

Supporting Information for

Azo dyes containing 1,3,4-thiadiazole fragment: synthesis, properties

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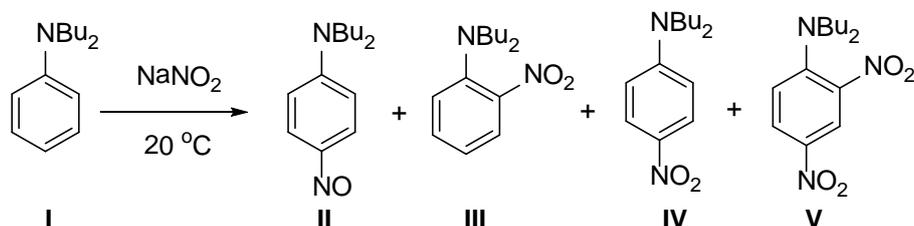
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¹H, ¹⁹F and ¹³C NMR spectra were recorded on a Bruker Avance-300 (300.13 MHz for ¹H and 282.36 13 MHz for ¹⁹F), Bruker Avance-400 (400.13 MHz for ¹H and 100.61 MHz for ¹³C) and Bruker DRX-500 (500 MHz for ¹H, 126 MHz for ¹³C) spectrometers. Chemical shifts (δ) of ¹H and ¹³C are given in ppm relative to TMS using the solvent signals as the internal standard ($\delta_{\text{H}} = 2.04$ ppm, $\delta_{\text{C}} = 29.8$ and 206.3 ppm for acetone-d₆, $\delta_{\text{H}} = 2.50$ ppm, $\delta_{\text{C}} = 39.5$ ppm for DMSO-d₆, $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.2$ ppm for CDCl₃), the internal standard for ¹⁹F spectra was C₆F₆ ($\delta = -162.9$ ppm). IR spectra were recorded using a spectrometer Tensor-27 (Bruker) for samples pelleted with KBr (0.25%). UV-VIS spectra were registered in a quartz cuvette on a Varian Cary 5000 spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a NETZSCH STA 409 instrument at a heating rate of 10 °C/min under He flow 30 mL/min. Temperature and heat flow calibration was calibrated according to ISO 11357-1 standard by the temperatures and enthalpies of phase transitions of standard substances from calibration set from NETZSCH (C₆H₅CO₂H (99,5%), RbNO₃ (99,99%), In (99,99%), Sn (99,99%), Bi (99,9995%), Zn (99,999%). The obtained data were processed using NETZSCH Proteus Thermal Analysis software.

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Interaction of N,N-di-*n*-butylaniline with sodium nitrite in the presence of sulfuric acid.

The formation of N,N-dialkyldinitroanilines, as well as mononitro derivatives of N,N-di-*n*-butylaniline under similar conditions has not been found in the literature. We studied the interaction of N,N-di-*n*-butylaniline (**I**) with NaNO₂ in dilute H₂SO₄ at room temperature (Scheme 1).



Scheme 1

Initially, an aqueous solution of NaNO₂ was added to solution **I** in 50% H₂SO₄ or in a mixture of 50% H₂SO₄ and an organic solvent. When the molar ratio of **I**/NaNO₂ was ~ 1: 1.2, the reaction mixture contained mainly unreacted aniline **I** (according to ¹H NMR data) and N,N-di-*n*-butyl-4-nitrosoaniline (**II**), mono nitro products: N,N-di-*n*-butyl-2-nitroaniline (**III**) and N,N-di-*n*-butyl-4-nitroaniline (**IV**) (in a ratio of ~ 1: 1.7), and trace amounts of N,N-di-*n*-butyl-2,4-dinitroaniline (**V**) after 12 min (Table 1, entry 1). Increasing of the time to 1 h and a change in the order of mixing the reagents, that is, the addition of amine **I** into a solution of NaNO₂ in dilute H₂SO₄, significantly changed the ratio of the products (Table 1, entry 2). Although a significant amount of starting amine **I** did not react, as in entry 1, nitroso compound **II** was not observed. The content of dinitro product **V** is significantly increased due to the nitration of mononitroanilines **III** and **IV**. The conversion of aniline **I** (entry 3) for 12 min is significant increased when the use of acetone as an organic solvent and the molar ratio **I**/NaNO₂/H₂SO₄ equal to ~1:1:3. Moreover, nitrosoaniline **II** is the main product. Increasing of sulfuric acid (up to 6, entry 4) led to decreasing of the conversion of **I** almost twice with the formation of the same products. With the addition of dioxane, as well as acetone, the main components of the reaction mixture were the starting amine **I** and the nitrosation product **II** (entry 5). Complete conversion of aniline **I** was achieved with the addition of acetone and the ratio of reagents **I**/NaNO₂/H₂SO₄ equal to ~ 1:1.5:3 (entry 6). Compounds **II-IV** were isolated in the yields 39%, 14%, and 25%, respectively.

In order to obtain dinitroaniline **V** as the main product, the molar ratio **I**/NaNO₂ was increased to ~1:9. The substrate **I** was added to a solution of NaNO₂ in dilute H₂SO₄ (50%) and kept at ~ 50 °C for half an hour. In this case, the main product is compound **V** (75% according to ¹H NMR data), while only *o*-nitroaniline **III** (13%) was observed as a minor component. Nitro compounds **V** and **III** were obtained in 53% and 8% yields, respectively. Previously, compound **V** was obtained from 2,4-dinitrofluorobenzene by heating with tri-*n*-butylamine in DMF¹ or di-*n*-butylamine in DMSO²; from 2,4-dinitrochlorobenzene with di-*n*-butylamine in DMSO³ or with tetra-*n*-butylammonium hydroxide in sulfolane at high temperature⁴.

Thus, it is shown that N,N-di-*n*-butyl-4-nitrosoaniline and *o*- and *p*-nitro products are formed under the action NaNO₂ to N,N-di-*n*-butylaniline in dilute H₂SO₄ or in its mixture with an organic solvent for 12 min. Increasing of the time up to 1 h leads to the appearance of N,N-di-*n*-butyl-2,4-dinitroaniline, which becomes dominant when using a 9-fold of NaNO₂ and an elevated temperature.

Individual compounds were isolated by column chromatography on silica gel 60–100 μm.

N,N-di-*n*-butyl-4-nitrosoaniline II⁵, **N,N-di-*n*-butyl-2-nitroaniline III** and **N,N-di-*n*-butyl-4-nitroaniline IV**^{6,7}. Aniline **I** (98 mg, 0.5 mmol) was dissolved in acetone (1 mL) then 50% H₂SO₄ (0.1 mL) was added, a solution of NaNO₂ (49 mg, 0.7 mmol) in water (0.1 mL) was quickly added, and then mixture was stirring for 12 min at a temperature of 20 °C. The reaction mixture was poured into water, extracted with CH₂Cl₂ (3 × 10 ml), dried with MgSO₄, the drying agent was filtered off, the solvent was removed on a rotary evaporator, and a mixture of compounds **II-IV** (102 mg) was obtained as a brown oil. Individual compounds were isolated by column chromatography (eluent: ethyl acetate-hexane, 1:10).

Table 1 Conditions and results of the conversion of aniline **I** under the action of NaNO₂ in the presence of H₂SO₄ at ambient temperature

No	Reagents: mg, (mmol), solvent, mL	Time, min	Composition according to ¹ H NMR*	Weight of crude product, mg
1	I 190 (0.9); NaNO ₂ 70 (1.0) 50% H ₂ SO ₄ 2 mL/H ₂ O 0.2 mL	12 min	I 50%, II 22%, III 9%, IV 15%, V 1%	191
2	I 104 (0.5); NaNO ₂ 40 (0.6) 50% H ₂ SO ₄ 2 mL/H ₂ O 0.3 mL	60 min	I 58%, III 15%, IV 3%, V 24%	90
3	I 92 (0.4); NaNO ₂ 34 (0.5) 50% H ₂ SO ₄ 0.1 mL/H ₂ O 0.1 mL, Acetone 1 mL	12 min	I 23%, II 43%, III 11%, IV 20%	89
4	I 96 (0.5); NaNO ₂ 36 (0.5) 50% H ₂ SO ₄ 0.2 mL/H ₂ O 0.1 mL, Acetone 1 mL	12 min	I 42%, II 38%, III 6%, IV 13%	106
5	I 100 (0.5); NaNO ₂ 37 (0.5) 50% H ₂ SO ₄ 0.1 mL/H ₂ O 0.1 mL, Dioxane 1 mL	12 min	I 31%, II 49%, III 5%, IV 13%	106
6	I 98 (0.5); NaNO ₂ 49 (0.7) 50% H ₂ SO ₄ 0.1 mL/H ₂ O 0.1 mL, Acetone 1 mL	12 min	II 47%, III 16%, IV 33%	102

* Trace amounts of products missing up to 100% are N-butylaniline and its nitration products.

N,N-di-*n*-butyl-4-nitrosoaniline II⁵, 43 mg (39%), green oil. ¹H NMR (400 MHz, CDCl₃ δ (ppm), J/Hz): 8.81 (br s, 1H, Ar-H), 6.61 (br s, 3H, Ar-H), 3.40 (t, 4H, *J*_{HH} = 7.8, H-7a, H-7b, H-7'a, H-7'b), 1.63 (pen, 4H, *J*_{HH} = 7.7, H-8a, H-8b, H-8'a, H-8'b), 1.38 (sex, 4H, *J*_{HH} = 7.4, H-9a, H-9b, H-13a, H-13b), 0.97 (t, 6H, *J*_{HH} = 7.4, H-10a, H-10b, H-10c, H-14a, H-14b, H-14c). ¹³C NMR (126 MHz, CDCl₃ δ, ppm): 162.9 (s, 1C, C-4), 154.0 (s, 1C, C-1), 141.7 (br s, 2C, C-3, C-5), 110.1 (br s, 2C, C-2, C-6), 51.4 (s, 2C, C-7, C-11), 29.5 (s, 2C, C-8, C-12), 20.3 (s, 2C, C-9, C-13), 14.0 (s, 2C, C-10, C-14). UV (EtOH) λ nm (lg ε): 238 (1.13), 275 (1.40), 431 (2.17). IR (KBr) ν 1600 (N=O), 1107 (C-N(=O)). Found: C, 72.20; H, 9.67; N, 11.50. C₁₄H₂₂N₂O requires C, 71.76; H, 9.46; N, 11.95%.

N,N-di-*n*-butyl-2-nitroaniline III, 16 mg (14%), yellow oil. ¹H NMR (400 MHz, CDCl₃ δ (ppm), J/Hz): 7.66 (dd, 1H, *J*_{HH} = 1.5, 8.1, H-3), 7.38 (ddd, 1H, *J*_{HH} = 1.5, 7.3, 8.5, H-5), 7.12 (dd, 1H, *J*_{HH} = 1.0, 8.5, H-6), 6.88 (ddd, 1H, *J*_{HH} = 1.0, 7.3, 8.1, H-4), 3.08 (t, 4H, *J*_{HH} = 7.2, H-7a, H-7b, H-7'a, H-7'b), 1.48 (pen, 4H, *J*_{HH} = 7.2, H-8a, H-8b, H-8'a, H-8'b), 1.26 (sex, 4H, *J*_{HH} = 7.2, H-9a, H-9b, H-9'a, H-9'b), 0.87 (t, 6H, *J*_{HH} = 7.3, H-10a, H-10b, H-10c, H-10'a, H-10'b, H-10'c). ¹³C NMR (126 MHz, CDCl₃ δ, ppm): 145.3 (s, 1C, C-1), 143.1 (s, 1C, C-2), 132.7 (s, 1C, C-5), 126.0 (s, 1C, C-3), 122.2 (s, 1C, C-4), 119.7 (s, 1C, C-6), 52.3 (s, 2C, C-7, C-7'), 29.6 (s, 2C, C-8, C-8'), 20.3 (s, 2C, C-9, C-9'), 14.0 (s, 1C, C-10, C-10').

N,N-di-*n*-butyl-4-nitroaniline IV^{6,7}, 30 mg (25%), yellow oil. ¹H NMR (400 MHz, CDCl₃ δ (ppm), J/Hz): 8.09 (d, 2H, *J*_{HH} = 9.5, H-2, H-6), 6.54 d, 2H, *J*_{HH} = 9.5, H-5, H-3), 3.36 (t, 4H, *J*_{HH} = 7.7, H-7a, H-7b, H-7'a, H-7'b), 1.60 (pen, 4H, *J*_{HH} = 7.7, H-8a, H-8b, H-8'a, H-8'b), 1.38 (sex, 4H, *J*_{HH} = 7.4, H-9a, H-9b, H-9'a, H-9'b), 0.98 (t, 6H, *J*_{HH} = 7.3, H-10a, H-10b, H-10c, H-10'a, H-10'b, H-10'c).

N,N-di-*n*-butyl-2,4-dinitroaniline V⁴. NaNO₂ (314 mg, 4.6 mmol) was dissolved in 50% H₂SO₄ (3 mL) and aniline **1** (106 mg, 0.5 mmol) was added, the mixture was stirring for 30 min at a temperature of ~ 50 °C. The reaction mixture was extracted with CH₂Cl₂ (3 × 10 mL), washed with water (2×10 mL), a extract was dried with MgSO₄, the drying agent was filtered off, the solvent was removed on a rotary evaporator, and a mixture of compounds **III** and **V** (131 mg) was obtained as a brown oil. Individual compounds were isolated by column chromatography (eluent: ethyl acetate-hexane, 1:10). Compound **III**, 10 mg (8%) (characteristics are given above).

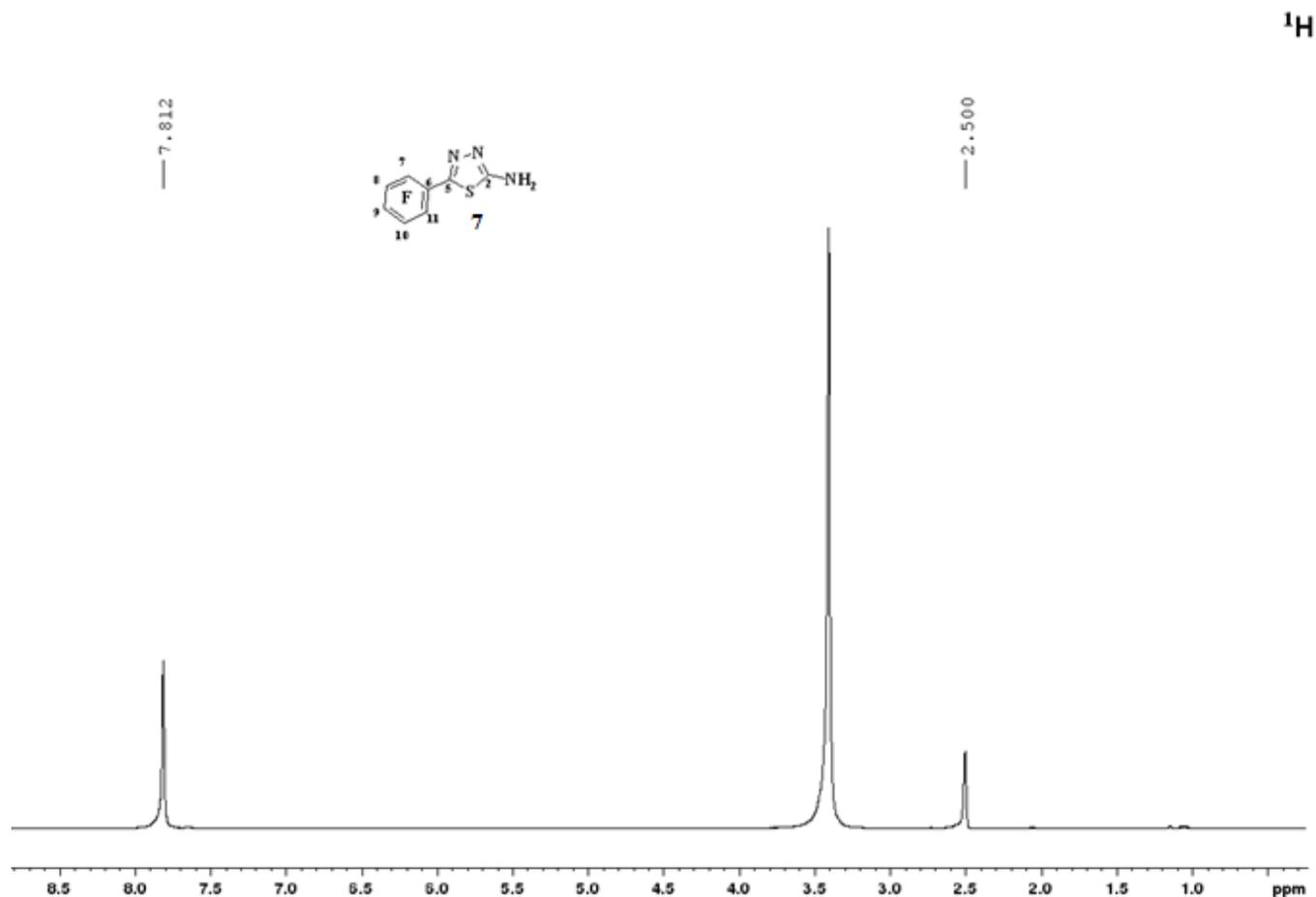
N,N-di-*n*-butyl-2,4-dinitroaniline V⁴, 81 mg (53%), yellow oil. ¹H NMR (400 MHz, CDCl₃ δ (ppm), J/Hz): 8.62 (d, 1H, *J*_{HH} = 2.8, H-3), 8.17 (dd, 1H, *J*_{HH} = 2.8, 9.5, H-5), 7.06(d, 1H, *J*_{HH} = 9.5, H-

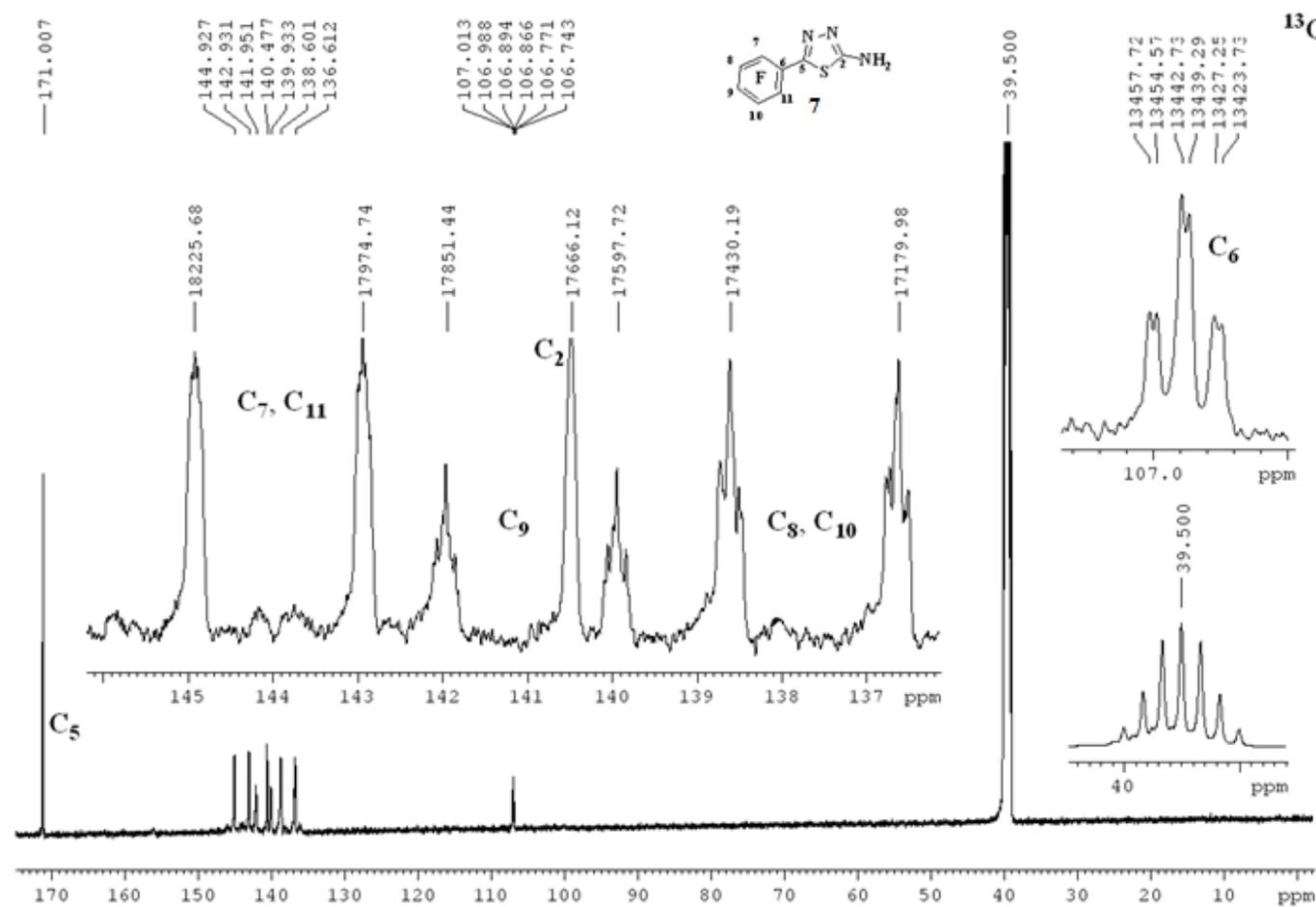
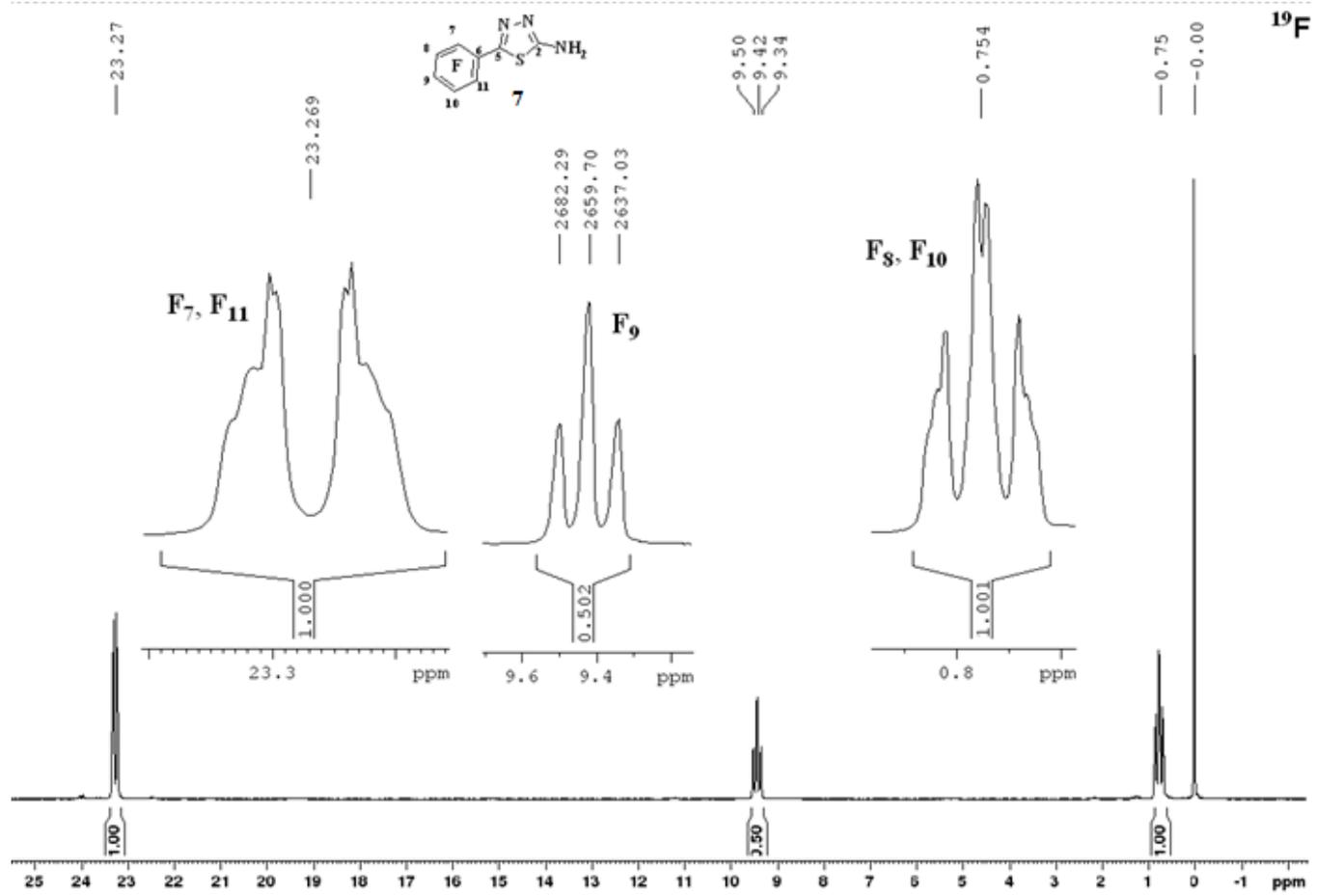
6), 3.26 (t, 4H, $J_{HH} = 7.3$, H-7a, H-7b, H-7'a, H-7'b), 1.58 (pen, 4H, $J_{HH} = 7.4$, H-8a, H-8b, H-8'a, H-8'b), 1.28 (sex, 4H, $J_{HH} = 7.5$, H-9a, H-9b, H-9'a, H-9'b), 0.89 (t, 6H, $J_{HH} = 7.4$, H-10a, H-10b, H-10c, H-10'a, H-10'b, H-10'c).

