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A ruthenium-catalyzed coupling of alkynes with 1,3-diketones

Megan K. Pennington-Boggio, Brian L. Conley, Travis J. Williams*

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA

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ABSTRACT

Ruthenium(III) chloride hydrate is a convenient catalyst for the addition of active methylene compounds to aryl alkynes. These reactions are rapid, operationally simple, and high yielding in cases. Most significantly, no precautions are required to exclude air or water from the reactions. All reagents are commercially available at reasonable prices, and the reactions can be conducted in disposable glassware with minimal solvent.

1. Introduction

The Conia-Ene reaction (equation 1) is an electrocyclic transformation in which an enolate reacts with a pi system to form a new C–C bond. Conceptually, a Conia-Ene reaction is similar to alkylating a ketone with an alkene or alkyne, with the latter representing a graceful strategy to "vinylate" adjacent to a carbonyl group. These reactions occur thermally at high temperature (c.f. 200 °C) [1]. Due to their synthetic utility, several examples of catalyzed Conia-Ene reactions have been reported.

There are many elegant examples of transition metal catalysts for the intramolecular Conia-type ene reaction. Some examples include reactions involving gold [2], palladium/ytterbium [3], and copper/silver [4] systems. Additionally, some of these methods have been demonstrated for use in complex [5] and asymmetric [3,6] applications.

By contrast, there are fewer reports of the analogous intermolecular ene-based coupling reaction (equation 2). Only a few catalytic solutions to this reaction are reported. These are limited to indium(III) triflate [7], indium(III) trifluoromethylsulfonamide [8], a rhenium-based system [9], and a recently reported hydro(trispyrazolyl)borato-ruthenium(II) complex [10].

Whereas the solutions to the intermolecular coupling variant of this reaction are few, and the existing solutions involve forcing conditions in cases, we proposed that a dual site ruthenium, boron catalyst [11] might be a convenient solution because of its ability to simultaneously bind and activate both reactive partners. We found, however, that commercially available ruthenium(III) chloride is a superior catalyst for this transformation and affords uncharacteristically mild intermolecular ene-type coupling reactions for a variety of terminal alkynes and 1,3-dicarbonyl compounds. Thus we report here operationally simple, inexpensive, and mild conditions for the ene-type coupling shown in equation 2.

We report herein the results of our study of commercial $RuCl_3 \cdot 3H_2O$ as a mild and convenient catalyst for coupling of alkenes with 1,3-diketones. These reactions are high yielding in cases, and, most notably, are easily executed on the benchtop with commercially available materials under mild and inexpensive conditions.

2. Results and discussion

2.1. Discovery and optimization

Initially we discovered that two ruthenium, boron complexes, $[(py)_2BMe_2]Ru(cym)Cl$ and $\{[(py)_2BMe(\mu\text{-}OH)]Ru(MeCN)_3\}^+ \ ^-OTf$ [12] (py = 2-pyridyl, cym = h^6-*p*-cymene), catalyze the ene-type coupling between phenylacetylene and acetylacetone in modest yield (Table 1, entries 1, 2). Further experiments revealed that a variety of ruthenium complexes also affect this transformation when modified with silver hexafluorophosphate, including $[(p\text{-cymene})RuCl_2]_2$, $[(COD)RuCl_2]_2$, $[(CO)_3RuCl_2]_2$, $(Ph_3P)_3RuCl_2$, and $[(CO)_3RuCl_2]_2$, but notably, $RuCl_3 \cdot 3H_2O$ provides the highest yield (Table 1, entries 3–4 and Table S1). In light of this observation, we considered that a $Ru(acac)_3$ (acac = acetylacetonate) species,

* Corresponding author. Fax: +1 213 740 6679.
E-mail address: travisw@usc.edu (T.J. Williams).

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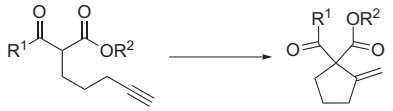


Equation 1. A Conia-Ene reaction.

generated in situ, might be responsible for the reactivity, but we observe no coupling when $Ru(acac)_3$ is used as the catalyst precursor (entry 5). This reaction results in the formation of 10% product with the addition of $AgOCOCF_3$ (entry 6). No reaction was observed in the absence of ruthenium (entry 7), and the incorporation of a silver salt seems essential (entry 8). The addition of $AgOCOCF_3$ instead of $AgPF_6$ produces similar results (entries 4 and 9).

