

Supporting Information

Pd-Catalyzed Intramolecular Sequential Heck Cyclization and Oxidation Reactions: A Facile Pathway for the Synthesis of Substituted Cycloheptenone with Computational Studies

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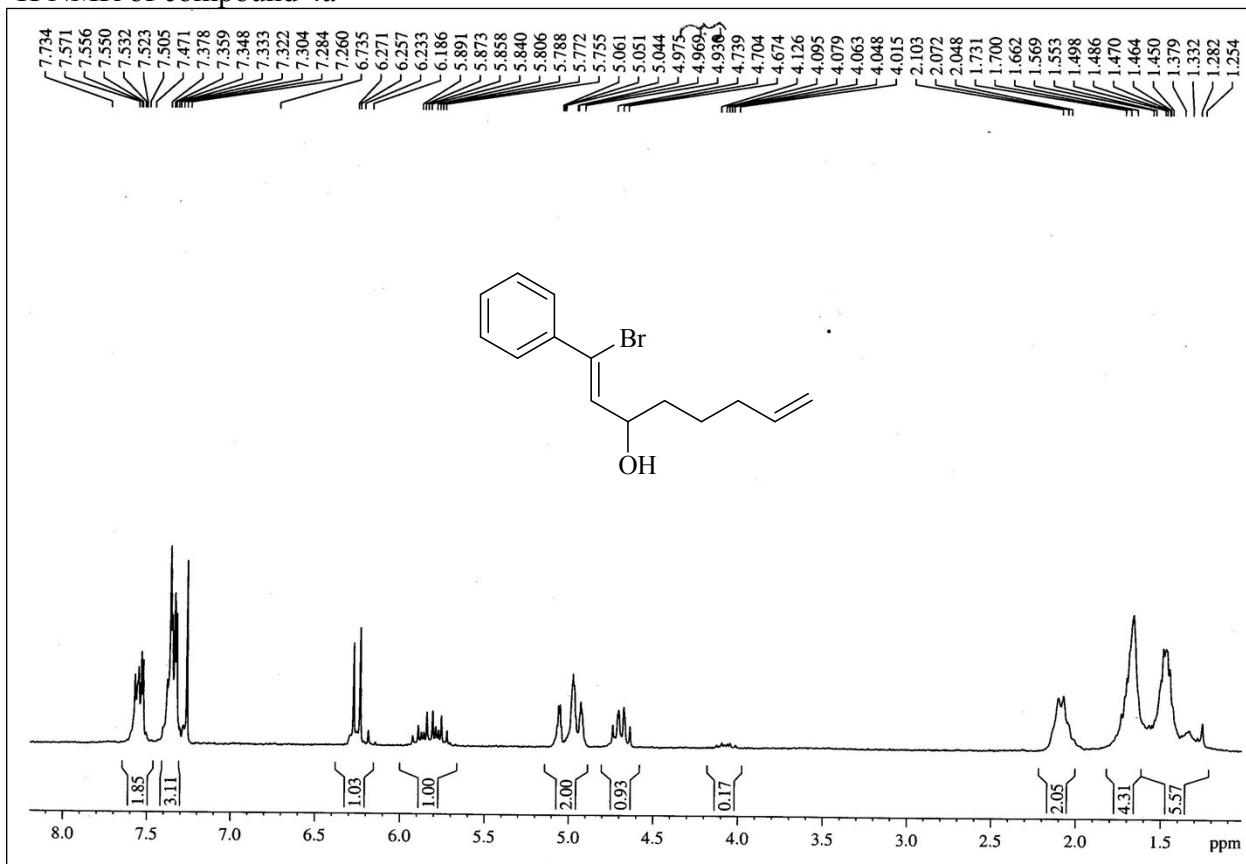
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A. General remarks

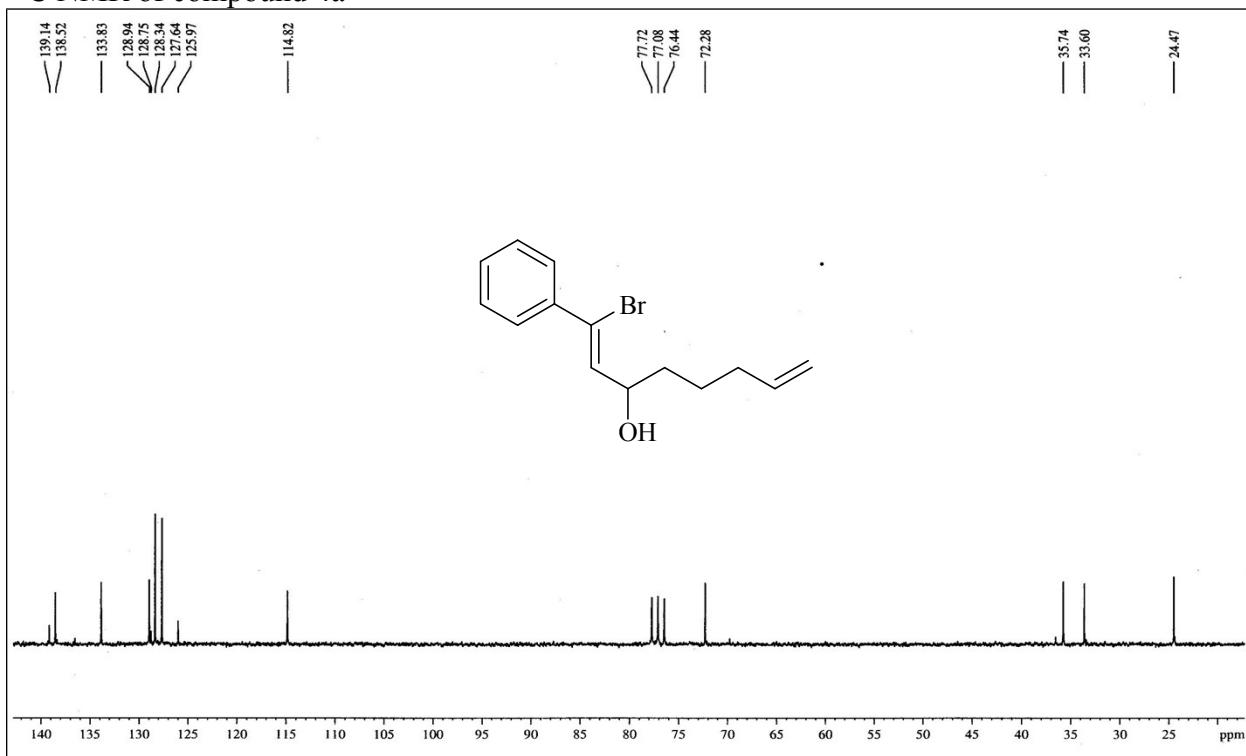
All reactions were carried out using oven-dried glassware. Commercial grade reagents were used without further purification. Solvents were dried and distilled following usual protocols prior to use. All yields refer to isolated yields after column purification. Column chromatography was carried out using Silica gel (60-120 mesh) purchased from Rankem, India. TLC was performed on aluminium-backed plates coated with Silica gel 60 with F254 indicator (Merck). The ¹H NMR spectra were measured with Bruker-200 (200 MHz) or Bruker-400 (400 MHz) and ¹³C NMR spectra were measured with Bruker-200 (50 MHz) or Bruker-400 (100 MHz) using CDCl₃. Coupling constants in ¹H NMR are in Hz. Elemental analyses were carried out in Perkin-Elmer 2400 instrument in the analytical lab of chemistry department, IIT, Kharagpur.

B. Spectra for the compounds 4a-m, 5a and 6a-m

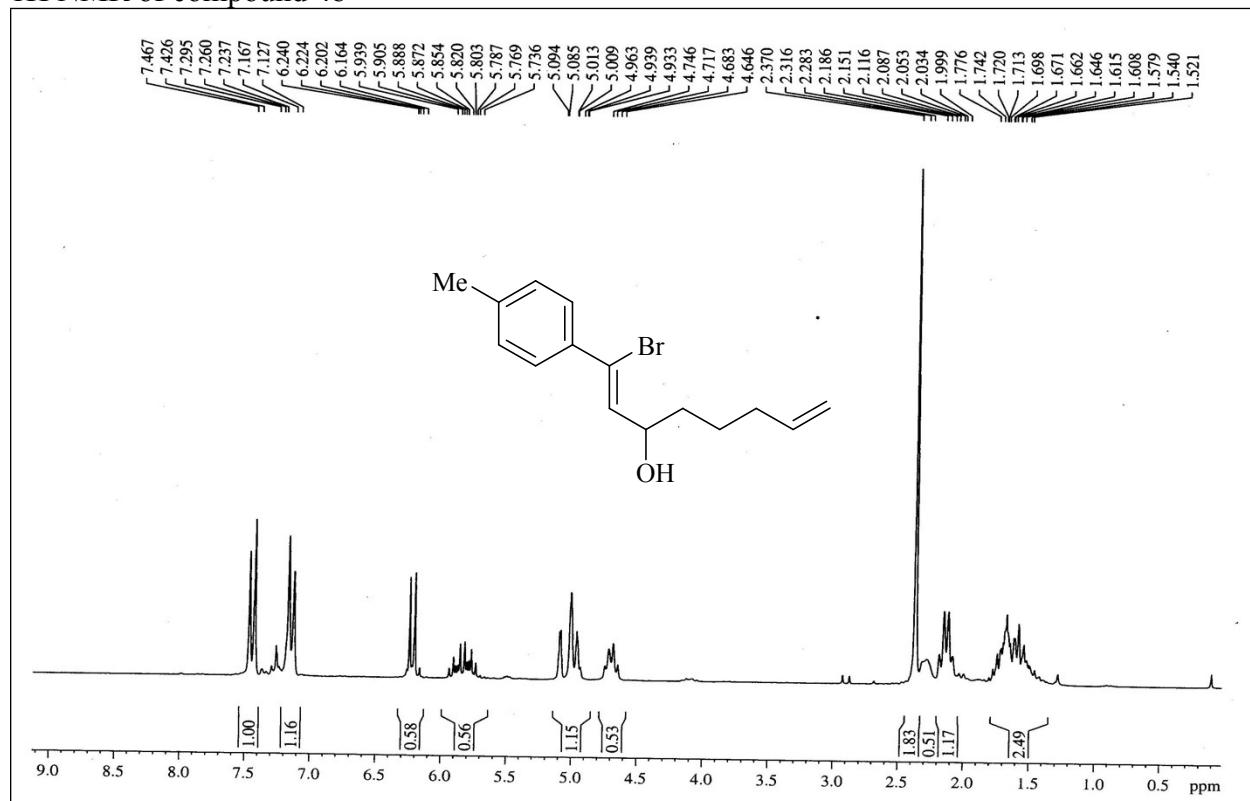
¹H NMR of compound 4a



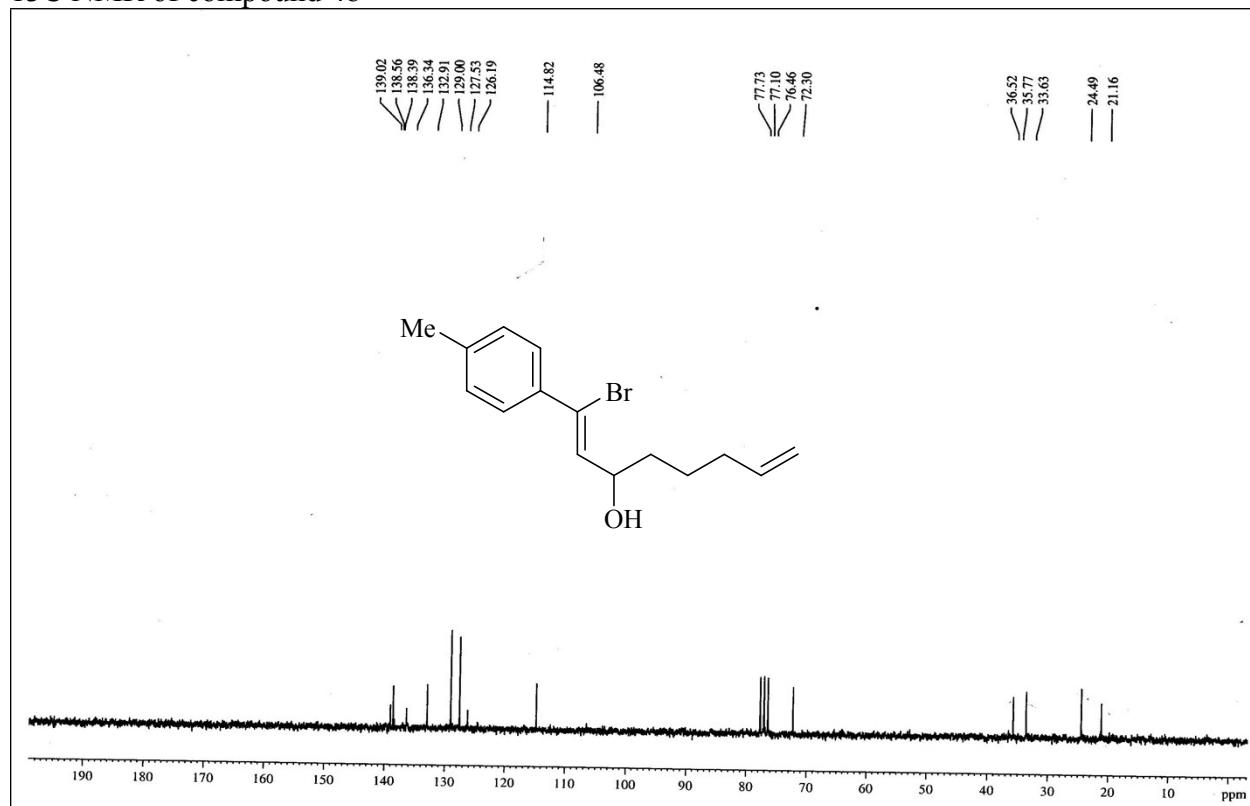
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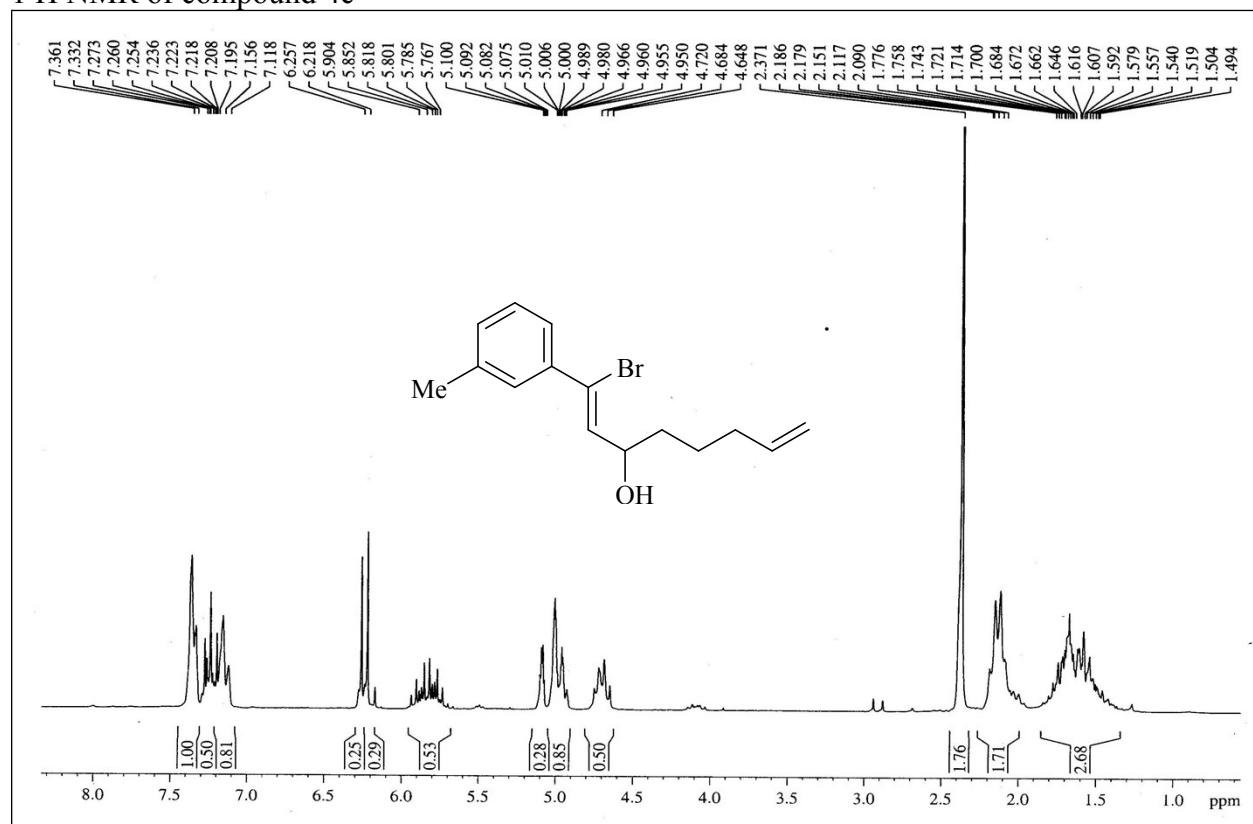
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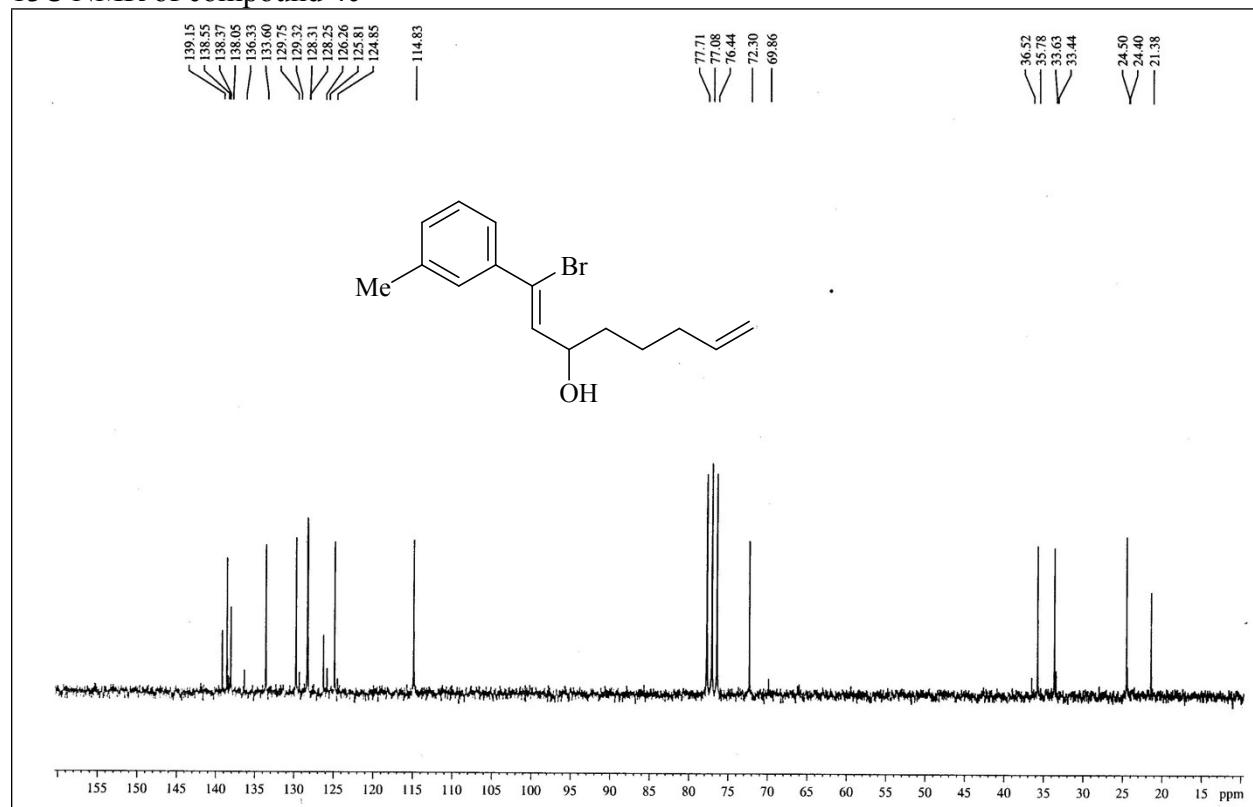
13C NMR of compound 4b



