Iranian Journal of Organic Chemistry Vol. 2, No. 4 (2010) 509-514

Efficient synthesis of stable trihydropyrrolo[1, 2-*a*][1,10]phenanthrolines via a domino-Knoevenagel-cyclization

Reza Heydari*, and Batool Tahamipour
Department of Chemistry, The University of Sistan and Balouchestan, P. O. Box 98135-674, Zahedan, Iran.

Abstract: 1-[4-methylphenacyl]-1,10-phenanthrolinium N-ylide, reacts with CH acids such as malonitrile or ethyl cyanoacetate and aromatic aldehydes via a domino-Knoevenagel cyclization to produce a new class of 9,9-dicyano (or 9-cyano-9-ethoxy carbonyl) -10-(aryl)-11-(4-methylbenzoyl) -8a,10,11–trihydro- pyrrolo[1,2-a][1,10] phenanthrolines as stable helical compounds in a simple and efficient protocol in excellent yields.

Keywords: Trihydropyrrolo[1,2-a][1,10]phenanthrolines , [1,10]phenanthrolinium N-ylide, Domino-Knoevenagel -condensation, Helical chirality, Multicomponent reaction.

Introduction

Cycloimmonium ylides, obtained from various synthetic methods, form a well-known class of zwitterionic compounds that display interesting chemical behaviors [1,2]. The chemistry of cycloimmonium ylides has been widely studied by several groups [3]. The research has focused especially of the pyridinium systems [4], diazinium systems [5] and quinolinium [6] and isoquinolinium [7] substrates. In the last decade, interest in [1,10]phenanthrolinium N-ylides has been increased and, as result, the synthesis of new heterocyclic systems of phenanthroline have been reported [8]. The extended heteroaromatic systems namely pyrrolo[1,2-*a*][1,10]phenanthrolines, presents helical chirality, like that of the helicene-type compounds. These polycyclic compounds are very interesting molecules not only from chemical viewpoint (synthesis, reactivity, stereochemistry, etc.) but also for their industrial applications [9,10]. For instance some soluble pyrrolo[1,2-*a*][1,10]phenanthroline derivatives are very promising candidates for use in organic light emitting diodes (OLEDs) [11]. Owing to the increasing importance of these *N*-heterocycles in the field of technology, the synthesis of new derivatives of these heterocycles is highly desirable. In continuing our interest in [1,10]phenanthroline reactions [12], we succeed in contribution of 1-(4-methylphenacyl)-1,10-phenanthrolinium bromide **3**, that obtained by refluxing 1,10-Phenanthroline monohydrate **1** and 2-bromo-4'-methylacetophenone **2**, in a new multi-component one-pot Knoevenagel condensation giving 9,9-dicyano-10-(aryl)-11-(4-methylbenzoyl) 8a,10,11-trihydro pyrrolo[1,2-*a*][1,10]phenanthrolines **6a-c** or 9-cyano-9-ethoxy carbonyl -10-(aryl)-11- (4-methylbenzoyl) -8a,10,11-trihydropyrrolo [1,2-*a*][1,10] phenanthrolines **6e,d** as novel stable helical macromolecules (Scheme **1**).

Results and discussion

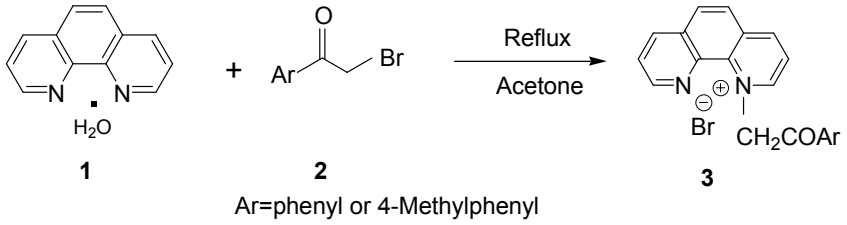
The structure of the 1-(4-methylphenacyl)-1, 10-phenanthrolinium bromide **3** was assigned by elemental analysis and NMR spectroscopy. In the ^{1}HNMR spectrum of salt **3**, recorded in DMSO-d_6, the methylenic hydrogens appeared as a broad singlet peak. This is due to non-planarity of the phenanthroline salt, as reported recently [8c].

