

## Aerobic Oxidation of Alkenes Mediated by Rhodium(III) Porphyrin Complexes in Water

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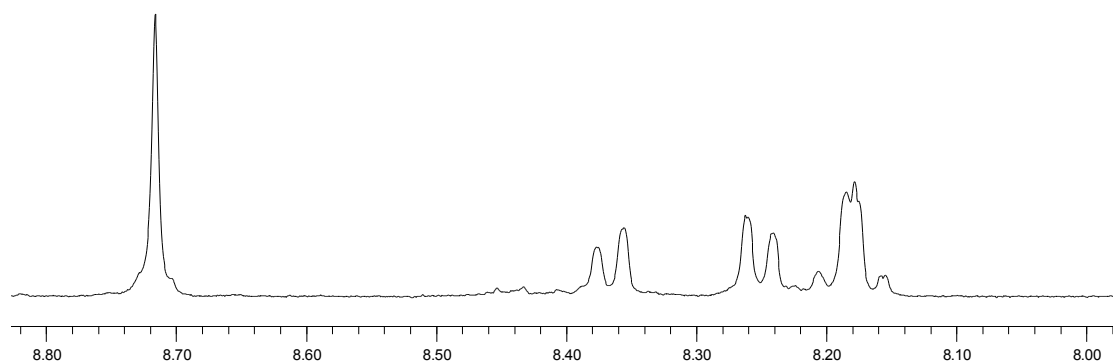
**General:** D<sub>2</sub>O and CDCl<sub>3</sub> were purchased from Cambridge Isotope Laboratory Inc; tetra p-sulfonatophenyl porphyrin from Tokyo Chemical Industry (TCI); (Rh(CO)<sub>2</sub>Cl)<sub>2</sub> from Strem Chemicals Inc; and all other chemicals were purchased from Aldrich or Alfa Aesar unless otherwise noted and used as received. <sup>1</sup>H NMR spectra were recorded on a Bruker AVII<sup>+</sup>-400 spectrometer at ambient temperature and the chemical shifts were referenced to 3-trimethylsilyl-1 propanesulfonic acid sodium salt. GC-MS results were obtained by the Agilent 7890A/5975C GC/MSD system equipped with the DB-17MS(30m, 0.25mm, 0.25um) column.

**Preparation of Na<sub>3</sub>[(TSPP)Rh<sup>III</sup>(D<sub>2</sub>O)<sub>2</sub>] (1):** Synthesis and the equilibrium distribution of [(TSPP)Rh<sup>III</sup>(D<sub>2</sub>O)<sub>2</sub>]<sup>-3</sup>, [(TSPP)Rh<sup>III</sup>(D<sub>2</sub>O)(OD)]<sup>-4</sup>, and [(TSPP)Rh<sup>III</sup>(OD)<sub>2</sub>]<sup>-5</sup> were reported in the previously published papers.<sup>1-3</sup> <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz) δ(ppm): 9.15 (s, 8H, pyrrole), 8.44 (d, 8H, o-phenyl, J<sub>H-1H</sub>=8Hz), 8.25 (d, 8H, m-phenyl, J<sub>H-1H</sub>=8Hz).

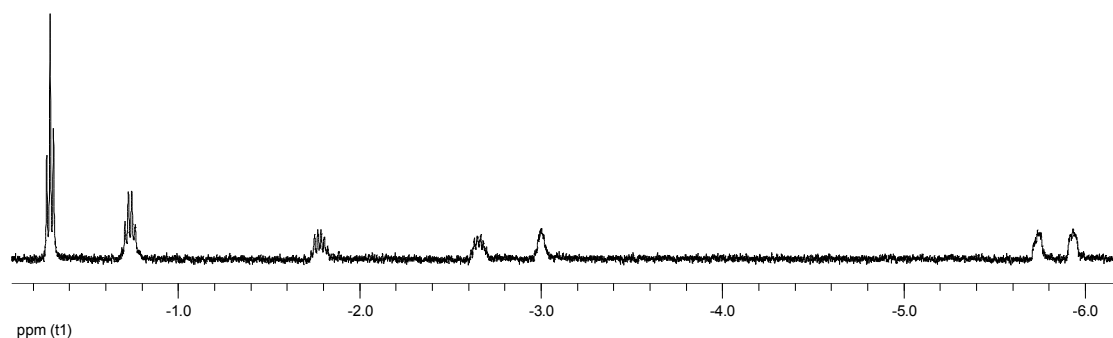
**Typical procedure for Preparation of (TSPP)Rh-CH<sub>2</sub>CH(OD)R in water:**<sup>4</sup> Alkenes (0.3mmol) and **1** (1.1mg, 0.001mmol) were dissolved in 0.5 mL borate buffer D<sub>2</sub>O solution (pH = 9.0) in vacuum adapted NMR tubes at room temperature, respectively. The biphasic solution was shaken for a while, and the progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. The chiral center β-carbon (CH<sub>2</sub>-C\*H(OD)-R) gives diastereotopic protons at neighboring positions. The spectral data are given in the following.

**Reaction of (TSPP)Rh<sup>III</sup> with pentene to produce (TSPP)Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> in D<sub>2</sub>O:** The reaction of **1** with pentene yields 92% of Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> and 3% of Rh-CH<sub>2</sub>C(O)(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>, with 5% (TSPP)Rh<sup>III</sup> remaining. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ(ppm):

8.71(8H, pyrrole), 8.40-8.12(16H, phenyl), -5.93(m, 1H<sub>A</sub>), -5.74(m, 1H<sub>B</sub>), -3.00(m, 1H),  
-2.64(m, 1H<sub>A</sub>), -1.78(m, 1H<sub>B</sub>), -0.73(m, 2H), -0.29(t, 3H).

