

Mizoroki–Heck and Sonogashira Cross-Couplings Catalyzed by CNC Palladium Pincer Complexes in Organic and Aqueous Media

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The catalytic activity of two CNC palladium pincer complexes is evaluated in two fundamental C–C bond-forming reactions: *Mizoroki–Heck* and *Sonogashira* cross-couplings. After several optimization attempts and a brief comparison with a PCN pincer catalyst, a number of arylated alkenes and diarylethynes are synthesized by procedures based on the catalytic use of the above mentioned CNC Pd pincers in H₂O and DMF.

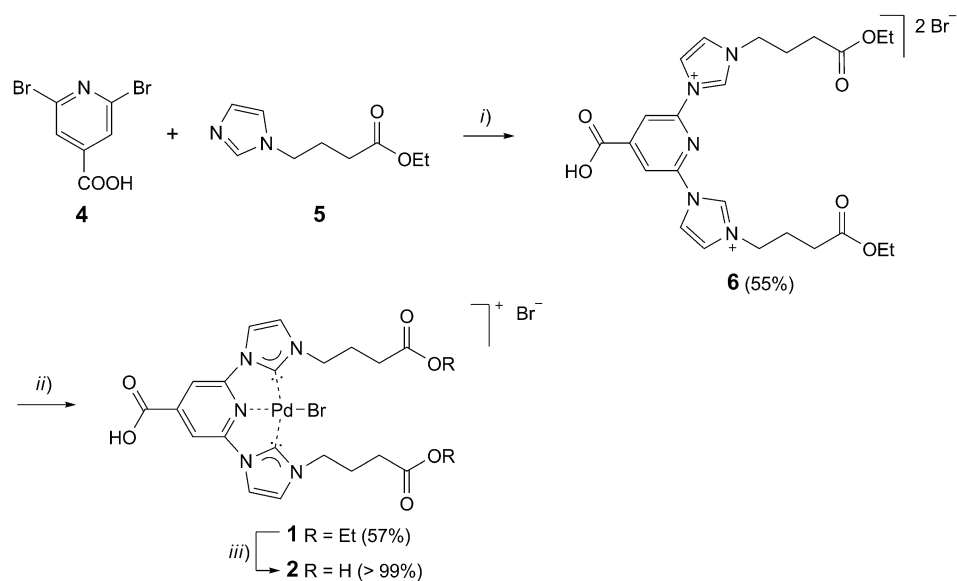
Introduction. – *Mizoroki–Heck* and *Sonogashira* coupling reactions are amongst the most important transformations based on Pd catalysts. Much effort has been devoted to the expansion of the scope of these two C–C bond forming reactions by means of several catalytic systems [1]. A particular area of interest in this context has been the use of pincer-type palladacycles in lieu of other well-established procedures relying on the combination of Pd salts, and Ph₃P or NHC ligands. Indeed, pincer Pd complexes have provided higher catalytic efficiencies (in terms of TON or TOF values) and, in some cases, allowed for the use of more convenient, sustainable media [2].

Following our research on the catalytic properties of CNC-type pincers [3], we envisaged the application of pincers **1** and **2** (*Scheme*) as catalysts in *Heck* and *Sonogashira* coupling reactions. The most remarkable results are reported in this article.

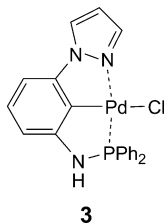
Results and Discussion. – The presence of polar COOMe and COOH groups in the structures of **1** and **2** accounted for a high solubility in polar solvents and even hydrophilicity, and, therefore, H₂O was selected as a suitable solvent to conduct the initial experiments in both coupling reactions. Multiple advantages can be gained by this way of proceeding, and several reports on the combination of pincer-type catalysts and aqueous solutions for *Suzuki* couplings have appeared in the literature [4]. However, very scarce examples of a combination of *Sonogashira* and *Mizoroki–Heck* reactions were described [5].

Encouraged by these findings, we attempted at performing alkenylation of 4-bromoacetophenone with styrene (*Heck*). Several base/solvent systems were tested, and the results were compared with those obtained with unsymmetrical PCN pincer **3**.

