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Synthesis of a new series of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene) benzohydrazides using a deep eutectic solvent as solvent/catalyst under sonication

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ABSTRACT

We report here the preparation of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide compounds in good to excellent yields (83–98%) within a short reaction time (10–15 min), through a clean and efficient procedure. Seventeen new compounds were synthesized and fully characterized by FT-IR, NMR, and HRMS. The deep eutectic solvent can be recovered easily by phase extraction and can be reused up to several times without any significant loss of catalytic activity. Additionally, the method has a wide substrate scope and provides an accessible route for the large-scale direct synthesis of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazides.

1. Introduction

Deep eutectic solvents (DESs) have known as a new generation of ionic liquid attracting much interest in the field of organic synthesis and sustainable chemistry [1, 2, 3, 4, 5, 6, 7, 8, 9]. DESs are non-volatile substances with some typical characteristic as nonflammability, thermal stability, simple preparation and purification, low cost, biodegradation. DESs generally are formed by the mixture of hydrogen bond donor (HBD) molecules with choline chloride or halide salts [10, 11, 12, 13, 14, 15]. Recently, DESs have been applied to many applications such as electrochemistry, gas adsorption, extraction [16], metal processing, catalysis, drug solubilization vehicles [17], fuel [18], and biodiesel [19]. However, a few studies were reported for using DES as a catalyst or solvent in chemical reactions [2, 20, 21, 22, 23, 24, 25].

Hydrazides and related compounds have attracted significant attention as useful building blocks for the assembly of various heterocyclic compounds which are found to possess anti-tumoral, anti-convulsant, anti-microbial, analgesic, anti-tubercular, and anti-inflammatory activities [26, 27, 28, 29]. Additionally, hydrazides are also essential precursors in the synthesis of hydrazones and heterocyclic compounds [30, 31]. As a result, several synthesis approaches have been developed for the construction of these hydrazides [32]. However, the problem of using the excess organic solvent or catalyst and the high temperature for the transformation remains to be solved.

Herein, we report the use of DESs composed of choline chloride and oxalic acid in the synthesis of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene) benzohydrazide compounds. DES plays dual roles in this synthetic process, such as the homogeneous catalyst and the liquid solvent. This is the first time DESs have been used as catalyst/solvent for the synthesis of benzohydrazides.

2. Results and discussion

First of all, DESs were synthesized according to the previous procedure [22]. Next, 2-hydroxy-5-iodobenzohydrazide (4) was synthesized from salicylic acid *via* three steps as described in Scheme 1. Subsequently, the effect of solvents on the synthesis of 2-hydroxy-5-iodo-*N*'-(1-phenylethylidene)benzohydrazide was investigated (Table 1). The desired product was obtained in moderate to good yield under the polar solvents, while low yields were observed when non-polar solvents were employed (Table 1, entries 1–10). These results exhibited that the polar of the solvent had a strong influence on the reaction yield. Thus, we decided to use DESs as a solvent/catalyst, and the desired product was afforded in excellent yield. No product was obtained in the absence of a solvent. After the solvent screening, DES from choline chloride and oxalic acid showed the best catalytic activity for this reaction.

The catalytic activity of DES in the reaction of 2-hydroxy-5-

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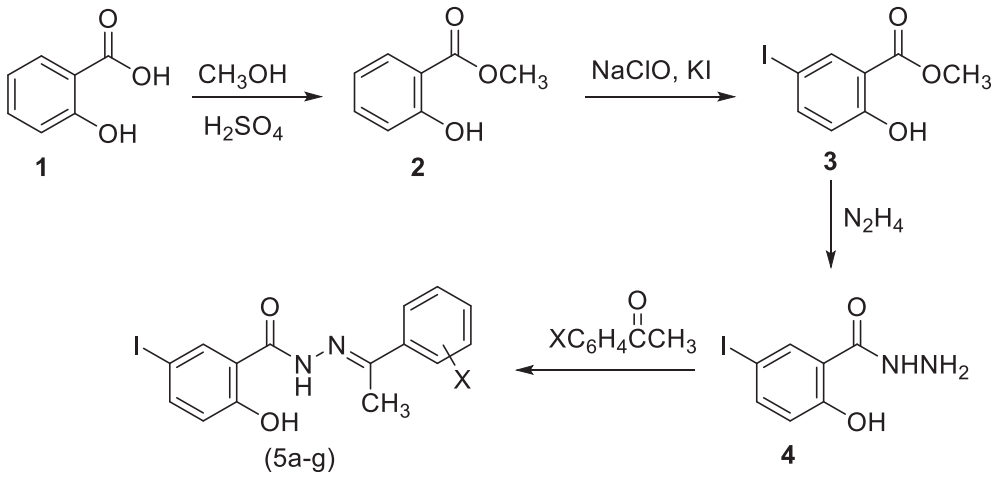

Scheme 1. Synthetic pathway of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide compounds.

