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Brönsted acid-surfactant-combined ionic liquid catalyzed green synthesis of 2-alkyl and 2-arylbenzothiazoles in water: Reusable catalyst and metal-free conditions

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ABSTRACT

An efficient Brönsted acid-surfactant-combined ionic liquid (BASILs) catalyzed cyclocondensation of 2-aminothiophenol with a variety of aldehydes in water is described. This protocol was successfully conducted under metal-free conditions at ambient temperature and produced 2-alkyl and 2-arylbenzothiazole products in high to excellent yields (up to 98%). The catalyst was reusable at least four times without significant loss of activity.

1. Introduction

Benzothiazoles are well established as an important class of ubiquitous heterocyclic substances, present as molecules or molecular skeletons in many valuable bioactive natural products, medicines and material sciences [1–11]. For examples, Thioflavin-T (ThT) (**1**) is a fluorescent dye, used for staining Aβ plaque in postmortem brains [5] and selective recognition of RNA G-quadruplexes6, benzothiazole-2,6-diamine (**2**) revealed as dual DNA gyrase and topoisomerase IV inhibitors [7], zopolrestat (**3**) is used for the treatment of diabetes [8] and benzothiazole (**4**) exhibit antibacterial activity [9]. Some benzothiazole derivatives have been applied as amyloid imaging agents for the treatment of Alzheimer's disease such as [^{11}C]PIB (Pittsburgh compound B, **5**) [10] and 6-(3-[^{18}F]fluoro-2-hydroxypropyl)-substituted 2-pyridylbenzothiazoles (**6**) [11] (Fig. 1).

This diversity in application strongly supports the development of synthetic benzothiazoles. Typically, benzothiazole ring construction methods involve the transition metals-catalyzed intramolecular cyclization of *o*-haloanilides or their derivatives [12], which are not commercial available starting material and the cyclocondensation of *o*-aminothiophenols with aldehydes, carboxylic acids or their derivatives and alcohols [13] (Scheme 1a). However, these previous methods always employ toxic and/or hazardous transition metal catalysts and organic solvents. Some methods require harsh reaction conditions to furnish the high yield of desirable products, including high temperature, microwave radiation and/or corrosive acids that caused substrate and application limitations [12a,12c,12,12h,13b]. Moreover, transition metal complexes are unstable, expensive, difficult to handle and not reusable. They are also environmentally unfriendly with the potential to leave toxic traces in the intended and waste products. Novel methods under mild conditions without transition metal catalysts for the synthesis of 2-substituted benzothiazoles would circumvent these concerns.

Brönsted acidic ionic liquids (BAILs) [14] have been used as powerful acid-catalysts in many organic reactions. They are privileged catalysts with non-toxic, environment-friendly, stable, reusable, inexpensive, and produce products of high purity and yields. Besides, they exhibit a high water solubility that could extremely compatible with reaction mixture in water system. Water is an abundant renewable resource and would which avoid the production of environmentally harmful waste as well as process cost. Numerous versatile organic syntheses employ water as a solvent [13h,15]. In 2010, Bahrami et al. reported the use of SDS to catalyze the synthesis of 2-arylbenzothiazole from *o*-aminothiophenol and aromatic aldehydes in water [13h]. Recently, our group employed BAILs, [bsmim][HSO_4] (**I**) to be an efficient and reusable catalyst in water for the synthesis of dipyrromethanes *via* double Friedel-Crafts reaction of aldehydes and pyrrole [14b]. Herein, we demonstrate a novel strategy for the green synthesis of 2-aryl- and 2-akylbenzothiazoles *via* Friedel-Crafts cyclocondensation of *o*-aminothiophenol with a variety of aldehyde substrates employing Brönsted acid-surfactant-combined ionic liquids (BASILs) as an efficient and reusable catalyst in water and *tert*-butyl hydroperoxide (TBHP) as an

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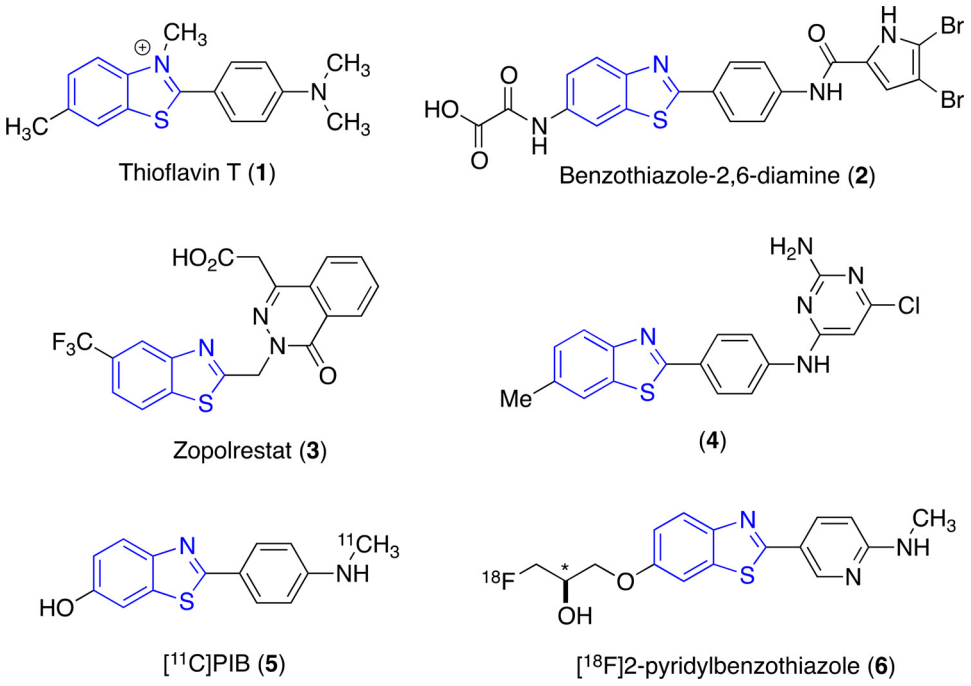
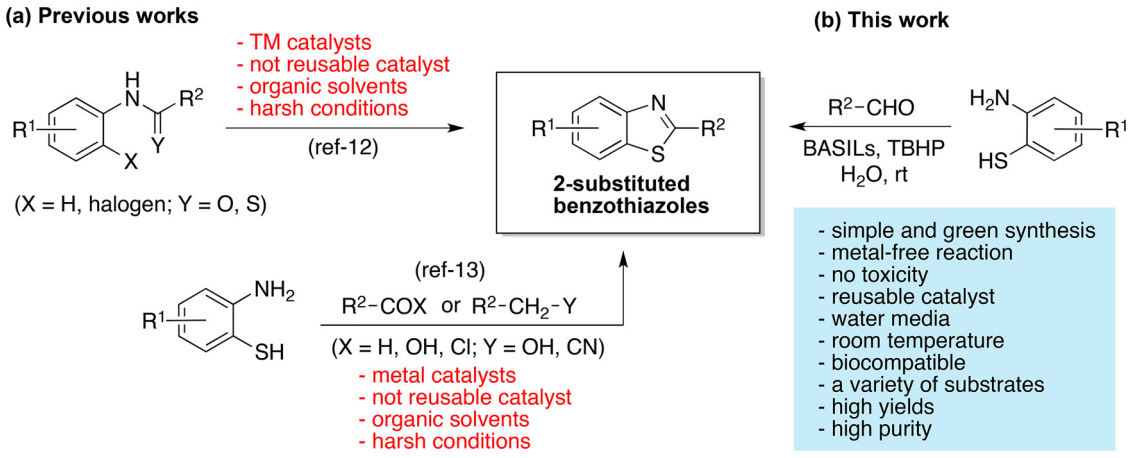


Fig. 1. Examples of versatile benzothiazole derivatives.



Scheme 1. Synthetic methods for the synthesis of 2-sunstituted benzothiazoles, (a) previous works, (b) this work.

oxidant at room temperature (Scheme 1b).

2. Experimental section

2.1. Materials and methods

All chemicals were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at Burapha University using a BRUKER AVANC (400 MHz). Light microscopy was detected at Burapha University using light microscope Olypus BX51. High-resolution mass spectra (HRMS) data were recorded at Mahidol University using a Bruker Daltonics-micrOTOF-Q. Infrared spectra were determined on a PERKIN ELMER FT/IR-2000S spectrophotometer. Analytical thin-layer chromatrography (TLC) was conducted on pre-coated TLC plates; silica gel 60F-254 [E. Merck, Darmstadt, Germany]. Open-column chromatography was carried out using silica gel 60 PF254 [E. Merck, Darmstadt, Germany]. Melting points were measured using a Melting point apparatus (Griffin) and are uncorrected.

2.2. Catalyst preparation

2.2.1. Synthesis of 1-Alkyl-1H-imidazoles

To a solution of 1-bromoalkane (10.0 g) in CH_3CN (20.0 mL) was added imidazole (1.00 eq.) and K_2CO_3 (3.00 eq.) at room temperature, respectively. The reaction mixture was stirred at room temperature for 24 h. Then, water (100 mL) was added and the mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic layer was dried over sodium sulfate anhydrous. The solvent was removed by using rotary evaporator. The residue was concentrated under reduced pressure and purified by column chromatography (SiO_2, 10–100 % ethyl acetate/*n*-hexane) to give the 1-alkyl-1*H*-imidazoles as products.

