Pergamon

Tetrahedron 58 (2002) 6901–6906

TETRAHEDRON

Vinylphosphonium salt mediated simple synthesis of 7-oxo-7*H*-pyrido[1,2,3-*cd*]perimidine derivatives. Dynamic NMR spectroscopic study of prototropic tautomerism in ethyl 1*H*-perimidine-2-carboxylate

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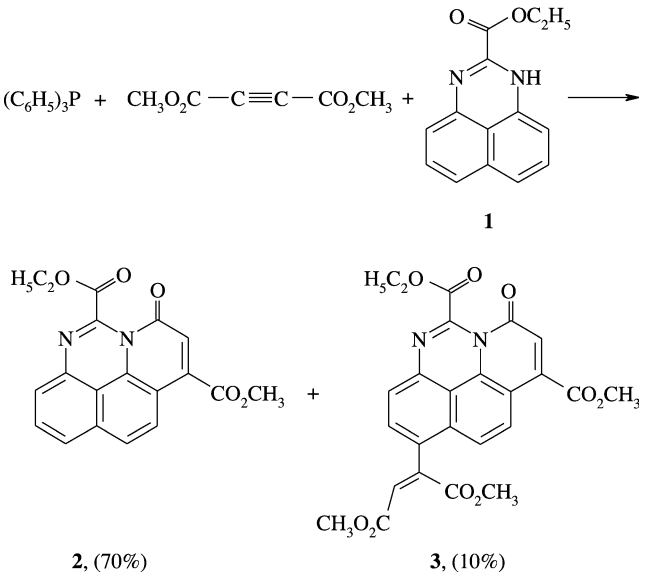
Received 20 December 2001; revised 2 May 2002; accepted 27 June 2002

Abstract—The reactive 1:1 intermediate produced in the reaction between dimethyl acetylenedicarboxylate and triphenylphosphine was trapped by ethyl 1*H*-perimidine-2-carboxylate to yield 5-ethyl 9-methyl 7-oxo-7*H*-pyrido[1,2,3-*cd*]perimidine-5,9-dicarboxylate and 5-ethyl 9-methyl 1-[3-methoxy-1-(methoxycarbonyl)-3-oxo-1-propenyl]-7-oxo-7*H*-pyrido[1,2,3-*cd*]perimidine-5,9-dicarboxylate in nearly 7:1 ratio and overall good yields. The first of these compounds is quantitatively converted to ethyl 10-[(2-ethoxy-2-oxoacetyl)amino]-2-hydroxybenzo[*h*]quinoline-4-carboxylate by refluxing in water-saturated chloroform, while the later compound remained unchanged under the same reaction conditions. The free-energy barrier ($\Delta G^{\neq}$) for prototropic tautomerism in ethyl 1*H*-perimidine-2-carboxylate is determined by dynamic ^{1}H NMR studies to be 50.6 kJ mol^{-1}. The methylene protons of 5-ethyl 9-methyl 7-oxo-7*H*-pyrido[1,2,3-*cd*]perimidine-5,9-dicarboxylate are diastereotopic as a result of peri interaction of carboethoxy group with the adjacent carbonyl bond. The free-energy barrier for conformational racemization of this compond is 56.3 kJ mol^{-1}.

1. Introduction

Perimidines (*peri*-naphtho-fused pyrimidine systems) are of interest because they constitute an important class of natural and non-natural products, many of which exhibit useful biological activity.[1] The interest in pyrido-fused perimidine derivatives stems from the appearance of these heterocyclic systems in many biologically active compounds.[1,2] Consequently, there has been an ongoing interest in the synthesis of perimidine ring structures.[1–5]

As part of our current studies on the development of new routes in heterocyclic and carbocyclic synthesis,[6–9] we now report the reaction between ethyl 1*H*-perimidine-2-carboxylate **1** and dimethyl acetylenedicarboxylate (DMAD) in the presence of triphenylphosphine. Thus, reaction of DMAD with triphenylphosphine in the presence of a strong NH-acid such as **1** afforded the functionalized 7-oxo-7*H*-pyrido[1,2,3-*cd*]-perimidine derivatives **2** and **3** in a 7:1 ratio (Scheme 1).



Scheme 1.