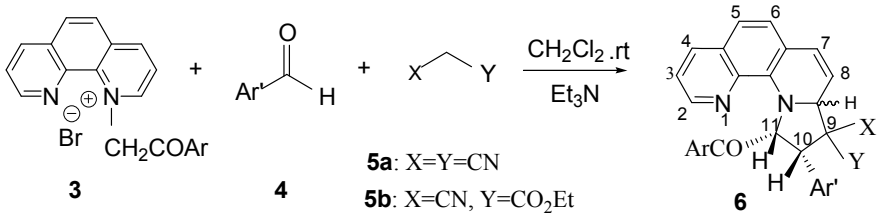
1-(4-methylphenacyl)-1,10-phenanthrolinium bromide **3**, can react with aromatic aldehyde derivatives **4** and CH acids such as malonitrile **5a** or ethyl cyanoacetate **5b** in the presence of triethylamine as base, to afford **6a-d** as new macromolecules in excellent yields .A proposed mechanism is shown in Scheme **2** in agreement with the predicted structure (Scheme **2**).

Herein, 1,10-phenanthrolinium *N*-ylide **8**, which generated *in situ* in the presence of base, attacks to the Knoevenagel's intermediate **7**, that generated simultaneously. Then cyclization will occur to give desired product. This product, against similar

*Corresponding author. Tel: +(98) 541 2446565; E-Mail: heydari@hamoon.usb.ac.ir

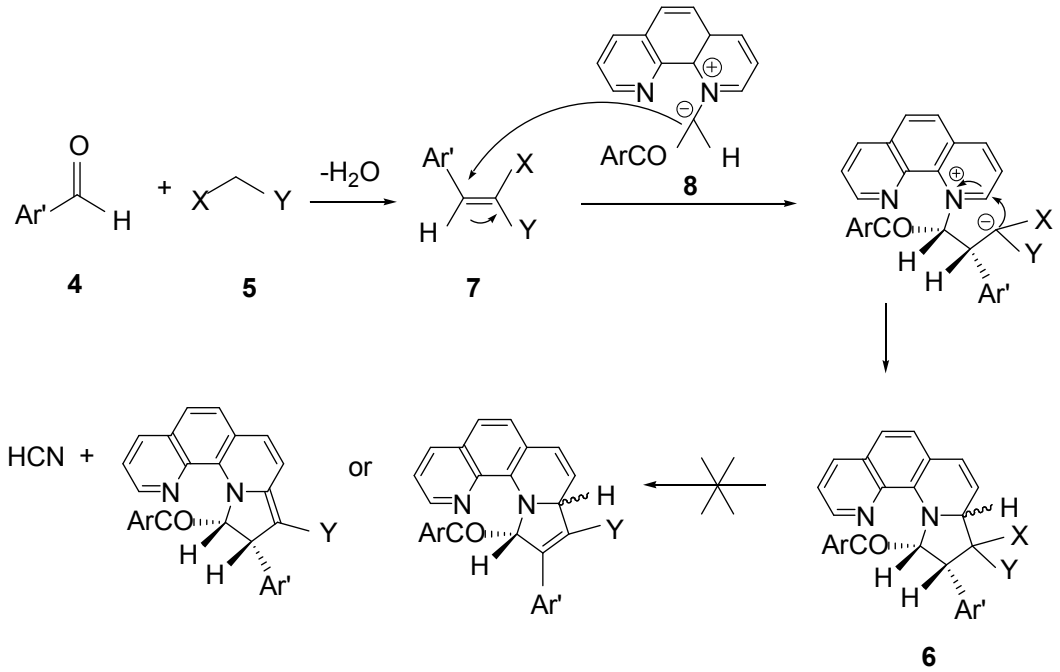
compound [8b], is so stable that could not remove any by-product by the action of triethylamine, or in the presence of air.





6	Ar'	X	Y	Yield%
a	Phenyl	CN	CN	80
b	3-Methylphenyl	CN	CN	85
c	3-Pyridyl	CN	CN	80
d	3-Chlorophenyl	CN	CO_2Et	86
e	1-Naphthyl	CN	CO_2Et	82

Scheme 1. Reaction of 1-(4-methylphenacyl)-1,10-phenanthrolinium bromide **3**, with aromatic aldehydes **4** and CH acids **5**.



