Highly Regio- and Stereoselective Synthesis of *Z*-Trisubstituted Alkenes via Propyne Bromoboration and Tandem Pd-Catalyzed Cross-Coupling

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Supporting Information

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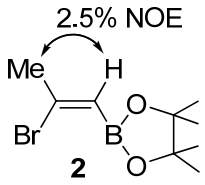
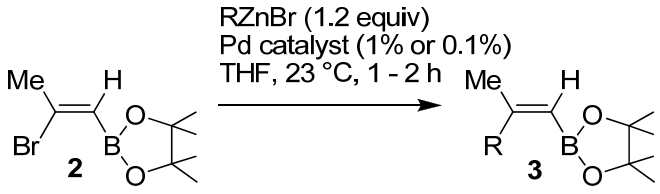
General. All reactions were run in flame-dried glassware under Argon atmosphere. THF and ether were distilled from sodium and benzophenone. CH_2Cl_2 was distilled from CaH_2. Zn dust was activated by rinsing with dilute HCl[i] and flame-dried under vacuum prior to use. $ZnBr_2$ was flamed-dried under vacuum. Except for 5-iodo-2-methyl-2-pentene, 1-iodo-3-decyne, (*E*)-1-iodo-2-methyl-1-octene and (*E*)-3-*tert*-butyldimethylsilyloxy-1-iodo-propene, the starting materials were purchased from commercial sources and used as received. 5-Iodo-2-methyl-2-pentene[ii], 1-iodo-3-decyne[iii], (*E*)-1-iodo-2-methyl-1-octene[iv] and (*E*)-3-*tert*-butyldimethylsilyloxy-1-iodo-propene [v] were prepared according to literature procedures. Reactions were monitored by TLC and GC analyses. GC analysis was performed on HP6890 Gas Chromatograph using an HP-5 capillary column (30 m × 0.32 mm, 0.5 μM film) packed with SE-30 on Chromosorb W. Column chromatography was carried out on 230-400 mesh silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-Inova-300 and Bruker-ARX-400. LRMS and HRMS were obtained on Hewlett Packed 5995 GC-MS and Finnigan MATL95 mass spectrometers, respectively.

(*Z*)-2-(2'-Bromo-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2)



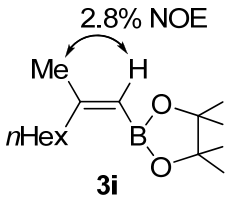
Propyne gas was slowly introduced to a graduated or marked flask or Schlenk tube at -78 °C, which was quickly condensed into liquid. Volume of the liquefied propyne can be easily measured by the graduation or markings (in this case: 1.14 mL, 20 mmol). Cooled dry CH_2Cl_2 (10 mL) was then added slowly to make a solution. To this stirred solution of propyne in CH_2Cl_2 was added a solution of BBr_3 (2.08 mL, 22 mmol) in dry CH_2Cl_2 (20 mL) at -78 °C. After 1h at -78 °C, the reaction mixture was warmed to 23 °C, kept at this temperature for 1 h, and added to a solution of pinacol (2.84 g, 24 mmol) in dry CH_2Cl_2 (20 mL) at -78 °C. The resultant reaction mixture was warmed to 23 °C, stirred for 1 h, washed with brine, and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, 50:1 hexane-EtOAc) to give 4.20 g (85%) of the title compound as colorless liquid. The above obtained compound **2** are ≥ 98% pure determined by ^1H and ^{13}C NMR analysis. Compound **2** is very stable and can be stored in air at 23^oC for days without any change according to NMR analysis. ^1H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 12 H, CH_3), 2.38 (s, 3H, CH_3), 5.82 (s, 1H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.66, 32.93, 83.47, 119.25, 139.33; HRMS calcd for $C_9H_{16}BBrO_2$ $[M]^+$: 246.0427. Found 246.0426.

General procedure A: Negishi cross-coupling of alkyl-, alkenyl-, and arylzinc bromides with (*Z*)-2-(2'-Bromo-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxa -borolane (2)



To a stirred solution of **2** (0.25 g , 1 mmol) and $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) in dry THF (2 mL) was added a solution of organozinc reagent (1.2 mmol) at 0°C. The resultant reaction mixture was stirred at 23°C for 1 h, quenched with 0.5 M HCl, extracted with ether, washed successively with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, 50:1 hexane-EtOAc) afforded the compounds **3**, which are ≥ 98% pure determined by ^1H and ^{13}C NMR analysis.

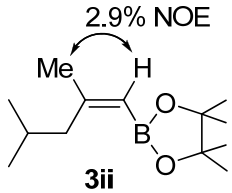
(*Z*)-2-(2'-methyl-1-octenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**)



3i

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and *n*-hexylzinc bromide (1.2 mmol, generated by treating *n*-hexyllithium (0.52 mL, 1.2 mmol, 2.3 M solution in hexanes) with a solution of $ZnBr_2$ (0.27 g, 1.2 mmol) in dry THF (2 mL) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.24 g (87%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.2-1.35 (m, 6H), 1.23 (s, 12H), 1.35-1.45 (m, 2H), 1.83 (d, *J* = 1.2 Hz, 3H), 2.38 (t, *J* = 7.2 Hz, 2H), 5.10 (q, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.05, 22.57, 24.74(4C), 26.35, 28.79, 28.94, 31.62, 35.90, 82.37(2C), 113-116(br s), 163.66. HRMS calcd for $C_{15}H_{29}BO_2$ $[M]^+$: 252.2261 Found 252.2268.

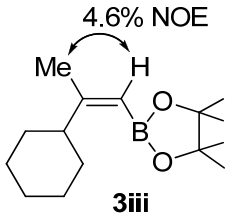
(*Z*)-2-(2,4-dimethyl-1-pentenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ii**)



3ii

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and *i*-butylzinc bromide (1.2 mmol, generated by treating *i*-butylmagnesium bromide (0.6 mL, 1.2 mmol, 2.0 M solution in Et_2O) with a solution of $ZnBr_2$ (0.27 g, 1.2 mmol) in dry THF (2 mL) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.193 g (86%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, *J* = 6.6 Hz, 3H), 1.22 (s, 12H), 1.7-1.8 (m, 1H), 1.80 (d, *J* = 1.5 Hz, 3H), 2.73 (d, *J* = 7.5 Hz, 2H), 5.13 (q, *J* = 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.34(2C), 24.70(4C), 26.59, 27.09, 44.87, 82.34(2C), 113-117(br s), 162.13. HRMS calcd for $C_{13}H_{25}BO_2$ $[M]^+$: 224.1948 Found 224.1958.

(*Z*)-2-(2'-cyclohexyl-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3iii**)

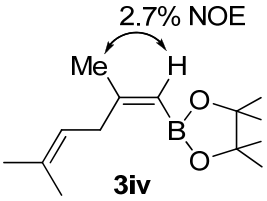


3iii

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and cyclohexylzinc bromide (1.2 mmol, generated by treating cyclohexylmagnesium

bromide (0.6 mL, 1.2 mmol, 2.0 M solution in Et_2O) with a solution of $ZnBr_2$ (0.27 g, 1.2 mmol) in dry THF (2 mL) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.21 g (84%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.1-1.35 (m, 5H), 1.24 (s, 12H), 1.5-1.55 (m, 2H), 1.6-1.8 (m, 3H), 1.76 (d, *J* = 1.5 Hz, 3H), 2.98 (tt, J_1 = 3.3 Hz, J_2 = 11.8 Hz, 1H), 5.03 (q, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.33, 24.72(4C), 26.20, 26.48(2C), 31.97(2C), 43.71, 82.35(2C), 111-115(br s), 167.93. HRMS calcd for $C_{15}H_{27}BO_2$ $[M]^+$: 250.2142 Found 250.2143.

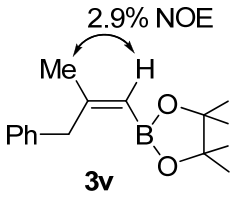
(*Z*)-2-(2,5-dimethyl-1,4-hexadienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3iv**)



3iv

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and (3-methyl-2-butenyl)zinc bromide (1.2 mmol, generated by treating 1-bromo-3-methyl-2-butene (0.18 g, 0.14 mL, 1.2 mmol) with Zn dust (0.156 g, 2.4 mmol) in dry THF (2 mL))[vi] gave the title compound as colorless oil. Yield: 0.187 g (79%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25(s, 12H), 1.68 (s, 3H), 1.70 (s, 3H), 1.83 (s, 3H), 3.12 (d, *J* = 7.6 Hz, 2H), 3.09 (s, 1H), 5.1-5.2 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.69, 24.69(4C), 25.73, 26.15, 35.22, 82.45(2C), 112-116(br s), 122.40, 132.31, 162.44. HRMS calcd for $C_{14}H_{25}BO_2$ $[M]^+$: 236.1948 Found 236.1961.

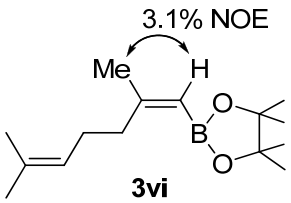
(*Z*)-2-(2-methyl-3-phenyl-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3v**)



3v

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and benzylzinc bromide (1.2 mmol, generated by treating benzyl bromide (0.20 g, 0.14 mL, 1.2 mmol) with Zn dust (0.156 g, 2.4 mmol) in dry THF (2 mL))[vi] gave the title compound as colorless oil. Yield: 0.214 g (83%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 12H), 1.76 (s, 3H), 3.76 (s, 2H), 5.25 (s, 1H), 7.1-7.25 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.77(4C), 26.00, 42.28, 82.68(2C), 115-117(br s), 125.84, 128.16(2C), 128.80(2C), 140.29, 161.15. HRMS calcd for $C_{16}H_{23}BO_2$ $[M]^+$: 258.1791 Found 258.1783.

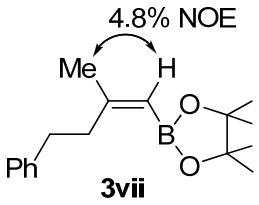
(*Z*)-2-(2,6-dimethyl-1,5-heptadienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3vi**)



3vi

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and (4-methyl-3-pentenyl)zinc bromide (1.2 mmol, generated by treating 2-iodo-2-methyl-2-pentene (0.25 g, 1.2 mmol) with *t*-BuLi (1.47 mL, 2.5 mmol, 1.7 M solution in pentane) in dry Et_2O (2 mL) for 30 min at -78°C, followed by treating with $ZnBr_2$ (0.27 g, 1.2 mmol) for 30 min at 0°C)[vii] gave the title compound as colorless oil. Yield: 0.183 g (73%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (s, 12H), 1.58 (s, 3H), 1.64 (s, 3H), 1.82 (s, 3H), 2.06 (q, *J* = 8 Hz, 2H), 2.37 (t, *J* = 8 Hz, 2H), 5.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.51, 24.71(4C), 25.63, 26.46, 27.62, 36.14, 82.37, 114.0(br s), 124.16, 131.32, 162.91. HRMS calcd for $C_{15}H_{27}BO_2$ $[M]^+$: 250.2104 Found 250.2118

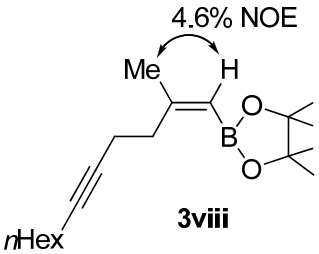
(*Z*)-2-(2-methyl-4-phenyl-1-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3vii**)



3vii

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and phenethylzinc bromide (1.2 mmol, generated by treating (2-iodoethyl)benzene (0.28 g, 1.2 mmol) with *t*-BuLi (1.47 mL, 2.5 mmol, 1.7 M solution in pentane) in dry Et_2O (2 mL) for 30 min at -78°C, followed by treating with $ZnBr_2$ (0.27 g, 1.2 mmol) for 30 min at 0°C) [vii] gave the title compound as colorless oil. Yield: 0.207 g (76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 12 H), 1.97 (s, 3H), 2.80 (m, 4H), 5.24 (s, 1H), 7.20 (m, 1H), 7.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.75(4C), 26.65, 35.82, 38.28, 82.42, 114.0(br s), 125.55, 128.06(2C), 128.37(2C), 142.27, 162.53. HRMS calcd for $C_{17}H_{25}BO_2$ $[M]^+$: 272.1948 Found 272.1971.

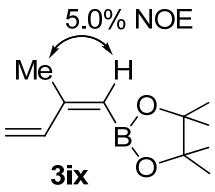
(*Z*)-2-(2-methyl-1-dedecen-5-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3viii**)



3viii

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and 3-decynylzinc bromide (1.2 mmol, generated by treating 2-iodo-3-decyne (0.37 g, 1.2 mmol) with *t*-BuLi (1.47 mL, 2.5 mmol, 1.7 M solution in pentane) in dry Et_2O (2 mL) for 30 min at -78°C, followed by treating with $ZnBr_2$ (0.27 g, 1.2 mmol) for 30 min at 0°C)[vii] gave the title compound as colorless oil. Yield: 0.198 (79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J* = 6.8 Hz, 3H), 1.22-1.36 (m, 20H), 1.40 (m, 2H), 1.87 (s, 3H), 2.10 (m, 2H), 2.25 (m, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 5.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.00, 18.74(2C), 22.52, 24.71(4C), 26.64, 28.48, 29.04, 31.33, 35.34, 79.68, 80.44, 82.49, 115.0(br s), 161.56. HRMS calcd for $C_{19}H_{33}BO_2$ $[M]^+$: 304.2574 Found 304.2559.

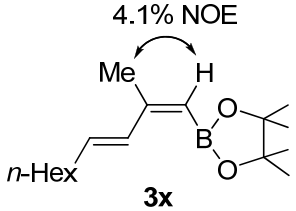
(*Z*)-2-(2'-methyl-1,3-butadienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ix**)



3ix

General procedure A starting from **2** (0.25 g, 1 mmol), 0.1% Pd(*t*-$Bu_3P)_2$ (0.1 mL, 0.01 M solutions in THF, 0.001mmol) and vinylzinc bromide (1.2 mmol, generated by treating vinylmagnesium bromide (1.2 mL, 1.2 mmol, 1.0 M solution in THF) with a solution of $ZnBr_2$ (0.27 g, 1.2 mmol) in dry THF (2 mL) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.16 (82%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (s, 12H), 1.99 (d, *J* = 1.5 Hz, 1H), 5.24 (dt, J_1 = 1.5 Hz, J_2 = 7.5 Hz, 1H), 5.36 (q, *J* = 1.5 Hz, 1H), 5.37(dd, J_1 = 1.2 Hz, J_2 = 17.7 Hz, 1H), 7.32 (dd, J_1 = 7.8 Hz, J_2 = 17.7) Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.91, 24.81(4C), 82.92(2C), 116.51, 118-122(br s), 137.86, 155.35. HRMS calcd for $C_{11}H_{19}BO_2$ $[M]^+$: 194.1478 Found 194.1499.

(*Z*)-4,4,5,5-tetramethyl-2-((1*Z*,3*E*)-2-methyl-1,3-decadienyl)-1,3,2-dioxaboralane (3x)

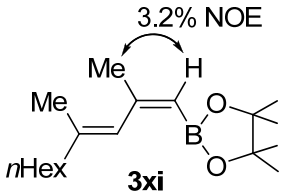


3x

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and (*E*)-1-octenylzinc bromide (1.2 mmol, generated by treating (*E*)-(1-iodo-1-octene (0.30 g, 1.2 mmol) with *n*-BuLi (0.53 mL, 1.3 mmol, 2.5 M solution in hexanes) in dry THF (2 mL) for 30 min at -78°C, followed by treating with $ZnBr_2$ (0.27 g, 1.2 mmol) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.267 g (96%). ^{1}H NMR

(400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.2-1.3 (m, 18H), 1.3-1.4 (m, 2H), 1.94 (s, 3H), 2.1-2.25 (m, 2H), 5.84 (dt, *J* = 15.6, 6.8 Hz, 1H), 7.00 (d, *J* = 16, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.00, 22.52, 22.72, 24.72(4C), 28.85, 28.99, 31.68, 32.91, 82.63(2C), 114-116(br s), 131.21, 135.18, 155.59; HRMS calcd for $C_{18}H_{33}BO_2$ $[M]^+$: 278.2417 Found 278.2411.

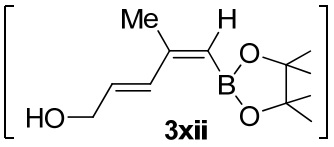
2-((1*Z*,3*E*)-2,4-dimethyl-1,3-decadienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3xi**)



3xi

General procedure A starting from **2** (0.25 g, 1 mmol), 0.1% Pd(*t*-$Bu_3P)_2$ (0.1 mL, 0.01 M solutions in THF, 0.001mmol) and (*E*)-(2-methyl-1-octenyl)zinc bromide (1.2 mmol, generated by treating (*E*)-(1-iodo-2-methyl-1-octene (0.30 g, 1.2 mmol) with *n*-BuLi (0.53 mL, 1.3 mmol, 2.5 M solution in hexanes) in dry THF (2 mL) for 30 min at -78°C, followed by treating with $ZnBr_2$ (0.27 g, 1.2 mmol) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.24 g (83%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.9 Hz, 3H), 1.2-1.4 (m, 6H), 1.24 (s, 12H), 1.4-1.5 (m, 2H), 1.74 (d, *J* = 1.2 Hz, 3H), 2.00 (d, *J* = 1.5 Hz, 3H), 2.04 (t, *J* = 6.9 Hz, 2H), 5.20 (q, *J* = 1.5 Hz, 1H), 6.27 (q, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.08, 18.17, 22.57, 24.84(4C), 27.39, 27.75, 28.96, 31.80, 41.03, 82.49(2C), 116-119(br s), 126.46, 139.13, 157.21; HRMS calcd for $C_{18}H_{33}BO_2$ $[M]^+$: 292.2574 Found 292.2559.

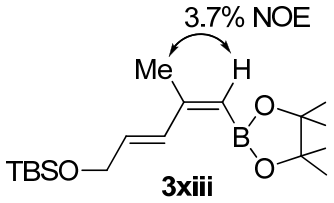
(2*E*,4*Z*)-4-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-2,4-dien-1-ol (3xii)



3xii

Compound **3xi** was generated from **1** and was used for synthesis of **4xi** without further purification. Experimental details are illustrated in the procedure for synthesizing **4xi** at page S13.

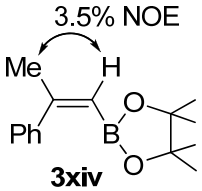
***tert*-Butyldimethyl((2*E*,5*Z*)-5-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-hexadienyloxysilane (3xiii)**



3xiii

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and (*E*)-(3-(*tert*-butyldimethylsilyloxy)-1-propenyl)zinc bromide (1.2 mmol, generated by treating (*E*)-tert-butyl(3-iodoallyloxy)dimethylsilane (0.358 g, 1.2 mmol) with *n*BuLi (0.53 mL, 1.3 mmol, 2.5 M solution in hexanes) in dry THF (2 mL) for 30 min at -78°C, followed by treating with $ZnBr_2$ (0.27 g, 1.2 mmol) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.31 g (90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.10 (s, 6H), 0.92 (s, 9H), 1.26 (s, 12 H), 1.97 (s, 3H), 4.30 (m, 2H), 5.28 (s, 1H), 5.91 (dt J_1 = 4.8 Hz, J_2 = 16 Hz, 1H), 7.22 (d J = 16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.21(2C), 18.43, 22.89, 24.79(4C), 26.03(3C), 63.75, 82.82, 124.0(br s), 130.55, 132.13, 154.86. HRMS calcd for $C_{18}H_{35}BO_3Si$ $[M]^+$: 338.2449 Found 338.2443.

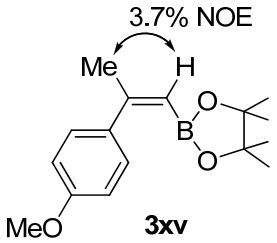
(*Z*)-2-(2'-phenyl-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3xiv)



3xiv

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and phenylzinc bromide (1.2 mmol, generated by treating phenylmagnesium bromide (0.4 mL, 1.2 mmol, 3.0 M solution in Et_2O) with a solution of $ZnBr_2$ (0.27 g, 1.2 mmol) in dry THF (2 mL) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.21 g (86%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (s, 12H), 2.24 (d, J = 1.2 Hz, 3H), 5.50 (q, J = 1.2 Hz, 3H), 7.25-7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.50(4C), 27.63, 82.83(2C), 115-119(br s), 127.32, 127.46(4C), 143.01, 157.54. HRMS calcd for $C_{15}H_{21}BO_2$ $[M]^+$: 244.1635 Found 244.1648.

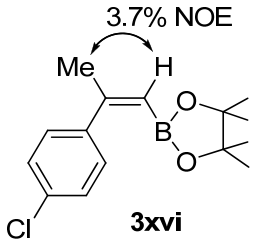
(*Z*)-2-(2'-(4-methoxyphenyl)-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3xv**)



3xv

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and 4-methoxyphenylzinc bromide (1.2 mmol, generated by treating 4-methoxyphenylmagnesium bromide (2.4 mL, 1.2 mmol, 0.5 M solution in THF) with a solution of $ZnBr_2$ (0.27 g, 1.2 mmol) in dry THF (2 mL) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.249 g (87%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 12H), 2.20 (d, *J* = 1.2 Hz, 3H), 3.79 (s, 3H), 5.41 (q, *J* = 1.2 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.48(4C), 27.57, 55.02, 82.74(2C), 112.70(2C), 115-117(br s), 128.74(2C), 135.25, 156.92, 159.04. HRMS calcd for $C_{16}H_{23}BO_3$ $[M]^+$: 274.1740 Found 274.1765.

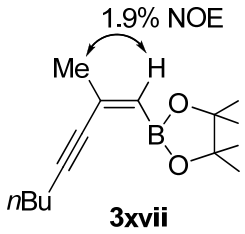
(*Z*)-2-(2'-(4-chlorophenyl)-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3xvi**)



3xvi

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and 4-chlorophenylzinc bromide (1.2 mmol, generated by treating 4-chlorophenylmagnesium bromide (1.2 mL, 1.2 mmol, 1.0 M solution in Et_2O) with a solution of $ZnBr_2$ (0.27 g, 1.2 mmol) in dry THF (2 mL) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.24 g (85%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (s, 12H), 2.19 (d, *J* = 1.2 Hz, 3H), 5.49 (q, *J* = 1.2 Hz, 1H), 7.25 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.54(4C), 27.67, 82.99(2C), 116-120(br), 127.61(2C), 128.94(2C), 133.00, 141.40, 156.44. HRMS calcd for $C_{15}H_{20}BO_2Cl$ $[M]^+$: 278.1245 Found 278.1255.

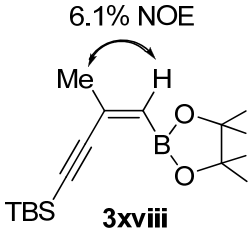
(*Z*)-2-(2'-methyl-1-octen-3-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3xvii**)



3xvii

General procedure A starting from **2** (0.25 g, 1 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and 1-hexynylzinc bromide (1.2 mmol, generated by treating 1-hexyne (0.10 g, 1.2 mmol) with *n*-BuLi (0.53 mL, 1.3 mmol, 2.5 M solution in hexanes) in dry THF (2 mL) for 30 min at -78°C, followed by treating with $ZnBr_2$ (0.27 g, 1.2 mmol) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.21 g (83%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 12H), 1.35-1.6 (m, 4H), 1.96 (d, *J* = 1.5 Hz, 3H), 2.34 (t, *J* = 6.9 Hz, 3H), 5.49 (q, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.59, 19.24, 21.83, 24.75(4C), 27.74, 30.59, 81.76, 82.91(2C), 94.64, 139.26. HRMS calcd for $C_{15}H_{25}BO_2$ $[M]^+$: 248.1948 Found 248.1933.

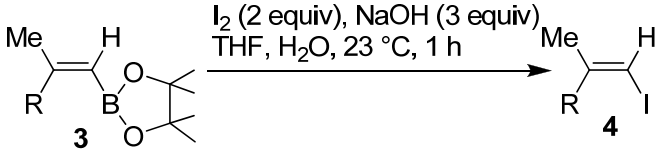
(*Z*)-2-(4-(*tert*-butyldimethylsilyl)-2-methylbut-1-en-3-ynyl)-4,4,5,5-tetramethyl-1,3, 2-dioxaboralane (**3xviii**)



3xviii

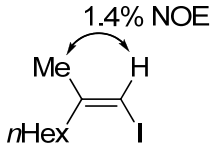
General procedure A starting from **2** (0.50 g, 2 mmol), 0.1% Pd(*t*-$Bu_3P)_2$ (0.1 mL, 0.01 M solutions in THF, 0.001mmol) and ((*tert*-butyldimethylsilyl)ethynyl)zinc bromide (3.0 mmol, generated by treating (*tert*-butyldimethylsilyl)ethyne (0.42 g, 3.0 mmol) with *n*-BuLi (1.2 mL, 3.0 mmol, 2.5 M solution in hexanes) in dry THF (4 mL) for 30 min at -78°C, followed by treating with $ZnBr_2$ (0.676 g, 3.0 mmol) for 30 min at 0°C) gave the title compound as colorless oil. Yield: 0.551 g (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 6H), 0.94 (s, 9H), 1.22 (s, 12H), 1.97 (s, 3H), 5.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.75, 16.62, 24.75, 26.10, 27.56, 83.00, 96.63, 106.25, 126.02, 138.23. HRMS calcd for $C_{17}H_{31}BO_2Si$ $[M]^+$: 306.2186 Found 306.2153.

General procedure B for iodinolysis of boronates[viii]



To a stirred solution of boronate **3** (0.5 mmol) in THF (1 mL) was added a solution of NaOH (0.5 mL, 1.5 mmol, 3 M in water). The resultant mixture was stirred for 10 min at 23°C, followed by dropwise addition of a solution of I_2 (0.25 g, 1 mmol) in THF (5 mL). After 1 h at 23°C, the reaction mixture was quenched with aqueous $Na_2S_2O_3$, extracted with ether, washed successively with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (silica gel, hexanes, for case of **4xii**, hexane-EtOAc 100:1 was used; for case of **4xv**, hexane-EtOAc 50:1 was used;) afforded the compounds **4**, which are ≥ 98% pure determined by ^1H and ^{13}C NMR analysis..

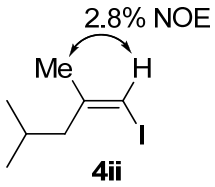
(*Z*)-1-iodo-2-methyl-1-octene (**4i**)



4i

General procedure B starting from **3i** (0.13 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.11 g (86%); ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.25-1.5 (m, 8H), 1.88 (d, *J* = 1.5 Hz, 3H), 2.20 (t, *J* = 7.2 Hz, 2H), 5.82 (q, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.08, 22.59, 23.25, 26.90, 28.96, 31.68, 38.64, 73.77, 147.80.

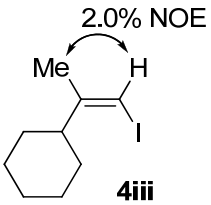
(*Z*)-1-iodo-2,3-dimethyl-1-butene (**4ii**)



4ii

General procedure B starting from **3ii** (0.11 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.09 g (82%); ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, *J* = 6.8 Hz, 6 H); 1.86 (s, 3H); 1.90 (m, 1H); 2.12 (d, *J* = 7.2 Hz, 2H); 5.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.22(C), 23.75, 26.65, 47.09, 75.16, 146.66. HRMS calcd for $C_7H_{13}I$ $[M]^+$: 224.0062 Found 224.0062.

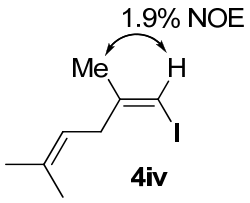
(*Z*)-(1-iodo-1-propen-2-yl)cyclohexane (**4iii**)



4iii

General procedure B starting from **3iii** (0.13 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.11 g (88%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.1-1.45 (m ,5H), 1.55-1.65 (m, 2H), 1.65-1.85 (m, 3H), 1.78 (d, J = 1.5 Hz, 3H), 2.54 (tt, J_1 = 3.0 Hz, J_2 = 11.7 Hz, 1H) , 5.76 (q, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.14, 26.01, 26.14(2C), 29.93(2C), 46.57, 73.91, 151.11. HRMS calcd for $C_9H_{15}I$ $[M]^+$: 250.0218 Found 250.0199.

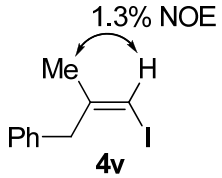
(*Z*) 1-iodo-2,5-dimethyl-1,4-hexadiene (**4iv**)



4iv

General procedure B starting from **3iv** (0.12 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.10 g (84%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (s, 3H), 1.72 (s, 3H), 1.85 (s, 3H), 2.91 (d, J = 6.9 Hz), 5.05-5.15 (m, 1H), 5.82 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.05, 23.17, 25.76, 37.91, 73.33, 119.69, 133.79, 147.03; HRMS calcd for $C_8H_{13}I$ $[M]^+$: 236.0062. Found 236.0061.

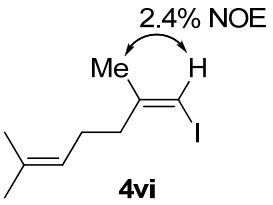
(*Z*)-(3-iodo-2-methylallyl)benzene (**4v**)



4v

General procedure B starting from **3v** (0.13 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.10 g (81%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85 (s, 3H), 3.62 (s, 2H), 6.07 (s, 1H), 7.2-7.4 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.07, 44.66, 75.54, 126.43, 128.46(2C), 128.53(2C), 138.17, 146.57. HRMS calcd for $C_{10}H_{11}I$ $[M]^+$: 257.9905. Found 257.9931.

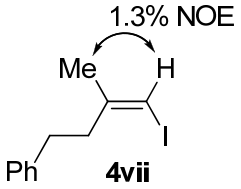
(*Z*)-1-iodo-2,6-dimethyl-1,5-heptadiene (**4vi**)



4vi

General procedure B starting from **3vi** (0.13 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.11 g (87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.65 (s, 3 H), 1.70 (s, 3H), 2.10 (m, 2H), 2.25 (m, 2H), 5.15 (t, *J* = 5.0 Hz, 1H), 5.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.67, 23.41, 25.55, 25.68, 38.74, 123.19, 132.32; 147.29.

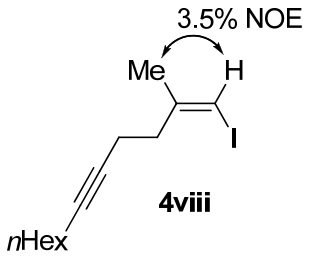
(*Z*)-(4-iodo-3-methyl-3-butenyl)benzene (**4vii**)



4vii

General procedure B starting from **3vii** (0.14 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.11 g (80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97 (s, 3H), 2.60 (m, 2H), 2.80 (m, 2H), 5.97 (s, 1H), 7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.55, 33.14, 40.64, 74.91, 125.95, 128.30(2C), 128.32(2C), 141.17, 146.69; HRMS calcd for $C_{11}H_{13}I$ $[M]^+$: 272.0062. Found 272.0081.

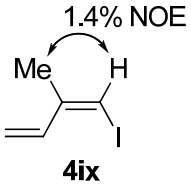
(*Z*)-1-iodo-2-methyl-1-dodecen-5-yne (**4viii**)



4viii

General procedure B starting from **3viii** (0.15 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.14 g (90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.26-1.40 (m, 6H), 1.45 (m, 2H), 1.90 (s, 3H), 2.11 (t, *J* = 2.0 Hz), 2.25 (m, 2H), 2.35 (m, 2H), 5.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.01, 16.60, 18.70, 22.51, 23.48, 28.48, 31.31, 37.98, 75.18, 78.63, 80.93, 146.07. $C_{13}H_{21}I$ $[M]^+$: 304.0688. Found 304.0660.

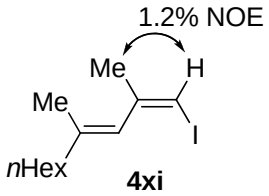
(*Z*)-1-iodo-2-methyl-1,3-butadiene (**4ix**)



4ix

General procedure B starting from **3ix** (0.10 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.08 g (84%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97 (d, *J* = 1.2 Hz, 3H), 5.32 (dt, J_1 = 1.2 Hz, J_2 = 9.6 Hz, 1H), 5.42 (dt, J_1 = 1.2 Hz, J_2 = 17.4 Hz, 1H), 6.68 (q, *J* = 1.2 Hz, 1H), 6.73 (ddd, J_1 = 1.2 Hz, J_2 = 11.1 Hz, J_3 = 17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.42, 79.92, 118.24, 138.20, 142.08.

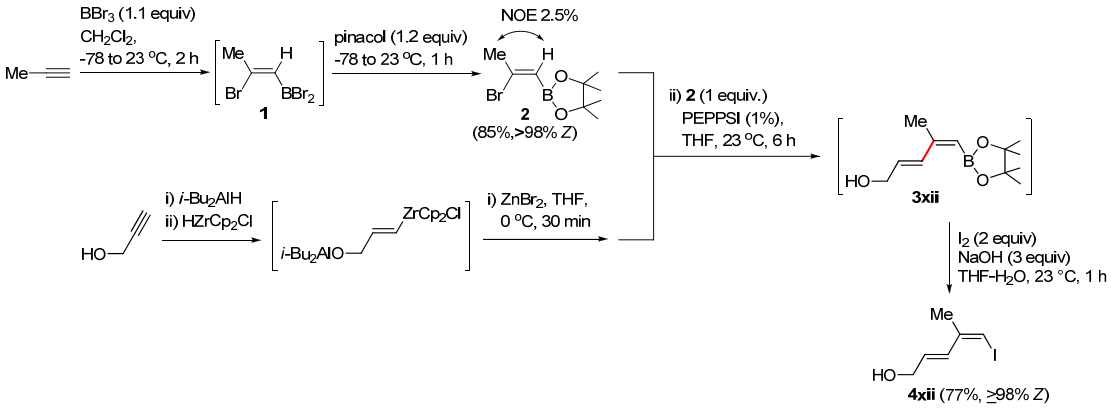
(1*Z*,3*E*)-1-iodo-2,4-dimethyl-1,3-decadiene (**4xi**)



4xi

General procedure B starting from **3xi** (0.15 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.12 g (81%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.9 Hz, 3H), 1.25-1.4 (m, 6H), 1.4-1.55 (m, 2H), 1.68 (d, *J* = 1.2 Hz, 3H), 1.98 (d, *J* = 1.5 Hz, 3H), 2.08 (t, *J* = 7.5 Hz, 2H), 5.64 (q, *J* = 1.2 Hz, 1H), 5.98 (q, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.12, 17.93, 22.66, 24.64, 27.71, 28.89, 31.75, 39.86, 76.35, 126.52, 140.29, 145.29; HRMS calcd for. $C_{12}H_{21}I$ $[M]^+$: 292.0688. Found 292.0678.

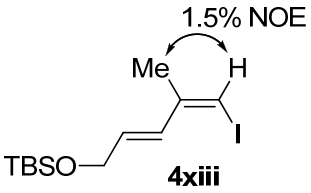
(2*E*,4*Z*)-5-iodo-4-methylpenta-2,4-dien -1-ol (**4xii**)



To $ZrCp_2Cl_2$ (1.93 g, 6.6 mmol) in dry THF (6 mL) cooled to 0°C was added slowly a solution of *i*-Bu_2AlH (6.6 mL, 6.6 mmol, 1 M solution in hexanes). The resultant

suspension was stirred for 30 min at 0°C, followed by addition of (3-butynyloxy)diisobutylaluminum (6 mmol) prepared by mixing propargyl alcohol (0.34 mL, 6.0 mmol) and *i*-Bu_2AlH (6.0 mL, 6.0 mmol, 1 M solution in hexanes) in dry THF (6 mL) for 30 min at -78°C. The resultant mixture was warmed to room temperature and stirred 1h at 23°C, cooled to 0°C, followed by addition of a solution of $ZnBr_2$ (1.35 g, 6 mmol) in dry THF (6 mL). After 30 min at 0°C, a solution of (*Z*)-2-(2'-Bromo-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) (4 mmol, prepared from propyne (0.16 g, 4.0 mmol) and BBr_3 (1.1 g, 4.4 mmol) in dry CH_2Cl_2) in dry THF (2 mL) and PEPPSI^{TM}-IPr (41 mg, 0.06 mmol). After 6 h at 23°C, a solution of NaOH (0.72 g, 18 mmol) in water (4 mL) and I_2 (3.05 g, 12 mmol) was added. The mixture was stirred 2h at 23°C, quenched with 0.5 M HCl, extracted with ether, washed with saturated $Na_2S_2O_3$, $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, EtOAc−hexanes 1:2) afforded the title compound 0.69 g (77%), which is ≥ 98% pure determined by ^1H and ^{13}C NMR analysis. ^1H NMR (300 MHz, $CDCl_3$) δ 1.98 (s, 3H), 4.29 (t, *J* = 5.4 Hz, 2H), 6.04 (dt, J_1 = 5.1 Hz, J_2 = 15.6 Hz, 1H), 6.16 (s, 1H), 6.64 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ21.05, 62.93, 79.63, 131.97, 133.25, 141.14. HRMS calcd for. C_6H_9IO $[M]^+$: 223.9698. Found 223.9678.

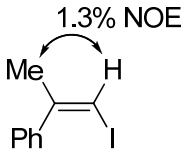
tert-Butyl((2*E*,5*Z*)-6-iodo-5-methyl-2,5-hexadienyloxy)dimethylsilane (**4xiii**)



4xiii

General procedure B starting from **3xiii** (0.17 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.14 g (84%); ^1H NMR (400 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.95 (s, 9H), 1.96 (s, 3H), 4.30 (dd, J_1 = 1.2 Hz, J_2 = 4.4 Hz, 2H), 5.96 (dt, *J* = 4.8 Hz, J = 15.6 Hz, 1H), 6.09 (s, 1H), 6.67 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.21(2C), 18.35, 21.08, 25.96(3C), 63.32, 78.76, 130.80, 133.87, 141.40.

(*Z*)-(1-iodo-1-propen-2-yl)benzene (**4xiv**)

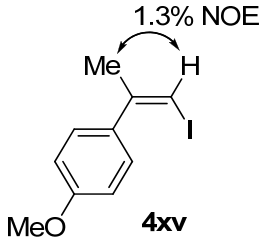


4xiv

General procedure B starting from **3xiv** (0.12 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.11 g (86%); ^1H NMR (300 MHz, $CDCl_3$) δ 2.26 (d, *J* = 1.2 Hz, 3H), 6.32 (q, *J* = 1.2 Hz,

1H), 7.25-7.35 (m, 2H), 7.35-7.45 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.52, 77.43, 127.35(2C), 127.59, 128.22(2C), 142.83, 148.19.

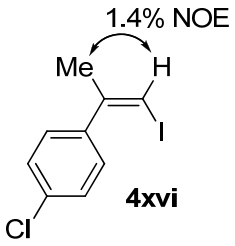
(*Z*)-(1-iodo-1-propen-2-yl)-4-methoxybenzene (**4xv**)



4xv

General procedure B starting from **3xv** (0.14 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.12 g (89%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (d, *J* = 1.2 Hz, 3H), 3.86 (s, 3H), 6.26 (q, *J* = 1.2 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.44, 55.12, 74.30, 113.42(2C), 128.64(2C), 134.80, 147.42, 158.84; HRMS calcd for. $C_{10}H_{11}IO$ $[M]^+$: 273.9855. Found 273.9878.

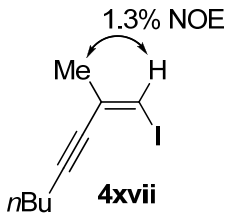
(*Z*)-(1-iodo-1-propen-2-yl)-4-chlorobenzene (**4xvi**)



4xvi

General procedure B starting from **3xvi** (0.14 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield: 0.12 g (85%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (d, *J* = 1.2 Hz, 3H), 6.32 (q, *J* = 1.5 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.41, 77.43, 128.50(2C), 128.87(2C), 133.40, 141.11, 147.02. C_9H_8ICl $[M]^+$: 277.9359. Found 277.9368.

(*Z*)-1-iodo-2-methyl-1-octen-3-yne (**4xvii**)

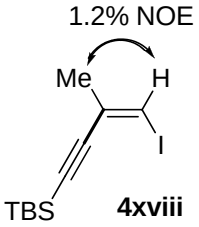


4xvii

General procedure B starting from **3xvii** (0.12 g, 0.5 mmol), NaOH (0.5 mL, 1.5 mmol, 3 M in water) and I_2 (0.25 g, 1 mmol) gave the title compound as colorless oil. Yield:

0.11 g (87%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.4-1.65 (m, 4H), 1.97 (d, *J* = 1.2 Hz, 3H), 2.38 (t, *J* = 7.2 Hz, 2H), 6.28 (q, *J* = 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.58, 19.24, 21.91, 24.95, 30.51, 81.93, 82.42, 96.92, 132.41; HRMS calcd for $C_9H_{13}I$ $[M]^+$: 248.0062. Found 248.0068.

