Enamine-Functionalized Oligopyridines as Convenient Intermediates for the Synthesis of Carbaldehyde Derivatives

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Abstract: A series of enamine-substituted bipyridine, biquinoline and o-phenanthroline chromophores has been synthesized and fully characterized. The para regioselectivity of the functionalization is discussed on the basis of 2D NOESY correlation and X-ray diffraction analysis. Absorption and emission spectroscopic studies allow a comparison of the acceptor strength of the heterocyclic core (bipyridine > phenanthroline > bipyridine). These enamine derivatives are key intermediates for a straightforward preparation of the corresponding dicarbaldehyde-bisimine compounds.

Key words: heterocycles, imines, ligands, aldehydes, chromophores

Heterocyclic bisimines are widely used ligands for metal ion complexation and powerful building blocks for the synthesis of molecular materials with a wide range of physical properties, such as electron transfer, photovoltaism, light-harvesting, magnetic or nonlinear optical (NLO) properties. In the latter field, we have demonstrated that 4,4′-functionalized-2,2′-bipyridines are efficient chromophores for the design of dipolar and octupolar NLO-phores. Carbalddehyde-substituted oligopyridines can be considered as useful precursors for the elaboration of these chromophores. To this end, we preliminarily reported a convenient two-step method for the preparation of 4,4′-dicarbaldehyde-2,2′-bipyridine via enamination of 4,4′-dimethyl-2,2′-bipyridine. We describe here the generalization of this methodology to different bisimine ligands such as bipyridines, annelated biquinolines and o-phenanthrolines. The regioselectivity of the enamination is discussed on the basis of 2D NMR studies or X-ray diffraction analysis. The absorption and emission spectroscopic properties of the enamine intermediates, which can be regarded as simple push-pull chromophores in which the donor (NMe₂) and the acceptor (pyridine) moieties are connected through an alkenyl bridge, is also discussed.

The transformation of an activated methyl group into an enamine by means of formamide acetals or aminals is well-established. This reaction has been first developed by Bredereck with methyl-substituted heteroarenes. Based on this results, we have extended the methodology to a series of methyl substituted bis-heterocyclic ligands such as 4,4′-dimethyl[2,2′]bipyridine (1a), 4,4′,6,6′-tetramethyl[2,2′]bipyridine (2a), 4,4′-dimethyl[3,3′]dimethylenebiquinoline (3a) and 3,4,7,8-tetramethyl-o-phenanthroline (4a).

Treatment of 1a–4a with the commercially available ‘Bredereck’s reagent’ (tert-butoxybis(dimethylaminomethane) in refluxing DMF led to the formation of the enamines 1b–4b in good to excellent yields (84 and 95%) (Scheme 1). The same reaction was successfully applied to the 4-methyl-4′-alkenyl-2,2′-bipyridines 5a–6a which gave rise to the corresponding mono-enamine derivatives 5b–6b in 82–85% yields.

These compounds were fully characterized by means of NMR, high-resolution mass spectrometry, absorption and emission spectroscopies. The E configuration of the enamine double bond was unambiguously established by 1H NMR, based on the determination of the coupling constant JCH=CH = 14 Hz (Table 1).

It is worth noting that in the case of 2a and 4a containing four methyl groups, the enamination regioselectively occurred at the para position of the pyridine rings. Even under more drastic conditions (large excess of Bredereck’s Reagent, longer reaction times) further functionalisation of the other methyl groups could not be detected. The highly selective nature of this reaction was clearly evidenced by 2D NOESY correlation and X-ray diffraction analysis in the case of 2b, and 4b (vide supra) respectively.

The 2D NOESY correlation spectrum of 2b exhibits...
through space correlation between the vinylic H\(_7\) proton and the pyridine H\(_3\) and H\(_5\) protons (Figure 1), strongly suggesting that the functionalization occurs selectively in the para position. Furthermore, this regioselectivity was unambiguously confirmed by the coupling of the remaining methyl group with only H\(_5\), and not with H\(_3\).

