Supporting Information

Z-Selective synthesis of vinyl boronates through Fe-catalyzed alkyl radical addition

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General Information

NMR spectra were recorded on a 400 MHz instrument at ambient temperature in $CDCl_3$ or CD_2Cl_2 as solvent. ^1H NMR chemical shifts (δ, ppm) were measured relative to tetramethylsilane (TMS) signal in $CDCl_3$ (0.00 ppm) unless otherwise stated. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR chemical shifts (δ, ppm) are reported relative to $CDCl_3$ signal (77.16 ppm) unless otherwise stated.

Unless otherwise noted, all chemicals were commercially available and were used as received without further purifications. Solvents were purified using a two-column solid-state purification system and transferred to glove box without exposure to air by the aid of a Straus flask. Zn powder (<10μ, 98%+) was purchased from Aldrich. Anhydrous dimethylacetamide (DMA) (99.8% purity) was commercially purchased and stored under nitrogen. Iron(II) triflate ($FeOTf_2$, 98% purity) was purchased from Aldrich or Acros. All the Z/E ratios are determined by ^1H NMR analysis after purification of the compounds.

Experimental protocols

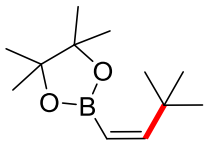
General procedure for the reaction with tertiary and secondary alkyl halides (General procedure A)

Zinc powder (25.5 mg, 0.39 mmol) was put in a 10 mL dry vial equipped with a stirring bar inside the glovebox. DMA (0.25 mL, 0.5 M) and TMSI (0.52 mg 0.0026 mmol) were added to this vial. The mixture was vigorously shaked until the disappearance of the white fume. $FeOTf_2$ (9.2 mg, 20 mol%), ethynyl boronic pinacolester (20 mg, 0.13 mmol) and the alkyl halide (0.39 mmol) were added. The vial was then sealed and its content was allowed to stir overnight (16-20 h) at 50°C. The mixture was quenched with water. *n*-Dodecane (29.5 µL, 0.13 mmol) was added as an internal standard, and the mixture was extracted into ca. 4 mL of ethyl acetate. The organic layer was analyzed by GC-MS. It was then dried over sodium sulfate and the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography (ethyl acetate/hexanes).

General procedure for the reaction with primary alkyl halides (General procedure B)

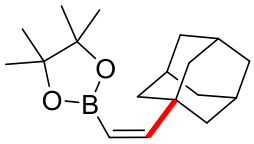
Zinc powder (25.5 mg, 0.39 mmol) was put in a 10 mL dry vial equipped with a stirring bar inside the glovebox. DMA (0.25 mL, 0.5 M) and TMSI (0.52 mg 0.0026 mmol) were added to this vial. The mixture was vigorously shaked until the disappearance of the white fume. The iron complex **4** (5 mol%), ethynyl boronic pinacolester (20 mg, 0.13 mmol) and the alkyl halide (0.39 mmol) were added. The vial was then sealed and its content was allowed to stir overnight (16-20 h) at 50°C. The mixture was quenched with water. *n*-Dodecane (29.5 µL, 0.13 mmol) was added as an internal standard, and the mixture was extracted into ca. 4 mL of ethyl acetate. The organic layer was analyzed by GC-MS. It was then dried over sodium sulfate and the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography (ethyl acetate/hexanes).

Synthesis of (Z)-2-(3,3-dimethylbut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)



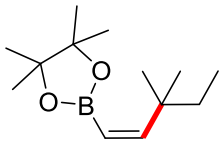
The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (25.9mg, 95%, Z:E: 44:1). ^{1}H NMR and ^{13}C NMR data were consistent with literature.[1]

Synthesis of 2-((Z)-2-((-adamantan-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)



The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (34.1mg, 91%, Z:E: 28:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.07 (d, J = 15.1 Hz, 1H), 5.19 (d, J = 15.1 Hz, 1H), 1.99 (d, J = 4.3 Hz, 3H), 1.72 (dd, J = 11.9, 4.3 Hz, 12H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 159.44, 83.35, 41.96, 36.79, 28.55, 24.83. HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for C18H29BO2+ 288.2255; Found 288.2253.

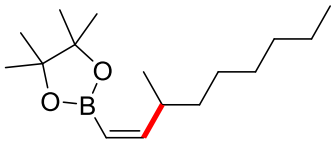
Synthesis of (Z)-2-(3,3-dimethylpent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)



The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (11.7mg, 40%, Z:E: 18:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.19 (d, J = 15.0 Hz, 1H), 5.27 (d, J = 15.1 Hz, 1H), 1.40 (q, J = 7.5 Hz, 2H), 1.30 (s, 12H), 1.07 (s, 3H), 0.84 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101

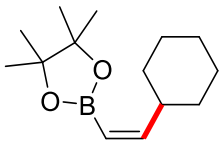
MHz, Chloroform-d) δ 158.57, 83.27, 38.23, 35.60, 26.96, 24.81, 8.97. ^{11}B NMR (128 MHz, Chloroform-d) δ 30.76. HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C13H26BO2+ 225.2020; Found 225.2025.

Synthesis of (Z)-4,4,5,5-tetramethyl-2-(3-methylnon-1-en-1-yl)-1,3,2-dioxaborolane (3d)



The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (26.6mg, 77%, Z:E: 13:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.15 (dd, J = 13.5, 9.8 Hz, 1H), 5.26 (d, J = 13.5 Hz, 1H), 2.90 (td, J = 6.7, 3.4 Hz, 1H), 1.27 (p, J = 4.3 Hz, 25H), 0.96 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 161.15, 82.67, 37.21, 35.96, 31.90, 29.34, 27.27, 24.87, 24.72, 22.69, 21.22, 14.10. HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for C16H31BO2+ 266.2412; Found 266.2412.

Synthesis of (Z)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)

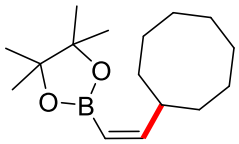


The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (22.7mg, 74%, Z:E: 8:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.27 (dd, J = 13.5, 9.3 Hz, 1H), 5.24 (dd, J = 13.6, 0.9 Hz, 1H), 2.73 (dtd, J = 14.1, 11.3, 10.7, 3.6 Hz, 1H), 1.84 – 1.53 (m, 8H), 1.28 (d, J = 1.3 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.59, 82.74, 40.59, 33.33, 26.02, 25.76, 24.81. HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for C14H25BO2+ 236.1942; Found 236.1941.

Synthesis of **(Z)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)** in a gram scale

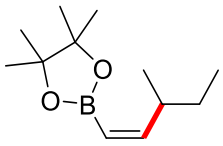
Zinc powder (941.96 mg, 14.4 mmol) was put in a 10 mL dry vial equipped with a stirring bar inside the glovebox. DMA (9.2 mL, 0.5 M) and TMSI (19.19 mg 0.095 mmol) were added to this vial. The mixture was vigorously shaked until the disappearance of the white fume. $FeOTf_2$ (339.8 mg, 20 mol%), ethynyl boronic pinacolester (1 g, 4.8 mmol) and the alkyl halide (3.028 g, 14.4 mmol) were added. The vial was then sealed and its content was allowed to stir overnight (16-20 h) at 50°C. The mixture was quenched with water. The mixture was extracted with ethyl acetate, the combined organic layers were dried over sodium sulfate and the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography (ethyl acetate/hexanes 1:9) Off white oil (793.4mg, 70%, Z:E: 8:1) .

Synthesis of (Z)-2-(2-cyclooctylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)



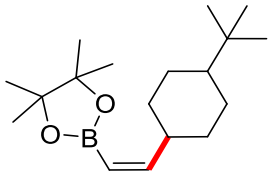
The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (19.2mg, 56%, Z:E: 20:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.34 (d, J = 3.6 Hz, 1H), 5.17 (d, J = 13.3 Hz, 1H), 3.07 (qt, J = 9.6, 3.4 Hz, 1H), 1.72 – 1.47 (m, 14H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 161.92, 82.72, 39.32, 33.18, 26.76, 25.38, 24.88. ^{11}B NMR (128 MHz, Chloroform-d) δ 29.91. HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for C16H29BO2+ 264.2255; Found 264.2255.

Synthesis of (Z)-4,4,5,5-tetramethyl-2-(3-methylpent-1-en-1-yl)-1,3,2-dioxaborolane (3g)



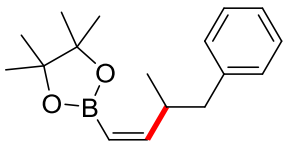
The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (19.7mg, 72%, Z:E: 13:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.13 (dd, J = 13.5, 9.8 Hz, 1H), 5.27 (d, J = 13.5 Hz, 1H), 2.80 (tt, J = 9.0, 6.1 Hz, 1H), 1.33 – 1.20 (m, 12H), 0.95 (d, J = 6.6 Hz, 3H), 0.84 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.71, 82.71, 37.68, 29.96, 24.89, 24.70, 20.92, 11.78. ^{11}B NMR (128 MHz, Chloroform-d) δ 29.96. HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C12H24BO2+ 211.1864; Found 211.1864.

Synthesis of (Z)-2-(2-(4-(tert-butyl)cyclohexyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)



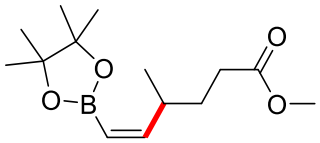
The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (37.2mg, 98%, Z:E: 9:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.83 (dd, J = 13.7, 9.4 Hz, 1H), 5.36 (d, J = 13.6 Hz, 1H), 1.88 – 1.62 (m, 6H), 1.61 – 1.53 (m, 4H), 1.28 (d, J = 2.7 Hz, 12H), 0.86 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 158.28, 82.71, 48.36, 34.59, 32.49, 27.51, 24.80, 22.14, 14.11. ^{11}B NMR (128 MHz, Chloroform-d) δ 29.61. HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C18H34BO2+ 293.2646; Found 293.2648.

Synthesis of (Z)-4,4,5,5-tetramethyl-2-(3-methyl-4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (3i)



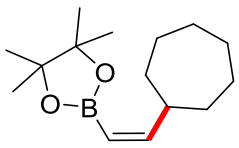
The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (14.1mg, 40%, Z:E: 7:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 – 7.17 (m, 5H), 6.28 (dd, J = 13.5, 9.6 Hz, 1H), 5.29 (d, J = 13.4 Hz, 1H), 3.31 (dq, J = 9.6, 6.9 Hz, 1H), 2.61 (ddd, J = 61.7, 13.3, 7.2 Hz, 2H), 1.27 (d, J = 2.2 Hz, 11H), 0.98 (d, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.16, 140.77, 129.32, 127.96, 125.64, 82.79, 43.82, 37.80, 24.86, 20.19. ^{11}B NMR (128 MHz, Chloroform-d) δ 29.89. HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for C17H25BO2+ 272.1942; Found 272.1951.

Synthesis of methyl (S,Z)-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (3j)



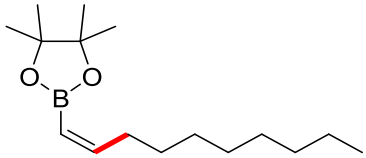
The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 8:2). Off white oil (13.24mg, 38%, Z:E: 11:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.11 (dd, J = 13.5, 10.0 Hz, 1H), 5.33 (d, J = 13.5 Hz, 1H), 4.32 (dd, J = 8.2, 4.6 Hz, 2H), 3.66 (s, 3H), 3.02 – 2.85 (m, 1H), 2.30 (t, J = 7.9 Hz, 2H), 1.82 – 1.64 (m, 2H), 1.27 (s, 12H), 1.01 (d, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 174.41, 159.30, 130.90, 128.82, 82.87, 51.38, 35.87, 32.23, 31.93, 24.87, 24.75, 21.16. ^{11}B NMR (128 MHz, Chloroform-d) δ 29.93. HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C14H26BO4+ 269.1919; Found 269.1917.

Synthesis of (Z)-2-(2-cycloheptylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)



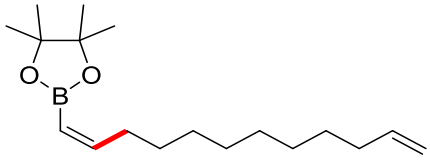
The synthesis was done following the general procedure A. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (23.0mg, 70.8%, Z:E: 13:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.36 (dd, J = 13.4, 9.7 Hz, 1H), 5.18 (d, J = 13.4 Hz, 1H), 2.92 (tq, J = 9.8, 5.0, 3.8 Hz, 1H), 1.77 – 1.40 (m, 7H), 1.28 (s, 17H). ^{13}C NMR (101 MHz, Chloroform-d) δ 161.28, 82.72, 41.93, 35.12, 28.60, 26.58, 24.83. ^{11}B NMR (128 MHz, Chloroform-d) δ 29.67. HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C15H28BO2+ 251.2177; Found 251.2178.

Synthesis of (Z)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)



The synthesis was done following the general procedure B. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (26.6mg, 77%, Z:E: 10:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.46 (dt, J = 15.0, 7.8 Hz, 1H), 5.35 (d, J = 13.5 Hz, 1H), 2.41 (q, J = 7.3 Hz, 2H), 1.28 (d, J = 8.7 Hz, 24H), 0.90 (d, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.28, 82.76, 32.20, 31.93, 29.71, 29.47, 29.41, 29.29, 29.08, 24.84, 24.02, 22.70, 14.12. ^{11}B NMR (128 MHz, Chloroform-d) δ 34.43, 29.93. HRMS m/z: [M + H]+ Calcd for C16H32BO2+ 267.2490; Found 267.2485.

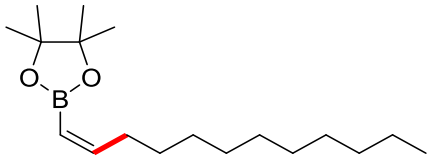
Synthesis of (Z)-2-(dodeca-1,11-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)



The synthesis was done following the general procedure B. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (23.2mg, 61%, Z:E: 10:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.44 (dt, J = 14.2, 7.3 Hz, 1H), 5.82 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.33 (dt, J = 13.4, 1.4 Hz, 1H), 5.04 – 4.89 (m, 2H), 2.04 (qd, J = 7.6, 3.8

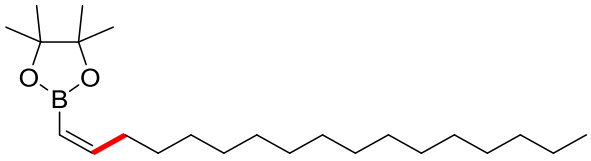
Hz, 2H), 1.45 – 1.20 (m, 27H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.21, 139.22, 114.05, 82.79, 33.83, 32.39, 29.40, 29.34, 29.13, 28.95, 24.81, 23.98. ^{11}B NMR (128 MHz, Chloroform-d) δ 34.52, 29.97. HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for $C_{18}H_{33}BO_2$+ 292.2568; Found 292.2573.

Synthesis of (Z)-2-(dodec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)



The synthesis was done following the general procedure B. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (13.4mg, 35%, Z:E: 13:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.45 (dt, J = 14.3, 7.5 Hz, 1H), 5.34 (dt, J = 13.5, 1.4 Hz, 1H), 2.41 (qd, J = 7.3, 1.4 Hz, 2H), 1.28 (d, J = 3.8 Hz, 28H), 0.90 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.28, 82.76, 32.20, 31.93, 29.66, 29.63, 29.48, 29.45, 29.37, 29.07, 24.84, 24.81, 22.69, 14.12. ^{11}B NMR (128 MHz, Chloroform-d) δ 30.02. HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C18H36BO2+ 295.2803; Found 295.2798.

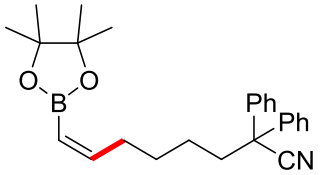
Synthesis of (Z)-2-(heptadec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)



The synthesis was done following the general procedure B. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (14.7mg, 31%, Z:E: 9:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.45 (dt, J = 14.2, 7.5 Hz, 1H), 5.35 (dd, J = 13.5, 1.5 Hz, 1H), 2.49 – 2.35 (m, 2H), 1.29 (q, J = 6.2, 4.9 Hz, 38H), 0.90 (t, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.29, 82.76, 43.93, 32.45, 32.20, 31.94, 29.71, 29.67, 29.47, 29.43, 29.37, 29.18, 29.08, 24.84, 24.82, 22.70, 14.12. ^{11}B NMR (128 MHz, Chloroform-d) δ 34.55,

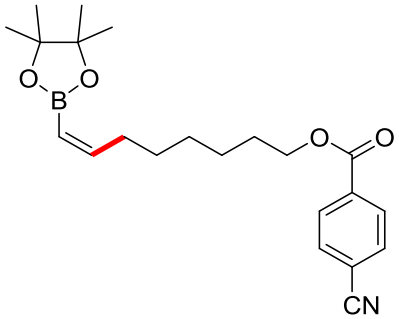
30.04. HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C24H48BO2+ 379.3742; Found 379.3735.

Synthesis of (Z)-2,2-diphenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-enenitrile (3p)



The synthesis was done following the general procedure B. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 8:2). Off white oil (31.8mg, 61%, Z:E: 10:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.24 (m, 10H), 6.39 (dt, J = 14.2, 7.5 Hz, 1H), 5.35 (d, J = 13.5 Hz, 1H), 2.48 – 2.33 (m, 7H), 1.68 – 1.43 (m, 9H), 1.25 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 154.26, 140.38, 128.94, 128.80, 128.56, 128.35, 127.96, 127.76, 126.88, 126.83, 82.84, 51.80, 39.46, 31.63, 29.27, 24.83. ^{11}B NMR (128 MHz, Chloroform-d) δ 29.95. HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C26H33BNO2+ 402.2599; Found 402.2599.

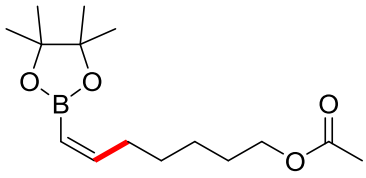
Synthesis of (Z)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-yl 4-cyanobenzoate (3q)



The synthesis was done following the general procedure B. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 8:2). Off white oil (10.7mg, 21.5%, Z:E: 8:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 – 8.10 (m, 2H), 7.77 (dd, J = 8.4, 1.8 Hz, 2H), 6.44 (dt, J = 14.2, 7.4 Hz, 1H), 5.36 (dt, J = 13.5, 1.3 Hz, 1H), 4.42 – 4.33 (m, 2H), 2.49 – 2.38 (m, 2H), 1.80 (p, J = 7.2, 6.8 Hz, 4H), 1.54 – 1.37 (m, 10H), 1.28 (s, 14H). ^{13}C NMR (101

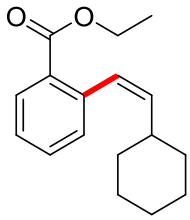
MHz, Chloroform-d) δ 154.79, 134.32, 132.20, 130.06, 118.02, 116.29, 82.81, 65.98, 32.03, 29.26, 28.63, 28.55, 25.79, 24.85. ^{11}B NMR (128 MHz, Chloroform-d) δ 29.99. HRMS (APPI/LTQ-Orbitrap) m/z: [M + K]+ Calcd for $C_{22}H_{30}BNO_4K$+ 422.1899; Found 422.1833.

Synthesis of (Z)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-en-1-yl acetate (3r)



The synthesis was done following the general procedure B. The crude residue was purified via column chromatography over silica gel (hexanes:ethyl acetate 9:1). Off white oil (9.28mg, 25.3%, Z:E: 11:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.43 (dt, J = 14.2, 7.4 Hz, 1H), 5.36 (dt, J = 13.5, 1.3 Hz, 1H), 4.07 (t, J = 6.8 Hz, 2H), 2.42 (qd, J = 7.2, 1.3 Hz, 2H), 2.06 (d, J = 1.9 Hz, 3H), 1.71 – 1.57 (m, 4H), 1.27 (d, J = 9.1 Hz, 15H). ^{13}C NMR (101 MHz, Chloroform-d) δ 171.20, 154.65, 82.81, 64.59, 31.90, 29.40, 29.21, 28.94, 28.60, 28.34, 25.89, 25.24, 24.83, 21.01. ^{11}B NMR (128 MHz, Chloroform-d) δ 33.68, 29.93. HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for C15H27BO4+ 282.1997; Found 282.2792.

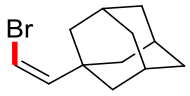
Synthesis of ethyl (Z)-2-(2-cyclohexylvinyl)benzoate (5)



To a solution of ethyl 2-bromobenzoate (64.6 mg, 0.282 mmol) and potassium carbonate (116.92 mg, 0.84 6mmol) in degassed dioxane/water (1.6 mL, 1/1 ratio) was added molecule **3a** (100 mg, 0.423 mmol) and tetrakis(triphenylphosphine)palladium(0) (16.34 mg, 0.0142 mmol) at room temperature. Then the mixture was heated to 95°C for 1 hour. After quenching with water, the mixture was extracted with ethyl acetate and concentrated, obtaining the crude product, which was

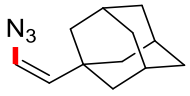
purified by chromatography (hexanes/ethyl acetate 4:1) to afford a pure compound **5** as a off yellow liquid (56.3 mg, yield: 60%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 (dd, J = 7.8, 1.4 Hz, 1H), 7.47 (dd, J = 7.6, 1.4 Hz, 1H), 7.36 – 7.26 (m, 2H), 6.75 (d, J = 11.6 Hz, 1H), 5.54 (t, J = 10.9 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.36 – 2.17 (m, 1H), 1.77 – 1.60 (m, 7H), 1.39 (t, J = 7.1 Hz, 3H), 1.33 – 1.27 (m, 3H), 1.18 (d, J = 7.4 Hz, 5H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.39, 139.37, 137.77, 131.41, 130.54, 130.15, 126.81, 126.50, 60.80, 36.87, 33.24, 25.99, 25.62, 14.29. HRMS (ESI/QTOF) m/z: [M + Na]+ Calcd for C17H22NaO2+ 281.1512; Found 281.1515.

Synthesis of 1-((Z)-2-bromovinyl)adamantine (6)



Molecule **3b** (100 mg, 0.35 mmol) was dissolved in 4 mL of diethyl ether and cooled to -20°C. A solution of Br_2 (55.9 mg, 0.35 mmol) in DCM (0.35 mL) was added dropwise over 15 minutes, then the mixture was stirred for additional 15 minutes. A solution of NaOMe (44 mg, 0.77 mmol) in MeOH (0.26 mL) was added and after 30 minutes the reaction was quenched with benzoic acid (20 equiv.) in DCM (3.4 mL). Purification by flash chromatography (hexanes/ethyl acetate from 0% to 20% of EA). Colorless liquid (71.7mg, yield 85%). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.10 (d, J = 13.7 Hz, 1H), 5.93 (d, J = 13.7 Hz, 1H), 2.02 (t, J = 3.1 Hz, 3H), 1.79 – 1.60 (m, 10H). 13C NMR (101 MHz, Chloroform-d) δ 148.73, 102.44, 41.61, 37.71, 36.62, 28.20. HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for C12H17+ 161.1330; Found 161.1322.

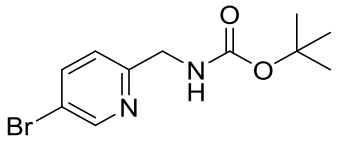
Synthesis of 1-((Z)-2-azidovinyl)adamantine (7)



Molecule **3b** (100 mg, 0.35 mmol), NaN_3 (34 mg, 0.53 mmol) and $CuSO_4$ (33.5 mg, 0.21 mmol) were dissolved in 3 mL of MeOH and stirred at room temperature for one night. The mixture is then concentrate under reduced pressure, dissolved in DCM and washed with water and brine. The residue is dried with anhydrous sodium sulfate, concentrated and purified by flash chromatography

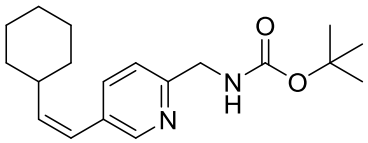
to obtain a white solid (61 mg, 85.8%). ^{1}H NMR (400 MHz, Chloroform-d) δ 5.97 (d, J = 8.5 Hz, 1H), 4.56 (d, J = 8.5 Hz, 1H), 2.05 – 1.90 (m, 3H), 1.79 – 1.57 (m, 10H), 1.45 – 1.17 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 130.22, 123.05, 42.14, 36.77, 34.88, 28.60. HRMS (APPI/LTQ-Orbitrap) m/z: [M]+ Calcd for C12H17N+ 175.1356; Found 175.1355.

Synthesis of tert-butyl ((5-bromopyridin-2-yl)methyl)carbamate (13)



5-bromopicolinonitrile (5 g, 27 mmol), $NiCl_2{*}6H_2O$ (10 mol%), $BocO_2$ (2 equiv.) and methanol (100 mL) were put in a flask which was then cooled to 0°C. Sodium boron hydride (7 equiv.) was then added portion-wise over 2h. After one additional hour of stirring at 15°C, the mixture was poured into ice-water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography giving the desired product as a white solid (4.46g, yield:57.2%). ^{1}H NMR (400 MHz, Methanol-d4) δ 8.57 (d, J = 2.4 Hz, 1H), 7.97 (dd, J = 8.4, 2.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 4.32 (s, 2H), 3.33 (dt, J = 3.3, 1.7 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, Methanol-d4) δ 157.82, 157.07, 149.40, 139.66, 122.47, 118.55, 79.15, 44.72, 27.34. Melting point: 92-94 °C.

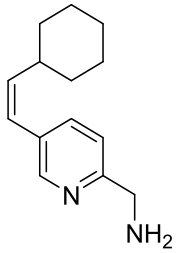
Synthesis of tert-butyl (Z)-((5-(2-cyclohexylvinyl)pyridin-2-yl)methyl)carbamate (14)



To a solution of **13** (30.44 mg, 0.106 mmol) and potassium carbonate (49.2 mg, 0.356 mmol) in degassed 1,2-dimethoxyethane/ethanol/water (0.8 mL, 1/0.5/1 ratio) was added molecule **3a** (50 mg, 0.212 mmol) and tetrakis(triphenylphosphine)palladium(0) (34.78 mg, 0.142 mmol) at room

temperature. Then the mixture was heated to 95°C for 1 hour. After quenching with water, the mixture was extracted with ethyl acetate and concentrated, obtaining the crude product, which was purified by chromatography (hexanes/ethyl acetate 4:1) to afford a pure compound **14** as a colorless liquid (48.1 mg, yield: 72%). ^{1}H NMR (CDCl3, 400 MHz): δ 8.45 (1H, s), 7.53 (1H, d), 7.24 (1H, d), 6.24 (1H, d), 5.62 (1H, t), 4.44 (2H, d), 2.48 (1H, m), 1.69 (5H, m), 1.46 (9H, s), 1.21 (6H, m), 5.53-5.61 (1H,bs). ^{13}C NMR (101 MHz, Chloroform-d) δ 156.00, 155.21, 148.88, 141.15, 136.42, 132.16, 122.94, 121.13, 79.48, 45.58, 37.09, 33.10, 29.70, 28.42, 25.91, 25.56. HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for C19H29N2O2+ 317.2224; Found 317.2222.

Synthesis of (Z)-(5-(2-cyclohexylvinyl)pyridin-2-yl)methanamine (9)



A solution of **14** (150 mg, 0.5 mmol) in DCM (5 mL) and trifluoroacetic acid (4 mL) was stirred for 45 minutes at room temperature, after which the solvent was evaporated. Ethyl ether (10 mL) was added, and the solvent was evaporated again. The residue was dissolved in DCM (20 mL), washed with saturated aqueous of sodium bicarbonate, dried with anhydrous sodium sulfate, and the solvent was evaporated to give product **9** in a quantitative yield as a green liquid (100 mg, quantitative yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.47 (s, 1H), 7.53 (dd, J = 8.0, 2.1 Hz, 1H), 7.31 – 7.22 (m, 1H), 6.25 (d, J = 11.7 Hz, 1H), 5.61 (dd, J = 11.7, 10.2 Hz, 1H), 4.00 (s, 2H), 2.49 (tdd, J = 10.7, 7.3, 3.2 Hz, 1H), 2.02 (d, J = 21.9 Hz, 2H), 1.78 – 1.63 (m, 5H), 1.36 – 1.11 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-d) δ 159.39, 149.00, 140.97, 136.39, 131.86, 123.05, 120.80, 37.09, 33.11, 29.70, 25.91, 25.57. HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C14H21N2+ 217.1699; Found 217.1701.

Analysis of the cis/trans ratio of compound 3h

Compound **3h** was obtained as a mixture of different isomers. (Figure S1).

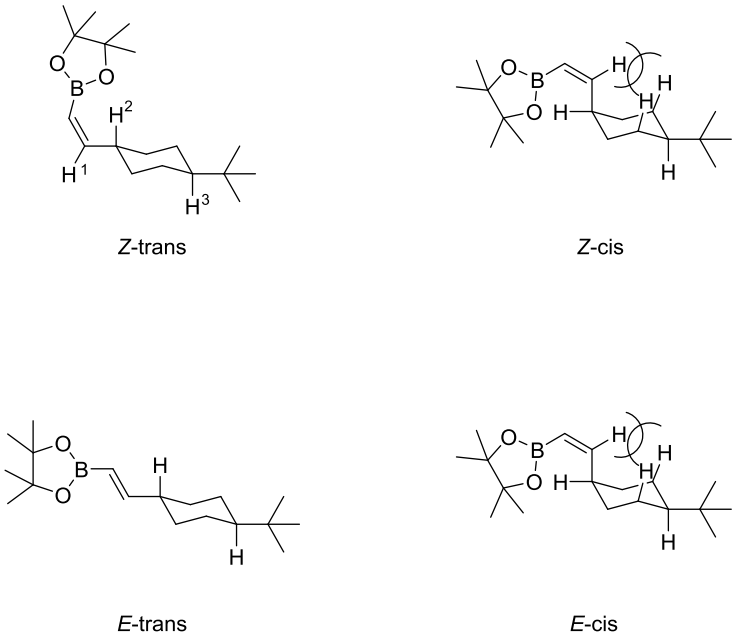


Figure S1. Four different possible isomers of compound **3h**

From ^{1}H NMR analysis it was possible to know the *E*/*Z* ratio of the double bond. A COSY-NMR analysis was used to determine the ratio of cis- and trans-isomer of Z-**3h** (Figure S2)

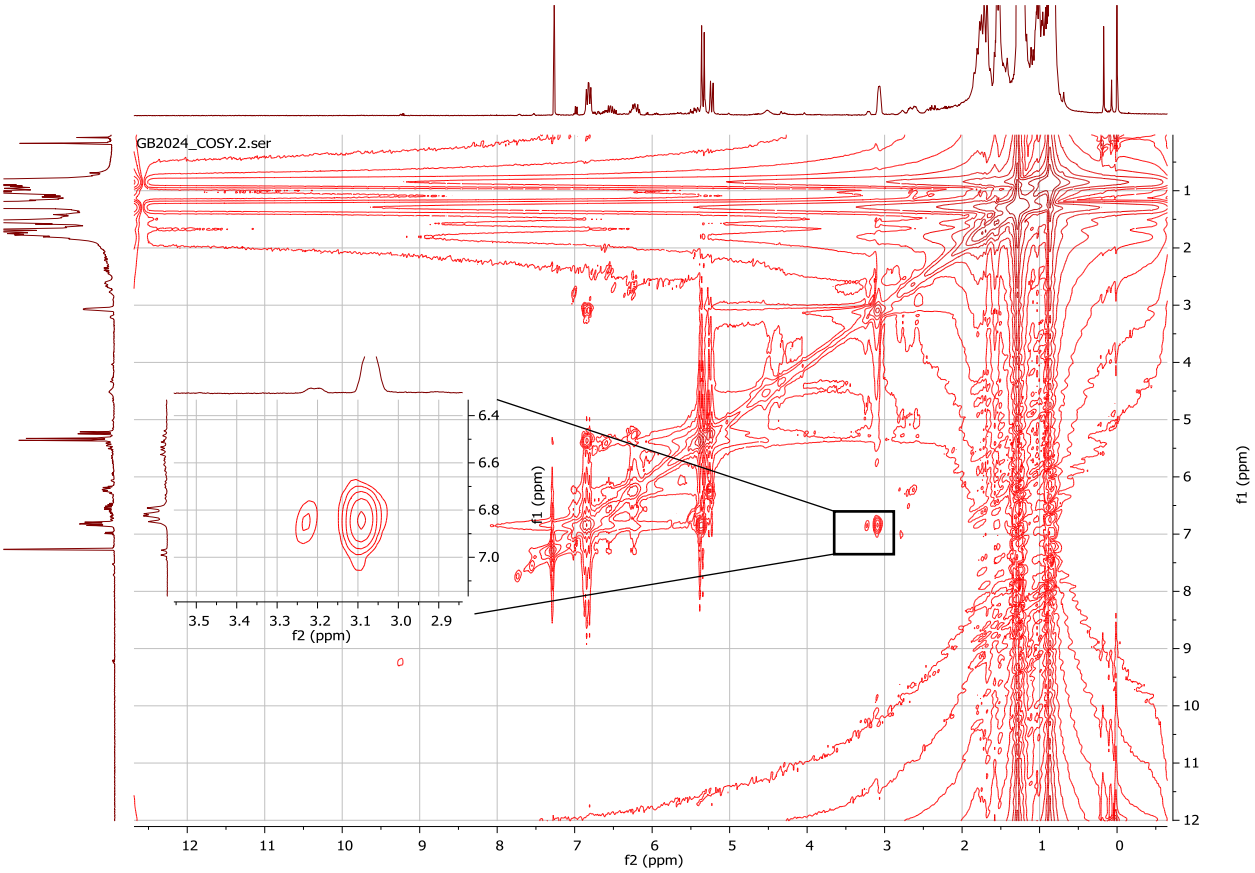


Figure S2. COSY spectrum of molecule **3h**

At 3.07 ppm (Figure S2) is the signal of the allylic hydrogen (H2, Figure S1) that has a correlation with the signal of the sp^2 hydrogen of the double bond (H1, Figure S1). Another peak at 3.20 ppm also correlates with the same sp^2 hydrogen. The ratio of the two allylic hydogens is 14:1. Thus, the reaction has a diasetereoselectivity of 14:1.

