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Bicyclic 1,2,3-Triazolium ionic liquids as a novel ionic liquid based catalytic systems for the preparation of spirobenzo[f]pyrano[3, 2-c]chromene derivatives under ultrasonic irradiation conditions

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Original Research

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Abstract:

A novel ionic liquid, 2-butyl-4, 5, 6, 7-tetrahydro-2H-[1, 2, 3]triazolo[1, 5-a]pyridin-8-ium hydrogen sulfate, was synthesized and employed as an efficient catalyst in the high-yield synthesis of spiro compounds featuring the benzo[f]pyrano[3,2-c]chromene scaffold. Through a three-component reaction involving 1-hydroxy-3H-benzo[f]chromen-3-one, malononitrile, and 1-benzylindoline-2,3-dione in ethanol under reflux and ultrasonic irradiation, 10 distinct compounds were successfully obtained in excellent yields ranging from 86% to 97%. The products were characterized comprehensively by Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), and CHN analysis. Notably, the protocol offers an efficient, non-chromatographic method for separation and purification, ensuring high-yield productivity and operational simplicity, making it a highly advantageous approach for synthesizing spiro compounds.

Keywords: Benzo[f]pyrano[3,2-c]chromene; Catalyst; Ionic liquid; 1-hydroxy-3H-benzo[f]chromen-3-one; Spiro compounds

1. Introduction

As high-potential materials, ionic liquids serve as exceptional catalysts in organic synthesis, offering many advantages that have propelled them to the forefront of modern chemical methodologies. One key advantage lies in their tunable physicochemical properties, allowing for tailoring to specific reaction requirements. With negligible vapor pressure, ionic liquids create reaction environments with enhanced safety and reduced environmental impact. Their high thermal stability enables their application in a wide temperature range, accommodating diverse synthetic processes. Importantly, ionic liquids exhibit unique solvation properties, facilitating increased substrate accessibility and selectivity in catalyzed reactions. Their recyclability further underscores their sustainability, contributing to green chemistry practices. As versatile and efficient catalysts, ionic liquids continue to revolutionize organic synthesis, offering a sustainable and effective alternative in the pursuit of novel and efficient chemical transformations. Owning this interesting knowledge about ionic liquids, we wish to expand their application to multi-component reactions for the synthesis of pyran heterocycles [1–13].

On the other hand, spiro compounds, characterized by a fused-ring structure where two or more rings share a single common atom, exhibit a fascinating array of properties that make them intriguing subjects in various scientific domains. Their distinctive three-dimensional architecture imparts stability and often enhances bioactivity, making spiro compounds valuable in drug discovery and medicinal chemistry. The presence of a spiro center introduces chirality, contributing to their potential as versatile building blocks for asymmetric synthesis. Spiro compounds frequently display unique electronic properties, influencing their reactivity and

applications in materials science. Additionally, the spiro motif imparts rigidity to the molecular framework, influencing conformational preferences and enhancing the compound's overall structural diversity. These inherent properties position spiro compounds as versatile and valuable entities in the synthesis of diverse molecular architectures with applications ranging from pharmaceuticals to materials [12–17]. The synthesis of spiro compounds involves diverse methods, and the choice of a synthetic route depends on the specific spiro compound desired. Here are a few common synthetic routes: [2+2] cycloaddition reactions, Diels-Alder reactions, asymmetric cycloadditions, transition metal-catalyzed reactions, multicomponent reactions, and cascade reactions. It's important to note that the choice of synthetic route depends on factors such as the specific spiro compound targeted, the desired stereochemistry, and the availability of starting materials. The field of spiro compound synthesis continues to evolve with new methodologies and strategies [12–18].
On the other hand, the synthesis of pyrano [3, 2-c] chromene heterocycles involves various methods, and the route choice often depends on the desired substitution pattern and functional groups. One common approach utilizes a multicomponent reaction of 4-hydoxycoumarin, carbonyl compounds, and an active methylene. This multi-component reaction forms the pyran ring through condensation and cyclization steps. To date, different strategies have been reported for the synthesis of pyrano [3, 2-c] chromene derivatives using catalytic systems, including Fe_3O_4@SiO_2-propyl covalent dapsone-copper complex [18], L-arginine modified graphene oxide [19], tetramethylguanidine hydrochloride/sorbitol [20], SMPSMA@Fe_3O_4 [21], Zn_2SnO_4-SnO_2 nano-composite [22], MgO [23], and so-on.
In this scientific paper, we explore the synthesis and applications of ionic liquid **A2** for the synthesis of **1a-10a**. Our focus encompasses the innovative use of ionic liquids as reaction media in multi-component reactions, aiming to unveil new pathways and enhance the efficiency of diverse synthetic processes.

