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ORIGINAL ARTICLE

A synthesis of thioxo[3.3.3]propellanes from acenaphthoquinone-malononitrile adduct, primary amines and CS_2 in water

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KEYWORDS

[3.3.3]Propellane;
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Knoevenagel condensation;
Acenaphthoquinone

Abstract Novel thioxo[3.3.3]propellanes were synthesized in moderate to good yields *via* reactions of aromatic or aliphatic amines and carbon disulfide with the Knoevenagel adduct resulting from acenaphthoquinone and malononitrile in water at room temperature. The merit of this reaction is highlighted by its high atom-economy, chemo-selectivity, and lack of metal promoters. The structures of the products were established by IR, NMR, and single crystal X-ray analyses.

1. Introduction

Propellane systems are defined as tricyclic compounds containing three nonzero bridges and one zero bridge between a pair of bridgehead carbons (Ginsburg, 1975). They have significant chemical and physical properties due to their fascinating topology (Navarro and Reisman, 2012; Pihko and Koskinen, 2005; Wiberg, 1989). Due to their occurrence in several natural products and bioactive compounds, they found applications in medicinal chemistry (Qian-Cutrone et al., 1994; Dave et al., 2004; Miao et al., 2013). Since the propellanes discovery in 1965 (Nerdel et al., 1965), the commonest processes reported for their synthesis involve Diels–Alder reactions (Nicolaou et al., 2002), palladium (Trost and Shi 1991) or manganese catalyzed transformations (Asahi and Nishino 2008), rearrangement of spiro-ketones (Fitjer et al., 1994), nucleophilic substitutions of alkenes (Jamrozik et al., 1995), photochemical addition reactions (Navarro and Reisman 2012), and MCR methodologies (Rezvanian et al., 2012; Zhang and Yan 2013; Alizadeh et al., 2015).

Sulfur heterocycles have been widely explored as new materials due to their superconducting, optical, and electronic switching properties (Bendikov et al., 2004; Nielser et al., 2000; Konstantinova et al., 2004; Attanasi et al., 2009; Wang et al., 2011; Shi et al., 2011). Despite the importance of organo-sulfur compounds, there are relatively few protocols for construction of C–S bonds compared to C–N and C–O bond-forming methods. Recently, carbon disulfide was used as sulfur reagent in constructing various sulfur heterocyclic systems (Clegg et al., 2010; Maddani and Prabhu 2010; Ma et al., 2011; Özkay et al., 2016; Charitos et al., in press).

Dithiocarbamate salts, obtained from amines and CS_2, have wide impacts in environmental chemistry (Kanchi et al., 2014). These salts react with different electrophiles including electron-deficient alkenes

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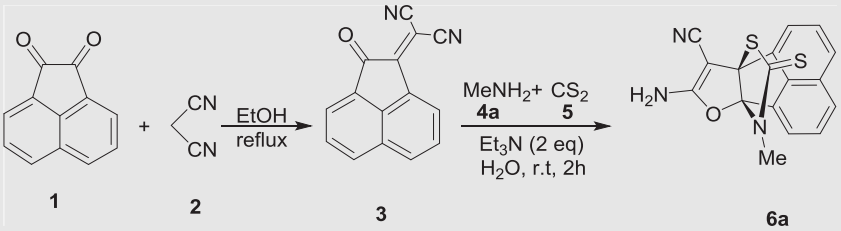
(Saidi et al., 2006; Bardajee et al., 2011), electron-rich alkenes (Ziyaei-Halimehjani et al., 2010, 2013), 2-chloro-1,3-dicarbonyl compounds (Yavari et al., 2010a), aldehydes and ketones (Ziyaei-Halimehjani et al., 2012), maleic anhydride (Ziyaei-Halimehjani and Hosseinkhany, 2015), fumaryl chloride (Alizadeh and Zohreh 2009), alkyl halides (Azizi et al., 2006), epoxides (Ziyaei-Halimjani and Saidi 2006; Azizi et al., 2007), divinyl sulfone and sulfoxides (Ziyaei-Halimehjani et al., 2016), β-nitrostyrene derivatives (Ghabraie et al., 2013), itaconic anhydride (Yavari et al., 2010b), electron-deficient chlorobenzenes (Ranjbar-Karimi et al., 2014) and 2-chloroacetamides (Yurttaş et al., 2014; Abu-Mohsen et al., 2015). To the best of our knowledge, there is no published report on the reaction between CS_2 and amines in the presence of cyanochalcones.

As part of our current studies in the synthesis of heterocyclic [3.3.3] propellanes and 1,3-dithiolanes compounds (Yavari et al., 2007, 2010c; Yavari and Beheshti 2011; Diyanatizadeh and Yavari 2016), we herein report on the synthesis of a novel class of thioxo[3.3.3]propellanes by a simple and one pot three-component reaction involving aliphatic and aromatic amines, carbon disulfide, and Knoevenagel condensation product of acenaphthoquinone and malononitrile in water at room temperature.

