Electronic Supplementary Informations

Polyethylene Glycol-Functionalized Benzylidene Cyclopentanone Dyes for Two-Photon Excited Photodynamic Therapy

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Two-photon absorption (TPA) characterization

TPA cross-section (σ) values of compounds in n-octanol (2×10^{-4} M) were determined using the two-photon excited fluorescence (TPEF) technique following the experimental protocol described in detail by Xu and Webb.[1] The excitation light sources were a mode-locked Tsunami Ti:sapphire laser (720–880 nm, 80 MHz, <130 fs). Two-photon excited fluorescence spectra were recorded in a direction perpendicular to the laser beam using a fiber spectrometer (Ocean Optics USB2000 CCD) as detector. Rhodamine B in methanol solution (10^{-4} M) was used as reference, whose σ values in the range of 720-880 nm was reported by Xu and Webb.[1] The σ values of dyes **A1-B4** were calculated according to equation (1) by comparing their TPEF intensities with that of Rhodamine B under the same measurement conditions.[2]

$$\sigma_s = \frac{S_s \Phi_r \varphi_r C_r}{S_r \Phi_s \varphi_s C_s} \sigma_r \qquad (1)$$

Here, the subscripts r and s stand for the reference and sample, respectively. *S* is the integral area of the two-photon-excited fluorescence. *Φ* is the fluorescence quantum yield. *φ* is the overall fluorescence collection efficiency of the experimental apparatus. *C* is the number density of the molecules in solution.

To avoid any contribution from other photophysical or photochemical processes, the intensity of input pulses were adjusted to a proper regime to ensure a quadratic dependence of the fluorescence intensity versus excitation pulse energy. It is shown in Fig. S1 that slopes around 2 are obtained for all dyes in the logarithmic plots of the fluorescence intensities induced by TPA *vs.* excitation intensities at 800 nm.

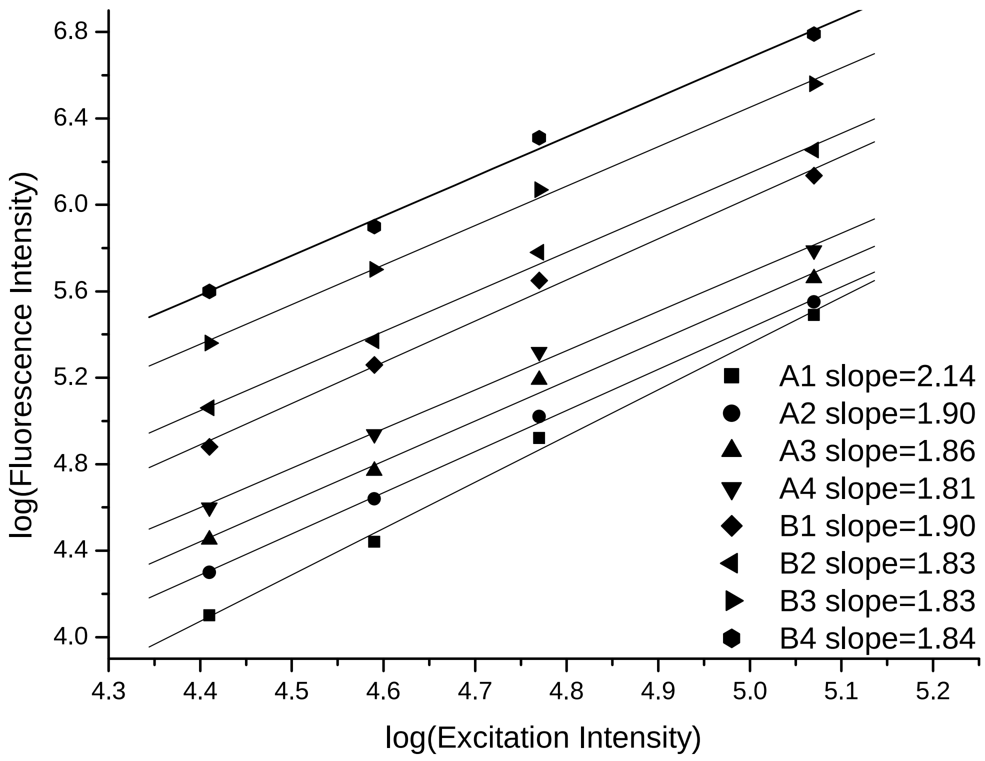


Fig. S1 Logarithmic plots of the fluorescence intensities induced by TPA *vs.* excitation intensities at 800 nm of dyes **A1-B4** in n-octanol (2×10^{-4} M).