As shown in *Table 1*, only carbonate bases, and DMF and H₂O as solvents provided (*E*)-4-acetylstilbene at the preliminary assays (*Entries 1* and *6*, resp.). The optimization

Scheme. Synthesis of CNC Pincer Complexes **1** and **2**

i) Sealed tube, 150°, 24 h. *ii*) Pd(OAc)₂, DMSO, r.t., 3 h; 50° 12 h; 155°, 1 h. *iii*) 2M HCl, EtOH, 80°, 24 h.



protocol was performed according to the aforementioned parameters, and factors such as metal counterion, catalyst loading, temperature, reaction time or additives were varied. K₂CO₃ turned out to be crucial for the reaction outcome (*Entries 6–14*), as well as the applied temperature for both solvents (130°, *Entry 9* vs. *7* and *8*, and *Entry 13* vs. *6*). After tuning of the reaction time, it was possible to further reduce the amount of the pincer catalyst when using DMF (*Entry 12* vs. *11*) and addition of Bu₄N⁺ F[–] (TBAF) improved significantly the yield from the aqueous reaction system (*Entry 13* vs. *14*). Finally, it was clear from the results that CNC Pd complexes **1** and **2** behaved as more efficient catalysts for *Heck* arylation than PCN pincer **3**, and comparatively better yields were obtained with catalyst **1** compared to **2** in both solvents (*Entries 12* and *14*).

To define the scope of the method and for a better comparison of the catalytic properties exhibited by both pincer complexes, the optimized reaction conditions were applied to a number of alkenes and aryl bromides. With regard to the reactions conducted in aqueous media, and in spite of its higher hydrophilicity, a look at the results displayed in *Table 2* allows us to conclude that tricarboxy derivative **2** is less

Table 1. *Selected Mizoroki–Heck Arylations*

Entry	Reaction conditions (i)	Yields [%] ^{a)} of product in the presence of		
		1	2	3
1 ^{b)}	Na ₂ CO ₃ , DMF, 140°, 19 h	40	44	45
2 ^{b)}	K ₃ PO ₄ , DMF, 140°, 19 h	– ^{c)}	– ^{c)}	< 5
3 ^{b)}	Et ₃ N, DMF, 110°, 24 h	– ^{c)}	– ^{c)}	– ^{c)}
4 ^{b)}	CS ₂ CO ₃ , toluene, 110°, 24 h	– ^{c)}	– ^{c)}	– ^{c)}
5 ^{b)}	Et ₃ N, toluene, 110°, 24 h	– ^{c)}	– ^{c)}	– ^{c)}
6 ^{b)}	K ₂ CO ₃ , H ₂ O, 100°, 4 h	10	8	< 5
7 ^{b)}	K ₂ CO ₃ , DMF, 150°, 4 h	– ^{c)}	– ^{c)}	18
8 ^{b)}	K ₂ CO ₃ , DMF, 80°, 4 h	– ^{c)}	– ^{c)}	– ^{c)}
9 ^{d)}	K ₂ CO ₃ , DMF, 130°, 4 h	55	– ^{c)}	– ^{c)}
10 ^{d)}	K ₂ CO ₃ , DMF, 130°, 9 h	76	61	– ^{c)}
11 ^{d)}	K ₂ CO ₃ , DMF, 130°, 22 h	> 99	92	41
12 ^{c)}	K ₂ CO ₃ , DMF, 130°, 22 h	> 99	92	69
13 ^{d)}	K ₂ CO ₃ , H ₂ O, 130°, 22 h	44	40	13
14 ^{d)}	K ₂ CO ₃ , Bu ₄ NF(TBAF), H ₂ O, 130°, 22 h	67	40	< 5

^{a)} Determined by ¹H-NMR spectroscopy on the basis of the amount of starting aryl bromide. Diethylene glycol dimethyl ether was used as internal standard. ^{b)} One equiv. of aryl bromide, 1.5 equiv. of styrene, 2.0 equiv. of base and 2 mol-% of the Pd pincer were used. ^{c)} Only starting material was recovered. ^{d)} One equiv. of aryl bromide, 1.5 equiv. of styrene, 2.0 equiv. of base, and 1 mol-% of the Pd pincer were used. ^{e)} One equiv. of aryl bromide, 1.5 equiv. of styrene, 2.0 equiv. of base, and 0.5 mol-% of the Pd pincer were used.