Compounds 1b and 4b gave suitable crystals for X-ray diffraction analysis. ORTEP drawings are depicted in Figures 2 and 3, respectively. Crystal data and refinement parameters are listed in Table 2. The bipyridine derivative 1b adopts a classical transoid arrangement due to the repulsion of the nitrogen lone pairs with a symmetry centre in the middle of the C(1)–C(1\(_3\)) bond.\(^7c,12\) The E configuration of the enamine double bonds is clearly confirmed for both compounds, as well as the selective para functionalization in 4b. The C=C double bonds of the enamine moieties in 1b and 4b adopt an s-cis conformation with respect to C3–C4 and C7–C8/C4–C3 respectively. This contrasts with the s-trans conformation recently reported for 4,4\(^′\)-dibutylaminostyril[2,2\(^′\)]bipyridine.\(^7c\) In 1b, the enamine double bonds lie perfectly in the plane of the pyridine ring, whereas the structure of 4b reveals a substantial twist with dihedral angles between the double bonds and the phenanthroline plane of ca. 25 and 50°, one enamine group being more distorted than the other. These distortions could be explained by steric hindrance between either the phenanthroline bridging protons (H\(_5\), H\(_6\)) or the methyl groups (C19, C20) with the enamine vinylic protons. For both compounds, classical bond lengths of about 1.34 for the enamine double bonds (1b, C6–C7; 4b, C15–C16/C17–C18) and 1.46 for the C6–C3 (1b) and C15–C4/C17–C7 (4b) are observed.

Table 1  Selected NMR, UV-Visible and Fluorescence Data

<table>
<thead>
<tr>
<th>Ligand</th>
<th>(J_{CH=CH}/Hz)</th>
<th>(\lambda_{max}/nm)</th>
<th>(\varepsilon/L\cdot mol^{-1} \cdot cm^{-1})</th>
<th>(\lambda_{em}/nm)</th>
<th>Stokes Shift/nm</th>
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<tbody>
<tr>
<td>1b</td>
<td>13.6</td>
<td>345</td>
<td>38000</td>
<td>449</td>
<td>104</td>
</tr>
<tr>
<td>2b</td>
<td>13.7</td>
<td>340</td>
<td>31000</td>
<td>453</td>
<td>113</td>
</tr>
<tr>
<td>3b</td>
<td>13.8</td>
<td>385</td>
<td>14000</td>
<td>519</td>
<td>134</td>
</tr>
<tr>
<td>4b</td>
<td>13.8</td>
<td>352 (368)</td>
<td>25500</td>
<td>470</td>
<td>102</td>
</tr>
</tbody>
</table>

Figure 2 ORTEP drawing of compound 1b. Selected bond lengths (): N2–C7, 1.357(4); C7–C6, 1.339(4); C6–C3, 1.458(4); C1–C1\(_3\), 1.493(6).

Figure 1 Determination of the regioselectivity by means of the NOE correlation.
The UV-visible spectra of 1b–4b recorded in dichloromethane (Table 1 and Figure 4) exhibit absorption bands that are sensitive to the nature of the bisimine moieties. The optical spectra of the push-pull bipyridines 1b and 2b are characterized by an intense intraligand charge transfer transition (ICT) at ca. 340 nm. The phenanthroline derivative 4b has a slightly red-shifted ICT band when compared to 1b and 2b. Noteworthy is the substantial bathochromic shift of the charge-transfer transition in 3b centered at 385 nm, which is consistent with the lower π* level in 2,2′-biquinolines. This very broad band overlaps with another low-energy band assigned to the π→π* biquinoline excitation (λ = 350 nm), a transition which is also expected to occur in this region. The bathochromic shift allows a rough estimate of the relative values of the acceptor strengths in the order biquinoline > phenanthroline > bipyridine. Photoluminescence is observed for the four compounds in dichloromethane solution at room temperature (Table 1 and Figure 4). A substantial red shift in the emission wavelength of the biquinoline derivative 3b is also found when compared to those of 1b and 2b (Δλ = 70 nm) and 4b (Δλ = 50 nm).

