Diastereoselective Synthesis of γ-Dispiroiminolactone Bearing Naphthalene or Bipyridine Pendant Groups

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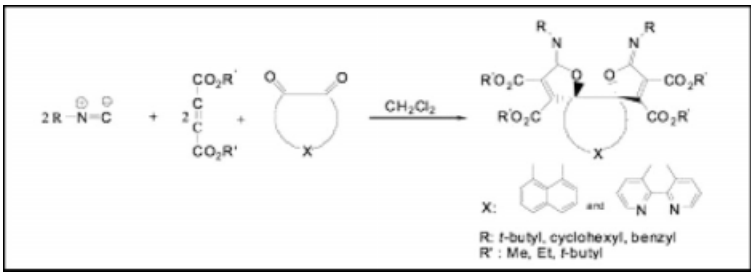
Received December 2, 2008
DOI 10.1002/jhet.164
Published online 25 August 2009 in Wiley InterScience (www.interscience.wiley.com).



Diastereoselective γ-dispiroiminolactone products **4a–m** were obtained from a condensation of the highly reactive 1:1 intermediate of isocyanides and acetylenic esters with aromatic α-dicarbonyls compounds **3a, b**.

J. Heterocyclic Chem., **46**, 843 (2009).

INTRODUCTION

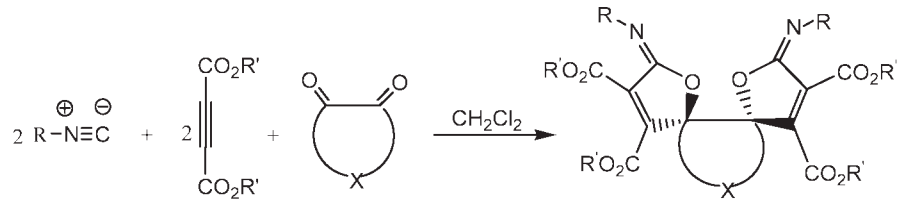
γ-Spirolactones and iminolactones are heterocyclic compounds obtained via ''one pot'' multicomponents condensation reaction [1,2]. They are generally used as precursors for the preparation of a wide range of compounds including antibacterial agents [3a]. Moreover, the ease of hydrolysis of iminolactones to spirolactones affords a number of biologically active natural products such as kijanolide, tetranolide, and chlorothricolide [3b–d]. Multicomponent reactions [4,5] are commonly used approaches for production of iminolactones by virtue of their convergence, facile execution, and generally proceed with high yields [1,2]. Recently, we have reported a series of iminolactones from the reaction of isocyanide with activated acetylenic esters in the presence of carbonyl compounds [6–8]. Intimately related condensation is the reaction of isocyanide with acetylenic diesters and carbonyl compounds affording *gama*-spiroiminolactones [1,2,9]. Continuing with our investigation of this reaction with activated α-diketones, we examined the reaction of 1,2-dicarbonyl groups of acenaphthenequinone and phendione with acetylenic esters in the presence of variety isocyanides and successfully prepared the γ-dispiroiminolactone derivatives reported herein.

RESULTS AND DISCUSSION

The reaction of alkyl isocyanides with dialkyl acetylenedicarboxylates in the presence of 1,2-diketones, acenaphthenequinone and phendione afford new γ-dispiroiminolactone products **4a–m** (Scheme 1). Such condensation reaction generally yields the γ-spiroiminolactone analogues [8–11]. For example, when the α-ketoester or α-ketoamide is used, the carbonyl of the ester or the amide functionality is not involved in the reaction [10]. This reaction is molar ratio dependent and influenced by the ratio of the dicarbonyl compounds to the isocyanide and the dialkyl acetylenedicarboxylate. The reaction of the preformed highly reactive zwitterionic intermediate with activated α-dicarbonyl ketone at 1:1:1 molar ratio of reactants **1**, **2**, and **3** favors γ-spiroiminolactones, whereas at 2:2:1 molar ratio the reaction yields γ-dispiroiminolactones [12]. We utilized the 2:2:1 molar ratio of reactants resulting in the participation of both carbonyl groups and the formation of γ-dispiroiminolactone products, **4a–f** and **4g–m** from acenaphthenequinone and phendione, respectively. The products are obtained as diastereoselective racemic mixture based on NMR and X-ray data (see Experimental section).

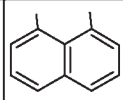
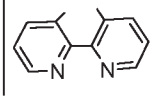
The reported products **4a–m** are stable solids and their structures determined by IR, ^{1}H, ^{13}C NMR, and

Scheme 1



1	R
a	*t*-butyl
b	cyclohexyl
c	benzyl

2	R'
a	Me
b	Et
c	*t*-butyl

3	X
a	
b	

4	3	R	R'	(%) yield
a	a	benzyl	Me	93
b	a	cyclohexyl	Me	88
c	a	cyclohexyl	Et	80
d	a	t-butyl	Me	91
e	a	*t*-butyl	Et	96
f	a	*t*-butyl	*t*-butyl	91
g	b	benzyl	Me	80
h	b	benzyl	Et	94
i	b	benzyl	*t*-butyl	79
j	b	cyclohexyl	Me	74
k	b	cyclohexyl	Et	84
l	b	cyclohexyl	*t*-butyl	79
m	b	*t*-butyl	Et	90

Mass spectrometry with **4a** and **4h** structurally authenticated by single X-ray single crystal diffraction. The ^{1}H NMR spectrum of compound **4a** exhibited two singlets arising from the methyl of the ester groups [δ 3.38 ppm (6H, s, 2OMe), 3.90 ppm (6H, s, 2OMe)] and one singlet [δ 4.55 ppm (4H, s, 2CH$_2$)] due to the methylene of the benzyl groups. The aromatic region of ^{1}H NMR spectrum clearly accounts for the protons associated with the aromatics of benzyl and naphthal moieties. The ^{13}C NMR data displays 19 distinct signals consistent with the structure of **4a**. The characteristic signal resulting from the spiro carbon was identified at δ 101.18 ppm. In addition, FTIR spectrum of compound **4a** showed strong absorptions at 1749 and 1733 cm^{-1} relevant to the ester groups and 1683 cm^{-1} attributed to C=N (see Experimental section). The mass spectrum of compound **4a** displayed a molecular ion peak of 700 (*m*/*z*). Single crystal of compound **4a** was grown from dichloromethane/ethanol (1:3) solution and the X-ray structure is in agreement with the NMR data for γ-dispiroiminolactone (Fig. 1).

