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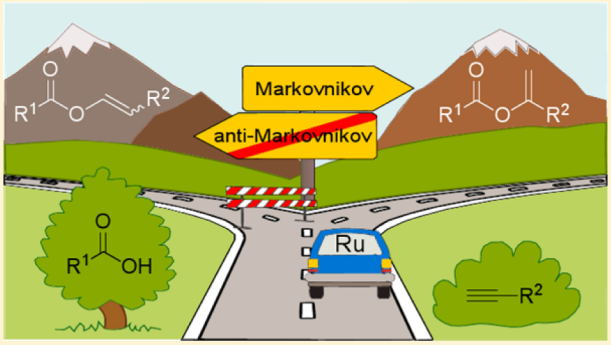
Regioselective Formation of Enol Esters from the Ruthenium-Catalyzed Markovnikov Addition of Carboxylic Acids to Alkynes

Janine Jeschke, Christian Gäbler, and Heinrich Lang*

Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry, Inorganic Chemistry, 09107 Chemnitz, Germany

Supporting Information

ABSTRACT: The ruthenium complexes $[Ru(CO)_2(P(p\text{-}C_6H_4\text{-}X)_3)_2(O_2CPh)_2]$ (**1a**, X = CF_3; **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. Catalyst screening revealed a significant influence of phosphine's electronic nature on 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.

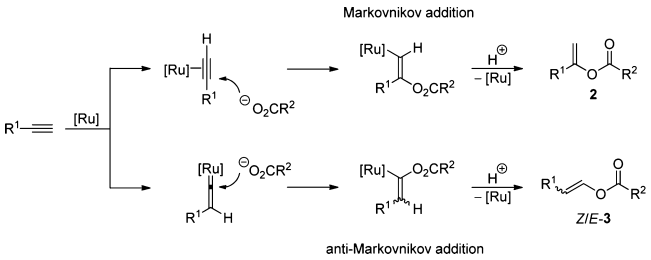


INTRODUCTION

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-type[5] 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 enolates[8] 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 ruthenium-catalyzed enol ester synthesis in the 1980s,[11] a variety of transition metal complexes have been investigated, including rhodium,[12] rhenium,[13] iridium,[14] palladium,[15] gold,[16] and bimetallic[17] catalysts. However, because of 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 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

Scheme 1. Proposed Mechanism for the Regioselective Ru-Catalyzed Formation of Enol Esters[23]



to the metal center.[19,20] The η^2-alkyne binding mode leads to a nucleophilic attack at the C_1 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]

Much effort has been invested in adjusting the selectivity in enol ester synthesis. Successful approaches include control of the selectivity by the solvent,[24] the ligands,[25] 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

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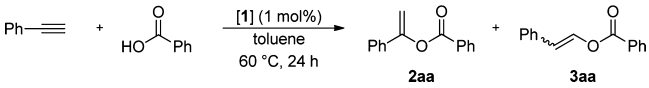
systems lead to the formation of the anti-Markovnikov species.[29] Another challenge is that the Markovnikov selective catalysts often require quite harsh reaction conditions or suffer from poor selectivities in the conversion of aromatic alkynes.[23−28]

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 the type $[Ru(CO)_2(PR^1_3)_2(O_2CR^2)_2]$ (R^1, R^2 = aryl, alkyl).[30,31] In continuation of our studies, we herein describe the successful application of ruthenium complexes $[Ru(CO)_2(P(p\text{-}C_6H_4\text{-}X)_3)_2(O_2CPh)_2]$ (**1a**, X = CF_3; **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 $[Ru(CO)_2(P(p\text{-}C_6H_4\text{-}X)_3)_2(O_2CPh)_2]$[31] (**1a**, X = CF_3; **1b**, X = Cl; **1c**, X = H; **1d**, X = Me; **1e**, X = OMe) in enol ester synthesis, the common addition of benzoic acid to phenylacetylene was chosen as the 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 were determined by ^{1}H NMR spectroscopy, applying acenaphthene as the internal standard.