Table 2. *Mizoroki–Heck Cross-Coupling in H₂O Catalyzed by CNC Pd Pincer Complexes 1 and 2*

Entry	R ¹	R ²	Yields [%] ^{a)} ^{b)} of product in the presence of	
			1	2
1	Ac	Ph	67	40
2	Me	COO ^t Bu	22	< 5 ^{c)}
3	NO ₂	MeO	70	< 5 ^{c)}
4	NO ₂	COO ^t Bu	48	< 5 ^{c)}

^{a)} Determined by ¹H-NMR spectroscopy on the basis of the amount of starting aryl bromide. Diethylene glycol dimethyl ether was used as internal standard. ^{b)} One equiv. of aryl bromide, 1.5 equiv. of alkene, 2.0 equiv. of K₂CO₃, and 1 mol-% of the Pd pincer were used. Reactions were performed in screw-capped tubes. ^{c)} Only traces of the coupling product were detected.

efficient than diester **1**. However, the catalytic behavior of the latter should be pointed out in view of the scarcity of examples reported [5c].

The similarity between the properties of both pincer catalysts was observed in the reactions performed in DMF. As shown in *Table 3*, moderate to good yields were obtained in all cases, although the presence of electron-withdrawing groups in the bromoarene provided better results (e.g., *Entries 1* and *6* vs. *Entry 5*), probably due to a faster oxidative addition step [6].

Table 3. Mizoroki–Heck Cross-Coupling in DMF Catalyzed by CNC Pd Pincer Complexes **1** and **2**

Entry	R ¹	R ²	Yields [%] ^{a)} of product in the presence of	
			1	2
1	Ac	Ph	> 99	92
2	Ac	COO ^t Bu	50	29
3	Me	Ph	60	40
4	Me	COO ^t Bu	85	79
5	MeO	Ph	41	7
6	CN	COO ^t Bu	98	56

^{a)} Determined by ¹H-NMR spectroscopy on the basis of the amount of starting aryl bromide. Diethylene glycol dimethyl ether was used as internal standard. ^{b)} One equiv. of aryl bromide, 1.5 equiv. of alkene, 2.0 equiv. of K₂CO₃, and 1 mol-% of the Pd pincer were used. Reactions were performed in screw-capped tubes.

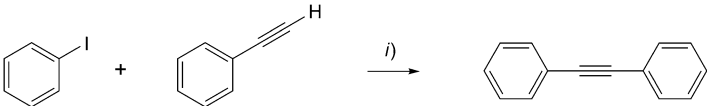
The coupling between alkynes and aryl iodides (*Sonogashira*) was the next process in which the catalytic efficiencies of complexes **1** and **2** were evaluated. Both the Cu-free and the Cu co-catalyzed versions were assayed, and again special attention was directed to reactions conducted in H₂O. Taking iodobenzene and phenylacetylene as model substrates, a number of assays compiled in *Table 4* were performed, and, to our pleasure, an procedure conducted in H₂O under mild conditions turned out to be most effective (*Entry 5*). On the other hand, all attempts to further reduce the catalyst loading below 1 mol-% failed.

The optimized aqueous conditions were applied to several electronically and sterically differing iodoarenes. The results are collected in *Table 5*.

The results revealed that, as in the previous *Mizoroki–Heck* reaction, diarylethynes were produced in almost all cases with better yields by using Pd pincer **1**, and a similar trend that relates significant decreases in conversion rates to iodoarenes bearing electron-donating (MeO or NH₂) groups was also observed.