Table 1
The effect of solvents on the synthesis of 2-hydroxy-5-iodo-*N*'-(1-phenylethylidene)benzohydrazide (5a).

Entry[a]	Type of solvent	Solvents	Isolated yield (%)[b]
1	Polar protic	Ethanol	85
2		*n*-Butanol	65
3		Acetonitrile	42
4	Polar aprotic	DMF	71
5		DMSO	80
6		THF	49
7	Non polar	Dichloromethane	40
8		Toluene	37
9		Hexane	0
10		1,4-Dioxane	35
11	Deep euctectic solvent	[ChCl][oxalic acid]	98
12		[ChCl][benzoic acid]	96
13		$[ChCl][ZnCl_2]_2$	93
14		$[Uera]_4[ZnCl_2]$	85
15		$[Ethylen\ glycol]_4[ZnCl_2]$	90

[a] Reaction conditions: A mixture of 2-hydroxy-5-iodobenzohydrazide (0.239 g, 0.5 mmol), acetophenone (0.060 g, 0.5 mmol) and 1.5 mL solvents was sonicated at room temperature for 10 min.
[b] Yield of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide was recrystallized from ethanol.

Table 2
Comparison of catalysts on the synthesis of 2-hydroxy-5-iodo-*N*'-(1-phenylethylidene)benzohydrazide.

Entry	Type of catalysts	Catalysts	Isolated yield[c] (%)
1	Deep euctectic solvent[a]	[ChCl][oxalic acid]	98
2		[ChCl][benzoic acid]	96
3		$[ChCl][ZnCl_2]_2$	93
4		$[Uera]_4[ZnCl_2]$	85
5		$[Ethylen\ glycol]_4[ZnCl_2]$	90
6	Metal salts[b]	$AlCl_3$	53
7		$FeCl_3$	41
8		$ZnCl_2$	51
9		$Cu(CH_3COO)_2$	36
10	Brønsted acids[b]	H_2SO_4	91
11		HCl	87
12		CF_3COOH	85
13		CH_3COOH	85

[a] Reaction conditions: A mixture of 2-hydroxy-5-iodobenzohydrazide (0.239 g, 0.5 mmol), acetophenone (0.060 g, 0.5 mmol) and 1.5 mL DES was sonicated at room temperature for 10 min.
[b] Reaction conditions: A mixture of 2-hydroxy-5-iodobenzohydrazide (0.239 g, 0.5 mmol), acetophenone (60 g, 0.5 mmol), catalysts (0.05 mmol) and 1.5 mL ethanol was sonicated at room temperature for 10 min.
[c] Yield of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide was recrystallized from ethanol.

iodobenzohydrazide and acetophenone was also compared with that of other homogeneous catalysts, we tried to use Brønsted or Lewis acids in ethanol for improvement the reaction yields. However, Lewis acids were not good for the present method afforded the expected product in moderate yields (Table 2, entries 6–9). The reaction could smoothly provide the product with good yield when Brønsted acids were employed in this method (Table 2, entries 10–13). However, the best yield was obtained in the presence of [ChCl][oxalic acid] under room temperature sonication. The reaction time was optimized, and the best yield was obtained in only 10 min sonication.

With the optimized conditions, the scope of the acetophenones in the reaction was extended (Fig. 1). As shown in Table 4, the desired products were obtained in good to excellent yields. The substituent in the benzene ring of acetophenones was found to have little effect on the reaction rate. Substituted acetophenones bearing both electron-rich groups and electron-poor groups in the aromatic ring could effectively afford the desired products in excellent yields (>85%). When the acetophenone bearing the strong electron-withdrawing group such as NO_2 at *meta* position, the product was obtained in lower yield. However, an excellent yield of 94% was observed when the NO_2 group at *meta* position was replaced by a Br group (Table 3, entry 9). It is worth noting that aromatic heterocyclic methyl ketones were successfully employed as the substrates to give the desired products with excellent yields (Table 3, entries 12–16).

The comparison of our work with previous literature is described in Table 4. The synthesis of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide in the presence of DES afforded the desired product in excellent yield (Table 4, entry 3). The previous reports showed that synthesis of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide also delivered the expected product in good yields but those reports still suffered intrinsic drawbacks such as the requirement of long reaction time and volatile organic solvent (Table 4, entries 1–2).