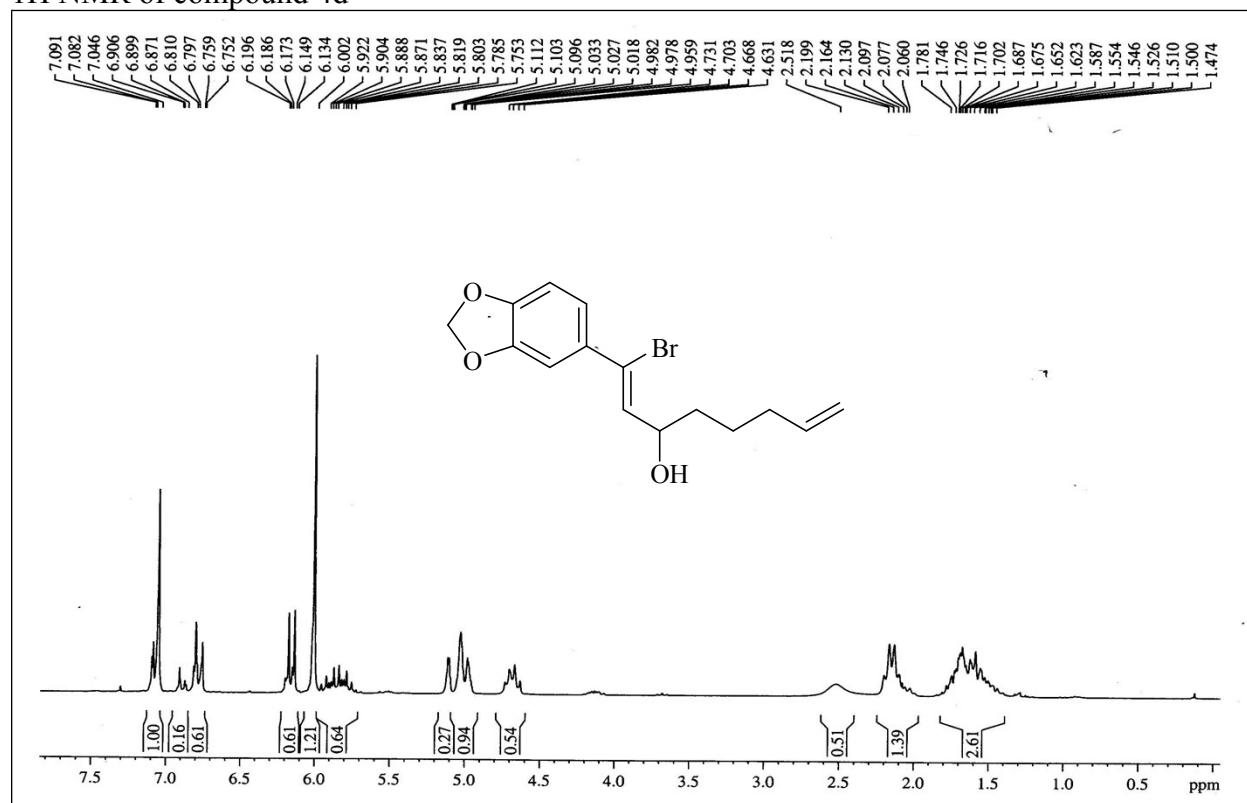
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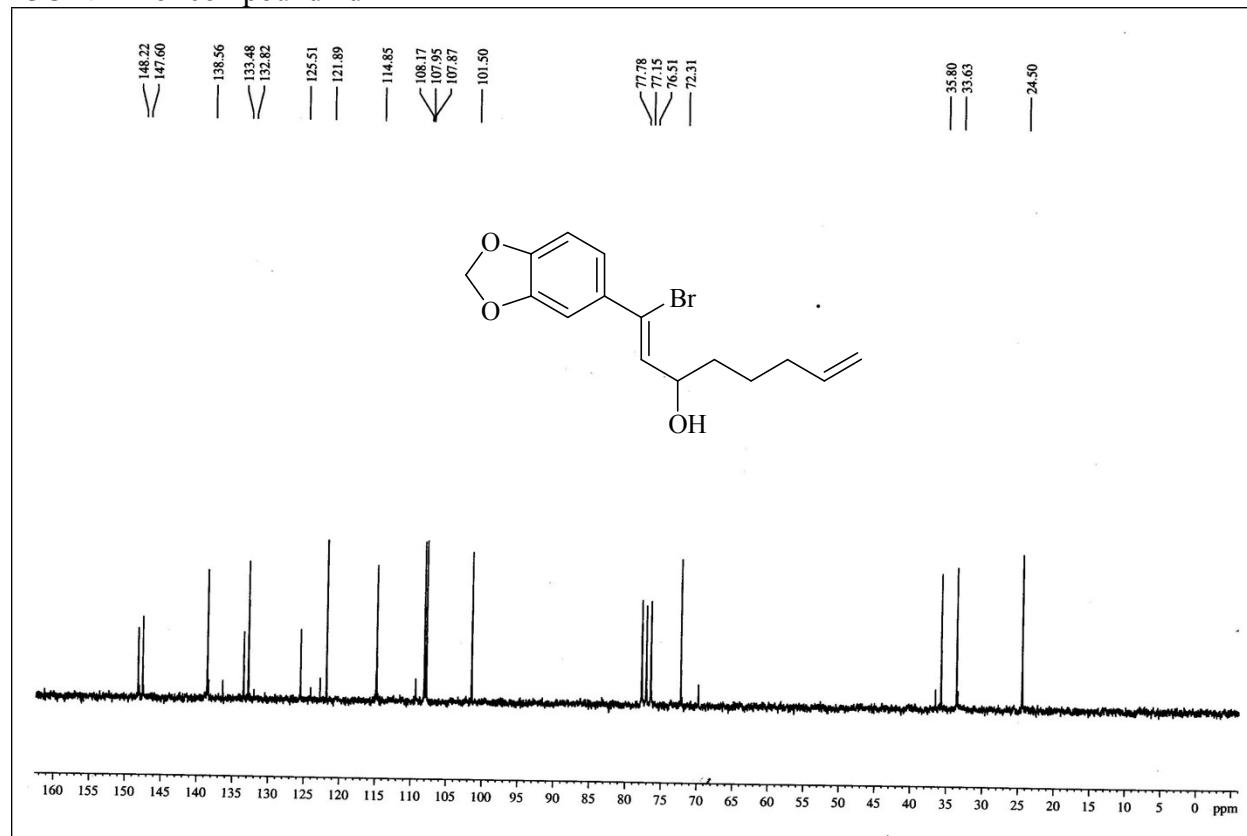
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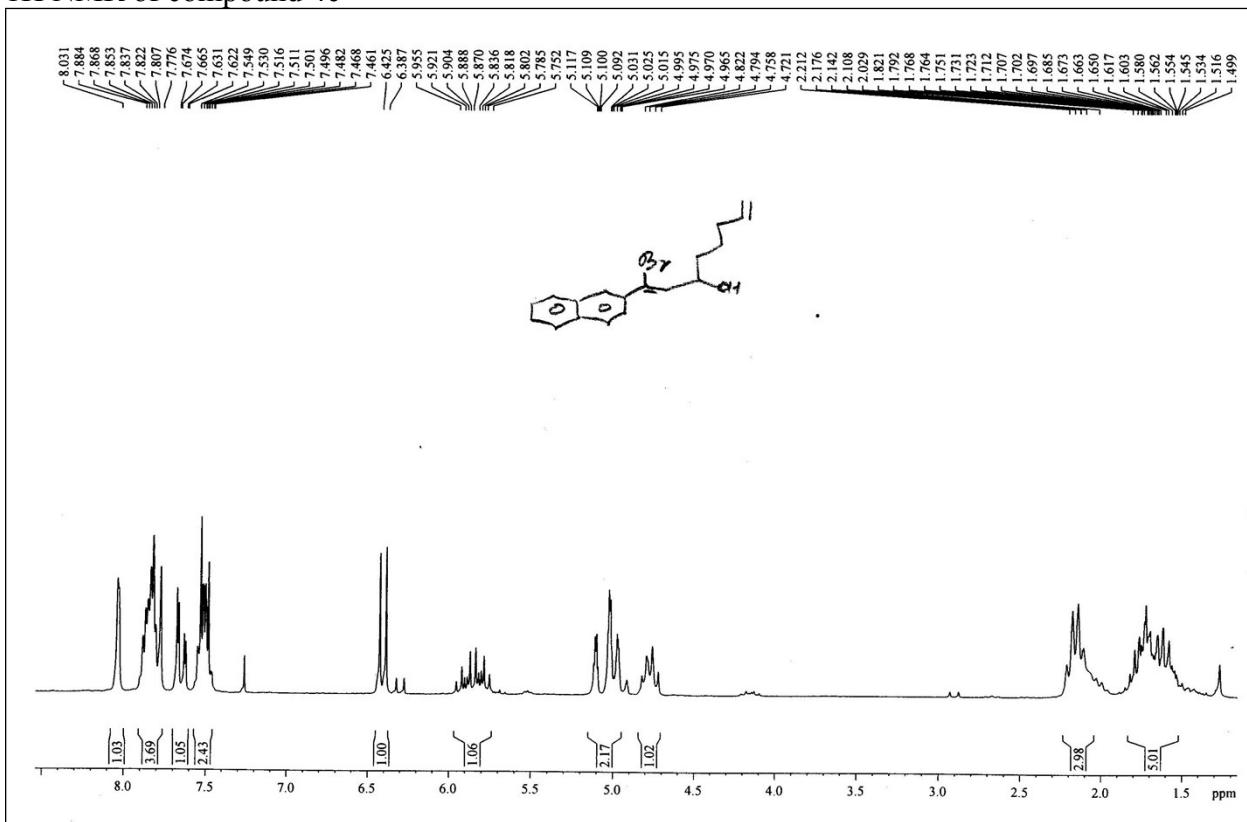
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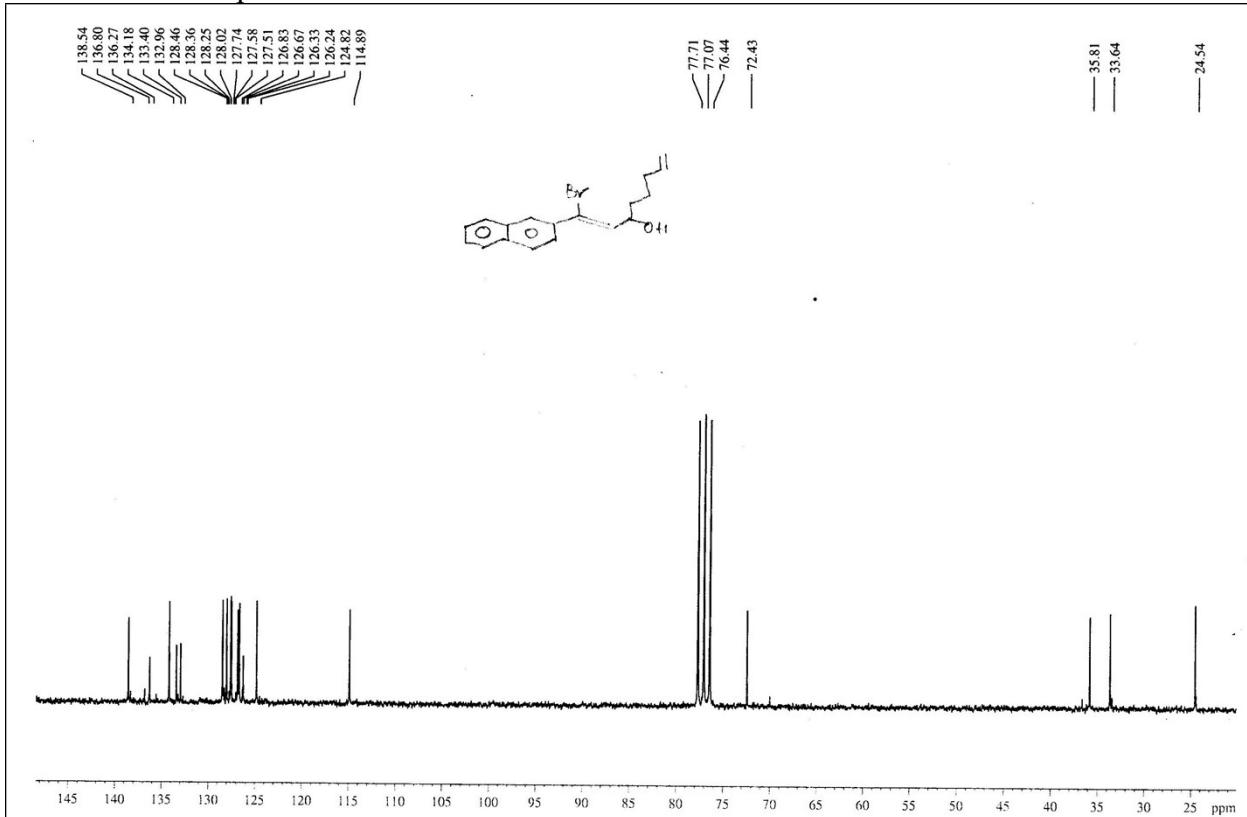
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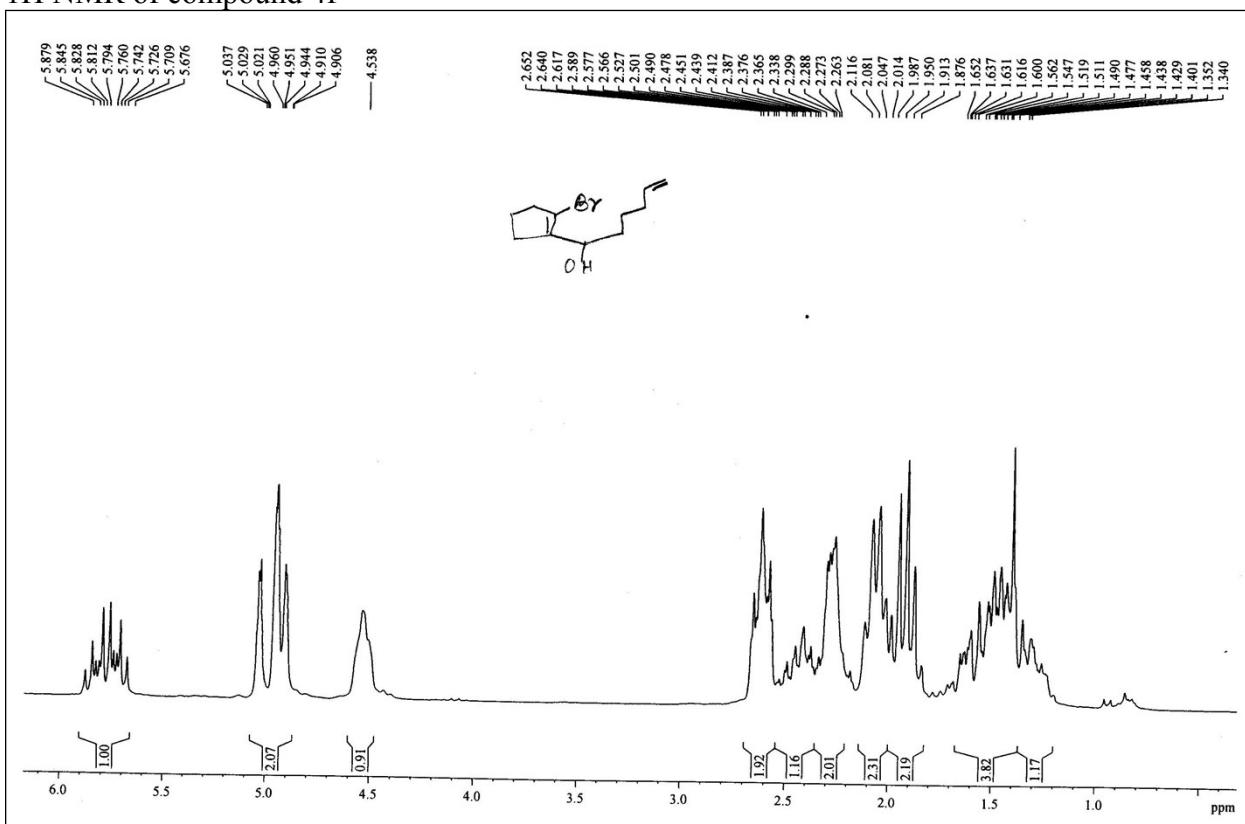
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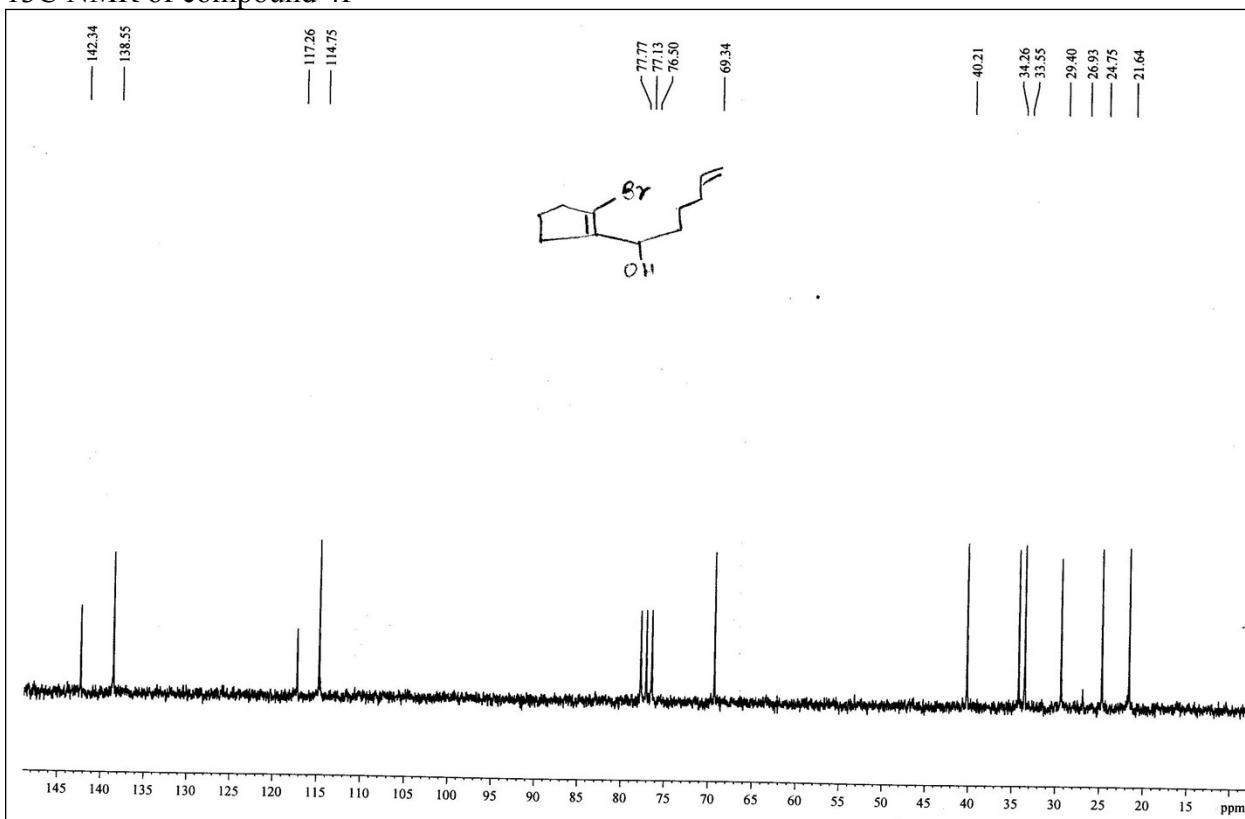