Compounds 1b–5b were then converted to their carbaldehyde derivatives 1c–5c in good yield (60 to 80%) upon oxidative cleavage of the enamine double bonds by sodium periodate in aqueous THF solution at 40 °C (Scheme 3). The overall yields of this two steps synthesis from dimethyl-substituted bisimines are fairly good, from 50 to 70%. Classically, the formation of such 4,4′-dicarbalddehyde oligopyridines from the corresponding dimethyl precursors requires either: (i) a multistep procedure involving oxidation of the methyl fragments to carboxylic acids, esterification, reduction to alcohol and finally controlled oxidation to aldehyde; or (ii) direct oxidation by selenium dioxide or benzeneselenic anhydride. However, these two methods cannot be applied to the synthesis of methylated derivatives such as 2c, due to the poor regioselectivity of the oxidation processes. A comparison of the different synthetic methods (Table 3) shows that our alternative methodology is more efficient in the case of bipyridines and gives comparable yields in the case of biquinolines and o-phenanthrolines. Moreover, the use of highly toxic selenium reagents is avoided. Finally, the enamine formation step allows the regioselective synthesis of derivatives 2c and 4c, without undesirable transformation of the other methyl substituents.

**Scheme 3**
In summary, we have demonstrated a successful, high yield, approach for the design of new bis-enamine bidentate chromophores and fluorophores. These compounds are good synthons for the synthesis of the corresponding carbaldehyde derivatives. This route represents a good alternative to the other methods, since it allows the generation of these aldehydes in better overall yields and high regioselectivities. The synthetic procedure reported in this paper offers the opportunity to build more extended push-pull chromophores via the versatile dialdehyde precursors.

All reactions were routinely performed under argon using Schlenk techniques. NMR spectra ($^1$H, $^{13}$C) were recorded at r.t. on a Bruker DPX 200 (operating at 200.12 MHz for $^1$H and 50.33 MHz for $^{13}$C). NMR data are listed in parts per million (ppm) and are reported relative to tetramethylsilane ($^1$H, $^{13}$C). UV/Vis spectra were recorded on a Kontron UVIKON 941 spectrophotometer in diluted CH$_2$Cl$_2$ solution (ca. 10$^{-5}$ mol.L$^{-1}$). Fluorescence experiments were performed in dilute CH$_2$Cl$_2$ solution (ca. 10$^{-5}$ mol.L$^{-1}$) using a PTI spectrometer. IR spectra were recorded in KBr pellets using a Nico.

### Table 2 Selected Crystallographic Data and Collection Parameters for Compounds 1b and 4b

<table>
<thead>
<tr>
<th>Compounds</th>
<th>1b</th>
<th>4b</th>
</tr>
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<tbody>
<tr>
<td>Formula</td>
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<td>C$<em>{22}$H$</em>{26}$N$_4$</td>
</tr>
<tr>
<td>M/</td>
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<td>346.47</td>
</tr>
<tr>
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<td>0.42 × 0.35 × 0.35</td>
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<tr>
<td>Color</td>
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<td>Yellow-green</td>
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<td>Monoclinic</td>
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<tr>
<td>Space group</td>
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<td>P2$_1$/a</td>
</tr>
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<td>8.819(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>8.610(4)</td>
<td>16.154(4)</td>
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<tr>
<td>c/Å</td>
<td>12.238(9)</td>
<td>13.830(3)</td>
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<tr>
<td>$\beta/^\circ$</td>
<td>100.46(4)</td>
<td>101.07(2)</td>
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<tr>
<td>V/Å$^3$</td>
<td>828.3(7)</td>
<td>1933.6(8)</td>
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<tr>
<td>Z</td>
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<td>4</td>
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<tr>
<td>$\lambda$(MoK$\alpha$)/</td>
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<td>0.71069</td>
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<tr>
<td>$\mu$/cm$^{-1}$</td>
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<tr>
<td>F(000)</td>
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<td>744</td>
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<tr>
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<td>D$_g$/g.cm$^{-3}$</td>
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<td>0 to 11, 0 to 20, –17 to 17</td>
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<td>237</td>
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<tr>
<td>Reflections measured</td>
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<td>4213</td>
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<tr>
<td>Reflections</td>
<td>874</td>
<td>2124</td>
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### Table 3 Comparison of the Different Synthetic Methods