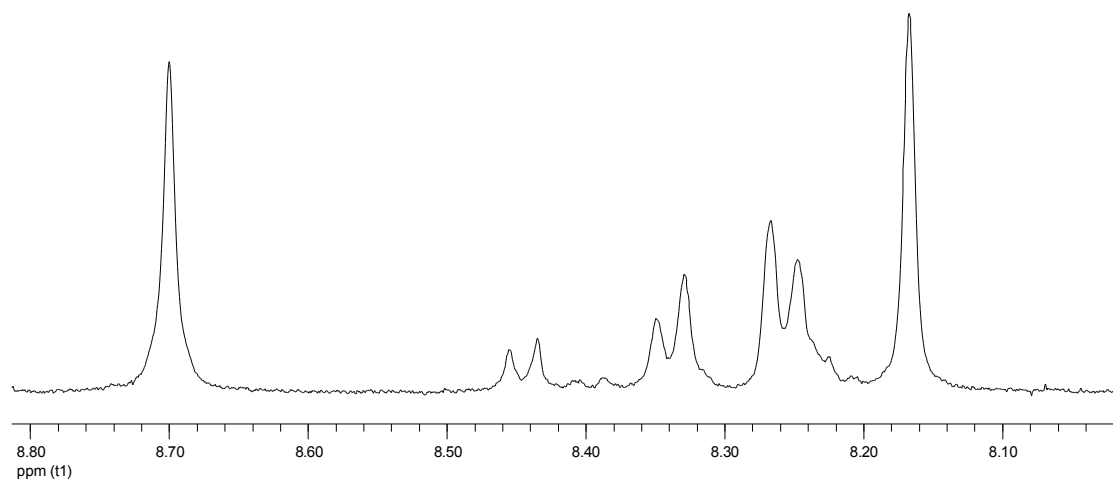


<sup>1</sup>H NMR spectra of pyrrole and phenyl hydrogens of Rh-CH<sub>2</sub>CH(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> in D<sub>2</sub>O

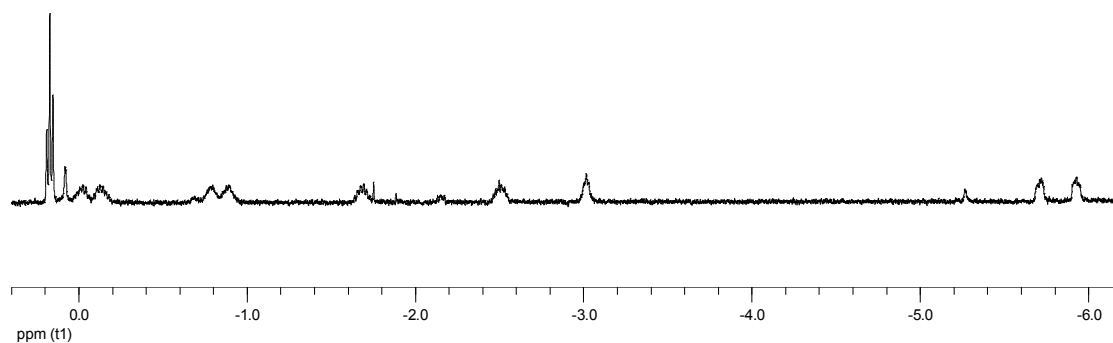


<sup>1</sup>H NMR spectra of -CH<sub>2</sub>CH(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> in Rh-CH<sub>2</sub>CH(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> in D<sub>2</sub>O

**Reaction of (TSPP)Rh<sup>III</sup> with hexene to produce (TSPP)Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> in D<sub>2</sub>O:** The reaction of **1** with hexene yields 80% of Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> and 6% of Rh-CH<sub>2</sub>C(O)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, with 14% (TSPP)Rh<sup>III</sup> remaining. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ(ppm): 8.70(8H, pyrrole), 8.38-8.12(16H, phenyl), -5.93(m, 1H<sub>A</sub>), -5.71(m, 1H<sub>B</sub>), -3.02(m, 1H), -2.50(m, 1H<sub>A</sub>), -1.69(m, 1H<sub>B</sub>), -0.89(m, 1H<sub>A</sub>), -0.79(m, 1H<sub>B</sub>), -0.13 (m, 1H<sub>A</sub>), -0.02(m, 1H<sub>B</sub>), 0.17(t, 3H).

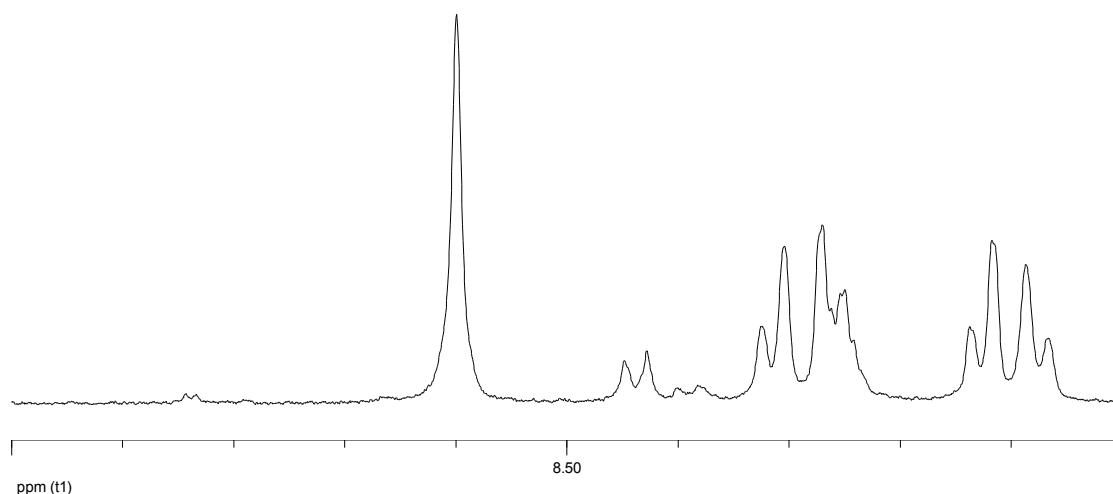


$^1\text{H}$  NMR spectra of pyrrole and phenyl hydrogens of  $\text{Rh-CH}_2\text{CH(OD)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{D}_2\text{O}$