Pertinent structural information is deduced from solution NMR for these class of compounds (**4a–m**). For example, the benzylic methylene proton signals for the compounds derived from the benzyl cyanide are diagnostic of the symmetry of the molecules. The mode of splitting is associated with spatial arrangement of the α-diketonic derived building block. The products bearing acenaphthenequinone derived moiety (**4a–f**) display one singlet accounting for four magnetically equivalent protons for the benzylic methylenes (C$_2$ symmetry). On the other hand for the products bearing pyridyl (**4g–m**), the benzylic methylene protons appear as an AB-quartet. The NMR mode of splitting is related to the lack of C$_2$ symmetry in the molecule associated with the formation of nonaromatic six-membered ring. Variable temperature ^{1}H NMR was performed on the model compounds, **4a** and **4h** and no dynamic effect was observed reflecting the structural rigidity of these compounds. The stereochemistry of all reported products are comparable with compound **4a** or **4h** obtained as racemate.

It is noteworthy to mention that the solvent has an effect on the reaction yield with good yields could be obtained using nonpolar solvents, such as benzene and toluene. However, some of the products in this work (e.g., **4a–i**) were obtained from a reaction using dichloromethane at 38°C for 27 h. Optimization of the reaction conditions was investigated and higher yields were obtained using dichloromethane and benzene mixture (1:4) at 75°C for 48 h. All the synthesized products,

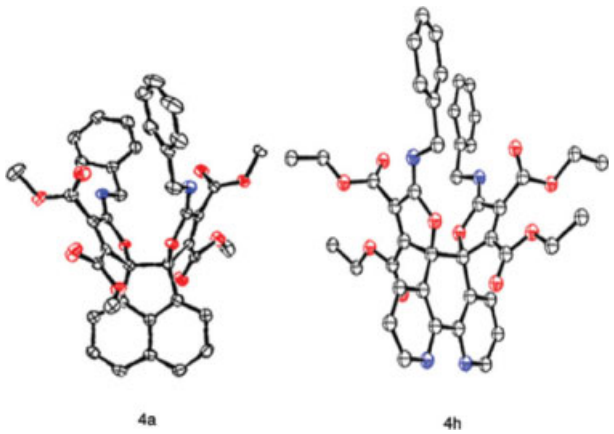
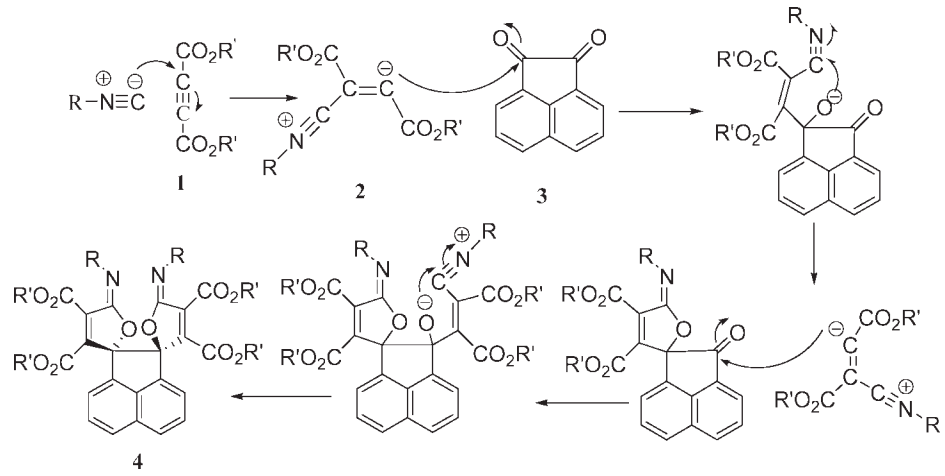


Figure 1. X-ray structure of **4a** and **4h** as model compounds. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 2



4a–f were fully characterized and the formation can be rationalized by the mechanism shown in Scheme 2.

EXPERIMENTAL

Starting materials, dialkyl acetylenedicarboxylates; *tert*-butyl, cyclohexyl, and benzyl isocyanides; acenaphthenequinone and phendione were purchased from Fluka, Buchs, and Switzerland, and used as received. Melting point and IR spectra were measured on an Electrothermal 9100 apparatus and on Shimadzu IR-470 spectrometer. Elemental analysis for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. The ^{1}H and ^{13}C NMR spectra were measured using Bruker DRX-500 AVANCE instrument in $CDCl_3$ at 300.1 and 75.5 MHz, respectively. Mass spectra were recorded on a Shimadzu GC/MS QP 1100 EX mass spectrometer operating at an ionization potential of 70 ev. X-ray diffracted intensities were measured from single crystals at 100 K on an Oxford Diffraction Gemini-R Ultra CCD diffractometer using monochromatized Cu-Kα (λ = 1.54178 Å). A partial projections of the heterocyclic rings with their atomic numbering are depicted in Figure 2. The interatomic distances and angles for each heterocyclic ring in compounds **4a** and **4h** are depicted in Table 1 and 2.