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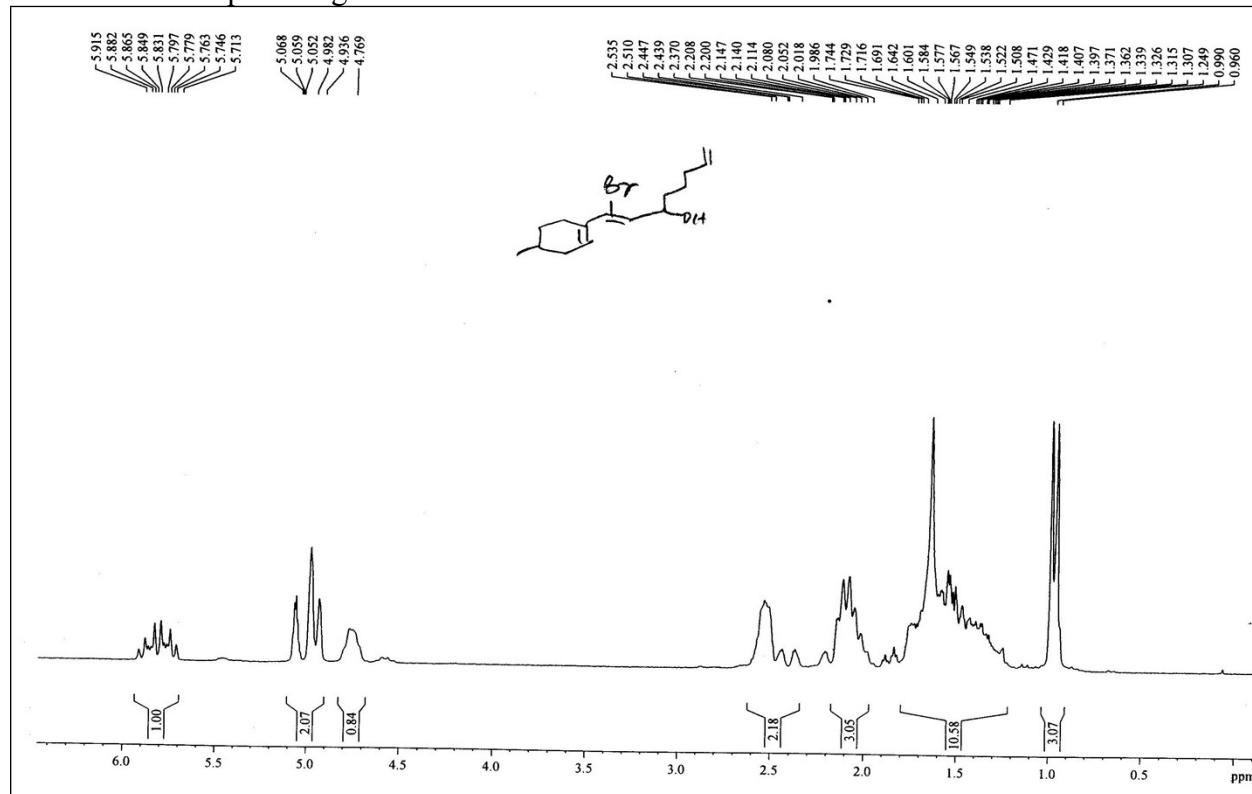
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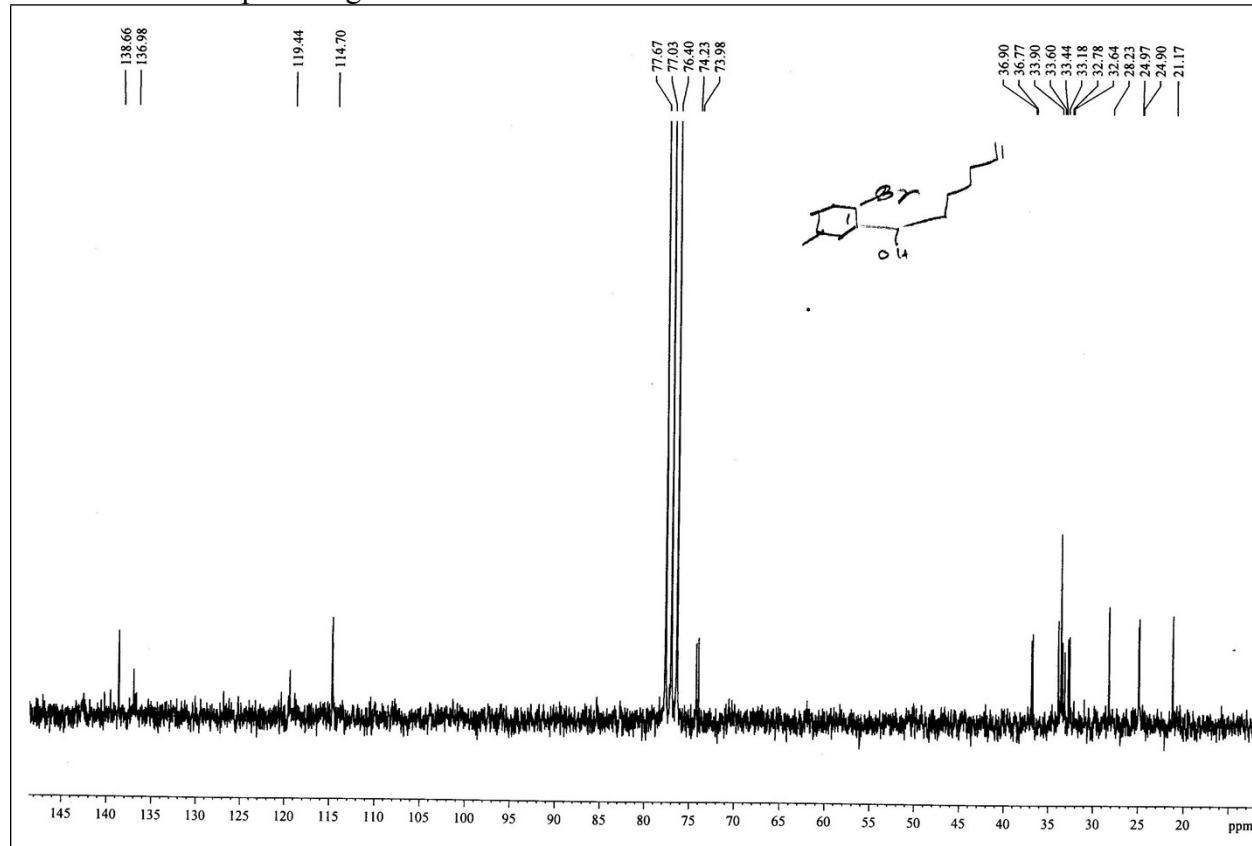
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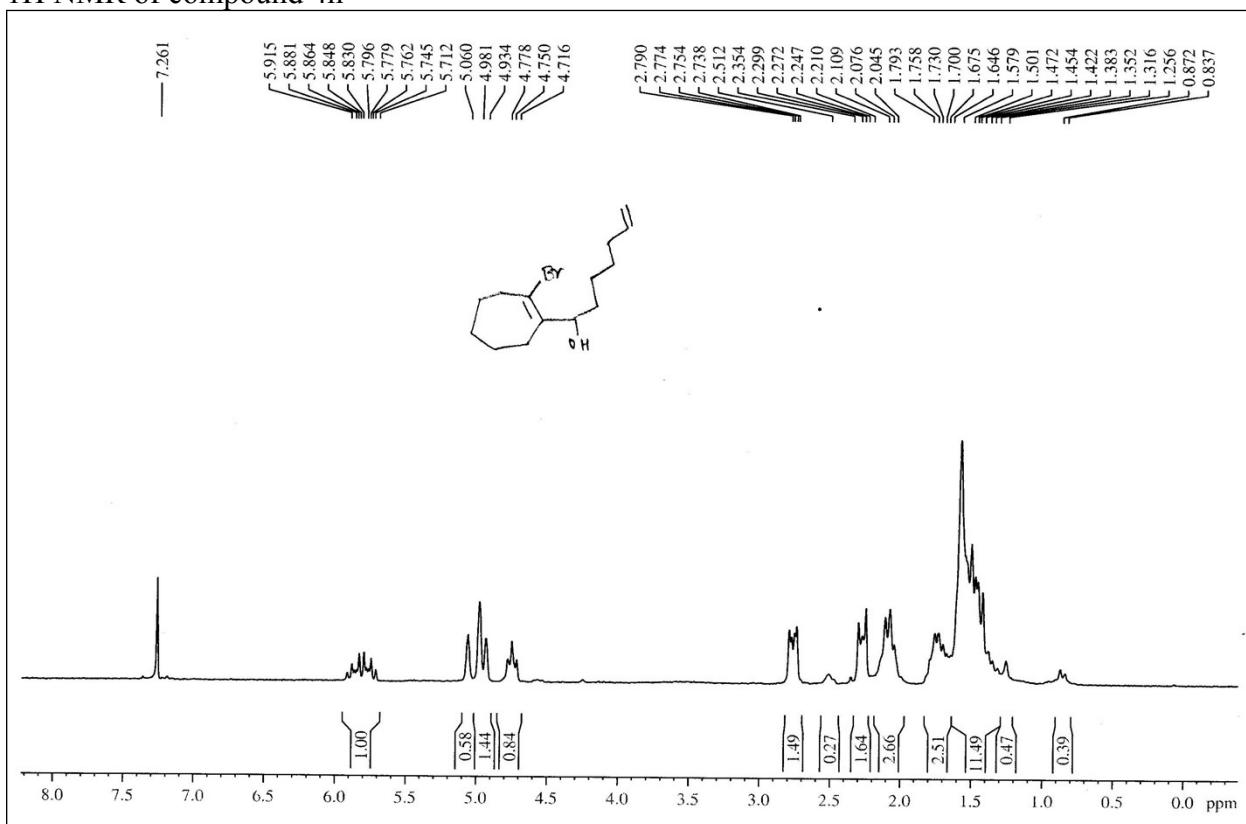
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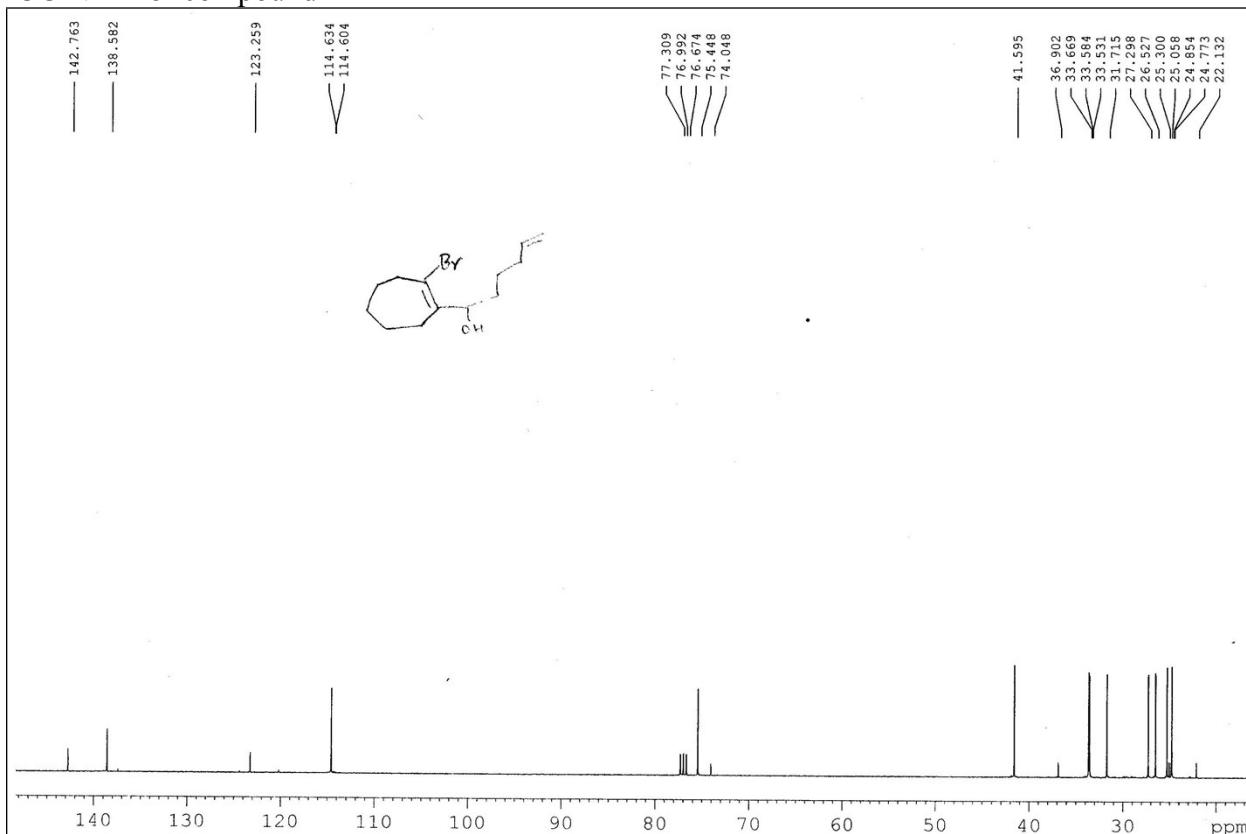
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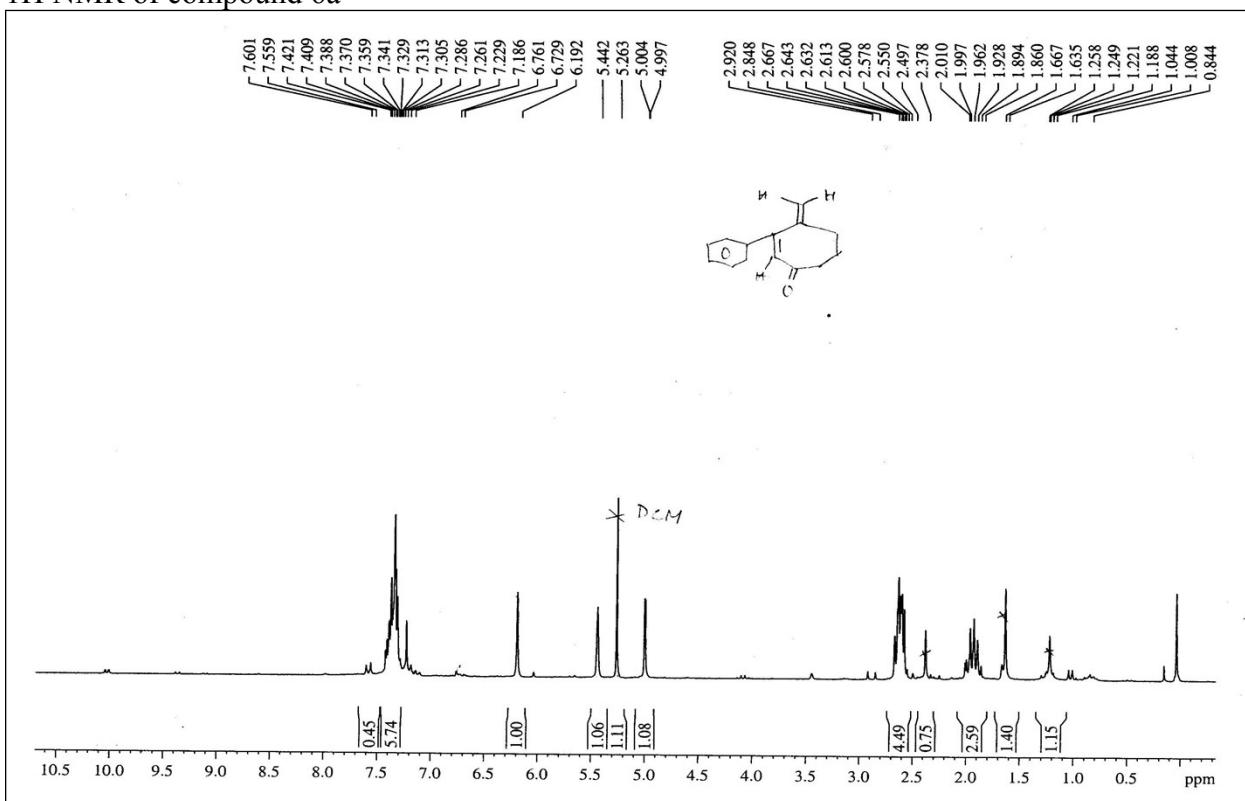
