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Tropylium Ion Catalyzes Hydration Reactions of Alkynes

Giulia Oss,[a] Junming Ho*[a] and Thanh Vinh Nguyen*[a]

Abstract: The hydration of alkynes is one of the most atom-economic and versatile synthetic protocols to access carbonyl compounds. This fundamental reaction, however, often requires transition-metal catalysts or harsh reaction conditions to promote the addition of water to the carbon-carbon triple bond. In this work, we demonstrate for the first time that the non-benzenoid aromatic tropylium ion can be used as an organic Lewis acid promoter for the hydration of alkynes under simple reaction conditions with excellent outcomes.

Introduction

The fundamental hydration reaction of alkynes to carbonyl compounds remain a versatile chemical process to access valuable synthetic substrates as well as an interesting reactivity probe for a range of catalytic systems.[1] This reaction is commonly utilized in organic synthesis due to its atom-economic nature.[1c] Although the reaction is exergonic, it often requires a catalyst to speed up the hydration of alkynes.[1] In the past two decades, the reaction has long departed from its original mercury-promoted process[2] with recent developments on more environmentally benign methods.[1] These developments have focused on two distinct angles of the reaction: activating alkyne substrate[1c] or stimulating the 'hydrative' reaction medium.[3] The first research direction typically involves activation of alkynes with transition-metal catalysts containing Au,[4] Ag,[5] Ru,[6] Pd,[7] Fe,[8] Cu[9], Co[10] and other metals.[11] More recently, there has been a number of interesting hydration processes promoted by Brønsted acid catalytic systems.[12] However, these methods are generally limited in scope[12c,12g,12h] or require complicated reaction setups[7c,12c,12i] with long reaction times in toxic or expensive solvents.[12f,12h] Therefore, it is still of significant interest to develop new methods that do not involve precious and toxic metal-catalysts and solvents, or have broader reaction and substrate scopes. Herein, we report the successful utilization of tropylium tetrafluoroborate, a readily available salt of a stable carbocation, as an organic Lewis acid to efficiently promote the hydration reaction of alkynes with excellent outcomes (Figure 1).

The non-benzenoid aromatic tropylium ion[13] has 6π electron and a positive charge fully delocalized on a conjugated planar seven-carbon system.[14] It therefore fulfills Hückel's rule of aromaticity and possesses a unique combination of stability and reactivity. Based on our previous works with tropylium-promoted

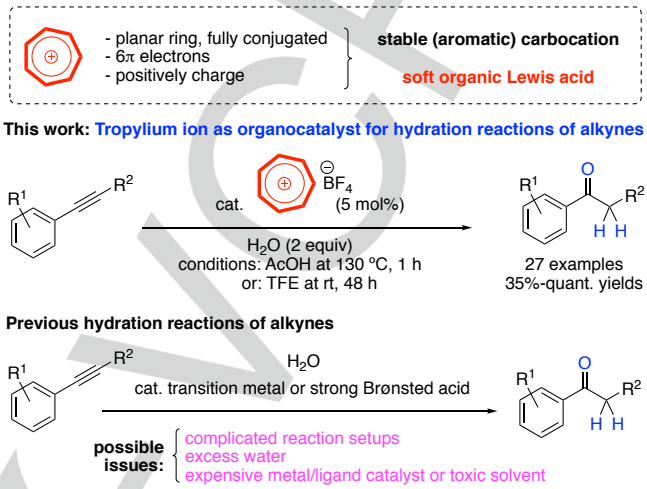

Figure 1. Tropylium-catalyzed hydration of alkynes.

chemistry[15] and synthetic applications of Lewis acid/base systems,[16] we believe that tropylium ion could serve as a Lewis acid promoter for the hydration of alkynes.[15d] Specifically, the tropylium cation may enhance the Brønsted acidity of water or the protic solvent, in a *Lewis acid assisted Brønsted acid catalytic* pathway,[17] to facilitate the alkyne hydration reaction. Previous Brønsted acid catalyzed hydration methods normally employed strongly acidic conditions with special co-activators[3c] such as ionic liquid solvents,[3a,3b] perfluorinated reagents or solvents[12f] or metal Lewis acids.[17] Herein, we demonstrate for the first time that tropylium tetrafluoroborate[18] can be used as an efficient organic promoter for the metal-free hydration reaction of alkynes using a cheap solvent and simple reaction setups. Our combined NMR and computational studies revealed interesting activation mechanisms by the tropylium ion, which will spur further research into the applications of tropylium ion in catalytic chemistry.

Results and Discussion

Gratifyingly, our initial test reactions using tropylium tetrafluoroborate (**2**) as a catalyst for the hydration reaction of phenylacetylene (**1a**) met with instant success (Table 1). Under pressurized microwave-assisted high temperature conditions in toluene, **1a** smoothly reacted with water to form acetophenone (**2a**) with 80% conversion within one hour in the presence of 5 mol% catalyst **2** (entry 1, Table 1). We subsequently did a quick solvent screening study[19] and found that reactions in no solvent, alcohols, dichloroethane, acetonitrile as well as toluene gave unsatisfactory conversion of **1a** to the product (entries 1-6). Acetic acid, however, turned out to be a very good solvent for this reaction (entry 7, Table 1). Variations of the tropylium

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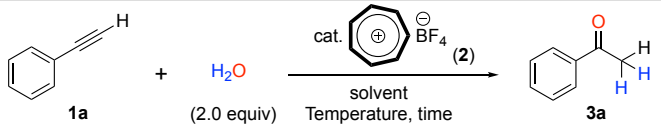
[**] Experimental procedures, characterization data and spectroscopic data are available free of charge.