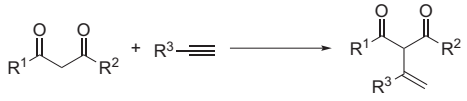
The reaction proceeds in a variety of solvents, or with no solvent at all (Table 1, entries 4, 10–12). We find that the shortest reaction times and highest yields are obtained using a minimal volume of diethyl ether. Further, a small amount of water significantly accelerates the reaction rate; two equivalents relative to diketone seems optimal (entries 4, 13–14).

Finally, we observe that although three equivalents of alkyne relative to the diketone is optimal for reaction time; the reaction proceeds to completion with only 1.5 equivalents (Table 1, entry 15). The need for excess alkyne arises from a side reaction in which some alkyne is hydrolyzed to the corresponding methyl ketone, as is evident from the formation of acetophenone from phenylacetylene as determined by GC/MS and NMR [13]. Electron-rich alkynes are more susceptible to this side reaction as evident from NMR quantification, and it appears to be faster in the presence of $AgPF_6$ as opposed to $AgOCOCF_3$.

It is important to note that while the solvents used in this study were rigorously anhydrous to allow for the quantification of added water, we observe that these reactions can be run with benchtop grade solvent without the need for additional water. For example, repeating the reaction in Table 1, entry 4 in this way gives an 87% isolated yield.

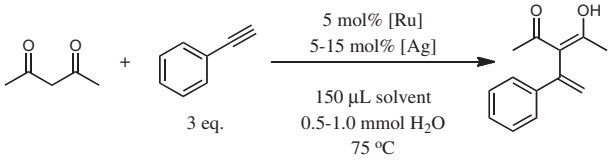
2.2. Alkyne scope

A number of aryl alkynes afford good yield of ene-type coupling products under our optimized conditions (Table 2). Our parent case, entry 1, affords coupling product in 88% isolated yield. Electron-rich and electron-poor alkynes both participate successfully. However, the electron-rich alkynes are more reactive towards the alkyne hydrolysis side reaction. Entries 2 and 3 show that although these reactions are somewhat slower than the parent, they proceed in desirable yields. For example, a reaction of 4-ethynyltoluene (**3**) proceeds to completion to give **4** in 2 h, and the analogous 1-ethynyl-4-methoxybenzene (**5**) requires 6 h to convert to **6**. In all cases, reactions of electron-rich alkynes do not reach completion with only 3 equivalents of alkyne when $AgPF_6$ is utilized. Even with the use of $AgOCOCF_3$, the corresponding aryl ketones are produced in quantities detectable by GC/MS. Our conditions are compatible with ethyne-pendant heterocycles and anilines: entries 6 and 7 show the results of these experiments. These conditions are not compatible with internal alkynes such as 1-phenylpropyne.



Equation 2. An intermolecular carbonyl ene reaction.

Table 1
Condition Optimization.



Entry	[Ru]	[Ag]	H_2O (eq.)	Solvent	Time (h)	Yield (%)[a]
1	$[(py)_2BMe_2]Ru(cym)Cl$	$AgPF_6$	2	Et_2O	2	52
2	$\{[(py)_2BMe(\mu\text{-}OH)]Ru(MeCN)_3\}^+ {}^-OTf$	None	2	Et_2O	2	10
3	$[(CO)_3RuCl_2]_2$	$AgPF_6$	2	Et_2O	2	82
4	$RuCl_3\cdot 3H_2O$	$AgPF_6$	2	Et_2O	2	90
5	$Ru(acac)_3$	None	2	Et_2O	2	0
6	$Ru(acac)_3$	$AgOCOCF_3$	2	Et_2O	2	10
7	None	$AgPF_6$	2	Et_2O	2	0
8	$RuCl_3\cdot 3H_2O$	None	2	Et_2O	2	9
9	$RuCl_3\cdot 3H_2O$	$AgOCOCF_3$	2	Et_2O	2	92
10	$RuCl_3\cdot 3H_2O$	$AgPF_6$	2	CH_2Cl_2	2	53
11	$RuCl_3\cdot 3H_2O$	$AgPF_6$	2	None	2	69
12	$RuCl_3\cdot 3H_2O$	$AgPF_6$	2	C_6H_6	2	45
13	$RuCl_3\cdot 3H_2O$	$AgPF_6$	0	Et_2O	2	6
14	$RuCl_3\cdot 3H_2O$	$AgPF_6$	1	Et_2O	2	84
15	$RuCl_3\cdot 3H_2O$[b]	$AgPF_6$	2	Et_2O	5.5	92

[a] Yield determined by NMR using nitromethane as internal standard.
[b] 1.5 eq. Phenylacetylene.