According to a previous report, the cis or trans isomer might be assigned by comparing the difference of the ^{1}H NMR shift of H2 and H3 (Figure S1).[2] Unfortunately, in the present case, the H3 signal overlaps with the other signals of the cyclohexyl moiety and cannot be identified. Nevertheless, previous reports of substituted cyclohexanes show that a hydrogen on a cyclohexyl ring is more shielded if it is in axial position than in an equatorial position.[3,4] Moreover, according to a previous report,[2] reaction of 4-substituted cyclohexyl radical should give rise to the more stable trans isomer. Therefore we assign the major product as the trans-isomer.

References

(1) Ohmura, T.; Yamamoto, Y.; Miyaura, N. Rhodium- or Iridium-Catalyzed Trans-Hydroboration of Terminal Alkynes, Giving (Z)-1-Alkenylboron Compounds. *J. Am. Chem. Soc.* **2000**, *122* (20), 4990–4991. https://doi.org/10.1021/ja0002823.

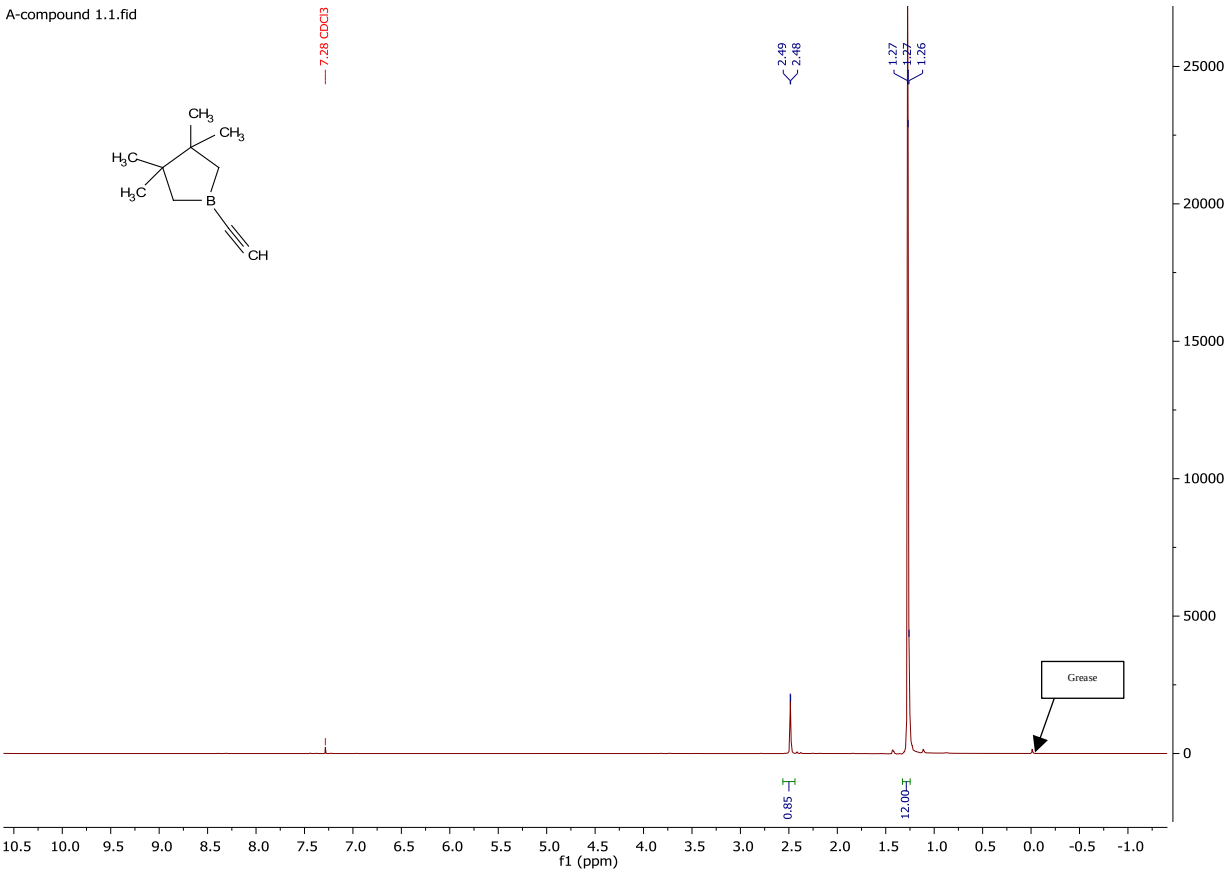
(2) Perez Garcia, P. M.; Di Franco, T.; Orsino, A.; Ren, P.; Hu, X. Nickel-Catalyzed Diastereoselective Alkyl–Alkyl Kumada Coupling Reactions. *Org. Lett.* **2012**, *14* (16), 4286–4289. https://doi.org/10.1021/ol302067b.

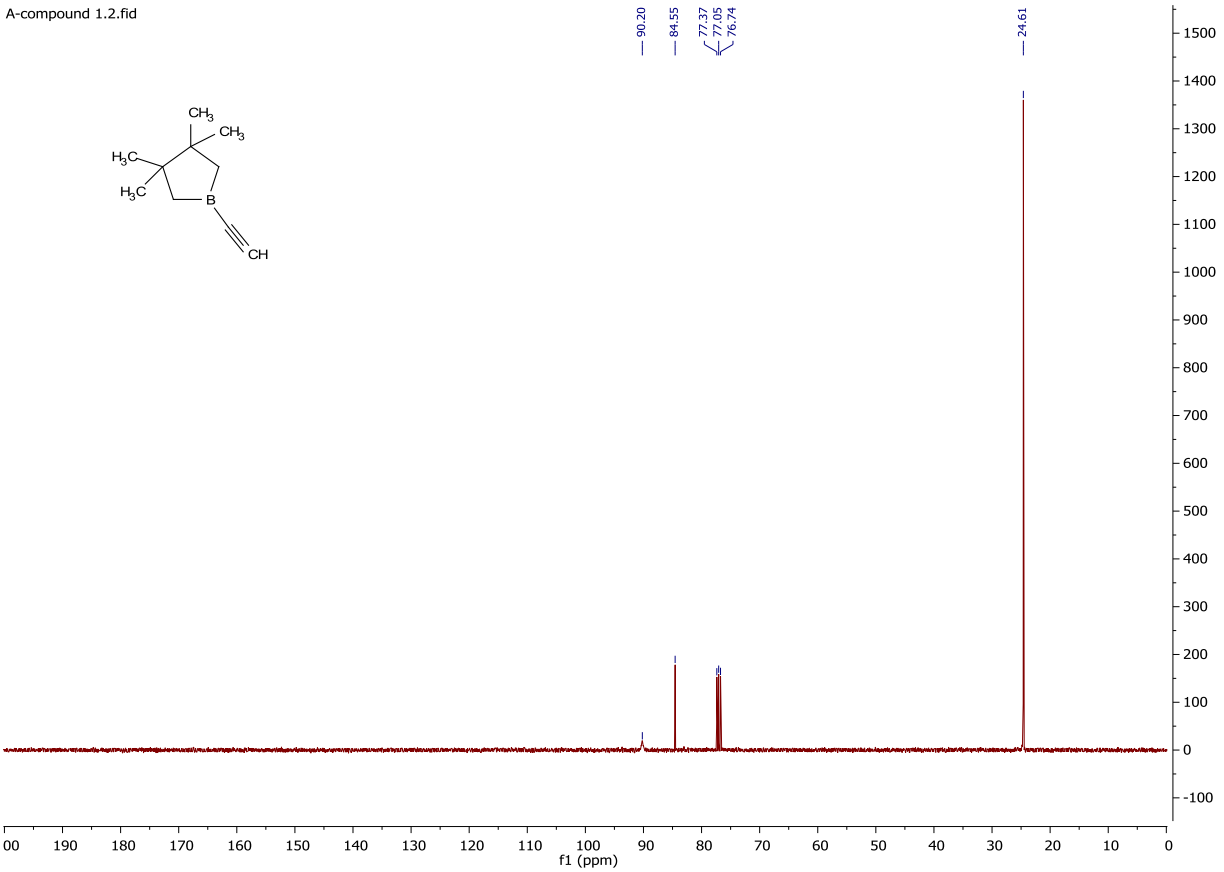
(3) Abraham, R. J.; Byrne, J. J.; Griffiths, L.; Perez, M. 1H Chemical Shifts in NMR: Part 23, the Effect of Dimethyl Sulphoxide versus Chloroform Solvent on 1H Chemical Shifts. *Magn. Reson. Chem.* **2006**, *44* (5), 491–509. https://doi.org/10.1002/mrc.1747.

(4) Hanessian, S.; Dhanoa, D. S.; Beaulieu, P. L. Synthesis of Carbocycles from ω-Substituted α,β-Unsaturated Esters via Radical-Induced Cyclizations. *Can. J. Chem.* **1987**, *65* (8), 1859–1866. https://doi.org/10.1139/v87-312.

NMR spectra

Molecule 1

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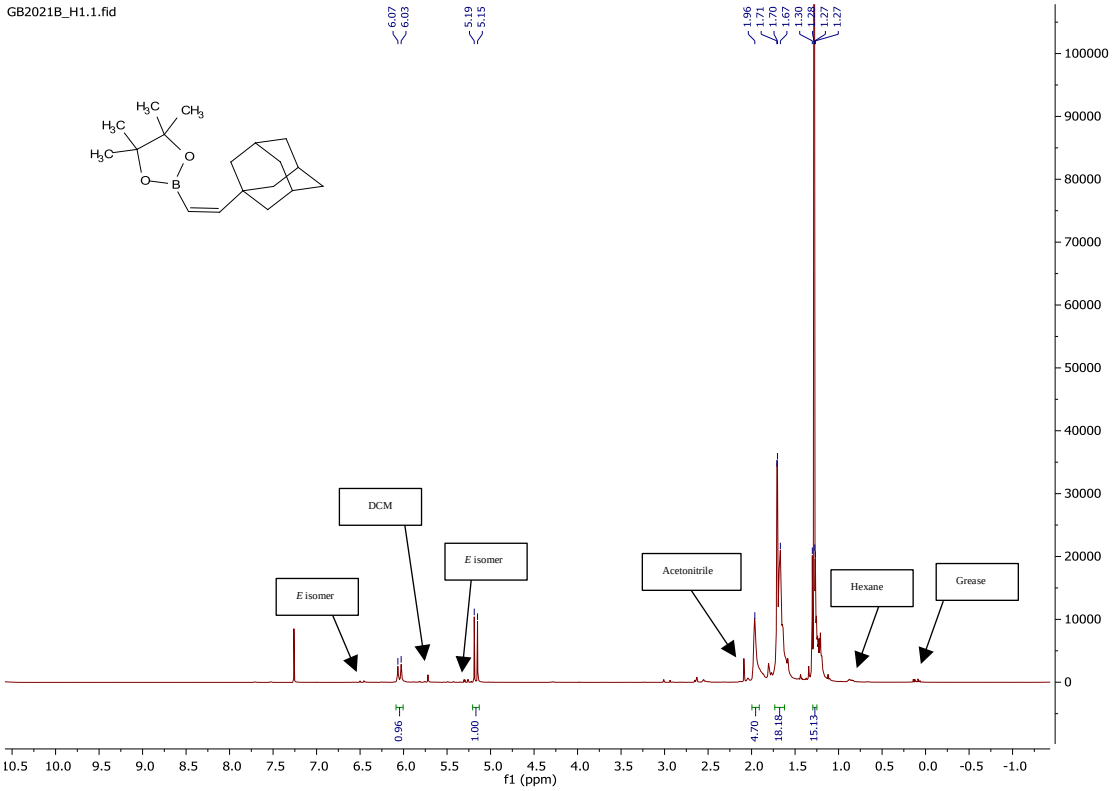
f1 (ppm)

Molecule 3b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1.27
1.27
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E isomer
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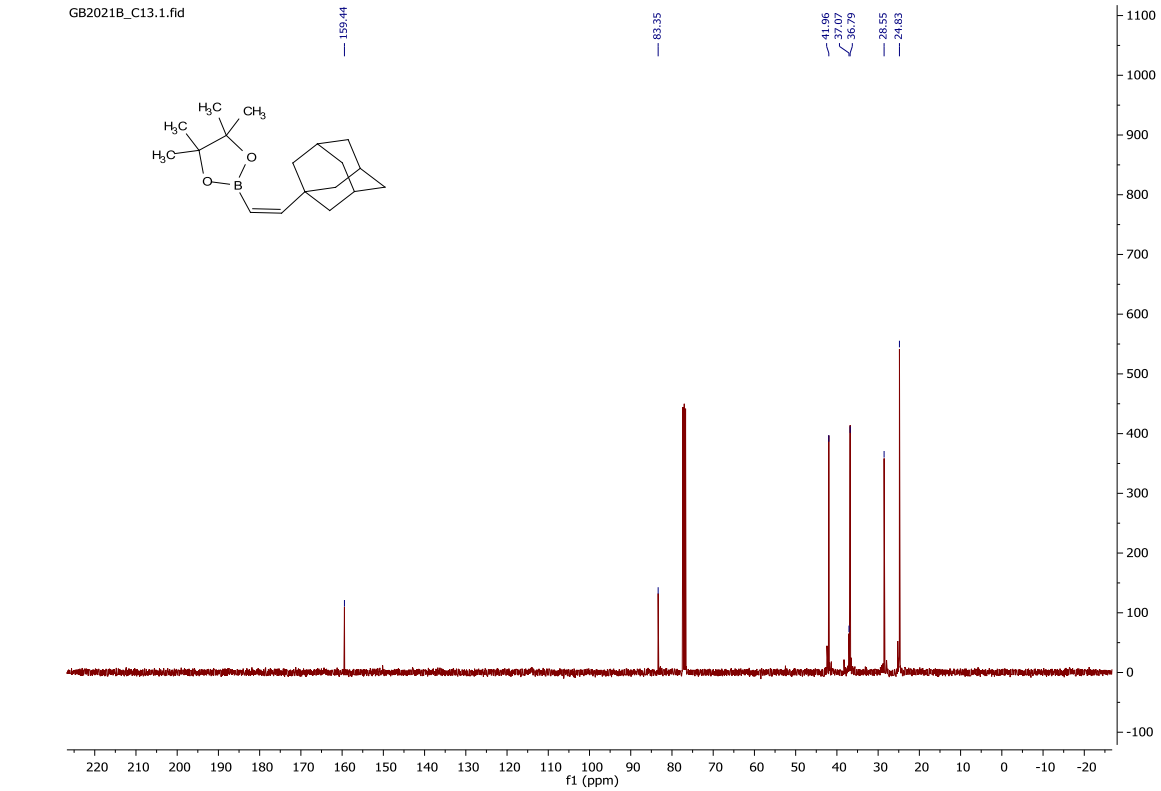
15.13
f1 (ppm)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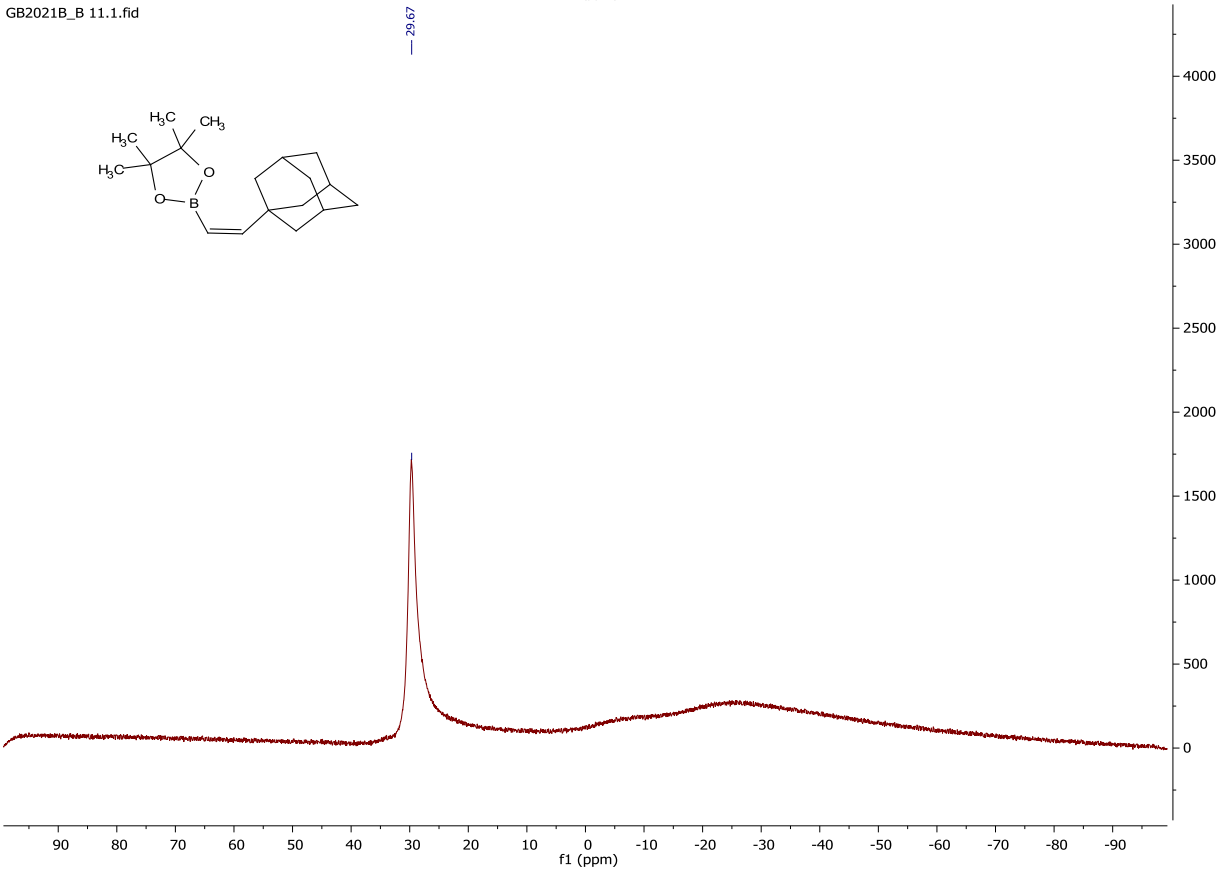
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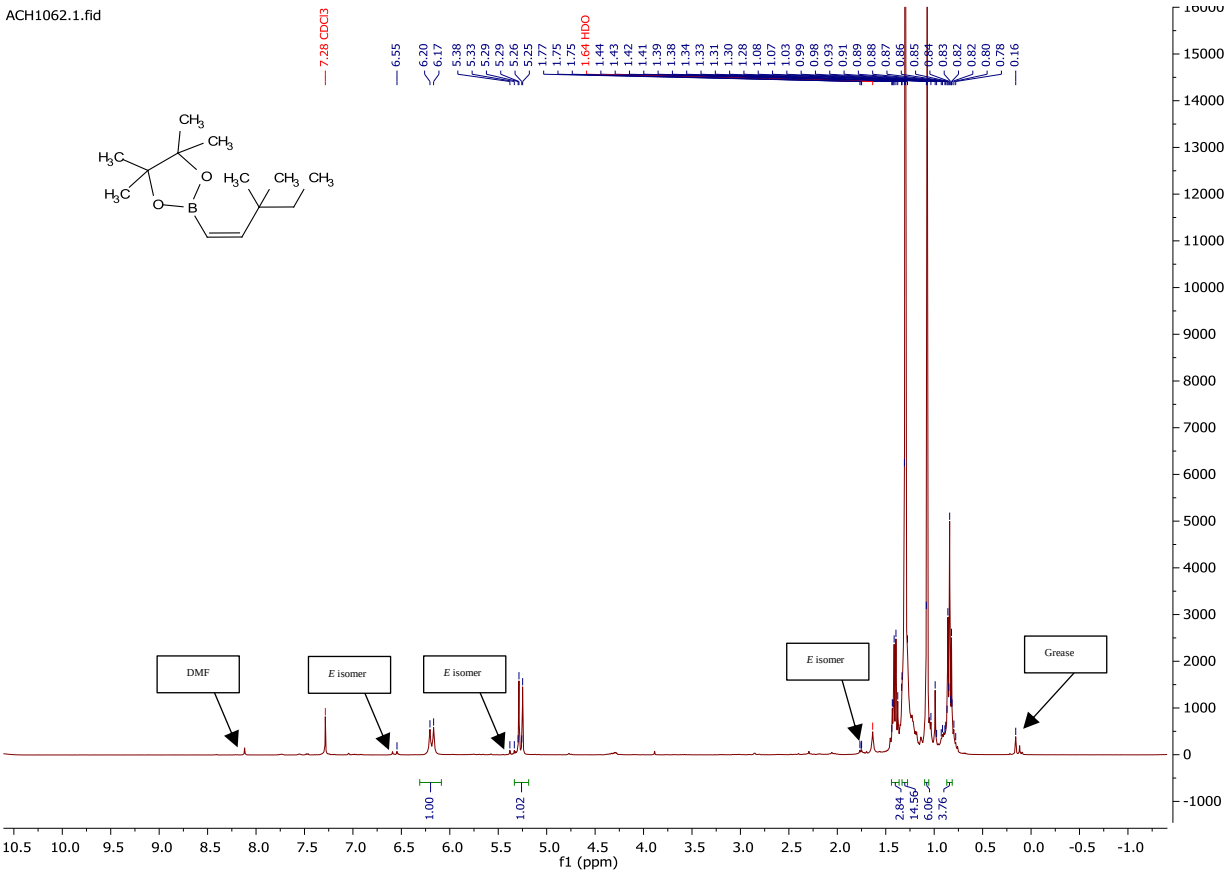
29.67
f1 (ppm)

Molecule 3c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1.38
1.34
1.33
1.31
1.30
1.28
1.08
1.07
1.03
0.99
0.98
0.93
0.91
0.89
0.88
0.87
0.86
0.85
0.84
0.83
0.82
0.82
0.80
0.78
0.16
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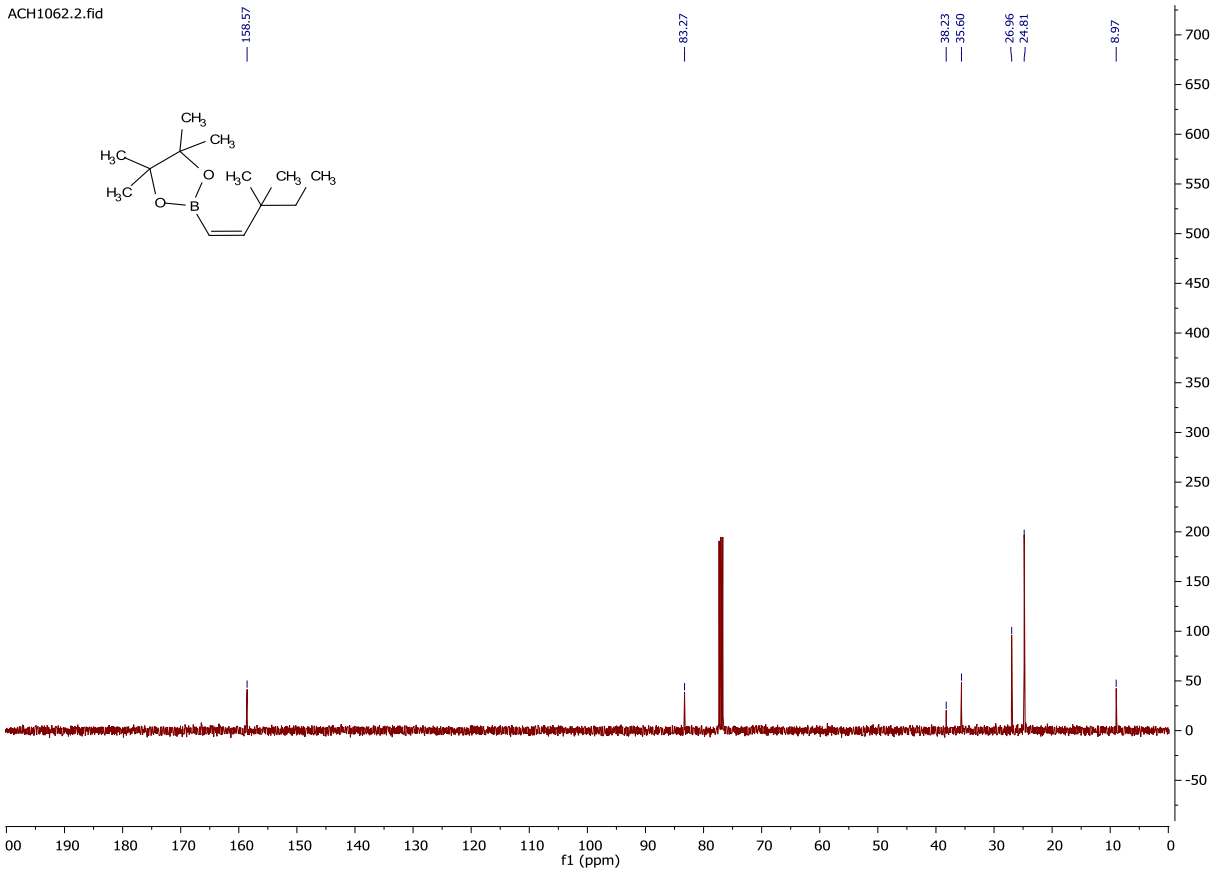
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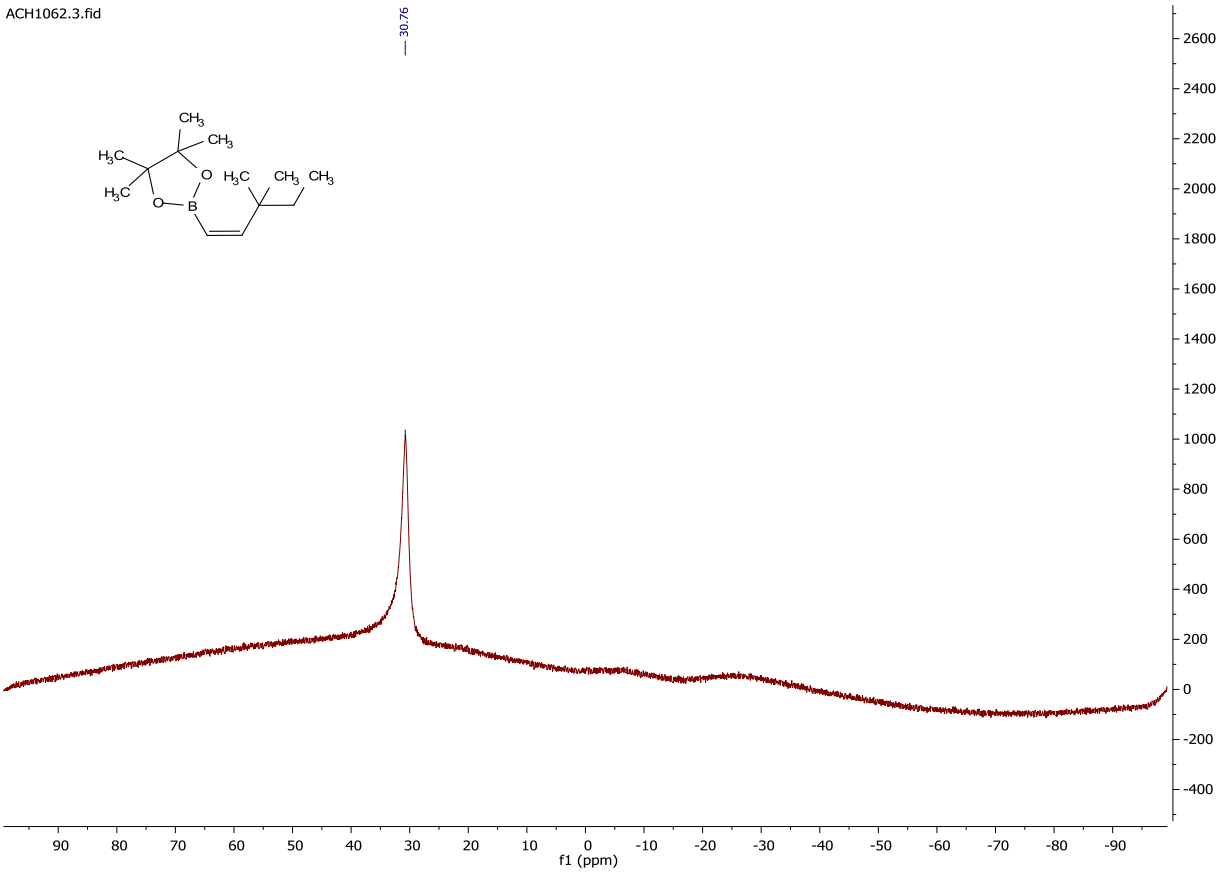
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-200
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90
80
70
60
50
40
30
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-70
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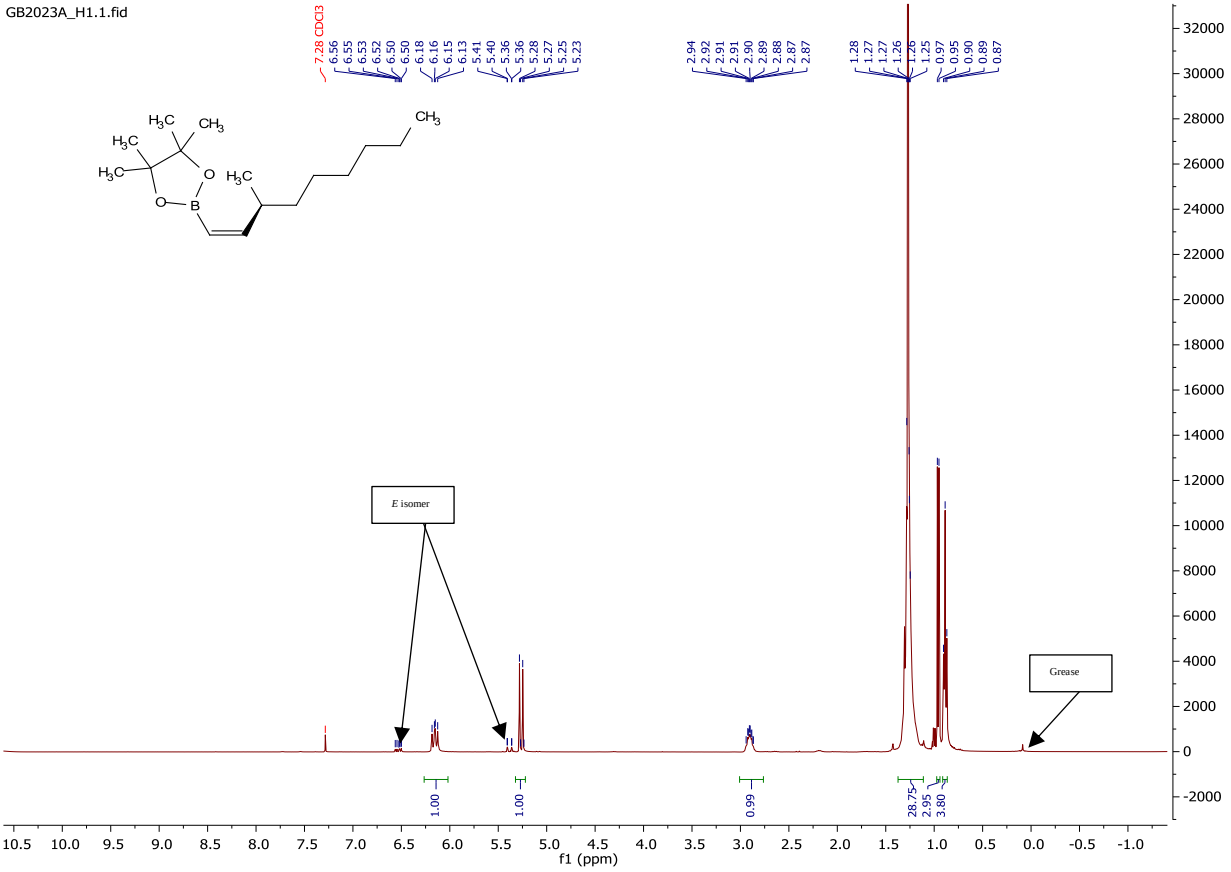
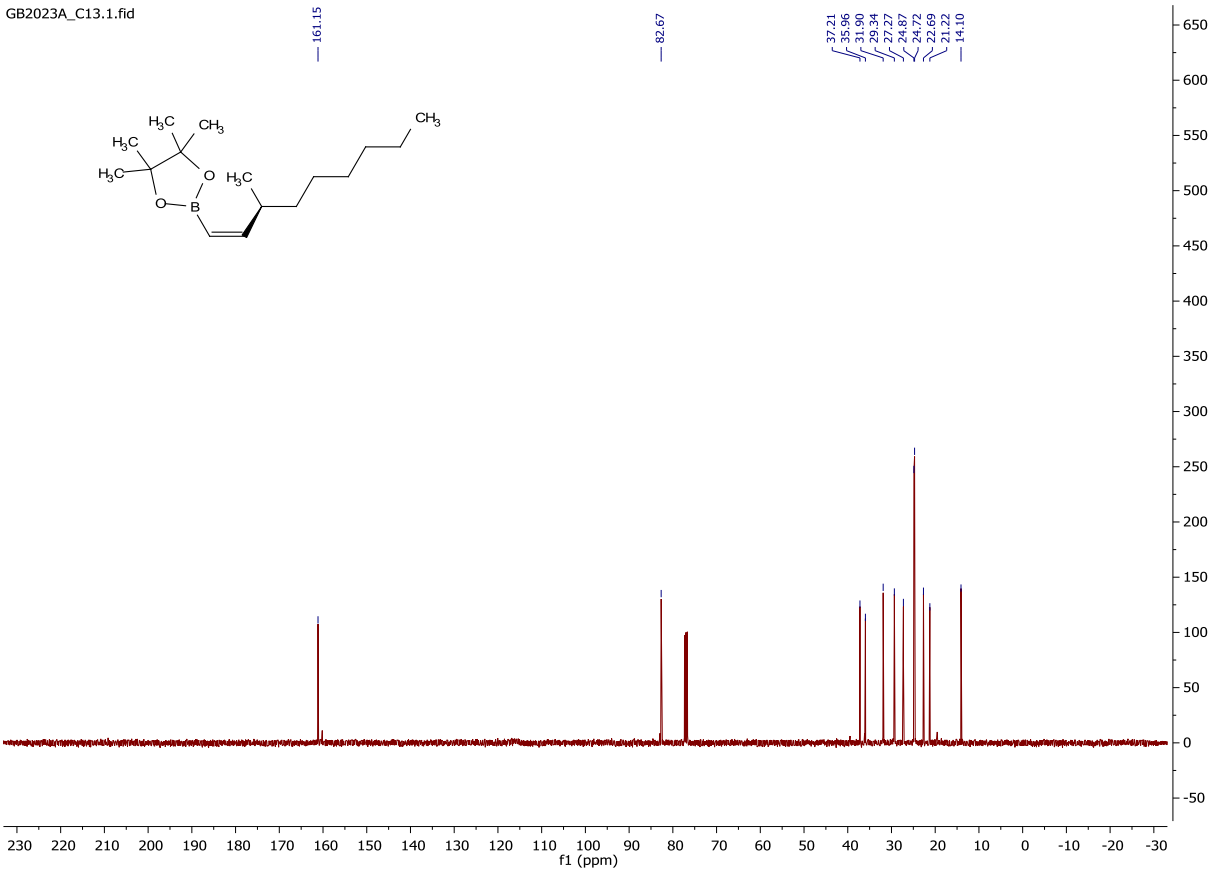
f1 (ppm)

