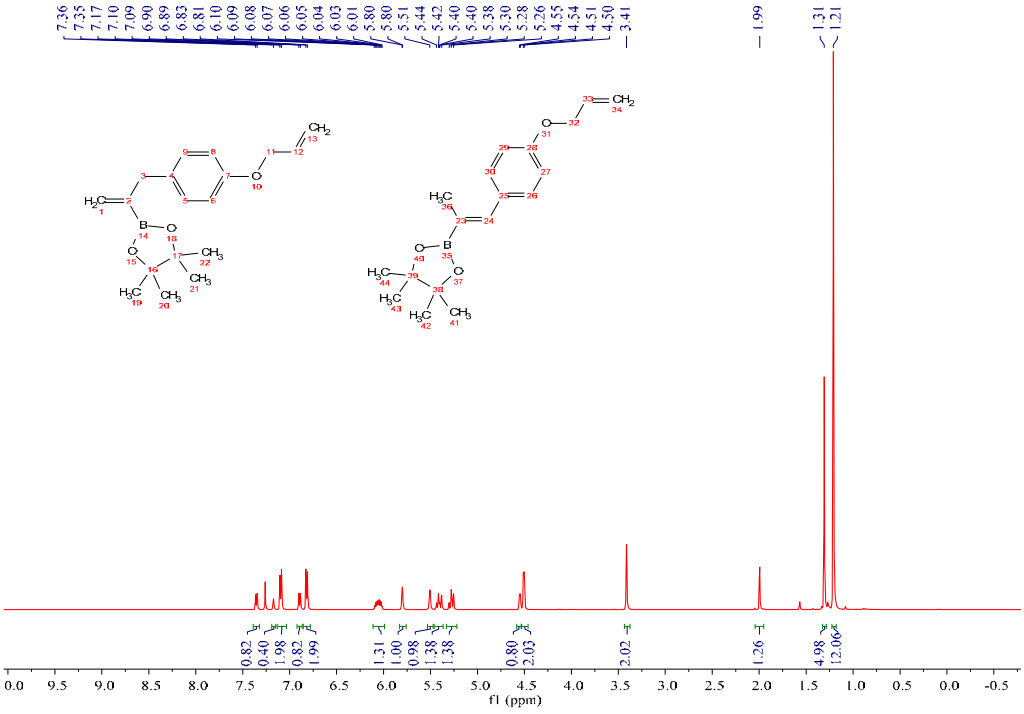
^{13}C NMR Spectra of **2/3j**



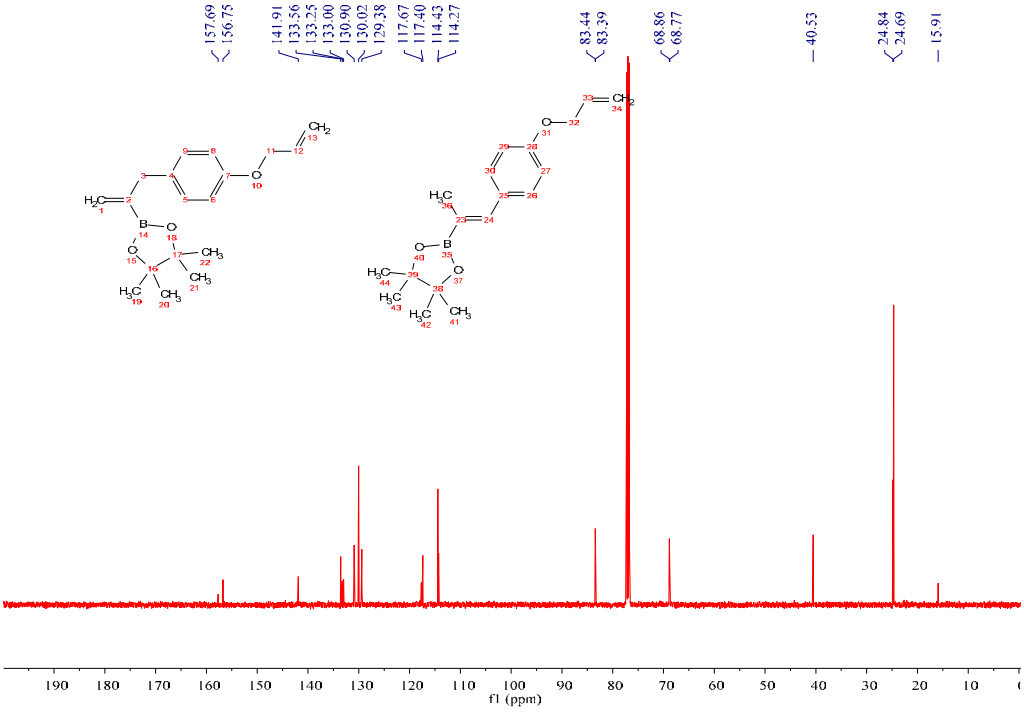
^{11}B NMR Spectra of **2/3j**



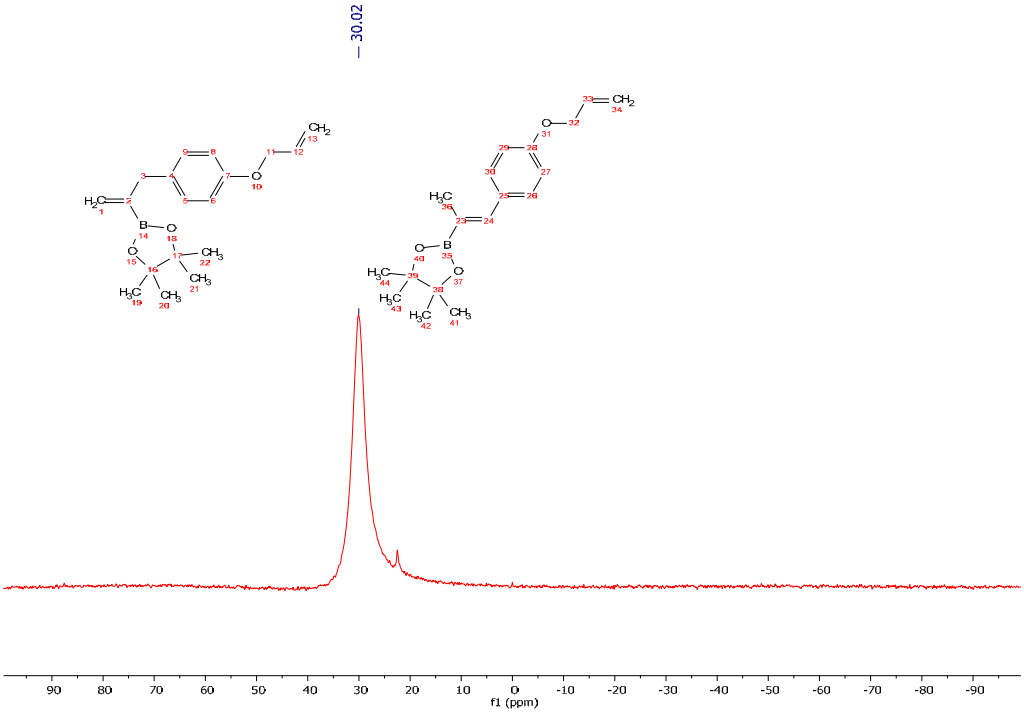
