Studies of the Solvatochromic Emission Properties of *N*-Aroylurea Derivatives II: Influence of Hydrogen-Bonding Interactions

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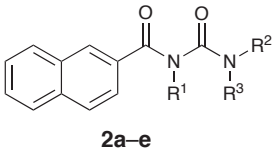
Electronic Supplementary Information (ESI)

Table of contents



2a–e

a: $R^1 = R^2 = H$; $R^3 = CH_3$ (18%)
b: $R^1 = H$; $R^2 = R^3 = CH_3$ (32%)
c: $R^1 = R^2 = R^3 = CH_3$ (24%)
d: $R^2 = H$; $R^1 = R^3 = -CH_2-$ (49%)
e: R^1 = 2-Naphthoyl; $R^2 = R^3 = CH_3$ (3%)

1. ^{1}H-NMR spectroscopy and X-ray diffraction analysis

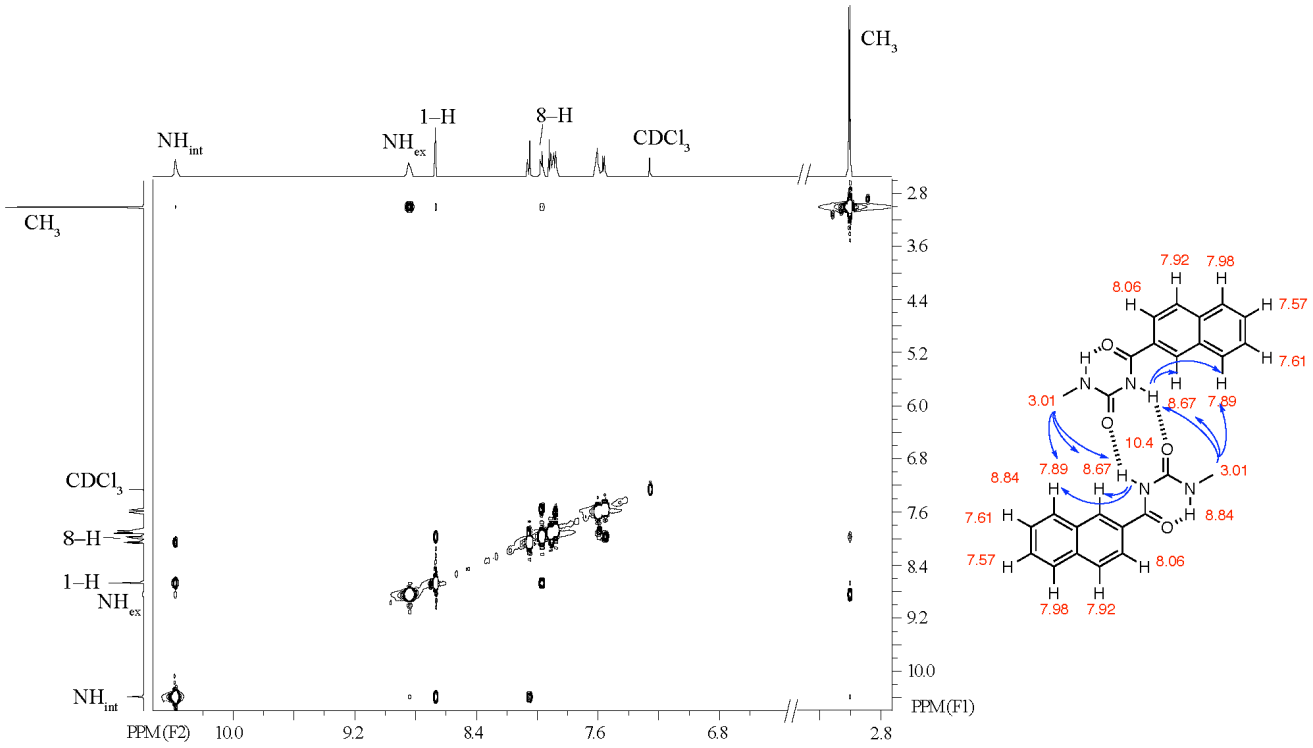


Fig. S1 NOESY spectra of **2a** in $CDCl_3$ at room temperature (600 MHz) and proposed structural alignment of **2a**, based on the observed NOE-signals.

X-ray diffraction analysis. Single crystals of **2a** and **2d** were measured on a STOE IPDS at 150 K. Single crystal measurements of **2b** and **2c** were performed with a SIEMENS SMART 1K CCD diffractometer at 176 and 170 K, respectively. The structures were determined by direct methods using the program SHELXS.[1] Refinement was performed on F^2 values using the program SHELXL-97.[1] Hydrogen atoms were geometrically positioned and were constrained. The NH hydrogen atom was refined for **2b**. The crystal packing of **2b** shows solvent accessible channels along the c-axis direction. The solvent contribution was subtracted from the observed reflection intensities with the program PLATON/SQUEEZE.[2] The crystal data and the structure refinement details are given in Table S1.

Table S1. Crystal data and structure refinement details of compounds **2a**, **2b**, **2c** and **2d**.

	2a	**2b**	**2c**	**2d**
Molecular Formula	$C_{13}H_{12}N_2O_2$	$C_{14}H_{14}N_2O_2$	$C_{15}H_{16}N_2O_2$	$C_{14}H_{12}N_2O_2$
Temperature / K	150	176	170	150
Wavelength / Å	0.71069	0.71073	0.71073	0.71069
Space group	Monoclinic, $P2_1/c$ (No. 14)	Trigonal, $R\bar{3}$ (No. 148)	Triclinic, $P\bar{1}$ (No. 2)	Monoclinic, $P2_1/c$ (No. 14)
Unit cell dimensions	a = 9.334 (2) Å b = 5.641 (1) Å c = 21.879 (4) Å β = 99.26 (3)°	a = 39.138 (2) Å b = 39.138(2) Å c = 4.3831(3) Å	a = 10.4212 (6) Å b = 11.4181 (7) Å c = 12.0437 (7) Å α = 68.743(1)° β = 89.477(1)° γ = 89.526(1)°	a = 12.559 (3) Å b = 6.7160 (10) Å c = 14.191 (3) Å β = 94.61 (3)°
Volume / Å^3	1137.0 (4)	5814.6 (7)	1335.51 (14)	1193.1 (4)
Z	4	18	4	4
Calculated density / g·cm^{-1}	1.392	1.245	1.275	1.338
Absorption coefficient / mm^{-1}	0.092	0.085	0.086	0.091
F (000)	480	2304	544	480
Meausured θ range	$3.13 \le \theta \le 27.91$	$1.80 \le \theta \le 27.00$	$1.81 \le \theta \le 26.10$	$2.88 \le \theta \le 27.96$
Limiting indices	$-12 \ge h \ge 12$ $-7 \ge k \ge 7$ $-28 \ge l \ge 28$	$-50 \le h \le 49$ $-49 \le k \le 50$ $-5 \le l \le 5$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-14 \le l \le 14$	$-16 \le h \le 16$ $0 \le k \le 8$ $0 \le l \le 18$
Reflections collected / unique	11382 / 2569	19858 / 2697	13253 / 5035	9994 / 2724
R_{int}	0.0391	0.1043	0.0478	0.0629
Data / restraints/ parameters	2569 / 0 / 202	2697 / 0 / 169	5035 / 0 / 350	2724 / 0 / 209
Goodness of fit on F^2	0.951	1.028	1.076	0.987
R values [$I \ge 2\sigma$ (I)]	$R_1 = 0.0347$ $wR_2 = 0.0878$	$R_1 = 0.0687$ $wR_2 = 0.1288$	$R_1 = 0.0693$ $wR_2 = 0.1072$	$R_1 = 0.0541$ $wR_2 = 0.1430$
R values (all data)	$R_1 = 0.0573$ $wR_2 = 0.0947$	$R_1 = 0.1545$ $wR_2 = 0.1528$	$R_1 = 0.1284$ $wR_2 = 0.1219$	$R_1 = 0.0882$ $wR_2 = 0.1570$
Final Fourier residuals	0.3 –0.2 eÅ^{-3}	0.210 –0.213 eÅ^{-3}	0.2 –0.2 eÅ^{-3}	0.5 –0.2 eÅ^{-3}

