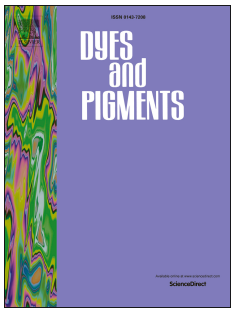
Accepted Manuscript



An environmentally friendly approach to the green synthesis of azo dyes with aryltriazenes via ionic liquid promoted C-N bonds formation

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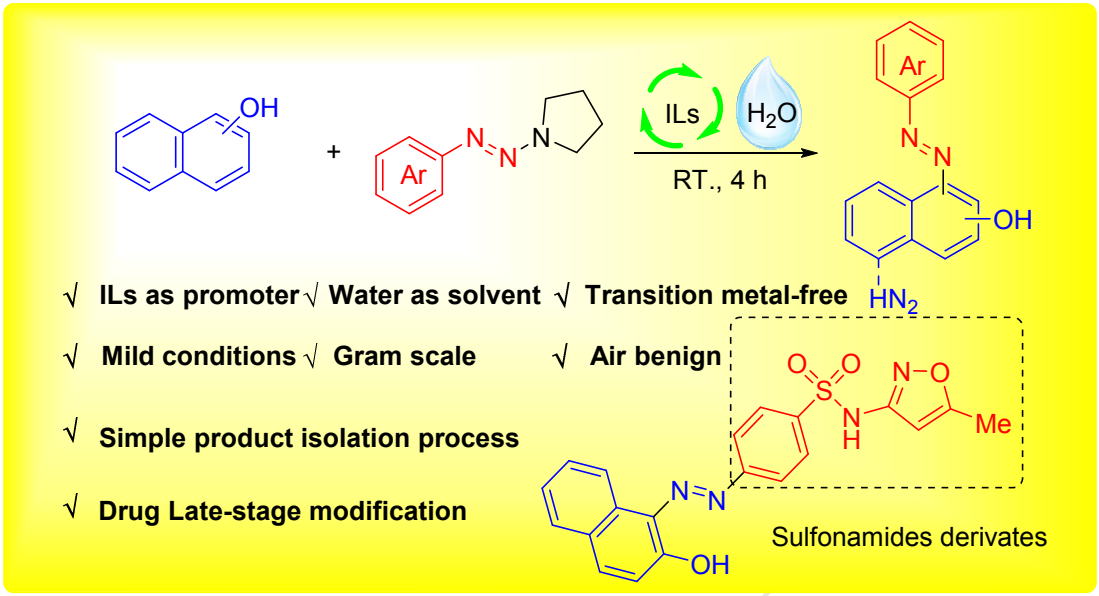

An environmentally friendly approach to the green synthesis of azo dyes with aryltriazenes via ionic liquid promoted C-N bonds formation

Yonghong Zhang[a,d*], Yonghong Liu[a], Xiaoqian Ma[a], Xia Ma[a], Bin Wang[b], Hongguang Li[c], Yan Huang[a*], Chenjiang Liu[a,b,d*]

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KEYWORDS: *azo dyes, ionic liquids, environmentally friendly, aryltriazenes*

ABSTRACT

An efficient and green approach for the synthesis of azo dyes has been developed via the Brønsted acidic ionic liquid (IL) promoted diazo coupling reaction of naphthols with aryltriazenes. The reaction was carried out with the aryltriazenes as diazotizing agents, the Brønsted acidic ionic liquids as the promoter, and water as the green solvent at room temperature under air and metal-free conditions. Notably, the attractive advantages of the process include mild conditions with excellent yields, simple product isolation process, large-scale experiment, late-stage modification of pharmaceutical and recyclability of the promoter. In addition, the UV-vis spectral characteristics of the azo-dyes were investigated in DMSO.

1. Introduction

Azo compounds are attractive targets for organic synthesis methodology due to their widespread applications in many areas of technology and medicine [1]. Particularly attractive are azo dyes, which are utilized as building blocks for dyeing textile fibers [2, 3], pharmaceuticals [4, 5], organic synthesis [5, 6], and optic/photoelectric materials [7, 8]. Because of their value in dyes, pigments and advanced materials, the construction of azo dye compounds has attracted considerable interests [1, 9-15]. Most of these protocols, however, involve harsh reaction conditions, such as low temperature, use of instability of aryl diazonium salts and toxic solvents as well as generate low yields and require long reaction times [16].

