Supporting Information

to the article

Title: Synthesis, structure, and stereospecific cross-[2 + 2] photocycloaddition of pseudodimeric complexes based on ammonioalkyl derivatives of styryl dyes

Authors: Sergey P. Gromov,*[,a,b] Artem I. Vedernikov,[a] Sergey K. Sazonov,[a] Lyudmila G. Kuz'mina,[c] Natalia A. Lobova,[a] Yuri A. Strelenko[d] and Judith A. K. Howard[e]

[a]*Photochemistry Center, Russian Academy of Sciences, ul. Novatorov 7A-1, Moscow 119421, Russian Federation;*[b]*Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russian Federation;*[c]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prosp. 31, Moscow 119991, Russian Federation;* [d]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, Moscow 119991, Russian Federation;* [e]*Chemistry Department, Durham University, South Road, Durham DH1 3LE, United Kingdom*

spgromov@mail.ru

Journal: New Journal of Chemistry

Table of Contents

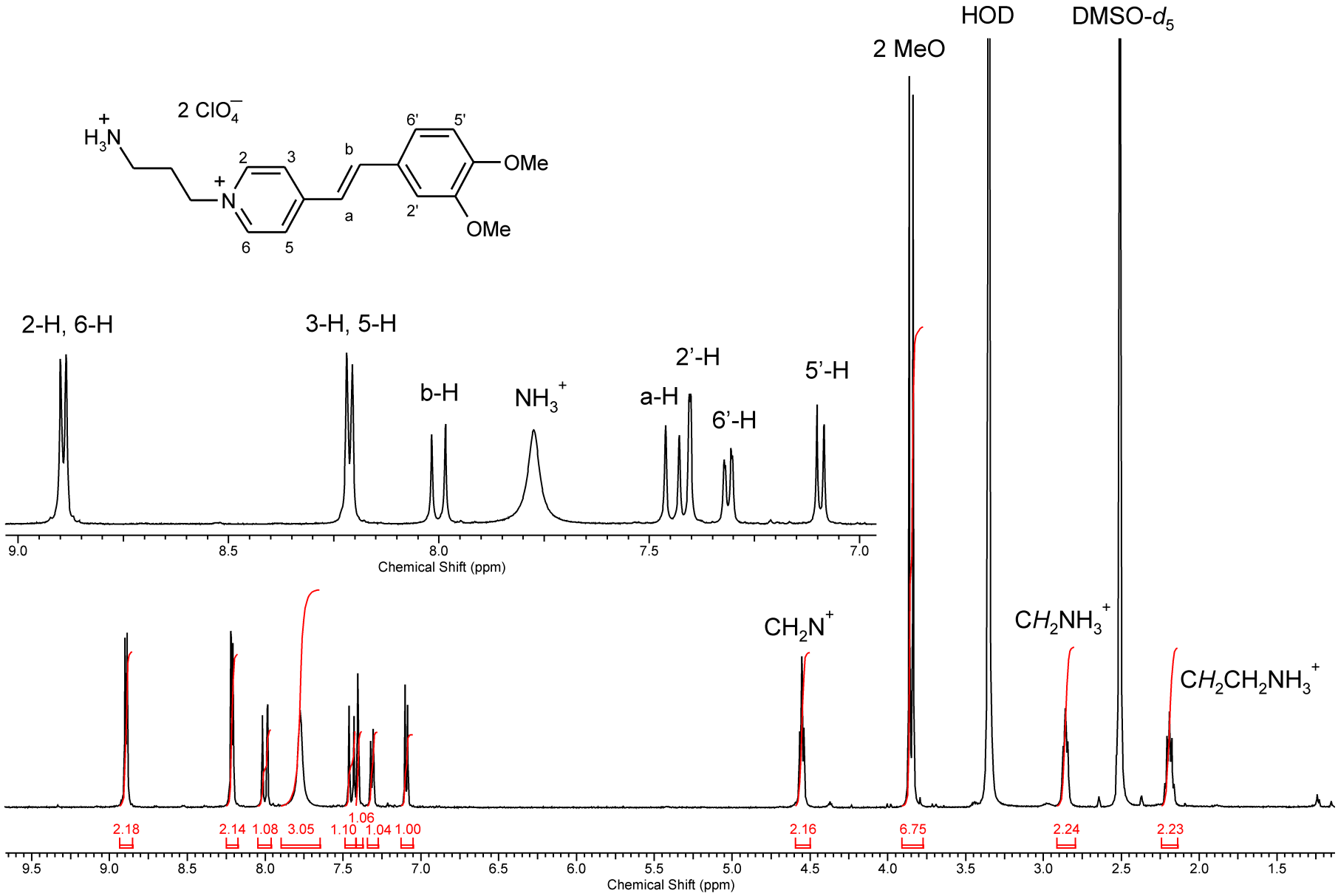

Fig. S1 ^{1}H NMR spectrum of dye **1a** (500.13 MHz, DMSO-d_6, 23 °C).

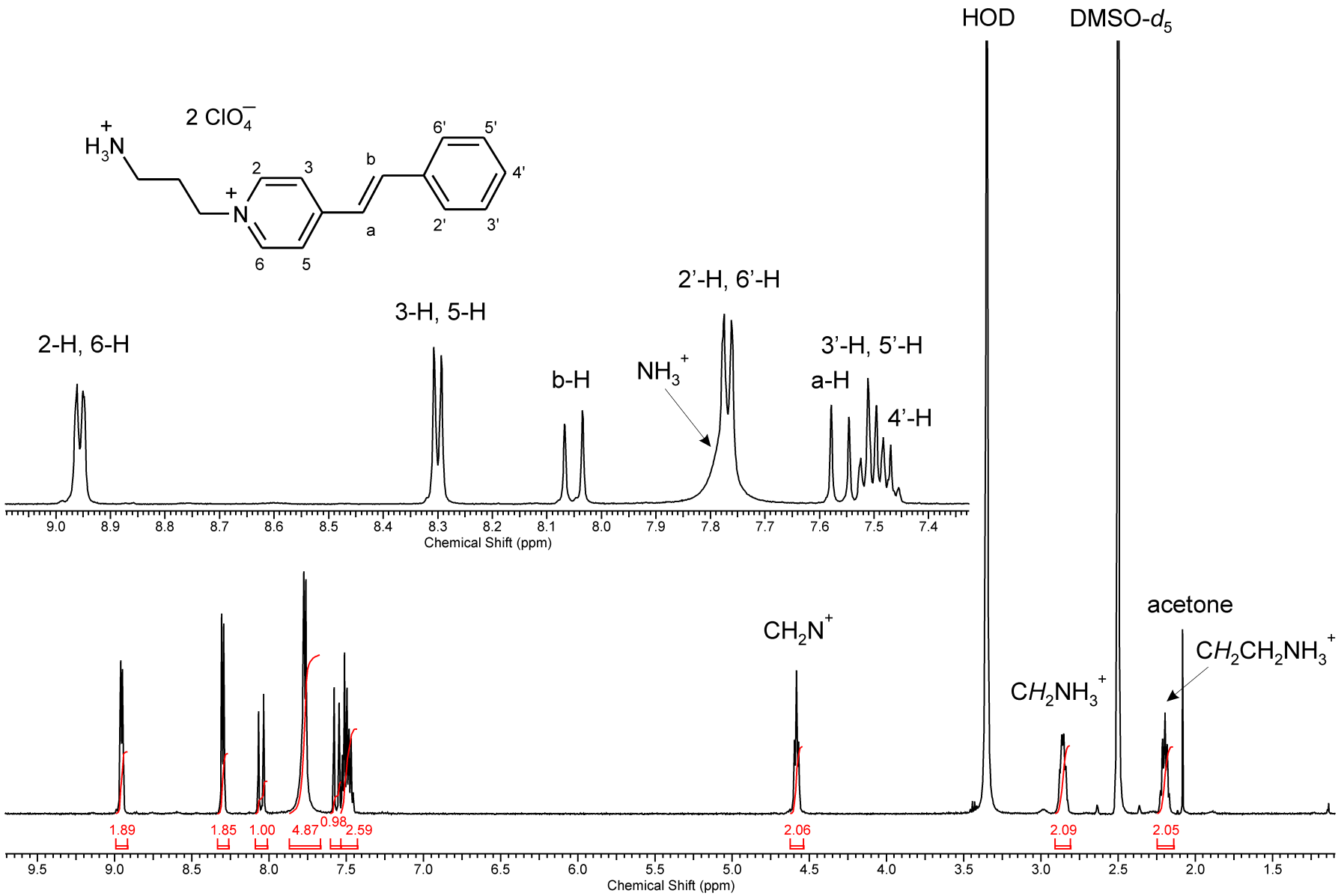

Fig. S2 ^{1}H NMR spectrum of dye **1b** (500.13 MHz, DMSO-d_6, 25 °C).

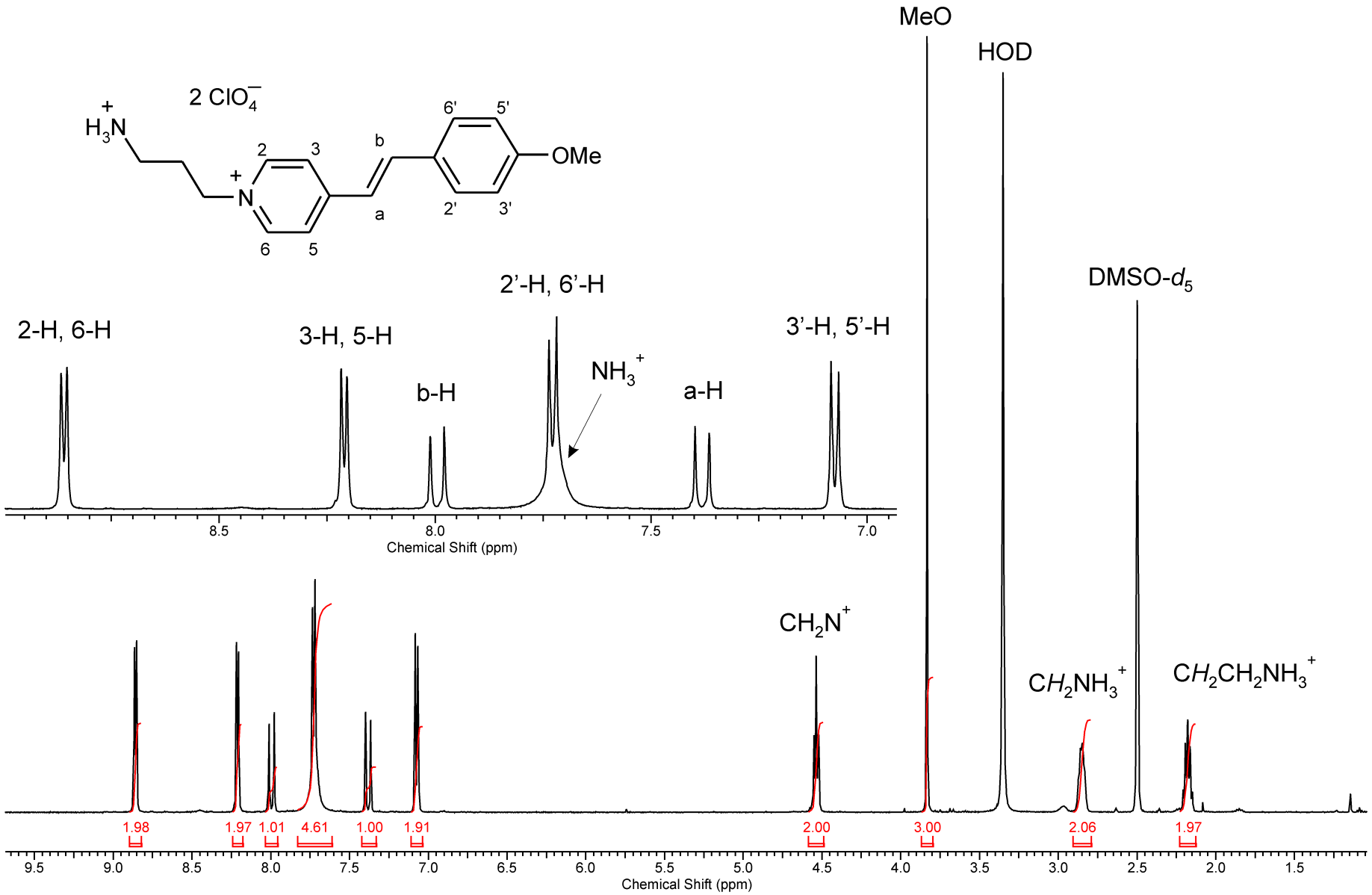

Fig. S3 ^{1}H NMR spectrum of dye **1c** (500.13 MHz, DMSO-d_6, 25 °C).

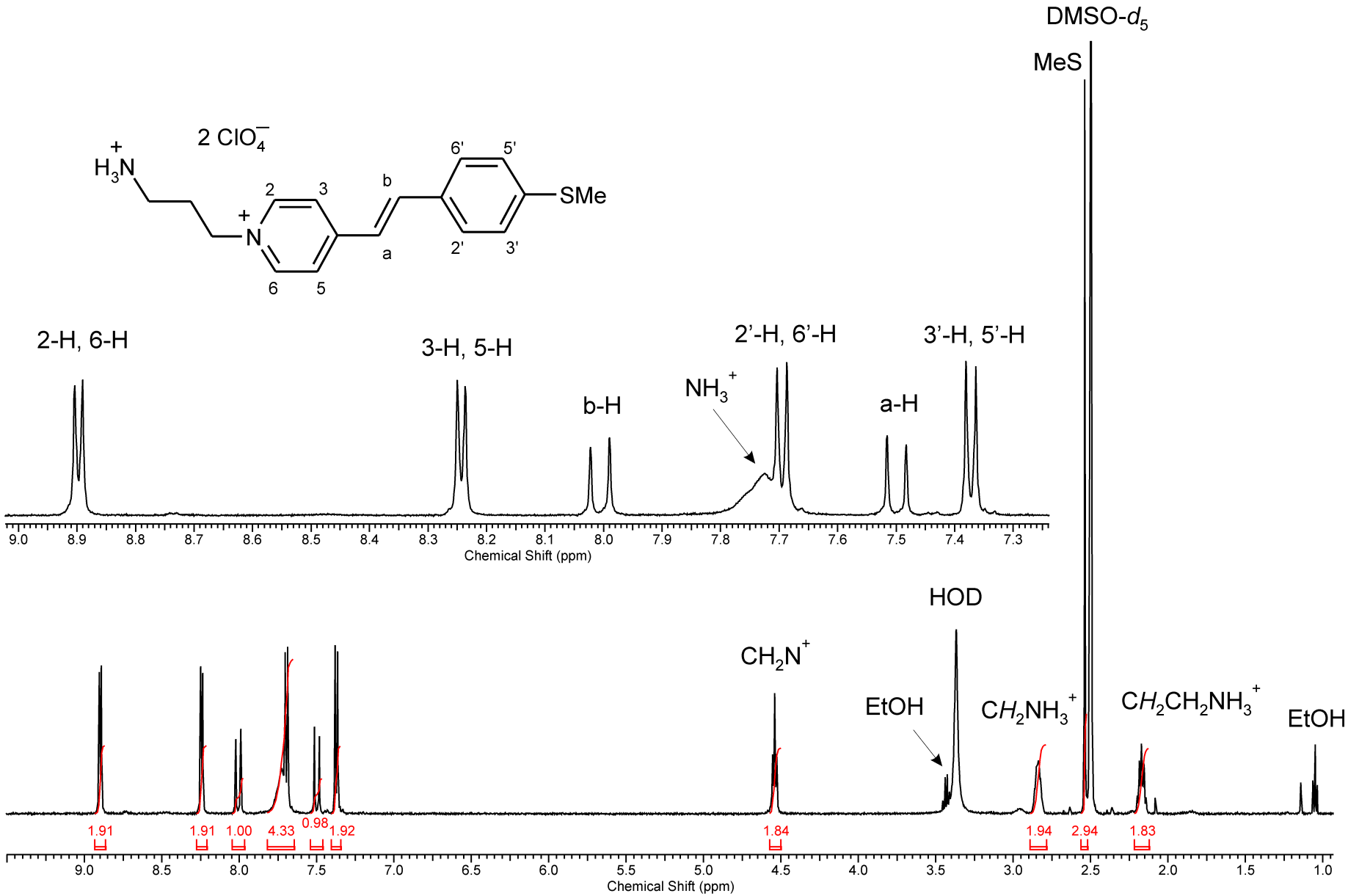

Fig. S4 ^{1}H NMR spectrum of dye **1d** (500.13 MHz, DMSO-d_6, 25 °C).

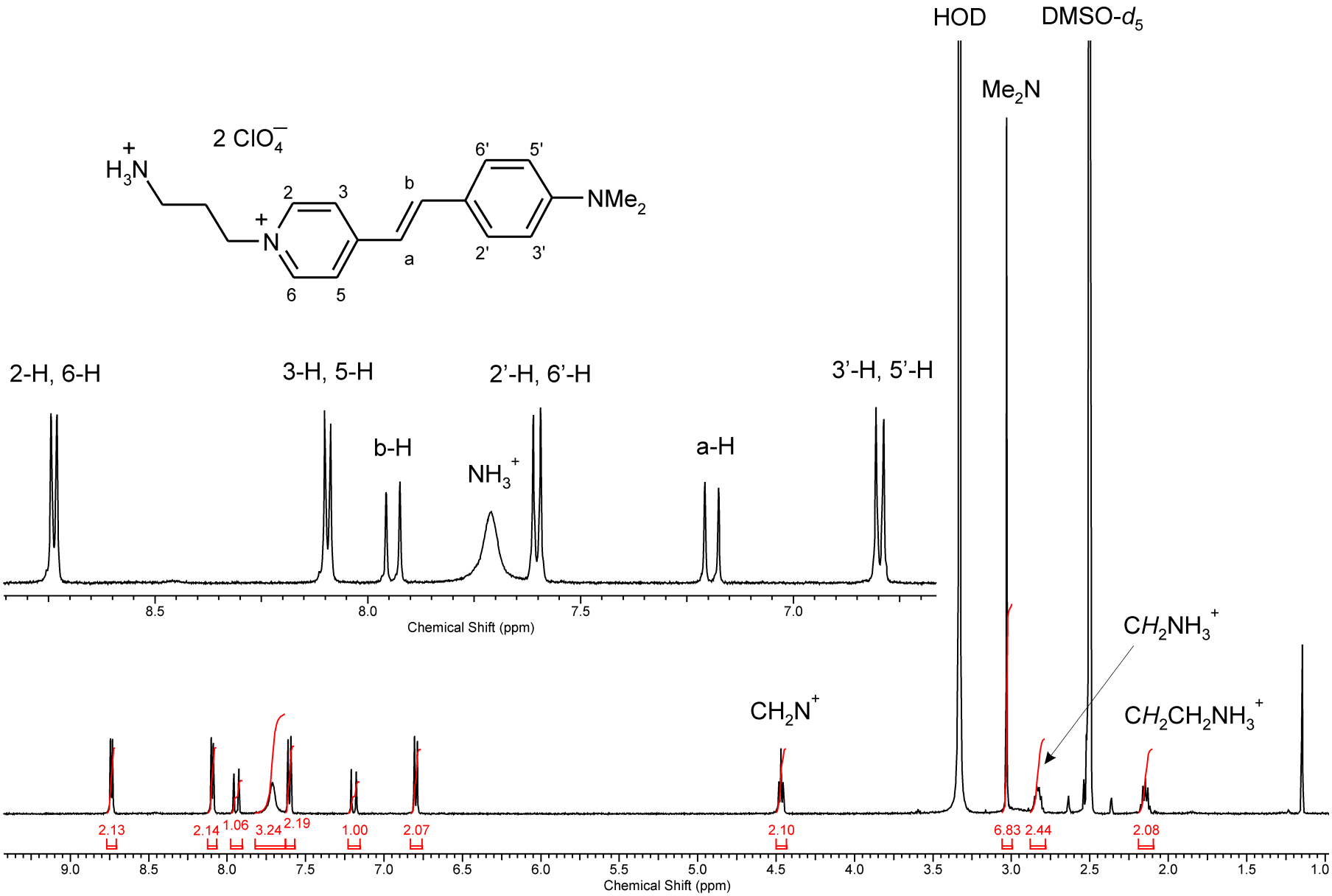

Fig. S5 ^{1}H NMR spectrum of dye **1e** (500.13 MHz, DMSO-d_6, 24 °C).

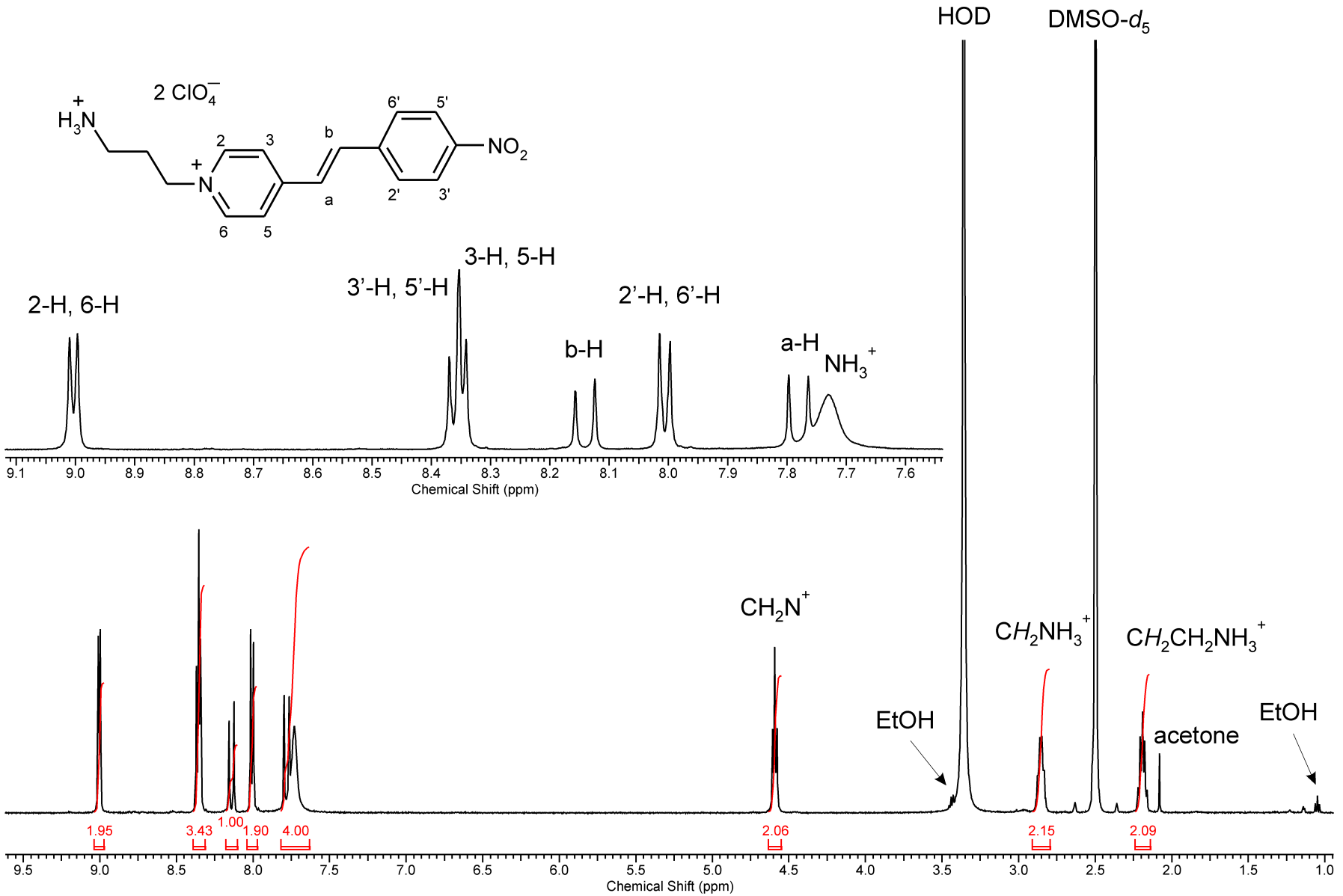

Fig. S6 ^{1}H NMR spectrum of dye **1f** (500.13 MHz, DMSO-d_6, 25 °C).

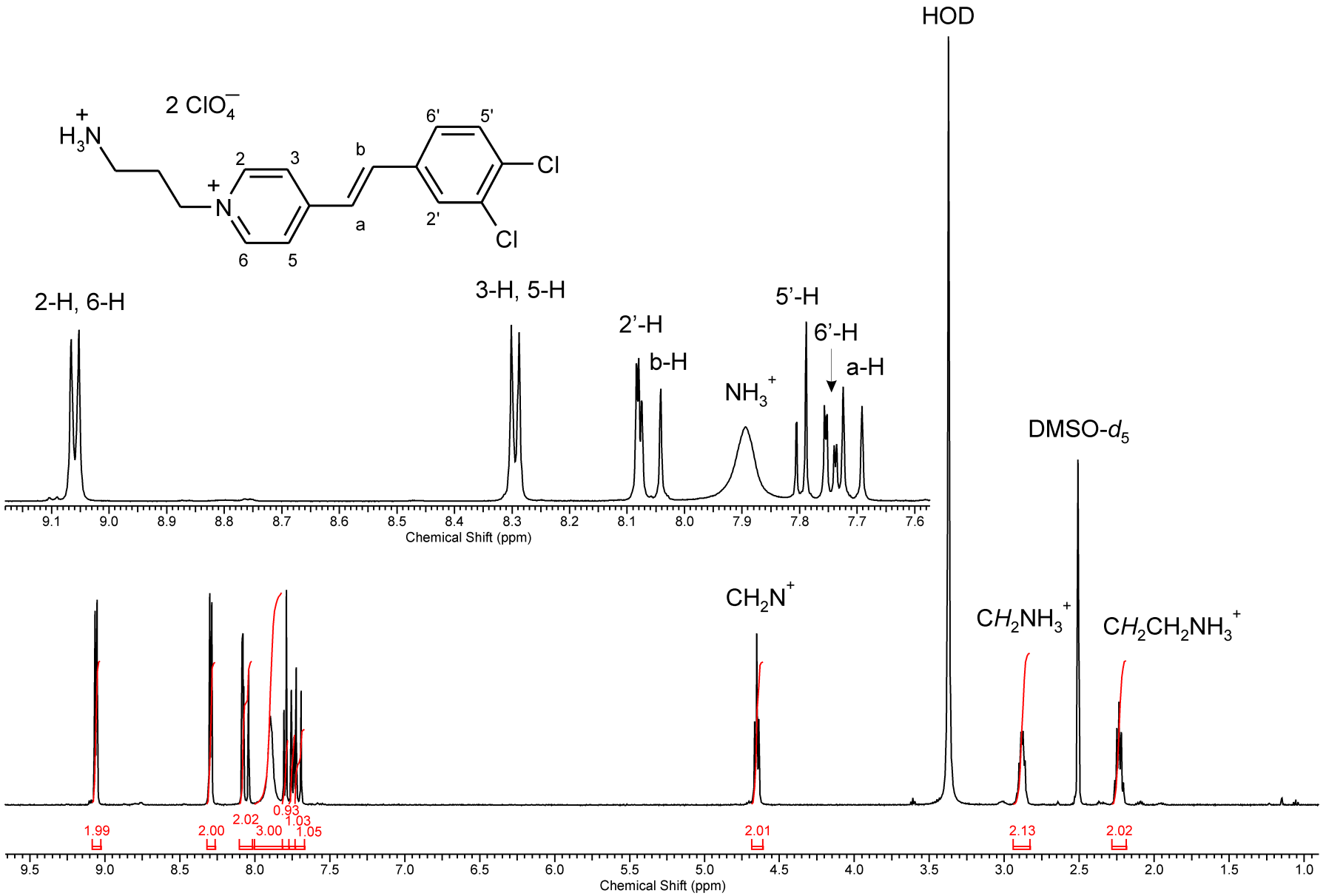

Fig. S7 ^{1}H NMR spectrum of dye **1g** (500.13 MHz, DMSO-d_6, 25 °C).

