# N, N, N', N'-Tetrabromobenzene-1,3-disulfonamide and Poly(N-bromo-Nethylbenzene-1,3-disulfonamide) as Mild and Efficient Catalysts for Solvent-free Synthesis of *N*-Cyclohexyl-2-aryl(alkyl)-imidazo[1,2-*a*] pyridin-3-amine Derivatives

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Received August 28, 2012 DOI 10.1002/jhet.1875 Published online 00 Month 2014 in Wiley Online Library (wileyonlinelibrary.com).  $NH_2$ 1 2 3 TBBDA or Neat PBBS R1 = aryl, alkyl R<sub>2</sub>= alicyclic 4(a-q) Br N-Br Br O O Ó Ο̈́Ό

N-Cyclohexyl-2-aryl(alkyl)-imidazo[1,2-a]pyridin-3-amine derivatives have been synthesized in good to high yields from o-aminopyridine, aromatic and aliphatic aldehydes, and cyclohexyl isocyanide in the presence of N, N, N', N'-tetrabromobenzene-1,3-disulfonamide and poly(N-bromo-N-ethylbenzene-1,3disulfonamide) as catalysts, at room temperature under solvent-free conditions.

PBBS

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## **INTRODUCTION**

TBBDA

Synthesis of organic molecules via green, mild, and simple procedures is currently receiving considerable attention. Also, reducing or eliminating the use and generation of hazardous substances is a goal of green chemistry. The development of simple, versatile, and environmentally friendly processes or methodologies for widely used organic compounds from readily available reagents is one of the major challenges for chemists in organic synthesis. Organic compounds containing nitrogen are widespread in numerous natural products and widely used as various artificial chemicals. Heterocyclic compounds always attribute remarkable attention in pharmaceutical industry because of their wide therapeutic values. Among them, imidazo[1,2-a]pyridines are a class of nitrogen bridgehead heterocycles that have received considerable attention because of their interesting biological activities [1]. Imidazo[1,2-a] pyridines have been shown to possess a broad range of biological activities and have been investigated for treatment of conditions such as gastric disease [2,3], heart diseases [4], migraines [5], viral diseases [6-10], HIV-1 inhibitors [11], and activity against the colon cancer cell lines HT-29 and Caco-2 [12]. The most common route for the preparation of imidazo[1,2-a]pyridines involves the condensation of o-aminopyridine, aldehydes, and isocyanides in the presence of a catalyst [13-24]. However, some of these condensations have some demerits such as the requirement of expensive and excess amount of catalyst,

longer time, difficulties in work-up procedure, and harsh reaction conditions [25,26]. Because of the interesting properties of imidazo[1,2-*a*]pyridines, the development of synthetic methods that enable a facile access to this heterocycle is desirable.

#### **RESULTS AND DISCUSSION**

In continuation of our interest in the application of N,N,N', N'-tetrabromobenzene-1,3-disulfonamide (TBBDA) and poly (N-bromo-N-ethylbenzene-1,3-disulfonamide) (PBBS) in organic synthesis [27–39], we herein report a simple and improved protocol for the synthesis N-cyclohexyl-2-aryl (alkyl)-imidazo[1,2-a]pyridin-3-amines in good to high yields, from o-aminopyridine, aromatic and aliphatic aldehydes, and cyclohexyl isocyanide (Scheme 1). TBBDA and PBBS play an especially important role as Lewis acid catalysts in the chemistry of these compounds. Therefore, we describe herein an efficient process for the synthesis of N-cyclohexyl-2-aryl(alkyl)-imidazo[1,2-a]pyridin-3-amine derivatives.

The advantages of TBBDA and PBBS are as follows:

- 1. The preparation of TBBDA and PBBS are easy.
- 2. TBBDA and PBBS are stable under atmospheric conditions for 2 months.
- After completion of the reaction, the catalysts are recovered and can be reused several times without decreasing the yield.

Initially, we decided to explore the role of our catalysts in various solvents and various conditions for the synthesis of *N*-cyclohexyl-2-phenylimidazo[1,2-*a*]pyridin-3-amines

Scheme 1. Synthesis of imidazo[1,2-a]pyridine derivatives.





