1,3-Dipolar cycloaddition reactions of 1-(3-nitrophenacyl)-1,10-phenanthrolinium *N*-ylide with activated alkynes

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Dedicated to Professor Alexandru Balaban on his 75th birthday

(received 06 Dec 04; accepted 22 Apr 05; published on the web 12 May 05)

Abstract

The 3+2 cycloaddition reaction of 1-(3-nitrophenacyl)-1,10-phenanthrolinium ylide **4** with activated alkynes gave pyrrolo[1,2-a][1,10]phenanthrolines **7a-e**. The reaction of *N*-ylide **4** with DMAD, under controlled conditions, gave regioselectively the primary cycloadduct *trans*-**5a** which, in the presence of triethylamine, rearranged regio- and stereoselectively to *trans*-**6a**. Evidence for the helical chirality of pyrrolophenanthrolines **7b-e** was obtained by NMR spectroscopy.

Keywords: 1,10-Phenanthrolinium *N*-ylide, 1,3-dipolar cycloaddition, regio- and stereoselectivity, pyrrolophenanthrolines, helical chirality

Introduction

The use of heteroaromatic *N*-ylides as 1,3-dipoles has gained increasing interest due to the possibility of obtaining new condensed heterocyclic structures difficult to obtain by other methods.[1-5] The dipolar 3+2 cycloaddition of dipolarophiles to heteroaromatic *N*-ylides raises interesting regio- and stereoselectivity problems.[5-9] Recently, the synthesis of a new heterocyclic system, namely pyrrolo[1,2-a][1,10]phenanthroline, by 1,3-dipolar cycloaddition of 1,10-phenanthrolinium *N*-ylides with acetylenic dipolarophiles, was described.[9-12] The extended heteroaromatic system presents helical chirality, like that of the helicene-type compounds.[13]

Herein we describe the reaction of 1-(3-nitrophenacyl)-1,10-phenanthrolinium *N*-ylide (**4**) with activated alkynes giving new pyrrolo[1,2-a][1,10]phenanthrolines **7a-d**.