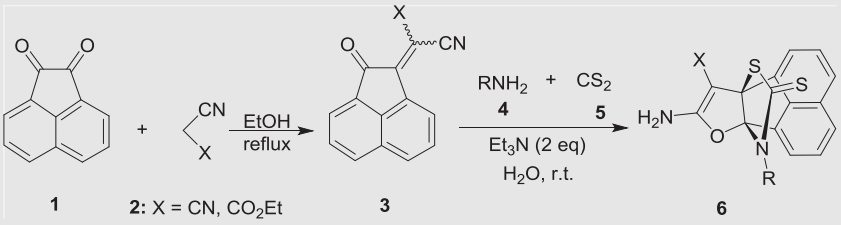
Table 1 Formation of product **6a** under different reaction conditions.[a]



Entry	Solvent	Time (h)	Yield[b] (%)
1	THF	4	60
2	MeOH	5	55
3	EtOH	5	52
4	H_2O	2	71
5	CH_2Cl_2	4	46

[a] Reaction conditions: **3** (0.230 g, 1 mmol), **4a** (0.031 g, 1 mmol), **5** (0.114 g, 1.5 mmol), Et_3N (0.202 g, 2 mmol), solvent (5 mL), room temperature.
[b] Isolated yield.

Table 2 Synthesis of thioxo[3.3.3]propellane derivatives **6**.[a]



Entry	X	R	Product	Yield[b] (%)	Time (h)
1	CN	Me	**6a**	71	2
2	CN	Et	**6b**	74	3
3	CN	Pr	**6c**	71	4
4	CN	Bu	**6d**	79	4
5	CN	Bn	**6e**	68	3
6	CN	4-Cl-C_6H_4-CH_2	**6f**	80	2
7	CN	2,4-Cl_2-C_6H_3-CH_2	**6g**	91	1
8	CN	Ph	**6h**	85	5
9	CN	4-MeO-C_6H_4	**6i**	88	1
10	CN	4-Me-C_6H_4	**6j**	82	2
11	CO_2Et	Et	**6k**	75	3
12	CO_2Et	4-Cl-C_6H_4-CH_2	**6l**	77	2
13	CO_2Et	4-MeO-C_6H_4	**6m**	83	1

[a] Reaction conditions: **3** (0.230 g, 1 mmol), **4** (1 mmol), **5** (0.114 g, 1.5 mmol), Et_3N (0.202 g, 2 mmol), H_2O (5 mL), room temperature.
[b] Isolated yield.

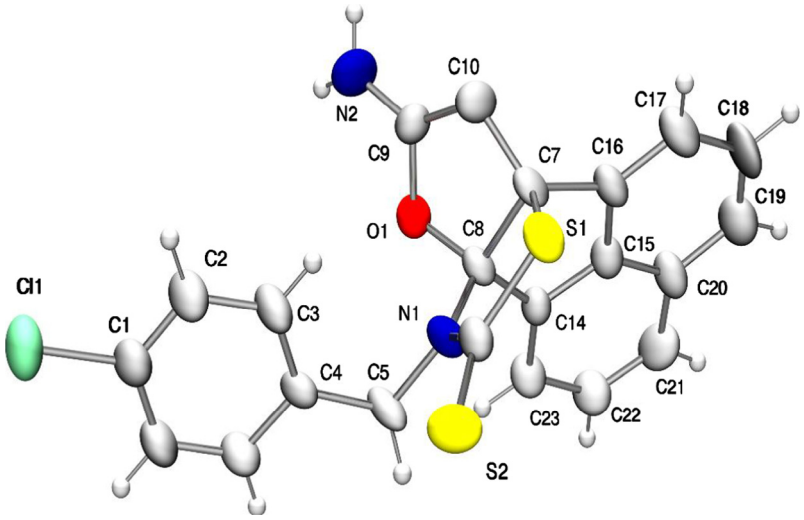


Figure 1 Molecular structure and numbering scheme of **6l**; the thermal ellipsoids are drawn at the 40% probability level.