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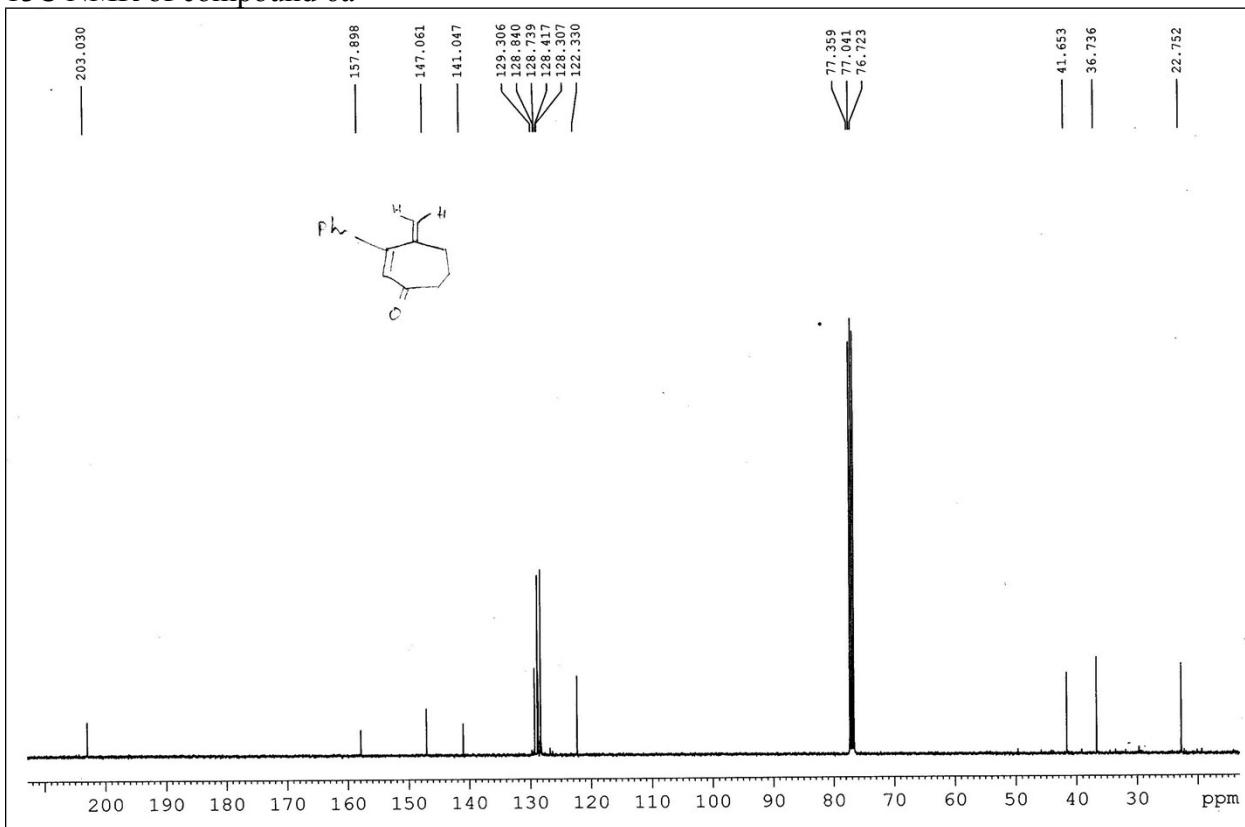
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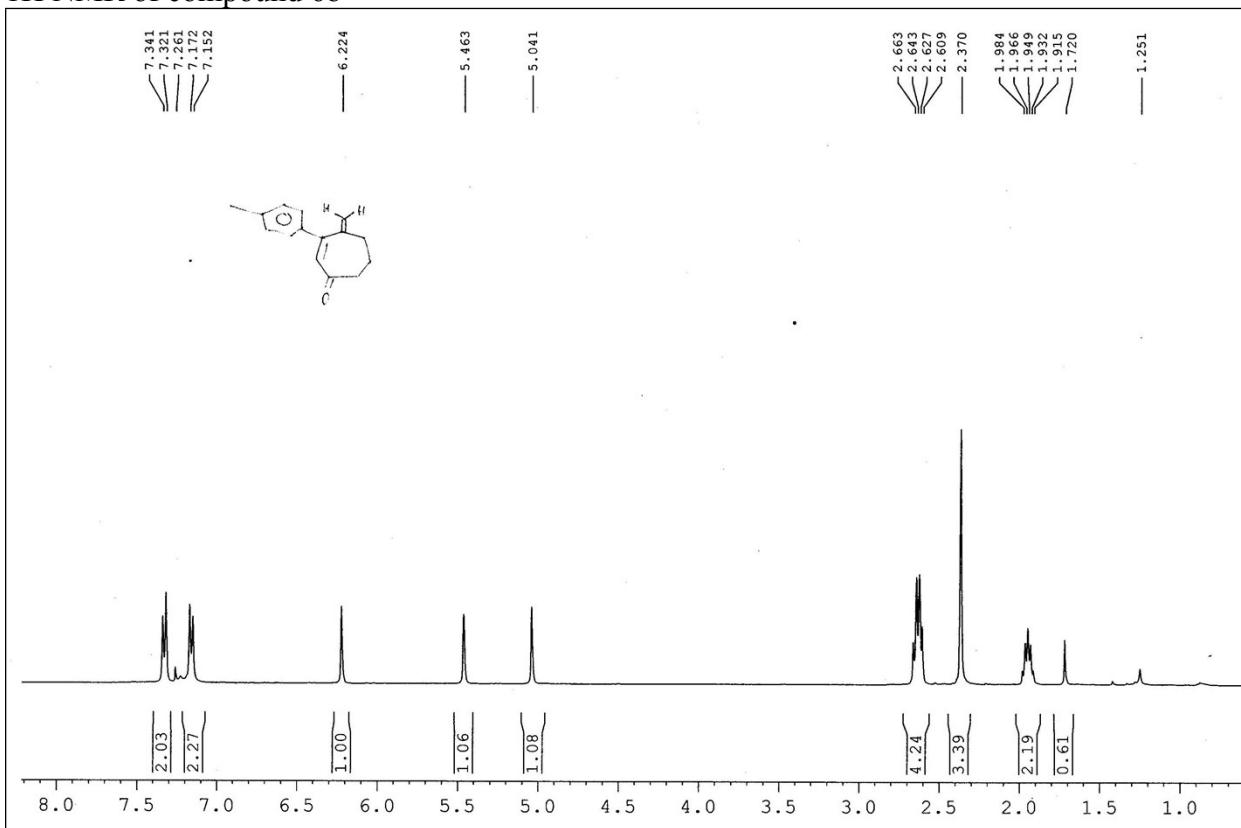
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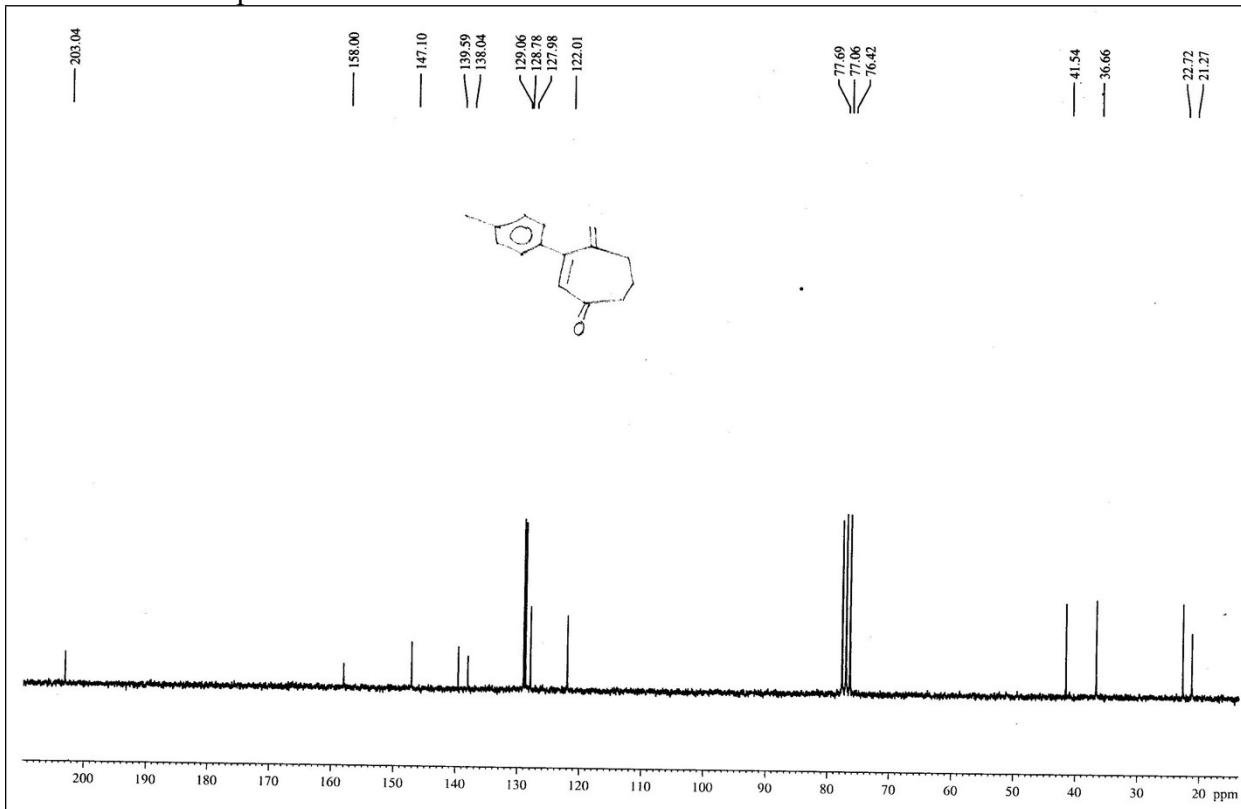
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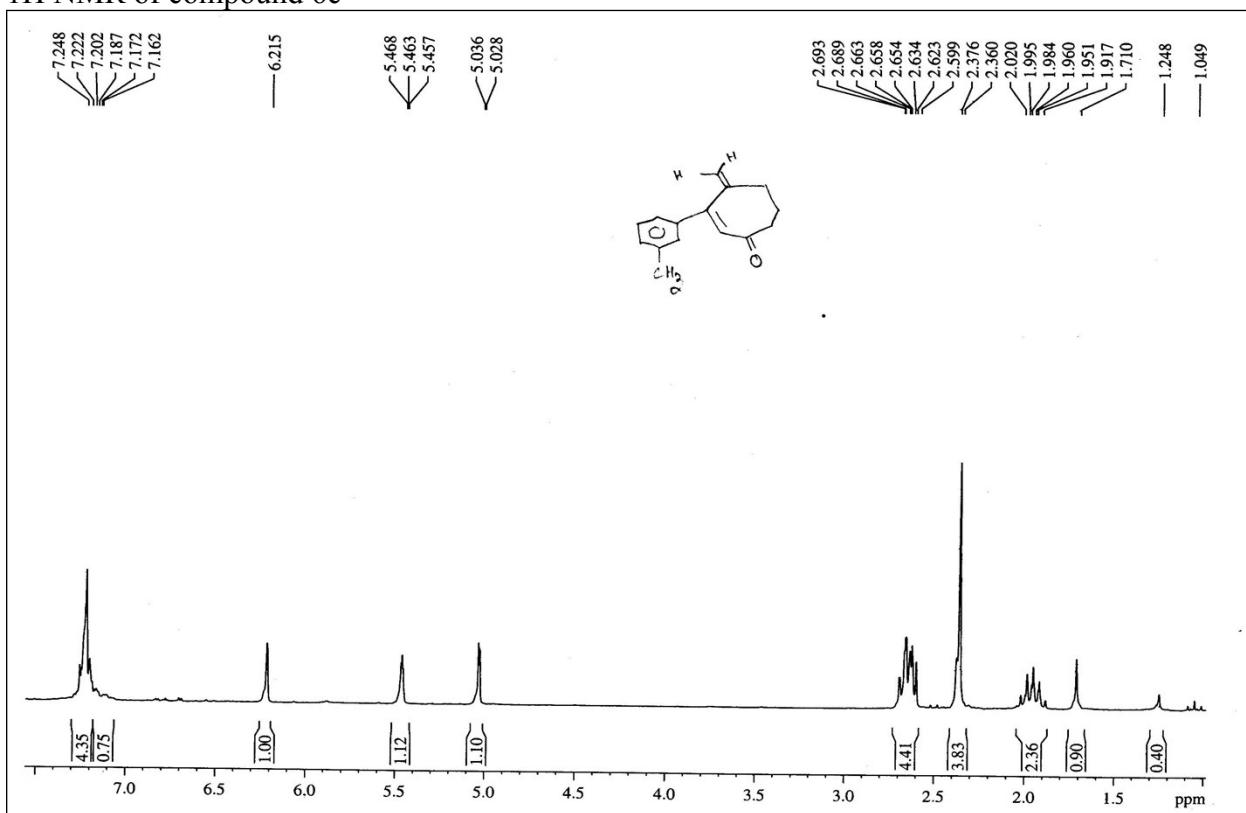
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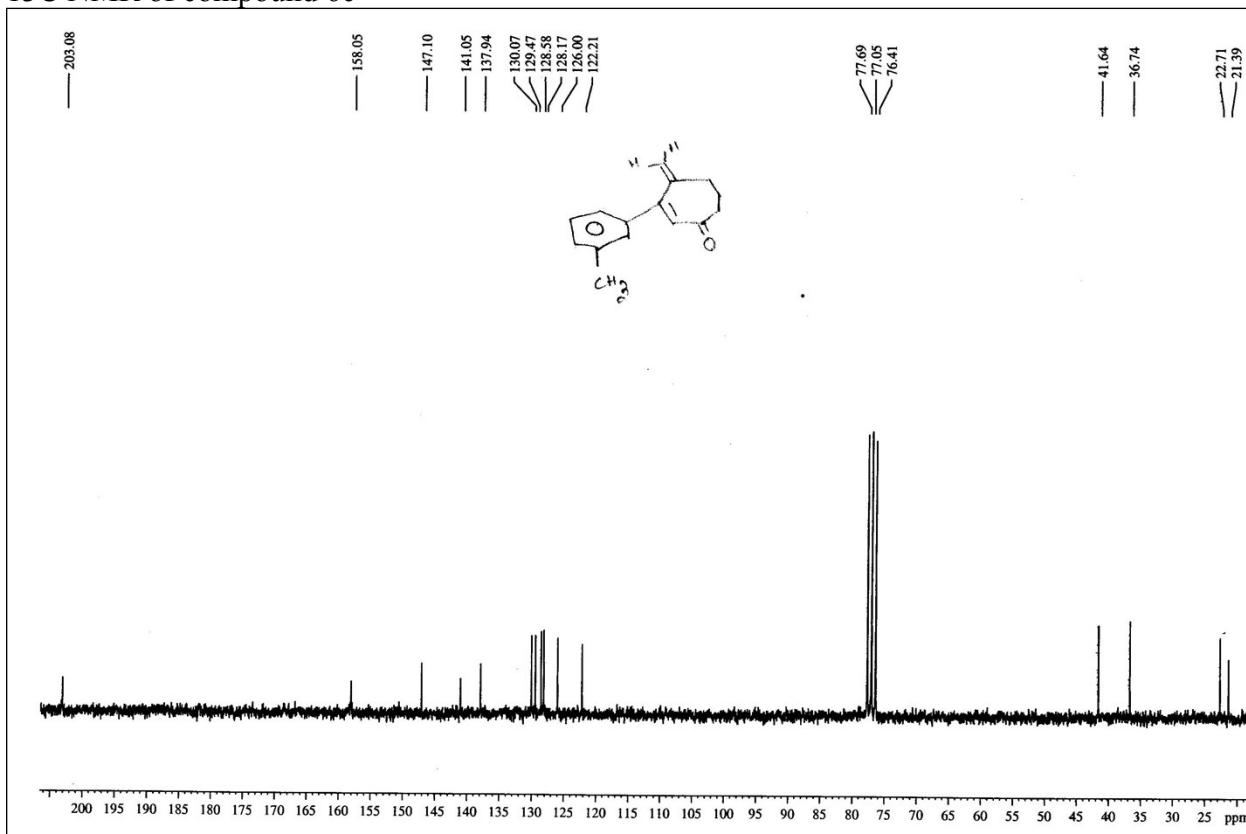
