

Supplementary Material

New "turn-off" fluorescence sensors to detect vapors of nitro-explosives on the basis of 4,6-bis[5-(heteroaryl)thiophen-2-yl] substituted 5-(4-tert-butylphenyl)pyrimidines

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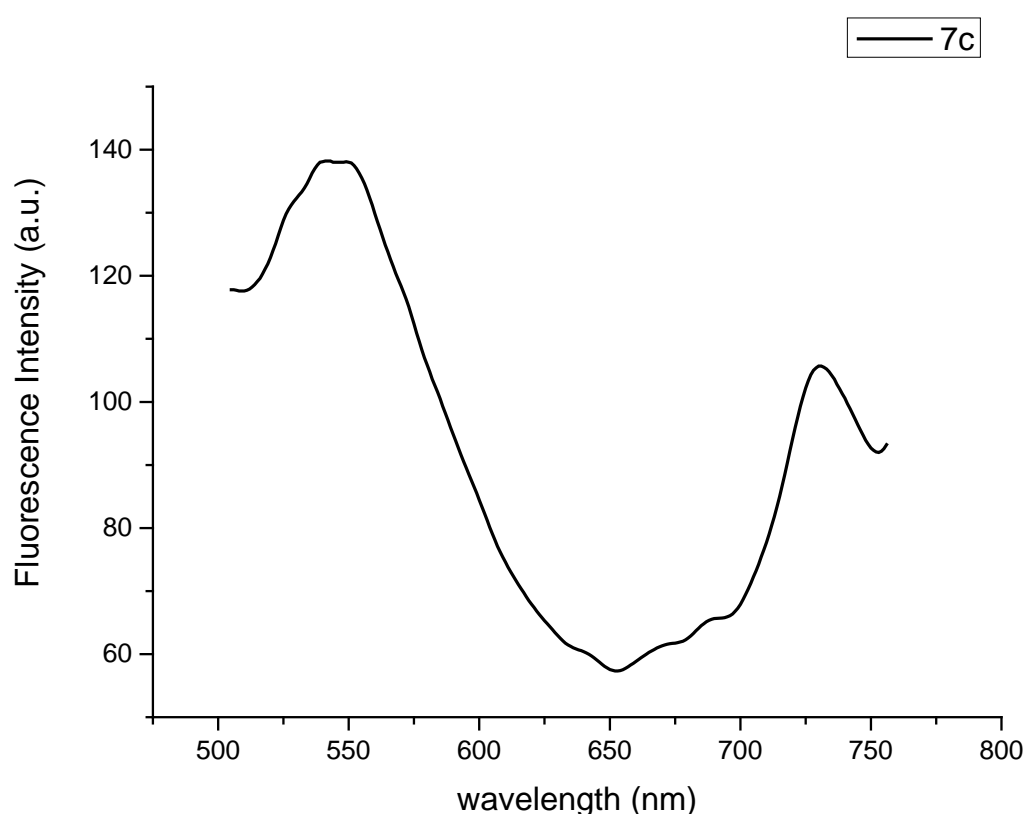


Figure S1. Solid-state fluorescence spectra of compound **7c**.