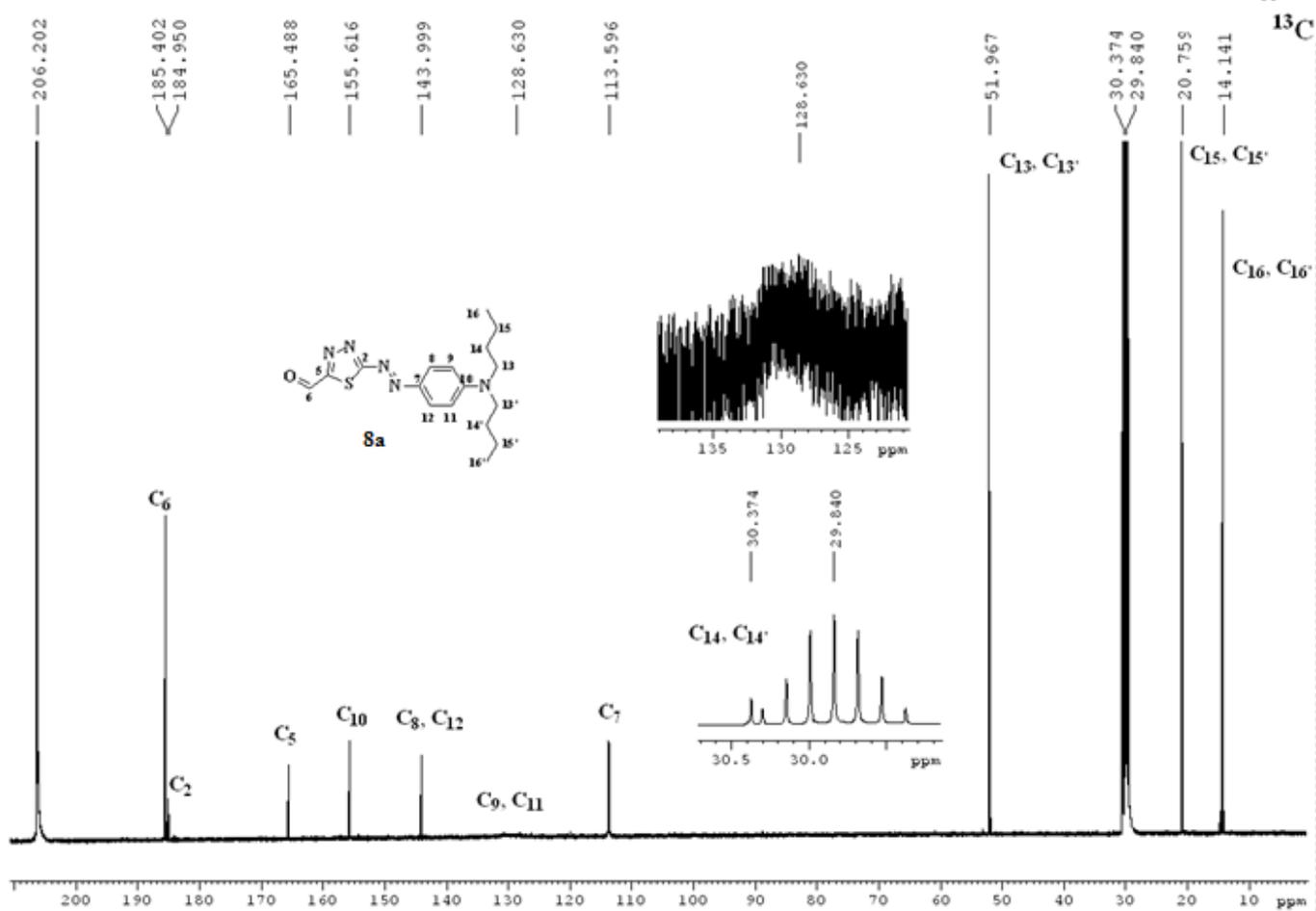
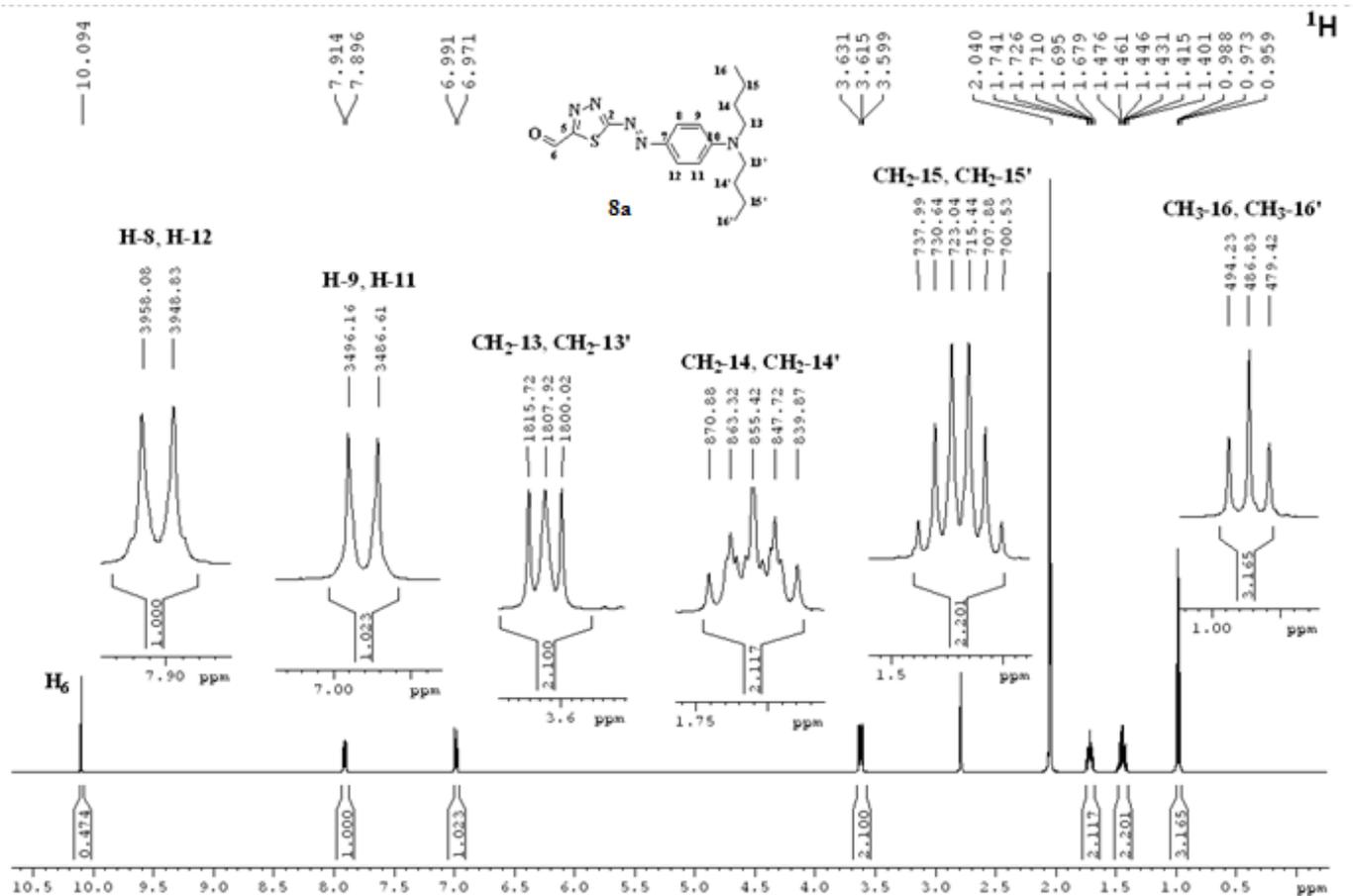
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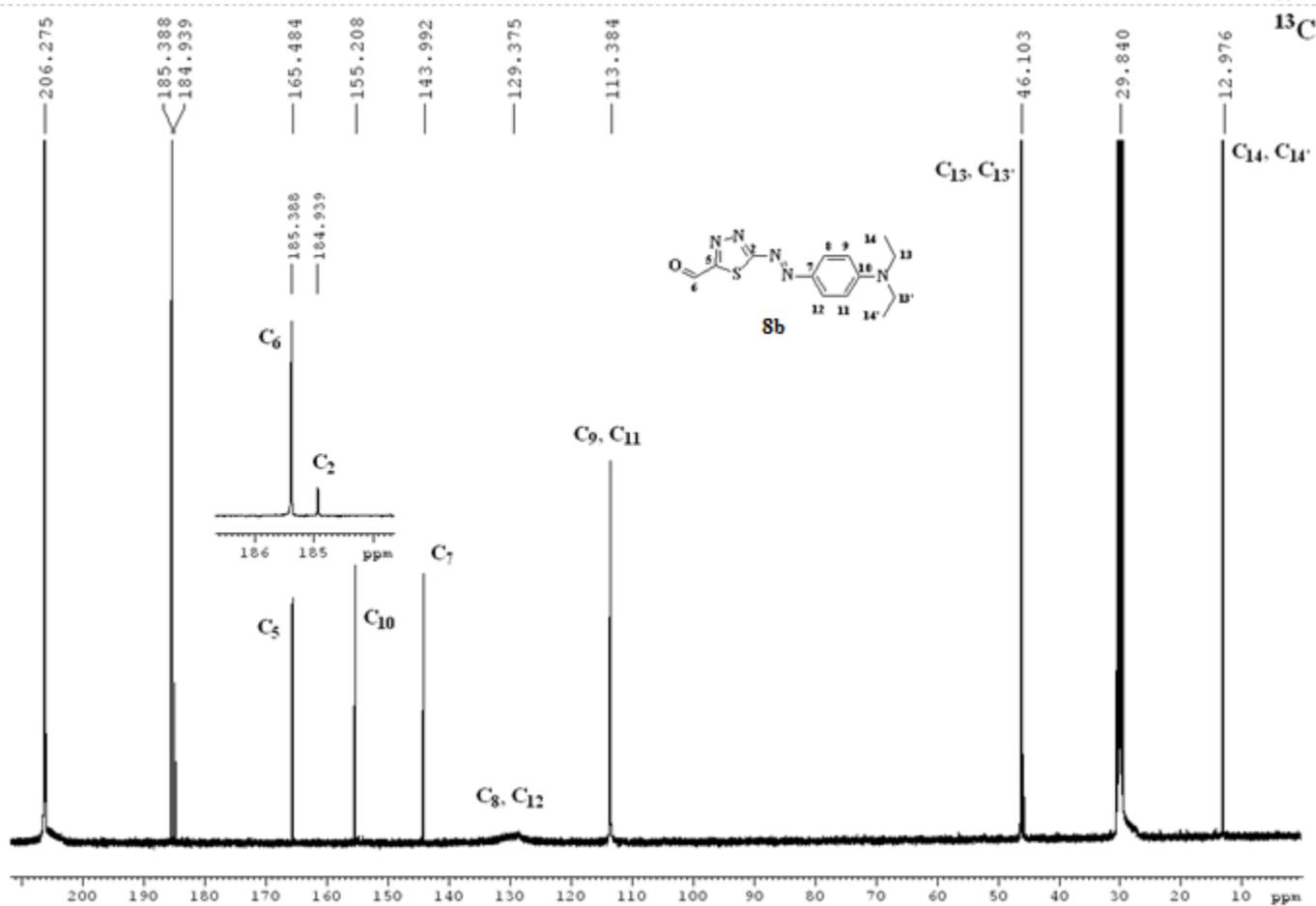
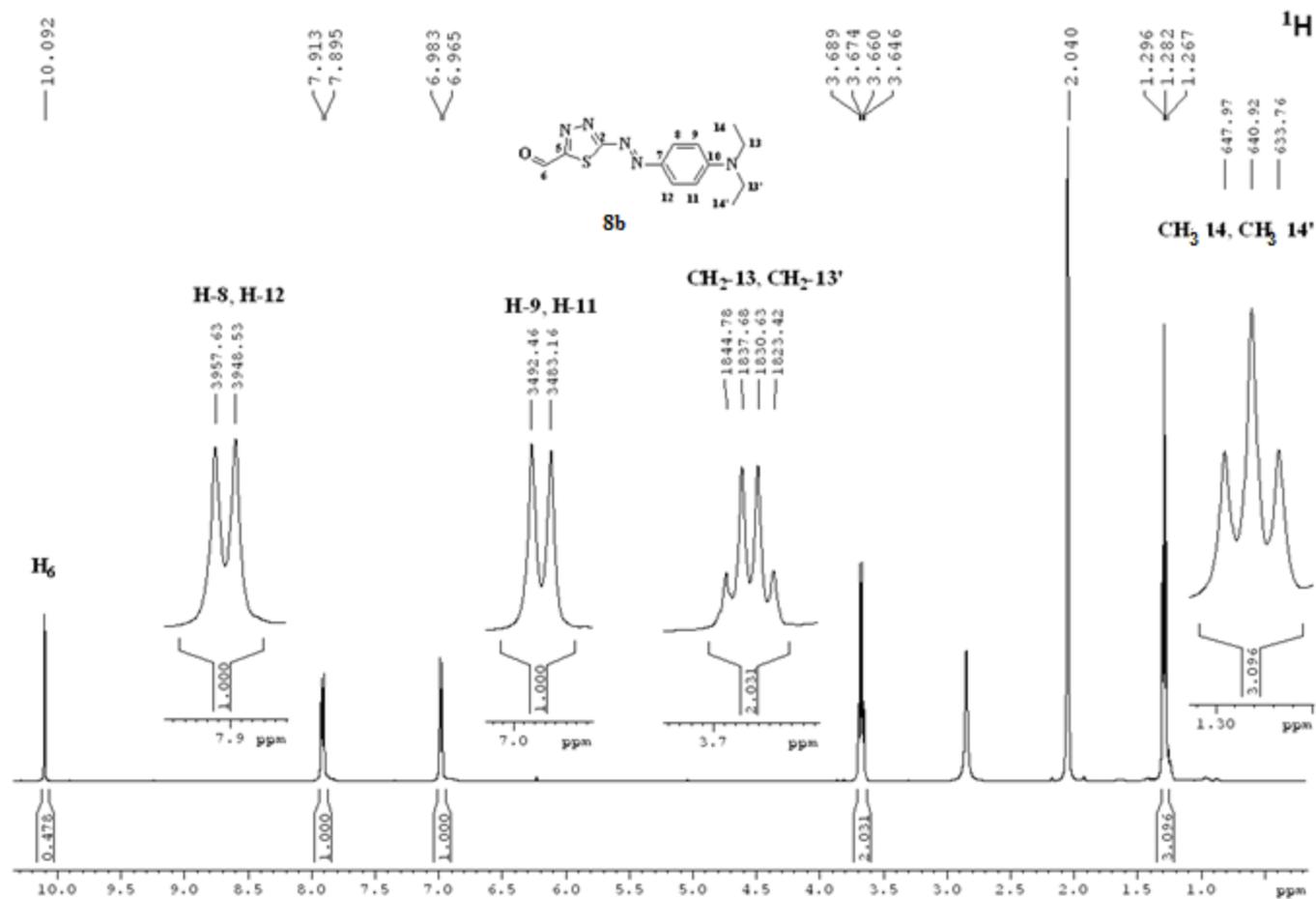
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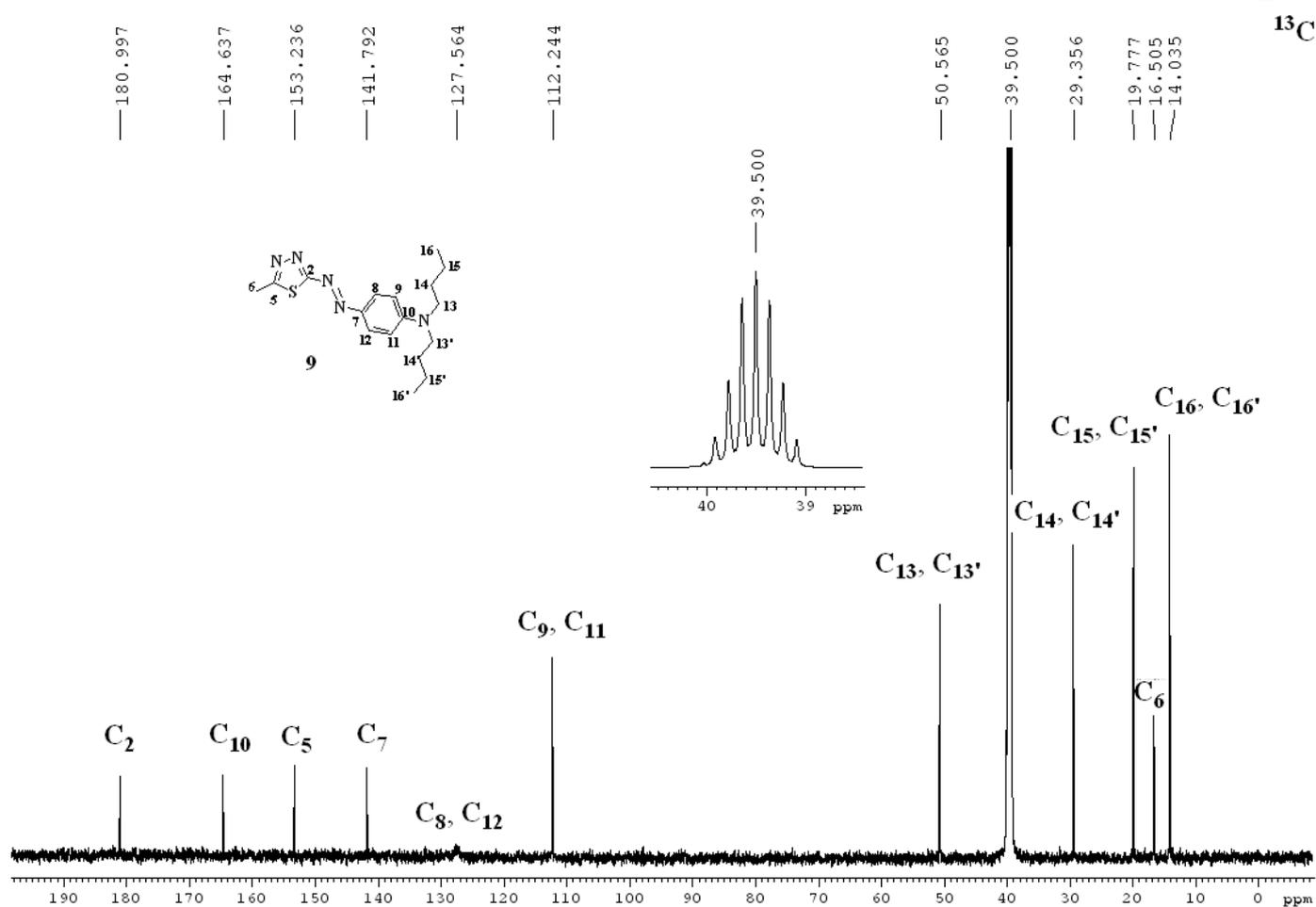
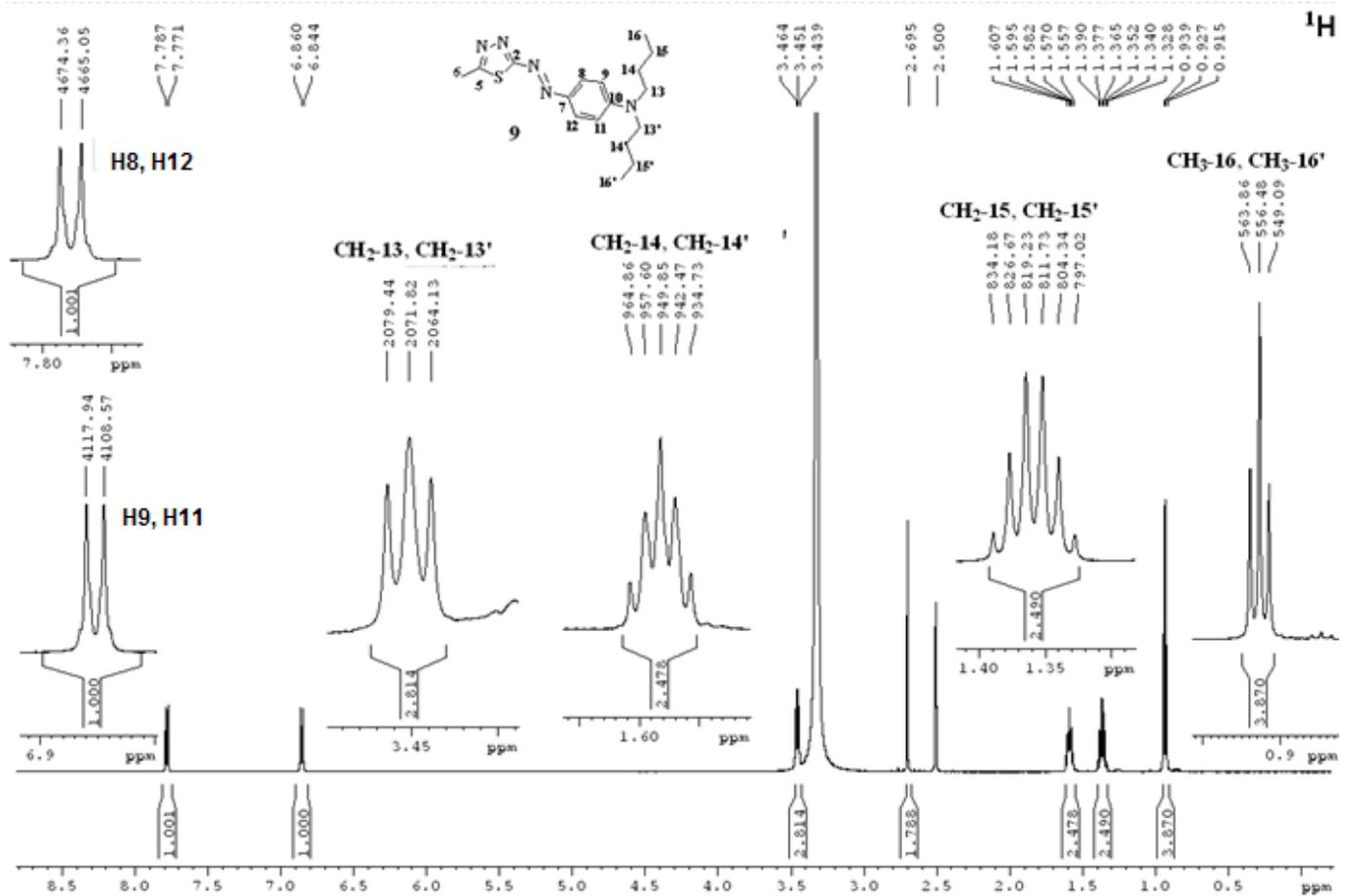
^1H and ^{13}C NMR spectra of azo compounds