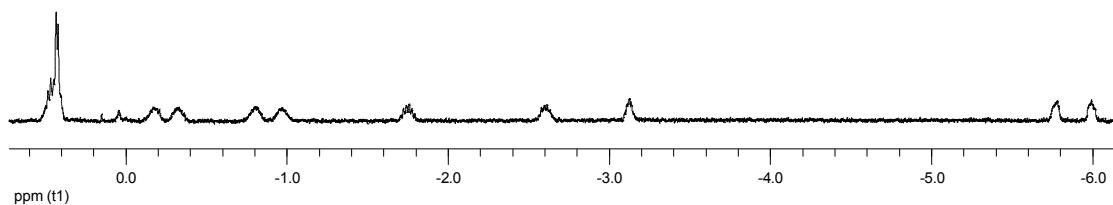


$^1\text{H}$  NMR spectra of  $-\text{CH}_2\text{CH(OD)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{Rh-CH}_2\text{CH(OD)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{D}_2\text{O}$

**Reaction of  $(\text{TSPP})\text{Rh}^{\text{III}}$  with heptene to produce  $(\text{TSPP})\text{Rh-CH}_2\text{CH(OD)(CH}_2)_4\text{CH}_3$  in  $\text{D}_2\text{O}$ :**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta(\text{ppm})$ : 8.60(8H, pyrrole), 8.32-8.07(16H, phenyl), -5.99(m, 1H<sub>A</sub>), -5.77(m, 1H<sub>B</sub>), -3.12(m, 1H), -2.60(m, 1H<sub>A</sub>), -1.75(m, 1H<sub>B</sub>), -0.97(m, 1H<sub>A</sub>), -0.80(m, 1H<sub>B</sub>), -0.32(m, 1H<sub>A</sub>), -0.18(m, 1H<sub>B</sub>), 0.43(m, 2H), 0.47(t, 3H).

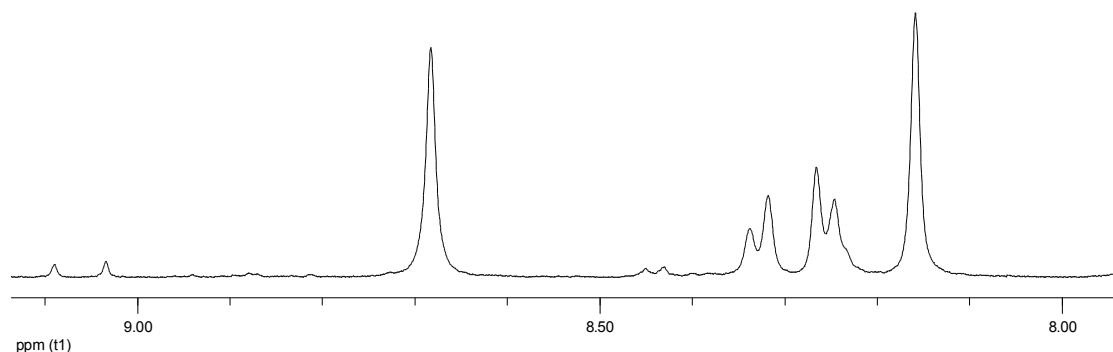


$^1\text{H}$  NMR spectra of pyrrole and phenyl hydrogens of  $\text{Rh-CH}_2\text{CH(OD)CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{D}_2\text{O}$

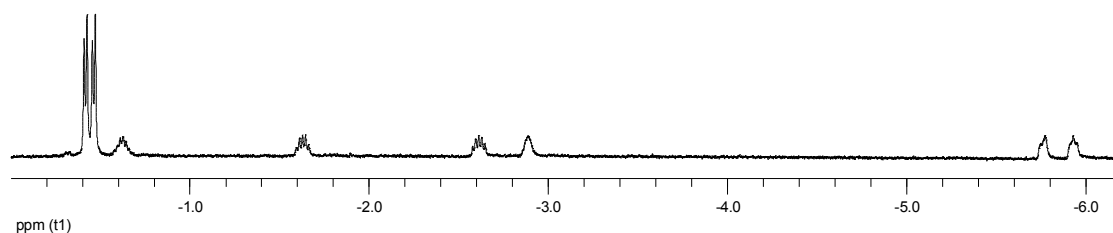


$^1\text{H}$  NMR spectra of  $-\text{CH}_2\text{CH(OD)CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{Rh-CH}_2\text{CH(OD)CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{D}_2\text{O}$ .

**Reaction of  $(\text{TSPP})\text{Rh}^{\text{III}}$  with 4-methyl-1-pentene to produce  $(\text{TSPP})\text{Rh-CH}_2\text{CH(OD)CH}_2\text{CH(CH}_3)_2$  in  $\text{D}_2\text{O}$ :**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta(\text{ppm})$ : 8.68(8H, pyrrole), 8.40-8.15(16H, phenyl), -5.93(m, 1H<sub>A</sub>), -5.77(m, 1H<sub>B</sub>), -2.89(m, 1H), -2.61(m, 1H<sub>A</sub>), -1.63(m, 1H<sub>B</sub>), -0.62(m, 1H), -0.46(d, 3H), -0.41(d, 3H).