2.2.1.1. 1-Octyl-1H-imidazole. CAS Number 21252-69-7; 44% yield (6.4075 g) as a pale yellow oil; R_f = 0.32 (100% EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, J = 6.5 Hz), 1.19–1.34 (m, 10 H), 1.71–1.82 (m, 2 H), 3.91 (t, 2H, J = 7.0 Hz), 6.90 (s, 1 H), 7.04 (s, 1 H), 7.45 (s, 1 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.92, 22.47, 26.41, 28.90, 28.96, 30.94, 31.59, 46.91, 118.67, 129.05, 136.89.

2.2.1.2. 1-Decyl-1H-imidazole. CAS Number 33529-02-1; 50% yield (5.0969 g) as a pale yellow oil; R_f = 0.44 (100% EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 6.5 Hz), 1.18–1.36 (m, 14 H), 1.71–1.81 (m, 2 H), 3.92 (t, 2H, J = 7.0 Hz), 6.90 (s, 1 H), 7.05 (s, 1 H), 7.45 (s, 1 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.03, 22.59, 26.49, 29.00, 29.19, 29.36, 29.41, 31.02, 31.79, 46.98, 118.71, 129.21, 136.97.

2.2.1.3. 1-Dodecyl-1H-imidazole. CAS Number 4303-67-7; 52% yield (4.9294 g) as a pale yellow oil; R_f = 0.37 (100% EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, J = 6.5 Hz), 1.23–1.31 (m, 18 H), 1.72–1.81 (m, 2 H), 3.91 (t, 2H, J = 7.0 Hz), 6.89 (s, 1 H), 7.05 (s, 1 H), 7.47 (s, 1 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.91, 22.63, 26.66, 29.08, 29.29, 29.42, 29.51, 29.59 (2 × C), 31.08, 31.92, 47.13, 118.70, 129.47, 137.09.

2.2.1.4. 1-Tetradecyl-1H-imidazole. CAS Number 54004-47-6; 59% yield (5.7256 g) as a pale yellow oil; R_f = 0.38 (100% EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 6.5 Hz), 1.18–1.36 (m, 22 H), 1.71–1.81 (m, 2 H), 3.92 (t, 2H, J = 7.5 Hz), 6.90 (s, 1 H), 7.05 (s, 1 H), 7.46 (s, 1 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.07, 22.65, 26.52, 29.03, 29.31, 29.39, 29.48, 29.56, 29.60 (2 × C), 29.64, 31.04, 31.89, 47.02, 118.73, 129.22, 136.98.

*2.2.2. Synthesis of **IV, V, VI** and **VII***

To a solution of 1-alkyl-1*H*-imidazole (1.00 g) in CH_3CN (4.00 mL) was added 1,4-butanesultone (1.10 eq.) in portions at room temperature. The reaction mixture was heated to 80 °C with stirring for 48 h, and then cooled to room temperature resulting in white precipitate. The white precipitate was filtered and washed with ethyl acetate (3 × 5 mL) to remove any unreacted starting materials, and then the precipitate was dried in a vacuum to give the zwitterion compound as a white solid. Then a mixture of zwitterion compound (500 mg) in anhydrous toluene (5.00 mL) was added a stoichiometric amount of trifluoromethane sulfonic acid (TfOH) (1.00 eq.) in portions at room temperature. The reaction was then stirred at 80 °C for 24 h. After complete the reaction anhydrous toluene was removed by rotary evaporator to obtain compounds **IV, V, VI** and **VII** as products.

*2.2.2.1. 1-Butylsulfonic-3-octyl-1H-imidazolium trifluoromethanesulfonate **(IV)**: 99% yield*. (0.7340 g) as a brown oil; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3H, J = 6.5 Hz), 1.15–1.35 (m, 10 H), 1.56 (quint, 2H, J = 7.5 Hz), 1.78 (quint, 2H, J = 7.5 Hz), 1.89 (quint, 2H, J = 7.5 Hz), 2.55–2.62 (m, 2 H), 4.09–4.25 (m, 4 H), 7.80 (s, 2 H), 9.22 (s, 1 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 14.28, 21.79, 22.44, 25.92, 28.72, 28.82, 28.85, 29.74, 31.56, 48.94, 49.34, 50.80, 122.89 (2C), 136.43.

*2.2.2.2. 1-Butylsulfonic-3-decyl-1H-imidazolium trifluoromethanesulfonate **(V)**: 95% yield*. (0.6834 g) as a brown oil; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3H, J = 6.5 Hz), 1.15–1.32 (m, 14 H), 1.56 (quint, 2H, J = 7.5 Hz), 1.78 (quint, 2H, J = 7.5 Hz), 1.89 (quint, 2H, J = 7.5 Hz), 2.58 (t, 2H, J = 7.5 Hz), 4.10–4.25 (m, 4 H), 7.80 (s, 2 H), 9.22 (s, 1 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 14.32, 21.83, 22.51, 25.94, 28.78, 28.85, 29.03, 29.23, 29.32, 29.75, 31.71, 48.95, 49.34, 50.80, 122.89 (2C), 136.42.

*2.2.2.3. 1-Butylsulfonic-3-dodecyl-1H-imidazolium trifluoromethanesulfonate **(VI)**: 99% yield*. (0.6982 g) as a brown oil; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3H, J = 7.0 Hz), 1.16–1.33 (m, 18 H), 1.56 (quint, 2H, J = 7.5 Hz), 1.72–1.84 (m, 2 H), 1.89 (quint, 2H, J = 7.5 Hz), 2.56 (t, 2H, J = 7.5 Hz), 4.15 (t, 2H, J = 7.5 Hz), 4.19 (t, 2H, J = 7.5 Hz), 7.79 (s, 2 H), 9.21 (s, 1 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 14.33, 21.84, 22.52, 25.96, 28.79, 28.85, 29.14, 29.24, 29.38, 29.44 (2C), 29.76, 31.72, 48.31, 49.34, 50.80, 74.87, 122.90 (2C), 136.43.

*2.2.2.4. 1-Butylsulfonic-3-tetradecyl-1H-imidazolium trifluoromethanesulfonate **(VII)**: 99% yield*. (0.6971 g) as a brown oil; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3H, J = 7.0 Hz), 1.13–1.35 (m, 22 H), 1.55 (quint, 2H, J = 7.5 Hz), 1.78 (quint, 2H, J = 7.5 Hz), 1.89 (quint, 2H, J = 7.5 Hz), 2.45–2.58 (m, 2 H), 4.15 (t, 2H, J = 7.5 Hz), 4.19 (t, 2H, J = 7.5 Hz), 7.80 (s, 2 H), 9.22 (s, 1 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 14.31, 21.85, 22.52, 25.97, 28.82, 28.87, 29.15, 29.26, 29.40, 29.46 (2C), 29.50 (2C), 29.78, 31.74, 48.96, 49.34, 50.80, 122.90 (2C), 136.44.

*2.2.3. Synthesis of 1-Dodecyl-1H-imidazolium trifluoromethanesulfonate **(VIII)***

A mixture of 1-dodecylimidazole (500 mg, 2.12 mmol) in anhydrous CH_2Cl_2 (5.00 mL) was added a stoichiometric amount of trifluoromethanesulfonic acid (TfOH) (188 µL, 2.12 mmol) in portions at 0 °C and stirred at room temperature for 24 h. After complete the reaction, dichloromethane was removed by rotary evaporator to obtain **[dodecim] [OTf] (VIII)** in 98% yield (0.8050 g) as a white solid; m.p. 68–70 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 0.85 (t, 3H, J = 7.0 Hz), 1.15–1.35 (m, 18 H), 1.74–1.83 (m, 2 H), 4.17 (t, 2H, J = 7.5 Hz), 7.69 (s, 1 H), 7.78 (s, 1 H), 9.11 (s, 1 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 13.89, 22.06, 25.52, 28.32, 28.68, 28.79, 28.90, 28.98 (2C), 29.39, 31.27, 48.55, 119.90, 121.97, 135.17.

2.3. General procedure for the synthesis of 2-substituted benzothiazoles

To a suspension of [bsdodecim][OTf]* (10 mol%, 52.2 mg) in water (1.0 mL) was added aldehyde (8) (1.0 mmol), 2-aminothiophenol (7) (1.0 mmol) and *tert*-butyl hydrogenperoxide (TBHP) (1.0 mmol, 159 µL) at room temperature, respectively. The mixture suspension was stirred at room temperature for 1.5 h. Then, the mixture was extracted with ethyl acetate (3 × 2 mL). The combined organic layer was concentrated using rotary evaporator. The crude residue was purified by column chromatography (SiO_2, 2–20% ethyl acetate/*n*-hexane as eluent depend on each derivatives) or recrystallization to give the desired products (9a-9x).

**Recycling experiment*. After completion of the reaction, the remaining catalyst in aqueous solution could be reused directly by adding substrates in the next run without purification.

*2.3.1. 2-Phenylbenzothiazole **(9a)***

[4h,12b,13c–e] CAS Number 883-93-2; 98% yield (0.2067 g) as a white solid; m.p. 120–122 °C; R_f = 0.36 (2% EtOAc/*n*-hexane); IR (KBr): 1479, 1434, 1314, 1226, 964, 766, 732, 688, 624 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.40 (t, 1H, J = 7.6 Hz), 7.47–7.55 (m, 4 H), 7.92 (d, 1H, J = 8.0 Hz), 8.06–8.14 (m, 3 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 121.54, 123.16, 125.11, 126.23, 127.48 (2C), 128.94 (2C), 130.88, 133.54, 134.99, 154.07, 167.98.