2. Results and discussion

Ethyl 1*H*-perimidine-2-carboxylate **1** is a readily available heterocyclic compound, which can be obtained from naphthalene-1,8-diamine and ethyl oxalyl chloride. Although physicochemical data show that the NH-proton in perimidines, as in imidazoles, migrates rapidly between

Keywords: ethyl 1*H*-perimidine-2-carboxylate; dynamic NMR spectroscopy; benzoquinolines; prototropic tautomerism; aromatic substitution.

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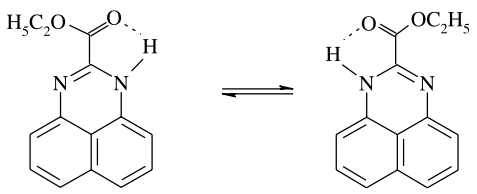
PII: S0040-4020(02)00759-7



1a **1b**

Scheme 2.

the two nitrogen atoms[1] (degenerate tautomerism of the amidine type) (Scheme 2), there are no published experimental data on the free-energy barrier of prototropic tautomerism in 2-substituted perimidines by NMR spectroscopy. We now report the prototropic tautomerism in ethyl 1*H*-perimidine-2-carboxylate **1** on the basis of its dynamic 500 MHz ^{1}H NMR spectrum.

Although the ^{1}H and ^{13}C NMR spectra of perimidine itself are consistent with a symmetrical structure, reflecting rapid prototropic tautomerism between the annular nitrogen atoms, the ^{1}H and ^{13}C NMR spectrum of compound **1** shows some very broad signals at ambient temperature. The low-temperature (213 K) spectra of **1** are consistent with an unsymmetrical structure, which is the result of slow prototropic tautomerism between the annular nitrogen atoms. The ^{1}H NMR spectra of **1** at various temperatures are shown in Fig. 1.

The ^{1}H NMR spectrum of **1** in $CDCl_3$ at room temperature (25°C) exhibited a fairly broad resonance arising from the CH-4 and CH-9 protons. By increasing the temperature to 50°C, a fairly sharp doublet ($^3J_{HH}$=6.9 Hz) was observed. At −60°C, the signals appear as two fairly sharp doublets (^3J=5.6, 6.9 Hz). Increasing the temperature results in coalescence of the two doublets (T_c=−5±1°C).

Although no extensive line-shape analysis for **1** was undertaken, the variable temperature spectra allowed us to calculate the free energy barriers $\Delta G^{\neq}$ (if not the enthalpy and entropy of activation) for the dynamic NMR process in **1**. From coalescence of the C_4 and C_9 protons of compound **1**, and using the expression, $k = \pi\Delta\nu/\sqrt{2}$, we calculate that the first-order rate constant (k) for dynamic NMR effect in **1** is 733 s^{-1}. Application of the absolute rate theory with a transmission coefficient of 1 gives the free energy of activation ($\Delta G^{\neq}$) as 50.6±2 kJ mol^{-1} for compound **1**, where all known sources of errors are estimated and included.[10] The experimental data available are not suitable for obtaining meaningful values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ even though the errors in $\Delta G^{\neq}$ are not large.[11]