Scheme 2. Proposed mechanism

The structure of compound **6a** was determined on the basis of its elemental analyses, mass spectroscopy, ^{1}H and ^{13}C NMR and IR spectroscopic data. The ^{1}H NMR spectrum of **6a** exhibited two distinct doublet signals arising from C-10-H and C-11-H (δ = 3.81, 6.73) ppm, respectively. *Cis* vicinal geometry of these protons is confirmed with respect to the coupling constant of *cis* dihydropyrrolo ring protons in similar structure. (*J*=8.3) [13]. Characteristic signal for C-8a-H were observed at δ = 6.27 ppm as a doublet of doublet signal (J_1 = 2.2, J_2 = 1.4 Hz) that confirm with coupling constant in similar structure [14]. In the ^{1}H-NMR spectra of compounds **6d,e** recorded in $CDCl_3$, diastereotopic methylenic protons of the ester group appeared as ABX_3 patterns. This behavior can be explained by non-planarity between pyrrolic and pyridinic moieties, which imparts helical chirality to the molecules of **6d,e**. The ^{13}C-NMR spectrum of **6a** showed 27 distinct resonances in agreement with the proposed structure.

The close values of the chemical shifts in the ^{13}C-NMR spectrum (δ = 112.83 and 113.37 ppm) of the two carbonitrile groups represent a strong evidence that they are grafted on pyrrole ring. Also the IR spectrum showed an CN absorption at ν=2247 cm^{-1}. The mass spectrum of **6a** displayed the molecular ion [M$^+$] signal at m/z = 466 which is consistent with the product structure. Any initial fragmentation involves ring fragmentation.

Experimental

General Procedure

Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a JASCO FT-IR spectrometer, respectively. Also, the ^{1}H and ^{13}C NMR spectra were obtained with a BRUKER DRX-500 AVANCE instrument using $CDCl_3$ as the applied solvent and TMS as internal standard at 500.1 and 125.8 MHz, respectively. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. In addition, the mass spectra were recorded on Shimadzu GCMS-QP5050A mass spectrometer operating at an ionization potential of 70 eV. [1, 10]-Phenanthroline, 2'-bromo-4-methylacetophenone, malonitrile, ethyl cyanoacetate and aldehyde derivatives were purchased from Merck and Aldrich companies and used without further purification.

1-(4-methylphenacyl)-1,10-phenanthrolinium bromide (3):

1 g (5 mmol) [1,10]-phenanthroline mono hydrate and 1 g (5 mmol) 2'-bromo-4-methylacetophenone in 50 mL acetone were refluxed for 12 hrs. The precipitate was filtered by suction and washed with acetone. Yield 86 % (1.69 gr), m.p 220-222 °C. IR (KBr) (ν_{max}, cm^{-1}): 1472, 1606 (s, C=C), 1697(s, C=O). ^{1}H NMR (500.1MHz; $CDCl_3$): δ_H 2.45 (3H, s, CH_3), 7.26 (2H, bs, CH_2), 7.50 (2H, d, J=7.9Hz, C-3'-H,C-5'-H), 7.85 (1H, dd, J_1=4.2, J_2=8.1Hz, C-8-H), 8.06 (2H, d, *J*=8.0, C-5-H, C-6-H), 8.40 (2H, d, *J*=7.9, C-2'-H, C-6'-H), 8.43 (1H, dd, J_1=4.1, J_2=1.0, C-9-H), 8.55 (1H, dd, J_1=8.0, J_2=5.5, C-3-H), 8.7(1H, dd, J_1=8.0, J_2=1.0, C-7-H), 9.54 (1H, dd, J_1=8.0, J_2=1.0, C-4-H), 9.65 (1H, dd, J_1=5.5, J_2=1.0Hz, C-2-H). ^{13}C NMR (125.8 MHz, $CDCl_3$): 22.23 (CH_3), 70.44(CH_2), 125.50 (C-8), 126.33 (C-3), 127.79 (C-5), 129.11 (3', 5'), 130.68 (2', 6'), 131.46 (C-6), 132.25, 132.54, 132.79 ,137.12, (C-4a, C-6a, C-10-a, C-10-b), 138.75, 139.27 (C-1',C-4'), 145.64 (C-7), 148.88 (C-4), 149.52 (C-9), 152.86 (C-2), 191.17 (CO). MS (m/z, %): 395 (M+2, 4), 394 (M+1, 6), 393 (M+, 8.5), 382 (14), 372 (18), 368 (100), 358 (27), 341 (31), 314 (100), 297 (48), 285 (38), 264 (64), 255 (37), 212 (100), 180 (100). Anal. Calcd for $C_{21}H_{17}BrN_2O$ (393): C, 64.12; H, 4.32; Br, 20.10; N, 7.12. Found: C, 64.19; H, 4.45; Br, 20.05; N, 7.16.

