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One-pot synthesis of α,β-unsaturated ketones through sequential alkyne dimerization/hydration reactions using the Hoveyda–Grubbs catalyst†

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Herein we report a sequential one-pot alkyne dimerization/hydration protocol for the regioselective synthesis of α,β-unsaturated ketones in quantitative yields. The alkyne dimerization reactions of terminal arylacetylenes proceeded with high regioselectivity in the presence of the Hoveyda–Grubbs 2nd generation catalyst (1 mol%) and tricyclohexylphosphine (4 mol%). The hydration reactions of *in situ* formed 1-aryl-3-*en*-1-ynes proceeded very rapidly in the presence of CCl_3COOH/*p*-TsOH·H_2O, yielding the corresponding unsaturated ketones within 15 minutes in quantitative yields. Different arylacetylene derivatives were converted to the corresponding α,β-unsaturated ketones in quantitative yields (94–95%) using sequential one-pot alkyne dimerization/hydration reactions.

1. Introduction

Unsaturated ketones (enones) are important building blocks for the synthesis of various functional molecules such as enols, α-siloxyamides, α-hydroxyamides, hydroborate derivatives and chiral alcohols.[1–4] To date, several different strategies have been reported in the literature for the synthesis of α,β and β,γ unsaturated ketones.[3–7] Various starting materials including allyl alcohol, propargyl alcohol, saturated ketones, ketone-stabilized phosphonium ylides, enol ethers, and alkynes have been used in the construction of enone derivatives through catalytic or non-catalytic synthesis protocols.[8–13] Among these starting materials, alkynes emerge as valuable starting materials for the construction of unsaturated ketones through combined catalytic transformation reactions.[14] The early examples of unsaturated ketone synthesis protocols utilize isomerization of propargylic alcohols to enones in the presence of a ruthenium catalyst.[15] In 2012, hydroacylation of internal alkynes with aldehyde derivatives in the presence of Ru/CeO_2 and phosphine derivatives gave the corresponding α,β-unsaturated ketones in moderate yields.[16] The reaction of terminal alkynes and water in the presence of $[CpRu(NCMe)_3^+PF_6^-]$ and *para*-toluenesulfonic acid yielded β,γ-unsaturated ketone derivatives *via* a one-pot procedure. The reaction mechanism proceeds through *in situ* formation of head-to-head dimerization of alkynes, followed by the generation of bis-carbene derivatives.[17] The reaction then proceeds through oxidation of the intermediates, yielding β,γ-unsaturated ketone. This study showed that not only alkynes but 1,3-enynes can be used as starting materials for the synthesis of α,β- and β,γ-unsaturated ketone derivatives. $PtCl_2$/CO and IPrAuCl/AgOTf catalyzed hydration reactions of 1-aryl-3-*en*-1-ynes selectively gave α,β- and β,γ-unsaturated ketone derivatives based on the catalyst and the reaction conditions.[18] In 2014, the same strategy was applied for the synthesis of 2-*en*-1,4-dicarbonyl derivatives through hydrative oxidation of 1,3-enynes.[19]

To date, several approaches have been reported in the literature for the selective synthesis of 1,3-enynes.[20] Among the reported synthesis strategies, the dimerization of terminal alkynes emerges as an efficient catalytic reaction for the selective formation of 1,3-enynes. Several different transition metal complexes including Co, Ru, Fe, Zr, Pd and Au have been reported as efficient catalysts for the dimerization of terminal alkynes.[21–27] Among these transition metal-based catalysts, ruthenium exhibits high regioselectivity in the dimerization of alkynes.[28–30] Ruthenium based Grubbs type catalysts are known to catalyze various non-metathetic reactions including alkyne dimerization, cyclotrimerization, alkyne–carboxylic acid addition reactions and reduction of alkenes.[31–42] During the last decade, our research group has focused on non-metathetic tandem reactions using Grubbs type catalysts.[31–42] Grubbs 2nd and Grubbs 3rd generation catalysts are efficient catalysts for alkyne dimerization reactions.[36–39] Recent studies proved that the addition of coordinating molecules such as pyridine and phosphine can tune the chemoselectivity and regioselectivity of dimerization reactions.[37,38]