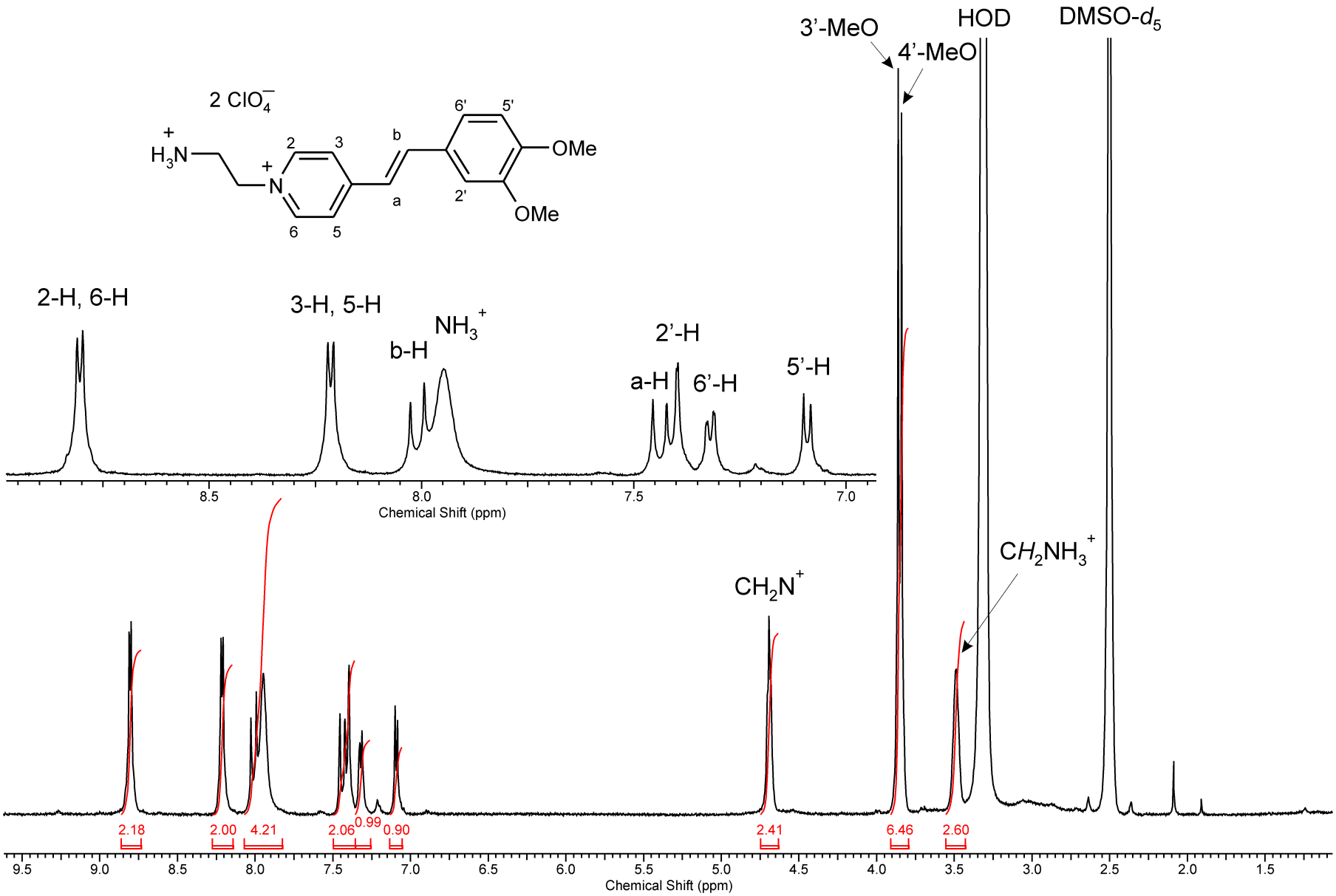

Fig. S8 ^{1}H NMR spectrum of dye **1h** (500.13 MHz, DMSO-d_6, 30 °C).

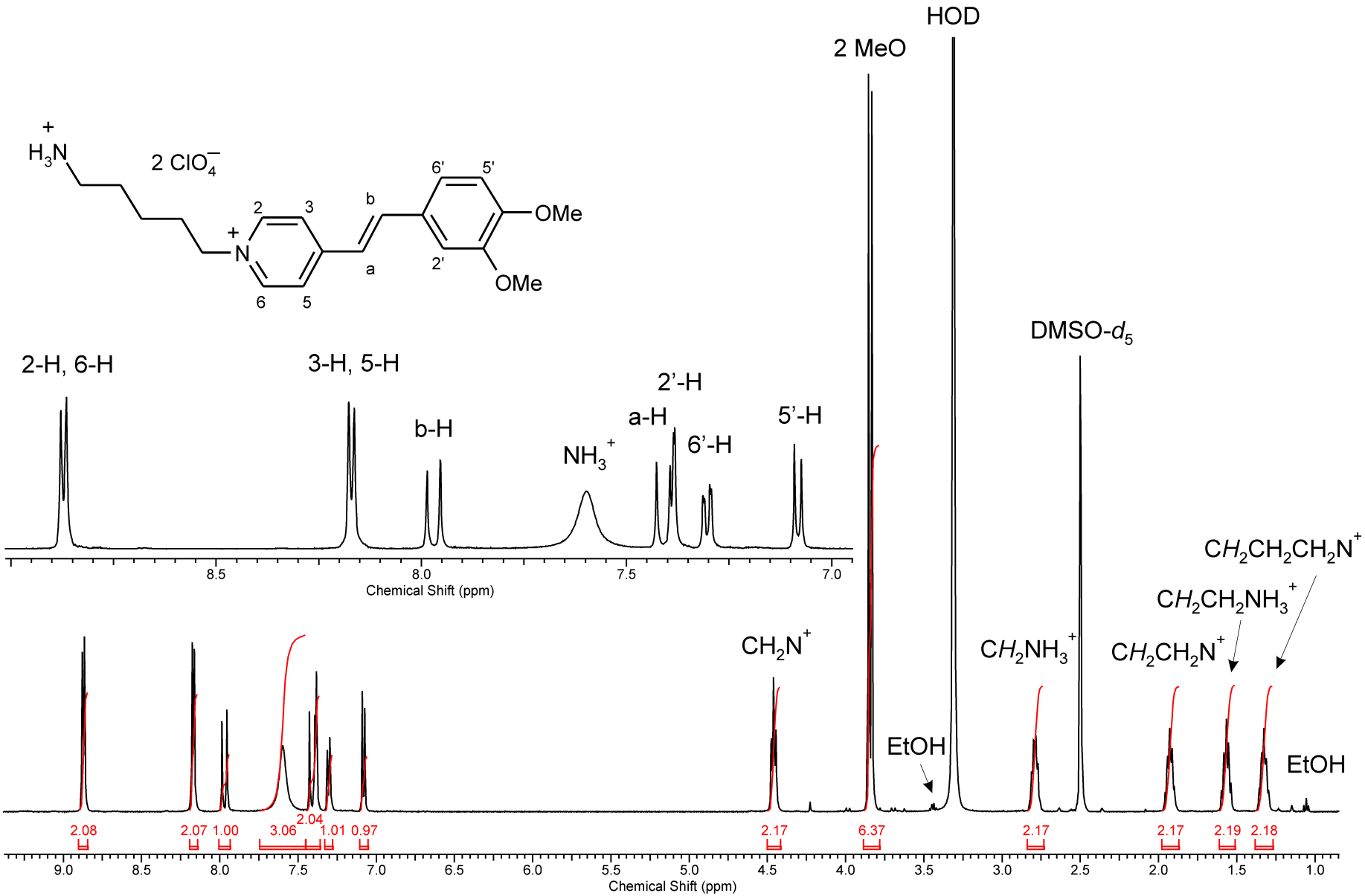

Fig. S9 ^{1}H NMR spectrum of dye **1i** (500.13 MHz, DMSO-d_6, 25 °C).

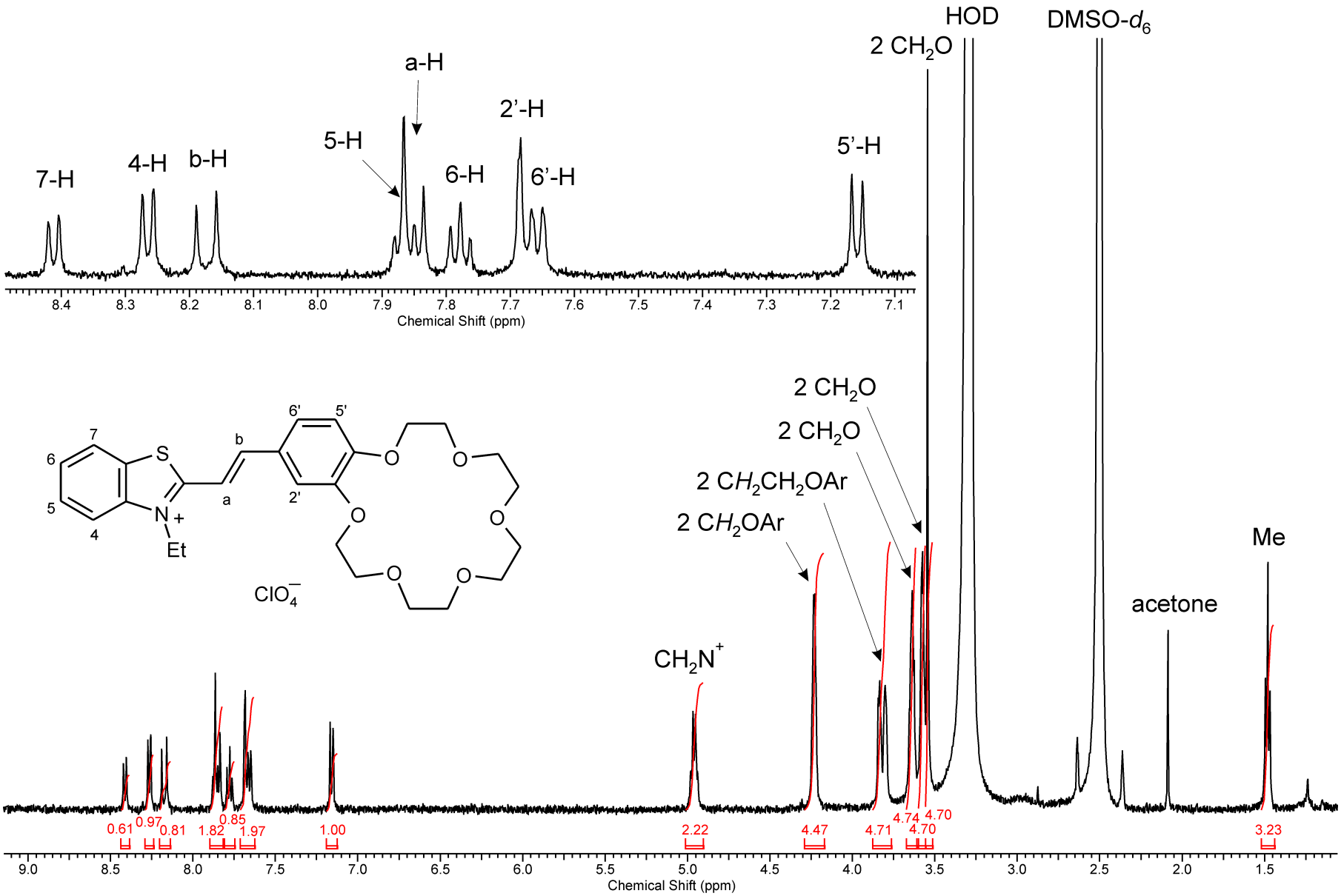

Fig. S10 ^{1}H NMR spectrum of dye **2c** (500.13 MHz, DMSO-d_6, 30 °C).

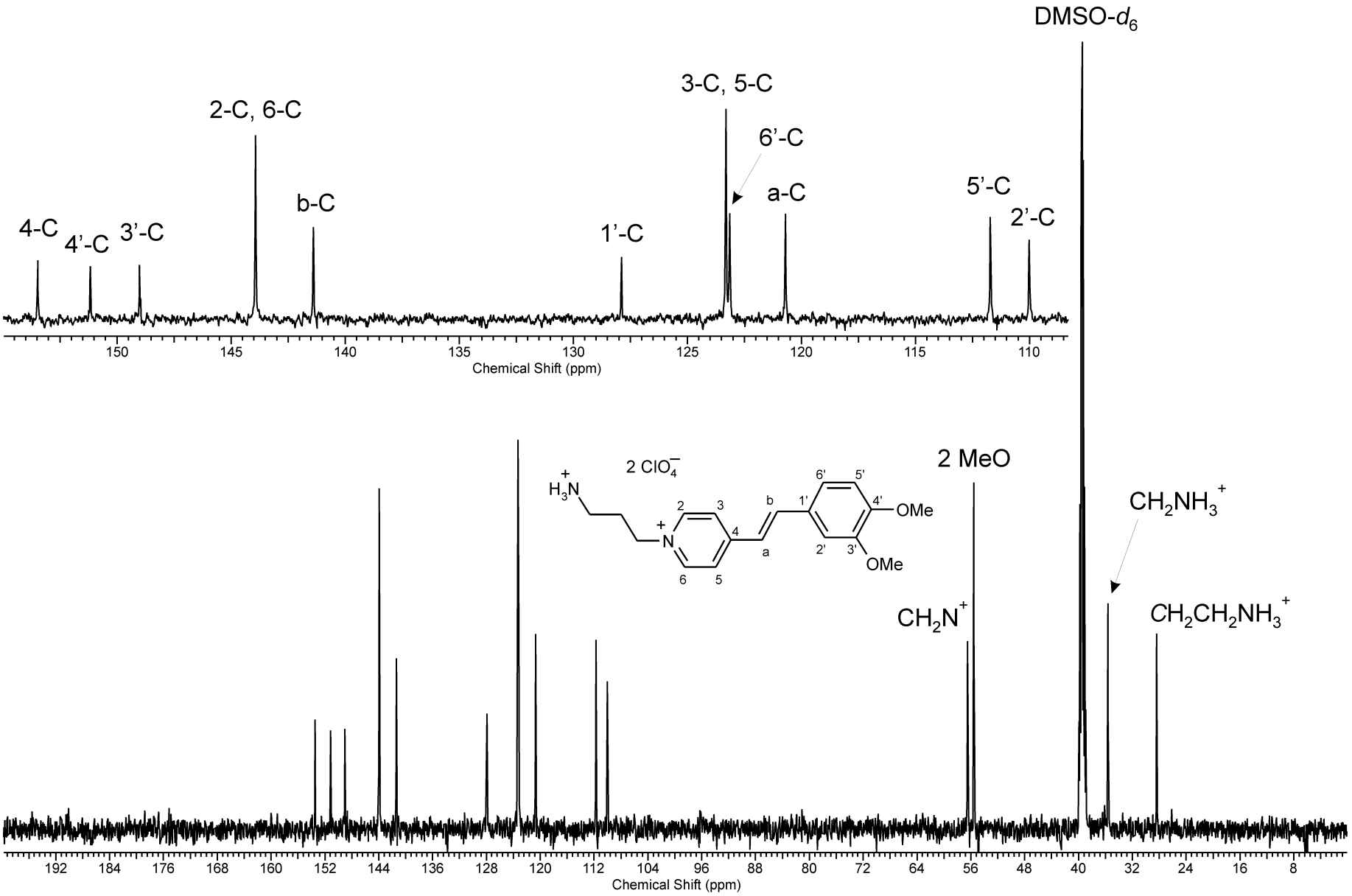

Fig. S11 ^{13}C NMR spectrum of dye **1a** (125.76 MHz, DMSO-d_6, 30 °C).

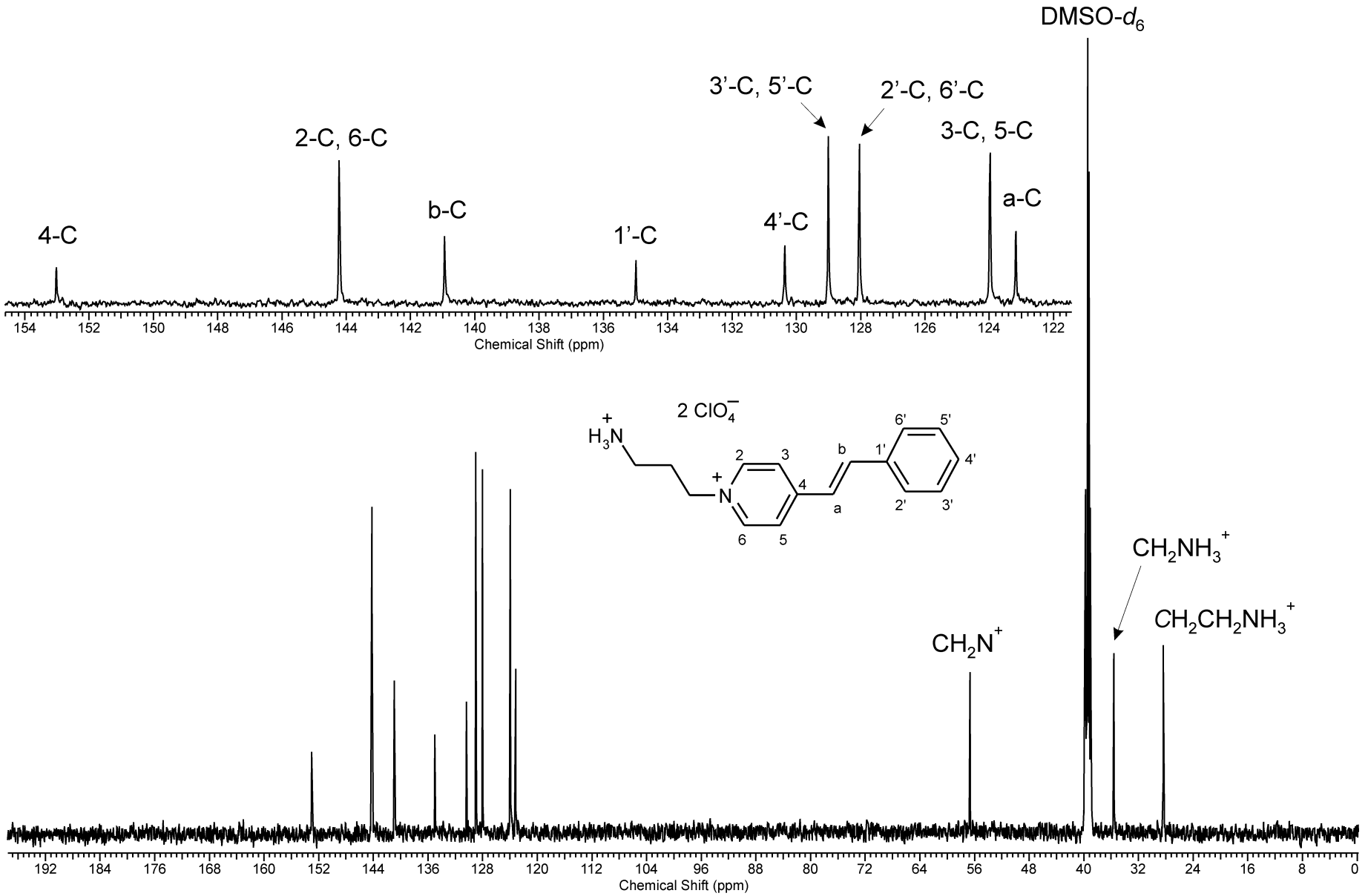

Fig. S12 ^{13}C NMR spectrum of dye **1b** (125.76 MHz, DMSO-d_6, 30 °C).

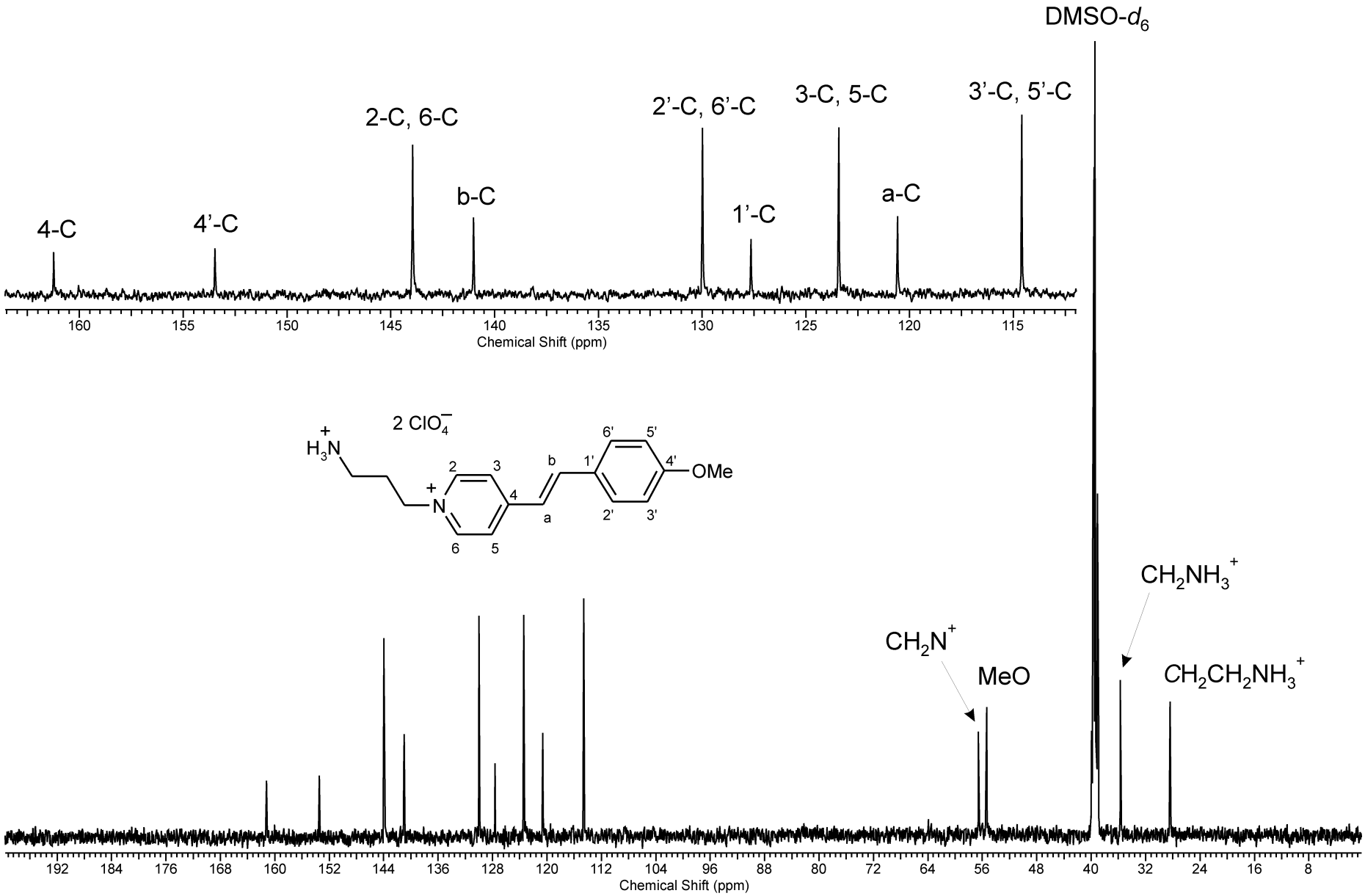

Fig. S13 ^{13}C NMR spectrum of dye **1c** (125.76 MHz, DMSO-d_6, 30 °C).

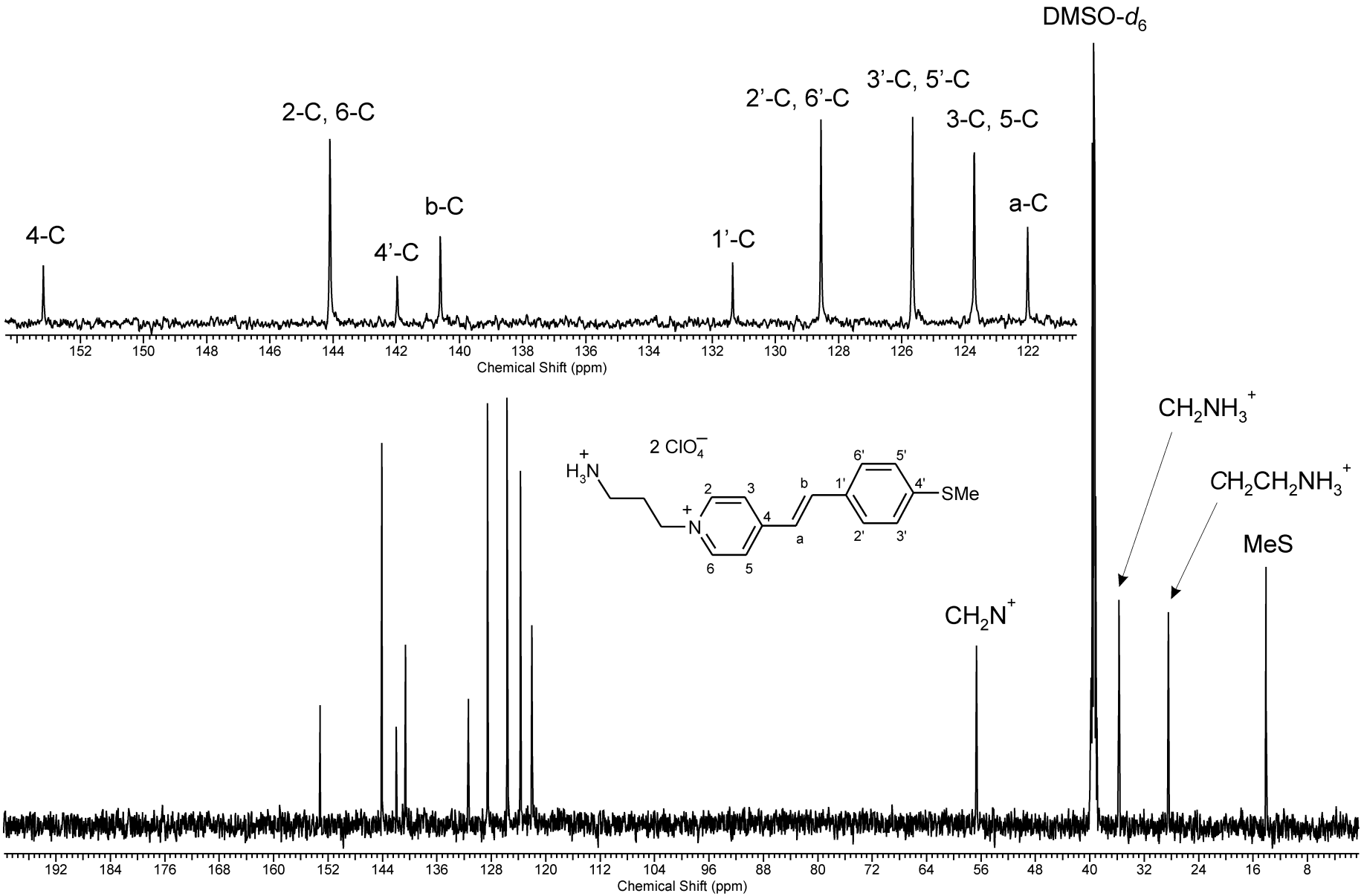

Fig. S14 ^{13}C NMR spectrum of dye **1d** (125.76 MHz, DMSO-d_6, 27 °C).

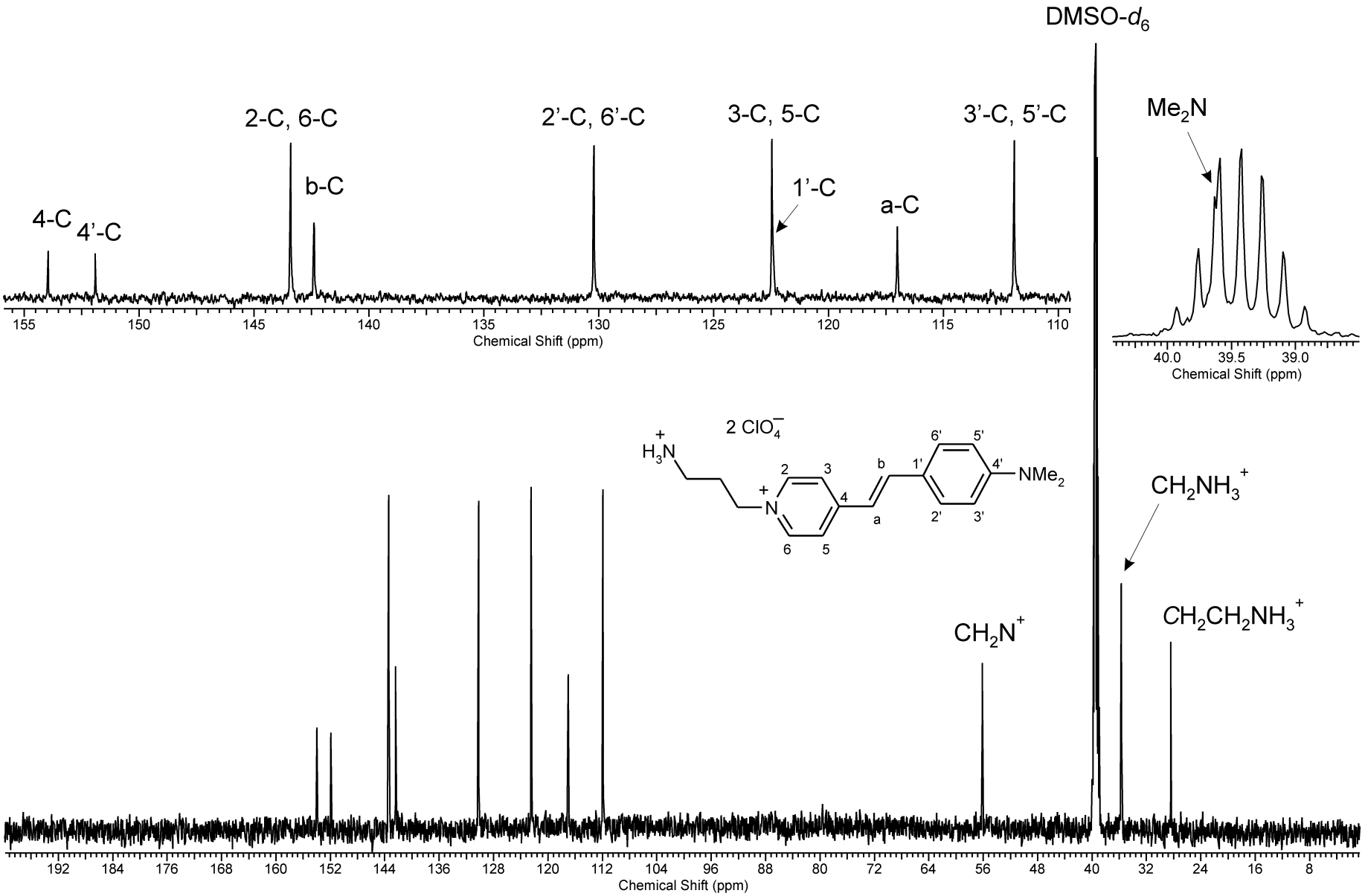

Fig. S15 ^{13}C NMR spectrum of dye **1e** (125.76 MHz, DMSO-d_6, 25 °C).

