Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Unusual fluorescene emission from ethynyltriphenylene substituted diacetylenic molecular hinge. Formation of intramolecular excimer

Ritesh Nandy and Sethuraman Sankararaman*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

sanka@iitm.ac.in

Supporting Information: **Page**

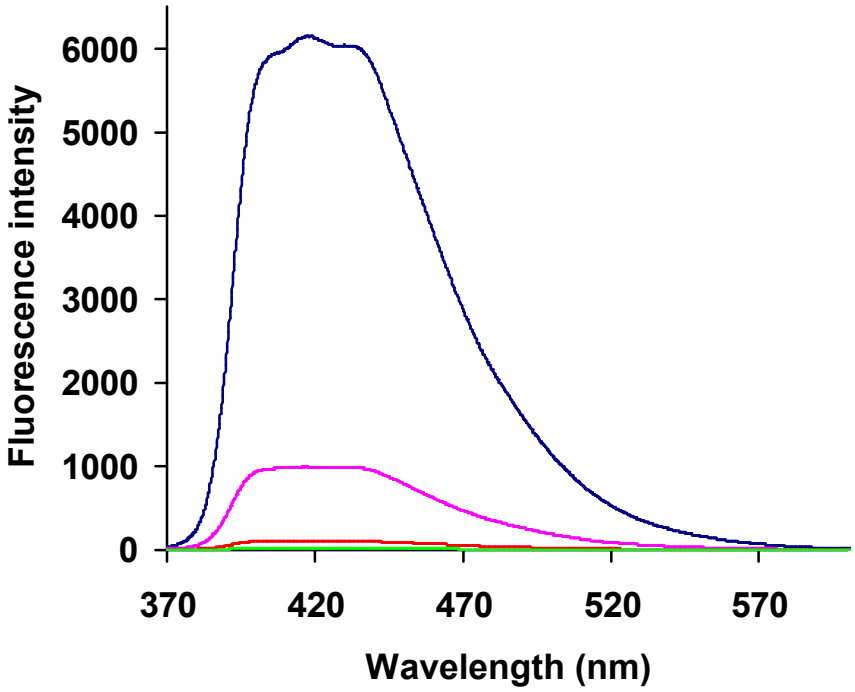


Figure S1. Effect of concentration on the fluorescence emission of **1** in CH_2Cl_2. 10^{-5} M (blue), 10^{-6} M (magenta), 10^{-7} M (red), 10^{-8} M (green). λ_{ex} = 312 nm.

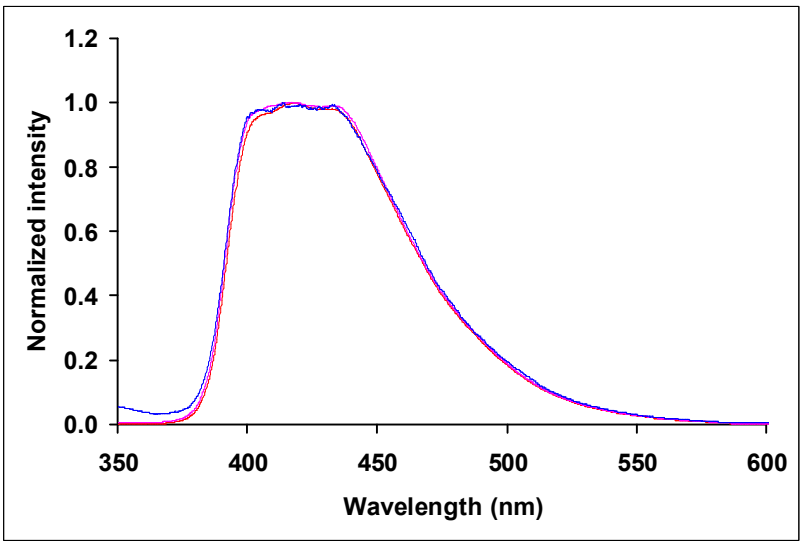


Figure S1a: Normalized intensity plot of the data from Figure S1.

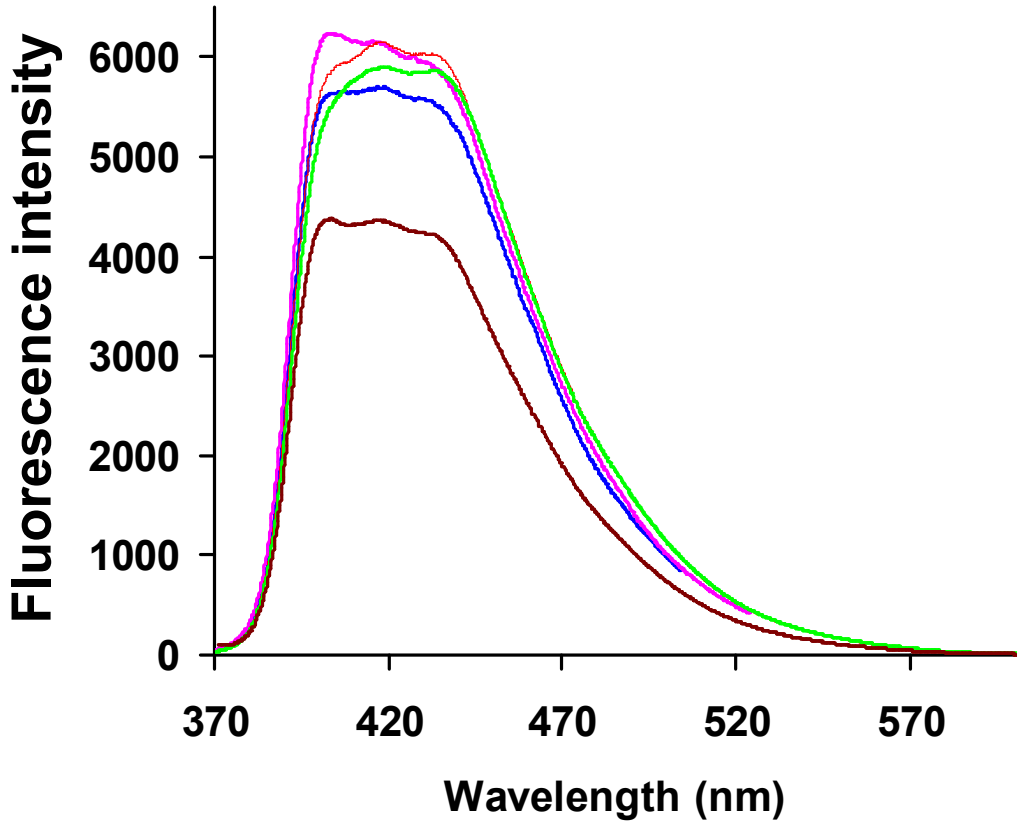


Figure S2. Effect of excitation wavelength on the fluorescence emission of **1** in CH_2Cl_2. λ_{ex} (nm) = 257 (blue), 267 (magenta), 312 (red), 332 (green), 361 (brown).

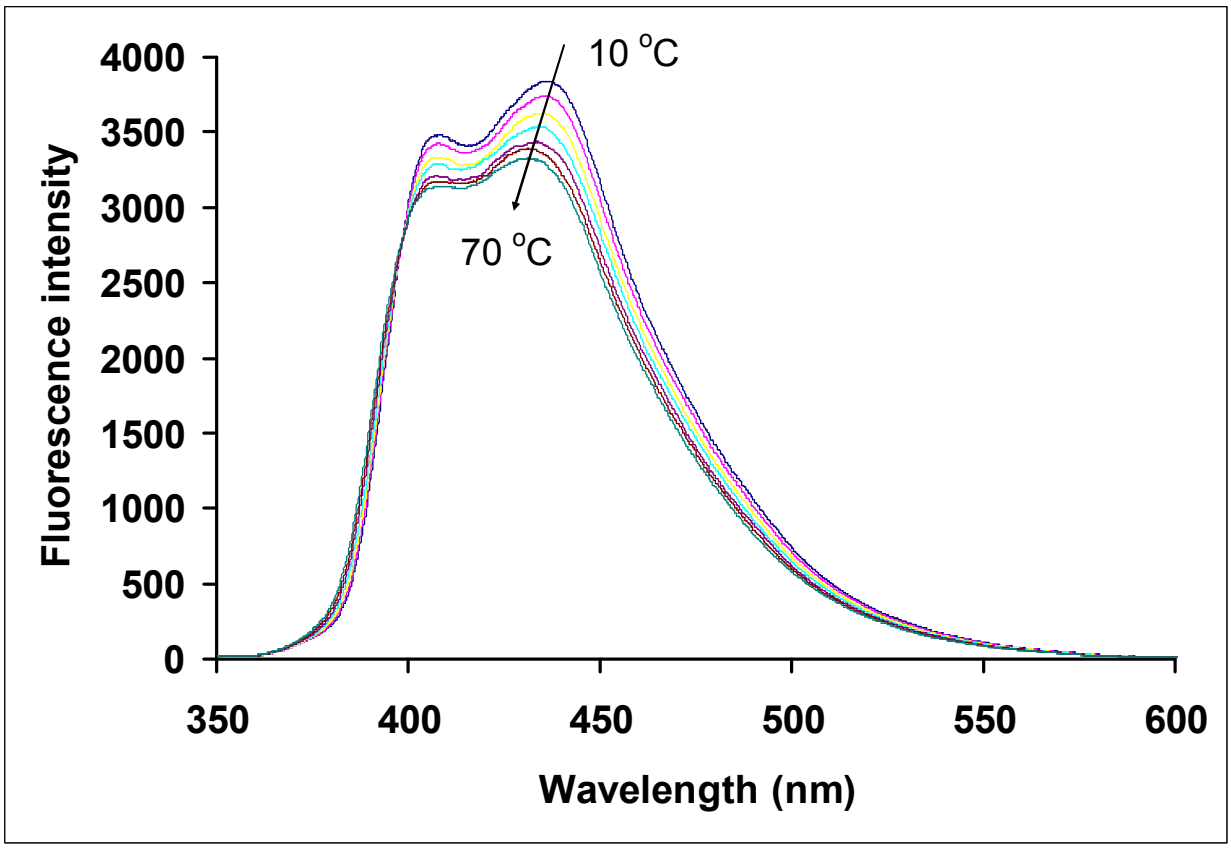


Figure S3. Effect of temperature on the fluorescence of **1** in cyclohexane in the temperature range +10 to + 70 °C. λ_{ex} = 314 nm.

