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Efficient polymeric catalyst for one-pot synthesis of acenaphtho[1,2-*b*]pyrroles

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Abstract Some new derivatives of acenaphtho[1,2-*b*]furans have been synthesized efficiently by one-pot reaction of (acenaphthylen-1-yloxy)trimethylsilane, various aldehydes, and isocyanides in the presence of silica-supported ionic liquid.

Keywords One-pot synthesis · Acenaphtho[1,2-*b*]furan · Silica-supported ionic liquid

Introduction

Fused furans are among the most important heterocyclic compounds with widespread occurrence in nature [1, 2]. The pharmacological and biological activities of furan derivatives have induced and encouraged a large number of research groups to develop new synthetic approaches with the aim of obtaining more pharmacologically and biologically effective compounds [3–5]. Among these various strategies, isocyanide-based multicomponent reactions, introduced in the 1990s by Passerini [6], have attracted specific attention [7–12]. Furthermore, ionic liquids have recently become powerful alternatives to conventional molecular organic solvents due to

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some of their unique advantages such as undetectable vapor pressures and ability to dissolve many organic and inorganic substances [13]. Additionally, ionic liquids are readily recycled and tunable to specific chemical tasks. One type is Brønsted acidic task-specific ionic liquids. Among ionic liquids, those possessing HSO_4^- as a counteranion have found broad applications in organic synthesis, acting as both solvents and catalysts. Recently, immobilization processes of acidic ionic liquids on solid supports have been designed [14–18]. Heterogenization of catalysts and reagents can offer important advantages in handling, separation, and reuse procedures.

In previous studies [19, 20], we reported catalyst-free synthesis of acenaphtho[1,2-*b*]furan compounds employing isocyanide, aldehyde, and silyl enol of acenaphthylen-1(2*H*)-one. However, chemical yields were not sustainable. Accordingly, in this study, we examined various ionic liquids to improve the efficiency of our synthetic method. Among the ionic liquids used, supported ionic liquid **d** was found to be the best choice and was used for synthesis of compounds **7a–k** (Scheme 1). In all cases, the efficiencies of catalyzed and noncatalyzed reactions were compared (Table 1).