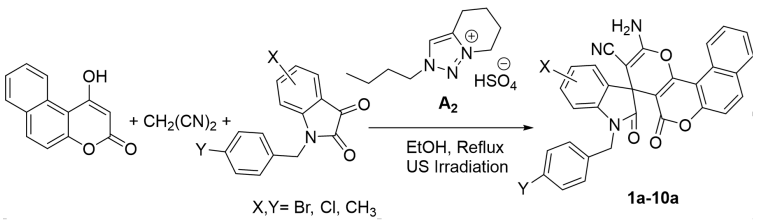
2. Experimental

2.1 Reagents and instrumentation

All materials, including reagents and solvents used for the reaction and purification steps, were purchased from commercial sellers. Instruments: Bruker Avance DPX 500 MHz instrument for NMR spectra (Recorded in deuterated dimethyl sulfoxide (DMSO-d6) as solvent), Heraeus CHN-O-Rapid analyzer for elemental analysis. The thin layer chromatography (TLC) was done on silica plates as the solid support using hexane/ethyl acetate (90/10) as the eluting solvent. TGA was done using TA (Q600) instrumentation. Infrared spectra were obtained using a Thermo (AVATAR) instrument and were recorded as KBr disks. Melting points were taken on an Electrothermal IA9100 melting point apparatus and are uncorrected. Ultrasonication was carried out using ultrasound cleaning bath KQ-250 DE apparatus with 40 kHz frequency and 250 W power.

2.2 Synthesis of ionic liquid (A2)

Note: The ionic liquid prepared here was synthesized following the reported literature with some modifications [24, 25].
First step: sodium azide (10 mmol) was mixed with 1-bromobutane (10 mmol) in CH_3CN as solvent (20 mL) and stirred at room temperature for 20 h. Next, 6-chlorohex-1-yne (10 mmol), triethylamine (6 mmol), and CuI (1 mmol) were added to the mixture and stirred again for 20 h at room temperature. Afterward, the reaction was concentrated under reduced pressure, and 1-butyl-4-(4-chlorobutyl)-1H-1, 2, 3-triazole (Scheme 2, **A1**) as a product of this step was purified using a plate chromatography technique (EtOAc/hexane: 15/85) (Isolated yield: 91%).
Second step: A1 (5 mmol) and KI (4 mmol) were mixed in CH_3CN (25 mL) and refluxed for 15 h. afterward, the mixture was filtered, and the solvent was evaporated and diluted in toluene (25 mL). After the addition of 5 mmol of H_2SO_4, the mixture was stirred at room temperature for 5 h. Finally, the mixture was concentrated under reduced pressure and extracted with CH_2Cl_2 (3 × 5 mL). The desired product **(A2)** was achieved after solvent evaporation in vacuo (Isolated yield according to 5 mmol of **A1**: 98%).
2-Butyl-4, 5, 6, 7-tetrahydro-2H- [1, 2, 3] triazolo [1, 5-a] pyridin-8-ium hydrogen sulfate (Scheme 2, A2): ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.02 (t, J = 5.7 Hz, 3H, CH_3,), 1.42-1.77 (m, 6H), 2.95-2.99 (m, 2H), 3.39 (t, J = 5.8 Hz, 2H), 4.59-4.69 (m, 4H), 8.89 (s, 1H), 10.53 (brs, 1H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 17.4, 19.6, 20.1, 20.3, 21.0, 27.2, 59.0, 59.7, 134.4, 151.8 ppm; CHNS elemental analysis found: C, 43.28; H, 6.87; N, 15.14; S, 11.58. FT-IR (KBr): 3613, 2933, 2892, 1714, 1650, 1351, 1235, 1187, 1036, 978, 928, 842, 798, 702 cm^{-1}. The pH value of ionic liquid in water (Concentration:1 mol/L) was determined as 1.58 by a pH meter (Horiba model F-52).
$BaSO_4$ test:
One mmol (0.277 g) of A2 was dissolved in 20 mL of water, and subsequently, a solution of $BaCl_2$ (1.5 mmol of $BaCl_2$ in 30 mL of water) was added to that slowly. The reaction was allowed to be stirred at room temperature. The wight