*2.3.2. 2-(4'-Chlorophenyl)benzothiazole **(9b)***

[4g,12a,13c] CAS Number 6265-91-4; 91% yield (0.2214 g) as a white solid; m.p. 104–106 °C; R_f = 0.38 (2% EtOAc/*n*-hexane); IR (KBr): 1475, 1436, 1400, 1316, 1251, 965, 829, 756, 732, 483 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.40 (t, 1H, J = 7.6 Hz), 7.48 (d, 2H, J = 8.4 Hz), 7.51 (t, 1H, J = 7.2 Hz), 7.91 (d, 1H, J = 8.0 Hz), 8.03 (d, 2H, J = 8.4 Hz), 8.07 (d, 1H, J = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 121.61, 123.26, 125.37, 126.44, 128.66 (2C), 129.22 (2C), 132.06, 135.01, 136.98, 154.02, 166.56.

*2.3.3. 2-(4'-Fluorophenyl)benzothiazole **(9c)***

[13k,13o], CAS Number 1629-26-1; 90% yield (0.2054 g) as a white solid; m.p. 100–102 °C; R_f = 0.38 (2% EtOAc/*n*-hexane); IR (KBr): 1483, 1436, 1316, 1229, 967, 837, 756, 729, 500 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.19 (t, 2H, J = 8.6 Hz), 7.39 (t, 1H, J = 7.6 Hz), 7.50 (t, 1H, J = 7.6 Hz), 7.91 (d, 1H, J = 8.0 Hz), 8.04–8.12 (m, 3 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 116.08 (d, 2C_o-F, J = 22.0 Hz), 121.55, 123.13, 125.18, 126.35, 129.45 (d, 2C_m-F, J = 8.0 Hz), 129.89 (d, C_p-F,

J = 4.0 Hz), 134.99, 154.03, 164.39 (d, C–F, J = 251 Hz), 166.66.

2.3.4. 2-(2',4'-Dichlorophenyl)benzothiazole (9d)

[4g,13j,13p], CAS Number 6265-90-3; 98% yield (0.2732 g) as a yellow solid; m.p. 134–136 °C; R_f = 0.48 (2% EtOAc/*n*-hexane); IR (KBr): 1585, 1483, 1377, 1317, 1260, 1107, 1061, 966, 860, 827, 754, 725 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.41 (dd, 1H, J = 8.4, 2.0 Hz), 7.45 (t, 1H, J = 8.4 Hz), 7.54 (t, 1H, J = 8.4 Hz), 7.57 (d, 1H, J = 2.0 Hz), 7.96 (d, 1H, J = 8.0 Hz), 8.13 (d, 1H, J = 8.0 Hz), 8.23 (d, 1H, J = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 121.38, 123.46, 125.60, 126.42, 127.55, 130.54, 130.78, 132.50, 133.29, 136.01, 136.60, 152.31, 162.91.

2.3.5. 2-(3'-Nitrophenyl)benzothiazole (9e)

[12m,13c–d,13k,13p], CAS Number 22868-33-3; 92% yield (0.2353 g) as a yellow solid; m.p. 164–166 °C; R_f = 0.42 (10% EtOAc/*n*-hexane); IR (KBr): 1530, 1347, 761, 729, 670 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.46 (t, 1H, J = 7.2 Hz), 7.55 (t, 1H, J = 7.2 Hz), 7.70 (t, 1H, J = 8.0 Hz), 7.96 (d, 1H, J = 8.0 Hz), 8.13 (d, 1H, J = 8.4 Hz), 8.34 (dd, 1H, J = 8.0, 1.2 Hz), 8.43 (d, 1H, J = 7.6 Hz), 8.94 (s, 1 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 120.82, 122.02, 122.94, 124.95, 125.72, 126.54, 130.69, 132.88, 134.08, 134.50, 148.24, 153.06, 164.38.

2.3.6. 2-(4'-Nitrophenyl)benzothiazole (9f)

[4c-d,4h,12k,13c,13g–i,13p–q], CAS Number 22868-34-4; 94% yield (0.2388 g) as a yellow solid; m.p. 212–214 °C; R_f = 0.52 (10% EtOAc/*n*-hexane); IR (KBr): 1521, 1349, 852, 765, 686 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.47 (t, 1H, J = 7.6 Hz), 7.56 (t, 1H, J = 7.6 Hz), 7.96 (d, 1H, J = 8.0 Hz), 8.13 (d, 1H, J = 8.0 Hz), 8.27 (d, 2H, J = 8.8 Hz), 8.36 (d, 2H, J = 8.8 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 122.23, 123.21, 124.18 (2C), 126.04, 126.76, 128.13 (2C), 134.91, 138.18, 148.69, 153.32, 164.54.

2.3.7. 4-(2-Benzothiazolyl)benzoic acid (9g)

[13r] CAS Number 2182-78-7; 90% yield (0.2293 g) as a white solid; m.p. 286–288 °C; R_f = 0.21 (40% EtOAc/*n*-hexane); IR (KBr): 3037, 1679, 1406, 1288, 971, 857, 772, 751, 719, 693 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.44 (t, 1H, J = 8.0 Hz), 7.54 (t, 1H, J = 8.4 Hz), 7.95 (d, 1H, J = 8.0 Hz), 8.13 (d, 1H, J = 8.0 Hz), 8.19–8.26 (m, 4 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 122.51, 123.22, 125.99, 126.90, 127.35 (2C), 130.29 (2C), 132.96, 134.76, 136.43, 153.53, 166.16, 166.67.

2.3.8. Methyl 4-(2-benzothiazolyl)benzoate (9h)

[12m,13q] CAS Number 2182-77-6; 92% yield (0.2466 g) as a white solid; m.p. 160–162 °C; R_f = 0.50 (10% EtOAc/*n*-hexane); IR (KBr): 1721, 1482, 1406, 1281, 1111, 968, 859, 771, 697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 3.96 (s, 3 H), 7.43 (t, 1H, J = 7.2 Hz), 7.53 (t, 1H, J = 7.2 Hz), 7.94 (d, 1H, J = 8.0 Hz), 8.11 (d, 1H, J = 8.4 Hz), 8.17 (m, 4 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 52.32, 121.69, 123.54, 125.68, 126.57,127.39 (2C), 130.22 (2C), 131.99, 135.21, 137.37, 154.02, 166.36, 166.55.

2.3.9. 2-(4-Hydroxyphenyl)benzothiazole (9i)

[4e,4g,12e,13e,13h,13p], CAS Number 6265-55-0; 90% yield (0.2033 g) as a white solid; m.p. 214–216 °C; R_f = 0.32 (20% EtOAc/*n*-hexane); IR (KBr): 2996, 2592, 1606, 1434, 1286, 1226, 827, 757 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ_H 6.94 (d, 2H, J = 8.8 Hz), 7.41 (t, 1H, J = 7.2 Hz), 7.51 (t, 1H, J = 6.8 Hz), 7.94 (d, 2H, J = 8.4 Hz) 7.98 (d, 1H, J = 8.0 Hz), 8.09 (d, 1H, J = 7.6 Hz), 10.24 (brs, 1 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 116.56 (2C), 122.52, 122.77, 124.56, 125.32, 126.85, 129.52 (2C), 134.61, 154.22, 161.02, 167.94.

2.3.10. 2-(4'-Methoxyphenyl)benzothiazole (9j)

[4e,12a–b,12f–g12k–m,13c,13g–h,13k,13o,13q], CAS Number 6265-92-5; 92% yield (0.2229 g) as a white solid; m.p. 114–116 °C; R_f = 0.26 (5% EtOAc/*n*-hexane); IR (KBr): 1606, 1485, 1435, 1311, 1262, 1227, 1172, 1027, 969, 832, 757 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 3.89 (s, 3 H), 7.01 (d, 2H, J = 8.8 Hz), 7.36 (t, 1H, J = 8.0 Hz), 7.47 (t, 1H, J = 8.0 Hz), 7.88 (d, 1H, J = 8.0 Hz), 8.03 (d, 1H, J = 8.8 Hz), 8.04 (d, 2H, J = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 55.41, 114.29 (2C), 121.44, 122.75, 124.71, 126.13, 126.39, 129.03 (2C), 134.80, 154.16, 161.84, 167.78.

2.3.11. 2-(3',4'-Dimethoxyphenyl)benzothiazole (9k)

[4c,4e,4g,13a,13p], CAS Number 6638-45-5; 80% yield (0.2167 g) as a white solid; m.p. 124-126 °C; R_f = 0.42 (20% EtOAc/*n*-hexane); IR (KBr): 1602, 1525, 1483, 1434, 1265, 1146, 1024, 760 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 3.96 (s, 3 H), 4.02 (s, 3 H), 6.94 (d, 1H, J = 8.4 Hz), 7.36 (t, 1H, J = 7.6 Hz), 7.48 (t, 1H, J = 7.6 Hz), 7.60 (dd, 1H, J = 8.4, 2.0 Hz), 7.71 (d, 1H, J = 1.6 Hz), 7.87 (d, 1H, J = 8.0 Hz), 8.04 (d, 1H, J = 8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 55.90, 56.00, 109.64, 110.89, 121.06, 121.39, 122.66, 124.79, 126.15, 126.42, 134.70, 149.21, 151.49, 153.87, 167.85.

