

Supporting Information

Circularly polarized luminescent organogel based on Pt(II) complex possessing phenylisoxazoles

Toshiaki Ikeda, Kyohei Hirano and Takeharu Haino*

Department of Chemistry, Graduate School of Science, Hiroshima University

Higashi-hiroshima 739-8526 (Japan)

e-mail: haino@hiroshima-u.ac.jp; Fax: +81-82-424-0724; Tel: +81-82-424-7427.

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Analysis of isodesmic self-assembly by ¹H NMR experiments: Hyperbolic curves were obtained by plotting of compound concentrations vs ¹H NMR chemical shifts (δ) of the aromatic protons. The curve-fitting analysis of the plots was carried out on the basis of an isodesmic association model, which is a type of unlimited self-association where the addition of each successive monomer to polymer involves an equal association constant ($K_2 = K_3 = \dots = K_n = K_i$).¹ The fitting functions are given by equation 1 for NMR experiments. δ denotes apparent chemical shifts obtained from spectra; δ_m and δ_a are chemical shifts for a monomer and self-assembled species, respectively. K_i is the association constant; and c is the total concentration of a compound. The complexation-induced shift $\Delta\delta$ displays the difference between δ_m and δ_a .

$$\delta(c) = \delta_m + (\delta_a - \delta_m) \left(1 + \frac{1 - \sqrt{4K_i c + 1}}{2K_i c} \right) \quad (1)$$

Analysis of cooperative self-assembly by temperature-dependent UV-vis absorption spectra:

Degree of aggregation (α_{agg}) were calculated from the following equation 2:

$$\alpha_{agg}(T) = \frac{\varepsilon(T) - \varepsilon_m}{\varepsilon_a - \varepsilon_m} \quad (2)$$

where $\varepsilon(T)$ is the measured extinction coefficient at the absolute temperature T ; ε_m and ε_a are the extinction coefficients of the monomer and fully aggregated state, respectively. The latter two values could be determined from the data or were determined by extrapolation of the measured extinction coefficient to their asymptotic value at high and low temperature, respectively. Non-sigmoidal melting curves were obtained by plotting of $\alpha_{agg}(T)$ vs T . The curve-fitting analysis of the plots was carried out on the basis of van der Schoot mathematical model.²

In the elongation regime, $\alpha_{agg}(T)$ is given by the following equation 3:

$$\alpha_{agg}(T) = \alpha_{sat} \left(1 - \exp \left[\frac{-\Delta H_e}{RT_e^2} (T - T_e) \right] \right) \quad (3)$$

where ΔH_e is the molecular enthalpy release due to noncovalent interactions during elongation, T_e is the elongation temperature and R is the gas constant. α_{sat} is introduced as a parameter to ensure that $\alpha_{agg}(T)/\alpha_{sat}$ does not exceed unity. At temperatures above the elongation temperature T_e (i.e., the nucleation regime) the fraction of aggregated molecules is described by equation 4:

$$\alpha_{agg}(T) = K_a^{\frac{1}{3}} \exp \left[\left(\frac{2}{3} K_a^{\frac{1}{3}} - 1 \right) \frac{h_e}{RT_e^2} (T - T_e) \right] \quad (4)$$

where K_a is the dimensionless equilibrium constant of the activation step at T_e . The average length of the stack, $\langle N_n(T_e) \rangle$, averaged over the nucleated species, at the elongation temperature is given by equation 5:

$$\langle N_n(T_e) \rangle = \frac{1}{K_a^{\frac{1}{3}}} \quad (5)$$

Hence, a higher degree of cooperativity is expressed in a smaller K_a value and will lead to a larger nucleus before elongation sets in. In the elongation regime the number-averaged degree of polymerization, averaged over all active species, $\langle N_n \rangle$, is given by equation 6:

$$\langle N_n \rangle = \frac{1}{K_a^{\frac{1}{2}}} \frac{\alpha_n}{\alpha_{sat} - \alpha_n} \quad (6)$$

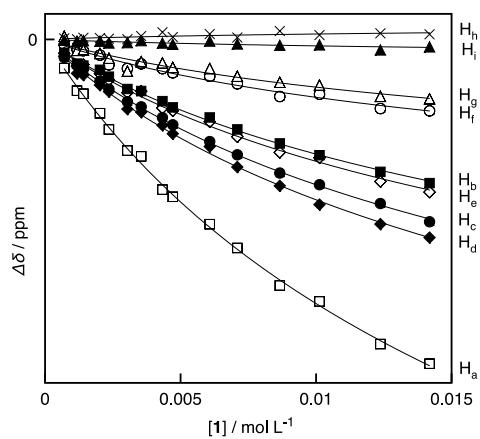


Figure S1. Non-linear curve fitting of the self-assembly of **1** using ^1H NMR in chloroform-*d* at 25 °C. The lines display fitting curves based on isodesmic model.

