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# Methylenepyran based dipolar and quadrupolar dyes: synthesis, electrochemical and photochemical properties

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### A R T I C L E I N F O

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### ABSTRACT

This paper presents the synthesis of a series of push–pull and quadrupolar  $\pi$ -conjugated structures incorporating pro-aromatic methylenepyran electron-donor groups and various electron-attracting groups. Some of the methylenepyran derivatives were oxidized by I<sub>2</sub> to give, after reduction by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, bismethylenepyran compounds via successive steps.

The electrochemical redox properties of methylenepyrans **5**–**9** and extended bismethylenepyrans **10**, **14**, and **15** determined by cyclic voltammetry indicate the formation of redox bistable systems with high bistability. Oxidation of the dimers obtained from **5** to **9** was also described. All compounds are colored and slightly fluorescent (except some bismethylenepyran derivatives). Some compound second-order non-linear optical properties were investigated, and large positive values of  $\mu\beta$  were obtained. A positive dimer effect was also observed for bispyran derivatives.

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### 1. Introduction

Donor–acceptor  $\pi$ -conjugated (D– $\pi$ –A) materials with both electron-donating and electron-accepting groups linked by a  $\pi$ -conjugated bridge have been extensively studied during the past decades due to their useful applications as sensitizers for dye-sensitized solar-cells (DSSCs),<sup>1</sup> emitters of organic light emitting diodes (OLEDs),<sup>2</sup> and various fluorescence sensors.<sup>3</sup>

Push-pull molecules with large delocalized  $\pi$ -electron systems are also typical second and third order nonlinear optic (NLO) chromophores.<sup>4</sup> Quadrupolar D- $\pi$ -A- $\pi$ -D structures also exhibit third order NLO properties. Second-order NLO materials have found applications in green lasers obtained from red sources through frequency doubling, in second-harmonic generation microscopy or in terahertz wave generation.<sup>5</sup> Third order NLO, in particular twophoton absorption (TPA) materials have also attracted considerable attention due to their applications in photodynamic therapy, confocal microscopy, optical power limiting and 3D data storage, and microfabrication.<sup>6</sup> Unlike inorganic materials, organic compounds used for NLO applications offer several advantages, such as easy syntheses, well-defined structure, easily tunable properties,

0040-4020/\$ – see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2013.07.066 and large optical nonlinearities and responses.  $\gamma$ -Methylenepyrans are versatile six-membered heterocycles with a pro-aromatic electron-donor character. It is well-known that chromophores incorporating aromatic subunits display lower  $\beta$  values than the corresponding polyenes of the same conjugation length, since their ground states are usually dominated by neutral, aromatic forms that lose resonance energy on charge separation.<sup>7</sup> One way to circumvent this drawback consists of incorporating a molecular fragment whose aromaticity will increase upon charge transfer. In this context,  $\gamma$ -methylenepyrans, which acquire the aromatic character of pyrylium upon internal charge transfer, are particularly attracting as donor part in push-pull structures. The use of such molecular fragments in the structure of NLO chromophores has already been described in the literature.<sup>8</sup> Moreover,  $\pi$ -conjugated structures incorporating  $\gamma$ -methylenepyran building blocks have also been described as interesting redox systems.<sup>9</sup> In particular, it has been described that oxidative dimerization of methylenepyrans bearing exocyclic ferrocenyl groups leads to the formation of bispyrilium salts via a radical cation intermediate. Subsequent deprotonation led to extended diferrocenylbispyran, which were then oxidized into unsaturated bispyrilium salts.<sup>10</sup>

On the other hand, diazines are six-membered aromatics with two nitrogen atoms. Three different structures can be distinguished based on the relative position of the nitrogen atoms: pyridazine (1,2-diazine), pyrimidine (1,3-diazine), and pyrazine (1,4-diazine). Diazines are very attractive electron accepting building blocks for





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the synthesis of push–pull, quadrupolar, and octupolar structures. Such structures exhibit high fluorescence due to internal charge transfer, important TPA properties and can be used as dyes for DSSCs.<sup>11–13</sup> The possibility to protonate, form hydrogen bonds, and chelate the diazine rings also present additional advantages.

Recently, some of us have described the NLO properties of two pyrimidine  $\gamma$ -methylenepyran derivatives.<sup>14</sup> In the present article, we describe the synthesis, the electrochemical and the optical properties of a series of push–pull, bispush–pull, and quadrupolar structures with an extended  $\pi$ -conjugated core incorporating  $\gamma$ -methylenepyrans as electron-donating parts and various electron-accepting groups, in particular diazine rings.

### 2. Results and discussion

### 2.1. Synthesis

The key intermediate for synthesis of push-pull structures is alkyne **4**. This compound can be obtained in two steps from 4-trimethylsilylethynyl-benzaldehyde **1** and phosphonium salt  $2^{15}$  (Scheme 1). The first step is a Wittig reaction<sup>16</sup> leading to intermediate **3** with good yield and the second step consists of the deprotection of the trimethylsilyl group with quasi-quantitative yield.

It has been reported that alkynyldiazines can be obtained from iododiazines by Sonogashira cross-coupling under mild synthetic conditions with good yield.<sup>18</sup> Similar conditions were used to synthesize building block **4** and a variety of monoiodo and diiododiazines leading to push–pull structures **11–13** and quadrupolar compounds **14**. **15**, with moderate to good yield (Scheme 3).

Dithiafulvenes and methylenepyrans have been reported to dimerize in the presence of oxidant by oxidative coupling via a radical cation intermediate.<sup>10b,19</sup> This method was used with some of the methylenepyrans described (compounds **5**–**9**) using diiode as oxidant (Scheme 4). Addition of a reducing agent ( $Na_2S_2O_3$ ) to the reaction mixture gave bismethylenepyran coupling products **16**–**20**, with moderate yield. This suggests that under such oxidative conditions, the formation of the dimers proceeds from the following successive steps: (1) dimerization of compounds **5**–**9** via a radical cation intermediate leading to bispyrylium salts. (2) Deprotonation of the salts to give bismethylenepyrans **16**–**20**. (3) Oxidation of the neutral dimers to dicationic pyrylium species, which were then reduced by  $Na_2S_2O_3$  to give bismethylenepyrans **16**–**20**.

