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Ultrasound-promoted Brønsted acid ionic liquid-catalyzed hydrothiocyanation of activated alkynes under minimal solvent conditions†

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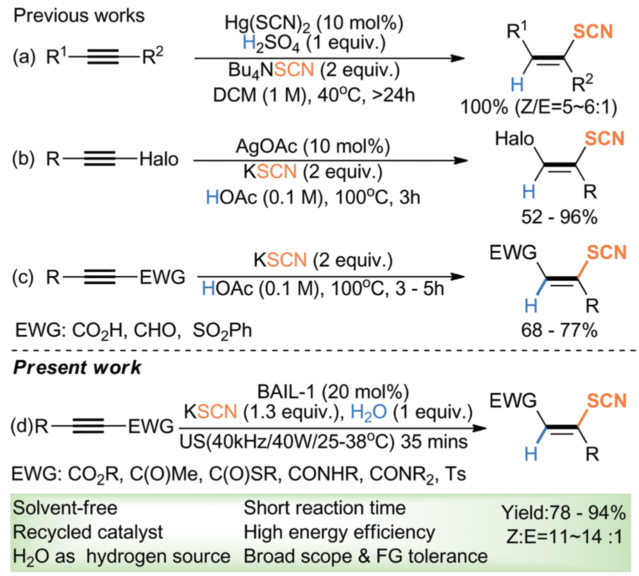
By using water as the hydrogen source, an eco-friendly and practical protocol for the synthesis of *Z*-vinyl thiocyanates through ultrasound-promoted Brønsted acid ionic liquid-catalyzed hydrothiocyanation of activated alkynes under minimal solvent conditions has been developed. This process effectively avoids the use of organic solvents, metal catalysts and harsh reaction conditions. This reaction shows attractive characteristics such as operational simplicity, broad substrate scope with good to excellent yields, ease of scale-up and high energy efficiency and recyclable and reusable catalysts.

Introduction

Sulphur-containing organic compounds are extremely valuable because of their abundance in numerous natural products, pharmaceuticals and agrochemicals.[1] Among them, organic thiocyanates not only display a variety of biological activities but also serve as versatile building blocks and synthetic intermediates in organic synthesis.[2] Over the past few decades, many impressive achievements have been made in the preparation of alkyl and aromatic thiocyanates.[2a,b,3] However, the construction of vinyl thiocyanates,[4] especially for thermodynamically unfavored *Z* isomers has rarely been achieved. A conventional method for the preparation of vinyl thiocyanates is the nucleophilic substitution of vinyl halides with thiocyanate salts.[5] However, the pre-installation of a halogen atom at an expected position remains a formidable challenge. In 1985, Cousseau first reported the synthesis of vinyl thiocyanates through Hg(II)-catalyzed thiocyanation of alkynes with Bu_4NSCN and H_2SO_4 in dichloromethane (Scheme 1a).[6] However, this strategy suffers from the usage of toxic metal catalysts, the limitations of the substrate scope, low atom economy and *Z*/*E* selectivity. Jiang and Wu reported silver-catalyzed thiocyanation of haloalkynes with KSCN at 100 °C in acetic acid to give *Z*-vinyl thiocyanates (Scheme 1b).[7] Maddi Sridhar Reddy treated electron-deficient alkynes with KSCN at 100 °C in acetic acid to form *Z*-vinyl thiocyanates.[8] Although these methods are representative of considerably advanced methods, both approaches employed a large amount of acetic acid as the reaction medium and a hydrogen source as well as a high temperature to facilitate the hydrothiocyanation, which requires an excess amount of an inorganic base to neutralize the acidic solution leading to not only environmental issues



Scheme 1 Synthesis of *Z*-vinyl thiocyanates.

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but also high cost. Therefore, the development of an eco-friendly and efficient methodology for the construction of *Z*-vinyl thiocyanates is highly desirable.

With its natural abundance, low cost and eco-friendly properties, water has been an attractive solvent[9] and reagent[10] for many organic synthesis reactions. We are well aware that in the presence of activated alkenes or alkynes, water can be used as the hydrogen source (generated *in situ* from self-ionization of water) for sulfa-Michael addition. For example, Wang *et al.* have pioneered the aqueous sulfonylation of activated alkenes with water as the H-atom source under mild conditions to afford various mono-substituted ethyl sulfones.[11] Recently, our group reported the aqueous sulfonylation reactions of activated alkynes with water as the hydrogen source.[12] However, excessive activated alkenes or activated alkynes are required in these transformations, which result in considerable waste of starting materials, increased cost and environmental burden. To the best of our knowledge, there exists no example of hydrothiocyanation of electron-deficient alkynes with water as the hydrogen source under eco-friendly reaction conditions.