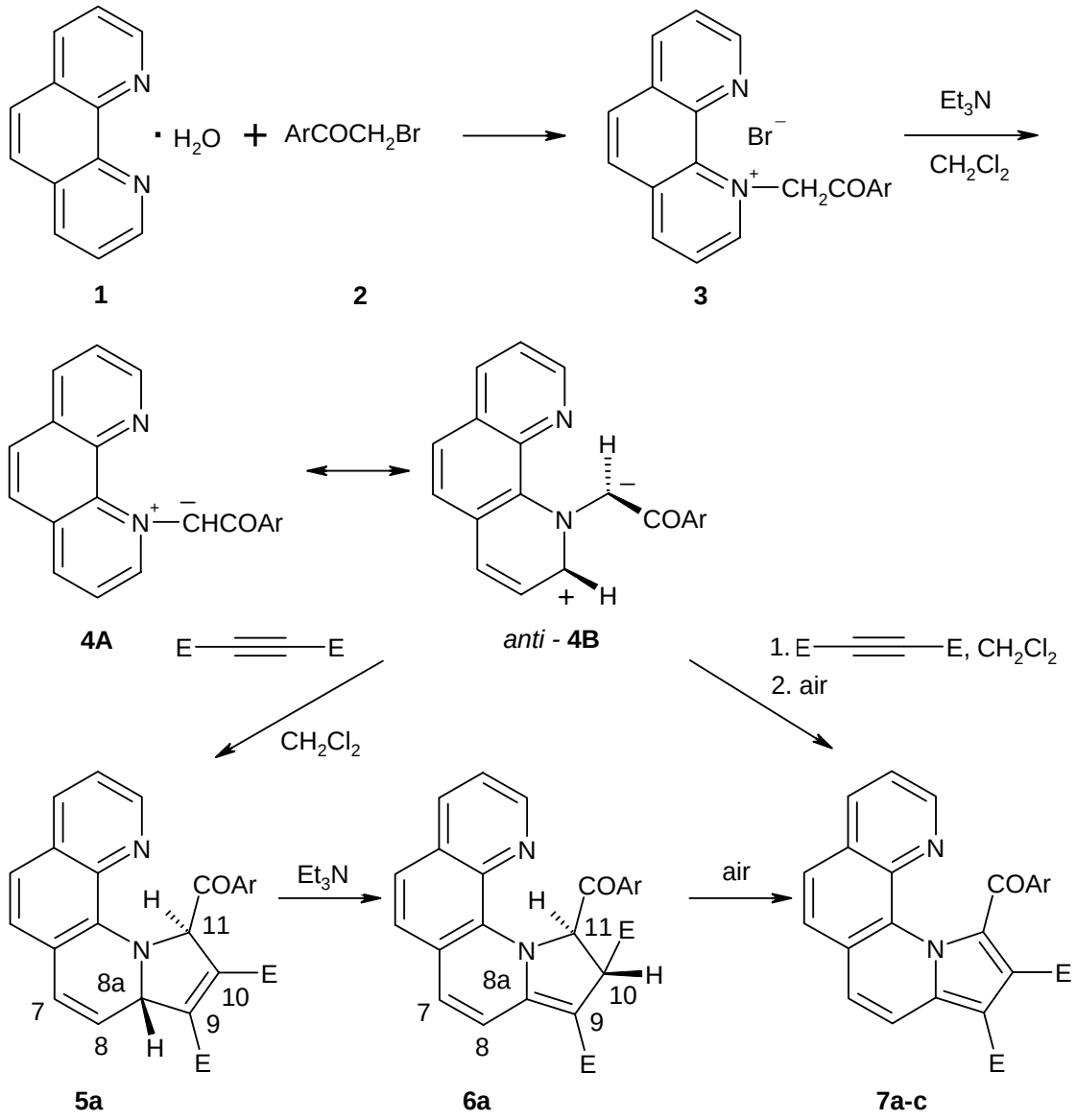
Results and Discussion

1-[2-(3-Nitrophenyl)-2-oxoethyl]-1,10-phenanthrolinium bromide (**3**) was obtained by refluxing 1,10-phenanthroline monohydrate (**1**) and 2-bromo-3'-nitroacetophenone (**2**) in acetone. The structure of the cycloimmonium bromide was assigned by elemental analysis and NMR spectroscopy. In the ^{1}H-NMR spectrum of salt **3** recorded in DMSO-d_6, the methylenic protons appeared as a broad singlet. This is due to non-planarity of the phenanthroline, as we reported recently.[14]

The 1,10-phenanthrolinium *N*-ylide **4**, being unstable, was generated *in situ* by deprotonation of the cycloimmonium salt **3** with triethylamine. The ylide **4** can react with acetylenic dipolarophiles as 1,3-dipole. Treatment of the ylide **4** with dimethyl, diethyl or diisopropyl esters of acetylenedicarboxylic acid in methylene chloride, in the presence of triethylamine, followed by evaporation and refluxing of the residue in ethanol gave pyrrolophenanthrolines **7a-c** in yields of over 75%. We consider that the formation of compounds **7a-c** implies the rearrangement of the primary cycloadducts **5** to dihydroderivatives **6** followed by dehydrogenation in the presence of air (Scheme 1).

The 1-[2-(3-nitrophenyl)-2-oxoethyl]-1,10-phenanthrolinium bromide **3** and dimethyl acetylenedicarboxylate (DMAD) gave, in the presence of triethylamine, the primary cycloadduct *trans*-**5a**. The reaction was performed at 0 °C in methylene chloride using a strictly equimolar ratio between **3** and triethylamine. We have isolated and characterized only the primary cycloadduct *trans*-**5a**.

The purity of *trans*-**5a**, based on ^{1}H-NMR spectroscopy is ca. 95%. The primary cycloadduct is stable in the solid state but in solution, in the presence of triethylamine, rearranges regio- and stereoselectively to give *trans*-**6a**.



Scheme 1. Ar: 3-$NO_2C_6H_4$; E: **a**: CO_2CH_3, **b**: $CO_2C_2H_5$, **c**: $CO_2CH(CH_3)_2$.

The structure of *trans*-**5a** was assigned on the basis of the coupling constants of the hydrogen atoms from the pyrroline and phenanthroline moieties, ^{1}H-NMR chemical shifts of CH and NCH groups, as well as ^{13}C-NMR chemical shifts of the carbonyl groups.