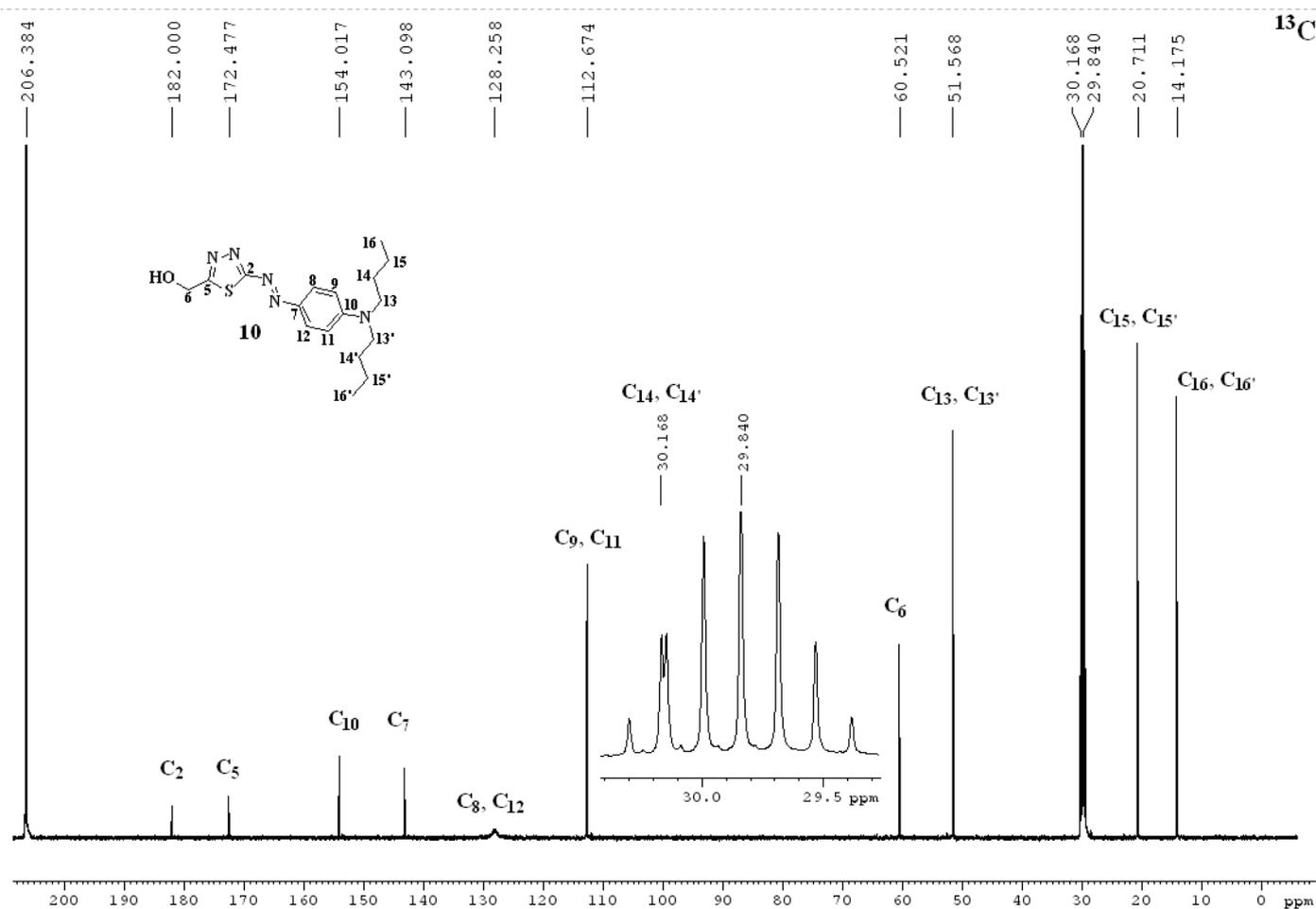
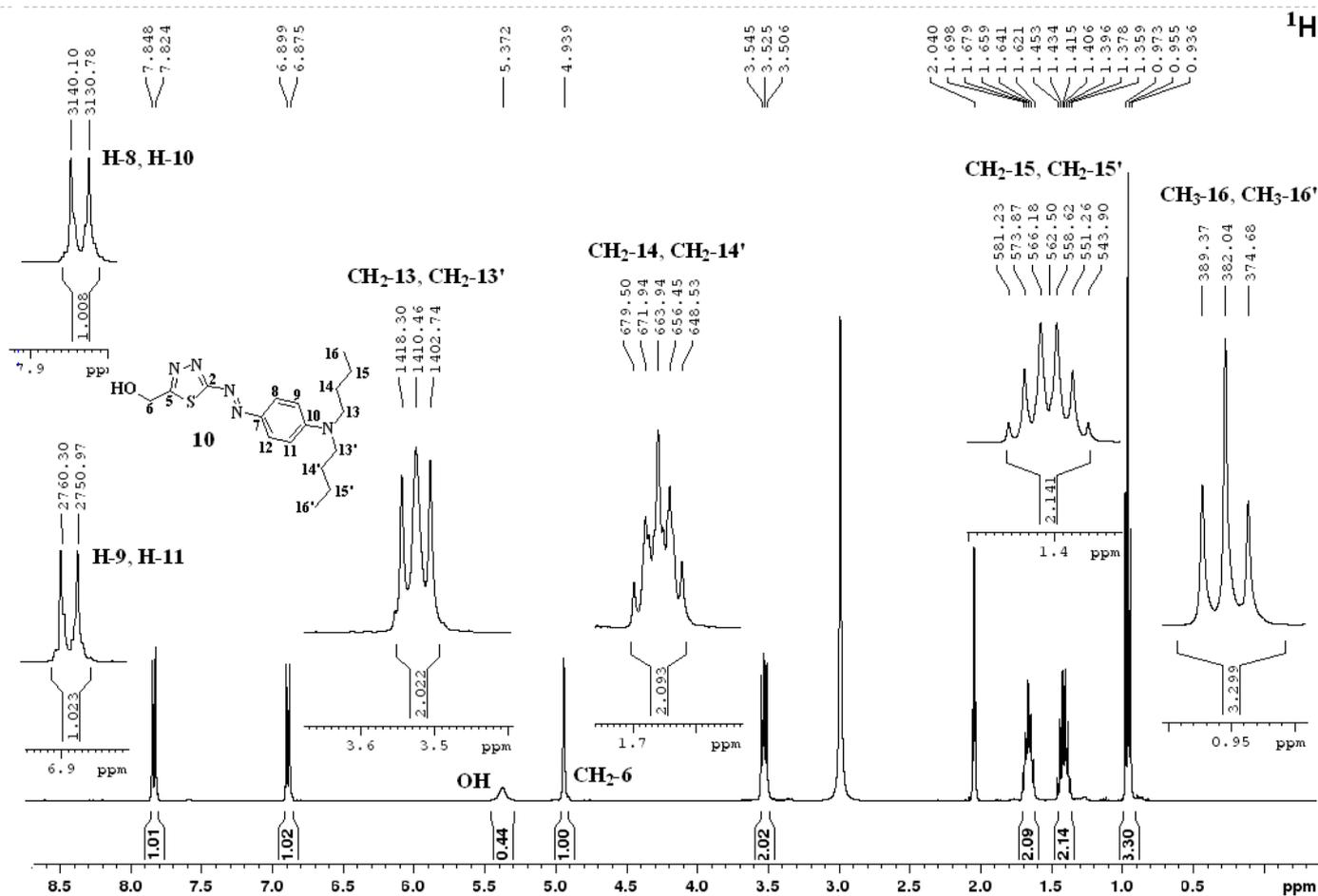


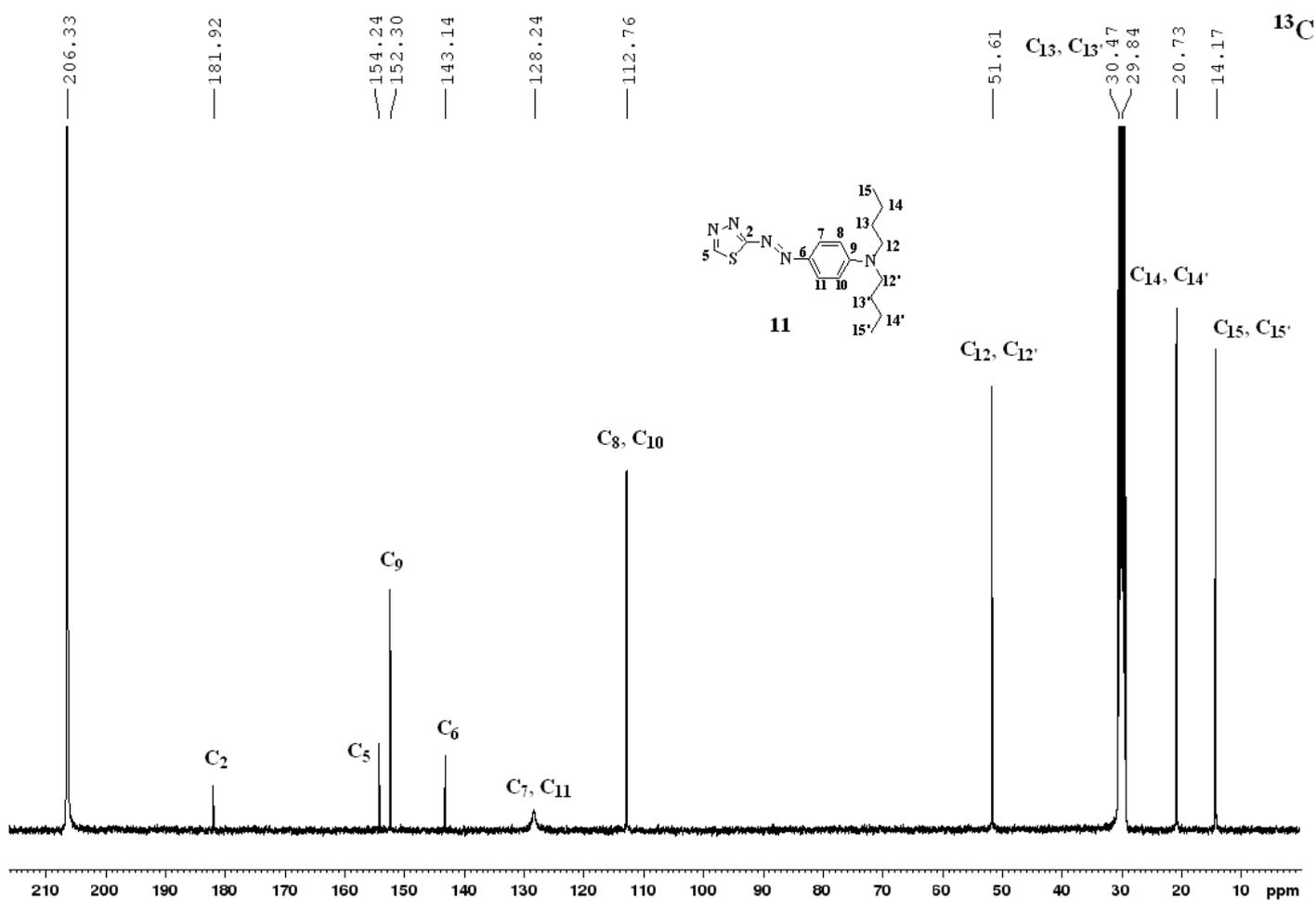
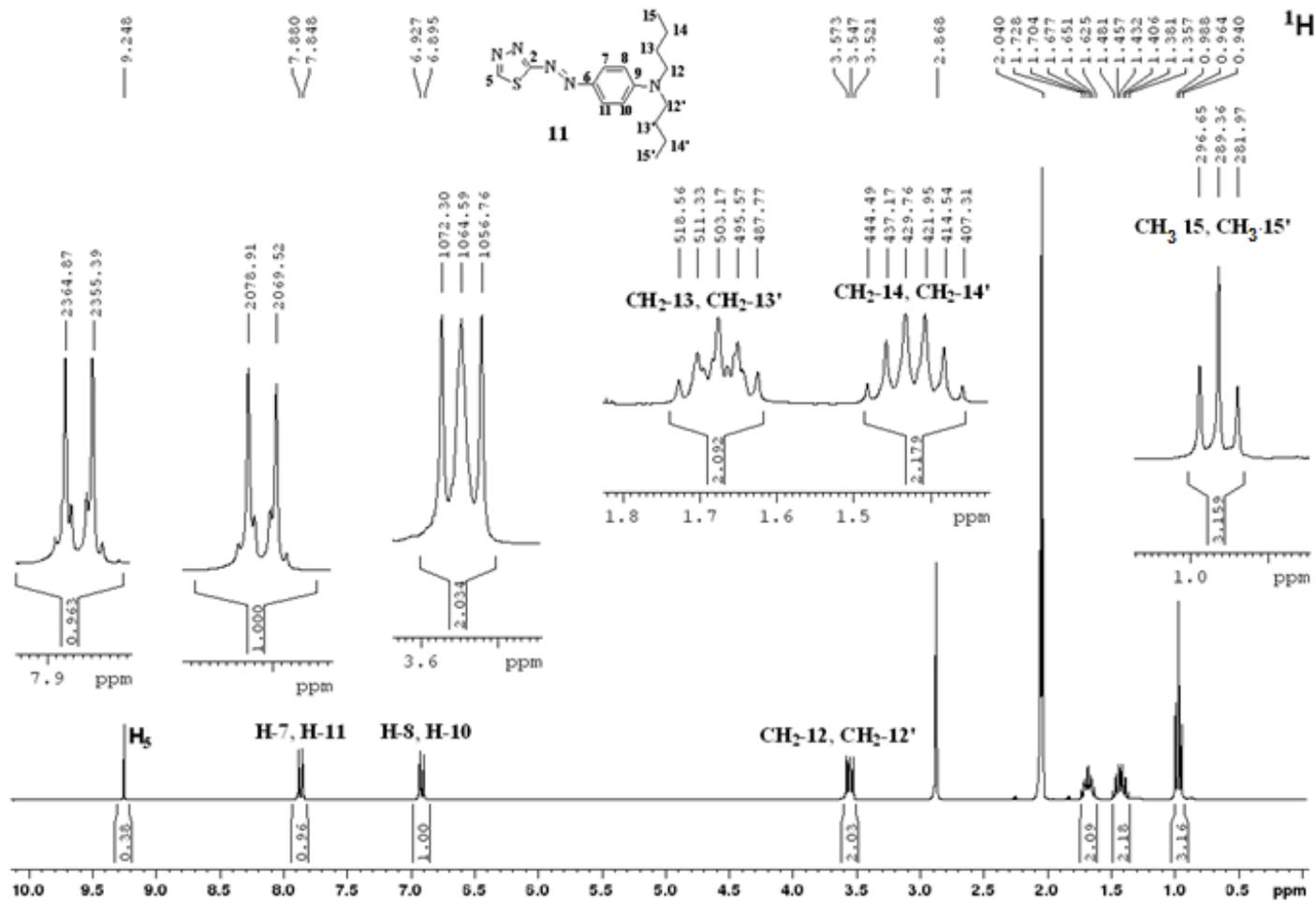


