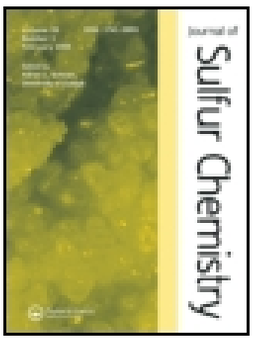

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A one-pot synthesis of novel cyclic ketene dithioacetals from Nef-isocyanide-Perkow adduct

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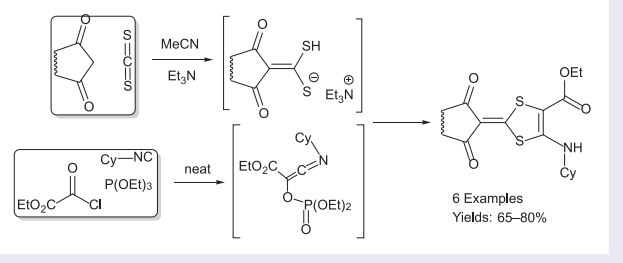
ABSTRACT

A novel synthesis of cyclic ketene dithioacetals through the reaction between phosphorous-based ketenimines [generated *in situ* from Nef-isocyanide-Perkow reaction], cyclic 1,3-dicarbonyl compounds, and carbon disulfide at room temperature, in moderate to good yields (65–80%), is described.



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Nef-isocyanide-Perkow reaction; ketene dithioacetal; active methylene compounds; carbon disulfide; polarized double bond

Highlights

The reaction of phosphorous-based ketenimines with cyclic 1,3-dicarbonyl compounds and carbon disulfide at room temperature leads to the formation of novel cyclic ketene dithioacetals in moderate to good yields.

1. Introduction

Functionalized ketene dithioacetals have emerged as versatile intermediates in organic synthesis [1–3]. Extensive research, since the last decade, has given rise to new prospects in their chemistry. Among them, acceptor-substituted ketene dithioacetals have proven to be especially important in the construction of a diverse array of substituted carbo- and heterocyclic compounds [4–7]. Ketene dithioacetals can be classified on the basis of their substitution patterns at the α-position of the ketene dithioacetal functionality. For instance,

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α-oxo ketene dithioacetals, which bear a carbonyl group at the α-C atom, are versatile intermediates in organic synthesis and their preparation and diverse applications, especially serving as 1,3-electrophilic three-carbon synthones have been reviewed in detail [8–11].

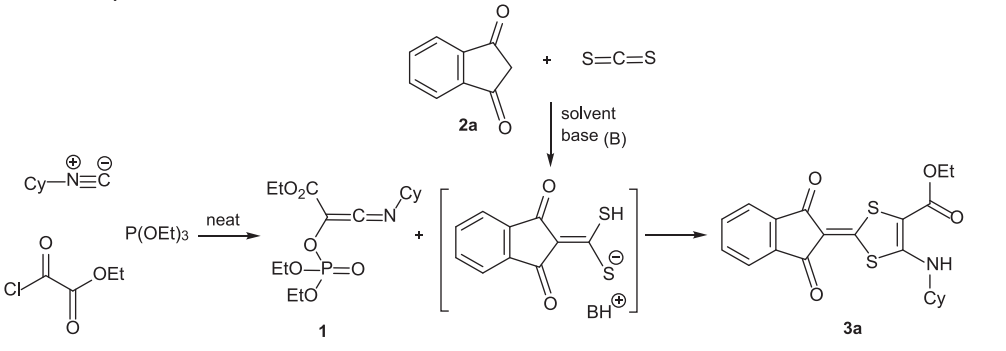
A general method for the synthesis of functionalized ketene dithioacetals involves the condensation of an active methylene compound with carbon disulfide (CS_2) in the presence of a suitable base followed by S-alkylation. These condensations have been performed by a variety of base reagents such as sodium hydride, potassium hydroxide, potassium *tert*-butoxide, *n*-butylithium, lithium dialkylamides, and potassium carbonate [12–15]. Moreover, the preparation of ketene dithioacetals containing active methylene groups, under phase transfer catalysis, has been reported [16]. Geminal dithiolates react readily with electrophiles such as alkyl halides, 1,2-dibromoethane and 1,3-dibromopropane to form bis(alkylsulfanyl) derivatives, dithiolanes, and dithianes, respectively [17].