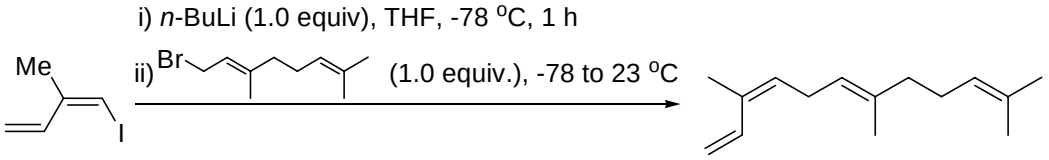
(*Z*)-(4-(tert-butyldimethylsilyl)-1-iodo-2-methyl-1-buten-3-yne (**4xviii**)



4xviii

General procedure B starting from **3xviii** (0.545 g, 1.78 mmol), NaOH (0.214 g, 5.34 mmol, in 1.5 mL water) and I_2 (0.904 g, 3.56 mmol in 6 mL THF) gave the title compound as colorless oil. Yield: 0.457 g (84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 6H), 1.00 (s, 9H), 1.22 (s, 12H), 1.98 (s, 3H), 6.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.69, 16.61, 24.66, 26.15, 84.76, 99.13, 106.49, 131.98. HRMS calcd for $C_{11}H_{19}ISi$ $[M]^+$: 306.2585. Found 306.2599.

(3*Z*,6*E*)-3,7,11-trimethyl-1,3,6,10-dodecatetraene (**6**)

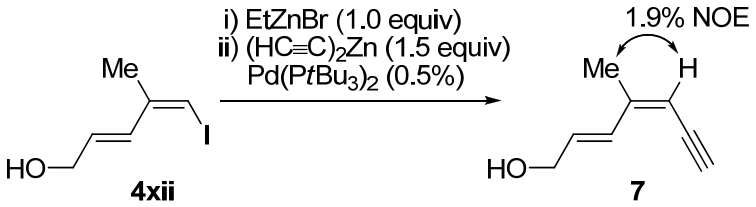


4ix

6 (3*Z*, 6*E*)-α-farnesene
(80%, ≥98% pure)

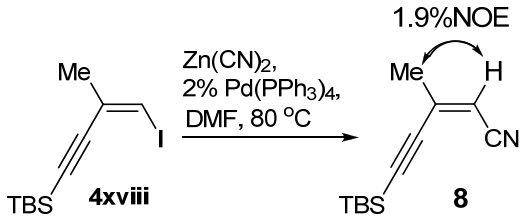
To a stirred solution of (*Z*)-1-iodo-2-methyl-1,3-butadiene (0.11 g, 0.55 mmol) in THF (2 mL) cooled to -78°C was added *n*BuLi (0.24 mL, 0.6 mmol, 2.5 M solution in hexanes). The resultant mixture was stirred 15 min at -78°C followed by addition of a solution of geranyl bromide (0.11 g, 0.5 mmol) in dry THF (2 mL).The mixture was stirred 1 h at 23°C, quenched with water, extracted with ether, washed successively with brine, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (silica gel, hexanes) afforded the title compound 0.084 g (82%), which is ≥ 98% pure determined by ^{1}H and ^{13}C NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (s, 3H), 1.64 (d, *J* = 0.9 Hz, 3H), 1.68 (d, *J* = 0.9 Hz, 3H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.95-2.15 (m, 4H), 2.87 (t, *J* = 6.9 Hz, 2H), 5.05-5.15 (m, 3H), 5.21 (dd, J_1 = 1.2 Hz, J_2 = 17.1 Hz, 1H), 5.36 (t, *J* = 6.9 Hz, 3H), 6.81 (ddd, J_1 = 0.9 Hz, J_2 = 11.1 Hz, J_3 = 17.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.09, 17.67, 19.75, 25.70, 26.34, 26.65, 39.65, 113.46, 122.34, 124.24, 129.73, 131.43, 131.91, 133.65, 135.66.

(2*E*,4*Z*)-4-methyl-2,4-heptadien-6-yn-1-ol (7)



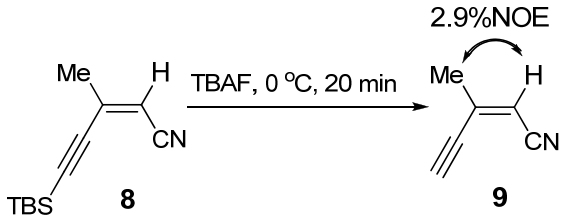
To a solution of (2*E*,4*Z*)-5-iodo-4-methyl-2,4-pentadien-1-ol **4xii** (0.21 g, 0.94 mmol) cooled to 0°C was added Et_2Zn (0.98 mL, 0.98 mmol, 1.0 M solution in hexanes). The mixture was stirred 30 min at 0°C followed by addition of a solution of Pd(*t*-$Bu_3P)_2$ (0.5 mL, 0.01 M solutions in THF, 0.005mmol) in dry THF (1 mL) and diethynylzinc (1.4 mL, 1.4 mmol, 1.0 M solution in hexanes). After 2 h at 23°C reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, 2:1 hexane:EtOAc) afforded the title compound 0.11 g (94%), which is ≥ 98% pure determined by ^1H and ^{13}C NMR analysis. ^1H NMR (300 MHz, $CDCl_3$) δ 1.92 (s, 3H), 3.20 (s, 1H), 4.30 (d, *J* = 5.7 Hz, 2H), 5.41 (s, 1H), 6.03 (dt, J_1 = 6.0 Hz, J_2 = 15.6 Hz, 1H), 6.97 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.16, 63.20, 80.84, 82.49, 107.61, 129.05, 132.21, 146.74.

(Z)-5-(tert-butyldimethylsilyl)-3-methyl-2-penten-4-ynenitrile (8)



To a solution of **4xviii** (350 mg, 1.14 mmol) and $Zn(CN)_2$ (174 mg, 1.48 mmol) in dry DMF (2 mL) was added $Pd(PPh_3)_4$ (26 mg, 0.023 mmol) at 23°C. The reaction mixture was stirred at 80°C for 3 h. Then, it was diluted with Et_2O (60 mL), washed with water (2 x 15 mL), dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (silica gel, 20:1 hexane:EtOAc) afforded the title compound 225 mg (96%) as colorless oil which is ≥ 98% pure determined by ^1H and ^{13}C NMR analysis. ^1H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 6H), 0.94 (s, 9H), 2.00 (s, 3H), 5.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.14, 16.33, 23.39, 25.80, 101.85, 104.09, 105.07, 116.19, 141.84. HRMS calcd for $C_{12}H_{19}NSi$ $[M]^+$: 205.1287. Found 205.1298.

(*Z*)-3-methyl-2-penten-4-ynenitrile (9)



To a cooled (0 °C) solution of **8** (223 mg, 1.09 mmol) in THF (2 mL) was add TBAF (1.14 mL, 1.14 mmol, 1M solution in THF). The resultant mixture was stirred at 0°C for 20 min,concentrated under vacumm and column chromatography (silica gel, 20:1 Et_2O:pentane) gave the title compound 84 mg (85%) as colorless oil which is ≥ 98% pure determined by ^1H and ^{13}C NMR analysis. ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 3.60 (s, 1H), 5.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.46, 80.37, 87.83, 105.27, 116.08, 141.39. HRMS calcd for C_6H_5N $[M]^+$: 91.0422. Found 91.0401.

Reference

[i] R. L. Shriner, F. W. Neumann, *Org. Synth.* **1955**, Coll. Vol. III, p73.
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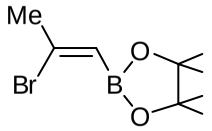
[viii] C. Morrill, R. H. Grubbs, *J. Org. Chem.* **2003**, *68*, 6031–6034.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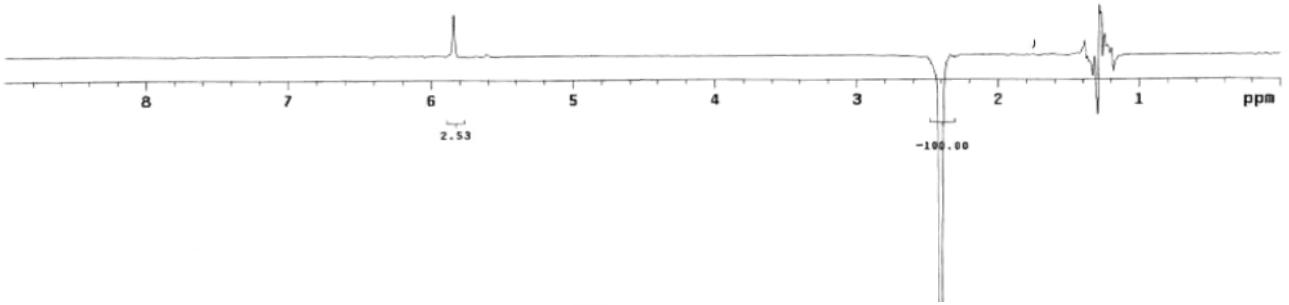
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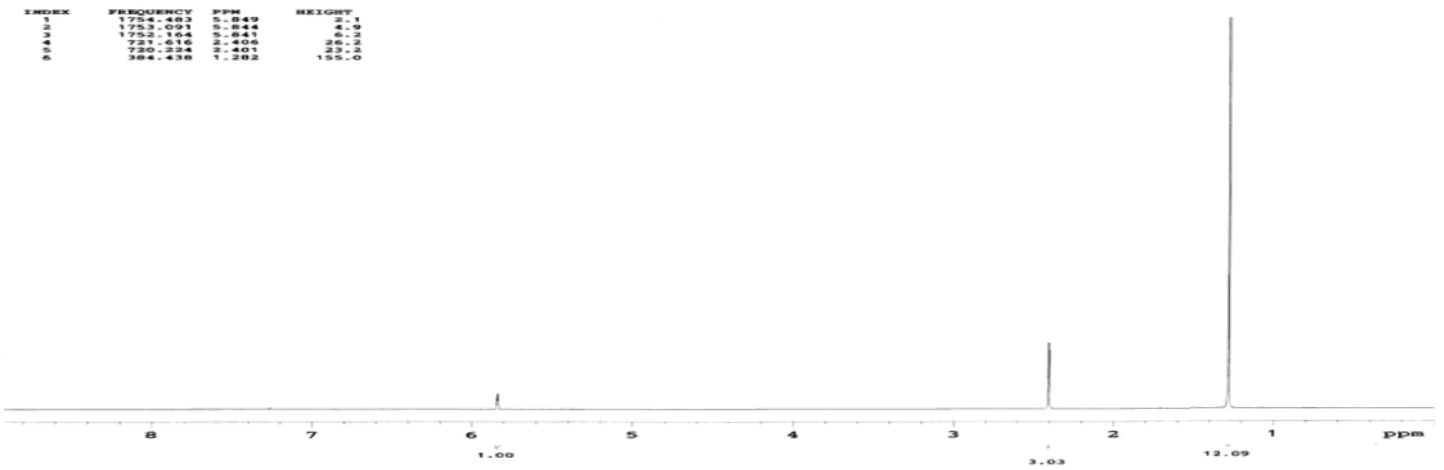
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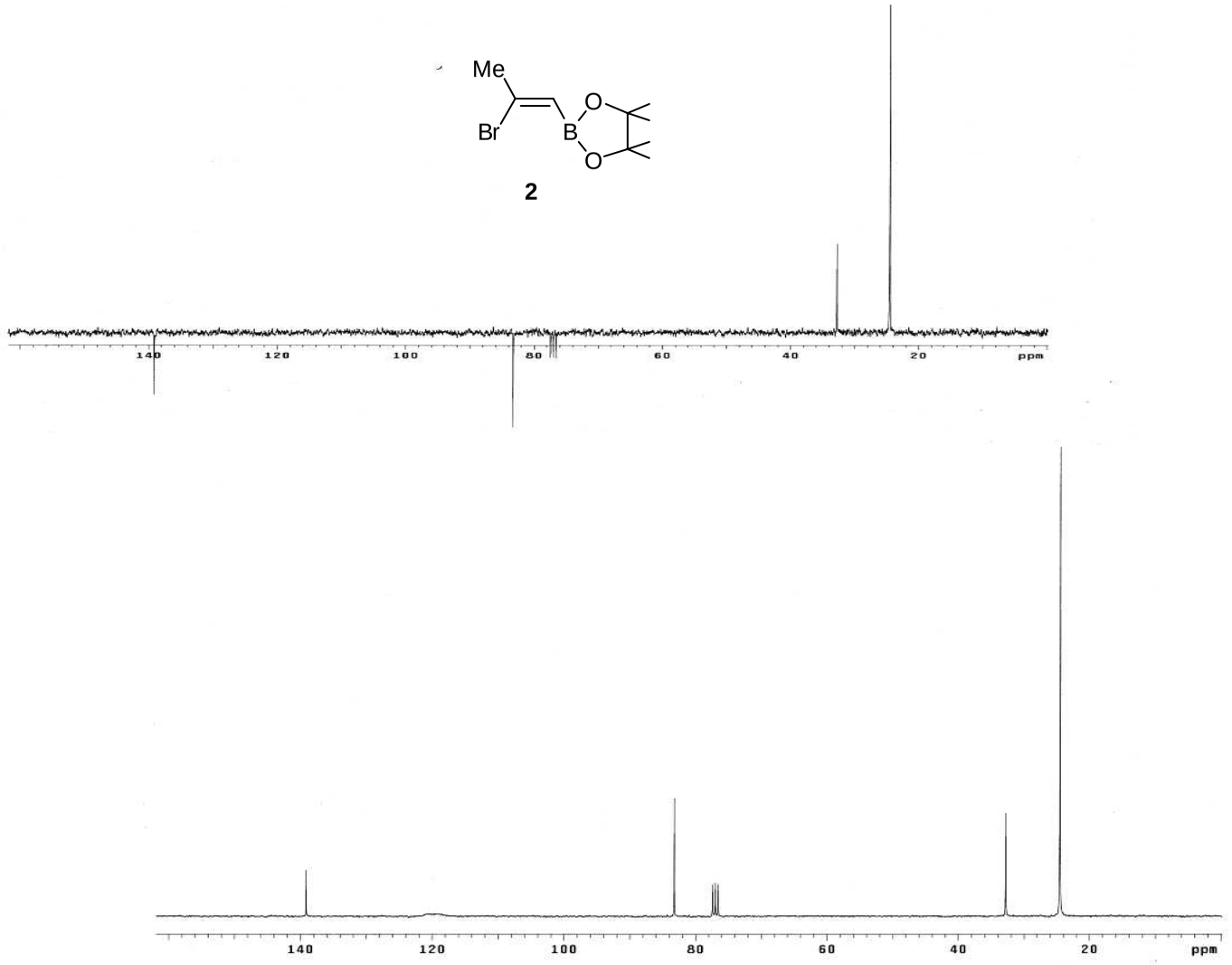
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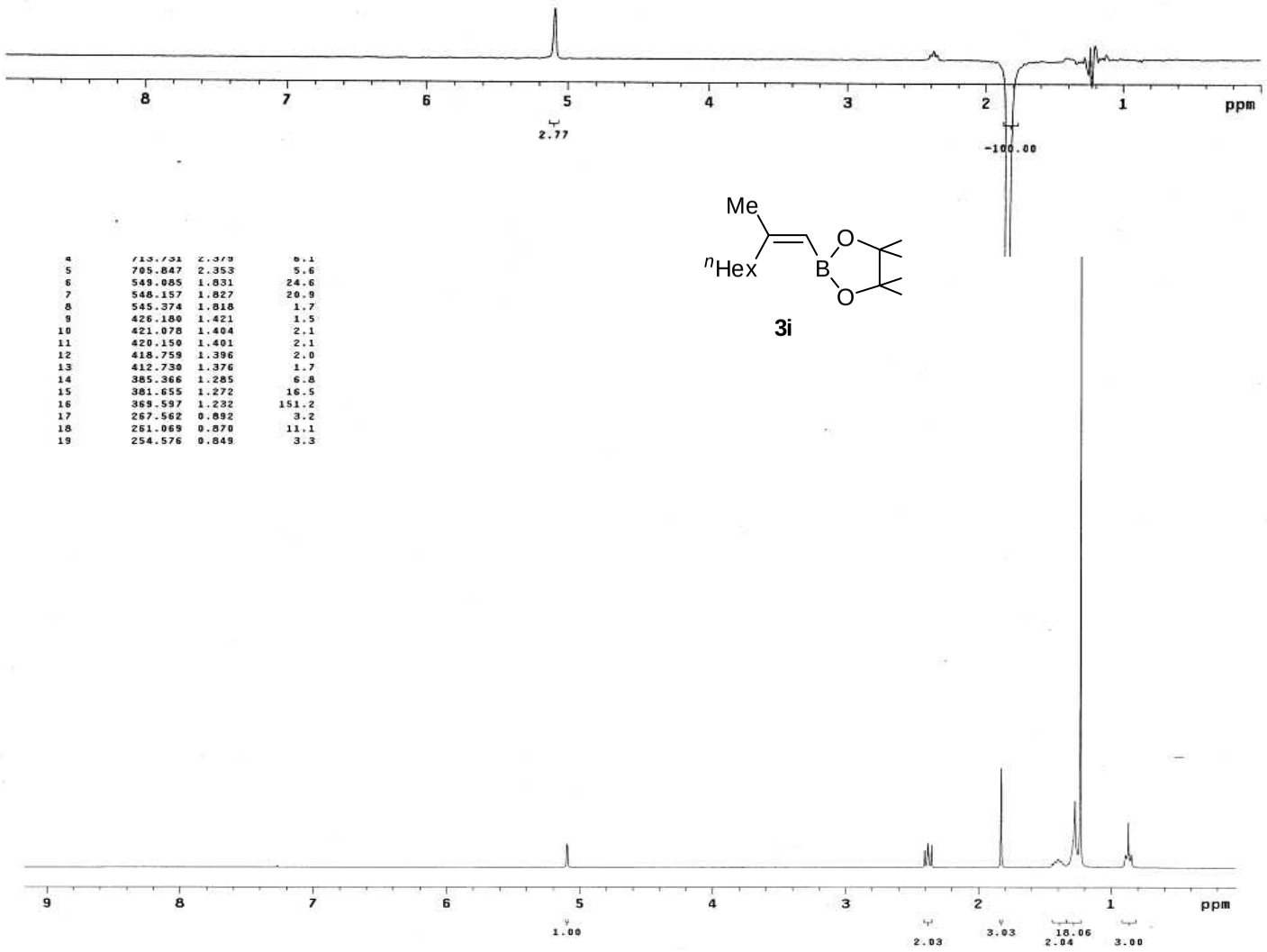

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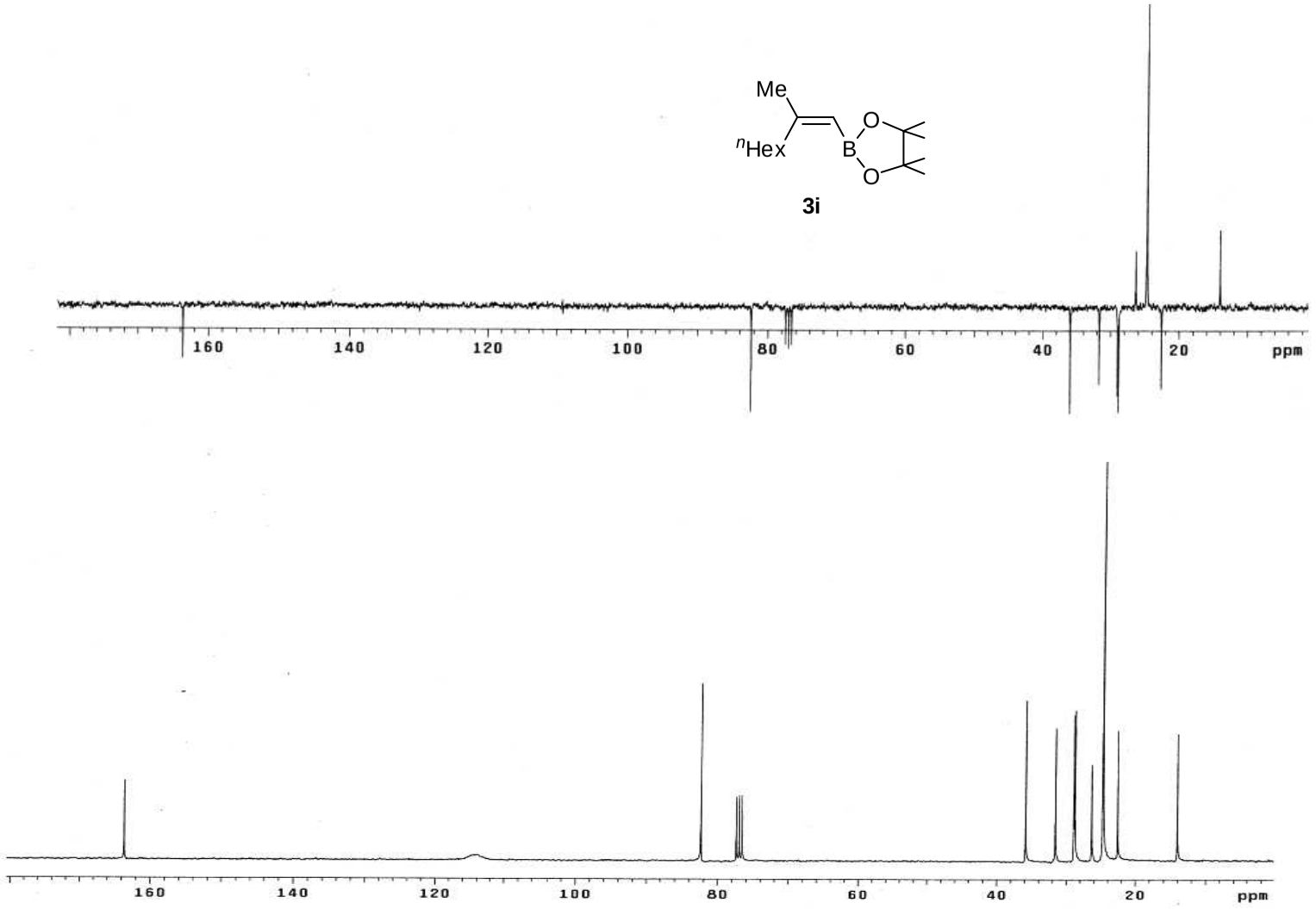
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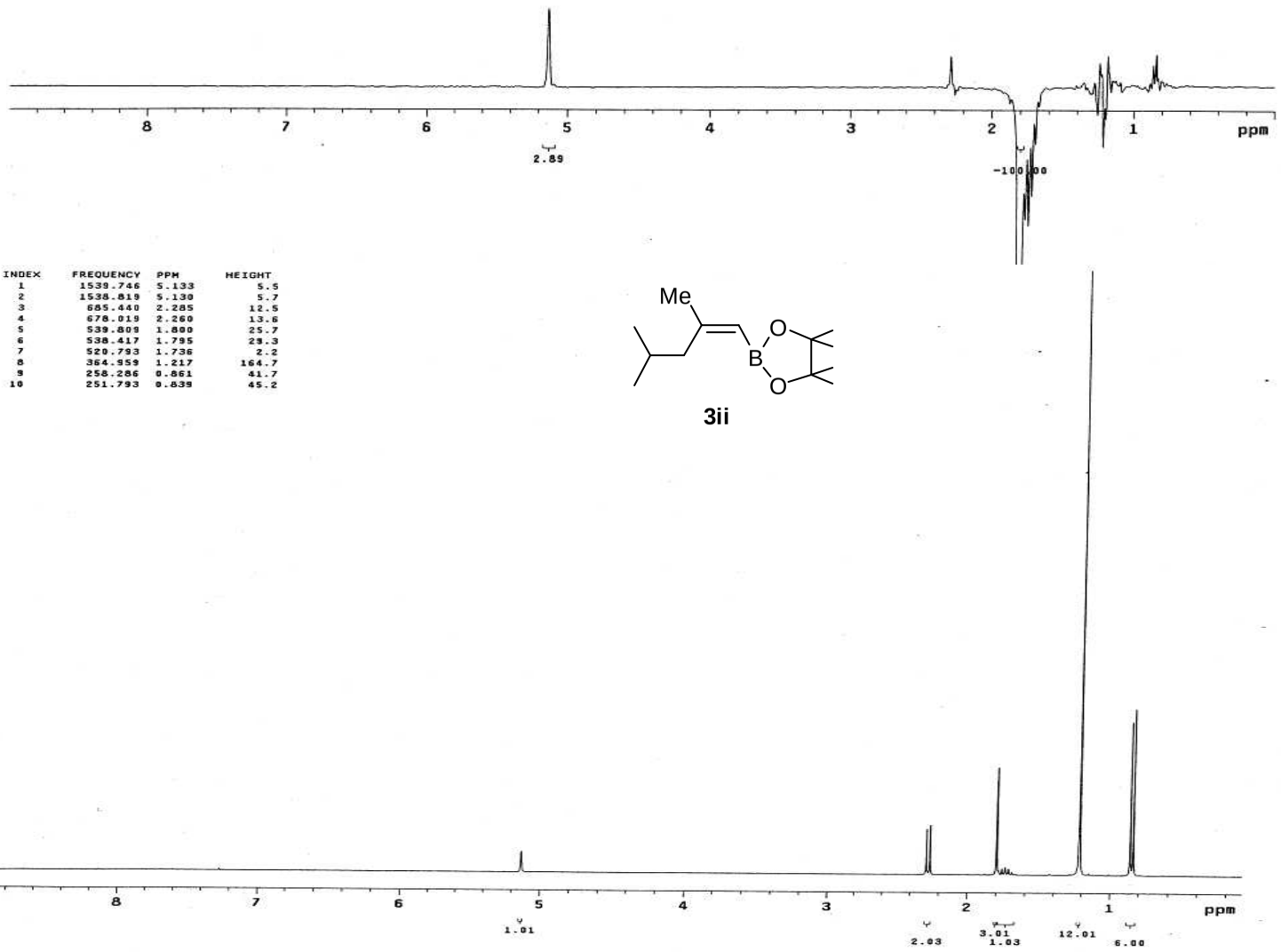
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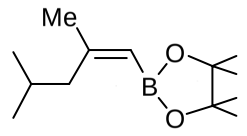

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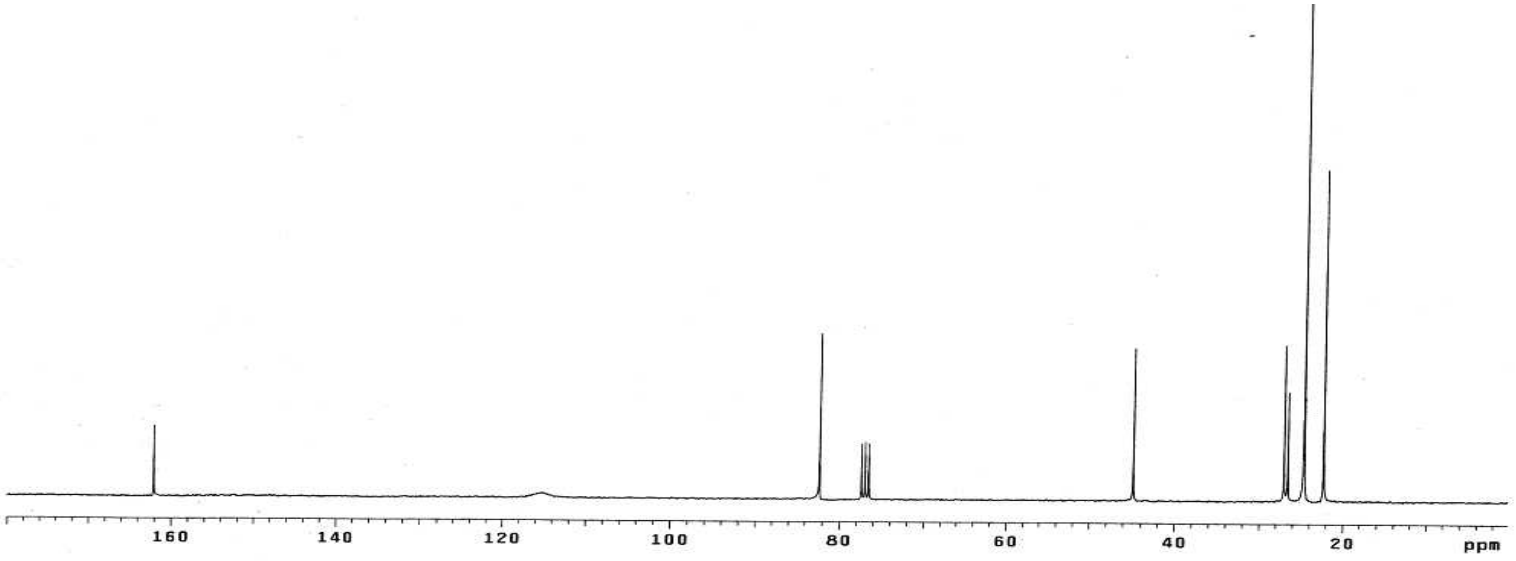

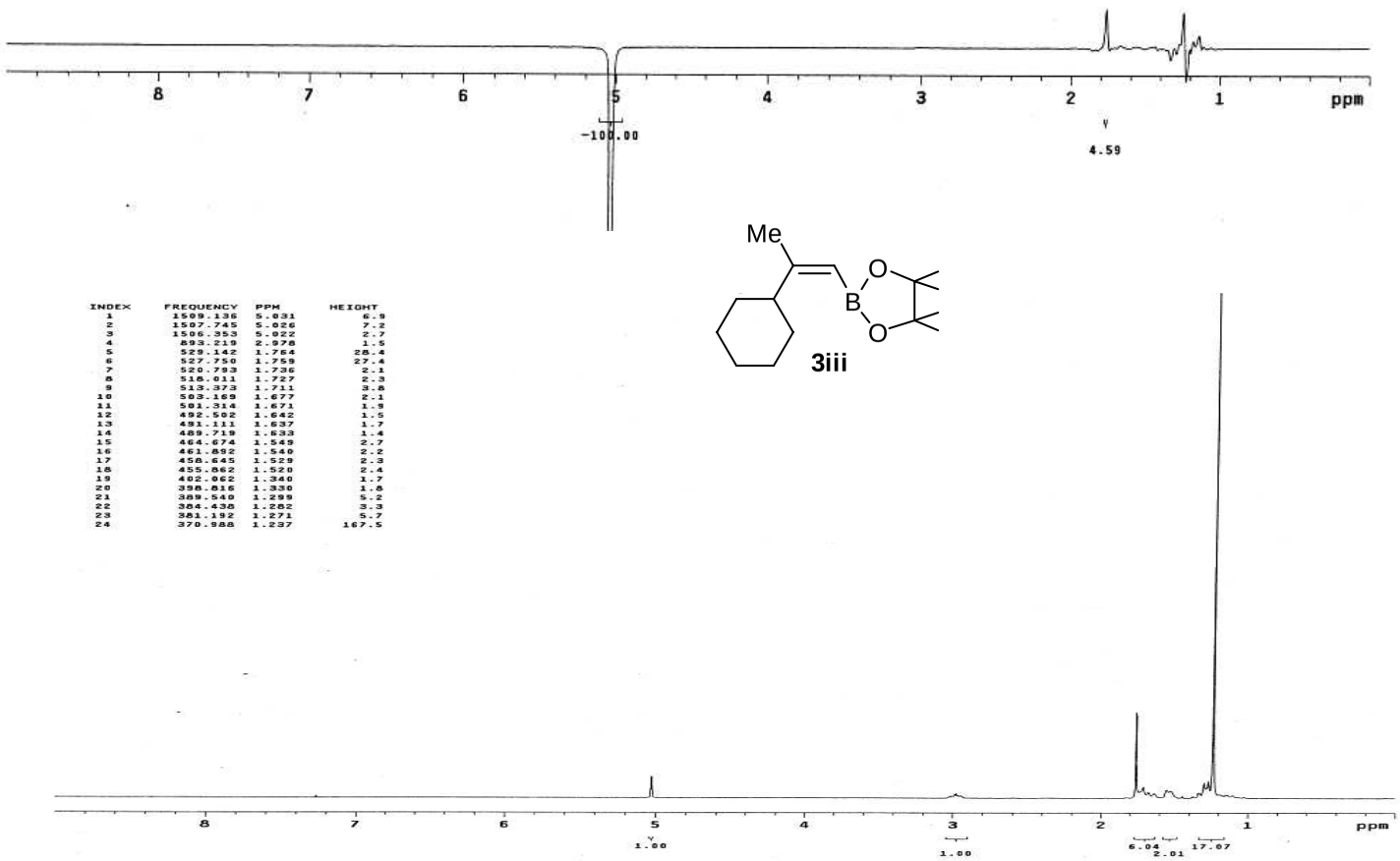

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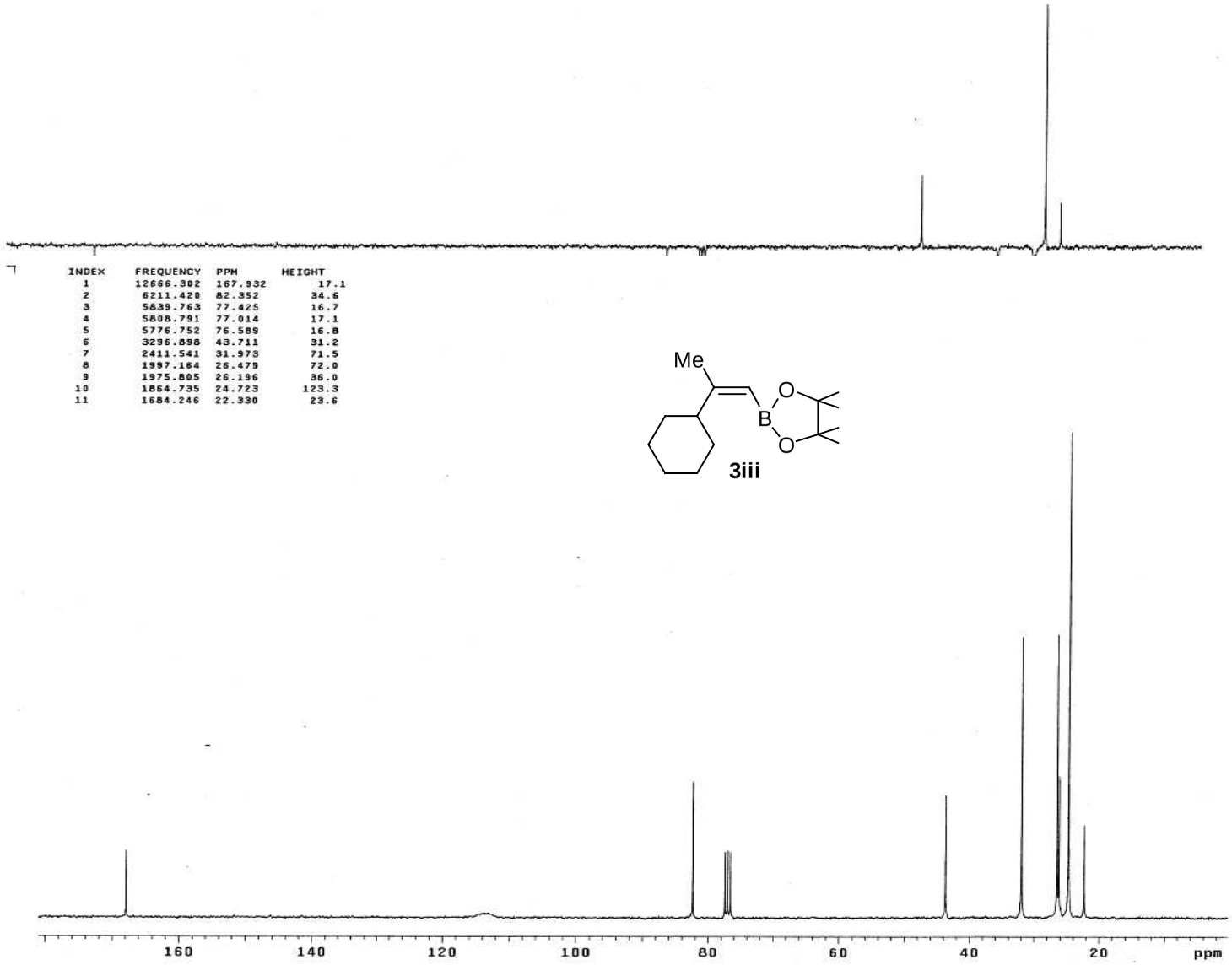
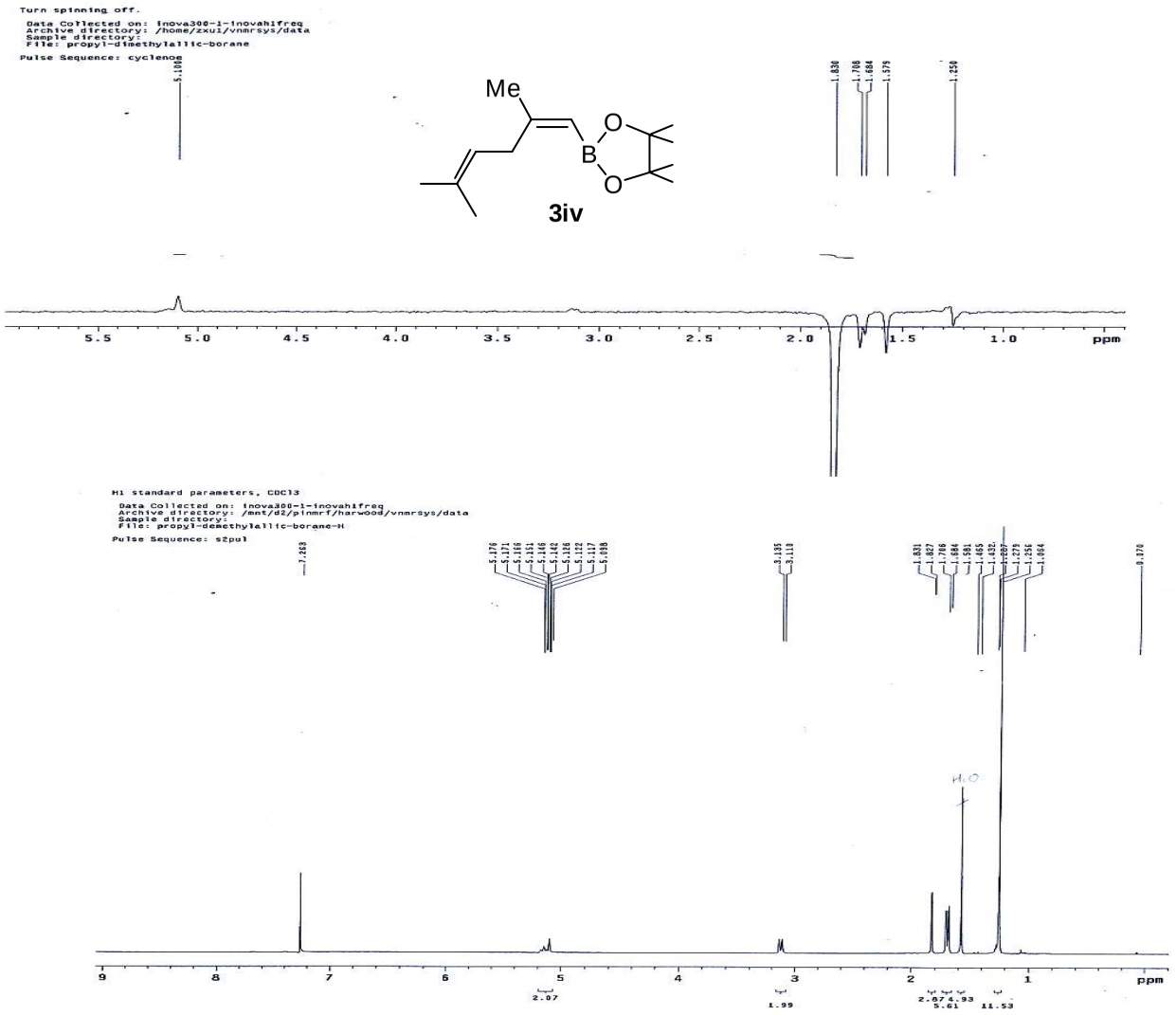
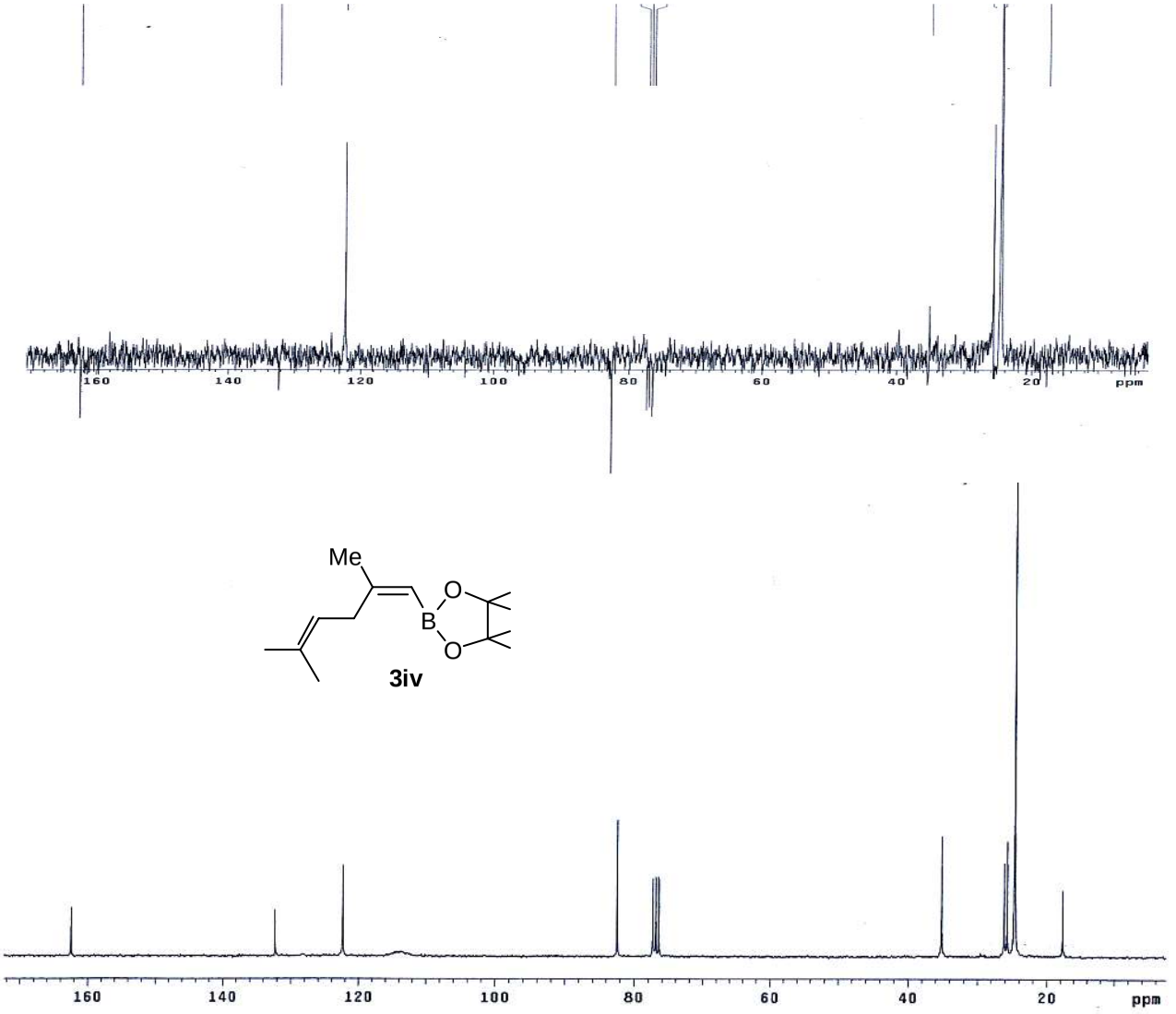
2	1507.745	5.026	7.2
3	1506.353	5.022	2.7
4	893.219	2.978	1.5
5	529.142	1.764	28.4
6	527.750	1.759	27.4
7	520.793	1.736	2.1
8	516.011	1.727	2.3
9	513.373	1.711	3.8
10	503.169	1.677	2.1
11	501.314	1.671	1.9
12	492.502	1.642	1.5
13	491.111	1.637	1.7
14	489.719	1.633	1.4
15	464.674	1.549	2.7
16	461.892	1.540	2.2
17	458.645	1.529	2.3
18	455.862	1.520	2.4
19	402.062	1.340	1.7
20	398.816	1.330	1.8
21	389.540	1.299	5.2
22	384.436	1.282	3.3
23	381.192	1.271	5.7
24	370.988	1.237	167.5

