


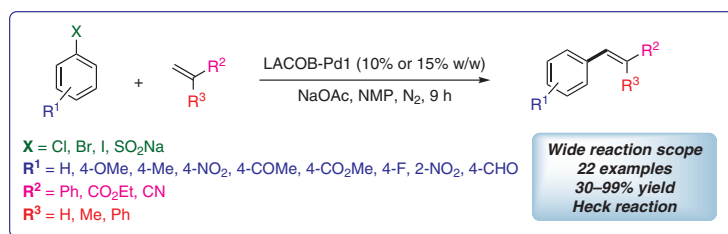
Palladium Nanoparticles Anchored on Magnesium Organosilicate: An Effective and Selective Catalyst for the Heck Reaction

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Abstract A new and effective palladium catalyst supported on a magnesium organosilicate for application in the Heck reaction is presented. A group of compounds comprising 22 examples were synthesized in moderate to high yields (up to 99%) within a short time. The palladium supported on magnesium organosilicate catalyst was characterized as an amorphous solid by SEM, containing around 33% of palladium inside the solid, and even with this low quantity of palladium, the catalyst was very efficient in the Heck reaction. Besides, based on the Scherrer equation, the crystallite size of the synthesized palladium nanoparticles was ultrasmall (around 1.3 nm). This strategy is a simple and efficient route for the formation of C–C bonds via the Heck cross-coupling reaction.

Key words cross-coupling, Heck reaction, palladium, heterogeneous catalyst, organosilicates

The palladium-catalyzed arylation of olefins, known as Heck reaction, is a selective method for the formation of a new C–C bond.¹ The Heck reaction has been intensively studied and used for the synthesis of pharmaceutical products (Figure 1, **I**, **II**).² Besides, some styrene derivatives are also ubiquitous molecules in nature (**III**, **IV**).³ Recent developments have shown that many challenges in organic synthesis can be overcome through the Heck reaction, such as asymmetric synthesis,⁴ reactions with Csp³ organic halides,⁵ and even highly stereoselective reactions.⁶ However, in the majority of cases, Heck cross-coupling reactions are carried out by using high-cost palladium catalysts.⁷ Nowadays, researchers are putting efforts into the development of environmentally friendly heterogeneous palladium catalysts with excellent recyclability and negligible leaching, thereby reducing costs (catalysts and the process) and environmental pollution.⁸

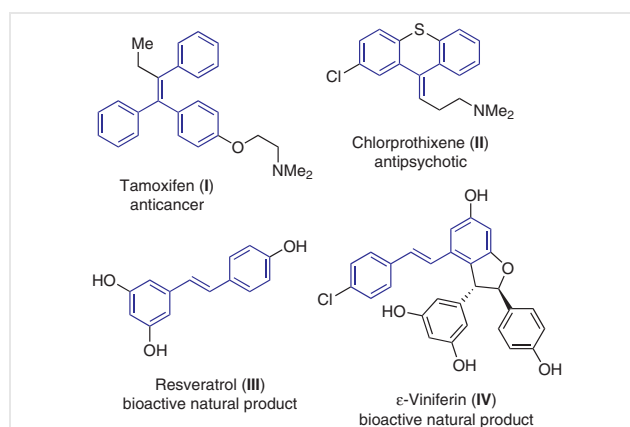


Figure 1 Bioactive molecules containing styrene nucleus

Over the past decades, solid supports such as alumina,⁹ silica,¹⁰ mesoporous materials,¹¹ active carbon and graphene,¹² polymers,¹³ and magnetic nanoparticles¹⁴ have been employed in material sciences and chemistry to obtain heterogeneous catalysts. Because of the range of solid supports presented, various methodologies have been described in the literature for the heterogenization of homogeneous catalysts. The classical Lindlar catalyst is an example of a heterogeneous catalyst that consists of palladium deposited on calcium carbonate and is widely used in hydrogenation industrial processes.¹⁵ In this sense, Xu and co-workers performed the Heck reaction using Pd@PANI as a heterogeneous catalyst.¹⁶

The introduction of new and stable heterogeneous catalytic supports is a popular research topic in the science of catalysis. In this category of supports, phyllosilicates have become important and efficient tools in catalytic organic synthesis, the most important being the synthetic talc (magnesium organosilicates).¹⁷ It is used as a fine powder in

the paper, rubber, cosmetic, and pharmaceutical industries, because of its inertness, whiteness, low thermal and electrical conductivity, and adsorption capacity of organic substances.¹⁸ Although magnesium organosilicates with organic functionalities have been reported in the literature, there are limited studies on the applications of this material in organic reactions. Thus, as part of our investigation into efficient synthetic methodologies, we wish to introduce a practical and low-cost heterogeneous catalytic support in organic synthesis affording a wide spectrum of use.