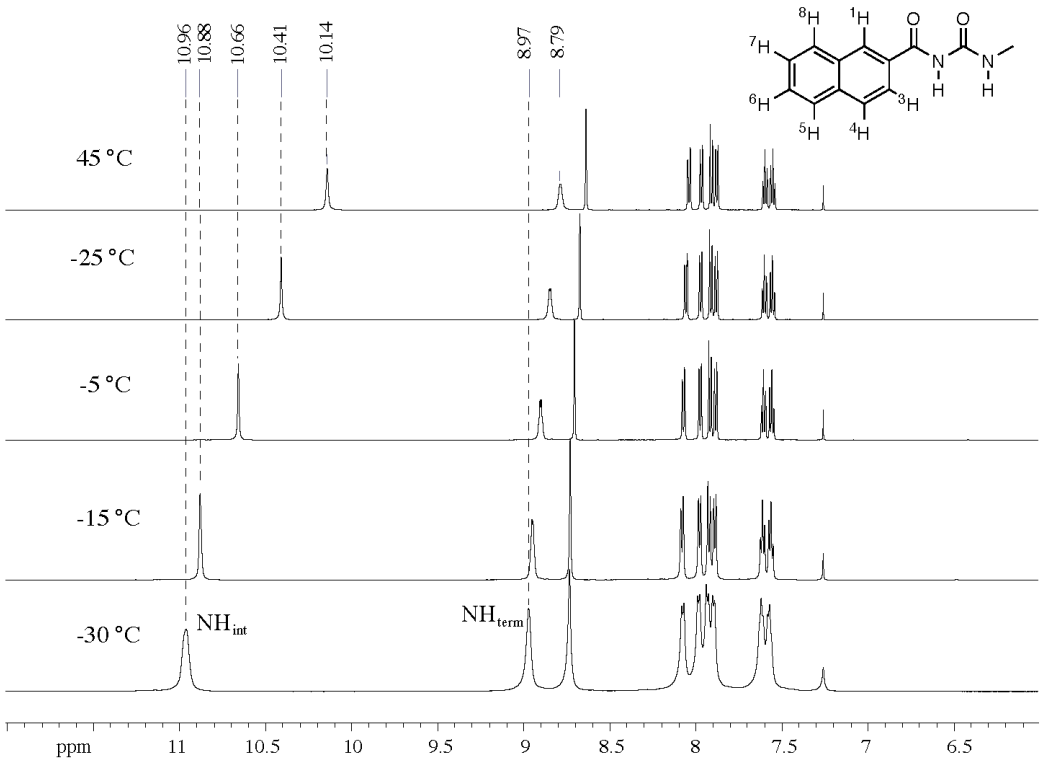


Fig. S2 ^{1}H-NMR spectra of **2a** in $CDCl_3$ at different temperatures (600 MHz).

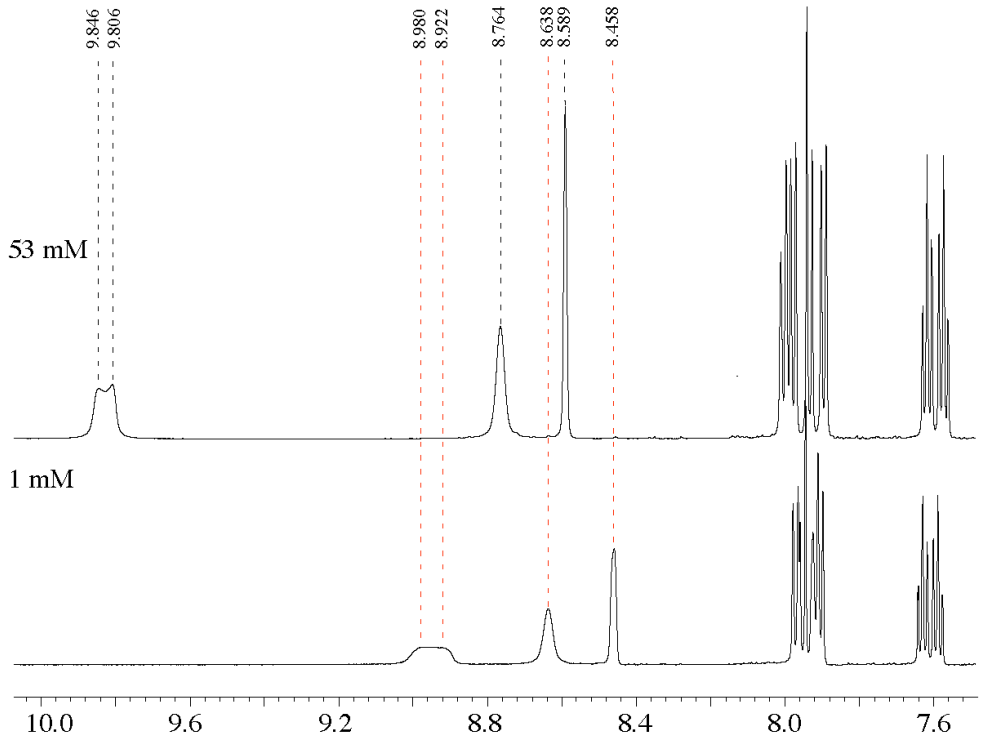


Fig. S3 ^{1}H-NMR spectra of **2a** in $CDCl_3$ at different concentrations (600 MHz) .

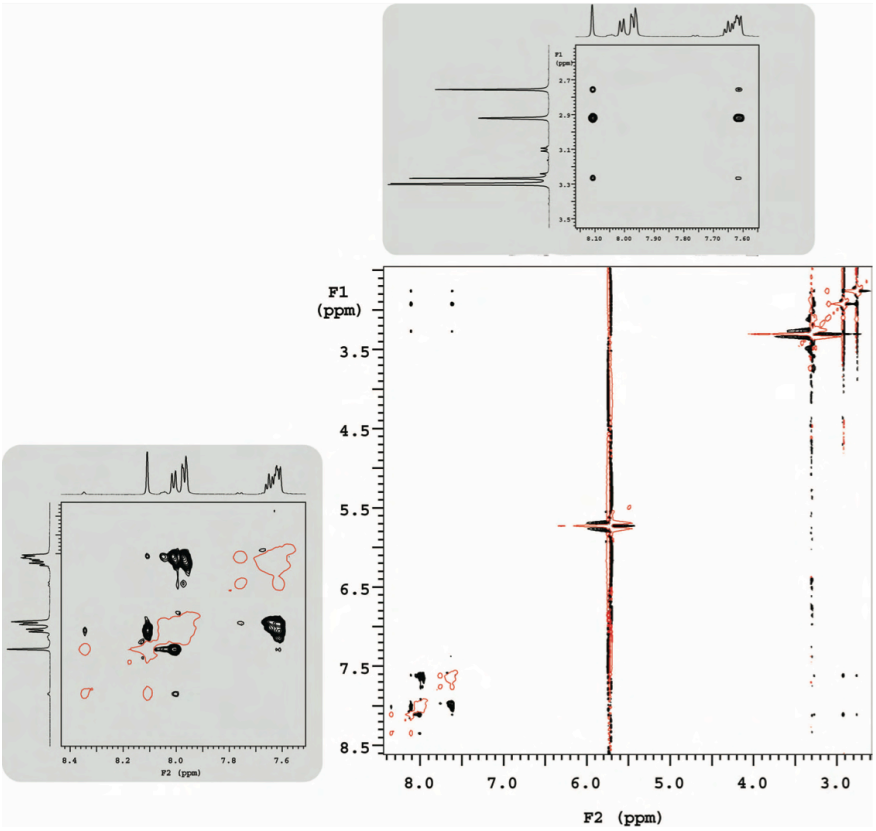


Fig. S4 ROESY data of **2c** in d_4-MeOD at –80 °C (600 MHz).