General synthetic procedure exemplified by 9,9-dicyano-10-(phenyl) -11-(4-methylbenzoyl)-8a,10,11-trihydropyrrolo[1,2-a][1,10] phenanthroline (6a):

1-(4-Methylphenacyl)-1,10-phenanthrolinium bromide (2 mmol, 0.758g) benzaldehyde (2.2 mmol, 0.23g) and malonitrile (2.2mmol, 0.14g) were suspended in 25 mL of methylene chloride. Then (2.5 mmol, 0.25g) of triethylamine dissolved in 5 mL of methylene chloride were added under stirring, over 5 minutes at ambient temperature. 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 washed with ethyl acetate and air dried to afford desired product.

This compound was obtained as bright orange powder in 80% yield, (0.74g), mp: 138-140 °C, IR (KBr) (ν_{max}, cm^{-1}): 1453, 1605 (s, C=C), 1686(s, C=O), 2247 (m, CN). ^{1}H NMR (500.1MHz; $CDCl_3$): δ_H 2.38 (3H, s, CH_3), 3.81 (1H, d, *J* = 8.3 Hz, C-10-H), 5.92 (1H, dd, J_1 = 9.9, J_2 = 2.2 Hz, C-8-H), 6.27 (1H, dd, J_1 = 2.2, J_2 = 1.4 Hz, C-8a-H), 6.73 (1H, d, *J* = 8.4 Hz, C-11-H), 6.84 (1H, dd, J_1 = 9.9, J_2 = 1.4 Hz, C-7-H), 7.02 (1H, dd, J_1 = 8.2, J_2 = 3.8 Hz, C-3-H), 7.11(2H, m, C-3"-H, C-5"-H), 7.12 (1H, d, *J* = 8.2 Hz, C-5-H), 7.18 (1H, d, *J* = 8.2 Hz, C-6-H), 7.40-7.43 (3H, m, C-3'-H, C-4'-H,

C-5'-H), 7.51 (1H, dd, J_1 = 3.8 Hz, J_2 = 1.3 Hz, C-2-H), 7.55-7.57(2H, m, C-2'-H, C-6'-H), 7.62 (2H, d, J_1 = 7.2 Hz, C-2"-H, C-6"-H), 7.88 (1H, dd, J_1 = 8.1, J_2 = 1.3 Hz, C-4-H). ^{13}C NMR (125.8 MHz, $CDCl_3$): 22.05 (CH_3), 49.47 (C-9), 57.07 (C-10), 69.51 (C-8a), 73.61 (C-11), 112.83, 113.37 (2CN), 116.72 (C-8), 117.77 (C-7), 118.28 (C-6a), 121.23 (C-3), 127.47 (C-5) 129.28 (C-3" ,5"), 129.33 (C-2' ,6'), 129.51 (C-3' ,5'), 129.81 (C-2",6"), 130.19 (C-4'), 130.68 (C-4a), 131.69 (C-6), 132.69 (C-1'), 132.98 (C-4"), 136.72 (C-4), 137.53 (C-6b), 138.32 (C-4b), 143.93 (C-1"), 145.47 (C-2), 196.26 (CO). MS (m/z, %): 466 (M+, 5.5), 433 (4%), 360 (12), 347 (10), 299 (100), 271 (33), 245 (13), 180 (100), 153 (35), 140 (37), 119 (100), 91 (100), 77 (100). Anal. Calcd for $C_{31}H_{22}N_4O$ (466): C, 79.82; H, 4.72; N, 12.01. Found: C, 79.88; H, 4.67; N, 12.11.