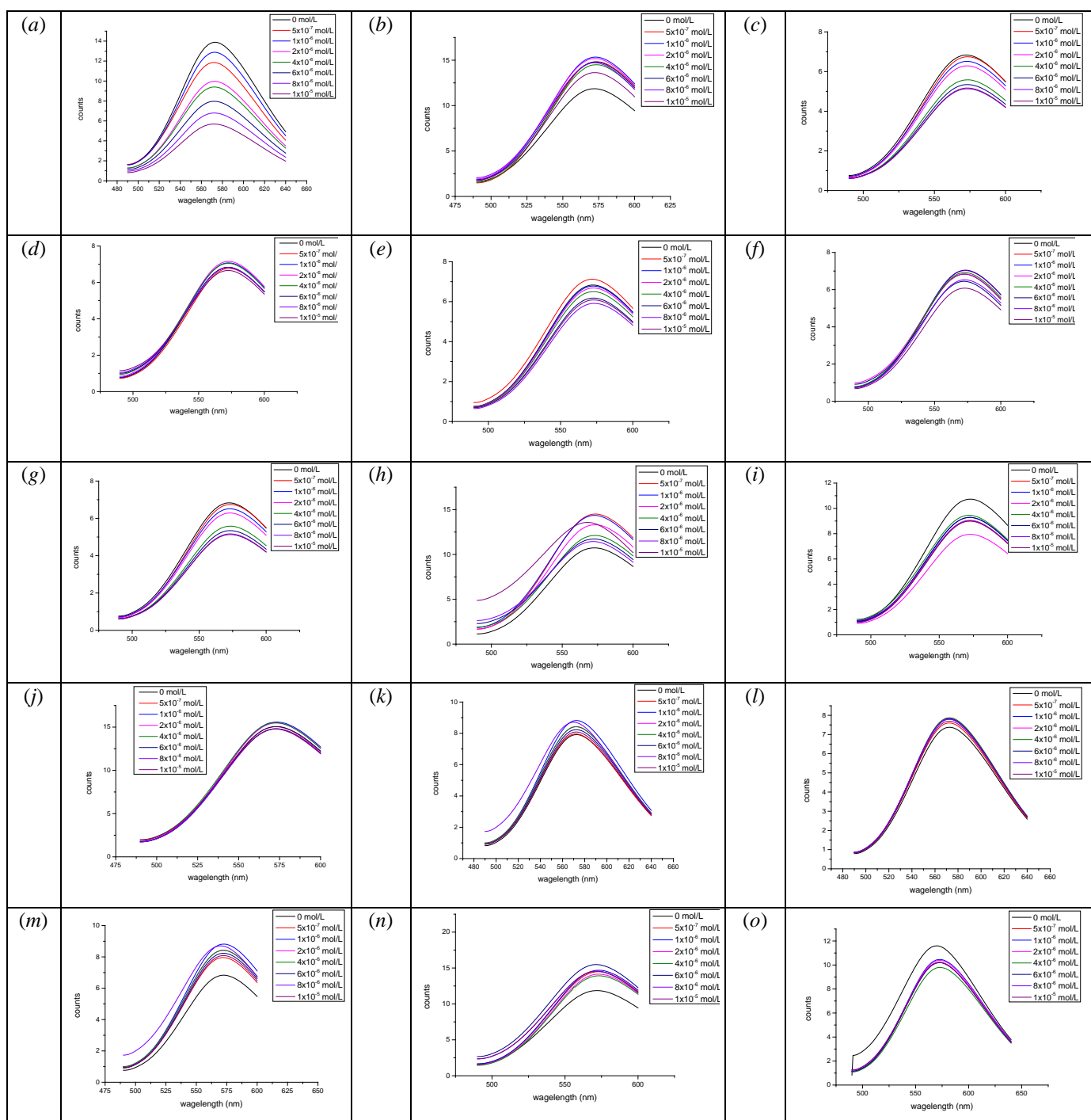


Figure S2. Fluorescence quenching studies of **7a** (1.0×10^{-6} mol/L) recorded in the presence of various amounts of NB (a), 1,3-DNB (b), 1,3,5-TNB (c), 2-NP (d), 4-NP (e), 2,4-DNP (f), PA (g), SA (h), 4-NT (i), 2,4-DNT (j), TNT (k), DNAN (l), TNAN (m), TATB (n) and DDBu (o) for which 433 nm was taken as the excitation wavelength.

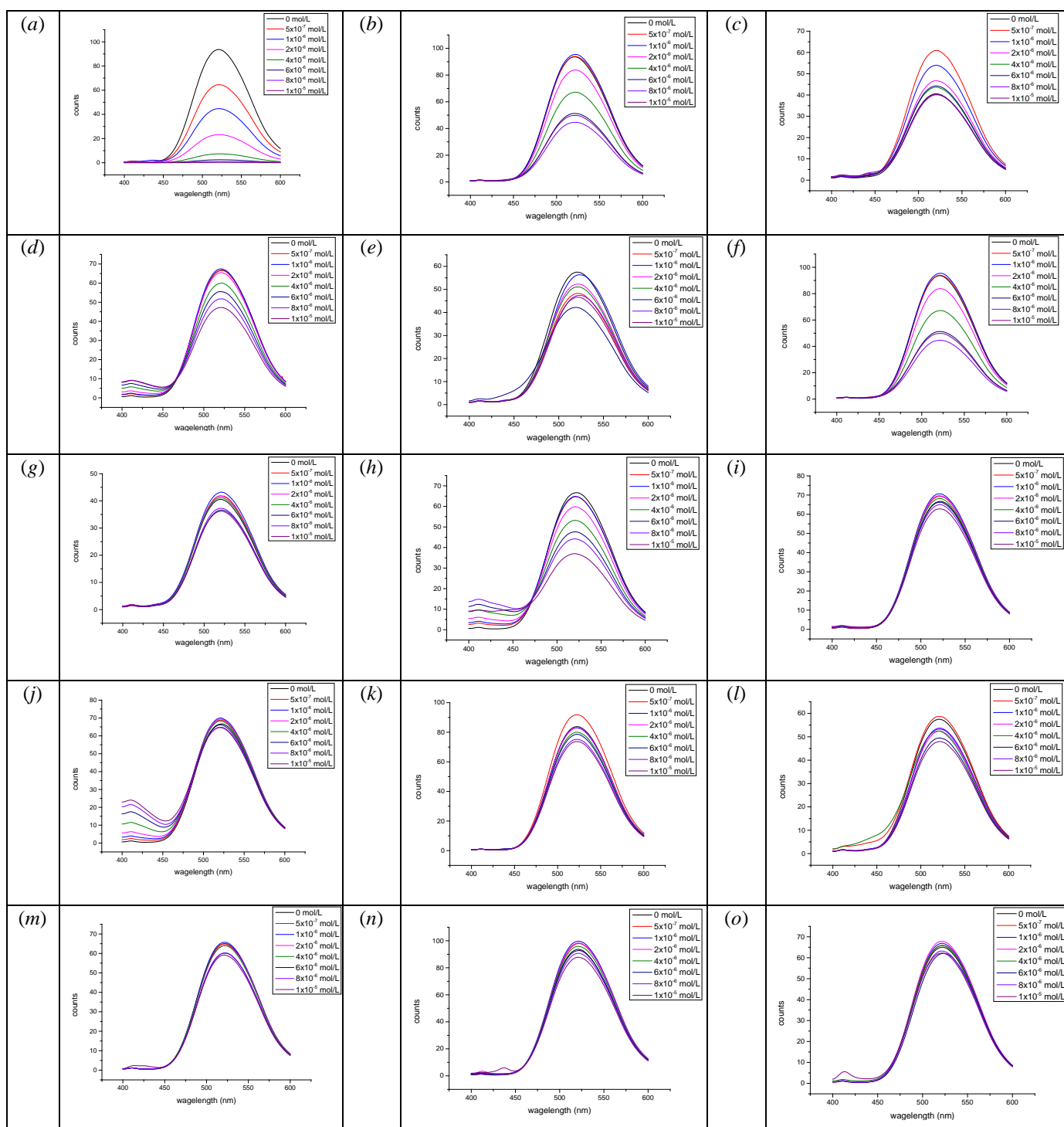


Figure S3. Fluorescence quenching studies of **7b** (1.0×10^{-6} mol/L) recorded in the presence of various amounts of NB (a), 1,3-DNB (b), 1,3,5-TNB (c), 2-NP (d), 4-NP (e), 2,4-DNP (f), PA (g), SA (h), 4-NT (i), 2,4-DNT (j), TNT (k), DNAN (l), TNAN (m), TATB (n) and DDBu (o) for which 412 nm was taken as the excitation wavelength.