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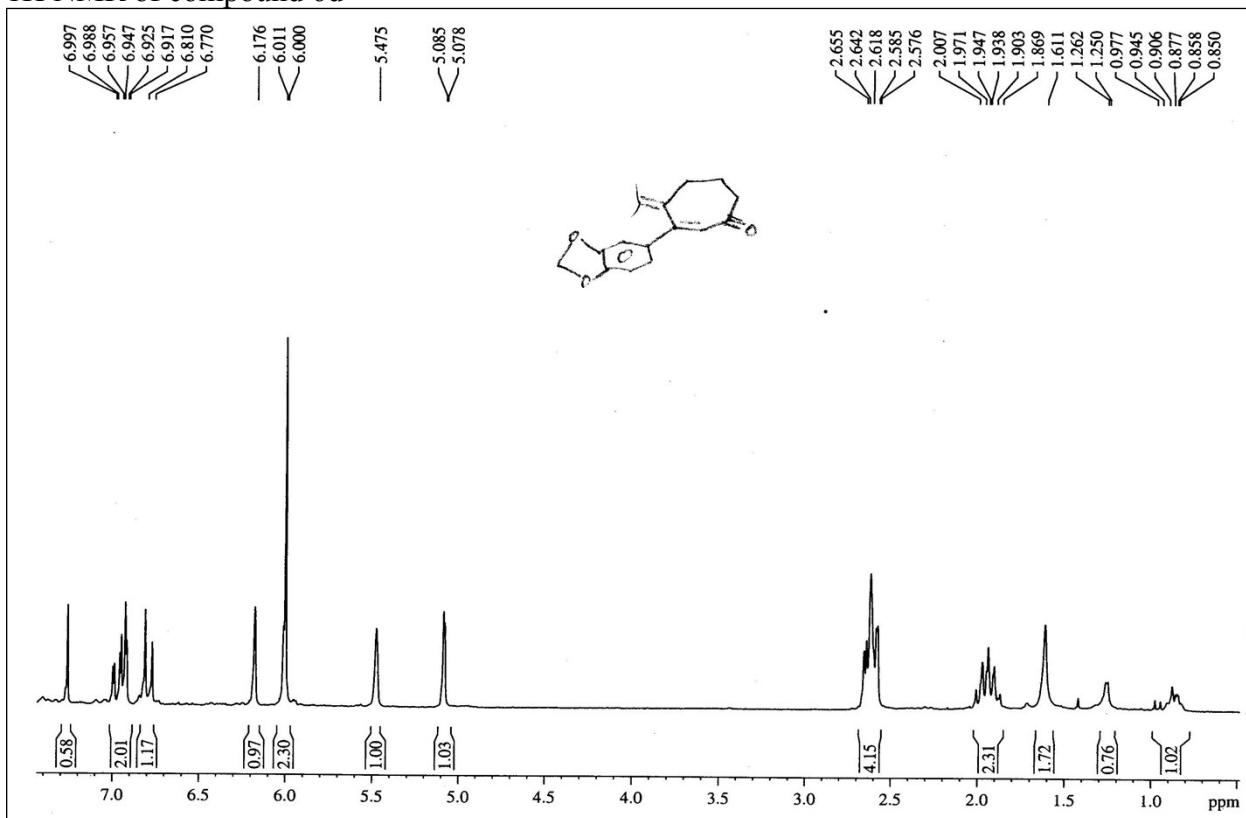
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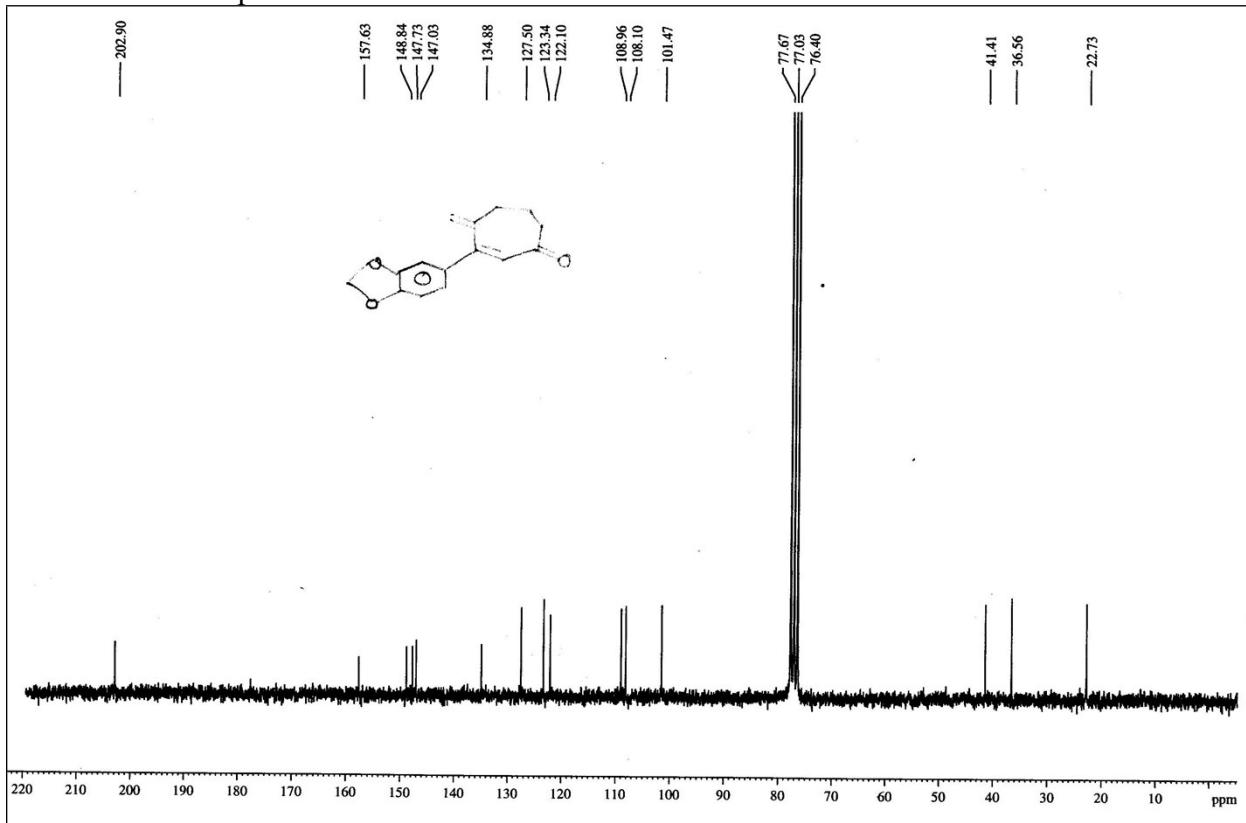
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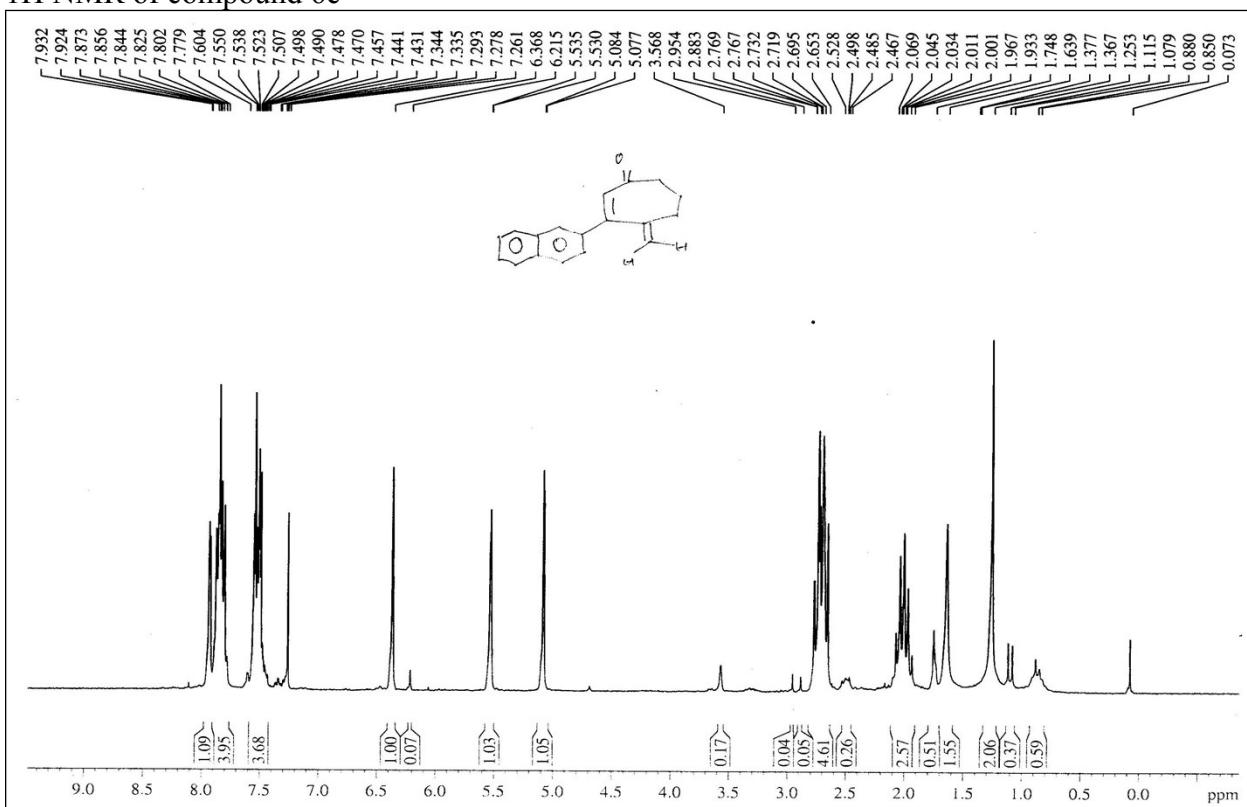
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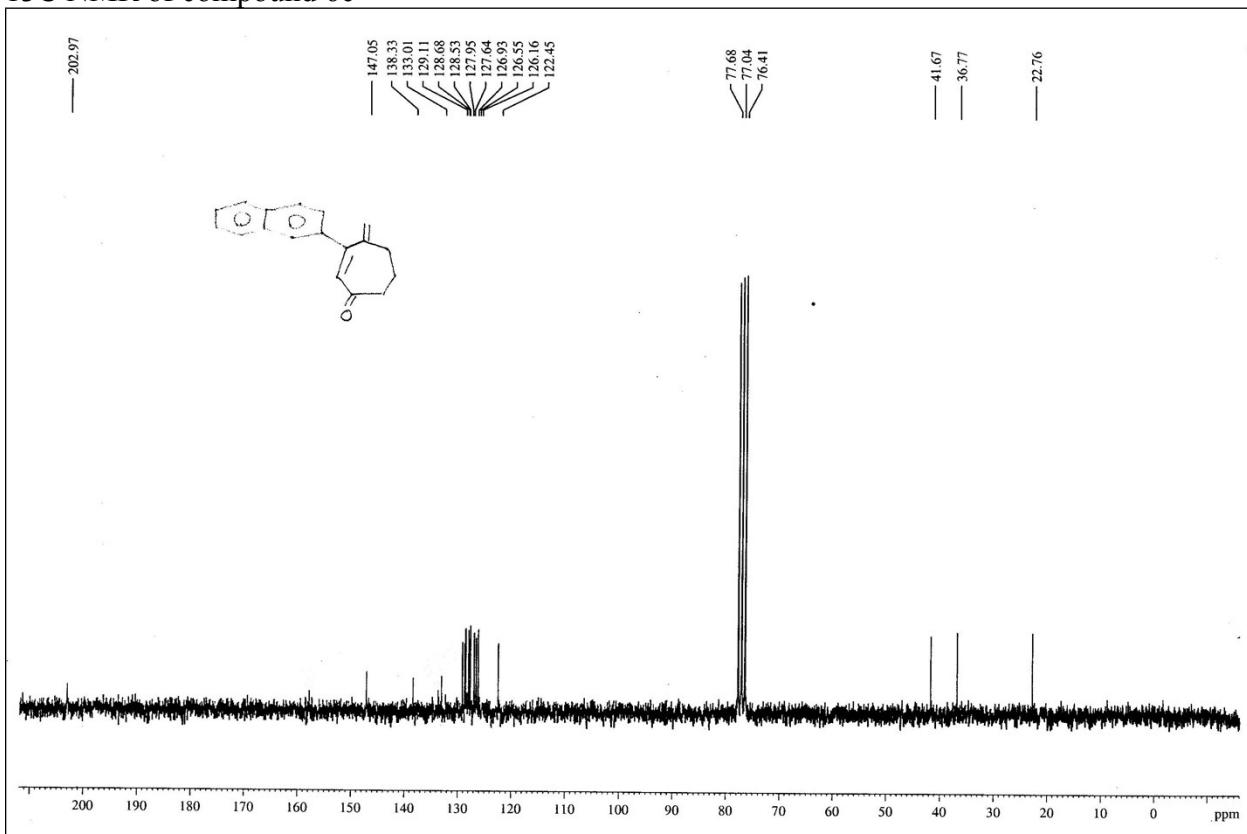
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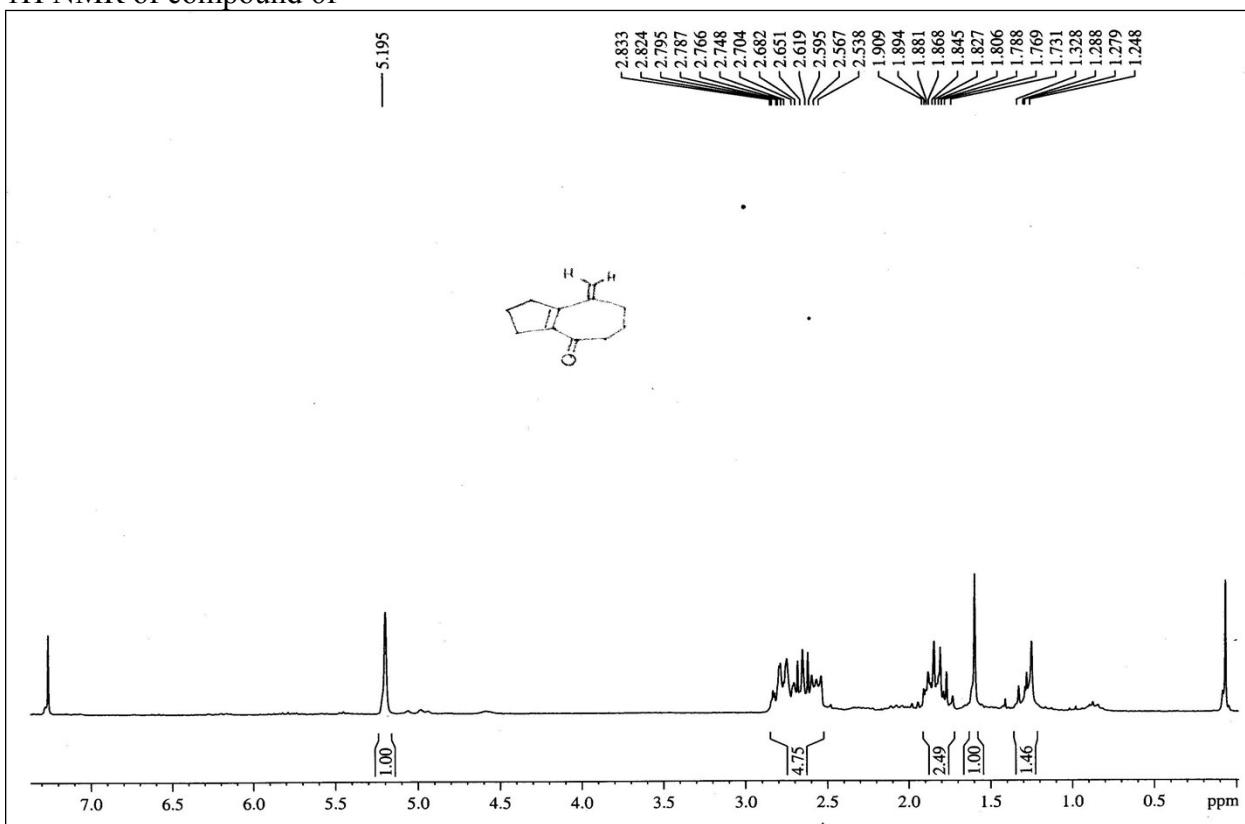
