Article

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The Synthesis of 2,11-Diamino-4,9-diphenyl-4,9-dihydrobenzo [f] pyrano[3,2-h] chromene-3,10-dicarbonitrile Derivatives using Triethanolammonium Acetate as a Green Ionic Liquid

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Triethanolammonium acetate [TEA][HOAc] was used as a green ionic liquid and successfully utilized for the multi-component synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano [3,2-h]chromene-3,10-dicarbonitrile derivatives as new compounds by the reaction of 2,3-naphthalenediol with malononitrile and various aldehydes. Mild reaction conditions and high yields are some of the advantages of this method. These compounds were identified by IR, NMR spectroscopy and mass analysis.

Keywords: Ionic liquid; Triethanolammonium acetate; 2,11-Diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile; One-pot synthesis.

INTRODUCTION

Ionic liquids (ILs) find increasing applications in many fields of chemistry and industry due to their chemical and thermal stability, low vapor pressure, and high ionic conductivity.[1]

In the past few years, ILs have been popularly used for organic synthesis as environmentally friendly solvents, for catalysis, and also as media for extraction processes.[2–10] Perhaps the best way in which an IL can be used in catalysis is as a combined catalyst and solvent. Since the melting points of ILs are low, they can act as solvents for diverse reactions. Such reactions often give selectivity and reactivity different from those with conventional organic solvents. Therefore, ILs have been classified as "green solvents".[11] Reports indicate that a variety of reactions can be performed in ILs ranging from electrophilic reactions,[12,13] hydrogenation,[14] Wittig reaction,[15] heterocyclic synthesis,[16,17] and nucleophilic substitution reactions.[18,19] The early use of ILs as catalysts was merely based on their role as polar media to facilitate organic reactions.[20–26]

2,11-Diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile derivatives are an important class of organic compounds because of their use as drugs, pesticides, analogs of natural compounds, dyes, and other materials with practical importance.[27–32]

Previously, these derivatives were synthesized in two steps. The first step consisted in preparing and isolating arylmethylene malononitrile, and the second step involved the reaction of this compound with the corresponding phenol or naphthol.[33–35]

In this paper, we report the use of triethanolammonium acetate [TEA][HOAc] as a green IL and catalyst (Scheme 1) for the synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile derivatives by the reaction of 2,3-naphthalenediol with malononitrile and aldehydes (Scheme 2) with excellent yields.[36]

RESULTS AND DISCUSSION

This IL contains hydroxyl and ammonium groups, which could be coordinated with the hydrogens on the active methylene group of malononitrile and the carbonyl group of the aromatic aldehydes (Scheme 3).

At first, the reaction of naphthalene-2,3-diol with benzaldehyde and malononitrile was selected as a model reaction. Then, in order to optimize the reaction

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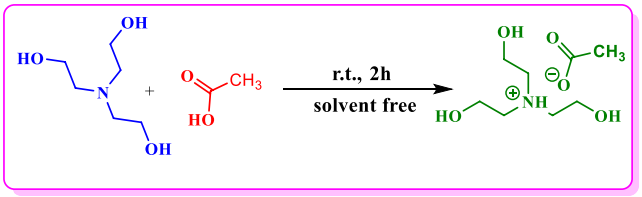
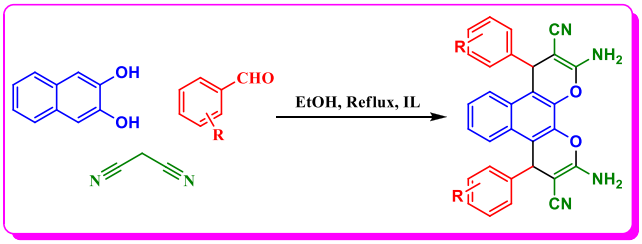
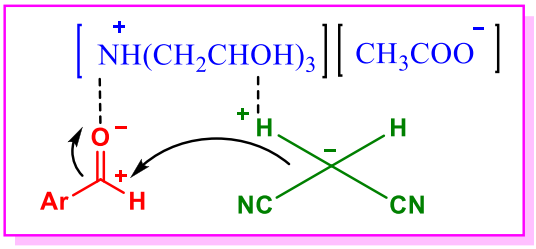


Scheme 1. Synthesis of triethanolammonium acetate [TEA][HOAc].