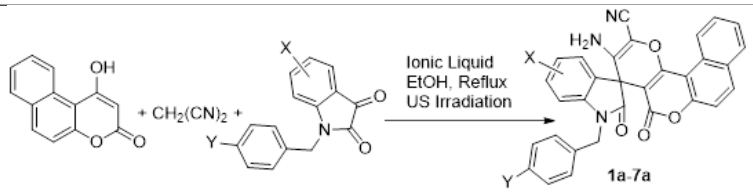
Scheme 1. Preparation of **1a-10a**.

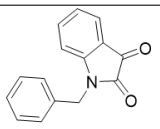
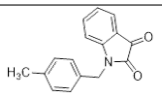
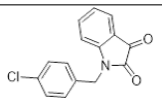
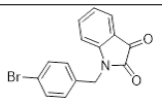
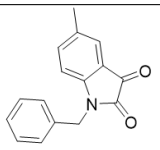
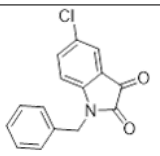
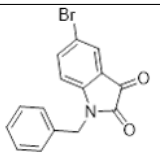
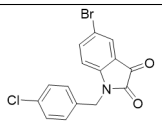
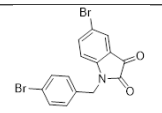
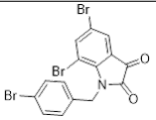
solid was filtered, washed with water and ethanol, dried, and accurately weighed ($BaSO_4$ Yield for fresh ionic liquid: 0.2321 g, ≥ 99; for recovered ionic liquid 0.2219 ≥ 95).

General procedure for the preparation of 1a-10a:

In a 100 mL balloon coupled with a condenser containing EtOH (20 mL), 1-hydroxy-3H-benzo [f] chromen-3-one (1 mmol), malononitrile (1 mmol), and 1-benzylindoline-2, 3-dione (1 mmol), ionic liquid (0.5 mmol) was added. The mixture was irradiated in the water bath of the ultrasonic cleaner at reflux condition for a period as indicated in Table 1. As the reactions were completed (monitored by TLC), the solvent was concentrated, and the crude product

Table 1. Preparation of **1a-7a**.



Product	Substrate	Time (h)	Yield (%)[a]
1a		2	87, 86, 85, 85, 84, 84, 83, 81, 80, 80, 79
2a		2.3	86
3a		1.8	91
4a		1.8	93
5a		2.5	94
6a		1.5	93
7a		1.5	95
8a		1.5	93
9a		1.4	94
10a		1.3	97

[a]Isolated yields. Yields for 10 times recovery in the synthesis of **1a**

was washed with ethanol to afford the pure product.

2-Amino-1'-benzyl-2', 5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline]-3-carbonitrile **(Table 1, Product 1a): Solid powder, M. p. :** 251-253 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.43 (d, J = 11.2 Hz, 1H), 4.49 (d, J = 11.2 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 7.21-7.25 (m, 3H), 7.31 (d, J = 7.8 Hz, 2H), 7.39-7.48 (m, 6H), 7.63 (d, J = 8.6 Hz, 1H), 7.69-7.74 (m, 2H), 7.93 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H) ppm; 13C-NMR (100 MHz, DMSO-d6): δ = 71.2, 91.7, 95.3, 101.2, 123.9, 126.2, 127.3, 127.6, 127.8, 128.2, 128.4, 128.6, 128.9, 129.1, 129.3, 129.6, 129.9, 130.6, 131.4, 132.2, 133.2, 134.9, 136.7, 138.7, 149.2, 153.5, 155.4, 166.7, 179.7 ppm; MASS (m/e): 520 (M++Na); Elemental analysis: Found: C, 74.81; H, 3.93; N, 8.42% $C_{31}H_{19}N_3O_4$; requires: C, 74.84; H, 3.85; N, 8.45%. FT-IR (KBr): 3534, 3528, 3079, 2956, 2297, 1742, 1678, 1625, 1529, 1495, 1389, 1179, 1103, 1069, 1015, 908, 863, 829, 781 cm^{-1}.