Molecule 3d

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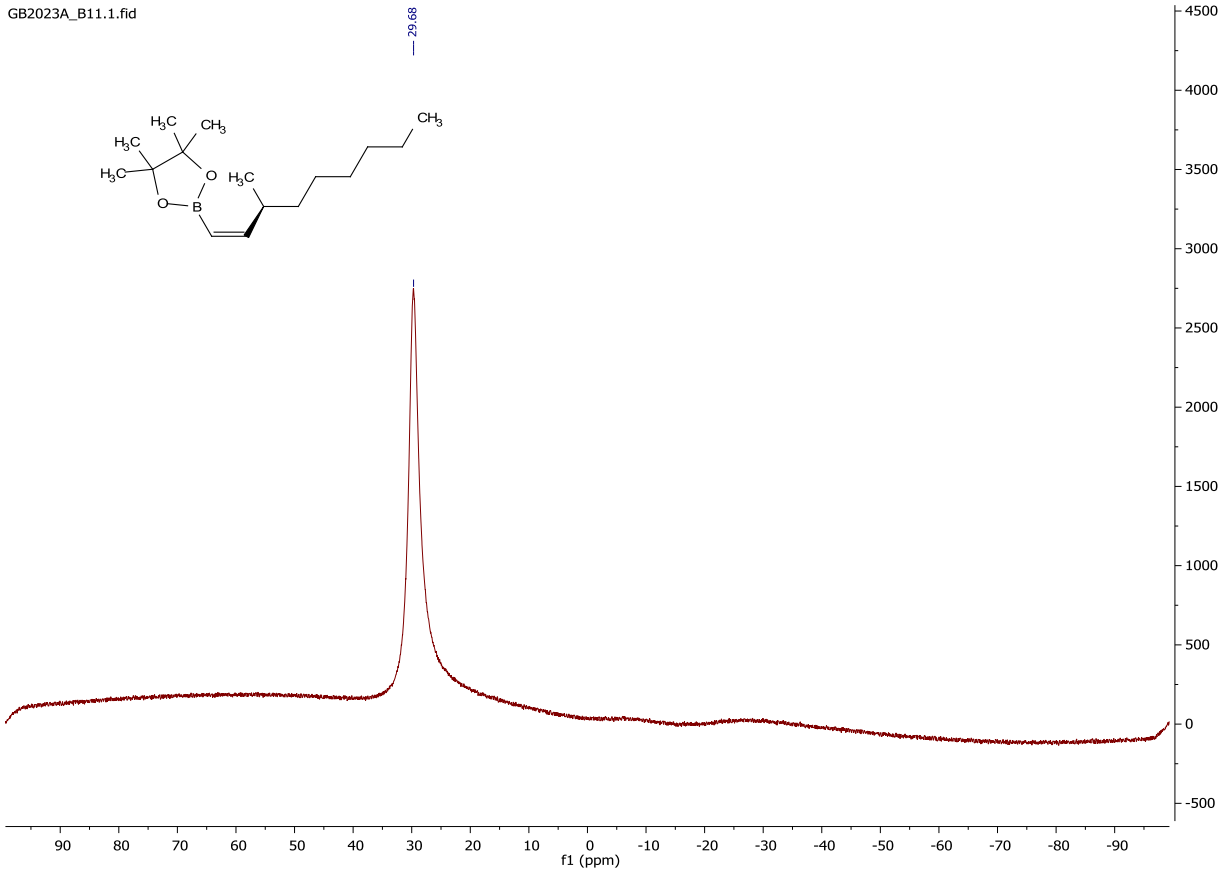
f1 (ppm)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H3C
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1500
1000
500
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90
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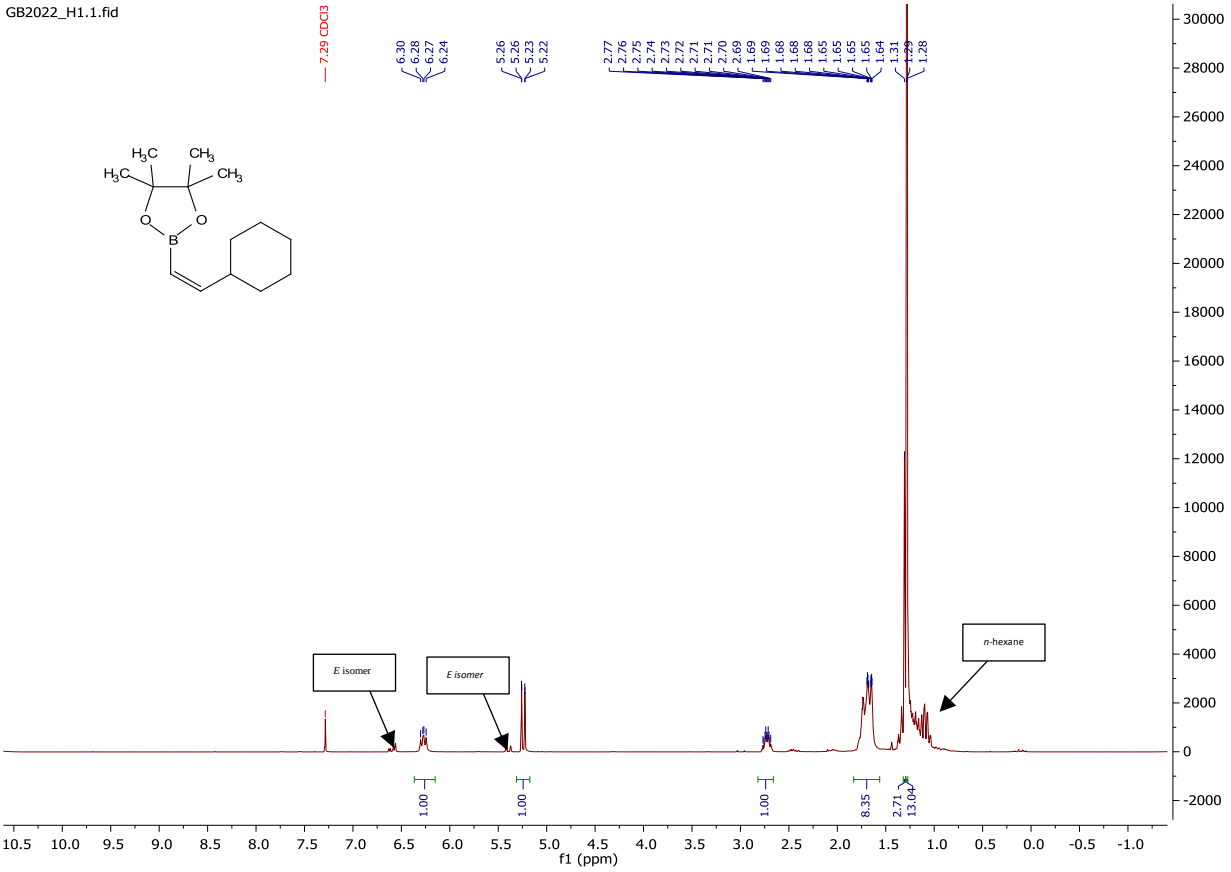
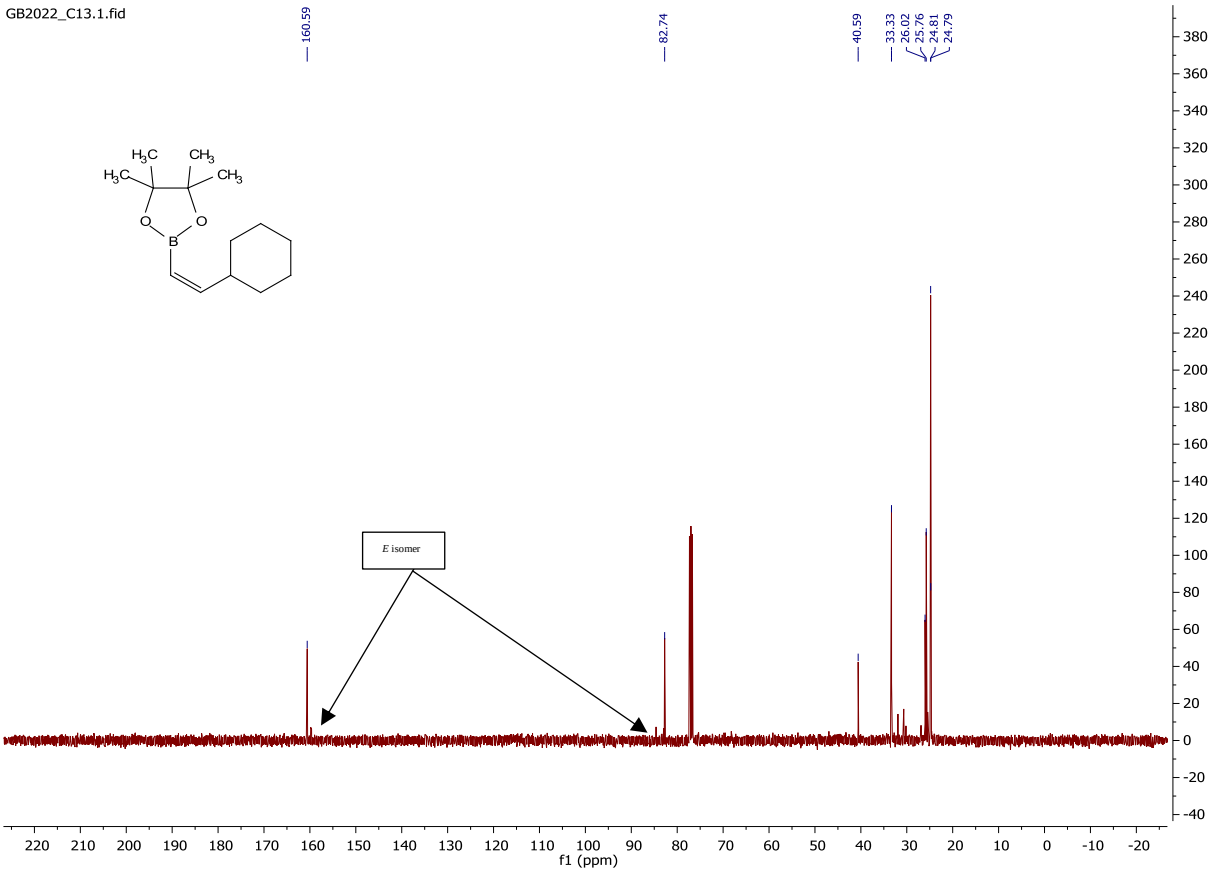
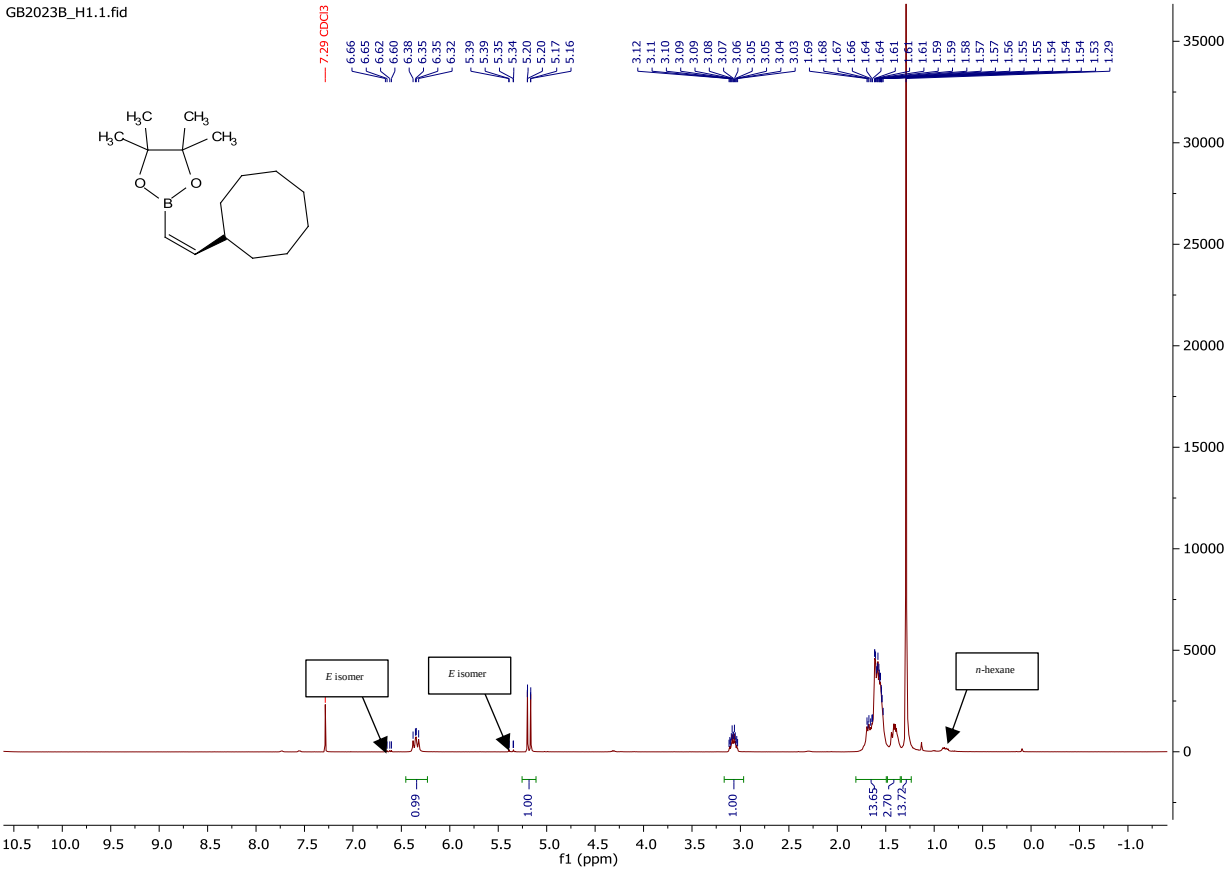
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

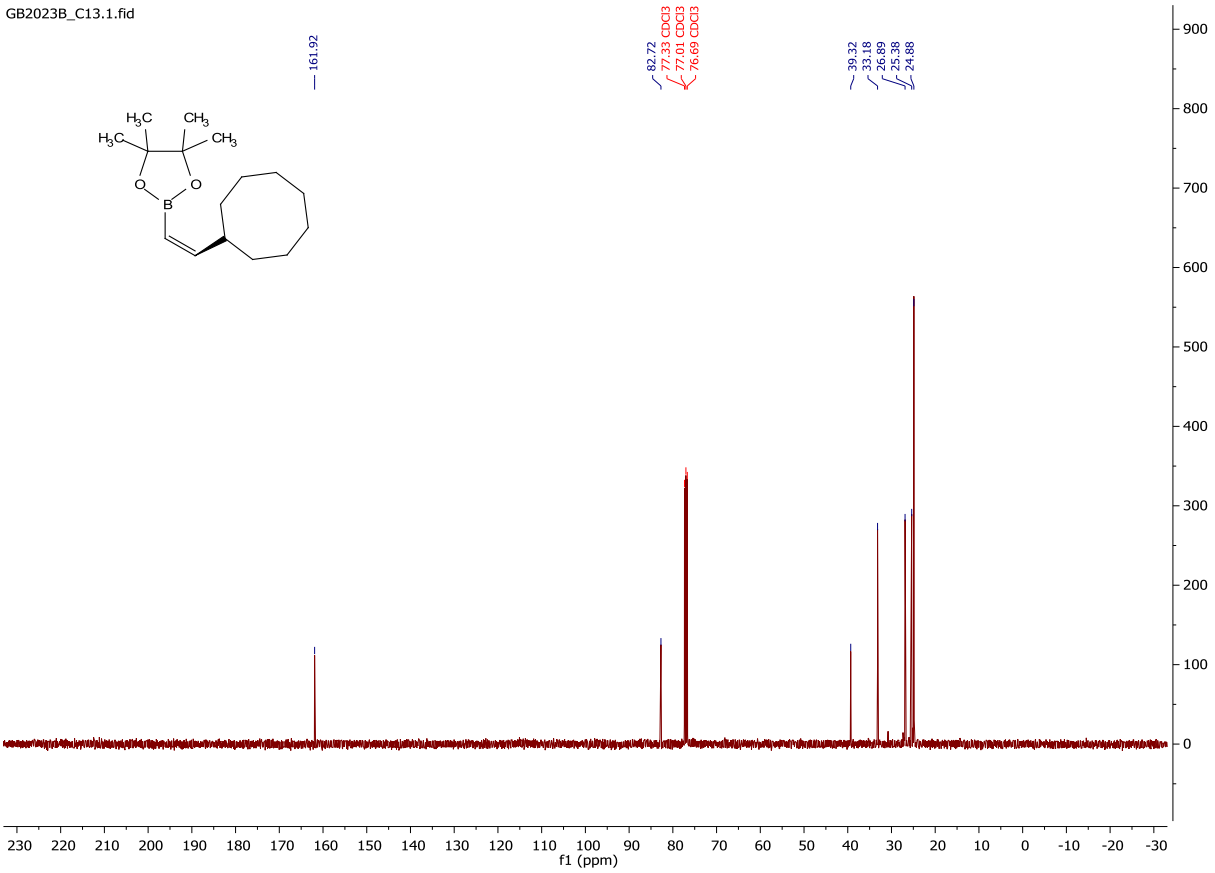
Molecule 3e

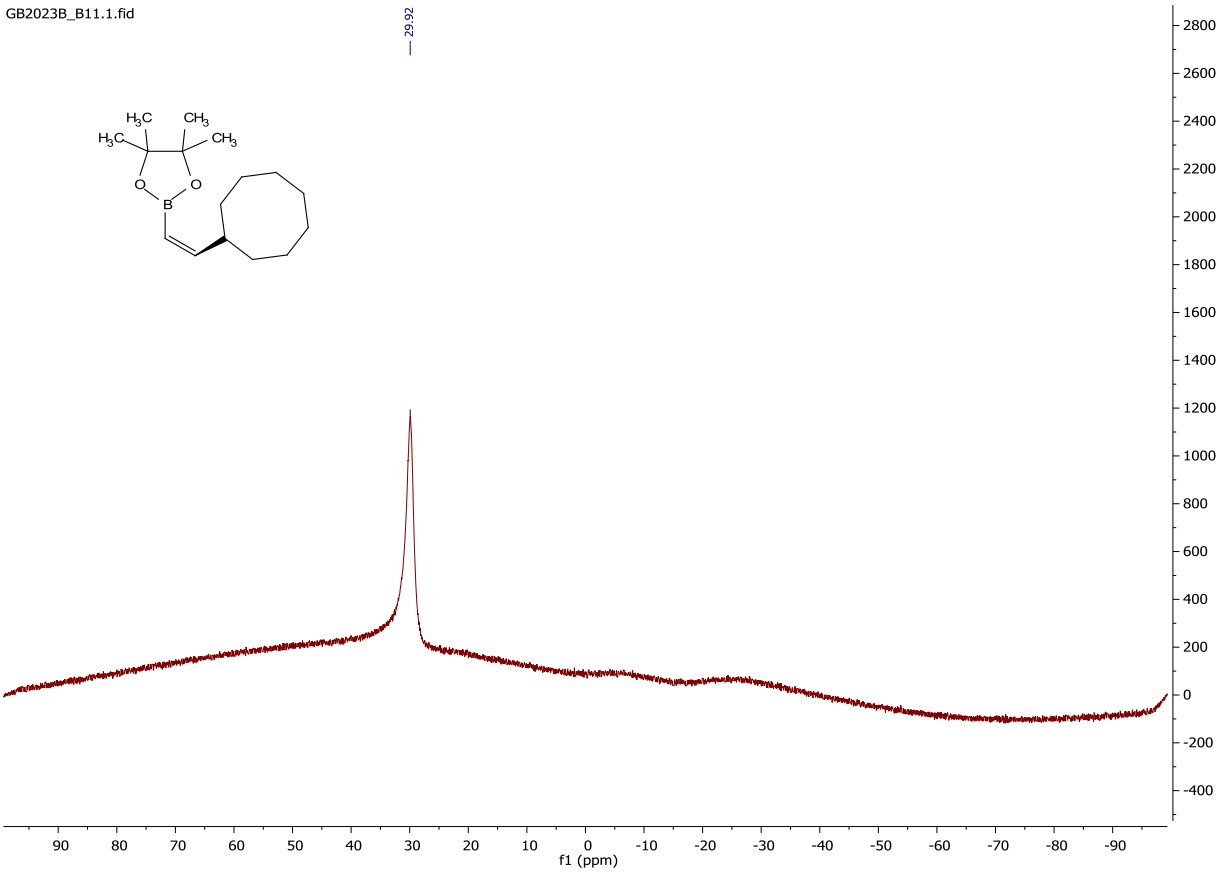

GB2022_H1.1.fid
7.29 CDCl3
6.30
6.28
6.27
6.24
5.26
5.26
5.23
5.22
2.77
2.76
2.75
2.74
2.73
2.72
2.71
2.71
2.70
2.69
1.69
1.69
1.68
1.68
1.68
1.65
1.65
1.65
1.65
1.64
1.31
1.29
1.28
E isomer
E isomer
n-hexane
1.00
1.00
1.00
8.35
2.71
13.04
f1 (ppm)


GB2022_C13.1.fid
160.59
82.74
40.59
33.33
26.02
25.76
24.81
24.79
H3C
CH3
H3C
CH3
O
O
B
E isomer
f1 (ppm)

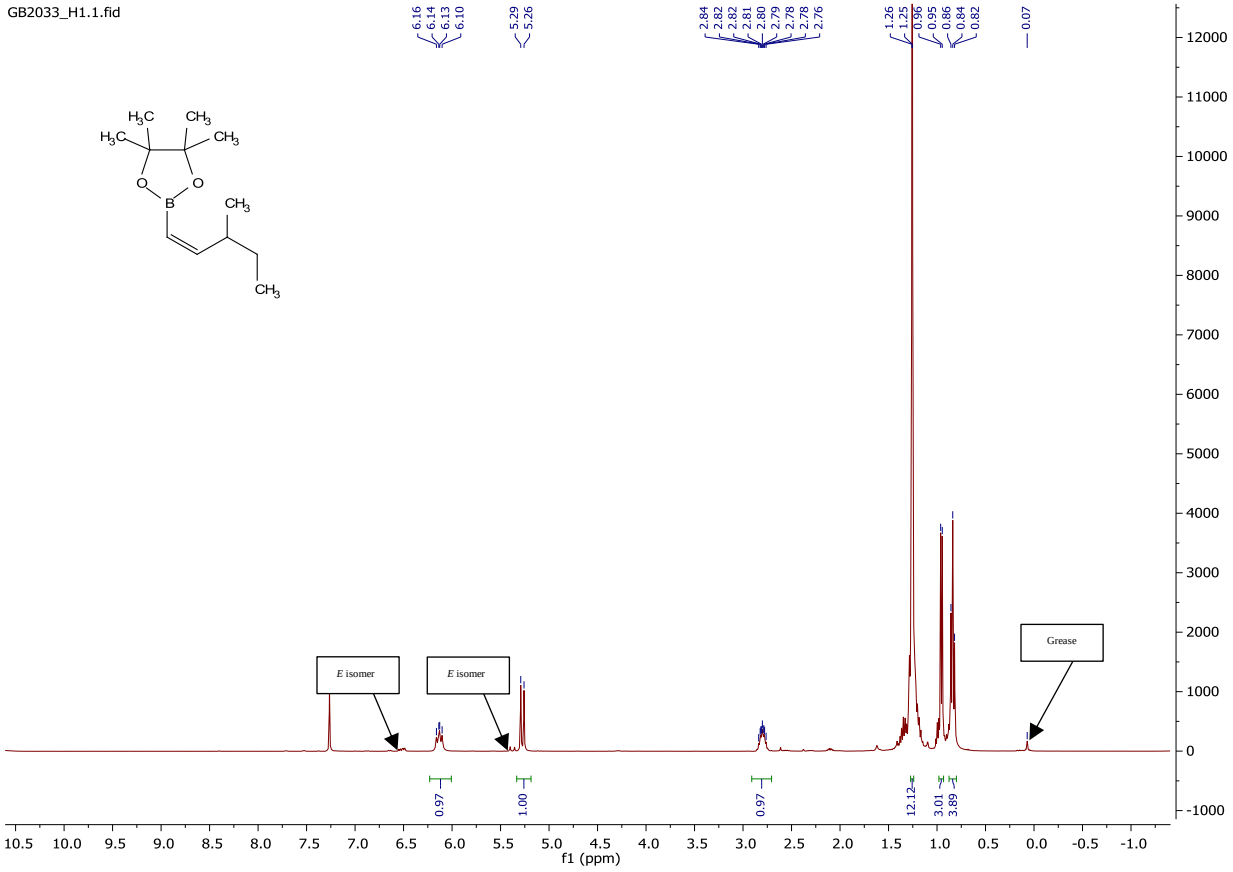
Molecule 3f

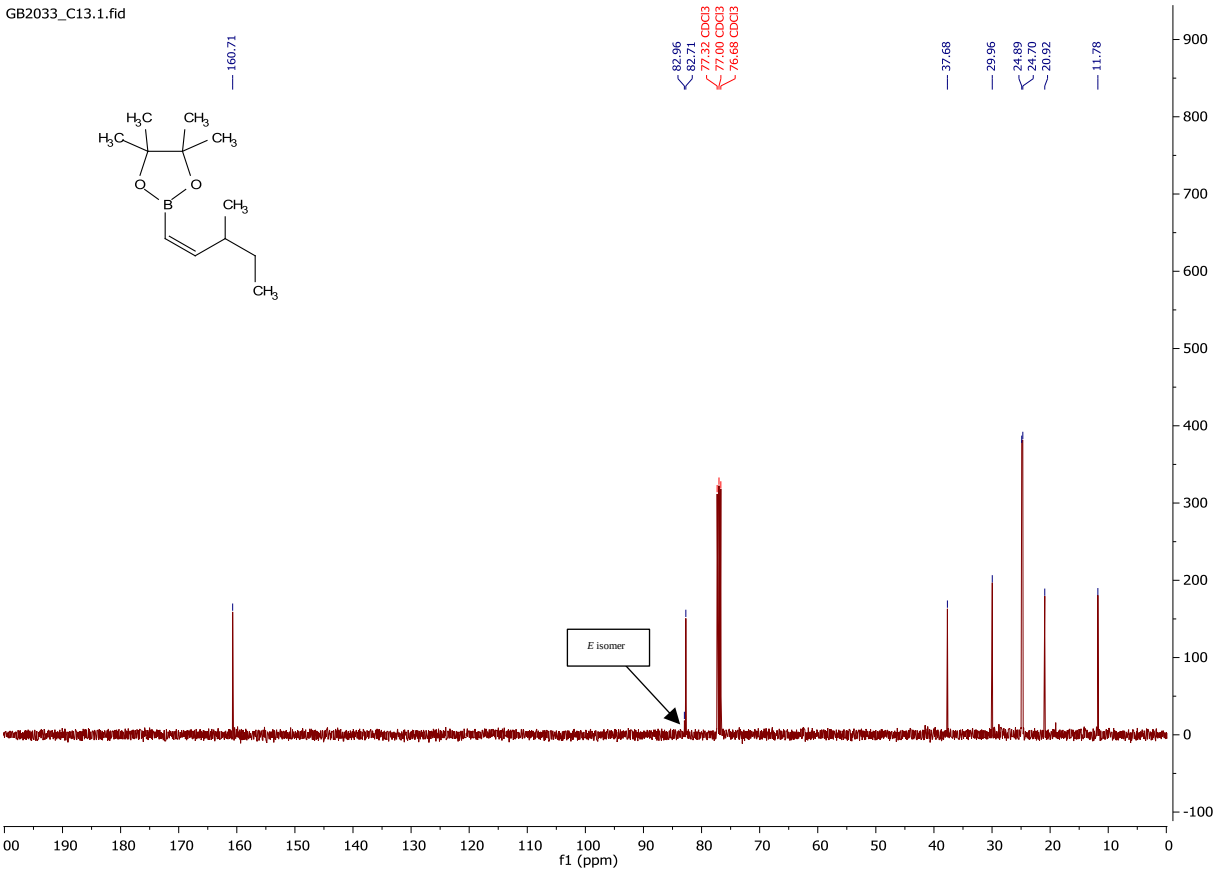

GB2023B_H1.1.fid
7.29 CDCl3
E isomer
E isomer
n-hexane
0.99
1.00
1.00
13.65
2.70
13.72
f1 (ppm)

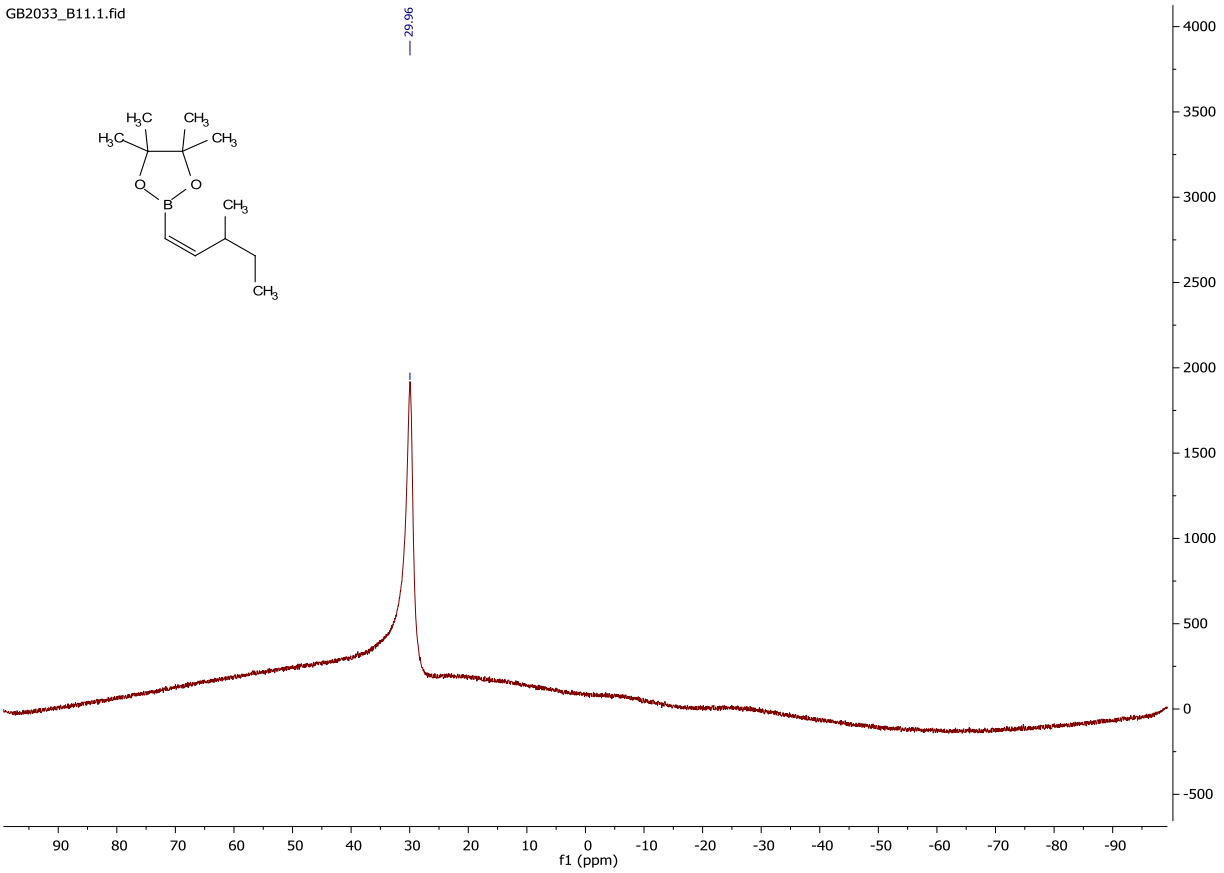

GB2023B_C13.1.fid
161.92
82.72
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
39.32
33.18
26.89
25.38
24.88
H3C
CH3
H3C
CH3
O
O
B
900
800
700
600
500
400
300
200
100
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


