

Synthesis of $\text{TMS}^{\text{PS}}\text{PS}_3\text{H}_3$ ligand and monoanion $(\text{TMS}^{\text{PS}}\text{PS}_3)\text{Mn}^{\text{III}}\text{-alkyl/alkynyl complexes}$

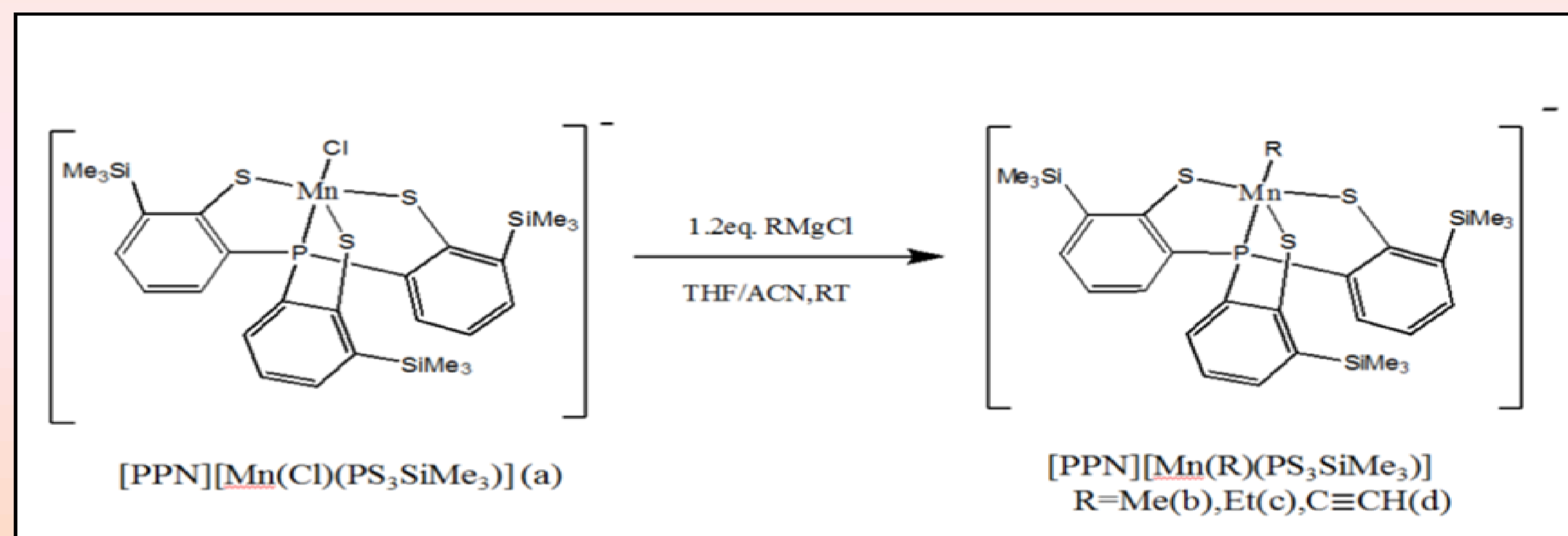
$\text{TMS}^{\text{PS}}\text{PS}_3$ 配位基合成和含磷、硫錳三價烷基/炔基化合物之反應性探討

摘要:

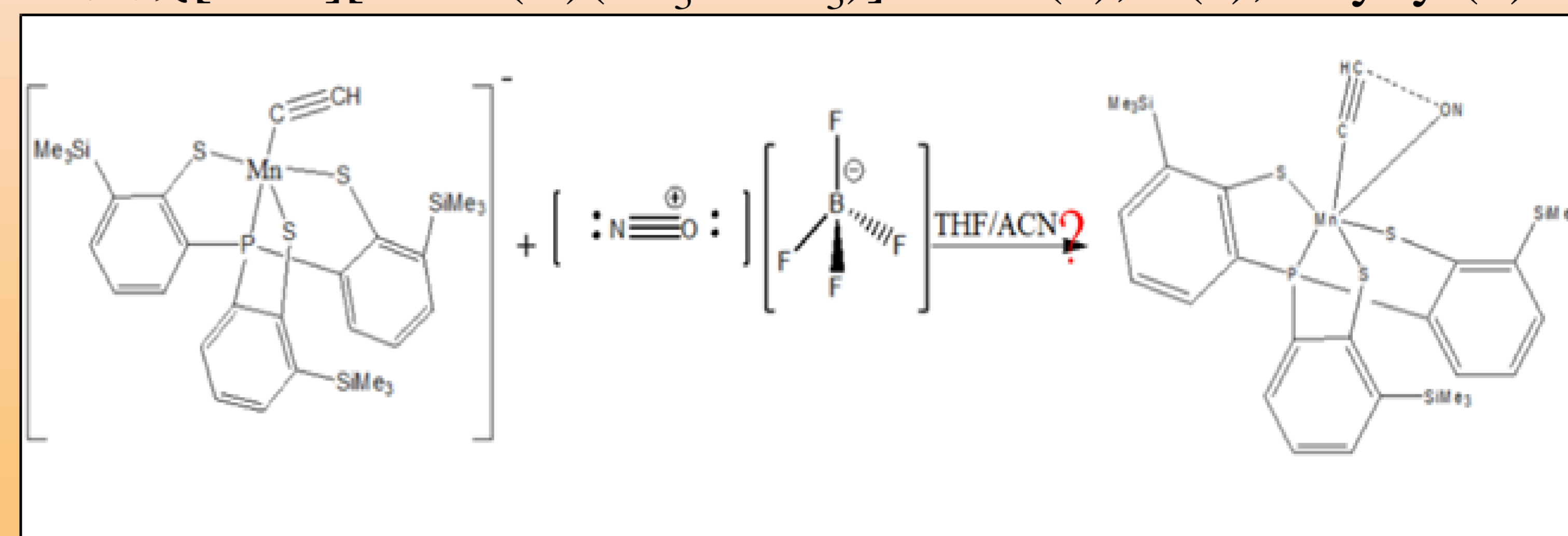
利用 $[\text{PPN}][\text{Mn}(\text{Cl})(\text{PS}_3\text{SiMe}_3)]$ (a; $\text{PS}_3\text{SiMe}_3 = \text{P}(\text{C}_6\text{H}_3\text{-3-SiMe}_3\text{-2-S})_3$) 作為起始物和Grignard試劑(RMgCl , $\text{R} = \text{Me, Et or Ethynyl}$) 進行反應，成功合成出一系列五配位烷基的錳金屬化合物 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{R})(\text{PS}_3\text{SiMe}_3)]$ ($\text{R} = \text{Me(b), Et(c) or Ethynyl(d)}$)。

