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RESEARCH ARTICLE

Tetra-*n*-buylammonium fluoride: Efficient catalyst for the one-pot synthesis of 5-aryl-2*H*-1,2,3-triazole-4-carbonitrile derivatives

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Abstract

TBAF has been found to catalyze the Knoevenagel condensation between aromatic aldehyde and nitrile derived active methylene compounds and this has led to a one-pot synthesis of 5-aryl-2*H*-1,2,3-triazole-4-carbonitrile derivatives at room temperature.

Introduction

Knoevenagel condensation is one of the most important and widely used methods for the formation of C-C bonds.[1] It has been used for the synthesis of fine chemicals[2] and several pharmaceutical drug substance[3] such as atorvastatin, pioglitazone, pregabalin, lumefantrine, entacapone etc. Also, the Knoevenagel adduct itself has remarkable biological properties[4] and arylcyanoacrylamides are the inhibitors of dengue & west nile virus proteases.[5] Numerous reagents have been reported to catalyze the Knoevenagel condensation.[6] In these literature reports we have found that fluoride ion efficiently catalyze the Knoevenagel condensation between aromatic aldehyde and nitrile derived active methylene compounds but it proceeded under microwave or ultrasound irradiation condition. Recently, Mogilaiah *et al*[7] reported the ammonium fluoride[7a] and sodium fluoride[7b] catalyzed Knoevenagel condensation under microwave condition. In 2005, Li and co-workers[8] described a synthesis of arylmethylenemalononitriles using KF-Al_2O_3 catalyst under ultrasound irradiation. These reactions have several advantages but it requires harsh reaction conditions. The fluoride ion mediated Knoevenagel reaction was not further explored. 1,2,3-(*NH*)-Triazole is the core moiety in several therapeutic agents.[9] Among these analogs, 5-aryl-2*H*-1,2,3-triazole-4-carbonitrile derivatives are important one because it used for optical brighteners for lacquers, natural or synthetic fibers & films[10] and HER2 tyrosine kinase inhibitors.[11] Several methods are available for the synthesis of 5-aryl-2*H*-1,2,3-triazole-4-carbonitrile derivatives.[11,12] But all of the reported methods require two stages i.e. Knoevenagel condensation[12] or cyanation[11] followed by cycloaddition reactions. Recently, Muthusubramanian *et al*[13] described a one-pot synthesis of these analogs through cycloaddition followed by elimination reactions from aldehyde in water under reflux condition. Specifically they demonstrated an in-situ preparation of Knoevenagel adduct. In the present

work, we reported the mild, efficient and thermal-free synthesis of 5-aryl-2*H*-1,2,3-triazole-4-carbonitrile derivatives. The obtained results are presented here.

Material and Methods

^{1}H NMR spectra were recorded on 400 or 300 MHz and ^{13}C NMR spectra were recorded on 100 or 75 MHz in DMSO-d_6 or $CDCl_3$ using 300 MHz or 400 MHz spectrometer. Chemical shifts are reported in δ (ppm) relative to TMS. Electrospray ionization (ESI) mass spectra were obtained on Agilent mass spectrometer. Infrared spectra were recorded on a Shimadzu FT-IR instrument (KBr pellet). Melting points were determined on a melting point apparatus (Inlab Pvt Ltd, India) equipped with a thermometer and were uncorrected. Elemental analyses were performed on a Perkin-Elmer 2400 Series II Elemental CHNS analyzer. TLC analysis performed on Silica gel-G plates (Merck).

General procedure for the synthesis of Knoevenagel adducts ***(3a, 3b, 3e and 3f)***

To a solution of benzaldehyde (1.06 g, 10 mmol) and active methylene compounds (12 mmol) in THF (10 mL) was added TBAF (1M solution in THF, 10 mol%, 1 mL) under stirring at room temperature. The reaction mixture was stirred at room temperature of 1 h. TLC confirms the completion of reaction. The resultant mixture was poured into ice water (50 mL) and the obtained solid was filtered and washed thoroughly with water. Dried and get the product in pure form. The spectral data of **3a**, **3b**, **3e** and **3f** were consistent with the literature report.[7a, 17]

*General procedure for the synthesis of 5-aryl-2H-1,2,3-triazole-4-carbonitrile derivatives (****4****)*

To a solution of aldehyde (10 mmol), 2-(phenylsulfonyl)acetonitrile (12 mmol) and trimethylsilyl azide (15 mmol) in THF (10 mL) was added TBAF (1M solution in THF, 20 mol%) under stirring at room temperature. The resultant mixture was stirred at room temperature and progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into ice-water (50 mL). The mixture was extracted with ethyl acetate (2 x 100 mL) and the combined organic layer was washed with water (2 x 100 mL) then brine solution (1 x 50 mL). Evaporated to dryness and the product was obtained in the pure form.

