

Article

Synthesis of Alpha Olefins: Catalytic Decarbonylation of Carboxylic Acids and Vegetable Oil Deodorizer Distillate (VODD)

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Abstract: Decarbonylation of carboxylic acids provides an effective protocol for producing alpha olefins; however, previous literature has focused on the palladium-bisphosphine catalysts and has only sporadically studied the palladium-monophosphine catalyst. To investigate the catalytic activity of the palladium-monophosphine catalyst on decarbonylation of carboxylic acids, new monophosphine ligands were synthesized (NP-1, NP-2, CP-1 and CP-2). By employing (1–3 mol%) palladium-naphthylphosphine catalysts, various carboxylic acids were converted into corresponding alpha alkenes with good yields and selectivity within a short period of time. Vegetable oil deodorizer distillate (VODD), which is a by-product from the vegetable oil refinery process, was found to be rich in free fatty acids and there is great interest in turning vegetable oil deodorizer distillate into value-added compounds. It is noteworthy that our catalytic system could be applied to convert vegetable oil deodorizer distillate (VODD) into diesel-like hydrocarbons in a good yield.

Keywords: palladium; decarbonylation; diesel-like hydrocarbons; carboxylic acid; vegetable oil deodorizer distillate



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1. Introduction

Owing to the depletion of fossil fuels, there is a growing demand for the exploration of alternative renewable energy sources [1–4]. Biomass-derived hydrocarbons (diesel-like hydrocarbons) are believed to be a good alternative for fossil fuels since they could be readily obtained by cracking or decarbonylation/decarboxylation of a biomass such as vegetable oils. Cracking of vegetable oil results in the production of a broad range of hydrocarbons with different numbers of carbon chains. Compared to cracking, decarbonylation/decarboxylation of biomass-derived carboxylic acids is particularly attractive since substrates are inexpensive and are readily available from various natural sources [1], and highly selective alkenes can be obtained. In addition to acting as transportation fuels, biomass-derived alpha olefins are important precursors for various industrial chemicals, such as surfactants, plasticizers, and polymers [5–8]. In the past decade, extensive studies that focused on the development of heterogeneous catalytic decarbonylation/decarboxylation reactions were carried out, and TiO [5–9], Pd/C [10–15], Pd/Al₂O₃ [16,17], Pt/Al₂O₃ [18–20], Ni/SiO₂ [15], Ru/C [15], Rh/C [15], Os/C [15], and WO_x-Al₂O₃ [21] were found to convert fatty acids into alkanes and alkenes in response to harsh reaction conditions (>300 °C) [2]. Therefore, homogeneous catalytic systems were explored [4] and palladium [22–31], nickel [32–34], iridium [35,36], rhodium [22], and iron [37] converted various carboxylic acids into alkenes. Palladium catalysts showed superior catalytic activity over the other metals described, resulting in a continuous effort to explore various palladium catalysts on the decarbonylation reactions of carboxylic acids.

Miller [23] and Kraus [26] employed very low catalyst loading (0.01 mol% PdCl₂(PPh₃)₂) to catalyze a decarbonylation reaction at elevated temperatures (230–250 °C). Grubbs and

Stoltz [28] reported another example of low catalyst loading catalysis (0.05 mol% $\text{PdCl}_2(\text{PPh}_3)_2$ -Xantphos) with a portion-wise addition of acetic anhydride reported. Gooßen [24] and Scott [25] catalyzed a decarbonylation reaction under milder conditions, albeit by employing a higher catalyst loading (3 mol% Pd-DPEPhos) and with the use of an expensive high-boiling point solvent (DMPU). Jensen [30] reported the use of 0.5 mol% palladium-bisphosphine precatalyst to catalyze a decarbonylation reaction (Figure 1).