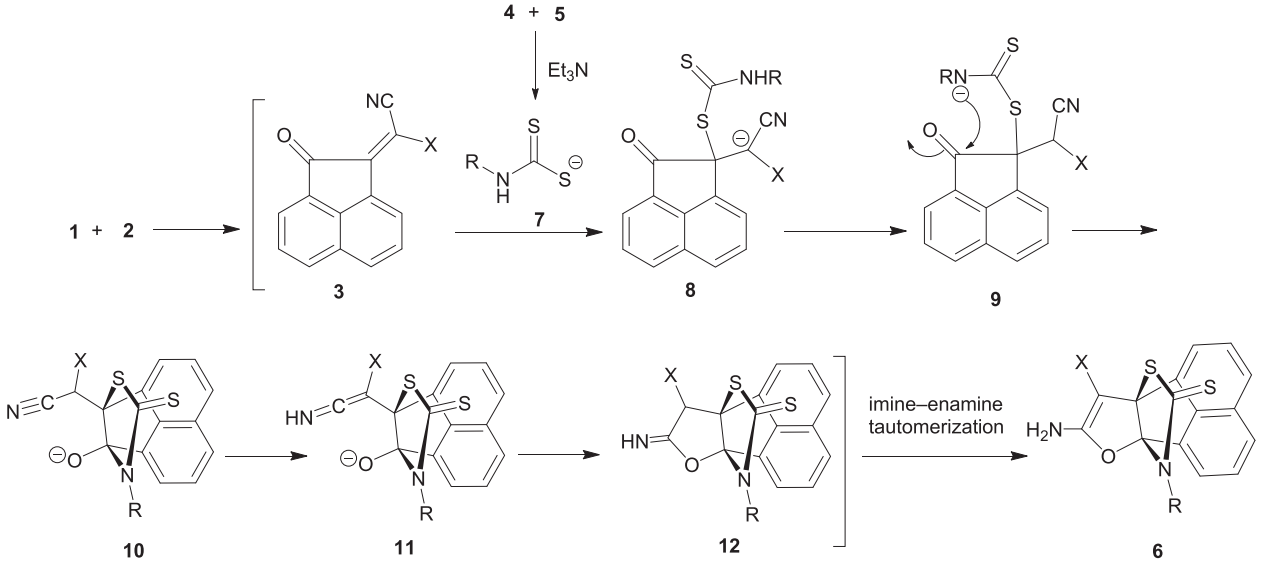
2. Results and discussion

Initially, the three-component reaction of methylamine, carbon disulfide and acenaphthoquinone-malononitrile adduct was investigated to establish the feasibility of the strategy and to optimize the reaction conditions. Different solvents such as H_2O, MeOH, EtOH, tetrahydrofuran (THF), and CH_2Cl_2 were explored. The results are summarized in Table 1. When the reaction was performed in H_2O in the presence of 2 equiv. of Et_3N as the base for 2 h, it was found that product **6a** was obtained in 71% yield (Table 1). Thus, the optimized reaction conditions used were 1 mmol of amines, 1.5 mmol of carbon disulfide, 2 mmol of Et_3N, and 1 mmol of acenaphthoquinone-malononitrile adduct in H_2O at room temperature.

Using the optimized reaction conditions for the formation of product **6a**, a range of aliphatic and aromatic amines were treated with CS_2 and **3** in H_2O for 1–5 h at room temperature to afford thioxo[3.3.3]propellane derivatives **6a–m** in moderate to good yields (Table 2).

The structures of products **6a–m** were deduced from their IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data, and by single-crystal X-ray analysis of **6l**. The mass spectrum of **6a** displayed molecular ion peak at m/z = 337. The IR spectrum of **6a** exhibited stretching bands for NH_2 (3325 and 3272 cm^{-1}), CN (2194 cm^{-1}), and C=S (1345 cm^{-1}) groups. The ^{1}H NMR spectrum of **6a** exhibited two sharp singlets (δ 3.54 and 7.99 ppm) for the methyl and NH_2 protons. The aromatic protons appeared at δ 7.56–8.11 ppm. The ^{1}H NMR spectra of **6b–g** were similar to those of **6a** except for the R groups which exhibited characteristic patterns (δ 4.09–5.43 ppm) for diastereotopic H_2C-N protons. In the ^{13}C NMR spectrum of these compounds, signals corresponding to the O–C–NH_2, and C=S groups were observed at about 166 and 199 ppm, respectively.

To extend the scope of these transformations, the reaction of **1** with ethyl cyanoacetate was attempted and the results are shown in Table 2 (Entries 11–13). Compounds **6k–m** was again fully characterized with their IR and NMR spectral data. Unequivocal evidence for the structure of **6l** was



Scheme 1 A plausible mechanism for the formation of products **6**.

obtained from single-crystal X-ray analysis. The ORTEP diagram of **6l** is shown in Fig. 1. The structure was deduced from the crystallographic data and those of **6a–k**, and **6m** were assumed to be analogous on account of their similar NMR spectra.

A plausible mechanism for the formation of products **6a–m** is shown in Scheme 1. It is conceivable that the dithiocarbamate **7** undergoes *S*-Michael addition upon **3** to afford intermediate **8**, which undergoes proton-transfer reaction to produce **9**. Intermediate **9** undergoes intermolecular nucleophilic attack of nitrogen atom upon the carbonyl group to generate **10**, which is convert to ketenimine intermediate **11** by deprotonation of the RXCH-CN moiety of **10**. Then, *O*-cyclization of ketenimine **11** and subsequent imine-enamine tautomerization leads to the formation of thioxo[3.3.3]propellanes **6**.

3. Conclusion

In summary, we have developed a simple one-pot three-component reaction involving aromatic and aliphatic amines, carbon disulfide, and the Knoevenagel condensation product of acenaphthoquinone and malononitrile or ethyl cyanoacetate for the synthesis of a new series of thioxo[3.3.3]propellanes in water at room temperature. It is noteworthy that this reaction results in the sequential C-S, C–N, and C–O bond formation in a single pot. The advantages of this method include the good yields of products, mild and simple reaction conditions (no metal catalyst or inert atmosphere, water used as a green solvent), fairly broad substrate scope, and readily available starting materials, which make it an useful protocol for the synthesis of [3.3.3]propellane systems.

4. Experimental

Compound **3** was prepared from acenaphthoquinone and malononitrile (or ethyl cynoacetate) according to the literature (Mhaidat et al., 2007; Chen et al., 2014). Other materials were obtained from Merck and used without further purification. Elemental analyses for C, H, and N were performed using a *Heraeus CHN-O-Rapid* analyzer. FT-IR spectra were recorded on a Shimadzu *IR-460* instrument using the KBr self-supported pellet technique. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker *DRX-500 Avance* spectrometer at 500 and 125 MHz. NMR spectra were obtained in solution of DMSO-d_6 using tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on a *Finnigan-MAT-8430EI-MS* apparatus at ionization potential of 70 eV. The melting points of the products were determined in open capillary tubes by using *Electrothermal-9100* apparatus. Column chromatography was performed using silica (Merck #60). Silica plates (Merck) were used for TLC analysis.