Although several homogeneous catalysts exhibited high activity, these catalysts could not be recycled. The recyclability of DES was investigated in the model reaction over 5 successive runs (Fig. 2). The DES could be easily recovered and reused without any significant loss of catalytic activity after the fifth run (see Fig. 3).

3. Experimental

3.1. Chemicals and instrumentation

Salicylic acid (purity ≥99%), acetophenone (purity ≥98%), 4-

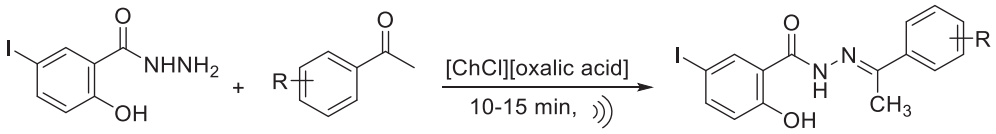

Fig. 1. Synthesis of various 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazides.

Table 3
Reaction scope of methyl ketones on the synthesis of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide compounds.[a]

Entry	Ketones	Products	Time (min)	Isolated yield (%)[b]
1	Acetophenone	5a	10	98
2	4-Methylacetophenone	5b	15	91
3	4-Methoxyacetophenone	5c	15	94
4	4-Fluoroacetophenone	5d	10	90
5	4-Chloroacetophenone	5e	10	89
6	4-Bromoacetophenone	5f	10	95
7	4-Aminoacetophenone	5g	15	87
8	4-Nitroacetophenone	5h	10	88
9	3-Bromoacetophenone	5i	10	94
10	3-Nitroacetophenone	5j	10	83
11	2-Hydroxyacetophenone	5k	10	87
12	4-Acetylpyridine	5l	15	90
13	3-Acetylpyridine	5m	15	89
14	2-Acetylthiophene	5m	12	94
15	3-Acetylcoumarin	5o	10	96
16	3-Acetyl-6-bromocoumarin	5p	10	95
17	3-Acetyl-6-iodocoumarin	5q	10	95

[a] Reaction conditions: A mixture of 2-hydroxy-5-iodobenzohydrazide (0.239 g, 0.5 mmol), aromatic ketones (0.5 mmol), 1.5 mL [ChCl][oxalic acid] was sonicated at room temperature.

[b] Yield of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazides was recrystallized from ethanol.

Table 4
Comparison of the present method with previous reports in the synthesis of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide.

Entry	Catalyst	Condition	Yield (%)	Recycle run
1	CH_3COOH [32]	Refluxed (EtOH), 5–9 h	75–89	-
2	Catalyst-free [33]	Refluxed (EtOH), 2 h	76–88	-
3	DES (This work)	Ultrasound, 10–15 min	83–98	5th (5%)[a]

[a] The number in parenthesis is the drop in the reaction yield after the last run.

methylacetophenone (purity ≥95%), 4-methoxyacetophenone (purity ≥98%), 4-fluoroacetophenone (purity ≥99%), 4-chloroacetophenone (purity ≥97%), 4-bromoacetophenone (purity ≥98%), 4-aminoacetophenone (purity ≥99%), 4-nitroacetophenone (purity ≥98%), 3-bromoacetophenone (purity ≥99%), 3-nitroacetophenone (purity ≥98%), 2-hydroxyacetophenone (purity ≥98%), 4-acetylpyridine (purity ≥97%), 3-acetylpyridine (purity ≥98%), 2-acetylthiophene (purity ≥98%), 3-acetylcoumarin (purity ≥96%), 3-acetyl-6-bromocoumarin (purity ≥97%), 3-acetyl-6-iodocoumarin (purity ≥97%), choline chloride (purity ≥99%), urea (purity ≥98%), oxalic acid (purity ≥99%), benzoic acid (purity ≥99%), ethylene glycol (purity ≥99%), trifluoroacetic acid (purity ≥99%), potassium iodide, sodium hypochlorite solution, hydrazine monohydrate (purity ≥98%), aluminum chloride anhydrous (purity ≥99%), zinc chloride anhydrous (purity ≥97%), iron(III) chloride anhydrous (purity ≥99%), copper(II) acetate anhydrous (purity ≥98%) were purchased from Sigma-Aldrich (Singapore). Ethanol (water ≤0.10 %), *n*-butanol (water ≤0.10 %), acetonitrile (water ≤30 ppm), *N*,*N*-dimethylformamide (water ≤0.10 %), tetrahydrofuran (water ≤0.10 %), dimethyl sulfoxide (water ≤0.10 %), dichloromethane (water ≤0.10 %), toluene (water ≤0.05 %), *n*-hexane (water ≤0.005 %), 1,4-dioxane (water ≤0.02 %), methanol (water ≤0.10 %), sulfuric acid, hydrochloric acid, and acetic acid were purchased from Merck (Germany). Deuterated solvents DMSO-d_6 was purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