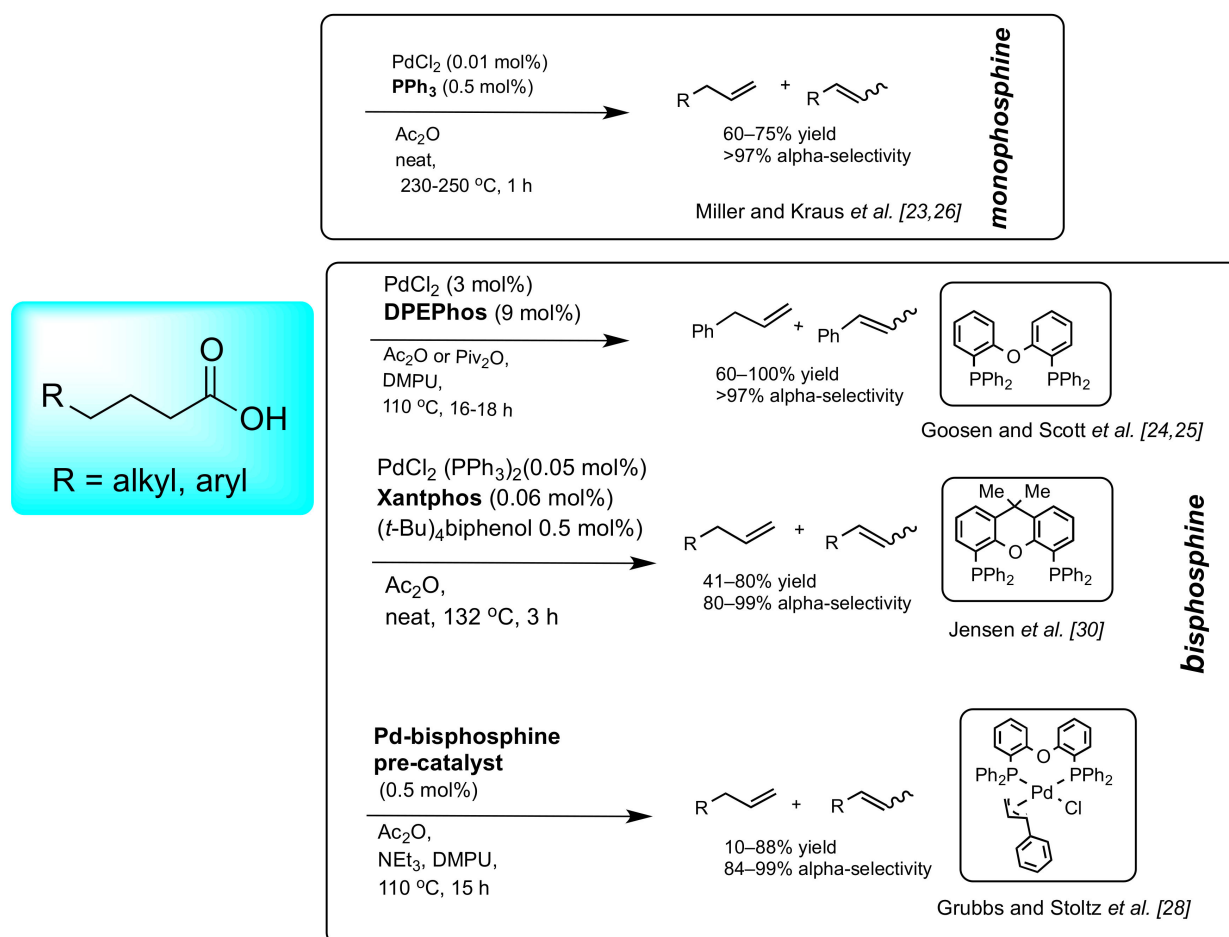
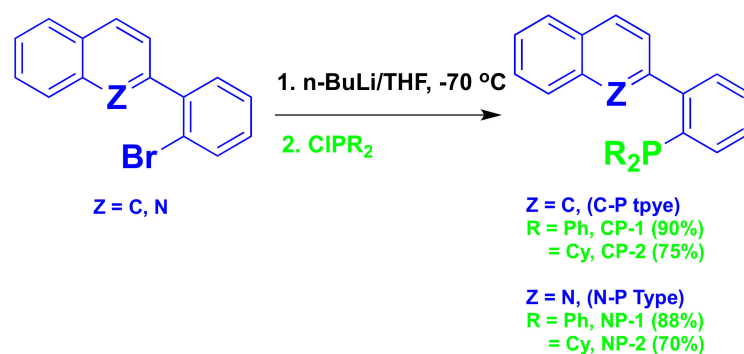


Figure 1. Palladium-catalyzed decarbonylation of carboxylic acids into olefins.

Despite this, palladium, in conjunction with strong coordination bisphosphine ligands (particularly biaryl ether ligands, DPEPhos, or XantPhos), were proven to be an effective catalyst in decarbonylation reactions to afford alkenes with good alpha-selectivity [38]. However, application of palladium-monophosphine catalysts remains sporadically studied. Cramer *et al.* investigated the palladium-catalyzed decarbonylation of biomass-derived hydrocinnamic acid to styrene [31]. Recently, Jensen *et al.* reported the benefit of hemilabile POP-type ligand (e.g., DPEPhos) in the deoxygenation of fatty acids reaction [39]. Their proposed mechanism involved the deliberation of phosphine ligands for provision of reaction vacant site and re-coordination of phosphine ligands for stabilization of intermediates. Inspired by computational studies by Cramer *et al.* and Jensen *et al.*, we developed N-P type monophosphines with quinoline-scaffold (NP-1 and NP-2) and C-P type Buchwald biarylmonophosphines [40] with naphthalene-scaffold (CP-1 and CP-2) (Scheme 1) and their corresponding palladium complexes crystalline structure are reported herein (Figure 2). We would like to (1) investigate any beneficial effects of hemilabile ligands towards the decarbonylation of carboxylic acids and (2) examine the feasibility of palladium-monophosphine catalyzed decarbonylation reactions.