^{1}H NMR Spectra of **2/3k**



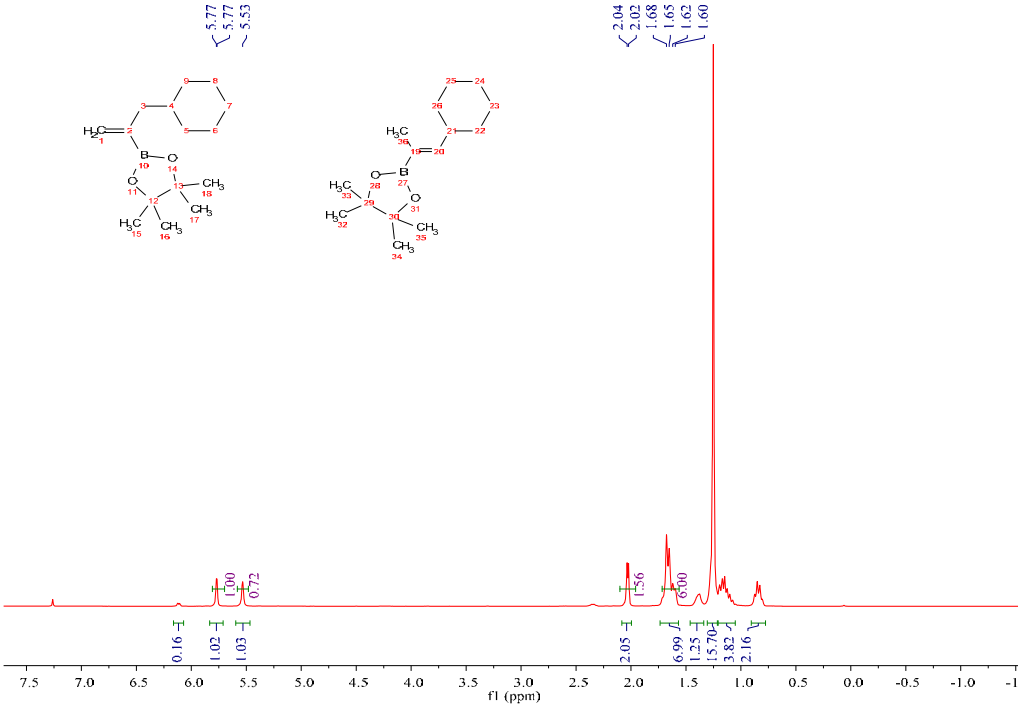
^{13}C NMR Spectra of **2/3k**



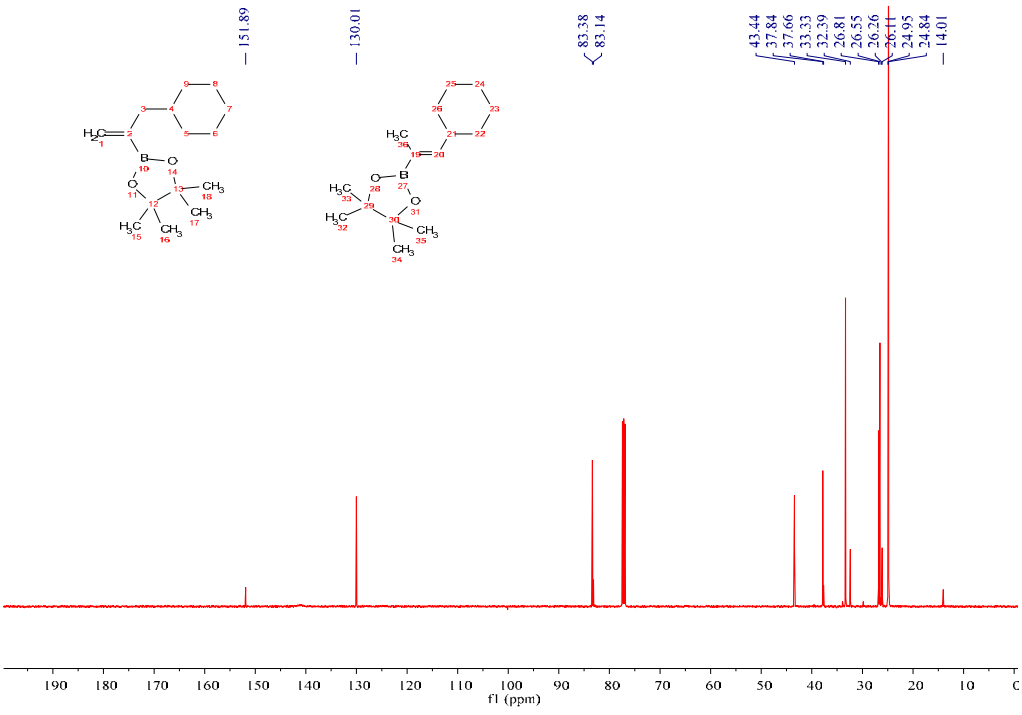
^{11}B NMR Spectra of **2/3k**



