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Synthesis of 1,3-Dialkyl-1,2,3-triazolium Ionic Liquids and Their Applications to the Baylis−Hillman Reaction

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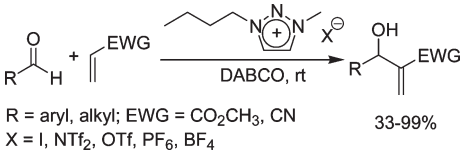
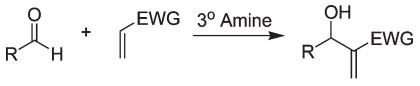


Novel 1,3-dialkyl-1,2,3-triazolium ionic liquids were synthesized via click reactions using 1-trimethylsilylacetylene and alkyl azides and were efficient reaction media for the Baylis−Hillman reaction. The problems associated with deprotonation of the C-2 hydrogen of [bmim][PF_6] could be suppressed in the reaction of [bmTr][PF_6] or [bmTr][NTf_2]. 1,3-Dialkyl-1,2,3-triazolium ionic liquids are chemically inert under basic conditions and more suitable media for the reactions involving bases than the common 1,3-dialkylimidazolium ionic liquids.

Introduction

The Baylis−Hillman reaction is one of the most important C−C bond-forming processes in modern organic synthesis.[1] This versatile reaction basically involves a reaction between an aldehyde and an activated alkene in the presence of a tertiary amine base to afford a densely functionalized product (Scheme 1). Since the Baylis−Hillman reaction was first reported by Baylis and Hillman in 1972,[2] it has attracted organic chemists' interest due to its inherent advantages, including a high atom economy, organocatalysis, mild reaction conditions, and wide functional group compatibility. However, this reaction sometimes has a long reaction time and moderate yields.[1] In particular, the reactions with acrylic esters were quite sluggish, and the hydrolysis of acrylic esters in aqueous media could be a potential side reaction.[3] To circumvent these problems, several reaction conditions have been developed using supercritical CO_2,[4] ultrasound,[5] microwave irradiation,[6] and ionic liquids.[7] Most notably, the use of ionic liquids as an alternate solvent has been extensively studied for the past decade.[7]

SCHEME 1. Baylis−Hillman Reaction



Ionic liquids (ILs) are defined as organic salts, mostly consisting of organic cations and inorganic anions, which melt below 100 °C. Since ethylammonium nitrate was first reported in 1914,[8] a number of cation types of ionic liquids have been developed, including imidazolium, pyridinium, ammonium, and phosphonium. Among them, imidazolium cations like 1-butyl-3-methylimidazolium ([bmim]) are the most commonly used as ionic liquids (**1**, Figure 1). However,

(1) For reviews, see: (a) Basavaiah, D.; Rao, K. V.; Reddy, R. J. *Chem. Soc. Rev.* **2007**, *36*, 1581–1588. (b) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811–891.

(2) (a) Baylis, A. B.; Hillman, M. E. D. Ger. Offen. 2 155 113, 1972. (b) Hillman, M. E. D.; Baylis, A. B. US Patent 3 743 669, 1973. (c) Morita, K.; Suzuki, Z.; Hirose, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2815. (d) Rauhut, M.; Currier, H. US Patent 3 074 999, 1963.

(3) (a) Yu, C.; Liu, B.; Hu, L. *J. Org. Chem.* **2001**, *66*, 5413–5418. (b) Krishna, P. R.; Manjuvani, A.; Kannan, V.; Sharma, G. V. M. *Tetrahedron Lett.* **2004**, *45*, 1183–1185.

(4) (a) Rose, P. M.; Clifford, A. A.; Rayner, C. M. *Chem. Commun.* **2002**, 968–969. (b) Chandrasekhar, S.; Narsihmulu, C.; Saritha, B.; Sultana, S. S. *Tetrahedron Lett.* **2004**, *45*, 5865–5867.

(5) Ge, S.-Q.; Hua, Y.-Y.; Xia, M. *Ultrason. Sonochem.* **2009**, *16*, 743–746.

(6) Kundu, M. K.; Mukherjee, S. B.; Balu, N.; Padmakumar, R.; Bhat, S. V. *Synlett* **1994**, 444.

(7) Chowdhury, S.; Mohan, R. S.; Scott, J. L. *Tetrahedron* **2007**, *63*, 2363–2389. and references therein.

(8) Sugden, S.; Wilkins, H. *J. Chem. Soc.* **1929**, 1291–1298. and references therein.

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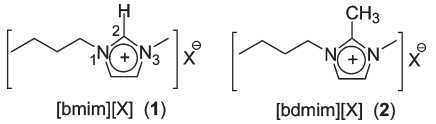
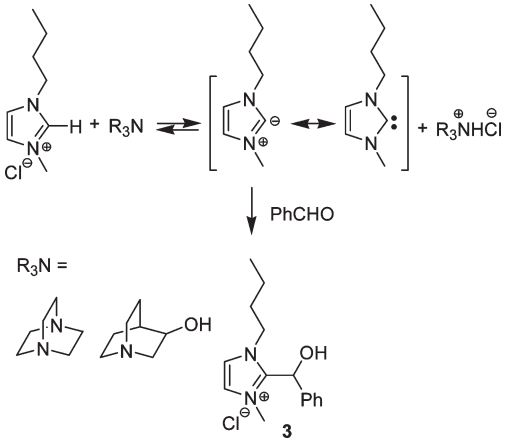


FIGURE 1. 1-Butyl-3-methylimidazolium ([bmim]) and 1-butyl-2,3-dimethylimidazolium ([bdmim]) ionic liquids.

SCHEME 2. Side Reaction of 1-Butyl-3-methylimidazolium ([bmim]) Ionic Liquid with Benzaldehyde



the C-2 proton of the 1,3-dialkylimidazolium cation is acidic and removed even under mild basic conditions.[9] The generated carbene, which could act as a ligand for metal catalysts, showed advantageous effects in the Heck reaction and in the Suzuki coupling.[7] However, the carbene significantly inhibited the desired chemical transformations in the Horner−Wadsworth−Emmons reaction, Knoevenagel condensation, Claisen−Schmidt condensation, and the Baylis−Hillman reaction.[7] In the case of the Baylis−Hillman reaction, deprotonation at the imidazolium C-2 position produced a nucleophile, which directly reacted with the aldehyde, leading to the adduct **3** (Scheme 2).[9] The undesired side reaction was partly suppressed by introducing a substituent at the C-2 position of imidazolium salts,[10] e.g., 1-butyl-2,3-dimethylimidazolium ([bdmim]) (**2**, Figure 1). However, the C-2 methyl group also undergoes slow proton exchange in the presence of triethylamine.[11] Therefore, there is a need for chemically inert ionic liquids suitable for reactions involving strong bases.[12]

In this context, we herein report the development of a chemically inert 1,2,3-triazolium-based ionic liquid and its application to the Baylis−Hillman reaction. The stereotype of our novel 1,2,3-triazolium ionic liquid is shown in Figure 2. The 1 and 3 positions of 1,2,3-triazolium[13] have been functionalized with *n*-butyl, methyl, or benzyl to maintain

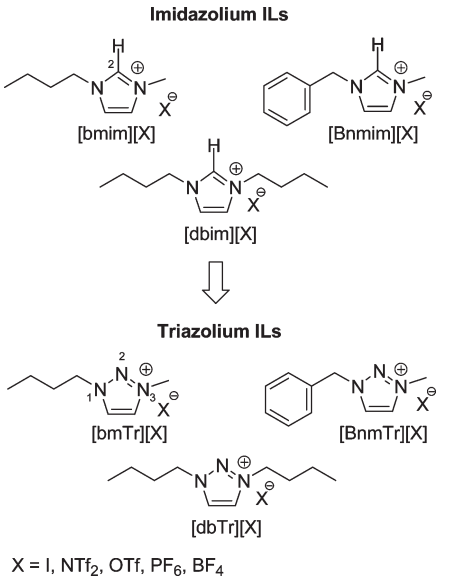
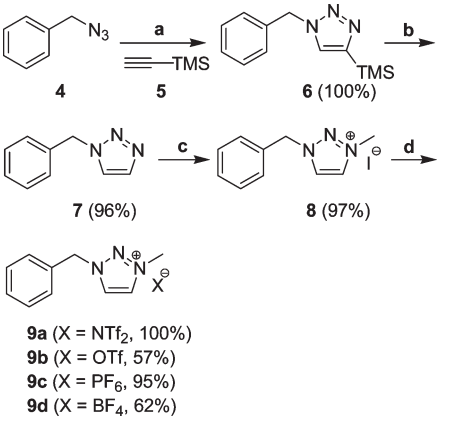


FIGURE 2. Design of 1,3-dialkyl-1,2,3-triazolium ionic liquids.