2-Amino-1'-(4-methylbenzyl)-2',5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline] -3-carbonitrile **(Table 1, Product 2a): Solid powder, M. p. :** 258-260 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.37 (s, 3H, CH_3), 4.42 (d, J = 11.0 Hz, 1H), 4.48 (d, J = 11.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.7 Hz, 2H), 7.38-7.48 (m, 6H), 7.62 (d, J = 8.3 Hz, 1H), 7.70-7.75 (m, 2H), 7.91 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 21.3, 70.1, 91.5, 95.8, 102.8, 124.2, 124.8, 126.3, 127.8, 128.3, 128.4, 128.7 128.8, 129.0, 129.3, 129.5, 129.8, 130.4, 131.4, 132.6, 133.2, 134.4, 136.5, 137.4, 138.2, 150.1, 153.7, 155.1, 168.7, 178.1 ppm; MASS (m/e): 534 (M++Na); Elemental analysis: Found: C, 75.19; H, 4.18; N, 8.24% $C_{32}H_{21}N_3O_4$; requires: C, 75.14; H, 4.14; N, 8.21%. FT-IR (KBr): 3534, 3512, 3073, 2931, 2300, 1745, 1678, 1623, 1594, 1488, 1362, 1282, 1148, 1101, 1063, 1017, 901, 903, 826, 786, 713 cm^{-1}.

2-Amino-1'-(4-chlorobenzyl)-2', 5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline] -3-carbonitrile (Table 1, Product 3a): Solid powder, M. p. : 263-265 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.56 (d, J = 11.6 Hz, 1H), 4.63 (d, J = 11.6 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.38-7.48 (m, 8H), 7.63 (d, J = 8.4 Hz, 1H), 7.71-7.76 (m, 2H), 7.93 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H) ppm; 13C-NMR (100 MHz, DMSO-d_6): δ = 73.2, 91.7, 95.9, 103.1, 124.7, 126.7, 127.5, 128.3, 128.6, 128.8, 128.9 129.1, 129.3, 129.4, 129.7, 130.1, 130.6, 131.5, 132.7, 133.2, 134.6, 136.7, 138.4, 144.7, 150.2, 153.7, 155.4, 168.9, 179.3 ppm; MASS (m/e): 554 (M++Na); Elemental analysis: Found: C, 70.07; H, 3.34; N, 7.83% $C_{31}H_{18}ClN_3O_4$; requires: C, 70.00; H, 3.41; N, 7.90%. FT-IR (KBr): 3568, 3517, 3056, 2905, 2301, 1749, 1676, 1619, 1594, 1508, 1373, 1289, 1217, 1179, 1068, 1025, 906, 827, 775, 702 cm^{-1}.

2-Amino-1'-(4-bromobenzyl)-2',5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline] -3-carbonitrile **(Table 1, Product 4a):** Solid powder, M. p. : 284-286 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.63 (d, J = 11.1 Hz, 1H), 4.69 (d, J = 11.1 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 7.37-7.48 (m, 8H), 7.58 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 8.2 Hz, 1H), 7.70-7.76 (m, 2H), 7.92 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 75.1, 92.0, 95.8, 103.4, 124.6, 126.8, 127.8, 128.6, 128.7, 128.8, 129.3, 129.5, 129.6, 129.8, 129.9, 130.3, 130.8, 131.4, 132.5, 133.4, 134.5, 136.8, 138.7, 146.4, 150.3, 153.4, 155.1, 168.1, 179.0 ppm; MASS (m/e): 599 (M++Na); Elemental analysis: Found: C, 64.57; H, 3.11; N, 7.21% $C_{31}H_{18}BrN_3O_4$; requires: C, 64.60; H, 3.15; N, 7.29%. FT-IR (KBr): 3561, 3553, 3053, 2276, 1746, 1689, 1658, 1604, 1531, 1496, 1366, 1164, 1066, 1024, 923, 874, 825, 780, 662 cm^{-1}.

