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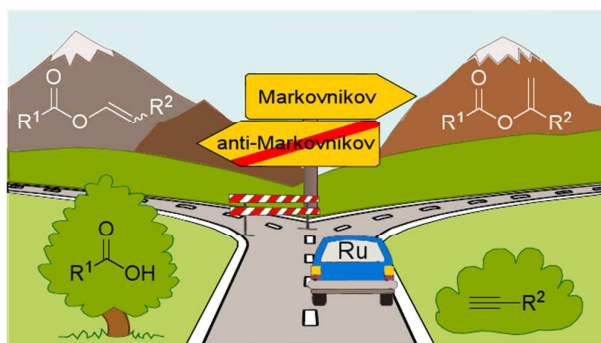
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ABSTRACT



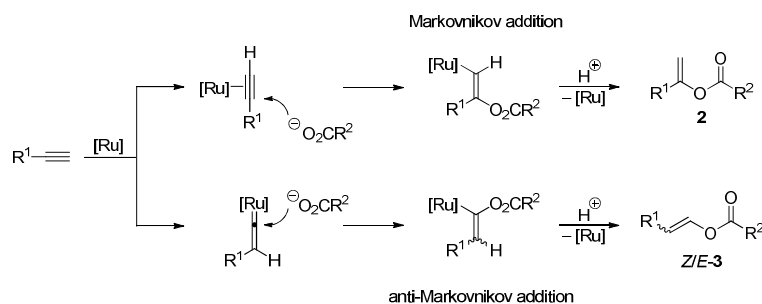
The ruthenium complexes $[\text{Ru}(\text{CO})_2(\text{P}(p\text{-C}_6\text{H}_4\text{-X})_3)_2(\text{O}_2\text{CPh})_2]$ (**1a**, X = CF₃; **1b**, X = Cl; **1c**, X = H; **1d**, X = Me; **1e**, X = OMe) were successfully applied in the regioselective Markovnikov addition of carboxylic acids to terminal alkynes, yielding valuable enol esters. The catalyst screening revealed a significant influence of the phosphine's electronic nature on the activity and selectivity. The highest activity was achieved with catalyst **1a**, featuring the most electron withdrawing phosphine ligand. Selectivity and activity could be further improved by the addition of catalytic amounts of AgOTf. Moreover, excellent selectivities with up to 99 % of the Markovnikov product were achieved. The electronic influence of the substrates on the reaction rate was quantified by Hammett plots. By the use of electron rich alkynes or highly acidic carboxylic acids the reaction rate could be increased. Hence, the addition of highly acidic pentafluorobenzoic acid to electron rich 4-methoxyphenylacetylene can even be carried out quantitatively at 25 °C within 4 h. Furthermore, a broad range of simple as well as electronically or sterically challenging substrates could be isolated in good to excellent yields with high regioselectivity and under mild reaction conditions (25–70 °C). The best reported activities and selectivities were obtained for the conversion of aromatic alkynes.

INTRODUCTION

Enol esters are valuable intermediates in a variety of organic synthetic methodologies. They are widely used as mild acylation reagents,¹ as substrates in asymmetric hydrogenation,² cycloaddition,³ aldol-⁴ and Mannich-type⁵ reactions and in vinyl arene synthesis by decarbonylative Heck-Mizoroki olefination.⁶ Moreover, vinyl esters such as vinyl acetate are also of considerable industrial interest as they are utilized as monomers in various polymerization reactions.⁷ Classical methods for the preparation of enol esters include the acylation of enolates⁸ and the acetoxymercuration of alkynes.⁹ However, these reactions require the use of toxic mercury salts or stoichiometric amounts of a strong acid or base. Therefore, the most straightforward and atom economic route to enol esters is the transition metal catalyzed addition of carboxylic acids to alkynes.¹⁰

Since the first reports on the ruthenium-catalyzed enol ester synthesis in the 1980ies,¹¹ a variety of transition metal complexes has been investigated, including rhodium,¹² rhenium,¹³ iridium,¹⁴ palladium,¹⁵ gold¹⁶ and bimetallic¹⁷ catalysts. But due to their high efficiency, excellent tolerance of functional groups and ease of preparation, ruthenium catalysts are still the most intensively studied and applied systems.¹⁸ Some ruthenium catalysts also allow a good control of the regio- and stereoselectivity, leading to the favored formation of one of the three possible isomers (Scheme 1). Thereby, the regioselectivity of the reaction is affected by the coordination mode of the alkyne to the metal center.^{19,20} The η^2 -alkyne binding mode leads to a nucleophilic attack at the C₁ position of the alkyne and hence the Markovnikov product is obtained.²¹ On the contrary, a tautomerization to the vinylidene analogue affords the anti-Markovnikov products by nucleophilic attack at the α -carbon.²²

Scheme 1. Proposed mechanism for the regioselective Ru-catalyzed formation of enol esters²³



Much effort has been invested to adjust the selectivity in enol ester synthesis. Successful approaches include the control of the selectivity by the solvent,²⁴ the ligands²⁵ or the addition of catalytic amounts of a Lewis acid or base.^{26,27} However, there are only few examples of catalysts that selectively promote the formation of Markovnikov products.^{23–28} Most known catalytic systems lead to the formation of the anti-Markovnikov species.²⁹ Another challenge is that the Markovnikov selective catalysts often require quite harsh reaction conditions or suffer from poor selectivities in the conversion of aromatic alkynes.^{23–28}

Recently, we reported on the synthesis of β -oxo esters by the Markovnikov addition of carboxylic acids to propargylic alcohols catalyzed by mononuclear ruthenium complexes of type $[\text{Ru}(\text{CO})_2(\text{PR}^1_3)_2(\text{O}_2\text{CR}^2)_2]$ ($\text{R}^1, \text{R}^2 = \text{aryl, alkyl}$).^{30,31} In continuation of our studies we herein describe the successful application of ruthenium complexes $[\text{Ru}(\text{CO})_2(\text{P}(p\text{-C}_6\text{H}_4\text{-X})_3)_2(\text{O}_2\text{CPh})_2]$ (**1a**, X = CF₃; **1b**, X = Cl; **1c**, X = H; **1d**, X = Me; **1e**, X = OMe) in the regioselective Markovnikov addition of carboxylic acids to terminal alkynes, yielding valuable enol esters. The electronic impact of the phosphine ligands as well as the effect of catalytic amounts of an additive on the reaction's activity and selectivity is discussed. Furthermore, the electronic influence of the substrates on the reaction rate is investigated.

RESULTS AND DISCUSSION

For the evaluation of the catalytic performance of organometallic ruthenium complexes $[\text{Ru}(\text{CO})_2(\text{P}(p\text{-C}_6\text{H}_4\text{-X})_3)_2(\text{O}_2\text{CPh})_2]$ ³¹ (**1a**, X = CF₃; **1b**, X = Cl; **1c**, X = H; **1d**, X = Me; **1e**, X = OMe) in the enol ester synthesis, the common addition of benzoic acid to phenylacetylene was chosen as model reaction. In the initial experiments, benzoic acid (1.0 mmol) and phenylacetylene (2.0 mmol) were dissolved in toluene (1 mL) and treated with 1.0 mol% of catalyst **1** for 24 h at 60 °C (Table 1).³² The efficiency and selectivity of the optimization reactions was determined by ¹H NMR spectroscopy applying acenaphthene as internal standard.

