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Recyclable $Pd(OAc)_2$/Ligand/$Al(OTf)_3$ Catalyst for the Homogeneous Methoxycarbonylation and Hydrocarboxylation Reactions of Phenylacetylene

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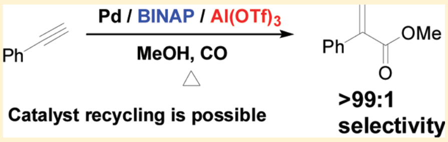
ABSTRACT: The Pd-catalyzed methoxycarbonylation reaction of phenylacetylene was studied making use of various promoters, including aluminum triflate and several other acid-type promoters of this reaction. The influence of the ligand (bidentate-type ligands and monodentate analogues) was found to be determinative of the success of the reaction. The catalyst was found to be recyclable through 10 catalytic runs. The unique results when using BINAP, relating to the selectivity for the branched product and the stability of the catalyst produced, led to a study on the sulfonated analogue thereof, with the intention of performing hydrocarboxylation reactions to directly prepare the carboxylic acid. The product obtained accordingly may be varied between the methyl ester or its carboxylic acid equivalent, depending on the solvent medium and the ligand employed.



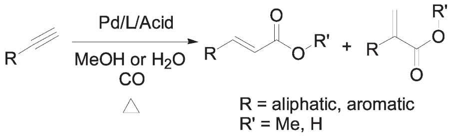
■ INTRODUCTION

The carbonylation of alkynes allows for the synthesis of α,β-unsaturated carboxylic esters or acids in an easy one-step synthesis (Scheme 1). The reaction occurs much in the same manner as for alkenes, a reaction that has been quite extensively studied.[1] The reaction requires the presence of a catalyst (usually Pd), carbon monoxide under pressure, methanol or water, and an acidic co-promoter. This reaction is of interest since methyl atropate (methyl 2-phenylacrylate) and its derivatives are potential precursors of nonsteroidal anti-inflammatories such as ibuprofen and naproxen.[2]

While several ligands have been applied to the catalytic conversion of phenylacetylene into its unsaturated ester derivatives, N-containing phosphine ligands have been shown to provide good catalysts in terms of stability and activity. Specifically, 2-pyridyldiphenylphosphine has earned a reputation for being particularly suited to this transformation.[3] Alternative systems have included iminophosphine-type analogues[4] and a PPh_3/pyridine carboxylic acid system.[5] Supported catalysts have also been applied with a fair degree of success.[6] When ligands do not possess the pyridyl moiety, poor results are generally noted.[7]

As with other alkoxycarbonylation-type chemistry with alkenes, the application of alkynes as substrates also calls for an acidic co-catalyst, typically a Brønsted acid. Recent work in our laboratories has involved the use of $Al(OTf)_3$ as a co-catalyst in the methoxycarbonylation of styrene and 1-pentene.[8] We hoped that this robust, recyclable co-catalyst would be useful in the methoxycarbonylation and hydrocarboxylation reactions of phenylacetylene and investigated its application in this reaction, discovering along the way that P−P bidentate ligands produce excellent catalysts in the presence of this co-promoter. We also demonstrate that the Pd-based catalyst derived from BINAP is stable and capable of being recycled a number of times.

Scheme 1. Methoxycarbonylation Reaction of Phenylacetylene



■ RESULTS AND DISCUSSION

Initial reactions using phenylacetylene were carried out under the conditions we earlier reported,[8] making use of $Al(OTf)_3$ as the co-catalyst in Pd-catalyzed reactions supported by PPh_3 as ligand. The system showed a complete lack of conversion of the phenylacetylene, a result also noted by others when using monodentate phosphine ligands.[9] Several changes to the reaction conditions, while retaining the monodentate ligand, were met with failure. Previous studies have shown 1,4-bis(diphenylphosphino)butane (dppb) to be active as a ligand in the methoxycarbonylation reaction of phenylacetylene.[10] We accordingly investigated a few bidentate-type ligands with varying bite angles (Table 1), including 1,2-bis(diphenylphosphino)benzene, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), and SiXantphos, in quite long-duration reactions (24 h).