GB2023B_B11.1.fid
29.92
H3C
CH3
H3C
CH3
O
O
B
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

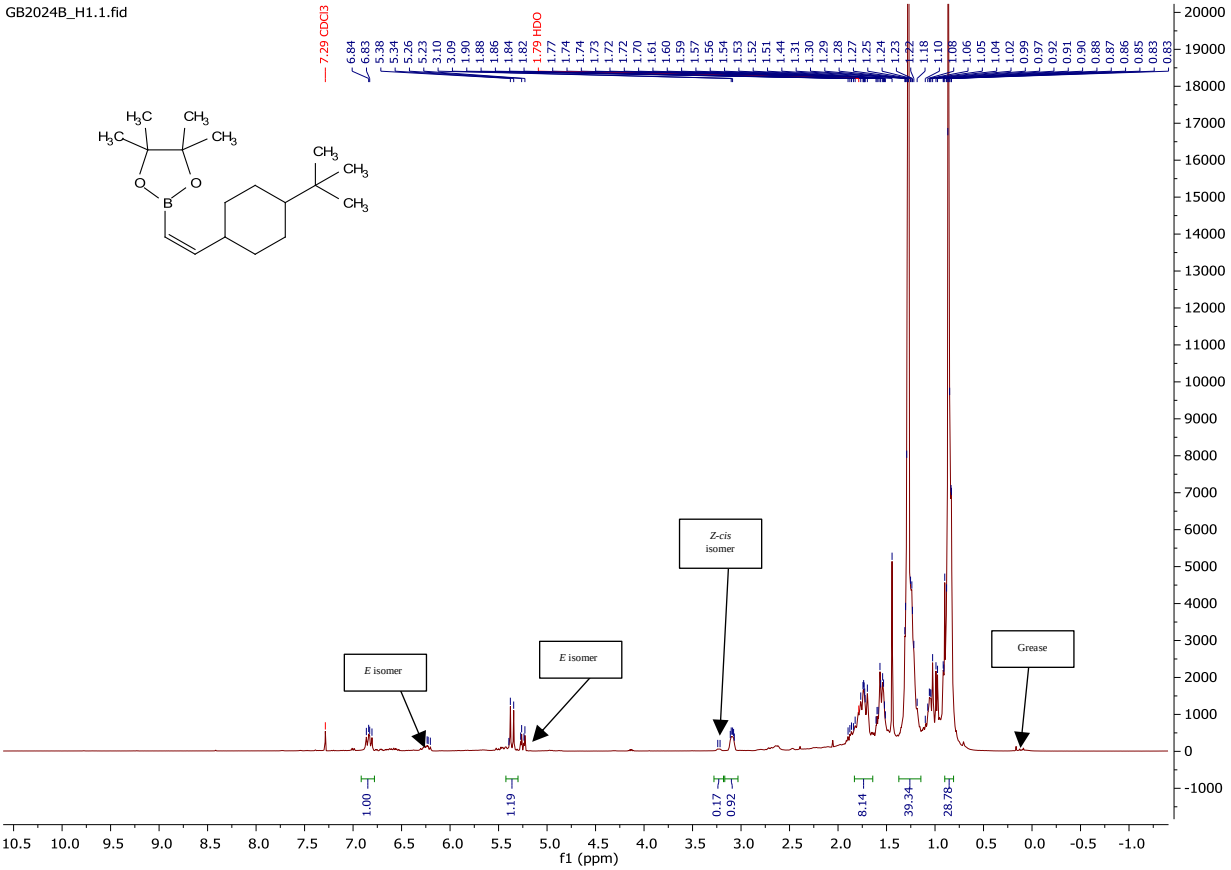
Molecule 3g

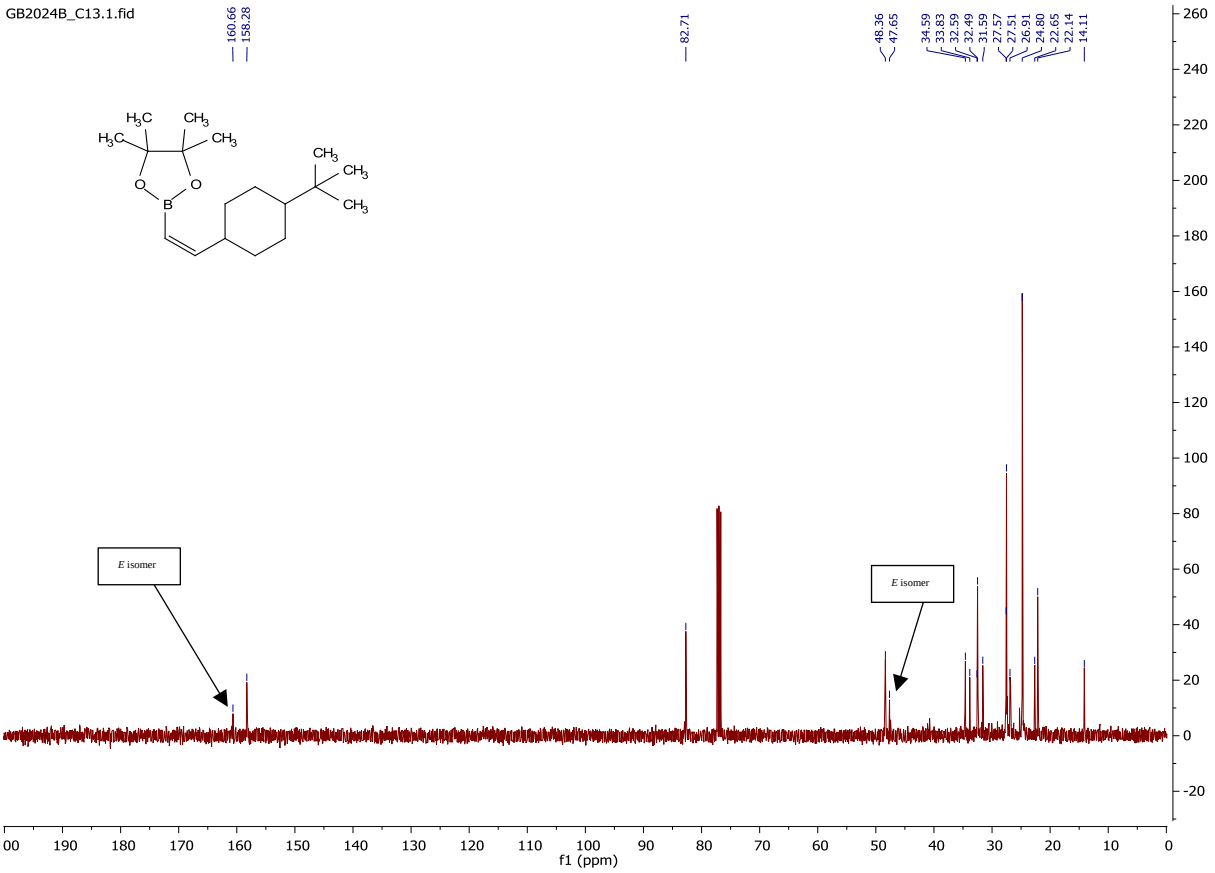

GB2033_H1.1.fid
6.16
6.14
6.13
6.10
5.29
5.26
2.84
2.82
2.82
2.81
2.80
2.79
2.78
2.78
2.76
1.26
1.25
0.96
0.95
0.86
0.84
0.82
0.07
E isomer
E isomer
Grease
0.97
1.00
0.97
12.12
3.01
3.89
f1 (ppm)

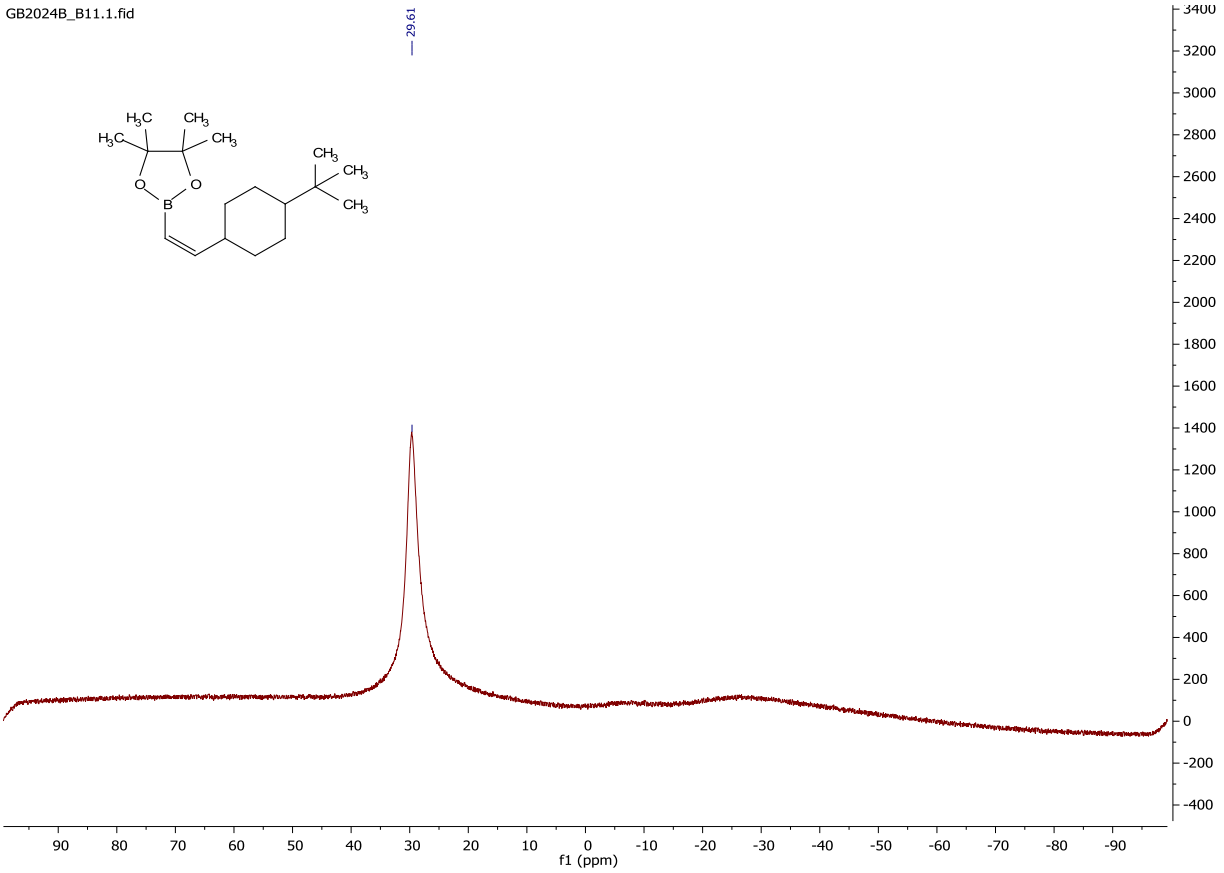

GB2033_C13.1.fid
160.71
82.96
82.71
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
37.68
29.96
24.89
24.70
20.92
11.78
E isomer
f1 (ppm)


GB2033_B11.1.fid
29.96
H3C
CH3
H3C
CH3
O
O
B
CH3
CH3
4000
3500
3000
2500
2000
1500
1000
500
0
-500
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

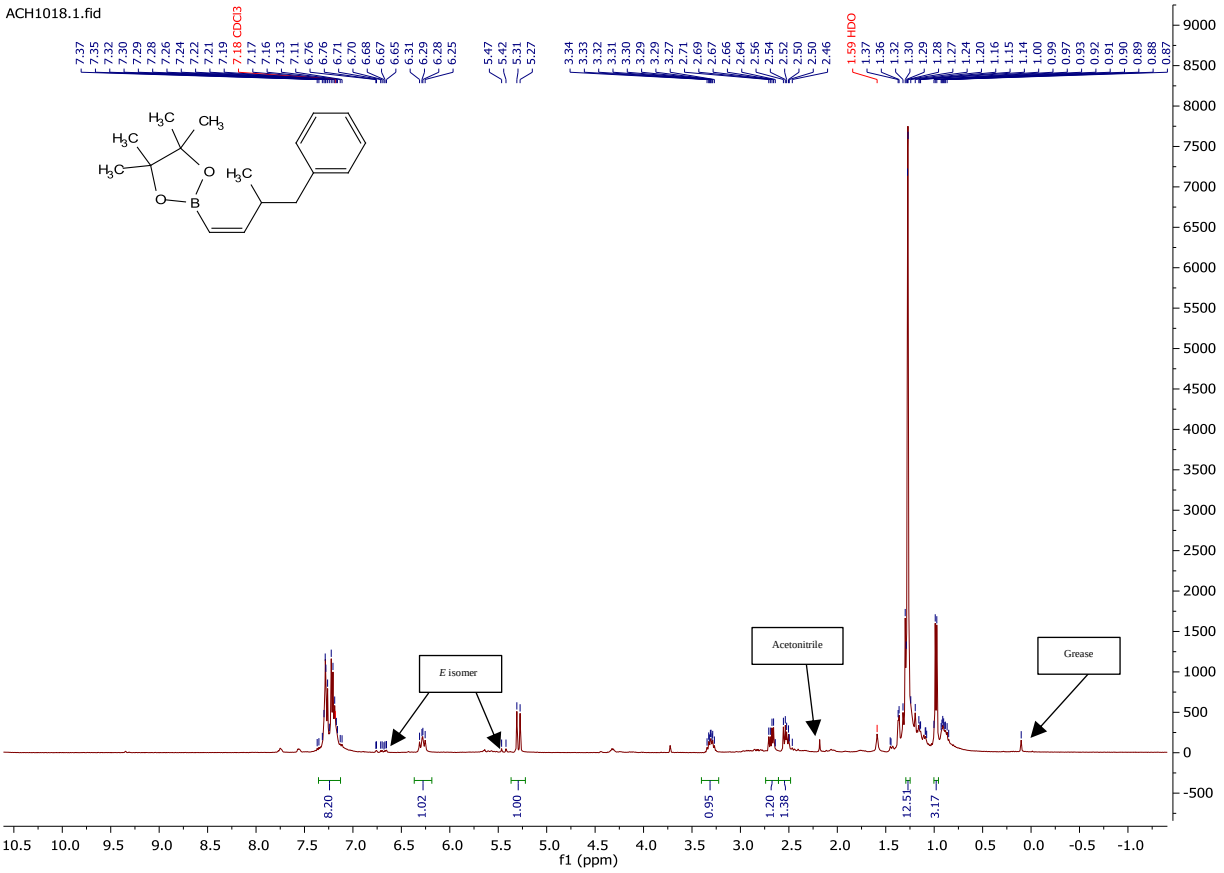
Molecule 3h

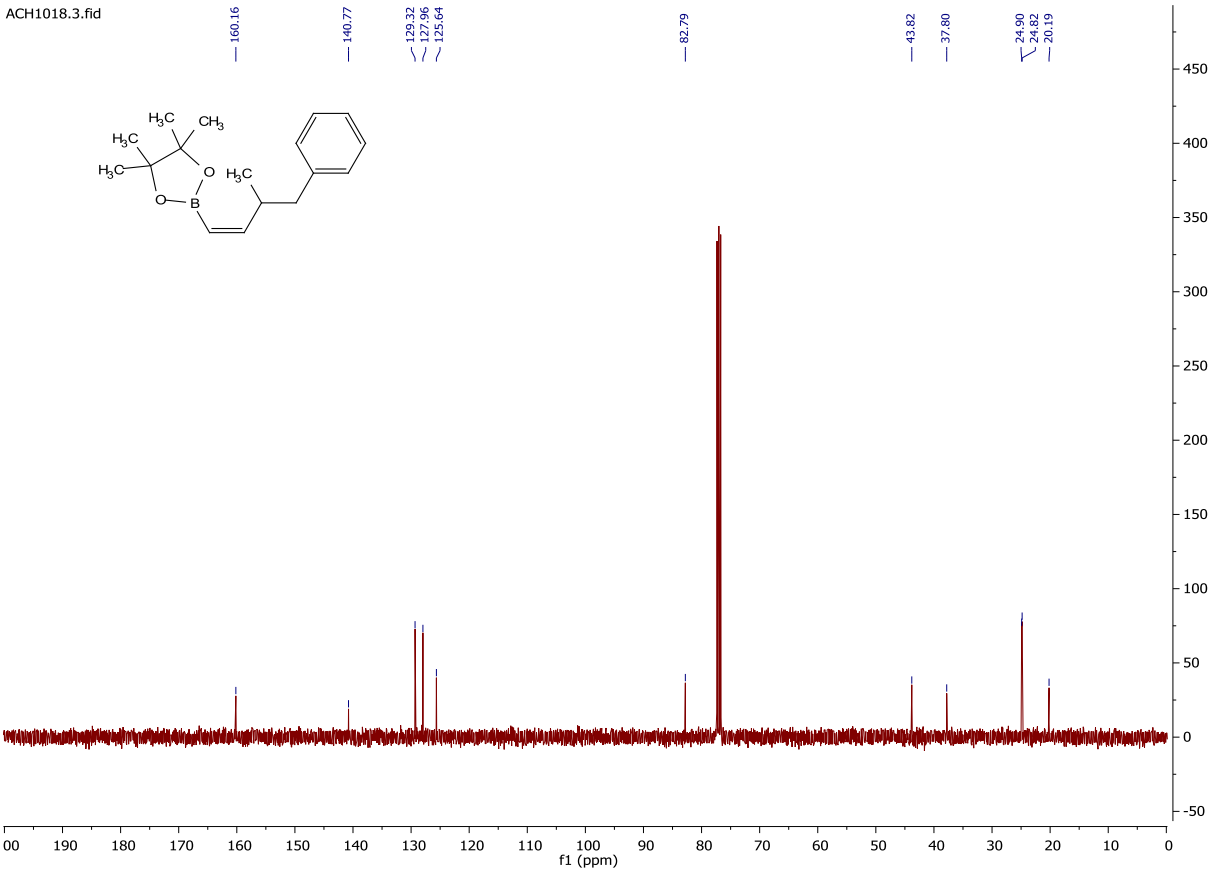

GB2024B_H1.1.fid
7.29 CDCl3
1.79 HDO
E isomer
E isomer
Z-cis isomer
Grease
1.00
1.19
0.17
0.92
8.14
39.34
28.78
f1 (ppm)

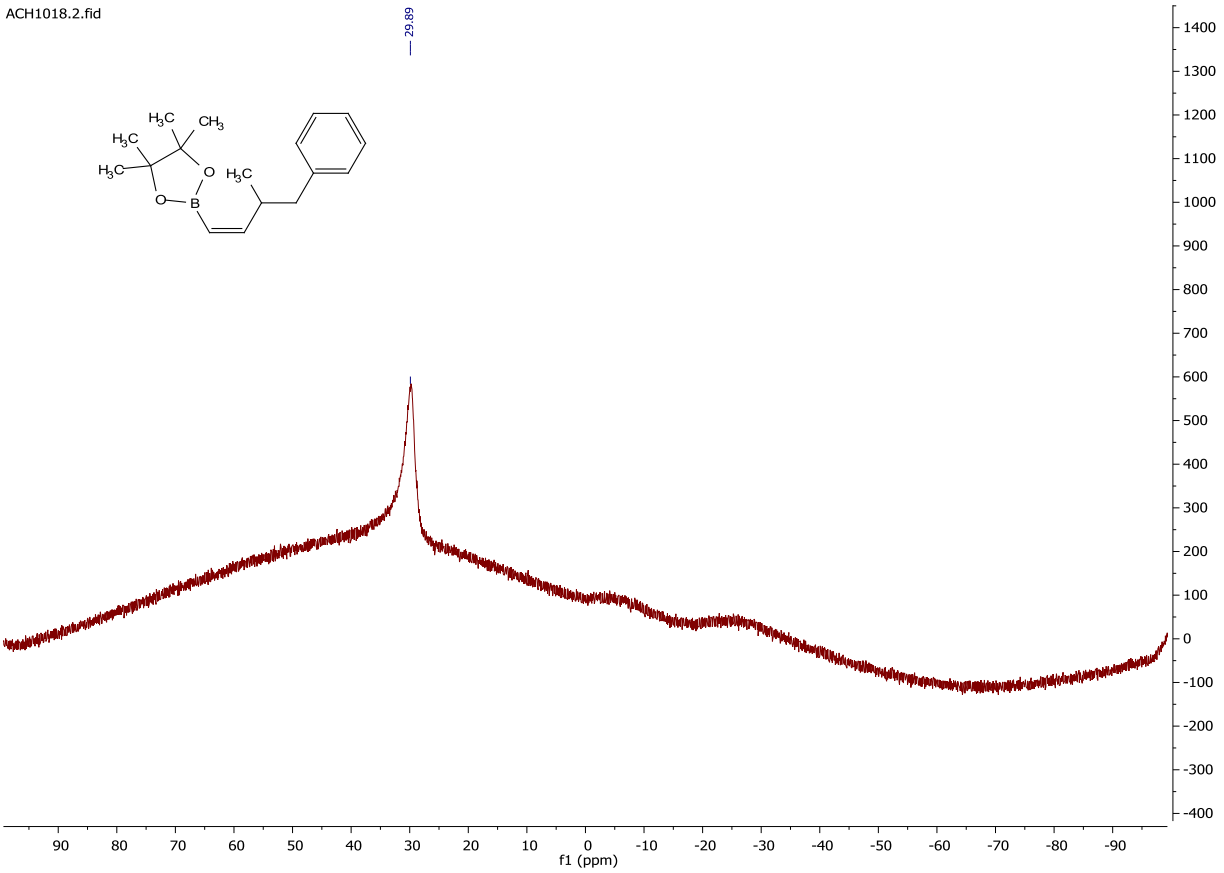

GB2024B_C13.1.fid
160.66
158.28
82.71
48.36
47.65
34.59
33.83
32.59
32.49
31.59
27.57
27.51
26.91
24.80
22.65
22.14
14.11
E isomer
E isomer
f1 (ppm)


GB2024B_B11.1.fid
29.61
f1 (ppm)

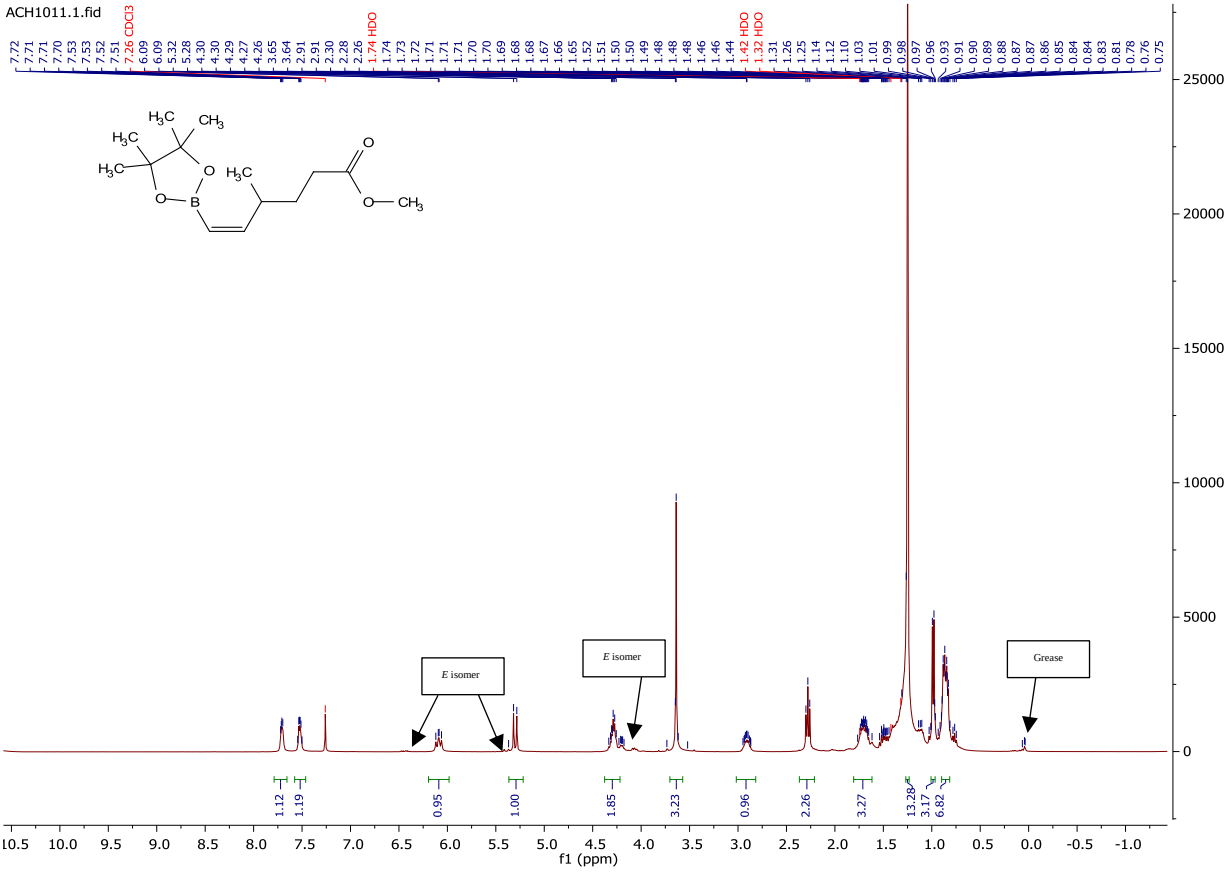
Molecule 3i

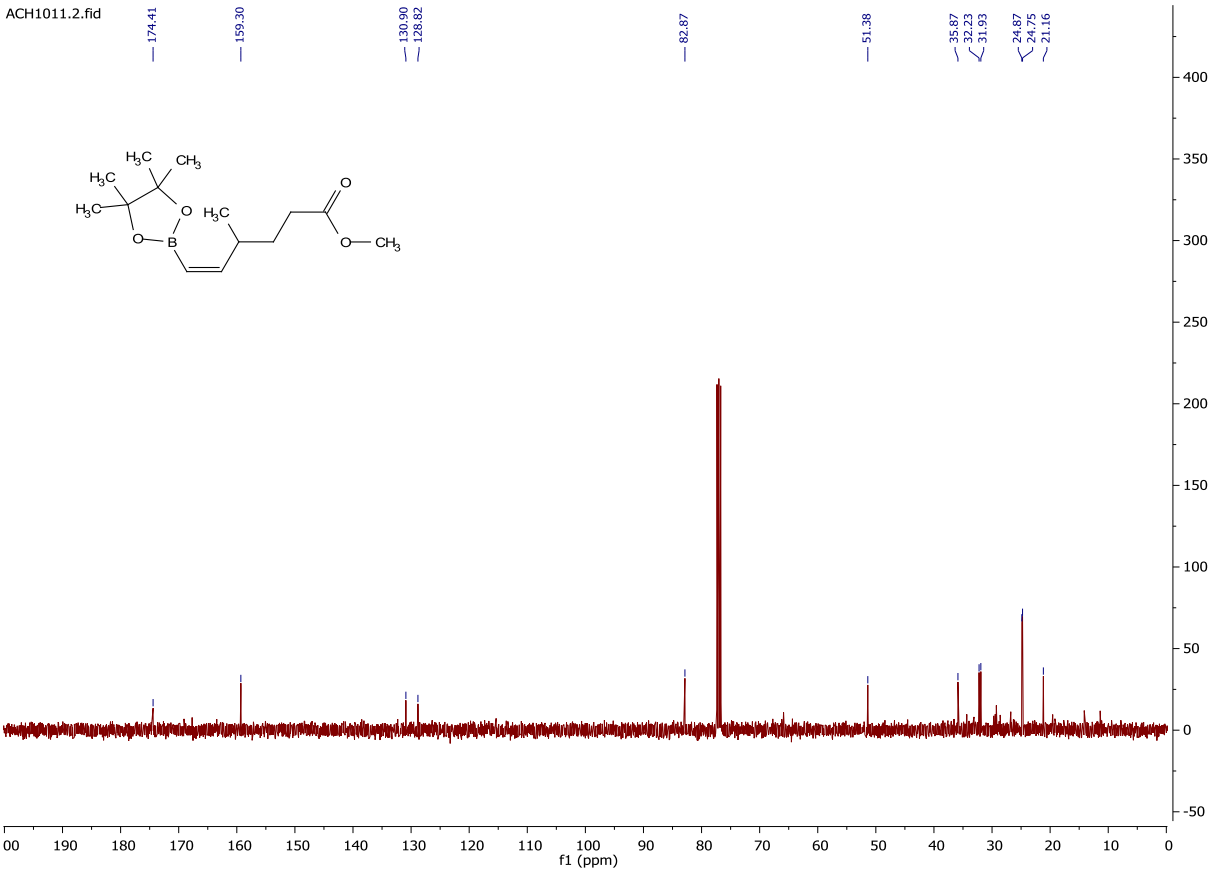

ACH1018.1.fid
CDCl3
HDO
E isomer
Acetonitrile
Grease
8.20
1.02
1.00
0.95
1.20
1.38
12.51
3.17
f1 (ppm)

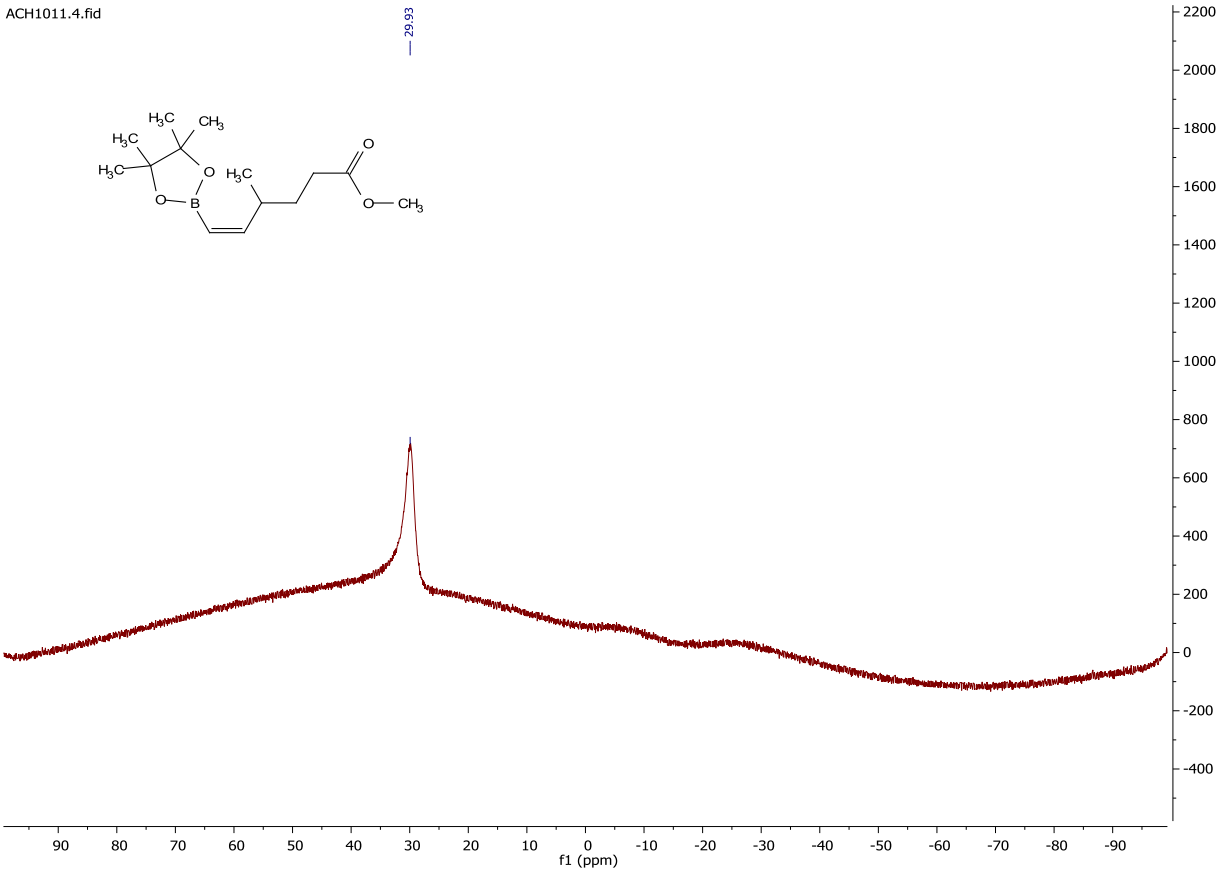

ACH1018.3.fid
160.16
140.77
129.32
127.96
125.64
82.79
43.82
37.80
24.90
24.82
20.19
f1 (ppm)