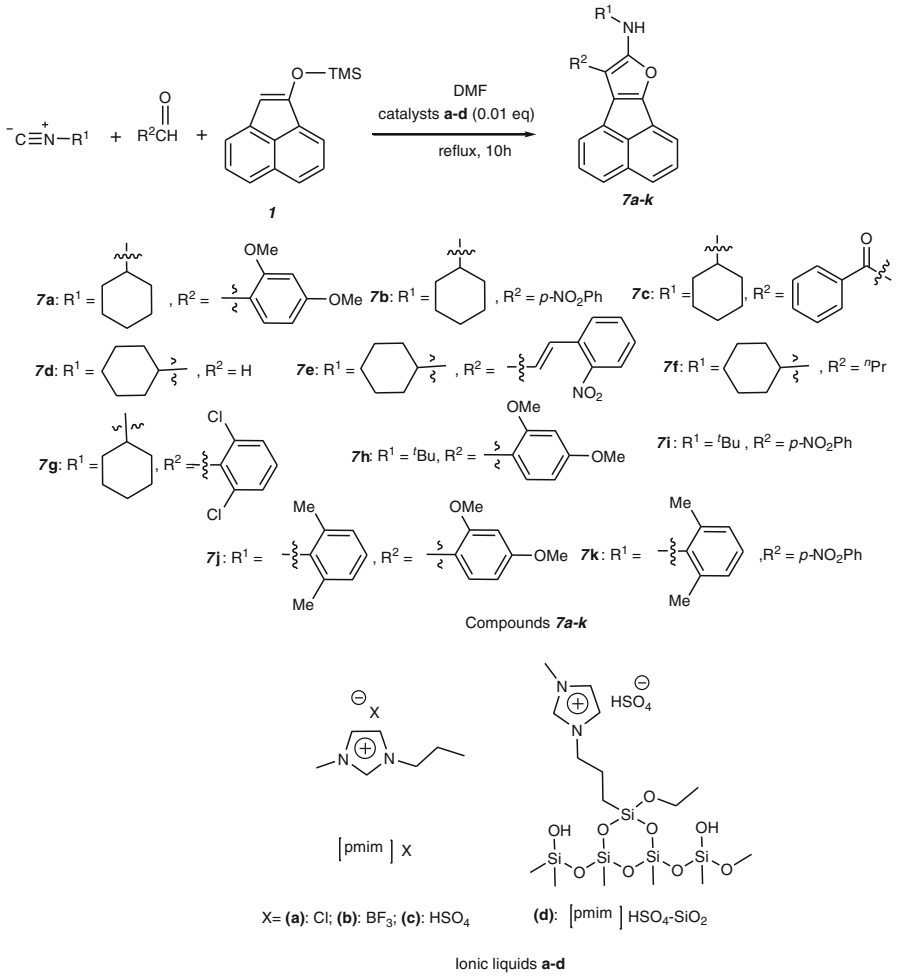
Experimental

Materials and methods

All products, except compounds **7h–k** [19, 20], are new and were characterized by infrared (IR), ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, and elemental micro analysis. ^{1}H NMR spectra were recorded on a Bruker AQSAVANCE 400-MHz spectrometer using tetramethylsilane (TMS) as internal standard ($CDCl_3$ solution). ^{13}C NMR spectra were recorded on a Bruker AQSAVANCE 100-MHz spectrometer ($CDCl_3$ solution). IR spectra were recorded from KBr disk on a Fourier-transform (FT)-IR Bruker Tensor. Gas chromatography/mass spectroscopy (GC/MS) spectra were recorded on an Agilent Technologies 6890 network GC system and an Agilent 5973 network mass-selective detector. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. (Acenaphthylen-1-yloxy)trimethylsilane (**1**), supported and unsupported ionic liquids were prepared according to the literature [21, 22].

General procedure for preparation of acenaphtho[1,2-*b*]pyrrole derivatives (**7a–k**)

To a magnetically stirred mixture of aldehyde (1 mmol) and catalyst (0.01 mmol) in DMF (40 mL) at 0 °C was dropwise added a solution of (acenaphthylen-1-yloxy)trimethylsilane (**1**) (1 mmol) in DMF (10 mL) over a 30-min period. Then, the mixture was allowed to warm to room temperature and treated with a solution of isocyanide (1.0 mmol) in DMF (10 mL). The mixture was refluxed for 10 h, cooled to room temperature, and filtered. The filtrate was extracted with



Scheme 1 Compounds **7a–k** prepared in the presence of ionic liquids **a–d**

dichloromethane (4 × 15 mL). After evaporation of solvent, the residue was washed with ether and crystallized from acetonitrile to give analytically pure product (**7a–k**).

*N-Cyclohexyl-9-(2,4-dimethoxyphenyl)acenaphtho[1,2-b]furan-8-amine (**7a**)*

Brown powder (97 %); m.p. 195–200 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,355 (N–H), 1,230 (C–O), 1,200 (C–O); ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.21–1.97 (10H, m, $5CH_2$), 3.52 (1H, m, N–CH), 3.75 (3H, s, OCH_3), 3.81 (3H, s, $-OCH_3$), 6.43 (1H, bs, NH), 6.62–7.81 (9H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 22.6, 28.7, 31.5, 49.6, 55.9, 56.2, 100.9, 107.1, 109, 117.8, 125.5, 127.3, 127.6, 128, 128.3, 129, 129.5, 133.5, 137.7, 139, 147.2, 158.4, 161.7; GC/MS: 425 (M^+); Anal. Calcd. for $C_{28}H_{27}NO_3$: C, 79.03; H, 6.40; N, 3.29 %. Found: C, 78.84; H, 6.35; N, 3.23 %.