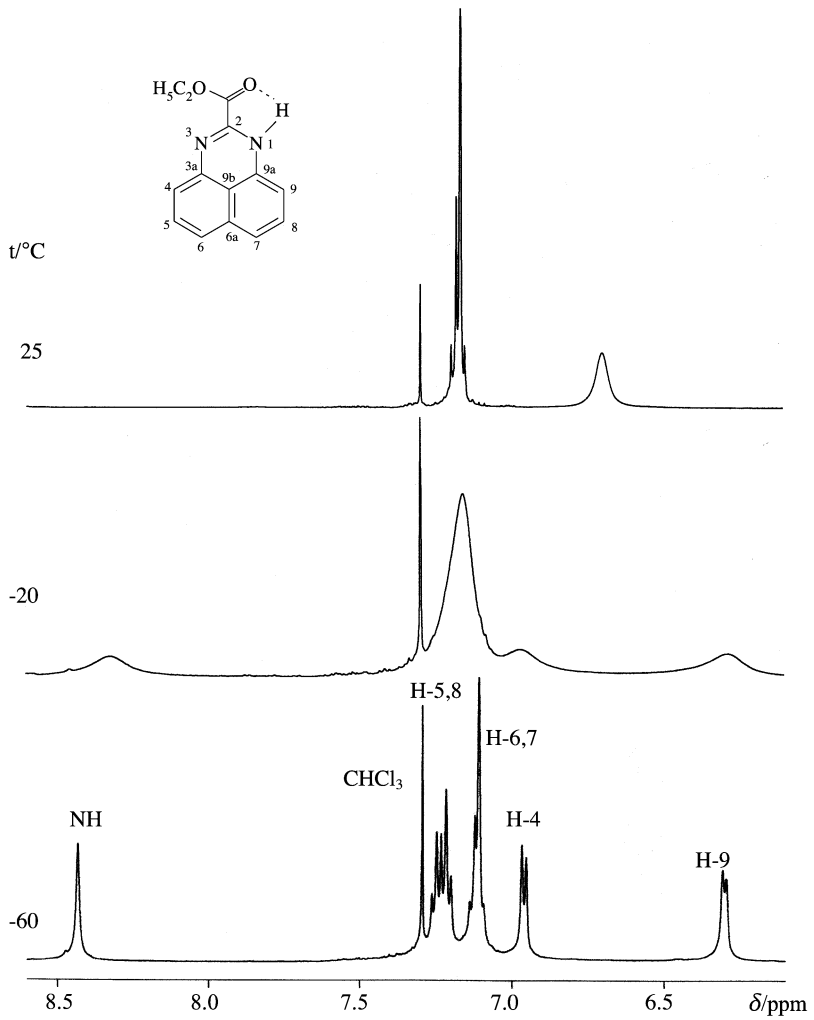
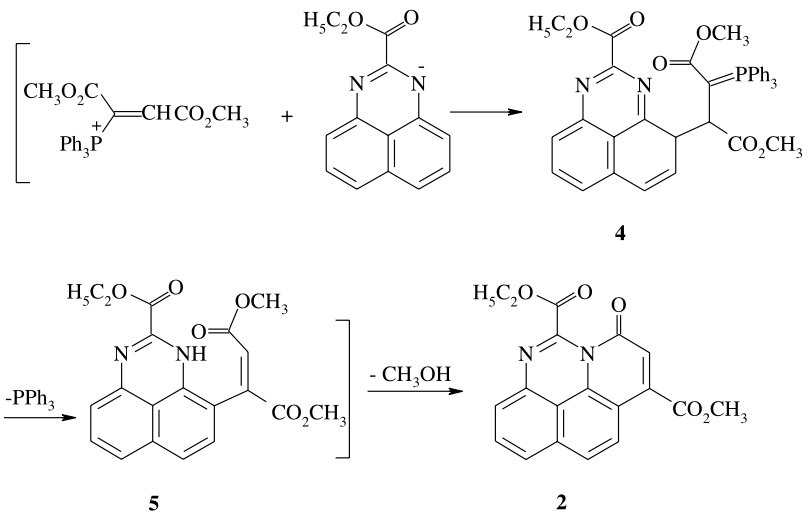


Figure 1. Variable-temperature 500 MHz ^{1}H NMR spectra of the aromatic region of compound **1** in $CDCl_3$.



Scheme 3.

The reaction of DMAD with ethyl 1*H*-perimidine-2-carboxylate **1** in the presence of triphenylphosphine proceeded in dichloromethane and then in boiling toluene. The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of two products, named **2** and **3**, which were separated by column chromatography. The structure of compound **2** was deduced from its elemental analyses and its high-field ^{1}H and ^{13}C NMR and IR spectral data. The mass spectra of the product displayed molecular ion peak at m/z=350. The ^{1}H and ^{13}C NMR spectroscopic data for **2** are given in Section 4. The ^{1}H NMR spectrum of **2** exhibited two sharp singlets, readily recognizable as arising from methoxy (δ=4.07 ppm) and olefinic (δ=7.37 ppm) protons, along with characteristic multiplets for ethoxy and aromatic protons. The ^{13}C NMR spectrum of **2** exhibited 19 distinct resonances in agreement with the unsymmetrical pyridoperimidine structure. The structure of **3** was deduced from its elemental analyses and its high-field ^{1}H and ^{13}C NMR and IR spectral data. The mass spectrum of the product displayed molecular ion peak at m/z=492. The (*Z*)-configuration of the carbon–carbon double bond in **3** is based on the chemical shift of the olefinic proton.[12] Partial assignments of the ^{1}H and ^{13}C NMR spectra of **2** and **3** are given in Section 4.