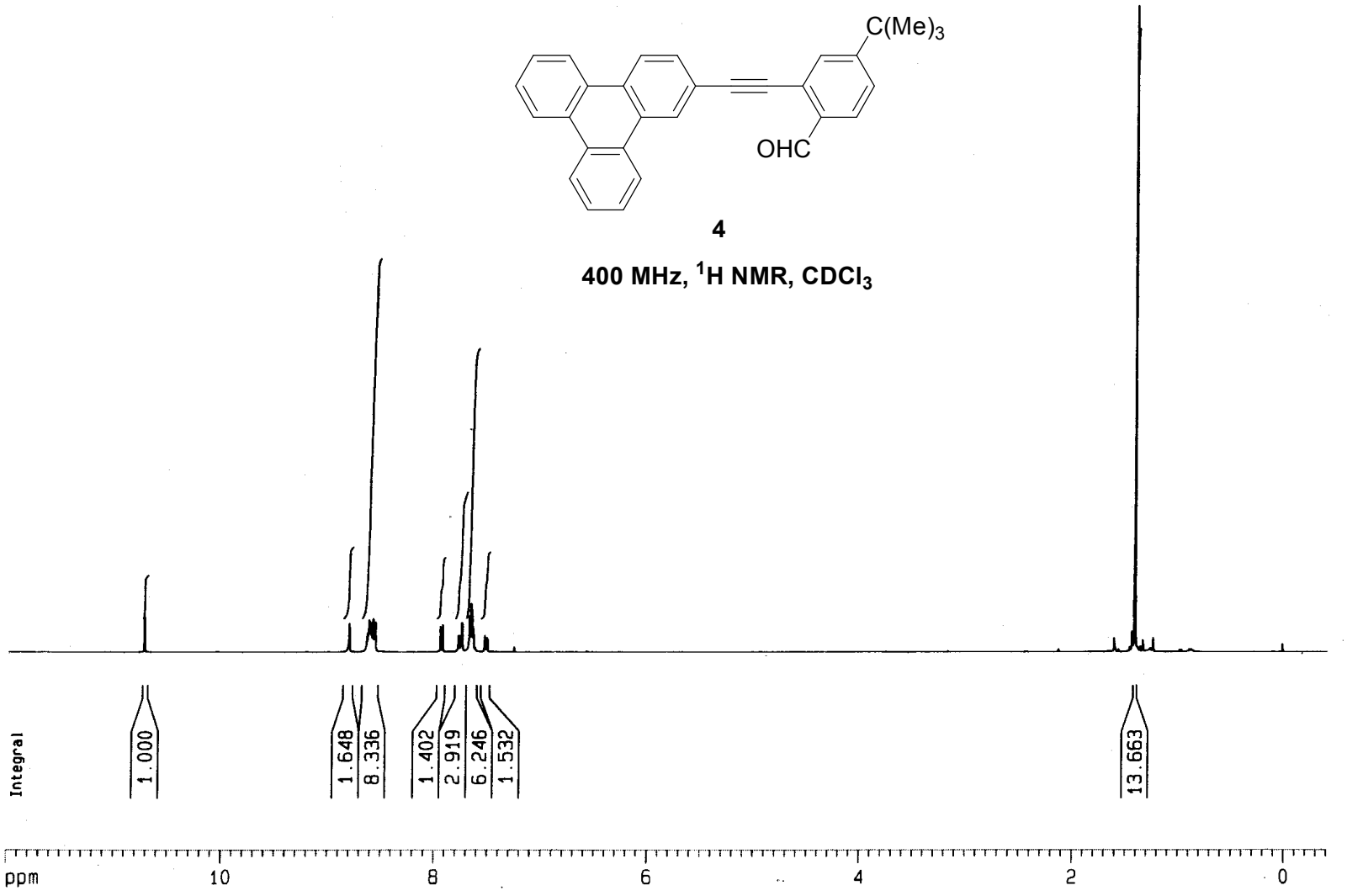


Figure S4. 400 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$.

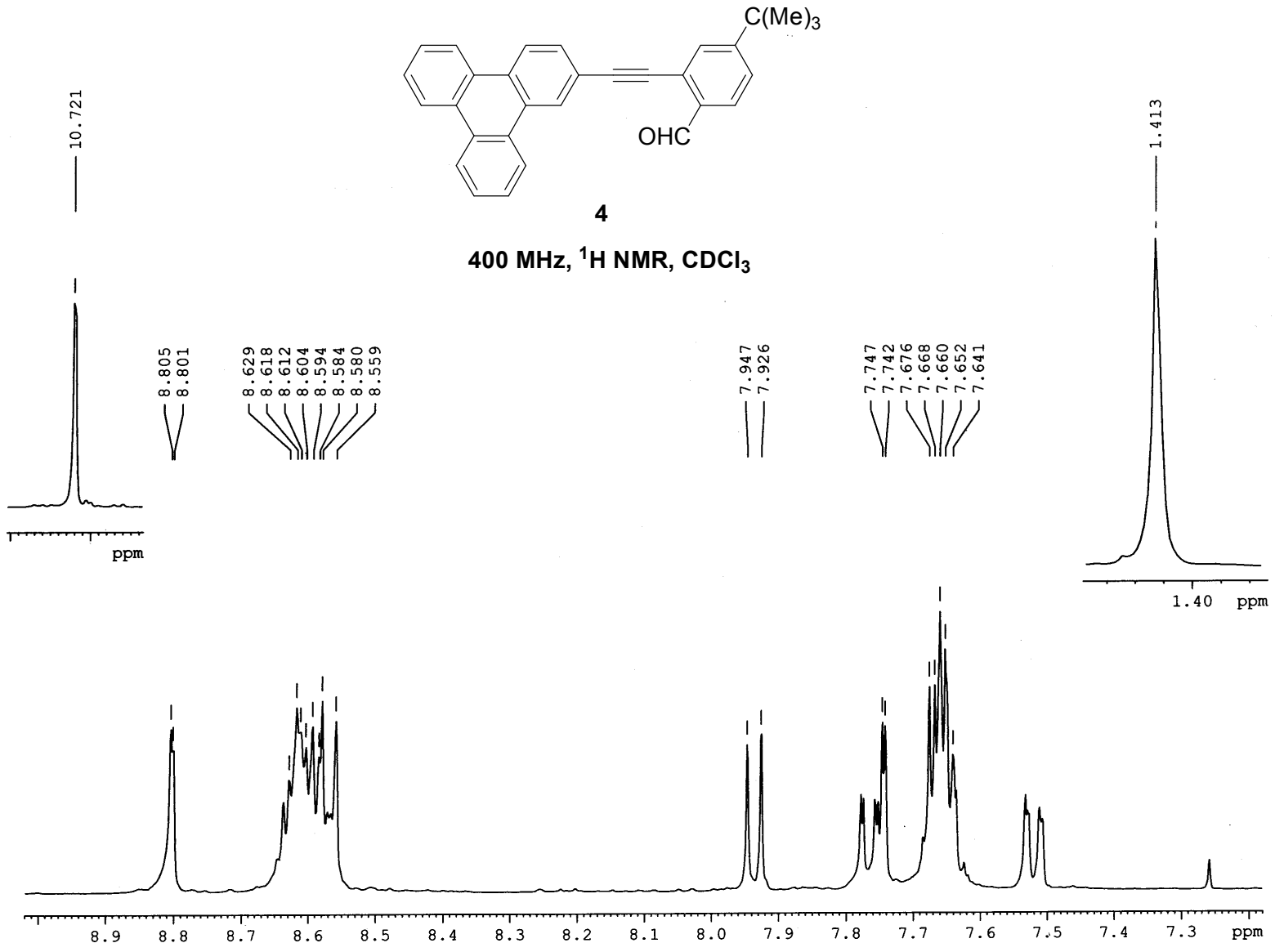


Figure S5. 400 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$. Aromatic region expanded.

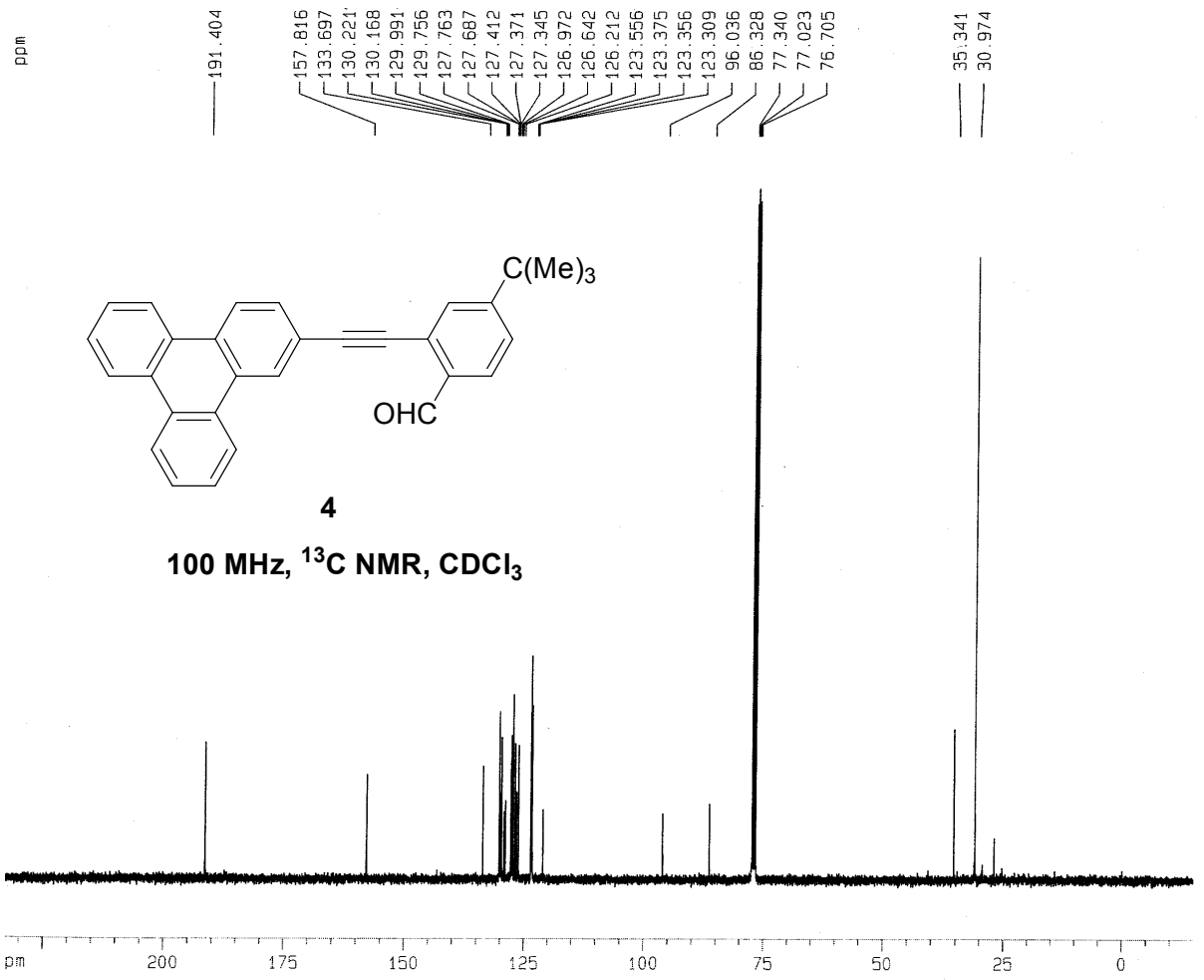


Figure S6. 100 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$.

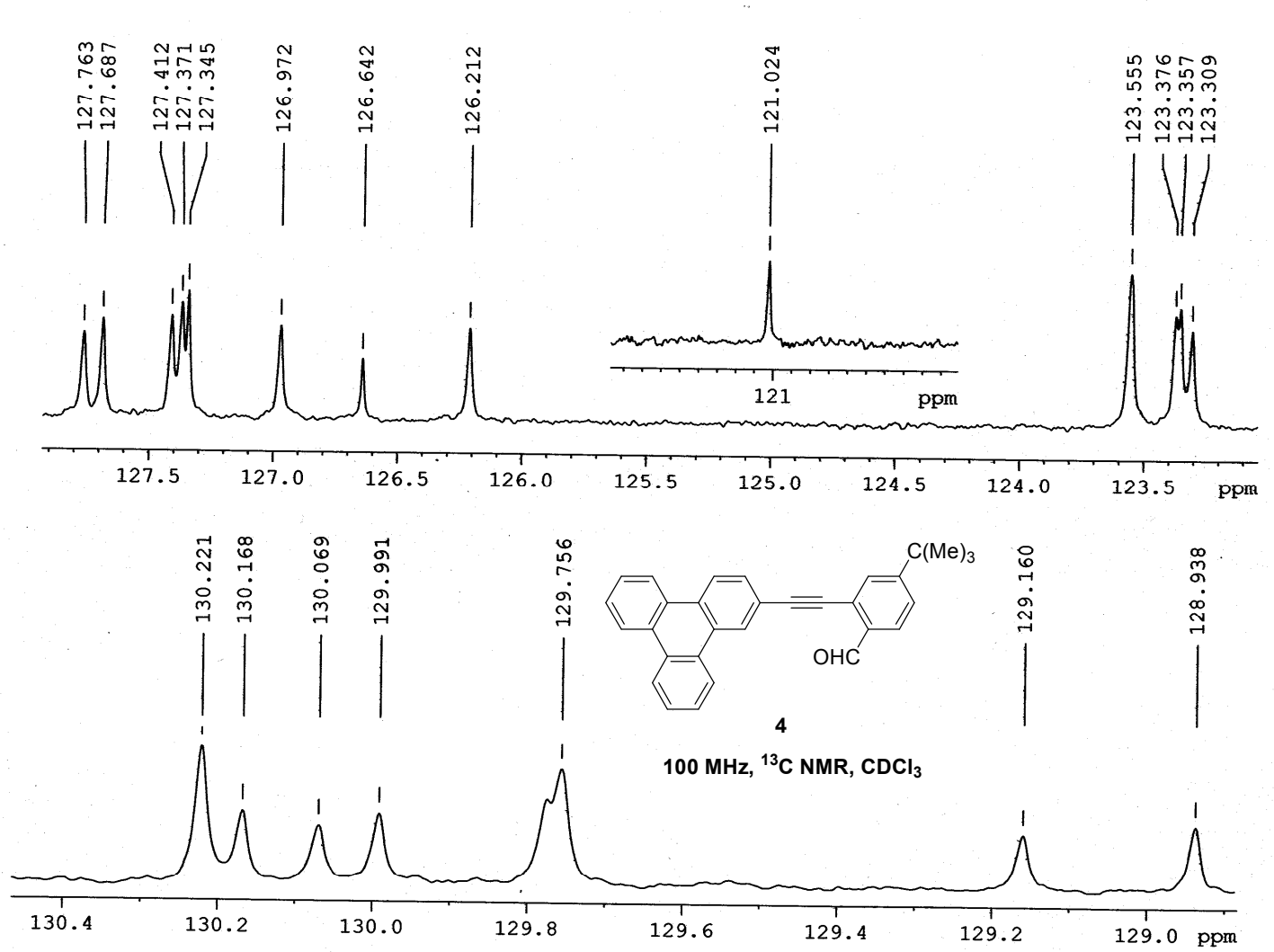


Figure S7. 100 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$. Aromatic region expanded.