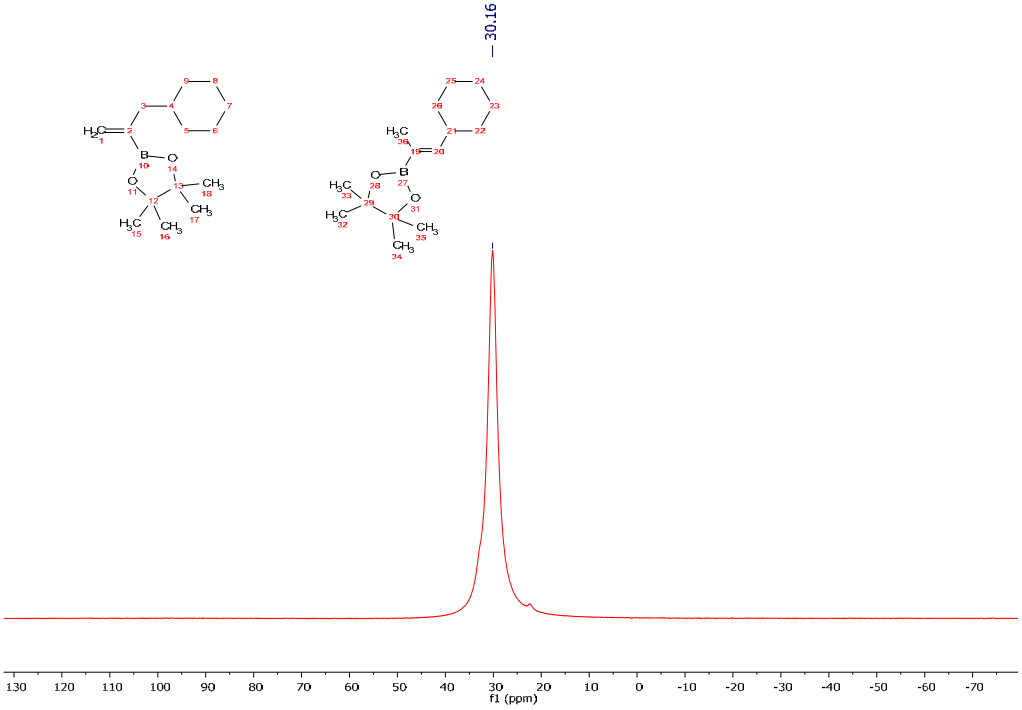
^{1}H NMR Spectra of **2/3l**



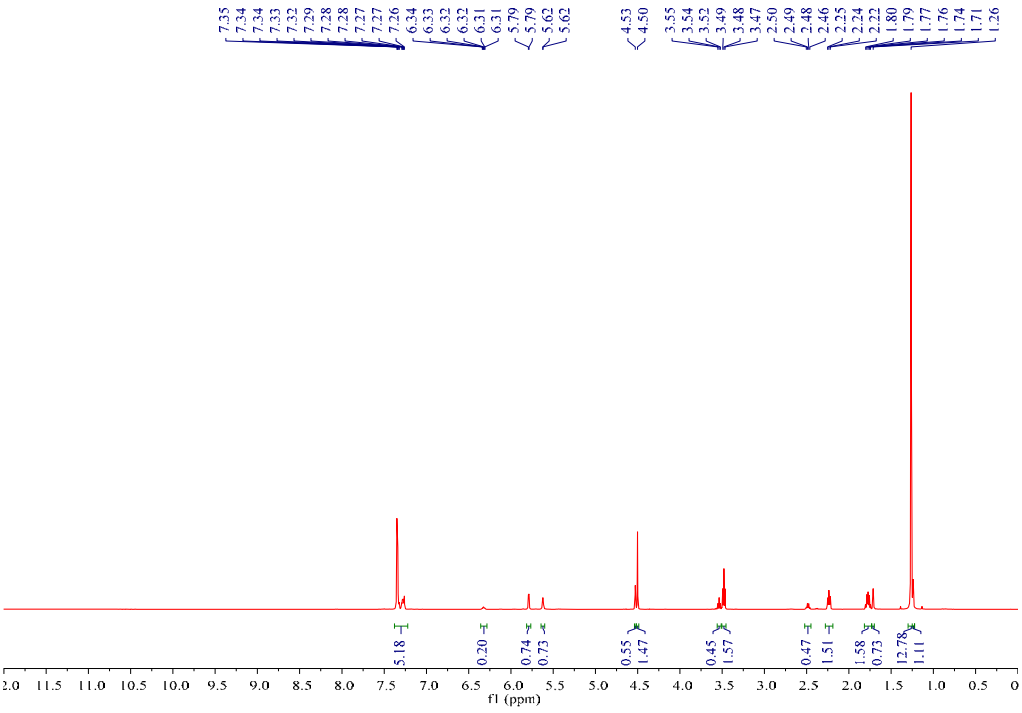
^{13}C NMR Spectra of **2/3l**



