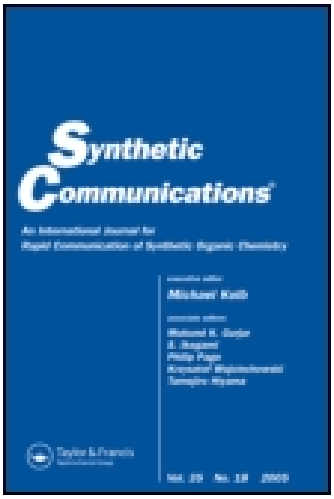

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Convenient One-Step Synthesis of cis-2,4,5-Triarylimidazolines from Aromatic Aldehydes with Urea

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CONVENIENT ONE-STEP SYNTHESIS OF *cis*-2,4,5-TRIARYLIMIDAZOLINES FROM AROMATIC ALDEHYDES WITH UREA

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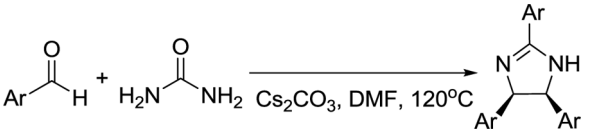
GRAPHICAL ABSTRACT



Abstract *A simple and efficient method has been developed for the synthesis of* cis-*2,4,5-triarylimidazolines based on a one-step procedure of aldehydes and urea in the presence of cesium carbonate.*

Keywords Aldehyde; cesium carbonate; imidazoline; urea

INTRODUCTION

2,4,5-Triarylimidazolines are good precursors for the synthesis of diarylethylenediamines, which have been employed as chiral ligands in enantioselective reactions after optical resolution.[1–11] The most important method for the synthesis of 2,4,5-triarylimidazolines is the reaction of aromatic aldehydes with ammonia to give the diimine compounds, *N,N′*-bis(arylmethylidene)arylmethanediamines, followed by heating with a strong base such as sodium amide or phenyllithium or heating at high temperature to form triarylimidazoline,[12–16] which often occurs in poor yield. Other methods have been reported for the synthesis of diimines using aldehydes and hexamethyldisilazane (HMDS) in the presence of Lewis acids such as $ZnCl_2$ or without any catalyst under solvent-free conditions using microwave irradiation.[17–19] Recently, one-step syntheses of 2,4,5-triarylimidazolines either from the corresponding aldehydes and HMDS with lithium bromide in dimethyl sulfoxide (DMSO)[20–22] or from aldehydes with a mixture of alumina with ammonium acetate under solvent-free conditions using microwave irradiation have

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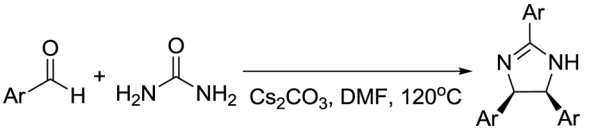


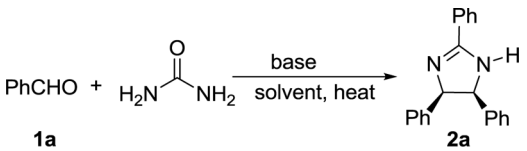
Scheme 1. Reaction of aromatic aldehydes with urea.

been reported.[23] Although these protocols provided access to triarylimidazolines, the development of simple and efficient methods is still strongly desirable. Herein, we report a one-step synthesis of *cis*-2,4,5-triarylimidazolines based on the reaction of aromatic aldehydes with urea and Cs_2CO_3 in *N,N*-dimethylformamide (DMF) (Scheme 1).

RESULTS AND DISCUSSION

The reaction of benzaldehyde **1a**, chosen as a model compound, was studied in the presence of several bases at solvents at different temperatures. Initially, we carried out the reaction of benzaldehyde **1a** (1.0 mmol) with urea (4.0 mmol) in the presence of cesium carbonate (2.0 mmol) in DMF at 100 °C (Table 1, entry 1). However, only 26% yield of *cis*-2,4,5,-triphenylimidazoline **2a** was obtained as determined by NMR. Then we raised the temperature and prolonged the reaction time; the corresponding yields increased (entries 2 and 4). Various ratios of benzaldehyde **1a** and urea as well as Cs_2CO_3 were checked, and the best yield was obtained when the ratio of **1a**/urea/Cs_2CO_3 was 1:4:2. The yield decreased when the amount of urea or

Table 1 Screen the reactions of benzaldehyde and urea under different conditions[a]