Table 1. Optimization of tropylium-catalyzed hydration reaction [a]



entry	mol% cat. **2**	solvent	T (°C)	t (h)	conv (%)
1	5	toluene	130	1	80
2	5	MeOH	130	1	17
3	5	EtOH	130	1	40
4	5	MeCN	130	1	37
5	5	DCE	130	1	43
6	5	no solvent	130	1	10
7[b]	**5**	**AcOH**	**130**	**1**	**100**
8	2	AcOH	130	1	57
9	1	AcOH	130	1	34
10	0.5	AcOH	130	1	13
11	-	AcOH	130	1	n.r.
12	5	AcOH	100	1	51
13	5	AcOH	100	2	70
14	5	AcOH	130	0.25	74
15	5	AcOH	130	0.5	87
16	5	AcOH	130	0.75	92
17[c]	5	AcOH	130	1	38
18[d]	5	AcOH	130	1	100
19	$Trop^{\oplus}Br^{\ominus}$	AcOH	130	1	100
20	$Trop^{\oplus}PF_6^{\ominus}$	AcOH	130	1	100
21	$Trop^{\oplus}ClO_4^{\ominus}$	AcOH	130	1	100
22[e]	TfOH (5)	AcOH	130	1	100
23[e]	HBF_4 (5)	AcOH	130	1	~90
24	NH_4BF_4 (5)	AcOH	130	1	< 5
25	KBF_4 (5)	AcOH	130	1	n.r.
26	$TrBF_4$ (5)	AcOH	130	1	~90
27	5	TFE	130	1	100
28	5	TFE	rt	72	100
29	10	TFE	rt	48	100
30[f]	5 + pyr1	TFE	130	1	< 5
31[g]	5 + pyr2	TFE	130	1	< 5

[a] Alkyne **1a** (1 mmol), water (2 mmol), tropylium tetrafluoroborate (**2**, 0.1 or 0.05 mmol) in solvent (0.5 mL) in a *pressurized* microwave (MW) reactor. [b] Conventional heating instead of MW irradiation gave similar results. [c] 0.5 mL AcOH and 0.5 mL water were used. [d] 0.5 mL AcOH and *no water* were used. [e] 5 mol% of Brønsted acid (HBF_4 or TfOH) was used instead of tropylium catalyst. [f] 5 mol% of 2,6-lutidine was used as proton sponge. [g] 5 mol% of 2,6-di(*tert*-butyl)pyridine was used as proton sponge.

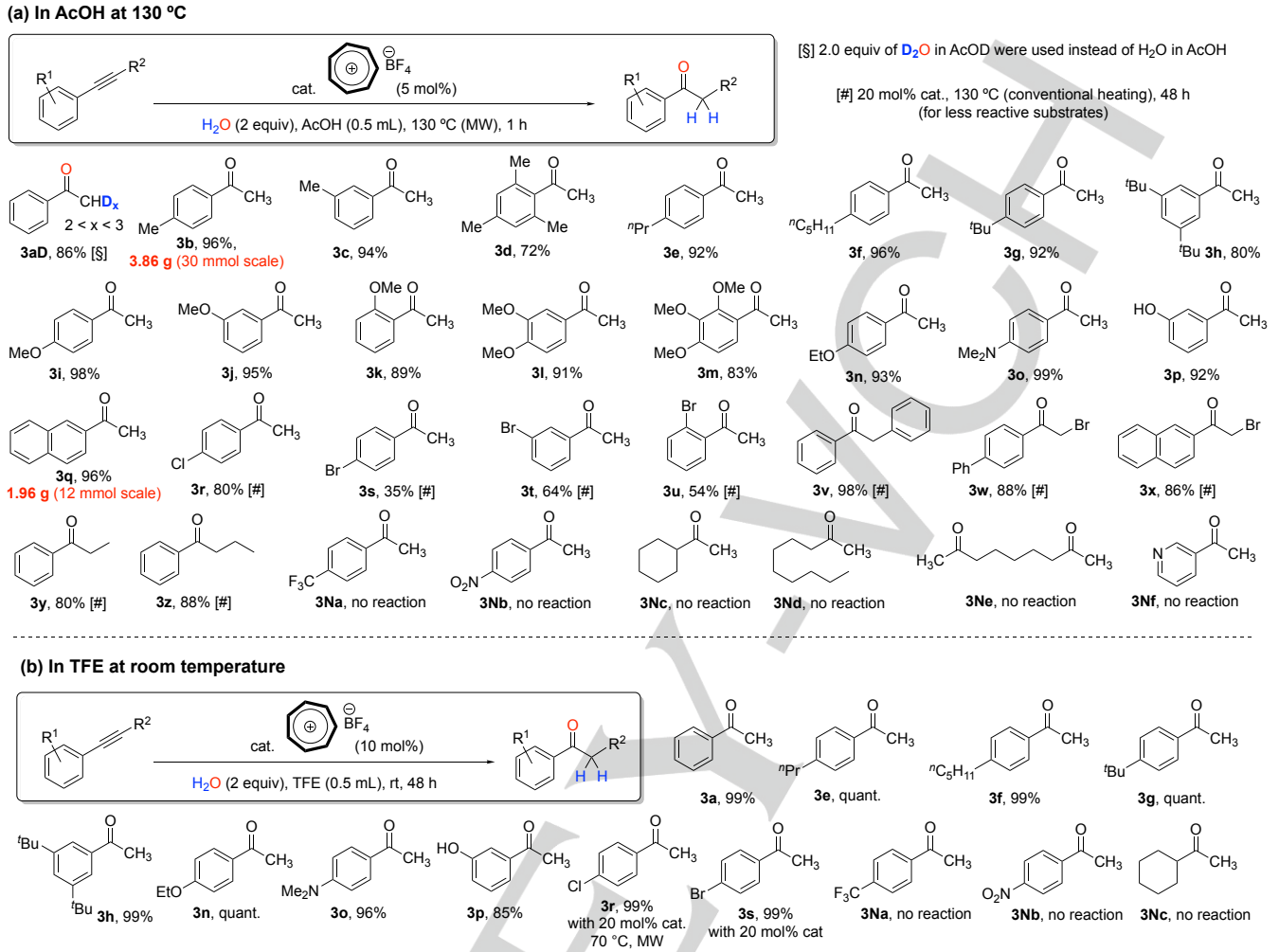
catalyst loading, reaction temperature and reaction time (entries 7-18) led to the conclusion that the reaction works optimally at 130 ºC after one hour of microwave irradiation or conventional heating with 5 mol% tropylium tetrafluoroborate (entry 7).[20] A control reaction without the catalyst showed no conversion of **1a** to product **3a** (entry 11).