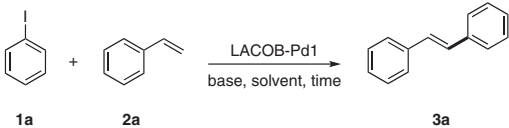
Because of their physicochemical properties, magnesium organosilicates could be a promising support for the synthesis of heterogeneous catalysts. Herein, we introduced synthetic talc as a novel, eco-friendly, and inexpensive heterogeneous catalytic support for the LACOB-Pd1 catalyst synthesis and its application in the Heck reaction. The LACOB-Pd1 catalyst is bench-stable and the reaction was performed with a broad substrate scope in a shorter time than in previous reports.¹⁹

We initially prepared the LACOB-Pd1 catalyst as described in the Experimental Section (see Supporting Information, SI). Then, the catalytic activity was assessed in the arylation reaction of various olefins by aryl halides. Initially, as presented in Table 1, we selected the reaction between iodobenzene (**1a**) and styrene (**2a**) for optimizing the reaction conditions. First, the Heck reaction was performed using two bases (K_2CO_3 and Et_3N) in EtOH as the solvent (entries 1 and 2). The Heck product **3a** was only observed when an inorganic base was employed (entry 1). We initially selected EtOH as the solvent due to its green properties. Thus, we increased the catalytic loading to 20% w/w, but this did not improve the yield (entry 3). To improve the results, we performed the reaction for 9 h and this produced a small increase in the yield (entry 4). On the basis of previous studies, we changed the base to NaOAc, the solvent to NMP, and the temperature to 110 °C and, gratifyingly, we obtained the Heck product in 83% yield (entry 5). The solvent is important in the Heck reaction and usually dipolar aprotic solvents are employed because these accelerate Pd^0 formation.²⁰

Following this satisfactory result, we assessed the efficiency of the LACOB-Pd1 catalyst by conducting a blank reaction (without catalyst), but no product was observed (Table 1, entry 6). Finally, we doubled the catalytic loading (entry 7) and obtained the Heck product quantitatively. It should be noted that the LACOB-Pd1 catalyst could be directly used in the Heck reaction and no previous treatment was needed to activate the catalyst.

The characteristics of the synthesized catalyst were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS) analyses (Figure 2). As shown in Figure 2A, two new reflections appear at $2\theta = 40.32^\circ$ and 46.44° for the LACOB-Pd1 catalyst, corresponding to the reflection planes (111) and

Table 1 Optimization of the Reaction Conditions^a

						
Entry	Base	LACOB-Pd1 (% w/w)	Solvent	Temp (°C)	Time (h)	Yield ^b (%)
1	K_2CO_3	5	EtOH	80	4	20
2	Et_3N	5	EtOH	80	4	0
3	K_2CO_3	20	EtOH	80	4	14
4	K_2CO_3	5	EtOH	80	9	45
5	NaOAc	5	NMP	110	9	83 ^c
6	NaOAc	–	NMP	110	9	0 ^c
7	NaOAc	10	NMP	110	9	>99 ^c

^a Reaction conditions: **1a** (1 equiv), **2a** (2 equiv), base (1 equiv), LACOB-Pd1, solvent.

^b Yield of isolated product.

^c Reaction performed with styrene (1.1 mmol) and base (1.5 mmol) under an N_2 atmosphere.

(200), which are characteristic of the face-centered cubic (fcc) structure of Pd nanoparticles.²¹ These data indicate that the Pd element exists in the form of Pd^0 and not Pd^{2+} .²² On the basis of the half-width of the (111) reflection, the average crystallite size (1.3 nm) of the synthesized palladium nanoparticles was estimated through the Scherrer equation.²³ The morphology of the LACOB-Pd1 catalyst was investigated by SEM analysis (Figure 2B) and showed that most of the prepared nanoparticles were formed uniformly.

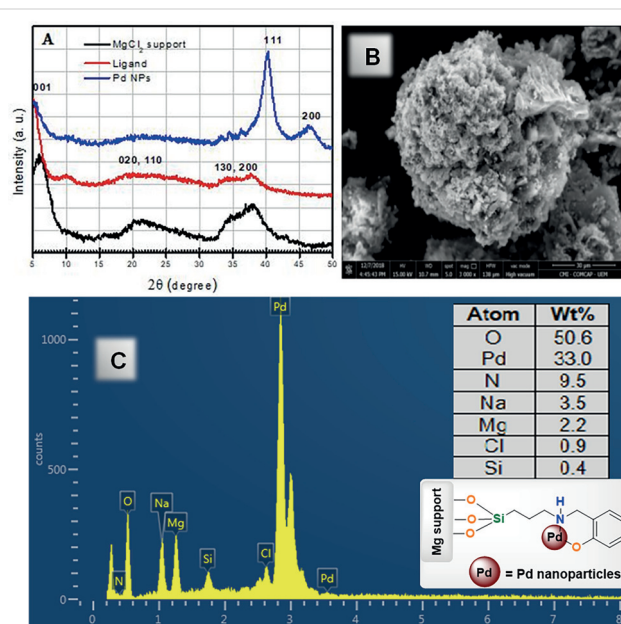


Figure 2 LACOB-Pd1 catalyst analysis by XRD (A), SEM (B), and EDS (C)

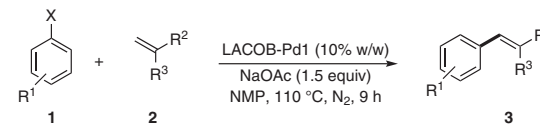
EDS of the catalyst is shown in Figure 2C. It clearly indicates the presence of Pd, along with other elements including oxygen, nitrogen, and magnesium.

