Electronic Supplementary Information for:

Structurally and Electronically Modulated Spin Interaction of Transient Biradicals in Two Photon-Gated Stepwise Photochromism

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1. ^{1}H NMR Spectra

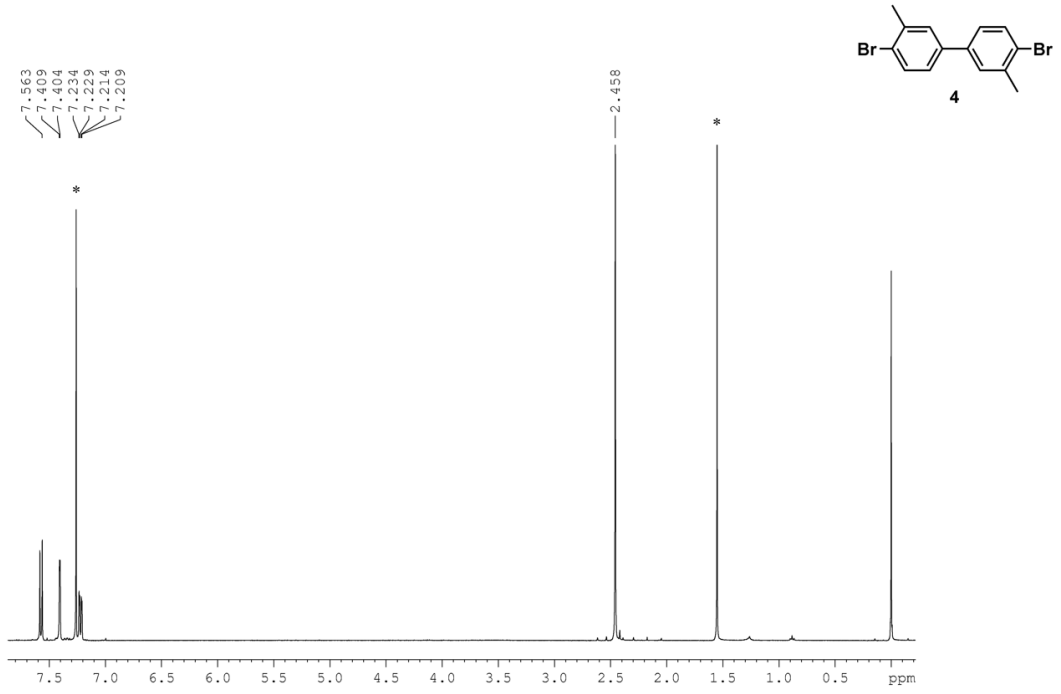

Fig. S1. ^{1}H NMR spectrum of **4** in $CDCl_3$ (* solvent peaks).

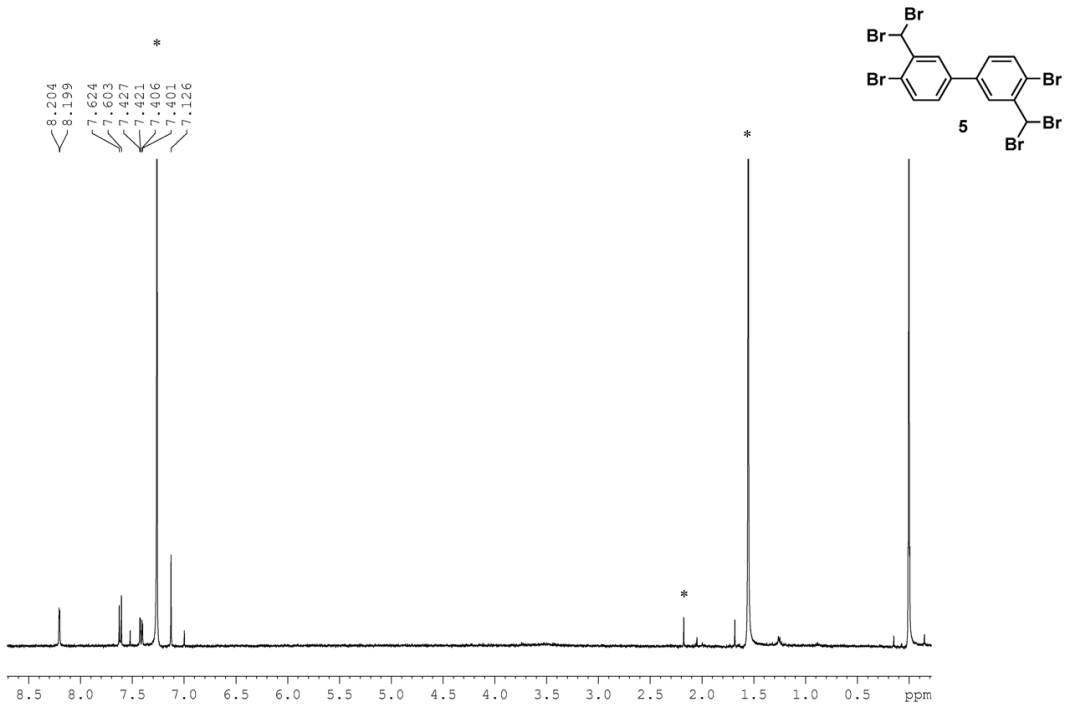

Fig. S2. ^{1}H NMR spectrum of **5** in $CDCl_3$ (* solvent peaks).

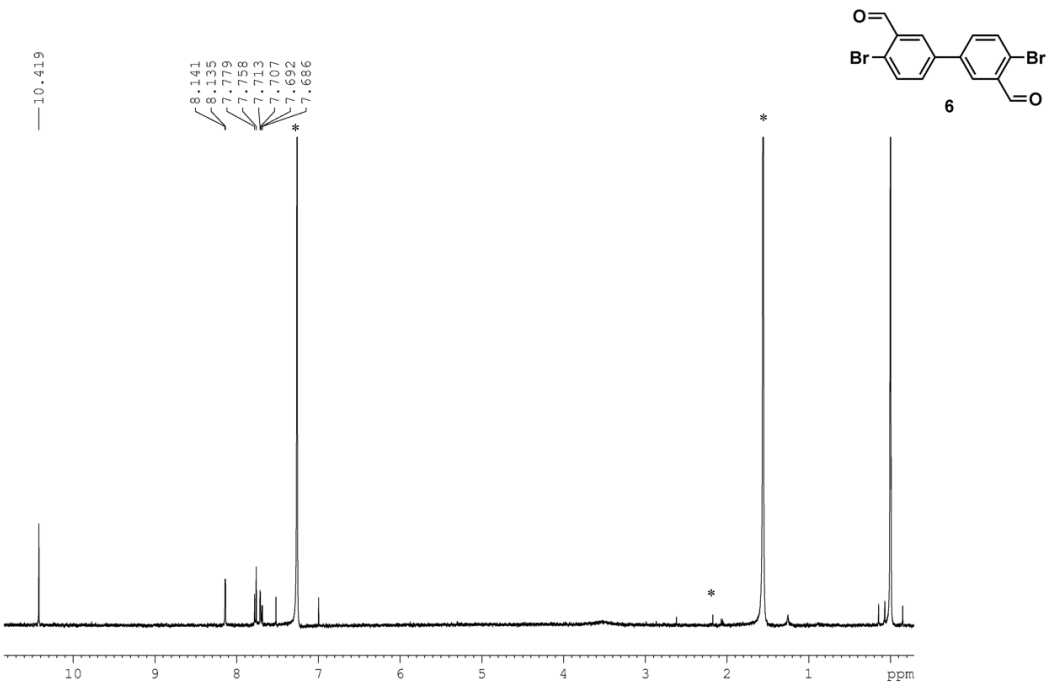

Fig. S3. ^{1}H NMR spectrum of **6** in $CDCl_3$ (***** solvent peaks).

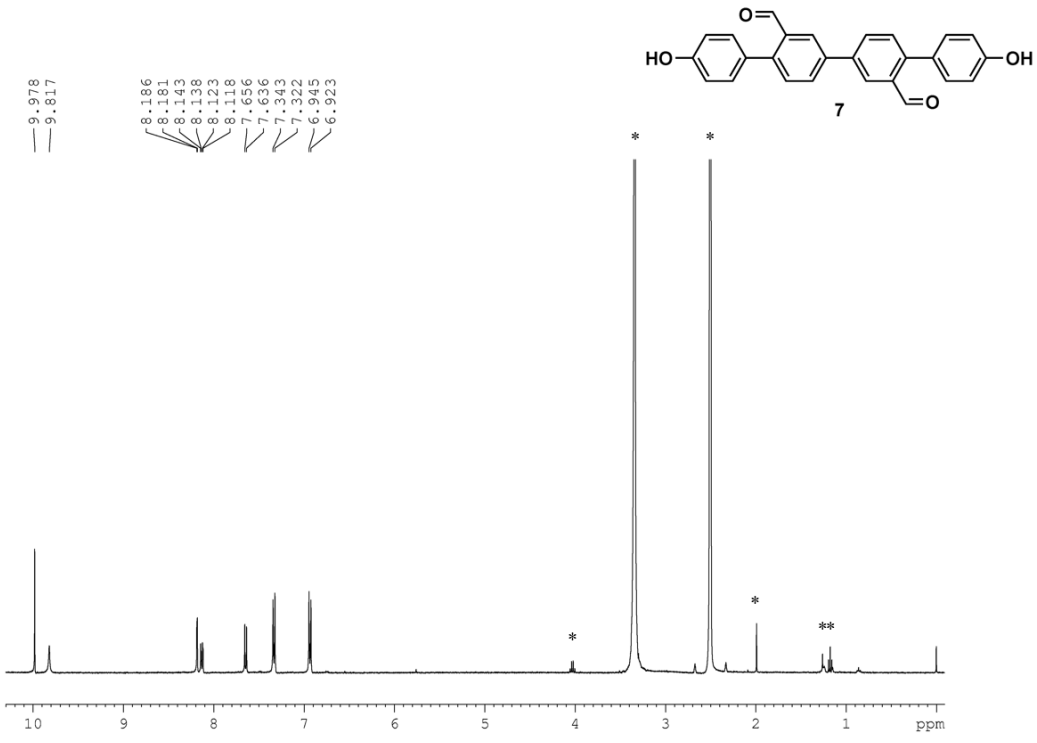

Fig. S4. ^{1}H NMR spectrum of **7** in DMSO–d_6 (***** solvent peaks).