Scheme 1. Synthesis pathway for mono-phosphines.

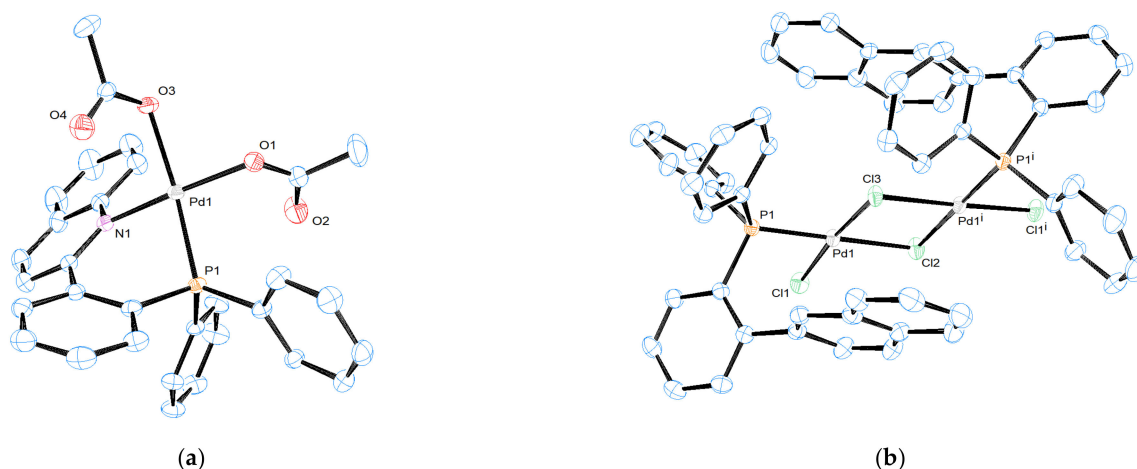
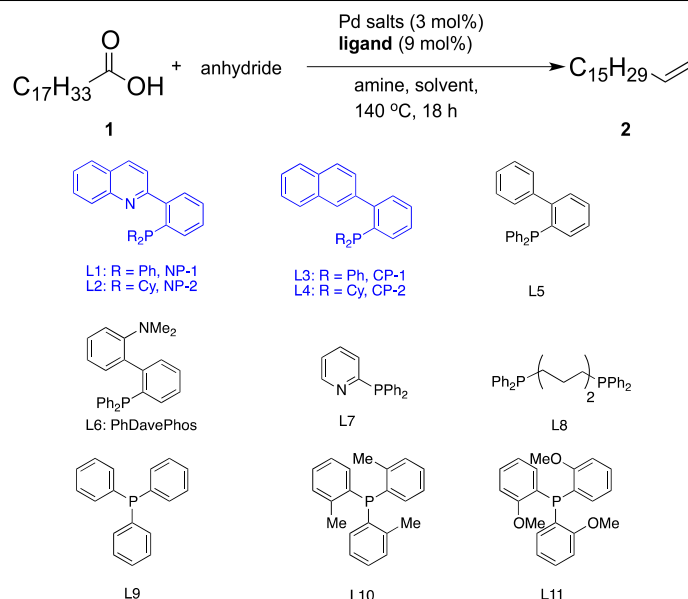


Figure 2. ORTEP drawing of Pd complexes. (a) Pd-NP-1. Selected bond lengths (\AA): Pd(1)-O(1) = 2.0164(15), Pd(1)-N(1) = 2.0601(16), Pd(1)-O(3) = 2.0901(13), Pd(1)-P(1) = 2.1885(4); (b) Pd-CP-1. Selected bond lengths (\AA): Pd(1)-P(1) = 2.2563(8), Pd(1)-Cl(1) = 2.2937(9), Pd(1)-Cl(3) = 2.3181(8), Pd(1)-Cl(2) = 2.4293(9), Cl(2)-Pd(1)ⁱ = 2.4293(9), Cl(3)-Pd(1)ⁱ = 2.3181(8). H atoms are omitted for clarity.