Having established the optimized reaction conditions, we performed the reaction with different haloarenes and olefins (Table 2). Initially, a catalytic loading of 10% w/w was established for all reactions; however, for some entries, 15% w/w was used to maximize the yields. As presented in Table 2, Heck cross-coupling products were achieved in yields up to 99%. As already described by Jagtap,²⁰ the less crowded structure is generally preferred in the Heck reaction, and the *trans* product is usually favored. The coupling reactions of the electron-deficient and electron-rich haloarenes with styrene provided the Heck products (entries 1, 4, 5, and 6) in excellent yields in the presence of electron-donating substituents (**3b** and **3c**). Moderate to good yields were obtained when weakly electron-withdrawing groups were employed (**3e–g**; entries 7–9). Interestingly, we noticed that α -methyl styrene and 1,1-diphenylethylene were unreactive, and, thus, no Heck product was obtained using these reagents (entries 2 and 3), probably due to increased steric hindrance of the starting materials. The application scope for olefins was also tested. To evaluate the efficacy of this method, the Heck reaction was investigated by using ethyl acrylate instead of styrene under the same reaction conditions (entries 10–16). Reactions of ethyl acrylate with electron-rich iodobenzenes afforded the corresponding products **3i** and **3j** in high yields (entries 11 and 12). 1-Iodo-2-nitrobenzene was found to be a suitable substrate for this reaction, giving product **3k** in 98% yield (entry 13). In the presence of iodobenzenes bearing electron-deficient substituents (entries 14–16), moderate to good yields were obtained for compounds **3l–n**. Aryl bromides were also employed, but only gave the Heck products in moderate yields (**3o** and **3p**; entries 17 and 18). The reactions of styrene with aryl chloride (entry 19) and benzenesulfinic acid sodium salt (entry 20) were also tested, but the Heck cross-coupling product was not obtained in these reactions, even after a reaction time of 24 hours.

Other unsaturated starting materials (e.g., acrylonitrile and cyclohex-2-en-1-one) were also tested in the Heck reaction (Table 2, entries 21 and 22); however, a product only emerged when acrylonitrile was used (**3q**). The moderate yield is explained by the conjugation of the double bond with the nitrile group, making nitrogen a strong ligand for palladium.

It should be noted that all alkene products were stereoselectively produced in the *E*-form. We did not observe any *cis*-isomer, indicating a very high selectivity degree for the catalyst (see SI). To prove this statement, the reaction between iodobenzene and styrene was performed under the same conditions as in Table 2, entry 1, and analyzed by ¹H NMR without further purification. The absence of the signal at $\delta = 6.60$ proves that the *cis*-isomer is not formed in the reaction (Figure 3).

Table 2 LACOB-Pd1-Catalyzed Heck Cross-Coupling of Aryl Halides **1** with Olefins **2**^a



Entry	R ¹	X	R ² , R ³	3 : Yield ^b (%)
1	H	I	Ph, H	3a : >99
2	H	I	Ph, Me	trace
3	H	I	Ph, Ph	trace
4	4-OMe	I	Ph, H	3b : >99 ^c
5	4-Me	I	Ph, H	3c : 88 ^c
6	4-NO ₂	I	Ph, H	3d : 30
7	4-COMe	I	Ph, H	3e : 65
8	4-CO ₂ Me	I	Ph, H	3f : 50 ^c
9	4-F	I	Ph, H	3g : 87 ^c
10	H	I	CO ₂ Et, H	3h : 82
11	4-OMe	I	CO ₂ Et, H	3i : 99 ^c
12	4-Me	I	CO ₂ Et, H	3j : 98 ^c
13	2-NO ₂	I	CO ₂ Et, H	3k : 98
14	4-COMe	I	CO ₂ Et, H	3l : 81 ^c
15	4-CO ₂ Me	I	CO ₂ Et, H	3m : 88 ^c
16	4-F	I	CO ₂ Et, H	3n : 68 ^c
17	4-CHO	Br	Ph, H	3o : 55 ^c
18	4-CHO	Br	CO ₂ Et, H	3p : 63 ^c
19	4-CHO	Cl	Ph, H	no reaction ^{c,d}
20	H	SO ₂ Na	Ph, H	no reaction ^c
21	H	I	CN, H	3q : 57
22	H	I	cyclohexenone	trace

^a Reaction conditions: **1** (1 equiv), **2** (1.1 equiv), NaOAc (1.5 equiv), LACOB-Pd1 (0.1 equiv, 10% w/w), NMP, 110 °C, 9 h, under N₂.

