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Development of an Improved Rhodium Catalyst for *Z*-Selective Anti-Markovnikov Addition of Carboxylic Acids to Terminal Alkynes

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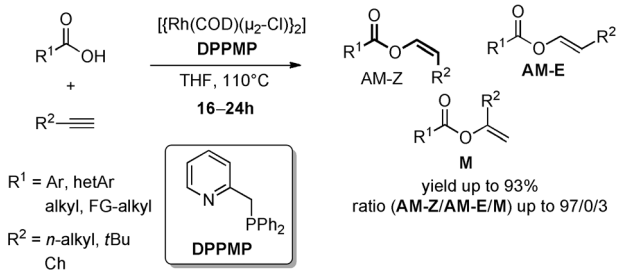
Abstract: To develop more active catalysts for the rhodium-catalyzed addition of carboxylic acids to terminal alkynes furnishing anti-Markovnikov *Z* enol esters, a thorough study of the rhodium complexes involved was performed. A number of rhodium complexes were characterized by NMR, ESI-MS, and X-ray analysis and applied as catalysts for the title reaction. The systematic investigations revealed that the presence of chloride ions decreased the catalyst activity. Conversely, generating and applying a mixture of two rhodium species, namely, $[Rh(DPPMP)_2][H(benzoate)_2]$ (DPPMP = diphenylphosphinomethylpyridine) and $[\{Rh(COD)(\mu_2\text{-benzoate})\}_2]$, provided a significantly more active catalyst. Furthermore, the addition of a catalytic amount of base (Cs_2CO_3) had an additional accelerating effect. This higher catalyst activity allowed the reaction time to be reduced from 16 to 1–4 h while maintaining high selectivity. Studies on the substrate scope revealed that the new catalysts have greater functional-group compatibility.

Keywords: chemoselectivity · enol esters · homogeneous catalysis · N,P ligands · rhodium

Introduction

The addition of carboxylic acids to terminal alkynes catalyzed by transition metal complexes[1] (hydro-oxycarbonylation) is an efficient, atom-economic method for the preparation of enol esters,[2] which are widely used as monomers for polymerization,[3] mild acylating agents,[4] and as substrates for asymmetric branched-selective hydroformylation.[5] Following the first report of this reaction in 1983 by Shvo et al. employing $[Ru_3(CO)_{12}]$ as catalyst,[6] most notable improvements were made by using ligand-modified ruthenium catalysts to afford selectively either the Markovnikov (**M**) and/or anti-Markovnikov (**AM-Z**, **AM-E**) enol esters (Scheme 1).[7] Furthermore, iridium,[8] rhenium,[9] palladium,[10] and gold[11] catalysts have been used for the intermolecular addition, while the use of rhodium catalysts was restricted to the intramolecular version of this reaction, yielding alkylidene lactones.[12] Only a single report of a polyphosphine-modified rhodium catalyst for intermolecular Markovnikov-selective addition has been made.[13]

Recently, we reported the first rhodium catalyst for general and selective intermolecular anti-Markovnikov addition of carboxylic acids to terminal alkynes, yielding valuable *Z* enol esters.[14] Key to the reaction was the P,N ligand 2-diphenylphosphinomethylpyridine (DPPMP).[15] This catalyst was applied to a broad range of substrates, and its utility was recently demonstrated by its application in the total synthesis of (+)-patulolide C, which exhibits both antifungal and antibacterial activity.[5b] Although high selectivity for the anti-Markovnikov *Z* enol ester (**AM-Z**) over the other possible isomers (**M** and **AM-E**) was usually achieved, long reaction times (16–24 h) were necessary to obtain the coupling products in high yield, and thus the utility of this methodology for sensitive and unstable substrates is limited. Herein, we report the development of improved rhodium catalysts that promote the formation of *Z* enol esters in high yields after only 1–4 h, while maintaining high regioselectivity and functional group compatibility.



Scheme 1. *Z*-selective *anti*-Markovnikov rhodium-catalyzed addition of carboxylic acids to alkynes using $[\{Rh(COD)(\mu_2\text{-Cl})\}_2]$ and DPPMP.

Results and Discussion

In our previous report,[14] the active catalyst was expected to be the neutral complex $[\{Rh(DPPMP)(\mu_2\text{-Cl})\}_2]$. The pro-

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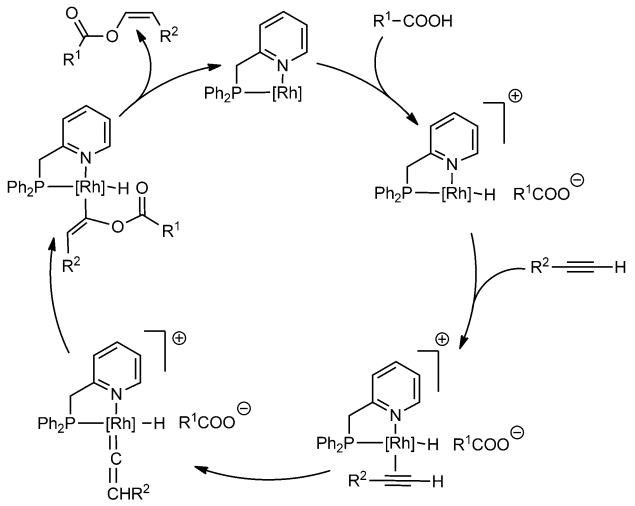
posed mechanism (Scheme 2) commenced with oxidative addition of the carboxylic acid to the Rh^I center forming a cationic rhodium hydride complex.[13] Since internal alkynes did not show any reactivity, we suggested that η^2 coordination of the alkyne to the metal center was followed by a rearrangement to an η^1-vinylidene rhodium species.[16] This could be attacked by the carboxylate at the more electrophilic carbon atom, followed by reductive elimination to afford the *Z* anti-Markovnikov product (**AM-Z**). The *Z* stereochemistry results from minimization of steric repulsion between the R^2 group and the bulky rhodium catalyst.[17]



Scheme 2. Proposed mechanism for the rhodium-catalyzed intermolecular hydro-oxycarbonylation reaction yielding the *Z* anti-Markovnikov product.[14]

However, systematic investigations of the in situ reaction of the precursor complex $[\{Rh(COD)(\mu_2\text{-}Cl)\}_2]$ (cod = 1,5-cyclooctadiene) with DPPMP showed that the complex formed was not as expected $[\{Rh(DPPMP)(\mu_2\text{-}Cl)\}_2]$, but almost quantitatively the salt $[Rh(DPPMP)_2][Rh(COD)Cl_2]$ (**1**), which was characterized by X-ray crystallography (Figure 1). This compound consists of a cationic Rh^I 16-electron complex with two DPPMP ligands in a nearly square planar geometry and an anionic rhodium complex[18] in which a 16-electron Rh^I center is chelated by COD and covalently bound to two Cl ligands. NMR analysis of this complex in THF gave broad signals, which was not the case in CH_2Cl_2 (Figure 2). Dynamic ligand exchange between the less stable Rh–N bond and THF might be the cause of this behavior.

These NMR observations are consistent with the strong influence of the nature of the solvent on the regioselectivity and yield of the reaction between benzoic acid and 1-octyne (Table 1)[14,19] and direct employment of isolated complex **1** in the coupling between benzoic acid and 1-octyne in THF at 110 °C (Table 2, entry 1 and 2) led to analogous results to those described in our first report.

The ^{31}P NMR spectrum of the reaction mixture $[\{Rh(COD)(\mu_2\text{-}Cl)\}_2]$:DPPMP:benzoic acid:1-octyne (1:2:100:150) in THF (Figure 3) showed after 30 min at room temperature the starting material (complex **1**, 19%) and two new species (38 and 27%). Interestingly, no hydrides were observed. X-ray crystallography of one of the new complexes (**2**, 27%) showed that it is an 18-electron cationic Rh^{III} species bearing two DPPMP ligands and two covalently bound Cl ligands (Figure 1). The anion consists of a deprotonated "dimer" of the substrate benzoic acid. It seems that the chlorine atoms stem from the initially formed $[Rh(DPPMP)_2][Rh(COD)Cl_2]$ (**1**). As expected, since **2** is an electronically saturated complex, it shows low activity under the standard conditions (Table 2, entry 3).

The use of cationic diolefin precursors instead of neutral dimeric complexes has been shown to be beneficial in several cases, for example, in the enantioselective ring-opening reaction of oxabicyclic alkenes.[20] This and the knowledge that the rhodium(I) complex **1** formed in situ contains a cationic Rh^I species prompted us to prepare the complex $[Rh(DPPMP)(diolefin)]BF_4$. Such a complex could be directly used in catalysis to avoid the formation of inactive complexes such as **2**, since the reaction medium is free of chlorine ions. The cationic complexes $[Rh(DPPMP)(NBD)]BF_4$ (**3**) (NBD = norbornadiene) and $[Rh(DPPMP)(COD)]BF_4$ (**4**) were synthesized by a reported method using [Rh(diolefin)(acac)] (acac = acetylacetonate) as starting material[21] and characterized by X-ray crystallography (Figure 4). Unfortunately, they displayed only low catalytic activity (Table 2, entries 4 and 5).