2. Results and Discussion

Oleic acid—a major component present in vegetable oils, such as peanut oil (up to 71.1%) and almond oil (up to 67.2%) [41]—was chosen as a model substrate to optimize reaction conditions. By screening different Pd-sources (Table 1, entries 1–7), PdCl_2 in conjunction with NP-1 gave trace amounts of the desired product (11%) (Table 1, entry 1). Changing the PPh_2 moiety of ligand to PCy_2 showed an adverse effect on the product yield and no decarbonylation reaction occurred (Table 1, entry 2). Employing $\text{Pd}(\text{COD})\text{Cl}_2$ with ligand NP-1 (30%) yielded promising results (Table 1, entry 7). Increasing the amount of acetic anhydride did not increase the product yields (Table 1, entries 7–9) and thus two equivalents of anhydride were applied. Amines are crucial for stabilizing palladium-active species and help to enhance selectivity of the reaction [25], hence different amines were tested (Table 1, entries 10–13). Three equivalents of *N,N*-diisopropylethylamine (DIPEA) were found to enhance the yields of alkenes significantly (Table 1, entry 13). The C-O bonds of fatty acids are not easily broken and therefore excessive acid anhydride was needed for activation [39] (Table 1, entries 13–14).

Table 1. Optimization of the Pd-catalyzed decarbonylation of carboxylic acids. ¹

Entry	Pd Source (mol%)	Ligand (mol%)	Additive ² (Equiv.)	Amine ³ (Equiv.)	Solvent ⁴	Yield, % ⁵
1	PdCl ₂ (3)	L1 (9)	Ac ₂ O (2)	NEt ₃ (1)	DMAc	11
2	PdCl ₂ (3)	L2 (9)	Ac ₂ O (2)	NEt ₃ (1)	DMAc	n.r. ⁶
3	Pd(OAc) ₂ (3)	L1 (9)	Ac ₂ O (2)	NEt ₃ (1)	DMAc	n.r.
4	Pd(TFA) ₂ (3)	L1 (9)	Ac ₂ O (2)	NEt ₃ (1)	DMAc	n.r.
5	[Pd(cinnamyl)Cl] ₂ (1.5)	L1 (9)	Ac ₂ O (2)	NEt ₃ (1)	DMAc	n.r.
6	Pd(acac) ₂ (3)	L1 (9)	Ac ₂ O (2)	NEt ₃ (1)	DMAc	n.r.
7	Pd(COD)Cl ₂ (3)	L1 (9)	Ac ₂ O (2)	NEt ₃ (1)	DMAc	30
8	Pd(COD)Cl ₂ (3)	L1 (9)	Ac ₂ O (4)	NEt ₃ (1)	DMAc	28
9	Pd(COD)Cl ₂ (3)	L1 (9)	Ac ₂ O (6)	NEt ₃ (1)	DMAc	24
10	Pd(COD)Cl ₂ (3)	L1 (9)	Ac ₂ O (2)	NPr ₃ (1)	DMAc	33
11	Pd(COD)Cl ₂ (3)	L1 (9)	Ac ₂ O (2)	NPr ₃ (2)	DMAc	35
12	Pd(COD)Cl ₂ (3)	L1 (9)	Ac ₂ O (2)	NPr ₃ (3)	DMAc	41
13	Pd(COD)Cl ₂ (3)	L1 (9)	Ac ₂ O (2)	DIPEA (3)	DMAc	47
14	Pd(COD)Cl ₂ (3)	L1 (9)	—	DIPEA (3)	DMAc	n.r.
15	Pd(COD)Cl ₂ (3)	L3 (9)	Ac ₂ O (2)	DIPEA (3)	DMAc	68
16	Pd(COD)Cl ₂ (3)	L3 (9)	Piv ₂ O (2)	DIPEA (3)	DMAc	57
17	Pd(COD)Cl ₂ (3)	L3 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	70
18	Pd(COD)Cl ₂ (3)	L3 (9)	Bz ₂ O (1)	DIPEA (3)	DMAc	49
19	Pd(COD)Cl ₂ (3)	L3 (9)	Bz ₂ O (2)	DIPEA (3)	Toluene	53
20	Pd(COD)Cl ₂ (3)	L3 (9)	Bz ₂ O (2)	DIPEA (3)	CPME	55
21	Pd(COD)Cl ₂ (3)	L3 (9)	Bz ₂ O (2)	DIPEA (3)	γ-butyrolactone	28
22	Pd(COD)Cl ₂ (3)	L3 (9)	Bz ₂ O (2)	DIPEA (3)	DMPU	54
23	Pd(COD)Cl ₂ (3)	L3 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	72
24	Pd(COD)Cl ₂ (3)	—	Bz ₂ O (2)	DIPEA (3)	DMAc	18
25 #	Pd(COD)Cl ₂ (3)	L1 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	57
26 #	Pd(COD)Cl ₂ (3)	L2 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	46
27 #	Pd(COD)Cl ₂ (3)	L3 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	68
28	Pd(COD)Cl ₂ (3)	L3 (3)	Bz ₂ O (2)	DIPEA (3)	DMAc	36
29	Pd(COD)Cl ₂ (3)	L3 (6)	Bz ₂ O (2)	DIPEA (3)	DMAc	47
30	Pd(COD)Cl ₂ (3)	L3 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	70
31	Pd(COD)Cl ₂ (3)	L4 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	n.r.
32	Pd(COD)Cl ₂ (3)	L5 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	63
33	Pd(COD)Cl ₂ (3)	L6 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	56
34	Pd(COD)Cl ₂ (3)	L7 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	38
35	Pd(COD)Cl ₂ (3)	L8 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	29
36	Pd(COD)Cl ₂ (3)	L9 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	42
37	Pd(COD)Cl ₂ (3)	L10 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	n.r.
38	Pd(COD)Cl ₂ (3)	L11 (9)	Bz ₂ O (2)	DIPEA (3)	DMAc	n.r.