2.3. Diketone scope

A number of 1,3-diketone compounds participate efficiently in coupling reactions under our reaction conditions (Table 3); β-ketoesters participate less efficiently (37% yield by NMR, see Supporting information). The products of reactions with β-ketoesters and 3-substituted 1,3-diketones (entries 2 and 3) are susceptible to retro-Claisen type decomposition to give deacylated products with internal alkenes (Scheme 1). This decomposition is promoted by water, and the use of only 1 equivalent of water relative to diketone is beneficial. These reaction conditions are not useful for the functionalization of β-ketophosphonates, β-cyanoketones, β-nitroketones, or α,β-unsaturated-β-aminoketones.

In cases where $R^2 = Ph$ (entries 4, 5), coupling is high-yielding and involves a subsequent isomerization of the initially formed diene to an internal alkene, either stepwise or through a [1,5] hydride shift (Scheme 2). Entry 4 shows all of the possibilities available along these lines: **21** is converted to **22** under our conditions, then **22** converts to isomers **23E** and **23Z**. By contrast, when $R^1 = R^2 = Ph$ (**24**), a single, isomerized product is collected in 90% yield (entry 5).

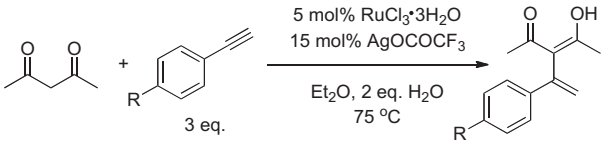
2.4. Scalability

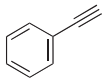
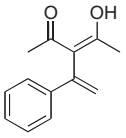
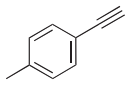
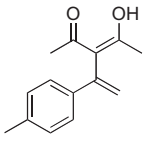
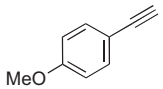
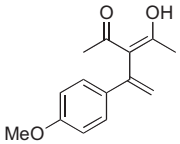
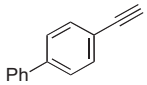
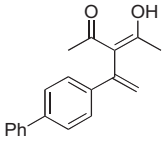
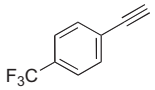
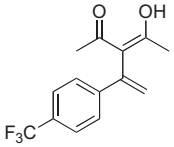
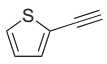
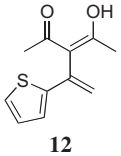
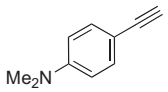
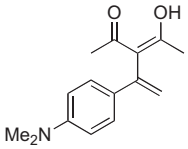
We have observed that our reaction conditions can be scaled up to 1 g with no appreciable loss of yield (Scheme 3). This is indicative of homogeneous catalysis, and is an essential part of the practicality of these conditions.

3. Conclusion

In conclusion, we have developed new catalytic conditions for the ene-type coupling reaction of alkynes with 1,3-diketones. These reactions proceed at mild temperature under air and in the presence of water with relatively low catalyst loading and minimal solvent waste. While there are other known catalysts for

Table 2
Alkyne scope.[a]

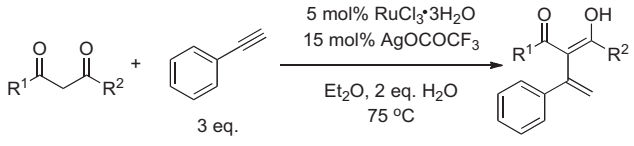


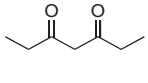
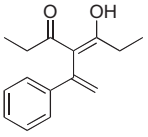
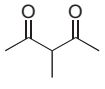
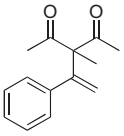
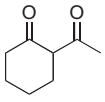
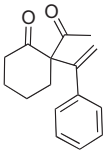
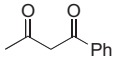
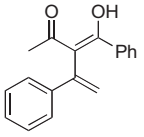
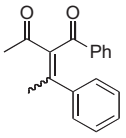
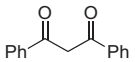
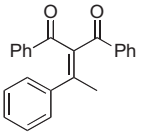
Entry	Substrate	Product	Time (h)	Yield (%)[b]
1	 **1**	 **2**	2	88 (92)
2	 **3**	 **4**	3	77 (95)
3	 **5**	 **6**	6	82 (96)
4	 **7**	 **8**	4	92
5	 **9**	 **10**	2	68 (83)
6	 **11**	 **12**	8	36 (45)
7	 **13**	 **14**	24	41 (50)

