

Supporting Information for

Regio- and Stereoselective Hydrostannation of Allenes Using Dibutylstannane (Bu₂SnH) and Successive Coupling with Aromatic Halides

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Analysis:

IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All ¹H and ¹³C NMR spectra were recorded with a JEOL JMTC-400/54/SS (400 and 100 MHz, respectively) in deuteriochloroform (CDCl₃) containing 0.03% (w/v) of tetramethylsilane as internal standard. ¹¹⁹Sn NMR (148 MHz) spectra were obtained in deuteriochloroform (CDCl₃) with Me₄Sn in THF-*d*₈ as external standard. Mass spectra were recorded on a JEOL JMS-DS-303 spectrometer. Column chromatography was performed by using Fuji Davison silica gel FL-100DX. Purification of products by recycle GPC system was performed by JAPAN ANALYTICAL INDUSTRY CO., LTD. LC-908. Yields were determined by ¹H NMR using internal standard. Stereochemistry of products was determined by NOE-difference spectrum or coupling constant of ¹H NMR.

Materials:

Di-*n*-butyltin dihydride (*n*-Bu₂SnH₂) was prepared by the reduction of di-*n*-butyltin dichloride (*n*-Bu₂SnCl₂) with LiAlH₄.¹ Di-*n*-butyliodotin hydride (*n*-Bu₂SnIH) was synthesized *in situ* by the redistribution reaction between Bu₂SnI₂ and Bu₂SnH₂.²

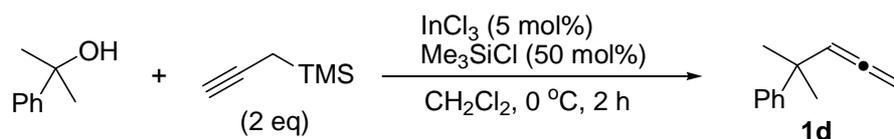
THF was purchased in dehydrated form.

Undeca-1,2-diene (Octylallene) (1a) was prepared according to the known procedures.³

Propa-1,2-dienyl-cyclohexane (Cyclohexylallene) (1b) was prepared by similar method to octylallene (1a).

4,4-Dimethyl-penta-1,2-diene (Tert-butylallene) (1c) was prepared according to the known procedure.⁴

4-Methyl-4-Phenyl-penta-1,2-diene (1d) was prepared according to our reported method.⁵ To the mixture of InCl₃ (0.275 g, 1.25 mmol) and propargyl trimethylsilane (68% purity 8.40g, 50.8 mmol) and chlorotrimethylsilane (1.39 g, 12.8 mmol) in dry dichloromethane (45 mL) was added dropwise 2-phenyl-propan-2-ol (2.98 g, 22 mmol) at 0 °C under nitrogen. After stirring at 0 °C for 2 h, the reaction mixture was warmed up to rt and then diluted with saturated NaHCO₃(aq) and extracted by Hexane/AcOEt= 9/1. The combined organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography eluting with hexane and then distilled under reduced pressure. (100 °C/ 8 mmHg, 1.87 g, 54% yield)



4-Butoxy-buta-1,2-diene (Butoxymethylallene) (1e) was prepared according to the known procedure.⁶

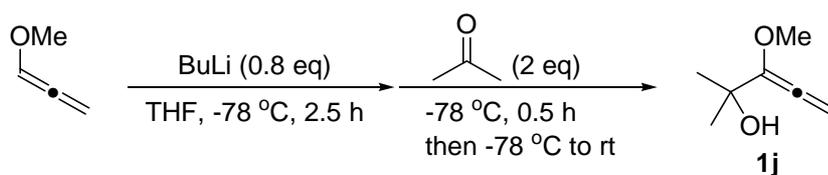
1-Methoxy-propa-1,2-diene (Methoxyallene) (1f) was prepared according to the known procedure.⁷

Cyclonona-1,2-diene (1g) was prepared according to the known procedures.⁸

3-Methoxy-undeca-1,2-diene (1h) was prepared according to the known procedures.⁹

Vinylidene-cyclohexane (1i) was prepared according to the known procedures.¹⁰

3-Methoxy-2-methyl-penta-3,4-dien-2-ol (1j) was known compound. To the stirred solution of 1-Methoxy-propa-1,2-diene (1f) (3.48 g, 49.7 mmol) in THF (40 mL) was added dropwise a 1.6 M BuLi in hexane (26 mL, 41.6 mmol) at -78 °C. After stirring at -78 °C for 2.5 h, acetone (6.32 g, 108.8 mmol) was added dropwise to this solution. Stirring was continued for 0.5 h at -78 °C and then warmed up to rt. The reaction mixture was diluted with water and extracted by diethyl ether. The combined organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by distillation under reduced pressure. (28 °C/0.05 mmHg, 2.79g, 52% yield)



Unless otherwise noted, materials obtained from commercial supplier were used without further purification.

Typical experimental procedures:

Hydrostannation of allenes using Bu₂SnIH

A 10 mL of round bottom flask was dried by flame under nitrogen atmosphere. After nitrogen was filled, THF (1.0 mL) was added. Bu₂SnH₂ (0.117 g, 0.5 mmol) and Bu₂SnI₂ (0.243 g, 0.5 mmol) were added successively to generate Bu₂SnIH by the redistribution reaction. To the mixture was added allene **1d** (0.158 g, 1.0 mmol) and resulting mixture was stirred at rt for 44 h when IR absorption of Sn-H at 1855 cm⁻¹ disappeared. To the resulting solution was added CHCl₃ (5 mL) to completely decompose the remained tin hydride and volatiles were removed under reduced pressure. Product **2d** was determined by ¹H NMR. Purification was performed by silica gel column chromatography eluting with hexane. Further purification was performed by recycle GPC eluting with CHCl₃. (0.130 g, 25%)

Synthesis of multisubstituted alkenes

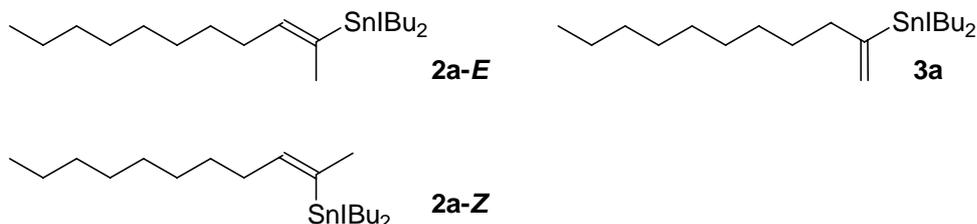
A 10 mL of round bottom flask was dried by flame under nitrogen atmosphere. After nitrogen was filled, THF (1.0 mL) was added. Bu₂SnH₂ (0.117 g, 0.5 mmol) and Bu₂SnI₂ (0.243 g, 0.5 mmol) were added to generate Bu₂SnIH by the redistribution reaction. To the mixture was added allene **1f** (0.070 g, 1.0 mmol) and resulting mixture was stirred at rt for 12 h when IR absorption of Sn-H at 1855 cm⁻¹ disappeared. [In the case of applying initiator, 1M Et₃B solution (0.1 mL) was added after the addition of allenes.] PhI (0.204 g, 1.0 mmol), Pd₂(dba)₃-CHCl₃ (0.010 g, 1 mol%) and 1M Bu₄NF solution in THF (3.0 mL) were added and the mixture was stirred at 65 °C for 24 h. After the reaction, resulting solution was filtrated by cerite. After concentration of the filtrate, yield of product **5f** was determined by ¹H NMR. Further purification was performed by silica gel column chromatography eluting with hexane/AcOEt = 95/5 followed by distillation under reduced pressure. (0.070 g, 48%)

Hydrostannation of Octylallene (**1a**) using Bu₃SnH in the presence of Et₃B

A 10 mL of round bottom flask was dried by flame under nitrogen atmosphere. After nitrogen was filled, hexane (1.0 mL), Bu₃SnH (0.291 g, 1.0 mmol) and allene **1a** (0.152 g, 1.0 mmol) were added successively. To the mixture was added 1M Et₃B solution in hexane (0.1 mL) and resulting mixture was stirred at rt for 90 h. To the resulting solution was added CHCl₃ (5 mL) to decompose the remained tin hydride and volatiles were removed under reduced pressure. Products were determined by ¹H NMR.

Physical and spectral data:

2-(Di-*n*-butyliodostannyl)-undec-2-ene (**2a**) and 2-(Di-*n*-butyliodostannyl)-undec-1-ene (**3a**)



These compounds were not purely isolated and were obtained as mixture of regio- and stereoisomers. (**2a-E:2a-Z:3a** = 39:34:27); See NMR spectrum. The observed data was shown below.

Colorless liquid

IR (neat) 1612 (C=C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 6.14 (tq, $J = 7.2$ and 1.5 Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 191.8$ Hz, 1H, SnC=CH **2a-Z**), 5.76 (d, $J = 1.0$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 203.6$ Hz, 1H, SnC=CH **3a**), 5.69 (tq, $J = 6.8$ and 1.7 Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 105.6$ Hz, 1H, SnC=CH **2a-E**), 5.32 (d, $J = 1.0$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 88.5$ Hz, 1H, SnC=CH **3a**), 2.38 (t, $J = 7.5$ Hz, 2H, **3a**), 2.16 (dt, $J = 7.5$ and 6.8 Hz, 2H, C=CCH₂, **2a-E**), 2.03 (s, $^3J(^{119}\text{Sn}-^1\text{H}) = 58.0$ Hz, 3H, SnCCH₃, **2a-E**), 2.00 (dt, $J = 7.5$ and 7.2 Hz, 2H, C=CCH₂, **2a-Z**), 1.93 (d, $^4J(^1\text{H}-^1\text{H}) = 1.0$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 62.3$ Hz, 3H, SnCCH₃, **2a-Z**), 1.73-1.19 (m, 74H), 0.96-0.85 (m, 27H, SnCH₂CH₂CH₂CH₃, **2a-E**, **2a-Z**, **3a**)

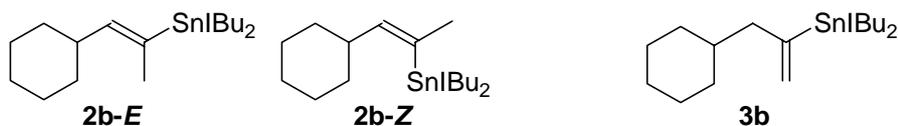
^{13}C NMR (CDCl_3 , 100 MHz) δ 153.25 (**3a**), 143.86 (**2a-E**), 142.04 (**2a-Z**), 136.25 (**2a**), 135.92 (**2a**), 126.90 (**3a**), 39.90 (**3a**), 35.60 (**2a**), 31.88, 31.87, 31.84, 29.87, 29.54, 29.50, 29.46, 29.40, 29.34, 29.28, 29.24, 29.17, 29.08, 29.06, 28.44, 26.77, 26.58, 26.56, 22.67, 18.48, 17.90, 16.86, 16.25, 14.11, 13.58, 13.56

^{119}Sn NMR (CDCl_3 , 148 MHz) δ 23.75, 19.02, 17.01

MS (EI, 70 eV) m/z 457 (M^+ - Bu, 100), 387 (M^+ - I, 8), 247 (ISn, 21), 177 (BuSn, 6), 69 (23), 55 (27)

Anal. calcd for $\text{C}_{19}\text{H}_{39}\text{ISn}$: C, 44.47; H, 7.66, found: C, 44.54; H, 7.56.

2-(Di-*n*-butylstannyl)-1-cyclohexyl-prop-1-ene (2b)
and **2-(Di-*n*-butylstannyl)-1-cyclohexyl-prop-2-ene (3b)**



These compounds were not purely isolated and were obtained as mixture of regio- and stereoisomers. (**2b-E:2b-Z:3b** = 44:44:12); See NMR spectrum. The observed data was shown below.

Colorless liquid

IR (neat) 1624 (C=C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 5.97 (dq, $^3J(^1\text{H}-^1\text{H})= 9.7$ Hz, $^4J(^1\text{H}-^1\text{H})= 1.7$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 191.3$ Hz, 1H, SnC=CH, **2b-Z**), 5.71 (d, $J= 1.4$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 244$ Hz, 1H, SnC=CH, **3b**), 5.49 (dq, $^3J(^1\text{H}-^1\text{H})= 8.7$ Hz, $^4J(^1\text{H}-^1\text{H})= 1.7$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 102.9$ Hz, 1H, SnC=CH, **2b-E**), 5.36 (d, $J= 1.4$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 90.3$ Hz, 1H, SnC=CH, **3b**), 2.46-2.38 (m, 1H, **2b-E**), 2.28 (d, $J= 7.0$ Hz, 2H, **3b**), 2.00 (d, $^4J(^1\text{H}-^1\text{H})= 1.7$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 59.4$ Hz, 3H, SnCCH₃, **2b-Z**), 1.95 (d, $^4J(^1\text{H}-^1\text{H})= 1.7$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 64.2$ Hz, 3H, SnCCH₃, **2b-E**), 1.81-1.02 (m, 68H), 0.98-0.89 (m, 18H, SnCH₂CH₂CH₂CH₃, **2b-E**, **2b-Z**, **3b**)

^{13}C NMR (CDCl_3 , 100 MHz) δ 151.96 (**3b**), 149.27 (**2b-E**), 147.74 (**2b-Z**), 134.24 (**2b**), 133.85 (**2b**), 128.08 (**3b**), 48.20 (**3b**), 45.63 (**2b-Z**), 37.24 (**2b-E**), 37.33 (**3b**), 33.23, 33.19, 33.15, 33.04, 32.68, 32.65, 32.61, 32.48, 29.29, 29.18, 29.12, 29.07, 29.04, 28.99, 28.88, 26.91, 26.84, 26.56, 26.50, 26.42, 26.78, 26.19, 25.97, 25.81, 25.69, 25.66, 18.59, 17.94, 16.84, 16.23, 13.55

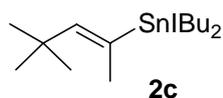
^{119}Sn NMR (CDCl_3 , 148 MHz) δ 25.32, 16.52, 16.06

MS (EI, 70 eV) m/z 427 ($\text{M}^+ - \text{Bu}$, 100), 357 ($\text{M}^+ - \text{I}$, 8), 247 (ISn, 21), 123 ($\text{M}^+ - \text{Bu}_2\text{ISn}$, 17), 81 (47), 55 (25)

HRMS calcd for $\text{C}_{13}\text{H}_{24}\text{ISn}$: 426.9945, found: m/z 426.9951 (EI, ($\text{M}^+ - \text{Bu}$), + 0.7 mmu)

Anal. calcd for $\text{C}_{17}\text{H}_{33}\text{ISn}$: C, 42.27; H, 6.89, found: C, 42.03; H, 6.85.