2. Absorption and steady-state emission properties in different solvents

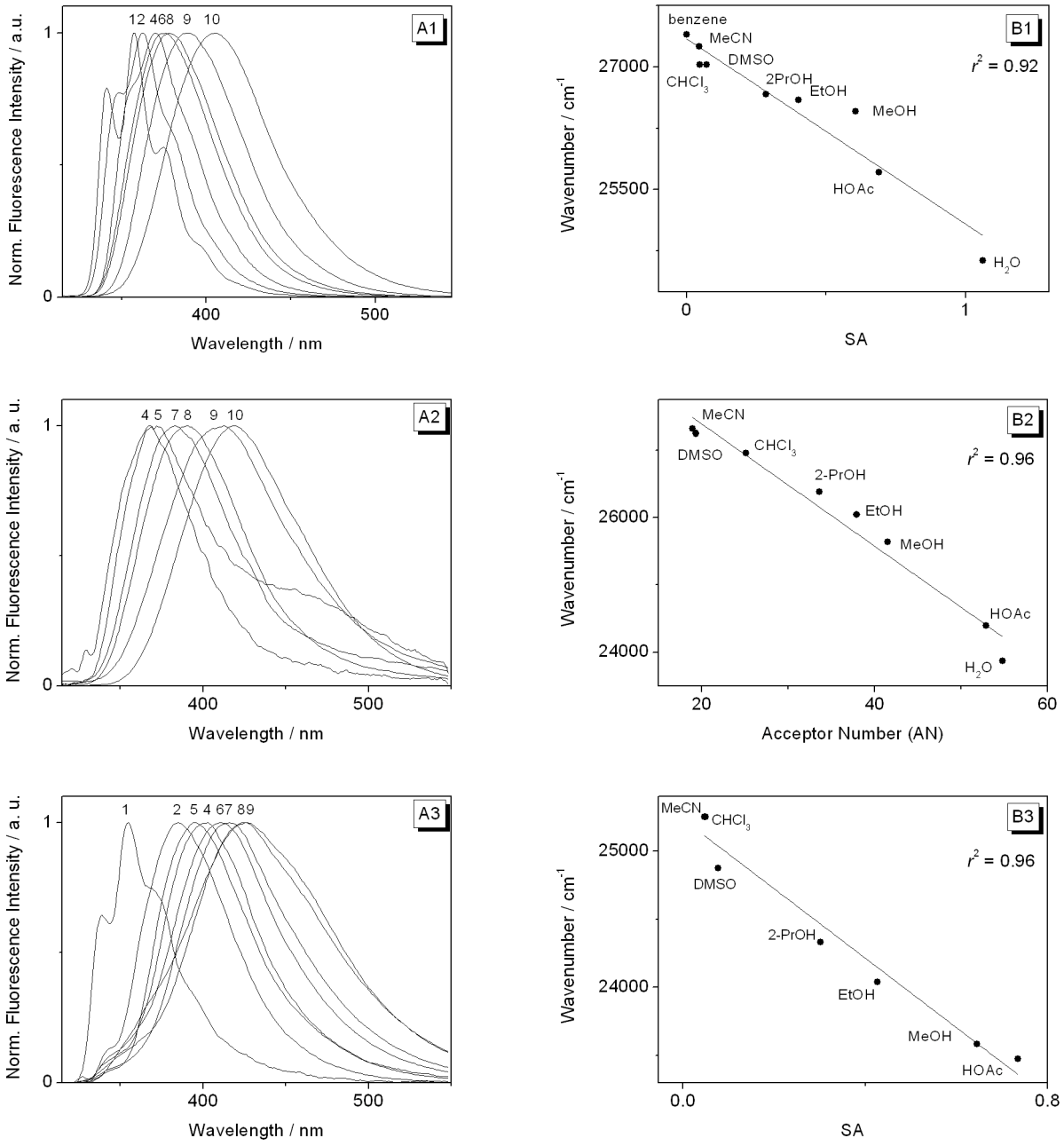


Fig. S5 A: Normalized emission spectra of **2a** (1), **2c** (2) and **2e** (3) (**2a**, **2c**: λ_{ex} = 280 nm; **2e**: λ_{ex} = 290 nm, 1: cyclohexane; 2: benzene; 3: MeCN; 4: DMSO; 5: $CHCl_3$; 6: 2-PrOH; 7: EtOH; 8: MeOH; 9: HOAc; 10: H_2O). B: Correlation of the emission maxima (in cm^{-1}) of **2a**, **2c** and **2e** with the acidity (SA) and acceptor number (AN) of the solvent.

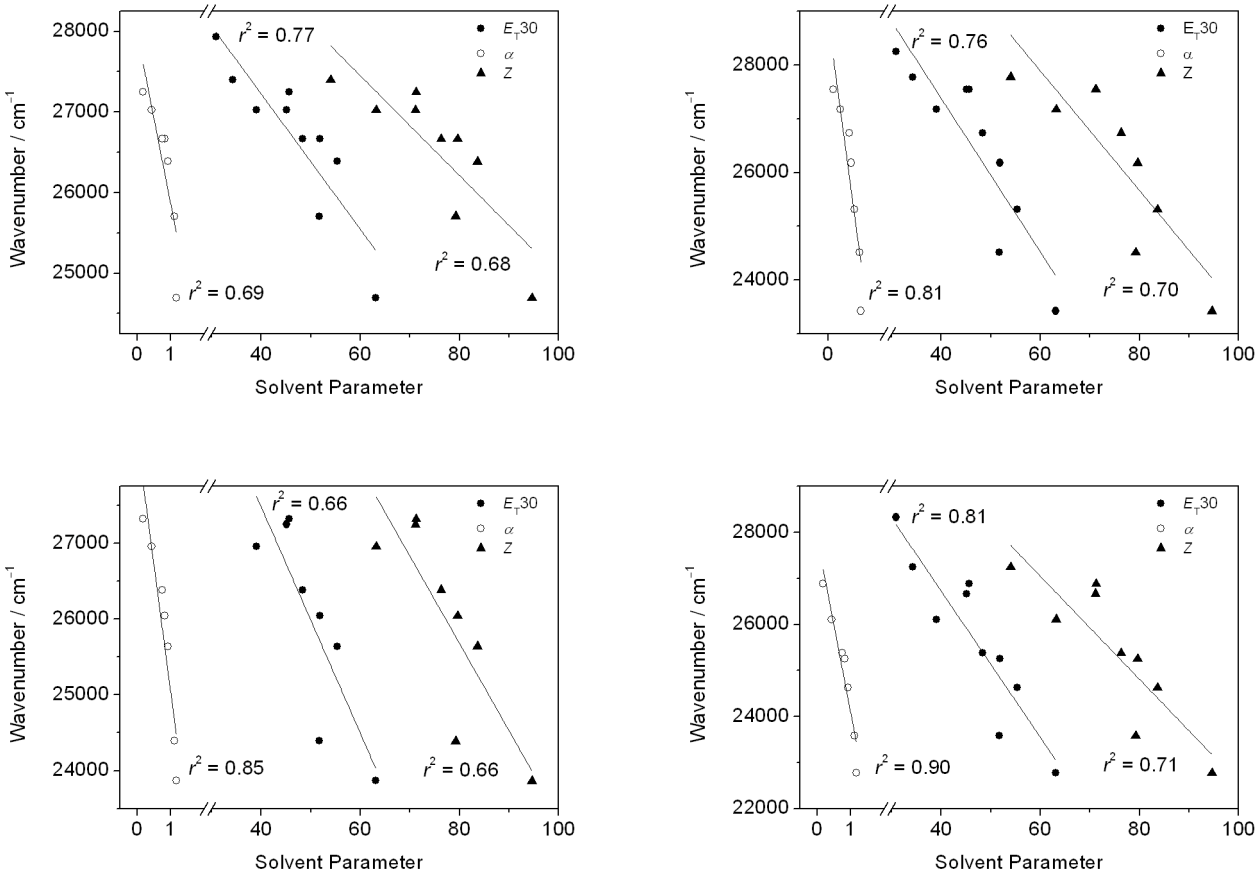


Fig. S6 Correlation of the emission maxima (in cm^{-1}) of **2a**, **2b, 2c** and **2d** with the E_T30, α and Kosower (Z) parameters of the solvent.

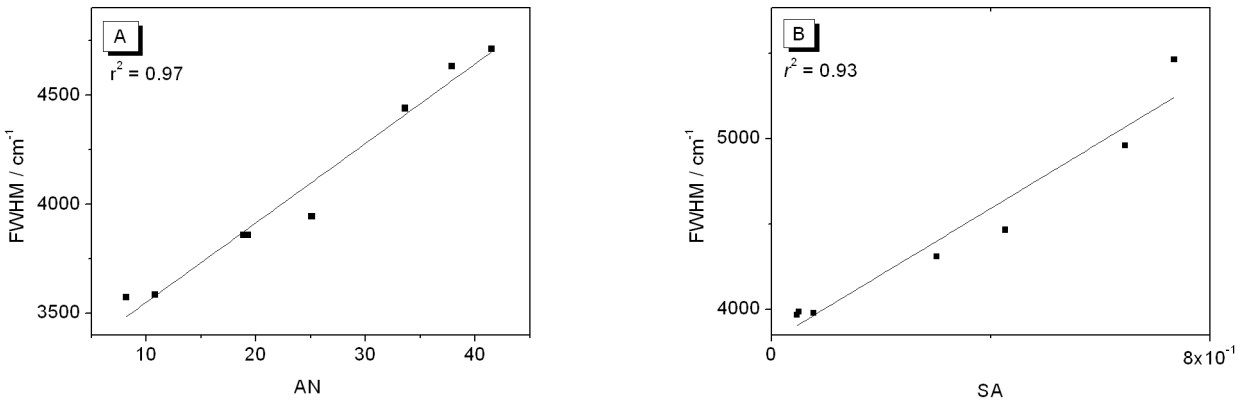


Fig. S7 Correlation of the FWHM (in cm^{-1}) of **2b** (A) and **2e** (B) with the acceptor number (AN) and the acidity (SA) of the solvent.

