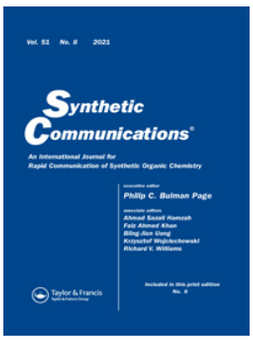

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Dimethylurea/L-tartaric acid as deep eutectic solvent for one-pot synthesis of 2-(methylamino)-3-nitrospiro-[chromene] and *N*-methyl-3-nitro-4*H* chromen-2-amines

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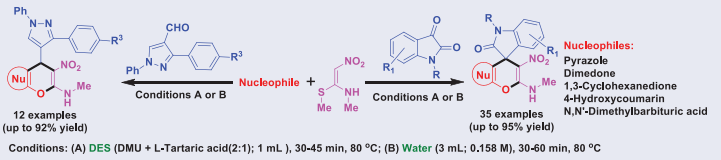
ABSTRACT

An application of dimethyl urea and L-tartaric acid as deep eutectic solvent (DES) is demonstrated for the synthesis of 2-(methylamino)-3-nitrospiro[chromene] and *N*-methyl-3-nitro-4*H*-chromen-2-amines by a reaction of substituted isatins/pyrazole aldehydes, nucleophiles and (E)-N-methyl-1-(methylthio)-2-nitroethenamine. Systematic studies proved that the dimethyl urea and L-tartaric acid in 2:1 ratio at 80 °C is suitable to give the desired products in good yields in shorter period of reaction time (45 min). This method was extended for water as reaction medium and good yields of the products was obtained in 1 h.

GRAPHICAL ABSTRACT



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KEYWORDS
Chromenes; catalyst-free; deep eutectic solvent (DES); spirooxindoles; water

Introduction

The development of environmentally benign methods is the need of the hour. Over the years, many non-conventional reaction media like the use of water,[1a] glycerol,[1b] ionic liquids,[1c] perfluorinated,[1d] supercritical fluids[1e] and deep eutectic solvents (DES) have been developed. Among these, DES (popularly known as twenty-first century solvents) are gaining attention recently in biocatalysis,[2a] separation technology,[2b,c] electrochemistry[2d,e] and organic synthesis (cross-coupling,[2f] multicomponent, condensation and Michael addition reactions).[2g,h,i,j] DES are proven to be relatively cheaper, nontoxic and biodegradable[2a,b] compared to ionic liquids. DES are obtained by mixing two or three safe hydrogen bond donors and hydrogen-bond acceptors as biodegradable components (from the natural source) in different ratios at room temperature or by heating (below 100 °C).[2]

Though many organic compounds are insoluble in water, the natural abundance, nontoxic, and non-flammable properties make water as a preferred reaction

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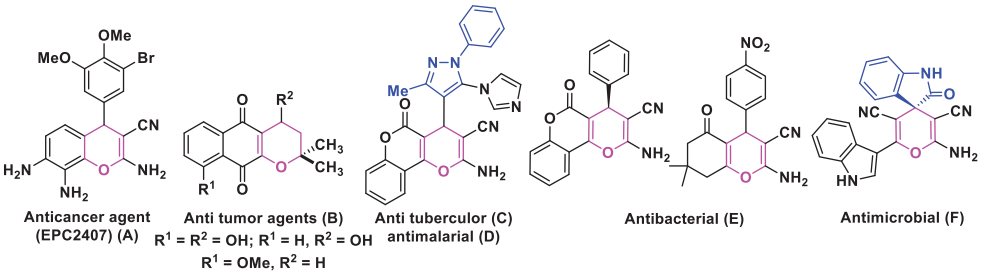


Figure 1. Biologically active chromene and spirochromene heterocyclic compounds.

medium.[3–6], it is the first priority solvent because of the development of "on-water" and "in-water" concepts in which the formation of aggregates *via* hydrophobic interactions with organic molecules is the key for the formation of product in organic transformation.[5,7]