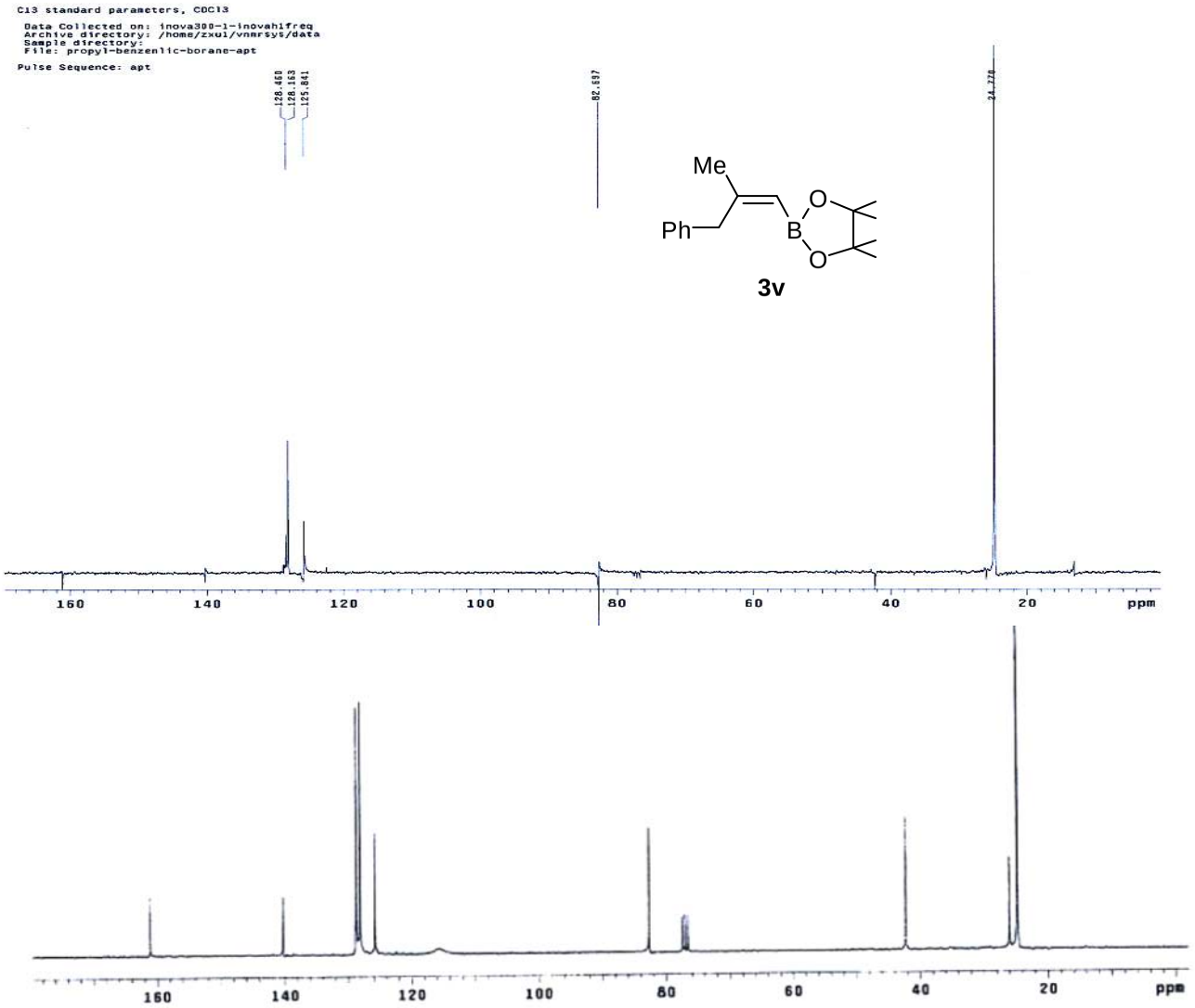


INDEX	FREQUENCY	PPM	HEIGHT
1	12666.302	167.932	17.1
2	6211.420	82.352	34.6
3	5839.763	77.425	16.7
4	5808.791	77.014	17.1
5	5776.752	76.589	16.8
6	3296.898	43.711	31.2
7	2411.541	31.973	71.5
8	1997.164	26.479	72.0
9	1975.805	26.196	36.0
10	1864.735	24.723	123.3
11	1684.246	22.330	23.6


Turn spinning off.
Data Collected on: inova300-1-inovahlfreq
Archive directory: /home/zxu1/vnmrsys/data
Sample directory:
File: propyl-dimethylallic-borane
Pulse Sequence: cyclenoe
Me
B
O
O
3iv
ppm
H1 standard parameters, CDCl3
Data Collected on: inova300-1-inovahlfreq
Archive directory: /mnt/d2/pinmrf/harwood/vnmrsys/data
Sample directory:
File: propyl-dimethylallic-borane-H
Pulse Sequence: s2pul
H2O
ppm


160
140
120
100
80
60
40
20
ppm
Me
O
B
O
3iv
160
140
120
100
80
60
40
20
ppm


9
8
7
6
5
4
3
2
1
ppm
2.85
-100.06
H1 standard parameters, CDCl3
Data Collected on: inova300-1-inovahlfreq
Archive directory: /mnt/d2/pinmrf/harwood/vnmrsys/data
Sample directory:
File: propyl-benzenlc-borane-H
Pulse Sequence: s2pul
7.288
7.285
7.272
7.266
5.851
5.247
3.764
1.768
1.763
1.637
1.298
1.231
Me
Ph
B
O
O
3v
5.47
1.00
2.03
2.92
11.59


C13 standard parameters, CDCl3
Data Collected on: inova300-1-inovahifreq
Archive directory: /home/zxu1/vnmrsys/data
Sample directory:
File: propyl-benzenlic-borane-apt
Pulse Sequence: apt
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128.163
125.841
82.697
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Me
Ph
B
O
O
3v
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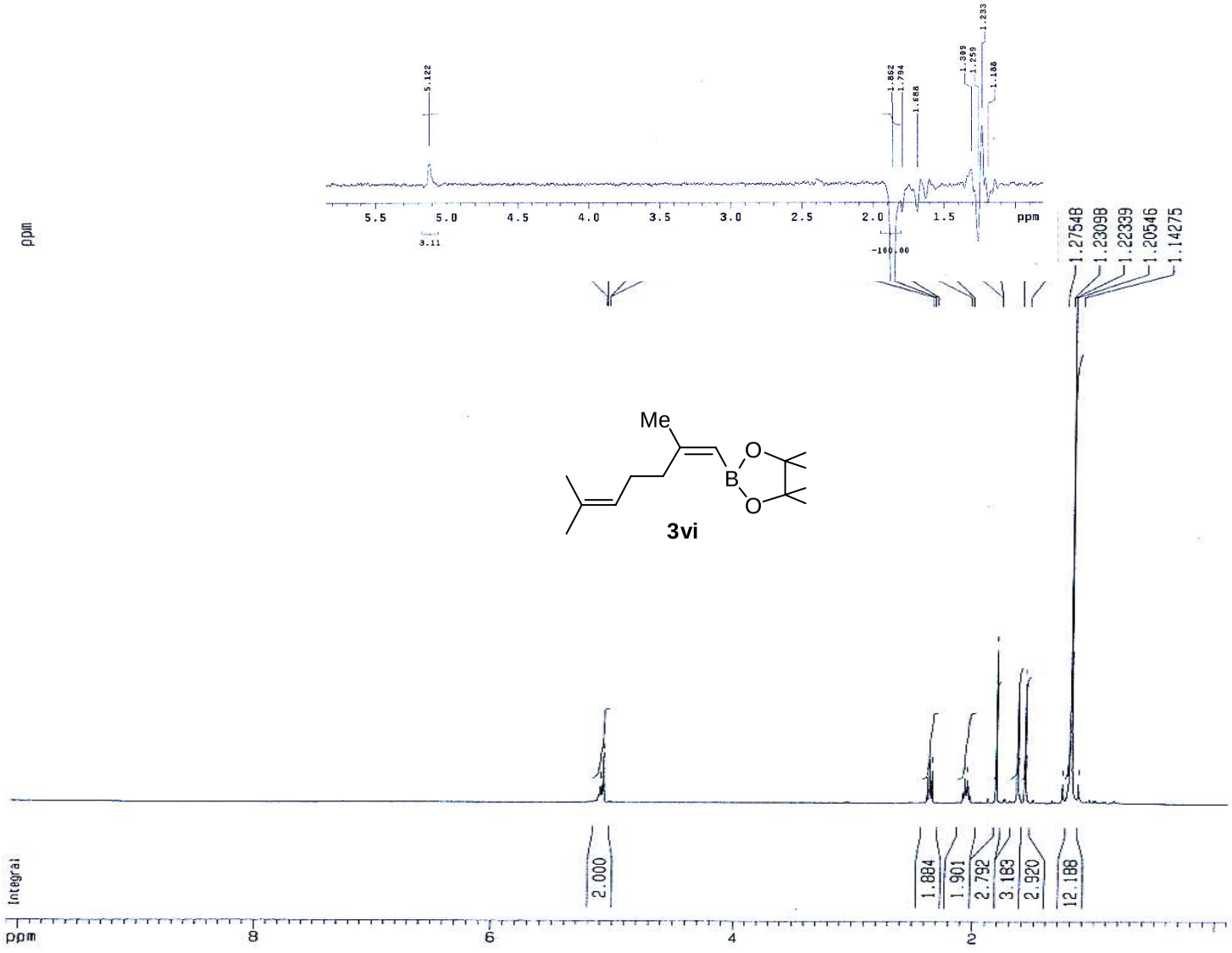
140
120
100
80
60
40
20
ppm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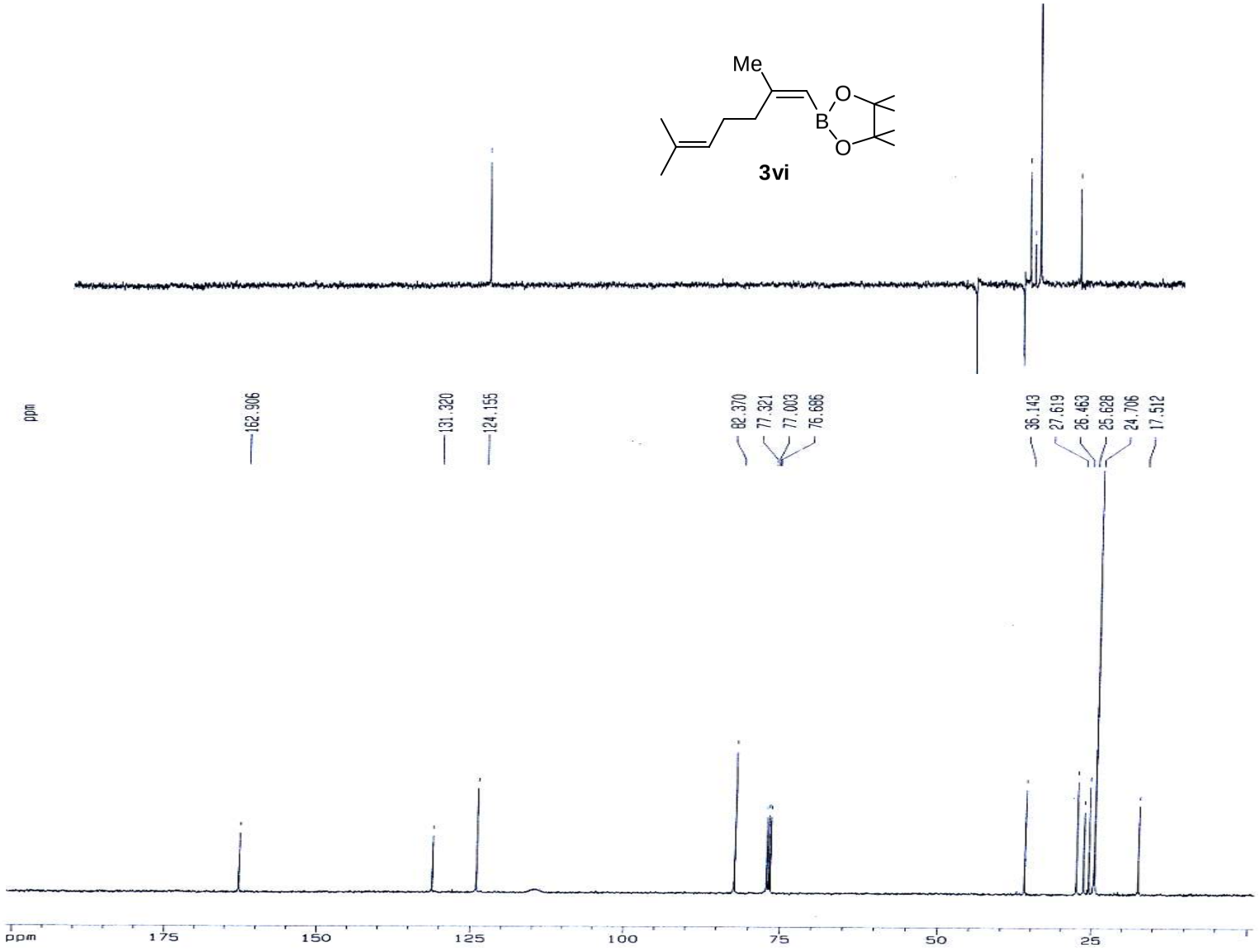
1.862
1.794
1.688
1.309
1.259
1.233
1.186
ppm
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
3.11
-100.00
1.27548
1.23098
1.22339
1.20546
1.14275
Me
O
B
O
3vi
Integral
2.000
1.884
1.901
2.792
3.183
2.920
12.188
ppm
8
6
4
2

Highly Regio- and Stereoselective Synthesis of *Z*-Trisubstituted Alkenes via Propyne Bromoboration and Tandem Pd-Catalyzed Cross-Coupling

Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



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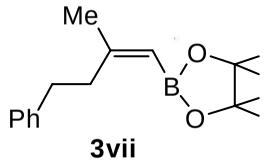
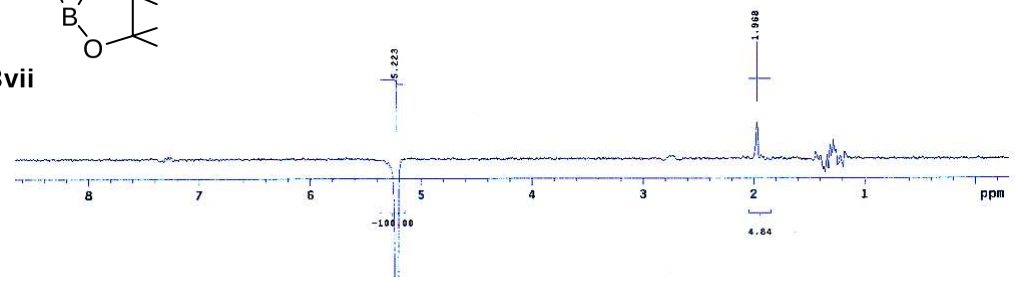
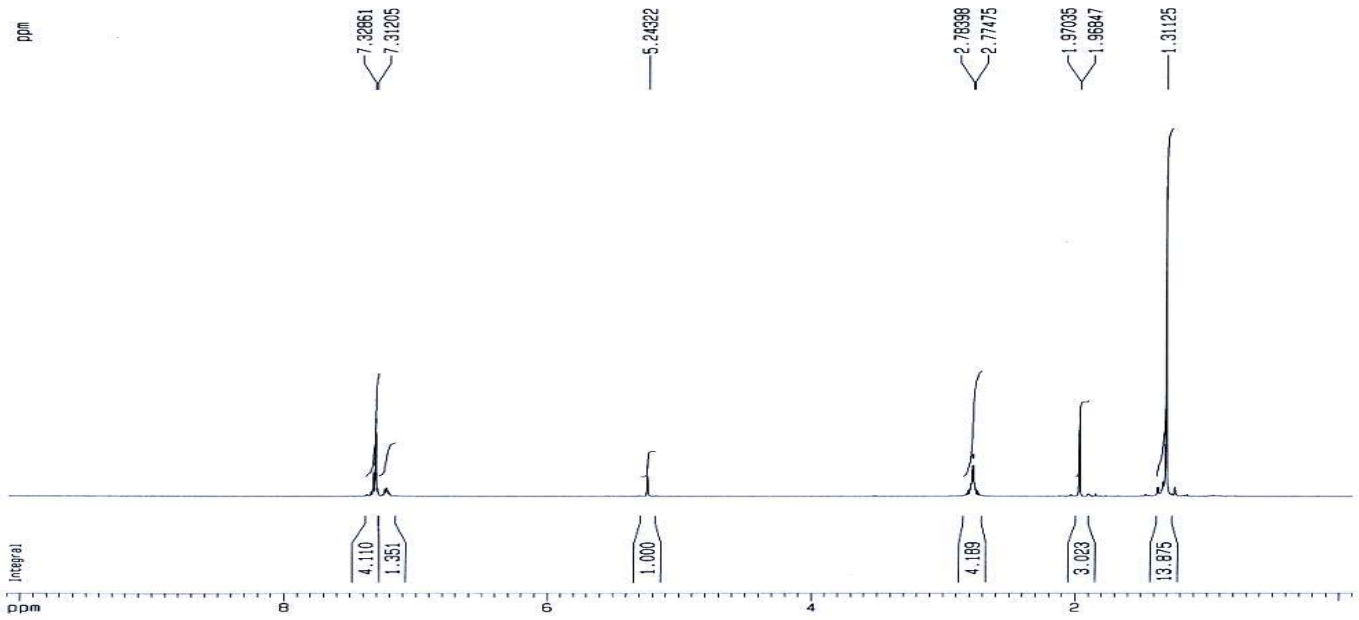
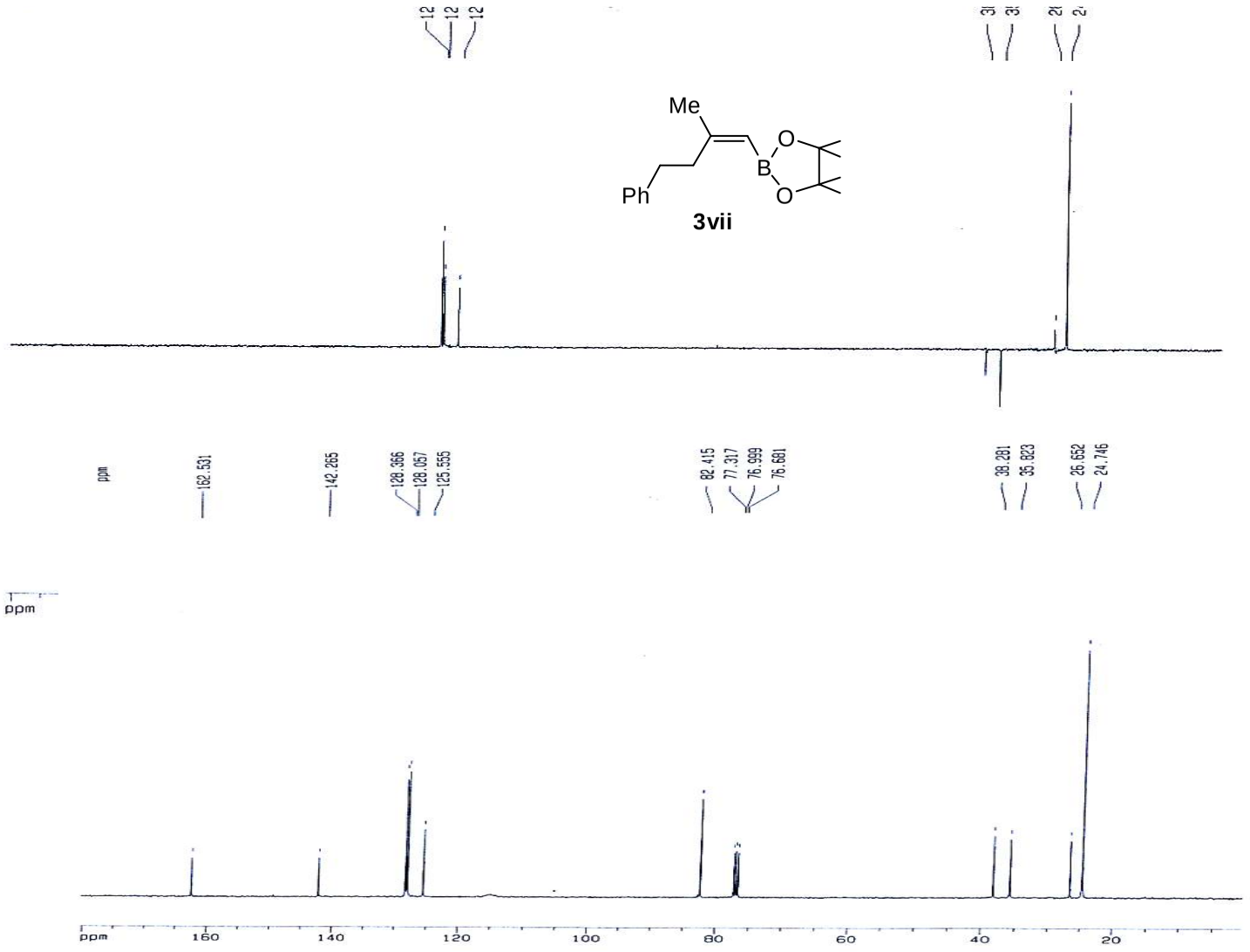


3vii



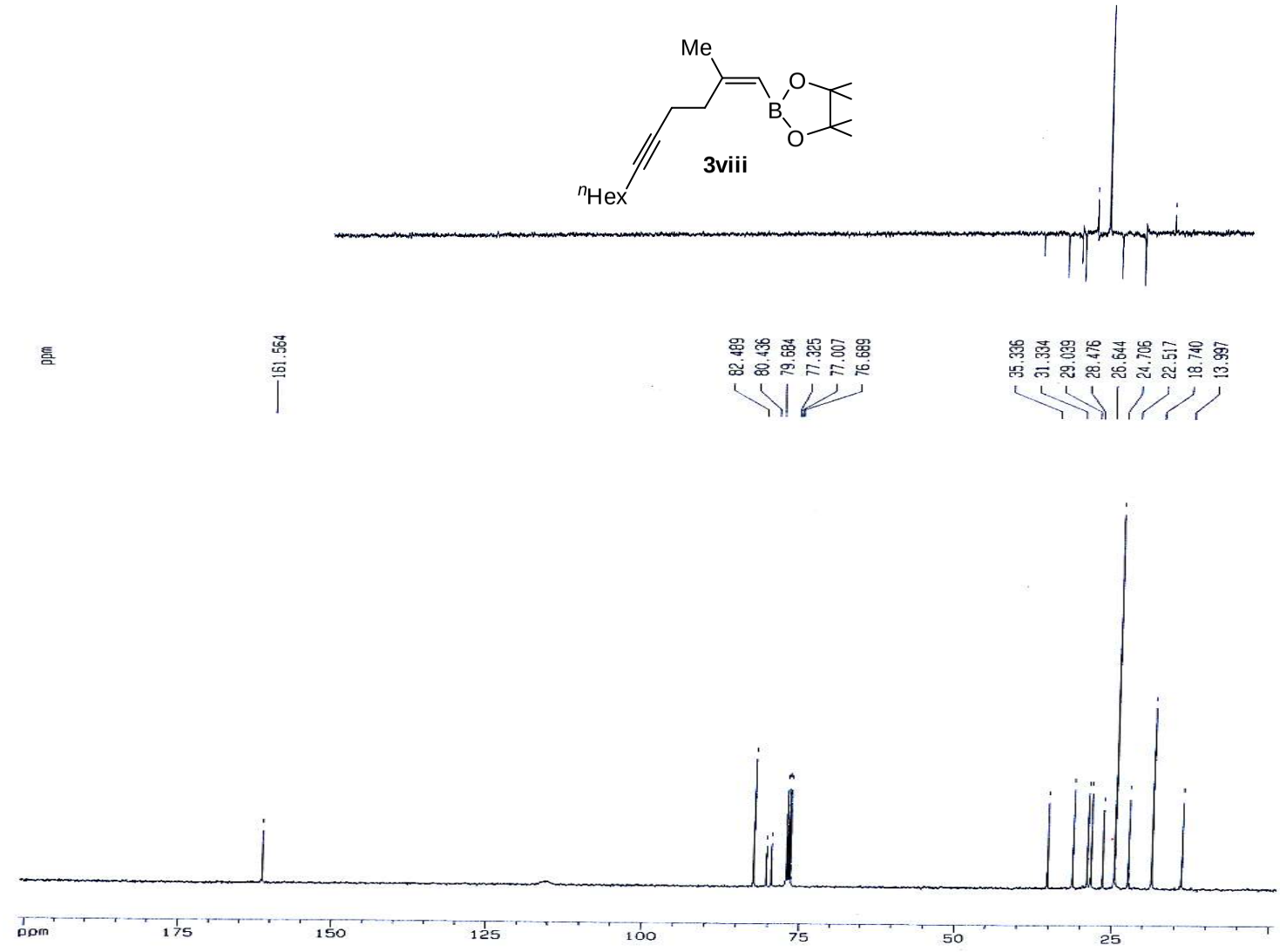


Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*

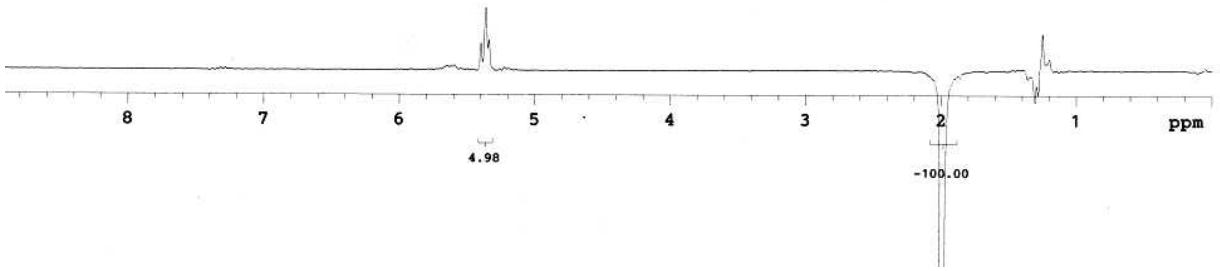


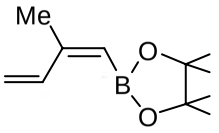

5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
4.55
ppm
5.14389
2.56032
2.54178
2.52325
2.26631
2.24801
2.11547
2.09868
2.08145
1.86504
1.43778
1.41946
1.35559
1.33941
1.31913
1.30276
1.28676
1.22110
0.87396
0.85748
0.83980
Me
O
B
O
3viii
nHex
Integral
1.000
2.070
2.141
2.245
2.943
2.399
21.052
3.808
ppm
8
6
4
2

Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



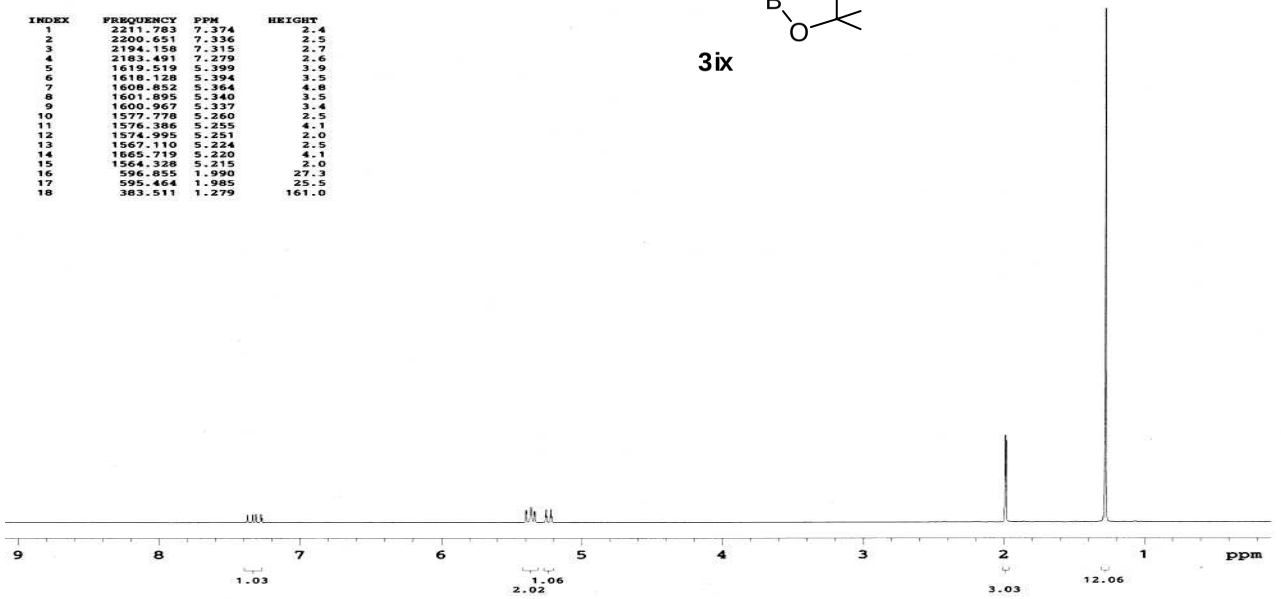
Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*





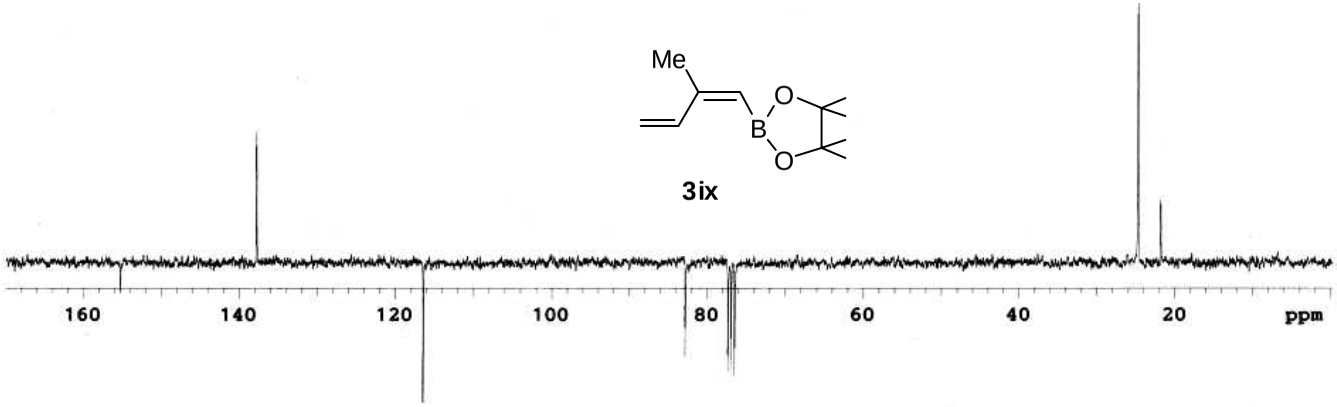
3ix

INDEX	FREQUENCY	PPM	HEIGHT
1	2211.783	7.374	2.4
2	2200.651	7.336	2.5
3	2194.158	7.315	2.7
4	2183.491	7.279	2.6
5	1619.519	5.399	3.9
6	1618.128	5.394	3.5
7	1608.852	5.364	4.8
8	1601.895	5.340	3.5
9	1600.967	5.337	3.4
10	1577.778	5.260	2.5
11	1576.386	5.255	4.1
12	1574.995	5.251	2.0
13	1567.110	5.224	2.5
14	1565.719	5.220	4.1
15	1564.328	5.215	2.0
16	596.855	1.990	27.3
17	595.464	1.985	25.5
18	383.511	1.279	161.0



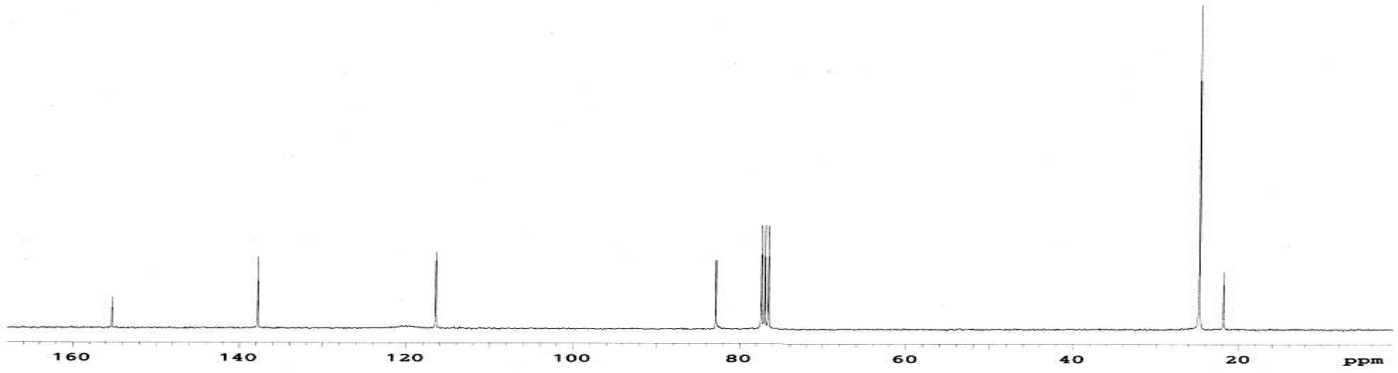
Highly Regio- and Stereoselective Synthesis of *Z*-Trisubstituted Alkenes via Propyne Bromoboration and Tandem Pd-Catalyzed Cross-Coupling

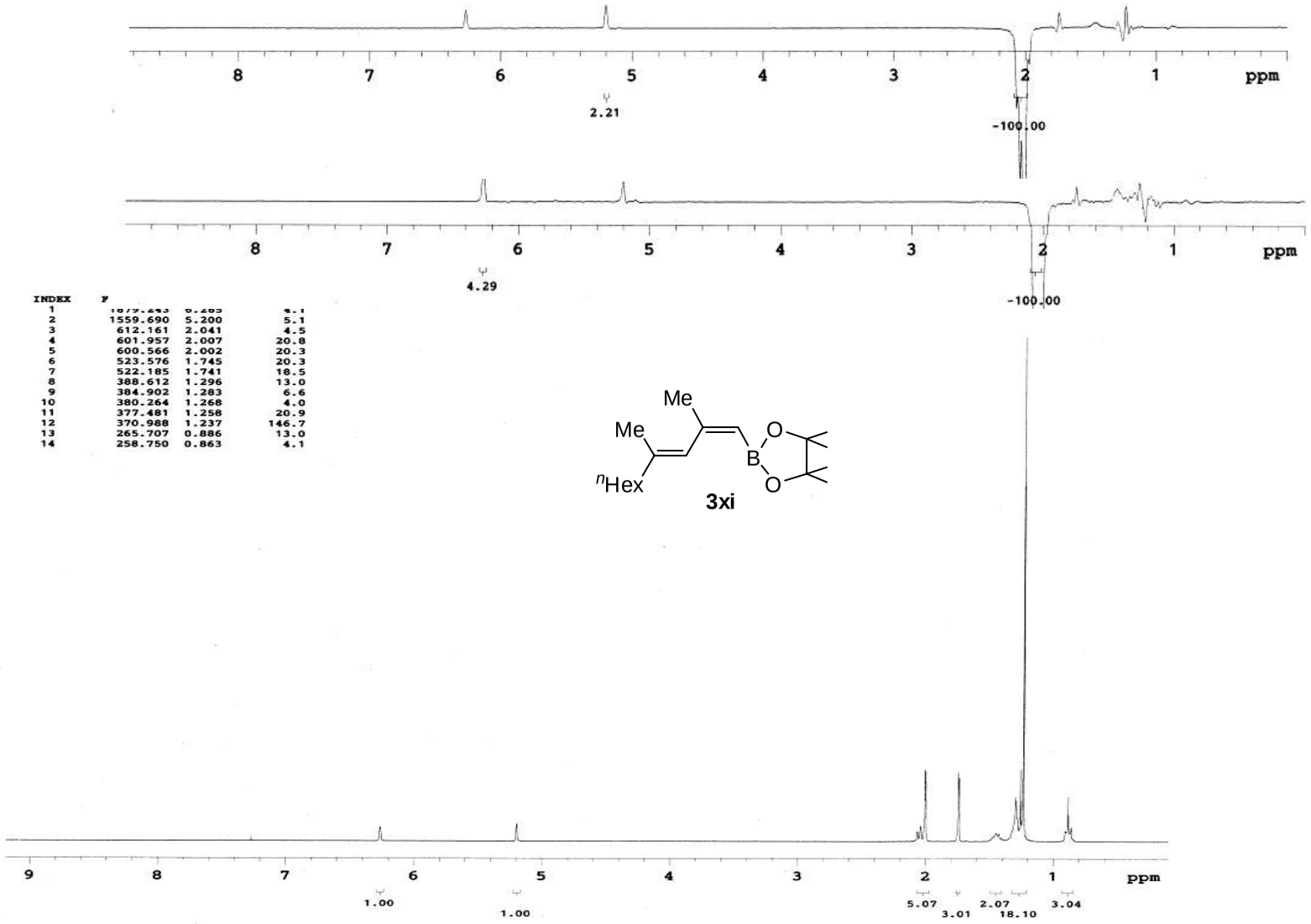
Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