比較化合物(a)和這些五配位烷基的錳金屬UV-Vis光譜，當Cl-被給予電子能力較強的配位基取代時，存在於化合物(a)中低能量躍遷(750nm)會往短波長移動。

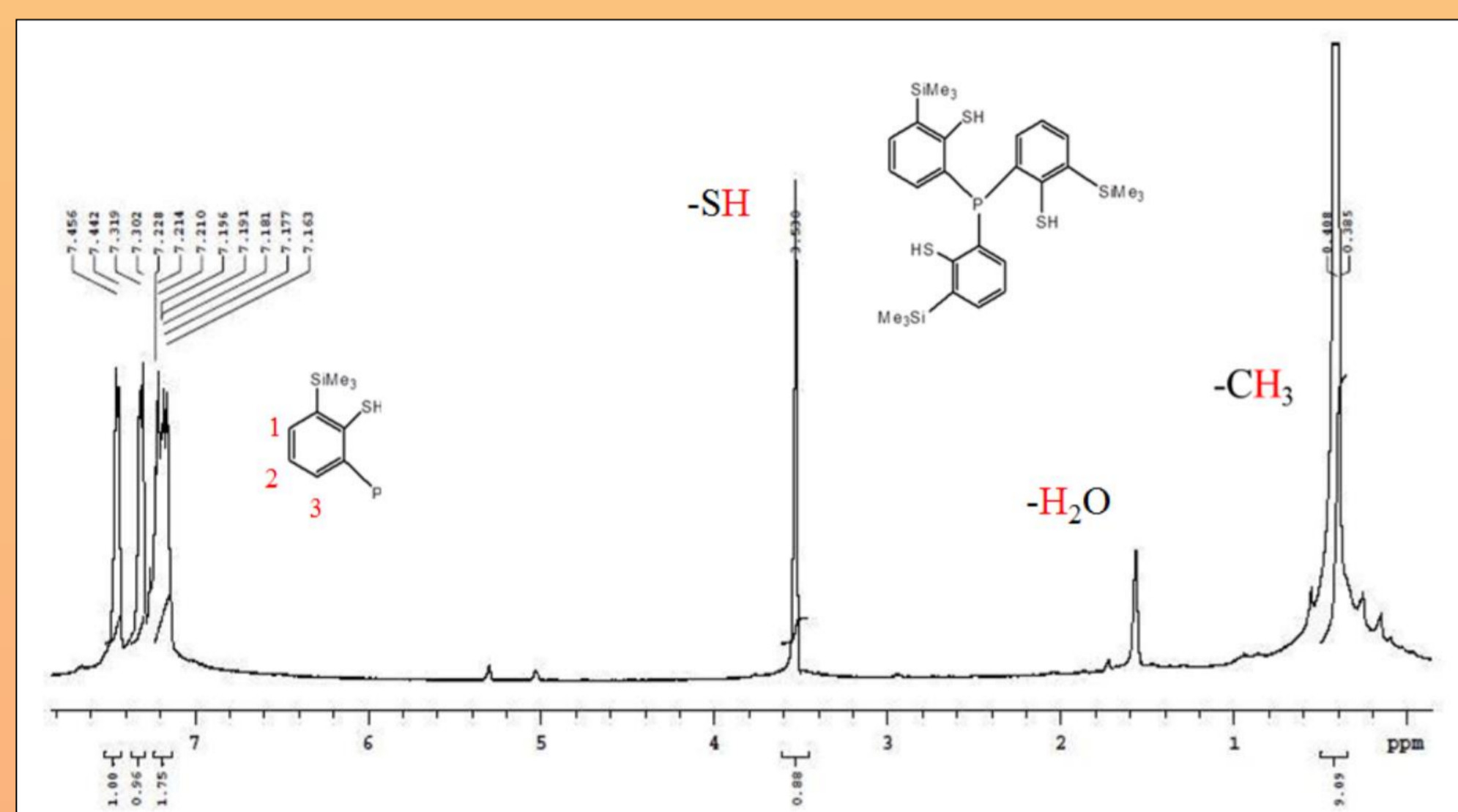
目前主要探討 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)]$ 的性質，其晶體生成後並不會受到空氣、水氣的影響，較有利做後續的驗證；而我們發現其化合物格外穩定，利用較具活性的分子和化合物做反應，而其反應性仍在進行中。