While 1,2-bis(diphenylphosphino)benzene provided no conversion to the desired product, BINAP- and SiXantphos-based catalysts afforded 100% conversion of the starting material, but in reactions in which less than 100% selectivity was shown to the anticipated ester product. In these cases, a diester byproduct was isolated (Scheme 2).

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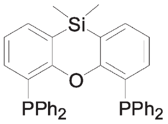
Table 1. Methoxycarbonylation Reaction of Phenylacetylene Using Bidentate Ligands[a]

Entry	Ligand	Bite angle[b]	%Conv[c]	%Select[d]	*b*:*l*
1	$(Ph_2P)Ph(PPh_2)$	83°	0	-	-
2	BINAP	92°	100	90	>99:1
3		108°	100	30[e]	1.9:1

[a] Reaction conditions: 0.045 mmol of $Pd(OAc)_2$, 0.18 mmol of ligand, 0.09 mmol of $Al(OTf)_3$, 2.25 mmol of phenylacetylene, 5.75 mL of MeOH, 35 bar of CO, 80 ± 2 °C internal temperature, 24 h. [b] Reference 1. Standardized P—M—P angles from X-ray structures and calculations. [c] Conversion of starting material. [d] Conversion to ester products (selectivity) as determined by ^1H and ^{13}C NMR spectroscopy and quantitative GC-FID analysis. [e] Secondary reactions accounted for diminished selectivities (see discussion in the main text).

Scheme 2. Diester Formation by Secondary Methoxycarbonylation

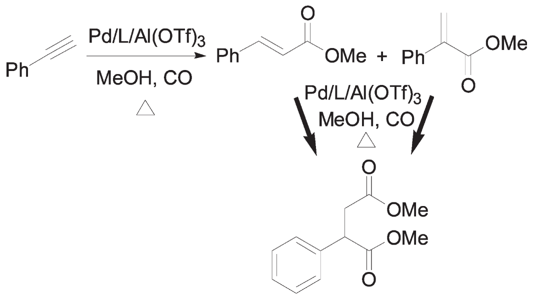
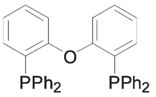
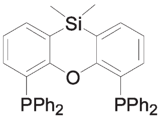
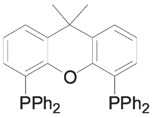
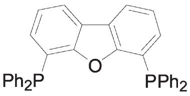


Table 2. Methoxycarbonylation Reaction of Phenylacetylene Using Varying Bidentate Ligands at 0.1% Pd Loading[a]

Entry	Ligand	Bite angle[b]	Yield[c] (%)	*b*:*l*[d]
1	$(Ph_2P)Ph(PPh_2)$	83°	0	–
2	BINAP	92°	99	>99:1
3		102°	85[e]	1.6:1
4		108°	53	1.9:1
5		112°	42	2.4:1
6		132°	3[e]	>99:1

[a] Reaction conditions: Pd:substrate 1:1000; 0.0111 mmol of $Pd(OAc)_2$, 0.0444 mmol of ligand, 0.0222 mmol of $Al(OTf)_3$, 11.1 mmol of phenylacetylene, 4.7 mL of MeOH, 35 bar of CO, 80 ± 2 °C internal temperature, 3 h. [b] Reference 1. Standardized P—M—P angles from X-ray structures and calculations. [c] Isolated yields. [d] Branched/linear selectivites are based on ^1H and ^{13}C NMR spectroscopy and quantitative GC-FID analysis. [e] Formation of Pd black was noted.

Since, in principle, both the linear and branched monoesters could provide the diester product upon secondary methoxycarbonylation (Scheme 2), each of these substances was subjected to reaction under the conditions detailed in Table 1. It was found that the reaction leading to the diester product proceeds preferentially via the branched α,β-unsaturated monoester intermediate (methyl atropate). This became clear as the rate of reaction of the branched substrate was approximately 5 times faster than that of the linear analogue (methyl cinnamate), in competitive reactions containing 1:1 mixtures of the two monoesters.