The chromenes and spirochromenes are well-known scaffolds in medicinal chemistry. Chromene derivatives (A and B) show anticancer properties[8,9] and C–F are reported for their antimicrobial,[10] anti-tubercular, antimalarial,[11] antibacterial,[12] anti-apoptotic (Bcl-2 proteins),[13] anti-fungal,[14] anti-rheumatic,[15] anti-hyperglycemic and α-glucosidase inhibitory activities.[16] Some of these compounds play a key role in the central nervous system, possess excellent binding capacity toward many receptors in the biological systems and are used as cosmetics, pigments and biodegradable agrochemicals[17a] (Fig. 1). The chromene and spirochromenes are synthesized in many conditions including magnetic graphitic carbon nitride as heterogeneous catalyst,[17b] urea and choline chloride as deep eutectic solvent.[17c]

Nitroolefin *N,S* acetals (NMSM)[18a] have been found as interesting building blocks used for the synthesis of five- and six-membered heterocyclic compounds. NMSM possesses unique structural features of having electrophilic and nucleophilic vicinal carbons because of the presence of alkylamino (electron donating) and nitro group (electron withdrawing) on an olefinic system.[18b] There have been reports on the synthesis of chromenes using NMSM with aldehydes and different nucleophiles. The methods are known so far include solvent and catalyst-free conditions at 110 °C,[18c] 6,6′-thiobis(-methylene)-β-cyclodextrin dimer,[18d] and poly(-oligo ethylene glycol methacrylate)-*g*-supported coated double hydroxides (LDHs-*g*-POEGMA)[18e] as reusable promoters, silica-supported tungstic acid (STA) as a heterogeneous catalyst,[18f] microwave irradiation in the presence of NH_4OAc,[18g] $ZnCl_2$, and $InCl_3$ as acid catalysts,[18h–18i] H_2O and triethylamine in ethanol,[18j–18k] However, only two methods have been reported for the synthesis of spirochromenes so far. One of them is $InCl_3$-mediated reaction of NMSM, isatin and pyrazolone as nucleophile by Perumal and coworkers[19a] and the second report is by the Saigal group in EtOH reflux conditions (i.e., the reaction of cyclic-1,3-dinucleophiles, isatin and NMSM)[19b] (Fig. 2). Though these reports are good methods for the generation of complex spiro compounds from NMSM, the reaction times are relatively high. Considering this, and in continuation with our efforts of developing synthetic methods under homogeneous conditions,[20a,b] we applied our reported condition (L-Proline and Melamine; 3:1 in DMSO, RT) for this reaction but the attempts were futile even at 80 °C (Scheme 1). In addition, as mentioned in the introduction part,

