

An Imidazolium-Based Phosphinite Ionic Liquid (IL-OPPh₂) as a Reusable Reaction Medium and Pd^{II} Ligand in Heck Reactions of Aryl Halides with Styrene and *n*-Butyl Acrylate

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A new imidazolium-based phosphinite ionic liquid (IL-OPPh₂) is reported as an effective reusable medium and suitable Pd^{II} ligand for C–C bond formation through Heck coupling reactions of aryl iodides, bromides and also chlorides with styrene and *n*-butyl acrylate. The ionic liquid, still con-

taining its corresponding Pd^{II} complex, was easily recovered and reused in several runs without losing its efficiency.

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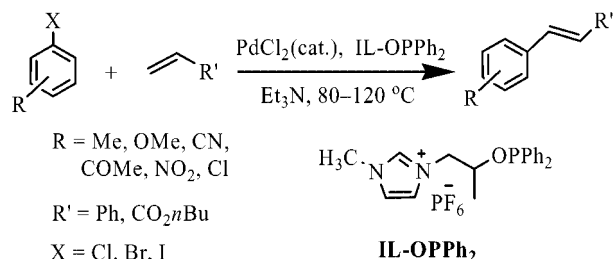
Introduction

Catalytic carbon–carbon bond-forming coupling reactions have emerged as exceedingly important methodologies for the preparation of unsaturated carbon skeletons of organic molecules. The use of phosphanes in Pd-catalysed Heck reactions provides an efficient route for the synthesis of substituted olefins through cross-coupling of aryl halides and olefins.^[1–6] In the case of the less reactive aryl bromides and aryl chlorides, electron-rich bulky tertiary phosphanes are usually used as ligands.^[2] As well as recent developments in catalytic carbon–carbon coupling reactions involving new ligands^[7–10] or bases,^[11] alongside techniques such as microwave irradiation^[12] or the use of supported reagents, complex matrices immobilized on silica,^[13] polymers and PEG,^[14] ionic liquids have also been considered as potential tools for this purpose.^[15] As far as we know, imidazolium-based ionic liquids are either used as media^[16] or used as ligands in complexation with palladium compounds in different C–C coupling bond formation reactions.^[17–19]

Results and Discussion

We have recently reported the preparation of a new imidazolium-based phosphinite ionic liquid (Scheme 1, IL-OPPh₂) and its application as a reaction medium and reagent for bromination and thiocyanation of alcohols and of trimethylsilyl and tetrahydropyranyl ethers.^[20] Since this

ionic liquid can play a dual role both as reaction medium and also – through the phosphinite group that it bears – as a potential complexing agent, we decided to apply it in conjunction with Pd^{II} salts for Heck C–C bond-formation reactions. This dual property offers the potential for recycling of the ionic liquid together with its corresponding catalytic Pd^{II} complex, which should thus eliminate wastage both of the ligand and also of the Pd compound. Here we report on the successful application of this ionic liquid both as solvent and as a ligand for efficient Heck coupling reactions of aryl iodides and bromides at 80 °C, and also of chlorides at 120 °C, with styrene and *n*-butyl acrylate in the presence of catalytic amounts of PdCl₂ and Et₃N (Scheme 1).



Scheme 1.

The desired products were isolated simply by diethyl ether extraction. The use of this ionic liquid also allows the use of solvents such as DMF or DMAc, otherwise widely employed in Heck reactions, to be avoided. Of the Pd^{II} compounds we have studied as catalysts, PdCl₂ proved to be the most effective under our reaction conditions (Table 1).