5-Phenyl-2H-1,2,3-triazole-4-carbonitrile ***(4a)***: White solid; mp 161-163 °C; R_f 0.33 (DCM/MeOH, 95:5); IR (KBr) 2875, 2245, 1615, 1515, 1275 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.47-7.52 (m, 3H), 7.95-7.96 (m, 2H); δ_C (100 MHz, $CDCl_3$) 113.3, 117.1, 126.7, 126.8, 129.3, 130.4, 147.5; Anal. Calcd. For $C_9H_6N_4$: C, 63.52; H, 3.55; N, 32.92. Found: C, 63.48; H, 3.54; N, 32.89%; ESI-m/z calcd for $[C_9H_6N_4 - H]^+$ 169.1, found 169.1.

5-(4-Chlorophenyl)-2H-1,2,3-triazole-4-carbonitrile ***(4b)***: White solid; mp 183-184 °C; R_f 0.26 (DCM/MeOH, 95:5); IR (KBr) 2880, 2247, 1616, 1513, 1271 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 7.67 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 7.6 Hz, 2H); δ_C (100 MHz, DMSO-d_6) 113.1, 116.5, 125.1, 128.6, 129.5, 135.1, 145.8; Anal. Calcd. For $C_9H_5ClN_4$: C, 52.83; H, 2.46; N, 27.38%. Found: C, 52.79; H, 2.45; N, 27.34; ESI-m/z calcd for $[C_9H_5ClN_4 - H]^+$ 203.0, found 203.0.

5-p-Tolyl-2H-1,2,3-triazole-4-carbonitrile ***(4c)***: White solid; mp 173-174 °C; R_f 0.38 (DCM/MeOH, 95:5); IR (KBr) 2873, 2240, 1613, 1510, 1275 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 2.39 (s, 3H), 7.43 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 16.47 (bs, 1H); δ_C (100 MHz, $CDCl_3$) δ 21.0, 112.9, 116.3, 122.7, 126.4, 129.8, 140.8; Anal. Calcd. For $C_{10}H_8N_4$: C, 65.21; H, 4.38; N, 30.42. Found: C, 65.16; H, 4.30; N, 30.39; ESI-m/z calcd for $[C_{10}H_8N_4 - H]^+$ 183.1, found 183.1.

5-(4-Methoxyphenyl)-2H-1,2,3-triazole-4-carbonitrile ***(4d)***: White solid; mp 196-199 °C; R_f 0.27 (DCM/MeOH, 95:5); IR (KBr) 2881, 2251, 1619, 1515, 1281 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.81 (s, 3H), 7.05 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H); δ_C (100 MHz, $CDCl_3$) 54.2, 112.4, 115.6, 116.5, 125.2, 127.3, 159.3; Anal. Calcd. For $C_{10}H_8N_4O$: C, 59.99; H, 4.03; N, 27.99. Found: C, 59.95; H, 4.02; N, 27.96%; ESI-m/z calcd for $[C_{10}H_8N_4O - H]^+$ 199.1, found 199.1.

5-(4-Fluoro-3-methoxyphenyl)-2H-1,2,3-triazole-4-carbonitrile ***(4e)***: White solid; mp 161-162 °C; R_f 0.23 (DCM/MeOH, 95:5); IR (KBr) 2879, 2245, 1622, 1524, 1286 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 3.93 (s, 3H), 7.50 (t, J = 8.6 Hz, 2H), 7.64 (d, J = 8.4 Hz, 1H), 16.51 (bs, 1H); δ_C (100 MHz, $CDCl_3$) 56.2, 111.8, 113.0, 116.7, 116.9,

119.5, 123.1, 147.6, 148.2, 153.4; Anal. Calcd. For $C_{10}H_7FN_4O$: C, 55.05; H, 3.23; N, 25.68. Found: C, 55.01; H, 3.22; N, 25.64%; ESI-m/z calcd for $[C_{10}H_7FN_4O - H]^+$ 217.1, found 217.1.