Variation of the reaction conditions for the preparation of $[Rh(DPPMP)(COD)]BF_4$ (**4**), that is, fast addition of HBF_4 and stirring at room temperature instead of dropwise addition of the acid at 0 °C, led surprisingly to the formation of an Rh^{III} hydride complex $[Rh(DPPMP)_2H(FBF_3)]BF_4$ (**5**), which could be

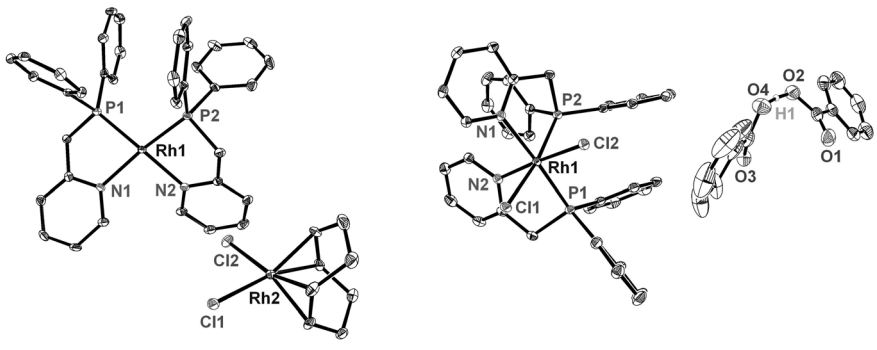


Figure 1. X-ray crystal structure of $[Rh(DPPMP)_2][Rh(COD)Cl_2]$ (**1**) and $[Rh(DPPMP)_2Cl_2][H(benzoate)_2]$ (**2**); ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

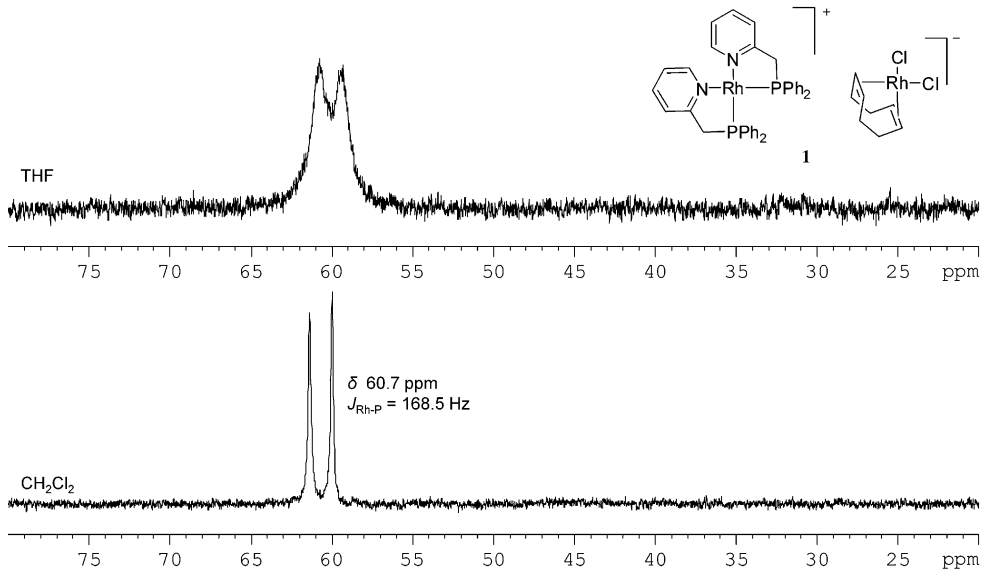
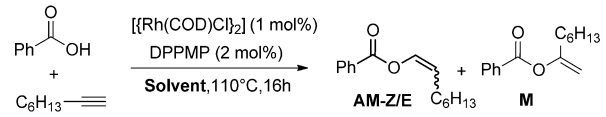


Figure 2. a) ^{31}P NMR spectrum of the mixture of [{Rh(COD)(μ$_2$-Cl)}$_2$] (0.0044 mmol), DPPMP (0.0088 mmol), and 0.4 mL of deuterated THF at room temperature. b) ^{31}P NMR spectrum of [Rh(DPPMP)$_2$][Rh(COD)Cl$_2$] (**1**) in deuterated CH_2Cl_2.

Table 1. Addition of benzoic acid to 1-octyne in various solvents.



Entry	Solvent	**AM-Z**/**AM-E**/**M**[a]	Yield [%][b]
1	THF	94/3/3	90
2	Et_2O	44/12/44	<10
3	CH_2Cl_2	37/22/41	<10
4	toluene	51/13/36	18

[a] Determined by integration of the ethylenic protons in the ^{1}H NMR spectrum of the crude mixture. [b] Yield of isolated product.

characterized by X-ray crystallography (Figure 5). Obviously, HBF_4 underwent an oxidative addition, resulting in the formation of an Rh–H bond (δ_H(RhH) = −20.81 ppm, Figure 6) and a Rh–F bond to one of the BF_4 counterions.

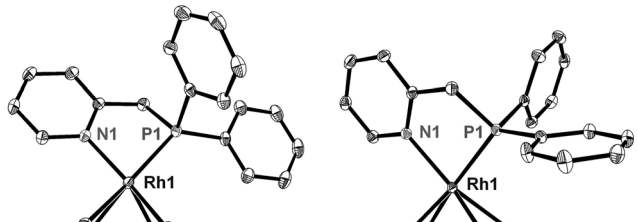


Figure 4. X-ray crystal structures of [Rh(DPPMP)(NBD)]BF_4 (**3**) and [Rh(DPPMP)(COD)]BF_4 (**4**); ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

To the best of our knowledge, such Rh complexes have never been observed with common diphosphines. This result

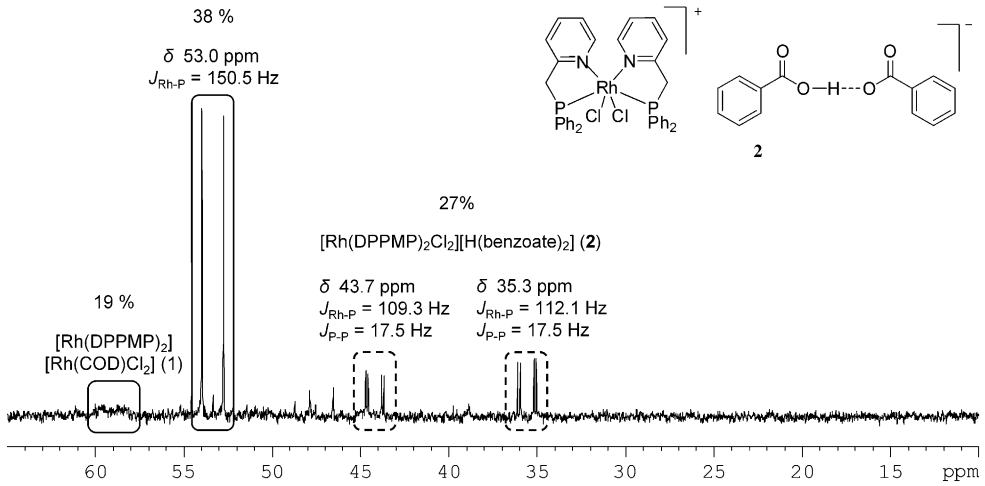
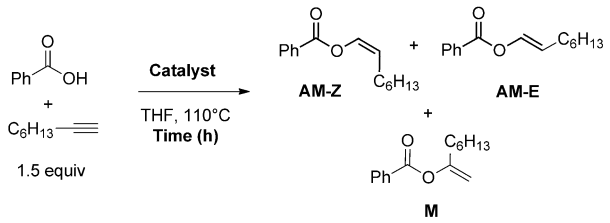


Figure 3. ^{31}P NMR spectrum of the reaction mixture of [{Rh(COD)(μ$_2$-Cl)}$_2$] (0.0044 mmol), DPPMP (0.0088 mmol), benzoic acid (0.44 mmol), and 1-octyne (0.66 mmol) in 0.4 mL of deuterated THF at room temperature.

