

Table 1 Coupling of aldehyde, alkyne, and amine catalyzed by Au/IRMOF-3 in 1,4-dioxane^a

$$\text{R}^1\text{-CHO} + \text{R}^2\text{R}^3\text{NH} + \text{R}^4\text{-C}\equiv\text{C-H} \xrightarrow[\text{Au/IRMOF-3}]{\text{dioxane } 120/150^\circ\text{C}} \text{R}^1\text{-CH(R}^2\text{R}^3\text{)-C(R}^4\text{)=C-NR}^2\text{R}^3$$

Entry	Cat.	R ¹	R ² R ³ NH	R ⁴	T ^b (h)	Conv./Yield ^c (%)
1	4.6%Au/IRMOF-3	Ph	Piperidine	Ph	0.5	77.0
2	4.6%Au/IRMOF-3	4-MeC ₆ H ₄	Piperidine	Ph	12	70.6
3	4.6%Au/IRMOF-3	4-MeOC ₆ H ₄	Piperidine	Ph	12	38.6
4	4.6%Au/IRMOF-3	3-ClC ₆ H ₄	Piperidine	Ph	12	95.4
5	4.6%Au/IRMOF-3	Cyclohexyl	Piperidine	Ph	12	98.9
6	4.6%Au/IRMOF-3	Heptyl	Piperidine	Ph	12	96.3
7	4.6%Au/IRMOF-3	Ph	Pyrrolidine	Ph	12	91.2
8	4.6%Au/IRMOF-3	Ph	Morpholine	Ph	12	54.6
9	4.6%Au/IRMOF-3	Ph	Diethylamine	Ph	12	26.6
10	4.6%Au/IRMOF-3	Ph	Piperidine	4-MeC ₆ H ₄	12	86.4
11	4.6%Au/IRMOF-3	Ph	Piperidine	4-EtC ₆ H ₄	12	70.6
12	4.6%Au/IRMOF-3	Ph	Piperidine	4-ButC ₆ H ₄	12	28.5
13	4.6%Au/IRMOF-3	Ph	Piperidine	Hexyl	12	62.1
14	4.6%Au/IRMOF-3	Ph	Piperidine	(CH ₃) ₃ Si	12	56.6
15	0.6%Au/IRMOF-3	Ph	Piperidine	Ph	12	98.0
16	0.6%Au/IRMOF-3	4-MeC ₆ H ₄	Piperidine	Ph	24	75.0
17	0.6%Au/IRMOF-3	3-ClC ₆ H ₄	Piperidine	Ph	24	40.3
18	0.6%Au/IRMOF-3	Cyclohexyl	Piperidine	Ph	24	98.2
19	0.6%Au/IRMOF-3	Heptyl	Piperidine	Ph	24	97.6
20	3.2%Au/IRMOF-3	Ph	Piperidine	Ph	10	98.0
21	3.2%Au/IRMOF-3	4-MeC ₆ H ₄	Piperidine	Ph	24	65.2
22	3.2%Au/IRMOF-3	3-ClC ₆ H ₄	Piperidine	Ph	24	30.0
23	3.2%Au/IRMOF-3	Cyclohexyl	Piperidine	Ph	24	98.5
24	3.2%Au/IRMOF-3	Heptyl	Piperidine	Ph	24	96.8

^a Reaction conditions: aldehyde (0.250 mmol), amine (0.300 mmol), alkyne (0.325 mmol), catalyst (0.07 g), the reaction temperatures are 120, 150, and 150 °C on 4.6%Au/IRMOF-3, 0.6%Au/IRMOF-3, and 3.2%Au/IRMOF-3 catalysts, respectively. ^b The reaction time was not optimization. ^c GC yield or conversion based on aldehydes, the product was determined by GC-MS, and ¹H-NMR.

bearing electron-withdrawing groups (Table 1, entry 4) afforded a better yield than those bearing electron-donating groups (Table 1, entries 2 and 3) when 4.6%Au/IRMOF-3 catalyst was used, however, the employment of 0.6%Au/IRMOF-3 (Table 1, entry 17 vs. 16) and 3.2%Au/IRMOF-3 (Table 1, entry 22 vs. 21) gave the opposite results. The A^3 coupling reaction was reported to be highly affected by the nature of aldehydes, and the reactivity of aldehydes could be affected by the employed catalyst.^{4,6,14,22,29} Kidwai *et al.* found that aryl aldehydes possessing electron-withdrawing groups afforded a better yield than that with an electron-donating group bound to the benzene ring which required longer reaction time with metallic Au nanoparticles as catalyst.¹¹ Wei and Li reported that both aromatic and aliphatic aldehydes were able to undergo the corresponding A^3 coupling with the catalyst of AuBr_3 .⁴ They found that electron-withdrawing groups displayed high reactivities, however, electron-rich groups bound to the benzene ring decreased the reactivity and required a longer reaction time. The decreased yield for aliphatic aldehydes was caused by the trimerization of aliphatic aldehydes with homogeneous gold salts. Zhang and Corma found that benzaldehyde with electron-donating groups react smoothly, while substitution of electron-withdrawing groups on the benzene ring decreases the reactivity with the catalyst of Au/CeO_2 .¹⁴ Based on the above results, we may presume that the activity difference could be due to the different properties (e.g., different oxidation states) between 4.6%Au/IRMOF-3 and 0.6%Au/IRMOF-3, 3.2%Au/IRMOF-3 catalysts.

With the catalyst of 4.6%Au/IRMOF-3, the reaction with secondary amines proceeded smoothly to afford the corresponding propargylamines (Table 1, entries 1, 7–9). Among the various amines tested, alicyclic amines such as piperidine, pyrrolidine, and morpholine gave good conversions of benzaldehyde, whereas the diethylamine afforded a lower conversion. This was probably due to the iminium ions generated from alicyclic amines and benzaldehyde which are more stable than that generated from dialkyl amine and benzaldehyde.

A variety of aromatic alkynes were coupled with benzaldehyde and piperidine in the presence of the 4.6%Au/IRMOF-3 catalyst. It was found that straight-chain alkyl substituted phenylacetylene showed decreasing conversion of benzaldehyde with increasing chain length, the conversions were 86.4%, 70.6% and 28.5% for methyl, ethyl, and butyl phenylacetylene, respectively (Table 1, entries 10–12). Clearly, when increasing the steric hindrance of alkynes, it gave a decrease in conversion. The reaction was found to be highly affected by the steric hindrance of the alkynes, which was probably ascribed to the limitation effect of the IRMOF-3 channels. Aliphatic alkynes such as 1-octyne and (trimethylsilyl)acetylene also afforded moderate conversions of benzaldehyde with 62.1% and 56.6%, respectively (Table 1, entries 13 and 14).

The reusability studies of 4.6%Au/IRMOF-3, 0.6%Au/IRMOF-3, and 3.2%Au/IRMOF-3 were carried out on the A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene. The results are summarized in Table 2. The fresh 4.6%Au/