3. Time-resolved emission properties in different solvents

Table S2. Emission Lifetimes of **2a**, **2c** and **2d** in Different Solvents.

	Solvent	λ_{FL} / nm	τ_1 / ns (%)[a]	τ_2 / ns (%)[a]	τ_3 / ns (%)[a]	χ^2
2a[b]	$CHCl_3$	366	4.9 ± 0.1 (100 ± 1)	--	--	0.967
2a[b]	C_6H_{12}	355	--	9.1 ± 0.1 (100 ± 1)	--	1.036
2c	MeOD	360	0.9^{fixed} (98 ± 1)[c]	5.8 ± 0.1 (2 ± 1)	--	1.108
2c	MeOD	390	0.9^{fixed} (98 ± 1)[c]	3.1 ± 0.2 (2 ± 1)	--	0.960
2c	MeOD	420	0.9^{fixed} (99 ± 1)[c]	3.7 ± 0.4 (1 ± 1)	--	1.093
2c	MeCN	360	0.3 ± 0.1 (100 ± 2)	--	--	1.057
2c	MeCN	390	0.2 ± 0.1 (100 ± 3)	6.4 ± 0.3 (< 1)	--	1.016
2d	$CHCl_3$	350	1.0^{fixed} (66 ± 3)[d]	2.8 ± 0.1 (19 ± 1)	6.5 ± 0.3 (14 ± 2)	0.944
2d	$CHCl_3$	380	1.1 ± 0.1 (90 ± 1)	3.6 ± 0.2 (10 ± 1)	--	0.944
2d	$CHCl_3$	410	1.2 ± 0.1 (94 ± 1)	3.6 ± 0.2 (6 ± 1)	--	1.043
2d	C_6H_{12}	350	0.2 ± 0.1 (90 ± 10)	7.3 ± 0.4 (4 ± 1)	18.0 ± 0.4 (4 ± 1)	0.990
2d	C_6H_{12}	365	0.1 ± 0.1 (100 ± 20)	7.5 ± 0.7 (2 ± 1)	17.2 ± 0.7 (1 ± 1)	1.149

[a] The values in parentheses correspond to pre-exponential factors expressed in percentages when the decay was fit to the sum of two exponentials; $c = 10^{-5}$ M, $\lambda_{ex} = 280$ nm; [b] lifetimes did not change with varying the detection wavelength; [c] lifetime is fixed to the average of the lifetimes obtained at different timescales; [d] lifetime was fixed to the one obtained when collecting up to 10,000 counts; decay adequately fit to a single exponential or a sum of two exponentials: --.

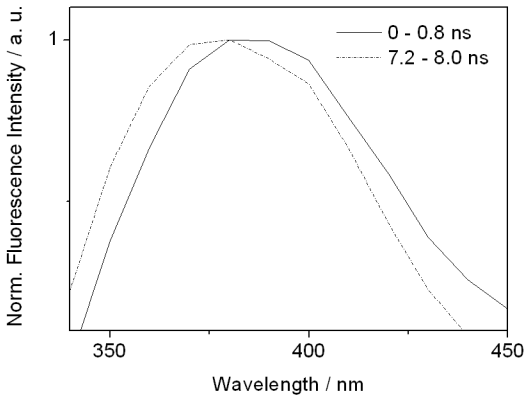


Fig. S8 Time-resolved emission spectra (TRES) of **2c** in methanol ($c = 10^{-5}$ M, $\lambda_{ex} = 280$ nm) at given delays after the excitation pulse.

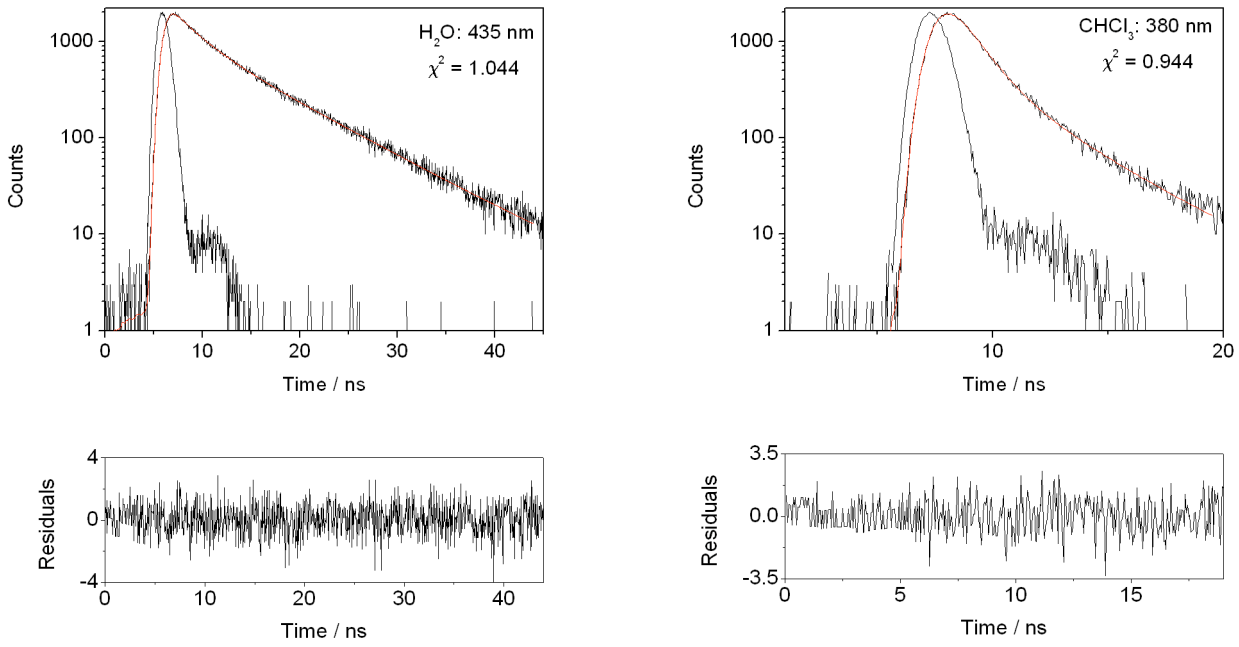


Fig. S9 Fluorescence decays of **2d** in H_2O (τ_1 = 2.5 ns, 52%; τ_2 = 8.0 ns, 48%) and $CHCl_3$ (τ_1 = 1.1 ns, 90%; τ_2 = 3.6 ns, 10%) ($c = 10^{-5}$ M, λ_{ex} = 280 nm, 50 ns) collected at given emission wavelength and the instrument response function (IRF). Continuous red lines correspond to the fits of the experimental data to the theoretical model. Residuals between the fits and the experimental data are shown below the main figure.

