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Heck Reactions of α- or β-Substituted Enol Ethers with Aryl Bromides Catalysed by a Tetraphosphane/Palladium Complex – Direct Access to Acetophenone or 1-Arylpropanone Derivatives

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cis,*cis*,*cis*-1,2,3,4-Tetrakis(diphenylphosphanylmethyl)cyclopentane/$[PdCl(C_3H_5)]_2$ efficiently catalyses the Heck reaction of α- and β-substituted enol ethers with aryl bromides. The arylation of 1-phenyl-1-(trimethylsilyloxy)ethylene led directly to the 2-aryl-1-phenylethanones. Similar reaction rates were observed with electron-rich, electron-deficient or sterically congested aryl bromides. Heck reaction with benzyl isopropenyl ether gave a mixture of isomers. However, this mixture gave selectively the 1-arylpropanones after hydrolysis. Employing β-methoxystyrene, 3-ethoxyacrylonitrile or methyl 3-methoxyacrylate, the regioselective α-arylation of these enol ethers was observed in all cases, but mixtures of (*Z*) and (*E*) isomers were generally obtained, which in many cases yielded a single ketone product after acid treatment. The stereoselectivity of this reaction depends on steric and electronic factors, and better stereoselectivities in favour of (*Z*) isomers were observed with electron-rich or sterically congested aryl bromides. Higher yields were obtained for this reaction with electron-rich or sterically congested aryl bromides than with electron-poor aryl bromides. These observations suggest that the rate-limiting step of the catalytic cycle is not the oxidative addition of the aryl bromide to the palladium complex with these substituted enol ethers.

Introduction

The Heck vinylation reaction is one of the most powerful methods for the formation of C–C bonds.[1] The efficiency of several catalysts for the reaction of aryl halides with acrylates or styrene derivatives has been studied in detail. On the other hand, the reaction involving disubstituted alkenes has attracted less attention. These alkenes are generally less reactive than terminal alkenes, mainly for steric reasons. Most of the results described with disubstituted alkenes were obtained with the activated electron-poor methacrylates, α-methylstyrene, cinnamates, crotonates or benzalacetone.[2–4] Only a few results have been obtained with α- or β-substituted enol ethers.[5–16] For electronic reasons, enol ethers are less reactive than electron-poor alkenes. Therefore, the arylation of α- or β-substituted enol ethers is generally very slow, requires the use of reactive but expensive aryl iodides, quite high catalyst loadings and often the presence of additives in the reaction mixture. Most of theses arylations were performed with simple palladium salts or palladium associated with PPh_3. For example, in 1982 Kuwajima et al. reported the arylation of α-substituted silyl enol ethers. With $PdCl_2[P(o\text{-}Tol)_3]_2$ as the catalyst in the presence of a stoichiometric amount of Bu_3SnF, the 1-arylpropanone derivatives were obtained in moderate to good yields.[5a] They postulated a silyl-stannyl exchange followed by palladium-catalysed arylation. Recently, isopropenyl acetate was also used as a vinylation agent. The vinylation was performed with Bu_3SnOMe as an additive and 2-dimethylamino-2′-diphenylphosphanyl-1,1′-biphenyl associated with $Pd_2(dba)_3$ as the catalyst.[6] Cacchi and coworkers described the arylation of an α-methoxyacrylate with aryl iodides as substrates, palladium acetate (3 mol-%) as the catalyst and tetrabutylammonium chloride as an additive.[7a] A similar reaction with Pd/C as the catalyst has also been described.[7b] A 1-acetylvinyl benzoate derivative was arylated with a variety of aryl iodides in low to moderate yields with $Pd(OAc)_2$ as the catalyst.[8] With alkoxystyrenes, arylation or diarylation products were obtained in low to good yields with $Pd(OAc)_2/PPh_3$ as the catalyst.[9] 1-Butoxyprop-1-ene reacts with iodobenzene or 4-bromonitrobenzene employing $Pd(PPh_3)_4$ (1 mol-%), but mixtures of isomers and

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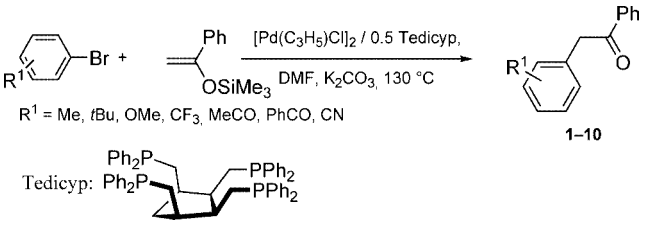
low yields were obtained.[12] The reaction of ethyl (*E*)-3-ethoxyacrylate and iodobenzene, 4-iodoanisole or 3-iodopyridine can be performed with Pd/C (5%) as the catalyst.[13] Finally, the reaction involving 3,3,3-trifluoro-1-methoxypropene and iodobenzene, 1-iodo-4-nitrobenzene, 3-iodopyridine or 1-bromo-4-iodobenzene with $Pd(OAc)_2$ (3 mol-%)/PPh_3 (6 mol-%) as the catalyst and Ag_2CO_3 as the base (1 equiv.) gave the corresponding 1-aryl-3,3,3-trifluoro-1-methoxyprop-1-enes in good yields.[14]

To the best of our knowledge, the Heck reaction involving the commercially available β-methoxystyrene or 3-ethoxyacrylonitrile has not been described, and relatively few results have been reported with silyl or benzyl enol ethers.[9] Therefore, there still remains a need for a general and simple protocol for Heck reactions in the presence of α- or β-substituted enol ethers, especially with aryl bromides. Moreover, this protocol should not employ toxic or expensive additives such as Bu_3SnF, Bu_3SnOMe or Ag_2CO_3. In addition, for the effective use of β-substituted enol ethers in synthesis, the regioselectivity of the arylation is important.