^b Yield of isolated product.

^c Reaction performed with LACOB-Pd1 (15% w/w).

^d Reaction time: 24 h.

Due to the high cost of palladium salts, we sought to recycle and reuse the catalyst in the Heck reaction. Since the LACOB-Pd1 catalyst is insoluble in NMP, we reacted iodobenzene with styrene under the standard conditions (Scheme 1). At the end of the first reaction, the catalyst was recovered by simple centrifugation, then successively rinsed with ethyl acetate, distilled water (to remove excess base), and acetone, and finally dried at room temperature. Another reaction was then performed again under the previous conditions. Unfortunately, the catalyst could only be recovered once, since the yield decreased by 33% in the second cycle.

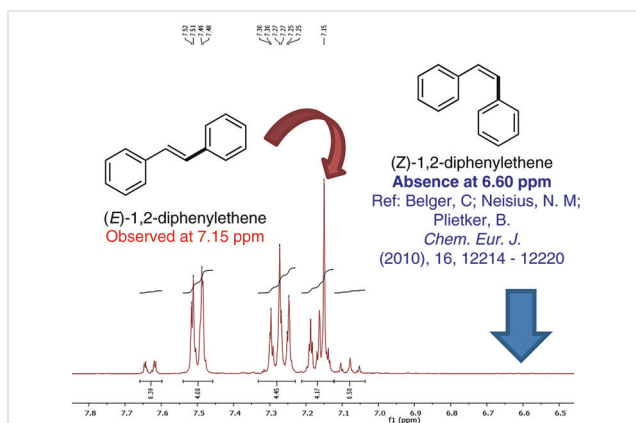
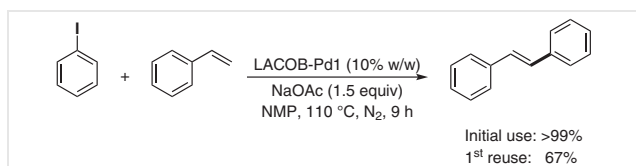


Figure 3 ^1H NMR spectrum of the crude reaction mixture when using iodobenzene and styrene, showing the absence of the *cis*-isomer



Scheme 1 Recyclability of the LACOB-Pd1 catalyst in the Heck cross-coupling reaction

In conclusion, we introduced a new and selective palladium catalyst anchored on synthetic talc. The LACOB-Pd1 catalyst is accessible, well defined, and stable in air and its synthesis is very simple and practical. It was effectively applied in the Heck reaction using many haloarenes and olefins, with moderate to excellent yields obtained. Regarding its reusability, this was only possible for the first cycle, although this does not depreciate the procedure. We are actively expanding the scope and use of this immobilized palladium catalyst to other cross-coupling and related reactions.

The catalyst preparation was carried out using dry starting material under pressure. All other reactions were carried out using chemical reagents and solvents without any specific treatment. The reactions were monitored by TLC (MACHEREY-NAGEL, SIL G/UV₂₅₄) and were visualized by fluorescence quenching with UV light at 254 nm. The purification of the compounds was performed by column chromatography using hexane/EtOAc. ^1H and ^{13}C NMR spectra were recorded of samples in CDCl_3 on a Bruker (300 MHz and 75 MHz, respectively) spectrometer. The IR spectra were recorded on a Jasco FT/IR 4100 type A spectrophotometer.

LACOB-Pd1 Catalyst

The magnesium organosilicate support synthesis was performed following the reports published by Jasra et al.¹⁷ In a beaker, MgCl_2 (8.36 g) was dissolved in methanol (200 mL) and the solution was stirred at 25 °C. In another beaker, APTES (9.8 g, 10.35 mL) was placed in methanol (50 mL). This solution was added dropwise to the MgCl_2 solution.

This mixture formed a white suspension. Then, 0.5 M NaOH solution was slowly added until the pH reached 10.5 under stirring at 25 °C. The suspension obtained was aged for 1 week at 25 °C and the gel formed was centrifuged, washed with distilled H_2O , and dried at 65 °C. Then, in a flask, the magnesium organosilicate support (0.1 g) and KOH (0.1 g, dissolved in distilled H_2O) were placed in ethanol (5 mL) and the mixture was stirred for 10 min. Subsequently, salicylaldehyde (0.1 g, 94 μL) was added and the mixture was stirred at 25 °C for 2 h. NaBH_4 was added until the solution became white and turbid. The reaction was stirred overnight. After this period, the white solid was centrifuged and washed with distilled H_2O to give the ligand. The LACOB-Pd1 catalyst was prepared to treat all the resulting support that was obtained with NaOH (0.1 g) in ethanol (5 mL) and the mixture was stirred at 25 °C for 15 min. Then, $\text{Pd}(\text{OAc})_2$ (0.1 g) was added and the mixture was stirred for 2 h. The black solid that formed was centrifuged and washed with chloroform.