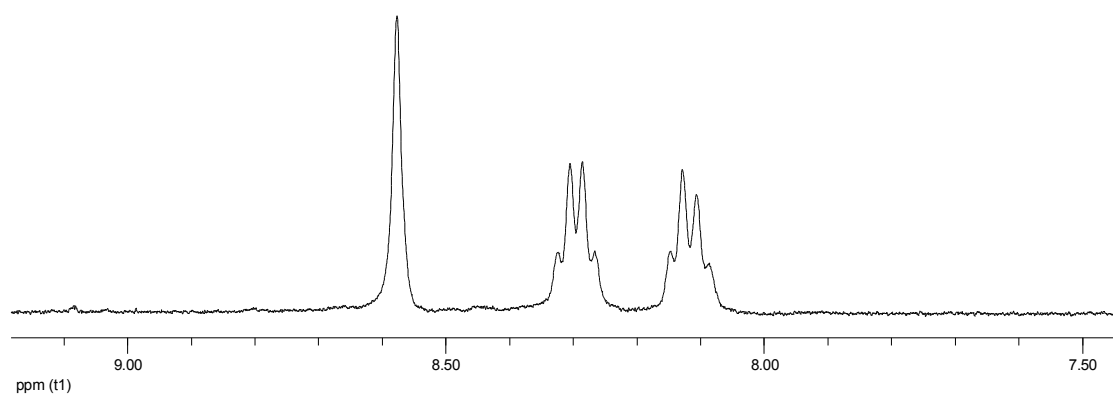
$^1\text{H}$  NMR spectra of pyrrole and phenyl hydrogens of  $\text{Rh-CH}_2\text{CH(OD)CH}_2\text{CH(CH}_3)_2$  in  $\text{D}_2\text{O}$



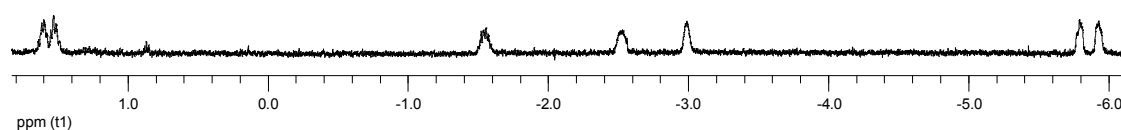
$^1\text{H}$  NMR spectra of  $-\text{CH}_2\text{CH}(\text{OD})\text{CH}_2\text{CH}(\text{CH}_3)_2$  in  $\text{Rh}-\text{CH}_2\text{CH}(\text{OD})\text{CH}_2\text{CH}(\text{CH}_3)_2$  in  $\text{D}_2\text{O}$

**Reaction of  $(\text{TSPP})\text{Rh}^{\text{III}}$  with 3-buten-1-ol to produce  $(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{OD})\text{CH}_2\text{CH}_2\text{OH}$**

**in  $\text{D}_2\text{O}$ :**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ (ppm): 8.58(8H, pyrrole), 8.40-8.00(16H, phenyl), -5.93(m, 1H<sub>A</sub>), -5.78(m, 1H<sub>B</sub>), -2.98(m, 1H), -2.51(m, 1H<sub>A</sub>), -1.55(m, 1H<sub>B</sub>), 1.53(m, 1H<sub>A</sub>), 1.60(m, 1H<sub>B</sub>).



$^1\text{H}$  NMR spectra of pyrrole and phenyl hydrogens of  $\text{Rh}-\text{CH}_2\text{CH}(\text{OD})\text{CH}_2\text{CH}_2\text{OD}$  in  $\text{D}_2\text{O}$

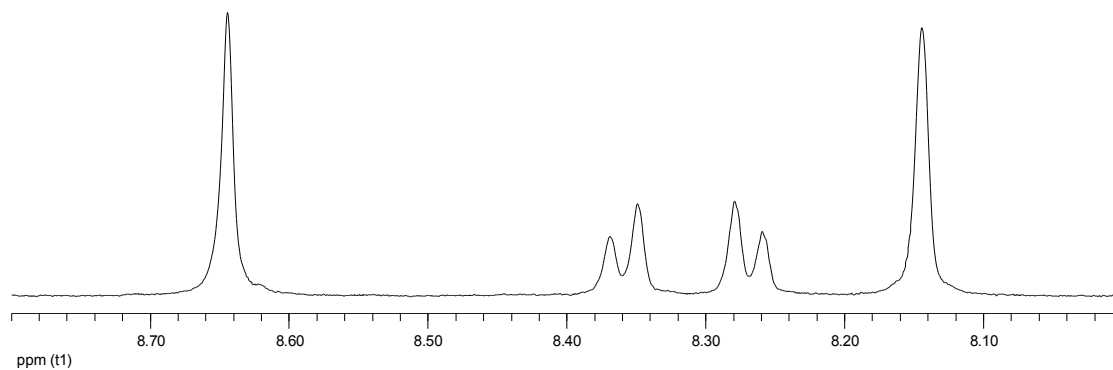


$^1\text{H}$  NMR spectra of  $-\text{CH}_2\text{CH}(\text{OD})\text{CH}_2\text{CH}_2\text{OD}$  in  $\text{Rh}-\text{CH}_2\text{CH}(\text{OD})\text{CH}_2\text{CH}_2\text{OD}$  in  $\text{D}_2\text{O}$