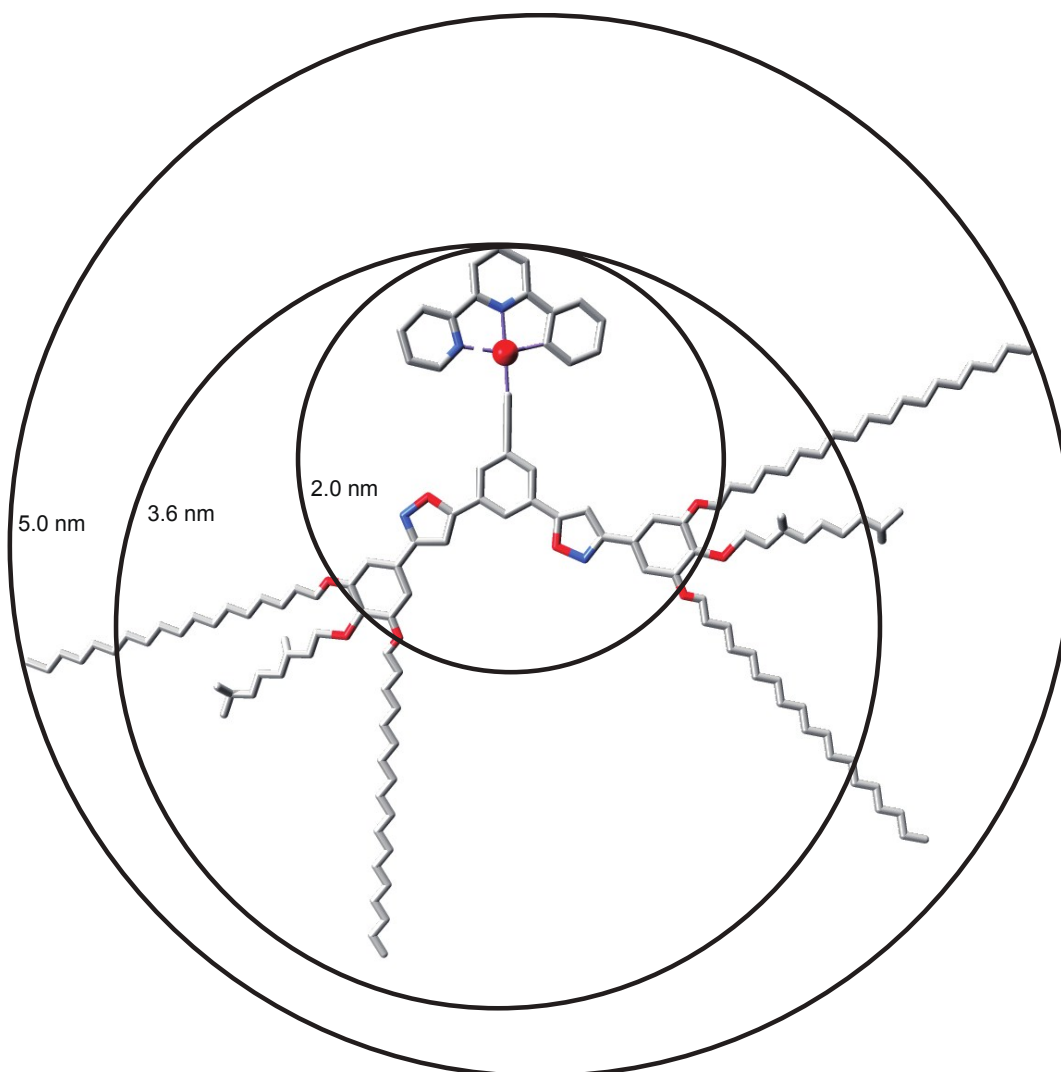


Figure S2. Molecular model of compound **1**. The length displays the diameter of the circle.

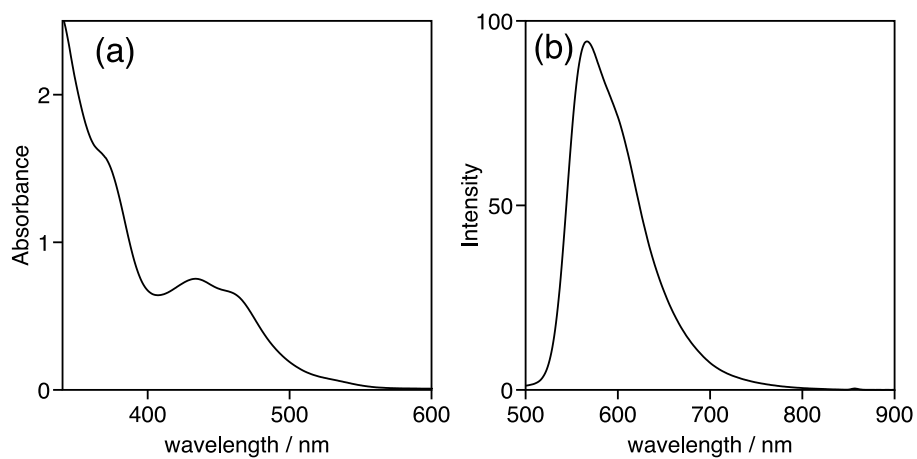


Figure S3. (a) UV-vis absorption and (b) emission spectra of **1** in chloroform at 25 °C. $[1] = 1.7 \times 10^{-4} \text{ mol L}^{-1}$.

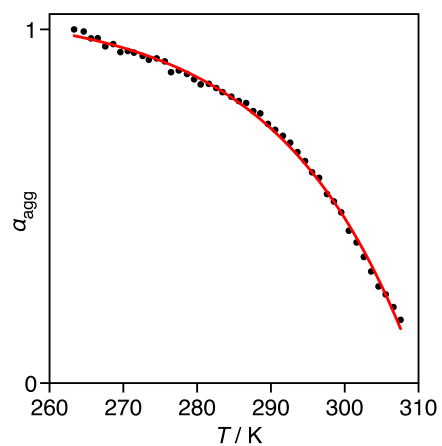


Figure S4. Plot of the degree of aggregation (α_{agg}) at 430 nm of **1** in MCH vs temperature. $[1] = 1.5 \times 10^{-4} \text{ mol L}^{-1}$. A Curve shows the fitting curve based on van der Schoot's model.