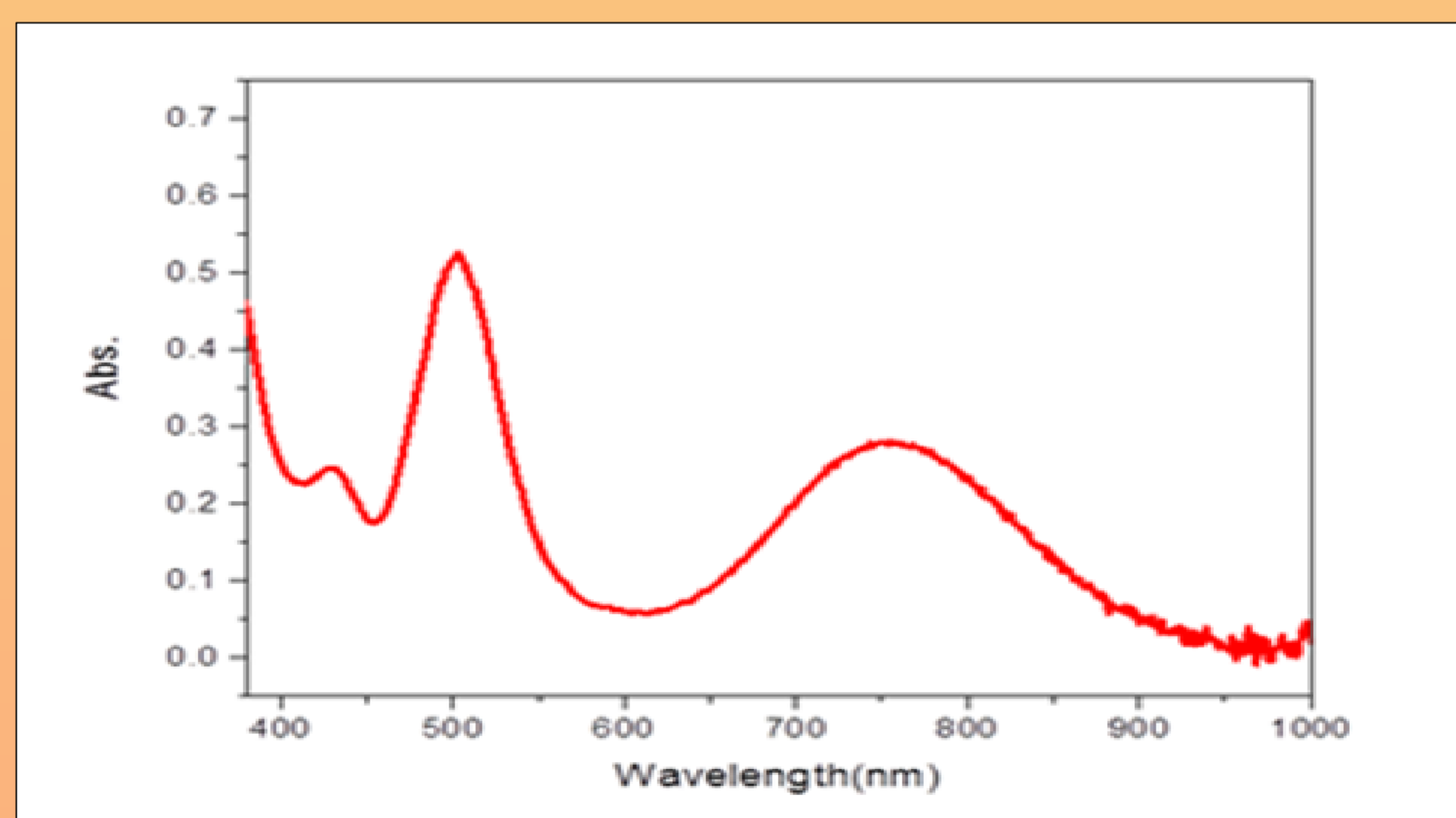
合成 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{R})(\text{PS}_3\text{SiMe}_3)]$ $\text{R} = \text{Me(b), Et(c), Ethynyl(d)}$