(Table 2, entry 4a) used as a model compound. In the absence of a catalyst, no product was observed, even after prolonged reaction time (Table 1, entry 1). Because the synthesis of *N*-cyclohexyl-2-phenylimidazo[1,2-*a*]pyridin-3-amines failed in the absence of a catalyst, the effect of catalyst was also investigated in various conditions, and the results are presented in (Table 1). With respect to the solvent system, the best results were achieved using ethanol (Table 1, entry 7). In recent years, the synthesis of compounds under solvent-free conditions is an important task in heterocyclic synthesis. Therefore, we decided to repeat this reaction under solvent-free reaction with various ratios of catalysts. We found that the reaction was rapid and gave good to high yields of the products when using TBBDA (0.05 g) and PBBS (60 min, 95%, entry 16).

To test the generality and versatility of this new procedure in the synthesis of *N*-cyclohexyl-2-aryl(alkyl)-imidazo[1,2*a*]pyridin-3-amines, we examined a number of aliphatic and aromatic aldehydes and cyclohexyl isocyanide under optimized conditions (Table 2).

As shown in Table 2, a series of aromatic, aliphatic, and heterocyclic aldehydes underwent electron-withdrawing and electron-donating groups reaction with *o*-aminopyridine and cyclohexyl isocyanide smoothly to afford a wide range of substituted *N*-cyclohexyl-2-aryl(alkyl)-imidazo[1,2-*a*] pyridin-3-amine derivatives in good to high yields in the presence of TBBDA and PBBS as catalysts. The nature and electronic properties of the aldehyde substrates affect the conversion rate. Aromatic aldehydes react faster than the aliphatic aldehydes.

It is likely that these catalysts release  $Br^+$  *in situ*, which can act as an electrophilic species. Therefore, the mechanism shown in Scheme 2 can be suggested for the conversion of the *o*-aminopyridine, various aliphatic and aromatic aldehydes, and cyclohexyl isocyanide to *N*-cyclohexyl-2-aryl(alkyl)-imidazo[1,2-*a*]pyridin-3-amine derivatives.

#### CONCLUSION

In summary, in this study we have introduced a new and useful catalytic application of TBBDA and PBBS as efficient catalysts for the synthesis of aliphatic and aromatic imidazo[1,2-*a*]pyridine derivatives, from the reaction of aldehydes, *o*-aminopyridine, and cyclohexyl isocyanide under solvent-free conditions. Moreover, the method has advantages in terms of high yields of products, short reaction time, operational simplicity, and easy workup product.

### EXPERIMENTAL

All commercially available chemicals were obtained from Merck and Fluka companies and used without further purification unless otherwise stated. Nuclear magnetic resonance, <sup>1</sup>H, and

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Entry	Solvent/condition	TBBDA/PBBS	Time (h)	Yield (%)
1	EtOH	_	24	0/0
2	EtOH	0.01/0.01	10	15/8
3	EtOH	0.02/0.04	10	30/20
4	EtOH	0.03/0.05	10	40/25
5	EtOH	0.04/0.07	10	40/30
6	EtOH	0.05/0.08	10	65/35
7	EtOH	0.1/0.12	10	65/60
8	CH <sub>3</sub> CN	0.05/0.07	8	35/20
9	CH <sub>3</sub> CO <sub>2</sub> Et	0.05/0.07	5	50/50
10	H <sub>2</sub> O	0.05/0.07	4	15/10
11	$CH_2Cl_2$	0.05/0.07	3.5	40/30
12	Neat	_	24	0/0
13	Neat	0.01/0.01	2	15/5
14	Neat	0.02/0.04	2	30/15
15	Neat	0.03/0.05	2	55/30
16	Neat	0.05/0.07	1	95/90
17	Neat	0.06/0.08	2	94/65
18	Neat	0.1/0.12	2	94/85

 Table 1

 Optimization of reaction conditions for the synthesis of *N*-cyclohexyl-2-phenylimidazo[1,2-a]pyridin-3-amine

<sup>a</sup>Standardization of reaction conditions: benzaldehyde (1 mmol), o-aminopyridine (1 mmol), cyclohexyl isocyanide (1 mmol).

<sup>13</sup>CNMR spectra were recorded on Bruker Avance 300 FT NMR spectrometers. Infrared (IR) spectroscopy was conducted on a Perkin Elmer GX FTIR spectrometer. Mass spectra were recorded on a Shimadzu QP 1100 BX Mass Spectrometer. Elemental analyses (C, H, and N) were performed with a Heraeus CHN-Rapid analyzer.