2. Results and discussion

As part of our current studies on the development of new routes to synthesis of ketenimines, imidoyl chlorides [18–21], and ketene dithioacetals [22]; here we report the reaction of these intermediates toward phosphorylated hydroxyketenimine, formed via a Nef-Perkow cascade involving isocyanides as starting material, to provide cyclic ketene dithioacetals. Herein, we report a method for the synthesis of a variety of five-membered cyclic ketene dithioacetals **3a**–**f** using condensation of active methylene compounds **2** and CS_2 in the presence of phosphorylated hydroxyketenimine **1.**

We started our study in the reaction of phosphorylated hydroxyketenimines (**1**) and 1,3-indandione (**2a**) in the presence of carbon disulfide, at room temperature in different solvent systems, and the results are given in Table 1. The use of MeCN instead of EtOH and THF as solvents in the presence of KOH (1 equiv.) at ambient temperature for 4 h, led to

Table 1. Optimization of the reaction conditions.[a]



Entry	Solvent	Base (x eq.)	Yield (%)[b]
1	EtOH	KOH (1)	20
2	THF	KOH (1)	30
3	MeCN	KOH (1)	45
4	MeCN	DBU (1)	50
5	MeCN	Et_3N (1)	73
6	MeCN	Et_3N (2)	80

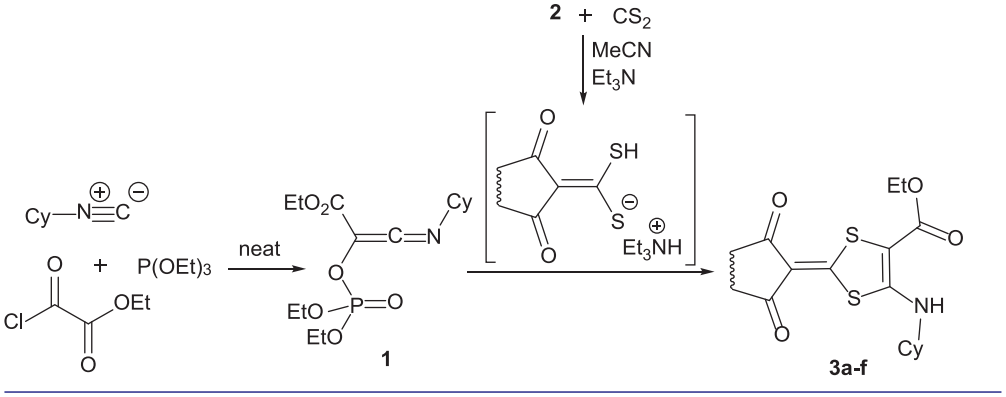
[a]Reaction conditions: (i) **1** Ref. [23]; (ii) **2a** (1 mmol), CS_2 (1.2 mmol), solvent (3 mL) and base (1 or 2 mmol) at r.t., 4 h.
[b]Isolated yield.

an improved 45% yield (Entries 1, 2 and 3). Compound **3a** was obtained in a better yield (73%) using Et_3N (Entry 5). These results encouraged us to further optimize the reaction conditions by increasing the Et_3N loading. The conversion proceeded in an improved yield (80%) with 2 equivalents of Et_3N (Entry 6). In the presence of this amount of Et_3N, the reaction was complete after 4 h at room temperature.

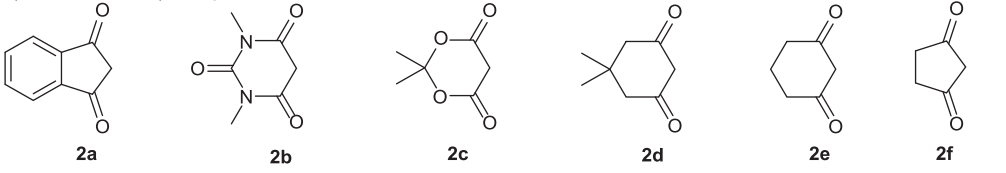
With the suitable reaction conditions in hand, we next explored the protocol with phosphorylated hydroxyketenimines (**1**), variety of five- and six-membered cyclic of the 1,3-dicarbonyl compounds (**2**), carbon disulfide in the presence of Et_3N with MeCN in 4 h. As shown in Table 2, these reactions led to the formation of ketene dithioacetals in 65–80% yields.

A plausible mechanism for the formation of products **3** is shown in Scheme 1. The addition of isocyanide to acyl chloride (Nef-isocyanide reaction) leads to imidoyl chlorides,

Table 2. Synthesis of cyclic ketene dithioacetals **3a–f**.