If the ionic liquid is used in an amount equimolar with the Pd^{II} catalyst, a sticky mass is produced and the reaction does not take place. In comparison with the reported metal phosphane complexes, the complex produced between this

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Table 1. Effect of the catalyst on the Heck reaction between bromobenzene and styrene.^[a]

Entry	Catalyst	Yield (%) ^[b]
1	none	0
2	PdCl ₂	100
3	Pd(OAc) ₂	15
4	PdCl ₂ (CH ₃ CN) ₂	60

[a] Reaction conditions: 0.03 mmol of catalyst, 0.5 mmol of IL-OPPh₂, 1.0 mmol of bromobenzene, 2.0 mmol of styrene and 2.0 mmol of Et₃N at 80 °C. [b] GC yields with *n*-octane as internal standard.

phosphinite ionic liquid and Pd^{II} has high stability towards oxygen and moisture. Little difference in the yields and times of the reactions was observed when oxygen was excluded from the reaction system.

Of the bases studied in the reaction between bromobenzene and styrene in the presence of PdCl₂ in this ionic liquid, Et₃N and NaOAc were found to be more efficient, probably thanks to their solubility in the reaction medium (Table 2). We therefore selected Et₃N as the most suitable base under our reaction conditions.

Table 2. Effects of different bases on the reaction between bromobenzene and styrene.^[a]

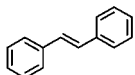
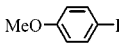
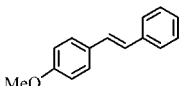
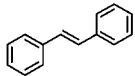
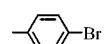
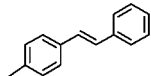
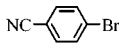
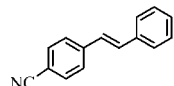
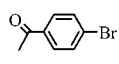
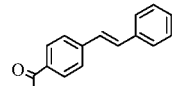
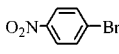
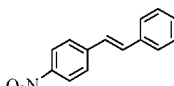
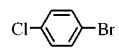
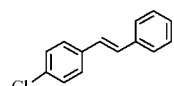
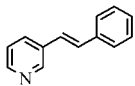
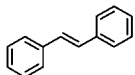
Entry	Base	Time [h]	Yield (%) ^[b]
1	none	12	0
2	Na ₂ CO ₃	12	10
3	CS ₂ CO ₃	12	70
4	NaOAc	5	100
5	Et ₃ N	1	100

[a] Reaction conditions: 0.5 mmol of IL-OPPh₂, 0.03 mmol of PdCl₂, 1.0 mmol of bromobenzene, 2.0 mmol of styrene and 2.0 mmol of base. [b] GC yield with *n*-octane as an internal standard.

Under our optimized reaction conditions (0.5 mmol IL-OPPh₂, 0.03 mmol of PdCl₂ and 2.0 mmol of Et₃N), the desired products were obtained in excellent yields both from a wide array of aryl iodides and bromides with styrene at 80 °C and also from chlorides at 120 °C (Table 3). Iodobenzene and 4-iodoanisole, for example, had been completely converted into the coupled products after 0.5 and 1 h, respectively (Table 3, Entries 1, 2). Remarkably, the catalytic system was equally efficient with the electron-neutral bromides: complete conversion had been achieved in the reactions of bromobenzene and 4-bromotoluene with styrene after 1 h (Table 3, Entries 3, 4). With electron-deficient bromides, elongations of the reaction times were observed, along with the decrement of the yields of the products. This is most probably due to the poorer solubilities of 4-bromobenzonitrile, 4-bromoacetophenone and 1-bromo-4-nitrobenzene in this ionic liquid (Table 3, Entries 5–7).

As illustrated in Table 3, Entry 9, these Heck cross-coupling reactions based on the PdCl₂/IL-OPPh₂ complex were also applicable to heteroaryl halides. Use of 3-bromopyridine and styrene as substrates gave a satisfactory result and the desired product was isolated in 65% yield.

Table 3. PdCl₂/IL-OPPh₂-catalysed Heck reactions between aryl halides and styrene.