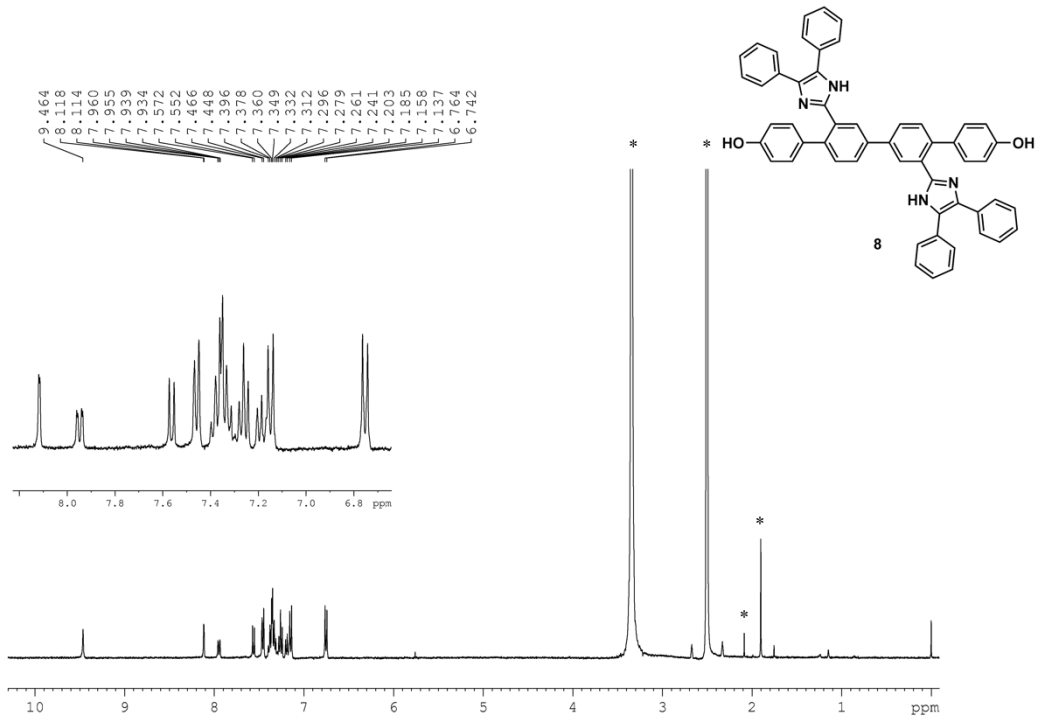

Fig. S5. [1]H NMR spectrum of **8** in DMSO–d_6 (* solvent peaks).

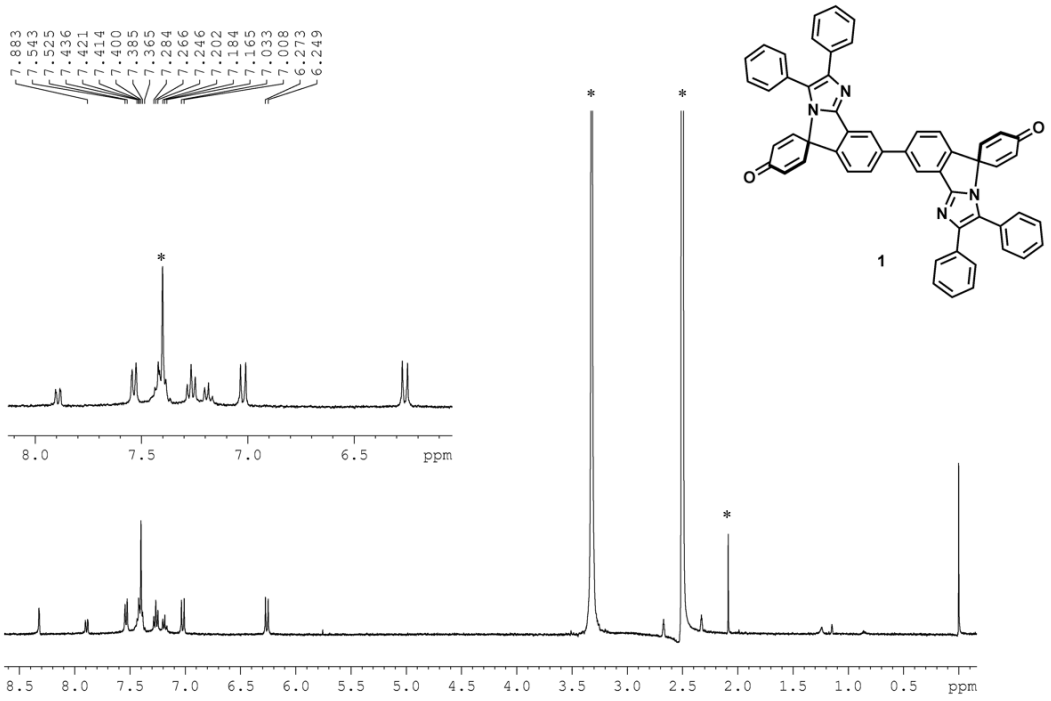

Fig. S6. [1]H NMR spectrum of **1** in DMSO–d_6 (* solvent peaks).

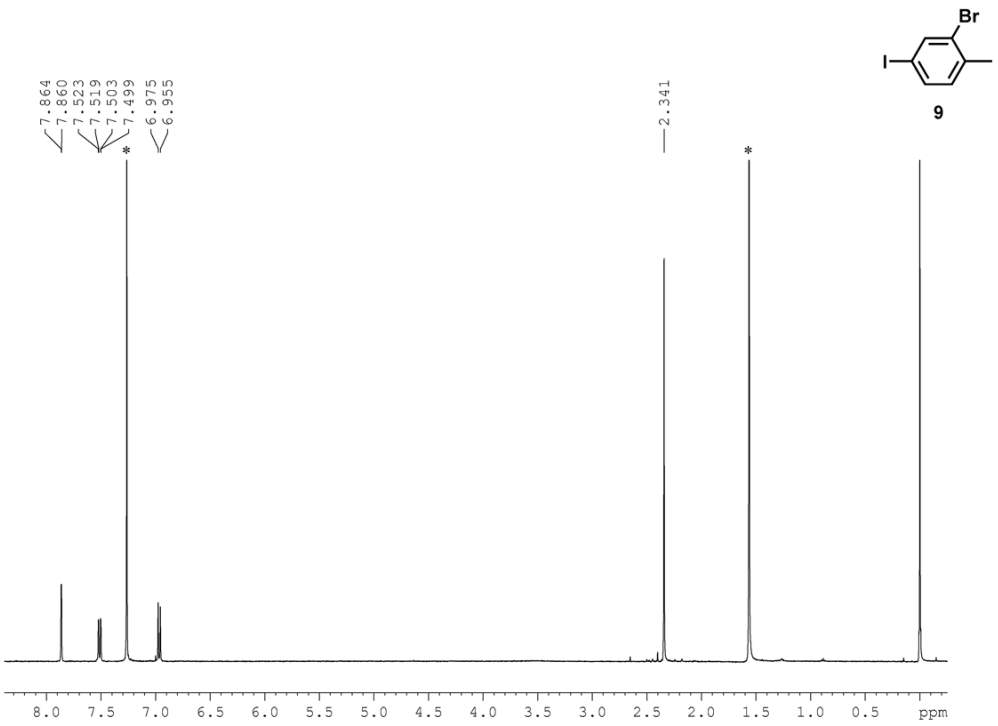

Fig. S7. ^{1}H NMR spectrum of **9** in $CDCl_3$ (* solvent peaks).

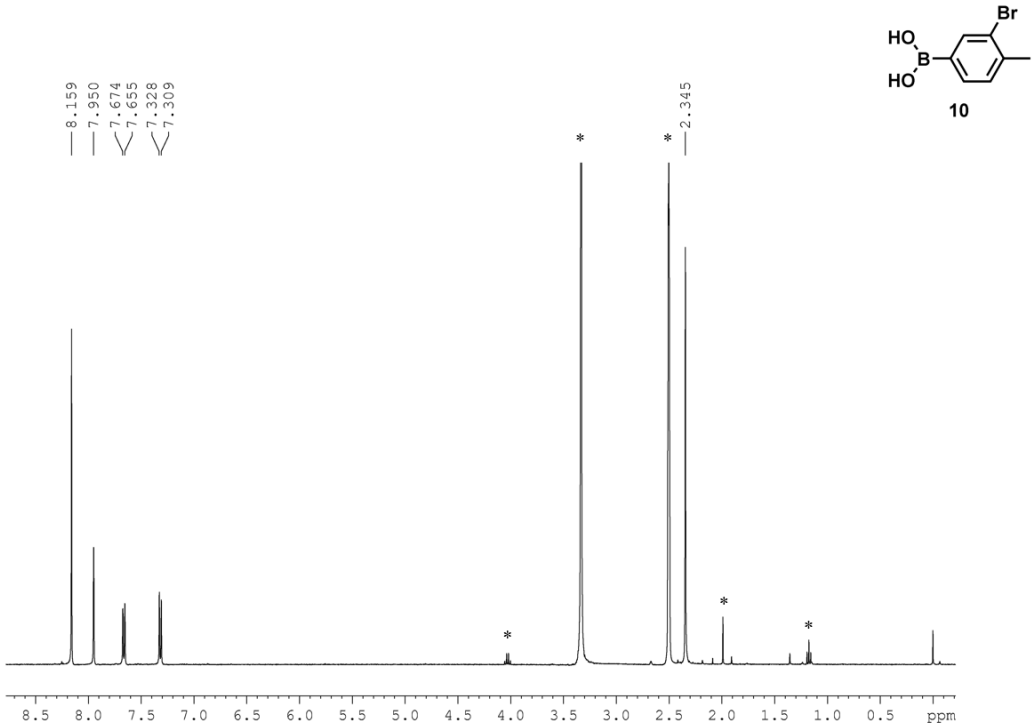

Fig. S8. ^{1}H NMR spectrum of **10** in DMSO–d_6 (* solvent peaks).

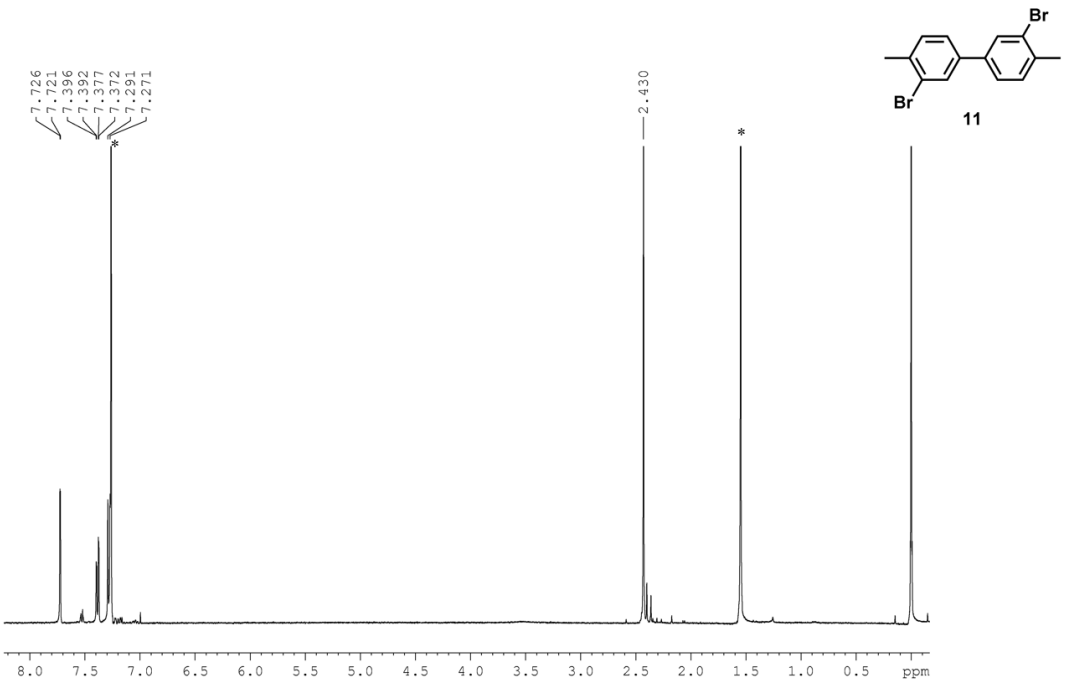

Fig. S9. ^{1}H NMR spectrum of **11** in $CDCl_3$ (* solvent peaks).