The most characteristic feature of *trans*-**5a** is the large homoallylic coupling, $J_{11,8a}$ = 7.3 Hz. The vicinal and allylic coupling constants of the protons in the position 8a (δ = 6.38 ppm, dt), 8 (δ = 5.93 ppm, dd) and 7 (δ = 6.54 ppm, dd) of *trans*-**5a** were found to be 2.7 and 2.3 Hz, respectively. The close values of the chemical shifts in the ^{13}C-NMR spectrum (δ = 162.8 and 163.5 ppm) of the two carbonyl ester groups represent ~~a~~ strong evidence that they are grafted on a double bond.

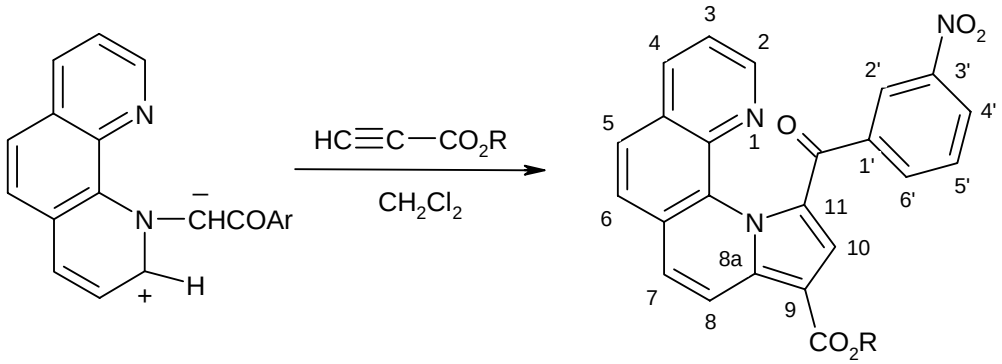
The chemical shift of the ketone group (δ = 193.3 ppm) of *trans*-**5a** is deshielded by ca. 10 ppm compared to those of the corresponding aromatic analogues **7b,c** (solvent $CDCl_3$). This indicated that the COAr group is linked to a Csp^3.

The primary cycloadduct *trans*-**5a** rearranged regio- and stereoselectively, in solution, in the presence of triethylamine, to 1,2-dihydroderivative *trans*-**6a**. Most probably, by the action of triethylamine, the deprotonation occurred at H-11 and the resulting allylic carbanion isomerised and then was protonated to give *trans*-**6a**.

In solution, in the presence of air, the compound *trans*-**6a** aromatized to **7a**. The structure of *trans*-**6a** was assigned by NMR spectroscopy. Thus, in the ^{1}H-NMR spectrum, a vicinal coupling constant of 4.5 Hz between H-10 (δ = 4.02 ppm, d) and H-11 (δ = 7.68 ppm, d) was observed. On the basis of the constant value, a *trans* configuration has been assigned. The different values of the chemical shifts of the carbonyl in the ester groups (δ = 165.8 and δ = 173.3 ppm) indicated that they are grafted on sp^2 and sp^3 carbon atoms, respectively. Supplementary evidence for the structures of *trans*-**5a** and *trans*-**6a** was given by COSY and HETCOR experiments.

The formation of stereoisomer *trans*-**5a** shows that the 1,3-dipolar cycloaddition is stereoselective and that the *N*-ylide participates in the reaction in the *anti* configuration.

The 1,3-dipolar cycloaddition between ylide **4** and activated unsymmetrical alkynes was regiospecific and the pyrrolophenanthroline derivatives **7d,e** were obtained (Scheme 2).



4 **7d,e**

R: Et, *i*Pr

Scheme 2

The structures of the pyrrolophenanthrolines **7a-e** were assigned by elemental analysis and NMR spectroscopy.

In the ^{1}H-NMR spectra of compounds **7b,d**, recorded in $CDCl_3$, the methylenic protons of the ester group appeared as ABX_3 patterns. In the case of the compounds **7c** and **7e** the methyl groups in each isopropyl radical were found to be non-equivalent in the ^{1}H-NMR.

