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# Prediction of photophysical properties of pyrimidine chromophores using Taguchi method.

Charline Denneval,<sup>1</sup> Sylvain Achelle,<sup>2\*</sup> Christine Baudequin,<sup>1</sup> and Françoise Robin-le Guen.<sup>2</sup>

<sup>1</sup> Normandie Univ. COBRA, UMR 6014 et FR 3038; Univ. Rouen; INSA Rouen; CNRS, IRCOF, 1 rue Tesnière, 76821 Mont Saint Aignan Cedex, France

<sup>2</sup> Institut des Sciences Chimiques de Rennes UMR CNRS 6226, IUT de Lannion, rue Edouard Branly, BP 30219, F22302 Lannion Cedex, France

Corresponding author: [sylvain.achelle@univ-rennes1.fr](mailto:sylvain.achelle@univ-rennes1.fr) Tel: +33 (0)2 96 46 94 48 Fax : + 33 (0)2 96 46 93 54.

**Abstract**

This paper presents the photophysical properties of a series of pyrimidine chromophores. The influence of three parameters has been studied: the nature of the electron-donating group and of the  $\pi$ -conjugated linker as well as the substituted position of the pyrimidine core (2, 4 and 6 position). Taguchi design of experiment combined with analysis of variance methodologies have been employed. This approach has permitted to highlight the main factor affecting the absorption and emission wavelengths of the studied compounds. Absorption maxima of this family of compounds can be predicted with relatively good precision ( $\pm 18$  nm). The emission maxima can be also predicted, however the precision is lower ( $\pm 39$  nm). Taguchi methodology has been also employed with these families of compounds to optimize the intramolecular charge transfer estimated by emission solvatochromy.

**Key words:** Pyrimidine, Photophysical Properties, Intramolecular Charge Transfer, Design of Experiment, Dyes

**1. Introduction**

Donor-acceptor  $\pi$ -conjugated (D- $\pi$ -A) materials, also called push-pull materials, with both electron-donating and electron-withdrawing groups linked by a  $\pi$ -conjugated bridge have been extensively studied during the past decades [1]. In such molecules, Intramolecular Charge Transfer (ICT) that occurs can be easily illustrated by two limiting resonance forms (aromatic and quinoid/zwitterionic arrangements) [2]. Push-pull structures have found useful applications in fluorescent dyes and sensors [3], sensitizers for Dye-Sensitized Solar-Cells (DSSCs) [4] and emitters for Organic Light-Emitting Diodes (OLED) [5]. This molecular design is also typical of second and third order Non-Linear Optical (NLO) chromophores [6]. Second order NLO materials have found applications in green laser obtained from red sources through frequency doubling, in second-harmonic generation microscopy or in terahertz wave

generation [7]. Third order NLO, in particular two-photon absorption (TPA) materials have also attracted considerable attention due to their applications in photodynamic therapy, confocal microscopy, optical power limiting, 3D data storage and microfabrication [8]. In case of second order NLOphores, the NLO answer ( $\mu\beta$ ) is directly related to the intensity of the ICT phenomena [9].

Pyrimidine, which is a highly  $\pi$ -deficient heterocycle, can be used as electron-withdrawing part in push-pull structure. The ability of protonation, hydrogen bond formation and chelation of the nitrogen atoms of the pyrimidine ring are also of great importance: such derivatives could be therefore used for the formation of supramolecular assemblies and as sensors. The use of pyrimidine ring in the structure of  $\pi$ -conjugated materials has been recently reviewed [10]. During the past decade, hundreds of pyrimidine chromophores have been designed. In particular numerous arylpyrimidine derivatives have been studied as fluorescent dyes [11]. Moreover, it should be noted that 4,6-di(arylvinyl)pyrimidine is now a well established structure of TPA dyes [12]. Recently, the second order NLO properties of 4-arylvinylpyrimidine have been also studied [13].

Even if the solvent polarity affects the absorption spectra of push-pull compounds [14], the emission solvatochromism is generally more intense. Broad structureless red shifted emission is observed on increasing the solvent polarity along with a successive decrease in the fluorescence intensity. This solvatochromic behavior results from the stabilization of the highly polar emitting state by polar solvents [15]. Therefore studying the emission solvatochromism is a way to evaluate ICT upon excitation in push-pull structures. Different scales have been described for quantification of solvent polarity [16], one of them is the Dimroth-Reichardt ( $E_T(30)$ ) polarity scale based on the solvatochromic method [17].

Taguchi robust design method is a combination of mathematical and statistical techniques used in an empirical study [18]. The Taguchi design of experiment method has become a

standard method to enhance the quality of products and processes. In principle, the Taguchi's design of experiments is used to get information such as main effects and interaction effects of design parameters from minimum number of experiments. It consists in an experimental strategy in which the effects of multiple factors are studied simultaneously by running tests with the core factors at various levels. In the Taguchi approach, experiments are designed using special orthogonal arrays that allow the parameter space to be examined by performing a limited number of experiments. It is therefore economical for characterizing a complicated process. Fewer experiments are required to study all levels of all input parameters, and filters out some effects due to statistical variation. Taguchi design of experiments method has been widely used in chemistry for the optimization of synthetic procedure [19]. However, only few examples of statistical studies dedicated to the photophysical data of series of dyes have been described. Bureš and coworkers used statistical treatment to rationalize the photophysical data of a series of heterocyclic compounds [20], and more recently, Chen *et al* described the optimization of luminescence properties of materials by design of experiments methodologies [21]

The aim of the work described in this paper is to predict the absorption and emission maxima and to optimize ICT, estimated by the importance of emission solvatochromism, of a series of pyrimidine chromophores (Figure 1). The influence of three parameters has been studied: the nature of the electron-donating group and of the  $\pi$ -conjugated linker as well as the substituted position of the pyrimidine core (2, 4 and 6 position).

<Figure1>

## 2. Materials and method

### 2.1. method

In order to predict the absorption and emission maxima and to optimize ICT in pyrimidine chromophores, three parameters have been studied: the nature of the electron-donating group,

the nature of the  $\pi$ -conjugated linker and the substituted position of the pyrimidine core. For each parameter, three levels have been considered (Table 1). The orthogonal array of  $L_9$  type was used and is represented in Table 2, where column D is used as control to check if there are interactions between factors A-C. The corresponding compounds are represented in Figure 2. It should be noted that in case of compound **3**, for solubility reasons, the methoxy groups have been replaced by hexyloxy group. This modification is supposed to have a negligible influence on the photophysical parameters studied.

<Table 1>

<Table 2>

<Figure 2>

## 2.2. General experimental

All solvents were reagent grade. The starting materials were purchased from Sigma-Aldrich or Acros and used without further purification. For air and moisture-sensitive reactions, all glassware pieces were flame-dried and cooled under nitrogen. NMR spectra were recorded in  $CDCl_3$ , on a Bruker Advance 300 spectrometer ( $^1H$  at 300 MHz and  $^{13}C$  at 75 MHz). The chemical shifts  $\delta$  are reported in ppm relative to the residual solvent ( $CHCl_3$ ). The coupling constants  $J$  are given in Hz. In the  $^1H$  NMR spectra, the following abbreviations are used to describe the peak patterns: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet). In the  $^{13}C$  NMR spectra, the nature of the carbons (C, CH,  $CH_2$  or  $CH_3$ ) was determined by performing a JMOD experiment. Melting points ( $^{\circ}C$ ) were measured on a Kofler hot-stage with a precision of 2 degrees ( $\pm 2^{\circ}C$ ). High-resolution mass analyses were performed at the "Centre Régional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes1) using a Bruker MicroTOF-Q II apparatus. Analytical thin layer chromatographies (TLC) were performed on silica gel plates (Merck 60F254) and compounds were visualized

by irradiation with UV light at 254 and 365 nm. Flash chromatography was performed using silica Acros SI 60 (60-200 mesh ASTM). UV-Visible spectra were recorded on a Varian Cary 50 scan spectrophotometer. Fluorescence spectroscopy studies were conducted on a Varian Cary Eclipse spectrophotometer. Compounds were excited at their absorption maxima (band of lowest energy) for recording the emission spectra. All solutions were measured with optical densities below 0.1. Fluorescence quantum yield ( $\pm 10\%$ ) determined relative to quinine sulfate in 1 M H<sub>2</sub>SO<sub>4</sub> ( $\Phi_F = 0.54$ ) or harmane in 0.1 M H<sub>2</sub>SO<sub>4</sub> as standard ( $\Phi_F = 0.83$ ). Stokes shifts were calculated considering the lowest energetic absorption band.

### 2.3. Synthesis

Compounds **1** [22], **2** [23], **3** [24], **5** [13a], **6** [11a], **9** [22] have been synthesized according to reported methods. The synthetic routes to chromophores **4**, **7**, **8** and **12** are reported in schemes 1-4.

<Scheme 1>

<Scheme 2>

<Scheme 3>

<Scheme 4>

### 2.4. General Knoevenagel condensation procedure

A stirred mixture of methylpyrimidine derivative (1.5 mmol) and corresponding aldehyde (1.5 mmol) in aqueous sodium hydroxide (5 M, 15 mL) containing Aliquat 336 (64 mg, 0.15 mmol) was heated under reflux for 3 h. The mixture was allowed to cool, the precipitate was filtered off, and washed with water.

### 2.5. Synthesis of **4**

Compound **4** was synthesized according to general Knoevenagel condensation procedure and the crude product was purified by column chromatography (SiO<sub>2</sub>, AcOEt/Petroleum Ether,

1:1); yellow solid; 216 mg; yield 64%; mp : 149-152°C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.01 (s, 6H), 6.71 (d, 1H,  $J = 9.0$  Hz), 7.01 (t, 1H,  $J = 4.8$  Hz), 7.03 (d, 1H,  $J = 16.2$  Hz), 7.53 (d, 2H,  $J = 9.0$  Hz), 7.92 (d, 1H,  $J = 16.2$  Hz), 8.65 (d, 2H,  $J = 4.8$  Hz);  $^{13}\text{C}$  NMR and JMOD (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7 (C), 156.9 (CH), 151.1 (C), 138.5 (CH), 129.1 (C), 124.1 (C), 122.5 (CH), 117.6 (CH), 112.1 (CH), 40.2 ( $\text{CH}_3$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{15}\text{N}_3$ : C, 74.64; H, 6.71; N, 18.65. Found C, 74.51; H, 6.95; N, 18.37.

