ChemPubSoc Europe

DOI: 10.1002/ejoc.201501583

EurJOC European Journal of Organic Chemistry

Full Paper

Ruthenium Catalysis

Ruthenium-Catalyzed Hydrocarboxylation of Internal Alkynes

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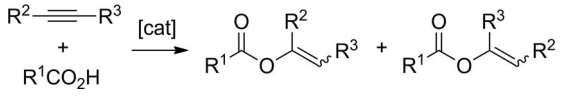
Abstract: The application of the highly efficient ruthenium catalyst $[Ru(CO)_2\{P(p\text{-}CF_3\text{–}C_6H_4)_3\}_2(O_2CPh)_2]$ (**1**) in the selective *syn*-addition of carboxylic acids to internal alkynes, yielding valuable trisubstituted enol esters with (*E*)-configuration, is described. All reactions feature excellent stereoselectivities and good regioselectivities. The regioselectivity is dictated by electronic and steric aspects of the alkyne substituents and the acidity of the carboxylic acid. The catalytic activity can be significantly increased by the addition of catalytic amounts of $B(C_6F_5)_3$. Relative to known catalysts for the synthesis of (*E*)-enol esters, this methodology offers improved selectivity and requires lower catalyst loadings. Moreover, a broad range of alkynes and carboxylic acids can be successfully converted to their corresponding (*E*)-enol esters in high yields.

Introduction

The transition metal-catalyzed hydrocarboxylation of alkynes is the most efficient and atom economic approach for the synthesis of valuable enol esters.[1,2] Such esters can be applied as monomers in numerous polymerization reactions[3,4] and are important intermediates in organic synthesis.[5–11] The first metal found to catalyze this reaction was mercury.[12–14] However, due to its high toxicity, alternatives to mercury have been explored with an emphasis on both effectivity and lack of toxicity.[15–17] Today, the most widely applied catalysts in the addition of carboxylic acids to alkynes are ruthenium complexes.[18–25] However, most of these catalysts fail to enable hydrocarboxylation of internal alkynes since their conversion requires much higher activation energies, the result of significant steric barriers.[26–28] Another challenge involves the control of selectivity; this is especially relevant to the addition of carboxylic acids to unsymmetrically substituted internal alkynes, as this reaction can render up to four isomers whose separation is difficult to achieve (Scheme 1).[29]



Scheme 1. Addition of carboxylic acids to unsymmetrically substituted internal alkynes.

To date only few active catalysts for the hydrocarboxylation of internal alkynes have been developed, including ruthenium,[30–34] palladium,[35,36] silver[37] and gold[38,39] metal complexes. The best catalytic activities have been reported for the gold complexes $[Au(PPh_3)Cl]$[38] and $[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$[39] {IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene}. However, these catalysts lead to the selective formation of (*Z*)-configured enol esters. To the best of our knowledge, the only catalyst reported to favor formation of (*E*)-enol esters is $Ru_3(CO)_{12}$.[32–34] However, this approach requires high catalyst loadings and renders poor reaction selectivity.

Recently, we demonstrated that the mononuclear ruthenium complex $[Ru(CO)_2\{P(p\text{-}CF_3\text{–}C_6H_4)_3\}_2(O_2CPh)_2]$ (**1**) is a highly efficient and selective catalyst for the addition of carboxylic acids to terminal alkynes and propargylic alcohols under mild reaction conditions.[40–42] In continuing these studies, we have investigated the catalytic activity of **1** for hydrocarboxylation of challenging internal alkynes. Herein, the effect of catalytic amounts of various additives on reaction efficiency and selectivity as well as substrate scope is explored and discussed.

Results and Discussion

To study the activity and selectivity of $[Ru(CO)_2\{P(p\text{-}CF_3\text{–}C_6H_4)_3\}_2(O_2CPh)_2]$ (**1**) (Figure 1) in the addition of carboxylic acids to internal alkynes, the conversion of benzoic acid with symmetrically substituted 3-hexyne was selected as a model reaction. Toluene was chosen as solvent since it had proven to be the best solvent for this catalytic system.[40–42] By applying 1.0 mol-% of catalyst **1**, a conversion of 70 % was reached after 6 h at 140 °C (Table 1, Entry 1). Interestingly, this reaction led to the formation of (*E*)-**2a** as the exclusive product.[43] Relative to our previously reported protocol for the conversion of terminal alkynes, higher reaction temperatures were required due to the increased activation energy.[42]

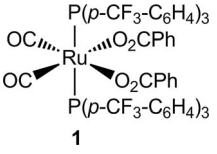


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Figure 1. Structure of catalyst **1**.

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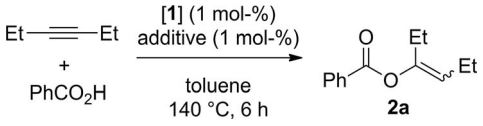
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201501583.

Table 1. Influence of additives on the catalytic performance of **1** in the addition of benzoic acid to 3-hexyne.[a]