ACH1018.2.fid
29.89
H3C
CH3
H3C
H3C
O
H3C
O
B
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

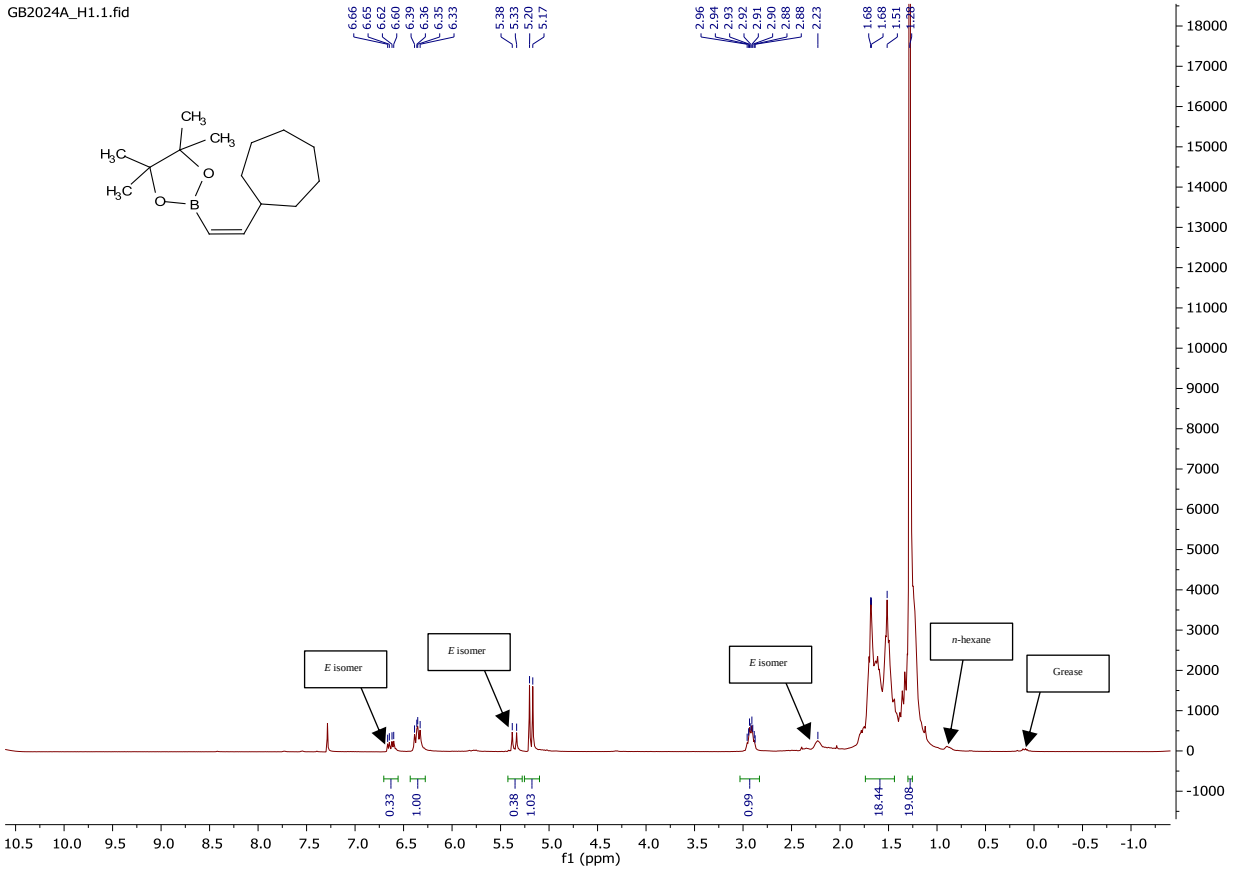
Molecule 3j

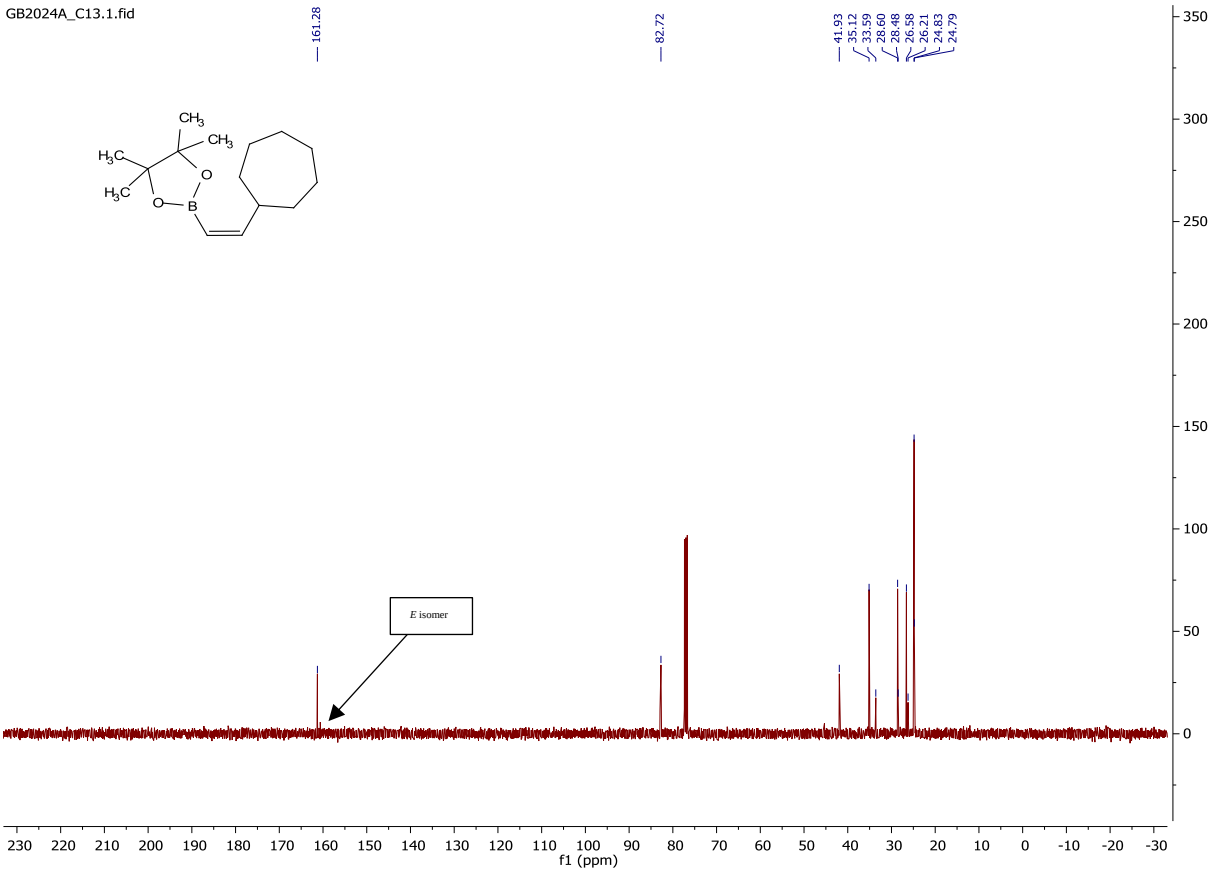


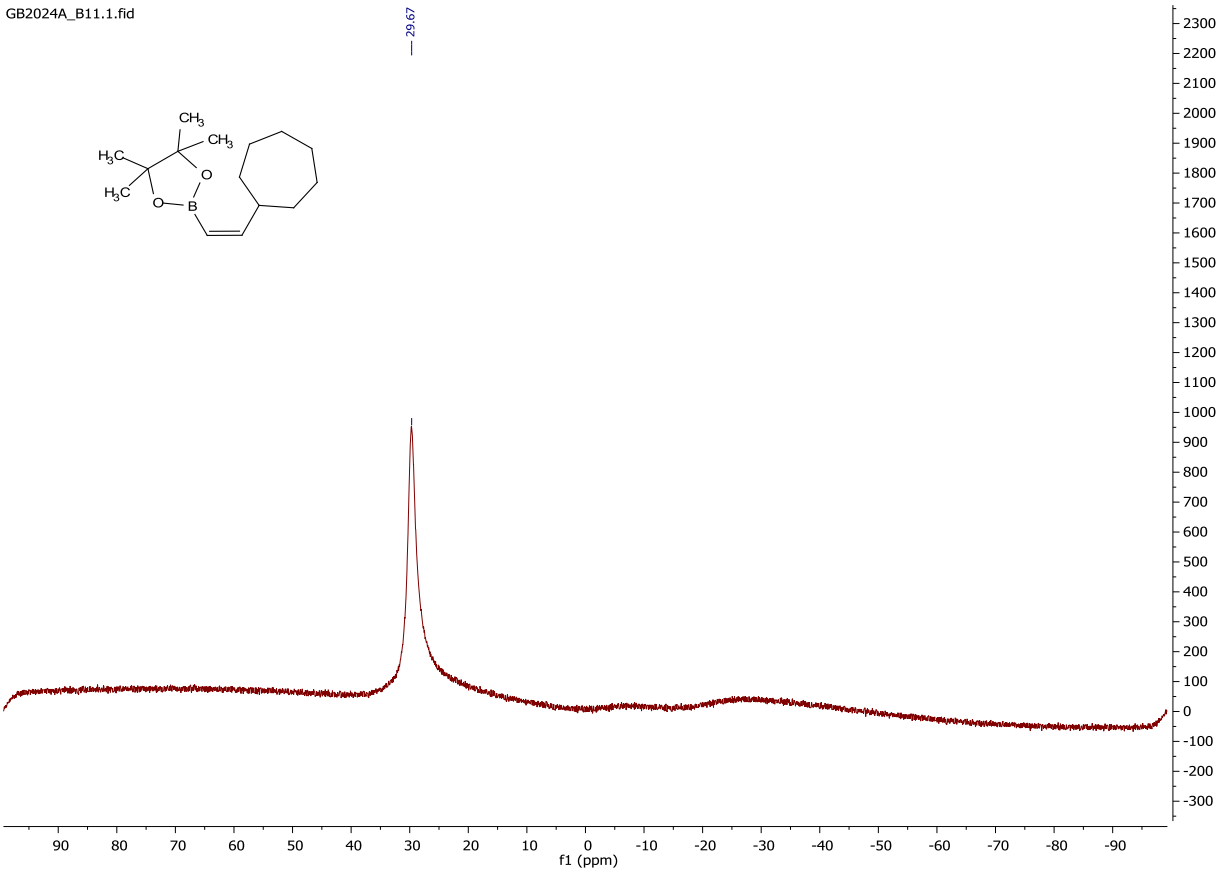

ACH1011.2.fid
174.41
159.30
130.90
128.82
82.87
51.38
35.87
32.23
31.93
24.87
24.75
21.16
f1 (ppm)


ACH1011.4.fid
29.93
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

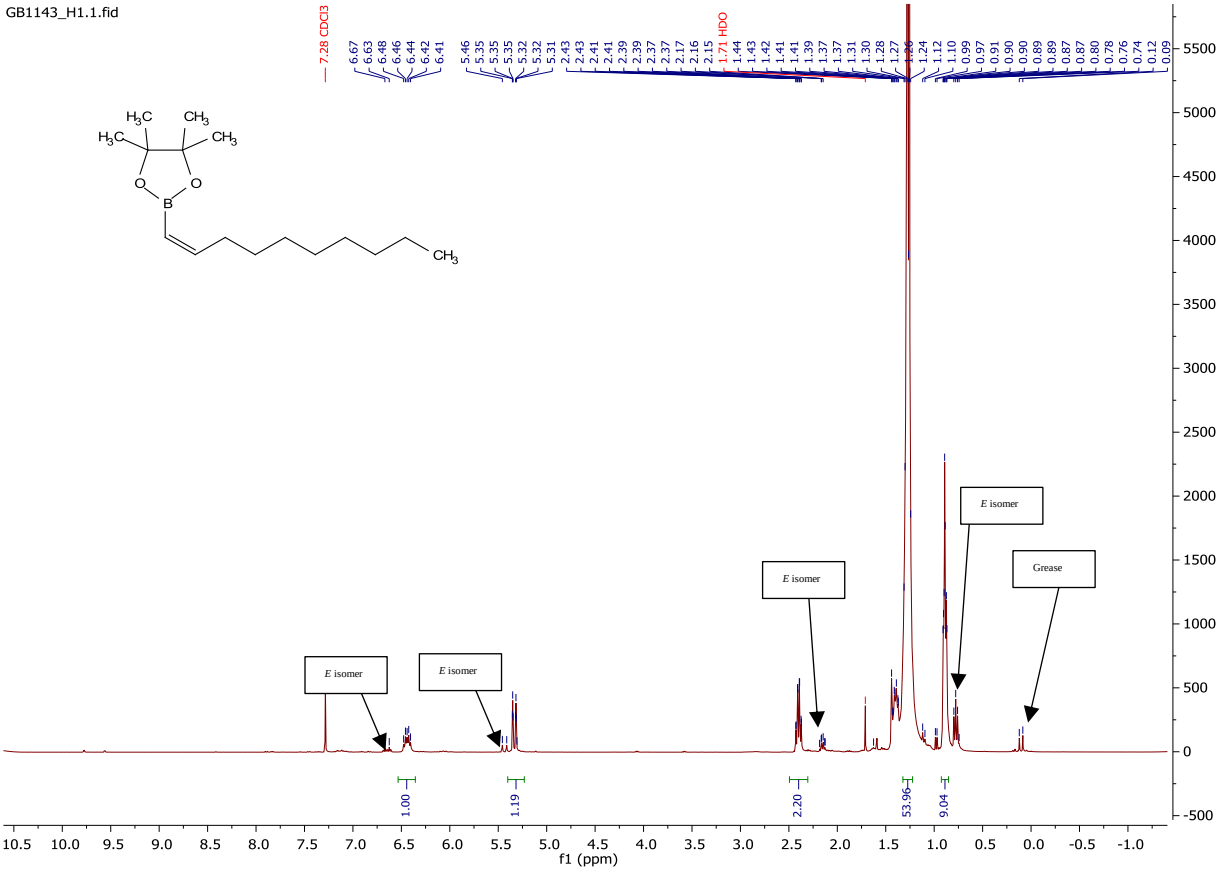
Molecule 3k

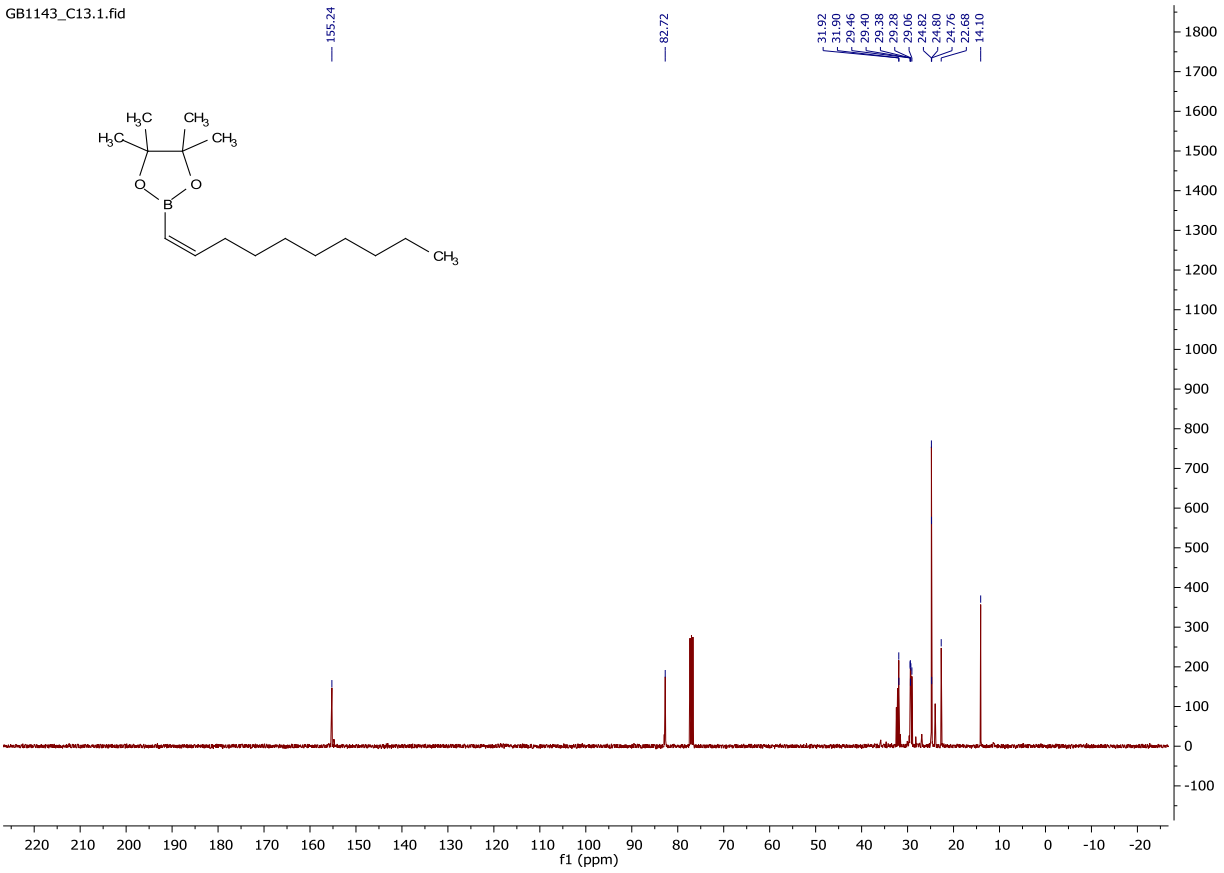

GB2024A_H1.1.fid
6.66
6.65
6.62
6.60
6.39
6.36
6.35
6.33
5.38
5.33
5.20
5.17
2.96
2.94
2.93
2.92
2.91
2.90
2.88
2.88
2.23
1.68
1.68
1.51
1.26
CH3
CH3
H3C
H3C
O
O
B
E isomer
E isomer
E isomer
n-hexane
Grease
0.33
1.00
0.38
1.03
0.99
18.44
19.08
f1 (ppm)

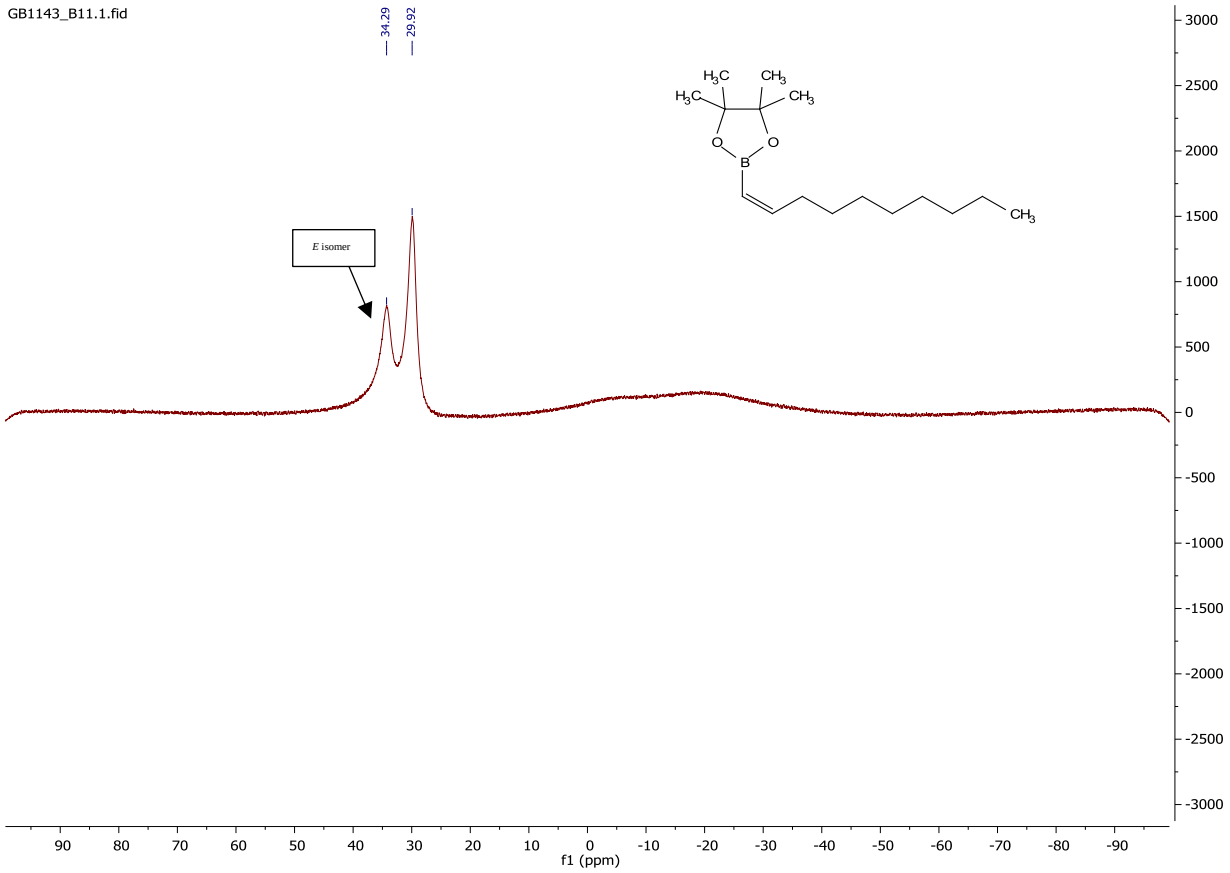

GB2024A_C13.1.fid
161.28
82.72
41.93
35.12
33.59
28.60
28.48
26.58
26.21
24.83
24.79
E isomer
f1 (ppm)


GB2024A_B11.1.fid
29.67
CH3
CH3
H3C
H3C
O
O
B
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

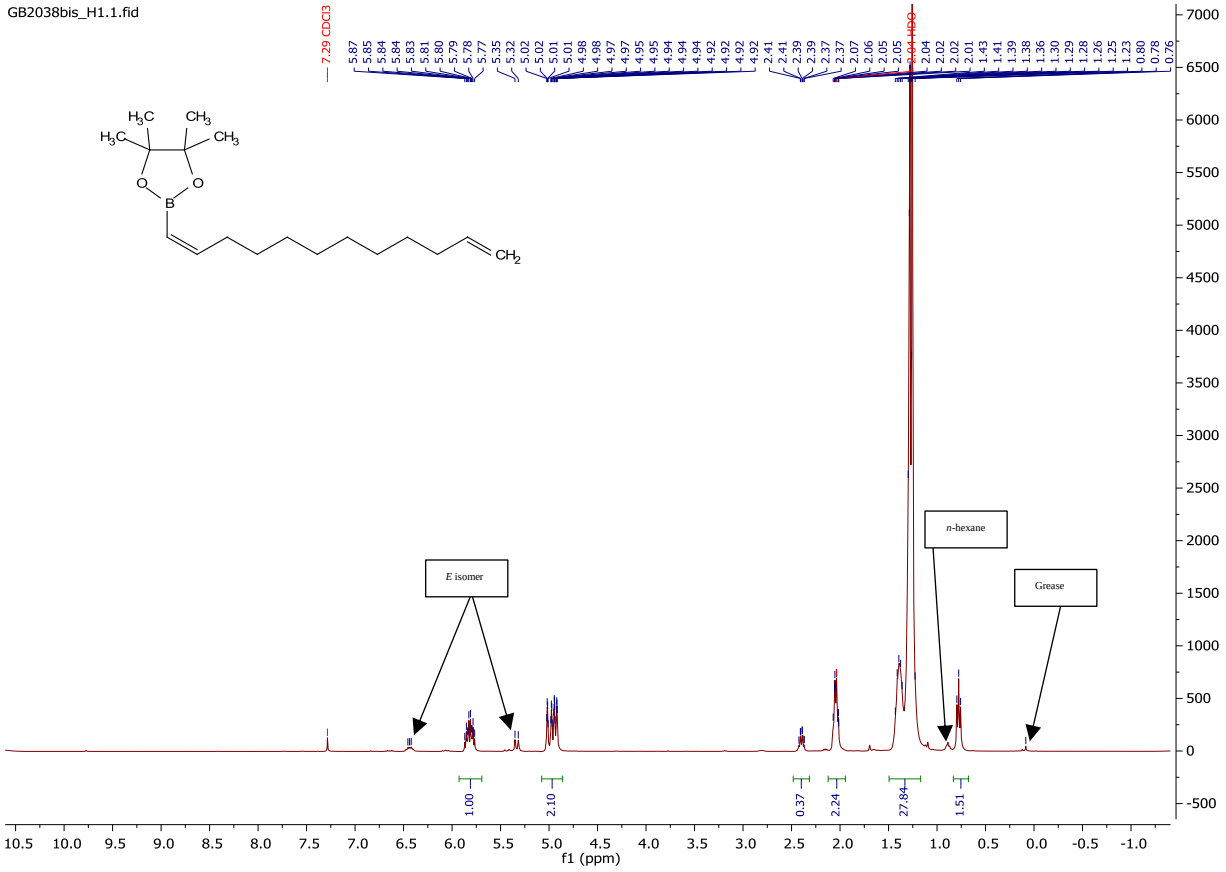
Molecule 3l

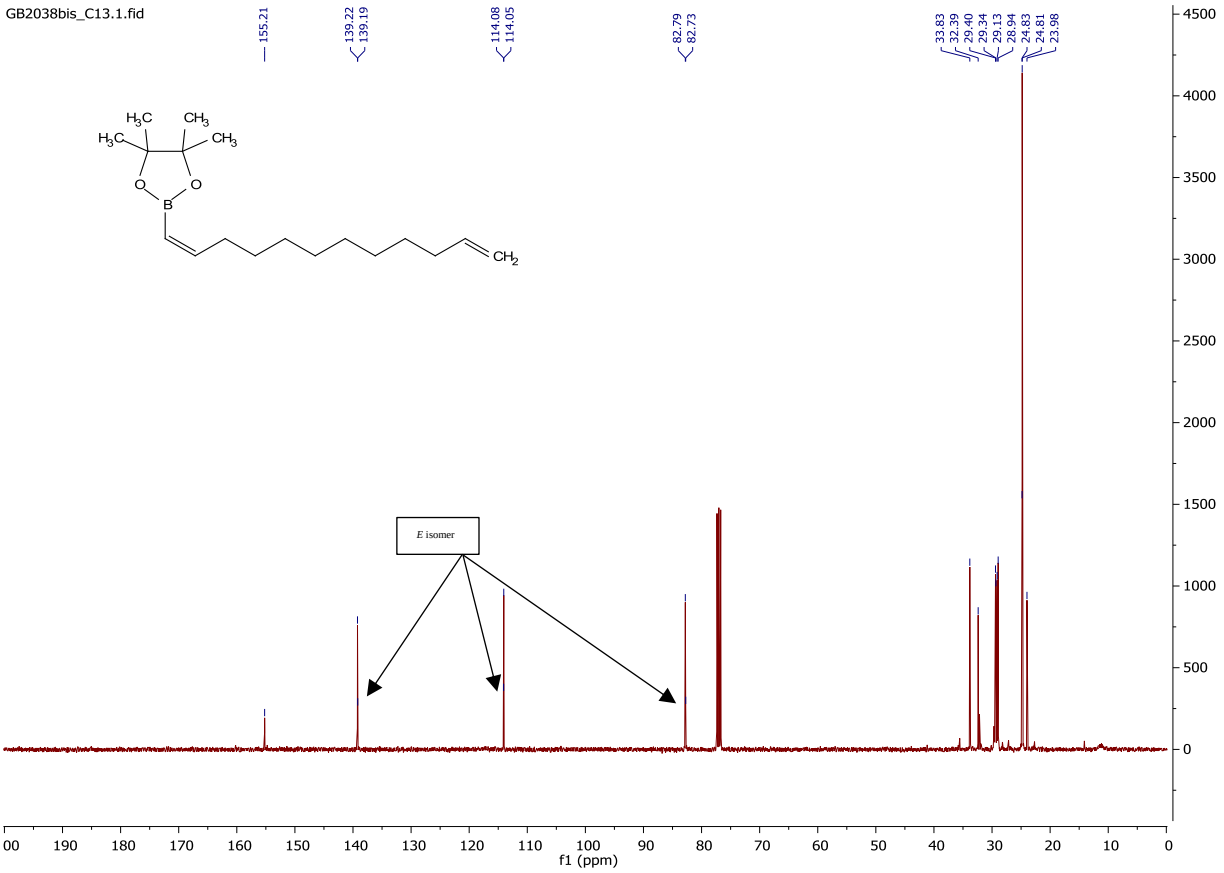

GB1143_H1.1.fid
7.28 CDCl3
1.71 HDO
E isomer
E isomer
E isomer
E isomer
Grease
1.00
1.19
2.20
53.96
9.04
f1 (ppm)

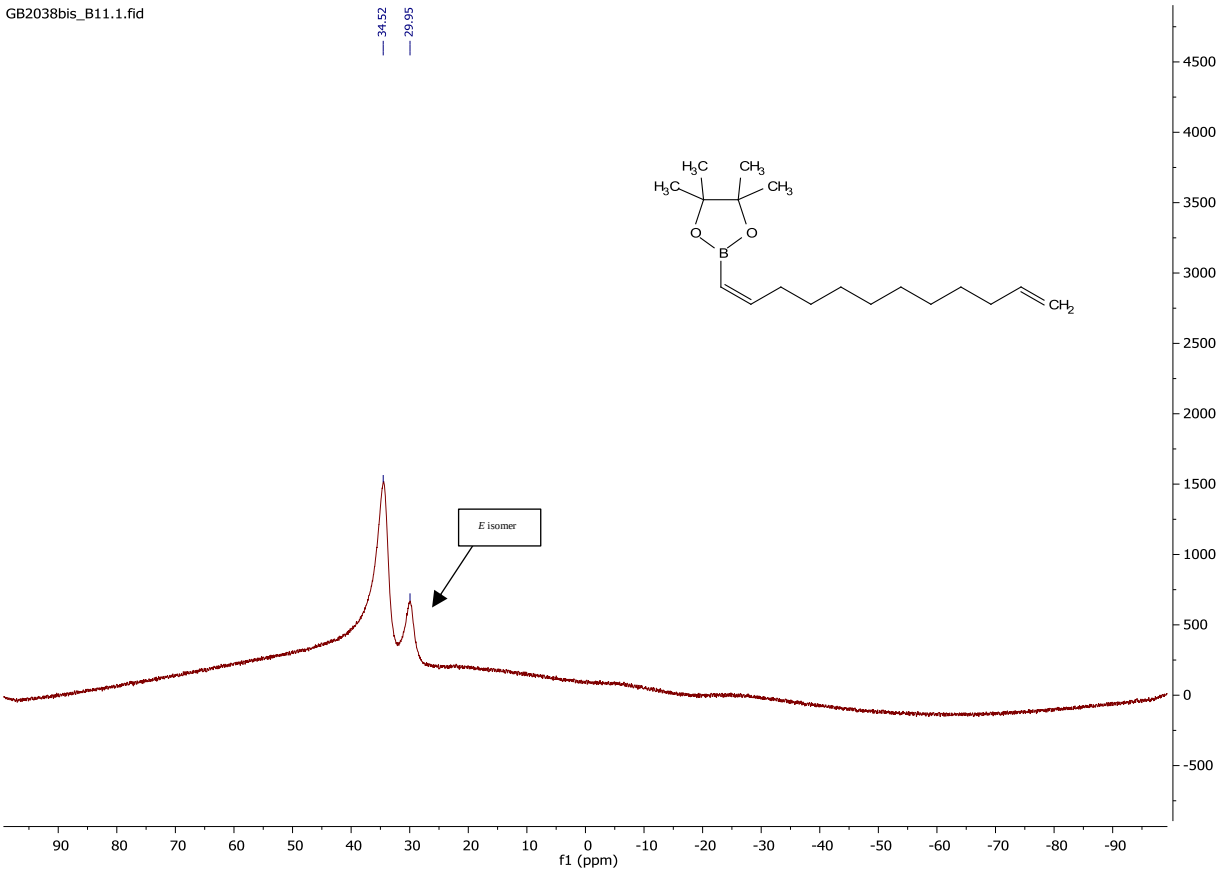

GB1143_C13.1.fid
155.24
82.72
31.92
31.90
29.46
29.40
29.38
29.28
29.06
24.82
24.80
24.76
22.68
14.10
H3C
CH3
H3C
CH3
O
O
B
CH3
f1 (ppm)


GB1143_B11.1.fid
34.29
29.92
E isomer
H3C
CH3
H3C
CH3
O
O
B
CH3
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