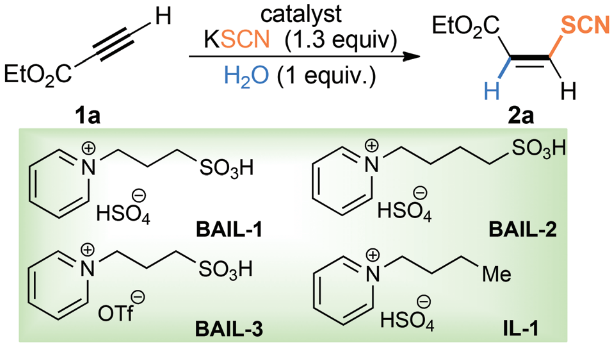
Brønsted acid ionic liquid (BAIL) catalyzed reaction has drawn increased attention in recent years.[13] These reactions usually require minimal solvent, since a mixture composed of BAIL, substrate, and product plays the role of a solvent, and the BAIL catalyst can be easily recycled. In light of the above-mentioned points and also in continuation of our ongoing research in green organic synthesis,[14] we herein report for the first time the ultrasound-promoted (Principle 6, design for energy efficiency) Brønsted acid ionic liquid-catalyzed (Principle 7, use of renewable feedstocks and Principle 9, catalysis) hydrothiocyanation of activated alkynes with water as a hydrogen source (Principle 5, safer solvents and auxiliaries) under minimal solvent conditions (Principle 1, prevention), affording the corresponding vinyl thiocyanates in good *Z*-selectivity (Scheme 1d).

Results and discussion

Initially, we conducted the hydrothiocyanation of ethyl propiolate (**1a**) using KSCN (1.3 equiv.) with acetic acid (1 equiv.) as the promoter in water (1 mL) at room temperature, and a 28% yield of (*Z*)-ethyl 3-thiocyanatoacrylate (**2a**) and a 4% yield of propiolic acid as the by-product based on 32% conversion of the starting material **1a** were obtained after 12 hours (Table 1, entry 1). Further investigation indicated that the employment of common protonic acids (TFA, $PhCO_2H$, TsOH and HCl) brought a trace amount or poor yields of **2a** (entries 2–5). Fortunately, the first breakthrough was achieved when **1a** was treated with KSCN (1.3 equiv.), BAIL-1 (1 equiv.) and water (1 equiv.) at room temperature under minimal solvent conditions (entry 6). Encouraged by this result, various ionic-liquids were further investigated. As anticipated, the ionic liquid played a pivotal role in the outcome of the process, since related acidic ionic-liquid other than BAIL-1 resulted in lower yields (entries 7 and 8), and no expected product was produced when employing aprotic ionic liquids (entries 9 and 10). We were pleased to find that decreasing the loading of BAIL-1 from stoichiometric to catalytic amounts (20 mol%) did not affect the reaction outcome (entries 6 *vs.* 11 and 12). However, a further decrease of BAIL-1 loading to 10 mol% resulted in a low yield of **2a** (entry 13). Changing KSCN to NaSCN or NH_4SCN produced a slightly lower yield of **2a** (entries 14 and 15, respectively). The increase in the amounts of KSCN (1.3 equiv. → 1.5 equiv.), **1a** (1 equiv. → 3.5 equiv.) and water (1 equiv. → 3 equiv.) as well as the reaction temperature elevation (r.t. → 60 °C) did not appear to significantly improve the outcomes (entries 16–19). It was clear that conventional stirring was not ideal to promote this chemical process. By copying the best conventional stirring conditions (entry 12), the multicomponent reaction was further optimized by ultrasonic radiation. To our delight, ultrasonic radiation (40 kHz/40 W) employed under the same reaction parameters for 35 minutes resulted in 95% yield. This preferable result may be attributed to the cavitation effect of ultrasound irradiation.[15] Subsequent evaluation on the effect of ultrasonic power and frequency revealed that such reaction is sensitive to ultrasonic radiation energy variation (entries 20–24) and 40 kHz/40 W was appropriate for the hydrothiocyanation reaction (entry 20). No reaction occurred in the absence of Brønsted acid, and the starting material **1a** was quantitatively recovered (entry 25).