All new compounds were soluble in THF, chloroform, and dichloromethane and were characterized using <sup>1</sup>H and <sup>13</sup>C NMR and high-resolution mass analysis. These materials were also perfectly stable in the solid state and did not require special storage conditions.



Scheme 1. Reagents and conditions: (i) *n*-BuLi, THF, −78 °C→rt, 2 h (ii) K<sub>2</sub>CO<sub>3</sub>, MeOH/CH<sub>2</sub>Cl<sub>2</sub>, rt, overnight.

The intermediate **4** can be involved in a copper/palladiumcatalyzed Sonogashira cross-coupling reaction with a variety of substituted bromobenzenes (Scheme 2).<sup>17</sup> Compounds **5–8** have been obtained in moderate to good yield. It should be noted that a small proportion of dimer **10** is systematically formed during the reaction, even when using  $Pd(PPh_3)_4$  instead of  $Pd(PPh_3)_2Cl_2$  as palladium catalyst. Aldehyde **8** can be used in a Knoevenagel condensation reaction with malononitrile leading to dicyano derivative **9**.

#### 2.2. Electrochemical studies

The redox properties of the series of pyrans **5–9** and **11–13**, extended bispyrans **10**, **14**, and **15**, and diarylacetylene bispyran **16–20** (Table 1 and Fig. 1) were investigated by cyclic voltammetry in  $CH_2Cl_2$  in the presence of  $NBu_4BF_4$  as supporting electrolyte. All potentials are given versus  $FeCp_2^+/FeCp_2$  couple.

The cyclic voltammogram of  $\mathbf{9}$  (Fig. 1a) shows an irreversible anodic peak at 0.31 V and, on the reverse scan, an irreversible



Scheme 2. Reagents and conditions: (i) bromobenzene derivative, Pd(PPh\_3)<sub>2</sub>Cl<sub>2</sub>, Cul, THF, NHiPr<sub>2</sub>, 60 °C, overnight (ii) 2 equiv malononitrile, AcOH/AcONa, benzene, reflux, 5 h.



Scheme 3. Reagents and conditions (i) iododiazine, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, THF, NEt<sub>3</sub>, rt, overnight.



Scheme 4. Reagents and conditions (i) I2, CH2Cl2, rt, overnight (ii) Na2S2O3.

cathodic peak is observed at -0.85 V. As previously described for the pyridyl, phenyl, and ferrocenyl methylenepyrans,<sup>10,16</sup> these observations are consistent with the formation of a pyrylium radical cation **9**<sup>+</sup>, which is transformed into a bispyrylium compound **9**<sup>2+</sup>

#### Table 1

Electrochemical data for pyran and bispyran compounds, (*E* vs, FeCp<sub>2</sub><sup>+</sup>/FeCp<sub>2</sub>) in  $CH_2Cl_2$  with  $NBu_4BF_4$  as supporting electrolyte at 0.1 V s<sup>-1</sup>

	$E_{\rm pa}(1)/V^{\rm a}$	$E_{\rm pc}$ (2)/V <sup>b</sup>	$E_{1/2}$ (3)/V, ( $\Delta E_{1/2}$ /mV)
5	0.31	-0.87	
6	0.32	-0.86	
7	0.32	-0.89	
8	0.32	-0.88	
9	0.31	-0.85	
10	0.31	-0.84	
11	0.31	-0.84	
12	0.34	-0.85	
13	0.35	-0.87	
14	0.33	-0.84	
15	0.33	-0.83	
16			-0.16, (63)
17			-0.16, (63)
18			-0.16, (98)
19			-0.17, (102)
20			-0.15, (70)

<sup>a</sup> Irreversible peak.

<sup>b</sup> Irreversible peak on the reverse cathodic scan.

 $(\sigma_{C-C} \text{ bond making})$ . This dication is irreversibly reduced at -0.85 V to a dipyranyl radical, which evolves into the initial methylenepyran **9** through the breaking of a  $\sigma_{C-C}$  bond. Unlike the chemical oxidation by I<sub>2</sub>, the deprotonation to bismethylenepyran was not observed. As indicated in Table 1, the whole series of pyran compounds **5–9** exhibited a similar behavior. As expected, our molecular redox systems displayed high bi-stability properties, as shown by the peak separation value  $\Delta E = E_{\text{pa}} (1) - E_{\text{pc}} (2)$  of 1.16 V found between the irreversible reduction and oxidation peak observed for compound **9**.

Extended bismethylenepyrans **10**, **14**, and **15** displayed essentially an identical behavior (Table 1), as shown by their voltammograms exhibiting an irreversible oxidation peak and an irreversible reduction peak at potential values very similar to those of compounds **5–9**. Such electrochemical behavior that was already observed,<sup>14</sup> differs from that of other methylenepyrans bearing alkenyl spacers, for which dimerization did not occur.<sup>9,20</sup> Previous voltammetry studies have shown that vinylogues of bispyrans can be sequentially oxidized to pyranyl–pyrylium radical cations and then to pyrylium dications.<sup>9,20</sup> Based on the substitution of the exocyclic carbon, the oxidation of the bispyrans proceeded either via two separated one electron reversible waves or via coalescence of the two reversible waves indicating that the removal of the two electrons occurred at a close potential.<sup>10b,20b</sup>

The cyclic voltammogram of bispyran **20** (Fig. 1b) shows a reversible system at  $E_{1/2}$  (3)=-0.15 V ( $\Delta E_{1/2}$ =70 mV). The redox behavior of **20** resulting in the formation of the bispyrylium cation **20**<sup>2+</sup> suggests that the system  $E_{1/2}$  (3) corresponds to two singleelectron waves coalescing to one two-electron oxidation wave (compression of potential). As shown in Table 1, a comparable reversible system was observed with the whole series of bispyrans **16**-**20** (-0.17 V< $E_{1/2}$  (3)<-0.15 V). Finally, comparison of the potential values shows that the dimers **16**-**20** have been oxidized at a potential lower than that of their corresponding monomer **5**-**9**. This explains the oxidation of the bismethylenepyrans formed by deprotonation during the I<sub>2</sub> oxidative coupling. Therefore, the isolation of dimers **16**-**20** required the use of a reducing agent.