Table 2. Addition of benzoic acid to 1-octyne with different rhodium catalysts under standard conditions.[a]



Entry	Catalyst	Time [h]	**AM-Z**/**AM-E**/**M**[b]	Yield [%][c]
1	[{Rh(COD)(μ_2-Cl)}$_2$]/DPPMP[d]	16	91/3/6	84
2	[Rh(DPPMP)$_2$][Rh(COD)Cl$_2$] (**1**)	16	92/3/5	87
3	[Rh(DPPMP)$_2$Cl$_2$][H(benzoate)$_2$] (**2**)	16	26/–/69	~5
4	[Rh(DPPMP)(NBD)]BF$_4$ (**3**)	16	–/–/12	50
5	[Rh(DPPMP)(COD)]BF$_4$ (**4**)	16	11/44/45	38
6	[Rh(DPPMP)$_2$H(FBF$_3$)]BF$_4$ (**5**)	16	–/–/100	18
7	[Rh(DPPMP)$_2$][H(benzoate)$_2$] (**6**)	16	89/2/9	92
8	[Rh(DPPMP)$_2$][H(benzoate)$_2$] (**6**)/ [{Rh(COD)(μ_2-benzoate)}$_2$] (**7**)[e]	4	95/2/3	98
9	[Rh(DPPMP)(COD)]BF$_4$ (**4**)/Cs$_2$CO$_3$	2	94/3/3	98
10	[Rh(COE)$_2$(acac)]/DPPMP[f]	2	95/2/3	95
11	[Rh(COE)$_2$(acac)]/DPPMP/Cs$_2$CO$_3$[f]	1	96/2/2	95

[a] Reaction conditions: 0.0044 mmol of "Rh precursor", 0.44 mmol of benzoic acid and 0.66 mmol of 1-octyne in 0.7 mL of THF were heated in a closed Schlenk vessel at 110 °C for 1 to 16 h.[b] **AM-Z**/**AM-E**/**M** ratio determined by integration of the ethylenic protons in the ^{1}H NMR spectrum of the crude mixture. [c] Yield of isolated product. [d] Results included in our previous report.[14] [e] Obtained by mixing [Rh(COD)(acac)] and DPPMP (1 equiv relative to "Rh") with benzoic acid (4 equiv) at 50 °C. [f] Precomplexation with benzoic acid (50 equiv) at room temperature in THF was done prior to addition of 1-octyne.

is highly interesting, since we postulated the formation of an analogous species on oxidative addition of benzoic acid in our proposed mechanism (see Scheme 2).[14,22]

Isolated complex **5** was employed as a catalyst in the title reaction, but it showed only moderate catalytic activity (Table 2, entry 6). Interestingly, with this rhodium species selective formation of the Markovnikov regioisomer was observed, albeit in low yield (18%). This result led us to directly replace HBF$_4$ by benzoic acid. Indeed, after treating [[Rh(COD)(acac)]] and DPPMP with benzoic acid (4 equiv) in THF at 50 °C, we were able to isolate complex [Rh(DPPMP)$_2$][H(benzoate)$_2$] (**6**; Figure 7). In this case, hydride formation was not observed, and this suggests that no oxidative addition occurred. Complex **6** is a cationic 16-electron Rh^I species coordinated by two DPPMP ligands in a square-planar geometry with benzoic acid/benzoate dimer counterion. Since complexes **1** and **6** consist of the same cationic species but different counterions, complex **6** was tested in catalysis. However, this species performed with similar activity and regioselectivity as our original system (cf. Table 2, entries 2 and 7).[23]

The stoichiometry of the reaction to form complex **6**, that is, [Rh(COD)(acac)], DPPMP (1 equiv), and an excess of benzoic acid (4 equiv), suggested that another rhodium species must be formed. This species bears no DPPMP ligand, since no signals in the ^{31}P NMR spectrum other than those of cationic [Rh(DPPMP)$_2$]$^+$ were observed. The ^{1}H NMR spectrum of the reaction mixture and the ESI-MS analysis (mass numbers 332 and 664) suggested the formula "[Rh(COD)benzoate]" (**7**). By reaction of [Rh(COD)(acac)] with benzoic acid in THF we were able to isolate and characterize species **7**. The structure of the neutral benzoate-bridged complex dimer [{Rh(COD)(μ_2-benzoate)}$_2$] (**7**) is shown in Figure 8. The in situ reaction of [Rh(COD)(acac)] with one equivalent of DPPMP in the presence of benzoic acid and 1-octyne (forming theoretically a mixture of complexes **6** and **7** in 1:1 ratio) surprisingly showed much higher activity in the hydro-oxycarbonylation reaction (Table 2, entry 8). We isolated the

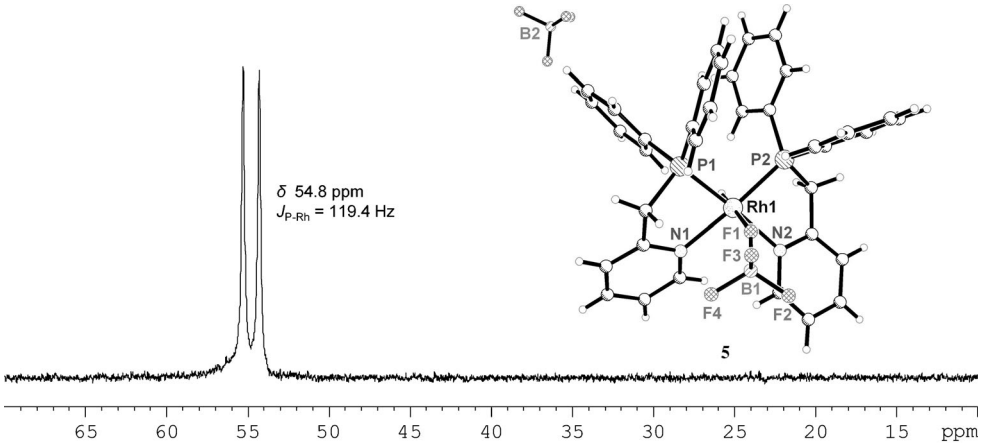


Figure 5. ^{31}P NMR spectrum of [Rh(DPPMP)$_2$H(FBF$_3$)]BF$_4$ (**5**) in deuterated THF and its X-ray crystal structure; ORTEP, 30% probability ellipsoids.

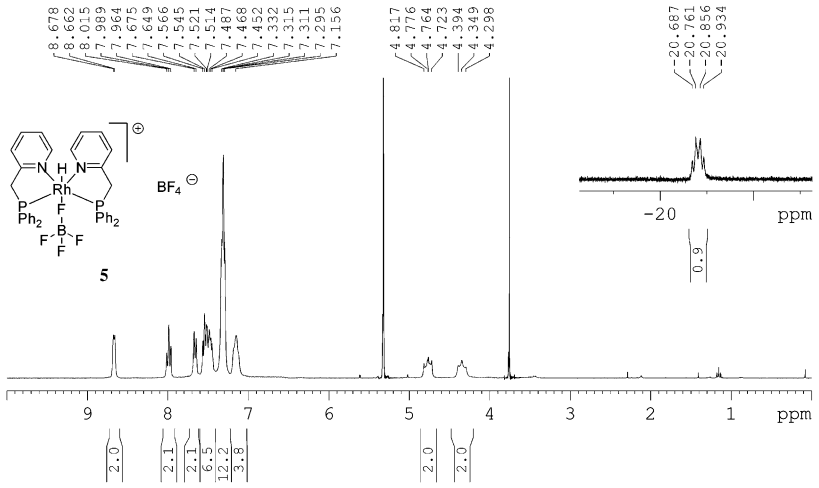


Figure 6. ^{1}H NMR spectrum of $[Rh(DPPMP)_2H(FBF_3)]BF_4$. The inset shows the hydride region.

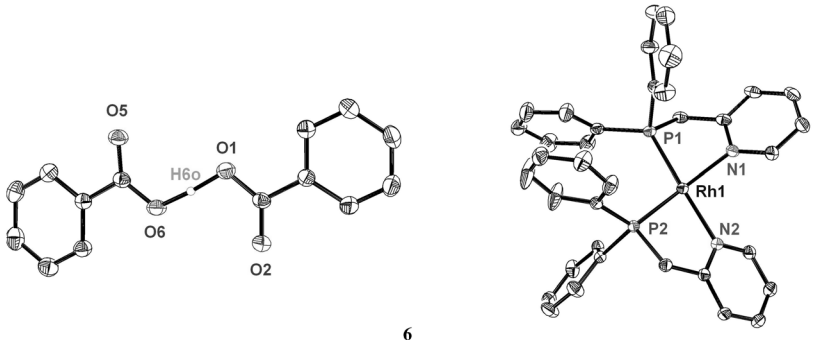


Figure 7. X-ray crystal structure of $[Rh(DPPMP)_2][H(benzoate)_2]$ (**6**); ORTEP, 30% probability ellipsoid.