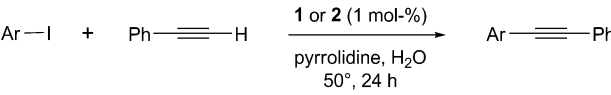
3. Conclusions. – In summary, two CNC Pd pincer complexes based on NHC moieties were applied as catalysts for *Mizoroki–Heck* and *Sonogashira* coupling reactions. In addition to a more efficient *Heck* protocol in DMF, in both cases, procedures in H₂O were carried out, thus adding more examples to a scarcely explored area of research. Despite a higher hydrophilicity due to the presence of several COOH groups in its structure, catalyst **2** behaved less efficiently than its diester counterpart **1**. A comparison with the catalytic ability of a Pd PCN pincer in *Heck* arylation was also

Table 4. Selected Sonogashira Cross-Coupling Assays



Entry	Reaction conditions (i)	Yields [%] ^{a)} of product in the presence of	
		1	2
1 ^{b)}	Pyrrolidine, 100°, 6 h	60	69
2 ^{c)}	Et ₃ N (3.0 equiv.), CuI (5 mol-%), MeCN, r.t., 24 h	9	15
3 ^{c)}	K ₂ CO ₃ (2.0 equiv.), CuI (2 mol-%), H ₂ O, r.t., 4 h	21	9
4 ^{d)}	K ₃ PO ₄ (1.4 equiv.), CuI (5 mol-%), DMF, 80°, 5 h	32	21
5 ^{c)}	Pyrrolidine (1.0 equiv.), H ₂ O, 50°, 24 h	97	82
6 ^{c)}	Pyrrolidine (1.0 equiv.), H ₂ O, 50°, 24 h	50	19

^{a)} Determined by ¹H-NMR spectroscopy on the basis of the amount of starting aryl iodide. Diethylene glycol dimethyl ether was used as internal standard. ^{b)} One equiv. of PhI, 1.5 equiv. of phenylacetylene, and 1 mol-% of the Pd pincer were used. ^{c)} One equiv. of PhI, 1.4 equiv. of phenylacetylene, and 1 mol-% of the Pd pincer were used. ^{d)} One equiv. of phenyl iodide, 1.2 equiv. of phenylacetylene, and 1 mol-% of the Pd pincer were used. ^{e)} One equiv. of phenyl iodide, 1.4 equiv. of phenylacetylene, and 0.5 mol-% of the Pd pincer were used.

Table 5. Sonogashira Coupling in H₂O Catalyzed by CNC Pd Pincer Complexes **1** and **2**


Entry	Coupling product	Yields [%] ^{a)} ^{b)} of product in the presence of	
		1	2
1	PhC≡CPh	97	82
2	4-NO ₂ -C ₆ H ₄ C≡CPh	> 99	95
3	(Naphthalen-1-yl)-C≡CPh	47	45
4	4-MeO-C ₆ H ₄ C≡CPh	31	31
5	2-Me-C ₆ H ₄ C≡CPh	98	30
6	4-NH ₂ -C ₆ H ₄ C≡CPh	18	23
7	3-Me-C ₆ H ₄ C≡CPh	79	55
8	4-Cl-C ₆ H ₄ C≡CPh	93	< 5 ^{c)}

^{a)} Determined by ¹H-NMR spectroscopy on the basis of the amount of starting aryl iodide. Diethylene glycol dimethyl ether was used as internal standard. ^{b)} One equiv. of aryl iodide, 1.4 equiv. of phenylacetylene, and 1 mol-% of the Pd pincer were used. ^{c)} Only traces of the coupling product were detected.

provided, and the scope of the presented *Heck* and *Sonogashira* protocols was defined by a series of arylated alkenes and diarylacetylenes, respectively.

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Experimental Part

General. All reagents were purchased and used as received. Drying of org. extracts during workup of reaction mixtures was performed with anh. Na_2SO_4 . Evaporation of solvents was achieved with a rotary evaporator. TLC: silica gel (SiO_2); and visualization with UV light. Flash chromatography (FC): SiO_2 . M.p.: *Gallenkamp* in cap. tubes; uncorrected. ^1H - and ^{13}C -NMR spectra: *Bruker AC-300* at 300 and 63 MHz, resp; chemical shifts (δ) in ppm downfield from Me_4Si , and referring to the residual solvent CDCl_3 as internal standard ($\delta(\text{H})$ 7.26 for ^1H and $\delta(\text{C})$ 77.0 for ^{13}C); coupling constants (J) in Hz.