3ix

INDEX	FREQUENCY	PPM	HEIGHT
1	11716.866	155.345	10.4
2	10397.909	137.858	24.1
3	8787.392	116.505	25.9
4	6254.140	82.919	23.5
5	5839.763	77.425	35.1
6	5807.723	77.000	35.2
7	5776.752	76.589	34.9
8	1871.143	24.808	110.6
9	1652.206	21.905	19.6

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6
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2
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ppm
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4.29
-100.00
INDEX
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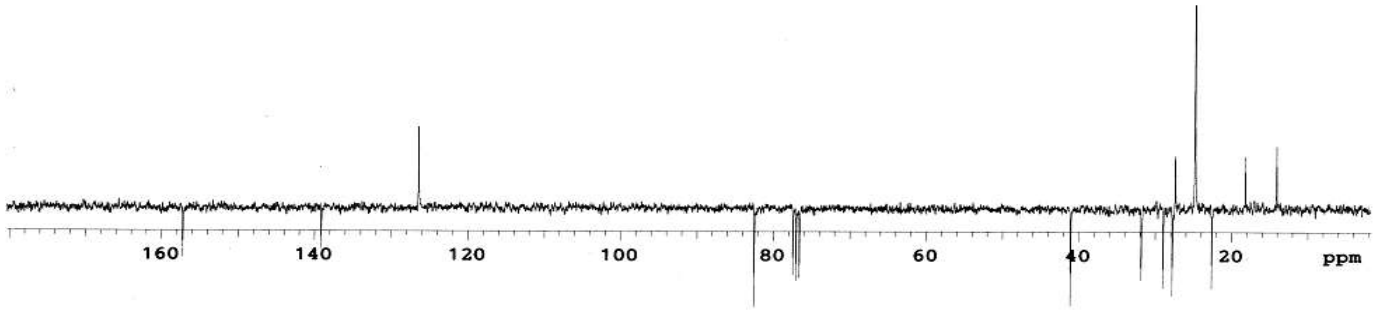
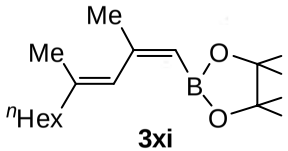
2 1559.690 5.200 5.1
3 612.161 2.041 4.5
4 601.957 2.007 20.8
5 600.566 2.002 20.3
6 523.576 1.745 20.3
7 522.185 1.741 18.5
8 388.612 1.296 13.0
9 384.902 1.283 6.6
10 380.264 1.268 4.0
11 377.481 1.258 20.9
12 370.988 1.237 146.7
13 265.707 0.886 13.0
14 258.750 0.863 4.1
Me
Me
nHex
B
O
O
3xi
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
5.07
3.01
2.07
18.10
3.04

Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



4	6222.100	82.494	42.4
5	5839.763	77.425	29.7
6	5807.723	77.000	30.4
7	5775.684	76.575	29.4
8	3095.050	41.035	36.2
9	2398.726	31.803	34.0
10	2184.061	28.957	35.8
11	2093.283	27.753	33.4
12	2065.515	27.385	26.8
13	1873.279	24.836	119.9
14	1702.401	22.571	34.6
15	1370.259	18.167	23.1
16	1061.612	14.075	30.0



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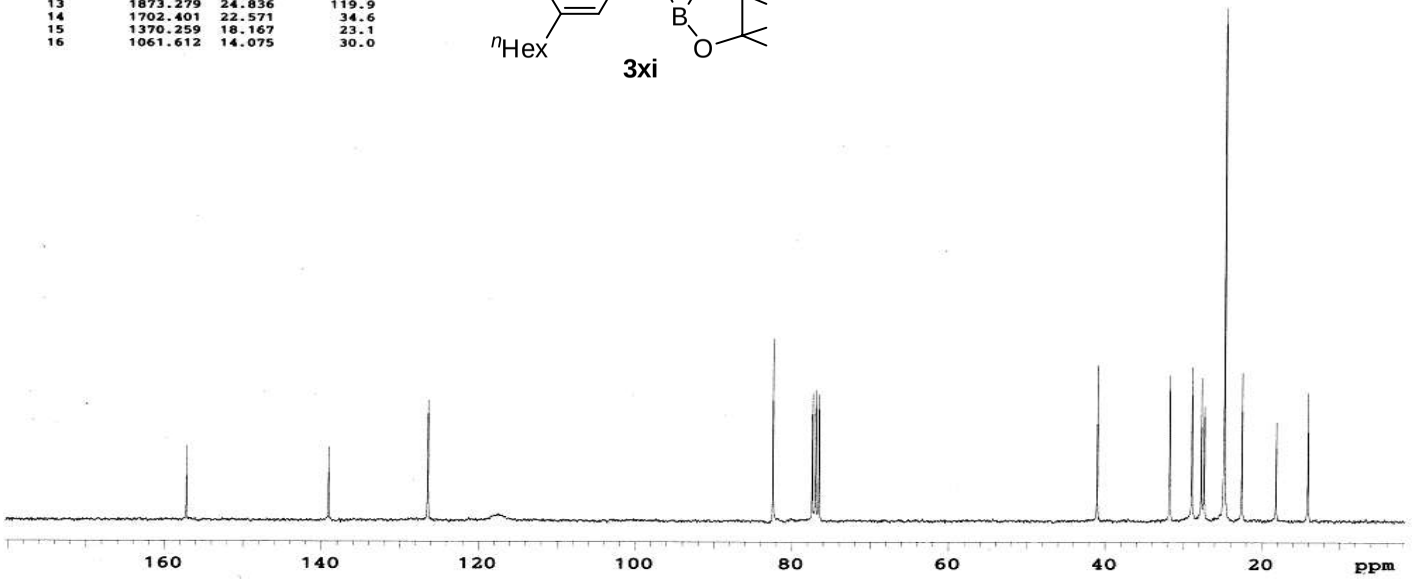
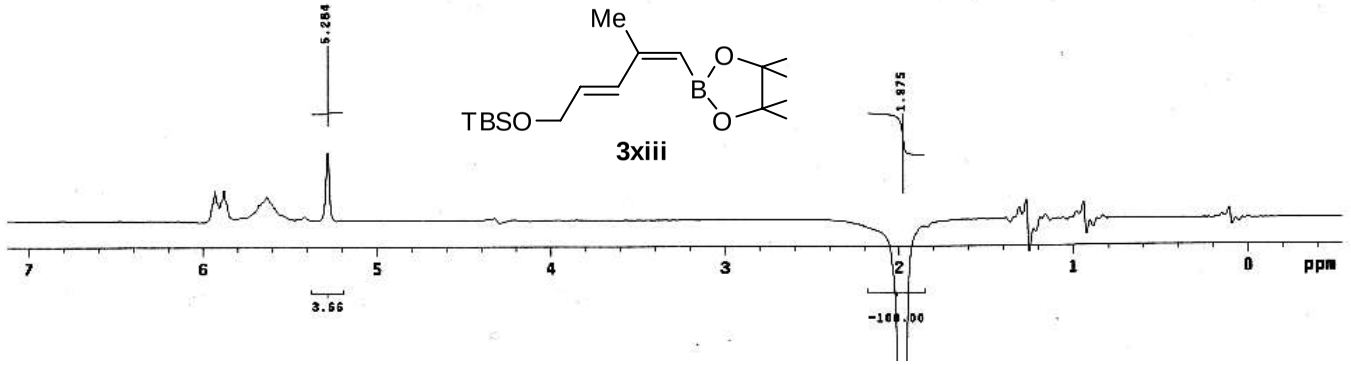
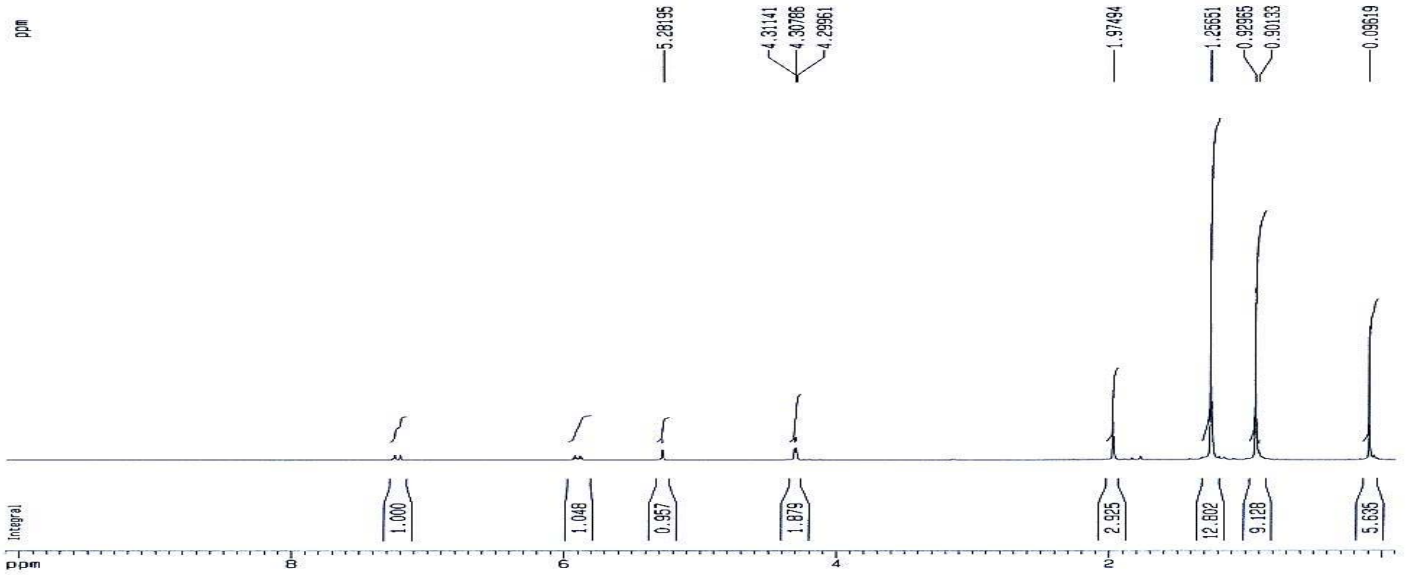
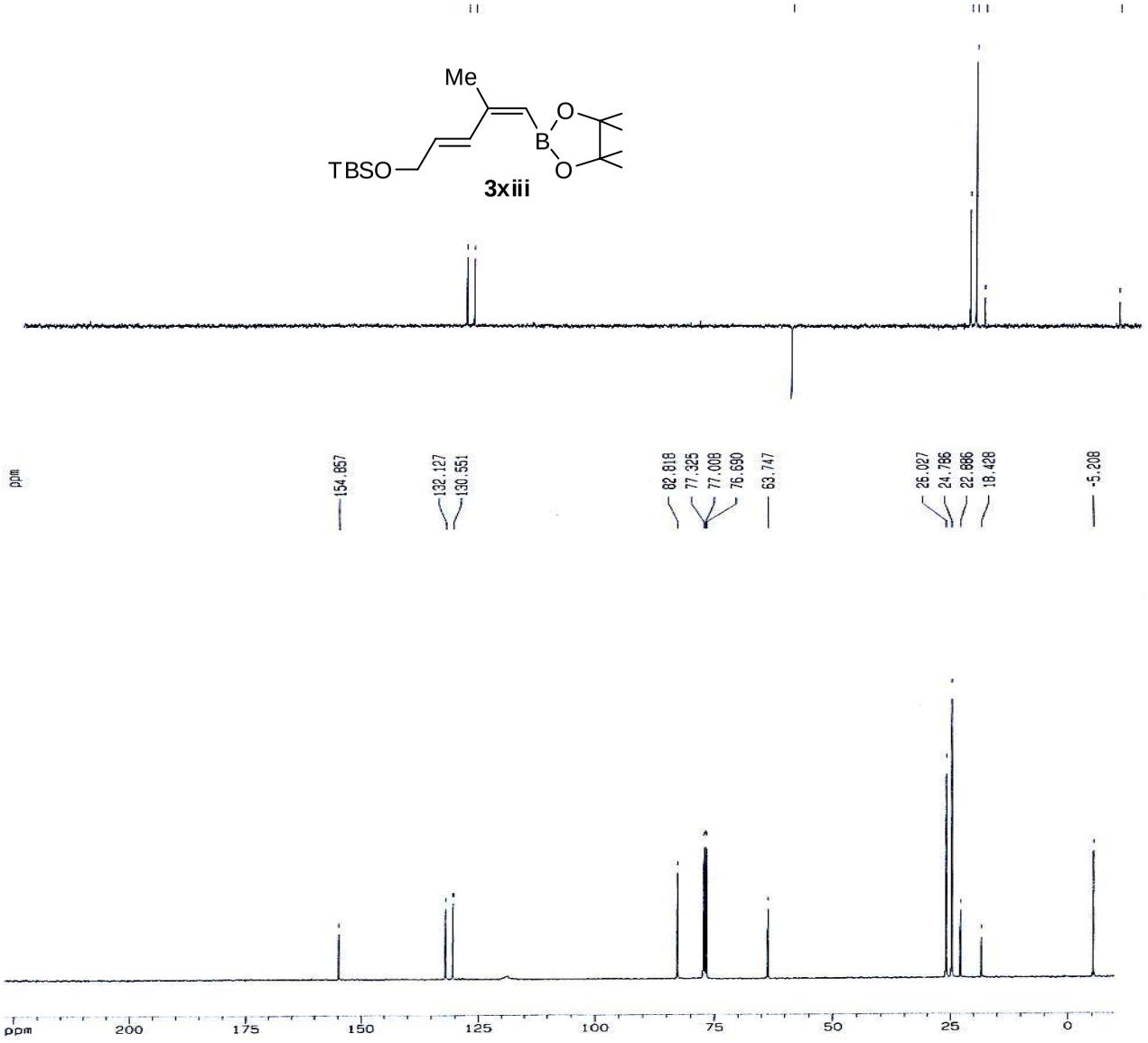


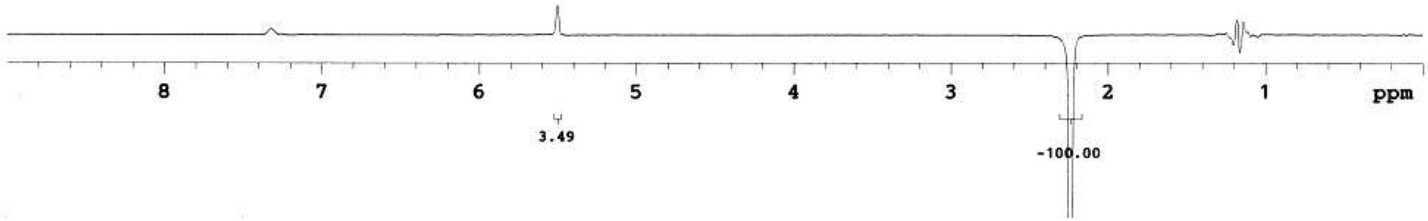
Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



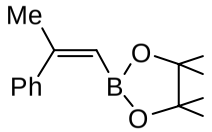


Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*





INDEX	FREQUENCY	PPM	HEIGHT
1	2196.941	7.324	8.5
2	2194.622	7.316	10.1
3	2190.448	7.302	8.4
4	2189.520	7.299	9.1
5	2184.419	7.282	7.4
6	1650.593	5.503	7.3
7	1649.202	5.498	7.4
8	671.062	2.237	24.5
9	669.671	2.233	24.5
10	350.581	1.169	146.7



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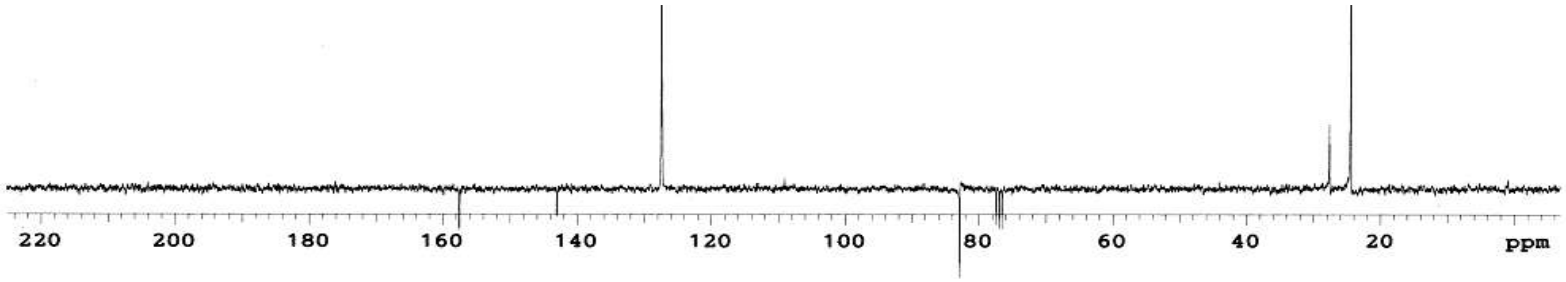
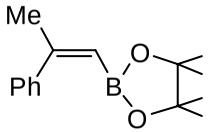
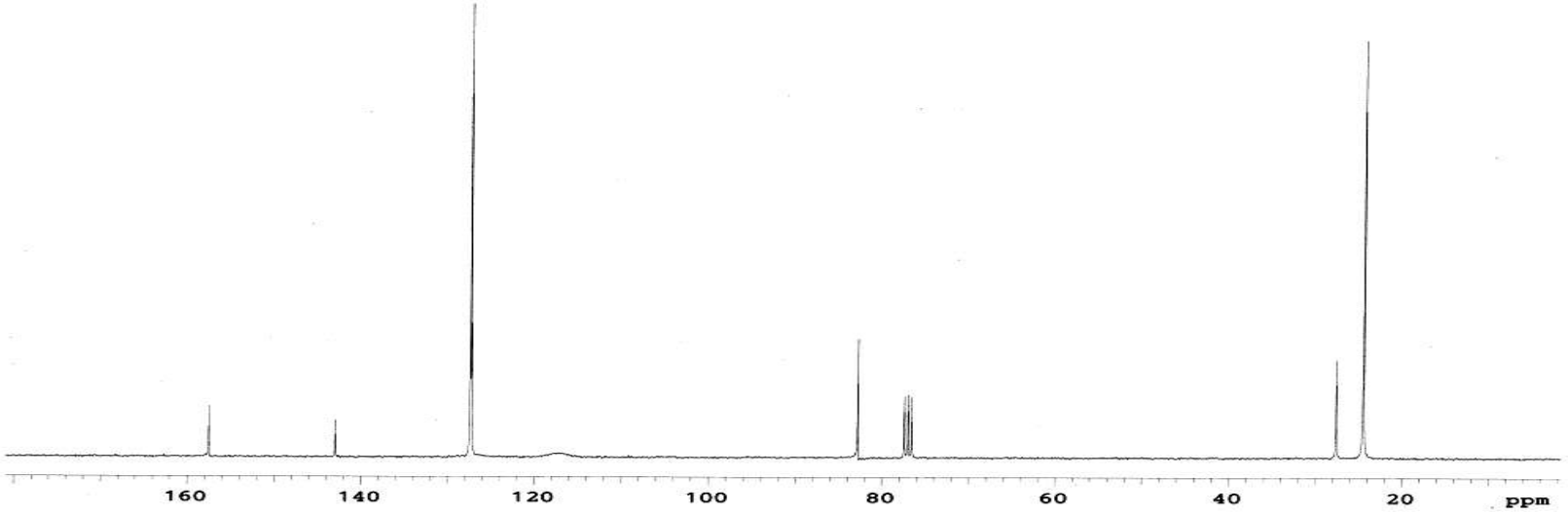
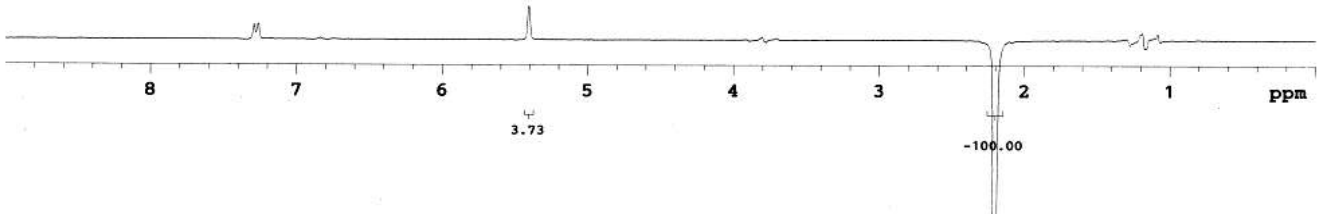


INDEX	FREQUENCY	PPM	HEIGHT
1	11882.404	157.539	12.7
2	10786.655	143.012	9.2
3	9614.011	127.465	113.7
4	9603.331	127.323	33.5
5	6247.732	82.834	29.8
6	5839.763	77.425	15.3
7	5807.724	77.000	15.7
8	5775.684	76.575	15.2
9	2083.671	27.626	24.5
10	1847.647	24.496	104.8

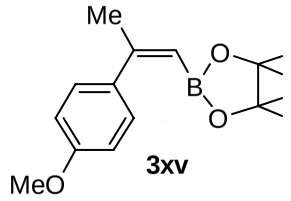


3xiv





INDEX	FREQUENCY	PPM	HEIGHT
1	2187.202	7.292	9.6
2	2178.389	7.262	10.8
3	2049.455	6.832	9.7
4	2040.643	6.803	8.4
5	1138.102	3.794	38.1
6	659.467	2.199	18.1
7	658.540	2.195	19.0
8	353.828	1.180	114.1



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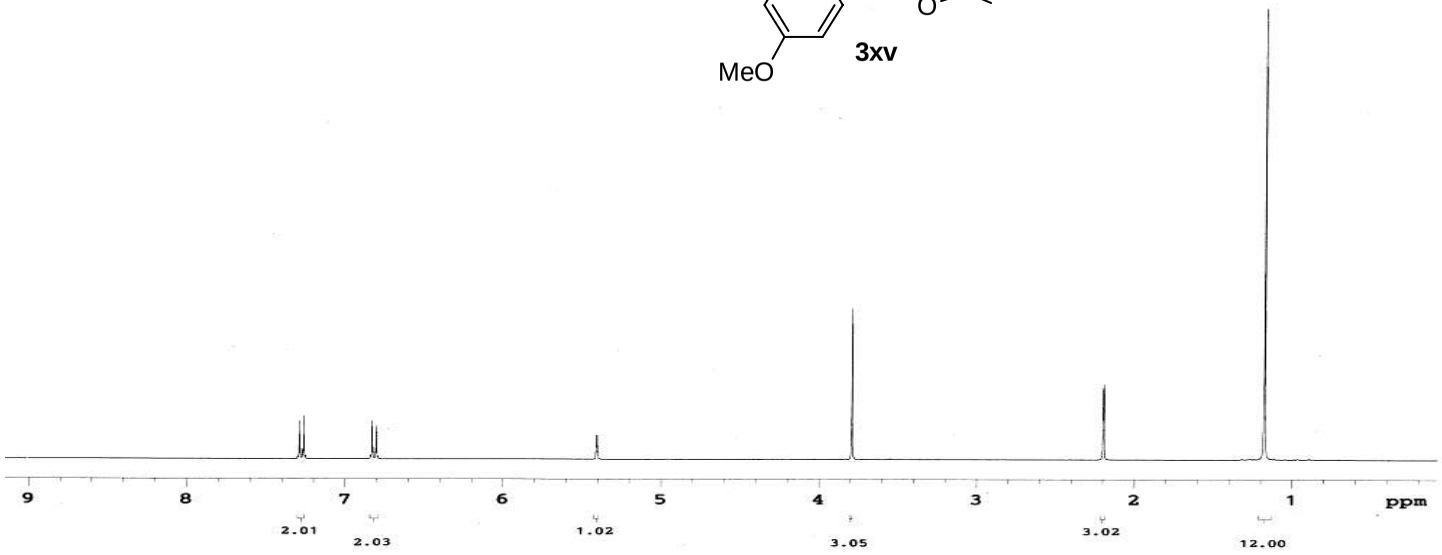

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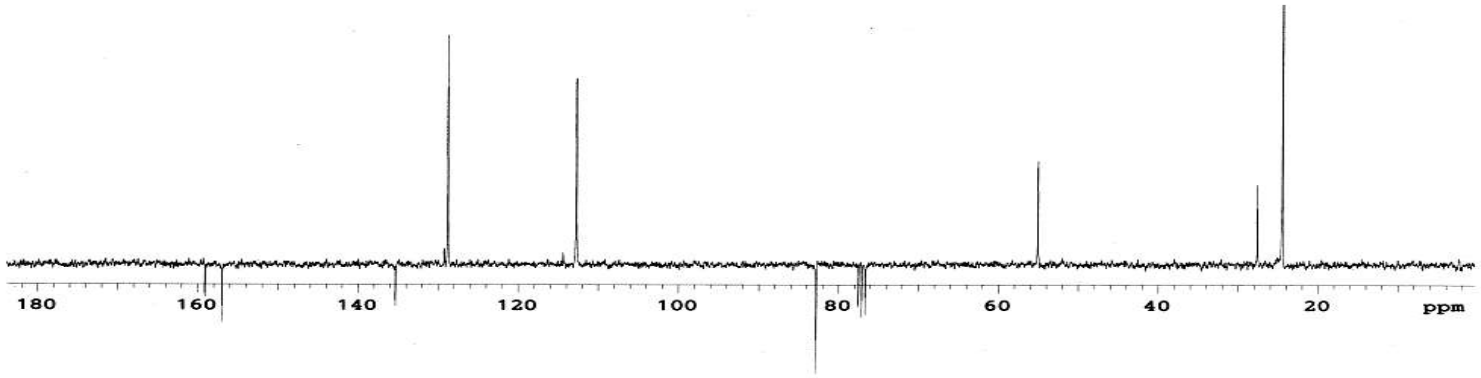
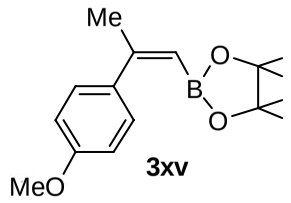


6	6240.257	82.735	37.3
7	5839.763	77.425	13.0
8	5807.724	77.000	13.4
9	5775.685	76.575	13.2
10	4150.216	55.024	26.0
11	2079.400	27.569	25.6
12	1846.580	24.482	98.4



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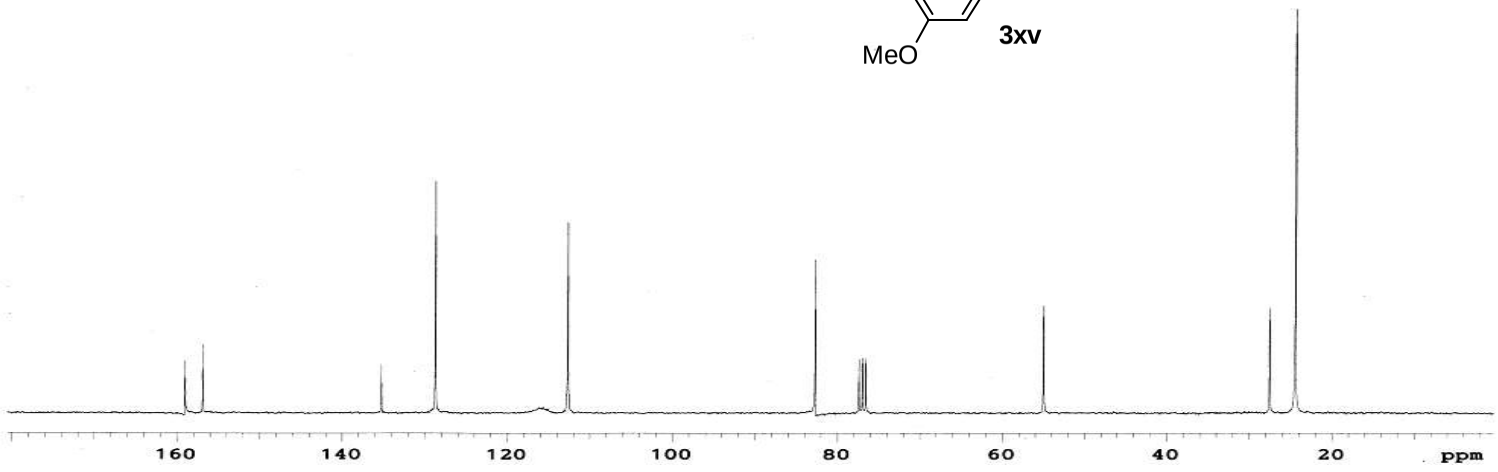
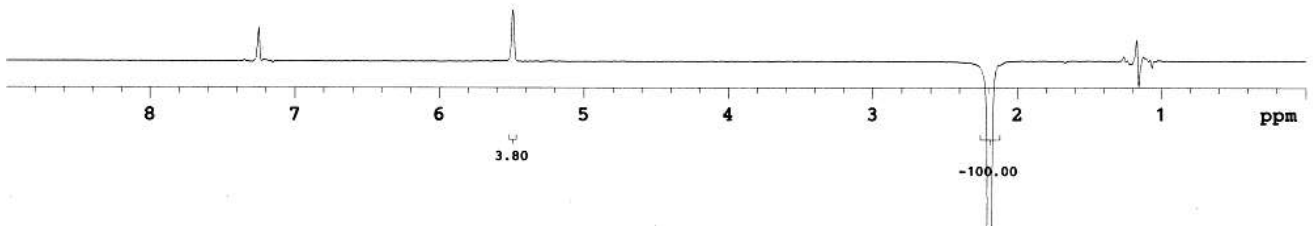
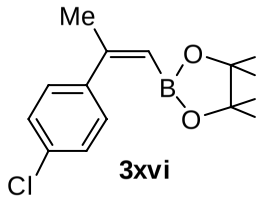




INDEX	FREQUENCY	PPM	HEIGHT
1	2174.679	7.250	48.0
2	1647.810	5.493	5.8
3	1646.419	5.489	5.9
4	656.685	2.189	21.9
5	655.293	2.185	22.0
6	348.726	1.163	140.9



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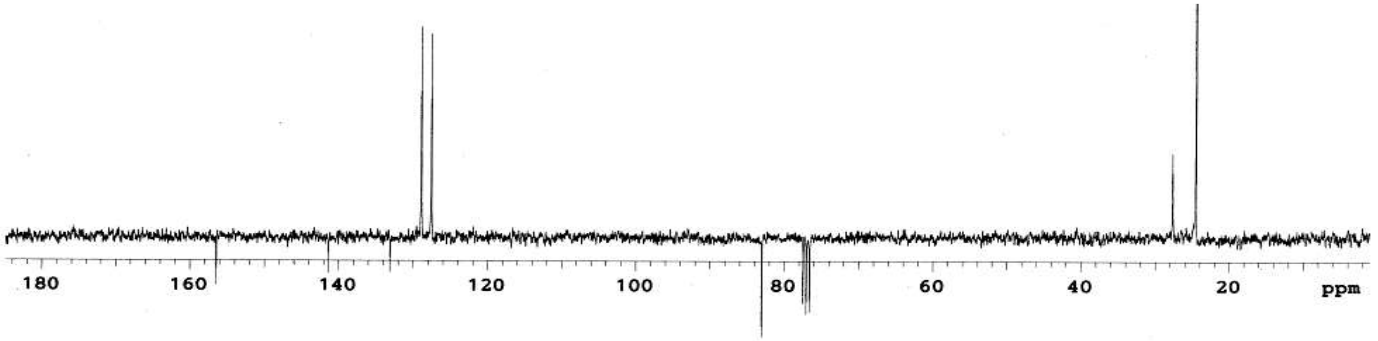
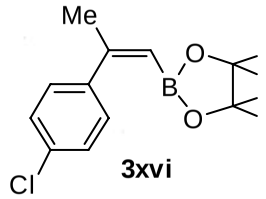


1	11799.101	156.435	13.7
2	10664.904	141.398	10.2
3	10039.067	133.100	9.9
4	9725.080	128.937	52.1
5	9624.690	127.606	49.2
6	6259.480	82.989	33.5
7	5839.763	77.425	23.7
8	5807.723	77.000	24.5
9	5775.684	76.575	24.1
10	2086.875	27.668	25.2
11	1850.851	24.539	102.2



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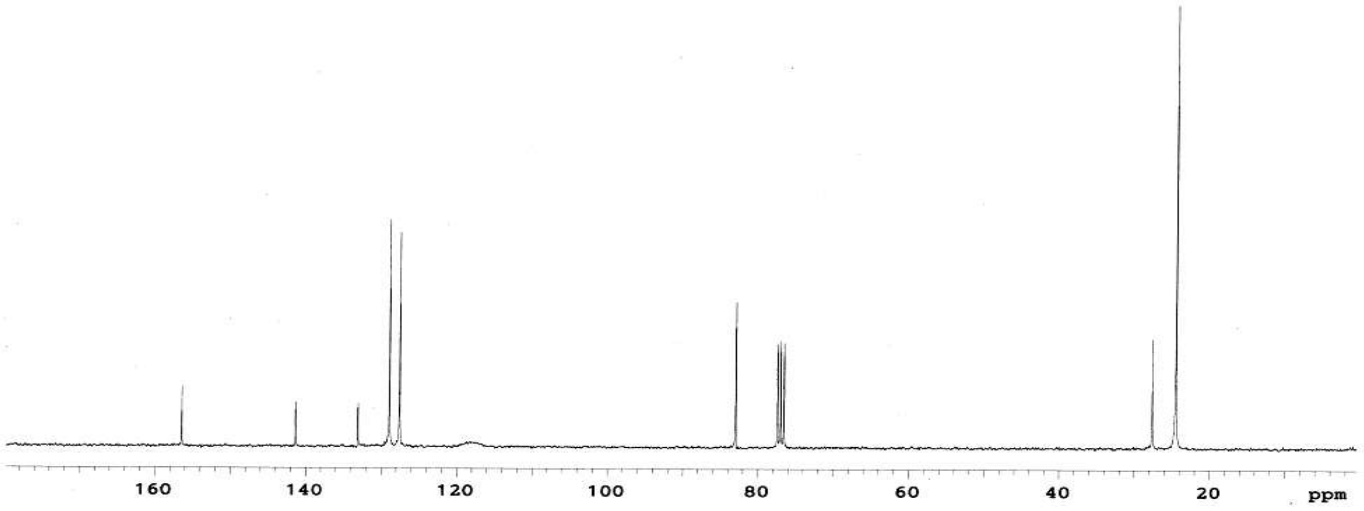
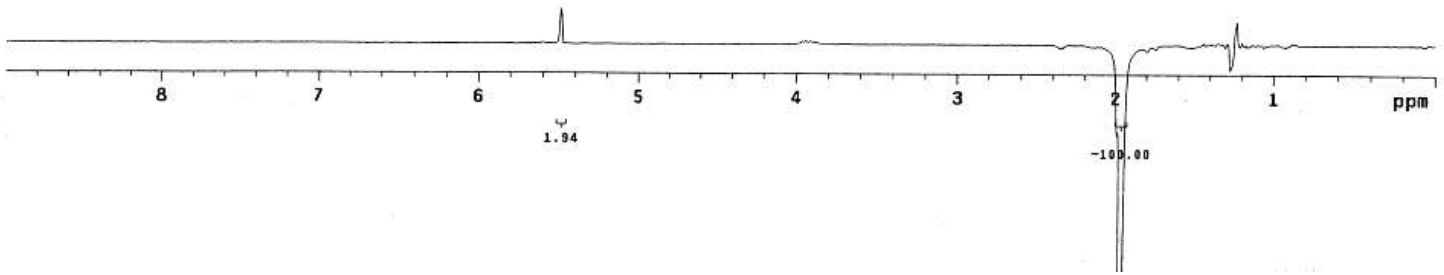
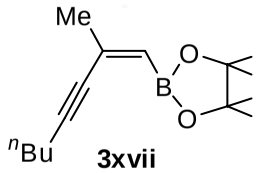




INDEX	FREQUENCY	PPM	HEIGHT
1	1646.419	5.489	6.0
2	1645.028	5.484	6.7
3	708.629	2.362	4.7
4	702.136	2.341	10.6
5	695.179	2.318	5.9
6	588.507	1.962	23.0
7	587.116	1.957	26.4
8	452.616	1.509	5.8
9	450.297	1.501	5.2
10	447.050	1.490	5.8
11	440.093	1.467	4.7
12	375.626	1.252	151.2
13	279.157	0.931	8.9
14	272.200	0.907	16.5
15	265.243	0.884	7.5