[a] Conditions: 0.5 mmol acetylacetone, 1.5 mmol alkyne, 150 μL diethyl ether, 1.0 mmol H_2O.
[b] Isolated yield. NMR Yield in parentheses.

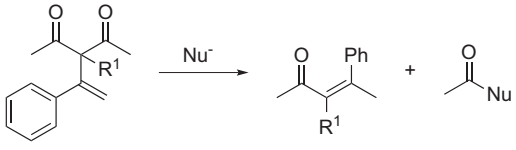
this reaction, our conditions have advantages over each. The rhenium catalyst involves significantly greater cost, and though the cost of both the indium and hydro(trispyrazolyl)borato-ruthenium(II) catalysts are similar all three must be prepared

Table 3
Diketone scope.[a]

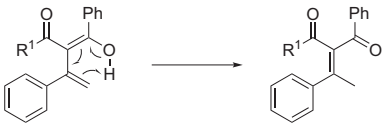


Entry	Substrate	Product	Time (h)	Yield (%)[b]
1	 **15**	 **16**	2	78 (83)
2[c]	 **17**	 **18**	15	44 (50)
3[c]	 **19**	 **20**	15	50 (54)
4	 **21**	 **22 +**  **23ZE** 9 **22**:13 **23Z**: 4 **23E**	4	90 (95)
5	 **24**	 **25**	4	90 (98)

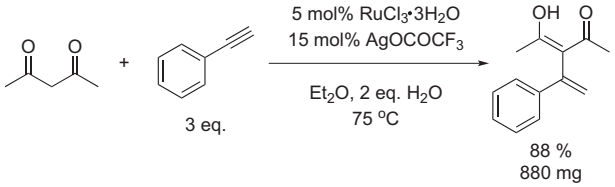
[a] Conditions: 0.5 mmol diketone, 1.5 mmol phenylacetylene, 150 μL diethyl ether, 1.0 mmol H_2O.
[b] Isolated yield. NMR Yield in parentheses.
[c] 1 eq. (0.5 mmol) H_2O.



Scheme 1. Retro-Claisen decomposition of 3-substitued 1,3-diketones.



Scheme 2. Isomerization in cases where R^2 = Ph.



Scheme 3. Parent reaction on 1 g scale.

and conducted under inert atmosphere with rigorously dried materials. Our system is not limited by this need and is therefore more practically applicable. Additionally, all catalytic materials are commercially available and the conditions are applicable to a diverse variety alkynes and diketones. Thus, these conditions present a very convenient approach to the "vinylation" of diketone systems.

4. Materials and methods

4.1. Materials and instrumentation

Deuterated NMR solvents were purchased from Cambridge Isotopes Laboratories and were used as received. Reagents were purchased from Sigma–Aldrich Co., Alfa-Aesar, Strem Chemicals, Inc., Combi-Blocks, Inc., or and TCI America and used as received. ^{1}H, ^{19}F and ^{13}C NMR spectra were obtained on a Varian 400-MR spectrometer (400 MHz in ^{1}H, 100 MHz in ^{13}C) or a Varian 500 spectrometer (500 MHz in ^{1}H, 125 MHz in ^{13}C). All ^{1}H and ^{13}C chemical shifts are referenced to the residual ^{1}H or ^{13}C solvent (relative to TMS) and reported in units of ppm. Infrared spectra were acquired on a Bruker OPUS FT-IR spectrometer. Benzene and diethyl ether were dried by refluxing over sodium and benzophenone, dichloromethane was distilled from calcium hydride. Column chromatography was done in automation using the Teledyne CombiFlash Rf 200 system using hexane and ethyl acetate. High-resolution ESI mass spectra were recorded at the University of California, Riverside.