**Typical procedure for the preparation of** *N***-cyclohexyl-2-phenylimidazo[1,2-***a***]<b>pyridine-3-amine.** To a mixture of *o*-amino pyridine (1 mmol, 0.108 g), benzaldehyde (1 mmol, 0.106 g), and cyclohexyl isocyanide (1 mmol, 0.109 g) was added a catalytic amount of TBBDA (0.905 mmol, 0.05 g) or [PBBS] (0.07 g), and the mixture was stirred for an appropriate

Synthesis of <i>tr</i> -cyclonexyr-2-ary(arkyt)-innuazo(1,2-ar)pythan-5-annie detroatives.							
			TBBDA		PBBS		
Entry	Aldehyde	Product	Time (min)	Yield(%)	Time (min)	Yield(%)	Ref.
4a	СНО	N N NH	60	95	70	90	11
4b	NC		55	90	80	85	11
4c	СІСНО		25	85	65	80	11

 Table 2

 Synthesis of *N*-cyclohexyl-2-aryl(alkyl)-imidazo[1,2-*a*]pyridin-3-amine derivatives.

(Continues)

Table 2
(Continued)

			TBBDA		PBBS		
Entry	Aldehyde	Product	Time (min)	Yield(%)	Time (min)	Yield(%)	Ref.
4d	H <sub>3</sub> CO		30	90	90	75	11
4e	СНО	HO N NH	50	94	75	85	11
4f	онс		100	70	40	45	_
4g	СНО	N N NH	60	80	110	60	_
4h	H <sub>3</sub> C	NH NH NH	90	90	50	65	_
4i	H <sub>3</sub> CO H <sub>3</sub> CO OCH <sub>3</sub>	NH OCH <sub>3</sub> NH OCH <sub>3</sub>	55	85	120	70	_

(Continues)

		()	Continued)				
	Aldehyde	Product	TBBDA		PBBS		
Entry			Time (min)	Yield(%)	Time (min)	Yield(%)	Ref.
4j	O <sub>2</sub> N CHO		12	90	35	60	11
4k	H <sub>3</sub> C.N CHO CH <sub>3</sub>	N N NH CH <sub>3</sub> CH <sub>3</sub>	30	94	60	90	11
41	CI		40	90	55	75	11
4m	СНО		65	85	80	80	_
4n	СНО	N N NH	65	88	60	75	
40	СНО	N N NH	80	95	90	85	_
4p	/СНО	N N NH	75	80	70	80	_

Table 2

(Continued)								
		Product	TBBDA		PBBS			
Entry	Aldehyde		Time (min)	Yield(%)	Time (min)	Yield(%)	Ref.	
4q		N N NH	50	75	75	50	_	

Table 2

The products were characterized by comparing their spectroscopic and physical data with those of the samples synthesized by a reported procedure.

time (Table 2). The progress of the reaction was monitored by TLC (*n*-hexane/ethyl acetate, 2:1). After completion of the reaction,  $CH_2Cl_2$  (10 mL) was added, and the catalyst was removed by filtration. Evaporation of the solvent under reduced pressure gave the crude product. The crude product was purified by TLC using *n*-hexane/ethyl acetate (70:60) as the eluent system to afford the *N*-cyclohexyl-2-phenylimidazo[1,2-*a*]pyridin-3-amine (95%).

*if.* 2,2'-(1,4-Phenylene)bis(*N*-cyclohexylimidazo[1,2-*a*] pyridin-3-amine) (Table 2, entry **4f**). Colorless crystal (70%): mp 260–262°C (dec). [Found: C, 76.48; H, 7.22; N, 16.74. C<sub>32</sub>H<sub>36</sub>N<sub>6</sub> requires C, 76.16; H, 7.19; N, 16.65%]; IR (KBr) ( $\nu_{max}$ /cm<sup>-1</sup>): 3195 (NH), 2925, 1613. <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  (ppm) 1.11–2.20 (20H, m, 10CH<sub>2</sub> of cyclohexyl), 4.20 (2H, s, br, CH-N), 5.11 (2H, d, *J* = 6 Hz NH-C), 6.81 (2H, t, *J* = 2.2 Hz), 7.10 (2H, t, *J* = 6.2 Hz H-Ar), 7.53–7.62 (4H, m, Ar-H), 7.70 (2H, d, *J* = 1.1 Hz), 7.82 (2H, d, *J* = 2.4 Hz); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm C}$  (ppm) 23.66, 23.79, 31.04 (carbons of cyclohexyl), 50.41 (CH-N of cyclohexyl), 123.27, 123.59, 125.72, 126.63, 126.87, 128.78, 129.86, 133.11, 136.82, 148.15 (C-Ar).

