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Natural eutectic salts catalyzed one-pot synthesis of 5-arylidene-2-imino-4-thiazolidinones

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Abstract The rapid, very simple and green one-pot synthesis of 5-arylidene-2-imino-4-thiazolidinones by condensation of the thioureas with chloroacetyl chloride and an aldehyde in natural deep eutectic solvent with good to excellent yields is described.

Keywords Thiazolidinones · One-pot synthesis · Deep eutectic solvent · Green chemistry

Introduction

Due to the growing concern for the influence of the organic harmful solvents on the environment, organic reactions in green media have attracted considerable attention for organic chemists in recent years. Green chemistry is an innovative way for designing simple chemical processes and methods in order to eliminate or reduce the use of hazardous and toxic chemicals at any stage of production in the industry or laboratory [1].

Ionic liquids are considered as green alternative media for volatile organic solvents because of their low vapor pressures. They also have several other attractive properties, including chemical and thermal stability, nonflammability, high ionic conductivity, and a wide electrochemical potential window. Unfortunately, the high cost and toxicity of some aquatic species are the main disadvantages of these green solvents, which has limited their applications in laboratory and industry [2, 3]. Deep eutectic solvents (DESs), eutectic mixtures of an ammonium salt and a hydrogen-bond donor compound such as urea, acid, amine, and salts, developed by Abbott and co-workers [4, 5], are alternatives to ionic liquids.

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These eutectic mixtures are attractive alternatives to room temperature ionic liquids, as DESs can be less expensive, more synthetically available, nontoxic, and biodegradable [4–7].

Thiazolidin-4-ones derivatives constitute an important class of heterocyclic compounds due to their applications in organic synthesis, dyes, and in diverse biological and pharmaceutical activities [8–16]. Several synthetic routes have been developed for the preparation of substituted 2-imino-thiazolidin-4-ones [11, 17–25]. The most common synthetic pathway is the cyclization of substituted thioureas with a halo acetic acid derivative to form the corresponding 2-imino-thiazolidin-4-one derivatives [26–28]. However, most methods use a two- or three-step procedure and only one example used one-pot multicomponent reactions for the synthesis of 5-arylidene-2-imino-4-thiazolidinones under microwave irradiation [29]. During the course of our study on the environmentally benign organic synthesis, we have been particularly interested in one-pot synthesis of some novel 5-arylidene-2-imino-4-thiazolidinones derivatives under green reaction media in order to develop environmentally benign reactions [30–32].

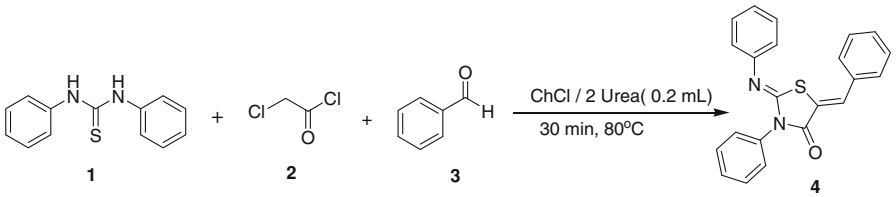
Results and discussion

The general synthetic strategy employed for preparation is based on one-pot reaction of thiourea, chloroacetyl chloride, and aromatic aldehydes in natural deep eutectic solvent.

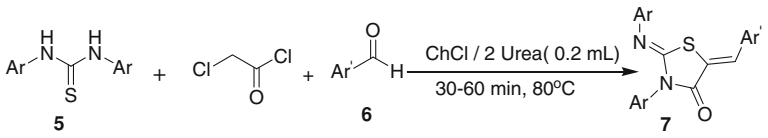
First, we embarked upon a series of experiments to establish the optimum conditions on the model reaction. Our first finding showed that three component reaction of *N*,*N*′-diphenylthiourea [33] **1** (1 mmol) with chloroacetyl chloride **2** (1.2 mmol) and benzaldehyde **3** (1 mmol) in urea/choline chloride (2:1)-based solvent (0.2 mL) under thermal heating at 80 °C for 30 min was an excellent reaction condition, and 5-benzylidene-3-phenyl-2(phenylimino)thiazolidin-4-one **4** was obtained in 94 % yield (Scheme 1).