Sonogashira Coupling Catalyzed by Pincers 1 or 2. General Procedure. Pincer complex **1** or **2** (1 mol-% Pd) was added to a mixture of aryl iodide (1 mmol), phenylacetylene (1.4 mmol), pyrrolidine (1 mmol), and H_2O (1.5 ml) in a round-bottom flask open to the atmosphere. After stirring for 24 h at 50° , the mixture was cooled, and H_2O (5 ml) was added. The aq. layer was extracted with AcOEt (4×6 ml). The combined org. extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was dissolved in CDCl_3 and analyzed by ^1H -NMR using diethylene glycol dimethyl ether as an internal standard, thus confirming the identity of every product in comparison with spectroscopic data in the literature.

1,2-Diphenylethyne (= *1,1'-(Ethyne-1,2-diyl)bisbenzene*) [7]. ^1H -NMR: 7.27–7.24 (*m*, 6 H); 7.48–7.43 (*m*, 4 H). ^{13}C -NMR: 89.4; 123.3; 128.2; 128.3; 131.6.

1-(Phenylethynyl)naphthalene [8]. ^1H -NMR: 7.29–7.45 (*m*, 4 H); 7.45–7.60 (*m*, 2 H); 7.60–7.69 (*m*, 2 H); 7.70–7.85 (*m*, 3 H); 8.45 (*d*, $J = 8.4$, 1 H). ^{13}C -NMR: 87.5; 94.3; 120.9; 123.4; 125.2; 126.2; 126.4; 126.7; 128.2; 128.3; 128.4; 128.7; 130.3; 131.6; 133.1; 133.2.

1-Methoxy-4-(phenylethynyl)benzene [8]. ^1H -NMR: 3.82 (*s*, 3 H); 6.88 (*dt*, $J = 6.8$, 2.1, 2 H); 7.29–7.39 (*m*, 3 H); 7.42–7.58 (*m*, 4 H). ^{13}C -NMR: 55.3; 88.0; 89.3; 114.0; 115.3; 123.6; 127.9; 128.3; 131.4; 133.0; 159.6.

1-Methyl-2-(phenylethynyl)benzene [8]. ^1H -NMR: 2.50 (*s*, 3 H); 7.08–7.21 (*m*, 3 H); 7.25–7.35 (*m*, 3 H); 7.44–7.55 (*m*, 3 H). ^{13}C -NMR: 20.7; 88.3; 93.3; 123.0; 123.5; 125.5; 128.1; 128.2; 128.3; 129.4; 131.4; 131.8; 140.1.

1-Methyl-3-(phenylethynyl)benzene [9]. ^1H -NMR: 2.23 (*s*, 3 H); 7.03 (*d*, $J = 8.0$, 1 H); 7.11 (*t*, $J = 8.0$, 1 H); 7.26–7.20 (*m*, 5 H); 7.44–7.40 (*m*, 2 H). ^{13}C -NMR: 21.2; 89.0; 89.6; 123.0; 123.4; 128.2; 128.3; 128.4; 128.6; 128.7; 129.1; 131.6; 137.8.

4-(Phenylethynyl)benzenamine [10]. ^1H -NMR: 3.81 (*s*, 2 H); 6.63 (*d*, $J = 8.2$, 2 H); 7.30–7.43 (*m*, 5 H); 7.50–7.60 (*m*, 2 H). ^{13}C -NMR: 87.4; 90.2; 112.5; 114.8; 123.9; 127.7; 128.3; 131.3; 132.9; 146.7.

1-Nitro-4-(phenylethynyl)benzene [7]. ^1H -NMR: 7.40–7.37 (*m*, 3 H); 7.57–7.55 (*m*, 2 H); 7.67 (*d*, $J = 8.6$, 2 H); 8.22 (*d*, $J = 8.6$, 2 H). ^{13}C -NMR: 87.6; 94.6; 122.0; 123.6; 128.5; 129.2; 130.2; 131.8; 132.2; 146.9.