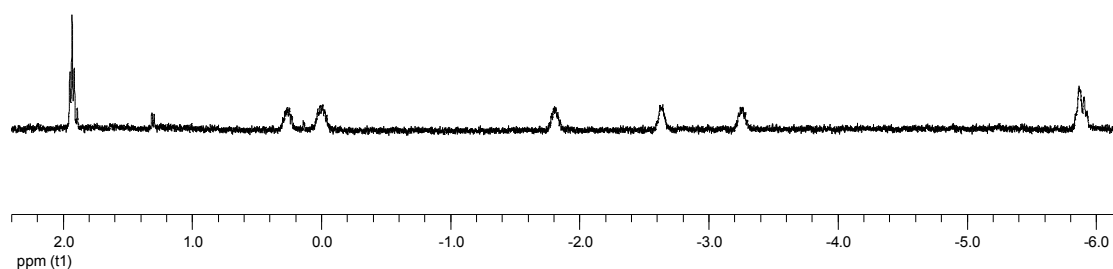
**Reaction of  $(\text{TSPP})\text{Rh}^{\text{III}}$  with 4-penten-1-ol to produce  $(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{OD})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  in  $\text{D}_2\text{O}$ :**

The reaction of **1** with 4-penten-ol turns out to be a complete conversion to  $\text{Rh}-\text{CH}_2\text{CH}(\text{OD})(\text{CH}_2)_2\text{CH}_2\text{OD}$  without any observation of  $\text{Rh}-\text{CH}_2\text{C}(\text{O})(\text{CH}_2)_2\text{CH}_2\text{OD}$  or remaining  $(\text{TSPP})\text{Rh}^{\text{III}}$ . As a result, the product 5-hydroxy-2-pentanone was the only product quantitatively from the thermal dissociation of  $\text{Rh}-\text{CH}_2\text{CH}(\text{OD})(\text{CH}_2)_2\text{CH}_2\text{OD}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ (ppm): 8.65(8H, pyrrole),

8.40-8.10(16H, phenyl), -5.90 — -5.88 (m, 2H), -3.25(m, 1H), -2.63(m, 1H<sub>A</sub>), -1.80(m, 1H<sub>B</sub>),  
0.0 (m, 1H<sub>A</sub>), 0.27 (m, 1H<sub>B</sub>), 1.93 (t, 3H).



<sup>1</sup>H NMR spectra of pyrrole and phenyl hydrogens of Rh-CH<sub>2</sub>CH(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OD in D<sub>2</sub>O

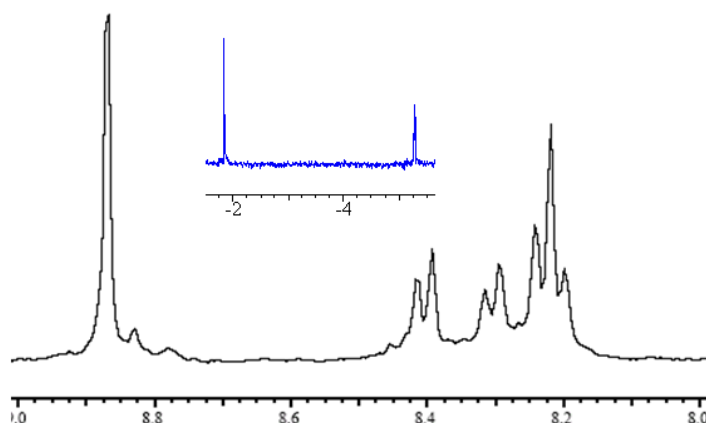


<sup>1</sup>H NMR spectra of -CH<sub>2</sub>CH(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OD in Rh-CH<sub>2</sub>CH(OD)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OD in D<sub>2</sub>O

***Typical procedure for independent preparation of (TSPP)Rh-CH<sub>2</sub>C(O)R in water:***

Ketones (0.3mmol) and **1** (1.1mg, 0.001mmol) were dissolved in 0.5 mL borate buffer D<sub>2</sub>O solution (pH = 9.0) in vacuum adapted NMR tubes at room temperature, respectively. Notably, 2-pentanone was dissolved in D<sub>2</sub>O solution, while 2-hexanone and D<sub>2</sub>O formed a biphasic solution. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. The spectral data of (TSPP)Rh-CH<sub>2</sub>C(O)R are given in the following.

***(TSPP)Rh-CH<sub>2</sub>C(O)CH<sub>3</sub>:***



<sup>1</sup>H NMR of the (TSPP)Rh-CH<sub>2</sub>C(O)CH<sub>3</sub> from reaction of (TSPP)Rh<sup>I</sup> with ClCH<sub>2</sub>C(O)CH<sub>3</sub> in water, which is identical with compound formed by reaction of (TSPP)Rh<sup>III</sup> with acetone.

***(TSPP)Rh-CH<sub>2</sub>C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>:***

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ(ppm): 8.85(8H, pyrrole), 8.46-8.18(16H, phenyl), -5.29(m, 2H), -2.15(m, 2H), -0.59(m, 2H), -0.23(t, 3H).

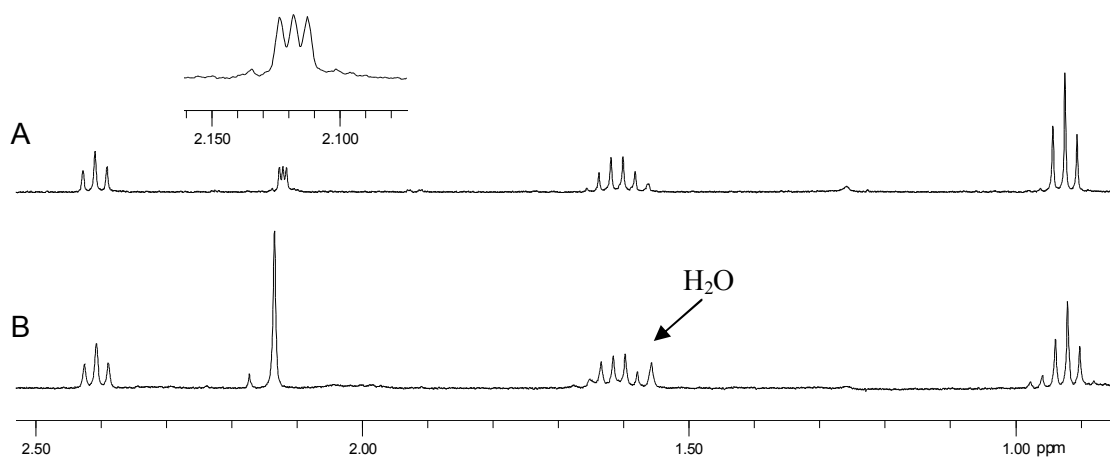
***(TSPP)Rh-CH<sub>2</sub>C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>:***

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ(ppm): 8.85(8H, pyrrole), 8.46-8.18(16H, phenyl), -5.32(m, 2H), -2.16(m, 2H), -0.69(m, 2H), 0.09(m, 5H).