### 2.6. Synthesis of **10**

Compound **10** was synthesized according to general Knoevenagel condensation procedure and the crude product was purified by column chromatography ( $\text{SiO}_2$ , AcOEt/Petroleum Ether, 1:1); cream solid; 172 mg; yield 44%;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 (t, 1H,  $J = 4.8$  Hz), 7.22 (d, 1H,  $J = 16.2$  Hz), 7.48 (d, 1H,  $J = 8.7$  Hz), 7.52 (d, 2H,  $J = 8.7$  Hz), 7.91 (d, 1H,  $J = 16.2$  Hz), 8.72 (d, 2H,  $J = 4.8$  Hz);  $^{13}\text{C}$  NMR and JMOD (75 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7 (C), 157.1 (CH), 136.8 (CH), 134.9 (C), 132.0 (CH), 129.0 (CH), 128.1 (CH), 123.1 (C), 118.7 (CH); Anal. Calcd for  $\text{C}_{12}\text{H}_9\text{BrN}_2$ : C, 55.20; H, 3.47; N, 10.73. Found C, 55.15; H, 3.56; N, 10.57.

### 2.7. General Suzuki cross-coupling reaction procedure

A stirred mixture of halogeno derivative (1 mmol), corresponding phenylboronic acid (1.2 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (58 mg, 0.05 mmol), aqueous 1 M sodium carbonate (1 mmol, 1 mL) and ethanol (1 mL) in degassed toluene (10 mL) was heated under nitrogen for 24 h (40h in case of **12**). The reaction mixture was cooled, filtered, and dissolved with a mixture of EtOAc and water 1:1 (50 mL) and the organic layer separated. The aqueous layer was extracted with EtOAc (2  $\times$  25 mL). The combined organic extracts were dried with  $\text{MgSO}_4$  and the solvents evaporated.

### 2.8. Synthesis of **7**



Compound **7** was synthesized according to general Suzuki cross coupling reaction procedure and the crude product was purified by column chromatography (SiO<sub>2</sub>, AcOEt/Petroleum Ether, 1:1); yellow solid; 296 mg; yield 70%; mp : 182-186°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.10-7.03 (m, 3H), 7.16-7.12 (m, 7H), 7.31-7.28 (m, 4H), 7.52 (d, 2H, *J* = 8.7 Hz), 7.62 (d, 2H, *J* = 8.4 Hz), 7.69 (d, 2H, *J* = 8.4 Hz), 8.03 (d, 1H, *J* = 16.2 Hz), 8.74 (d, 2H, *J* = 4.8 Hz); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>) δ 165.0 (C), 157.1 (CH), 147.6 (C), 147.5 (C), 141.3 (C), 137.8 (CH), 134.5 (C), 134.1 (C), 129.3 (CH), 128.2 (CH), 127.6 (CH), 127.0 (CH), 126.9 (CH), 124.6 (CH), 123.7 (CH), 123.1 (CH), 118.4 (CH); HRMS (ESI<sup>+</sup>, ASAP) *m/z* calculated for C<sub>30</sub>H<sub>24</sub>N<sub>3</sub> [M+H]<sup>+</sup> 426.1970, found 426.1968.

### 2.9. Synthesis of **11**

Compound **11** was synthesized according to general Suzuki Cross coupling reaction procedure and the crude product was purified by column chromatography (SiO<sub>2</sub>, AcOEt/Petroleum Ether, 1:9); pale yellow solid; 250 mg; yield 70%; mp : 147-149°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.20-7.10 (m, 8H), 7.37-7.31 (m, 4H), 7.65 (s, 1H), 7.94 (d, 2H, *J* = 8.7 Hz), 8.96 (s, 1H); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>) δ 165.1 (C), 161.5 (C), 158.9 (CH), 151.3 (C), 146.7 (C), 129.7 (CH), 128.4 (CH), 127.5 (C), 125.7 (CH), 124.4 (CH), 121.3 (CH), 115.8 (CH); HRMS (ESI<sup>+</sup>, ASAP) *m/z* calculated for C<sub>22</sub>H<sub>17</sub>ClN<sub>3</sub> [M+H]<sup>+</sup> 358.1106, found 358.1109.

### 2.10. Synthesis of **8**

To a stirred mixture of compound **11** (150 mg, 0.42 mmol), sodium hydrogenocarbonate (43 mg, 0.50 mmol) and Pd-C (5 mg, 0.04 mmol) in EtOH (5 mL), dihydrogen was introduced in bubbles at rt for 20 h. The mixture was then filtered with celite and the solvent removed. The crude product was purified by column chromatography (SiO<sub>2</sub>, AcOEt/Petroleum Ether, 1:4); yellow solid; 124 mg; yield 92%; mp : 104-107°C; <sup>1</sup>H NMR

(300 MHz, CDCl<sub>3</sub>)  $\delta$  7.08-7.17 (m, 8H), 7.25-7.33 (m, 4H), 7.61 (d,  $J$  = 5 Hz, 1H), 7.95 (d,  $J$  = 8.7 Hz, 2H), 8.67 (d,  $J$  = 5 Hz, 1H), 9.19 (s, 1H); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  163.3 (C), 158.9 (CH), 157.0 (C), 150.7 (CH), 146.9 (CH), 129.5 (CH), 128.9 (C), 128.1 (CH), 125.4 (CH), 124.0 (CH), 121.7 (CH), 116.1 (C); HRMS (ESI<sup>+</sup>, ASAP)  $m/z$  calculated for C<sub>22</sub>H<sub>17</sub>N<sub>3</sub> [M+H]<sup>+</sup> 324.1501, found 324.1511

### 2.11. Synthesis of **12**

Compound **12** was synthesized according to general Suzuki Cross coupling reaction procedure and the crude product was purified by crystallization from of mixture of DCM/pentane; orange solid; 261 mg; yield 34%; mp : 125-130°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.03-7.05 (m, 6H), 7.12-7.16 (m, 12H), 7.26-7.32 (m, 9H), 7.51 (d,  $J$  = 8.7 Hz, 4H), 8.13 (d,  $J$  = 8.7 Hz, 4H), 8.15 (d,  $J$  = 8.7 Hz, 4H), 7.95 (d,  $J$  = 15.9 Hz, 2H), 9.12 (s, 1H); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  162.9 (C), 158.8 (C), 147.8 (C), 147.6 (C), 141.7 (CH), 136.8 (CH), 134.1 (C), 133.8 (C), 129.5 (CH), 128.3 (CH), 127.7 (CH), 127.0 (CH), 125.5 (CH), 124.7 (CH), 123.7 (CH), 123.3 (CH), 116.6(CH); HRMS (ESI<sup>+</sup>, ASAP)  $m/z$  calculated for C<sub>56</sub>H<sub>42</sub>N<sub>4</sub> [M+H]<sup>+</sup> 771.3480, found 771.3488.

## 3. Results and discussion

The UV-Vis and photoluminescence (PL) spectroscopic data of compounds **1-9** measured in dichloromethane at 25 °C are presented in table 3. Analyses have been carried out using low concentration solutions in order to avoid self-absorption effect. As an example, the spectra for derivative **9** are shown in Figure 3. All compounds are photostable during photophysical experiments.

<Table 3>

<Figure 3>

The absorption and emission maxima have been studied according to Taguchi methodology and analysis of variance (ANOVA) was conducted to determine the significance of each factor. For absorption, the effects of each level of each factor are presented in Table 4 and the results of ANOVA calculations are given in Table 5. The average absorption wavelength is 367 nm. As shown in Table 4, the diphenylamino group (level 3 of factor A) is the substituent leading to the most red-shifted absorption. 2-substituted pyrimidine (level 1, factor B) are the most blue shifted whereas 4,6-disubstituted derivatives (level 3, factor B) are the most red shifted. Concerning the  $\pi$ -conjugated core, phenylenevinylene derivatives (level 2, factor C) are the most red shifted.

Similar tables for emission are given in supporting information, the average emission wavelength is 476 nm. It should be noted that the substitution position of the pyrimidine core affect differently the absorption and the emission: 4-monosubstituted derivatives (level 2, factor B) are more red shifted in emission than 4,6-disubstituted pyrimidines (level 3, factor B).

Either for  $\lambda_{\text{abs}}$  and  $\lambda_{\text{em}}$ , the influence of residue is low (below 3.3%) indicating that there is no interaction between the three factors studied. The F-ratio test was conducted to evaluate the effect of each factor on the signal/noise ratio. For absorption, the three factors A, B and C have F-ratios superior to the F-value for a 90% confidence level ( $F\text{-value}_{0,9} = 9$ ) making them significant. For emission, only factors A and C are significant. As shown in table 4, the nature of the electron-donating group (factor A, 48.0%) and the substituted position of the pyrimidine ring (factor B, 28.4%) are the main factor influencing the absorption wavelength. The emission wavelength mainly depends on the nature of the  $\pi$ -conjugated core (factor C, 45.3%) and of the electron-donating group (factor A, 44.3%).

The absorption wavelengths calculated according to the average value and the effects of the corresponding level of each factor (Table 4) are in good agreement with experimental values

for the compounds described in the literature ( $\Delta\lambda < 18$  nm, see supporting information). For emission, the differences between calculated and experimental values are a bit higher ( $\Delta\lambda < 39$  nm, see supporting information) in particular for the most red-shifted compounds.

<Table 4>

<Table 5>

In an effort to gain further insight into the photophysical process within this series of pyrimidine push-pull chromophores, we investigated the emission behavior of compounds **1-9** in different aprotic solvents. The results of these investigations are summarized in Table 6. As an example the emission spectra in various solvents for compound **6** are shown in Figure 3. For all compounds, the emission maxima were plotted *versus* the Dimroth-Reichardt polarity parameter ( $\Delta E_T(30)$ ). In all case a good linearity was obtained (see supporting information). The slopes of the corresponding regression lines (SP) are good indications of the intensity of the ICT into the chromophores. The highest value of SP is observed for compound **5**.

<Table 6>

<Figure 4>

The ANOVA method was employed to study the influence of each factor on the value of SP in a similar manner than for absorption and emission maxima. The results are given in Tables 7 and 8. The average value of SP is 1.73. Once again, the influence of the residue is low (2.1%). Two factors significantly explain SP according to their F-ratios: the nature of the electron-donating group (factor A, 46.8 %) and of the  $\pi$ -conjugated core (factor C, 40.4%). The substituted position of the pyrimidine ring seems to be less important. According to Table 7, the optimal configuration consists in diphenylamino donor groups (level 3 factor A) linked to a 4-6-disubstituted pyrimidine (level 3 factor B) by a biphenylenevinylene bridge (level 3

factor C). The corresponding structure (compound **12**) exhibits a higher SP value than compounds **1-9** which validates the methodology.

<Table 7>

<Table 8>

#### 4. Conclusion

To conclude, we have shown that Taguchi design of experiment methodology can be efficiently applied to predict the photophysical properties (absorption and emission maxima) of a family of pyrimidine chromophores. ICT in these compounds estimated by emission solvatochromy has been also optimized using the same approach. Taguchi design of experiment methodology appears useful to study the influence various parameters involved in the photophysical properties of a series of dyes and to identify quickly the optimized chromophore. This strategy could be applied to other family of chromophores.