The behavior can be explained by non-coplanarity between pyrrolic and pyridinic moieties, rendering helical chirality to the molecules of **7b,c**, at room temperature.[9] This behavior renders

the molecular framework chiral, thereby explaining the non-equivalence of the diastereotopic methylene and methyl (in the isopropyl group) protons in the ^{1}H-NMR spectra. Recently, this hypothesis was confirmed by X-ray analysis.[15]

Because of the low solubility of compound **7a** in $CDCl_3$, the NMR spectrum was performed in a $CDCl_3$ + TFA mixture. We have observed that the coupling constant between protons H-2 and H-3 in $CDCl_3$ (compounds **7b-e**) was 4.3 Hz, whereas in $CDCl_3$ + TFA (compound **7a**) the respective constant is 6.2 Hz. The same coupling constant of ~ 6.2 Hz was observed when ^{1}H-NMR spectra of compounds **7b-e** were recorded in $CDCl_3$ + TFA. Also, a strong deshielding was observed at protons H-2, H-3 and H-4, respectively ($\Delta\delta > 0.85$ ppm). Both the coupling constant and the deshielding of protons H-2, H-3 and H-4 may be explained as due to protonation of the nitrogen atom (N-1) in the presence of trifluoracetic acid (TFA).

Conclusions

The pyrrolo[1,2-a][1,10]phenanthroline derivatives **7a-d** were obtained by 1,3-dipolar cycloaddition between 1,10-phenanthrolinium ylide **4** and activated alkynes.

The reaction of *N*-ylide **4** with DMAD gave regioselectively the primary cycloadduct *trans*-**5a** which rearranged regio- and stereoselectively to *trans*-**6a** in the presence of triethylamine.

Based on ^{1}H-NMR chemical shift non-equivalence of prochiral groups (ethyl, isopropyl) the pyrrolo[1,2-a][1,10]phenanthrolines **7b-e** were found to possess helical chirality.

Experimental Section

General Procedures. Melting points were determined on a Boëtius hot plate and are uncorrected. Mass spectra were recorded using a VG-QMD-1000 Carlo Erba instrument. The IR spectra were recorded on a Nicolet Impact 410 spectrometer, in KBr pellets. The NMR spectra were recorded on a Varian Gemini 300 BB instrument, operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Supplementary evidence was given by HETCOR and COSY experiments.

1-[2-(3-Nitrophenyl)-2-oxoethyl]-1,10-phenanthrolinium bromide (3). 5 g (25 mmol) 1,10-phenanthroline hydrate and 4.9 g (20 mmol) 2'-bromo-3-nitroacetophenone in 80 mL acetone were refluxed for 12 hrs. The precipitate was filtered by suction and washed with acetone. Yield 76 %, m.p. 215-217 °C (from ethanol). *Anal.* Calcd.$C_{20}H_{14}BrN_3O_3$: C 56.65; H 3.32; Br 18.84; N 9.90. Found: C 56.80; H 3.62; Br 18.27; N 10.18. IR (KBr, cm^{-1}) 863; 1229; 1355; 1531; 1703; 2819; 2986; 3081. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38 (2H, bs, CH_2); 7.90 (1H, dd, *J* = 8.2, 4.3 Hz, H-8); 8.07 (1H, t, *J* = 8.0 Hz, H-5'); 8.46 (1H, dd, *J* = 4.4, 1.8 Hz, H-9); 8.48; 8.53 (2H, 2d, *J* = 8.9 Hz, H-5, H-6); 8.64-8.71 (3H, m, H-3, H-4', H-6'); 8.80 (1H, dd, *J* = 8.2, 1.8 Hz, H-7); 8.87 (1H, t, *J* = 2.0 Hz, H-2'); 9.65 (1H, dd, *J* = 8.2, 1.4 Hz, H-4); 9.71 (1H, dd, *J* = 5.9, 1.4 Hz, H-2).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 69.4 (CH_2); 122.5 (C-2'); 124.9 (C-3); 125.5 (C-8); 127.0 (C-6); 128.3 (C-5'); 130.7 (C-5); 131.3 (C-4'); 131.5, 132.0, 136.0, 138.2 (C-4a, C-6a, C-10a, C-10b); 134.3 (C-6'); 135.5 (C-1'); 138.1(C-7); 148.3 (C-4); 148.4 (C-3'); 148.8 (C-9); 152.1 (C-2); 189.1 (CO).