Table 1. Catalyst Screening in the Addition of Benzoic Acid to Phenylacetylene to Give 2aa and 3aa[a]



			selectivity [%][c]		
entry	catalyst	yield [%][b]	**2aa**	(*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

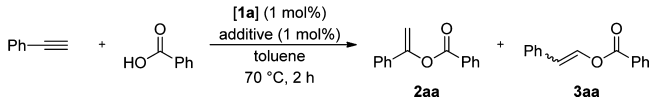
[a]Reaction conditions: benzoic acid (1.0 mmol), phenylacetylene (2.0 mmol), acenaphthene (0.5 mmol), **1** (1.0 mol %), toluene (1 mL), 60 °C, 24 h. [b]Total yield determined by ^{1}H NMR spectroscopy applying acenaphthene as internal standard. [c]Relative ratio of isomers determined by ^{1}H NMR spectroscopy.

From Table 1, it can be seen that all tested catalysts (**1a−e**) lead to the 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 $P(p\text{-}C_6H_4\text{-}CF_3)_3$ the most electron-withdrawing phosphine ligand. On the contrary, an enhanced selectivity for 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 the highest activities were observed in nonpolar solvents like carbon tetrachloride, toluene, or a toluene/cyclohexane mixture (1:1, v:v). 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).

To further improve the selectivity for the Markovnikov product, we tested the effect of catalytic amounts of various additives in the addition of benzoic acid to phenylacetylene. 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 Na_2CO_3, 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 Na_2CO_3 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 $BF_3{\cdot}Et_2O$. 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]



			selectivity [%][c]		
entry	additive	yield [%][b]	**2aa**	(*Z*)-**3aa**	(*E*)-**3aa**
1		29	66	27	7
2	Na_2CO_3	30	67	26	7
3	Cs_2CO_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	$BF_3{\cdot}Et_2O$	26	96	0	4
9	$Li(B[C_6F_5]_4){\cdot}2Et_2O$	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 ^{1}H NMR spectroscopy applying acenaphthene as internal standard. [c]Relative ratio of isomers determined by ^{1}H NMR spectroscopy. [d]Reaction performed without catalyst.

From Table 2, it can be seen that, compared to the absence of any additive (Entry 1, Table 2), the addition of inorganic bases Na_2CO_3 and Cs_2CO_3 did not show any effect on activity or selectivity (Entries 2 and 3, Table 2). The addition of organic bases led to a decline of the activity, probably due to 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 $BF_3{\cdot}Et_2O$ (Entries 8 and 9, Table 2). An additional accelerating

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effect was observed for TfOH (Entry 10, Table 2). On the basis of the excellent results for TfOH, several triflates were tested, among which AgOTf resulted in a further improvement of the activity.[33] Additionally, whether AgOTf exhibits a catalytic activity by itself was also investigated, but no conversion was detected without the use 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), but the best results in terms of activity and selectivity were still reached with 1 mol % of AgOTf.

Besides productivity, the effect of AgOTf on catalytic activity was also 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

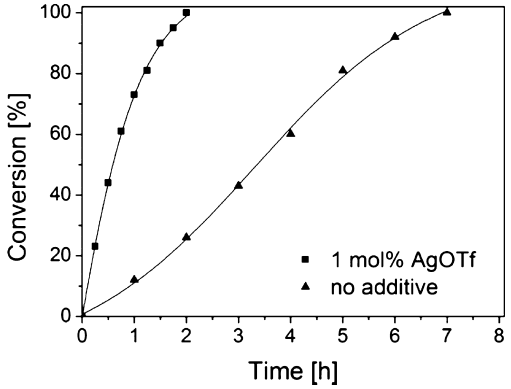

Figure 1. Effect of AgOTf on the reaction profile in the addition of benzoic acid to phenylacetylene catalyzed by **1a** at 70 °C in toluene. Please notice that upon addition of AgOTf solely **2aa** is formed, whereas without additive, a mixture of the three isomers **2aa**:(*Z*)-**3aa**:(*E*)-**3aa**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

additive shows an induction period at the beginning of the conversion and complete conversion after 7 h at 70 °C. However, no induction period is observed with the addition of AgOTf.[33] Instead, a considerably higher reaction rate is seen, and full conversion is already reached after 2 h.