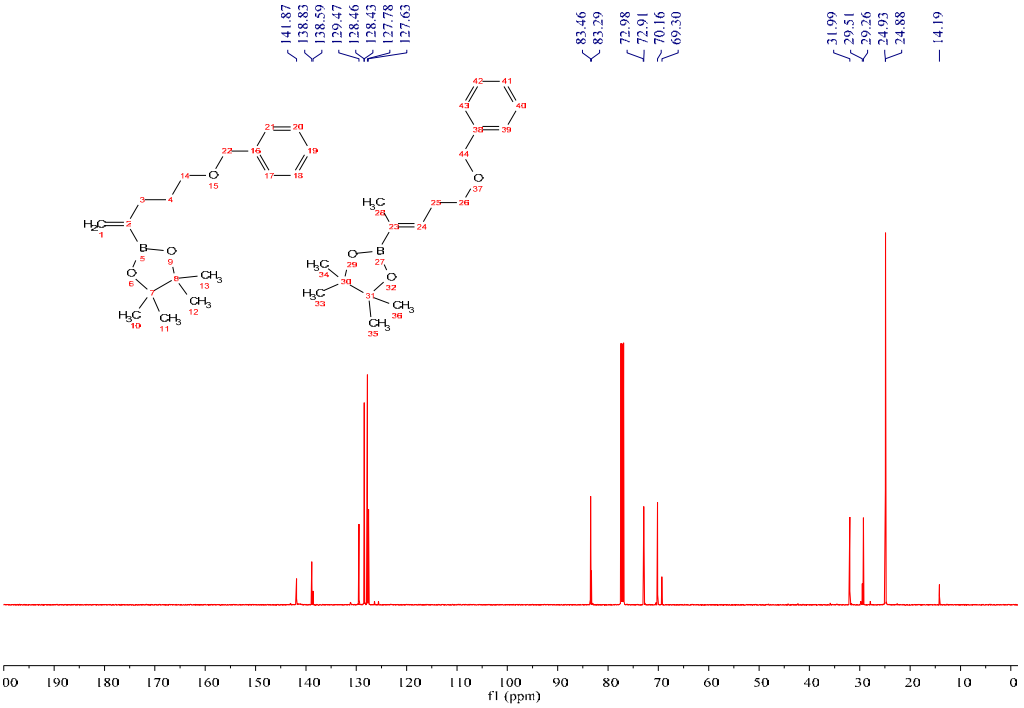
^{11}B NMR Spectra of **2/3l**



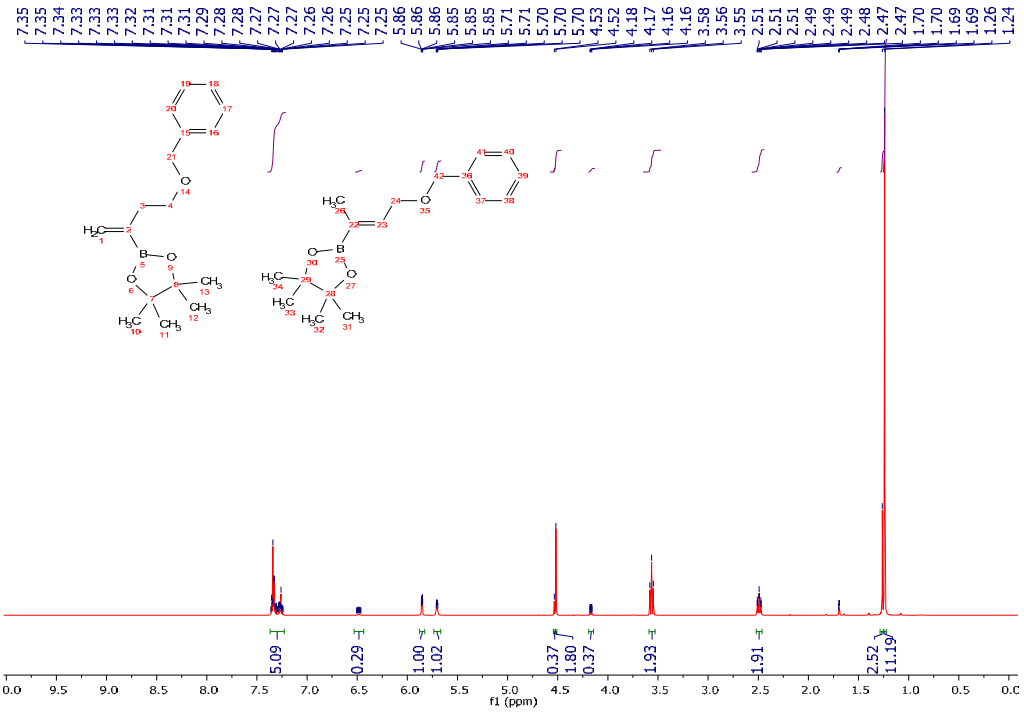
^{1}H NMR Spectra of **2/3m**



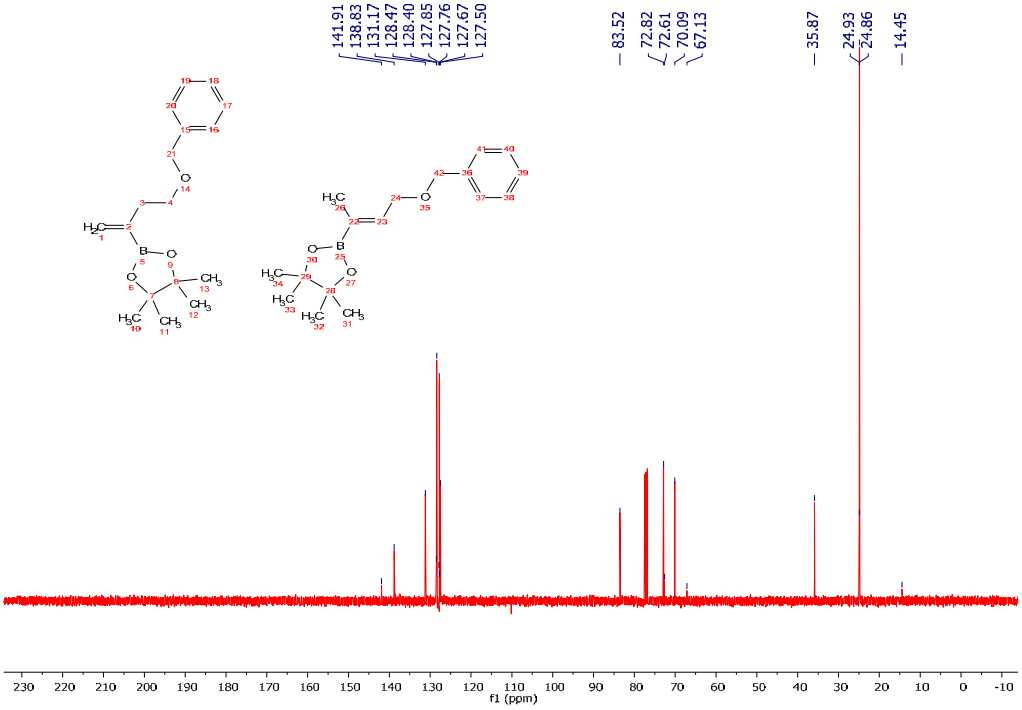