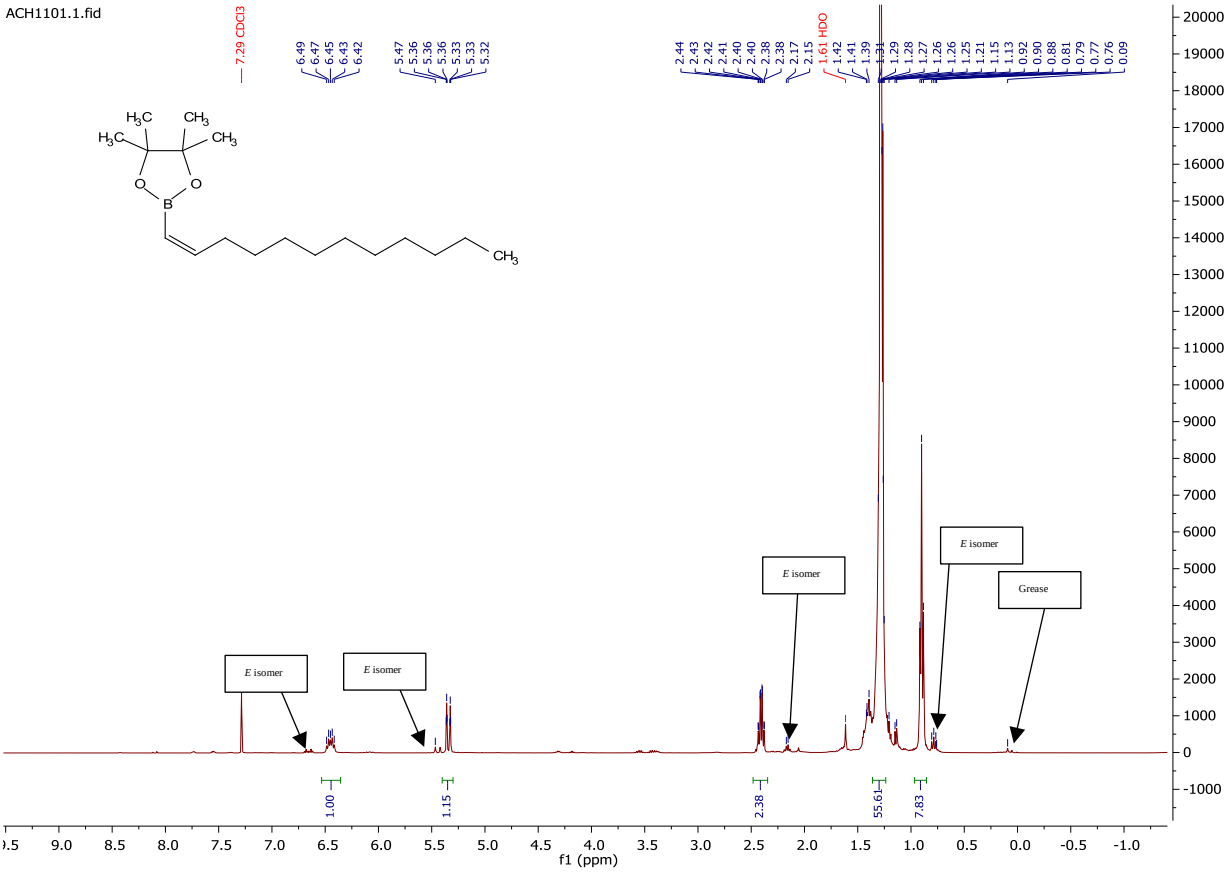
Molecule 3m

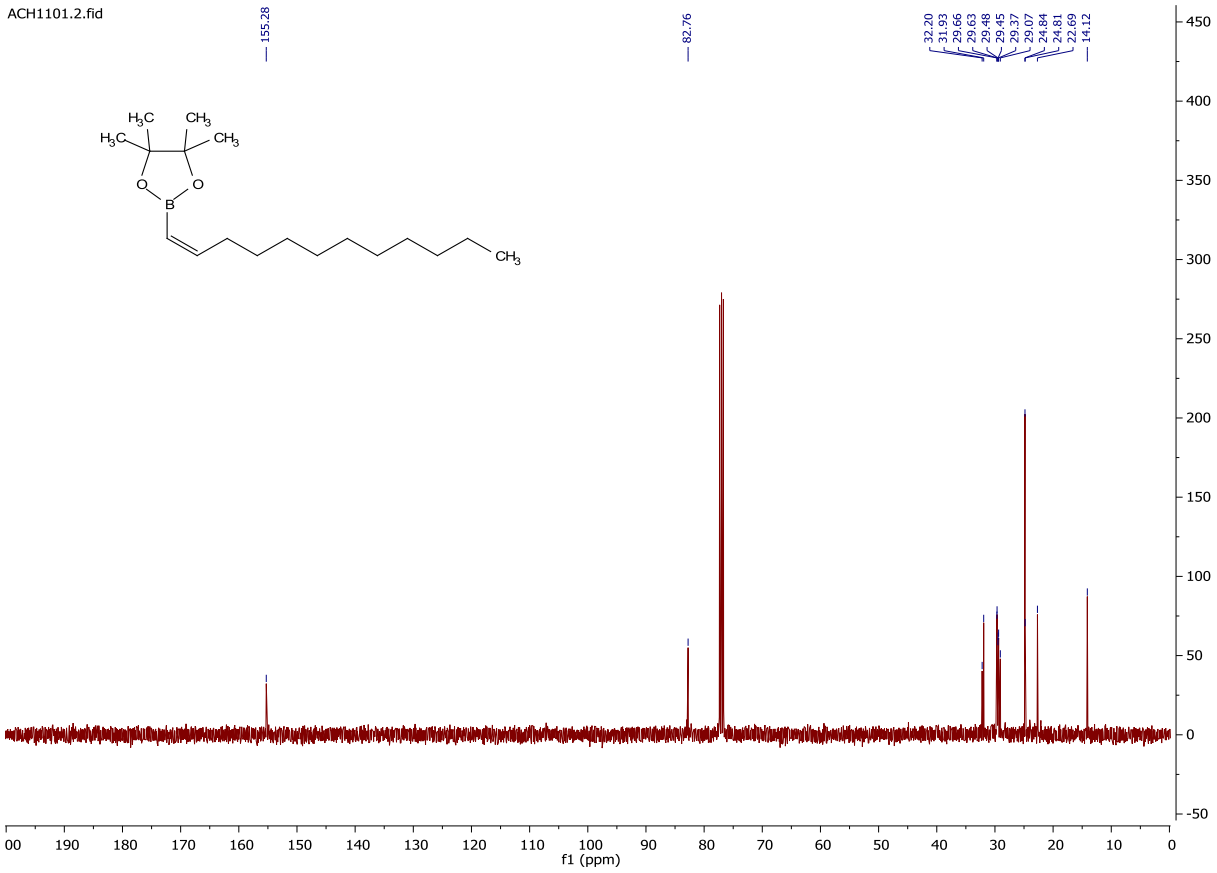

GB2038bis_H1.1.fid
7.29 CDCl3
2.04 H2O
n-hexane
E isomer
Grease
1.00
2.10
0.37
2.24
27.84
1.51
f1 (ppm)

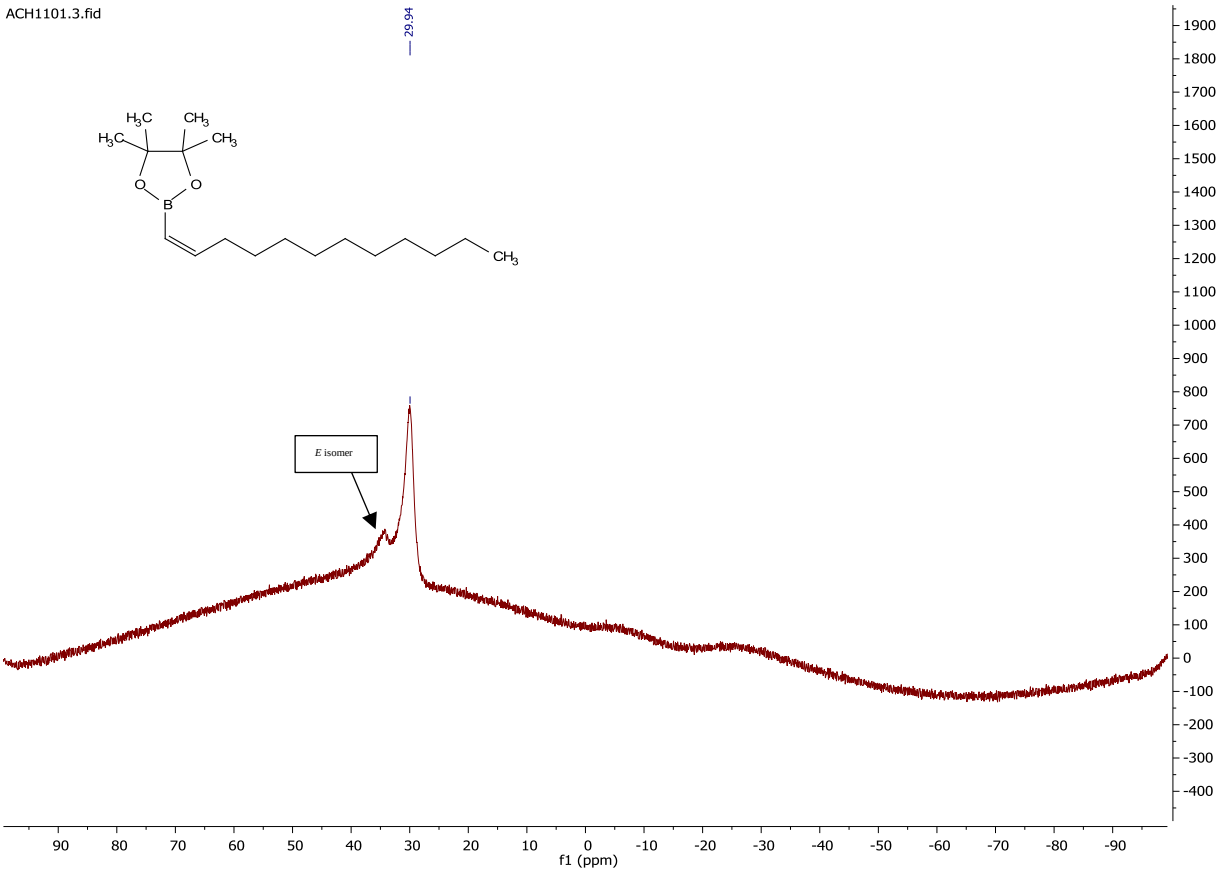

GB2038bis_C13.1.fid
155.21
139.22
139.19
114.08
114.05
82.79
82.73
33.83
32.39
29.40
29.34
29.13
28.94
24.83
24.81
23.98
H3C
CH3
H3C
CH3
O
O
B
CH2
E isomer
4500
4000
3500
3000
2500
2000
1500
1000
500
0
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


GB2038bis_B11.1.fid
34.52
29.95
H3C
CH3
H3C
CH3
O
O
B
CH2
E isomer
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

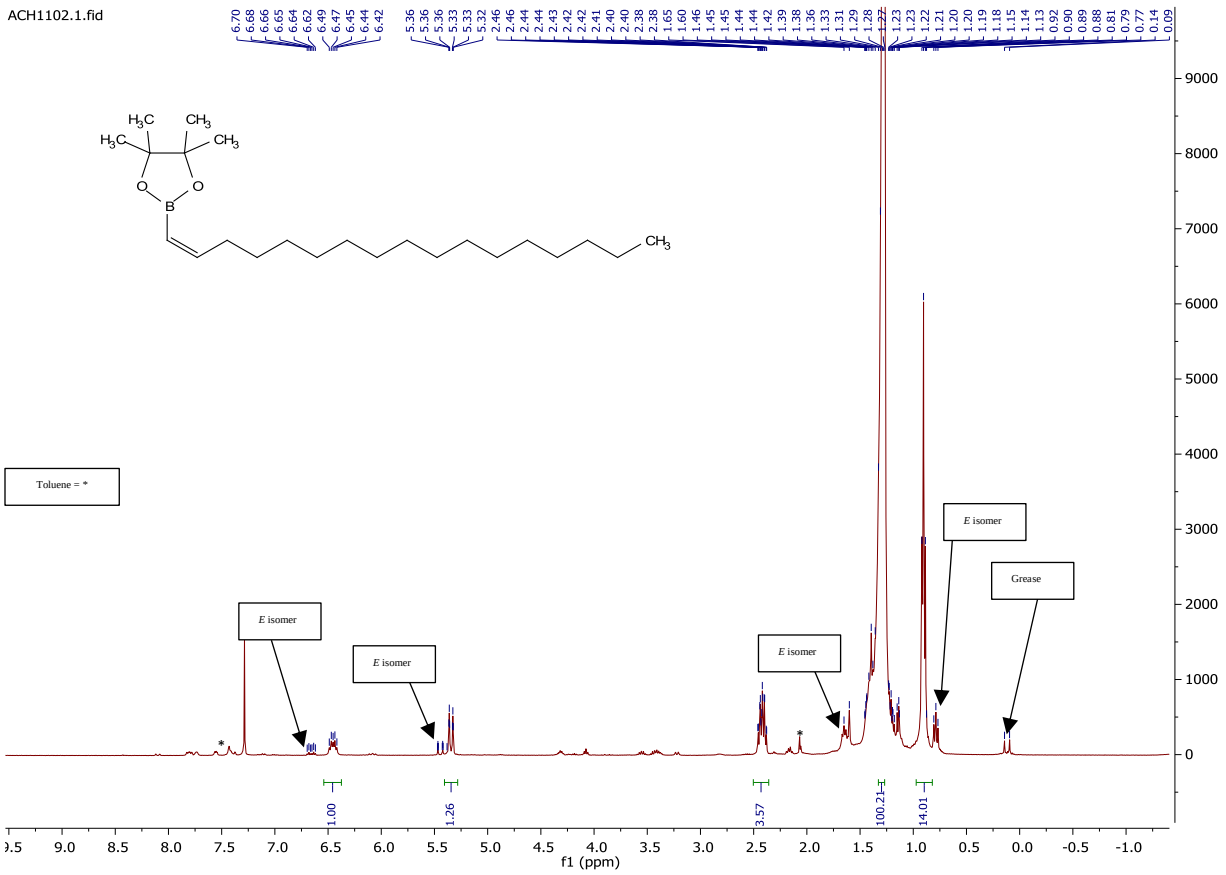
Molecule 3n

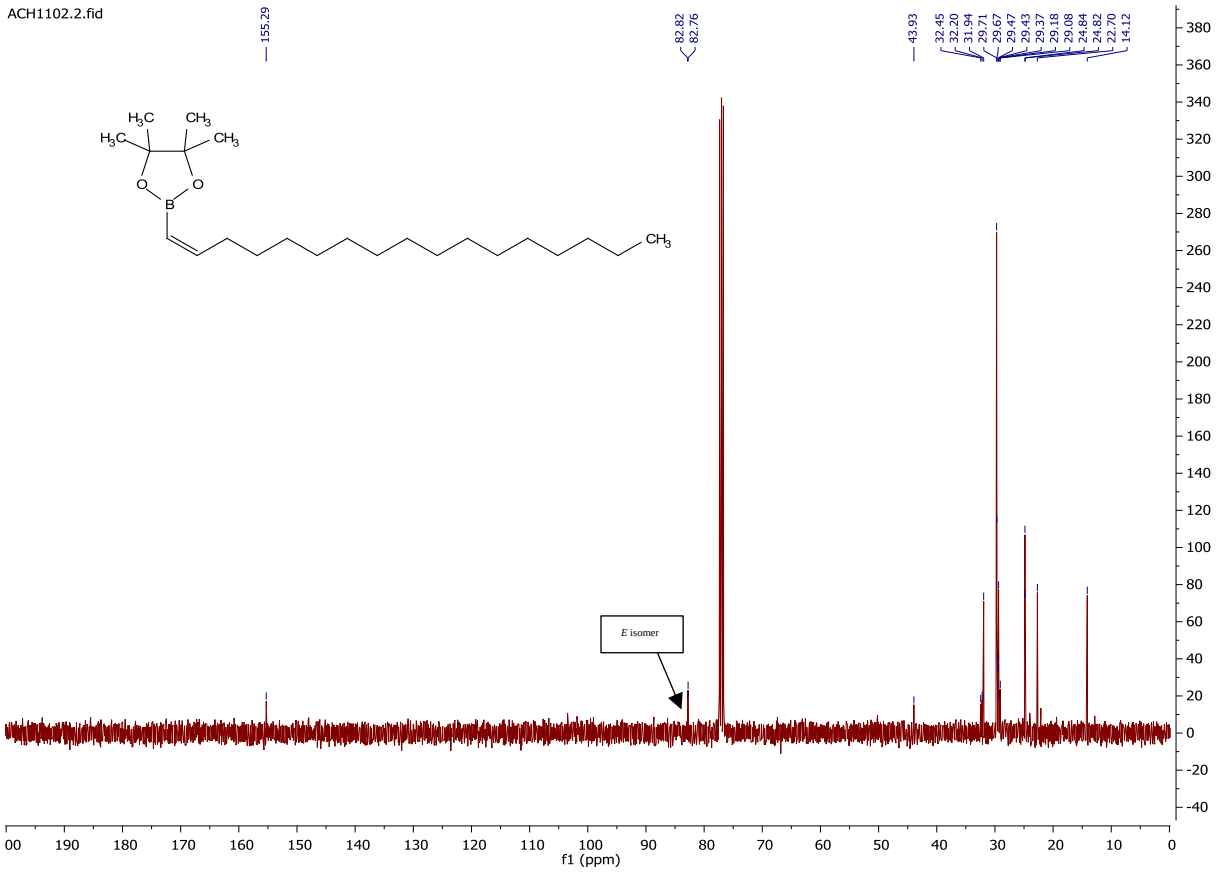

ACH1101.1.fid
7.29 CDCl3
6.49
6.47
6.45
6.43
6.42
5.47
5.36
5.36
5.36
5.33
5.33
5.32
2.44
2.43
2.42
2.41
2.40
2.40
2.38
2.38
2.17
2.15
1.61 HDO
1.42
1.41
1.39
1.31
1.29
1.28
1.27
1.26
1.26
1.25
1.21
1.15
1.13
0.92
0.90
0.88
0.81
0.79
0.77
0.76
0.09
H3C
CH3
H3C
CH3
O
O
B
CH3
E isomer
E isomer
E isomer
E isomer
Grease
1.00
1.15
2.38
55.61
7.83
f1 (ppm)

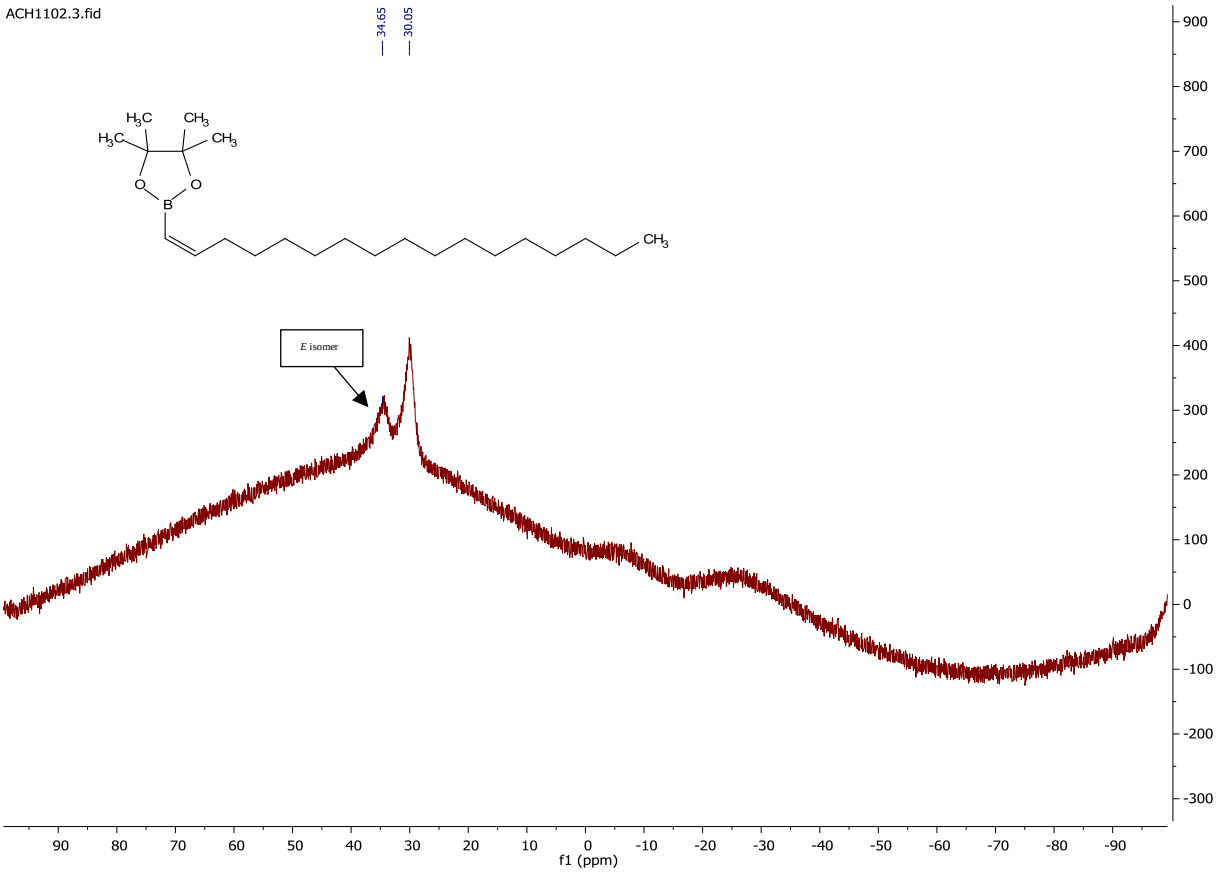

ACH1101.2.fid
155.28
82.76
32.20
31.93
29.66
29.63
29.48
29.45
29.37
29.07
24.84
24.81
22.69
14.12
H3C
CH3
H3C
CH3
O
O
B
CH3
450
400
350
300
250
200
150
100
50
0
-50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


ACH1101.3.fid
29.94
E isomer
f1 (ppm)

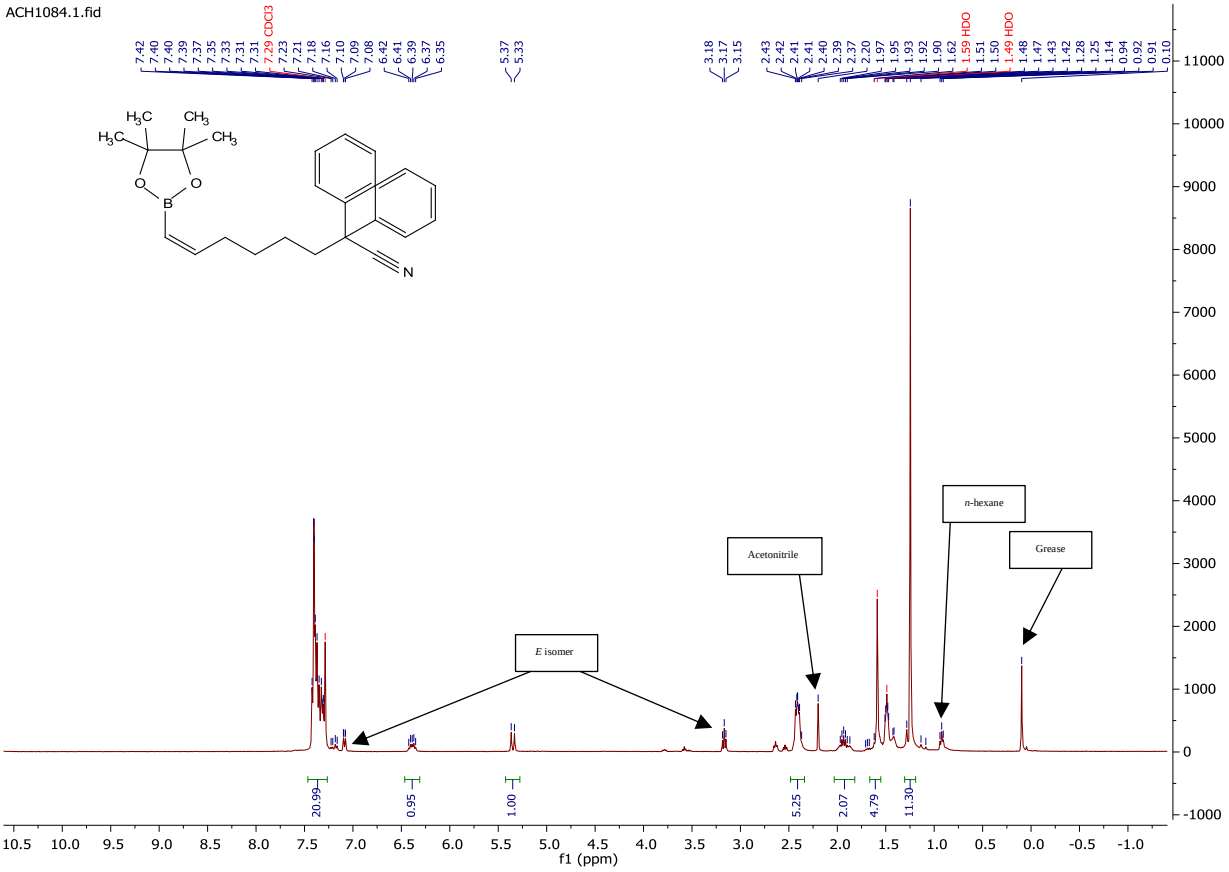
Molecule 3o

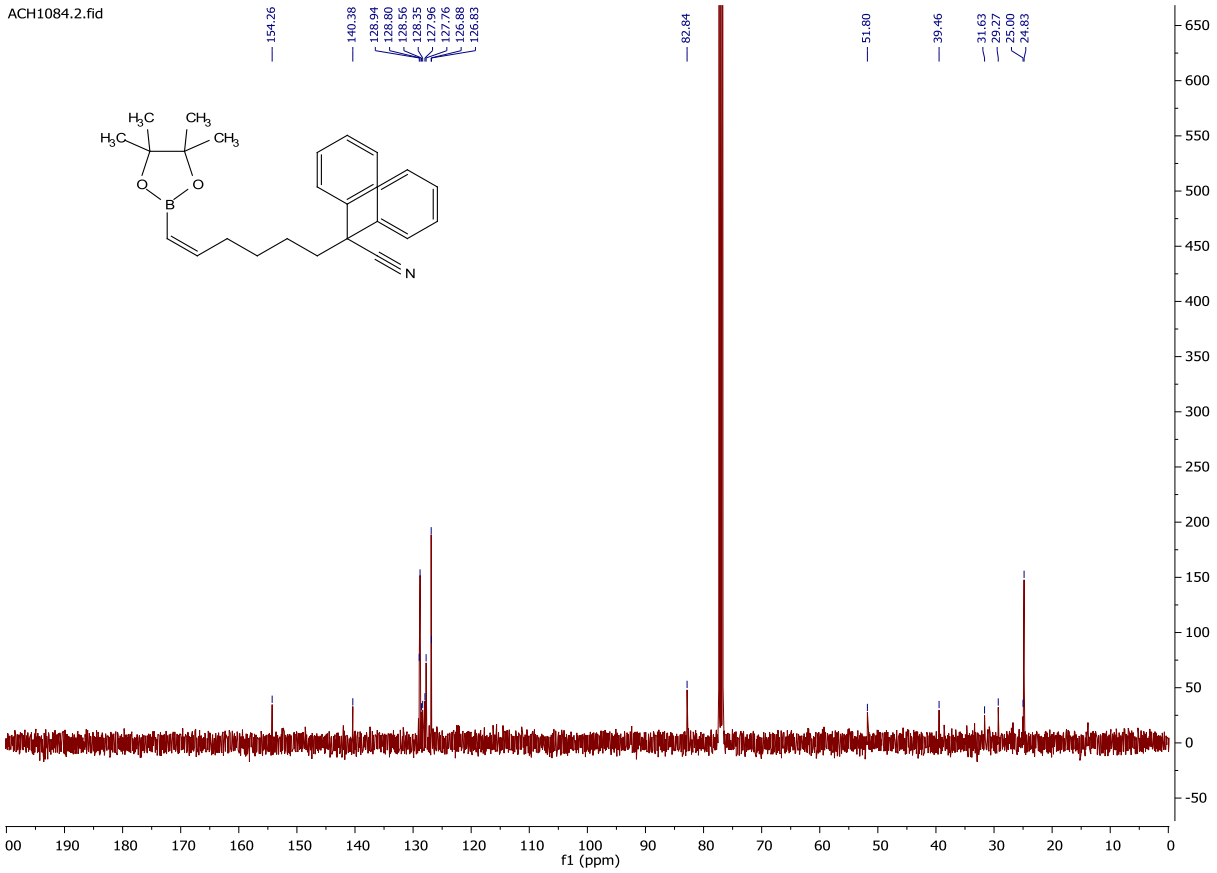

ACH1102.1.fid
Toluene = *
E isomer
E isomer
E isomer
E isomer
Grease
1.00
1.26
3.57
100.21
14.01
f1 (ppm)

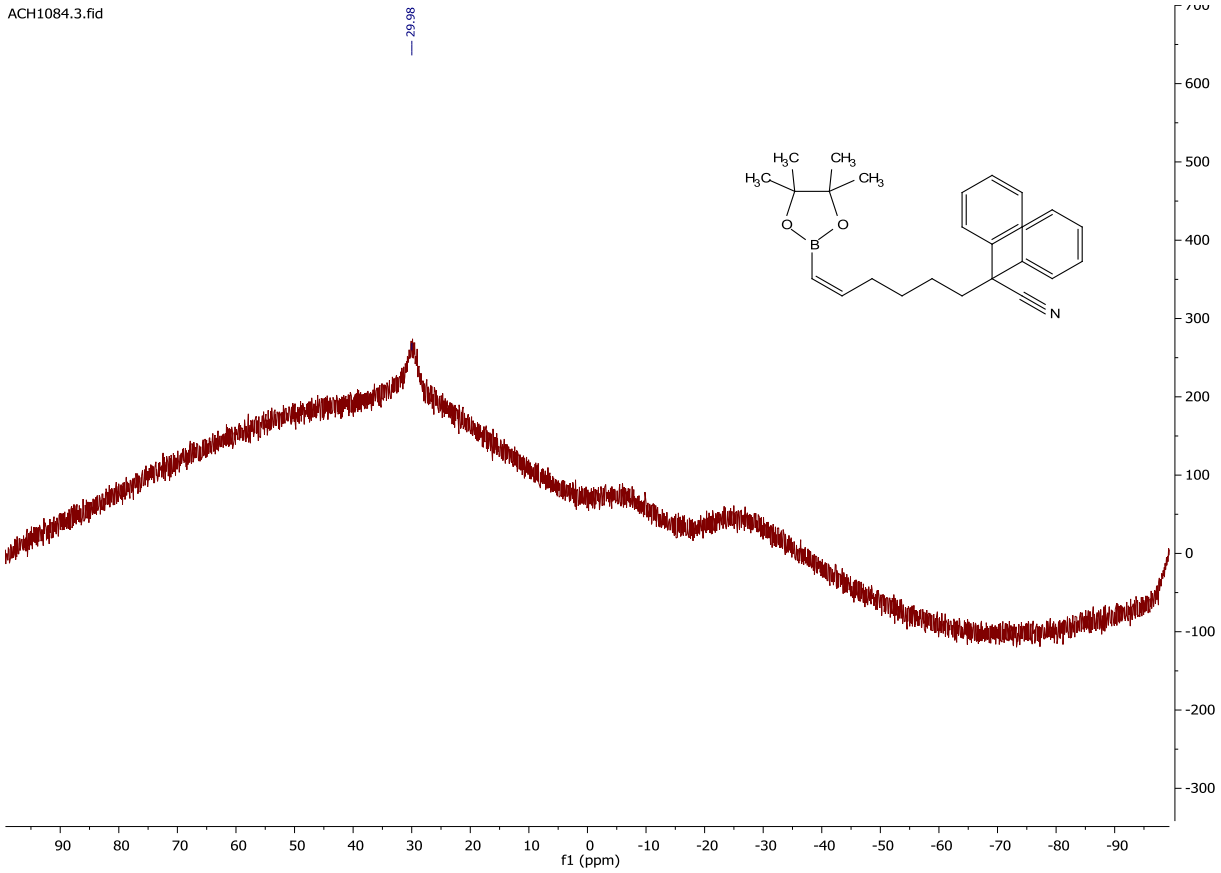

ACH1102.2.fid
155.29
82.82
82.76
43.93
32.45
32.20
31.94
29.71
29.67
29.47
29.43
29.37
29.18
29.08
24.84
24.82
22.70
14.12
H3C
CH3
H3C
CH3
O
O
B
CH3
E isomer
f1 (ppm)


ACH1102.3.fid
34.65
30.05
H3C
CH3
H3C
CH3
O
O
B
CH3
E isomer
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