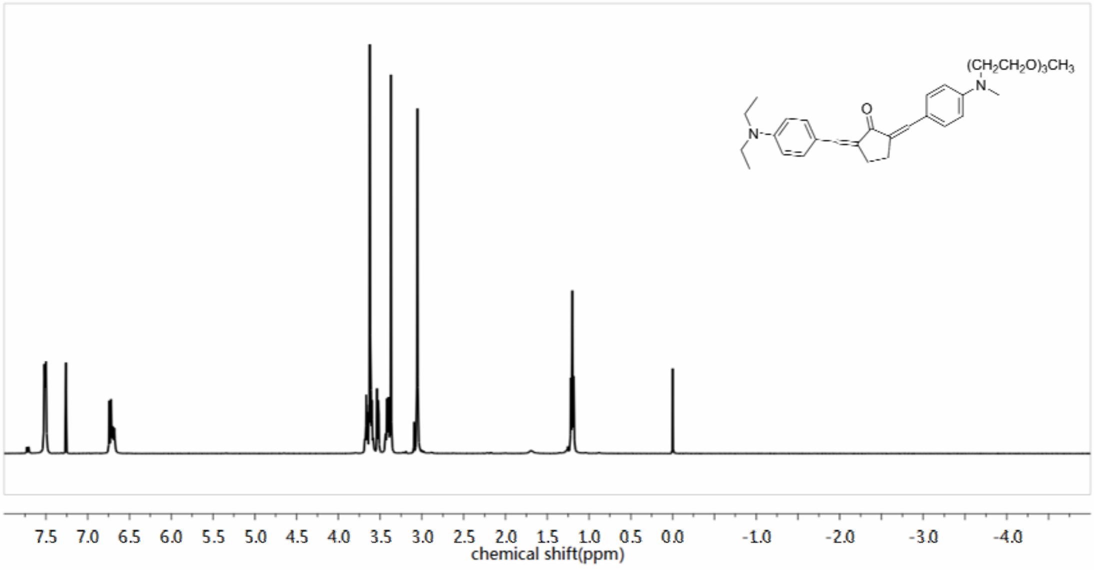
Reference:

1. C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481.

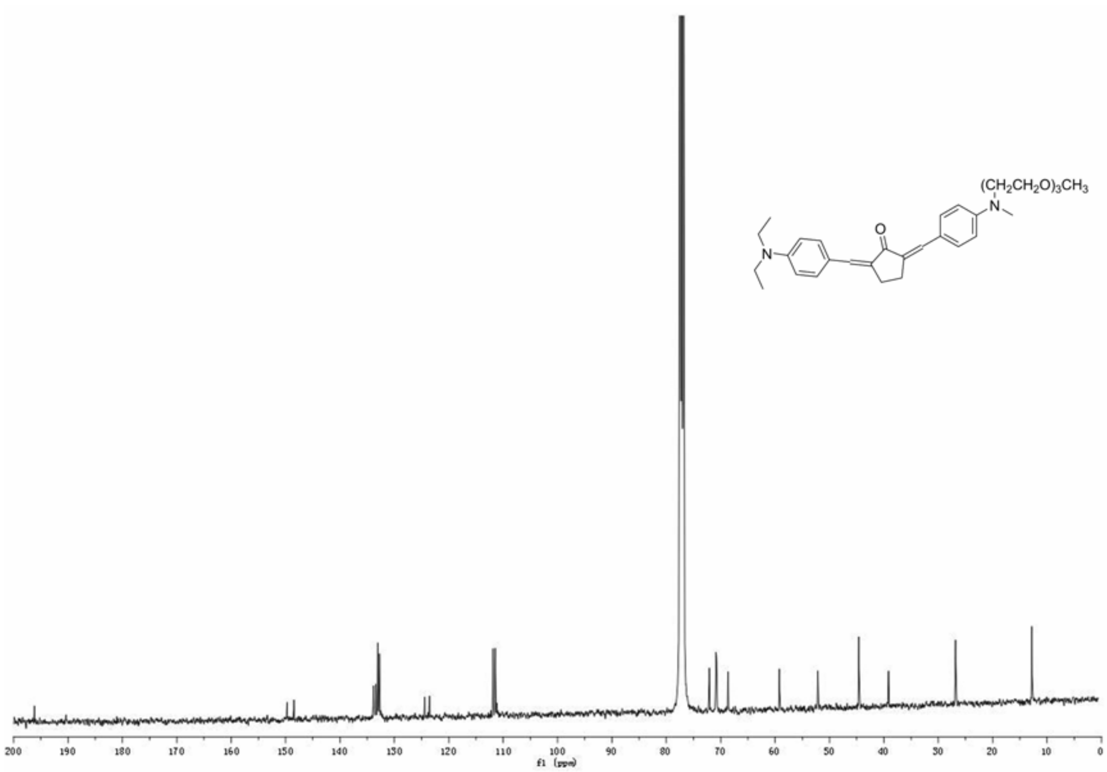
2. M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z.-Y. Hu, D. McCord-Maughon, T. C. Parker, H. Röckel, S. Thayumanavan, S. R. Marder, D. Beljonne and J.-L. Brédas, *J. Am. Chem. Soc.* 2000, **122**, 9500.