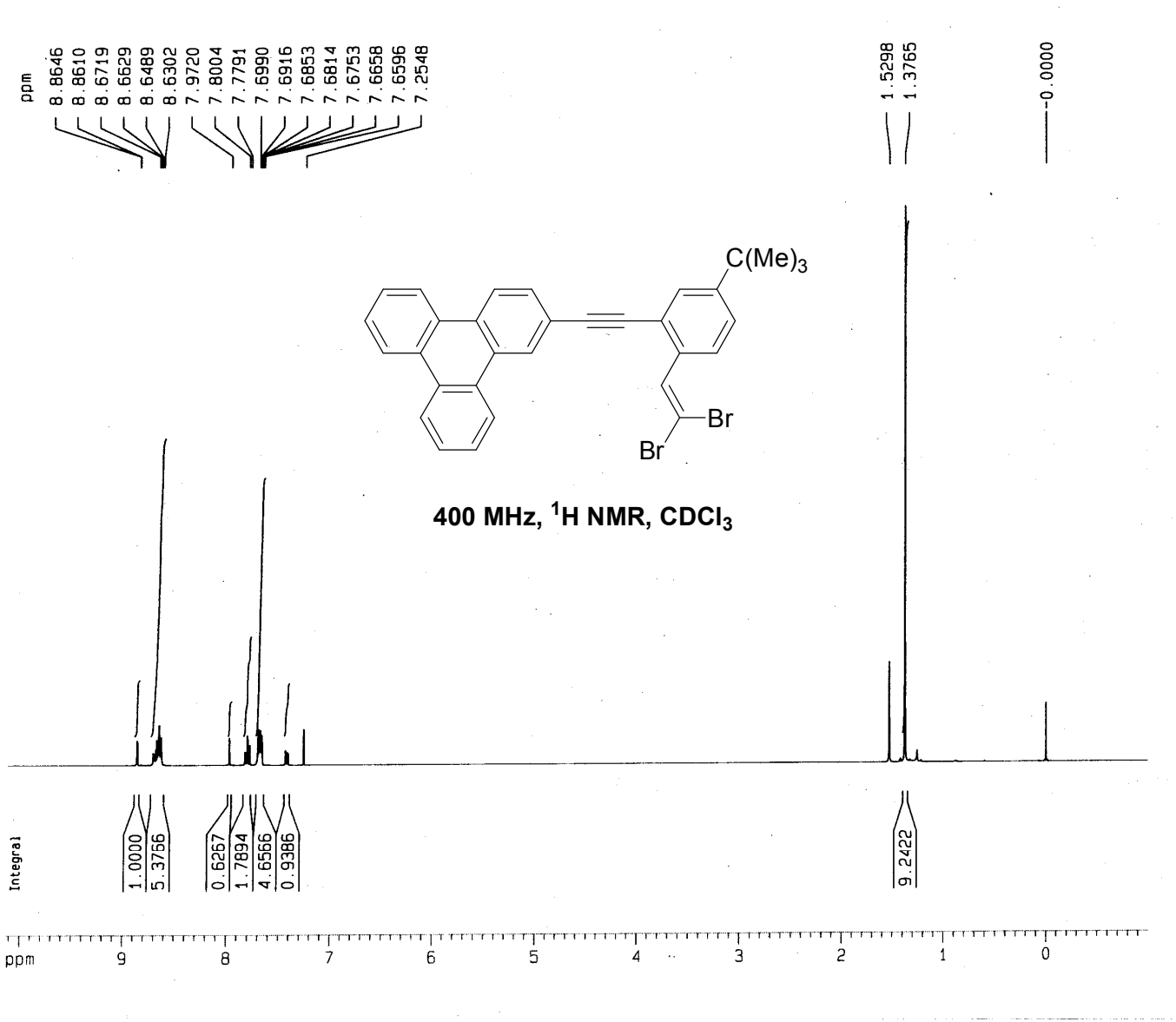


Figure S8. 400 MHz ^{1}H NMR spectrum of 2-(5-*tert*-butyl-2-(1,1-dibromovinyl)phenylethynyl) triphenylene in $CDCl_3$.

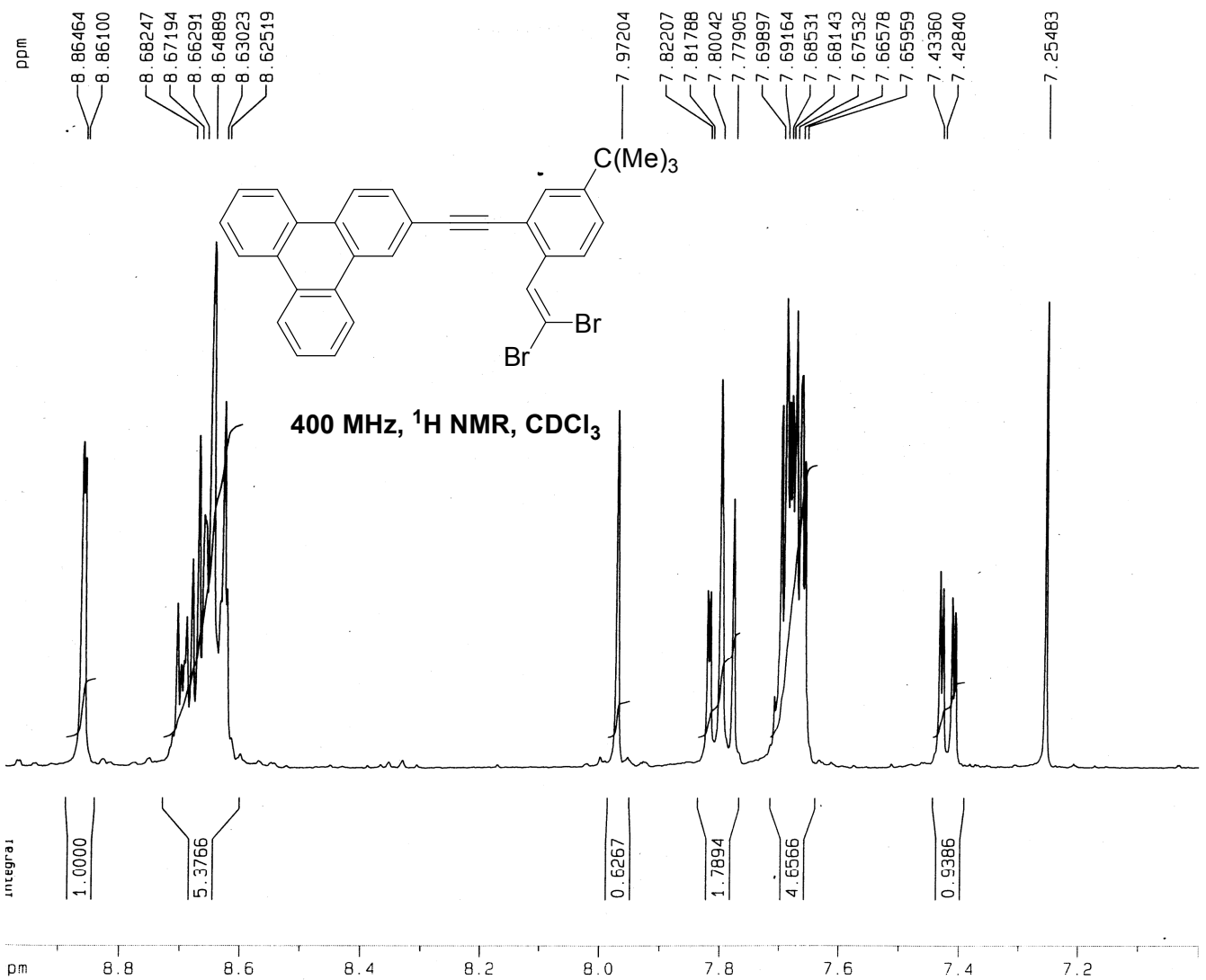


Figure S9. 400 MHz ^{1}H NMR spectrum of 2-(5-*tert*-butyl-2-(1,1-dibromovinyl)phenylethynyl) triphenylene in $CDCl_3$. (Aromatic region)

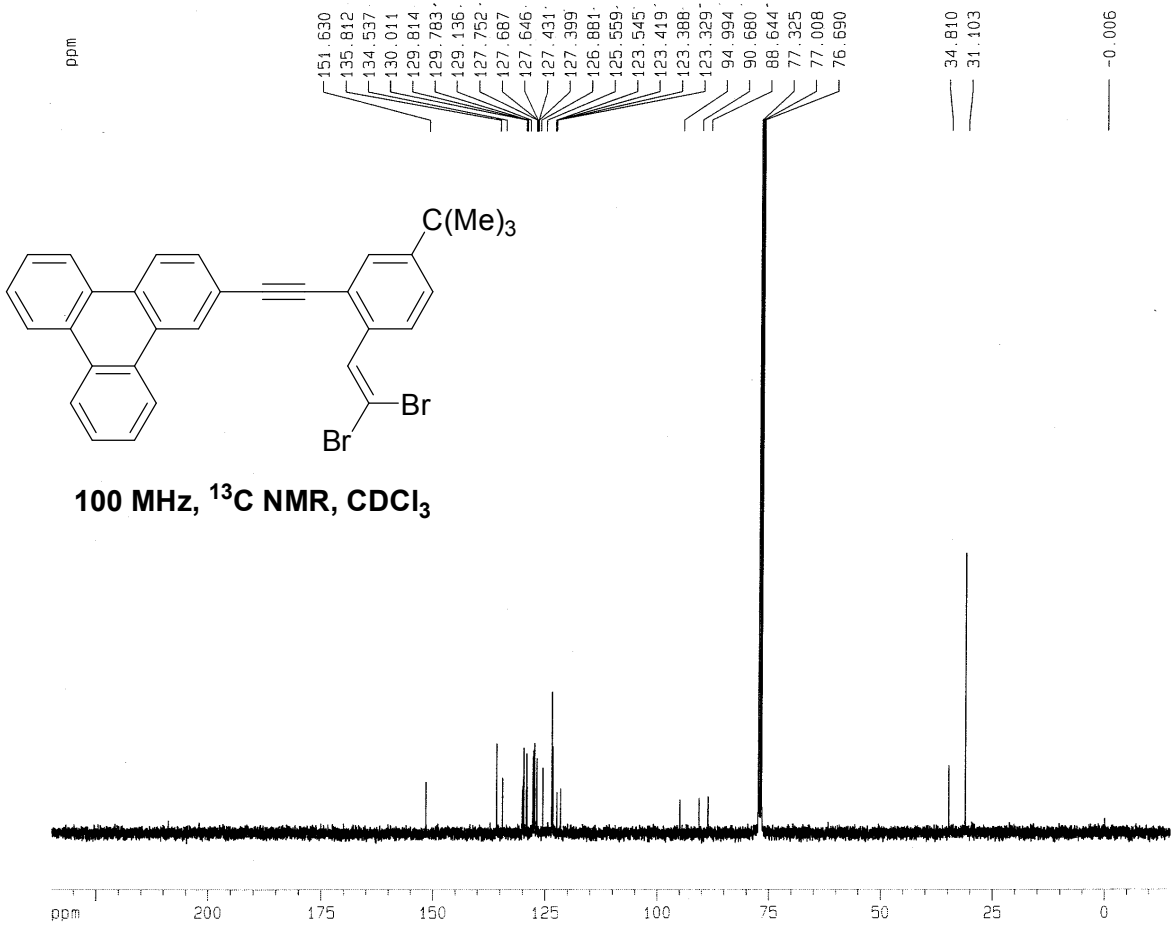


Figure S10. 100 MHz ^{13}C NMR spectrum of 2-(5-*tert*-butyl-2-(1,1-dibromovinyl)phenylethynyl) triphenylene in $CDCl_3$