2.3.12. 2-(3'-Methoxy-4'-hydroxyphenyl)benzothiazole (9l)

[4e,12e] CAS Number 36341-25-0; 87% yield (0.2231 g) as a white solid; m.p. 164–166 °C; R_f = 0.60 (10% EtOAc/*n*-hexane); IR (KBr): 3099, 1605, 1585, 1527, 1480, 1428, 1287, 1198, 757 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 4.03 (s, 3 H), 6.02 (s, 1 H), 7.01 (d, 1H, J = 8.0 Hz), 7.36 (t, 1H, J = 7.6 Hz), 7.47 (t, 1H, J = 7.6 Hz), 7.55 (dd, 1H, J = 8.4, 1.6 Hz), 7.72 (d, 1H, J = 1.6 Hz), 7.88 (d, 1H, J = 8.0 Hz), 8.03 (d, 1H, J = 8.0 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 55.72, 110.21, 115.91, 121.25, 121.96, 122.27, 124.37, 124.83, 126.34, 134.18, 148.09, 150.05, 153.65, 167.50; HRMS (ESI) m/z $C_{14}H_{11}NO_2S$ $[M+H]^+$ calcd 258.0589, found 258.0587.

2.3.13. 2-(2-Pyridyl)benzothiazole (9m)

[4h,12e,12l,13h], CAS Number 716-80-3; 87% yield (0.1839 g) as a brow solid; m.p. 130–132 °C; R_f = 0.42 (10% EtOAc/*n*-hexane); IR (KBr): 1585, 1566, 1509, 1458, 1435, 1318, 996, 980, 738, 759, 741, 729 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.37–7.46 (m, 2 H), 7.51 (t, 1H, J = 7.6 Hz), 7.86 (td, 1H, J = 7.6, 1.2 Hz), 7.97 (d, 1H, J = 8.4 Hz), 8.10 (d, 1H, J = 8.0 Hz), 8.38 (d, 1H, J = 8.0 Hz), 8.69 (d, 1H, J = 4.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 120.63, 121.90, 123.46, 125.13, 125.53, 126.15, 136.01, 136.87, 149.51, 151.26, 154.16, 169.25.

2.3.14. 2-(2-Furyl)benzothiazole (9n)

[4h,12b,12e,12l–m,13a,13h,13o], CAS Number 1569-98-9; 81% yield (0.1634 g) as a white solid; m.p. 100–102 °C; R_f = 0.53 (10% EtOAc/*n*-hexane); IR (KBr): 1505, 1012, 896, 759, 592, 434 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 6.60 (dd, 1H, J = 3.6, 1.6 Hz), 7.20 (d, 1H, J = 3.2 Hz), 7.38 (t, 1H, J = 7.6 Hz), 7.49 (t, 1H, J = 7.2 Hz), 7.61 (s, 1 H), 7.89 (d, 1H, J = 8.0 Hz), 8.05 (d, 1H, J = 8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 111.31, 112.41, 121.45, 122.99, 125.07, 126.35, 134.16, 144.57, 148.63, 153.63, 157.43.

2.3.15. 2-(3-Indolyl)benzothiazole (9o)

[13q] CAS Number 31224-76-7; 51% yield (0.1273 g) as a brown solid; m.p. 144–146 °C; R_f = 0.13 (10% EtOAc/*n*-hexane); IR (KBr): 3400, 3216, 2923, 1551, 1439, 1246, 747 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.28–7.39 (m, 3 H), 7.44 (d, 1H, J = 8.0 Hz), 7.47 (t, 1H, J = 7.2 Hz), 7.89 (d, 1H, J = 7.6 Hz), 7.96 (d, 1H, J = 2.4 Hz), 8.05 (d, 1H, J = 8.0 Hz), 8.46 (d, 1H, J = 7.2 Hz), 8.88 (brs, 1 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 110.46, 112.37, 120.73, 121.17, 121.59, 121.73, 122.77, 124.21, 124.58, 126.13, 128.91, 133.05, 136.82, 153.75, 162.90; HRMS (ESI) m/z $C_{15}H_{10}N_2S$ $[M+H]^+$ calcd 251.0643, found 251.0642.

*2.3.16. 2-(2-Pyrrolyl-N-Boc)benzothiazole (**9p**)*

52% yield (0.1560 g) as a yellow oil; R_f = 0.52 (10% EtOAc/*n*-hexane); IR (KBr): 2980, 1748, 1316, 1145, 939, 848, 825, 759, 730 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.37 (s, 9 H), 6.30 (t, 1H, J = 3.2 Hz), 6.71 (dd, 1H, J = 3.6, 1.6 Hz), 7.39 (td, 1H, J = 7.2, 1.2 Hz), 7.46 (dd, 1H, J = 3.2, 1.6 Hz), 7.49 (td, 1H, J = 7.2, 1.2 Hz), 7.89 (d, 1H, J = 8.0 Hz), 8.04 (d, 1H, J = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 27.54 (3C), 84.55, 110.90, 118.87, 121.28, 123.08, 125.04, 125.06, 126.14, 126.60, 135.59, 148.69, 153.10, 159.77; HRMS (ESI) m/z $C_{16}H_{16}N_2SO_2$ $[M + Na]^+$ calcd 323.0830, found 323.0837.

*2.3.17. 2-(2-Pyrrolyl)benzothiazole (**9q**)*

[4h,13a], CAS Number 54584-09-7; 11% yield (0.0215 g) as a yellow oil; R_f = 0.35 (10% EtOAc/*n*-hexane); IR (KBr): 3193, 2923, 1571, 1492, 1440, 1105, 1041, 913, 755, 726 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 6.33 (dd, 1H, J = 6.0, 2.4 Hz), 6.85 (brs, 1 H), 6.98 (brs, 1 H), 7.32 (t, 1H, J = 7.6 Hz), 7.44 (t, 1H, J = 7.8 Hz), 7.83 (d, 1H, J = 8.0 Hz), 7.90 (d, 1H, J = 8.0 Hz), 9.85 (brs, 1 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 110.65, 112.57, 121.51, 121.75, 122.16, 124.50, 126.23 (2C), 133.86, 153.38, 160.50 ppm; HRMS (ESI) m/z $C_{11}H_8N_2S$ $[M+H]^+$ calcd 201.0486, found 201.0490.

*2.3.18. 2-Isobutylbenzothiazole (**9r**)*

CAS Number 17229-77-5; 69% yield (0.1314 g) as a yellow oil; R_f = 0.23 (2% EtOAc/*n*-hexane); IR (KBr): 2958, 1519, 1436, 759, 729 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.04 (d, 6H, J = 6.4 Hz), 1.17–2.29 (m, 1 H), 2.99 (d, 2H, J = 7.2 Hz), 7.35 (t, 1H, J = 7.6 Hz), 7.45 (t, 1H, J = 7.6 Hz), 7.84 (d, 1H, J = 8.0 Hz), 7.98 (d, 1H, J = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 22.26 (2C), 29.54, 43.13, 122.28, 122.47, 124.48, 125.68, 135.17, 153.24, 171.03; HRMS (ESI) m/z $C_{11}H_{13}NS$ $[M+H]^+$ calcd 192.0847, found 192.0842.

*2.3.19. 2-Propylbenzothiazole (**9s**)*

[12j] CAS Number 17229-76-4; 40% yield (0.0709 g) as a yellow oil; R_f = 0.30 (2% EtOAc/*n*-hexane); IR (KBr): 2962, 1520, 1436, 759, 729 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.06 (t, 3H, J = 7.6 Hz), 1.91 (sex, 2H, J = 7.6 Hz), 3.10 (t, 2H, J = 7.6 Hz), 7.34 (t, 1H, J = 7.2 Hz), 7.45 (t, 1H, J = 7.6 Hz), 7.84 (d, 1H, J = 8.0 Hz), 7.97 (d, 1H, J = 8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 13.62, 23.01, 36.14, 121.38, 122.42, 124.52, 125.76, 135.06, 153.17, 172.09.

*2.3.20. Benzothiazole (**9t**)*

[12a,12e,13e], CAS Number 95-16-9; 76% yield (0.1021 g) as a yellow oil; R_f = 0.32 (10% EtOAc/*n*-hexane); IR (KBr): 3062, 1456, 1425, 874, 758, 728 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.45 (t, 1H, J = 7.6 Hz), 7.53 (t, 1H, J = 7.6 Hz), 7.97 (d, 1H, J = 8.0 Hz), 8.15 (d, 1H, J = 8.4 Hz), 9.00 (s, 1 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 121.79, 123.59, 125.45, 126.08, 133.67, 153.26, 153.72.

*2.3.21. 2-Cyclohexylbenzothiazole (**9u**)*

[12j] CAS Number 40115-03-5; 66% yield (0.1424 g) as a yellow oil; R_f = 0.22 (2% EtOAc/*n*-hexane); IR (KBr): 2926, 2852, 1473, 1449, 759, 738 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.29–1.38 (m, 1 H), 1.42 (dm, 1H, J = 12.8 Hz), 1.48 (dm, 1H, J = 12.4 Hz), 1.61 (dm, 1H, J = 12.0 Hz), 1.67 (dm, 1H, J = 12.0 Hz), 1.77 (dm, 1H, J = 12.8 Hz), 1.89 (dm, 2H, J = 13.2 Hz), 2.21 (dm, 2H, J = 12.4 Hz), 3.06–3.15 (m, 1 H), 7.34 (t, 1H, J = 8.0 Hz), 7.44 (t, 1H, J = 8.4 Hz), 7.85 (d, 1H, J = 8.0 Hz), 7.97 (d, 1H, J = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_H 25.66, 25.93 (2C), 33.28 (2C), 43.28, 121.39, 122.42, 124.35, 125.64, 134.41, 152.98, 177.40.