9,9-dicyano-10-(3-methylphenyl)-11-(4-methylbenzoyl)-8a,10,11-trihydropyrrolo [1,2-a][1,10] phenanthroline, (6b):

This compound was obtained as bright yellow powder in 85% yield (0.78g), mp: 147-149 °C, IR (KBr) (ν_{max}, cm^{-1}): 1453, 1606 (s, C=C), 1686 (s, C=O), 2245 (m, CN). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 2.37(3H, s, CH_3), 2.39 (3H, s, CH_3), 3.77 (1H, d, J = 8.4 Hz, C-10-H), 5.91 (1H, dd, J_1 = 9.9, J_2 = 2.2 Hz, C-8-H) 6.26 (1H, dd, J_1 = 2.2, J_2 = 1.6 Hz, C-8a-H), 6.71 (1H, d, J = 8.4 Hz, C-11-H), 6.82 (1H, dd, J_1 =9.9, J_2 = 1.6 Hz, C-7-H), 7.01 (1H, dd, J_1 = 8.2, J_2 = 4.1 Hz, C-3-H), 7.10 (2H, d, J_2 = 8.0 Hz, C-3"-H, C-5"-H), 7.12 (1H, d, J = 8.2 Hz, C-5-H), 7.17 (1H, d, J = 8.2 Hz, C-6-H), 7.23(1H, d, J=7.7, C-4'-H), 7.29-7.31 (2H, m, C-2'-H, C-5'-H), 7.38 (1H, d, J=7.8, C-6'-H), 7.49 (1H, dd, J_1 = 4.1, J_2 = 1.46 Hz, C-2-H), 7.62 (2H, d, J = 8.0 Hz, C-2"-H, C-6"-H), 7.88 (1H, dd, J_1 = 8.2 , J_2 = 1.46 Hz, C-4-H) ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.82, 22.05 ($2CH_3$), 49.51 (C-9), 56.99 (C-10), 69.46 (C-8a), 73.60 (C-11), 112.86, 113.46 (2CN), 116.78 (C-8), 117.73 (C-7), 118.29 (C-6a), 121.22 (C-3), 126.15, 127.46 (C-5,6), 129.27 (C-3" ,5"), 129.49 (C-2" ,6"), 129.64, 130.06 (C-2', 4'), 130.67 (C-3'), 130.95, 131.65 (C-5', 6'),132.56, 133.07 (C-1',4"), 136.69 (C-4), 137.55 (C-1"), 138.37 (C-4a), 139.57 (C-6b), 143.86 (C-4b), 145.44 (C-2), 195.91 (CO). MS (m/z, %): 480 (M^+, 6), 479 (7), 433 (7), 419 (14), 361 (14), 284 (20), 271 (28), 245(13), 195(22), 180 (100), 119 (100), 91 (80). Anal. Calcd for $C_{32}H_{24}N_4O$ (480): C, 80.00; H, 5.00; N, 11.66 Found: C, 80.09; H, 4.94; N, 11.58.

9,9-dicyano-10-(3-pyridyl)-11-[(4-methylbenzoyl]-8a,10,11-trihydropyrrolo[1,2-a][1,10]phenanthroline (6c):