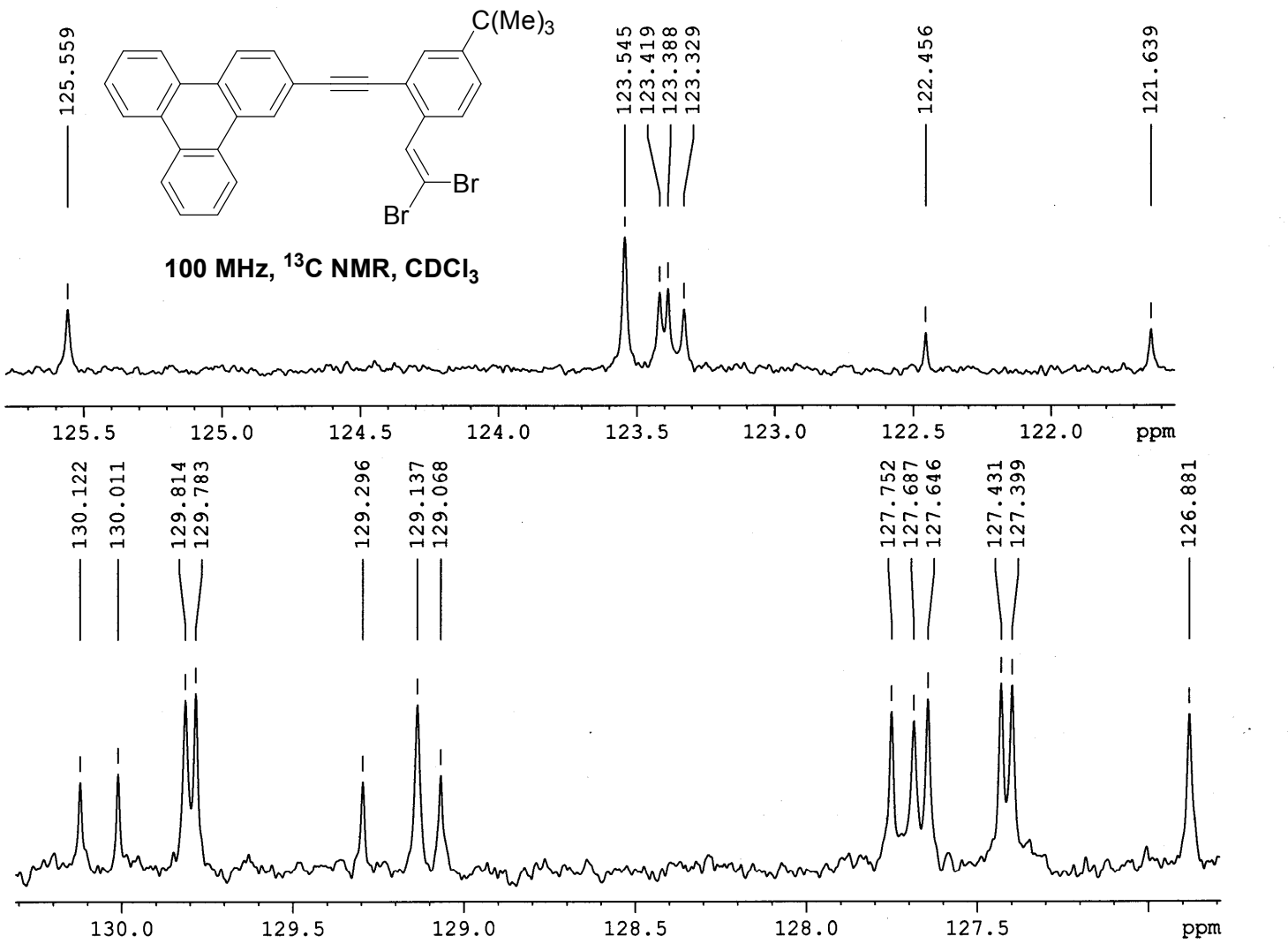


Figure S11. 100 MHz ^{13}C NMR spectrum of 2-(5-*tert*-butyl-2-(1,1-dibromovinyl)phenylethynyl) triphenylene in $CDCl_3$. (Aromatic region).

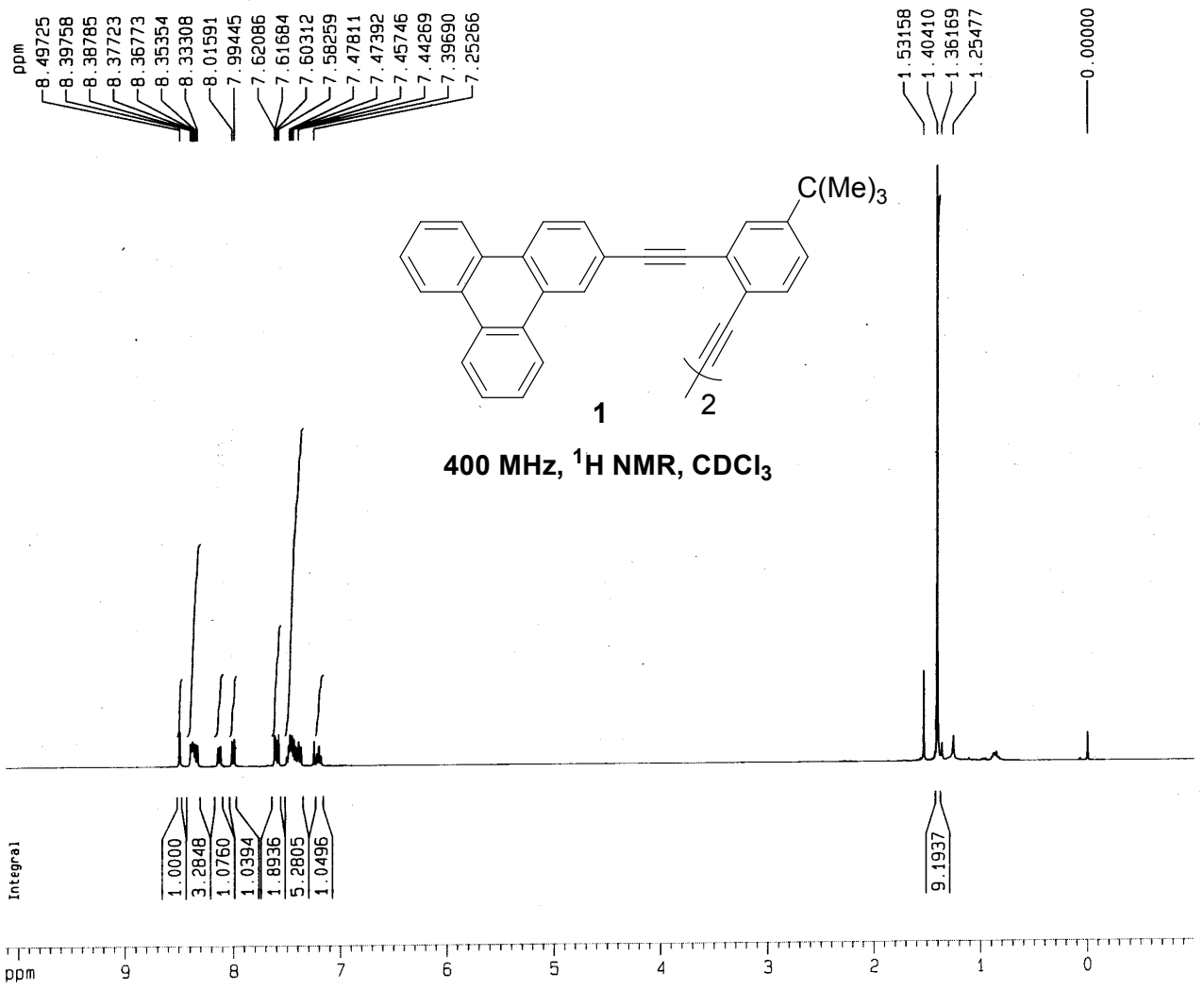


Figure S12. 400 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$.

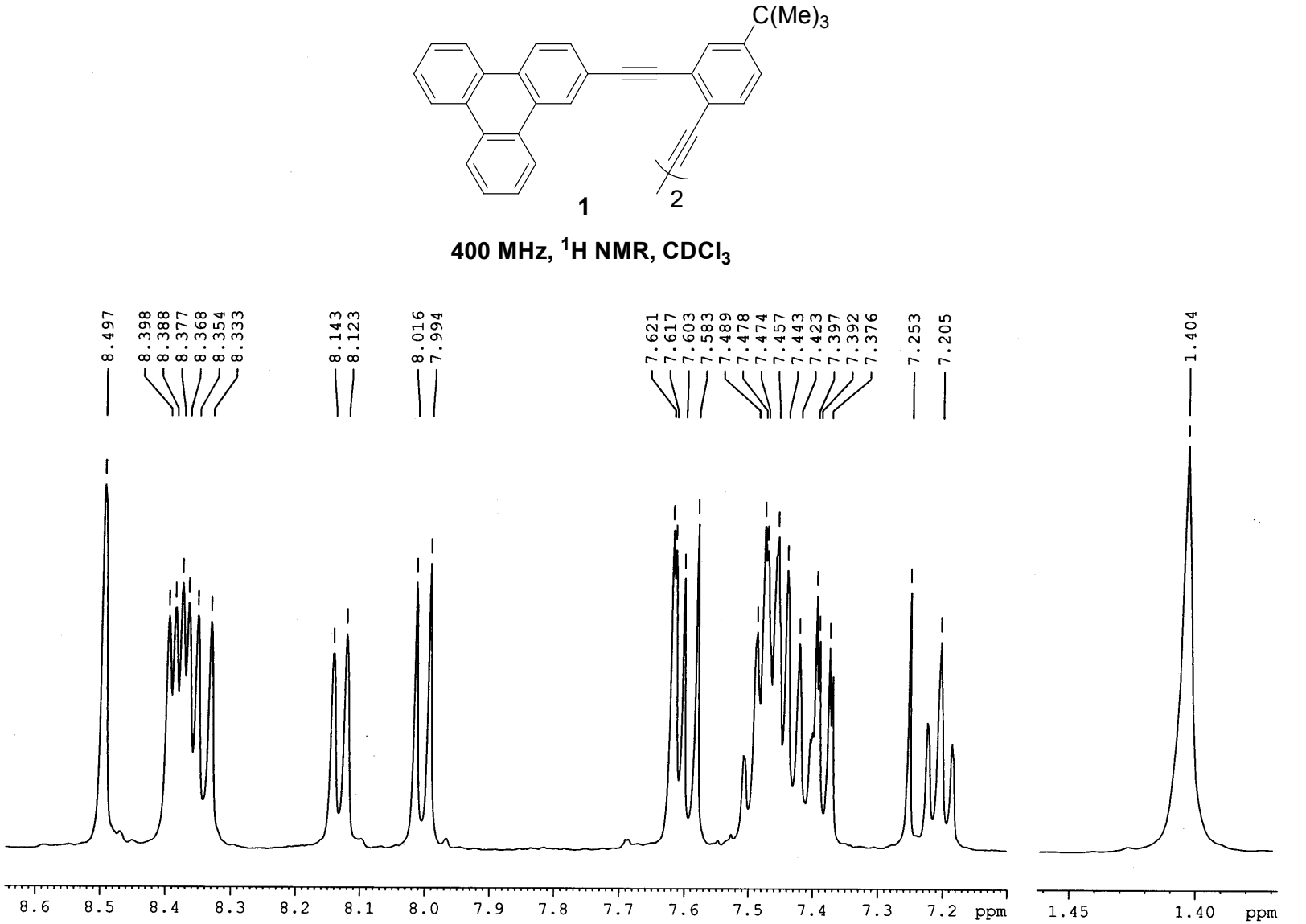


Figure S13. 400 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$. Aromatic region expanded.