Entry	Ar-X	Product	Time [h]	Yield [%] ^[a]
1			0.5	97
2			1	95
3			1	91
4			1	90
5			10	88
6			10	72 (80) ^[b]
7			15	60 (70) ^[b]
8			10	90
9			17	65 (70) ^[b]
10			48 ^[c]	90

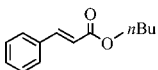
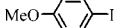
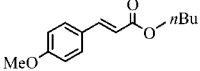
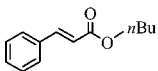
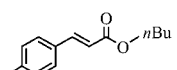
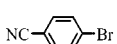
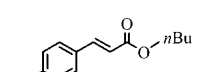
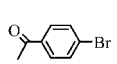
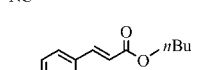
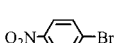
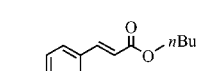
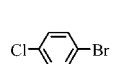
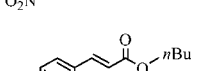
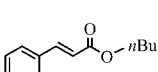
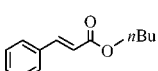
[a] All products are known compounds and were identified by comparison of their physical or spectroscopic data with those for known samples.^[21–23] [b] Data in the brackets show the GC yields with *n*-octane as an internal standard. [c] The reaction went to completion at 120 °C.

The use of this system for the coupling of chlorobenzene and styrene at 120 °C was also successful (Table 3, Entry 10). In these reactions, no formation of 1,1-diarylethylene compounds as side products was observed.

In an additional series of experiments we also studied the coupling reactions between aryl halides and *n*-butyl acrylate. A methodology similar to that described for styrene was also employed for this purpose, and the results of this study are presented in Table 4.

The *trans* products, as confirmed by ¹H NMR analysis, were obtained exclusively in all the cases that we present in this article. The remaining mixture of ionic liquid and its corresponding Pd^{II} complex was washed with water to re-

Table 4. PdCl₂/IL-OPPh₂-catalysed Heck reactions between aryl halides and *n*-butyl acrylate.

Entry	Ar-X	Product	Time [h]	Yield [%] ^[a]
1			0.25	95
2			0.5	90
3			3	90
4			3	90
5			8	88
6			10	69 (75) ^[b]
7			10	59 (70) ^[b]
8			7	95
9			15	60 (70) ^[b]
10			36 ^[c]	95

[a] All products are known compounds and were identified by comparison of their physical or spectroscopic data with those for known samples.^[21–23] [b] The data in the brackets are GC yields with *n*-octane as internal standard. [c] The reaction went to completion at 120 °C.

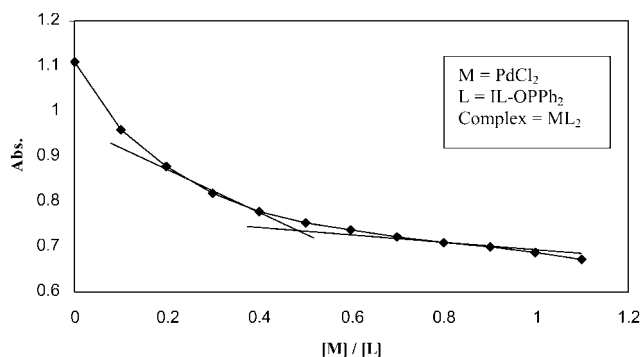
move the produced triethylammonium halide and could be reused for six runs in the reaction between bromobenzene and styrene without losing its efficiency, giving *trans*-stilbene (Table 5).

Table 5. Coupling of bromobenzene with styrene in the presence of recycled ionic liquid and its Pd complex.^[a]

Cycle	Conversion (%)	Yield (%) ^[b]
1	100	91
2	100	91
3	100	93
4	100	90
5	100	90
6	100	92
7	90	84

[a] All the reactions were performed with Et₃N as base at 80 °C over 1 h. [b] Isolated yields.

In order to gain insight into the nature of the catalyst, the ionic liquid and Pd^{II} were mixed in the ratio of 2:1 in two separate reaction mixtures, Et₃N (2 equiv.) was added to one of them, and both reaction mixtures were heated to 80 °C. The complexes obtained from these reactions showed similar reactivities when they were used as catalysts in the coupling reaction between styrene and bromobenzene at 80 °C. The ¹H NMR spectra of these complexes each showed the presence of the C(2)-H unit of the imidazolium group, which indicates that the carbon (2) of the imidazolium group does not take part in the complex formation and that two molecules of the phosphinite ionic liquid and Pd^{II} form a ML₂ complex. The absence of formation of a carbene-type complex with this phosphinite ionic liquid is probably due to the low probability of the formation of a seven-membered ring in the ML complex. The use of the mole ratio method^[24] for the complex formation between this IL and PdCl₂ in the presence of triethylamine is in good agreement with the ML₂ structure for this complex (Figure 1).