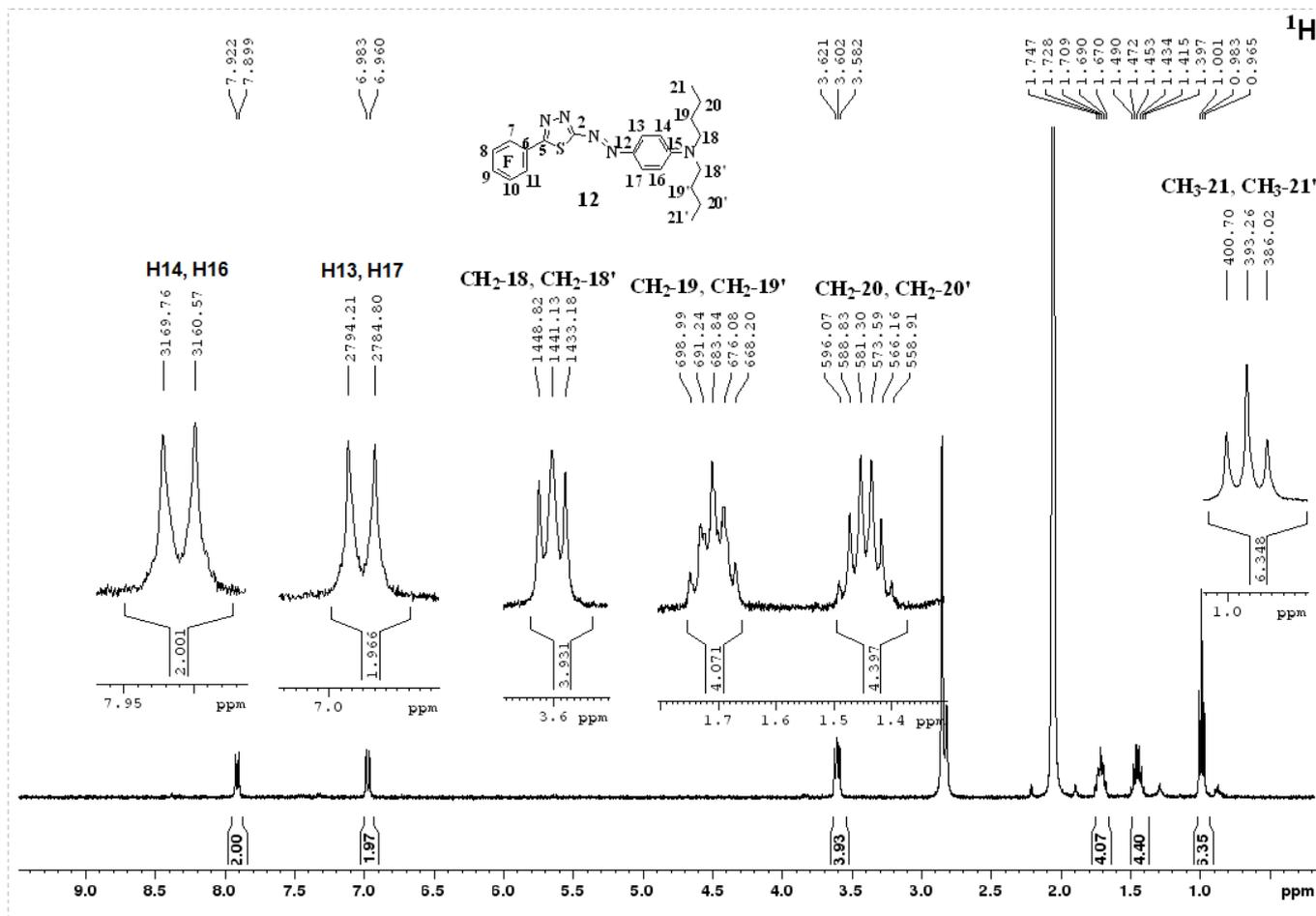


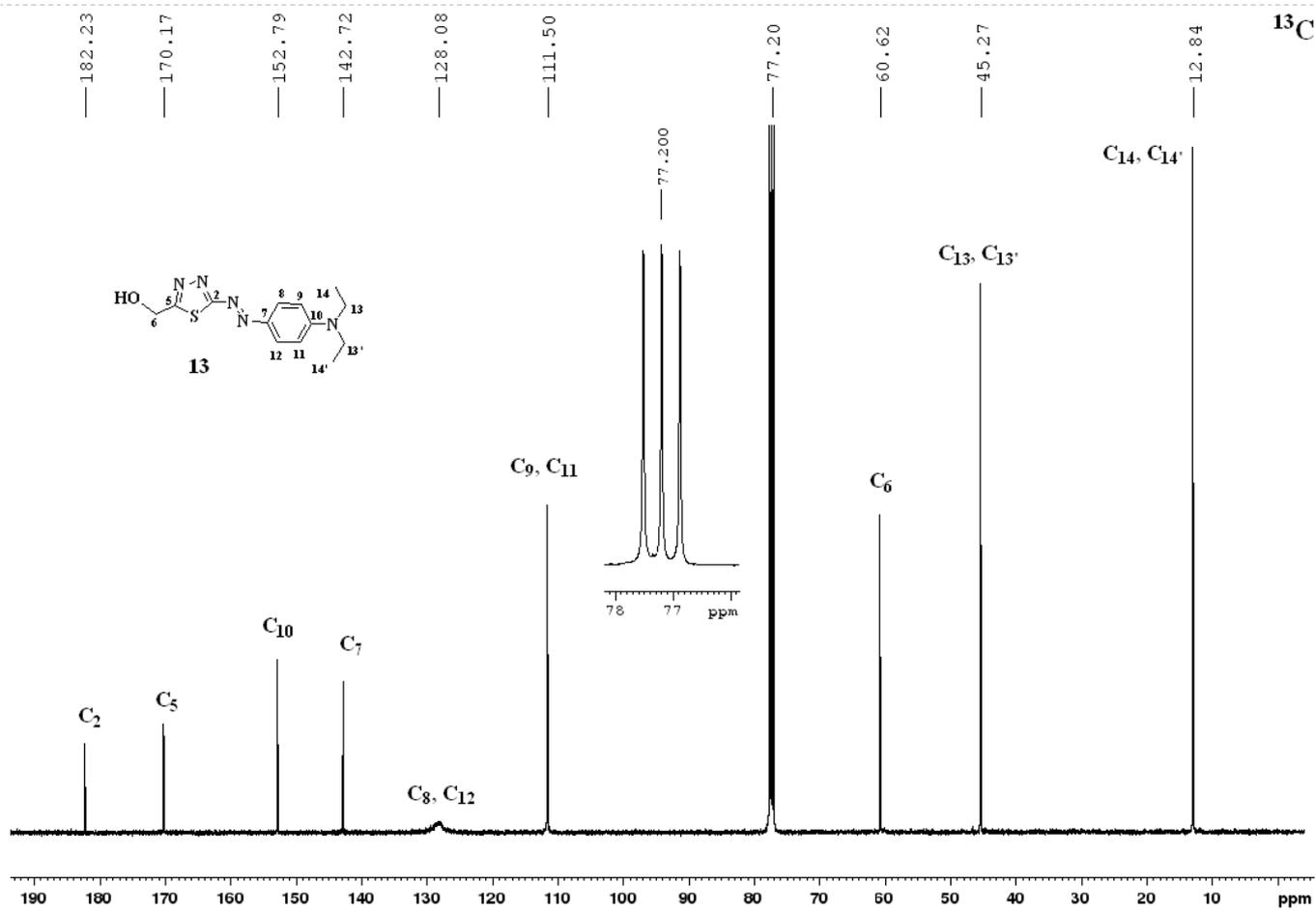
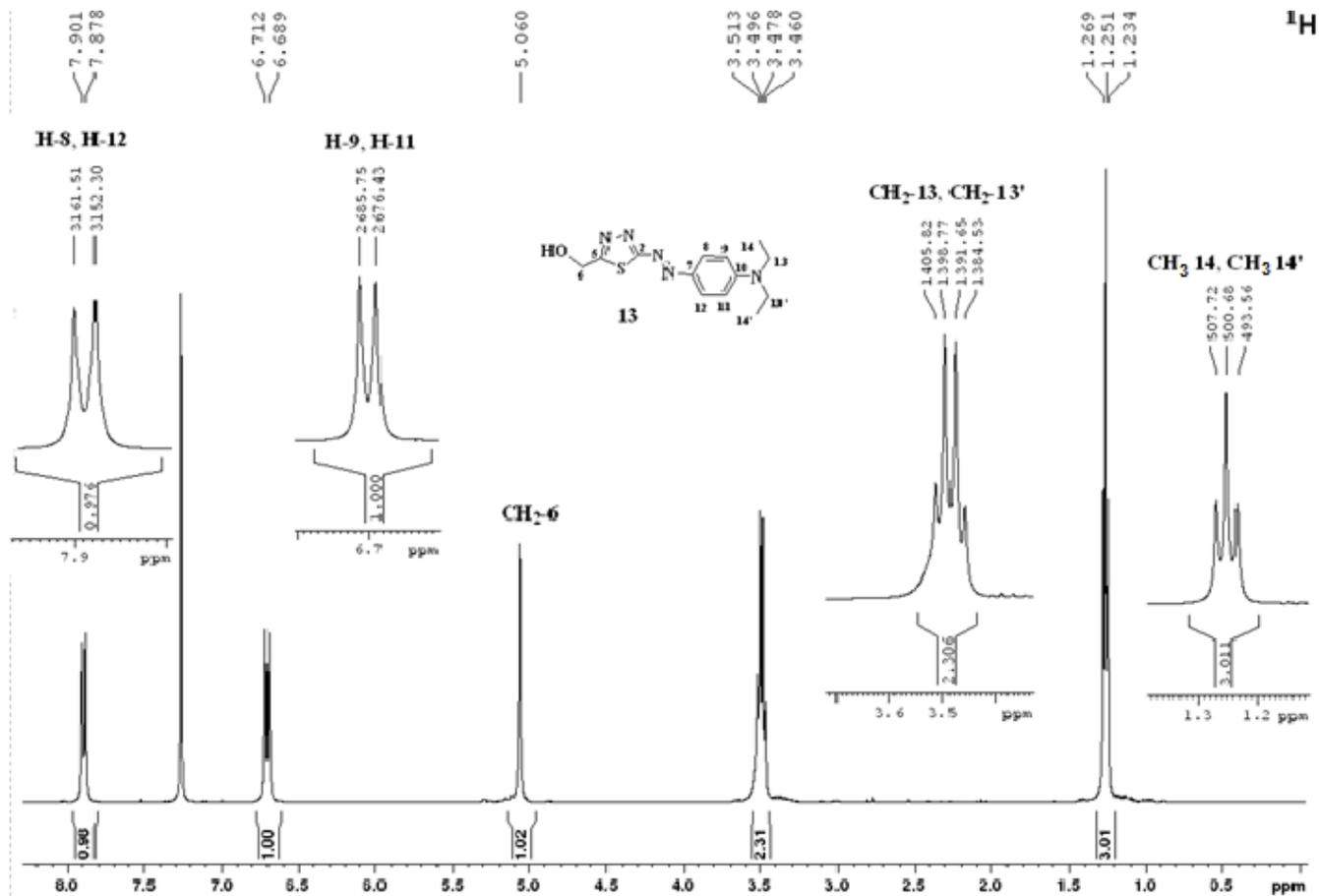


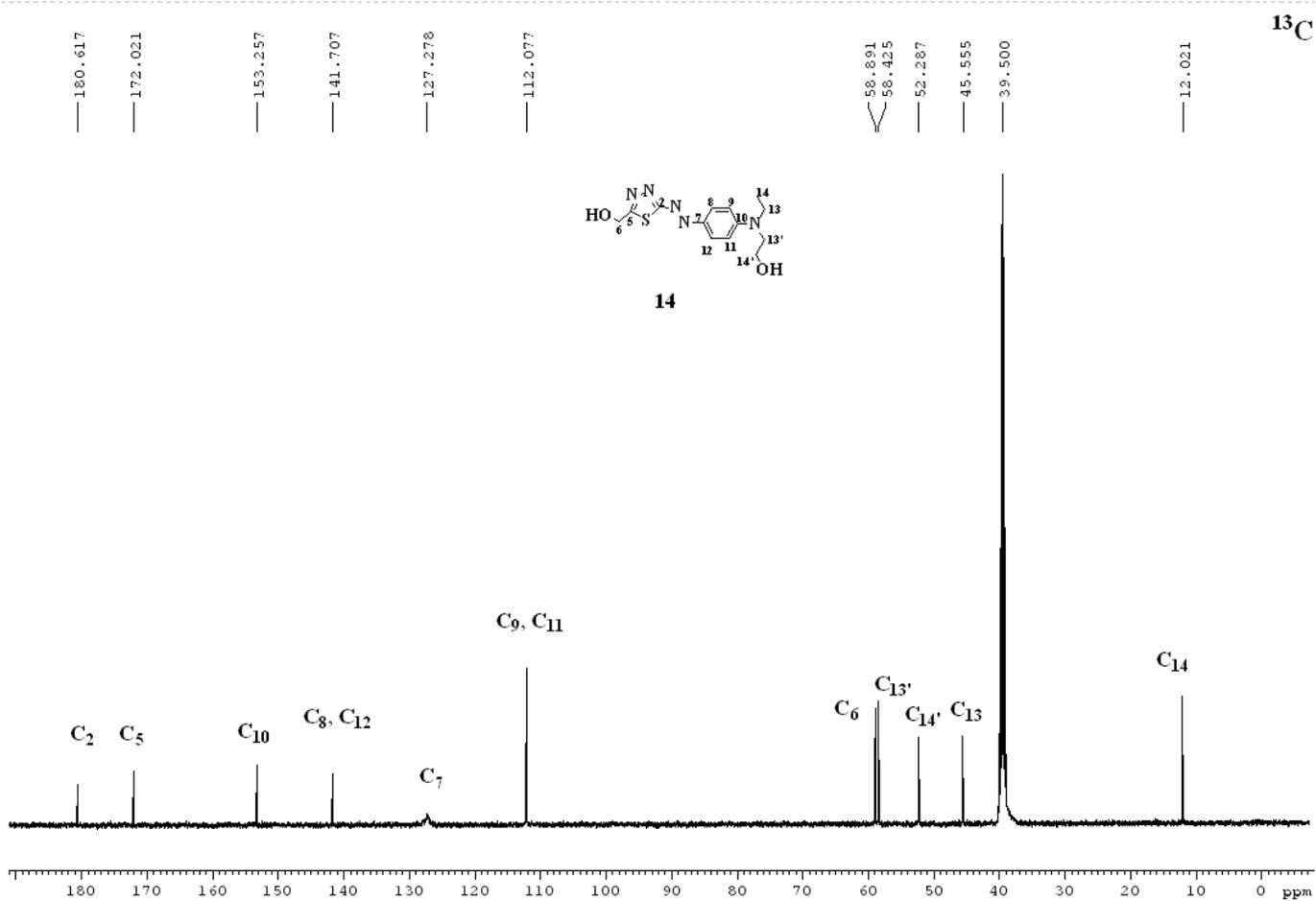
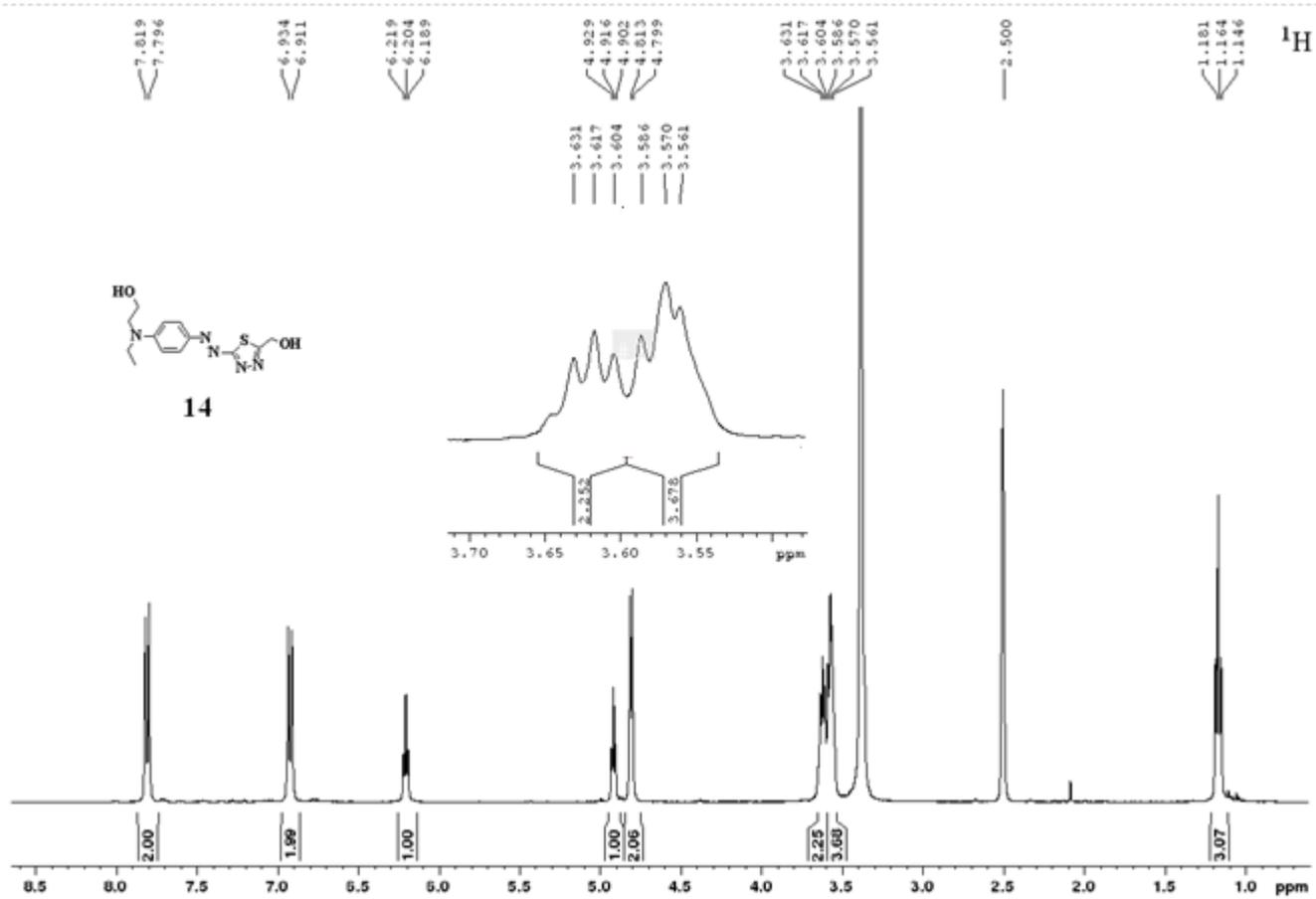


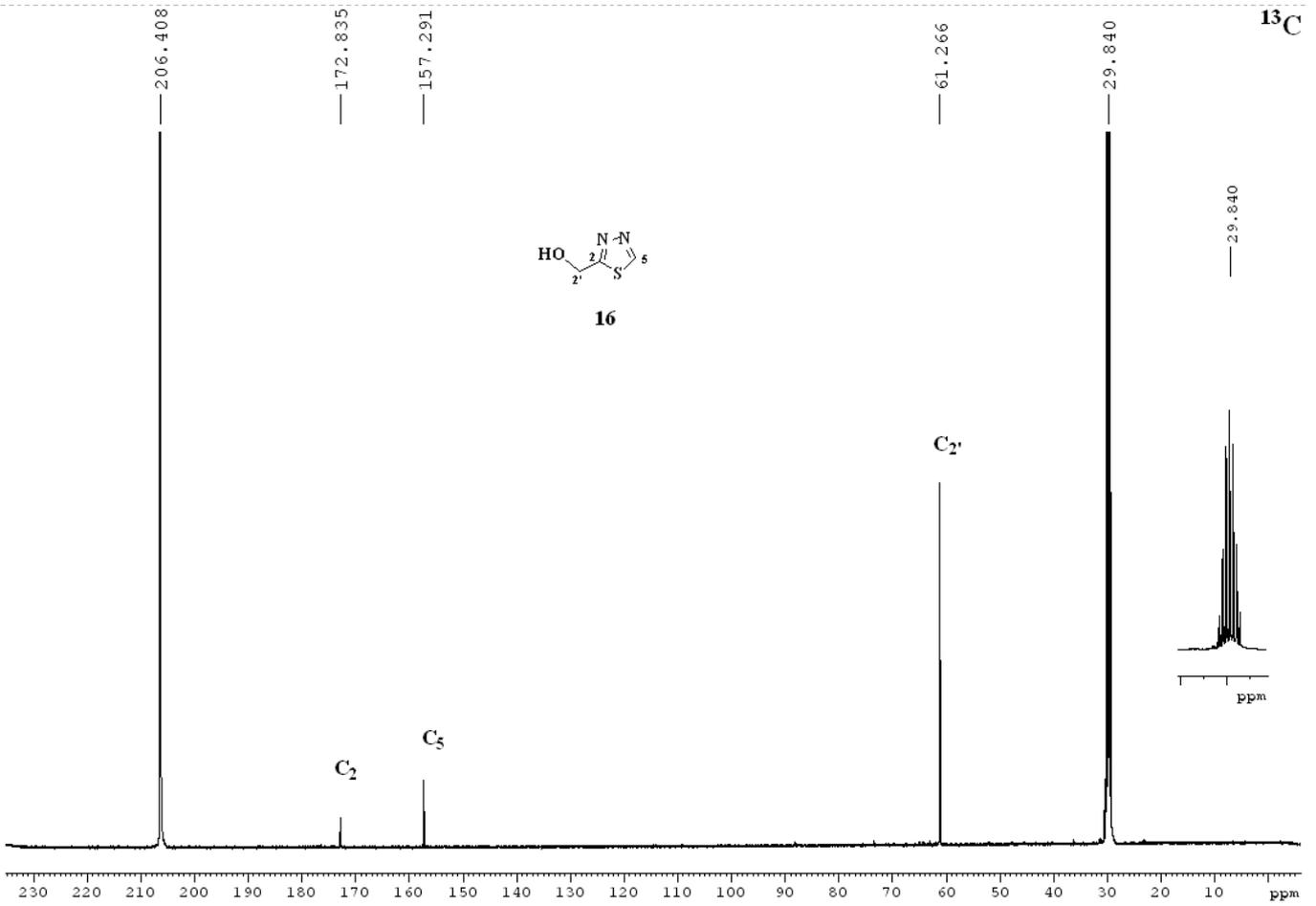
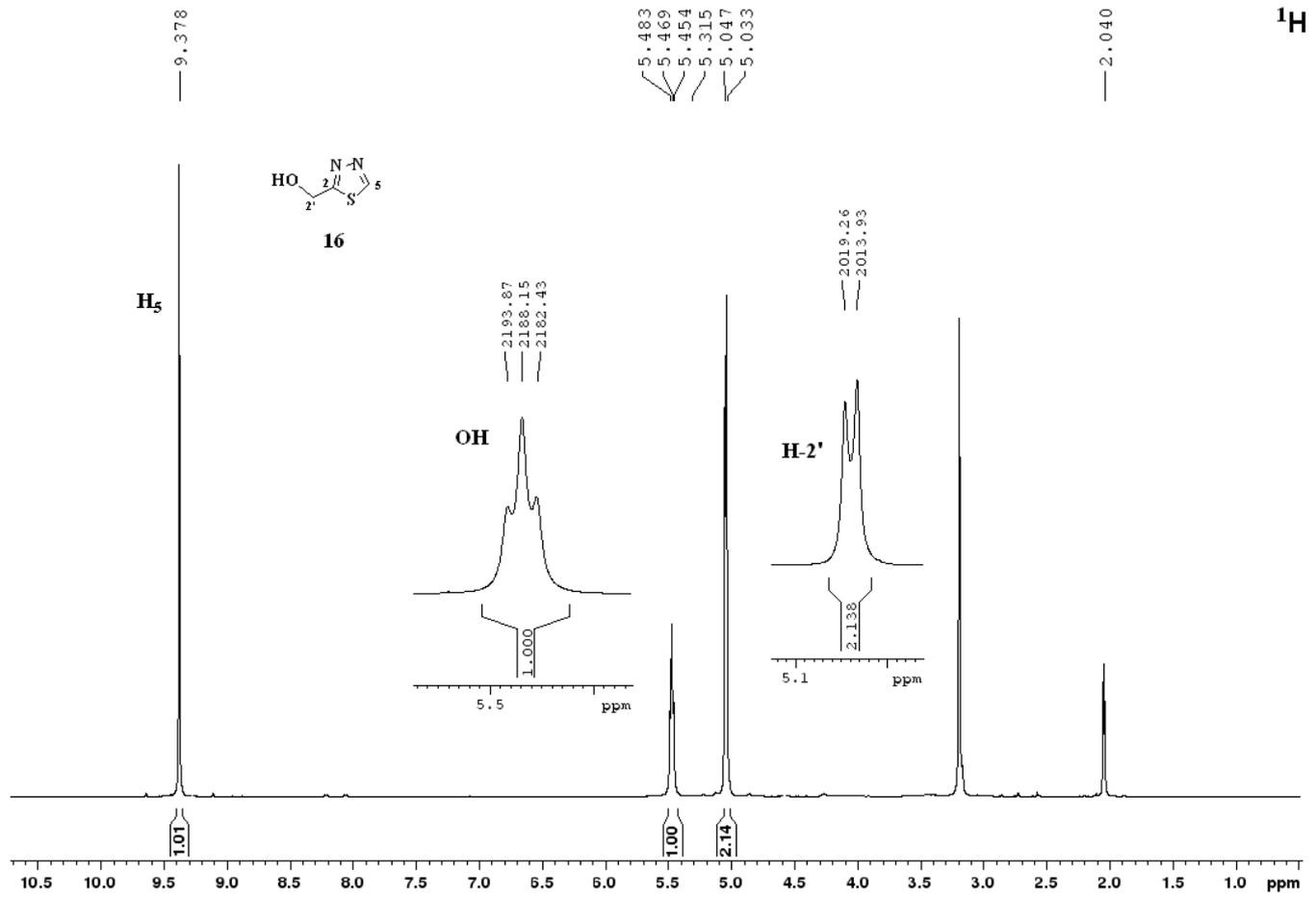