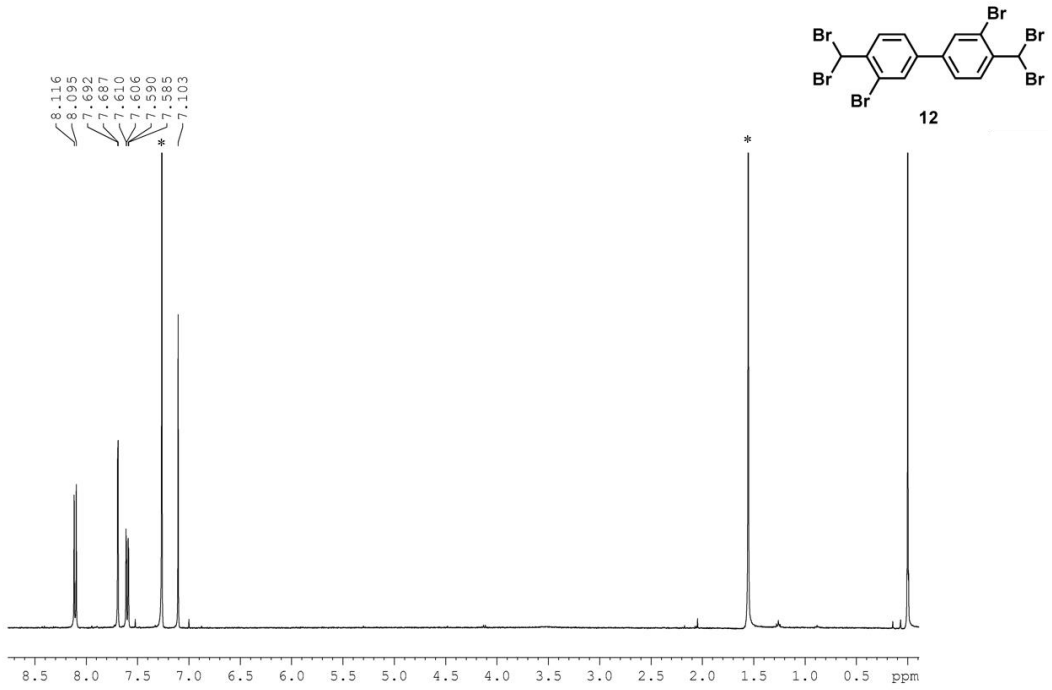

Fig. S10. ^{1}H NMR spectrum of **12** in $CDCl_3$ (* solvent peaks).

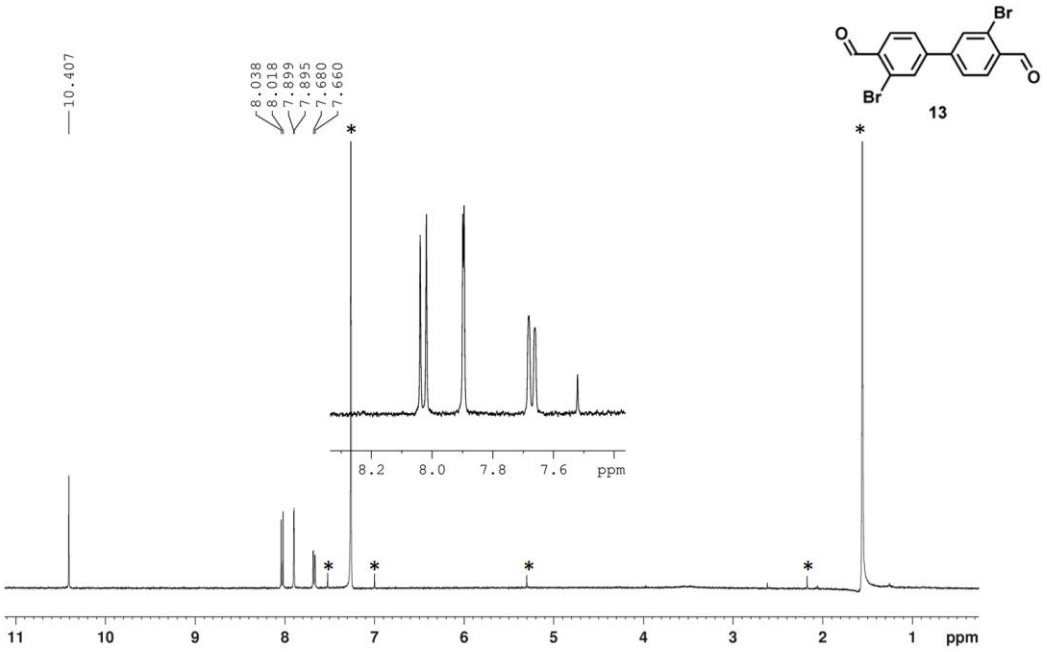

Fig. S11. ^{1}H NMR spectrum of **13** in $CDCl_3$ (* solvent peaks).

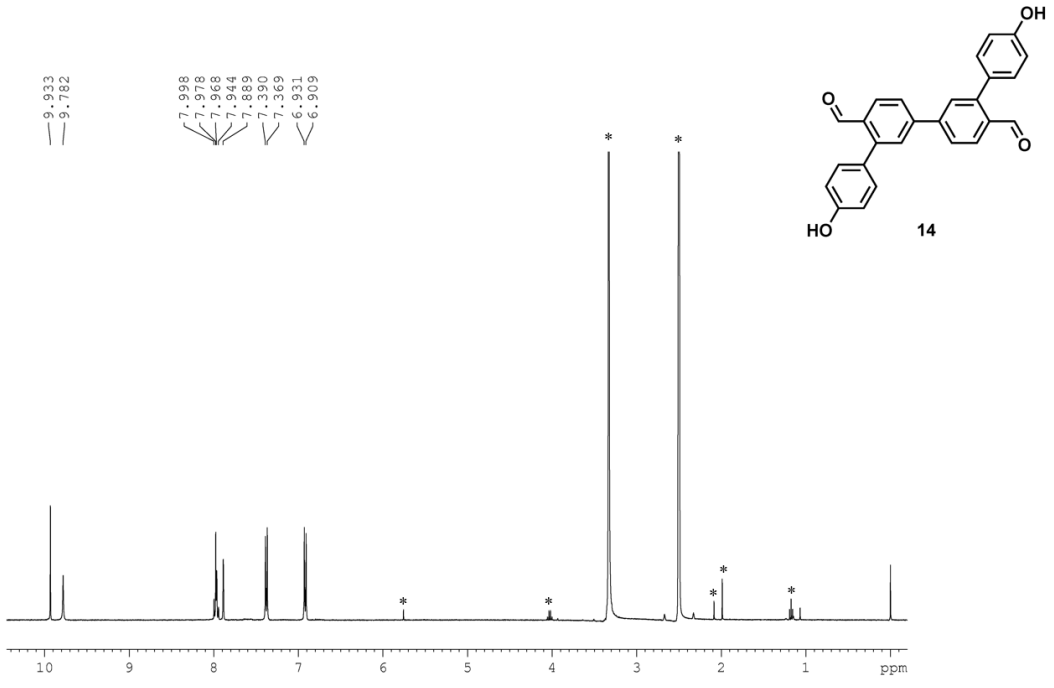

Fig. S12. ^{1}H NMR spectrum of **14** in DMSO–d_6 (* solvent peaks).

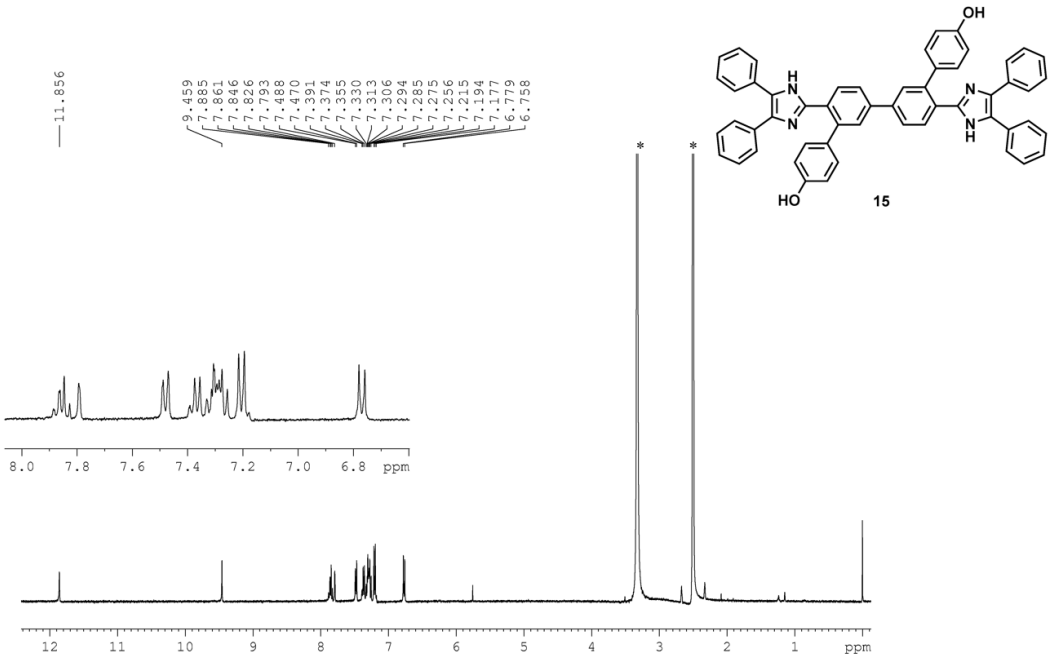

Fig. S13. [1]H NMR spectrum of **15** in DMSO–d_6 (* solvent peaks).

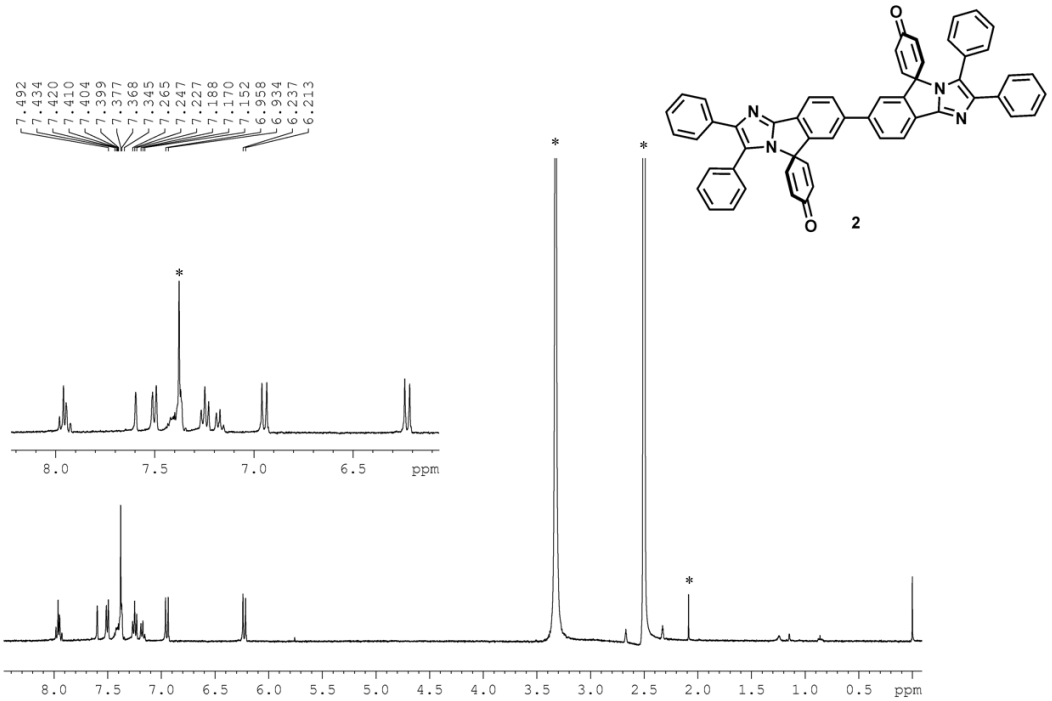

Fig. S14. [1]H NMR spectrum of **2** in DMSO–d_6 (* solvent peaks).