Styrenes 3 by Heck Reaction; General Procedure

In a 5 mL flask were placed the palladium catalyst (10% or 15% w/w), the alkene **2** (1.1 mmol), the haloarene **1** (1 mmol), and NaOAc (1.5 mmol). The mixture was magnetically stirred in NMP (4 mL) at 110 °C in an oil bath for 9 h under a N_2 atmosphere. The progress of the reaction was monitored by TLC (hexane/EtOAc, 90:10). After this time, the solution was cooled to room temperature, diluted with EtOAc (20 mL), and washed with H_2O (3×20 mL). The organic phase was separated, dried over Na_2SO_4 , and concentrated under vacuum. The obtained products were purified by column chromatography (silica gel, hexane/EtOAc, 90:10).

(E)-1,2-Diphenylethene (**3a**)¹⁶

White solid; yield: 178 mg (>99%); mp 130 °C.

IR (KBr): 3020, 1596, 1495, 1451, 963, 764, 690 cm^{-1} .

^1H NMR (300 MHz, CDCl_3): δ = 7.54–7.52 (m, 4 H), 7.39–7.35 (dd, J = 10.5, 4.8 Hz, 4 H), 7.28–7.26 (m, 2 H), 7.12 (s, 2 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 137.55, 128.92, 127.87, 126.75.

MW: 180.25 g/mol, $\text{C}_{14}\text{H}_{12}$.

(E)-1-Methoxy-4-styrylbenzene (**3b**)¹⁶

White solid; yield: 208 mg (>99%); mp 131 °C.

^1H NMR (300 MHz, CDCl_3): δ = 7.52–7.45 (m, 4 H), 7.38–7.33 (m, 2 H), 7.27–7.22 (m, 1 H), 7.11–6.96 (q, J = 16.3 Hz, 2 H), 6.94–6.89 (m, 2 H), 3.84 (s, 3 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 159.49, 137.84, 130.34, 128.86, 128.40, 127.92, 127.43, 126.81, 126.45, 114.33, 55.54.

MW: 210.27 g/mol, $\text{C}_{15}\text{H}_{14}\text{O}$.

(E)-1-Methyl-4-styrylbenzene (**3c**)¹⁶

White solid; yield: 171 mg (88%); mp 112 °C.

^1H NMR (500 MHz, CDCl_3): δ = 7.52–7.51 (d, J = 7.4 Hz, 2 H), 7.43–7.42 (d, J = 8.1 Hz, 2 H), 7.37–7.34 (dd, J = 10.6, 4.7 Hz, 2 H), 7.27–7.24 (dd, J = 8.7, 6.0 Hz, 1 H), 7.19–7.17 (d, J = 7.9 Hz, 2 H), 7.12–7.05 (m, 2 H), 2.37 (s, 3 H).

^{13}C NMR (125 MHz, CDCl_3): δ = 137.55, 137.52, 134.58, 129.40, 128.65, 127.73, 127.40, 126.44, 126.40, 21.25.

MW: 194.28 g/mol, $\text{C}_{15}\text{H}_{14}$.

(E)-1-Nitro-4-styrylbenzene (**3d**)¹⁶

Yellow solid; yield: 68 mg (30%); mp 159 °C.

¹H NMR (300 MHz, CDCl₃): δ = 8.25–8.21 (m, 2 H), 7.66–7.63 (m, 2 H), 7.58–7.55 (m, 2 H), 7.44–7.33 (m, 3 H), 7.32–7.26 (d, *J* = 16.3 Hz, 1 H), 7.18–7.12 (d, *J* = 16.3 Hz, 1 H).

¹³C NMR (75 MHz, CDCl₃): δ = 146.96, 144.06, 136.38, 133.52, 129.12, 129.07, 129.01, 127.24, 127.08, 126.49, 124.37.

MW: 225.25 g/mol, C₁₄H₁₁NO₂.

(*E*)-1-(4-Styrylphenyl)ethanone (3e)²⁴

Light yellow solid; yield: 144 mg (65%); mp 146 °C.

¹H NMR (300 MHz, CDCl₃): δ = 7.98–7.95 (m, 2 H), 7.61–7.54 (m, 4 H), 7.42–7.37 (m, 2 H), 7.34–7.28 (m, 1 H), 7.27–7.11 (dd, *J* = 32.0, 15.9 Hz, 2 H), 2.62 (s, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 197.76, 142.21, 136.88, 136.12, 131.66, 129.10, 129.02, 128.55, 127.63, 127.04, 126.71, 26.83.

MW: 222.29 g/mol, C₁₆H₁₄O.

Methyl (*E*)-4-Styrylbenzoate (3f)²⁵

Light yellow solid; yield: 119 mg (50%); mp 157 °C.