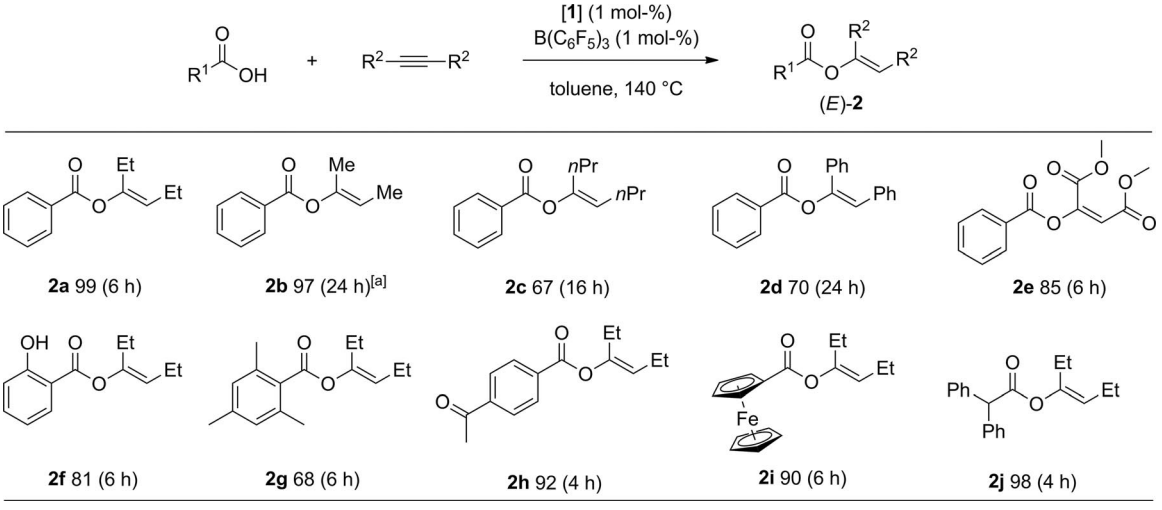
Entry	Additive	Yield[b] [%]	Selectivity [%][c] (*Z*)-**2a**	(*E*)-**2a**
1	–	70	0	100
2	Na_2CO_3	69	0	100
3	DMAP	41	0	100
4	KOTf	86	1	99
5	$Mg(OTf)_2$	85	1	99
6	AgOTf	55	55	45
7	$AgPF_6$	73	2	98
8	$AgNO_3$	82	2	98
9	$AgBF_4$	90	0	100
10	$B(C_6F_5)_3$	100	0	100

[a] Reaction conditions: benzoic acid (1.0 mmol), 3-hexyne (1.5 mmol), **1** (1.0 mol-%), additive (1.0 mol-%), acenaphthene (0.5 mmol), toluene (1 mL), 140 °C, 6 h. [b] Total yield determined by ^{1}H NMR spectroscopy using acenaphthene as an internal standard. [c] Relative ratio of isomers determined by ^{1}H NMR spectroscopy.

In former studies on the preparation of enol esters it could be shown that the addition of catalytic amounts of Lewis acids or bases can significantly enhance the reaction rate or allow for control of the selectivity.[23,25,36,38,42] To improve the activity, the impact of diverse additives (1.0 mol-%) was examined (Table 1). From Table 1 it is obvious that the addition of bases such as Na_2CO_3 or 4-(dimethylamino)pyridine (DMAP) had no impact on catalytic performance (Table 1, Entry 2) or even led to a drop of activity (Table 1, Entry 3). On the contrary, the addition of triflates like KOTf or $Mg(OTf)_2$ resulted in a slight increase in yields (Table 1, Entries 4 and 5). However, when the reaction was performed in the presence of AgOTf reaction selectivity was reversed and (*Z*)-**2a** was observed as the main isomer (Table 1, Entry 6). A possible explanation for this finding might be that initially formed (*E*)-product isomerizes to the (*Z*)-isomer. This hypothesis is especially compelling since trifluoromethanesulfonic acid and their metal salts are known to catalyze this reaction.[38,44] Other silver compounds gave again (*E*)-**2a** as major product with excellent selectivities of up to 100 % (Table 1, Entries 7–9). The best set of reaction conditions, in terms of activity and selectivity, was achieved upon addition of $B(C_6F_5)_3$ (Entry 10).[45] The accelerating effect of $B(C_6F_5)_3$ may be the result of π-coordination of the boron to the triple bond, since $B(C_6F_5)_3$ is known to activate alkynes towards nucleophilic attack.[46,47] Moreover, $B(C_6F_5)_3$ can also enhance the acidity of the carboxylic acid via carbonyl oxygen coordination.[47–49] Due to its accelerating effect all following reactions of symmetrically substituted internal alkynes were carried out in the presence of 1.0 mol-% **1** and $B(C_6F_5)_3$, respectively.

To assess the substrate scope of this reaction as well as its tolerance for various functional groups, diverse symmetrically substituted internal alkynes were reacted with carboxylic acids (Scheme 2). Reactions were monitored on the basis of regular sampling by ^{1}H NMR spectroscopy in order to optimize the reaction times. All products of this substrate screening were isolated in good to excellent yields (67–99 %) and were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Additionally, novel compounds were characterized by high resolution mass spectrometry (HRMS).

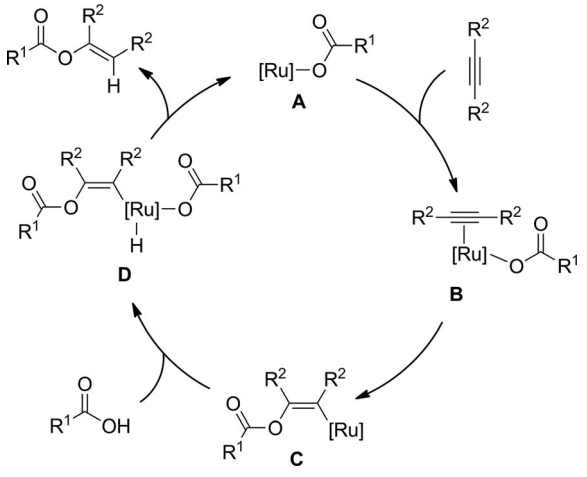
Several aliphatic alkynes of different chain lengths were examined, revealing that conversion of 4-octyne (**2c**, Scheme 2) needed significantly longer reaction times than did 3-hexyne (**2a**). Correspondingly, the smallest substrate, 2-butyne (**2b**), could be successfully converted at a decreased reaction temperature of 120 °C. Not surprisingly, the reaction of sterically more challenging diphenylacetylene (**2d**) required the longest reaction time of 24 h, whereas dimethyl acetylenedicarboxylate (**2e**) was smoothly converted within 6 h. In addition to the substrate scope of the alkyne, reaction tolerance of various carboxylic acids was investigated. Hereby, not only *para*-substituted