Figure 1. Mole ratio plot for complex formation between PdCl₂ and IL at 267 nm in relation to λ_{max} of the ligand.

Comparison of our results (Table 1, Table 2) with those based on the use of ionic liquids in other reaction systems show the advantages of the present method. The use of 10 mol% of Pd(OAc)₂ and immobilized ionic liquid on SiO₂ in *n*-dodecane at 150 °C, for example, allowed the coupling only of aryl iodides and bromides with alkyl acrylates,^[21] the reaction between PhCl and *n*-butyl acrylate in the presence of 0.5 mol-% of Pd(dba)₂ and equimolar amounts of a phosphane-imidazolium salt system in DMAc at 120 °C gave only a 13% yield of the coupled product,^[17a] while use of Pd nanoparticles dispersed in BMI·PF₆ produced the coupled products of ArX (X = I, Br) with *n*-butyl acrylate at 130 °C after 14 h in 77–87% isolated yields.^[16]

Conclusions

In summary, the use of this easily prepared phosphinite ionic liquid (IL-OPPh₂) both as the reaction medium and as the ligand in Pd^{II}-catalysed Heck reactions provides a useful method for the efficient coupling of ArX (X = Cl, Br and I) with styrene and *n*-butyl acrylate. The reusability

of this phosphinite ionic liquid and its IL/Pd^{II} complex in a mixture can also be regarded as strong practical advantages of this new Heck method.

Experimental Section

Chemicals were obtained from Fluka or Merck. The progress of reactions was followed by TLC on silica gel SILG/UV 254 plates. IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance DPX 250 FT-NMR spectrometer (δ in ppm). Melting points were determined with a Büchi 510 instrument in open capillary tubes and are uncorrected. All yields refer to the isolated products. Evaporation of solvents was performed at reduced pressure, with a Büchi rotary evaporator. The absorbance measurements as a function of time, at a fixed wavelength, were made with a Shimadzu UV-1601PC spectrophotometer interfaced with a Pentium 200 MHz computer.

Typical Procedure for the Heck Reaction between Bromobenzene and Styrene: PdCl₂ (0.03 mmol, 5.3 mg) and Et₃N (2 mmol, 0.27 mL) were placed in a flask containing the phosphinite ionic liquid (0.5 mmol, 0.23 g). The flask was placed in an 80 °C oil bath, the mixture was stirred for 15 min, and bromobenzene (1 mmol, 0.105 mL) and styrene (2 mmol, 0.22 mL) were then added to the mixture. GC and TLC of the reaction mixture showed the completion of the reaction after 1 h. After completion of the reaction, the mixture was allowed to cool to room temperature and *trans*-stilbene was extracted with diethyl ether (3 × 5 mL). Evaporation of the solvent, followed by chromatography on a short column of silica gel, gave *trans*-stilbene (0.162 g, 91%).

Typical Procedure for the Heck Reaction between Bromobenzene and *n*-Butyl Acrylate: PdCl₂ (0.03 mmol, 5.3 mg) and Et₃N (2 mmol, 0.27 mL) were added at 80 °C to a flask containing phosphinite ionic liquid (0.5 mmol, 0.23 g), the mixture was stirred for 15 min, and bromobenzene (1 mmol, 0.105 mL) and *n*-butyl acrylate (2 mmol, 0.28 mL) were then added. GC and TLC of the reaction mixture showed the completion of the reaction after 3 h. After completion of the reaction, the mixture was allowed to cool to room temperature and butyl *trans*-cinnamate was extracted with diethyl ether (3 × 5 mL). Evaporation of the solvent, followed by chromatography on a short column of silica gel, gave butyl *trans*-cinnamate (90%).

