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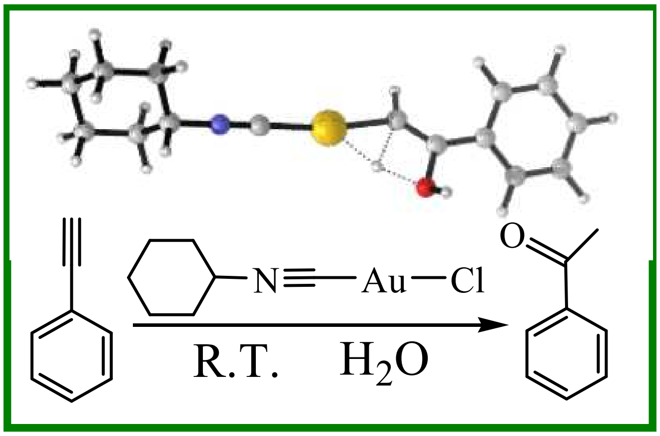

Gold (I) isocyanide show highly catalytic ability for the hydration of different alkynes at room temperature.

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ARTICLE TYPE

Hydration of alkynes at room temperature catalyzed by gold (I) isocyanide compounds

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An effective method using gold (I) isocyanide complexes as catalysts for the transformation of various alkynes to the corresponding ketones has been successfully developed. The hydration process proceeds smoothly at room temperature with quite high yield (up to 99%). The catalytic center is isocyanide-Au(I)$^+$ cation. Further theoretical research reveals a direct hydration mechanism by H_2O, and the rate-determining step has an energy barrier of 23.7 kcal/mol. These results show a good example to reduce unnecessary step and achieve milder reaction conditions at the same time for the hydration of alkynes.

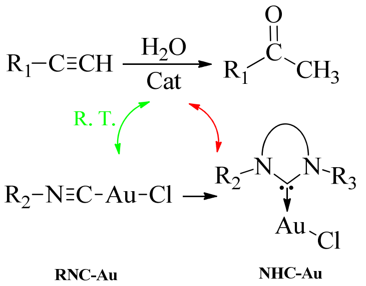
Introduction

The addition of water to alkynes is an environmentally friendly method to prepare ketones with 100% atomic economy. However, the traditional alkyne hydration was realized by using mercury (II) salts, a highly toxic compound, as catalyst. [1] Even though different Brønsted acids were also found to have catalytic activity for the hydration of alkynes,[2-4] the processes require, in most cases, stoichiometric or excess amounts of acids and only electron-rich alkynes as the substrates can lead to high conversions.

To overcome the disadvantages of mercury (II) salts and Brønsted acids, a variety of organometallic catalysts were explored, such as compounds containing Pt,[5] Ag,[6, 7] Ru,[8,9] Au, and even biomimetic catalysts.[10] Among them, the unique catalytic ability of gold (I) and gold (Ⅲ) has attracted many attentions, because gold centers show high affinity to activate C≡C triple bonds by nucleophilic attack. Though gold compounds were thought to be potential and excellent catalysts for alkynes hydration,[11,12] most of the reactions catalyzed by gold compounds require high reaction temperature, such as 120℃ for the hydration catalyzed by gold *N*-heterocyclic carbenes (Au-NHC)/$AgSbF_6$,[12,13] Au-NHC/$HSbF_6$,[11] and Au-NHC@porous organic polymers,[14] 100~150℃ for Bis(phosphane) gold(I),[15] 100 ℃ for $NaAuCl_4$,[16] 80 ℃ for Au-NHC[17] and Au-SH/SO_3H-PMO(Et),[8] 70℃ for $(Ph_3P)AuCH_3$ in the presence of H_2SO_4,[18] 65 ℃ for abnormal Au-NHC,[19] and reflux temperature.[20-24] Obviously, it is still a challenge to develop more effective gold catalysts for alkynes hydration at room temperature.

In the past decade, an increasing number of studies have focused on the preparation of gold isocyanide complexes (Au-RNC) and the investigation of their structure and properties.[25-27] But so far, Au-RNC complexes were mainly used as the starting materials for the synthesis of other novel catalysts. [28] Among the complexes obtained via Au-RNC, Au-NHC represents a kind of the most extensively studied compounds in organometallic chemistry and catalysis (Scheme 1).[29-39] To realize the reported catalytic ability of Au-NHC for the hydration of alkynes, high reaction temperatures are needed to obtain satisfactory conversions [11-14, 17, 19-23]. As far as we known[40], there was almost no example that Au-RNC complex was directly used as catalyst in not only alkynes hydration but also other reactions.