Scheme 2. Synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene -3,10-dicarbonitrile derivatives using triethanolammonium acetate.



Scheme 3. Triethanolammonium acetate [TEA][HOAc] coordinated with malononitrile and aldehydes.

conditions, the effect of temperature, amount of catalyst, and kinds of solvent on the model reaction was studied. The obtained results are summarized in Tables 1–3. Among the solvents H_2O/ethanol (1:1), ethanol, H_2O and PEG, ethanol was found to be the best solvent in this reaction (Table 1, entry 3). As shown in Tables 2 and 3, the best reaction conditions were obtained in ethanol under reflux conditions in the presence of 0.143% of the catalyst. The model reaction was also tested under solvent-free conditions; but the yield of product was low in comparison with that with the solvent.

Table 1. Effect of various solvents on the synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo[f] pyrano [3,2-h]chromene-3,10-dicarbonitrile using [TEA][HOAc] (0.143 mol%)

Entry	Solvent	Time (h)	Yield[a] (%)
1	Solvent-free	2	30
2	H_2O–ethanol (1:1)	2	85
3	Ethanol	1	95
4	H_2O	2	40
5	PEG (300)	2	90

[a] Isolated yield.

Table 2. Effect of amount of the catalyst on the synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile

Entry	Catalyst (mol %)	Time (h)	Yield[a] (%)
1	0.047	1	80
2	0.095	1	80
3	0.143	1	95

[a] Isolated yield.

To show the generality of the catalyst, various aromatic aldehydes containing electron-withdrawing and electron-donating groups and halogens were tested under these reaction conditions (Table 4). Electron-withdrawing substituents (such as NO_2) on the aldehyde increase the reaction time, and electron-donating substituents (such as OMe) on the aldehyde decrease the reaction time (Table 4, entries 5 and 6).

Various catalysts were tested in the synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile under optimal conditions in ethanol as solvent in comparison with [TEA][HOAc]. As shown in Table 5, [TEA][HOAc] was the best catalyst in the synthesis of the products under these reaction conditions.

In a possible mechanism that is supported by the literature[37] and shown in Scheme 4, at first malononitrile reacts with the carbonyl group of the aldehyde which is activated by the tri-ethanol ammonium acetate

Table 3. Effect of temperature on the synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo [f] pyrano [3,2-h]chromene-3,10-dicarbonitrile

Entry	Temperature (°C)	Time (h)	Yield[a] (%)
1	r.t.	6.5	60
2	60	3	85
3	70	1	90
4	Reflux	1	95

[a] Isolated yield.

Table 4. Synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile derivatives using [TEA][HOAc] as a green ionic liquid catalyst

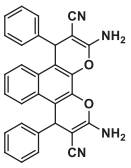
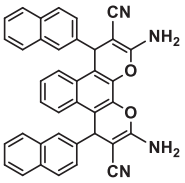
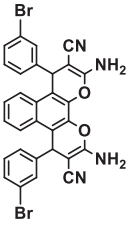
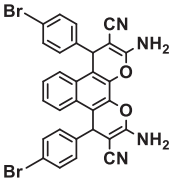
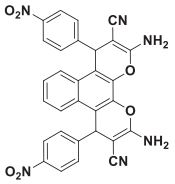
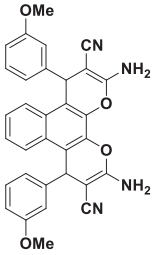
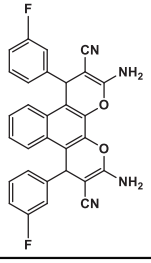
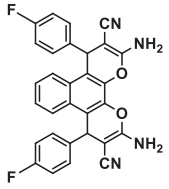
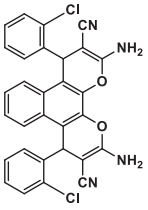
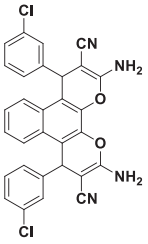
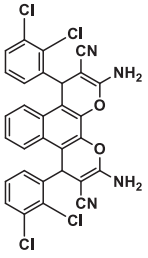
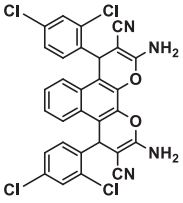
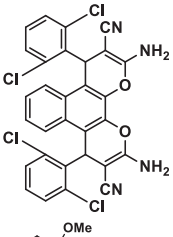
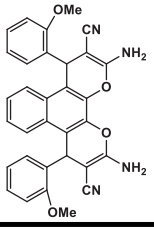
Entry	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
1		60	95	315 (dec.) (>300 [33])
2		360	70	279–281
3		150	90	321–323
4		60	95	332
5		20	85	337–342
6		120	67	306
7		390	85	316–319