From a sustainable and green chemistry viewpoint, the use of the combination of water and ionic liquids in organic synthesis has attracted much attention in recent years [17-20]. As a green, inexpensive, non-flammable and nontoxic solvent, water has been widely used as an alternative to traditional organic solvents in organic transformations due to its fascinating advantages of low cost, environmental benignity, inherent safety, biocompatibility, unique physical and chemical properties [21-25]. On the other hand, ionic liquids (ILs) features many fascinating advantages over traditional reaction media or catalyst such as their unique physical and chemical properties of nonvolatility, thermal stability, recyclability, and tunable chemistry [26-28]. Furthermore, acidic functionalized ionic liquids have been recognized as acceptable reaction catalysts or media, which combined the catalytic advantages of Brønsted acid and unique properties of ionic liquids [29-31].

Aryltriazenes, as a very useful and versatile class of compounds with intriguing structural and chemical properties, have been extensively explored in organic synthesis due to their superior stability and reactivity [32-36]. Among these transformations, the diazotization reaction with aryltriazenes represents atom-economic strategy for C–N bond formation

[20, 37-43], compared with that utilized in arylation reaction [44-65]. However, in general, most of those reactions involving transition metal catalyst, harsh reaction conditions, volatile acid promoter and organic solvent. Recently, we developed a novel and green combination of water/ionic liquids/aryltriazenes for the synthesis of azo compounds [20]. In continuation of our interest in triazene chemistry and green organic synthesis with ionic liquilds [20, 36, 43], we envisioned that azo dyes could be synthesized by diazo coupling reaction of aryltriazene with naphthol in aqueous media under metal-free and mild conditions.

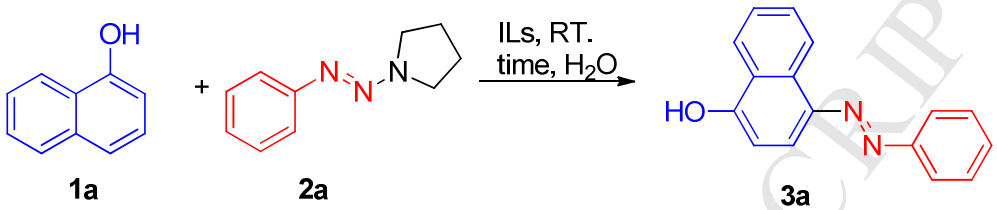
2. Results and discussion

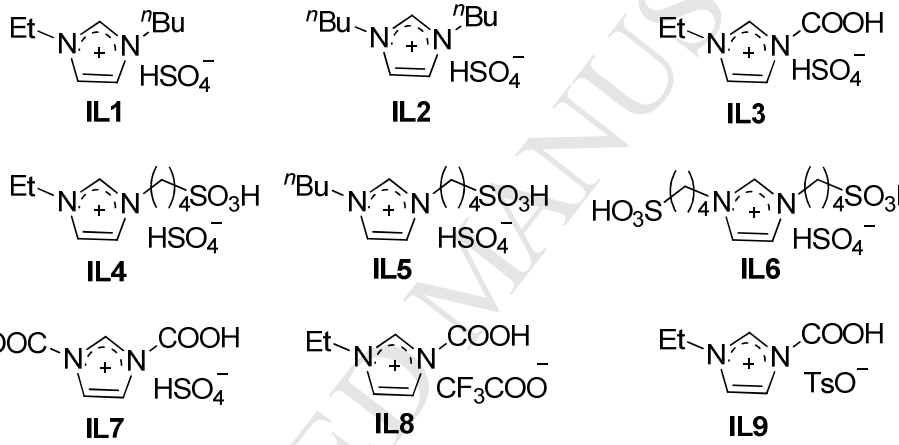
2.1 Optimization of the reaction conditions