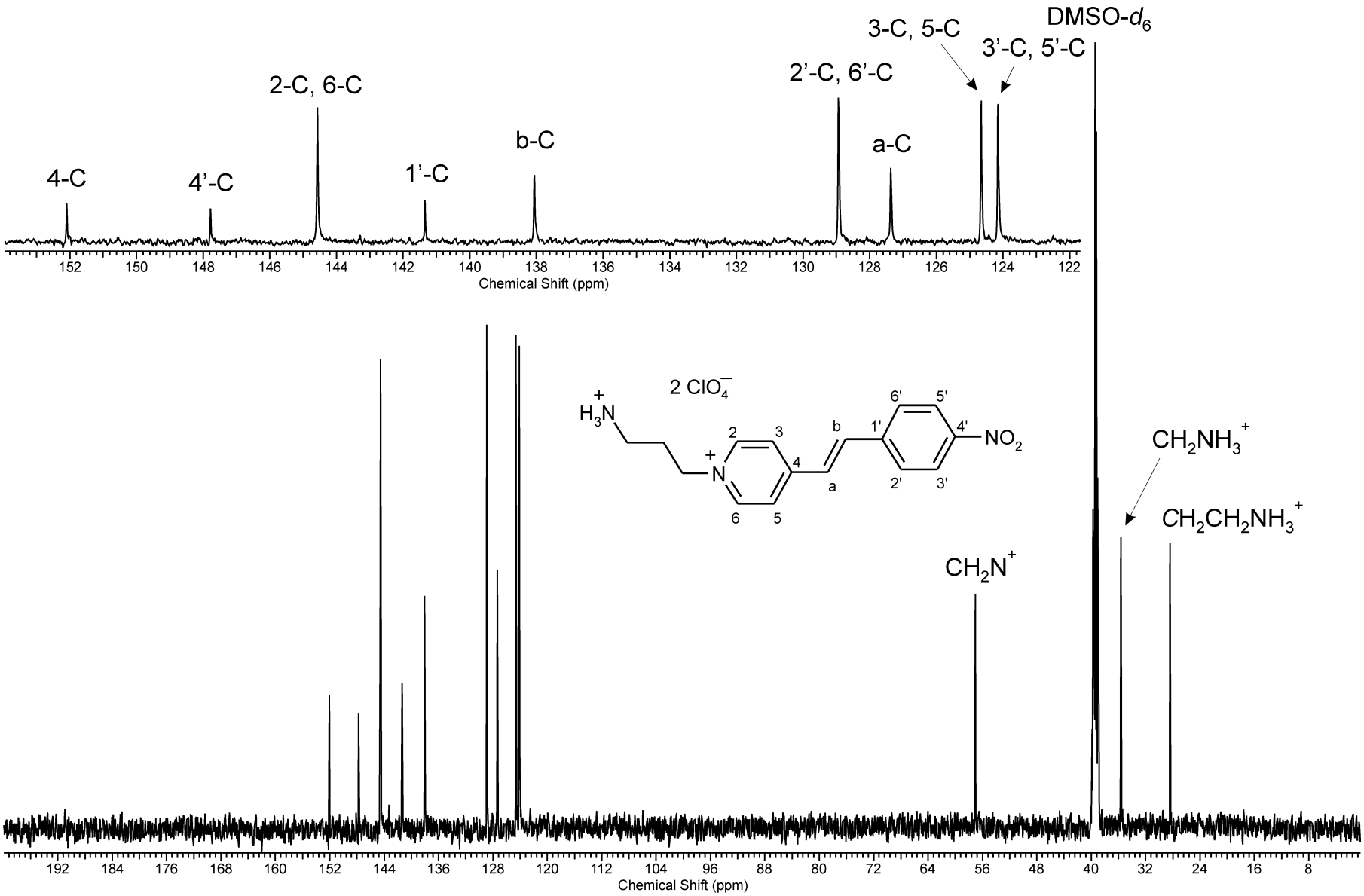

Fig. S16 ^{13}C NMR spectrum of dye **1f** (125.76 MHz, DMSO-d_6, 30 °C).

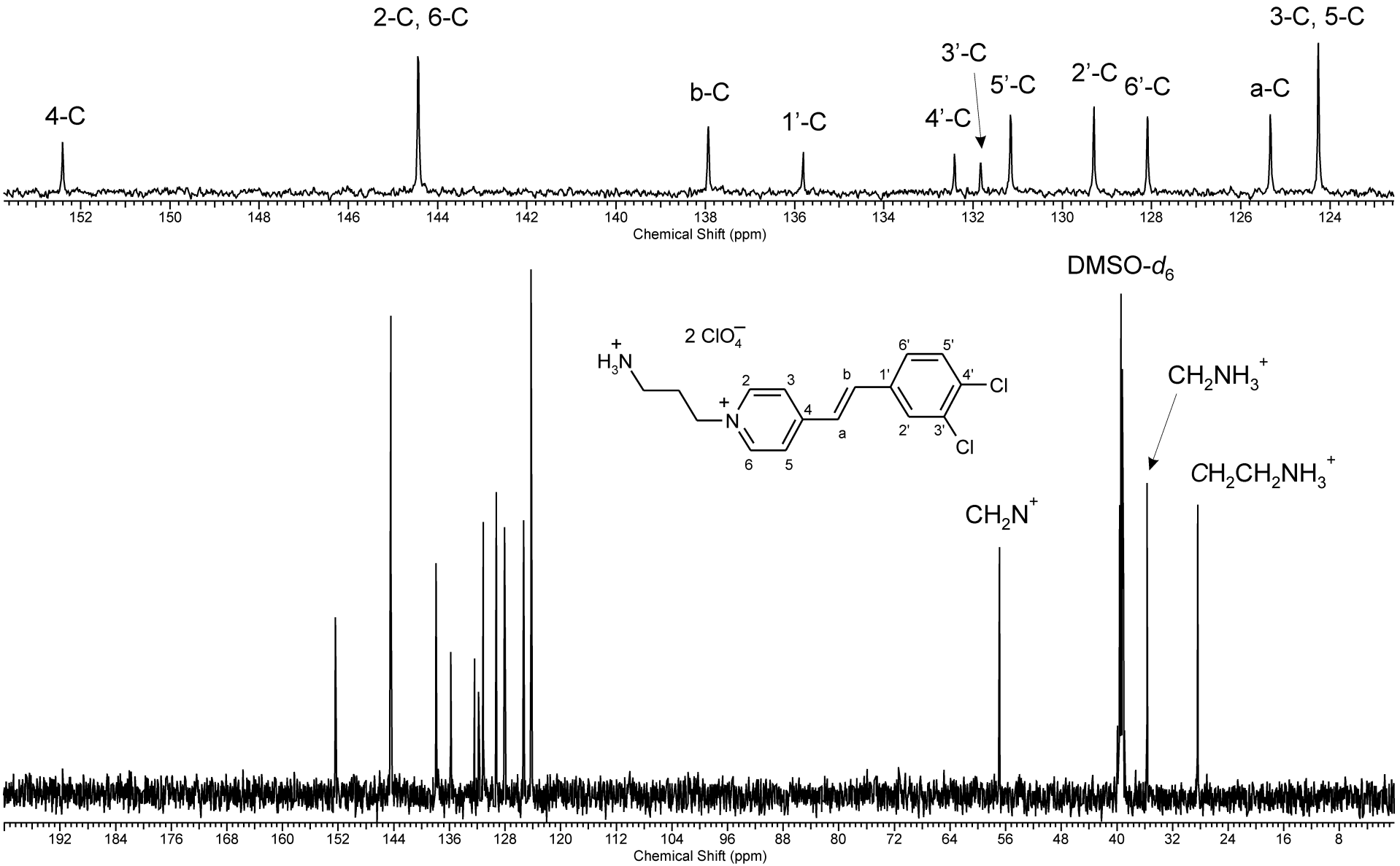

Fig. S17 ^{13}C NMR spectrum of dye **1g** (125.76 MHz, DMSO-d_6, 30 °C).

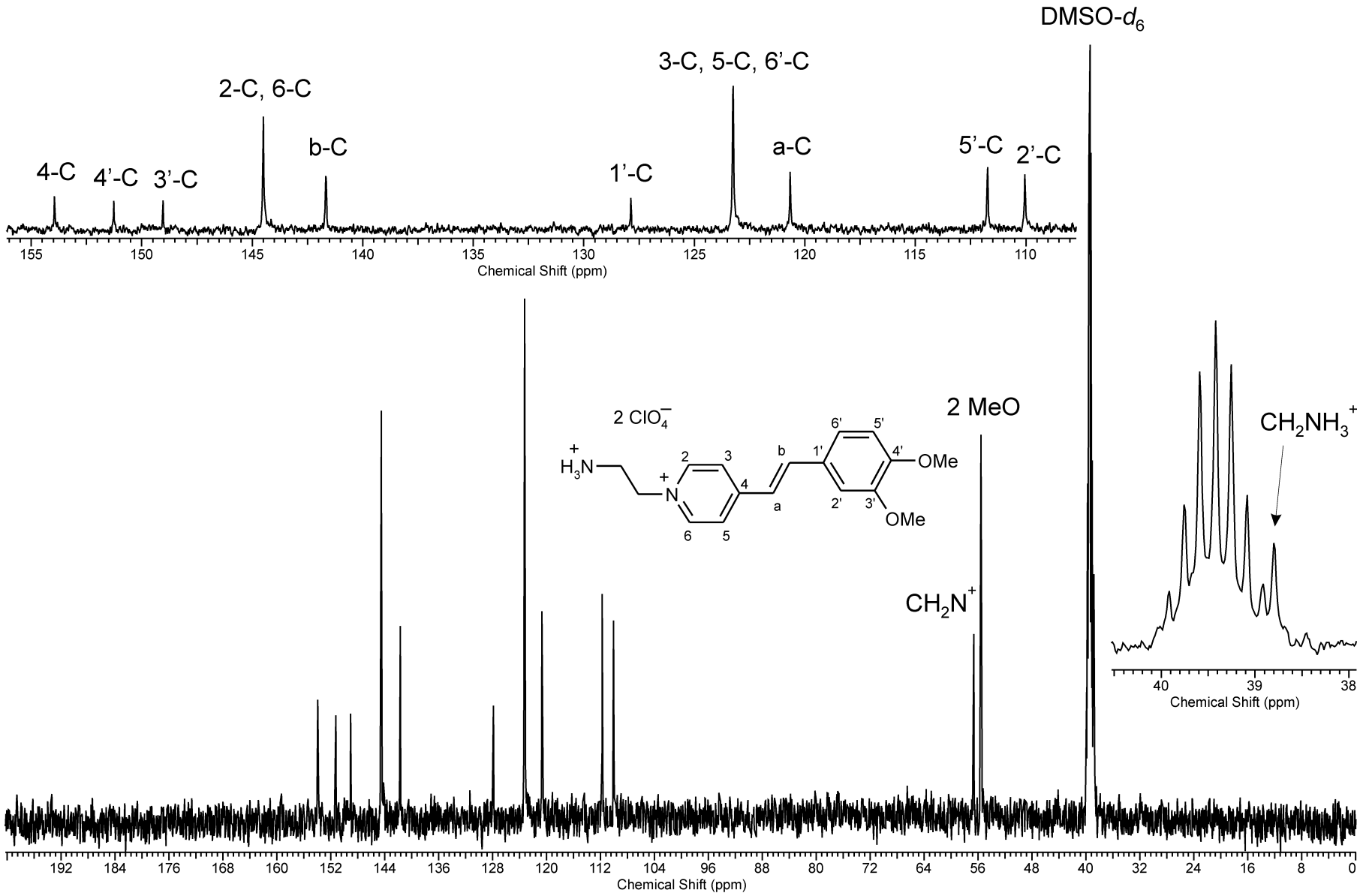

Fig. S18 ^{13}C NMR spectrum of dye **1h** (125.76 MHz, DMSO-d_6, 30 °C).

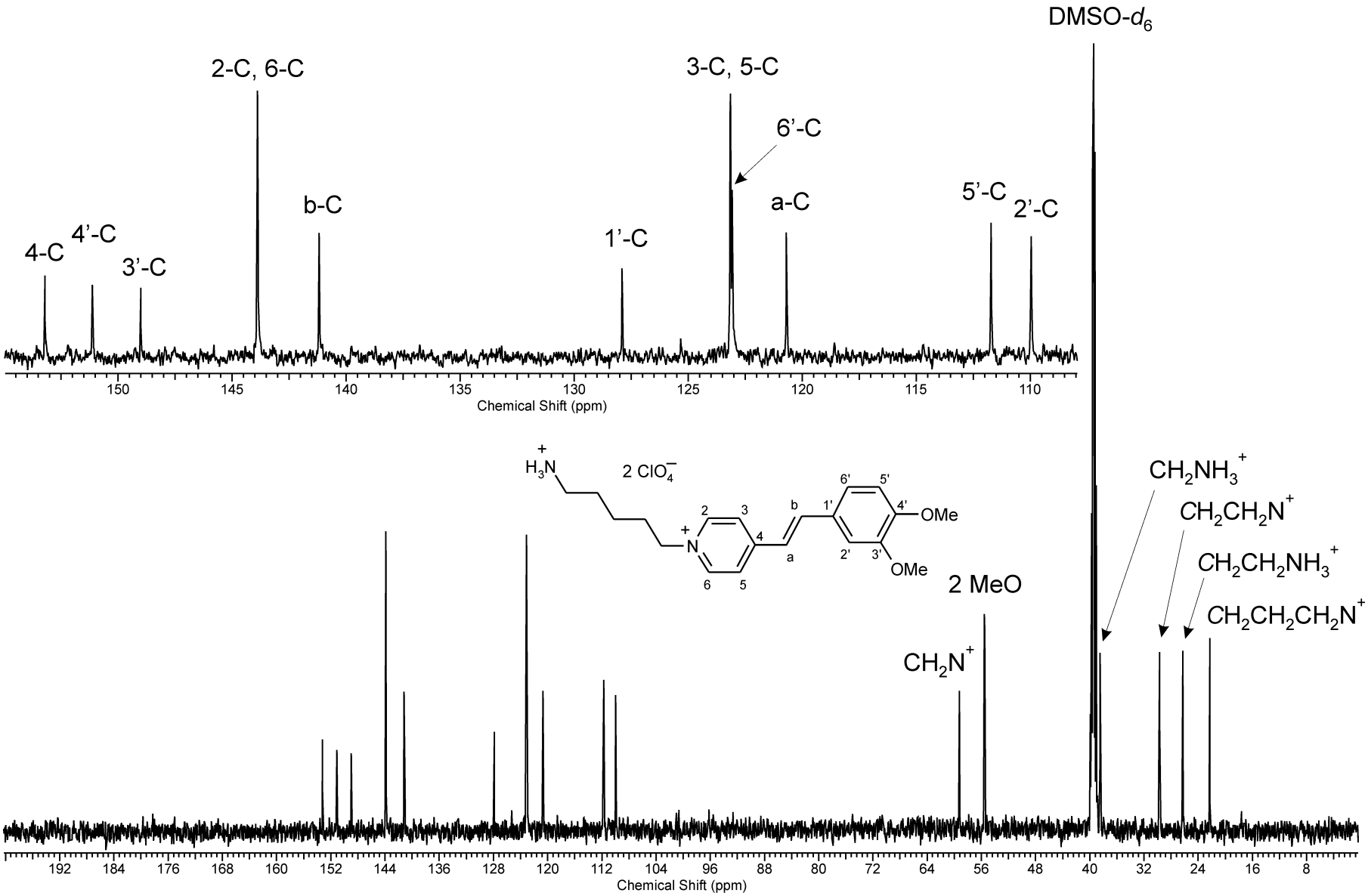

Fig. S19 ^{13}C NMR spectrum of dye **1i** (125.76 MHz, DMSO-d_6, 30 °C).

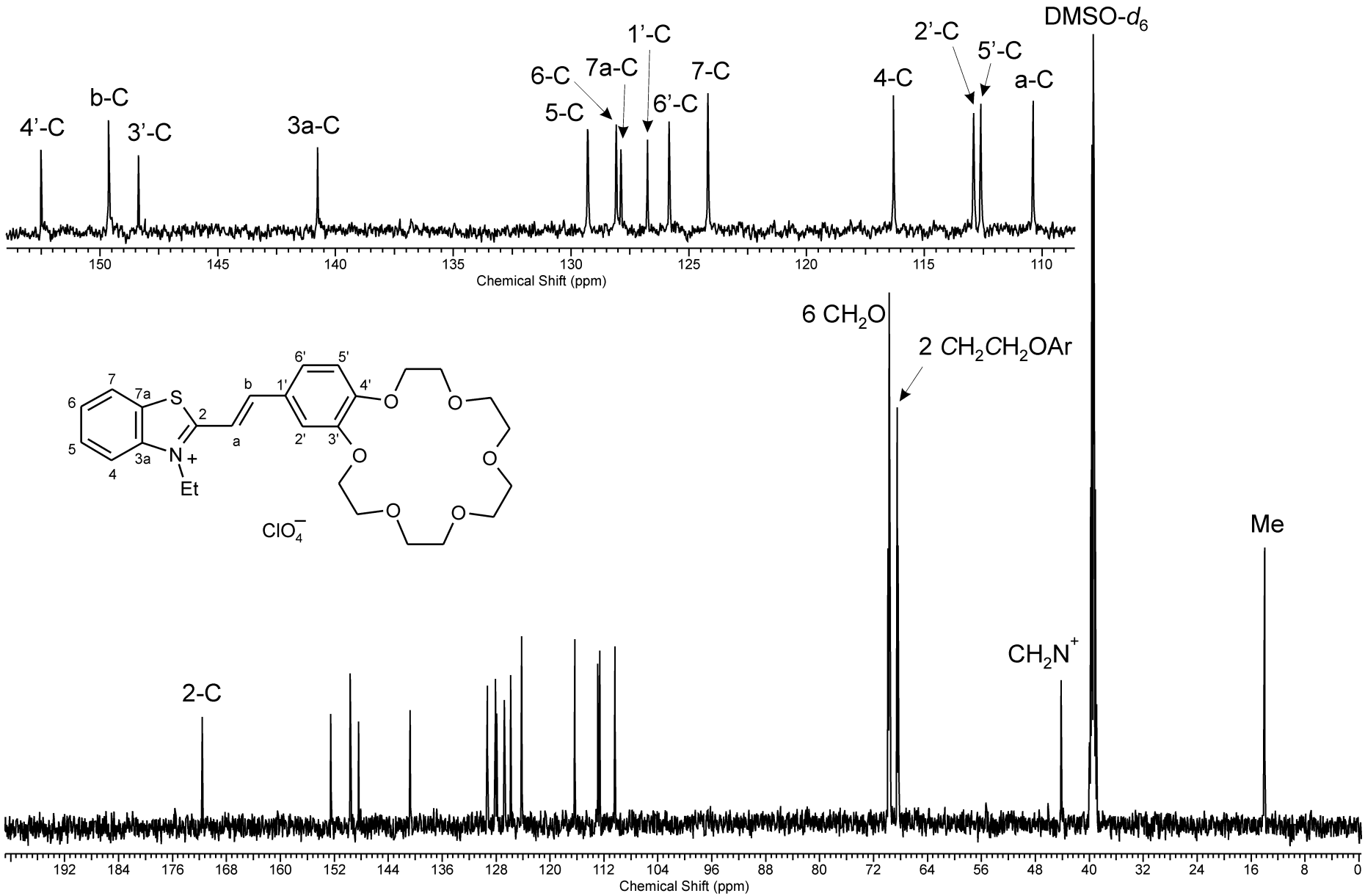

Fig. S20 ^{13}C NMR spectrum of dye **2c** (125.76 MHz, DMSO-d_6, 30 °C).

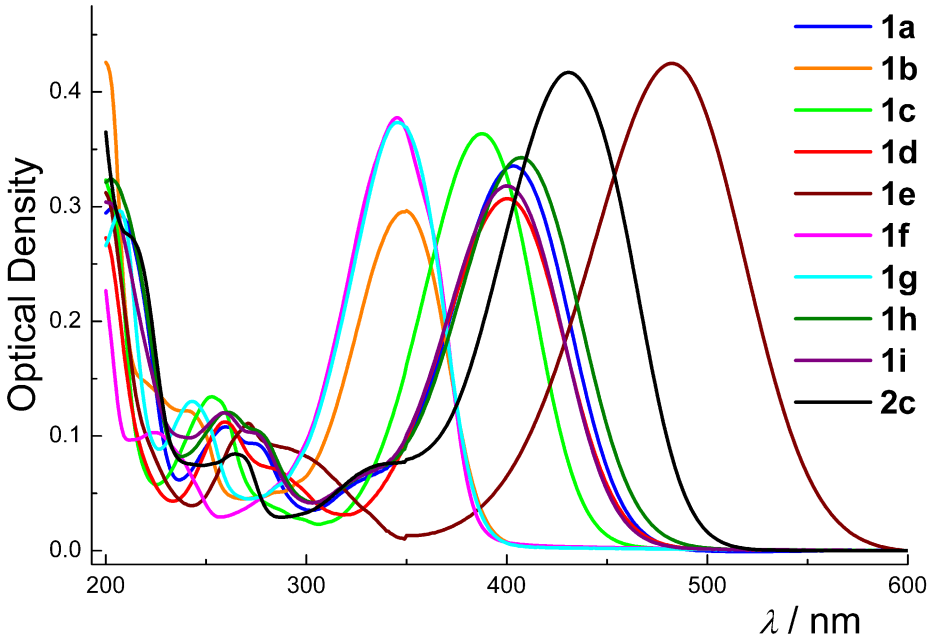

Fig. S21 Absorption spectra of dyes **1a–i** and **2c** (MeCN, C_{dye} = 1×10^{-5} M, 1-cm quartz cell, ambient temperature).

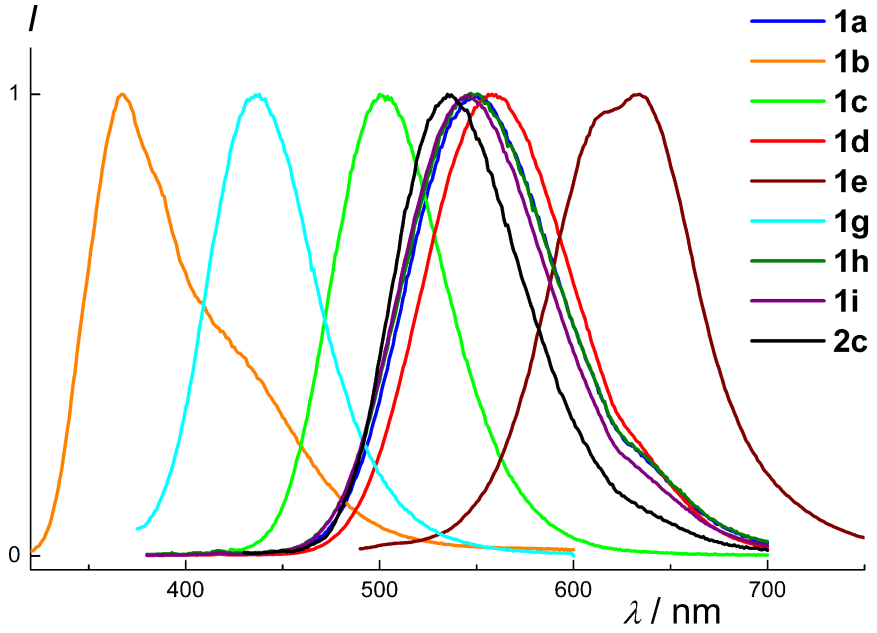

Fig. S22 Normalized emission spectra of dyes **1a–e,g–i** and **2c** (MeCN, C_{dye} = 1×10^{-5} M, 1-cm quartz cell, ambient temperature). Excitation 310 nm (**1b**), 330 nm (**1g**), 370 nm **(1a,c,d,h,i**), 420 nm (**2c**), and 470 nm (**1e**). Dye **1f** does not fluoresce.

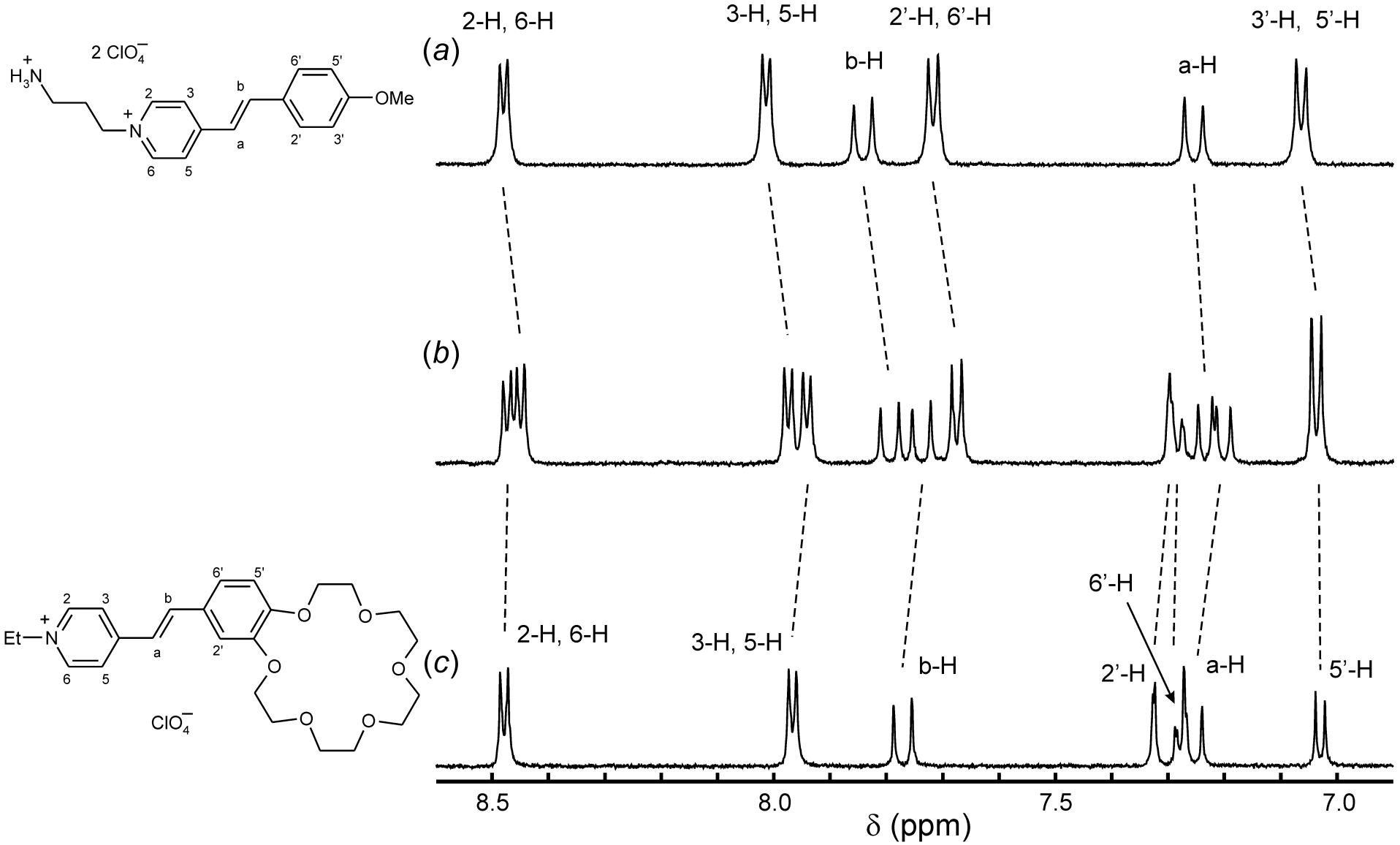

Fig. S23 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1c**, (*b*) a 1:1 mixture of dyes **1c** and **2a**, and (*c*) dye **2a** (C_{dye} = 1×10^{-3} M) (500.13 MHz, MeCN-d_3, 30 °C).