***trans*-Dimethyl 11-[(3-nitrophenyl)carbonyl]-8a,11-dihydropyrrolo[1,2-*a*][1,10]phen-anthroline -9,10-dicarboxylate (5a).** 2.2 g (5 mmol) cycloimmonium bromide **3** and 5.5 mmol DMAD were suspended in 25 mL of methylene chloride. The mixture was cooled at 0 °C (ice bath), then 5 mmol of triethylamine dissolved in 5 mL of methylene chloride were added under stirring, over 5 minutes. Stirring was continued for 15 minutes and then the reaction mixture was washed with water and the solvent removed at room temperature. The residue was triturated with ethanol, filtered and air dried. The product *trans*-**5a**, obtained in 92 % yield, being too unstable to be analyzed by elemental analysis or melting point, was fully characterized by NMR spectroscopy. IR (KBr, cm^{-1}) 831; 1103; 1206; 1350; 1458; 1532; 1700; 1728; 1747; 2784; 2950; 3089. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.57, 3.88 (6H, 2s, 2Me); 5.93 (1H, dd, *J* = 9.7, 2.3 Hz, H-8); 6.38 (1H, dt, *J* = 7.3, 2.7, 2.3 Hz, H-8a); 6.54 (1H, dd, *J* = 9.7, 2.7 Hz, H-7); 6.77 (1H, d, *J* = 7.3 Hz, H-11); 7.05 (1H, dd, *J* = 8.3, 4.2 Hz, H-3); 7.12, 7.18 (2H, 2d, *J* = 8.2 Hz, H-6, H-5); 7.54 (1H, dd, *J* = 4.2, 1.7 Hz, H-2); 7.72 (1H, t, *J* = 8.0 Hz, H-5'); 7.90 (1H, dd, *J* = 8.3, 1.7 Hz, H-4); 8.38- 8.46 (2H, m, H-4', H-6'); 8.91 (1H, t, H-2'). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 52.5, 52.7 (2 Me); 68.0 (C-8a); 75.9 (C-11); 117.6, 126.8 (C-6, C-5); 120.0 (C-7); 120.7, 129.3, 137.9, 138.1, 138.5, 138.7, 140.4 (C-10, C-9, C-6a, C-4a, C-4b, C-6b, C-1'); 120.9 (C-3); 123.6 (C-2'); 126.4 (C-8); 126.5 (C-4'); 129.5 (C-5'); 134.4 (C-6'); 144.8 (C-2); 148.4 (C-3'); 162.8, 163.5 (10-CO_2Me); 193.3 (COAr).

***trans*-Dimethyl 11-[(3-nitrophenyl)carbonyl]-10,11-dihydropyrrolo[1,2-*a*][1,10]phenanthro-line-9,10-dicarboxylate (6a).** 0.5 g *trans*-**5a** dissolved in 10 mL of methylene chloride was treated with 0.1 mL triethylamine, under cooling, in an ice bath. After 5 minutes of stirring, the solvent was removed at room temperature. The residue was triturated with methanol and filtered. The product *trans*-**6a**, obtained as yellow crystals, being too unstable to be analyzed by elemental analysis or melting point, was fully characterized by NMR spectroscopy. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.70, 3.85 (6H, 2s, 2Me); 4.09 (1H, d, *J* = 4.5 Hz, H-10); 7.22 (1H, dd, *J* = 8.2, 4.2 Hz, H-3); 7.37, 7.47 (2H, 2d, *J* = 8.5 Hz, H-6, H-5); 7.44 (1H, d, *J* = 9.6 Hz, H-7); 7.58 (1H, d, *J* = 4.5 Hz, H-11); 7.80 (1H, t, *J* = 8.0 Hz, H-3'); 7.89 (1H, d, *J* = 9.6 Hz, H-8); 7.92 (1H, dd, *J* = 4.2, 1.8 Hz, H-2); 8.02 (1H, dd, *J* = 8.2, 1.8 Hz, H-4); 8.48-8.56 (2H, m, H-4', H-6'); 9.10 (1H, t, *J* = 2.0 Hz, H-2'). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 49.6 (C-10); 50.4, 52.4 (2Me); 71.0 (C-11); 88.2 (C-9); 119.7 (C-8); 121.0, 126.8 (C-6, C-5); 121.9 (C-3); 119.5, 122.2, 130.3, 131.1, 135.2, 137.2 (C-8a, C-6a, C-4a, C-4b, C-6b, C-1'); 124.0 (C-2'); 127.5 (C-4'); 130.1 (C-5'); 134.9 (C-6'); 136.4 (C-7); 136.7 (C-4); 146.3 (C-2); 148.6 (C-3'); 165.8 (9-COOMe); 173.3 (10-COOMe); 188.0 (COAr).