***Typical procedure for thermal dissociation of (TSPP)Rh-CH<sub>2</sub>CH(OD)R to produce ketones quantitatively in water:*** The Rh-CH<sub>2</sub>CH(OD)R complexes were prepared from the reactions of Rh-OD with excess of alkenes in weak basic condition which exclusively converted (TSPP)Rh<sup>III</sup> into Rh-CH<sub>2</sub>CH(OD)R. The excess of alkenes and solvent D<sub>2</sub>O were pumped out, fresh D<sub>2</sub>O was added into the NMR tube and subjected to three freeze-pump-thaw cycles. The initial <sup>1</sup>H NMR was recorded to show the formation of Rh-CH<sub>2</sub>CH(OD)R and a clean range from 0 to 4 ppm. The sample Rh-CH<sub>2</sub>CH(OD)R was heated in a water bath at 60°C for a period of hours, and the progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. When the reactions reach completion where all Rh-CH<sub>2</sub>CH(OD)R were converted to ketones and (TSPP)Rh<sup>I</sup> which shows a characteristic <sup>1</sup>H NMR singlet peak at 8.31 ppm, the product ketones were extracted by CDCl<sub>3</sub>. A parallel

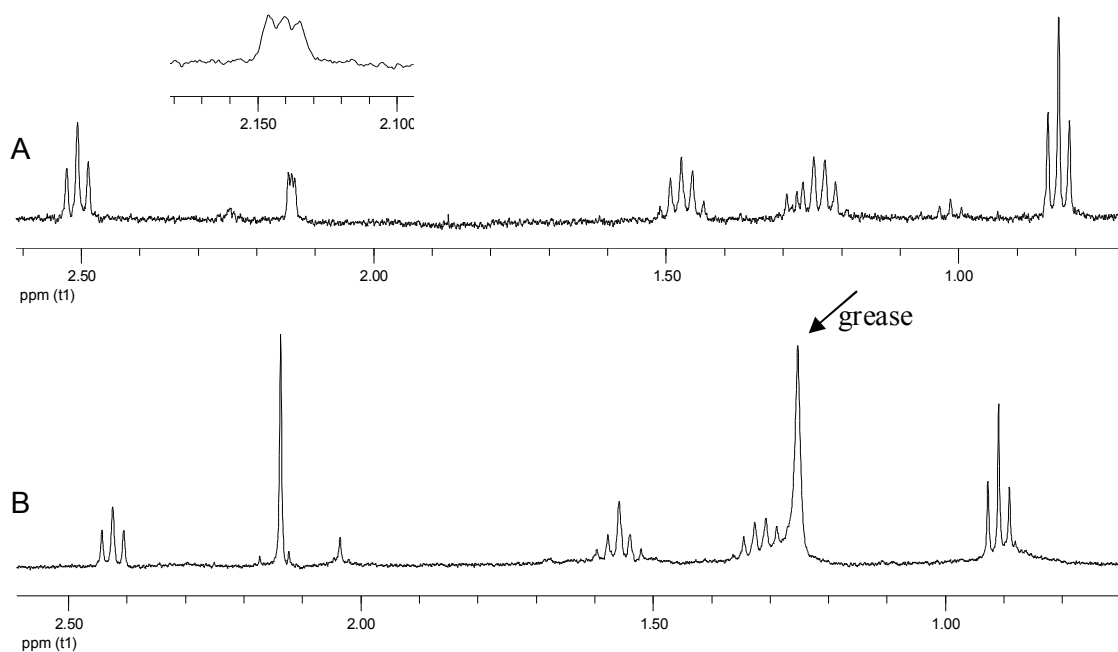
sample of Rh-CH<sub>2</sub>CH(OH)R dissolved in H<sub>2</sub>O was also heated under the same reaction condition, and extracted by CDCl<sub>3</sub>. The <sup>1</sup>H NMR spectra for the product ketones are given in the following.

**Pentanone (CH<sub>3</sub>C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>):**



<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) spectrum of pentanone produced from thermal dissociation of (TSPP)Rh-CH<sub>2</sub>CH(OH)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> in D<sub>2</sub>O and H<sub>2</sub>O. A) CH<sub>2</sub>(D)C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> in D<sub>2</sub>O; B) CH<sub>3</sub>C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (obtained in H<sub>2</sub>O).