¹H NMR (300 MHz, CDCl₃): δ = 8.05–8.02 (m, 2 H), 7.59–7.53 (t, *J* = 8.2 Hz, 4 H), 7.41–7.36 (dd, *J* = 10.1, 4.6 Hz, 2 H), 7.33–7.27 (ddd, *J* = 11.7, 5.7, 2.8 Hz, 1 H), 7.26–7.10 (q, *J* = 16.3 Hz, 2 H), 3.93 (s, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 167.11, 142.03, 136.95, 131.43, 130.24, 129.00, 128.46, 127.76, 127.46, 127.01, 126.54, 52.31.

MW: 238.29 g/mol, C₁₆H₁₄O₂.

(*E*)-1-Fluoro-4-styrylbenzene (3g)¹⁶

White solid; yield: 172 mg (87%).

¹H NMR (300 MHz, CDCl₃): δ = 7.53–7.47 (m, 4 H), 7.41–7.36 (t, *J* = 7.4 Hz, 2 H), 7.31–7.27 (dd, *J* = 7.4, 5.3 Hz, 1 H), 7.13–7.00 (m, 4 H).

¹³C NMR (75 MHz, CDCl₃): δ = 164.18, 160.91, 137.37, 133.74, 133.69, 128.94, 128.70, 128.67, 128.26, 128.15, 127.90, 127.68, 126.66, 115.99, 115.70.

MW: 198.24 g/mol, C₁₄H₁₁F.

Ethyl Cinnamate (3h)¹

Yellow oil; yield: 144 mg (82%).

¹H NMR (300 MHz, CDCl₃): δ = 7.72–7.67 (d, *J* = 16.0 Hz, 1 H), 7.54–7.50 (m, 2 H), 7.39–7.35 (dd, *J* = 6.5, 3.6 Hz, 3 H), 6.47–6.42 (d, *J* = 16.0 Hz, 1 H), 4.30–4.23 (q, *J* = 7.1 Hz, 2 H), 1.37–1.32 (t, *J* = 7.2 Hz, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 167.25, 144.83, 134.65, 130.45, 129.09, 128.27, 118.46, 60.73, 14.54.

MW: 176.22 g/mol, C₁₁H₁₂O₂.

Ethyl (*E*)-3-(4-Methoxyphenyl)acrylate (3i)²⁶

Light yellow oil; yield: 204 mg (99%).

¹H NMR (300 MHz, CDCl₃): δ = 7.66–7.61 (d, *J* = 16.0 Hz, 1 H), 7.47–7.44 (m, 2 H), 6.91–6.84 (m, 2 H), 6.33–6.27 (d, *J* = 16.0 Hz, 1 H), 4.28–4.21 (q, *J* = 7.1 Hz, 2 H), 3.81 (s, 3 H), 1.34–1.30 (t, *J* = 7.2 Hz, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 167.55, 161.53, 144.46, 129.90, 127.35, 115.90, 114.50, 60.53, 55.53, 14.56.

MW: 206.24 g/mol, C₁₂H₁₄O₃.

Ethyl (*E*)-3-(*p*-Tolyl)acrylate (3j)²⁶

Light yellow oil; yield: 186 mg (98%).

¹H NMR (300 MHz, CDCl₃): δ = 7.68–7.63 (d, *J* = 16.0 Hz, 1 H), 7.41–7.38 (d, *J* = 8.2 Hz, 2 H), 7.17–7.15 (m, 2 H), 6.41–6.36 (d, *J* = 16.0 Hz, 1 H), 4.28–4.21 (q, *J* = 7.1 Hz, 2 H), 2.34 (s, 3 H), 1.34–1.30 (t, *J* = 7.2 Hz, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 167.39, 144.81, 140.80, 131.93, 129.82, 128.27, 117.35, 60.60, 21.65, 14.56.

MW: 190.24 g/mol, C₁₂H₁₄O₂.

Ethyl (*E*)-3-(2-Nitrophenyl)acrylate (3k)²⁷

Yellow oil; yield: 217 mg (98%).

¹H NMR (300 MHz, CDCl₃): δ = 8.08–7.97 (dd, *J* = 19.1, 12.0 Hz, 2 H), 7.66–7.59 (m, 2 H), 7.56–7.47 (ddd, *J* = 13.9, 7.2, 4.0 Hz, 1 H), 6.36–6.30 (d, *J* = 15.8 Hz, 1 H), 4.27–4.20 (q, *J* = 7.1 Hz, 2 H), 1.32–1.28 (t, *J* = 7.1 Hz, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 165.99, 148.44, 140.02, 133.79, 130.68, 130.52, 129.31, 125.06, 123.43, 61.09, 14.42.

MW: 221.21 g/mol, C₁₁H₁₁NO₄.

Ethyl (*E*)-3-(4-Acetylphenyl)acrylate (3l)²⁸

Light yellow solid; yield: 177 mg (81%); mp 38 °C.