Scheme 2. Substrate screening for conversion of symmetrically substituted internal alkynes. Reaction conditions: carboxylic acid (1.0 mmol), alkyne (1.5 mmol), **1** (1.0 mol-%), $B(C_6F_5)_3$ (1.0 mol-%), toluene (1 mL), 140 °C, isolated yields, optimized reaction times are given in parentheses. [a] Reaction performed at 120 °C.

benzoic acids (**2g**,**h**), but also, single or double *ortho*-substituted carboxylic acids (**2f**,**g**) were converted in very good yields. Reactions involving electron-deficient acids gave excellent results (**2h**), whereas electron-rich substrates correlated to slightly reduced yields (**2g**). In addition, the reaction proceeded smoothly in the presence of ferrocenecarboxylic acid (**2i**) and was not affected by functional groups like the free hydroxyl group of salicylic acid (**2f**). In addition, aliphatic acids such as diphenylacetic acid (**2j**) were also found to be well tolerated.

Of particular note in the conversion of all symmetrically substituted internal alkynes is that only a single isomer bearing the (*E*)-configuration was obtained. Hence, the reaction proceeds by a *syn*-addition of the carboxylic acid to the alkyne. This can be rationalized by insertion of the coordinated triple bond into the Ru–O bond as presented in complex **C** (Scheme 3).



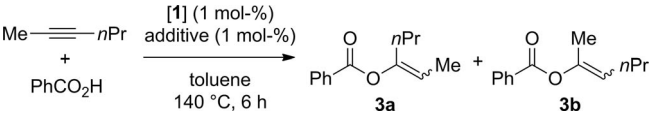
Scheme 3. Proposed mechanistic cycle for enol ester generation.[34]

In cases **2f**–**j** (Scheme 2), when carboxylic acids other than benzoic acid were applied, the formation of up to 2 % of the benzoate product **2a** was observed, presumably arising from conversion of the benzoate ligands on initial catalyst **1**.[40–42] Compared to previously reported results on the formation of (*E*)-isomers, the current conditions employing **1** and $B(C_6F_5)_3$ led to higher selectivities while using both lower catalyst loadings and similar or even reduced reaction times.[32–34]

Having demonstrated that, with catalyst **1**, a broad range of symmetrically substituted internal alkynes could be successfully converted to isomerically pure (*E*)-enol esters, we were encouraged to study the reaction with unsymmetrically substituted internal alkynes. Consequently, the influences of several additives on the activities and selectivities achievable in the addition of benzoic acid to 2-hexyne were investigated (Table 2).

In the absence of additive, hydrocarboxylation of 2-hexyne with benzoic acid proceeded with a conversion of 63 % after 6 h at 140 °C (Table 2, Entry 1); this is comparable to the reaction with symmetrically substituted 3-hexyne (Table 1, Entry 1). In considering the selectivity of the reaction, it is notable that

Table 2. Influence of additives on the catalytic performance of **1** in the addition of benzoic acid to 2-hexyne.[a]



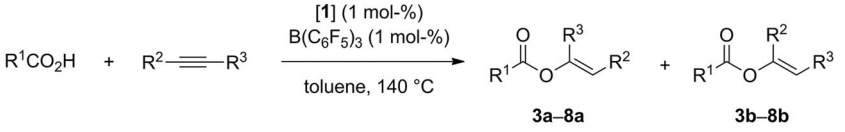
Entry	Additive	Yield[b] [%]	Selectivity [%][c] (*Z*)-**3a**	(*E*)-**3a**	(*Z*)-**3b**	(*E*)-**3b**
1	–	63	0	68	0	32
2	Na_2CO_3	73	0	68	0	32
3	DMAP	35	0	67	0	33
4	KOTf	76	5	61	5	29
5	$Mg(OTf)_2$	100	3	63	3	30
6	AgOTf	61	36	9	41	14
7	$AgPF_6$	75	13	49	16	21
8	$AgNO_3$	92	0	68	0	32
9	$AgBF_4$	46	7	57	7	29
10	$B(C_6F_5)_3$	100	0	69	0	31

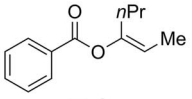
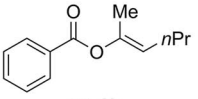
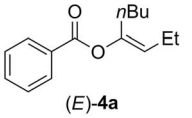
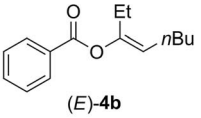
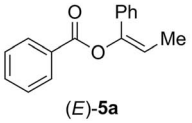
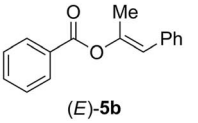
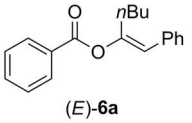
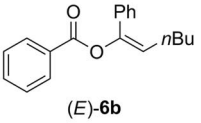
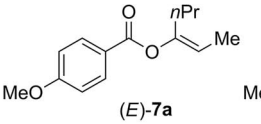
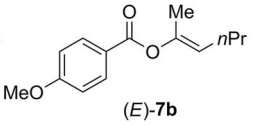
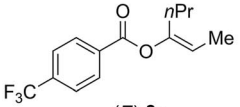
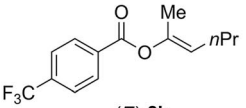
[a] Reaction conditions: benzoic acid (1.0 mmol), 2-hexyne (1.5 mmol), **1** (1.0 mol-%), additive (1.0 mol-%), acenaphthene (0.5 mmol), toluene (1 mL), 140 °C, 6 h. [b] Total yield determined by ^{1}H NMR spectroscopy using acenaphthene as an internal standard. [c] Relative ratio of isomers determined by ^{1}H NMR spectroscopy.