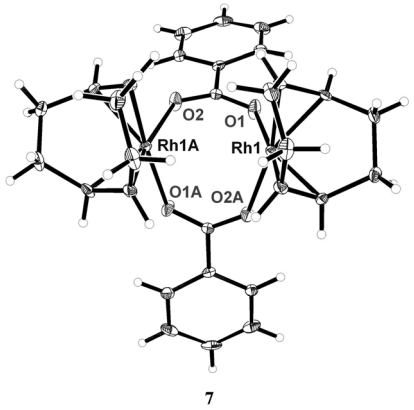
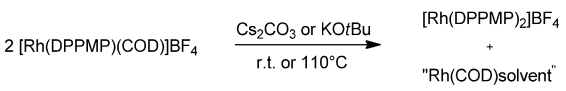


Figure 8. Crystal structure of $[\{Rh(COD)(\mu_2\text{-benzoate})\}_2]$ (**7**); ORTEP, 30% probability ellipsoid.

coupling product in excellent yield after only 4 h at 110 °C without any loss of selectivity. Since complex **6** alone did not show higher activity, we concluded that the observed increase in reaction rate must be due to the presence of complex **7**.[24,25] It is possible that the accelerating effect of **7** is merely due to a more efficient proton transfer between benzoic acid and benzoate. Furthermore, it is known that addition of catalytic amount of base (e.g., Cs_2CO_3) has an accelerating effect in related coupling reactions, as found in our recent enantioselective coupling between allenes and carboxylic acids affording branched allylic esters.[26] It is also known that addition of bases to cationic Rh^I complexes can lead to the formation of trinuclear Rh complexes.[27] Hence, we tested the effect of addition of base to the inactive cationic complexes **3** and **4** (see above). Indeed, with the $[Rh(DPPMP)(COD)]BF_4$ (**4**)/Cs_2CO_3 system, the reaction time could be reduced to 2 h without any loss of selectivity (Table 2, entry 9). In a detailed investigation on the influence of base, employing $[Rh(DPPMP)(COD)]BF_4$ (**4**) as starting material and Cs_2CO_3 or KO*t*Bu, we observed the formation of a mixture of $[Rh(DPPMP)_2]BF_4$ and a second Rh complex without DPPMP as ligand (stoichiometry suggests "Rh(COD)(solvent)"; Scheme 3). We believe that anion exchange for



Scheme 3. Formation of $[Rh(DPPMP)_2]BF_4$ and "Rh(COD)solvent" from $[Rh(DPPMP)(COD)]BF_4$ by addition of base (Cs_2CO_3 or KO*t*Bu).

benzoate in both complexes led to formation of an active system analogous to the mixture of complexes **6** and **7** (Table 2, entry 8). The origin of the accelerating effect of the base (Cs_2CO_3) can be attributed to the presence of carboxylates, which are more nucleophilic than carboxylic acids.[28,29]

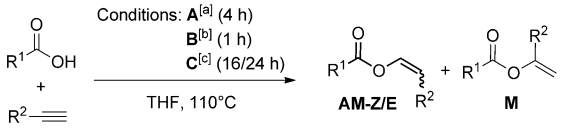
The role of the chelating COD ligand in the reaction has not yet been clarified. The structure of complex **7** suggests that COD remains free in solution during the reaction, which we expected from our experience to affect negatively the activity of the catalyst. Hence, we decided to form the catalyst from the corresponding cyclooctene complex $[Rh(COE)_2(acac)]$ with one equivalent of DPPMP in the presence of an excess of benzoic acid (4 or 50 equiv compared to Rh; Table 2, entry 10). Direct comparison with entry 8 of Table 2 shows that the reaction time can be reduced to 2 h. This could be further improved by adding a catalytic amount of Cs_2CO_3 (2 mol%), which resulted in an overall

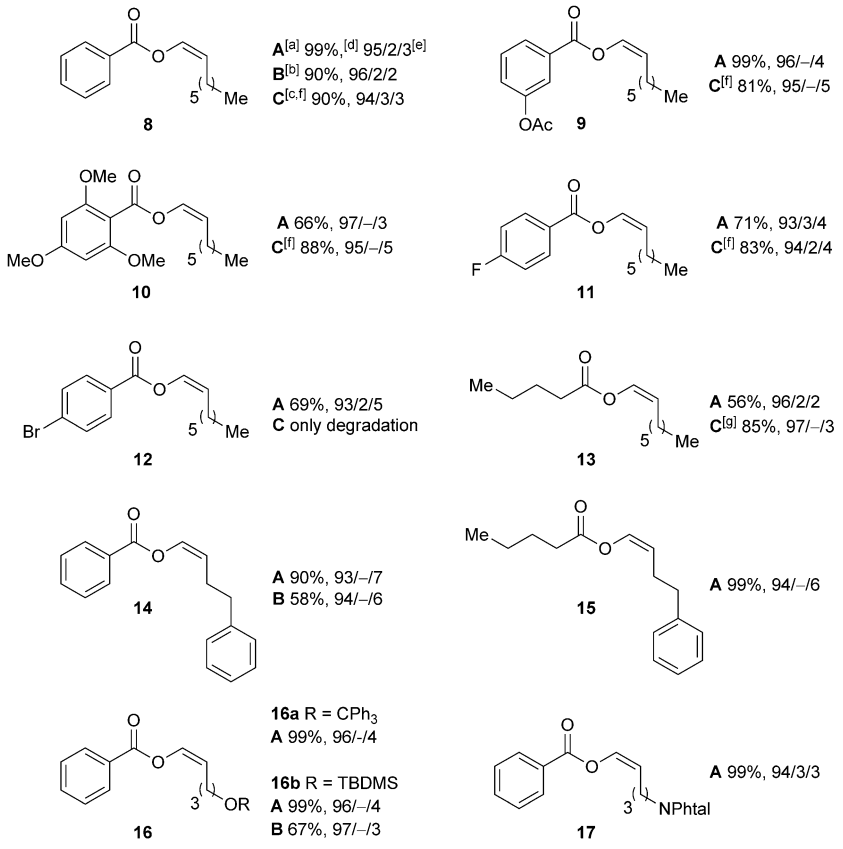
reaction time of 1 h with even better selectivity (Table 2, entry 11).[29]

These new rhodium catalyst systems were then applied to the preparation of various enol esters (Table 3). However, since the $[Rh(COE)_2(acac)]$-based catalysts appeared to be highly sensitive[30] (Table 2, entries 10 and 11), we mainly focused on the more robust and convenient $[Rh(DPPMP)_2][H(benzoate)_2]$ (**6**)/$[\{Rh(COD)(\mu_2\text{-benzoate})\}_2]$ (**7**) catalyst system (Table 2, entry 8), obtained in situ by treating [Rh(COD)(acac)] with DPPMP and benzoic acid in THF at 50 °C prior to addition of the terminal alkyne (Table 3, conditions **A**).[31] Various substituted aromatic carboxylic acids and an aliphatic acid were well tolerated, and enol esters **8**–**13** were obtained in comparable yields and selectivities to those obtained after 16 h of reaction in our original protocol (conditions **C**, Table 3).[14,31] Enol ester **12** derived from *p*-bromobenzoic acid could be obtained in good yield (69 %). This compound was not accessible by previously reported procedure **C**. Indeed, the long reaction time (16 h) induced nearly complete degradation of the product. This result demonstrates the usefulness of the more active catalyst system for organic synthesis.

Furthermore, we extended the scope of the reaction to functionalized and heteroatom-containing terminal alkynes, and the corresponding enol esters **14**–**17** were isolated in excellent yield and very high regioselectivity. Enol esters **14** and **16b** were also obtained after 1 h by using $[Rh(COE)_2(acac)]$/DPPMP catalyst in the presence of Cs_2CO_3 (procedure **B**), but while the regioselectivities were identical, the yields were significantly lower.

Table 3. Rhodium-catalyzed intermolecular hydro-oxycarbonylation reaction.





[a] After reaction of [Rh(COD)(acac)] (0.0088 mmol) with DPPMP (0.0088 mmol) and carboxylic acid (0.44 mmol) in THF (0.7 mL) at 50 °C (in situ formation of complexes **6** and **7**), alkyne (0.66 mmol) was added and the reaction mixture heated at 110 °C in a closed Schlenk vessel for 4 h (see Experimental Section for more details). [b] After reaction of $[Rh(COE)_2(acac)]$ (0.0088 mmol) with DPPMP (0.0088 mmol), carboxylic acid (0.44 mmol) and Cs_2CO_3 (0.0088 mmol) in THF (0.7 mL) at room temperature, alkyne (0.66 mmol) was added and the reaction mixture heated at 110 °C in a closed Schlenk vessel for 1 h (see Experimental Section for more details). [c] $[\{Rh(COD)(\mu_2\text{-Cl})\}_2]$ (0.0044 mmol), DPPMP (0.0088 mmol), carboxylic acid (0.44 mmol) and alkyne (0.66 mmol) were heated at 110 °C in THF (0.4 mL) in a closed Schlenk vessel during 16–24 h.[14] [d] Yield of isolated product after purification by chromatography on SiO_2. [e] Ratio **AM-Z**/**AM-E**/**M** determined by GC analyses and/or integration of the ethylenic protons in the ^1H NMR spectrum of the crude mixture. [f] 16 h of reaction. [g] 24 h of reaction.