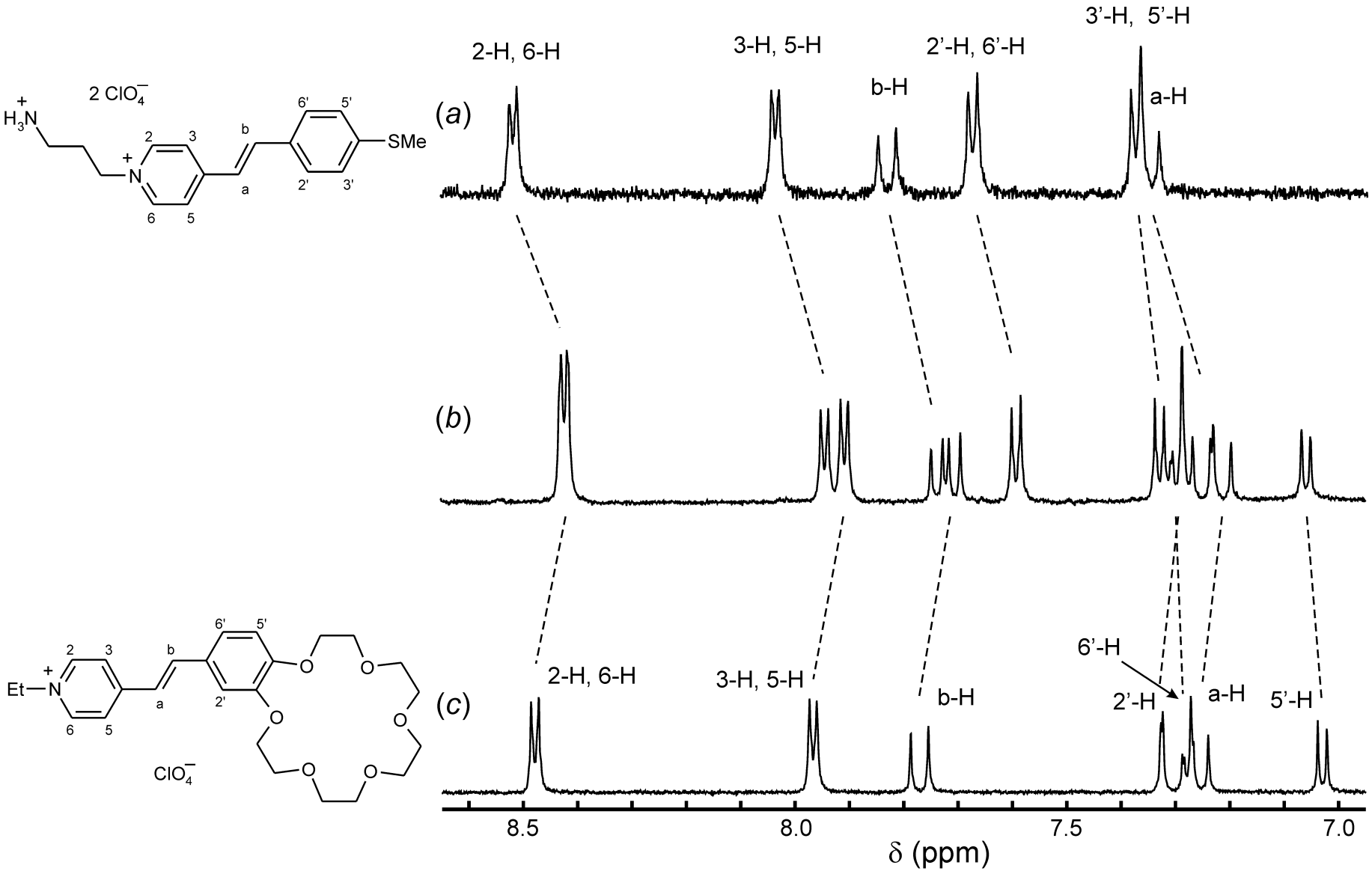

Fig. S24 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1d**, (*b*) a 1:1 mixture of dyes **1d** and **2a**, and (*c*) dye **2a** (C_{dye} = 1×10^{-3} M) (500.13 MHz, MeCN-d_3, 30 °C).

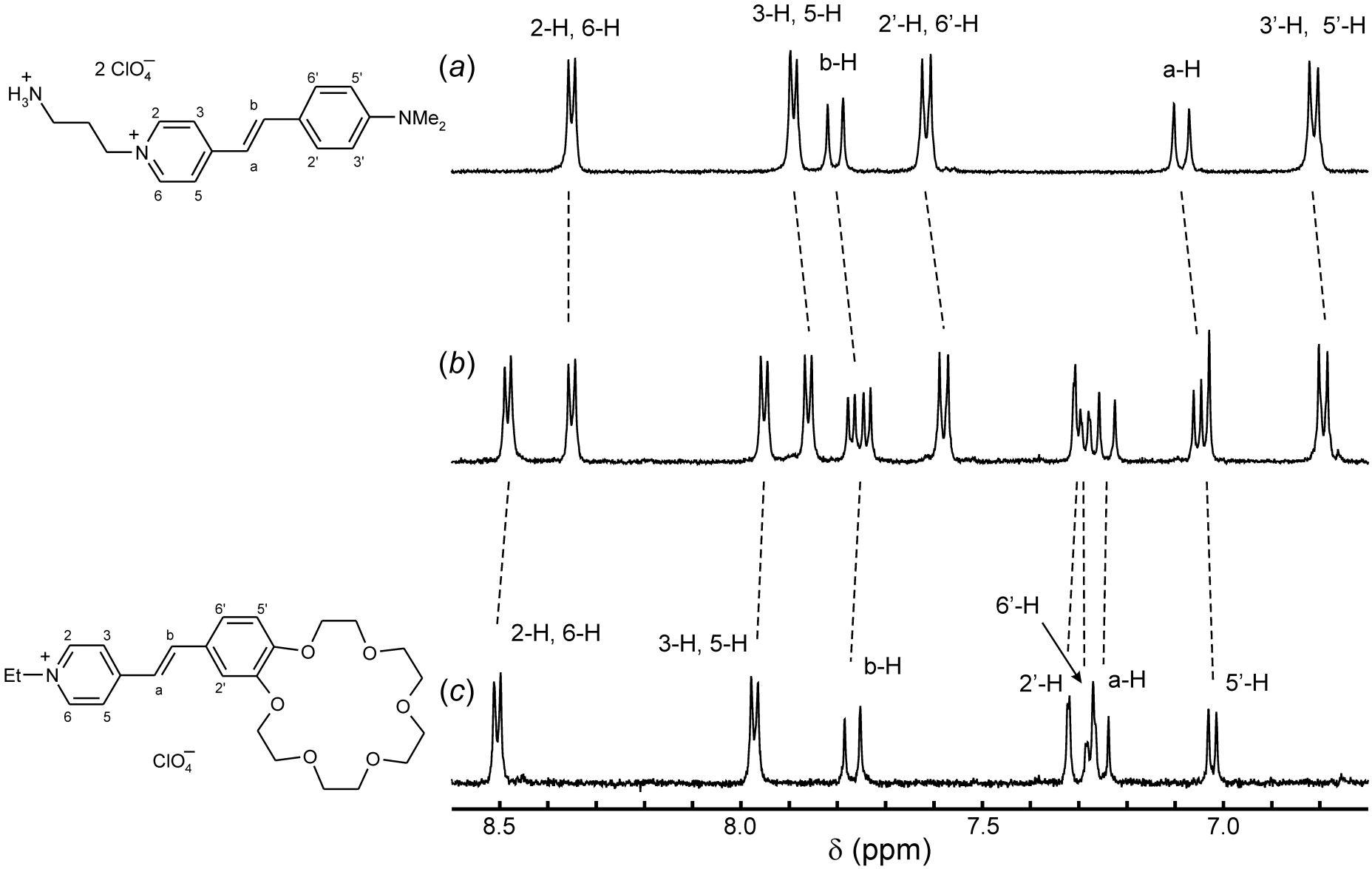

Fig. S25 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1e**, (*b*) a 1:1 mixture of dyes **1e** and **2a**, and (*c*) dye **2a** (C_{dye} = 1×10^{-3} M) (500.13 MHz, MeCN-d_3, 30 °C).

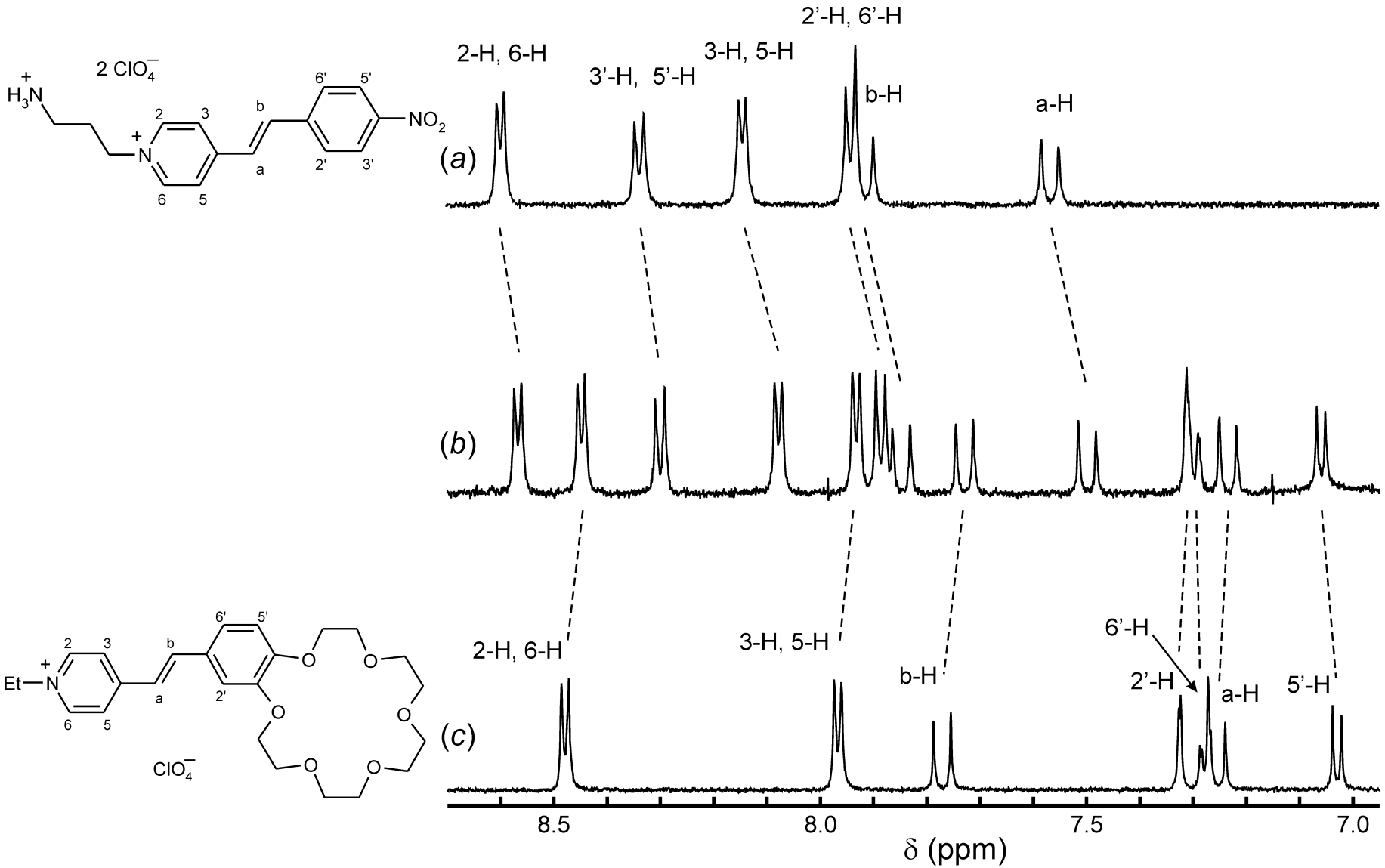

Fig. S26 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1f**, (*b*) a 1:1 mixture of dyes **1f** and **2a**, and (*c*) dye **2a** (C_{dye} = 1×10^{-3} M) (500.13 MHz, MeCN-d_3, 30 °C).

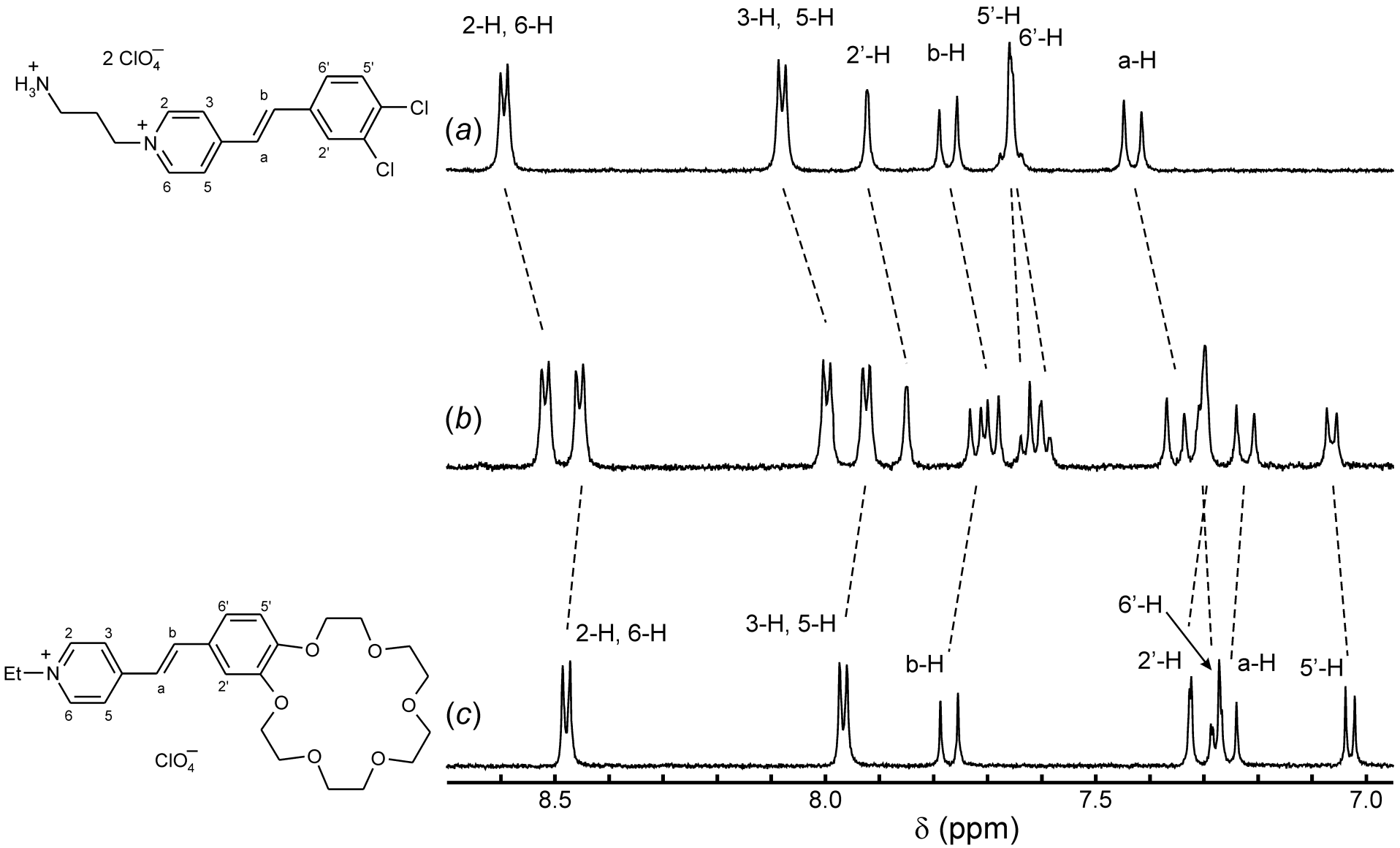

Fig. S27 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1g**, (*b*) a 1:1 mixture of dyes **1g** and **2a**, and (*c*) dye **2a** (C_{dye} = 1×10^{-3} M) (500.13 MHz, MeCN-d_3, 30 °C).

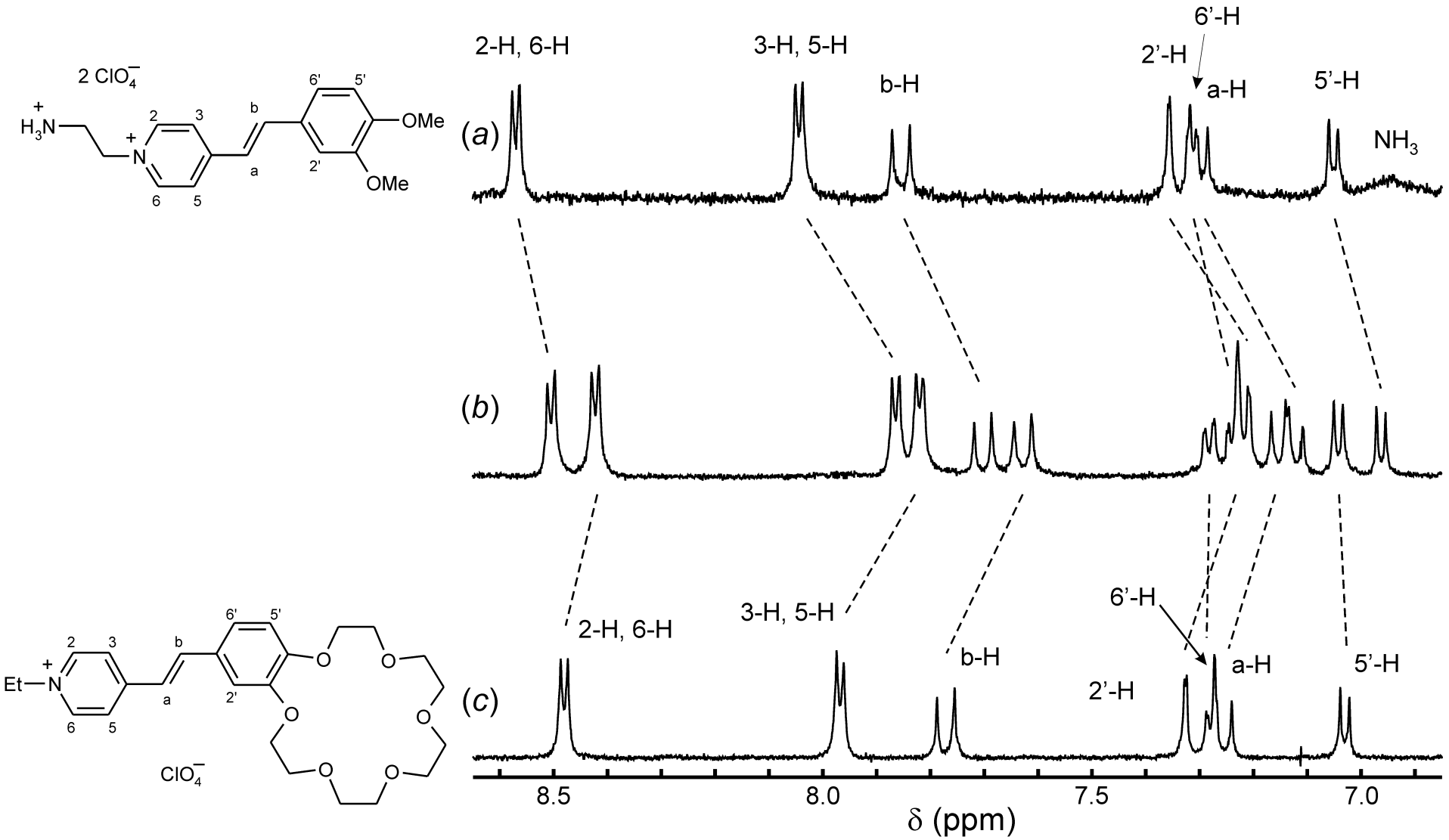

Fig. S28 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1h**, (*b*) a 1:1 mixture of dyes **1h** and **2a**, and (*c*) dye **2a** (C_{dye} = 1×10^{-3} M) (500.13 MHz, MeCN-d_3, 30 °C).

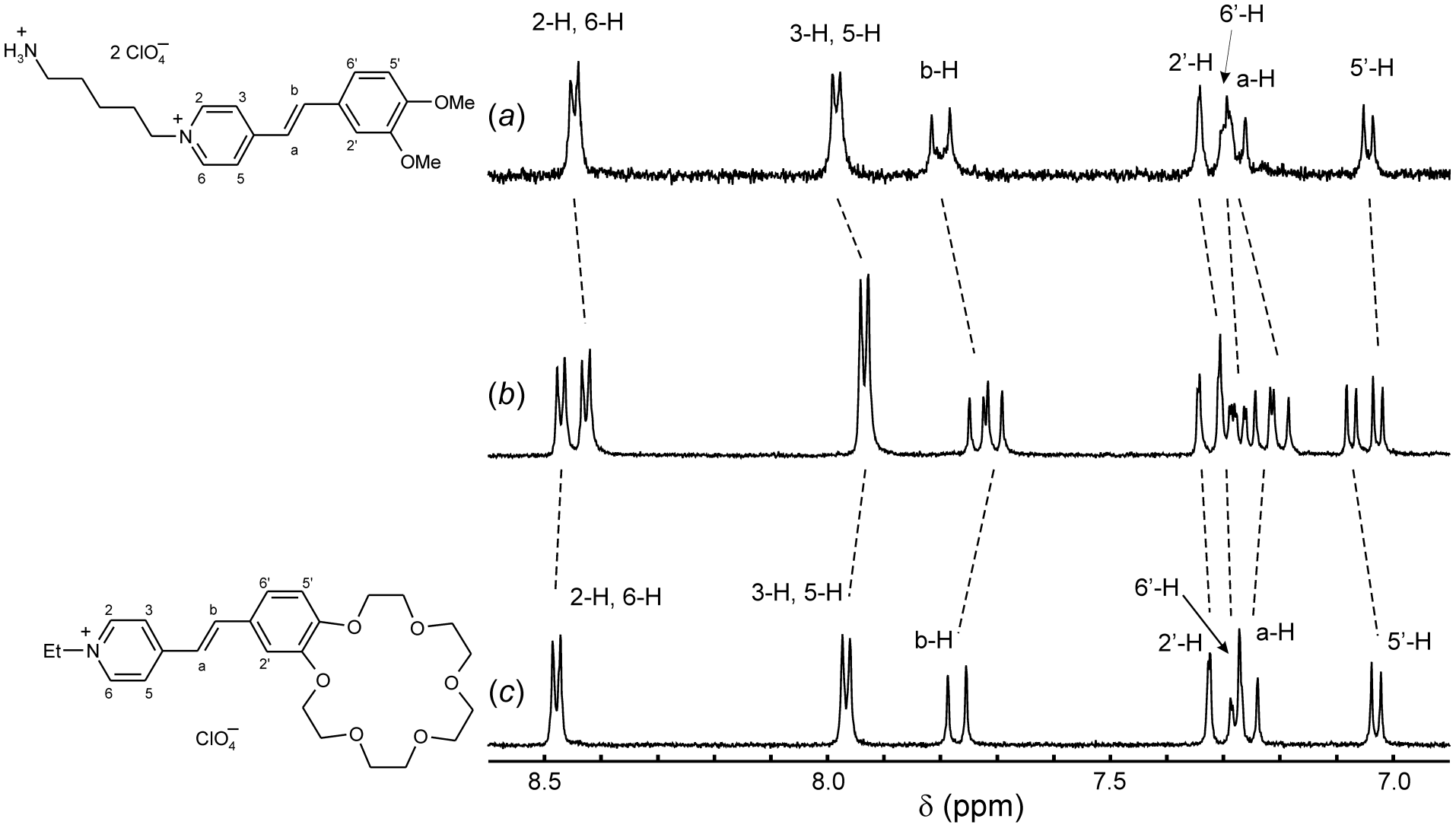

Fig. S29 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1i**, (*b*) a 1:1 mixture of dyes **1i** and **2a**, and (*c*) dye **2a** (C_{dye} = 1×10^{-3} M) (500.13 MHz, MeCN-d_3, 30 °C).

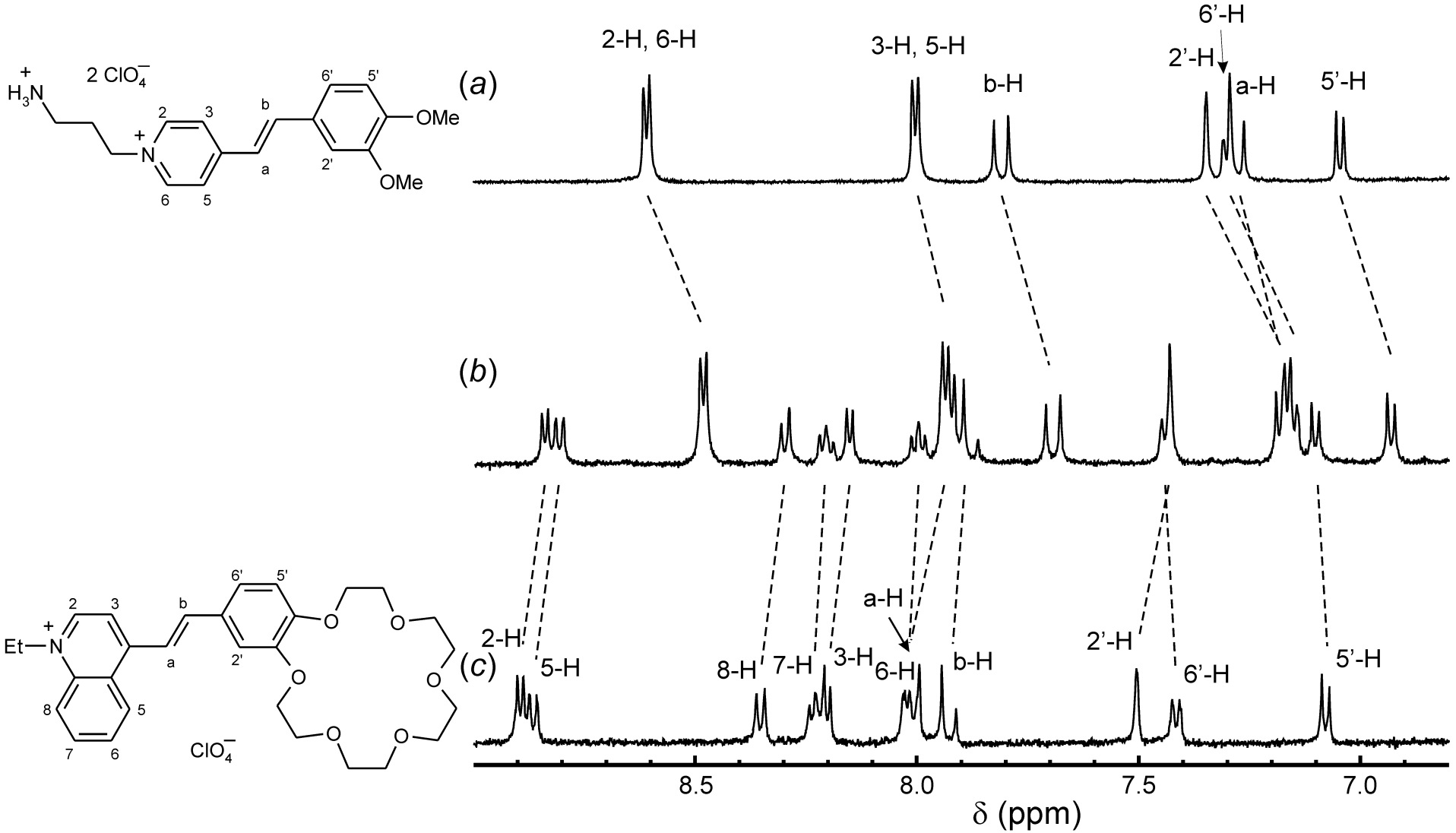

Fig. S30 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1a**, (*b*) a 1:1 mixture of dyes **1a** and **2b**, and (*c*) dye **2b** (C_{dye} = 1×10^{-3} M) (500.13 MHz, MeCN-d_3, 30 °C).