After determining the optimized reaction conditions, we investigated the generality and scope of the one-pot three-component reaction with a variety of thiourea **5** and various aldehydes **6** to give 5-arylidene-2-imino-4-thiazolidinones **7** (Scheme 2).

As shown in Table 1, the yield of the products is not affected by the nature of the thiourea. In the case of thiourea with electron-donating and electron-withdrawing



Scheme 1 The model reaction for optimization of reaction conditions



Scheme 2 Synthetic pathway of thiazolidinone derivatives

Table 1 Diverse derivatives of 5-arylidene-2-imino-4-thiazolidinones **7**

Entry	Ar	Ar'	Mp (°C)	Yield (%)
1	Ph	Ph	214–216 (216) [26]	94
2	Ph	4-Cl-Ph	227–229	85
3	Ph	4-OCH_3-Ph	203–205	70
4	Ph	2-OH-Ph	254–256	80
5	Ph	4-OH-Ph	319–321	72
6	4-Cl-Ph	4-Cl-Ph	168–170	83
7	4-Cl-Ph	2,6-di-Cl-Ph	196–198	80
8	4-Et-Ph	4-Cl-Ph	198–200	87
9	4-But-Ph	3-NO_2-Ph	145–147	80
10	4-But-Ph	Indole-3-yl	236–238	67
11	2,3-di-CH_3-Ph	4-Cl-Ph	225–227	80
12	2,3-di-CH_3-Ph	2-OH-Ph	252–254	75
13	2,3-di-CH_3-Ph	2,4-di-OH-Ph	189–191	70
14	2,4,6-tri-CH_3-Ph	Ph	224–226	80
15	2,4,6-tri-CH_3-Ph	2-OH-Ph	302–304	73
16	2,4,6-tri-CH_3-Ph	4-CH_3-Ph	197–199	75
17	2,4,6-tri-CH_3-Ph	4-OCH_3-Ph	202–203	73

Isolated yield (%)

groups, as well as hindered groups, gave the desired product in good yields. The scope of the simple reaction was extended to aldehyde substrates, and the results indicated that commercially available aromatic aldehydes were good substrates and gave the products in good yields. The structure of all compounds was established by analysis of their ^{1}H and ^{13}C NMR spectroscopy as well as microanalysis data. The *Z* configuration of the exocyclic C=C bond was assigned on the basis of ^{1}H NMR spectroscopy, according to literature data for analogous 4-thiazolidinones [10, 29, 32].

Experimental

All chemicals including (2-hydroxyethyl)trimethylammonium chloride (known as choline chloride) were purchased from Merck or Fluka. Melting points were determined using an electro-thermal digital apparatus and are uncorrected. Purity of the compound was checked by Thin Layer Chromatography (TLC) using ethyl

acetate/petroleum ether (1:10 v/v) as an eluent. IR spectra were prepared on a galaxy series FT–IR 5000 spectrophotometer using KBr discs. ^{1}H NMR spectra were recorded on Bruker spectrophotometer (300 MHz) in DMSO d_6 or $CDCl_3$ using TMS as an internal standard. Microanalyses were performed by the Elemental Analyzer (Elemental, Vario EL III) at the Arak University. The microanalyses results agreed favorably with the calculated values.

General procedure for synthesis of 5-arylidene-2-imino-4-thiazolidinones (4)

A mixture of aldehyde (1 mmol), thiourea (1 mmol), and chloroacetyl chloride (1.2 mmol) in urea–choline chloride (2:1), (0.2 mL) was added to a test tube with a magnetic stirring bar. The test tube was heated in an oil bath at 80 °C for 30–60 min (progress of the reaction was followed by TLC) and then was slowly cooled to room temperature. The resulting precipitate was filtered, and washed with hot water and ethanol to give pure thiazolidinones. For most of the reactions, appropriate recrystalization from $CHCl_3$ was used for further purification.

