Tetrahedron 65 (2009) 8120–8124

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

An efficient three-component protocol for the synthesis of novel spiro-oxazinobarbiturates

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ARTICLE INFO

Article history:
Received 3 May 2009
Received in revised form 15 July 2009
Accepted 30 July 2009
Available online 3 August 2009

Keywords:
Activated acetylenes
Alloxan
Azines
Multicomponent reactions
Spiro compounds

ABSTRACT

Some novel spiro-oxazinobarbiturate derivatives have been successfully synthesized in a one-pot, three-component cascade reaction from various azines (pyridine, isoquinoline, quinoline and phenanthridine), 1,3-dimethylalloxan, and several activated acetylenes (alkyl propiolates, dialkyl acetylenedicarboxylates, and butyne-2-one). The high bond forming efficiency (formation of new C–N, C–C, and C–O bonds) of this reaction makes it attractive for the synthesis of spiro-oxazinobarbiturates in a single operation.

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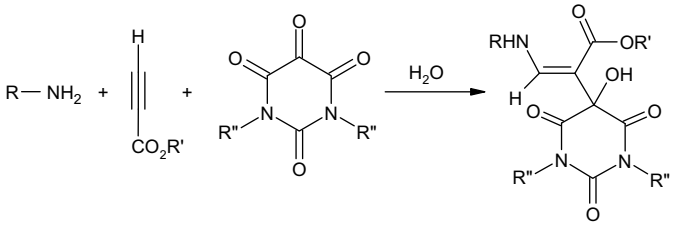
1. Introduction

One-pot multicomponent strategies are used to improve the efficiency of chemical reactions whereby multiple carbon–carbon and carbon–heteroatom and stereocenters are formed in a single operation without the need to isolate intermediates and represent an efficient approach to the synthesis of complex molecular structures based on simple organic building blocks.[1–6]

Barbiturates possess a rather wide range of therapeutic activities.[7] In particular, drugs belonging to this class of compounds have been used for more than a century as hypnotics and anticonvulsants. Pharmaceutical industries market more than 50 barbiturate derivatives under various trade names.[8] On the other hand, spirooxazines represent an important class of photochromic compounds.[9] They belong to the class of compounds that exhibit both normal and reverse photochromism.[10]

Extensive work has been done by many groups on the reactivities of 1,4-dipoles derived from activated acetylenic compounds and nitrogen heterocycles.[11] These studies have led to a number of interesting carbon–carbon bond forming reactions and heterocyclic constructions.[12]

Our group recently reported a three-component reaction of primary amine with alkyl propiolates in the presence of alloxans (Scheme 1).[13] The reaction proceeds through the Michael addition of a primary amine to the terminal carbon of active alkyne followed by the efficient aldol-like reaction of the resulting β-aminoacrylate with the central carbonyl group of alloxan.



Scheme 1.

After reporting the reaction shown in Scheme 1, herein we report an efficient and operationally convenient approach to the synthesis of spiro-oxazinobarbiturates **4** containing the [1,3]oxazino[2,3-*a*]azine skeleton based on the cascade reactions of various azines **1** with activated acetylenes **2** in the presence of

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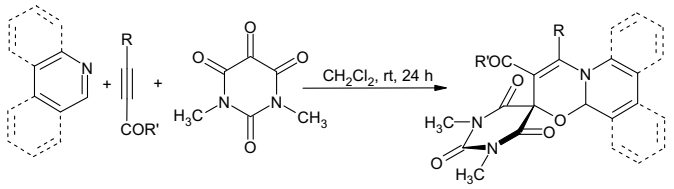
doi:10.1016/j.tet.2009.07.091

Table 1
Three-component condensation reactions of azines, activated acetylenes, and 1,3-dimethylalloxan