*2.3.22. 6-Chloro-2-phenylbenzothiazole (**9v**)*

[12f,12g,12j,12l-m,13d,13k–l,13o], CAS Number 952-16-9; 75% yield (0.1849 g) as a white solid; m.p. 130–132 °C; R_f = 0.38 (2% EtOAc/*n*-hexane); IR (KBr): 1543, 1478, 1434, 1265, 1223, 1072, 969, 884, 808, 764, 688, 628 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.36 (dd, 1H, J = 8.8, 2.0 Hz), 7.48–7.53 (m, 3 H), 7.81 (d, 1H, J = 8.8 Hz), 8.04–8.10 (m, 3 H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 122.29, 123.89, 125.65, 127.33 (2C), 129.48 (2C), 131.42, 131.82, 132.51, 133.26, 154.46, 169.68.

*2.3.23. 6-Chloro-2-(4'-chlorophenyl)benzothiazole (**9w**)*

81% yield (0.2249 g) as a white solid; m.p. 142–144 °C; R_f = 0.38 (2% EtOAc/*n*-hexane); IR (KBr): 1474, 1431, 1402, 1094, 968, 831, 797, 623, 482 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.38 (d, 1H, J = 8.4 Hz), 7.48 (d, 2H, J = 8.4 Hz), 7.82 (d, 1H, J = 8.8 Hz), 8.02 (d, 2H, J = 8.4 Hz), 8.05 (brs, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 122.24, 123.01, 125.80, 128.65 (2C), 129.26 (2C), 131.62, 132.44, 133.19, 137.38, 154.79, 168.36; HRMS (ESI) m/z $C_{13}H_7Cl_2NS$ $[M+H]^+$ calcd 279.9755, found 279.9757.

*2.3.24. 6-Chloro-2-(4-methoxyphenyl)benzothiazole (**9x**)*

[12l] CAS Number 92161-46-1; 73% yield (0.1998 g) as a yellow solid; m.p. 142–144 °C; R_f = 0.10 (10% EtOAc/*n*-hexane); IR (KBr): 1262, 969, 883, 831, 809, 629 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 3.89 (s, 3 H), 7.00 (d, 2H, J = 8.8 Hz), 7.32 (dd, 1H, J = 8.8, 2.0 Hz), 7.78 (d, 1H, J = 8.4 Hz), 8.00 (brs, 1 H), 8.02 (d, 2H, J = 8.4 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6): δ_C 56.01, 115.30 (2C), 122.32, 124.16, 125.62, 129.54 (3C), 131.73, 133.49, 155.07, 162.57, 169.89.

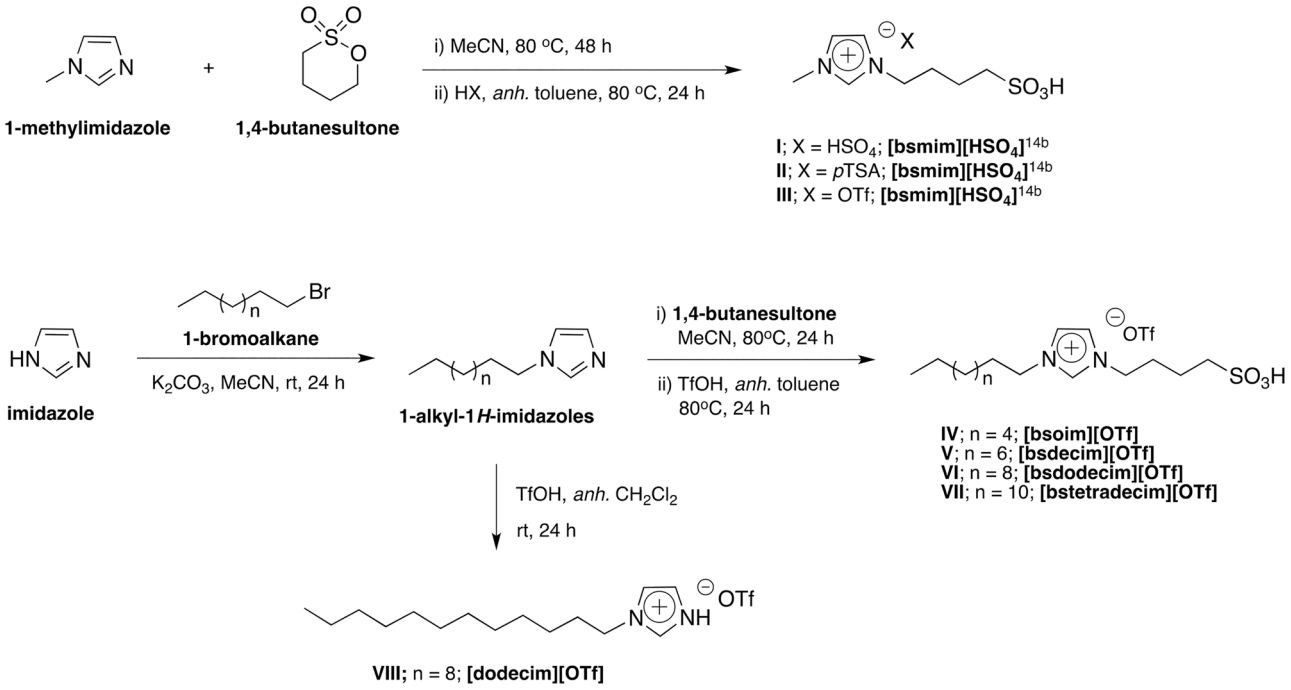
3. Results and Discussion

Preparation of a series of BAILs (**I-III**) and BASILs (**IV-VIII**) based-imidazolium cation employed the method according to previous report [14b] (Scheme 2) and investigated as catalysts for the synthesis of 2-substituted benzothiazoles *via* condensation of *o*-aminothiophenol with a variety of aldehydes in water at ambient temperature.

The reaction of *o*-aminothiophenol (**7a**, 1.0 mmol) and benzaldehyde (**8a**, 1.0 mmol) was chosen as a model to test the activity of catalysts in water at room temperature (Table 1). Benzothiazole **9a** was a desirable product, formed through benzothiazoline intermediate **10a** under oxidation [13c,13h]. Initial experiment, the control reaction was examined in the absence of a catalyst and oxidant for 3 h and resulted in an incomplete reaction with only trace amounts of the desirable product **9a** (6%) and intermediate **10a** in 76% (entry 1). Subsequently, 10 mol% of various catalysts were substituted and compared under the otherwise same conditions (entries 1-13). Transition metal complex such as $FeCl_3{\cdot}6H_2O$ was tested for comparison and yielded the desired product **9a** in only 34% with no intermediate **10a** (entry 2). BAILs **I-III** [14b] (entries 3-5) derived from methylimidazolium cation gave low yields of **9a** (7-17%) and intermediate **10a** was found as a major product (64-83%). This is probably due to poor solubility of substrates and intermediate in water system reflect in low yield of the desirable product **9a** (Fig. 2a). However, the highest total yield (94%) was found with catalyst **III**, which consists of OTf anion (entry 5). This suggests that the counter anion plays a significant role in this protocol and OTf anion showed the highest efficiency. Encouraged by these results, subsequent experiments were explored using long alkyl-chain Brönsted acidic ionic liquids with OTf anion **IV-VIII** under the otherwise same conditions (entries 6-10). Indeed, organic substrates were quite miscible with water as a yellow turbid emulsion (Fig. 2b) and the yield of **9a** slightly higher with catalysts **IV-VII**, but not catalyst **VIII**. Particularly, catalyst **VI** consist of C12 hydrocarbon chain was the most efficiency to provide the best yield of **9a** in 55% (45% of **10a**, entry 8), and it was found that shorter and longer alkyl chains of catalyst produced the product **9a** in lower yields.

Chemical yield of **9a** with catalyst **VI** increased by 70% after reaction time was increased to 12 h (27% of **10a**, entry 11) and by 96% after 24 h (entry 12). This indicated that in order to produce an excellent yield of **9a** with catalyst **VI** in water and without an oxidant longer reaction times are required.

While short reaction time (1.5 h) in the absence of oxidant, yield of



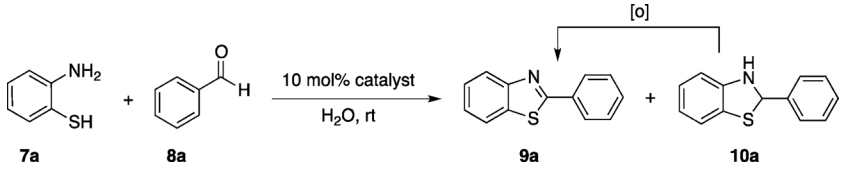
Scheme 2. Synthesis and structures of the BAILs (**I-III**) and BASILs (**IV-VIII**).

9a was found only 22% (77% of **10a**, Table 2, entry 1). To further optimization with 1.5 h of reaction time, oxidant was employed and the better yield of **9a** was occurred (Table 2). Hydrogen peroxide (H_2O_2, 1.0 eq.) improved yield of **9a** to 67% along with 26% of **10a** (entry 2). Yields of **9a** were highest at 98% when 1.0 eq. TBHP was used (entry 3). Yields of **9a** declined (64%) and **10a** in 28% (entry 4) with a reduction of TBHP to 0.5 eq. Decreasing the amount of catalyst **VI** to 5 mol% reduced **9a** to 80% with only trace amounts of **10a** (4%, entry 5). Finally, further confirmation the catalytic activity of catalyst **VI**, the reaction was evaluated under oxidant (TBHP, 1.0 eq.) without catalyst and resulted in lower yields of both **9a** and **10a** (entries 6 and 7).

To confirm that catalyst **VI**-induced the formation of micelles or colloidal dispersions in water, a reaction mixture was detected by light microscopic technique and the result revealed the formation of colloidal particles (Fig. 2c). These stable spherical colloidal particles play a crucial role in rapidly stimulating the reaction in water, as in the case of LASC, SDS, DBSA and sodium stearate [13h,15].