Both experimental and theoretical researches in this paper show, to our surprise, that Au-RNC has excellent activity in catalyzing the hydration of alkynes at room temperature. It is a good example that avoids the using of complicated catalysts and eliminates harsh reaction conditions in the hydration of alkynes (Scheme 1).



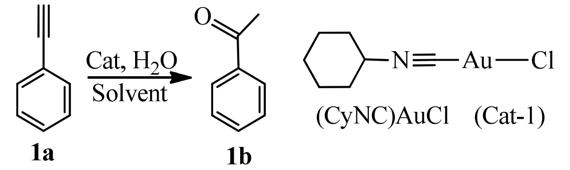
Scheme 1 The relation between Au-RNC and Au-NHC and their catalytic ability for the hydration of alkynes.

Results and Discussion

Hydration of phenylacetylene catalyzed by gold isocyanide

Two simple gold isocyanide complexes (RNC)AuCl (R=Cy, 2,6-$Me_2C_6H_3$) were synthesized according to the literature procedures (See supplementary information for detailed synthetic procedures and characterizations).[31, 34, 38] The hydration of phenylacetylene (**1a**) catalyzed by (CyNC)AuCl (**Cat-1**) was selected as a probe to investigate the activity of the catalyst (Table 1). No acetophenone (**1b**) was observed when **Cat-1** was used as catalyst alone (entry 1). As we known, the active center of gold (I) complexes in many reactions should be gold (I) cation.[41] To release the gold cation, some weakly coordinating anions (such as SbF_6^-, BF_4^-, $B(C_6H_5)_4^-$, and $B(C_6F_5)_4^-$) were added into the reaction system (entries 2-5). Though $AgSbF_6$ itself can be used as catalyst for the hydration of alkynes,[7] almost no ketone was produced in our research when using **Cat-1**/$AgSbF_6$ as catalyst because the reaction temperature is far low than that in the reference.[7] Among these anions (SbF_6^-, BF_4^-, $B(C_6H_5)_4^-$, and $B(C_6F_5)_4^-$), only $B(C_6F_5)_4^-$ which has the weakest coordination ability gives satisfactory result (entry 5). To exclude the possibility of $KB(C_6F_5)_4$ acting as catalyst, reaction with only $KB(C_6F_5)_4$ was also performed and no product was observed (entry 6). All the results above indicated that the active center in this reaction system should be $(CyNC)Au^+$ cation (**Cat-1**$^+$).

Table 1. Optimization of the Hydration Conditions [a]

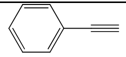
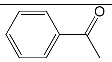
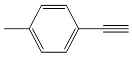
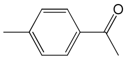
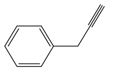
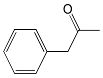
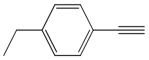
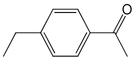
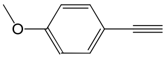
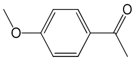
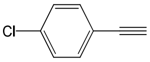
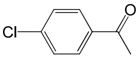
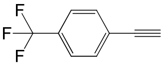
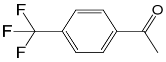
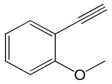
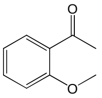
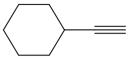
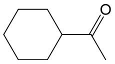
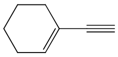
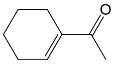
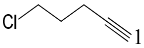
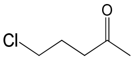
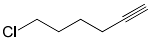
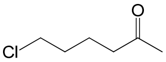
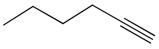
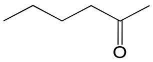
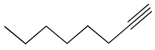
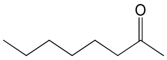
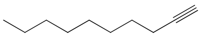
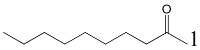
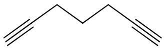
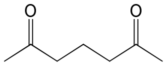
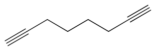
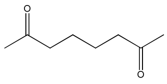