General procedures. The solution of alkyl isocyanide (1 mmol) in 3 mL of CH_2Cl_2 was slowly added dropwise to the mixture of acenaphthenequinone (0.5 mmol) and DMAD (1 mmol) in 20 mL of dry CH_2Cl_2 for 5 min at room temperature. The reaction mixture was heated to 38°C for 28 h. The crude product was collected by filtration and crystallized from dichloromethane-methanol (1:3) and washed with cold diethyl ether (2 × 5 mL).

Bis(Dimethyl-5-benzyl-5H-6H′)-dispiro[furan-2,5′-acenaphthenequinone]-3,3′,4,4′-tetracarboxylate (4a). Light brown powder, yield: 0.32 g (91%), m.p. 203–205°C, IR (KBr) (υ_{max}, cm^{-1}): 1744 and 1729 (4C=O), 1689 (2C=N). ^{1}H NMR: (300 MHz, $CDCl_3$): δ_H 3.38 (6H, s, 2OMe), 3.90 (6H, s, 2OMe), 4.55 (4H, s, $2CH_2$ of benzyl), 7.22–7.32 (10H, m, 10CH), 7.34 (2H, d, J = 7.0 Hz, 2CH), 7.64 (2H, t, J = 7.0 Hz, 2CH), 7.93 (2H, d, J = 8.0 Hz, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 51.72 ($2NCH_2$), 52.53 and 53.36 (4OMe), 101.18 (2Cspiro), 120.33, 126.86, 126.91, 127.92, 127.75, 128.36, 128.51, 130.64, 134.90, 136.37, 138.70, and 144.10 (C=$C_{iminolactone}$ and C_{arom}), 156.26 (N=$C_{iminolactone}$), 160.29 and 161.35 (4C=O of esters). MS (*m*/*z*, %): 701 (M^+ + 1) (1), 700 (M^+ +3), 684 (1), 669 (1), 641 (2), 609 (6), 577 (1), 533 (3), 121 (4), 105 (3), 91 (100). Anal. Calcd for $C_{40}H_{32}N_2O_{10}$ (700.69): C, 68.57; H, 4.60; N, 4.00%; Found: C, 68.39; H, 4.58; N, 4.03%.

Bis(Dimethyl-5-cyclohexyl-5H-6H′)-dispiro[furan-2,5′-acenaphthenequinone]-3,3′,4,4′-tetracarboxylate (4b) Yellow powder, yield: 0.31 g (91%), m.p. 233–236°C, IR (KBr) (λ_{max}, cm^{-1}): 1749 and 1738 (4C=O), 1695 (2C=N). ^{1}H NMR: (300 MHz, $CDCl_3$): δ_H 1.19–1.77 (20H, m, $10CH_2$), 3.43 (6H, s, 2OMe), 3.55 (1H, m, N—CH), 3.94 (6H, s, 2OMe), 7.37 (2H, d, J = 7.0 Hz, 2CH), 7.63 (2H, t, J = 7.1 Hz, 2CH), 7.91 (2H, d, J = 7.0 Hz, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_c 24.82, 25.52 and 32.83 ($5CH_2$ of cyclohexyl), 52.54 and 53.24 (4OMe), 57.35 (2N—*C*H), 100.23 ($2C_{spiro}$), 120.10,

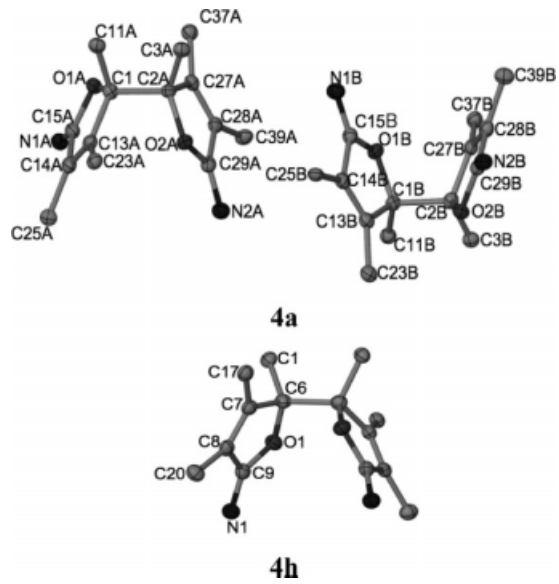


Figure 2. Asymmetric unit projections and atoms numbering of each heterocyclic ring in the structures of compounds **4a** and **4h**.

126.65, 128.46, 130.50, 135.51, 136.85, 137.70, and 143,33 (C=$C_{iminolactone}$ and C_{arom}), 154.98 (2C=$N_{iminolactone}$), 160.15 and 161.66 (4C=O of esters). MS (*m/z*, %): 685 (M^+ +1, 10), 684 (M^+, 18), 602 (12), 543 (16), 417 (3), 83 (44), 59 (17), 55(100). Anal. Calcd for $C_{38}H_{40}N_2O_{10}$ (684.73): C, 66.65; H, 5.89; N, 4.09%; Found: C, 65.87; H, 6.02; N, 4.15%.