Preparation of deep eutectic solvent

The general route for the synthesis of the ionic liquid was as follow: choline chloride (100 mmol) was mixed with urea (200 mmol) and heated to ca. 100 °C in air with stirring until a clear colorless liquid was obtained.

Entry 1: (2Z,5Z)-5-benzylidene-3-phenyl-2-(phenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.00$–7.94 (m, 15H), 8.13 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 121.1$, 121.2, 124.9, 128.1, 129.0, 129.1, 129.3, 129.4, 129.9, 130.0, 131.6, 133.6, 134.6 (CH=C), 148.1, 151.2 (C=N), 166.4 (C=O); IR (KBr, cm^{-1}): 1,639 (C=N), 1,712 (C=O), Anal. Calcd for $C_{22}H_{16}N_2OS$: C, 74.13; H, 4.52; N, 7.86; S, 9.00. Found: C, 74.41; H, 4.61; N, 7.98; S, 9.21.

Entry 2: (2Z,5Z)-5-(4-chlorobenzylidene)-3-phenyl-2-(phenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.98$–7.60 (m, 14H), 7.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 121.0$, 121.9, 125.0, 128.0, 129.0, 129.3, 129.4, 130.1, 131.1, 131.3, 132.1,134.5 (CH=C), 135.9, 147.9, 150.7 (C=N), 166.2 (C=O); IR (KBr, cm^{-1}): 1,650 (C=N), 1,716 (C=O), Anal. Calcd for $C_{22}H_{15}N_2OSCl$: C, 67.70; H, 3.87; N, 7.17; S, 8.20. Found: C, 67.86; H, 3.97; N, 7.01; S, 8.41.

Entry 3: (2Z,5Z)-5-(4-methoxybenzylidene)-3-phenyl-2-(phenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.85$ (s, 3H), 6.96–7.56 (m, 14H), 7.85 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.4$, 114.6, 118.3, 121.2, 124.8, 126.4, 128.1, 128.3, 128.9, 129.3, 131.4, 132.0, 134.9, 148.4, 151.3, 161.0, 166.6; IR (KBr, cm^{-1}): 1,640 (C=N), 1,710 (C=O), Anal. Calcd for $C_{23}H_{18}N_2O_2S$: C, 71.48; H, 4.69; N, 7.25; S, 8.30. Found: C, 71.27; H, 4.60; N, 7.30; S, 8.37.

Entry 4: (2Z,5Z)-5-(2-hydroxybenzylidene)-3-phenyl-2-(phenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 6.72$–7.41 (m, 14H), 8.11 (s, 1H), 9.45 (1H, brs, OH); IR (KBr, cm^{-1}): 1,691 (C=N), 1,714 (C=O), 3,260 (OH), Anal. Calcd for $C_{22}H_{16}N_2O_2S$: C, 70.95; H, 4.33; N, 7.52; S, 8.61. Found: C, 70.72; H, 4.55; N, 7.61; S, 8.49.

Entry 5: (2Z,5Z)-5-(4-hydroxybenzylidene)-3-phenyl-2-(phenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 6.88$–7.58 (m, 14H), 7.72 (s, 1H), 10.26 (s, 1H, OH); ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 117.1$, 121.2, 124.7, 125.1, 129.0, 129.5, 129.9, 131.4, 132.6, 135.5, 148.5, 151.1, 160.0, 166.3 (C=O), Anal. Calcd for $C_{22}H_{16}N_2O_2S$: C, 70.95; H, 4.33; N, 7.52; S, 8.61. Found: C, 80.10; H, 4.21; N, 7.47; S, 8.75.