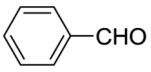
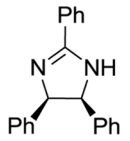
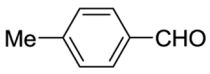
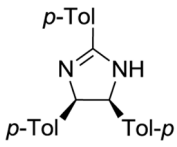
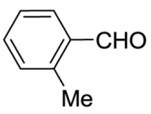
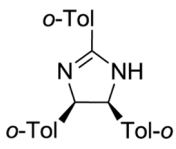
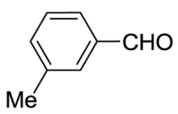
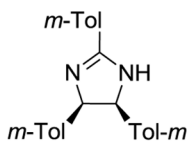
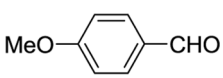
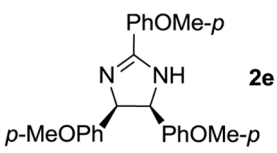
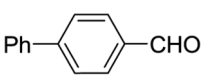
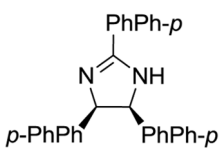
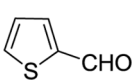
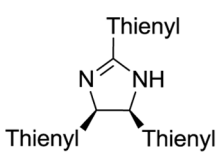
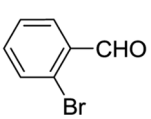
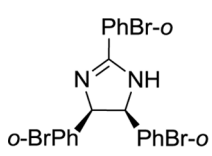


Entry	Base	Solvent	Temp.	Time	Yield of **2a** (%)[b]
1	Cs_2CO_3	DMF	100 °C	24 h	26
2	Cs_2CO_3	DMF	120 °C	24 h	46
3	—	DMF	120 °C	24 h	9
4	Cs_2CO_3	DMF	120 °C	36 h	78
5	K_2CO_3	DMF	120 °C	36 h	56
6	K_3PO_4	DMF	120 °C	36 h	64
7	AcONa	DMF	120 °C	36 h	23
8	Cs_2CO_3	NMP	120 °C	36 h	51
9	Cs_2CO_3	Toluene	120 °C	36 h	30
10	Cs_2CO_3	1,4-Dioxane	120 °C	36 h	26

[a]The reactions were performed with 1.0 mmol aldehyde **1a**, 4.0 mmol urea, and 2.0 mmol base in 2 mL solvent.

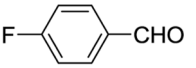
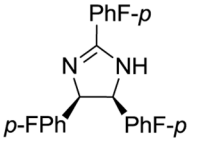
[b]Determined by ^1H NMR using CH_2Cl_2 as internal standard.

Table 2. Reactions of aldehyde **1** and urea to synthesize imidazoline **2**

Entry	Substrate **1**	Product		Yield (%)[a]
1			**2a**	78(73)
2			**2b**	79(70)
3			**2c**	82(78)
4			**2d**	72(65)
5			**2e**	82(79)
6			**2f**	62(56)
7			**2g**	50(42)
8			**2h**	60(52)

(*Continued*)

Table 2. Continued

Entry	Substrate **1**	Product	Yield (%)[a]
9		 **2i**	47(40)

[a]NMR yields, isolated yields are given in parentheses.

Cs_2CO_3 was reduced. In addition, when the amount of urea was increased to 6 equivalents, the yield of **2a** also decreased. It is important to note that only a trace of the desired product was obtained in the absence of Cs_2CO_3 (entry 3). Next, the applicability of other bases and solvents was also evaluated. Clearly, Cs_2CO_3 proved to be superior to K_3PO_4 and K_2CO_3 (entries 4–6). NaOAc gave poor yield (entry 7). The solvent did have a great effect on the reaction. Besides DMF, 1-methyl-2-pyrrolidinone (NMP) was also effective for the reaction (entry 8). When toluene and dioxane were used as solvents, the reactions gave poor yields, which were supposed to be because urea does not dissolve in such solvents (entries 9 and 10). When DMSO was used as a solvent, we did not observe any of the desired product **2a**; only the (*E*)-(2-(methylsulfinyl)vinyl)benzene[24] was obtained in 86% yield, which demonstrated the aldo-type reaction between aldehyde and DMSO in the presence of Cs_2CO_3.