Bis(Diethyl-5-cyclohexyl-5H-6H′)-dispiro[furan-2,5′-acenaphthenequinone]-3,3′,4,4′-tetracarboxylate (4c) Pale white powder, yield: 0.36 g (96%), m.p. 230–233°C, IR (KBr) (υ_{max}, cm^{-1}): 1742 and 1733 (4C=O), 1683 (2C=N). ^{1}H NMR: (300 MHz, $CDCl_3$): δ_H 0.51 (3H, t, *J* = 5.4 Hz, 2OCH2*CH*$_3$), 1.14–1.75 (20H, m, 10CH_2), 1.35 (3H, t, *J* = 5.4 Hz, 2OCH_2CH_3), 3.68 (1H, m, N—CH), 4.37 (4H, m, 2OCH_2), 4.41 (4H, m, 2OCH_2), 7.35 (2H, d, *J* = 7.0 Hz, 2CH), 7.59 (2H, t, *J* = 7.0 Hz, 2CH), 7.86 (2H, d, *J* = 7.0 Hz, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_c 12.75 and 13.93 (4OCH_2CH_3), 24.83, 25.63 and 33.10 (5CH_2 of cyclohexyl), 57.1 (2N*C*Me_3), 61.16 and 62.37 (4OCH_2CH_3), 100.39 (2C_{spiro}), 119.85, 126.15, 128.28, 130.45, 134.00, 136.19, 137.93, and 142.93 (C=$C_{iminolactone}$ and C_{arom}), 154.10 (2C=$N_{iminolactone}$), 159.77 and 161.58 (4C=O of esters). MS (*m/z*, %): 742 (M^+ +2, 3), 741 (M^+ +1, 6), 740 (M^+, 13), 658 (8), 613 (4), 585 (38), 83 (35), 55 (100). Anal. Calcd for $C_{42}H_{48}N_2O_{10}$ (740.33): C, 68.09; H, 6.53; N, 3.78%; Found: C, 68.15; H, 6.49; N, 3.83%.

Bis(Dimethy-5-tert-butylimino-5H-6H′)-dispiro[furan-2,5′-acenaphthenequinone]-3,3′,4,4′-tetracarboxylate (4d). Yellow crystals, yield: 0.59 g (93%), m.p. 207–210°C, IR (KBr) (λ_{max}, cm^{-1}): 1749 and 1733 (4C=O), 1683 (2C=N). ^{1}H NMR: (300 MHz, $CDCl_3$): δ_H 1.27 (18H, s, 2C*Me*$_3$), 3.34 and 3.91 (6H, 2s, 4OMe), 7.30 (2H, d, *J* = 7.0 Hz, 2CH), 7.60 (2H, t, *J* = 7.4 Hz, 2CH), 7.89 (2H, d, *J* = 8.2Hz, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_c 29.40 (2C*Me*$_3$), 52.07 and 52.98 (4OMe), 55.03 (N*C*Me_3), 100.81 (2C_{spiro}), 119.23, 126.21, 128.31, 130.30, 137.34, 137.53, 137.85, and 141.56 (C=$C_{iminolactone}$ and C_{arom}), 151.57 (2C=$N_{iminolactone}$), 160.17 and 162.41 (4C=O of esters). MS (*m/z*, %): 632 (M^+, 3), 576 (31), 561 (5), 502 (7), 444 (13), 429 (8), 419 (4), 397 (5), 297 (4), 213 (27), 57 (100). Anal. Calcd for $C_{34}H_{36}N_2O_{10}$ (632.24): C, 64.55; H, 5.74; N, 4.43%; Found: C, 64.48; H, 5.80; N, 4.21%.

Bis(Diethyl-5-tert-butylimino-5H-6H′)-dispiro[furan-2,5′-acenaphthenequinone]-3,3′,4,4′-tetracarboxylate (4e). Yellow crystals, yield: 0.39 g (88%), m.p. 197–200°C, IR (KBr) (υ_{max}, cm^{-1}): 1747 and 1731 (4C=O), 1680 (2C=N), ^{1}H NMR: (300 MHz, $CDCl_3$): δ_H 1.27 (18H, s, 2C*Me*$_3$), 1.30 (6H, t, *J* = 7.1 Hz, 2OCH_2*CH*$_3$), 1.37 (6H, t, *J* = 7.0 Hz, 2OCH_2*CH*$_3$), 4.33 (4H, m, 2OCH_2), 4.43 (4H, m, 2OCH_2), 7.28 (2H, d, *J* = 6.9 Hz, 2CH), 7.56 (2H, t, *J* = 7.4 Hz, 2CH), 7.85 (2H, d, *J* = 8.2 Hz, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_c 12.6 and 14.1 (4OCH_2*CH*$_3$), 29.5 (2C*Me*$_3$), 54.9 (2N*C*Me_3), 126.95, 128.25, 130.35, 137.65, 137.97, 138.37, and 141.76 (C=$C_{iminolactone}$ and C_{arom}), 151.75 (2C=$N_{iminolactone}$), 159.80 and 162.06 (4C=O of esters). MS (*m/z*, %): 689 (M^+ +1, 4), 688 (M^+, 8), 632 (98), 576 (17), 559 (64), 503 (36), 385 (36), 57 (100). Anal. Calcd for $C_{38}H_{44}N_2O_{10}$ (688.30): C, 66.26; H, 6.44; N, 4.07%; Found: C, 66.50; H, 6.51; N, 3.89%.