(E)-2-(Di-*n*-butylstannyl)-4,4-dimethyl-pent-2-ene (2c)



Colorless liquid

IR (neat) 1604 (C=C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 5.59 (q, $^4J(^1\text{H}-^1\text{H})= 1.9$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 115.9$ Hz, 1H, SnC=CH_c), 2.09 (d, $^4J(^1\text{H}-^1\text{H})= 1.9$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 70.0$ Hz, 3H, SnCCH₃), 1.66-1.30 (m, 12H, SnCH₂CH₂CH₂CH₃), 1.15 (s, 9H, ^tBu), 0.92 (t, $J= 7.2$ Hz, 6H, SnCH₂CH₂CH₂CH₃)

^{13}C NMR (CDCl_3 , 100 MHz) δ 152.50, 136.17, 35.32, 30.74, 29.01, 26.53, 19.96, 16.45, 13.58

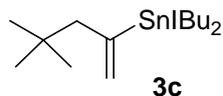
^{119}Sn NMR (CDCl_3 , 148 MHz) δ 29.75

MS (EI, 70 eV) m/z 401 (M^+ - Bu, 100), 361 (Bu_2ISn , 6), 331 (M^+ - I, 11), 247 (ISn , 31), 97 (M^+ - Bu_2ISn , 34), 57 (Bu, 30)

HRMS calcd for $\text{C}_{11}\text{H}_{22}\text{ISn}$: 400.9788, found: m/z 400.9782 (EI, (M^+ - Bu), - 0.6 mmu)

Anal. calcd for $\text{C}_{15}\text{H}_{31}\text{ISn}$: C, 39.42; H, 6.84, found: C, 39.41; H, 6.71.

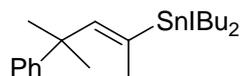
(E)-2-(Di-*n*-butylstannyl)-4,4-dimethyl-pent-1-ene (3c)



This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture were shown below.

^1H NMR (CDCl_3 , 400 MHz) δ 5.79 (d, $J= 1.2$ Hz, 1H, C=CH), 5.57 (d, $J= 1.2$ Hz, 1H, C=CH)

(E)-2-(Di-*n*-butyliodostannyl)-4-methyl-4-phenyl-pent-2-ene (2d)



Colorless liquid

IR (neat) 1601 (C=C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 7.35 (m, 2H, Ph), 7.29 (m, 2H, Ph), 7.17 (m, 1H, Ph), 5.98 (q, $^4J(^1\text{H}-^1\text{H})=1.9$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})=107.2$ Hz, 1H, $\text{SnC}=\text{CH}_c$), 1.52 (d, $J=1.9$ Hz, 3H, $\text{C}=\text{CCH}_3$), 1.46 (s, 6H, $\text{PhC}(\text{CH}_3)_2$), 1.67-1.32 (m, 12H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.94 (t, $J=7.3$ Hz, 6H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)

^{13}C NMR (CDCl_3 , 100 MHz) δ 152.39, 149.72, 138.69, 128.18, 125.96, 125.47, 41.97, 31.03, 29.04, 26.53, 20.11, 16.52, 13.61

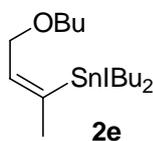
^{119}Sn NMR (CDCl_3 , 148 MHz) δ 25.92

MS (EI, 70 eV) m/z 520 (M^+ , 0.12), 463 ($\text{M}^+ - \text{Bu}$, 100), 393 ($\text{M}^+ - \text{I}$, 20), 361 (Bu_2ISn , 20), 247 (ISn , 19), 159 ($\text{M}^+ - \text{Bu}_2\text{ISn}$, 24), 119 ($\text{C}(\text{CH}_3)_2\text{Ph}$, 100), 91 (37)

HRMS calcd for $\text{C}_{16}\text{H}_{24}\text{ISn}$: 462.9944, found: m/z 462.9940 (EI, ($\text{M}^+ - \text{Bu}$), -0.4 mmu)

Anal. calcd for $\text{C}_{20}\text{H}_{33}\text{ISn}$: C, 46.28; H, 6.41, found: C, 46.44; H, 6.34.

(Z)-3-(Di-*n*-butyliodostannyl)-1-butoxy-but-2-ene (2e)



This compound was isolated including small amount of **3e**.

Colorless liquid

IR (neat) 1635 (C=C), 1095 (C-O-C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 6.28 (m, $^3J(^{119}\text{Sn}-^1\text{H})=189.6$ Hz, 1H, $\text{SnC}=\text{CH}_f$), 4.14-4.08 (m, 2H, $\text{C}=\text{CCH}_2\text{O}$), 3.62 (t, $J=7.3$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.17 (q, $^4J(^1\text{H}-^1\text{H})=1.9$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})=61.8$ Hz, 3H, SnCCH_3), 1.76-1.28 (m, 16H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.96 (t, $J=7.3$ Hz, 3H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.91 (t, $J=7.3$ Hz, 6H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)

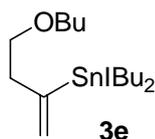
^{13}C NMR (CDCl_3 , 100 MHz) δ 133.19, 131.13, 71.47, 70.45, 30.36, 28.73, 28.61, 26.36, 22.00, 18.84, 13.82, 13.66

MS (EI, 70 eV) m/z 431 ($\text{M}^+ - \text{Bu}$, 56), 361 (Bu_2ISn , 78), 247 (ISn , 20), 177 (BuSn , 15), 127 ($\text{M}^+ - \text{Bu}_2\text{ISn}$, 23), 71 (100), 57 (27)

HRMS calcd for $\text{C}_{16}\text{H}_{34}\text{OISn}$: 489.0676, found: m/z 489.0674 (CI, ($\text{M}^+ + \text{H}$), -0.3 mmu)

Anal. calcd for $\text{C}_{16}\text{H}_{33}\text{OISn}$: C, 39.46; H, 6.83, found: C, 39.31; H, 6.86.

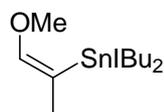
(Z)-3-(Di-*n*-butyliodostannyl)-1-butoxy-but-1-ene (3e)



This compound was a minor product and was not purely isolated. The identifiable signals in the crude mixture were shown below.

^1H NMR (CDCl_3 , 400 MHz) δ 5.98 (d, $^2J(^1\text{H}-^1\text{H})= 1.5$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 193.7$ Hz, 1H, $\text{SnC}=\underline{\text{CH}}_t$), 5.85 (d, $^2J(^1\text{H}-^1\text{H})= 1.5$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 88.9$ Hz, 1H, $\text{SnC}=\underline{\text{CH}}_c$), 3.49 (t, $J= 7.3$ Hz, 2H, OCH_2), 3.49 (t $J= 5.8$ Hz, 2H, OCH_2), 2.64 (t, $^3J(^1\text{H}-^1\text{H})= 5.8$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 71.5$ Hz, 2H, SnCCH_2)
 ^{13}C NMR (CDCl_3 , 100 MHz) δ 136.41, 71.59, 70.88, 40.11, 31.06, 28.98, 26.45, 19.80, 19.09, 13.84, 13.61.

(Z)-2-(Di-*n*-butyliodostannyl)-1-methoxy-prop-1-ene (2f)



This compound was decomposed by silica gel column chromatography and was isolated by GPC.
Colorless liquid

IR (neat) 1631 (C=C), 1141 (C-O-C) cm^{-1}

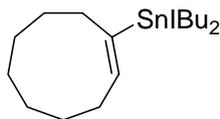
^1H NMR (CDCl_3 , 400 MHz) δ 6.46 (q, $^4J(^1\text{H}-^1\text{H})= 1.7$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 127.5$ Hz, 1H, $\text{SnC}=\underline{\text{CH}}_t$), 3.53 (s, 3H, OCH_3), 1.84 (d, $^4J(^1\text{H}-^1\text{H})= 1.7$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 61.8$ Hz, 3H, SnCCH_3), 1.64-1.31 (m, 12H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.91 (t, $J= 7.3$ Hz, 6H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)

^{13}C NMR (CDCl_3 , 100 MHz) δ 150.87, 111.74, 58.79, 28.93, 26.37, 18.15, 17.73, 13.59

MS (EI, 70 eV) m/z 375 ($\text{M}^+ - \text{Bu}$, 100), 335 (58), 305 ($\text{M}^+ - \text{I}$, 23), 247 (ISn, 42), 151 (48), 57 (Bu, 73)

HRMS calcd for $\text{C}_8\text{H}_{16}\text{OISn}$: 374.9268, found: m/z 374.9291 (EI, (M^+), + 2.3 mmu).

(E)-1-(Di-n-butylidostannyl)-cyclonon-1-ene (2g)



Colorless liquid

IR (neat) 1608 (C=C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 5.88 (t, $^3J(^1\text{H}-^1\text{H})= 8.2$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 101.9$ Hz, 1H, $\text{SnC}=\text{CH}_c$), 2.53 (t, $^3J(^1\text{H}-^1\text{H})= 5.6$ Hz, $^3J(^{119}\text{Sn}-^1\text{H})= 87.7$ Hz, 2H, SnCCH_2), 2.33-2.23 (m, 2H, $\text{SnC}=\text{CCH}_2$), 1.70-1.33 (m, 22H), 0.92 (t, $J= 7.3$ Hz, 6H, CH_3)

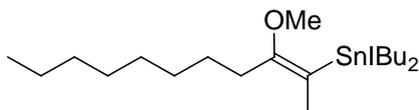
^{13}C NMR (CDCl_3 , 100 MHz) δ 143.62, 142.90, 31.03, 29.14, 27.69, 26.66, 26.02, 25.71, 25.32, 24.70, 16.62, 13.59

^{119}Sn NMR (CDCl_3 , 148 MHz) δ 24.25

MS (EI, 70 eV) m/z 427 ($\text{M}^+ - \text{Bu}$, 100), 361 (M^+ , 14), 247 (24), 123 ($\text{M}^+ - \text{SnIBu}_2$, 68), 81 (90), 67 (35)

HRMS calcd for $\text{C}_{13}\text{H}_{24}\text{ISn}$: 426.9945, found: m/z 426.9940 (EI, ($\text{M}^+ - \text{Bu}$), - 0.5 mmu).

(Z)-2-(Di-n-butylidostannyl)-3-methoxy-undec-2-ene (2h)



This compound is unstable and was not purely isolated. This compound was decomposed by silica gel column chromatography. The identifiable signals in the crude mixture after GPC were shown below.

Colorless liquid

IR (neat) 1643 (C=C), 1092 (C-O-C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 3.45 (s, 3H, OCH_3), 2.32 (t, 7.3 Hz, 2H, $\text{C}=\text{CCH}_2$), 1.86 (s, $^3J(^{119}\text{Sn}-^1\text{H})= 69.1$ Hz, 3H, SnCCH_3), 1.67-1.19 (m, 24H), 0.94-0.84 (m, 9H, CH_3 of C_8H_{17} and $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)

^{13}C NMR (CDCl_3 , 100 MHz) δ 158.25, 114.12, 55.76, 31.78, 29.35, 29.19, 28.99, 28.92, 27.09, 26.34, 25.12, 22.59, 18.65, 16.81, 14.04, 13.59

^{119}Sn NMR (CDCl_3 , 148 MHz) δ 33.01

MS (EI, 70 eV) m/z 544 (M^+ , 0.37), 487 ($\text{M}^+ - \text{Bu}$, 50), 455 (80), 431 (24), 417 ($\text{M}^+ - \text{I}$, 12), 361 (Bu_2ISn , 83), 335 (53), 265 (30), 247 (ISn , 78), 151 (36), 57 (Bu , 100), 41 (26)

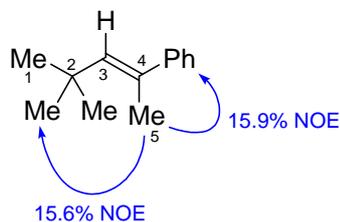
HRMS calcd for $\text{C}_{16}\text{H}_{32}\text{IOSn}$: 487.0520, found: m/z 487.0527 (EI, ($\text{M}^+ - \text{Bu}$), + 0.7 mmu).

(E)-2,2-Dimethyl-4-phenyl-pent-3-ene (5c)

15.9% NOE was observed at Ph by irradiation at 5-H (2.14 ppm).

15.6% NOE was observed at 1-H (1.21 ppm) by irradiation at 5-H (2.14 ppm).

No NOE was observed at 3-H (5.73 ppm) by irradiation at 5-H (2.14 ppm).



Colorless liquid

IR (neat) 1597 (C=C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 7.35-7.18 (m, 5H, Ph), 5.73 (q, $J= 1.5$ Hz, 1H, C=CH), 2.14 (d, $J= 1.5$ Hz, 3H, C=CCH₃), 1.21 (s, 9H, tBu)

^{13}C NMR (CDCl_3 , 100 MHz) δ 146.10, 139.27, 134.28, 128.03, 126.31, 125.91, 32.65, 30.93, 17.18

MS (EI, 70 eV) m/z 174 (M^+ , 45), 159 ($\text{M}^+ - \text{Me}$, 100), 117 ($\text{M}^+ - \text{CMe}_3$, 59)

HRMS calcd for $\text{C}_{13}\text{H}_{18}$: 174.1409, found: m/z 174.1412 (EI, (M^+), + 0.3 mmu)

Anal. calcd for $\text{C}_{13}\text{H}_{18}$: C, 89.59; H, 10.41, found: C, 89.55; H, 10.48.

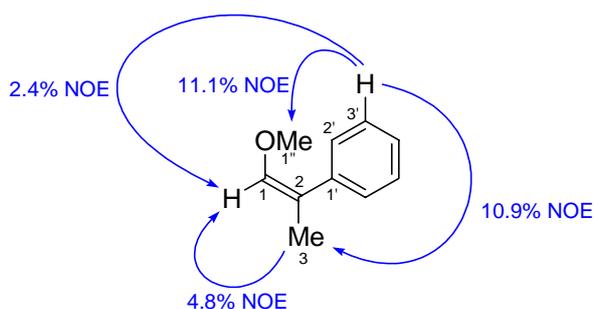
(Z)-1-Methoxy-2-phenyl-propene (5f)

4.8% NOE was observed at 1-H (6.12 ppm) by irradiation at 3-H (1.92 ppm).

11.1% NOE was observed at OMe (3.67 ppm) by irradiation at 3'-H (7.34-7.28 ppm).

10.9% NOE was observed at 3-H (1.92 ppm) by irradiation at 3'-H (7.34-7.28 ppm).

Little NOE was observed at 1-H (6.12 ppm) by irradiation at 3'-H (7.34-7.28 ppm).