5-(3,4,5-Trimethoxyphenyl)-2H-1,2,3-triazole-4-carbonitrile ***(4f)***: White solid; mp 222-224 ^oC; R_f 0.25 (DCM/MeOH, 95:5); IR (KBr) 2865, 2241, 1628, 1521, 1219 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.71 (s, 3H), 3.76 (s, 6H), 7.04 (s, 2H); δ_C (100 MHz, $CDCl_3$) 55.9,* 60.7, 103.8, 113.1, 116.5, 121.6, 139.3, 147.6, 153.5; Anal. Calcd. For $C_{12}H_{12}N_4O_3$: C, 55.38; H, 4.65; N, 21.53. Found: C, 55.33; H, 4.64; N, 21.51%; ESI-m/z calcd for $[C_{12}H_{12}N_4O_3 - H]^+$ 259.1, found 259.1. (* Two carbons)

5-(4-(Methylthio)phenyl)-2H-1,2,3-triazole-4-carbonitrile ***(4g)***: White solid; mp 189-190 ^oC; R_f 0.28 (DCM/MeOH, 95:5); IR (KBr) 2882, 2243, 1615, 1510, 1273 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.53 (s, 3H), 7.34 (d, J = 7.9 Hz, 2H), 7.86 (d, J = 7.9 Hz, 2H); δ_C (100 MHz, $CDCl_3$) 14.9, 113.3, 116.4, 126.1, 126.9, 141.9; Anal. Calcd. For $C_{10}H_8N_4S$: C, 55.54; H, 3.73; N, 25.91%. Found: C, 55.50; H, 3.72; N, 25.89; ESI-m/z calcd for $[C_{10}H_8N_4S - H]^+$ 215.0, found 215.0.

5-(4-Fluorophenyl)-2H-1,2,3-triazole-4-carbonitrile ***(4h)***: White solid; mp 191-192 ^oC; R_f 0.22 (DCM/MeOH, 95:5); IR (KBr) 2884, 2240, 1618, 1517, 1280 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 7.30 (d, 2H, J = 7.9 Hz), 7.80 (d, 2H, J = 8.1 Hz), 12.3 (br, 1H). ESI-m/z calcd for $[C_9H_5FN_4 - H]^+$ 187.0, found 187.0.

5-(2-Fluorophenyl)-2H-1,2,3-triazole-4-carbonitrile ***(4i)***: White solid; mp 180-182 ^oC; R_f 0.21 (DCM/MeOH, 95:5); IR (KBr) 2881, 2251, 1619, 1515, 1281 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 7.43-7.53 (m, 2H), 7.64-7.69 (m, 1H), 7.80 (t, J = 7.5 Hz, 1H), 16.65 (bs, 1H); δ_C (100 MHz, $CDCl_3$) 112.2, 114.2, 116.5, 119.1, 125.1, 129.8, 132.5, 142.4, 159.5; Anal. Calcd. For $C_9H_5FN_4$: C, 57.45; H, 2.68; N, 29.78. Found: C, 57.41; H, 2.67; N, 29.74%; ESI-m/z calcd for $[C_9H_5FN_4 - H]^+$ 187.0, found 187.0.

5-Furan-2-yl-2H-[1,2,3]triazole-4-carbonitrile ***(4j)***: Light yellow solid; R_f 0.25 (DCM/MeOH, 95:5); δ_H (400 MHz, DMSO-d_6) 6.75 (dd, 1H, J = 1.8H, 3.4Hz), 7.10 (d, 1H, J = 3.6 Hz), 7.80 (d, 1H, J = 1.6 Hz); δ_C (100 MHz, DMSO-d_6) 111.3, 112.3, 112.6, 115.1, 138.6, 141.5, 145.1; Anal. Calcd. For $C_7H_4N_4O$: C, 52.50; H, 2.52; N, 34.99. Found: C, 52.58; H, 2.54; N, 35.03%; ESI-m/z calcd for $[C_7H_4N_4O - H]^+$ 159.0, found 159.0.

5-(Thiophen-2-yl)-2H-1,2,3-triazole-4-carbonitrile ***(4k)***: Yellow solid; mp 194-196 ^oC; R_f 0.20 (DCM/MeOH, 95:5); IR (KBr) 2873, 2244, 1624, 1528, 1217 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.21 (m, 1H), 7.62 (b, 1H), 7.74 (b, 1H); δ_C (100 MHz, $CDCl_3$) 112.5, 115.3, 126.9, 127.4, 128.5, 129.1, 142.7. Anal. Calcd. For $C_7H_4N_4S$: C, 47.72; H, 2.29; N, 31.80. Found: C, 47.68; H, 2.28; N, 31.77%; ESI-m/z calcd for $[C_7H_4N_4S - H]^+$ 175.0, found 175.0.