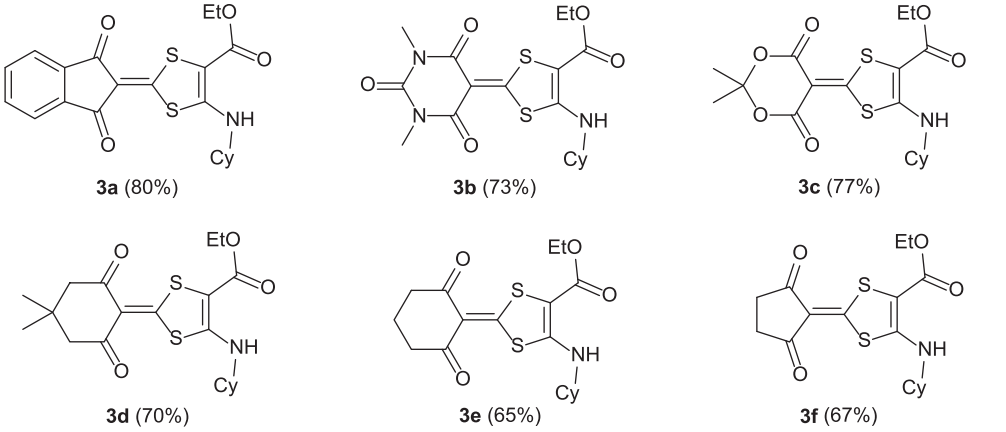


Cyclic 1,3-dicarbonyl compounds **2a–f**



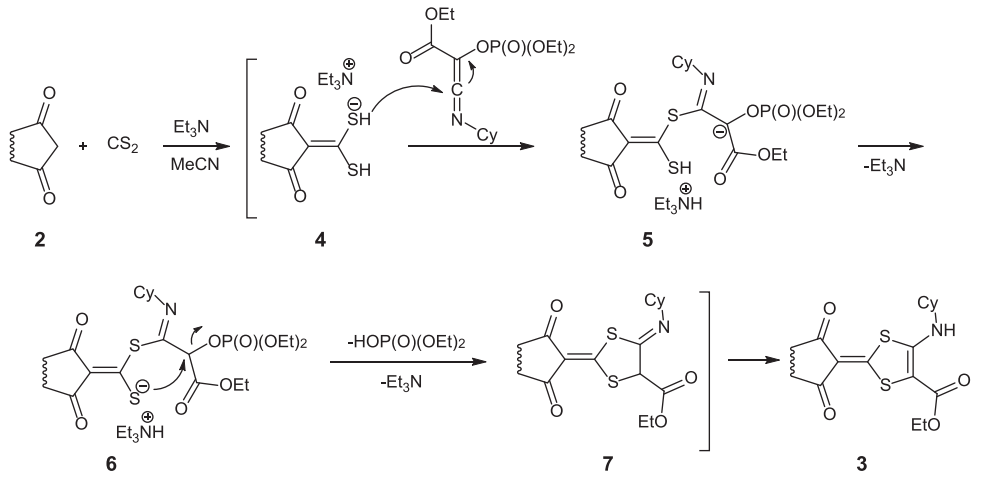
2a **2b** **2c** **2d** **2e** **2f**

Products **3a–f**



3a (80%) **3b** (73%) **3c** (77%)

3d (70%) **3e** (65%) **3f** (67%)



Scheme 1. Proposed mechanism for the formation of products **3**.

which can later be treated with triethyl phosphite to afford ketenimines in a Perkow-type reaction. Then, the reaction of triethylammonium salt **4** with ketenimine gives intermediate **5**, which is converted into intermediate **6** by the proton transfer reaction. This intermediate undergoes removal of phosphate with intramolecular cyclization and tautomerization to give product **3**.

3. Conclusion

In conclusion, we have described the synthesis of functionalized cyclic ketene dithioacetals by a novel multicomponent process, which proceeds under mild conditions and furnished the products in satisfactory isolated yields. The methodology involves an initial Nef-isocyanide-Perkow reaction to produce a phosphorous-based ketenimine, which was then allowed to react with a 'bis-thiol' derivative generated *in situ* from a cyclic 1,3-dioxo compound and carbon disulfide. The structures of six novel dithioacetals thus prepared were perfectly described by analytical data.

