# Biphasic Palladium-Catalyzed Hydroesterification in a Polyol Phase: Selective Synthesis of Derived Monoesters

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The palladium-catalyzed hydroesterification reaction was performed with polyols and olefins in a liquid/liquid biphasic system composed of unreacted polyol on the one hand and apolar reaction products/organic solvents on the other hand. The palladium-based catalyst was immobilized in the polyol phase thanks to the use of cationic triarylphosphines possessing pendent protonated amino groups in the acidic reaction medium or to the sulfonated phosphine TPPTS (trisodium triphenylphosphine-3,3',3''-trisulfonate). Owing to the insolubility of the products in the catalytic phase, this approach allowed the synthesis of monoesters of polyols with high selectivities as well as the easy separation of the catalyst through simple decantation.

## Introduction

Esters derived from polyols have found several applications as lubricants,<sup>[1]</sup> surfactants emulsifiers,<sup>[2]</sup> and plasticizers.<sup>[3]</sup> Their access is straightforward and particularly relevant from a sustainable point of view from simple esterification reactions with long-chain fatty acids resulting from vegetable oils. As natural acids more commonly contain very long alkyl chains, shorter chains have to be obtained from acids from a petroleum source.  $C_7-C_{11}$  acids are thus typically synthesized from  $C_6-C_{10}$ olefins through the "oxo process", which involves a two-step hydroformylation/oxidation process. Interested in the field of polyol functionalization, we recently targeted to access derived monoesters from the hydroesterification reaction.<sup>[4]</sup> This palladium- or cobalt-catalyzed reaction allows straightforward access to esters from alcohols, carbon monoxide, and olefins. This transformation is, moreover, highly atom economical, as all the reactants are fully incorporated in the final product and no salt is formed as a side product. This reaction has been well studied with methanol, and notably, methyl propionate is now industrially produced from the methoxycarbonylation of ethylene.<sup>[5]</sup> The nature of the olefin has been largely varied, but variation of the alcohol and more precisely the use of polyols have attracted much less attention. Several patents describe

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the cobalt-catalyzed hydroesterification of olefins with polyols.<sup>[6]</sup> Ethylene glycol<sup>[7]</sup> and cellulose<sup>[8]</sup> have also been acylated by using the olefin hydroesterification reaction with palladiumbased catalysts in a homogeneous phase.

Polyols are hydrophilic and essentially insoluble in apolar organic solvents. We thus anticipated that a biphasic hydroesterification reaction with the catalyst immobilized in the polyol phase could be setup if the reaction products were sufficiently lipophilic. The hydroesterification reaction has been scarcely performed under biphasic conditions for the conversion of aliphatic olefins or styrenic compounds with simple alcohols. The reaction products are soluble in alcohols such as methanol and ethanol, and thus, biphasic systems have been obtained from the use of an immiscible tertiary solvent such as ionic liquids<sup>[9]</sup> or supercritical CO2.<sup>[10]</sup> Water cannot be used because of the possible hydrolysis of the esters and/or potential hydrocarboxylation. Our aim was to show that polyols, more than simple reactants, can advantageously also act as a polar phase in a biphasic hydroesterification reaction. Such an approach has, for example, been successfully applied in other metal- and basecatalyzed transformations in glycerol.[11] Taking advantage of this behavior, we particularly concentrated our efforts on the development of appropriate ligands soluble in a polyol phase for easy catalyst separation from the products by simple phase decantation, an important issue if expensive metals are employed for synthesis. From a synthetic point of view, this procedure is, in addition, expected to allow improved selectivities for monoesters through extraction of the products from the catalytic phase.