2-Amino-1'-benzyl-5'-methyl-2', 5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3 '-indoline] -3-carbonitrile **(Table 1, Product 5a):** Solid powder, M. p. : 241-243 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 2.26 (s, 3H, CH_3), 4.44 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 11.6 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.09 (s, 1H), 7.21-7.26 (m, 3H), 7.29 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 8.6 Hz, 1H), 7.44-7.47 (m, 5H), 7.63 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.6 Hz, 1H) ppm; ^{13}C-NMR (100 MHz, DMSO-d6): δ = 21.6, 70.1, 91.2, 94.2, 103.2, 114.2, 117.4, 124.6, 125.1, 126.8, 127.8, 128.6, 129.1, 129.4, 129.6, 130.4, 131.4, 132.4, 133.0, 133.2, 136.8, 137.8, 138.6, 150.0, 153.2, 155.4, 168.0, 179.3 ppm; MASS (m/e): 534 (M++Na); Elemental analysis: Found: C, 75.07; H, 4.07; N, 8.11% $C_{32}H_{21}N_3O_4$; requires: C, 75.14; H, 4.14; N, 8.21%. FT-IR (KBr): 3558, 3510, 3074, 2949, 2297, 1744, 1667, 1604, 1525, 1496, 1366, 1271, 1164, 1064, 1056, 922, 874, 825, 780 cm^{-1}.

2-Amino-1'-benzyl-5'-chloro-2', 5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline]-3-carbonitrile **(Table 1, Product 6a):** Solid powder, M. p. : 279-281 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.46 (d, J = 11.3 Hz, 1H), 4.55 (d, J = 11.3 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 7.21-7.26 (m, 3H), 7.30 (d, J = 7.8 Hz, 2H), 7.40-7.48 (m, 5H), 7.53 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 8.29 (s, 1H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 70.7, 91.7, 94.6, 104.3, 126.8, 127.6, 127.8, 128.4, 129.1, 129.3, 129.4, 129.7, 129.8, 130.4, 130.6, 131.2, 131.4, 132.4, 133.4, 134.6, 135.2, 136.7, 138.7, 144.5, 151.2, 153.5, 155.7, 168.7, 179.9 ppm; MASS (m/e): 554 (M++Na); Elemental analysis: Found: C, 69.92; H, 3.36; N, 7.88% $C_{31}H_{18}ClN_3O_4$; requires: C, 70.00; H, 3.41; N, 7.90%. FT-IR (KBr): 3533, 3501, 3070, 2949, 2286, 1754, 1686, 1578, 1495, 1368, 1287, 1163, 1099, 1061, 1018, 929, 857, 805, 770, 763 cm^{-1}.

2-Amino-1'-benzyl-5'-bromo-2', 5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline] -3-carbonitrile **(Table 1, Product 7a)**: Solid powder, M. p. : 293-295 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.46 (d, J = 11.3 Hz, 1H), 4.55 (d, J = 11.3 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 7.21-7.26 (m, 3H), 7.30 (d, J = 7.8 Hz, 2H), 7.40-7.48 (m, 5H), 7.53 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 8.39 (s, 1H) ppm; 13C-NMR (100 MHz, DMSO-d_6): δ = 71.2, 91.8, 94.2, 104.5, 126.8, 127.7, 127.8, 128.2, 129.2, 129.3, 129.5, 129.8, 129.9, 130.3, 130.7, 131.4, 131.7, 132.3, 133.5, 134.7, 135.3, 136.5, 138.8, 146.6, 151.0, 153.4,

155.2, 168.3, 179.7 ppm; MASS (m/e): 599 (M++Na); Elemental analysis: Found: C, 64.53; H, 3.09; N, 7.24% $C_{31}H_{18}BrN_3O_4$; requires: C, 64.60; H, 3.15; N, 7.29%. FT-IR (KBr): 3536, 3503, 3072, 2285, 1741, 1656, 1604, 1581, 11485, 1369, 1284, 1169, 1094, 1063, 932, 845, 775, 687 cm^{-1}.