Under the optimized condition, a study on the substrate scope was carried out, and the results are summarized in Table 2. The reaction of aldehyde **1** with urea exhibited a broad scope. As shown in Table 2 (entries 1–5), the reactions using various aromatic aldehydes having electron-donating groups (entries 2–6) proceeded well to give the corresponding imidazolines in good yields. The reaction of thiophene aldehyde with urea gave the corresponding imidazolines in good yield (entry 7). The

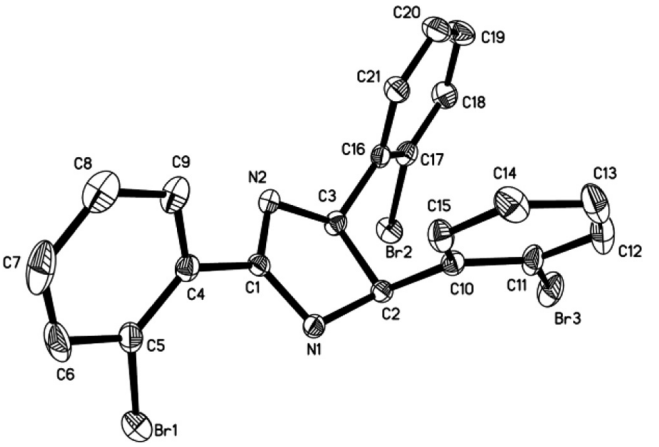


Figure 1. Configuration of **2h** in crystalline form.

reactions of 2-bromobenzaldehyde or 4-fluorobenzaldehyde with urea afforded the corresponding imidazolines in moderated yields (entries 8 and 9). It should be noted that if using *p*-chlorobenzaldehyde and *p*-bromobenzaldehyde as substrates, almost no imidazoline product was obtained but other uncharacterized products formed in the reaction. The imidazolines obtained in the reaction were confirmed to have *cis* geometry by comparison of the ^{1}H NMR spectral data of imidazolines **2** with the reported data.[9,15,21] In addition, the *cis* geometry of **2h** was further confirmed by x-ray crystallography (Fig. 1).

In summary, we have described a general one-pot method for the convenient synthesis of imidazoline derivatives via cooperative Cs_2CO_3 cyclization of aldehydes and urea. The yields are essentially moderate to good, and the configuration of products was always 100% favoring *cis* fashion. The application and further study are in progress in this laboratory.

EXPERIMENTAL

All the reactions were carried out in predried a screw-capped test tube with a Teflon-lined septum. DMF, toluene, 1,4-dioxane, and DMSO were freshly distilled. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Jeol 300 NMR spectrometer at ambient temperature with $CDCl_3$ as the solvent and TMS as internal standard. The melting points were measured on an X-4 digital melting-point apparatus and are uncorrected. Electrospray ionization–mass spectrometry (ESI-MS) were obtained on a Bruker Esquire-Lc/MSn spectrameter. Flash column chromatography was performed using silica gel (200–300 mesh).

Typical Procedure for Preparation of *cis*-2,4,5-Tris(*o*-tolyl)-imidazoline (2c)

2-Methylbenzaldehyde **1c** (1.0 mmol, 0.12 g), urea (4.0 mmol, 0.24 g), and Cs_2CO_3(2.0 mmol, 0.65 g) were dissolved in DMF (2 mL) in a sealed tube. The mixture was stirred at room temperature for 10 min and then heated at 120 °C for 36 h. The mixture was worked up with water (5 mL) at 0 °C, extracted by ethyl ether, and then dried with anhydrous sodium sulfate. The obtained organic solution was concentrated under vacuum to leave a residue, which was purified by silica-gel column chromatography (hexane/EtOAc 3/1) to afford 88 mg (78%) of *cis*-**2c**. White solid, mp 159–160 °C; IR (KBr): 3561, 3218, 2145, 1637, 1504, 1438, 1246, 1016 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 2.20 (s, 6H, C*H*$_3$), 2.69 (s, 3H, C*H*$_3$), 5.03 (s, 1H, *H*NCH), 5.67 (s, 2H, C*H*Ar), 6.82–6.96 (m, 6H, *H*-Ar), 7.06–7.11 (m, 2H, *H*-Ar), 7.24–7.38 (m, 3H, *H*-Ar), 7.70 (d, $J = 7.6$ Hz, 1H, *H*-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.54 (s, *C*H$_3$), 21.92 (s, *C*H$_3$), 70.89 (br, s, N*C*HAr), 125.39, 125.91, 126.88, 128.58, 129.72, 129.93, 130.82, 131.39, 135.10, 137.20, 137.45 (*Ar*), 165.51 (NH*C*N); ESI-MS: $m/z = 341.3$ ($[M + H]^+$). HRMS calcd. for $C_{24}H_{24}N_2$, 340.1939; found 340.1943.