## **Results and Discussion**

The palladium-catalyzed hydroesterification reaction involves the use of phosphorus-based ligands to stabilize low-valent palladium species and to allow the formation of reactive or-



ganometallic species.<sup>[4]</sup> Among these ligands, triphenylphosphine is the simplest, and this widely available ligand has proven to be one of the best and simplest ligands to obtain high catalytic activities in the methoxycarbonylation of  $\alpha$ -olefins. In the case of the hydroesterification reaction of 1-octene with isosorbide, the best results in terms of catalytic activity were obtained with this ligand combined with Pd(OAc)<sub>2</sub> and PTSA (4-toluenesulfonic acid) as an acid cocatalyst.<sup>[12]</sup> Aiming at immobilizing the catalyst in the polyol phase, we thus targeted the use of polar ionic triarylphosphines. Phosphines that bear pendent basic amino groups particularly attracted our attention (Scheme 1). In the presence of an excess amount of an



Scheme 1. Hydrophilic phosphorus-based ligands used in the biphasic hydroesterification reaction.

acid cocatalyst used to promote the hydroesterification reaction, the amino groups are protonated, which thus leads to the formation of highly polar ligands. The hydrophilicity of these ionic ligands has been previously exploited to promote the hydroxycarbonylation of olefins under aqueous biphasic conditions.<sup>[13]</sup> In addition, the commercially available TPPTS (trisodium triphenylphosphine-3,3',3''-trisulfonate) ligand bearing sulfonate groups was also evaluated. One can expect good solubility of the catalyst from the use of ionic ligands associated to palladium in a polyol phase along with low solubility in an apolar solvent, which thus allows biphasic processes.

Ligand L3 was synthesized according to an already-reported procedure.<sup>[14]</sup> Ligands L1 and L2 are new and were synthesized in two steps (Scheme 2). In THF, 1-(4-bromophenyl)-*N*,*N*-dimethylmethanamine was lithiated with tBuLi (2 equiv.), and the organolithium reagent thus obtained was treated separately with chlorodiphenylphosphine and dichlorophenylphosphine at -80 °C. After aqueous workup under oxygen-free conditions, the two phosphines were ob-

tained as pure oily compounds that contained less than 3% of phosphine oxide. Ligands L1–L3 are air sensitive and are easily oxidized and should be stored under an oxygen-free atmosphere.

The first catalytic experiments were setup with ethylene glycol and 1-octene as model substrates (Scheme 3, see also Table 1). The catalyst combination was obtained from a mixture of Pd(OAc)<sub>2</sub> (0.2 mol%) asCHEMSUSCHEM Full Papers

sociated with an unoptimized excess of 8 equivalents of phosphines **L1–L3** or TPPTS. An excess amount of monophosphine is classically used in hydroesterification reactions to counterbalance ligand degradation thus to ensure catalyst stability during the reaction.<sup>[12]</sup> An excess amount of PTSA was also used as a cocatalyst for the formation of a palladium hydride species. With all four ligands, the catalytic mixtures proved to be very soluble at room temperature in ethylene glycol (2.1 mL) thus to give pale-yellow solutions. The apolar phase was composed of 1-octene (2 mL, 500 equiv. relative to Pd) and an added organic solvent (1 v/v of 1-octene) to facilitate product extraction from the polyol phase. The reactions were run under CO pressure

(4.0 MPa) at 90 °C for 20 h, and the conversion of 1octene was quantified by GC.

The biphasic mixture was made up of ethylene glycol on the one hand and toluene/1-octene on the other hand, and it could be decanted quickly at room temperature. Protonated phosphines L1, L2, and L3 and TPPTS were clearly located in the polar phase, as shown by analysis of the two layers by <sup>31</sup>P NMR spectroscopy. After the catalytic reactions were run, the biphasic solutions were retained. GC analysis of the two layers evidenced the presence of the ester products essentially in the toluene apolar phase.

The hydroesterification reaction with ethylene glycol and 1octene yielded a mixture of mono- and diesters with linear and branched aliphatic chains (see Scheme 3). The measured linear to branched (sum of the three possible branched isomers) ratios measured for the experiments were dependent on the nature of the ligand used. L1, L2, L3, and PPh<sub>3</sub> gave ratios close to 75:25, a commonly obtained value for the hydroesterification reaction of  $\alpha$ -olefins with a Pd/PPh<sub>3</sub>/sulfonic acid catalytic system.<sup>[4,12]</sup> The TPPTS ligand afforded higher selectivities



Scheme 2. Synthesis of ligands L1 and L2.



Scheme 3. The hydroesterification reaction with 1-octene and ethylene glycol. PTSA = p-toluenesulfonic acid.