According to the literatures [13,15] and our experiment results, we suggest a mechanism for the formation of benzothiazole in Scheme 3. A long alkyl-chain acidic ionic liquid acts both as Brönsted acid to activate substrates and as a surfactant to form micelle in water. Hydrophobic substrates were concentrated inside the hydrophobic core of the catalyst, allowing the reaction to take place more easily. With hydrophilic Brönsted acid activating aldehyde substrate at oxygen atom

Table 1
Optimization of the reaction.[a]



7a **8a** **9a** **10a**

Entry	Catalyst	Time (h)	Yield (%) [b]		
			9a	**10a**	**Total**
1	–	3.0	7	76	83
2	$FeCl_3.6H_2O$	3.0	34	0	34
3	**I**, [bsmim][HSO_4]	3.0	7	64	71
4	**II**, [bsmim][*p*TSA]	3.0	17	69	86
5	**III**, [bsmim][OTf]	3.0	11	83	94
6	**IV**, [bsocim][OTf]	3.0	26	69	95
7	**V**, [bsdecim][OTf]	3.0	21	75	96
8	**VI**, [bsdodecim][OTf]	3.0	55	45	100
9	**VII**, [bstetradecim][OTf]	3.0	20	71	91
10	**VIII**, [dodecim][OTf]	3.0	3	90	93
11	**VI**, [bsdodecim][OTf]	12.0	70	27	97
12	**VI**, [bsdodecim][OTf]	24.0	96	0	96

[a] All reactions were conducted with *o*-aminothiophenol (**7a**, 1.0 mmol), benzaldehyde (**8a**, 1.0 mmol), catalyst (10 mol%) in water (1.0 mL) at room temperature for.1.5–24.0 h.
[b] Isolated yield.

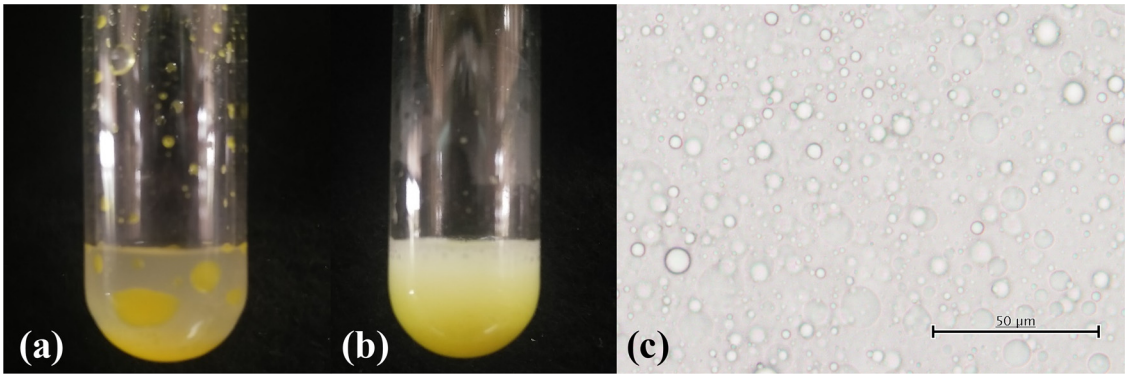
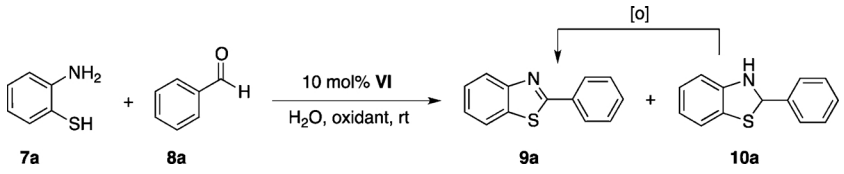


Fig. 2. (a) Reaction mixture of catalyst **III** and substrates in water. (b) Reaction mixture of catalyst **VI** and substrates in water. (c) Spherical colloidal partials of the reaction mixture of substrates and catalyst **VI** in water, detected by light microscopy.

Table 2
Optimization of the reaction with oxidant.[a]

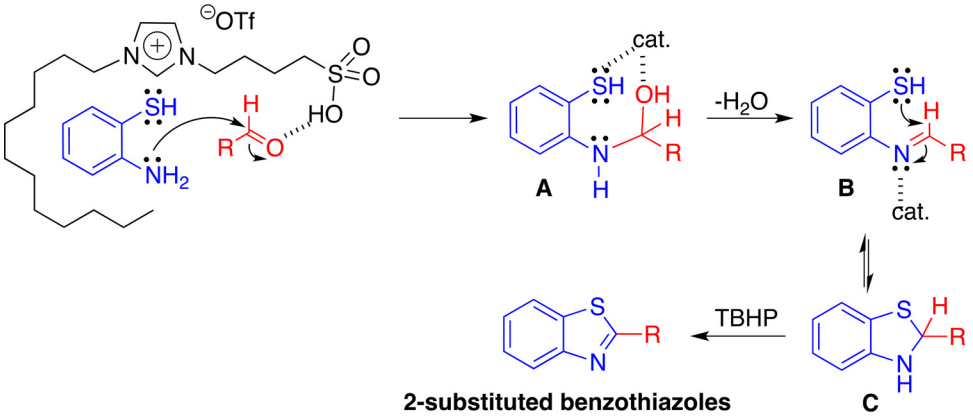


Entry	Oxidant (eq.)	Time (h)	Yield (%)[b]		
			9a	**10a**	**Total**
1	–	1.5	22	77	99
2	H_2O_2 (1.0)	1.5	67	26	83
3	TBHP (1.0)	1.5	98	0	98
4	TBHP (0.5)	1.5	64	28	92
5[c]	TBHP (1.0)	1.5	80	4	84
6[d]	TBHP (1.0)	1.5	26	7	33
7[e]	TBHP (1.0)	4.5	32	24	56

[a] All reactions were conducted with *o*-aminothiophenol (**7a**, 1.0 mmol), benzaldehyde (**8a**, 1.0 mmol), catalyst **VI** (10 mol%), oxidant (0.5–1.0 equivalent) in water (1.0 mL) at room temperature for 1.5 h.
[b] Isolated yield.
[c] 5 mol% of catalyst **VI**.
[d] Without catalyst.
[e] Stirred for 3.0 h without catalyst and then 1.5 h after adding TBHP.

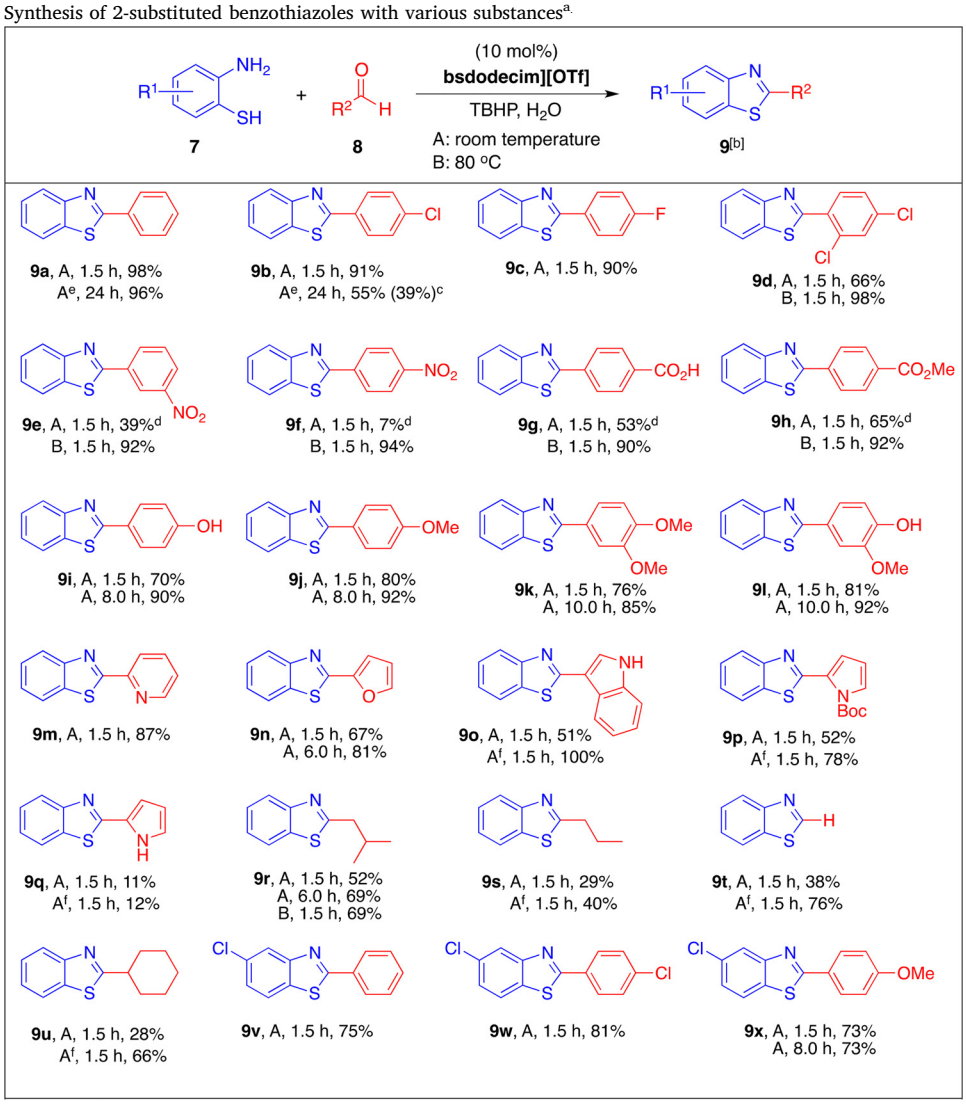
forming an intermediate **A**, dehydration and cyclization take place to form intermediate **B** and **C**, respectively. Finally, TBHP oxidizes intermediate **C** to produce the corresponding 2-substituted benzothiazoles.