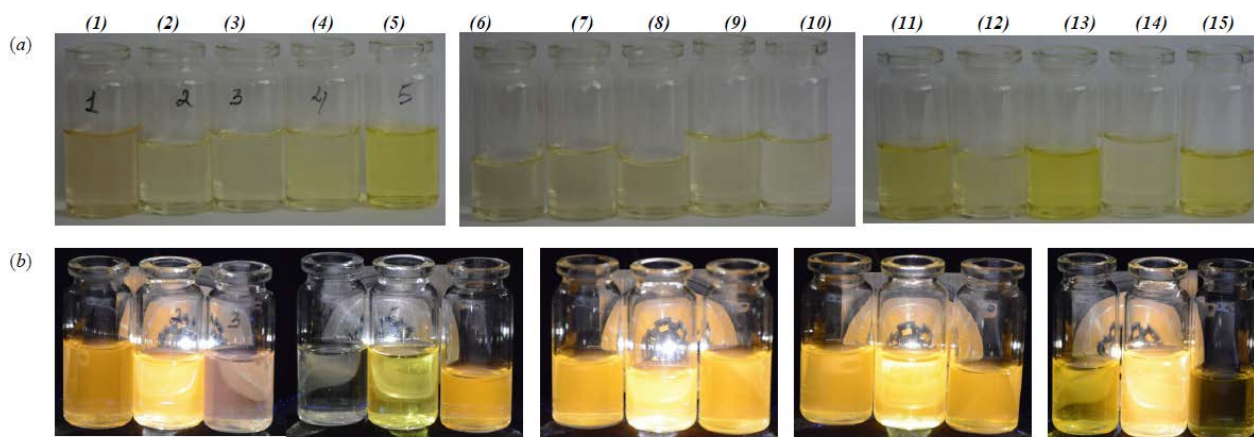


Figure S4. Photographs of solution **7a** ($c = 1.0 \times 10^{-6}$ M) with the presence of solution **TNT** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (1), solution **7a** with the presence of solution **4-NT** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (2), solution **7a** with the presence of solution **2-NP** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (3), solution **7a** with the presence of solution **NB** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (4), solution **7a** with the presence of solution **PA** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (5), solution **7a** with the presence of solution **DDBu** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (6), solution **7a** with the presence of solution **DNAN** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (7), solution **7a** with the presence of solution **1,3-DNB** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (8), solution **7a** with the presence of solution **TATB** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (9), solution **7a** with the presence of solution **4-NP** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (10), solution **7a** with the presence of solution **TNAN** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (11), solution **7a** with the presence of solution **1,3,5-TNB** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (12), solution **7a** with the presence of solution **2,4-DNP** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (13), solution **7a** with the presence of solution **2,4-DNT** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (14), solution **7a** with the presence of solution **SA** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (15): before radiation (a – no emission) and during radiation (b – emission, $\lambda_{\text{ex}} = 400$ nm) at room temperature.

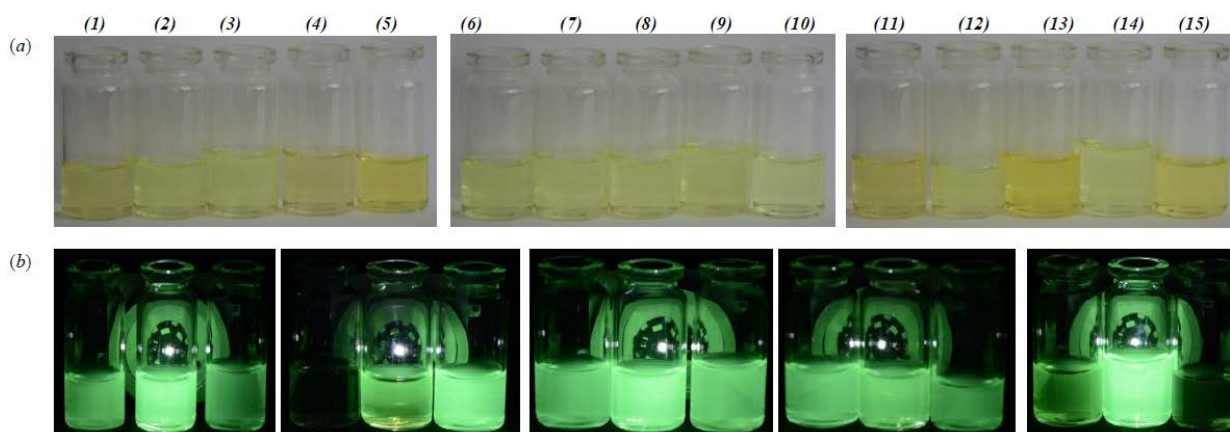


Figure S5. Photographs of solution **7b** ($c = 1.0 \times 10^{-6}$ M) with the presence of solution **TNT** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (1), solution **7b** with the presence of solution **4-NT** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (2), solution **7b** with the presence of solution **2-NP** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (3), solution **7b** with the presence of solution **NB** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (4), solution **7b** with the presence of solution **PA** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (5), solution **7b** with the presence of solution **DDBu** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (6), solution **7b** with the presence of solution **DNAN** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (7), solution **7b** with the presence of solution **1,3-DNB** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (8), solution **7b** with the presence of solution **TATB** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (9), solution **7b** with the presence of solution **4-NP** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (10), solution **7b** with the presence of solution **TNAN** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (11), solution **7b** with the presence of solution **1,3,5-TNB** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (12), solution **7b** with the presence of solution **2,4-DNP** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (13), solution **7b** with the presence of solution **2,4-DNT** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (14), solution **7b** with the presence of solution **SA** ($c = 1.0 \times 10^{-6}$ M) in acetonitrile (15): before radiation (a – no emission) and during radiation (b – emission, $\lambda_{\text{ex}} = 400$ nm) at room temperature.

Details for the determination and calculation of the detection limits of the fluorophore to nitro compounds in acetonitrile solution.

Detection limit of the fluorophore to the analyte in acetonitrile solution was determined and calculated according to the following functions:

$$s_b = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (1)$$

$$S = \frac{\Delta I}{\Delta c} \quad (2)$$

$$DL = \frac{3s_b}{S} \quad (3)$$

Firstly, the standard deviation (S_b) was calculated by measuring the intensity of the fluorophore in blank solution for more than 10 times and then got the average intensity (\bar{x}). By fitting the data into Function 1, the value of standard deviation (S_b) was obtained. Secondly, a certain amount of analyte such as NB, 1,3-DNB, 1,3,5-TNB, 2-NP, 4-NP, 2,4-DNP, PA, SA, 4-NT, DNT, TNT, DNAN, TNAN, TATB or DDBu was added into the blank solution and the resulting variation of the intensity (Δc) was recorded. By fitting the data into Function 2, where ΔI is the variation of intensity, and Δc is the variation of quencher concentration, the value of precision S was calculated. Finally the detection limit, DL, was calculated according to Function 3.