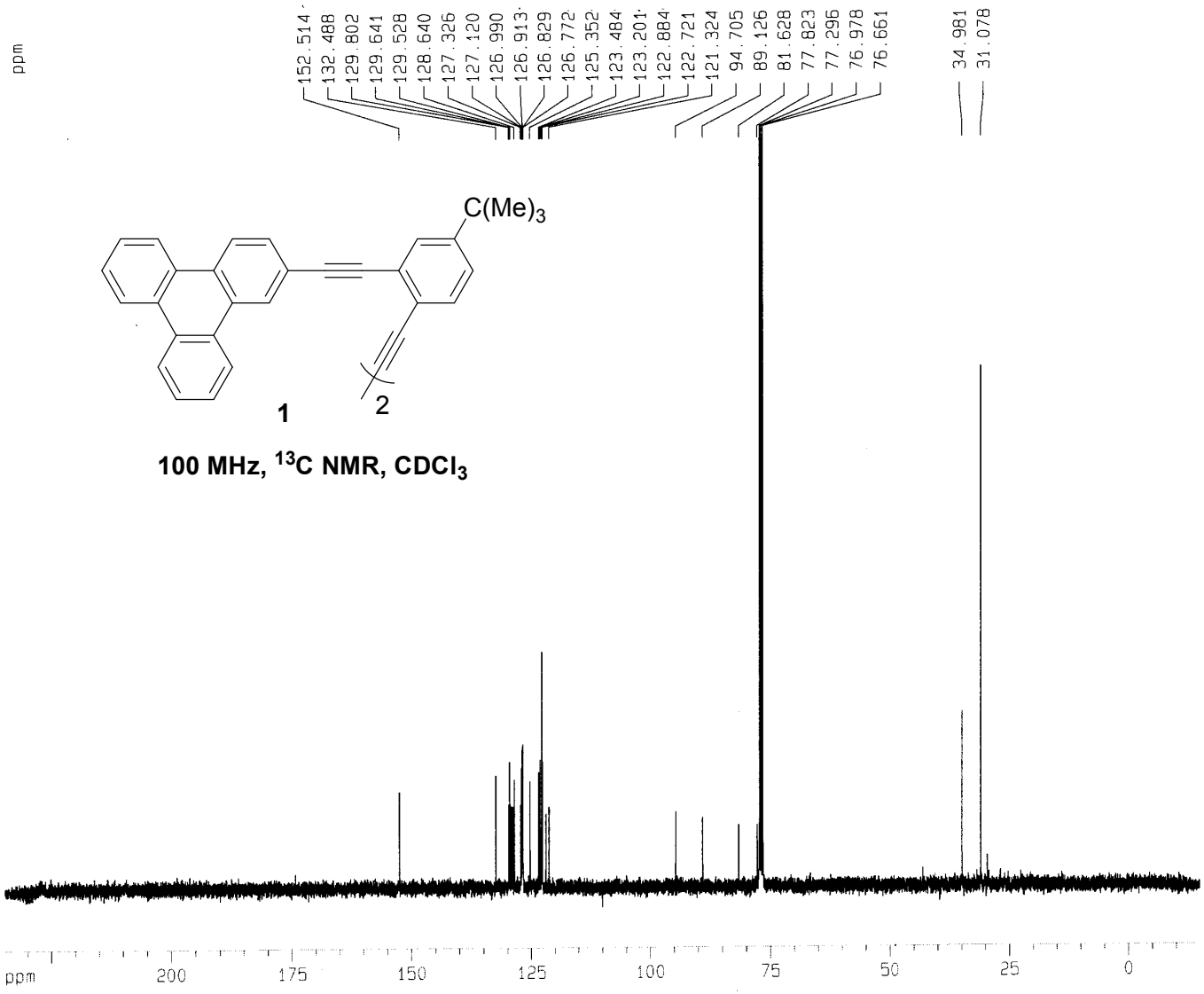


Figure S14. 100 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$

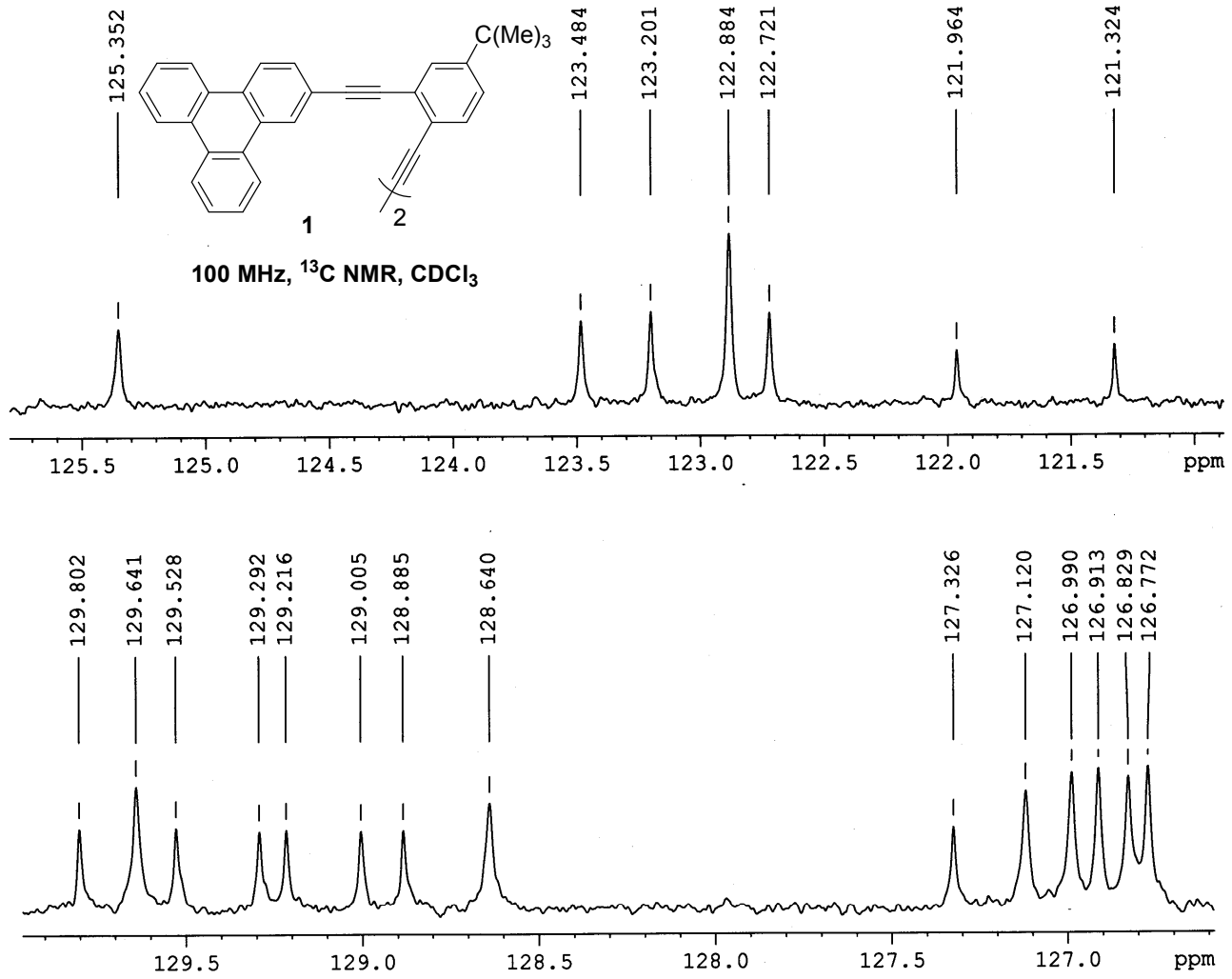


Figure S15. 100 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$. Aromatic region expanded.

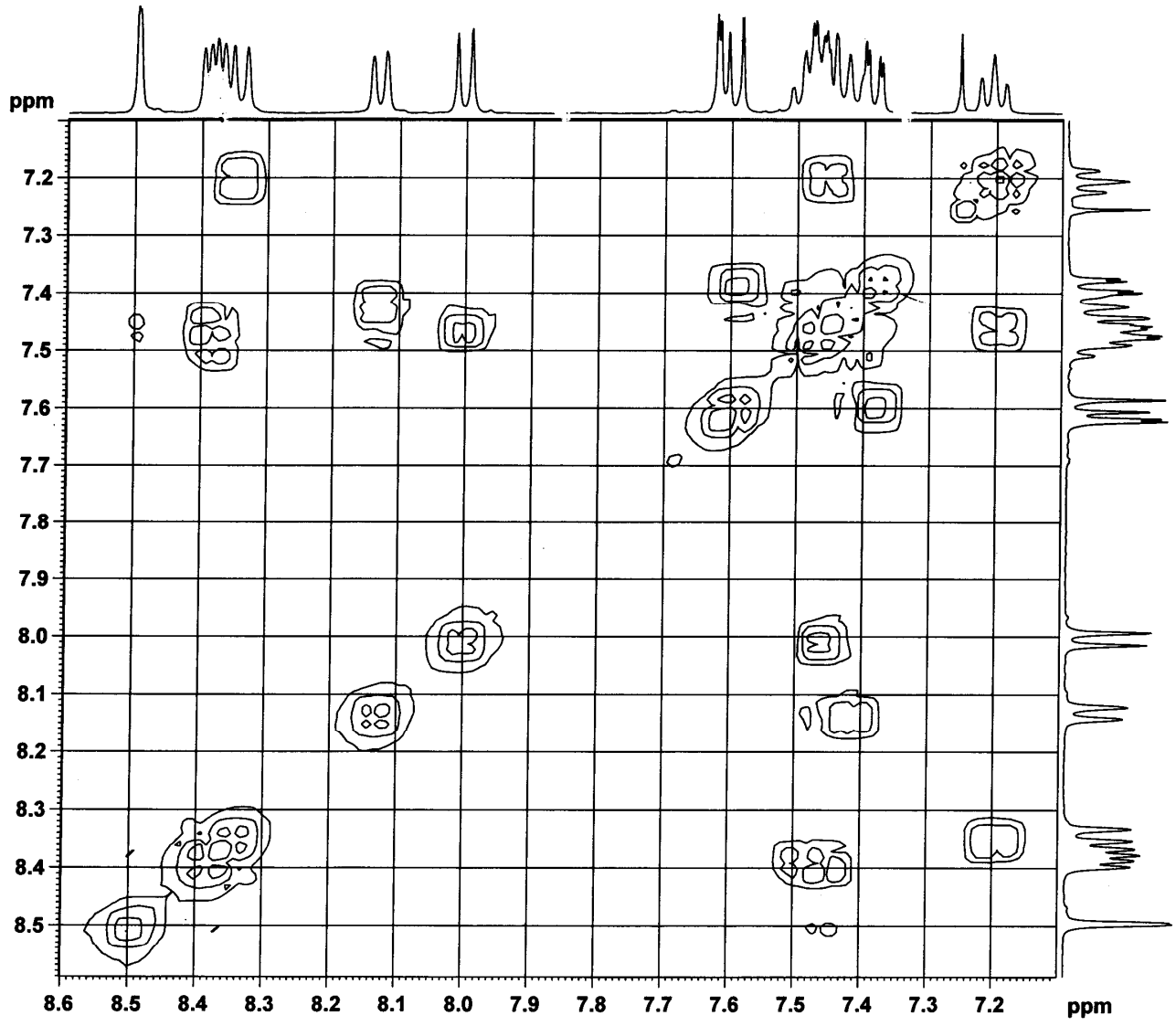


Figure S16. ^{1}H-^{1}H COSY spectrum of **1** in $CDCl_3$.