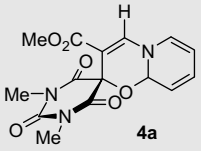
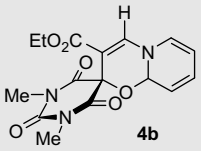
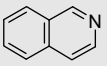
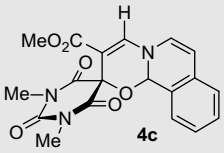
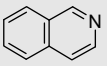
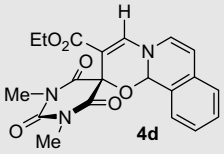
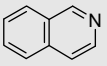
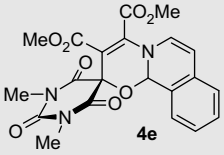
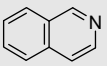
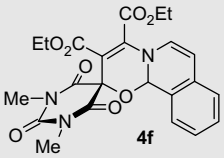
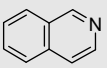
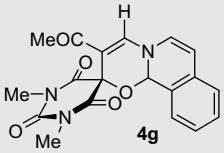
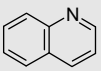
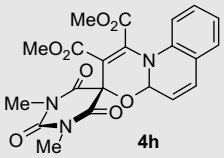
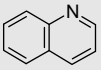
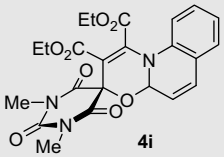
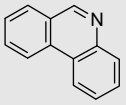
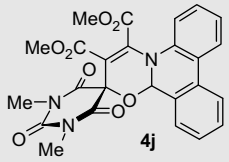
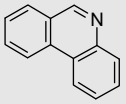
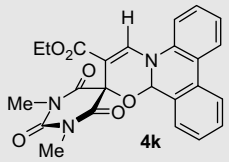
Entry	Azine	R	R′	Product	Yield[a] (%)
1		H	OMe	 **4a**	75
2		H	OEt	 **4b**	73
3		H	OMe	 **4c**	80
4		H	OEt	 **4d**	81
5		CO_2Me	OMe	 **4e**	78
6		CO_2Et	OEt	 **4f**	75
7		H	Me	 **4g**	80
8		CO_2Me	OMe	 **4h**	69
9		CO_2Et	OEt	 **4i**	65

Table 1 (*continued*)

Entry	Azine	R	R′	Product	Yield[a] (%)
10		CO_2Me	OMe	 **4j**	67
11		H	OEt	 **4k**	65

[a] Refers to purified yield. Compound purity is >95% as determined by ^{1}H NMR.

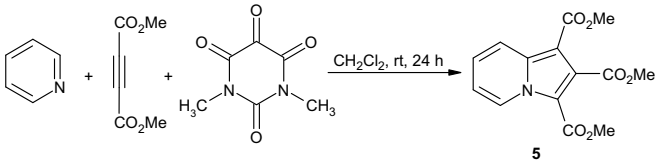
1,3-dimethylalloxan **3**. Carotti and his co-workers reported the first synthesis of spiro-derivatives of [1,3]oxazino[2,3-*a*]isoquinoline and [1,3]oxazino[2,3-*a*]quinoline as heterocyclic steroids.[14] Later, they examined the catalytic reduction of these oxasteroids.[15]

2. Results and discussion

In an exploratory experiment, a solution of pyridine and methyl propiolate in dry CH_2Cl_2 was treated with 1,3-dimethylalloxan at room temperature for 24 h (Table 1, Entry 1). Afterward, the solvent was removed and the residue was subjected to column chromatography to yield the methyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,9a*H*-spiro[pyrido[2,1-*b*][1,3]oxazine-2,5′-pyrimidine]-3-carboxylate **4a** as colorless crystals in 75% yield. We then successfully performed the reaction between another various active azines **1**, activated acetylenes **2**, and 1,3-dimethylalloxan **3** leading to the formation of spiro-oxazinobarbiturates **4** in 65–81% yields and the full results are summarized in Table 1.