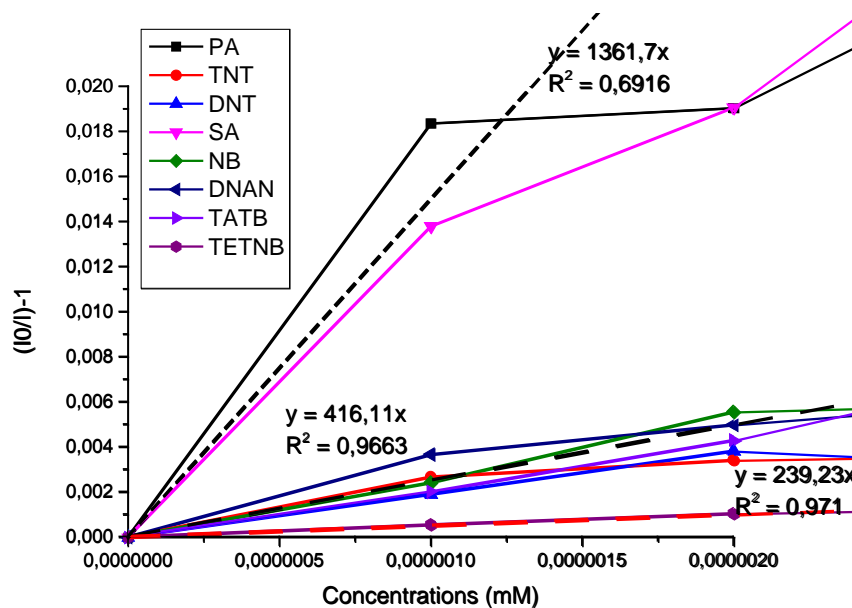


Figure S6. The Stern–Volmer plots as function of NB, 1,3-DNB, 1,3,5-TNB, 2-NP, 4-NP, 2,4-DNP, PA, SA, 4-NT, 2,4-DNT, TNT, DNAN, TNAN, TATB and DDBu concentration in CH₃CN, with an excitation wavelength of 433 nm for **7a** solution.

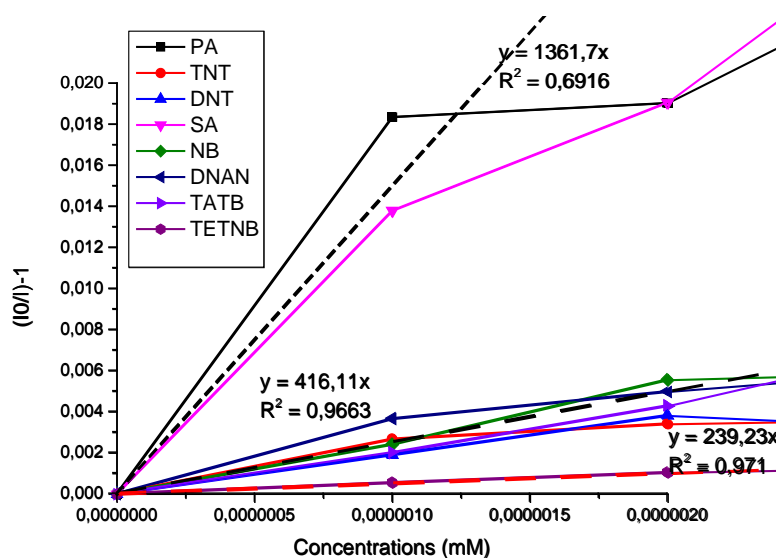
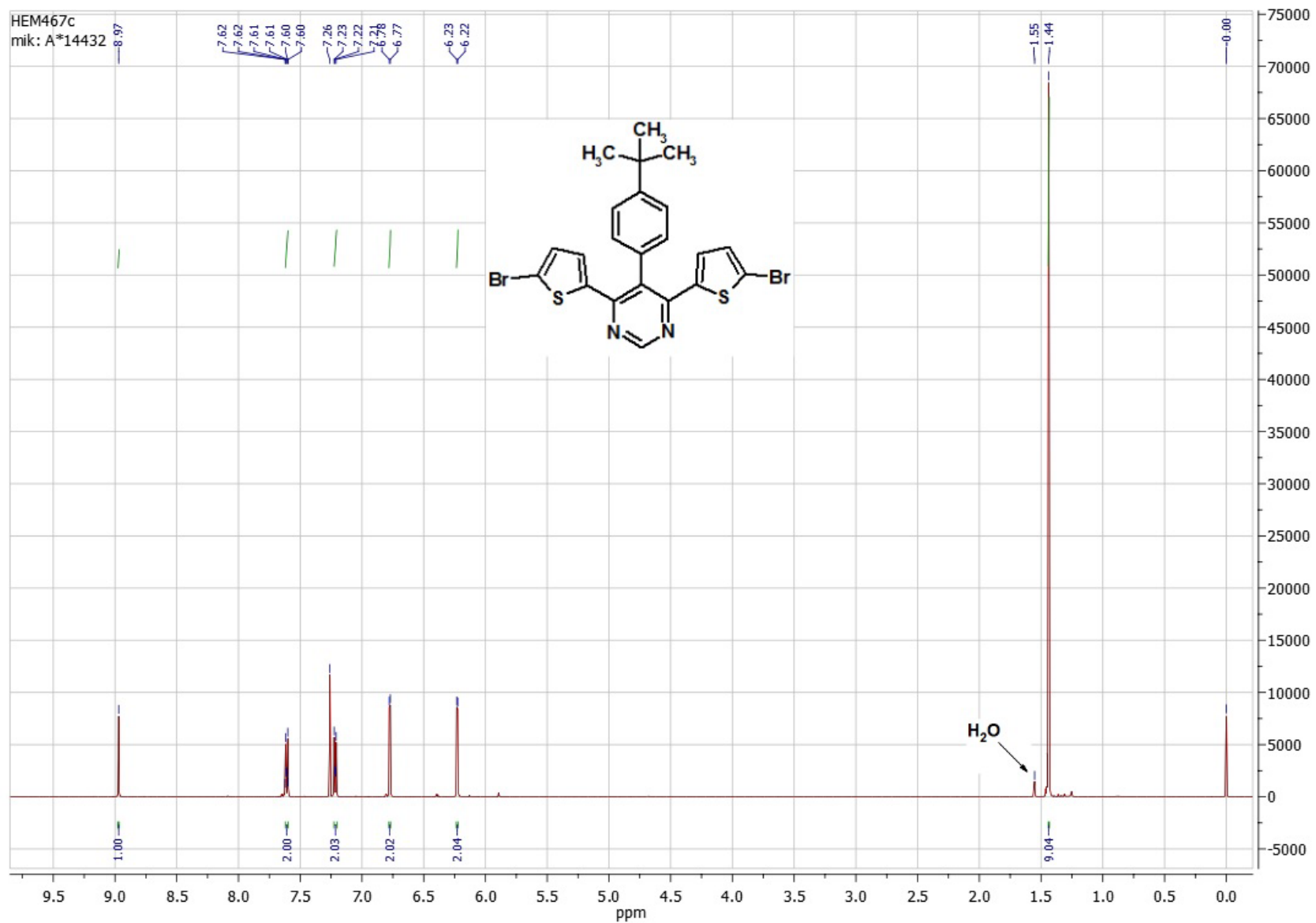