General procedure for diesters of 11-[(3-nitrophenyl)carbonyl]-pyrrolo[1,2-a][1,10]phenanthroline-9,10-dicarb-oxylic acid (7a-c)

2.2 g (5 mmol) phenanthrolinium salt **3** were suspended in 25 mL of dichloromethane and then 5.5 mmol of dimethyl (or diethyl, diisopropyl) acetylenedicarboxylate were added. Under vigorous stirring 0.75 mL (5 mmol) of triethylamine (dissolved in 5 mL methylene chloride) were added drop wise. After 20 min the reaction mixture was washed twice with water and the solvent evaporated. The residue was refluxed in ethanol for an hour and the precipitate was isolated by filtration.

Dimethyl 11-[(3-nitrophenyl)carbonyl]-pyrrolo[1,2-*a*][1,10]phenanthroline-9,10-dicarboxyl-ate (7a). The product was recrystallized from nitromethane and yellow crystals were obtained. Yield 75 %, mp 286-8 °C. *Anal.* Calcd.$C_{26}H_{17}N_3O_7$: C 64.60; H 3.54; N 8.69. Found: C 64.91; H 3.80; N 8.97. MS *m*/*z*: 483 (M, 5.1 %), 361 (100.0 %). IR (KBr, cm^{-1}) 846; 1104; 1219; 1350; 1460; 1536; 1655; 1704; 1736; 2948; 2997; 3086. ^{1}H-NMR (300 MHz, $CDCl_3$ + TFA) δ 3.85, 4.07 (6H, 2s, $2CH_3$); 7.60 (1H, t, *J* = 8.0 Hz, H-5'); 7.77-7.81 (1H, m, H-4'); 7.95 (1H, d, *J* = 9.6 Hz, H-7); 8.22 (1H, dd, *J* = 8.1, 6.3 Hz, H-3); 8.25-8.29 (2H, m, H-2', H-6'); 8.30, 8.37 (2H, 2d, *J* = 8.9 Hz, H-6, H-5); 8.60 (1H, d, *J* = 9.6 Hz, H-8); 9.15 (1H, dd, *J* = 8.1, 1.1 Hz, H-4); 9.38 (1H, dd, *J* = 6.3, 1.1 Hz, H-2). ^{13}C-NMR (75 MHz, $CDCl_3$ + TFA) δ 52.8, 53.6 (2 CH_3); 94.0 (C-9); 117.6, 120.0, 122.5, 126.3, 126.9, 128.4, 130.5 (C-11, C-10, C-8a, C-6a, C-4a, C-4b, C-6b); 120.2, 125.7 (C-7, C-3); 124.4 (C-2'); 124.6 (C-8); 125.9 (C-5); 126.5 (C-4'); 130.2 (C-6); 130.6 (C-5'); 131.2 (C-6'); 142.8 (C-1'); 144.2 (C-2); 147.5 (C-4); 148.2 (C-3'); 163.8, 165.8 (CO_2CH_3); 181.6 (COAr).

Diethyl 11-[(3-nitrophenyl)carbonyl]-pyrrolo[1,2-*a*][1,10]phenanthroline-9,10-dicarboxyl-ate (7b). The product was recrystallized from nitromethane and yellow crystals were obtained. Yield 84 %; mp 263-5 °C. *Anal.* Calcd. $C_{28}H_{21}N_3O_7$: C 65.75; H 4.14; N 8.22. Found: C 66.11; H 4.33; N 8.47. MS *m*/*z*: 511 (M, 7.8 %), 389 (100.0 %). IR (KBr, cm^{-1}) 844; 1106; 1211; 1346; 1454; 1533; 1655; 1711; 1730; 2897; 2982; 3103. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.09 (3H, t, *J* = 7.1 Hz , 10-CH_2CH_3); 1.38 (3H, t, *J* = 7.1 Hz, 9-CH_2CH_3); 3.79-3.98 (2H, m, 10-CH_2CH_3, ABX_3 system); 4.36-4.44 (2H, m, 9-CH_2CH_3, ABX_3 system); 7.37 (1H, dd, *J* = 8.2, 4.3 Hz, H-3); 7.70 (1H, t, *J* = 8.0 Hz, H-5'); 7.75 (1H, d, *J* = 9.2 Hz, H-7); 7.84, 7.91 (2H, 2d, *J* = 8.6 Hz, H-6, H-5); 8.01 (1H, dd, *J* = 4.3, 1.7 Hz, H-2); 8.21 (1H, dd, *J* = 8.2, 1.7 Hz, H-4); 8.43-8.48 (2H, m, H-4', H-6'); 8.60 (1H, d, *J* = 9.2 Hz, H-8); 8.98 (1H, t, *J* = 1.9 Hz, H-2'). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.7; 14.3 (2 CH_3); 60.4; 61.6 (2 CH_2); 104.5 (C-9); 120.5 (C-8); 122.7 (C-3); 124.5 (C-2'); 125.6, 127.0 (C-6, C-5); 125.5, 126.1, 127.9, 128.8, 129.2, 137.1, 137.5 (C-11, C-10, C-8a, C-6a, C-4a, C-4b, C-6b); 126.4 (C-7); 126.6 (C-4'); 129.4 (C-5'); 135.5 (C-6'); 136.5 (C-4); 139.8 (C-1'); 145.5 (C-2); 148.2 (C-3'); 163.3, 165.4 ($CO_2CH_2CH_3$); 181.5 (COAr).