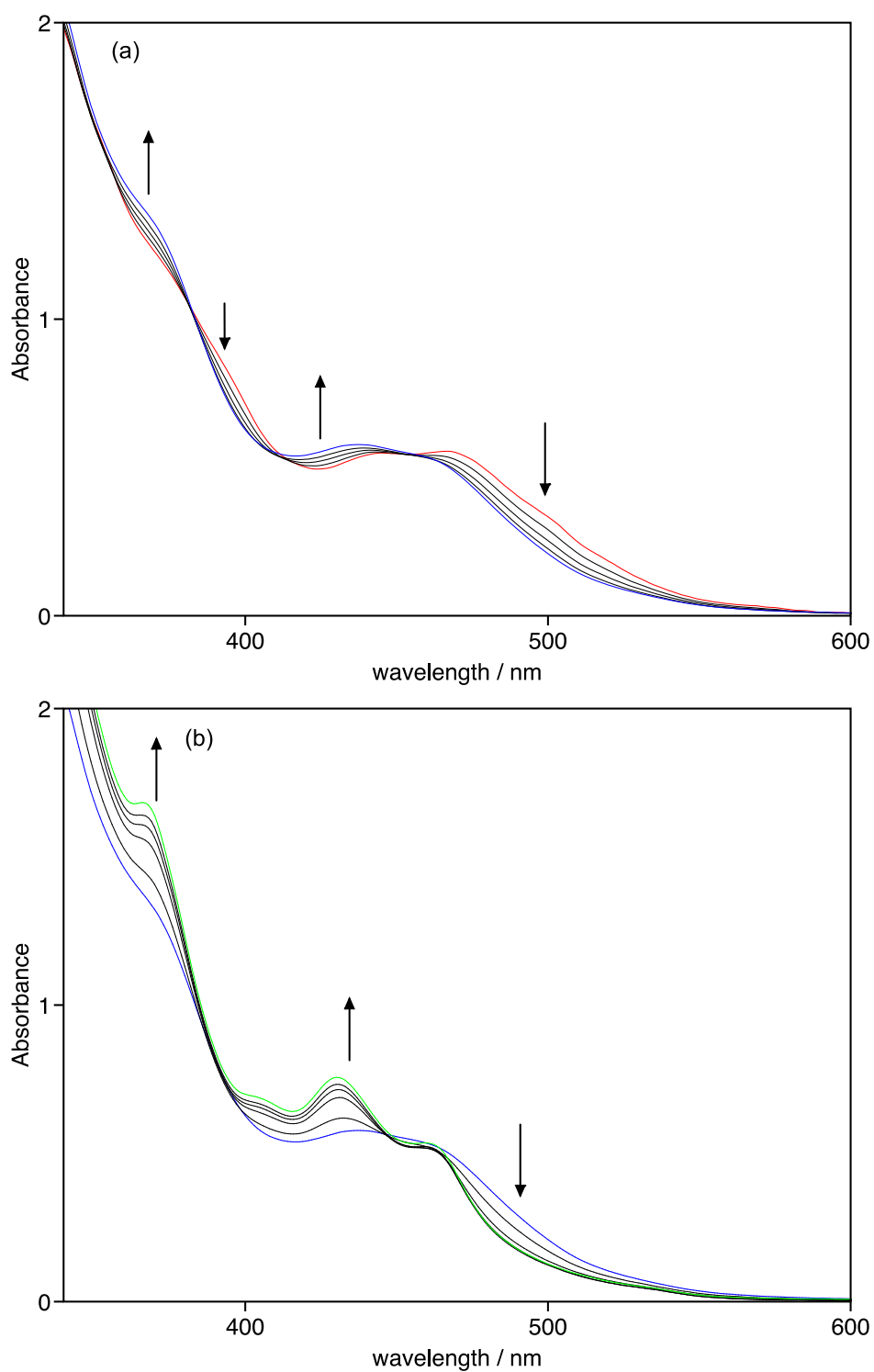
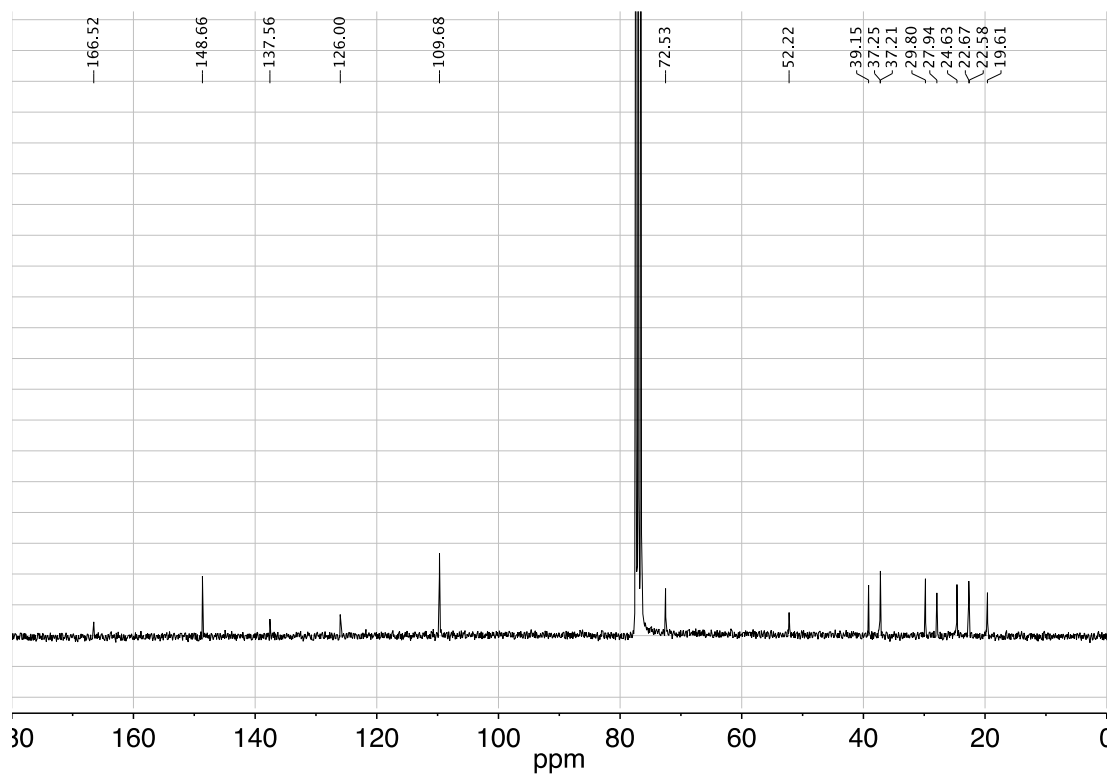
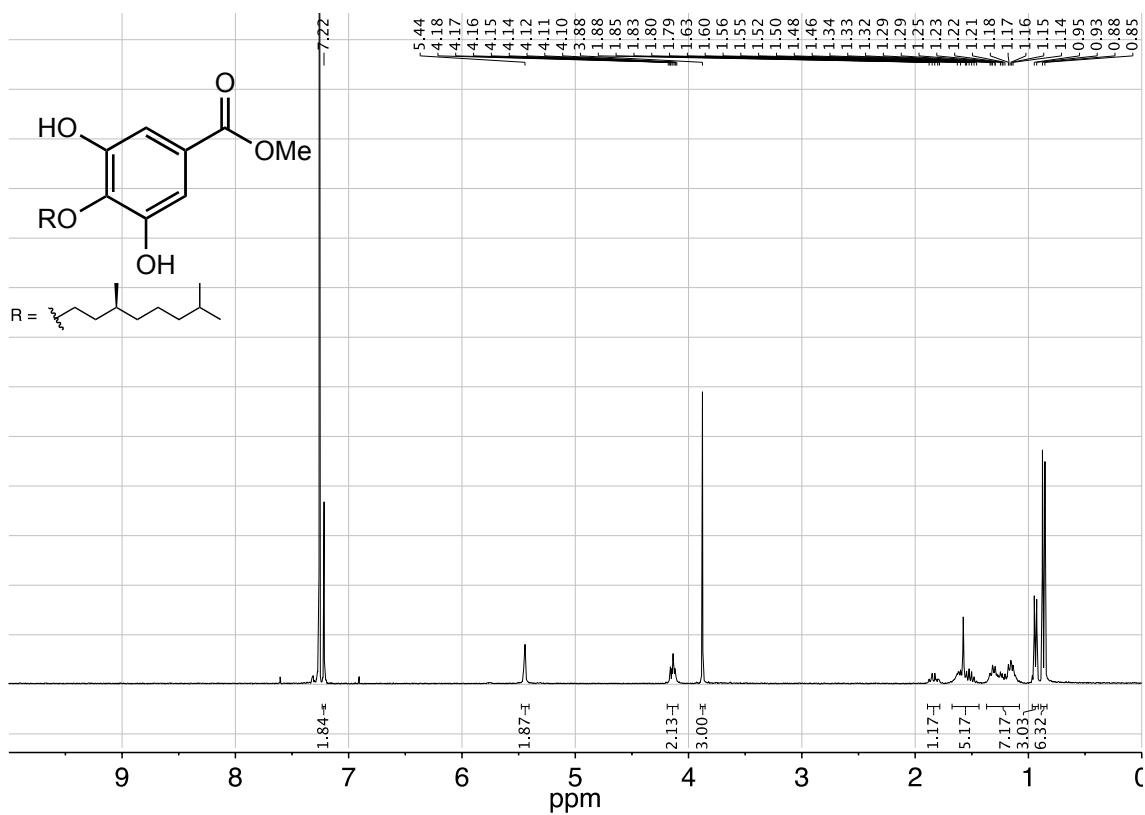


Figure S5. Temperature-dependent UV-vis absorption spectra of **1** in MCH. The spectra were recorded every 10 °C. The arrows indicate the change in the spectra as the temperature decrease from (a) 80 to 40 and (b) 40 to -10 °C. Red, blue, and green lines display the spectra at 80, 40, and -10 °C, respectively. $[1] = 1.5 \times 10^{-4} \text{ mol L}^{-1}$.