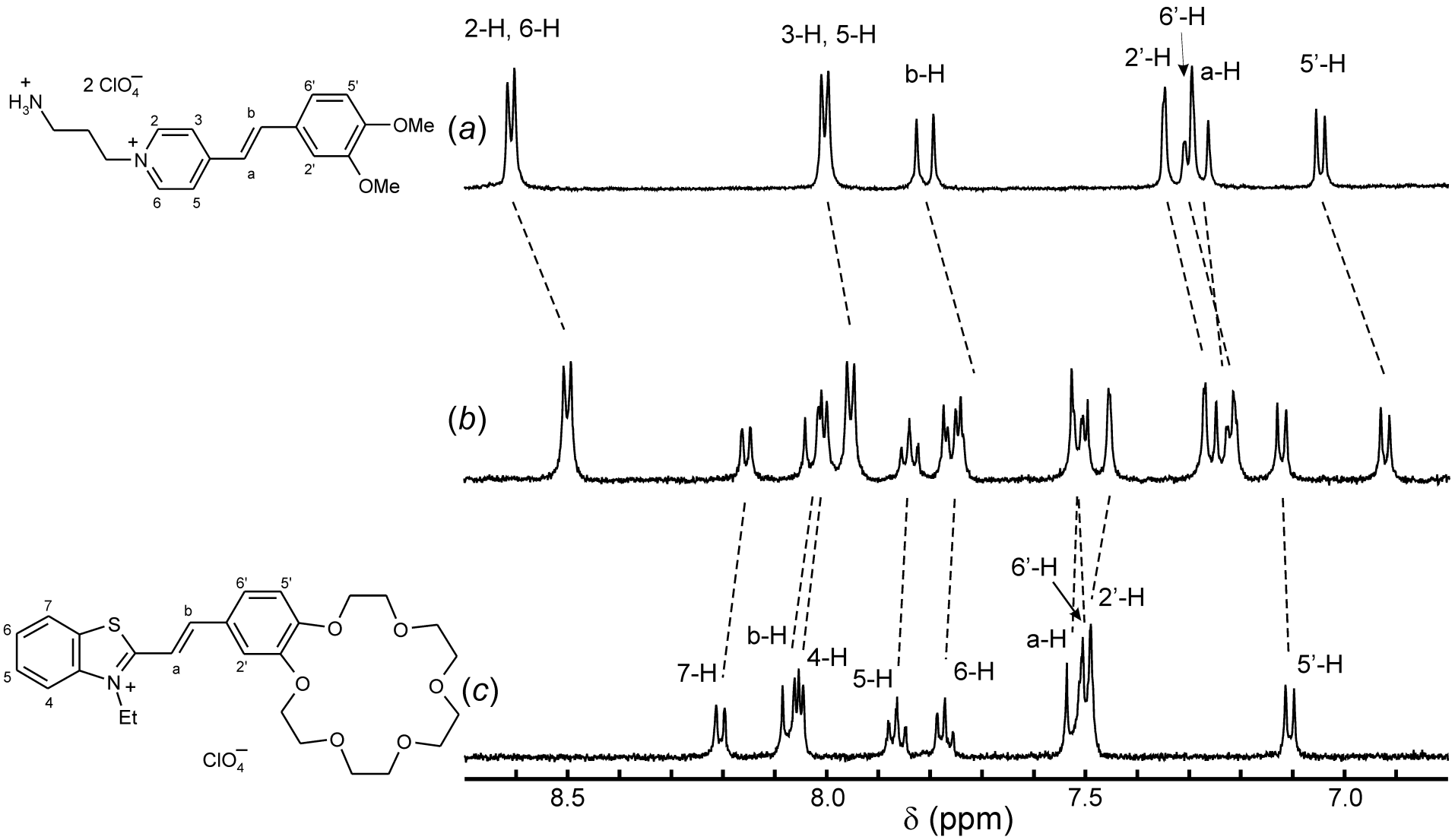

Fig. S31 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1a**, (*b*) a 1:1 mixture of dyes **1a** and **2c**, and (*c*) dye **2c** (C_{dye} = 1×10^{-3} M) (500.13 MHz, MeCN-d_3, 30 °C).

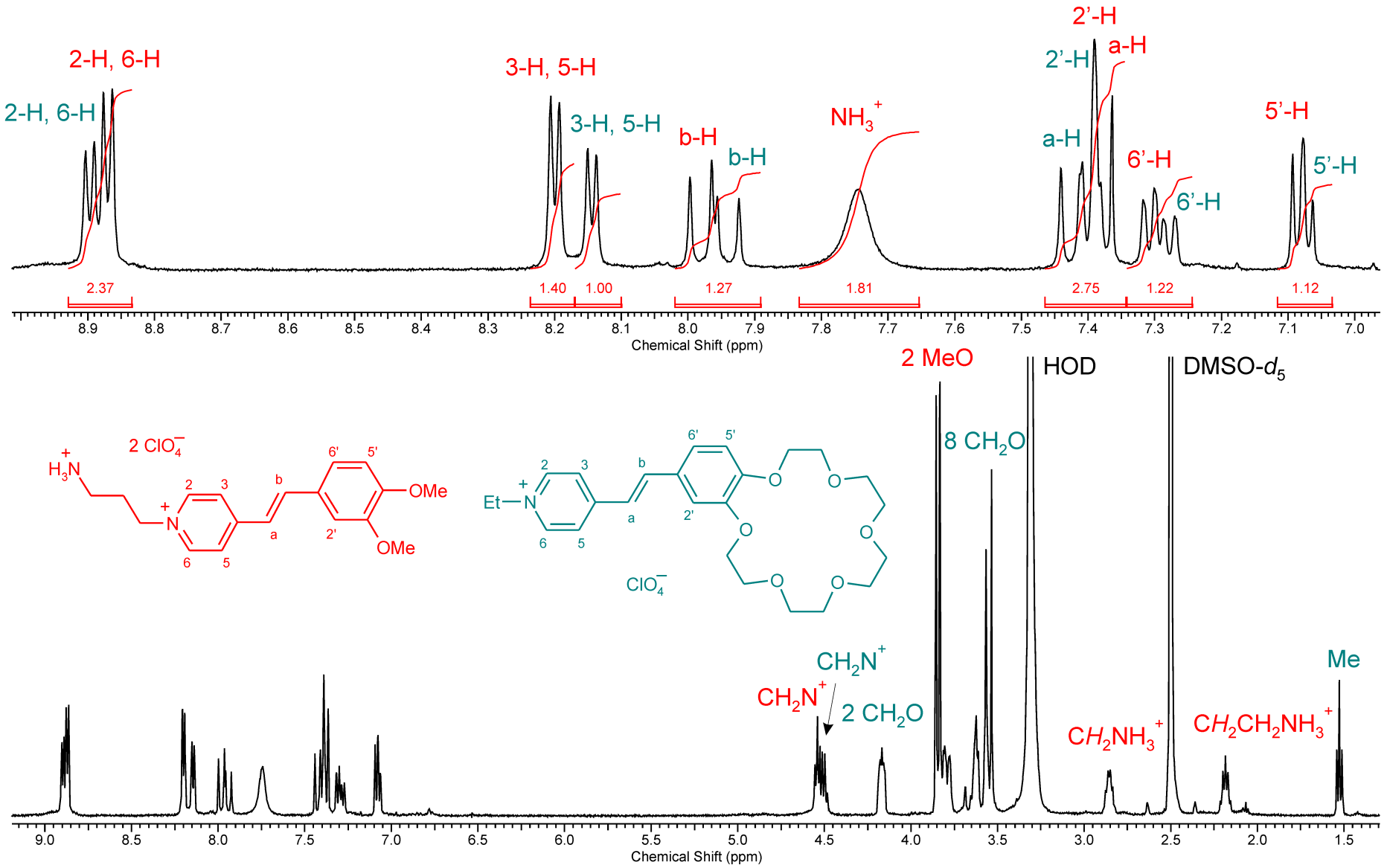

Fig. S32 ^{1}H NMR spectrum of complex (**1a**)$_{1.5}$·**2a**, which was obtained by crystallization (500.13 MHz, DMSO-d_6, 30 °C). In DMSO-d_6, the complex is destroyed to form a mixture of free dyes **1a** and **2a**.

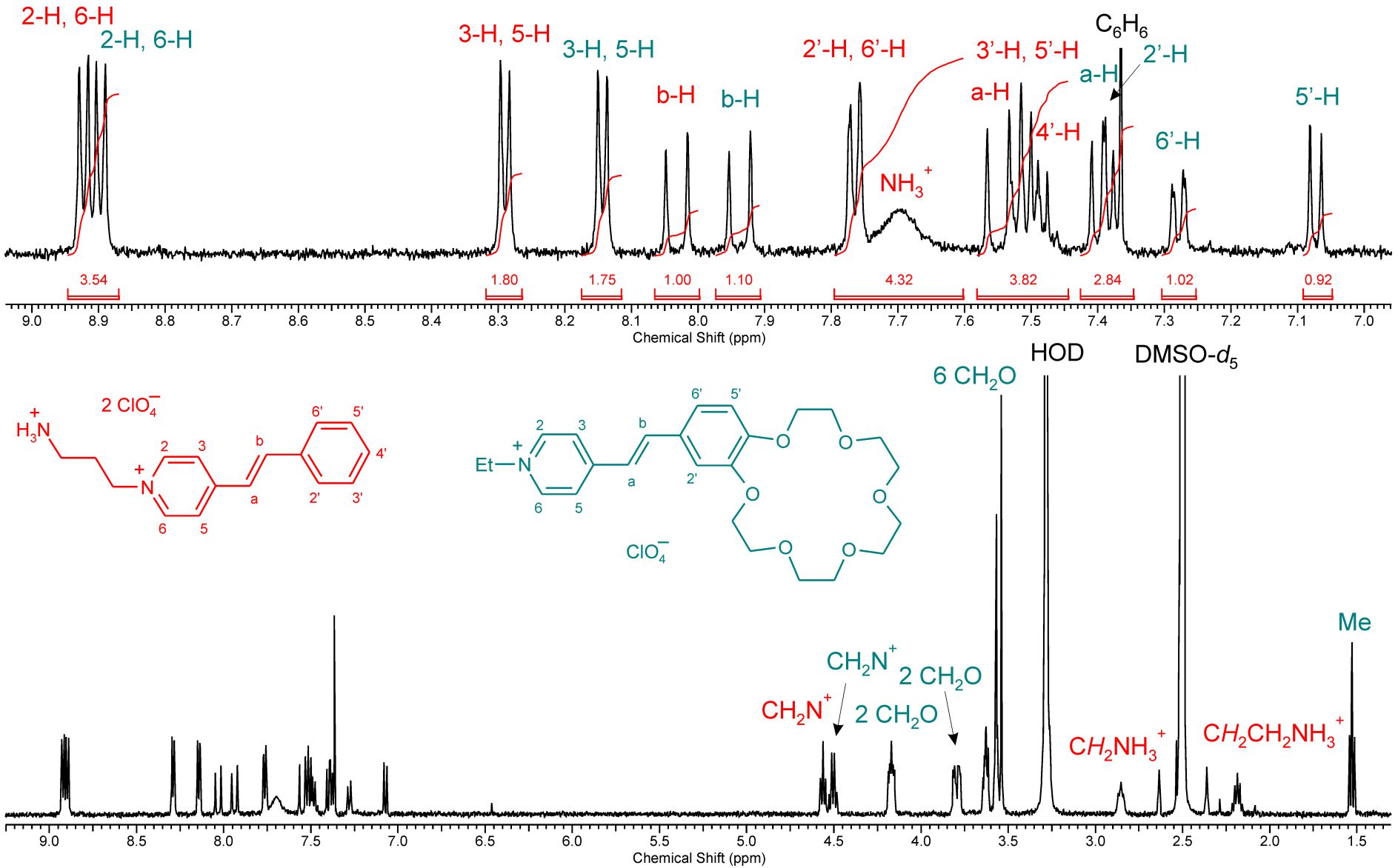

Fig. S33 ^{1}H NMR spectrum of complex **1b**·**2a**, which was obtained by crystallization (500.13 MHz, DMSO-d_6, 30 °C). In DMSO-d_6, the complex is destroyed to form a mixture of free dyes **1b** and **2a**.

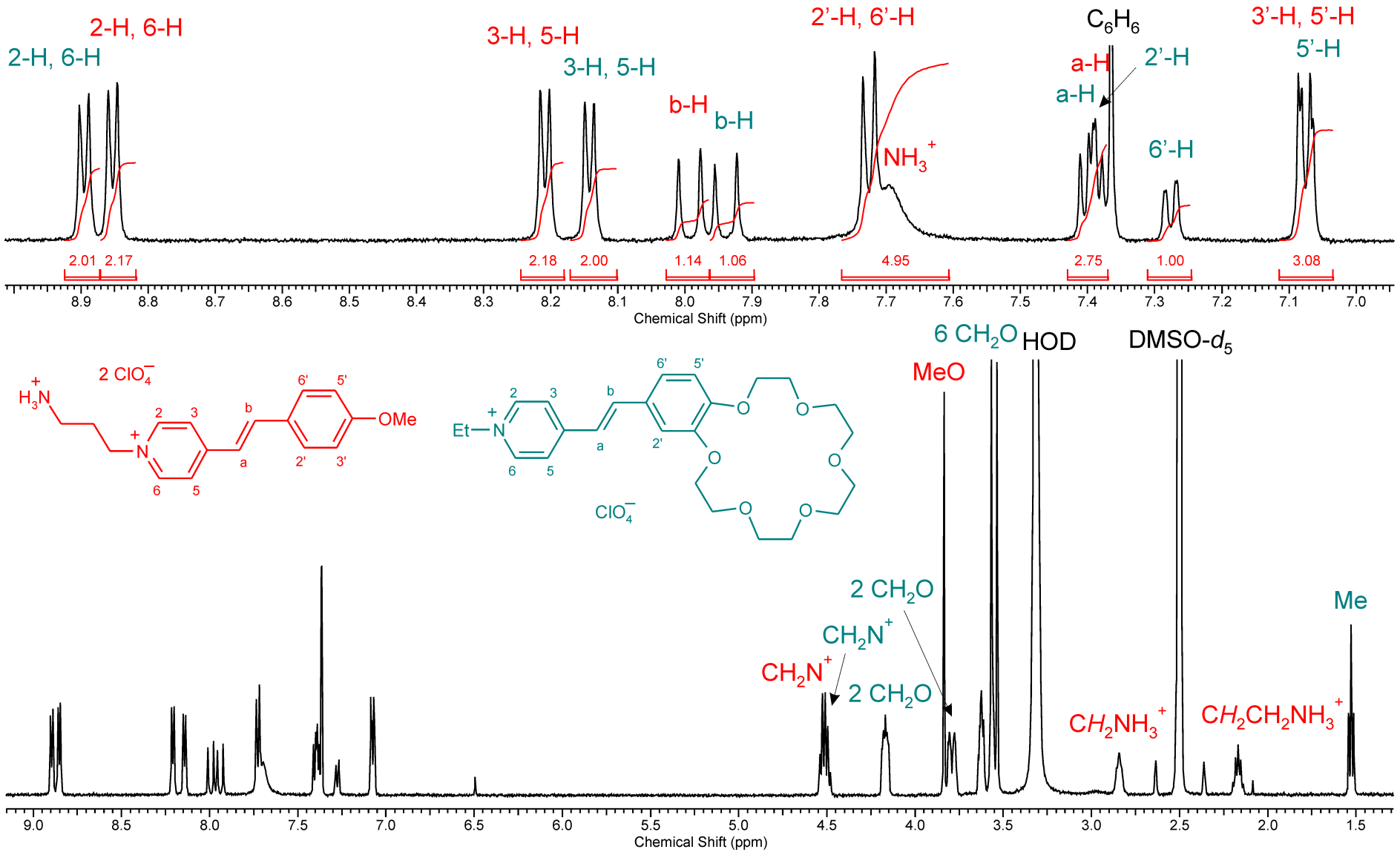

Fig. S34 ^{1}H NMR spectrum of complex **1c**·**2a**, which was obtained by crystallization (500.13 MHz, DMSO-d_6, 29 °C). In DMSO-d_6, the complex is destroyed to form a mixture of free dyes **1c** and **2a**.

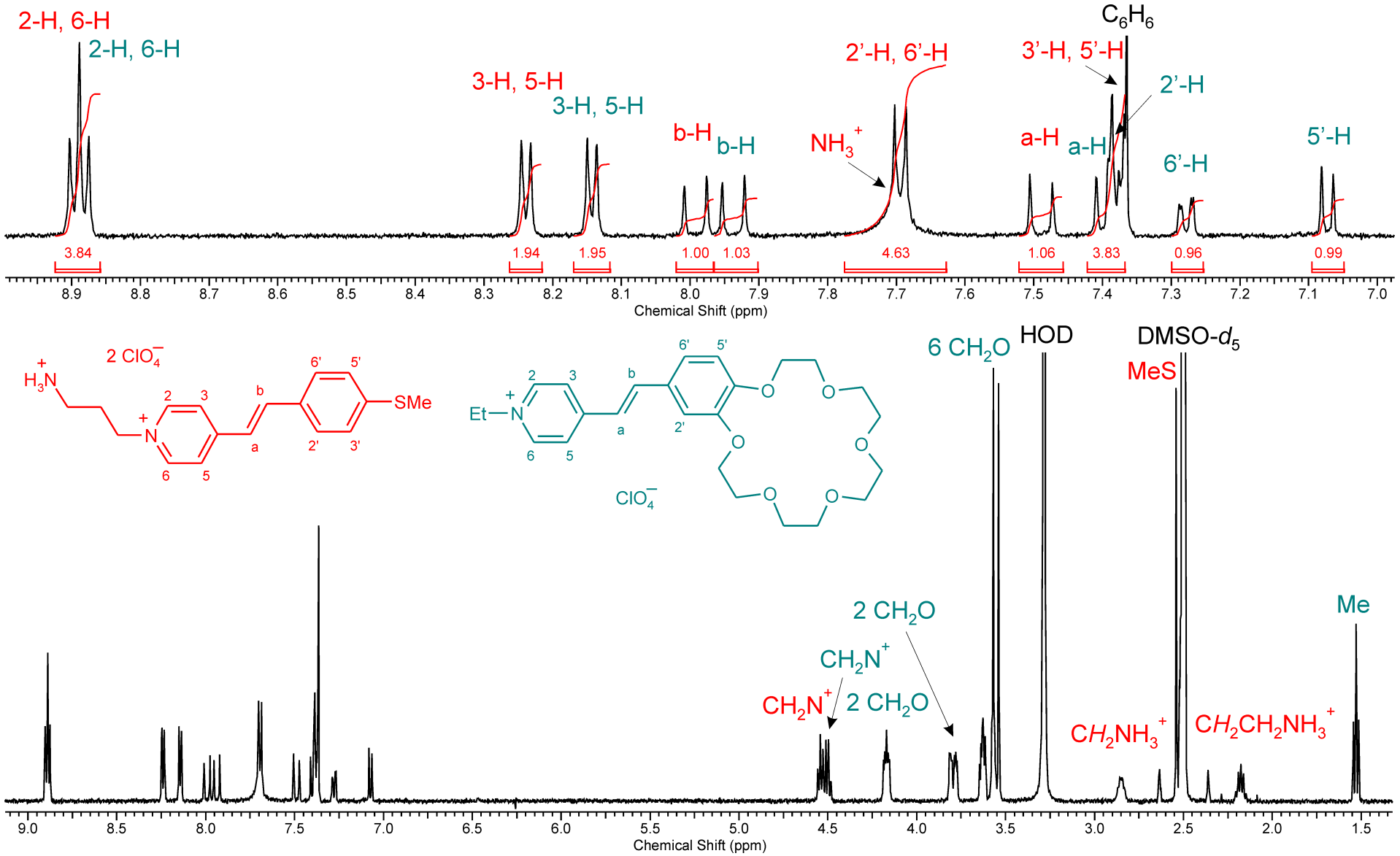

Fig. S35 ^{1}H NMR spectrum of complex **1d**·**2a**, which was obtained by crystallization (500.13 MHz, DMSO-d_6, 30 °C). In DMSO-d_6, the complex is destroyed to form a mixture of free dyes **1d** and **2a**.

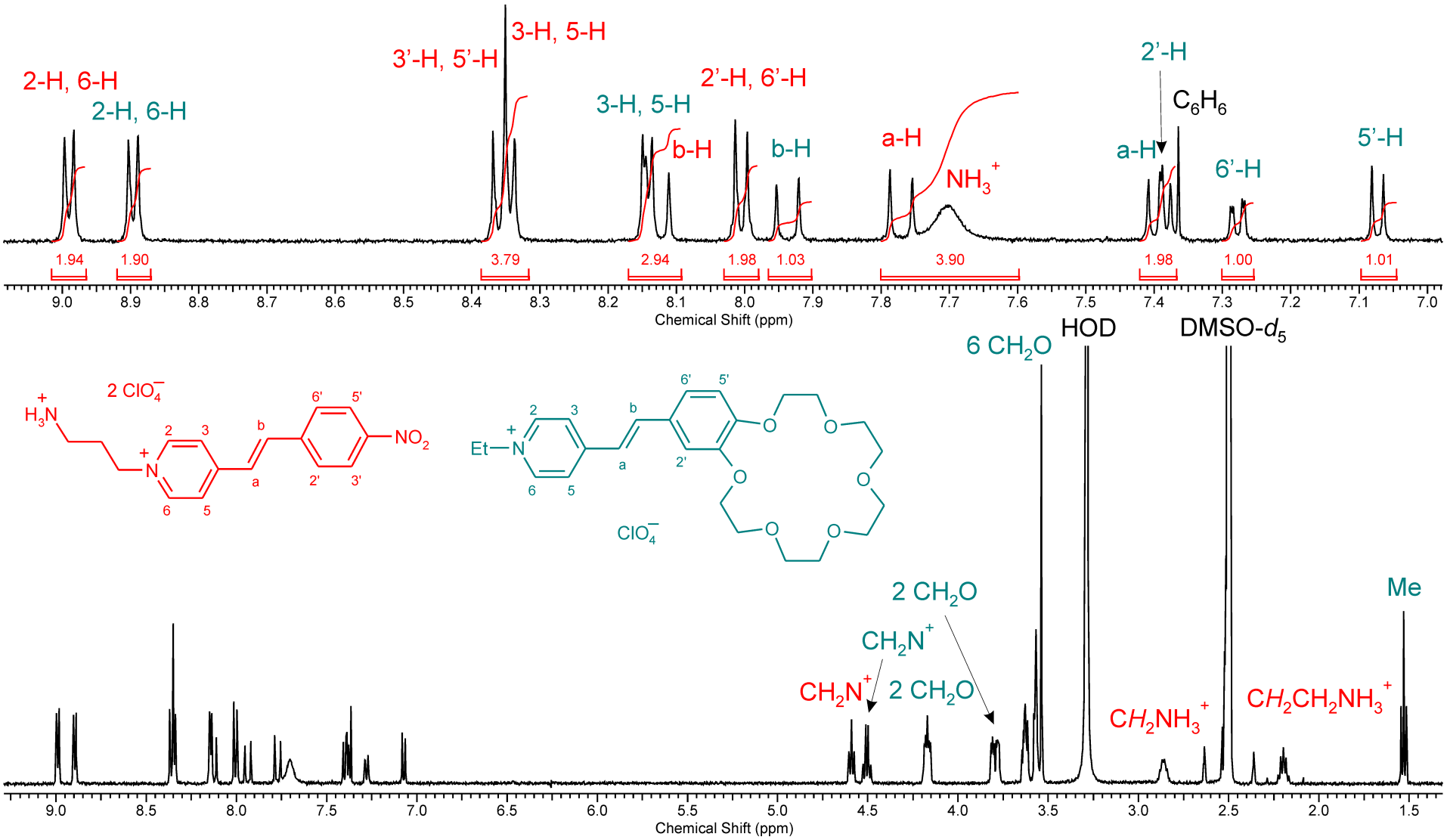

Fig. S36 ^{1}H NMR spectrum of complex **1f**·**2a**, which was obtained by crystallization (500.13 MHz, DMSO-d_6, 30 °C). In DMSO-d_6, the complex is destroyed to form a mixture of free dyes **1f** and **2a**.

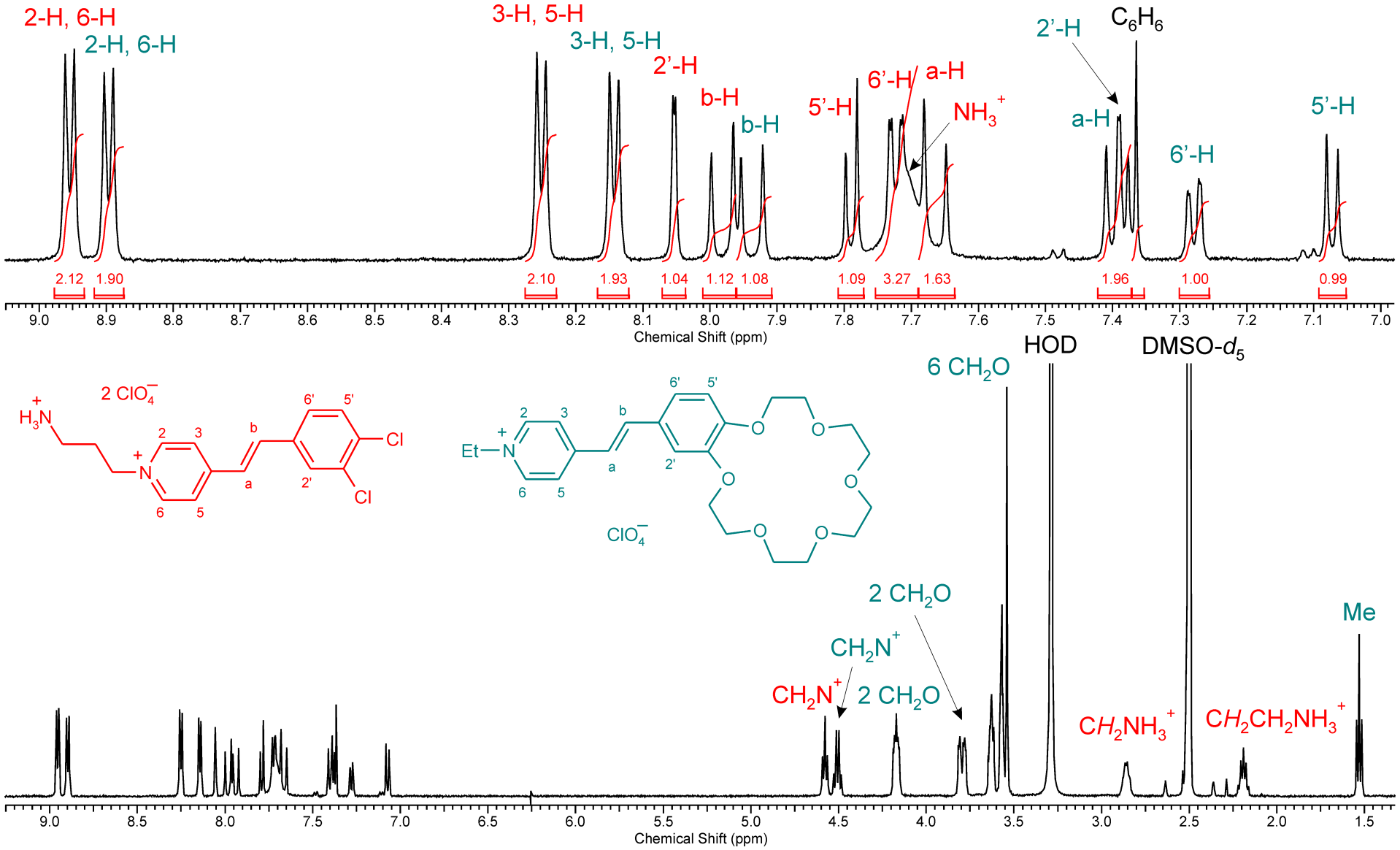

Fig. S37 ^{1}H NMR spectrum of complex **1g**·**2a**, which was obtained by crystallization (500.13 MHz, DMSO-d_6, 30 °C). In DMSO-d_6, the complex is destroyed to form a mixture of free dyes **1g** and **2a**.