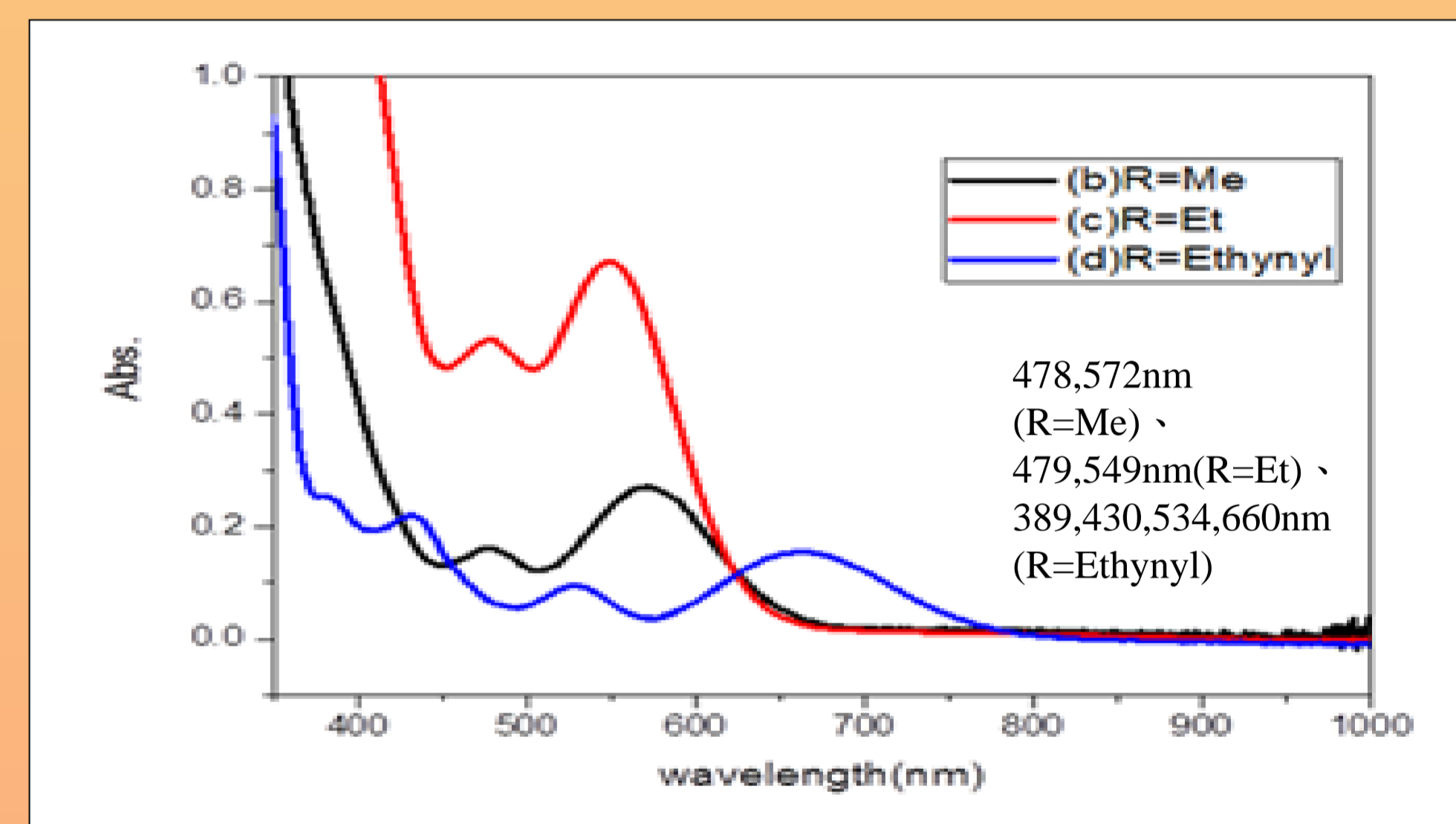
合成 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)] + \text{NOBF}_4$