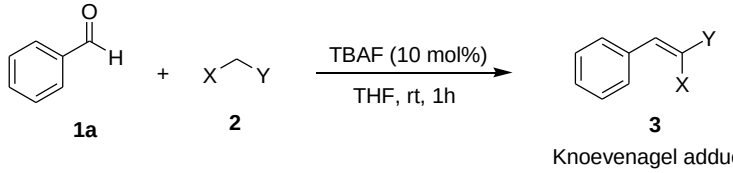
5-(Thiophen-3-yl)-2H-1,2,3-triazole-4-carbonitrile ***(4l)***: Pale yellow solid; mp 201-203 ^oC; R_f 0.26 (DCM/MeOH, 95:5); IR (KBr) 2872, 2243, 1626, 1525, 1215 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 7.60 (d, J = 4.7 Hz, 1H), 7.85 (t, J = 4.7 Hz, 1H), 8.18 (s, 1H); δ_C (100 MHz, DMSO-d_6) 113.3, 115.6, 125.5, 125.9, 126.3, 129.0, 141.9; Anal. Calcd. For $C_7H_4N_4S$: C, 47.72; H, 2.29; N, 31.80. Found: C, 47.67; H, 2.28; N, 31.76%; ESI-m/z calcd for $[C_7H_4N_4S - H]^+$ 175.0, found 175.0.

5-(Thiazol-2-yl)-2H-1,2,3-triazole-4-carbonitrile ***(4m)***: Pale yellow solid; mp 196-197 ^oC; R_f 0.24 (DCM/MeOH, 80:20); IR (KBr) 2874, 2247, 1632, 1534, 1222 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 8.04 (d, J = 3.2 Hz, 1H), 8.13 (d, J = 3.2 Hz, 1H); δ_C (75 MHz, DMSO-d_6) 112.0, 114.8, 124.3, 125.4, 126.5, 142.0; Anal. Calcd. For $C_6H_3N_5S$: C, 40.67; H, 1.71; N, 39.53. Found: C, 40.63; H, 1.71; N, 39.49%; ESI-m/z calcd for $[C_6H_3N_5S - H]^+$ 176.0, found 176.0.

Result and Discussion

Tetra-*n*-butylammonium fluoride (TBAF) is an efficient catalyst for the various kinds of chemical transformation.[14] But it cannot be studied the alkene formation like Knoevenagel reaction. We planned to study the efficacy of TBAF in Knoevenagel condensation reaction. Initially the reaction between benzaldehyde (**1a**) and malononitrile (**2a**) was carried out with 10 mol% of TBAF in THF at room temperature. The reaction was preceded smoothly and yielded 95% of the product, **3a,** even after 1h. This result encouraged us to test the efficacy of TBAF in Knoevenagel condensation, numbers of active methylene compounds was allowed to react with benzaldehyde (**1a**) in the presence of TBAF and the results are presented in Table 1. Here we have seen that TBAF catalyzed Knoevenagel condensation is successful only when the active methylene compound contains at least one cyano group as the activating group (**Table-1**, products **3a**, **3b**, **3e** and **3f**).

Table-1 TBAF catalyzed Knoevenagel condensation



1a **2** **3**

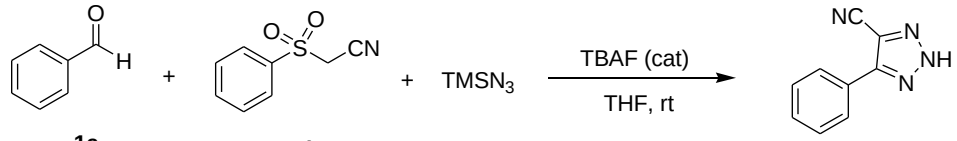
Knoevenagel adduct

Product	X	Y	Yield (%)[a]
3a	CN	CN	95
3b	$C_6H_5SO_2$	CN	99
3c	CH_3CO	CH_3CO	N/R
3d	CH_3CO	$COOCH_3$	N/R
3e	$COOCH_3$	CN	88
3f	$COOC_2H_5$	CN	86
3g	C_6H_5CO	$COOC_2H_5$	N/R