^{1}H NMR and ^{13}C NMR Spectra of compounds A4-B4

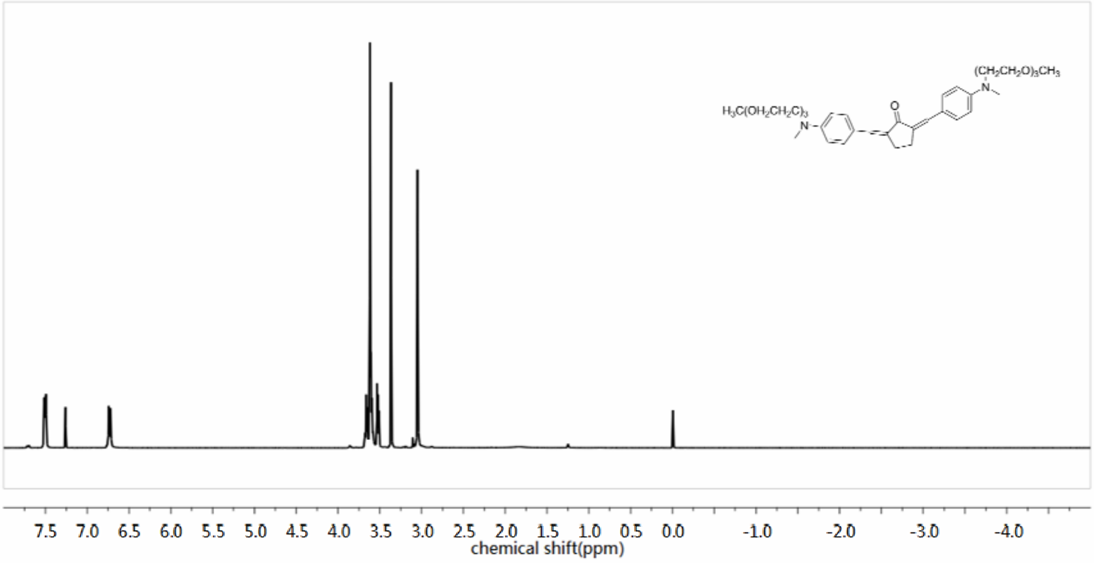
1. ^{1}HNMR spectrum of dye **A1** ($CDCl_3$, 400MHz)



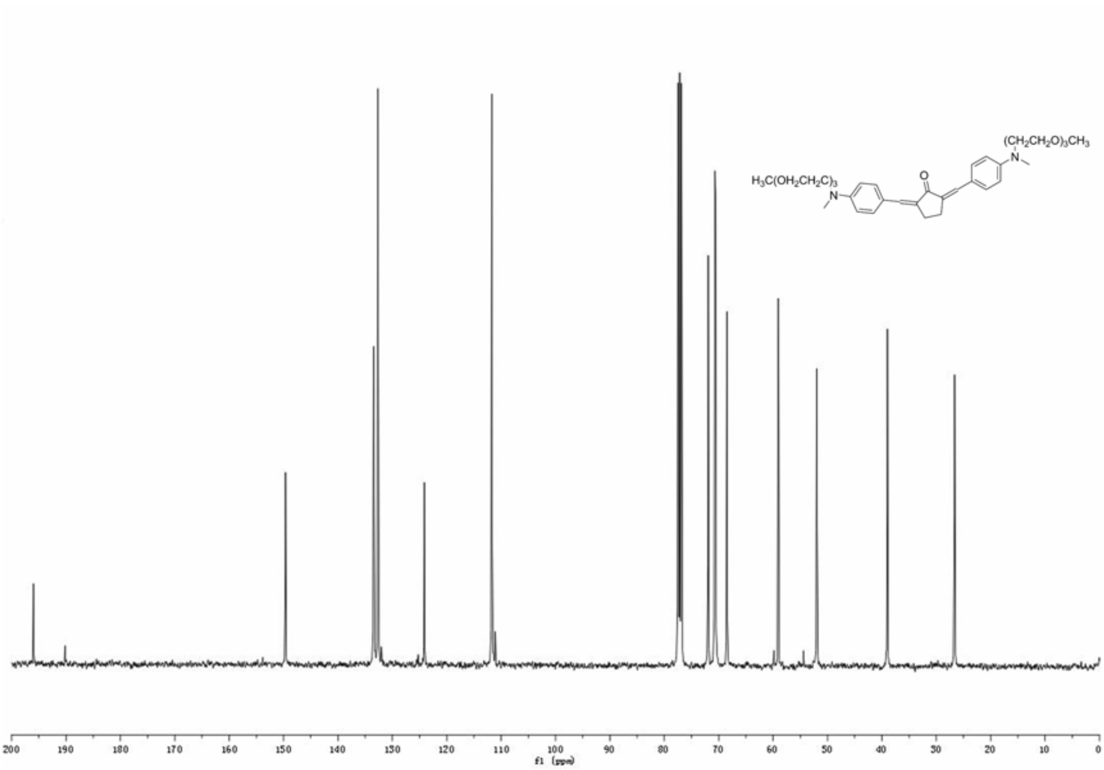
2. ^{13}CNMR spectrum of dye **A1** ($CDCl_3$, 400MHz)



3. ^{1}HNMR spectrum of dye **A2** ($CDCl_3$, 400MHz)



4. ^{13}CNMR spectrum of dye **A2** ($CDCl_3$, 400MHz)