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Table 1. Hydroesterification of 1-octene and ethylene glycol with triarylphosphines. <sup>[a]</sup>						
Ligand	Conversion of 1-octene [%] <sup>[b]</sup>	Octene iso- mers <sup>[b,c]</sup> [%]	Yield [ monoester <sup>[b]</sup>	%] diester <sup>[b]</sup>	Selectivity mono- ester <sup>[d]</sup> [%]	Linear/branched <sup>[e]</sup>
L3	37	5	28	2	91	76:24
L2	70	8	39	21	65	73:27
L1	99	7	62	29	68	74:26
TPPTS	72	9	41	21	66	55:45
PPh₃	99	6	26	64	29	72:28

[a] The reactions were performed with 1-octene (2 mL, 12.7 mmol), toluene (2 mL), ethylene glycol (2.1 mL, 37.6 mmol),  $Pd(OAc)_2$  (0.2 mol% with respect to 1-octene), ligand (8 equiv. with respect to Pd), PTSA (35 equiv. with respect to Pd), and CO (4.0 MPa) at 90 °C for 20 h. [b] Determined by GC. [c] Octene isomers represent part of the isomerized olefin (100×amount of internal olefin/initial amount of olefin). [d] Selectivity=100× amount of monoester/(amount of monoester+amount diester). [e] Linear/branched=ratio linear/(sum of branched isomers) calculated for the monoesters.

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which strongly suggests good immobilization of the palladium species in the polar phase (Figure 1).

Inductively coupled plasma (ICP) analysis of the organic phases obtained from the reactions with these three ligands evidenced palladium and phosphorus contents below the detection limit of 1 ppm, which thus indicated very low catalyst leaching in the apolar phase. On the other hand, the run with PPh<sub>3</sub> afforded a strongly colored

toward the branched isomers. A non-negligible part of the converted 1-octene was found in the corresponding internal olefins obtained according to a well-known palladium hydride catalyzed isomerization reaction. Finally, it should be noted that ethylene glycol was partially dimerized to give diethylene glycol. This side reaction is due to the presence of PTSA that acts as an acid catalyst for this transformation, but this reaction, however, remained guite limited under the reaction conditions used. At 90 °C, less than 2% of ethylene glycol was dimerized. The conversions of 1-octene were complete upon using more lipophilic ligand L1 and PPh<sub>3</sub>. For the extreme values obtained with ligands bearing dimethylamino groups, conversions of 99 and 37% were obtained with the use of L1 and L3, respectively. This difference in activity could be attributed to the more or less marked amphiphilic character of the phosphines. The more ionic the phosphine, the better the immobilization of the catalyst in the bulk of the polar phase. By analogy to aqueous biphasic catalysis, better immobilization in the polar phase does not favor high reaction rates as a consequence of mass-transfer limitations. The TPPTS ligand bearing strongly electron-withdrawing sodium sulfonate groups gave activities that were in between those of L1 and L2. The selectivity of monoesters depended on the degree of advancement of the reaction: the lower the conversion of 1-octene, the higher the expected selectivity for the monoester. The selectivity for the monoester was, for example, higher with ligand L3 than with ligand L2 at 37 and 70% 1-octene conversion, respectively. However, the nature of the ligand involved in the biphasic catalytic transformations also played a non-negligible role. Ligands L2 and L1 afforded narrow selectivities for the monoester at rather different conversions of 1-octene (70 and 99%, respectively). To assess the importance of the biphasic nature of this catalytic system on the selectivity for the monoester, we performed a catalytic run with PPh<sub>3</sub>. With this ligand, complete conversion of 1-octene was obtained, but the proportion of diester was increased. This positive effect of biphasic catalysis on the selectivity is, of course, of interest for the selective synthesis of monoesters. Noteworthy is the color of the polyol and organic phases at the end of the reaction. The runs performed with TPPTS, L2, and L3 showed a well-colored ethylene glycol phase with a clear and colorless apolar phase,



Figure 1. Crude reaction mixture obtained with ligand L2 (left) and PPh<sub>3</sub> (right). For clarity, the crude mixture with PPh<sub>3</sub> was diluted with toluene and ethylene glycol.

apolar phase, which thus showed, as expected, very important leaching of palladium species in the product-containing layer. Less-polar ligand L1 showed intermediate behavior with an intensively colored ethylene glycol phase and a pale-yellow apolar phase.