**Figure 1.** General structure of the studied dyes.

**Figure 2.** Chromophores **1, 2, 3, 4, 5, 6, 7, 8, 9**

**Figure 3.** Absorption (broken line) and emission spectra (solid line) of chromophores **9**

**Figure 4.** Normalized emission spectra of chromophore **6** in various solvents.

**Scheme 1.** Synthesis of compound **4**

**Scheme 2.** Synthesis of compound **7**.

**Scheme 3.** Synthesis of compound **8**.

**Scheme 4.** Synthesis of compound **12**.

**Table 1.** Parameters and their values corresponding to their levels to be studied in experiments.

**Table 2.** Experimental layout using the  $L_9$  orthogonal array.

**Table 3.** UV/Vis and photoluminescence (PL) data

**Table 4.** Effect of each level of each factor on  $\lambda_{\text{abs}}$  in nm

**Table 5.** Analysis of variance (ANOVA) for on  $\lambda_{\text{abs}}$  in nm.

**Table 6.** Emission solvatochromic range of pyrimidine chromophores **1-9** and **12** in various aprotic solvents

**Table 7.** Effect of each level of each factor on SP

**Table 8.** Analysis of variance of SP

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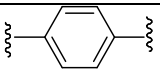
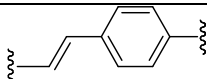

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Parameter	Levels		
	1	2	3
A: Nature of electron-donating group	OMe	NMe <sub>2</sub>	NPh <sub>2</sub>
B: Substituted positions of the pyrimidine core.	2	4	4 and 6
C: Nature of $\pi$ -conjugated linker			

Compound	A	B	C	D
<b>1</b>	1	1	1	1
<b>2</b>	1	2	2	2
<b>3</b>	1	3	3	3
<b>4</b>	2	1	2	3
<b>5</b>	2	2	3	1
<b>6</b>	2	3	1	2
<b>7</b>	3	1	3	2
<b>8</b>	3	2	1	3
<b>9</b>	3	3	2	1

Compd <sup>a</sup>	UV/vis $\lambda_{max}$ , nm	PL		Stokes shift
	( $\epsilon$ , M <sup>-1</sup> ·cm <sup>-1</sup> )	$\lambda_{max}$ , nm	$\Phi_F$ <sup>b</sup>	cm <sup>-1</sup>
<b>1</b>	283 (26600)	356	<0.01	7245
<b>2</b>	338 (28500)	418	<0.01	5662
<b>3<sup>b</sup></b>	373 (60500)	483	0.59	6106
<b>4</b>	251 (18900), 379 (31900)	472	0.01	5199
<b>5<sup>c</sup></b>	296 (24600), 386 (32400)	570	0.66	8362
<b>6</b>	299 (16000), 378 (38100)	429	0.72	3145
<b>7</b>	303 (38400), 373 (36500)	530	0.60	7942
<b>8</b>	300 (13000), 367 (31400)	482	0.55	6501
<b>9<sup>b</sup></b>	301 (38900), 427 (47600)	540	0.55	4901

<sup>a</sup> All spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> solutions at room temperature at  $c = 1.0 \times 10^{-5}$  M to  $3.0 \times 10^{-5}$  M for absorption and  $c = 1.0 \times 10^{-6}$  M to  $3.0 \times 10^{-6}$  M for emission. <sup>b</sup> Fluorescence quantum yield ( $\pm 10\%$ ) determined relative to quinine sulfate in 1 M H<sub>2</sub>SO<sub>4</sub> ( $\Phi_F = 0.54$ ) or harmane in 0.1 M H<sub>2</sub>SO<sub>4</sub> as standard ( $\Phi_F = 0.83$ ). <sup>b</sup> data from ref [24]. <sup>c</sup> data from ref [13a].

factor	$S^a$	dof <sup>b</sup>	$V^c$	F-ratio <sup>d</sup>	Explained % <sup>e</sup>
A	5856	2	2928	35.6	48.0
B	3462	2	1731	21.1	28.4
C	2713	2	1356	16.5	22.2
Residue	164	2	82		1.3
Total	12281	8			100

<sup>a</sup> Sum of squared deviations from the mean. <sup>b</sup> degree of freedom. <sup>c</sup> variance: mean of squares per dof. <sup>d</sup> ratio between squared deviation and the mean of square residue. <sup>e</sup> relative effects of the factors on  $\lambda_{\text{abs}}$ .



	A		B		C	
	Average	Effect	Average	Effect	Average	Effect
1	331	-36	345	-22	343	-24
2	381	14	364	-3	381	14
3	389	22	393	26	377	10

	<i>n</i> -heptane $\Delta E_T(30)^a = 0.0$	Toluene $\Delta E_T(30)^a = 13.6$	THF $\Delta E_T(30)^a = 27.2$	CH <sub>2</sub> Cl <sub>2</sub> $\Delta E_T(30)^a = 40.7$	DMSO $\Delta E_T(30)^a = 59.0$	SP <sup>b</sup>
	$\lambda_{em}$ (nm)	$\lambda_{em}$ (nm)	$\lambda_{em}$ (nm)	$\lambda_{em}$ (nm)	$\lambda_{em}$ (nm)	
<b>1</b>	- <sup>c</sup>	- <sup>c</sup>	352	356	- <sup>c</sup>	0.30
<b>2</b>	384	401	410	418	427	0.70
<b>3</b>	405	422	458	483	509	1.85
<b>4</b>	423	439	460	472	497	1.25
<b>5</b>	453	490	554	569	632	3.01
<b>6</b>	373	403	431	435	480	1.70
<b>7</b>	418	458	498	530	566	2.52
<b>8</b>	400	430	456	482	509	1.85
<b>9</b>	443	476	515	540	584	2.38
<b>12</b>	440	481	545	585	623	3.43

<sup>a</sup> Dimroth–Reichardt polarity parameter, J·mol<sup>-1</sup>. <sup>b</sup> SP: slope of the regression line  $\lambda_{em}$  (nm) versus  $\Delta E_T(30)$  in nm mol J<sup>-1</sup>. <sup>c</sup> due to very low emission intensity no emission maxima can be obtained.

	A		B		C	
	Average	Effect	Average	Effect	Average	Effect
1	0.95	-0.78	1.36	-0.37	1.28	-0.45
2	1.99	0.26	1.85	0.12	1.44	-0.29
3	2.25	0.52	1.98	0.25	2.46	0.73

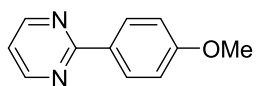
Factor	$S^a$	dof <sup>b</sup>	$V^c$	F-ratio <sup>d</sup>	Explained % <sup>e</sup>
A	2.834	2	1.42	22.3	46.8
B	0.645	2	0.32	5.10	10.7
C	2.444	2	1.22	19.3	40.4
Residue	0.127	2	0.03		2.1
Total	6.051	8			100

<sup>a</sup> Sum of squared deviations from the mean. <sup>b</sup> degree of freedom, <sup>c</sup> variance: mean of squares per dof. <sup>d</sup> ratio between squared deviation and the mean of square residue. <sup>e</sup> relative effects of the factors on SP.

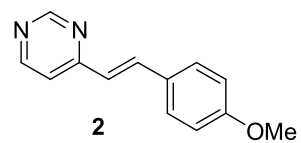


R = electron-donating group

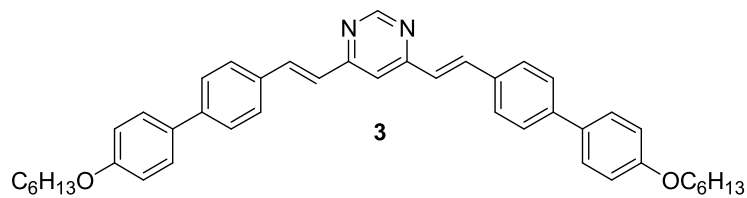
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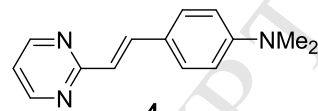
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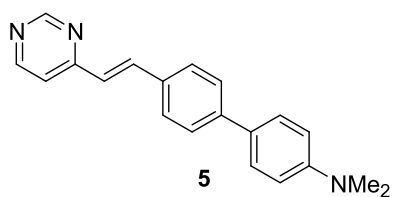
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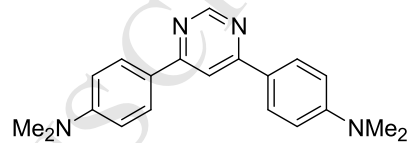
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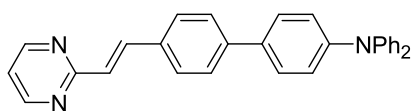
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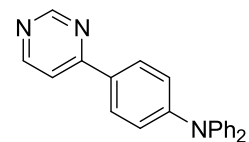
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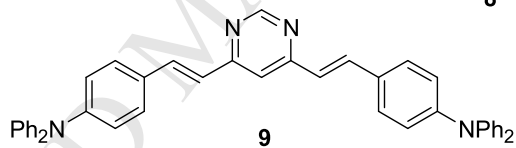
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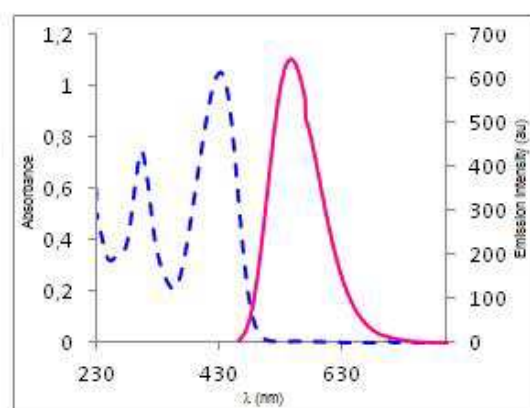
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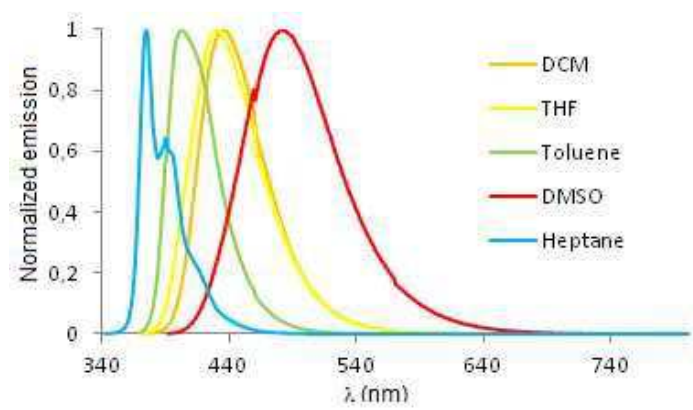