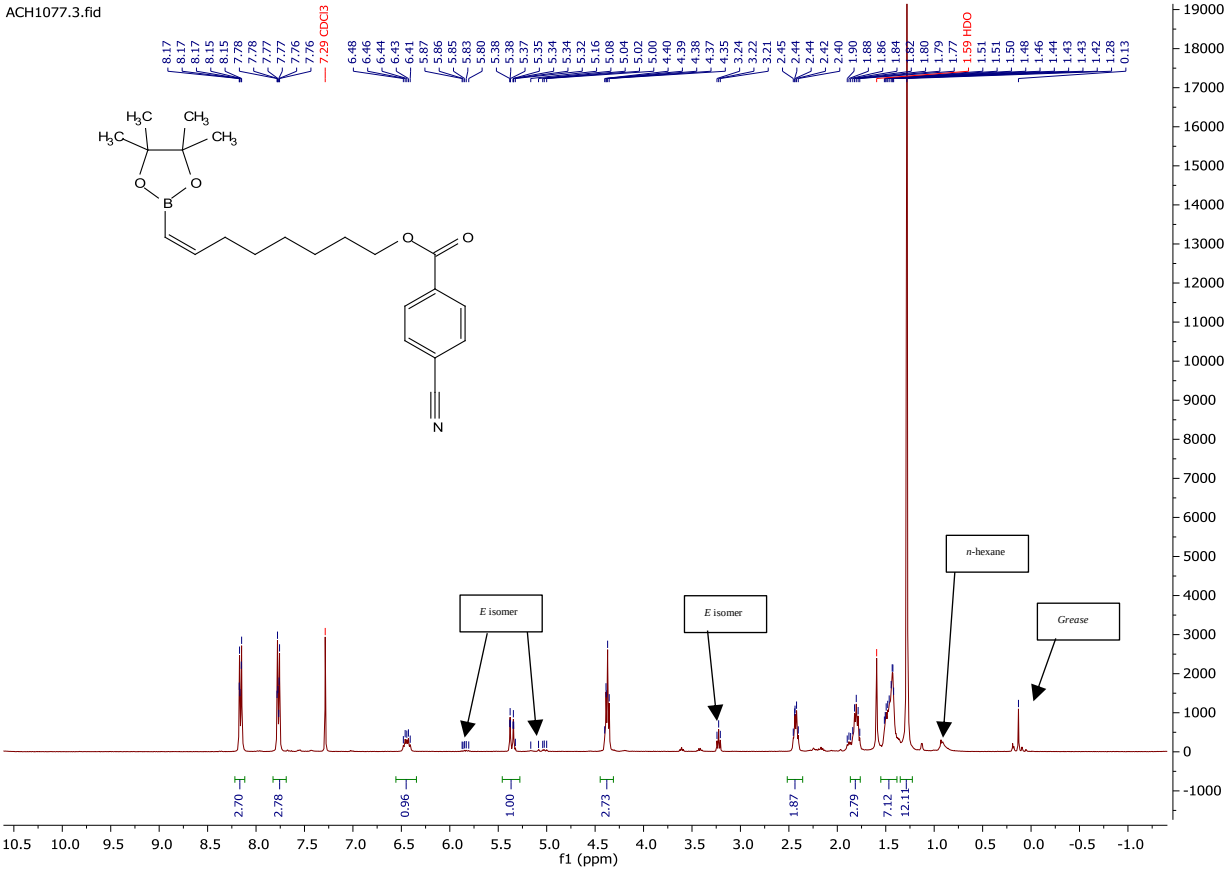
Molecule 3p

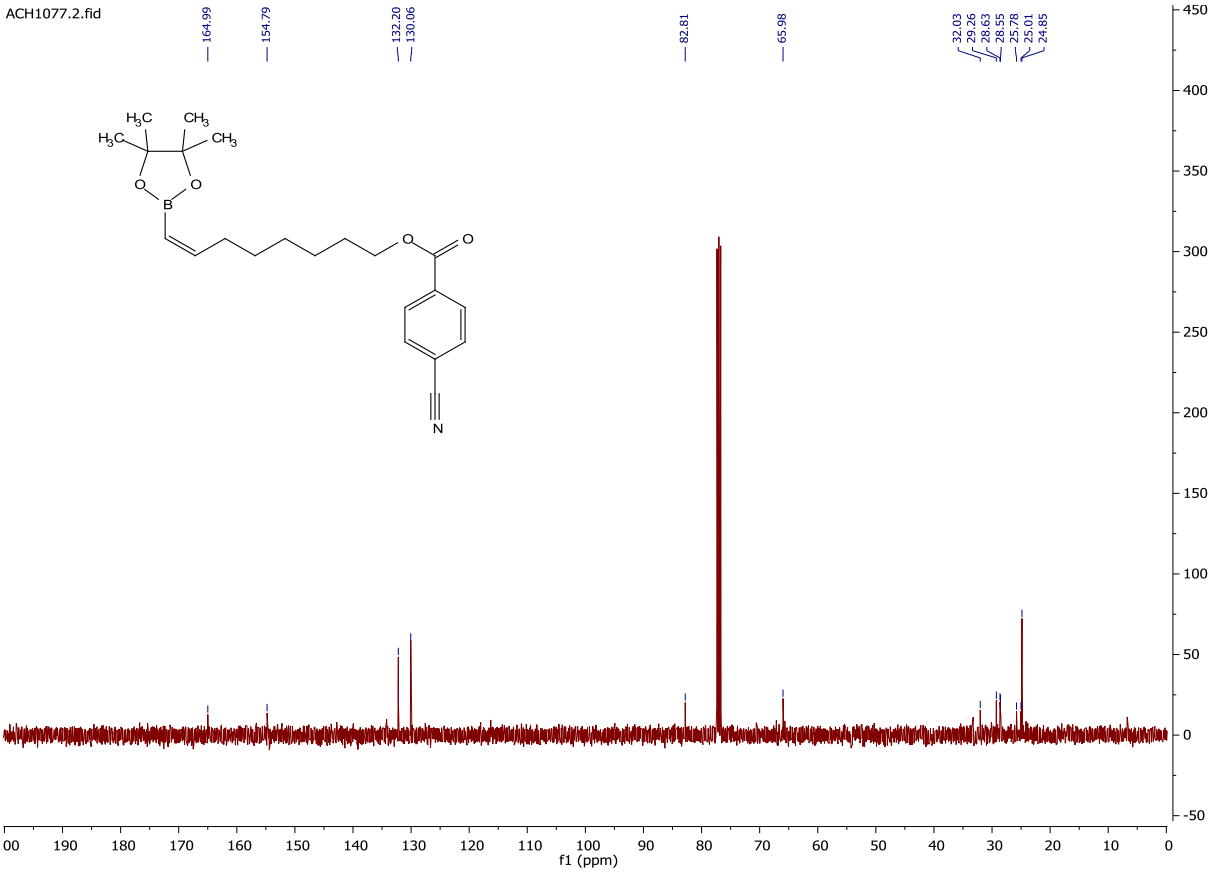

ACH1084.1.fid
CDCl3
HDO
HDO
E isomer
Acetonitrile
n-hexane
Grease
20.99
0.95
1.00
5.25
2.07
4.79
11.30
f1 (ppm)

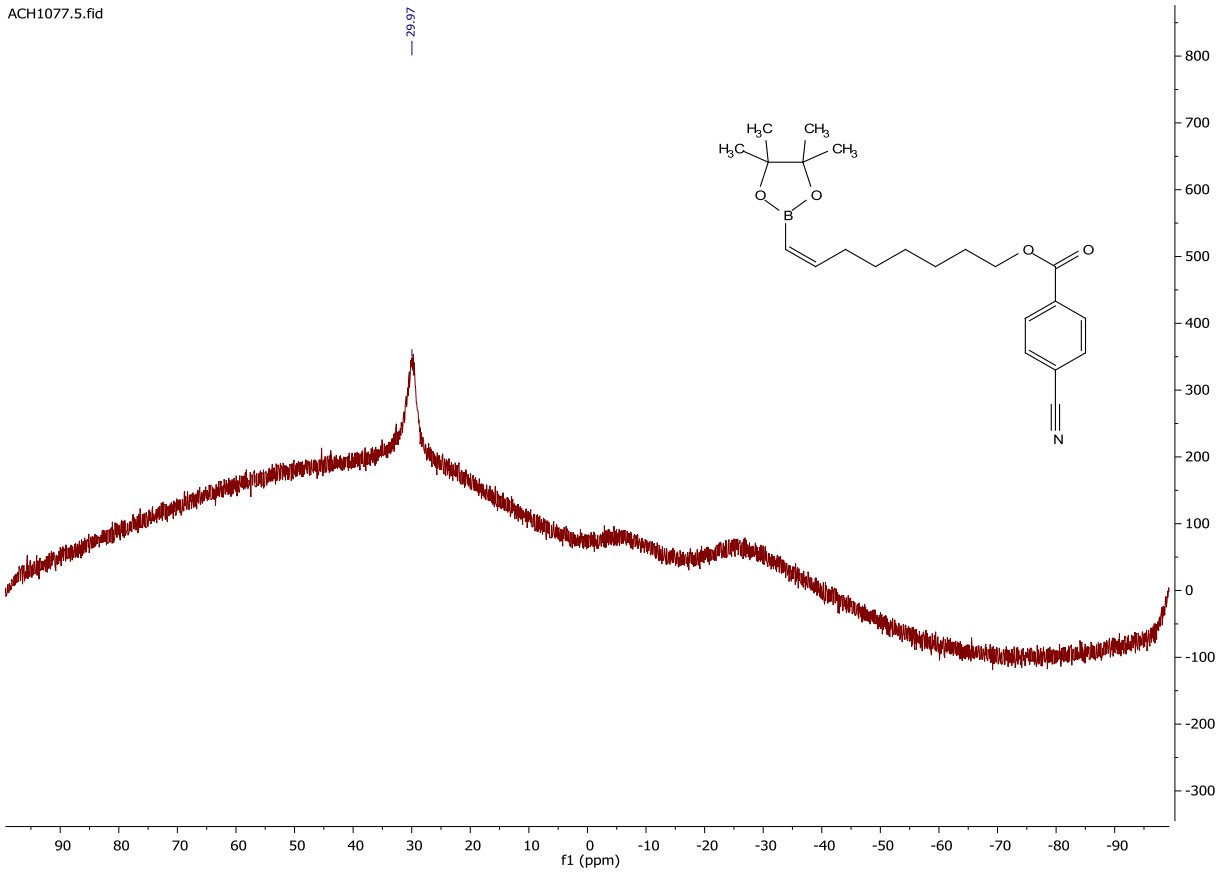

ACH1084.2.fid
154.26
140.38
128.94
128.80
128.56
128.35
127.96
127.76
126.88
126.83
82.84
51.80
39.46
31.63
29.27
25.00
24.83
H3C
CH3
H3C
CH3
O
O
B
N
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


ACH1084.3.fid
29.98
H3C
CH3
H3C
CH3
O
O
B
N
600
500
400
300
200
100
0
-100
-200
-300
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

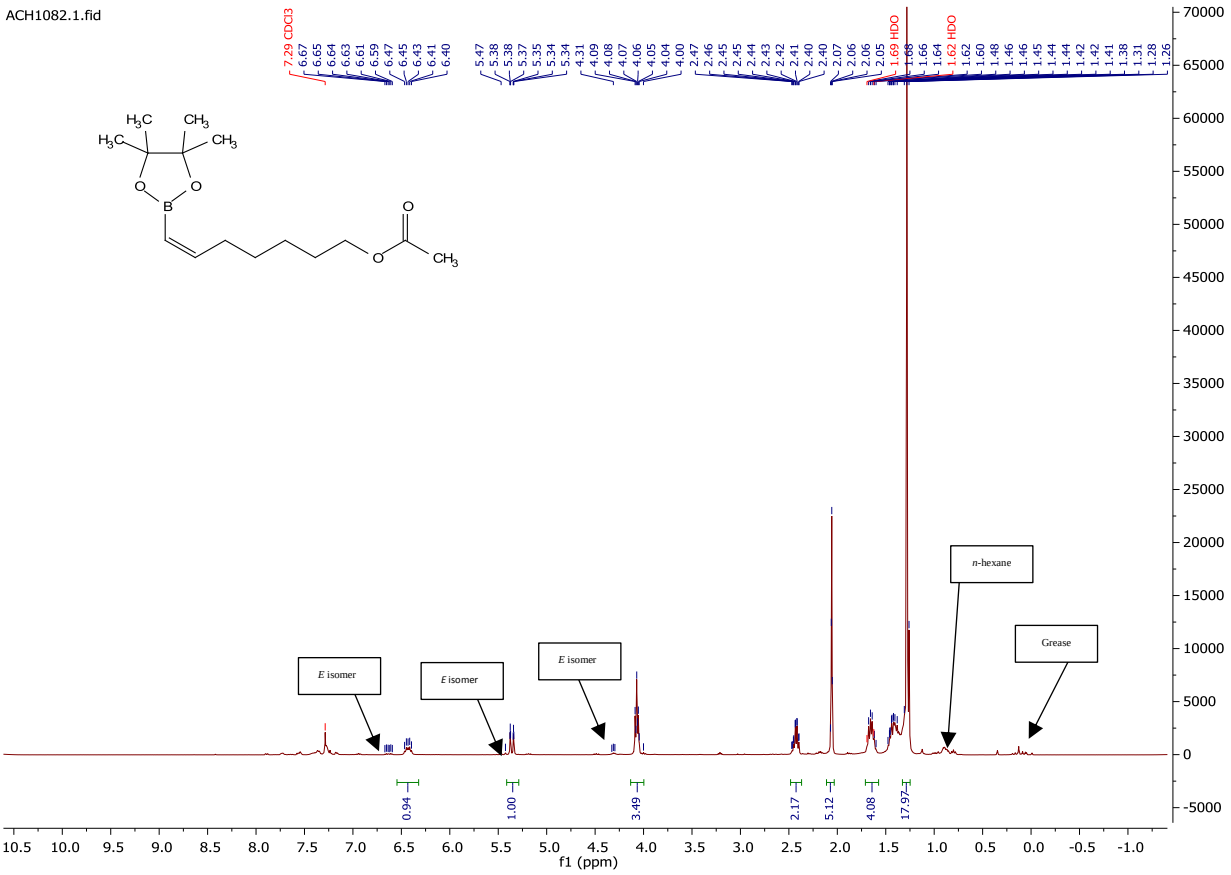
Molecule 3q

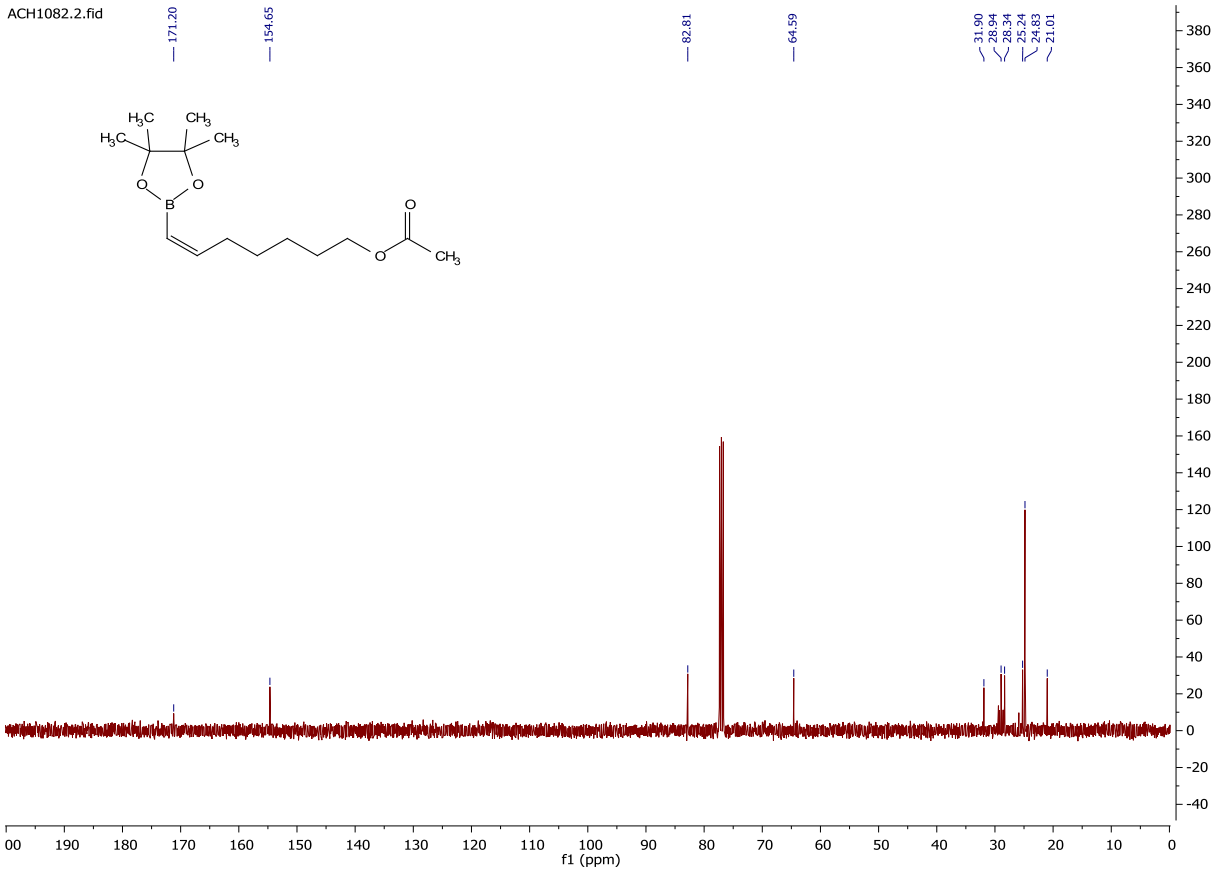


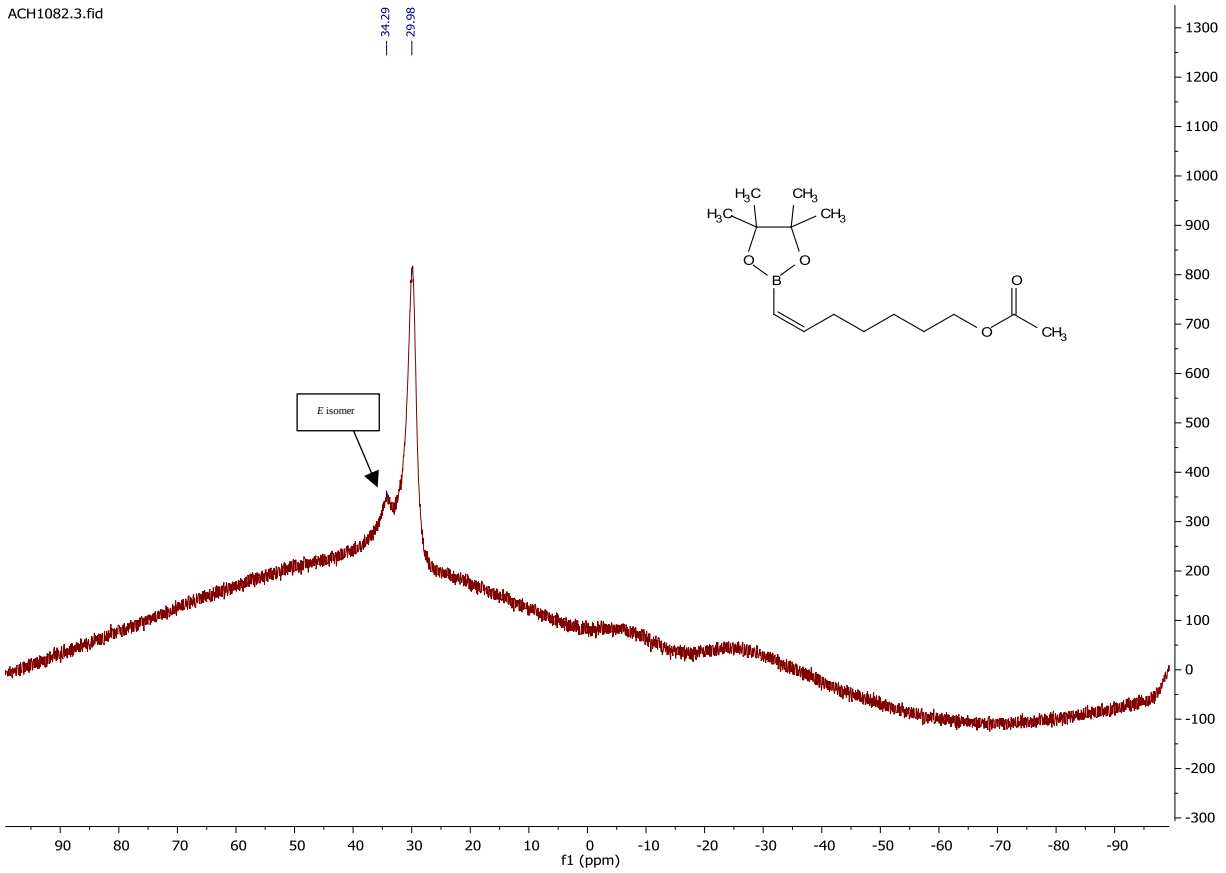

ACH1077.2.fid
164.99
154.79
132.20
130.06
82.81
65.98
32.03
29.26
28.63
28.55
25.78
25.01
24.85
H3C
CH3
H3C
CH3
O
O
B
O
O
N
450
400
350
300
250
200
150
100
50
0
-50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


ACH1077.5.fid
29.97
800
700
600
500
400
300
200
100
0
-100
-200
-300
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)
H3C
CH3
H3C
CH3
O
O
B
O
O
N

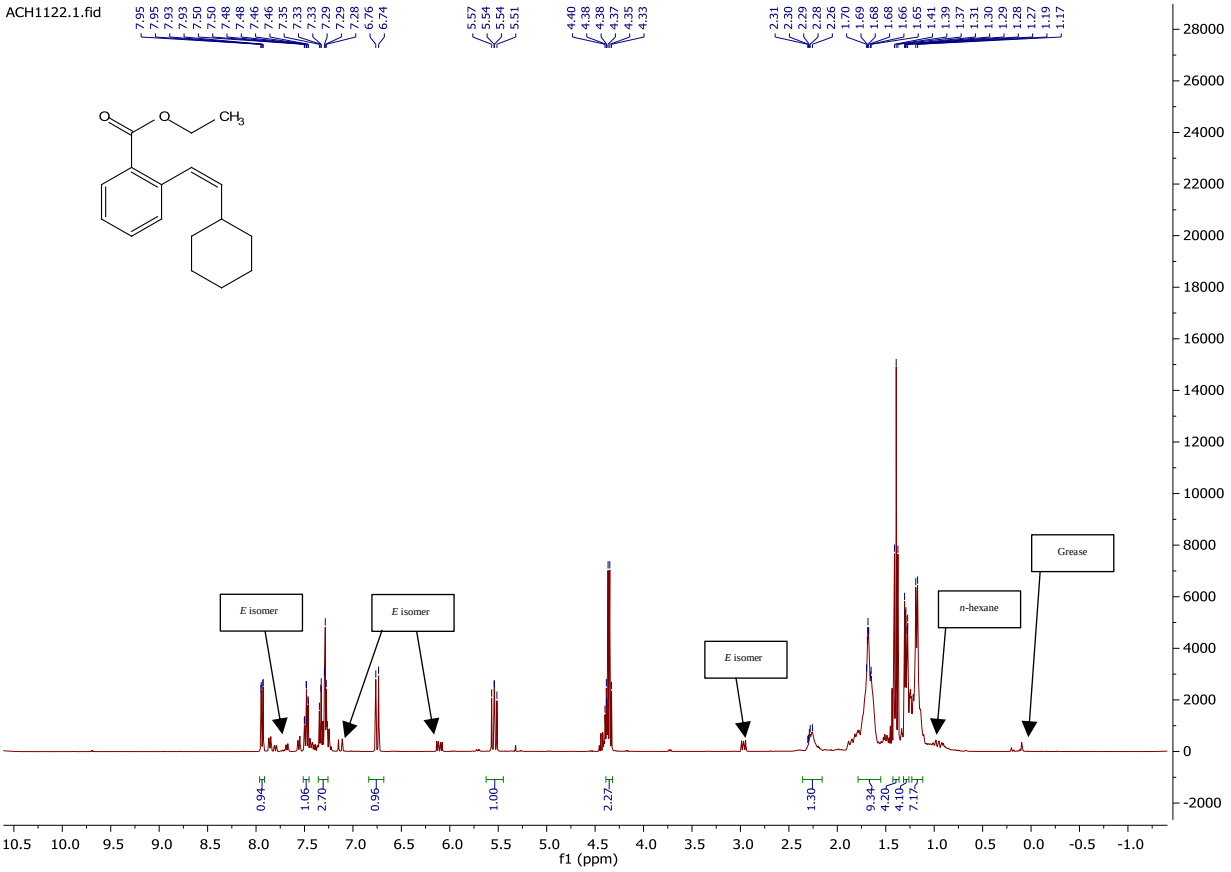
Molecule 3r

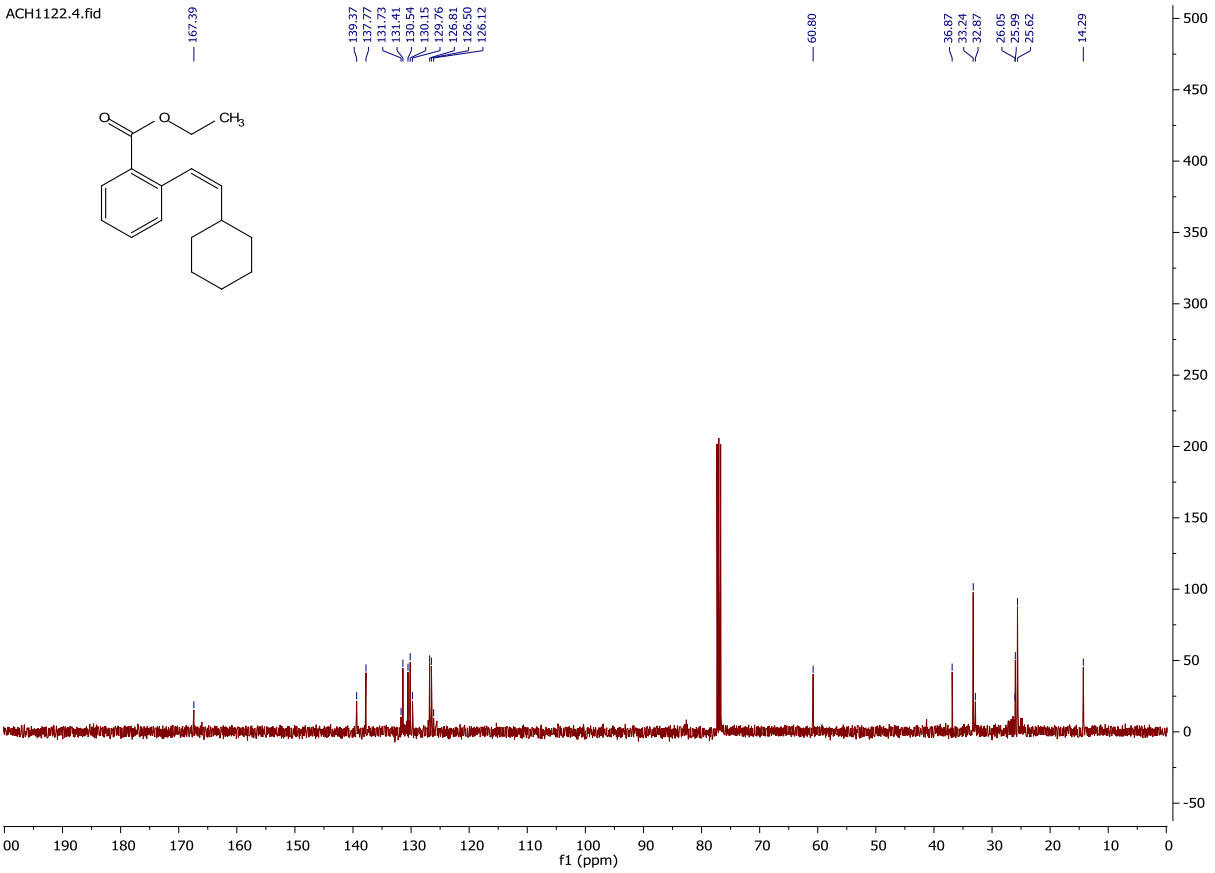

ACH1082.1.fid
7.29 CDCl3
1.69 HDO
1.62 HDO
E isomer
E isomer
E isomer
n-hexane
Grease
0.94
1.00
3.49
2.17
5.12
4.08
17.97
f1 (ppm)


ACH1082.2.fid
171.20
154.65
82.81
64.59
31.90
28.94
28.34
25.24
24.83
21.01
f1 (ppm)

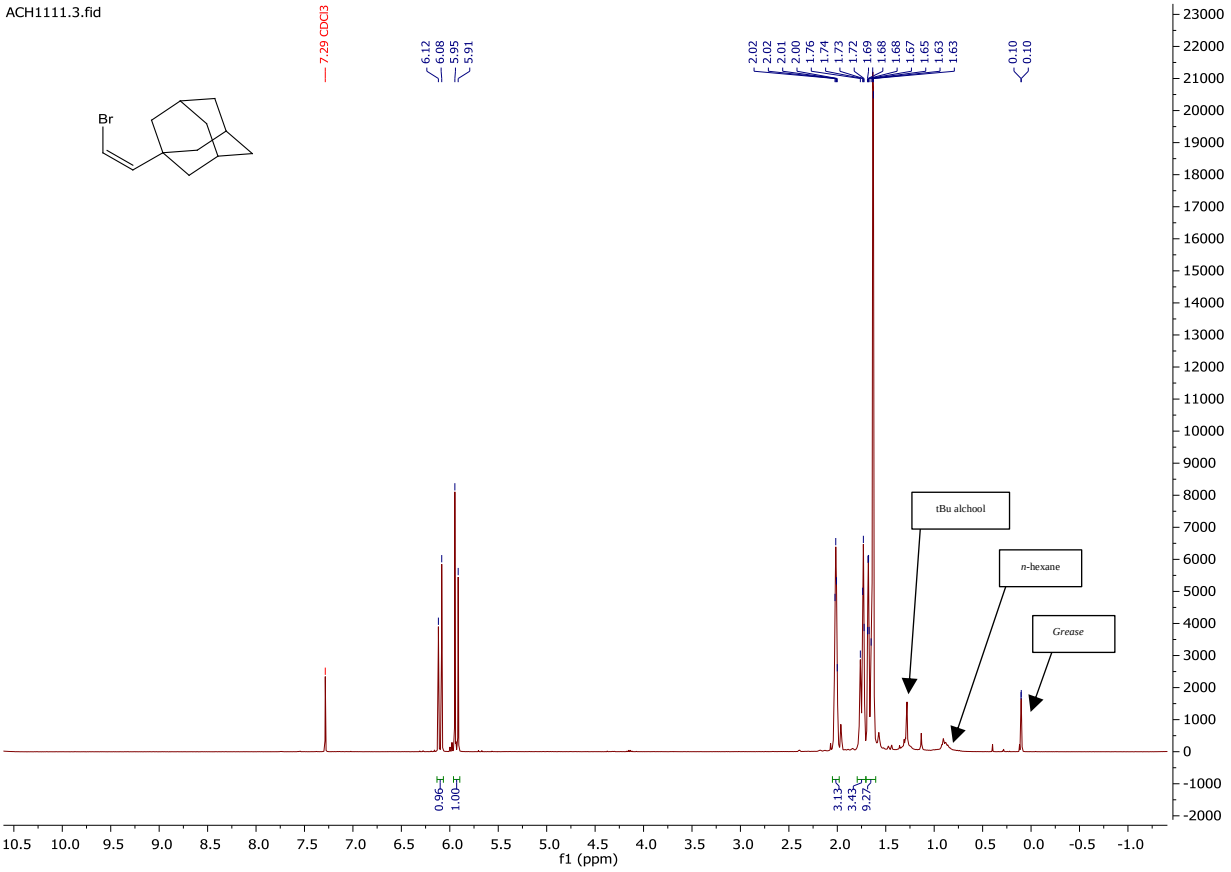

ACH1082.3.fid
34.29
29.98
E isomer
f1 (ppm)