only two out of four possible isomers were formed in a ratio of 2:1 for **3a**:**3b**. The products formed (**3a**,**b**) both possess the (*E*)-configuration indicating a *syn*-addition of the carboxylic acid. None of the additives tested led to an improvement in selectivity. In fact, the addition of several triflates (Table 2, Entries 4–6), $AgPF_6$ (Table 2, Entry 7) and $AgBF_4$ (Table 2, Entry 9) diminished reaction selectivity. Full conversion within 6 h was obtained upon addition of $B(C_6F_5)_3$ (Table 2, Entry 10). Because of the enhanced activity and the unchanged selectivity of 2:1 for (*E*)-**3a**:(*E*)-**3b**, all further reactions with unsymmetrically substituted internal alkynes were performed in the presence of $B(C_6F_5)_3$ additive.

In the substrate screening reactions with unsymmetrically substituted internal alkynes only the two *syn*-addition products with (*E*)-configuration have been observed. As a result, it appears that the regioselectivity of nucleophilic attack by the carboxylic acid is subject to the influence of triple bond substituents (Table 3). The more different the electronic or steric demands of the alkyne substituents are, the greater the regioselectivity of the reaction is likely to be. The highest selectivity was obtained for the conversion of 1-phenyl-1-hexyne (Table 3, Entry 4), whereas the lowest selectivity was observed for the reaction of 3-octyne (Table 3, Entry 2). Rotem and Shvo have performed a similar addition of benzoic acid to 1-phenyl-1-heptyne with $Ru_3(CO)_{12}$ as the catalyst, but observed the formation of all four possible isomers, in addition to two rearranged products of type $R^1CO_2CH{=}CR^2R^3$.[33] In addition to the alkyne substituents, the acidity of the carboxylic acid also appears to exert a small influence. Consequently, reaction regioselectivity may be slightly improved via the use of more acidic acids (Table 3, Entries 5 and 6).

Table 3. Substrate screening for the conversion of unsymmetrically substituted internal alkynes.[a]



Entry	Product	Time [h]	Yield [%][b]	Ratio[c]
1	 (*E*)-**3a**  (*E*)-**3b**	6	99	67:33
2	 (*E*)-**4a**  (*E*)-**4b**	16	73	56:44
3	 (*E*)-**5a**  (*E*)-**5b**	8	97	67:33
4	 (*E*)-**6a**  (*E*)-**6b**	16	80	72:28
5	 (*E*)-**7a**  (*E*)-**7b**	6	91	62:38
6	 (*E*)-**8a**  (*E*)-**8b**	6	96	72:28

[a] Reaction conditions: carboxylic acid (1.0 mmol), alkyne (1.5 mmol), **1** (1.0 mol-%), $B(C_6F_5)_3$ (1.0 mol-%), acenaphthene (0.5 mmol), toluene (1 mL), 140 °C. [b] Isolated yield. [c] Relative ratio of isomers determined by ^1H NMR spectroscopy.

Conclusions

We demonstrate herein that $[Ru(CO)_2\{P(p\text{-}CF_3\text{–}C_6H_4)_3\}_2(O_2CPh)_2]$ (**1**) is a highly efficient and selective catalyst for the hydrocarboxylation of internal alkynes to give trisubstituted enol esters. All reactions proceeded by a *syn*-addition of the carboxylic acid and hence, led to selective formation of the (*E*)-configured products. Consequently, the conversion of symmetrically substituted alkynes resulted in generation of a single product with 100 % stereoselectivity. Conversely, the reaction of unsymmetrically substituted alkynes afforded two regioisomers. Regioselectivity was found to be influenced by electronic and steric effects associated with the alkyne substituents as well as the acidity of the carboxylic acid. Furthermore, the catalytic activity could be significantly increased by the addition of catalytic $B(C_6F_5)_3$ which had no impact upon reaction selectivity. Relative to previously reported catalysts for the formation of (*E*)-enol esters,[32–34] our catalytic system requires lower catalyst loadings, is highly selective, and broadly applicable to the conversion of diverse internal alkynes and carboxylic acids en route to enol esters.

Experimental Section

General Information: Compound **1** was prepared according to a previously published procedure.[40] Toluene was dried using a solvent purification system (MB SPS-800, MBraun). Acenaphthene was purified by sublimation at 75 °C (1.0 mbar). All other chemicals were purchased from commercial suppliers and were used without further purification. For column chromatography silica with a particle size of 40–60 μm [230–400 mesh (ASTM), Macherey–Nagel] was used. NMR spectra were recorded with a Bruker Advance III 500 spectrometer operating at 500.3 MHz for ^1H 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 [^1H NMR, $CHCl_3$ δ = 7.26; $^{13}C(^1H)$ NMR, $CDCl_3$ δ = 77.16 ppm]. High resolution mass spectra were recorded with a Bruker Daltonite micrOTOF-QII spectrometer using electro-spray ionization (ESI).