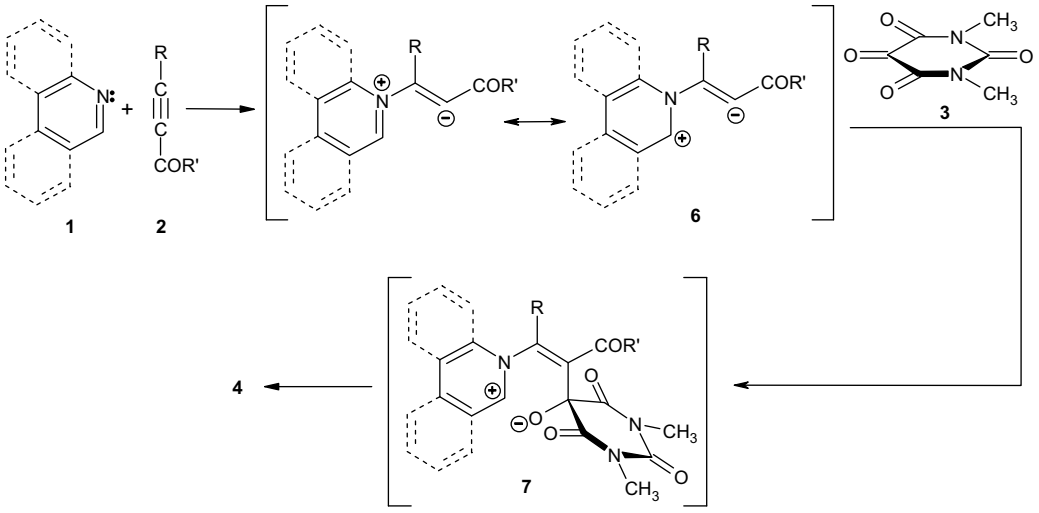
The structures of compounds **4a**–**k** were deduced from their elemental analyses and their FTIR, ^{1}H NMR, and ^{13}C NMR spectra. For example, the ^{1}H NMR spectrum of **4a** exhibited four signals identified as two *N*-methyl (δ_H 3.33 and 3.35 ppm) protons, methoxy (δ_H 3.62 ppm) and vinylic methine (δ_H 7.88 ppm) proton, along with multiplets for the four vinylic and one allylic methines of pyridine residue (δ_H 5.14–5.38 and 6.20–6.39 ppm). The ^{1}H decoupled ^{13}C NMR spectra of **4a** showed 15 distinct resonances, which confirmed the proposed structure.

The scope and limitations of this three-component reaction were explored by using five activated acetylenes and four active azine derivatives. The results show that the three-component reaction is quite general with butyne-2-one, alkyl propiolates, and dialkyl acetylenedicarboxylates affording the expected spiro-oxazinobarbiturates **4** in good yields. Note that even moderate yields are synthetically useful because these reactions form complex structures and a number of bonds are formed. Also, we examined the scope of reactive azines in the three-component reaction. As shown in Table 1, the pyridine and a variety of structurally diverse benzopyridines are used in this protocol with excellent



5

Scheme 2.



Scheme 3.

results. Our attempts to carry out this reaction under the same reaction conditions with other vicinal tricarbonyl compounds such as alloxan, ninhydrin, and diethylketomalonate were not successful and unfortunately the reactions led to intractable mixtures. Under similar reaction condition, starting with pyridine, dimethyl acetylenedicarboxylate, and 1,3-dimethylalloxane, the trimethyl indolizine-1,2,3-tricarboxylate **5**[16–19] was isolated in 39% yield with the exception of 1,3-dimethylalloxane, which did not enter into the same reaction (Scheme 2).

Although the mechanistic details of all the reactions are not known, the formation of these heterocycles tabulated in Table 1 can be rationalized by initial formation of a highly reactive 1:1 zwitterionic intermediate **6** by the Michael-type addition reaction[20] of the azine **1** with the activated acetylene **2**, which adds to the central carbonyl group of 1,3-dimethylalloxan **3** leading to a dipolar species **7**. Cyclization of the latter leads to the spiro-oxazinobarbiturates **4** (Scheme 3).

3. Conclusion

In conclusion we have achieved an efficient process for the synthesis of functionalized spiro-oxazinobarbiturate derivatives starting from readily available reagents. The reaction is very simple from the experimental point of view and allows the creation of a spiro-fused oxazinobarbiturate ring with concomitant formation of one new C–C bond, one C–N, and one C–O bond (three new bonds) in a single operation.

4. Experimental

4.1. General

Melting points were measured on a Büchi 535 apparatus and are uncorrected. Elemental analyses were performed using an elementar vario EL *III* instrument. FTIR spectra were recorded on a Bruker Equinox-55 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 Avance spectrometer at 400.13 and 100.77 MHz, respectively, with $CDCl_3$ as solvents and calibrated using residual undeuterated solvent as an internal reference. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254) and visualized with UV light. All chemical reagents were obtained from Aldrich, Merck, Fluka or Acros and were used without further purification.