We commenced our study using 1-phenyltriazene (**1a**) and 1-naphthol (**2a**) as model substrates (Table 1). Initially, we examined the influence of the promoter Brønsted acidic ionic liquids with different counter cations and anions (Table1, entries 1-9). The results show that **IL9** with moderate acidity was superior to the others (Table 1, entry 9), as the desired product (*E*)-4-(phenyldiazenyl)naphthalen-1-ol (**3a**) was produced in 97% isolated yield. Since ionic liquids not only act as promoter but also as a phase transfer catalyst in this reaction. As IL9 has a 4-methylbenzenesulfonate anion, it helps to enhance the solubility of the substrate. Furthermore, increasing and reducing the amount of IL9 led to a relatively lower yield. Because the increase in the amount of promoter will lead to poor selectivity and some by-products, reducing the amount of promoter will also reduce the reaction efficiency. Further study showed that only a trace amount of product was formed under solvent-free conditions, which might be due to the insolubility of the substrates and promoter (entry 12). By further screening the amount of triazene (entry 13), water (entry 14) and the reaction time (entries 15, 16), the optimum reaction conditions were obtained. The optimal reaction conditions are therefore as follows:

1-phenyltriazene (0.2 mmol), 1-naphthol (0.2 mmol), promoter **IL9** (0.2 mmol) in water (1 mL) at room temperature under air with a reaction time of 4 hours.

Table 1. Optimization of reaction conditions.





Entry[a]	Triazene	ILs/mmol	Time/h	Solvent	Yield/%[b]
1	0.2 mmol	**IL1** (0.2)	4	H_2O	79
2	0.2 mmol	**IL2** (0.2)	4	H_2O	81
3	0.2 mmol	**IL3** (0.2)	4	H_2O	83
4	0.2 mmol	**IL4** (0.2)	4	H_2O	80
5	0.2 mmol	**IL5** (0.2)	4	H_2O	67
6	0.2 mmol	**IL6** (0.2)	4	H_2O	73
7	0.2 mmol	**IL7** (0.2)	4	H_2O	76
8	0.2 mmol	**IL8** (0.2)	4	H_2O	70
9	0.2 mmol	**IL9** (0.2)	4	H_2O	97

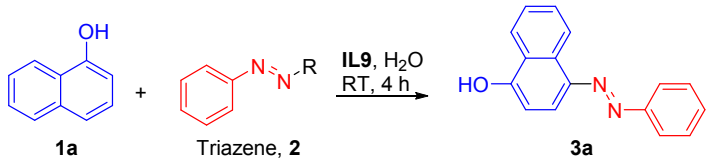
10	0.2 mmol	**IL9** (0.22)	4	H_2O	94
11	0.2 mmol	**IL9** (0.16)	4	H_2O	90
12	0.2 mmol	**IL9** (0.2)	4	-	Trace
13	0.22 mmol	**IL9** (0.2)	4	H_2O	94
14	0.2 mmol	**IL9** (0.2)	4	H_2O 0.5 mL	95
15	0.2 mmol	**IL9** (0.2)	3	H_2O	91
16	0.2 mmol	**IL9** (0.2)	5	H_2O	98

[a] Conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **IL** (0.2 mmol), H_2O (1 mL), at room temperature, 4 h; [b] Isolated yields.

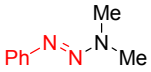
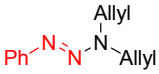
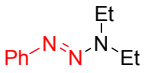
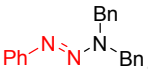
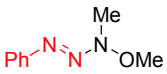
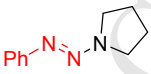
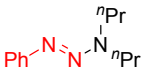
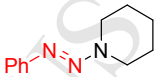
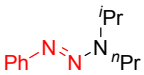
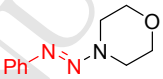
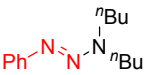
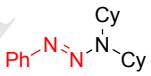
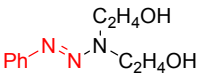
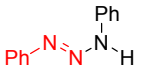
2.2 Optimization of *N*-substituted 1-aryltriazenes