Spectral Data for Products

***trans*-Stilbene:**^[22] M.p. ref.^[22] 123–124 °C; found 122–123 °C. ¹H NMR (250 MHz, CDCl₃): δ = 7.53 (d, J = 7.5 Hz, 4 H), 7.45 (t, J = 7.5 Hz, 4 H), 7.35 (t, J = 7.5 Hz, 2 H), 7.26 (s, 2 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 139.5, 130.5, 128.5, 126.7, 128.5 ppm.

***trans*-4-Methylstilbene:**^[23] M.p. ref.^[23] 117–118 °C; found 117.5–118 °C. ¹H NMR (250 MHz, CDCl₃): δ = 7.42 (d, J = 8.5 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.20 (t, J = 7.5 Hz, 2 H), 7.15 (t, J = 6.5 Hz, 1 H), 7.05 (d, J = 8.0 Hz, 2 H), 6.96 (d, J = 16.5 Hz, 1 H), 6.90 (d, J = 16.5 Hz, 1 H), 2.30 (s, 3 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 136.7, 136.3, 134.2, 130.5, 129.8, 128.7, 127.8, 127.2, 126.0, 126.0, 23.0 ppm.

***trans*-4-Methoxystilbene:**^[23] M.p. ref.^[23] 135.4–137.1 °C; found 136–137 °C. ¹H NMR (250 MHz, CDCl₃): δ = 7.42 (d, J = 7.5 Hz, 2 H), 7.37 (d, J = 8.5 Hz, 2 H), 7.28 (t, J = 7.5 Hz, 2 H), 7.18 (t, J = 6.5 Hz, 1 H), 6.99 (d, J = 16.0 Hz, 1 H), 6.89 (d, J = 16.5 Hz, 1 H), 6.80 (d, J = 8.5 Hz, 2 H), 3.77 (s, 3 H) ppm. ¹³C NMR

(60 MHz, CDCl₃): δ = 160.5, 138.8, 130.9, 129.5, 128.0, 127.5, 127.0, 126.5, 126.0, 116.5, 57.5 ppm.

***trans*-4-Cyanostilbene:**^[23] ¹H NMR (250 MHz, CDCl₃): δ = 7.45–7.60 (m, 6 H), 7.49 (t, J = 7.5 Hz, 2 H), 7.40 (t, J = 7.45 Hz, 1 H), 7.20 (d, J = 16.5 Hz, 1 H), 7.02 (d, J = 16.5 Hz, 1 H) ppm.

***trans*-4-Acetylstilbene:**^[23] M.p. ref.^[23] 138.7–144.8 °C; found 140–144 °C. ¹H NMR (250 MHz, CDCl₃): δ = 7.90 (d, J = 8.0 Hz, 2 H), 7.70 (d, J = 8.0 Hz, 2 H), 7.40 (d, J = 8.0 Hz, 2 H), 7.30–7.35 (m, 3 H), 7.20 (d, J = 16.5 Hz, 1 H), 7.01 (d, J = 16.5 Hz, 1 H), 2.15 (s, 3 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 194.5, 144.5, 137.9, 137.5, 130.7, 129.8, 129.8, 128.0, 127.8, 127.0, 125.0, 30.5 ppm.

***trans*-4-Nitrostilbene:**^[23] M.p. ref.^[23] 156–157 °C; found 155–157 °C. ¹H NMR (250 MHz, CDCl₃): δ = 8.40 (d, J = 9.3 Hz, 2 H), 7.80 (d, J = 9.3 Hz, 2 H), 7.71 (d, J = 7.3 Hz, 2 H), 7.45–7.55 (m, 3 H), 7.37 (d, J = 16 Hz, 1 H), 7.23 (d, J = 16.5 Hz, 1 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 152.2, 149.9, 140.5, 135.5, 130.1, 129.0, 128.5, 128.0, 127.0, 125.5 ppm.