In order to obtain stable and efficient palladium catalysts, we have prepared the tetraphosphane ligand, *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphanylmethyl)cyclopentane or Tedicyp[17] (Scheme 1). The presence of four phosphanes close to the metal centre seems to increase the stability of the catalyst. The palladium is shown by NMR to circulate around the 4 phosphorus atoms under the "pressure to coordinate" of the 4 phosphanyl groups maintained in a half-space. This pressure to coordinate in a half-space might be responsible for the easy reductive elimination step for several cross-coupling reactions. We have already reported the results obtained for allylic substitution,[18] Suzuki or Negishi cross-coupling,[19,20] Sonogashira alkynylation[21] and the direct arylation of furans[22] with Tedicyp as the ligand. We have also reported several results for the Heck vinylation.[18,23–26] We had observed that with our catalyst, good results could be obtained for the reaction of *n*-butyl vinyl ether or ethylene glycol vinyl ether with aryl bromides.[24] Satisfactory results in terms of substrate/catalyst ratio have also been obtained for the reaction with disubstituted alkenes such as methyl crotonate, ethyl cinnamate or benzalacetone.[25] We have also recently reported preliminary results with β-substituted enol ethers.[26] In the present report, in order to further establish the requirements for a successful Heck reaction with our catalytic system, we describe the reaction of a variety of aryl bromides with the α- or β-substituted enol ethers, 1-phenyl-1-(trimethylsilyloxy)ethylene, benzyl isopropenyl ether, β-methoxystyrene, 3-ethoxyacrylonitrile or methyl 3-methoxyacrylate.



Scheme 1. Heck reactions with 1-phenyl-1-(trimethylsilyloxy)ethylene.

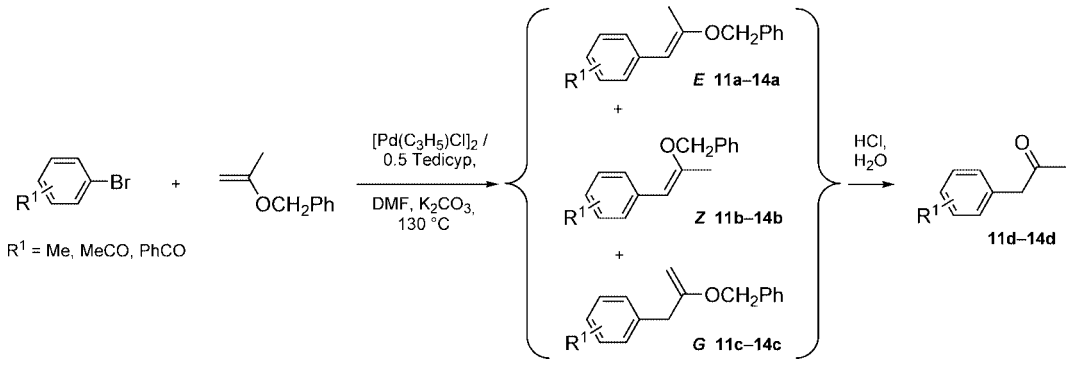
Results and Discussion

The regioselectivity of insertion in the Heck reaction is controlled both by the electronic properties of the alkenes and by steric factors. Electron-poor alk-1-enes such as acrylates, acrylonitrile or styrene generally lead very selectively to the β-arylated alkenes. On the other hand, electron-rich alk-1-enes such as *n*-butyl vinyl ether often give mixtures of α- and β-arylated alkenes.[1] Electronic effects do indeed play a major role in the arylation of enol ethers. With our Tedicyp/palladium catalyst, we had observed with *n*-butyl vinyl ether that, in all cases, mixtures of linear and branched products were obtained.[24a] For these reasons, the regioselectivity of reaction with the unsymmetrical 1,2-disubstituted alkenes β-methoxystyrene, 3-ethoxyacrylonitrile and methyl 3-methoxyacrylate can be predicted and should lead to regioselective α-insertions on these enol ethers. With the 1,1′-disubstituted alkenes 1-phenyl-1-(trimethylsilyloxy)-

Table 1. Heck reactions with 1-phenyl-1-(trimethylsilyloxy)ethylene, catalysed by the Tedicyp-palladium complex (Scheme 1).[a]

Entry	Aryl halide	Substrate/catalyst	Product	% Yield[b]
1	4-bromobenzophenone	100	**1**	100 (83)
2	4-bromobenzophenone	1000	**1**	11
3	4-bromoacetophenone	100	**2**	90 (78)
4	1-bromo-4-(trifluoromethyl)benzene	50	**3**	100 (82)
5	1-bromo-4-(trifluoromethyl)benzene	100	**3**	64
6	4-bromobenzonitrile	50	**4**	99 (80)
7	4-bromobenzonitrile	100	**4**	36
8	1-bromo-4-*tert*-butylbenzene	50	**5**	90 (78)
9	1-bromo-2-(trifluoromethyl)benzene	50	**6**	96 (83)
10	1-bromonaphthalene	50	**7**	100 (88)
11	1-bromonaphthalene	100	**7**	56
12	2-bromotoluene	25	**8**	77 (65)
13	2-bromoanisole	50	**9**	92 (81)
14	1-bromo-2,4,6-trimethylbenzene	50	**10**	88 (80)

[a] Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp (1:2), see ref.[17], ArBr (1 equiv.), 1-phenyl-1-(trimethylsilyloxy)ethylene (2 equiv.), K_2CO_3 (2 equiv.), DMF, 20 h, 130 °C and under argon. [b] Yields were determined by GC, and yields in parentheses refer to isolated yields.



Scheme 2. Heck reactions with benzyl isopropenyl ether.