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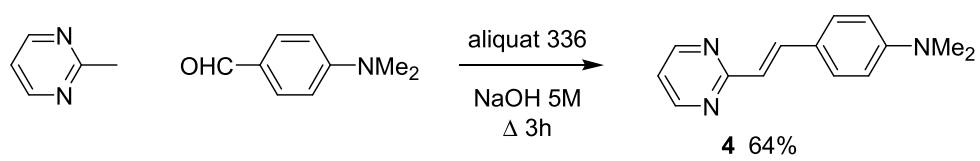


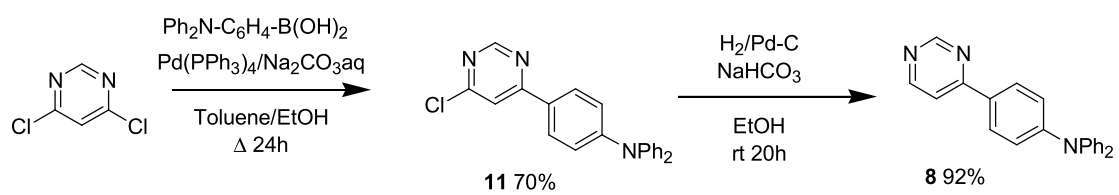
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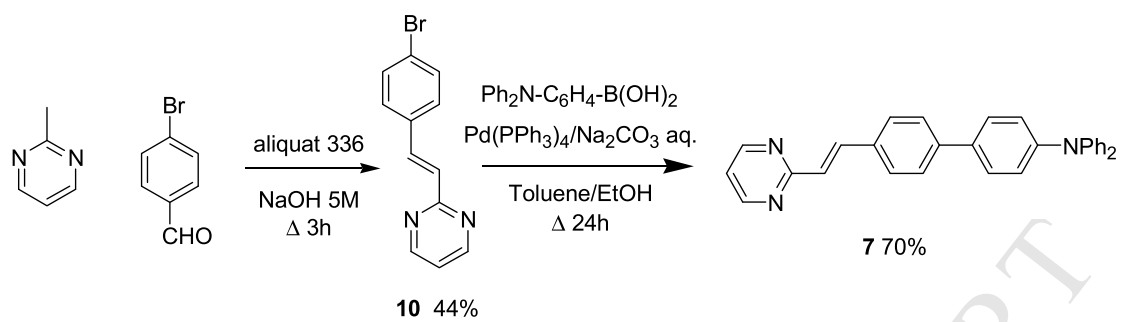


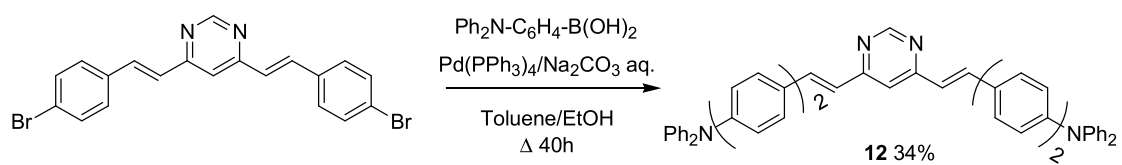






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The photophysical properties of pyrimidine chromophores have been studied.

The influence of three parameters has been studied by Taguchi methodology.

Internal charge transfer estimated by emission solvatochromy has been optimized.

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# Prediction of photophysical properties of pyrimidine chromophores using Taguchi method.

Charline Denneval,<sup>1</sup> Sylvain Achelle,<sup>2\*</sup> Christine Baudequin,<sup>1</sup> and Françoise Robin-le Guen.<sup>2</sup>

<sup>1</sup> Normandie Univ. COBRA, UMR 6014 et FR 3038; Univ. Rouen; INSA Rouen; CNRS, IRCOF, 1 rue Tesnière, 76821 Mont Saint Aignan Cedex, France

<sup>2</sup> Institut des Sciences Chimiques de Rennes UMR CNRS 6226, IUT de Lannion, rue Edouard Branly, BP 30219, F22302 Lannion Cedex, France

Corresponding author: sylvain.achelle@univ-rennes1.fr Tel: +33 (0)2 96 46 94 48 Fax : + 33 (0)2 96 46 93 54.

## Electronic supporting informations

Effect of each level of each factor on $\lambda_{em}$ in nm	S1
Analysis of variance (ANOVA) for on $\lambda_{em}$ in nm.	S2
Calculated and experimental photophysical data (in CH <sub>2</sub> Cl <sub>2</sub> ) from literature of some pyrimidine chromophores.	S2
$\lambda_{em}$ (nm) versus $\Delta E_T(30)$ (J/mol) for compounds 1-9 and 12	S3
Copy of <sup>1</sup> H and <sup>13</sup> C NMR spectra of compounds 4, 7, 8 and 10-12	S6
References	S11

**Table S1.** Effect of each level of each factor on  $\lambda_{em}$  in nm

	A		B		C	
	Average	Effect	Average	Effect	Average	Effect
1	419	-57	453	-24	424	-52
2	492	16	490	14	477	0

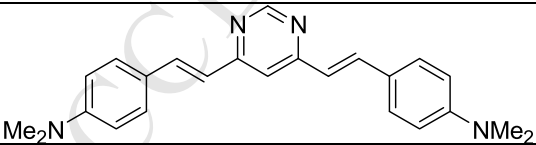
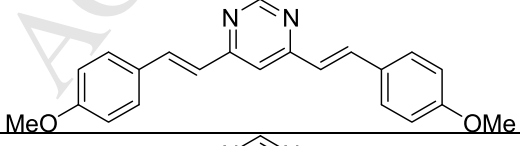
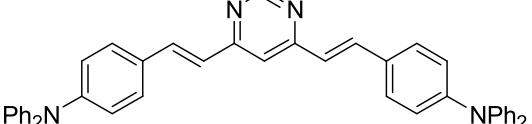
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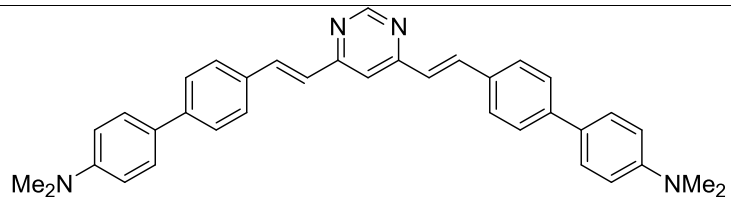
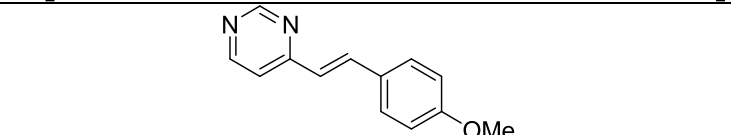
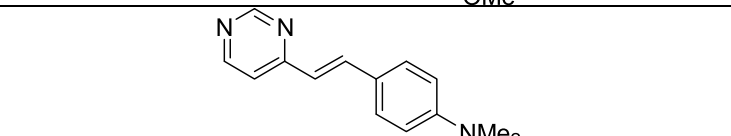
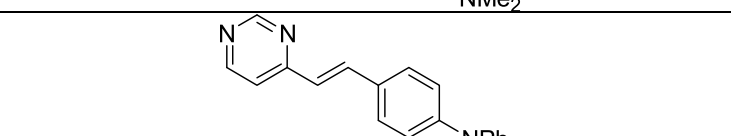
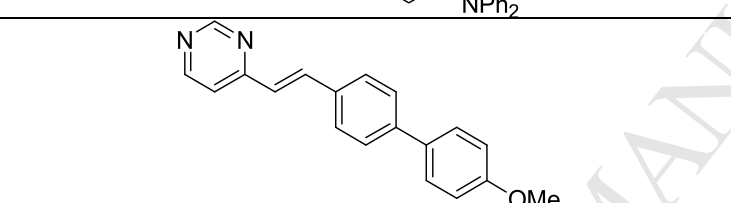
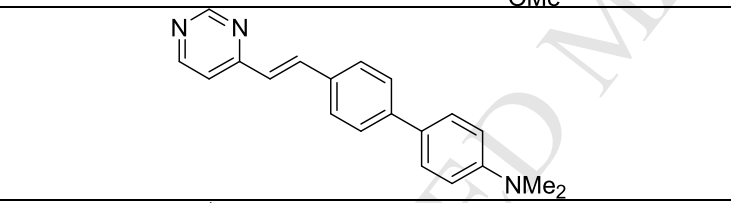
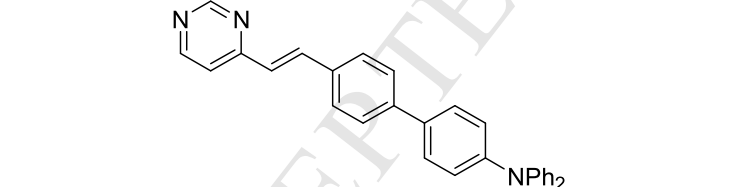
**Table S2.** Analysis of variance (ANOVA) for on  $\lambda_{em}$  in nm.

Factor	S <sup>a</sup>	dof <sup>b</sup>	V <sup>c</sup>	F-ratio <sup>d</sup>	Explained % <sup>e</sup>
A	15672	2	7836	13.2	44.3
B	2520	2	1260	2.13	7.1
C	16017	2	8009	13.5	45.3
Residue	1183	2	591		3.3
Total	35394	8			100