4.2. Typical procedure for preparation of methyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,9a*H*-spiro[pyrido[2,1-*b*][1,3]oxazine-2,5′-pyrimidine]-3-carboxylate (4a)

To a magnetically stirred solution of pyridine (0.079 g, 1.0 mmol) and methyl propiolate (0.084 g, 1.0 mmol) in 10 mL of dry CH_2Cl_2 was added 1,3-dimethylalloxan (0.170 g, 1.0 mmol) at room temperature (25 °C). The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure and the viscous residue was purified by column chromatography (Merck 230–400 mesh) using *n*-hexane/EtOAc (3:1) as eluent to give **4a** as colorless prisms (0.250 g, 75%). Mp 176–178 °C; R_f (30% EtOAc/*n*-hexane) 0.46; FTIR (KBr) (ν_{max}, cm^{-1}): 1743, 1686, 1660 (C=O), 1596 (C=C); δ_H (400 MHz, $CDCl_3$) 3.33 (3H, s, NCH_3), 3.35 (3H, s, NCH_3), 3.62 (3H, s, OCH_3), 5.14–5.38 (2H, m, N–C*H*=C*H*), 6.20–6.39 (3H, m, C*H*=C*H*–C*H*–O), 7.88 (1H, s, =CH); δ_C (100.6 MHz, $CDCl_3$) 168.4, 166.8, 165.1, 150.6, 143.0, 128.2, 126.2, 114.8, 105.2, 101.1, 80.2, 73.2, 51.8, 29.5, 29.1; Anal. Calcd for $C_{15}H_{15}N_3O_6$ (333.29): C, 54.05; H, 4.54; N, 12.61%. Found: C, 53.98; H, 4.52; N, 12.57%.

4.3. Ethyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,9a*H*-spiro[pyrido[2,1-*b*][1,3]oxazine-2,5′-pyrimidine]-3-carboxylate (4b)

Colorless prisms (0.253 g, 73%); mp 197–199 °C; R_f (30% EtOAc/*n*-hexane) 0.48; FTIR (KBr) (ν_{max}, cm^{-1}): 1738, 1687, 1655 (C=O), 1598 (C=C); δ_H (400 MHz, $CDCl_3$) 1.19 (3H, t, *J* 7.1 Hz, CH_3), 3.32 (3H, s, NCH_3), 3.38 (3H, s, NCH_3), 4.09 (2H, q, *J* 7.1 Hz, OCH_2), 5.13–5.40 (2H, m, N–C*H*=C*H*), 6.19–6.39 (3H, m, C*H*=C*H*–C*H*–O), 7.90 (1H, s, =CH); δ_C (100.6 MHz, $CDCl_3$) 168.3, 166.8, 165.2, 150.6, 143.0, 128.3, 126.2, 115.0, 105.2, 101.2, 80.1, 73.3, 60.7, 29.4, 29.1, 14.2; Anal. Calcd for $C_{16}H_{17}N_3O_6$ (347.32): C, 55.33; H, 4.93; N, 12.10%. Found: C, 55.35; H, 4.90; N, 12.15%.

4.4. Methyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,11b*H*-spiro[1,3-oxazino[2,3-*a*]isoquinoline-2,5′-pyrimidine]-3-carboxylate (4c)

Colorless flakes (0.306 g, 80%); mp 226–228 °C; R_f (30% EtOAc/*n*-hexane) 0.47; FTIR (KBr) (ν_{max}, cm^{-1}): 1696, 1680, 1622 (C=O); δ_H (400 MHz, $CDCl_3$) 3.33 (3H, s, NCH_3), 3.42 (3H, s, NCH_3), 3.68 (3H, s,

OCH_3), 5.76 (1H, d, *J* 7.5 Hz, N–CH=C*H*), 6.42 (1H, d, *J* 7.5 Hz, N–C*H*=CH), 6.80 (1H, s, N–CH–O), 7.05–7.30 (4H, m, C_6H_4), 7.93 (1H, s, =CH); δ_C (100.6 MHz, $CDCl_3$) 168.8, 166.7, 165.2, 150.7, 142.8, 130.3, 129.7, 127.1, 127.0, 126.6, 125.4, 125.2, 104.8, 103.4, 80.5, 73.9, 51.7, 29.5, 29.1; Anal. Calcd for $C_{19}H_{17}N_3O_6$ (383.35): C, 59.53; H, 4.47; N, 10.96%. Found: C, 59.48; H, 4.48; N, 11.00%.