Although we have not yet established the mechanism of the reaction between triphenylphosphine and DMAD in the presence of 1*H*-perimidine-2-carboxylate **1** in an experimental manner, a possible explanation is proposed in Scheme 3. On the basis of well-established chemistry of trivalent phosphorus nucleophiles,[13–20] it is reasonable to assume that compound **2** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acid **1**, followed by electrophilic attack of the vinyltriphenylphosphonium cation on the aromatic ring at the *ortho* position relative to the strong activating group. The 7-oxo-7*H*-pyrido[1,2,3-*cd*]perimidine derivative **2** is presumably produced by intramolecular lactamization of the unsaturated triester **5** (Scheme 3).

The most noteworthy feature of the ^{1}H NMR spectrum of **2** in $CDCl_3$ at room temperature (25°C) is the methylene

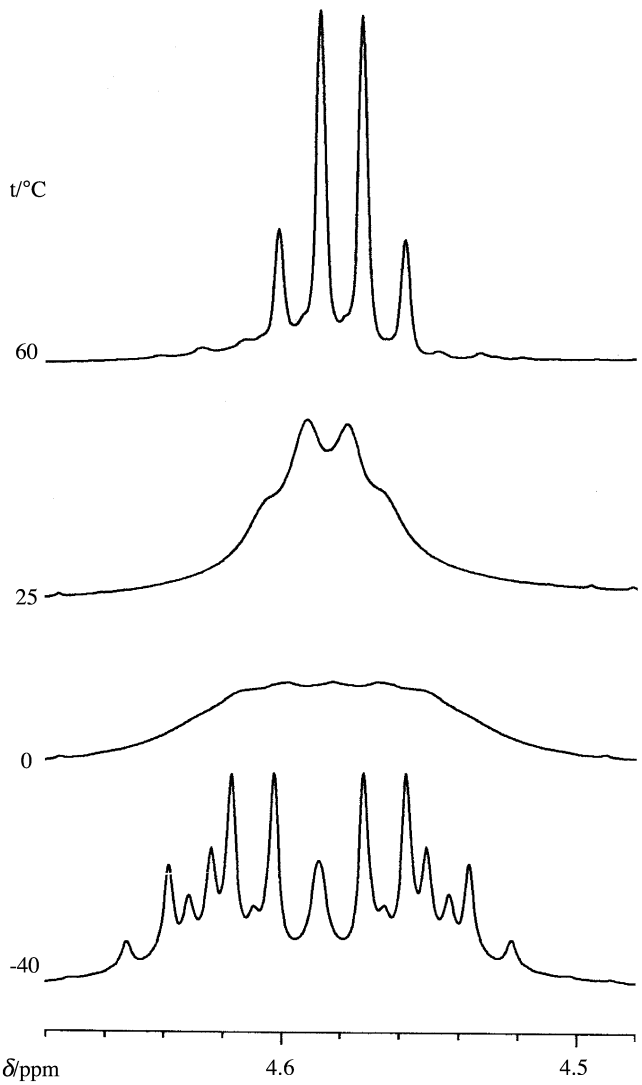
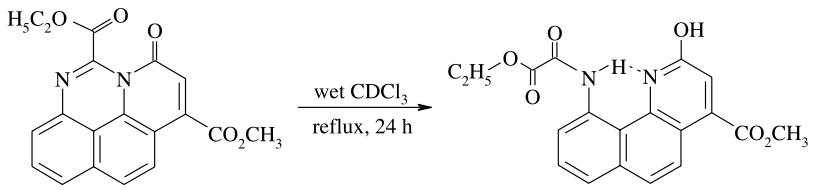


Figure 2. Variable-temperature 500 MHz ^{1}H NMR spectra of the methylene group of compound **2** in $CDCl_3$.