4. Experimental

4.1. General

All purchased solvents and chemicals were of analytical grade and used without further purification. Phosphorylated hydroxyketenimines **1** were prepared according to literature [23]. Melting points: *Electrothermal-9100* apparatus. IR Spectra: *Shimadzu-IR-460* spectrometer; $\bar{\upsilon}$ in cm^{-1}. ^{1}H NMR and ^{13}C NMR Spectra: Bruker *DRX-500 Advance* instrument using $CDCl_3$ as the applied solvent and TMS as the internal standard at 500.1 and 125.7 MHz, respectively.; δ in ppm, J in Hz. Mass spectra were recorded on a *Finnigan-MAT-8430EI-MS* mass spectrometer; at an ionization potential 70 eV; in m/z (rel. %). Elemental analyses for C, H, and N were performed using a *Heraeus CHN-O-Rapid* analyzer.

4.2. General procedure for preparation (3a–3f)

A mixture of 1,3-dicarbonyl compound (1 mmol) with carbon disulfide (0.091, 1.2 mmol) and Et_3N (0.202 g, 2 mmol) in MeCN (4 mL) was stirred for 2 h at room temperature. A solution of ketenimine **1** (1 mmol) in MeCN (1 mL) was then added. After 4 h, the solvent was removed under reduced pressure and the residue was purified by preparative TLC (SiO_2; AcOEt/hexane 1:2).

4.2.1. Ethyl 5-(cyclohexylamino)-2-(1,3-dioxo-1H-inden-2(3H)-ylidene)-1,3-dithiole-4-carboxylate (3a)

Yellow powder. M.p. 227–228°C. Yield: 0.33 g (80%). IR (KBr) (ν_{max}/cm^{-1}): 3452 (NH), 1730 (C=O), 1640 (C=O), 1126 (C−O). ^{1}H NMR (500 MHz, DMSO-d_6): 1.25–1.29 (2H, *m*, CH_2); 1.37 (3H, *t*, $J = 7.1$, Me); 1.38–1.45 (2H, *m*, CH_2); 1.55–1.65 (2H, *m*, CH_2); 1.79–1.83 (2H, *m*, CH_2); 2.07–2.09 (2H, *m*, CH_2); 3.42 (1H, *br s*, CH); 4.30 (2H, *q*, $J = 7.1$, CH_2O); 7.62–7.64 (2H, *m*, 2 CH); 7.77–7.80 (2H, *m*, 2 CH), 8.14 (1H, *d*, $J = 8.3$, NH).^{13}C NMR (125 MHz, DMSO-d_6): 14.4 (Me); 24.3 (2 CH_2); 25.1 (CH_2); 33.2 (2 CH_2); 57.8 (CH); 60.0 (CH_2O); 122.1 (CH); 122.2 (CH); 133.5 (CH); 133.9 (CH); 133.7 (C); 140.2 (C); 140.6 (C); 140.9 (C); 159.5 (C); 159.7 (C); 167 (C=O); 187.7 (C=O); 187.8 (C=O). MS (EI, 70 eV): *m*/*z* (%) = 415 (100, M^+), 370 (20), 342 (25), 322 (15), 311 (20), 283 (10), 219 (35), 141 (60), 132 (35), 98 (15), 83 (45), 55 (30). Anal. Calcd (%) for $C_{21}H_{21}NO_4S_2$ (415.53): C 60.70, H 5.09, N, 3.37. Found: C 60.86, H 5.11, N 3.40.

4.2.2. Ethyl 5-(cyclohexylamino)-2-(tetrahydro-1,3-dimethyl-2,4,6-trioxopyrimidin-5(6H)-ylidene)-1,3-dithiole-4-carboxylate (3b)

