An efficient, catalyst- and solvent-free synthesis of imidazo[1,2-*a*]pyridines and 2,4-disubstituted thiazoles on grinding

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An efficient synthesis of imidazo[1,2-*a*]pyridines and 2,4-disubstituted thiazoles in excellent yield under catalyst- and solvent-free conditions at room temperature on grinding has been developed. The important features of this method are that it is reasonably fast, very clean, high yielding, simple workup and environmentally benign.

Keywords: imidazo[1,2-*a*]pyridines, 2,4-disubstituted thiazoles, grinding, solvent-free synthesis, catalyst-free synthesis

Imidazo[1,2-*a*]pyridine derivatives exhibit diverse biological activities.[1,2] The typical procedure for the synthesis of these compounds involves a condensation reaction of an α-bromocarbonyl compound with 2-aminopyridine derivatives in neutral,[3] weak basic organic solvents at elevated temperature.[4] These compounds were also synthesised by solid support[5] and using catalysts, such as Al_2O_3[6] and $TiCl_4$.[7]

Moreover, the thiazole ring system is also a useful structural element in medicinal chemistry.[8-10] One of the most common approaches for the synthesis of thiazoles involves the reaction of readily available α-haloketones with thioureas/thioamides in the presence of various promoting agents, such as ammonium 12-molybdophosphate,[11] β-cyclodextrin,[12,13] iodine,[14] [bbim]BF_4,[15] and with the aid of microwave.[16]

In recent years, significant articles have appeared reporting solid-state reactions by grinding.[17-21] Most of these reactions are carried out at room temperature in absolutely solvent-free environment using only a mortar and pestle, and therefore the common merit of these processes is that they are efficient, economical, and environmentally friendly.

In continuation of our interest in green chemistry,[22-26] we herein developed a green, simple and practical method for the synthesis of imidazo[1,2-*a*]pyridines and 2,4-disubstituted thiazoles under catalyst- and solvent-free conditions (Schemes 1 and Scheme 2).

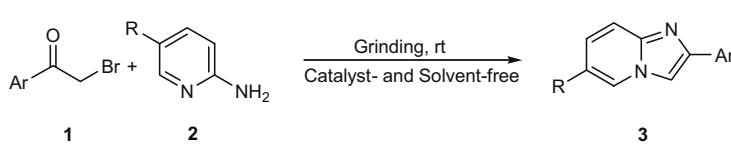
Initially, 1 mmol each of α-bromoacetophenone and 2-aminopyridine as a model reaction were heated at 60 °C in ethanol. After 1 h, only 61% of the desired product of 2-phenylimidazo[1,2-*a*]pyridine (**3a**) was obtained. In an attempt to improve the yields and acknowledging the benefits of grinding,[27-32] the model reaction was performed under catalyst- and solvent-free conditions. To keep this method economical, all the ingredients of the reaction were taken in a glass mortar, mixed thoroughly and ground well at room temperature. It was observed that the mixture which was initially in a partial liquid state, solidified during the process of grinding to a light yellow solid mass and thin layer chromatography (TLC), at this moment, indicated the conversion to **3a** in 90% yield.

A variety of substrates were submitted to this reaction conditions and the desired products **3** were obtained in excellent yields (Table 1). It is evident that electron rich and electron deficient α-bromoacetophenone reacted smoothly with 2-aminopyridine and 2-amino-5-methylpyridine to afford the desired products in excellent yields.

Table 1 Synthesis of imidazo[1,2-*a*]pyridines[a]

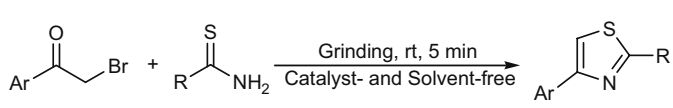
Entry	α-bromoketone	R	Time/min	Product	Yield/%[b]
1	C_6H_5	H	20	**3a**	90
2	*p*-OMe–C_6H_4	H	10	**3b**	95
3	*p*-Cl–C_6H_4	H	30	**3c**	90
4	C_6H_5	Me	10	**3d**	91
5	*p*-OMe–C_6H_4	Me	20	**3e**	94
6	*p*-Cl–C_6H_4	Me	25	**3f**	90

[a]Reaction conditions: α–bromoketone (1 mmol) and 2–aminopyridine (1 mmol) on grinding at room temperature.
[b]Isolated yields.