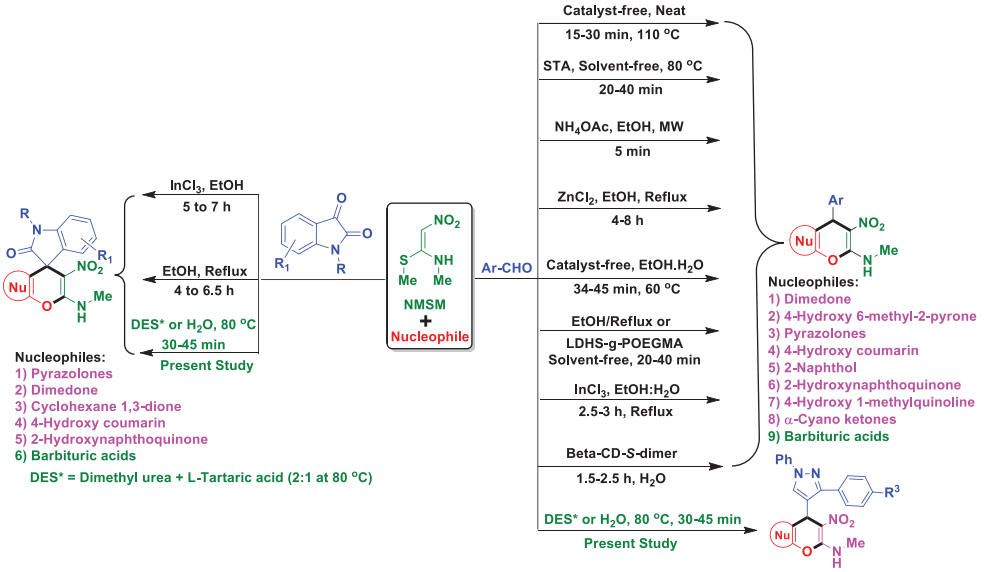
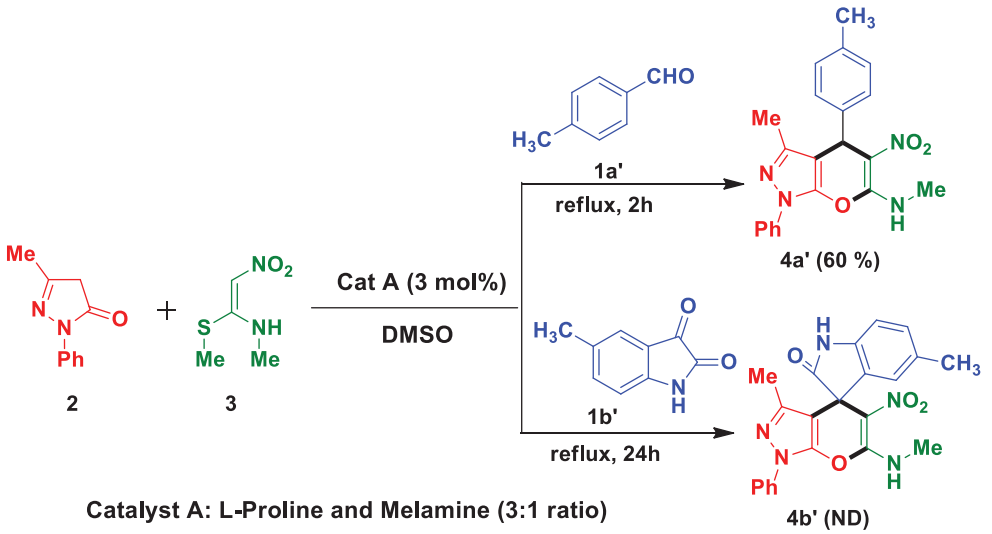


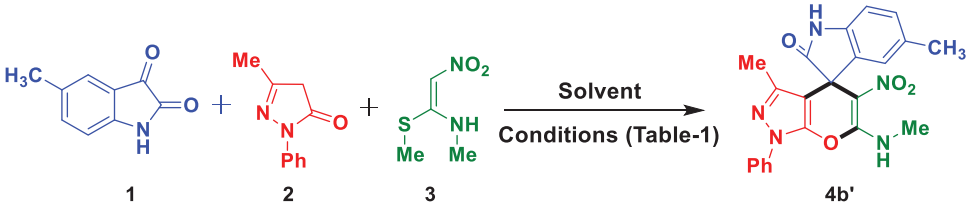
Figure 2. Closely related literature methods for the synthesis of chromene and spirochromenes and present study.[19]



Scheme 1. One-pot three-component synthesis of chromene and spirochromenes.

the DES are finding a lot of applications in organic synthesis and have been used for multicomponent reactions. However, to the best of our knowledge, there is no report so far on the use of DES for the generation of spiro compounds using NMSM as starting material. In this context, herein we wish to report a new method for the construction of chromene and spirochromene/spirooxindole derivatives using deep eutectic solvent (DES)/water as green reaction medium in short reaction times (both methods) with excellent yields.

Table 1. Optimization of the reaction conditions for the synthesis of compound **4b'**.



