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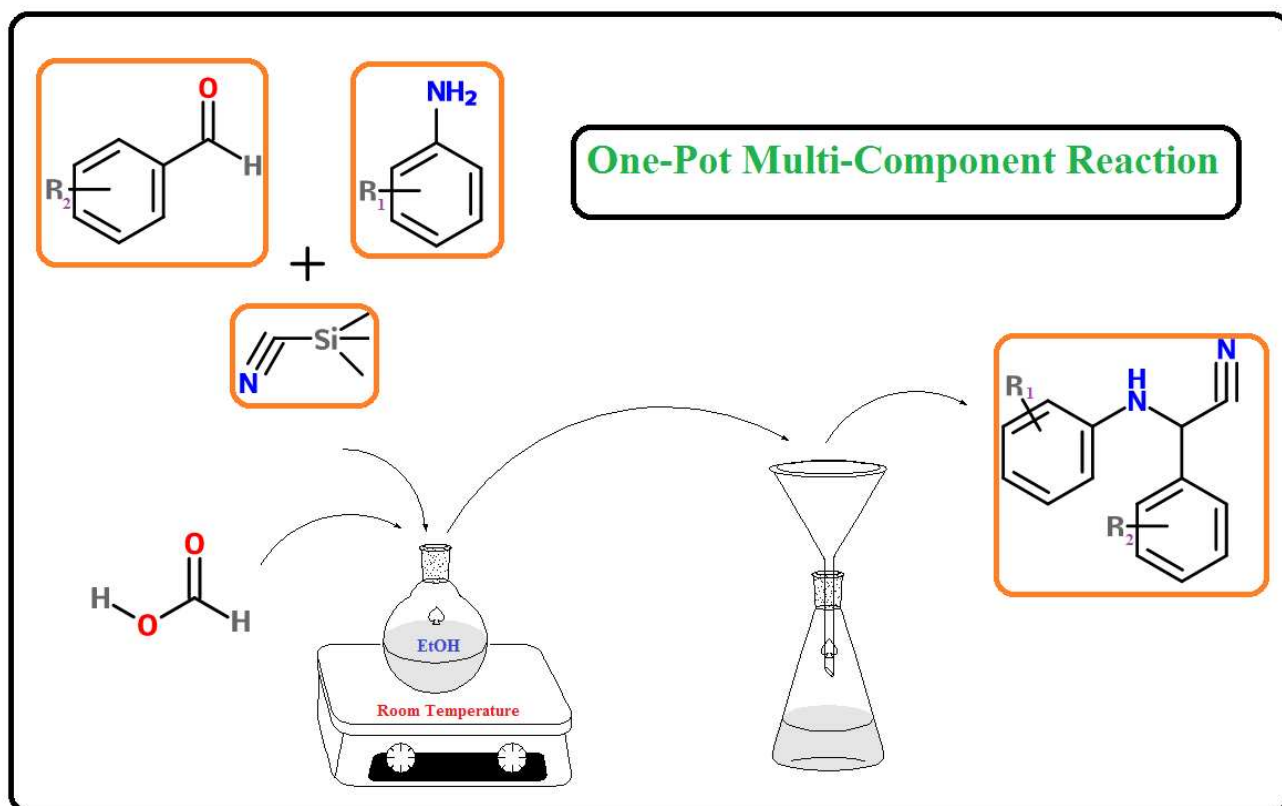
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Graphical Abstract

Aqueous formic acid: an efficient, inexpensive and environmentally friendly organocatalyst for three-component Strecker synthesis of α -aminonitriles and imines with excellent yields.

Hossein Ghafuri,^{*a} Mahdi Roshani^a

^a Department of Chemistry, Iran University of Science and Technology, 16846 Tehran, Iran e-mail: ghafuri@iust.ac.ir



Text: Aqueous Formic acid (37%) was effectively used as catalyst in Strecker reaction to afford α -aminonitriles and imines in high yields.

ARTICLE

Aqueous formic acid: an efficient, inexpensive and environmentally friendly organocatalyst for three-component Strecker synthesis of α -aminonitriles and imines with excellent yields

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Hossein Ghafuri,^{*a} Mahdi Roshani^a

Aqueous Formic acid (37%) which is an efficient, inexpensive and environmentally friendly organocatalyst was used in Strecker reaction to afford α -aminonitriles and imines. Reaction was carried out under mild condition and room temperature in high yields. We obtained α -aminonitriles derives by using of trimethylsilyl cyanide through Strecker reaction. The most important feature of formic acid as a catalyst is affordability and availability.