¹ Reaction conditions: 0.5 mmol oleic acid, 3 mol% Pd salts, 9 mol% ligand, 2–6 equiv. anhydride, 1–3 equiv. amine, 1 mL solvent, 140 °C, 18 h. ² Ac₂O = Acetic anhydride, Bz₂O = Benzoic anhydride, Piv₂O = Pivalic anhydride. ³ NEt₃ = Triethylamine, NPr₃ = Tripropylamine, DIPEA = *N,N*-diisopropylethylamine. ⁴ CPME = Cyclopentyl methyl ether; DMPU = *N,N'*-Dimethylpropyleneurea; DMAc = *N,N*-Dimethylacetamide. ⁵ Calibrated GC yield % by GC-FID against dodecane as internal standard. ⁶ n.r. = No reaction. # Reaction time = 6 h.

With the optimized reaction conditions we then examined the catalytic activity of our N-P and C-P type ligands. However the N-P type ligand (NP-1) gave inferior results (47%, Table 1, entry 13) than the C-P type ligand (CP-1) (68%, Table 1, entry 15). The crystalline structure indicated that relative strong Pd-N bond (bond length = 2.06 Å) was formed. The Pd-N bond may not favour the dissociation and re-coordination of ligands to stabilize the reaction intermediates. Meanwhile, monodentate CP-1 may offer the flexibility for dissociation of ligands in order to provide vacant sites and re-coordinate to stabilize the palladium catalyst (Figure 2).

Thus, we employed CP-1 as a ligand and examined different anhydrides (Table 1, entries 15–18) as well as solvents (Table 1, entries 19–23) to modify our catalytic system. Two equivalents of benzoic anhydrides were found to give the highest yield (Table 1, entry 17: 70%) among screened anhydride sources. *N,N'*-Dimethylpropyleneurea (DMPU) was reported as an appropriate solvent that commonly used in Pd-bisphosphine-catalyzed decarbonylation of carboxylic acids; however, it gave an inferior performance (Table 1, entry 22: 54%) in our catalytic system while *N,N*-Dimethylacetamide (DMAc) gave superior results (Table 1, entry 23: 72%). Several other green solvents [42,43], such as cyclopentyl methyl ether (CPME) (Table 1, entry 20: 55%) and γ -butyrolactone (Table 1, entry 21: 28%), were examined but their results were inferior to DMAc.

With promising results in hand, we then compared the catalytic activity of our developed and synthesized monophosphines to other commercially available monophosphine ligands (Table 1, entries 24–38). Firstly, ligands were found to be crucial towards the decarbonylation reaction to afford desired alkenes. Then we found that Pd(COD)Cl₂ with CP-1 gave the highest catalytic activity when compared to other commercially available ligands (Table 1, entries 30–38). A lesser amount of ligand would decrease product yields significantly (3 mol% = 36%; 6 mol% = 47%; 9 mol% = 70%, Table 1, entries 28–30). Furthermore, the reaction time could be shortened to six hours without diminishing product yields (18 h: 70%; 6 h: 68%, Table 1, entries 27 and 30). With the optimized reaction conditions, we examined the catalytic activities of our developed monophosphines. Naphthyl-scaffold monophosphines were found to give superior results to the quinoyl-scaffold monophosphines (Table 1, entries 25–27).