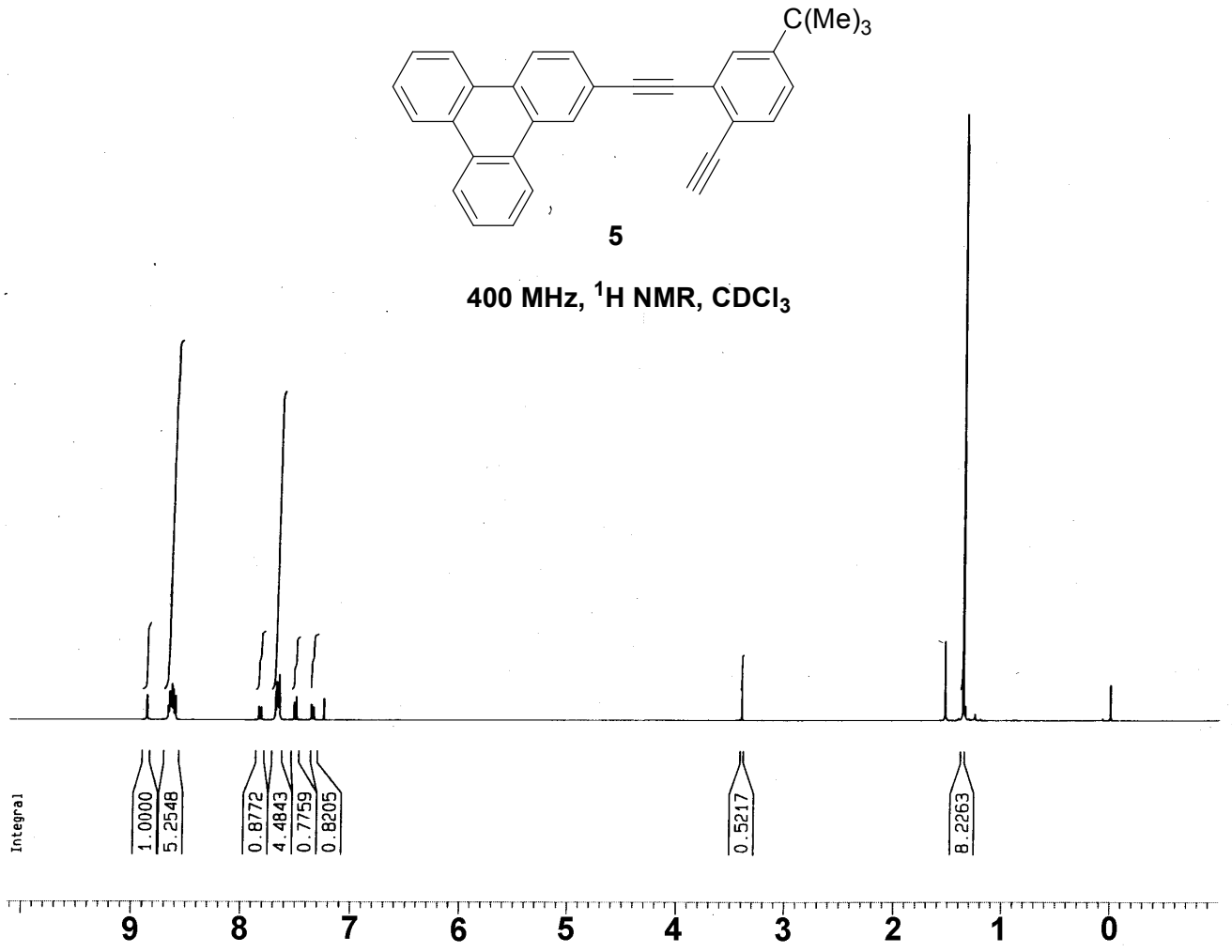


Figure S17. 400 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$.

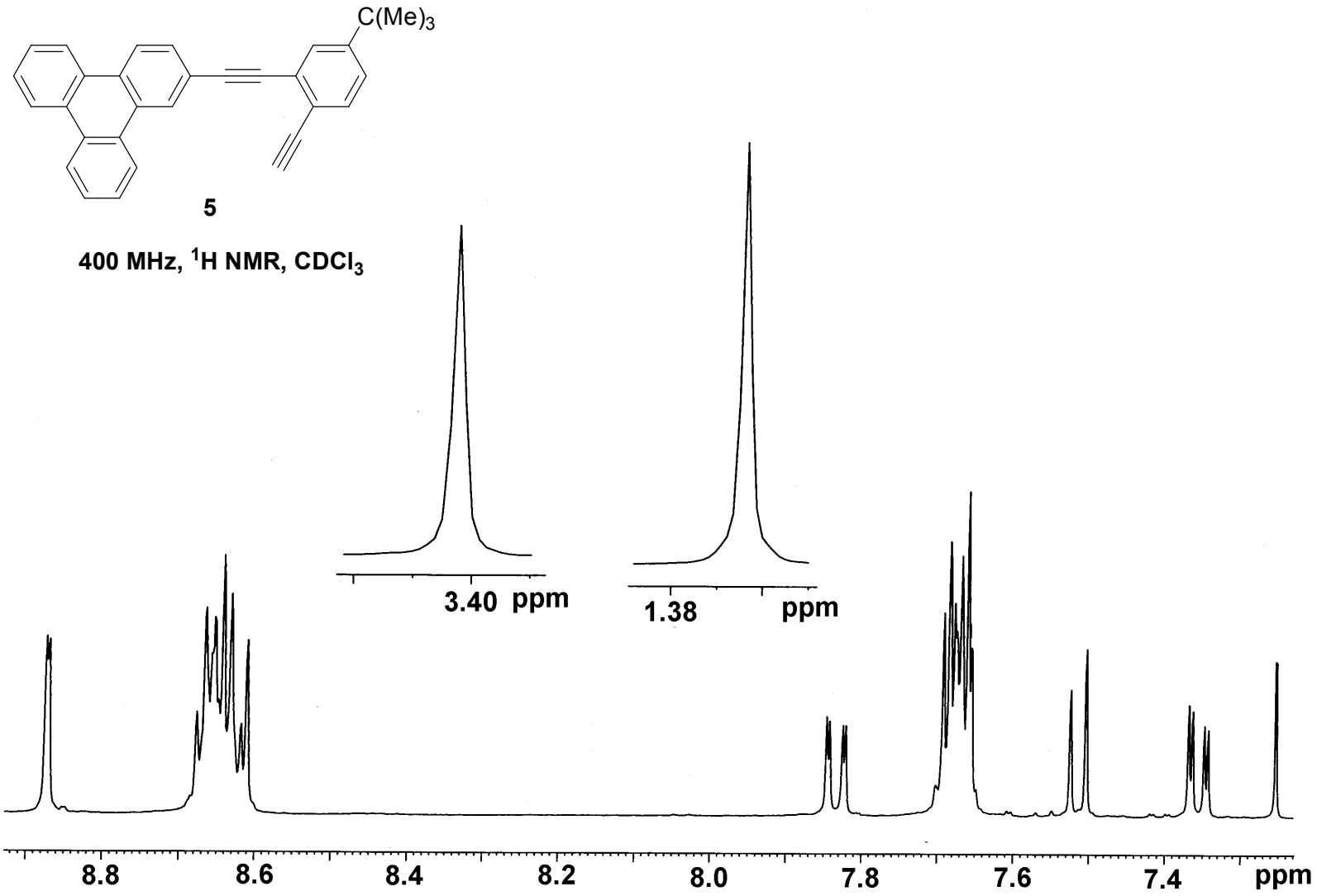


Figure S18. 400 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$. Aromatic region expanded.

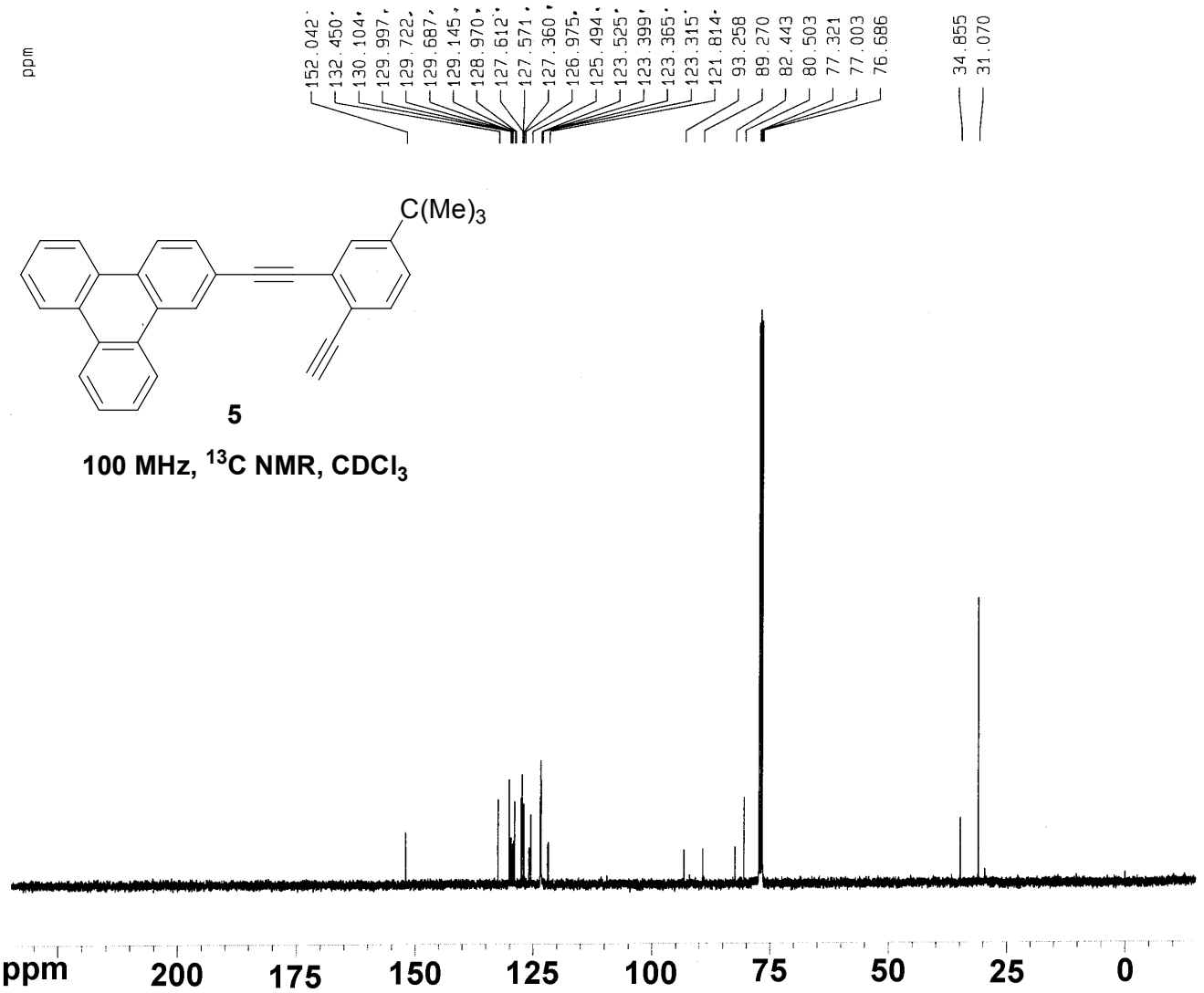


Figure S19. 100 MHz ^{13}C NMR spectrum of **5** in $CDCl_3$.