Under the optimized conditions, we firstly optimized the *N*-substituted groups of 1-phenyltriazenes (Table 2). For acyclic substitution, the substrates with various linear and branched chains, such as diethyl-, dimethyl-, methoxy-methyl-, dipropyl-, diisopropyl- and dibutyl-amino groups, could produce the desired product in good yields (entries 1-7). Furthermore, both free alcohol (entry 7) and diversified reactive groups (entries 8, 9) were tolerated as *N*-substituents in this transformation. Besides acyclic substituents, cyclic ones were also scrutinized (entries 10-13) and found that the ring size exhibited almost no obvious influence on the reaction efficiency (entries 10, 11). The cyclic *N*-morpholinyl group, which containing an additional heteroatom, also provided a good yield (entry 12). What's more, the compound with two separate cyclohexyl rings on the nitrogen atom was efficient as well (entry 13). Besides the sp^3 substituent groups, the sp^2 ones could also afforded the desired product in good yield (entry 14). Consequently, (*E*)-1-(phenyldiazenyl)pyrrolidine (**2a**) was chosen as the optimal as diazotizing agents with pyrrolidinyl as leaving group.

Table 2. Optimization of *N*-substituted 1-pheyltriazenes.



1a Triazene, **2** **3a**

Entry[a]	Triazene	yield[b]	Entry[a]	Triazene	yield[b]
1		80%	8		65%
2		84%	9		82%
3		82%	10		97%
4		85%	11		92%
5		88%	12		89%
6		86%	13		85%
7		70%	14		73%

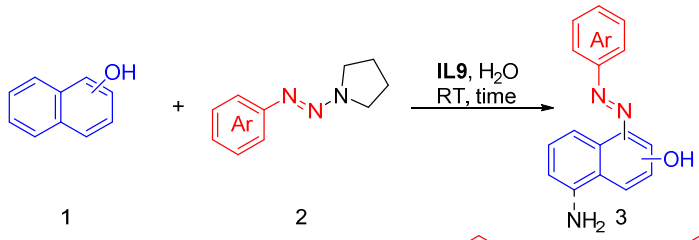
[a] Conditions: **1a** (0.2 mmol), **2** (0.2 mmol), **IL9** (0.2 mmol), H_2O (1 mL), at room temperature, 4 h; [b] Isolated yields.

2.3 **Substrate scope of naphthol and 1-aryltriazenes**

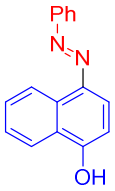
Once different *N*-substituted groups of 1-pheyltriazenes were systematically investigated, we moved to examine the substrate scope of naphthol and 1-aryltriazenes with different aryl substitutions (Table 3). First, different naphthols were tested. Both 1-naphthol and 2-naphthol could afford the corresponding azo dyes in excellent yields. Subsequently, 2-naphthol **1b** was then selected as ideal coupling partners for the coupling reactions with various aryltriazenes. 1-Aryltriazenes bearing a broad range of different *ortho*, *meta*, and *para* substituents were all compatible under the optimized conditions to afford the corresponding azo products in good to excellent yields. The nature of the substituents on

the benzene rings of aryltriazenes had no obvious effects on the effciency of the reaction. A series of functional groups, such as methyl (**3c**, **3f**, **3h**), methoxy (**3d**, **3k**), *iso*-propyl (**3n**), *tert*-butyl (**3i**), trifluoromethyl (**3n**), fluoro (**3e**, **3l**), chloro (**3g**), and carboxyl acid (**3o**) were tolerated under the optimal reaction conditions, and the desired products were obtained in 83-99% yields. Bearing a strong electron-withdrawing group like trifluoromethyl (**3n**), and carboxyl acid (**3p**) gave lower yields than other *para*-substituted compounds under modified reaction conditions. It is worth mentioning that the substrates with halogen substitutions at different positions of phenyl ring of triazenes could be well transformed (**3e**, **3l**, **3g**, **3m**), which showed that this method has great potential in further transformation. In addition, the compound containing an active hydrogen group, such as carboxyl acid (**3o**), also performed well, which is a big challenge under many common coupling reactions. Polysubstituted triazene could also afford desired product (**3p**) in good yield, which shown that the steric hindrance have seldom effect. Besides mono-substituted naphthols, multi-substituted naphthol was also studied, 5-amino-1-naphthol can be reacted with 2 equivalent of phenyl triazene to afforded 5-amino-4,8-bis((*E*)-phenyldiazenyl)naphthalen-1-ol with 33% isolated yield (**4a**). The UV-visible absorption spectra of these dyes were measured by a UV-vis spectrometer in DMSO at a concentration of 1×10^{-5} $molL^{-1}$ (Table 3, SI). As expected, these arylazo-substituted naphthols all have strong light absorptivity in visible range. The maximum absorption band of each dyes appeares in 400-600 nm with a large molar absorption coefficient ($\varepsilon > 10^4$ $Lmol^{-1}cm^{-1}$) at the corresponding peaks, which is fully matches the reported results in the literature [66].