### 2.3. Linear and nonlinear optical properties

The UV/vis and photoluminescence (PL) spectroscopic data of various oligomers carried out in dichloromethane at 25 °C are presented in Table 2. The measurements were performed using low concentration solutions  $(1.0 \times 10^{-5} - 3.0 \times 10^{-5} \text{ M} \text{ for UV/vis})$ 



**Fig. 1.** Cyclic voltammograms of (a) pyran **9** in CH<sub>2</sub>Cl<sub>2</sub>+NBu<sub>4</sub>BF<sub>4</sub> (T=293 K, C=8.00.10<sup>-4</sup> M,  $\nu$ =0.1 V s<sup>-1</sup>, WE:Pt) and (b) bispyran **20** in CH<sub>2</sub>Cl<sub>2</sub>+NBu<sub>4</sub>BF<sub>4</sub> (T=293 K, C=2.00.10<sup>-4</sup> M,  $\nu$ =0.1 V s<sup>-1</sup>, WE:Pt).

Table 2 UV/vis and photoluminescence (PL) data in  $CH_2Cl_2$  solution

Compd	UV/vis $\lambda_{max}$ , nm ( $\varepsilon$ , mM <sup>-1</sup> cm <sup>-1</sup> )	PL $\lambda_{max}$ , nm	Stokes shift cm <sup>-1</sup>
5	414 (40.5)	555	6137
6	432 (34.1)	551	4999
7	403 (33.9)	457	2932
8	422 (23.9)	610	7303
9	361 (40.5), 463 (34.9)	528	2657
10	437 (71.4)	534	4157
11	414 (28.3)	537	5533
12	409 (15.4)	514	4995
13	414 (32.1)	495	3953
14	441 (54.6)	614	6389
15	429 (52.4)	557	5357
16	361 (26.2), 453sh (23.5)	576	4714
17	371 (19.5), 454sh (25.5)	a	a
18	360 (18.9), 425sh (16.4)	a	a
19	355 (32.3), 446sh (25.8)	a	a
20	366 (54.9), 470sh (25.7)	a	a

<sup>a</sup> No emission signal has been detected.

measurements and  $1.0 \times 10^{-6} - 3.0 \times 10^{-6}$  M for PL measurements). For example, the spectra of the derivatives **5**, **9**, and **14** are shown in Fig. 1. Under these conditions, self-absorption effects were not observed. All compounds were photo-stable under the analysis conditions (Fig. 2).

All compounds showed absorption wavelengths ( $\lambda_{max}$ ) in the visible region (403-463 nm). In all cases, a second or even a third absorption band of higher energy could be observed. All compounds, except bispyrans 17–20, were slightly fluorescent in the green to orange region (495-614 nm) with emission quantum yield below 0.01. In general, large Stokes shifts were obtained for the compounds under investigation. This observation indicates significant differences (vibrational, electronic, geometric) between the Franck–Condon state and the excited state. When comparing the UV/vis spectra of compounds 5–9. a red shift of the visible absorption band was observed upon increase of the electronattracting strength of the aromatic groups. As expected, the dicyano derivative **9** exhibited the highest value of  $\lambda_{abs}$ . As a result of the extension of the conjugation, compound 10 exhibited a red shifted absorption compared to structures substituted by moderately attracting groups (5 and 7). The position of the visible absorption band of the diazine derivatives **11–13** (409–414 nm) indicates that the diazinyl groups exhibit an electron-attracting strength similar to that of a *p*-cyanophenyl group (compound 5:  $\lambda_{abs}$ =414 nm). In case of dimers **14** and **15** the two methylenepyran parts are not conjugated due to 2,4 (or 6,4) substitution of the pyrimidine ring, however a bathochromic effect is observed in comparison with compounds 12 and 13. Oxidative coupling



Fig. 2. Normalized UV/vis (solid line) and emission spectra (broken line) of compounds 5, 14, and 16.

products (**16–20**) spectra also show a red-shifted visible absorption band compared to those of the compounds **5–7**, **9**, and **11** with noteworthy broadened peaks.

Second-order nonlinear properties were studied in CHCl<sub>3</sub> solution using the electric-field-induced second-harmonic generation technique (EFISH), which provides information about the scalar product  $\mu\beta$  (2 $\omega$ ) of the vector component of the first hyperpolarisability tensor  $\beta$  and the dipole moment vector.<sup>21</sup> This product is derived according to Eq. 1 and considering  $\gamma_0(-2\omega,\omega,\omega,0)$ , the third-order term, as negligible for the push–pull compounds under consideration. This approximation is usually used for push–pull organic and organometallic molecules.

$$\gamma_{\text{FFISH}} = \mu\beta/5kT + \gamma_0(-2\omega,\omega,\omega,0) \tag{1}$$

Measurements are performed at 1907 nm, obtained from a Raman-shifted Nd:YAG<sup>+</sup> laser source, which allowed us to work in conditions far from the resonance peaks of the compounds we were investigating (**5**–**7**, **9**, **11**, and **16**). It should be noted that the sign and values of  $\mu\beta$  depend on the 'direction' of the transition implied in the NLO phenomena and on the direction of the ground-state dipole moment. When  $\beta$  and  $\mu$  are a parallel (antiparallel), positive (negative) maxima  $\mu\beta$  values are obtained.