<table>
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<th>Entry</th>
<th>Compound</th>
<th>Previous synthesis yield (%)</th>
<th>This work yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dmbpy (1a)</td>
<td>22$^{16b}$, 34$^{16b}$ (i), 13$^{17a}$ (ii)</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>Tmbpy (2a)</td>
<td>43$^{16c}$ (i)</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>Dmabiq (3a)</td>
<td>40$^{17c}$ (ii)</td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>Dmbiq</td>
<td>68$^{16a}$ (ii)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Dmphen</td>
<td>65$^{17b}$ (ii)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tmphen (4a)</td>
<td>–</td>
<td>61</td>
</tr>
</tbody>
</table>
let 205 FTIR. HRMS spectrometry measurements (FAB, EI) were performed at the Centre Regional de Mesures Physiques de l’Ouest (Rennes, France).

Crystal Structure Analysis
The samples were studied on an automatic diffractometer CAD4 NONIUS with graphite monochromatized MoKα radiation.30 The cell parameters are obtained by fitting a set of 25 high-theta reflections. After Lorenz and polarization corrections,30 the structure was solved with SIR-97,31 which reveals the non-hydrogen atoms of the structure. After anisotropic refinement, all the hydrogen atoms are found with a Fourier Difference. The whole structure was refined with SHELXL9732 by the full-matrix least-square techniques (use of F magnitude; x, y, z, (i) for C, N and O atoms, x, y, z in riding mode for H atoms). ORTEP views realized with PLATON98.24 All the calculations were performed on a Silicon Graphics Indy computer. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no 189533 and 189534 for compounds 1b and 4b, respectively.

4,4′-Bis(N,N-dimethylaminovinyl)-3,3′-dimethylene-2,2′-biquinoline (3b)
Using the same procedure described for 2a, compound 3b was isolated from 3a (1.40 g, 4.5 mmol). Yield: 1.59 g (84%); red brown powder.1

1H NMR (CDCl3): δ = 8.25 (d, J = 8.8 Hz, 2 H, H5, H6), 8.06 (s, 2 H, H1, H7), 7.79 (d, J = 8.4, 8.3 Hz, 2 H, 2 H), 7.66 (td, J = 8.2, 8.2 Hz, 2 H, 2 H), 7.54 (td, J = 8.3, 8.3 Hz, 1 H, =CH styryl), 7.15 (d, J = 7.2 Hz, 2 H, H3), 5.43 (d, J = 13.8 Hz, 2 H, H14), 3.20 (s, 4 H, CH2), 2.91 (s, 12 H, NCH3).


UV/Vis (CH3Cl2): λmax (εmax) = 340 nm (31000 Lmol-1 cm-1).

Emission (CH3Cl2): λem = 450 nm.

4,4′-Bis(N,N-dimethylaminovinyl)-3,3′-dimethylene-2,2′-biquinoline (3a)

In a Schlenk flask, 1,2-cyclohexanénone (1.16 g, 10 mmol) and 2′-aminoacetoephone hydrochloride (3.55 g, 20 mmol) were mixed from Aldrich and used as received.2

4,4′-Dimethyl-3,3′-dimethyl-2,2′-biquinoline (1a) and 3,4,7,8-tetramethyl-2,2′-biquinoline (14a) were purchased from Aldrich and used as received.

4,4′-Dimethyl-3,3′-dimethylene-2,2′-biquinoline (1a)
In a Schlenk flask, 1,2-cyclohexanénone (1.16 g, 10 mmol) and 2′-aminoacetoephone hydrochloride (3.55 g, 20 mmol) were mixed with 2-methoxethanol (30 mL) and the mixture was heated under reflux for 48 h. After cooling to r.t., the solvent was removed under vacuum and the residue dissolved in CH2Cl2. The organic layer was refluxed for 48 h. After cooling to r.t., the solvent was removed under vacuum.