^{13}C NMR Spectra of **2/3m**



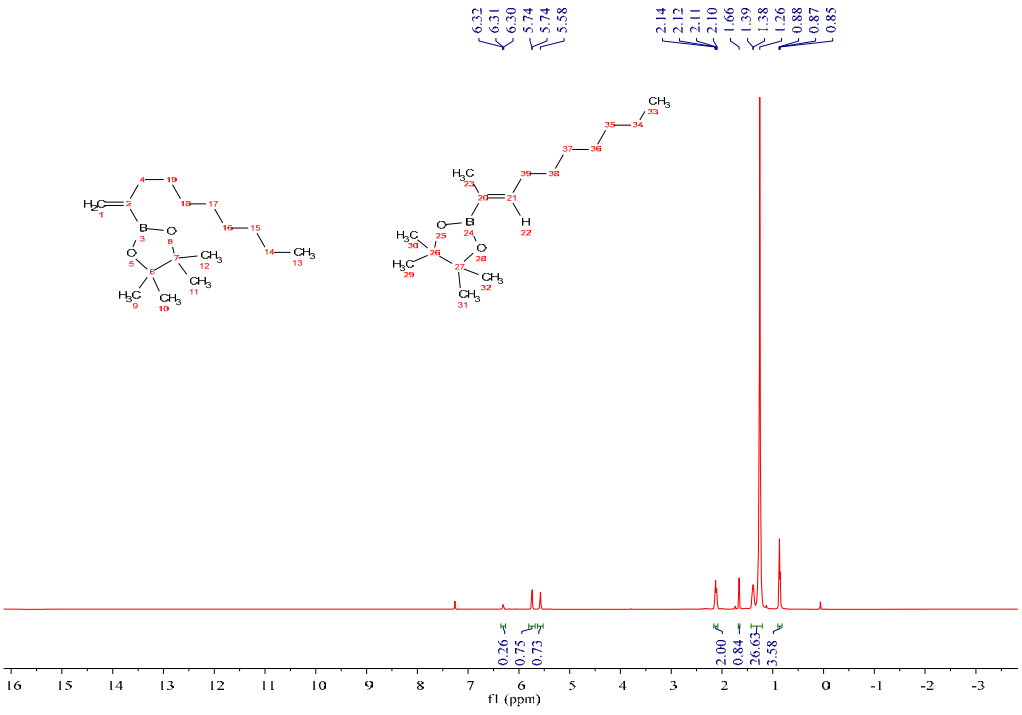
^{1}H NMR Spectra of **2/3n**



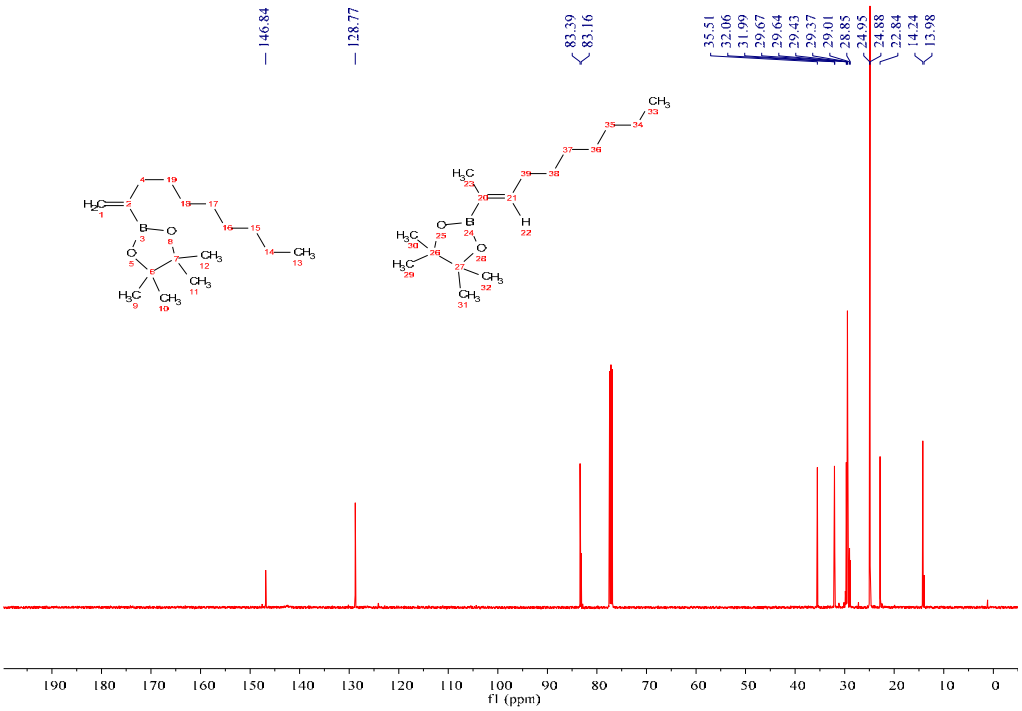
^{13}C NMR Spectra of **2/3n**