4. Studies in media with different viscosity and temperature

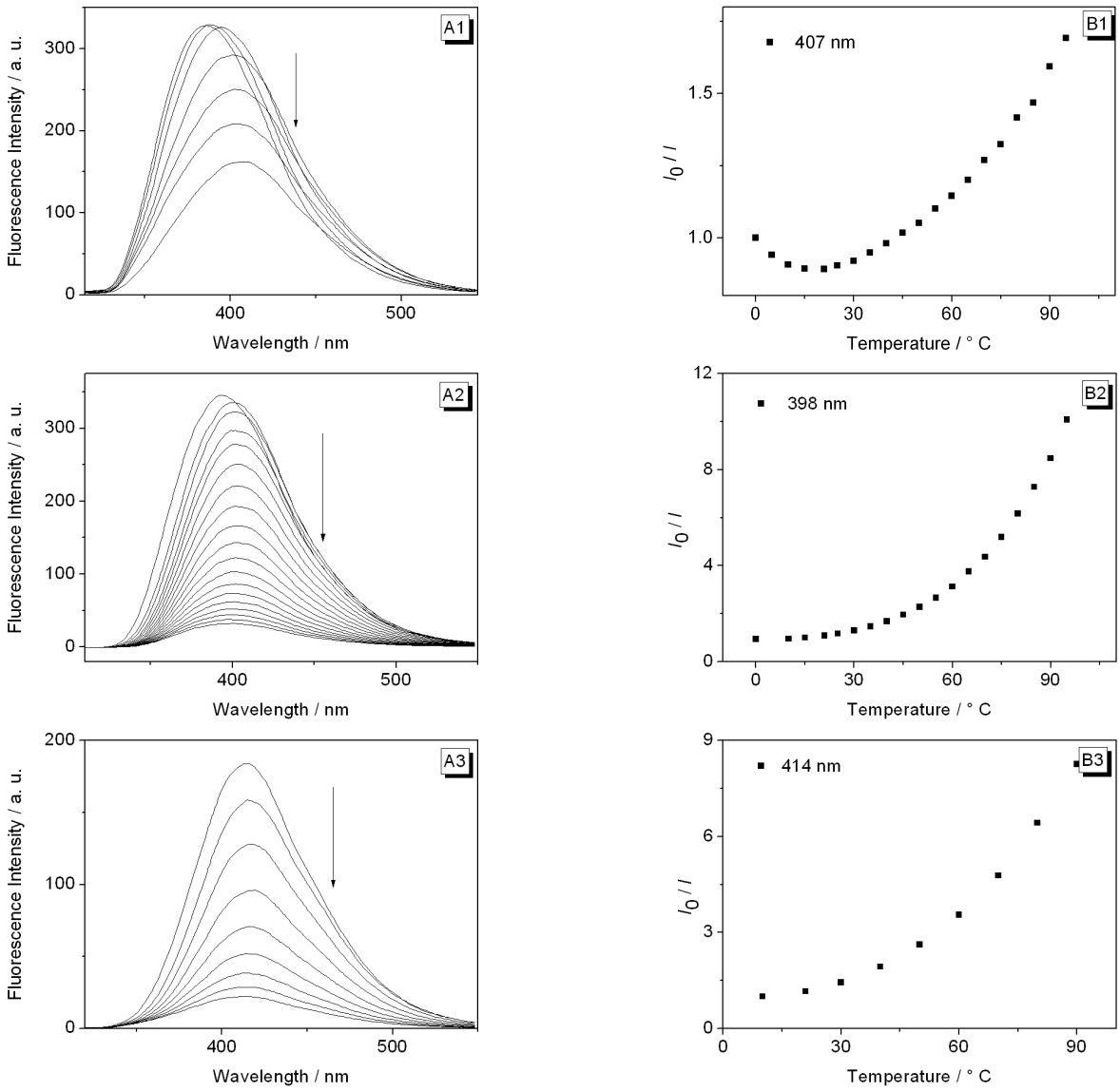


Fig. S10 A: Emission spectra of **2b** (1), **2c** (2) and **2d** (3) ($c < 10^{-4}$ M in glycerol; **2c**: λ_{ex} = 280 nm, **2b**, **2d**: λ_{ex} = 285 nm) at different temperatures. B: Plot of I_0/I versus the temperature of the solution (I_0 = emission intensity at $T = 0$ °C).

Table S3. Emission Lifetimes of **2c**–**2d** in Glycerol Solution at Different Temperatures.

	T / °C	λ_{FL} / nm	τ_1 / ns (%)[a]	τ_2 / ns (%)[a]	τ_3 / ns (%)[a]	χ^2
2c	100	375	0.8 ± 0.1 (97 ± 1)	2.7 ± 0.3 (3 ± 2)	10^{fixed} (< 1)[b]	1.039
2c	100	400	0.6 ± 0.1 (99 ± 1)	--	6.2 ± 0.5 (1 ± 1)	1.060
2c	50	375	0.3 ± 0.1 (64 ± 8)	3.0 ± 0.1 (35 ± 1)	10^{fixed} (< 1)[b]	1.040
2c	50	400	0.3 ± 0.1 (51 ± 9)	2.9 ± 0.1 (46 ± 1)	7^{fixed} (3 ± 1)[b]	1.037
2c	0	375	1.1 ± 0.1 (35 ± 3)	3.4 ± 0.1 (51 ± 3)	10^{fixed} (14 ± 1)[b]	0.981
2c	0	400	1.4^{fixed} (26 ± 3)[b]	4.3 ± 0.2 (48 ± 1)	10.6 ± 0.3 (26 ± 2)	0.996
2d	100	385	0.7 ± 0.1 (96 ± 1)	--	8.0 ± 0.1 (4 ± 1)	1.003
2d	100	410	0.7 ± 0.1 (99 ± 1)	--	7.6 ± 0.2 (1 ± 1)	1.031
2d	50	385	0.5 ± 0.1 (36 ± 4)	2.9 ± 0.1 (60 ± 1)	9^{fixed} (4 ± 1)[b]	1.109
2d	50	410	2.2 ± 0.4 (52 ± 31)	3.6 ± 0.6 (46 ± 31)	8^{fixed} (2 ± 1)[b]	1.098
2d	0	385	1.9 ± 0.2 (49 ± 5)	5.8 ± 0.9 (43 ± 2)	13 ± 1 (14 ± 5)	1.028
2d	0	410	--	5.3 ± 0.2 (57 ± 2)	12.8 ± 0.2 (43 ± 2)	1.026

[a] The values in parentheses correspond to pre-exponential factors expressed in percentages when the decay was fit to the sum of two or three exponentials; $c < 10^{-4}$ M, λ_{ex} = 280 nm; [b] lifetimes were fixed based on the trend observed with increasing temperature for the same emission wavelength; decay adequately fit to the sum of two exponentials: --.

Table S4. Emission Lifetimes of **2a**, **2c** and **2d** in Ethanol at Different Temperatures.

	T / °C	λ_{FL} / nm	τ_1 / ns (%)[a]	τ_2 / ns (%)[a]	τ_3 / ns (%)[a]	χ^2
2a	20	375	--	8.1 ± 0.6 (84 ± 27)	12 ± 3 (16 ± 27)	1.073
2a	–40	350	0.3[fixed] (54 ± 3)[b]	8.2 ± 0.3 (39 ± 2)	16 ± 2 (6 ± 3)	0.946
2a	–40	375	--	9.4 ± 0.1 (100 ± 1)	--	1.092
2a	–80	350	1.4 ± 0.1 (60 ± 1)	8.6 ± 0.5 (35 ± 2)	20 ± 3 (5 ± 3)	0.993
2a	–80	375	--	10.9 ± 0.1 (100 ± 1)	--	1.153
2a	–80	400	1.3 ± 0.1 (–32 ± 2)	11.1 ± 0.1 (68 ± 1)	--	1.151
2c	20	380	1.0 ± 0.1 (99 ± 1)	--	12.0 ± 0.5 (1 ± 1)	1.082
2c	0	380	1.8 ± 0.1 (98 ± 1)	7.2 ± 0.8 (2 ± 1)	--	1.002
2c	–40	380	0.4 ± 0.2 (20 ± 9)	5.1[fixed] (70 ± 2)	8.7 ± 0.4 (10 ± 2)	0.980
2c	–40	410	--	5.3 ± 0.1 (100 ± 1)	--	0.937
2c	–80	380	1.1[fixed] (39 ± 1)[c]	9.6 ± 0.1 (61 ± 1)	--	1.139
2c	–80	410	1.2 ± 0.2 (–19 ± 2)	9.8 ± 0.1 (81 ± 1)	--	1.054
2d	20	390	1.3 ± 0.1 (91 ± 1)	4.3 ± 0.1 (9 ± 1)	--	1.031
2d	0	390	2.0 ± 0.1 (78 ± 1)	5.1 ± 0.1 (22 ± 2)	--	0.965
2d	–40	360	0.3 ± 0.1 (77 ± 5)	4.8[fixed] (15 ± 1)[d]	15.2 ± 0.1 (8 ± 1)	1.113
2d	–40	390	--	4.8 ± 0.1 (58 ± 1)	12[fixed] (42 ± 1)[d]	0.972
2d	–40	420	0.6 ± 0.2 (–26 ± 7)	4.8 ± 0.3 (33 ± 1)	11.8 ± 0.2 (40 ± 2)	1.071
2d	–80	360	0.7 ± 0.1 (79 ± 2)	3.7 ± 0.2 (12 ± 1)	16[fixed] (8 ± 1)[e]	1.114
2d	–80	390	1.6 ± 0.1 (34 ± 2)	8.1 ± 0.3 (35 ± 1)	16[fixed] (32 ± 1)[e]	1.063
2d	–80	420	0.6 ± 0.1 (–55 ± 2)	8.7 ± 0.7 (18 ± 2)	15.9 ± 0.4 (27 ± 3)	1.124

[a] The values in parentheses correspond to pre-exponential factors expressed in percentages when the decay was fit to the sum of two or three exponentials; $c = 10^{-5}$ M, **2a**, **2c**, **2d**: λ_{ex} = 280 nm, **2e**: λ_{ex} = 310 nm; [b] lifetime was fixed because of a large error of A when τ_1 = 0.32 ns; [c] lifetime was fixed to the lifetime obtained at 350 nm at –80 °C; [d] lifetime was fixed to the lifetime obtained at 420 nm at –40 °C; [e] lifetime was fixed to the lifetime obtained at 420 nm at –80 °C; decay adequately fit to a single exponential or a sum of two exponentials: --.