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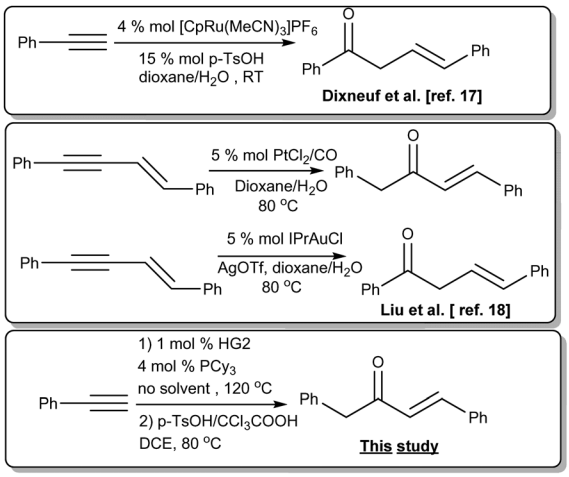


Scheme 1 Different strategies for the synthesis of unsaturated ketones.

To date, only a few studies utilized 1,3-enynes as starting materials (or reaction intermediate) to build α,β- and β,γ-unsaturated ketone derivatives (Scheme 1).[17–19] To the best of our knowledge, there are no reports in the literature on the synthesis of α,β-unsaturated ketones using sequential one-pot alkyne dimerization/hydration reactions.

In this study, we have developed a novel strategy for the synthesis of α,β-unsaturated ketones using sequential alkyne dimerization/hydration reactions. The dimerization of arylalkynes in the presence of the Hoveyda–Grubbs 2nd generation catalyst (1% mol) and PCy_3 (4% mol) yielded *Z*-selective dimers (up to 99% *Z* isomer) within 2 hours of reaction time. The *in situ* formed dimers were reacted with the *p*-toluenesulfonic acid/trichloroacetic acid mixture to yield α,β-unsaturated ketones within 15 minutes of reaction time. Different arylacetylene derivatives were tested under optimized reaction conditions.

2. Experimental section

All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. The *Z*-selective Hoveyda–Grubbs catalyst (Ru–*Z*) and Hoveyda–Grubbs 2nd generation catalyst (HG2) were purchased from Sigma-Aldrich. The Grubbs 2nd generation analog [Ru = $CHPhCl_2(PCy_3)(IPr)$] was synthesized according to the literature.[43] Gas chromatography–mass spectrometry (GC-MS) analyses were performed with a Shimadzu GC-MS 2010 Plus using a Restek Rxi-5Sil column (30 m × 0.25 mm × 0.25 μm) in the temperature range of 50–320 °C with a constant helium flow rate of 1 mL min^{-1}. ^1H and ^{13}C NMR spectra were recorded at 25 °C with a Bruker GmbH 400 MHz high performance digital FT-NMR spectrometer using $CDCl_3$ as the NMR solvent.

2.1. Representative procedure for alkyne dimerization reactions

A Schlenk reactor was charged with phenylacetylene (**1a**, 1.6 mmol, 175 μL), Hoveyda–Grubbs 2nd generation catalyst (HG2) (0.016 mmol, 0.01 g) and tricyclohexylphosphine (PCy_3) (0.064 mmol, 0.018 g) under a nitrogen atmosphere. The reactor was sealed with a rubber septum and taken to a pre-heated oil bath at 120 °C. Aliquots were taken at 30 minute intervals and analysed by GC-MS. The tip of a GC syringe was plunged into the reaction mixture gently and the syringe tip was purged in methanol (GC/HPLC grade) in vials for GC-MS analysis. Once the conversion of phenylacetylene has reached a plateau, the reaction mixture was cooled to room temperature and the product was separated using dry column vacuum chromatography (DCVC)[44] using a gradient eluent (2% v/v), starting from *n*-hexane (100%). The polarity of the solvent was increased gradually by increasing the ethyl acetate content of the mixture (2% v/v increment for each addition). The isolated compound was characterized by ^1H and ^{13}C NMR analyses.