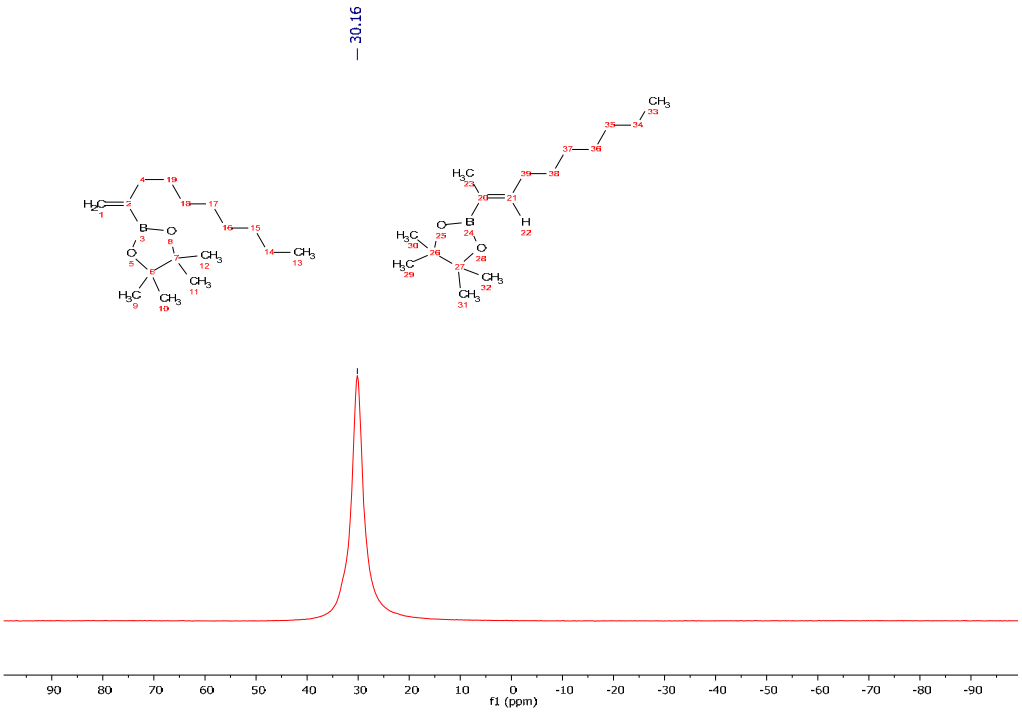
^{1}H NMR Spectra of **2/3o**



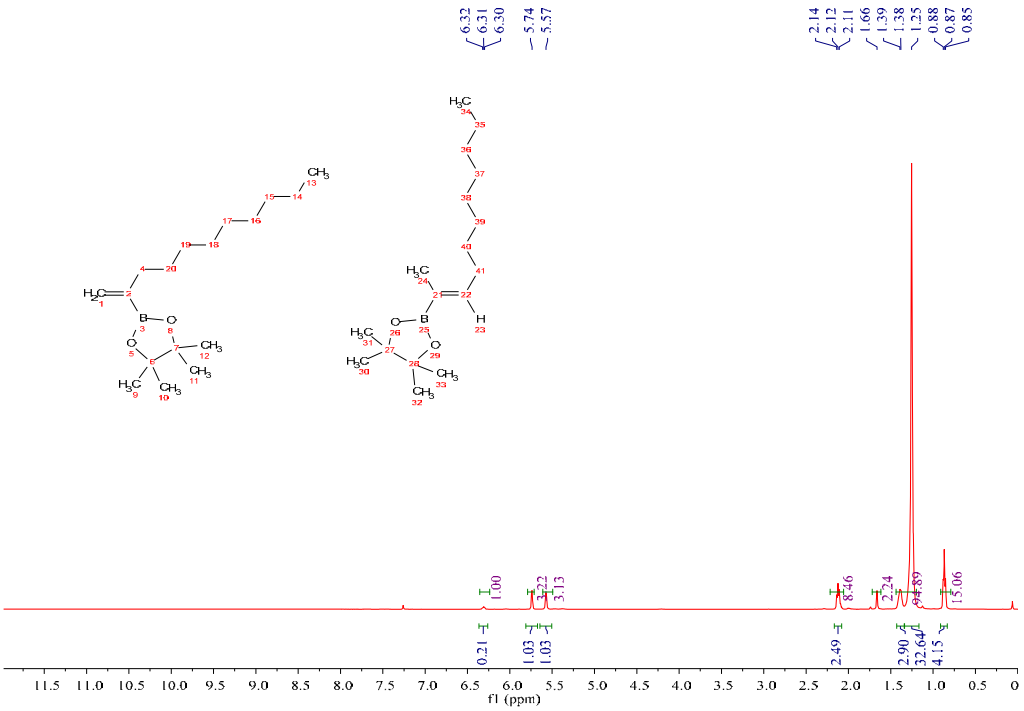
^{13}C NMR Spectra of **2/3o**



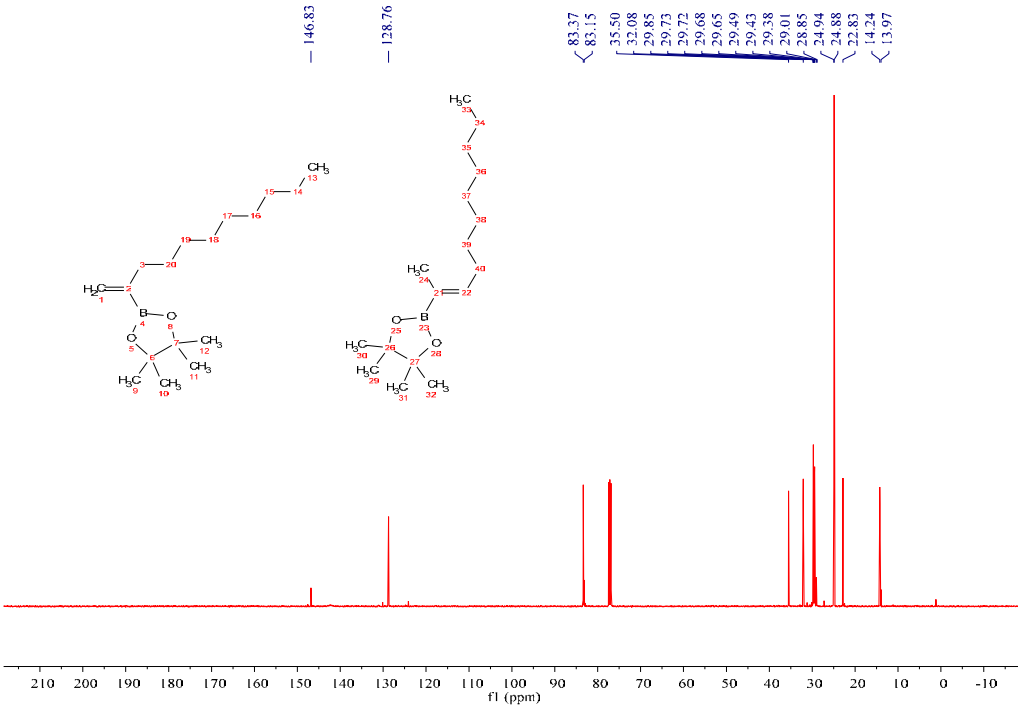