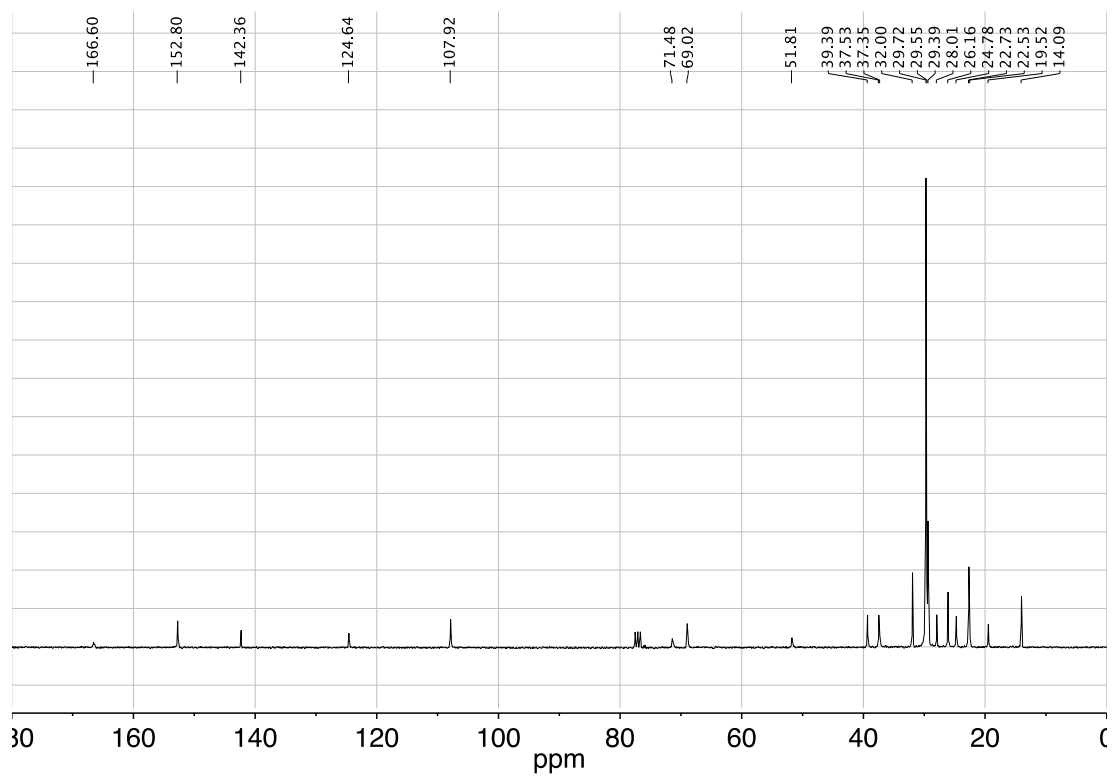
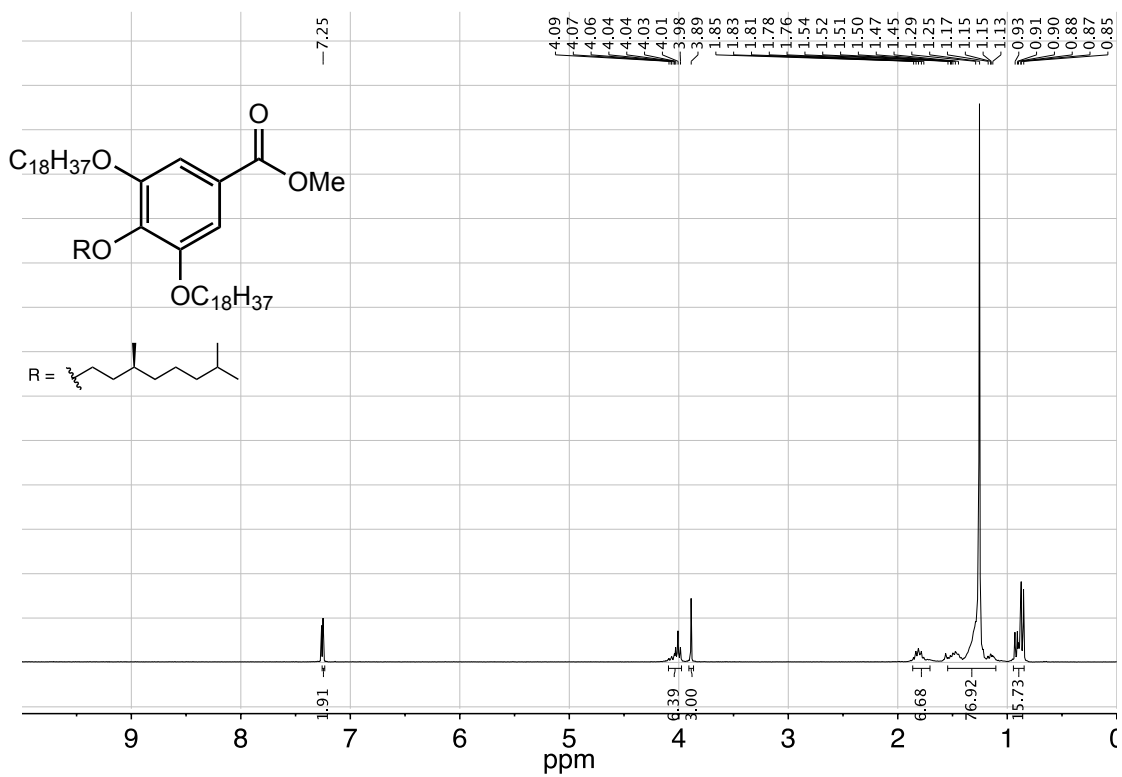
Reference

- 1) *Supramolecular Polymers, 2nd ed.*; Ciferri, A., Ed.; CRC Press - Taylor & Francis: Boca Raton, FL, **2005**.
- 2) M. M. J. Smulders, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.*, **2008**, *130*, 606.