1 **2** **3**

Scheme 1 Synthesis of imidazo[1,2-*a*]pyridine derivatives from α-bromoacetophenone and 2-aminopyridine on grinding.



1 **4** **5**

Scheme 2 Synthesis of 2,4-disubstituted thiazole derivatives from α-bromoacetophenone and thiourea/thioamide on grinding.

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Encouraged by our success, we also investigated the reaction of α-bromoacetophenone with thiourea/thioamide on grinding at room temperature under catalyst- and solvent-free conditions. However, the problem in the grinding reaction is that the starting materials soon become a tough waxy substance that is hard to grind. To overcome this, we added three drops of water to the mixture until the substrates form a paste-like product that was easily ground. And, the process gave the corresponding product 4-phenylthiazol-2-amine (**5a**) as short as 5 min in 94% yield.

Next, we explored the scope and generality of this present protocol for the synthesis of various 2,4-disubstituted thiazoles (Table 2). As expected, a variety of α-bromoacetophenone bearing either electron-donating (Table 2, entries 9–12) or electron-withdrawing (Table 2, entries 5–8) groups on aromatic ring underwent smooth transformation to the corresponding products **5** in excellent yields when they reacted with thiourea/thioamide. The substitution group on the phenyl ring did not make any difference in the reaction. In all cases, the corresponding products were afforded as short a reaction time as 5 min in excellent yields. Moreover, the reaction of α-bromo-4-nitroacetophenone with thioacetamide and thiobenzamide was conducted successfully in 88% and 92% yields, respectively (Table 2, entries 13–14). To the best of our knowledge, it was little reported that a reaction could be conducted within 5 min; except, Kabalka[16] reported microwave promoted synthesis of thiazoles. Compared to the reaction carried out by microwave irradiation, this procedure is completely free from organic solvents during the reaction.

In conclusion, we have developed a simple and efficient method for the synthesis of imidazo[1,2-*a*]pyridine and 2,4-disubstituted thiazole derivatives on grinding at room temperature under catalyst- and solvent-free conditions. The mildness of the conversion, experimental simplicity, compatibility with various functional groups, efficient yields, short reaction times, and the easy workup procedure, makes this procedure attractive to synthesise a variety of these derivatives.

Experimental

Chemicals were purchased and used without further purification. All the melting points were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured on a FT-Bruker AT-300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in Hz. IR spectra was recorded on a AVATAR 370 FI-IR Spectrophotometer. Mass spectra were measured with Thermo Finnigan LCQ-Advantage. Elemental analyses were carried out using a Carlo-Erba EA1112 instrument. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

General procedure for preparation of **3a–f**

A mixture of α-bromoketone (**1**) (1 mmol), and 2-aminopyridine (**2**) (1 mmol) is ground at room temperature with a glass pestle in the glass mortar. The progress of the reaction was monitored by TLC. After completion of the reaction, the product was washed with dehydrated alcohol or ethyl acetate (3 × 10 mL). The combined organic solvent was removed under vacuum to obtain the crude solid product. The crude product was further purified by silica gel column chromatography using ethyl acetate–petroleum ether (1 : 3) as eluent to afford the pure product. The physical and spectra data of the compounds **3a–f** are as follows.