1 2 3 4b'

Entry	Solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	DMSO [L-proline and melamine (3:1)]	rt	24	ND
2	DMSO [L-proline and melamine (3:1)]	80	24	ND
3	EtOH	50	6	50
4	MeOH	80	6	Trace
5	EtOH	80	6	70
6	Urea + ChCl (1:1)	80	1	ND
7	Urea + ChCl (2:1)	80	1	ND
8	Urea + $ZnCl_2$ (2:1)	80	1	trace
9	DMU + $ZnCl_2$ (1:1)	80	1	20
10	DMU + $ZnCl_2$ (2:1)	80	1	55
11	DMU + $ZnCl_2$ (3:1)	80	1	40
12	DMU + ChCl (1:1)	80	1	70
13	DMU + ChCl (2:1)	80	1	60
14	DMU + ChCl (3:1)	80	1	50
15	$SnCl_2$ + ChCl (1:1)	80	1	50
16	$SnCl_2$ + ChCl (2:1)	80	1	80
17	$SnCl_2$ + ChCl (3:1)	80	1	70
18	Ethylene glycol + ChCl (2:1)	80	1	80
19	$ZnCl_2$ + ChCl (2:1)	80	1	25
20	L-tartaric acid + ChCl (2:1)	80	1	50
21	Proline + Oxalic acid (1:1)	80	1	30
22	Proline + L-tartaric acid (1:1)	80	1	70
23	DMU + Oxalic acid (1:1)	80	1	50
24	DMU + Oxalic acid (2:1)	80	1	60
25	DMU + Oxalic acid (3:1)	80	1	55
26	DMU + Citric acid (1:1)	80	0.5	75
27	DMU + Citric acid (2:1)	80	0.5	85
28	DMU + Citric acid (3:1)	80	0.5	80
29	DMU + L-tartaric acid (1:1)	80	0.5	80
30	DMU + L-tartaric acid (2:1)	80	0.5	90
31	DMU + L-tartaric acid (3:1)	80	0.5	85
32	H_2O (3 mL; 0.158 M)	80	1	95

All the reactions were performed with 0.475 mmol of isatin.
[a]Isolated yields.

Results and discussion

Owing to the biological importance of chromene and spirochromenes and in our continuous interest in sustainable organic transformations, we planned for the synthesis of chromene and spirochromenes using (E)-N-methyl-1-(methylthio)-2-nitroethenamine. Initially, a model reaction of aldehyde (**1a'**), pyrazole (**2**) and (E)-N-methyl-1-(methylthio)-2-nitroethenamine (**3**) in presence of L-proline and melamine (3:1 ratio) as catalyst in DMSO at room temperature[20b] could not afford the final product but the same reaction under heating conditions (80 °C) gave **4a'** in 60% yield in 2 h. After confirmation of the product, similar conditions were applied for isatin (**1b**') but the desired product (**4b**') was not formed even after prolonged reaction time (24 h) (Scheme 1). Then the above reaction was carried out in Ethanol under catalyst-free condition (50 °C