2.2. Representative procedure for hydration reactions of 1,3-enynes

A Schlenk reactor was charged with (*Z*)-but-1-*en*-3-yne-1,4-diyldibenzene (**2a**) (1.6 mmol, 0.33 g) and dissolved in dichloroethane (4 mL). *p*-Toluenesulfonic acid monohydrate (1.6 mmol, 0.30 g) and trichloroacetic acid (4.8 mmol, 0.78 g) were added to the reactor and the reaction mixture was transferred to a pre-heated oil bath at 80 °C. After 15 minutes of reaction time, enyne (**2a**) was completely consumed. The reactor was cooled to room temperature. The reaction mixture was diluted with dichloromethane (4 mL) and vacuum-filtrated. The filtered reaction mixture was extracted with saturated $NaHCO_3$ solution (20 mL × 2) and deionized water (20 mL × 1). The organic layer was separated and the solvent was evaporated using a rotary evaporator. The viscous yellow/brown oil was dissolved in ethyl acetate (2 mL) and loaded on Celite. Celite was added to a silica gel column and the final product was purified using dry column vacuum chromatography using *n*-hexane and ethyl acetate, starting from 100% *n*-hexane. The polarity of the mobile phase was gradually increased (2%) using ethyl acetate. The isolated product was characterized using ^1H and ^{13}C NMR.

2.3. Representative procedure for one-pot synthesis of α,β-unsaturated ketones

A Schlenk reactor was charged with phenylacetylene (1.6 mmol, 175 μL), Hoveyda–Grubbs 2nd generation catalyst (HG2) (0.016 mmol, 0.01 g) and tricyclohexylphosphine (PCy_3) (0.064 mmol, 0.018 g) under a nitrogen atmosphere. The reactor was sealed with a rubber septum and transferred to a pre-heated oil bath at 120 °C. The aliquots were taken at regular intervals from the reaction mixture and analyzed by GC-MS. Once all the phenylacetylene was consumed, the temperature of the oil bath was decreased to 80 °C and the viscous oily dimerization product in the reactor was dissolved in dichloroethane (4 mL). *p*-Toluenesulfonic acid monohydrate (1.6 mmol, 0.30 g) and trichloroacetic acid (4.8 mmol, 0.78 g) were added to the reactor and the reaction mixture was magnetically stirred. After 15 minutes, all the enyne product (**2a**) was converted to the desired α,β-unsaturated ketone (**3a**). The reaction mixture was cooled to room temperature and then

dichloromethane (4 mL) was added to the reactor. The reaction mixture was filtered under vacuum. The filtered reaction mixture was extracted with saturated $NaHCO_3$ solution (20 mL × 2) and deionized water (20 mL × 1). The organic layer was separated and the solvent was evaporated using a rotary evaporator. The viscous yellow/brown oil was dissolved in ethyl acetate (2 mL) and loaded on Celite. Celite was added to a silica gel column and the final product was purified using dry column vacuum chromatography using *n*-hexane and ethyl acetate, starting from 100% *n*-hexane. The polarity of the mobile phase was gradually increased (2%) using ethyl acetate. The isolated product was characterized using ^1H and ^{13}C NMR.

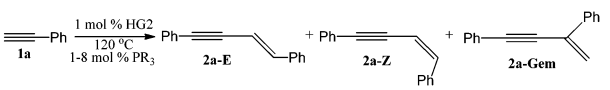
3. Results and discussion

For the last decade, there has been tremendous interest in the development of atom-efficient tandem and one-pot catalytic reactions.[40] As a part of our ongoing efforts to develop efficient one-pot sequential reactions to build advanced molecular structures, our research group was focused on ruthenium catalyzed alkyne dimerization reactions and alkyne hydration reactions.[38,39] The selective hydration of the α- or β-carbon of the alkyne moiety of 1,3-enynes can give α,β- or β,γ-unsaturated ketones as reported in the literature.[18,19] Therefore, the effective combination of alkyne dimerization and hydration reactions can be used for the efficient synthesis of unsaturated ketone derivatives *via* a one-pot procedure. We have chosen commercially available Grubbs type ruthenium catalysts for the *in situ* generation of 1,3-enynes through dimerization reactions. Instead of expensive gold-based hydration catalysts,[45] the *p*-toluenesulfonic acid/trichloroacetic acid binary mixture was chosen for the alkyne hydration reactions based on their effectiveness on the hydration reactions of various alkynes.[42] For this purpose, three different ruthenium catalysts: Grubbs 2nd generation (G2), Hoveyda–Grubbs 2nd generation (HG2), and *Z*-selective Hoveyda–Grubbs catalysts (Ru–Z) were chosen and tested in alkyne dimerization reactions of various alkynes (Scheme 2). As reported in the literature, the reactions of arylalkynes in the presence of the HG2 catalyst using various solvents (toluene, THF, dichloromethane) have yielded cyclotrimerization products. However, the selectivity of HG2 can be tuned for the selective generation of dimerization products by the introduction of σ-donor ligands to the reaction media.[38]