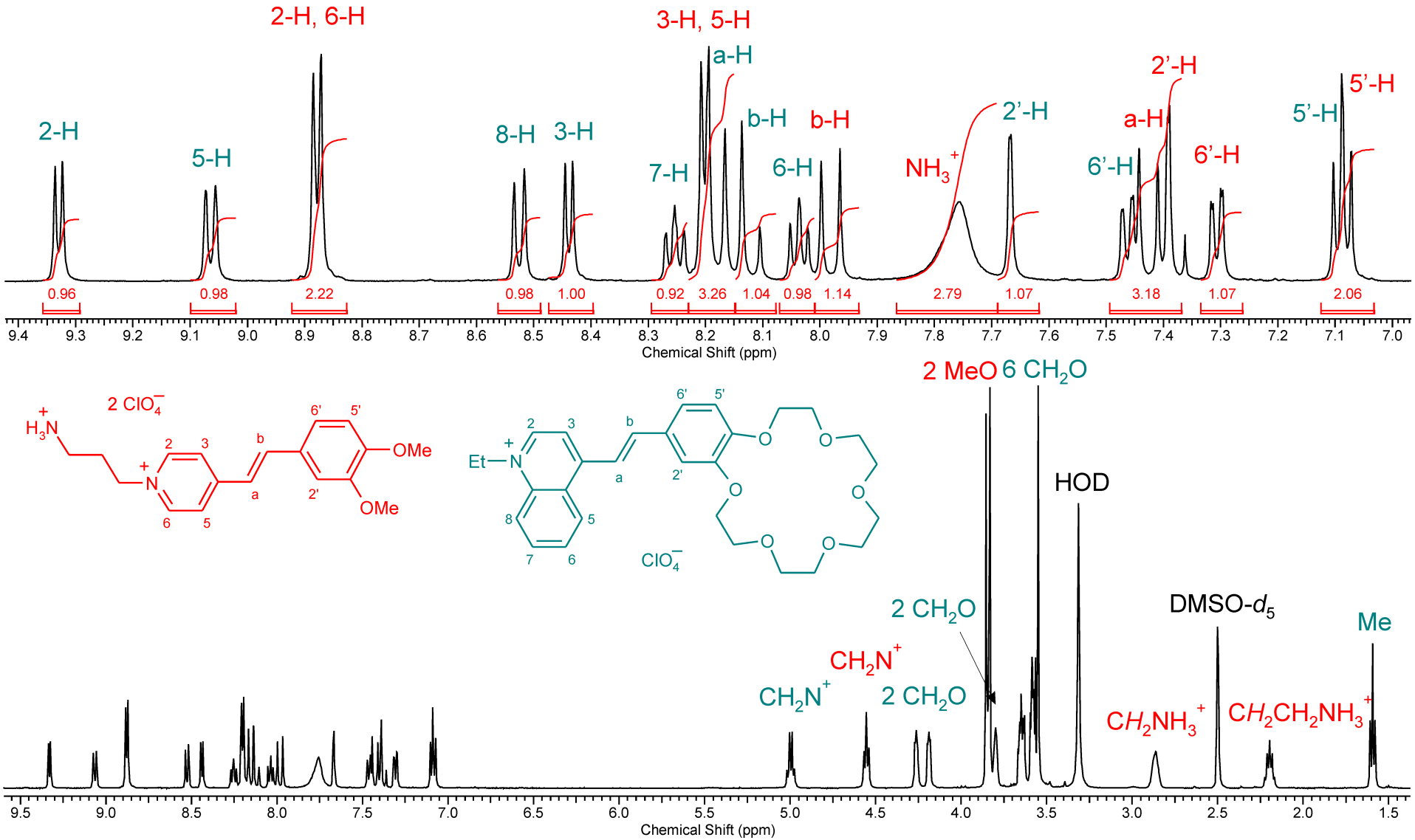

Fig. S38 ^{1}H NMR spectrum of complex **1a**·**2b**, which was obtained by crystallization (500.13 MHz, DMSO-d_6, 30 °C). In DMSO-d_6, the complex is destroyed to form a mixture of free dyes **1a** and **2b**.

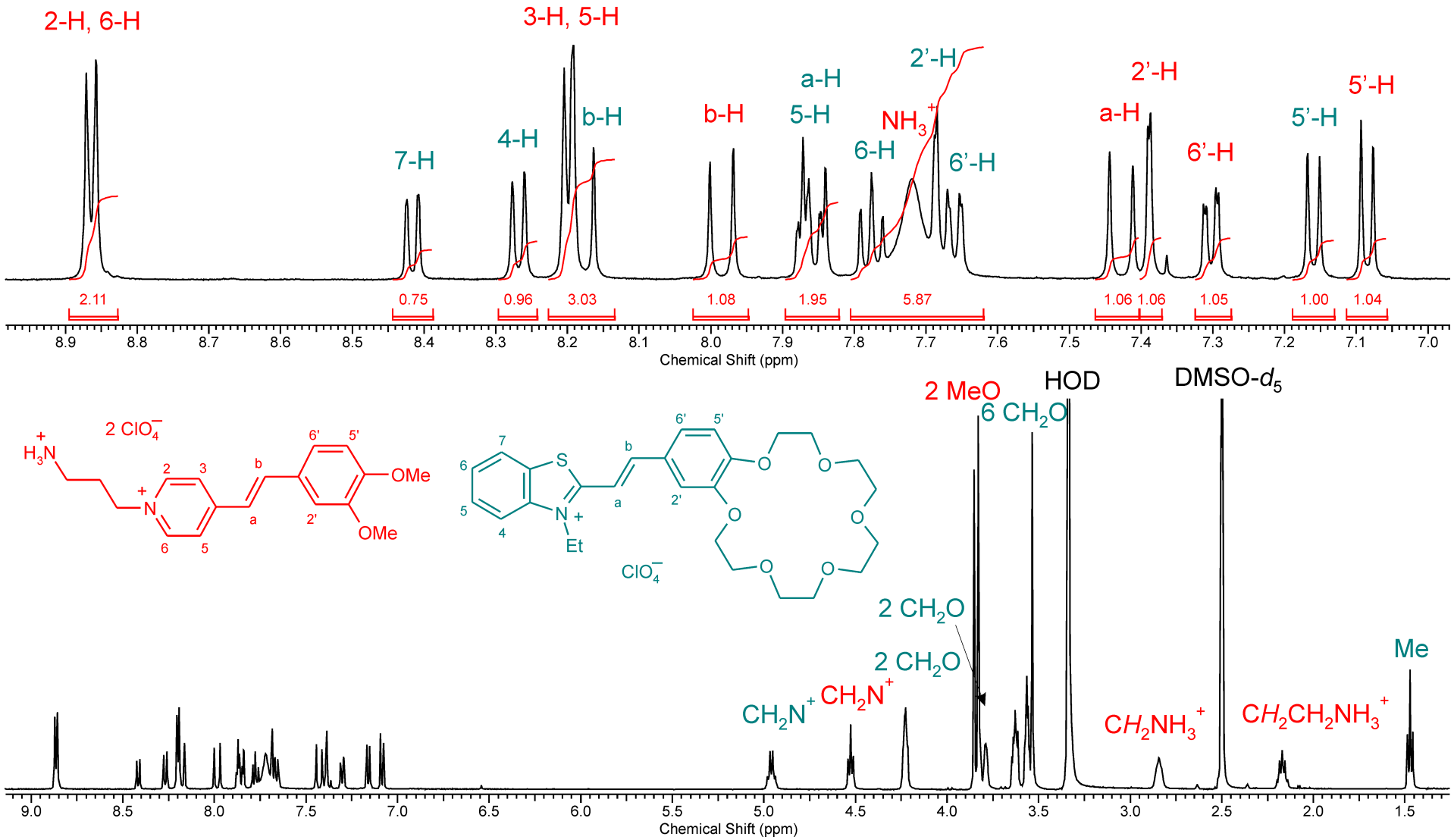

Fig. S39 ^{1}H NMR spectrum of complex **1a**·**2c**, which was obtained by crystallization (500.13 MHz, DMSO-d_6, 30 °C). In DMSO-d_6, the complex is destroyed to form a mixture of free dyes **1a** and **2c**.

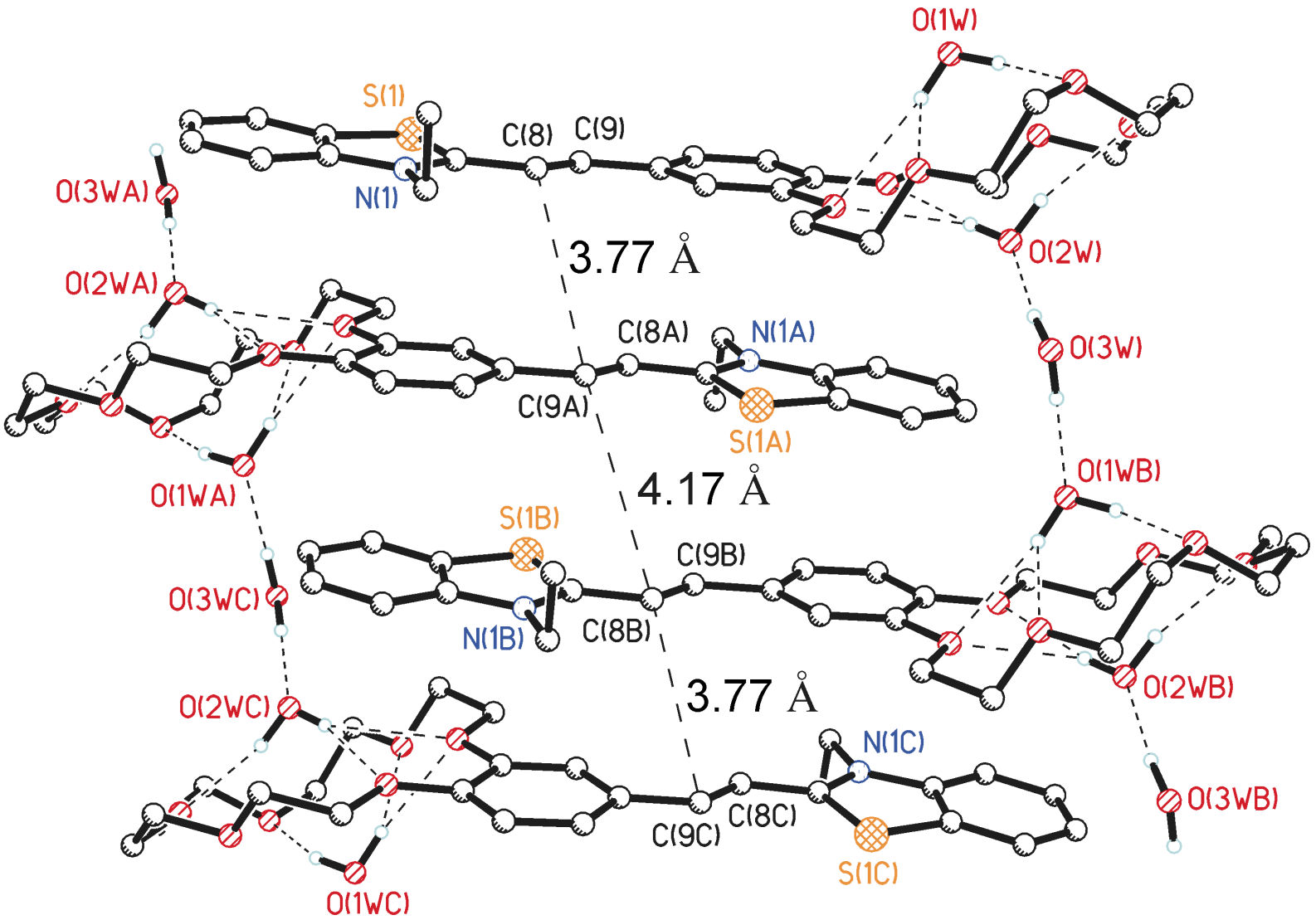

Fig. S40 Head-to-tail stack of dye cations in structure **2c**·$C_4H_8O_2$·$3H_2O$.

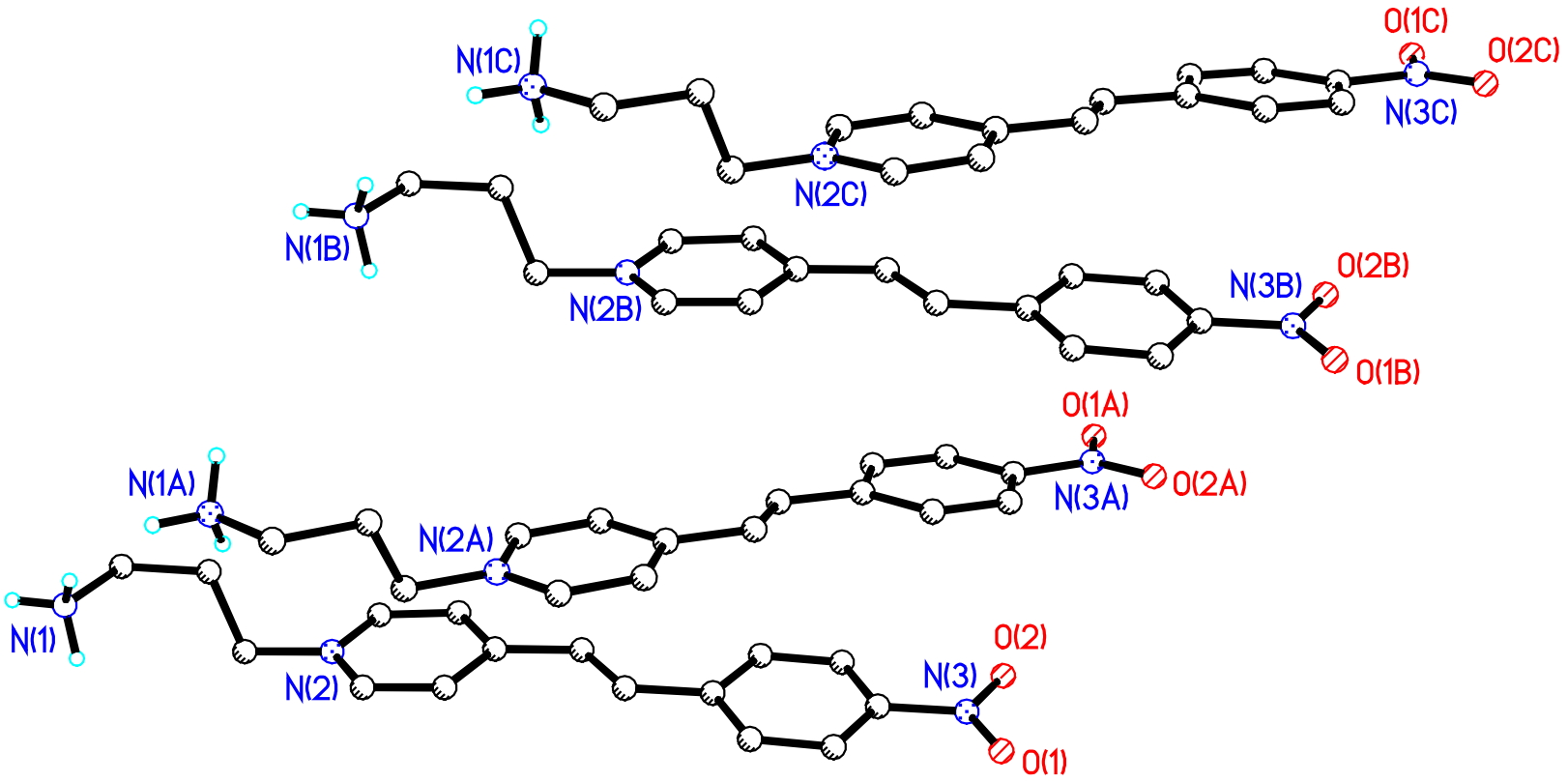

Fig. S41 Head-to-head stack of dye cations in structure **1f**·0.25H_2O.

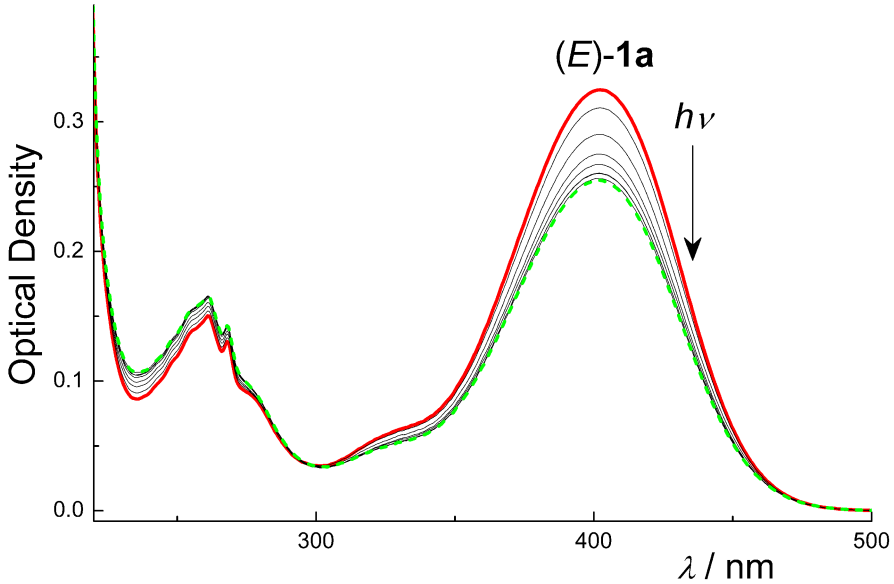

Fig. S42 Photolysis of solution of dye **1a** for 0, 1, 3, 6, 10, 20, 30, and 50 min (MeCN, $C_{\mathbf{1a}} = 9.66\times10^{-5}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **1a**.

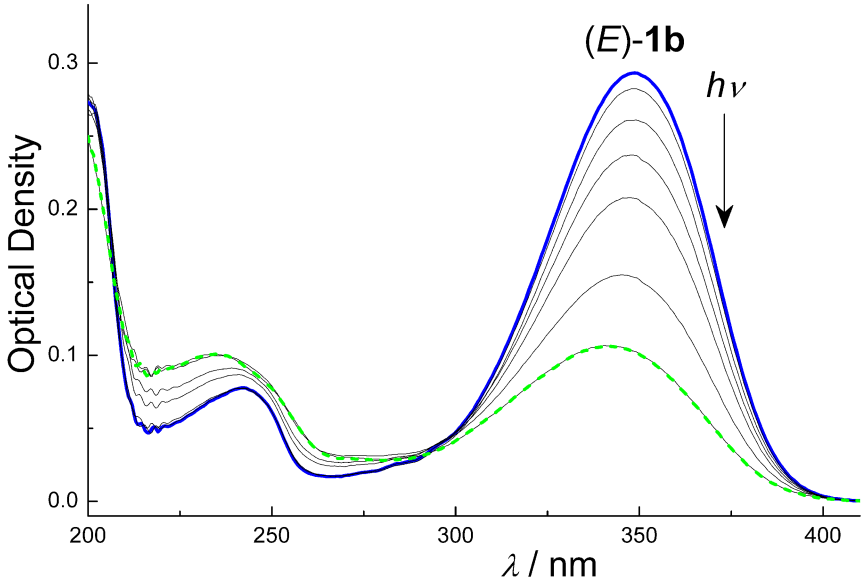

Fig. S43 Photolysis of solution of dye **1b** for 0, 1, 3, 6, 10, 20, and 80 min (MeCN, $C_{\mathbf{1b}} = 9.86\times10^{-5}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **1b**.

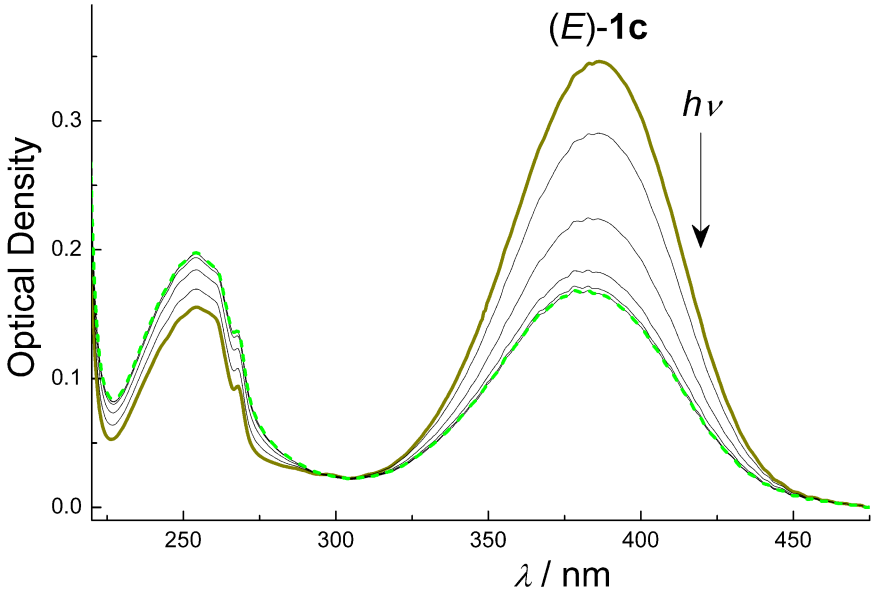

Fig. S44 Photolysis of solution of dye **1c** for 0, 1, 3, 6, 10, and 20 min (MeCN, $C_{\mathbf{1c}}$ = 9.50×10^{-5} M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **1c**.

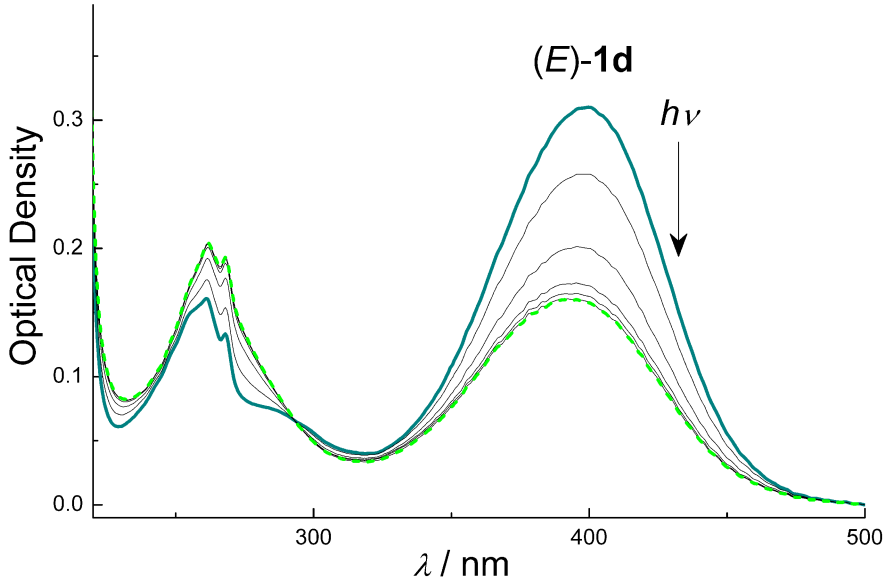

Fig. S45 Photolysis of solution of dye **1d** for 0, 1, 3, 6, 10, and 20 min (MeCN, $C_{\mathbf{1d}}$ = 1.01×10^{-4} M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **1d**.

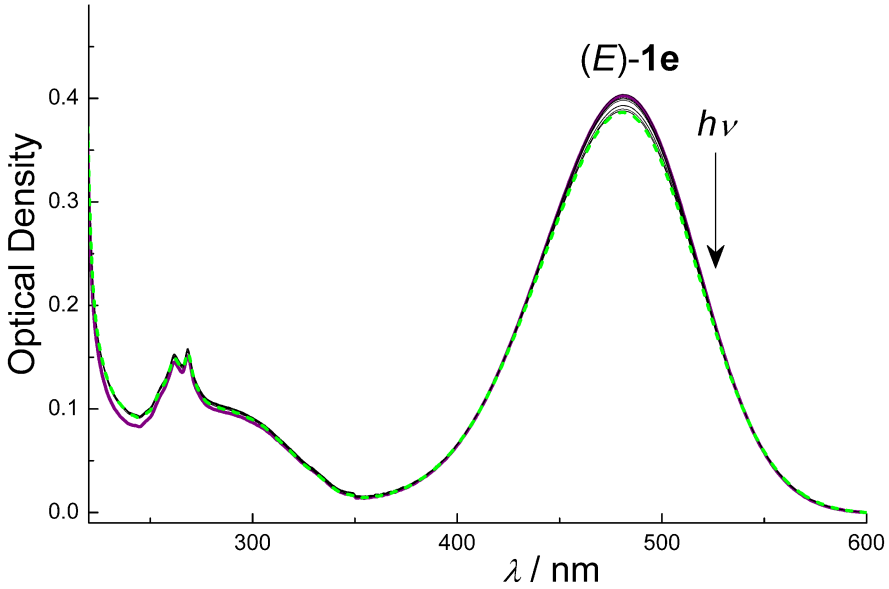

Fig. S46 Photolysis of solution of dye **1e** for 0, 1, 3, 6, 10, 20, 30, 50, 80, and 110 min (MeCN, $C_{\mathbf{1e}}$ = 1.03×10^{-4} M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **1e**.

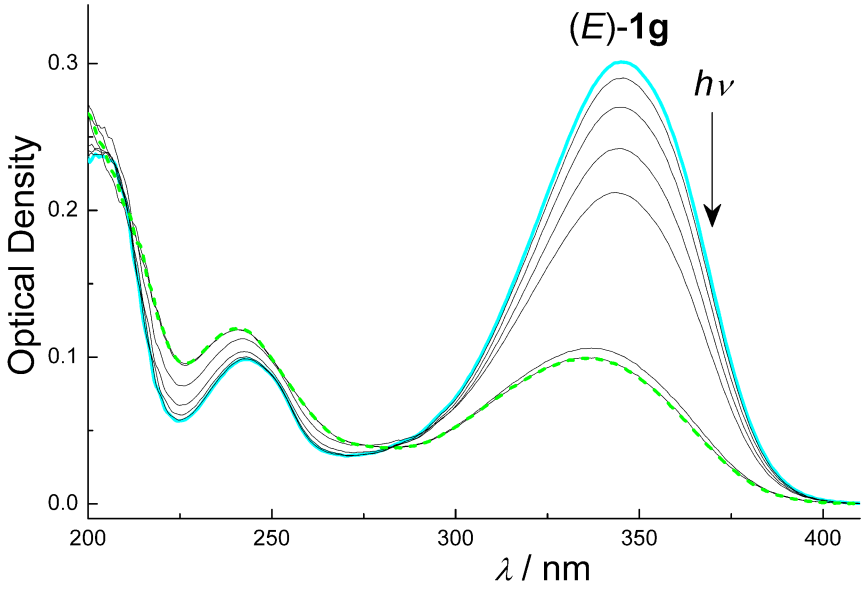

Fig. S47 Photolysis of solution of dye **1g** for 0, 1, 3, 6, 10, 50, and 80 min (MeCN, $C_{\mathbf{1g}}$ = 8.05×10^{-5} M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **1g**.

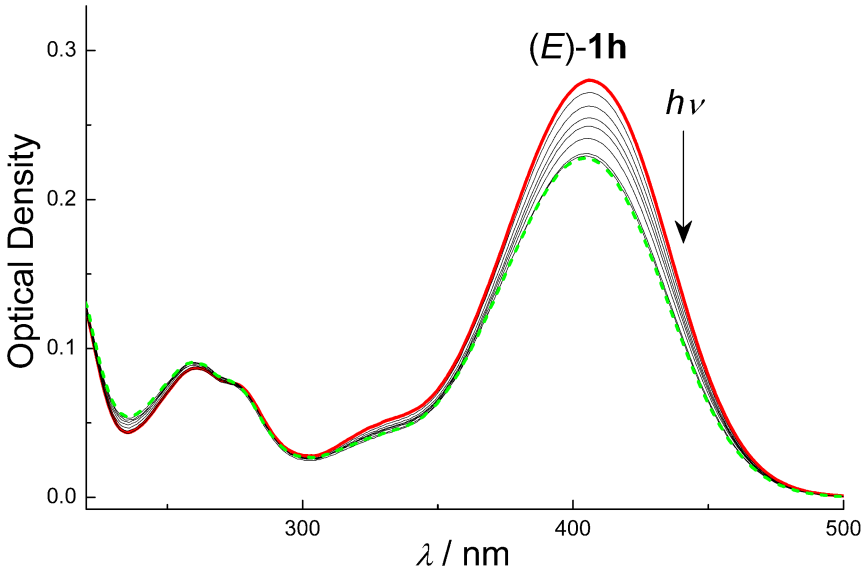

Fig. S48 Photolysis of solution of dye **1h** for 0, 1, 3, 6, 10, 20, 50, and 80 min (MeCN, $C_{\mathbf{1h}}$ = 8.16×10^{-5} M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **1h**.

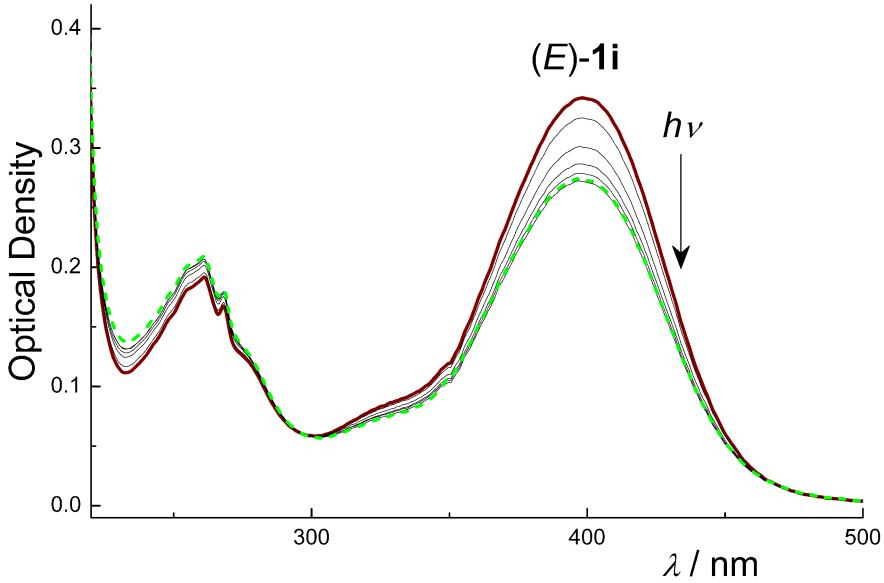

Fig. S49 Photolysis of solution of dye **1i** for 0, 1, 3, 6, 10, and 20 min (MeCN, $C_{\mathbf{1i}}$ = 1.07×10^{-4} M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **1i**.