Bis(Di-tert-butyl-5-tert-butylimino-5H-6H′)-dispiro[furan-2,5′-acenaphthenequinone]-3,3′,4,4′-tetracarboxylate (4f). Yellow crystals, yield: 0.32 g (80%), m.p. 210–213°C, IR (KBr) (υ_{max}, cm^{-1}): 1743 and 1726 (4C=O), 1678 (2C=N). ^{1}H NMR: (300 MHz, $CDCl_3$): δ_H 0.80 (18H, s, 2CMe_3), 1.25 (18H, s, 2NCMe_3), 1.60 (18H, s, 2CMe_3), 7.53 (2H, d, *J* = 6.9 Hz, 2CH), 7.69 (2H, t, *J* = 7.0 Hz, 2CH), 7.97 (2H, d, *J* = 8.0 Hz, 2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_c 27.13 and 28.14 (4OCMe_3), 29.53 (2NCMe_3), 54.89 (2N*C*Me_3), 82.00 and 83.05 (4O—*C*Me_3), 99.86 (2C_{spiro}), 122.76, 126.57, 128.42, 130.63, 134.36, 137.82, 139.34, and 142.86 (C=$C_{iminolactone}$ and C_{arom}), 158.64 (2C=$N_{iminolactone}$), 160.77 and 161.40 (4C=O of esters). MS (*m/z*, %): 643 (6), 531 (7), 476 (5), 358 (4), 314 (9), 234 (5), 57 (100). Anal. Calcd for $C_{46}H_{60}N_2O_{10}$ (800): C, 69.00; H, 7.50; N, 3.50%; Found: C, 70.13; H, 7.61; N, 3.42%. Anal. Calcd for $C_{46}H_{60}N_2O_{10}$ (800.98): C, 68.98; H, 7.55; N, 3.50%; Found: C, 69.30; H, 7.60; N, 3.53%.

Bis(dimethyl 5-benzylimino-5H,6H′)-dispiro(furan-2,5′-[1,10]phenanthroline)-3,3′,4,4′-tetracarboxylate (4g). Brown powder; yield: 0.29 g (80%), m.p. 94–97°C, IR (KBr) (υ_{max}, cm^{-1}): 1740 and 1732 (4C=O), 1687 (2C=N). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 3.29 (6H, s, 2 OMe), 3.84 (6H, s, 2 OMe), 4.71 (4H, AB quartet, 2 CH_2 of benzyl), 7.21–7.31 (14H, m, 14 CH_{arom}), 8.86 (2H, dd, J_1 = 4.0, J_2 = 2.0 Hz, 2 CH_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 52.37 (2 NCH_2), 52.78 and 53.26 (4 OMe), 91.32 (2 C_{spiro}), 124.36, 126.86, 127.94, 128.18, 128.31, 133.10, 133.66, 139.07, 146.73, 150.53, and 151.28 (C=$C_{iminolactone\ ring}$ and C_{arom}), 155.09 (2C=$N_{iminolactone}$), 160.06 and 160.87 (4C=O of esters). MS (*m/z*, %): 729 (M^+ +1, 2), 728 (M^+, 3), 669 (8), 610 (17), 587 (3), 452 (11), 321 (8), 179 (8), 91 (58). Anal. Calcd for $C_{40}H_{32}N_4O_{10}$ (728.70): C, 65.93; H, 4.43; N, 7.69%; Found: C, 65.78; H, 4.52; N, 7.57%.

Bis(diethyl 5-benzylimino-5H,6H′)-dispiro(furan-2,5′-[1,10]phenanthroline)-3,3′,4,4′-tetracarboxylate (4h). Pale yellow powder; yield: 0.37 g (94%), m.p. 176–179°C, IR (KBr) (υ_{max}, cm^{-1}): 1737 and 1733 (4C=O), 1686 (2C=N); ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 0.87 (6H, t, *J* = 7.1 Hz, 2 OCH_2*CH*$_3$), 1.28 (6H, t, *J* = 7.1 Hz, 2 OCH_2*CH*$_3$), 3.82 (4H, ABX_3 system, 2 O*C*H_2CH_3), 4.34 (4H, ABX_3 system, 2 O*C*H_2CH_3), 4.71 (4H, AB quartet, 2 CH_2 of benzyl), 7.24–7.38 (14H, m, 14 CH_{arom}), 8.93 (2H, t, *J* = 6.2 Hz, 2 CH_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 13.36 and 13.92 (4 OCH_2*CH*$_3$), 52.22 (2 NCH_2), 62.30 and 62.56 (4 O*C*H_2CH_3), 91.34 (2 C_{spiro}), 124.67, 126.83, 127.96, 128.08, 128.29, 128.67, 133.91, 139.23, 146.25, 150.86, and 151.81 (C=$C_{iminolactone\ ring}$ and C_{arom}), 155.26 (2C=$N_{iminolactone}$), 159.62 and 160.56 (4C=O of esters). MS (*m/z*, %): 784 (M^+, 8), 694 (12), 132 (4), 91 (100), 65 (4), 44 (4). Anal. Calcd for $C_{44}H_{40}N_4O_{10}$ (784.81): C, 67.34; H, 5.14; N, 7.14%; Found: C, 67.46; H, 5.23; N, 7.02%.

Bis(di-tert-butyl 5-benzylimino-5H,6H′)-dispiro(furan-2,5′-[1,10]phenanthroline)-3,3′,4,4′-tetracarboxylate (4i). Light brown crystals; yield: 0.35 g (79%), m.p. 138–141°C, IR (KBr) (υ_{max}, cm^{-1}): 1738 and 1718 (4C=O), 1687 (2C=N); ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 1.09 (18H, s, 2 C*Me*$_3$), 1.53 (18H, s, 2 C*Me*$_3$), 4.74 (4H, AB quartet, 2 CH_2 of benzyl), 7.28–7.44 (14H, m, CH_{arom}), 9.02 (2H, d, *J* = 3.7 Hz, 2 CH_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 27.32 and 27.92 (4 O*C*Me_3), 51.79 (2 N—*C*H_2), 84.74 and 85.89 (4 O*C*Me_3), 91.83 (2 C_{spiro}), 125.10, 126.75, 127.69, 127.86, 128.04, 128.34, 128.83, 133.12, 138.85, 144.59, and 151.35 (C=$C_{iminolactone\ ring}$ and C_{arom}), 158.77 (2C=$N_{iminolactone}$), 160.16 and 161.69 (4C=O of esters). MS (*m/z*, %): 896 (M^+, 4), 795 (2), 704 (3), 670 (16), 537 (8), 444 (4), 200 (1), 105 (5), 91 (15), 56 (43), 44 (77), 41 (100). Anal. Calcd for $C_{52}H_{56}N_4O_{10}$ (897.02): C, 69.63; H, 6.29; N, 6.25%; Found: C, 69.65; H, 6.36; N, 6.21%.