Table 1. Catalyst screening in the addition of benzoic acid to phenylacetylene to give **2aa** and **3aa**^a

Reaction scheme: Phenylacetylene (Ph-C≡CH) + Benzoic acid (HO-C(=O)Ph) $\xrightarrow[\text{60 } ^\circ\text{C, 24 h}]{\text{[1] (1 mol\%) , toluene}}$ 2aa (Markovnikov product) + 3aa (anti-Markovnikov product).

Entry	Catalyst	Yield [%] ^b	2aa	Selectivity [%] ^c (Z)-3aa	(E)-3aa
1	1a	100	74	20	6
2	1b	89	81	14	5
3	1c	86	91	7	2
4	1d	73	86	11	3
5	1e	62	97	2	1

^a Reaction conditions: benzoic acid (1.0 mmol), phenylacetylene (2.0 mmol), acenaphthene (0.5 mmol), **1** (1.0 mol%), toluene (1 mL), 60 °C, 24 h. ^b Total yield determined by ¹H NMR spectroscopy applying acenaphthene as internal standard. ^c Relative ratio of isomers determined by ¹H NMR spectroscopy.

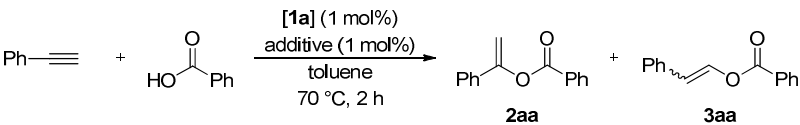
From Table 1 it can be seen that all tested catalysts **1a–e** lead to a favored formation of the Markovnikov product **2aa**. Furthermore, a correlation between the basicity of the phosphine ligands and the activity and selectivity of the resulting catalysts **1a–e** could be established. The highest activity is achieved with catalyst **1a**, which features with P(*p*-C₆H₄-CF₃)₃ the most electron withdrawing phosphine ligand. On the contrary, an enhanced selectivity for the Markovnikov product **2aa** is obtained with increasing basicity of the phosphine ligands.

For further optimization reactions the most active catalyst **1a** was chosen. The solvent screening revealed that in non-polar solvents like carbon tetrachloride, toluene or a toluene/cyclohexane mixture (1:1, v:v) the highest activities were observed. Although the toluene/cyclohexane mixture gave the best Markovnikov selectivity of 79 %, we continued with the usage of toluene due to its highest observed activity (Table S1, Supporting Information).

In order to further improve the selectivity for the Markovnikov product, the effect of catalytic amounts of various additives in the addition of benzoic acid to phenylacetylene was tested. Gooßen *et al.* could control the regioselectivity by the addition of various bases.²⁷ Whereas, the Markovnikov addition was observed in the presence of inorganic bases like Na₂CO₃, the reverse regioselectivity was obtained by the addition of organic bases like 4-*N,N*-dimethylaminopyridine (DMAP).²⁷ The effect of additives in the enol ester synthesis was also studied by Tripathy and Bhattacharjee.²⁶ Interestingly, their catalytic system leads to the opposite regioselectivity for the addition of Na₂CO₃ compared to the results of Gooßen. However, they could also achieve a high selectivity for the Markovnikov products in the presence of the Lewis acid BF₃·Et₂O. Inspired by these results,

we explored the impact of 1 mol% of various additives on the selectivity of our catalytic system in the addition of benzoic acid to phenylacetylene (Table 2).

Table 2. Influence of additives on the catalytic performance of **1a** in the addition of benzoic acid to phenylacetylene^a



Entry	Additive	Yield [%] ^b	Selectivity [%] ^c		
			2aa	(<i>Z</i>)- 3aa	(<i>E</i>)- 3aa
1	–	29	66	27	7
2	Na ₂ CO ₃	30	67	26	7
3	Cs ₂ CO ₃	29	66	27	7
4	NEt ₃	26	62	31	7
5	DMAP	2	50	50	0
6	AgNO ₃	18	50	33	17
7	AgI	35	60	31	9
8	BF ₃ ·Et ₂ O	26	96	0	4
9	Li(B[C ₆ F ₅] ₄)·2Et ₂ O	25	92	4	4
10	TfOH	85	99	0	1
11	KOTf	41	89	9	2
12	AgOTf	100	99	0	1
13 ^d	AgOTf	0	0	0	0
14	Mg(OTf) ₂	39	87	9	4
15	Yb(OTf) ₃	54	100	0	0

^a Reaction conditions: benzoic acid (1.0 mmol), phenylacetylene (2.0 mmol), acenaphthene (0.5 mmol), **1a** (1.0 mol%), additive (1.0 mol%), toluene (1 mL), 70 °C, 2 h. ^b Total yield determined by ¹H NMR spectroscopy applying acenaphthene as internal standard. ^c Relative ratio of isomers determined by ¹H NMR spectroscopy.

^d Reaction performed without catalyst.

From Table 2 it can be seen that compared to the waiving of any additive (Entry 1, Table 2), the addition of the inorganic bases Na_2CO_3 and Cs_2CO_3 did not show any effect on the activity nor selectivity (Entries 2 and 3, Table 2). The addition of organic bases led to a decline of the activity, probably due to the coordination to the ruthenium ion/center (Entries 4 and 5, Table 2). However, an obvious increase of the selectivity for the Markovnikov product was obtained by adding Lewis acids like $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (Entries 8 and 9, Table 2). An additional accelerating effect was observed for TfOH (Entry 10, Table 2). Based on the excellent results for TfOH, several triflates were tested, among which AgOTf resulted in a further improvement of the activity.³³ Additionally, it was examined whether AgOTf exhibits a catalytic activity by itself, but no conversion was detected without usage of a ruthenium catalyst (Entry 13, Table 2). The effect of the amount of the various triflates on the productivity was also explored (Table S2, Supporting Information), but the best results in terms of activity and selectivity were still reached with 1 mol% of AgOTf.

Besides the productivity, the effect of AgOTf on the catalytic activity was examined. Therefore, the reaction of benzoic acid with phenylacetylene was followed over time with and without the addition of AgOTf (Figure 1). The reaction profile without additive shows an induction period at the beginning of the conversion and a complete conversion after 7 h at 70 °C. However, no induction period is observed for the addition of AgOTf.³³ Instead, a considerably higher reaction rate and full conversion already after 2 h is reached.

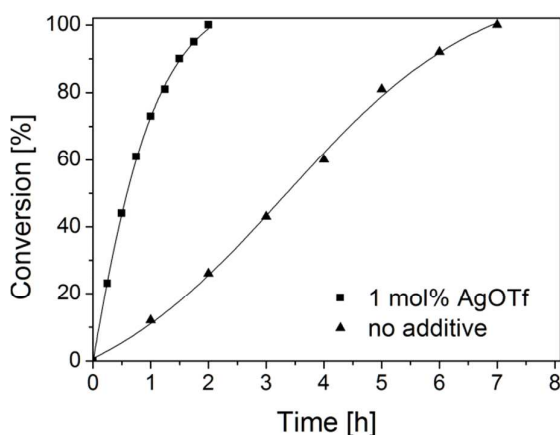


Figure 1. Effect of AgOTf on the reaction profile in the addition of benzoic acid to phenylacetylene catalyzed by **1a** at 70 °C in toluene. Please, notice that upon addition of AgOTf solely **2aa** is formed, while without additive a mixture of the three isomers **2aa**:(*Z*)-**3aa**:(*E*)-**3aa** in the ratio of 70:24:6 is produced (the graph contains the sum of all three isomers).