UV/Vis (CH3Cl2): λmax (εmax) = 340 nm (31000 Lmol-1 cm-1).

Emission (CH3Cl2): λem = 450 nm.

4,4′-Bis(N,N-dimethylaminovinyl)-3,3′-dimethylene-2,2′-biquinoline (3b)

Using the same procedure described for 2a, compound 3b was isolated from 3a (1.40 g, 4.5 mmol).

Yield: 1.59 g (84%); red brown powder.

1H NMR (CDCl3): δ = 8.34 (d, J = 8.3 Hz, 1 H, H10), 8.16 (d, J = 8.3, 8.3 Hz, 2 H, H3, H4), 7.56 (td, J = 8.3, 8.3 Hz, 1 H, H5), 7.42 (d, J = 13.8 Hz, 2 H, H14), 5.43 (d, J = 13.8 Hz, 2 H, H14), 3.20 (s, 4 H, CH2), 2.91 (s, 12 H, NCH3).


UV/Vis (CH3Cl2): λmax (εmax) = 340 nm (31000 Lmol-1 cm-1).

Emission (CH3Cl2): λem = 450 nm.

4,7-Bis(N,N-dimethylaminovinyl)-3,8-dimethyl-1,10-phenanthroline (4b)

Using the same procedure described for 2a, compound 4b was isolated from 4a (0.50 g, 2.12 mmol).

Yield: 0.69 g (94%); green powder.

1H NMR (CDCl3): δ = 8.79 (s, 2 H, H5, H6), 8.08 (s, 2 H, H1, H7), 6.70 (d, J = 13.8 Hz, 2 H, H10), 5.27 (d, J = 13.8 Hz, 2 H, H14), 7.38 (s, 12 H, NCH3), 2.37 (s, 6 H, Me).

HRMS (EI): m/z calc for [M + H]+ (C22H17N2): 347.2236; found: 347.2251.

UV/Vis (CH3Cl2): λmax (εmax) = 352 nm (25500 Lmol-1 cm-1).

Emission (CH3Cl2): λem = 470 nm.

4-[(p-N,N-Dimethylaminostyryl)-4′-(N,N-dimethylaminovinyl)-2,2′-bipyridine (5b)

To a solution of 4-[(p-N,N-Dimethylaminostyryl)-4′-methyl-2,2′-bipyridine (5a) (0.50 g, 1.60 mmol) in DMF (10 mL) was added under argon the Bredereck’s reagent [4-tert-butoxybis(dimethylamino)methane] (0.56 g, 3.2 mmol). The mixture was refluxed for 18 h. After cooling down to r.t., the pale orange mixture was hydrolyzed by addition of H2O (20 mL) and extracted with CH2Cl2 (4 × 10 mL). The organic phase was dried (MgSO4) and the solvent removed under vacuum. The resulting orange solid was recrystallized from CH2Cl2–Et2O to give the desired product.

Yield: 0.50 g (85%); brown powder.

1H NMR (CDCl3): δ = 8.56 (d, J = 5.3 Hz, 1 H, H7), 8.43 (d, J = 1.2 Hz, 1 H, H6), 8.37 (d, J = 5.3 Hz, 1 H, H8), 8.13 (d, J = 1.8 Hz, 1 H, H5), 7.44 (d, J = 8.8 Hz, 2 H, C8H2), 7.38 (d, J = 16.1 Hz, 1 H, =CH styryl), 7.30 (dd, J = 5.3, 1.2 Hz, 1 H, H5), 7.20 (d, J = 13.6 Hz, 1 H, H4), 6.97 (dd, J = 5.3, 1.8 Hz, 1 H, H4), 6.89 (d, J = 16.1 Hz, 1 H, =CH styryl), 6.70 (d, J = 8.8 Hz, 2 H, C8H2), 5.08 (d, J = 13.6 Hz, 1 H, H4), 2.98 (s, 6 H, NCH3), 2.87 (s, 6 H, NCH3).