2 **6**, (95%)

Scheme 4.

protons of the ethoxy group which exhibit a broad quartet at δ=4.58 ppm. At −40°C, a fairly sharp (AB)X_3 pattern was observed for the two diastereotopic methylene protons. Increasing the temperature results in coalescence of the two double quartets (T_c=0±1°C). A fairly sharp quartet was observed at about 60°C (see Fig. 2). The dynamic ^{1}H NMR effect in **2** can be described in terms of hindered rotation of the carboethoxy group around the C–CO bond which is attributed to *peri* interaction of the carboethoxy substituent and adjacent carbonyl group. At low temperatures, rotation is slow on the NMR timescale and the protons of the methylene group become diastereotopic. At temperatures above coalescence, rotation is too fast, and a fairly broad quartet is observed.

Although an extensive line-shape analysis in relation to the dynamic ^{1}H NMR effect observed for **2** was not undertaken, the variable temperature spectra allowed us to calculate the free energy barriers $\Delta G^{\neq}$ (if not the enthalpy and entropy of activation) for the dynamic NMR process in **2**. From coalescence of the two diastereotopic protons of the ethoxy group, and using the expression, $k = (\pi/\sqrt{2})\sqrt{\Delta\nu^2 + 6J^2}$,[21] we calculate that the first-order rate constant (k) for the dynamic NMR effect in **2** is 95 s^{-1}. Application of the absolute rate theory with a transmission coefficient of 1 gives the free energy of activation ($\Delta G^{\neq}$) as 56.3±2 kJ mol^{-1}, where all known sources of errors are estimated and included.[10]

When compound **2** was refluxed in water-saturated chloroform, ^{1}H NMR spectroscopy showed nearly quantitative conversion to ethyl 10-[(2-ethoxy-2-oxoacetyl)amino]-2-hydroxybenzo[*h*]quinoline-4-carboxylate **6** (Scheme 4).

Structure **6** was assigned to the isolated product on the basis of its elemental analyses and its ^{1}H and ^{13}C NMR and IR spectral data. The mass spectrum of the product displayed molecular ion peak at m/z=368. The ^{1}H NMR spectrum of compound **6** exhibited a sharp singlet for the methoxy (δ=4.09 ppm) protons, along with characteristic multiplets for the ethoxy and aromatic protons. Two fairly broad singlets were observed at δ=7.95 and 16.70 ppm, arising from OH and NH protons, respectively. The ^{13}C NMR spectrum of compound **6** exhibited 19 distinct resonances in agreement with the benzoquinoline structure. Partial assignments of the ^{1}H and ^{13}C NMR spectra of **6** are given in Section 4.

3. Conclusions

We have found that the reaction of ethyl 1*H*-perimidine 2-carboxylate with dimethyl acetylenedicarboxylate in the presence of triphenylphosphine leads to a simple synthesis of 7-oxo-7*H*-pyrido[1,2,3-*cd*]perimidine derivatives. 5-Ethyl 9-methyl 7-oxo-7*H*-pyrido[1,2,3-*cd*]perimidine-5,9-dicarboxylate is quantitatively converted to ethyl 10-[(2-ethoxy-2-oxoacetyl)amino]-2-hydroxybenzo[*h*]quinoline-4-carboxylate by refluxing in water-saturated chloroform. The methylene protons of the former compound are diastereotopic as a result of *peri* interaction of carboethoxy group with the adjacent carbonyl bond. The free-energy barrier ($\Delta G^{\neq}$) for conformational racemization of this compound is determined by dynamic ^{1}H NMR studies to be 56.3 kJ mol^{-1}. The free-energy barrier for prototropic tautomerism in ethyl 1*H*-perimidine 2-carboxylate is 50.6 kJ mol^{-1}.

4. Experimental

4.1. General

Naphthalene-1,8-diamine, ethyl oxalyl chloride, dimethyl acetylenedicarboxylate and triphenylphosphine were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 70 eV. ^{1}H and ^{13}C NMR spectra were measured ($CDCl_3$ solution) with a Brucker DRX-500 AVANCE spectrometer at 500.1 and 125.8 MHz, respectively. IR spectra were recorded on a Shimadzu IR-460 spectrometer. Chromatography columns were prepared from Aldrich silica gel 70–230 mesh.