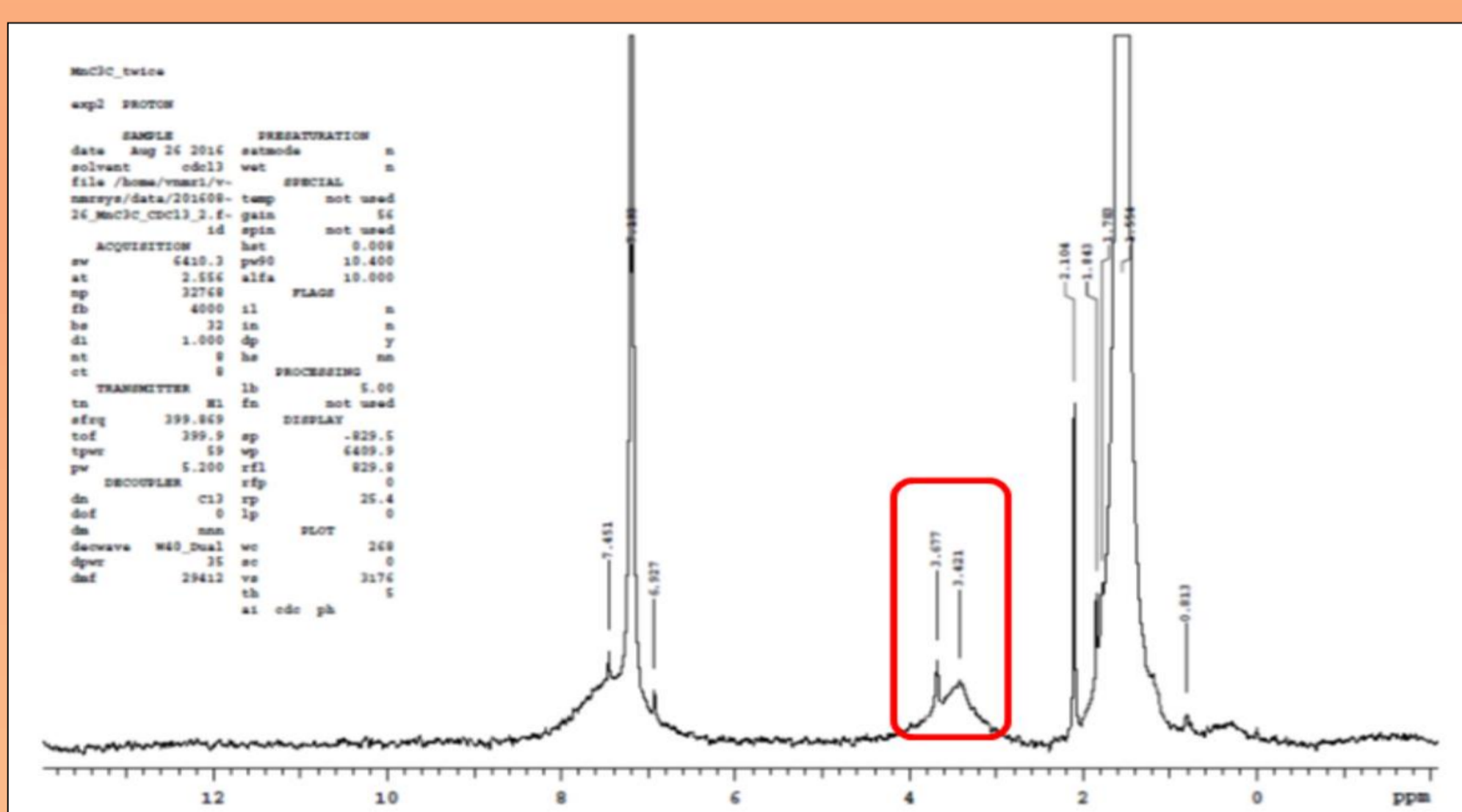
圖(1) $^1\text{H-NMR}$ 圖譜 $\text{P}(\text{C}_6\text{H}_3\text{-3-SiMe}_3\text{-2-SH})_3$



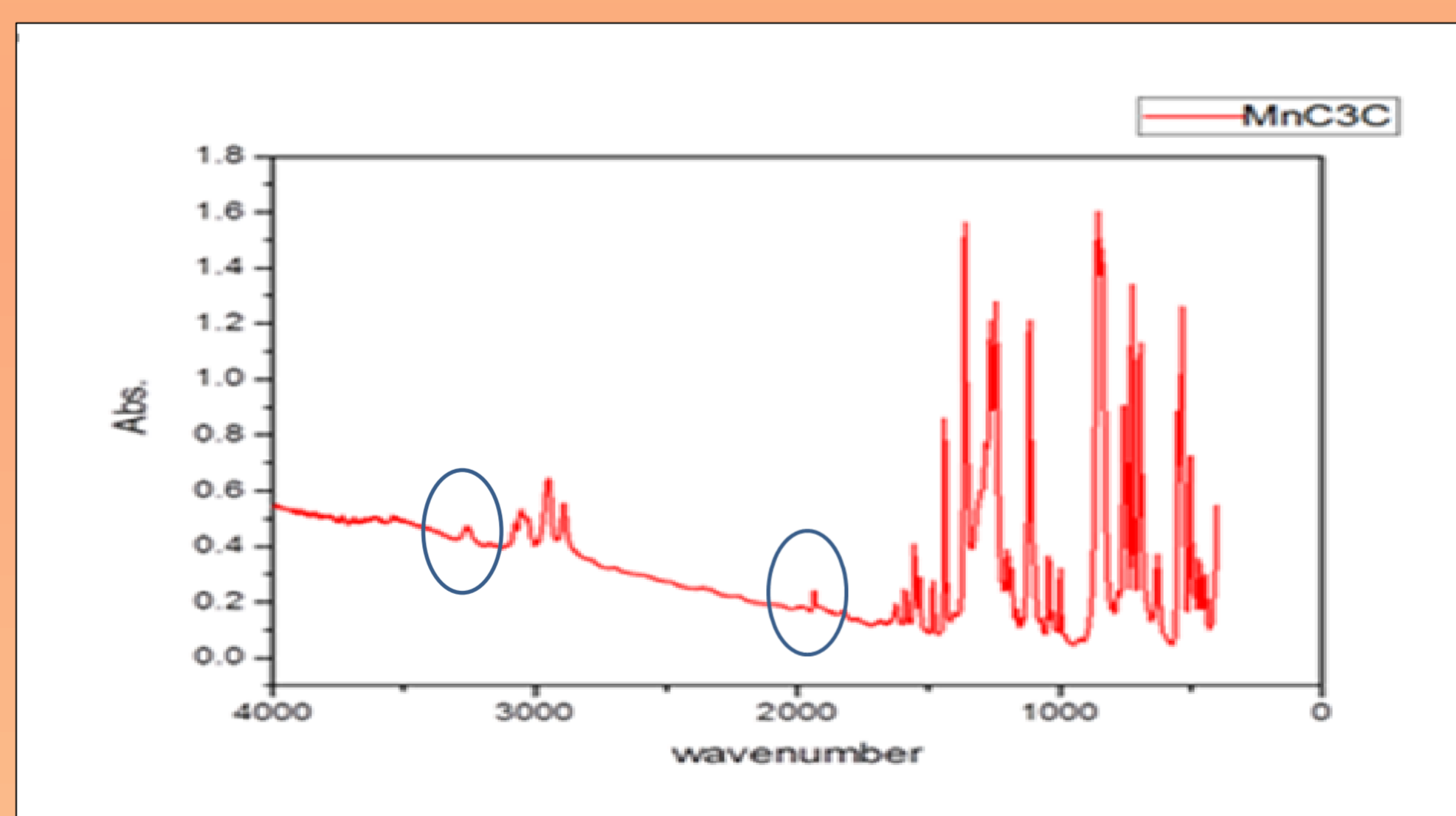
圖(2) UV-Visble $[\text{PPN}][\text{Mn}(\text{Cl})(\text{PS}_3\text{SiMe}_3)]$ in DCM $[\lambda_{\text{max}}, \text{nm}(\epsilon, \text{cm}^{-1}, \text{M}^{-1})]: 429(2005), 502(4206), 755(2267)$