*4.1. Synthesis of thioxo[3.3.3]propellane derivatives (**6a–m**)*

Compound **3** (1 mmol, 0.230 g) was added to a stirred solution of amine (1 mmol), CS_2 (1.5 mmol, 0.114 g), and Et_3N (2 mmol, 0.202 g) in H_2O (5 mL) at room temperature. After completion of the reaction [about 1–5 h, TLC (*n*-hexane/EtOAc, 1:1) monitoring], the mixture filtered and the precipitate purified by flash column chromatography on silica gel using EtOAc/*n*-hexane (1:1) as eluent (for compound **6a-6e** and **6k**) or recrystallization from EtOAc (for compounds **6f–6j**, **6l**, and **6m**) to afford the pure product **6**.

*4.2. 8-Amino-12-methyl-11-thioxo-9a,6b-(epithiomethanoimino) acenaphtho[1,2-b]furan-9-carbonitrile **6a***

Violet solid (0.24 g, 71%). mp: 254–258 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 3.54 (3 H, s, Me), 7.57 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.69 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.76 (1 H, t, ^3J = 8.0 Hz, Ar-H), 7.93 (1 H, d, ^3J = 8.0 Hz, Ar-H), 7.99 (2 H, s, NH_2), 8.02 (1 H, d, ^3J = 7.0 Hz, Ar-H), 8.09 (1 H, d, ^3J = 8.0 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 34.3 (Me), 58.9 (C-S), 73.4 (*C*CN), 117.7 (CN), 119.2 (OCN), 119.8 (CH), 122.3 (CH), 126.0 (CH), 129.0 (CH), 129.9 (CH), 130.5 (CH), 132.5 (C), 134.6 (C), 135.5 (C), 143.0 (C), 166.5 (CNH_2), 196.6 (C=S). IR (KBr) (ν_{max}, cm^{-1}): 3325 and 3272 (NH_2), 2194 (CN), 1656 (OC=C), 1593, 1429 (C=C_{Ar}), 1345 (C=S). EI-MS: *m*/*z* (%) = 337 (M^+, 30), 322 (100), 280 (20), 256 (56), 229 (40), 178 (10), 154 (15), 127 (9). Anal. Calc. for $C_{17}H_{11}N_3OS_2$ (337.42): C, 60.52; H, 3.29; N, 12.45. Found: C, 60.82; H, 3.32; N, 12.53%.

*4.3. 8-Amino-12-ethyl-11-thioxo-9a,6b-(epithiomethanoimino) acenaphtho[1,2-b]furan-9-carbonitrile **6b***

Cream color solid (0.26 g, 74%). mp: 257–260 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 1.28 (3 H, t, ^3J = 7.0 Hz, Me), 4.12–4.26 (2 H, AB-m, $\Delta\upsilon_{AB}$ = 42.0 Hz, CH_2) 7.55 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.68 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.76 (1 H, t, ^3J = 7.7 Hz, Ar-H), 7.93 (1 H, d, ^3J = 8.3 Hz, Ar-H), 7.99 (2 H, s, NH_2), 8.09 (2 H, t, ^3J = 7.5 Hz, 2 Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 13.5 (Me), 42.3 (CH_2), 58.4 (C_{-S}), 73.2 (*C*CN), 117.1 (CN), 119.2 (OCN), 119.8 (CH), 121.7 (CH), 125.8 (CH), 128.3 (CH), 129.4 (CH), 130.5 (CH), 131.8 (C), 134.1 (C), 135.5 (C), 142.5 (C), 165.8 (CNH_2), 196.2 (C=S). IR (KBr) (ν_{max}, cm^{-1}): 3275 and 3196 (NH_2), 2197 (CN), 1657 (OC=C), 1596, 1434 (C=C_{Ar}), 1384 (C=S). EI-MS: *m*/*z* (%) = 351 (M^+, 28), 323 (100), 291 (23), 267 (60), 240 (23), 189 (15), 165 (13). Anal. Calc. for $C_{18}H_{13}N_3OS_2$ (351.44): C, 61.52; H, 3.73; N, 11.96. Found: C, 61.80; H, 3.81; N, 12.00%.

*4.4. 8-Amino-12-propyl-11-thioxo-9a,6b-(epithiomethanoimino) acenaphtho[1,2-b]furan-9-carbonitrile **6c***

Colorless solid (0.26 g, 71%). mp: 250–252 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 0.95 (3 H, t, ^3J = 7.2 Hz, Me), 1.66–1.91 (2 H, AB-m, $\Delta\upsilon_{AB}$ = 114.5 Hz, CH_2), 3.93–4.16 (2H, AB-m, $\Delta\upsilon_{AB}$ = 93.9 Hz, CH_2-N), 7.55 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.67 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.75 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.91 (1 H, d, ^3J = 7.5 Hz, Ar-H), 7.98 (2 H, s, NH_2), 8.04 (1 H, d, ^3J = 7.0 Hz, Ar-H), 8.08 (1 H, d, ^3J = 7.5 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 12.5 (Me), 21.4 (CH_2), 48.5 (CH_2), 58.4 (C-S), 73.1 (*C*CN), 117.1 (CN), 118.9 (OCN), 119.1 (CH), 121.6 (CH), 125.3 (CH), 128.3 (CH), 129.3 (CH), 129.8 (CH), 131.9 (C), 134.1 (C), 135.2 (C), 142.5 (C), 165.8 (CNH_2), 196.5 (C=S). IR (KBr) (ν_{max}, cm^{-1}): 3314 and 3265 (NH_2), 2197 (CN), 1659 (OC=C), 1594, 1436 (C=C_{Ar}), 1385 (C=S). EI-MS: *m*/*z* (%) = 365 (M^+, 25), 321 (100), 289 (31), 265 (61), 238 (44), 187 (10), 163 (24), 136 (9). Anal. Calc. for $C_{19}H_{15}N_3OS_2$ (365.47): C, 62.44; H, 4.14; N, 11.50. Found: C, 62.70; H, 4.22; N, 11.56%.