4.1.1. Ethyl 1*H*-perimidine 2-carboxylate (1). To a magnetically stirred solution of naphthalene-1,8-diamine (3.2 g, 0.02 mol) and triethylamine (8.1 g, 0.08 mol) in dichloromethane (40 mL) was added dropwise a mixture of ethyl oxalyl chloride (2.7 g, 0.02 mol) in dichloromethane (10 mL) at −5°C for 15 min. The reaction mixture was stirred for 40 min and then warmed up to room temperature and stirred for 12 h. Then, the reaction mixture was washed successively with water (3×50 mL), and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator to give a red solid (4.7 g, 98%). The residual solid recrystallized from hexane–ethyl acetate (1:2) as red crystals, mp 212–215°C. IR (KBr) (ν_{max}, cm^{-1}): 3305 (NH), 1704 (C=O), 1585 (C=N). Anal. Calcd for $C_{14}H_{12}N_2O_2$ (240.26): C, 69.98; H, 5.03; N, 11.66%. Found: C, 69.9; H, 5.1; N, 11.7%. ^{1}H NMR (298 K): δ 1.50

(3H, t, J=7.1 Hz, CH_3), 4.53 (2H, q, J=7.1 Hz, CH_2), 6.67 (2H, br s, CH-4,9), 7.19 (4H, m, 4CH), 8.15 (1H, very br s, NH). ^{1}H NMR (213 K): δ 1.47 (3H, t, J=7.1 Hz, CH_3), 4.51 (2H, q, J=7.1 Hz, CH_2), 6.30 (1H, d, J=5.6 Hz, CH-9), 6.96 (1H, d, J=6.9 Hz, CH-4), 7.12 (2H, m, CH-6,7), 7.25 (2H, m, CH-5,8), 8.43 (1H, s, NH). ^{13}C NMR (298 K): δ 14.14 (CH_3), 63.78 (CH_2), 112.00 (very br, CH-4,9), 121.23 (br, CH-6,7), 123.18 (C-9b), 128.39 (CH-5,8), 135.54 (C-6a), 140.00 (C-3a,9a), 143.71 (C-2), 161.26 (C=O).

4.2. General procedure for preparation of 2 and 3

To a magnetically stirred solution of triphenylphosphine (0.262 g, 1 mmol) and ethyl 1*H*-perimidine-2-carboxylate (0.24 g, 1 mmol) in dichloromethane (4 mL) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) in dichloromethane (2 mL) at −5°C for 10 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 5 h. The solvent was evaporated and then toluene (5 mL) was added and the mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography using hexane–ethyl acetate (2:1) as eluent. The solvent was removed under reduced pressure and products were obtained.

4.2.1. 5-Ethyl 9-methyl 7-oxo-7*H*-pyrido[1,2,3-*cd*]perimidine-5,9-dicarboxylate (2). Yellow crystals, mp 212–214°C (from 1:2 hexane–ethyl acetate), yield 0.24 g, 70%. IR (KBr) (ν_{max}, cm^{-1}): 1728 and 1662 (C=O). MS, *m/z* (%): 350 (M$^+$, 100), 322 (10), 305 (18), 291 (22), 278 (50), 250 (38), 219 (45), 191 (20), 164 (28). Anal. Calcd for $C_{19}H_{14}N_2O_5$ (350.33): C, 65.14; H, 4.03; N, 8.00%. Found: C, 65.2; H, 4.1; N, 8.1%. ^{1}H NMR (298 K): δ 1.49 (3H, t, J=7.2 Hz, CH_3), 4.07 (3H, s, OCH_3), 4.58 (2H, br q, J=7.2 Hz, OCH_2), 7.37 (1H, s, CH), 7.69 (1H, d, J=9.1 Hz, CH), 7.76 (1H, dd, ^2J=5.6 Hz, ^3J=3.0 Hz, CH), 7.83 (1H, d, J=5.6 Hz, CH), 7.84 (1H, d, J=3.0 Hz, CH), 8.34 (1H, d, J=9.1 Hz, CH). ^{13}C NMR: δ 13.48 (CH_3), 52.82 (OCH_3), 62.55 (OCH_2CH_3), 109.89 and 115.81 (2C), 120.32, 122.16, 122.83, 123.56, 125.15 and 130.26 (6CH), 132.54, 132.97, 137.59, 138.91 and 141.10 (5C), 157.27, 161.11 and 164.58 (3C=O).