To check the influence of AgOTf on the activity of the other catalysts featuring more basic phosphine ligands, additional reaction profiles for the conversion of benzoic acid with phenylacetylene catalyzed by **1c** and **1e** were recorded (Figure S3, Supporting Information). The basicity of the phosphine ligand clearly affects the activity of the resulting catalyst, whereby with increasing basicity a distinct drop of the catalytic activity is observed. Independently of the phosphine ligands, a high selectivity for the Markovnikov product was obtained for all catalysts by the addition of AgOTf. Complex **1a** in combination with AgOTf still showed the best catalytic performance in enol ester synthesis. It is also interesting to note that for all examined catalysts no induction period at the beginning of the conversion was detected. For this reason it is very likely that AgOTf promotes the formation of the catalytically active species.

Finally, temperature dependent reaction profiles for the conversion of benzoic acid with phenylacetylene to afford **2aa** catalyzed by **1a**/AgOTf were studied (Figure 2). As it was already presented in Figure 1, complete conversion was achieved after 2 h at 70 °C. By lowering the reaction temperature to 60 °C, nearly the fourfold reaction time is needed to reach almost full conversion. A further decrease of temperature is not appropriate as quite low productivities were obtained at 50 °C. Apparently, the activity of the catalytic system is reduced for longer reaction times.

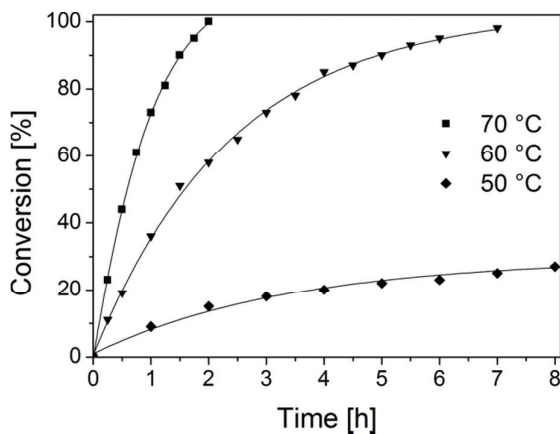


Figure 2. Temperature dependent reaction profiles for the addition of benzoic acid to phenylacetylene yielding **2aa** catalyzed by **1a** in combination with 1 mol% of AgOTf.

After optimization of the reaction conditions, the electronic impact of the substrates in the enol ester synthesis was explored. Therefore, a correlation of the Hammett value σ_p and the reaction rates in the conversion of a series of *para*-substituted phenylacetylenes and benzoic acids was investigated (Figure 3). The negative ρ value ($\rho = -0.294$) for the addition of benzoic acid to *para*-substituted phenylacetylenes $p\text{-Y-C}_6\text{H}_4\text{-C}\equiv\text{CH}$ ($\text{Y} = \text{OMe}, \text{Me}, \text{H}, \text{Cl}, \text{CF}_3$) reveals electron rich alkynes to increase the reaction rate. This observation can be explained by a facilitated coordination of an electron rich C_3C triple bond to the electrophilic ruthenium atom. On the contrary, for the reaction of *para*-substituted benzoic acids $p\text{-Z-C}_6\text{H}_4\text{-CO}_2\text{H}$ ($\text{Z} = \text{OMe}, \text{Me}, \text{H}, \text{Cl}, \text{CF}_3$) with phenylacetylene a positive ρ value ($\rho = +0.061$) was observed. A possible interpretation of these Hammett data might be that the carboxylic acid is involved in the alkyne activation. Thus, the coordination of more electron-deficient carboxylic acids to ruthenium, e.g. by carboxylate exchange,³⁰ probably accelerates the alkyne activation by increasing the electrophilicity of ruthenium. From the ρ values it can also be concluded that the electronic effect of the substituents at the alkyne are more decisive on the product formation than that of the carboxylic acids. Therefore, the activation of the alkyne is considered to be the rate-determining step in the enol ester synthesis.

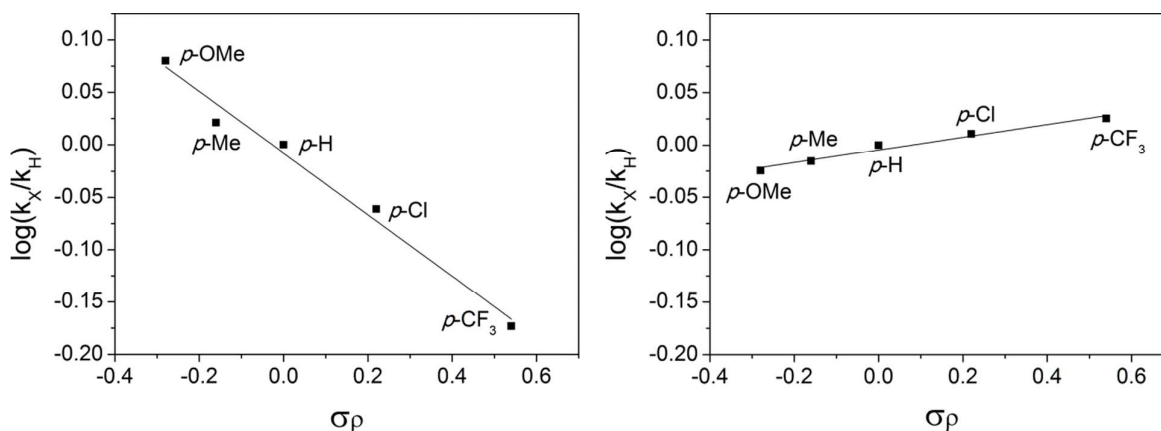
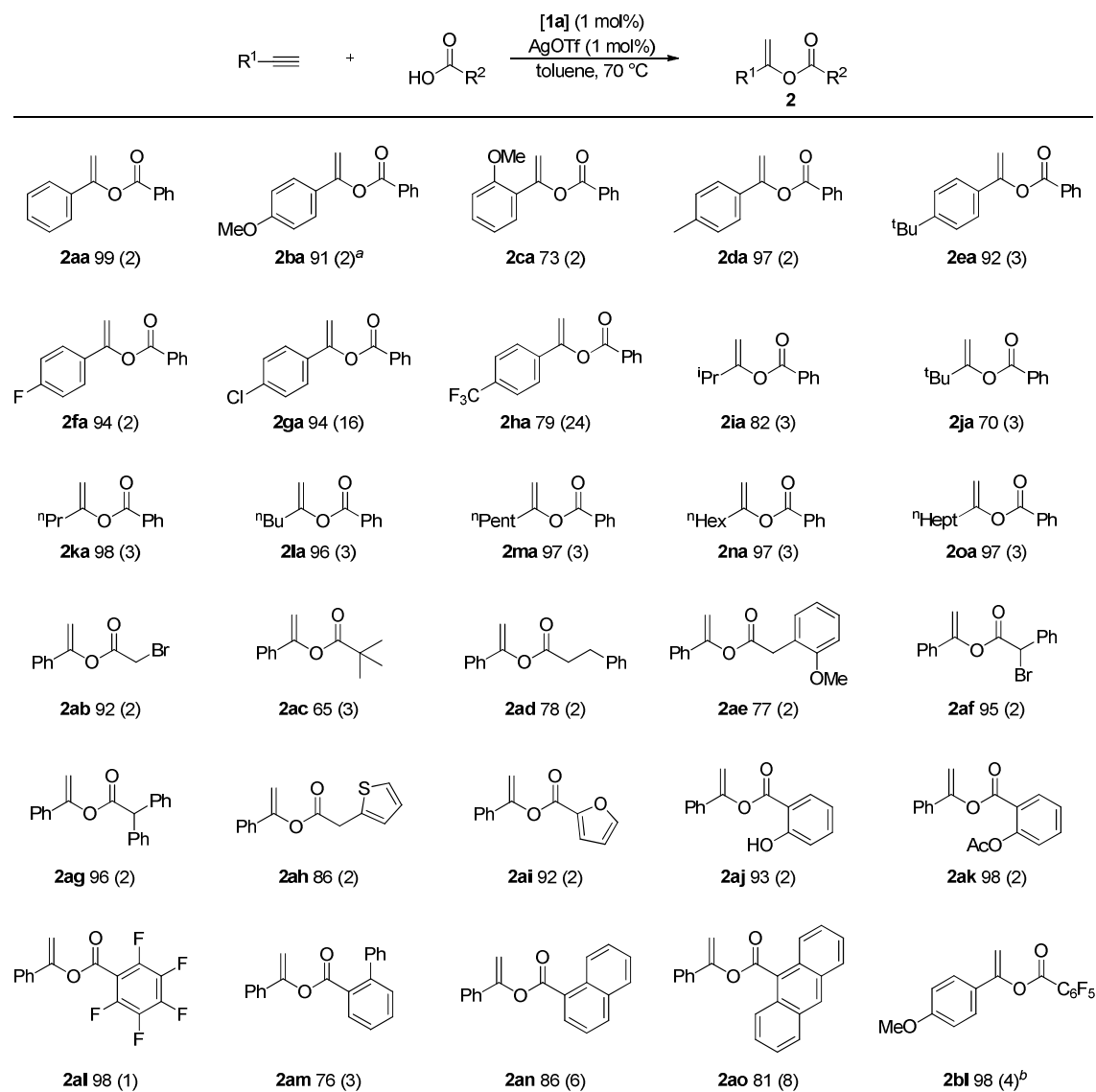


