

# Efficient and Stereoselective Synthesis of Yellow Scale Pheromone via Alkyne Haloboration, Zr-Catalyzed Asymmetric Carboalumination of Alkenes (ZACA Reaction), and Pd-Catalyzed Tandem Negishi Coupling

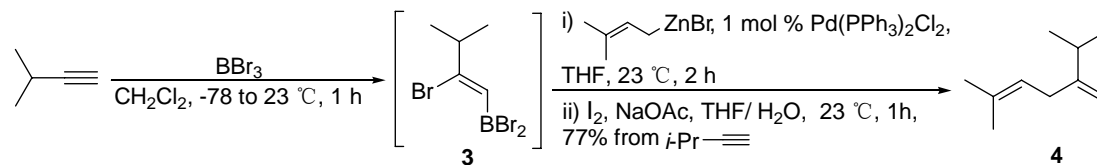
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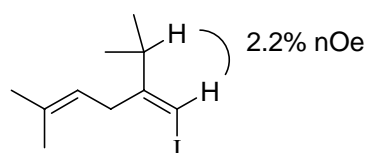
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**General.** All reactions were run in flame-dried glassware under Argon atmosphere. THF and ether were distilled from sodium and benzophenone. CH<sub>2</sub>Cl<sub>2</sub> was distilled from CaH<sub>2</sub>. Zn dust was activated by rinsing with dilute HCl<sup>1</sup> and flame-dried under vacuum prior to use. ZnBr<sub>2</sub> was flamed-dried under vacuum. (-)-(NMI)<sub>2</sub>ZrCl<sub>2</sub><sup>2</sup> was prepared as reported in the literature. Amano PS lipase from *Pseudomonas Cepacia* was purchased from Aldrich and used as received. Reactions were monitored by TLC and GC analysis of reaction aliquots. GC analysis was performed on an 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. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian-Inova-300 spectrometer. LRMS and HRMS were obtained on Hewlett Packed 5995 GC-MS and Finnigan MATL95 mass spectrometers, respectively. Optical rotations were performed on an Autopol III automatic polarimeter.

**Representative Procedure for Alkyne Haloboration, Pd-Catalyzed Allyl–Alkenyl Coupling, and Iodinolysis. Conversion of 3-Methyl-1-butyne to (1E)-1-Iodo-2-isopropyl-5-methyl-1,4-hexadiene (4).**



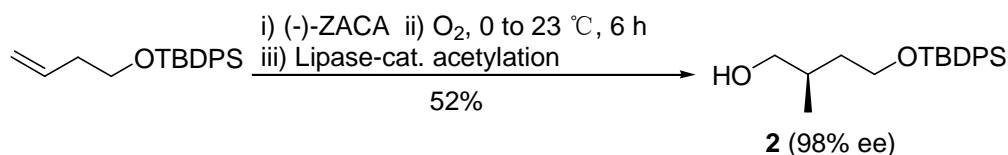
To a stirred solution of  $\text{BBr}_3$  (10.0 mL, 10.0 mmol, 1 M in  $\text{CH}_2\text{Cl}_2$ ) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added 3-methyl-1-butyne (0.82 g, 12.0 mmol, dissolved in 20 mL  $\text{CH}_2\text{Cl}_2$ ) at  $-78$  °C. The resultant solution was stirred at  $-78$  °C for 30 min, at 23 °C for another 30 min, and cooled to  $-78$  °C again. After adding 2 mL of dry THF and  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.07 g, 0.1 mmol) to the above solution, the resultant mixture was warmed to 23 °C, and 3-methyl-2-butenylzinc bromide (12.0 mmol, generated by treating 1-bromo-3-methyl-2-butene (1.79 g, 1.4 mL, 12.0 mmol) with Zn dust (1.56 g, 24.0 mmol) in THF (30 mL))<sup>3</sup> was added. After stirring the mixture for 2 h at 23 °C, a solution of  $\text{I}_2$  (5.08 g, 20.0 mmol) in THF (10 mL) and NaOAc (1.23 g, 15.0 mmol) in  $\text{H}_2\text{O}$  (5 mL) were added successively at 0 °C. The reaction mixture was stirred at 23 °C for 1 h, treated with sodium thiosulfate (15 mL, 25% solution in water) to decompose the residual  $\text{I}_2$ , and extracted with ether. The combined organic layer was washed with brine, dried, concentrated under vacuum, and purified by column chromatography (silica gel, hexanes) to give (1E)-1-iodo-2-isopropyl-5-methyl-1,4-hexadiene (**4**) as colorless oil. Yield: 2.0 g (77%). The 1E geometry was established by nOe measurement. Its isomeric purity was  $\geq 98\%$  by  $^{13}\text{C}$  NMR.



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.04 (d,  $J = 6.9$  Hz, 6 H), 1.71 (s, 6 H), 2.45–2.5 (m, 1 H), 2.96 (d,  $J = 6.9$ , 2 H), 5.03 (t,  $J = 1.5$  Hz, 1 H), 5.95 (s, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  18.13, 21.58, 25.63, 35.49, 35.77, 74.34, 120.69, 132.91, 156.47. MS (CI): 263 (7), 209 (57), 137(100), 95 (18), 69 (34); HRMS calcd for  $\text{C}_{10}\text{H}_{17}\text{I}$   $[\text{M}]^+$ :

264.0375. Found 264.0378.

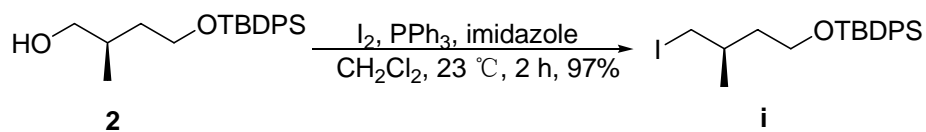
**(2R)-4-tert-Butyldiphenylsilyloxy-2-methyl-1-butanol (2).**



To 100 mg (0.15 mmol) of (-)-(NMI)<sub>2</sub>ZrCl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added Me<sub>3</sub>Al (4.5 mL, 45 mmol, neat (Caution: Highly pyrophoric!)) at 23 °C. To the resultant orange mixture was added via cannula 4.65 g (15 mmol) of 4-tert-butyl-1-butene in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The resultant solution was cooled to -78 °C and 0.13 mL (7.5 mmol) H<sub>2</sub>O was carefully added to the mixture. Then, the system was warmed to 23 °C. After stirring for 5 h, the reaction mixture was treated with a vigorous stream of O<sub>2</sub> bubbled through a needle for 1 h at 0 °C, and stirred further for 5 h at 23 °C under O<sub>2</sub>. The reaction mixture was quenched with 2 N NaOH, extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with water, dried, concentrated and purified by column chromatography (silica gel, 90/10 hexanes–EtOAc) to give the title compound mixed with its *S* isomer as colorless oil. Yield: 4.2 g (82%), 72% ee by Mosher ester analysis.

To 2.4 g (7 mmol) of the crude product of 72% ee obtained above in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were added 0.21 g of Amano PS lipase (30 mg/ mmol substrate) and 3.5 mL (35 mmol) of vinyl acetate. After stirring for 24 h at 23 °C, at which time 35% of the substrate was acetylated, the reaction mixture was filtered, concentrated and purified by column chromatography (silica gel, 97/ 3 hexanes–EtOAc) to afford the desired compound **2** as colorless oil. Yield: 1.51 g (63%). 98% ee by Mosher ester analysis.  $[\alpha]_D^{23}$ : +6.9° (c 1.0, CHCl<sub>3</sub>)<sup>4</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.92 (d, *J* = 6.9 Hz, 3 H), 1.09 (s, 9 H), 1.5-1.55 (m, 1 H), 1.6-1.7 (m, 1 H), 1.8-1.9 (m, 1 H), 2.69 (br, s, 1 H), 3.5-3.55 (m, 2 H), 3.7-3.85 (m, 2 H), 7.4-7.5 (m, 6 H), 7.7-7.75 (m, 4 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 17.07, 19.05, 26.74 (3 C), 33.76, 36.66, 62.42, 68.14, 127.64 (4 C), 129.65 (2 C), 133.35 (2 C), 135.50 (4 C).

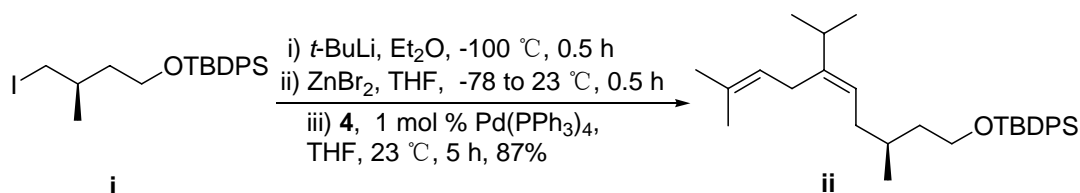
**(3*R*)-4-Iodo-3-methyl-1-butyl *tert*-Butyldiphenylsilyl Ether.**



To a mixture of 0.41 g (6.0 mmol) of imidazole and 1.44 g (5.5 mmol) of PPh<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added 1.47 g (5.8 mmol) of I<sub>2</sub> at 0 °C. After stirring for 15 min at 0 °C, 1.58 g (4.6 mmol) of **2** in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to above solution. The mixture was stirred for 2 h at 23 °C, then, it was quenched with water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried, concentrated and purified by column chromatography (silica gel, 99/1 hexanes–EtOAc) to give the title compound as colorless oil. Yield: 2.0 g (95%)

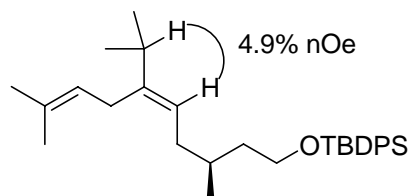
<sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>) δ 1.05 (d, *J* = 6.3 Hz, 3 H), 1.16 (s, 9 H), 1.55-1.6 (m, 1 H), 1.7-1.8 (m, 1 H), 3.2-3.35 (m, 2 H), 3.79 (t, *J* = 6.0 Hz, 2 H), 7.45-7.5 (m, 6 H), 7.75-7.8 (m, 4 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 18.09, 19.21, 20.71, 26.92 (3 C), 31.35, 38.94, 61.51, 127.71 (4 C), 129.66 (2 C), 133.73 (2 C), 135.55 (4 C).

***O*-*tert*-Butyldiphenylsilyl-protected (3*S*, 5*E*)-3, 9-Dimethyl-6-isopropyl- 5, 8-decadien-1-ol.**



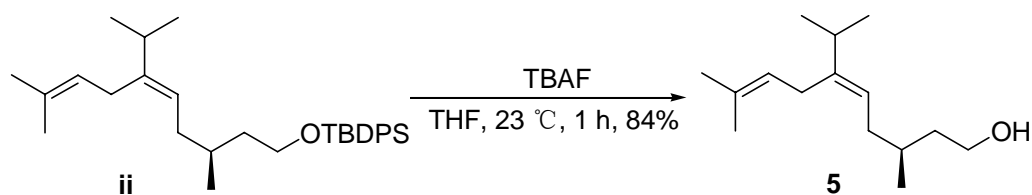
To 2.0 g (4.4 mmol) of (3*R*)-4-iodo-3-methyl-1-butyl *tert*-butyldiphenylsilyl ether in Et<sub>2</sub>O (10 mL) was added *t*-BuLi (5.3 mL, 9.1 mmol, 1.7 M in pentane) at -100 °C. After stirring for 30 min at -100 °C, the mixture was transferred to 1.2 g (5.3 mmol) of ZnBr<sub>2</sub> in THF (10 mL) at -78 °C. After stirring for 15 min at -78 °C, the mixture was slowly warmed to 23 °C during 15 minutes. In another flask, **4** (0.77 g, 2.92 mmol) was dissolved in THF (10 mL) and treated consecutively with Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.03 mmol) and organozinc reagent prepared as described above at 23 °C. After stirring for 5 h, the reaction was quenched with water, extracted with Et<sub>2</sub>O, washed with brine, dried, concentrated, and purified by column chromatography (silica gel,

90/10 hexanes–EtOAc ) to give the title compound as colorless oil. Yield: 1.18 g (87%). The 5*E* geometry was established by nOe measurement. Its isomeric purity was  $\geq 98\%$  by  $^{13}\text{C}$  NMR.

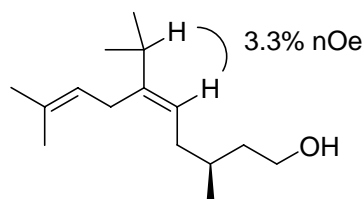


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86 (d,  $J = 6.6$  Hz, 3 H), 1.04 (d,  $J = 7.5$  Hz, 6 H), 1.25-1.45 (m, 2 H), 1.7-1.75 (m, 1 H), 1.73 (d,  $J = 5.4$  Hz, 6 H), 1.8-2.0 (m, 2H), 2.2-2.25 (m, 1H), 2.72 (d,  $J = 6.9$  Hz, 2H), 3.7-3.75 (m, 2 H), 4.95-5.05 (m, 1H), 5.16 (t,  $J = 7.2$  Hz, 1 H), 7.35-7.45 (m, 6 H), 7.7-7.75 (m, 4 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  17.93, 19.30, 19.82, 22.15, 25.83, 26.98(3 C), 34.57, 35.10, 39.54, 62.42, 121.01, 123.89, 127.67(4 C), 129.58(2 C), 130.83, 134.26(2 C), 135.67(4 C), 145.53; MS (CI): 463 (1.1), 405 (9.6), 205 (74.5), 151 (58.9), 111 (100), 109 (29.5); HRMS calcd for  $\text{C}_{31}\text{H}_{46}\text{OSi}$   $[\text{M}]^+$ : 462.3318. Found 462.3322.