Entry 6: (2Z,5Z)-5-(4-chlorobenzylidene)-3-(4-chlorophenyl)-2-(4-chlorophenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.91$–7.55 (m, 12H), 7.80 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 121.1$, 122.4, 129.3, 129.4, 129.5, 129.6, 130.5, 130.8, 131.2, 131.8, 132.7, 135.0 (CH=C), 136.2, 146.3, 151.0 (C=N), 165.9 (C=O); IR (KBr, cm^{-1}): 1,652 (C=N), 1,715 (C=O), Anal. Calcd for $C_{22}H_{13}N_2OSCl_3$: C, 57.47; H, 2.85; N, 6.09; S, 6.97. Found: C, 57.19; H, 2.99; N, 6.15; S, 6.84.

Entry 7: (2Z,5Z)-5-(2,6-di-chlorobenzylidene)-3-(4-chlorophenyl)-2-(4-chlorophenylimino) thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.85$–7.56 (m, 11H), 7.82 (s, 1H); IR (KBr, cm^{-1}): 1,633 (C=N), 1,712 (C=O), Anal. Calcd for $C_{22}H_{12}N_2OSCl_4$: C, 53.47; H, 2.45; N, 5.67; S, 6.49. Found: C, 53.69; H, 2.30; N, 5.51; S, 6.51.

Entry 8: (2Z,5Z)-5-(4-chlorobenzylidene)-3-(4-ethylphenyl)-2-(4-ethylphenylimino) thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ (t, 6H, $J = 7.2$ Hz), 2.73 (q, 4H, $J = 9.5$ Hz), 6.92–7.48 (m, 12H), 7.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.3$, 28.3, 120.9, 121.7, 122.2, 127.0, 127.7, 128.6, 128.8, 129.0, 129.3,129.6, 129.7, 131.1, 131.4, 131.7, 132.2, 132.8, 135.7, 136.7, 140.9, 145.0, 145.6, 150.3 (C=N), 166.4 (C=O); IR (KBr, cm^{-1}): 1,645 (C=N), 1,705 (C=O), Anal. Calcd for $C_{26}H_{23}N_2OSCl$: C, 69.86; H, 5.19; N, 6.27; S, 7.17. Found: C, 69.6; H, 5.34; N, 6.46; S, 6.91.

Entry 9: (2Z,5Z)-5-(3-nitrobenzylidene)-3-(4-butylphenyl)-2-(4-butylphenylimino) thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.97$ (t, 6H, $J = 6.9$ Hz), 1.35–1.45 (m, 4H), 1.58–1.68 (m, 4H), 2.61–2.71 (m, 4H), 6.89–8.23 (m, 12H), 8.33 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.0$, 22.4, 22.5, 33.3, 33.6, 35.1, 35.4, 120.7, 123.8, 124.6, 125.2, 127.6, 127.9, 129.3, 129.4, 130.1, 131.9, 134.7, 135.5, 139.9, 143.9, 145.4, 148.6, 149.3, 166.0 (C=O); IR (KBr, cm^{-1}): 1,643 (C=N), 1,718 (C=O), Anal. Calcd for $C_{30}H_{31}N_3O_3S$: C, 70.15; H, 6.08; N, 8.18; S, 6.24. Found: C, 69.90; H, 6.25; N, 8.01; S, 6.11.

Entry 10: (2Z,5Z)-5-(1H-indole-3-yl)methylene)-3-(4-butylphenyl)-2-(4-butylphenylimino) thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.93$ (t, 6H, $J = 7.7$ Hz), 1.28–1.45 (m, 4H), 1.57–1.68 (m, 4H), 2.61–2.66 (m, 4H), 6.94–7.85 (m, 13H), 8.18 (s, 1H), 8.91 (1H, brs, NH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.9$, 14.0, 22.3, 22.4, 33.2, 33.6, 35.1, 35.4, 111.6, 112.4, 115.8, 118.7, 121.0, 121.4, 123.2, 123.6, 126.5, 127.0, 127.7, 129.1, 129.2, 132.5, 135.7, 139.3, 143.6, 146.2, 151.3, 166.8; IR (KBr, cm^{-1}): 1,637 (C=N), 1,689 (C=O), 3,263 (NH), Anal. Calcd for $C_{32}H_{33}N_3OS$: C, 75.70; H, 6.55; N, 8.28; S, 6.32. Found: C, 75.94; H, 6.39; N, 8.34; S, 6.49.