Table 1 Catalytic efficiencies of ionic liquids **a**–**d** for preparation of compound **7a**[a]

Entry	Catalyst	Time (h)	Yield (%)[b]
1	–	10	39
2	[pmim]HSO_4-SiO_2	10	97
3	[pmim]HSO_4	10	76
4	[pmim]BF_4	10	67
5	[pmim]Cl	10	64
6	Silica support	10	51

[a] Reaction conditions: 1.0 equiv. of silyl enol of acenaphthylen-1(2*H*)-one, 1.0 equiv. of 2,4-dimethoxybenzaldehyde, 1.0 equiv. of isocyanocyclohexane, 10 mol % of catalyst, 50 mL of DMF as solvent, at refluxing condition

[b] Isolated yields

*N-Cyclohexyl-9-(4-nitrophenyl)acenaphtho[1,2-b]furan-8-amine (**7b**)*

Brown powder (95 %); m.p. 209–214 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,281 (N–H), 1,541 (N–O), 1,360 (N–O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.24–2.09 (10H, m, $5CH_2$), 3.60 (1H, m, N–CH), 4.92 (1H, bs, NH), 7.72–8.35 (10H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 24.5, 26.1, 30.5, 30.8, 33.2, 51.3, 110.7, 121.4, 125.1, 125.7, 127.6, 127.9, 129.1, 129.6, 130.3, 132.7, 135.1, 135.9, 137.4, 139.3, 141.5, 149.3, 154.8, 159.7, 175.4; GC/MS: 410 (M^+); Anal. Calcd. for $C_{26}H_{22}N_2O_3$: C, 76.08; H, 5.40; N, 6.82 %. Found: C, 75.91; H, 5.34; N, 6.76 %.

*(8-(Cyclohexylamino)acenaphtho[1,2-b]furan-9-yl)(phenyl)methanone (**7c**)*

Brown powder (94 %); m.p. 181–184 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,350 (N–H), 1,690 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.20–2.01 (10H, m, $5CH_2$), 3.53 (1H, m, N–CH), 6.16 (1H, bs, NH), 7.70–8.04 (11H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 20.6, 26.6, 33.9, 47.1, 109.7, 120.2, 124.3, 125.7, 127.2, 127.9, 128.1, 128.5, 129.5, 133.1, 133.7, 135.1, 139.2, 149.3, 151.8, 190.7; GC/MS: 393 (M^+); Anal. Calcd. for $C_{27}H_{23}NO_2$: C, 82.42; H, 5.89; N, 3.56 %. Found: C, 82.30; H, 5.81; N, 3.52 %.

*N-Cyclohexylacenaphtho[1,2-b]furan-8-amine (**7d**)*

Brown powder (92 %); m.p. 161–163 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,364 (N–H); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.22–2.05 (10H, m, $5CH_2$), 3.51 (1H, m, N–CH), 4.76 (1H, s, =CH–), 6.09 (1H, bs, NH), 7.78–7.93 (6H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 24.3, 29.0, 33.6, 49.3, 104.8, 113.4, 127.3, 129.5, 129.9, 130.4, 131.7, 135.1, 138.9, 145.3, 150.2; GC/MS: 289 (M^+); Anal. Calcd. for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84 %. Found: C, 82.95; H, 6.60; N, 4.81 %.

*9-(2-Nitrostyryl)-N-cyclohexylacenaphtho[1,2-b]furan-8-amine (**7e**)*

Brown powder (91 %); m.p. 189–192 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,363 (N–H), 1,535 (N–O), 1,354 (N–O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.29–2.01 (10H, m,

$5CH_2$), 3.53 (1H, m, N–CH), 6.05 (1H, bs, NH), 7.16 (1H, d, $J = 12.4$ Hz, ArC=CH), 7.65–8.40 (11H, m, Ar–H and ArCH=C); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 26.2, 31.6, 35.1, 53.3, 111.6, 124.6, 128.6, 129.1, 130.9, 131.6, 131.8, 132.2, 132.5, 133.1, 134.2, 137.6, 137.7, 139.3, 141.9, 143.2, 150.3, 151.7; GC/MS: 436 (M^+); Anal. Calcd. for $C_{28}H_{24}N_2O_3$: C, 77.04; H, 5.54; N, 6.42 %. Found: C, 76.76; H, 5.47; N, 6.35 %.