For a greater ability to critically assess the bidentate ligands, lower catalyst loadings (0.1%) were employed to afford incomplete conversion of the substrate in a given period of time (Table 2). In general, all of the ligands tended to favor formation of the branched ester, varying from moderate selectivity (Table 2, entries 3−5) to essentially complete selectivity (Table 2, entries 2 and 6). The ligands used here possess similar electronic characteristics, differing mainly in their bite angles. These data point to a rather determinative effect of the bite angle on the reactivity of the catalyst as reflected by the yields and upon the branched/linear selectivity. However, binding of the ring O atom to the Pd atom in the case of the diphenyl ether- and Xantphos-derived ligands may also play a role.

Given the overall excellent results secured with BINAP as ligand, we further probed this reaction, among others, by varying the catalyst loading (Table 3). No Pd black was obtained in any of the runs, indicating the inherent stability of the system. At higher catalyst loadings (Table 2, entries 1 and 2), fairly substantial conversion of the monoester product into the diester analogue was noted, in reactions performed over 24 h. Shorter reaction times (Table 3, entry 3) essentially precluded the formation of this byproduct, which was also not formed at lower catalyst loadings, presumably because of significant differences in its rate of formation in comparison to that of the mono ester. A reaction performed in the absence of Pd catalyst gave essentially no conversion of the substrate to product (Table 3, entry 8). The

Table 3. Methoxycarbonylation Reaction of Phenylacetylene Using BINAP As Ligand at Varying Catalyst Loadings[a]

entry	Pd:substrate	conv (%)	product[b] (%)	diester[b] (%)	*b*:*l*[b]	time (h)	TOF[c] (× 10^2)
1	1:50[a]	100	84	10	>99:1	24	
2	1:500	100	79	19	>99:1	24	
3	1:500	100	98	1	>99:1	3	
4	1:1000	100	99	0	>99:1	3	
5	1:1000	99	99	0	>99:1	1.5	
6	1:5000	67	67	0	>99:1	3	11.2
7	1:10 000	34	34	0	>99:1	3	11.3
8	0:10 000[d]	<1	<1	0		3	
9	1:10 000[e]	12	12	0	>99:1	3	4.0
10	1:10 000[f]	48	48	0	>99:1	3	16.0
11	1:10 000[f]	88	88	0	>99:1	15	
12	1:20 000[f]	80	65[g]	0	>99:1	15	10.7

[a] Reaction conditions: 0.225 mmol of $Pd(OAc)_2$, 0.90 mmol of BINAP, 0.45 mmol of $Al(OTf)_3$, 1.125 mmol of phenylacetylene, 5.9 mL of MeOH, 35 bar of CO, 80 ± 2 °C internal temperature, total volume ca. 6 mL. The amount of catalyst (including $Pd(OAc)_2$, $Al(OTf)_3$, and ligand) was reduced in later runs. [b] Conversion to and selectivity for ester products as determined by ^{1}H and ^{13}C NMR spectroscopy and GC-FID analysis. [c] TOF is the mean turnover frequency calculated over the duration of the reaction: TOF = mol product/mol Pd/h. [d] Reaction run in the absence of Pd to test for reactor memory effect. [e] Reaction run in the absence of $Al(OTf)_3$. [f] Reaction run using 8 equiv of $Al(OTf)_3$. [g] Byproduct formation accounted for 15% of the starting material converted, evidenced by late peaks in the GC trace indicating uncharacterized higher-boiling materials.