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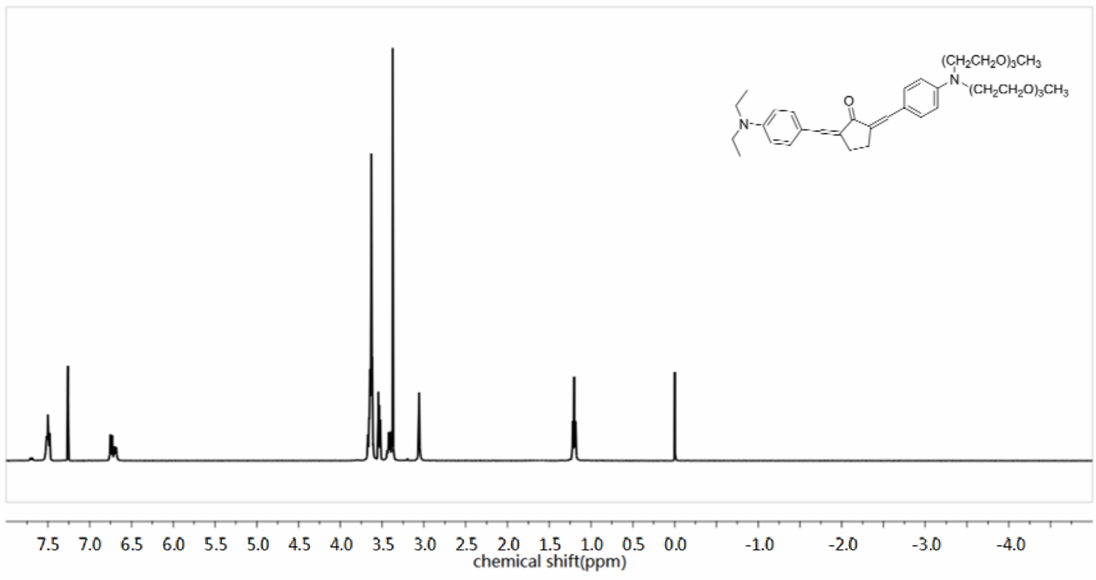
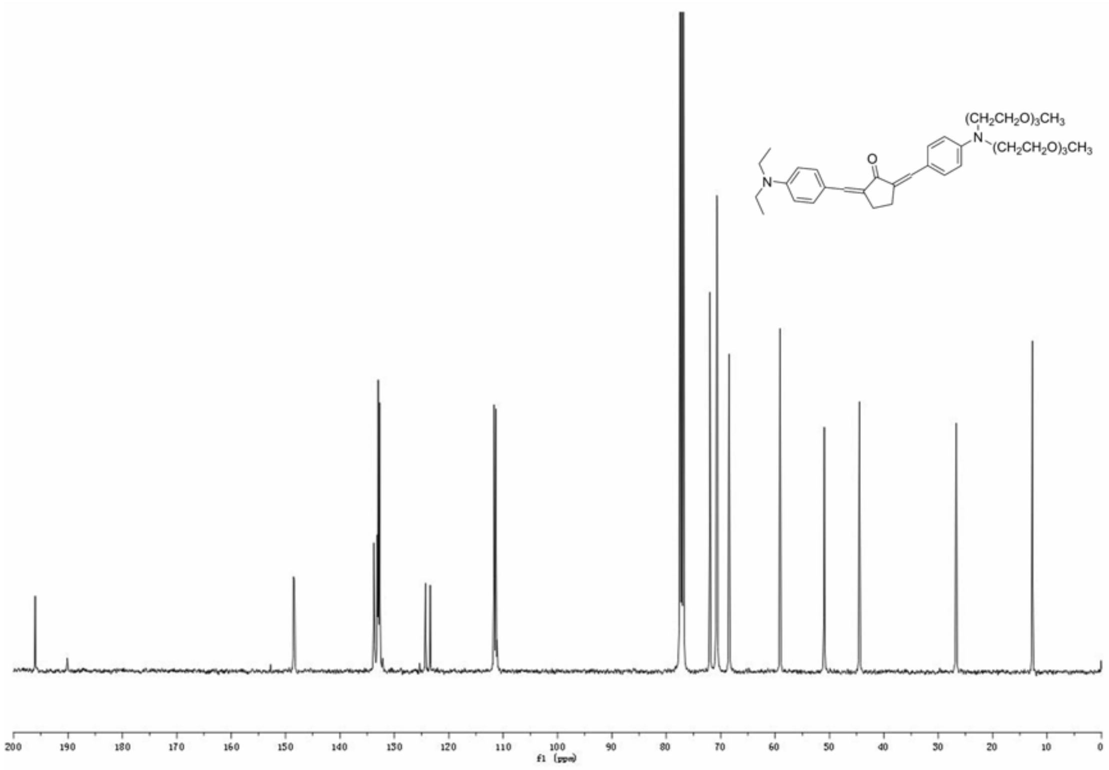
5. ^{1}HNMR spectrum of dye **A3** ($CDCl_3$, 400MHz)



6. ^{13}CNMR spectrum of dye **A3** ($CDCl_3$, 400MHz)