General Procedure for the Catalytic Reactions: In a screw-capped vial and under an atmosphere of argon the carboxylic acid (1.0 mmol), the alkyne (1.5 mmol), the ruthenium catalyst **1** (0.01 mmol, 1.0 mol-%), the additive (0.01 mmol, 1.0 mol-%) and acenaphthene (77 mg, 0.5 mmol) were dissolved in toluene (1 mL). The sealed vial was immersed in a heating mantle preheated to 140 °C and stirred for 4–24 h. The progress of the reaction was monitored by regular sampling and analysis by ^{1}H NMR spectroscopy applying acenaphthene as an internal standard. Analytically pure products were isolated by column chromatography on silica gel (volume: 3 × 7 cm) using *n*-hexane/ethyl acetate (99:1, v/v) as eluent. All catalytic results have been verified by at least two independent experiments.

Characterization Data of Catalysis Products

(*E*)-Hex-3-en-3-yl Benzoate (2a): Benzoic acid (122 mg, 1.0 mmol) was reacted with 3-hexyne (123 mg, 1.5 mmol) for 6 h at 140 °C, yielding **2a** as a yellow liquid after appropriate work-up (203 mg, 99 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 1.05 [t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3], 1.08 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 2.13 (dt, $J_{H,H}$ = 7.6, $J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 2.40 (q, $J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 5.22 [t, $J_{H,H}$ = 7.7 Hz, 1 H, =CH(Et)], 7.42–7.48 (m, 2 H, *m*-CH/Ph), 7.54–7.60 (m, 1 H, *p*-CH/Ph), 8.07–8.12 (m, 2 H, *o*-CH/Ph) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 11.8, 14.6, 19.9, 22.5, 119.1, 128.5, 129.9, 130.3, 133.2, 150.0, 165.5 ppm. HRMS (ESI-TOF): calcd. for $C_{13}H_{16}O_2Na$ [M + Na]$^+$ 227.1043, found 227.1026.

(*E*)-But-2-en-2-yl Benzoate (2b): Benzoic acid (122 mg, 1.0 mmol) was reacted with 2-butyne (81 mg, 1.5 mmol) for 24 h at 120 °C, yielding **2b** as a pale yellow liquid after appropriate work-up (171 mg, 97 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 1.70 (dq, $J_{H,H}$ = 7.1, $J_{H,H}$ = 1.1 Hz, 3 H, CH_3), 1.98 (dq, $J_{H,H}$ = 2.3, $J_{H,H}$ = 1.1 Hz, 3 H, CH_3), 5.30 [qq, $J_{H,H}$ = 7.1, $J_{H,H}$ = 1.1 Hz, 1 H, =CH(Me)], 7.42–7.48 (m, 2 H, *m*-CH/Ph), 7.54–7.59 (m, 1 H, *p*-CH/Ph), 8.05–8.11 (m, 2 H, *o*-CH/Ph) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 11.9, 15.1, 112.2, 128.5, 129.9, 130.3, 133.2, 146.1, 165.4 ppm. The analytical data are in agreement with ref.[50]

(*E*)-Oct-4-en-4-yl Benzoate (2c): Benzoic acid (122 mg, 1.0 mmol) was reacted with 4-octyne (165 mg, 1.5 mmol) for 16 h at 140 °C, yielding **2c** as a yellow liquid after appropriate work-up (155 mg, 67 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.41–1.56 (m, 4 H, CH_2), 2.07–2.14 (m, 2 H, CH_2), 2.37 (t, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 5.27 [t, $J_{H,H}$ = 7.8 Hz, 1 H, =CH(*n*Pr)], 7.43–7.48 (m, 2 H, *m*-CH/Ph), 7.55–7.60 (m, 1 H, *p*-CH/Ph), 8.07–8.11 (m, 2 H, *o*-CH/Ph) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 13.81, 13.83, 20.3, 23.0, 28.7, 31.1, 118.3, 128.5, 130.0, 130.4, 133.2, 149.0, 165.5 ppm. The analytical data are in agreement with ref.[33]

(*E*)-1,2-Diphenylvinyl Benzoate (2d): Benzoic acid (122 mg, 1.0 mmol) was reacted with diphenylacetylene (267 mg, 1.5 mmol) for 24 h at 140 °C, yielding **2d** as a yellow liquid after appropriate work-up (210 mg, 70 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 6.69 [s, 1 H, =CH(Ph)], 7.23–7.28 (m, 5 H, CH/Ph), 7.33–7.37 (m, 3 H, CH/Ph), 7.51–7.56 (m, 4 H, CH/Ph), 7.63–7.68 (m, 1 H, CH/Ph), 8.22–8.25 (m, 2 H, CH/Ph) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 120.3, 127.4, 128.4, 128.5, 128.6, 128.9, 129.0, 129.1, 129.8, 130.2, 133.5, 134.4, 134.7, 147.8, 165.2 ppm. The analytical data are in agreement with ref.[32,33]

Dimethyl 2-(Benzoyloxy)maleate (2e): Benzoic acid (122 mg, 1.0 mmol) was reacted with dimethyl acetylenedicarboxylate (213 mg, 1.5 mmol) for 6 h at 140 °C, yielding **2e** as a yellow liquid after appropriate work-up (224 mg, 85 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 3.80 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.23 (s, 1 H, =CH), 7.45–7.51 (m, 2 H, *m*-CH/Ph), 7.60–7.66 (m, 1 H, *p*-CH/Ph), 8.05–8.10 (m, 2 H, *o*-CH/Ph) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 52.4, 53.1, 115.5, 127.8, 128.8, 130.5, 134.5, 147.6, 161.8, 163.7, 164.4 ppm. The analytical data are in agreement with ref.[33]