**(3*S*, 5*E*)- 3, 9-Dimethyl-6-isopropyl-5, 8-decadien-1-ol (5).**

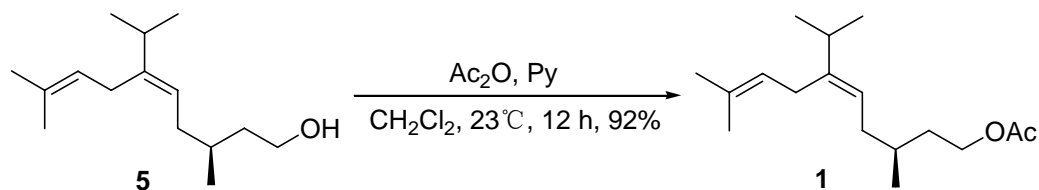


To 1.39 g (3.0 mmol) of *O-tert*-butyldiphenylsilyl-protected (3*S*, 5*E*)-3, 9-dimethyl-6-isopropyl-5, 8-decadien-1-ol in THF (5 mL) was added dropwise TBAF (3.6 mL, 3.6 mmol, 1M in THF) at 0°C, and the resultant mixture was stirred for 1 h at 23 °C. The reaction was quenched with water, extracted with  $\text{Et}_2\text{O}$ , washed with brine, dried, concentrated, and purified by column chromatography (silica gel, 90/10 hexanes–EtOAc) to give the title compound as colorless oil. Yield: 0.56 g (84%). The 5*E* geometry was established by nOe measurement. Its isomeric purity was  $\geq 98\%$  by  $^{13}\text{C}$  NMR.

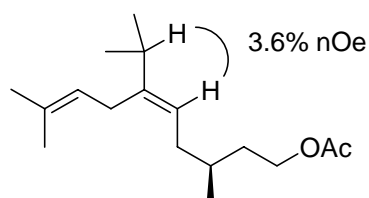


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.97 (d,  $J = 6.3$  Hz, 3 H), 1.06 (d,  $J = 6.9$  Hz, 6 H), 1.35-1.5 (m, 2 H), 1.65-1.7 (m, 1 H), 1.74 (d,  $J = 6.6$  Hz, 6 H), 1.9-2.15 (m, 2H), 2.25-2.35 (m, 1H), 2.78 (d,  $J = 7.2$  Hz, 2H), 3.7-3.8 (m, 2 H), 5.05-5.1 (m, 1 H), 5.22 (t,  $J = 7.2$  Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  17.89, 19.30, 19.77, 22.09, 25.79, 28.50, 30.54, 34.57, 35.05, 39.73, 61.40, 120.72, 123.76, 130.96, 145.85;  $[\alpha]_D^{23}$ :  $-7.1^\circ$  (c 1.0,  $\text{CHCl}_3$ ).

**(3S, 5E)-3, 9-Dimethyl-6-isopropyl-5, 8-decadienyl Acetate (1).**



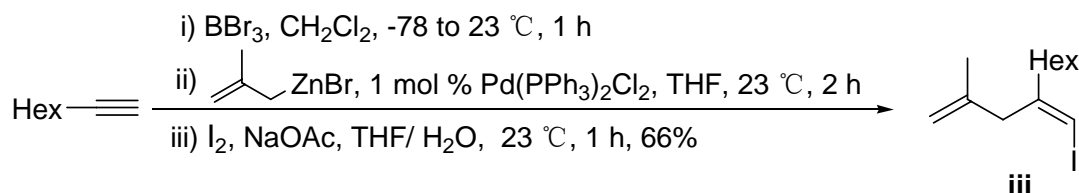
To a solution of **5** (0.45 g, 2.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) were added  $\text{Ac}_2\text{O}$  (0.41 g, 0.38 mL, 4.0 mmol) and pyridine (0.19 g, 0.20 mL, 2.4 mmol) at  $23^\circ\text{C}$ . After stirring for 12 h at  $23^\circ\text{C}$ , the reaction mixture was quenched with water, extracted with ether, washed with sat.  $\text{NaHCO}_3$  solution and brine, dried, concentrated and purified by column chromatography (silica gel, 90/10 hexanes–EtOAc) to give the title compound as colorless oil. Yield: 0.49 g (92%). The *5E* geometry was established by nOe measurement. Its isomeric purity was  $\geq 98\%$  by  $^{13}\text{C}$  NMR.



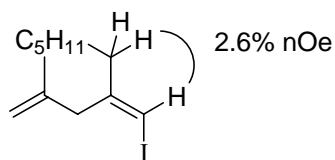
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.90 (d,  $J = 6.3$  Hz, 3 H), 0.98 (d,  $J = 6.6$  Hz, 6 H), 1.35-1.4 (m, 1 H), 1.45-1.65 (m, 2 H), 1.66 (d,  $J = 6.6$  Hz, 6 H), 1.7-2.05 (m, 2H), 2.04 (s, 3H), 2.2-2.25 (m, 1H), 2.70 (d,  $J = 6.9$  Hz, 2H), 4.05-4.1 (m, 2 H), 4.95-5.0

(m, 1 H), 5.13 (t,  $J = 7.2$  Hz 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  17.71, 19.38, 20.93, 21.89, 25.61, 28.31, 30.65, 34.40, 34.70, 35.12, 63.02, 120.28, 123.52, 130.80, 145.83, 171.11;  $[\alpha]_{\text{D}}^{23}$ :  $-12.3^\circ$  (c 1.0, hexanes).

**(1Z)-1-Iodo-2-hexyl-4-methyl-1, 4-pentadiene.**

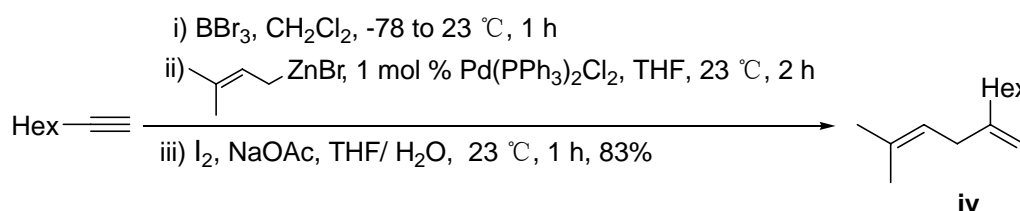


The title compound was synthesized according to the **Representative Procedure for Alkyne Haloboration, Pd-Catalyzed Allyl–Alkenyl Coupling, and Iodinolysis**. To a stirred solution of  $\text{BBr}_3$  (1.0 mL, 1.0 mmol, 1 M in  $\text{CH}_2\text{Cl}_2$ ) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added dropwise 1-octyne (0.11 g, 0.15 mL, 1.0 mmol) at  $-78$  °C. The resultant solution was stirred at  $-78$  °C for 30 min, at  $23$  °C for another 30 min, and cooled to  $-78$  °C again. After adding 0.5 mL of dry THF and  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (7 mg, 0.1 mmol) to the above solution, the resultant mixture was warmed to  $23$  °C, and 2-methylallylzinc bromide [1.2 mmol, generated by treating 3-bromo-2-methylpropene(0.14 g, 0.12 mL, 1.2 mmol) with Zn dust (0.16 g, 2.4 mmol) in THF (5 mL)]<sup>3</sup> was added. After stirring the mixture for 2 h at  $23$  °C, a solution of  $\text{I}_2$  (0.51 g, 2.0 mmol) in THF (2 mL) and NaOAc (0.12 g, 1.5 mmol) in  $\text{H}_2\text{O}$  (1 mL) were added successively at  $0$  °C. The reaction mixture was stirred at  $23$  °C for 1 h, treated with sodium thiosulfate (5 mL, 25% solution in water) to decompose the residual  $\text{I}_2$ , and extracted with ether. The combined organic layer was washed with brine, dried, concentrated under vacuum, and purified by column chromatography (silica gel, hexanes) to give the (1Z)-1-iodo-2-hexyl-4-methyl-1, 4-pentadiene as colorless oil. Yield: 0.195g (66%). The 1Z geometry was established by nOe measurement. Its isomeric purity was  $\geq 98\%$  by  $^{13}\text{C}$  NMR.



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J = 7.2$  Hz, 3 H),  $\delta$  1.25-1.45 (m, 8 H), 1.70 (s, 3 H), 2.13 (t,  $J = 7.2$  Hz, 2 H), 2.95 (s, 2 H), 4.72 (s, 1 H), 4.80 (s, 1 H), 6.02 (s, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.15, 22.25, 22.65, 25.68, 27.81, 28.95, 31.69, 36.72, 45.54, 76.66, 112.15, 142.08, 149.62. HRMS calcd for  $\text{C}_{12}\text{H}_{21}\text{I}$   $[\text{M}]^+$ : 292.0688. Found 292.0689.

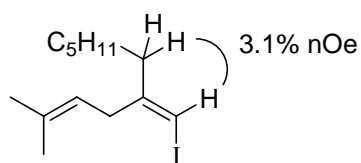
**(1Z)-1-Iodo-2-hexyl-5-methyl-1,4-hexadiene.**



The title compound was synthesized according to the **Representative Procedure for Alkyne Haloboration, Pd-Catalyzed Allyl–Alkenyl Coupling, and Iodolysis**. To a stirred solution of  $\text{BBr}_3$  (1.0 mL, 1.0 mmol, 1 M in  $\text{CH}_2\text{Cl}_2$ ) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added dropwise 1-octyne (0.11 g, 0.15 mL, 1 mmol) at  $-78$  °C. The resultant solution was stirred at  $-78$  °C for 30 min, at 23 °C for another 30 min, and cooled to  $-78$  °C again. After adding 0.5 mL of dry THF and  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (7 mg, 0.1 mmol) to the above solution, the resultant mixture was warmed to 23 °C, and 3-methyl-2-butenylzinc 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 (0.16 g, 2.4 mmol) in THF (5 mL)]<sup>3</sup> was added. After stirring the mixture for 2 h at 23 °C, a solution of  $\text{I}_2$  (0.51 g, 2.0 mmol) in THF (2 mL) and NaOAc (0.12 g, 1.5 mmol) in  $\text{H}_2\text{O}$  (1 mL) were added successively at 0 °C. The reaction mixture was stirred at 23 °C for 1 h, treated with sodium thiosulfate (5 mL, 25% solution of water) to decompose the residual  $\text{I}_2$ , and extracted with ether. The combined organic layer was washed with brine, dried, concentrated under vacuum, and purified by column chromatography (silica gel, hexanes) to give the (1Z)-1-iodo-2-hexyl-5-methyl-1,



4-hexadiene as colorless oil. Yield: 0.255g (83%). The 1Z geometry was established by nOe measurement. Its isomeric purity was  $\geq 98\%$  by  $^{13}\text{C}$  NMR.

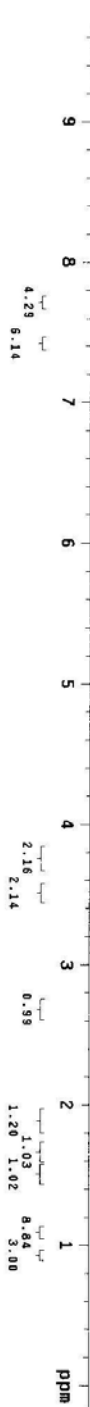
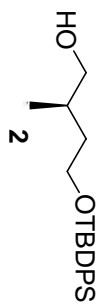
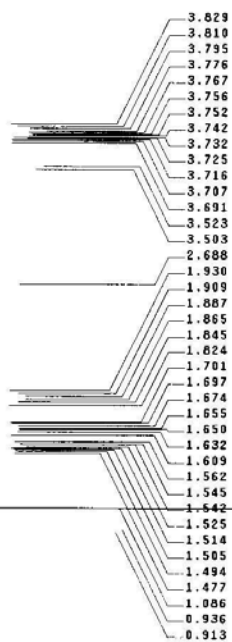
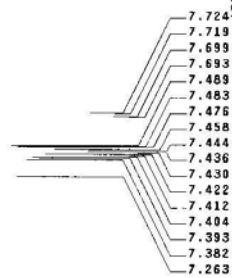


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 7.2$  Hz, 3 H),  $\delta$  1.25-1.45 (m, 8 H), 1.71 (d,  $J = 1.5$  Hz, 6 H), 2.16 (t,  $J = 6.3$  Hz, 6 H), 2.92 (d,  $J = 6.9$ , 2 H), 5.0-5.1 (m, 1 H), 5.85 (s, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.01, 18.10, 22.49, 25.68, 27.56, 28.76, 31.52, 36.39, 37.09, 73.98, 120.05, 133.39, 151.09. HRMS calcd for  $\text{C}_{13}\text{H}_{23}\text{I}$   $[\text{M}]^+$ : 306.0844. Found 306.0834.

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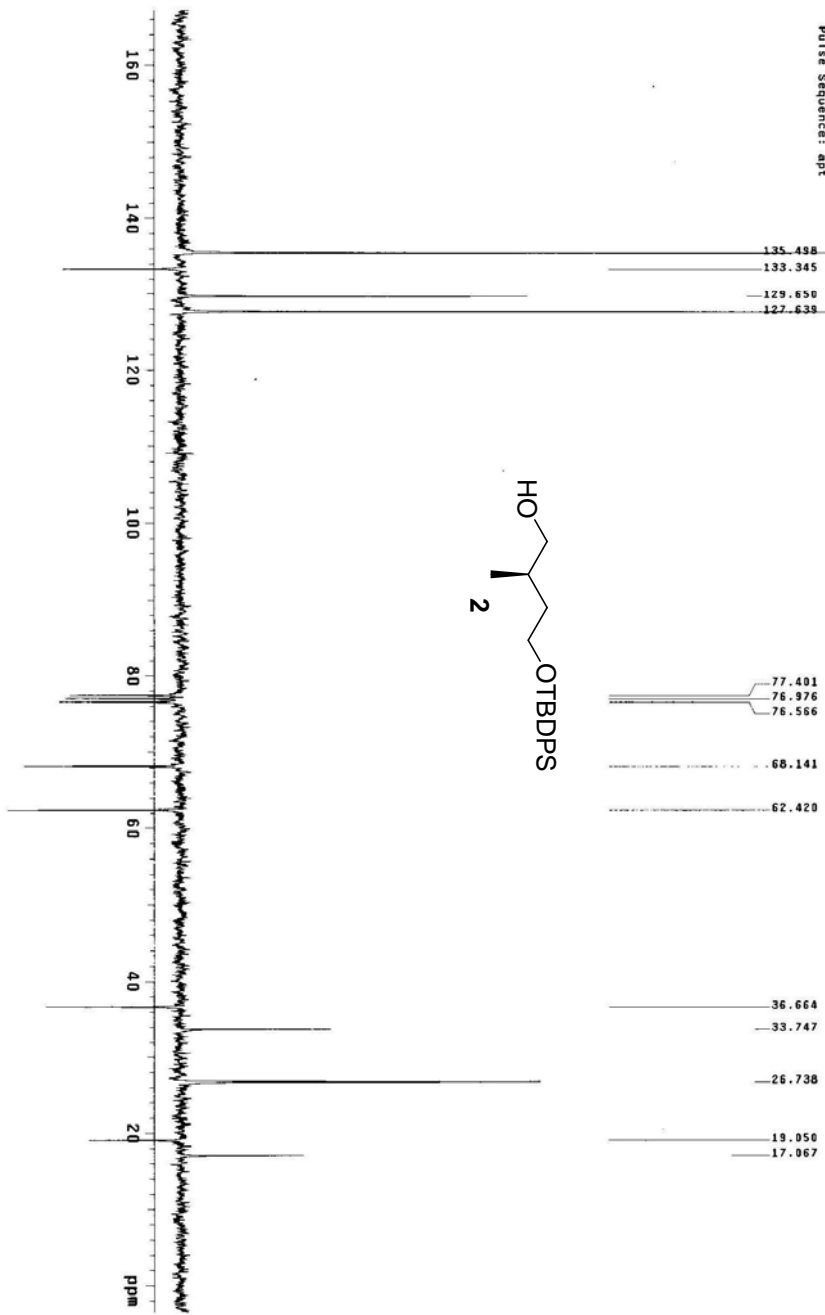
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2. Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermuehle, D.; Kruger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590.
3. Negishi, E.; Matsushita, H.; Okukado, N. *Tetrahedron Lett.* **1981**, *22*, 2715.
4. Huang, Z.; Tan, Z.; Novak, T.; Zhu, G.; Negishi, E. *Adv. Synth. Catal.* **2007**, *349*, 539.