Yellow powder. M.p. 205–207°C. Yield: 0.31 g (73%). IR (KBr) (ν_{max}/cm^{-1}): 3452 (NH), 1739 (C=O), 1701 (C=O), 1226 (C−N). ^{1}H NMR (500 MHz, DMSO-d_6): 1.25–1.30 (2H, *m*, CH_2); 1.37 (3H, *t*, $J = 7.1$, Me); 1.39–1.45 (2H, *m*, CH_2); 1.55–1.65 (2H, *m*, CH_2); 1.79–1.83 (2H, *m*, CH_2); 2.05–2.09 (2H, *m*, CH_2); 3.42 (6H, *s*, 2 Me); 3.46 (1H, *br s*, CH); 4.30 (2H, *q*, $J = 7.1$, CH_2O); 7.98 (1H, *d*, $J = 8.2$, NH). ^{13}C NMR (125 MHz, DMSO-d_6): 13.9 (Me); 22.5 (2 CH_2); 27.1 (CH_2); 28.4 (Me); 28.5 (Me); 33.5 (2 CH_2); 47.5 (CH); 59.2 (CH_2O); 103.8 (C); 121.3 (C); 154.5 (C); 158.3 (C); 160.89 (C=O); 166.42 (C=O); 166.9 (C=O); 170.1 (C=O). MS (EI, 70 eV): *m*/*z* (%) = 425 (80, M^+), 380 (20), 368 (15), 342 (25), 327 (15), 311 (100), 283 (20), 229 (35), 141 (65), 98 (25), 83 (55), 55 (40). Anal. Calcd (%) for $C_{18}H_{23}N_3O_5S_2$ (425.52): C 50.81, H 5.45, N 9.87. Found: C 51.04, H 5.48, N 9.91.

4.2.3. Ethyl 5-(cyclohexylamino)-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-1,3-dithiole-4-carboxylate (3c)

Yellow powder. M.p. 201–204°C. Yield: 0.31 g (77%). IR (KBr) (ν_{max}/cm^{-1}): 3452 (NH), 1670 (C=O). ^{1}H NMR (500 MHz, DMSO-d_6): 1.25–1.30 (2H, *m*, CH_2); 1.34 (3H, *t*, $J = 7.1$, Me); 1.38–1.44 (2H, *m*, CH_2); 1.60–1.65 (2H, *m*, CH_2); 1.73 (6H, *s*, 2 Me); 1.77–1.79 (2H, *m*, CH_2); 2.00–2.07 (2H, *m*, CH_2); 3.43 (1H, *br s*, CH); 4.30 (2H, *q*, $J = 7.1$, CH_2O); 7.99 (1H, *d*, $J = 8.4$, NH). ^{13}C NMR (125 MHz, DMSO-d_6): 13.9 (Me); 24.6 (2 CH_2); 25.5 (2 Me); 27.4 (CH_2); 32.7 (2 CH_2); 57.2 (CH); 60.1 (CH_2O); 92.8 (C); 94.0 (C); 104.3 (C); 160.6 (C); 161.6 (C); 162.4 (C=O); 163.7 (C=O); 171.8 (C=O). MS (EI, 70 eV): *m*/*z* (%) = 413 (90, M^+), 377 (30), 349 (10), 311 (100), 264 (10), 229 (40), 200 (20), 173 (5),

145 (25), 117 (15), 83 (25), 55 (45). Anal. Calcd (%) for $C_{18}H_{23}NO_6S_2$ (413.51): C 52.28, H 5.61, N 3.39. Found: C 52.53, H 5.64, N 3.42.

4.2.4. Ethyl 5-(cyclohexylamino)-2-(4,4-dimethyl-2,6-dioxocyclohexylidene)-1,3-dithiole-4-carboxylate (3d)

Yellow powder. M.p. 156–158°C. Yield: 0.28 g (70%). IR (KBr) (ν_{max}/cm^{-1}): 3450 (NH), 1689 (C=O), 1659 (C=O), 1118 (C−O). ^{1}H NMR (500 MHz, DMSO-d_6): 1.12 (6H, *s*, 2 Me); 1.20–1.30 (2H, *m*, CH_2); 1.35 (3H, *t*, J = 7.1, Me); 1.36–1.45 (2H, *m*, CH_2); 1.63–1.65 (2H, *m*, CH_2); 1.76–1.78 (2H, *m*, CH_2); 2.06–2.08 (2H, *m*, CH_2); 2.53 (4H, *s*, 2 CH_2); 3.48 (1H, *br s*, CH); 4.30 (2H, *q*, J = 7.1, CH_2O); 7.96 (1H, *d*, J = 8.3, NH). ^{13}C NMR (125 MHz, DMSO-d_6): 14.4 (Me); 24.3 (2 CH_2); 25.1 (C); 28.4 (Me); 28.5 (Me); 30.8 (CH_2); 33.2 (2 CH_2); 50.6 (2 CH_2); 56.8 (CH); 60.8 (CH_2O); 116.6 (C); 140.3 (C); 161.2 (C); 164.1 (C); 167.1 (C=O); 193.7 (C=O); 193.8 (C=O). MS (EI, 70 eV): *m*/*z* (%) = 409 (100, M^+), 364 (20), 326 (35), 311 (85), 283 (15), 267 (40), 214 (35), 195 (10), 141 (55), 126 (25), 98 (15), 83 (50), 54 (65). Anal. Calcd (%) for $C_{20}H_{27}NO_4S_2$ (409.56): C 58.65, H 6.64, N 3.42. Found: C 58.51, H 6.66, N 3.44.