The recycling performance of catalyst **VI** was investigated using model reaction. After the complete reaction (Table 2, entry 3), **9a** was separated from the water layer by simple extraction with ethyl acetate (3 × 2 mL). Catalyst **VI** contained in the water layer was reused by directly adding substrates for the next cycles. Catalyst **VI** was reused for at least four cycles without apparent loss of catalytic activity and yields of **9a** remained unchanged at 98, 96, 97 and 98% for four cycles respectively. Finally, NMR analysis confirmed analysis confirmed catalyst **VI** retained its structure following for four cycles of use.



Scheme 3. Proposed mechanism for the synthesis of 2-substituted benzothiazole in water using [bsdodecim][OTf] as catalyst.

Table 3
Synthesis of 2-substituted benzothiazoles with various substances[a].



[a]All reactions were conducted with 2-aminothiophenol (**1**, 1.0 mmol) and aldehyde (**2**, 1.0 mmol) using 10 mol% of [bsdodecim][OTf] and 1.0 eq. TBHP in 1.0 ml of water; [b]Isolated yield; [c]benzothiazoline intermediate; [d]solidity; [e]without TBHP; [f]2 eq. of aldehyde.
Conditions A. Reaction was performed at room temperature; **Condition B.** Reaction was performed at 80 °C.

This protocol could be applied to a variety of either aliphatic, aromatic and heteroaromatic aldehyde substrates to provide the corresponding desirable products in good to excellent yields depending on steric hindrance, electronic properties and solubility of substrates (Table 3). Aromatic aldehydes with nonpolar electron-withdrawing substituents (-Cl, -F), including benzaldehyde proceed smoothly to produce excellent yields of products **9a-9c** within 1.5 h at room temperature (90-98%, condition A). Remarkably, when the reaction was performed in the absence of an oxidant (TBHP), a prolonged reaction time (24 h) was necessary to produce an excellent yield of **9a** (96%) and a moderate yield of **9b** (55%) with 39% of a benzothiazoline intermediate. A sterically hindered group at *ortho*-position on benzene ring of benzaldehyde reduced the yield of **9d** to 66% (condition A), but at a high reaction temperature (80 °C, condition B) yield improved to 98%. Under condition A, aromatic aldehydes with polar electron-withdrawing substituents (-NO_2, -CO_2H, -CO_2Me), poor solubility and solidify during the reaction, gave products **9e**, **9 g** and **9 h** in moderate yields (39–65%) and only trace amount of **9e** (7%). Heating to 80 °C (condition B) improved solubility of substrates and yields of products **9e-9 h** to 90–94%. Notably, the ester functional group, which was easily hydrolyzed under acid conditions, tolerated this catalyst even under heating conditions. Aromatic aldehydes with electron-donating substituents produced the target products **9i-9 l** in high yields (70–81%) within 1.5 h at room temperature (condition A) and yields improved even more (85–92%) when the reaction time was increased to 8–10 h. Heteroaromatic aldehyde substrates were investigated also with this protocol and produced the desired products in moderate (**9n-9p**, 51–67%) to high yields (**9 m**, 87%) under condition A for 1.5 h. Yield of **9n** was enhanced to 81% when reaction time was 8.0 h. Aldehyde substrates of 2.0 eq was employed to provide higher yields of **9o** (100%) and **9p** (78%). In contrast, a poor yield of **9q** (11%) was obtained from pyrrole-2-carbaldehyde substrate even with 2.0 eq. of aldehyde. This was likely due to the strong pH effect of nitrogen atom on substrates allowing for easy attachment to an acid-catalyst reducing catalytic activity [16]. Interestingly, aliphatic aldehyde substrates were incorporated well enough to generate acceptable yields of **9 r-9 u** (28–52%, condition A, 1.5 h). A higher yield of **9 r** (69%) resulted when reaction time was 8.0 h at room temperature or temperature was maintained under 80 °C for 1.5 h (condition B). In the presence of 2.0 eq. of aldehyde substrates yields of **9 s-9 u** increased to 40, 76 and 66%, respectively. In addition, when 4-chloro-2-aminothiophenol was employed as the substrate, the products **9v-9x** were readily produced in

high yields (75, 81 and 73%, respectively) within 1.5 h. However, yield of **9x** (73%) did not improve even at a prolonged reaction period (8.0 h).

4. Conclusion

In summary, we have developed a green and efficient method for the synthesis of 2-substituted benzothiazoles from *o*-phenylenediamine with a wide range of aliphatic, aromatic and heteroaromatic aldehyde substrates using Brönsted acid-surfactant-combined ionic liquids (BASILs) as a reusable catalyst in water under metal-free conditions at ambient temperature. The BASILs, named [bsdodecim][OTf] was the most efficient reusable catalyst to provide the corresponding desirable products in high to excellent yields.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2018.06.017.

References

[1] (a) A. Rouf, C. Tanyeli, Eur. J. Med. Chem. 97 (2015) 911–927;
(b) C.E. Blunt, C.C. Nawrat, L. LeBozec, M. Liutkus, Y. Liu, W. Lewis, C.J. Moody, Synlett 27 (2016) 37–40.

[2] (a) R.S. Keri, M.R. Patil, S.A. Patil, S. Budagumpi, Eur. J. Med. Chem. 89 (2015) 207–251;
(b) J. Mizoule, B. Meldrum, M. Mazadier, M. Croucher, C. Ollat, A. Uzan, J.J. Legrand, C. Gueremy, G. Le Fur, Neuropharmacology 24 (1985) 767–773.

[3] (a) S.-J. Ji, H.-B. Shi, Dyes Pigm. 70 (2006) 246–250;
(b) V.O. Rodionov, S.I. Presolski, S. Gardinier, Y.H. Lim, M.G. Finn, J. Am. Chem. Soc. 129 (2007) 12696–12704;
(c) S. Yao, K.J. Schafer-Hales, K.D. Belfield, Org. Lett. 9 (2007) 5645–5648.

[4] (a) S. Aiello, G. Wells, E.L. Stone, H. Kadri, R. Bazzi, D.R. Bell, M.F.G. Stevens, C.S. Matthews, T.D. Bradshaw, A.D. Westwell, J. Med. Chem. 51 (2008) 5135–5139;
(b) D. Loos, E. Sidoova, V. Sutoris, Molecules 4 (1999) 81–93;
(c) S.-J. Choi, H.J. Park, S.K. Lee, S.W. Kim, G. Han, H.-Y.P. Choo, Bioorg. Med. Chem. 14 (2006) 1229–1235;
(d) E. Kashiyama, I. Hutchinson, M.-S. Chua, S.F. Stinson, L.R. Phillips, G. Kaur, E.A. Sausville, T.D. Bradshaw, A.D. Westwell, M.F.G. Stevens, J. Med. Chem. 42 (1999) 4172–4184;
(e) Y.M. Ha, J.Y. Park, Y.J. Park, D. Park, Y.J. Choi, J.M. Kim, E.K. Lee, Y.K. Han, J.-A. Kim, J.Y. Lee, H.R. Moon, H.Y. Chung, Bioorg. Med. Chem. Lett. 21 (2011) 2445–2449;
(f) D.O. Koltun, T.A. Marquart, K.D. Shenk, E. Elzein, Y. Li, M. Nguyen, S. Kerwar, D. Zeng, N. Chu, D. Soohoo, J. Hao, V.Y. Maydanik, D.A. Lustig, K.J. Ng, H. Fraser, J.A. Zablocki, Bioorg. Med. Chem. Lett. 14 (2004) 549–552;
(g) K.M. Khan, F. Rahim, S.A. Halim, M. Taha, M. Khan, S. Perveen, Zaheer-ul-Haq, M.A. Mesaik, M.I. Choudhary, Bioorg. Med. Chem. 19 (2011) 4286–4294;
(h) P.J. Palmer, R.B. Trigg, J.V. Warrington, J. Med. Chem. 14 (1971) 248–251;
(i) C.G. Mortimer, G. Wells, J.-P. Crochard, E.L. Stone, T.D. Bradshaw, M.F.G. Stevens, A.D. Westwell, J. Med. Chem. 49 (2006) 179–185;
(j) J.M. Bergman, P.J. Coleman, C. Cox, G.D. Hartman, C. Lindsley, S.P. Mercer, A.J. Roecker, D.B. Whitman, PCT Int. Appl. (2006) WO 2006127550.

[5] (a) H. Naiki, K. Higuchi, M. Hosokawa, T. Takeda, Anal. Biochem. 177 (1989) 244–249;
(b) M. Biancalana, S. Koide, Biochem. Biophys. Acta 1804 (2010) 1405–1412;
(c) A. Srivastava, P.K. Singh, M. Kumbhakar, T. Mukherjee, S. Chattopadyay, H. Pal, S. Nath, Chemistry 16 (2010) 9257–9263;
(d) D.J. Linderg, M.S. Wranne, M.G. Gatty, F. Westerlund, E.K. Esbjorner, Biochem. Biophys. Res. Commun. 458 (2015) 418–423.