This compound was obtained as dark yellow powder in 80% yield (0.71g) mp:159-161 °C, IR (KBr) (ν_{max}, cm^{-1}): 1456, 1606 (s, C=C), 1674(s, C=O), 2251 (m, CN). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 2.19 (3H, s, CH_3) 3.67 (1H, d, J = 8.5 Hz, C-10-H), 5.75 (1H, dd, J_1 = 9.9, J_2 = 2.1 Hz, C-8-H), 6.06 (1H, dd, J_1 = 2.1, J_2 = 1.4 Hz, C-8a-H) 6.55 (1H, d, J = 8.4 Hz, C-11-H), 6.68 (1H, dd, J_1 =9.9, J_2 = 1.4 Hz, C-7-H), 6.9 (1H, dd, J_1 = 8.1, J_2 = 3.8 Hz, C-3-H), 6.95 (2H, d, J=8.0, C-3"-H, C-5"-H), 6.96 (1H, d, J = 8.1 Hz, C-5-H), 7.02 (1H, d, J = 8.1 Hz, C-6-H), 7.23-7.26 (1H, m, C-5'-H), 7.40-7.42 (2H, d,J=7.9, C-2"-H, C-6"-H), 7.42 (1H, dd, J_1 = 3.8, J_2 = 1.3 Hz, C-2-H), 7.75 (1H, dd, J_1 = 8.1, J_2 = 1.3 Hz, C-4-H), 7.87 (1H, d, J = 7.9 Hz, C-6'-H), 8.46-8.50 (2H, m, H-2', H-4') ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.89 (CH_3), 48.91 (C-9), 54.11 (C-10), 68.87 (C-8a), 73.35 (C-11), 112.41, 112.68 (2CN), 116.35 (C-8), 117.96 (C-7), 118.07 (C-6a), 121.31 (C-3), 124.31 (C-5'), 127.30 (C-5), 128.79 (C-1'), 129.13 (C-3",5"), 129.59 (C-2",6"), 130.53 (C-4a), 131.67 (C-6), 132.54 (C-4"), 135.43 (C-1"), 136.26 (C-6'), 136.72 (C-4), 137.45 (C-6b), 144.18 (C-4b), 145.52 (C-2), 150.56 (C-2'), 151.33 (C-4'), 195.26 (CO). MS (m/z, %): 467 (M^+, 1), 464 (8), 375 (7), 289 (55), 258(13), 245(14), 230(13), 180 (100), 154 (30), 119 (95), 91(73). Anal. Calcd for $C_{30}H_{21}N_5O$ (467): C, 77.08; H, 4.49; N, 14.98. Found: C, 77.12; H, 4.42; N, 14.88.

9-cyano-9-ethoxycarbonyl-10-(3-chlorophenyl)-11-(4-methylbenzoyl)-8a,-10,11 trihydro pyrrolo [1,2-a][1,10]phenanthroline (6d):

This compound was obtained as bright yellow powder in 86% yield, (0.94g), mp: 170-172 °C. IR (KBr) (ν_{max}, cm^{-1}): 1125,1292 (s, C-O), 1456, 1606 (s, C=C), 1684 (s, C=O ketone), 1740 (s, C=O ester), 2247 (m, CN) .^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.30 (3H, t, J=7.1, OCH_2CH_3), 2.38 (3H, s, CH_3), 4.05 (1H, d, J = 8.4 Hz, C-10-H), 4.27-4.35 (2H, m, OCH_2CH_3) 5.73 (1H, dd, J_1 = 10.0, J_2 = 2.1 Hz, C-8-H) 6.10 (1H, dd, J_1 = 2.0, J_2 = 1.9 Hz, C-8a-H), 6.64 (1H, d, J = 8.4 Hz, C-11-H), 6.71(1H, dd, J_1 =10.0, J_2 = 1.7 Hz, C-7-H), 6.99 (1H, dd, J_1 = 8.3, J_2 = 4.1 Hz, C-3-H), 7.02 (1H, d, J = 8.2 Hz, C-5-H), 7.12 (2H, d, J=8.1, C-3"-H, C-5"-H), 7.13 (1H, d, J = 8.2 Hz, C-6-H), 7.28-7.31 (2H, m, C-5'-H, C-6'-H), 7.42-7.43 (2H, m, C-2'-H, C-4'-H), 7.53 (1H, dd, J_1 = 4.1, J_2 = 1.6 Hz, C-2-H), 7.63 (2H, d, J_1 = 8.1 Hz, C-2"-H, C-6"-H), 7.84 (1H, dd, J_1= 8.3, J_2=1.6 Hz, C-4-H) ^{13}C NMR (125.8 MHz, $CDCl_3$): 14.52 (CH_3), 22.02 (CH_3), 54.44 (C-9), 62.51 (C-10), 64.05(CH_2), 70.29 (C-8a), 72.43 (C-11), 116.29 (CN), 117.00 (C-8), 118.08 (C-7), 118.43 (C-6a), 121.00 (C-3), 127.43, 127.47 (C-5' ,6') , 129.29 (C-3" ,5"), 129.41

(C-5),129.46 (C-2",6"), 129.83(C-4a), 130.57 (C-2', C-4'), 130.65 (C-6), 133.38 (C-4"), 135.04 (C-1'), 136.62, 137.27 (C-1",C-3'), 137.66 (C-4), 138.96 (C-6b), 143.60 (C-4b), 145.17 (C-2), 165.04 (CO ester), 195.58 (CO ketone). MS (m/z, %): 548 (M^+, 10) , 518 (10), 473 (25), 427 (42), 354 (100), 312 (42), 291 (75), 180 (100), 91(100), 77 (40). Anal. Calcd for $C_{33}H_{26}N_3O_3Cl$(547.5): C, 72.32; H, 4.74; N, 7.67. Found: C, 72.28; H, 4.80; N, 7.63.