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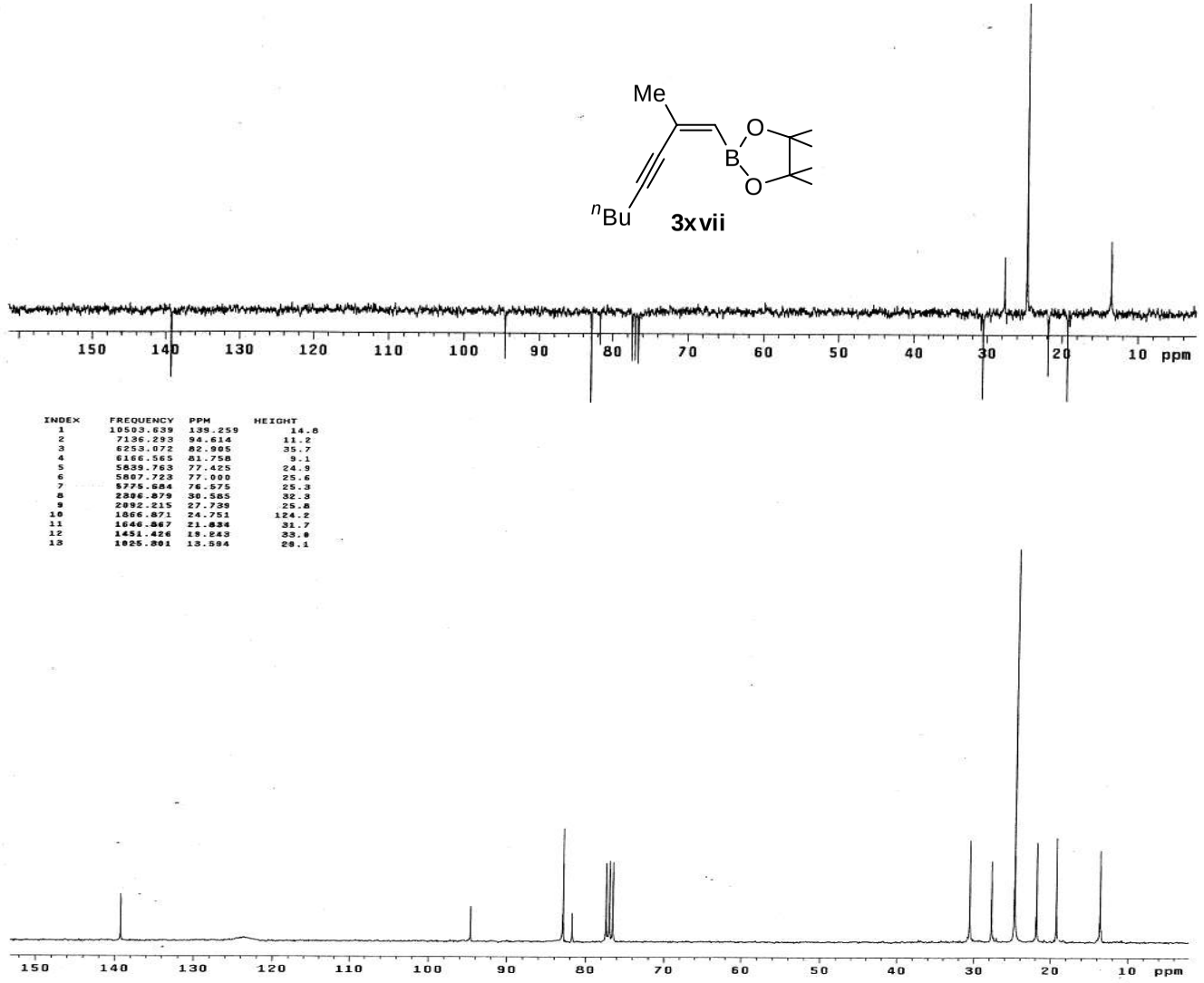
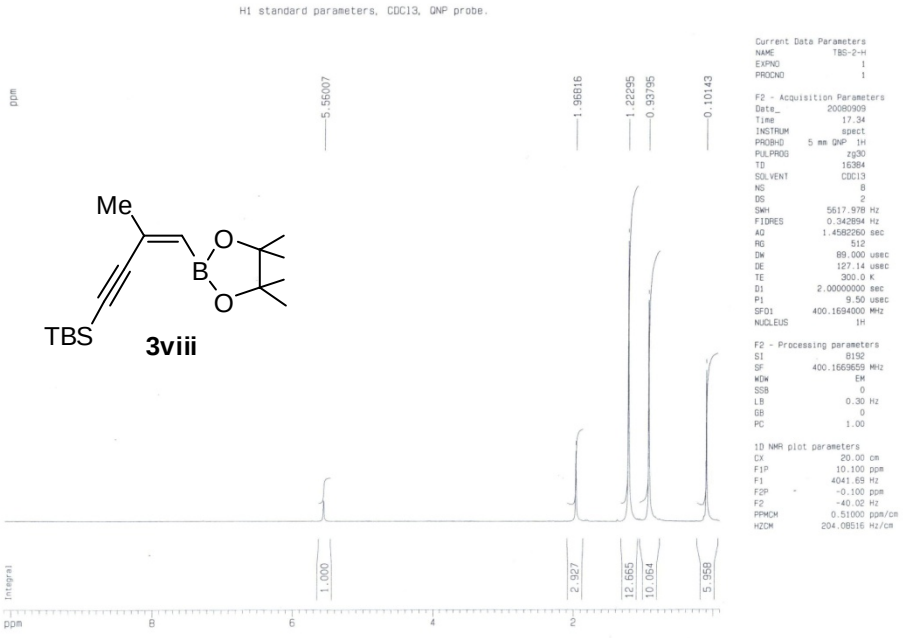
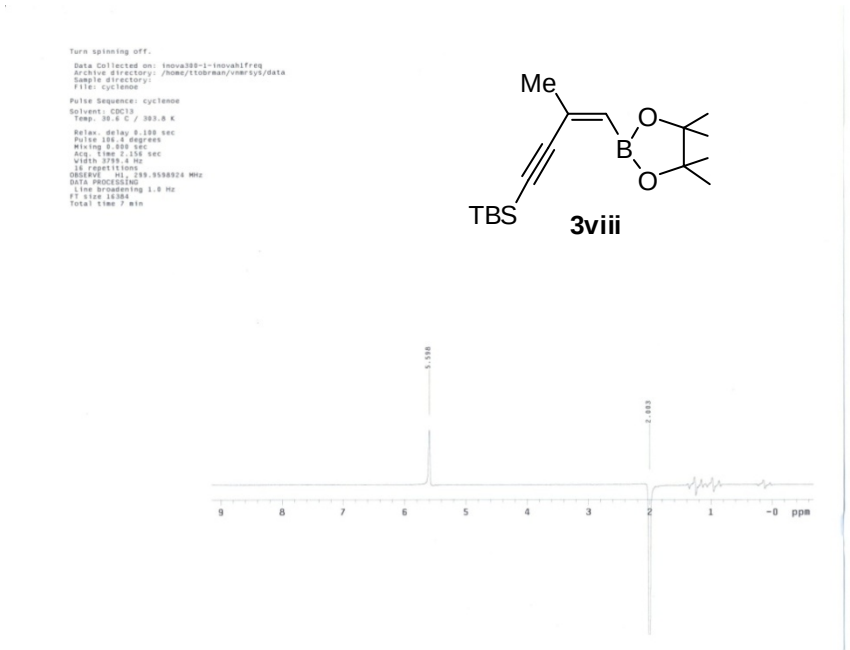


INDEX	FREQUENCY	PPM	HEIGHT
1	10503.639	139.259	14.8
2	7136.293	94.614	11.2
3	6253.072	82.905	35.7
4	6166.565	81.758	9.1
5	5839.763	77.425	24.9
6	5807.723	77.000	25.6
7	5775.684	76.575	25.3
8	2306.879	30.585	32.3
9	2092.215	27.739	25.8
10	1866.871	24.751	124.2
11	1646.867	21.834	31.7
12	1451.426	19.243	33.9
13	1025.301	13.594	28.1

Highly Regio- and Stereoselective Synthesis of *Z*-Trisubstituted Alkenes via Propyne Bromoboration and Tandem Pd-Catalyzed Cross-Coupling

Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*





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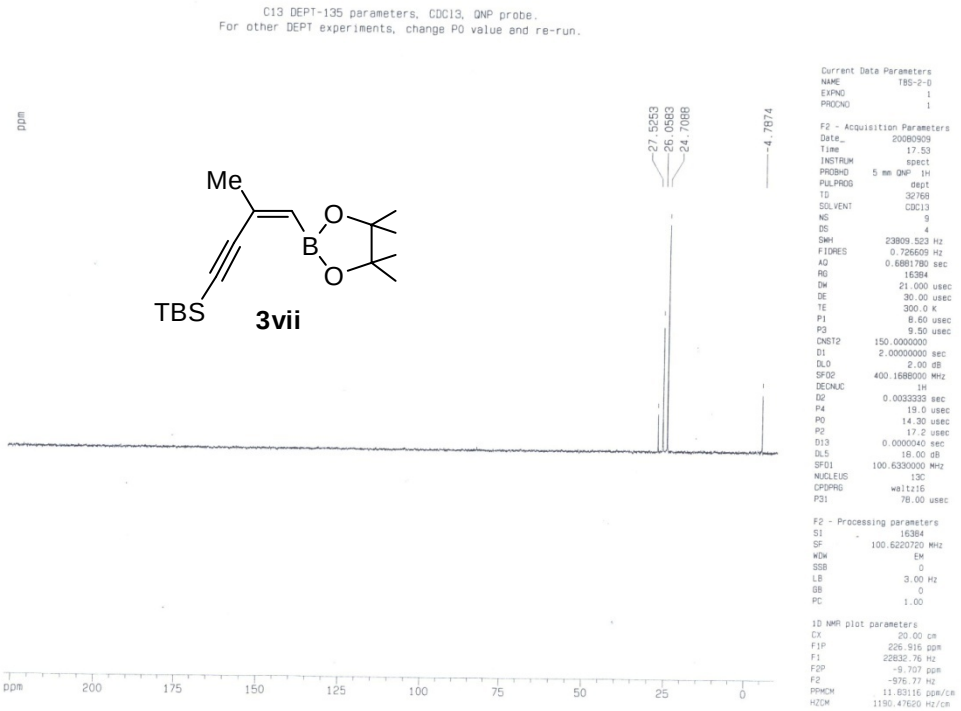

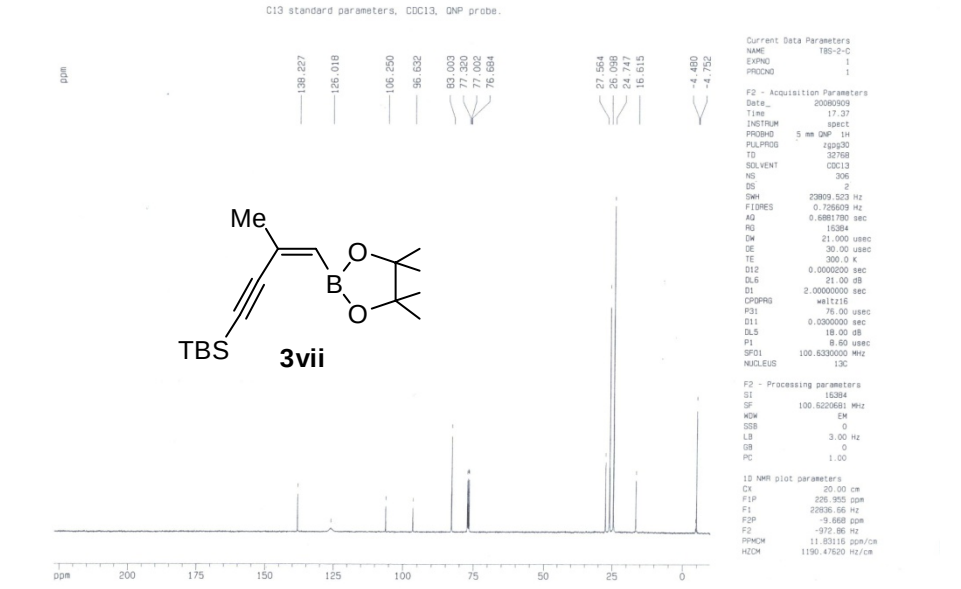

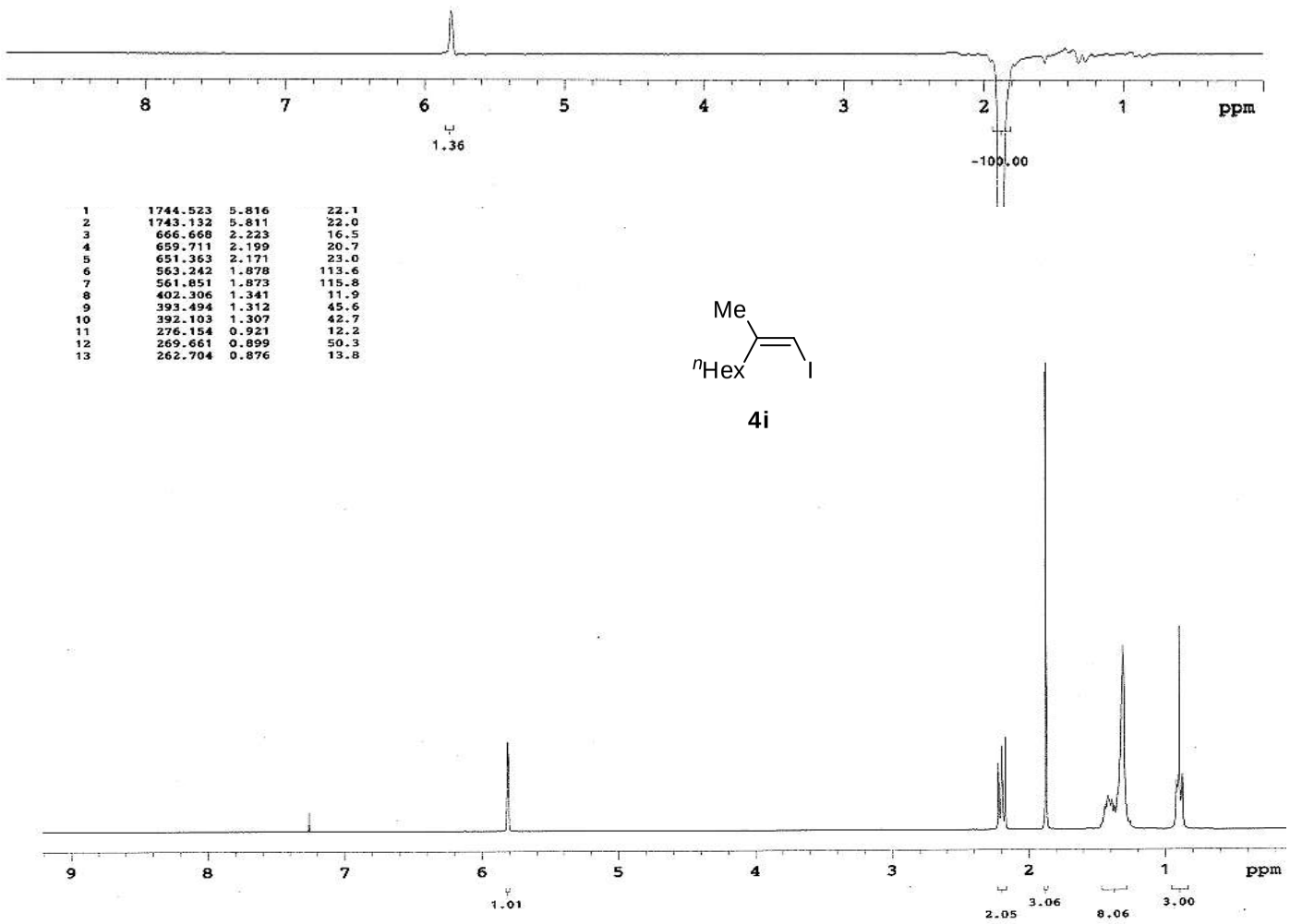
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3 666.668 2.223 16.5
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5 651.363 2.171 23.0
6 563.242 1.878 113.6
7 561.851 1.873 115.8
8 402.306 1.341 11.9
9 393.494 1.312 45.6
10 392.103 1.307 42.7
11 276.154 0.921 12.2
12 269.661 0.899 50.3
13 262.704 0.876 13.8
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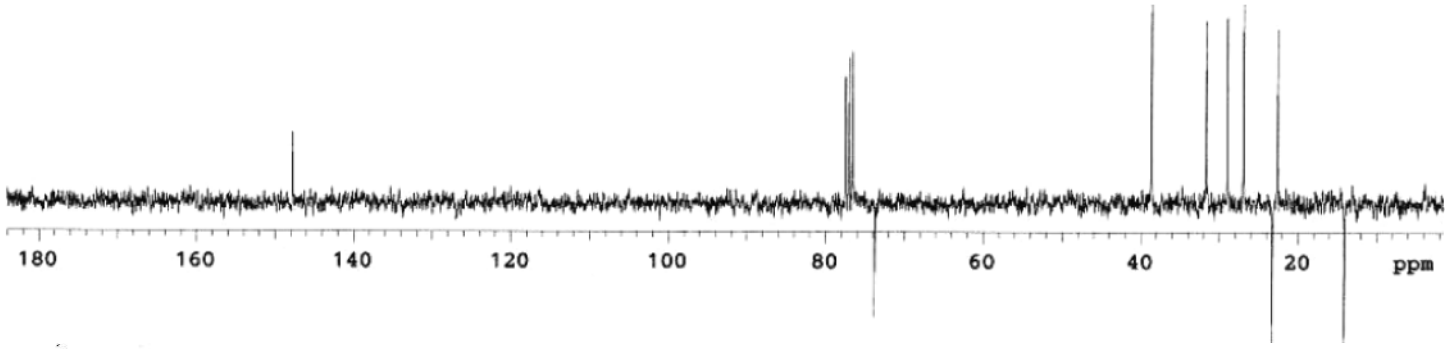
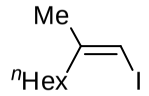


INDEX	FREQUENCY	PPM	HEIGHT
1	11147.632	147.798	25.0
2	5839.763	77.425	38.5
3	5807.723	77.000	39.3
4	5775.684	76.575	38.7
5	5564.223	73.772	53.1
6	2914.561	38.642	60.7
7	2389.114	31.675	49.7
8	2184.061	28.957	48.8
9	2029.204	26.904	50.5
10	1753.665	23.250	40.3
11	1703.469	22.585	46.3
12	1061.612	14.075	44.8



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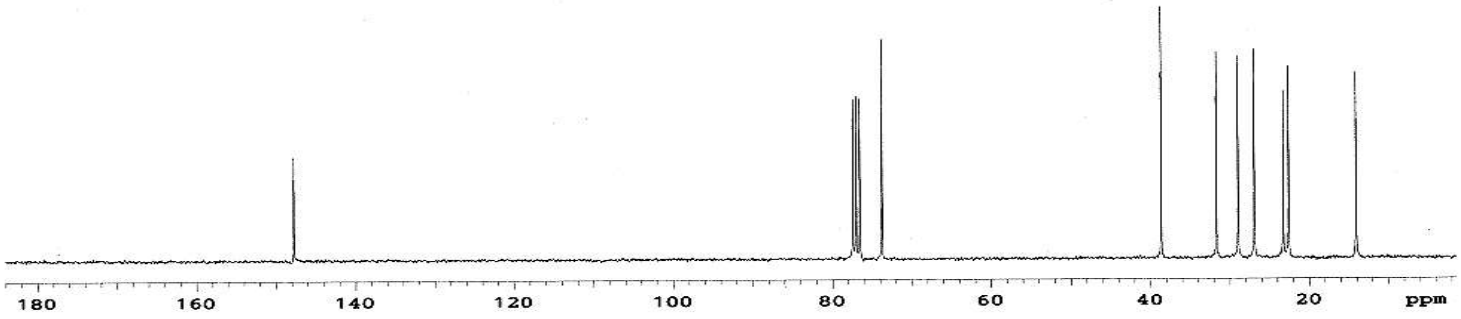
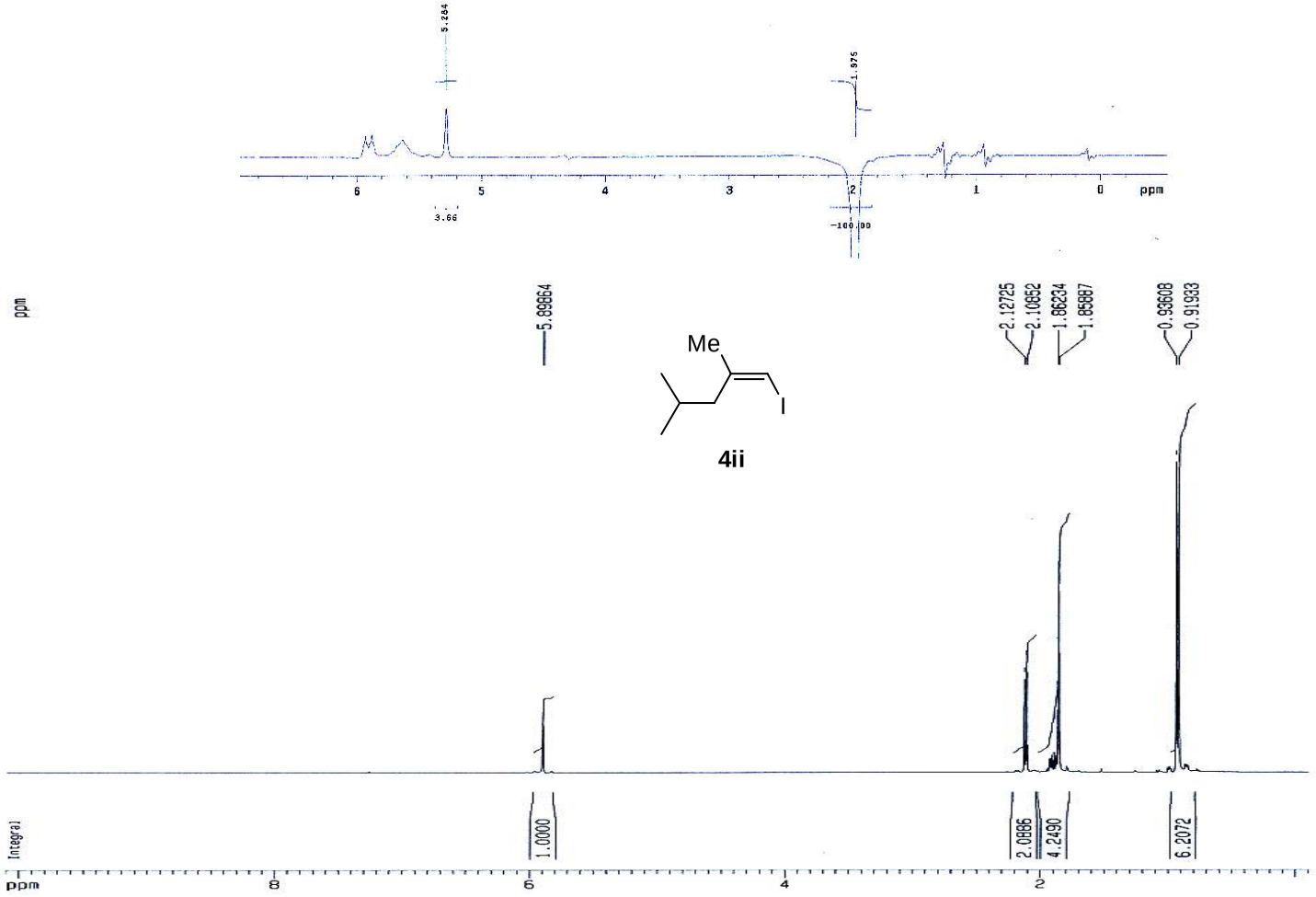
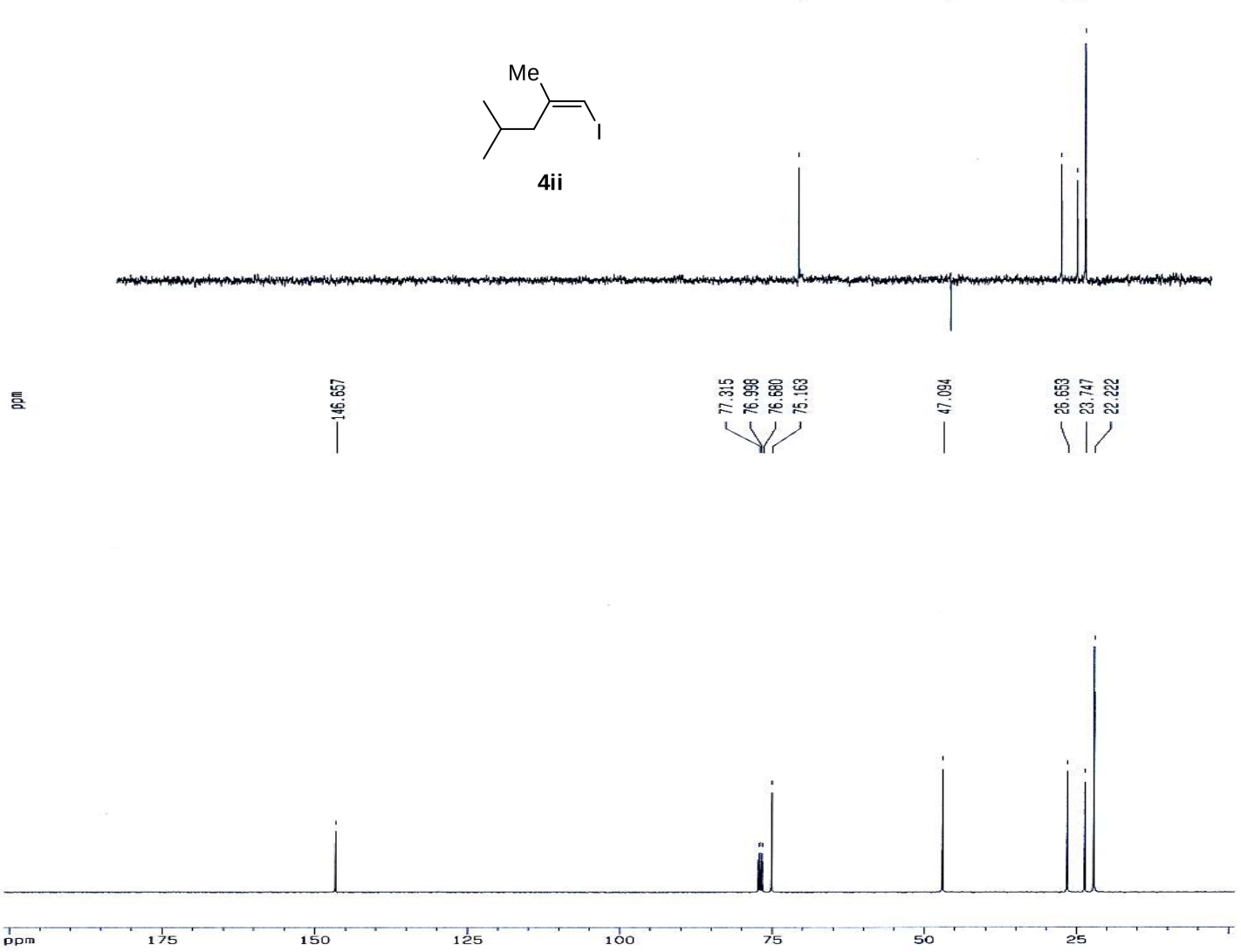


Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*

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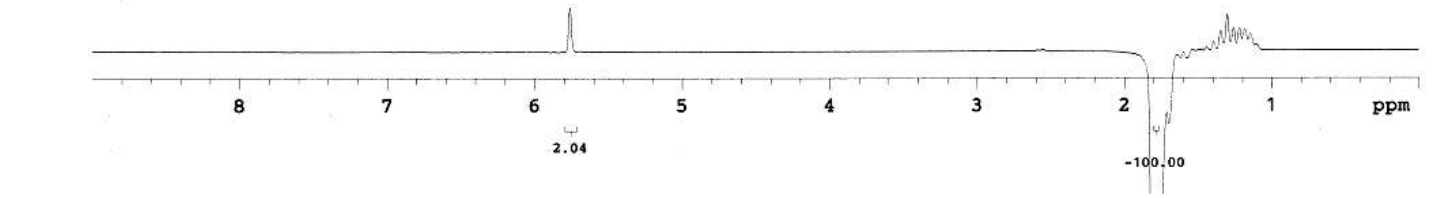
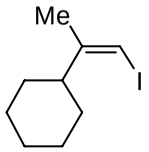


INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	1730.365	5.769	7.6	39	368.205	1.228	9.1
2	1728.974	5.764	21.7	40	364.959	1.217	8.6
3	1727.583	5.759	21.8	41	356.147	1.187	5.8
4	1726.191	5.755	7.7	42	352.900	1.176	4.5
5	772.633	2.576	3.4	43	343.624	1.146	4.3
6	764.748	2.550	4.1				
7	761.038	2.537	7.7				
8	757.792	2.526	3.8				
9	749.443	2.498	4.4				
10	543.983	1.814	4.7				
11	540.736	1.803	7.1				
12	538.881	1.797	6.0				
13	537.490	1.792	7.4				
14	534.707	1.783	101.8				
15	533.316	1.778	96.7				
16	528.214	1.761	8.9				
17	525.431	1.752	8.9				
18	521.721	1.739	4.2				
19	520.330	1.735	3.6				
20	518.474	1.728	3.6				
21	517.083	1.724	3.1				
22	509.198	1.698	3.3				
23	507.807	1.693	3.7				
24	506.416	1.688	4.2				
25	504.561	1.682	3.5				
26	482.299	1.608	7.3				
27	480.907	1.603	6.9				
28	476.269	1.588	3.2				
29	468.385	1.561	9.4				
30	419.223	1.398	5.0				
31	416.440	1.388	6.8				
32	406.700	1.356	6.0				
33	403.454	1.345	9.1				
34	401.135	1.337	4.9				
35	391.395	1.305	9.3				
36	389.076	1.297	8.5				
37	379.800	1.266	9.9				
38	377.017	1.257	9.2				



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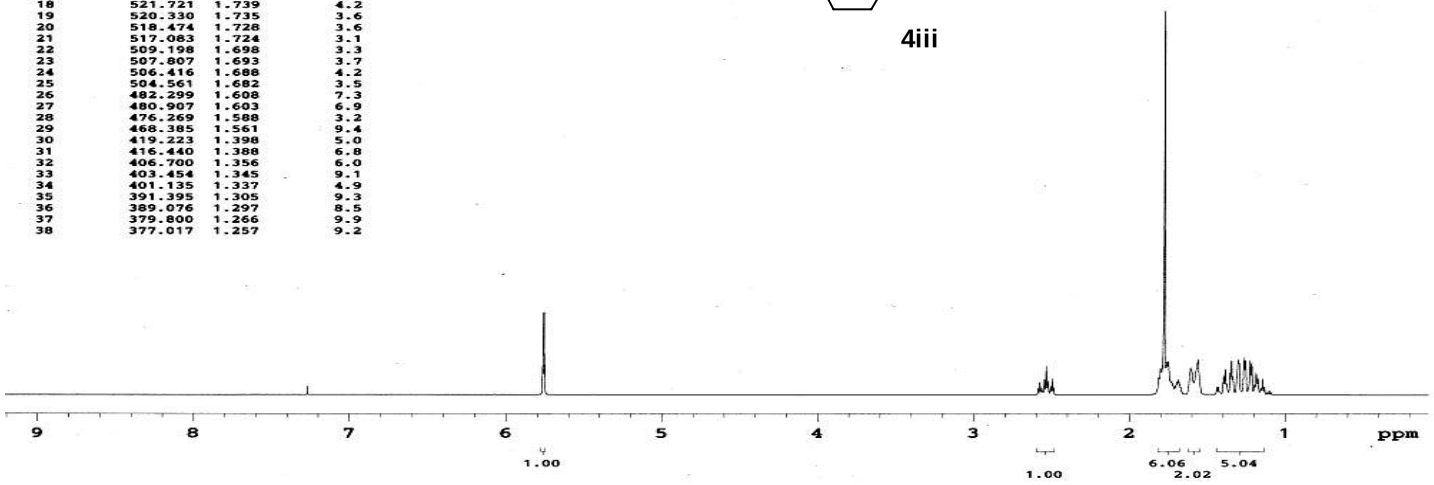
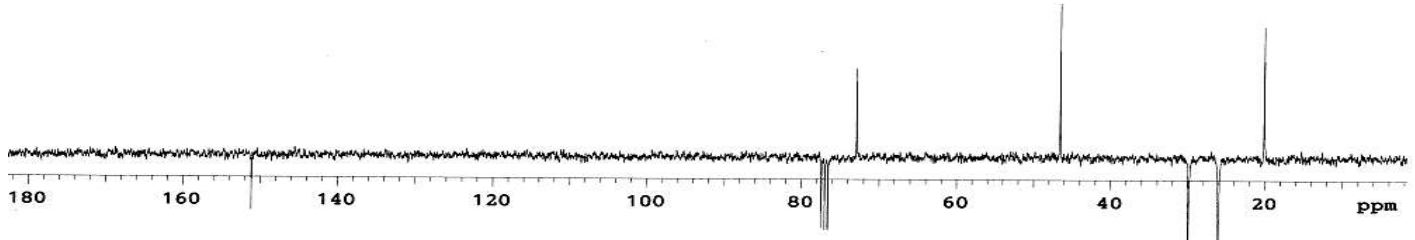
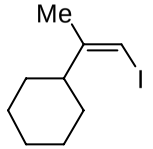




INDEX	FREQUENCY	PPM	HEIGHT
1	11397.940	151.111	16.3
2	5838.695	77.411	19.9
3	5806.655	76.986	20.0
4	5725.484	76.575	19.8
5	5499.077	72.908	39.6
6	3511.963	46.557	38.7
7	2257.752	29.934	99.2
8	1971.533	26.139	88.1
9	1961.921	26.012	47.9
10	1518.709	20.135	32.3



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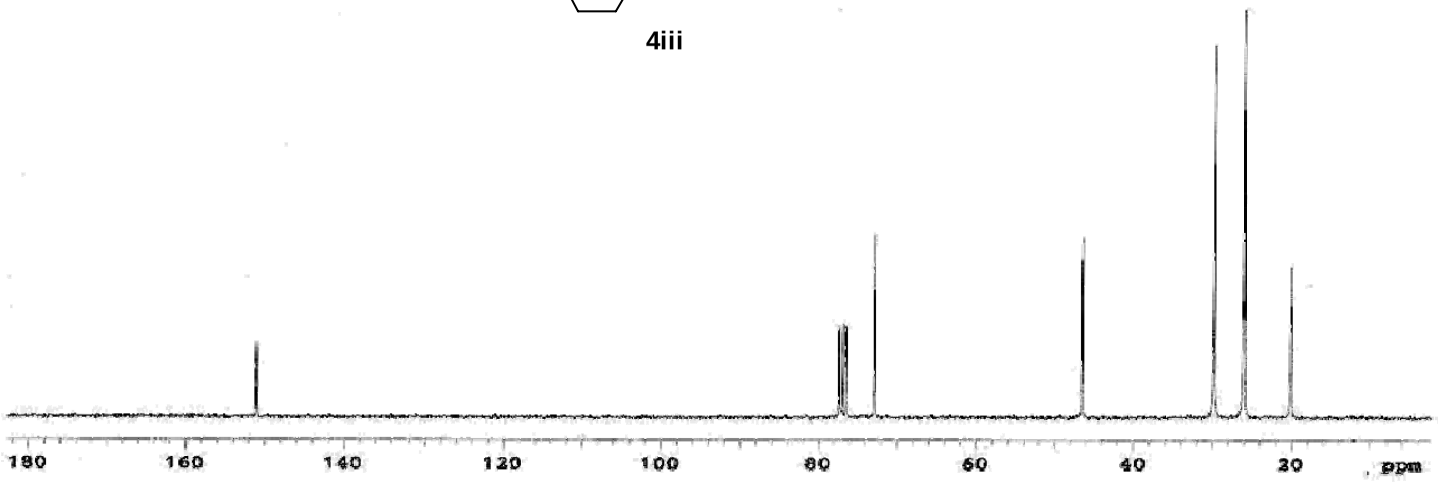
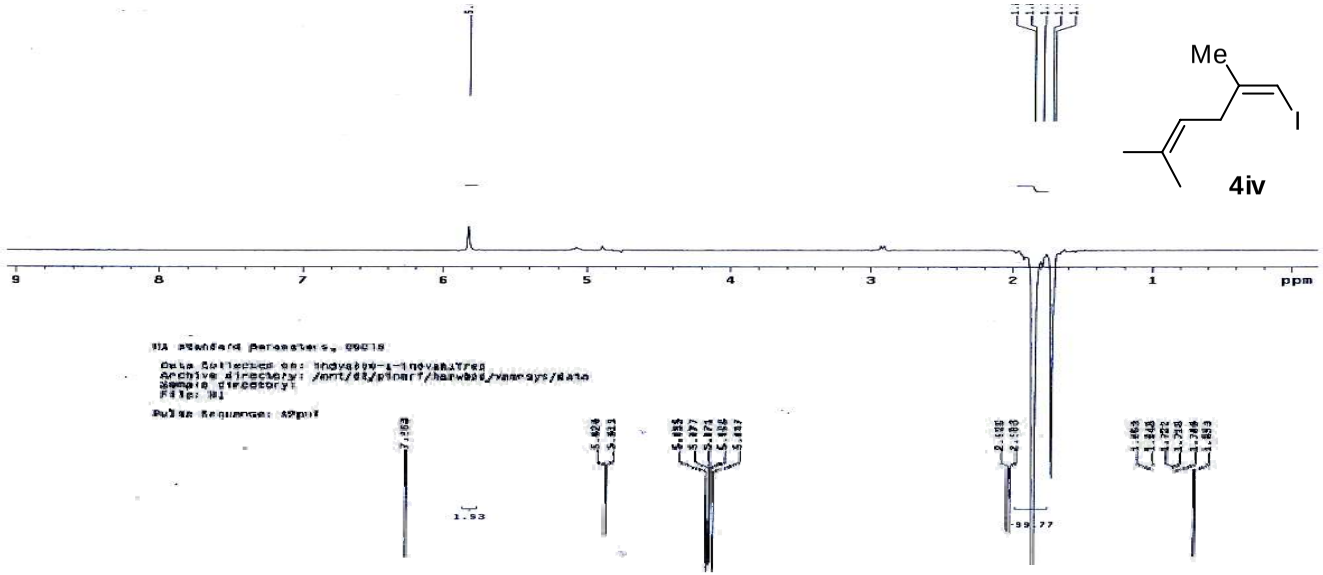
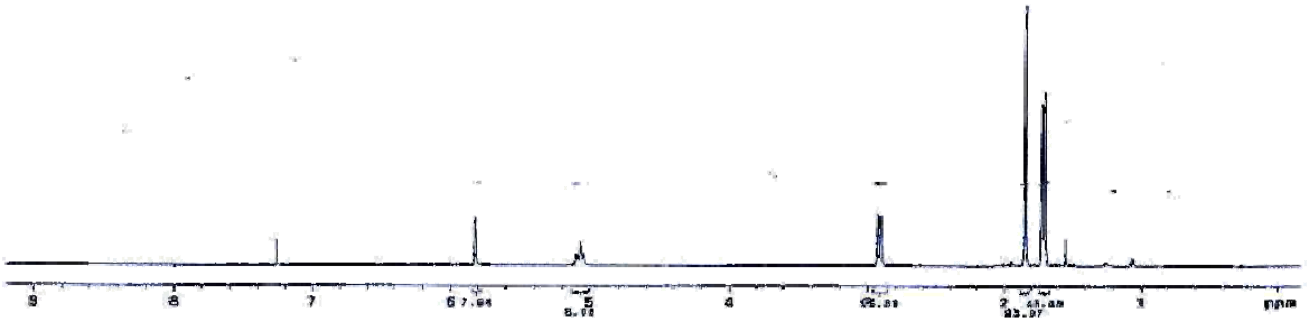
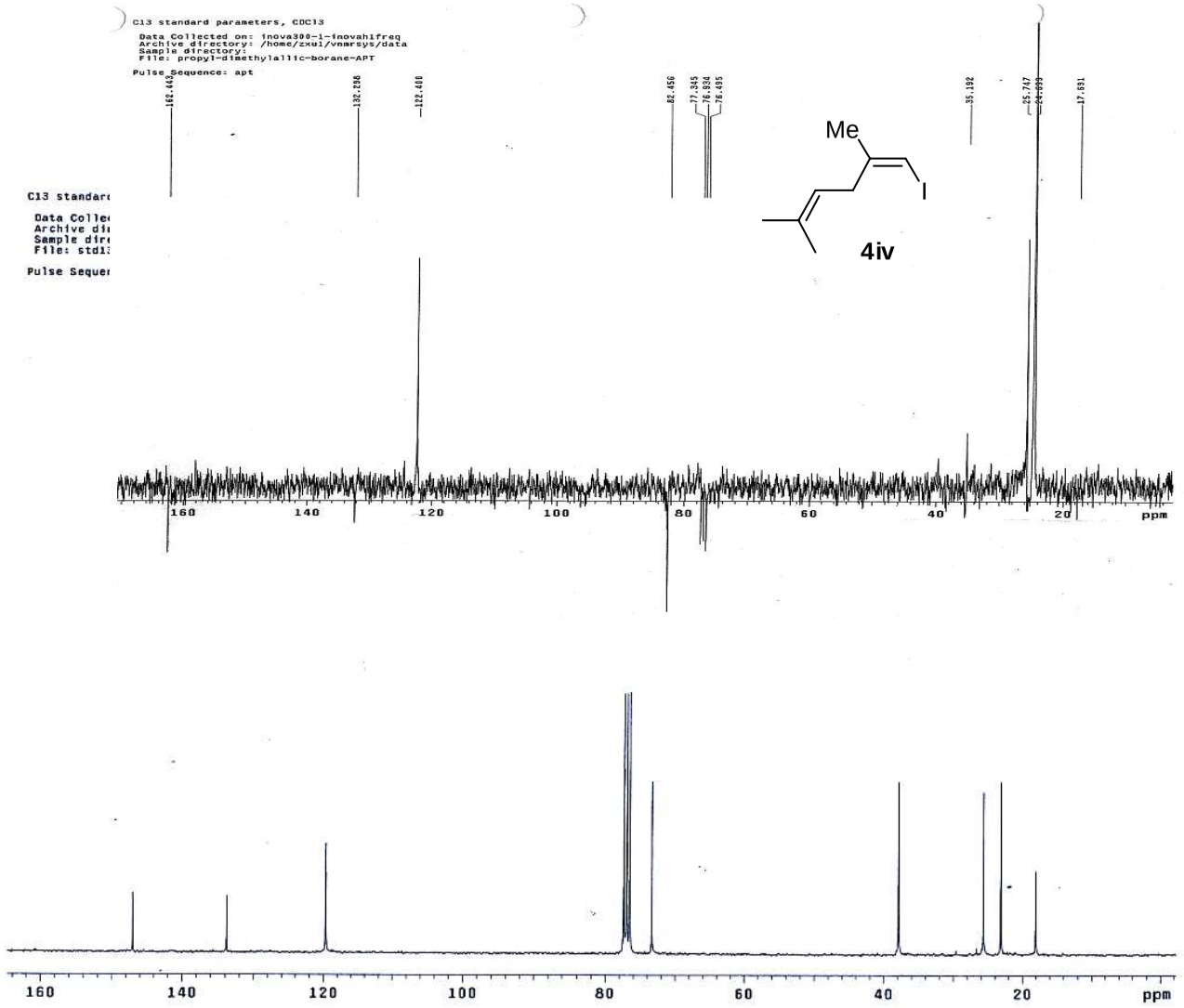


Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



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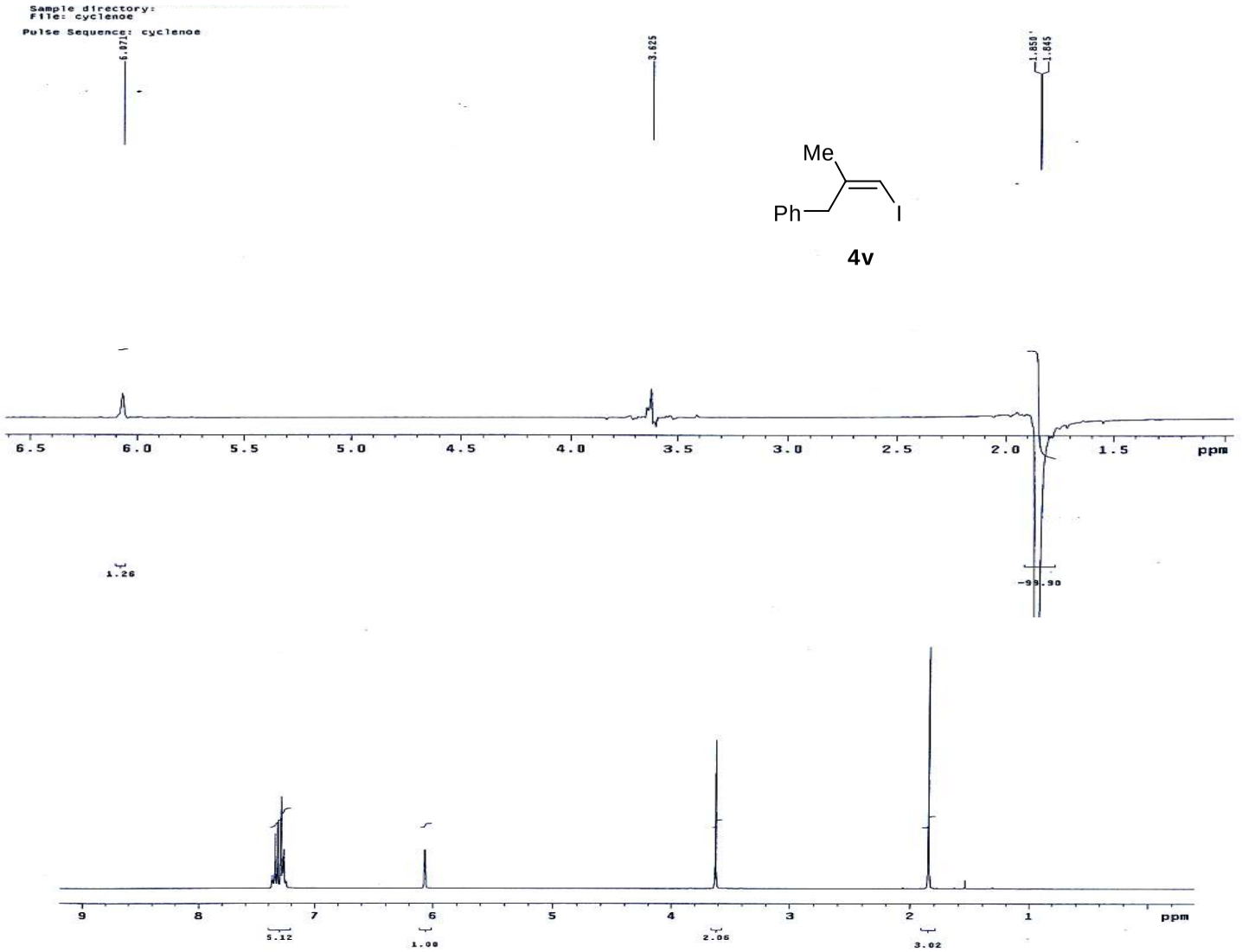
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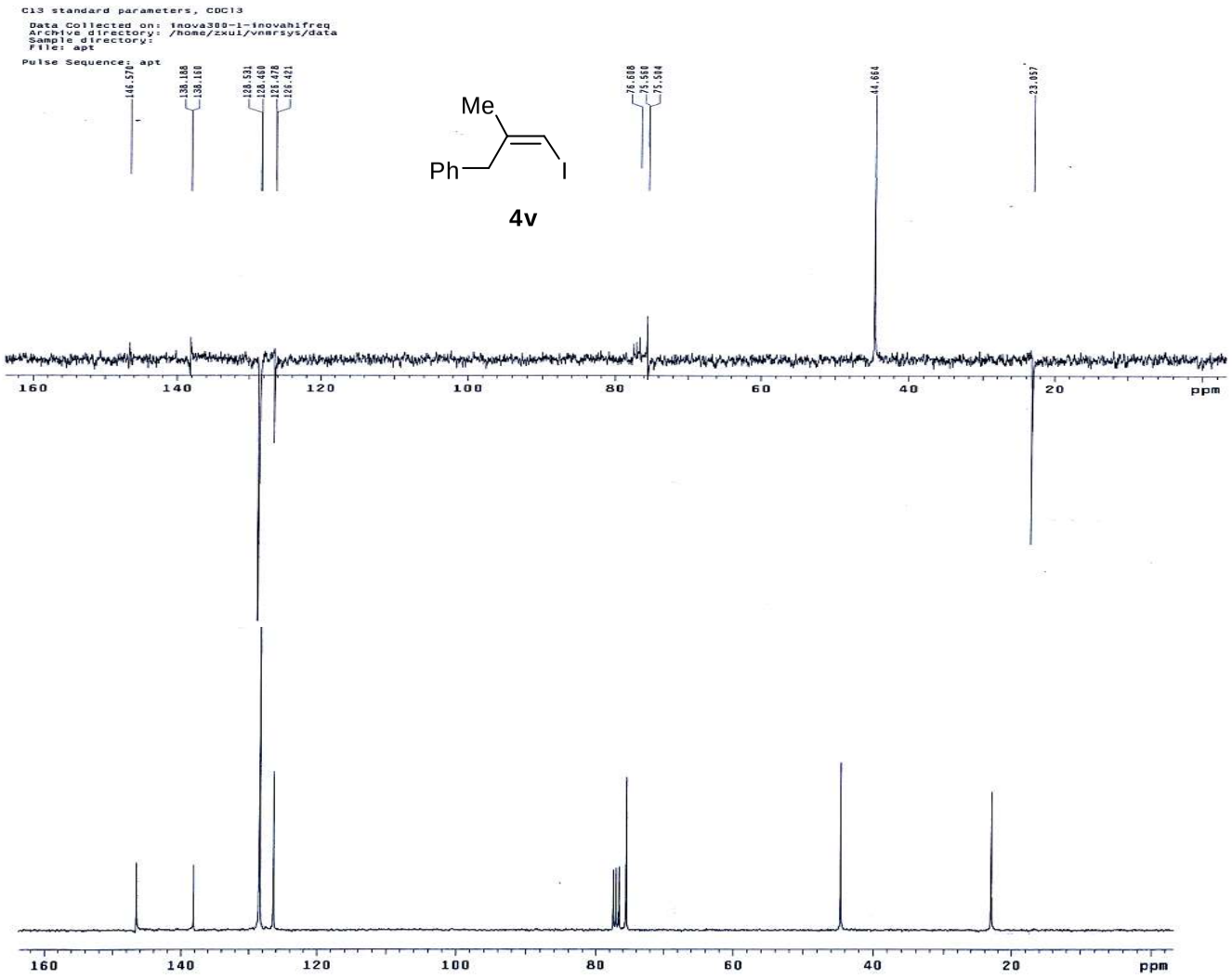
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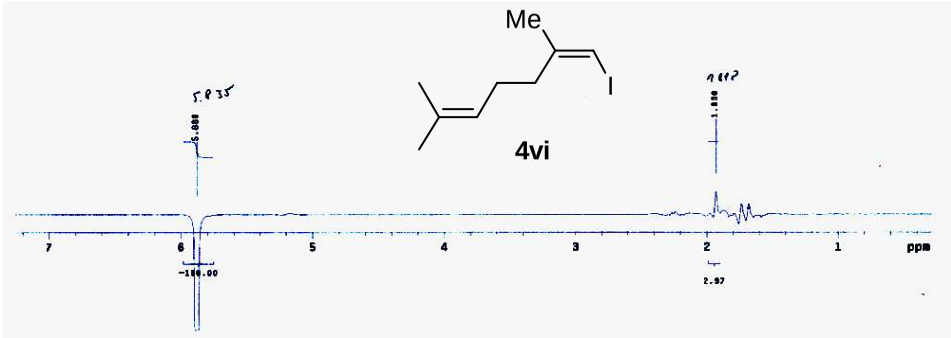
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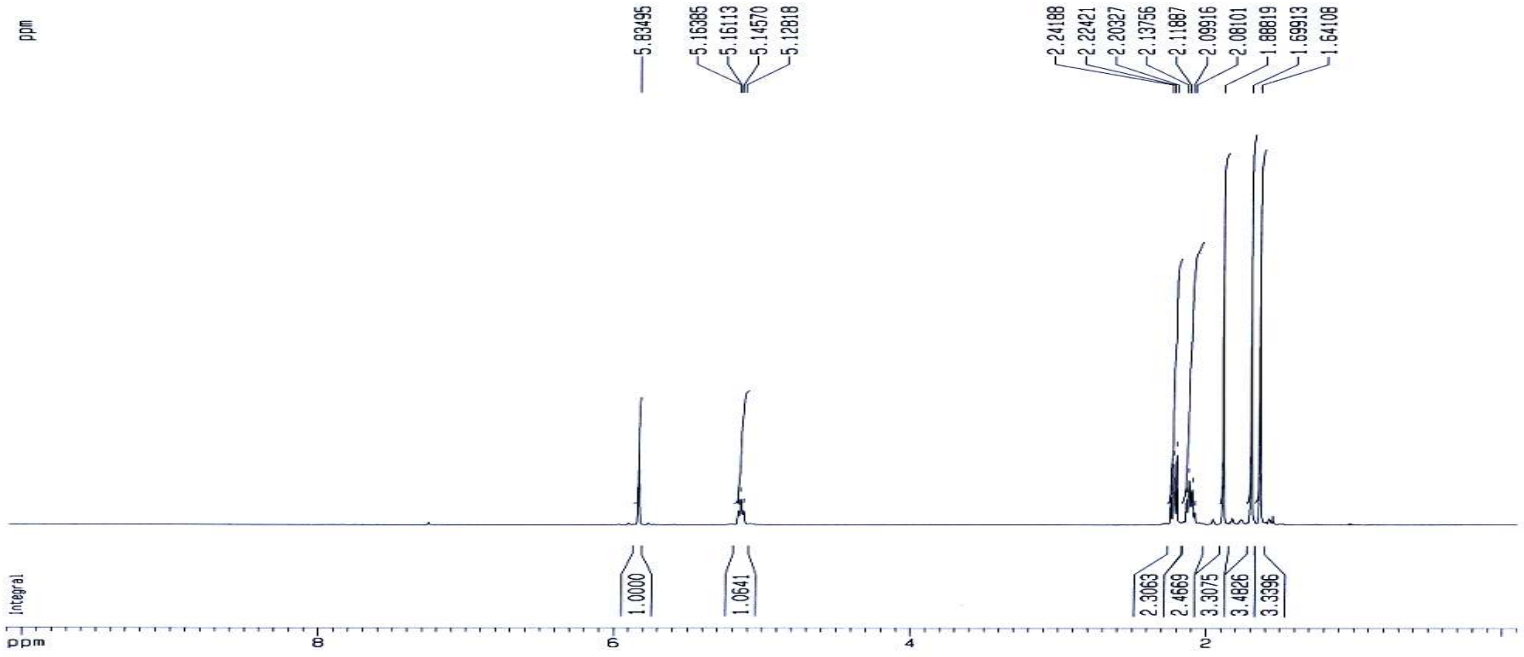
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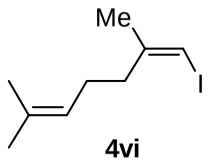
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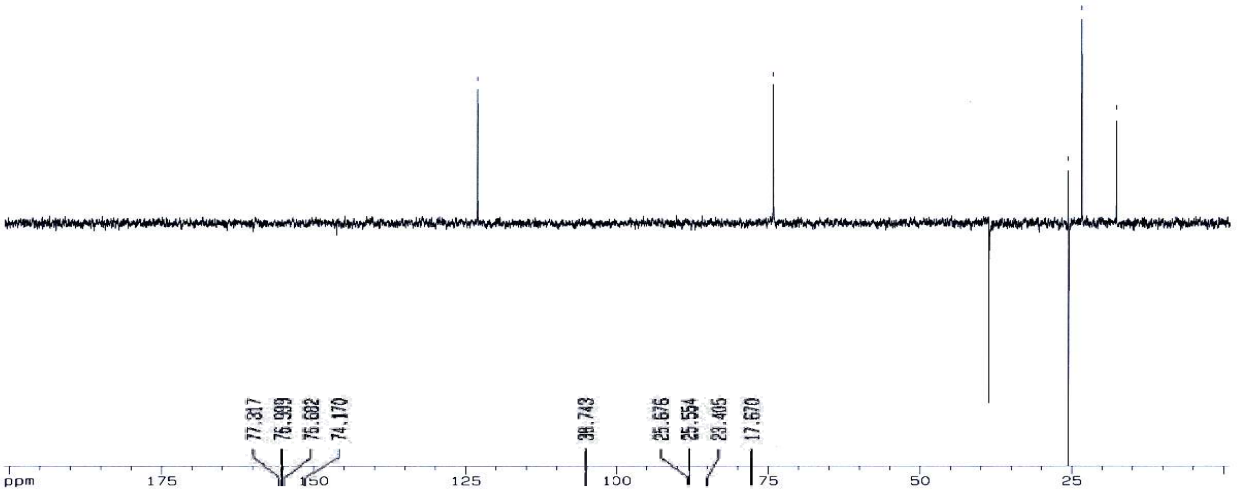
4vi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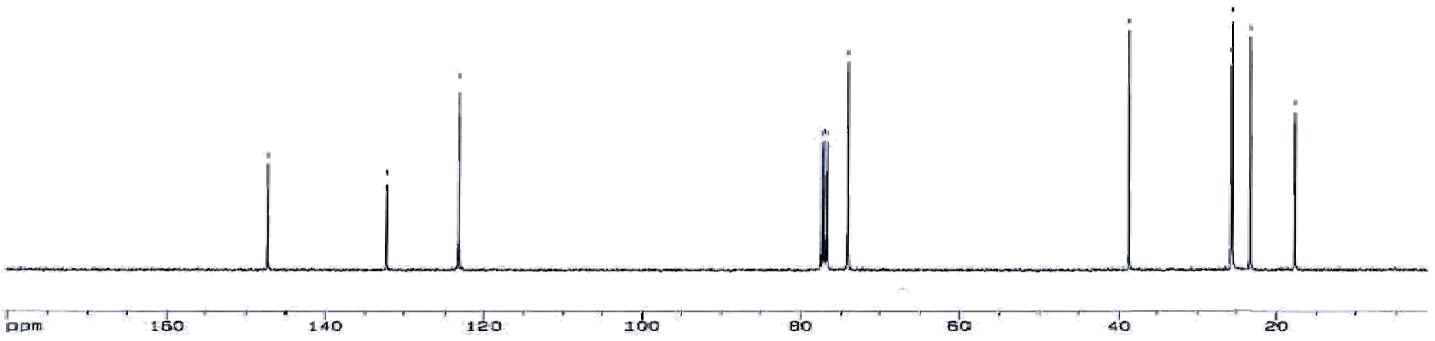
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40
20

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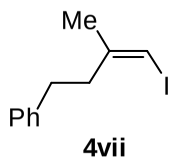
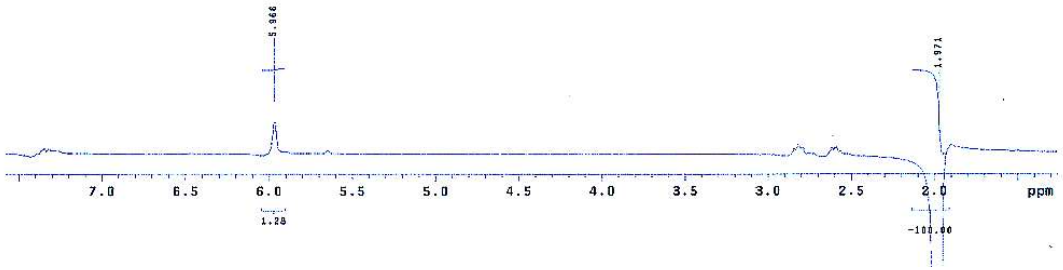
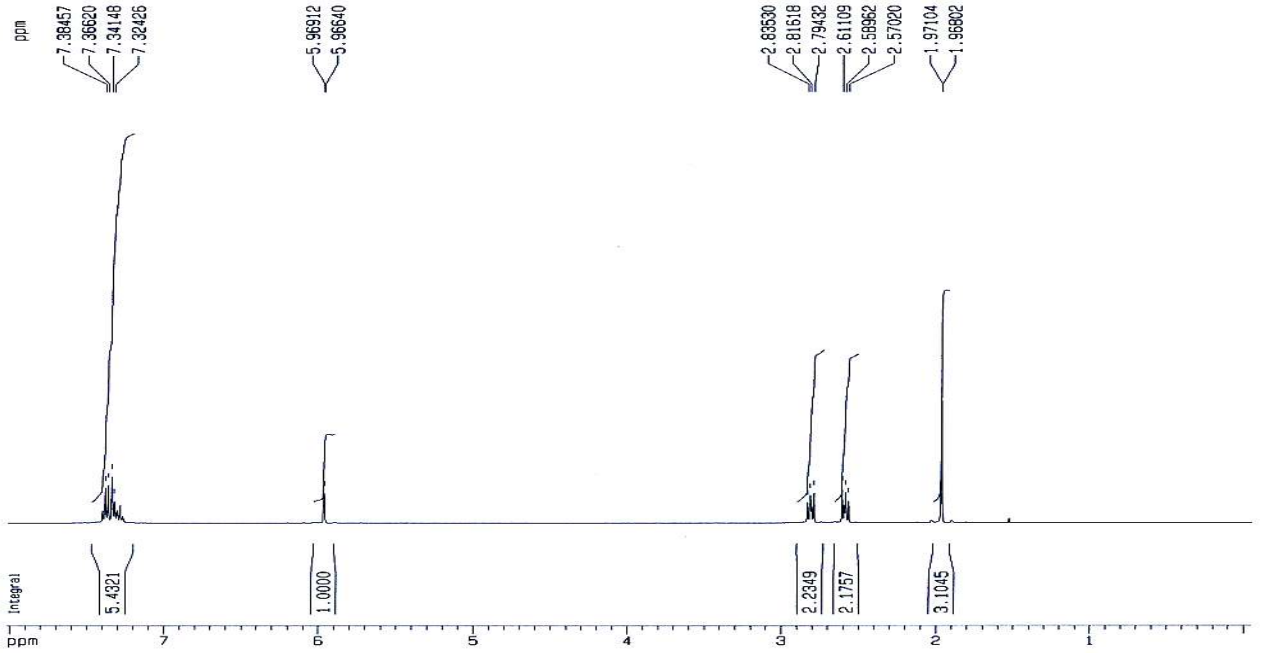
Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



4vii





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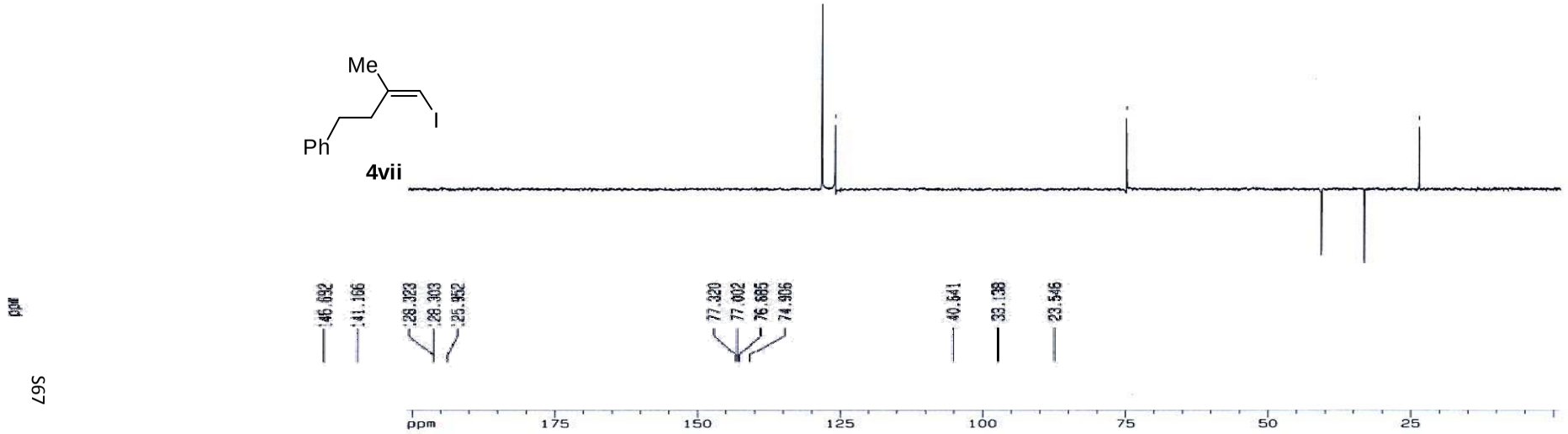
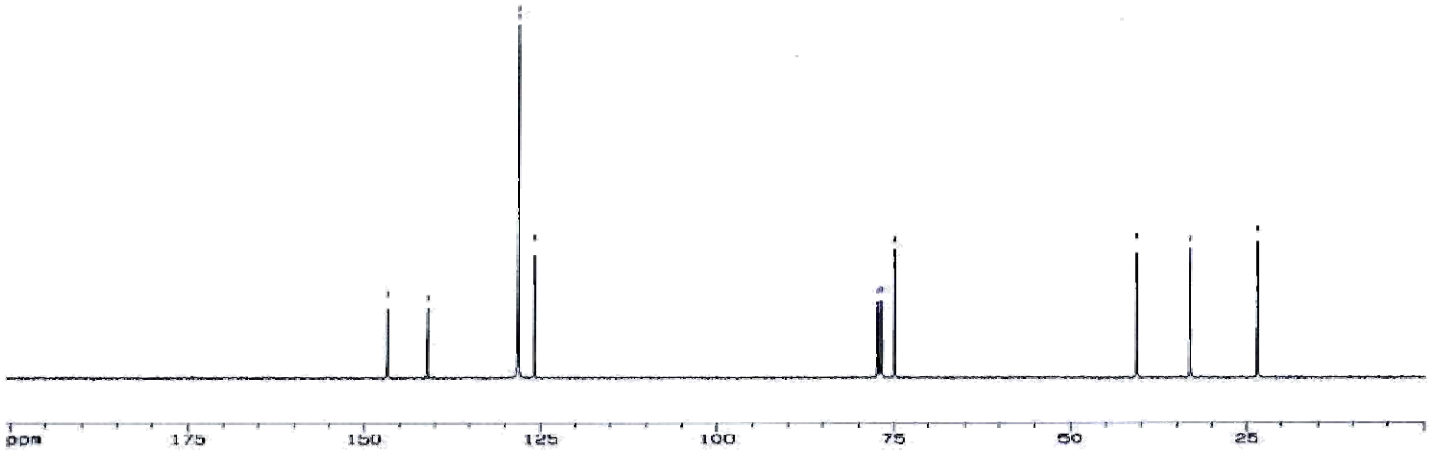
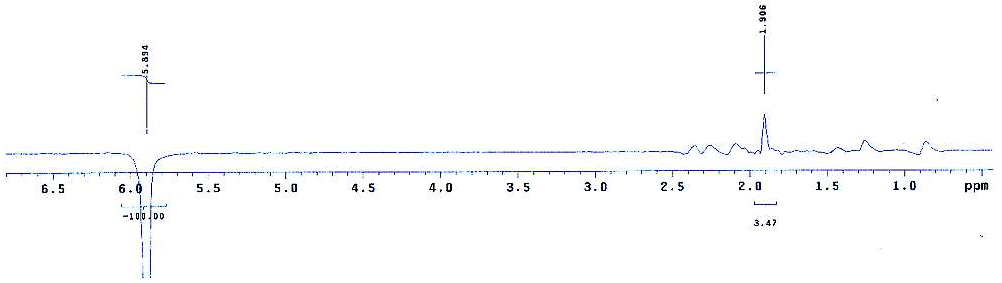
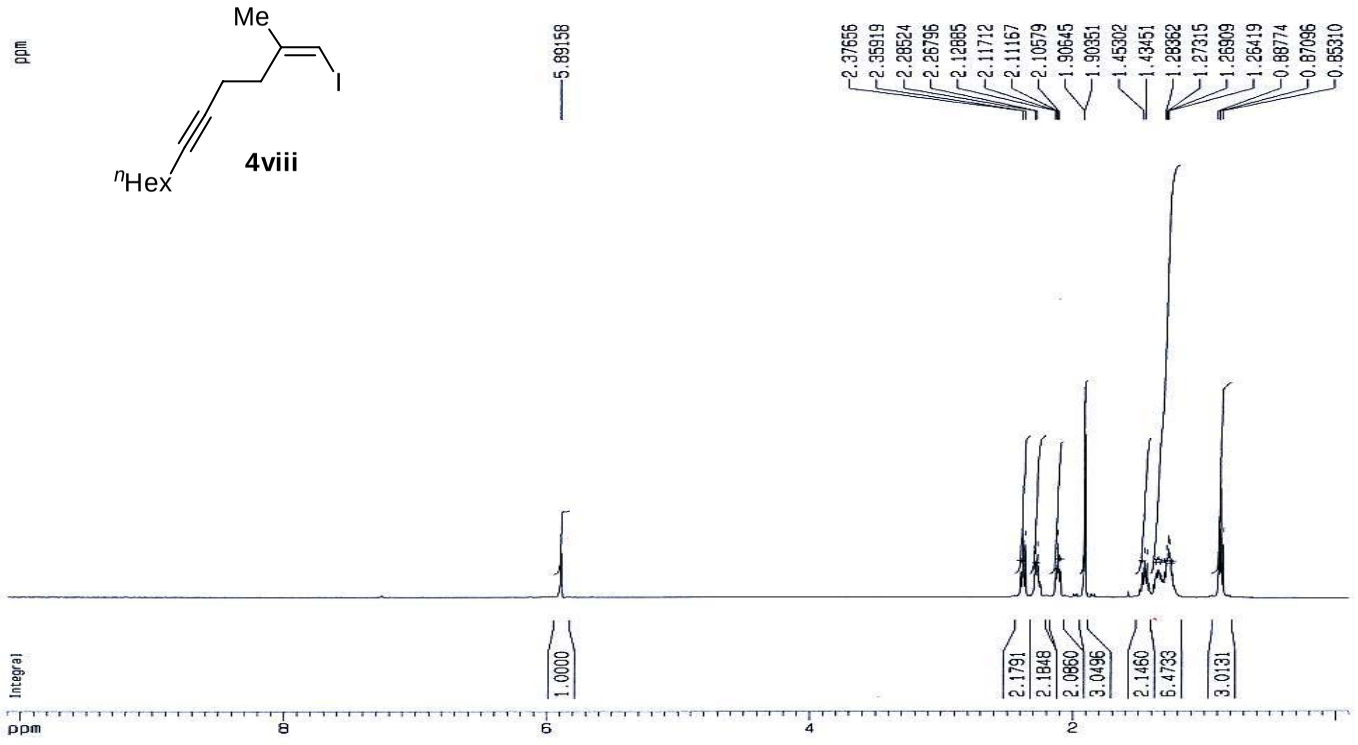




Highly Regio- and Stereoselective Synthesis of *Z*-Trisubstituted Alkenes via Propyne Bromoboration and Tandem Pd-Catalyzed Cross-Coupling

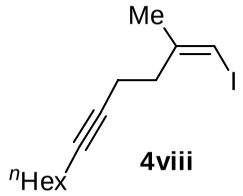
Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



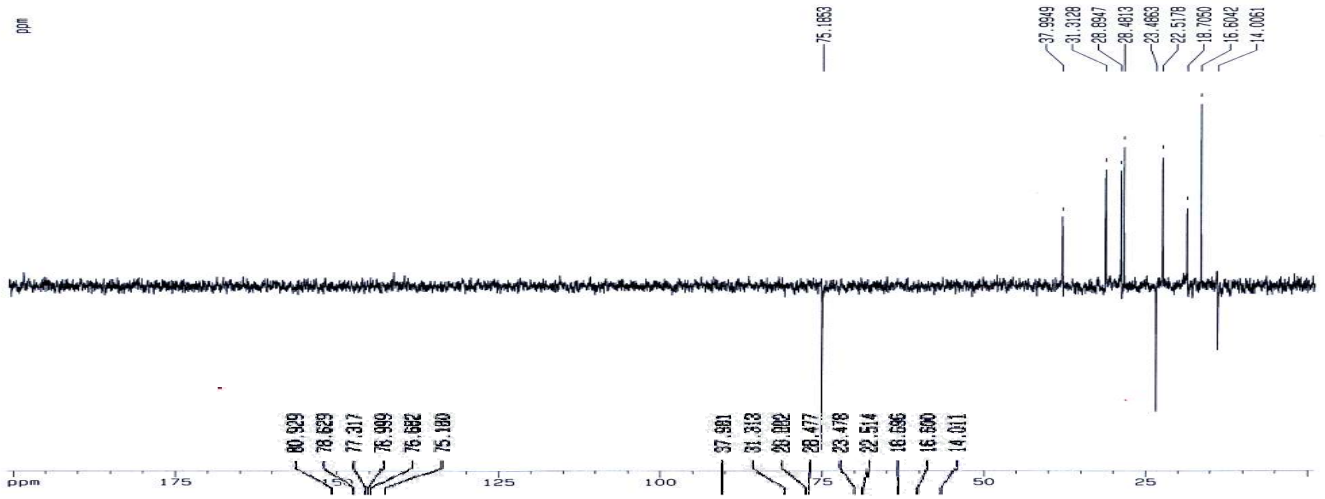


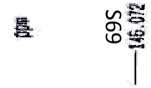
Highly Regio- and Stereoselective Synthesis of *Z*-Trisubstituted Alkenes via Propyne Bromoboration and Tandem Pd-Catalyzed Cross-Coupling

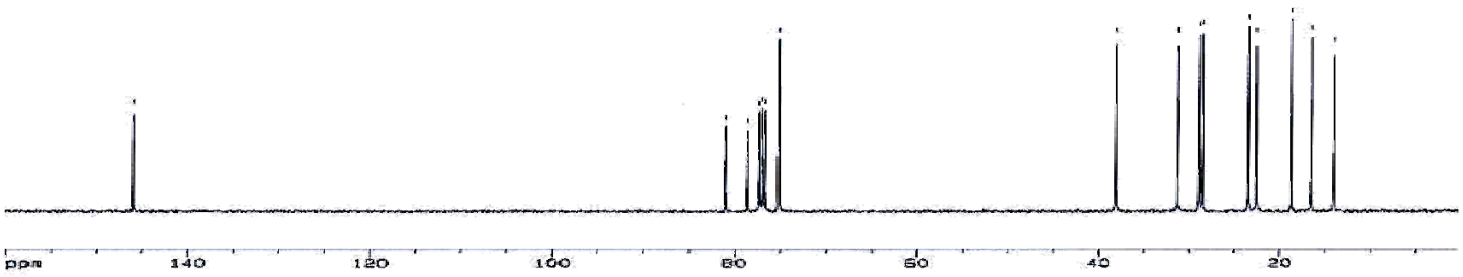
Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*

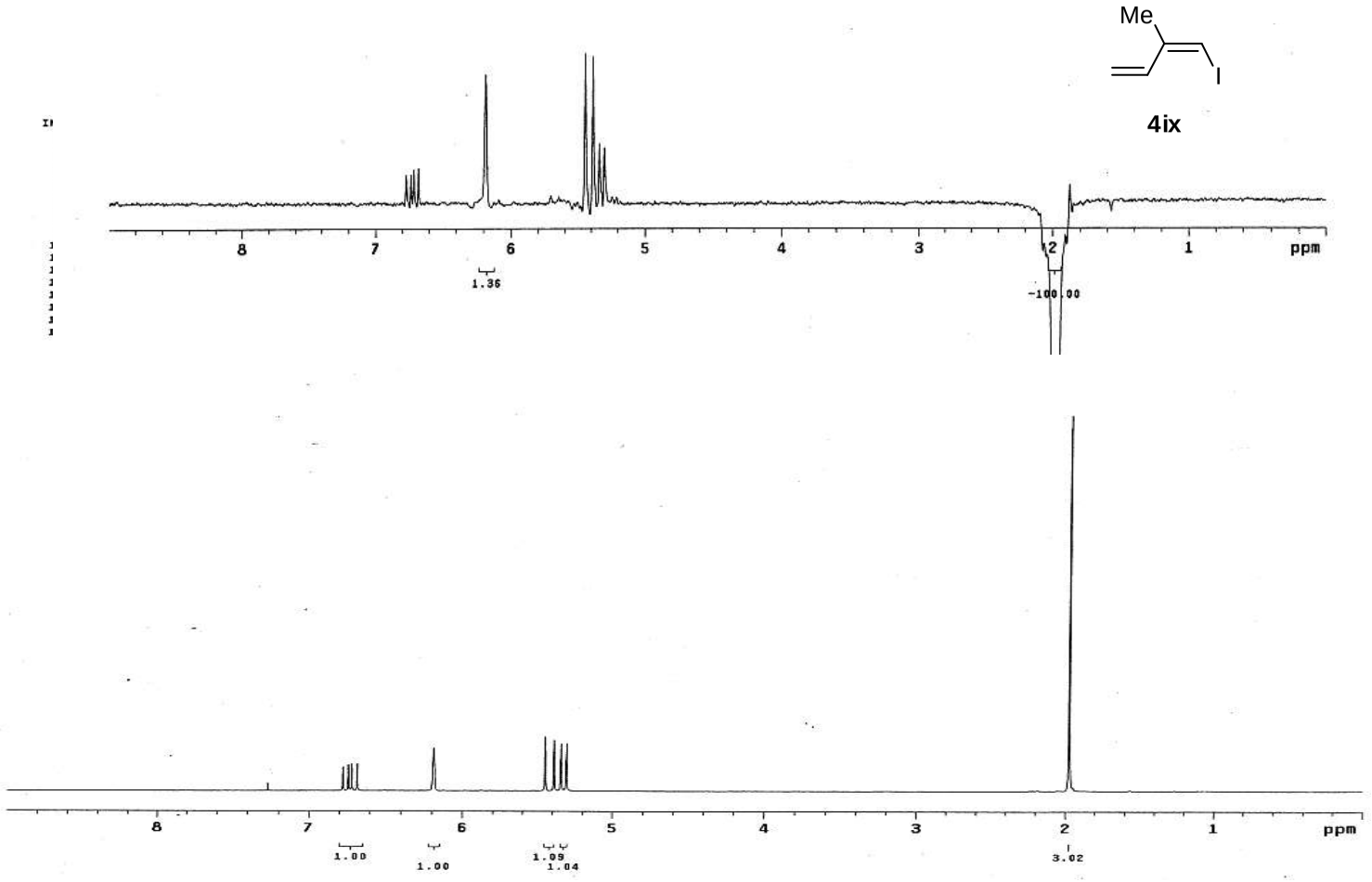


4viii





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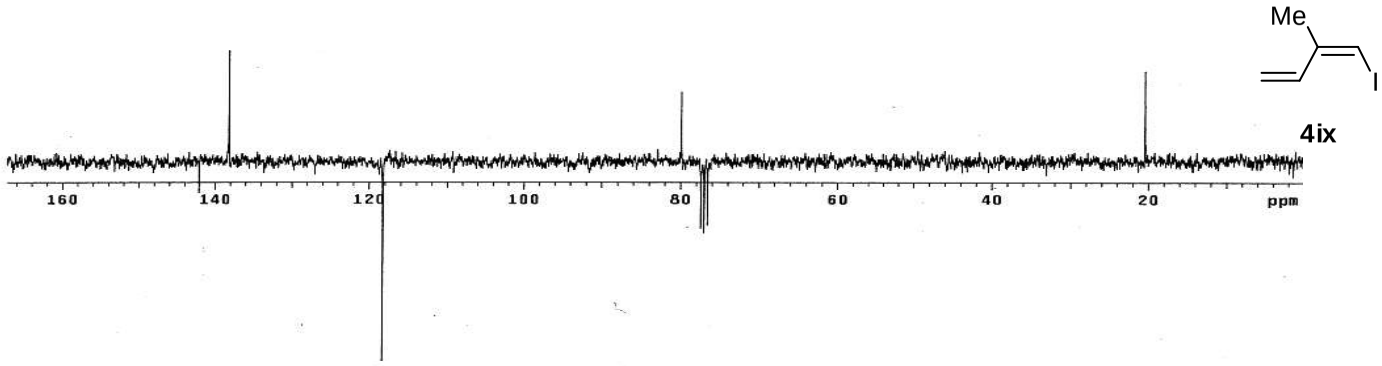
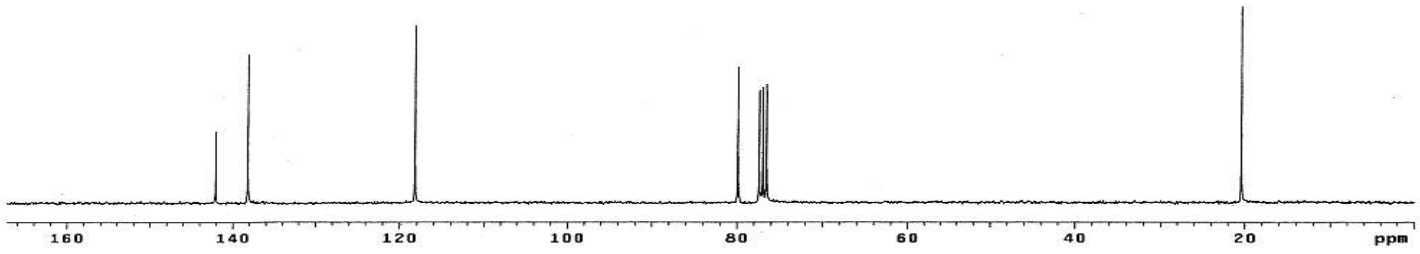
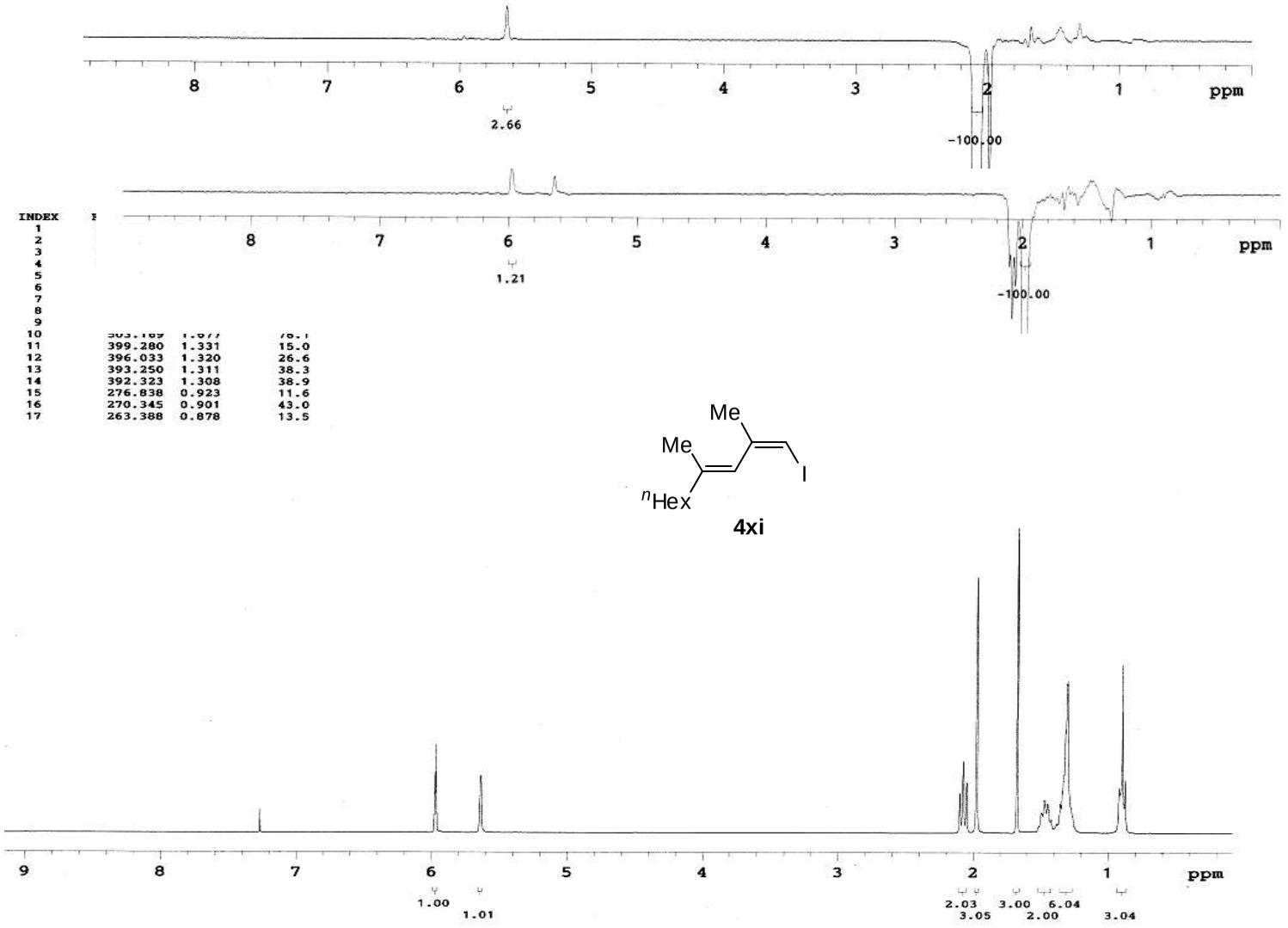