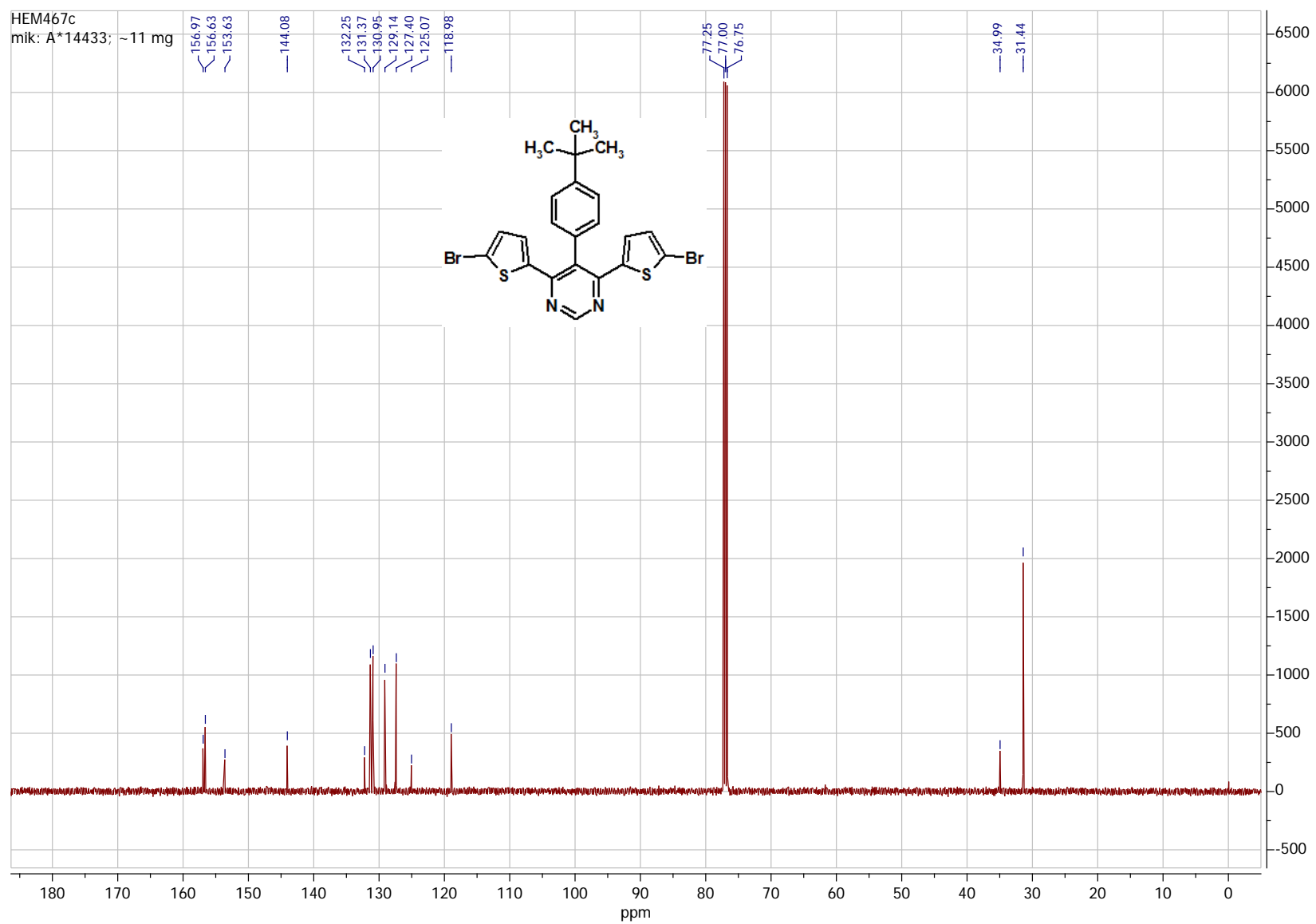
Figure S7. The Stern–Volmer plots as function of NB, 1,3-DNB, 1,3,5-TNB, 2-NP, 4-NP, 2,4-DNP, PA, SA, 4-NT, 2,4-DNT, TNT, DNAN, TNAN, TATB and DDBu concentration in CH₃CN, with an excitation wavelength of 412 nm for **7b** solution.