4.5. Ethyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,11b*H*-spiro[1,3-oxazino[2,3-*a*]isoquinoline-2,5′-pyrimidine]-3-carboxylate (4d)

Colorless flakes (0.321 g, 81%); mp 197–199 °C; R_f (30% EtOAc/*n*-hexane) 0.51; FTIR (KBr) (ν_{max}, cm^{-1}): 1690, 1679 (C=O); δ_H (400 MHz, $CDCl_3$) 1.21 (3H, t, *J* 7.1 Hz, CH_3), 3.33 (3H, s, NCH_3), 3.42 (3H, s, NCH_3), 4.08–4.16 (2H, ABX_3 system, OCH_2), 5.75 (1H, d, *J* 7.5 Hz, N–CH=C*H*), 6.43 (1H, d, *J* 7.5 Hz, N–C*H*=CH), 6.81 (1H, s, N–CH–O), 7.05–7.29 (4H, m, C_6H_4), 7.95 (1H, s, =CH); δ_C (100.6 MHz, $CDCl_3$) 168.9, 166.8, 164.6, 150.7, 142.7, 130.3, 129.7, 127.1, 127.0, 126.7, 125.4, 125.2, 104.7, 103.6, 80.5, 73.9, 60.7, 29.5, 29.1, 14.2; Anal. Calcd for $C_{20}H_{19}N_3O_6$ (397.38): C, 60.45; H, 4.82; N, 10.57%. Found: C, 60.50; H, 4.81; N, 10.54%.

4.6. Dimethyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,11b*H*-spiro[1,3-oxazino[2,3-*a*]isoquinoline-2,5′-pyrimidine]-3,4-dicarboxylate (4e)

Colorless flakes (0.344 g, 78%); mp 207–209 °C; R_f (30% EtOAc/*n*-hexane) 0.52; FTIR (KBr) (ν_{max}, cm^{-1}): 1743, 1686, 1671 (C=O); δ_H (400 MHz, $CDCl_3$) 3.30 (3H, s, NCH_3), 3.41 (3H, s, NCH_3), 3.68 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 5.88 (1H, d, *J* 7.7 Hz, N–CH=C*H*), 6.39 (1H, d, *J* 7.7 Hz, N–C*H*=CH), 6.59 (1H, s, N–CH–O), 7.11–7.35 (4H, m, C_6H_4); δ_C (100.6 MHz, $CDCl_3$) 168.3, 165.8, 164.2, 162.6, 150.6, 146.1, 130.1, 129.7, 128.0, 127.3, 125.6, 124.7, 123.5, 106.6, 105.9, 80.9, 73.9, 53.6, 52.5, 29.5, 29.0; Anal. Calcd for $C_{21}H_{19}N_3O_8$ (441.39): C, 57.14; H, 4.34; N, 9.52%. Found: C, 57.20; H, 4.33; N, 9.50%.

4.7. Diethyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,11b*H*-spiro[1,3-oxazino[2,3-*a*]isoquinoline-2,5′-pyrimidine]-3,4-dicarboxylate (4f)