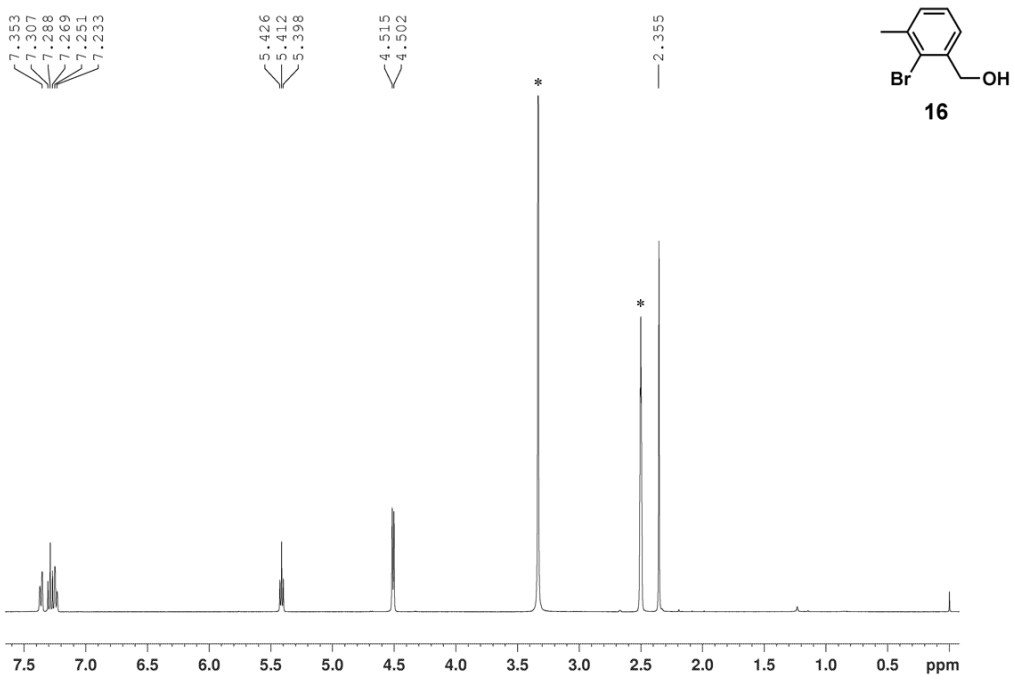

Fig. S15. ^{1}H NMR spectrum of **16** in DMSO–d_6 (* solvent peaks).

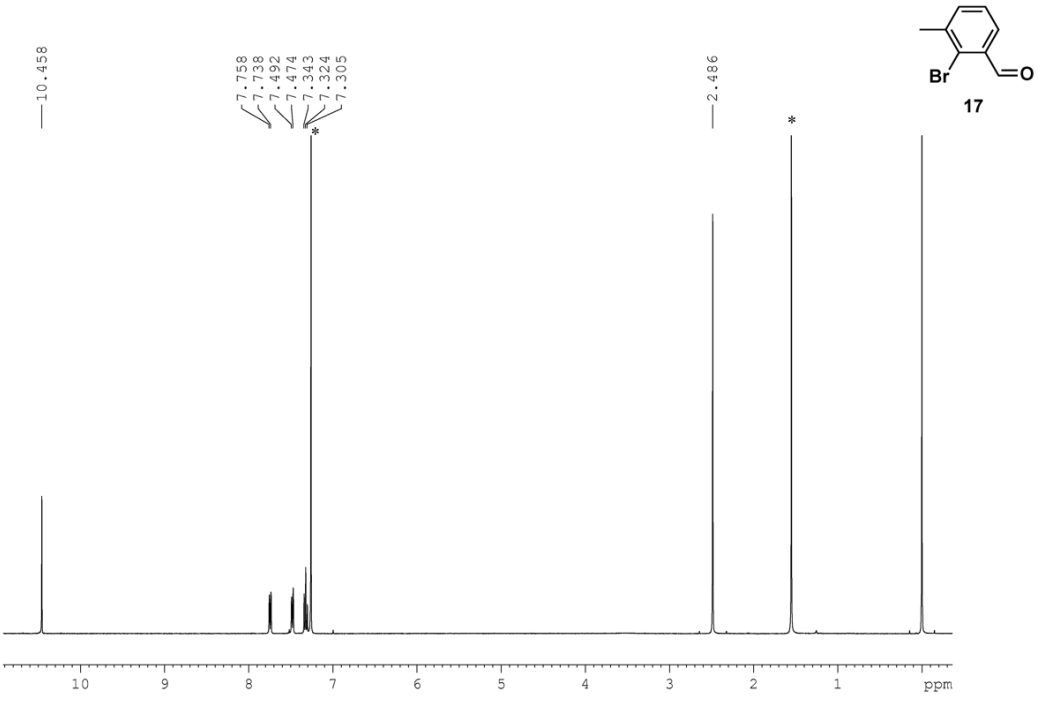

Fig. S16. ^{1}H NMR spectrum of **17** in $CDCl_3$ (* solvent peaks).

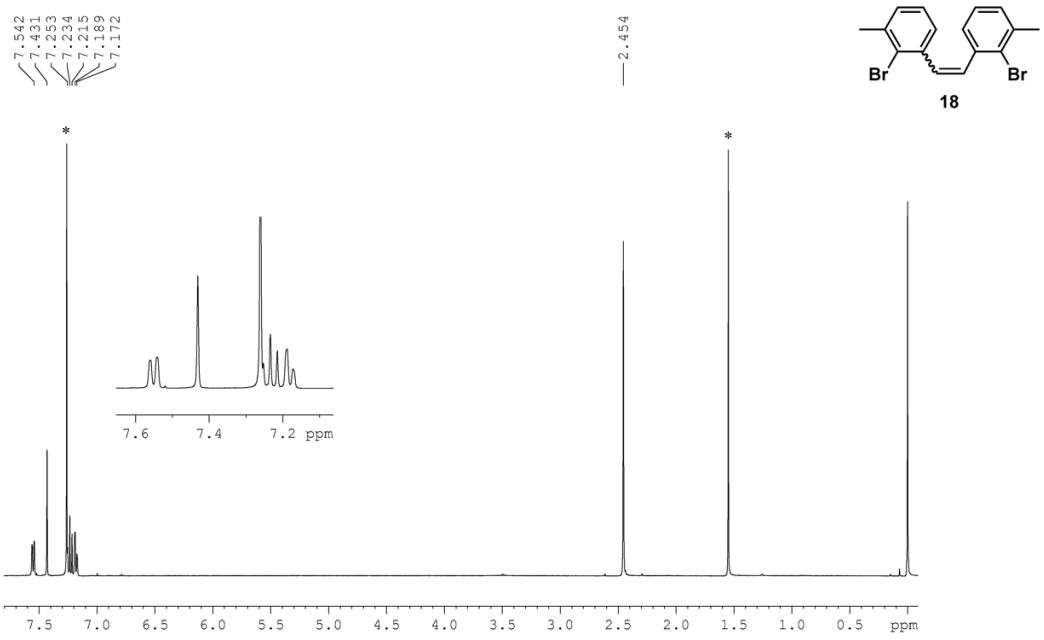

Fig. S17. ^{1}H NMR spectrum of **18** in $CDCl_3$ (* solvent peaks).

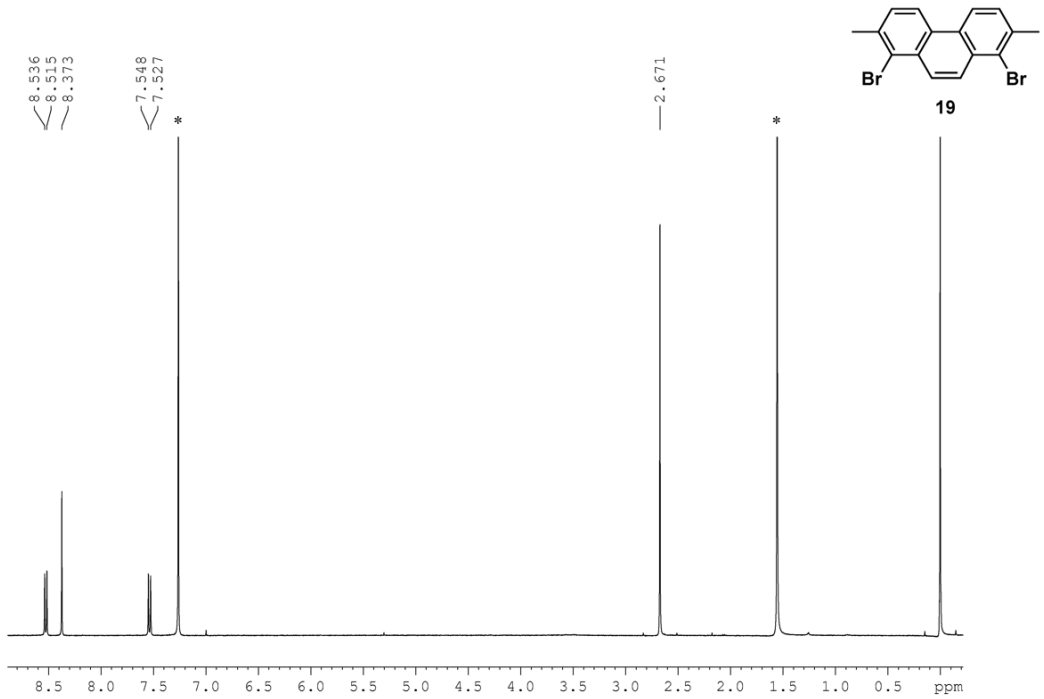

Fig. S18. ^{1}H NMR spectrum of **19** in $CDCl_3$ (* solvent peaks).

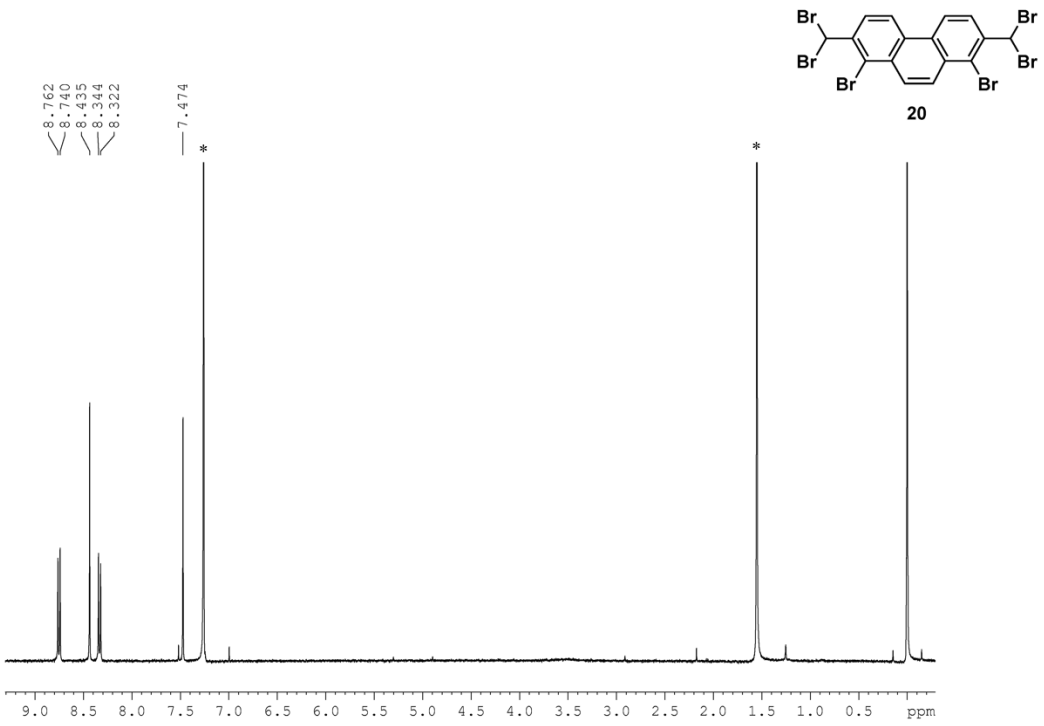

Fig. S19. ^{1}H NMR spectrum of **20** in $CDCl_3$ (* solvent peaks).