Entry	Catalyst (mol) [b]	Solvent	Conv. (%) [c]
1	5% Cat-1	Methanol	NR
2	5% Cat-1+5% $AgSbF_6$	Methanol	0.6
3	5% Cat-1+5% KBF_4	Methanol	3.7
4	5% Cat-1+5% $KB(C_6H_5)_4$	Methanol	1.5
5	5% Cat-1+5% $KB(C_6F_5)_4$	Methanol	99.9
6	5% $KB(C_6F_5)_4$	Methanol	NR
7[d]	5% Cat-1+5% $KB(C_6F_5)_4$	Methanol	99.9
8[e]	5% Cat-1+5% $KB(C_6F_5)_4$	Methanol	32.2
9[f]	5% Cat-1+5% $KB(C_6F_5)_4$	Methanol	5.0
10	1% Cat-1+1% $KB(C_6F_5)_4$	Methanol	20.2
11[f]	1% Cat-1+1% $KB(C_6F_5)_4$	Methanol	<1.0
12	5% Cat-1+5% $KB(C_6F_5)_4$	Ethanol	27.2
13	5% Cat-1+5% $KB(C_6F_5)_4$	Hexane	25.7
14	5% Cat-1+5% $KB(C_6F_5)_4$	Dioxane	10.1
15	5% Cat-1+5% $KB(C_6F_5)_4$	Acetone	3.4
16	5% Cat-1+5% $KB(C_6F_5)_4$	THF	0.8
17	5% Cat-1+5% $KB(C_6F_5)_4$	None	57.0

[a] Reaction condition: phenylacetylene (0.5mmol), solvent(0.5ml), H_2O(0.5ml), room temperature, 24h. [b] The catalyst amount is based on the molar percent to 1a. [c] Conversion of 1a determined by GC. [d] Methanol(0.5ml) and H_2O(1.0ml); [e] Methanol(1.0ml) and H_2O(0.5ml); [f] Methanol(2.0ml) and H_2O(0.5ml).

Using environmentally preferable solvent is quite important for a green process. The solvents screening experiments on methanol, ethanol, hexane, dioxane, acetone and THF show that reaction performed in methanol give best result (entries 5, 12~16 in Table 1). Using methanol as solvent is quite green according to the framework for the environmental assessment of solvents [42], Sanofi's solvent selection guide [43], and the EHS assessment for alternative solvents [44]. The amounts of solvent have obvious influence on the conversion of phenylacetylene. Comparing with the standard condition, increasing the amount of methanol results in low conversion of the reactant (entries 5, 7~9).

Table 2. Hydration of various alkynes catalyzed by Cat-1[a]

Entry	Reactant	Product	Yield (%)[b]
1	 1a	 1b	>99
2	 2a	 2b	>99 (96)
3	 3a	 3b	>99
4	 4a	 4b	>99 (95)
5	 5a	 5b	>99 (97)
6[c]	 6a	 6b	63
7[c]	 7a	 7b	8 [5][d]
8	 8a	 8b	>99 (99)
9	 9a	 9b	>99 (95)
10	 10a	 10b	>99 (98)
11	 11a	 11b	>99
12	 12a	 12b	>99 (99)
13	 13a	 13b	>99 (98)
14	 14a	 14b	97
15	 15a	 15b	>99 (99)
16[c]	 16a	 16b	97 (95)
17[c]	 17a	 17b	98 (97)

[a] Reaction condition: alkyne (1.0 mmol), Cat-1 (0.05mmol), $KB(C_6F_5)_4$ (0.05mmol), H_2O(1.0 ml), methanol (1.0 ml), room temperature, 24h. [b]

Yield determined by GC with biphenyl as internal standard. Isolated yields are shown in parenthesis. [c] 10% mol catalyst, 48h. [d] Reaction time: 48h [24h].

It has been found that some alkynes can be converted into vinyl ether intermediate by the addition of methanol to the C≡C bond, and vinyl ether can then be hydrolyzed into ketone [11, 12]. The catalysis reported here should not proceed in such a pathway, because no any vinyl ethers were detected by GC-MS during the reactions of all the substrates investigated here (Tables 1 and 2). Furthermore, when only H_2O was used as both solvent and reactant, the reaction conversion still can reach 57.0% in 24h (entry 17 in Table 1).