4.5. 8-Amino-12-butyl-11-thioxo-9a,6b-(epithiomethanoimino) acenaphtho[1,2-b]furan-9-carbonitrile ***6d***

Colorless solid (0.30 g, 79%). mp: 248–251 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 0.92 (3 H, t, ^3J = 7.3 Hz, Me), 1.38 (2 H, six, ^3J = 7.2 Hz, CH_2), 1.63–1.87 (2 H, AB-m, $\Delta\upsilon_{AB}$ = 104.7 Hz, CH_2), 3.95–4.20 (2 H, AB-m, $\Delta\upsilon_{AB}$ = 96.0 Hz, CH_2-N), 7.55 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.66 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.74 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.89 (1 H, d, ^3J = 8.0 Hz, Ar-H), 7.98 (2 H, s, NH_2), 8.02 (1 H, d, ^3J = 7.0 Hz, Ar-H), 8.06 (1 H, d, ^3J = 8.0 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 14.0 (Me), 19.7 (CH_2), 28.7 (CH_2), 46.8 (CH_2), 58.4 (C-S), 73.1 (*C*CN), 117.7 (CN), 119.1 (OCN), 119.2 (CH), 121.6 (CH), 125.3 (CH), 128.1 (CH), 129.1 (CH), 129.2 (CH), 131.9 (C), 134.1 (C), 135.2 (C), 142.4 (C), 165.8 (CNH_2), 196.5 (C=S). IR (KBr) (υ_{max}, cm^{-1}): 3316 and 3262 (NH_2), 2194 (CN), 1658 (OC=C), 1594, 1437 (C=C_{Ar}), 1383 (C=S). EI-MS: *m*/*z* (%) = 379 (M^+, 20), 335 (100), 303 (14), 279 (47), 252 (36), 220 (16), 177 (20), 150 (10), 44 (9). Anal. Calc. for $C_{20}H_{17}N_3OS_2$ (379.50): C, 63.30; H, 4.52; N, 11.07. Found: C, 63.61; H, 4.60; N, 11.15%.

4.6. 8-Amino-12-benzyl-11-thioxo-9a,6b-(epithiomethanoimino) acenaphtho[1,2-b]furan-9-carbonitrile ***6e***

Pink solid (0.28 g, 68%). mp: 249–252 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 5.43 (2 H, AB-q, ^2J = 16.5 Hz, $\Delta\upsilon_{AB}$ = 43.8 Hz, CH_2-N), 7.07 (2 H, d, ^3J = 7.2 Hz, 2 Ar-H), 7.20 (3 H, m, 3 Ar-H), 7.56 (1 H, t, ^3J = 7.6 Hz, Ar-H), 7.60 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.69 (1 H, t, ^3J = 7.6 Hz, Ar-H), 7.84 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.92 (1 H, d, ^3J = 8.00 Hz, Ar-H), 7.96 (2 H, s, NH_2), 8.02 (1 H, d, ^3J = 8.0 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 51.3 (CH_2), 59.1 (C-S), 73.1 (*C*CN), 117.6 (CN), 119.5 (OCN), 119.9 (CH), 122.6 (CH), 126.1 (CH), 127.6 (CH), 128.0 (2 CH), 128.5 (2 CH), 128.9 (CH), 129.6 (CH), 129.7 (CH), 130.3 (C), 132.5 (C), 134.6 (C), 135.7 (C), 143.1 (C), 166.5 (CNH_2), 197.9 (C=S). IR (KBr) (υ_{max}, cm^{-1}): 3295 and 3230 (NH_2), 2190 (CN), 1650 (OC=C), 1595, 1433 (C=C_{Ar}), 1378 (C=S). EI-MS: *m*/*z* (%) = 413 (M^+, 30), 369 (100), 337 (20), 261 (15), 247 (40), 220 (16), 105 (22), 77 (8). Anal. Calc. for $C_{23}H_{15}N_3OS_2$ (413.51): C, 66.81; H, 3.66; N, 10.16. Found: C, 67.12; H, 3.73; N, 10.20%.

4.7. 8-Amino-12-(4-chlorobenzyl)-11-thioxo-9a,6b-(epithiomethanoimino)acenaphtho[1,2-b]furan-9-carbonitrile ***6f***

Colorless solid (0.36 g, 80%). mp: 241–246 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 5.43 (2 H, t, ^2J = 17.0 Hz, $\Delta\upsilon_{AB}$ = 17.9 Hz, CH_2-N), 7.11 (2 H, d, ^3J = 8.3 Hz, 2 Ar-H), 7.29 (2 H, d, ^3J = 8.3 Hz, 2 Ar-H), 7.60 (2 H, m, 2 Ar-H), 7.69 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.89 (1 H, d, ^3J = 7.2 Hz, Ar-H), 7.92 (1 H, d, ^3J = 8.0 Hz, Ar-H), 7.96 (2 H, s, NH_2), 8.03 (1 H, d, ^3J = 8.0 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 49.2 (CH_2), 58.5 (C-S), 73.6 (*C*CN), 117.1 (CN), 118.9 (OCN), 119.2 (CH), 121.9 (CH), 126.1 (CH), 128.4 (2 CH), 128.5 (3 CH), 128.8 (CH), 129.0 (CH), 130.4 (C), 131.9 (C), 134.0 (C), 134.4 (C), 135.0 (C), 142.5 (C), 165.8 (CNH_2), 197.5 (C=S). IR (KBr) (υ_{max}, cm^{-1}): 3315 and 3265 (NH_2), 2195 (CN), 1654 (OC=C), 1592, 1432 (C=C_{Ar}), 1374 (C=S). EI-MS: *m*/*z* (%) = 447 (M^+, 40), 403 (100), 371 (37), 336 (14), 260 (15), 246 (9), 219 (42), 195 (54), 90 (12). Anal. Calc. for $C_{23}H_{14}ClN_3OS_2$ (447.96): C, 61.67; H, 3.15; N, 9.38. Found: C, 61.95; H, 3.22; N, 9.45%.