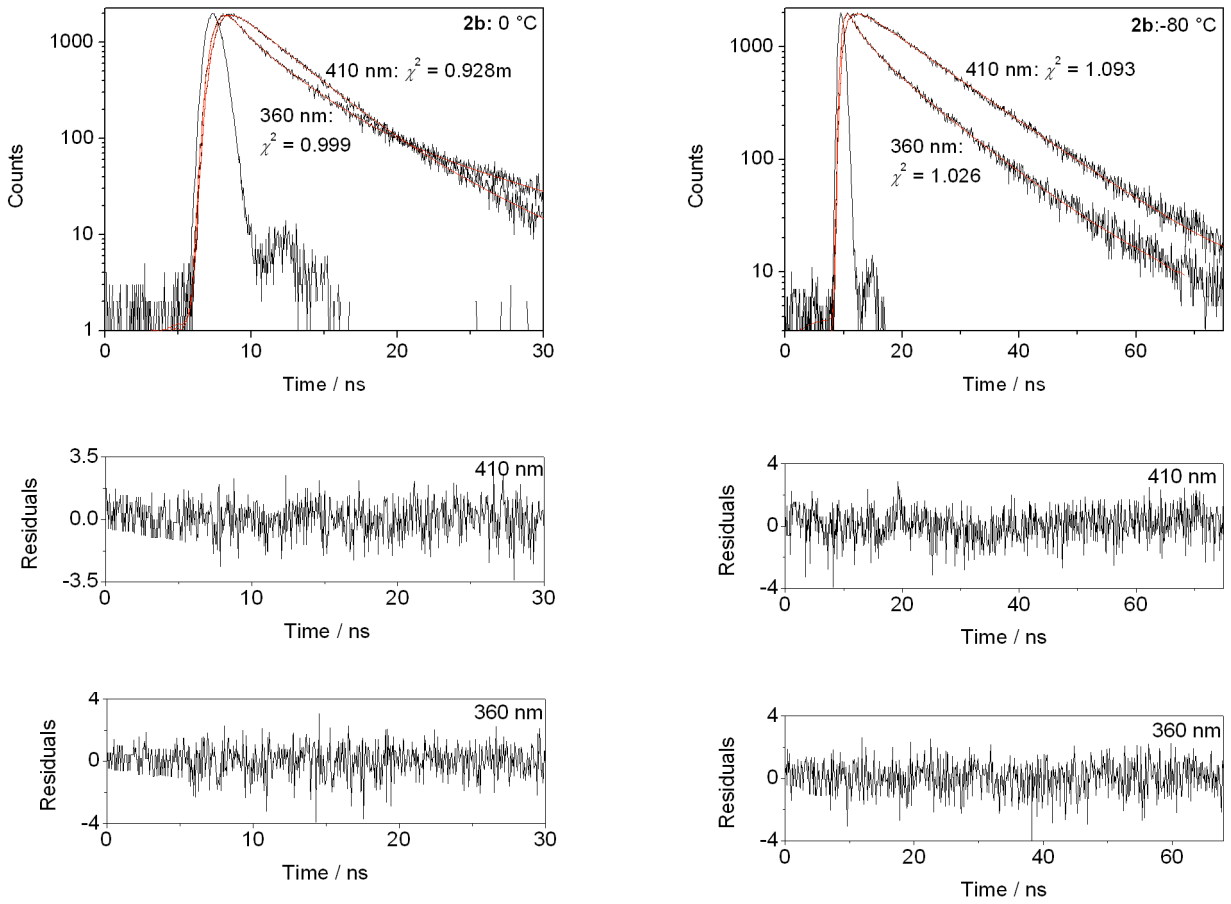


Fig. S11 Fluorescence decays of **2b** in ethanol at different temperatures (c = 10^{-5} M, λ_{ex} = 280 nm) collected at given emission wavelength and the IRF [0 °C (360 nm): τ_1 = 1.0 ns, 33%; τ_2 = 3.0 ns, 59%; τ_3 = 10.0 ns, 7%; 0 °C (410 nm): τ_1 = 1.0 ns, –29%; τ_2 = 2.9 ns, 62%; τ_3 = 6.2 ns, 9%; –80 °C (360 nm): τ_1 = 2.0 ns, 38%; τ_2 = 6.4 ns, 31%; τ_3 = 12.0 ns, 32%; –80 °C (410 nm): τ_1 = 1.4 ns, –36%; τ_3 = 11.8 ns, 64%]. Continuous red lines correspond to the fits of the experimental data. Residuals between the fits and the experimental data are shown below the main figure.

5. ^{1}H-NMR and ^{13}C-NMR data of 2a–e

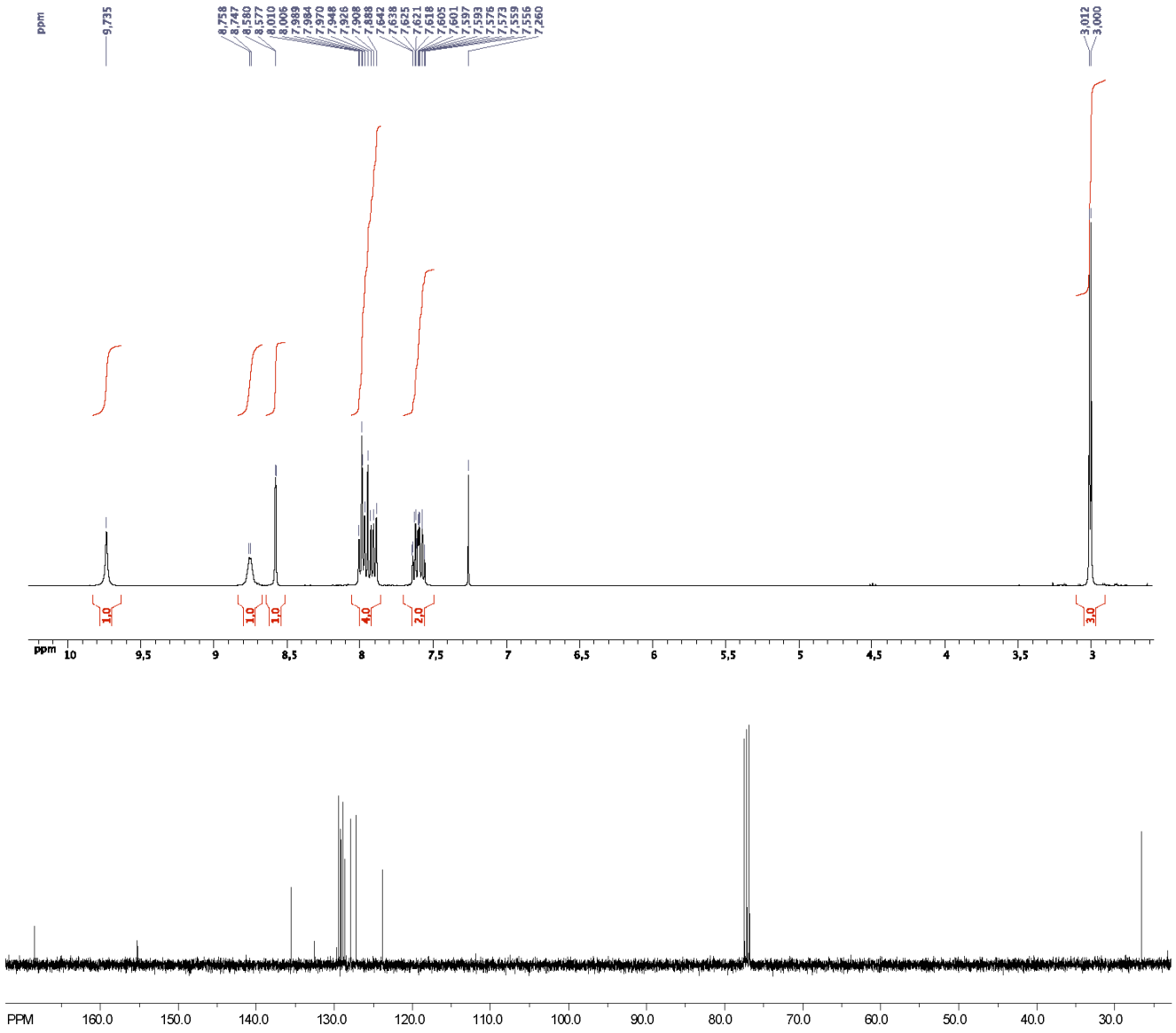


Fig. S12 ^{1}H- and ^{13}C-NMR spectra of **2a** in $CDCl_3$.