*N-Cyclohexyl-9-propylacenaphtho[1,2-b]furan-8-amine (**7f**)*

Brown powder (95 %); m.p. 174–176 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,360 (N–H); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.92 (3H, t, $J = 7.8$ Hz, CH_3–C–C), 1.25–2.11 (10H, m, $5CH_2$), 1.85 (2H, m, C–CH_2–C), 2.70 (2H, t, $J = 7.8$ Hz, C–CH_2–C), 3.48 (1H, m, N–CH), 5.06 (1H, bs, NH), 7.69–7.92 (6H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 17.1, 20.3, 26.7, 28.6, 30.1, 33.6, 51.7, 113.1, 121.1, 127.6, 129.9, 131.7, 132.4, 132.4, 132.7, 137.3, 141.5, 141.8, 149.7; GC/MS: 331 (M^+); Anal. Calcd. for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23; %. Found: C, 83.21; H, 7.54; N, 4.12 %.

*9-(2,6-Dichlorophenyl)-N-cyclohexylacenaphtho[1,2-b]furan-8-amine (**7g**)*

Brown powder (95 %); m.p. 182–186 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,359 (N–H); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.22–2.00 (10H, m, $5CH_2$), 3.52 (1H, m, N–CH), 6.22 (1H, bs, NH), 7.23–7.89 (9H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 25.5, 31.3, 34.4, 52.5, 113.9, 129.6, 131.4, 131.6, 131.7, 132.4, 132.4, 133.1, 134.8, 136.7, 136.9, 138.7, 140.9, 142.5; GC/MS: 433 (M^+); Anal. Calcd. for $C_{26}H_{21}Cl_2NO$: C, 71.89; H, 4.87; N, 3.22 %. Found: C, 71.74; H, 4.81; N, 3.17 %.

*N-tert-Butyl-9-(2,4-dimethoxyphenyl)acenaphtho[1,2-b]furan-8-amine (**7h**)*

Brown powder (93 %); m.p. 135–138 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,364 (N–H), 1,210 (C–O), 1,200 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.18 (9H, s, $C(CH_3)_3$), 3.70 (3H, s, OCH_3), 3.74 (3H, s, –OCH_3), 5.41 (1H, bs, NH), 6.59–7.71 (9H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 30.7, 51.3, 57.6, 57.9, 102.6, 108.8, 10.7, 119.5, 127.2, 129, 129.3, 129.7, 130.0, 130.7, 131.2, 135.2, 139.4, 140.7, 148.9, 160.1, 163.4; GC/MS: 399 (M^+); Anal. Calcd. for $C_{26}H_{25}NO_3$: C, 78.17; H, 6.31; N, 3.51 %. Found: C, 78.01; H, 6.24; N, 3.45 %.

*N-tert-Butyl-9-(4-nitrophenyl)acenaphtho[1,2-b]furan-8-amine (**7i**)*

Brown powder (78 %); m.p. 146–148 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,364 (N–H), 1,550 (N–O), 1,343 (N–O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.17 (9H, s, $C(CH_3)_3$), 6.43 (1H, bs, NH), 7.76–8.30 (10H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 31.8, 53.9, 113.1, 123.7, 127.5, 128.1, 130.0, 130.3, 131.5, 132, 132.7, 135.1, 137.5, 138.3, 139.8, 141.7, 143.9, 151.7, 157.2, 162.1, 177.8; GC/MS: 384 (M^+); Anal. Calcd. for $C_{24}H_{20}N_2O_3$: C, 74.98; H, 5.24; N, 7.29 %. Found: C, 74.71; H, 5.16; N, 7.19 %.