INDEX	FREQUENCY	PPM	HEIGHT
1	10716.167	142.077	18.1
2	10423.540	138.197	37.3
3	8918.754	118.247	44.6
4	6027.728	79.917	34.2
5	5838.695	77.411	28.4
6	5807.723	77.000	29.1
7	5775.684	76.575	29.9
8	1540.068	20.419	49.3

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392.323 1.308 38.9
276.838 0.923 11.6
270.345 0.901 43.0
263.388 0.878 13.5
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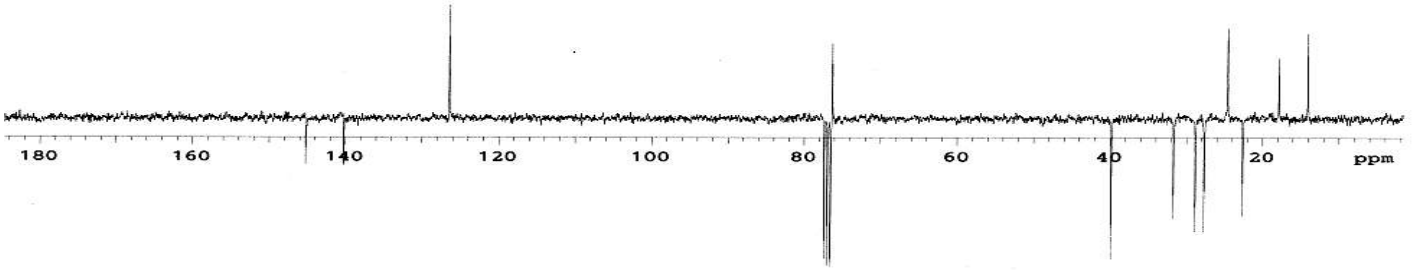
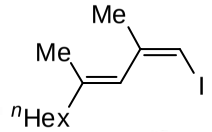


INDEX	FREQUENCY	PPM	HEIGHT
1	10958.599	145.291	20.2
2	10581.602	140.293	21.9
3	9542.455	126.516	41.0
4	5839.763	77.425	67.0
5	5807.723	77.000	68.8
6	5775.684	76.575	69.7
7	5758.596	76.349	49.7
8	3006.407	39.860	54.1
9	2394.454	31.746	47.1
10	2178.721	28.886	48.0
11	2090.079	27.711	45.3
12	1858.327	24.638	39.3
13	1708.809	22.656	42.9
14	1352.103	17.926	28.9
15	1064.816	14.118	41.8



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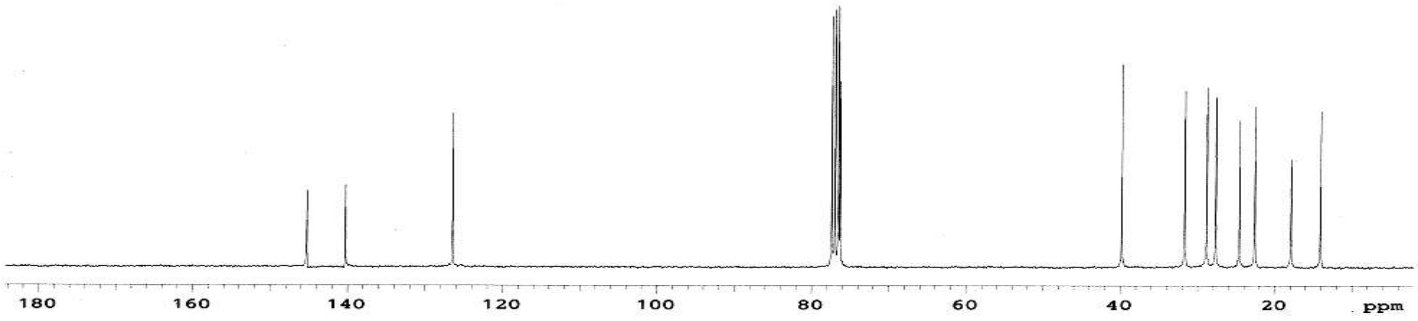

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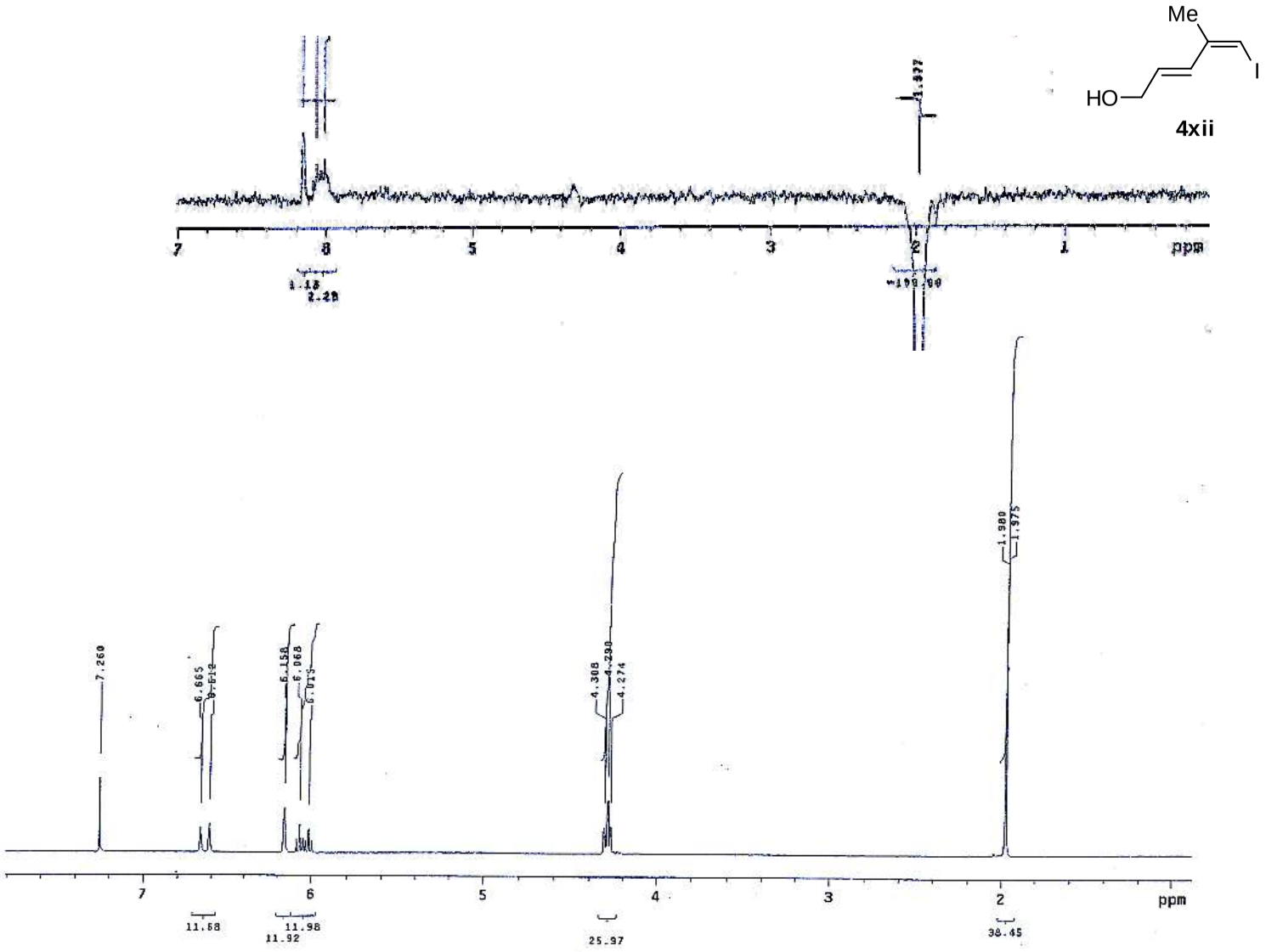

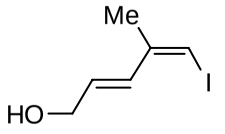
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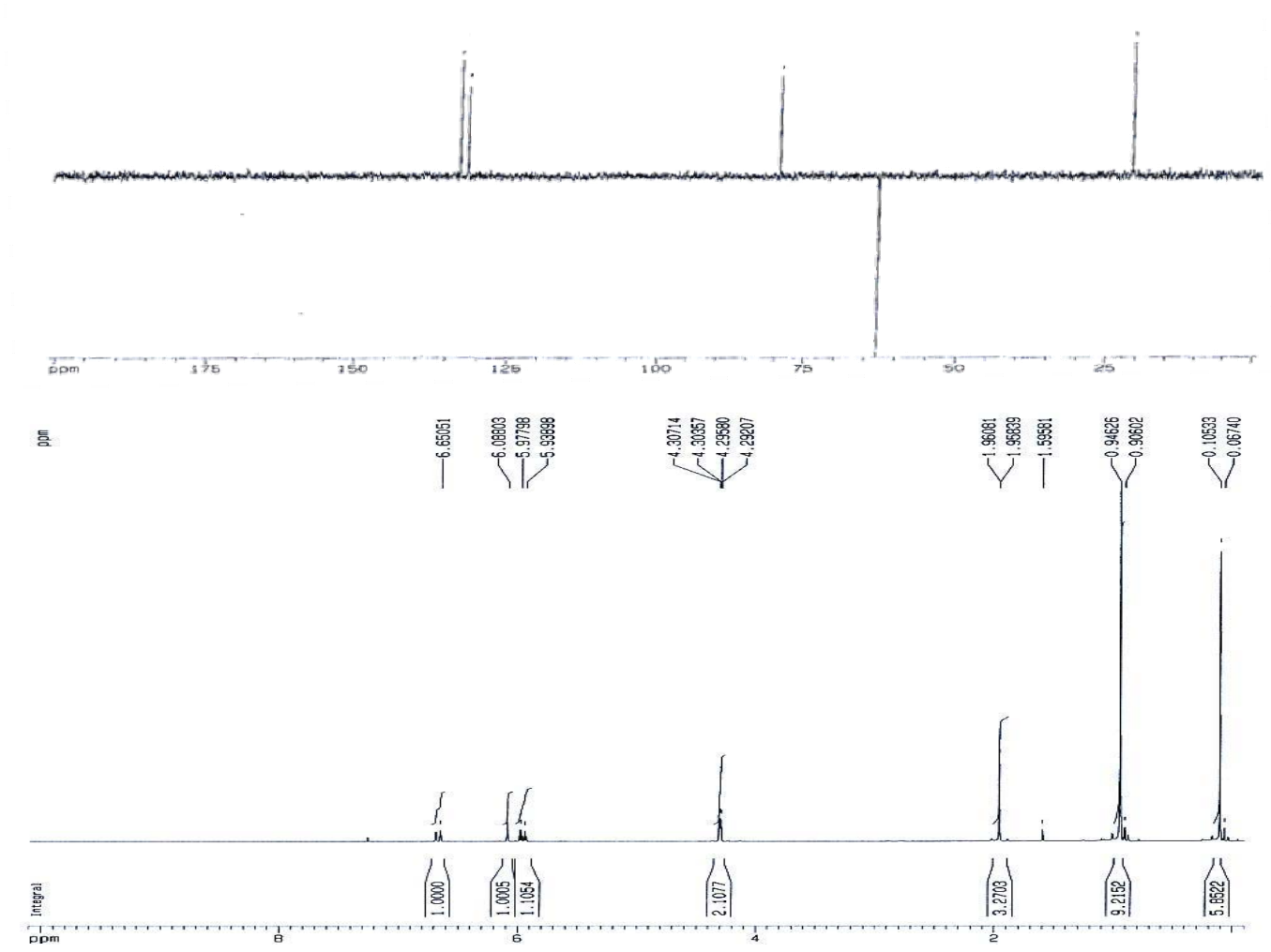
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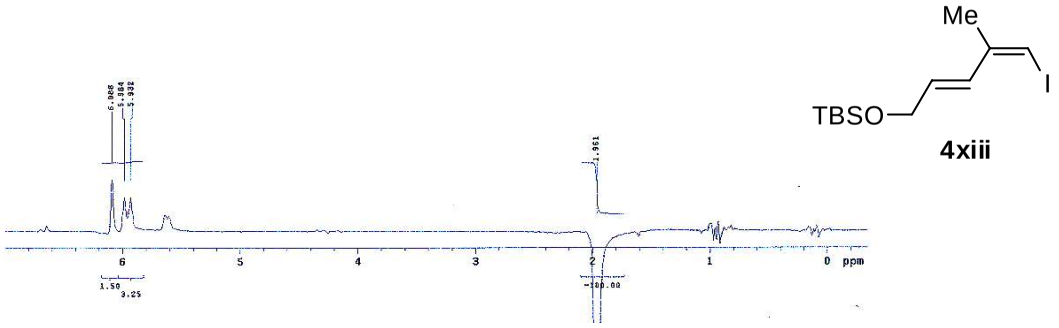
Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



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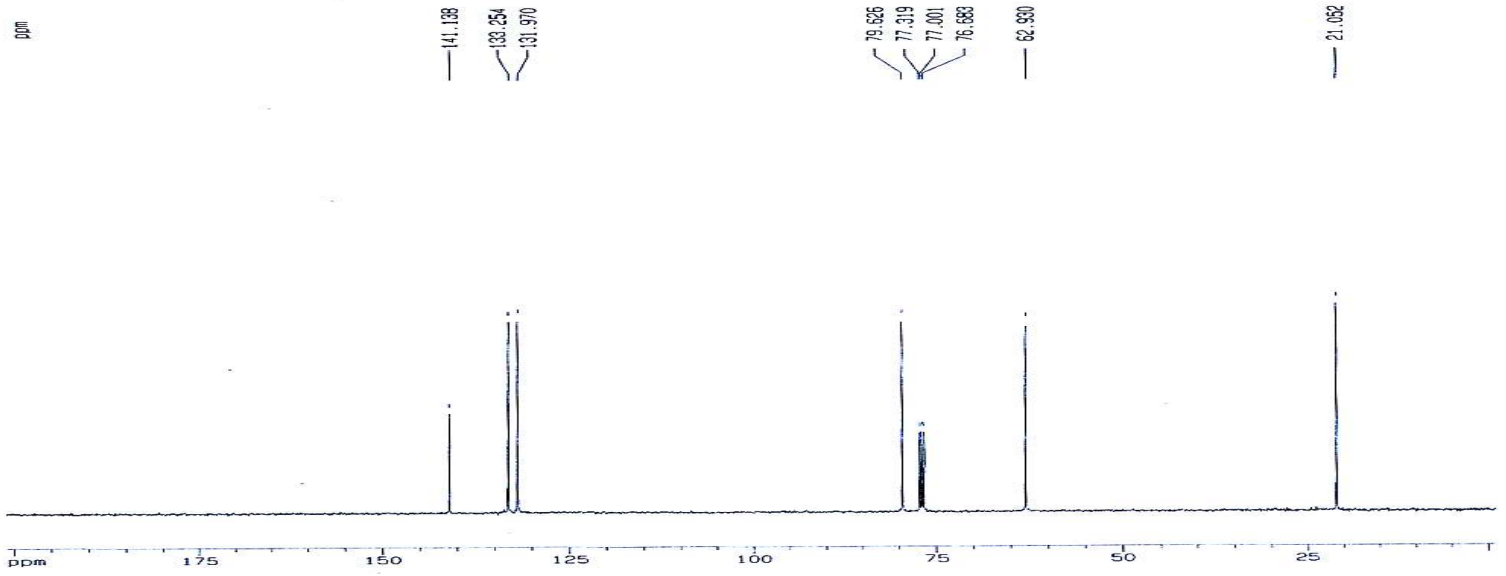

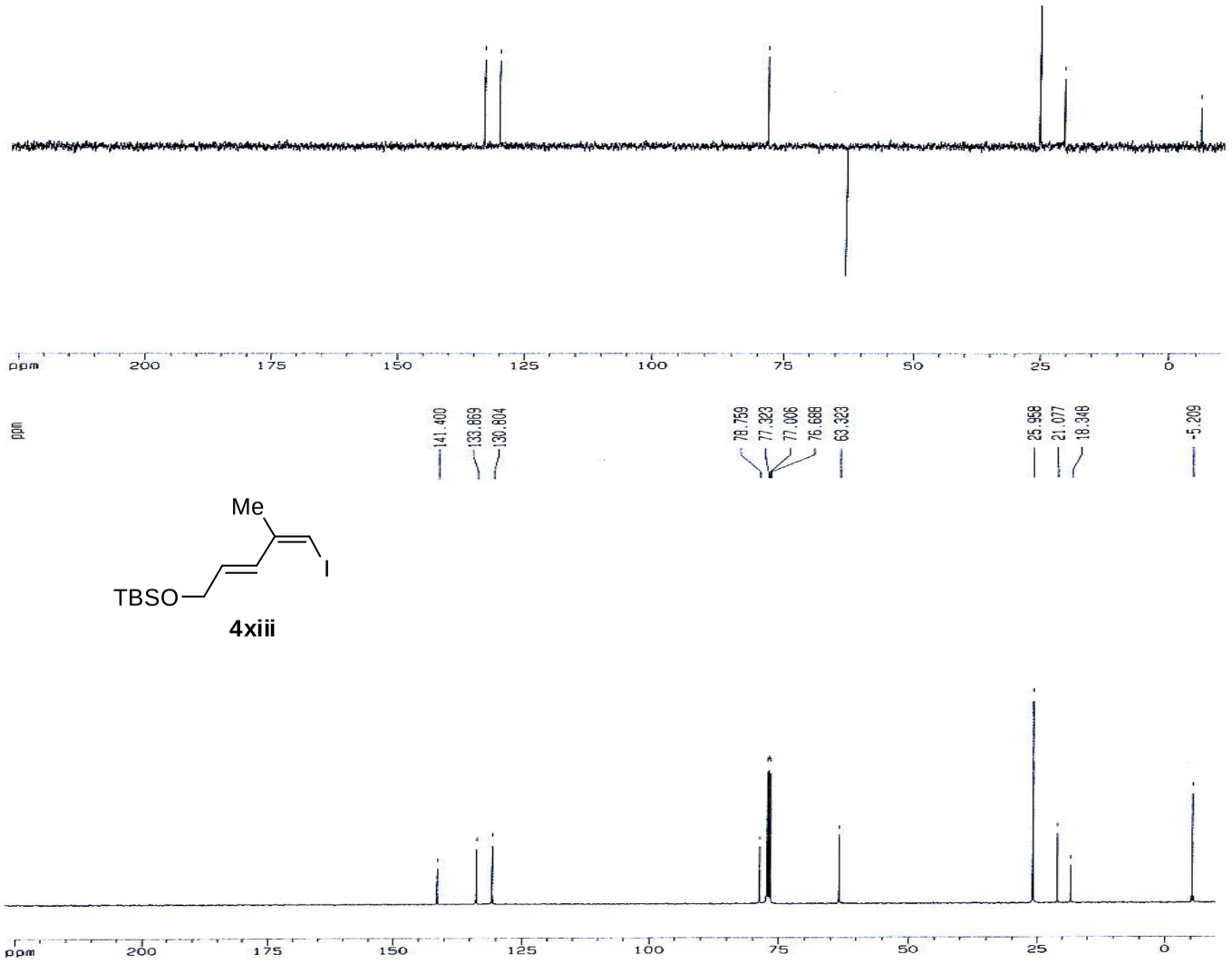
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63.323
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Me
I
TBSO
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ppm
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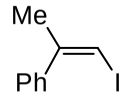
50
25
0

Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



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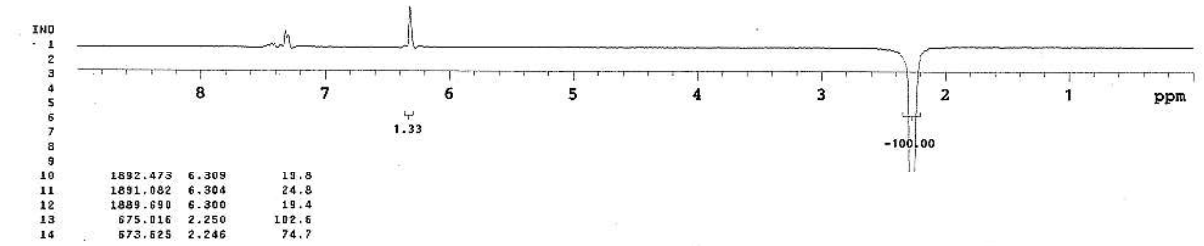

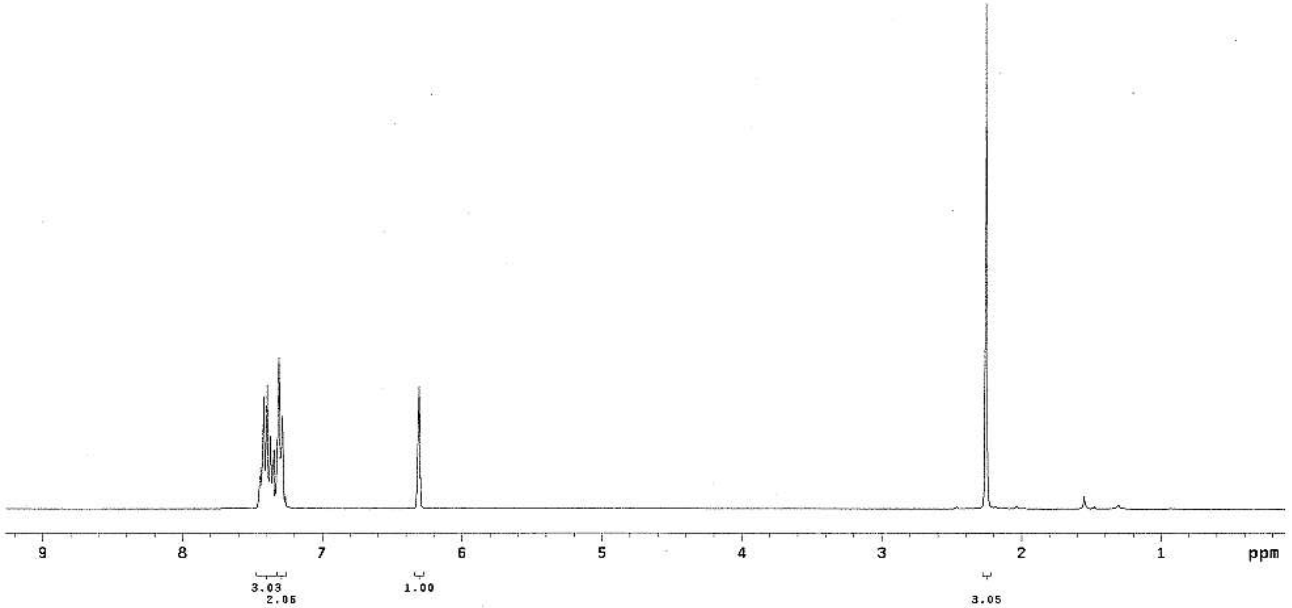

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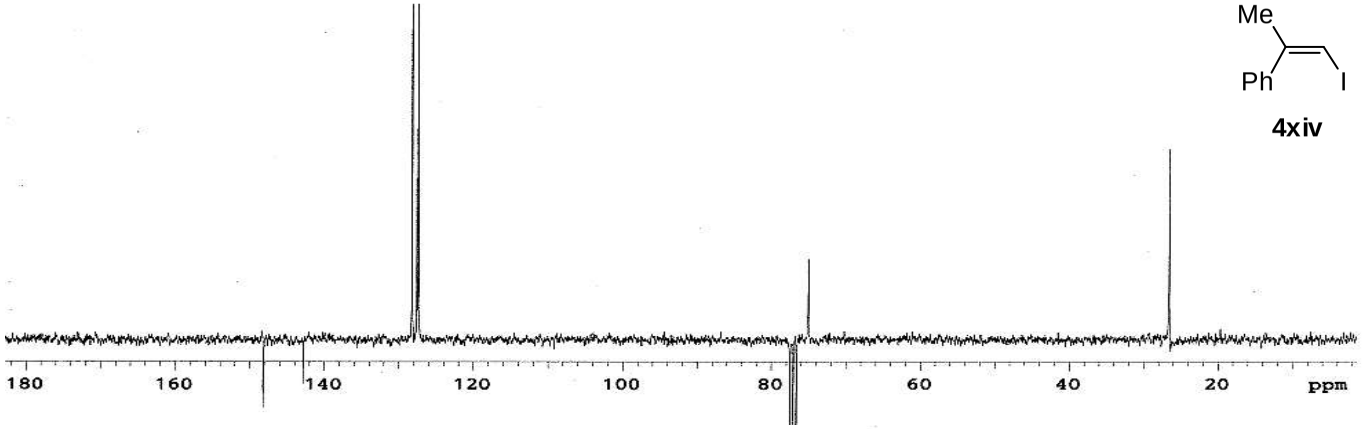
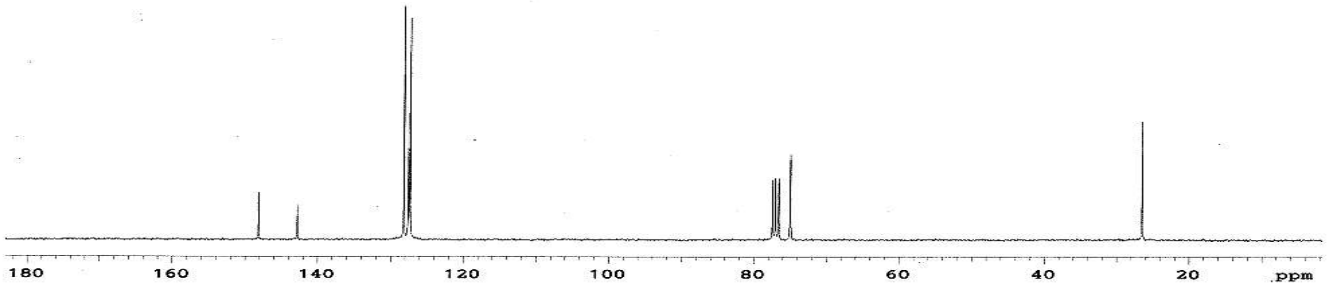


4xiv

INDEX	FREQUENCY	PPM	HEIGHT
1	11177.536	148.194	13.7
2	10772.771	142.828	10.2
3	9670.614	128.215	68.4
4	9623.623	127.592	36.9
5	9605.467	127.351	64.9
6	5839.763	77.425	17.6
7	5807.724	77.000	18.1
8	5775.684	76.575	18.0
9	5655.002	74.975	25.1
10	2000.369	26.521	34.8



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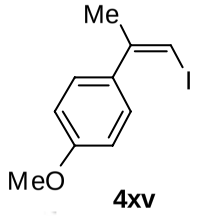

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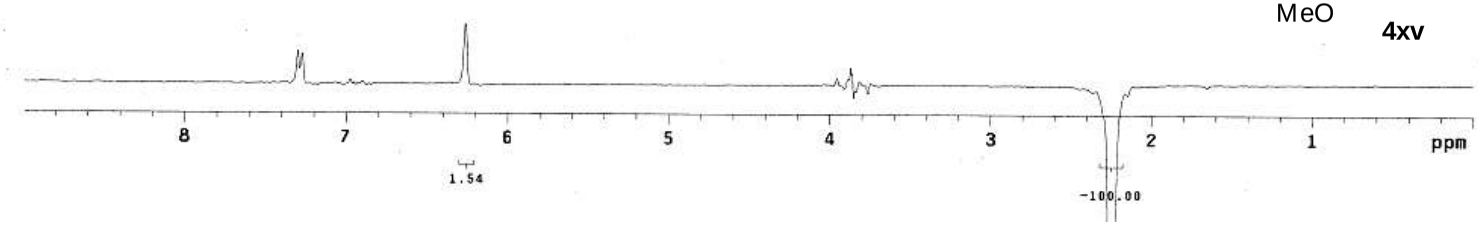
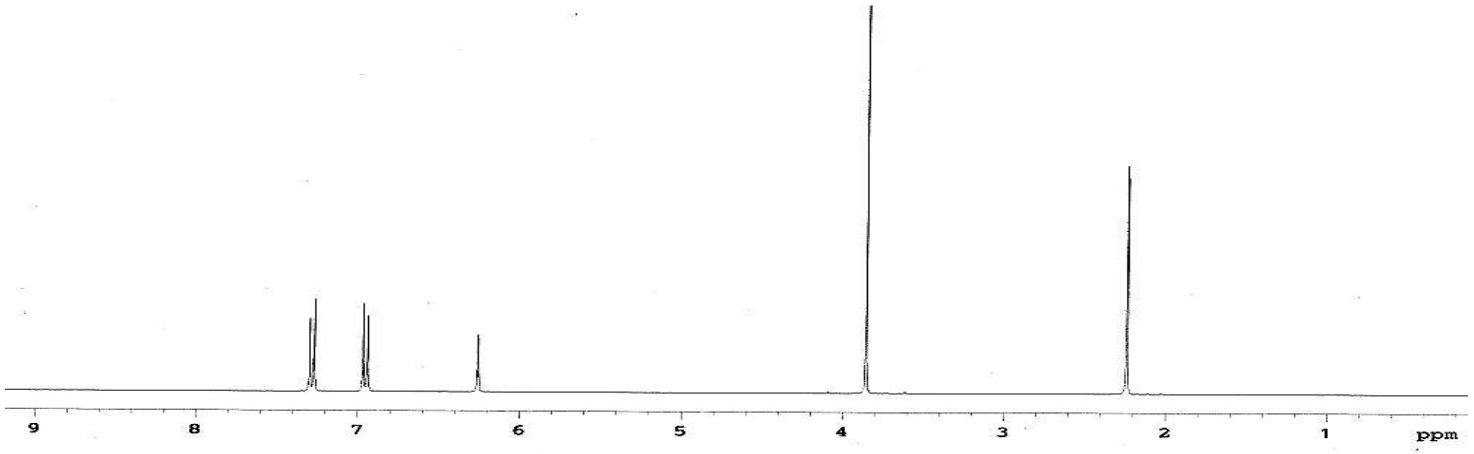


INDEX	FREQUENCY	PPM	HEIGHT
1	2189.520	7.299	19.3
2	2180.708	7.270	24.4
3	2090.269	6.968	23.2
4	2081.457	6.939	20.0
5	1878.779	6.263	15.0
6	1877.388	6.259	14.1
7	1157.581	3.859	102.6
8	672.917	2.243	60.2
9	671.526	2.239	56.9



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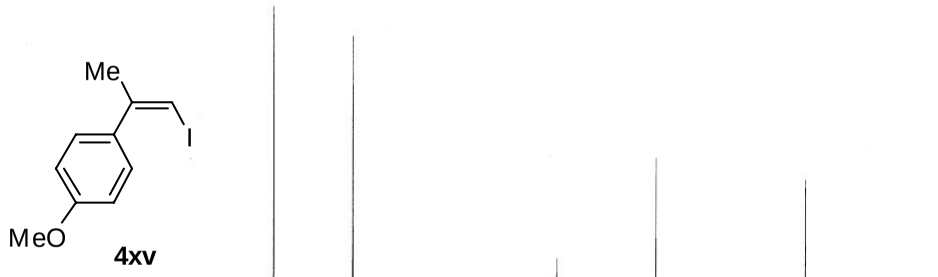
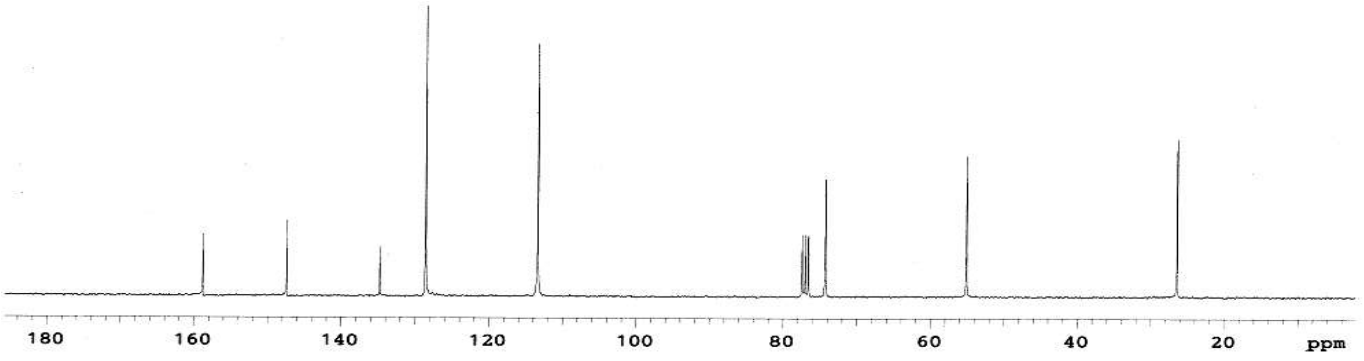
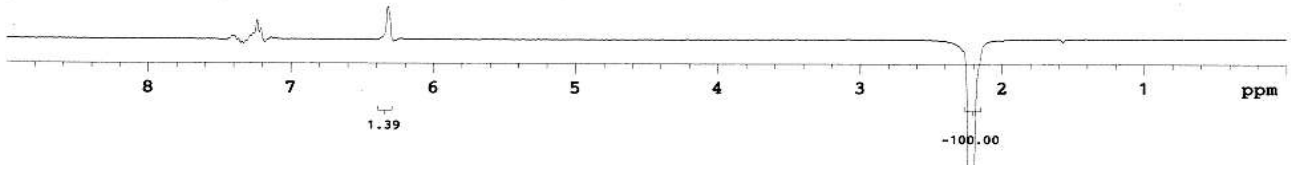
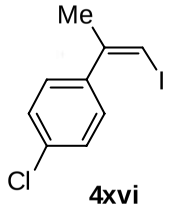


INDEX	FREQUENCY	PPM	HEIGHT
1	11980.658	158.842	13.9
2	11118.797	147.415	17.1
3	10167.225	134.799	11.2
4	9702.653	128.640	65.7
5	8554.573	113.418	57.3
6	5839.763	77.425	14.1
7	5807.724	77.000	14.3
8	5775.685	76.575	13.9
9	5603.740	74.296	26.7
10	4157.692	55.124	31.9
11	1993.961	26.436	35.8





INDEX	FREQUENCY	PPM	HEIGHT
1	2214.565	7.383	24.3
2	2205.753	7.353	34.8
3	2169.577	7.233	31.3
4	2161.229	7.205	21.2
5	1894.548	6.316	20.7
6	663.178	2.211	79.3
7	661.786	2.206	57.1



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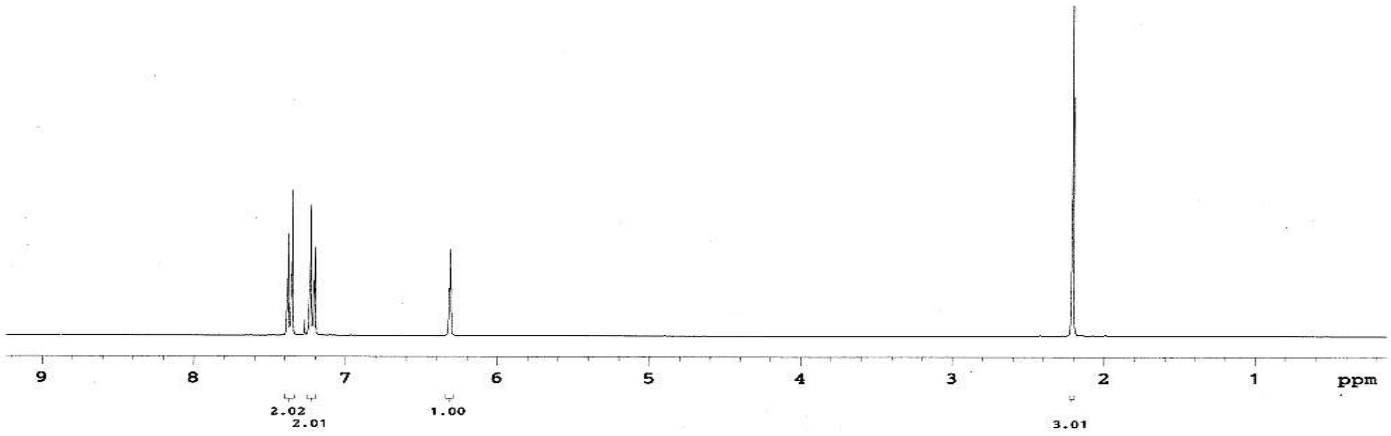
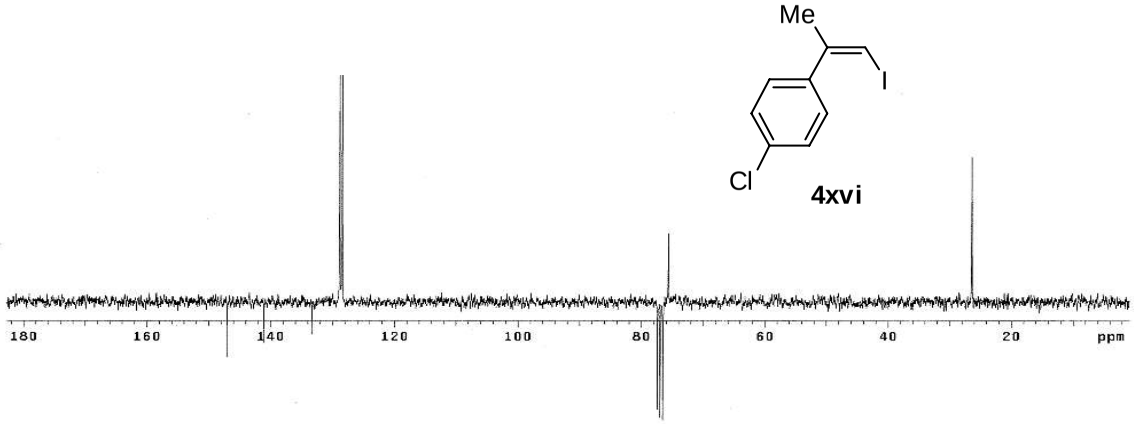
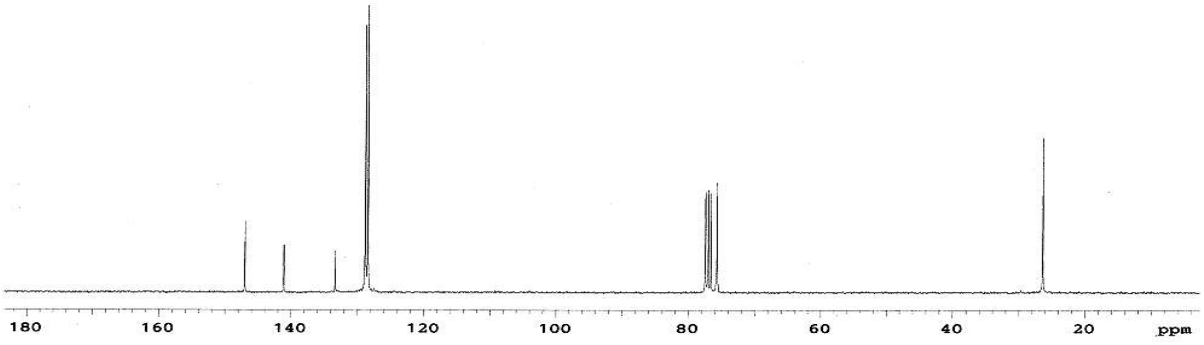