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and an aq solution of NaIO₄ (1 M; 8 g, 37 mmol) was added dropwise. In a Schlenk flask, 4,4′-bis(N,N-dimethylaminovinyl)-2,2′-bipyridine (6b) to a solution of 4-[p-(Octyloxy)styryl]-4′-(N,N-dimethylaminovinyl)-2,2′-bipyridine (6a) (0.30 g, 0.75 mmol) in DMF (3 mL) was added under argon the Bredereck's reagent [tert-butoxy(dimethyl) methanol] (0.56 g, 3.2 mmol). The mixture was refluxed for 18 h. After cooling down to r.t., the pale orange mixture was hydrolyzed by addition of H₂O (20 mL) and extracted with CH₂Cl₂ (4×5 mL). The organic phase was dried (MgSO₄) and the solvent removed under vacuum. The resulting orange solid was recrystallized from CH₂Cl₂–Et₂O to give the desired product.

Yield: 0.28 g (82%); yellow-brown powder.

1H NMR (CDCl₃): δ = 8.53 (d, J = 5.1 Hz, 1 H, H₁), 8.40 (s, 1 H, H₄), 8.32 (d, J = 5.3 Hz, 1 H, H₂), 8.09 (s, 1 H, H₅), 7.42 (d, J = 8.7 Hz, 2 H, C₆H₄), 7.34 (dd, J = 16.4 Hz, 1 H, H₇), 7.25 (dd, J = 5.1, J = 1.4 Hz, 1 H, H₆), 7.14 (d, J = 13.6 Hz, 1 H, H₈), 6.92 (dd, J = 5.3, J = 1.5 Hz, 1 H, H₉), 6.90 (d, J = 16.4 Hz, 1 H, H₁₀), 6.84 (d, J = 8.7 Hz, 2 H, C₆H₄), 5.04 (d, J = 13.6 Hz, 2 H, H₁₀), 3.95 (t, J = 7.5 Hz, 2 H, OCH₃), 2.86 (s, 6 H, NCH₃), 1.73 (m, 2 H, CH₂), 1.24 (m, 10 H, 5 CH₂), 0.82 (m, 3 H, Me).

13C NMR (CDCl₃): δ = 159.7, 157.1, 155.6, 149.3, 148.9, 148.8, 145.9, 143.4, 132.8, 128.9, 128.4, 123.9, 120.5, 118.2, 117.9, 114.8 (2 C), 94.5, 68.1, 40.6, 31.8, 29.4, 29.3 (2 C), 26.0, 22.7, 14.1.

IR (KBr): 1730 (C=O) cm⁻¹.

UV/Vis (CH₂Cl₂): εₘₐₓ = 388 nm (31000 L.mol⁻¹.cm⁻¹), 350 nm (sh).

4,4′-Dicarbaldehyde-6,6′-dimethyl-2,2′-bipyridine (2c) In a Schlenk flask, 4,4′-bis(N,N-dimethylaminovinyl)-6,6′-[dimethyl(2,2′-bipyridine (0.32 g, 1 mmol) in THF (180 mL) was iso- lated from 3b (0.75 g, 1.78 mmol) after precipitation from THF–pentane. The product was dissolved in CH₂Cl₂ (40 mL) and washed with H₂O (2×50 mL). The organic phase was dried (MgSO₄), filtered, and the solvent removed under vacuum. The product then was reprecipitated from THF–pentane, the desired compound was finally obtained as a pale-yellow microcrystalline powder (0.14 g, 60% yield).

Yield: 0.11 g (64%); orange powder.

IR (KBr): 1716 (C=O) cm⁻¹.

UV/Vis (CH₂Cl₂): λₘₐₓ (εₘₐₓ) = 382 nm (30000 L.mol⁻¹.cm⁻¹).

Acknowledgments

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References


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Convenient Intermediates for the Synthesis of Carbaldehyde Derivatives


(25) Other sources of NaIO₄ gave only poor yield.