*9-(2,4-Dimethoxyphenyl)-N-(2,6-dimethylphenyl)acenaphtho[1,2-b]furan-8-amine (**7j**)*

Brown powder (96 %); m.p. 163–167 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,451 (N–H), 1,130 (C–O), 1,200 (C–O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 2.36 (6H, s, 2Me), 3.57 (3H, s, OCH_3), 3.62 (3H, s, –OCH_3), 6.74 (1H, bs, NH), 6.43–7.84 (12H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 18.4, 58.7, 59.5, 104.7, 110.9, 112.8, 121.5, 121.6, 128.4, 129.8, 130.2, 130.5, 130.9, 131.2, 131.8, 133.9, 134.4, 138.4, 142.6, 142.6, 144.8, 152.1, 163.3, 166.6; GC/MS: 447 (M^+); Anal. Calcd. for $C_{30}H_{25}NO_3$: C, 80.51; H, 5.63; N, 3.13 %. Found: C, 80.46; H, 5.58; N, 3.02 %.

*N-(2,6-Dimethylphenyl)-9-(4-nitrophenyl)acenaphtho[1,2-b]furan-8-amine (**7k**)*

Brown powder (94 %); m.p. 142–144 °C; FT-IR (KBr) (ν_{max}, cm^{-1}): 3,237 (N–H), 1,501 (N–O), 1,418 (N–O); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 2.21 (6H, s, 2Me), 6.86 (1H, bs, NH), 7.52–8.27 (13H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 22.4, 113.1, 122.7, 125.7, 129.6, 129.7, 130.5, 130.4, 130.7, 130.8, 131.9, 134.0, 134.1, 138.6, 142.2, 142.8, 145.2, 147.6, 152.3, 153.5; GC/MS: 432 (M^+); Anal. Calcd. for $C_{28}H_{20}N_2O_3$: C, 77.76; H, 4.66; N, 6.48 %. Found: C, 77.58; H, 4.43; N, 6.41 %.

Results and discussion

An equal stoichiometric ratio of silyl enol of acenaphthylen-1(2*H*)-one (**1**), 2,4-dimethoxybenzaldehyde, and isocyanocyclohexane and 10 mol % of ionic liquid catalyst was used for the model reaction. To find the most efficient catalyst, three ionic liquids: [pmim]Cl (1-propyl-3-methylimidazolium–Cl) (**a**), [pmim]BF_4 (1-propyl-3-methylimidazolium–BF_4) (**b**), and [pmim]HSO_4 (1-propyl-3-methylimidazolium–HSO_4) (**c**), possessing different counteranions (Scheme 1), were comparatively used to catalyze the model reaction. As seen in Table 1, among the ionic liquid catalysts (**a**–**c**) employed, [pmim]HSO_4 showed the best catalytic efficiency.