4-Ethynyl-1,1′-biphenyl was synthesized according to literature procedures [14].

4.2. Standard procedure

To a vial containing a magnetic stir bar, ruthenium(III) chloride hydrate (6.5 mg, 25 μmol, 5 mol%) and silver(I) trifluoroacetate (16.6 mg, 75 μmol, 15 mol%) is added diethyl ether (150 μL) and water (18 μL, 1.0 mmol). Diketone (0.50 mmol) and alkyne (1.50 mmol) are added to the vial. The reaction is then stirred at 75 °C for the specified time. Products were isolated by column chromatography using a hexane/ethyl acetate gradient.

Only 1 eq. of H_2O was used for compounds **18** and **20**.

4.2.1. 4-Hydroxy-3-(1-phenylvinyl)pent-3-en-2-one (*2*)

Adduct **2** was prepared according to the standard procedure using acetylacetone (50.0 mg, 51.1 μL, 0.50 mmol) and phenylacetylene (**1**, 153.2 mg, 164.7 μL, 1.50 mmol), and stirring for 2 h. **2** was isolated as a yellow oil in 88% yield. Data are consistent with a known compound [7a].

4.2.2. 4-Hydroxy-3-(1-(p-tolyl)vinyl)pent-3-en-2-one (*4*)

Adduct **4** was prepared according to the standard procedure using acetylacetone (50.0 mg, 51.1 μL, 0.50 mmol) and *p*-tolylacetylene (**3**, 174.2 mg, 190.2 μL, 1.50 mmol), and stirring for 3 h. **4** was isolated as a yellow oil in 77% yield. Data are consistent with a known compound [10].

4.2.3. 4-Hydroxy-3-(1-(4-methoxyphenyl)vinyl)pent-3-en-2-one (*6*)

Adduct **6** was prepared according to the standard procedure using acetylacetone (50.0 mg, 51.1 μL, 0.50 mmol) and 1-ethynyl-4-methoxybenzene (**5**, 198.2 mg, 194.5 μL, 1.50 mmol), and stirring for 6 h. **6** was isolated as a pale yellow solid in 82% yield. Data are consistent with a known compound [10].

4.2.4. 3-(1-([1,1′-Biphenyl]-4-yl)vinyl)-4-hydroxypent-3-en-2-one (*8*)

Adduct **8** was prepared according to the standard procedure using acetylacetone (50.0 mg, 51.1 μL, 0.50 mmol) and 4-ethynyl-1,1′-biphenyl (**7**, 267.3 mg, 1.50 mmol), and stirring for 4 h. **8** was isolated as a yellow solid in 92% yield.

M.P. = 75–78 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.024 (s, 6H), 5.264 (s, 1H), 5.966 (s, 1H), 7.362 (tt, J = 1.2 Hz, 7.4 Hz, 1H), 7.429–7.468 (m, 2H), 7.498–7.524 (m, 2H), 7.577–7.615 (m, 4H), 16.659 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 23.8, 118.5, 126.498, 127.1, 127.6, 127.7, 129.0, 138.7, 140.5, 143.2, 191.5; FT-IR (KBr/cm^{-1}) ν = 3032, 1598, 1487, 1246, 909, 774, 743, 729; HR-MS (+ESI): m/z = 279.1380 g/mol, calc'd. for $C_{19}H_{19}O_2^+$ $[MH]^+$: 279.1380 g/mol.

4.2.5. 4-Hydroxy-3-(1-(4-(trifluoromethyl)phenyl)vinyl)pent-3-en-2-one (*10*)

Adduct **10** was prepared according to the standard procedure using acetylacetone (50.0 mg, 51.1 μL, 0.50 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene (**9**, 255.2 mg, 244.7 μL, 1.50 mmol), and stirring for 2 h. **10** was isolated as a yellow semi-solid in 68% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.979 (s, 1H), 5.373 (s, 1H), 6.004 (s, 1H), 7.543 (d, J = 8.2 Hz, 2H), 7.613 (d, J = 8.2 Hz, 2H), 16.668 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.8, 113.4, 120.8, 124.2 (q, J_{CF} = 272 Hz), 125.9 (q, J_{CF} = 4 Hz), 126.3, 130.3 (q, J_{CF} = 32 Hz), 142.7, 143.3, 191.5; ^{19}F NMR: ($CDCl_3$, 500 MHz, ref. $CFCl_3$) δ −63.12; FT-IR (KBr/cm^{-1}) ν = 3094, 2928, 1617, 1326, 1122, 1068, 1015, 853; HR-MS (+ESI): m/z = 271.0946 g/mol, calc'd. for $C_{14}H_{14}F_3O_2^+$ $[MH]^+$: 271.0940 g/mol.