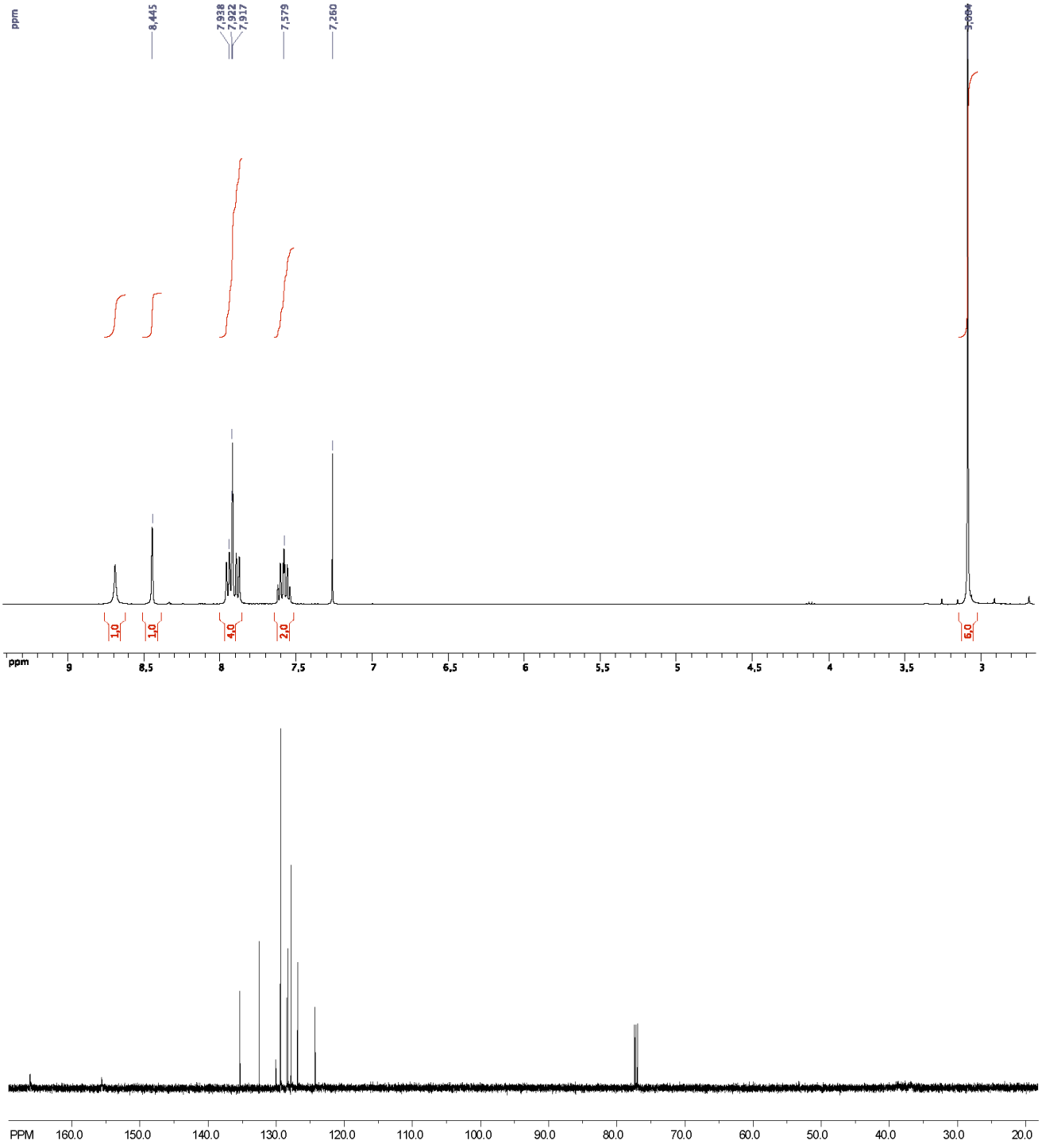


Fig. S13 ^{1}H- and ^{13}C-NMR spectra of **2b** in $CDCl_3$.

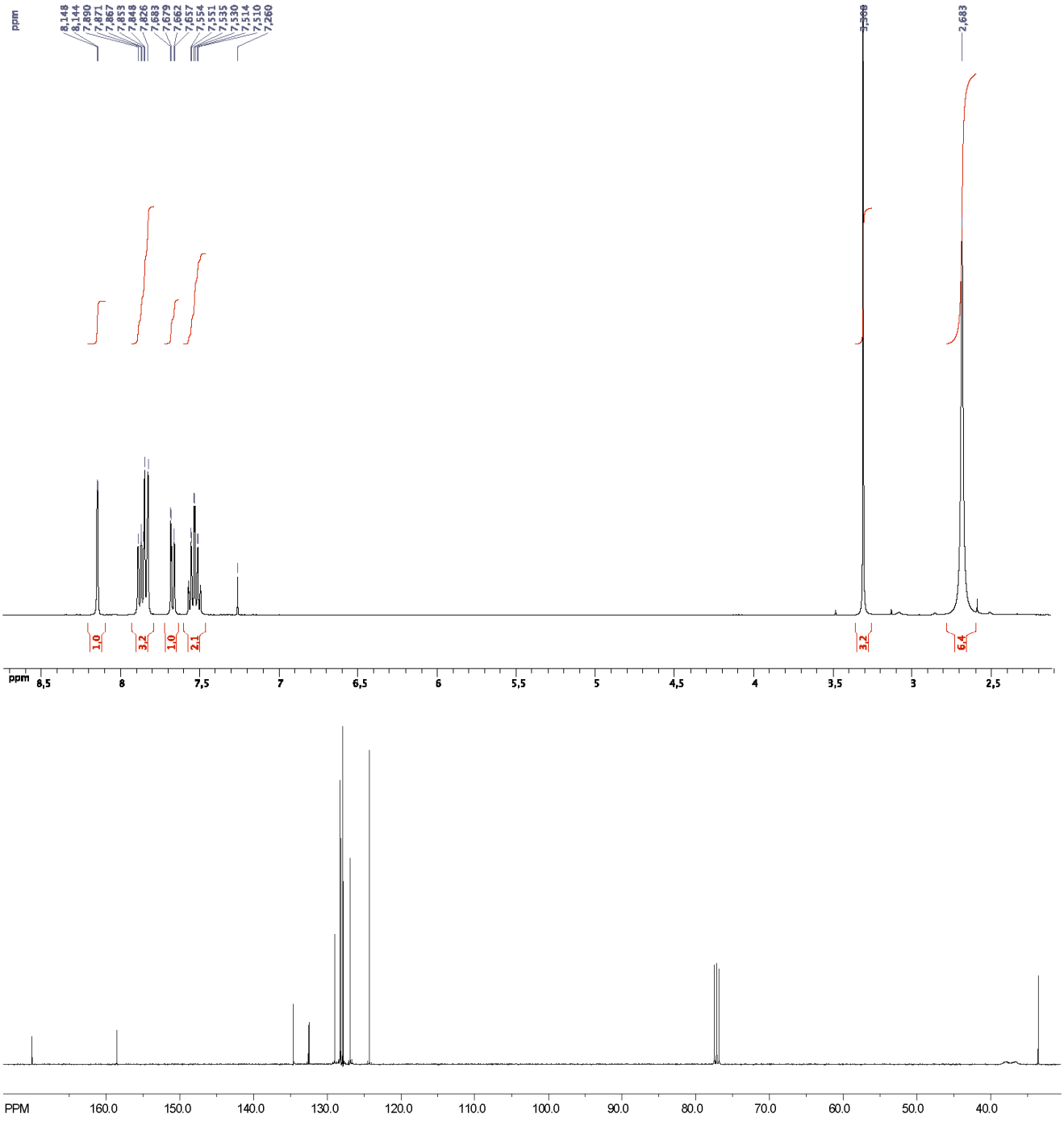


Fig. S14 ^{1}H- and ^{13}C-NMR spectra of **2c** in $CDCl_3$.