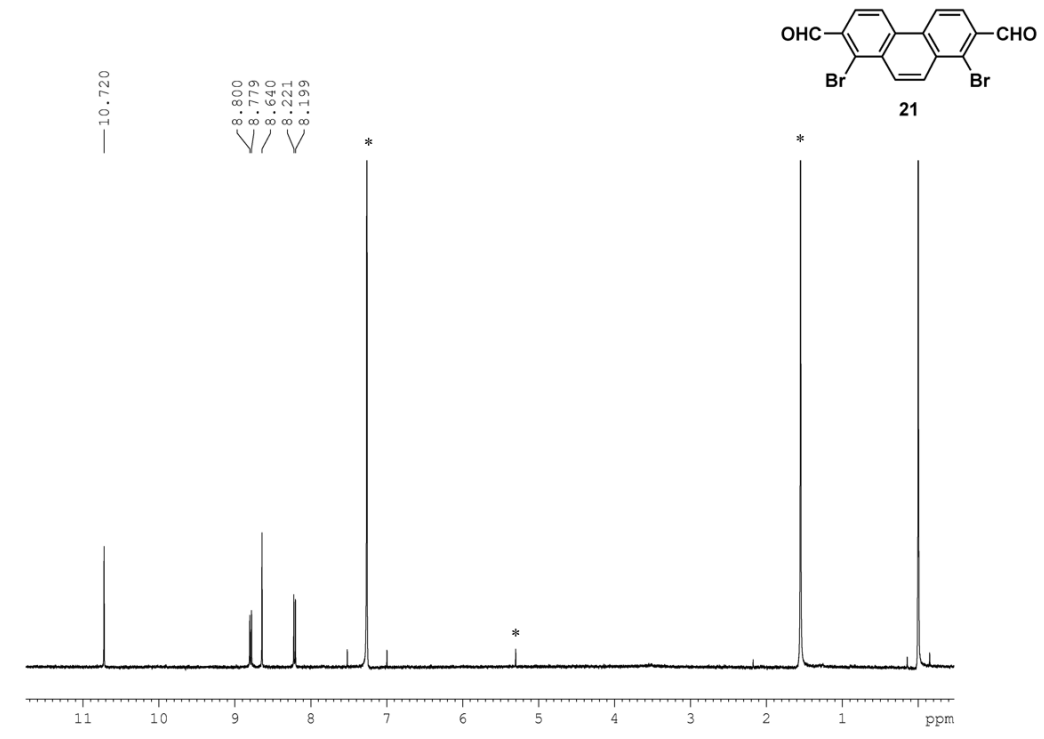

Fig. S20. ^{1}H NMR spectrum of **21** in $CDCl_3$ (* solvent peaks).

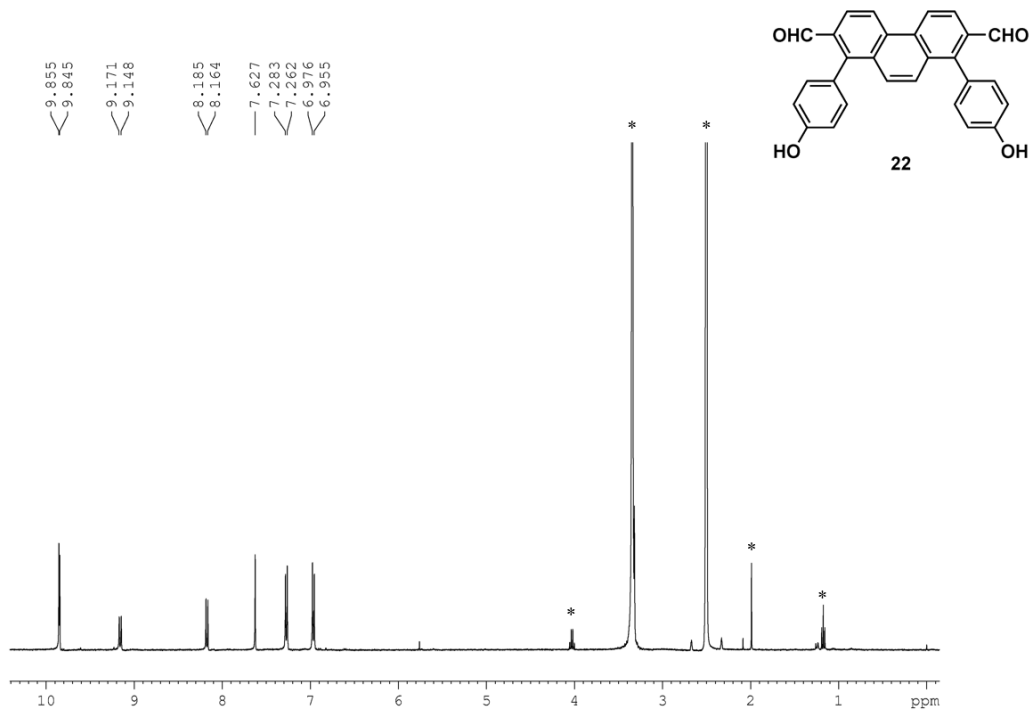

Fig. S21. [1]H NMR spectrum of **22** in DMSO–d_6 (* solvent peaks).

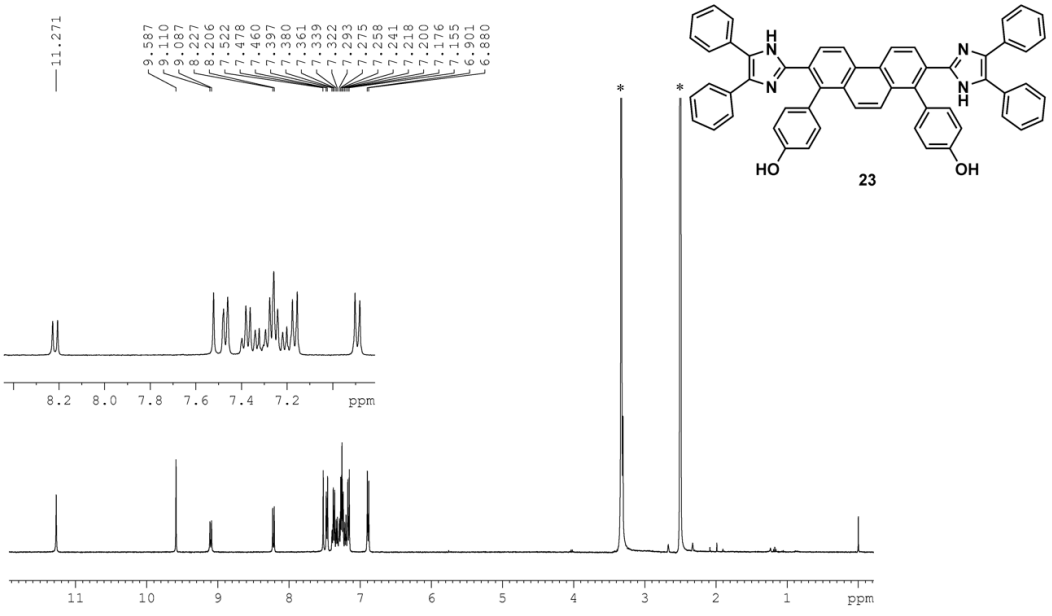

Fig. S22. [1]H NMR spectrum of **23** in DMSO–d_6 (* solvent peaks).

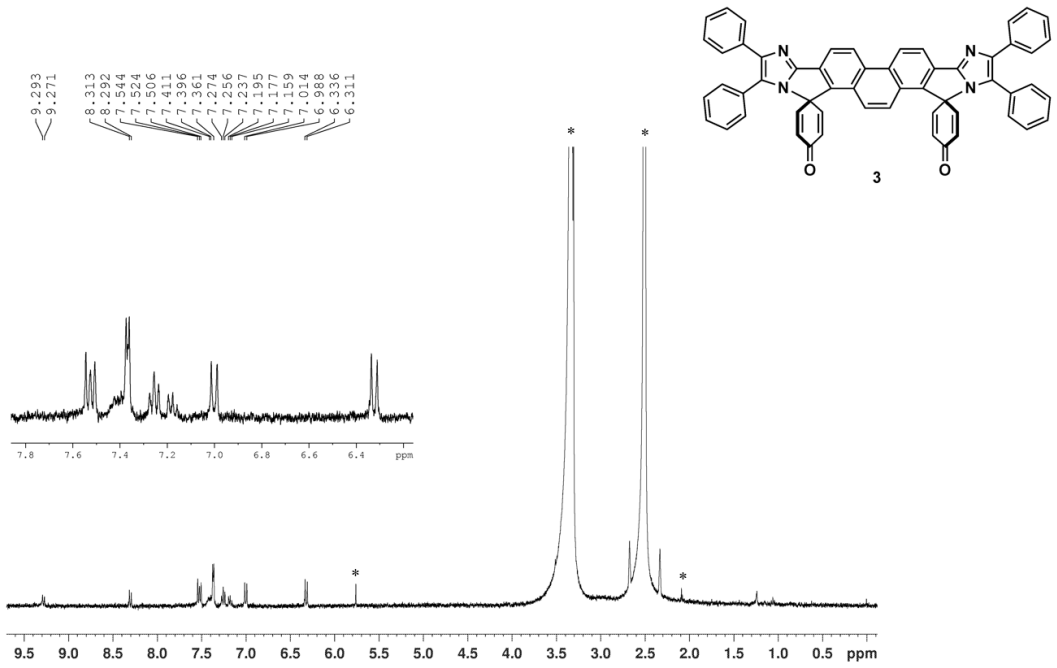

Fig. S23. [1]H NMR spectrum of **3** in DMSO–d_6 (* solvent peaks).