The reactions were conducted on an Elma S30H Ultrasonic cleaning unit (ultrasonic frequency = 37 kHz). Analytical thin-layer chromatography (TLC) was performed on F-254 silica gel coated aluminum plates from Merck (Germany). Melting points were recorded with a Buchi B-545 melting point Apparatus. Fourier transform infrared (FTIR) spectra were measured on a Bruker E400 FT-IR spectrometer using potassium bromide pellets. Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were acquired on a Bruker Avance II 500 MHz NMR spectrometer. Chemical shifts were quoted in parts per million (ppm) and referenced to the appropriate solvent peak. High-resolution mass spectrometry (HRMS) was conducted in negative ionization mode on an Agilent 1200 series high-performance liquid chromatography coupled to a Bruker micrOTOF-QII EIS mass spectrometer detector.

3.2. General procedure for the synthesis of deep eutectic solvents

3.2.1. [ChCl][oxalic acid]

A mixture of choline chloride (3.0 mmol, 0.420 g) and oxalic acid (3.0 mmol, 0.450 g) was stirred at 100 °C until a clear colorless liquid was obtained.

3.2.2. [ChCl][benzoic acid]

A mixture of choline chloride (3.0 mmol, 0.420 g) and benzoic acid (3.0 mmol, 0.366 g) was stirred at 100 °C until a clear colorless liquid was obtained.

3.2.3. [ChCl][$ZnCl_2$]$_2$

A mixture of choline chloride (2.0 mmol, 0.280 g) and zinc chloride (4.0 mmol, 0.544 g) was stirred at 100 °C until a clear colorless liquid was obtained.

3.2.4. [Uera]$_4$[$ZnCl_2$]

A mixture urea (4.0 mmol, 0.240 g) and zinc chloride (1.0 mmol, 0.136 g) were stirred at 100 °C until a clear colorless liquid was obtained.

3.2.5. [Ethylen glycol]$_4$[$ZnCl_2$]

A mixture ethylene glycol (4.0 mmol, 0.248 g) and zinc chloride (1.0 mmol, 0.136 g) were stirred at 100 °C until a clear colorless liquid was obtained.

3.2.6. General procedure for the synthesis of 2-hydroxy-5-iodo-N'-(1-arylethylidene)benzo-hydrazide compounds

A mixture of 2-hydroxy-5-iodobenzohydrazide (0.239 g, 0.5 mmol), acetophenone (0.060 g, 0.5 mmol) and 1.5 mL DES was sonicated at room temperature for an appropriate time. The reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with water (5 mL). The residue was filtered and purified by recrystallizing from ethanol to give the desired product. The structure of the product was characterized by FT-IR, NMR, and MS. For the recycling test, DES was dried under vacuum for 6 h and used for next run without any further purification. ^{1}H and ^{13}C NMR spectra were included in supporting information.

3.2.7. (E)-2-Hydroxy-5-iodo-N'-(1-phenylethylidene)benzohydrazide (5a)

Melting point: 179–180 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3295, 3040,