Table 4. Methoxycarbonylation Reaction of Phenylacetylene Using BINAP As Ligand with Different Co-catalysts[a]

entry	co-catalyst	product[b] (%)	*b*:*l*	TOF[c] (× 10^2)
1	$Al(OTf)_3$	34	>99:1	11.3
2	$La(OTf)_3$	25	>99:1	8.3
3	$Hf(OTf)_4$	22	>99:1	7.3
4	*p*-TsOH	19	>99:1	6.3
5	HOTf	15	>99:1	5.0
6	MSA	11	>99:1	3.7
7	TFA	3	>99:1	1.0

[a] Reaction conditions: Pd:substrate 1:10 000; 0.000 55 mmol of $Pd(OAc)_2$, 0.0022 mmol of BINAP, 0.0011 mmol of co-catalyst added, 5.5 mmol of phenylacetylene, 5.3 mL of MeOH, 35 bar of CO, 80 ± 2 °C internal temperature, 3 h, total volume ca. 6 mL. [b] Conversion to ester products as determined by ^{1}H and ^{13}C NMR spectroscopy and GC-FID analysis. [c] TOF is the mean turnover frequency calculated over the duration of the reaction: TOF = mol product/mol Pd/h.

effect of the $Al(OTf)_3$ is neatly demonstrated by entry 9, where catalyst activity is compromised by the absence of this co-catalyst. What little activity there was may possibly be ascribed to the water–gas shift reaction ($H_2O + CO \rightarrow H_2 + CO_2 \rightarrow H_2CO_3$), which would generate weak Brønsted acidity. The catalyst remained stable and active, even at very low loadings, but required the presence of additional co-catalyst (entries 10–12) to secure reasonable catalyst activity. It is clear when comparing the turnover frequencies calculated for entries 7 and 9 that the additional co-catalyst provides a more active catalyst system. At 0.01% Pd, increased acid (entry 11) as well as increased time (entry 12) showed that excellent activity was still obtainable even at such low Pd loadings.

The influence of the co-catalyst was investigated making use of other triflate salts as well as some Brønsted acids (Table 4). Here, as previously noted,[8] $Al(OTf)_3$ provided the most active catalyst of the series of co-catalysts employed. What was also striking is that no Pd black was observed in any of these reactions, indicating a very stable Pd/ligand system. It is also evident that the acid did not play a role in determining the selectivity to product in the reaction as the *b*:*l* ratio remained the same throughout.

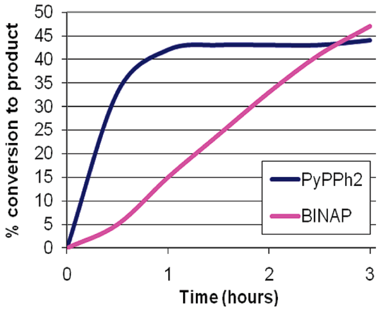


Figure 1. CO uptake curves for BINAP and $PyPPh_2$.

$PyPPh_2$ is a ligand of choice in Brønsted acid co-catalyzed methoxycarbonylation reactions of phenylacetylene.[11] Unfortunately, this ligand is not a simple replacement for the BINAP ligand that fared so well in the present study. Optimization0 of the reaction conditions for this ligand, but using $Al(OTf)_3$ as co-catalyst, afforded a highly active but relatively unstable catalyst (Figure 1). The catalytic system provides the ester with good selectivity (Table 5), possibly by acting as a (hemilabile) bidentate ligand. Despite much effort, Pd black continued to precipitate from the reaction mixture in our hands when using $Al(OTf)_3$ as the co-catalyst, even when applying excess ligand and acid catalyst, changes that have led to more stable catalysts in other instances.[8] This presumably accounts for the precipitous decline in CO uptake as noted in Figure 1. $PyPPh_2$ is a monodentate ligand that is held to act in a hemilabile fashion.[12] It may be that the added Al ion coordinates to the N atom of the pyridyl moiety at some stage of the catalytic cycle, leading to catalyst destabilization. We accordingly concentrated our efforts on BINAP-type ligands.