Figure 3. Hammett plots for the conversion of *para*-substituted phenylacetylenes $p\text{-Y-C}_6\text{H}_4\text{-C}\equiv\text{CH}$ ($\text{Y} = \text{OMe}, \text{Me}, \text{H}, \text{Cl}, \text{CF}_3$) with benzoic acid (left; $y = -0.294x - 0.008$, $R^2 = 0.979$) and the conversion of *para*-substituted benzoic acids $p\text{-Z-C}_6\text{H}_4\text{-CO}_2\text{H}$ ($\text{Z} = \text{OMe}, \text{Me}, \text{H}, \text{Cl}, \text{CF}_3$) with phenylacetylene (right; $y = 0.061x - 0.005$, $R^2 = 0.964$) in toluene.

To assess the substrate scope as well as the tolerance of the reaction towards functional or sterically demanding groups a substrate screening was carried out under optimized reaction conditions at 70 °C applying 1.0 mol% of **1a** and AgOTf, respectively. Scheme 2 reveals that diverse aliphatic and aromatic alkynes and carboxylic acids can be converted to enol esters in good to excellent isolated yields.

Scheme 2. Substrate Scope in the Enol Ester Synthesis



Reaction conditions: carboxylic acid (1.0 mmol), acetylene (2.0 mmol), **1a** (1.0 mol%), AgOTf (1.0 mol%), toluene (1 mL), 70 °C, isolated yield, optimized reaction times are given in parentheses. ^a Reaction performed at 60 °C. ^b Reaction performed at 25 °C.

The substrate screening of the electronically modified aromatic alkynes **2aa–ah** confirms the findings from the Hammett plot. Whereas substrates with electron donating substituents can even be successfully converted at a decreased reaction temperature of 60 °C in 2 h (**2ab**), electron deficient alkynes need significantly longer reaction times (**2ag,ah**). Next to *para*-substituted phenylacetylenes, also substituents in *ortho*-position are well tolerated (**2ac**). The conversion of aliphatic alkynes (**2ai–ao**) was usually completed within 3 h, whereby branched as well as linear alkynes of various chain lengths could be reacted without drop of the yields.

The generality of the carboxylic acid allows the successful conversion of various aliphatic (**2ab–ag**), aromatic (**2ah–ao**) and even heterocyclic compounds (**2ah,ai**). As estimated from the Hammett plot, strong acidic acids are converted preferably (**2al, 2af**). When a highly acidic acid like pentafluorobenzoic acid is converted with an electron rich alkyne like 4-methoxyphenylacetylene, the reaction can even be carried out quantitatively at 25 °C within 4 h (**2bl**). Moreover, the reaction also proceeds smoothly in the presence of sterically demanding substrates (**2an,ao**) and various functionalities like ester (**2ak**), ether (**2ba**), halide (**2ab**) and even hydroxy groups (**2aj**) are tolerated. It is also important to note that for all reactions applying a carboxylic acid apart from benzoic acid, the formation of up to 2 % of the benzoate product **2aa** is observed. The reason for this is that the benzoate ligands bound to the initial catalyst complex **1a** can also be converted during the reaction. Thereby, the formation of the minor product **2aa** could either arise from an intramolecular attack of the already bounded benzoate group to the activated alkyne or from an exchange of the carboxylates followed by an intermolecular nucleophilic attack.³⁰

In comparison to already known catalytic systems,^{14b,16,18d,23–28} catalyst **1a** exhibits productivities, for both simple and electronically or sterically challenging substrates that often match or even exceed those reported in literature. Up to now, the conversion of aromatic alkynes often suffered from poor selectivities, high temperatures or long reaction times.^{23–28} With our catalytic system the addition of benzoic acid to phenylacetylene proceeds smoothly within 2 h at 70 °C, yielding 99 % of isolated Markovnikov product **2aa**. Compared to established catalysts, we obtained the best reported catalytic results for this reaction (Table 3).

Table 3. Comparison of the isolated yields of **2aa** in the addition of benzoic acid to phenylacetylene for literature known catalytic systems

Entry	Catalyst	T [° C]	c _[cat] [mol%] ^a	t [h]	Yield [%] ^b	Reference
1	1a	70	1.0	2	99	this work
2	RuHCl(CO)(PCy ₃) ₂	90–95	2.0	8–12	98	[24]
3	Ru(CO) ₃ (PCy ₃) ₂	75	1.0	5	87	[25]
4	[Ru(PPh ₃) ₂ (CH ₃ CN) ₃ Cl][BPh ₄]	80	1.0	17	75	[26]
5	<i>trans</i> -[RuCl ₂ (η ³ :η ³ -C ₁₀ H ₁₆)(PPh ₃)]	60	2.0	24	60	[23]
6	[RuCl ₂ (<i>p</i> -cymene)] ₂ /PFur ₃	70	0.8	16	53	[27]

^a Based on [Ru]. ^b Isolated yield of isomer **2aa**.