As L2 appeared to be a good compromise between catalytic activity and quality of the biphasic phase, we thus studied the reaction with this ligand. To achieve higher selectivities for the monoesters, we used higher ethylene glycol/1-octene ratios. As shown in Table 2, this logically allowed a higher selectivity for the monoester but also a better conversion of 1-octene (Table 2, entry 1 vs. Table 1, entry 2). Very similar yields were also found with pentane and ether as co-solvents. The latter allowed us to reach 92% selectivity for the monoester at 87% olefin conversion, and similar results were obtained with the TPPTS ligand (Table 2, entry 4). The use of another acid source did not allow any improvement. Methanesulfonic acid led to conversions that were similar to those obtained with PTSA, but lower selectivities for the monoesters were obtained. Hydrochloric acid led to less-active catalytic species but proved to be useful to synthesize esters with more of a branched structure (54% branched). Interestingly, SnCl<sub>2</sub> allowed access to a higher proportion of linear esters (90% linear), albeit in lower yields. In that particular case, in addition to SnCl<sub>2</sub>, a stoichiometric amount of PTSA to fully protonate the phosphine was used, and this resulted in a colorless organic phase at the end of the reaction.

According to the biphasic hydroesterification procedure, monoesters of ethylene glycol are efficiently obtained from the reaction with  $\alpha$ -olefins that bear 6 to 10 carbon atoms (see Table 3, entries 1–3). A lower reactivity was obtained with 1-decene, presumably because of the lower solubility of this



Table 2. Optimization of the hydroesterification reaction with 1-octene and ethylene glycol with ligand L2. <sup>[a]</sup>							
Entry	Acid	Solvent	Conversion of 1-octene <sup>[b]</sup> [%]	Octene iso- mers <sup>[c]</sup> [%]	Yield [ monoester <sup>[b]</sup>	%] diester <sup>[b]</sup>	Selectivity mono- ester <sup>[d]</sup> [%]
1	PTSA	toluene	88	8	62	17	78
2	PTSA	pentane	79	11	55	12	82
3	PTSA	Et₂O	87	6	73	6	92
4 <sup>[e]</sup>	PTSA	Et <sub>2</sub> O	86	9	68	4	94
5	MsOH	Et <sub>2</sub> O	79	<2	52	23	69
6	HCI	Et <sub>2</sub> O	59	3	52	4	93
7	SnCl <sub>2</sub> <sup>[f]</sup>	Et <sub>2</sub> O	36	2	32	< 2	95

[a] The reactions were performed with 1-octene (1 mL, 6.4 mmol), co-solvent (1 mL), ethylene glycol (4 mL, 75.2 mmol), Pd(OAc)<sub>2</sub> (0.2 mol% with respect to 1-octene), **L2** (8 equiv. with respect to Pd), acid (27 equiv. with respect to Pd), and CO (4.0 MPa) at 90 °C for 20 h. MsOH = methanesulfonic acid. [b] Determined by GC. [c] Octene isomers represent the part of isomerized olefin (100×amount of internal olefin/initial amount of olefin). [d] Selectivity = 100×amount of monoester/(amount of monoester + amount diester). [e] With TPPTS in place of **L2**. [f] The reaction was performed with PTSA (2 equiv. with respect to Pd).

Entry	Polyol	Olefin	Olefin conver- sion <sup>[b]</sup> [%]	Selectivity monoester <sup>[c]</sup> [%] (Yield [%]) <sup>[d]</sup>
1	ethylene glycol	1-octene	87	94 (74)
2	ethylene glycol	1-hexene	85	97 (69)
3	ethylene glycol	1-decene	68	>98 (57)
4	1,3-propanediol	1-octene	87	94 (67)
5	1,4-butanediol	1-octene	89	94 (n.d. <sup>[e]</sup> )
6	isosorbide	1-octene	70	92 (58)
7	glycerol	1-octene	72	85 (57)

 $Pd(OAc)_2$  (0.2 mol% with respect to olefin), TPPTS (8 equiv. with respect to Pd), acid (11 equiv. with respect to Pd), and CO (4.0 MPa) at 90 °C for 20 h. [b] Determined by GC. [c] Selectivity = 100 × amount of monoester/(amount of monoester + amount diester). [d] Yield of isolated product after extraction and evaporation of the volatiles.[e] Not determined.