H1 standard parameters, CDCl3  
Data collected on: inovas30-1-inovahlfrq  
Archive directory: /mnt/dz/p1mr-f/barwood/vmrsvs/data  
Sample directory:  
File: H1  
Pulse Sequence: szpul



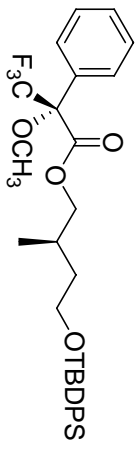


C13 standard parameters, CDCl3  
Data Collected on: innova300-1-1novah1f1req  
Archive directory: /home/znou/vmr/sys/data  
File: apt  
Pulse Sequence: apt

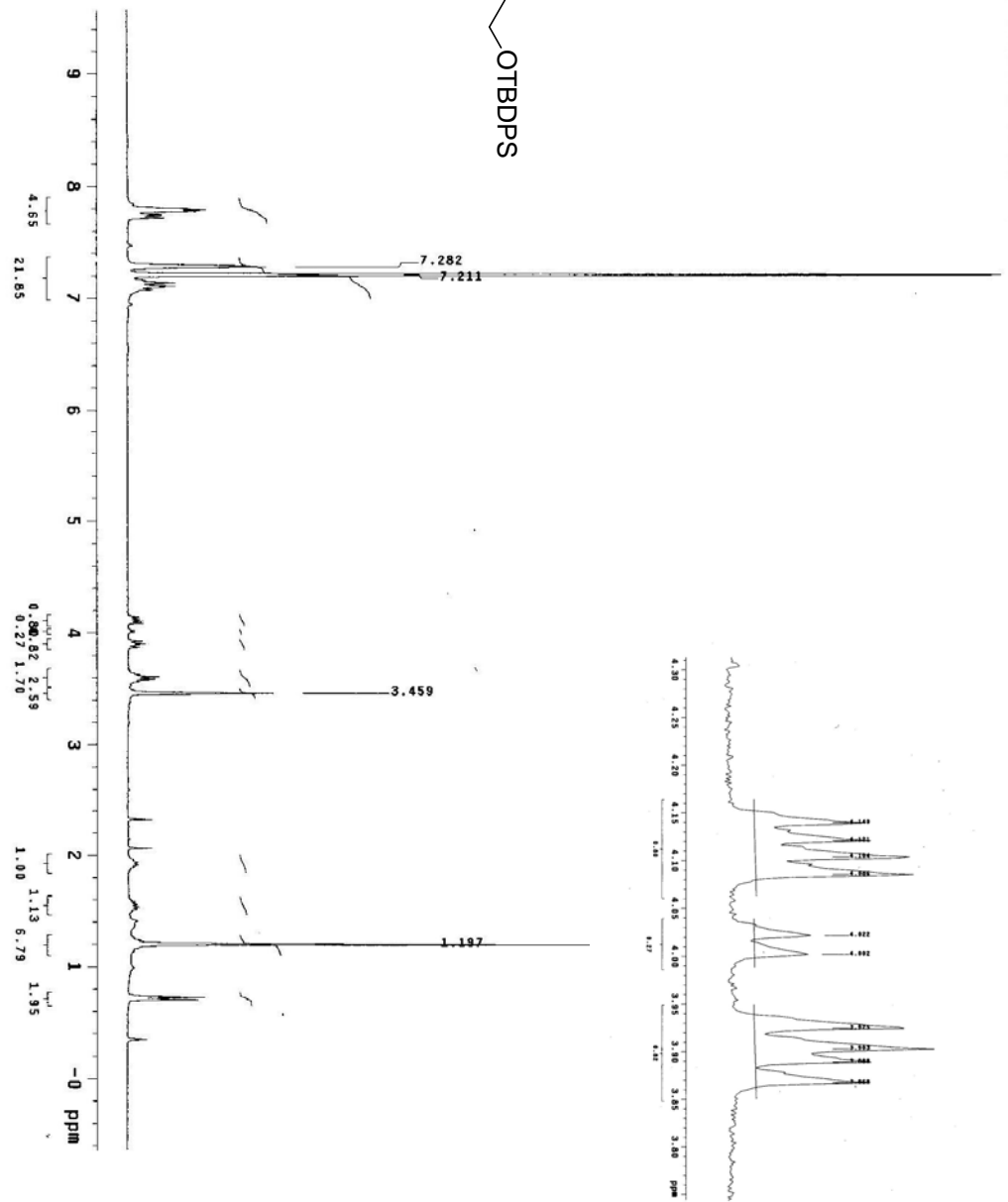


H1 standard parameters, CDCl3  
 Data Collected on: /home300-1-100001/frag  
 Archive directory: /mnt/d2/p1mr/f/harwood/vnmrSYS/data  
 Sample directory:  
 File: H1

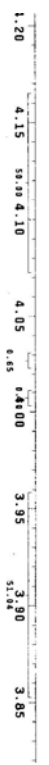
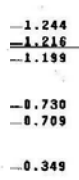
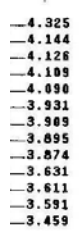
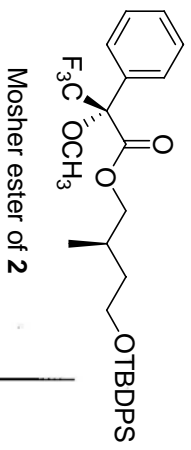
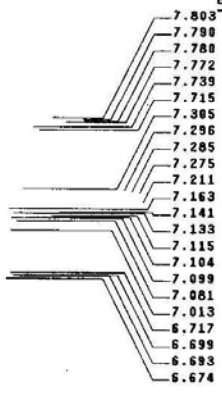
Pulse Sequence: s2pul  
 Solvent: CDCl3  
 Relax. delay 2.000 sec  
 Pulse 28.8 degrees  
 Acq. 3750  
 Uch 3750 2.133 sec  
 64 repetitions  
 OBSERVE H1 299.9598319 MHz  
 DATA PROCESSING  
 Line broadening 0.2 Hz  
 FT size 16384  
 Total time 0 min



Mosher ester of 2



H1 standard parameters, CDCl3  
 Data Collected on: Inova300-1-InovaHitF6q  
 Archive directory: /mnt/dz/p1/mr7/halwood/vmr/sys/data  
 Sample directory:  
 File: H1  
 Pulse Sequence: szpu1

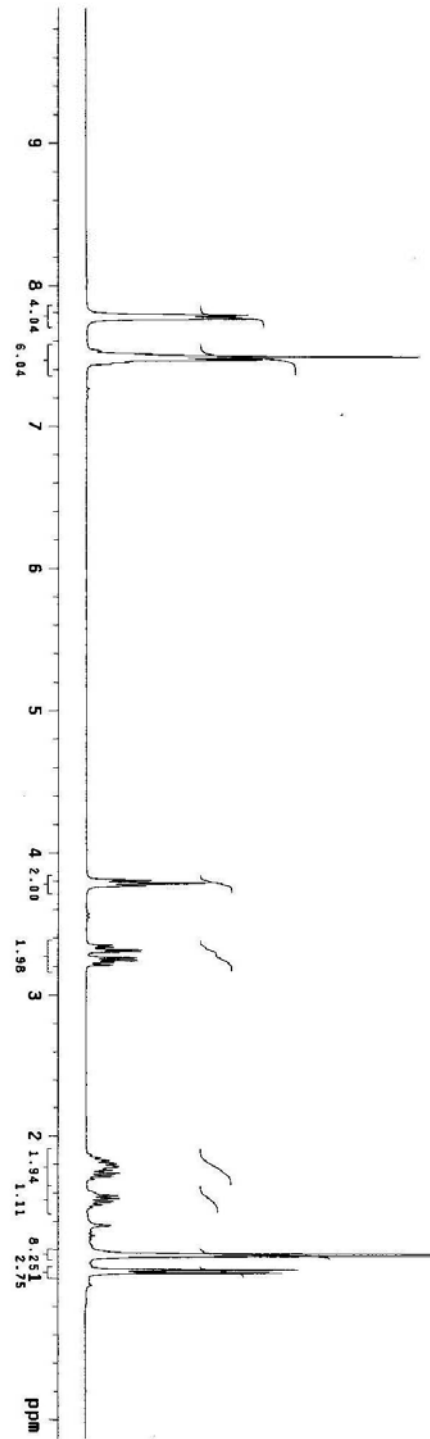
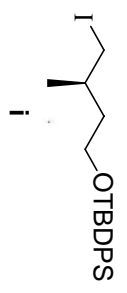


H1 standard parameters, CQC13  
 Data collected on: Inova300-1-InovaHTReg  
 Archive directory: /mnt/d2/pinmr/Harwood/vmr/sys/data  
 Sample directory:  
 File: H1  
 Pulse Sequence: s2pu1

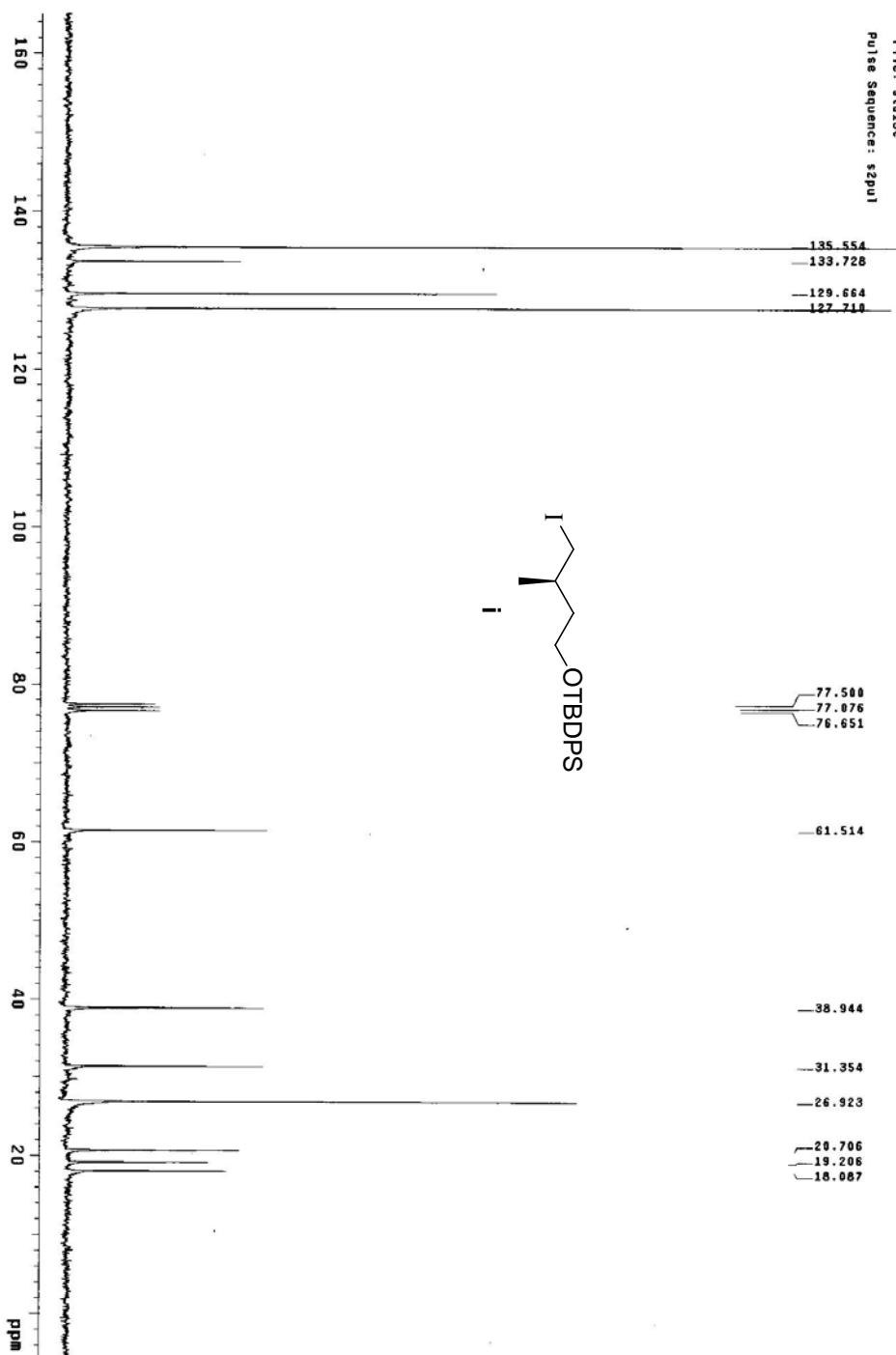
7.781  
 7.776  
 7.756  
 7.507  
 7.490  
 7.469  
 7.450

3.607  
 3.787  
 3.767  
 3.350  
 3.336  
 3.317  
 3.303  
 3.260  
 3.241  
 3.228  
 3.209