INDEX	FREQUENCY	PPM	HEIGHT
1	11088.893	147.019	19.9
2	10643.545	141.114	13.2
3	10061.495	133.397	11.6
4	9719.741	128.866	75.0
5	9691.973	128.498	80.6
6	5839.763	77.425	28.2
7	5807.724	77.000	28.7
8	5775.684	76.575	27.8
9	5709.469	75.697	30.8
10	1991.825	26.408	43.3



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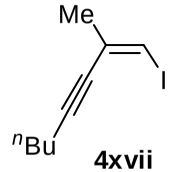

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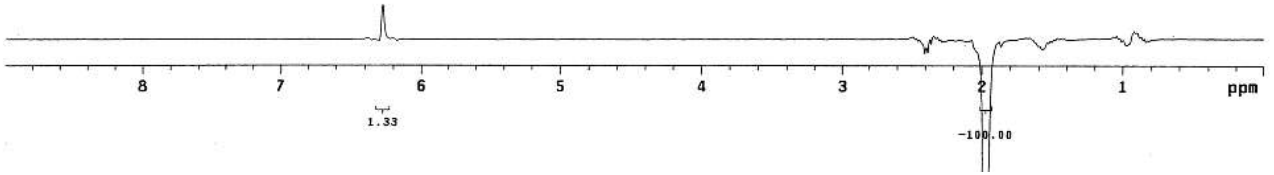
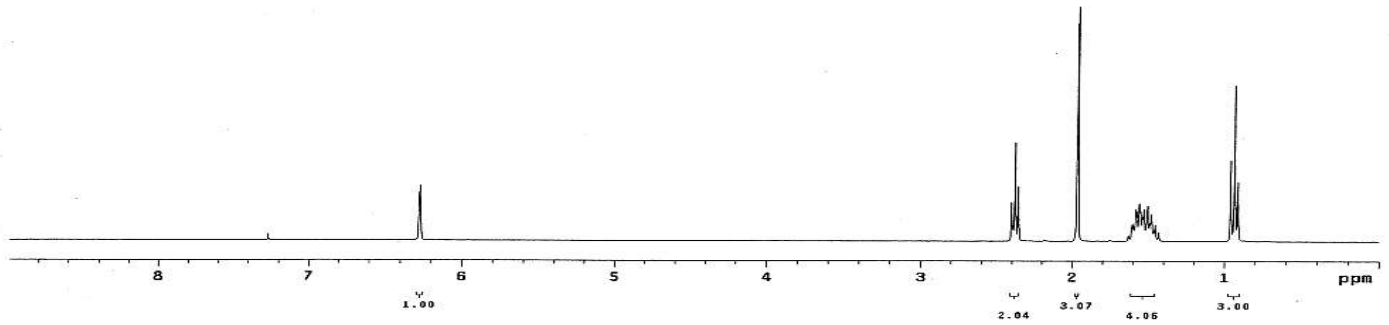
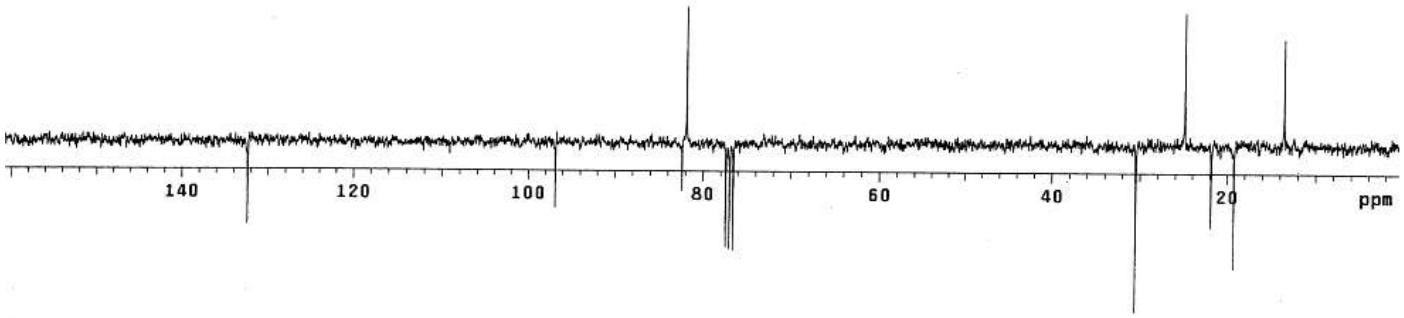


INDEX	FREQUENCY	PPM	HEIGHT
1	1883.881	6.280	12.0
2	1882.480	6.276	13.7
3	721.616	2.406	9.7
4	714.659	2.383	24.4
5	707.702	2.359	13.6
6	591.754	1.973	53.5
7	589.898	1.967	57.6
8	474.414	1.582	8.0
9	472.559	1.575	7.5
10	468.385	1.561	9.4
11	467.457	1.558	9.4
12	465.602	1.552	7.5
13	460.036	1.534	7.3
14	459.109	1.531	8.0
15	451.688	1.506	8.9
16	288.897	0.963	20.1
17	281.940	0.940	38.4
18	274.519	0.915	14.8

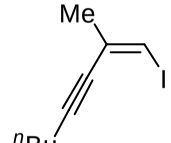


Highly Regio- and Stereoselective Synthesis of *Z*-Trisubstituted Alkenes via Propyne Bromoboration and Tandem Pd-Catalyzed Cross-Coupling

Chao Wang, Tomas Tobrman, Zhaoqing Xu, and Ei-ichi Negishi*



INDEX	FREQUENCY	PPM	HEIGHT
1	9986.736	132.496	19.9
2	7310.374	96.922	17.2
3	6216.760	82.423	14.0
4	6179.381	81.928	49.9
5	5839.763	77.425	35.1
6	5807.723	77.000	35.6
7	5775.684	76.575	35.1
8	2301.539	30.514	52.4
9	1881.822	24.956	49.6
10	1652.206	21.905	43.7
11	1451.426	19.243	46.0
12	1024.233	13.579	48.1



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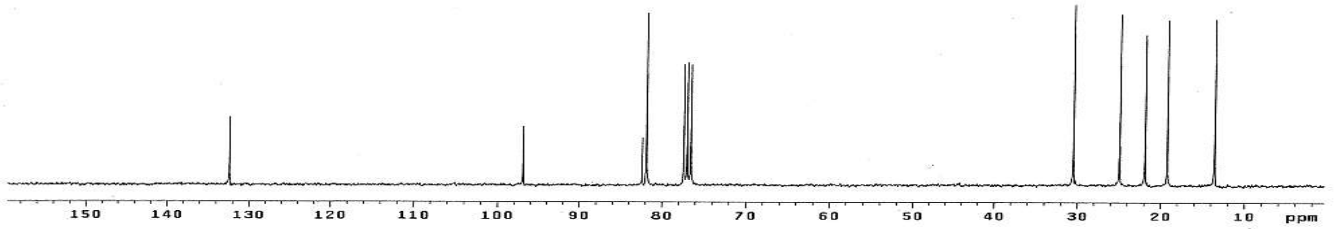

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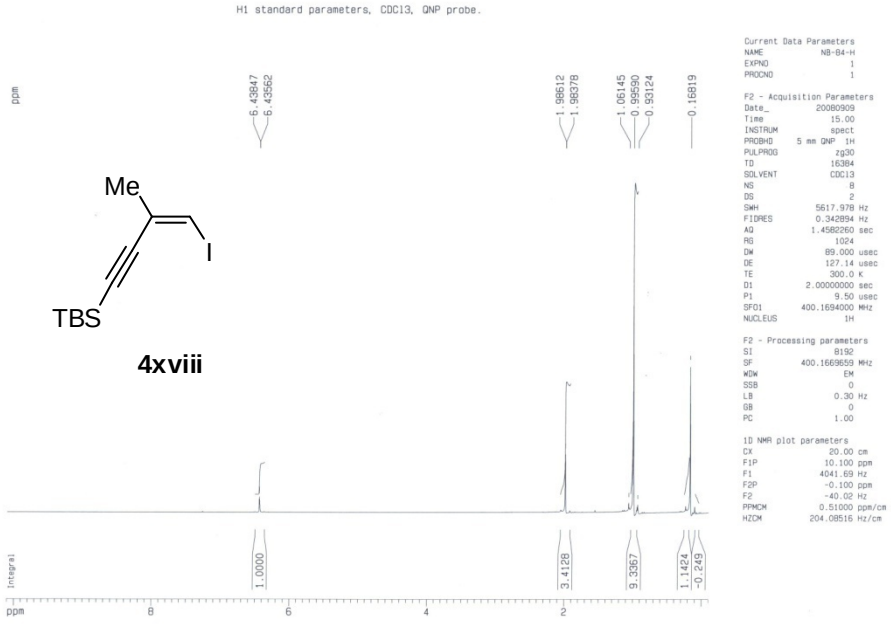

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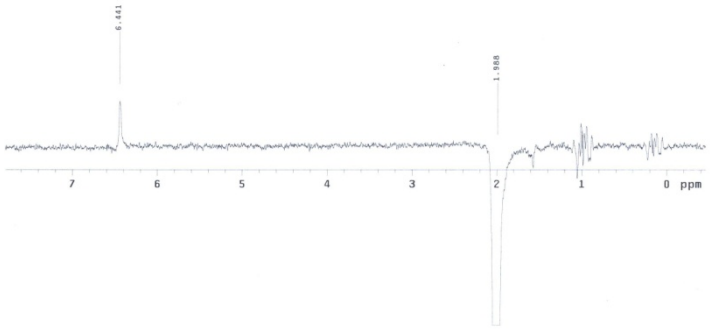

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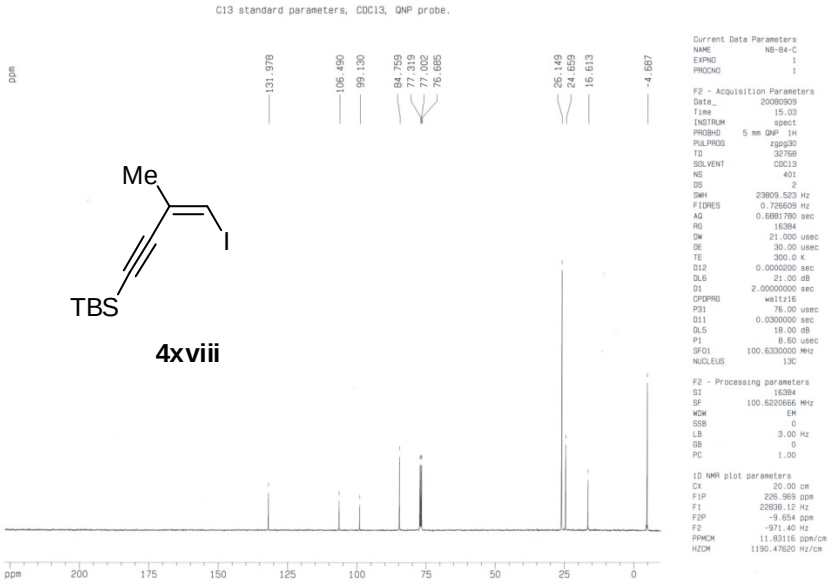

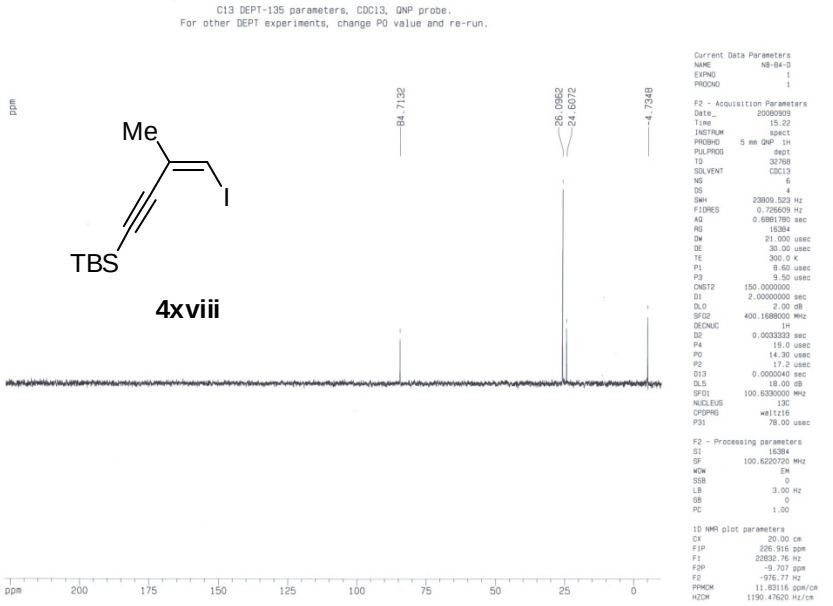

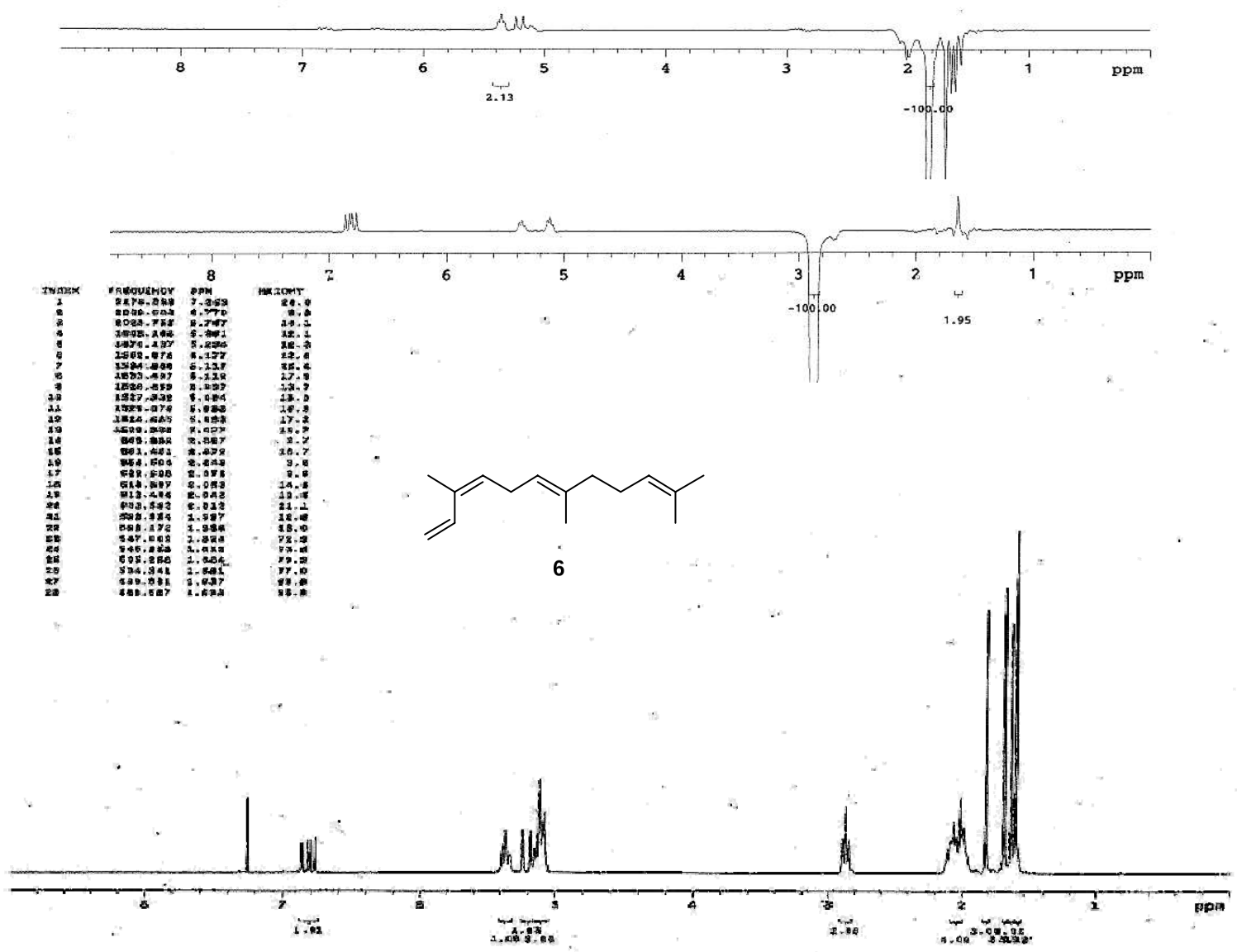
8
7
6
5
4
3
2
1
ppm
2.13
-100.00
1.95
6

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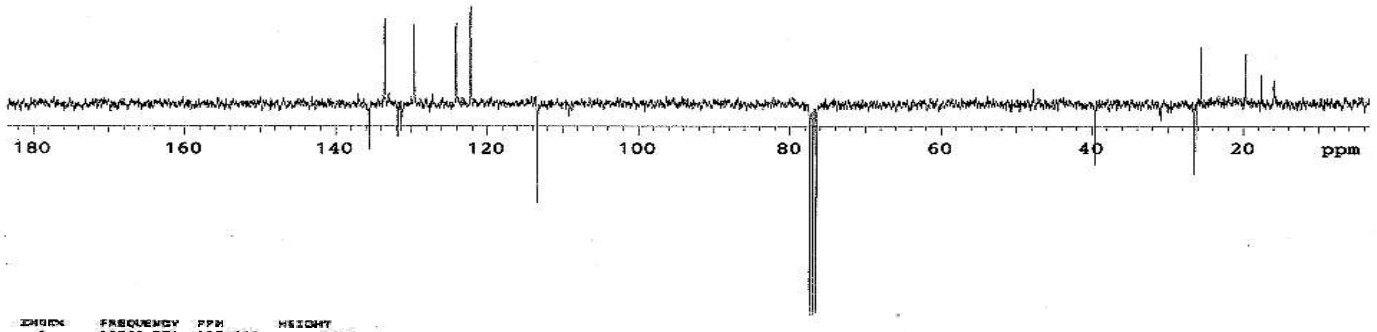
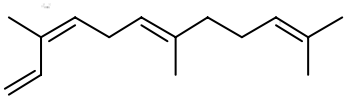


INDEX	FREQUENCY	PPM	HEIGHT
1	19824.971	135.660	30.4
2	19666.715	134.577	58.5
3	19249.350	131.811	17.8
4	19213.949	131.568	17.2
5	17784.667	121.780	26.3
6	17670.510	120.996	54.8
7	17627.491	120.702	41.9
8	17357.779	118.851	41.9
9	11339.752	77.625	99.6
10	11307.723	77.390	61.9
11	11275.684	76.875	77.8
12	11190.287	76.647	44.1
13	11100.958	75.648	50.6
14	10964.464	75.037	41.6
15	10838.415	74.780	43.6
16	10686.873	73.753	40.5
17	10382.880	71.972	31.1
18	10213.256	70.868	25.3



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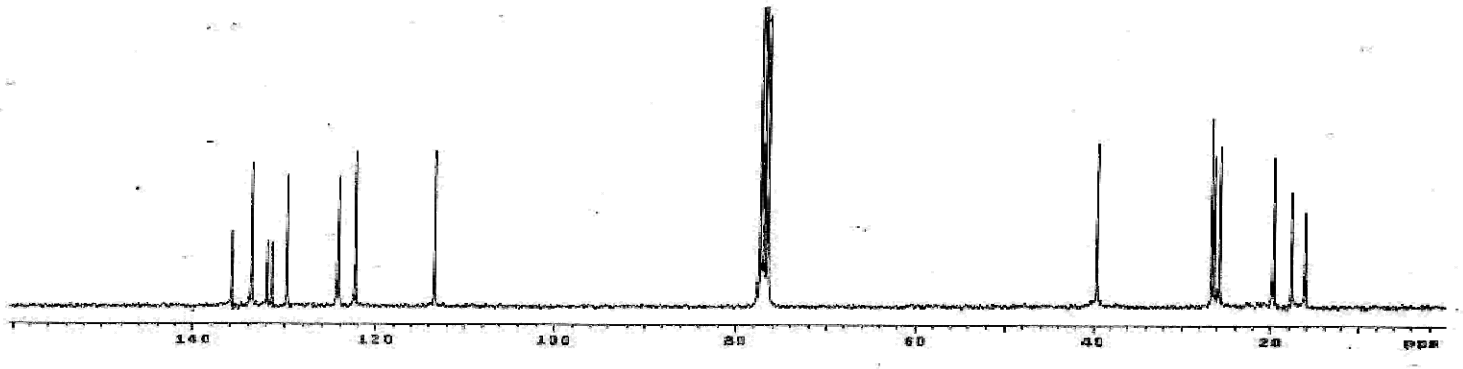
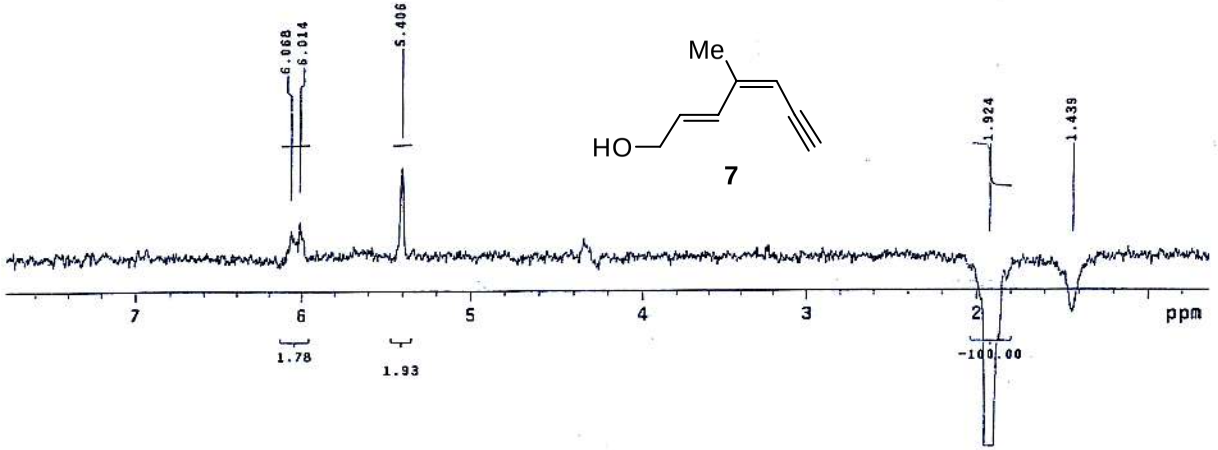
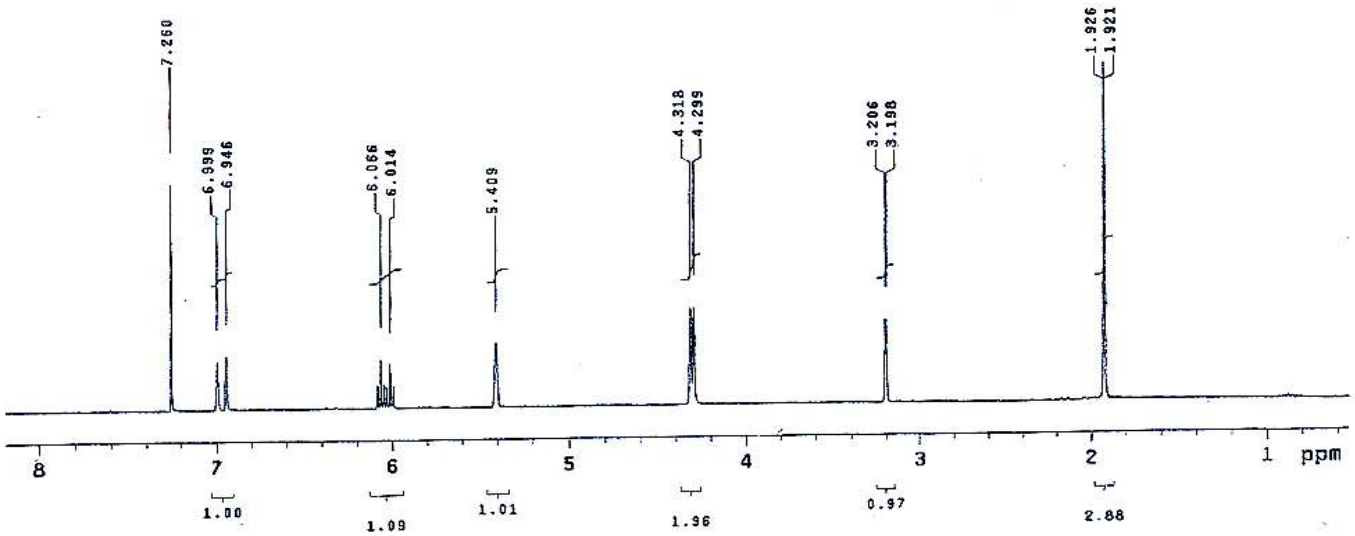
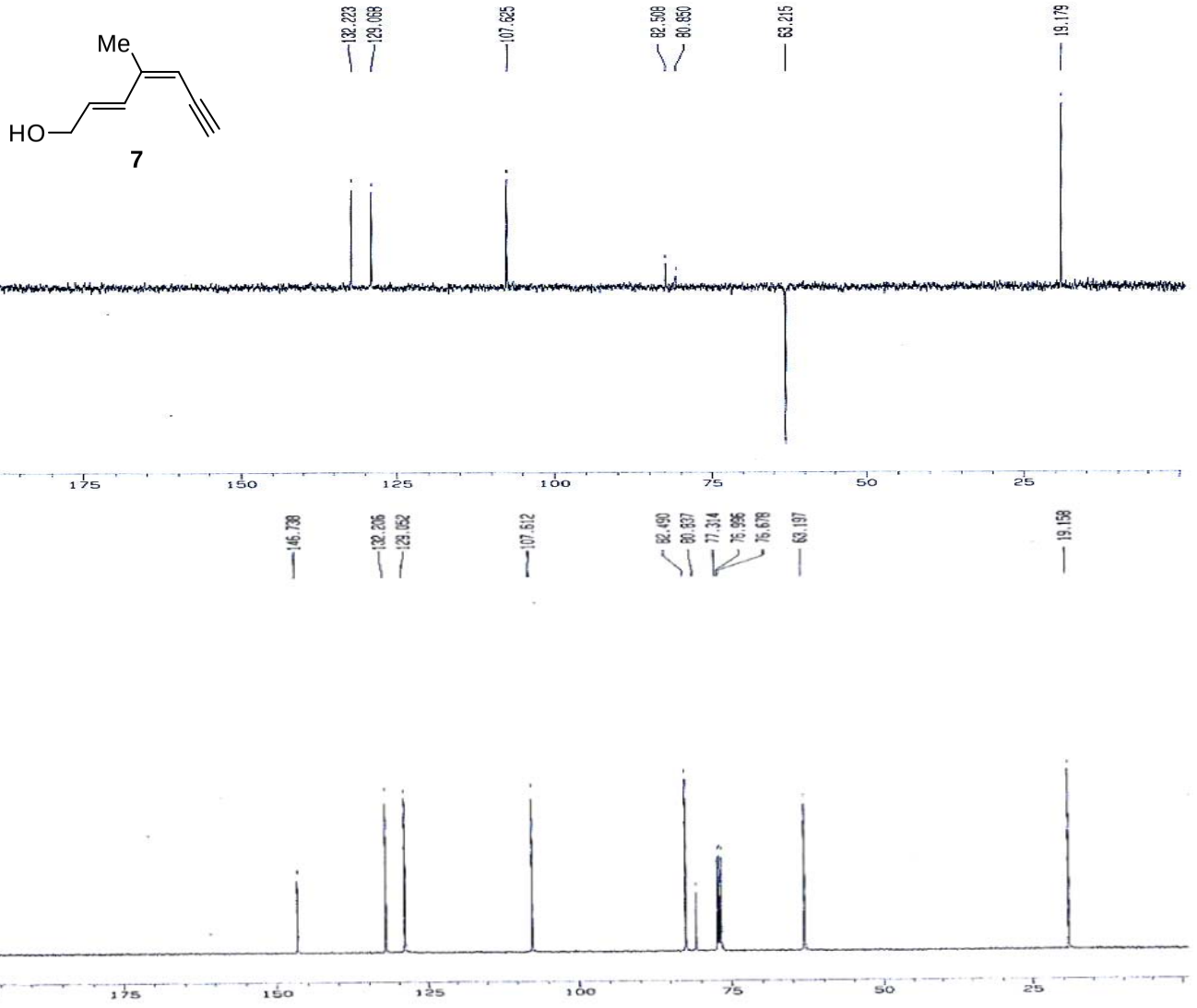



6.068
6.014
5.406
1.924
1.439
Me
HO
7
7
6
5
4
3
2
ppm
1.78
1.93
-100.00


7.260
6.999
6.946
6.066
6.014
5.409
4.318
4.299
3.206
3.198
1.926
1.921
8
7
6
5
4
3
2
1
ppm
1.00
1.09
1.01
1.96
0.97
2.88


Me
HO
7
132.223
129.069
107.625
82.598
80.650
63.215
19.179
ppm
175
150
125
100
75
50
25
146.738
132.206
129.052
107.612
82.490
80.837
77.314
76.996
76.678
63.197
19.158
ppm
175
150
125
100
75
50
25

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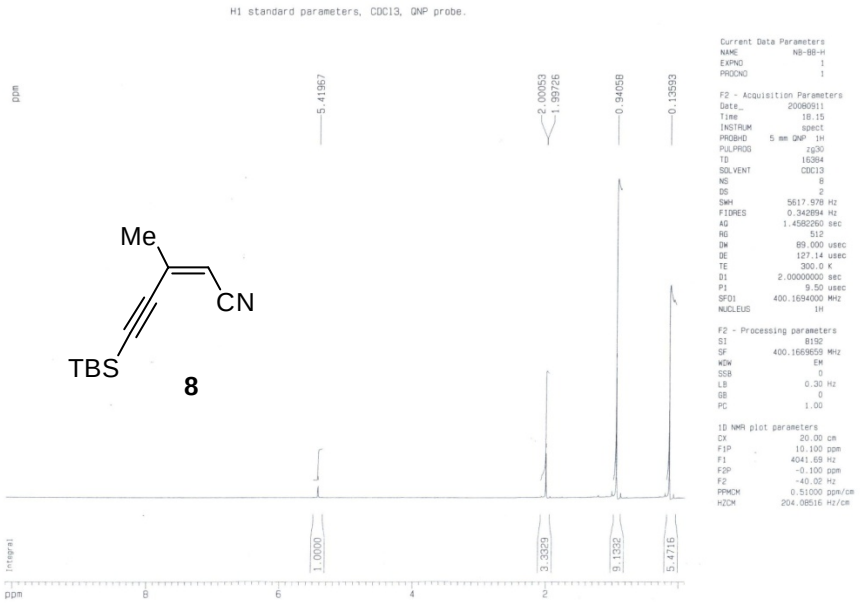

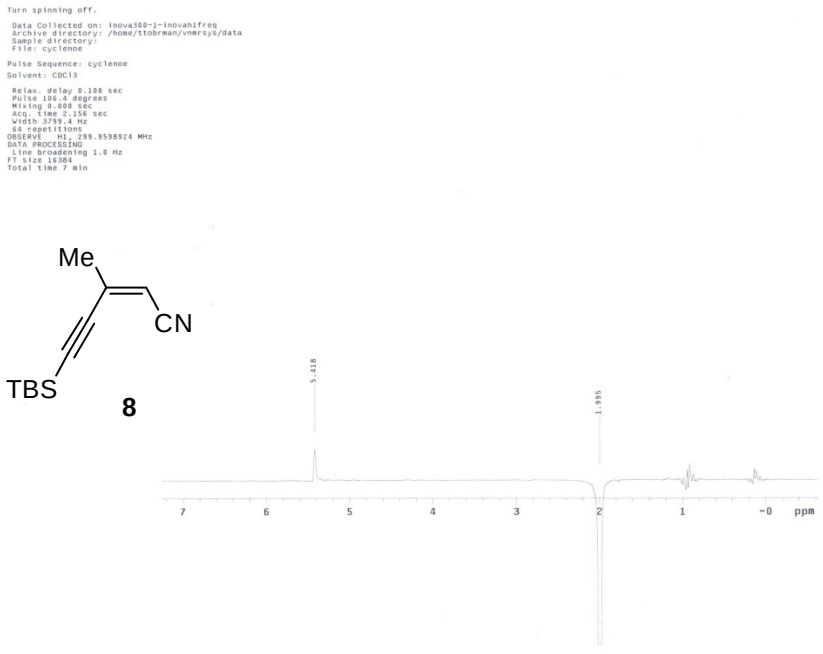

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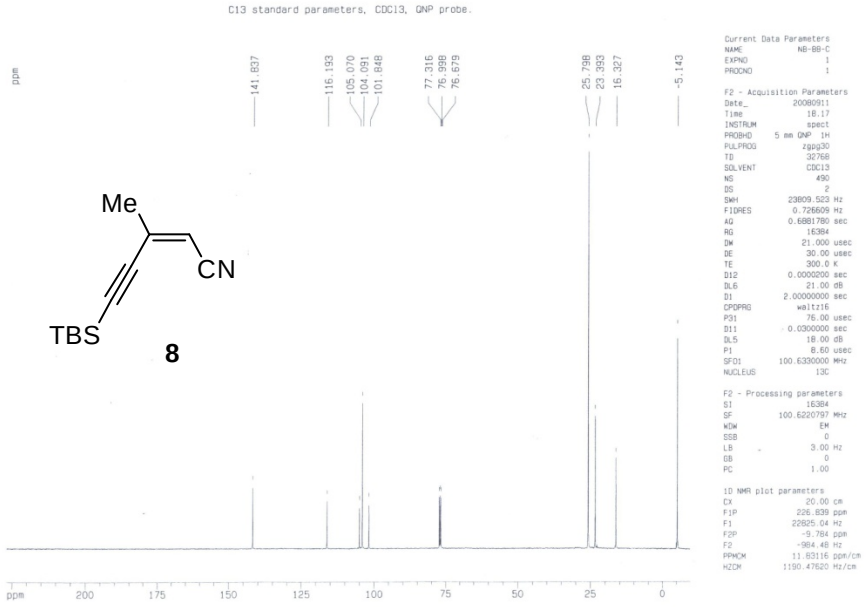

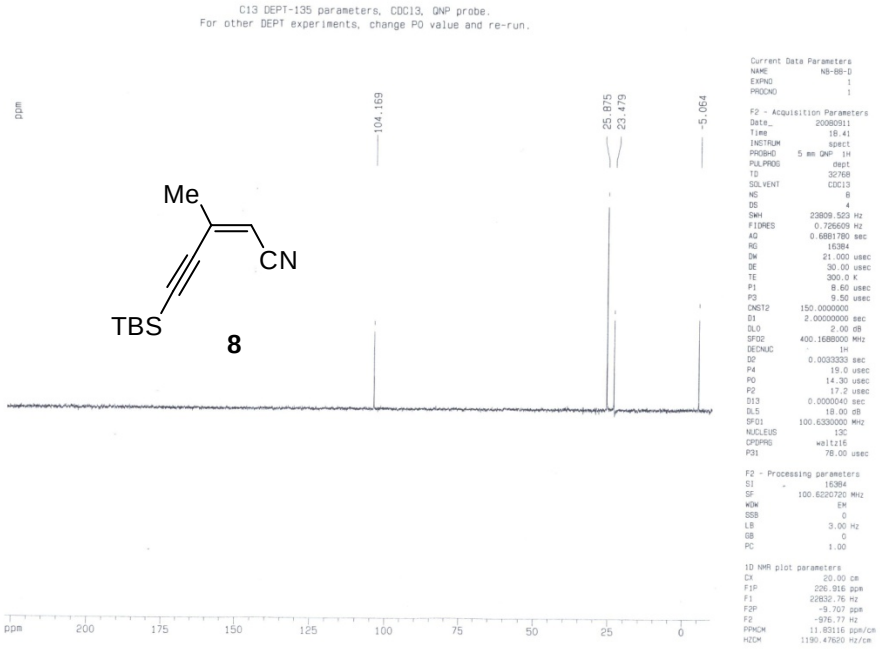

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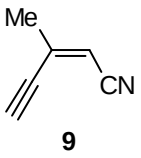

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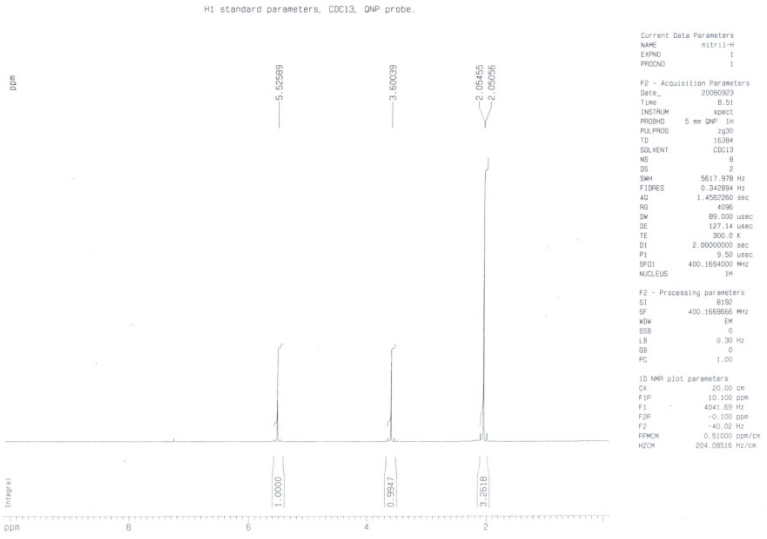

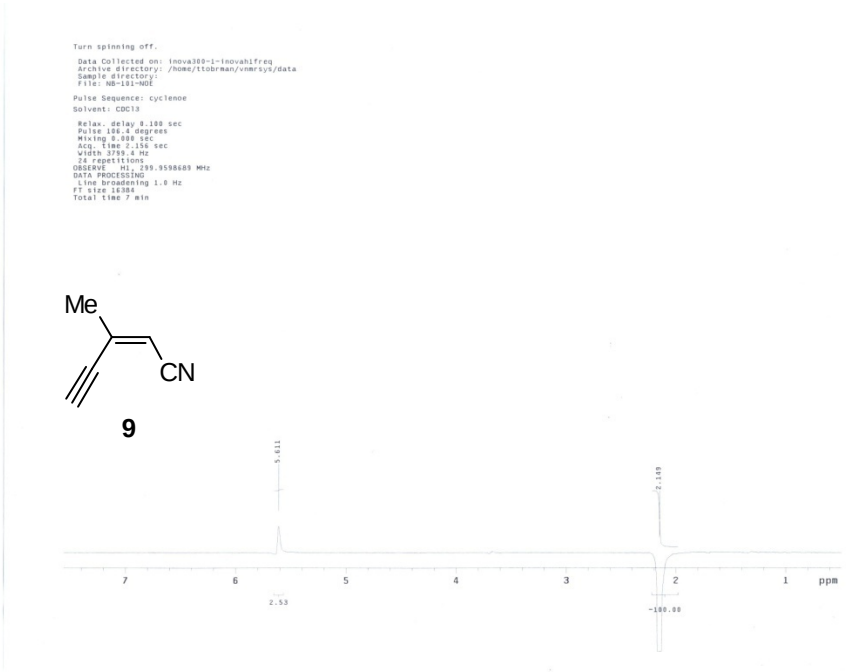

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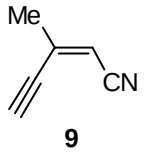

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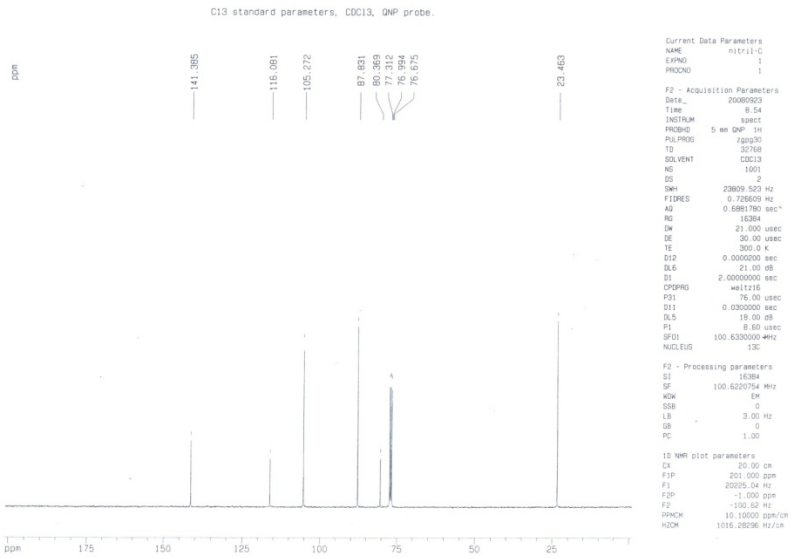

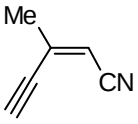

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