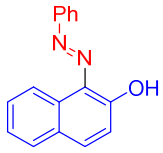
Table 3. Substrate scope of the Brønsted acidic ionic liquid promoted diazenylation of naphthol with various substituted aryltriazenes.



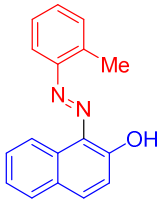
1 2 3



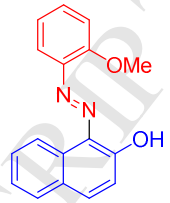
3a, 97%, RT, 4 h
$\lambda_{max,abs}$ = 498 nm



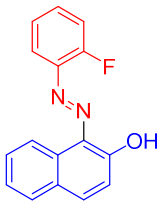
3b, 98%, RT, 4 h
$\lambda_{max,abs}$ = 482 nm



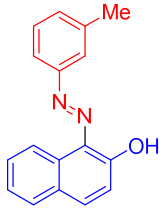
3c, 99%, RT, 4 h
$\lambda_{max,abs}$ = 490 nm



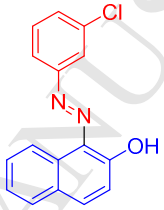
3d, 99%, RT, 4 h
$\lambda_{max,abs}$ = 500 nm



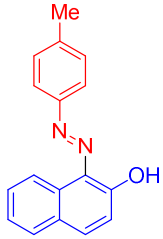
3e, 89%, 60 °C, 2.5 h
$\lambda_{max,abs}$ = 480 nm



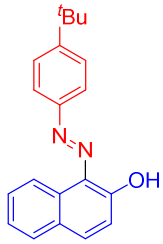
3f, 98%, RT, 4 h
$\lambda_{max,abs}$ = 484 nm



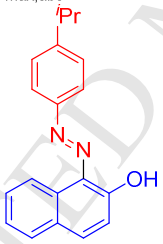
3g, 98%, RT, 4 h
$\lambda_{max,abs}$ = 480 nm



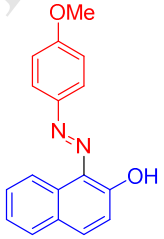
3h, 99%, RT, 4 h
$\lambda_{max,abs}$ = 480 nm



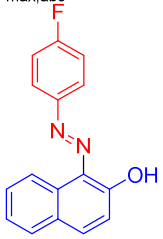
3i, 99%, RT, 12 h
$\lambda_{max,abs}$ = 486 nm



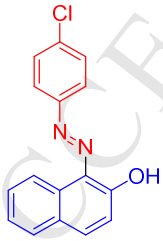
3j, 94%, RT, 4 h
$\lambda_{max,abs}$ = 486 nm



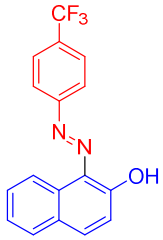
3k, 99%, RT, 4 h
$\lambda_{max,abs}$ = 464 nm



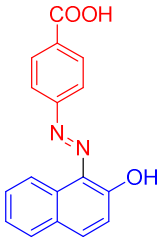
3l, 96%, RT, 12 h
$\lambda_{max,abs}$ = 464 nm



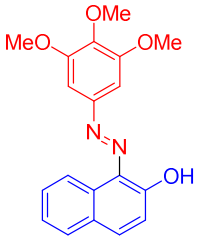
3m, 98%, RT, 12 h
$\lambda_{max,abs}$ = 482 nm