CONCLUSION

Ruthenium complexes [Ru(CO)₂(P(*p*-C₆H₄-X)₃)₂(O₂CPh)₂] (**1a**, X = CF₃; **1b**, X = Cl; **1c**, X = H; **1d**, X = Me; **1e**, X = OMe) were found to be highly efficient catalysts in the atom-economic addition of carboxylic acids to terminal alkynes, yielding synthetically valuable enol esters. For all tested catalysts the formation of the Markovnikov products was favored. The activity and selectivity of the catalysts could be successfully tuned by the basicity of the phosphine ligands. The highest activity was achieved with catalyst **1a**, featuring the most electron deficient phosphine ligand. However, an enhanced selectivity for the Markovnikov product was observed with increasing basicity of the phosphine ligands. The selectivity as well as the activity could be further improved by the addition of catalytic amounts of AgOTf. The best catalytic performance was achieved with catalyst **1a** in combination with 1 eq. AgOTf.

The electronic influence of the substrates on the reaction rate was quantified by Hammett studies for the conversion of *para*-substituted phenylacetylenes and benzoic acids. The results indicate an increased reaction rate for the conversion of electron rich phenylacetylenes or benzoic acids with electron withdrawing substituents. By converting an electron rich alkyne and a highly acidic carboxylic acid, the reaction can even be carried out quantitatively within 4 h at 25 °C. Additionally, a broad range of facile as well as challenging substrates could be successfully converted under mild conditions, including aliphatic and aromatic alkynes and carboxylic acids. All reactions proceeded smoothly in short reaction times with high regioselectivity for the Markovnikov products. Furthermore, various common functional groups like esters, ethers, halides, and even sensitive hydroxy groups

were tolerated. For the conversion of aromatic alkynes the best catalytic performance reported in literature was obtained.^{23–27} Further investigations on the conversion of internal alkynes are underway.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Compounds **1a–e** were prepared according to previously published procedures.³¹ Toluene was dried by a solvent purification system. Acenaphthene was purified by sublimation at 75 °C (1.0 mbar). All other chemicals were purchased from commercial suppliers and used without further purification. For column chromatography silica with a particle size of 40–60 µm (230–400 mesh ASTM) was used. NMR spectra were recorded with a spectrometer operating at 500.3 MHz for ¹H and 125.7 MHz for ¹³C{¹H} spectra in the Fourier transform mode at 298 K. Chemical shifts are reported in δ (ppm) downfield from tetramethylsilane with the solvent as reference signal (¹H NMR, CHCl₃ δ 7.26; ¹³C{¹H} NMR, CDCl₃ δ 77.16). High resolution mass spectra were recorded with a time-of-flight (TOF) spectrometer using electro-spray ionization (ESI).

General Procedure for the Catalytic Reaction. In a screw-capped vial and under an atmosphere of argon the carboxylic acid (1.0 mmol), the alkyne (2.0 mmol), the ruthenium catalyst **1** (0.01 mmol), the additive (0.01 mmol), and acenaphthene (77 mg, 0.5 mmol) as internal standard were dissolved in toluene (1 mL). The sealed vial was immersed in a heating mantle preheated to 70 °C and stirred for 1–24 h. The progress of the reaction was monitored by regular sampling and analysis by ¹H NMR spectroscopy applying acenaphthene as internal standard. Analytically pure products were isolated by column chromatography on silica gel. All catalytic results have been verified by at least two independent experiments.

Hammett Study: Alkyne. In a screw-capped vial and under an atmosphere of argon the respective *para*-substituted phenylacetylene *p*-Y-C₆H₄-C≡CH (Y = OMe, Me, H, Cl, CF₃) (2.0 mmol), benzoic acid (122 mg, 1.0 mmol), **1a** (13.32 mg, 0.01 mmol), AgOTf (2.56 mg, 0.01 mmol), and acenaphthene (77 mg, 0.5 mmol) as internal standard were dissolved in toluene (1 mL). The sealed vial was immersed in a heating mantle preheated to 60 °C. The reaction was monitored by ¹H NMR spectroscopy applying acenaphthene as internal standard in 15 min intervals. The *k*_x was estimated from a first-order plot of ln[product] vs reaction time rather than ln[benzoic acid] vs reaction time because the ¹H NMR integration of the product signals (=CH₂) was more accurate.

Hammett Study: Carboxylic Acid. In a screw-capped vial and under an atmosphere of argon the respective *para*-substituted benzoic acid *p*-Z-C₆H₄-CO₂H (Z = OMe, Me, H, Cl, CF₃) (1.0 mmol), phenylacetylene (204 mg, 2.0 mmol), **1a** (13.32 mg, 0.01 mmol), AgOTf (2.56 mg, 0.01 mmol), and acenaphthene (77 mg, 0.5 mmol) as internal standard were dissolved in toluene (20 mL). The sealed vial was immersed in a heating mantle preheated to 80 °C. The reaction was monitored by ¹H NMR spectroscopy applying acenaphthene as internal standard in 30 min intervals. The *k_x* was estimated from a first-order plot of ln[product] vs reaction time rather than ln[carboxylic acid] vs reaction time because the ¹H NMR integration of the product signals (=CH₂) was more accurate.

Characterization Data of Catalysis Products

1-Phenylvinyl benzoate (**2aa**)^{14,16,18b,18c,23–27,29b,29c,29e}

Benzoic acid (122 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (221 mg, 99 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 5.21 (d, *J* = 2.2 Hz, 1H), 5.63 (d, *J* = 2.3 Hz, 1H), 7.33–7.41 (m, 3H), 7.51–7.56 (m, 2H), 7.56–7.60 (m, 2H), 7.62–7.68 (m, 1H), 8.21–8.27 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 102.4, 125.0, 128.68, 128.74, 129.1, 129.6, 130.3, 133.7, 134.4, 153.3, 164.9.

1-(4-Methoxyphenyl)vinyl benzoate (**2ba**)^{18b,18c,23,24,26}

Benzoic acid (122 mg, 1.0 mmol) was converted with 4-methoxyphenylacetylene (264 mg, 2.0 mmol) for 2 h at 60 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as yellow liquid (231 mg, 91 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 3.80 (s, 3H), 5.07 (d, *J* = 2.2 Hz, 1H), 5.48 (d, *J* = 2.2 Hz, 1H), 6.85–6.90 (m, 2H), 7.46–7.55 (m, 4H), 7.61–7.67 (m, 1H), 8.18–8.24 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 55.4, 100.5, 114.1, 126.5, 127.1, 128.7, 129.7, 130.2, 133.6, 153.1, 160.3, 164.9.

1-(2-Methoxyphenyl)vinyl benzoate (2ca)

Benzoic acid (122 mg, 1.0 mmol) was converted with 2-methoxyphenylacetylene (264 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using cyclohexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as yellow liquid (185 mg, 73 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 3.84 (s, 3H), 5.32 (d, *J* = 1.3 Hz, 1H), 5.73 (d, *J* = 1.4 Hz, 1H), 6.91–6.96 (m, 2H), 7.28–7.32 (m, 1H), 7.43–7.46 (m, 1H), 7.47–7.52 (m, 2H), 7.58–7.64 (m, 1H), 8.16–8.20 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 55.7, 106.8, 111.5, 120.6, 123.6, 128.5, 128.6, 130.0, 130.1, 130.2, 133.4, 150.6, 157.2, 164.9. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₆H₁₄O₃Na 277.0835; Found 277.0833.