(*E*)-Hex-3-en-3-yl 2-Hydroxybenzoate (2f): Salicylic acid (138 mg, 1.0 mmol) was reacted with 3-hexyne (123 mg, 1.5 mmol) for 6 h at 140 °C, yielding **2f** as a yellow liquid after appropriate work-up (178 mg, 81 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 1.06 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.08 (t, $J_{H,H}$ = 7.6 Hz, 3 H, CH_3), 2.14 (dt, $J_{H,H}$ = 7.6, $J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 2.40 (q, $J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 5.25 [t, $J_{H,H}$ = 7.7 Hz, 1 H, =CH(Et)], 6.90 (ddd, $J_{H,H}$ = 8.1, 7.3, 1.0 Hz, 1 H, CH/Ph), 7.00 (dd, $J_{H,H}$ = 8.4, $J_{H,H}$ = 0.8 Hz, 1 H, CH/Ph), 7.48 (ddd, $J_{H,H}$ = 8.8, 7.4, 1.7 Hz, 1 H, CH/Ph), 7.91 (dd, $J_{H,H}$ = 8.0, 1.7 Hz, 1 H, CH/Ph) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 11.8, 14.5, 19.9, 22.5, 112.5, 117.8, 119.3, 119.8, 130.3, 136.1, 149.5, 162.1, 169.4 ppm. HRMS (ESI-TOF): calcd. for $C_{13}H_{16}O_3Na$ [M + Na]$^+$ 243.0992, found 243.1009.

(*E*)-Hex-3-en-3-yl 2,4,6-Trimethylbenzoate (2g): 2,4,6-Trimethylbenzoic acid (164 mg, 1.0 mmol) was reacted with 3-hexyne (123 mg, 1.5 mmol) for 6 h at 140 °C, yielding **2g** as a yellow solid after appropriate work-up (167 mg, 68 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 1.07 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.12 (t, $J_{H,H}$ = 7.6 Hz, 3 H, CH_3), 2.15 (dt, $J_{H,H}$ = 7.6, $J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 2.30 (s, 3 H, CH_3), 2.38 (s, 6 H, CH_3), 2.42 (q, $J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 5.24 [t, $J_{H,H}$ = 7.7 Hz, 1 H, =CH(Et)], 6.87–6.89 (m, 2 H, CH/Ph) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 12.2, 14.6, 19.9, 20.0, 21.2, 22.8, 119.2, 128.6, 131.0, 135.2, 139.4, 150.2, 169.1 ppm. HRMS (ESI-TOF): calcd. for $C_{16}H_{23}O_2$ [M + H]$^+$ 247.1693, found 247.1700.

(*E*)-Hex-3-en-3-yl 4-Acetylbenzoate (2h): 4-Acetylbenzoic acid (164 mg, 1.0 mmol) was reacted with 3-hexyne (123 mg, 1.5 mmol) for 4 h at 140 °C, yielding **2h** as a yellow liquid after appropriate work-up (226 mg, 92 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 1.05 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.07 (t, $J_{H,H}$ = 7.6 Hz, 3 H, CH_3), 2.13 (dt, $J_{H,H}$ = 7.5, $J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.40 (q, $J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.64 [s, 3 H, $C(O)CH_3$], 5.23 [t, $J_{H,H}$ = 7.7 Hz, 1 H, =CH(Et)], 8.00–8.04 (m, 2 H, CH/Ph), 8.14–8.18 (m, 2 H, CH/Ph) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 11.9, 14.6, 19.9, 22.4, 27.0, 119.4, 128.4, 130.2, 134.1, 140.5, 150.0, 164.7, 197.6 ppm. HRMS (ESI-TOF): calcd. for $C_{15}H_{19}O_3$ [M + H]$^+$ 247.1329, found 247.1365.

(*E*)-Hex-3-en-3-yl Ferrocene Carboxylate (2i): Ferrocene carboxylic acid (230 mg, 1.0 mmol) was reacted with 3-hexyne (123 mg, 1.5 mmol) for 6 h at 140 °C, yielding **2i** as an orange solid after appropriate work-up (281 mg, 90 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 1.05 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.11 (t, $J_{H,H}$ = 7.6 Hz, 3 H, CH_3), 2.12 (dt, $J_{H,H}$ = 7.5, $J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.37 (q, $J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 4.24 (s, 5 H, C_5H_5), 4.41–4.43 (m, 2 H, C_5H_4), 4.84–4.86 (m, 2 H, C_5H_4), 5.16 [t, $J_{H,H}$ = 7.7 Hz, 1 H, =CH(Et)] ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 12.0, 14.7, 20.0, 22.6, 69.9, 70.5, 71.2, 71.6, 118.9, 150.0, 170.7 ppm. HRMS (ESI-TOF): calcd. for $C_{17}H_{21}FeO_2$ [M + H]$^+$ 313.0886, found 313.0898.

(*E*)-Hex-3-en-3-yl 2,2-Diphenylacetate (2j): Diphenylacetic acid (212 mg, 1.0 mmol) was reacted with 3-hexyne (123 mg, 1.5 mmol) for 4 h at 140 °C, yielding **2j** as a yellow liquid after appropriate work-up (288 mg, 98 %). ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.01 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 2.07 (dt, $J_{H,H}$ = 7.6, $J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 2.27 (q, $J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 5.09–5.13 [m, 2 H, =CH(Et), $CH(Ph)_2$], 7.27–7.31 (m, 2 H, CH/Ph), 7.33–7.42 (m, 8 H, CH/Ph) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 11.7, 14.5, 19.8, 22.3, 57.2, 118.9, 127.4, 128.7, 128.8, 138.7, 150.0, 171.3 ppm. HRMS (ESI-TOF): calcd. for $C_{20}H_{23}O_2$ [M + H]$^+$ 295.1693, found 295.1699.