Table 4. Continued

Entry	Product	Time (min)	Yield[a] (%)	M.p. °C (Lit.)
8		390	73	244–248 (241 [36])
9		60	72	317
10		360	76	338–341
11		60	69	314
12		240	84	327–330
13		180	74	316
14		150	76	311–313

[a] Isolated yield.

Table 5. Effect of various catalysts on the synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo [f] pyrano [3,2-h]chromene-3,10-dicarbonitrile

Catalyst (mol %)	Time (h)	Yield[a] (%)
Fe_2O_3 nanoparticle	2.5	40
$ZnFe_2O_3$ nanoparticle	2.5	45
Al_2O_3 nanoparticle	3	10
IL $[HN^+(CH_2CH_2OH)_3][CH_3COO^-]$	1	95
IL $[HN^+(CH_2CH_2OH)_3][HSO_4^-]$	2.5	49
IL$[HN^+(Et)_3][CH_3COO^-]$	1	64
TCCA	3	32
PBNS	3	20

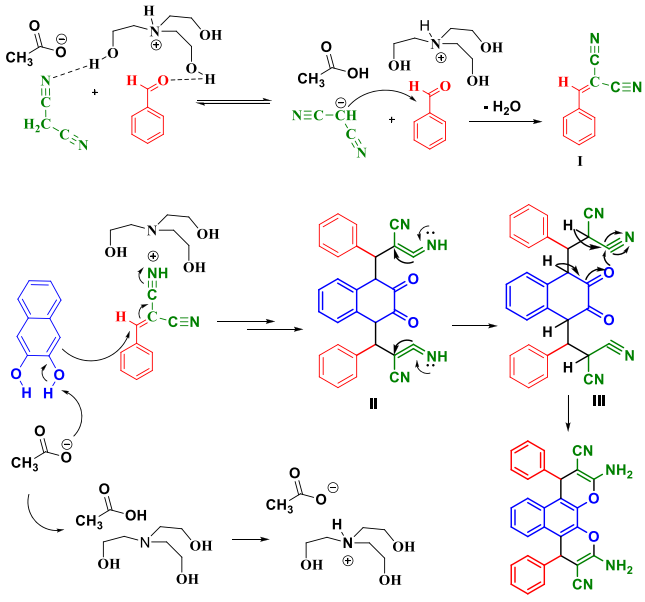
[a] Isolated yield.

as an acidic IL to give intermediate **I** after removing one molecule of H_2O. 2,3-Naphthalenediol attacks the cyanoolefin compound (**I**) as a Michael acceptor to give **II**, which converts to **III**. Finally, intramolecular cyclocondensation reaction of **III** affords the desired product (Scheme 4).

EXPERIMENTAL

Typical procedure for the preparation of triethanolammonium acetate [TEA][HOAc]

To a 250-mL flask was added triethanolamine (1 mmol) and acetic acid (1 mmol) at room temperature within 2 h to give [TEA][HOAc] as a light yellow viscous liquid.