[a]Isolated yield, N/R - no reaction

It can be seen that 3-phenyl-2-(phenylsulfonyl)acrylonitrile was isolated in 99% under this reaction condition (**Table-1**, **3b**). It was used as an intermediate[13] or starting material[15] for the preparation of 5-aryl-2*H*-1,2,3-triazole-4-carbonitriles. In 2005, Fringuelli *et al*[16] reported the TBAF catalyzed synthesis of 4-aryl-1*H*-1,2,3-triazoles from 2-aryl-1-nitroethenes and trimethylsilyl azide under solvent free condition. Compiling of all these reports and results we decided to prepare the 5-aryl-2*H*-1,2,3-triazole-4-carbonitriles under one-pot condition i.e. addition of trimethylsilyl azide into the above reaction mixture. A mixture of benzaldehyde (1 equ), 2-(phenylsulfonyl)acetonitrile (1 equ) and $TMSN_3$ (1.5 equ) were reacted with 10 mol% of TBAF (1M in THF solution) at room temperature for 5 h, it gave 72% of 5-phenyl-2*H*-1,2,3-triazole-4-carbonitrile (**Scheme-1**, **4a**) and similar results obtained even the reaction continued for 24h. The same reaction condition was followed with the use of 20 mol% of TBAF instead of 10 mol%, complete conversion was observed and the product **4a** was isolated in 90% after 1h (**Scheme-1**). This reaction proceeds through the Knoevenagel condensation, [3+2] cycloaddition followed by elimination of phenylsulfinic acid.

Scheme-1 TBAF mediated one-pot synthesis of 5-phenyl-2*H*-1,2,3-triazole-4-carbonitrile

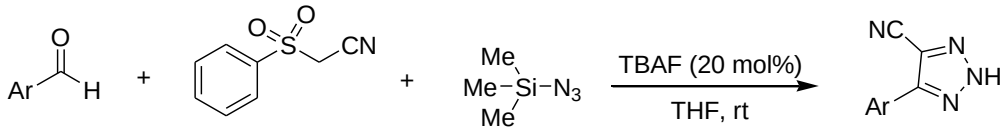


1a **2b** **4a**

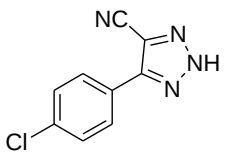
TBAF (**10 mol%**), 5h 72% of **4a**
TBAF (**20 mol%**), 1h 90% of **4a**

Using the optimized reaction condition several aromatic and heteroaromatic aldehydes were reacted with 2-(phenylsulfonyl)acetonitrile in TBAF catalyst and the results are shown in **scheme-2**.

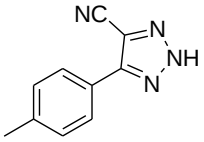
Scheme-2 One-pot synthesis of 5-aryl-2*H*-1,2,3-triazole-4-carbonitrile derivatives



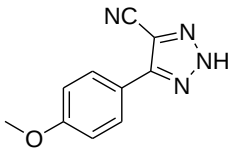
1 **2b** **4**



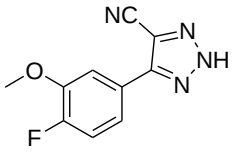
98%, 4b, 1h



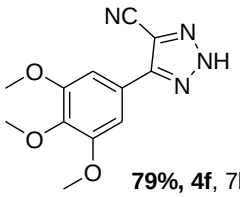
88%, 4c, 3h



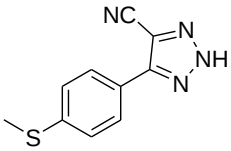
81%, 4d, 5h



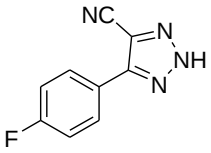
91%, 4e, 2h



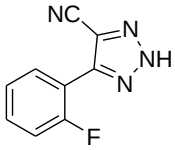
79%, 4f, 7h



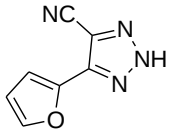
84%, 4g, 3h



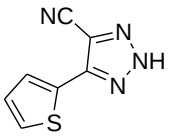
89%, 4h, 1h



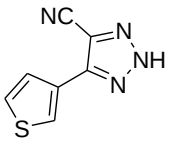
82%, 4i, 1h



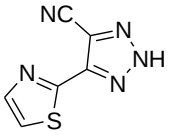
65%, 4j, 5h



71%, 4k, 5h



74%, 4l, 5h



69%, 4m, 5h

The reaction proceeded efficiently in the range of aromatic and heteroaromatic aldehydes. Heteroaromatic aldehydes provided lesser yield (**4j** to **4m**, 65-74%) as compared to aromatic aldehydes (**4a** to **4i**, 79-98%). The aldehyde component contains fluoride, chloride and methylthio substituent reacts faster than methoxy substituents and heteroaromatic aldehydes. All the synthesized triazole analogs were characterized by mass, ^{1}H-NMR, ^{13}C-NMR and IR spectroscopic techniques.

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