To determine the influence of AgOTf on the activity of 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). The basicity of the phosphine ligand clearly affects the activity of the resulting catalyst, whereby increasing basicity results in the observation of a distinct drop in the catalytic activity. 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 already presented in Figure 1, complete conversion was achieved after 2 h at 70 °C. By lowering the reaction temperature to 60 °C, a nearly 4-fold reaction time is needed to reach almost full conversion. Further decreasing the temperature is not

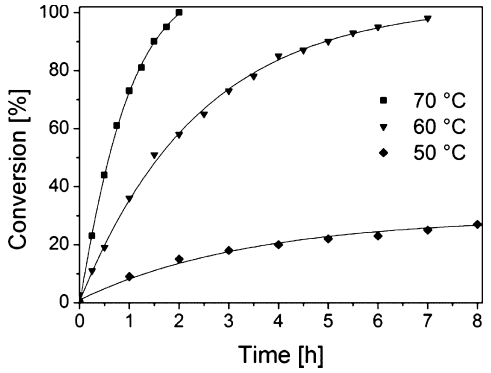

Figure 2. Temperature-dependent reaction profiles for the addition of benzoic acid to phenylacetylene yielding **2aa** catalyzed by **1a** in combination with 1 mol % of AgOTf.

appropriate as quite low productivities were obtained at 50 °C. Apparently, the activity of the catalytic system is reduced for longer reaction times.

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_ρ and the reaction rates in the conversion of a series of *para*-substituted phenylacetylenes and benzoic acids were investigated (Figure 3). The negative ρ value ($\rho = -0.294$) for the addition of benzoic acid to *para*-substituted phenylacetylenes *p*-Y-C_6H_4-C≡CH (Y = OMe, Me, H, Cl, 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,C triple bond to the electrophilic ruthenium atom. On the contrary, for the reaction of *para*-substituted benzoic acids *p*-Z-C_6H_4-CO_2H (Z = OMe, Me, H, Cl, 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.

To assess the substrate scope as well as the tolerance of the reaction toward functional or sterically demanding groups, we carried out substrate screening under optimized reaction conditions at 70 °C by 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.

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**, **2ah**). Next to *para*-substituted phenylacetylenes, substituents in the *ortho*-position are also 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 a reduction in the yields.