Scheme 4. Proposed mechanism for the synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydroben zo [f] pyrano [3,2-h]chromene-3,10-dicarbonitrile derivatives using Triethanolammonium acetate.

Typical procedure for the preparation of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h] chromene-3,10-dicarbonitrile derivatives

To a mixture of 2,3-naphthalenediol (1 mmol), malononitrile (2 mmol), aldehydes (2 mmol), and ethanol (3 mL) in a round-bottom flask, 0.143 mol % of triethanolammonium acetate [TEA][HOAc] as a green IL catalyst was added. The resulting mixture was first stirred magnetically in ethanol as solvent under reflux conditions for an appropriate time (Table 4). After completion of the reaction as observed by thin-layer chromatography (TLC; *n*-hexane/ethyl acetate: 2/1), the solid was washed three times with a 5% aqueous solution of alcohol and recrystallized from 95% aqueous ethanol. The spectra of compounds have been reported in supporting information.

Spectral data of the compounds

2,11-Diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 1*): m.p: 315°C (dec.). FT-IR ν (cm^{-1}): 3488, 3377, 3249 (NH_2) 2188 (CN); ^{1}HNMR (DMSO-d_6, 90 MHz): δ (ppm): 5.23 (s, 2H), 6.88–7.62 (m, 14H), 10.28 (s, 4H).

2,11-Diamino-4,9-di(naphthalen-2-yl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 2*): m.p: 279–281°C (dec.). FT-IR ν (cm^{-1}): 3466, 3374 (NH_2), 2197 (CN). ^{1}HNMR (DMSO-d_6, 400 MHz): δ (ppm): 5.45 (s, 2H), 6.96 (s, 2H), 7.17 (s, 2H), 7.27 (s, 4H), 7.46 (s, 2H), 7.67 (s, 2H), 7.81 (s, 6H), 10.33 (s, 4H). ^{13}CNMR (DMSO-d_6, 100 MHz): δ (ppm): 38.6, 57.6, 109.9, 116.8, 120.4, 123.3, 124.3, 124.9, 125.7, 126.3, 127.4, 128.6, 131.2, 131.8, 132.8, 139.0, 142.9, 145.0, 159.6; MS: *m/z* = 568 [M^+].

2,11-Diamino-4,9-bis(3-bromophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 3*): m.p: 321–323°C (dec.). FT-IR ν (cm^{-1}): 3454, 3331, 3196 (NH_2), 2197 (CN). ^{1}HNMR (acetone, 500 MHz): δ (ppm): 5.47 (s, 2H), 6.23 (s, 2H), 6.31 (s, 1H), 7.25–7.30 (m, 2H), 7.36–7.42 (m, 6H), 7.51 (s, 1H) 7.55 (s, 2H), 7.91–7.93 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ (ppm): 38.4, 59.2, 117.3, 120.6, 122.9, 124.9, 126.9, 127.0, 127.7, 130.4, 130.7, 131.9, 137.7, 148.5, 160.1; MS: *m/z* = 626 [M^+].

2,11-Diamino-4,9-bis(4-bromophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 4*): m.p: 332°C (dec.). FT-IR ν (cm^{-1}): 3448, 3331, 3190 (NH_2), 2194 (CN). ^{1}HNMR (DMSO-d_6, 500 MHz): δ (ppm): 5.35 (s, 2H), 6.86 (s, 1H), 7.17 (d, J = 8.5 Hz, 4H), 7.30–7.31 (m, 2H), 7.42 (d, J = 8.5 Hz, 4H), 7.74–7.78 (m, 2H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 38.3, 59.0, 115.8, 117.4, 120.6, 120.8, 124.9, 126.9, 127.5, 127.7, 130.1, 132.6, 137.6, 145.2, 159.9; MS: m/z = 626 [M^+].