alkene in ethylene glycol. Keeping 1-octene as the reactant, the reaction was further studied with various polyols resulting from agroresources. 1,3-Propanediol and 1,4-butanediol are, for example, straightforwardly accessible from glucose through fermentation processes.<sup>[15]</sup> The hydroesterification with these two diols and 1-octene allowed high conversions, and the results compare well with those obtained with ethylene glycol (Table 3, entry 1 vs. entries 4 and 5). Conversions of 1-octene proved to be rather high, and the selectivities for monoesters were higher than 90%. However, the mixtures of esters were easily separated from the polyol phase in the cases of ethylene glycol and 1,3-propanediol, but only one phase was obtained at the end of the reaction with 1,4-butanediol, which thus impeded the separation procedure. Isosorbide, a diol accessible from double dehydration of sorbitol, has a melting point of 63 °C and is thus a liquid at 90 °C (Table 3, entry 6). The reaction was thus run with this diol in pure form by using the biphasic procedure with 1-octene. The reaction proved to be efficient and selective toward the synthesis of the corresponding monoesters. As isosorbide is a nonsymmetric molecule with two nonequivalent hydroxyl groups, a complex mixture of two monoesters with either linear or branched structures was ob-

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tained. Saponification followed by GC analysis allowed the linear/branched ratio of 65:35 to be determined. At the end of the reaction, the unreacted isosorbide precipitated along with the catalyst. The colorless liquid organic layer containing the esters was thus simply extracted and separated from the catalyst through filtration. Finally, the reaction was also performed with glycerol as a liquid higher polyol (Table 3, entry 7). The secondary hydroxyl groups of glycerol showed very limited reactivity, and 1-monoglycerides were obtained as the main reaction

products. The linear/branched ratio was fully comparable to that obtained with ethylene glycol or with other polyols if the TPPTS ligand was used (60:40 with glycerol).

# Conclusions

The palladium-catalyzed hydroesterification reaction was efficiently performed under polyol/organic phase biphasic conditions. Noteworthy is that the catalyst was immobilized in the polyol phase. The immiscibility of the catalyst with the organic solvent and organic products formed allowed an easy separation of the catalystFor this purpose, hydrophilic dimethylaminocontaining monophosphines protonated in the presence of acids were efficiently used, as was the trisodium triphenylphosphine-3,3',3''-trisulfonate (TPPTS)

ligand . The protocol allowed efficient synthesis of monoesters derived from agro-based polyols with high selectivities, which thus showed that concepts of biphasic catalysis can be applied to polyol/organic systems in carbonylation reactions, for which the polyol acts as both the catalyst immobilization phase and the reactant.

# **Experimental Section**

### Experimental procedure for the hydroesterification of olefins with ethylene glycol (Table 1, ligand L2)

A 25 mL Parr mechanically stirred stainless-steel autoclave was charged with Pd(OAc)<sub>2</sub> (6.1 mg, 0.03 mmol), ligand L2 (0.24 mmol), and PTSA (180 mg, 0,96 mmol). The reactor was then purged by vacuum/dry nitrogen (3×). Distilled and degassed ethylene glycol (2.1 mL, 37.6 mmol), ether (2 mL), and 1-octene (2 mL, 12.7 mmol) were transferred by cannula from a Schlenk tube to the stainless-steel autoclave, and the mixture was stirred at room temperature for 5 min. CO (4.0 MPa) was introduced, and the reactor was heated to 90 °C and stirred at 1300 rpm. After 20 h, the reactor was cooled, and the excess amount of CO was vented. The mixture was



diluted with ether (10 mL), dodecane (250  $\mu$ L) was introduced (internal standard for GC analysis), and the organic layer was extracted and analyzed by GC. ICP analysis was performed on the sample.

### General procedure to isolate the esters (Table 3)

The crude product was extracted with ether  $(2 \times 10 \text{ mL})$ . The ether phase was washed with distilled water (10 mL), and the resulting solution was dried (MgSO<sub>4</sub>) and filtered. The volatiles were finally evaporated under reduced pressure to afford the mixture of esters as a colorless liquid.