1.825  
 1.804  
 1.782  
 1.759  
 1.737  
 1.715  
 1.579  
 1.559  
 1.536  
 1.367  
 1.160  
 1.055  
 1.034

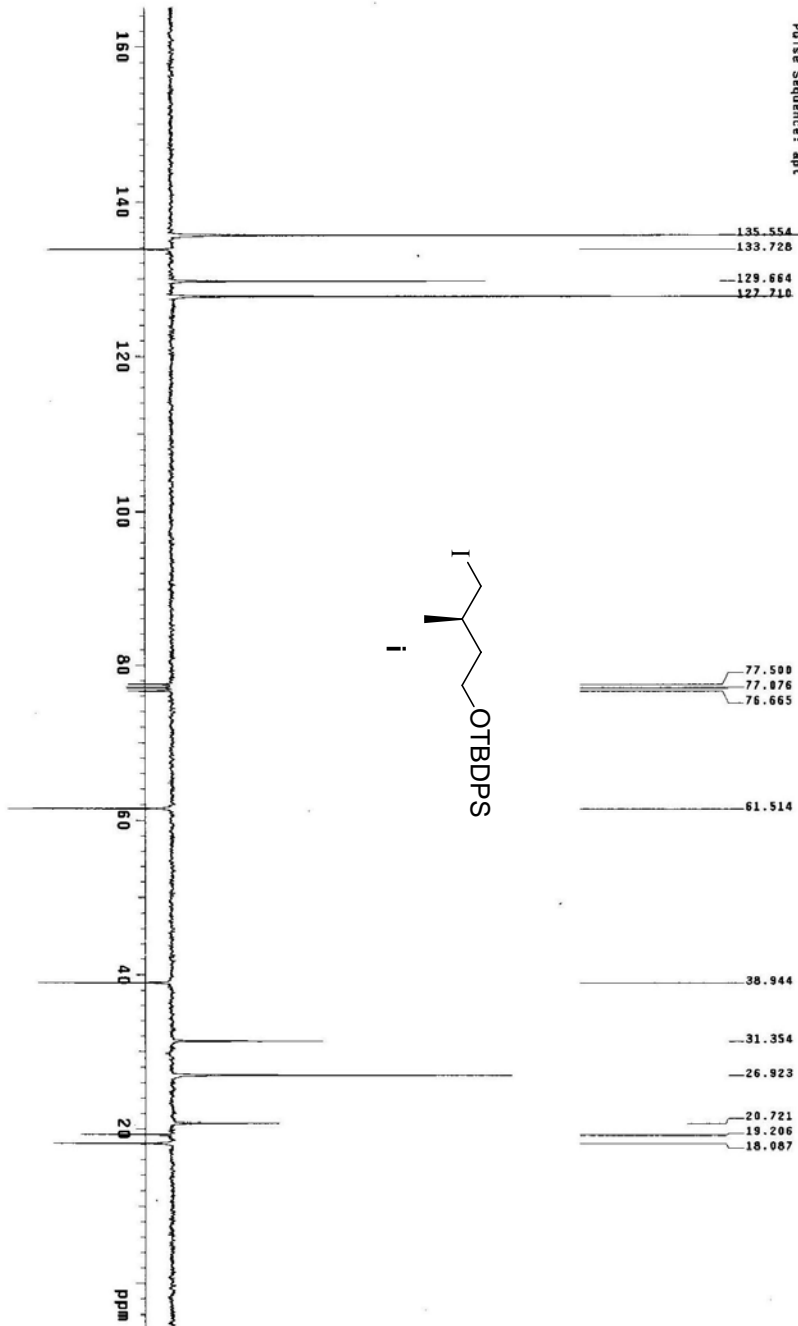


C13 standard parameters, C0013  
Data collected on: Inova300-1-InovaHfrad  
Archive directory: /mnt/d2/pimrr/harwood/vnmr-sys/data  
Sample directory: /mnt/d2/pimrr/harwood/vnmr-sys/data  
File: std13c  
Pulse Sequence: s2pul

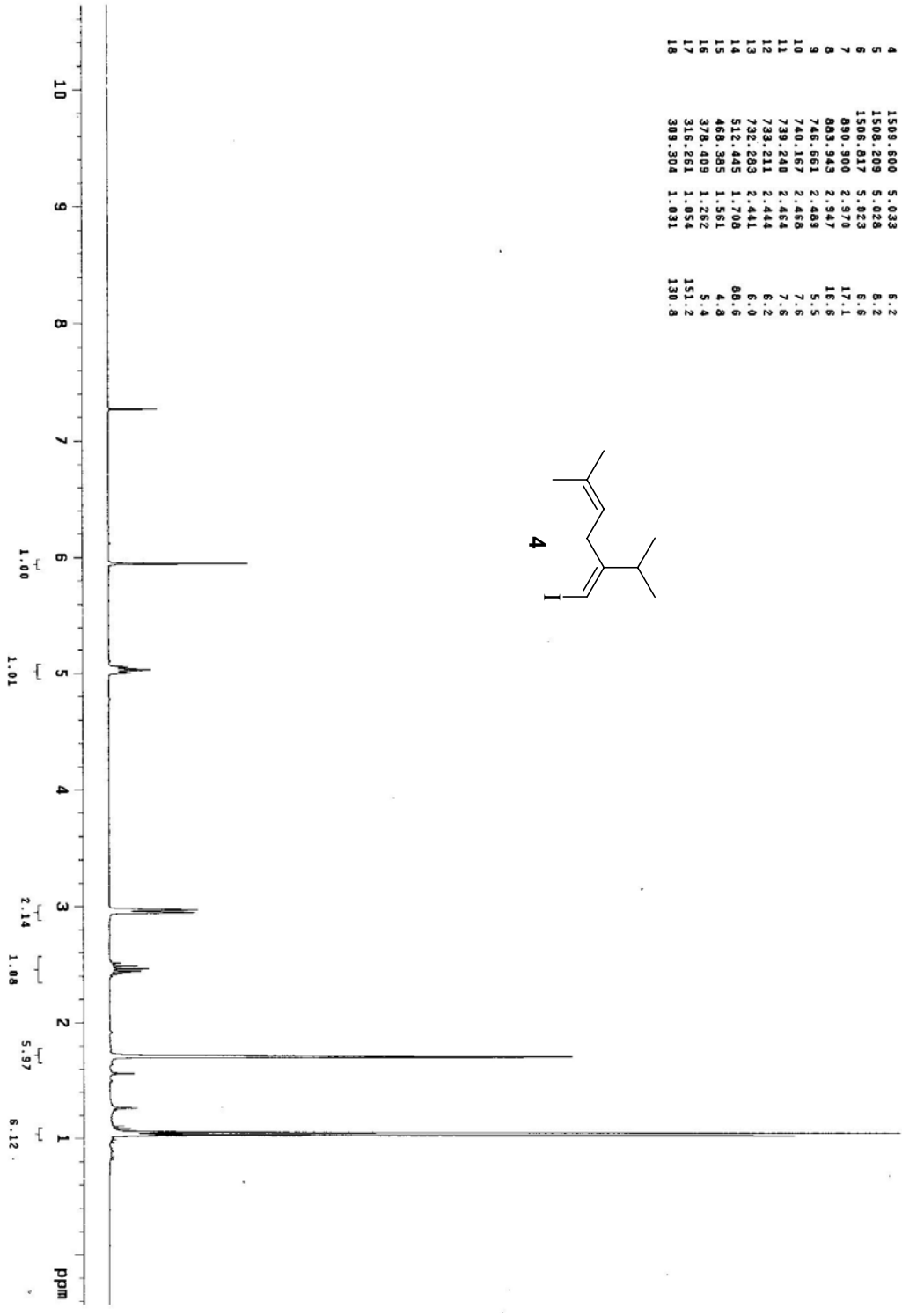
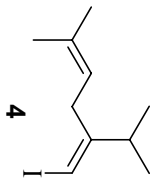




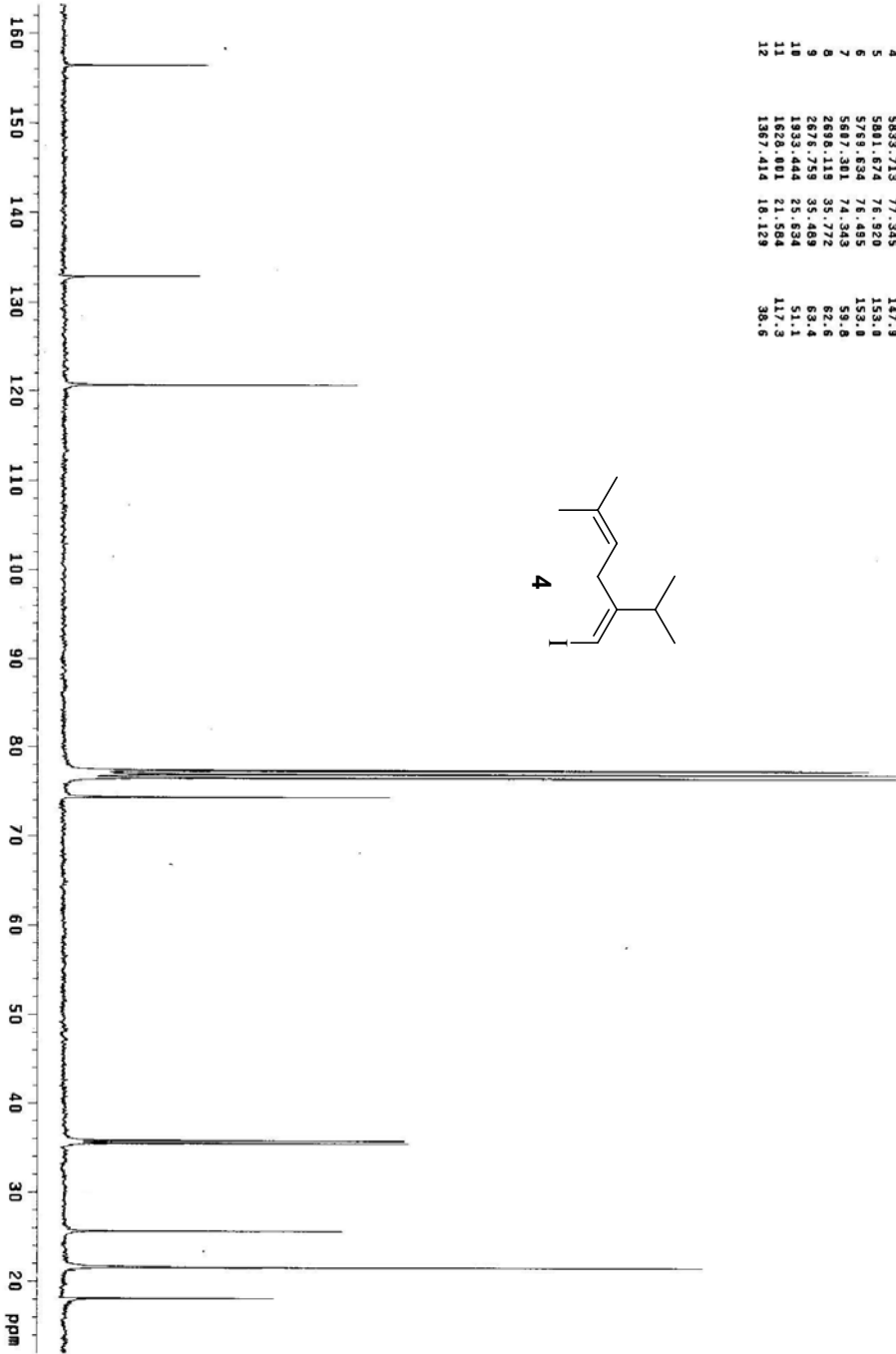
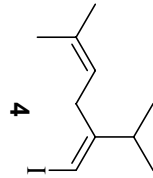
C13 standard parameters, CDCl3  
Data Collected on: nov38e-1-novahl1freq  
Acquisition Date: 11/11/00  
Sample directory: /home/ksul/vnmr5y/data  
File: TBDS-homocall1c-1-APT  
Pulse Sequence: apt



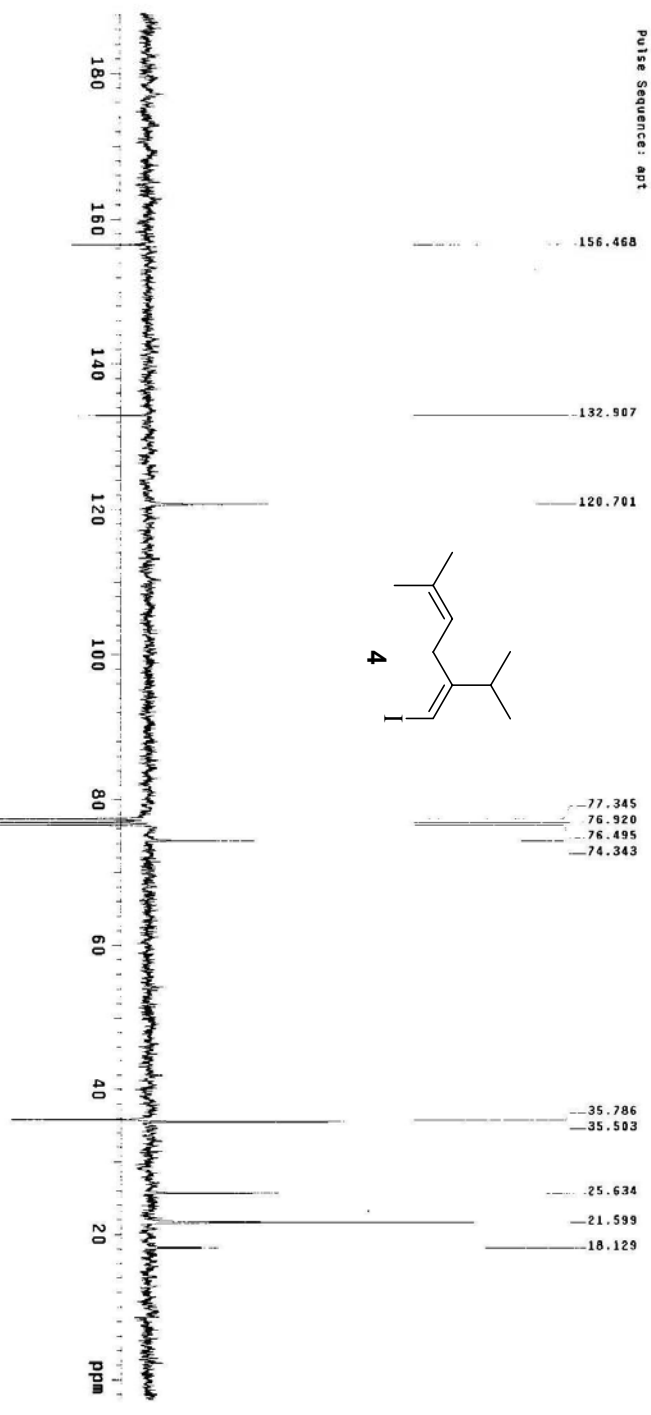
INDEX	FREQUENCY	PM	HEIGHT
1	2180.708	7.270	9.5
2	1784.165	5.948	26.7
3	1793.238	5.945	26.4
4	1509.600	5.033	6.2
5	1508.209	5.028	6.2
6	1506.817	5.023	5.6
7	890.900	2.970	17.1
8	893.943	2.947	16.6
9	746.651	2.468	5.5
10	740.167	2.468	7.6
11	739.248	2.464	7.6
12	739.211	2.444	6.2
13	732.283	2.441	6.0
14	512.445	1.708	88.6
15	468.385	1.581	4.8
16	378.409	1.262	5.4
17	316.261	1.054	151.2
18	389.304	1.031	138.8