SCHEME 3. Synthesis of 1-Benzyl-3-methyl-1,2,3-triazolium Ionic Liquids [BnmTr][X][a]



[a]Reagents and conditions: (a) $CuSO_4$, sodium ascorbate, *t*-BuOH/H_2O (1/1), rt, 1 d; (b) TBAF, THF, rt, 6 h; (c) CH_3I, 80 °C, 17 h; (d) **9a**: $LiNTf_2$, H_2O, 40 °C, 1 d; **9b**: KOTf, H_2O, 40 °C, 1 d; **9c**: $LiPF_6$, H_2O, 40 °C, 1 d; **9d**: $AgBF_4$, H_2O, 40 °C, 1 d.

similar ionic liquid properties and structural features to conventional [bmim] cations, while the problematic acidic C-2 proton of 1,3-dialkylimidazolium cation has been replaced by the nitrogen of the 1,3-dialkyl-1,2,3-triazolium cation to obtain the stability under basic conditions. Since the properties of ionic liquids can be controlled to a large degree by varying the nature of either the cation or the anion, it is particularly interesting to test whether the introduction of a third nitrogen impacts the chemical or physical properties or charge distribution of the ring relative to the 1,3-imidazole.

Results and Discussion

Synthesis of 1,2,3-Triazolium Ionic Liquid. The 1-benzyl-3-methyl-1,2,3-triazolium salts ([BnmTr][X]) were easily accessed by Cu-catalyzed Huisgen 1,3-dipolar cycloaddition using benzyl azide (**4**) and 1-trimethylsilylacetylene (**5**) (Scheme 3), which proved useful for the synthesis of unsymmetrically substituted

(9) (a) Santos, L. S.; Da Silveira Neto, B. A.; Consorti, C. S.; Pavam, C. H.; Almeida, W. P.; Coelho, F.; Dupont, J.; Eberlin, M. N. *J. Phys. Org. Chem.* **2006**, *19*, 731–736. (b) Aggarwal, V. K.; Emme, I.; Mereu, A. *Chem. Commun.* **2002**, 1612–1613.

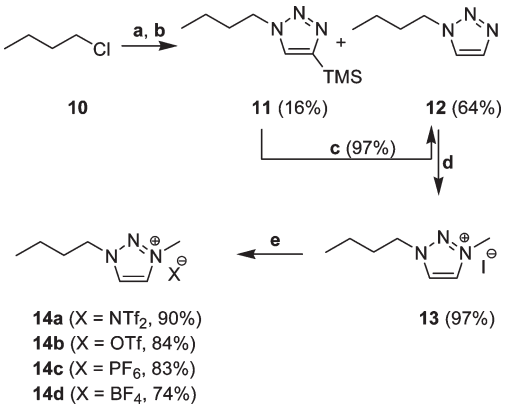
(10) Hsu, J.-C.; Yen, Y.-H.; Chu, Y.-H. *Tetrahedron Lett.* **2004**, *45*, 4673–4676.

(11) Handy, S. T.; Okello, M. *J. Org. Chem.* **2005**, *70*, 1915–1918.

(12) Jurčík, V.; Wilhelm, R. *Green Chem.* **2005**, *7*, 844–848.

(13) For 1,3,4-trialkyl-1,2,3-triazolium and pyrrolidine-tethered 1,3,4-trialkyl-1,2,3-triazolium, see: (a) Hanelt, S.; Liebscher, J. *Synlett* **2008**, 1058–1060. (b) Yacob, Z.; Shah, J.; Leistner, J.; Liebscher, J. *Synlett* **2008**, 2342–2344.

SCHEME 4. Synthesis of 1-Butyl-3-methyl-1,2,3-triazolium Ionic Liquids ([bmTr][X])[a]

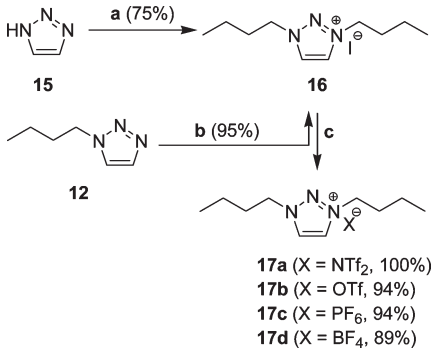


[a]Reagents and conditions: (a) NaN_3, DMF, 80 °C, 20 h; (b) **5**, CuI, DMF, 80 °C, 40 h; (c) TBAF, THF, rt, 6 h.; (d) CH_3I, 80 °C, 1 d; (e) **14a**: $LiNTf_2$, H_2O, 40 °C, 1 d; **14b**: KOTf, H_2O, 40 °C, 1 d; **14c**: $LiPF_6$, H_2O, 40 °C, 1 d; **14d**: $AgBF_4$, H_2O, 40 °C, 1 d.

1,3-dialkyl-1,2,3-triazolium because direct alkylation of the 1*H*-1,2,3-triazole generally produces mixtures of regioisomers or symmetrically dialkylated products. The "click" reaction of benzyl azide (**4**) and 1-trimethylsilylacetylene (**5**) provided complete conversion to triazole **6**, the TMS of which was removed by TBAF. 1-Benzyl-1,2,3-triazole (**7**) was quaternized at N-3 by reaction with equivalent amounts of methyl iodide under neat reaction conditions at 80 °C to afford 1,2,3-triazolium iodide salt **8** in nearly quantitative yield and high purity. Not surprisingly, this iodide salt has a rather high melting point (127.5−129.5 °C). Metathesis of **8** with $LiNTf_2$, KOTf, $LiPF_6$, or $AgBF_4$ in water afforded new quaternary salts **9a**−**d** in moderate to excellent yields. Compounds **9a** and **9b** are liquids at room temperature. Compounds **9c** and **9d** are solids that melt below 100 °C. Our 1,2,3-triazolium salts **9c** and **9d** have slightly lower melting points (**9c**: 90.5 °C, **9d**: 74.3 °C) compared to the corresponding imidazolium salts (e.g., 1-benzyl-3-methylimidazolium hexafluorophosphate ([Bnmim][PF_6]): 130.6 °C,[14] 1-benzyl-3-methylimidazolium tetrafluoroborate ([Bnmim][BF_4]): 77 °C[15]).

Next, we prepared 1-butyl-3-methyl-1,2,3-triazolium salts, which are structurally similar to the most commonly used [bmim] ionic liquids. The 1-butyl-3-methyl-1,2,3-triazolium salts ([bmTr][X]) (**14a**−**d**) were prepared in three steps (Scheme 4). The *n*-butyl azide was generated in situ from *n*-butyl chloride (**10**) and NaN_3, whereupon it was captured by 1-trimethylsilylacetylene via a Cu-catalyzed "click" reaction. Unlike the click reaction using benzyl azide (**4**), the click reaction with *n*-butyl azide led to the formation of the 4-TMS-substituted 1,2,3-triazole product **11** and 4,5-unsubstituted 1,2,3-triazole analogue **12**. The subsequent deprotection of TMS converted **11** to **12**, which was readily quaternized with methyl iodide under neat conditions at 80 °C in 97% yield. The regiochemistry of *N*-methylation was unambiguously determined by 1D-NOE experiments (see the Supporting Information). Finally, the desired [bmTr] salts (**14a**−**d**) were obtained by a metathesis reaction of iodide salt **13** with $LiNTf_2$, KOTf, $LiPF_6$, or $AgBF_4$. All of the synthesized [bmTr] salts **13** and **14a**−**d** were liquids at room temperature when they were

SCHEME 5. Synthesis of 1,3-Dibutyl-1,2,3-triazolium Ionic Liquids ([dbTr][X])[a]



[a]Reagents and conditions: (a) NaH, *n*-butyl iodide (5 equiv), CH_3CN, 80 °C, 19 h; (b) *n*-butyl iodide (1 equiv), neat, 80 °C, 15 h; (c) (**17a**) $LiNTf_2$, H_2O, 40 °C, 15 h; (**17b**) KOTf, H_2O, 40 °C, 11 h; (**17c**) $LiPF_6$, H_2O, 40 °C, 22 h; (**17d**) $AgBF_4$, H_2O, 40 °C, 20 h.