Substrate scope of the gold isocyanide catalysts

To explore the substrate scope of this catalytic system, the hydration of different alkynes was investigated under the standard conditions (Table 2). **Cat-1** shows excellent catalytic reactivity at room temperature for a wide range of substrates, including electron-rich and electron-deficient alkynes, aromatic and none-aromatic alkynes. Total seventeen alkynes were investigated, and the isolated or GC yields of fifteen alkynes are larger than 95%. For relatively electron-deficient alkynes, such as **6a**, only 63% yield was obtained (entry 6). Further increase in the electron withdrawing ability of the substituent by CF_3 results in quite slow reaction rate. The GC yield of **7b** is only 5% in 24 hours and 8% in 48 hours (entry 7). For electron-donating alkynes, **5a** and **8a**, satisfactory isolated yields (>97%) were obtained, especially when the methoxyl is located at ortho-position (entries 5 and 8). No matter the C≡C triple bond binds with aromatic ring or alkane, the reactions perform quite well. Besides alkynes, the hydration of diynes, such as **16a** and **17a**, can also be well catalyzed by gold isocyanide with high yields at room temperature (entries 16 and 17).

In addition to **Cat-1**, another gold isocyanide (2,6-$Me_2C_6H_3$-NC)AuCl (**Cat-2**) was also investigated and its catalytic ability was compared with that of **Cat-1** (Figure 1). Though the activity of **Cat-2** is a little weaker than that of **Cat-1**, the reaction catalyzed by **Cat-2** can still proceed quite well at room temperature (Table S1 in supplementary information).

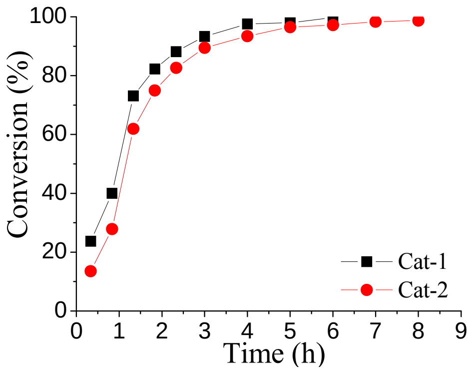


Fig. 1. Kinetic plot of conversion of 5a with respect to time under standard condition.

Another route to synthesize these ketones is the catalytic aerobic oxidation of alcohols. [45-53] It should be noticed that the only byproduct is water for an ideal oxidation process, and some of these oxidations can be performed at room temperature. [45-49] However, $NaNO_2$ [48, 49] or excess amounts of bases [45-47, 50, 51] are usually indispensable in these aerobic oxidations. Though some of the alcohols used in the oxidation routes are cheaper than the alkynes in the hydration routes, the following characteristics of the route reported here make itself a more green choice for the synthesis of ketones: 100% atomic economy, mild reaction condition, environmentally preferable solvent, no need of acids or bases.

Hydration mechanism of the reaction catalyzed by gold isocyanide

It has been found in literature that alkynes with methanol as solvent can be hydrated to the expected ketones via vinyl ether intermediates.[11, 12] However, for the hydration catalyzed by the gold isocyanide complexes (Cat-1 and Cat-2), no any signal of vinyl ether intermediates was detected by GC-MS analysis. Besides, the reaction still can perform well without the addition of methanol (entries 13 and 14, Table 1). These two evidences above imply a direct hydration of alkynes by H_2O.[7] To further understand the hydration mechanism catalyzed by the gold isocyanide, a DFT based theoretical investigation was performed (see supplementary information for computational details) (Figure 2). According to the known knowledge of other Au(I) catalysts[41] and results listed in Table 1, the active center in the reaction should be (Cy-N≡C)Au^+ (**Cat-1**$^+$) cation.