2-Phenylimidazo[1,2-a]pyridine (**3a**): White solid, m.p. 136–137 °C (lit.[27] 131–133 °C); IR ν (cm^{-1}): 2925, 2857, 1738, 1625, 1511, 1460, 1383, 1269, 1201, 1122, 1081, 1040, 744, 688, 458. ^{1}H NMR: δ 8.12 (dd, *J* = 1.04, 1.03 Hz, 1H), 7.98–7.96 (m, 2H), 7.88 (s, 1H), 7.64 (d, *J* = 9.14 Hz, 1H), 7.45 (t, *J* = 7.22 Hz, 2H), 7.35 (d, *J* = 7.33 Hz, 1H), 7.20–7.17 (m, 1H), 6.79 (d, *J* = 6.78 Hz, 1H). ^{13}C NMR: δ 145.8, 145.7, 133.8, 128.7, 127.9, 126.0, 125.6, 124.6, 117.5, 112.4, 108.1. MS-ESI: *m/z* (%): 195 (100).

2-(4-Methoxyphenyl)imidazo[1,2-a]pyridine (**3b**): White solid, m.p. 135–136 °C (lit.[28] 133–134 °C); IR ν (cm^{-1}): 2961, 2838, 1612, 1548, 1482, 1371, 1285, 1244, 1175, 1110, 1077, 1030, 924, 838, 743, 631, 536, 446. ^{1}H NMR: δ 8.09 (d, *J* = 6.77 Hz, 1H), 7.89 (dd, *J* = 1.95, 1.94 Hz, 2H), 7.77 (s, 1H), 7.61 (d, *J* = 9.08 Hz, 1H), 7.17–7.15 (m, 1H), 6.97 (dd, *J* = 1.97, 1.94 Hz, 2H), 6.76 (dd, *J* = 0.82, 0.81 Hz, 1H), 3.85 (s, 3H, OCH_3). ^{13}C NMR: δ 159.6, 145.64, 145.57, 127.3, 126.4, 125.4, 124.5, 117.2, 114.1, 112.3, 107.2, 55.3.

2-(4-Chlorophenyl)imidazo[1,2-a]pyridine (**3c**): White solid, m.p. 207–209 °C (lit.[29] 201 °C); IR ν (cm^{-1}): 2917, 1632, 1471, 1369, 1250, 1202, 1089, 1009, 933, 830, 742, 598, 510. ^{1}H NMR: δ 8.09 (d, *J* = 6.78 Hz, 1H), 7.87 (d, *J* = 8.52 Hz, 2H), 7.82 (s, 1H), 7.61 (d, *J* = 9.15 Hz, 1H), 7.39 (d, *J* = 8.52 Hz, 2H), 7.17 (t, *J* = 7.17 Hz, 1H), 6.77 (t, *J* = 6.60 Hz, 1H). ^{13}C NMR: δ 145.7, 144.6, 133.6, 132.3, 128.9, 127.2, 125.6, 124.9, 117.5, 112.6, 108.2.

6-Methyl-2-phenylimidazo[1,2-a]pyridine (**3d**): White solid, m.p. 171–173 °C (lit.[6] 172–173 °C); IR ν (cm^{-1}): 2921, 1628, 1525, 1471, 1418, 1342, 1259, 1206, 1159, 1079, 846, 805, 768, 715, 685, 571, 506. ^{1}H NMR: δ 7.95 (d, *J* = 7.05 Hz, 2H), 7.83 (s, 1H), 7.73 (s, 1H), 7.53 (d, *J* = 9.09 Hz, 1H), 7.44 (t, *J* = 6.63 Hz, 2H), 7.33 (d, *J* = 6.44 Hz, 1H), 7.00 (d, *J* = 8.82 Hz, 1H). ^{13}C NMR: δ 145.4, 144.7, 133.9, 128.7, 127.84, 127.78, 125.9, 123.3, 122.0, 116.7, 107.9, 18.0.

2-(4-Methoxyphenyl)-6-methylimidazo[1,2-a]pyridine (**3e**): White solid, m.p. 179–181 °C; IR ν (cm^{-1}): 2926, 1612, 1546, 1483, 1413, 1341, 1301, 1246, 1174, 1103, 1023, 839, 794, 744, 710, 591, 528. ^{1}H NMR: δ 7.88 (d, *J* = 2.26 Hz, 2H), 7.86 (d, *J* = 2.11 Hz, 1H), 7.68 (s, 1H), 7.51 (d, *J* = 9.48 Hz, 1H), 7.01 (d, *J* = 1.57 Hz, 2H), 6.96 (dd, *J* = 2.10, 2.06 Hz, 1H), 3.85 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3). ^{13}C NMR: δ 159.5, 145.3, 144.6, 127.7, 127.2, 126.6, 123.3, 121.9, 116.5, 114.1, 107.0, 55.3, 18.1. MS-ESI: *m/z* (%): 239 (100). Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92. Found: C, 75.66; H, 5.85%.