TABLE 1. Thermal Decomposition Temperatures of 1,2,3-Triazolium Salts

entry	ionic liquids[a]	T_d[b] (°C)
1	[BnmTr][I] (**8**)	178
2	[BnmTr][NTf_2] (**9a**)	278
3	[BnmTr][OTf] (**9b**)	160
4	[BnmTr][PF_6] (**9c**)	287
5	[BnmTr][BF_4] (**9d**)	284
6	[bmTr][I] (**13**)	196
7	[bmTr][NTf_2] (**14a**)	333
8	[bmTr][OTf] (**14b**)	170
9	[bmTr][PF_6] (**14c**)	355
10	[bmTr][BF_4] (**14d**)	340
11	[dbTr][NTf_2] (**17a**)	350
12	[dbTr][OTf] (**17b**)	195
13	[dbTr][PF_6] (**17c**)	341
14	[dbTr][BF_4] (**17d**)	345

[a][BnmTr] = 1-benzyl-3-methyl-1,2,3-triazolium, [bmTr] = 1-butyl-3-methyl-1,2,3-triazolium, [dbTr] = 1,3-dibutyl-1,2,3-triazolium. [b]Thermal decomposition temperature.

TABLE 2. Miscibility[a] of Various Ionic Liquids in Organic Solvents with Dielectric Constant ε[b]

ionic liquids[c]	hexane	Et_2O	EtOAc	CH_2Cl_2	H_2O
[BnmTr][NTf_2] (**9a**)	nm	nm	m	m	nm
[BnmTr][OTf] (**9b**)	nm	nm	m	m	pm
[bmTr][I] (**13**)[d]	nm	nm	nm	m	pm
[bmTr][NTf_2] (**14a**)	nm	nm	m	m	nm
[bmTr][OTf] (**14b**)	nm	nm	m	m	pm
[bmTr][PF_6] (**14c**)[d]	nm	nm	m	m	nm
[bmTr][BF_4] (**14d**)	nm	nm	m	m	m
[dbTr][I] (**16**)	nm	nm	m	m	m
[dbTr][NTf_2] (**17a**)	nm	m	m	m	nm
[dbTr][OTf] (**17b**)	nm	nm	m	m	pm
[dbTr][PF_6] (**17c**)	nm	nm	m	m	nm
[dbTr][BF_4] (**17d**)	nm	nm	m	m	m

[a]m = miscible, nm = nonmiscible, pm = partially miscible. [b]Dielectric constant ε at 20 °C; hexane = 1.89; Et_2O = 4.34; EtOAc = 6 (25 °C); CH_2Cl_2 = 9.08; H_2O = 78.54. [c][BnmTr] = 1-benzyl-3-methyl-1,2,3-triazolium, [bmTr] = 1-butyl-3-methyl-1,2,3-triazolium, [dbTr] = 1,3-dibutyl-1,2,3-triazolium. [d]Miscibility was checked when ionic liquids melted.

(14) Peng, J. J.; Li, J. Y.; Bai, Y.; Gao, W. H.; Qiu, H. Y.; Wu, H.; Deng, Y.; Lai, G. Q. *J. Mol. Catal. A: Chem.* **2007**, *278*, 97–101. [Bnmim][PF_6] is commercially available, and the melting point obtained from the Aldrich database is 136 °C.

(15) SakiZdeh, K.; Olson, L. P.; Cowdery-Corvan, P. J.; Ishida, T.; Whitcomb, D. R. US Patent 7 163 786, 2007. [Bnmim][BF_4] is commercially available, and the melting point obtained from Aldrich database is 77 °C.

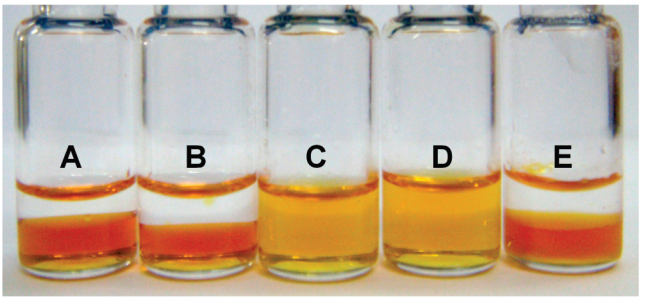
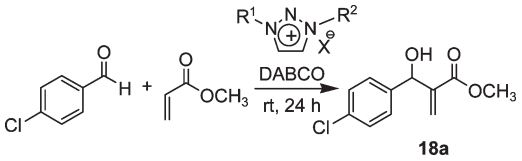


FIGURE 3. Miscibility of [bmTr][PF_6] in common organic solvents. Picture was taken when IL melted: (A) hexane (top layer) and [bmTr][PF_6] (bottom layer); (B) Et_2O (top layer) and [bmTr][PF_6] (bottom layer); (C) EtOAc and [bmTr][PF_6] (miscible); (D) CH_2Cl_2 and [bmTr][PF_6] (miscible); (E) H_2O (top layer) and [bmTr][PF_6] (bottom layer).

TABLE 3. Baylis–Hillman Reactions of *p*-Chlorobenzaldehyde and Methyl Acrylate in Various 1,2,3-Triazolium Ionic Liquids[a]



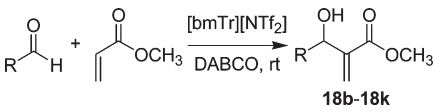
entry	ionic liquid	R_1	R_2	yield (%)
1	[BnmTr][NTf_2] (**9a**)	benzyl	methyl	61
2	[BnmTr][OTf] (**9b**)	benzyl	methyl	77
3	[bmTr][I] (**13**)	*n*-butyl	methyl	46
4	[bmTr][NTf_2] (**14a**)	*n*-butyl	methyl	83
5	[bmTr][OTf] (**14b**)	*n*-butyl	methyl	63
6	[bmTr][PF_6] (**14c**)	*n*-butyl	methyl	96
7	[bmTr][BF_4] (**14d**)	*n*-butyl	methyl	80
8	[dbTr][I] (**16**)	*n*-butyl	*n*-butyl	74
9	[dbTr][NTf_2] (**17a**)	*n*-butyl	*n*-butyl	91
10	[dbTr][OTf] (**17b**)	*n*-butyl	*n*-butyl	77
11	[dbTr][PF_6] (**17c**)	*n*-butyl	*n*-butyl	80
12	[dbTr][BF_4] (**17d**)	*n*-butyl	*n*-butyl	83
13	[bmim][PF_6]			67
14	[bmim][NTf_2]			68

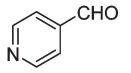
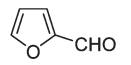
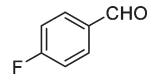
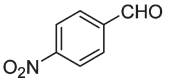
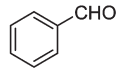
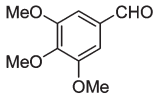
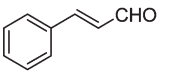
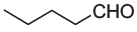
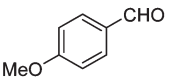
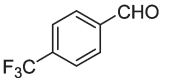
[a]Reaction conditions: *p*-chlorobenzaldehyde (144 mg, 1.00 mmol), methyl acrylate (173 mg, 2.01 mmol), DABCO (230 mg, 2.01 mmol), ionic liquid (0.1 mL), room temperature, 24 h.

prepared. Interestingly, **13** and **14c** were solidified very slowly and melted at 42 and 47 °C, respectively. Once they melted, they remained liquid for several hours at room temperature. This phenomenon was also reported for the imidazolium-based [mPhmim][PF_6] ionic liquid having mp close to room temperature. It was also used as a solvent for the Baylis–Hillman reaction.[12]

The 1,3-dibutyl-1,2,3-triazolium salts ([dbTr][X]) (**17a–d**) were prepared via direct alkylation. 1*H*-1,2,3-Triazole (**15**) was treated with 1 equiv of NaH before the addition of excess *n*-butyl iodide in the CH_3CN (Scheme 5). We obtained the desired dialkylated product **16** as a sole product in 75% yield in one step from commercially available 1*H*-1,2,3-triazole (**15**). Alternatively, **16** could be synthesized from 1-butyl-1,2,3-triazole (**12**) using 1 equiv of *n*-butyl iodide under neat conditions in 95% yield. Metathesis of **16** in the presence of $LiNTf_2$, KOTf, $LiPF_6$, or $AgBF_4$ provided the desired [dbTr] salts **17a–d** as ionic liquids.