2-Amino-5'-bromo-1'-(4-chlorobenzyl)-2', 5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline] -3-carbonitrile **(Table 1, Product 8a):** Solid powder, M. p. : >300 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.63 (d, J = 11.6 Hz, ^{1}H), 4.74 (d, J = 11.6 Hz, 1H), 7.12 (d, J = 8.3 Hz, 1H), 7.31 (d, J = 7.8 Hz, 2H), 7.40-7.49 (m, 7H), 7.54 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H), 8.28 (s, 1H) ppm; 13C-NMR (100 MHz, DMSO-d_6): δ = 76.3, 92.1, 94.6, 104.8, 126.7, 127.8, 128.3, 128.6, 129.4, 129.7, 129.8, 130.2, 130.4, 130.9, 131.6, 131.7, 132.4, 133.5, 134.7, 135.3, 136.6, 138.8, 144.6, 146.8, 151.3, 153.7, 155.4, 168.7, 180.2 ppm; MASS (m/e): 633 (M++Na); Elemental analysis: Found: C, 60.88; H, 2.84; N, 6.92% $C_{31}H_{17}BrClN_3O_4$; requires: C, 60.95; H, 2.81; N, 6.88%. FT-IR (KBr): 3578, 3514, 3088, 2290, 1753, 1689, 1624, 1594, 1500, 1377, 1245, 1179, 1116, 1067, 1021, 916, 828, 779, 729, 693 cm^{-1}.

2-Amino-5'-bromo-1'-(4-bromobenzyl)-2', 5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline]-3-carbonitrile **(Table 1, Product 9a):** Solid powder, M. p. : >300 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.66 (d, J = 11.2 Hz, 1H), 4.77 (d, J = 11.2 Hz, 1H), 7.19 (d, J = 8.3 Hz, 1H), 7.39-7.49 (m, 7H), 7.58-7.61 (m, 3H), 7.64 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 8.37 (s, 1H) ppm; 13C-NMR (100 MHz, DMSO-d_6): δ = 78.1, 92.4, 94.8, 105.1, 126.6, 127.7, 128.3, 128.6, 129.5, 129.7, 130.2, 130.4, 130.8, 131.7, 131.9, 132.0, 132.4, 133.7, 134.7, 135.6, 136.6, 138.4, 146.6, 146.9, 151.2, 153.6, 155.2, 169.1, 180.4 ppm; MASS (m/e): 678 (M++Na); Elemental analysis: Found: C, 56.75; H, 2.66; N, 6.47% $C_{31}H_{17}Br_2N_3O_4$; requires: C, 56.82; H, 2.61; N, 6.41%. FT-IR (KBr): 3537, 3530, 3075, 2283, 1744, 1667, 1621, 1586, 1506, 1378, 1170, 1055, 1011, 9018, 804, 702 cm^{-1}.

2-Amino-5', 7'-dibromo-1'-(4-bromobenzyl)-2', 5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline] -3-carbonitrile **(Table 1, Product 10a):** Solid powder, M. p. : >300 ^{O}C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.65 (d, J = 11.3 Hz, 1H), 4.75 (d, J = 11.3 Hz, 1H), 7.39-7.49 (m, 7H), 7.59 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.69 (s, 1H), 7.74 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.43 (s, 1H) ppm; 13C-NMR (100 MHz, DMSO-d_6): δ = 78.8, 92.6, 94.6, 105.0, 126.5, 127.8, 128.3, 128.7, 129.7, 130.3, 130.8, 131.0, 131.7, 132.0, 132.3, 132.8, 133.9, 134.7, 135.7, 136.6, 138.5, 146.8, 146.9, 147.5, 151.3, 153.8, 155.4, 169.7, 180.6 ppm; MASS (m/e): 757 (M++Na); Elemental analysis: Found: C, 50.63; H, 2.16; N, 5.65% $C_{31}H_{16}Br_3N_3O_4$; requires: C, 50.71; H, 2.20; N, 5.72%. FT-IR (KBr): 3532, 3510, 3079, 2293, 1754, 1673, 1607, 1581, 1490, 1369, 1165, 1100, 1059, 1009, 923, 866, 842, 771, 684 cm^{-1}.