Introduction

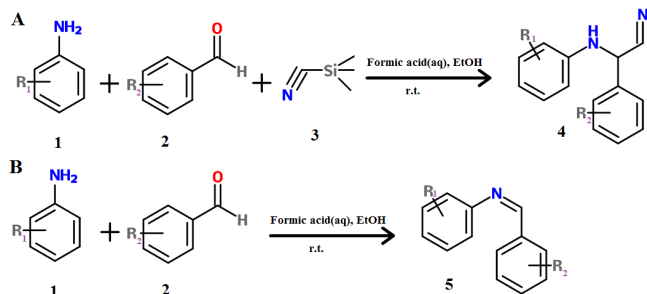
Strecker reaction is a significant and useful reaction in organic chemistry. This reaction afford α -aminonitriles which are versatile intermediates that can be used for synthesis of building blocks such as α -amino acids, 1,2-diamines, and nitrogen-containing heterocycles.¹ As you know strecker reaction is a significant step in the preparation of pharmaceuticals such as Saframycin A,² Ecteinascidin 743,³ and Phtalascidin.⁴ In the classic strecker reaction researchers use HCN, KCN or NaCN as cyanide sources⁵⁻¹³ but these sources are toxic. In order to overcome safety problems, various cyanide sources such as Bu₃SnCN,¹⁴ K₄[Fe (CN)₆]¹⁵ and TMSCN¹⁶ have been used for strecker reaction. Among of these cyanide sources which can attack as nucleophile to different electrophiles, trimethylsilyl cyanide (TMSCN) is a significant one, due to its safety, efficiency and availability. It is noteworthy that TMSCN cannot transfer to electrophiles by itself and need a catalyst in order to its activation. Therefore a wide range of acid catalysts have been used¹⁷⁻²² but many of them have disadvantages such as: long reaction time, toxicity and high price of catalyst. For example TiO₂ (P 25) which has been used as catalyst for this reaction is expensive and is not environmentally friendly.²³ In order to overcome these issues and to facilitate product formation, we decided to use aqueous

formic acid as catalyst in the synthesis of α -aminonitriles and imine compounds. Formic acid is an important intermediate in chemical synthesis and occurs naturally, most notably in ant venom²⁴ and Urtica. Its name comes from the Latin word for ant, Formica, referring to its early Isolation by the distillation of ant bodies. Urtica is a genus of flowering plants in the family Urticaceae. Many species have stinging hairs and may be called nettles or stinging nettles, although the latter name applies particularly to Urtica dioica. In synthetic organic chemistry, formic acid is often used as a source of hydride ion. The Eschweiler-Clarke reaction and the Leuckart-Wallach reaction are examples of this application. It, or more commonly its azeotrope with triethylamine, is also used as a source of hydrogen in transfer hydrogenation. Like acetic acid and trifluoroacetic acid, formic acid is commonly used as a volatile pH modifier in HPLC and capillary electrophoresis. As mentioned below, formic acid may serve as a convenient source of carbon monoxide by being readily decomposed by sulfuric acid.

Furthermore, effect of formic acid on growth, nutrient digestibility, Intestine mucosa morphology, and meat yield of broilers a positive effect of formic acid on intestine mucosa was investigated in some papers.²⁵ using formic acid as reductant in combination with an catalyst, for the transfer hydrogenation of α -substituted acetophenones,²⁶ β -keto esters²⁷ and nitroarenes to

anilines²⁸ were also investigated. Reduction of alkynes can selectively produce cis,trans-alkenes and alkanes.²⁹ And also using formic acid for oxidation of alkynes to α -dicarbonyl in high yields has been studied.³⁰ In comparison to other acid catalysts, formic acid is very environmentally friendly and effective.

Herein, we wish to report a superior, green, and facile synthesis of α -aminonitriles and imines compounds through strecker reaction of aromatic aldehydes, aniline derivatives and trimethylsilyl cyanide at room temperature in high yields (Scheme 1).