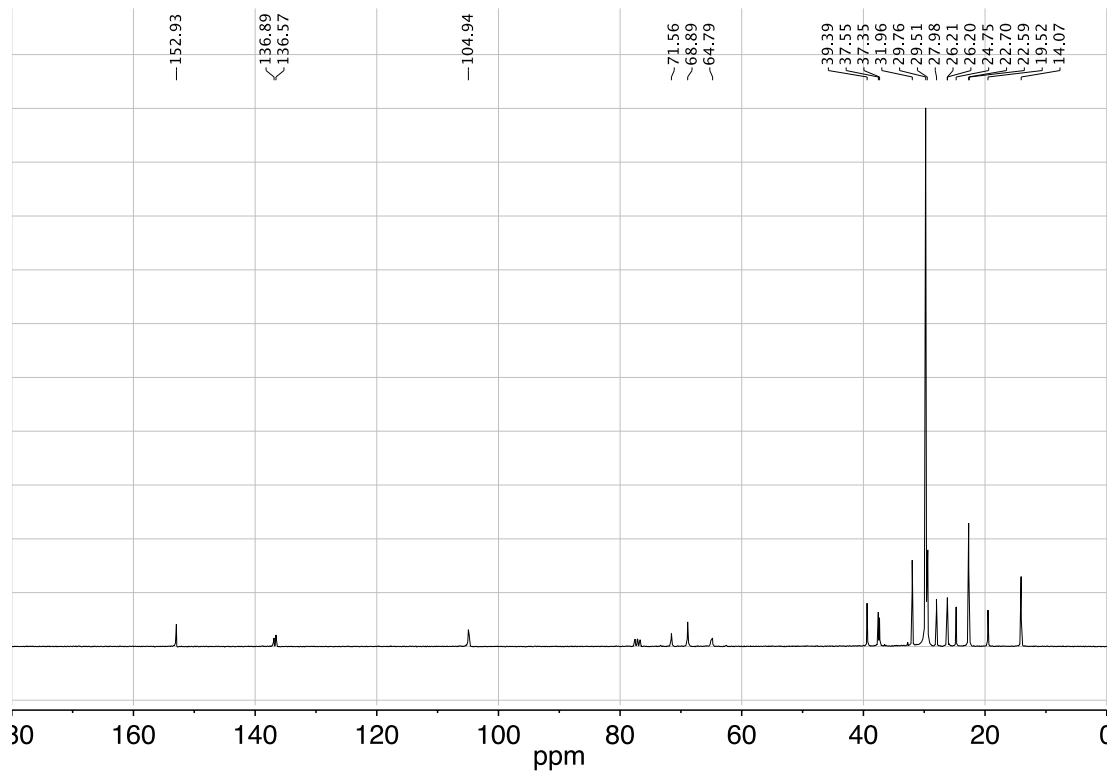
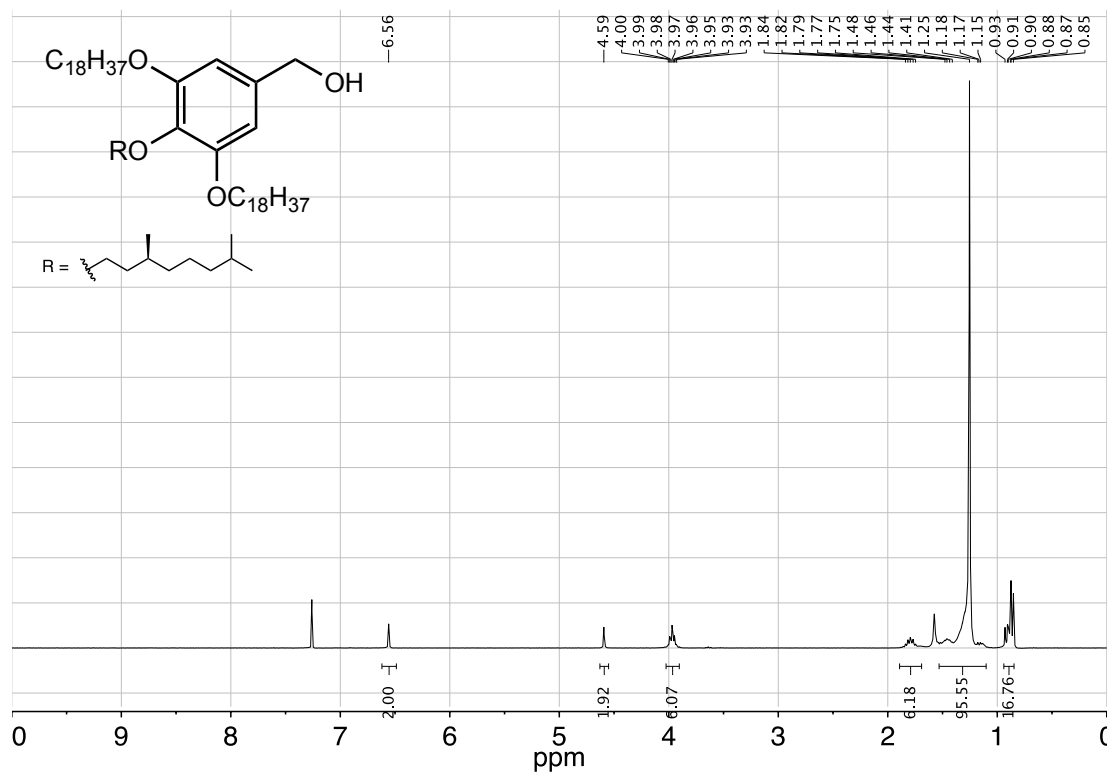
Methyl 3,5-dihydroxy-4-((S)-3,7-dimethyloctyloxy)benzoate (2)