2,11-Diamino-4,9-bis(4-nitrophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 5*): m.p: 337–342°C (dec.). FT-IR ν (cm^{-1}): 3445, 3365, 3191 (NH_2), 2190 (CN); ^{1}HNMR (DMSO, 500 MHz): δ (ppm): 5.59 (s, 2H), 7.00 (s, 1H), 7.31 (d, J = 3.0 Hz, 2H), 7.56 (d, J = 8.5 Hz, 4H), 7.74–7.75 (m, 2H), 8.11 (d, J = 8.5 Hz, 4H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 31.4, 57.6, 116.7, 120.6, 124.6, 124.9, 125.0, 125.0, 127.5, 129.0, 137.6, 147.0, 152.9, 160.1; MS: m/z = 558 [M^+].

2,11-Diamino-4,9-bis(3-methoxyphenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 6*): m.p: 306°C (dec.); FT-IR ν (cm^{-1}): 3451, 3335, 3191 (NH_2), 2193 (CN); ^{1}HNMR (DMSO, 500 MHz): δ (ppm): 3.66 (s, 6H), 5.33 (s, 2H), 6.76 (m, 8H), 7.19 (m, 2H), 7.35 (m, 2H), 7.83 (m, 2H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 38.9, 55.7, 59.6, 112.5, 113.9, 117.6, 119.9, 120.8, 124.8, 126.7, 127.8, 130.8, 137.5, 147.4, 160.1, 160.2; MS: m/z = 528 [M^+].

2,11-Diamino-4,9-bis(3-fluorophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 7*): m.p: 316–319°C (dec.). FT-IR ν (cm^{-1}): 3460, 3388, 3332, 3199 (NH_2), 2197 (CN); ^{1}HNMR (DMSO-d_6, 500 MHz): δ (ppm): 5.39 (s, 2H), 6.81 (m, 3H), 6.96 (m, 1H), 7.07 (m, 2H), 7.21 (m, 3H), 7.33 (m, 3H), 7.42 (s, 1H), 7.80 (m, 2H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 37.6, 58.3, 66.3, 113.7, 116.4, 119.7, 123.1, 124.0, 126.0, 126.9, 130.9, 136.9, 147.8, 159.2, 161.0, 163.4; MS: m/z = 504 [M^+].

2,11-Diamino-4,9-bis(4-fluorophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 8*): m.p: 243–248°C (dec.). FT-IR ν (cm^{-1}): 3476, 3385, 3333, 3241, (NH_2), 2219 (CN). ^{1}HNMR (DMSO-d_6, 500 MHz): δ (ppm): 5.27 (s, 2H), 6.51 (s, 1H), 6.51 (s, 1H), 6.82–6.94 (m, 7H), 7.24 (s, 1H), 7.36 (s, 4H), 7.63 (s, 2H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 32.8, 51.1, 95.9, 99.5, 114.2, 115.8, 116.7, 122.1, 130.0, 131.3, 145.7, 151.3, 152.6; MS: m/z = 504 [M^+].

2,11-Diamino-4,9-bis(2-chlorophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 9*): m.p: 317°C (dec.); FT-IR ν (cm^{-1}): 3471, 3439, 3375, 3187 (NH_2), 2193 (CN); ^{1}HNMR (DMSO-d_6, 500 MHz): δ (ppm): 5.72 (s, 2H), 6.84 (s, 3H), 6.94 (s, 1H), 7.21 (m, 6H), 7.35 (d, J = 3 Hz, 2H), 7.43 (s, 2H), 7.60 (s, 2H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 36.5, 58.0, 116.8, 120.1, 124.2, 127.0, 127.7, 129.1, 129.6, 130.6, 131.2, 132.0, 137.9, 142.6, 160.0; MS: m/z = 538 [M^+].

2,11-Diamino-4,9-bis(3-chlorophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 10*): m.p: 338–341°C (dec.); FT-IR ν (cm^{-1}): 3451, 3329, 3193 (NH_2), 2199 (CN). ^{1}HNMR (DMSO-d_6, 500 MHz): δ (ppm): 5.41 (s, 2H), 6.81 (m, 3H), 7.19–7.35 (m, 9H), 5.41 (s, 2H), 7.81 (s, 2H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 38.4, 59.2, 117.3, 120.5, 124.9, 126.6, 127.0, 127.5, 127.6, 127.8, 131.6, 134.2, 137.8, 148.3, 160.1; MS: m/z = 536 [M^+].