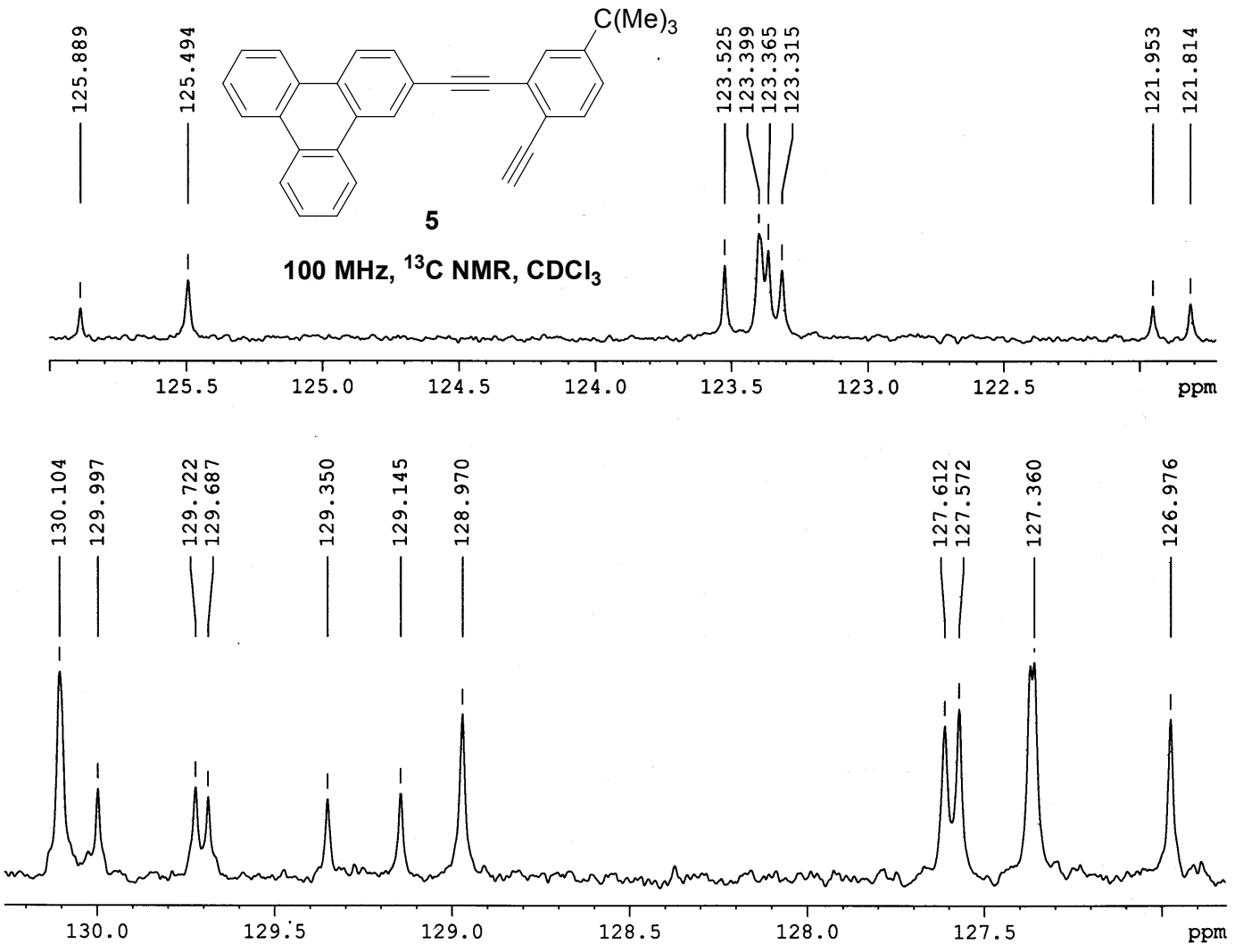


Figure S20. 100 MHz ^{13}C NMR spectrum of **5** in $CDCl_3$. Aromatic region expanded.

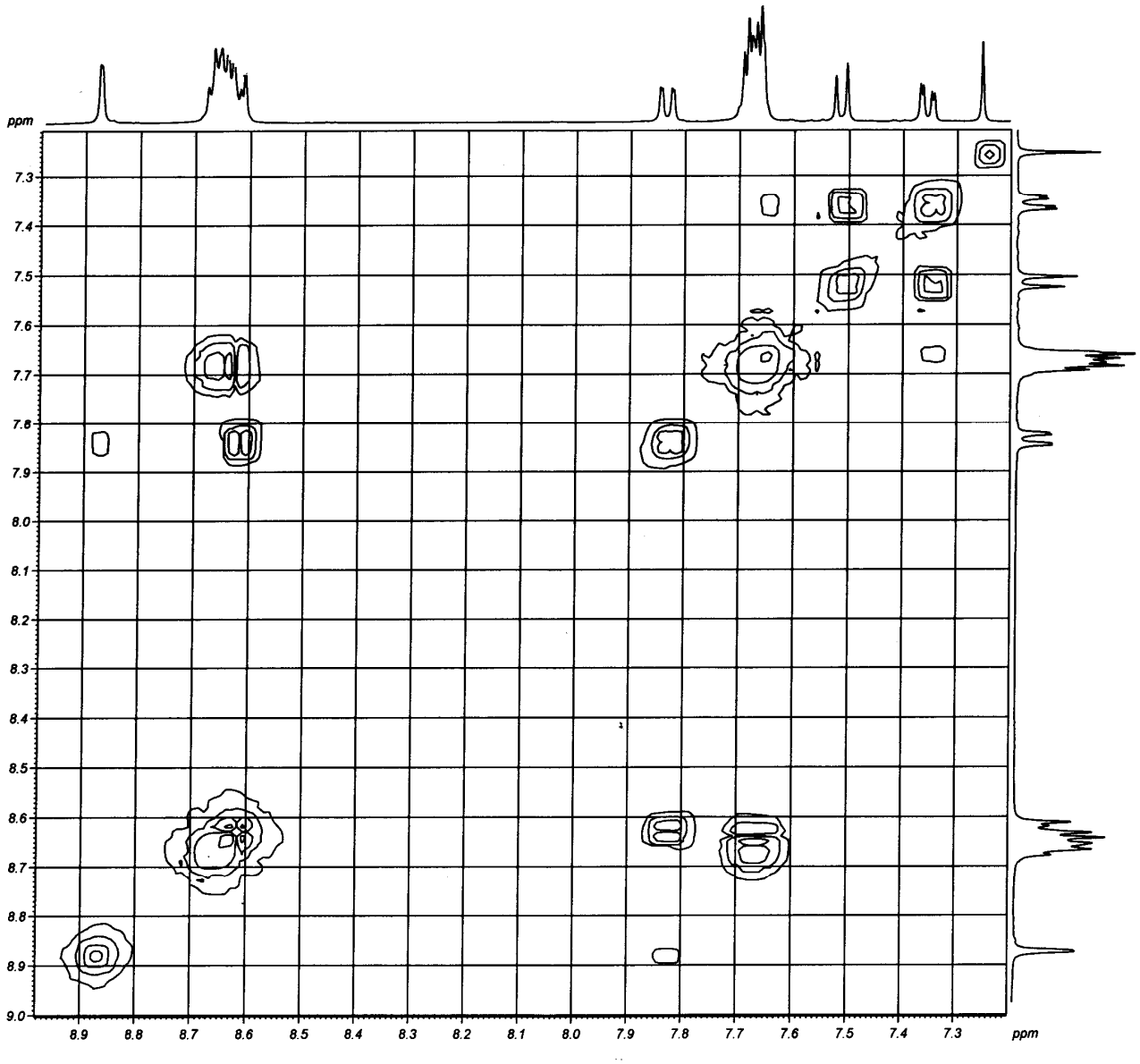


Figure S21. ^{1}H-^{1}H COSY spectrum of **5** in $CDCl_3$.

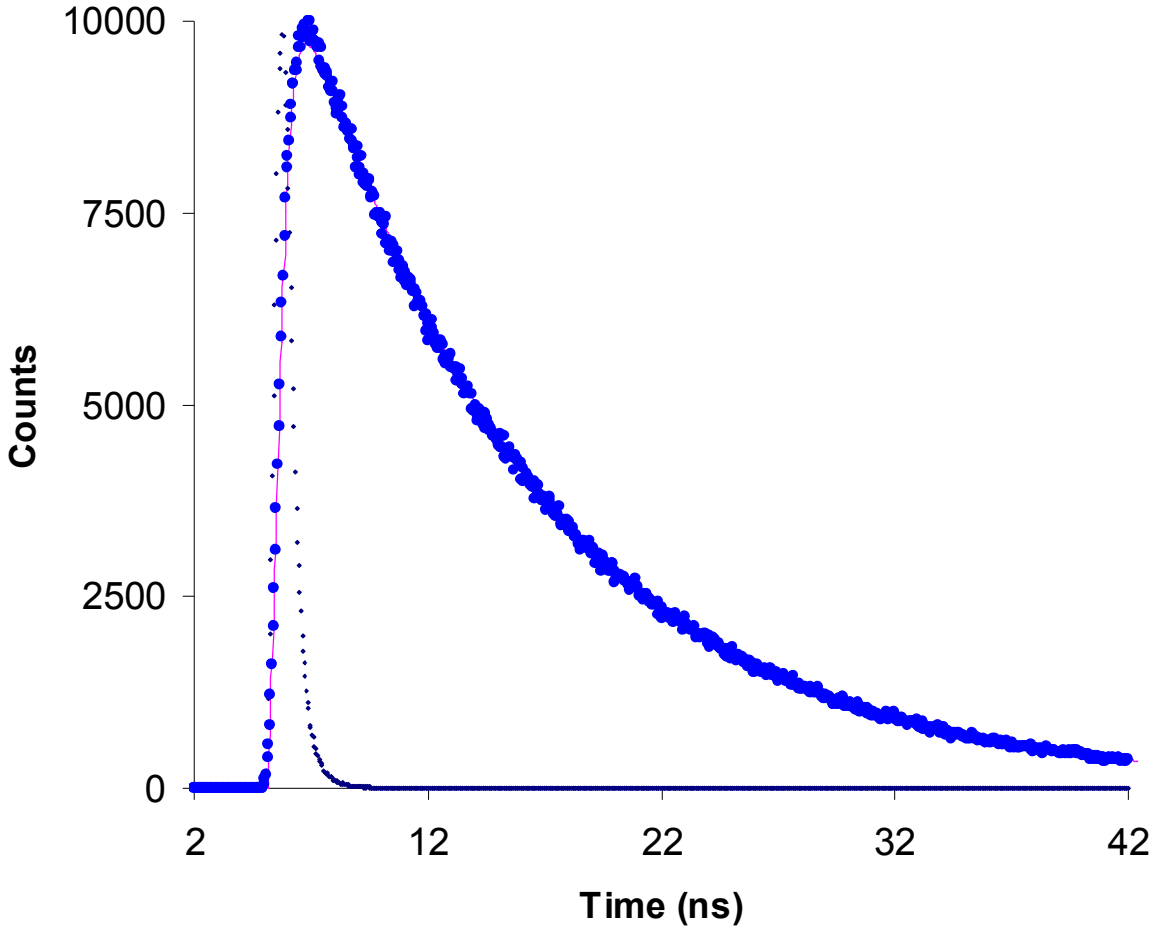


Figure S22. Fluorescence decay of **5** in degassed cyclohexane. Lamp pulse profile (black ++), raw decay data (blue **), single exponential fit (magenta line). λ_{ex} = 340 nm and λ_{obs} = 375 nm. Fluorescence lifetime τ = 10.37 ns, χ^2 = 1.26.