Interestingly, the use of an excess amount of water was not favorable for the tropylium-catalyzed reaction (entry 17, Table 1). When the reaction was carried out without the addition of water (entry 18, Table 1), the hydration reaction still took place with the formation of acetic anhydride by-product from the sacrificial role of acetic acid (see page S3 in the SI). Since the formation of acetic anhydride is undesirable, the addition of water is deemed necessary for the hydration reaction. Different counterions had no effect on the performance of the tropylium catalysts (entries 19-21, Table 1).

The use of strong Brønsted acids such as triflic acid (pKa_{water} = -14.7)[21] or HBF_4 (pKa_{water} = -0.44)[22] as catalysts can also promote the smooth conversion of **1a** to **3a** (entries 22 and 23), albeit only ~ 90% conversion in the later case. The weakly (Brønsted) acidic ammonium tetrafluoroborate only gave a very poor conversion (entry 24, Table 1). Potassium tetrafluoroborate could not catalyze the reaction but the (Lewis) acidic tritylium tetrafluoroborate resulted in a good conversion of alkyne **1a** to product **3a** (entries 25-26).

Li and co-workers recently reported in an interesting study that triflic acid can facilitate the hydration reactions of alkyenes at ambient temperature (reactive substrates) or 70 ºC (less reactive substrates) in TFE.[12f] TFE solvent actually played a role in lowering the activation energy for these reaction compared to ethanol.[12f] Therefore, we decided to explore the possibility of using this perfluorinated solvent to carry out our catalytic reactions under milder conditions. Gratifyingly, a quick optimization (entries 27-29, Table 1) showed that tropylium catalyst **2** can also promote the hydration reaction of alkyne **1a** at room temperature in TFE with reaction time comparable to what reported by Li and co-workers with 20 mol% triflic acid catalyst.[12f] Thus, we have developed *two practical protocols* to facilitate the hydration reaction of alkynes, one at elevated temperature in the inexpensive and abundantly available acetic acid solvent (entry 7, Table 1) and the other at room temperature in TFE (entry 29, Table 1).

Subsequent substrate scope studies using the first method showed that this tropylium-catalyzed hydration protocol worked efficiently with a wide range of different alkynes (Scheme 1a).[20] All phenylacetylenes with electron-neutral or electron-donating substituents were hydrated smoothly to their corresponding acetophenones (**3a**-**3q**, Scheme 1a) in excellent yields using the optimized reaction conditions (entry 7, Table 1). Phenylacetylenes with halogen substituents seemed to be less reactive under the standard reaction settings; hence they were converted to the acetophenone products using more forcing



Scheme 1. Substrate scope of the tropylium-catalyzed hydration reaction

conditions (**3r**-**3u**, Scheme 1a).[20] Similarly, non-terminal aromatic alkynes required longer reaction times and higher catalyst loading to afford the products in high to excellent yields (**3v**-**3z**, Scheme 1a). Non-aromatic alkynes and aromatic alkynes with strong electron-withdrawing substituents such as the CF_3 or nitro group could not be hydrated using this tropylium-catalyzed procedure (**3Na**-**3Nf**), hinting that a π *electron-rich aromatic system on the substrate is required for the tropylium activation*. This is consistent with a Brønsted acid catalyzed pathway since the more electron-rich the substrate is, the higher its proton affinity and the lower the thermodynamic barrier for proton transfer. Despite this limitation, the substrate scope clearly demonstrates the superior synthetic value and versatility of the tropylium-catalyzed system in comparison to previous transition metal-free methods.[12]