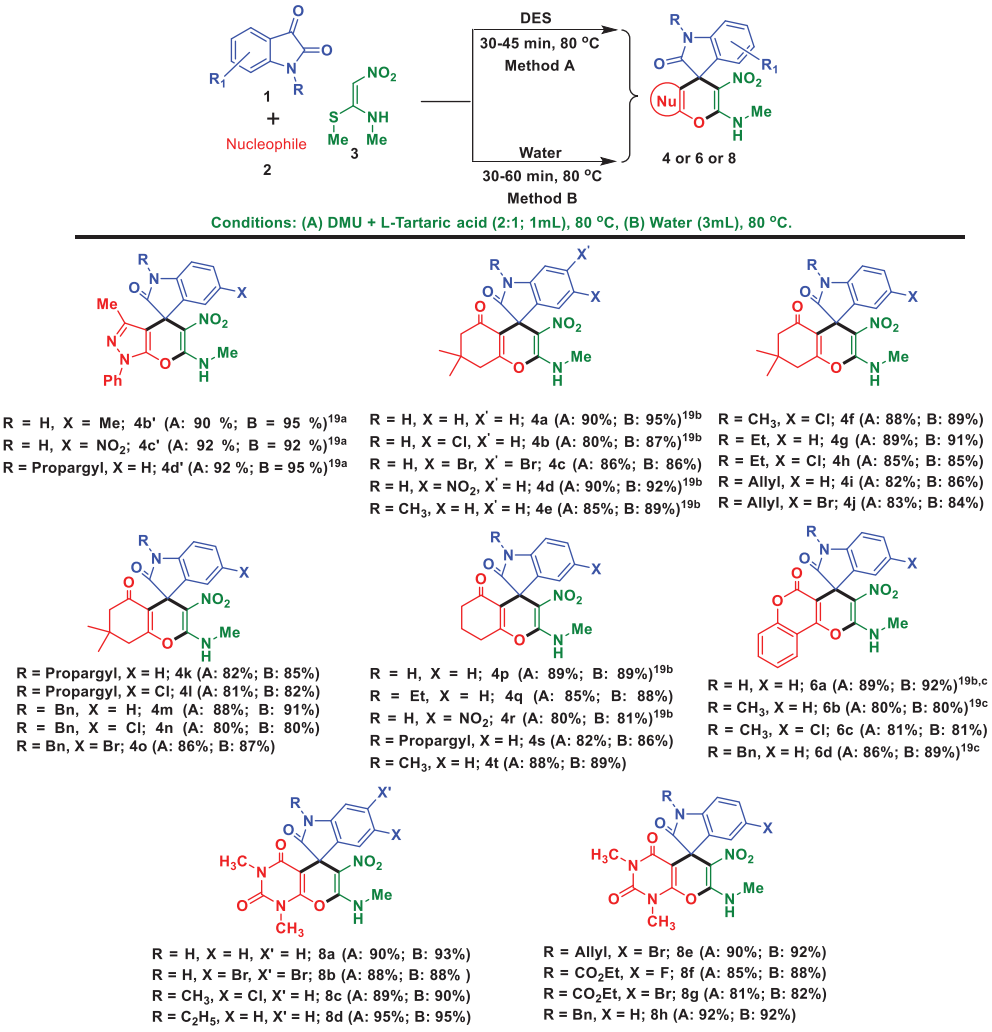


Figure 3. Various spirochromene derivatives (**4**–**8**) under optimized reaction conditions.

in 6 h)[19b] leading to the formation of the product **4b'** in 50% yield (Table–1; entry-**3**). The formation of the desired product was confirmed by ^{1}H, ^{13}C NMR and mass spectral data.

After confirmation of the product, the next task was to optimize the reaction conditions. Thus, the reaction was carried out in methanol and ethanol at 80 °C without catalyst (Table–1, entries **4**–**5**) in which EtOH could give the desired product **4b'** in 70% yield in 6 h. Toward finding the best reaction conditions (time and yield), we choose deep eutectic solvent as a reaction medium. Accordingly, the above reaction was performed using urea-choline chloride and urea-$ZnCl_2$ as deep eutectic solvent (Table–1, entries **6**–**8**). However, both the conditions fail to give the desired product (**4b'**). Then, efforts were continued using different combinations of DES [DMU + $ZnCl_2$, DMU + ChCl, $SnCl_2$ + ChCl, Ethylene glycol + ChCl, $ZnCl_2$ + ChCl, L-tartaric acid + ChCl, Proline + Oxalic acid and Proline + L-tartaric acid] in different ratio (Table–1, entries **9**–**22**), which afford desired product in 20-80% yields in 60 min at