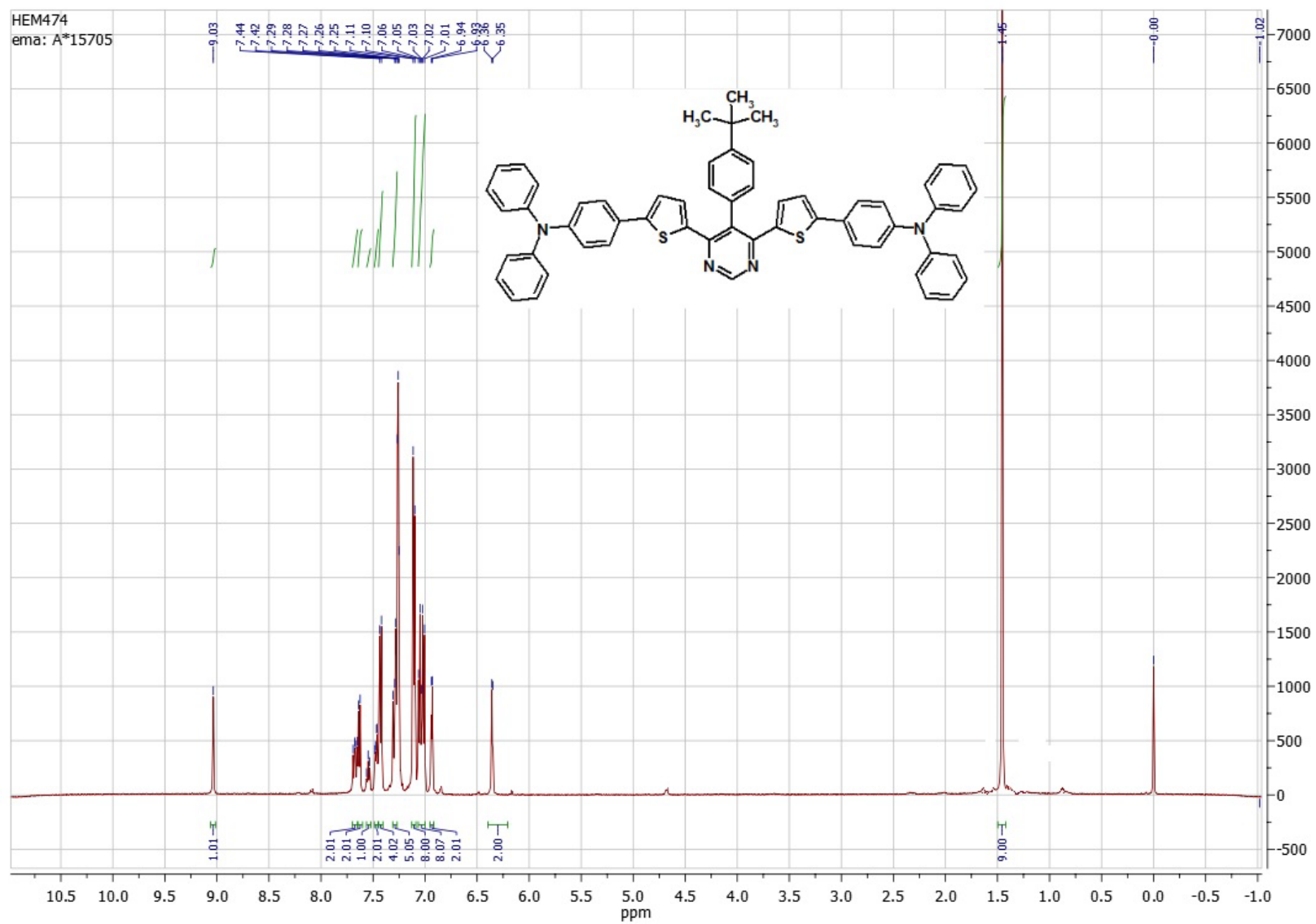
Figure S8. Photograph (from the website <http://nitroscan.pro>.) of the portable sniffer «Nitroscan» for detecting of nitroaromatic explosives in vapor phase (Plant «Promautomatika», Ekaterinburg, Russia).



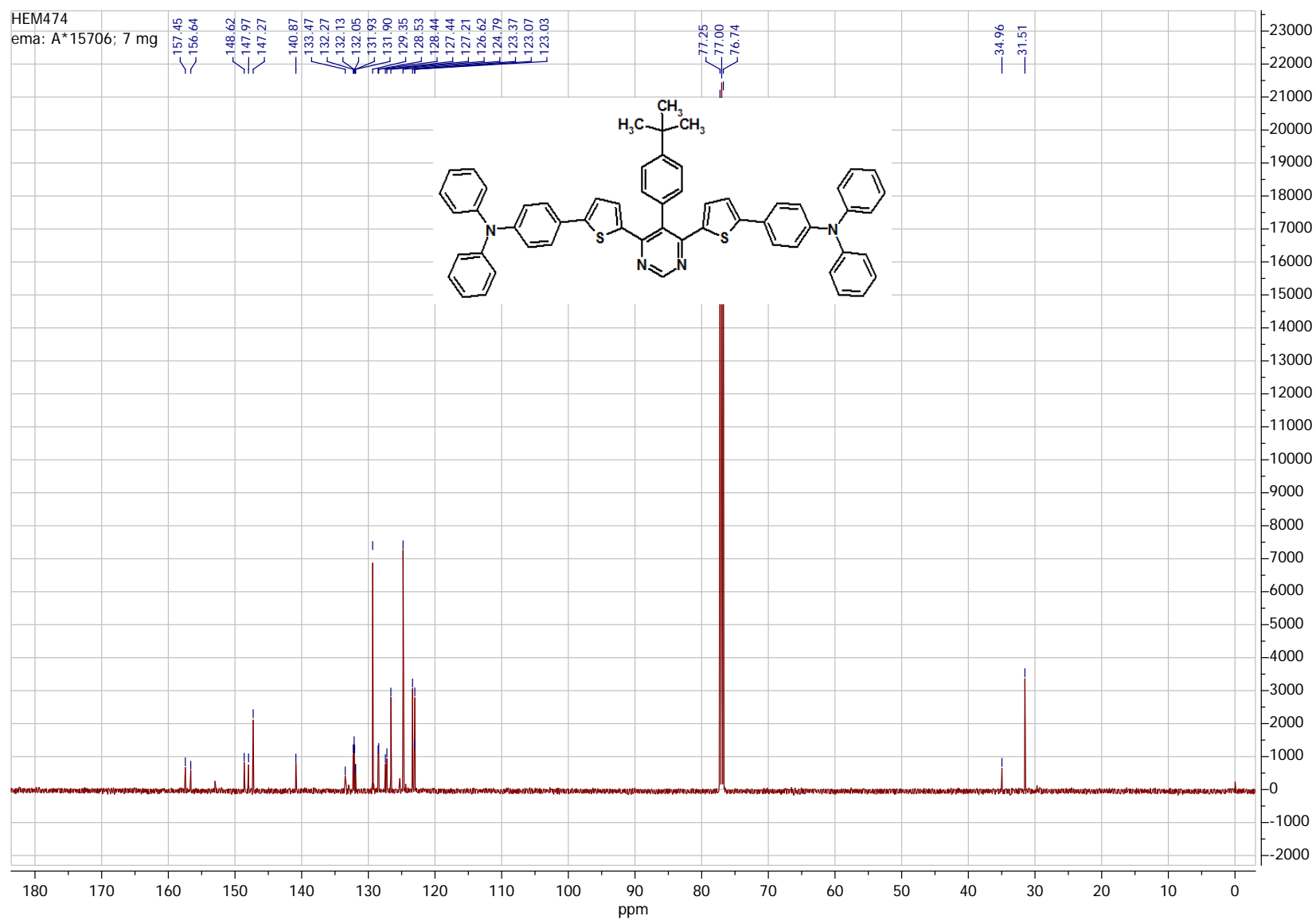
^1H NMR (500 MHz, CDCl_3) spectrum of **5**.