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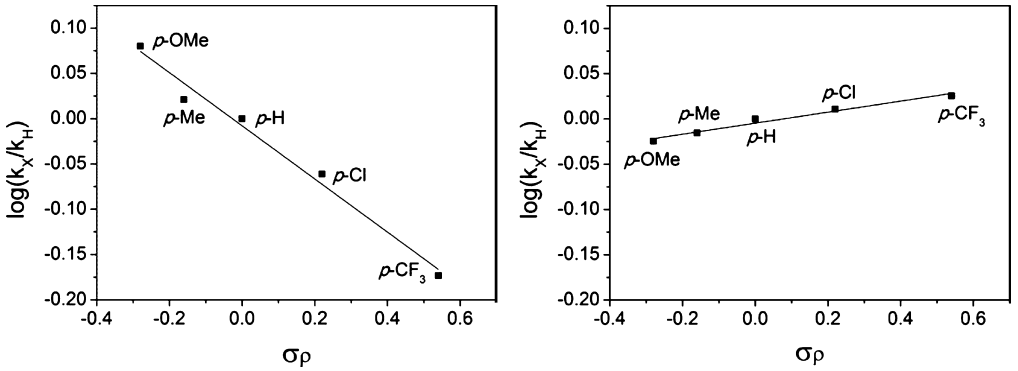
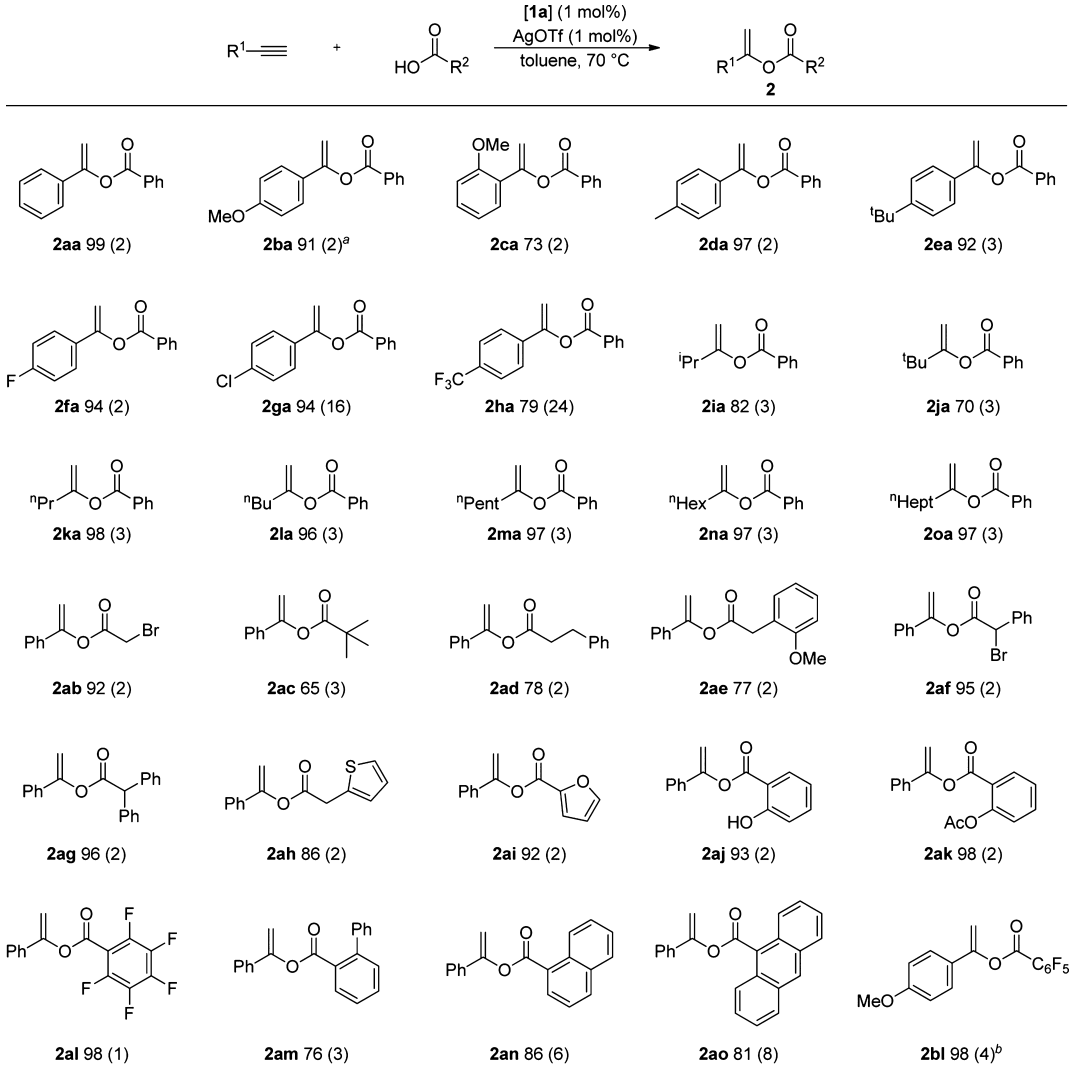


Figure 3. Hammett plots for the conversion of *para*-substituted phenylacetylenes *p*-Y-C_6H_4-C≡CH (Y = OMe, Me, H, Cl, CF_3) with benzoic acid (left; $y = -0.294x - 0.008$, $R^2 = 0.979$) and the conversion of *para*-substituted benzoic acids *p*-Z-C_6H_4-CO_2H (Z = OMe, Me, H, Cl, CF_3) with phenylacetylene (right; $y = 0.061x - 0.005$, $R^2 = 0.964$) in toluene.

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 generality of the carboxylic acid allows the successful conversion of various aliphatic (**2ab**–**ag**), aromatic (**2ah**–**ao**), and even heterocyclic compounds (**2ah**, **2ai**). As estimated from the Hammett plot, strong acidic acids are preferably converted (**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

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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]	ref
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	$[Ru(PPh_3)_2(CH_3CN)_3Cl][BPh_4]$	80	1.0	17	75	26
5	*trans*-$[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)]$	60	2.0	24	60	23
6	$[RuCl_2(p\text{-cymene})]_2/PFur_3$	70	0.8	16	53	27

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

smoothly in the presence of sterically demanding substrates (**2an**, **2ao**) 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 the literature. To date, 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).