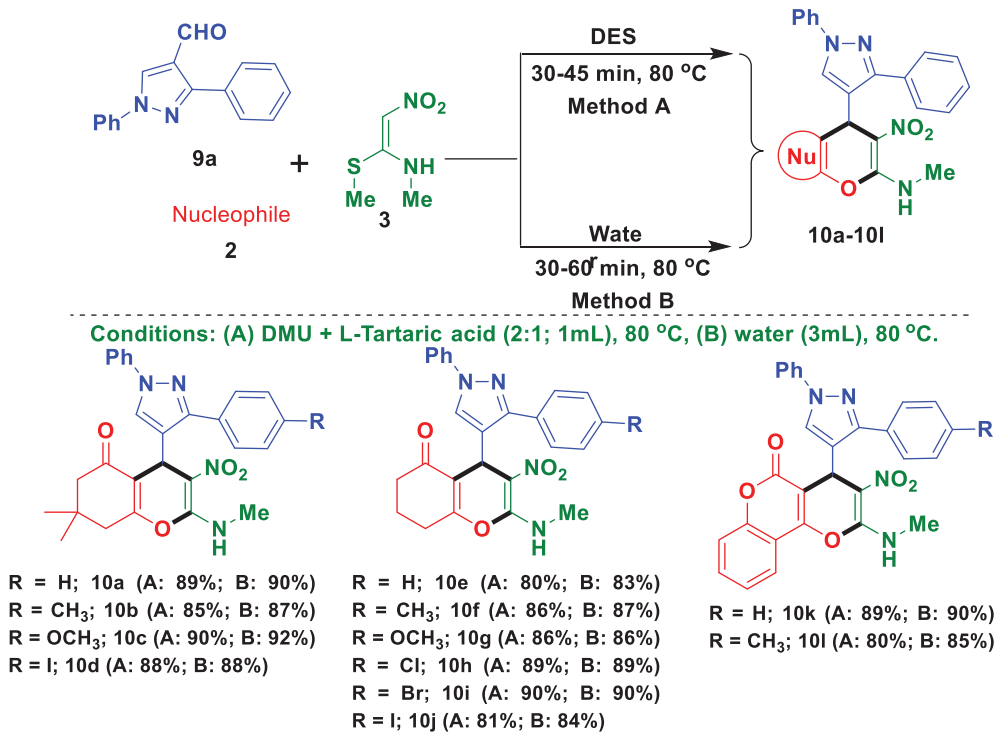


Figure 4. Synthesis of chromene derivatives (**10a–l**) under optimized condition.

80 °C. Following these results, changing the reaction medium to dimethyl urea + oxalic acid, dimethyl urea + citric acid and dimethyl urea + L-tartaric acid in different combinations gave product **4b'** in good yields in 30 min at 80 °C (Table–1, entries **23–31**). Among the screened combinations, dimethyl urea + L-tartaric acid (2:1) was found to be superior in terms of product yield (90%) and reaction time (30 min) at 80 °C. To explore further to find a green method, the same experiment was performed using water as solvent at 80 °C. To our delight, the product **4b'** was obtained in 95% in 1 h (Table–1; entry-32).

With the optimization condition in hand, protocol was explored for structurally different isatins (substitution on the aromatic ring and nitrogen), nucleophiles (pyrazole, dimedone, 1,3-cyclohexanedione, 4-hydroxy coumarin and N,N′-dimethyl barbituric acid) and (E)-N-methyl-1-(methylthio)-2-nitroethenamine under both conditions (both in DES and water) to a library of spirochromene hybrids with good yields as shown in Figure 3. The structures of all the obtained products were confirmed by NMR and mass spectra (for detail See ESI). Keeping in view of the biological activity of pyrazole-chromene hybrids C, D (in Fig. 1), we extended this method for the synthesis of different chromene hybrids with pyrazole moiety. Thus, the reaction of pyrazole aldehyde (**9a**; prepared *via* literature methods) dimedone (**2**), and (E)-N-methyl-1-(methylthio)-2-nitroethenamine (**3**) under the optimized reaction conditions in DES and water (as reaction media) gave the products with excellent yields up to 92% (Figure 4) in shorter reaction times. Later, various nucleophiles (dimedone, 1,3-cyclohexanedione and