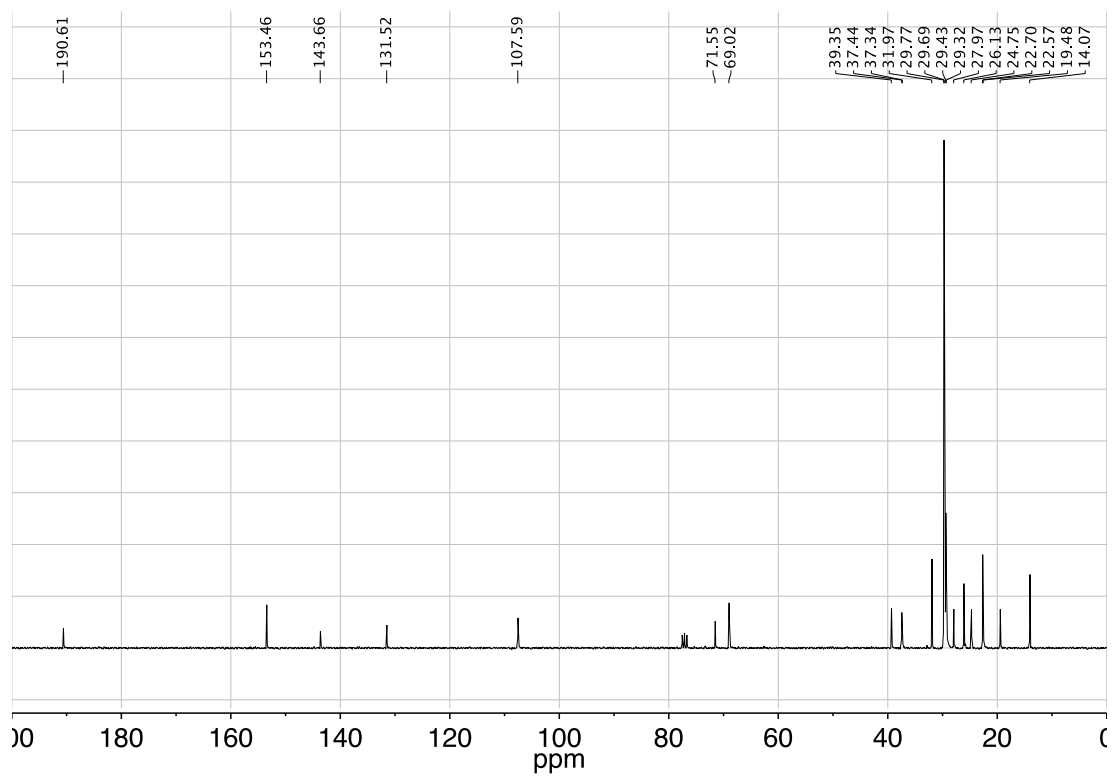
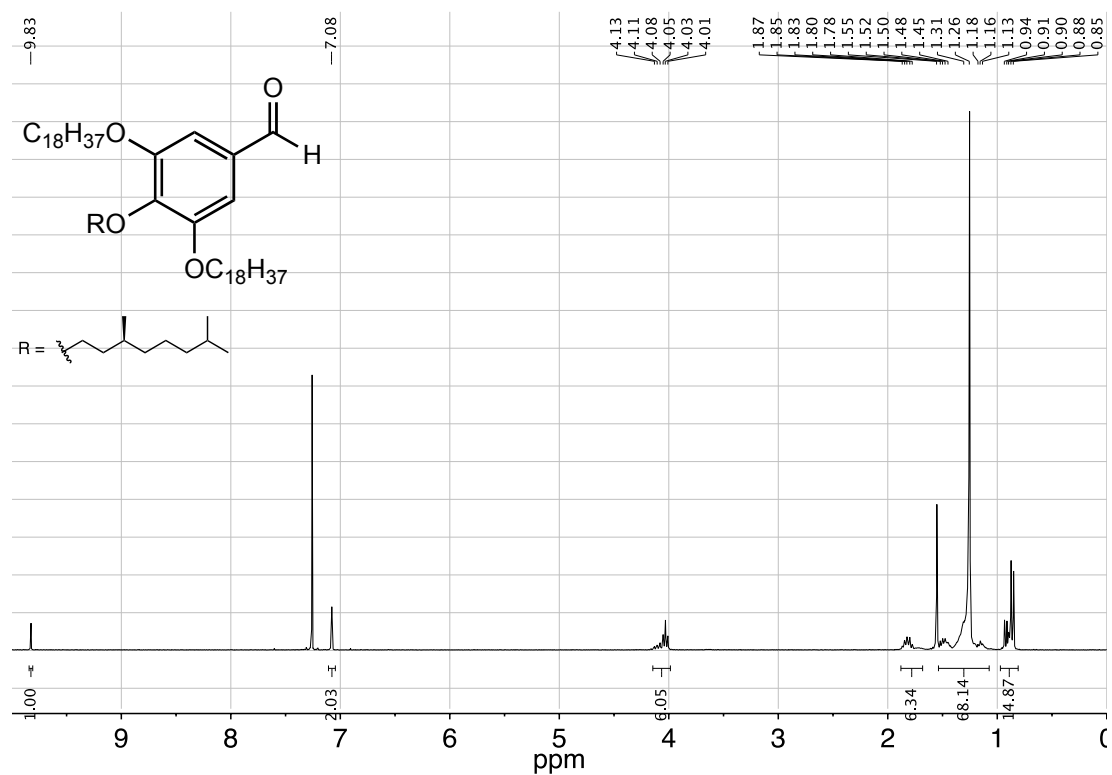
Methyl 4-((S)-3,7-dimethyloctyloxy)-3,5-bis(octadecyloxy)benzoate (3)



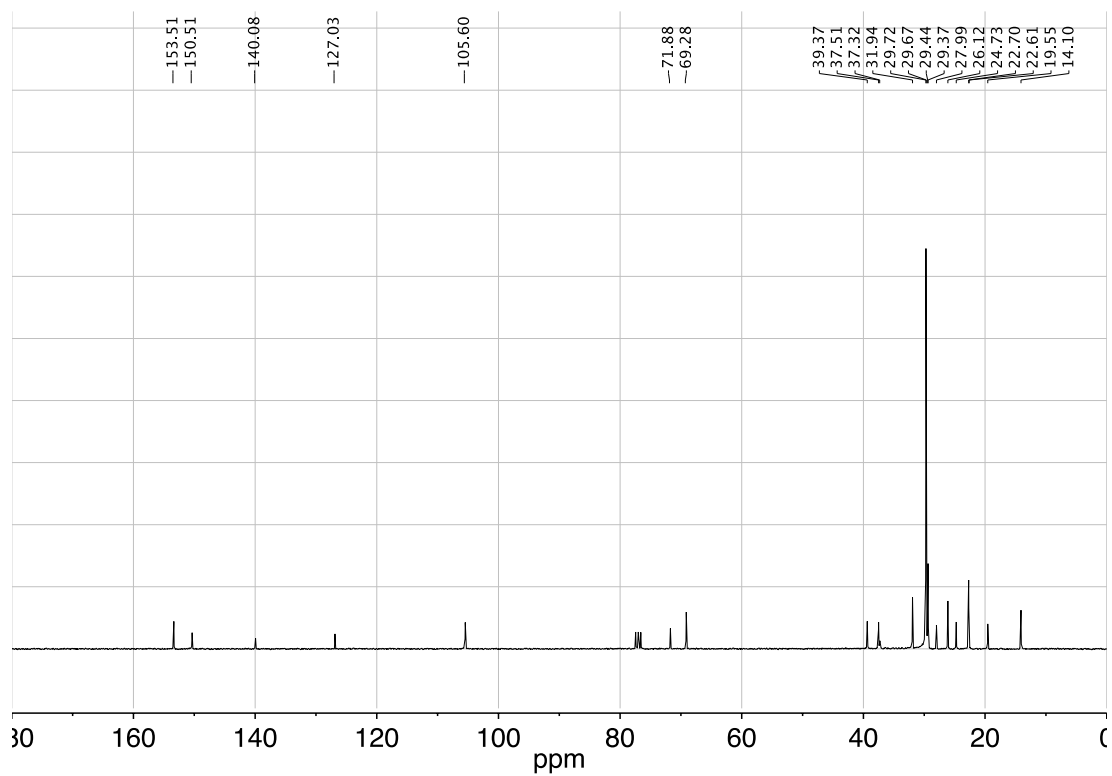
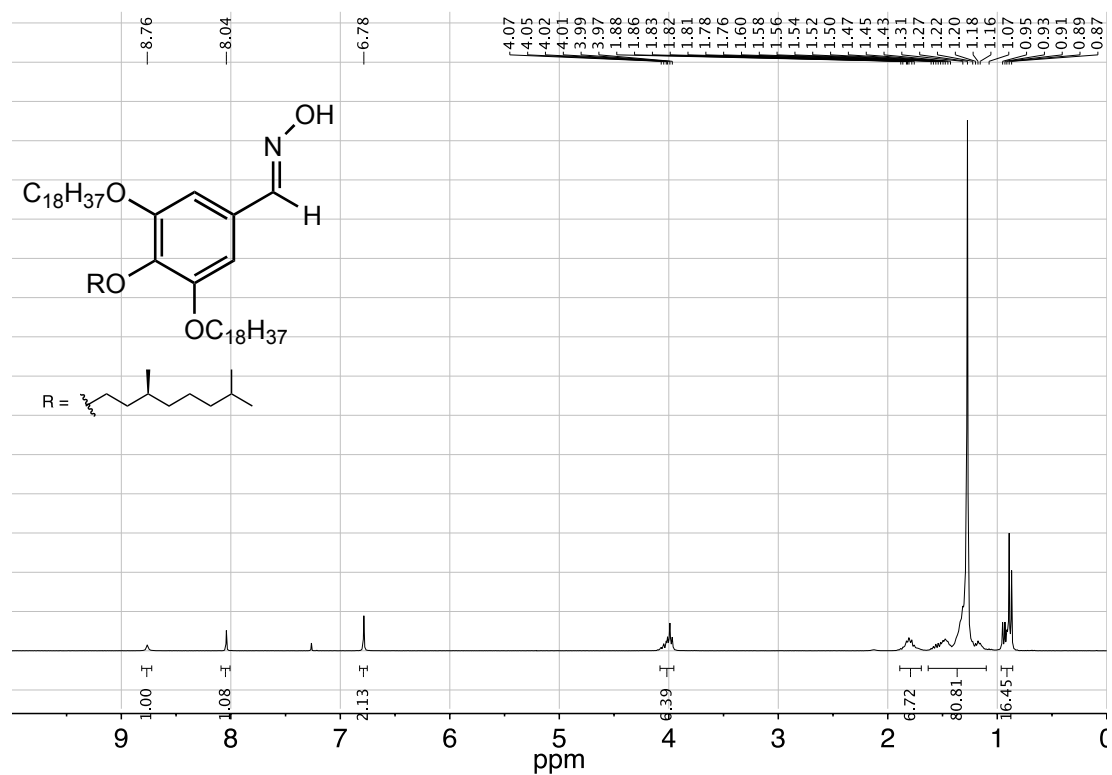
(4-((S)-3,7-Dimethyloctyloxy)-3,5-bis(octadecyloxy)phenyl)methanol (4)