***trans*-4-Chlorostilbene:**^[23] ¹H NMR (250 MHz, CDCl₃): δ = 7.80 (d, J = 7.3 Hz, 2 H), 7.65 (d, J = 8.5 Hz, 2 H), 7.30–7.44 (m, 5 H), 7.20 (s, 2 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 140.0, 137.9, 135.5, 131.3, 129.9, 129.5, 128.2, 127.5, 127.0, 125.5 ppm.

***trans*-3-Styrylpyridine:**^[23] M.p. ref.^[23] 78.6–81.6 °C; found 79–81 °C. ¹H NMR (250 MHz, CDCl₃): δ = 8.70 (s, 1 H), 8.50 (d, J = 4.8 Hz, 1 H), 7.90 (d, J = 8.3 Hz, 1 H), 7.65 (d, J = 7.3 Hz, 2 H), 7.30 (t, J = 7.3 Hz, 2 H), 7.15–7.25 (m, 2 H), 7.08 (d, J = 16.5 Hz, 1 H), 6.90 (d, J = 16.0 Hz, 1 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 150.5, 149.5, 138.8, 135.0, 133.3, 130.0, 129.7, 127.6, 126.0, 125.0, 121.0 ppm.

Butyl *trans*-Cinnamate:^[23] ¹H NMR (250 MHz, CDCl₃): δ = 7.80 (d, J = 16 Hz, 1 H), 7.66 (m, 2 H), 7.43 (m, 3 H), 6.75 (d, J = 16 Hz, 1 H), 4.45 (t, J = 6.8 Hz, 2 H), 2.65 (m, J = 7.3 Hz, 2 H), 1.80 (m, J = 7.3 Hz, 2 H), 1.05 (t, J = 7.3 Hz, 3 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 170.5, 151.5, 140.8, 135.6, 130.2, 129.5, 120.8, 71.6, 35.0, 22.2, 15.5 ppm.

Butyl *trans*-4-Methylcinnamate:^[23] ¹H NMR (250 MHz, CDCl₃): δ = 7.87 (d, J = 16 Hz, 1 H), 7.55 (d, J = 8.5 Hz, 2 H), 7.25 (d, J = 8.5 Hz, 2 H), 6.60 (d, J = 16 Hz, 1 H), 4.90 (t, J = 6.5 Hz, 2 H), 2.80 (s, 3 H), 1.99 (m, J = 6 Hz, 2 H), 1.20 (m, J = 7.3 Hz, 2 H), 0.88 (t, J = 7.5 Hz, 3 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 175.5, 150.6, 144.5, 130.0, 129.0, 128.5, 119.0, 70.5, 41.3, 25.7, 17.5, 13.0 ppm.

Butyl *trans*-4-Methoxycinnamate:^[23] ¹H NMR (250 MHz, CDCl₃): δ = 1.07 (t, J = 7.5 Hz, 3 H), 1.30–1.42 (m, 2 H), 1.59–1.70 (m, 2 H), 3.67 (s, 3 H), 4.05 (t, J = 6.7 Hz, 2 H), 6.46 (d, J = 16.0 Hz, 1 H), 6.70–6.90 (m, 2 H), 7.35–7.50 (m, 2 H), 7.65 (d, J = 16.0 Hz, 1 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 12.05, 21.20, 35.67, 44.34, 60.19, 110.05, 118.05, 125.08, 126.72, 150.21, 159.09, 162.43 ppm.

Butyl *trans*-4-Cyanocinnamate:^[23] M.p. ref.^[23] 43.5–46.9 °C; found 44–46 °C. ¹H NMR (250 MHz, CDCl₃): δ = 7.82–7.69 (m, 5 H), 6.90 (d, J = 16 Hz, 1 H), 5.45 (t, J = 6.6 Hz, 2 H), 2.23 (m, J = 7.3 Hz, 2 H), 1.99 (m, J = 7.3 Hz, 2 H), 1.07 (t, J = 7.3 Hz, 3 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 184.5, 163.3, 151.2, 145.5, 133.7, 128.2, 121.9, 119.0, 86.5, 42.8, 25.5, 16.7 ppm.