### Synthesis of ligand L2

A 250 mL Schlenk tube equipped with a magnetic stirring bar was charged with 1-(4-bromophenyl)-N,N-dimethylmethanamine (3.3 g, 15.41 mmol). The Schlenk tube was purged with nitrogen by using vacuum/N<sub>2</sub> cycles (3×), and degassed diethyl ether (50 mL) was added to the flask by cannula. The resulting homogeneous solution was cooled down to -78 °C. A solution of 1.6 M tert-butyllithium in pentane (20 mL, 32 mmol) was then added dropwise while maintaining the temperature. A yellowish precipitate was formed, and the solution was stirred at -78 °C for 2 h under an atmosphere of nitrogen. Dichlorophenylphosphine (1000 µL, 7.37 mmol) was added dropwise by syringe, and the solution was kept at room temperature and stirred overnight. Degassed water (50 mL) was added, followed by degassed dichloromethane (50 mL). After decantation, the organic layer was extracted, and the aqueous phase was further extracted with degassed dichloromethane (2×25 mL). The organic layer was dried (MgSO<sub>4</sub>), and after filtration (under an atmosphere of nitrogen) the volatiles were evaporated. The product was finally obtained as a pale-yellow oil (2.16 g, 80%). The oxide-free ligand was obtained through a reduction step with HSiCl<sub>3</sub> according to a reported procedure.<sup>[14]</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 2.27$  (s, 12 H, CH<sub>3</sub>), 3.44 (s, 4 H, CH<sub>2</sub>), 7.31 ppm (m, 13 H,  $H_{arom}$ ). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 45.43$  (s, 4C, CH<sub>3</sub>), 64.07 (s, 2C,  $CH_2$ ), 128.46 (d,  $J_{P,C} = 6.8 \text{ Hz}$ , 2C,  $CH_{meta}$ ), 128.62 (s, 1C,  $CH_{para}$ ), 129.25 (d,  $J_{P,C} = 7.1$  Hz, 4C, CH<sub>meta</sub>), 133.67 (d,  $J_{P,C} = 19.4$  Hz, 2C, CH<sub>ortho</sub>), 133.73 (d, J<sub>PC</sub> = 19.7 Hz, 4C, CH<sub>ortho</sub>), 135.88 (d, J<sub>PC</sub> = 10.4 Hz, 2C, C<sub>ipso</sub>), 137.52 (d, J<sub>P,C</sub> = 10.9 Hz, 1C, C<sub>ipso</sub>), 139.54 ppm (s, 1C, CCH<sub>2</sub>). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>):  $\delta = -6.7$  ppm.

#### Synthesis of ligand L1

The ligand was synthesized accordingly to the protocol used for the synthesis of **L2**. The reaction was set up with 1-(4-bromophen-yl)-*N*,*N*-dimethylmethanamine (1,3 g, 6 mmol), 1.6 m *tert*-butyllithium in pentane (9 mL, 14.4 mmol), and chlorodiphenylphosphine (1100 µL, 6 mmol). The product was finally obtained as a pale-yellow oil (1.78 g, 91 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.28 (s, 6 H, CH<sub>3</sub>), 3.45 (s, 2 H, CH<sub>2</sub>), 7.28–7.37 ppm (m, 14 H, H<sub>arom</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 45.42 (s, 4 C, CH<sub>3</sub>), 64.04 (s, 2 C, CH<sub>2</sub>), 128.48 (d, J<sub>PC</sub> = 7.1 Hz, 4 C, CH<sub>meta</sub>), 128.67 (s, 2 C, CH<sub>para</sub>), 129.29 (d, J<sub>PC</sub> = 7,1 Hz, 2 C, CH<sub>meta</sub>), 133.71 (d, J<sub>PC</sub> = 19.4 Hz, 4 C, CH<sub>ortho</sub>), 137.73 (d, J<sub>PC</sub> = 19.6 Hz, 4 C, CH<sub>ortho</sub>), 135.92 (d, J<sub>PC</sub> = 10.4 Hz, 2 C, C<sub>ipso</sub>), 137.33 (d, J<sub>PC</sub> = 10.9 Hz, 2 C, C<sub>ipso</sub>), 139.50 (s, 1 C, CCH<sub>2</sub>). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  = -6.0 ppm.

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