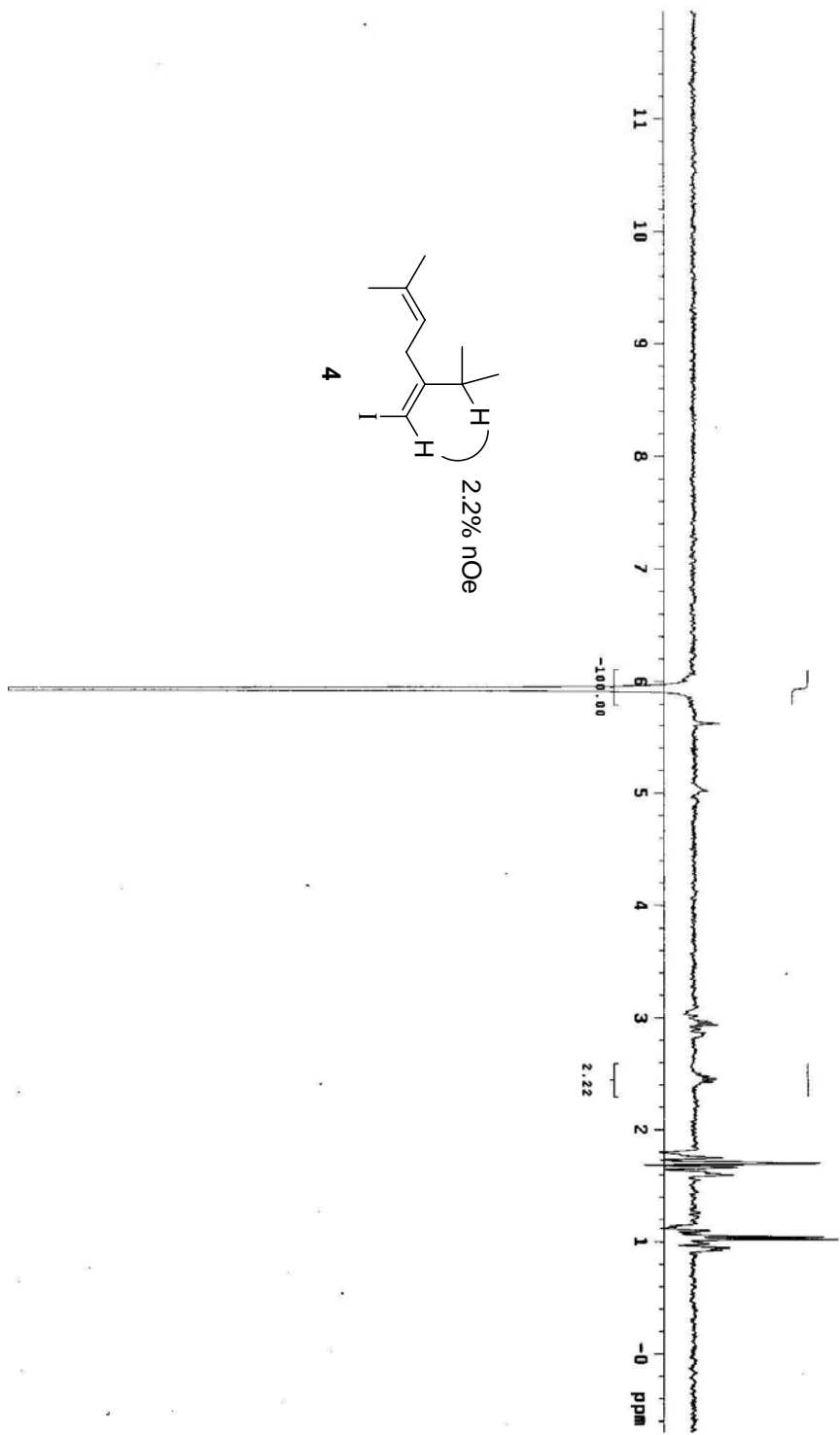


INDEX	FREQUENCY	PPM	HEIGHT
1	11801.595	155.468	26.3
2	11024.474	132.907	24.9
3	9182.865	120.587	59.7
4	5833.713	77.345	147.8
5	5881.674	76.520	153.0
6	5789.634	76.485	153.0
7	5687.381	74.343	59.8
8	2696.119	35.772	62.6
9	2676.759	35.659	63.4
10	1933.444	25.634	51.1
11	1626.081	21.564	117.3
12	1367.414	18.129	36.6



C13 standard parameters, CDCl3  
Data collected on: inovas30-1-inovahifreq  
Archive directory: /home/zxui/nmr/sys/data  
Sample directory:  
File: apt  
Pulse Sequence: apt

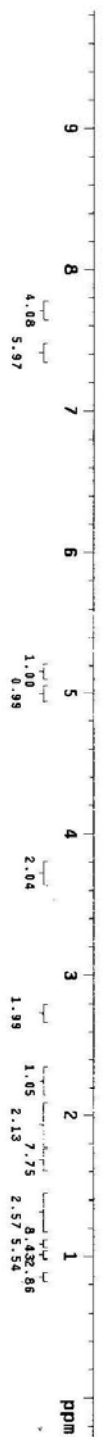
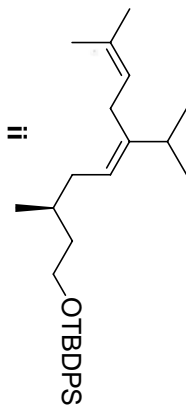
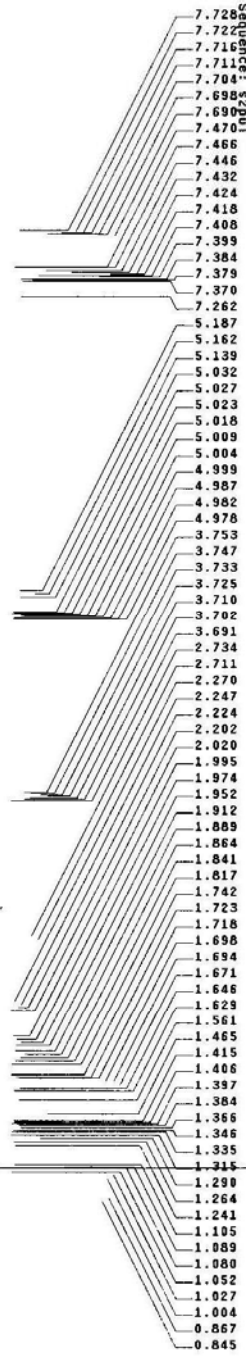


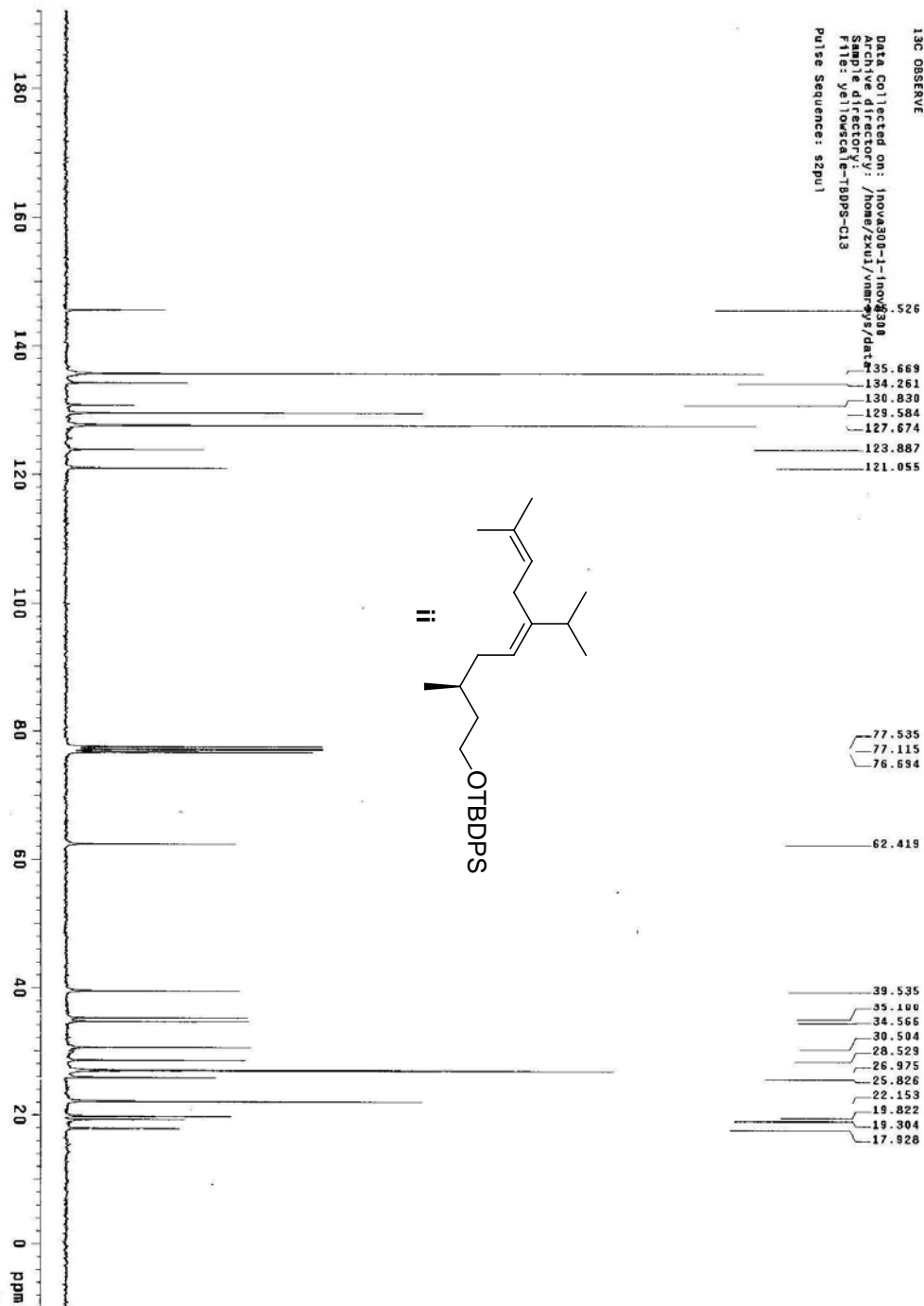


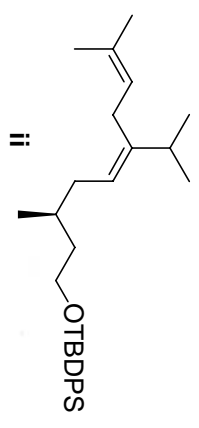
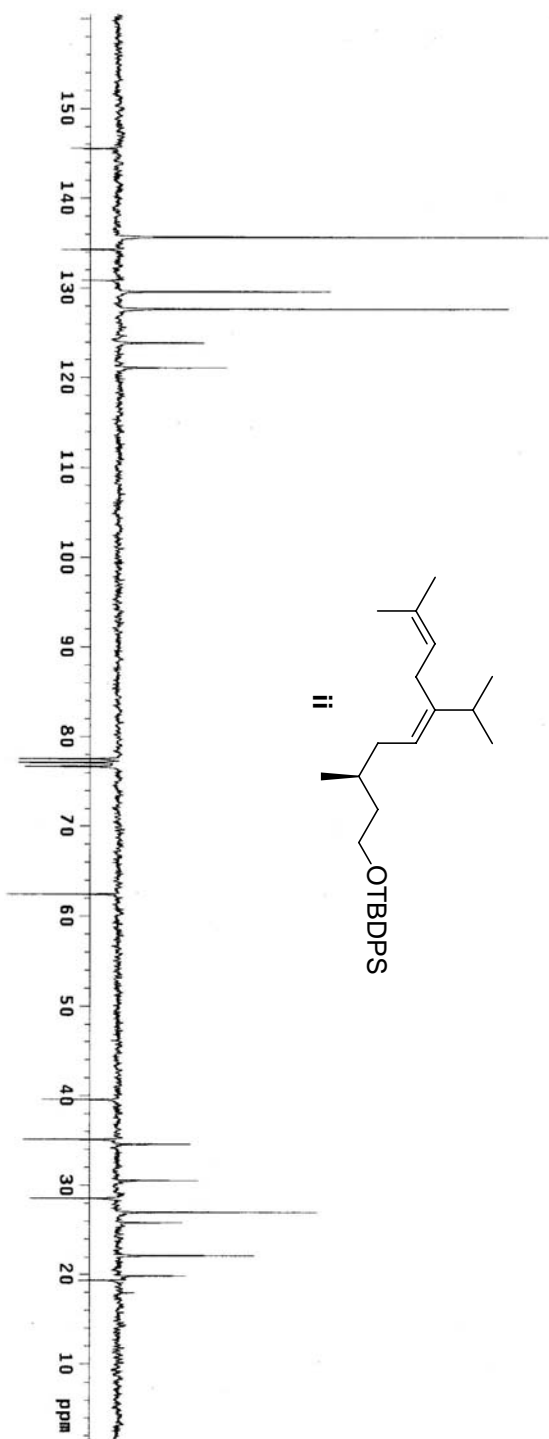
H1 standard parameters, CDC13