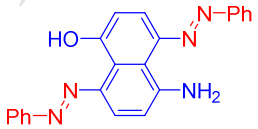
3n, 93%, 80 °C, 12h
$\lambda_{max,abs}$ = 478 nm



3o, 83%, 80°C, 12h
$\lambda_{max,abs}$ = 474 nm



3p, 96%, RT, 3 h
$\lambda_{max,abs}$ = 480 nm

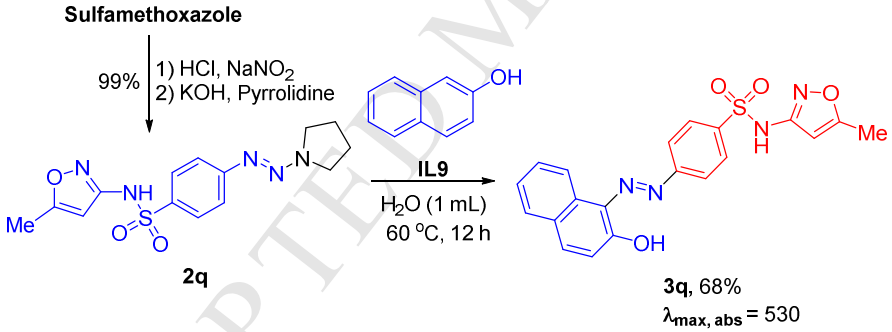


4a, 33%, 60 °C, 12 h
$\lambda_{max,abs}$ = 482 nm

[a] Reaction condition: 0.2 mmol of **1** and 0.2 mmol of **2** in the presence of **IL9** (0.2 mmol) in H_2O (1 mL) at room temperature for 4 h.

2.4 **Pharmaceutical derivatives late-stage diazenylation reaction**

To determine the practical utility of this protocol, we undertook a late-stage diazenylation reaction of drug molecule for the purposes of preparing pharmaceutical derivatives (Scheme 1). As a useful bacteriostatic antibiotic, sulfamethoxazole was smoothly converted into the corresponding (*E*)-*N*-(5-methylisoxazol-3-yl)-4-(pyrrolidin-1-yldiazenyl)benzenesulfonamide **2q** in quantitative yield. Upon subject this triazene-based drug to our diazenylation protocol, (*E*)-4-((2-hydroxynaphthalen-1-yl)diazenyl)-*N*-(5-methylisoxazol-3-yl)benzenesulfonamide **3q** was obtained in 68% yield. This synthetic method demonstrates the applicability of this diazenylation protocol for efficient preparation of lead compounds.

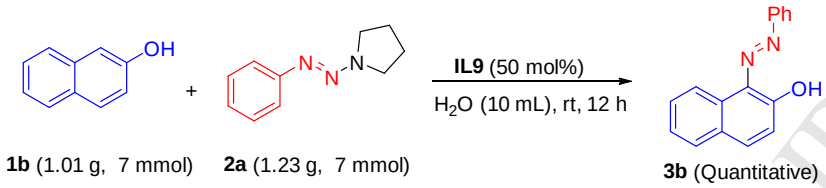


Scheme 1. Pharmaceutical derivatives late-stage diazenylation reaction.

2.5 **Gram scale experiment**

In order to further demonstrate the practicability of this direct diazenylation protocol, gram-scale operation was carried out under modified reaction conditions. When the reaction of naphthalen-2-ol **1b** and phenyl triazene **2a** was enlarged to 7.0 mmol scale, the desired azo dye **3b** was obtained in quantitative yield under these green and easily

handled reaction conditions, in which 50 mol% of the promoter **IL9** and 10 mL water was sufficient (Scheme 2).



1b (1.01 g, 7 mmol) **2a** (1.23 g, 7 mmol) **3b** (Quantitative)

Scheme 2. Gram scale experiment for the synthesis of (*E*)-1-(phenyldiazenyl)naphthalen-2-ol.