TABLE 4. Baylis–Hillman Reactions with Methyl Acrylate and Various Aldehydes in [bmTr][NTf_2] (14a)[a]

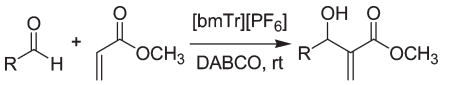


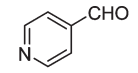
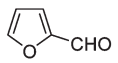
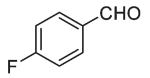
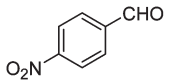
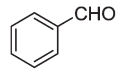
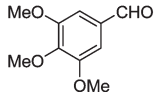
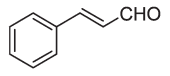
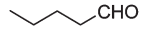
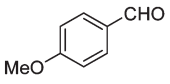
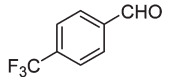
Entry	RCHO	Product	Time (h)	Yield (%)
1		**18b**	0.3	87
2		**18c**	4.5	74
3		**18d**	24	88
4		**18e**	0.3	85
5		**18f**	24	81
6		**18g**	66	81
7		**18h**	24	55
8		**18i**	72	33
9		**18j**	72	39
10		**18k**	2	64

[a]Reaction conditions: aldehyde (1.00 mmol), methyl acrylate (173 mg, 2.01 mmol), DABCO (230 mg, 2.01 mmol), [bmTr][NTf_2] (0.1 mL), room temperature.

The three types of 1,2,3-triazolium salts, including [BnmTr], [bmTr], and [dbTr] have been synthesized: **9a**, **9b**, **14a**, **14b**, **14d**, **16**, and **17a–d** are liquids at room temperature; **9c**, **9d**, **13**, and **14c**, solid salts at room temperature, melt below 100 °C. Therefore, all 1,2,3-triazolium salts except **8** may be classified as ionic liquids. Water content of some prepared triazolium salts are given in the Experimental Section, and their thermal decomposition temperatures were determined by thermogravimetric analysis and described in Table 1. The thermal stabilities of the 1,2,3-triazoliun compounds might be a concern because they contain three nitrogens. However, they show good thermal stabilities up to 355 °C (Table 1, entry 9). The thermal stabilities of the prepared 1,2,3-triazolium salts depend on the anion species. Iodide and TfO^- dramatically reduce the thermal stability with the onset of decomposition occurring approximately 100 °C below the corresponding ionic liquids with PF_6^-, Tf_2N^-, BF_4^- anions. Relative anion stabilities have been suggested as PF_6^-, Tf_2N^-, $BF_4^- \gg TfO^-$, I^-.

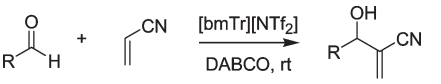
TABLE 5. Baylis−Hillman Reactions with Methyl Acrylate and Various Aldehydes in [bmTr][PF_6] (14c)[a]

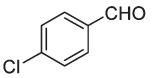
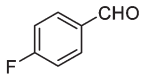
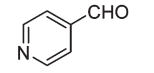
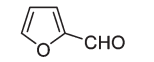
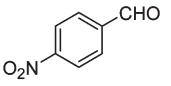
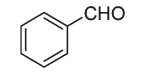
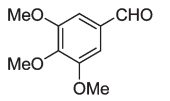
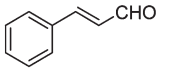
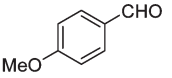
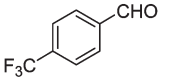


Entry	RCHO	Product	Time (h)	Yield (%)
1		**18b**	0.3	93
2		**18c**	4.5	86
3		**18d**	24	80
4		**18e**	0.3	79
5		**18f**	24	77
6		**18g**	66	81
7		**18h**	24	66
8		**18i**	47	47
9		**18j**	50	41
10		**18k**	0.25	67

[a]Reaction conditions: aldehyde (1.00 mmol), methyl acrylate (173 mg, 2.01 mmol), DABCO (230 mg, 2.01 mmol), [bmTr][PF_6] (0.1 mL), room temperature.

TABLE 6. Baylis−Hillman Reactions with Acrylonitrile and Various Aldehydes in [bmTr][NTf_2] (14a) [a]



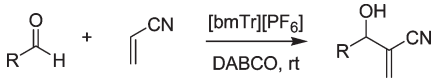
Entry	RCHO	Product	Time (h)	Yield (%)
1		**19a**	3	99
2		**19b**	24	99
3		**19c**	0.05	99
4		**19d**	1.5	96
5		**19e**	0.05	92
6		**19f**	16	97
7		**19g**	5.5	79
8		**19h**	9	80
9		**19i**	65	99
10		**19j**	0.17	99

[a]Reaction conditions: aldehyde (1.00 mmol), acrylonitrile (107 mg, 2.01 mmol), DABCO (230 mg, 2.01 mmol), [bmTr][NTf_2] (0.1 mL), room temperature.

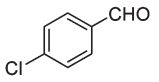
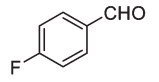
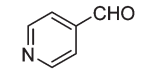
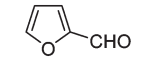
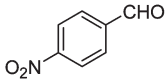
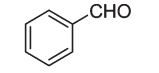
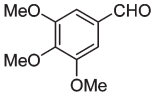
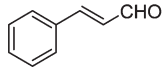
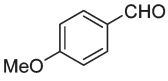
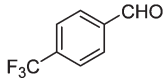
In general, the product and byproduct can be separated from ionic liquid media by simple extraction with organic solvents, which enables ionic liquids to be recycled. The solubility of ionic liquid in organic solvents is an important factor for recycling. Thus, we tested the solubilities of 1,2,3-triazolium ionic liquids in several common organic solvents (Table 2). The solubilities increase with the dielectric constant of the solvents. The ionic salts do not dissolve in hexane or Et_2O, but their solubilities increase in CH_2Cl_2 or ethyl acetate. The solubility in H_2O depends on the anion of the ionic liquid. The NTf_2 salts and the PF_6 salts are not miscible with H_2O, but the BF_4 salts are. The miscibility of the representative 1,2,3-triazolium ionic liquid [bmTr][PF_6] is shown in Figure 3. With the novel ionic liquids in hand, we then shifted our focus to the feasibility of the Baylis−Hillman reaction in a variety of 1,2,3-triazolium ionic liquids.

Baylis−Hillman Reaction in 1,2,3-Triazolium Ionic Liquid. To compare the reaction rates in these novel ionic liquids, we first examined the Baylis−Hillman reaction of *p*-chlorobenzaldehyde (1 mmol), methyl acrylate (2 mmol), and DABCO (2 mmol) in the presence of 1,2,3-triazolium ionic liquids (0.1 mL). All reactions were performed at ambient temperature for 24 h, and the product **18a** was purified by column chromatography. [bmTr][I] (**13**) and [bmTr][PF_6] (**14c**) were loaded as a liquid after slight warming. All 1,2,3-triazolium ionic liquids were good reaction media for the Baylis−Hillman reaction (Table 3). The results clearly demonstrate that the Baylis−Hillman reaction can be greatly accelerated in [bmTr][NTf_2] (**14a**), [bmTr][PF_6] (**14c**), and [dbTr][NTf_2] (**17a**) (entries 4, 6, and 9). In particular, we were interested in the comparison of [bmim][PF_6], [bmim][NTf_2], and our 1,2,3-triazolium ionic liquids. Thus, the Baylis−Hillman reaction in [bmim][PF_6] or [bmim][NTf_2] was conducted under the same reaction conditions (entries 13 and 14). As expected, almost all 1,2,3-triazolium ionic liquids except [BnmTr][NTf_2] (**9a**), [bmTr][I] (**13**), and [bmTr][OTf] (**14b**)

TABLE 7. Baylis–Hillman Reactions with Acrylonitrile and Various Aldehydes in [bmTr][PF_6] (14c)[a]



19a-19j

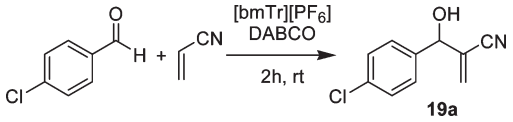
Entry	RCHO	Product	Time (h)	Yield (%)
1		**19a**	3	99
2		**19b**	24	99
3		**19c**	0.05	99
4		**19d**	1.5	51
5		**19e**	0.05	97
6		**19f**	16	99
7		**19g**	5.5	99
8		**19h**	9	87
9		**19i**	65	98
10		**19j**	0.17	93

[a]Reaction conditions: aldehyde (1.00 mmol), acrylonitrile (107 mg, 2.01 mmol), DABCO (230 mg, 2.01 mmol), [bmTr][PF_6] (0.1 mL), room temperature.

provided better yields than [bmim][PF_6] (74–96% vs 67%). In particular, the 1,2,3-triazolium ionic liquids with the same PF_6 anion (entries 6 and 11) afforded better yields than [bmim][PF_6] (96% and 80% vs 67%). Presumably, the problems associated with deprotonation of C-2 hydrogen of [bmim] cation could be suppressed in the reaction of [bmTr] or [dbTr].