2,11-Diamino-4,9-bis(2,3-dichlorophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 11*): m.p: 314°C (dec.). FT-IR ν (cm^{-1}): 3472, 3327, 3190 (NH_2), 2196 (CN). ^{1}HNMR (DMSO-d_6, 500 MHz): δ (ppm): 5.79 (s, 2H), 6.87 (s, 2H), 6.96-7.02 (m, 1H), 7.21 (m, 3H), 7.31 (m, 2H), 7.45 (m, 2H), 7.52 (m, 2H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 37.3, 57.4, 116.4, 120.0, 123.9, 127.1, 127.5, 129.8, 130.0, 130.1, 130.2, 133.0, 137.8, 145.1, 160.0; MS: m/z = 606 [M^+].

2,11-Diamino-4,9-bis(2,4-dichlorophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 12*): m.p: 320–330°C (dec.). FT-IR ν (cm^{-1}): 3471, 3333, 3187 (NH_2), 2194 (CN); ^{1}HNMR (DMSO-d_6, 500 MHz): δ (ppm): 5.73 (s, 2H), 6.93 (s, 1H), 7.23-7.30 (m, 5H), 7.38 (d, J = 3Hz, 2H), 7.54–7.55 (m, 2H), 7.61 (m, 2H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 31.5, 57.4, 116.3, 120.0, 124.0, 127.0, 127.4, 129.3, 129.9, 132.6, 132.9, 133.2, 137.8, 141.7, 159.8; MS: m/z = 606 [M^+].

2,11-Diamino-4,9-bis(2,6-dichlorophenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 13*): m.p: 316°C (dec.). FT-IR ν (cm^{-1}): 3473, 3382 (NH_2), 2178 (CN); ^{1}HNMR (Aceton, 500 MHz): δ (ppm): 6.21 (s, 2H), 6.30 (s, 2H), 7.23–7.34 (m, 7H), 7.56–7.61 (m, 3H), 7.70 (d,

J = 8 Hz, 2H); ^{13}CNMR (DMSO-d_6, 125 MHz): δ (ppm): 36.2, 53.6, 111.3, 114.5, 120.3, 123.1, 124.7, 125.2, 125.7, 127.6, 129.7, 130.3, 131.7, 135.2, 138.3, 141.1, 145.4, 161.0; MS: m/z = 606 [M^+].

2,11-Diamino-4,9-bis(2-methoxyphenyl)-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile (*Table* 4, *entry 14*): m.p: 311–313°C (dec.); FT-IR ν (cm^{-1}): 3470, 3330, 3189 (NH_2), 2192 (CN); ^{1}HNMR (DMSO-d_6, 400 MHz): δ (ppm): 3.83 (s, 6H), 5.63 (s, 2H), 6.76 (s, 3H), 6.87 (m, 2H), 7.04–7.06 (m, 4H), 7.19 (m, 2H), 7.35–7.37 (m, 2H), 7.77 (m, 2H); ^{13}CNMR (DMSO-d_6, 100 MHz): δ (ppm): 32.4, 55.8, 66.3, 111.8, 116.6, 120.0, 121.0, 123.4, 125.7, 126.9, 128.2, 128.6, 132.7, 137.0, 155.8, 159.6; MS: m/z = 528 [M^+].

CONCLUSION

In this work, we reported the catalytic application of triethanolammonium acetate [TEA][HOAc] as a green IL and catalyst in the synthesis of 2,11-diamino-4,9-diphenyl-4,9-dihydrobenzo[f]pyrano[3,2-h]chromene-3,10-dicarbonitrile derivatives by the one-pot three-component condensation reaction of 2,3-naphthalenediol, malononitrile, and various aldehydes with good to excellent yields and in short reaction times in ethanol under reflux conditions.

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Supporting information

Additional supporting information is available in the online version of this article.

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