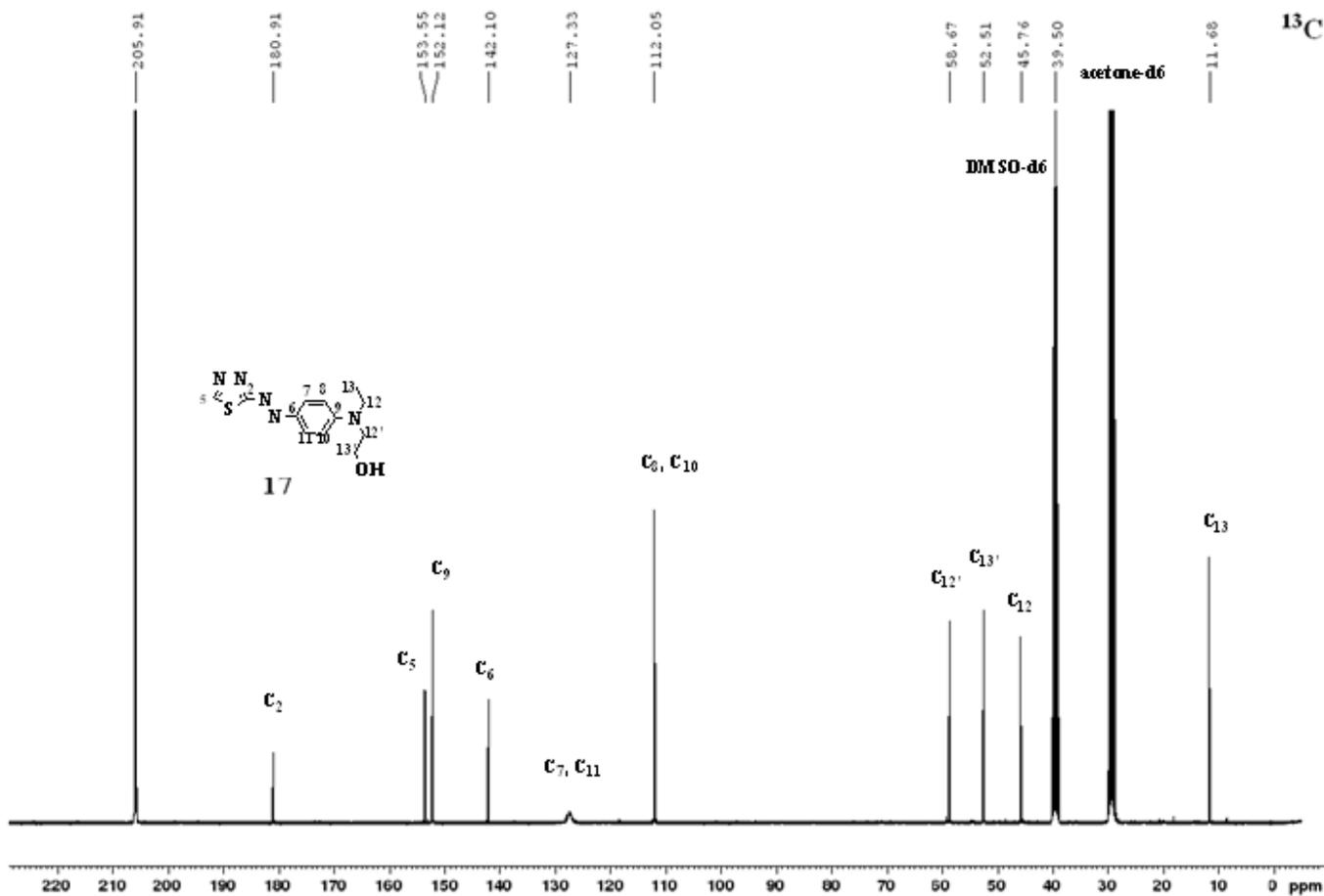
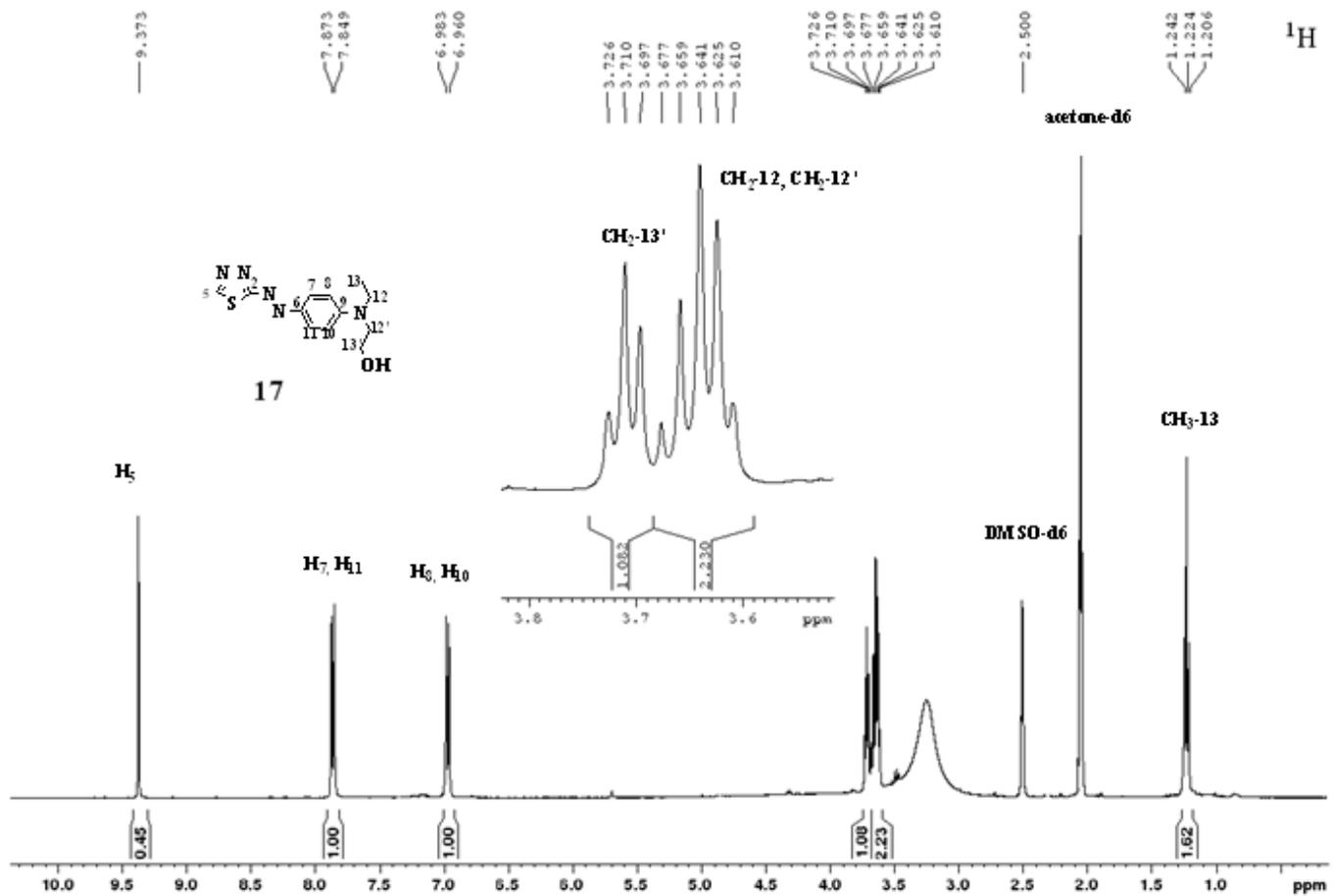


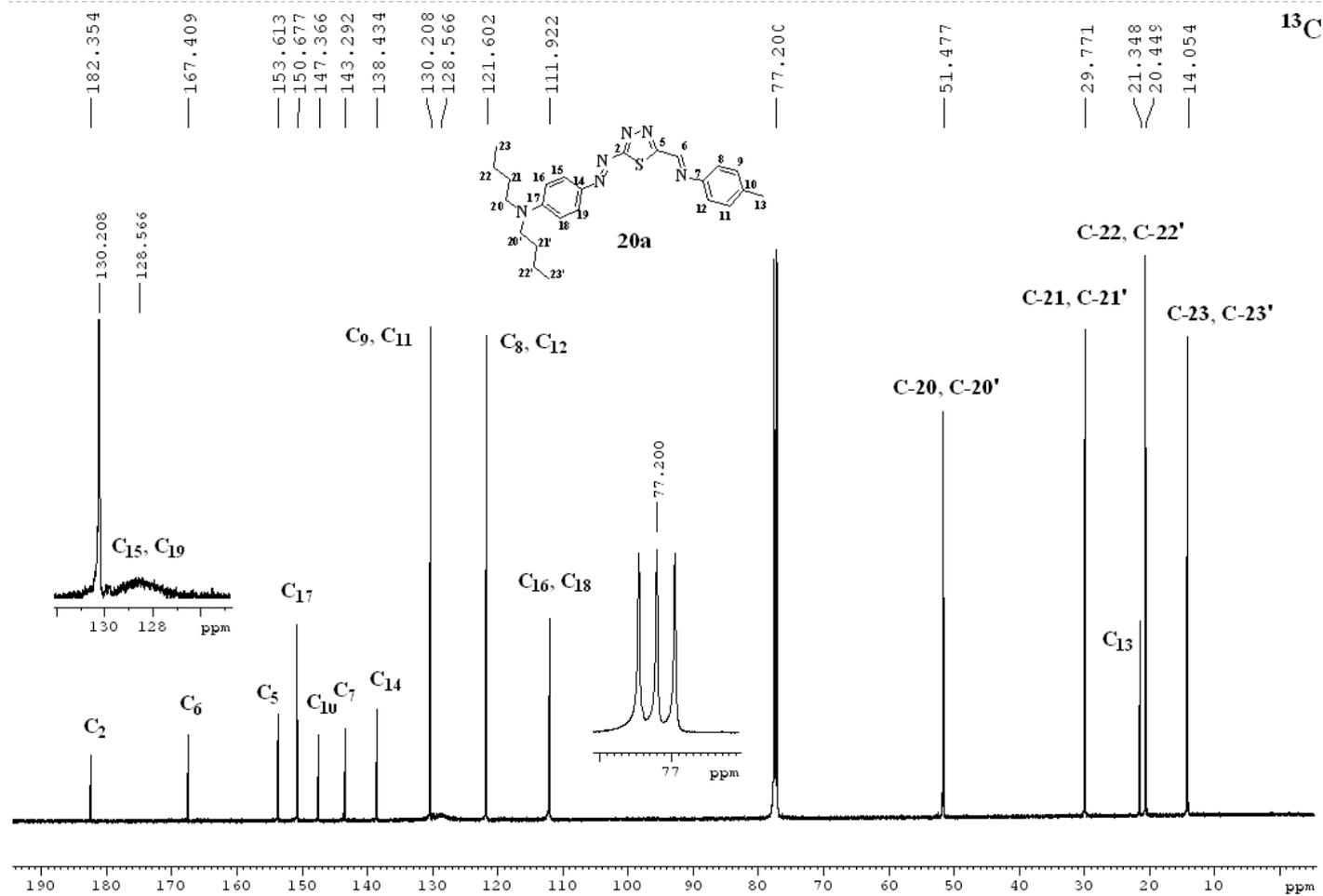
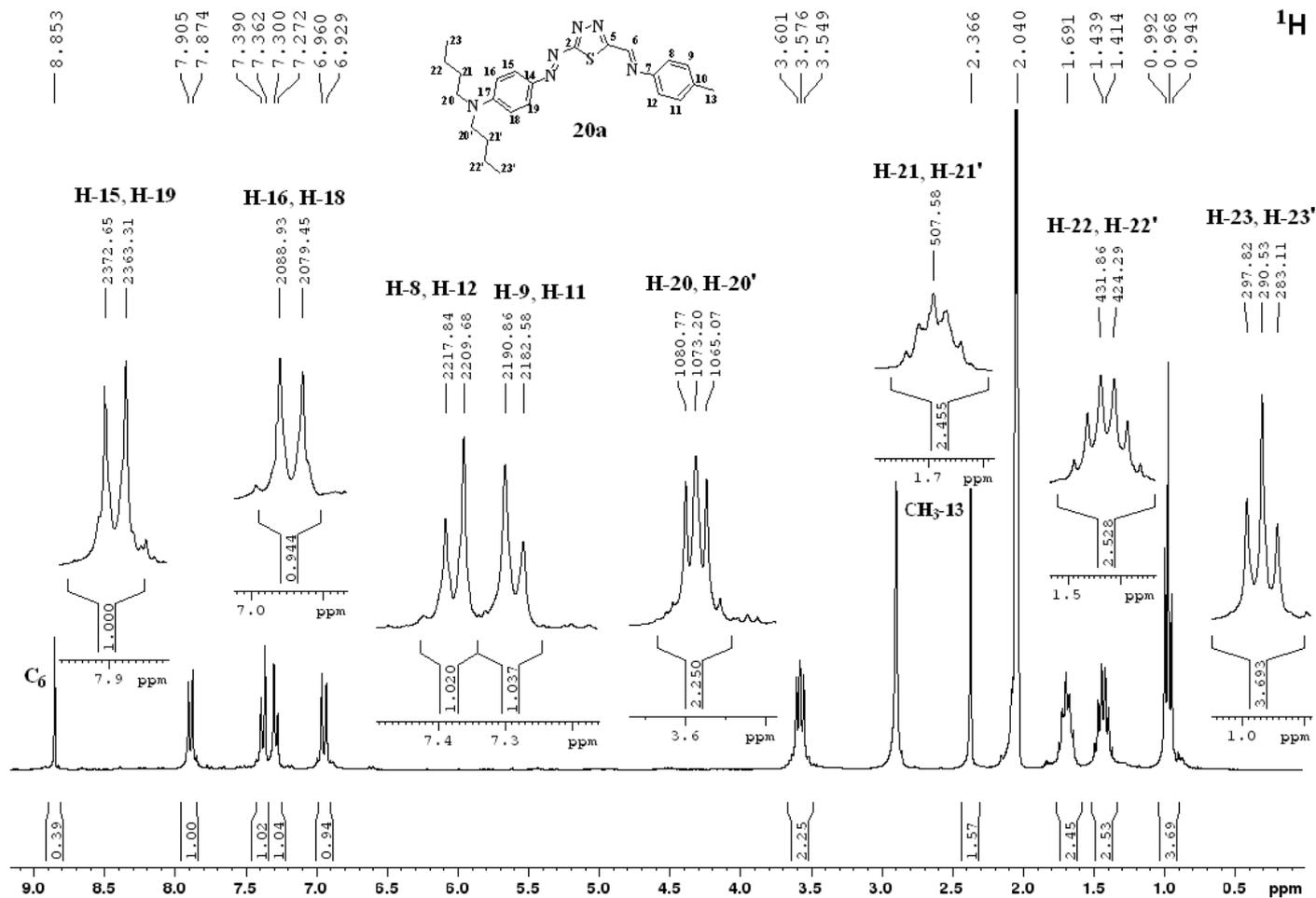


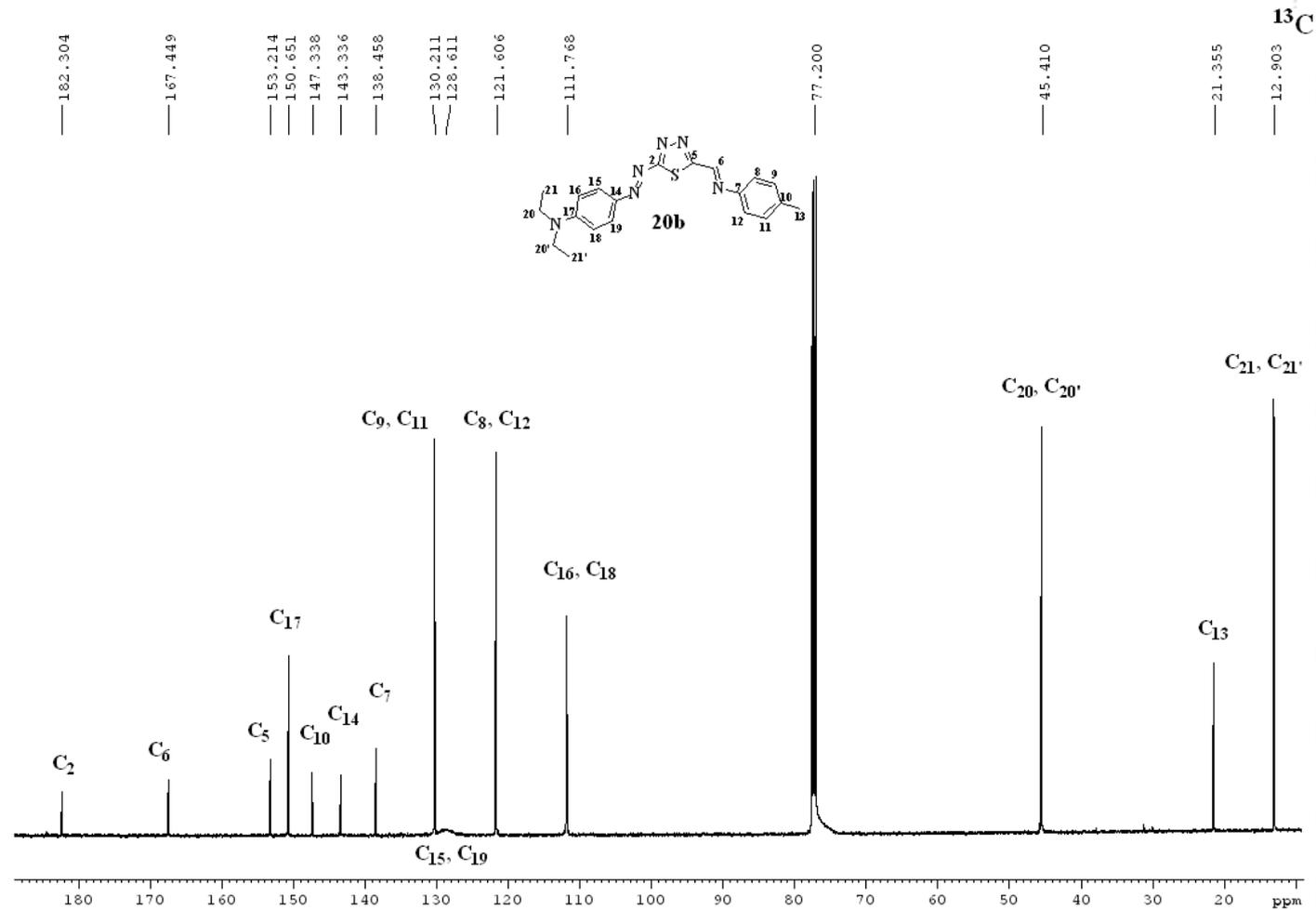
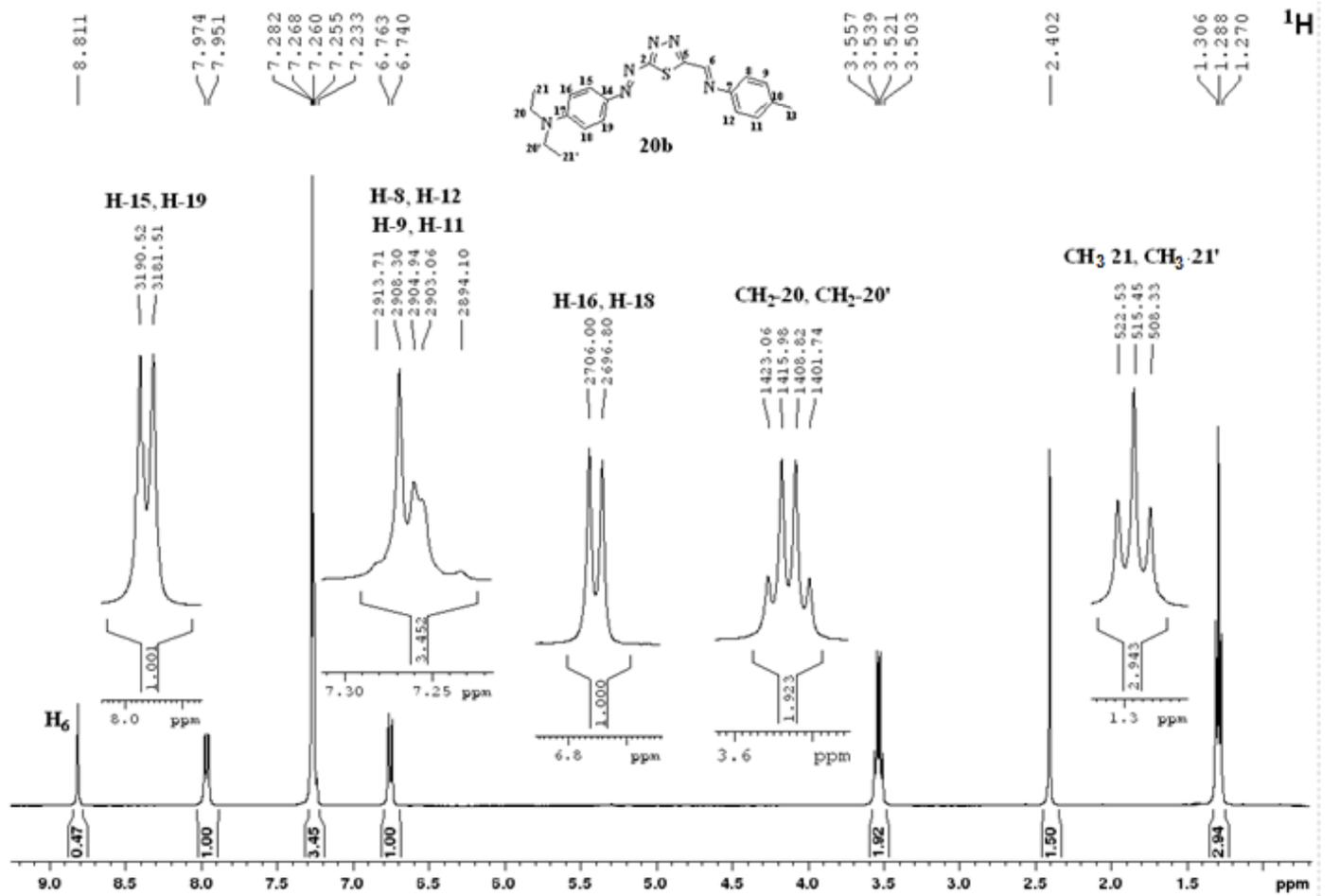