Scheme 1. The Strecker reaction of carbonyl compounds and amines with TMSCN catalyzed by formic acid (A), synthesis of imines by formic acid (B).

Results and discussion

Synthesis of α -amino nitriles catalyzed by formic acid

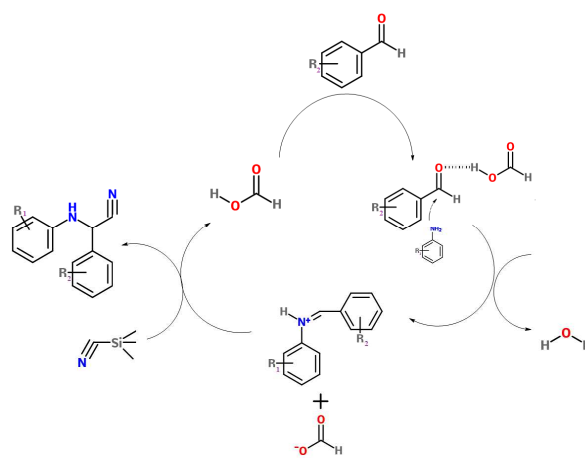
According to our previous studies concerning the use of aqueous formic acid as an efficient acid catalyst for diastereoselective synthesis of β -amino carbonyl derivatives³¹ we used this green acid catalyst for strecker reaction. In order to optimize reaction condition we considered the reaction of 4-chlorobenzaldehyde, aniline and TMSCN (mol ratio 1:1:1.2) in the presence of formic acid as a model reaction. The results have been showed in Table 1. As you see in Table 1 we haven't desired yield in the absence of formic acid even after 24h, so the use of catalyst is necessary for reaction progress. Increasing the amount of catalyst increases the yield of reaction until catalyst amount reaches 20%mol. The higher amount of 20%mol causes gradual decrease in yield of reaction. Therefore the optimize amount of catalyst is 20%mol. Monitoring of reaction condition shows that in the presence of ethanol as solvent, reaction will progress in a better way rather than solvent-free condition. This result inspires us to developed optimized condition to other aromatic carbonyl compounds and amines for synthesis of α -aminonitriles (Table 2) and imines (Table3).

Table 1. Screening of formic acid amount for Strecker reaction of 4-chlorobenzaldehyde and aniline with TMSCN.

Entry	Amount of formic acid (mol %)	Solvent	Time(min)	Yield(%) ^a
1	0	-	24h	Trace
2	5	-	19h	48
3	10	-	12h	63
4	15	EtOH	1h	75
5	20	EtOH	5	99
6	25	EtOH	30	85
7	30	EtOH	50	60

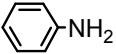
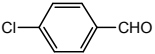
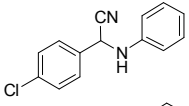
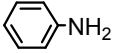
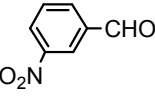
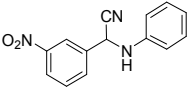
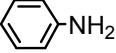
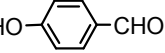
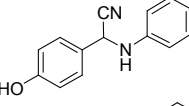
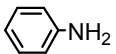
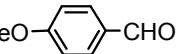
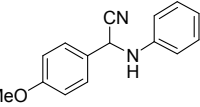
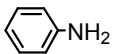
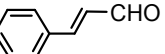
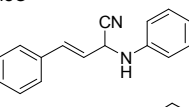
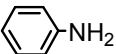
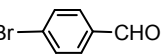
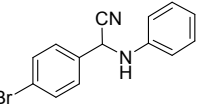
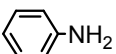
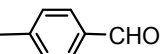
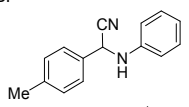
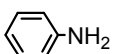
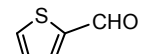
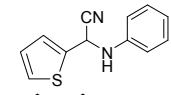
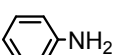
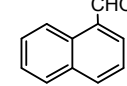
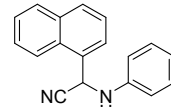
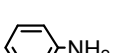
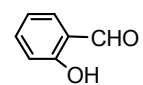
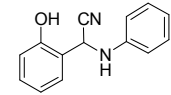
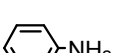
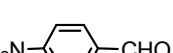
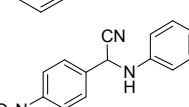
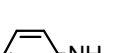
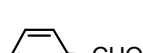
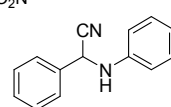
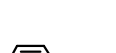
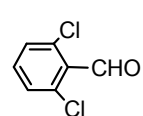
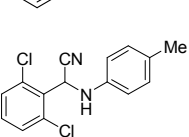
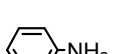
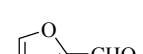
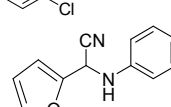
^a Reaction conditions: 1 mmol of 4-chlorobenzaldehyde, 1 mmol of aniline and 130 μ l of TMSCN at room temperature. solvent is 2ml EtOH.