2-(4-Chlorophenyl)-6-methylimidazo[1,2-a]pyridine (**3f**): White solid, m.p. 239–240 °C (lit.[6] 240–242 °C); IR ν (cm^{-1}): 2921, 1635, 1540, 1465, 1409, 1257, 1206, 1090, 1010, 944, 835, 803, 734, 511. ^{1}H NMR: δ 7.89 (d, *J* = 2.83 Hz, 2H), 7.88 (s, 1H), 7.75 (s, 1H), 7.54 (t, *J* = 6.05 Hz, 1H), 7.39 (d, *J* = 8.53 Hz, 2H), 7.05 (d, *J* = 9.34 Hz, 1H), 2.33 (s, 3H, CH_3). ^{13}C NMR: δ 144.8, 144.4, 133.5, 132.5, 128.9, 128.1, 127.1, 123.3, 122.3, 116.8, 107.9, 18.1.

General procedure for preparation of **5a–n**

A mixture of α-bromoketone (**1**) (1 mmol), thiourea/thioamide (**4**) (1 mmol) and three drops of water is ground at room temperature with a glass pestle in the glass mortar for 5 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the product was washed with dehydrated alcohol or ethyl acetate (3 × 10 mL). The combined organic solvent was removed under vacuum to obtain the crude solid product. The crude product was further purified by silica gel column chromatography using ethyl acetate–petroleum ether as eluent to afford the pure product. The physical and spectra data of the compounds **5a–n** are as follows.

4-Phenylthiazol-2-amine (**5a**): White solid, m.p. 150–151 °C (Lit.[15] 150–151 °C); IR ν (cm^{-1}): 3432, 2974, 1624, 1524, 1388, 1337, 1045, 670. ^{1}H NMR: δ 7.81–7.78 (m, 2H, ArH), 7.42-7.37 (m, 2H, ArH), 7.33–7.28 (m, 1H, ArH), 6.74 (s, 1H, thiazole), 5.05 (br s, 2H, NH_2). ^{13}C NMR: δ 167.3, 151.3, 134.7, 128.5, 127.7, 126.0, 102.7. MS-EI: *m/z* (%): 176 (100), 134 (59), 89 (12).

N,4-Diphenylthiazol-2-amine (**5b**): White solid, m.p. 135–136 °C (Lit.[30] 135–136 °C); IR ν (cm^{-1}): 3432, 2927, 1606, 1562, 1461, 1422, 1310, 692. ^{1}H NMR: δ 7.89–7.86 (m, 2H, ArH), 7.60 (s, 1H, ArH), 7.44–7.30 (m, 7H, ArH), 7.10–7.06 (m, 1H, thiazole), 6.84 (br s, 1H, NH). ^{13}C NMR: δ 164.4, 151.3, 140.2, 134.5, 129.3, 128.5, 127.8, 126.0, 122.9, 118.1, 101.7.

2-Mmethyl-4-phenylthiazole (**5c**): White solid, m.p. 67–69 °C (Lit.[15] 67–68 °C); IR ν (cm^{-1}): 3436, 2924, 1640, 1387, 1169, 1028, 676. ^{1}H NMR: δ 7.89–7.86 (m, 2H, ArH), 7.42–7.37 (m, 3H, ArH), 7.33–7.27 (m, 1H, ArH), 2.75 (s, 3H, CH_3). ^{13}C NMR: δ 165.7, 155.1, 134.5, 128.6, 127.8, 126.3, 112.1, 19.2.