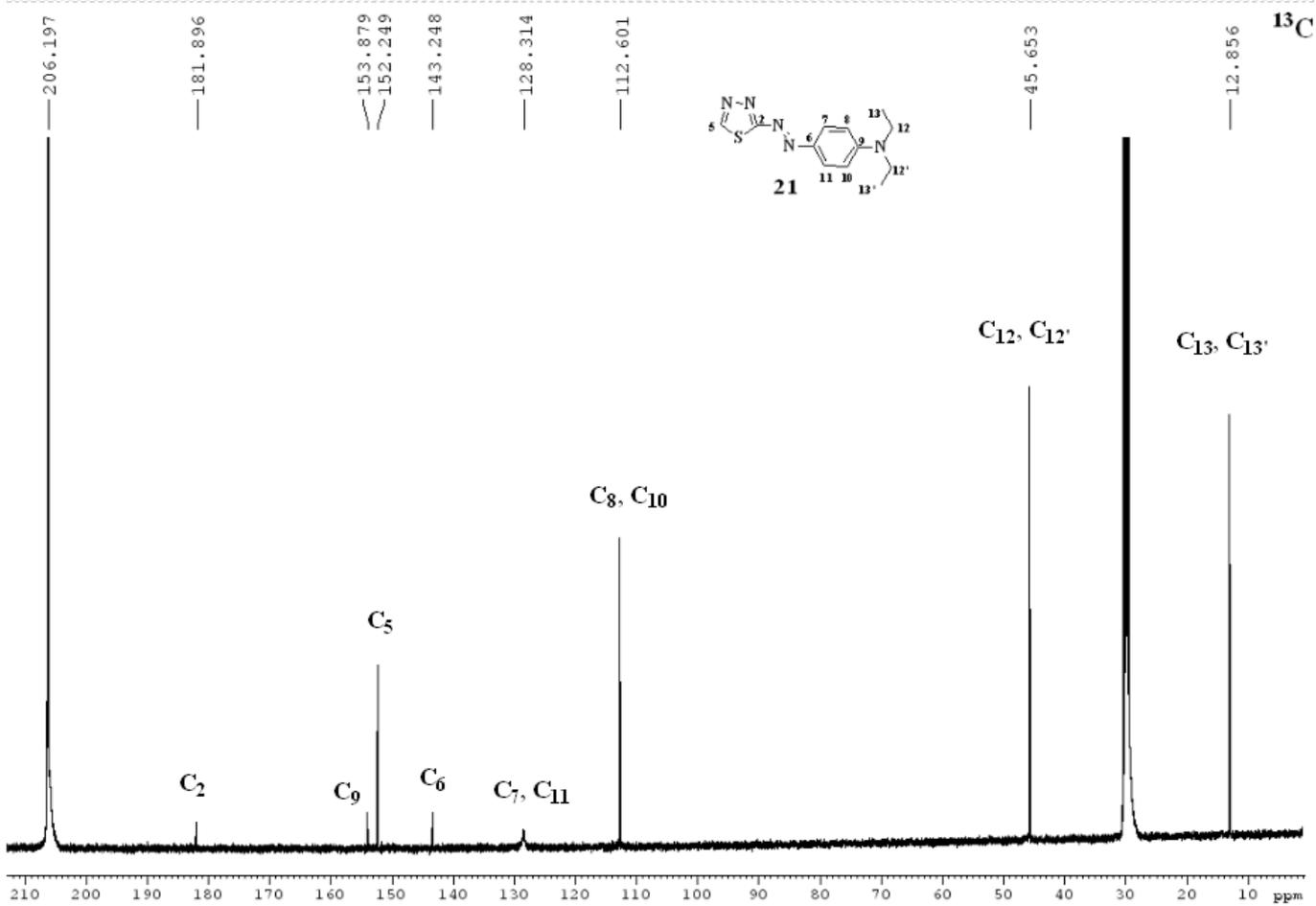
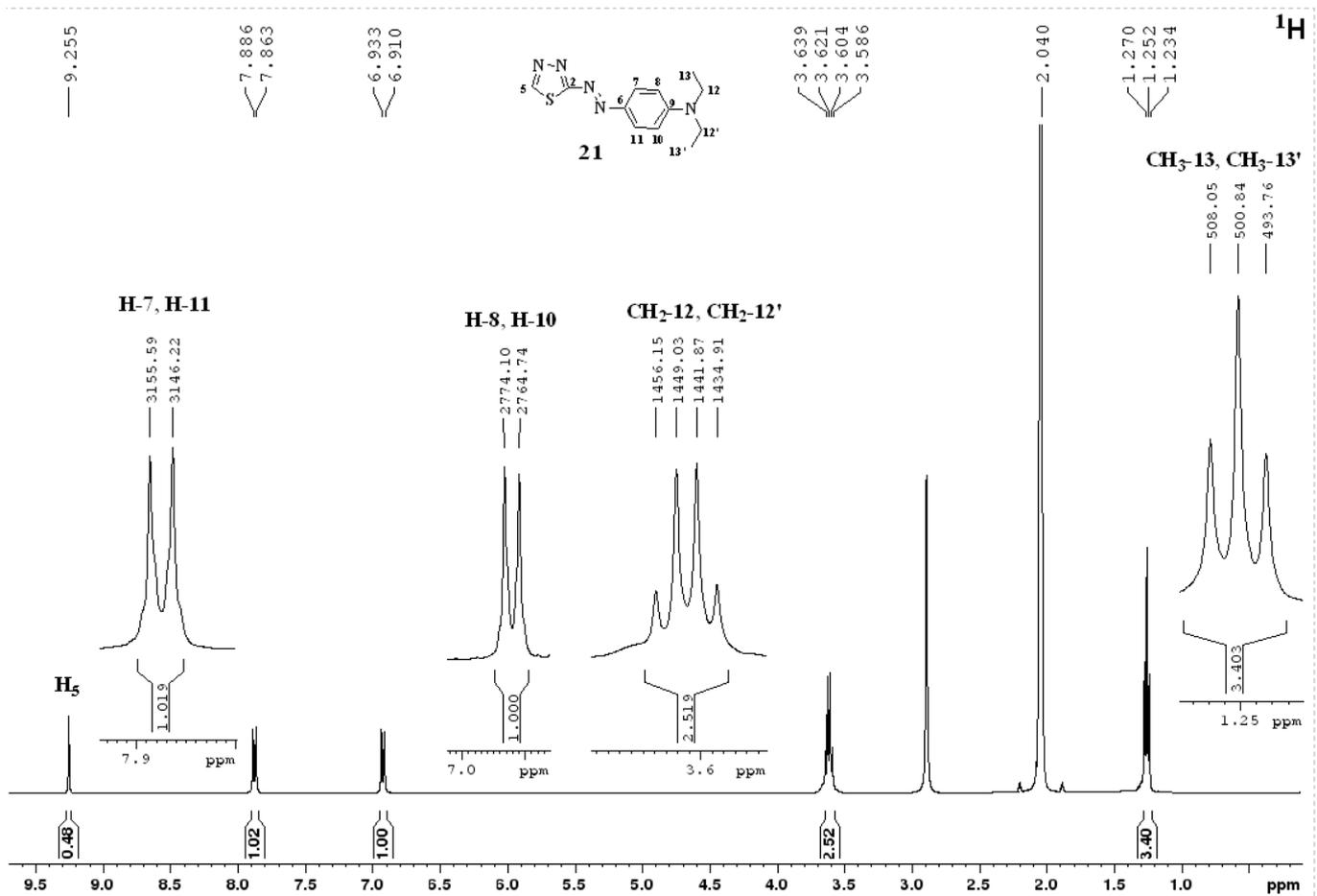


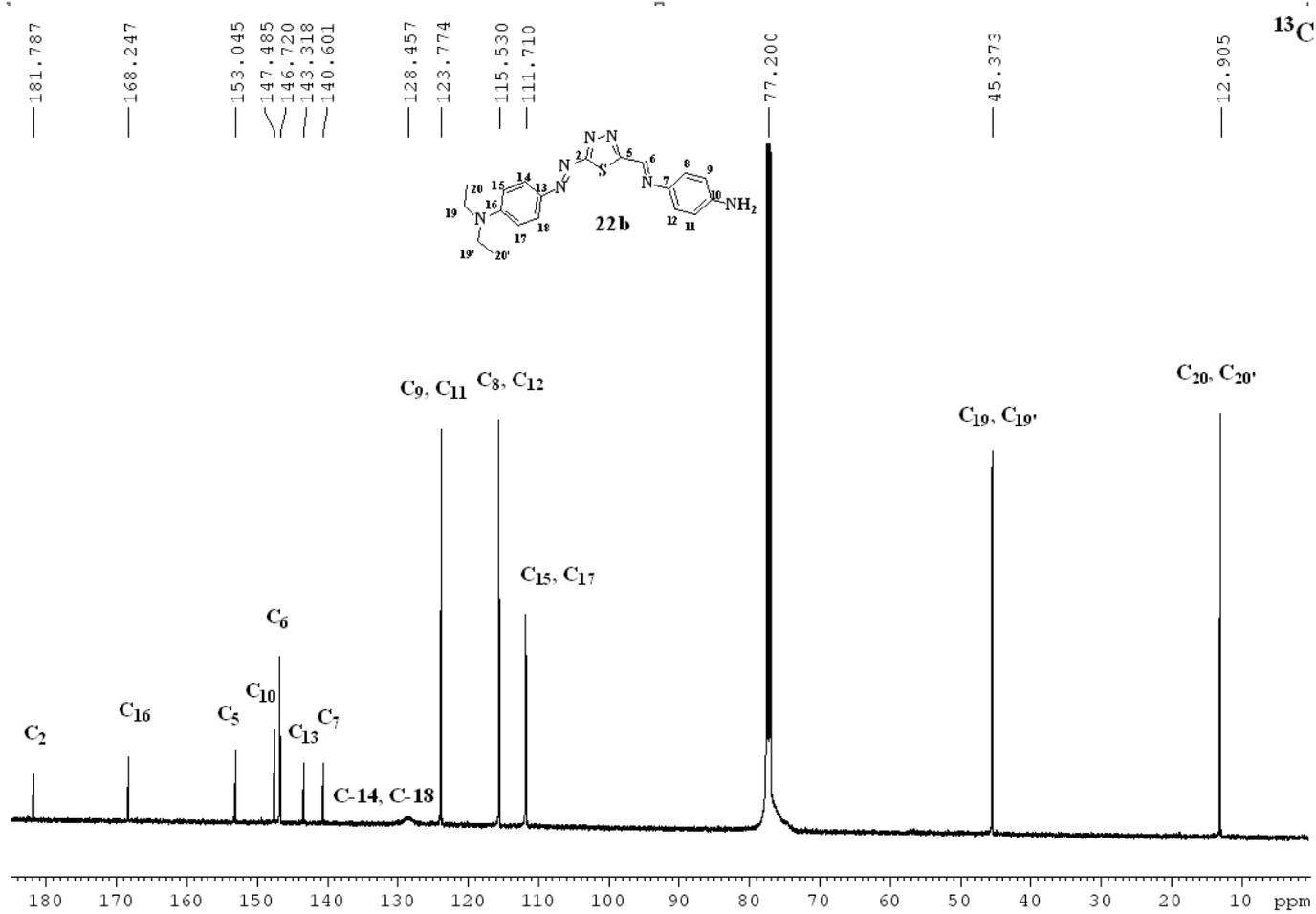
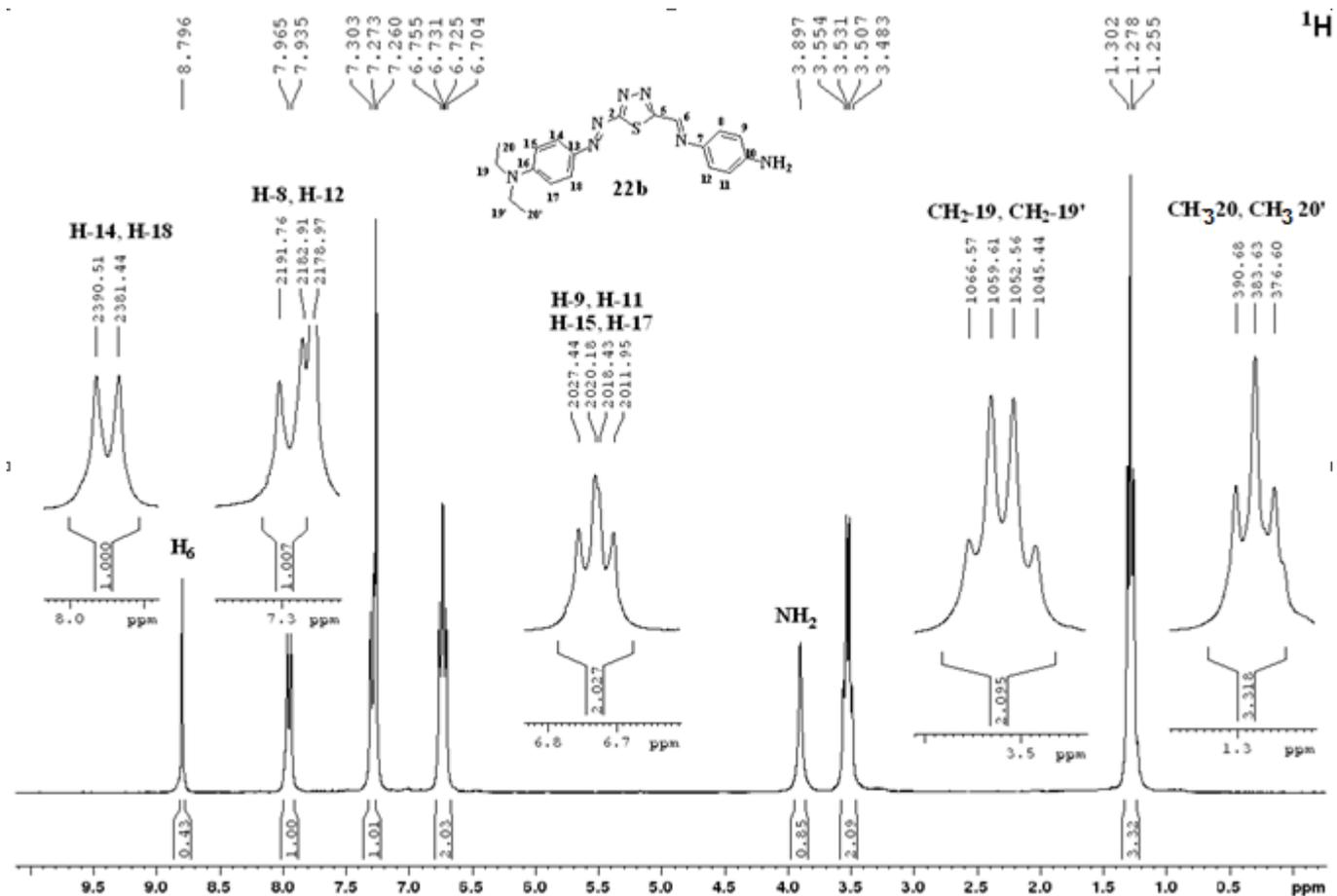


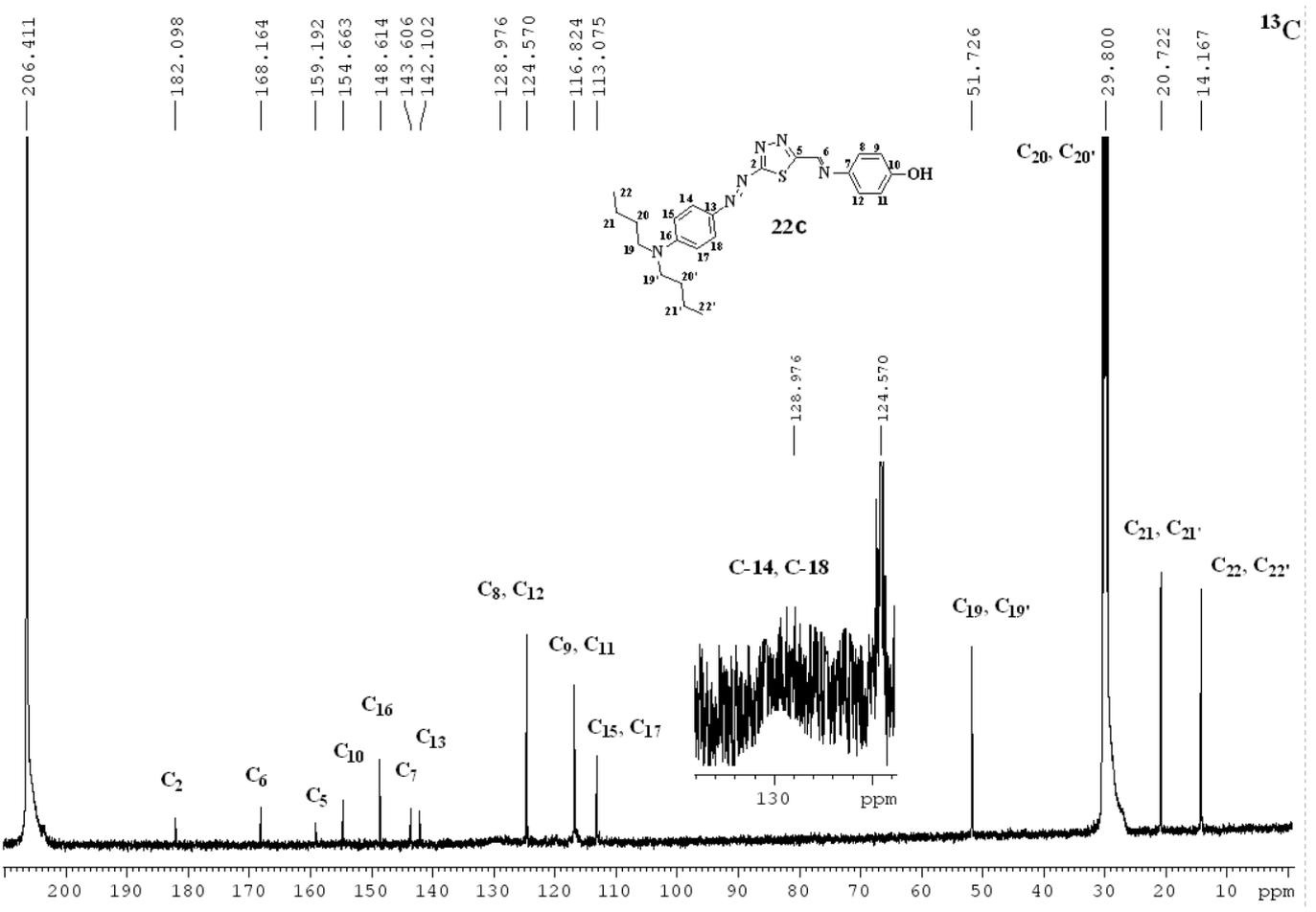
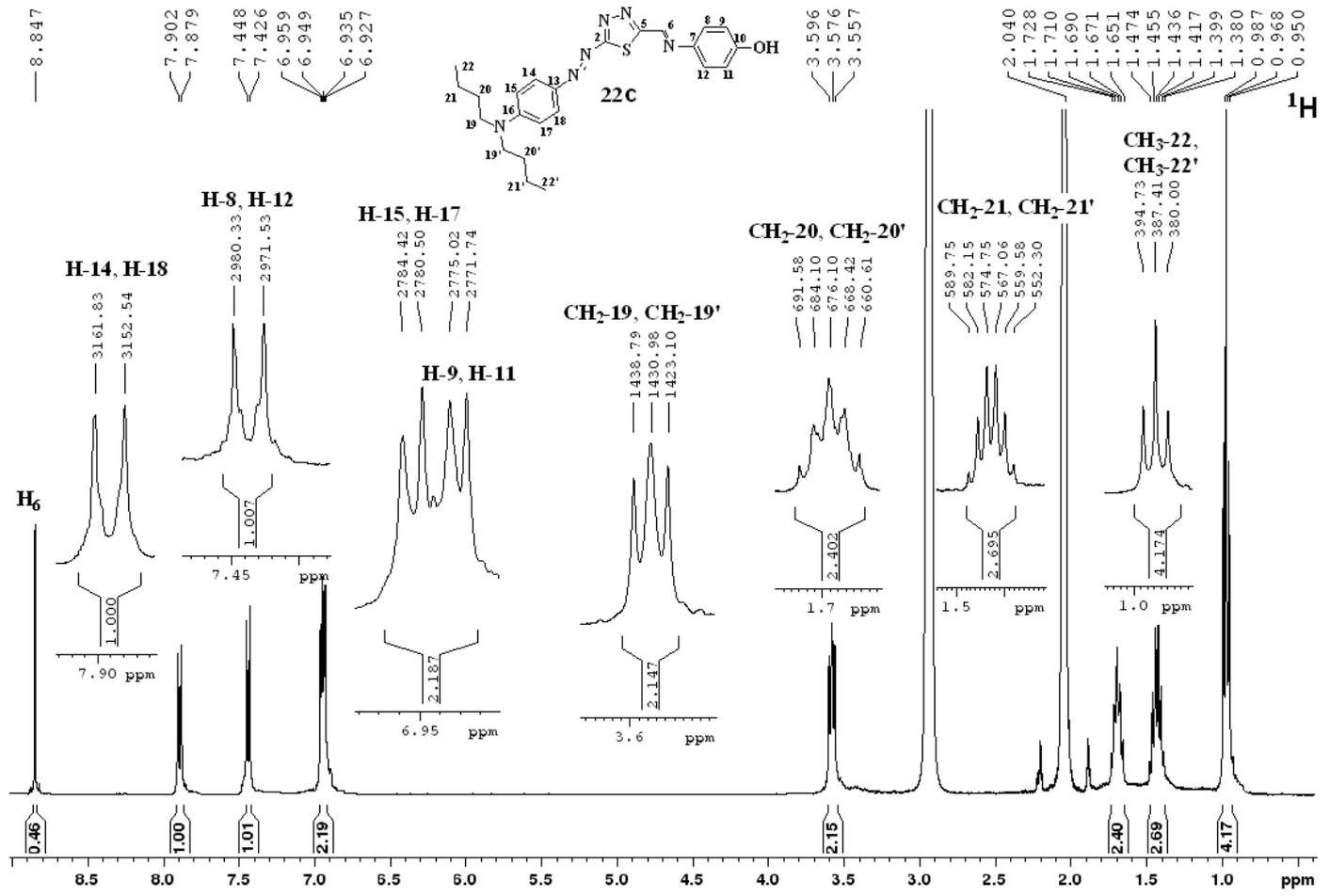