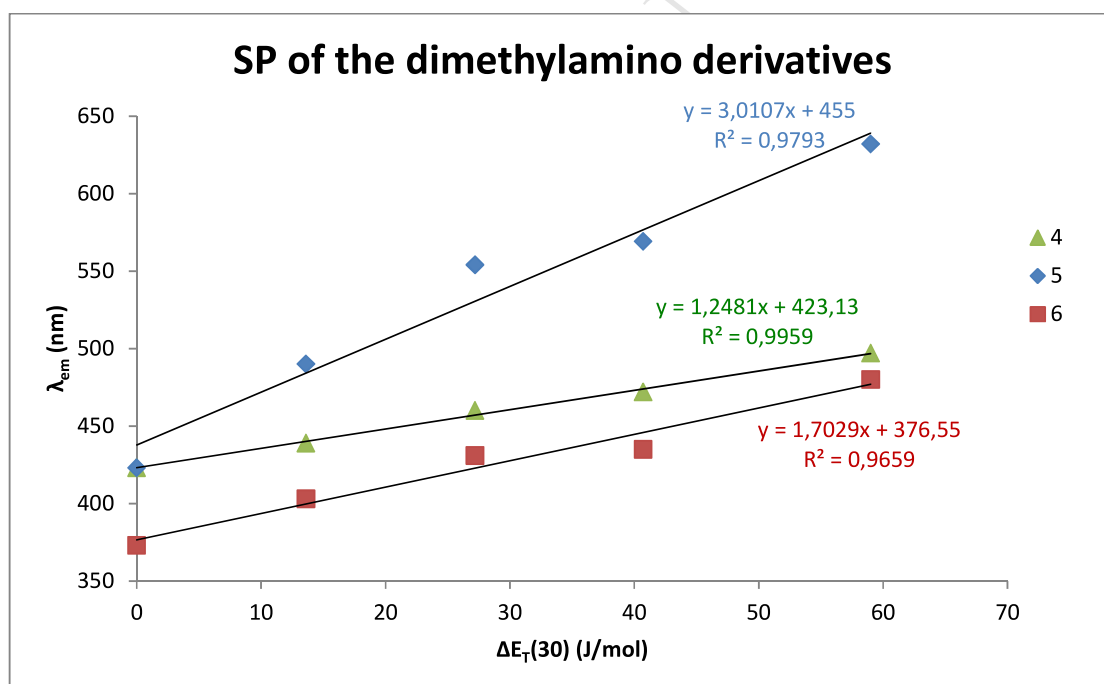
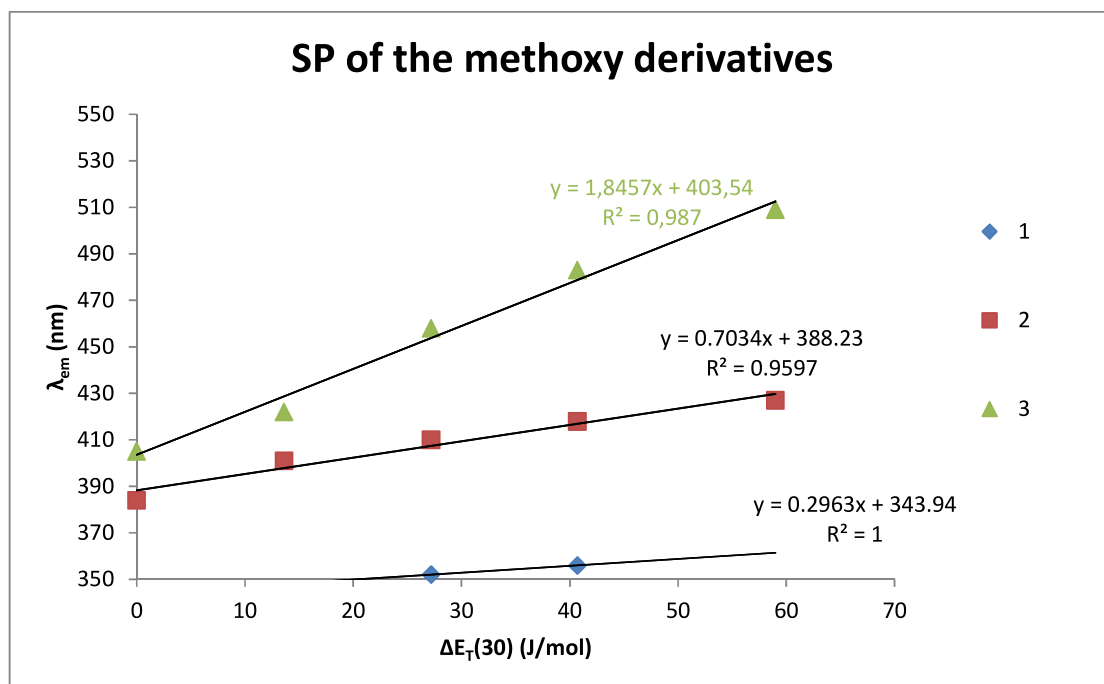
<sup>a</sup> Sum of squared deviations from the mean <sup>b</sup> degree of freedom <sup>c</sup> variance: mean of squares per dof <sup>d</sup>ratio between squared deviation and the mean of square residue <sup>e</sup> relative effects of the factors on  $\lambda_{em}$ .

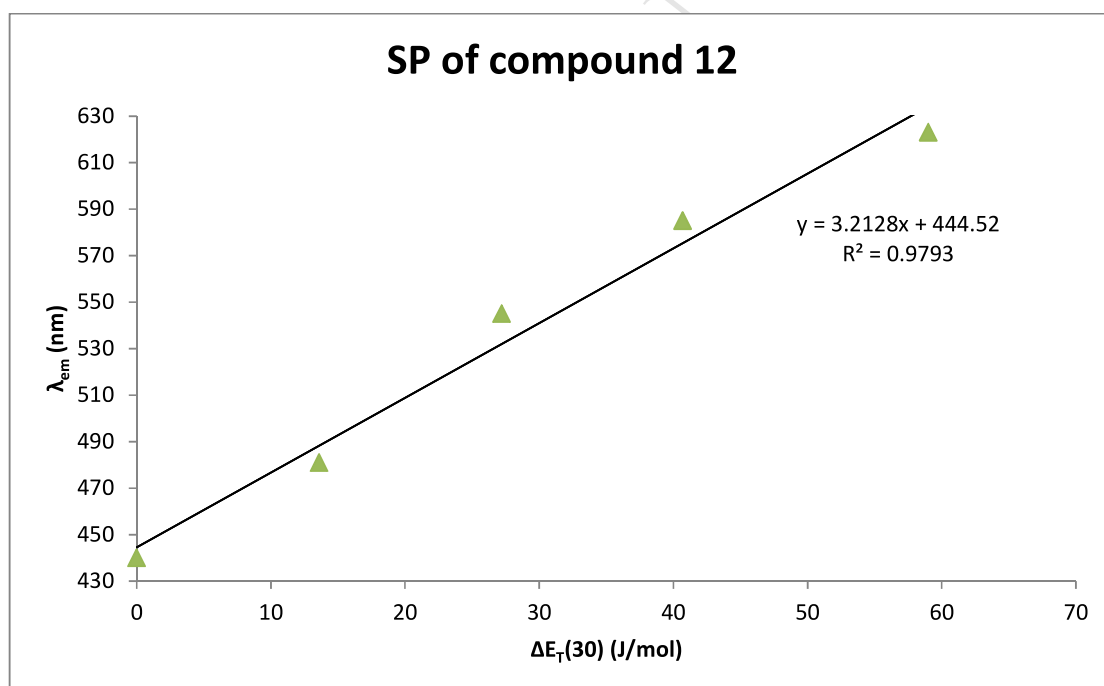
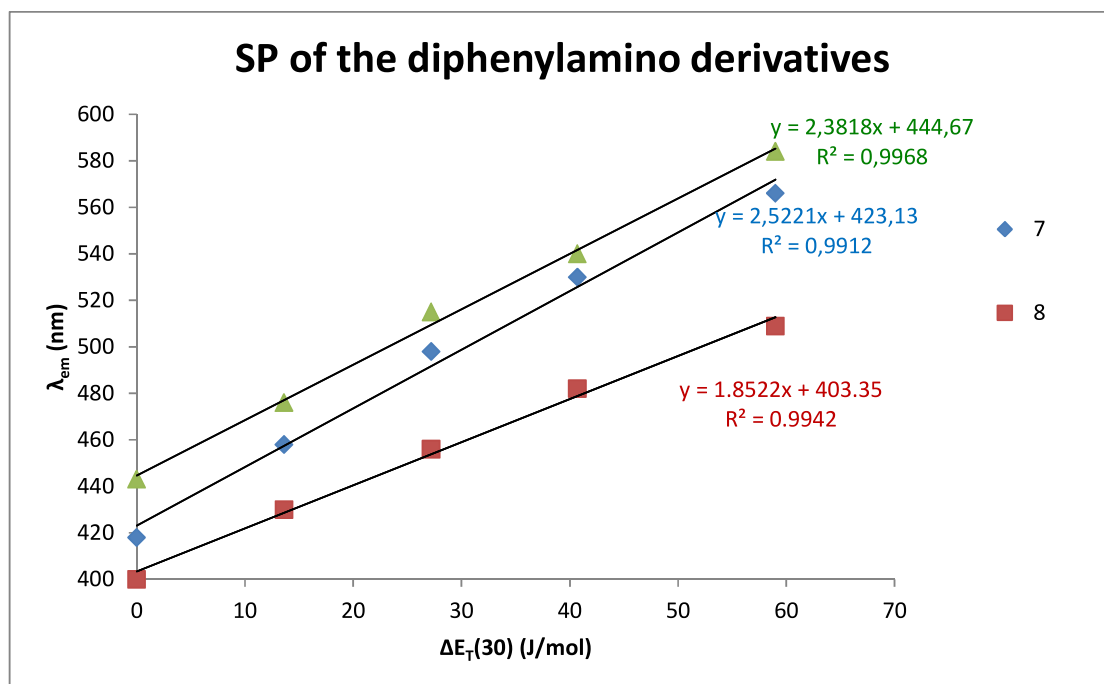
**Table S3.** Calculated and experimental photophysical data (in CH<sub>2</sub>Cl<sub>2</sub>) from literature of some pyrimidine chromophores.<sup>1</sup>