Using the optimal reaction conditions, we investigated various electron-deficient alkynes so as to gauge the scope of this hydrothiocyanation reaction. To our delight, propargylic carboxylates with various carbon chain lengths and isomeric structures smoothly undergo hydrothiocyanation to deliver the *Z*-thiocyano enoates in excellent yields (**2a**–**2o**). Meanwhile, many valuable functional groups such as alkyl (**2a**–**2d**), benzyl (**2e**), phenemyl (**2f**), cyclohexyl (**2g**), phenyl (**2h**), free OH (**2i**), ether (**2j** and **2k**), sulfonate ester (**2l**), cyano (**2m**), bromine (**2n**) and azide group (**2o**) were well compatible with the optimal reaction conditions. The hydrothiocyanation of the polycyclic and heteroaromatic motifs proceeded well to produce the expected products in good to excellent yields (**2p**–**2s**), thus further enhancing the synthetic utility of our present protocol. A series of natural product derivatives underwent the present reaction well, generating the target products in good yields (**2t**–**2v**). In addition, the reaction also permitted the use of thermodynamically more stable internal propargylic carboxylates, and good yields were obtained (**2w**–**2aa**). Neither the steric factor nor the electronic effect of β-substituted ethyl propiolate had significant influence on this difunctionalization reaction. It is worth noting that acetylenes substituted with electron-withdrawing groups, such as acetyl (**2ab**), thioester (**2ac** and **2ad**), amide (**2ae**–**2ag**) and sulfonic ester (**2ah**), all produced the desired products in good to excellent yields, which highlighted this difunctionalization reaction as a useful approach for producing various vinyl thiocyanates. No reaction occurred when ethyl 3-phenylpropiolate was used as the substrate. The hydrothiocyanation of propiolaldehyde or propiolic acid gave a trace amount of the corresponding thiocyanated product.

Table 1 Optimization of reaction conditions[a]



Entry	Acid (equiv.)	Conditions	Con.[b] (%)	Yield[b] (%)	Z/E[b]
1	HOAc (1)	Stirring, r.t., 12 h	32	28	12/1
2[c]	TFA (1)	Stirring, r.t., 12 h	Trace	Trace	—
3[c]	$PhCO_2H$ (1)	Stirring, r.t., 12 h	25	18	10/1
4[c]	TsOH (1)	Stirring, r.t., 12 h	27	20	12/1
5[c]	HCl (1)	Stirring, r.t., 12 h	38	31	11/1
6	BAIL-1 (1)	Stirring, r.t., 12 h	54	44	12/1
7	BAIL-2 (1)	Stirring, r.t., 12 h	39	33	11/1
8	BAIL-3 (1)	Stirring, r.t., 12 h	20	15	11/1
9	IL-1 (1)	Stirring, r.t., 12 h	0	N.D	N.D
10	IL-2 (1)	Stirring, r.t., 12 h	0	N.D	N.D
11	BAIL-1 (0.5)	Stirring, r.t., 12 h	52	44	13/1
12	BAIL-1 (0.2)	Stirring, r.t., 12 h	54	44	12/1
13	BAIL-1 (0.1)	Stirring, r.t., 12 h	40	32	13/1
14[d]	BAIL-1 (0.2)	Stirring, r.t., 12 h	44	37	12/1
15[e]	BAIL-1 (0.2)	Stirring, r.t., 12 h	40	32	12/1
16[f]	BAIL-1 (0.2)	Stirring, r.t., 12 h	51	44	13/1
17[g]	BAIL-1 (0.2)	Stirring, r.t., 12 h	48	37	12/1
18[h]	BAIL-1 (0.2)	Stirring, r.t., 12 h	51	42	13/1
19	BAIL-1 (0.2)	Stirring, 60 °C, 12 h	55	43	11/1
20	**BAIL-1 (0.2)**	**US (40 kHz/40 W/25–38 °C), 35 min**	**99**	**95**	**13/1**
21	BAIL-1 (0.2)	US (40 kHz/50 W/25–42 °C), 35 min	99	95	13/1
22	BAIL-1 (0.2)	US (40 kHz/30 W/25–36 °C), 35 min	89	84	13/1
23	BAIL-1 (0.2)	US (28 kHz/40 W/25–38 °C), 35 min	76	69	13/1
24	BAIL-1 (0.2)	US (68 kHz/40 W/25–43 °C), 35 min	99	94	11/1
25	—	US (40 kHz/40 W/25–38 °C), 35 min	0	N.D	N.D

[a] Unless otherwise specified, the reactions were carried out in a vial in the presence of **1a** (0.1 mmol), KSCN (0.13 mmol), water (1 equiv.) and acid. The temperatures of ultrasonic reactions (entries 20–25) were detected by using a thermometer. [b] Estimated by ^1H NMR using diethyl phthalate as an internal reference. [c] 1 ml water was used as the solvent. [d] 1.3 equiv. of NaSCN was used. [e] 1.3 equiv. of NH_4SCN was used. [f] 1.5 equiv. of KSCN. [g] 3.5 equiv. of **1a** and 1 equiv. of KSCN were used. [h] 3 equiv. of H_2O was used. IL-2: [Emim][OTf].