*4g. N*-Cyclohexyl-2-phenethylimidazo[1,2-*a*]pyridin-3amine (Table 2, entry **4g**). Colorless crystal (80%): mp 203–206°C (dec). [Found: C, 79.26; H, 7.92; N, 13.25.  $C_{21}H_{25}N_3$  requires C, 78.96; H, 7.89; N, 13.15%]; IR (KBr) ( $v_{max}/cm^{-1}$ ): 3125 (NH), 2905, 1623. <sup>1</sup>H NMR (200 MHz, DMSO- $d_6$ ):  $\delta_{\rm H}$  (ppm) 1.12–2.11 (10H, m, 5CH<sub>2</sub> of cyclohexyl), 3.03 (2H, t, J=8.2 Hz CH<sub>2</sub>-CH<sub>2</sub>-Ar), 3.27 (2H, t, J=4 Hz CH<sub>2</sub>-CH<sub>2</sub>-Ar), 4.18 (1H, s, br, CH-N), 4.60 (1H, s, C-NH), 6.72 (1H, d, J=3.4 Hz Ar-H), 7.21–7.36 (5H, m, Ar-H), 7.43 (1H, t, J=3.3 Hz Ar-H), 7.88 (1H, d, J=3.4 Hz Ar-H), 8.10 (1H, s, J=5.4 Hz Ar-H). <sup>13</sup>C NMR (50 MHz, DMSO- $d_6$ ):  $\delta_{\rm C}$  (ppm) 24.77, 25.81, 29.73, 38.81, 38.86, 49.34 (CH-N of cyclohexyl), 124.16, 125.59, 126.19, 128.28, 128.82, 129.55, 130.05, 131.12, 133.86, 135.64, 136.82, 139.78, 140.80, 141.20, 146.91, 149.26 (C-Ar). **4**h. N-Cyclohexyl-2-(5-methylthiophen-2-yl)imidazo[1,2-*a*]

*4h. N*-Cyclohexyl-2-(5-methylthiophen-2-yl)imidazo[1,2-*a*] pyridin-3-amine (Table 2, entry **4h**). Colorless crystal (90%): mp 220–222°C (dec). [Found: 69.72; H, 6.85; N, 13.59.  $C_{18}H_{21}N_3S$  requires C, 69.42; H, 6.80; N, 13.49%]; IR (KBr) ( $\nu_{max}/cm^{-1}$ ): 3185 (NH), 2935, 1615; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  (ppm) 1.10–2.12 (10H, m, 5CH<sub>2</sub> of cyclohexyl), 2.42 (3H, s, CH<sub>3</sub>), 4.24 (1H, m, CH-N of cyclohexyl), 5.14 (1H, s br, CH-NH), 6.74 (1H, t, *J*=2.6 Hz Ar-H), 7.19 (1H, t, *J*=6.85 Hz Ar-H), 6.91, 6.92 (1H, d, *J*=1.9 Hz Ar-H), 7.03 (1H, d, *J*=1 3 Hz Ar-H), 7.20 (1H, t, Ar-H), 7.65 (1H, d, *J*=1 Hz Ar-H), 7.87 (1H, d, *J*=2 Hz Ar-H), 16.24 (methyl), 24.71, 25.75, 32.81 (carbons of

Scheme 2. Proposed mechanism for preparation of N-cyclohexyl-2-aryl(alkyl)-imidazo[1,2-a]pyridin-3-amine derivatives.



cyclohexyl), 56.25 (CH-N of cyclohexyl), 120.05, 124.25, 125.79, 128.74, 129.68, 132.07, 136.61, 139.15, 141.48, 146.35, 149.10 (C-Ar). *4i. N*-Cyclohexyl-2-(3,4,5-trimethoxyphenyl)imidazo[1,2-*a*]