3: Benzoic acid (122 mg, 1.0 mmol) was reacted with 2-hexyne (123 mg, 1.5 mmol) for 6 h at 140 °C, yielding a mixture of (*E*)-hex-2-en-3-yl benzoate (**3a**) and (*E*)-hex-2-en-2-yl benzoate (**3b**) as a yellow liquid after appropriate work-up (203 mg, 99 %, ratio **3a**:**3b** = 67:33). **3a**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.48–1.57 (m, 2 H, CH_2), 1.72 (d, $J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 2.37 (t, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 5.32 [q, $J_{H,H}$ = 7.1 Hz, 1 H, = $CH(CH_3)$], 7.43–7.48 (m, 2 H, *m*-CH/Ph), 7.55–7.60 (m, 1 H, *p*-CH/Ph), 8.06–8.11 (m, 2 H, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 11.9, 13.7, 20.2, 30.8, 112.7, 128.5, 130.0, 130.4, 133.2, 149.5, 165.5 ppm. HRMS (ESI-TOF): calcd. for $C_{13}H_{16}O_2Na$ $[M + Na]^+$ 227.1043, found 227.1068. **3b**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.42–1.50 (m, 2 H, CH_2), 1.98 (d, $J_{H,H}$ = 0.9 Hz, 3 H, CH_3), 2.08 (q, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 5.25 [t, $J_{H,H}$ = 7.8 Hz, 1 H, =CH(*n*Pr)], 7.43–7.48 (m, 2 H, *m*-CH/Ph), 7.55–7.60 (m, 1 H, *p*-CH/Ph), 8.06–8.11 (m, 2 H, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 13.8, 15.4, 22.8, 28.8, 117.8, 128.5, 130.0, 130.3, 133.2, 145.8, 165.4 ppm. The analytical data are in agreement with ref.[50]

4: Benzoic acid (122 mg, 1.0 mmol) was reacted with 3-octyne (165 mg, 1.5 mmol) for 16 h at 140 °C, yielding a mixture of (*E*)-oct-3-en-4-yl benzoate (**4a**) and (*E*)-oct-3-en-3-yl benzoate (**4b**) as a yellow liquid after appropriate work-up (170 mg, 73 %, ratio **4a**:**4b** = 56:44). **4a**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, $J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 1.05 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.33–1.42 (m, 4 H, CH_2), 2.10–2.17 (m, 2 H, CH_2), 2.38 (t, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 5.25 [t, $J_{H,H}$ = 7.8 Hz, 1 H, =CH(Et)], 7.43–7.49 (m, 2 H, *m*-CH/Ph), 7.55–7.60 (m, 1 H, *p*-CH/Ph), 8.07–8.11 (m, 2 H, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 14.0, 14.6, 20.1, 22.3, 22.4, 28.8, 119.8, 128.5, 130.0, 130.4, 133.2, 148.8, 165.5 ppm. HRMS (ESI-TOF): calcd. for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ 255.1356, found 255.1338. **4b**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.93 (t, $J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.07 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.42–1.51 (m, 4 H, CH_2), 2.09–2.15 (m, 2 H, CH_2), 2.40 (q, $J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 5.21 [t, $J_{H,H}$ = 8.2 Hz, 1 H, =CH(*n*Bu)], 7.43–7.49 (m, 2 H, *m*-CH/Ph), 7.55–7.60 (m, 1 H, *p*-CH/Ph), 8.07–8.11 (m, 2 H, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 11.8, 14.0, 22.5, 26.2, 29.3, 32.0, 117.6, 128.5, 130.0, 130.4, 133.2, 150.3, 165.5 ppm.

5: Benzoic acid (122 mg, 1.0 mmol) was reacted with 1-phenyl-1-propyne (174 mg, 1.5 mmol) for 8 h at 140 °C, yielding a mixture of (*E*)-1-phenylprop-1-en-1-yl benzoate (**5a**) and (*E*)-1-phenylprop-1-en-2-yl benzoate (**5b**) as a yellow liquid after appropriate work-up (230 mg, 97 %, ratio **5a**:**5b** = 67:33). **5a**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 1.92 (d, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 5.71 [q, $J_{H,H}$ = 7.4 Hz, 1 H, =CH(Me)], 7.27–7.41 (m, 4 H, CH/Ph), 7.46–7.54 (m, 3 H, CH/Ph), 7.58–7.65 (m, 1 H, *p*-CH/Ph), 8.13–8.19 (m, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 13.0, 114.9, 128.29, 128.33, 128.6, 130.0, 130.07, 130.10, 133.4, 134.5, 147.0, 165.6 ppm. HRMS (ESI-TOF): calcd. for $C_{16}H_{15}O_2$ $[M + H]^+$ 239.1067, found 239.1076. **5b**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 2.27 (d, $J_{H,H}$ = 1.0 Hz, 3 H, CH_3), 6.44 [s, 1 H, =CH(Ph)], 7.27–7.41 (m, 4 H, CH/Ph), 7.46–7.54 (m, 3 H, CH/Ph), 7.58–7.65 (m, 1 H, *p*-CH/Ph), 8.13–8.19 (m, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 17.4, 119.1, 127.0, 128.4, 128.5, 128.6, 128.9, 130.0, 133.5, 135.0, 148.3, 165.2 ppm.