Colorless liquid

bp 90 °C/ 4 mmHg

IR (neat) 1651 (C=C), 1146 (C-O-C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 7.62-7.58 (m, 2H, Ph), 7.34-7.28 (m, 2H, Ph), 7.20-7.15 (m, 1H, Ph), 6.12 (q, $J= 1.4$ Hz, 1H, C=CH), 3.67 (s, 3H, OCH₃), 1.92 (d, $J= 1.4$ Hz, 3H, C=CCH₃)

^{13}C NMR (CDCl_3 , 100 MHz) δ 144.56, 138.31, 127.89, 127.44, 126.00, 110.78, 60.11, 18.27

MS (EI, 70 eV) m/z 148 (M^+ , 72), 121 (100), 105 (55), 77 (Ph, 29)

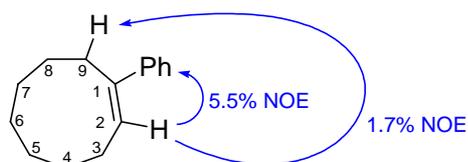
HRMS calcd for $\text{C}_{10}\text{H}_{12}\text{O}$: 148.0888, found: m/z 148.0883 (EI, (M^+), - 0.5 mmu)

Anal. calcd for $\text{C}_{10}\text{H}_{12}\text{O}$: C, 81.04; H, 8.16, found: C, 80.83; H, 7.92.

(E)-1-Phenyl-cyclononene (5g)

5.5% NOE was observed at Ph by irradiation at 2-H (5.87 ppm).

No NOE was observed at 9-H (2.32 ppm) by irradiation at 2-H (5.87 ppm).



Colorless liquid

bp 110 °C/ 0.3 mmHg

IR (neat) 1597 (C=C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 7.41-7.38 (m, 2H, Ph), 7.32-7.28 (m, 2H, Ph), 7.25-7.19 (m, 1H, Ph), 5.87 (t, J = 8.5 Hz, 1H, C=CH), 2.63 (t, J = 5.5 Hz, 2H, C=CPhCH₂), 2.32 (dt, J = 8.5 and 5.5 Hz, 2H, C=CHCH₂), 1.62-1.49 (m, 10H)

^{13}C NMR (CDCl_3 , 100 MHz) δ 143.49, 140.46, 128.73, 128.13, 126.38, 126.13, 28.86, 27.46, 26.62, 26.25, 25.69, 25.40, 25.14

MS (EI, 70 eV) m/z 200 (M^+ , 32), 185 (11), 172 (7), 157 (16), 143 (23), 129 (28), 118 (100), 91 (23)

HRMS calcd for $\text{C}_{15}\text{H}_{20}$: 200.1565, found: m/z 200.1574 (EI, (M^+), + 0.9 mmu)

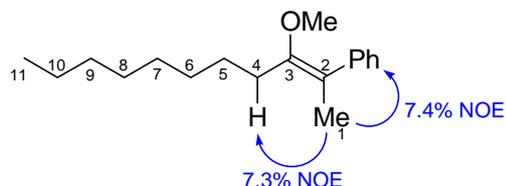
Anal. calcd for $\text{C}_{15}\text{H}_{20}$: C, 89.94; H, 10.06, found: C, 89.87; H, 10.21.

(Z)-3-Methoxy-2-phenyl-undec-2-ene (5h)

7.4% NOE was observed at Ph by irradiation at 1-H (1.95 ppm).

7.3% NOE was observed at 4-H (2.31 ppm) by irradiation at 1-H (1.95 ppm).

No NOE was observed at OMe (3.33 ppm) by irradiation at 1-H (1.95 ppm).



Colorless liquid

IR (neat) 1651 (C=C), 1092 (C-O-C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 7.31-7.29 (m, 4H, Ph), 7.20-7.14 (m, 1H, Ph), 3.33 (s, 3H, OCH₃), 2.31 (t, J = 7.5 Hz, 2H, C=CCH₂), 1.95 (s, 3H, C=CCH₃), 1.54 (tt, J = 6.8 and 7.5 Hz, 2H, C=CCH₂CH₂), 1.42-1.22 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H, CH₃ of C_8H_{17})

^{13}C NMR (CDCl_3 , 100 MHz) δ 152.17, 141.84, 128.33, 127.76, 125.73, 116.80, 56.94, 31.89, 29.53, 29.44, 29.31, 28.15, 27.39, 22.67, 18.81, 14.10

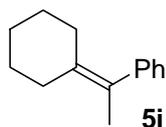
MS (EI, 70 eV) m/z 260 (M^+ , 94), 162 (28), 147 (42), 130 (100), 129 (60), 105 (36), 91 (38), 77 (Ph, 7)

HRMS calcd for $\text{C}_{18}\text{H}_{28}\text{O}$: 260.2140, found: m/z 260.2146 (EI, (M^+), + 0.6 mmu)

Anal. calcd for $\text{C}_{18}\text{H}_{28}\text{O}$: C, 83.02; H, 10.84, found: C, 82.93; H, 10.67.

(1-Phenyl-ethylidene)-cyclohexane (5i)

This compound was isolated with small amount of 1-cyclohexyl-1-phenyl-ethylene (6i).



Colorless liquid

bp 70 °C/ 0.4 mmHg

IR (neat) 1601 (C=C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 7.33-7.28 (m, 2H, Ph), 7.21-7.17 (m, 1H, Ph), 7.13-7.10 (m, 2H, Ph), 2.30 (t, $J = 5.8$ Hz, 2H, $\text{C}=\text{CCH}_2$), 1.99 (t, $J = 6.0$ Hz, 2H, $\text{C}=\text{CCH}_2$), 1.95 (s, 3H, CH_3), 1.64-1.40 (m, 6H, $\text{C}=\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$)

^{13}C NMR (CDCl_3 , 100 MHz) δ 145.29, 135.43, 128.39, 127.91, 126.60, 125.65, 31.90, 30.58, 28.46, 28.06, 26.85, 20.21

MS (EI, 70 eV) m/z 186 (M^+ , 100), 171 ($\text{M}^+ - \text{Me}$, 40), 143 (40), 129 (46), 118 (33), 105 (60), 91 (26)

HRMS calcd for $\text{C}_{14}\text{H}_{18}$: 186.1409, found: m/z 186.1412 (EI, (M^+), + 0.3 mmu).

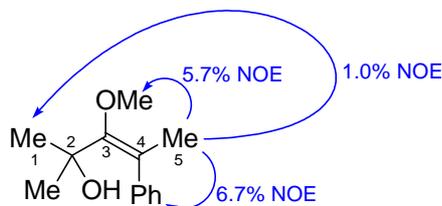
(E)-3-Methoxy-2-methyl-4-phenyl-pent-3-ene-2-ol (5j)

This compound was purified by column chromatography.

6.7% NOE was observed at Ph by irradiation at 5-H (1.98 ppm).

5.7% NOE was observed at OMe (3.78 ppm) by irradiation at 5-H (1.98 ppm).

No NOE was observed at 1-H (1.21 ppm) by irradiation at 5-H (1.98 ppm).



Yellow liquid

IR (neat) 3467 (O-H), 1651 (C=C), 1068 (C-O-C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 7.34-7.30 (m, 2H, Ph), 7.26-7.23 (m, 1H, Ph), 7.22-7.14 (m, 2H, Ph), 3.78 (s, 3H, OCH_3), 2.17 (s, 1H, OH), 1.98 (s, 3H, $\text{C}=\text{CCH}_3$), 1.21 (s, 6H, $\text{C}(\text{CH}_3)_2$)

^{13}C NMR (CDCl_3 , 100 MHz) δ 156.92, 142.18, 128.37, 128.25, 126.72, 121.76, 73.73, 61.40, 30.15, 21.72

MS (EI, 70 eV) m/z 206 (M^+ , 20), 173 (100), 159 ($\text{M}^+ - 2\text{Me} - \text{OH}$, 41), 131 (34), 105 (46)

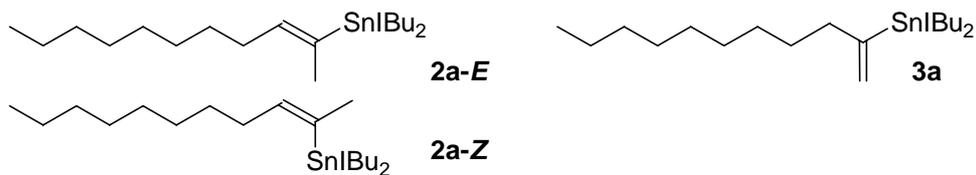
HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: 206.1307, found: m/z 206.1301 (EI, (M^+), - 0.6 mmu)

Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.69; H, 8.80, found: C, 75.85; H, 8.64.

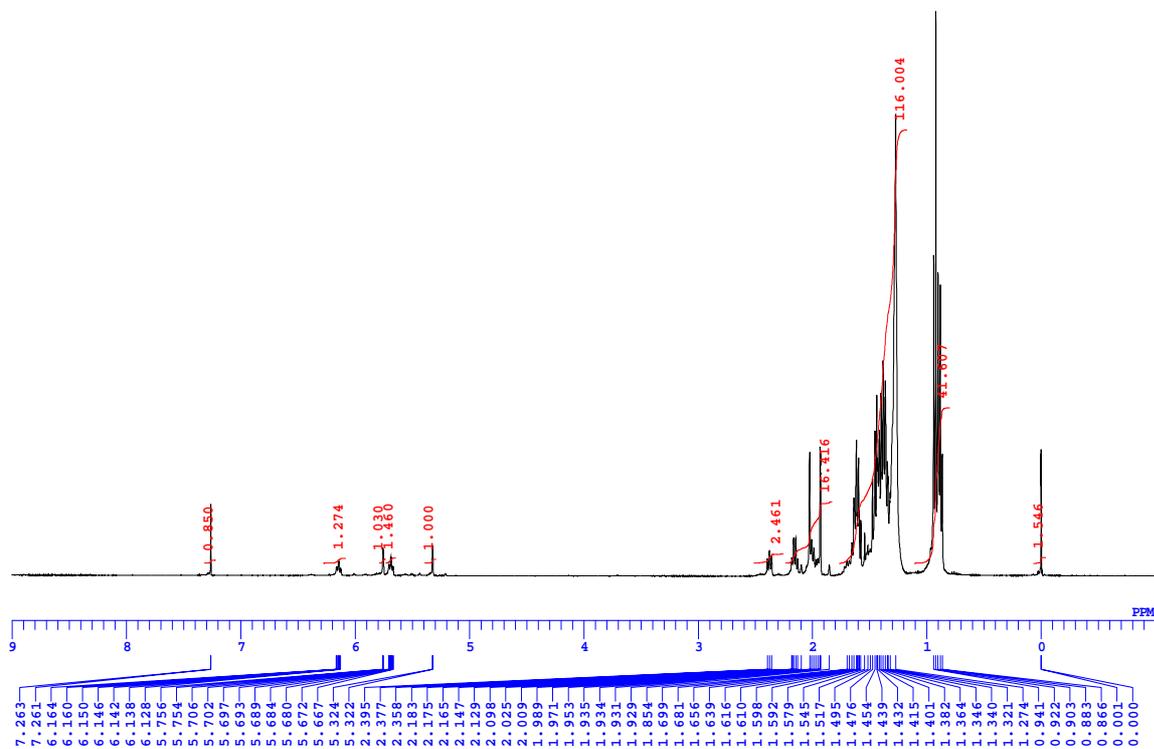
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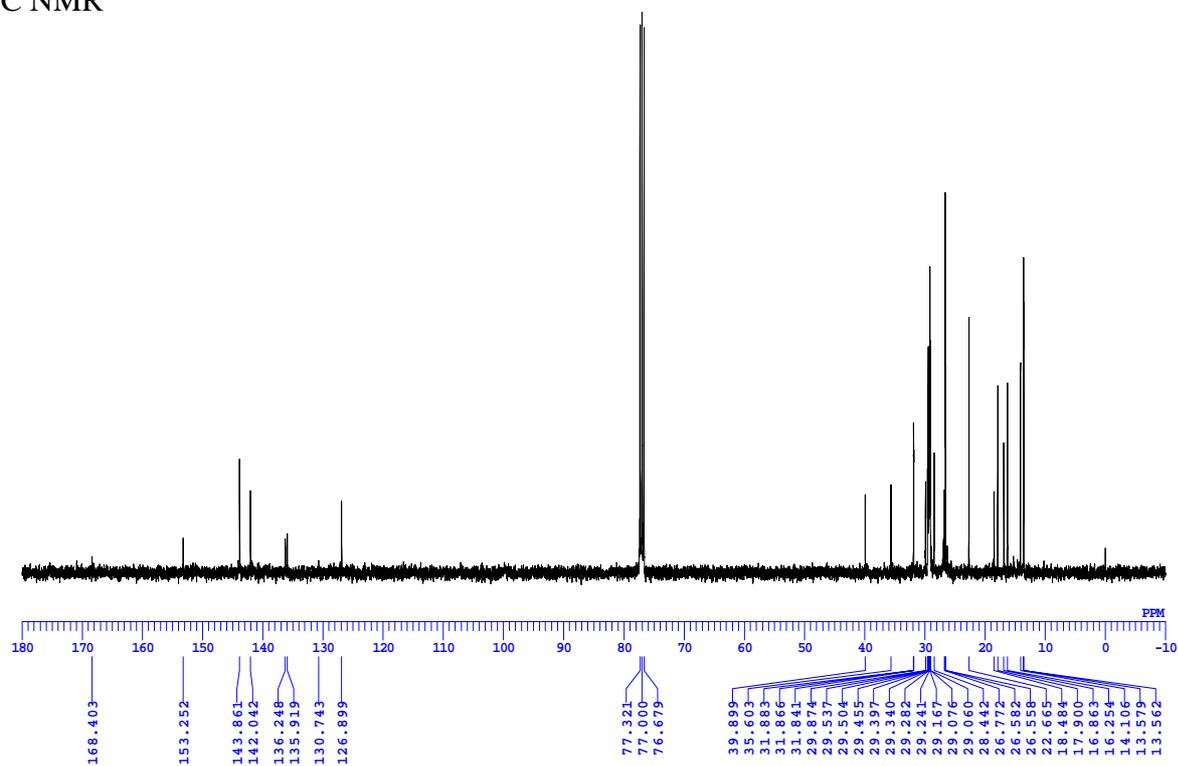
2a and 3a