Data Collected on: 1NOVA300-1-1NOVAH1F-req  
Archive directory: /mnt/d2/p1mmf/Barwood/vnmr/sys/data  
Sample directory:  
File: H1

Pulse Sequence: sspul



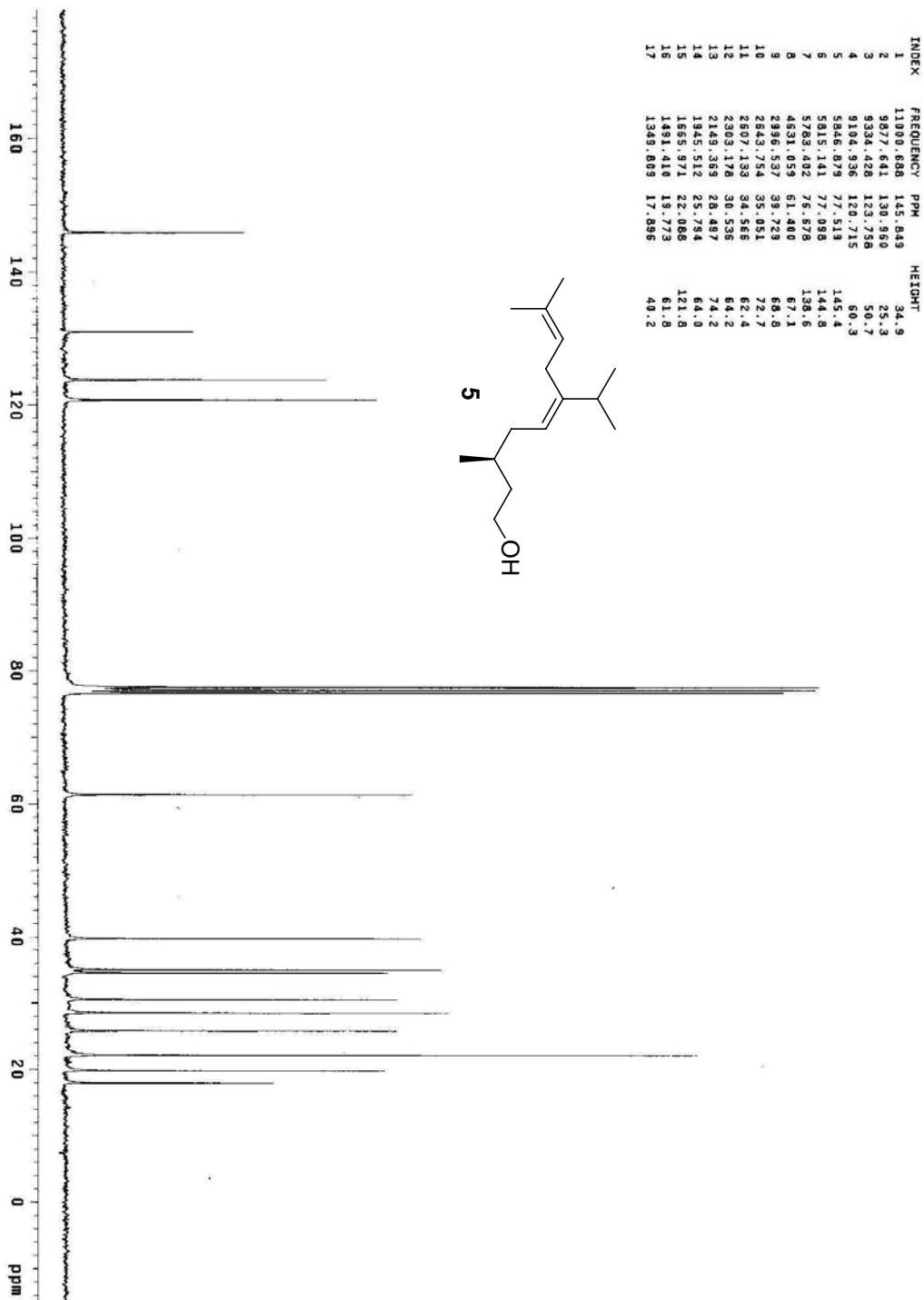




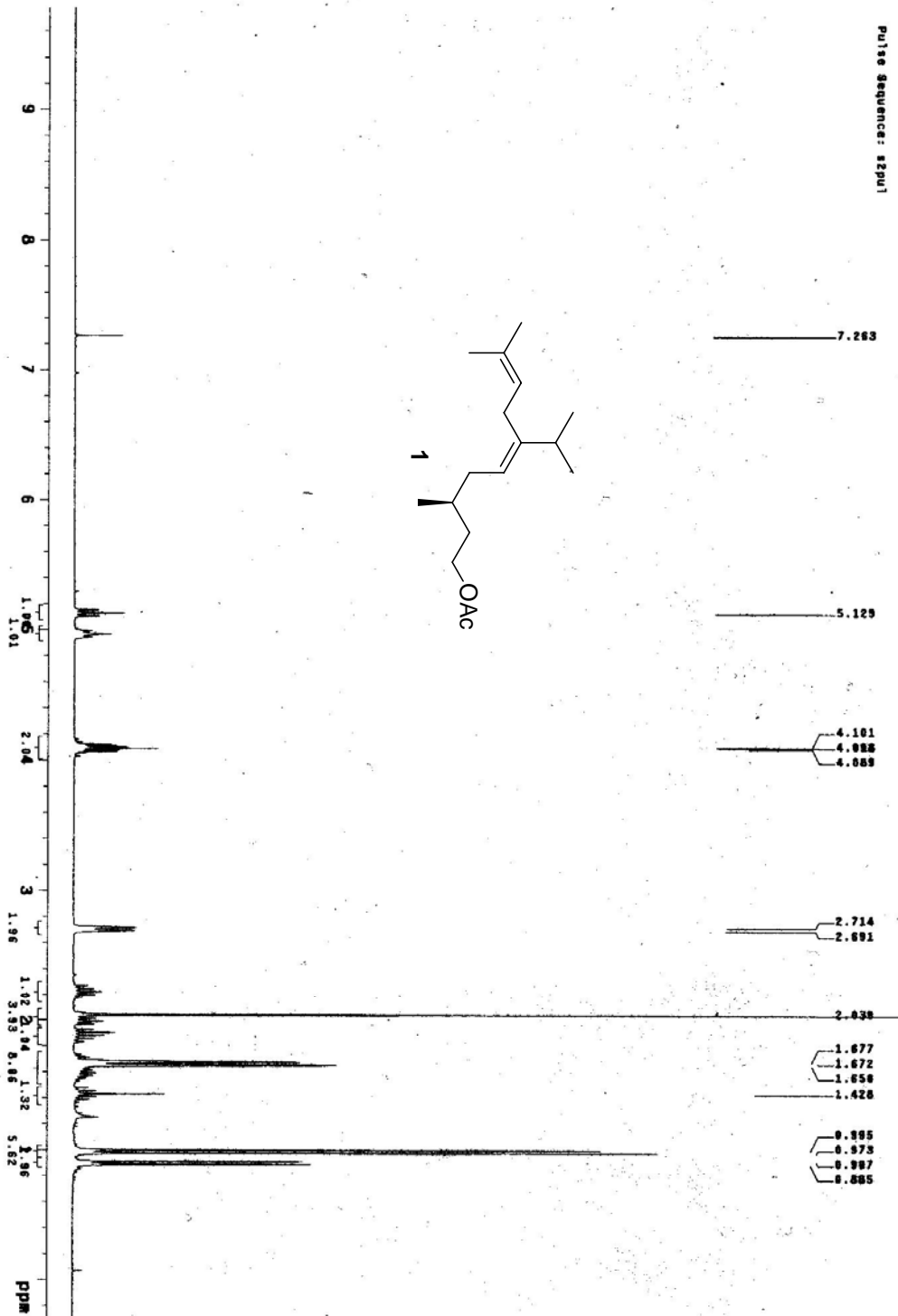






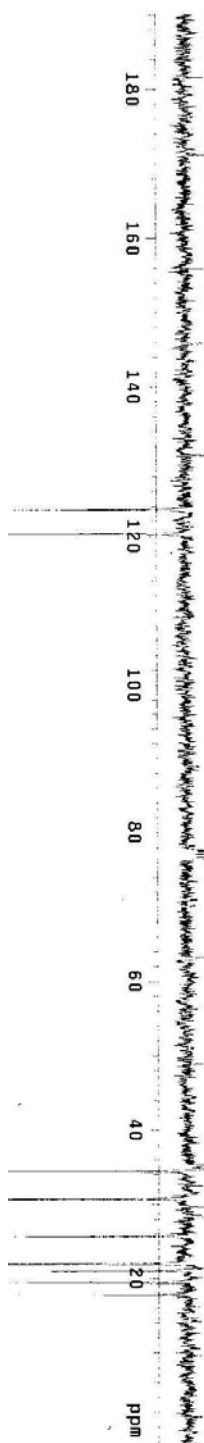
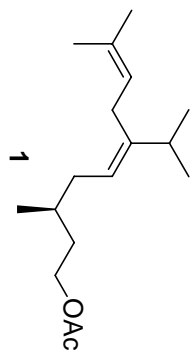


H1 standard parameters, CDCl3  
 Data Collected on: jnov300-1-1nov301f1q  
 Archive directory: /mnt/dz/pinart/nerwood/vmr/eys/data  
 Sample directory: /mnt/dz/pinart/nerwood/vmr/eys/data  
 File: H1  
 Pulse sequence: szpu1





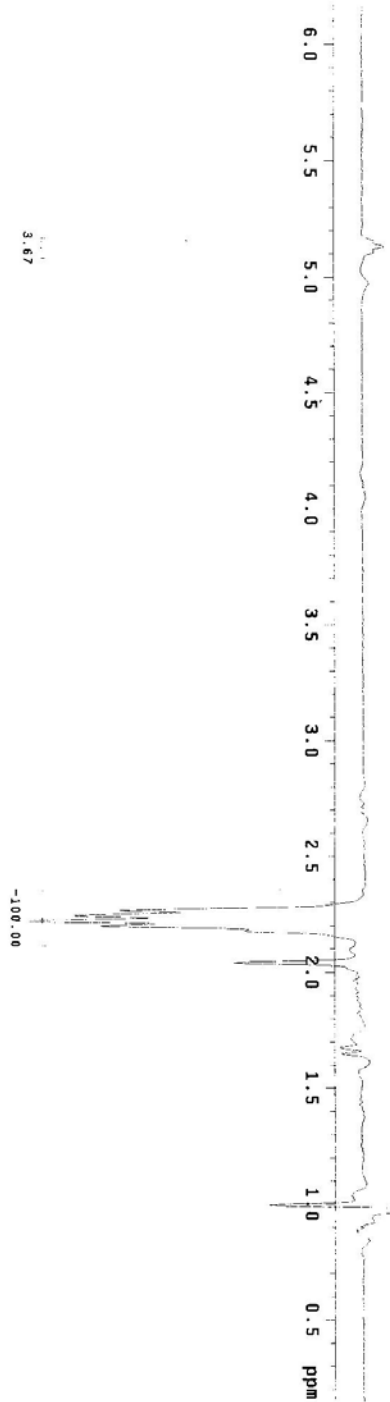
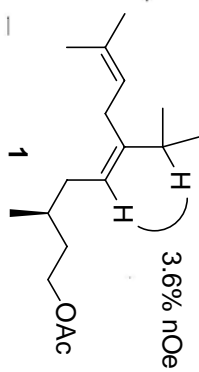
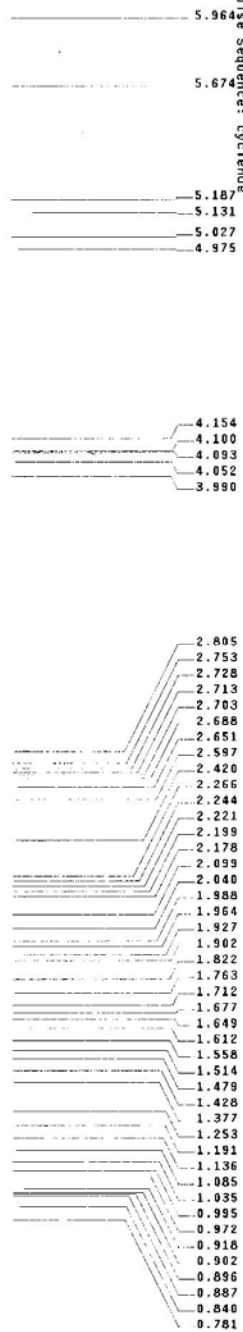
Cl3 standard parameters, C0C13  
Data Collected on: inovas03-1-inovahifred  
Archive directory: /home/zxul/vnmr.sys/data  
Sample directory:  
File: apt  
Pulse Sequence: apt