4.2.5. Ethyl 5-(cyclohexylamino)-2-(2,6-dioxocyclohexylidene)-1,3-dithiole-4-carboxylate (3e)

Yellow powder. M.p. 202–205°C. Yield: 0.24 g (65%). IR (KBr) (ν_{max}/cm^{-1}): 3450 (NH), 1689 (C=O), 1659 (C=O), 1118 (C−O). ^{1}H NMR (500 MHz, DMSO-d_6): 1.28–1.32 (2H, *m*, CH_2); 1.35 (3H, *t*, J = 7.1, Me); 1.36–1.48 (2H, *m*, CH_2); 1.62–1.65 (2H, *m*, CH_2); 1.75–1.78 (2H, *m*, CH_2); 1.79–1.92 (2H, *m*, CH_2); 1.99–2.09 (2H, *m*, CH_2); 2.62–2.65 (4H, *m*, 2CH_2); 3.47 (1H, *br s*, CH); 4.30 (2H, *q*, J = 7.1, CH_2O); 7.95 (1H, *d*, J = 8.2, NH). ^{13}C NMR (125 MHz, DMSO-d_6): 14.4 (Me); 19.7 (CH_2); 24.3 (2 CH_2); 25.2 (CH_2); 33.2 (2 CH_2); 36.9 (CH_2); 37.1 (CH_2); 57.8 (CH); 61.2 (CH_2O); 93.0 (C); 117.9 (C); 161.3 (C); 164.1 (C); 167.5 (C=O); 193.6 (C=O); 194.0 (C=O). MS (EI, 70 eV): *m*/*z* (%) = 381 (100, M^+), 336 (20), 298 (30), 283 (70), 239 (25), 195 (15), 185 (15), 141 (55), 83 (30), 55 (50). Anal. Calcd (%) for $C_{18}H_{23}NO_4S_2$ (381.51): C 56.67, H 6.08, N 3.67. Found: C 56.89, H 6.10, N 3.70.

4.2.6. Ethyl 5-(cyclohexylamino)-2-(2,5-dioxocyclopentylidene)-1,3-dithiole-4-carboxylate (3f)

Yellow powder. M.p.: 239–241°C. Yield: 0.27 g (67%). IR (KBr) (ν_{max}/cm^{-1}): 3434 (NH), 1675 (C=O), 1628 (C=O), 1182 (C−O). ^{1}H NMR (500 MHz, DMSO-d_6): 1.28 (3H, *t*, J = 7.0, Me); 1.38–1.46 (2H, *m*, CH_2); 1.49–1.55 (2H, *m*, CH_2); 1.65–1.68 (2H, *m*, CH_2); 1.94–1.96 (2H, *m*, CH_2); 2.42–2.43 (2H, *m*, CH_2); 2.58 (4H, *s*, 2 CH_2); 3.49 (1H, br *s*, CH); 4.27 (2H, *q*, J = 7.0, CH_2O); 8.10 (1H, *d*, J = 9.3, NH). ^{13}C NMR (125 MHz, DMSO-d_6): 14.4 (Me); 24.2 (2 CH_2); 25.1 (CH_2); 33.1 (CH_2); 34.1 (CH_2); 34.0 (2 CH_2); 57.8 (CH); 61.2 (CH_2O); 116.2 (C); 160.4 (C); 163.4 (C); 163.7 (C); 199.3 (C=O); 199.4 (C=O); 200.0 (C=O). MS (EI, 70 eV): *m*/*z* (%) = 367 (100, M^+), 344 (5), 320 (20), 285 (35), 256 (20), 234 (5), 210 (15), 173 (10), 141 (70), 113 (20), 83 (25), 55 (65). Anal. Calcd (%) for $C_{17}H_{21}NO_4S_2$ (367.48): C 55.56, H 5.76, N 3.81. Found: C 55.71, H 5.79, N 3.83.

Disclosure statement

No potential conflict of interest was reported by the authors.

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