We investigated aldehyde containing both electron-withdrawing and electron-donating groups. The results show that being electron-withdrawing or electron-donating does not determine the general trend of the reactivity. The reaction time for the Strecker reaction catalyzed by formic acid has a remarkable decrease in comparison to former methodologies^{20, 32}. According to the obtained results we present a plausible mechanism for synthesis of α -aminonitriles through strecker reaction catalyzed by aqueous formic acid (Scheme 2). The acidic hydrogen of formic acid active the carbonyl group of the aldehydes through hydrogen bonding for nucleophilic attack of amines to produce the corresponding imine. In the next step CN group of TMSCN attack to imine to produce α -aminonitriles. We synthesis imine separately and then add TMSCN to reaction pot. The product was same with concurrent manner which confirms that this mechanism is reliable.

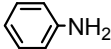
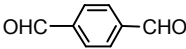
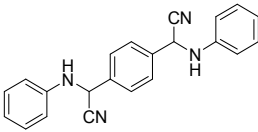
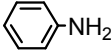

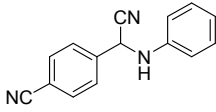
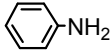
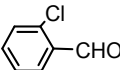
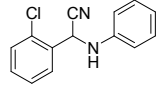
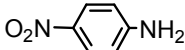
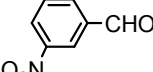
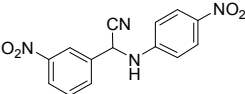
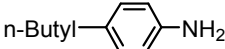
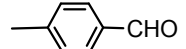
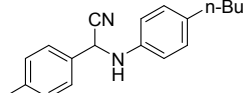
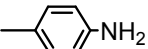
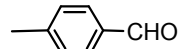
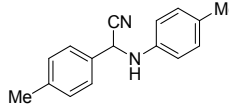
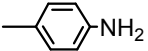
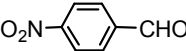
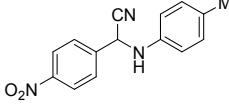
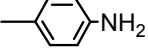
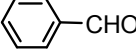
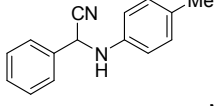
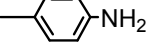

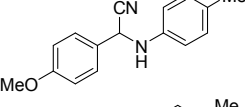
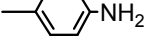
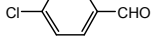
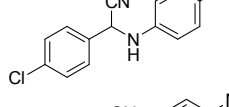
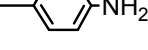
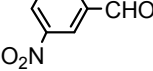
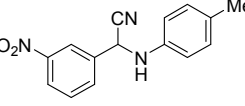


Scheme 2. The plausible mechanism for synthesis of α -aminonitriles through strecker reaction.

Table 2. Synthesis of α -aminonitriles through strecker reaction of aldehyde with amines and TMSCN catalyzed by aqueous formic acid.

Entry	Amine	Aldehyde	Product	Time (min)	Yield (%) ^a	Mp	Mp ^{ref}
1				5	94	108-110	110-112 ³³
2				55	96	86-89	86-88 ³³
3				26	98	117-120	120-122 ³⁴
4				32	94	96-98	94-97 ¹⁶
5				48	91	121-123	123-125 ³³
6				42	90	88-90	87-88 ³³
7				25	95	80-81	77-88 ³⁵
8				51	88	95-98	98-100 ³³
9				72	89	94-97	97-98 ³⁶
10				32	95	126-129	124-126 ³⁷
11				40	90	Oil	Oil ³³
12				40	76	78-80	80-82 ³⁸
13				54	89	71-73	73-76 ⁴⁰
14				36	84	61-64	64-67 ³⁸