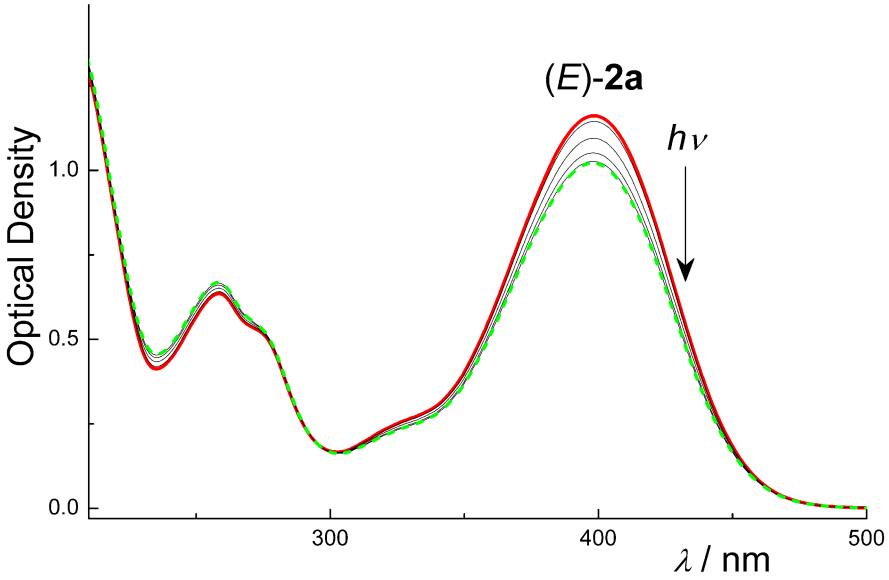

Fig. S50 Photolysis of solution of dye **2a** for 0, 1, 4, 9, and 20 min (MeCN, $C_{\mathbf{2a}}$ = 3.75×10^{-4} M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **2a**.

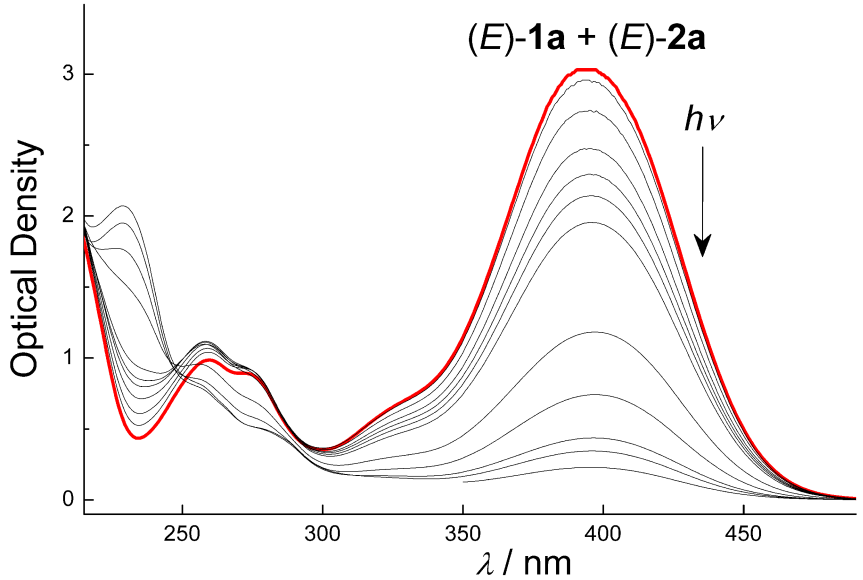

Fig. S51 Photolysis of solution of an equimolar mixture of dyes **1a** and **2a** for 0, 2, 5, 10, 15, 20, and 30 min and 2, 4, 8, 13, and 36 h (MeCN, $C_{\mathbf{1a}}$ = $C_{\mathbf{2a}}$ = 5×10^{-4} M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm).

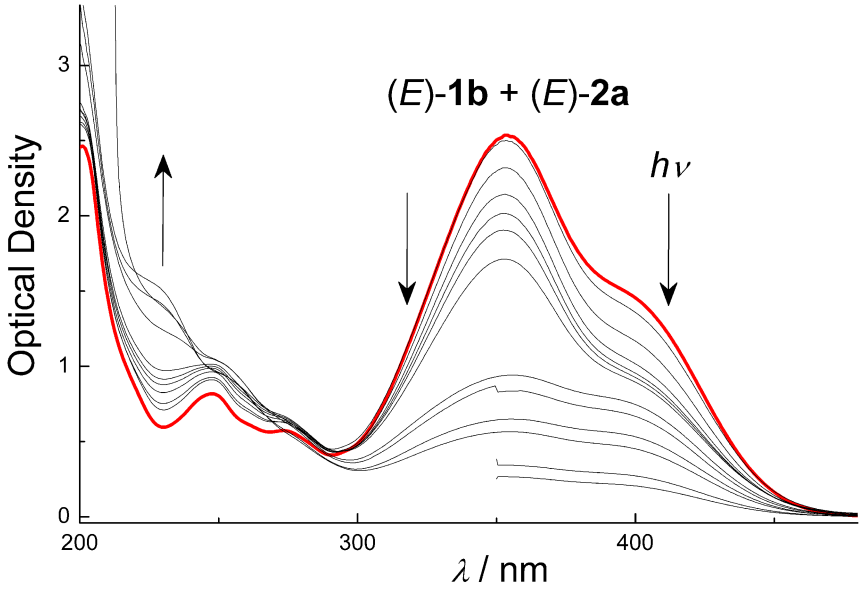

Fig. S52 Photolysis of solution of an equimolar mixture of dyes **1b** and **2a** for 0, 2, 5, 10, 15, 20, and 30 min and 2, 4, 8, 13, 36, and 60 h (MeCN, $C_{\mathbf{1b}} = C_{\mathbf{2a}} = 5\times10^{-4}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm).

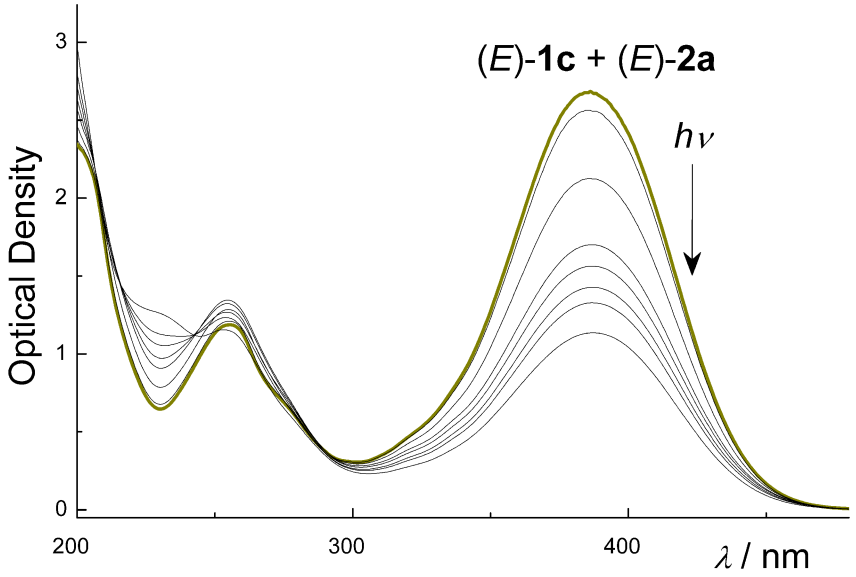

Fig. S53 Photolysis of solution of an equimolar mixture of dyes **1c** and **2a** for 0, 1, 6, 20, 40, and 80 min and 2 and 4 h (MeCN, $C_{\mathbf{1c}} = C_{\mathbf{2a}} = 5\times10^{-4}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm).

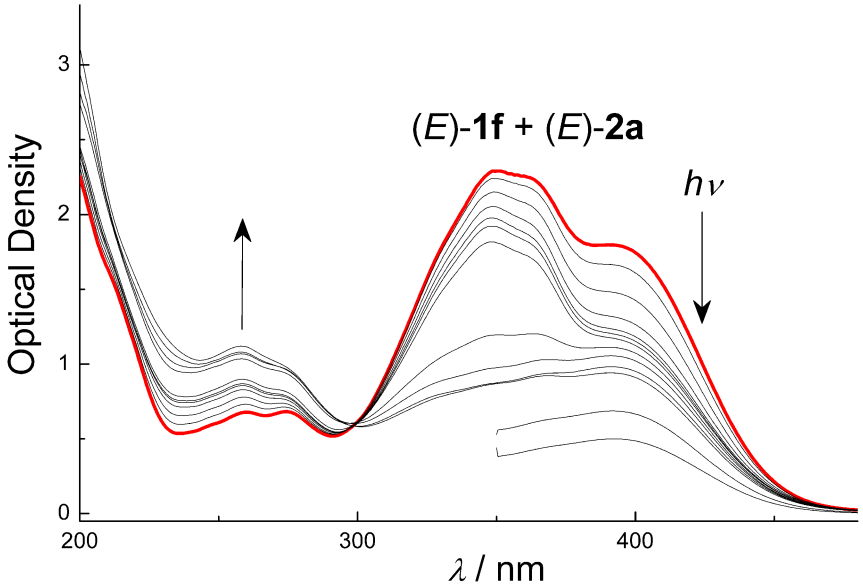

Fig. S54 Photolysis of solution of an equimolar mixture of dyes **1f** and **2a** for 0, 2, 5, 10, 15, 20, and 30 min and 2, 4, 8, 13, 36, and 60 h (MeCN, $C_{\mathbf{1f}} = C_{\mathbf{2a}} = 5\times10^{-4}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm).

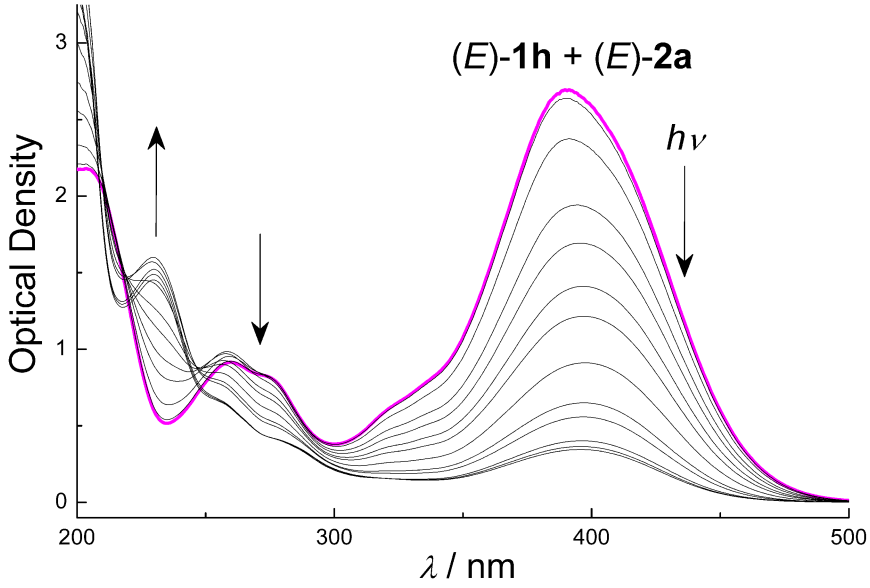

Fig. S55 Photolysis of solution of an equimolar mixture of dyes **1h** and **2a** for 0, 1, 6, 20, 40, and 80 min and 2, 4, 8, 16, 24, 34, and 52 h (MeCN, $C_{\mathbf{1h}} = C_{\mathbf{2a}} = 5\times10^{-4}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm).

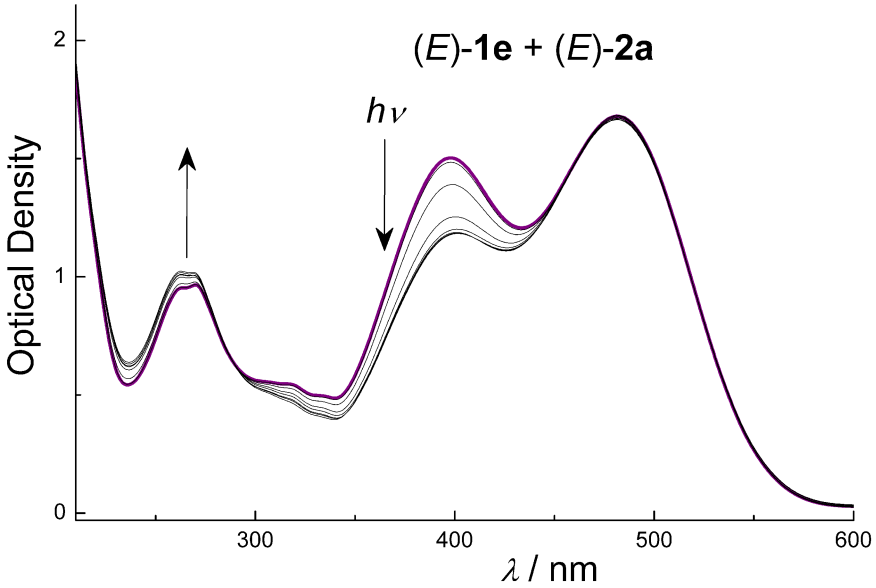

Fig. S56 Photolysis of solution of an equimolar mixture of dyes **1e** and **2a** for 0, 1, 6, 20, 40, and 80 min and 2 and 4 h (MeCN, $C_{\mathbf{1e}} = C_{\mathbf{2a}} = 5\times10^{-4}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm).

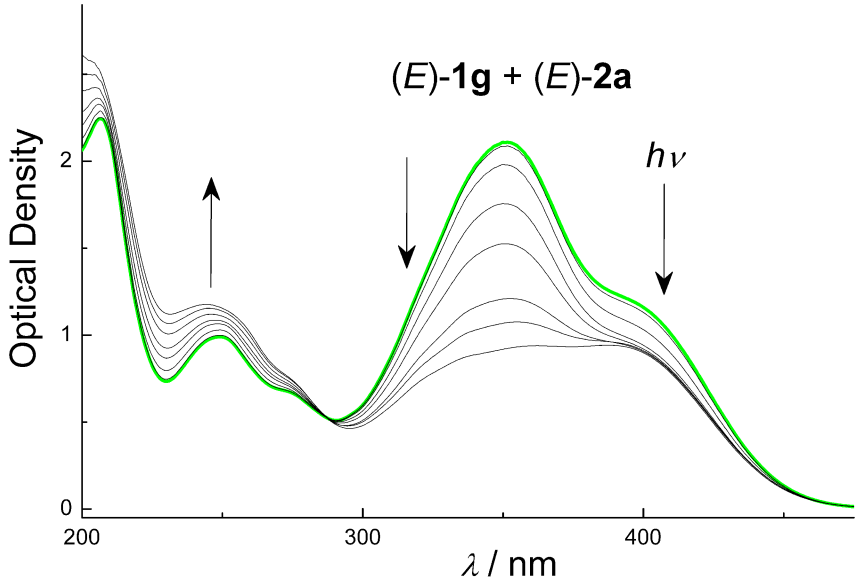

Fig. S57 Photolysis of solution of an equimolar mixture of dyes **1g** and **2a** for 0, 1, 6, 20, 40, and 80 min and 2 and 4 h (MeCN, $C_{\mathbf{1g}} = C_{\mathbf{2a}} = 5\times10^{-4}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm).

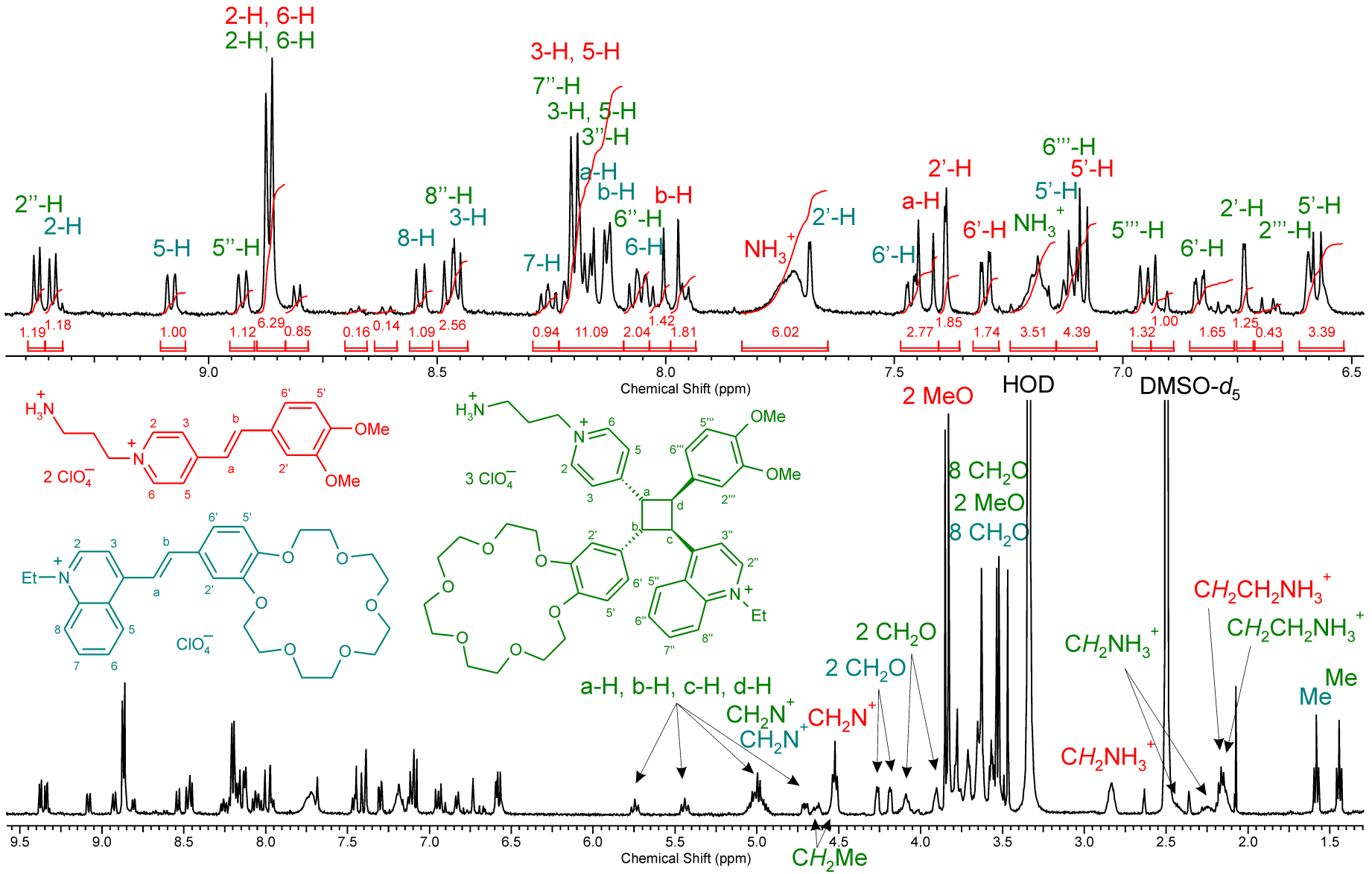

Fig. S58 ^{1}H NMR spectrum of a sample of 1:1 mixture of dyes **1a** and **2b**, which was irradiated with visible light for 290 h in MeCN and then redissolved in DMSO-d_6 (500.13 MHz, 30 °C).

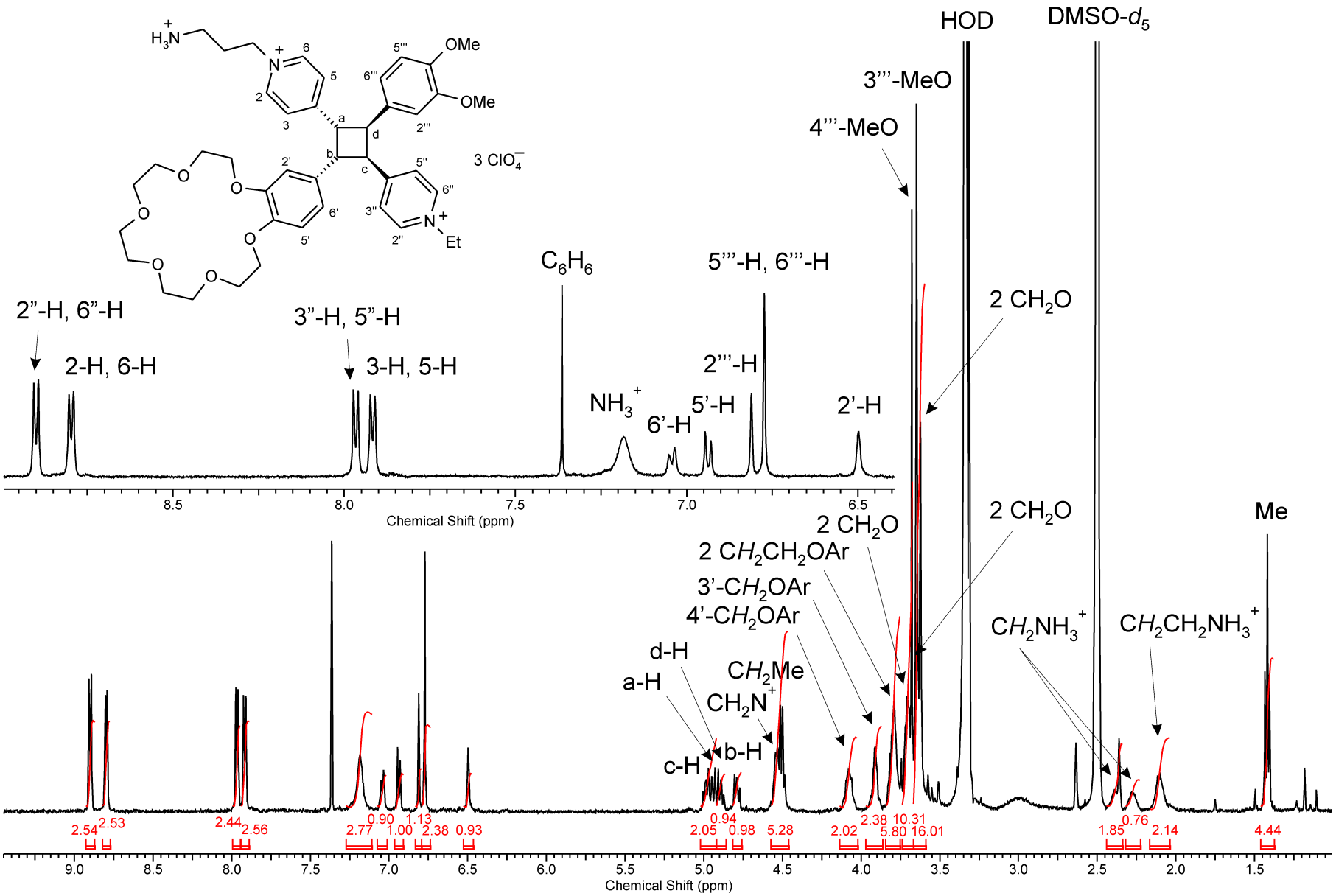

Fig. S59 ^{1}H NMR spectrum of cyclobutane *rctt*-**3a** (500.13 MHz, DMSO-d_6, 23 °C).

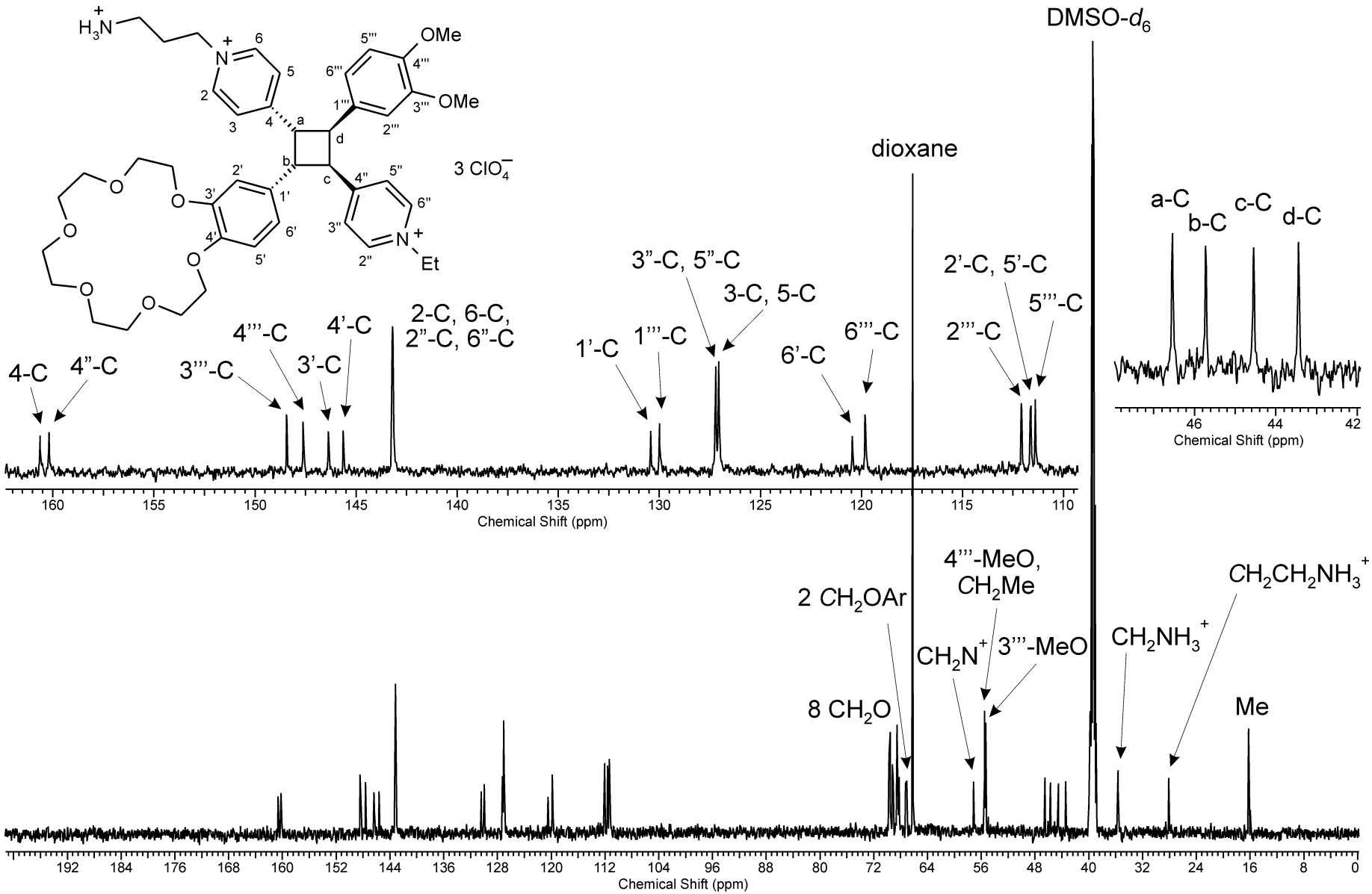

Fig. S60 ^{13}C NMR spectrum of cyclobutane *rctt*-**3a** (125.76 MHz, DMSO-d_6, 30 °C).