Conclusion

We have described a thorough investigation of the different complexes present and involved in the regioselective intermolecular rhodium-catalyzed addition of carboxylic acids to terminal alkynes using NMR and X-ray analyses. On the basis of these new results, we have developed improved rhodium catalysts which allow a considerable reduction of the reaction time (from 16–24 to 1–4 h), while maintaining high selectivities and yields. This allowed us to extend the scope to a variety of substrates including previously incompatible functionalities such as aryl bromides.

Experimental Section

Rhodium complexes: All syntheses were carried out under oxygen- and moisture-free conditions under argon by using standard Schlenk or drybox techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl immediately prior to use. $[D_8]$THF and CD_2Cl_2 were distilled from CaH_2. Subsequent removal of traces of oxygen for the deuterated

solvents was carried out by application of six freeze–pump–thaw cycles. ^{31}P, ^{13}C, ^{13}C DEPT, and ^{1}H NMR spectra were obtained on a Bruker ARX-300 or ARX-400 spectrometer at 297–298 K and were referenced internally to the deuterated solvent (^{13}C, CD_2Cl_2: $\delta_{reference}=54$ ppm, CD_3OD: $\delta_{reference}=49.2$ ppm) or to protic impurities in the deuterated solvent (^{1}H, $CDHCl_2$: $\delta_{reference}=5.31$ ppm, CD_3OD: $\delta_{reference}=3.32$ ppm). For ^{31}P NMR chemical shifts, 85% H_3PO_4 was used as external standard. The chemical shifts are given in parts per million (ppm). Mass spectra were recorded on a Time-of-Flight LC/MS 6210 (Agilent Technologies) with electrospray ionization (ESI-TOF).

Diffraction data were collected at low temperature on a Bruker Kappa APEX II Duo diffractometer by using $Mo_{K\alpha}$ radiation (**1**, **2**, **3**, **4**, **5**, and **7**) or $Cu_{K\alpha}$ radiation (**6**). The structures were solved by direct methods (SHELXS-97)[32] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[32] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in theoretical positions (except for [H(benzoate)$_2$] and H in **5**) and were refined by using the riding model. Contributions of solvent molecules were removed in **6** from the diffraction data with PLATON/SQUEEZE.[33]

Crystal data for [Rh(DPPMP)$_2$][Rh(COD)Cl$_2$] (1): $C_{46}H_{48}Cl_4N_2P_2Rh_2$; triclinic, space group $P\bar{1}$; $a=9.9958(4)$, $b=11.8465(5)$, $c=18.6006(9)$ Å; $\alpha=96.554(2)$; $\beta=100.135(2)$, $\gamma=96.327(2)°$; $V=2134.85(16)$ Å^3; $T=150(2)$ K; $Z=2$; $\rho_{calcd}=1.615$ g cm^{-3}; $\mu(Mo_{K\alpha})=1.135$ mm^{-1}; 31152 total data, $\Theta_{max}=25.65$; $R=0.0345$ for 6096 data with $I>2\sigma(I)$ of 7999 unique data and 505 refined parameters. The final $wR(F^2)$ value was 0.0695 ($I>2\sigma(I)$). The final R_1 value was 0.0578 (all data). The final $wR(F^2)$ value was 0.0761 (all data). The goodness of fit on F^2 was 1.002.

Crystal data for [Rh(DPPMP)$_2$Cl$_2$][H(benzoate)$_2$] (2): $C_{50}H_{43}Cl_2N_2O_4P_2Rh$; monoclinic, space group $P2_1/n$; $a=13.1720(3)$, $b=19.2018(4)$, $c=17.2098(4)$ Å; $\alpha=96.436(1)°$; $V=4325.37(17)$ Å^3; $T=150(2)$ K; $Z=4$; $\rho_{calcd}=1.492$ g cm^{-3}; $\mu(Mo_{K\alpha})=0.642$ mm^{-1}; 67152 total data, $\Theta_{max}=26.00$; $R=0.0288$ for 7283 data with $I>2\sigma(I)$ of 8492 unique data and 554 refined parameters. The final $wR(F^2)$ value was 0.0682 ($I>2\sigma(I)$). The final R_1 value was 0.0377 (all data). The final $wR(F^2)$ value was 0.0754 (all data). The goodness of fit on F^2 was 1.074.

Crystal data for [Rh(DPPMP)(NBD)]BF$_4$ (3): $C_{26}H_{26}BClF_4NPRh$; monoclinic, space group $P2_1/c$; $a=11.6191(1)$, $b=10.8508(1)$, $c=19.3404(2)$ Å; $\beta=91.400(1)°$, $V=2437.64(4)$ Å^3; $T=150(2)$ K; $Z=4$; $\rho_{calcd}=1.658$ g cm^{-3}; $\mu(Mo_{K\alpha})=0.923$ mm^{-1}; 22539 total data, $\Theta_{max}=26.50$; $R=0.0268$ for 4510 data with $I>2\sigma(I)$ of 5057 unique data and 328 refined parameters. The final $wR(F^2)$ value was 0.0668 ($I>2\sigma(I)$). The final R_1 value was 0.0321 (all data). The final $wR(F^2)$ value was 0.0715 (all data). The goodness of fit on F^2 was 1.026.

Crystal data for [Rh(DPPMP)(COD)]BF$_4$ (4): $C_{26}H_{28}BF_4NPRh$; orthorhombic, space group $Pbca$; $a=16.4506(3)$, $b=15.1037(3)$, $c=19.1085(4)$ Å; $V=4747.79(16)$ Å^3; $T=150(2)$ K; $Z=8$; $\rho_{calcd}=1.609$ g cm^{-3}; $\mu(Mo_{K\alpha})=0.834$ mm^{-1}; 53146 total data, $\Theta_{max}=27.10$; $R=0.0236$ for 4185 data with $I>2\sigma(I)$ of 5242 unique data and 335 refined parameters. The final R_1 value was 0.0382 (all data). The final $wR(F^2)$ value was 0.0590 (all data). The goodness of fit on F^2 was 1.032.

Crystal data for [Rh(DPPMP)$_2$H(FBF$_3$)]BF$_4$ (5): $C_{36}H_{32}B_2F_8H_1N_2P_2Rh$; monoclinic, space group $P2_1/n$; $a=9.0285(2)$, $b=22.1872(5)$, $c=17.7508(4)$ Å; $\beta=96.596(1)°$, $V=3532.25(14)$ Å^3; $T=150(2)$ K; $Z=4$; $\rho_{calcd}=1.565$ g cm^{-3}; $\mu(Mo_{K\alpha})=0.647$ mm^{-1}; 70949 total data, $\Theta_{max}=27.50$; $R=0.0266$ for 6457 data with $I>2\sigma(I)$ of 8108 unique data and 464 refined parameters. The final $wR(F^2)$ value was 0.0580 ($I>2\sigma(I)$). The final R_1 value was 0.0404 (all data). The final $wR(F^2)$ value was 0.0615 (all data). The goodness of fit on F^2 was 1.010.

Crystal data for [Rh(DPPMP)$_2$][H(benzoate)$_2$] (6): $C_{50}H_{43}N_2O_4P_2Rh$, triclinic, space group, $P\bar{1}$; $a=17.6242(3)$, $b=18.3121(3)$, $c=18.7849(3)$ Å; $\alpha=87.523(1)$, $\beta=68.317(1)$, $\gamma=73.565(1)°$; $V=5390.61(15)$ Å^3; $T=150(2)$ K; $Z=4$; $\rho_{calcd}=1.110$ g cm^{-3}, $\mu(Cu_{K\alpha})=3.424$ mm^{-1}; 54781 total data, $\Theta_{max}=61.21$; $R=0.0299$ for 14497 data with $I>2\sigma(I)$ of 16268 unique data and 1108 refined parameters. The final $wR(F^2)$ value was 0.0759 ($I>2\sigma(I)$). The final R_1 value was 0.0332 (all data). The final $wR(F^2)$ value was 0.0775 (all data). The goodness of fit on F^2 was 1.064.

Crystal data for [{Rh(COD)(μ_2-benzoate)}$_2$] (7): $C_{15}H_{17}O_2Rh$; orthorhombic, space group $Pbcn$; $a=17.9455(4)$, $b=8.1008(2)$, $c=17.7915(4)$ Å; $V=2586.4(1)$ Å^3; $T=150(2)$ K; $Z=8$; $\rho_{calcd}=1.706$ g cm^{-3}; $\mu(Mo_{K\alpha})=1.311$ mm^{-1}; 24982 total data, $\Theta_{max}=26.00$; $R=0.0374$ for 2342 data with $I>2\sigma(I)$ of 2526 unique data and 163 refined parameters. The final $wR(F^2)$ value was 0.1365 ($I>2\sigma(I)$). The final R_1 value was 0.0401 (all data). The final $wR(F^2)$ value was 0.1386 (all data). The goodness of fit on F^2 was 1.248.