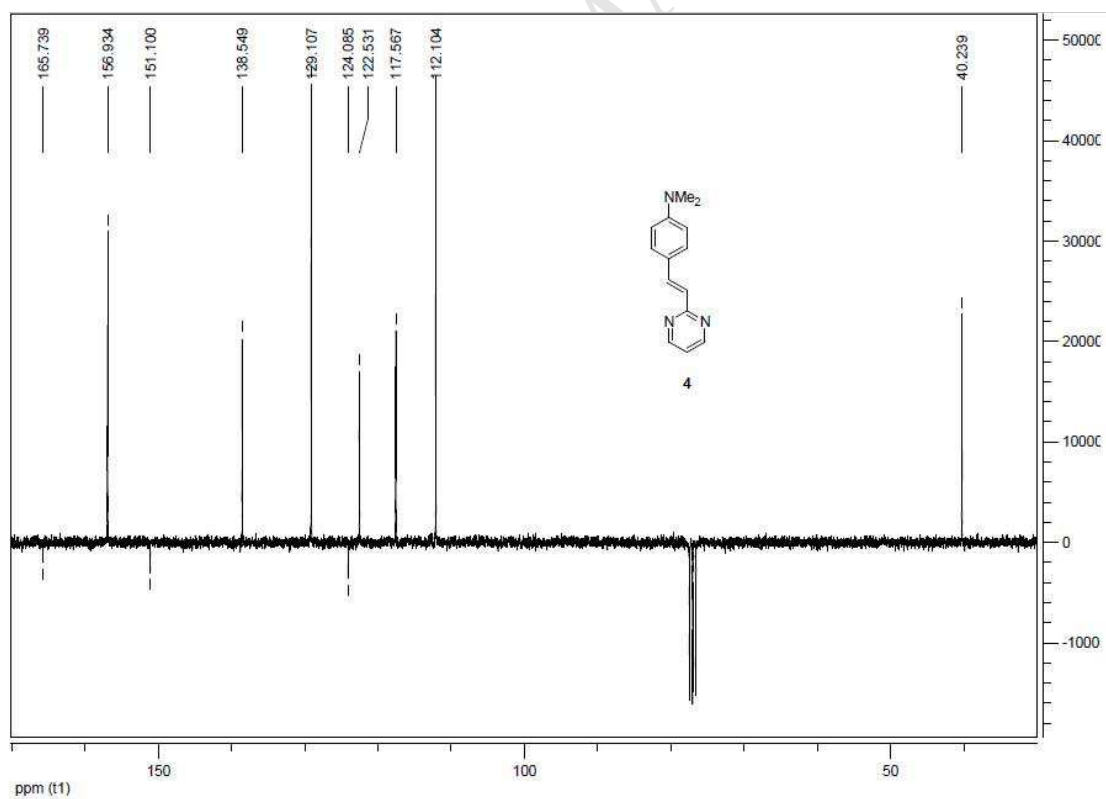
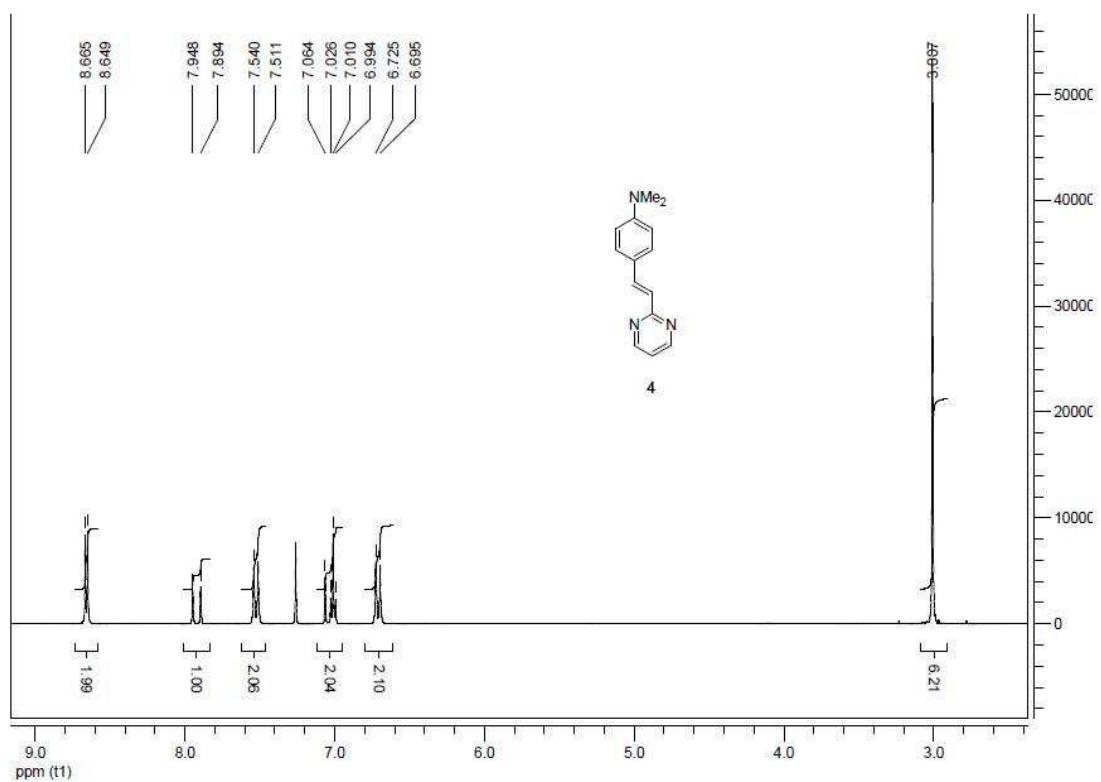
Compounds	Calculated $\lambda_{abs}$ in nm (experimental $\lambda_{abs}$ in nm)	Calculated $\lambda_{em}$ in nm (experimental $\lambda_{em}$ in nm)
	421 (429)	502 (530)
	371 (353)	429 (406)
	429 (427)	527 (540)

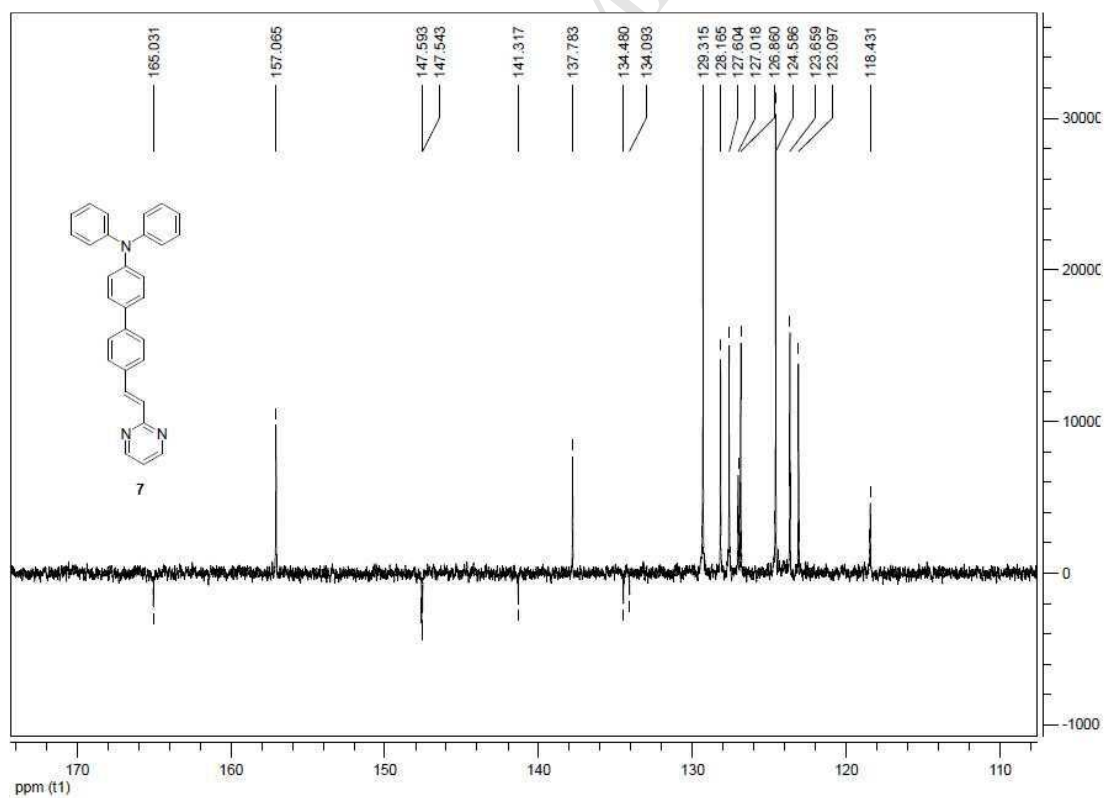
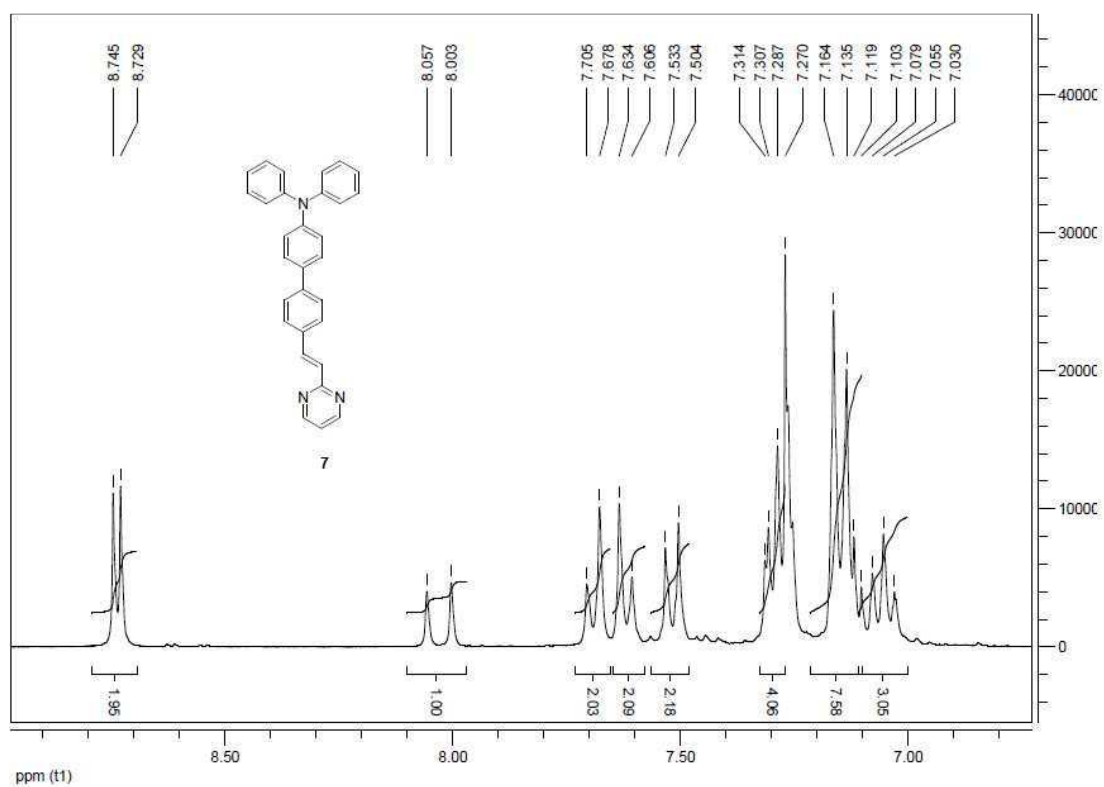
 <chem>CN(C)c1ccc(cc1)/C=C/C2=CN=CN=C2/C=C/c3ccc(cc3)N(C)C</chem>	417 (407)	553 (592)
 <chem>COC1=CC=C(C=C1)/C=C/C2=CN=CN=C2</chem>	342 (338)	433 (418)
 <chem>CN(C)C1=CC=C(C=C1)/C=C/C2=CN=CN=C2</chem>	392 (393)	506 (488)
 <chem>Nc1ccc(cc1)/C=C/C2=CN=CN=C2</chem>	400 (400)	531 (526)
 <chem>COC1=CC=C(C=C1)/C=C/C2=CN=CN=C2/C=C/c3ccc(cc3)C4=CC=C(C=C4)</chem>	338 (346)	484 (447)
 <chem>CN(C)C1=CC=C(C=C1)/C=C/C2=CN=CN=C2/C=C/c3ccc(cc3)C4=CC=C(C=C4)</chem>	388 (386)	557 (570)
 <chem>Nc1ccc(cc1)/C=C/C2=CN=CN=C2/C=C/c3ccc(cc3)C4=CC=C(C=C4)</chem>	396 (384)	582 (563)