Based on the screening above, we selected [bmTr][NTf_2] (**14a**) and [bmTr][PF_6] (**14c**) to explore the substrate scope of the Baylis–Hillman reaction. We then investigated the Baylis–Hillman reaction with a variety of aldehydes, such as aliphatic, aromatic, and α,β-unsaturated aldehydes in [bmTr][NTf_2] (**14a**) (Table 4) and [bmTr][PF_6] (**14c**) (Table 5). [bmTr][NTf_2] (**14a**) is a free-flowing liquid at room temperature and even at −78 °C. All reactions occurred smoothly under standard conditions, giving the corresponding products **18b–k**. The reaction rates were most rapid for substrates bearing 4-pyridyl or *p*-nitrophenyl groups (Table 4 and 5, entries 1 and 4). These results imply that

TABLE 8. Reuse of the Ionic Liquid [bmTr][PF_6][a]



19a

	isolated yield (%)	
cycle	method A[b]	method B[c]
1	95	99
2	89	99
3	98	100
4	100	100

[a]Reaction conditions: *p*-chlorobenzaldehyde (431 mg, 3.01 mmol), acrylonitrile (321 mg, 6.02 mmol), DABCO (690 mg, 6.03 mmol), [bmTr][PF_6] (0.3 mL), room temperature, 2 h. [b]IL was recovered by Et_2O extraction. [c]IL was recovered by column chromatography without extraction (see the Experimental Section).

the electron-withdrawing resonance effect of the nitro group in *p*-nitrobenzaldehyde and the nitrogen on the pyridine ring in 4-pyridinecarboxaldehyde is important in accelerating the Baylis–Hillman reaction. On the other hand, the aliphatic aldehyde (Table 4 and 5, entry 8) and aromatic aldehydes bearing electron-donating groups (Table 4 and 5, entries 6 and 9) react comparatively slowly and produce the corresponding adducts in moderate yields. The current substrate scope in [bmTr]-[NTf_2] (**14a**) and [bmTr][PF_6] (**14c**) is similar to that in [bmim]-[PF_6], but [bmTr][NTf_2] (**14a**) and [bmTr][PF_6] (**14c**) afford reliably higher yields than [bmim][PF_6].[16]

To demonstrate the extended applicability of [bmTr][NTf_2] (**14a**) and [bmTr][PF_6] (**14c**) for the Baylis–Hillman reactions, acrylonitrile was also tested as another Michael acceptor with various aldehydes (Table 6 and Table 7). Compared to methyl acrylate reactions, higher yields were achieved for all the reactions in a shorter reaction time. Regardless of substituents, almost all substrates were quantitatively converted to the desired Baylis–Hillman products. On the other hand, furfural only provided a moderate yield of the desired product **19d**, which was decomposed rapidly during the reaction (Table 7, entry 4). **19d** is rather unstable with [bmTr][PF_6] (**14c**) reaction conditions.[17] However, this decomposition was not observed in the [bmTr][NTf_2] (**14a**) reaction, and 96% of isolated yield was obtained (Table 6, entry 4).

Due to chemical stability and negligible volatility, ionic liquids are amenable to multiple recycling cycles, which considerably decrease the production of environmentally harmful waste and the cost of a process, two criteria for "green solvents". Thus, we tested the recycling of our novel [bmTr][PF_6] (**14c**) for the reaction of *p*-chlorobenzaldehyde and acrylonitrile. Upon the completion of the first reaction, the product was extracted from [bmTr][PF_6] (**14c**) with Et_2O and purified by column chromatography (method A). After drying the ionic liquid under reduced pressure, a second batch of aldehyde, acrylonitrile, and DABCO was added. During recycling, ^{1}H NMR analysis of the ionic liquid showed a trace of DABCO. Alternately, [bmTr][PF_6] (**14c**)

(16) Rosa, J. N.; Afonso, C. A. M.; Santos, A. G. *Tetrahedron* **2001**, *57*, 4189–4193.

(17) The rapid decomposition of the product **19d** was also reported in the literature; see: Aggarwal, V. K.; Emme, I.; Fulford, S. Y. *J. Org. Chem.* **2003**, *68*, 692–700.

was recovered without extraction by column chromatography (method B). In both methods, [bmTr][PF_6] (**14c**) could be recycled up to four times without significant loss in yield (Table 8).

Conclusions

We have developed 1,3-dialkyl-1,2,3-triazolium ionic liquids as stable and recyclable solvents. The applicability of the ionic liquids as new reaction media is shown for the Baylis−Hillman reaction. 1,3-Dialkyl-1,2,3-triazolium ionic liquids showed comparable properties to imidazolium ionic liquids in terms of thermal stability and miscibility. However, the 1,2,3-triazolium ionic liquids are chemically inert under basic condition, which makes them more suitable media for base-mediated reactions. They could be used as base-stable surrogates for imidazolium ionic liquids. Further applications of the 1,2,3-triazolium-based ionic liquids to other important reactions are underway in our laboratory.

Experimental Section

Synthesis of Ionic liquids. 1-Benzyl-4-trimethylsilyl-1,2,3-triazole (6). Benzyl azide (266 mg, 2.00 mmol), trimethylsilylacetylene (196 mg, 2.00 mmol), $CuSO_4$ (16 mg, 0.10 mmol), and sodium ascorbate (40 mg, 0.20 mmol) were suspended in a mixed solution of *tert*-butyl alcohol/water (4 mL, 1/1) at rt. After the mixture was stirred for 24 h, a brown crystalline solid precipitated from the reaction. Filtration and washing with water afforded **6** (460 mg, 100%) as a brown solid. TLC: R_f 0.14 (3:1 hexane/EtOAc). Mp: 54−56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1H), 7.39−7.35 (m, 3H), 7.27 (dd, 2H, J = 5.6, 1.6 Hz), 5.55 (s, 2H), 0.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 136.1, 130.2, 129.8, 129.7, 129.2, 54.6, 0.0. LRMS (FAB) m/z (rel int): 91 ([C_7H_7]$^+$, 63), 232 ([M + H]$^+$, 100). HRMS: m/z calcd for $C_{12}H_{18}N_3Si$ 232.1270, found 232.1270.

1-Benzyl-1,2,3-triazole (7). To a solution of triazole **6** (2.26 g, 9.78 mmol) in anhydrous THF (9.8 mL) was dropwise added TBAF (1 M in THF, 11.7 mL, 11.7 mmol). The reaction was monitored for the disappearance of starting materials by TLC. After 6 h at rt, the reaction mixture was concentrated in vacuo. Column chromatography on silica gel (3:1 hexane/EtOAc) afforded a desired triazole **7** (1.49 g, 96%) as a white solid. TLC: R_f 0.12 (3:1 hexane/EtOAc). Mp: 61−63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.47 (s, 1H), 7.38−7.36 (m, 3H), 7.28−7.25 (m, 2H), 5.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.9, 134.5, 129.3, 129.0, 128.2, 123.5, 54.2. LRMS (FAB) m/z (rel int): 91 ([C_7H_7]$^+$, 63), 160 ([M + H]$^+$, 80). HRMS: m/z calcd for $C_9H_{10}N_3$ 160.0875, found 160.0872.