^{11}B NMR Spectra of **2/3o**



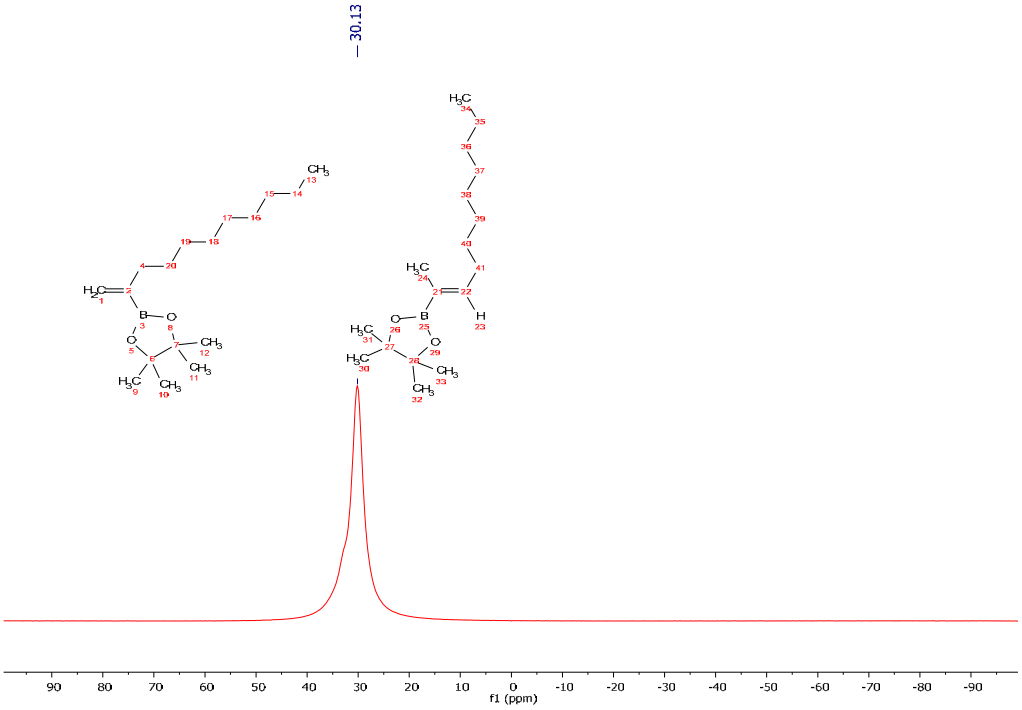
^{1}H NMR Spectra of **2/3p**



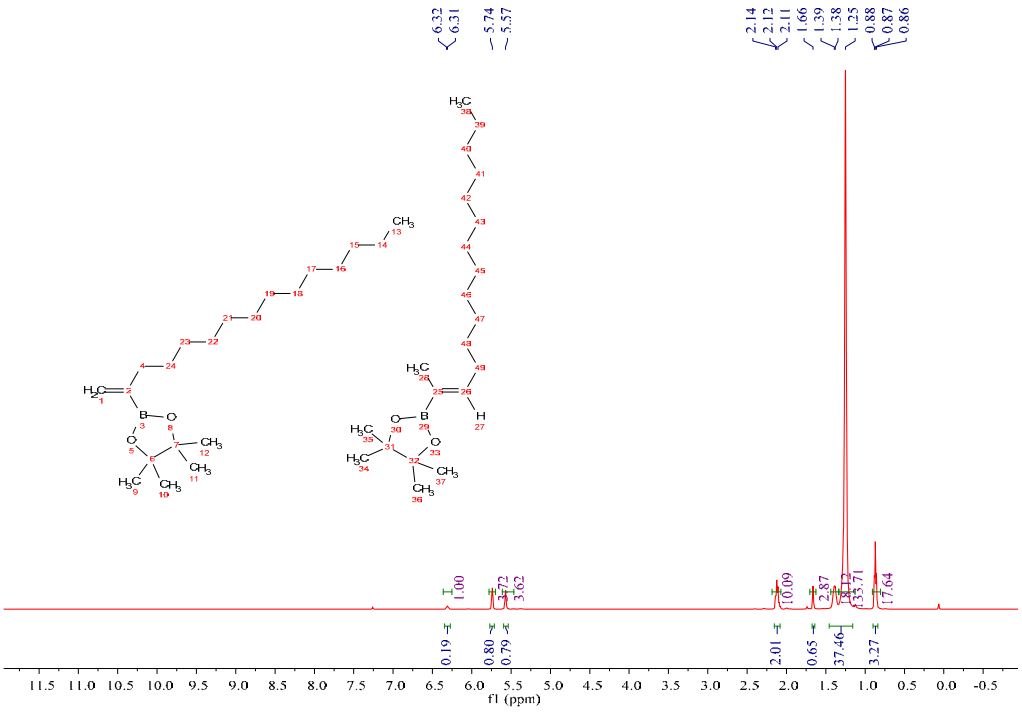
^{13}C NMR Spectra of **2/3p**