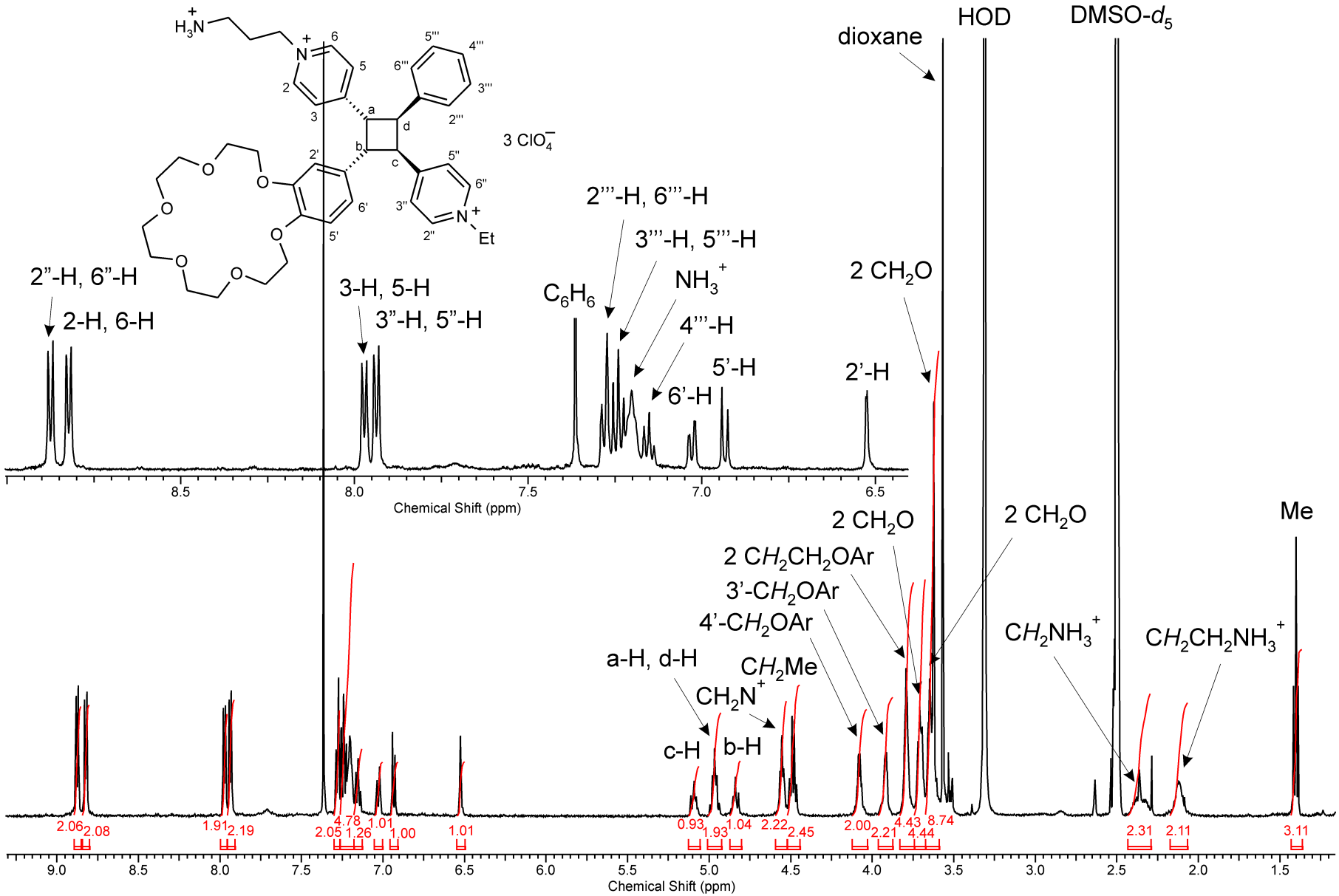

Fig. S61 ^{1}H NMR spectrum of of cyclobutane *rctt*-**3b** (500.13 MHz, DMSO-d_6, 25 °C).

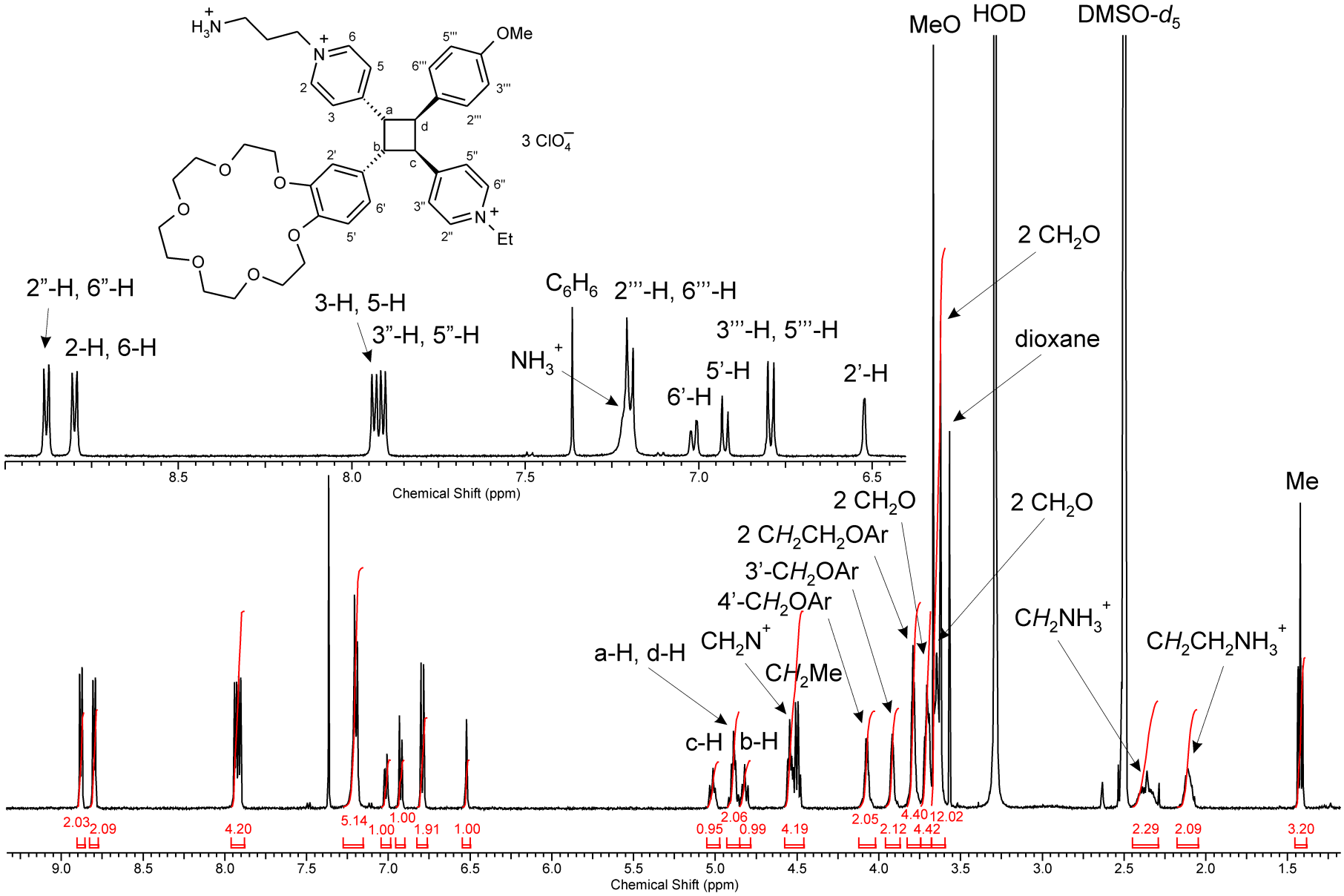

Fig. S62 ^{1}H NMR spectrum of cyclobutane *rctt*-**3c** (500.13 MHz, DMSO-d_6, 30 °C).

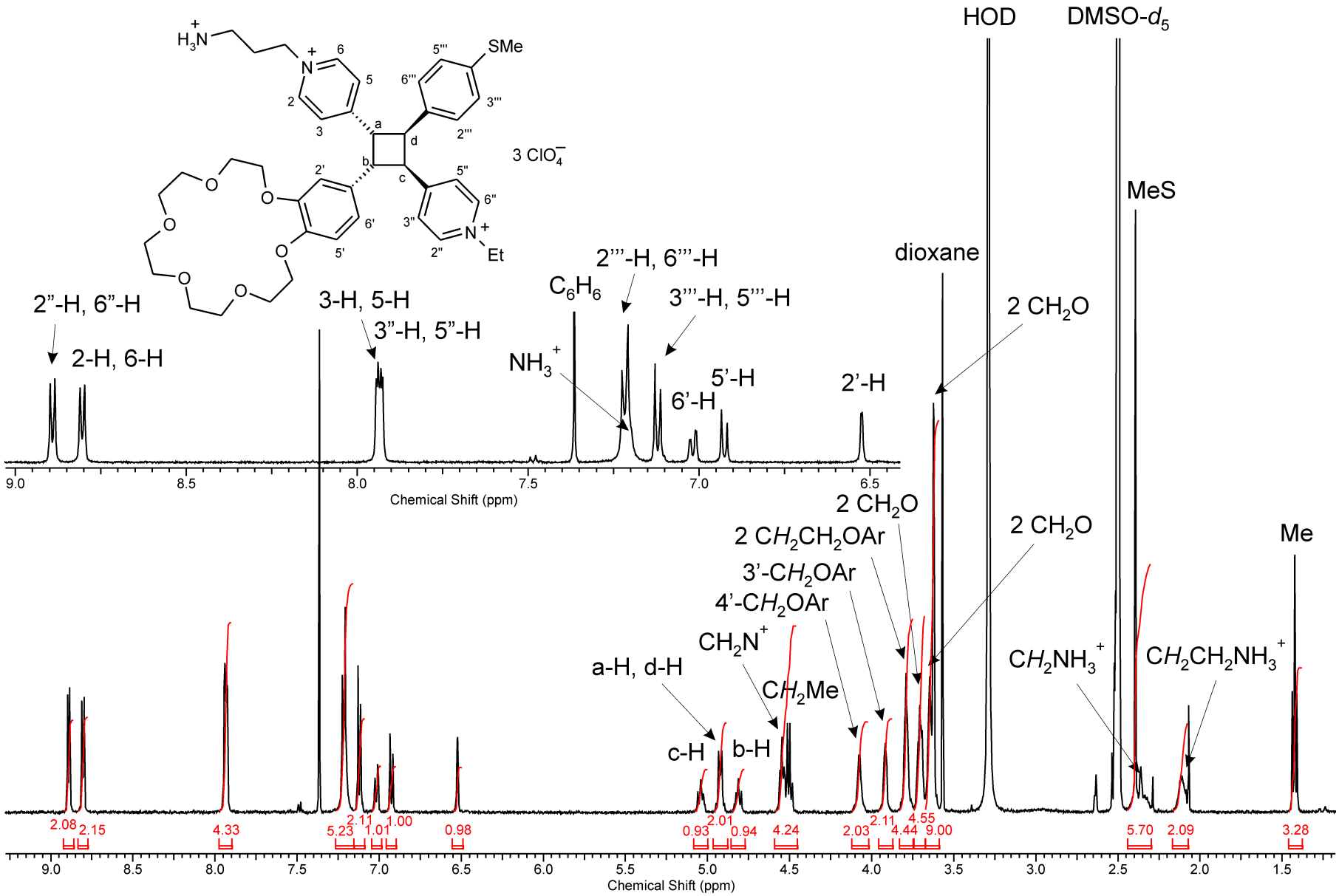

Fig. S63 ^{1}H NMR spectrum of of cyclobutane *rctt*-**3d** (500.13 MHz, DMSO-d_6, 30 °C).

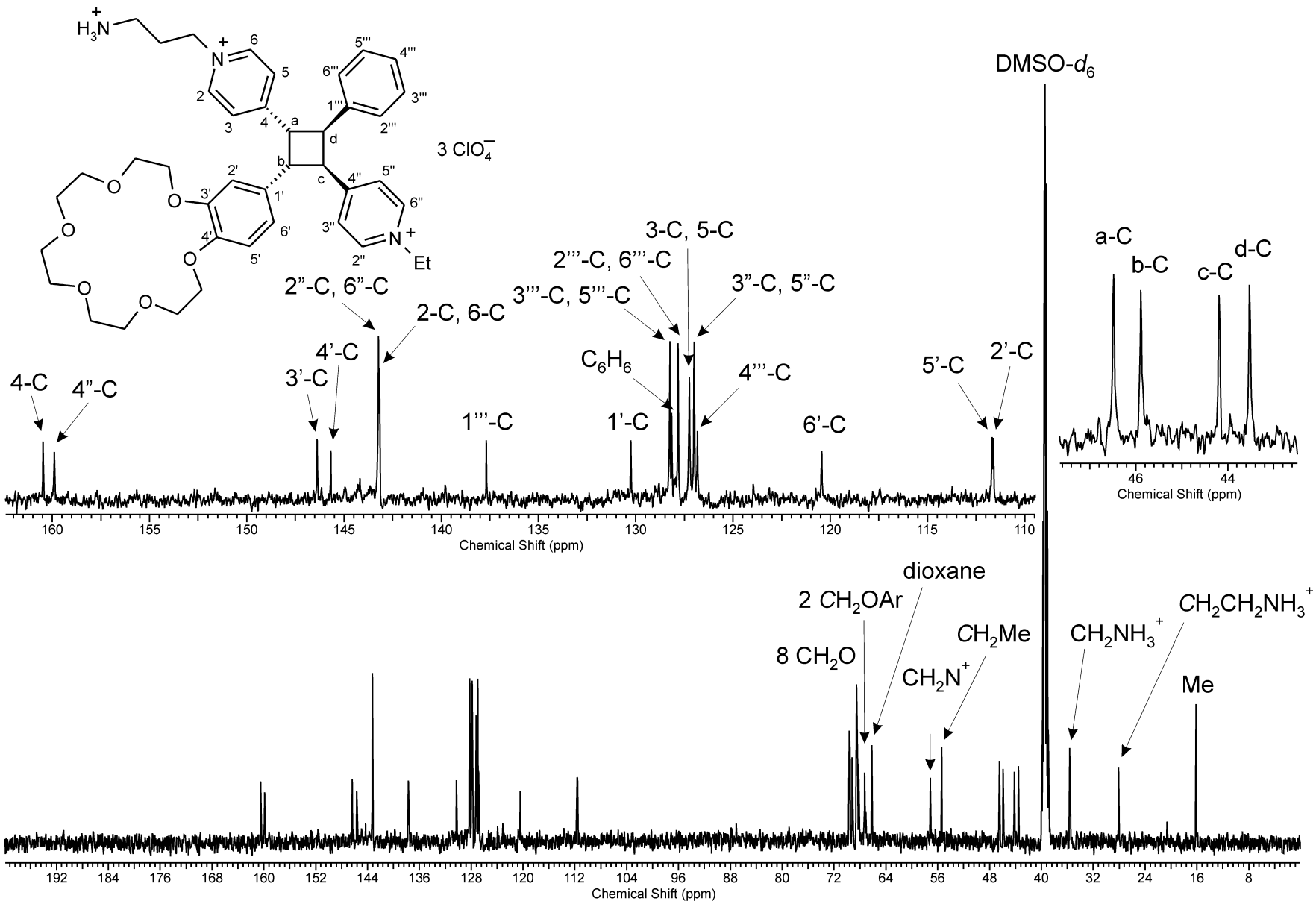

Fig. S64 ^{13}C NMR spectrum of cyclobutane *rctt*-**3b** (125.76 MHz, DMSO-d_6, 30 °C).

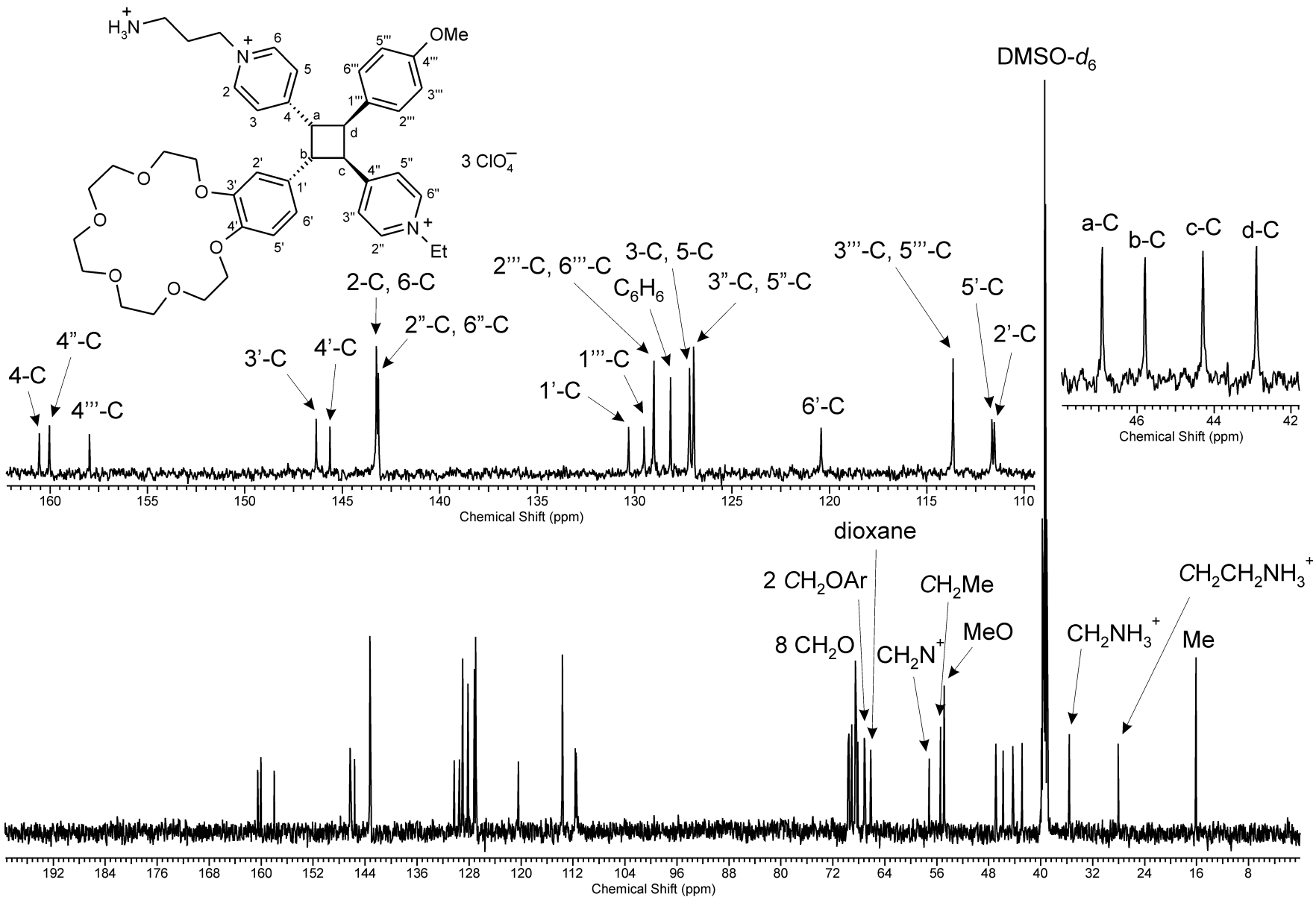

Fig. S65 ^{13}C NMR spectrum of cyclobutane *rctt*-**3c** (125.76 MHz, DMSO-d_6, 30 °C).

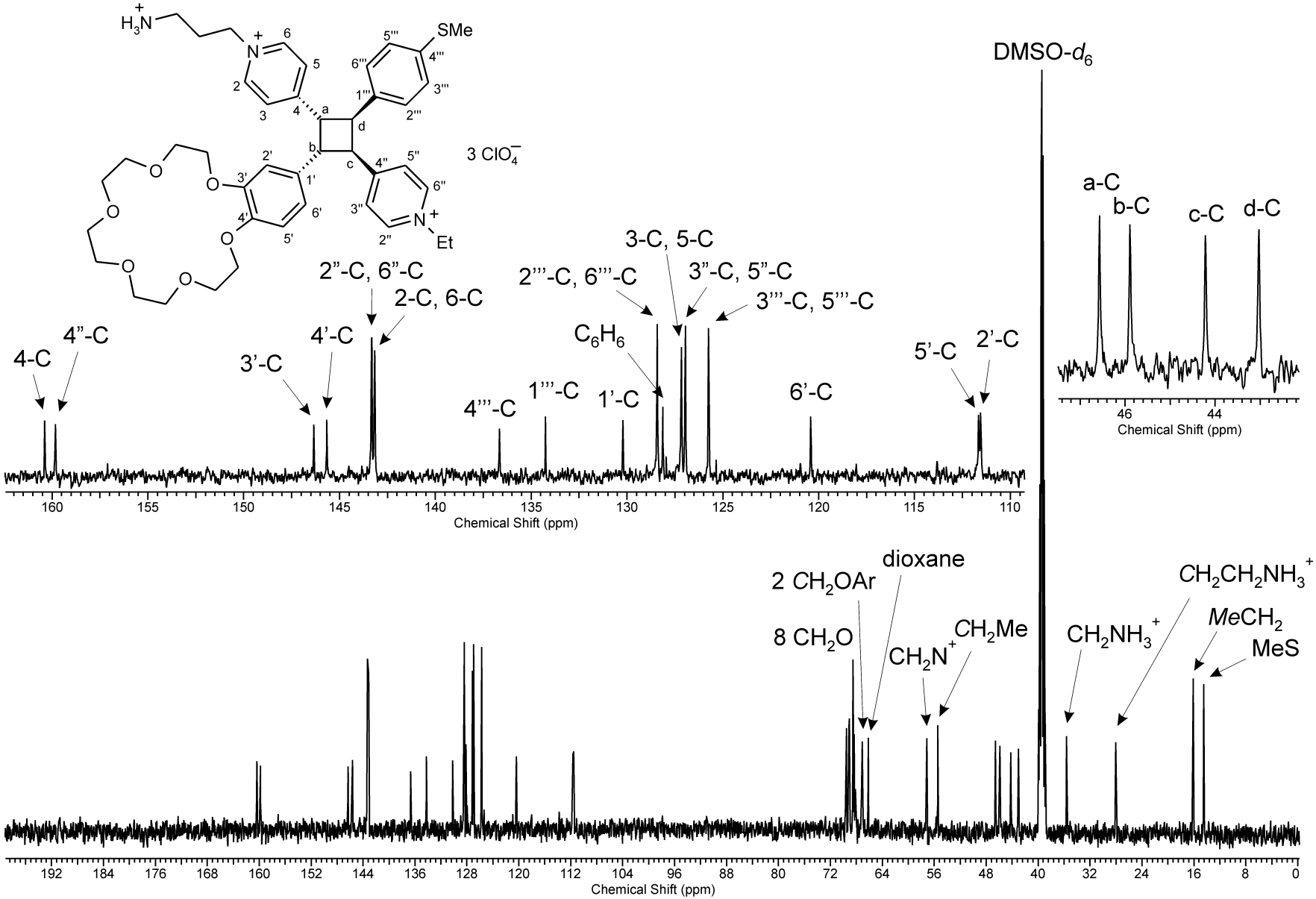

Fig. S66 ^{13}C NMR spectrum of cyclobutane *rctt*-**3d** (125.76 MHz, DMSO-d_6, 30 °C).

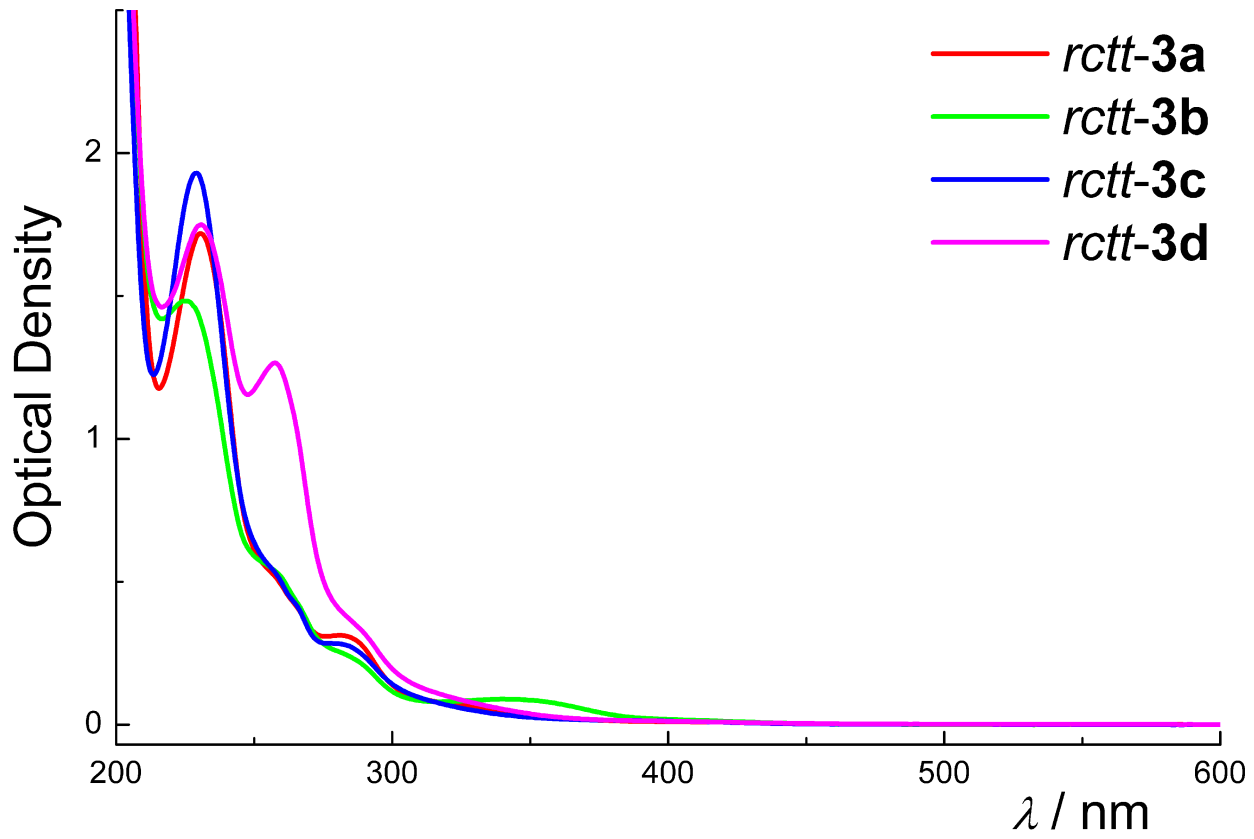

Fig. S67 Absorption spectra of cyclobutanes *rctt*-**3a–d** (MeCN, $C_{cyclobutane} = 5\times10^{-5}$ M, 1-cm quartz cell, ambient temperature).

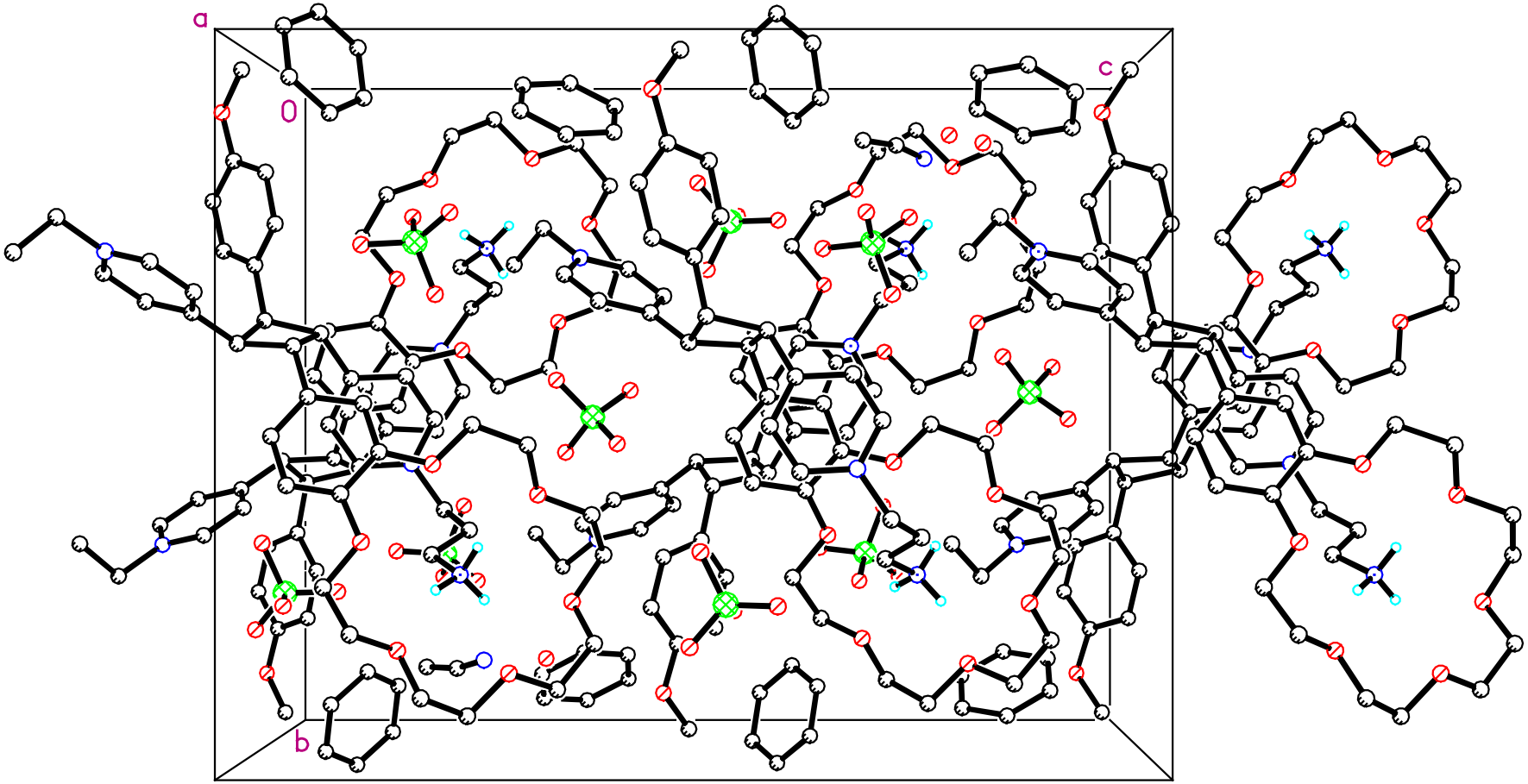

Fig. S68 Packing of *rctt*-**3c**·2C_6H_6·0.75MeCN·0.25H_2O.