4.8. 8-Amino-12-(2,4-dichlorobenzyl)-11-thioxo-9a,6b-(epithiomethanoimino)acenaphtho[1,2-b]furan-9-carbonitrile ***6g***

Colorless solid (0.44 g, 91%). mp: 252–257 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 5.39 (2 H, AB-q, ^2J = 17.4 Hz, $\Delta\upsilon_{AB}$ = 40.1 Hz, CH_2-N), 6.45 (1 H, d, ^3J = 8.5 Hz, Ar-H), 7.13 (1 H, d, ^3J = 8.5 Hz, Ar-H), 7.57 (1 H, t, ^3J = 7.50 Hz, Ar-H), 7.63 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.66 (1 H, s, Ar-H), 7.71 (2 H, t, ^3J = 7.50, 7.0 Hz, 2 Ar-H), 7.93 (1 H, d, ^3J = 8.0 Hz, Ar-H), 8.01 (2 H, s, NH_2), 8.03 (2 H, d, ^3J = 8.0 Hz, 2 Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 47.9 (CH_2), 59.1 (C-S), 74.5 (*C*CN), 117.3 (CN), 118.9 (OCN), 119.8 (CH), 121.9 (CH), 126.1 (CH), 127.9 (CH), 128.8 (CH), 129.0 (CH), 129.5 (C), 129.8 (CH), 130.4 (C), 131.7 (CH), 132.4 (C), 133.2 (C), 133.3 (CH), 134.4 (C), 135.1 (C), 142.8 (C), 166.3 (CNH_2), 198.3 (C=S). IR (KBr) (υ_{max}, cm^{-1}): 3310 and 3266 (NH_2), 2198 (CN), 1657 (OC=C), 1594, 1435 (C=C_{Ar}), 1375 (C=S). EI-MS: *m*/*z* (%) = 481 (M^+, 55), 436 (100), 404 (34), 369 (12), 334 (53), 258 (45), 244 (19), 218 (23), 191 (8), 86 (17). Anal. Calc. for $C_{23}H_{13}Cl_2N_3OS_2$ (482.40): C, 57.27; H, 2.72; N, 8.71. Found: C, 57.56; H, 2.80; N, 8.79%.

4.9. 8-Amino-12-phenyl-11-thioxo-9a,6b-(epithiomethanoimino) acenaphtho[1,2-b]furan-9-carbonitrile ***6h***

Cream color solid (0.34 g, 85%). mp: 248–251 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 6.36 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.29 (2 H, br s, 2 Ar-H), 7.48 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.60 (3 H, br s, 3 Ar-H), 7.64 (1 H, d, ^3J = 7.5 Hz, Ar-H), 7.72 (1 H, t, ^3J = 8.2 Hz, Ar-H), 7.92 (1 H, d, ^3J = 8.0 Hz, Ar-H), 8.01 (1 H, d, ^3J = 8.0 Hz, Ar-H), 8.06 (2 H, s, NH_2). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 59.4 (C-S), 75.0 (*C*CN), 117.7 (CN), 119.1 (OCN), 119.9 (CH), 121.9 (CH), 122.0 (CH), 126.2 (2 CH), 128.8 (CH), 129.4 (C), 130.4 (CH), 130.7 (CH), 130.9 (CH), 132.5 (C), 134.8 (C), 135.9 (C), 137.4 (2 CH), 143.1 (C), 166.6 (CNH_2), 199.4 (C=S). IR (KBr) (υ_{max}, cm^{-1}): 3316 and 3266 (NH_2), 2191 (CN), 1652 (OC=C), 1583, 1426 (C=C_{Ar}), 1335 (C=S). EI-MS: *m*/*z* (%) = 399 (M^+, 29), 355 (100), 323 (24), 311 (54), 279. (14), 202 (10), 165 (34), 150 (64), 108 (54), 76 (9). Anal. Calc. for $C_{22}H_{13}N_3OS_2$ (399.49): C, 66.15; H, 3.28; N, 10.52. Found: C, 66.48; H, 3.34; N, 10.60%.