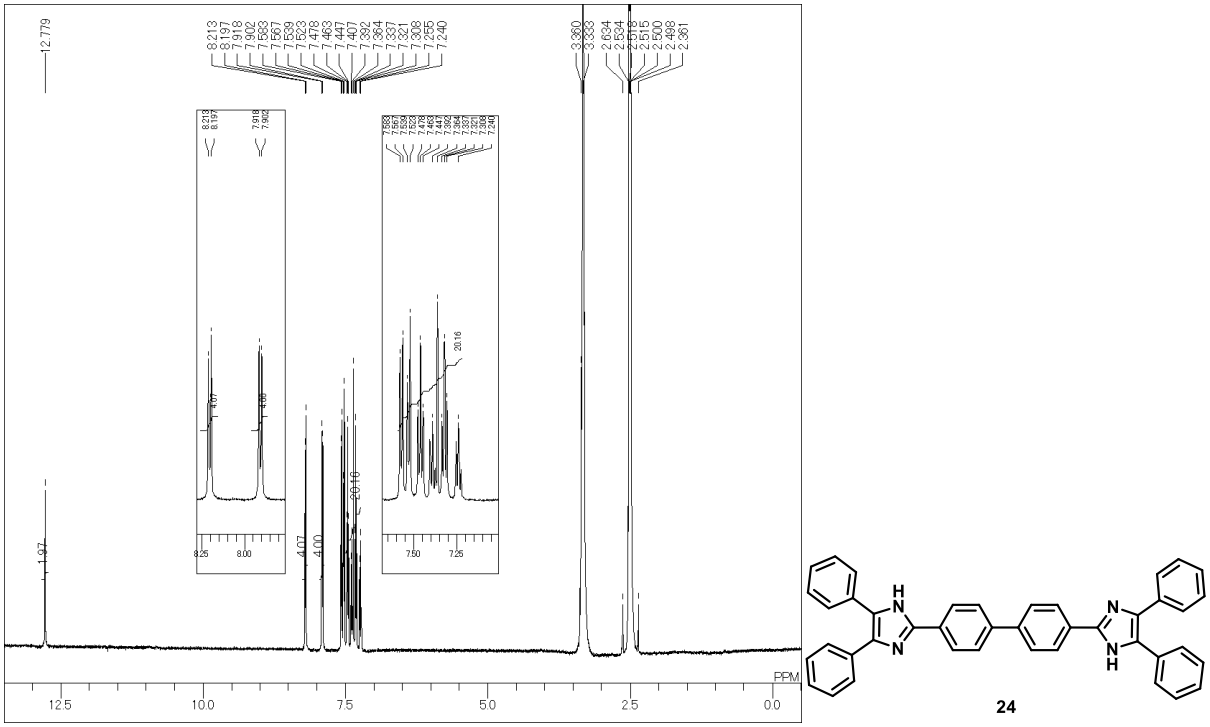

Fig. S24. [1]H NMR spectrum of **24** in DMSO–d_6 (* solvent peaks).

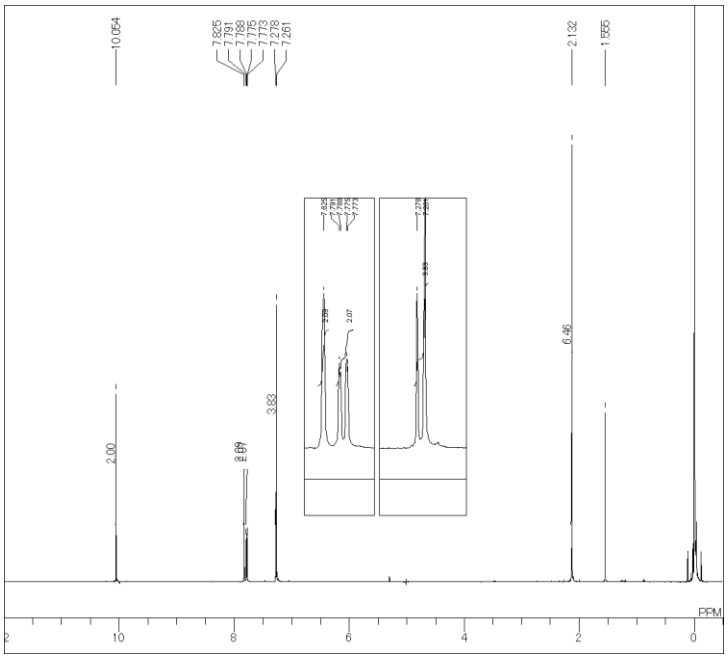

Fig. S25. ^{1}H NMR spectrum of **28** in $CDCl_3$ (* solvent peaks).

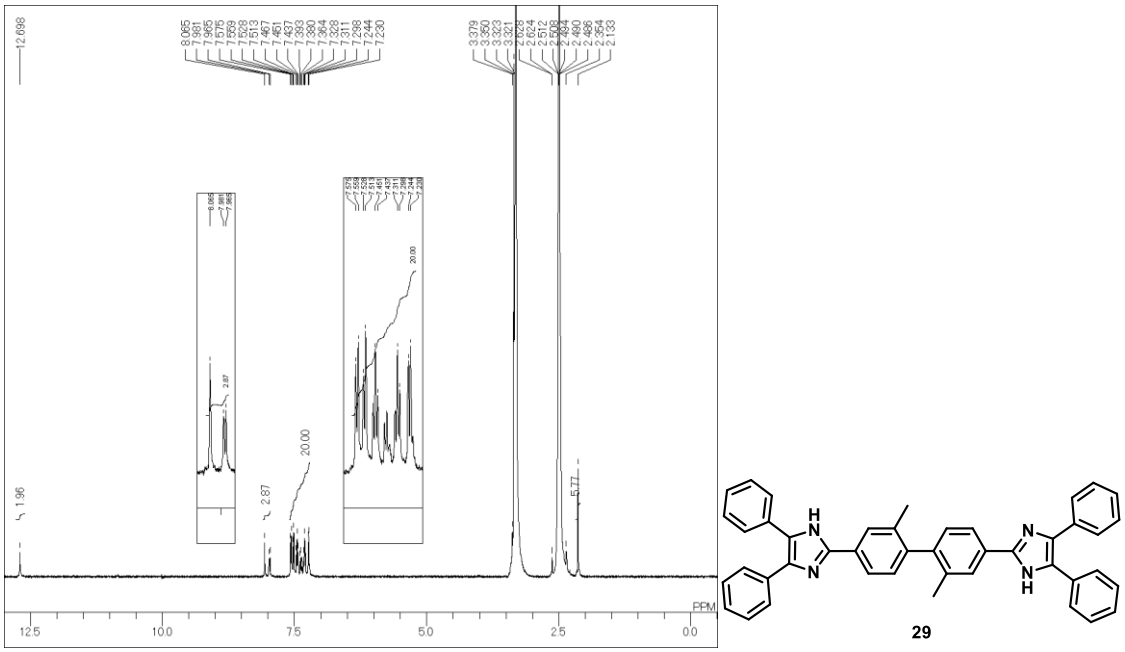

Fig. S26. ^{1}H NMR spectrum of **29** in DMSO–d_6 (* solvent peaks).

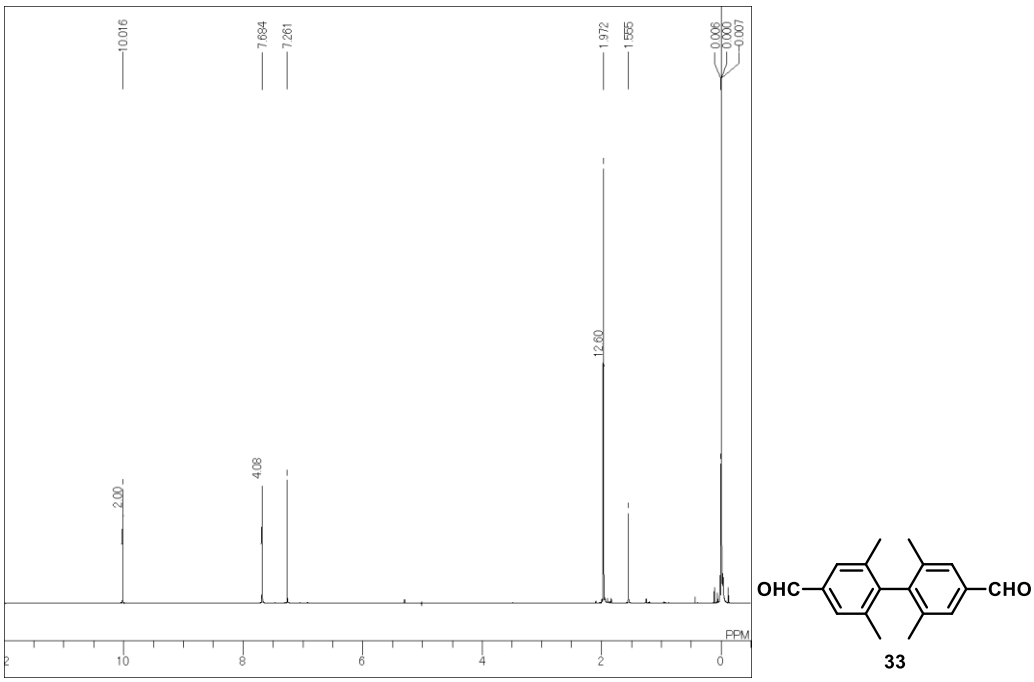

Fig. S27. ^{1}H NMR spectrum of **33** in $CDCl_3$ (* solvent peaks).

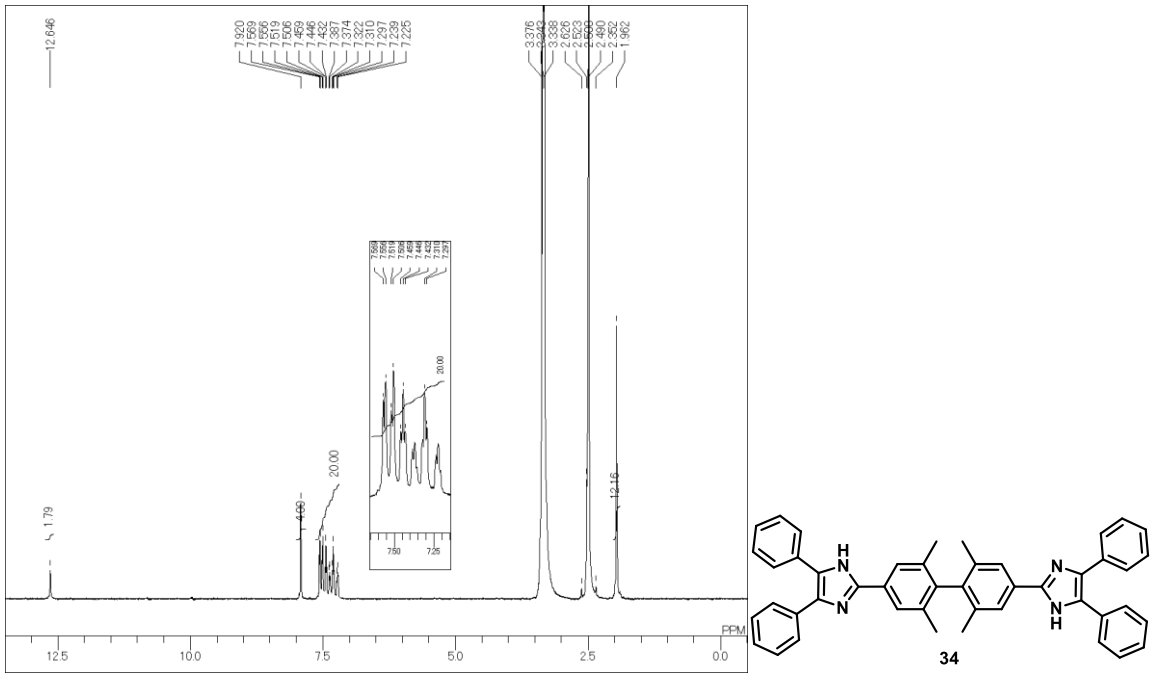

Fig. S28. ^{1}H NMR spectrum of **34** in DMSO–d_6 (* solvent peaks).