The  $\mu\beta$  values of compounds **5–7**, **9**, **11**, and **16** (Table 3) are positive indicating excited states more polarized than the ground state ( $\mu e > \mu g$ ). In addition, this implies that the ground and excited states are polarized in the same direction. The  $\mu\beta$  values observed are relatively high, and similar to or higher than Disperse Red 1, as reported in literature.<sup>22</sup> As expected, the trifluoromethyl derivative 6, which does not contain a mesomeric attracting group, exhibited the lowest  $\mu\beta$  value ( $\mu\beta$ =200×10<sup>-48</sup> esu). On the contrary the highest value was obtained for the dicyano derivative 9  $(\mu\beta=1150\times10^{-48} \text{ esu})$ , confirming the attracting strength of the malononitrile group.<sup>23</sup> Cyano derivatives **5** and pyrazinyl compound **11** exhibited similar  $\mu\beta$  values (350 and 380×10<sup>-48</sup> esu, respectively) confirming that the attracting strength of the pyrazine ring is similar to a *p*-cyanophenyl substituent. It should be noted that compound **11** displayed a higher  $\mu\beta$  value than that of 2-[2-(4-*N*,*N*-dimethylamino-phenyl)-vinyl]-pyrazine  $(230 \times 10^{-48} \text{ esu})^{3c}$ confirming the good donor strength of the methylenepyran part. When comparing the  $\mu\beta$  values of compounds **5** and **16**, the value obtained for compound **16** is more than the double that obtained for compound **5**, indicating a positive dimer effect  $(350 \times 10^{-48} \text{ esu})$ vs  $830 \times 10^{-48}$  esu). As the total dipole moment  $\mu$  depends on the dihedral angle  $\alpha$  formed by the two pyran units ( $\alpha$ =0 corresponds to an s-cis conformation and  $\mu$  is maximum,  $\alpha = 180^{\circ}$  corresponds to an s-trans conformation and  $\mu=0$ ), these results suggest that the dimer compounds exist in a pseudo *cisoid* staggered conformation, as found from X-ray analysis, for similar extended ferrocenyl disubstituted bispyran.<sup>10</sup> In such conformation, the conjugation between the two methylenepyran moieties via the central C-C bond is low and the two push-pull branches are globally pointing out in the same direction amplifying the NLO response. Similar enhancement of NLO response by dimerization has already been described for V-shaped binaphthol derivatives.<sup>24</sup> Finally it should be noted that the  $\mu\beta$  value observed for nitro derivative **7** is probably underestimated due to the possible aggregation at the concentration used for the measurement.

### **Table 3** $\mu\beta$ values for compounds **5–7**, **9**, **11**, **14**, and **16**

	5	6	7	9	11	16
$\mu\beta \ [10^{-48} \ \mathrm{esu}]^{\mathrm{a}}$	350	200	700	1150	380	830

<sup>a</sup>  $\mu\beta$  (2 $\omega$ ) at 1907 nm in CHCl<sub>3</sub>. Molecular concentrations used for the measurements were in the range  $10^{-3}$ – $10^{-2}$  M.  $\mu\beta\pm10\%$ .

### 3. Conclusion

In conclusion, we have successfully synthesized and characterized a series of push-pull and quadripolar structures incorporating methylenepyran as pro-aromatic electron-donating moieties. The redox properties were studied: cvclic voltammograms of pyrans and some bispyrans derivatives exhibited irreversible oxidation peak around 0.31 V and, on the reverse scan, an irreversible reduction peak around -0.85 V. As shown previously, the oxidation peak corresponds to the formation of a radical cation, which dimerizes to a bispyrilium salt ( $\sigma_{C-C}$  bond making) and the reduction peak to the formation of the initial compound ( $\sigma_{C-C}$  bond breaking). These redox systems have a high bi-stability as illustrated by the difference between the two potential values ( $\Delta E > 1.1$  V). I<sub>2</sub> oxidation of methylenepyrans followed by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> reduction resulted in the isolation of bismethylenepyran derivatives. These compounds were reversibly oxidized (two-electron wave) to bispyrylium cation. The optical properties have been also studied: all the compounds were colored and slightly fluorescent (except some bispyran derivatives). The second-order nonlinear optical properties have been investigated for some of the compounds and large of positive  $\mu\beta$  values were obtained. A positive dimer effect on the  $\mu\beta$ values was obtained for V-shaped bispyran derivatives Further investigations of this effect are currently underway.

### 4. Experimental section

#### 4.1. General methods

All solvents were reagent grade. The starting materials were purchased from Sigma-Aldrich or Acros and used without further purification. Compound 1 was obtained according to literature procedures.<sup>25</sup> For air and moisture-sensitive reactions, all glassware pieces were flame-dried and cooled under nitrogen. NMR spectra were recorded in CDCl<sub>3</sub>, on a Bruker Advance 300 spectrometer (<sup>1</sup>H at 300 MHz and  $^{13}$ C at 75 MHz). The chemical shifts  $\delta$  are reported in parts per million relative to the residual solvent (CHCl<sub>3</sub>). The coupling constants J are given in hertz. In the <sup>1</sup>H 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 <sup>13</sup>C NMR spectra, the nature of the carbons (C, CH, CH<sub>2</sub> or CH<sub>3</sub>) was determined by performing a JMOD experiment. Melting points (°C) were measured on a Kofler hot-stage with a precision of  $2^{\circ}$  ( $\pm 2^{\circ}$ 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 60F<sub>254</sub>) 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/ vis 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 for recording the emission spectra. All solutions were measured with optical densities below 0.1. Cyclic voltammetry experiments were performed on a µ-AUTOLAB III potentiostat monitored by a computer. All the potentials were standardized against the ferrocene-ferricenium couple. Ferrocene was added as an internal standard at the end of the experiments.

### **4.2.** [4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenylethynyl]-trimethyl-silane (3)

A *n*-BuLi solution (4 mL, 2.5 M in pentane, 9.9 mmol) was added to a solution of phosphonium salt **2** (5.26 g, 9 mmol) in THF (50 mL) at -78 °C under nitrogen. The reaction mixture was stirred at this temperature for 15 min, and 4-[(timethylsilyl)ethynyl]benzaldehyde **1** (1.82 g, 9 mmol) was added. The resulted mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed and the residue was purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:2) to give compound **3** as orange brown solid, yield 70% (2.6 g); mp: 124–125 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.25 (s, 9H), 5.88 (s, 1H), 6.39 (d, *J*=1.8 Hz, 1H), 6.95 (d, *J*=1.3 Hz, 1H), 7.30 (d, 2H, *J*=8.1 Hz), 7.41–7.47 (m, 8H), 7.70–7.75 (m, 4H); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.0 (C), 151.2 (C), 138.9 (C), 133.9 (CH), 133.7 (CH), 133.4 (C), 133.2 (C), 132.1 (CH), 130.2 (C), 129.4 (CH), 129.2 (CH), 128.7 (CH), 128.6 (CH), 127.5 (CH), 124.9 (CH), 124.6 (CH), 119.7 (C), 113.6 (CH), 108.5 (CH), 105.7 (C), 102.0 (CH), 94.3 (C), 0.1 (CH<sub>3</sub>). HRMS (ESI/ASAP) *m/z* calculated for C<sub>29</sub>H<sub>27</sub>OSi [M+H]<sup>+</sup>: 419.1831, found 419.1832.