We further extended our substrate scopes with the optimization reaction conditions obtained (Figure 3). Odd-numbered alkenes are valuable building blocks for various fine chemicals, but they are largely inaccessible and expensive. Even-numbered long-chain fatty acids could be easily accessed from vegetable oils [41]. Therefore, it is of great interest as to whether we could convert inexpensive, even-numbered, saturated fatty acids into value-added, odd-numbered alkenes. By applying our catalytic system, various even-numbered, long-chain fatty acids could be converted into odd-numbered alkenes in good yields and selectivity (Figure 3, entries 2–4). When the catalyst loading was lowered to 1 mol% Pd, even-numbered, long-chain fatty acids could still be smoothly converted into their corresponding odd-numbered alkenes in satisfactory yields (52%–63%). In addition to the saturated, long-chain fatty acids, 5-phenylvaleric acid and 5-(4-Fluorophenyl)valeric acid were also smoothly converted into corresponding alkenes (Figure 3, entries 7 and 8). Estragole (60%) (Figure 3, entry 5) and its derivatives (65%) (Figure 3, entry 6), which served as precursors for fungicide and fragrance [44], could be readily obtained via decarbonylation of 4-(4-methoxyphenyl)butyric acid and 4-(3,4-Dimethoxyphenyl)butyric acid, respectively. It is important to note that this study gives the first report of the synthesis of allylpyrene via decarbonylation of pyrenecarboxylic acid (60%) (Figure 3, entry 9).

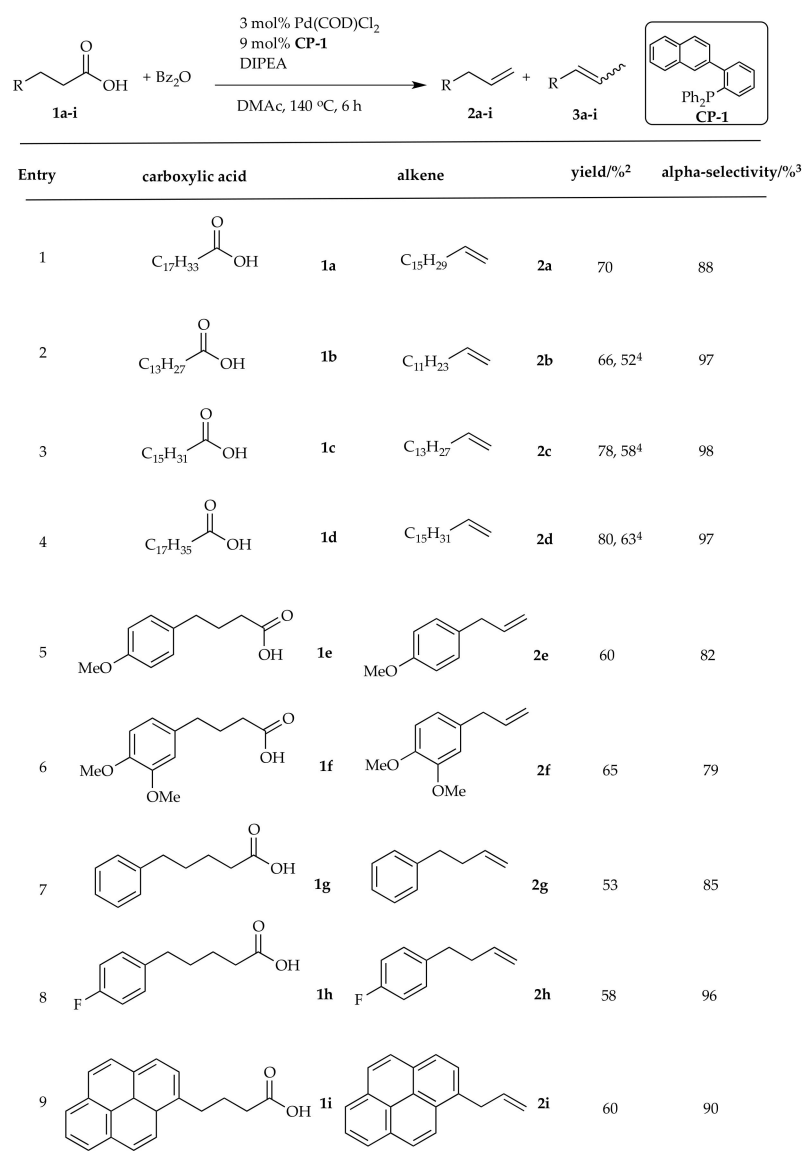
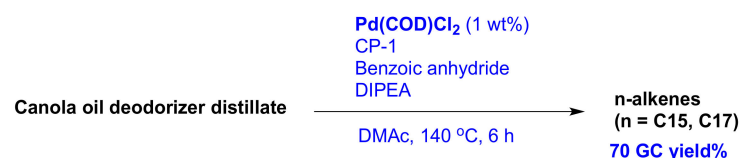