Our first attempts were focused on the optimization of alkyne dimerization reaction conditions using 1–8 mol% PCy_3 and 1 mol% Hoveyda–Grubbs 2nd generation catalyst in the absence of any solvents at 120 °C (Table 1). As can be seen in Table 1, the reaction yielded the dimerization product (**2a**) within 8 h in the presence of 1 mol% PCy_3 and 1 mol% HG2 with a product selectivity ratio of *Z*/*E*/*gem* of 85/10/5 (mol/mol/mol). The increment of PCy_3 loading to 4 mol% has drastically increased the *Z*-selectivity of the reaction and reduced the reaction time to 2 h. The reaction yielded **2a** with 99% *Z*-selectivity in the presence of 1 mol% HG2. The optimum phosphine loading was found to be 4 mol%, considering the reaction time, yield and regioselectivity of the reaction. As shown in Fig. 1, the olefinic proton signal appearing as doublets at 6.69–6.72 and 5.91–5.94 ppm with a *J*-value of 11.9 Hz confirmed the presence of *Z* (*cis*)-configuration of double bonds. On the next trial, the effect of the phosphine structure on the selectivity and yield of the reaction was investigated in detail and the results are given in Table 2. In the absence of phosphine, the reaction proceeded very slowly, yielding the cyclotrimerization product instead of the dimerization product using HG2 (1 mol%). The addition of triphenylphosphine (PPh_3) has drastically switched the selectivity towards the dimerization product, giving **2a** in 99% yield with a 97% *Z*-selectivity. The substitution of PPh_3 with a better σ-donor ligand, PCy_3, has decreased the reaction time to 2h and increased the *Z*-selectivity of the reaction up to 99%. Therefore, 4 mol% PCy_3 and 1 mol% Ru were used in further alkyne dimerization experiments.

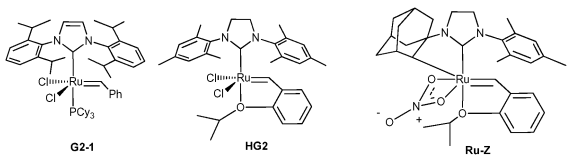
The Grubbs 2nd generation analog (G2-1), Hoveyda–Grubbs 2nd generation catalyst (HG2) and *Z*-selective Hoveyda–Grubbs catalyst (Ru–Z) were used in dimerization reactions of various alkynes including 1-phenylacetylene (**1a**), 4-ethynyl toluene (**1b**), 2-ethynyl toluene (**1c**) and 4-*tert*-butylphenylacetylene (**1d**) (Fig. 2). The effect of PCy_3 on product selectivity can be directly seen on HG2 and Ru–Z catalyzed reactions. In the absence of PCy_3, the reaction predominantly yielded cyclotrimerization products as the major reaction product. However, the addition of 4 mol% PCy_3 has switched the selectivity of the reaction towards the dimerization product **2a**. It is important to note that HG2 exhibited high *Z*-selectivity (99%, Table 3-entry 2) in the presence of 4 mol% PCy_3. In contrast to HG2, Ru–Z showed poor *Z*-selectivity under the same reaction conditions, yielding **2a** (85%) with a *Z*/*E*/*gem* selectivity of 61/36/3. The alkynes **1a–d** yielded the corresponding dimerization products **2a–d** (up to 99% yield) with high *Z*-selectivity (91–99%) using HG2 and G2 catalysts. The Ru–Z catalyst showed poor

Table 1 The effect of phosphine amount on the selectivity of the alkyne dimerization reactions



Entry	PCy_3 (mol%)	Time (h)	Conversion[a] (%)	*Z*/*E*/*gem*[a]
1	1	8	90	85/10/5
2	2	4	99	90/10/—
3	4	2	99	99/1/—
4	8	2	97	95/5/—

[a] Determined by GC-MS using n-tetradecane as the internal standard.



Scheme 2 Grubbs type ruthenium catalysts used in this study.