4.10. 8-Amino-12-(4-methoxyphenyl)-11-thioxo-9a,6b-(epithiomethanoimino)acenaphtho[1,2-b]furan-9-carbonitrile ***6i***

Light blue solid, 0.38 g, 88%. mp: 255–258 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 3.85 (3 H, s, OMe), 6.46 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.11 (2 H, d, ^3J = 7.0 Hz, 2 Ar-H), 7.20 (2 H, br s, 2 Ar-H), 7.51 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.62 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.70 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.92 (1 H, d, ^3J = 8.2 Hz, Ar-H), 8.01 (1 H, d, ^3J = 8.0 Hz, Ar-H), 8.06 (2 H, s, NH_2). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 55.4 (OMe), 58.7 (C-S), 73.9 (*C*CN), 115.1 (2CH), 117.1

(CN), 117.8 (2CH), 119.8 (OCN), 121.3 (CH), 125.4 (CH), 128.1 (CH), 128.7 (CH), 128.8 (C), 129.3 (CH), 131.6 (CH), 131.9 (C), 134.2 (C), 135.5 (C), 142.5 (C), 160.3 (C), 166.0 (CNH_2), 198.9 (C=S). IR (KBr) (ν_{max}, cm^{-1}): 3316 and 3280 (NH_2), 2194 (CN), 1658 (OC=C), 1591, 1429 (C=C_{Ar}), 1349 (C=S). EI-MS: *m/z* (%) = 429 (M^+, 28), 385 (100), 353 (77), 341 (81), 309 (83), 266 (85), 230 (97), 202 (79), 165 (90), 150 (84), 108 (75), 76 (80), 44 (18). Anal. Calc. for $C_{23}H_{15}N_3O_2S_2$ (429.51): C, 64.32; H, 3.52; N, 9.78. Found: C, 64.63; H, 3.61; N, 9.85%.

4.11. 8-Amino-11-thioxo-12-(p-tolyl)-9a,6b-(epithiomethanoimino)acenaphtho[1,2-b]furan-9-carbonitrile ***6j***

Violet solid (0.34 g, 82%). mp: 102–106 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 2.42 (3 H, s, Me), 6.42 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.17 (2 H, br s, 2 Ar-H), 7.38 (2 H, d, ^3J = 7.0 Hz, 2 Ar-H), 7.49 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.62 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.70 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.91 (1 H, d, ^3J = 8.2 Hz, Ar-H), 7.99 (1 H, d, ^3J = 8.0 Hz, Ar-H), 8.05 (2 H, s, NH_2). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 21.9 (Me), 59.3 (C-S), 74.8 (*C*CN), 117.7 (CN), 119.1 (CH), 119.8 (OCN), 122.0 (CH), 126.1 (2CH), 128.7 (CH), 129.4 (C), 130.0 (CH), 130.7 (C), 131.1 (C), 132.5 (2 CH), 134.7 (CH), 134.8 (C), 136.0 (C), 140.6 (CH), 143.1 (C), 166.6 (CNH_2), 199.3 (C=S). IR (KBr) (ν_{max}, cm^{-1}): 3294 and 3151 (NH_2), 2194 (CN), 1659 (OC=C), 1588, 1430 (C=C_{Ar}), 1337 (C=S). EI-MS: *m/z* (%) = 413 (M^+, 27), 369 (100), 337 (31), 325 (12), 293 (70), 278 (63), 242 (42), 214 (27), 177 (19), 162 (53), 120 (41), 88 (8), 74 (74). Anal. Calc. for $C_{23}H_{15}N_3OS_2$ (413.51): C, 66.81; H, 3.66; N, 10.16. Found: C, 67.13; H, 3.74; N, 10.23%.

4.12. Ethyl 8-amino-12-ethyl-11-thioxo-9a,6b-(epithiomethanoimino)acenaphtho[1,2-b]furan-9-carboxylate ***6k***

Light yellow solid (0.30 g, 75%). mp: 192–195 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 1.31 (6 H, t, ^3J = 7.0 Hz, 2 Me), 4.12–4.21 (2 H, AB-m, CH_2-N), 4.19 (2 H, br s, NH_2), 4.25 (2 H, q, ^3J = 7.0 Hz, O-CH_2), 7.63 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.71 (1 H, t, ^3J = 7.0 Hz, Ar-H), 7.73 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.86 (1 H, d, ^3J = 8.3 Hz, Ar-H), 8.04 (1 H, d, ^3J = 7.0 Hz, Ar-H), 8.06 (1 H, d, ^3J = 7.0 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 12.6 (Me), 15.7 (Me), 42.1 (CH_2), 58.1 (CH_2), 59.3 (C-S), 79.7 (*C*CO_2Et), 120.6 (CH), 121.2 (CH), 121.4 (OCN), 124.9 (CH), 128.1 (CH), 128.9 (CH), 129.6 (CH), 131.8 (C), 134.5 (C), 135.7 (C), 143.7 (C), 164.6 (C=O), 171.5 (CNH_2), 197.3 (C=S). IR (KBr) (ν_{max}, cm^{-1}): 3388 and 3215 (NH_2), 1681 (C=O), 1626 (OC=C), 1531, 1442 (C=C_{Ar}), 1379 (C=S). EI-MS: *m/z* (%) = 398 (M^+, 30), 353 (100), 309 (17), 277 (48), 249 (42), 223 (21), 172 (35), 148 (53), 121 (12), 15 (11). Anal. Calc. for $C_{20}H_{18}N_2O_3S_2$ (398.50): C, 60.28; H, 4.55; N, 7.03. Found: C, 60.55; H, 4.62; N, 7.10%.