Butyl *trans*-4-Acetylcinnamate:^[23] ¹H NMR (250 MHz, CDCl₃): δ = 8.11 (d, J = 8.5 Hz, 2 H), 7.89 (d, J = 15.5 Hz, 1 H), 7.72 (d, J = 8.5 Hz, 2 H), 6.92 (d, J = 16 Hz, 1 H), 5.35 (t, J = 7.5 Hz, 2 H), 3.98 (s, 3 H), 2.56 (m, J = 7.5 Hz, 2 H), 1.98 (m, J = 7.5 Hz, 2 H), 1.06 (t, J = 7.3 Hz, 3 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ =

195.5, 172.5, 155.0, 146.5, 141.5, 132.6, 130.8, 125.5, 88.3, 45.0, 33.4, 23.4, 16.0 ppm.

Butyl *trans*-4-Nitrocinnamate:^[23] M.p. ref.^[23] 59.6–64.4 °C; found 60–63 °C. ¹H NMR (250 MHz, CDCl₃): δ = 8.65 (d, J = 8.7 Hz, 2 H), 7.98–7.88 (m, 3 H), 7.09 (d, J = 15.5 Hz, 1 H), 5.65 (t, J = 7 Hz, 2 H), 2.45 (m, J = 7.8 Hz, 2 H), 1.86 (m, J = 7.5 Hz, 2 H), 1.08 (t, J = 7.5 Hz, 3 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 184.0, 166.5, 155.5, 138.7, 133.5, 129.5, 123.3, 87.7, 54.4, 28.8, 15.5 ppm.

Butyl *trans*-4-Chlorocinnamate:^[23] ¹H NMR (250 MHz, CDCl₃): δ = 1.09 (t, J = 7.4 Hz, 3 H), 1.44–1.51 (m, 2 H), 1.70–1.85 (m, 2 H), 3.99 (t, J = 6.7 Hz, 2 H), 5.87 (d, J = 16.0 Hz, 1 H), 7.43–7.50 (m, 2 H), 7.54–7.78 (m, 2 H), 7.89 (d, J = 16.0 Hz, 1 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 15.55, 25.15, 47.55, 74.66, 108.82, 125.50, 127.75, 130.14, 134.40, 152.13, 175.88 ppm.

Butyl *trans*-3-(Pyridin-3-yl)acrylate:^[23] ¹H NMR (250 MHz, CDCl₃): δ = 8.85 (s, 1 H), 8.72 (m, 1 H), 7.75 (d, J = 8.5 Hz, 1 H), 7.57 (d, J = 16 Hz, 1 H), 7.24 (m, 1 H), 6.79 (d, J = 16.5 Hz, 1 H), 5.09 (t, J = 6.5 Hz, 2 H), 2.23 (m, J = 7.3 Hz, 2 H), 1.78 (m, J = 7.3 Hz, 2 H), 1.04 (t, J = 7.3 Hz, 3 H) ppm. ¹³C NMR (60 MHz, CDCl₃): δ = 187.5, 172.2, 159.9, 138.8, 135.5, 128.5, 123.3, 111.4, 89.9, 56.6, 39.9, 28.4, 15 ppm.