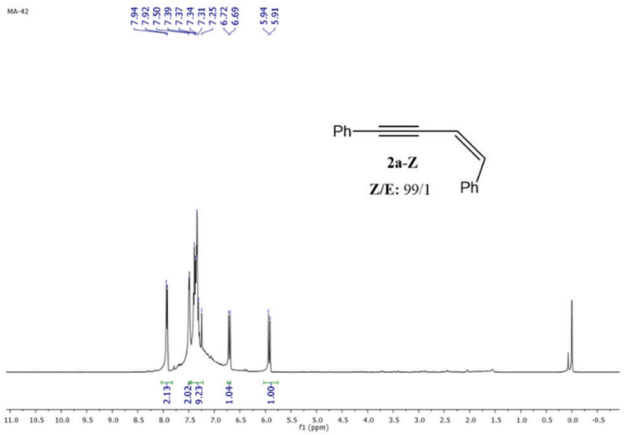
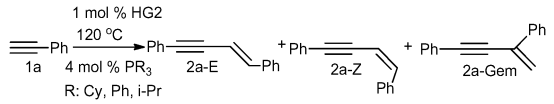


Fig. 1 ^{1}H NMR spectrum of the dimerization product (**2a**-*Z*) (400 MHz, $CDCl_3$)

Table 2 The effect of phosphine addition on the selectivity of the dimerization reaction



Entry	PR_3 (mol%)	Time (h)	Conversion[a] (%)	*Z*/*E*/*gem*[a]
1	—	12	80	85/10/5
2	PPh_3	4	99	97/3/—
3	PCy_3	2	99	99/1/—
4	$P(^{i-}Pr)_3$	2	97	95/5/—

[a] Determined by GC-MS using n-tetradecane as the internal standard.

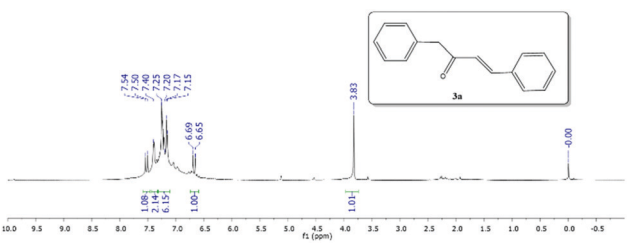


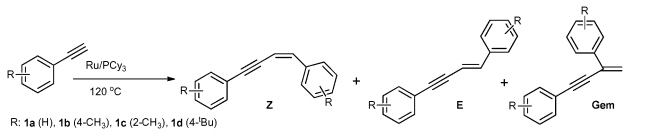
Fig. 2 ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$).

performance in terms of product selectivity, yielding a mixture of *Z*- and *E*-isomers of the dimerization product.

Once the dimerization reaction conditions were optimized, the hydration of the dimerization product **2a** was studied using different binary acid couples such as trichloroacetic acid/*p*-toluenesulfonic acid, acetic acid/*p*-toluenesulfonic acid and benzoic acid/*p*-toluenesulfonic acid under different reaction conditions.

The activity of *p*-toluenesulfonic acid/acetic acid in alkyne hydration reactions was previously reported by Liu *et al.*[46] However, the performance of the acid catalyst system needs to be improved for the hydration of 1,3-enynes. Therefore,

Table 3 Dimerization of arylalkynes in the presence of various ruthenium catalysts



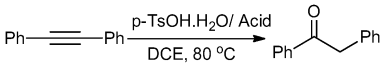
Entry	Alkyne	Cat.	PCy_3%	Time (h)	% Yield[a]	*Z*/*E*/*gem*[b]
1	**1a**	G2	—	24	80	85/10/5
2	**1a**	G2	4	2	97	99/1/—
3	**1a**	HG2	—	36	60[c]	80/20/—
4	**1a**	HG2	4	2	97	99/1/—
5	**1a**	Ru–Z	—	24	85[d]	61/36/1
6	**1a**	Ru–Z	4	2	96	73/26/1
7	**1b**	G2	4	2	97	92/8/—
8	**1b**	HG-2	4	2	97	93/7/—
9	**1b**	Ru–Z	4	2	96	74/24/4
10	**1c**	G2	4	2	97	91/6/3
11	**1c**	HG-2	4	2	96	92/7/1
12	**1c**	Ru–Z	4	4	90	61/36/1
13	**1d**	G2	4	4	97	96/2/2
14	**1d**	HG-2	4	4	98	99/1/—
15	**1d**	Ru–Z	4	4	95	55/41/4

[a] Isolated yield of the dimerization product. [b] Determined by GC-MS and ^{1}H NMR. [c] The cyclotrimerization (CT) product was formed as a side product (40% GC yield). [d] The CT product was formed (15% GC yield).

before proceeding enyne hydration experiments, we have tested the activity of acid mixtures on the hydration reaction of diphenylacetylene, known as a challenging alkyne substrate for hydration reactions. The results are given in Table 4.