Table 2. Heck reactions with benzyl isopropenyl ether, catalysed by the Tedicyp-palladium complex (Scheme 2).[a]

Entry	Aryl halide	Substrate/catalyst	Ratio of isomers (**a/b/c**) (Scheme 2)[c]	Isolated product	% Yield[b]
1	4-bromobenzophenone	50	49:39:12	**11d**	70 (66)
2	4-bromobenzophenone	100	50:31:19	**11d**	25
3	4-bromoacetophenone	50	49:42:9	**12d**	100 (84)
4	bromobenzene	50	54:36:10	**13d**	32 (27)
5	4-bromotoluene	50	30:23:47	**14d**	58 (52)

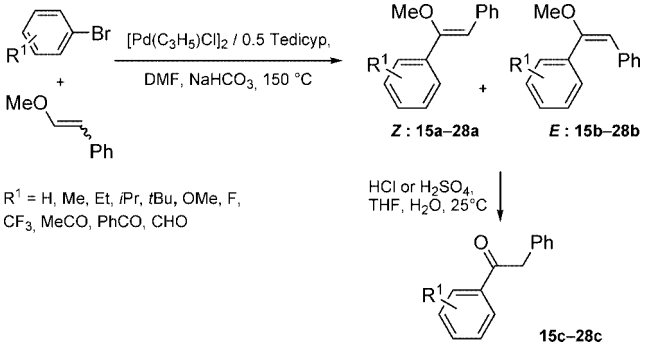
[a] Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp (1:2), see ref.[17], ArBr (1 equiv.), benzyl isopropenyl ether (2 equiv.), K_2CO_3 (2 equiv.), DMF, 20 h, 130 °C and under argon. [b] Yields were determined by GC, and yields in parenthesis are isolated yields. [c] The **a/b/c** ratio was calculated from ^1H NMR of the crude mixtures.

ethylene and benzyl isopropenyl ether, the arylation will be regioselective in favour of carbon 2, but mixtures of (*Z*) and (*E*) isomers should be observed.

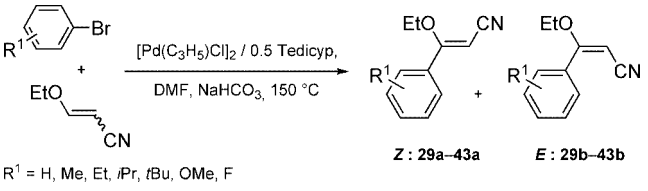
First we examined the reactivity of the two α-substituted enol ethers, 1-phenyl-1-(trimethylsilyloxy)ethylene (Scheme 1, Table 1) and benzyl isopropenyl ether with various aryl bromides (Scheme 2, Table 2). For this study, based on previous results,[25,26] DMF was chosen as the solvent. The reactions were performed under argon employing a 1:2 ratio of $[Pd(C_3H_5)Cl]_2$/Tedicyp as the catalyst. As to the arylation of 1-phenyl-1-(trimethylsilyloxy)ethylene, a wide array of electronically and sterically diverse aryl bromides were successfully directly converted into the corresponding 2-arylacetophenone derivatives under these reaction conditions. The 2-aryl-1-phenyl-1-(trimethylsilyloxy)ethylenes were not observed due to their low stability. As apparent from Table 1, for this arylation, quite similar results were obtained with electron-poor, electron-rich or sterically congested aryl bromides. For example, 1-bromo-4-(trifluoromethyl)benzene, 1-bromo-4-(*tert*-butyl)benzene and 1-bromo-2,4,6-trimethylbenzene gave products **3**, **5** and **10** in 82, 78 and 80% yield, respectively, with 2 mol-% of catalyst (Table 1, Entries 4, 8 and 14). This observation indicates that, with this hindered alkene, the oxidative addition of the aryl bromide to palladium is not rate limiting.

In general, the arylation of benzyl isopropenyl ether gave lower yields than did the reactions performed with 1-phenyl-1-(trimethylsilyloxy)ethylene (Scheme 2, Table 2). With this alkene, mixtures of (*Z*) and (*E*) isomers were obtained, and the formation of a third isomer due to the migration of the double bond was also observed. However, the hydrolysis of these mixtures led selectively to the corresponding 1-arylpropanones. With 2 mol-% of catalyst, products **11d**–**14d** were obtained in 27–84% yield. Better results were obtained with the electron-poor aryl bromides 4-bromoacetophenone or 4-bromobenzophenone than with bromobenzene.

We then studied the reactivity of three β-substituted enol ethers (see Schemes 3, 4, 5, Tables 3, 4, and 5). First we examined the reactivity of β-methoxystyrene (*Z*/*E* = 2:98) with 1-bromo-4-(*tert*-butyl)benzene with a few bases at 100–150 °C in DMF. Low conversions were observed in the presence of 1 mol-% of catalyst with K_2CO_3, Na_2CO_3 or NaOAc as bases or at 100–130 °C. The best yield was ob-

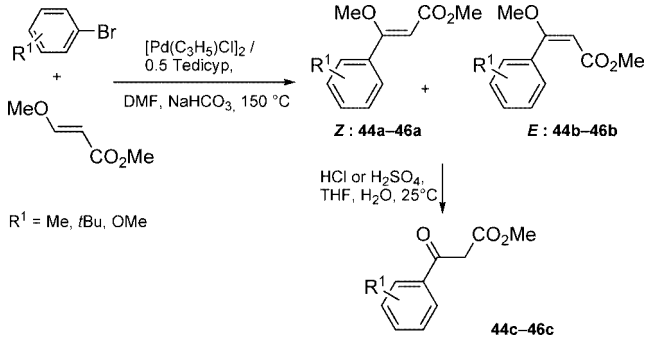


Scheme 3. Heck reactions with β-methoxystyrene.



Scheme 4. Heck reactions with (*E*)-3-ethoxyacrylonitrile.

tained with $NaHCO_3$ at 150 °C. Next, we examined the reaction of β-methoxystyrene with several aryl bromides employing 1 mol-% of catalyst (Scheme 3, Table 3, Entries 1–14). As expected with this alkene, we observed a regioselective addition to the aryl bromides to give the corresponding β-aryl-β-methoxystyrene derivatives. However, this reaction was not stereospecific, as the starting material β-methoxystyrene contained only 2% of the (*Z*) isomer, and the products were mixtures of (*Z*) and (*E*) isomers. The Tedicyp-Pd catalyst system is tolerant of a variety of aryl bromides for the reaction with β-methoxystyrene. Electron-poor aryl bromides such as 4-bromoacetophenone and 4-bromobenzaldehyde led to the coupling products **15a/15b** and **16a/16b**, respectively, in lower conversions and yields than the reactions performed with electron-rich 1-bromo-4-(*tert*-butyl)benzene, 4-bromotoluene or 4-bromoanisole (Table 3, Entries 1–7). This observation indicates that the rate-limiting step of the reaction with this enol ether is not the oxidative addition of the aryl bromide to the palladium complex but probably the insertion of the enol ether in the Ar–Pd bond. We also studied the influence of *ortho*-substit-



Scheme 5. Heck reactions with methyl (*E*)-3-methoxyacrylate.