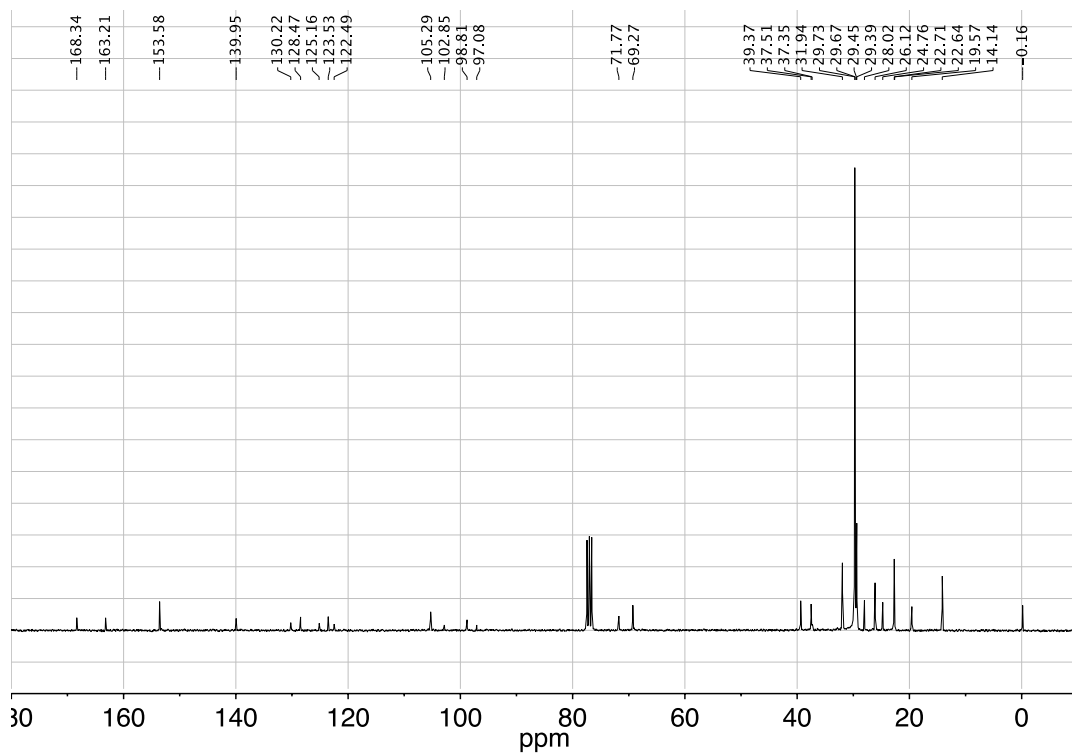
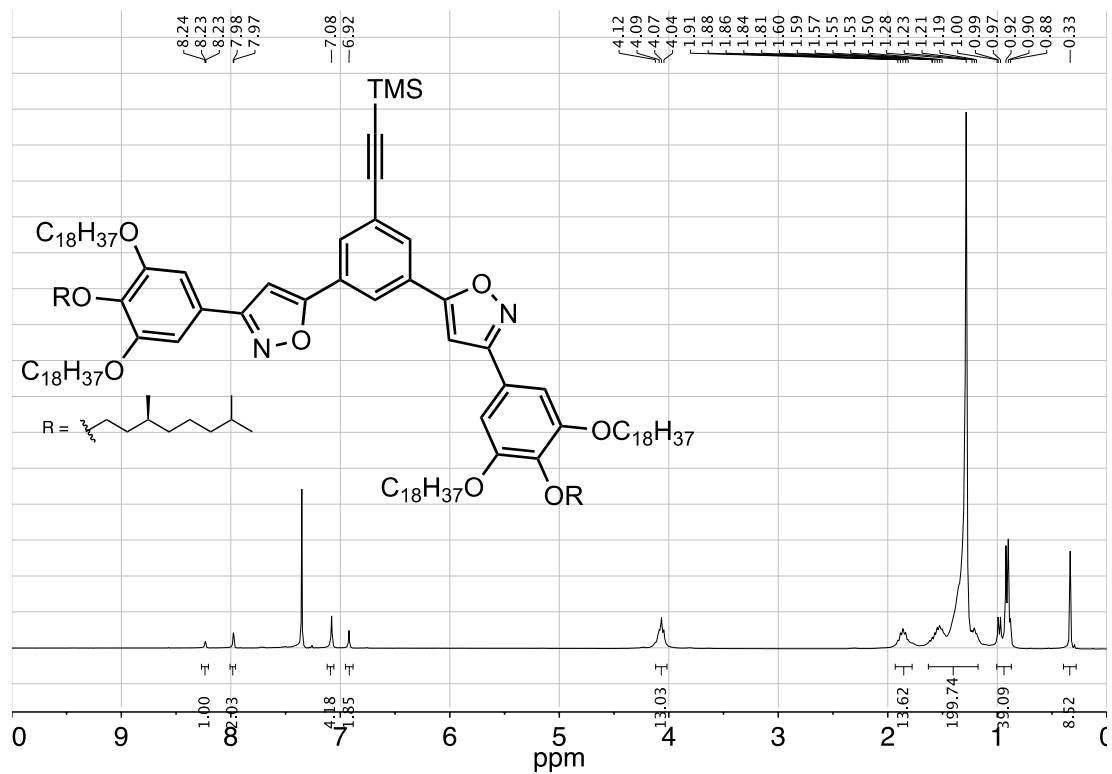
4-((S)-3,7-Dimethyloctyloxy)-3,5-bis(octadecyloxy)benzaldehyde (5)