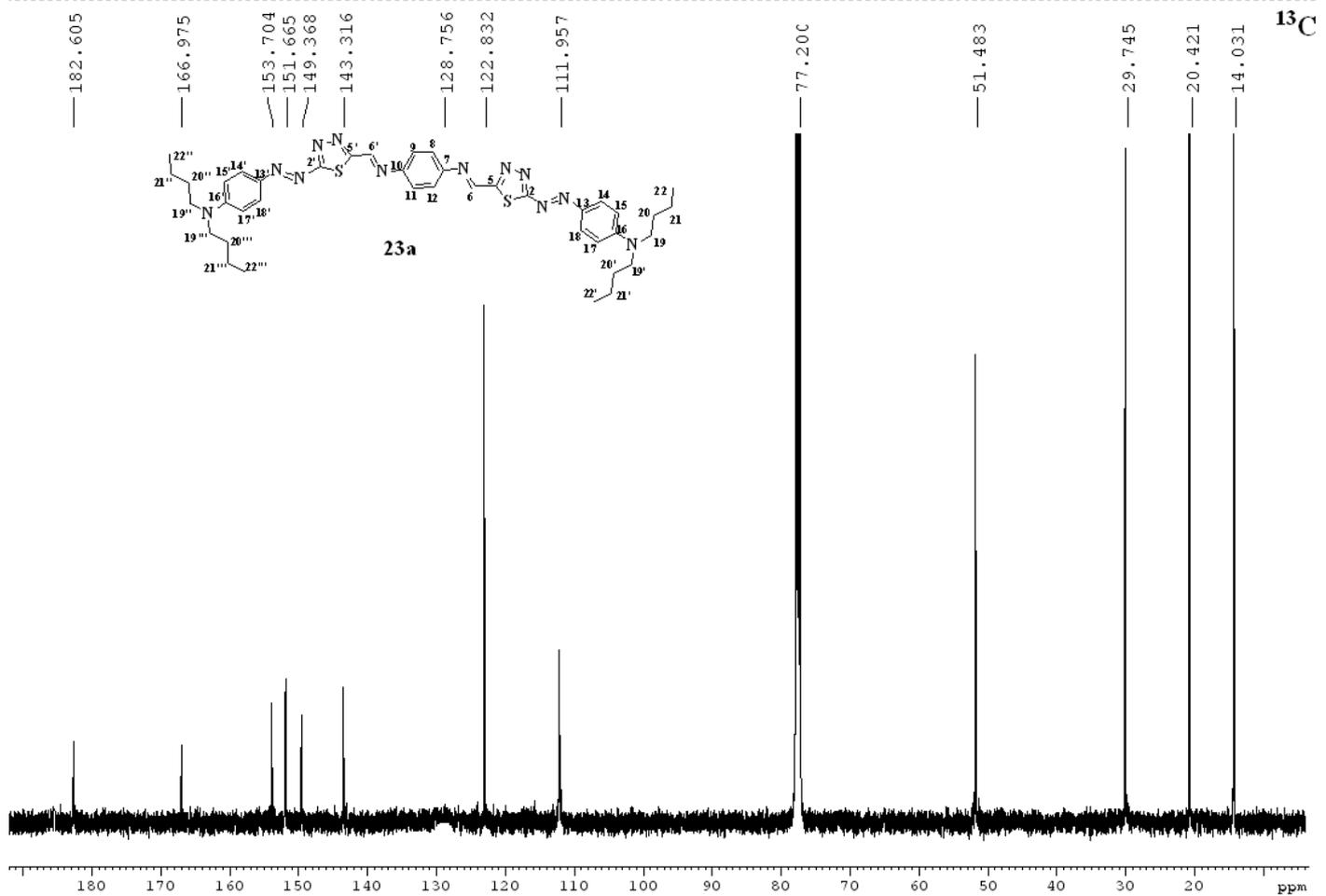
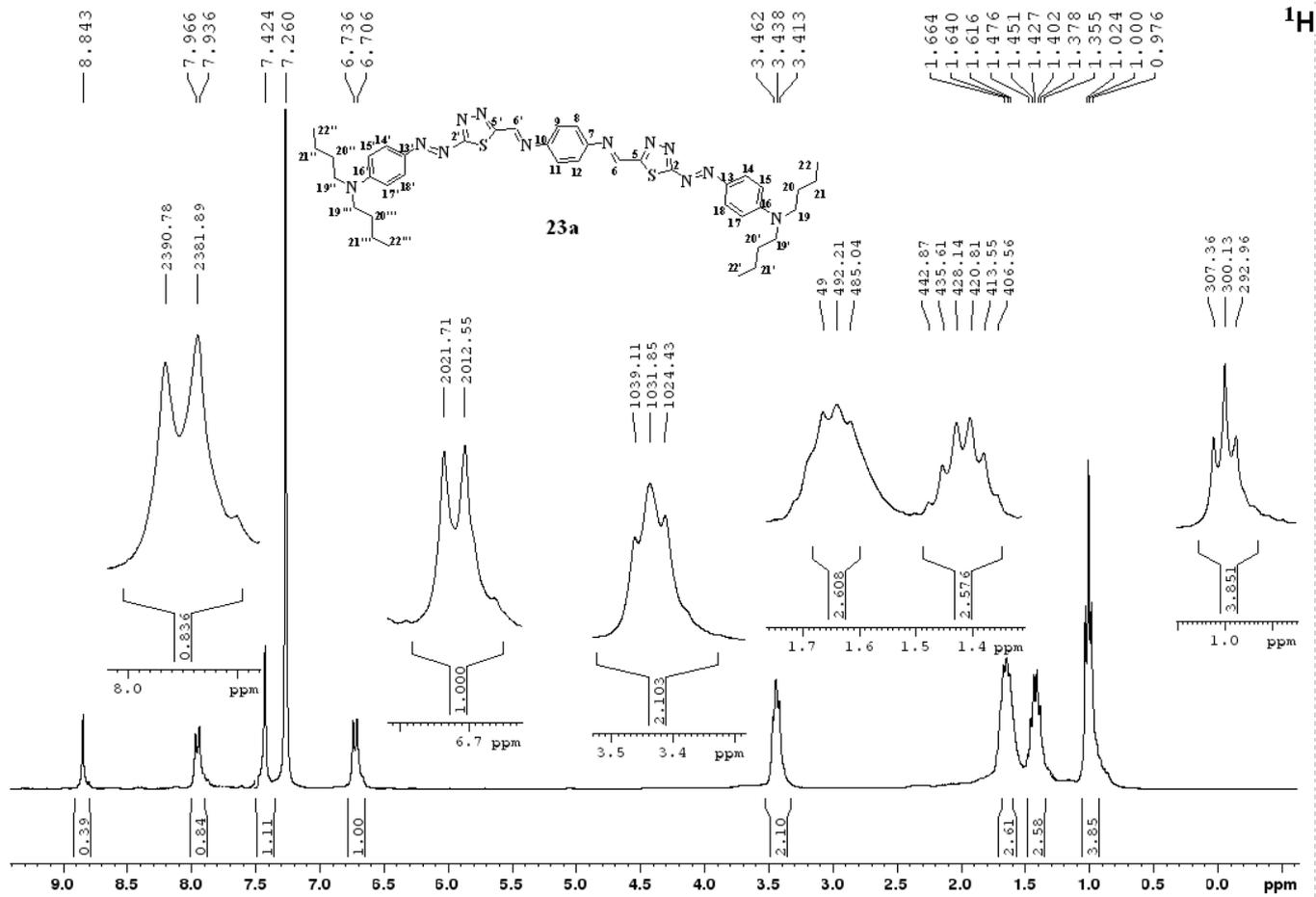


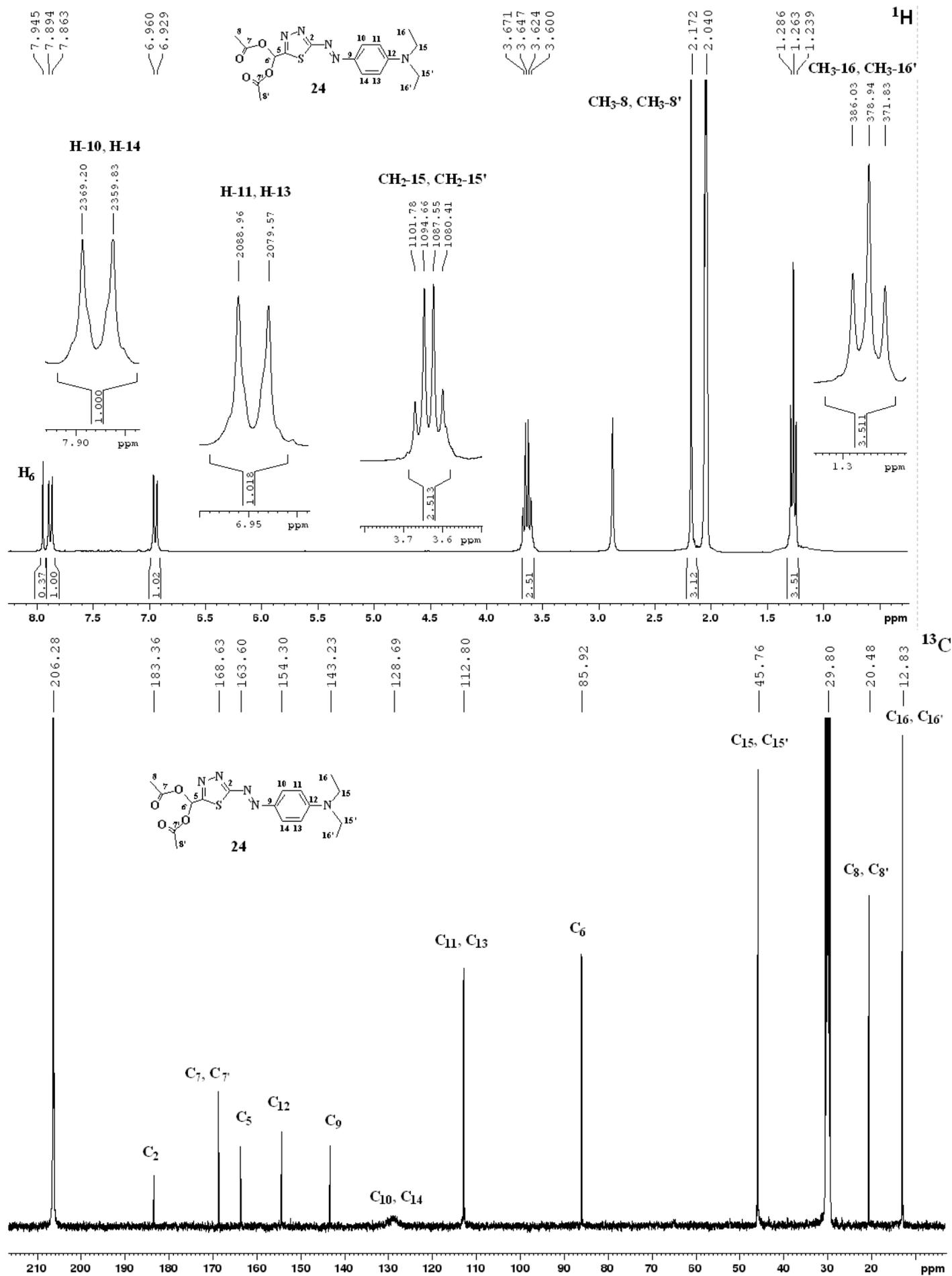












Crystal Packing of azo compounds

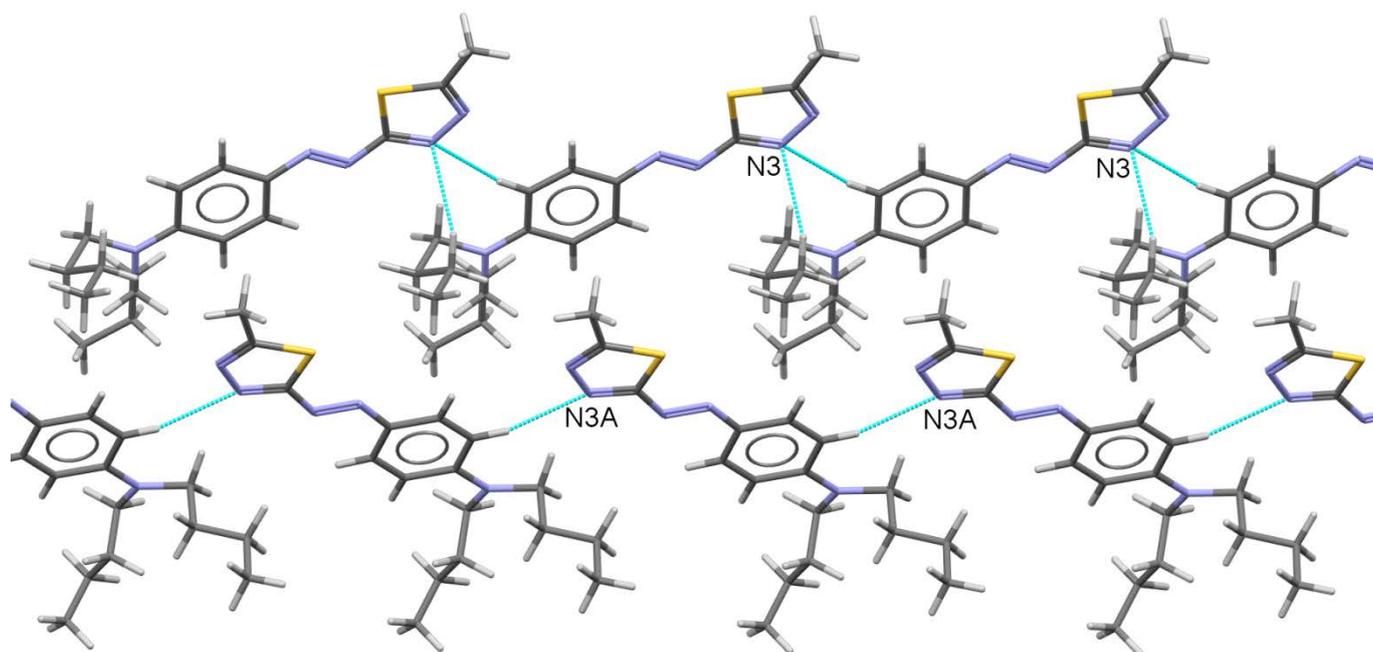


Fig. S1 Crystal packing of dye 9.

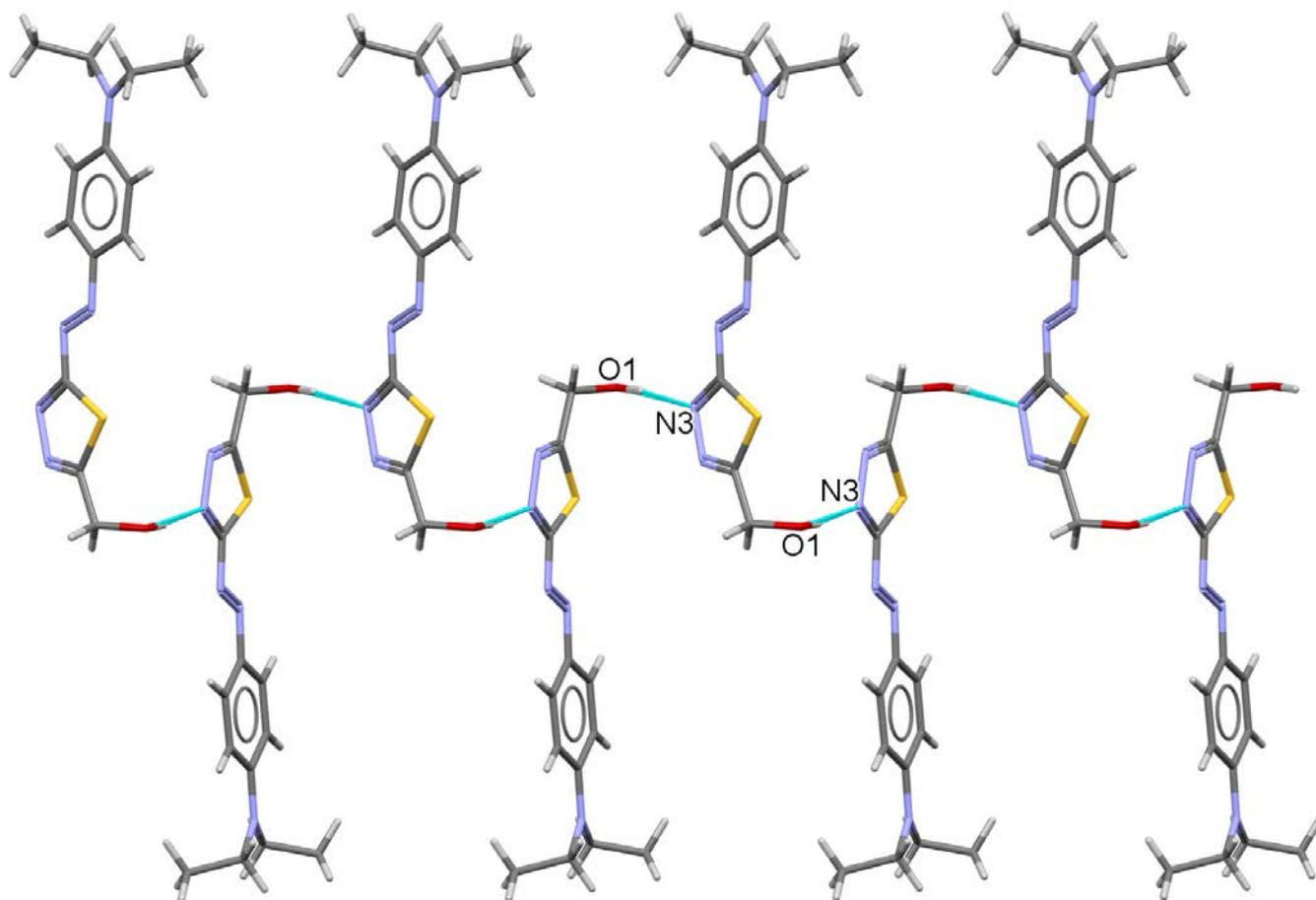


Fig. S2 Crystal packing of azo dye 13.

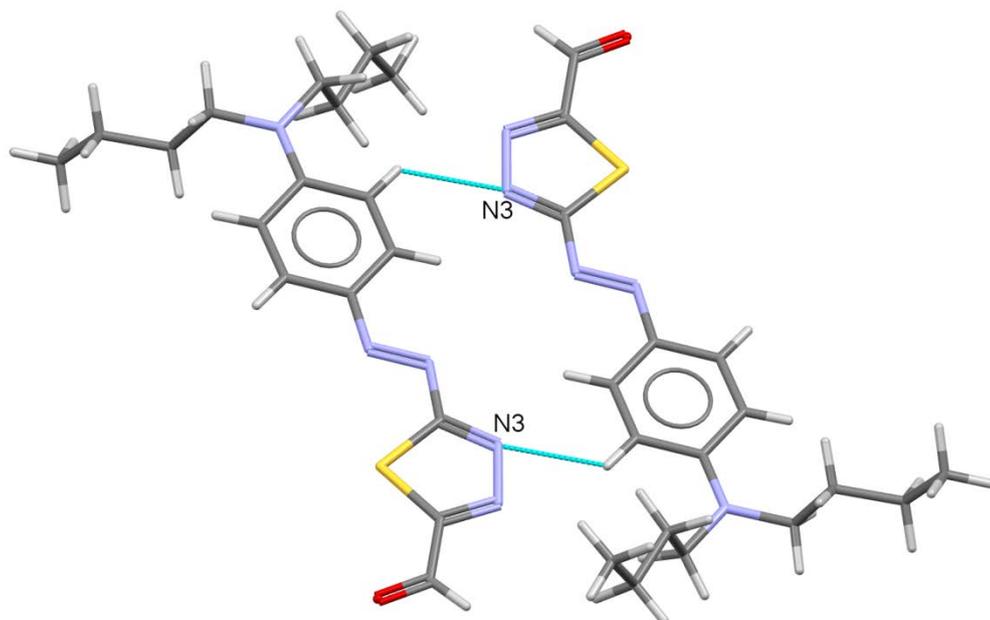


Fig. S3 Crystal packing of azo dye **8a**.