### 4.3. 4-(4-Ethynyl-benzylidene)-2,6-diphenyl-4H-pyran (4)

Potassium carbonate (K<sub>2</sub>CO<sub>3</sub> (0.91 g, 6.6 mmol)) was added to a solution of compound **3** (2.53 g, 6 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (2:1, 100 mL). The mixture was stirred at room temperature overnight under air, diluted with CH<sub>2</sub>Cl<sub>2</sub>, and washed with water. The organic layer was separated, dried over MgSO<sub>4</sub>, and evaporated under vacuum leading to compound **4**, an orange brown solid, yield 94% (1.94 g); mp: 135–136 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.12 (s, 1H), 5.90 (s, 1H), 6.40 (d, *J*=1.8 Hz, 1H), 6.97 (d, *J*=1.3 Hz, 1H), 7.34 (d, 2H, *J*=8.2 Hz), 7.40–7.49 (m, 8H), 7.73–7.78 (m, 4H); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.2 (C), 151.2 (C), 139.3 (C), 133.9 (CH), 133.7 (CH), 133.4 (C), 133.2 (C), 132.3 (CH), 130.4 (C), 129.4 (CH), 129.2 (CH), 128.7 (CH), 128.6 (CH), 127.5 (CH), 125.0 (CH), 124.6 (CH), 118.6 (C), 113.4 (CH), 108.5 (CH), 101.9 (CH), 84.2 (C), 77.2 (C). HRMS (ESI/ASAP) *m/z* calculated for C<sub>26</sub>H<sub>18</sub>O [M]<sup>+</sup>: 346.1358, found 346.1360.

### 4.4. General procedure A for Sonogashira cross-coupling reaction

Bromobenzene derivatives (0.5 mmol), compound **4** (173 mg, 0.5 mmol), Cul (5 mg, 5 mol %), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (18 mg, 5 mol %) were added to a mixture of THF (5 mL) and *i*-Pr<sub>2</sub>NH (5 mL). The suspension was stirred at 60 °C overnight under nitrogen atmosphere. The resulting solution was diluted with a mixture of water and dichloromethane (1:1, 20 mL) and the organic layer separated. The aqueous layer was extracted with dichloromethane (2×20 mL). The combined organic extracts were dried over MgSO<sub>4</sub>, filtered, and evaporated.

## **4.5. 4-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenyl-ethynyl]-benzonitrile** (5)

Orange solid; obtained according to the general procedure A and purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1); yield 70% (157 mg); mp: 241–242 °C; <sup>1</sup>H NMR (300 MHz, THF- $d_8$ )  $\delta$  6.16 (s, 1H), 6.83 (s, 1H), 7.29 (s, 1H), 7.69–7.58 (m, 10H), 7.83 (d, *J*=8.1 Hz, 2H), 7.92 (d, *J*=8.1 Hz, 2H), 8.02 (d, *J*=6.9 Hz, 4H); <sup>13</sup>C NMR and JMOD (75 MHz, THF- $d_8$ )  $\delta$  154.8 (C), 152.7 (C), 141.4 (C), 134.9 (C), 134.6 (C), 133.6 (CH), 133.4 (CH), 133.2 (CH), 132.1 (C), 126.4 (CH), 125.9 (CH), 120.2 (C), 119.4 (C), 115.1 (CH), 113.2 (C), 110.1 (CH), 103.3 (CH), 95.5 (C), 89.5 (C). HRMS (ESI/ASAP) *m/z* calculated for C<sub>33</sub>H<sub>22</sub>NO [M+H]<sup>+</sup>: 448.1701, found 448.1701.

### **4.6. 4-**[**4-**(**4-**Nitro-phenylethynyl)-benzylidene]-2,6-diphenyl-**4***H*-pyran (6)

Dark-red solid; obtained according to general procedure A and purified by column chromatography (SiO<sub>2</sub>, hexane/CH<sub>2</sub>Cl<sub>2</sub>, 1:1); yield 62% (145 mg); mp: 260–261 °C; <sup>1</sup>H NMR (300 MHz, THF- $d_8$ )

δ 6.17 (s, 1H), 6.84 (d, *J*=1.9 Hz, 1H), 7.30 (d, *J*=1.8 Hz, 1H), 7.57–7.71 (m, 10H), 7.91 (d, *J*=8.9 Hz, 2H), 8.03 (d, *J*=7.2 Hz, 4H), 8.43 (d, *J*=8.9 Hz, 2H); <sup>13</sup>C NMR: no measurement due to the low solubility of the compound. HRMS (ESI/ASAP) *m*/*z* calculated for C<sub>32</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 468.1600, found 468.1606.

### 4.7. 2,6-Diphenyl-4-[4-(4-trifluoromethyl-phenylethynyl)benzylidene]-4*H*-pyran (7)

Yellow solid; obtained according to general procedure A and purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1); yield 68% (167 mg); mp: 244–245 °C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  5.97 (s, 1H), 6.50 (s, 1H), 7.06 (s, 1H), 7.56–7.42 (m, 10H), 7.64 (d, *J*=8.7 Hz, 2H), 7.68 (d, *J*=8.7 Hz, 2H), 7.83–7.80 (m, 4H); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  153.3, 151.3, 139.4, 133.3, 133.0, 131.8, 131.7, 130.5, 129.5, 129.1, 128.6, 127.6, 125.3, 125.34, 125.29, 125.2, 124.9, 124.5, 118.9, 113.4, 108.5, 101.8, 92.3, 88.1. HRMS (ESI/ASAP) *m/z* calculated for C<sub>33</sub>H<sub>22</sub>OF<sub>3</sub> [M+H]<sup>+</sup>: 491.1623, found 491.1621.