Diisopropyl11-[(3-nitrophenyl)carbonyl]-pyrrolo[1,2-*a*][1,10]phenanthroline-9,10-dicarboxylate (7c). The product was recrystallized from nitromethane and yellow crystals were obtained. Yield 80 %; mp 229-232 °C; *Anal.* Calcd.$C_{30}H_{25}N_3O_7$: C 66.78; H 4.67; N 7.79. Found: C 67.05; H 4.97; N 8.11. MS *m*/*z*: 540 (M, 11.9 %), 417 (100.0 %). IR (KBr, cm^{-1}) 844;

1106; 1220; 1346; 1453; 1532; 1651; 1705; 2875; 2982; 3086. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.95, 1.09 (6H, 2d, *J* = 6.3 Hz, 10-$CH(CH_3)_2$); 1.38, 1.41 (6H, 2d, *J* = 6.3 Hz, 9-$CH(CH_3)_2$); 4.79 (1H, sep, *J* = 6.3 Hz, 10-$CH(CH_3)_2$); 5.32 (1H, sep, *J* = 6.3 Hz, 9-$CH(CH_3)_2$); 7.37 (1H, dd, *J* = 8.1, 4.3 Hz, H-3); 7.70 (1H, t, *J* = 8.0 Hz, H-5'); 7.75 (1H, d, *J* = 9.3 Hz, H-7); 7.84, 7.92 (2H, 2d, *J* = 8.6 Hz, H-6, H-5); 7.95 (1H, dd, *J* = 4.3, 1.7 Hz, H-2); 8.21 (1H, dd, *J* = 8.1, 1.7 Hz, H-4); 8.43-8.48 (2H, m, H-4', H-6'); 8.61 (1H, d, *J* = 9.3 Hz, H-8); 8.98 (1H, dd, *J* =1.8 Hz, H-2'). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.1, 21.4, 22.0, 22.1 ($4CH_3$); 68.1, 69.8 ($2CHMe_2$); 104.8 (C-9); 120.5 (C-8); 122.6 (C-3); 124.6 (C-2'); 125.4 (C-5); 126.0 (C-7); 126.1, 126.2, 127.8, 128.7, 128.8, 137.0, 137.3 (C-11, C-10, C-8a, C-6a, C-4a, C-4b, C-6b); 126.5 (C-4'); 126.9 (C-6); 129.4 (C-5'); 135.7 (C-6'); 136.4 (C-4); 139.7 (C-1'); 145.3 (C-2); 148.2 (C-3'); 162.9, 165.0 ($CO_2CH(CH_3)_2$); 181.4 (COAr).

General procedure for monoesters of 11-[(3-nitrophenyl)carbonyl]-pyrrolo[1,2-a][1,10]phenanthroline-9-carboxylic acid (7d,e)

2.2 g (5 mmol) phenanthrolinium salt **3** were suspended in 25 mL of dichloromethane and then 6 mmol of ethyl or isopropyl propiolate were added. Under vigorous stirring 0.7 mL (5 mmol) of triethylamine (dissolved in 10 mL of methylene chloride) were added drop wise. After 20 min the reaction mixture was washed with water and the solvent evaporated. The residue was purified by column chromatography on neutral Al_2O_3 using CH_2Cl_2 as eluent.