Entry 11: (2Z,5Z)-5-(4-chlorobenzylidene)-3-(2,3-dimethylphenyl)-2-(2,3-dimethylphenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.06$ (s, 3H), 2.23 (s, 3H), 2.31 (s, 3H), 2.40 (s, 3H), 6.74–7.41 (m, 10H), 7.80 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.9$, 14.4, 20.3, 20.5, 117.9, 122.1, 125.9, 126.0, 126.7, 126.8, 128.3, 129.3, 130.0, 131.3, 131.4, 132.1, 133.8, 134.7 (CH=C), 135.8, 137.9, 138.6, 146.5, 150.2 (C=N), 166.2 (C=O); IR (KBr, cm^{-1}): 1,649 (C=N), 1,720 (C=O), Anal. Calcd for $C_{26}H_{23}N_2OSCl$: C, 69.86; H, 5.19; N, 6.27; S, 7.17. Found: C, 70.05; H, 5.01; N, 6.22; S, 7.34.

Entry 12: (2Z,5Z)-5-(2-hydroxybenzylidene)-3-(2,3-dimethylphenyl)-2-(2,3-dimethylphenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.96$ (s, 3H), 2.11 (s, 3H), 2.22 (s, 3H), 2.33 (s, 3H), 6.67–7.28 (m, 10H), 8.03 (s, 1H), 10.49 (1H, brs, OH); ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 13.9$, 14.4, 20.3, 20.5, 116.4, 117.9, 120.1, 120.3, 120.7, 126.3, 126.4, 126.6, 126.7, 127.0, 127.8, 128.8, 131.0, 132.3, 134.8 (CH=C),135.0, 137.9, 138.3, 147.0, 150.2 (C=N), 157.3, 166.1 (C=O); IR (KBr, cm^{-1}): 1,646 (C=N), 1,715 (C=O), 3,221 (brs, OH), Anal. Calcd for $C_{26}H_{24}N_2O_2S$: C, 72.87; H, 5.64; N, 6.54; S, 7.48. Found: C, 72.70; H, 5.50; N, 6.69; S, 7.42.

Entry 13: (2Z,5Z)-5-(2,4-dihydroxybenzylidene)-3-(2,3-dimethylphenyl)-2-(2,3-dimethylphenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, DMSO): $\delta = 1.91$ (s, 3H), 2.08 (s, 3H), 2.20 (s, 3H), 2.23 (s, 3H), 6.41–7.29 (m, 9H), 7.98 (s, 1H), 10.20 (brs, OH), 10.43(brs, OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.8$, 14.3, 19.0, 20.3, 117.8, 126.1, 126.2, 126.6, 126.9, 127.5, 130.7,135.0, 135.1, 137.7, 138.2, 147.1, 155.1, 171.9 (C=O); IR (KBr, cm^{-1}): 1,691 (C=N), 1,712 (C=O), 3,381 (OH), Anal. Calcd for $C_{26}H_{24}N_2O_3S$: C, 70.25; H, 5.44; N, 6.30; S, 7.21. Found: C; 70.48; H, 5.59; N, 6.39; S, 7.02.