## **4.8. 4-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenyl-ethynyl]-benzaldehyde (8)**

Orange solid; obtained according to general procedure A and purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:2); yield 75% (169 mg); mp: 250–251 °C; <sup>1</sup>H NMR (300 MHz, THF- $d_8$ )  $\delta$  6.16 (s, 1H), 6.83 (s, 1H), 7.30 (s, 1H), 7.70–7.56 (m, 10H), 7.86 (d, *J*=7.8 Hz, 2H), 8.09–8.01 (m, 6H), 10.16 (s, 1H); <sup>13</sup>C NMR and JMOD (75 MHz, THF- $d_8$ )  $\delta$  191.8 (C), 154.8 (C), 152.6 (C), 141.2 (C), 137.5 (C), 134.9 (C), 134.7 (C), 133.2 (CH), 132.0 (C), 130.8 (CH), 130.7 (CH), 130.5 (CH), 130.1 (CH), 130.0 (CH), 129.1 (CH), 126.3 (CH), 125.9 (CH), 120.5 (C), 115.2 (CH), 110.1 (CH), 106.0 (C), 103.3 (CH), 95.1 (C), 90.2 (C). HRMS (ESI/ASAP) *m/z* calculated for C<sub>33</sub>H<sub>23</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 451.1698, found 451.1703.

### **4.9.** 2-{4-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenylethynyl]-benzylidene}-malononitrile (9)

The compound 8 (165 mg, 0.37 mmol), malononitrile (49 mg, 0.74 mmol, 2 equiv), AcONa (1 mg), and AcOH (5-6 drops) were dissolved in benzene (10 mL) to form a suspension that was refluxed for 5 h. The reaction mixture was then allowed to cool; the solvent was evaporated and the residue was purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 3:2 then Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1). Yield 45% (83 mg) as a dark-red solid. Mp: 208–209 °C <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 5.95 (s, 1H), 6.49 (d, 1H, *J*=2 Hz), 7.06 (d, 1H, *J*=2 Hz), 7.42–7.52 (m, 8H), 7.54 (d, 2H, *J*=8 Hz), 7.67 (d, 2H, J=8 Hz), 7.78 (s, 1H), 7.78-7.84 (m, 4H), 7.91 (d, 2H, J=8 Hz); <sup>13</sup>C NMR and JMOD (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  159.1 (CH), 153.8 (C), 151.8 (C), 140.3 (C), 133.7 (C), 133.4 (C), 132.6 (CH), 132.5 (CH), 131.2 (CH), 130.6 (C), 130.4 (C), 130.0 (CH), 129.7 (CH), 129.1 (CH), 128.1 (CH), 125.4 (CH), 125.0 (CH), 119.0 (C), 114.4 (C), 113.8 (CH), 113.2 (C), 109.0 (CH), 102.3 (CH), 96.05 (C), 89.4 (C), 82.9 (C). HRMS (ESI/ASAP) *m*/*z* calculated for C<sub>36</sub>H<sub>23</sub>N<sub>2</sub>O [M–H]<sup>+</sup>: 499.1810, found 499.1807.

### 4.10. Butadiyne derivative (10)

Red solid; obtained as by-product during the procedure B. Yield 5–15% (17–52 mg); mp: 257–258 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  5.91 (s, 2H), 6.43 (s, 2H), 7.00 (s, 2H), 7.52–7.37 (m, 20H), 7.78–7.76 (m, 8H); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.3 (C), 151.3 (C), 139.7 (C), 134.2 (CH), 133.3 (C), 133.1 (C), 132.7 (CH), 130.7 (C), 129.5 (CH), 129.2 (CH), 128.7 (CH), 127.6 (CH), 125.0 (CH), 124.6 (CH), 118.3 (C), 113.4 (CH), 108.6 (CH), 102.0 (CH), 82.6 (C), 74.7 (CH). HRMS (ESI/ASAP) *m/z* calculated for C<sub>52</sub>H<sub>35</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 691.2631, found 691.2630.

### 4.11. General procedure B for Sonogashira cross-coupling reaction

Compound **4** (1 equiv per iodine atom), NEt<sub>3</sub> (0.5 mL), Cul (6 mol %), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (6 mol %) were added to iododiazine (1 mmol) in THF (5 mL). The suspension was stirred at room temperature overnight under nitrogen atmosphere. The suspension was then diluted with a mixture of water and dichloromethane (1:1, 20 mL) and the organic layer separated. The aqueous layer was extracted with dichloromethane (2×20 mL). The combined organic extracts were dried over MgSO<sub>4</sub>, filtered, and evaporated.

# **4.12. 2-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenyl-ethynyl]-pyrazine (11)**

Orange solid; obtained according to the general procedure B and purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1 then CH<sub>2</sub>Cl<sub>2</sub>, then CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 95:5); yield 48% (203 mg); mp: 156–157 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.91 (s, 1H), 6.43 (s, 1H), 7.01 (s, 1H), 7.46–7.40 (m, 8H), 7.59 (d, 2H, *J*=8 Hz), 7.77–7.76 (m, 4H), 8.48 (s, 1H), 8.58 (s, 1H), 8.77 (s, 1H); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.4 (C), 151.4 (C), 147.7 (CH), 144.5 (CH), 142.5 (CH), 140.7 (C), 140.2 (C), 133.3 (C), 133.1 (C), 132.4 (CH), 130.9 (C), 129.5 (CH), 129.2 (CH), 128.69 (CH), 128.66 (CH), 127.6 (CH), 125.0 (CH), 124.6 (CH), 117.8 (C), 113.3 (CH), 108.6 (CH), 101.9 (CH), 94.3 (C), 86.2 (C). HRMS (ESI/ASAP) *m/z* calculated for C<sub>30</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 425.1654, found 425.1757.