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15				40	68 ^b	159-160	157-160 ⁴⁰
16				39	86	107-109	109-111 ³⁸
17				16	89	64-65	63-66 ³²
18				*	*	-	-
19				*	*	-	-
20				46	86	103-106	104-106 ³⁸
21				40	80	85-88	83-85 ³⁸
22				13	80	104-107	107-109 ³⁸
23				67	96	103-105	100-103 ³⁹
24				48	95	81-83	83-85 ³³
25				52	88	112-114	114-116 ³⁹

^a Reaction conditions: 1 mmol of aldehyde, 1 mmol of aniline, 130 μl TMSCN, 2 ml EtOH as solvent and 30 μl formic acid at room temperature. *No Reaction. ^b Reaction conditions: 1 mmol of aldehyde, 2 mmol of aniline, 260 μl TMSCN, 2 ml EtOH as solvent and 30 μl formic acid at room temperature. *No Reaction

In order to show the efficiency of formic acid as a convenient catalyst for strecker reaction we compare our results with other results which has been reported using various catalysts in **Table 3**.

Table 3. Comparison of the catalytic efficiency of formic acid with other catalysts for Strecker reaction.


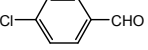
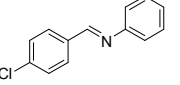

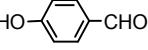
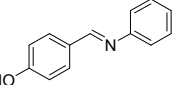

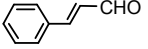
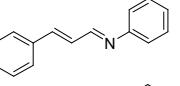

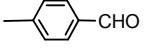
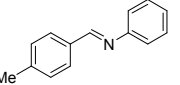

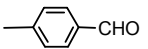
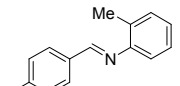

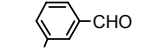
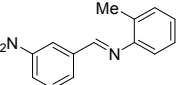
Entry	Catalyst	Solvent	Time (min)	Yield (%) ^a	Ref
1	Formic acid	EtOH	5	99	This work
2	Sn-Montmorillonite	-	6	90	41
3	MCM-41-SO ₃ H	EtOH	30	98	33
4	PEG-OSO ₃ H	H ₂ O	10	92	42
5	B-MCM-41	EtOH	90	98	43
6	Ga-TUD	-	30	92	11
7	PVP-SO ₂	CH ₂ Cl ₂	6h	89	44

^a 4-Chlorobenzaldehyde (1 mmol), aniline (1 mmol), TMSCN (1.2 eq) and 2 ml of ETOH as solvent were used at rt.

Synthesis of imines (5) catalyzed by aqueous formic acid

We investigated the imine formation from aldehydes **2** and amines **1** in the presence of aqueous formic acid as catalyst. The reaction condition of imines and α -aminonitriles was same. The result have been summarized in **Table 4**. It is noteworthy that separation of product is very simple.

Table 4. Synthesis of imines through reaction of aldehydes with amines catalyzed by aqueous formic acid.

Entry	Amine	Aldehyde	product	Time (min)	Yield (%) ^a	Mp	Mp ^{ref}
1				1	99	64-65	62-64 ³⁸
2				1	81	190-193	193-194 ⁴⁵
3				1	96	102-104	100-102 ⁴⁶
4				1	96	38-41	37-38 ⁴⁷
5				1	96	71-73	72-74 ³⁸
6				No reaction	No reaction	-	-

^a Aldehyde (1 mmol), aniline (1 mmol), 2ml EtOH as solvent and formic acid(30 μ l) were used at rt.

Conclusion

In conclusion aqueous formic acid has been demonstrated to be an effective and inexpensive catalyst for synthesis of α -amino nitriles and imines through strecker reaction in high yield and mild condition. To conclude, easy work up, low cost of catalyst and high efficiency make our method to be efficient and practical for synthesis of α -amino nitriles and imines.

Experimental

All chemicals were purchased from Merck or Aldrich and used as received. Melting points were determined using an Electro thermal 9100 apparatus. FT-IR spectra were recorded as

KBr pellets on a Shimadzu FT IR-8400S spectrometer. Analytical TLC was carried out using Merck 0.2 mm silica gel 60 F-254 Al-plates. ¹H NMR (500 MHz) and ¹³C NMR (125 or 75 MHz) spectra were obtained using Bruker DRX-500 Avance and Bruker DRX-300 Avance spectrometers at ambient temperature, respectively.