Figure 3. Pd-catalyzed decarbonylation of carboxylic acids to alpha alkenes. ¹ Reaction conditions: 0.5 mmol carboxylic acid, 3 mol% Pd(COD)Cl₂, 9 mol% CP-1, 2 equiv. Benzoic anhydride, 3 equiv. DIPEA, 1 mL DMAc, 140 °C, 6 h. ² Isolated yield. ³ alpha-selectivity was determined by ¹H NMR. ⁴ 1 mol% Pd(COD)Cl₂ (Pd:L = 1:3) were employed.

Vegetable oil deodorizer distillate (VODD), a by-product of the vegetable oil refinery process [45,46], was found to be rich in free fatty acids. Thus, there is great interest in turning vegetable oil deodorizer distillate into value-added compounds. Extensive studies were done on the heterogeneous catalytic deoxygenation of biomass-derived fatty acids to produce alkanes/alkenes [47]. Studies on the homogeneous catalytic decarbonylation of vegetable oil deodorizer distillate to produce biomass-derived hydrocarbons (diesel-like hydrocarbons) were rarely found. Therefore, we envisaged a probe of the industrial application of our catalytic system using vegetable oil deodorizer distillate as a model compound. Food-grade canola oil deodorizer distillate was chosen for the investigation, and its free fatty acid content was found to be 50 wt% by titration [48]. To further identify the composition of fatty acids in the canola oil deodorizer distillate, canola oil deodorizer distillate was under acid-transesterification, followed by GC analysis [49]. It was found to mainly consist of C18:1 (oleic acid, see supporting information on Table S1 for the fatty acid profile).

We then applied our catalysts to catalyze industrial canola oil deodorizer distillate as a feedstock to obtain olefins. 1 wt% Pd(COD)Cl₂ with naphthalyl-scaffold monophosphine CP-1 was employed to catalyze the decarbonylation reaction. We found that our catalysts could catalyze the decarbonylation process of canola oil deodorizer distillate smoothly to afford olefins that mainly consist of C17-alkenes in good yield (70%) (see supporting information Figure S3 for the GCMS profile) in six hours (Scheme 2).



Scheme 2. Pd(COD)Cl₂ catalyzed decarbonylation of canola oil deodorizer distillate using CP-1 as ligand.

3. Experimental

3.1. General Procedures for the Optimization of Reaction Conditions

An array of Schlenk tubes were charged with a magnetic stirrer bar (4 mm × 10 mm) and were evacuated and backfilled with nitrogen (3 cycles). The Schlenk tubes were charged with Pd sources (3 mol%) and ligands (3–9 mol%), followed by the addition of 1 mL solvent by syringe, and was stirred for 1 min. The Schlenk tubes were then added with oleic acid (0.5 mmol), anhydride sources (0.5–3 mmol) and amines (0.5–1.5 mmol). This batch of Schlenk tube was resealed and magnetically stirred in a preheated 140 °C oil bath for 6–18 h. The reactions were allowed to reach room temperature. Ethyl acetate (~4 mL) and water (~2 mL) were added. Next, an internal standard (dodecane) was added to the organic layer and was subjected to GC-FID analysis to calculate the GC yield%.

3.2. General Procedures for the Pd-Catalyzed Decarbonylation of Carboxylic Acids

An array of Schlenk tubes were charged with magnetic stirrer bar (4 mm × 10 mm) and were evacuated and backfilled with nitrogen (3 cycles). The Schlenk tubes were charged with Pd(COD)Cl₂ (3 mol%) and ligand CP-1 (9 mol%), followed by the addition of 1 mL DMac by syringe and stirred for 1 min. The Schlenk tubes were then added with carboxylic acids substrates (0.5 mmol), benzoic anhydride (1 mmol) and DIPEA (1.5 mmol). This batch of Schlenk tube was resealed and magnetically stirred in a preheated 140 °C oil bath for 6 h. The reactions were allowed to reach room temperature. Ethyl acetate (~4 mL) and water (~2 mL) were added. The organic layer was concentrated under reduced pressure and was purified by flush column chromatography.