Table 1

Interatomic distances (*l*, Å) and bond angles (ϕ, °) around the heterocyclic rings in compound **4a**.

O(1A)-C(15A)	1.375 (3)
O(1A)-C(1A)	1.455 (3)
O(2A)-C(29A)	1.373 (3)
O(2A)-C(2A)	1.455 (3)
N(1A)-C(15A)	1.254 (3)
N(2A)-C(29A)	1.260 (3)
C(1A)-C(13A)	1.513 (3)
C(1A)-C(11A)	1.515 (3)
C(1A)-C(2A)	1.605 (3)
C(2A)-C(3A)	1.509 (3)
C(2A)-C(27A)	1.518 (3)
C(15A)-O(1A)-C(1A)	109.72 (16)
C(29A)-O(2A)-C(2A)	110.08 (16)
O(1A)-C(1A)-C(13A)	103.36 (16)
O(1A)-C(1A)-C(11A)	112.28 (17)
C(13A)-C(1A)-C(11A)	116.41 (18)
O(1A)-C(1A)-C(2A)	109.10 (17)
C(13A)-C(1A)-C(2A)	111.96 (18)
C(11A)-C(1A)-C(2A)	103.78 (17)
O(2A)-C(2A)-C(3A)	114.32 (18)
O(2A)-C(2A)-C(27A)	102.95 (16)
C(3A)-C(2A)-C(27A)	112.53 (17)
O(2A)-C(2A)-C(1A)	108.03 (16)
C(3A)-C(2A)-C(1A)	104.42 (17)
C(27A)-C(2A)-C(1A)	114.84 (18)
N(1A)-C(15A)-O(1A)	126.8 (2)
N(1A)-C(15A)-C(14A)	125.2 (2)
O(1A)-C(15A)-C(14A)	108.00 (18)
C(28A)-C(27A)-C(37A)	128.1 (2)
C(28A)-C(27A)-C(2A)	109.55 (19)
C(37A)-C(27A)-C(2A)	122.29 (19)
C(27A)-C(28A)-C(29A)	109.1 (2)
C(27A)-C(28A)-C(39A)	131.5 (2)
C(29A)-C(28A)-C(39A)	119.43 (19)
N(2A)-C(29A)-O(2A)	126.9 (2)
N(2A)-C(29A)-C(28A)	125.5 (2)
O(2A)-C(29A)-C(28A)	107.58 (19)
O(1B)-C(15B)	1.374 (3)
O(1B)-C(1B)	1.449 (3)
O(2B)-C(29B)	1.375 (3)
O(2B)-C(2B)	1.447 (3)
N(1B)-C(15B)	1.251 (3)
N(2B)-C(29B)	1.259 (3)
C(1B)-C(11B)	1.512 (3)
C(1B)-C(13B)	1.525 (3)
C(1B)-C(2B)	1.616 (3)
C(2B)-C(3B)	1.507 (3)
C(2B)-C(27B)	1.517 (3)
C(15B)-O(1B)-C(1B)	109.60 (16)
C(29B)-O(2B)-C(2B)	109.70 (16)
O(1B)-C(1B)-C(11B)	112.61 (18)
O(1B)-C(1B)-C(13B)	103.22 (17)
C(11B)-C(1B)-C(13B)	117.29 (19)
O(1B)-C(1B)-C(2B)	108.59 (17)
C(11B)-C(1B)-C(2B)	103.50 (18)
C(13B)-C(1B)-C(2B)	111.59 (18)
O(2B)-C(2B)-C(3B)	114.58 (17)
O(2B)-C(2B)-C(27B)	103.43 (17)
C(3B)-C(2B)-C(27B)	113.43 (18)
O(2B)-C(2B)-C(1B)	109.00 (17)
C(3B)-C(2B)-C(1B)	104.30 (18)
C(27B)-C(2B)-C(1B)	112.27 (18)
N(1B)-C(15B)-O(1B)	126.7 (2)
N(1B)-C(15B)-C(14B)	125.3 (2)
O(1B)-C(15B)-C(14B)	107.94 (18)
C(28B)-C(27B)-C(37B)	124.5 (2)
C(28B)-C(27B)-C(2B)	109.39 (19)
C(37B)-C(27B)-C(2B)	126.04 (19)
C(27B)-C(28B)-C(29B)	108.5 (2)
C(27B)-C(28B)-C(39B)	129.3 (2)
C(29B)-C(28B)-C(39B)	121.8 (2)
N(2B)-C(29B)-O(2B)	125.4 (2)
N(2B)-C(29B)-C(28B)	126.4 (2)
O(2B)-C(29B)-C(28B)	108.13 (19)

The interatomic distances and angles for each heterocyclic ring in compound **4a** is depicted in Table 1.