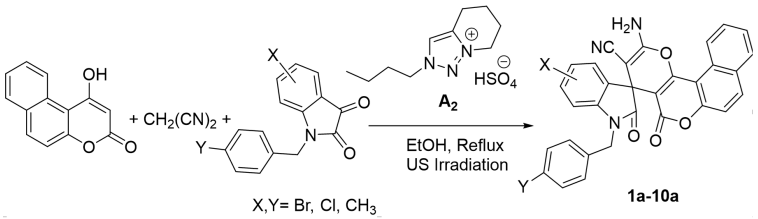
3. Results and discussion

3.1 Ionic liquids: preparation and characterization

Scheme 2 represents the preparation of ionic liquid A2. The successful synthesis of ionic liquid was confirmed by their ^{1}H-NMR spectra and CHNS analysis. In the ^{1}H-NMR spectrum of sample A2, the broad peak located in δ = 10.53 ppm is related to the proton of the HSO_4 group. One proton in the triazole ring appeared at δ = 8.89 ppm as a singlet. The barium sulfate ($BaSO_4$) test confirmed that the ionic liquid A2 is suitably synthesized and purified, and each molar mass of ionic liquid contains an equal molar ratio (1 mol) of hydrogen sulfate ions.

Ionic liquid catalyzed preparation of spiro-compounds

After the successful synthesis of A2 ionic liquid, the A2 catalyzed three-component reaction of 1-hydroxy-3H-benzo [f] chromen-3-one, malononitrile, and 1-benzylindoline-2, 3-dione lead to the synthesis of 2-amino-1'-benzyl-2', 5-dioxo-5H-spiro [benzo [f] pyrano [3, 2-c] chromene-4, 3'-indoline] -3-carbonitrile **(1a)** was chosen as a model to be used for the founding of the optimized reaction condition. In the beginning, the effect of factors on the rate and productivity of the reaction, such as different solvents, temperature, and catalyst dosage, was screened (Table 2). In the absence of the catalyst and at room temperature no progress to the productivity was achieved. A moderate yield of **(1a)** was achieved under solvent-free (49%) conditions. When the media is a solvent with a low boiling point (e. g. , Hexane Et_2O CH_2Cl_2), no product is formed. In polar aprotic solvents, moderate yield of product was achieved (EtOAc (21%), CH_3CN (34%), DMF (64%). The reaction in water has a yield (H_2O, 37%) but is not interesting. Higher yields of **(1a)** were produced when CH_3OH (78%) and EtOH (87%) were chosen as the reaction media. Accordingly, EtOH was selected as the suitable solvent for the reaction media. In continuation, the tests were also carried out using different catalyst dosages (0.5 mmol: 87%, 0.25 mmol: 53%, 0.75 mmol: 89%, 1 mmol: 86%). Based on our experimental observations, it



Scheme 2. Schematic preparation of **A1** and ionic liquid **A2**.

Table 2. The experimental tests used for the optimization condition in the synthesis of **1a**.

Catalyst Dosage (mmol)/Solvent (25 mL)/Temperature (°C)	Time (h)	Yield (%)*
-/ EtOH / r.t.	5	-
-/ EtOH / Reflux	5	-
0.5 / - /100	1	49
0.5 / H_2O / Reflux	2	37
0.5 / CH_3OH / Reflux	2	78
0.5 / EtOAc / Reflux	4	21
0.5 / CH_3CN / Reflux	4	34
0.5 / DMF / Reflux	2	64
0.5 / Hexane / Reflux	6	-
0.5 / Toluene / Reflux	3	59
0.5 / Et_2O / Reflux	7	-
0.5 / CH_2Cl_2 / Reflux	8	-
0.5 / EtOH / Reflux	2	87
0.25 / EtOH / Reflux	3	53
0.75 / EtOH / Reflux	2	89
1 / EtOH / Reflux	2	86