cis-2,4,5,-Triphenyl-imidazoline (2a)[9]

Yield 73%; white solid, mp 160–162 °C; IR (KBr): 3717, 3027, 1668, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 5.45 (s, 2H, C*H*Ph), 6.93–7.03 (m, 10 H, *H*-Ar),

7.47–7.50 (m, 3 H, *H*-Ar), 7.97 (d, $J = 7.9$ Hz, 2 H, *H*-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 71.15 (br, s, N*C*HPh), 126.91, 127.37, 127.62, 127.75, 128.78, 130.16, 131.20, 139.10 (*Ph*), 164.59 (NH*C*N); ESI-MS: $m/z = 299.2$ ($[M + H]^+$).

cis-2,4,5-Tris(*p*-tolyl)imidazoline (2b)[21]

Yield 70%; white solid, mp 178–180 °C; IR (KBr): 3616, 3168, 1607, 1564, 1512, 1465, 1109 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 2.18 (s, 6H, C*H*$_3$), 2.43 (s, 3H, C*H*$_3$), 5.40 (s, 2H, C*H*Ar), 6.85 (s, 8H, *H*-Ar), 7.29 (d, $J = 7.9$ Hz, 2H, *H*-Ar), 7.86 (d, $J = 7.9$ Hz, 2H, *H*-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.13 (s, *C*H$_3$), 21.60 (s, *C*H$_3$), 70.11 (br, s, N*C*HAr), 127.25, 127.54, 128.40, 129.36, 136.20, 136.25, 141.28 (*Ar*), 164.37 (NH*C*N); ESI-MS: $m/z = 341.2$ ($[M + H]^+$).

cis-2,4,5-Tris(*m*-tolyl)imidazoline (2d)

Yield 65%; light yellow solid, mp 156–158 °C; IR (KBr): 3581, 3227, 1637, 1481, 693 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 2.13 (s, 6H, C*H*$_3$), 2.43 (s, 3H, C*H*$_3$), 5.32 (s, 2H, C*H*Ar), 5.53 (br, s, 1H, N*H*C), 6.74–6.81 (m, 6H, *H*-Ar), 6.89–6.95 (m, 2H, *H*-Ar), 7.34–7.39 (m, 2H, *H*-Ar), 7.73 (d, $J = 6.5$ Hz, 1H, *H*-Ar), 7.86 (s, 1H, *H*-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.31 (s, *C*H$_3$), 21.46 (s, *C*H$_3$), 124.27, 124.71, 127.44, 128.14, 128.32, 128.57, 130.19, 131.83, 137.06, 138.53, 139.11 (*Ar*), 164.54 (NH*C*N); ESI-MS: $m/z = 341.3$ ($[M + H]^+$). HRMS calcd. for $C_{24}H_{24}N_2$, 340.1939; found 340.1941.

cis-2,4,5-Tris(*p*-methoxyphenyl)imidazoline (2e)[21]

Yield 79%; white solid, mp 162–164 °C; IR (KBr): 3618, 3205, 1627, 1509, 1257, 994 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TMS): 3.65 (s, 6H, C*H*$_3$), 3.84 (s, 3H, C*H*$_3$), 5.28 (s, 2H, C*H*Ar), 6.57 (d, $J = 8.6$ Hz, 4H, *H*-Ar), 6.84 (d, $J = 8.6$ Hz, 4H, *H*-Ar), 6.93 (d, $J = 8.9$ Hz, 2H, *H*-Ar), 7.88 (d, $J = 8.9$ Hz, 2H, *H*-Ar); ^{13}C NMR (75 MHz, $CDCl_3$): 55.12 (s, O*C*H$_3$), 55.43 (s, O*C*H$_3$), 69.93 (br, s, N*C*HAr), 113.07, 113.89, 122.74, 128.62, 128.85, 131.57, 158.31, 161.75 (*Ar*), 163.91 (NH*C*N); ESI-MS: $m/z = 389.2$ ($[M + H]^+$).

cis-2,4,5-Tris(*p*-phenylphenyl)imidazoline (2f)