9-cyano-9-ethoxycarbonyl-10-(naphthyl)-11-(4-methylbenzoyl)8a,-10,11-trihydropyrrolo[1,2-a][1,10]phenanthroline (6e):

This compound was obtained as dark yellow powder in 82% yield (0.92g), mp: 167-169 °C , IR (KBr) (ν_{max}, cm^{-1}): 1125, 1242 (s, C-O), 1455, 1508 (s, C=C), 1670 (s, C=O ketone), 1732 (C=O ester), 2245 (m, CN). ^1H NMR (500.1 MHz, $CDCl_3$): δ_H 1.00 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 2.21 (3H, s,CH_3), 4.02-4.17 (2H, m, OCH_2CH_3), 5.04 (1H, d, *J* = 7.9 Hz, C-10-H), 5.73 (1H, dd, J_1 = 9.9, J_2 = 2.0 Hz, C-8-H), 6.37 (1H, dd, J_1 = 2.0, J_2 = 1.5 Hz, C-8a-H) 6.73 (1H, dd, J_1 =9.9, J_2 = 1.5 Hz, C-7-H), 6.86 (1H, d, *J* = 7.8 Hz, C-11-H), 6.90 (2H, d, *J*=7.9 Hz, C-3"-H ,C-5"-H), 6.98 (1H, dd, J_1 = 8.2, J_2 = 3.9 Hz, C-3-H), 7.04 (1H, d, *J* = 8.1 Hz, C-5-H), 7.15 (1H, d, *J* = 8.1 Hz, C-6-H), 7.38-7.41 (2H, m, CH naphthyl), 7.52 (1H, dd, J_1 = 3.9, J_2 = 1.4 Hz, C-2-H), 7.53-7.56 (2H, m, CH naphthyl), 7.61 (1H, m, CH naphthyl), 7.81 (1H, d, *J*=7.6 Hz, CH naphthyl), 7.84 (1H, m, CH naphthyl), 7.85 (2H, d, *J* = 7.9 Hz, C-2"-H, C-6"-H), 8.2 (1H, dd, J_1 = 8.2, J_2 = 1.4 Hz, C-4-H) ^{13}C NMR (125.8 MHz, $CDCl_3$): 14.52 (CH_3), 22.02 (CH_3), 48.67 (C-9), 63.11 (C-10), 63.92(CH_2), 72.11 (C-8a), 73.00 (C-11), 116.74 (CN), 116.83 (C-8), 118.44 (C-7), 118.52 (C-6a), 120.96 (C-3), 122.55, 125.73, 126.11, 126.59, 126.96 (5C Naphtyl), 127.47 (C-5), 129.06 (C-3" ,5"), 129.14 (C-2" ,6"), 129.32, 129.68, 130.42 (3C Naphtyl), 130.67 (C-4a), 131.59 (C-6), 132.83 (C-4"),133.27, 134.19 (2C Naphthyl), 136.57 (C-4), 137.78 (C-6b), 139.25 (C-4b), 143.18 (C-1"), 145.23 (C-2), 165.85(CO, ester), 196.99 (CO, ketone). MS (m/z, %): 563 (M^+, 2), 502 (2), 384 (4), 314 (8), 291 (12), 251 (54), 193(28), 180 (94), 152 (26), 119 (100), 91 (42). Anal. Calcd for $C_{37}H_{29}N_3O_3$ (563): C, 78.86; H, 5.15; N, 7.46. Found: C, 78.79; H, 5.20; N, 7.41.

Conclusion

In summary, we have developed a facile and efficient synthetic method for preparation of substituted 9, 9-dicyano (or 9-cyano-9-ethoxycarbonyl) -8a, 10, 11-trihydropyrrolo [1,2-*a*][1,10]phenanthroline derivatives via a new multi-component Knoevenagel condensation. This one-pot MCR by contrast to the multi-step syntheses requires minimal work-up and generated products in excellent yields.

Acknowledgements

We gratefully acknowledge financial support from the Research Council of University of Sistan and Balouchestan.