Ethyl 11-[(3-nitrophenyl)carbonyl]-pyrrolo[1,2-a][1,10]phenanthroline-9-carboxylate (7d). The product was recrystallized from an acetonitrile and ethanol mixture. Yellow crystals were obtained. Yield 42 %; mp 227-229 °C. *Anal.* Calcd. $C_{25}H_{17}N_3O_5$: C 68.33; H 3.90; N 9.56. Found: C 68.66; H 4.11; N 9.82. MS *m*/*z*: 439 (M, 9.1 %), 317 (100.0 %). IR (KBr, cm^{-1}) 842; 1053; 1224; 1348; 1443; 1532; 1653; 1705; 2866; 2976; 3077. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.43 (3H, t, *J* = 7.1 Hz, CH_3); 4.38-4.47 (2H, m, *J* = 7.1 Hz, CH_2); 7.37 (1H, dd, *J* = 8.0, 4.5 Hz, H-3); 7.57 (1H, s, H-10); 7.74 (1H, d, *J* = 9.3 Hz, H-7); 7.75 (1H, t, *J* = 9.0 Hz, H-5'); 7.81, 7.89 (2H, 2d, *J* = 8.5 Hz, H-6, H-5); 8.18-8.22 (2H, m, H-4, H-2), 8.48-8.56 (2H, m, H-4', H-6'); 8.59 (1H, d, *J* = 9.3 Hz, H-8); 9.07 (1H, t, *J* = 1.9 Hz, H-2'). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.5 (CH_3); 60.2 (CH_2); 106.5 (C-9); 120.0 (C-8); 121.7 (C-10); 122.5 (C-3); 124.5 (C-2'); 124.8, 126.6 (C-6, C-5); 125.5, 127.8, 129.2, 131.4, 137.7, 138.9 (C-11, C-8a, C-6a, C-4a, C-4b, C-6b); 125.2 (C-7); 126.1 (C-4'); 129.5 (C-5'); 135.6 (C-4); 136.1 (C-6'); 139.4 (C-1'); 146.0 (C-2); 148.4 (C-3'); 164.3 (CO_2Et); 182.4 (COAr).

Isopropyl 11-[(3-nitrophenyl)carbonyl]-pyrrolo[1,2-a][1,10]phenanthroline-9-carboxylate (7e). The product was recrystallized from nitromethane and yellow crystals were obtained. Yield 37 %; mp 178-180 °C. *Anal.* Calcd. $C_{26}H_{19}N_3O_5$: C 68.87; H 4.22; N 9.27. Found: C 69.11; H 4.35; N 9.51. MS *m*/*z*: 453 (M, 3.8 %), 289 (100.0 %). IR (KBr, cm^{-1}) 841; 1101; 1236; 1349; 1447; 1535; 1648; 1691; 2872; 2998; 3076. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.41, 1.43 (6H, 2d, *J* = 6.2 Hz, $2CH_3$); 5.34 (1H, sep, *J* = 6.2 Hz, $CHMe_2$); 7.41 (1H, dd, *J* = 8.1, 4.5 Hz, H-3); 7.56 (1H, s, H-10); 7.78 (1H, d, *J* = 9.2 Hz, H-7); 7.79 (1H, t, *J* = 7.9 Hz, H-5'); 7.86, 7.95 (2H, 2d, *J* = 8.6 Hz, H-6, H-5); 8.22-8.27 (2H, m, H-4, H-2); 8.50-8.58 (2H, m, H-4', H-6'); 8.63 (1H, d, *J* =

9.2 Hz, H-8); 9.06 (1H, t, *J* = 1.9 Hz, H-2'). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 22.0 (2 Me); 67.3 ($CHMe_2$); 106.8 (C-9); 119.9 (C-8); 121.5 (C-10); 122.3 (C-3); 124.6 (C-2'); 125.0, 126.5 (C-6, C-5); 125.3, 127.6, 129.0, 131.2, 137.5, 138.7 (C-11, C-8a, C-6a, C-4a, C-4b, C-6b); 125.8 (C-7); 126.5 (C-4'); 129.3 (C-5'); 135.4 (C-4); 135.9 (C-6'); 139.3 (C-1'); 145.8 (C-2); 148.2 (C-3'); 163.7 (CO_2iPr); 182.0 (COAr).

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