General procedure for synthesis of α -amino nitriles **4** catalysed by formic acid

A mixture of aldehyde **2** (1 mmol), amine **1** (1 mmol), trimethylsilyl cyanide (130 μ l), 30 μ l of formic acid (20 mol %) and 2 ml of ETOH as solvent was stirred vigorously in a 5 mL round bottom flask equipped with a magnetic bar at room

temperature for a sufficient amount of time. After completion of the reaction as monitored by TLC the solid product was filtered, washed with deionized water, and dried.

General procedure for synthesis of imines **5** catalysed by formic acid

A mixture of aldehyde **2** (1 mmol), amine **1** (1 mmol), 30 μ l of formic acid (20 mol %) and 2 ml of ETOH as solvent was stirred vigorously in a 5 mL round bottom flask equipped with a magnetic bar at room temperature for a sufficient amount of time. After completion of the reaction as monitored by TLC the solid product was filtered, washed with deionized water, and dried.

Spectral data of representative compounds:

2-Anilino-2-(4-methoxy phenyl) acetonitrile (Table 2, entry4):

IR(KBr): 3347, 2299 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 3.72 (s, 3H), 3.89 (br s, 1H), 5.36 (d, 1H, J = 6.6 Hz), 6.63 (d, 2H, J = 8.2 Hz), 6.89-6.99 (m, 3H), 7.29 (d, 2H, J = 8.2 Hz), 7.82 (d, 2H, J = 8.2 Hz).

2-Anilino-2-(4-chloro phenyl) acetonitrile (Table 2, entry 1):

IR (KBr): 3291, 2268 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 3.74 (br s, 1H), 5.33 (d, 1H, J = 6.0 Hz), 6.76 (d, 2H, J = 7.9 Hz), 6.93 (t, 1H, J = 7.3 Hz), 7.39 (t, 2H, J = 8.1 Hz), 7.85 (d, 2H, J = 8.9 Hz), 8.07 (d, 2H, J = 8.5 Hz).

2-Anilino-2-(4-cyano phenyl) acetonitrile (Table 2, entry22):

IR (KBr): 3324, 2257 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 4.37 (br s, 1H), 5.86 (s, 1H), 6.90(d, 2H, J = 7.8 Hz), 7.01 (t, 1H, J = 7.6 Hz), 7.33 (t, 2H, J = 7.8 Hz), 7.92 (s, 4H).

2-Anilino-2-(4-methyl phenyl) acetonitrile (Table 2, entry7):

IR (KBr): 3298, 2273 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 2.61 (s, 3H) 4.03 (br s, 1H), 5.40 (s, 1H), 6.85 (d, 2H, J = 8.2 Hz), 6.91 (t, 1H, J = 7.4 Hz), 7.37-7.41 (m, 4H), 7.86 (d, 2H, J = 7.8 Hz).

2-Anilino-2-(phenyl) acetonitrile (Table 2, entry18):

IR (KBr): 3358, 2263 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 4.23 (d, J=8.34 Hz, 1H), 5.42 (d, J=8.44 Hz, 1H), 6.87 (d, J=7.75 Hz, 2H), 7.06 (t, J=7.42 Hz, 1H), 7.49 (m, 2H), 7.66 (m, 3H), 7.78 (m, 2H).

2-Anilino-2-(furfuryl) acetonitrile (Table 2, entry20):

IR (KBr): 3358, 3093 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 4.62 (br s, 1H), 5.72 (s, 1H), 6.44 (d, J=4.9 Hz, 1H), 6.61 (t, J=4.9 Hz, 1H), 6.91 (d, J=7.8 Hz, 2H), 6.96 (t, J=7.8 Hz, 1H), 7.47 (t, J=7.8 Hz, 2H), 7.81 (d, J=4.9 Hz, 1H).