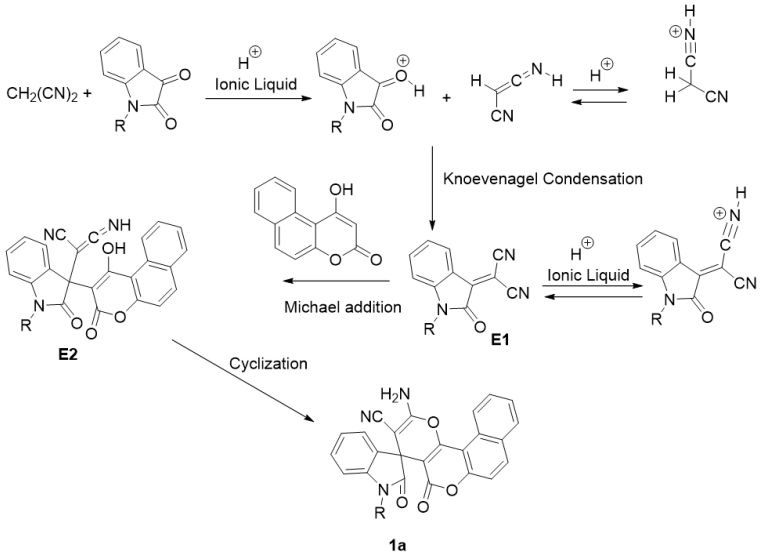
*Isolated Yields; All reactions were done under ultrasonic irradiation condition in an US bath

could be concluded that 0.5 mmol of the catalyst and EtOH at reflux conditions are favorable conditions for product formation.

In comparison, the use of some metal hydrogen sulfate as a catalyst, including $NaHSO_4$ (21%), $Mg(HSO_4)_2$ (41%), $Ca(HSO_4)_2$ (28%), $Al(HSO_4)_3$ (48%), and $Fe(HSO_4)_3$ (57%) do not perform better results. Thus, ionic liquid A2 is a better catalyst for promoting the synthesis of **(1a)**.

The progress of the reaction for the synthesis of **1a** could be started by the protonation and activation of starting materials, as shown in Scheme 3. Accordingly, the Knoevenagel condensation makes a new intermediate **(E1)**, which undergoes the Michael addition reaction to form an intermediate **(E2)**. Subsequently, the cyclization process makes the final product **(a1)**. The electron-withdrawing groups, such as Cl and Br atoms, increased the positive charge of the carbon center, and thus, the Knoevenagel condensation and the Michael addition reactions will proceed faster [21–23].

Next, some different varieties of 1-benzylindoline-2,



Scheme 3. Proposed mechanism for the preparation of **1a**.

3-dione were tested (Table 1). As observed, the substances substituted with electron-donating groups, such as CH_3, reacted at a lower rate while substituted substances with Cl and Br show higher activity, and thus, the reactions need lower times to be completed. The structures of all the synthesized products **(1a-10a)** were confirmed by their $^{1}H/^{13}C$-NMR, CHNS analysis, and melting point analysis. To investigate the possible stability of ionic liquid, after completion of the reaction, the solid was filtered and washed several times with ethanol. The filtrate was concentrated and used again for the synthesis of **1a**. The progress was repeated 10 times, and the results confirmed that the catalyst was stable during the reaction.

4. Conclusion

A new ionic liquid, referred to as **A2**, was first synthesized and subjected to detailed characterization using techniques like NMR, FT-IR, and CHNS elemental analysis, ensuring both the structure and composition were confirmed. Following this, a streamlined approach for the three-component synthesis of compounds **1a-10a** was introduced. This process involved the reaction of 1-hydroxy-3H-benzo [f] chromen-3-one, malononitrile, and 1-benzylindoline-2, 3-dione in ethanol, conducted under reflux with ultrasonic assistance. The use of ultrasonic irradiation notably enhanced the reaction, reducing the time required to obtain the products while maintaining high yields. The catalytic performance of ionic liquid **A2** proved to be highly effective, enabling efficient product formation. Moreover, **A2** was easily recoverable and demonstrated stable reusability across multiple cycles, preserving its catalytic properties, which highlights its potential as a sustainable catalyst in organic synthesis.

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Authors contributions

A. Fazlinia and F. H. Tavakoli designed and performed the experiments and analyzed the data. M. Ghashang is the corresponding author of the work, who has performed the materials and written the paper.

Availability of data and materials

The data that could support our findings are available in the text of this article.

Conflict of interests

The authors declare that they have no interest in influencing the work reported in this paper.

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