1-(4-Tolyl)vinyl benzoate (2da)^{18b,18c,24,29b}

Benzoic acid (122 mg, 1.0 mmol) was converted with 4-tolylacetylene (232 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as pale yellow liquid (230 mg, 97 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 2.35 (s, 3H), 5.12 (d, *J* = 2.2 Hz, 1H), 5.55 (d, *J* = 2.2 Hz, 1H), 7.13–7.18 (m, 2H), 7.42–7.46 (m, 2H), 7.49–7.54 (m, 2H), 7.61–7.67 (m, 1H), 8.18–8.23 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 21.4, 101.5, 125.0, 128.7, 129.4, 129.7, 130.3, 131.7, 133.7, 139.1, 153.4, 165.0.

1-(4-(*tert*-Butyl)phenyl)vinyl benzoate (2ea)

Benzoic acid (122 mg, 1.0 mmol) was converted with 4-*tert*-butylphenylacetylene (316 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as brown liquid (258 mg, 92 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 1.34 (s, 9H), 5.16 (d, *J* = 2.2 Hz, 1H), 5.59 (d, *J* = 2.2 Hz, 1H), 7.37–7.42 (m, 2H), 7.49–7.56 (m, 4H), 7.62–7.68 (m, 1H), 8.21–8.27 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 31.3, 34.7, 101.6, 124.8, 125.6, 128.7, 129.7, 130.2, 131.6, 133.6, 152.2, 153.4, 164.9. HRMS (ESI-TOF) *m/z*: (M + Na)⁺ Calcd for C₁₉H₂₀O₂Na 303.1356; Found 303.1353.

1-(4-Fluorophenyl)vinyl benzoate (2fa)^{24,26}

Benzoic acid (122 mg, 1.0 mmol) was converted with 4-fluorophenylacetylene (240 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as pale yellow liquid (227 mg, 94 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 5.16 (d, *J* = 2.3 Hz, 1H), 5.53 (d, *J* = 2.3 Hz, 1H), 7.01–7.07 (m, 2H), 7.49–7.55 (m, 4H), 7.63–7.67 (m, 1H), 8.17–8.24 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 102.3, 115.7 (d, *J*_{CF} = 21.9 Hz), 127.0 (d, *J*_{CF} = 8.5 Hz), 128.8, 129.5, 130.3, 130.8 (d, *J*_{CF} = 3.5 Hz), 133.8, 152.5, 163.3 (d, *J*_{CF} = 249 Hz), 164.9.

1-(4-Chlorophenyl)vinyl benzoate (2ga)³⁴

Benzoic acid (122 mg, 1.0 mmol) was converted with 4-chlorophenylacetylene (273 mg, 2.0 mmol) for 16 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as pale yellow liquid (243 mg, 94 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 5.21 (d, *J* = 2.4 Hz, 1H), 5.59 (d, *J* = 2.4 Hz, 1H), 7.30–7.36 (m, 2H), 7.45–7.50 (m, 2H), 7.50–7.56 (m, 2H), 7.62–7.68 (m, 1H), 8.18–8.23 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 102.9, 126.4, 128.8, 128.9, 129.3, 130.2, 133.0, 133.8, 135.0, 152.3, 164.8.

1-(4-(Trifluoromethyl)phenyl)vinyl benzoate (2ha)²⁴

Benzoic acid (122 mg, 1.0 mmol) was converted with 4-(trifluoromethyl)phenylacetylene (340 mg, 2.0 mmol) for 24 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (231 mg, 79 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 5.32 (d, *J* = 2.5 Hz, 1H), 5.70 (d, *J* = 2.5 Hz, 1H), 7.51–7.57 (m, 2H), 7.59–7.69 (m, 5H), 8.19–8.24 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 104.7, 124.0 (q, *J*_{CF} = 272 Hz), 125.4, 125.7 (q, *J*_{CF} = 3.8 Hz), 128.9, 129.1, 130.3, 130.9 (q, *J*_{CF} = 32.6 Hz), 134.0, 137.9, 152.1, 164.8.

3-Methylbut-1-en-2-yl benzoate (2ia)

Benzoic acid (122 mg, 1.0 mmol) was converted with 3-methyl-1-butyne (136 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/diethyl ether (10:1, v/v) as eluent, yielding the title compound as colorless liquid (156 mg, 82 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 1.15 (d, *J* = 6.8 Hz, 6H), 2.58 (hept, *J* = 6.8 Hz, 1H), 4.82–4.89 (m, 2H), 7.44–7.51 (m, 2H), 7.57–7.63 (m, 1H), 8.07–8.13 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 20.4, 32.6, 99.6, 128.6, 130.06, 130.09, 133.4, 161.6, 165.0. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₂H₁₄O₂Na 213.0886; Found 213.0903.

3,3-Dimethylbut-1-en-2-yl benzoate (2ja)^{12c,23,27,29e}

Benzoic acid (122 mg, 1.0 mmol) was converted with 3,3-dimethyl-1-butyne (164 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/diethyl ether (98:2, v/v) as eluent, yielding the title compound as colorless liquid (143 mg, 70 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 1.19 (s, 9H), 4.81 (d, *J* = 2.1 Hz, 1H), 4.99 (d, *J* = 2.1 Hz, 1H), 7.43–7.51 (m, 2H), 7.56–7.62 (m, 1H), 8.08–8.13 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 28.0, 36.6, 99.3, 128.6, 130.1, 130.3, 133.4, 162.8, 164.9.

Pent-1-en-2-yl benzoate (2ka)^{11b,11f,23}

Benzoic acid (122 mg, 1.0 mmol) was converted with 1-pentyne (136 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as pale yellow liquid (186 mg, 98 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 0.98 (t, *J* = 7.4 Hz, 3H), 1.52–1.62 (m, 2H), 2.30–2.35 (m, 2H), 4.82–4.85 (m, 1H), 4.86–4.88 (m, 1H), 7.44–7.49 (m, 2H), 7.56–7.61 (m, 1H), 8.07–8.11 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 13.6, 20.0, 35.6, 101.6, 128.6, 130.0, 130.1, 133.4, 156.7, 164.9.

Hex-1-en-2-yl benzoate (2la)^{16,23,24,26,28,29e}

Benzoic acid (122 mg, 1.0 mmol) was converted with 1-hexyne (164 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent,

yielding the title compound as pale yellow liquid (195 mg, 96 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.35–1.44 (m, 2H), 1.48–1.57 (m, 2H), 2.31–2.38 (m, 2H), 4.82–4.85 (m, 1H), 4.85–4.88 (m, 1H), 7.43–7.50 (m, 2H), 7.56–7.62 (m, 1H), 8.06–8.12 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 14.0, 22.3, 28.8, 33.3, 101.4, 128.6, 130.06, 130.10, 133.4, 157.0, 164.9.

Hept-1-en-2-yl benzoate (2ma)²⁵

Benzoic acid (122 mg, 1.0 mmol) was converted with 1-heptyne (192 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (98:2, v/v) as eluent, yielding the title compound as pale yellow liquid (212 mg, 97 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 0.88–0.92 (m, 3H), 1.31–1.38 (m, 4H), 1.50–1.59 (m, 2H), 2.31–2.37 (m, 2H), 4.82–4.85 (m, 1H), 4.85–4.88 (m, 1H), 7.44–7.50 (m, 2H), 7.55–7.62 (m, 1H), 8.06–8.11 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 14.1, 22.5, 26.4, 31.3, 33.5, 101.4, 128.6, 130.0, 130.1, 133.4, 157.0, 164.9.