Table 3. Heck reactions with β-methoxystyrene, catalysed by the Tedicyp-palladium complex (Scheme 3).[a]

Entry	Aryl halide	Substrate/catalyst	*Z*/*E* (**a**/**b**)[c]	Isolated product	% Yield[b]
1	4-bromoacetophenone	100	65:35	**15c**	58
2	4-bromobenzaldehyde	100	69:31	**16c**	60
3	1-bromo-4-(trifluoromethyl)benzene	250	73:27	**17c**	72
4	1-bromo-4-fluorobenzene	100	67:33	**18c**	78
5	4-bromotoluene	100	62:38	**19c**	80
6	1-bromo-4-(*tert*-butyl)benzene	100	63:37	**20c**	79
7	4-bromoanisole	100	54:46	**21c**	77[d]
8	2-bromo-6-methoxynaphthalene	100	51:49	**22c**	82
9	iodobenzene	100	33:67	**23c**	79
10	bromobenzene	100	66:34	**23c**	74
11	1-bromonaphthalene	100	57:43	**24c**	84
12	1-bromo-2-methylbenzene	100	62:38	**25c**	79
13	1-bromo-2,4,6-trimethylbenzene	100	100:0	**26c**	74[d]
14	1-bromo-2,6-diethyl-4-methylbenzene	100	100:0	**27c**	76
15	3-bromoquinoline	100	71:29	**28c**	73

[a] Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp (1:2), see ref.[17], ArX (1 equiv.), β-methoxystyrene (*Z*/*E* = 2:98, 2 equiv.), $NaHCO_3$ (2 equiv.), DMF, 20 h, 150 °C and under argon. [b] Isolated yields. [c] The *Z*/*E* was calculated with ^1H NMR of the crude mixtures. [d] The reaction was performed under similar conditions with $[Pd(C_3H_5)Cl]_2/PPh_3$ (1:4) as the catalyst and gave **21c** and **26c** in 16–25% yield.

Table 4. Heck reactions with 3-ethoxyacrylonitrile, catalysed by the Tedicyp-palladium complex (Scheme 4).[a]

Entry	Aryl halide	*Z*/*E* (**a**/**b**)[c]	Isolated product	% Yield[b]
1	1-bromo-4-fluorobenzene	12:88	**29a**, **29b**	79
2	4-bromotoluene	35:65	**30a**, **30b**	76
3	1-bromo-4-(*tert*-butyl)benzene	30:70	**31a**, **31b**	82
4	2-bromo-6-methoxynaphthalene	27:73	**32a**, **32b**	84
5	iodobenzene	40:60	**33a**, **33b**	80
6	bromobenzene	23:77	**33a**, **33b**	88
7	4-bromoanisole	24:76	**34a**, **34b**	85
8	3-bromotoluene	11:89	**35a**, **35b**	81
9	1-bromo-2-fluorobenzene	26:74	**36a**, **36b**	78
10	1-bromonaphthalene	75:25	**37a**, **37b**	81
11	2-bromotoluene	77:23	**38a**, **38b**	77
12	1-bromo-2,4,6-trimethylbenzene	66:34	**39a**, **39b**	73[d]
13	1-bromo-2,6-diethyl-4-methylbenzene	65:35	**40a**, **40b**	74
14	1-bromo-2,4,6-triisopropylbenzene	93:7	**41a**, **41b**	76
15	3-bromopyridine	9:91	**42a**, **42b**	78
16	3-bromoquinoline	10:90	**43a**, **43b**	80

[a] Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp (1:2), see ref.[17] (0.01 equiv.), ArX (1 equiv.), 3-ethoxyacrylonitrile (*Z*/*E* = 35:65, 2 equiv.), $NaHCO_3$ (2 equiv.), DMF, 20 h, 150 °C and under argon. [b] Isolated yields. [c] The *Z*/*E* was calculated from ^1H NMR of the crude mixtures. [d] The reaction was performed under similar conditions with $[Pd(C_3H_5)Cl]_2/PPh_3$ (1:4) as the catalyst and gave **39a**/**39b** in 38% yield.

Table 5. Heck reactions with methyl (*E*)-3-methoxyacrylate, catalysed by the Tedicyp-palladium complex (Scheme 5).[a]

Entry	Aryl halide	*Z*/*E* (**a**/**b**)[c]	Isolated product	% Yield[b]
1	1-bromo-4-(*tert*-butyl)benzene	49:51[d]	**44c**	62
2	4-bromoanisole	Nd[d,e]	**45c**	60[f]
3	2-bromotoluene	Nd[d,e]	**46c**	56

[a] Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp (1:2), see ref.[17] (0.01 equiv.), ArBr (1 equiv.), methyl (*E*)-3-methoxyacrylate (2 equiv.), $NaHCO_3$ (2 equiv.), DMF, 20 h, 150 °C and under argon. [b] Isolated yields. [c] The *Z*/*E* was calculated from ^{1}H NMR of the crude mixtures. [d] Partial deprotection into the corresponding ketones **c** was observed before treatment with HCl or H_2SO_4. [e] Not determined. [f] The reaction was performed under similar conditions with $[Pd(C_3H_5)Cl]_2/PPh_3$ (1:4) as the catalyst and gave **46c** in 18% yield.

uents on the aryl bromide for this reaction, and we observed that 1-bromonaphthalene, 1-bromo-2-methylbenzene or even 1-bromo-2,4,6-trimethylbenzene and 1-bromo-2,6-diethyl-4-methylbenzene gave similar yields than did 1-bromo-4-methylbenzene (Table 3, Entries 11–14). However, for steric reasons, with 1-bromo-2,4,6-trimethylbenzene and 1-bromo-2,6-diethyl-4-methylbenzene, the (*Z*) isomers **26a** and **27a**, respectively, were selectively obtained. The heteroaromatic substrate 3-bromoquinoline also led to the expected products **28a**/**28b** in good yield (Table 3, Entry 15). The mixtures of stereoisomers obtained with β-methoxystyrene were hydrolysed into the corresponding ketones with THF/H_2O/HCl (or H_2SO_4). If the regioselectivity of this reaction is important, the stereoselectivity is irrelevant, as the outcome of these reactions is the ketone product. It should be noted that the arylation of butyl 1-propenyl ether with iodobenzene with $Pd(PPh_3)_4$ as the catalyst gave a mixture of α- and β-arylated enol ethers.[12]