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- [1] a) I. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009; b) M. T. Reetz, in *Transition Metal Catalyzed Reactions* (Eds.: S. G. Davies, S.-I. Murahashi); Blackwell Science: Oxford, **1999**; c) G. T. Grisp, *Chem. Soc. Rev.* **1998**, *27*, 427; d) J. T. Link, L. E. Overman, in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, New York, **1998**; e) J. T. Link, L. E. Overman, *Chemtech* **1998**, *28*, 19; f) S. Brase, A. Meijere, in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. P. Diederich, J. Stang), Wiley-VCH, New York, **1998**; g) H. A. Dieck, R. F. Heck, *J. Org. Chem.* **1975**, *40*, 1083; h) H. A. Dieck, R. F. Heck, *J. Am. Chem. Soc.* **1974**, *96*, 1133.
- [2] A. F. Littke, G. C. Fu, *J. Org. Chem.* **1999**, *64*, 10.
- [3] G. P. F. Van Strijdonck, M. D. K. Boele, P. C. J. Kamer, J. G. de Vries, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.* **1999**, 1073.
- [4] Y. Bendavid, M. Portnoy, M. Gozin, D. Milstein, *Organometallics* **1992**, *11*, 1995.
- [5] M. Portnoy, Y. Bendavid, D. Milstein, *Organometallics* **1993**, *12*, 4734.
- [6] a) B. L. Shaw, S. D. Perera, *Chem. Commun.* **1998**, 1863; b) L. E. Overman, D. J. Poon, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 518; c) W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, *28*, 2; d) W. Cabri, I. Candiani, A. Bedeschi, *J. Org. Chem.* **1992**, *57*, 3558.
- [7] A. F. Littke, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 6989.
- [8] K. Selvakumar, A. Zapf, M. Beller, *Org. Lett.* **2002**, *4*, 3031.
- [9] J. Ch. Xiao, B. Twamley, J. M. Shreeve, *Org. Lett.* **2004**, *6*, 3845.
- [10] L. Xu, W. Chen, J. Xiao, *Organometallics* **2000**, *19*, 1123.
- [11] Q. Yao, E. P. Kinney, Z. Yang, *J. Org. Chem.* **2003**, *68*, 7528 and earlier references therein.
- [12] K. S. A. Vallin, P. Emilsson, M. Larhed, A. Hallberg, *J. Org. Chem.* **2002**, *67*, 6243.
- [13] B. Karimi, D. Enders, *Org. Lett.* **2006**, *8*, 1237.
- [14] a) Y. Uozumi, T. Watanabe, *J. Org. Chem.* **1999**, *64*, 6921–6923; b) L. Wang, Y. Zhang, Ch. Xie, Y. Wang, *Synlett* **2005**, *12*, 1861–1864.
- [15] V. Calo, A. Nacci, A. Monopoli, *Eur. J. Org. Chem.* **2006**, *17*, 3791–3802.
- [16] C. C. Cassol, A. P. Umpierre, G. Machado, S. I. Wolke, J. Dupont, *J. Am. Chem. Soc.* **2005**, *127*, 3298–3299.
- [17] a) Ch. Yang, H. M. Lee, S. P. Nolan, *Org. Lett.* **2001**, *3*, 1511–1514; b) J. Huang, S. Nolan, *J. Am. Chem. Soc.* **1999**, *121*, 9889–9890; c) H. M. Lee, S. P. Nolan, *Org. Lett.* **2000**, *2*, 2053–2055.
- [18] V. P. W. Böhm, W. A. Herrmann, *Chem. Eur. J.* **2000**, *6*, 1017.
- [19] H. M. Lee, S. P. Nolan, *Org. Lett.* **2000**, *2*, 2053.
- [20] N. Iranpoor, H. Firouzabadi, R. Azadi, *Tetrahedron Lett.* **2006**, *47*, 5531–5534.
- [21] H. Hagiwara, Y. Sugawara, K. Isobe, T. Hoshi, T. Suzuki, *Org. Lett.* **2004**, *6*, 2325–2328.
- [22] R. Barik, Ch. V. Kumar, P. K. Das, M. V. J. George, *J. Org. Chem.* **1985**, *50*, 4309.
- [23] Ö. Aksın, H. Türkmen, L. Artok, B. Çetinkaya, C. Ni, O. Büyükgüngörd, E. Ozkal, *J. Organomet. Chem.* **2006**, *691*, 3027–3036.
- [24] B. Gauguain, J. Barbet, N. Capelle, B. P. Roques, J. B. Le Pecq, *Biochemistry* **1978**, *17*, 5078–5088.

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