¹H NMR (300 MHz, CDCl₃): δ = 7.94–7.91 (m, 2 H), 7.67–7.62 (d, *J* = 16.1 Hz, 1 H), 7.57–7.55 (m, 2 H), 6.50–6.45 (d, *J* = 16.0 Hz, 1 H), 4.27–4.20 (q, *J* = 7.1 Hz, 2 H), 2.57 (s, 3 H), 1.33–1.28 (t, *J* = 7.1 Hz, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 197.47, 166.62, 143.15, 138.93, 138.10, 129.01, 128.28, 120.96, 60.92, 26.84, 14.46.

MW: 218.25 g/mol, C₁₃H₁₄O₃.

Methyl (*E*)-4-(3-Ethoxy-3-oxoprop-1-enyl)benzoate (3m)²⁹

White solid; yield: 206 mg (88%).

¹H NMR (300 MHz, CDCl₃): δ = 8.05–8.02 (d, *J* = 8.4 Hz, 2 H), 7.71–7.65 (d, *J* = 16.1 Hz, 1 H), 7.58–7.55 (d, *J* = 8.5 Hz, 2 H), 6.53–6.48 (d, *J* = 16.0 Hz, 1 H), 4.30–4.23 (q, *J* = 7.1 Hz, 2 H), 3.91 (s, 3 H), 1.35–1.31 (t, *J* = 7.1 Hz, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 166.73, 166.65, 143.34, 138.86, 131.49, 130.29, 128.09, 120.84, 60.95, 52.49, 14.48.

MW: 234.25 g/mol, C₁₃H₁₄O₄.

Ethyl (*E*)-3-(4-Fluorophenyl)acrylate (3n)¹

Light yellow oil; yield: 132 mg (68%).

¹H NMR (300 MHz, CDCl₃): δ = 7.65–7.60 (d, *J* = 16.0 Hz, 1 H), 7.52–7.45 (m, 2 H), 7.09–7.01 (m, 2 H), 6.36–6.31 (dd, *J* = 16.0, 0.5 Hz, 1 H), 4.28–4.21 (q, *J* = 7.1 Hz, 2 H), 1.34–1.29 (t, *J* = 7.1 Hz, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 167.03, 165.70, 162.37, 143.43, 130.91, 130.86, 130.15, 130.03, 118.21, 118.18, 116.33, 116.05, 60.72, 14.48.

MW: 194.21 g/mol, C₁₁H₁₁FO₂.

(*E*)-4-Styrylbenzaldehyde (3o)³⁰

Light yellow solid; yield: 114 mg (55%); mp 106 °C.

¹H NMR (300 MHz, CDCl₃): δ = 10.00 (s, 1 H), 7.89–7.86 (m, 2 H), 7.67–7.65 (d, *J* = 8.3 Hz, 2 H), 7.57–7.54 (m, 2 H), 7.43–7.31 (m, 3 H), 7.30–7.12 (dd, *J* = 38.6, 16.3 Hz, 2 H).

¹³C NMR (75 MHz, CDCl₃): δ = 191.89, 143.62, 136.74, 135.51, 132.40, 130.47, 129.06, 128.74, 127.52, 127.13.

MW: 208.26 g/mol, C₁₅H₁₂O.

Ethyl (E)-3-(4-Formylphenyl)acrylate (3p)²⁶

Light yellow solid; yield: 129 mg (63%); mp 49 °C.

¹H NMR (300 MHz, CDCl₃): δ = 10.03 (s, 1 H), 7.93–7.89 (m, 2 H), 7.74–7.67 (dd, *J* = 12.0, 10.0 Hz, 3 H), 6.58–6.53 (d, *J* = 16.0 Hz, 1 H), 4.33–4.25 (q, *J* = 7.2 Hz, 2 H), 1.38–1.33 (t, *J* = 7.2 Hz, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 191.76, 166.62, 143.07, 140.33, 137.30, 130.39, 128.70, 121.64, 61.08, 14.48.

MW: 204.23 g/mol, C₁₂H₁₂O₃.

Cinnamionitrile (3q)¹⁶

White solid; yield: 74 mg (57%).

¹H NMR (300 MHz, CDCl₃): δ = 7.48–7.43 (m, 5 H), 7.41–7.36 (d, *J* = 16.7 Hz, 1 H), 5.90–5.85 (d, *J* = 16.7 Hz, 1 H).

¹³C NMR (75 MHz, CDCl₃): δ = 150.80, 133.72, 131.47, 129.36, 127.62, 118.45, 96.54.

MW: 129.16 g/mol, C₉H₇N.