The first reaction protocol could also be easily employed in multiple-gram scale reactions, as demonstrated by two examples of alkynes **1b** and **1q** (Scheme 1a). These reactions were very high yielding, which confirm the practicality of the tropylium-catalyzed system. Furthermore, the hydration reaction of substrate **1a** with deuterated water reagent and acetic acid solvent also went smoothly to give deuterated acetophenone **3aD** in high yields (Scheme 1a). There were more than two deuteriums incorporated into **3aD**,[20] most likely due to further deuteration via the enolization of the ketone under acidic conditions.

Using the second method in TFE solvent at room temperature (entry 29, Table 1), a number of randomly selected alkyne substrates were hydrated smoothly and efficiently with 10 mol% of tropylium catalyst (**3a**, **3e**, **3f**, **3g**, **3h**, **3n**, **3o**, **3p**, Scheme 1b). Chloro- and bromo-substituted phenylacetylene required higher catalyst loading or elevated temperature to promote the reactions (**3r** and **3s**, Scheme 2c). Unfortunately the highly electron-deficient aromatic or aliphatic substrates (**3Na**, **3Nb**, **3Nc**) still did not react, even with 20 mol% catalyst at 70 ºC. Although these results showed that tropylium tetrafluoroborate does not provide superior reactions outcomes to triflic acid as reported by Li and co-workers,[12f] it is still synthetically convenient to use such a stable solid organic catalyst to setup this type of chemical transformation. The question remains as to

what is the origin of the catalytic action of tropylium ion in this type of reaction?

Mechanistic Studies

There are two possible explanations for the catalytic activity of tropylium tetrafluoroborate in the hydration reaction of alkynes: (i) the tropylium ion acts as a '*non-covalent*' Lewis acid to activate the alkyne substrate (Figure 2a) or (ii) the tropylium ions reacts with water or the solvent to facilitate the reaction via a *hidden Lewis acid assisted Brønsted acid catalytic pathway* (*vide infra*). Our initial NMR studies (Figure 2b) revealed aromatic interactions between tropylium ion and phenylacetylene, suggesting that tropylium might act as a non-covalent catalyst. Specifically, when present in a 20:1 mixture (to reflect the 5 mol% catalyst loading) with phenylacetylene **1a**, the tropylium ion signal showed an upfield shift, presumably due to π–π *interactions* between tropylium ion and phenylacetylene (spectrum 4, Figure 2a). Additionally, non-reactive substrates for the tropylium-promoted hydration reaction, for example alkynes **1Nb** and **1Nc**, showed much less significant chemical shift movements (spectra 7 and 8, Figure 2b). The π–π *interaction* between the tropylium ion to the benzene ring was also evidenced in the cases of styrene and ethylbenzene, where a C-C triple bond is absent (spectra 5 and 6, Figure 2b). At the NMR temperature (25 ºC), tropylium tetrafluoroborate seemed to be stable in the presence of water and acetic acid for several days (spectra 2 and 3).

Based on these NMR studies, we hypothesised that the tropylium ion can simultaneously activate water/acetic acid through electrostatic stabilization, and hold them in the close proximity to the alkyne substrate (complex **5**, Figure 2a) to promote the reaction. Thus, we subsequently employed DFT (M06-2X/6-31+G(d,p))[23] and high-level *ab initio* composite calculations (G3(MP2)-RAD(+))[24] to investigate the energetics of this process. Figure 2c illustrates the G3(MP2)-RAD(+)/SMD(Acetic Acid)[25] free energy profile[26] (in kJ mol^{-1}) for proton-coupled acetate addition to phenylacetylene in the absence and presence of tropylium ion. The calculations indicate that tropylium forms a very weak π–π complex with phenylacetylene (ΔG complexation *ca.* 3.4 kJ mol^{-1}), which is consistent with NMR studies. For this reason, the energies reported in Figure 2(c) are relative to *separate* reactants. We have located a concerted transition state where proton transfer from acetic acid is coupled with acetate addition in an asynchronous fashion. The free energy barrier associated with this transition state is about 160 kJ mol^{-1}, which is thermally inaccessible and is consistent with experimental observations (see entry 11, Table 1).