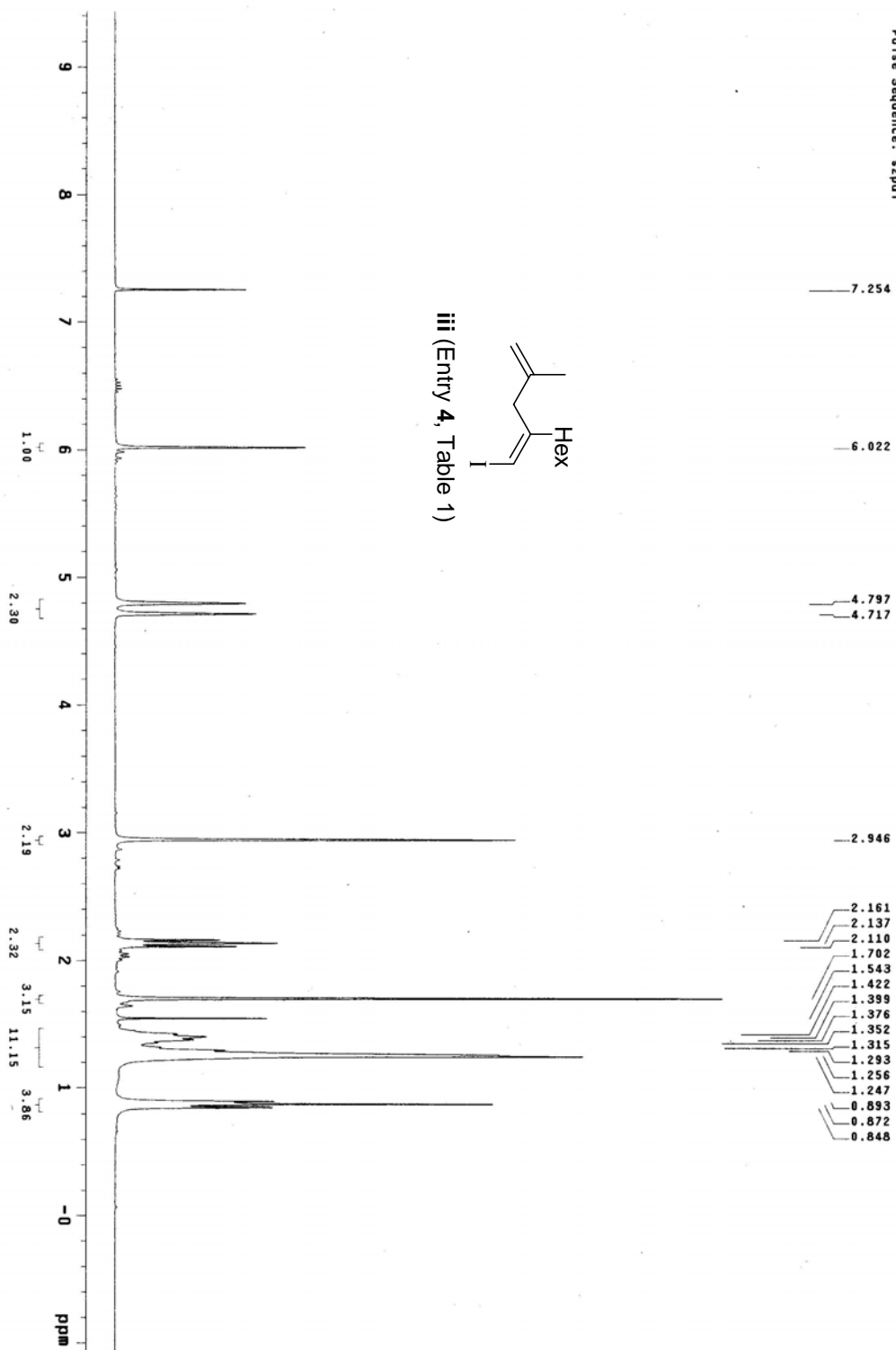
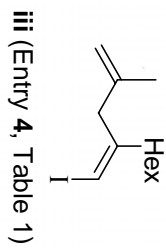
Turn spinning off.

Data Collected on: inovas300-1-inovahlfrsq  
Archive directory: /home/zxul/vnmr/sys/data  
Sample directory:  
File: cyclenoe

Pulse Sequence: cyclenoe

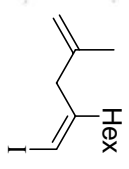
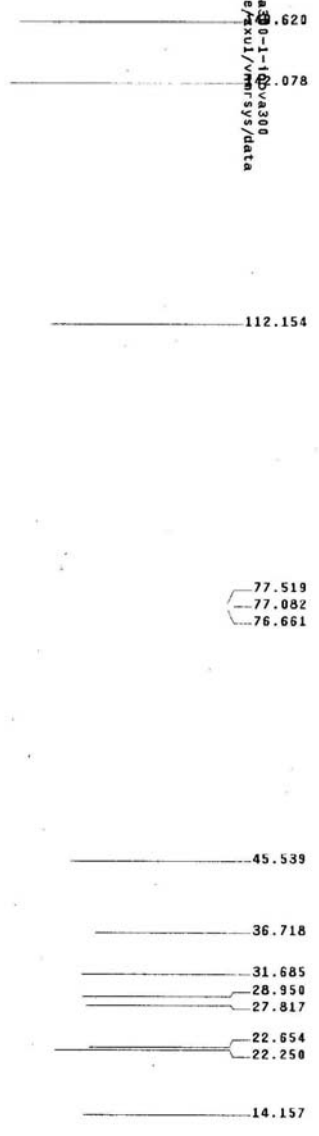


Data Collected on: inova300-1-inova300  
 Archive directory: /home/zxul/vnmrSYS/data  
 Sample directory:  
 File: PROTON  
 Pulse Sequence: szpul





13C OBSERVE  
Data Collected on: Inova 500-1-10va300  
Archive directory: /home/axul/vmr/sys/data  
Sample directory: /home/axul/vmr/sys/data  
File: CARBON  
Pulse Sequence: szpu1

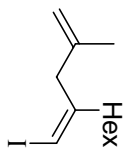


iii (Entry 4, Table 1)

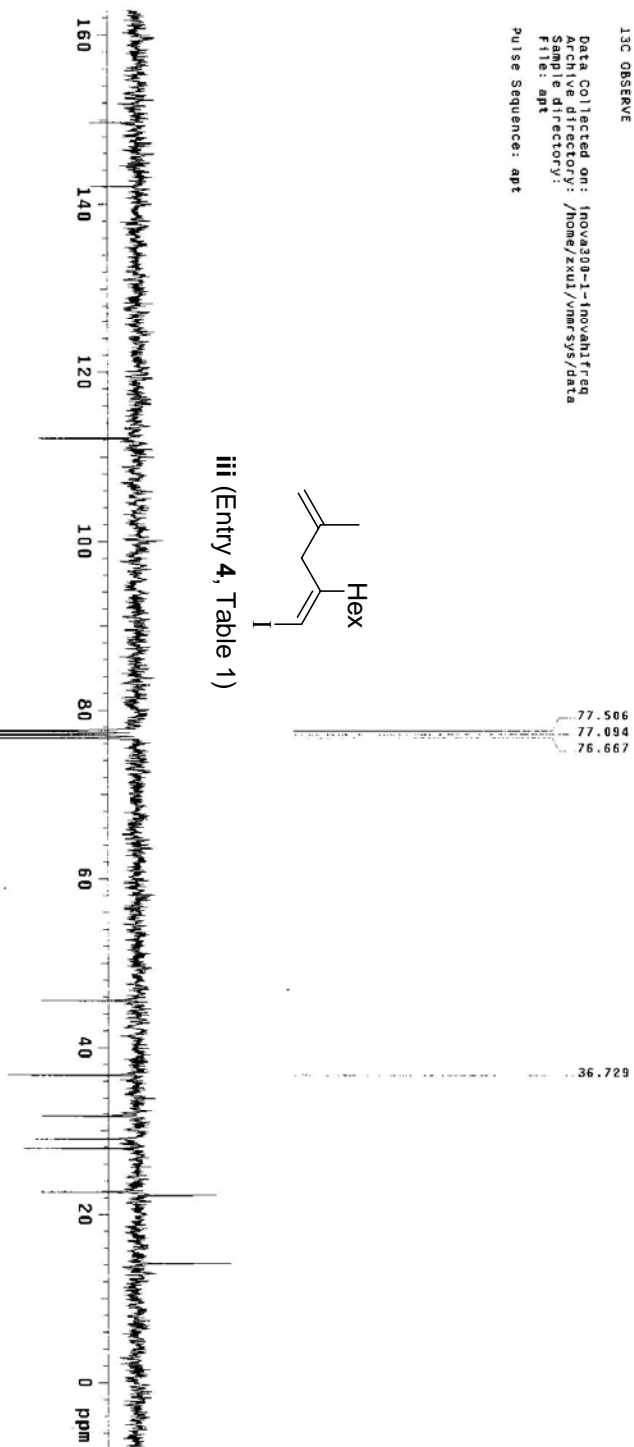


13C OBSERVE

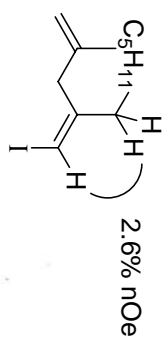
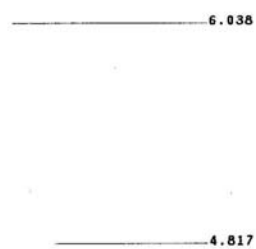
Data Collected on: inovas00-1-inovah1fraq  
Archive directory: /home/zxui/vnmr/sys/data  
Sample directory: /  
File: apt  
Pulse Sequence: apt



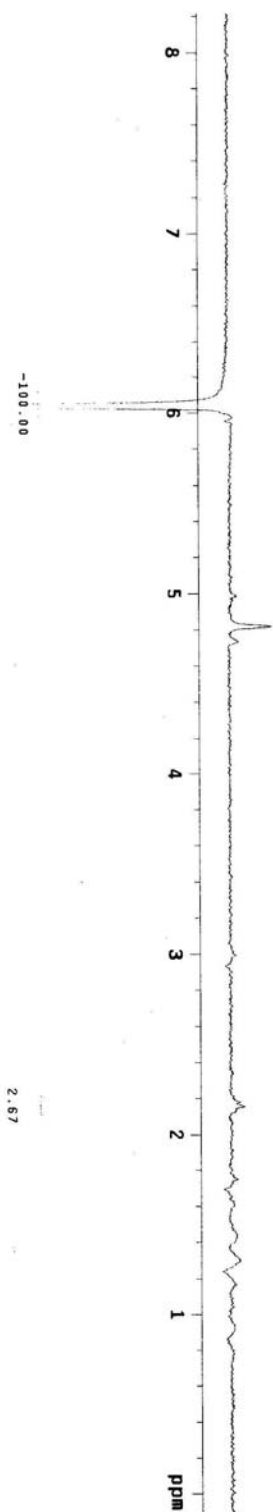
iii (Entry 4, Table 1)



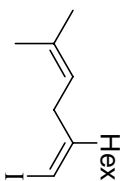
Turn spinning off.  
Data Collected on: inovas30-1-inovahi1freq  
Archive directory: /home/zxui/vnmrsws/data  
Sample directory:  
File: cyc1enoe  
Pulse Sequence: cycleenoe



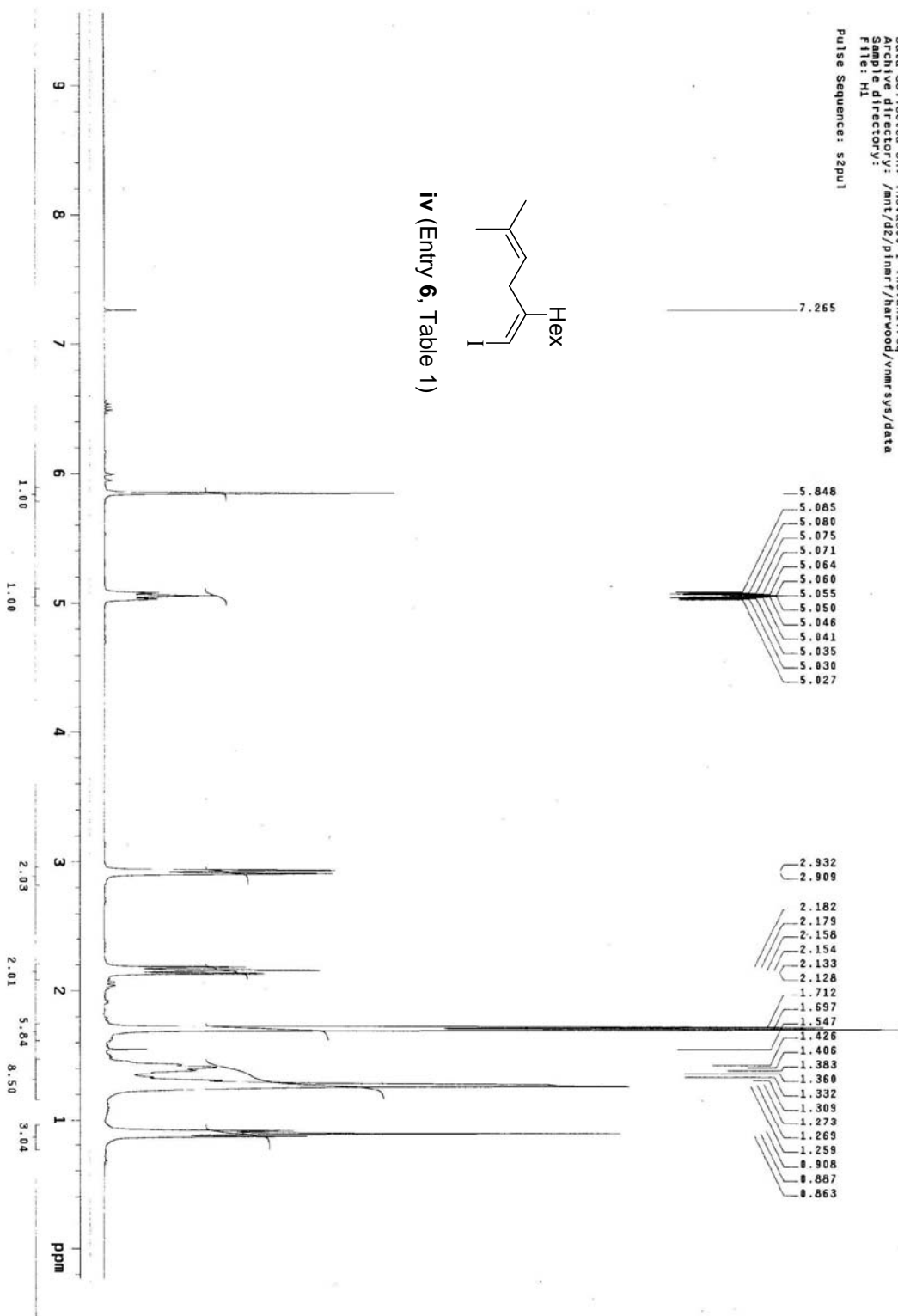
iii (Entry 4, Table 1)