### 4.13. 2-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenylethynyl]-4,6-dimethyl-pyrimidine (12)

Orange solid; obtained according to the general procedure B and purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1 then CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 95:5); yield 47% (213 mg); mp: 185–186 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.51 (s, 6H), 5.89 (s, 1H), 6.42 (s, 1H), 6.96 (s, 1H), 6.99 (s, 1H), 7.44–7.35 (m, 8H), 7.63 (d, 2H, *J*=8 Hz), 7.77–7.74 (m, 4H); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  167.0 (C), 153.3 (C), 152.8 (C), 151.3 (C), 140.0 (C), 133.3 (C), 133.1 (C), 132.8 (CH), 130.7 (C), 129.4 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 127.4 (CH), 125.0 (CH), 124.6 (CH), 118.7 (CH), 117.9 (C), 113.5 (CH), 108.6 (CH), 102.0 (CH), 88.6 (C), 87.8 (C). HRMS (ESI/ASAP) *m/z* calculated for C<sub>32</sub>H<sub>24</sub>N<sub>2</sub>O [M]<sup>+</sup>: 452.1889, found 452.1883.

### 4.14. 4-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenylethynyl]-6-methoxy-pyrimidine (13)

Orange solid; obtained according to the general procedure B and purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1); yield 65% (244 mg); mp: 155–156 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.00 (s, 3H), 5.89 (s, 1H), 6.41 (d, 1H, *J*=2 Hz), 6.88 (d, 1H, *J*=2 Hz), 6.99 (d, 1H, *J*=2 Hz), 7.38 (d, 2H, *J*=8 Hz), 7.44–7.40 (m, 6H), 7.56 (d, 2H, *J*=8 Hz), 7.77–7.74 (m, 4H), 8.76 (d, 1H, *J*=2 Hz); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  169.7 (C), 158.5 (CH), 153.4 (C), 151.4 (C), 150.7 (C), 140.3 (C), 133.3 (C), 133.1 (C), 132.5 (CH), 130.9 (C), 129.5 (CH), 129.2 (CH), 128.7 (CH), 128.6 (CH), 127.6 (CH), 125.0 (CH), 124.6 (CH), 117.6 (CH), 113.3 (CH), 110.3 (CH), 108.6 (CH), 101.9 (CH), 93.6 (C), 87.1 (C), 54.0 (CH<sub>3</sub>). HRMS (ESI/ASAP) *m/z* calculated for C<sub>31</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M–H]<sup>+</sup>: 455.1759, found 455.1751.

### 4.15. 4,6-Bis-[4-(2,6-diphenyl-pyran-4-ylidenemethyl)-phenylethynyl]-pyrimidine (14)

Red solid; obtained according to the general procedure B and purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 4:1 then CH<sub>2</sub>Cl<sub>2</sub>, then CH<sub>2</sub>Cl<sub>2</sub>/MeOH 93:7); yield 72% (554 mg); mp: 204 °C (dec); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.92 (s, 2H), 6.44 (s, 2H),

7.02 (s, 2H), 7.47–7.42(m, 17H), 7.61(d, 2H, J=8 Hz), 7.77–7.75 (m, 8H), 9.16 (s, 1H); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.6 (C), 151.5 (C), 151.0 (C), 140.8 (C), 133.2 (C), 133.0 (C), 132.7 (CH), 133.2 (C), 129.6 (CH), 129.3 (CH), 128.71 (CH), 128.68 (CH), 127.6 (CH), 125.4 (CH), 125.0 (CH), 124.6 (CH), 117.2 (C), 113.2 (CH), 108.6 (CH), 101.9 (CH), 95.9 (C), 87.2 (C). HRMS (ESI/ASAP) m/z calculated for C<sub>56</sub>H<sub>37</sub>N<sub>2</sub>O<sub>2</sub> [M–H]<sup>+</sup>: 769.2855, found 769.2849.

### 4.16. 2,4-Bis-[4-(2,6-diphenyl-pyran-4-ylidenemethyl)-phenylethynyl]-pyrimidine (15)

Red solid; obtained according to the general procedure B and purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1 then CH<sub>2</sub>Cl<sub>2</sub>, then CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1); yield 40% (307 mg); mp: 125–126 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  5.92 (s, 2H), 6.44 (s, 2H), 7.02 (s, 2H), 7.34 (d, 1H, *J*=5.1 Hz), 7.47–7.37 (m, 16H), 7.60 (d, 2H, *J*=8 Hz), 7.66 (d, 2H, *J*=8 Hz), 7.79–7.76 (m, 8H), 8.72 (d, 1H, *J*=5.1 Hz); <sup>13</sup>C NMR and JMOD (75 MHz, CDCl<sub>3</sub>)  $\delta$  157.4 (CH), 153.7 (C), 153.6 (C), 151.68 (C), 151.65 (C), 151.5 (C), 140.9 (C), 140.5 (C), 133.44 (C), 133.40 (C), 133.3 (CH), 133.2 (CH), 133.1 (CH), 133.0 (CH), 131.3 (C), 131.0 (C), 129.7 (CH), 129.6 (CH), 129.4 (CH), 129.3 (CH), 128.80 (CH), 128.77 (CH), 127.8 (CH), 127.7 (CH), 125.1 (CH), 124.7 (CH), 121.4 (CH), 117.8 (C), 117.4 (C), 113.5 (CH), 113.3 (CH), 108.81 (CH), 108.78 (CH) 102.11 (CH), 102.07 (CH), 95.9 (C), 89.4 (C), 88.6 (C), 87.2 (C). HRMS (ESI/ASAP) *m*/*z* calculated for C<sub>56</sub>H<sub>37</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 769.2855, found 769.2852.

### 4.17. General procedure C for oxidative coupling

 $I_2$  (255 mg, 1 mmol) was added to a solution of methylenepyran (compounds **5**–**9**) (0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). After being stirred at room temperature overnight, the resulting black greenish mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution (20 mL). The mixture was kept under stirring for another 1 h, and then the orange organic layer was separated, washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and concentrated in vacuo.