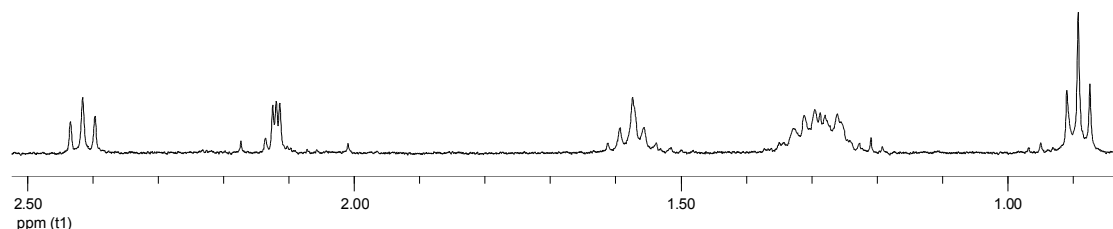
**Hexanone (CH<sub>3</sub>C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>):**





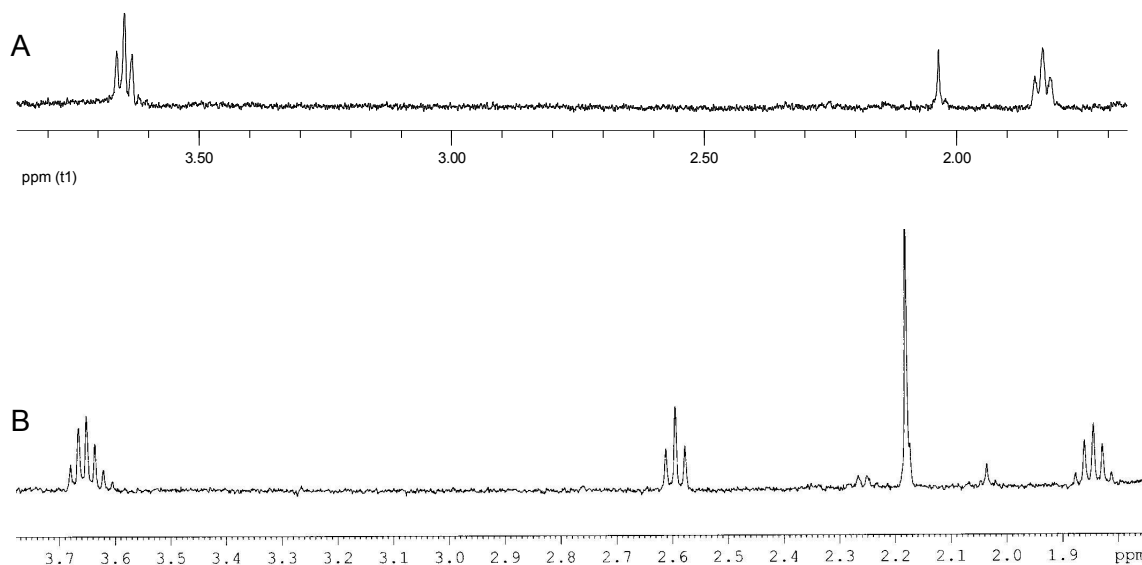
$^1\text{H}$  NMR (400 MHz) spectrum of hexanone produced from thermal dissociation of (TSPP)Rh- $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ . A)  $\text{CH}_2(\text{D})\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{D}_2\text{O}$ ; B)  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  (obtained in  $\text{H}_2\text{O}$ ) in  $\text{CDCl}_3$ .

**Heptanone ( $\text{CH}_2\text{DC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ):**



$^1\text{H}$  NMR (400 MHz) spectrum of heptanone ( $\text{CH}_2(\text{D})\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) produced from thermal dissociation of (TSPP)Rh- $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{D}_2\text{O}$ .

**5-hydroxy-2-pentanone ( $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ )**

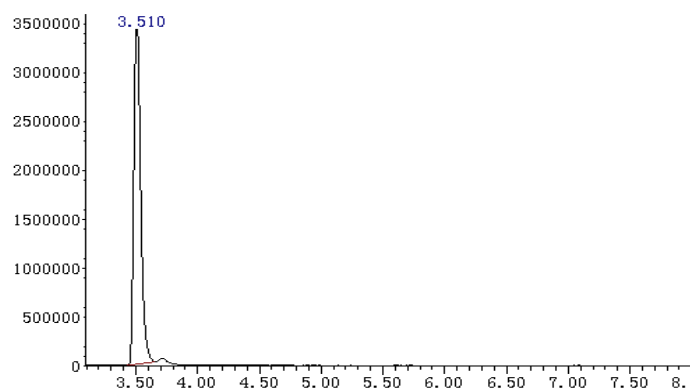


$^1\text{H}$  NMR (400 MHz) spectrum of 5-hydroxy-2-pentanone produced from thermal dissociation of (TSPP)Rh- $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ . A)  $\text{CD}_3\text{C}(\text{O})\text{CD}_2\text{CH}_2\text{CH}_2\text{OD}$  in  $\text{D}_2\text{O}$ ; B)  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  (obtained in  $\text{H}_2\text{O}$ ) in  $\text{CDCl}_3$ .

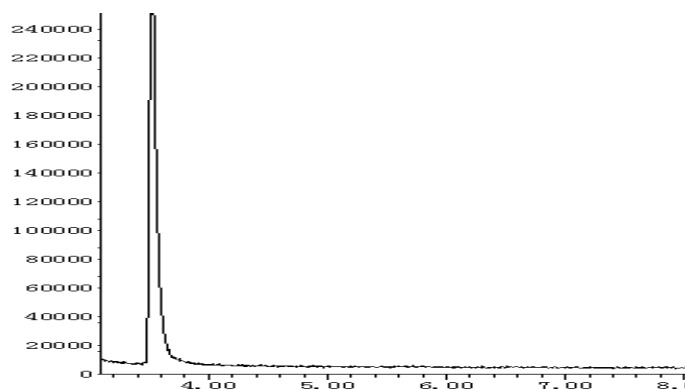
**GC-MS results.**

**Pentanone:** 2-pentanone obtained in  $\text{D}_2\text{O}$  and in  $\text{H}_2\text{O}$  respectively was extracted by  $\text{Et}_2\text{O}$  and