2, 4-Diphenylthiazole (**5d**): White solid, m.p. 90–91 °C (Lit.[31] 91–92 °C); IR ν (cm^{-1}): 3435, 2925, 1643, 1519, 1471, 1391, 1058, 673. ^{1}H NMR: δ 8.08–8.00 (m, 4H, ArH), 7.49–7.44 (m, 6H, ArH), 7.39–7.37 (m, 1H, thiazole). ^{13}C NMR: δ 167.8, 156.3, 134.5, 133.7, 130.0, 128.9, 128.7, 128.2, 126.6, 126.4, 112.6.

4-(4-Chlorophenyl)thiazol-2-amine (**5e**): White solid, m.p. 167–168 °C (Lit.[15] 163–164 °C); IR ν (cm^{-1}): 3433, 2924, 1628, 1532, 1466, 1395, 1041, 730. ^{1}H NMR: δ 7.74–7.70 (m, 2H, ArH), 7.38–7.33 (m, 2H, ArH), 6.73 (s, 1H, thiazole), 5.07 (br s, 2H, NH_2). ^{13}C NMR: δ 167.3, 150.2, 133.4, 133.1, 128.8, 127.3, 103.3.

4-(4-Chlorophenyl)-N-phenylthiazol-2-amine (**5f**): White solid, m.p. 144–146 °C; IR ν (cm^{-1}): 3383, 2974, 1559, 1473, 1399, 1304,

1089, 1053, 834, 691. ^{1}H NMR: δ 7.85–7.73 (m, 3H, ArH), 7.33–7.28 (m, 6H, ArH), 7.08–7.02 (m, 1H, thiazole), 6.77 (br s, 1H, NH). ^{13}C NMR: δ 164.8, 150.2, 140.2, 133.6, 133.1, 129.5, 128.8, 127.4, 123.2, 118.4, 102.2. Anal. Calcd for $C_{15}H_{11}ClN_2S$: C, 62.82; H, 3.87. Found: C, 62.77; H, 3.91%.

4-(4-Chlorophenyl)-2-methylthiazole (**5g**): White solid, m.p. 118–119 °C (Lit.[15] 111–112 °C); IR ν (cm^{-1}): 3442, 1647, 1523, 1391, 1166, 989, 672. ^{1}H NMR: δ 7.81 (d, *J* = 8.63 Hz, 2H, ArH), 7.37 (d, *J* = 8.63 Hz, 2H, ArH), 7.28 (s, 1H, thiazole), 2.76 (s, 3H, CH_3). ^{13}C NMR: δ 166.1, 153.9, 133.7, 133.0, 128.9, 127.6, 112.6, 19.3. MS-EI: *m/z* (%): 211 (42), 209 (100), 170 (40), 168 (100), 133 (36), 89 (27).

4-(4-Chlorophenyl)-2-phenylthiazole (**5h**): White solid, m.p. 131–132 °C (Lit.[32] 132–133 °C); IR ν (cm^{-1}): 3434, 2922, 1638, 1518, 1470, 1394, 1089, 1051, 760, 678. ^{1}H NMR: δ 8.06–8.02 (m, 2H, ArH), 7.96–7.93 (m, 2H, ArH), 7.48–7.43 (m, 5H, ArH), 7.41(s, 1H, thiazole). ^{13}C NMR: δ 168.1, 155.0, 133.9, 133.6, 133.0, 130.2, 129.0, 128.9, 127.7, 126.6, 113.0.

4-(4-Methoxyphenyl)thiazol-2-amine (**5i**): White solid, m.p. 208–209 °C (Lit.[30] 206–207 °C); IR ν (cm^{-1}): 3435, 2924, 1625, 1528, 1386, 1245, 1042, 670. ^{1}H NMR): δ 7.74–7.71 (m, 2H, ArH), 6.94–6.91 (m, 2H, ArH), 6.61 (s, 1H, thiazole), 5.03 (br s, 2H, NH_2), 3.85 (s, 3H, OCH_3). ^{13}C NMR: δ 167.1, 159.4, 150.9, 127.5, 127.3, 114.0, 101.0, 55.3.