**4i.** *N*-Cyclohexyl-2-(3,4,5-trimethoxyphenyl)imidazo[1,2-*a*] pyridin-3-amine (Table 2, entry **4h**). Colorless crystal (85%): mp 255–257°C (dec). [Found: C, 69.68; H, 7.03; N, 11.12.  $C_{22}H_{27}N_{3}O_{3}$  requires C, 69.27; H, 7.13; N, 11.02%]; IR (KBr) ( $v_{max}/cm^{-1}$ ): 3225 (NH), 2945, 1643; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  (ppm) 1.13–2.14 (10H, m, 5CH<sub>2</sub> of cyclohexyl), 3.85 (9H, s, OCH<sub>3</sub>), 4.20 (1H, m, CH-N of cyclohexyl), 5.19 (1H, d, *J*=7.4 Hz CH-NH), 6.92 (2H, s, H-Ar), 7.34 (1H, d, *J*=6.2 Hz Ar-H), 7.37 (1H, t, *J*=1.3 Hz Ar-H), 7.84 (1H, d, *J*=1.3 Hz Ar-H), 7.89 (1H, t, *J*=1.3 Hz Ar-H), <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm C}$  (ppm) 24.66, 24.79, 32.82 (carbons of cyclohexyl), 49.41 (CH-N of cyclohexyl), 54.66, 55.79, 111.27, 117.58, 125.72, 126.63, 126.87, 128.78, 129.66, 133.11, 136.82, 141.05, 141.30, 146.19, 150.15 (C-Ar). *4m. N*-Cyclohexyl-2-(naphthalen-1-yl)imidazo[1,2-*a*]

*4m. N*-Cyclohexyl-2-(naphthalen-1-yl)Imidazo[1,2-*a*] pyridin-3-amine (Table 2, entry **4m**). Yellow powder (85%): mp 243–245°C (dec). [Found: C, 81.25; H, 6.90; N, 12.34. C<sub>23</sub>H<sub>23</sub>N<sub>3</sub> requires C, 80.90; H, 6.79; N, 12.31%]; IR (KBr) ( $v_{max}/cm^{-1}$ ): 3205 (NH), 2915, 1623: <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> (ppm) 1.02–2.15 (10H, m, 5CH<sub>2</sub> of cyclohexyl), 4.21 (1H, m, CH-N of cyclohexyl), 4.41 (1H, s, *J*=6.7 Hz CH-NH), 6.99 (1H, t, *J*=8.5 Ar-H), 7.25–7.60 (8H, m, Ar-H), 7.88 (1H, d, *J*=3.1 Hz Ar-H); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> (ppm) 24.83, 24.88, 32.68 (carbons of cyclohexyl), 49.48 (CH-N of cyclohexyl), 120.01, 120.04, 124.51, 125.94, 128.42, 128.94, 130.24, 130.38, 132.19, 133.87, 134.04, 136.32, 136.36, 141.11, 149.04 (C-Ar). *An. N*-Cyclohexyl-2-hexylimidazo[1,2-*a*]pyridin-3-amine

*4n. N*-Cyclohexyl-2-hexylimidazo[1,2-*a*]pyridin-3-amine (Table 2, entry **4n**). Colorless crystal (88%): mp 145–147°C (dec). [Found: C, 76.31; H, 9.86; N, 14.16.  $C_{19}H_{29}N_3$  requires C, 76.21; H, 9.76; N, 14.03%]; IR (KBr) ( $v_{max}/cm^{-1}$ ): 3195 (NH), 2925, 1613: <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  (ppm) 0.92 (3H, t, CH<sub>3</sub> hexyl), 1.24–2.16 (18H, m, 5CH<sub>2</sub> of cyclohexyl and 4CH<sub>2</sub> hexyl), 2.75 (2H, t, *J* = 3.5 Hz CH<sub>2</sub>-Ar), 4.25 (1H, m, CH-N of cyclohexyl), 4.76 (1H, bs, C-NH), 6.82 (1H, t, *J* = 4.8 Hz Ar-H), 7.10 (1H, t, *J* = 2.8 Hz Ar-H), 7.77 (1H, d, *J* = 2.85 Hz Ar-H), 7.90 (1H, t, *J* = 2.1 Hz Ar-H); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm C}$  (ppm) 22.54, 24.40, 24.72, 25.80, 26.54, 31.75, 32.63, 33.88, 38.04, 49.39, 124.07, 125.36, 128.11, 128.89, 136.30, 148.17, 149.10 (C-Ar). *40. N*-Cyclohexyl-2-isobutylimidazo[1,2-*a*]pyridin-3-amine