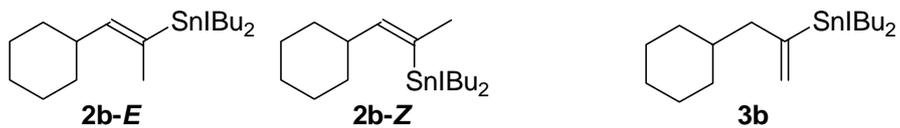
¹H NMR



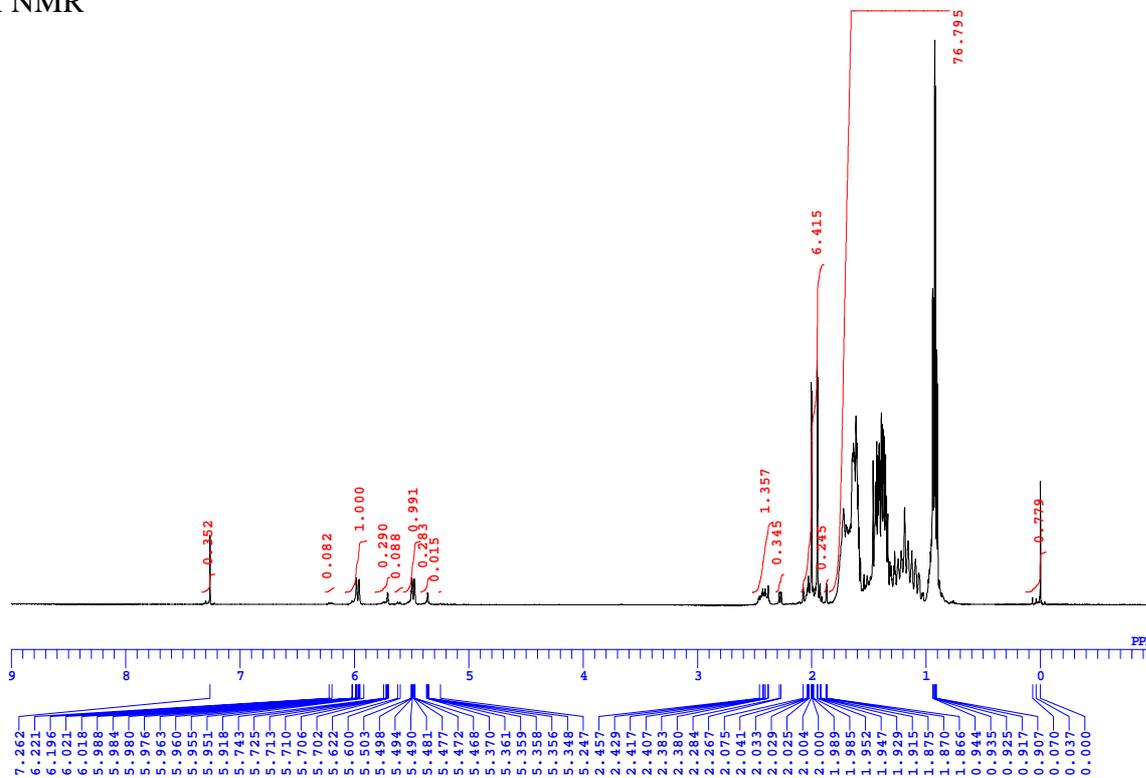
¹³C NMR



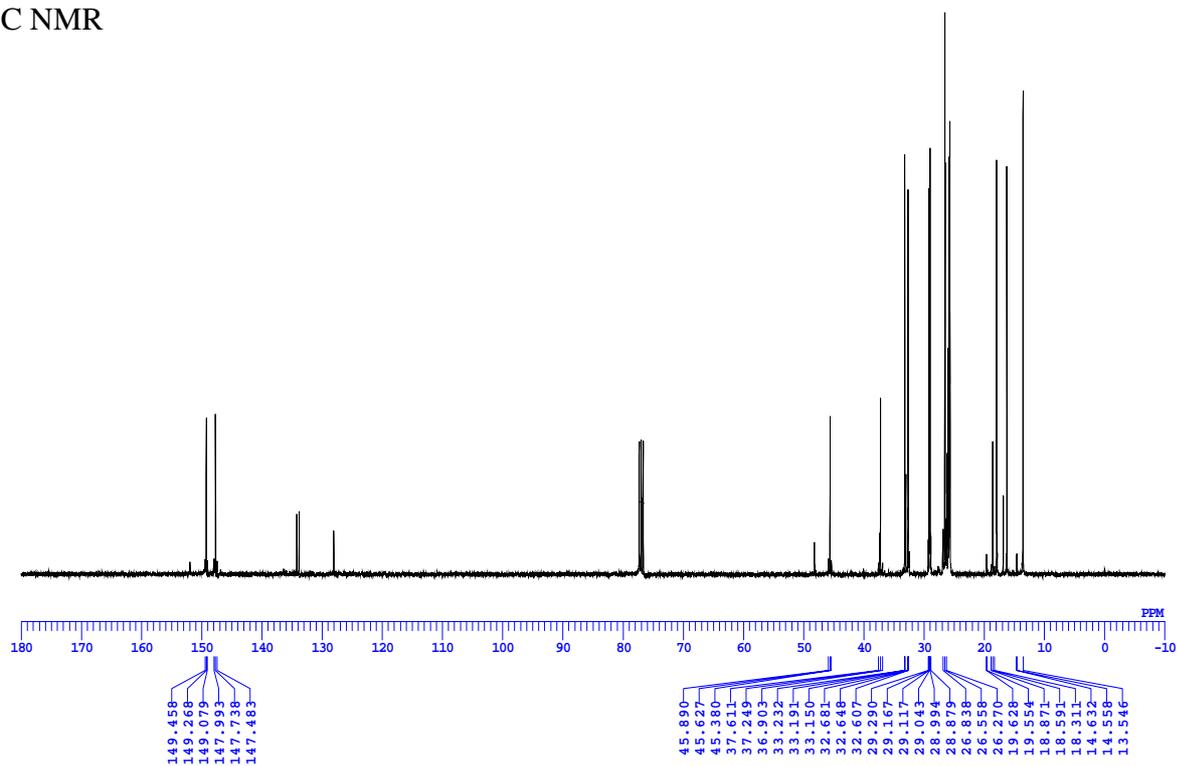
2b and 3b



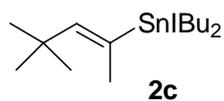
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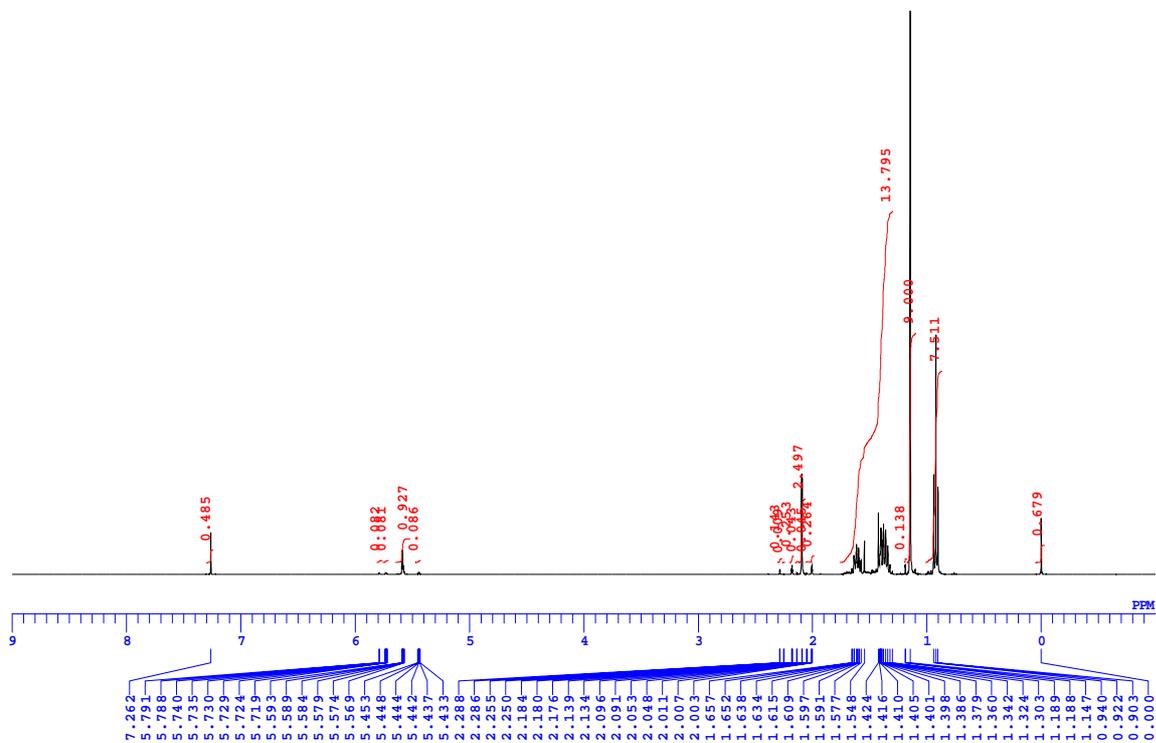
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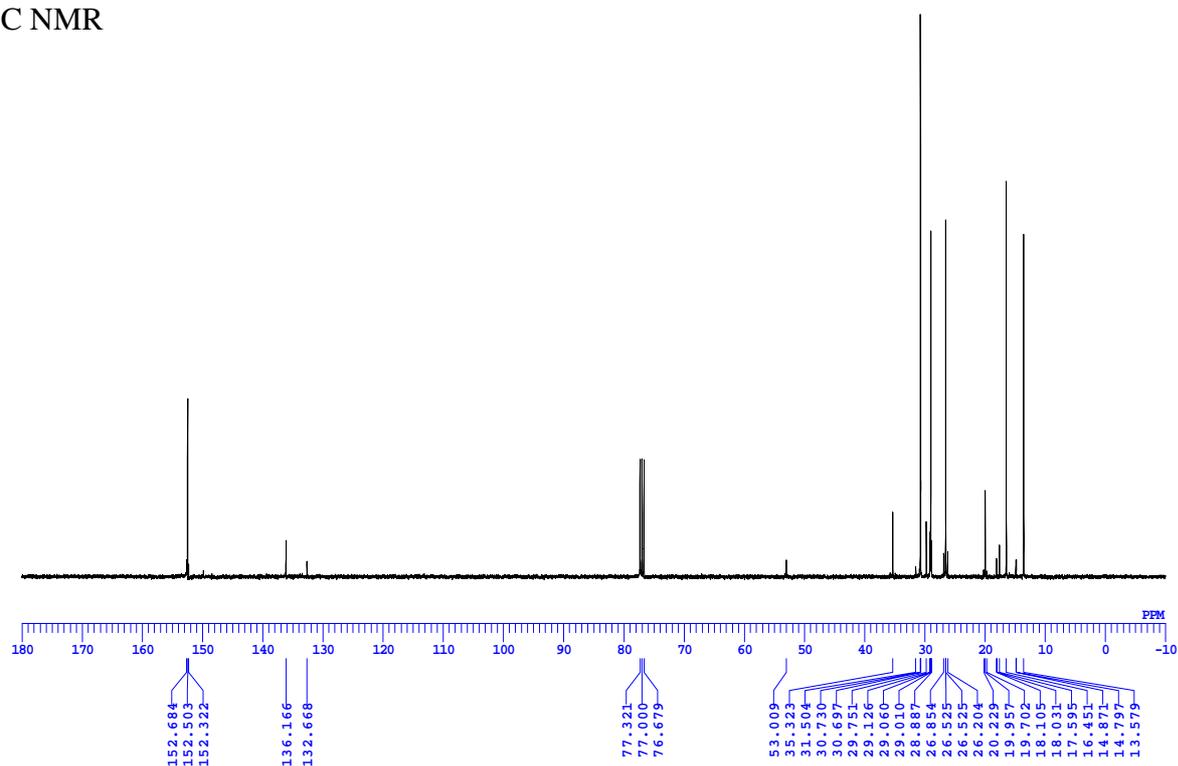
2c



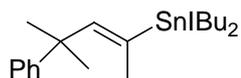
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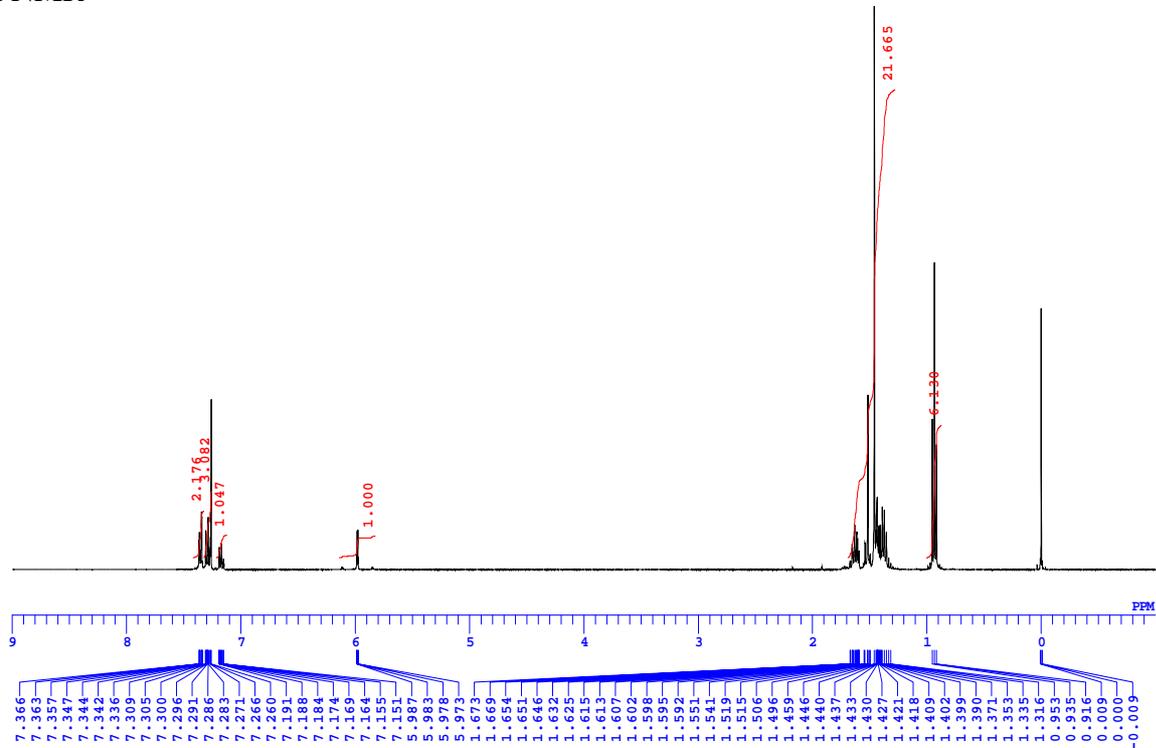
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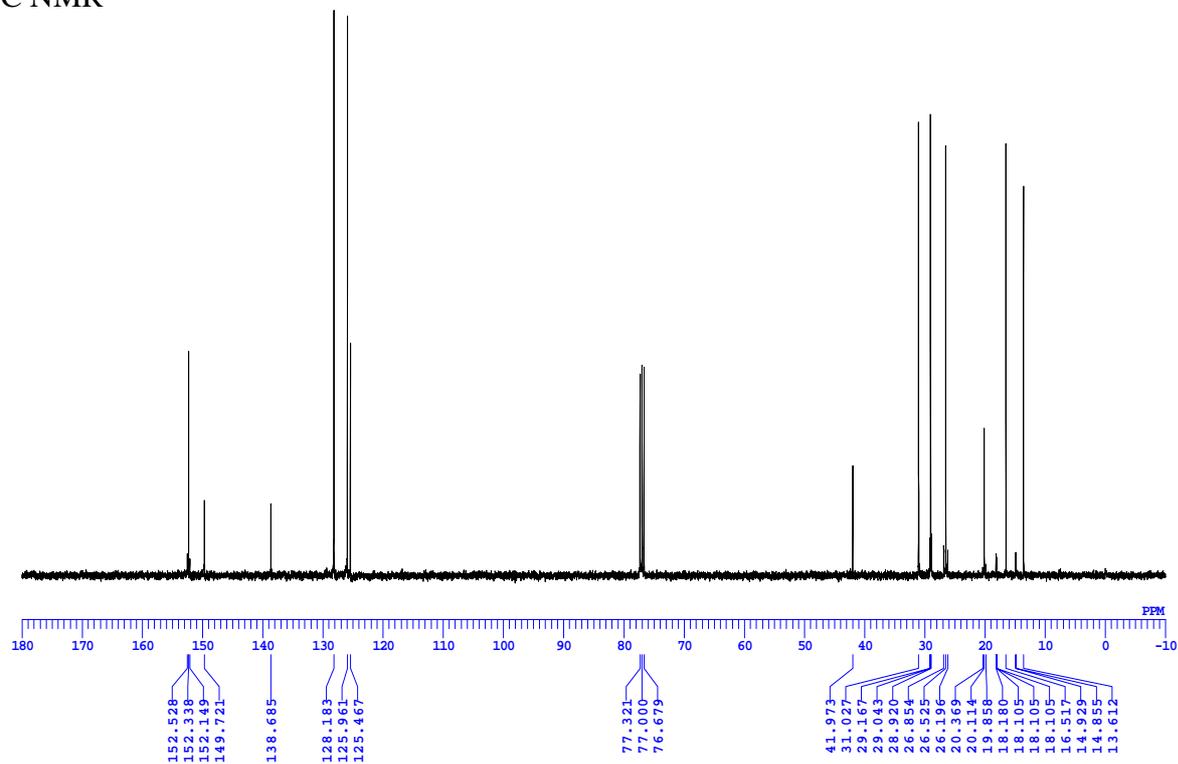
2d