Next, we studied the reactivity of 3-ethoxyacrylonitrile (Scheme 4, Table 4). With this enol ether, very low conversions were obtained with the electron-deficient aryl bromides 4-bromoacetophenone and 1-bromo-4-(trifluoromethyl)benzene. On the other hand, with 1-bromo-4-fluorobenzene, 4-bromotoluene, 1-bromo-4-(*tert*-butyl)benzene, 6-methoxy-2-bromonaphthalene and 4-bromoanisole complete conversions and good yields of arylated ethoxyacrylonitriles were obtained (Table 4, Entries 1–4 and 7). These *para*-substituted aryl bromides gave regioselectively 3-aryl-3-ethoxyacrylonitrile derivatives, but mixtures of (*Z*) and (*E*) isomers were obtained (12–35:65–88). With the *meta*-substituted 3-bromotoluene, the 3-arylated 3-ethoxyacrylonitriles **35a** and **35b** were also obtained in good yields and with a higher selectivity in favour of (*E*) isomer (89%, Table 5, Entry 8). As expected, the sterically congested aryl bromides 2-bromotoluene, 1-bromonaphthalene, 1-bromo-2,4,6-trimethylbenzene, 1-bromo-2,6-diethyl-4-methylbenzene and 1-bromo-2,4,6-triisopropylbenzene gave larger amounts of (*Z*) isomers (66–93%) for steric reasons (Table 5, Entries 10–14). On the other hand, with the π-electron-deficient heteroaromatic substrates 3-bromopyridine and 3-bromoquinoline, the (*E*) isomers were obtained with high selectivity (*Z*/*E* = 91:9 and 90:10, respectively, Table 5, Entries 15 and 16). The separation of (*Z*)- and (*E*)-3-aryl-3-ethoxyacrylonitriles was possible by chromatography on silica gel, so these compounds were not hydrolysed into the ketone. The formation of mixtures of isomers does not come from a secondary isomerisation of the products under the reaction conditions. Under the same conditions (catalyst, DMF, $NaHCO_3$ and 150 °C), we did not observe an isomerisation of pure (*E*)-**34b** into (E)-**34a** after 20 h.

Finally, we performed a few arylation reactions with methyl (*E*)-3-methoxyacrylate (Scheme 5, Table 5). In all cases, the formation of mixtures of (*Z*)- and (*E*)-3-aryl-3-methoxyacrylates **44a**–**46a** and **44b**–**46b**, respectively, was observed and a partial hydrolysis of the arylated enol ethers occurred during the Pd-catalysed reactions to directly give the methyl 3-aryl-3-oxopropionates **44c**–**46c**. The formation of unidentified side products was also observed with this alkene. Hydrolysis of these mixtures gave the methyl 3-aryl-3-oxopropionates **44c**–**46c** in moderate yields. A reaction was also performed with this 2-substituted enol ether with PPh_3 as the ligand, but a low yield was obtained, and large amounts of side products were formed with this catalytic system.

Conclusions

In summary, with the Tedicyp/palladium complex, the arylation of α- or β-substituted enol ethers with aryl bromides proceeds in good yields in most cases. 1-Phenyl-1-(trimethylsilyloxy)ethylene led directly to the 2-aryl-1-phenylethanones. On the other hand, the Heck reaction with benzyl isopropenyl ether led to mixtures of isomers. However, these mixtures gave selectively the 1-arylpropanones after hydrolysis. The Heck vinylation of several aryl bromides with β-substituted enol ethers has been performed in high regioselectivities and good yields. The reactivity of β-substituted enol ethers β-methoxystyrene, 3-ethoxyacrylonitrile and methyl (*E*)-3-methoxyacrylate has also been studied. In all cases, regioselective α-arylations of these enol ethers have been observed. The stereoselectivity of the reactions strongly depends on the electronic properties and the steric hindrance of the aryl bromides. As expected, larger amounts of (*Z*) isomers were obtained with sterically congested aryl bromides. Higher reaction rates were observed with the electron-rich aryl bromides than with electron-deficient ones. This observation indicates that the rate-limiting step of this reaction is not the oxidative addition of the aryl bromide to the palladium complex, but more likely, the insertion of the enol ether into the Ar–Pd bond of the intermediate Ar(X)Pd(RCH=CHOR′) to give Ar(R)CH–CH(PdX)(OR′). Steric factors may also be important for the reductive elimination step with our bulky tetraphosphane ligand. Steric strain is a driving force in many Pd-catalysed reactions. With our system, a catalytic intermedi-

ate might be a P_2PdArX(alkene) pentacoordinate complex with two arms of the ligand detached. Apart from achieving excellent regiocontrol, these reactions were performed in the absence of toxic or expensive additives and proceeded with aryl bromides, which are less expensive than aryl iodides. Another advantage is that 1-phenyl-1-(trimethylsilyloxy)ethylene, β-methoxystyrene, 3-ethoxy-acrylonitrile and methyl (*E*)-3-methoxyacrylate are commercially available. The hydrolysis of these arylated enol esters gives very simple access to a wide variety of acetophenone or 1-arylpropanone derivatives. This extension of the Heck methodology should increase the scope of this reaction.

Experimental Section

General Procedure: As a typical experiment, the reaction of the aryl halide (1 mmol), alkene (2 mmol) and K_2CO_3 (0.276 g, 2 mmol) or $NaHCO_3$ (0.168 g, 2 mmol) (see Table 1–Table 5) at 130 °C or 150 °C (see Table 1–Table 5) for 20 h in DMF (5 mL) in the presence of the *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphanylmethyl)-cyclopentane/$[PdCl(C_3H_5)]_2$ (1:2) complex[17] under argon afforded products after workup. Workup consisted of the addition of water (20 mL), extraction with dichloromethane (20 mL), separation, drying ($MgSO_4$) and concentration of the organic layer and purification of the crude material by chromatography on silica gel (pentane/ether). In some cases, the inseparable mixture of isomers was hydrolysed into the corresponding ketone with THF/H_2O/HCl. With 3-ethoxyacrylonirile, the separation by chromatography of the two stereoisomers formed was simple; therefore, they were not hydrolysed into the corresponding ketones.