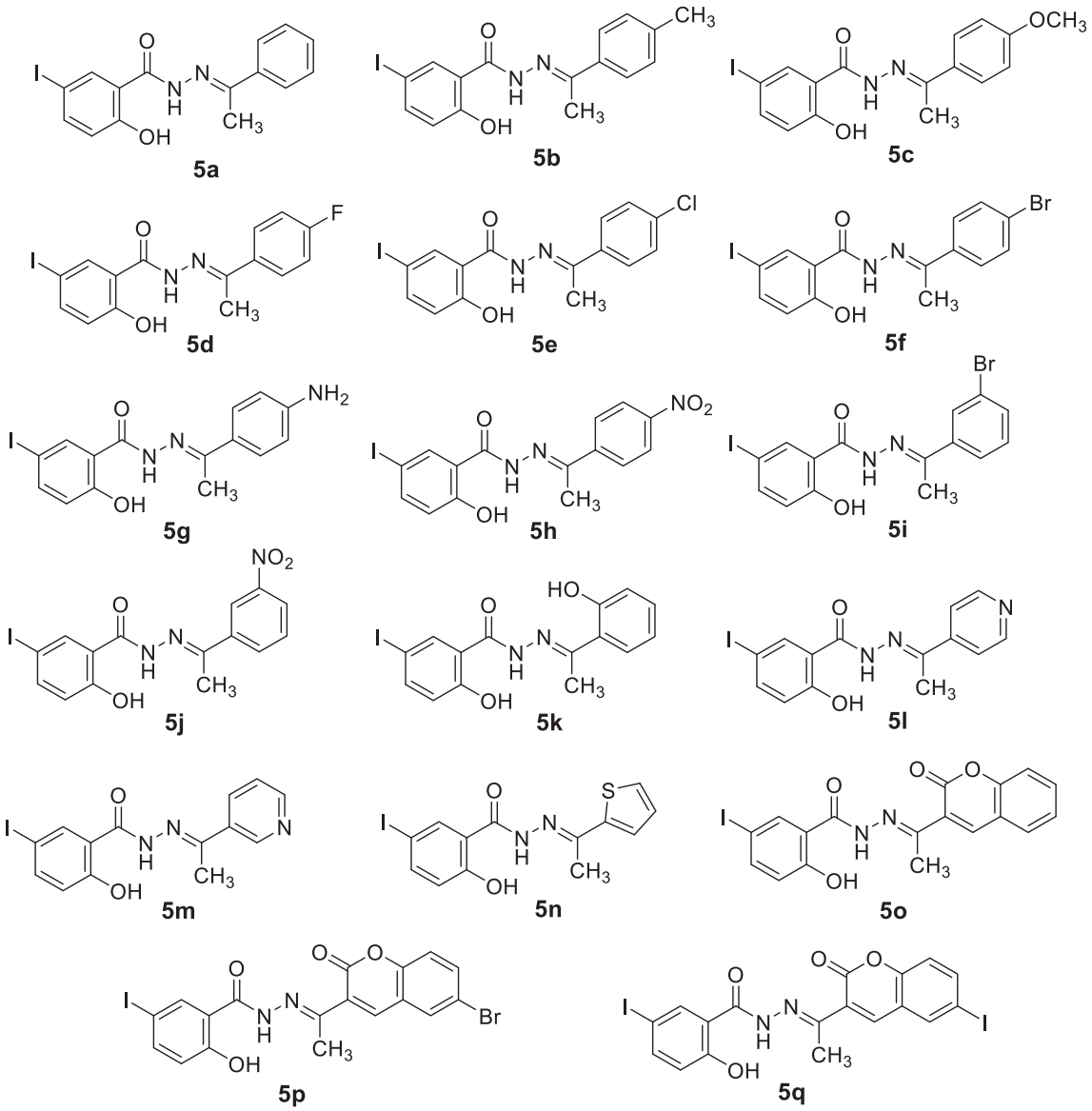

Fig. 2. The structures of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide compounds.

2917, 1643, 1566; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.06 (br), 11.29 (s, 1H), 7.87 (m, 2H), 7.73 (dd, J = 8.5, 2.0 Hz, 1H), 7.46 (m, 2H) 6.89 (d, J = 8.5 Hz, 1H), 8.23 (d, J = 2.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.6, 156.3, 152.9, 141.4, 138.5, 137.8, 129.5, 128.4, 126.5, 120.6, 119.6, 81.8, 13.9; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{14}IN_2O_2$ 381.0100; Found 380.9992.

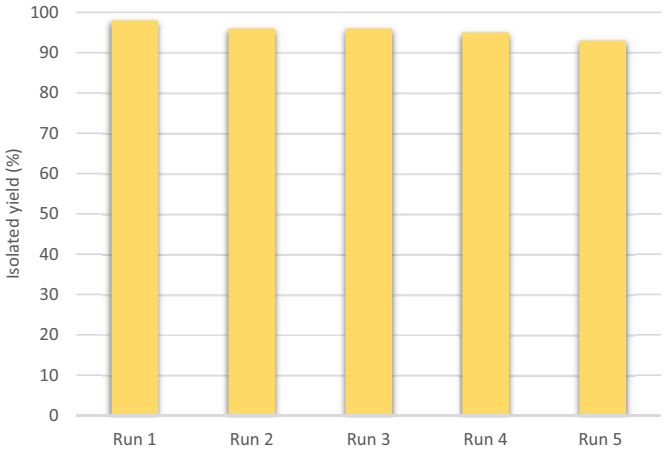

Fig. 3. Catalyst recycling studies.