2.6 **Recycling of IL9 in the synthesis azo dye 3b**

Stability and recyclability are crucial features for any ILs as a recyclable catalyst and media. In addition to the obvious environmentally friendly advantages, the use of recyclable ILs can considerably facilitate product purification. As shown in the diazenylation of 2-naphthol, our green promoter **IL9** is highly stable and is conveniently recycled and reused for at least six times without any significant loss of activity (Figure 1). Following each cycle, the product was isolated by direct filtration, and the **IL9** was recovered from the aqueous layer and reused for the next run after drying in vacuo. For the first cycle, the activity of **IL9** remained the same. In the subsequent cycles, the desired products could be obtained with high yields by extension of the reaction time from 4 to 6, 8 and 12 h. After that, slight decrease of activity is observed.

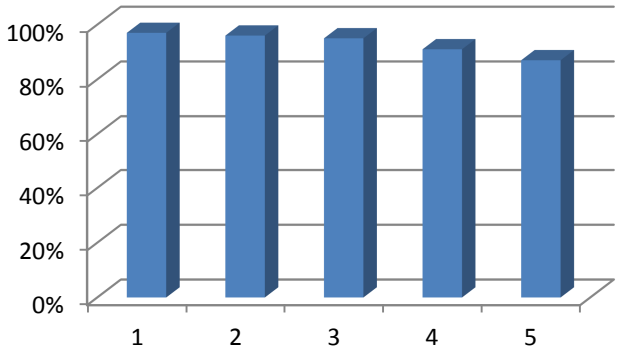
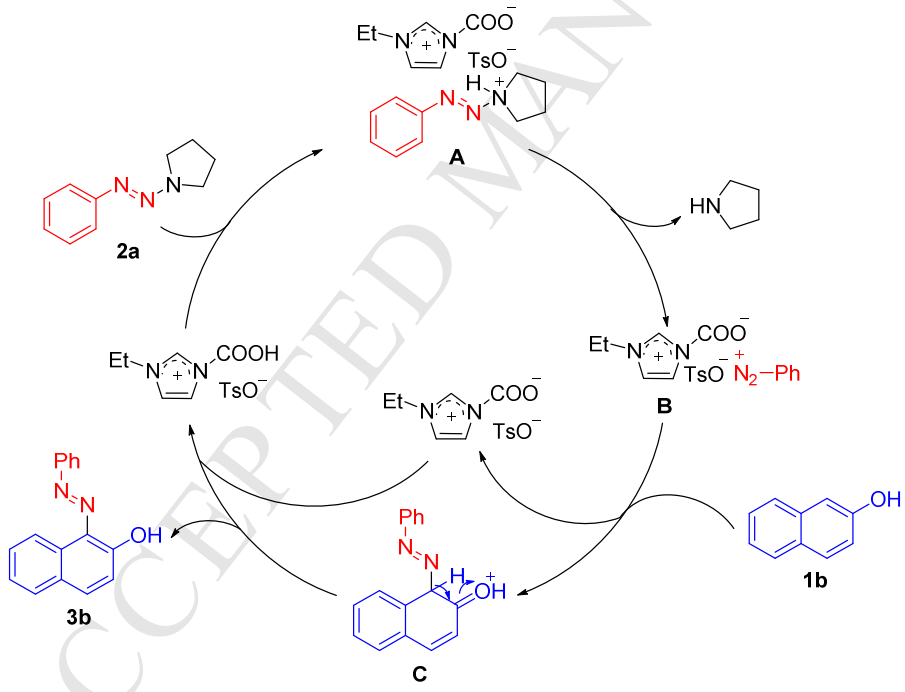


Figure 1. Recycling of **IL9** in the synthesis azo dye **3b**.

2.7 **Proposed reaction mechanism**

According to our previous work [20, 43], a plausible reaction pathway is proposed (Scheme 4). Initially, triazene **2a** was activated by Brønsted acidic **IL9** to afford ammonium salt **A**. Subsequently, intermediate **A** was then transformed into a soluble *N*-electrophilic, IL anion/phenyldiazonium cation ion pair **B** by the release of pyrrolidine. This species could react with nucleophilic naphthol derivatives to provide intermediate **C**. Finally, product **3b** was generated by the deprotonation of **C**, and promoter **IL9** was regenerated at same time.