Recycling of the Pd-BINAP catalyst was quite easy (Table 6), among others, given the high levels of stability of the catalyst when based on BINAP ligands. Various approaches were followed during the recycling, but all included distillation of the product from the crude mixture. For the experiments detailed in columns 1−6, an aqueous extraction of the residue also removed the $Al(OTf)_3$.[13] Columns 1 and 2 show the results of experiments where the Pd catalyst was recycled as a separate entity, with fresh co-catalyst, solvent, and substrate added. The results show retention of the activity of the catalyst but with attendant loss of selectivity for the branched isomer.

We reasoned that the loss of selectivity may arise due to loss of ligand through leaching or via oxidation of one or both of the P atoms on the BINAP and so added 0.1 equiv of ligand per Pd in each subsequent recycle (columns 3 and 4; the very small amounts of catalyst employed in these reactions precluded a spectroscopic conclusion on the matter of the ligand oxidation). Here, the activity of the catalyst diminishes with each cycle while selectivity is improved compared to the first set of recycling experiments. The diminished activity of the catalyst is seemingly in response to the added ligand and indicates that the putative loss of ligand may not require the addition of fresh ligand with each run. Accordingly, we added fresh ligand (again in the amount of 0.1 equiv per Pd) only after every third cycle (columns 5 and 6), allowing improved catalyst activity and selectivity for product. Semifinally (columns 7 and 8), the entire catalyst was recycled by simply distilling off all volatile components from the reaction vessel and resubmitting the total residue for a further reaction with fresh substrate and solvent. The overall trend here is similar to that demonstrated by the results contained in columns 1 and 2. Importantly, in no case was Pd black detected. Finally, the entire catalyst was recycled, and additional ligand was added after every third run, affording good retention of both activity of the catalyst and selectivity toward the branched ester product.

Table 5. Exploring $PyPPh_2$ As Ligand in the Phenylacetylene Reaction[a]

entry	Pd loading (mol %)	ligand equiv	acid equiv	yield (%)	*b*:*l*
1	0.04	16	8	99	99:1
2	0.02	16	8	57	99:1
3	0.02	32	16	99	99:1
4	0.01	32	16	42 (47)[b]	40:1
5	0.01	64	32	81	40:1

[a] Reaction conditions: identical to those indicated for Table 4, 3 h runs. Catalyst components were added as indicated in the table. [b] Yield in parentheses indicates an equivalent reaction run with 16 equiv of BINAP, with no Pd black formation.

Given the stability and activity noted with the Pd/BINAP/$Al(OTf)_3$ system, we investigated the use of sulfonated BINAP (known as BINAPS (Figure 2), prepared by sulfonation of BINAP naphthyl rings[14]) in polar mixed solvent systems containing water, with the possibility of forming the carboxylic acid instead of the methyl ester.

Mixed solvent systems were compared, using BINAP as a benchmark (Table 7, entries 1−3). Rather interestingly, no carboxylic acid products were identified, even when making use of 1:1 or 1:2 $MeOH/H_2O$ mixed solvents (entries 2 and 3), and only the methyl ester products were obtained. This situation changed when making use of BINAPS, where appreciable amounts of the carboxylic acid were generated in systems containing 50% or more of H_2O (entries 5−8). When reaching a ratio of 1:2 $MeOH/H_2O$ (entry 7), the ester was no longer detected in the product mixture. All the while, selectivity for the branched product (ester or acid) was maintained and the catalyst remained intact and active (see below). Additionally, the system tolerates

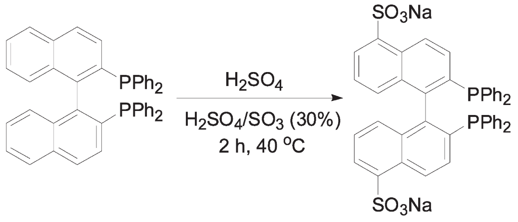


Figure 2. Sulfonation of BINAP.