4.2.6. 4-Hydroxy-3-(1-(thiophen-2-yl)vinyl)pent-3-en-2-one (*12*)

Adduct **12** was prepared according to the standard procedure using acetylacetone (50.0 mg, 51.1 μL, 0.50 mmol) and 2-ethynylthiophene (**11**, 162.2 mg, 146.2 μL, 1.50 mmol), and stirring for 8 h. **12** was isolated as an orange-brown oil 36% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.051 (s, 6H), 5.086 (s, 1H), 5.820 (s, 1H), 6.944 (d, J = 3.4 Hz, 1H), 6.976 (m, 1H), 7.227 (d, J = 4.9 Hz, 1H), 16.604 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.5, 113.9, 116.8, 125.3, 125.9, 128.0, 137.8, 145.5, 191.5; FT-IR (Neat/cm^{-1}) ν = 3105, 2925, 1609, 1395, 1247, 993, 915, 702; HR-MS (+ESI): m/z = 209.0637 g/mol, calc'd. for $C_{11}H_{13}O_2S^+$ $[MH]^+$: 209.0631 g/mol.

4.2.7. 3-(1-(4-(Dimethylamino)phenyl)vinyl)-4-hydroxypent-3-en-2-one (*14*)

Adduct **14** was prepared according to the standard procedure using acetylacetone (50.0 mg, 51.1 μL, 0.50 mmol) and 4-ethynyl-*N*,*N*-dimethylaniline (**13**, 213.3 mg, 1.50 mmol), and stirring for 24 h. **14** was isolated as a yellow solid in 41% yield.

M.P. = 38–41 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.995 (s, 6H), 2.976 (s, 6H), 5.009 (s, 1H), 5.729 (s, 1H), 6.680 (d, J = 9.1 Hz, 2H), 7.319 (d, J = 9.1 Hz, 2H), 16.596 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.6, 40.51, 112.3, 114.2, 114.4, 127.0, 127.7, 143.1, 150.5, 191.5; FT-IR (KBr/cm^{-1}) ν = 2919, 2808, 1757, 1606, 1552, 1364, 1171, 897, 820; HR-MS (+ESI): m/z = 246.1492 g/mol, calc'd. for $C_{15}H_{20}NO_2^+$ $[MH]^+$: 246.1489 g/mol.

4.2.8. 5-Hydroxy-4-(1-phenylvinyl)hept-4-en-3-one (**16**)

Adduct **16** was prepared according to the standard procedure using heptane-3,5-dione (**15**, 64.1 mg, 67.8 μL, 0.50 mmol) and phenylacetylene (**1**, 153.2 mg, 164.7 μL, 1.50 mmol), and stirring for 2 h. **16** was isolated as a yellow oil in 78% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.036 (t, J = 7.29 Hz, 6 H), 2.196 (b, 2H), 2.379 (b, 2H), 5.235 (s, 1H), 5.913 (s, 1H), 7.270–7.460 (m, 5H), 16.710 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 9.9, 29.5, 118.4, 126.1, 128.3, 128.8, 140.0, 143.1, 194.6; FT-IR (Neat/cm^{-1}) ν = 3084, 2978, 1598, 1492, 1199, 1065, 912, 781; HR-MS (+ESI): m/z = 231.1384 g/mol, calc'd. for $C_{15}H_{19}O_2^+$ $[MH]^+$: 231.1380 g/mol.

4.2.9. 3-methyl-3-(1-phenylvinyl)pentane-2,4-dione (**18**)

Adduct **18** was prepared according a modification of the standard procedure requiring only 1 eq. (9 μL) of H_2O and using 3-methylpentane-2,4-dione (**17**, 57.0 mg, 58.1 μL, 0.50 mmol) and phenylacetylene (**1**, 153.2 mg, 164.7 μL, 1.50 mmol), and stirring for 15 h. **18** was isolated as an orange-brown solid in 44% yield. Data are consistent with a known compound [7a].