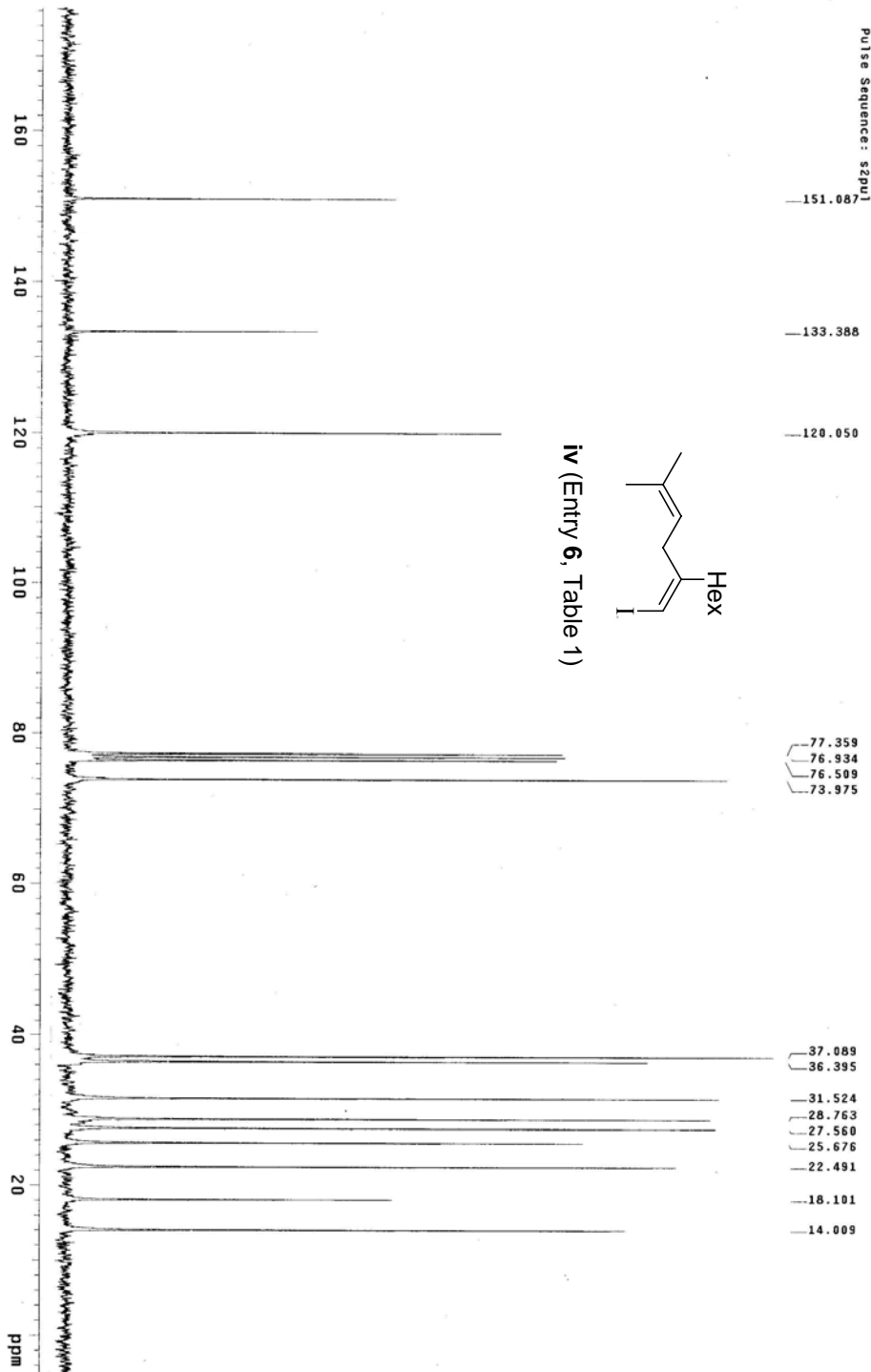
H1 standard parameters, CDCl3  
Data Collected on: Inova300-1-Inovaphireq  
Archive directory: /mnt/42/p1marf/harwood/vnmr/sy/data  
Sample directory:  
File: H1  
Pulse Sequence: s2pul1

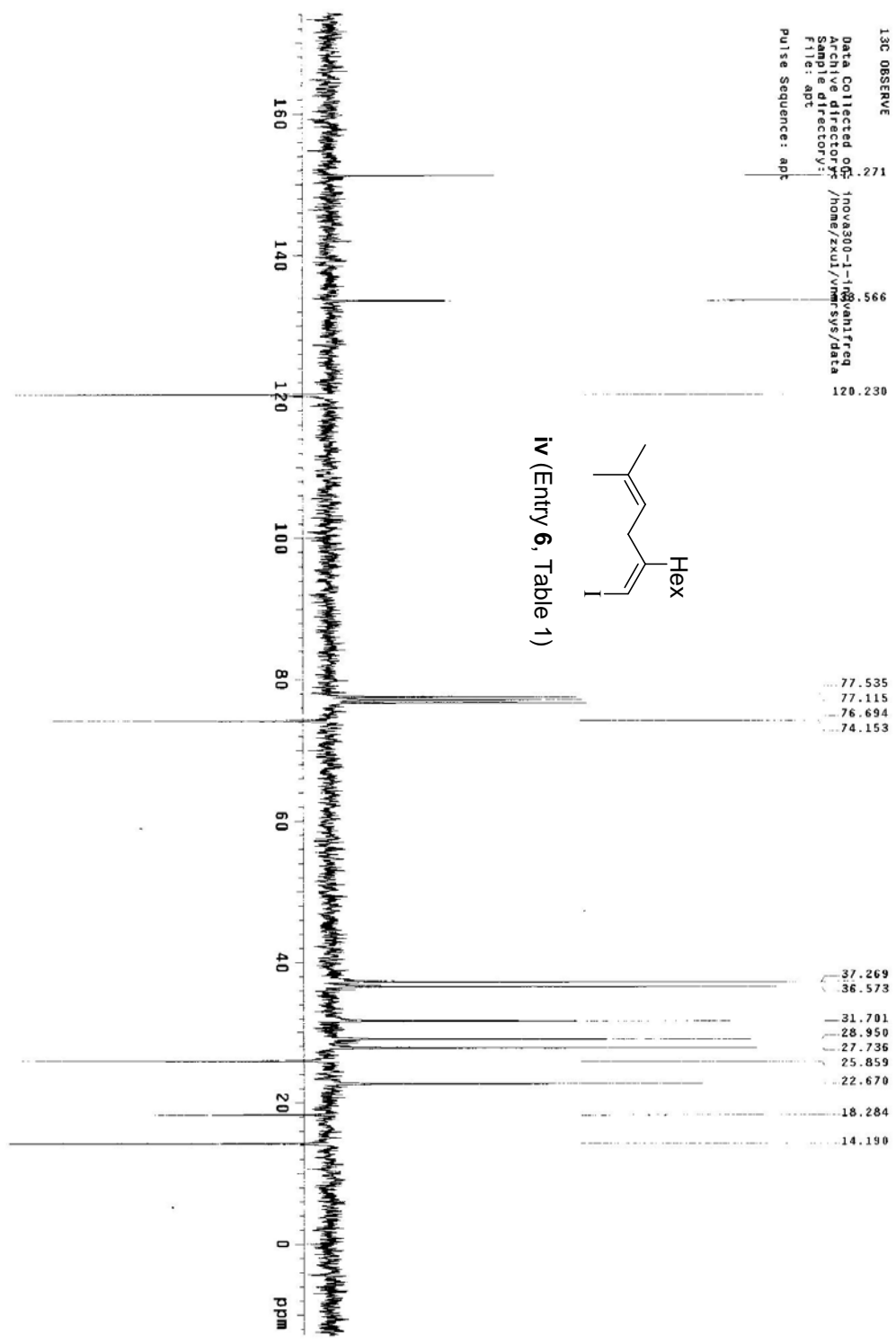


iv (Entry 6, Table 1)



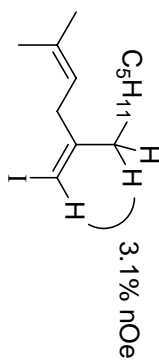
C13 standard parameters, C0C13  
Data Collected on: jnova300-1-inovahifreq  
Archive directory: /mnt/d2/pinart/harwood/vnmr-sys/data  
Sample directory: /mnt/d2/pinart/harwood/vnmr-sys/data  
File: std13c  
Pulse Sequence: szpu1



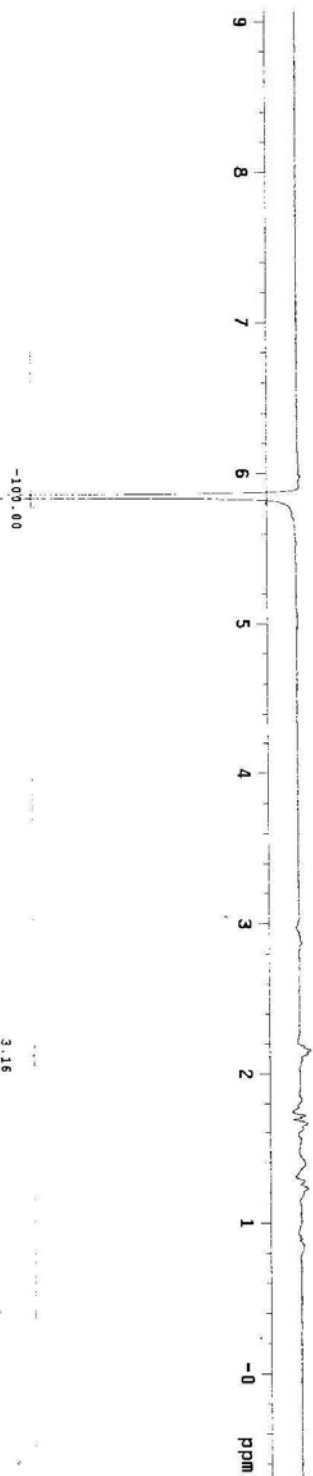


Turn spinning off.  
Data Collected on: jnov0300-1-jnovahi-freq  
Archive directory: /home/zxui/vnmrsws/data  
Sample directory:  
File: cyclenoe  
Pulse Sequence: cyclenoe

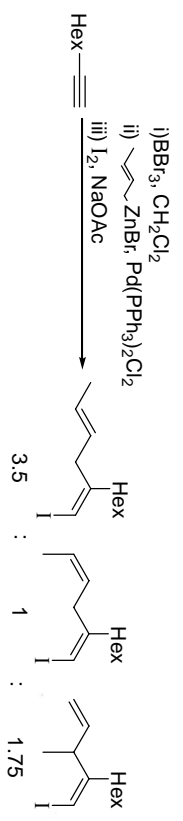
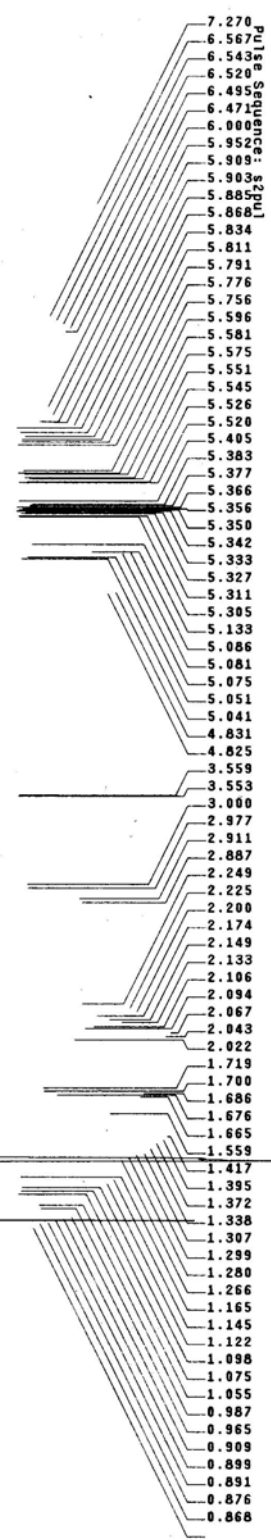
5.850



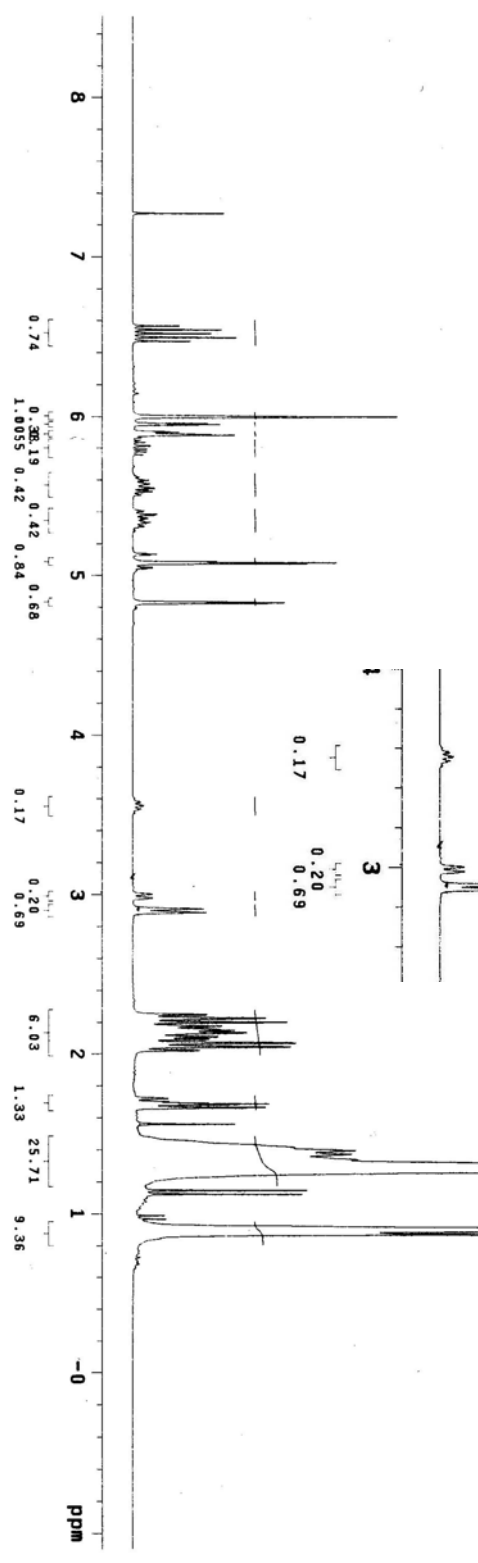
iv (Entry 6, Table 1)



Data Collected on: Inova300-1-Inova300  
 Archive directory: /home/zxui/vnmr/sys/data  
 Sample directory:  
 File: PROTON



Entry 5, Table 1





H1 standard parameters, CDCl3  
 Data Collected on: inovas300-2-inova300  
 Archive directory: /mnt/32/p1mr/f/harwood/vmr/sys/data  
 Sample directory:  
 File: PROTON  
 Pulse Sequence: szpu1