Table 6. Recycling Experiments When Using the Pd/BINAP/$Al(OTf)_3$ Catalyst[a]

	1[b]	2	3[c]	4	5[d]	6	7[e]	8	9[f]	10
run	yield	*b*:*l*	yield	*b*:*l*	yield	*b*:*l*	yield	*b*:*l*	yield	*b*:*l*
1	100	>99:1	100	>99:1	100	>99:1	100	>99:1	100	>99:1
2	100	50:1	88	90:1	100	99:1	99	50:1	100	>99:1
3	99	30:1	86	90:1	100	99:1	94	30:1	98	95:1
4	98	30:1	80	70:1	95	90:1	94	30:1	97	95:1
5	97	30:1	78	70:1	94	90:1	82	20:1	97	90:1
6	97	30:1	75	70:1	93	90:1	84	20:1	93	90:1
7	96	30:1	73	70:1	91	90:1	73	20:1	92	90:1
8	95	20:1	70	70:1	90	90:1	72	20:1	91	90:1
9	96	20:1	67	60:1	88	90:1	69	20:1	90	90:1
10	94	20:1	65	60:1	87	90:1	66	20:1	90	90:1

[a] Reaction conditions: Pd:substrate 1:1000; 0.0111 mmol of $Pd(OAc)_2$, 0.044 mmol of ligand, 0.0222 mmol of $Al(OTf)_3$, 11.1 mmol of phenylacetylene, 35 bar of CO, 82 ± 2 °C internal temperature, total volume 12 mL (MeOH used to make up to 12 mL). For recycling, the esters were distilled off and the $Al(OTf)_3$ was extracted using water. Fresh solvent and substrate were added for each run; ligand and $Al(OTf)_3$ were added as per the footnotes below. [b] No added ligand after recycle; added fresh solvent, substrate, and $Al(OTf)_3$. [c] 0.1 equiv of ligand added after each run in addition to fresh solvent, substrate, and $Al(OTf)_3$. [d] 0.1 equiv of ligand added after every third run in addition to fresh solvent, substrate, and $Al(OTf)_3$. [e] No additional ligand added; no additional $Al(OTf)_3$ added, only fresh solvent and substrate. [f] 0.1 equiv of ligand added after every third run in addition to fresh solvent and substrate; no added $Al(OTf)_3$.

Table 7. Comparative Study of BINAP and BINAPS with Varying Solvents[a]

entry	ligand	solvent	% product	*b*:*l*:acid[b]
1	BINAP	MeOH	99	>99:1:0
2	BINAP	1 MeOH:1 H_2O	95	>99:1:0
3	BINAP	1 MeOH:2 H_2O	100	>99:1:0
4	BINAPS	MeOH	95	>99:1:0
5	BINAPS	1 MeOH:1 H_2O	100	70:5:25
6	BINAPS	1 MeOH:1.5 H_2O	100	30:0:70
7	BINAPS	1 MeOH:2 H_2O	100	0:0:100
8	BINAPS	H_2O	100	0:0:100
9	BINAPS	1 H_2O:1 DME	100	0:0:100

[a] Reaction conditions: Pd:substrate 1:1000; 0.0111 mmol of $Pd(OAc)_2$, 0.044 mmol of ligand, 0.0222 mmol of $Al(OTf)_3$, 11.1 mmol of phenylacetylene, 10.8 mL of MeOH, 35 bar of CO, 82 ± 2 °C internal temperature, total volume ca. 12 mL. [b] Acid refers to the branched carboxylic acid (2-phenylacrylic acid).

the use of DME as co-solvent (entry 9), which may be useful for less soluble substrates.

Disappointingly, initial work performed to recycle the Pd/BINAPS system has not yet yielded fruitful results and exposes a potential weakness or limitation of the system. We are currently pursuing the recycling of this catalyst system.