4.2.10. 2-acetyl-2-(1-phenylvinyl)cyclohexanone (**20**)

Adduct **20** was prepared according to a modification of the standard procedure requiring only 1 eq. (9 μL) of H_2O and using 2-acetylcyclohexanone (**19**, 70.1 mg, 65.0 μL, 0.50 mmol) and phenylacetylene (**1**, 153.2 mg, 164.7 μL, 1.50 mmol), and stirring for 15 h. **20** was isolated as a yellow oil in 50% yield. Data are consistent with a known compound [10].

4.2.11. Reaction of **1** and **21** to form adducts **22**, **23E**, and **23Z**

Adducts **22** and **23EZ** were prepared according to the standard procedure using benzoylacetone (**21**, 81.1 mg, 0.50 mmol) and phenylacetylene (**1**, 153.2 mg, 164.7 μL, 1.50 mmol), and stirring for 4 h. The products were isolated as a yellow oil (**22**, **23E**) or a yellow solid (**23Z**). Products were collected in a combined yield of 124 mg (90%) with the ratio **22**:**23Z**:**23E** = 9:13:4. Each compound is separately characterized below. Olefin geometry assignments for **23E** and **Z** were made on the basis on 1D-NOE NMR experiments, see Supporting information.

4.2.12. 3-Hydroxy-1-phenyl-2-(1-phenylvinyl)but-2-en-1-one (**22**)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.046 (s, 3H), 5.130 (s, 1H), 5.786 (s, 1H), 7.221 (t, J = 8 Hz, 2 H), 7.279–7.350 (m, 4 H), 7.480 (d, J = 8 Hz, 2 H), 7.579 (d, J = 8 Hz, 2 H), 17.351 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 25.553, 113.333, 119.613, 126.351, 127.884, 128.194, 128.395, 128.891, 130.649, 140.422, 143.705, 183.487; FT-IR (Neat/cm^{-1}) ν = 3027, 1658, 1492, 1355, 1212, 1027, 913, 697; HR-MS (+ESI): m/z = 265.1227 g/mol, calc'd. for $C_{18}H_{17}O_2^+$ $[MH]^+$: 265.1223 g/mol.

4.2.13. (Z)-1-Phenyl-2-(1-phenylethylidene)butane-1,3-dione (**23Z**)

M.P. = 44–47 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.274 (s, 3H), 2.476 (s, 3H), 7.089 (s, 5H), 7.242–7.279 (m, 2H), 7.389 (t, J = 6.8 Hz, 1H), 7.704 (d, J = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 22.727, 31.059, 127.822, 128.310, 128.488, 128.550, 129.363, 133.313, 137.355, 139.841, 141.366, 151.449, 197.496, 198.781; FT-IR (KBr/cm^{-1}) ν = 3058, 1654, 1595, 1449, 1315, 1211, 865, 704; HR-MS (+ESI): m/z = 265.1227 g/mol, calc'd. for $C_{18}H_{17}O_2^+$ $[MH]^+$: 265.1223 g/mol.

4.2.14. (E)-1-Phenyl-2-(1-phenylethylidene)butane-1,3-dione (**23E**)

(Isolated as a mixture with *Z* isomer): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.868 (s, 3H), 2.049 (s, 3H), 7.331–7.353 (m, 2 H), 7.409–7.434 (m, 3H), 7.507 (t, J = 8 Hz, 2 H), 7.610 (apparent t, J = 8 Hz, 1 H), 8.009 (d, J = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 23.486, 31.005, 127.605, 128.991, 129.061, 129.162, 129.611, 133.955, 136.960, 140.987, 141.274, 148.266, 196.396, 200.624; FT-IR (Neat/cm^{-1}) ν = 2923, 1656, 1491, 1449, 1355, 1257, 1026, 700; GC/MS: calc'd.: 264.12 g/mol, found: 264.14 g/mol.

4.2.15. 1,3-diphenyl-2-(1-phenylethylidene)propane-1,3-dione (**25**)

Adduct **25** was prepared according to the standard procedure using dibenzoylmethane (**24**, 112.1 mg, 0.50 mmol) and phenylacetylene (**1**, 153.2 mg, 164.7 μL, 1.50 mmol), and stirring for 4 h. **25** was isolated as a yellow solid in 90% yield. Data are consistent with a known compound [9].

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2012.05.017.

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