3.3. General Procedures for the Pd-Catalyzed Decarbonylation of Canola Oil Deodorizer Distillates

A Schlenk tube was charged with a magnetic stirrer bar (4 mm × 10 mm) and was evacuated and backfilled with nitrogen (3 cycles). The Schlenk tube was charged with Pd(COD)Cl₂ (0.0043 g), ligand CP-1 (0.017 g) and 1 mL DMac was added by syringe and stirred for one minute. The Schlenk tube was then added with benzoic anhydrides (0.226 g, 1.0 mmol), DIPEA (0.36 mL, 1.5 mmol) and 0.5 mL canola oil deodorizer distillate (with 42 wt% oleic acid, equivalent to 0.74 mmol oleic acid). The Schlenk tube was resealed and magnetically stirred in a preheated 140 °C oil bath for 6 h. The reactions were allowed to reach room temperature. Ethyl acetate (~4 mL) and water (~2 mL) were added. Then, an internal standard (dodecane) was added to the organic layer and was subjected to GC-FID analysis to calculate GC yield%.

3.4. General Procedures for the Synthesis of NP Ligands

2-(2-Bromophenyl)quinoline (0.849 g, 3.0 mmol) was dissolved in freshly distilled THF (20 mL) at room temperature under a nitrogen atmosphere. The solution was cooled to −78 °C in a dry ice/acetone bath. Titrated *n*-BuLi (3.3 mmol) was added dropwise by

syringe. After the reaction mixture was stirred for 30 min at -78°C , chlorodiarylphosphine (0.66 mL, 3.3 mmol) in THF (5 mL) was added. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed under reduced pressure. After the solvent was removed under vacuum, the product was successively washed with cold MeOH/EtOH mixture. The product was then dried under vacuum. (See Supplementary Materials for detail characterization of ligands).

3.5. General Procedures for the Synthesis of CP Ligands

2-(2-Bromophenyl)naphthalene (0.849 g, 3.0 mmol) was dissolved in freshly distilled THF (20 mL) at room temperature under a nitrogen atmosphere. The solution was cooled to -78°C in a dry ice/acetone bath. Titrated *n*-BuLi (3.3 mmol) was added dropwise by syringe. After the reaction mixture was stirred for 30 min at -78°C , chlorodiarylphosphine (0.66 mL, 3.3 mmol) in THF (5 mL) was added. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed under reduced pressure. After the solvent was removed under vacuum, the product was successively washed with cold MeOH/EtOH mixture. The product was then dried under vacuum. (See Supplementary Materials for detail characterization of ligands).

3.6. General Procedures for Preparation of Palladium Complexes

$[\text{PdCl}_2(\text{C}_{28}\text{H}_{21}\text{P})]_2$, Pd-CP-1: $\text{Pd}(\text{COD})\text{Cl}_2$ (0.0071 g, 0.025 mmol and CP-1 (0.009 g, 0.025 mmol) were dissolved in freshly distilled dichloromethane (5 mL) under nitrogen at room temperature. The yellow solution was stirred for one hour. Then anhydrous hexane (2 mL) was slowly added for recrystallizing the pure product.

$\text{Pd}(\text{C}_{27}\text{H}_{20}\text{NP})(\text{CH}_3\text{CO}_2)_2$, Pd-NP-1: $\text{Pd}(\text{OAc})_2$ (0.0056 g, 0.025 mmol) and NP-1 (0.01 g, 0.025 mmol) were dissolved in freshly distilled dichloromethane (5 mL) under nitrogen at room temperature. The yellow solution was stirred for one hour. Then anhydrous hexane (2 mL) was slowly added for recrystallizing the pure product.

4. Conclusions

We synthesized the naphthalyl-scaffold and quinoline-scaffold of monophosphine ligands and demonstrated that (1–3 mol%) $\text{Pd}(\text{COD})\text{Cl}_2$ with naphthalyl-scaffold monophosphine CP-1 could be employed to convert various carboxylic acids into alkenes in good yields (up to 80%) and excellent alpha-selectivity (up to 98%) in six hours. It is noteworthy that our catalytic system could be applied to an industrial sample; we applied our catalyst to convert canola oil deodorizer distillate smoothly in order to afford the desired alkenes in a good yield (70%).

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11080876/s1>, Supplementary data (crystal structure data, NMR spectra) are included in supporting information. Crystallographic data for the palladium complex, Pd-CP-1 and Pd-NP-1, have been deposited with the CCDC. Deposition numbers: 2095371 and 2095373.

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Conflicts of Interest: The authors declare no conflict of interest.

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