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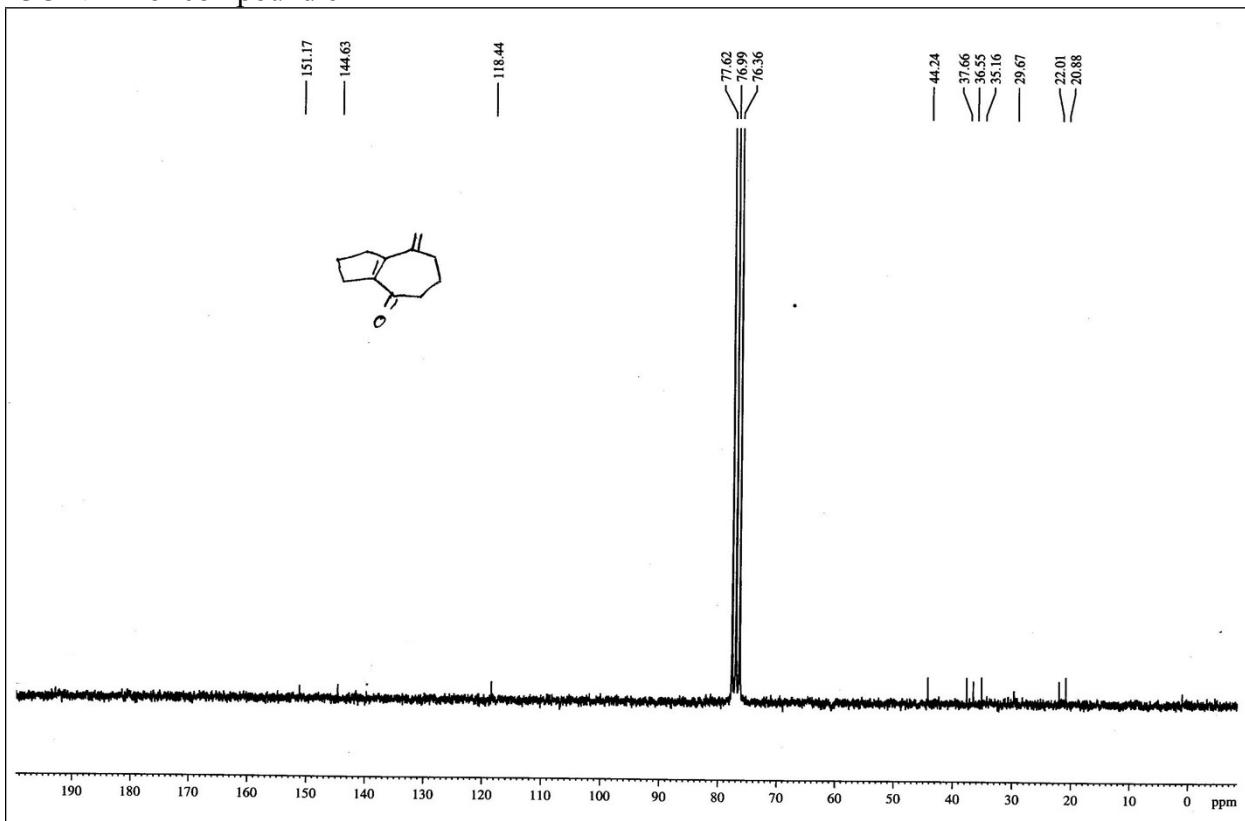
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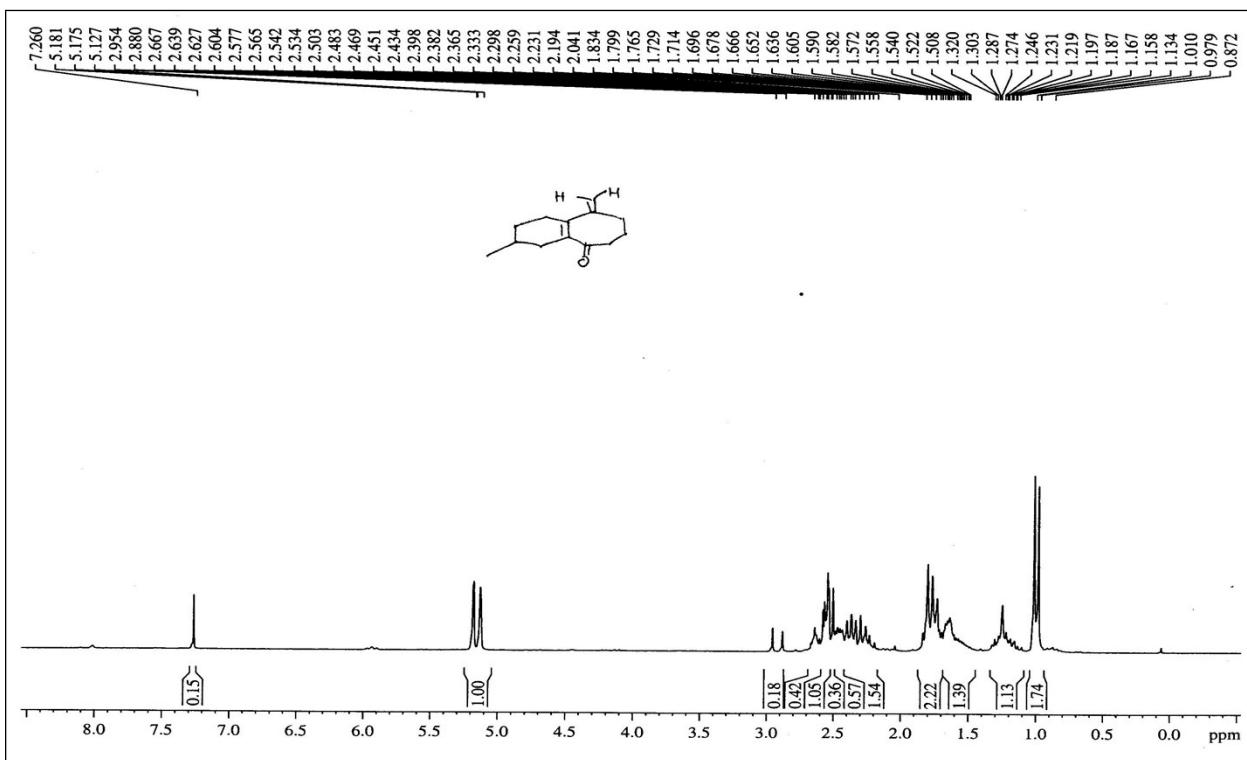
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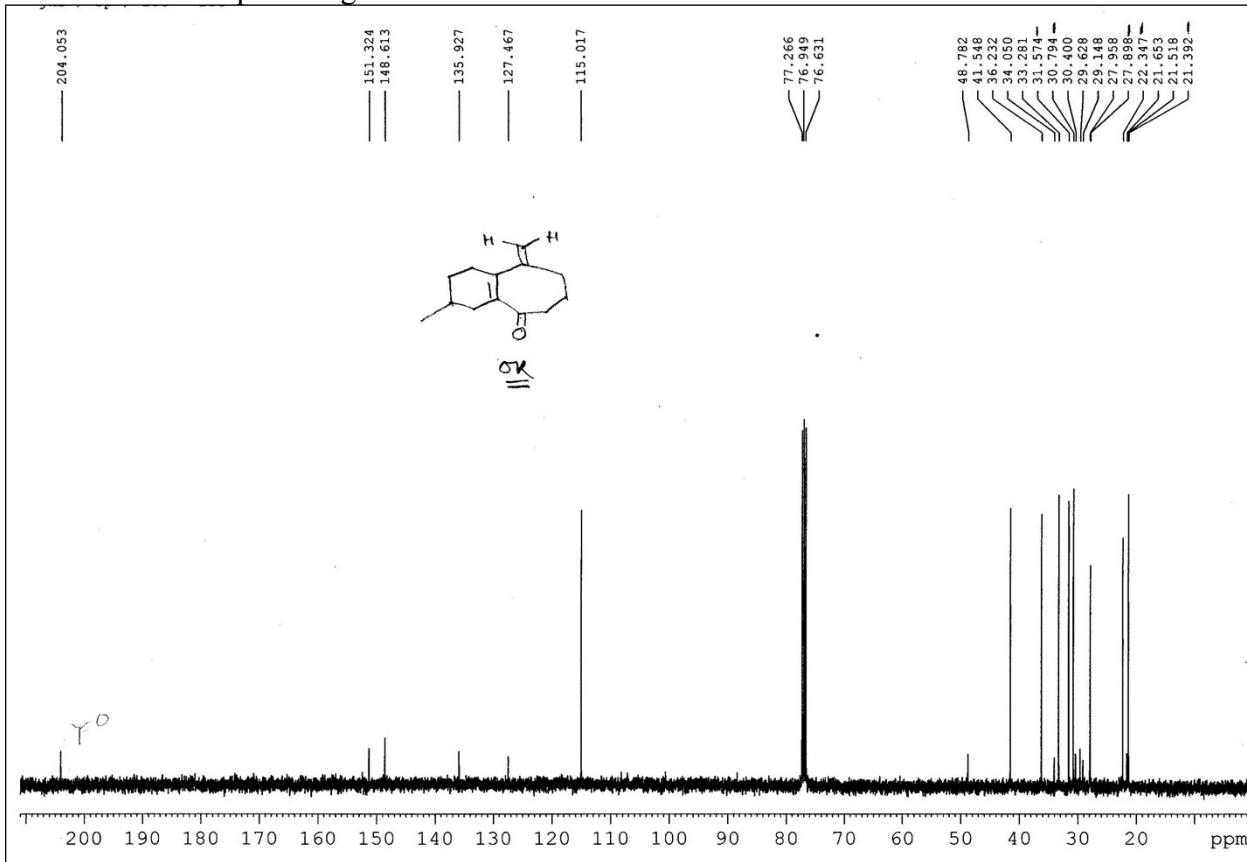
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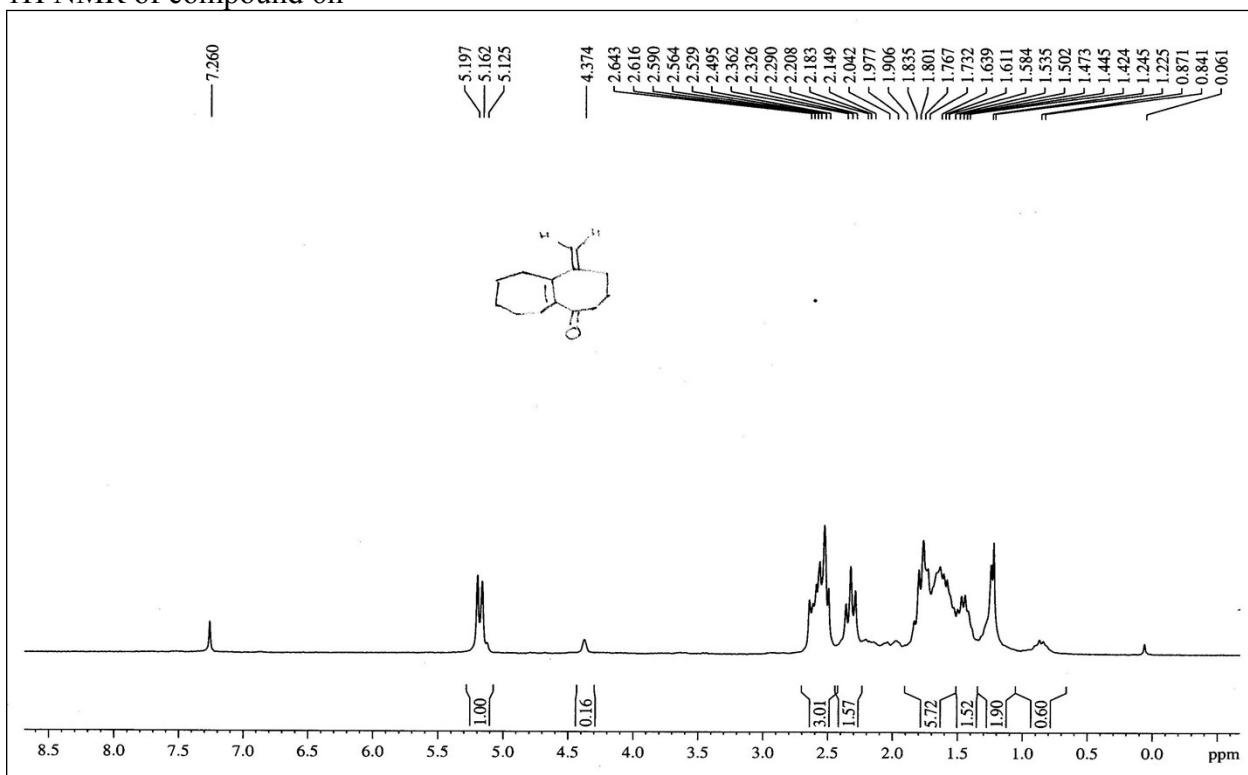
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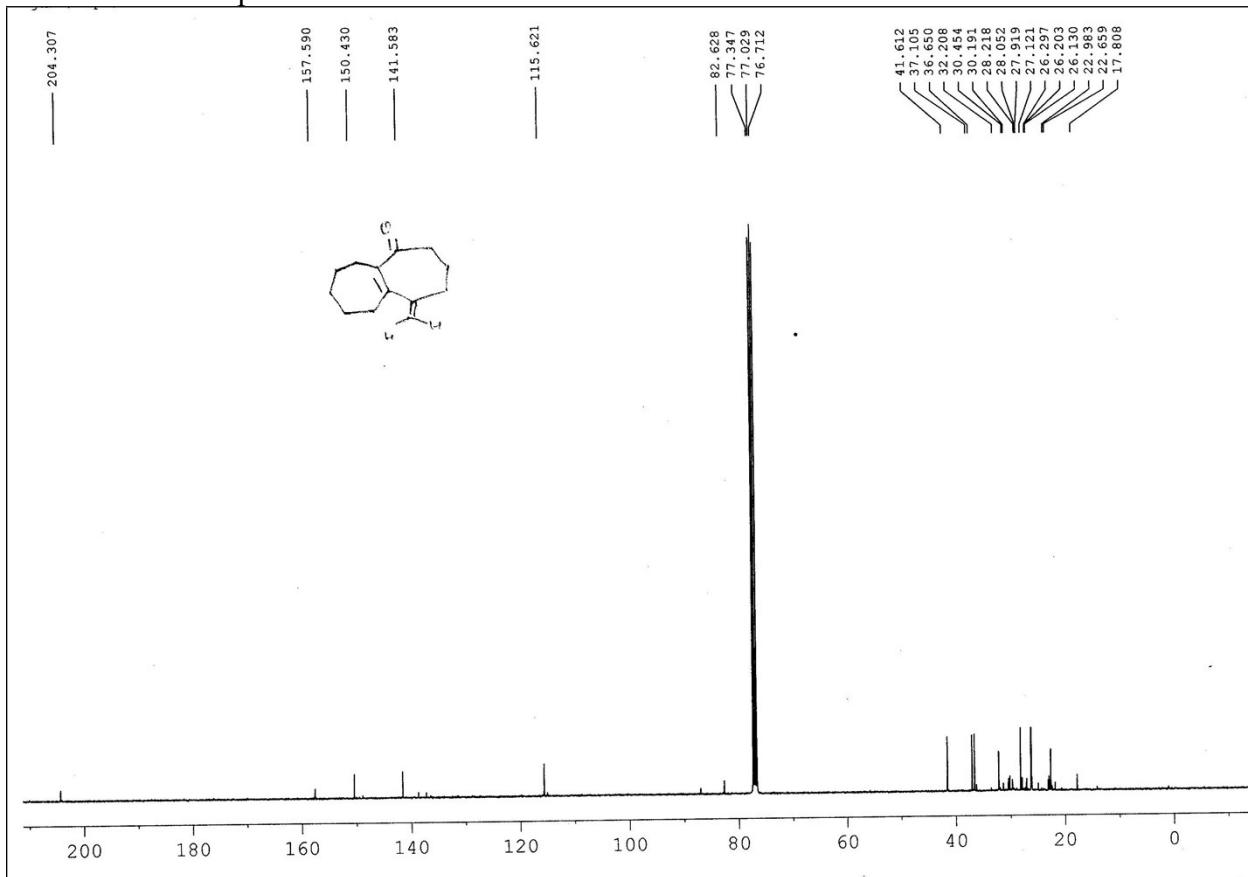
¹³C NMR of compound 6g