4-(4-Methoxyphenyl)-N-phenylthiazol-2-amine (**3j**): White solid, m.p. 139–140 °C (Lit.[30] 138–139 °C); IR ν (cm^{-1}): 3436, 2972, 1608, 1555, 1466, 1393, 1049, 678. ^{1}H NMR: δ 7.80–7.77 (m, 2H, ArH), 7.43–7.32 (m, 5H, ArH), 7.09–7.06 (m, 1H, thiazole), 6.95–6.92 (m, 2H, ArH), 6.69 (br s, 1H, NH), 3.84 (s, 3H, OCH_3). ^{13}C NMR: δ 164.2, 159.4, 151.1, 140.3, 129.4, 127.6, 127.3, 122.9, 118.1, 114.0, 100.0, 55.3. MS-EI: *m/z* (%): 282 (100), 165 (21), 149 (33), 77 (12).

4-(4-Methoxyphenyl)-2-methylthiazole (**5k**): White solid, m.p. 67–69 °C (Lit.[29] 67–68 °C); IR ν (cm^{-1}): 3434, 2926, 1612, 1505, 1249, 1173, 1032, 834, 747. ^{1}H NMR: δ 7.80 (d, *J* = 8.88 Hz, 2H, ArH), 7.16 (s, 1H, thiazole), 6.93 (d, *J* = 8.86 Hz, 2H, ArH), 3.83 (s, 3H, OCH_3), 2.75 (s, 3H, CH_3). ^{13}C NMR: δ 165.6, 159.5, 154.9, 127.59, 127.56, 114.0, 110.5, 55.3, 19.3.

4-(4-Methoxyphenyl)-2-phenylthiazole (**5l**): White solid, m.p. 127–129 °C (Lit.[29] 124–125 °C); IR ν (cm^{-1}): 3432, 2928, 1608, 1525, 1477, 1248, 1174, 1028, 836, 766, 690. ^{1}H NMR: δ 8.05–8.02 (m, 2H, ArH), 7.95–7.92 (m, 2H, ArH), 7.46–7.44 (m, 3H, ArH), 7.34 (s, 1H, thiazole), 6.99–6.96 (m, 2H, ArH), 3.86 (s, 3H, OCH_3). ^{13}C NMR: δ 167.7, 159.7, 156.1, 133.8, 130.0, 128.9, 127.8, 127.5, 126.6, 114.1, 110.9, 55.4.

2-Methyl-4-(4-nitrophenyl)thiazole (**5m**): Yellow solid, m.p. 141–143 °C (Lit.[29] 136 °C); IR ν (cm^{-1}): 3438, 2973, 1640, 1597, 1505, 1335, 1164, 1055, 847, 740, 659. ^{1}H NMR: δ 8.28 (d, *J* = 9.02 Hz, 2H, ArH), 8.05 (m, *J* = 9.01 Hz, 2H, ArH), 7.54 (s, 1H, thiazole), 2.80 (s, 3H, CH_3). ^{13}C NMR: δ 166.9, 152.7, 147.2, 140.3, 126.8, 124.2, 116.0, 19.4.

4-(4-Nitrophenyl)-2-phenylthiazole (**5n**): Yellow solid, m.p. 128–129 °C (Lit.[29] 122–123 °C); IR ν (cm^{-1}): 3434, 2924, 1599, 1510, 1338, 1104, 1054, 844, 734, 685. ^{1}H NMR: δ 8.31 (d, *J* = 8.69 Hz, 2H, ArH), 8.17 (d, *J* = 8.75 Hz, 2H, ArH), 8.07–8.04 (m, 2H, ArH) 7.69 (s, 1H, thiazole), 7.50–7.48 (m, 3H, ArH). ^{13}C NMR: δ 168.8, 153.8, 147.3, 140.3, 133.2, 130.6, 129.1, 127.0, 126.7, 124.2, 116.0. MS-EI: *m/z* (%): 282 (100), 252 (63), 236 (22), 149 (32), 89 (28).

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