CCDC 914756 (**1**), 914752 (**2**), 914753 (**3**), 914754 (**4**), 914750 (**5**), 914757 (**6**) and 914754 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Enol esters: Chromatographic purification of products was accomplished using Machery-Nagel silica gel 60 (230–400 mesh). TLC was performed on aluminum plates precoated with silica gel (Merk, 60 F_{254}), which were visualized by the quenching of UV fluorescence ($\lambda_{max}=254$ nm), and/or by staining with 1% w/v $KMnO_4$ in 0.5 M aqueous K_2CO_3 followed by heating. NMR spectra were acquired on a Bruker Avance 400 spectrometer (400 and 100.6 MHz for ^{1}H and ^{13}C respectively) and on a Varian Mercury (300 MHz and 75.5 MHz for ^{1}H and ^{13}C, respectively). All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signal at $\delta=7.26$ ppm (residual $CHCl_3$). All ^{13}C NMR spectra are reported in ppm relative to residual $CHCl_3$ ($\delta=77.16$ ppm) and were obtained with ^{1}H decoupling. High-resolution mass spectra were obtained on a Finnigan MAT 8200 instrument (CI/NH_3: 110 eV; EI: 70 eV).

[Rh(DPPMP)$_2$][Rh(COD)Cl$_2$] (1): A dry, argon-flushed Schlenk tube was charged with DPPMP (12 mg, 0.043 mmol), [{Rh(COD)(μ_2-Cl)}$_2$] (11 mg, 0.022 mmol), and THF (2 mL) under argon. A yellow precipitate formed after stirring at room temperature for 5 min. After stirring for 30 min, the solvent was removed and the residue washed with diethyl ether. Crystals of **1** suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution in THF/dichloroethane (17 mg, 85%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=8.50$ (d, $J=5.5$ Hz, 2H), 7.86–7.92 (m, 2H), 7.58 (d, $J=8.1$ Hz, 2H), 7.39–7.44 (m, 2H), 7.16–7.36 (m, 20H), 4.11 (br m, 8H), 2.32 (br s, 4H), 1.61 ppm (br d, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta=161.0$, 151.9, 139.0, 133.1, 132.6, 131.1, 128.8, 124.6, 124.1, 76.7, 44.4, 31.5 ppm; ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta=60.8$ ppm (d, $J_{P\text{-}Rh}=168.6$ Hz); MS (ESI-TOF): calcd for $[M]^+$ ($C_{36}H_{32}N_2P_2Rh$): 657.1090; found: 657.1086; calcd for $[M]^-$ ($C_8H_{12}Cl_2Rh$): 280.9377; found: 280.9368.

[Rh(DPPMP)Cl$_2$][(benzoate)$_2$H] (2): A dry, argon-flushed Schlenk tube was charged with [{Rh(COD)(μ_2-Cl)}$_2$] (2.2 mg, 0.0044 mmol), DPPMP (2.4 mg, 0.0088 mmol), and benzoic acid (54 mg, 0.44 mmol). 1-Octyne (98 μL 0.66 mmol) and freshly purified THF (0.4 mL) were then added under a flow of argon. The reaction mixture stirred for 30 min at room temperature. Small yellow crystals grew from the mixture after standing at room temperature for one or two days. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=9.65$–9.69 (m, 2H), 8.15–8.29 (m, 6H), 7.63–7.75 (m, 3H), 7.36–7.55 (m, 12H), 7.10–7.24 (m, 6H), 6.89–6.99 (m, 5H), 6.34 (t, $J=6.7$ Hz, 2H), 6.12 (d, $J=6.0$ Hz, 2H), 5.10–5.29 (m, 2H), 4.67–4.89 ppm (m, 2H); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta=43.3$ (dd, $J_{P\text{-}Rh}=109.5$ Hz, $J_{P\text{-}P}=17.5$ Hz), 36.6 ppm (dd, $J_{P\text{-}Rh}=112.0$ Hz, $J_{P\text{-}P}=17.4$ Hz); MS (ESI-TOF): calcd for $[M]^+$ ($C_{36}H_{32}Cl_2N_2P_2Rh$): 727.0467; found: 727.0475.

[Rh(DPPMP)(NBD)]BF$_4$ (3): A dry, argon-flushed Schlenk tube was charged with a solution of [Rh(NBD)(acac)] (89 mg) in THF (30 mL). After cooling the solution to −78 °C, a solution of DPPMP (83 mg) in THF (10 mL) was added dropwise over 15 min. After stirring at −78 °C for 30 min, HBF_4 in water (40%, 38 μL) was added at −78 °C. The mixture was stirred for 1 h from −78 °C to room temperature. The mixture was concentrated in vacuum, and the residue was washed with diethyl ether. A crystal suitable for X-ray crystallography was obtained by slow diffusion of diethyl ether into a solution in dichloroethane. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.86$–7.96 (m, 2H), 7.68 (d, $J=7.9$ Hz, 1H), 7.41–7.58 (m, 11H), 5.59 (s, 2H), 4.37 (s, 2H), 4.14 (br s, 3H), 4.11 (s, 1H), 1.70 ppm (d, $J=6.6$ Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta=161.8$, 150.3, 141.2, 132.8, 132.2, 129.9, 128.7, 125.2, 124.4, 92.6, 67.2, 64.2, 44.5,

41.0 ppm; ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 37.4$ ppm (d, $J_{P\text{-}Rh} = 169.8$ Hz); MS (ESI-TOF): calcd for $[M]^+$ ($C_{25}H_{24}NPRh$): 472.0696; found: 472.0704.

[Rh(DPPMP)(COD)]BF_4 (4): A dry, argon-flushed Schlenk tube was charged with [Rh(COD)(acac)] (124 mg, 0.4 mmol), and THF (40 mL) was added. After cooling the solution to −78 °C, a solution of DPPMP (110 mg, 0.4 mmol) in THF (10 mL) was added dropwise over 15 min. After stirring at −78 °C for 30 min, HBF_4 in water (40 %, 70 μL, 0.44 mmol) was added at −78 °C. The mixture was stirred for 1 h from −78 °C to room temperature. The mixture was concentrated in vacuum, and the residue washed with diethyl ether. Crystals of [Rh(DPPMP)-(COD)]BF_4 suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution in dichloroethane (210 mg, yield: 91 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.10$ (d, $J = 5.7$ Hz, 1H), 7.90 (tt, $J = 7.7$ Hz, 1.4 Hz, 1H), 7.60–7.67 (m, 5H), 7.41–7.59 (m, 7H), 5.54 (brs, 2H), 4.22 (d, $J = 11.1$ Hz, 2H), 3.90–3.93 (m, 2H), 2.48–2.59 (m, 4H), 2.29–2.35 ppm (m, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 150.7$, 141.1, 133.4, 132.6, 130.0, 128.6, 126.0, 124.8, 107.6, 78.1, 41.2, 32.8, 28.8 ppm; ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 42.8$ ppm (d, $J_{P\text{-}Rh} = 152.9$ Hz); MS (ESI-TOF): calcd for $[M]^+$ ($C_{26}H_{28}NPRh$): 488.1009; found: 488.1020.

[Rh(DPPMP)$_2$H(FB_3)]BF_4 (5): A dry, argon-flushed Schlenk tube was charged with DPPMP (70 mg, 0.25 mmol) and [Rh(COD)(acac)] (39 mg, 0.125 mmol), and THF (40 mL) was added under argon. After stirring for 5 min at room temperature, HBF_4 in water (40 %, 50 μL, 0.3 mmol) was added dropwise over 5 min, during which the yellow solid disappeared. After stirring for 2 h at room temperature, the solution was concentrated under vacuum. The light yellow solid was washed with diethyl ether (97 mg, 93 % yield). Crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution in dichloroethane. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.66$ (d, $J = 5.9$ Hz, 2H), 7.99 (t, $J = 7.4$ Hz, 2H), 7.65 (d, $J = 7.7$ Hz, 2H), 7.44–7.56 (m, 6H), 7.29–7.33 (m, 12H), 7.16 (t, $J = 9.2$ Hz, 4H), 4.76 (m, 2H), 4.34 (t, $J = 14.4$ Hz, 2H), −20.81 ppm (q, $J = 24.7$ Hz, 1H); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 54.8$ ppm (d, $J_{P\text{-}Rh} = 120.5$ Hz).