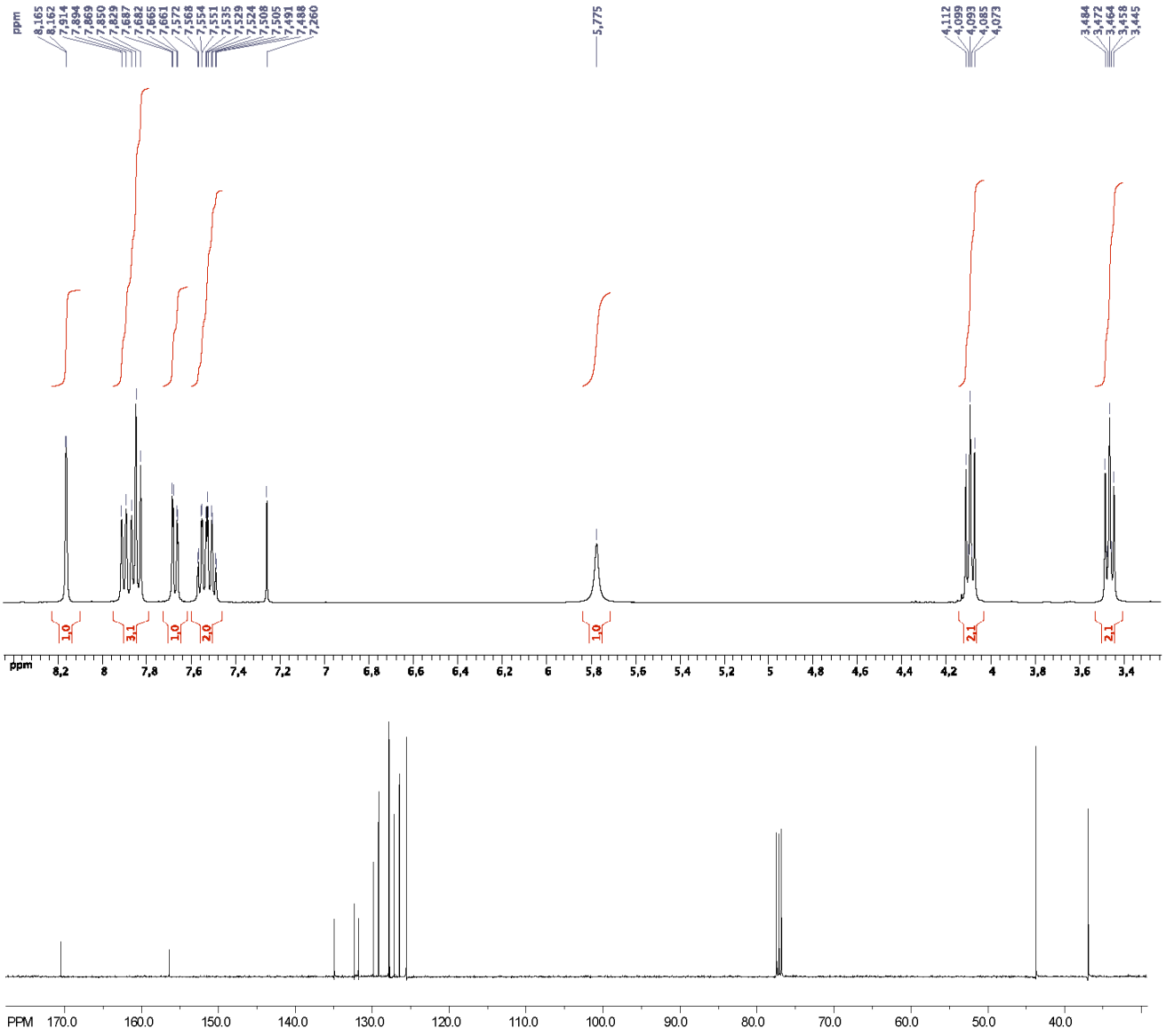


Fig. S15 ^{1}H- and ^{13}C-NMR spectra of **2d** in $CDCl_3$.

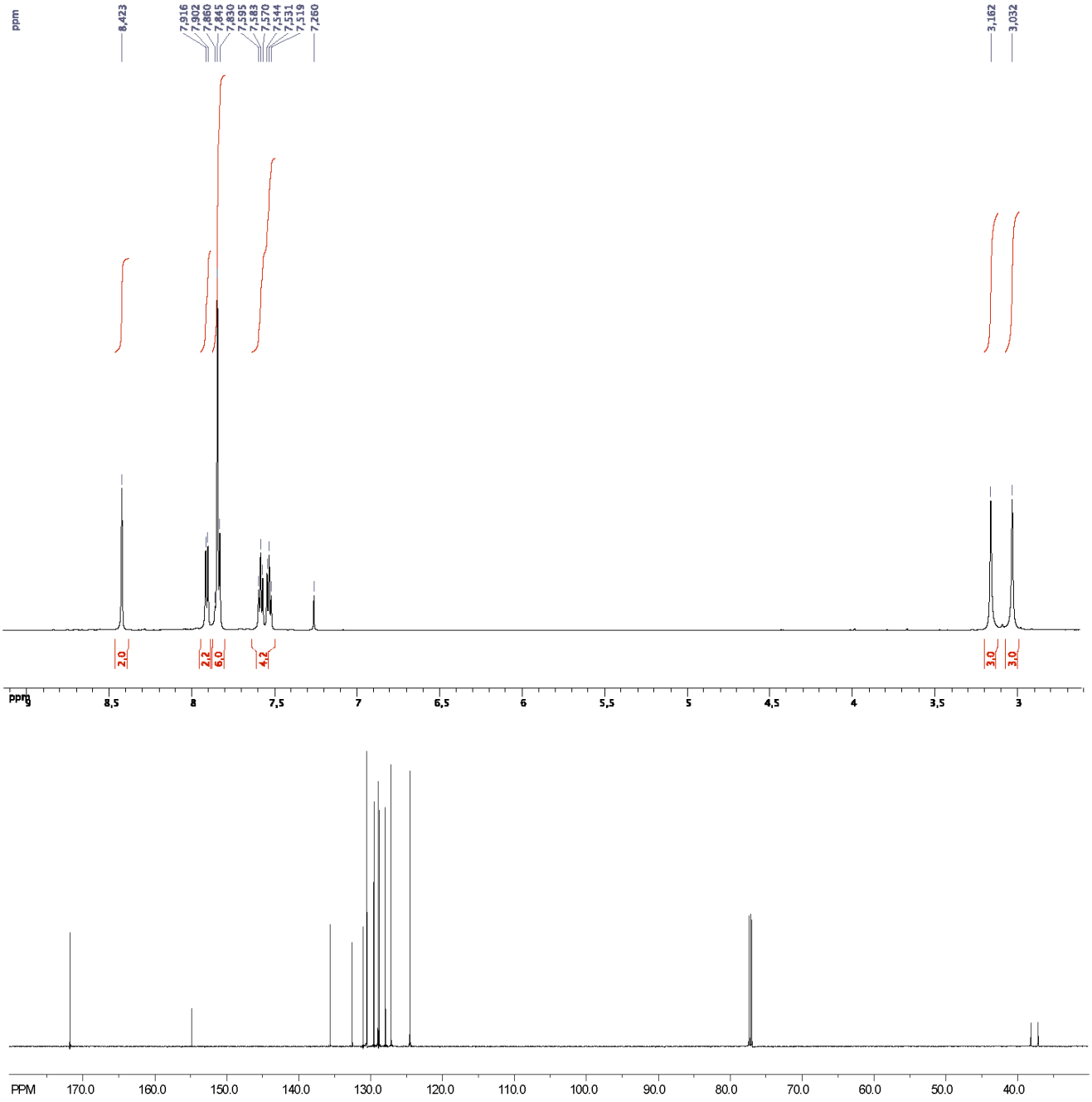


Fig. S16 ^{1}H- and ^{13}C-NMR spectra of **2e** in $CDCl_3$.

[1] G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112-122.
[2] A. L. Spek, *Acta Cryst*., 2009, **D65**, 148-155.