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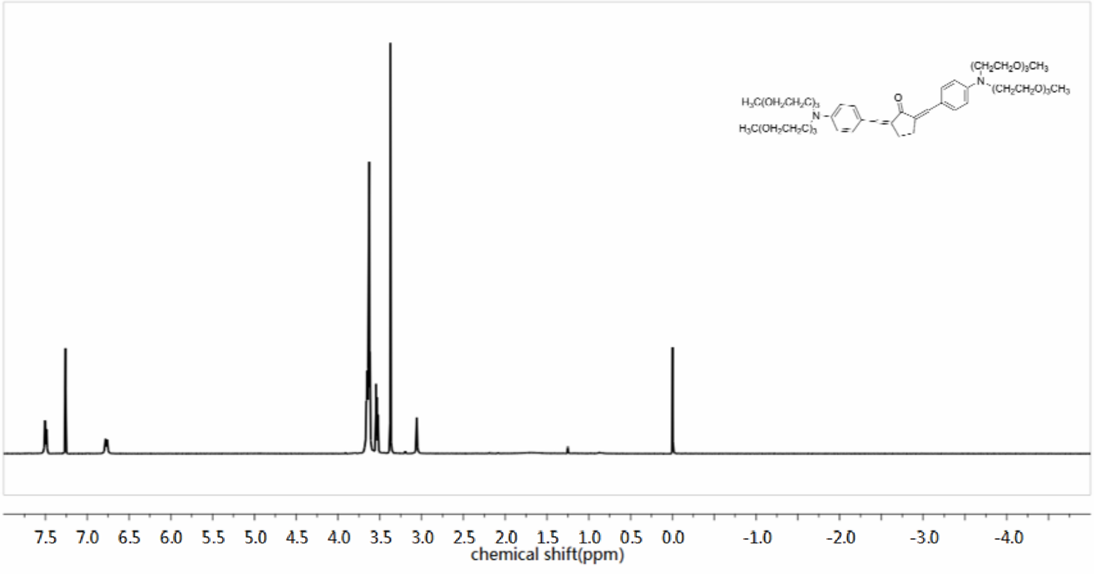
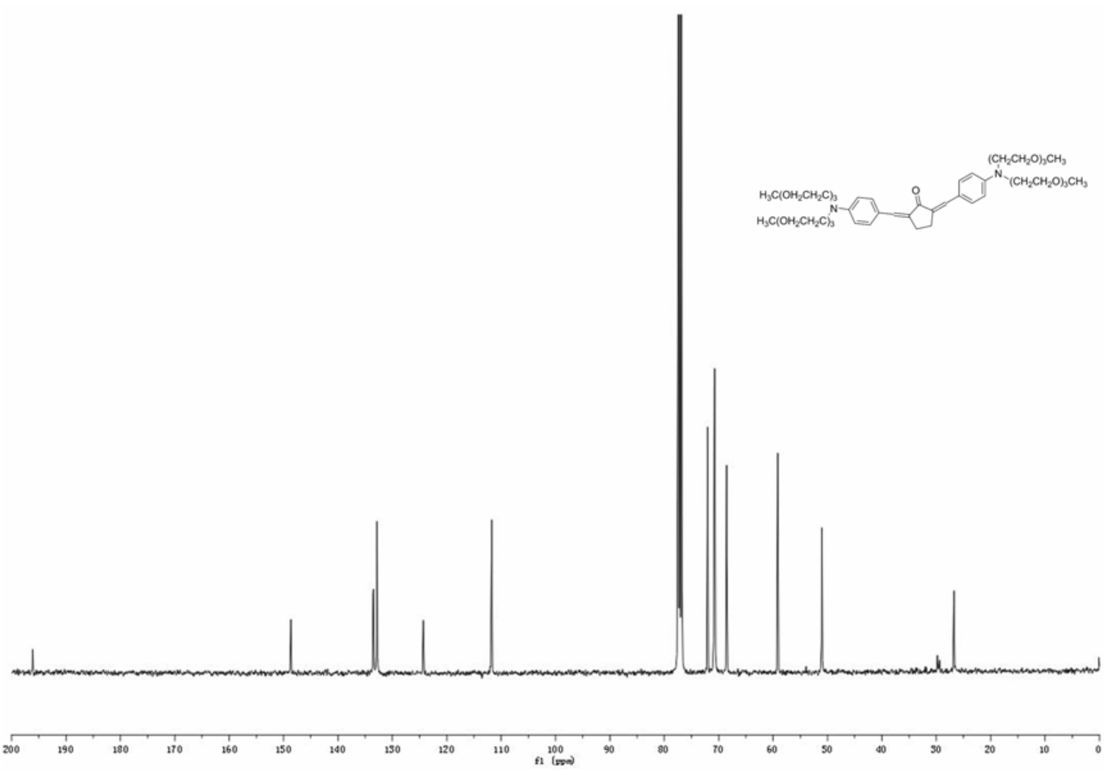
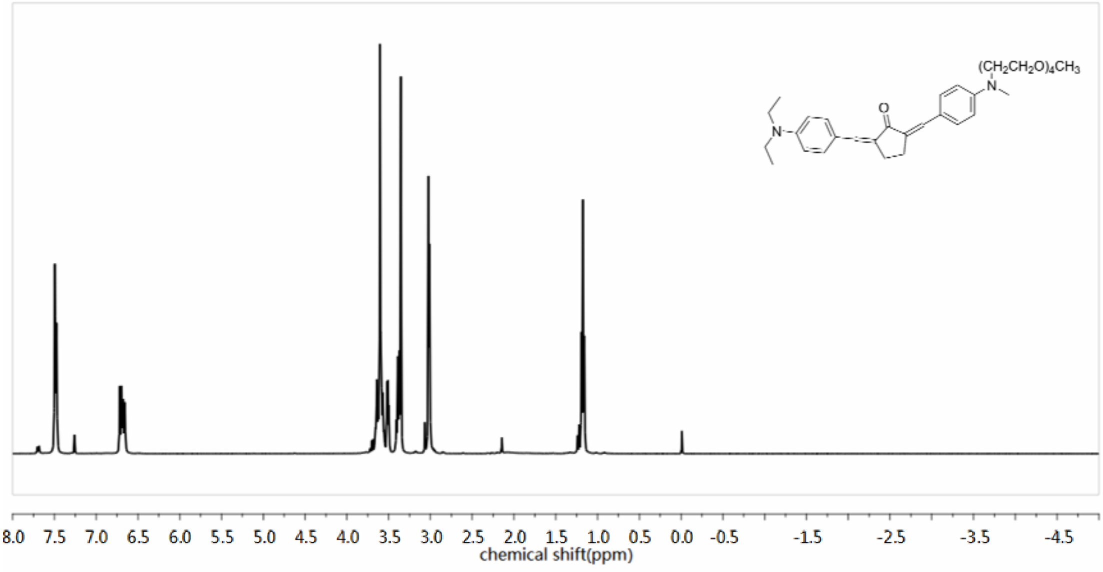
7. [1]HNMR spectrum of dye **A4** ($CDCl_3$, 400MHz)