CONCLUSIONS

The present study shows that the $Pd(OAc)_2$/BINAP/$Al(OTf)_3$ combination forms a stable catalyst capable of facilitating the methoxycarbonylation reaction of phenylacetylene to provide the branched ester product in high yield and selectivity. This catalyst can be recycled a number of times, with some small losses of activity and selectivity through 10 cycles. In the present system, the $Al(OTf)_3$ co-catalyst leads to the generation of catalysts that are more highly active than those generated from Brønsted acids under identical conditions. An advantage of the $Al(OTf)_3$-based system is its high potential for recycling.

EXPERIMENTAL SECTION

Instrumentation. NMR spectra were recorded on a Varian Gemini 2000 300 MHz instrument or on a Bruker Ultrashield 400 MHz spectrometer. MS data were recorded on a Thermo DFS magnetic sector instrument, while GC spectra were recorded on a Shimadzu GCMS-QP2010 instrument fitted with a quadrupole mass detector. A DB1MS 30 m analytical column (i.d.: 0.25 mm, film thickness: 0.25 mm) that separated the various compounds on the basis of boiling points was used. For quantitative data, flame ionization detection was employed.

Carbonylation Reactions. The carbonylation reactions were carried out in 50 mL stainless steel high-pressure reactors fitted with PTFE inserts. These reactors were heated using oil baths and stirred with the aid of magnetic stirrer bars. Typically, the calculated amounts of Pd catalyst, ligand, co-promoter, and substrate were dissolved in the solvent of interest as detailed in the tables, and the solution was introduced to the reactor vessel. The reactor was flushed three times with carbon monoxide, sealed, and pressurized to 35 bar or as otherwise indicated. The mixture was heated to the required temperature for the specified period of time. After cooling to room temperature, the reactor was depressurized and the product distilled from the catalyst under vacuum (150 °C, 0.01 mmHg), and the product was analyzed using ^1H and ^{13}C NMR spectroscopy and GC-FID analysis. The mean turnover frequencies (TOF = mol product/mol Pd/h) were calculated from the moles of isolated product.

Recycling. After completion of the reaction, the methanol solvent was removed under vacuum, and DCM (30 mL) was added to the residue. The solution was washed with water (3 × 10 mL), and the organic phase dried over magnesium sulfate. The solvent was removed under vacuum, and the residue dissolved in methanol and used in the next run. This process allowed recycling of the Pd/ligand part of the catalyst.

In instances where the entire catalyst mixture was recycled (i.e., Pd/ligand/Al), the residue was used directly after the vacuum distillation step.

Methyl cinnamate: ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.68 (d, 1H, J = 16.3 Hz), 7.50–7.48 (m, 2H), 7.37–7.34 (m, 3H), 6.42 (d, 1H, J = 16.3 Hz), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 167.3, 144.8, 134.2, 130.2, 128.8, 128.0, 117.7, 51.6.

Methyl atropate: ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.41–7.32 (m, 5H), 6.34 (d, 1H, J = 1.2 Hz), 5.87 (d, 1H, J = 1.2 Hz), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 167.2, 141.1, 136.5, 128.1, 128.0, 127.9, 126.7, 52.0.

Dimethyl 2-phenylsuccinate: ^1H NMR (300 MHz, $CDCl_3$) δ_H 7.31–7.22 (m, 5H), 4.08 (dd, 1H, J = 10.3 and 5.2 Hz), 3.78 (s, 6H), 3.18 (dd, 1H, J = 16.9 and 10.1 Hz), 2.63 (dd, 1H, J = 16.9 and 5.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 173.3, 171.8, 144.4, 128.7, 127.9, 127.5, 52.1, 51.7, 46.9, 37.4; CIMS m/z 223 $[M + H]^+$, 191; HRCIMS calculated for $C_{12}H_{14}O_4$ 223.0970, obtained 223.0968.

2-Phenylacrylic acid: Mp 103–105 °C; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 12.19 (s, 1H), 7.45–7.18 (m, 5H), 6.57 (br s, 1H), 6.04 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ 172.5, 140.6, 136.0, 129.5, 128.6, 128.3, 128.0 (lit.[15] ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 140.6, 136.0, 129.2, 128.4, 128.2, 128.0).

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