CONCLUSIONS

Ruthenium complexes $[Ru(CO)_2(P(p\text{-}C_6H_4\text{-}X)_3)_2(O_2CPh)_2]$ (**1a**, X = CF_3; **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 equiv of 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 the 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 ^{1}H and 125.7 MHz for $^{13}C\{^1H\}$ 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 (^{1}H NMR, $CHCl_3$ δ 7.26; $^{13}C\{^1H\}$ NMR, $CDCl_3$ 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, carboxylic acid (1.0 mmol), alkyne (2.0 mmol), ruthenium catalyst **1** (0.01 mmol), 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 ^{1}H 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-C_6H_4-C≡CH (Y = OMe, Me, H, Cl, CF_3) (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 ^{1}H 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 ^{1}H NMR integration of the product signals (=CH_2) 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-C_6H_4-CO_2H (Z = OMe, Me, H, Cl, CF_3) (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 ^{1}H NMR spectroscopy, applying acenaphthene as internal standard in 30 min intervals. The k_X was estimated from a first-order plot

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of ln[product] vs reaction time rather than ln[carboxylic acid] vs reaction time because the ^{1}H NMR integration of the product signals (=CH_2) was more accurate.

Characterization Data of Catalysis Products. *1-Phenylvinyl Benzoate (**2aa**).*[14,16,18b,c,23−27,29b,c,e] 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 a yellow liquid (221 mg, 99%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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,c,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 a yellow liquid (231 mg, 91%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a yellow liquid (185 mg, 73%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{16}H_{14}O_3Na$ 277.0835; found 277.0833.

*1-(4-Tolyl)vinyl Benzoate (**2da**).*[18b,c,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 a pale yellow liquid (230 mg, 97%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a brown liquid (258 mg, 92%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{19}H_{20}O_2Na$ 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 a pale yellow liquid (227 mg, 94%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a pale yellow liquid (243 mg, 94%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a yellow liquid (231 mg, 79%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a colorless liquid (156 mg, 82%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{12}H_{14}O_2Na$ 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 a colorless liquid (143 mg, 70%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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,f,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 a pale yellow liquid (186 mg, 98%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a pale yellow liquid (195 mg, 96%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a pale yellow liquid (212 mg, 97%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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,c,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 a yellow liquid (226 mg, 97%). ^{1}H NMR ($CDCl_3$, 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),

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7.44−7.50 (m, 2H), 7.56−7.62 (m, 1H), 8.06−8.13 (m, 2H). ^{13}C NMR ($CDCl_3$, 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 a pale yellow liquid (238 mg, 97%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a yellow liquid (222 mg, 92%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a yellow liquid (133 mg, 65%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a yellow solid (197 mg, 78%). Mp 50 °C. ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 a yellow liquid (207 mg, 77%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{17}H_{16}O_3Na$ 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 a colorless liquid (301 mg, 95%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{16}H_{11}O_2$ 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 a pale yellow liquid (300 mg, 96%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{22}H_{18}O_2Na$ 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 a yellow liquid (210 mg, 86%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{14}H_{12}O_2SK$ 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%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{13}H_{11}O_3$ 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 a yellow liquid (224 mg, 93%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{15}H_{12}O_3Na$ 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 a yellow liquid (277 mg, 98%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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: $[M + Na - C(O)CH_2]^+$ calcd for $C_{15}H_{12}O_3Na$ 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 an orange-brown solid (308 mg, 98%). Mp 67 °C. ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{15}H_7F_5O_2Na$ 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 a yellow liquid (228 mg, 76%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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,

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153.2, 166.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{16}O_2Na$ 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 a yellow liquid (235 mg, 86%). ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{19}H_{14}O_2Na$ 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 a yellow solid (261 mg, 81%). Mp 122 °C. ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{23}H_{17}O_2$ 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 a pale yellow solid (336 mg, 98%). Mp 99 °C. ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{16}H_{10}F_5O_3$ 345.0545; found 345.0542.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02293.

Additional catalytic results and the ^{1}H and ^{13}C{^{1}H} NMR spectra of all of the catalysis products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: heinrich.lang@chemie.tu-chemnitz.de. Phone: +49 (0) 371-531-21210. Fax: +49 (0)371-531-21219.

Notes

The authors declare no competing financial interest.

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