Yield 56%; light yellow solid, mp 130–132 °C; IR (KBr): 3593, 3251, 1638, 1484, 842, 794, 732, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 5.54 (s, 2H, C*H*Ar), 7.06 (d, $J = 8.2$ Hz, 3H, *H*-Ar), 7.25–7.48 (m, 18H, *H*-Ar), 7.64–7.74 (m, 4H, *H*-Ar), 8.08 (d, $J = 7.9$ Hz, 2H, *H*-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.54, 127.04, 127.18, 127.32, 127.47, 127.93, 128.10, 128.75, 129.07, 131.05, 138.20, 139.76, 140.29, 140.93, 144.07 (*Ar*), 164.43 (NH*C*N); ESI-MS: $m/z = 527.3$ ($[M + H]^+$). HRMS calcd. for $C_{39}H_{30}N_2$, 526.2409; found 526.2413.

cis-2,4,5-Tris(2-thienyl)imidazoline (2g)[21]

Yield 42%; light yellow solid, mp 138–140 °C; IR (KBr): 3679, 3216, 1627, 1479, 1138 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 5.40 (s, 1H, N*H*CPh), 5.63

(s, 2H, C*H*Ar), 6.76–6.83 (m, 4H, *H*-Ar), 7.06–7.14 (m, 3H, *H*-Ar), 7.51 (d, $J = 4.5$ Hz, 2H, *H*-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.03, 125.52, 126.46, 127.75, 128.23, 129.73, 133.11, 142.11 (*Ar*), 159.52 (NH*C*N); ESI-MS: $m/z = 317.1$ ($[M + H]^+$).

cis-2,4,5-Tris(*o*-bromophenyl)imidazoline (2h)

Yield: 52%; light yellow solid, mp 195–197 °C; IR (KBr): 3618, 3213, 1732, 1645, 1584, 1491, 1465, 1025 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 5.62 (br, s, 1H, *H*NCHAr), 6.03 (s, 2H, C*H*Ar), 6.89–6.94 (m, 2H, *H*-Ar), 7.01–7.06 (m, 2H, *H*-Ar), 7.26–7.44 (m, 6H, *H*-Ar), 7.67 (dd, $J = 7.9$ Hz, $J = .1.0$ Hz, 1H, *H*-Ar), 7.89 (dd, $J = 7.5$ Hz, $J = 1.7$ Hz, 1H, *H*-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.10 (br, s, N*C*HAr), 120.97, 124.18, 126.66, 127.79, 128.80, 130.34, 131.80, 132.10, 132.41, 133.84, 137.73 (*Ar*), 164.31 (NH*C*N); ESI-MS: $m/z = 536.8$ ($[M + H]^+$). HRMS calcd. for $C_{21}H_{15}Br_3N_2$, 531.8785; found 531.8782.

cis-2,4,5-Tris(*p*-flurophenyl)imidazoline (2i)[15]

Yield 40%; light yellow solid, mp 102–104 °C; IR (KBr): 3687, 2952, 1888, 1618, 1605, 1508, 1231, 849, 812 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 5.39 (s, 2H, C*H*Ar), 6.72–6.78 (m, 4H, *H*-Ar), 6.86–6.91 (m, 4H, *H*-Ar), 7.12–7.18 (m, 2H, *H*-Ar), 7.92–7.97 (m, 2H, *H*-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.73 (br, s, N*C*HAr), 114.75, 115.87, 126.13, 128.98, 129.49, 134.63, 161.61, 163.58 (*Ar*), 166.32 (NH*C*N); ESI-MS: $m/z = 353.2$ ($[M + H]^+$).

(*E*)-(2-(Methylsulfinyl)vinyl)benzene[24]

^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 2.63 (s, 3H, CH_3), 6.83 (d, $J = 15.4$ Hz, 1H, *H*CPh), 7.18 (d, $J = 15.4$ Hz, 1H, *H*CSOCH$_3$), 7.27–7.34 (m, 3H, *Ph*), 7.38–7.41 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.03 (*C*H$_3$), 127.74 (*C*HSOCH$_3$), 133.77(*C*HPh), 129.04, 129.85, 132.25, 136.46 (*Ph*); ESI-MS: $m/z = 167.1$ ($[M + H]^+$).

Compound 2h

$C_{42}H_{30}Br_6N_4$, crystallized in monoclinic, space group P2(1)/n with cell parameters: $a = 11.633$ (2), $b = 17.196$ (3), $c = 20.112$ (4)Å^3, $\alpha = 90.00$, $\beta = 93.68$ (3), $\gamma = 90.00$ °, $V = 4015.1$ (14) Å^3, $Z = 4$. CCDC 757397.

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