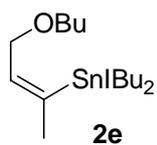
¹H NMR



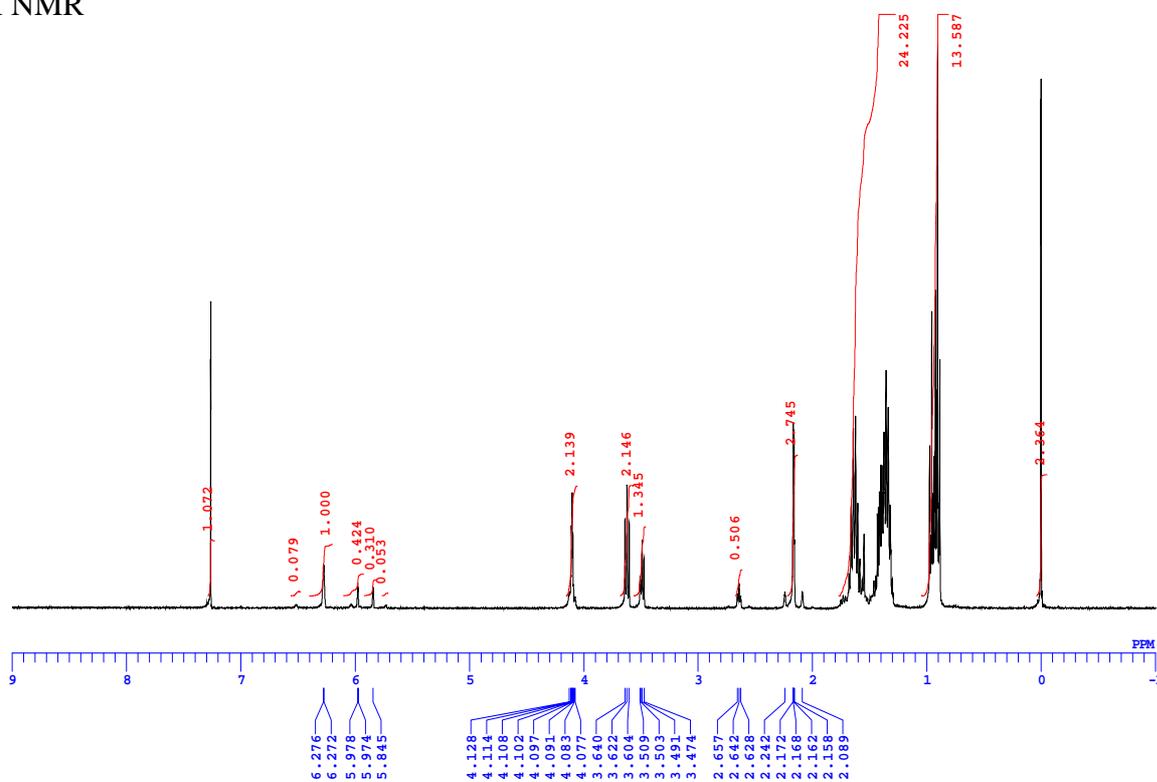
¹³C NMR



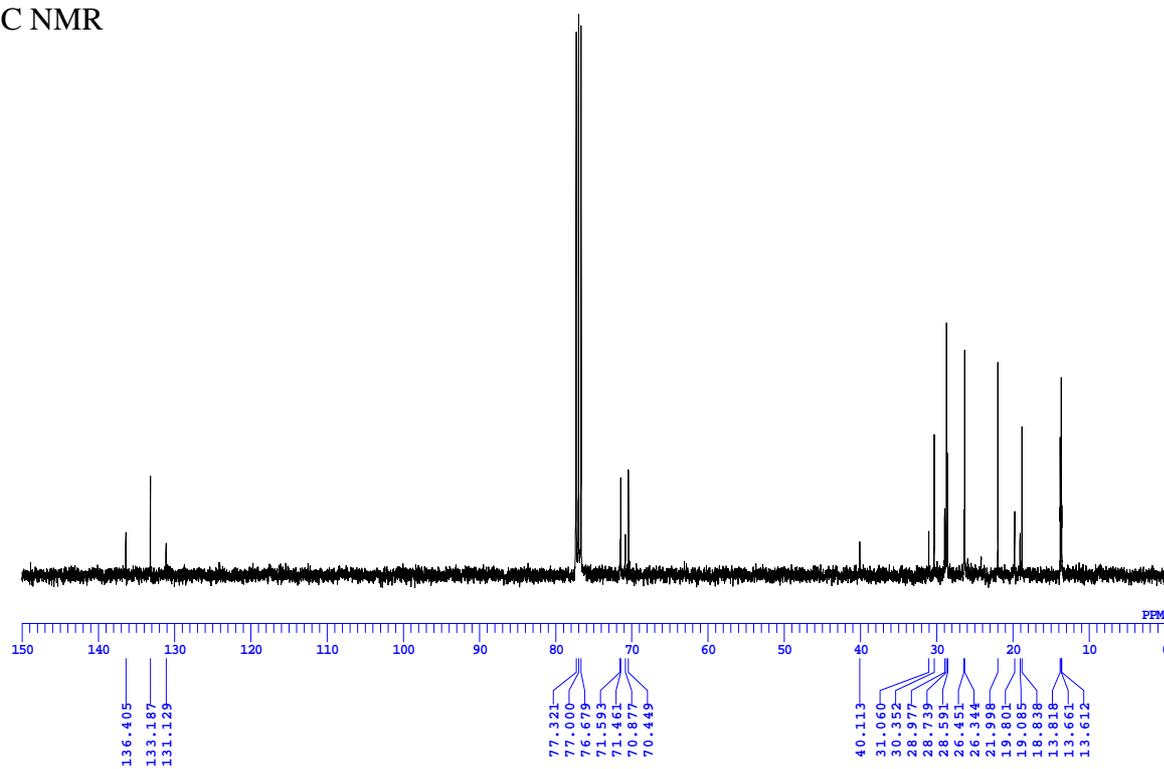
2e



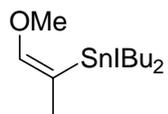
^1H NMR



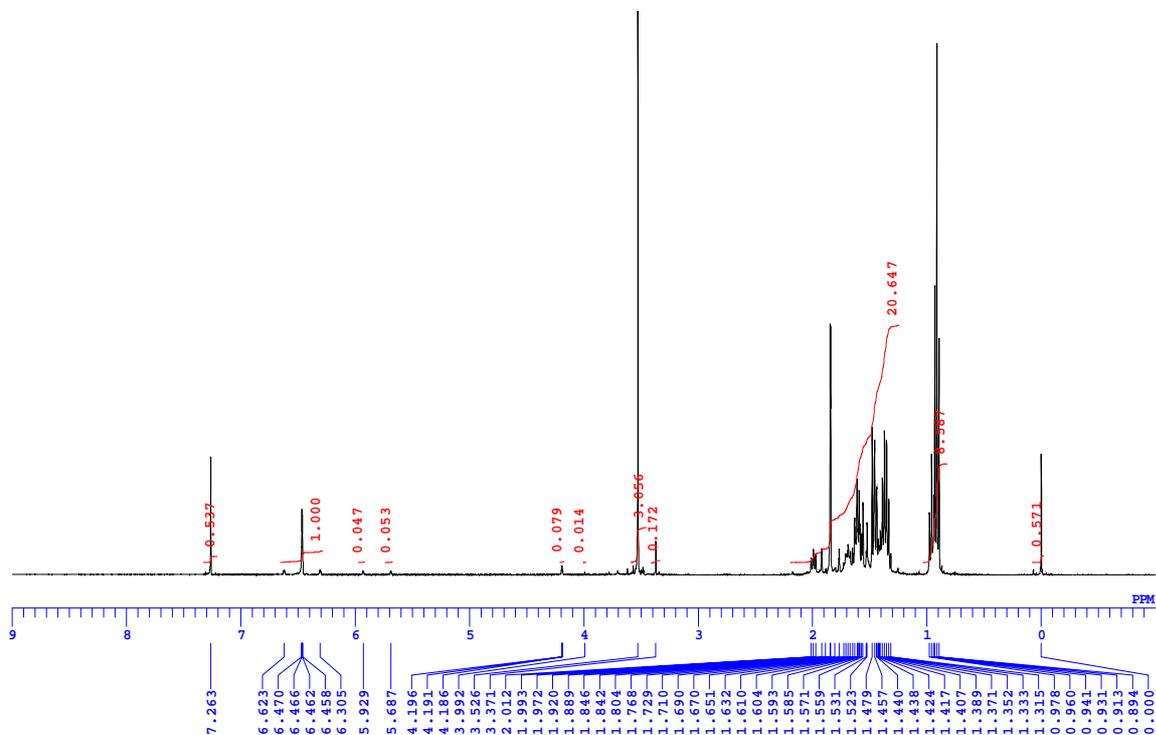
^{13}C NMR



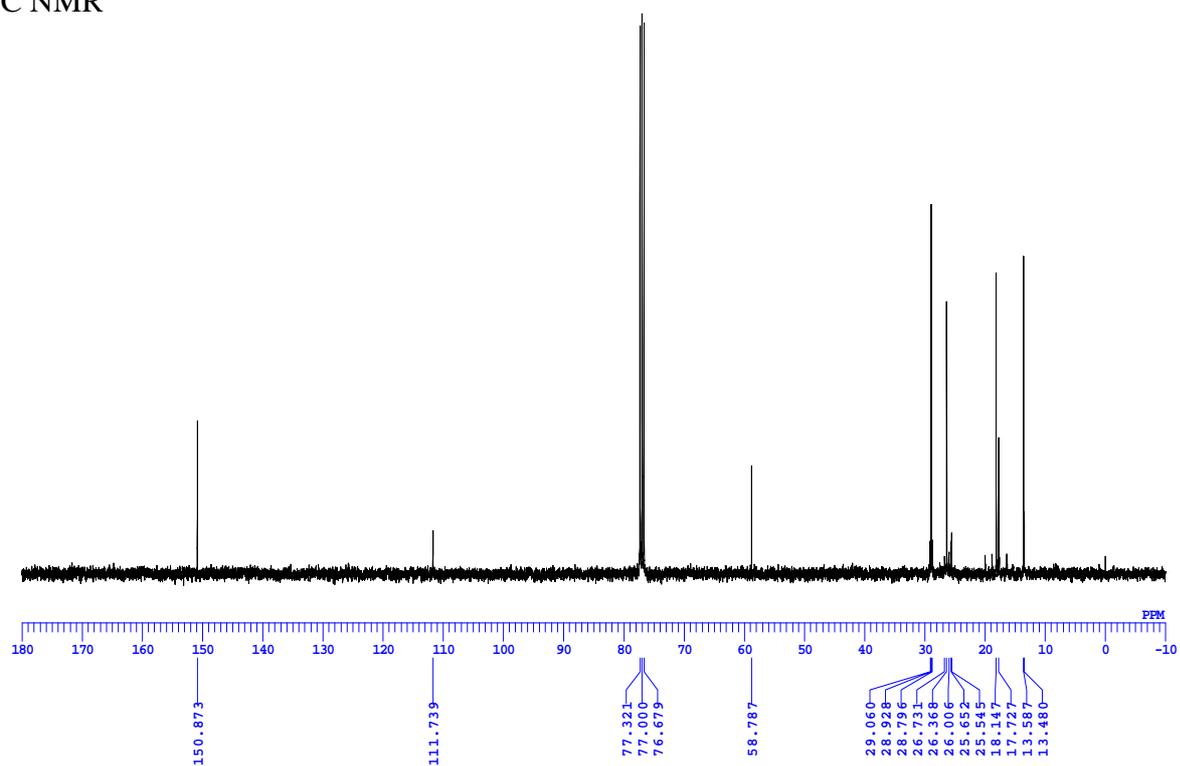
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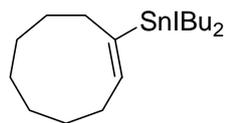
^1H NMR