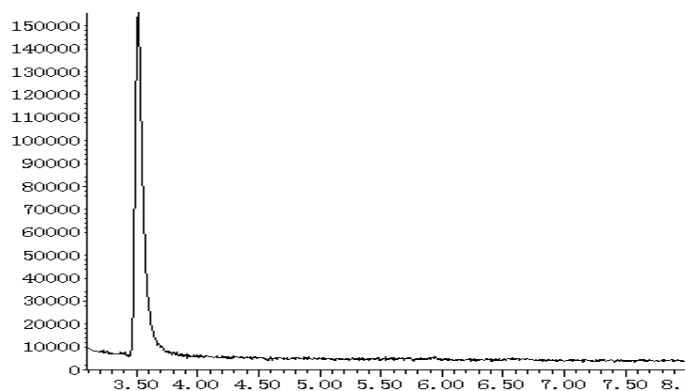
then examined by GC-MS. The formed products both share the same retention time with that of commercially available 2-pentanone. The parent ion peak ( $M^+$ ) of the product obtained in  $H_2O$  is 86.1, which conform with the exact mass of  $CH_3C(O)CH_2CH_2CH_3$ .  $M^+$  of the product obtained in  $D_2O$  is 87.1 associated with  $CH_2(D)C(O)CH_2CH_2CH_3$ , one deuterium substituent pentanone.



Commercial 2-pentanone

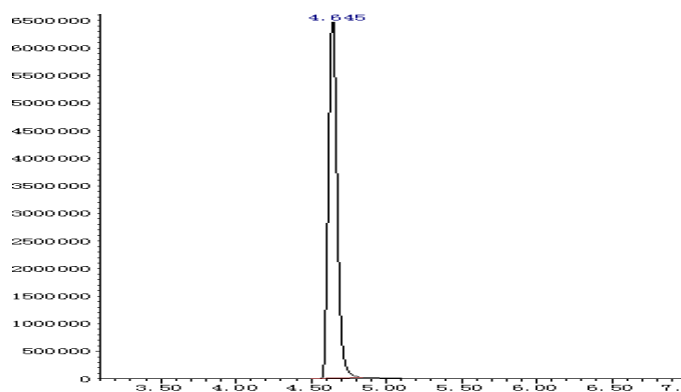


2-pentanone obtained in  $H_2O$

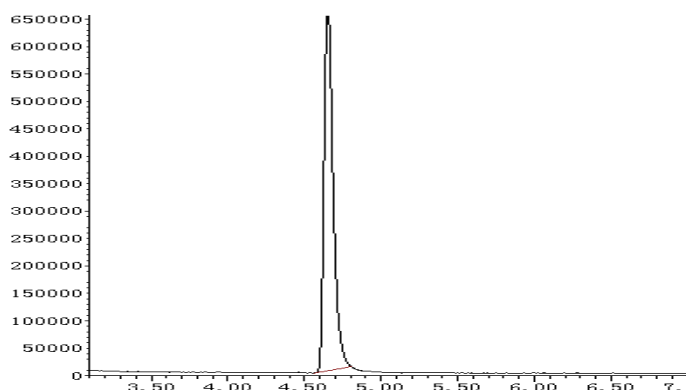


2-pentanone obtained in  $D_2O$

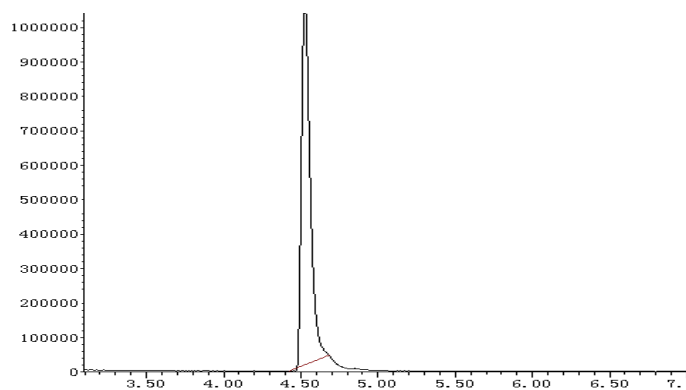
**Hexanone:** 2-hexanone obtained both in D<sub>2</sub>O and in H<sub>2</sub>O share the same retention time with that of commercially available 2-hexanone. M<sup>+</sup> of the product obtained in H<sub>2</sub>O is 100.1, which conform with the exact mass of CH<sub>3</sub>C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>. M<sup>+</sup> of the product obtained in D<sub>2</sub>O is 105.1 associated with CD<sub>3</sub>C(O)CD<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>.



Commercial 2-hexanone

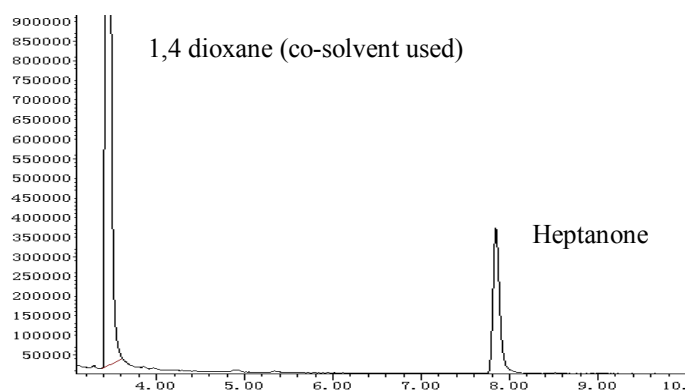


2-hexanone obtained in H<sub>2</sub>O



2-hexanone obtained in D<sub>2</sub>O

**Heptanone:**  $M^{\ddagger}$  of the product 2-heptanone obtained in  $D_2O$  is 115.1 associated with  $CH_2(D)C(O)CH_2CH_2CH_2CH_2CH_3$ .



#### References

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