Surprisingly, the calculations further indicate that when tropylium ion is present in a stacked conformation with phenylacetylene, the free energy barrier is slightly raised by 2 kJ mol^{-1}. Presumably, the concerted nature of the transition state (no charged intermediates) also means that electrostatic stabilization is not likely to play a significant role. We have also investigated the possibility of a stepwise process where the proton is initially transferred from acetic acid to phenylacetylene (**1a**) to form the ion pair **6**:**OAc** (Figure 2b). The potential energy scans (Figure S4 – see page S6 in the SI) suggest that the proton transfer is associated with spontaneous acetate addition,

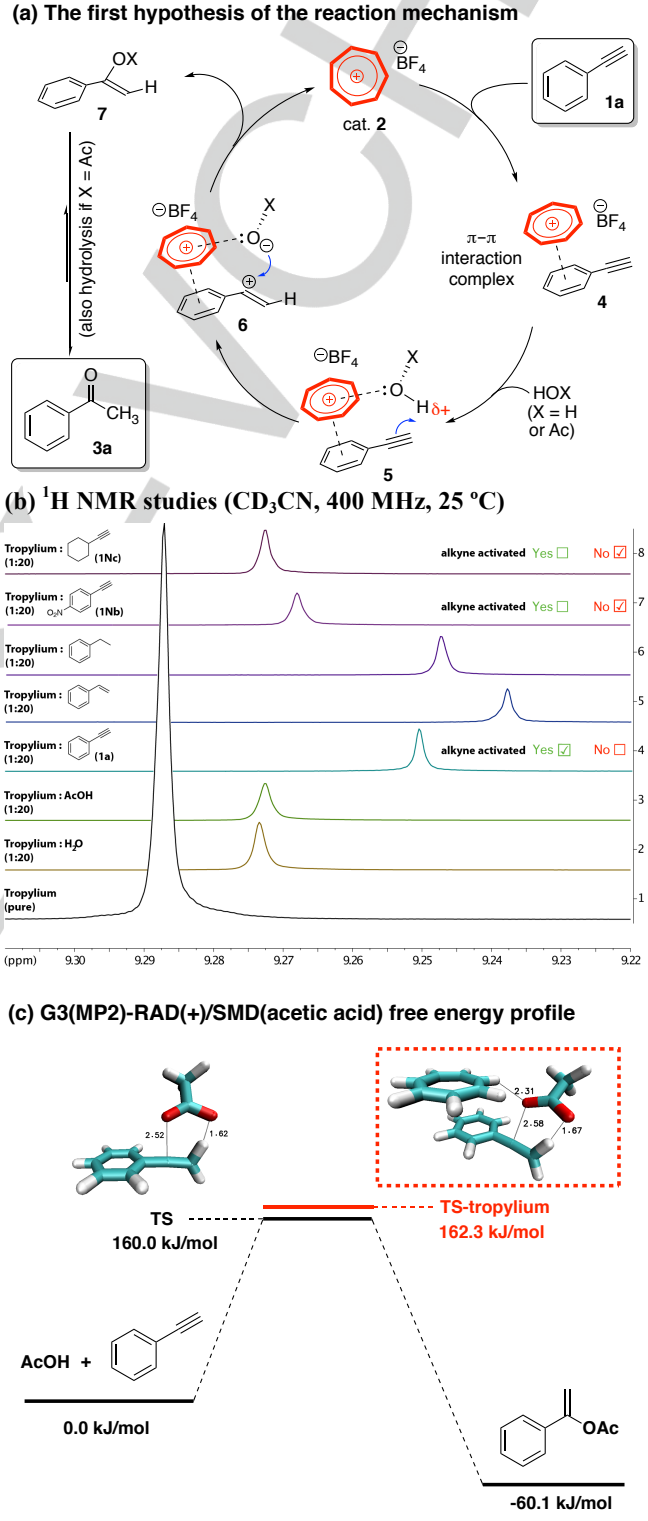


Figure 2. Mechanistic studies of the tropylium catalyzed hydration reaction.

which refutes a stepwise mechanism when tropylium is operating as a non-covalent catalyst. In brief, the results presented in Figure 2 and discussed here indicate the non-covalent catalytic pathway might not be the predominant route for this tropylium-promoted alkyne hydration reaction.

The *second proposed mechanism* was based on the common belief that tropylium tetrafluoroborate could react with water or acetic acid (pKa_{water} = 4.76)[27] to form hydrogen tetrafluoroborate (HBF_4) and OH/OAc substituted cycloheptatriene (also see Figure 2),[13c] thus catalyzing the reaction via a hidden Brønsted acid catalytic pathway. During our optimization work discussed in Table 1, we found that the addition of 2,6-lutidine or 2,6-di(*tert*-butyl)pyridine as bulky Brønsted bases stopped the reaction from working properly (entries 30 and 31, Table 1),[21] again hinting that this reaction might actually be Brønsted acid (HBF_4) catalysis assisted by Lewis acid (tropylium salt). *Would it really be the case?* To gain more insights into this hypothesis, we carried out a range of mechanistic studies using NMR spectroscopy (Figure 3) to look at how the tropylium ion interacts with all reaction components.

Much to our surprise, tropylium tetrafluoroborate was found to react directly with 2,6-lutidine (**8**) or 2,6-di(*tert*-butyl)pyridine (**10**) to presumably form the corresponding cycloheptatrienyl pyridinium salts (**9** and **11**, Figure 3). These chemical processes *ruled out the validity of the control experiments* carried out in entries 30-31 (Table 1) discussed above. The reaction with 2,6-lutidine occurred quickly even at room temperature (Eq. 2, spectrum 5) whereas 2,6-di(*t*-butyl)pyridine was more sluggish but one hour at 130 ºC completely converted tropylium salt to the inactive cycloheptatrienyl derivative (Eq. 1, spectrum 6).