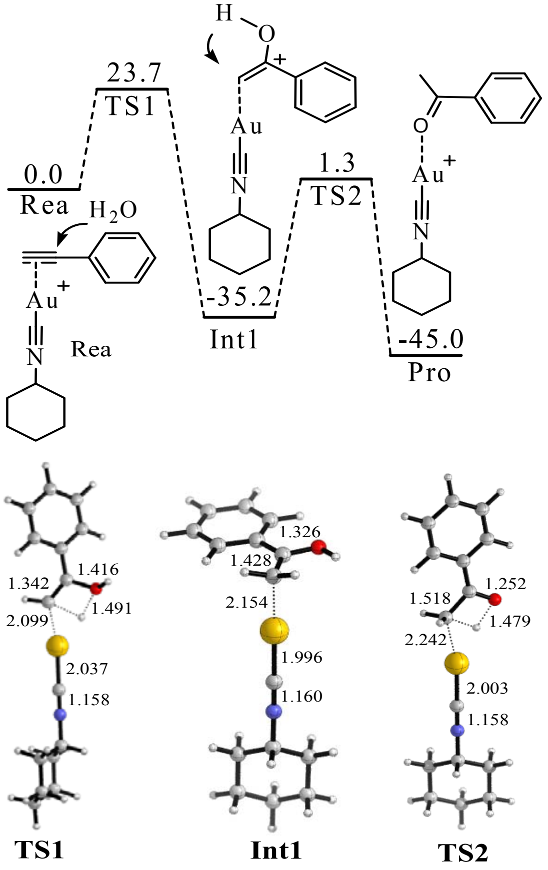


Fig. 2. Proposed mechanism of the hydration of phenylacetylene. The values in the reaction pathway are in kcal/mol. The other

values are bond length in Å.

The binding between **Cat-1**$^+$ and **1a** is found to be highly exothermic (-47.3 kcal/mol). With the assistance of **Cat-1**$^+$, H_2O can attack **1a** via a transition state TS1 (Figure 2). The barrier of TS1 is 23.7 kcal/mol. The C≡C triple bond of **1a** becomes almost a double bond in TS1 (length increasing from 1.212 to 1.342 Å). An enol form intermediate (Int1 or Int1') can be produced via TS1 (Figures 2 and 3). After that, enol-keto isomerisation via a proton transfer process (TS2 or TS2') takes place to generate the final product with a total energy change of -45.0 kcal/mol. However, the barrier of TS2 or TS2' is too high (36.5 or 37.6 kcal/mol) to support the room temperature hydration of 1a. Considering that the microenvironment of the reaction is full of water, water assisting enol-keto isomerisation process should be more feasible.[54-58] In this process, the proton of C-O-H transfers to the an explicit H_2O, and meanwhile, one proton of this explicit H_2O transfers to the terminal carbon of C=C bond. In this case, the transition from the Int1' hydrate (Int1'-W) to the final product only need to overcome a quite low barrier (22.5 kcal/mol of TS2'-W). Of course, if there are two or more explicit water molecules to join the process and assist the proton transfer, the barrier should be further reduced and smaller than 22.5 kcal/mol. [54-58] Thus, the rate-determining step of this hydration process should be H_2O attacking the C≡C triple bond with a barrier of 23.7 kcal/mol (Figure 2).

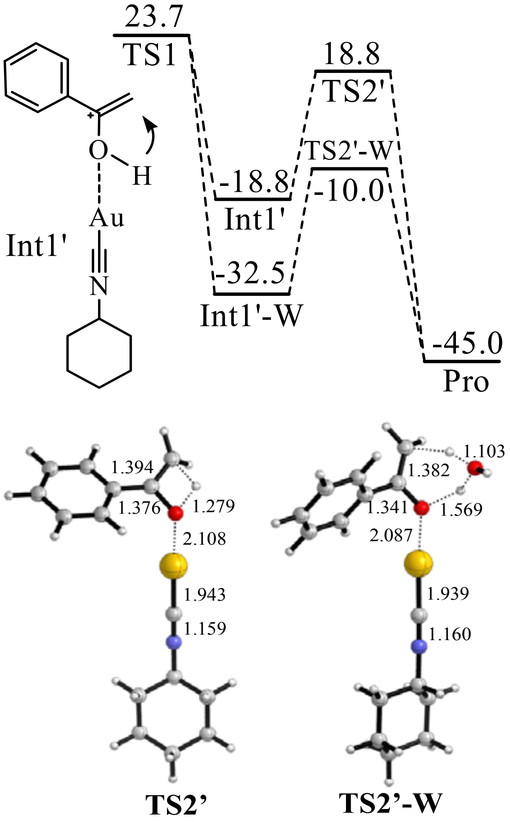


Fig. 3. Water-assisted enol-keto isomerisation in the hydration of phenylacetylene. The values in the reaction pathway are in kcal/mol. The other values are bond length in Å.