2-(4-Benzoylphenyl)-1-phenylethanone (1, Table 1, Entry 1): The reaction of 4-bromobenzophenone (0.261 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **1** in 83% (0.249 g) isolated yield as a white solid. M.p. 126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.5 Hz, 2 H), 7.81–7.76 (m, 4 H), 7.62–7.56 (m, 2 H), 7.50–7.40 (m, 4 H), 7.31 (d, J = 8.3 Hz, 2 H), 4.38 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.8, 196.3, 139.3, 137.6, 136.4, 136.2, 133.4, 132.3, 130.4, 130.0, 129.5, 128.7, 128.5, 128.2, 45.5 ppm. $C_{21}H_{16}O_2$ (300.35): calcd. C 83.98, H 5.37; found C 83.79, H 5.48.

2-(4-Acetylphenyl)-1-phenylethanone (2, Table 1, Entry 3): The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **2** in 78% (0.186 g) isolated yield.

1-Phenyl-2-(4-trifluoromethylphenyl)ethanone (3, Table 1, Entry 4): The reaction of 1-bromo-4-(trifluoromethyl)benzene (0.225 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded **3** in 82% (0.217 g) isolated yield.

4-(2-Oxo-2-phenylethyl)benzonitrile (4, Table 1, Entry 6): The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded **4** in 80% (0.177 g) isolated yield.

2-(4-*tert*-Butylphenyl)-1-phenylethanone (5, Table 1, Entry 8): The reaction of 1-bromo-4-(*tert*-butyl)benzene (0.213 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded **5** in 78% (0.197 g) isolated yield.

1-Phenyl-2-(2-trifluoromethylphenyl)ethanone (6, Table 1, Entry 9): The reaction of 1-bromo-2-(trifluoromethyl)benzene (0.225 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded **6** in 83% (0.219 g) isolated yield as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.3 Hz, 2 H), 7.70 (d, J = 8.2 Hz, 1 H), 7.63–7.49 (m, 4 H), 7.42 (m, 1 H), 7.31 (m, 1 H), 4.51 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.3, 136.4, 133.3, 133.1, 132.8, 131.8, 128.7, 128.2, 127.2, 126.1 (q, J = 6.1 Hz), 121.6 (q, J = 272.0 Hz), 42.4 ppm. $C_{15}H_{11}F_3O$ (264.24): calcd. C 68.18, H 4.20; found C 68.01, H 4.37.

2-(1-Naphthyl)-1-phenylethanone (7, Table 1, Entry 10): The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded **7** in 88% (0.217 g) isolated yield.

1-Phenyl-2-(*o*-tolyl)ethanone (8, Table 1, Entry 12): The reaction of 2-bromotoluene (0.171 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)-ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.04 mmol) afforded **8** in 65% (0.137 g) isolated yield.

2-(2-Methoxyphenyl)-1-phenylethanone (9, Table 1, Entry 13): The reaction of 2-bromoanisole (0.187 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded **9** in 81% (0.183 g) isolated yield.

1-Phenyl-2-(2,4,6-trimethylphenyl)ethanone (10, Table 1, Entry 14): The reaction of 1-bromo-2,4,6-trimethylbenzene (0.195 g, 1 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded **10** in 80% (0.191 g) isolated yield.

1-(4-Benzoylphenyl)propan-2-one (11d, Table 2, Entry 1): The reaction of 4-bromobenzophenone (0.261 g, 1 mmol), benzyl isopropenyl ether (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded, after hydrolysis, the corresponding ketone **11d** in 66% (0.157 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.33 (m, 14 H), 3.81 (s, 2 H), 2.22 (s, 3 H) ppm. Before hydrolysis, **11a** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.33 (m, 19 H), 5.44 (s, 1 H), 5.10 (s, 2 H), 2.14 (s, 3 H) ppm], **11b** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.33 (m, 19 H), 5.78 (s, 1 H), 4.93 (s, 2 H), 2.16 (s, 3 H) ppm], and **11c** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.33 (m, 19 H), 4.78 (s, 2 H), 4.12 (s, 1 H), 4.04 (s, 1 H), 3.55 (s, 2 H) ppm] were observed in a 49:39:12 ratio.

1-(4-Acetylphenyl)propan-2-one (12d, Table 2, Entry 3): The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), benzyl isopropenyl ether (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded, after hydrolysis, the corresponding ketone **12d** in 84% (0.148 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.5 Hz, 2 H), 7.36 (d, J = 8.5 Hz, 2 H), 3.81 (s, 2 H), 2.56 (s, 3 H), 2.22 (s, 3 H) ppm. Before hydrolysis, **12a** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.33 (m, 9 H), 5.41 (s, 1 H), 5.09 (s, 2 H), 2.56 (s, 3 H), 2.14 (s, 3 H) ppm], **12b** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.33 (m, 9 H), 5.75 (s, 1 H), 4.91 (s, 2 H), 2.56 (s, 3 H), 2.17 (s, 3 H) ppm], and **12c** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.33 (m, 9 H), 4.74 (s, 2 H), 4.10 (s, 1 H), 4.06 (s, 1 H), 3.55 (s, 2 H), 2.56 (s, 3 H) ppm] were observed in a 49:42:9 ratio.

1-Phenylpropan-2-one (13d, Table 2, Entry 4): The reaction of bromobenzene (0.157 g, 1 mmol), benzyl isopropenyl ether (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded, after hydrolysis, the corresponding ketone **13d** in 27% (0.037 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.33 (m, 5 H), 3.81 (s, 2 H), 2.22 (s, 3 H) ppm. Before hydrolysis, **13a** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.33 (m, 10 H), 5.41 (s, 1 H), 5.09 (s, 2 H), 2.14 (s, 3 H) ppm], **13b** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.33 (m, 10 H), 5.75 (s, 1 H), 4.91 (s, 2 H), 2.17 (s, 3 H) ppm], and **13c** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.33 (m, 10 H), 4.74 (s, 2 H), 4.10 (s, 1 H), 4.06 (s, 1 H), 3.51 (s, 2 H) ppm] were observed in a 54:36:10 ratio.