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Supporting Information

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References

- (1) Karimi, B.; Enders, D. *Org. Lett.* **2006**, *8*, 1237.
- (2) (a) Trost, B. M.; Knopf, J. D.; Brindle, C. S. *Chem. Rev.* **2016**, *116*, 15035. (b) Rousée, K.; Bouillon, J.-P.; Couve-Bonnaire, S.; Pannecoucke, X. *Org. Lett.* **2016**, *18*, 540.
- (3) Aukland, M. H.; Talbot, F. J. T.; Fernández-Salas, J. A.; Ball, M.; Pulis, A. P.; Procter, D. J. *Angew. Chem. Int. Ed.* **2018**, *57*, 9785; *Angew. Chem.* **2018**, *130*, 9933.
- (4) Patel, H. H.; Sigman, M. S. *J. Am. Chem. Soc.* **2015**, *137*, 3462.
- (5) Liu, X.-L.; Li, B.; Gu, Z.-H. *J. Org. Chem.* **2015**, *80*, 7547.
- (6) Cong, H.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *136*, 3788.
- (7) Littke, A. F.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 4176.
- (8) Sun, R.; Liu, B.; Li, B.-G.; Jie, S. *ChemCatChem* **2016**, *8*, 3261.
- (9) Wali, A.; Pillai, S. M.; Satish, S. *React. Kinet. Catal. Lett.* **1997**, *60*, 189.
- (10) Khajehzadeh, M.; Moghadam, M. *J. Organomet. Chem.* **2018**, *863*, 60.
- (11) Liu, Y.; Bai, X.; Li, S. *Microporous Mesoporous Mater.* **2018**, *260*, 40.
- (12) Taher, A.; Lee, D.-J.; Lee, I.-M.; Rahman, M. L.; Sarker, M. S. *Bull. Korean Chem. Soc.* **2016**, *37*, 1478.
- (13) Sato, T.; Ohno, A.; Sarkar, S. M.; Uozumi, Y.; Yamada, Y. M. A. *ChemCatChem* **2015**, *7*, 2141.
- (14) Ghorbani-Choghamarani, A.; Tahmasbi, B.; Noori, N.; Faryadi, S. C. *R. Chim.* **2017**, *20*, 132.
- (15) Huang, L.; Subramanian, R.; Wang, J.; Kwon Oh, J.; Ye, Z. *Mol. Catal.* **2020**, *488*, 110923.
- (16) Yu, L.; Huang, Y.; Wei, Z.; Ding, Y.; Su, C.; Xu, Q. *J. Org. Chem.* **2015**, *80*, 8677.
- (17) Patel, H. A.; Sharma, S. K.; Jasra, R. V. *J. Mol. Catal. A: Chem.* **2008**, *286*, 31.
- (18) Moura, K. O.; Pastore, H. O. *Microporous Mesoporous Mater.* **2014**, *190*, 292.
- (19) (a) Houdayer, A.; Schneider, R.; Billaud, D.; Ghanbaja, J.; Lambert, J. *Appl. Organomet. Chem.* **2005**, *19*, 1239. (b) Somjit, V.; Wong Chi Man, M.; Ouali, A.; Sangtrirutnugul, P.; Ervithayasuporn, V. *ChemistrySelect* **2018**, *3*, 753.
- (20) (a) Jagtap, S. *Catalysts* **2017**, *7*, 267. (b) Sherwood, J.; Clark, J. H.; Fairlamb, I. J. S.; Slattery, J. M. *Green Chem.* **2019**, *21*, 2164.
- (21) Khan, M.; Khan, M.; Kuniyil, M.; Adil, S. F.; Al-Warthan, A.; Alkhathlan, H. Z.; Tremel, W.; Tahir, M. N.; Siddiqui, M. R. H. *Dalton Trans.* **2014**, *43*, 9026.
- (22) Xuan, S.; Jiang, W.; Gong, X. *Dalton Trans.* **2011**, *40*, 7827.
- (23) Mekkaoui, A. A.; Jennane, S.; Aberkouks, A.; Boualy, B.; Mehdi, A.; Ait Ali, M.; El Firdoussi, L.; El Houssame, S. *Appl. Organomet. Chem.* **2019**, *33*, e5117.
- (24) Sore, H. F.; Boehner, C. M.; MacDonald, S. J. F.; Norton, D.; Fox, D. J.; Spring, D. R. *Org. Biomol. Chem.* **2009**, *7*, 1068.
- (25) Okita, T.; Asahara, K. K.; Muto, K.; Yamaguchi, J. *Org. Lett.* **2020**, *22*, 3205.
- (26) Ghasemzadeh, M. S.; Akhlaghinia, B. *Aust. J. Chem.* **2019**, *72*, 674.
- (27) Ren, G.; Cui, X.; Yang, E.; Yang, F.; Wu, Y. *Tetrahedron* **2010**, *66*, 4022.
- (28) Shao-Hsien, H. *Molecules* **2010**, *15*, 315.
- (29) Wei, Y.-L.; Li, Y.; Chen, Y.-Q.; Dong, Y.; Yao, J.-J.; Han, X.-Y.; Dong, Y.-B. *Inorg. Chem.* **2018**, *57*, 4379.
- (30) Balinge, K. R.; Bhagat, P. R. *Inorg. Chim. Acta* **2019**, *495*, 119017.