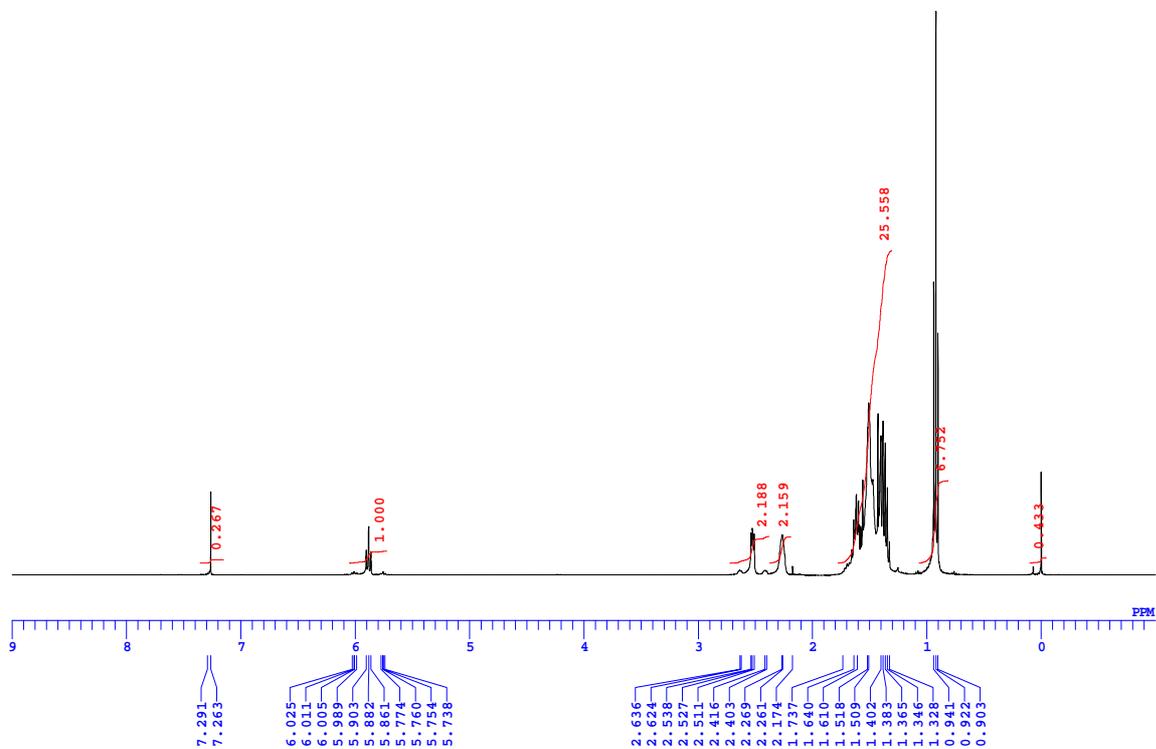
^{13}C NMR



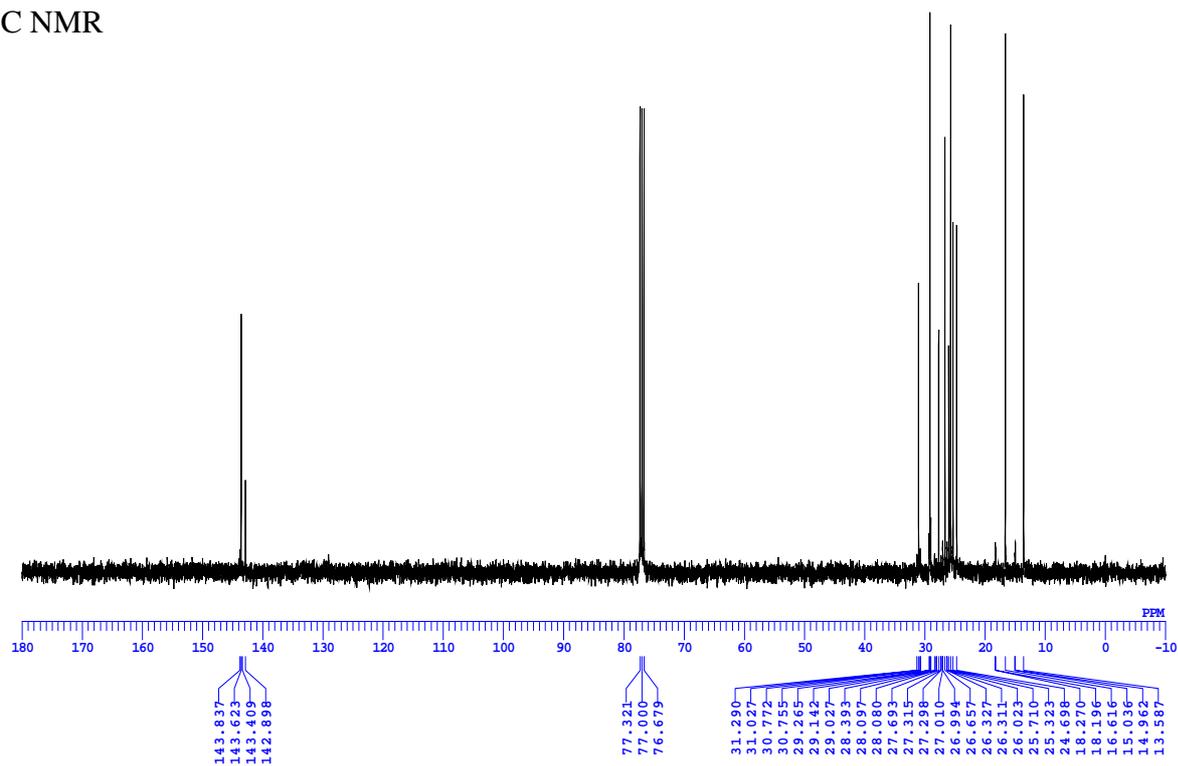
2g



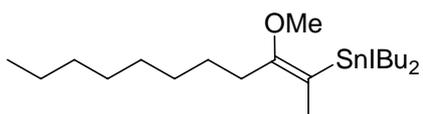
^1H NMR



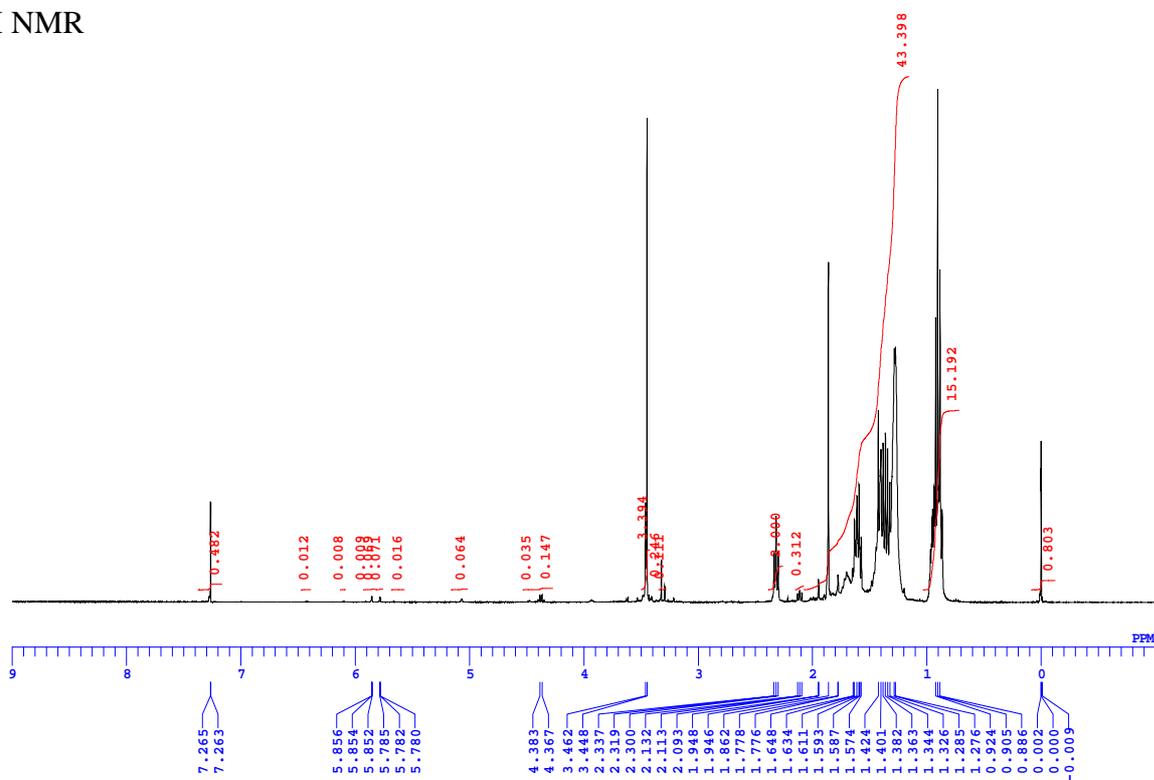
^{13}C NMR



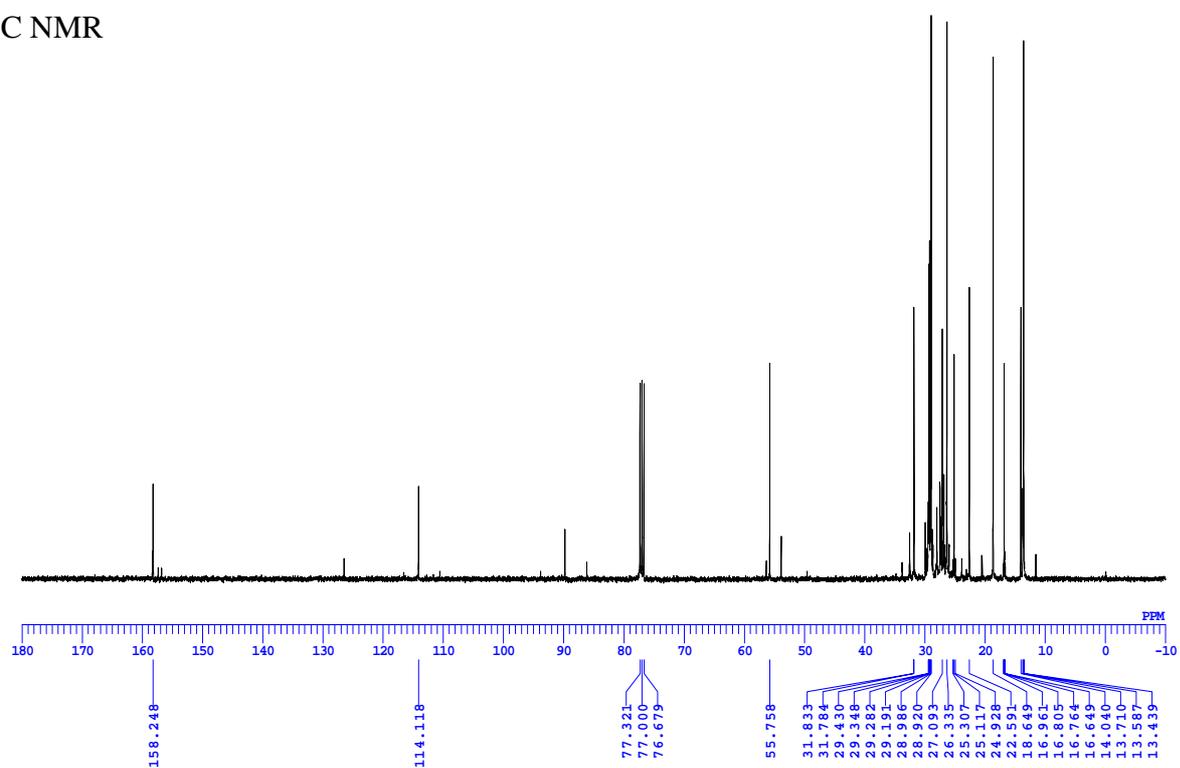
2h



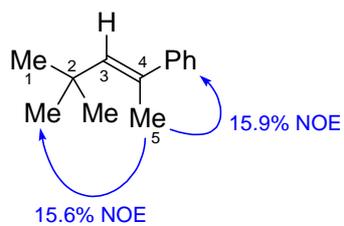
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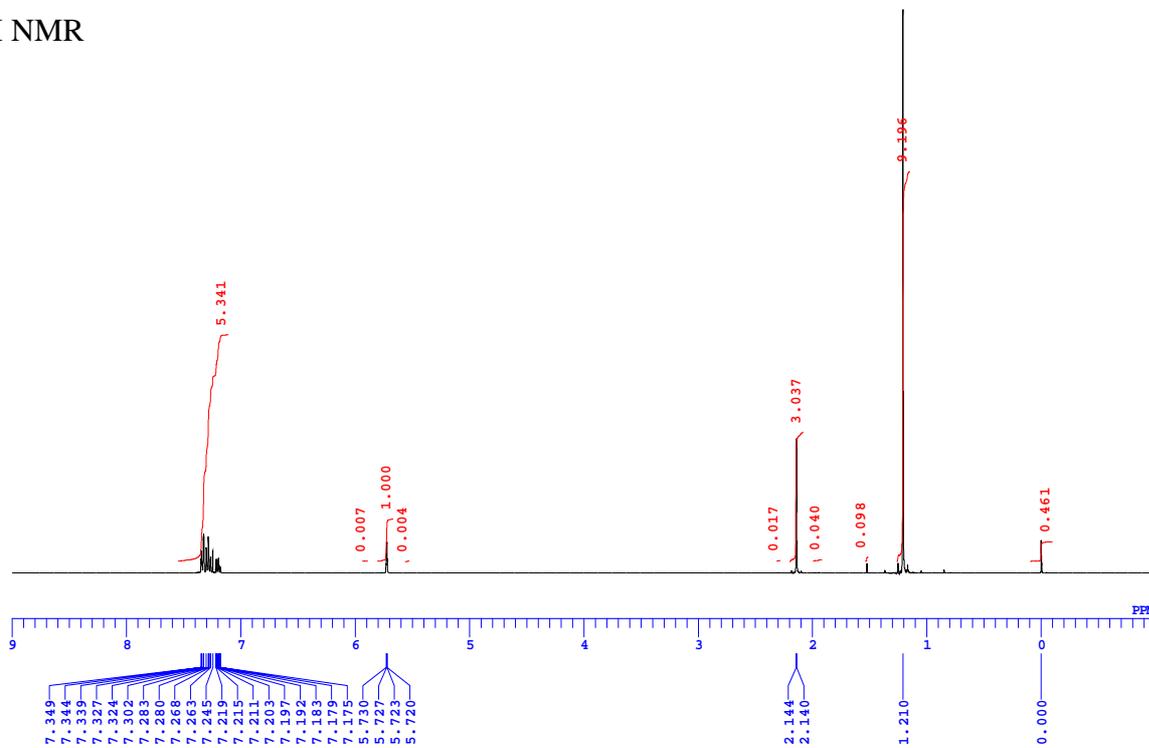
^{13}C NMR