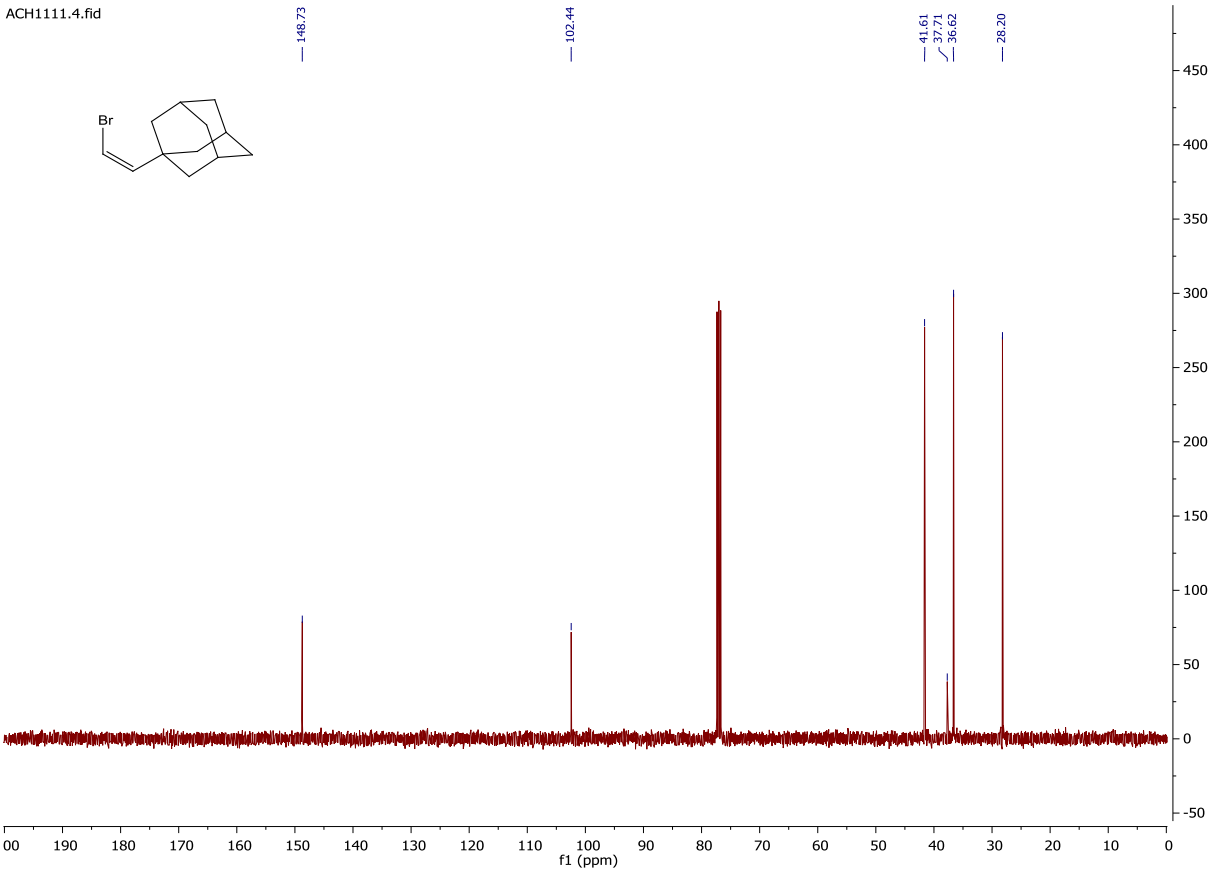
Molecule 5


ACH1122.1.fid
7.95 7.95 7.93 7.93 7.50 7.50 7.48 7.48 7.46 7.46 7.35 7.33 7.33 7.29 7.29 7.28 6.76 6.74
5.57 5.54 5.54 5.51
4.40 4.38 4.38 4.37 4.35 4.33
2.31 2.30 2.29 2.28 2.26 1.70 1.69 1.68 1.68 1.66 1.65 1.41 1.39 1.37 1.31 1.30 1.29 1.28 1.27 1.19 1.17
O
O
CH3
E isomer
E isomer
E isomer
n-hexane
Grease
0.94
1.06
2.70
0.96
1.00
2.27
1.30
9.34
4.20
4.10
7.17
f1 (ppm)

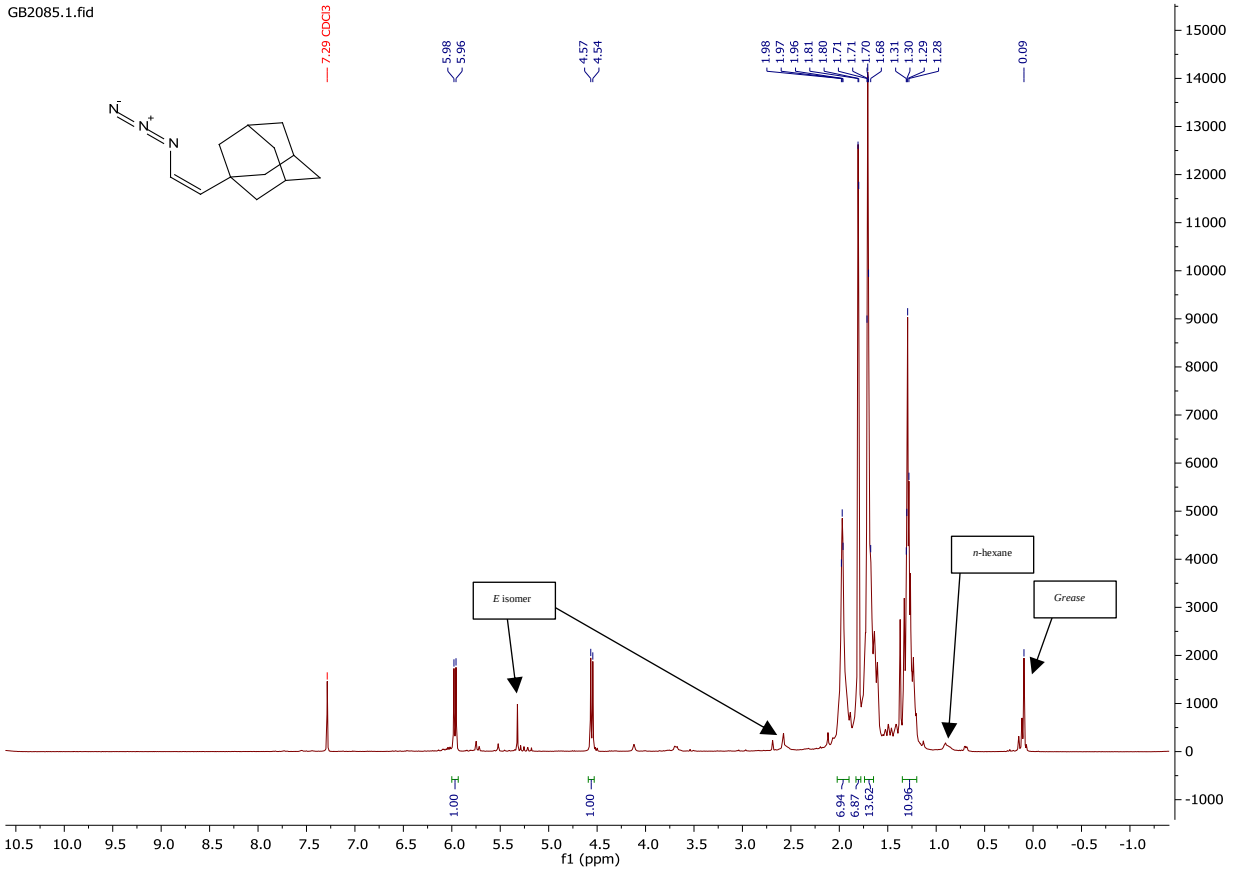

ACH1122.4.fid
167.39
139.37
137.77
131.73
131.41
130.54
130.15
129.76
126.81
126.50
126.12
60.80
36.87
33.24
32.87
26.05
25.99
25.62
14.29
O
O
CH3
500
450
400
350
300
250
200
150
100
50
0
-50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

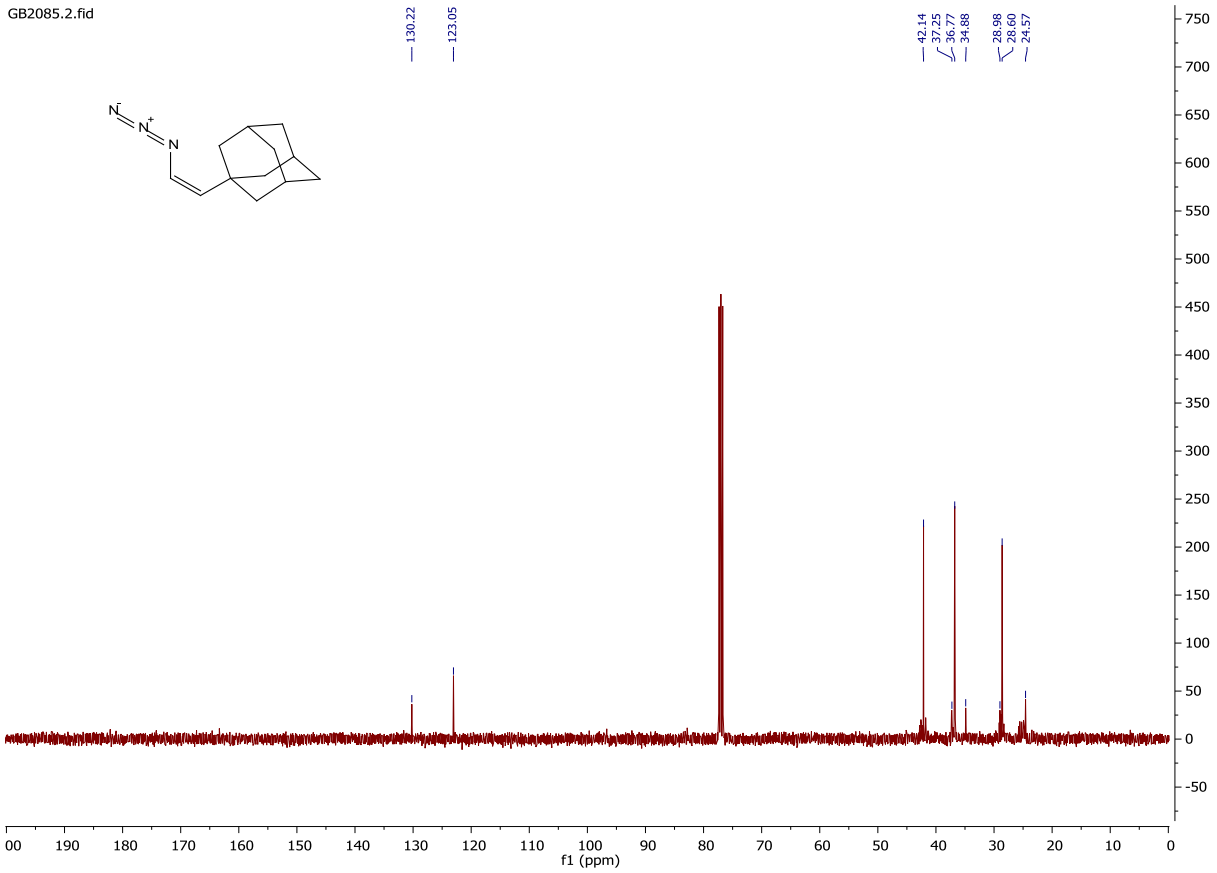
Molecule 6


ACH1111.3.fid
Br
7.29 CDCl3
6.12
6.08
5.95
5.91
2.02
2.02
2.01
2.00
1.76
1.74
1.73
1.72
1.69
1.68
1.68
1.67
1.65
1.63
1.63
0.10
0.10
tBu alchool
n-hexane
Grease
0.96
1.00
3.13
3.43
9.27
f1 (ppm)

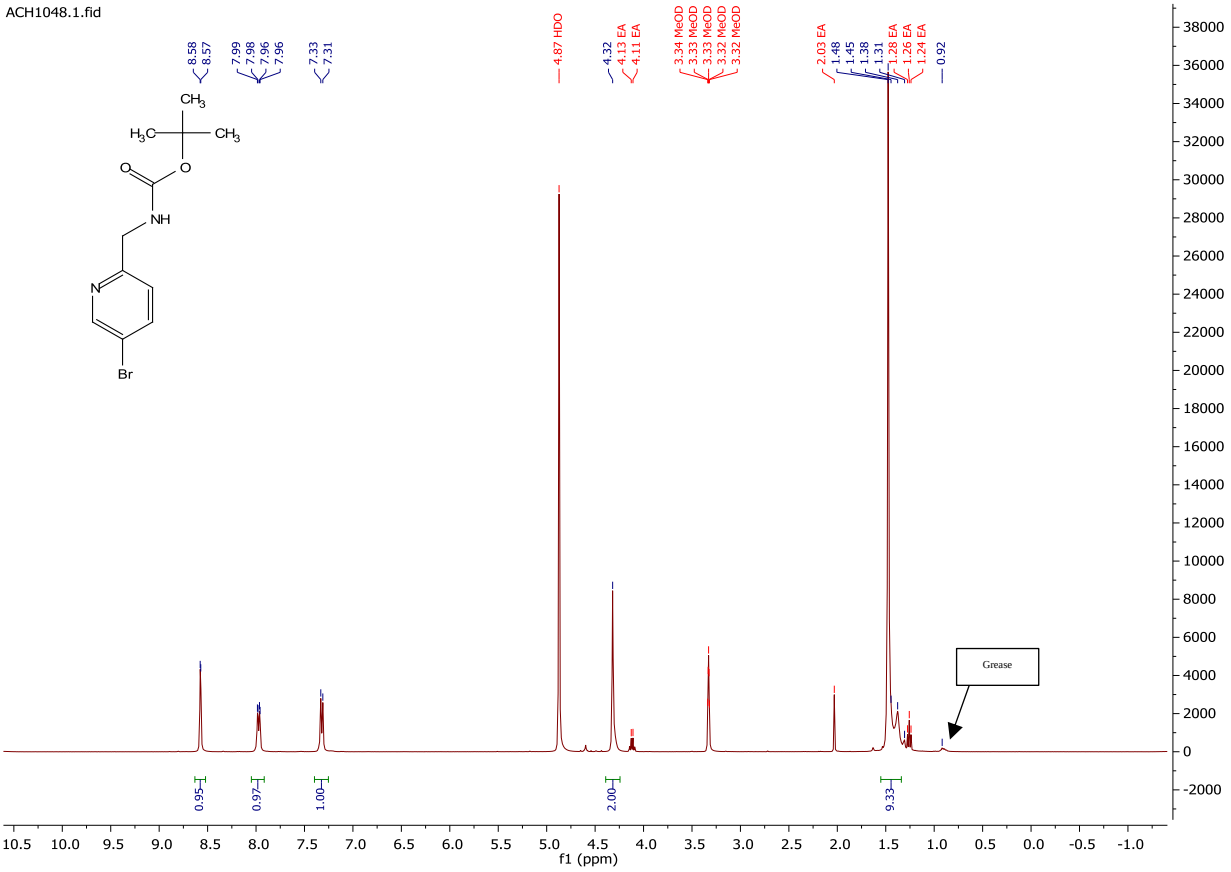

ACH1111.4.fid
148.73
102.44
41.61
37.71
36.62
28.20
Br
450
400
350
300
250
200
150
100
50
0
-50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

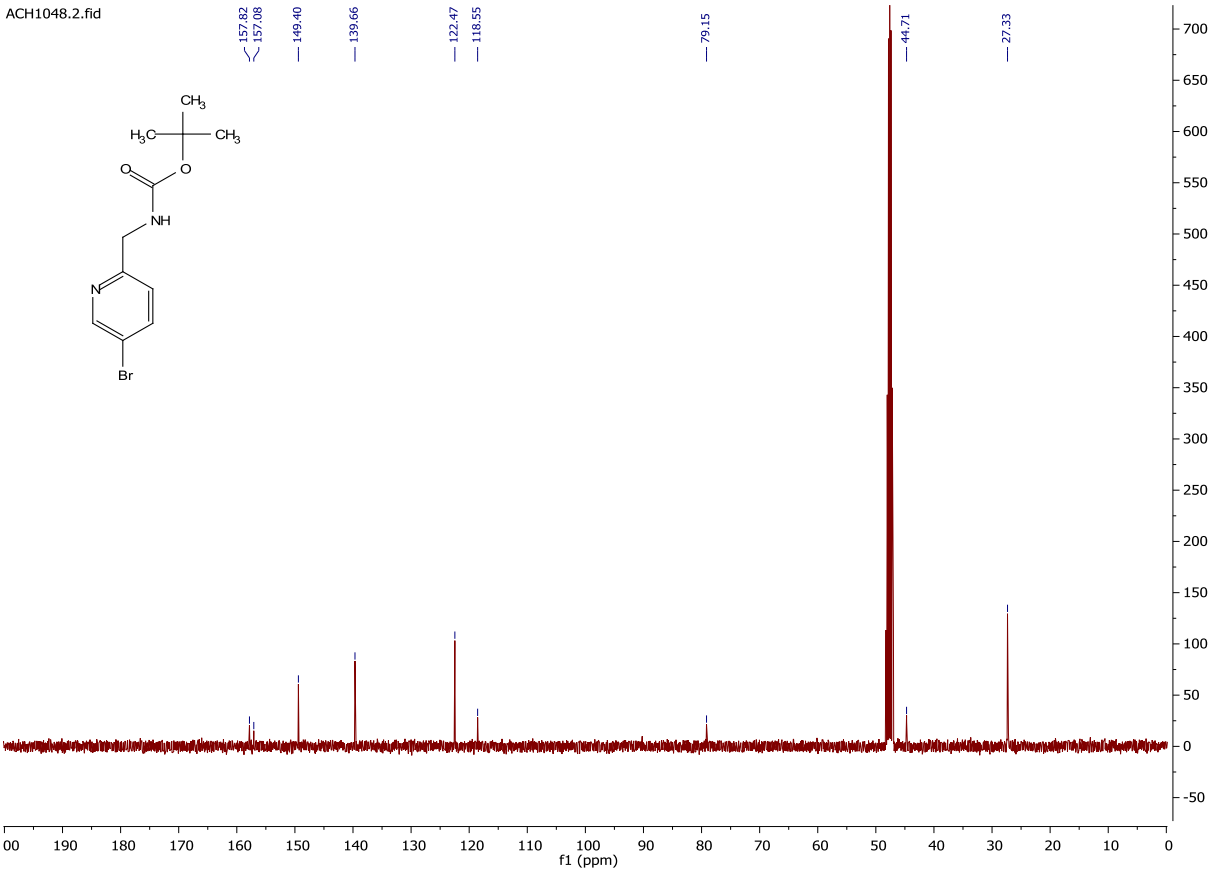
Molecule 7


GB2085.1.fid
7.29 CDCl3
5.98
5.96
4.57
4.54
1.98
1.97
1.96
1.81
1.80
1.71
1.71
1.70
1.68
1.31
1.30
1.29
1.28
0.09
E isomer
n-hexane
Grease
1.00
1.00
6.94
6.87
13.62
10.96
f1 (ppm)

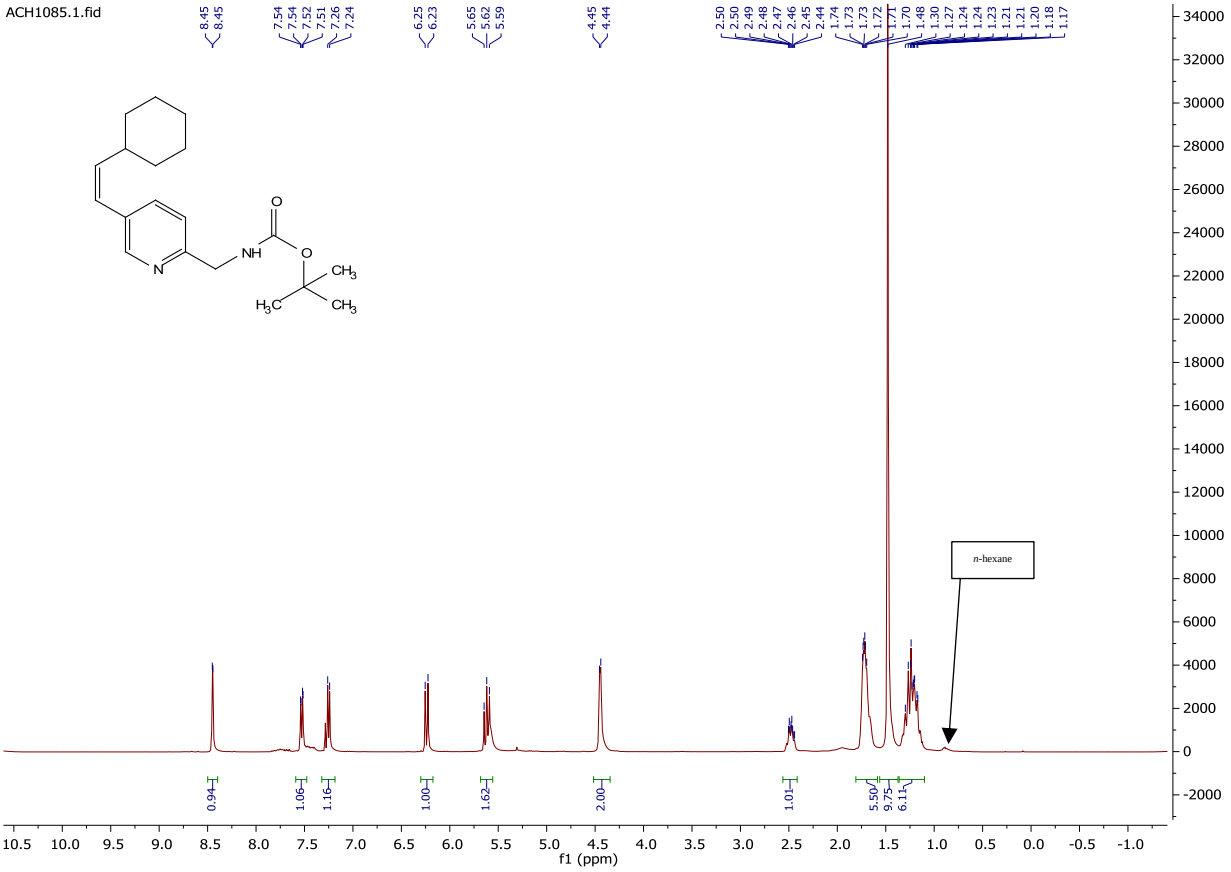

GB2085.2.fid
130.22
123.05
42.14
37.25
36.77
34.88
28.98
28.60
24.57
f1 (ppm)

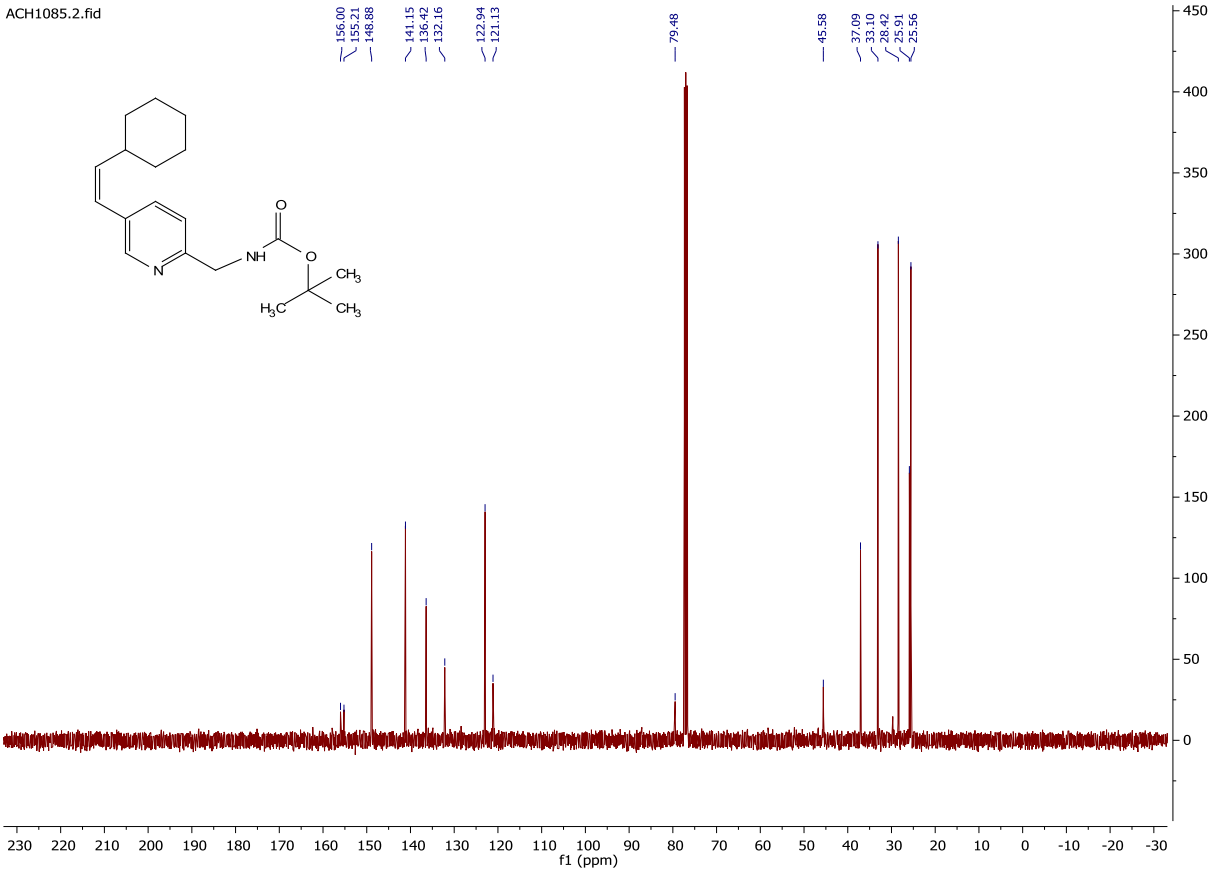
Molecule 13


ACH1048.1.fid
8.58
8.57
7.99
7.98
7.96
7.96
7.33
7.31
4.87 HDO
4.32
4.13 EA
4.11 EA
3.34 MeOD
3.33 MeOD
3.33 MeOD
3.32 MeOD
3.32 MeOD
2.03 EA
1.48
1.45
1.38
1.31
1.28 EA
1.26 EA
1.24 EA
0.92
Grease
0.95
0.97
1.00
2.00
9.33
f1 (ppm)

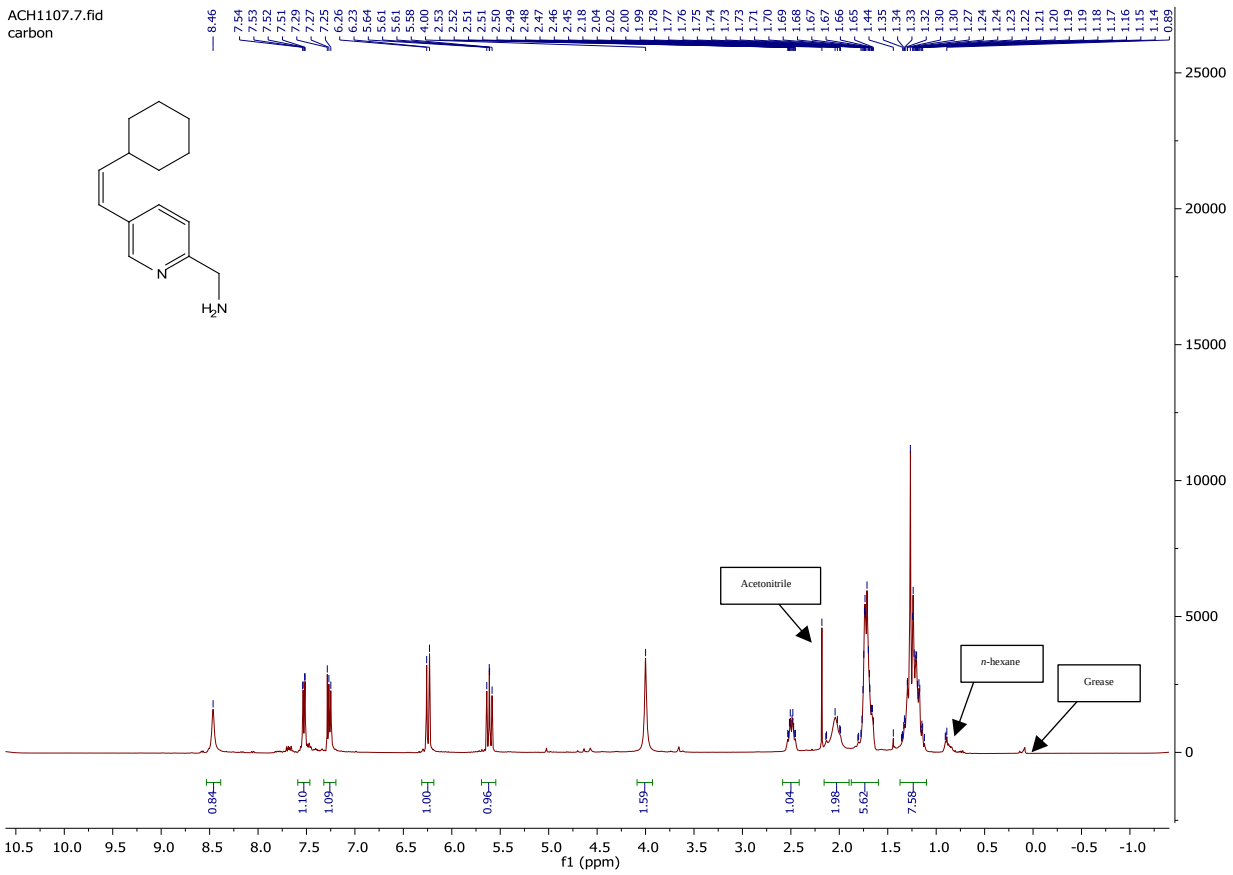

ACH1048.2.fid
157.82
157.08
149.40
139.66
122.47
118.55
79.15
44.71
27.33
CH3
H3C
CH3
O
O
NH
N
Br
f1 (ppm)

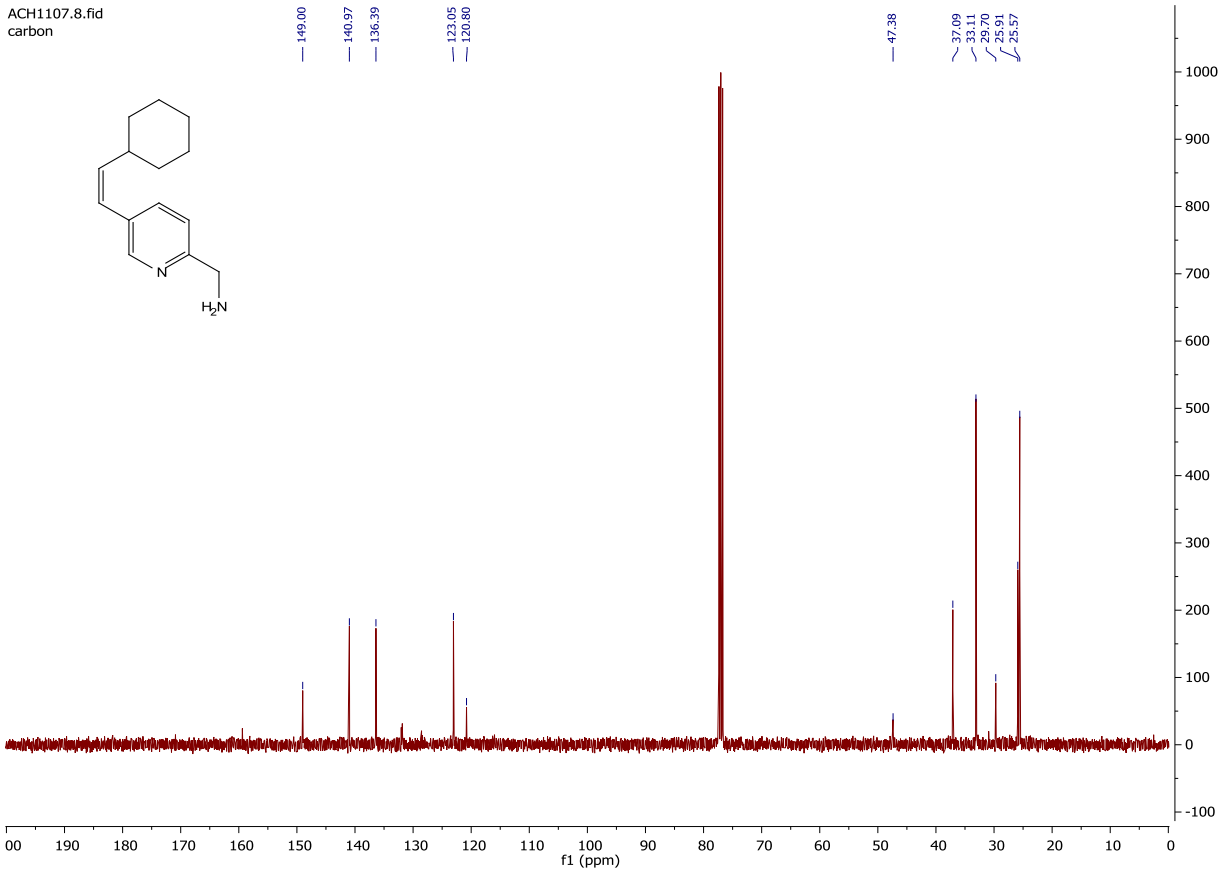
Molecule 14


ACH1085.1.fid
8.45
8.45
7.54
7.54
7.52
7.51
7.26
7.24
6.25
6.23
5.65
5.62
5.59
4.45
4.44
2.50
2.50
2.49
2.48
2.47
2.46
2.45
2.44
1.74
1.73
1.73
1.72
1.71
1.70
1.48
1.30
1.27
1.24
1.24
1.23
1.21
1.21
1.20
1.18
1.17
O
NH
O
N
CH3
H3C
CH3
n-hexane
0.94
1.06
1.16
1.00
1.62
2.00
1.01
5.50
9.75
6.11
f1 (ppm)


ACH1085.2.fid
156.00
155.21
148.88
141.15
136.42
132.16
122.94
121.13
79.48
45.58
37.09
33.10
28.42
25.91
25.56
O
NH
O
N
CH3
H3C
CH3
450
400
350
300
250
200
150
100
50
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

Molecule 9




ACH1107.8.fid
carbon
149.00
140.97
136.39
123.05
120.80
47.38
37.09
33.11
29.70
25.91
25.57
N
H2N
1000
900
800
700
600
500
400
300
200
100
0
-100
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)