1-*p*-Tolylpropan-2-one (14d, Table 2, Entry 5): The reaction of 4-bromotoluene (0.171 g, 1 mmol), benzyl isopropenyl ether (0.384 g, 2 mmol) and K_2CO_3 (0.276 g, 2 mmol) with the palladium complex (0.02 mmol) afforded, after hydrolysis, the corresponding ketone **14d** in 52% (0.077 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.33 (m, 4 H), 3.81 (s, 2 H), 2.22 (s, 3 H), 2.07 (s, 3 H) ppm. Before hydrolysis, **14a** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.33 (m, 9 H), 5.40 (s, 1 H), 5.04 (s, 2 H), 2.14 (s, 3 H), 2.07 (s, 3 H) ppm], **14b** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.33 (m, 9 H), 5.74 (s, 1 H), 4.90 (s, 2 H), 2.17 (s, 3 H), 2.07 (s, 3 H) ppm], and **14c** [^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.33 (m, 9 H), 4.77 (s, 2 H), 4.07 (s, 1 H), 3.97 (s, 1 H), 3.47 (s, 2 H), 2.07 (s, 3 H) ppm] were observed in a 30:23:47 ratio.

(*Z*)-1-(4-Acetylphenyl)-1-methoxy-2-phenylethene (15a) and (*E*)-1-(4-Acetylphenyl)-1-methoxy-2-phenylethene (15b, Table 3, Entry 1): The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **15a** and **15b** as a 65:35 mixture of isomers, as determined by ^{1}H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.25 [s, 1 H, C*H*=C (*Z*)], 5.90 [s, 1 H, C*H*=C (*E*)] ppm. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **1-(4-acetylphenyl)-2-phenylethanone** (**15c**) in 58% (0.138 g) isolated yield.

(*Z*)-1-(4-Formylphenyl)-1-methoxy-2-phenylethene (16a) and (*E*)-1-(4-Formylphenyl)-1-methoxy-2-phenylethene (16b, Table 3, Entry 2): The reaction of 4-bromobenzaldehyde (0.185 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **16a** and **16b** as a 69:31 mixture of isomers, as determined by ^{1}H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.30 [s, 1 H, C*H*=C (*Z*)], 5.93 [s, 1 H, C*H*=C (*E*)] ppm. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **4-(phenylacetyl)benzaldehyde** (**16c**) in 60% (0.135 g) isolated yield.

(*Z*)-1-Methoxy-2-phenyl-1-(4-trifluoromethylphenyl)ethene (17a) and (*E*)-1-Methoxy-2-phenyl-1-(4-trifluoromethylphenyl)ethene (17b, Table 3, Entry 3): The reaction of 1-bromo-4-(trifluoromethyl)benzene (0.225 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.004 mmol) afforded **17a** and **17b** as a 73:27 mixture of isomers, as determined by ^{1}H NMR on the crude mixture. Characteristic band of the mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.21 [s, 1 H, C*H*=C (*Z*)], 5.91 [s, 1 H, C*H*=C (*E*)]. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **2-phenyl-1-(4-trifluoromethylphenyl)ethanone** (**17c**) in 72% (0.190 g) isolated yield.

(*Z*)-1-(4-Fluorophenyl)-1-methoxy-2-phenylethene (18a) and (*E*)-1-(4-Fluorophenyl)-1-methoxy-2-phenylethene (18b, Table 3, Entry 4): The reaction of 1-bromo-4-fluorobenzene (0.175 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **18a** and **18b** as a 67:33 mixture of isomers, as determined by ^{1}H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.04 [s, 1 H, C*H*=C (*Z*)], 5.82 [s, 1 H, C*H*=C (*E*)]. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **1-(4-fluorophenyl)-2-phenylethanone** (**18c**) in 78% (0.167 g) isolated yield.

(*Z*)-1-Methoxy-1-(4-methylphenyl)-2-phenylethene (19a) and (*E*)-1-Methoxy-1-(4-methylphenyl)-2-phenylethene (19b, Table 3, Entry 5): The reaction of 4-bromotoluene (0.171 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **19a** and **19b** as a 62:38 mixture of isomers, as determined by ^{1}H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.04 [s, 1 H, C*H*=C (*Z*)], 5.78 [s, 1 H, C*H*=C (*E*)]. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **2-phenyl-1-(*p*-tolyl)ethanone** (**19c**) in 80% (0.168 g) isolated yield.

(*Z*)-1-(4-*tert*-Butylphenyl)-1-methoxy-2-phenylethene (20a) and (*E*)-1-(4-*tert*-Butylphenyl)-1-methoxy-2-phenylethene (20b, Table 3, Entry 6): The reaction of 1-bromo-4-(*tert*-butyl)benzene (0.213 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **20a** and **20b** as a 63:37 mixture of isomers, as determined by ^{1}H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.07 [s, 1 H, C*H*=C (*Z*)], 5.79 [s, 1 H, C*H*=C (*E*)]. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **1-(4-*tert*-butylphenyl)-2-phenylethanone** (**20c**) in 79% (0.199 g) isolated yield.

(*Z*)-1-Methoxy-1-(4-methoxyphenyl)-2-phenylethene (21a) and (*E*)-1-Methoxy-1-(4-methoxyphenyl)-2-phenylethene (21b, Table 3, Entry 7): The reaction of 4-bromoanisole (0.187 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **21a** and **21b** as a 54:46 mixture of isomers, as determined by ^{1}H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00 [s, 1 H, C*H*=C (*Z*)], 5.76 [s, 1 H, C*H*=C (*E*)]. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **1-(4-methoxyphenyl)-2-phenylethanone** (**21c**) in 77% (0.174 g) isolated yield.

(*Z*)-1-Methoxy-1-(6-methoxynaphthalen-2-yl)-2-phenylethene (22a) and (*E*)-1-Methoxy-1-(6-methoxynaphthalen-2-yl)-2-phenylethene (22b, Table 3, Entry 8): The reaction of 6-methoxy-2-bromonaphthalene (0.237 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **22a** and **22b** as a 51:49 mixture of isomers, as determined by ^{1}H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.23 [s, 1 H, C*H*=C (*Z*)], 5.90 [s, 1 H, C*H*=C (*E*)]. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **1-(6-methoxynaphthalen-2-yl)-2-phenylethanone** (**22c**) in 82% (0.226 g) isolated yield.