Colorless flakes (0.352 g, 75%); mp 161–163 °C; R_f (30% EtOAc/*n*-hexane) 0.53; FTIR (KBr) (ν_{max}, cm^{-1}): 1737, 1686 (C=O); δ_H (400 MHz, $CDCl_3$) 1.17 (3H, t, *J* 7.1 Hz, CH_3), 1.40 (3H, t, *J* 7.1 Hz, CH_3), 3.30 (3H, s, NCH_3), 3.41 (3H, s, NCH_3), 4.11 (2H, q, *J* 7.1 Hz, OCH_2), 4.43 (2H, m, ABX_3 system, OCH_2), 5.87 (1H, d, *J* 7.7 Hz, N–CH=C*H*), 6.40 (1H, d, *J* 7.7 Hz, N–C*H*=CH), 6.62 (1H, s, N–CH–O), 7.11–7.33 (4H, m, C_6H_4); δ_C (100.6 MHz, $CDCl_3$) 168.5, 165.9, 163.5, 162.1, 150.6, 146.4, 130.0, 129.8, 128.0, 127.2, 125.6, 124.7, 123.4, 106.2, 105.7, 80.8, 73.8, 63.0, 61.4, 29.4, 29.0, 13.9, 13.8; Anal. Calcd for $C_{23}H_{23}N_3O_8$ (469.44): C, 58.85; H, 4.94; N, 8.95%. Found: C, 58.87; H, 4.90; N, 9.01%.

4.8. 3-Acetyl-1′,3′-dimethyl-2′*H*,11b*H*-spiro[1,3-oxazino[2,3-*a*]isoquinoline-2,5′-pyrimidine]-2′,4′,6′-(1′*H*,3′*H*)-trione (4g)

Pale yellow flakes (0.293 g, 80%); mp 175–177 °C; R_f (30% EtOAc/*n*-hexane) 0.44; FTIR (KBr) (ν_{max}, cm^{-1}): 1690, 1665 (C=O); δ_H (400 MHz, $CDCl_3$) 2.20 (1H, s, CH_3), 3.32 (3H, s, NCH_3), 3.39 (3H, s, NCH_3), 5.66 (1H, d, *J* 7.7 Hz, N–CH=C*H*), 6.41 (1H, d, *J* 7.7 Hz, N–C*H*=CH), 6.77 (1H, s, N–CH–O), 7.20–7.27 (4H, m, C_6H_4), 7.96 (1H, s, =CH); δ_C (100.6 MHz, $CDCl_3$) 193.7, 168.7, 166.8, 150.7, 143.9, 130.1, 129.7, 127.3, 126.8, 126.5, 125.5, 125.4, 115.2, 105.9, 80.4. 74.2, 29.4, 29.0, 23.8; Anal. Calcd for $C_{19}H_{17}N_3O_5$ (367.35): C, 62.12; H, 4.66; N, 11.44%. Found: C, 62.17; H, 4.70; N, 11.41%.

4.9. Dimethyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,4a*H*-spiro[1,3-oxazino[3,2-*a*]quinoline-3,5′-pyrimidine]-1,2-dicarboxylate (4h)

Pale yellow prisms (0.304 g, 69%); mp 180–182 °C; R_f (30% EtOAc/*n*-hexane) 0.48; FTIR (KBr) (ν_{max}, cm^{-1}): 1749, 1738, 1680, 1656 (C=O); δ_H (400 MHz, $CDCl_3$) 3.28 (3H, s, NCH_3), 3.34 (3H, s, NCH_3), 3.73 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 5.75 (1H, d, *J* 4.2 Hz, N–C*H*–CH=CH), 5.91 (1H, dd, *J* 4.2 Hz, *J* 9.8 Hz, N–CH–C*H*=CH), 6.88 (1H, d, *J* 9.8 Hz, N–CH–CH=C*H*), 6.98–7.29 (4H, m, C_6H_4); δ_C (100.6 MHz, $CDCl_3$) 167.9, 165.0, 164.7, 163.2, 150.5, 145.9, 134.8, 130.2, 130.2, 128.6, 123.2, 121.4, 118.0, 116.8, 115.1, 80.2, 74.4, 53.4, 52.9, 29.5, 28.9; Anal. Calcd for $C_{21}H_{19}N_3O_8$ (441.39): C, 57.14; H, 4.34; N, 9.52%. Found: C, 57.11; H, 4.35; N, 9.55%.