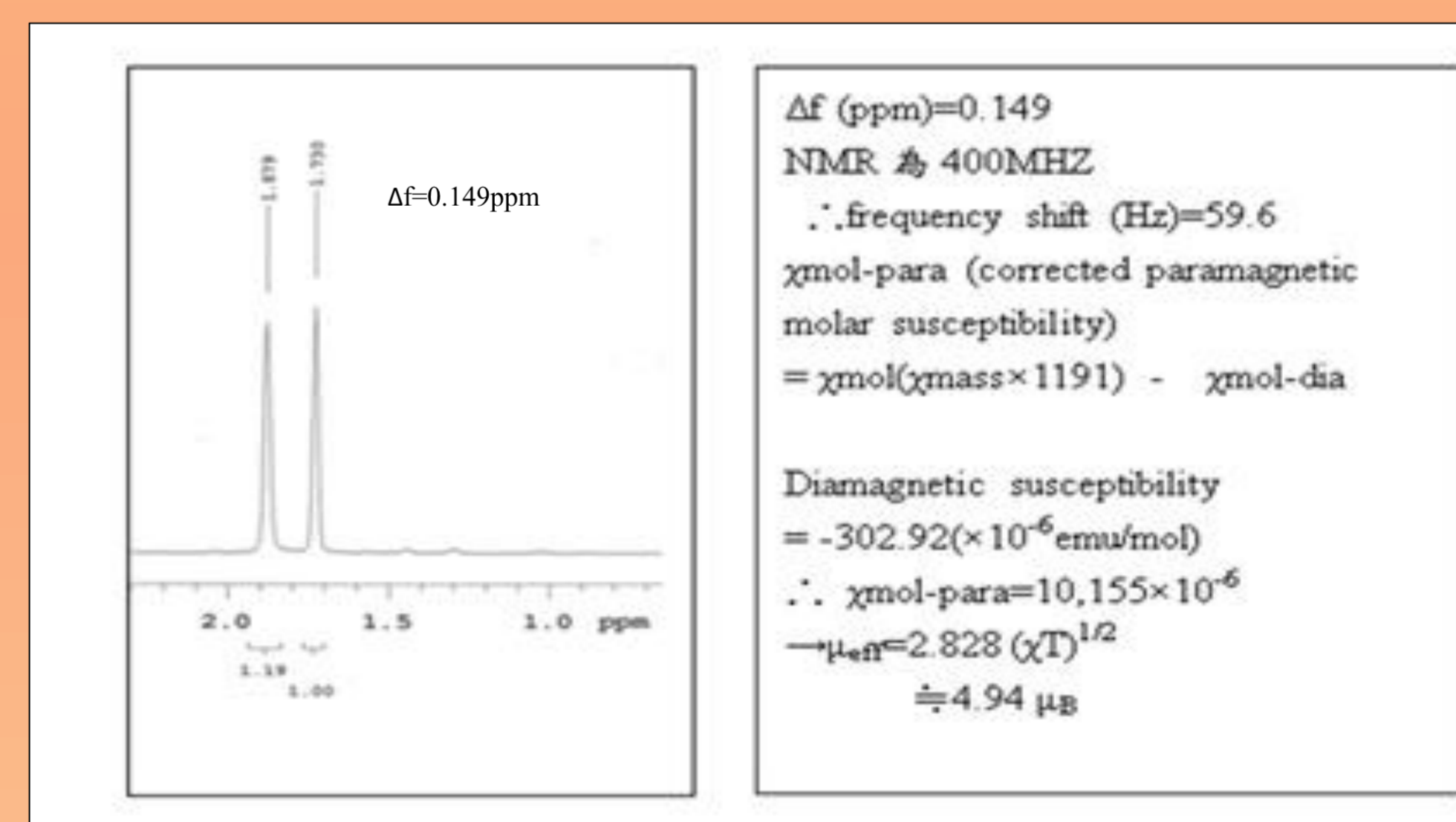
圖(3) UV-Visble $[\text{PPN}][\text{Mn}^{\text{III}}(\text{R})(\text{PS}_3\text{SiMe}_3)]$ $\text{R} = \text{Me(b), Et(c), Ethynyl(d)}$