1-Chloro-4-(phenylethynyl)benzene [7]. ^1H -NMR: 7.23–7.29 (*m*, 5 H); 7.37–7.48 (*m*, 4 H). ^{13}C -NMR: 88.2; 90.3; 121.8; 122.9; 128.3; 128.4; 128.6; 131.6; 132.7; 134.2.

Mizoroki–Heck Arylation Catalyzed by Pincers 1 or 2. General Procedure. A 10-ml screw-capped tube was charged with the aryl bromide (1 mmol), alkene (1.5 mmol), K_2CO_3 (2 mmol), catalyst **1** or **2** (0.5 mmol Pd), and dry DMF (2 ml). The mixture was stirred at 130° under Ar for 22 h. After cooling, H_2O (5 ml) was added, and the aq. layer was extracted with AcOEt (4×6 ml). The combined org. extracts were dried (Na_2SO_4) and evaporated *in vacuo*. The residue was dissolved in CDCl_3 and analyzed by ^1H -NMR (with bis(ethylene glycol) dimethyl ether as an internal standard), thus confirming the identity of every product in comparison with the spectroscopic data in the literature.

1-(4-Styrylphenyl)ethanone (= *1-[4-(E)-2-Phenylethenyl]phenyl]ethanone*) [11]. ^1H -NMR: 2.61 (*s*, 3 H); 7.17 (*d*, $J = 16.0$, 1 H); 7.22 (*d*, $J = 16.0$, 1 H); 7.25–7.40 (*m*, 3 H); 7.55 (*d*, $J = 8.2$, 2 H); 7.59 (*d*, $J = 8.2$, 2 H); 7.95 (*d*, $J = 8.2$, 2 H). ^{13}C -NMR: 26.6; 126.5; 126.8; 127.5; 128.3; 128.8; 128.9; 131.5; 136.0; 136.7; 142.0; 197.5.

tert-Butyl (E)-3-(4-Acetylphenyl)acrylate (= *tert-Butyl (2E)-3-(4-Acetylphenyl)prop-2-enoate*) [12]. ^1H -NMR: 1.53 (*s*, 9 H); 2.60 (*s*, 3 H); 6.45 (*d*, $J = 16.0$, 1 H); 7.57 (*d*, $J = 8.5$, 2 H); 7.59 (*d*,

$J = 16.0, 1 \text{ H}$); 7.95 ($d, J = 8.5, 2 \text{ H}$). $^{13}\text{C-NMR}$: 26.6; 28.1; 80.9; 122.7; 127.9; 128.7; 137.7; 139.0; 141.9; 165.7; 197.3.

1-(4-Methylstyryl)benzene (= *1-Methyl-4-[(E)-2-phenylethenyl]benzene*) [11]. $^1\text{H-NMR}$: 2.36 ($s, 3 \text{ H}$); 7.07 ($s, 2 \text{ H}$); 7.17 ($d, J = 8.0, 2 \text{ H}$); 7.24–7.26 ($m, 1 \text{ H}$); 7.35 ($d, J = 7.5, 2 \text{ H}$); 7.41 ($d, J = 8.1, 2 \text{ H}$); 7.51 ($d, J = 7.9, 2 \text{ H}$). $^{13}\text{C-NMR}$: 21.2; 126.3; 126.4; 127.4; 127.7; 128.6; 128.6; 129.3; 134.5; 137.4; 137.5.

tert-Butyl (E)-3-(4-Methylphenyl)acrylate (= *tert-Butyl (2E)-3-(4-Methylphenyl)prop-2-enoate*) [13]. $^1\text{H-NMR}$: 1.54 ($s, 9 \text{ H}$); 2.35 ($s, 3 \text{ H}$); 6.33 ($d, J = 16.0, 1 \text{ H}$); 7.16 ($d, J = 8.0, 2 \text{ H}$); 7.39 ($d, J = 8.0, 2 \text{ H}$); 7.58 ($d, J = 16.0, 1 \text{ H}$). $^{13}\text{C-NMR}$: 21.3; 28.1; 80.1; 118.9; 129.4; 131.8; 137.8; 140.1; 143.4; 166.4.