2. HR-ESI-TOF-MS Spectra

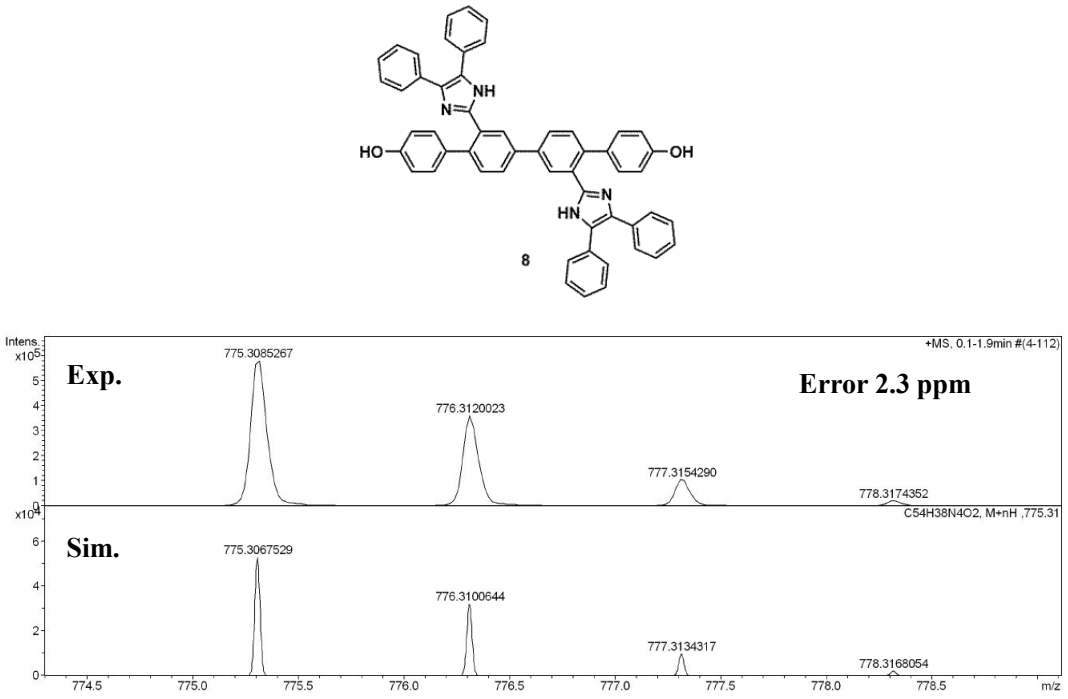

Fig. S29. HR-ESI-TOF MS spectra of **8**.

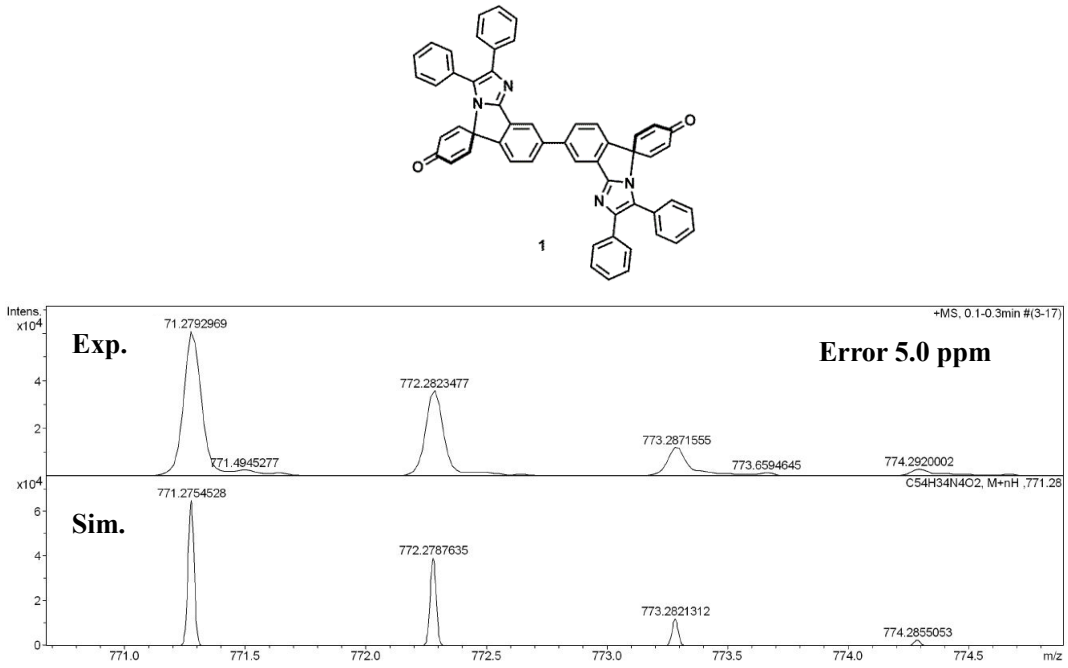

Fig. S30. HR-ESI-TOF MS spectra of **1**.

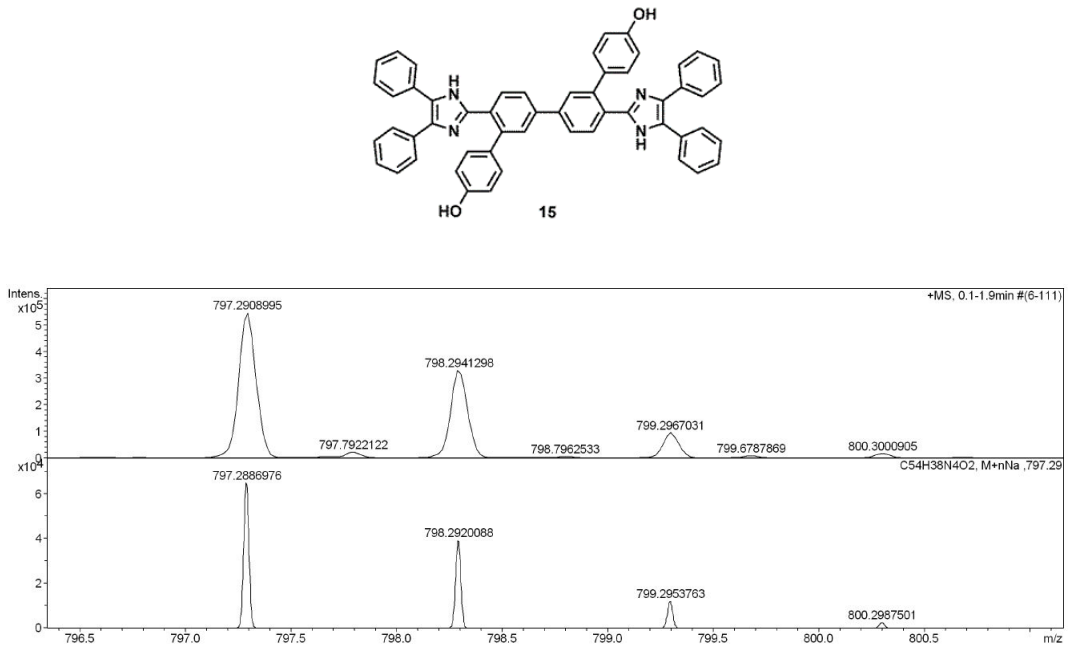

Fig. S31. HR-ESI-TOF MS spectra of **15**.

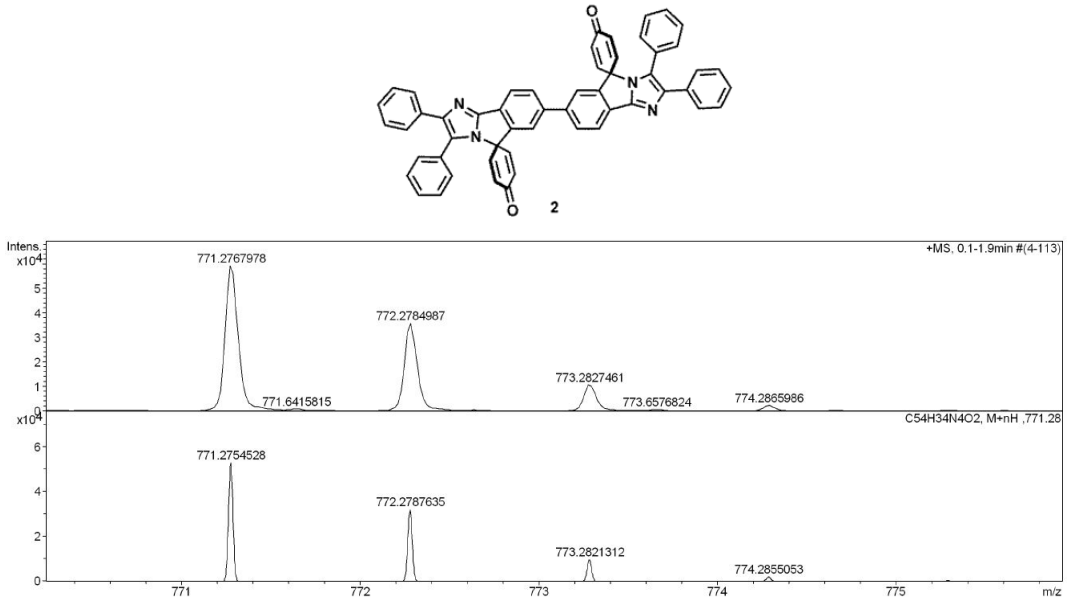

Fig. S32. HR-ESI-TOF MS spectra of **2**.

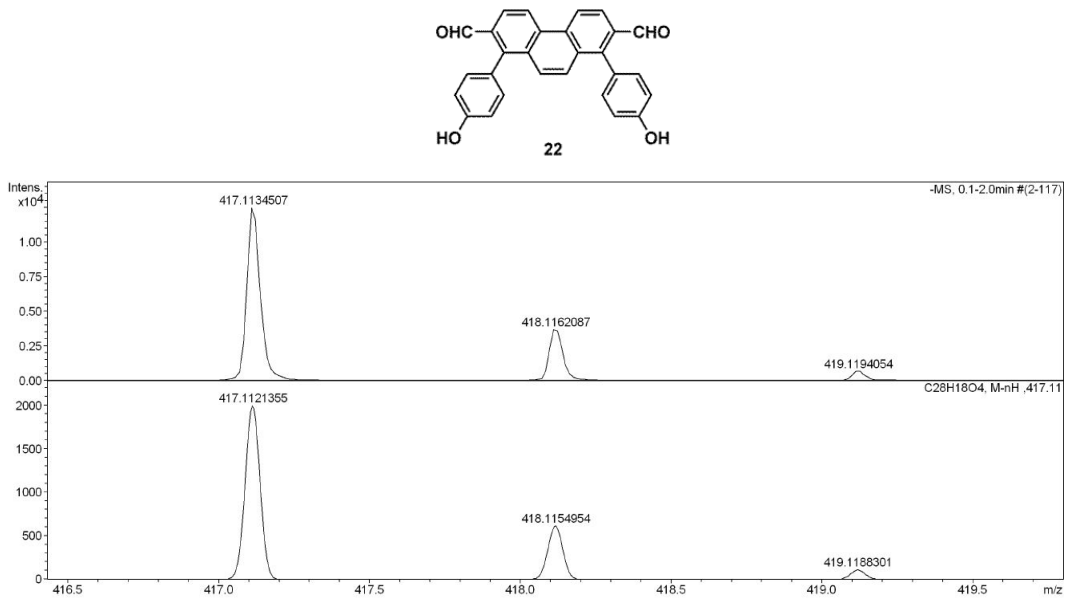

Fig. S33. HR-ESI-TOF MS spectra of **22**.