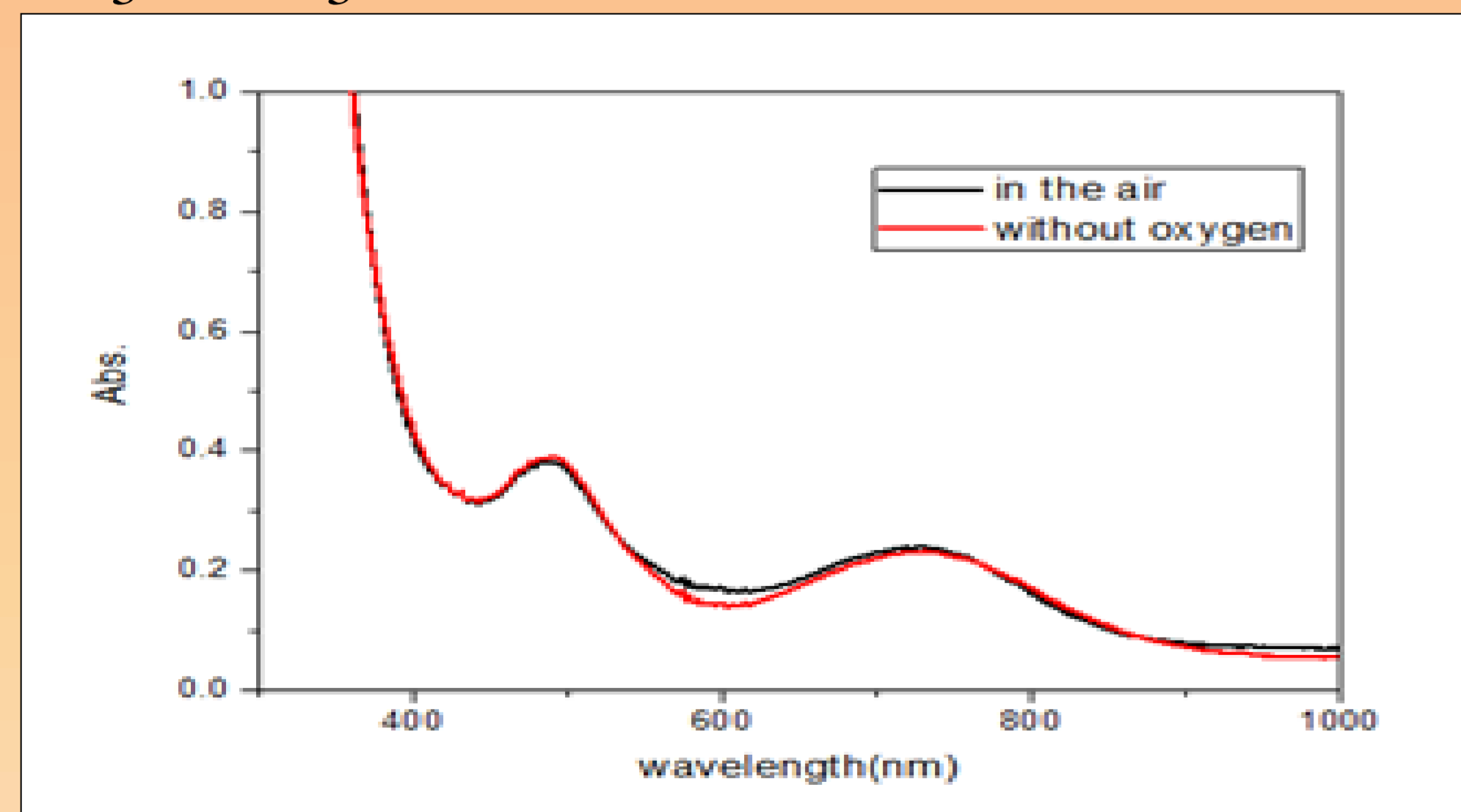
圖(4) $^1\text{H-NMR}$ 圖譜 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)]$