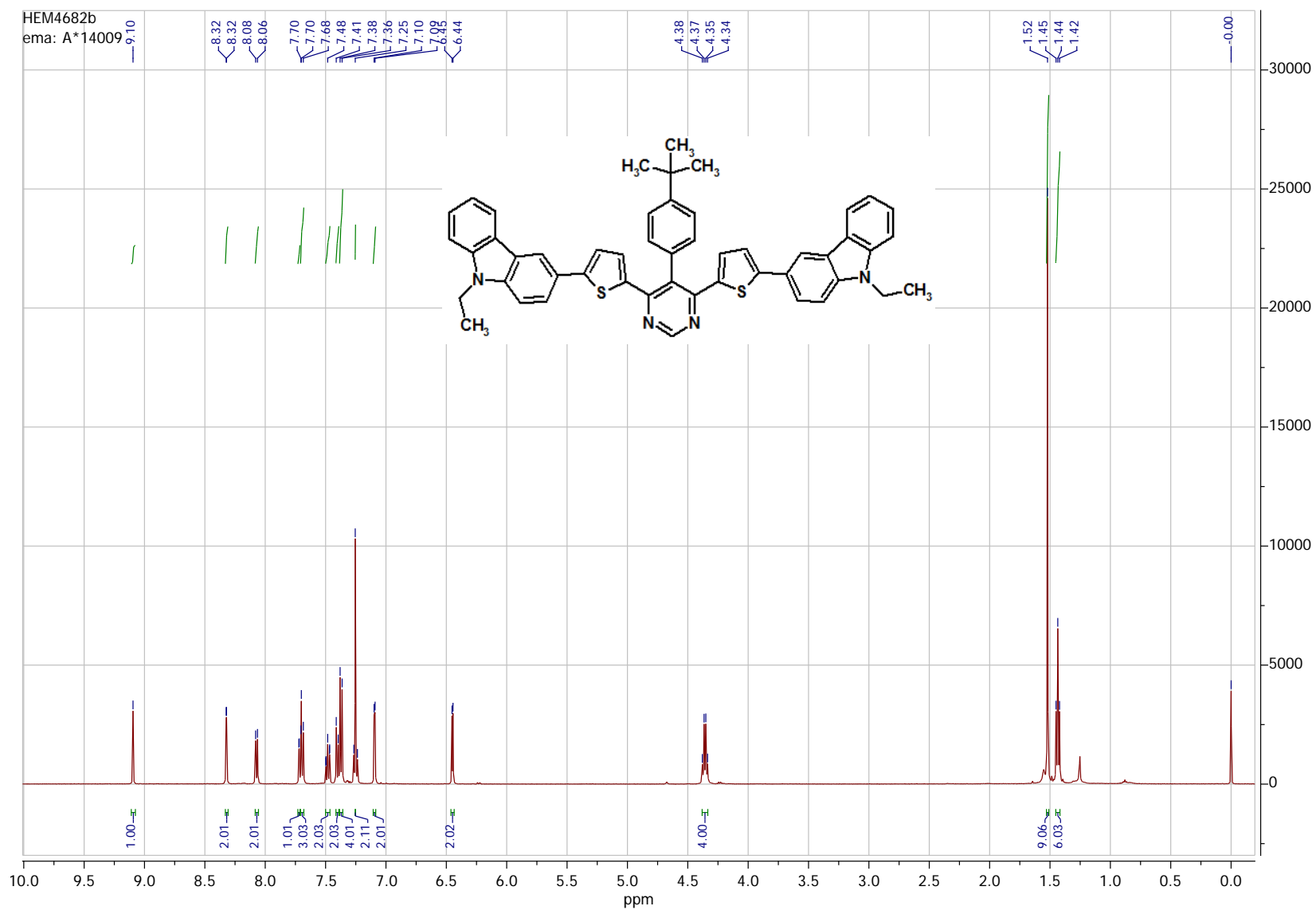
^{13}C NMR (126 MHz, CDCl_3) spectrum of **5**.