The acidity of carboxylic acid has a huge effect on the reactivity of the binary acid mixture in alkyne hydration reactions. As shown in Table 4, the acetic acid catalyzed reaction yielded the corresponding ketone 1,2-diphenylethanone in 24% yield. In contrast to the acetic acid (pK_a: 4.74)/*p*-toluenesulfonic acid catalyzed hydration reactions, the yield of the hydration product was increased to 55% when the same reaction was conducted using the benzoic acid (pK_a: 4.20)/*p*-toluenesulfonic acid mixture. The trichloroacetic acid (pK_a: 0.77)/*p*-toluenesulfonic acid mixture yielded the corresponding hydration product quantitatively within 15 minutes of reaction time. The most effective binary acid mixture was found to be trichloroacetic acid/*p*-toluenesulfonic acid and used in both hydration reactions of 1,3-enynes and one-pot dimerization/hydration reactions.

Table 4 Hydration of diphenylacetylene in the presence of binary acid mixtures



Entry	Acid	Solvent	Time	Conversion[a] (%)	Yield[b] (%)
1	CH_3COOH	DCE	4 hour	26	24
2	C_6H_5COOH	DCE	1 hour	59	55
3	CCl_3COOH	DCE	15 min	99	95

[a] Determined by GC-MS using *n*-tetradecane as the internal standard. [b] Isolated by simple extraction, isolated yield.

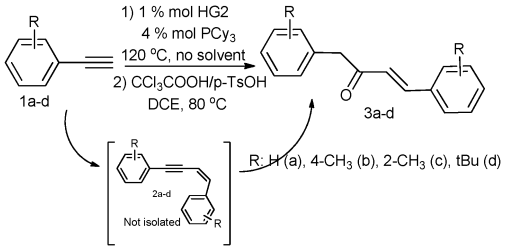
To test the regioselectivity of the hydration reaction, 1,4-diphenylbut-1-*en*-3-yne (**2a**) with different *Z*/*E* contents: *Z*-**2a** (99% *Z*, Table 3, entry 4) and *Z*/*E*-**2a** (61% *Z*, 36% *E*, Table 3, entry 5) were used in the hydration reaction in the presence of CCl_3COOH/*p*-TsOH in DCE at 80 °C (Scheme 3). All starting materials were consumed within 15 minutes of reaction time as confirmed by both GC-MS and TLC analyses.

The isolated hydration product **3a** was analyzed by ^1H NMR. It is interesting to note that, in both cases, the final α,β-unsaturated ketone (**3a**) derivative was found to have formed predominantly as an *E*-isomer (Fig. 2). The olefinic proton signals appearing at 6.65–6.69 (J = 16.2 Hz, 1H) and 7.52 (J = 16.2 Hz, 1H) confirmed that the configuration of the double bond was converted to an *E*-isomer during the hydration reaction. Identical ^1H NMR spectra were observed in both cases using 99% *Z*-**2a** or 61% *Z*-36% *E* **2a** isomers.

One-pot reactions were carried out under optimized reaction conditions for alkyne dimerization and hydration reactions using a variety of alkynes including phenylacetylene (**1a**), 4-ethynyltoluene (**1b**), 2-ethynyltoluene (**1c**) and 4-*tert*-butylphenylacetylene (**1d**) (Table 5). A Schlenk reactor was charged with **1a** and 1 mol% HG2 and 4 mol% PCy_3 under a nitrogen atmosphere and the reaction mixture was stirred at 120 °C without any solvent. The progress of the reaction was monitored by GC-MS. After complete conversion of the alkyne substrate, the temperature of the reaction mixture was decreased to 80 °C and the oily viscous dimer product (**2a**) was dissolved in DCE, *p*-toluenesulfonic acid (1.0 mol equivalent) and trichloroacetic acid (3.0 mol equivalent) and the reaction mixture was stirred under a nitrogen atmosphere. The progress of the reaction was monitored by both GC-MS and TLC analyses. After 15 minutes, **2a** was completely consumed to produce **3a** in quantitative yields. **3a** was isolated in 95% yield. 4-Ethynyl toluene (**1b**) and 2-ethynyl toluene (**1c**) were used in sequential dimerization/hydration reactions to monitor the effect of *para*- and *ortho*-substituents on reaction selectivity and yield. The hydration reaction proceeded smoothly with both *ortho*- and *para*-substituted arylacetylenes, giving unsaturated ketones in excellent yields.