Scheme 4. Proposed reaction mechanism

3. Experimental Section

3.1 Typical reaction procedure for the synthesis of azo dyes

A mixture of Brønsted acidic ionic liquid (0.20 mmol), naphthol (0.20 mmol), aryltriazene (0.20 mmol) and H_2O (1 mL) was added to a tube (25 mL), and then the mixture stirred at room temperature, some substrate bearing strong electron-withdrawing group need elevate temperature and prolong reaction time to improve yield. Reaction was monitored by TLC plate. After the reaction was complete, the resulting yellow precipitate isolated by filtration, the damp solid was washed with water (5 mL × 3) and cold ethanol (2 mL). The filter cake was dried in vacuo, and then the desired product azo dyes were obtained. If the product was oil, after the reaction was complete, water (5 mL) was added to the mixture, the mixture was extracted with EtOAc (5 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (2 mL ×x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product.

3.2 Pharmaceutical derivatives late-stage diazenylation reaction

A mixture of **IL9** (62.6 mg, 0.20 mmol), **1b** (28.8 mg, 0.20 mmol), **2q** (66.7 mg, 0.20 mmol) and H_2O (1 mL) was added to a tube (25 mL), and then the mixture stirred at 60 ^oC for 8 h. After the reaction was complete, the resulting precipitate isolated by filtration, the damp solid was washed with water (5 mL x 3) and ethanol (5 mL x 3) respectively, after drying in vacuo afford the desired product (*E*)-4-((1-hydroxynaphthalen-2-yl)diazenyl)-*N*-(5-methylisoxazol-3-yl)benzenesulfonamide **3q**: red solid (yield: 68%).

3.3 **Gram scale reaction**

(a) **IL9** dissolved in water; (b) The mixture of **IL9** and **1b**; (c) Reaction mixture **IL9, 1b** and **2a**;

(d) Reaction mixture (after reaction); (e) The product isolated by direct filtration; (f) The recovered **IL9** in aqueous.

To a 25 mL round-bottom flask was added **IL9** (1.10 g, 3.5 mmol), **1b** (1. 01 g, 7.0 mmol), **2a** (1. 23 g, 7.0 mmol) and H_2O (10 mL) sequentially, then the mixture was stirred at room temperature for 12 h. After the reaction was complete, the resulting precipitate isolated by filtration, the damp solid was recrystallized from EtOH to afford the corresponding product in quantitative yield.

3.4 **Recycling experiments**

A mixture of **IL9** (62.6 mg, 0.20 mmol), **1b** (28.8 mg, 0.20 mmol), **2a** (35.0 mg, 0.20 mmol), and H_2O (1 mL) was added to a tube (25 mL), and then the mixture stirred at room temperature for 1 h. After the reaction was complete, water (5 mL) was added to the mixture, the mixture was extracted with EtOAc (5 mL×3), and then the separated **IL9** from the water layer was reused for

the next reaction after drying in vacuo. The combined organic layer was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (2 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 20:1) to afford the desired product **3b**.

3.5 **UV–visible absorption spectra**

The UV–visible absorption spectra (200-800 nm) of azo dyes was measured by a UV-5300PC spectrophotometer in DMSO at concentration of 1×10^{-5} mol·L^{-1} at 25 ^{o}C.

4. Conclusions

In summary, we have developed an efficient and green method for the synthesis of azo dyes from aryltriazene and naphthol. The reaction was carried out with aryltriazenes as azo source, warer as green solvent, and Brønsted acidic ionic liquid as recyclable promoter at room temperature under mild conditions. Notably, Late-stage diazenylation of drugs and gram-scale operations were systematically established under mild conditions. Furthermore, the promoter **IL9** could be conveniently recycled and reused with the same efficacies for at least five cycles. The simple preparation of the starting material, a novel azo source, a cheap catalyst and the fairly mild reaction conditions without volatile organic solvents make this process effective and convenient for organic synthesis and industrial applications.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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Highlights

- Ionic liquid promoted diazo coupling reaction for the synthesis of azo dyes
- This green method featuring mild conditions, high yields and simple isolation process
- Drug modification and scale-up process demonstrate the practicability of the protocol