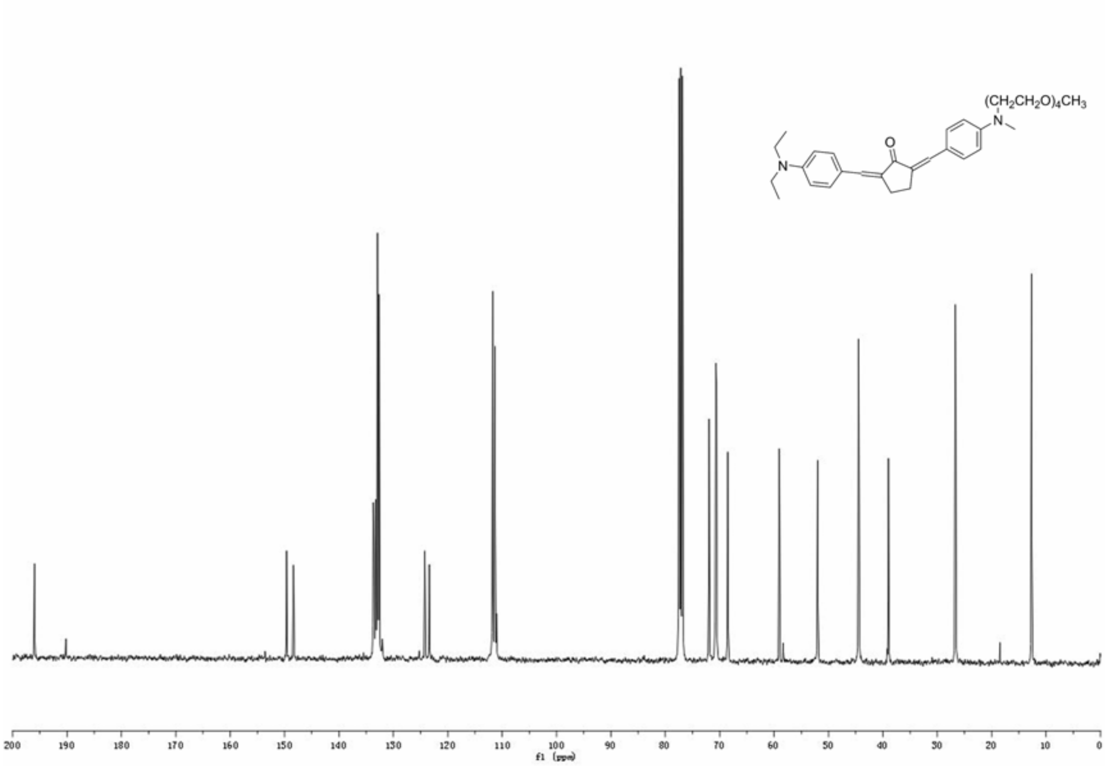
8. [13]CNMR spectrum of dye **A4** ($CDCl_3$, 400MHz)



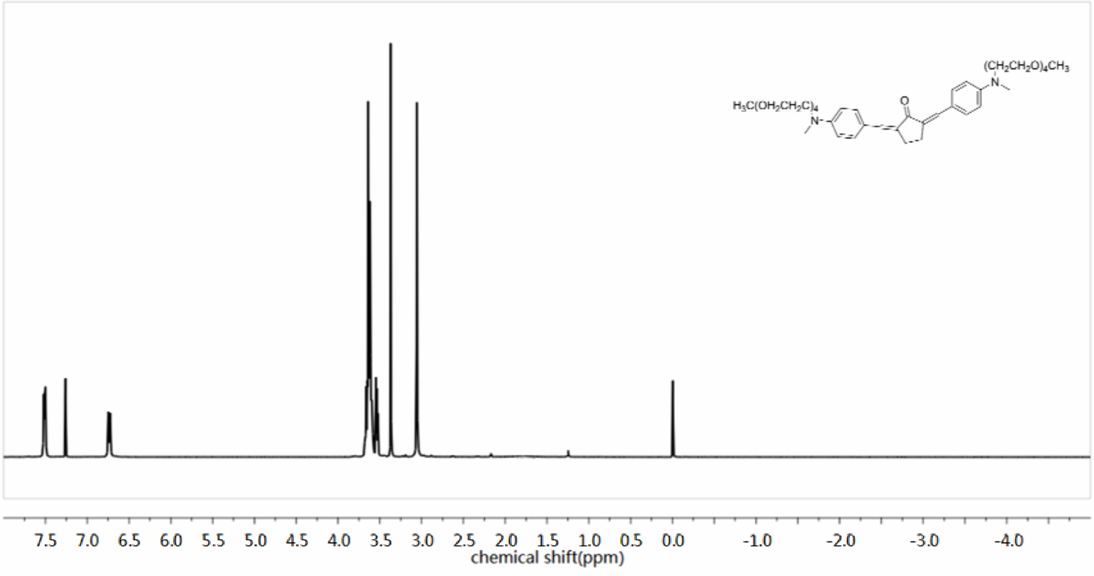
9. ^{1}HNMR spectrum of dye **B1** ($CDCl_3$, 400MHz)