1-(4-Methoxystyryl)benzene (= *1-Methoxy-4-[(E)-2-phenylethenyl]benzene*) [11]. $^1\text{H-NMR}$: 3.83 ($s, 3 \text{ H}$); 6.89 ($d, J = 8.8, 2 \text{ H}$); 6.98 ($d, J = 16.5, 1 \text{ H}$); 7.08 ($d, J = 16.4, 1 \text{ H}$); 7.25 ($t, J = 7.0, 1 \text{ H}$); 7.34 ($t, J = 7.5, 2 \text{ H}$); 7.44–7.50 ($m, 4 \text{ H}$). $^{13}\text{C-NMR}$: 55.3; 114.1; 126.3; 126.6; 127.2; 127.7; 128.2; 128.6; 130.2; 137.7; 159.3.

tert-Butyl (E)-3-(4-Cyanophenyl)acrylate (= *tert-Butyl (2E)-3-(4-Cyanophenyl)prop-2-enoate*) [13]. $^1\text{H-NMR}$: 1.53 ($s, 9 \text{ H}$); 6.44 ($d, J = 16.0, 1 \text{ H}$); 7.56 ($d, J = 15.8, 1 \text{ H}$); 7.58 ($d, J = 8.2, 2 \text{ H}$); 7.65 ($d, J = 8.2, 2 \text{ H}$). $^{13}\text{C-NMR}$: 28.1; 81.2; 113.0; 128.8; 131.6; 132.5; 139.0; 141.0; 165.3.

Mizoroki–Heck Arylation in Aqueous Media Catalyzed by Pincers **1 or **2**. General Procedure.** A dry 10-ml screw-capped tube was charged with the aryl bromide (1 mmol), alkene (1.5 mmol), K_2CO_3 (2 mmol), catalyst **1** or **2** (1 mmol Pd), TBAF (1 mmol), and dist. H_2O (2 ml). The mixture was stirred at 130° for 22 h. After cooling, H_2O (5 ml) was added, and the aq. layer was extracted with AcOEt ($4 \times 6 \text{ ml}$). The combined org. extracts were dried (Na_2SO_4) and evaporated *in vacuo*. The residue was dissolved in CDCl_3 and analyzed by $^1\text{H-NMR}$ (with bis(ethylene glycol) dimethyl ether as an internal standard), thus confirming the identity of every product in comparison with the spectroscopic data in the literature.

1-(4-Styrylphenyl)ethanone (= *1-[4-[(E)-2-Phenylethenyl]phenyl]ethanone*) [11].

tert-Butyl (E)-3-(4-Methylphenyl)acrylate (= *tert-Butyl (2E)-3-(4-Methylphenyl)prop-2-enoate*) [13].

1-(4-Nitrostyryl)benzene (= *1-Nitro-4-[(E)-2-phenylethenyl]benzene*) [12]. $^1\text{H-NMR}$: 7.14 ($d, J = 16.0, 1 \text{ H}$); 7.27 ($d, J = 16.0, 1 \text{ H}$); 7.33–7.42 ($m, 3 \text{ H}$); 7.55 ($d, J = 7.8, 2 \text{ H}$); 7.63 ($d, J = 8.8, 2 \text{ H}$); 8.22 ($d, J = 8.8, 2 \text{ H}$). $^{13}\text{C-NMR}$: 124.2; 126.4; 127.0; 127.1; 129.0; 129.0; 129.0; 133.4; 136.3; 144.0; 146.9.

tert-Butyl (E)-3-(4-Nitrophenyl)acrylate (= *tert-Butyl (2E)-3-(4-Nitrophenyl)prop-2-enoate*) [12]. $^1\text{H-NMR}$: 1.55 ($s, 9 \text{ H}$); 6.50 ($d, J = 15.9, 1 \text{ H}$); 7.61 ($d, J = 15.9, 1 \text{ H}$); 7.65 ($d, J = 7.8, 2 \text{ H}$); 8.24 ($d, J = 8.7, 2 \text{ H}$). $^{13}\text{C-NMR}$: 28.9; 82.0; 124.8; 125.3; 129.2; 141.2; 141.6; 149.0; 165.9.

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