Bis(dimethyl 5-cyclohexylimino-5H,6H′)-dispiro(furan-2,5′-[1,10]phenanthroline)-3,3′,4,4′-tetracarboxylate (4j). Pale yellow crystals; yield: 0.26 g (74%), m.p. 148–151°C, IR (KBr) (υ_{max}, cm^{-1}): 1681 and 1723 (4C=O), 1643 (2C=N). ^1H NMR (300.1 MHz, $CDCl_3$): δ_H 1.19–1.78 (20H, m, 10 CH_2 of cyclohexyl), 3.30 (6H, s, 2 OMe), 3.69 (2H, m, 2 NC*H*), 3.87 (6H, s, 2 OMe), 7.43 (2H, dd, J_1 = 4.0, J_2 = 7.5 Hz, 2 CH_{arom}), 7.63 (2H, d, J = 7.5 Hz, 2 CH_{arom}), 8.91 (2H, dd, J_1 = 9.2, J_2= 4.0 Hz, 2CH_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 24.69, 25.61 and 33.01 (10 *C*H_2 of cyclohexyl), 52.66 and 53.11 (4 OMe), 57.45 (2 N*C*H), 90.86 (2 C_{spiro}), 124.45, 128.97, 133.13, 134.35, 145.86, 150.59, and 151.16 (C=$C_{iminolactone\ ring}$ and C_{arom}), 152.53 (2C=$N_{iminolactone}$), 160.24 and 161.64 (4C=O of esters). MS (*m*/*z*, %): 714 (M^+ +2, 4), 713 (M^+ +1, 13), 712 (M^+, 27), 644 (6), 630 (5), 629 (12), 378 (10), 252 (17), 170 (27), 83 (43), 67 (33), 55 (100). Anal. Calcd for $C_{38}H_{40}N_4O_{10}$ (712.74): C, 64.04; H, 5.66; N, 7.86%; Found: C, 63.96; H, 5.70; N, 7.81%.

Bis(diethyl 5-cyclohexylimino-5H,6H′)-dispiro(furan-2,5′-[1,10]phenanthroline)-3,3′,4,4′-tetracarboxylate (4k). Brown crystals; yield: 0.32 g (84%), m.p. 65–68°C, IR (KBr) (υ_{max}, cm^{-1}): 1742 and 1730 (4C=O), 1685 (2C=N). ^1H NMR (300.1 MHz, $CDCl_3$): δ_H 0.80 (6H, t, J = 7.2 Hz, 2 OCH_2CH_3), 1.25 (6H, t, J = 7.2 Hz, 2 OCH_2CH_3), 1.21–2.14 (20H, m, 10 CH_2 of cyclohexyl), 3.59 (2H, m, 2 NC*H*), 3.78 (4H, m, 2 OCH_2CH_3), 4.30 (4H, m, 2 OCH_2CH_3), 7.37 (2H, dd, J_1 = 4.0, J_2 = 7.0 Hz, 2 $CH_{arom,}$), 7.53 (2H, d, J = 7.0 Hz, 2 CH_{arom}), 8.82 (2H, d, J = 4.0 Hz, 2 CH_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 13.32 and 13.91 (4 OCH_2CH_3), 24.34, 24.66, 25.60, 32.94, and 33.11 (10 *C*H_2 of cyclohexyl), 57.27 (2 N*C*H), 61.49 and 62.20 (4 OCH_2CH_3), 90.74 (2 C_{spiro}), 124.46, 129.32, 133.27, 133.54, 146.16, 150.15, and 151.03 (C=$C_{iminolactone\ ring}$ and C_{arom}), 152.87 (2C=$N_{iminolactone}$), 159.87 and 160.63 (4C=O of esters). MS (*m*/*z*, %): 769 (M^+ +1, 40), 768 (M^+, 82), 686 (36), 604 (27), 407 (14), 83 (29), 55 (100). Anal. Calcd for $C_{42}H_{48}N_4O_{10}$ (768.85): C, 65.61; H, 6.29; N, 7.29%; Found: C, 65.70; H, 6.32; N, 7.25%.

Bis(di-tert-butyl 5-cyclohexylimino-5H,6H′)-dispiro(furan-2,5′-[1,10]phenanthroline)-3,3′,4,4′-tetracarboxylate (4l). Pale yellow crystals; yield: 0.34 g (79%), m.p. 202–205°C, IR (KBr) (υ_{max}, cm^{-1}): 1744 and 1735 (4C=O), 1686 (2C=N); ^1H NMR (300.1 MHz, $CDCl_3$): δ_H 1.00 (18H, s, 2 C*Me*$_3$), 1.52 (18H, s, 2 C*Me*$_3$), 1.29–1.80 (20H, m, 10 CH_2 of cyclohexyl), 3.68 (2H, m, 2 NC*H*), 7.41 (2H, dd, J_1 = 4.7, J_2 = 7.9 Hz, 2 CH_{arom}), 7.64 (2H, dd, J_1 = 1.4, J_2 = 7.sz9 Hz, 2

Table 2

Interatomic distances (l, Å) and bond angles (ϕ, °) around the heterocyclic rings in compound **4h**.

O(1)-C(9)	1.380 (2)
O(1)-C(6)	1.456 (2)
N(1)-C(9)	1.257 (2)
C(6)-C(7)	1.527 (2)
C(6)-C(6)#1	1.565 (4)
C(9)-O(1)-C(6)	110.31 (13)
O(1)-C(6)-C(1)	108.71 (15)
O(1)-C(6)-C(7)	102.58 (14)
C(1)-C(6)-C(7)	112.03 (15)
O(1)-C(6)-C(6)#1	106.49 (13)
C(1)-C(6)-C(6)#1	114.00 (11)
C(7)-C(6)-C(6)#1	112.16 (18)
C(8)-C(7)-C(17)	127.54 (17)
C(7)-C(8)	1.330 (3)
C(7)-C(17)	1.477 (3)
C(8)-C(9)	1.463 (3)
C(8)-C(20)	1.497 (3)
C(8)-C(7)-C(6)	109.69 (16)
C(17)-C(7)-C(6)	122.72 (16)
C(7)-C(8)-C(9)	109.27 (16)
C(7)-C(8)-C(20)	130.36 (17)
C(9)-C(8)-C(20)	119.76 (16)
N(1)-C(9)-O(1)	126.46 (17)
N(1)-C(9)-C(8)	125.66 (17)
O(1)-C(9)-C(8)	107.87 (15)

The interatomic distances and angles for each heterocyclic ring in compound **4h** is depicted in Table 2.