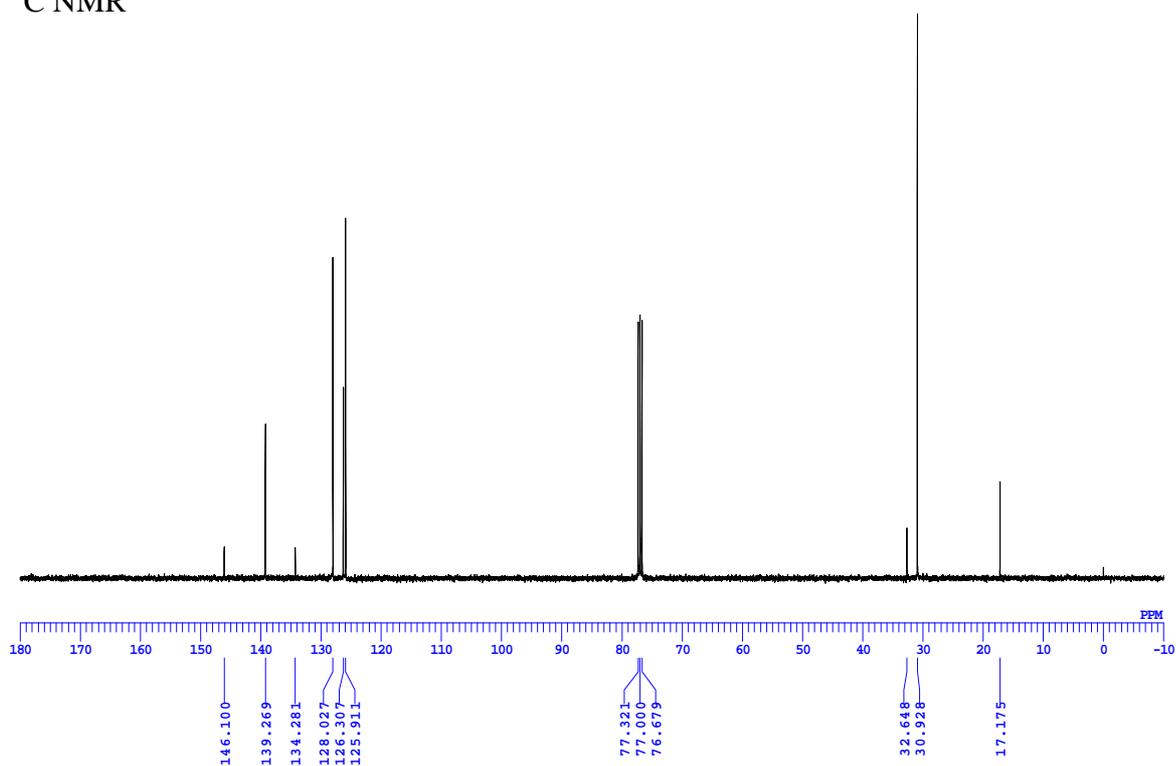
5c



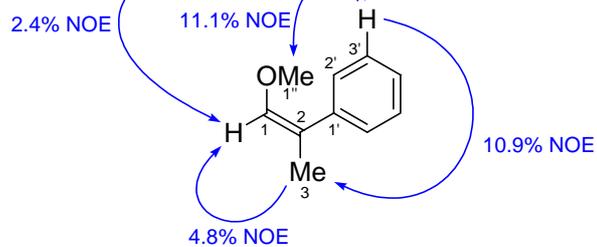
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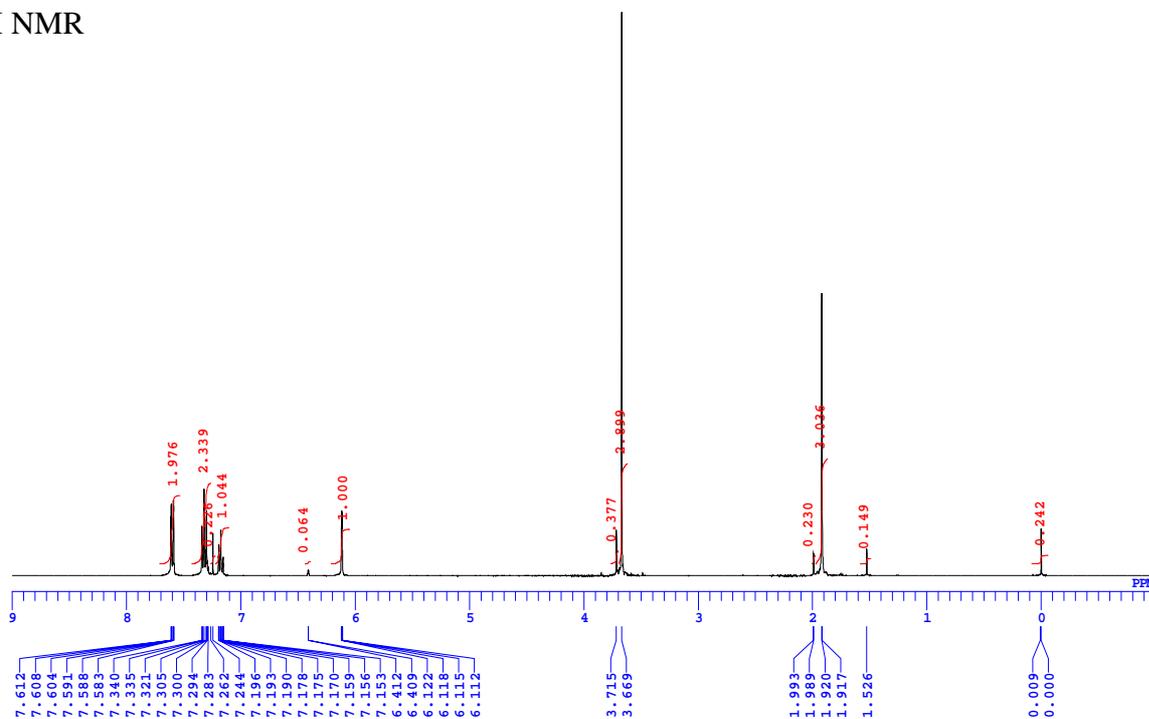
^{13}C NMR



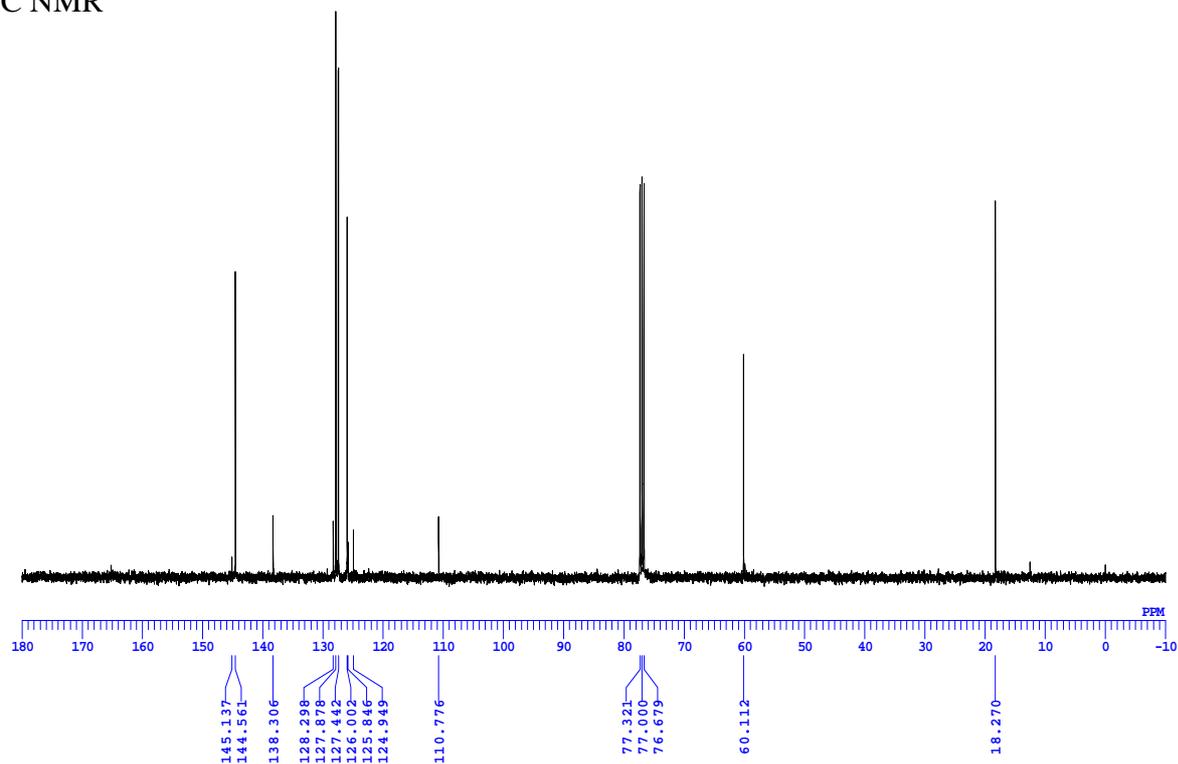
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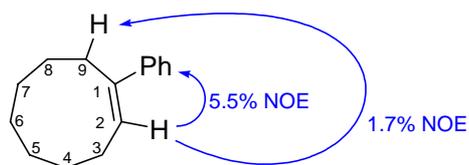
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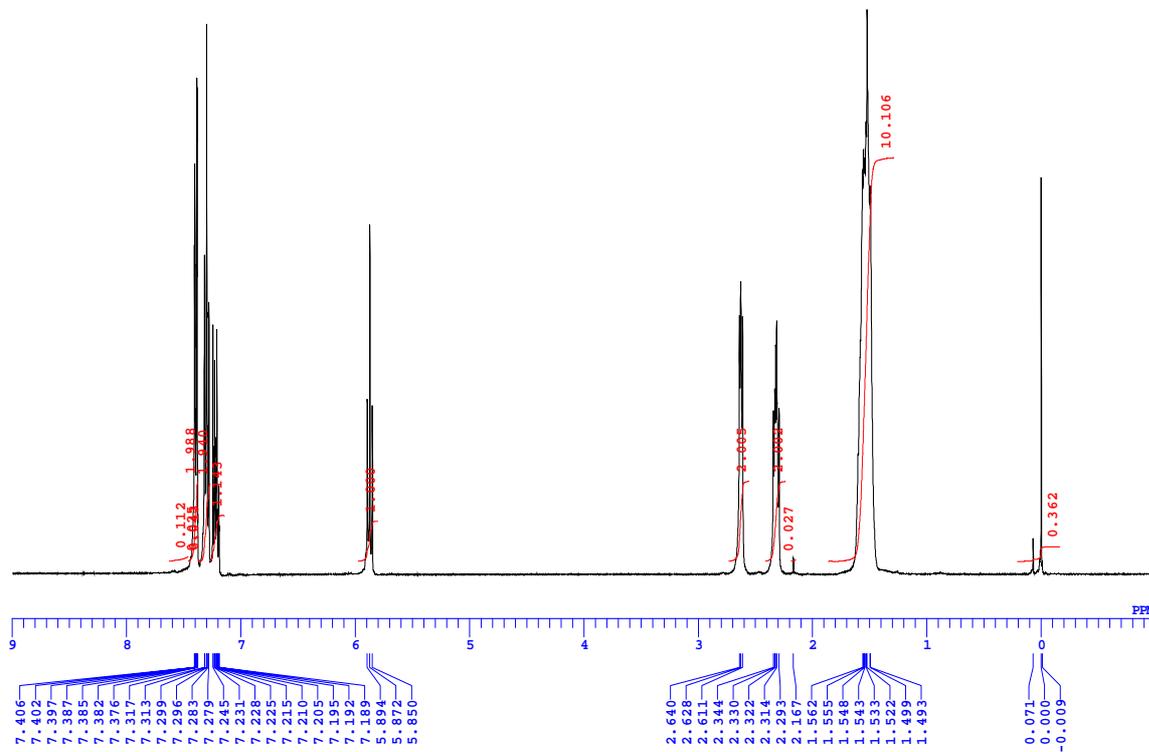
^{13}C NMR