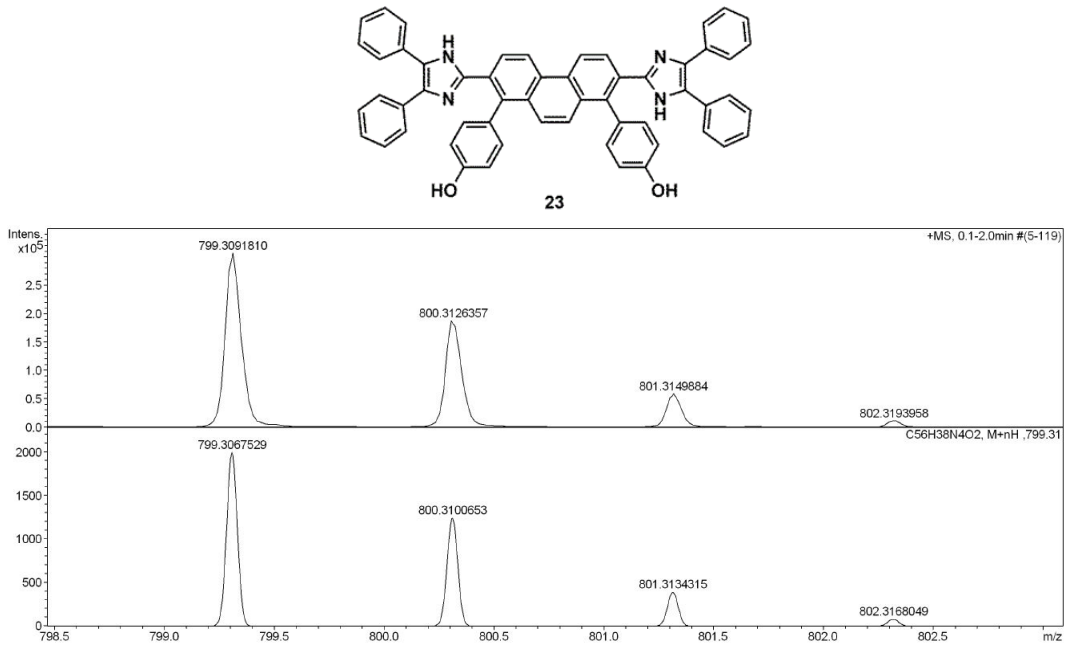

Fig. S34. HR-ESI-TOF MS spectra of **23**.

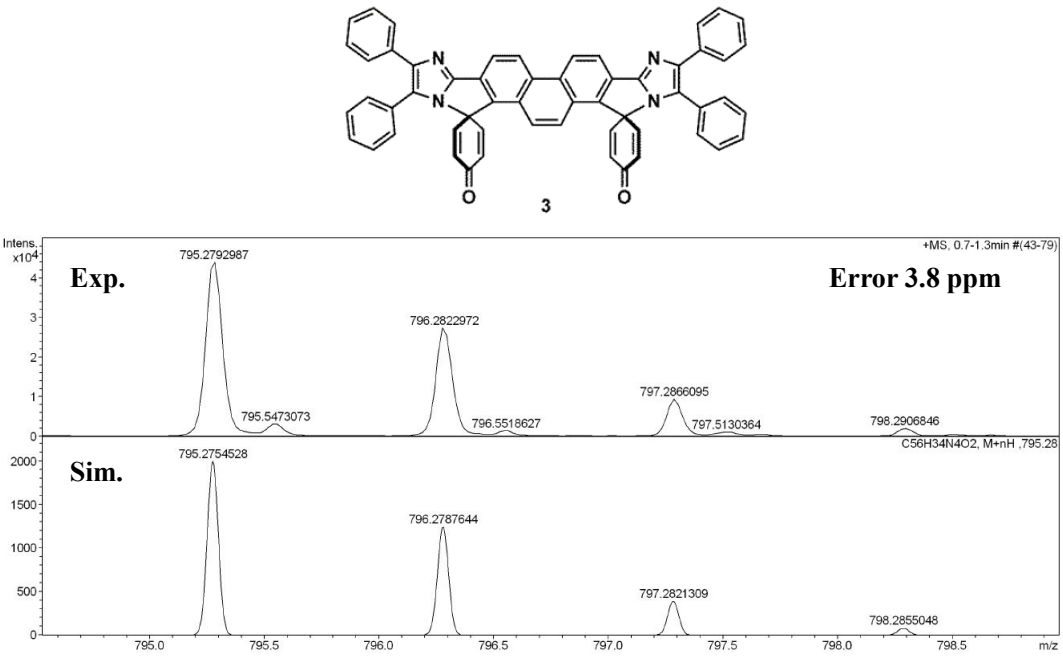

Fig. S35. HR-ESI-TOF MS spectra of **3**.

3. HPLC Chromatograms

HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25cm×4.6mm, 5μm particle) from Kanto Chemical Co., Inc. The HPLC analytical system consists of a pump unit (PU-2080 plus, JASCO), a photodiode array detector (MD-2018, JASCO), and a control unit (LCNetII/ADC, JASCO).

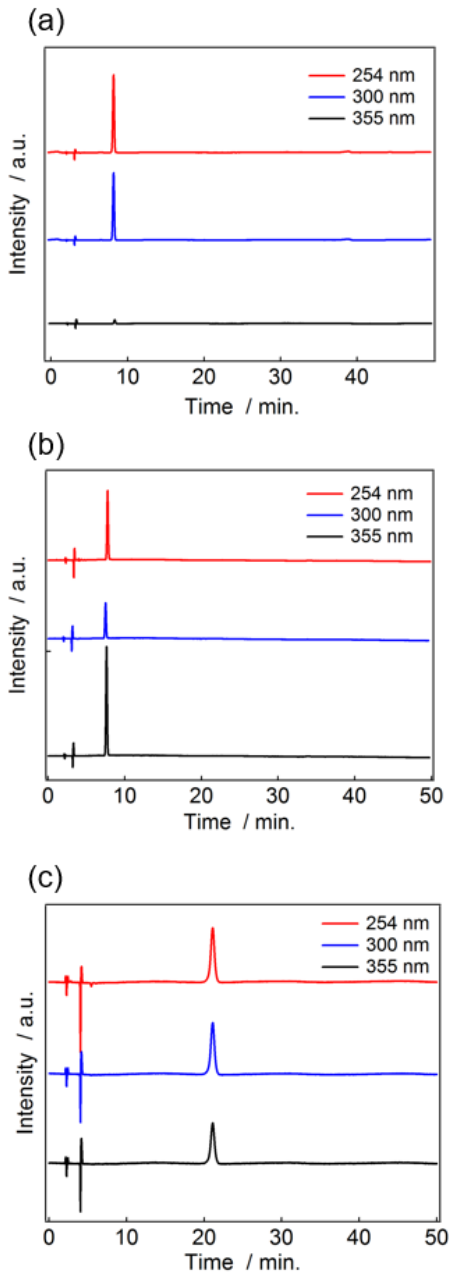

Fig. S36. HPLC charts of (a) **1**, 96 % purity, eluent; CH_3CN:H_2O=9:2, (b) **2**, 99 % purity, eluent; CH_3CN:H_2O=9:2, (c) **3**, 99 % purity, eluent; CH_3CN:H_2O=7:3, with a flow rate of 1.0 mL/min; detection wavelength, 254, 300 and 355 nm.

4. Transient Absorption Spectroscopy

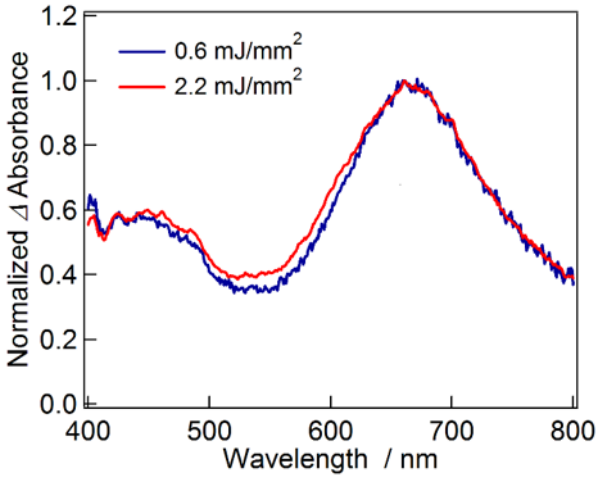

Fig. S37. Transient absorption spectra of **1** in benzene (7.2×10^{-5} M) at 10 ns after irradiation of 355-nm (5 ns) laser pulse. The power density was 0.6 mJ/mm^2 and 2.2 mJ/mm^2.

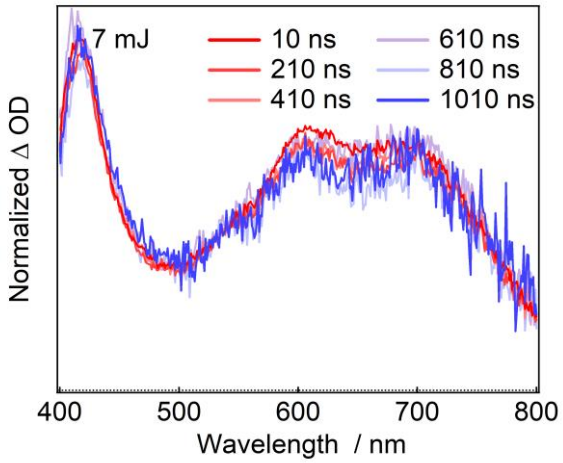

Fig. S38. Transient absorption spectra of **2** in benzene after irradiation of 355-nm (5 ns, 7 mJ) laser pulse.

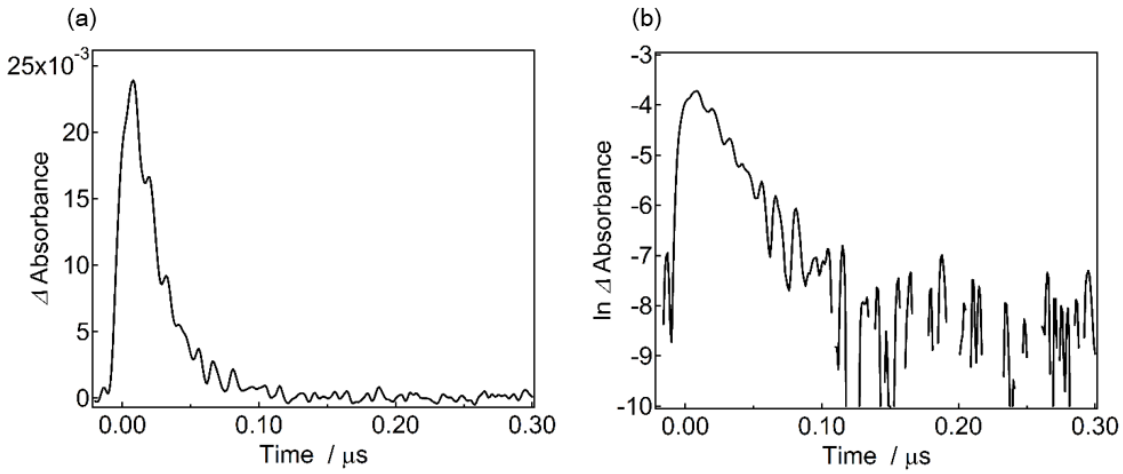

Fig. S39. (a) Decay profile (b) logarithmic decay profile of **3** in benzene after 355 nm, 5 ns laser pulse irradiation, observed at 600 nm. The excitation power density was 2.2 mJ/mm^2.