Another interesting pathway for the reaction of terminal alkyne using gold catalyst is gold(I) may react with terminal alkyne to produce gold vinylidenes ($LAu=C=CR_2$) intermediate and this intermediate can further react with other functional group, such as cycloisomerization of alkyne. [59, 60] The possibility of similar gold vinylidene (Rea'') reacting with H_2O was further investigated (Figure 4). It was found that the addition of H_2O to Rea'' is not easy because of a quite high barrier of TS1'' (51.4 kcal/mol). This energy barrier is 27.7 kcal/mol higher than that of TS1. Furthermore, the energy barrier for the proton transfer from C-O-H to the terminal carbon is 45.9 kcal/mol (TS2''), which is 9.4 kcal/mol higher than that of TS2. Hence, for the hydration of alkynes catalyzed by gold(I) isocyanide compounds, the reaction mechanism is more likely to be the pathway presented in Figures 2 and 3. The barrier height of rate-determining step for the pathway in Figures 2 and 3 is only 23.7 kcal/mol, and this barrier height is reasonable for the reaction to proceed readily at room temperature. [61]

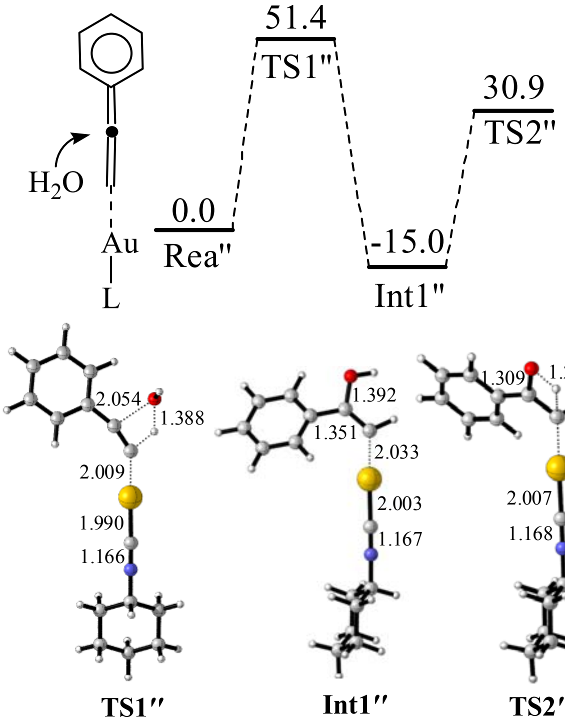


Fig. 4. Reaction between gold vinylidenes and H_2O. The values in the reaction pathway are in kcal/mol. The other values are bond length in Å.

Conclusions

In summary, the hydration of different alkynes was successfully performed at room temperature in the presence of gold isocyanide complexes. The substrates investigated here include electron-rich and electron-deficient alkynes, aromatic and none-aromatic alkynes. Isocyanide Au(I)$^+$ cation is extrapolated to be the active center that shows quite high catalytic ability for most of the substrates. Theoretical research further reveals the hydration mechanism which includes two steps: H_2O attacking the C≡C triple bond and explicit H_2O assisting the proton transfer to the C=C double bond.

Au-RNC, as a precursor for the synthesis of Au-NHC, [29-39] shows comparable catalytic ability to Au-NHC in the hydration of alkynes. This is a rare example that Au-RNC is used as catalyst directly to obtain satisfactory hydration results. Considering the simple structure and high reactivity of gold isocyanide, it deserves to receive more attention in other reactions. Because gold isocyanide is a homogeneous catalyst, developing a method to recycle it will bring a more green process. Supporting the gold isocyanide on zeolite [62] or ionic liquids [63-65] will be effective methods to reuse this compound.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and characterization results (^{1}H-NMR, ^{13}C-NMR, Elemental analysis, and MS); Hydration of various alkynes catalyzed by Cat-2; Computational methods and cartesians coordinates of the optimized structures. See DOI: 10.1039/b000000x/

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