4.2.2. 5-Ethyl 9-methyl 1-[3-methoxy-1-(methoxycarbonyl)-3-oxo-1-propenyl]-7-oxo-7*H*-pyrido[1,2,3-*cd*]perimidine-5,9-dicarboxylate (3). Yellow crystals, mp 230–232°C (from 1:2 hexane–ethyl acetate), yield 0.05 g, 10%. IR (KBr) (ν_{max}, cm^{-1}): 1724 (C=O ester), 1677 (C=O amide). MS, *m/z* (%): 492 (M$^+$, 32), 437 (100), 405 (20), 377 (10), 360 (5), 329 (5), 259 (6), 59 (20). Anal. Calcd for $C_{25}H_{20}N_2O_9$ (492.44): C, 60.97; H, 5.12; N, 5.69%. Found: C, 60.9; H, 5.1; N, 5.7%. ^{1}H NMR: δ 1.49 (3H, t, J=7.2 Hz, CH_3), 3.86, 3.88 and 4.08 (9H, 3 s, 3 OCH_3), 4.58 (2H, br q, J=7.2 Hz, OCH_2), 6.30 (1H, s, CH), 7.46(1H, s, CH), 7.84 (1H, d, J=7.9 Hz, CH), 7.92 (1H, d, J=7.9 Hz, CH), 8.04 (1H, d, J=9.4 Hz, CH), 8.53 (1H, d, J=9.4 Hz, CH). ^{13}C NMR: δ 13.45 (CH_3), 51.92, 52.54 and 52.93 ($3OCH_3$), 62.71 (OCH_2), 110.26 and 116.51 (2C), 120.58, 121.14, 121.79, 124.80 and 125.08 (5CH), 130.23 and 130.57 (2C), 130.68 (CH), 133.11, 138.78, 139.07, 141.84 and 145.07 (5C), 157.35, 160.91, 164.43, 164.46 and 166.71 (5C=O).

4.2.3. Ethyl 10-[(2-ethoxy-2-oxoacetyl)amino]-2-hydroxybenzo[*h*]quinoline-4-carboxylate (6). Compound **2** (0.1 g) was refluxed in water-saturated chloroform (10 mL) for 24 h. Then, dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residual solid (0.11 g) was recrystallized from hexane–ethyl acetate (1:2) as pale yellow crystals, mp 193–195°C, yield 95%. IR (KBr) (ν_{max}, cm^{-1}): 3425 (OH), 1700 and 1689 (C=O). MS, *m/z* (%): 368 (M$^+$, 10), 350 (25), 322 (5), 295 (100), 263 (34), 235 (20), 208 (12), 179 (14). Anal. Calcd for $C_{19}H_{16}N_2O_6$ (368.35): C, 61.96; H, 4.38; N, 7.61%. Found: C, 61.9; H, 4.4; N, 7.6%. ^{1}H NMR: δ 1.51 (3H, t, J=7.2 Hz, CH_3), 4.09 (3H, s, OCH_3), 4.54 (2H, q, J=7.2 Hz, OCH_2), 7.59 (1H, s, CH), 7.71 (1H, dd, ^3J=8.1 Hz, ^4J=2.0 Hz, CH), 7.73 (1H, dd, J=8.1 and 7.2 Hz, CH), 7.79 (1H, d, J=9.2 Hz, CH), 7.95 (1H, br s, OH), 8.50 (1H, d, J=9.2 Hz, CH), 8.96 (1H, dd, ^3J=7.2 Hz, ^4J=2.0 Hz, CH), 16.70 (1H, br s, NH···N). ^{13}C NMR: δ 14.08 (CH_3), 53.01 (OCH_3), 64.01 (OCH_2), 110.50 (CH), 117.03 (C), 118.22 (CH), 120.74 (C), 122.44, 124.33, 127.39 and 129.21 (4CH), 135.02, 137.19, 139.89 and 145.49 (4C), 153.86 (C–O), 157.89, 163.14 and 166.08 (3C=O).

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