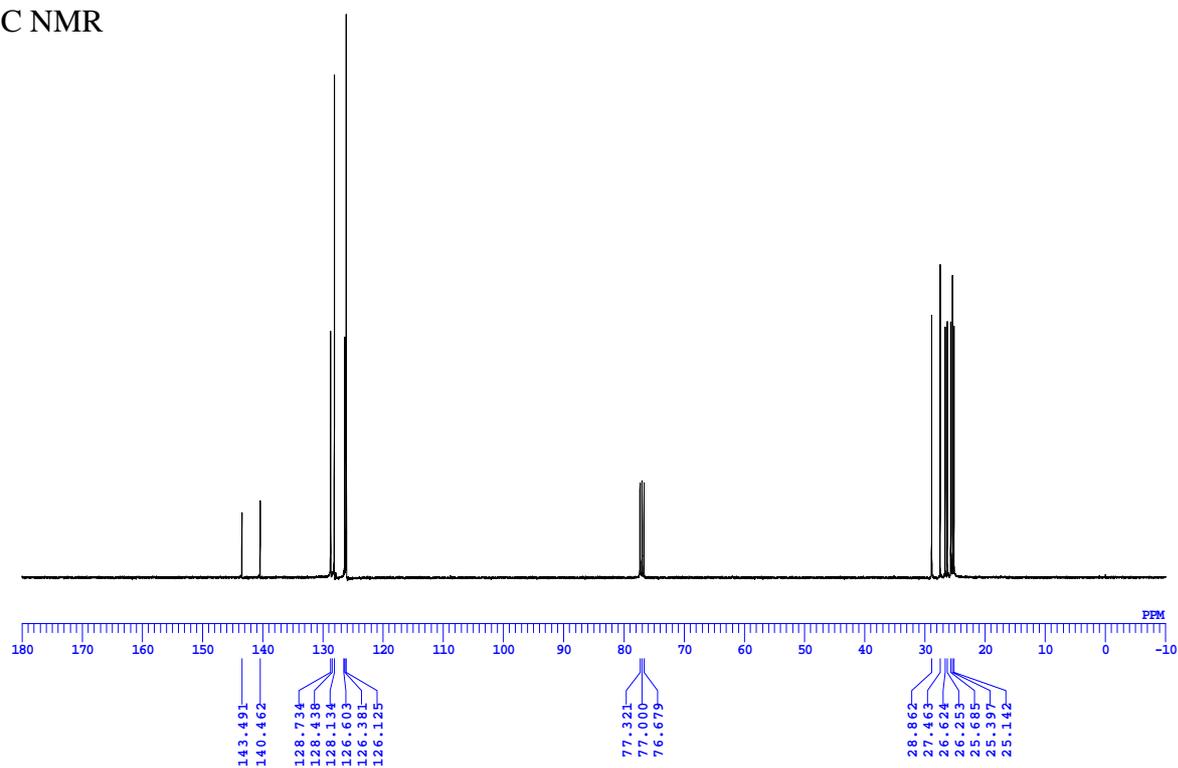
5g



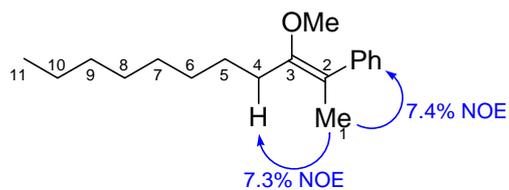
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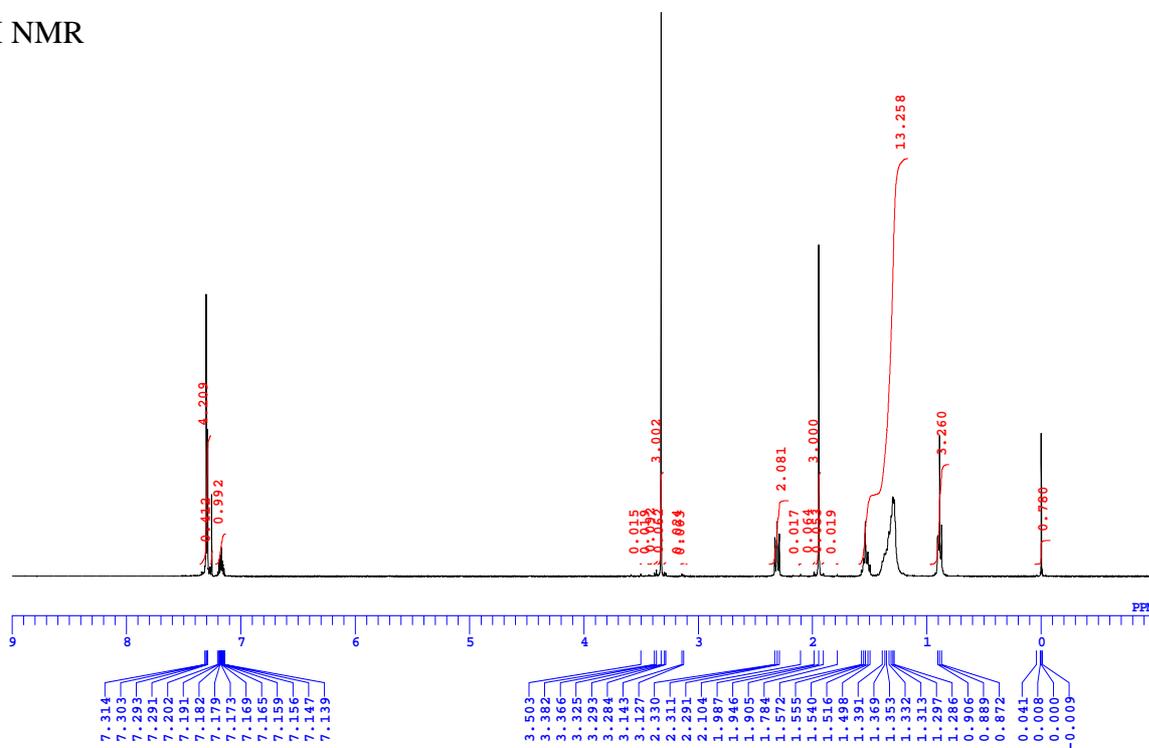
^{13}C NMR



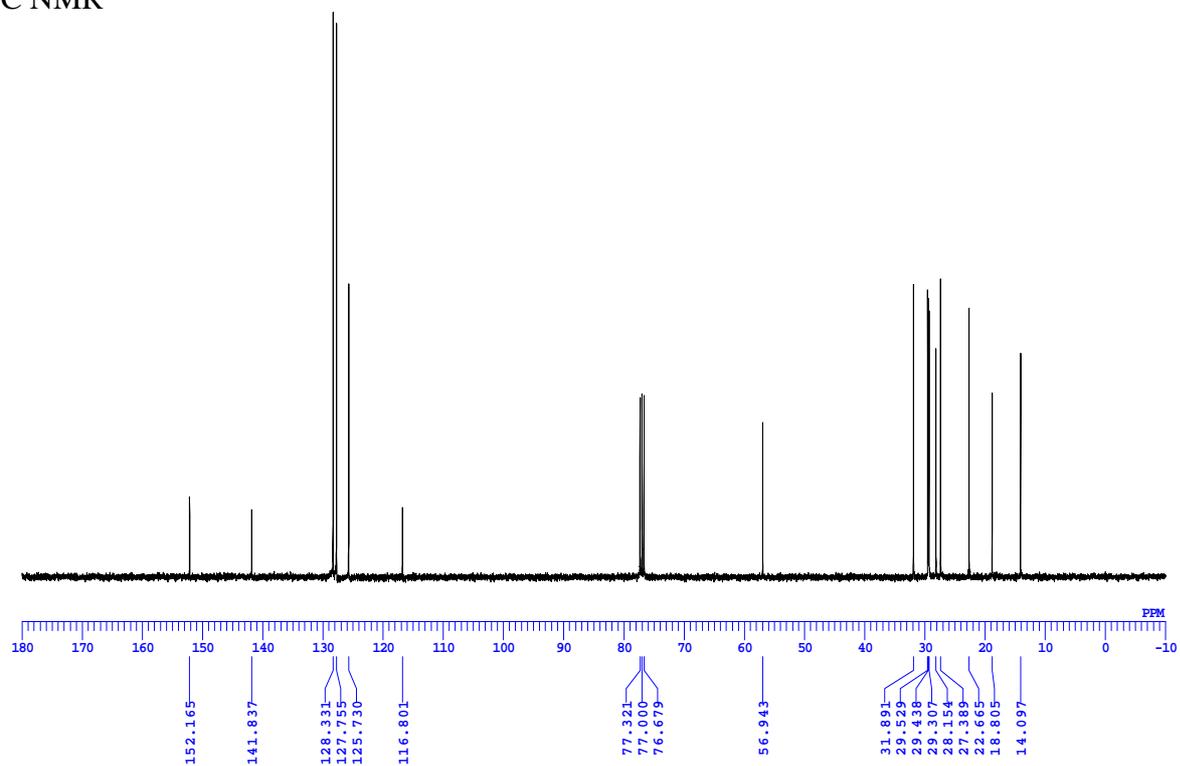
5h



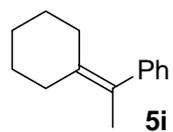
¹H NMR



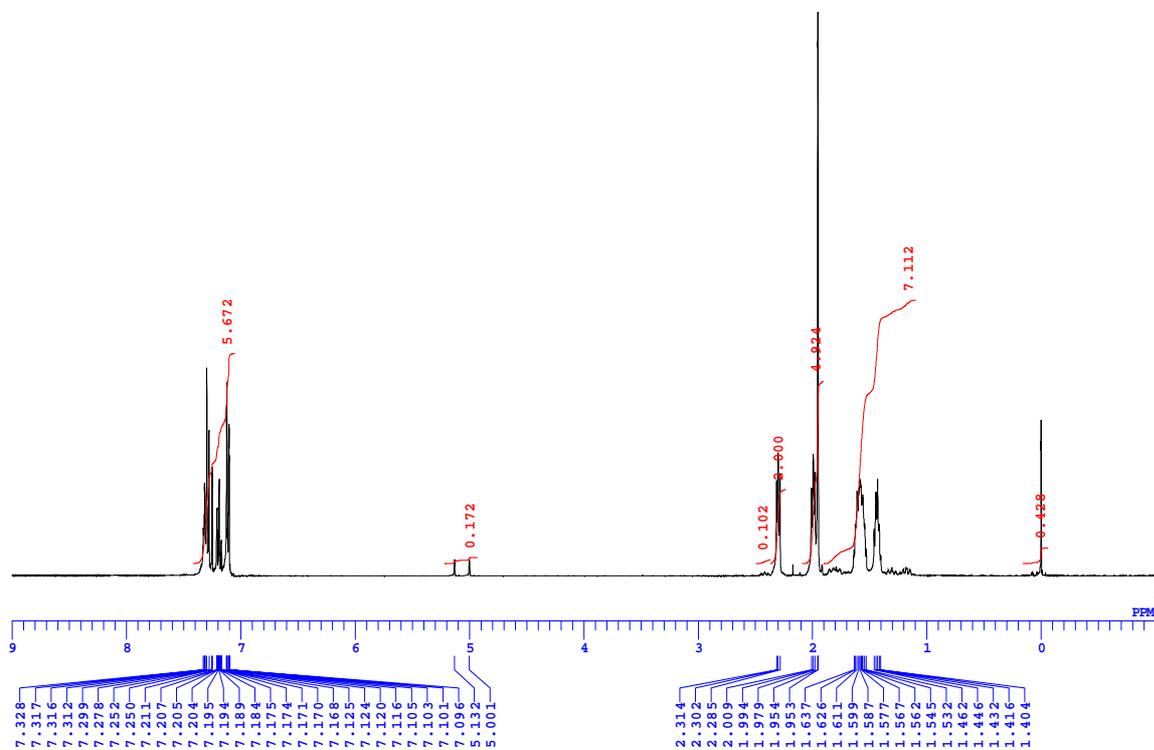
¹³C NMR



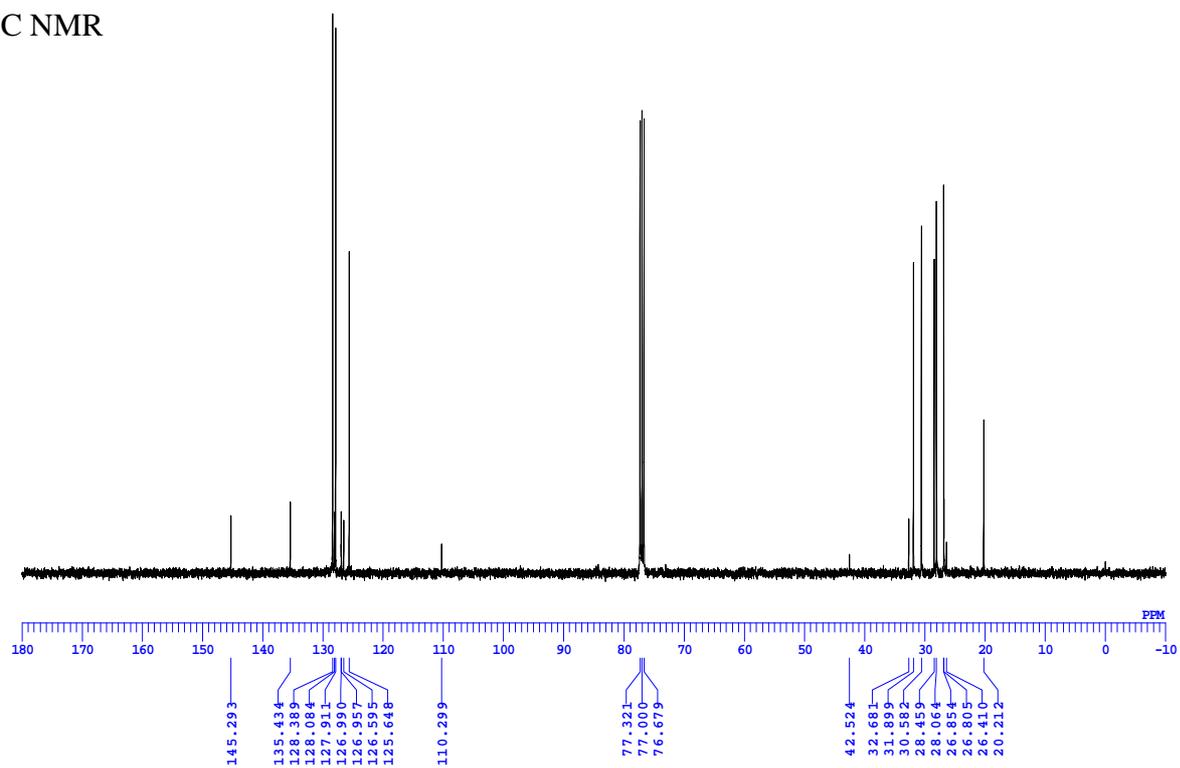
5i



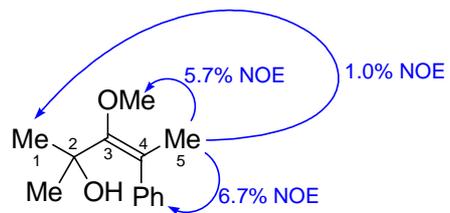
¹H NMR



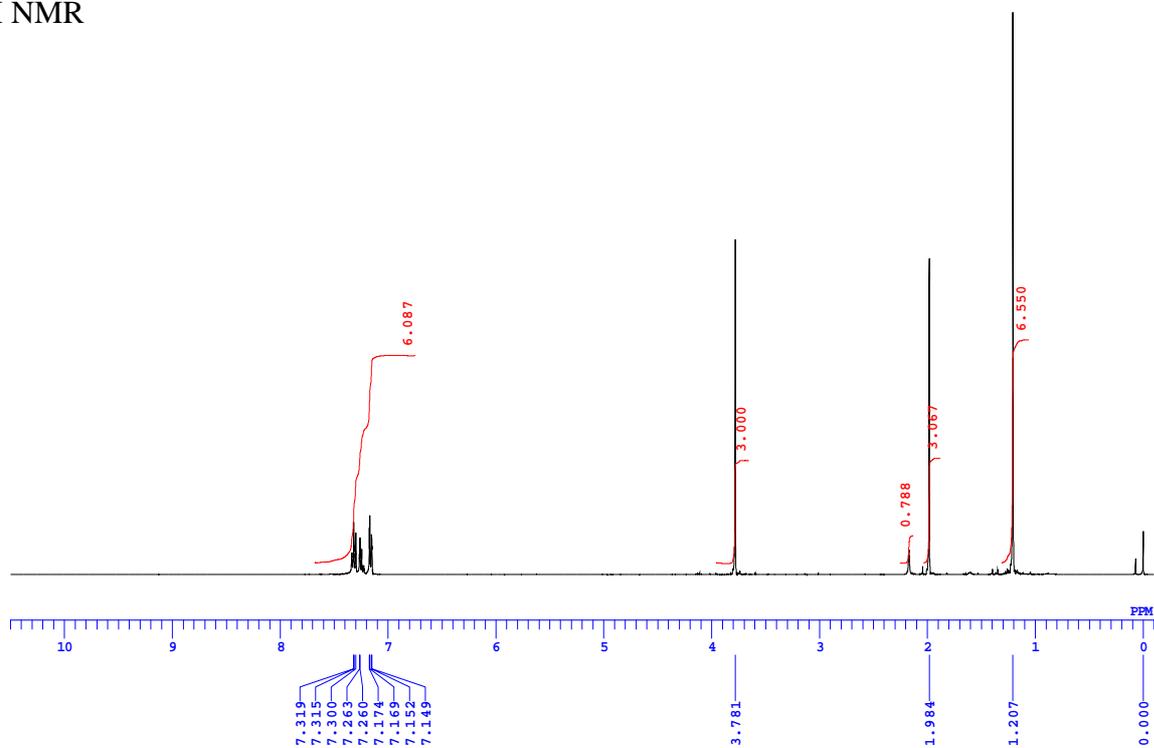
¹³C NMR



5j



^1H NMR



^{13}C NMR