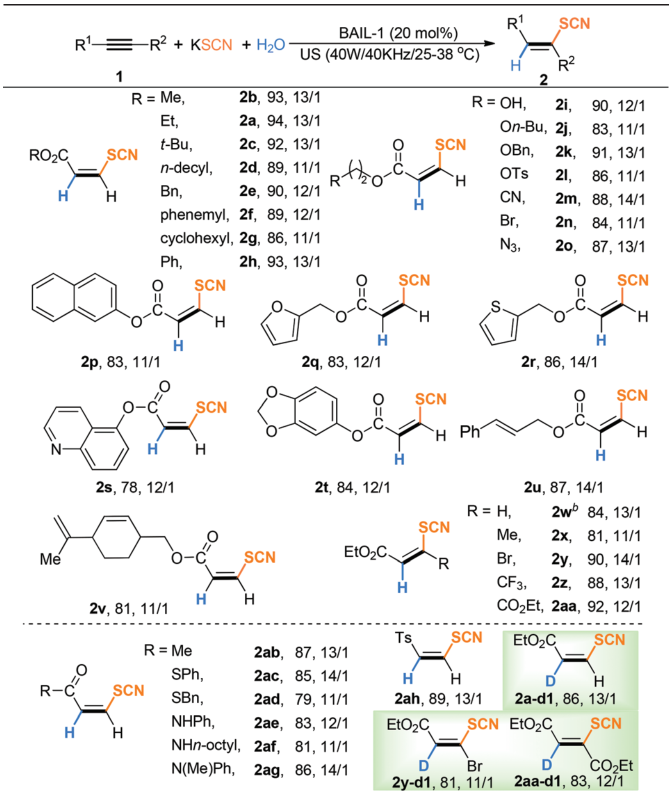
Deuterated vinyl compounds are important synthons for the construction of various deuterium labelled products, which are widely utilized in a variety of scientific fields like reaction mechanism research and biological research. Considering that deuteroxide is undoubtedly the cheapest deuterium source and is easy to handle, we performed the hydrothiocyanation reaction with D_2O as the D-atom source. Pleasingly, the desired β-deuterated vinyl thiocyanates (Table 2, **2a–d1**, **2y–d1** and **2aa–d1**) exclusively formed in excellent yield. These results clearly demonstrate that this protocol is amenable for the synthesis of deuterated vinyl compounds.

Once the substrate scope of this hydrothiocyanation reaction was established, it was important to evaluate the practical applicability of this green chemical process. Performing the reaction of **1a** (10 mmol) under optimal conditions provided the expected **2a** in 93% yield with high purity *via* simple filtration. From the viewpoint of resource reutilization and environmental benignancy, the employment of a catalyst would be favorable with simple separation and reuse. Therefore, the recyclability and reusability of BAIL-1 was evaluated under the standard conditions. At the end of each circulation, the catalyst was recycled through simple filtration and reused for the next run. This process could be repeated five times without significant influence on the yield of **2a** (Scheme 2).

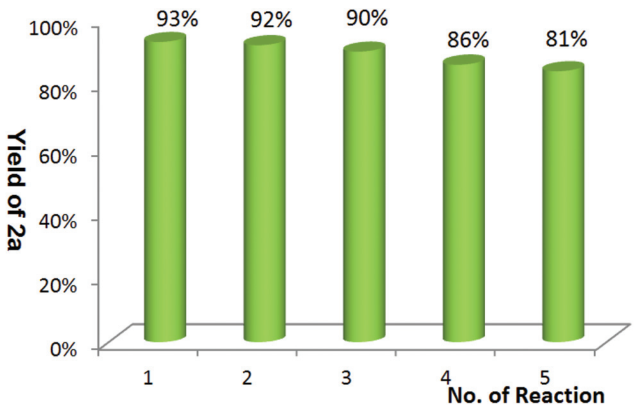
The energy expenditure for this ultrasound-promoted reaction was calculated. Compared with the traditional stirring procedure (1.3×10^3 kJ), the present ultrasound-promoted process has a lower amount of energy expenditure (84 kJ).[16]