40. N-Cyclohexyl-2-isobutylimidazo[1,2-*a*]pyridin-3-amine (Table 2, entry 40). Colorless crystal (95%): mp 110–112°C (dec). [Found: C, 75.55; H, 9.51; N, 15.38. C<sub>17</sub>H<sub>25</sub>N<sub>3</sub> requires C, 75.23; H, 9.28; N, 15.48%]; IR (KBr) ( $v_{max}/cm^{-1}$ ): 3305 (NH), 2895, 1643; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  (ppm) 1.01 (6H, d, *J* = 4.6 Hz C(CH<sub>3</sub>)<sub>2</sub>), 1.22–2.15 (10H, m, 5CH<sub>2</sub> of cyclohexyl), 2.34 (1H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 2.66 (1H, d, *J* = 3.1 Hz), 4.21 (1H, s br, CH-NH), 4.73 (1H, s, C-NH), 6.65 (1H, t, *J* = 2.4 Hz Ar-H), 6.91 (1H, t, *J* = 4 Hz Ar-H), 7.81 (1H, d, *J* = 1.4 Hz Ar-H), 7.84 (1H, d, *J* = 1.42 Hz Ar-H); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm C}$  (ppm) 17.71, 18.12, 20.05 (-CH<sub>2</sub>CH (CH<sub>3</sub>)<sub>2</sub>), 24.40, 25.21, 33.18 (carbons of cyclohexyl), 56.11 (CH-N of cyclohexyl), 112.95, 115.64, 122.11, 122.01, 126.13, 126.74, 128.37, 128.74, 132.35, 136.82, 145.88 (C-Ar). *4p. N*-Cyclohexyl-2ethylimidazo[1,2-*a*]pyridin-3-amine

*4p. N*-Cyclohexyl-2-ethylimidazo[1,2-*a*]pyridin-3-amine (Table 2, entry **4p**). Colorless crystal (80%): mp 140–142°C (dec). [Found: C, 74.33; H, 8.72; N, 17.37.  $C_{15}H_{21}N_3$  requires C, 74.03; H, 8.70; N, 17.27%]; IR (KBr) ( $\nu_{max}/cm^{-1}$ ): 3315 (NH), 2885, 1633; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> (ppm) 0.90 (3H, t, CH<sub>2</sub>-CH<sub>3</sub>), 1.06–1.74 (10H, m, 5CH<sub>2</sub> of cyclohexyl), 2.15 (2H, q, CH<sub>2</sub>CH<sub>3</sub>), 4.35 (1H, m, CH-N of cyclohexyl), 5.16 (1H, s br, CH-NH), 6.77 (1H, t, Ar-H), 7.01 (1H, t, Ar-H), 7.86 (1H, d,

Ar-H), 7.98 (1H, d, Ar-H); <sup>13</sup>C NMR (50 MHz, DMSO- $d_6$ ):  $\delta_C$  (ppm) 18.12, 21.05, 23.40, 25.31, 32.18 (carbons of cyclohexyl), 58.11 (CH-N of cyclohexyl), 122.01, 126.74, 128.37, 128.74, 132.35, 136.82, 145.88 (C-Ar).

132,35, 136.82, 145.88 (C-Ar). *4q. N*-Cyclohexyl-2-(2-(methylthio)ethyl)imidazo[1,2-*a*] pyridin-3-amine (Table 2, entry **4q**). Colorless crystal (75%): mp 203–206°C (dec). [Found: C, 66.59; H, 8.11; N, 14.54. C<sub>16</sub>H<sub>23</sub>N<sub>3</sub>S requires C, 66.39; H, 8.01; N, 14.52%]; IR (KBr) ( $\nu_{max}/cm^{-1}$ ): 3195 (NH), 2925, 1613; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  (ppm) 1.15– 1.74 (10H, m, 5CH<sub>2</sub> of cyclohexyl), 2.09 (3H, s, SCH<sub>3</sub>), 2.24 (4H, m, CH<sub>2</sub>-CH<sub>2</sub>-S), 4.10 (1H, m, CH-NH), 5.16 (1H, bs, NH-CH), 7.36–7.64 (3H, m, Ar-H), 8.10 (1H, d, Ar-H). <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\rm C}$  (ppm) 17.71, 18.26, 18.54 (carbons of thiomethyl propan), 24.40, 25.21, 33.18 (carbons of cyclohexyl), 56.11 (CH-N of cyclohexyl), 112.95, 115.64, 122.11, 122.01, 126.13, 126.74, 128.37, 128.74, 132.35, 136.82, 145.88 (C-Ar).

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