1-Benzyl-3-methyl-1,2,3-triazolium Iodide (8). In a screw cap vial, a mixture of **7** (1.97 g, 12.4 mmol) and iodomethane (1.76 g, 12.4 mmol) was stirred at 80 °C for 17 h. Upon completion of the reaction, the reaction mixture was concentrated in vacuo to afford analytically pure **8** (3.62 g, 97%) as a pale yellow solid. Mp: 127.5−129.5 °C. Water content (0.03%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (brs, 1H), 9.31 (brs, 1H), 7.61−7.58 (m, 2H), 7.44−7.42 (m, 3H), 5.97 (s, 2H), 4.51 (s, 3H). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.98 (d, 1H, J = 1.2 Hz), 8.86 (d, 1H, J = 1.2 Hz), 7.49−7.42 (m, 5H), 5.89 (s, 2H), 4.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 133.0, 132.1, 130.8, 129.2, 129.0, 128.8, 56.0, 40.0. LRMS (FAB) m/z (rel int): 91 ([C_7H_7]$^+$, 24), 174 ([$C_{10}H_{12}N_3$]$^+$, 100). HRMS: m/z calcd for $C_{10}H_{12}N_3$ 174.1031, found 174.1027.

1-Benzyl-3-methyl-1,2,3-triazolium Bis(trifluoromethylsulfonyl)-amide (9a). In a screw cap vial, a mixture of **8** (330 mg, 1.10 mmol) and $LiNTf_2$ (315 mg, 1.10 mmol) in deionized water (1.6 mL) was stirred at 40 °C for 24 h. Upon completion of the reaction, the reaction mixture was cooled to rt and extracted with CH_2Cl_2. The combined extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **9a** (496 mg, 100%) as a brown liquid. Water content (0.07%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, 1H, J = 1.6 Hz), 8.30 (d, 1H, J = 1.6 Hz), 7.43 (brs, 5H), 5.69 (s, 2H), 4.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.1, 130.7, 130.6, 130.5, 130.0, 129.6, 119.9 (q, J_{CF} = 319.1 Hz), 58.1, 40.7. LRMS (FAB) m/z (rel int): (pos) 91 ([C_7H_7]$^+$, 24), 174 ([$C_{10}H_{12}N_3$]$^+$, 100). HRMS: m/z calcd for $C_{10}H_{12}N_3$ 174.1031, found 174.1027. Anal. Calcd for $C_{12}H_{12}F_6N_4O_4S_2$: C, 31.72; H, 2.66; N, 12.33; S, 14.11. Found: C, 31.76; H, 2.70; N, 12.34; S, 14.37.

1-Benzyl-3-methyl-1,2,3-triazolium Trifluoromethylsulfonate (9b). In a screw cap vial, a mixture of **8** (1.00 g, 3.33 mmol) and KOTf (0.67 g, 3.33 mmol) in deionized water (4.8 mL) was stirred at 40 °C for 24 h. Upon completion of the reaction, the reaction mixture was cooled to rt and extracted with CH_2Cl_2. The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **9b** (0.62 g, 57%) as a brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (d, 1H, J = 1.6 Hz), 8.85 (d, 1H, J = 1.6 Hz), 7.51−7.49 (m, 2H), 7.41−7.39 (m, 3H), 5.81 (s, 2H), 4.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.4, 131.4, 131.0, 130.2, 129.7, 129.6, 120.7 (q, J_{CF} = 318.3 Hz), 57.7, 40.8. LRMS (FAB) m/z (rel int): (pos) 91 ([C_7H_7]$^+$, 30), 174 ([$C_{10}H_{12}N_3$]$^+$, 100). HRMS: m/z calcd for $C_{10}H_{12}N_3$ 174.1031, found 174.1035.

1-Benzyl-3-methyl-1,2,3-triazolium Hexafluorophosphate (9c). In a screw cap vial, a heterogeneous mixture of **8** (600 mg, 1.99 mmol) and $LiPF_6$ (309 mg, 1.99 mmol) in deionized water (2.0 mL) was stirred at 40 °C for 24 h. Upon completion of the reaction, the reaction mixture was cooled to rt, and extracted with CH_2Cl_2. The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **9c** (606 mg, 95%) as a yellow solid. Mp: 90.5−92.5 °C. Water content (0.02%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.27 (s, 1H), 7.45 (m, 5H), 5.70 (s, 2H), 4.36 (s, 3H). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.96 (d, 1H, J = 1.6 Hz), 8.84 (d, 1H, J = 1.6 Hz), 7.47−7.43 (m, 5H), 5.88 (s, 2H), 4.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 133.0, 132.1, 130.8, 129.2, 129.1, 128.8, 56.0, 39.5. LRMS (FAB) m/z (rel int): (pos) 91 ([C_7H_7]$^+$, 26), 174 ([$C_{10}H_{12}N_3$]$^+$, 100). HRMS: m/z calcd for $C_{10}H_{12}N_3$ 174.1031, found 174.1036. Anal. Calcd for $C_{10}H_{12}F_6N_3P$: C, 37.63; H, 3.79; N, 13.16. Found: C, 37.80; H, 3.88; N, 13.31.

1-Benzyl-3-methyl-1,2,3-triazolium Tetrafluoroborate (9d). In a screw cap vial, a heterogeneous mixture of **4** (806 mg, 2.68 mmol) and $AgBF_4$ (521 mg, 2.68 mmol) in deionized water (2.7 mL) was suspended at 40 °C for 24 h. Upon completion of the reaction, the reaction mixture was cooled to rt and extracted with CH_2Cl_2. The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **9d** (603 mg, 62%) as a white solid. Mp: 74.3−76.3 °C. Water content ($<$0.01%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, 1H, J = 1.6 Hz), 8.48 (d, 1H, J = 1.6 Hz), 7.48−7.45 (m, 2H), 7.45−7.42 (m, 3H), 5.72 (s, 2H), 4.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3, 131.7, 130.9, 130.1, 129.6, 129.5, 57.5, 40.4. LRMS (FAB) m/z (rel int): (pos) 91 ([C_7H_7]$^+$, 39), 174 ([$C_{10}H_{12}N_3$]$^+$, 100). HRMS: m/z calcd for $C_{10}H_{12}N_3$ 174.1031, found 174.1026. Anal. Calcd for $C_{10}H_{12}BF_4N_3$: C, 46.01; H, 4.63; N, 16.10. Found: C, 46.15; H, 4.57; N, 16.33.

1-Butyl-4-trimethylsilyl-1,2,3-triazole (11) and 1-Butyl-1,2,3-triazole (12). In a screw cap vial, a mixture of 1-chlorobutane (266 mg, 2.87 mmol) and sodium azide (476 mg, 7.32 mmol) in

DMF (3.7 mL) was stirred at 80 °C for 20 h. After the mixture was cooled to rt, trimethylsilylacetylene (359 mg, 3.66 mmol) and CuI (70 mg, 366 μmol) were added, and the solution was stirred at 80 °C for an additional 40 h. Upon completion of the reaction, the reaction mixture was cooled to rt and concentrated in vacuo. Column chromatography on silica gel (5:1 hexane/EtOAc) afforded desired compounds **11** (114 mg, 16%) and **12** (229 mg, 64%) as light-yellow liquids.

11. TLC: R_f 0.42 (3:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H), 4.38 (t, 2H, J = 7.4 Hz), 1.89 (m, 2H), 1.37 (sextet, 2H, J = 7.4 Hz), 0.96 (t, 3H, J = 7.4 Hz), 0.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 128.9, 49.7, 32.7, 20.0, 13.7, −0.9. LRMS (FAB) m/z (rel int): (pos) 198 ($[M + H]^+$, 100). HRMS: m/z calcd for $C_9H_{20}N_3Si$ 198.1427, found 198.1425.

12. TLC: R_f 0.16 (3:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.53 (s, 1H), 4.40 (t, 2H, J = 7.4 Hz), 1.90 (m, 2H), 1.36 (sextet, 2H, J = 7.4 Hz), 0.96 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0, 123.3, 50.1, 32.5, 19.9, 13.7. LRMS (FAB) m/z (rel int): (pos) 126 ($[M + H]^+$, 86). HRMS m/z calcd for $C_6H_{12}N_3$ 126.1031, found 126.1032.

1-Butyl-1,2,3-triazole (12). To a solution of triazole **11** (2.15 g, 10.9 mmol) in anhydrous THF (10.9 mL) was dropwise added TBAF (1 M in THF, 16.3 mL, 16.3 mmol). The reaction was monitored for the disappearance of starting materials by TLC. After 6 h at rt, the reaction mixture was concentrated in vacuo. Column chromatography on silica gel (3:1 hexane/EtOAc) afforded a desired triazole **12** (1.32 g, 97%) as a light-yellow liquid. TLC: R_f 0.16 (3:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.53 (s, 1H), 4.40 (t, 2H, J = 7.4 Hz), 1.90 (m, 2H), 1.36 (sextet, 2H, J = 7.4 Hz), 0.96 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0, 123.3, 50.1, 32.5, 19.9, 13.7. LRMS (FAB) m/z (rel int): (pos) 126 ($[M + H]^+$, 86). HRMS: m/z calcd for $C_6H_{12}N_3$ 126.1031, found 126.1032.