4.13. Ethyl 8-amino-12-(4-chlorobenzyl)-11-thioxo-9a,6b-(epithiomethanoimino)acenaphtho[1,2-b]furan-9-carboxylate ***6l***

Cream color solid (0.38 g, 77%). mp: 163–165 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 1.05 (3 H, t, ^3J = 7.0 Hz, Me), 4.21 (2 H, q, ^3J = 7.0 Hz, OCH_2), 4.22 (2 H, br s, NH_2), 5.42 (2 H, AB-q, ^2J = 17.0 Hz, $\Delta\upsilon_{AB}$ = 20.0 Hz, N-CH_2), 7.16 (2 H, d, ^3J = 7.5 Hz, 2 Ar-H), 7.30 (2 H, d, ^3J = 7.5 Hz, 2 Ar-H), 7.58 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.65 (1 H, t, ^3J = 7.5 Hz, Ar-H), 7.74 (1 H, d, ^3J = 7.0 Hz, Ar-H), 7.87 (1 H, d, ^3J = 8.0 Hz, Ar-H), 7.89 (1 H, d, ^3J = 7.5 Hz, Ar-H), 8.01 (1 H, d, ^3J = 8.0 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 15.8 (Me), 50.2 (CH_2), 60.4 (CH_2), 60.9 (C-S), 80.6 (*C*CO_2Et), 118.5 (OCN), 121.3 (CH), 122.2 (CH), 125.7 (CH), 128.7 (CH), 129.1 (2 CH), 129.3 (C), 129.6 (CH), 129.7 (C), 130.3 (CH), 132.4 (CH), 132.6 (C), 135.1 (C), 135.3 (CH), 136.1 (C), 144.3 (C), 165.8 (C=O), 171.4 (CNH_2), 199.2 (C=S). IR (KBr) (ν_{max}, cm^{-1}): 3388 and 3305 (NH_2), 1680 (C=O, OC=C), 1547, 1436 (C=C_{Ar}), 1327 (C=S). EI-MS: *m/z* (%) = 494 (M^+, 28), 449 (100), 405 (17), 373 (38), 338 (74), 262 (49), 248 (57), 221 (28), 189 (26), 174 (42), 132 (15), 100 (31). Anal. Calc. for $C_{25}H_{19}ClN_2O_3S_2$ (495.01): C, 60.66; H, 3.87; N, 5.66. Found: C, 60.97; H, 3.95; N, 5.73%.

4.13.1. X-ray Crystal-structure determination of compound ***6l***

The X-ray diffraction measurement was carried out on STOE IPDS 2T diffractometer with graphite-monochromated MoKα radiation. The single crystal suitable for X-ray analysis was obtained from DMSO/EtOAc solution and mounted on a glass fiber and used for data collection. Cell constants a = 15.837(3) Å, b = 14.091(3) Å, c = 11.496(2) Å, Alpha = 90°, Beta = 92.48° (3), Gamma = 90°, cell volume = 2563.0(9) Å3 and orientation matrixes for data collection were obtained by least-square refinement of the diffraction data from 3217 for compound **6l**. Diffraction data were collected in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA software package (Stoe and Cie, X–AREA Program, 2005). Numerical absorption correction was applied using X-Red32 software. The structure was solved by direct methods and subsequent difference Fourier maps and then refined on F2 by a full-matrix least-squares procedure using anisotropic displacement parameters. Atomic factors are from the International Tables for X-ray Crystallography. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. All refinements were performed using the X-STEP32, SHELXL-2014 and WinGX-2013.3 programs (Farrugia, 1999; Coppens et al., 1965; Burnett and Johnson, 1996; Macrae et al., 2006; Sheldrick, 2008). CCDC-1502615 contains the supplementary crystallographic data for this compound **6l**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

4.14. Ethyl 8-amino-12-(4-methoxyphenyl)-11-thioxo-9a,6b-(epithiomethanoimino)acenaphtho[1,2-b]furan-9-carboxylate ***6m***

Yellow solid (0.40 g, 83%). mp: 194–196 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 1.33 (3 H, br-m, Me), 3.85 (3 H, br-s, MeO), 4.01 (2 H, br-m, CH_2O), 4.21 (2 H, br-s, NH_2), 6.47 (1 H, br-m, Ar-H), 7.13 (2 H, br-m, 2 Ar-H), 7.22 (2 H, br-m, 2 Ar-H), 7.47 (1 H, br-m, Ar-H), 7.65 (1 H, br-m, Ar-H), 7.84 (1 H, br-m, Ar-H), 7.94 (1 H, d, ^3J = 8.2 Hz,

Ar-H), 8.1 (1 H, d, ^3J = 8.0 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 15.8 (Me), 56.5 (OMe), 60.0 (CH_2O), 64.0 (C-S), 80.7 (CCO_2Et), 115.6 (OCN), 115.7 (C), 121.3 (CH), 121.7 (C), 121.8 (C), 125.6 (CH), 128.5 (CH), 129.1 (C), 129.9 (2 CH), 130.2 (C), 132.3 (3 CH), 135.2 (CH), 136.4 (CH), 144.3 (C), 160.8 (C=O), 165.3 (CNH_2), 200.6 (C=S). IR (KBr) (ν_{max}, cm^{-1}): 3382 and 3278 (NH_2), 1686 (C=O), 1628 (C=C), 1530, 1428 (C=C_{Ar}), 1324 (C=S). EI-MS: m/z (%) = 476 (M^+, 34), 431 (100), 387 (68), 355 (52), 343 (63), 311 (12), 268 (36), 232 (41), 204 (75), 167 (27), 152 (12), 110 (45), 78 (15). Anal. Calc. for $C_{25}H_{20}N_2O_4S_2$ (476.57): C, 63.01; H, 4.23; N, 5.88. Found: C, 63.33; H, 4.31; N, 5.95%.

Appendix A. Supplementary material

The ^{1}H and ^{13}C NMR spectra of the products. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2017.01.010.

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