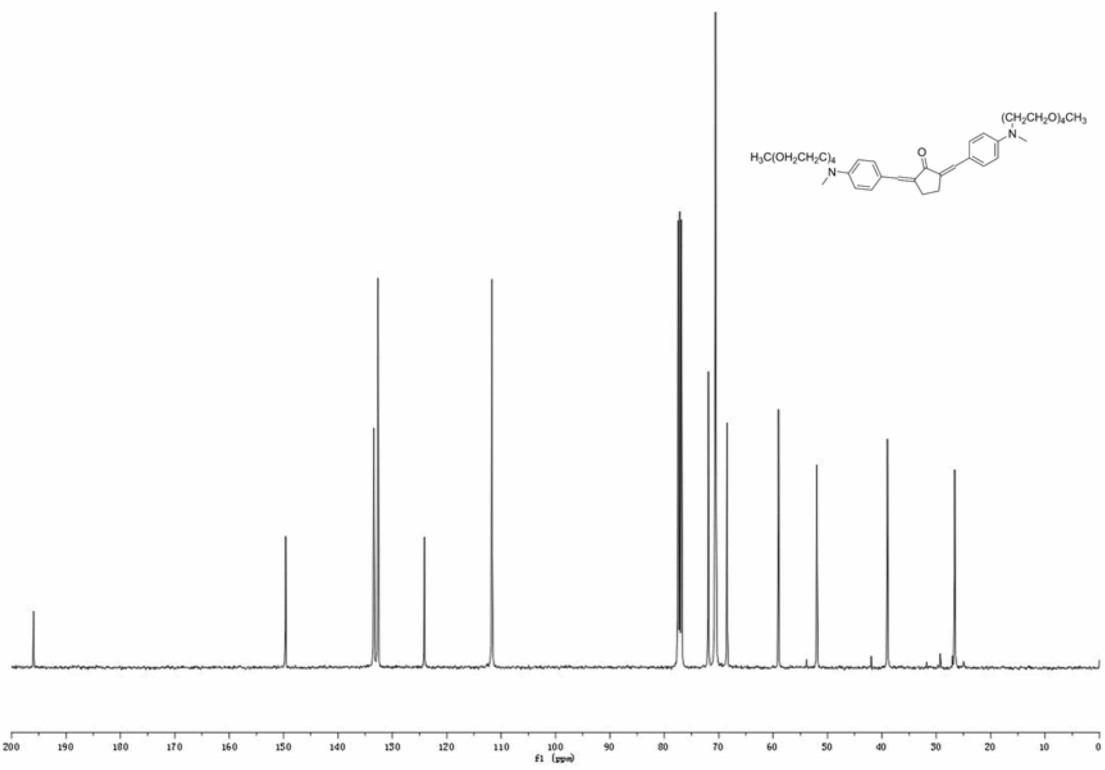
10. ^{13}CNMR spectrum of dye **B1** ($CDCl_3$, 400MHz)



11. [1]HNMR spectrum of dye **B2** ($CDCl_3$, 400MHz)



12. [13]CNMR spectrum of dye **B2** ($CDCl_3$, 400MHz)