1-Butyl-3-methyl-1,2,3-triazolium Iodide (13). In a screw cap vial, a mixture of **12** (3.52 g, 28.1 mmol) and iodomethane (3.99 g, 28.1 mmol) was stirred at 80 °C for 24 h. Upon completion of the reaction, the reaction mixture was concentrated in vacuo to afford analytically pure **13** (7.26 g, 97%) as a brown liquid. **13** was solidified very slowly. Mp: 42 °C. Water content (0.16%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (d, 1H, J = 1.6 Hz), 9.31 (d, 1H, J = 1.6 Hz), 4.74 (t, 2H, J = 7.4 Hz), 4.53 (s, 3H), 2.05 (m, 2H), 1.44 (sextet, 2H, J = 7.4 Hz), 1.00 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3, 131.4, 54.2, 41.3, 31.5, 19.4, 13.4. LRMS (FAB) m/z (rel int): (pos) 140 ($[C_7H_{14}N_3]^+$, 100). HRMS: m/z calcd for $C_7H_{14}N_3$ 140.1188, found 140.1186. Anal. Calcd for $C_7H_{14}IN_3$: C, 31.48; H, 5.28; N, 15.73. Found: C, 31.51; H, 5.24; N, 15.65.

1-Butyl-3-methyl-1,2,3-triazolium Bis(trifluoromethylsulfonyl)-amide (14a). In a screw cap vial, a mixture of **13** (43.1 mg, 161 μmol) and $LiNTf_2$ (46.3 mg, 161 μmol) in deionized water (0.8 mL) was stirred at 40 °C for 24 h. Upon completion of the reaction, the reaction mixture was cooled to rt and extracted with CH_2Cl_2. The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **14a** (60.9 mg, 90%) as a brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, 1H, J = 1.6 Hz), 8.44 (d, 1H, J = 1.6 Hz), 4.59 (t, 2H, J = 7.4 Hz), 4.38 (s, 3H), 2.02 (m, 2H), 1.42 (sextet, 2H, J = 7.4 Hz), 1.00 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5, 130.5, 119.9 (q, J_{CF} = 319.1 Hz), 54.2, 40.4, 31.2, 19.4, 13.2. LRMS (FAB) m/z (rel int): (pos) 140 ($[C_7H_{14}N_3]^+$, 100). HRMS: m/z calcd for $C_7H_{14}N_3$ 140.1188, found 140.1188. Anal. Calcd for $C_9H_{14}F_6N_4O_4S_2$: C, 25.72; H, 3.36; N, 13.33; S, 15.26. Found: C, 25.98; H, 3.27; N, 13.26; S, 15.36.

1-Butyl-3-methyl-1,2,3-triazolium Trifluoromethylsulfonate (14b). In a screw cap vial, a mixture of **13** (234 mg, 874 μmol) and KOTf (168 mg, 874 μmol) in deionized water (1.3 mL) was stirred at 40 °C for 24 h. Upon completion of the reaction, the reaction mixture was cooled to rt, and extracted with IPA/$CHCl_3$ (1/4). The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **14b** (213 mg, 84%) as a brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, 1H, J = 1.6 Hz), 8.90 (d, 1H, J = 1.6 Hz), 4.66 (t, 2H, J = 7.4 Hz), 4.44 (s, 3H), 2.03 (m, 2H), 1.42 (sextet, 2H, J = 7.4 Hz), 1.00 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.0, 131.1, 120.6 (q, J_{CF} = 318.2 Hz), 54.0, 40.6, 31.3, 19.4, 13.3. LRMS (FAB) m/z (rel int): (pos) 140 ($[C_7H_{14}N_3]^+$, 100). HRMS: m/z calcd for $C_7H_{14}N_3$ 140.1188, found 140.1186. Anal. Calcd for $C_8H_{14}F_3N_3O_3S$: C, 33.22; H, 4.88; N, 14.53. Found: C, 33.45; H, 5.05; N, 14.14.

1-Butyl-3-methyl-1,2,3-triazolium Hexafluorophosphate (14c). In a screw cap vial, a heterogeneous mixture of **13** (198 mg, 742 μmol) and $LiPF_6$ (115 mg, 742 μmol) in deionized water (1.5 mL) was stirred at 40 °C for 11 h. Upon completion of the reaction, the reaction mixture was cooled to rt and extracted with IPA/$CHCl_3$ (1/4). The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **14c** (176 mg, 83%) as a brown liquid. It was decolorized according to the literature.[18] Compound **14c** was solidified very slowly. Mp: 47 °C. Water content (< 0.01%). I^- content (178 ppm). Cl^- content (32 ppm). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, 1H, J = 1.2 Hz), 8.44 (d, 1H, J = 1.2 Hz), 4.58 (t, 2H, J = 7.4 Hz), 4.36 (s, 3H), 2.00 (m, 2H), 1.41 (sextet, 2H, J = 7.4 Hz), 0.98 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.8, 130.7, 54.1, 40.4, 31.3, 19.5, 13.4. LRMS (FAB) m/z (rel int): (pos) 140 ($[C_7H_{14}N_3]^+$, 100). HRMS: m/z calcd for $C_7H_{14}N_3$ 140.1188, found 140.1186. Anal. Calcd for $C_7H_{14}F_6N_3P$: C, 29.48; H, 4.95; N, 14.74. Found: C, 29.61; H, 4.95; N, 14.82.

1-Butyl-3-methyl-1,2,3-triazolium Tetrafluoroborate (14d). In a screw cap vial, a heterogeneous mixture of **13** (99.6 mg, 373 μmol) and $AgBF_4$ (73.3 mg, 373 μmol) in deionized water (0.8 mL) was suspended at 40 °C for 17 h. Upon completion of the reaction, the reaction mixture was cooled to rt and extracted with IPA/$CHCl_3$ (1/4). The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **14d** (62.6 mg, 74%) as a light-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.54 (s, 1H), 4.58 (t, 2H, J = 7.4 Hz), 4.36 (s, 3H), 1.99 (m, 2H), 1.41 (sextet, 2H, J = 7.4 Hz), 0.98 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.0, 130.9, 53.9, 40.2, 31.3, 19.5, 13.4. LRMS (FAB) m/z (rel int): (pos) 140 ($[C_7H_{14}N_3]^+$, 100). HRMS: m/z calcd for $C_7H_{14}N_3$ 140.1188, found 140.1182. Anal. Calcd for $C_7H_{14}BF_4N_3$: C, 37.04; H, 6.22; N, 18.51. Found: C, 37.49; H, 6.29; N, 18.01.

1,3-Dibutyl-1,2,3-triazolium Iodide (16). In a oven-dried flask, NaH (157 mg, 6.21 mmol) was suspended in anhydrous MeCN (5 mL) at 0 °C under nitrogen atmosphere. 1*H*-1,2,3-Triazole (358 mg, 5.18 mmol) was then added via syringe. After the mixture was stirred for 20 min, 1-iodobutane (4.81 g, 25.9 mmol) was added. The reaction mixture was stirred at 80 °C for 19 h. Upon completion of the reaction, the reaction mixture was cooled to rt. Column chromatography on silica gel (1:1 hexane/EtOAc → 4:1 CH_2Cl_2/MeOH) afforded a desired compound **16** (1.21 g, 75%) as a brown liquid. Water content (0.05%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 2H), 4.79 (t, 4H, J = 7.4 Hz), 2.05 (m, 4H), 1.42 (sextet, 4H, J = 7.4 Hz), 1.00 (t, 6H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.6, 54.3, 31.6, 19.5, 13.5. LRMS (FAB) m/z (rel int): (pos) 182 ($[C_{10}H_{20}N_3]^+$, 100). HRMS: m/z calcd for $C_{10}H_{20}N_3$ 182.1657, found 182.1651. Anal. Calcd for

(18) Earle, M. J.; Gordon, C. M.; Plechkova, N. J.; Seddon, K. R.; Welton, T. *Anal. Chem.* **2007**, *79*, 758–764.

$C_{10}H_{20}IN_3$: C, 38.85; H, 6.52; N, 13.59. Found: C, 39.32; H, 6.71; N, 12.94.