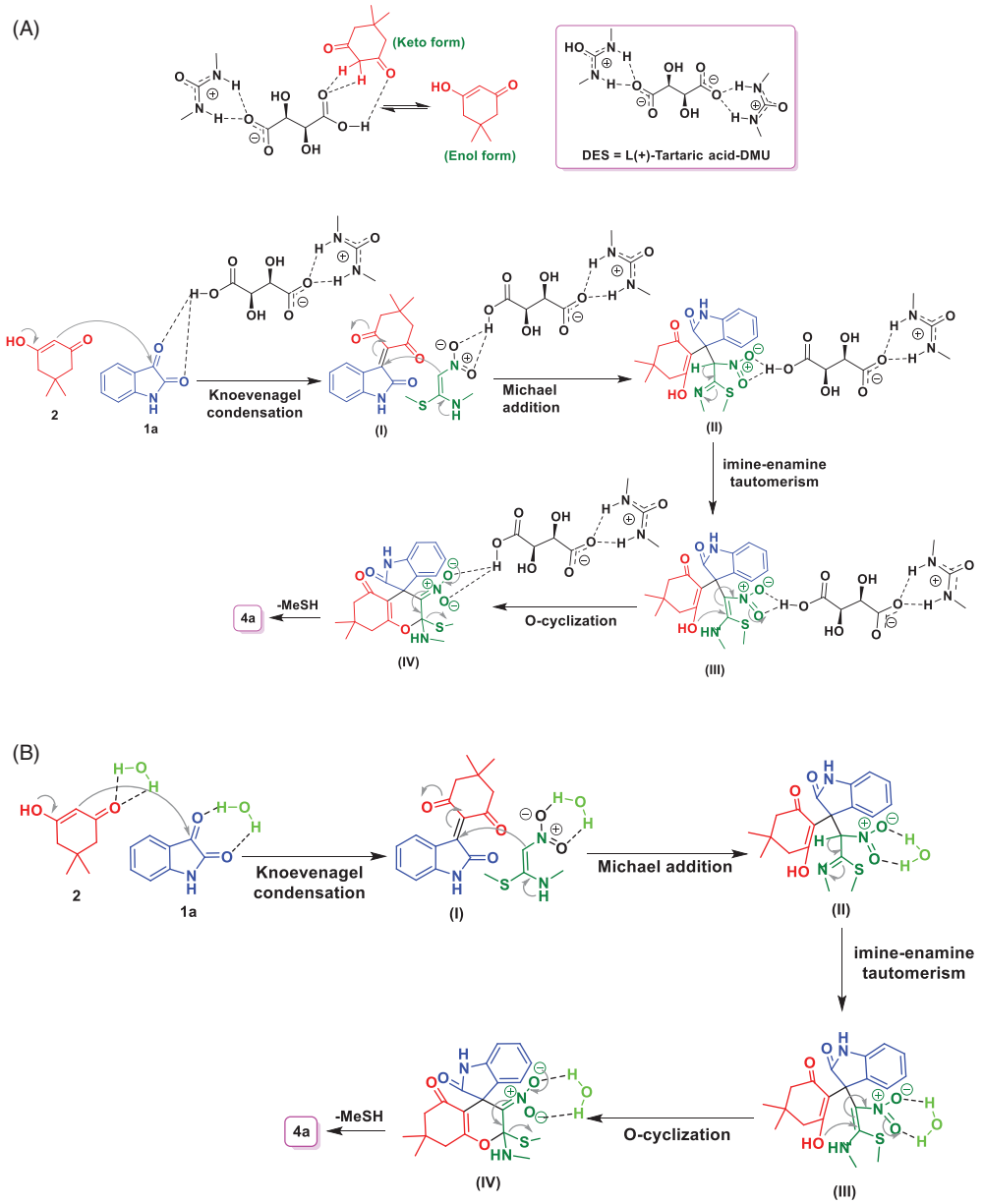


Figure 5. Plausible Mechanism for the reaction, (A) for DES and (B) for Water.