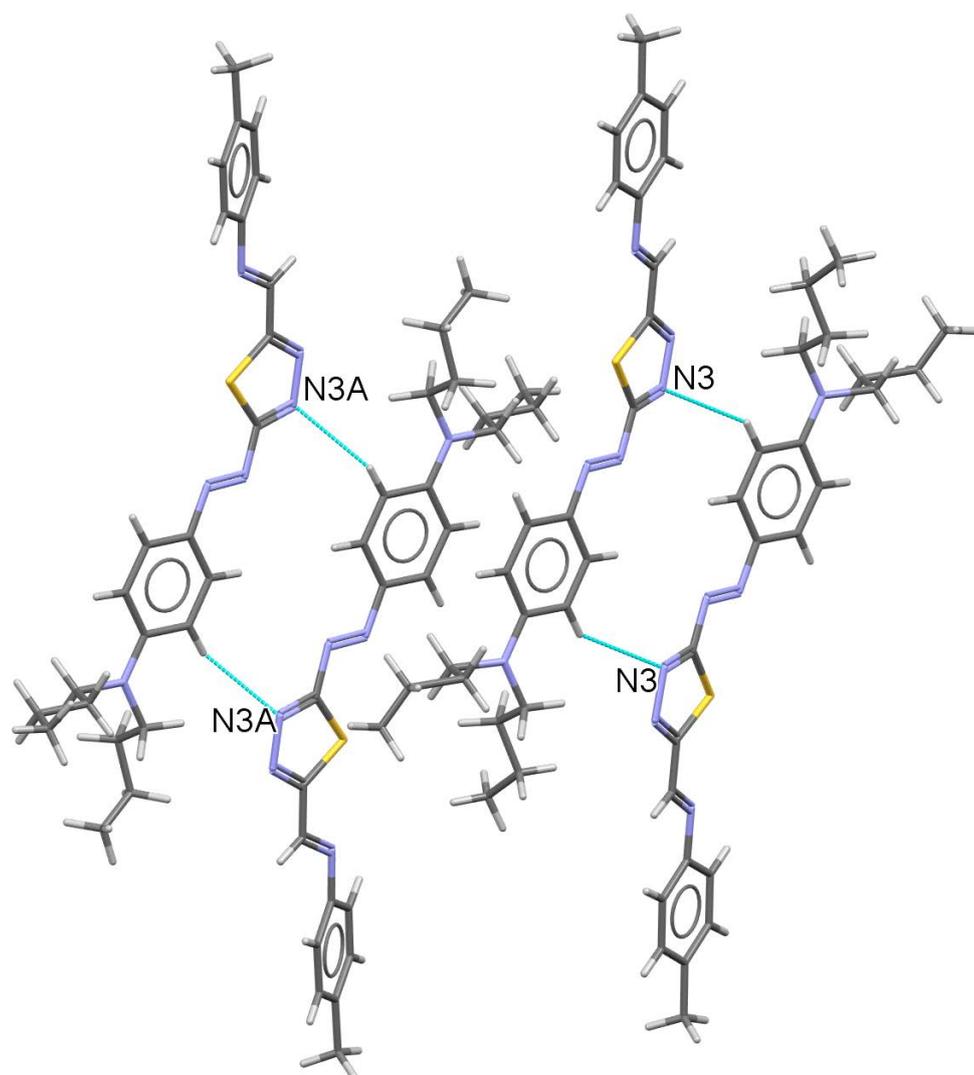


Fig. S3 Crystal packing of azo dye **20a**.

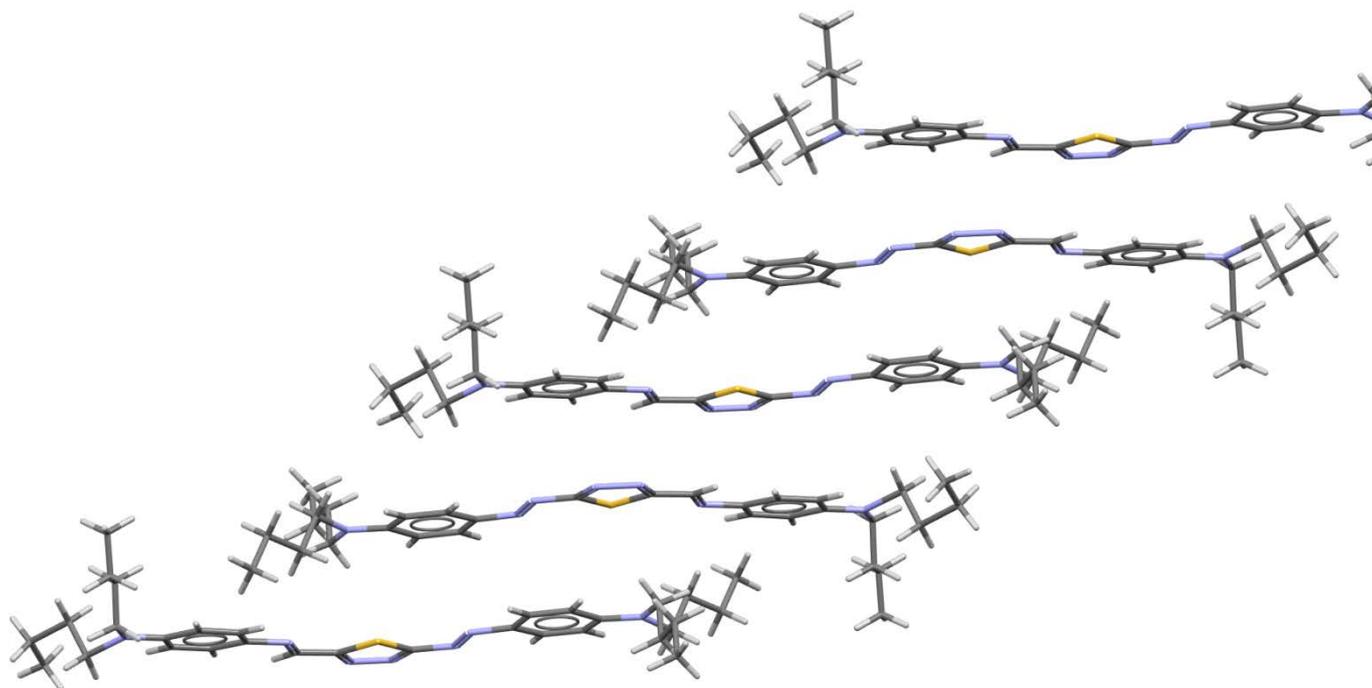


Fig. S5 Crystal packing of azo dye **15**.

Table S2 Crystal data and structure refinement parameters for compounds **9**, **13**, **15**, **20a** and **8a**.

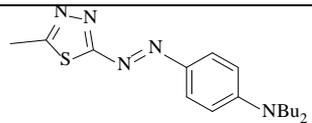
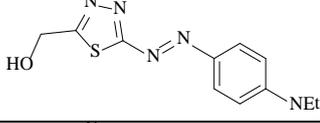
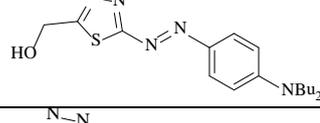
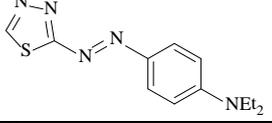
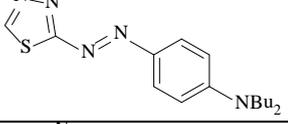
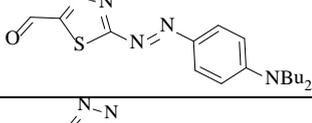
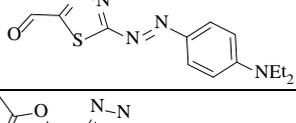
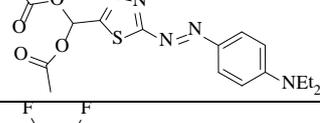
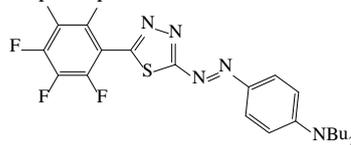
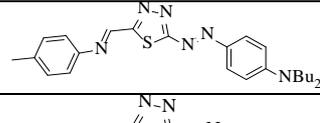
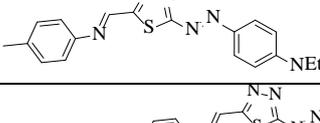
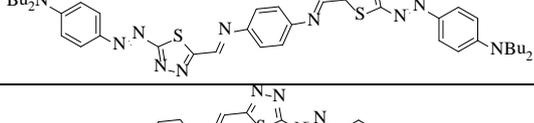
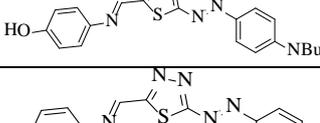
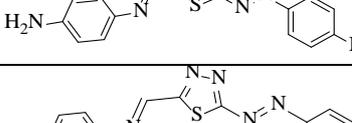
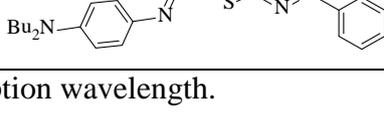
Compound	9	13	15
Empirical formula	C ₁₇ H ₂₅ N ₅ S	C ₁₃ H ₁₇ N ₅ OS	C ₃₁ H ₄₅ N ₇ S
Formula weight	331.48	291.38	547.80
Temperature K	200(2)	296(2)	296(2)
Wavelength Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	P-1	P2 ₁ 2 ₁ 2 ₁	P-1
Unit cell dimensions <i>a</i> Å	9.7724(6)	8.4561(2)	11.733(1)
<i>b</i> Å	14.406(1)	11.1718(3)	11.859(1)
<i>c</i> Å	14.710(1)	15.7263(5)	13.270(1)
α °	60.822(2)	90	107.133(4)
β °	88.336(2)	90	109.880(4)
γ °	84.707(3)	90	90.921(5)
Volume Å ³	1800.0(2)	1485.66(7)	1645.2(3)
Z	4	4	2
Density (calcd.) Mg.m ⁻³	1.223	1.303	1.106
Abs. coefficient mm ⁻¹	0.187	0.221	0.128
F(000)	712	616	592
Crystal size mm ³	0.06 x 0.4 x 0.9	0.10 x 0.80 x 0.80	0.04 x 0.38 x 0.48
Θ range for data collection °	1.6 – 25.0	2.2 - 29.3	1.7 – 25.0
Index ranges	-11 ≤ <i>h</i> ≤ 11, -17 ≤ <i>k</i> ≤ 17, -17 ≤ <i>l</i> ≤ 17	-11 ≤ <i>h</i> ≤ 11, -15 ≤ <i>k</i> ≤ 13, -20 ≤ <i>l</i> ≤ 21	-13 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 14, -15 ≤ <i>l</i> ≤ 15
Reflections collected	28978	17412	26178
Independent reflections	6362 R(int) = 0.043	3534 R(int) = 0.041	5789 R(int) = 0.056
Completeness to θ %	99.9	99.9	99.9
Data / restraints / parameters	6362 / 24 / 450	3534 / 7 / 186	5789 / 1 / 352
Goodness-of-fit on F^2	1.01	1.03	1.02
Final R indices $I > 2\sigma(I)$	R ₁ = 0.0632, wR ₂ = 0.1397	R ₁ = 0.0499, wR ₂ = 0.1299	R ₁ = 0.0632, wR ₂ = 0.1296
Final R indices (all data)	R ₁ = 0.1014, wR ₂ = 0.1682	R ₁ = 0.0613, wR ₂ = 0.1426	R ₁ = 0.1235, wR ₂ = 0.1585
Largest diff. peak / hole e.Å ⁻³	1.26 / -0.56	0.61 / -0.22	0.27 / -0.18

Table S2 (*continued*)

Compound	20a	8a
Empirical formula	C ₂₄ H ₃₀ N ₆ S	C ₁₇ H ₂₃ N ₅ OS
Formula weight	434.60	345.46
Temperature K	296(2)	200(2)
Wavelength Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 ₁ /c
Unit cell dimensions <i>a</i> Å	12.0068(5)	5.2794(7)
<i>b</i> Å	14.0117(5)	20.596(3)
<i>c</i> Å	14.8143(5)	16.720(2)
α °	80.584(2)	90
β °	83.282(2)	98.645(5)
γ °	89.786(2)	90
Volume Å ³	2441.5(2)	1797.4(4)
Z	4	4
Density (calcd.) Mg.m ⁻³	1.182	1.277
Abs. coefficient mm ⁻¹	0.155	0.194
F(000)	928	736
Crystal size mm ³	0.10 x 0.15 x 0.20	0.06 x 0.15 x 0.40
Θ range for data collection °	2.3 – 25.0	2.3 – 25.1
Index ranges	-14 ≤ <i>h</i> ≤ 14, -16 ≤ <i>k</i> ≤ 16, -17 ≤ <i>l</i> ≤ 17	-6 ≤ <i>h</i> ≤ 5, -24 ≤ <i>k</i> ≤ 24, -19 ≤ <i>l</i> ≤ 19
Reflections collected	40149	15733
Independent reflections	8605 R(int) = 0.048	3068 R(int) = 0.070
Completeness to θ %	99.8	96.2
Data / restraints / parameters	8605 / 1 / 582	3068 / 0 / 217
Goodness-of-fit on F^2	1.05	1.01
Final R indices $I > 2\sigma(I)$	R ₁ = 0.0588, wR ₂ = 0.1304	R ₁ = 0.0507, wR ₂ = 0.1036
Final R indices (all data)	R ₁ = 0.0965, wR ₂ = 0.1581	R ₁ = 0.1085, wR ₂ = 0.1291
Largest diff. peak / hole e.Å ⁻³	0.36, -0.23	0.28, -0.20

UV-Vis spectra of azo compounds

Table S3 UV-Vis data for dyes **8-13, 15, 20a, 20b, 21, 22b, 22c, 23a** and **24** in EtOH

No	Structure	λ_{\max} , nm	lg ϵ
9		502.6	4.56
13		502.6	5.60
10		503.3	4.63
21		503.3	5.63
11		504.0	5.61
8a		506.1	5.64
8b		506.6	5.64
24		516.7	5.57
12		532	1.68
20a		548.1	5.71
20b		548.4	5.71
23a		548.7	5.72
22c		549.2	5.52
22b		554.7	5.64
15		570.4	5.78

λ_{\max} : maximum absorption wavelength.

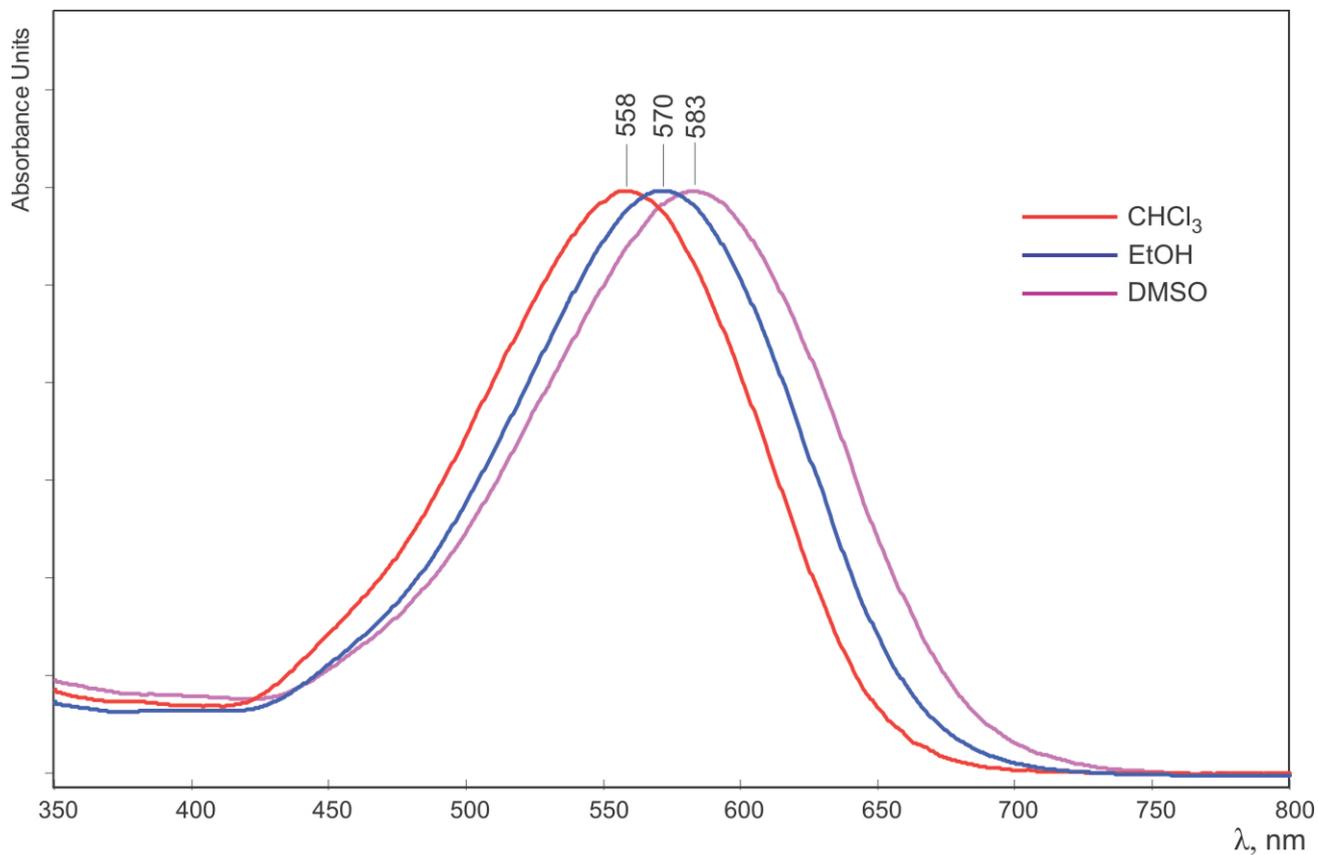


Fig. S6. Normalized absorption spectra of dye **15** in the visible region in various solvents.

TGA and DSC measurements for dyes

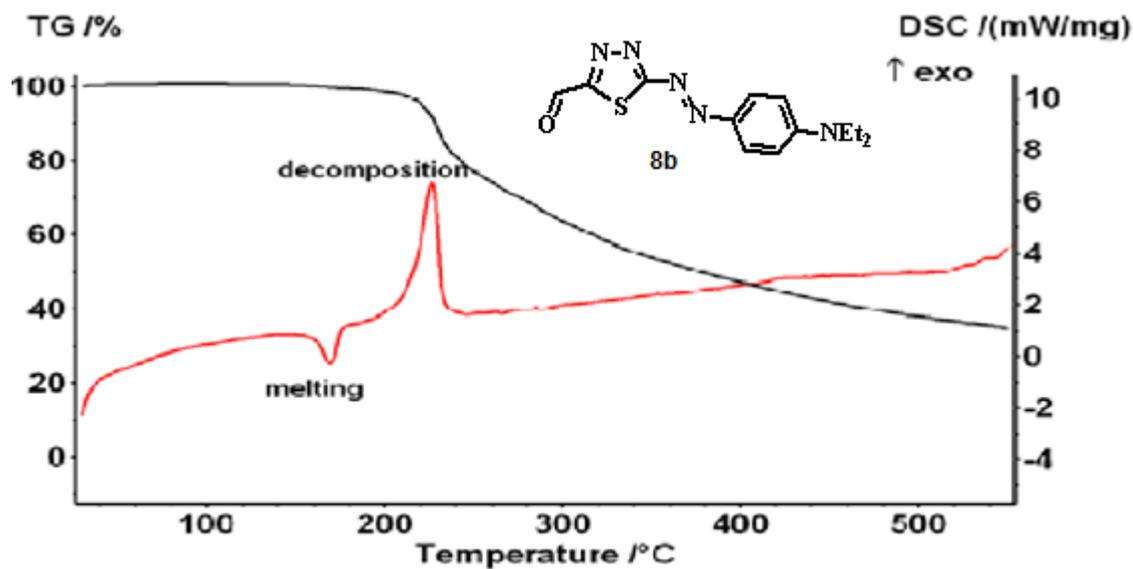


Fig. S7 TGA (____) and DSC (____) curves for dye **8b** (10 $^{\circ}\text{C}/\text{min}$)

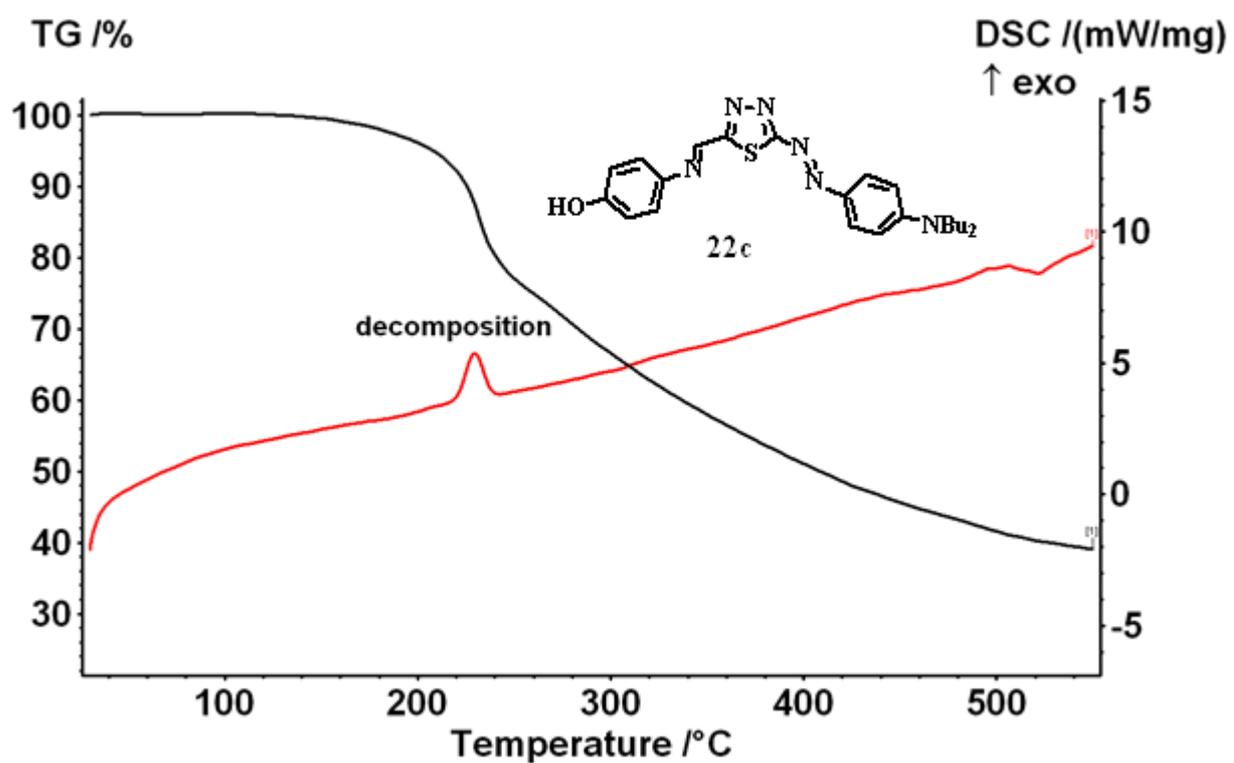


Fig. S8 TGA (____) and DSC(____) curves for dye **22c** (10 °C/min)