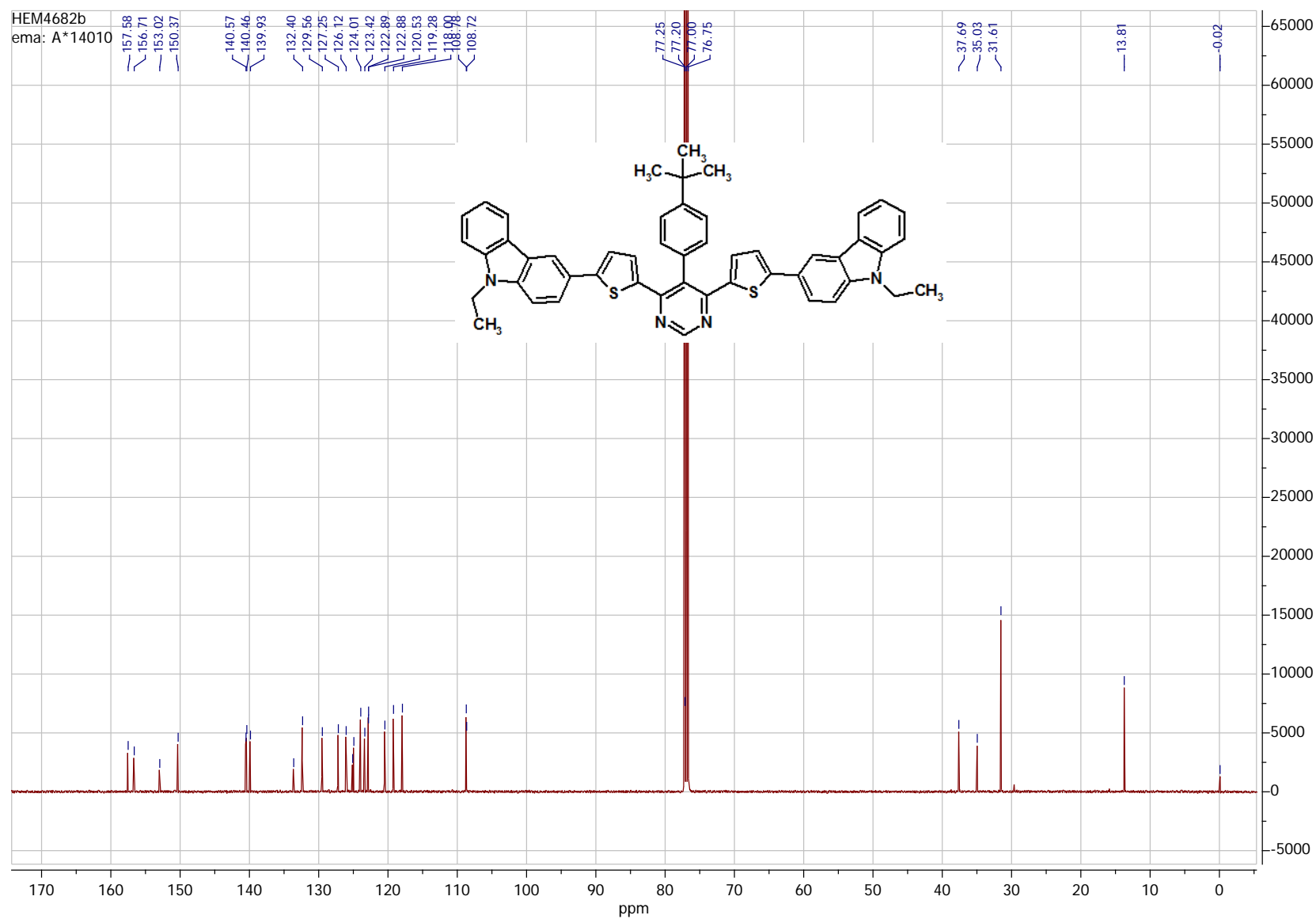
¹H NMR (500 MHz, CDCl₃) spectrum of **7a**.



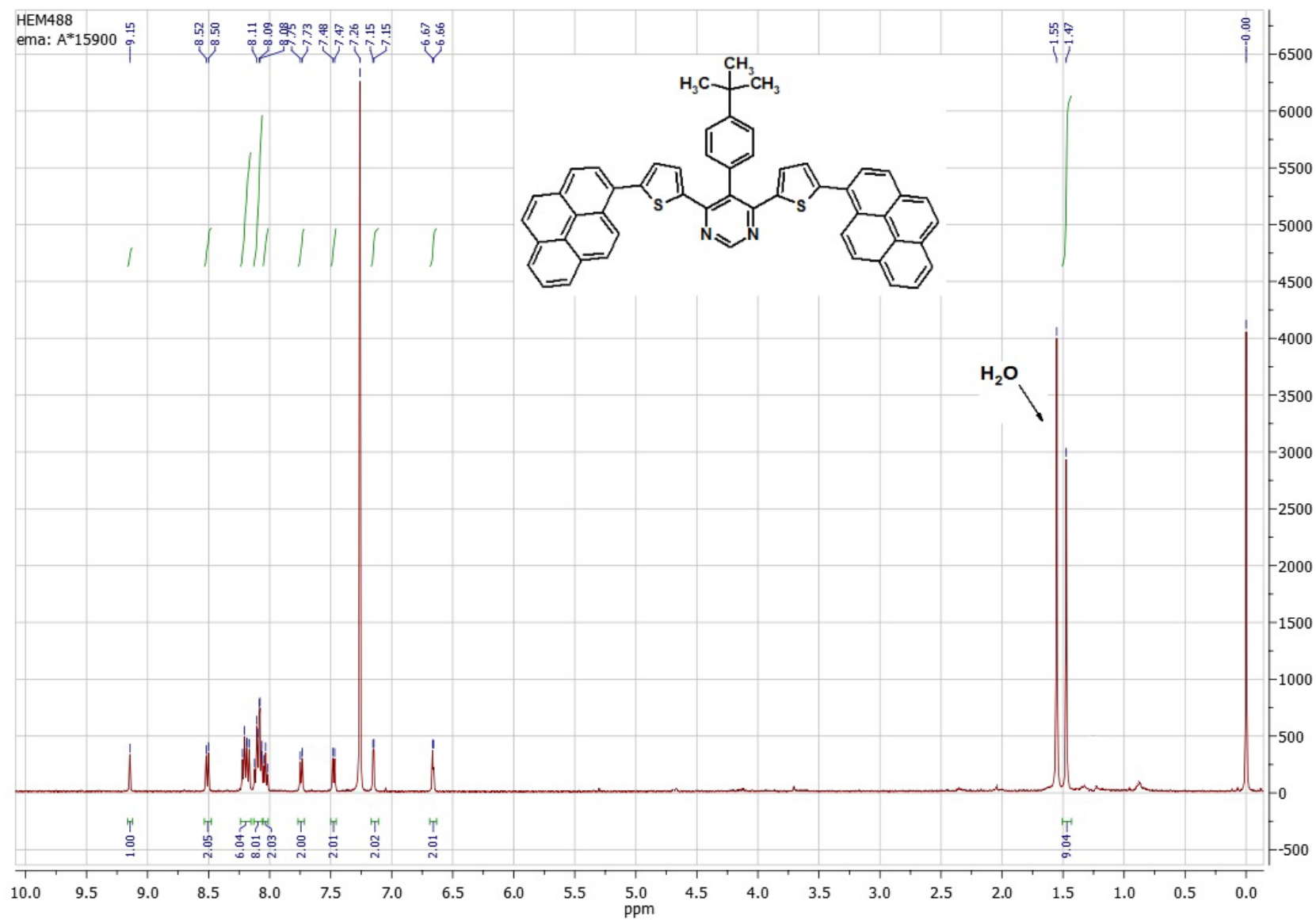
^{13}C NMR (126 MHz, CDCl_3) spectrum of **7a**.



^1H NMR (500 MHz, CDCl_3) spectrum of **7b**.



^{13}C NMR (126 MHz, CDCl_3) spectrum of **7b**.



^1H NMR (500 MHz, CDCl_3) spectrum of **7c**.