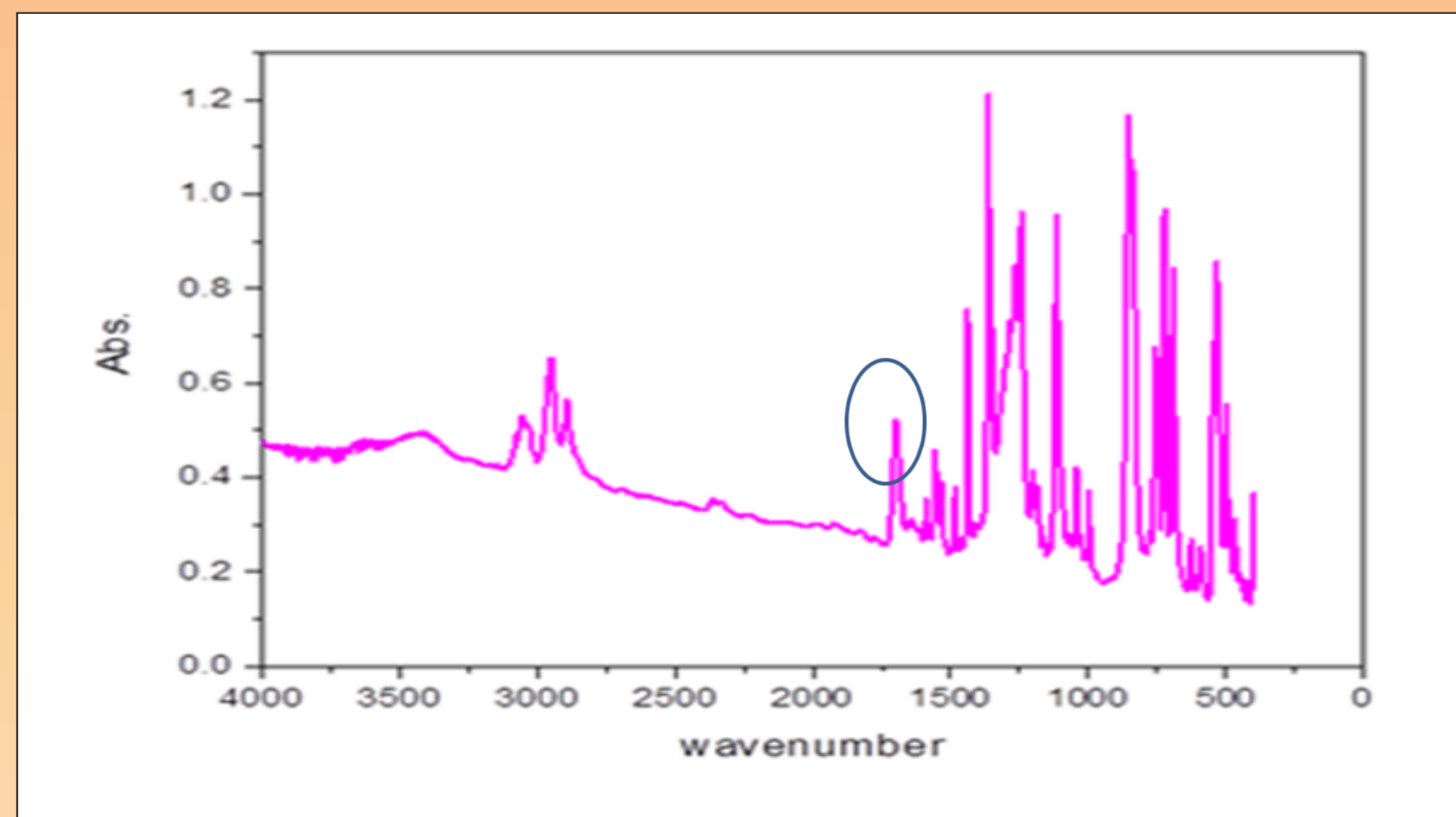
圖(5) 紅外線光譜圖 $[\text{PPN}][\text{Mn}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)]$



圖(6) 利用Evans Method之 $^1\text{H-NMR}$ 圖譜 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)]$



圖(7) UV-Visble光譜圖 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)] + \text{NOBF}_4$



圖(8) 紅外線光譜圖 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)] + \text{NOBF}_4$ in THF

結論: 藉由此研究，探討了配位基 $\text{P}(\text{C}_6\text{H}_3\text{-3-SiMe}_3\text{-2-SH})_3$ 之合成方式，並以核磁共振儀驗證之。以 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{Cl})(\text{PS}_3\text{SiMe}_3)]$ 作為起始物加入格林試劑(R-MgCl , $\text{R} = \text{Me, Et, Ethynyl}$)合成出一系列五配位的三價錳基金屬化合物。然而，我們集中於研究 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)]$ ，利用紫外光可見光光譜、傅立葉轉換紅外線光譜儀，以及核磁共振儀探討這些化合物的基本性質。接著嘗試 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)]$ 之反應性，加入 NOBF_4 後發現其化合物從深綠色轉變為紅棕色；日後會繼續探討 $[\text{PPN}][\text{Mn}^{\text{III}}(\text{C}\equiv\text{CH})(\text{PS}_3\text{SiMe}_3)]$ 的反應機制。

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- [1] Block E.; Ofori-Okai G.; Zubieta J. J. Am. Chem. Soc. 1989, 111, 2327.
- [2] Bain, G. A.; Berry, J. F. J. Chem. Educ. 2008, 85, 532.
- [3] Chang, H.-C.; Lo, F.-C.; Liu, W.-C.; Lin, T.-H.; Liaw, W.-F.; Kuo, T.-S.; Lee, W.-L. Inorg. Chem., 2012, 54, 5527.