4-((S)-3,7-Dimethyloctyloxy)-3,5-bis(octadecyloxy)benzaloxime (6)

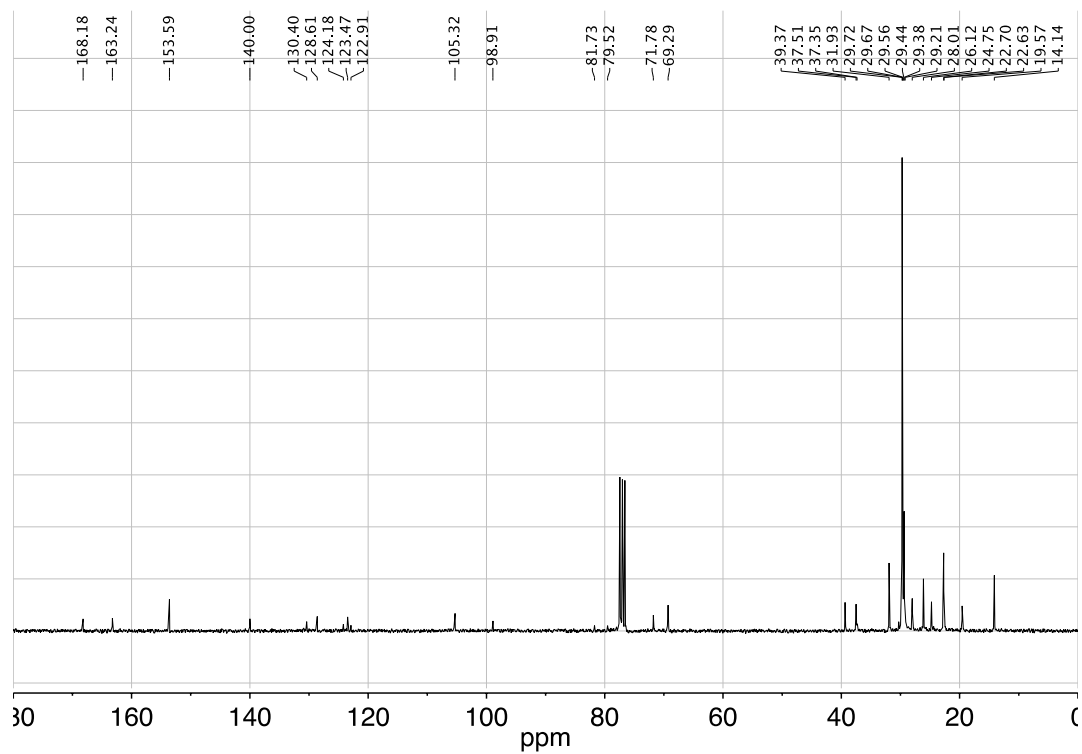
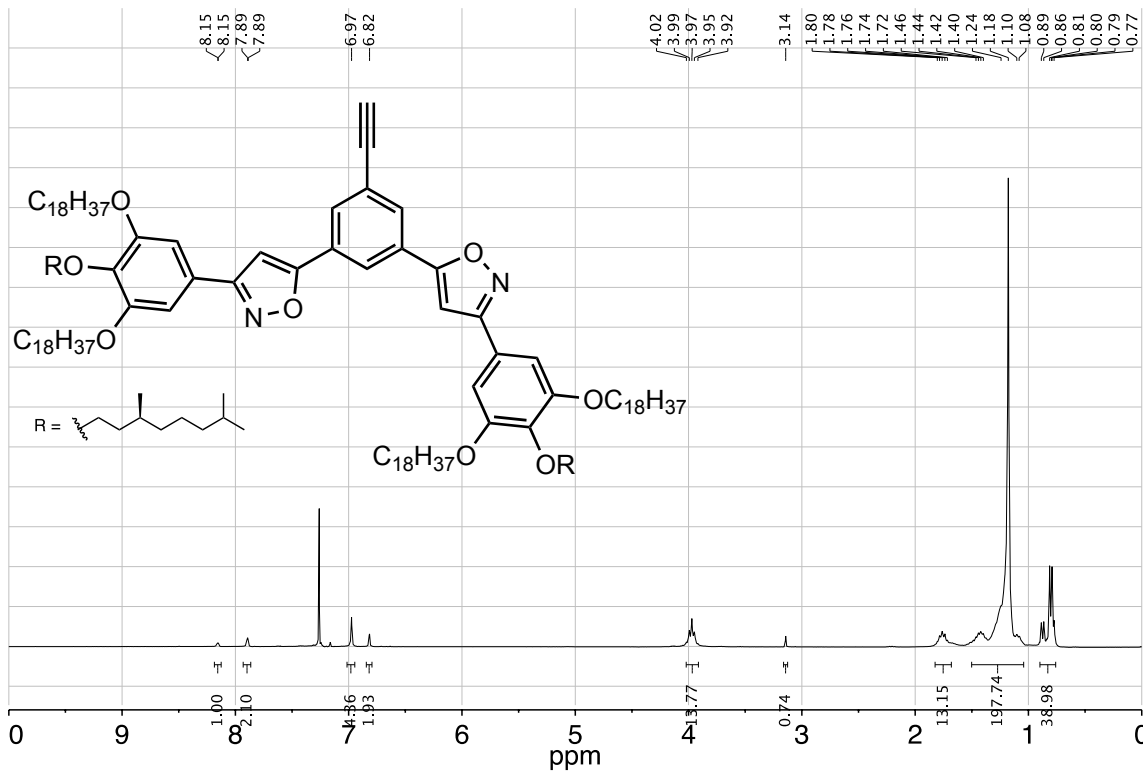


1-((Trimethylsilyl)ethynyl)-3,5-bis(4-((S)-3,7-dimethyloctyloxy)-3,5-bis(octadecyloxy)phenylisoxazolyl)benzene (8)



1-Ethynyl-3,5-bis(4-((S)-3,7-dimethyloctyloxy)-3,5-bis(octadecyloxy)phenylisoxazolyl)benzene

(9)



(6-Phenyl-2,2'-bipyridine)((3,5-bis(4-((S)-3,7-dimethyloctyloxy)-3,5-bis(octadecyloxy)phenylisoxazolyl)phenylethynyl)platinum (1)