¹H NMR of compound 6h



¹³C NMR of compound 6h



C. Computational details and analysis

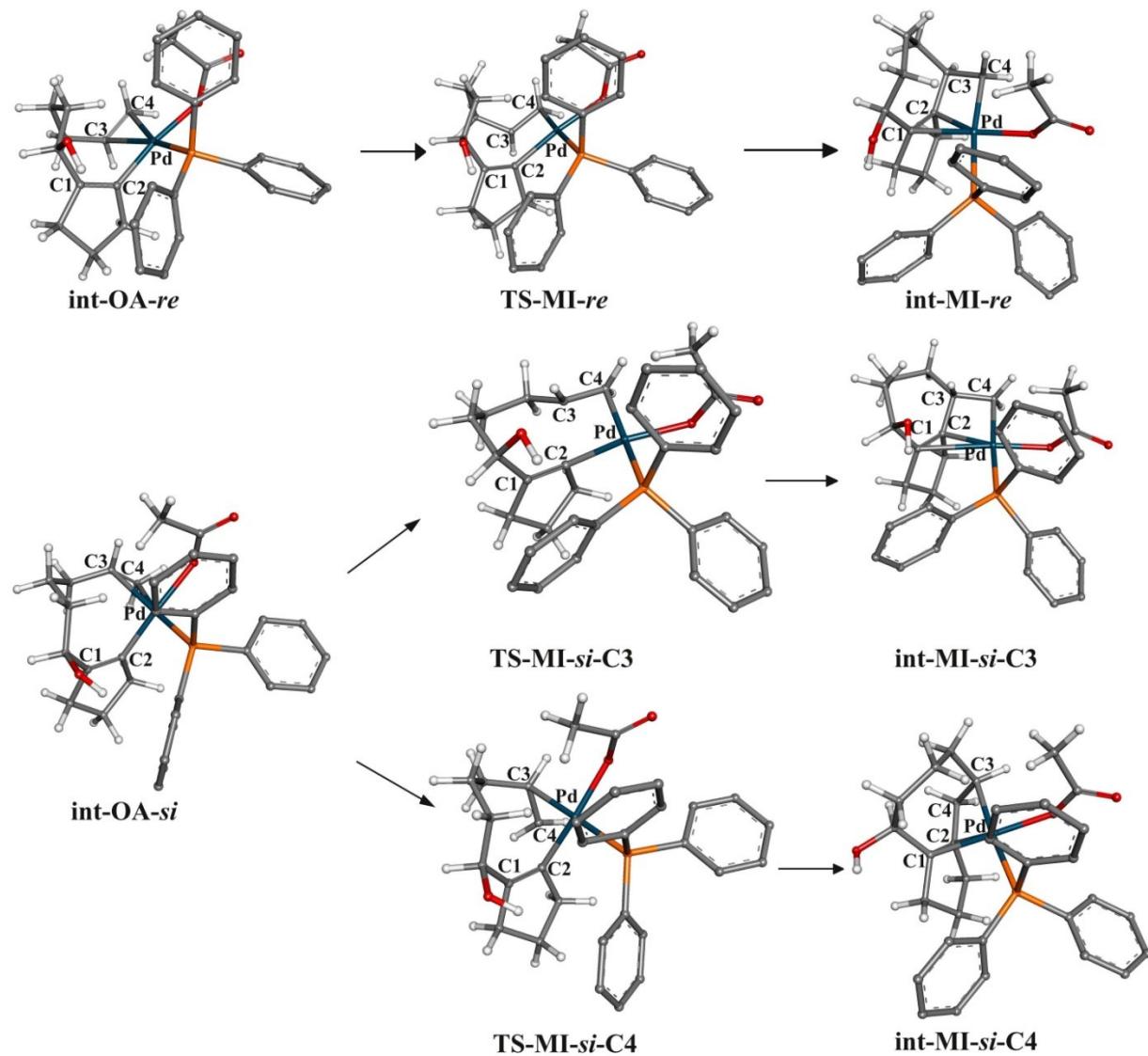


Figure SI1: Mechanism of Migratory Insertion catalyzed by $\text{Pd}(\text{OAc})\text{L}$ with optimized geometries

Table S1. The distances between the carbon atoms involved in the cyclization.

	int-OA- <i>re</i>		int-OA- <i>si</i>	
	C ₂ -C ₃ (d ₁)	C ₂ -C ₄ (d ₂)	C ₂ -C ₃ (d ₁)	C ₂ -C ₄ (d ₂)
Pd(OAc)L	2.88	3.56	3.10	3.03
Pd(Cl)L	2.74	3.50	3.13	3.02
PdL ₂	2.79	3.45	2.96	2.78
PdL	2.54	3.39	3.06	2.92

	TS (to <i>exo</i>)				TS (to <i>endo</i>)			
	<i>re</i>		<i>si</i>		<i>re</i>		<i>si</i>	
	C ₂ -C ₃ (d ₁)	C ₂ -C ₄ (d ₂)	C ₂ -C ₃ (d ₁)	C ₂ -C ₄ (d ₂)	C ₂ -C ₃ (d ₁)	C ₂ -C ₄ (d ₂)	C ₂ -C ₃ (d ₁)	C ₂ -C ₄ (d ₂)
Pd(OAc)L	1.94	2.83	2.01	2.77	Not possible	Not possible	2.69	1.84
Pd(Cl)L	1.95	2.85	2.00	2.75	Not possible	Not possible	2.76	1.93
PdL ₂	2.20	2.94	2.08	2.63	Not possible	Not possible	2.69	1.92
PdL	2.16	3.04	2.10	2.73	Not possible	Not possible	2.75	1.99