References

[1] Zugrăvescu, I.; & Petrovanu, M. *N-Ylides Chemistry*, McGraw-Hill Int, New York, **1976**.

[2] Padwa, A.; *1, 3-Dipolar Cycloaddition Chemistry*, John Wiley & Sons, New York, **1984**, 2, *chapter 12,* 277.

[3] (a) Vanecko, J. A.; Wan, H.; West, F. G. *Tetrahedron*, **2006**, 26, 1043. (b) Pinho e Melo, T. M. V. D. M. *Eur. J. Org. Chem.* **2006**, 2873.(c) Karafiloglou, P.; Surpateanu, G.; *Int. J. Quantum. Chem*, **2004**, 98, 456. (d) Sureshbabu, A. R.; Dhamodharan, R. *Synthetic Commun*, **2009**, 39, 2889. (e) Dumitrascu, F.; Georgescu, E.; Caira, M. R; *SYNLETT*, **2009**, 20, 3336.(f) Saravanan, P.; Sureshbabu, A. R.; Raghunathan, R. *Synthetic Commun*, **2010**, 40, 2329.(g) Kojima, S.; Fujitomo, K.; Itoh, Y.; Hiroike, K. *HETEROCYCLES*, **2006**, 67, 679.(h) Butler, R. N.; Coyne, A. G.; McArdle, P.; *J. Chem. Soc*., *Perkin Trans. 1*, **2001**, 1391.(i) Georgescu, E.; Draghici, C.; Iuhas, P. C.; *Arkivoc*, **2005**, (x), 95.

[4] (a) Dugstad, H.; Undheim, K.; *Synthetic Commun*, **2008**, 38, 1846.(b) Hayashi, N.; Kawajiri, N.; Uchida, T.; Matsumoto, K. *HETEROCYCLES,* **2005**, 66, 175.

[5] (a) Caprosu, M. D.; Butnariu, R. M.; Mangalagiu, I. *HETEROCYCLES*, **2005**, 65, 1871.(b) Fujii, H.; Kawano, I.; Iwafuji, K.; Sawae, Y.; Nagamatsu, K. *HETEROCYCLES*, **2006**, 70, 207.

[6] (a) Georgescu, E.; Caira, M. R. *SYNLETT*, **2009**, 11, 1795.(b)Toth, J.; Blasko, G.; Dancso, A.; Toke, L. *Synthetic Commun*, **2006**, 36, 3581.

[7] (a) Srinivasan, R.; Akila, S.; Caroline, J.; Balasubramanian, K. *Synthetic Commun*, **1998**, 28, 2245.(b) Kianmehr, E.; Faramarzi, R.; Estiri, H. *HETEROCYCLES*, **2009**, 78, 415.

[8] (a) Dumitrascu, F.; Mitan, C. I.; Drghici, C. *Tetrahedron Lett,* **2001**, 42, 8379. (b) Dumitrascu, F.; Draghici, C.; Caira, M. R. *Arkivoc*, **2005**, (x),

165. (c) Dumitrascu, F.; Caira, M. R.; Draghici, C. *J. Chem. Crystallogr,* **2004**, 34, 577. (d) Dumitraşcu, F.; Caira, M. R.; Draghici, C.; Caproiu, M. T.; Badoiu, A.; *Molecules*, **2005**, 10, 321.(e) Dumitrascu, F.; Caira, M. R.; Draghici, C. *Arkivoc,* **2010**, (ix), 97.

[9] Leontie, L.; Druta, I.; Danac, R.; Rusu, G. I. *Synth. Met*, **2005**, 155, 138.

[10] Prelipceanu, M.; Prelipceanu, O. S.; Leontie, L.; *Phys. Lett. A,* **2007**, 368, 331.

[11] Prelipceanu, M.; Prelipceanu, O. S. *Mater Sci Semicond Process*, **2007**, 10, 77.

[12] Maghsoodlou, M. T.; Tahamipour, B.; Marandi, G. *Arkivoc,* **2008**, (II), 153.

[13] Tsuge, O.; Kanemasa, S. *Bull. Chem. Soc. Jpn,* **1985**, 58, 3320.

[14] Maghsoodlou, M. T.; Khorassani, S. M. *J. Heterocyclic.Chem*, **2008**, 45, 289.