4.10. Diethyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,4a*H*-spiro[1,3-oxazino[3,2-*a*]quinoline-3,5′-pyrimidine]-1,2-dicarboxylate (4i)

Pale yellow prisms (0.305 g, 65%); mp 179–181 °C; R_f (30% EtOAc/*n*-hexane) 0.51; FTIR (KBr) (ν_{max}, cm^{-1}): 1740, 1676 (C=O); δ_H (400 MHz, $CDCl_3$) 1.15 (3H, t, *J* 7.1 Hz, CH_3), 1.41 (3H, t, *J* 7.1 Hz, CH_3), 3.30 (3H, s, NCH_3), 3.39 (3H, s, NCH_3), 4.08 (2H, q, *J* 7.1 Hz, OCH_2), 4.45 (2H, m, ABX_3 system, OCH_2), 5.79 (1H, d, *J* 4.2 Hz, N–C*H*–CH=CH), 5.88 (1H, dd, *J* 4.2 Hz, *J* 9.8 Hz, N–CH–C*H*=CH), 6.91 (1H, d, *J* 9.8 Hz, N–CH–CH=C*H*), 6.88–7.21 (4H, m, C_6H_4); δ_C (100.6 MHz, $CDCl_3$) 168.6, 166.2, 163.7, 163.1, 151.2, 146.5, 130.0, 129.9, 128.0, 127.4, 126.7, 125.3, 123.6, 107.2, 105.9, 81.0, 73.8, 63.0, 61.5, 29.3, 28.9, 13.9, 13.9; Anal. Calcd for $C_{23}H_{23}N_3O_8$ (469.44): C, 58.85; H, 4.94; N, 8.95%. Found: C, 58.87; H, 4.90; N, 9.01%.

4.11. Dimethyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,13b*H*-spiro[1,3-oxazino[3,2-*f*]phenanthridine-2,5′-pyrimidine]-3,4-dicarboxylate (4j)

Yellow prisms (0.329 g, 67%); mp 213–215 °C; R_f (30% EtOAc/*n*-hexane) 0.41; FTIR (KBr) (ν_{max}, cm^{-1}): 1737, 1682 (C=O); δ_H (400 MHz, $CDCl_3$) 3.26 (3H, s, NCH_3), 3.32 (3H, s, NCH_3), 3.71 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 5.93 (1H, s, N–CH–O), 6.70–8.38 (8H, m, $2C_6H_4$); δ_C (100.6 MHz, $CDCl_3$) 169.2, 166.9, 163.7, 163.1, 151.3, 140.5, 136.8, 133.7, 132.7, 131.5, 128.5, 128.6, 127.2, 126.1, 125.2, 124.6, 121.8, 120.1, 108.4, 83.7, 72.7, 53.1, 51.9, 29.3, 28.9; Anal. Calcd for $C_{25}H_{21}N_3O_8$ (491.44): C, 61.10; H, 4.31; N, 8.55%. Found: C, 61.17; H, 4.33; N, 8.60%.

4.12. Ethyl 1′,3′-dimethyl-2′,4′,6′-trioxo-1′,3′,4′,6′-tetrahydro-2′*H*,13b*H*-spiro[1,3-oxazino[3,2-*f*]phenanthridine-2,5′-pyrimidine]-3-carboxylate (4k)

Yellow prisms (0.290 g, 65%); mp 221–223 °C; R_f (30% EtOAc/*n*-hexane) 0.37; FTIR (KBr) (ν_{max}, cm^{-1}): 1685, 1672 (C=O); δ_H (400 MHz, $CDCl_3$) 1.20 (3H, t, *J* 7.1 Hz, CH_3), 3.39 (3H, s, NCH_3), 3.41 (3H, s, NCH_3), 4.11–4.20 (2H, ABX_3 system, OCH_2), 6.71 (1H, s, N–CH–O), 6.78–8.33 (9H, m, =CH+$2C_6H_4$); δ_C (100.6 MHz, $CDCl_3$) 166.4, 163.1, 161.7, 151.6, 139.2, 136.5, 133.2, 131.7, 131.3, 128.9, 127.7, 127.0, 126.2, 124.9, 124.1, 121.1, 120.5, 107.6, 84.0, 73.2, 61.3, 29.3, 28.8, 14.5; Anal. Calcd for $C_{24}H_{21}N_3O_6$ (447.44): C, 64.42; H, 4.73; N, 9.39%. Found: C, 64.37; H, 4.71; N, 9.44%.

Acknowledgements

We would like to thank Iran Polymer and Petrochemical Institute (IPPI) research council for the financial support.

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