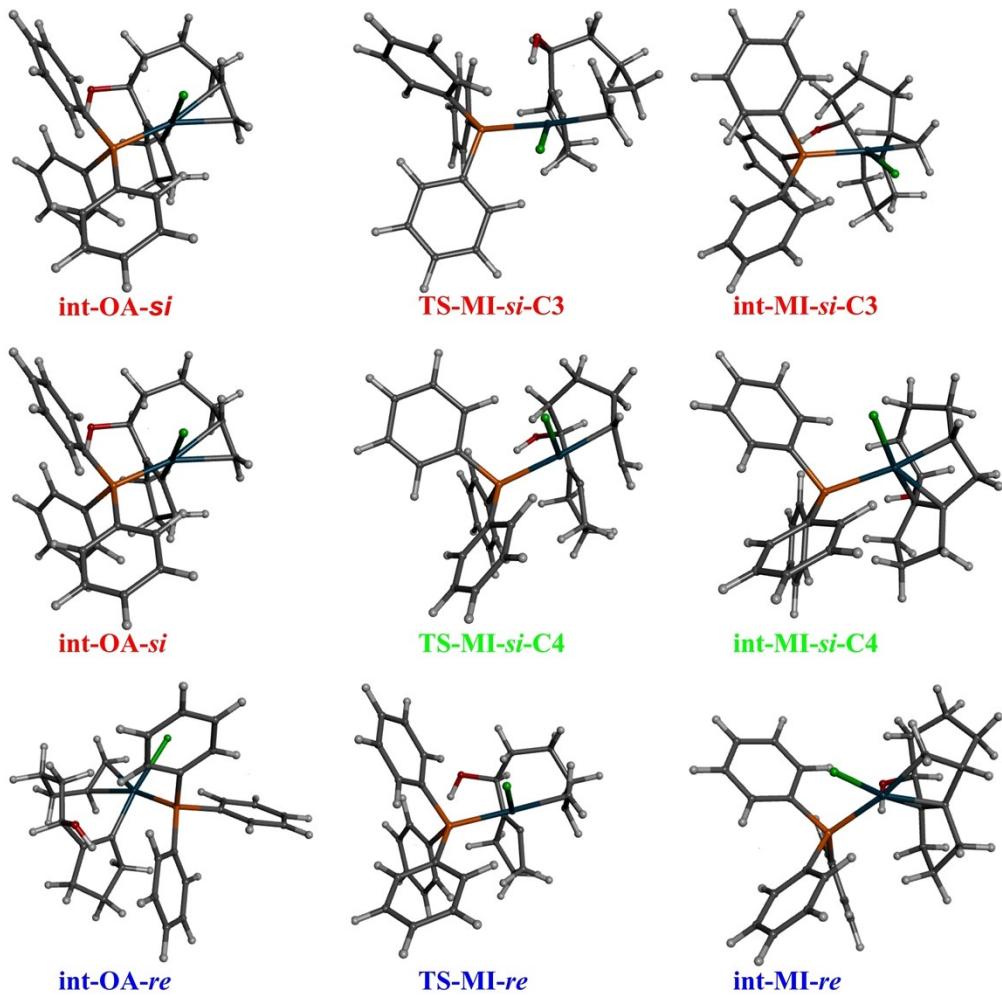


Figure SI2: Optimized geometries of *si* face 7-*exo* and 8-*endo* along with *re* face 7-*exo* migratory insertion by [Cl-Pd-PPh₃] catalyst

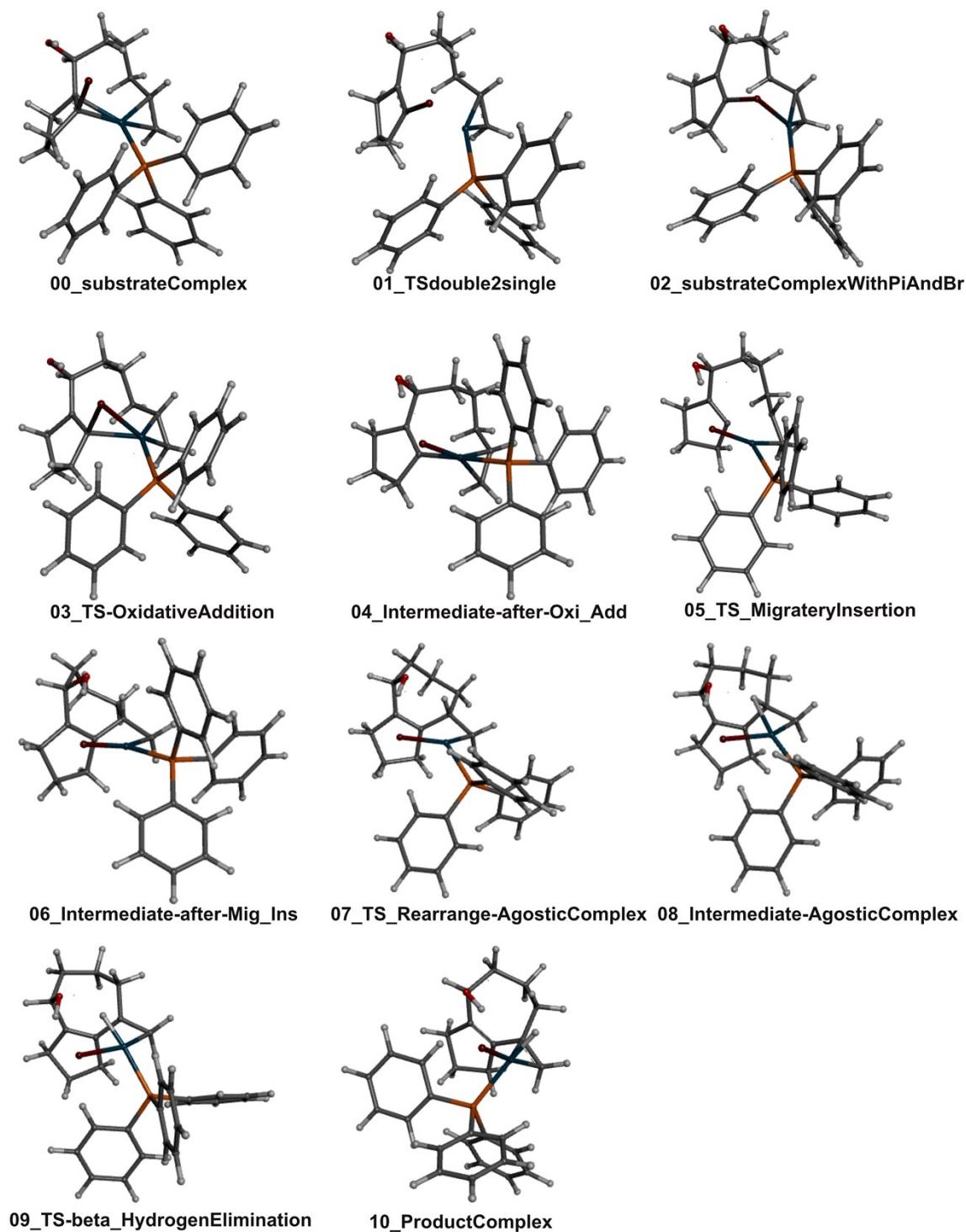


Figure SI3: Optimized geometries of *si* face 7-*exo* migratory insertion by $\text{Pd}(\text{PPh}_3)$ catalyst

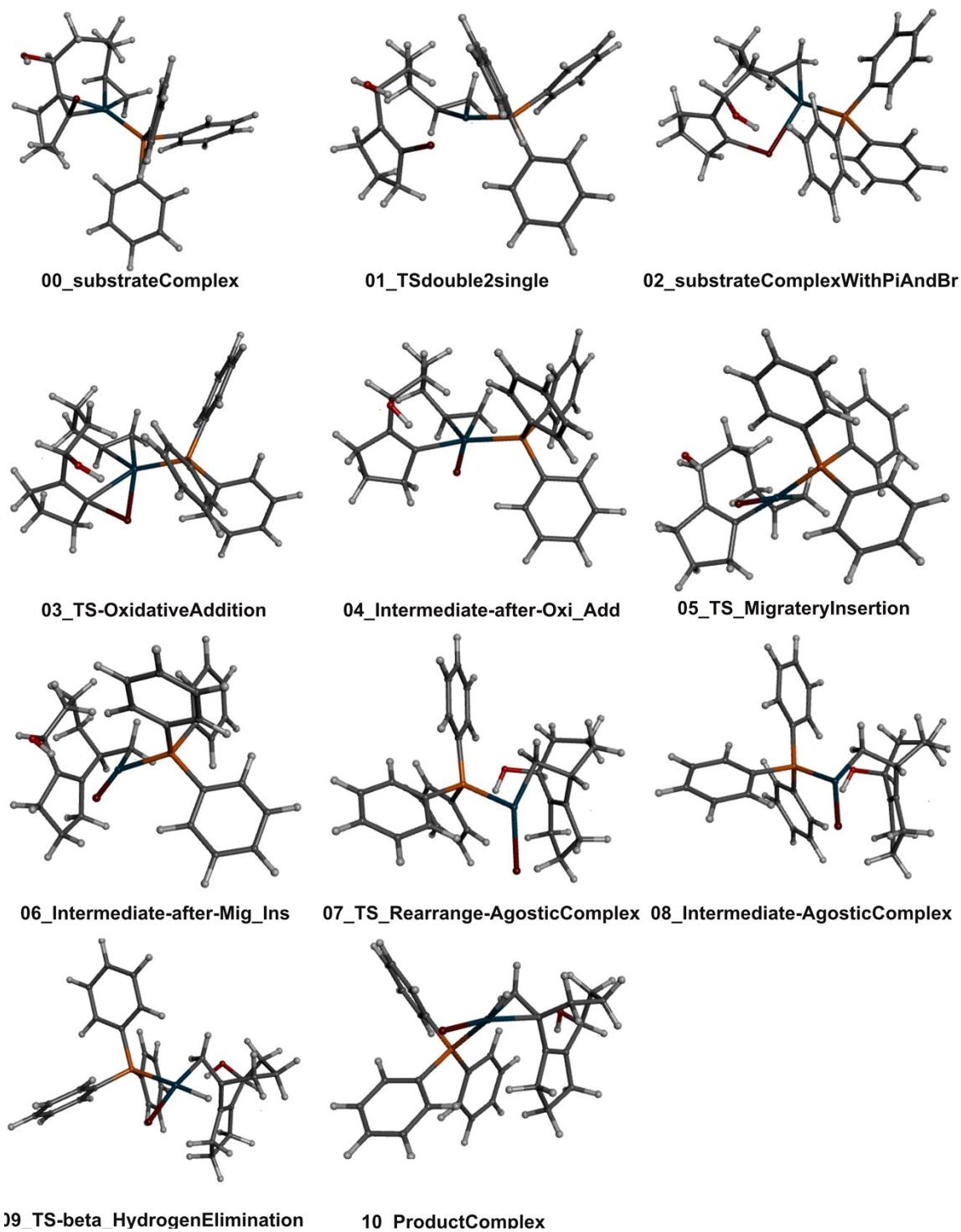


Figure SI4: Optimized geometries of *re* face 7-*exo* migratory insertion by $\text{Pd}(\text{PPh}_3)$ catalyst

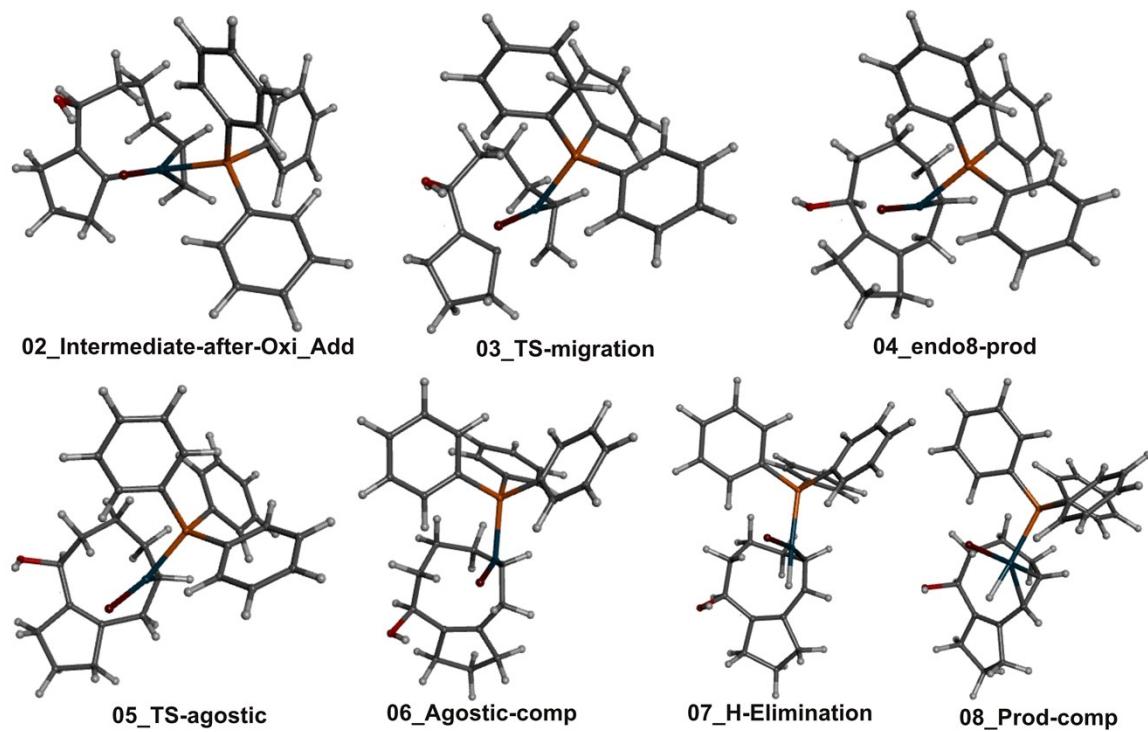


Figure SI5: Optimized geometries of *si* face 8-*endo* migratory insertion by Pd(PPh₃) catalyst

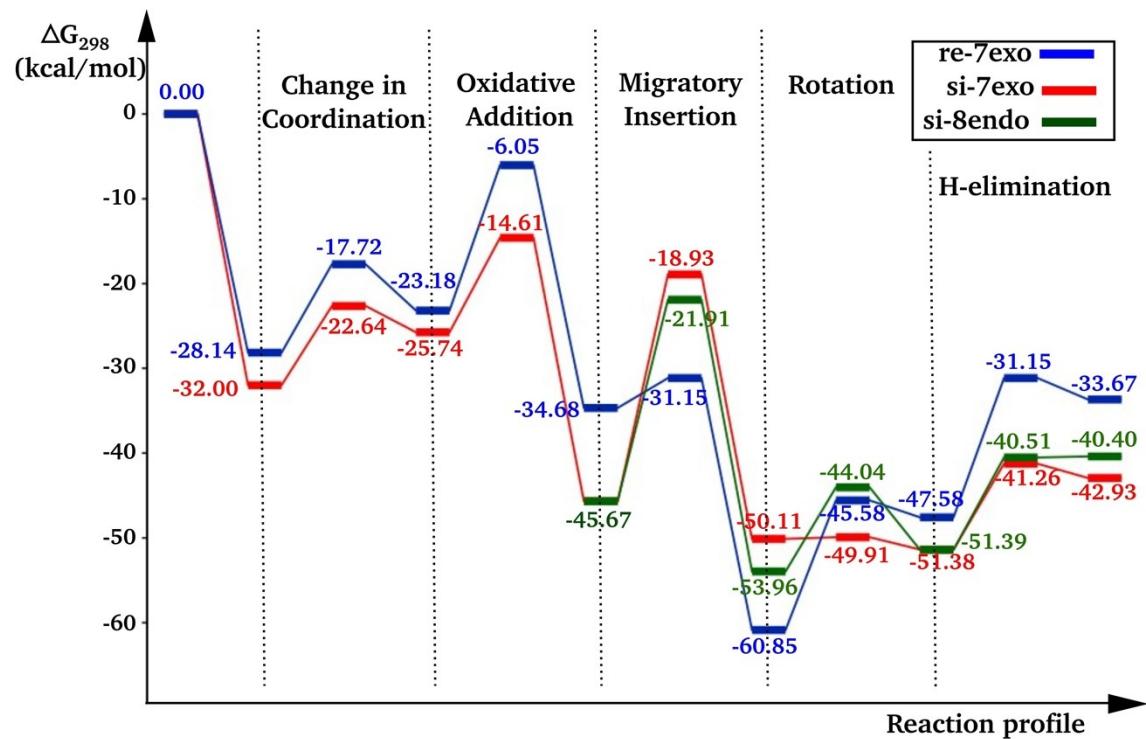


Figure SI6: Potential energy diagram of intramolecular Heck reaction by $\text{Pd}(\text{PPh}_3)$ catalyst [Substrate+ $\text{Pd}(\text{PPh}_3)$ is reference 0.00 kcal/mol]