It could be synthesized from *n*-butyl triazole **12**. In a screw cap vial, a mixture of **12** (36.5 mg, 292 μmol) and 1-iodobutane (53.7 mg, 292 μmol) was stirred at 80 °C for 14.5 h. Upon completion of the reaction, the reaction mixture was concentrated in vacuo to afford analytically pure **16** (86.0 mg, 95%) as a brown liquid.

1,3-Dibutyl-1,2,3-triazolium Bis(trifluoromethylsulfonyl)amide (17a). In a screw cap vial, a mixture of **16** (37.0 mg, 0.12 mmol) and $LiNTf_2$ (34.4 mg, 0.12 mmol) in deionized water (0.6 mL) was stirred at 40 °C for 15 h. Upon completion of the reaction, the reaction mixture was cooled to rt and extracted with IPA/$CHCl_3$ (1/4). The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **17a** (55.1 mg, 100%) as a brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 2H), 4.61 (t, 4H, J = 7.4 Hz), 2.03 (m, 4H), 1.42 (sextet, 4H, J = 7.4 Hz), 1.00 (t, 6H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.9, 119.9 (q, J_{CF} = 319.1 Hz), 54.3, 31.3, 19.5, 13.3. LRMS (FAB) m/z (rel int): (pos) 182 ($[C_{10}H_{20}N_3]^+$, 100). HRMS: m/z calcd for $C_{10}H_{20}N_3$ 182.1657, found 182.1661. Anal. Calcd for $C_{12}H_{20}F_6N_4O_4S_2$: C, 31.17; H, 4.36; N, 12.12; S, 13.87. Found: C, 31.55; H, 4.35; N, 12.07; S, 13.80.

1,3-Dibutyl-1,2,3-triazolium Trifluoromethylsulfonate (17b). In a screw cap vial, a mixture of **16** (328 mg, 1.06 mmol) and KOTf (204 mg, 1.06 mmol) in deionized water (1.5 mL) was stirred at 40 °C for 11 h. Upon completion of the reaction, the reaction mixture was cooled to rt and extracted with IPA/$CHCl_3$ (1/4). The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **17b** (331 mg, 94%) as a brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 2H), 4.68 (t, 4H, J = 7.4 Hz), 2.02 (m, 4H), 1.41 (sextet, 4H, J = 7.4 Hz), 0.99 (t, 6H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.0, 120.6 (q, J_{CF} = 318.2 Hz), 53.9, 31.3, 19.3, 13.2. LRMS (FAB) m/z (rel int): (pos) 182 ($[C_{10}H_{20}N_3]^+$, 100). HRMS: m/z calcd for $C_{10}H_{20}N_3$ 182.1657, found 182.1661. Anal. Calcd for $C_{11}H_{20}F_3N_3O_3S$: C, 39.87; H, 6.08; N, 12.68. Found: C, 39.89; H, 6.28; N, 13.08.

1,3-Dibutyl-1,2,3-triazolium Hexafluorophosphate (17c). In a screw cap vial, a heterogeneous mixture of **16** (362 mg, 1.17 mmol) and $LiPF_6$ (182 mg, 1.17 mmol) in deionized water (1.7 mL) was stirred at 40 °C for 22 h. Upon completion of the reaction, the reaction mixture was cooled to rt and extracted with IPA/$CHCl_3$ (1/4). The combined extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **17c** (359 mg, 94%) as a brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 2H), 4.61 (t, 4H, J = 7.4 Hz), 2.01 (m, 4H), 1.41 (sextet, 4H, J = 7.4 Hz), 0.99 (t, 6H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.9, 54.2, 31.4, 19.5, 13.4. LRMS (FAB) m/z (rel int): (pos) 182 ($[C_{10}H_{20}N_3]^+$, 100). HRMS m/z calcd for $C_{10}H_{20}N_3$ 182.1657, found 182.1661. Anal. Calcd for $C_{10}H_{20}F_6N_3P$: C, 36.70; H, 6.16; N, 12.84. Found: C, 36.68; H, 6.19; N, 12.90.

1,3-Dibutyl-1,2,3-triazolium Tetrafluoroborate (17d). In a screw cap vial, a heterogeneous mixture of **16** (279 mg, 903 μmol) and $AgBF_4$ (178 mg, 903 μmol) in deionized water (1.3 mL) was suspended at 40 °C. After being stirred for 20 h, the reaction mixture was cooled to rt and extracted with IPA/$CHCl_3$ (1/4). The combined organic extracts were washed with deionized water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was further dried in vacuo (0.3 mmHg) to afford analytically pure **17d** (217 mg, 89%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 2H), 4.62 (t, 4H, J = 7.4 Hz), 2.00 (m, 4H), 1.40 (sextet, 2H, J = 7.4 Hz), 0.98 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.1, 54.0, 31.4, 19.5, 13.4. LRMS (FAB) m/z (rel int): (pos) 182 ($[C_{10}H_{20}N_3]^+$, 100). HRMS: m/z calcd for $C_{10}H_{20}N_3$ 182.1657, found 182.1657. Anal. Calcd for $C_{10}H_{20}BF_4N_3$: C, 44.63; H, 7.49; N, 15.62. Found: C, 44.66; H, 7.41; N, 15.51.

General Procedure for the Baylis−Hillman Reaction of Aldehyde and Methyl Acrylate in Ionic Liquid. In a oven-dried flask, aldehyde (1.00 mmol) and DABCO (230 mg, 2.01 mmol) were dissolved in Ar-degassed [bmTr][PF_6] (**14c**) (0.1 mL). Methyl acrylate (173 mg, 2.01 mmol) was then added. The homogeneous mixture was stirred at ambient temperature, and the reaction progress was monitored by TLC. Upon completion of the reaction, the mixture was concentrated by rotary evaporation. Purification by silica flash chromatography afforded the desired compound (see the Supporting Information for characterization data).

General Procedure for the Baylis−Hillman Reaction of Aldehyde and Acrylonitrile in Ionic Liquid. In a oven-dried flask, aldehyde (1.00 mmol) and DABCO (230 mg, 2.01 mmol) were dissolved in Ar-degassed [bmTr][PF_6] (**14c**) (0.1 mL). Acrylonitrile (107 mg, 2.01 mmol) was then added. The homogeneous mixture was stirred at ambient temperature, and the reaction progress was monitored by TLC. Upon completion of the reaction, the mixture was concentrated by rotary evaporation. Purification by silica flash chromatography afforded the desired compound (see the Supporting Information for characterization data).

Reuse of [bmTr][PF_6] Ionic Liquid. In a oven-dried 1 mL round-bottom flask, 4-chlorobenzaldehyde (0.431 g, 3.01 mmol), acrylonitrile (321 mg, 6.02 mmol), and DABCO (690 mg, 6.03 mmol) were dissolved in [bmTr][PF_6] (**14c**) (409 mg, 0.3 mL). The homogeneous mixture was stirred at ambient temperature, and the reaction progress was monitored by TLC.

Method A. Upon completion of the reaction, Et_2O (5 mL) was added to the reaction mixture. The ionic liquid−Et_2O mixture was stirred for a couple of minutes and stopped. Then, the ionic liquid−Et_2O mixture clearly showed two separate layers, although $<$0.5 mL of ionic liquid was used. The upper Et_2O layer was carefully removed by decantation. This procedure was repeated five times. The combined Et_2O fractions were evaporated. Purification by silica flash chromatography (3:1 hexane/EtOAc) afforded the desired compound **19a** (553 mg, 95%). The ionic liquid was dissolved in CH_2Cl_2 and transferred to the 1 mL round-bottom flask for the second reaction. After evaporation of CH_2Cl_2, the recovered ionic liquid (414 mg) was dried in vacuo and reused for the next cycle.

Method B. Upon completion of the reaction, Purification by silica flash chromatography (3:1 hexane/EtOAc → MeOH) afforded the desired compound **19a** (577 mg, 99%) and ionic liquid (563 mg). The recovered ionic liquid was reused for the next cycle.

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Supporting Information Available: Spectroscopic data for all Baylis−Hillman products, 1D-NOE spectra of **13** and **9d**, TGA spectra, and ^{1}H and ^{13}C NMR spectra for **6**−**8**, **9a**−**d**, **11**−**13**, **14a**−**d**, **16**, **17a**−**d**, **18a**−**k**, **19a**−**j**. This material is available free of charge via the Internet at http://pubs.acs.org.