6: Benzoic acid (122 mg, 1.0 mmol) was reacted with 1-phenyl-1-hexyne (237 mg, 1.5 mmol) for 16 h at 140 °C, yielding a mixture of (*E*)-1-phenylhex-1-en-2-yl benzoate (**6a**) and (*E*)-1-phenylhex-1-en-1-yl benzoate (**6b**) as a yellow liquid after appropriate work-up (224 mg, 80 %, ratio **6a**:**6b** = 72:28). **6a**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.35–1.44 (m, 2 H, CH_2), 1.55–1.64 (m, 2 H, CH_2), 2.63–2.69 (m, 2 H, CH_2), 6.43 [s, 1 H, = CH(Ph)], 7.25–7.42 (m, 5 H, CH/Ph), 7.45–7.55 (m, 2 H, CH/Ph), 7.58–7.65 (m, 1 H, CH/Ph), 8.13–8.19 (m, 2 H, CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 13.9, 22.5, 29.1, 29.9, 119.3, 127.0, 128.3, 128.6, 128.9, 130.1, 133.4, 135.1, 151.9, 165.2 ppm. HRMS (ESI-TOF): calcd. for $C_{19}H_{21}O_2$ $[M + H]^+$ 281.1536, found 281.1551. **6b**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.92 (t, $J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 1.35–1.44 (m, 2 H, CH_2), 1.45–1.53 (m, 2 H, CH_2), 2.30–2.36 (m, 2 H, CH_2), 5.63 [t, $J_{H,H}$ = 7.8 Hz, 1 H, =CH(*n*Bu)], 7.25–7.42 (m, 5 H, CH/Ph), 7.45–7.55 (m, 2 H, CH/Ph), 7.58–7.65 (m, 1 H, CH/Ph), 8.13–8.19 (m, 2 H, CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.4, 27.0, 32.2, 120.8, 128.30, 128.32, 128.4, 128.6, 130.1, 133.3, 134.8, 146.4, 165.5 ppm.

7: 4-Methoxybenzoic acid (152 mg, 1.0 mmol) was reacted with 2-hexyne (123 mg, 1.5 mmol) for 6 h at 140 °C, yielding a mixture of (*E*)-hex-2-en-3-yl 4-methoxybenzoate (**7a**) and (*E*)-hex-2-en-2-yl 4-methoxybenzoate (**7b**) as a yellow liquid after appropriate work-up (213 mg, 91 %, ratio **7a**:**7b** = 62:38). **7a**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.94 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.48–1.55 (m, 2 H, CH_2), 1.70 (d, $J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 2.35 (t, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 3.86 (s, 3 H, OCH_3), 5.29 [q, $J_{H,H}$ = 7.1 Hz, 1 H, =CH(CH_3)], 6.90–6.94 (m, 2 H, *m*-CH/Ph), 8.01–8.04 (m, 2 H, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 11.9, 13.7, 20.2, 30.8, 55.5, 112.5, 113.8, 122.7, 132.0, 149.5, 163.6, 165.3 ppm. HRMS (ESI-TOF): calcd. for $C_{14}H_{18}O_3Na$ $[M + Na]^+$ 257.1148, found 257.1137. **7b**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.95 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.40–1.48 (m, 2 H, CH_2), 1.96 (d, $J_{H,H}$ = 0.9 Hz, 3 H, CH_3), 2.06 (q, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 3.86 (s, 3 H, OCH_3), 5.22 [t, $J_{H,H}$ = 7.8 Hz, 1 H, = CH(*n*Pr)], 6.90–6.94 (m, 2 H, *m*-CH/Ph), 8.01–8.04 (m, 2 H, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 13.8, 15.5, 22.9, 28.8, 55.5, 113.7, 117.6, 122.7, 132.0, 145.8, 163.6, 165.2 ppm.

8: 4-(Trifluoromethyl)benzoic acid (190 mg, 1.0 mmol) was reacted with 2-hexyne (123 mg, 1.5 mmol) for 6 h at 140 °C, yielding a mixture of (*E*)-hex-2-en-3-yl 4-(trifluoromethyl)benzoate (**8a**) and (*E*)-hex-2-en-2-yl 4-(trifluoromethyl)benzoate (**8b**) as a yellow liquid after appropriate work-up (262 mg, 96 %, ratio **8a**:**8b** = 72:28). **8a**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.95 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.47–1.56 (m, 2 H, CH_2), 1.72 (d, $J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 2.37 (t, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 5.34 [q, $J_{H,H}$ = 7.1 Hz, 1 H, =CH(CH_3)], 7.69–7.73 (m, 2 H, *m*-CH/Ph), 8.16–8.21 (m, 2 H, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 11.8, 13.7, 20.2, 30.7, 113.1, 123.8 (q, $J_{C,F}$ = 273 Hz, CF_3), 125.5–125.6 (m, *m*-CH/Ph), 130.4, 133.6, 134.7 (q, $J_{C,F}$ = 32.7 Hz, CCF_3), 149.4, 164.3 ppm. HRMS (ESI-TOF): calcd. for $C_{14}H_{15}F_3O_2Na$ $[M + Na]^+$ 295.0916, found 295.0920. **8b**: ^{1}H NMR (500.3 MHz, $CDCl_3$, 25 °C): δ = 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.41–1.49 (m, 2 H, CH_2), 1.98 (d, $J_{H,H}$ = 0.9 Hz, 3 H, CH_3), 2.06 (q, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 5.27 [t, $J_{H,H}$ = 7.8 Hz, 1 H, =CH(*n*Pr)], 7.69–7.73 (m, 2 H, *m*-CH/Ph), 8.16–8.21 (m, 2 H, *o*-CH/Ph) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 13.7, 15.3, 22.8, 28.8, 118.1, 123.8 (q, $J_{C,F}$ = 273 Hz, CF_3), 125.5–125.6 (m, *m*-CH/Ph), 130.4, 133.6, 134.7 (q, $J_{C,F}$ = 32.7 Hz, CCF_3), 145.7, 164.2 ppm.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of all catalysis products can be found in the Supporting Information.

Acknowledgments

The Fonds der Chemischen Industrie is gratefully acknowledged for financial support and for a Chemiefonds fellowship to J. J.

Keywords: Homogeneous catalysis · Hydrocarboxylation · Ruthenium · Carboxylic acids · Alkynes

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Received: December 17, 2015
Published Online: February 16, 2016