Oct-1-en-2-yl benzoate (2na)^{11f,12a,12c,18b,23,29e}

Benzoic acid (122 mg, 1.0 mmol) was converted with 1-octyne (220 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (98:2, v/v) as eluent, yielding the title compound as yellow liquid (226 mg, 97 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.24–1.40 (m, 6H), 1.49–1.58 (m, 2H), 2.31–2.36 (m, 2H), 4.83–4.85 (m, 1H), 4.85–4.87 (m, 1H), 7.44–7.50 (m, 2H), 7.56–7.62 (m, 1H), 8.06–8.13 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 14.2, 22.7, 26.6, 28.8, 31.7, 33.6, 101.5, 128.6, 130.02, 130.05, 133.4, 157.0, 164.9.

Non-1-en-2-yl benzoate (2oa)

Benzoic acid (122 mg, 1.0 mmol) was converted with 1-nonyne (248 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (98:2, v/v) as eluent, yielding the title compound as pale yellow liquid (238 mg, 97 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.22–1.40 (m, 8H), 1.48–1.60 (m, 2H), 2.30–2.39 (m, 2H), 4.80–4.85 (m, 1H), 4.85–4.88 (m, 1H), 7.44–7.50 (m, 2H), 7.56–7.62 (m, 1H), 8.06–8.13 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 14.2, 22.8, 26.7,

29.1, 29.2, 31.9, 33.6, 101.4, 128.6, 130.06, 130.11, 133.4, 157.0, 164.9. HRMS (ESI-TOF) m/z : $[M + Na]^+$
Calcd for $C_{16}H_{22}O_2Na$ 269.1512; Found 269.1536.

1-Phenylvinyl 2-bromoacetate (2ab)³⁵

2-Bromoacetic acid (139 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (222 mg, 92 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 4.02 (s, 2H), 5.11 (d, *J* = 2.6 Hz, 1H), 5.52 (d, *J* = 2.6 Hz, 1H), 7.30–7.41 (m, 3H), 7.49–7.55 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 25.5, 102.5, 125.0, 128.7, 129.4, 133.7, 152.9, 165.4.

1-Phenylvinyl pivalate (2ac)²⁵

Pivalic acid (102 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (133 mg, 65 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 1.36 (s, 9H), 4.98 (d, *J* = 2.0 Hz, 1H), 5.45 (d, *J* = 2.1 Hz, 1H), 7.29–7.38 (m, 3H), 7.43–7.49 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 27.3, 39.3, 101.9, 125.0, 128.6, 129.0, 134.9, 153.5, 176.7.

1-Phenylvinyl 3-phenylpropanoate (2ad)

3-Phenylpropanoic acid (150 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow solid (197 mg, 78 %). M.p.: 50 °C. ¹H NMR (CDCl₃, 500.3 MHz): δ 2.90–2.96 (m, 2H), 3.10 (t, *J* = 7.7 Hz, 2H), 5.01 (d, *J* = 2.2 Hz, 1H), 5.50 (d, *J* = 2.2 Hz, 1H), 7.27–7.41 (m, 10H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 30.9, 35.9, 102.2, 124.9, 126.5, 128.5, 128.6, 128.7, 129.0, 134.2, 140.2, 153.0, 171.1. HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $C_{17}H_{16}O_2Na$ 275.1043; Found 275.1028.

1-Phenylvinyl 2-(2-methoxyphenyl)acetate (2ae)

2-Methoxyphenylacetic acid (166 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (207 mg, 77 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 3.85 (s, 3H), 3.89 (s, 2H), 5.07 (d, *J* = 2.2 Hz, 1H), 5.51 (d, *J* = 2.2 Hz, 1H), 6.91–6.95 (m, 1H), 6.96–7.01 (m, 1H), 7.27–7.37 (m, 5H), 7.43–7.48 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 36.4, 55.4, 102.0, 110.5, 120.7, 122.6, 125.0, 128.4, 128.88, 128.9, 131.1, 134.4, 153.0, 157.6, 169.9. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₆O₃Na 291.0992; Found 291.0989.

1-Phenylvinyl 2-bromo-2-phenylacetate (2af)

α-Bromophenylacetic acid (215 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as colorless liquid (301 mg, 95 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 5.07 (d, *J* = 2.5 Hz, 1H), 5.51 (d, *J* = 2.5 Hz, 1H), 5.57 (s, 1H), 7.27–7.34 (m, 3H), 7.35–7.40 (m, 2H), 7.40–7.45 (m, 3H), 7.61–7.67 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 46.6, 102.5, 124.9, 128.7, 129.0, 129.1, 129.3, 129.7, 133.6, 135.3, 152.9, 166.4. HRMS (ESI-TOF) *m/z*: [M – HBr]⁺ Calcd for C₁₆H₁₁O₂ 235.0754; Found 235.0776.

1-Phenylvinyl 2,2-diphenylacetate (2ag)

Diphenylacetic acid (212 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as pale yellow liquid (300 mg, 96 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 5.04 (d, *J* = 2.3 Hz, 1H), 5.25 (s, 1H), 5.47 (d, *J* = 2.3 Hz, 1H), 7.21–7.25 (m, 4H), 7.27–7.34 (m, 3H), 7.34–7.39 (m, 4H), 7.39–7.44 (m, 4H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 57.1, 102.2, 124.9, 127.6, 128.4, 128.8, 128.9, 134.1, 138.0, 153.0, 170.5. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₂H₁₈O₂Na 337.1199; Found 337.1199.

1-Phenylvinyl 2-(thiophen-2-yl)acetate (2ah)

2-Thiopheneacetic acid (142 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (210 mg, 86 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 4.08 (d, *J* = 0.8 Hz, 2H), 5.08 (d, *J* = 2.3 Hz, 1H), 5.50 (d, *J* = 2.3 Hz, 1H), 7.00–7.03 (m, 1H), 7.04–7.07 (m, 1H), 7.27–7.29 (m, 1H), 7.31–7.34 (m, 3H), 7.38–7.42 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 35.6, 102.4, 124.9, 125.5, 127.1, 127.4, 128.6, 129.1, 134.1, 134.4, 153.0, 168.6. HRMS (ESI-TOF) *m/z*: [M + K]⁺ Calcd for C₁₄H₁₂O₂S 283.0190; Found 283.0176.

1-Phenylvinyl furan-2-carboxylate (2ai)

2-Furoic acid (112 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (197 mg, 92 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 5.19 (d, *J* = 2.4 Hz, 1H), 5.59 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 3.5 Hz, 1.8 Hz, 1H), 7.30–7.39 (m, 4H), 7.51–7.56 (m, 2H), 7.67 (dd, *J* = 1.7 Hz, 0.8 Hz, 1H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 102.7, 112.3, 119.5, 125.1, 128.7, 129.2, 134.2, 144.1, 147.3, 152.5, 156.7. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₁O₃ 215.0703; Found 215.0714.