To further investigate the possible role of ruthenium in hydration reactions, a control-experiment was carried out in the absence of HG2 (Table 6). For this purpose, isolated 1,3-enyne derivatives (**2a–d**) were reacted with CCl_3COOH/*p*-TsOH·H_2O in DCE at 80 °C under a nitrogen atmosphere. In addition, different acid mixtures of CH_3COOH/*p*-TsOH·H_2O and C_6H_5COOH/*p*-TsOH·H_2O were also tested in hydration reactions. In the case of the CH_3COOH/*p*-toluenesulfonic acid mixture, the conversion of **2a** was 40% even after 24 h of reaction time. The substitution of acetic acid with benzoic acid yielded the α,β-unsaturated ketone (**3a**) in 48% yield after 24 h of reaction time. As confirmed from previous experiments regarding diphenylacetylene, trichloroacetic acid efficiently catalyzed the hydration reaction, giving **3a** in quantitative yields within 15 minutes. The reaction proceeds very rapidly in the presence of trichloroacetic acid. It is important to note that sequential alkyne dimerization/hydration reactions or direct hydration reactions of isolated 1,3-enynes yielded the corresponding unsaturated ketone **3a** in quantitative yields in both cases. These results strongly suggest that ruthenium does not have a significant effect during the sequential reaction and is mainly responsible for alkyne dimerization reactions as the key catalyst.

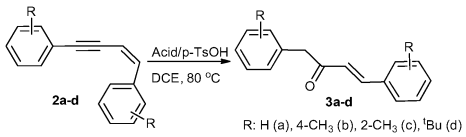
Table 5 One-pot sequential alkyne dimerization/hydration reactions



Entry	Alkyne	Time (h)	Conv.[a] (%)	Yield[b] (%)
1	**1a**	2.5	99	95
2	**1b**	2.5	99	95
3	**1c**	3	99	94
4	**1d**	4.5	99	95

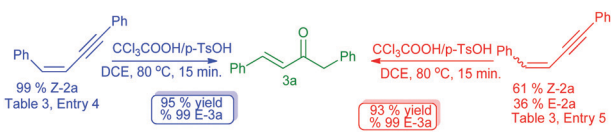
[a] The conversion of alkynes (**1a–d**) was determined by GC-MS using *n*-tetradecane as the internal standard. [b] Isolated yields of **3a–d**.

Table 6 Hydration of isolated enynes using binary acid mixtures



Entry	Dimer	Acid	Time	Conv.[a] (%)	Yield[b] (%)
1	**2a**	CH_3COOH	24 h	40	33
2	**2a**	C_6H_5COOH	24 h	50	48
3	**2a**	CCl_3COOH	15 min	99	95
4	**2b**	CCl_3COOH	15 min	99	96
5	**2c**	CCl_3COOH	20 min	99	95
6	**2d**	CCl_3COOH	15 min	99	96

[a] Determined by GC-MS using n-tetradecane as the internal standard. [b] Isolated yield.



Scheme 3 Synthesis of α,β-unsaturated ketone (**3a**) using isolated enynes with different *Z*/*E* isomer contents.

4. Conclusions

A novel sequential one-pot synthesis method utilizing alkyne dimerization/hydration reactions is presented for the regioselective synthesis of α,β-unsaturated ketones from arylalkyne derivatives. The combination of HG2/PCy_3 and CCl_3COOH/*p*-TsOH·H_2O through a one-pot sequential reaction gave the

corresponding α,β-unsaturated ketones in quantitative yields within 2.5–4 h. It is noteworthy that hydration reactions of 1,3-enynes showed high regioselectivity and no trace of β,γ-unsaturated ketone was observed during the hydration reactions.

Conflicts of interest

There are no conflicts to declare.

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