[Rh(DPPMP)$_2$][H(benzoate)$_2$] (6): A dry, argon-flushed Schlenk tube was charged with [Rh(COD)(acac)] (15 mg, 0.05 mmol), DPPMP (28 mg, 0.1 mmol), benzoic acid (25 mg, 0.2 mmol), and THF (3 mL). After stirring for 1 h at 50 °C, the solvent was removed, and the residue was recrystallized from diethyl ether and THF to yield 45 mg of [Rh(DPPMP)$_2$][H-(benzoate)$_2$] (yield: 88 %). Crystals of **6** suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution in THF. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 15.02$ (brs, 1H), 8.45 (d, $J = 5.5$ Hz, 2H), 8.04–8.08 (m, 4H), 7.81 (t, $J = 7.8$ Hz, 2H), 7.49 (d, $J = 7.9$ Hz, 2H), 7.14–7.44 (m, 28H), 4.02 ppm (t, $J = 5.6$ Hz, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 170.2$, 160.9, 151.9, 139.0, 135.9, 133.1, 132.6, 133.1, 131.0, 130.1, 128.7, 128.0, 124.4, 124.0, 44.2 ppm; ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 60.7$ ppm (d, $J_{P\text{-}Rh} = 168.9$ Hz); MS (ESI-TOF): calcd for $[M]^+$ ($C_{36}H_{32}N_2P_2Rh$): 657.1090; found: 657.1101.

[Rh(DPPMP)$_2$]BF_4: A dry, argon-flushed Schlenk tube was charged with $[Rh(COD)_2]BF_4$ (122 mg, 0.3 mmol) and DPPMP (167 mg, 0.6 mmol), and THF (15 mL) was added. After stirring for 1 h at room temperature and 30 min at 50 °C, the solvent was removed, and the residue was recrystallized from THF. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.49$ (d, $J = 5.5$ Hz, 2H), 7.86 (t, $J = 7.7$ Hz, 2H), 7.51 (d, $J = 7.7$ Hz, 2H), 7.16–7.41 (m, 22H), 4.07 ppm (t, $J = 5.7$ Hz, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 152.1$, 139.1, 133.2, 131.3, 128.9, 124.5, 124.2, 44.3 ppm; ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 60.8$ ppm (d, $J_{P\text{-}Rh} = 168.5$ Hz); MS (ESI-TOF): calcd for $[M]^+$ ($C_{36}H_{32}N_2P_2Rh$): 657.1090; found: 657.1092.

[{Rh(COD)(μ_2-benzoate)}$_2$] (7): A dry, argon-flushed Schlenk tube was charged with [Rh(COD)(acac)] (19 mg, 0.06 mmol) and benzoic acid (29 mg, 0.24 mmol), and THF (4 mL) was added. After stirring for 1 h at 100 °C the solvent was removed under vacuum and the residue recrystallized from $C_2H_4Cl_2$/hexane. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.76$–7.80 (m, 4H), 7.33–7.38 (m, 2H), 7.23–7.29 (m, 4H), 4.29 (s, 8H), 2.77–2.89 (m, 8H), 1.90 ppm (d, $J = 8.0$ Hz, 8H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 176.7$, 134.9, 131.7, 129.9, 128.2, 81.6, 74.9, 31.5 ppm; MS: (EI, 70 eV): *m*/*z* (%): 664 (0.5) $[M]^+$, 332 (8), 286 (2), 210 (3), 208 (4), 122 (93), 108 (4), 105 (100), 93 (12), 77 (82), 54 (73); HRMS (EI): calcd for $C_{30}H_{34}O_4Rh_2$: 664.05617; found: 664.05419 $[M]^+$.

Procedure A: A dry, argon-flushed 1 mL Schlenk vessel with a Teflon screw cap was charged with [Rh(COD)(acac)] (2.7 mg, 0.0088 mmol, 2.0 mol %), DPPMP (18, 2.4 mg, 0.0088 mmol, 2.0 mol %), and carboxylic acid (0.44 mmol). The flask was evacuated and filled with argon three times (note: this was done prior to addition of the carboxylic acid for liquid/volatile compounds). Freshly distilled THF (0.7 mL) was added under a flow of argon, and the flask sealed and immersed in a preheated oil bath (50 °C). The mixture was stirred for 30 min then allowed to reach room temperature. (ca. 10 min). Alkyne (0.66 mmol, 1.5 equiv) was added under a flow of argon, and the flask sealed and immediately immersed in a preheated oil bath (110 °C). The mixture was stirred for 4 h then allowed to reach room temperature (ca. 20 min), filtered through a pad of silica gel and washed with AcOEt (3 × 4 mL) to separate the catalyst. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel.

Procedure B: A dry, argon-flushed 1 mL Schlenk vessel with a Teflon screw cap was charged with $[Rh(COE)_2(acac)]$ (2.7 mg, 0.0088 mmol, 2.0 mol %), DPPMP (18, 2.4 mg, 0.0088 mmol, 2.0 mol %), Cs_2CO_3 (2.9 mg, 0.0088 mmol, 2.0 mol %), and carboxylic acid (0.44 mmol). The flask was evacuated and filled with argon three times (note: this was done prior to addition of the carboxylic acid for liquid/volatile compounds). Freshly distilled THF (0.7 mL) was added and the mixture was stirred for 10 min at room temperature. Alkyne (0.66 mmol, 1.5 equiv) was added under a flow of argon, and the flask sealed and immediately immersed in a preheated oil bath (110 °C). The mixture was stirred for 1 h then allowed to reach room temperature. (ca. 20 min), filtered through a pad of silica gel, and washed with AcOEt (3 × 4 mL) to separate the catalyst. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel.

Procedure C: A dry, argon-flushed 1 mL Schlenk vessel with a Teflon screw cap was charged with [{Rh(COD)(μ_2-Cl)}$_2$] (2.2 mg, 0.0044 mmol, 1.0 mol %), DPPMP (2.4 mg, 0.0088 mmol, 2 mol %), carboxylic acid (0.44 mmol), and alkyne (0.66 mmol). Freshly distilled THF (0.7 mL) was then added under a flow of argon and the Schlenk vessel was then sealed and immediately immersed in a preheated oil bath (110 °C). The mixture was stirred for 16–24 h, allowed to reach room temperature (ca. 20 min), filtered through a pad of silica gel, and washed with AcOEt (3 × 4 mL) to separate the catalyst. After removal of the solvent under reduced pressure, the crude product was analyzed by ^{1}H NMR and GC and purified by flash chromatography on silica gel.

(*Z*)-1-(Benzoyloxy)-1-octene (8): Procedure **A**: **AM-Z**/**AM-E**/**M** = 95/2/3, yield: 99 % (103 mg). Procedure **B**: **AM-Z**/**AM-E**/**M** = 95/–/5, yield: 95 % (99 mg). Procedure **C**: **AM-Z**/**AM-E**/**M** = 94/3/3, yield: 90 % (94 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 50/1, $R_f = 0.45$); obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.10$–8.13 (m, 2H), 7.57–7.62 (m, 1H), 7.45–7.51 (m, 2H), 7.27 (dt, $J = 6.4$, 1.5 Hz, 1H), 5.02 (td, $J = 7.5$, 6.4 Hz, 1H), 2.30 (qd, $J = 7.3$, 1.5 Hz, 2H), 1.28–1.50 (m, 8H), 0.86–0.92 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.6$, 134.1, 133.3, 129.8, 129.5, 128.5, 114.9, 31.6, 29.1, 28.8, 24.6, 22.6, 14.1 ppm.

(*Z*)-1-(3-Acetoxybenzoyloxy)-1-octene (9): Procedure **A**: **AM-Z**/**AM-E**/**M** = 96/–/4 yield: 99 % (129 mg). Procedure **C**: **AM-Z**/**AM-E**/**M** = 95/–/5, yield: 95 % (105 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 2/1, $R_f = 0.74$); obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.96$–8.00 (m, 1H), 7.80–7.83 (m, 1H), 7.46–7.52 (m, 1H), 7.34 (ddd, $J = 8.1$, 2.4, 1.1 Hz, 1H), 7.24 (dt, $J = 6.3$, 1.6 Hz, 1H), 5.03 (td, $J = 7.5$, 6.3 Hz, 1H), 2.33 (s, 3H), 2.28 (qd, $J = 7.3$, 1.6 Hz, 2H), 1.26–1.49 ppm (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 169.0$, 162.6, 150.7, 134.0, 131.0, 129.5, 127.2, 126.8, 123.0, 115.2, 31.6, 29.0, 28.8, 24.6, 22.5, 21.0, 14.0 ppm.