[6] S. Xu, J. Xiang, Q. Yang, H. Sun, A. Guan, L. Wang, Y. Liu, L. Yu, Y. Shi, H. Chen, Y. Tang, Sci. Rep. 6 (2016) 24793.

[7] M. Gjorgjieva, T. Tomasic, M. Barancokova, S. Katsamakas, J. Ilas, P. Tammela, L.P. Masic, D. Kikelj, J. Med. Chem. 59 (2016) 8941–8954.

[8] B.L. Mylari, E.R. Larson, T.A. Beyer, W.J. Zembrowski, C.E. Aldinger, M.F. Dee, T.W. Siegel, D.H. Singleton, J. Med. Chem. 34 (1991) 108–122.

[9] A. Ali, G.E. Taylor, D.W. Graham, PCT Int. Appl. (2001) WO 2001028561.

[10] (a) C.A. Mathis, Y. Wang, D.P. Holt, G.-F. Huang, M.L. Debnath, W.E. Klunk, J. Med. Chem. 46 (2003) 2740–2754;
(b) W.E. Klunk, H. Engler, A. Nordberg, Y. Wang, G. Blomqvist, D.P. Holt, M. Bergström, I. Savitcheva, G.-F. Huang, S. Estrada, B. Ausén, M.L. Debnath, J. Barletta, J.C. Price, J. Sandell, B.J. Lopresti, A. Wall, P. Koivistro, G. Antoni, C.A. Mathis, B. Långström, Ann. Neurol. 55 (2004) 306–319;
(c) M. Wang, M. Gao, B.H. Mock, K.D. Miller, G.W. Sledge, G.D. Hutchins, Q.-H. Zheng, Bioorg. Med. Chem. 14 (2006) 8599–8607.

[11] B.S. Lee, S.Y. Chu, H.R. Kwon, C.S. Park, U. Sirion, D. Brockschnieder, T. Dyrks, S.J. Oh, J.S. Kim, D.Y. Chi, Bioorg. Med. Chem. 24 (2016) 2043–2052.

[12] (a) T. Itoh, T. Mase, Org. Lett. 9 (2007) 3687–3689;
(b) Q. Ding, X.-G. Huang, J. Wu, J. Comb. Chem. 11 (2009) 1047–1049;
(c) P. Saha, T. Ramana, N. Purkait, M.A. Ali, R. Paul, T. Punniyamurthy, J. Org. Chem. 74 (2009) 8719–8725;
(d) M.D. Vera, J.C. Pelletier, J. Comb. Chem. 9 (2007) 569–570;
(e) D. Ma, S. Xie, P. Xue, X. Zhang, J. Dong, Y. Jiang, Angew. Chem. Int. Ed. 48 (2009) 4222–4225;
(f) K. Inamoto, C. Hasegawa, K. Hiroya, T. Doi, Org. Lett. 10 (2008) 5147–5150;
(g) Y. Cheng, J. Yang, Y. Qu, P. Li, Org. Lett. 14 (2012) 98–101;
(h) G. Evindar, R.A. Batey, J. Org. Chem. 71 (2006) 1802–1808;
(i) D.S. Bose, M. Idrees, J. Org. Chem. 71 (2006) 8261–8263;
(j) Y. Cheng, Q. Peng, W. Fan, P. Li, J. Org. Chem. 79 (2014) 5812–5819;
(k) R.G. Kalkhambkar, K.K. KLaali, Tetrahedron Lett. 53 (2012) 4212–4215;
(l) N. Park, Y. Heo, M.R. Kumar, Y. Kim, K.H. Song, S. Lee, Eur. J. Org. Chem. (2012) 1984–1993;
(m) X. Zhang, W. Zeng, Y. Yang, H. Huang, Y. Liang, Org. Lett. 16 (2014) 876–879.

[13] (a) R. Shelkar, S. Sarode, J. Nagarkar, Tetrahedron Lett. 54 (2013) 6986–6990;
(b) A.J. Blacker, M.M. Farah, M.I. Hall, S.P. Marsden, O. Saidi, J.M.J. Williams, Org. Lett. 11 (2009) 2039–2042;
(c) K. Bahrami, M.M. Khodaei, F. Naali, J. Org. Chem. 73 (2008) 6835–6837;
(d) A. Kumar, R.A. Maurya, P. Ahmad, J. Comb. Chem. 11 (2009) 198–201;
(e) H. Sharma, N. Singh, D.O. Jang, Green Chem. 16 (2014) 4922–4930;
(f) R. Fazaeli, H. Aliyan, Appl. Catal. A: Gen. 353 (2009) 74–79;
(g) S.M. Inamdar, V.K. More, S.K. Mandal, Tetrahedron Lett. 54 (2013) 579–583;
(h) K. Bahrami, M.M. Khodaei, A. Nejati, Green Chem. 12 (2010) 1237–1241;
(i) G.R. Bardajee, M. Mohammadi, H. Yari, A. Ghaedi, Chin. Chem. Lett. 27 (2016) 265–270;
(j) R. Kardanpour, S. Tangestaninejad, V. Mirkhani, M. Moghadam, I. Mohammadpoor-Baltork, F. Zadehahmadi, J. Solid State Chem. 235 (2016) 145–153;
(k) Y. Liao, H. Qi, S. Chen, P. Jiang, W. Zhou, G.-J. Deng, Org. Lett. 14 (2012) 6004–6007;
(l) H.-J. Lim, D. Myung, I.Y.C. Lee, M.H. Jung, J. Comb. Chem. 10 (2008) 501–503;
(m) M.S. Mayo, X. Yu, X. Zhou, X. Feng, Y. Yamamoto, M. Bao, Org. Lett. 16 (2014) 764–767;
(n) S.S. Panda, M.A. Ibrahim, A.A. Oliferenko, A.M. Asiri, A.R. Katritzky, Green Chem. 15 (2013) 2709–2712;
(o) Y. Sun, H. Jiang, W. Wu, W. Zeng, X. Wu, Org. Lett. 15 (2013) 1598–1601;
(p) H.Y. Guo, J.C. Li, Y.L. Shang, Chin. Chem. Lett. 20 (2009) 1408–1410;
(q) X. Wen, J.E. Bakali, R. Deprez-Poulain, B. Deprez, Tetrahedron Lett. 53 (2012) 2440–2443;
(r) T.B. Kumar, Ch. Sumanth, A.V.D. Rao, D. Kalita, M.S. Rao, K.B.C. Sekhar, K.S. Kumar, M. Pal, RSC Adv. 2 (2012) 11510–11519;
(s) R.N. Nadaf, S.A. Siddiqui, T. Daniel, R.J. Lahoti, K.V. Srinivasan, J. Mol, Catal. A Chem. 214 (2004) 155–160;
(t) X. Gao, B. Yu, Z. Yang, Y. Zhao, H. Zhang, L. Hao, B. Ham, Z. Liu, ACS Catal. 11 (2015) 6648–6652;
(u) X. Fan, Y. He, Y. Wang, Z. Xue, X. Zhang, J. Wang, Tetrahedron Lett. 52 (2011) 899–902.

[14] (a) A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis Jr, J. Am. Chem. Soc. 124 (2002) 5962–5963;
(b) W. Senapak, R. Saeeng, J. Jaratjaroonphong, T. Kasemsuk, U. Sirion, Org, Biomol. Chem. 14 (2016) 1302–1310;
(c) A.S. Amarasekara, Chem. Rev. 116 (2016) 6133–6183;
(d) F. Dong, F. Zhenghao, L. Zuliang, Catal. Commun. 10 (2009) 1267–1270;
(e) X. Liang, C. Qi, Catal. Commun. 12 (2011) 808–812;
(f) A. Zare, F. Abi, A.R. Moosavi-Zare, M.H. Beyzavi, M.A. Zolfigol, J. Mol. Liq. 178 (2013) 113–121;
(g) M. Vafaeezadeh, H. Alinezhad, J. Mol. Liq. 218 (2016) 95–105;
(h) A.K. Bagdi, A. Hajra, RSC Adv. 4 (2014) 23287–23291;
(i) Y. Jeong, J.-S. Ryu, J. Org. Chem. 75 (2010) 4183–4191;
(j) T. Chang, L. He, L. Bian, H. Han, M. Yuan, X. Gao, RSC Adv. 4 (2014) 727–731.

[15] (a) M. Shiri, M.A. Zolfigol, Tetrahedron 65 (2009) 587–598;
(b) K. Manabe, Y. Mori, T. Wakabayashi, S. Nagayama, S. Kobayashi, J. Am. Chem. Soc. 122 (2000) 7202–7207;
(c) K. Manabe, Y. Mori, S. Kobayashi, Tetrahedron 57 (2001) 2537–2544;
(d) Y. Ye, Q. Ding, J. Wu, Tetrahedron 64 (2008) 1378–1382;
(e) L.-M. Wang, N. Jiao, J. Qiu, J.-J. Yu, J.-Q. Liu, F.-L. Guo, Y. Liu, Tetrahedron 66 (2010) 339–343;
(f) F. Dong, F. Zhenghao, L. Zuliang, Catal. Commun. 10 (2009) 1267–1270;
(g) K. Pradhan, S. Paul, A.R. Das, Tetrahedron Lett. 54 (2013) 3105–3110;
(h) Y. Chen, Y. Zhao, J. Chen, K. Zhuo, J. Wang, J. Colloid Interface Sci. 364 (2011) 388–394;
(i) X.-F. Liu, L.-L. Dong, Y. Fang, J. Surfact Deterg 14 (2011) 497–504.

[16] W. Senapak, R. Saeeng, U. Sirion, RSC Adv. 7 (2017) 30380–30384.