2-Anilino-2-(2-chloro phenyl) acetonitrile (Table 2, entry23):

IR (KBr): 3367, 2253 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 3.92 (d, 1H, J = 7.5 Hz), 5.73 (d, 1H, J = 8.0 Hz), 6.74 (d, 2H, J = 8.0 Hz), 6.82 (t, 1H, J = 7.5 Hz), 7.29 (t, 2H, J = 8.0 Hz), 7.30-7.32 (m, 2H), 7.39-7.41 (m, 1H), 7.66-7.69 (m, 1H).

2-Anilino-2-(2-thienyl) acetonitrile (Table 2, entry 8):

IR (KBr): 3378, 2243 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 3.92 (d, J=8.73 Hz, 1H), 5.58 (d, J=9.35 Hz, 1H), 6.93 (d, J=7.72 Hz, 2H), 7.29 (t, J=7.43 Hz, 1H), 7.38 (q, J=2.96 Hz, 1H), 7.41–7.53 (m, 4H).

2-(4-methyl anilino)-2-(4-chloro phenyl) acetonitrile (Table 2, entry 24):

IR (KBr): 3351, 2893 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 3.22 (s, 3H), 4.06 (br s, 1H), 6.21 (s, 1H), 6.87 (d, J=7.8 Hz, 2H), 7.50 (d, J=7.9 Hz, 2H), 7.66 (d, J=8.2 Hz, 2H), 7.57 (d, J=8.1 Hz, 2H).

2-Anilino-2-(2, 6-dichloro phenyl) acetonitrile (Table 2, entry 25):

IR (KBr): 3391, 2223 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 5.23 (d, 1H, J = 10.7 Hz), 6.29 (d, 1H, J = 11.1 Hz), 6.86 (d, 2H, J = 8.7 Hz), 6.92 (t, 1H, J = 7.9 Hz), 7.27-7.34 (m, 3H), 7.41 (d, 2H, J = 7.6 Hz).

2-Anilino-2-cinnamyl acetonitrile (Table 2, entry 5):

IR (KBr): 3372, 2231 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 4.02 (br s, 1H), 5.39 (d, J = 1.6 Hz, 1H), 6.33 (dd, J = 5.2 Hz, J = 16.1 Hz, 1H), 6.97 (d, J = 8.1 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.36 (d, J = 16.1 Hz, 1H), 7.42–7.66 (m, 7H).

2-Anilino-2-(1-naphthyl) acetonitrile (Table 2, entry9):

IR (KBr): 3345, 2251 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 4.23 (d, J = 8.4 Hz, 1H), 6.26 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 7.7 Hz, 1H), 7.44 (t, J = 7.3 Hz, 2H), 7.63–7.69 (m, 3H), 8.1–8.25 (m, 4H).

2-(4-methyl anilino) phenyl acetonitrile (Table 2, entry22):

IR (KBr): 3335, 2239 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 2.43 (s, 3H), 3.83 (br s, 1H), 5.64 (s, 1H), 6.67 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 6.8 Hz, 3H), 7.84 (d, J = 5.7 Hz, 2H).

2-Anilino-2-(4-nitro phenyl) acetonitrile (Table 2, entry11):

IR (KBr): 3332, 2229 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 3.96 (d, 1H), 5.32 (d, J=8.3 Hz, 1H), 6.63 (d J=7.3 Hz, 2H), 6.81 (t, J=7.4 Hz, 1H), 7.29–7.34 (m, 3H), 7.79–7.81 (m, 2H), 8.29–8.31 (m, 2H).

2-Anilino-2-(4-bromo phenyl) acetonitrile (Table 2, entry22):

IR (KBr): 3305, 2309 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 4.07 (d, 1H, J = 8.9 Hz), 5.32 (d, 1H, J = 8.9 Hz), 6.88 (d, 2H, J = 8.6 Hz), 6.96 (t, 1H, J = 7.4 Hz), 7.29 (t, 2H, J = 8.4 Hz), 7.60 (d, 2H, J = 8.9 Hz), 7.69–7.72 (m, 2H).

(4-chloro-benzylidene)-Phenyl-amine (Table 4, entry 1):

IR (KBr): 3055, 1623 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.27-7.37 (m, 3H), 7.43–7.58 (m, 4H), 7.92 (d, J = 8.7 Hz, 2H), 8.93 (s, 1H).

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Notes and references

^a Department of Chemistry, Iran University of Science and Technology, 16846 Tehran, Iran e-mail: ghafuri@iust.ac.ir

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