3.2.8. (E)-2-Hydroxy-5-iodo-N'-(1-(p-tolyl)ethylidene)benzohydrazide (5b)

Melting point: 228–229 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3279, 3035, 2940, 1645, 1600; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.04 (br, 1H), 11.24 (s, 1H), 8.23 (s, J = 2.0 Hz, 1H), 7.76 (d, J = 8.5 Hz, 2H), 7.72 (dd, J = 8.5, 2.5 Hz, 1H), 7.26 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 1H), 2.35 (s, 1H), 2.32 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.6, 156.3, 152.9, 141.3, 139.2, 138.5, 135.0, 129.0, 126.4, 120.6, 119.6, 81.7, 20.9, 13.8; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{16}IN_2O_2$ 395.0256; Found 395.0247.

3.2.9. (E)-2-Hydroxy-5-iodo-N'-(1-(4-methoxyphenyl)ethylidene) benzohydrazide (5c)

Melting point: 222–223 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3279, 3063, 2931, 1643, 1605; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.05 (br, 1H), 11.21 (s, 1H), 8.23 (d, J = 2.0 Hz, 1H), 7.83 (d, J = 9.0 Hz, 2H), 7.71 (dd, J = 8.5, 2.0 Hz, 1H), 7.01 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 8.5 Hz, 1H), 3.82 (s, 1H), 2.31 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.0, 160.9,

156.8, 153.4, 141.8, 138.9, 130.6, 128.5, 121.1, 120.1, 114.3, 82.2, 55.7, 14.3; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{16}IN_2O_3$ 411.0206; Found 411.0158.

3.2.10. (E)-N'-(1-(4-fluorophenyl)ethylidene)-2-hydroxy-5-iodobenzohydrazide (5d)

Melting point: 234–235 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3295, 3102, 2930, 1643, 1605; ^1H NMR (500 MHz, DMSO-d_6) δ 12.04 (br, 1H), 11.27 (s, 1H), 8.22 (d, $J = 2.0$ Hz, 1H), 7.92 (dd, $J = 8.5$, 5.5 Hz, 2H), 7.72 (dd, $J = 8.5$, 2.0 Hz, 1H), 7.29 (dd, $J = 8.5$, 8.5 Hz, 2H), 6.88 (d, $J = 8.5$ Hz, 1H), 2.34 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.9 (*d*, $J = 245.5$ Hz), 160.6, 156.2, 151.9, 141.4, 138.5, 134.3 (d, $J = 11.0$ Hz), 128.7 (d, $J = 33.5$ Hz), 120.6, 119.6, 115.3 (d, $J = 86.0$ Hz) 81.7, 13.9; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}FIN_2O_2$ 399.0006; Found 399.0007.

3.2.11. (E)-N'-(1-(4-chlorophenyl)ethylidene)-2-hydroxy-5-iodobenzohydrazide (5e)

Melting point: 269–270 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3287, 3088, 2932, 1643, 1550; ^1H NMR (500 MHz, DMSO-d_6) δ 12.05 (br, 1H), 11.30 (s, 1H), 8.22 (s, 1H), 7.89 (d, $J = 8.0$ Hz, 2H), 7.73 (dd, $J = 8.5$, 1.5 Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 1H), 2.33 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.6, 156.2, 151.5, 141.4, 138.5, 136.6, 134.2, 128.4, 128.2, 120.6, 119.6, 81.8, 13.7; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}ClIN_2O_2$ 414.9710; Found 414.9674.

3.2.12. (E)-N'-(1-(4-bromophenyl)ethylidene)-2-hydroxy-5-iodobenzohydrazide (5f)

Melting point: 282 – 283 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3285, 3034, 2938, 1644, 1593; ^1H NMR (500 MHz, DMSO-d_6) δ 12.10 (s, 1H), 11.35 (s, 1H), 8.27 (d, $J = 2.0$ Hz, 1H), 7.87 (d, $J = 8.5$ Hz, 2H), 7.78 (dd, $J = 8.5$, 2.0 Hz, 1H), 7.71 (d, $J = 8.5$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.1, 156.7, 152.1, 141.9, 139.0, 137.5, 131.9, 129.0, 123.5, 121.1, 120.1, 82.3, 14.2; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}BrIN_2O_2$ 458.9205; Found 458.8999.

3.2.13. (E)-N'-(1-(4-aminophenyl)ethylidene)-2-hydroxy-5-iodobenzohydrazide (g)

Melting point: 242–243 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3440, 3298, 3201, 2932, 1634, 1577; ^1H NMR (500 MHz, DMSO-d_6) δ 11.10 (s, 1H), 8.21 (s, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 6.85 (d, $J = 8.5$ Hz, 1H), 6.58 (d, $J = 7.5$ Hz, 1H), 5.53 (s, 1H), 4.09 (d, $J = 5.0$ Hz, 1H), 3.17 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.5, 161.1, 157.0, 154.8, 150.9, 141.6, 138.7, 128.3, 125.2, 121.0, 120.1, 113.7, 82.0, 49.1, 14.1; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{15}IN_3O_2$ 396.0209; Found 396.0069.