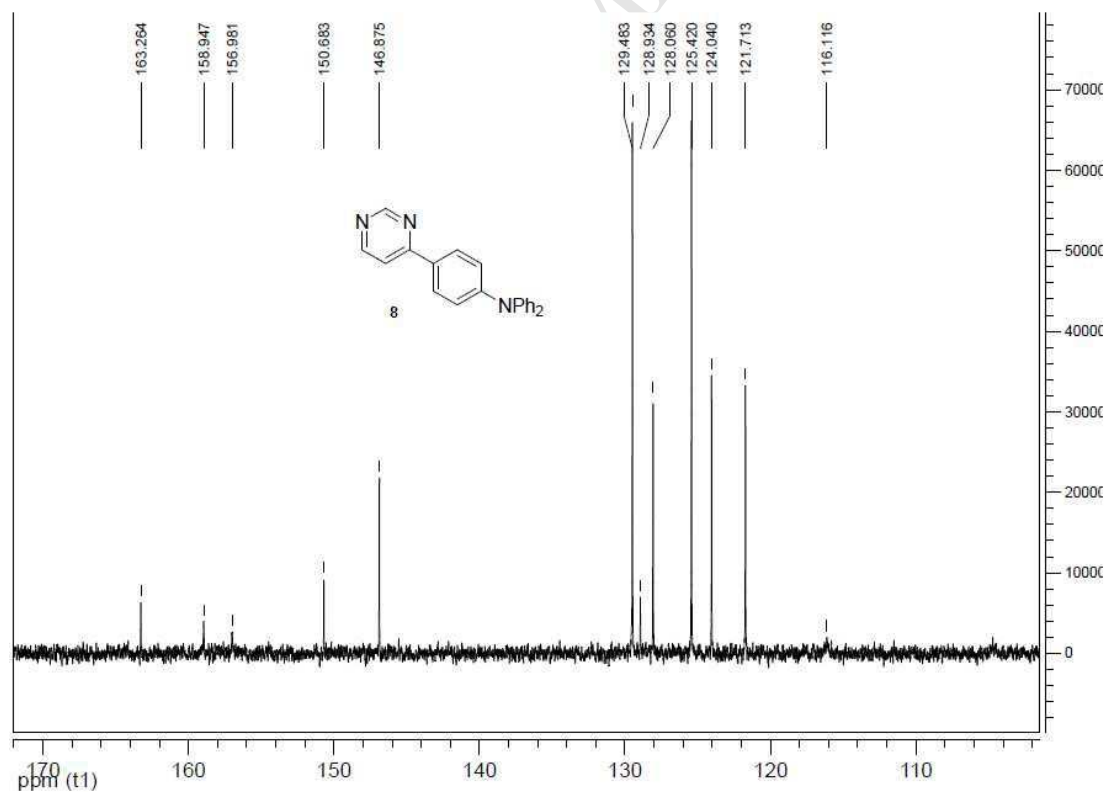
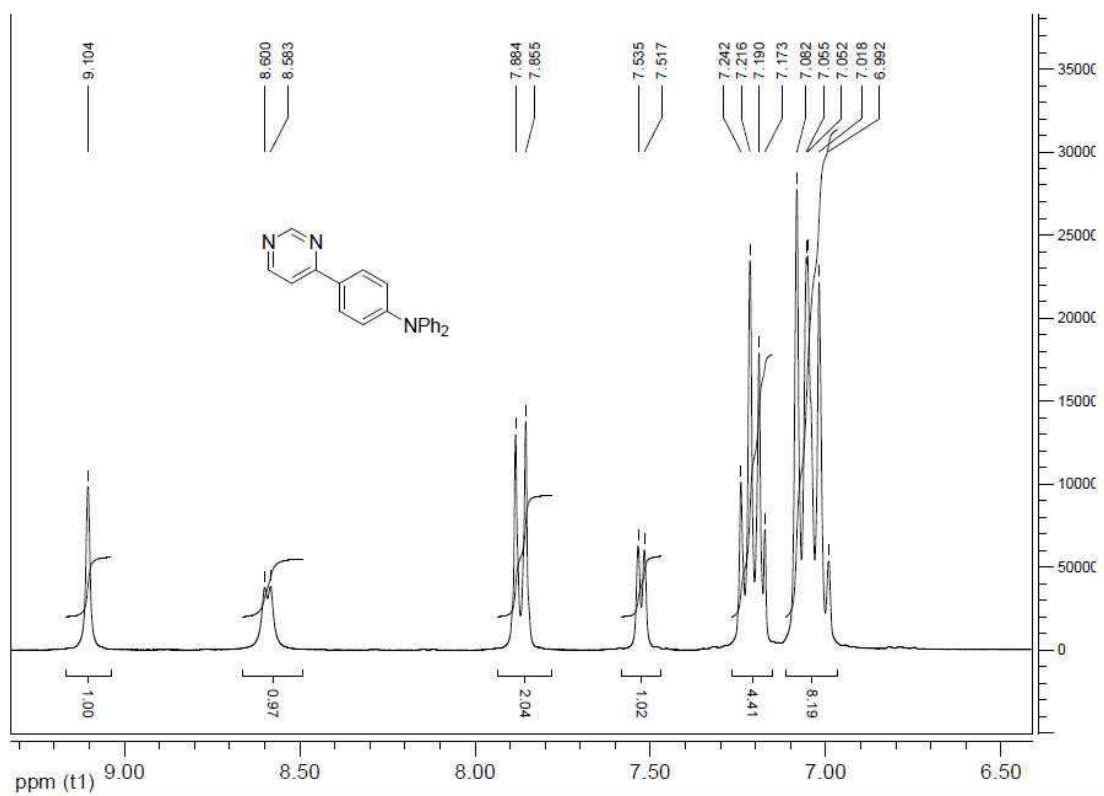