### 4.18. Bispyrane derivative (16)

Red solid; obtained according to the general procedure C and purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>); yield 45% (40 mg); mp: 188 °C (dec); <sup>1</sup>H NMR (300 MHz, THF- $d_8$ )  $\delta$  6.86 (s, 2H), 7.22 (s, 2H), 7.69–7.48 (m, 20H), 7.80 (d, *J*=8.4 Hz, 4H), 7.89 (d, *J*=8.4 Hz, 4H), 7.90 (d, *J*=6.9 Hz, 4H), 7.96 (d, *J*=6.9 Hz, 4H); <sup>13</sup>C NMR and JMOD (75 MHz, THF- $d_8$ )  $\delta$  154.2 (C), 153.4 (C), 143.9 (C), 134.9 (C), 133.6 (CH), 133.4 (CH), 133.1 (CH), 131.1 (CH), 130.7 (CH), 130.6 (CH), 130.1 (CH), 130.0 (CH), 125.5 (C), 126.0 (CH), 125.5 (C), 121.3 (C), 119.3 (C), 113.2 (C), 107.4 (CH), 105.5 (CH), 95.2 (C), 89.5 (C). HRMS (ESI/ASAP) *m/z* calculated for C<sub>66</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub> [M<sup>-</sup>]<sup>+</sup>: 892.3084, found 892.3090.

### 4.19. Bispyrane derivative (17)

Red solid; obtained according to the general procedure C and purified by column chromatography (SiO<sub>2</sub>, hexane/CH<sub>2</sub>Cl<sub>2</sub>, 1:1); yield 30% (28 mg); mp: 192 °C (dec); <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>)  $\delta$  6.85 (d, *J*=2.0 Hz, 1H), 7.23 (d, *J*=2.0 Hz, 1H), 7.50–7.68 (m, 10H), 7.40–7.49 (m, 4H), 7.95 (d, *J*=7.2 Hz, 2H), 8.40 (d, *J*=8.9 Hz, 2H); <sup>13</sup>C NMR (125 MHz, THF-*d*<sub>8</sub>)  $\delta$  154.2, 153.4, 148.7, 144.1, 134.9, 134.8, 133.6, 133.2, 131.5, 131.2, 130.7, 130.6, 130.1, 130.0, 126.1, 126.0, 125.4, 125.0, 121.2, 107.4, 105.6, 96.2, 89.3. HRMS (ESI/ASAP) *m/z* calculated for C<sub>64</sub>H<sub>40</sub>N<sub>2</sub>O<sub>6</sub> [M·]<sup>+</sup>: 932.2881, found 932.2880.

### 4.20. Bispyrane derivative (18)

Orange solid; obtained according to the general procedure C and purified by column chromatography (SiO<sub>2</sub>, Petroleum Ether/CH<sub>2</sub>Cl<sub>2</sub>,

2:1); yield 32% (31 mg); mp: 260 °C (dec); <sup>1</sup>H NMR (300 MHz, THFd<sub>8</sub>)  $\delta$  6.86 (s, 2H), 7.23 (s, 2H), 7.66–7.51 (m, 20H), 7.84 (s, 8H), 7.89 (d, *J*=7.8 Hz, 4H), 7.95 (d, *J*=6.9 Hz, 4H); <sup>13</sup>C NMR and JMOD (75 MHz, THF-d<sub>8</sub>)  $\delta$  154.2 (C), 153.4 (C), 143.7 (C), 134.9 (C), 134.8 (C), 133.2 (CH), 133.1 (CH), 131.1 (CH), 130.63 (CH), 130.58 (CH), 130.5 (C), 130.1 (CH), 130.0 (CH), 129.1 (C), 126.8 (CH), 126.7 (CH), 126.1 (CH), 126.0 (CH) 125.6 (C), 121.6 (C), 107.4 (CH), 105.6 (CH), 93.7 (C), 89.5 (C). HRMS (ESI/ASAP) *m*/*z* calculated for C<sub>66</sub>H<sub>40</sub>F<sub>6</sub>O<sub>2</sub> [M•]<sup>+</sup>: 978.2933, found 978.2931.

#### 4.21. Bispyrane derivative (19)

Red solid; obtained according to the general procedure C and purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>); yield 40% (36 mg); mp: 178 °C (dec); <sup>1</sup>H NMR (300 MHz, THF-*d*<sub>8</sub>)  $\delta$  6.87 (s, 2H), 7.23 (s, 2H), 7.67–7.51 (m, 20H), 7.83 (d, *J*=8.4 Hz, 4H), 7.88 (d, *J*=7.2 Hz, 4H), 7.96 (d, *J*=7.2 Hz, 4H), 8.04 (d, *J*=8.4 Hz, 4H), 10.1 (s, 2H); <sup>13</sup>C NMR and JMOD (75 MHz, THF-*d*<sub>8</sub>)  $\delta$  191.9 (CH), 154.2 (C), 153.4 (C), 143.7 (C), 137.5 (C), 134.9 (C), 133.2 (CH), 133.1 (CH), 131.1 (CH), 130.7 (CH), 130.6 (CH), 130.5 (C), 130.1 (CH), 130.0 (CH), 126.0 (CH), 125.6 (C), 121.6 (C), 107.4 (CH), 105.6 (CH), 94.8 (C), 90.2 (C). HRMS (ESI/ASAP) *m/z* calculated for C<sub>66</sub>H<sub>42</sub>O<sub>4</sub> [M<sup>·</sup>]<sup>+</sup>: 898.3083, found 898.3087.

### 4.22. Bispyrane derivative (20)

Dark-red solid; obtained according to the general procedure C and purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>); yield 25% (25 mg); mp: 174 °C (dec); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.60 (s, 2H), 6.98 (s, 2H), 7.47–7.37 (m, 20H), 7.63 (d, *J*=8.7 Hz, 4H), 7.76–68 (m, 10H), 7.89 (d, *J*=8.7 Hz, 4H); <sup>13</sup>C NMR and JMOD (75 MHz, THF-*d*<sub>8</sub>)  $\delta$  160.2 (CH), 154.3 (C), 153.5 (C), 144.0 (C), 134.9 (C), 133.5 (CH), 133.2 (CH), 132.6 (CH), 132.1 (CH), 131.1 (C), 130.8 (CH), 130.7 (CH), 130.0 (C), 126.0 (CH), 125.5 (CH), 125.4 (C), 121.4 (C), 115.3 (C), 114.3 (C), 107.4 (CH), 105.8 (CH), 96.1 (C), 90.3 (C), 84.0 (C). HRMS (ESI/ASAP) *m/z* calculated for C<sub>72</sub>H<sub>42</sub>N<sub>4</sub>O<sub>2</sub> [M<sup>-</sup>]<sup>+</sup>: 994.3308, found 994.3290.

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### Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.07.066.

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