3.2.14. (E)-2-Hydroxy-5-iodo-N'-(1-(4-nitrophenyl)ethylidene) benzohydrazide (5h)

Melting point: 259.5–260.5 °C; FT-IR (KBr, 4000-400 cm^{-1}): 3094, 1643, 1535; ^1H NMR (500 MHz, DMSO-d_6) δ 12.07 (br, 1H), 11.43 (s, 1H), 8.31 (d, $J = 8.5$ Hz, 2H), 8.22 (d, $J = 2.0$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 2H), 7.74 (dd, $J = 8.5$, 2.0 Hz, 1H), 6.89 (d, $J = 8.5$ Hz, 1H), 2.40 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.2, 156.7, 150.8, 148.1, 144.4, 142.1, 139.1, 128.1, 124.1, 121.1, 120.1, 82.3, 14.3; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{12}IN_3NaO_4$ 447.9770; Found 447.9718.

3.2.15. (E)-N'-(1-(3-bromophenyl)ethylidene)-2-hydroxy-5-iodobenzohydrazide (5i)

Melting point: 244 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3411, 3071, 2915, 1644, 1555, 616; ^1H NMR (500 MHz, DMSO-d_6) δ 12.01 (s, 1H), 11.30 (s, 1H), 8.21 (d, $J = 2.0$ Hz, 1H), 8.03 (s, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.71 (dd, $J = 8.5$, 2.0 Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.2, 156.7, 151.6, 141.9, 140.6, 139.0, 132.6, 131.1, 129.3, 126.1, 122.4, 121.1, 120.1, 82.2, 14.3; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{12}BrIN_2NaO_2$ 480.9025; Found 480.9023.

3.2.16. (E)-2-Hydroxy-5-iodo-N'-(1-(3-nitrophenyl)ethylidene) benzohydrazide (5j)

Melting point: 235 – 236 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3217, 1636, 1559; ^1H NMR (500 MHz, DMSO-d_6) δ 12.07 (s, 1H), 11.42 (s, 1H), 8.65 (s, 1H), 8.29 (m, 2H), 8.22 (d, $J = 2.0$ Hz, 1H), 7.77 (*d*, 8.0 Hz, 2H), 7.73 (dd, $J = 8.5$, 2.0 Hz, 1H), 6.89 (d, $J = 8.5$ Hz, 1H), 2.42 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.2, 156.4, 148.5, 142.0, 140.0, 139.1, 134.2, 133.3, 130.6, 124.4, 121.2, 121.1, 120.1, 82.3, 14.4; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{12}BrIN_2NaO_2$ 425.9951; Found 425.9924.

3.2.17. (E)-2-Hydroxy-N'-(1-(2-hydroxyphenyl)ethylidene)-5-iodobenzohydrazide (5k)

Melting point: 249–250 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3435, 3199, 2928, 1648, 1599; ^1H NMR (500 MHz, DMSO-d_6) δ 13.07 (s, 1H), 11.48 (s, 1H), 8.24–8.17 (m, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 6.95–6.82 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.3, 161.5, 159.1, 158.3, 157.1, 157.0, 142.4, 142.2, 138.82, 137.6, 131.9, 129.0, 120.5, 120.4, 120.1, 119.7, 119.1, 118.5, 117.8, 82.1, 81.53, 66.8, 13.8; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{13}IN_2NaO_3$ 418.9869; Found 418.9831.

3.2.18. (E)-2-Hydroxy-5-iodo-N'-(1-(pyridin-4-yl)ethylidene) benzohydrazide (5l)

Melting point: 244–245 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3451, 3247, 3071, 2884, 1663, 1548, 649; ^1H NMR (500 MHz, DMSO-d_6) δ 12.07 (s, 1H), 11.41 (s, 1H), 8.65 (d, $J = 4.5$ Hz, 2H), 8.21 (d, $J = 1.5$ Hz, 1H), 7.78 (d, $J = 5.0$ Hz, 2H), 7.74–7.69 (m, 1H), 6.88 (d, $J = 8.5$ Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.2, 156.8, 150.5, 145.3, 142.1, 139.1, 137.5, 121.0, 120.2, 82.2, 13.8; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{12}IN_3NaO_2$ 403.9872; Found 403.9770.