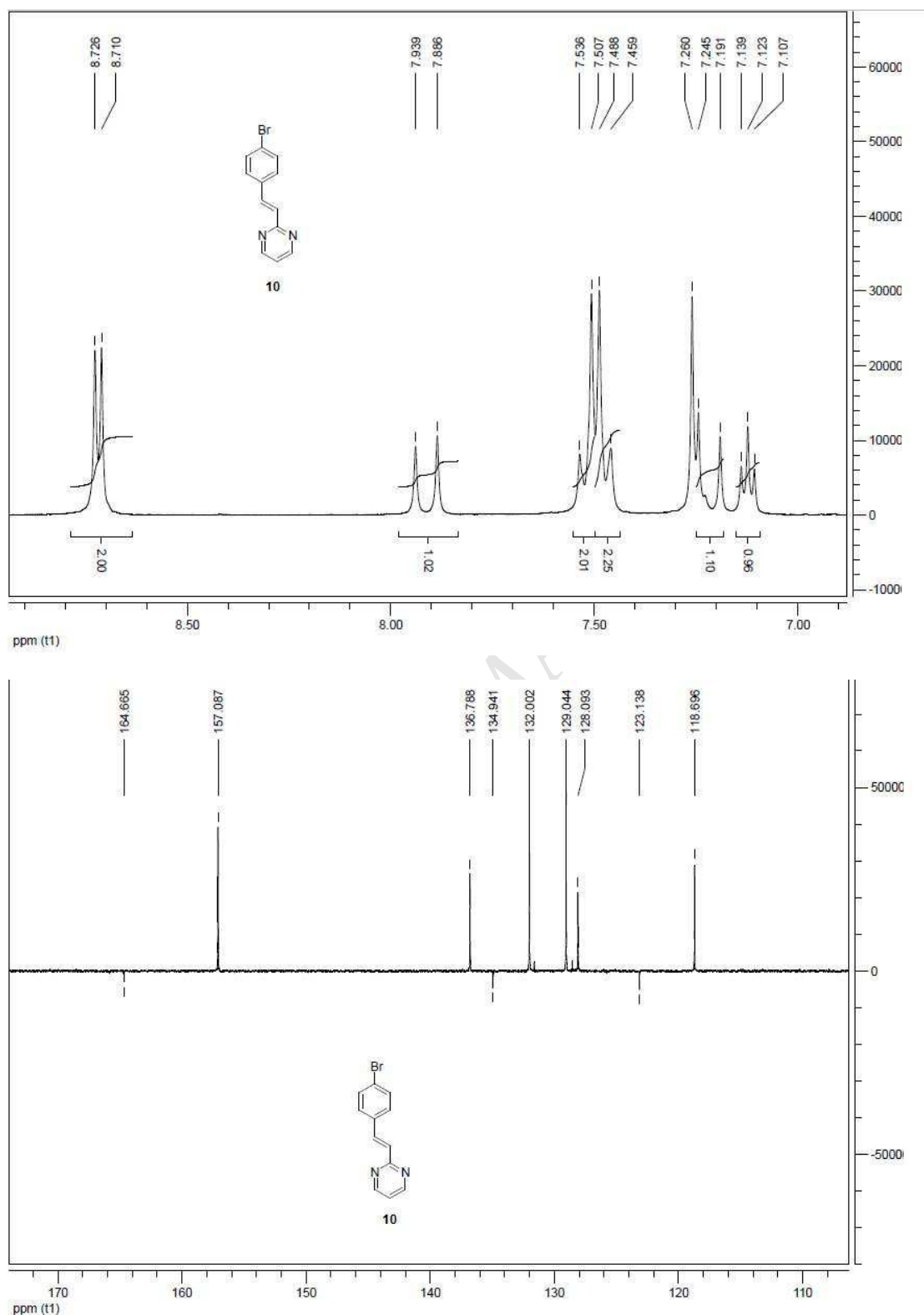


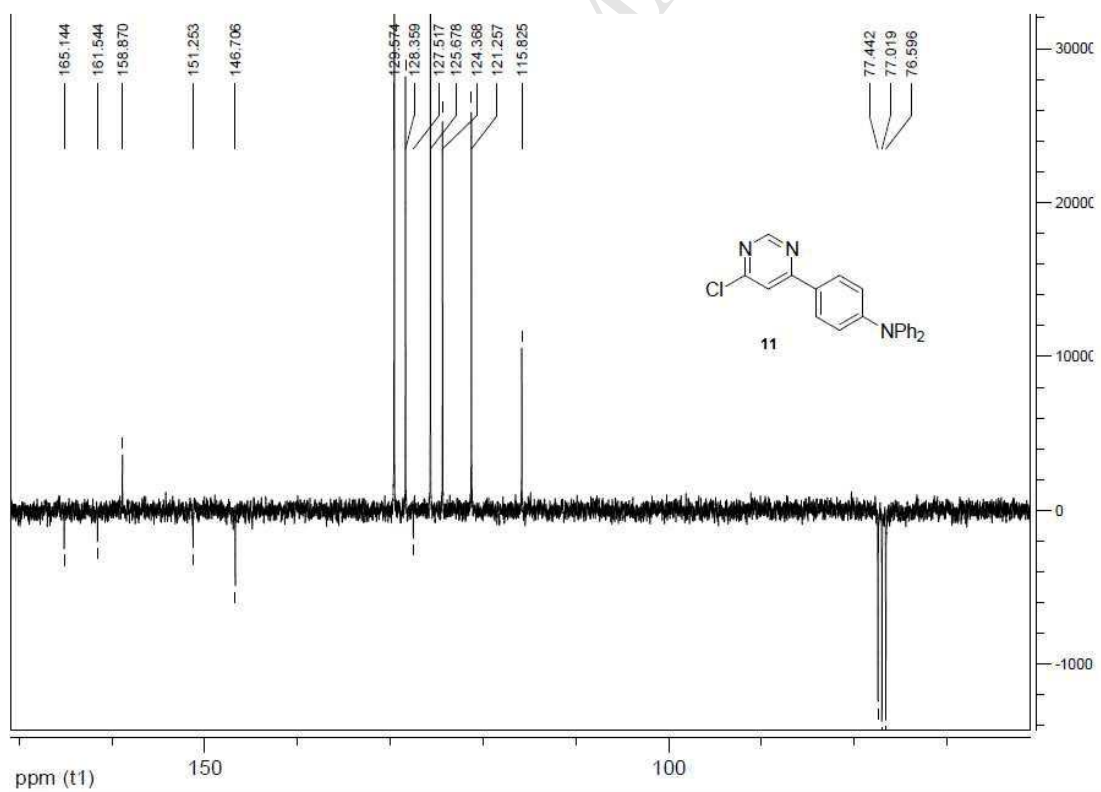
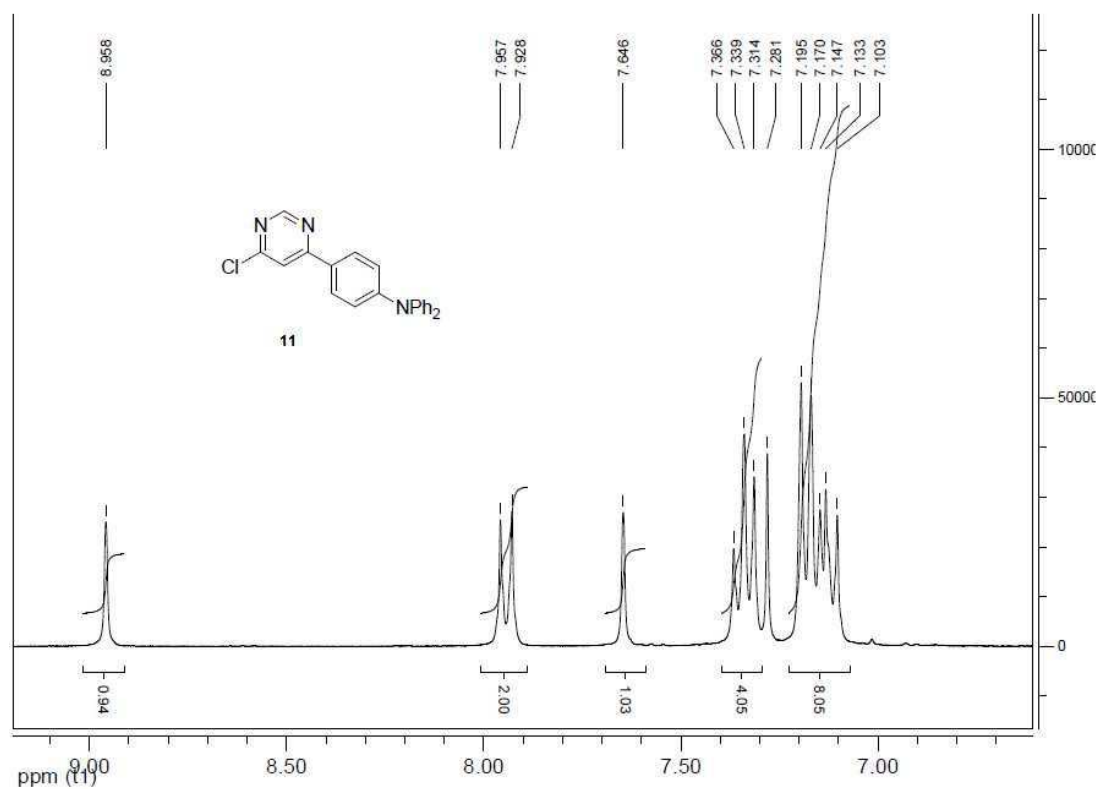


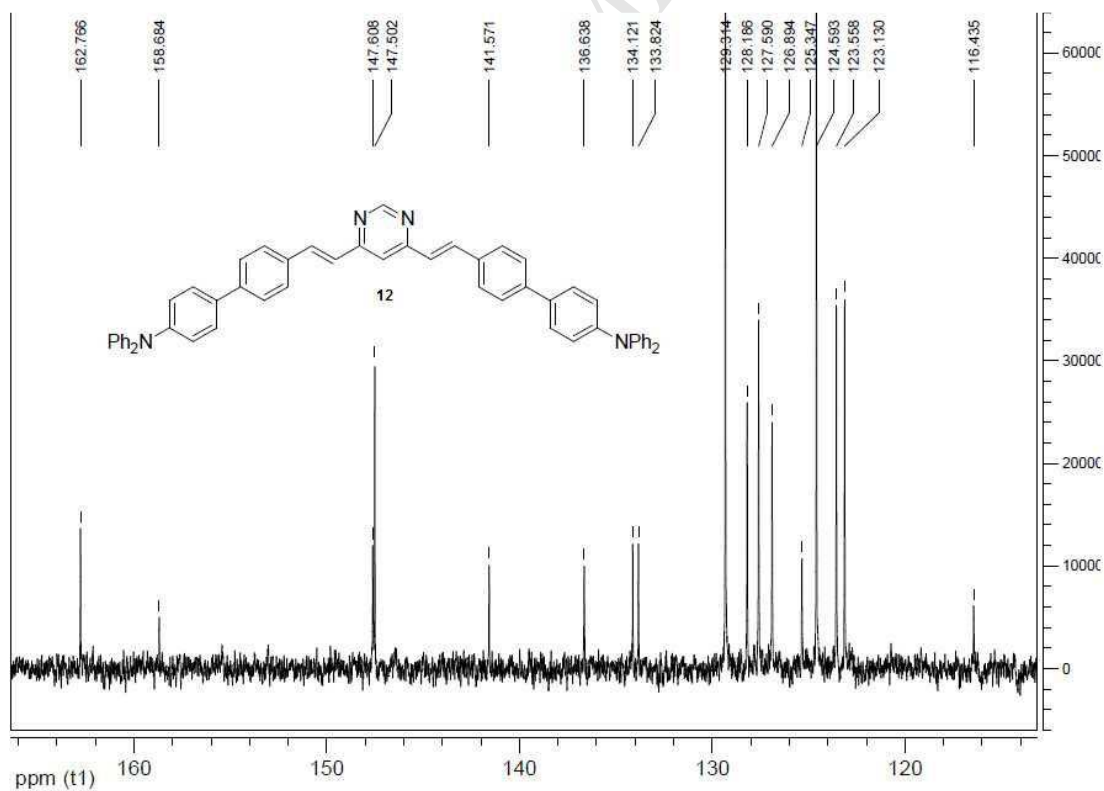
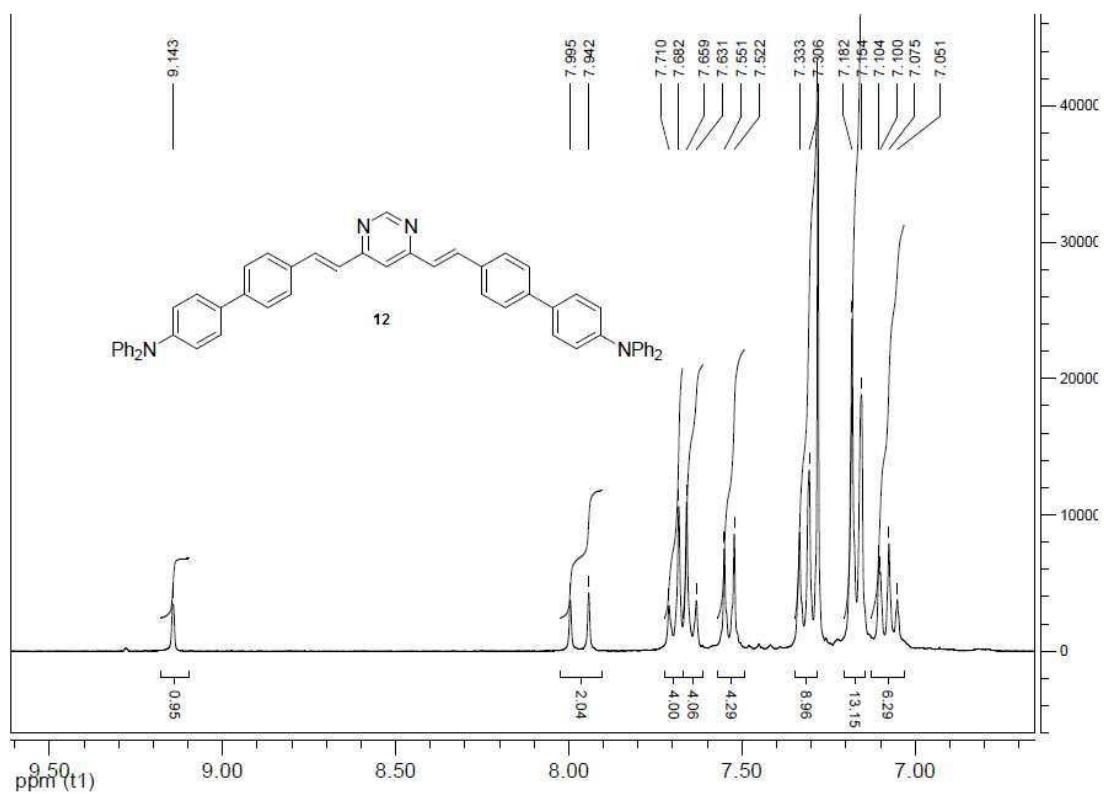














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<sup>1</sup> a) Achelle S, Barsella A, Baudequin C, Caro B, Robin-le Guen F. Synthesis and photophysical investigation of a series of push-pull arylvinylidiazine chromophores. *J Org Chem* 2012;77:4087-96. b) Achelle S, Nouira I, Pfaffinger B, Ramondenc Y, Plé N, Rodríguez-López J. V-shaped 4,6-bis(arylvinyl)pyrimidine oligomers: synthesis and optical properties. *J Org Chem* 2009;74:3711-7.

ACCEPTED MANUSCRIPT