Entry 14: (2Z,5Z)-5-benzylidene-3-(2,4,6-trimethylphenyl)-2-(2,4,6-trimethylphenylimino) thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.97$ (s, 6H), 2.12 (s, 6H), 2.30 (s, 3H), 2.45 (s, 3H), 6.82–7.63 (m, 9H), 7.90 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.7$, 18.3, 20.9, 21.3, 121.3, 128.1, 128.4, 129.0, 129.1, 129.7, 129.9, 130.1, 131.5, 133.6, 133.9, 135.8 (CH=C), 139.6, 143.3, 151.0 (C=N), 166.1 (C=O); IR (KBr, cm^{-1}): 1,645 (C=N), 1,720 (C=O), Anal. Calcd for

$C_{28}H_{28}N_2OS$: C, 76.33; H, 6.41; N, 6.36; S, 7.28. Found: C, 76.05; H, 6.52; N, 6.27; S, 7.35.

Entry 15: (2Z,5Z)-5-(2-hydroxybenzylidene)-3-(2,4,6-trimethylphenyl)-2-(2,4,6-trimethylphenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 2.00$ (s, 6H), 2.17 (s, 6H), 2.31 (s, 3H), 2.50 (s, 3H), 6.83–7.29 (m, 8H), 10.51 (s, 1H, OH); ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 17.6$, 18.1, 20.8, 21.0, 116.5, 119.7, 120.1, 133.5, 136.0, 139.1, 143.5, 150.2, 157.4 (C=N), 165.7 (C=O); IR (KBr, cm^{-1}): 1,639 (C=N), 1,718 (C=O), 3,186 (brs, OH); MS(*m/z*, %) : 456(M+), 278,160, Anal. Calcd for $C_{28}H_{28}N_2O_2S$: C, 73.65; H, 6.18; N, 6.14; S, 7.02. Found: C, 73.39; H, 6.28; N, 6.38; S, 6.88.

Entry 16: (2Z,5Z)-5-(4-methylbenzylidene)-3-(2,4,6-trimethylphenyl)-2-(2,4,6-trimethylphenylimino)thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.05$ (s, 6H), 2.23 (s, 12H), 2.38 (s, 3H), 6.76–7.40 (m, 8H), 7.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$); $\delta = 17.7$, 18.3, 20.9, 21.3, 21.5, 119.9, 128.3, 129.0, 129.7, 129.8, 130.2, 130.7, 131.8, 134.0, 135.8, 139.6, 140.6, 143.0, 166.1 (C=O); IR (KBr, cm^{-1}) 1,641 (C=N), 1,712 (C=O), Anal. Calcd for $C_{29}H_{30}N_2OS$: C, 76.61; H, 6.65; N, 6.16; S, 7.05. Found: C, 76.87; H, 6.74; N, 6.01; S, 7.18.

Entry 17: (2Z,5Z)-5-(4-methoxybenzylidene)-3-(2,4,6-trimethylphenyl)-2-(2,4,6-trimethylphenylimino) thiazolidin-4-one ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.16$ (s, 6H), 2.30 (s, 9H), 2.35 (s, 3H), 3.85 (s, 3H, OCH_3), 6.88–7.45 (m, 8H), 7.82 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.8$, 18.3, 21.0, 55.4, 114.6, 118.5, 126.3, 128.1, 129.0, 129.7, 130.6, 131.2, 132.1, 133.7, 135.9 (CH=C), 139.5, 143.8, 150.8, 160.9, 166.3 (C=O); IR (KBr, cm^{-1}) 1,639 (C=N), 1,705 (C=O), MS (*m/z*, %): 470 (M+), 278 (100), 202, Anal. Calcd for $C_{29}H_{30}N_2O_2S$: C, 74.01; H, 6.43; N, 5.95; S, 6.81. Found: C, 73.75; H, 6.51; N, 5.70; S, 6.98.

Conclusion

In summary, we have developed a mild and rapid procedure for green synthesis of various 4-thiazolidinones in good to excellent yields in natural deep eutectic solvent as a catalyst and reaction media. The reaction was carried out via a one-pot reaction of reactants in a green solvent followed by simple purification.

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