Mixtures of tropylium tetrafluoroborate and water or acetic acid in CD_3CN as NMR solvent remained unchanged after one hour at 130 ºC (spectra 2-3, Figure 3; also see page S3 in the SI) or several days at ambient temperature (see spectra 2 and 3, Figure 2b) without the formation of hydrogen tetrafluoroborate.

However, there was clear evidence that the tropylium ion interacts weakly with water or AcOH, as indicated by the upfield shifts of the tropylium signal when it was in 1:20 (equivalent to 5 mol% tropylium) mixtures with these nucleophilic molecules (even at room temperature, also see spectra 2-3, Figure 2b). Heating tropylium tetrafluoroborate to 130 ºC for one hour in pure d_4-acetic acid (CD_3COOD) led to the formation of a small amount (~ 5% of the original tropylium loading, i.e. in a catalytic reaction with 5 mol% tropylium, only ~ 0.25 mol% converted to this form) of cycloheptatriene adduct (see Eq. 4, spectrum 4, Figure 3). Such reaction was not observed for water (Eq. 3, spectrum 2).

Based on these collective NMR studies, we believe that the presence of the tropylium ion in acetic acid might have led to the formation of a small amount of a strong Brønsted acid (**13**, Figure 3) through a *Lewis acid assisted* pathway. Figure 4 provides additional computed thermodynamic data to help shed light on the mechanism of action of tropylium ion. Reactions (A) to (C) shows that tropylium ion enhances the transfer of a proton from acetic acid to phenylacetylene, forming vinyl cation intermediate **14** (Figure 4), through electrostatic stabilization (B) or adduct formation (C). In the former, the degree of stabilization is about 25 kJ mol^{-1}; however, the overall thermodynamic barrier is still exceedingly high at 187 kJ mol^{-1}. As such, tropylium ion is unlikely to act as a non-covalent catalyst. By comparison, in reaction (C) tropylium ion acts as a Lewis acid to stabilize the resulting acetate anion via adduct formation, and this significantly lowered the thermodynamic barrier by 90 kJ mol^{-1} to 122 kJ mol^{-1}, which is in the thermally accessible range. Reactions (D), (E) and (F) provide some hints with regards to the microspecies that may be involved in the proton transfer process. Notably, the calculations indicate that the free energy change for proton transfer from hydrogen tetrafluoroborate or tropylium acetic acid adduct **13** to substrate **1a** is approximately 30 kJ mol^{-1}, which is a four-fold reduction compared to (C).

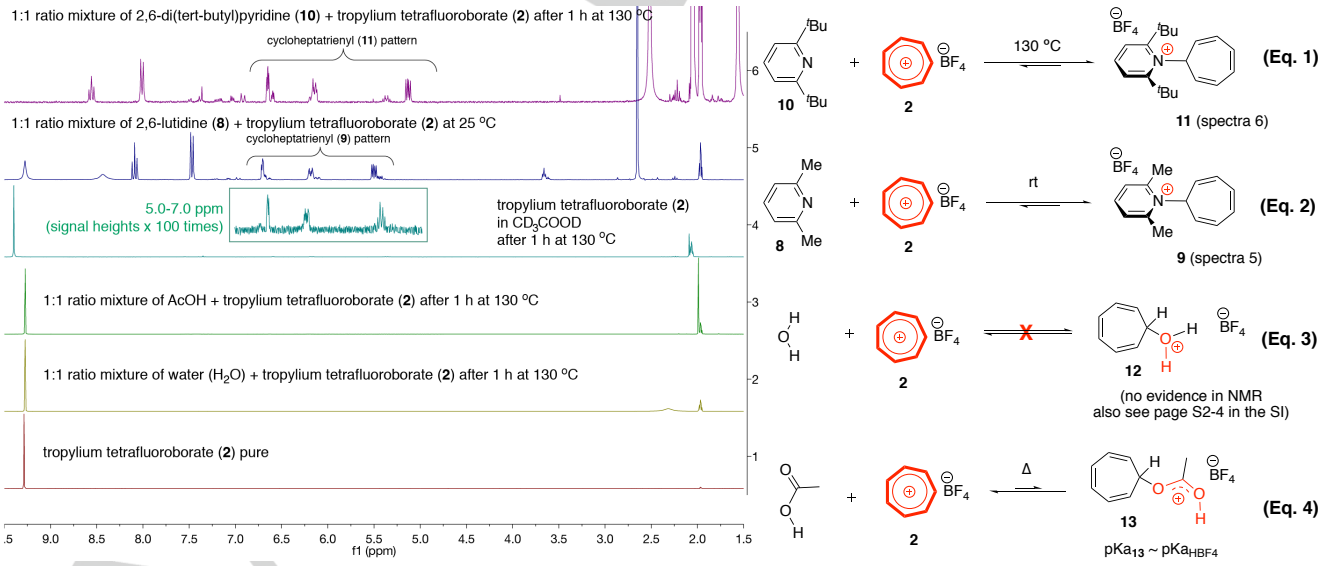


Figure 3. Interactions of tropylium ion with acetic acid and water: (left) NMR studies [^{1}H NMR, CD_3CN (except spectrum 4), 400 MHz, 25 ºC]; (right) Corresponding chemical reactions