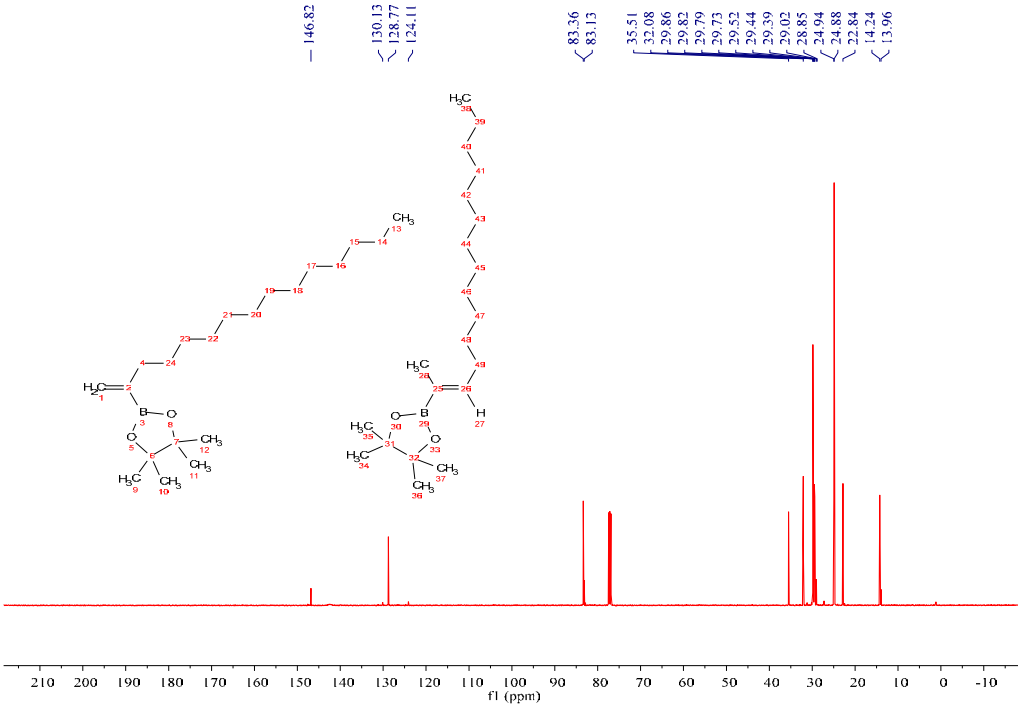
^{11}B NMR Spectra of **2/3p**



^{1}H NMR Spectra of **2/3q**



^{13}C NMR Spectra of **2/3q**



^{11}B NMR Spectra of **2/3q**