3.2.19. (E)-2-Hydroxy-5-iodo-N'-(1-(pyridin-3-yl)ethylidene) benzohydrazide (5m)

Melting point: 240–242 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3279, 3055, 2909, 1674, 1597, 633; ^1H NMR (500 MHz, (DMSO-d_6) δ 12.03 (s, 1H), 11.35 (s, 1H), 9.01 (s, 1H), 8.62 (s, 1H), 8.21 (s, 2H), 7.72 (d, $J = 7.5$ Hz, 1H), 7.48 (dd, $J = 7.0$, 4.8 Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.2, 156.8, 151.3, 150.6, 148.1, 142.0, 139.0, 134.3, 133.9, 124.0, 121.0, 120.1, 82.2, 14.3; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}IN_3O_2$ 382.0052; Found 382.0020.

3.2.20. (E)-2-Hydroxy-5-iodo-N'-(1-(thiophen-2-yl)ethylidene) benzohydrazide (5n)

Melting point: 267–268 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3424, 3073, 2930, 2574, 1639, 1564, 625; ^1H NMR (500 MHz, DMSO-d_6) δ 12.01 (s, 1H), 11.19 (s, 1H), 8.19 (d, $J = 2.0$ Hz, 1H), 7.71 (dd, $J = 8.5$, 2.0 Hz, 1H), 7.63 (d, $J = 5.0$ Hz, 1H), 7.55 (d, $J = 3.0$ Hz, 1H), 7.15–7.08 (m, 1H), 6.86 (d, $J = 8.5$ Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.8, 156.8, 150.1, 143.4, 141.8, 138.8, 129.7, 128.9, 128.1, 121.0, 120.1, 82.2, 14.8; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{11}IN_2NaO_2S$ 408.9484, Found 408.9345.

3.2.21. (E)-2-Hydroxy-5-iodo-N'-(1-(2-oxo-2H-chromen-3-yl)ethylidene) benzohydrazide (5o)

Melting point: 239–240 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3417, 3024, 1647, 1599, 628; ^1H NMR (500 MHz, DMSO-d_6) δ 12.07 (s, 1H), 11.39 (s, 1H), 8.30 (s, 1H), 8.22 (d, $J = 2.0$ Hz, 1H), 7.93 (d, $J = 7.5$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.69 (t, $J = 7.5$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 8.5$ Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.8, 154.0, 142.3, 142.0, 133.0, 129.8, 125.3, 121.0, 120.2, 119.3, 116.5; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{13}IN_2NaO_4$ 470.9818; Found 470.9823.

3.2.22. (E)-N'-(1-(6-bromo-2-oxo-2H-chromen-3-yl)ethylidene)-2-hydroxy-5-iodobenzohydrazide (5p)

Melting point: 249–250 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3417, 3054,

2912, 1547, 1472, 613.

^{1}H NMR (500 MHz, DMSO-d_6) δ 12.07 (s, 1H), 11.36 (s, 1H), 8.28–8.17 (m, 3H), 7.82 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.1, 159.3, 156.6, 153.0, 151.0, 146.1, 142.0, 140.8, 139.1, 137.1, 135.3, 131.7, 121.2, 120.1, 118.8, 116.8, 82.3, 16.2; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{12}BrIN_2NaO_4$ 548.8926; Found 548.8926.

3.2.23. (E)-2-Hydroxy-5-iodo-N'-(1-(6-iodo-2-oxo-2H-chromen-3-yl) ethylidene)benzohydrazide (5q)

Melting point: 262 °C; FT-IR (KBr, 4000–400 cm^{-1}): 3418, 3050, 2910, 1590, 1545, 610.

^{1}H NMR (500 MHz, DMSO-d_6) δ 12.07 (s, 1H), 11.36 (s, 1H), 8.33 (s, 1H), 8.21 (d, J = 2.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 10. Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.8, 159.3, 156.6, 153.6, 151.1, 146.9, 142.0, 140.9, 139.1, 137.7, 127.8, 121.6, 121.0, 120.1, 118.8, 89.0, 82.3, 16.3; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{12}I_2N_2NaO_4$ 596.8799; Found 596.8792.

4. Conclusions

We have developed a simple, clean, and cost-effective method for the synthesis of 2-hydroxy-5-iodo-*N*'-(1-arylethylidene)benzohydrazide. The as-prepared DES demonstrated remarkable potential catalyst/solvent; the desired products were obtained in excellent yield with short reaction time. The work-up simplicity, mild reaction conditions, high yields, and recyclability of the DES are the outstanding features of the current work.

Declarations

Author contribution statement

Phuong Tran: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

The Nguyen: Performed the experiments; Analyzed and interpreted the data.

Cong Nguyen: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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The authors declare no conflict of interest.

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