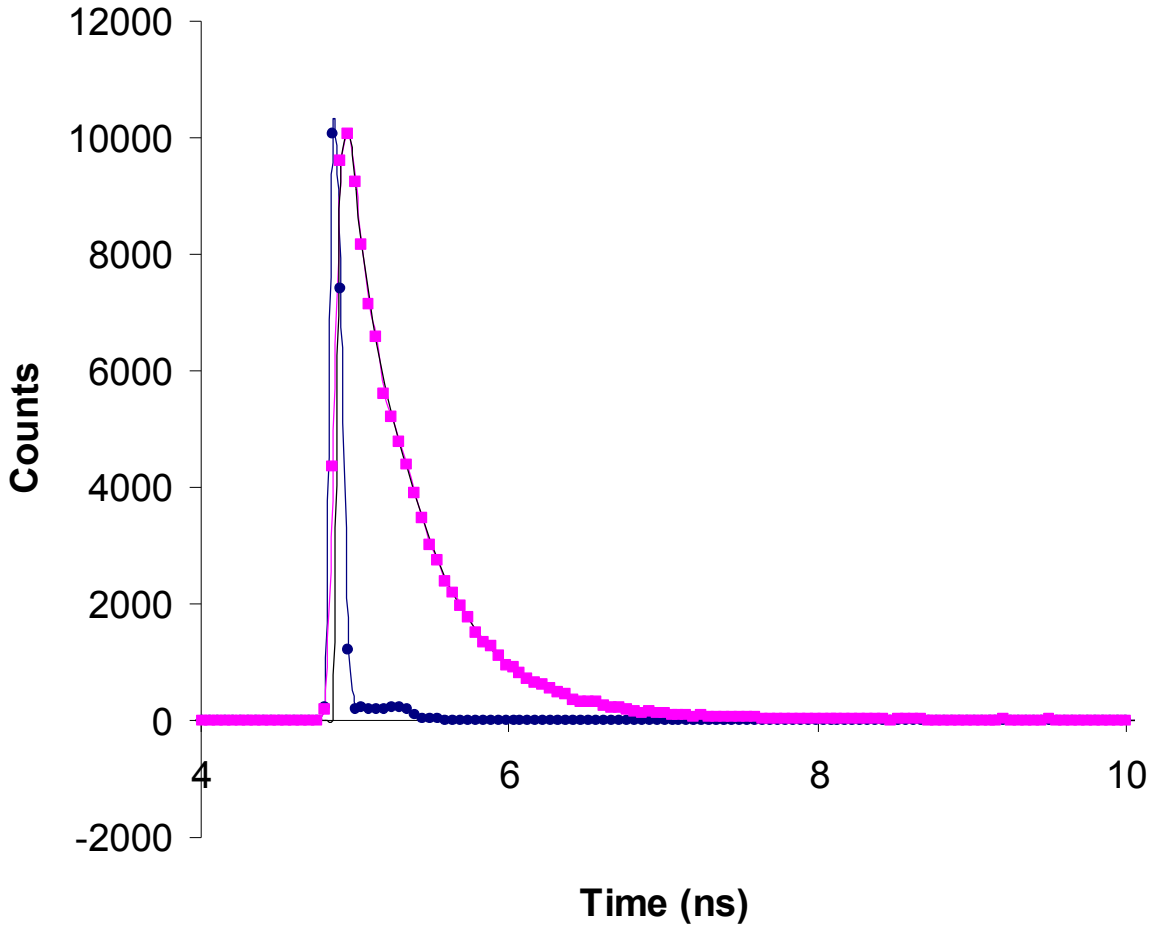


Figure S23. Fluorescence decay of **1** in degassed cyclohexane. Lamp pulse profile (blue *), raw decay data (magenta), bi-exponential fit (black line). λ_{ex} = 340 nm and λ_{obs} = 438 nm. Fluorescence lifetime τ_1 = 0.39 ns and τ_2 = 0.73 ns, χ^2 = 1.19.

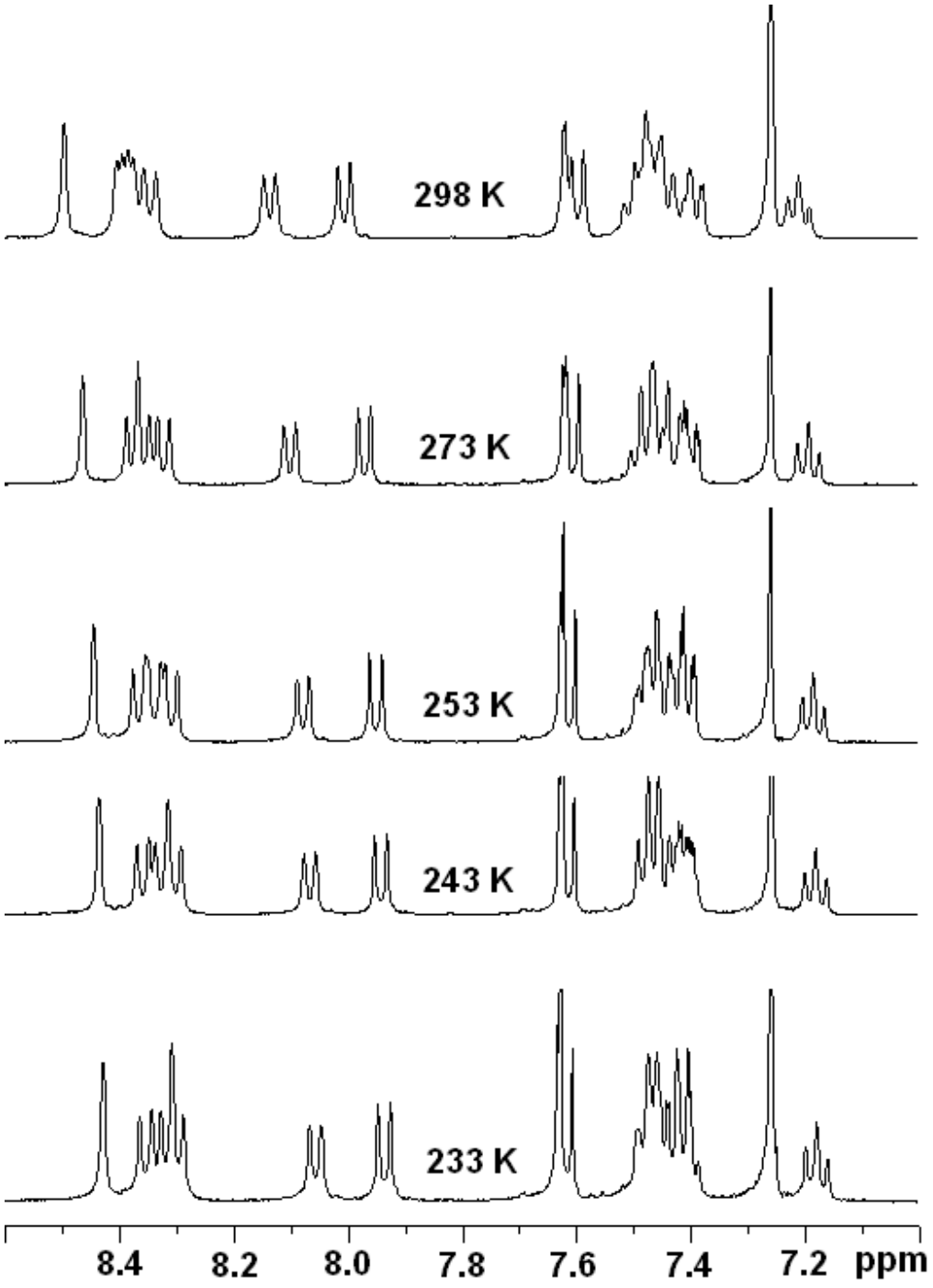
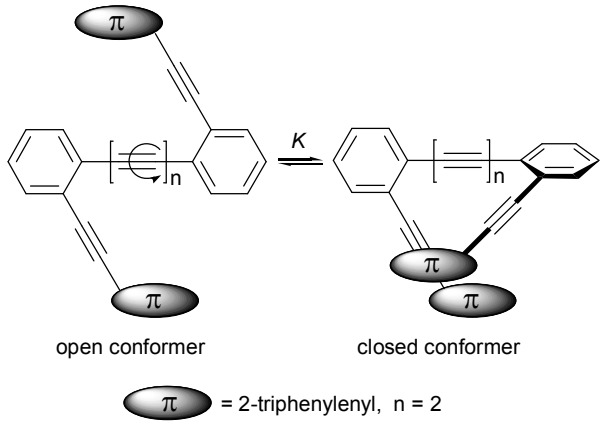


Figure S24. 400 MHz VT ^{1}H NMR of **1** in $CDCl_3$.

Calculation of equilibrium constant and other thermodynamic parameters from the VT NMR data.



For the above equilibrium in solution the observed chemical shift of any triphenylene proton in the NMR spectrum is an average chemical shift of the open and closed forms.

At a given temperature

$$\delta_{av} = X_o\delta_o + X_c\delta_c$$

Where δ_{av} is the observed chemical shift, δ_o is the chemical shift for open conformer and δ_c is the chemical shift for closed conformer. X_o and X_c are the mole fractions of the open and closed forms, respectively. The chemical shift of H1 proton of the model compound **6** was taken as δ_o (8.96 ppm) and the chemical shift of H1 of **1** at 233 K was taken as the chemical shift of H1 in the closed form (8.43 ppm). Since the chemical shifts were independent of temperature below 253 K, it is presumed that the equilibrium is shifted to far right such that the predominant species in solution at that temperature is only the closed form.

Therefore at 298 K

$$\delta_{av} = X_o\delta_o + X_c\delta_c$$

$$\delta_{av} = X_o\delta_o + (1\text{-}X_o)\delta c$$

$$8.50 = X_o(8.96) + (1\text{-}X_o)(8.43)$$

$$X_o = 0.13 \text{ and } X_c = 0.86$$

$$K = X_c/X_0 = 0.86/0.13 = 6.6$$

From the VT NMR data the equilibrium constant K at various temperature was calculated which are shown in Table S1.

Table S1. Data obtained from VT NMR and used in van't Hoff plot

T (K)	*K*	lnK(M^{-1})	1000/T
263	15.67	2.752	3.802
273	12.25	2.505	3.662
298	6.57	1.882	3.356
328	3.82	1.340	3.049
348	3.08	1.125	2.873
388	1.94	0.663	2.577

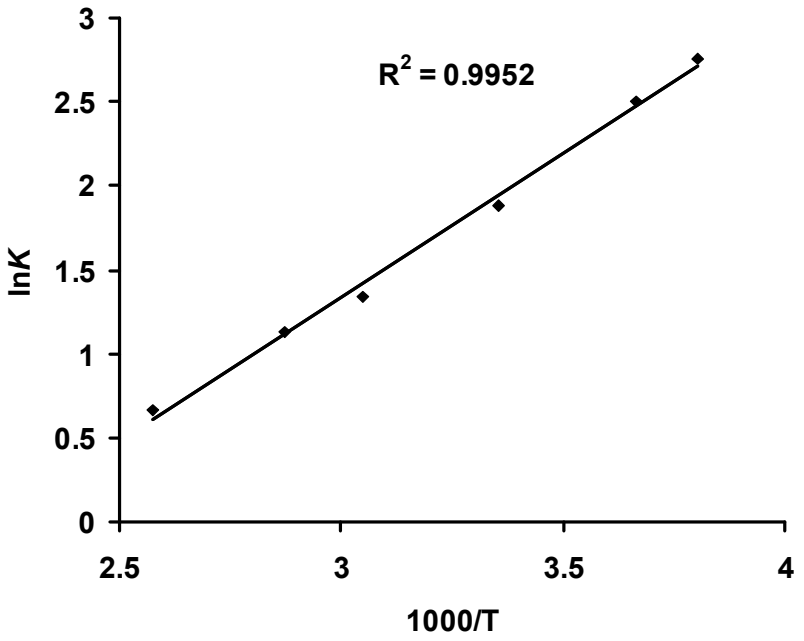


Figure S25. van't Hoff plot for the equilibrium of **1** between open and closed forms.

From the van't Hoff's plot of ln(*K*) vs (1000/T) a straight line was obtained.

Slope = - (ΔH/1000R) = 1.721.

Therefore, $\Delta H = - (1.721 \times 1000 \times 1.987)$ cal mol^{-1}
$= - 3.42$ kcal $mol^{-1} = -14.2$ kJ mol^{-1}

$\Delta G = -RT\ln(K)$

At 298 K, $\Delta G = - 1.987 \times 298 \times (\ln 6.57)$ cal mol^{-1}

$= - 1.114$ kcal $mol^{-1} = -4.6$ kJ mol^{-1}

$\Delta G = \Delta H - T\Delta S$

Substituting the values of ΔG, ΔH and T = 298 K

$\Delta S = -7.74$ cal $mol^{-1} = -32.2$ kJ mol^{-1} K^{-1}

Measurement of quantum yield of fluorescence:

Fluorescence quantum yields (ϕ_f) were measured in degassed cyclohexane using 9.10-diphenylanthracene as a reference sample as described by Lakowicz. The ϕ_f of 9,10-diphenylanthracene is 0.95 in cyclohexane. (Lakowicz, J. R., Principles of Fluorescence Spectroscopy, 2nd edition, Kluwer Academic, New York, 1999, pp 52-53).