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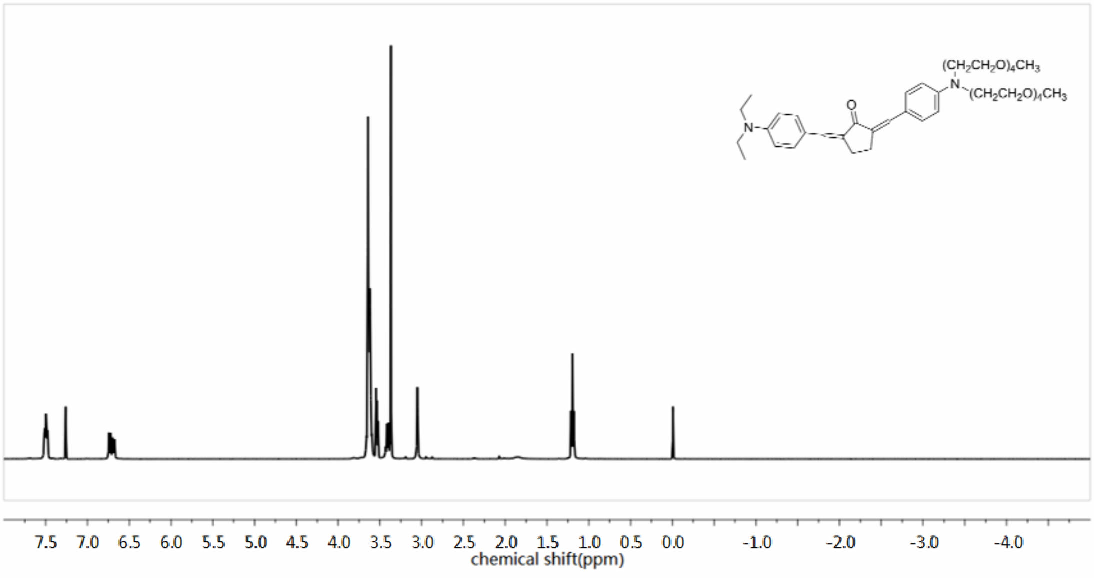
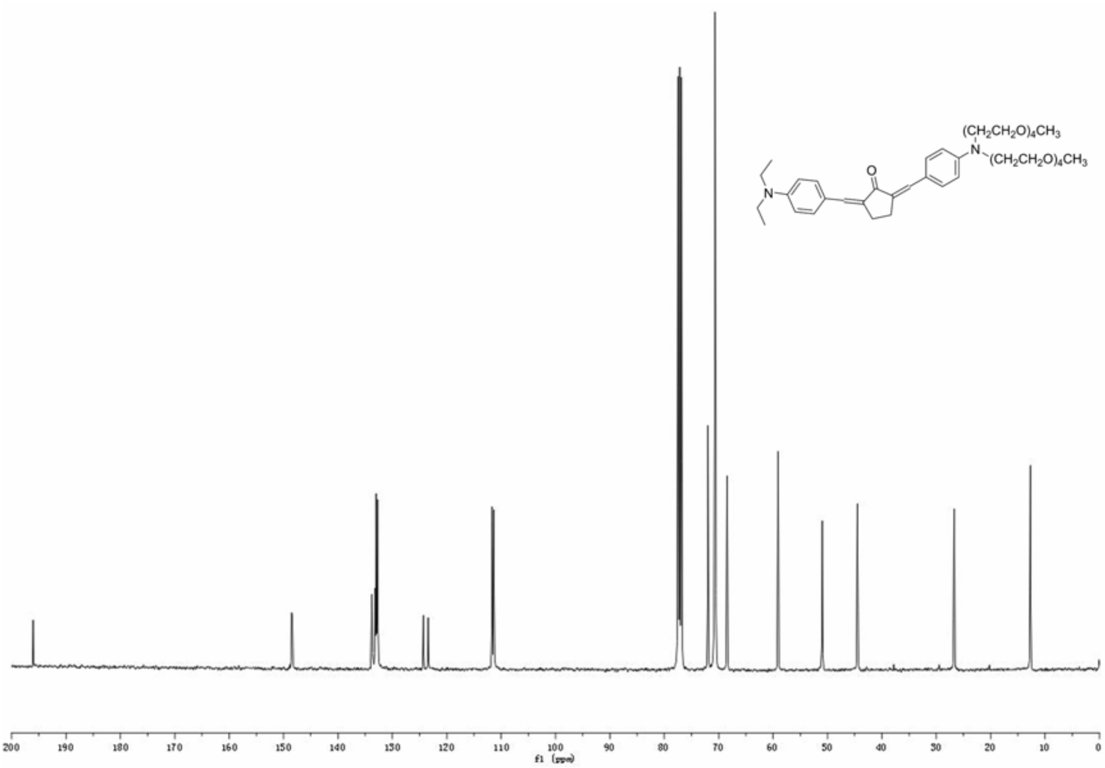
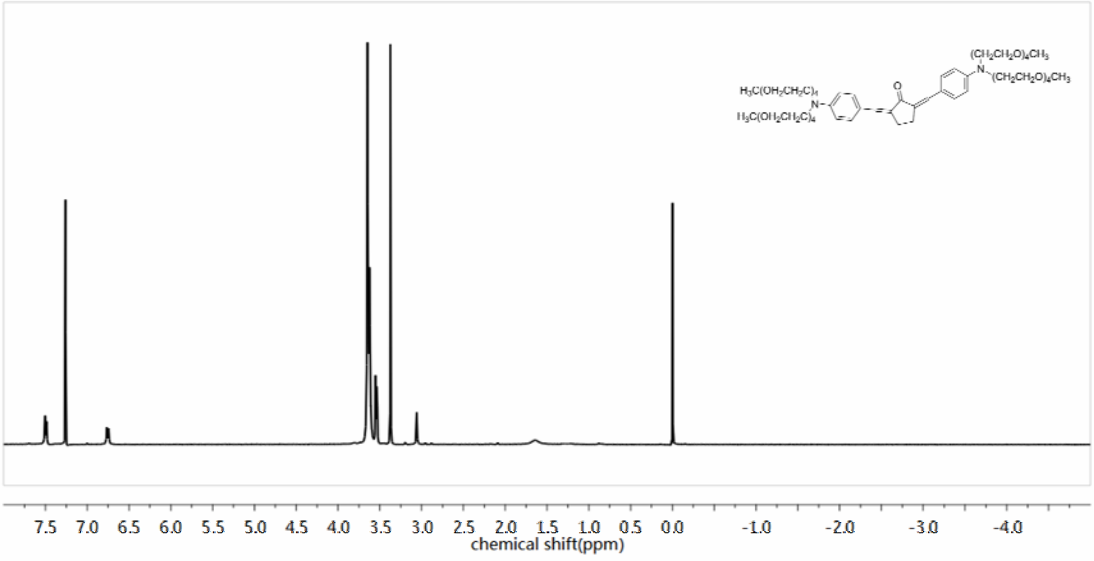
13. [1]HNMR spectrum of dye **B3** ($CDCl_3$, 400MHz)



14. [13]CNMR spectrum of dye **B3** ($CDCl_3$, 400MHz)



15. [1]HNMR spectrum of dye **B4** ($CDCl_3$, 400MHz)



16. [13]CNMR spectrum of dye **B4** ($CDCl_3$, 400MHz)