To gain some insight into the hydrothiocyanation reaction, we performed several controlled experiments. It was found that the addition of a radical scavenger (2 equiv. of TEMPO or

Table 2 Reaction scope[a]

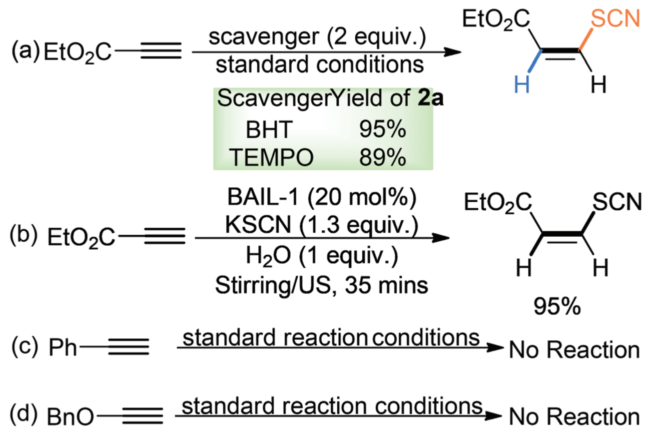


[a] All reactions were carried out in a vial in the presence of **1** (0.2 mmol), BAIL-1 (0.04 mmol), KSCN (0.26 mmol), H_2O (0.2 mmol), ultrasound conditions; isolated yields are reported. [b] Reactant is ethyl 3-(trimethylsilyl)propiolate.

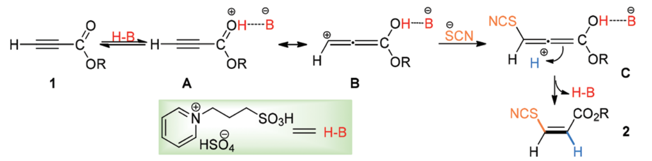


Scheme 2 Reusability of BAIL-1. Conditions: **1a** (10 mmol), BAIL-1 (2 mmol), KSCN (13 mmol), H_2O (10 mmol), ultrasound conditions, GC yields were reported.

BHT) had no effect on the reaction outcome, suggesting that a single electron transfer process might not be involved in this hydrothiocyanation reaction (Scheme 3a). When the hydrothiocyanation reaction was carried out under stirring and ultrasound mixing conditions, the yield of product **2a** was formed without any change. Taken together, these results convinced us that the ultrasound irradiation plays a key mechanical role in the transformation (Scheme 3b). No reaction occurred when phenylacetylene and ((ethynyloxy)methyl)benzene were used as the substrates (Scheme 3c and d), demonstrating that the electron-withdrawing group is essential for this reaction.



Scheme 3 Control experiments.



Scheme 4 Possible reaction mechanism.

According to the aforementioned experimental results and literature reports,[17] the presence of an acid is the key condition of this sulfa-Michael reaction. Initially, the activated alkyne **1** was reversibly protonated by the BAIL to generate a cationic intermediate **A**, which further tautomerized into the zwitterionic complex **B**. The nucleophilic thiocyanate ion attacked the β-carbon of intermediate **B** to produce an intermediate **C**. Finally, the capture of a proton which is dissociated from water by ultrasonic radiation occurred from the less hindered face of intermediate **C**, *trans* to SCN, thus leading to *Z*-vinyl thiocyanates **2** (Scheme 4).

Conclusions

In conclusion, we report for the first time the synthesis of *Z*-vinyl thiocyanates through ultrasound-promoted Brønsted acid ionic liquid-catalyzed hydrothiocyanation of activated alkynes with KSCN and water as the hydrogen source under minimal solvent conditions. In sharp contrast to traditional heating-conditions, the employment of ultrasonic radiation not only enhanced the reaction rate and efficiency but also reduced the side reactions. The desired products and catalyst can be readily separated by suction filtration. Other features of the process are as follows: (1) the abundance and accessibility of raw materials; (2) the usage of recyclable and reusable catalysts; (3) a wide substrate scope with good to high yields; (4) ease of scale-up; and (5) high energy efficiency. In addition, the reaction opens up a new avenue for cheap, convenient, and green synthesis of deuterium-labeled alkenes.

Conflicts of interest

There are no conflicts to declare.

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