1-Phenylvinyl 2-hydroxybenzoate (2aj)

Salicylic acid (138 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (224 mg, 93 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 5.22 (d, *J* = 2.5 Hz, 1H), 5.65 (d, *J* = 2.5 Hz, 1H), 6.99–7.03 (m, 1H), 7.05–7.09 (m, 1H), 7.35–7.43 (m, 3H), 7.53–7.59 (m, 3H), 8.12–8.16 (m, 1H), 10.52 (s, 1H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 102.9, 111.9, 118.0, 119.6, 124.9, 128.8, 129.4, 130.3, 133.9, 136.6, 152.8, 162.3, 168.7. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₅H₁₂O₃Na 263.0679; Found 263.0685.

1-Phenylvinyl 2-acetoxybenzoate (2ak)

2-Acetoxybenzoic acid (180 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 2 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (277 mg, 98 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 2.31 (s, 3H), 5.17 (d, *J* = 2.4 Hz, 1H), 5.63 (d, *J* = 2.4 Hz, 1H), 7.20 (dd, *J* = 8.1 Hz, 1.0 Hz, 1H), 7.32–7.43 (m, 4H), 7.53–7.58 (m, 2H), 7.65 (ddd, *J* = 8.1 Hz, 7.5 Hz, 1.7 Hz, 1H), 8.26 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 21.0, 102.5, 122.4, 124.2, 124.9, 126.3, 128.6, 129.1, 132.3, 133.8, 134.7, 151.3, 152.9, 162.6, 169.8. HRMS (ESI-TOF) *m/z*: [M + Na–C(O)CH₃]⁺ Calcd for C₁₅H₁₂O₃Na 263.0679; Found 263.0710.

1-Phenylvinyl 2,3,4,5,6-pentafluorobenzoate (2al)

Pentafluorobenzoic acid (212 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 1 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as orange-brown solid (308 mg, 98 %). M.p.: 67 °C. ¹H NMR (CDCl₃, 500.3 MHz): δ 5.24 (d, *J* = 2.7 Hz, 1H), 5.61 (d, *J* = 2.7 Hz, 1H), 7.36–7.42 (m, 3H), 7.52–7.58 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 103.2, 107.5–107.9 (m), 125.6, 128.8, 129.5, 133.4, 136.7–139.2 (m), 142.5–142.9 (m), 144.6–147.0 (m), 153.0, 157.1–157.4 (m). HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₅H₇F₅O₂Na 337.0258; Found 337.0290.

1-Phenylvinyl [1,1'-biphenyl]-2-carboxylate (2am)

1,1'-Biphenyl-2-carboxylic acid (198 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 3 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as eluent, yielding the title compound as yellow liquid (228 mg, 76 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 4.90 (d, *J* = 2.2 Hz, 1H), 5.42 (d, *J* = 2.2 Hz, 1H), 7.29–7.54 (m, 12H), 7.60–7.65 (m, 1H), 8.02–8.06 (m, 1H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 101.9, 125.0, 127.4, 127.5, 128.3, 128.5, 128.7, 128.9, 130.1, 130.4, 131.1, 131.8, 134.3, 141.1, 142.9, 153.2, 166.8. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₁H₁₆O₂Na 323.1043; Found 323.1039.

1-Phenylvinyl 1-naphthoate (2an)

1-Naphthoic acid (172 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 6 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/diethyl ether (4:1, v/v) as eluent, yielding the title compound as yellow liquid (235 mg, 86 %). ¹H NMR (CDCl₃, 500.3 MHz): δ 5.25 (d, *J* = 2.2 Hz, 1H), 5.66 (d, *J* = 2.2 Hz, 1H), 7.34–7.40 (m, 3H), 7.55–7.66 (m, 5H), 7.91–7.95 (m, 1H), 8.10–8.14 (m, 1H), 8.50–8.55 (m, 1H), 9.02–9.07 (m, 1H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 102.6, 124.7, 125.1, 125.8, 126.0, 126.6, 128.4, 128.76, 128.80, 129.1, 131.3, 131.9, 134.1, 134.5, 134.6, 153.5, 165.5. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₉H₁₄O₂Na 297.0886; Found 297.0918.

1-Phenylvinyl anthracene-9-carboxylate (2ao)

Anthracene 9-carboxylic acid (222 mg, 1.0 mmol) was converted with phenylacetylene (204 mg, 2.0 mmol) for 8 h at 70 °C. The product was purified by silica-gel column chromatography using *n*-hexane/diethyl ether (4:1, v/v) as eluent, yielding the title compound as yellow solid (261 mg, 81 %). M.p.: 122 °C. ¹H NMR (CDCl₃, 500.3 MHz): δ 5.53 (d, *J* = 2.6 Hz, 1H), 5.73 (d, *J* = 2.5 Hz, 1H), 7.39–7.43 (m, 3H), 7.51–7.60 (m, 4H), 7.64–7.68 (m, 2H), 8.05–8.09 (m, 2H), 8.16–8.21 (m, 2H), 8.60 (s, 1H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 102.8, 125.0, 125.5, 125.7, 126.9, 127.4, 128.8, 128.9, 129.4, 130.1, 131.2, 134.7, 153.6, 167.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₃H₁₇O₂ 325.1223; Found 325.1228.

1-(4-Methoxyphenyl)vinyl 2,3,4,5,6-pentafluorobenzoate (2bl)

Pentafluorobenzoic acid (212 mg, 1.0 mmol) was converted with 4-methoxyphenylacetylene (264 mg, 2.0 mmol) for 4 h at 25 °C. The product was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate (95:5, v/v) as eluent, yielding the title compound as pale yellow solid (336 mg, 98 %). M.p.: 99 °C. ¹H NMR (CDCl₃, 500.3 MHz): δ 3.83 (s, 3H), 5.12 (d, *J* = 2.7 Hz, 1H), 5.46 (d, *J* = 2.7 Hz, 1H), 6.88–6.93 (m, 2H), 7.44–7.50 (m, 2H). ¹³C NMR (CDCl₃, 125.7 MHz): δ 55.5, 101.2, 107.7–108.1 (m), 114.2, 126.0, 126.7, 136.7–139.2 (m), 142.5–142.9 (m), 144.6–147.0 (m), 152.9, 157.1–157.4 (m), 160.7. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₀F₅O₃ 345.0545; Found 345.0542.

ASSOCIATED CONTENT

Supporting Information

Additional catalytic results and the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of all catalysis products can be found in the supporting information.

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Notes

The authors declare no competing financial interest.

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(32) The reaction conditions were adopted from ref. 31. It was found that an acid/alkyne ratio of 1:2 is not mandatory for the reaction, as almost the same results were obtained by the usage of less alkyne (Table S4 in the Supporting Information).

(33) The positive impact of the AgOTf may arise from a combination of the following effects: *i*) alkyne coordination to Ag⁺ may facilitate the alkyne activation (see for example: Ishino, Y.; Nishiguchi, I.; Nakao, S.; Hirashima, T., *Chem. Lett.* **1981**, 641–644.), *ii*) exchange of triflate ions with the benzoate ligands bound to the catalyst may increase the electrophilicity of the ruthenium center, and *iii*) AgOTf may act as a phosphine scavenger and facilitate the generation of free coordination sites (cf. Altaf, M.; Stoeckli-Evans, H., *Polyhedron* **2010**, 29, 701–708; Meijboom, R.; Bowen, R. J.; Berners-Price, S. J., *Coord. Chem. Rev.* **2009**, 253, 325–342; Lettko, L.; Wood, J. S.; Rausch, M. D., *Inorg. Chim. Acta* **2000**, 308, 37–44.).

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