(*Z*)-1-(2,4,6-Trimethoxybenzoyloxy)-1-octene (10): Procedure **A**: **AM-Z**/**AM-E**/**M** 97/–/3, yield: 66 % (96 mg). Procedure **C**: **AM-Z**/**AM-E**/**M** = 95/–/5, yield: 88 % (128 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 3/1, $R_f = 0.38$); obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.15$ (dt, $J = 6.5$, 1.5 Hz, 1H), 6.11 (s, 2H), 4.95 (td, $J = 7.5$, 6.5 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 6H), 2.16 (qd, $J =$

7.5, 1.5 Hz, 2H), 1.43–1.20 (m, 8H), 0.91–0.83 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 163.1, 159.5, 134.8, 115.0, 105.2, 90.8, 56.1, 55.6, 31.8, 29.3, 29.0, 24.6, 22.7, 14.2 ppm.

(*Z*)-1-(4-Fluorobenzoyloxy)-1-octene (11): Procedure **A**: **AM-Z/AM-E/M** = 93/3/4, yield: 71% (78 mg). Procedure **C**: **AM-Z/AM-E/M** = 94/2/4, yield: 83% (91 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 50/1, R_f = 0.32); obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (m, 2H), 7.23 (dt, J = 6.5, 1.5, 1H), 7.15 (m, 2H), 5.01 (td, J = 7.5, 6.5, 1H), 2.27 (qd, J = 7.5, 1.5, 2H), 1.51–1.17 (m, 8H), 0.88 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2 (d, $^1J_{C\text{-}F}$ = 253 Hz), 162.8, 134.2, 132.6 (d, $^3J_{C\text{-}F}$ = 10 Hz), 125.9 (d, $^4J_{C\text{-}F}$ = 3 Hz), 115.9 (d, $^2J_{C\text{-}F}$ = 22 Hz), 115.2, 31.8, 29.3, 29.0, 24.8, 22.7, 14.2 ppm.

(*Z*)-Oct-1-en-1-yl 4-bromobenzoate (12): Procedure **A**: **AM-Z/AM-E/M** = 93/2/5, yield: 69% (97 mg). Purified by column chromatography on silica gel (eluent: hexanes/ACOEt 50/1, R_f = 0.35); obtained as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.98 (m, 2H), 7.60–7.64 (m, 2H), 7.24 (dt, J = 6.3, 1.6 Hz, 1H), 5.03 (td, J = 7.5, 6.4 Hz, 1H), 2.28 (qd, J = 7.3, 1.6 Hz, 2H), 1.26–1.50 (m, 8H), 0.86–0.92 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 134.0, 131.9, 131.3, 128.6, 128.4, 115.2, 31.6, 29.1, 28.8, 24.6, 22.6, 14.1 ppm. HRMS (CI): m/z calcd for $C_{15}H_{20}O_2Br$ $[M+H]^+$: 311.0647; found: 311.0645.

(*Z*)-1-(Valeroyloxy)-1-octene (13): Procedure **A**: **AM-Z/AM-E/M** = 96/2/2, yield: 56% (54 mg). Procedure **C**: **AM-Z/AM-E/M** = 97/–/3, yield: 85% (82 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 100/1, R_f = 0.49), obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (dt, J = 6.4, 1.6 Hz, 1H), 4.86 (td, J = 7.5, 6.4 Hz, 1H), 2.38–2.43 (m, 2H), 2.10–2.17 (m, 2H), 1.62–1.70 (m, 8H), 1.26–1.44 (m, 10H), 0.94 ppm (t, J = 7.3 Hz, 3H), 0.87–0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 134.0, 114.1, 33.8, 31.6, 29.1, 28.8, 26.8, 24.4, 22.6, 22.2, 14.0, 13.7 ppm.

(*Z*)-4-Phenylbut-1-en-1-yl benzoate (14): Procedure **A**: **AM-Z/AM-E/M** = 93/–/7, yield: 90% (102 mg), Procedure **B**: **AM-Z/AM-E/M** = 94/–/6, yield: 58% (66 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 100/1, R_f = 0.38); obtained as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09–8.13 (m, 2H), 7.60–7.65 (m, 1H), 7.47–7.52 (m, 2H), 7.20–7.35 (m, 6H), 5.08 (td, J = 7.3, 6.3 Hz, 1H), 2.79–2.84 (m, 2H), 2.63–2.70 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 163.4, 141.5, 134.6, 133.4, 129.9, 129.3, 128.5, 128.4, 128.4, 128.3, 126.0, 113.6, 35.4 ppm; HRMS (CI): m/z calcd for $C_{17}H_{20}O_2N$ $[M+NH_4]^+$ 270.1494 found 270.1493.

(*Z*)-4-Phenylbut-1-en-1-yl pentanoate (15): Procedure **A**: **AM-Z/AM-E/M** = 94/–/6, yield: 99% (103 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 100/1, R_f = 0.57); obtained as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.34 (m, 2H), 7.19–7.25 (m, 3H), 7.07 (dt, J = 6.3, 1.5 Hz, 1H), 4.93 (td, J = 7.4, 6.3 Hz, 1H), 2.71–2.76 (m, 2H), 2.48–2.54 (m, 2H), 2.38–2.42 (m, 2H), 1.63–1.71 (m, 2H), 1.35–1.48 (m, 2H), 0.95–0.99 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 141.5, 134.4, 128.4, 128.2, 125.9, 112.7, 35.3, 33.7, 26.7, 26.2, 22.2, 13.6 ppm. HRMS (CI): m/z calcd for $C_{15}H_{24}O_2N$ $[M+NH_4]^+$: 250.1807; found: 250.1807.

(*Z*)-1-(Benzoyloxy)-(5-*O*-triphenylmethyl)-1-pentene (16a): Procedure **A**: **AM-Z/AM-E/M** 96/–/4, yield: 99% (200 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 50/1, R_f = 0.39); obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (dd, J = 8.5, 1.4 Hz, 2H), 7.59–7.64 (m, 1H), 7.52–7.55 (m, 7H), 7.44–7.49 (m, 2H), 7.30–7.36 (m, 8H), 7.25–7.28 (m, 1H), 5.02 (td, J = 7.5, 6.4 Hz, 1H), 3.22 (t, J = 6.3 Hz, 2H), 2.51 (ddt, J = 7.5, 1.5 1.5 Hz, 2H), 1.81–1.90 ppm (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$): δ = 163.4, 144.3, 134.4, 133.3, 129.8, 129.3, 128.6, 128.5, 127.6, 126.8, 114.1, 86.4, 62.8, 29.6, 21.6 ppm. HRMS (CI): m/z calcd for $C_{31}H_{32}O_3N$ $[M+NH_4]^+$: 466.2382; found: 466.2380.

(*Z*)-1-(Benzoyloxy)-(5-*O*-tert-butyldimethylsilyl)-1-pentene (16b): Procedure **A**: **AM-Z/AM-E/M** = 96/–/4, yield: 99% (143 mg), Procedure **B**: **AM-Z/AM-E/M** = 97/–/3, yield: 67% (97 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 100/1, R_f = 0.35); obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09–8.12 (m, 2H), 7.56–7.61 (m, 1H), 7.43–7.48 (m, 2H), 7.28 (dt, J = 6.3, 1.5 Hz, 1H), 5.02 (td, J = 7.5, 6.3 Hz, 1H), 3.67 (t, J = 6.3 Hz, 2H), 2.37 (ddt, J = 7.5, 1.6, 1.6 Hz, 2H), 1.69–1.75 (m, 2H), 0.90 (s, 9H), 0.05 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 133.5, 130.0, 129.5, 128.6, 114.4, 62.6, 32.5, 26.0, 21.3, 18.4, −5.2 ppm; HRMS (CI): m/z calcd for $C_{18}H_{29}O_3Si$ $[M+H]^+$: 321.1886; found: 321.1890.

(*Z*)-1-(Benzoyloxy)-(5-*N*-phthalimide)-1-pentene (17): Procedure **A**: **AM-Z/AM-E/M** = 94/3/3, yield: 99% (149 mg). Purified by column chromatography on silica gel (eluent: hexanes/AcOEt 1/1, R_f = 0.82); obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–8.03 (m, 2H), 7.74–7.77 (m, 2H), 7.63–7.65 (m, 2H), 7.51–7.56 (m, 1H), 7.37–7.42 (m, 2H), 7.25 (dt, J = 6.4, 1.5 Hz, 1H), 5.00 (td, J = 7.4, 6.4 Hz, 1H), 3.69–3.74 (m, 2H), 2.32 (q, J = 7.5 Hz, 2H), 2.33 (q, J = 7.5 Hz, 2H), 1.80–1.88 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 163.1, 134.8, 133.7, 133.3, 131.9, 129.7, 129.1, 128.4, 123.0, 112.9, 37.4, 27.8, 22.0 ppm; HRMS (CI): m/z calcd for $C_{20}H_{18}O_4N$ $[M+H]^+$: 336.1236; found: 336.1232.

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