CH_{arom}), 8.89 (2H, dd, $J_1 = 1.4$, $J_2 = 4.7$ Hz, 2 CH_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 24.37, 24.47, 25.77, 32.96, and 33.23 (10 CH_2 of cyclohexyl), 27.29 and 27.96 (4 OC*Me*$_3$), 56.40 (2 N*C*H), 83.49 and 83.65 (4 O*C*Me$_3$), 90.51(2 C_{spiro}), 124.53, 130.10, 132.08, 133.71, 147.66, 149.78, and 150.71 (C=$C_{iminolactone\ ring}$ and C_{arom}), 153.03 (2C=$N_{iminolactone}$), 159.31 and 159.86 (4C=O of esters). MS (*m*/*z*, %): 880 (M^+, 2), 781 (4), 442 (2), 399 (3), 343 (3), 272 (4), 229 (3), 98(6), 83 (8), 57 (49), 44 (61). Anal. Calcd for $C_{50}H_{64}N_4O_{10}$ (881.06): C, 68.16; H, 7.32; N, 6.36%; Found: C, 68.07; H, 7.35; N, 6.40%.

Bis(diethyl 5-tert-butylimino-5H, 6H′)-dispiro(furan-2,5′-[1,10]phenanthroline)-3,3′,4,4′-tetracarboxylate (4m). Brown crystals; yield: 0.31 g (90%), m.p. 50–53°C, IR (KBr) (υ_{max}, cm^{-1}): 1738 and 1729 (4C=O), 1689 (2C=N); ^1H NMR (300.1 MHz, $CDCl_3$): δ_H 0.89 (6H, br s, 2 OCH_2CH_3), 1.23 (6H, br s, 2 OCH_2CH_3), 1.41 (18H, s, 2 C*Me*$_3$), 3.76 (4H, q, $J = 7.0$ Hz, 2 OCH_2CH_3), 4.31 (4H, q, $J = 7.0$ Hz, 2 OCH_2CH_3), 7.29–7.58 (4H, m, 4 CH_{arom}), 7.82 (2H, d, $J = 6.5$ Hz, 2 CH_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 13.37 and 13.84 (4 OCH_2CH_3), 29.53 (2 C*Me*$_3$), 55.25 (2 N*C*Me$_3$), 61.97 and 62.10 (4 O*C*H_2CH$_3$), 93.35 (2 C_{spiro}), 123.52, 125.59, 128.98, 130.33, 131.31, 133.42, 149.67, and 150.52 (C=$C_{iminolactone\ ring}$ and C_{arom}), 150.79 (2C=$N_{iminolactone}$), 159.92 and 161.01 (4C=O of esters). MS (*m*/*z*, %): 717 (M^+ +1, 28), 716 (M^+, 47), 702 (11), 660 (55), 603 (100), 515 (12), 406 (15), 297 (10), 57 (71). Anal. Calcd for $C_{38}H_{44}N_4O_{10}$ (716.78): C, 63.67; H, 6.19; N, 7.82%; Found: C, 63.60; H, 6.23; N, 7.78%.

Crystal/refinement details for 4a. $C_{40}H_{32}N_2O_{10}$, $M = 700.68$, $F(000) = 2928$ *e*, orthorhombic, $P2_12_12_1$ (No. 19), $Z = 8$, $T = 100(2)$ K, $a = 15.7294(1)$, $b = 20.0784(1)$, $c = 21.5051(1)$ Å, $V = 6791.77(6)$ Å^3; $D_c = 1.370$ g cm^{-3}; $\mu_{Cu} = 0.825$ mm^{-1}; $\sin\theta/\lambda_{max} = 0.5981$; N(unique) = 6631 (merged from 92696, $R_{int} = 0.0364$, $R_{sig} = 0.0148$), N_o ($I > 2\delta(I)$) = 6039; $R = 0.0324$, $wR2 = 0.0850$ (A,$B = 0.07, 0.67$), GOF = 1.002; $|\Delta_{\rho max}| = 0.26(4)$ e Å^{-3}. CCDC 662911.

Crystal/refinement details for 4h. $C_{44}H_{40}N_4O_{10}$, $M = 784.80$, $F(000) = 1648$ *e*, monoclinic, $C2/c$ (No. 15), $Z = 4$, $T = 100(2)$ K, $a = 17.6425(2)$, $b = 14.3501(1)$, $c = 16.1083(2)$ Å, $\beta = 109.573(1)°$, $V = 3842.51(7)$ Å^3; $D_c = 1.357$ g cm^{-3}; $\mu_{Cu} = 0.803$ mm^{-1}; $\sin\theta/\lambda_{max} = 0.5970$; N(unique) = 3399 (merged from 43440, $R_{int} = 0.0483$, $R_{sig} = 0.0319$), N_o ($I > 2\delta$ (I)) = 2349; $R = 0.0439$, $wR2 = 0.1107$ (A,$B = 0.078, 0$), GOF = 1.002; $|\Delta_{\rho max}| = 0.68(5)$ e Å^{-3}. CCDC 662912.

CCDC numbers 662911 and 662912 contains the crystallographic data for compounds **4a** and **4h**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments. We gratefully acknowledge support of this work by the Research Council of the University of Sistan and Baluchestan, Gonbad High Education Center, the Ministry of Science Research and Technology of Iran for a postgraduate research scholarship (to Faramarz Rostami Charati), and the University of Western Australia.

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