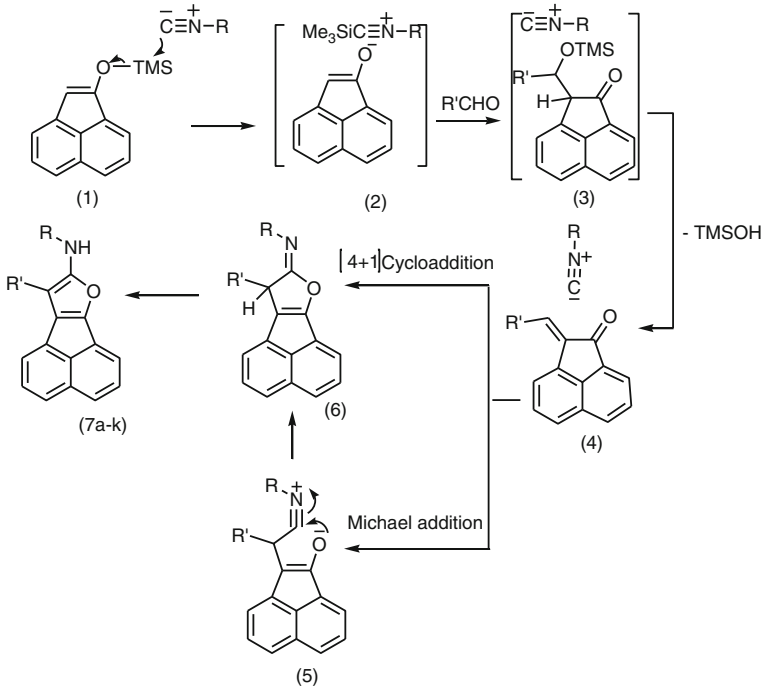
To investigate the effect of heterogenization on the catalytic behavior, the most active catalyst, [pmim]HSO_4 (**c**), was supported on modified silica to obtain the immobilized catalyst [pmim]HSO_4–SiO_2 (**d**). Immobilization on silica support enhanced the activity of the corresponding catalyst significantly (Table 1, entry 2). The higher activity of the immobilized catalyst [pmim]HSO_4–SiO_2 (**d**) could be attributed to the participation of SiO_2 in the catalytic process. To support this hypothesis, we used the silica support as catalyst under the same reaction conditions and showed that it could improve the efficiencies of the reactions compared with the noncatalyzed system (Table 1, compare entries 1 and 6). So, supported ionic liquid **d** was used to assess the generality and scope of the reaction with respect to the aldehyde and isocyanide components (Table 2). We examined various aliphatic aldehydes, such as α,β-unsaturated aldehydes as well as substituted aromatic aldehydes containing electron-withdrawing and electron-donating groups, and it was determined that all of them were well tolerated, affording expected products in

good yields. In addition, we applied aliphatic and aromatic isocyanides, and found that the reaction proceeded efficiently even with hindered aliphatic and aromatic isocyanides (Table 2, entries 8–11). As can be seen, all chemical yields were considerably improved in the presence of ionic liquid **d**, compared with those we obtained under noncatalyzed conditions.

Table 2 Comparison of ionic-liquid-catalyzed and noncatalyzed routes for preparation of compounds **7a–k**

Entry	Compound	Time (h)/yield (%)[a], catalyzed by catalyst **d**	Time (h)/yield (%)[a], not catalyzed
1	**7a**	10/97	10/44
2	**7b**	10/95	10/50
3	**7c**	10/94	10/40
4	**7d**	10/92	10/39
5	**7e**	10/91	10/37
6	**7f**	10/95	10/40
7	**7g**	10/92	10/40
8	**7h**	10/95	10/42
9	**7i**	10/93	10/44
10	**7j**	10/96	10/34
11	**7k**	10/94	10/36

[a] Isolated yields



Scheme 2 Proposed mechanism for the one-pot three-component synthesis of compounds **7a–k**

The effect of temperature was evaluated by carrying out the reaction at various temperatures. The chemical yields increased as the reaction temperature was raised. Hence, refluxing temperature was chosen as optimum temperature and applied for all reactions. Various solvents such as CH_2Cl_2, $CHCl_3$, ethanol, CH_3CN, and toluene were screened for the reaction, but DMF was found to be the best choice.

As established in our previous studies [19, 20], the first step of the mechanism involves nucleophilic attack of the isocyanide onto silyl enol ether (**1**), breaking the O–$SiMe_3$ bond to generate an active enol ion pair complex (**2**). Reaction of the enol with an aldehyde produces the aldol adduct (**3**), which, in turn, eliminates $(CH_3)_3SiOH$ to afford α,β-unsaturated ketone (**4**). Formation of the key iminolactone intermediate (**6**) is achieved either via [4 + 1] cycloaddition reaction or Michael-type addition of the isocyanide with concomitant intermolecular cyclization. Benefiting from delocalization stability, the iminolactone (**6**) isomerizes to form aminofuran heteroaromatic moiety (**7**) (Scheme 2).

Conclusions

One-pot three-component synthesis of some new derivatives of acenaphtho[1,2-*b*] furans efficiently proceeded in the presence of supported ionic liquid catalyst **d**. High chemical yields and short reaction times compared with those obtained in our previous work establish the very important role of the supported ionic liquid catalyst for one-pot synthesis of acenaphtho[1,2-*b*]furans.

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