4-hydroxy coumarin) were treated with pyrazole aldehyde and (E)-N-methyl-1-(methylthio)-2-nitroethenamine under optimized conditions to generate functionalized pyrazole-chromene hybrids with excellent yields both in DES and water (catalyst-free conditions). All the products obtained were characterized using spectroscopic data.

Based on the experimental observations, we propose plausible mechanisms as shown in Figure 5A and B. The DES induces the keto-enol tautomerism in dimedone. The activated dimedone (Enol form) undergo Knoevenagel condensation with isatin (The both carbonyl groups are associated with DES *via* intermolecular hydrogen bonding)

afforded intermediate (**I**), which act as Michael acceptor, the adduct (**I**) immediately undergoes Michael type addition with (E)-N-methyl-1-(methylthio)-2-nitroethenamine to generate intermediate (**II**). Subsequent imine-enamine tautomerism of (**II**) afforded intermediate (**III**) followed by intramolecular O-cyclization to give the product (**4a**). The water-mediated reaction follow the on-water concept.[21] The water induces enolization in dimedone. Simultaneously, the isatin is activated and reacts with enolic form of dimedone to give the Knoevenagel product followed by the Michael addition, imine-enamine tautomerism and O-cyclization, as shown in Figure 5B.

Conclusion

In summary, we have developed a new efficient protocol for the synthesis of chromene and spirochromene derivatives using dimethylurea/L-tartaric acid as a deep eutectic solvent. The reaction proceeds *via* Knoevenagel condensation, Michael addition, imine-enamine tautomerism followed by *O*-cyclization. This procedure offers notable advantages such as catalyst-free, environmentally benign reaction conditions and good yields of the products.

Experimental section

General procedure for the one-pot synthesis of chromene and spirochromenes

Method-A

A mixture of isatin/pyrazole aldehyde (0.475 mmol, 1 eq), Nucleophile (0.475 mmol, 1 eq) and (E)-N-methyl-1-(methylthio)-2-nitroethenamine (0.475 mmol, 1 eq) was stirred at 80 °C in DMU + L-tartaric acid (2:1) (DES, 1 mL). The progress of the reaction was monitored by TLC. After this period, the mixture was treated with water and extracted with EtOAc (2 × 10 mL). The collected organic phases were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. Evaporation of the solvent gave the crude product, which was further recrystallized from ethanol to afford the pure product.

Method-B

A mixture of isatin/pyrazole aldehyde (0.475 mmol, 1 eq), Nucleophile (0.475 mmol, 1 eq) and (E)-N-methyl-1-(methylthio)-2-nitroethenamine (0.475 mmol, 1 eq) was stirred at 80 °C in water. The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled and filtered. Then, the precipitate was washed with cold water (2 × 5 mL) and the crude product was recrystallized from ethanol to afford the pure product.

7,7-Dimethyl-2-(methylamino)-3-nitro-7,8-dihydrospiro[chromene-4,3'-indoline]-2',5(6H)-dione (4a):. Yield = A: 90%; B: 95% (Light yellow solid); m.p.: 302–304 °C, ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 1H), 10.44 (s, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.2 Hz, 1H), 6.80 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 3.11 (d, J = 4.4 Hz, 3H), 2.65 (q, J = 48.8 Hz, 2H), 2.13 (q, J = 53.6, 2H), 1.02 (s, 3H), 0.95 (s, 3H). ^{13}C NMR

(101 MHz, DMSO-d_6): δ 196.02, 178.26, 163.06, 157.59, 144.24, 130.99, 128.84, 122.86, 122.11, 113.07, 109.40, 107.88, 50.81, 49.18, 39.95, 31.85, 28.74, 27.92, 26.87. Mass (ESI-MS): *m/z* Calculated: 369.13; Observed: 395.1140 (M + Na).

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