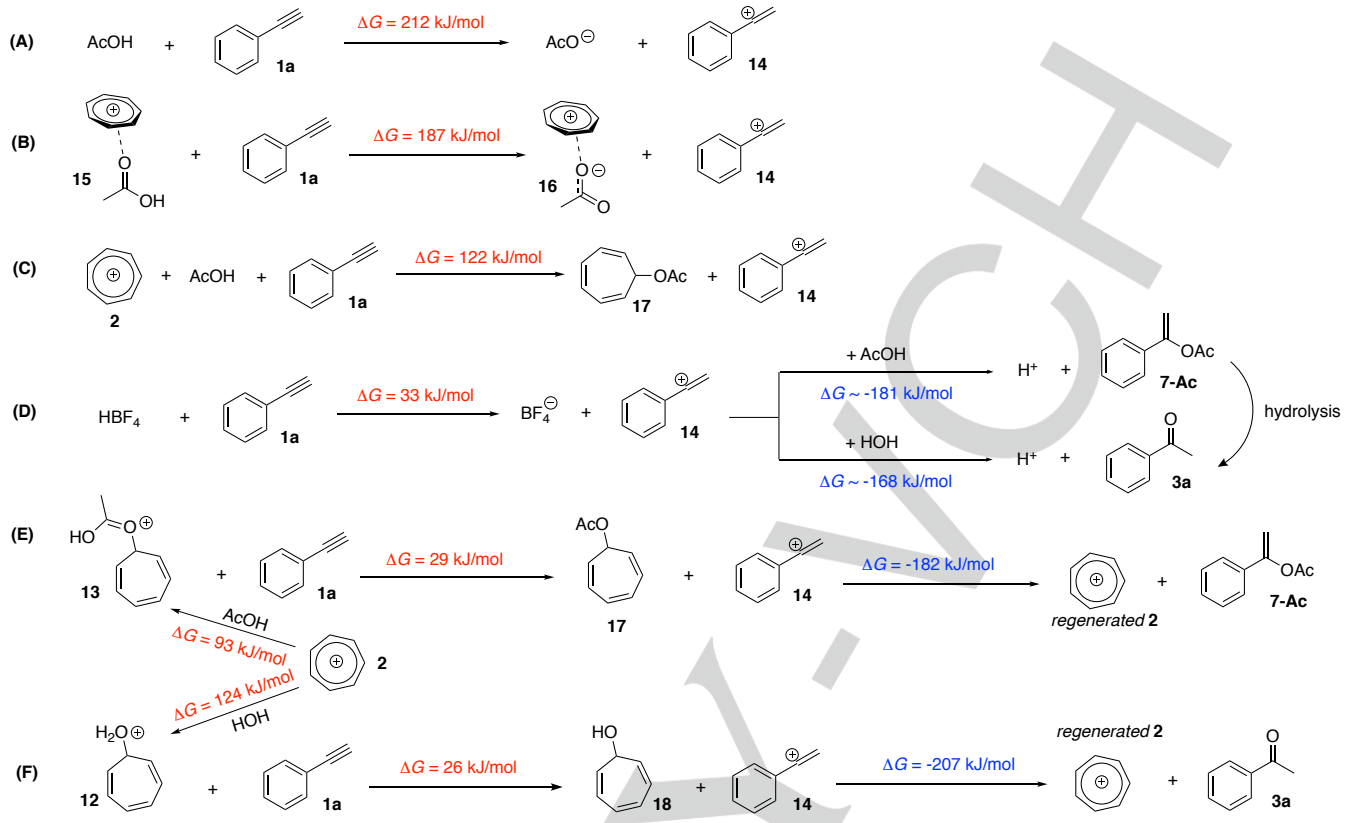


Figure 4. Thermodynamic data computed at the G3(MP2)-(RAD)(+)/SMD(acetic acid) level of theory.

As noted earlier, there is NMR evidence to support the presence of (*ca*. 5% of the total tropylium loading) **13** in a heated mixture of tropylium and acetic acid (see Figure 3). We hypothesise that upon proton transfer from **13** (or **12**, if any) to phenylacetylene **1a** to form vinyl cation **14**, this intermediate can further react with the generated by-products **17**/**18** to derive the product with the regeneration of tropylium ion. Another plausible pathway is the reaction of **14** with acetic acid or water (see reactions (D) in Figure 5), with the regeneration of the proton, which will then propagate the reaction. The data indicate that all of these processes are highly exergonic (ΔG < -160 kJ mol^{-1}), suggesting that they all are likely to be feasible pathways for the subsequent reactions after proton transfer.

To summarise, our combined experimental and computational investigations support a *Lewis acid assisted Brønsted acid catalytic mechanism*, where the Brønsted acidity of acetic acid and water is significantly enhanced through adduct formation with tropylium ion. We believe that the hydration reaction of alkynes in TFE medium (reported in Scheme 1b) proceeded in a similar fashion.

Conclusions

We have developed a new reaction protocol involves the tropylium ion as an organocatalyst to facilitate the conversion of alkynes to the corresponding ketone derivative using simple reaction setup with cheap and environmentally benign reagents and solvents. This tropylium-promoted reaction is particularly effective on aryl alkynes with excellent reaction outcomes, prompting further investigations into new synthetic applications of the tropylium ion in synthetic organic chemistry and organocatalysis.

Experimental Section

General Methods: Reactions, unless otherwise stated, were conducted under a positive pressure of dry nitrogen in oven-dried glassware. Microwave reactions were carried out in pressurized 10 mL microwave vials on CEM Discover – SP W/ACTIVENT 909155 or 10 mL vials on Anton Paar Monowave 300. Commercially available reagents were used as purchased unless otherwise noted. Analytical thin layer chromatography was performed using silica gel plates pre-coated with silica gel 60 F_{254} (0.2 mm). Flash chromatography employed 230-400 mesh silica-gel. Solvents used for chromatography are quoted as volume/volume ratios.

NMR spectroscopy was performed at 298 K using either a Bruker Avance III 300 (300.13 MHz, ^{1}H; 75.5 MHz, ^{13}C; BBFO probe), a Avance I 300 (300.13 MHz, ^{1}H; 75.5 MHz, ^{13}C; BBFO probe), a Avance III 400 (400.13 MHz, ^{1}H; 100.6 MHz, ^{13}C; BBFO probe or Prodigy cryoprobe), a Varian Mercury 300 (300.13 MHz, ^{1}H), a Varian Inova 400 (400.13 MHz, ^{1}H; 100.6 MHz, ^{13}C), or a Varian Inova 600 (600.13 MHz, ^{1}H; 150.0 MHz, ^{13}C). Data is expressed in parts per million (ppm) downfield shift from

tetramethylsilane with residual solvent as an internal reference (δ 7.26 ppm for chloroform, 5.27 ppm for dichloromethane, 1.94 ppm for acetonitrile, and 2.09 ppm for the toluene methyl group) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (J in Hz) and integration (number of protons). ^{13}C NMR spectra were recorded at 298 K with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ 77.2 ppm for the central peak of deuterated chloroform). Infrared spectra were obtained on a ThermoNicolet Avatar 370 FT-IR spectrometer and are reported in wavenumbers (cm^{-1}). HRMS were performed at the Bioanalytical Mass Spectrometry Facility within the Mark Wainwright Analytical Centre at the University of New South Wales on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) ion trap mass spectrometer.

General Procedure for the Tropylium-Catalyzed Hydration Reactions of Alkynes:

Procedure A: A mixture of alkyne **1** (1 mmol), water (2 mmol), tropylium tetrafluoroborate (0.05 mmol) and acetic acid (0.5 mL) was charged into a microwave vial (10 mL volume). The reaction vial was programmed in the microwave reactor to ramp rapidly from room temperature to the reaction temperature (~2 min) then hold at that temperature for 1 hour. The reaction vial was subsequently cooled down to room temperature. The reaction mixture was partitioned between DCM (10 mL) and sat. aq. $NaHCO_3$. The aqueous phase was further extracted with DCM (2 x 5 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduce pressure to give practically clean product **3**.

Procedure B: A mixture of alkyne **1** (1 mmol), water (2 mmol), tropylium tetrafluoroborate (0.2 mmol) and acetic acid (1 mL) was charged into a two-neck flask. The resulting mixture was heated to 130 °C for 48 h. The reaction was subsequently cooled down to room temperature. The reaction mixture was partitioned between DCM (10 mL) and sat. aq. $NaHCO_3$. The aqueous phase was further extracted with DCM (2 x 5 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduce pressure to give practically clean product **3**.

Procedure C: A mixture of alkyne **1** (1 mmol), water (2 mmol), tropylium tetrafluoroborate (0.1 mmol) and 2,2,2-trifluoroethanol (0.5 mL) was charged into a vial (4 mL volume). The reaction mixture was left stirring at room temperature for 48 h. The reaction mixture was filtered a short-plug of silica-gel then concentrated under reduce pressure to give practically clean product **3**.

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Keywords: tropylium • alkyne • hydration • organocatalysis • Lewis acid

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[18] Tropylium tetrafluoborate used in this project can either be purchased from chemical suppliers or synthesized in multiple-gram scale with an experimental protocol suitable for undergraduate laboratory; see: K. Conrow, *Org. Synth.* **1963**, *43*, 101. It is recrystallized twice to remove any trace of Bronsted acid impurities. .

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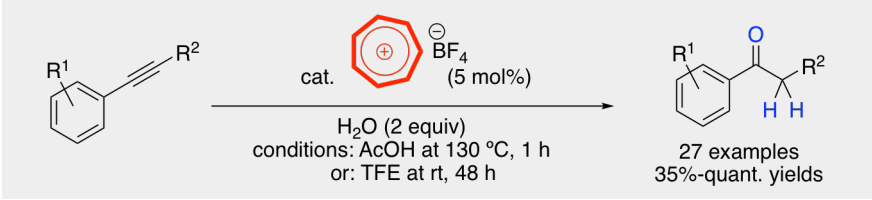

From Lewis to Brønsted: Tropylium ion acts as as Lewis acid to mediate the transition metal-free hydration of alkynes.

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