(*Z*)-1-Methoxy-1,2-diphenylethene (23a) and (*E*)-1-Methoxy-1,2-diphenylethene (23b, Table 3, Entry 9): The reaction of iodobenzene (0.204 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **23a** and **23b** as a 33:67 mixture of isomers, as determined by ^{1}H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.08 [s, 1 H, C*H*=C (*Z*)], 5.81 [s, 1 H, C*H*=C (*E*)]. This inseparable

mixture of isomers was hydrolysed into the corresponding ketone to give **1,2-diphenylethanone (23c)** in 79% (0.155 g) isolated yield.

(*Z*)-1-Methoxy-1-(naphthalen-1-yl)-2-phenylethene (24a) and (*E*)-1-Methoxy-1-(naphthalen-1-yl)-2-phenylethene (24b, Table 3, Entry 11): The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **24a** and **24b** as a 57:43 mixture of isomers, as determined by ^1H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^1H NMR (300 MHz, $CDCl_3$): δ = 6.12 [s, 1 H, C*H*=C (*Z*)], 5.76 [s, 1 H, C*H*=C (*E*)]. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **1-(naphthalen-1-yl)-2-phenylethanone (24c)** in 84% (0.207 g) isolated yield.

(*Z*)-1-Methoxy-1-(2-methylphenyl)-2-phenylethene (25a) and (*E*)-1-Methoxy-1-(2-methylphenyl)-2-phenylethene (25b, Table 3, Entry 12): The reaction of 2-bromotoluene (0.171 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **25a** and **25b** as a 62:38 mixture of isomers, as determined by ^1H NMR of the crude mixture: 62/38. Characteristic band of the mixture of isomers: ^1H NMR (300 MHz, $CDCl_3$): δ = 5.84 [s, 1 H, C*H*=C (*Z*)], 5.50 [s, 1 H, C*H*=C (*E*)]. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **2-phenyl-1-(*p*-tolyl)ethanone (25c)** in 79% (0.166 g) isolated yield.

(*Z*)-1-Methoxy-2-phenyl-1-(2,4,6-trimethylphenyl)ethene (26a, Table 3, Entry 13): The reaction of 1-bromo-2,4,6-trimethylbenzene (0.195 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **26a** exclusively, as determined by ^1H NMR of the crude material. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.10–6.90 (m, 3 H), 6.86 (s, 2 H), 6.77 (d, *J* = 7.0 Hz, 2 H), 5.89 (s, 1 H), 3.75 (s, 3 H), 2.28 (s, 3 H), 2.12 (s, 3 H). This product was hydrolysed into the corresponding ketone to give **2-phenyl-1-(2,4,6-trimethylphenyl)ethanone (26c)** in 74% (0.176 g) isolated yield.

(*Z*)-1-(2,6-Diethyl-4-methylphenyl)-1-methoxy-2-phenylethene (27a, Table 3, Entry 14): The reaction of 1-bromo-2,6-diethyl-4-methylbenzene (0.219 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **27a** exclusively, as determined by ^1H NMR of the crude material. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.15–6.90 (m, 3 H), 6.93 (s, 2 H), 6.76 (d, *J* = 7.0 Hz, 2 H), 5.89 (s, 1 H), 3.77 (s, 3 H), 2.58–2.40 (m, 4 H), 2.34 (s, 3 H), 1.06 (t, *J* = 7.7 Hz, 6 H) ppm. This product was hydrolysed into the corresponding ketone to give **1-(2,6-diethyl-4-methylphenyl)-2-phenylethanone (27c)** in 76% (0.202 g) isolated yield as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.17 (m, 5 H), 6.89 (s, 2 H), 4.00 (s, 2 H), 2.43 (q, *J* = 7.4 Hz, 4 H), 2.32 (s, 3 H), 1.16 (t, *J* = 7.4 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.5, 139.0, 138.7, 133.4, 133.3, 129.8, 128.5, 127.0, 126.7, 52.4, 26.1, 21.3, 15.7 ppm. $C_{19}H_{22}O$ (266.38): calcd. C 85.67, H 8.32; found C 85.90, H 8.57.

(*Z*)-1-Methoxy-2-phenyl-1-(quinolin-3-yl)ethene (28a) and (*E*)-1-Methoxy-2-phenyl-1-(quinolin-3-yl)ethene (28b, Table 3, Entry 15): The reaction of 3-bromoquinoline (0.208 g, 1 mmol), β-methoxystyrene (0.268 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **28a** and **28b** as a 71:29 mixture of isomers, as determined by ^1H NMR of the crude mixture. Characteristic band of the mixture of isomers: ^1H NMR (300 MHz, $CDCl_3$): δ = 6.31 [s, 1 H, C*H*=C (*Z*)], 6.01 [s, 1 H, C*H*=C (*E*)]. These compounds were characterized by hydrolysis into the corresponding ketone to give **2-phenyl-1-(quinolin-3-yl)ethanone (28c)** in 73% (0.180 g) isolated yield as a white solid. M.p. 116 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.46 (s, 1 H), 8.77 (s, 1 H), 8.15 (d, *J* = 7.8 Hz, 1 H), 7.94 (*J* = 7.9 Hz, 1 H), 7.83 (t, *J* = 7.4 Hz, 1 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.35–7.15 (m, 5 H), 4.41 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.4, 149.7, 149.4, 137.7, 133.7, 132.1, 129.4, 128.9, 128.8, 127.6, 127.2, 126.8, 46.0 ppm. $C_{17}H_{13}NO$ (247.29): calcd. C 82.57, H 5.30; found C 82.41, H 5.15.

(*Z*)-3-Ethoxy-3-(4-fluorophenyl)acrylonitrile (29a) and (*E*)-3-Ethoxy-3-(4-fluorophenyl)acrylonitrile (29b, Table 4, Entry 1): The reaction of 1-bromo-4-fluorobenzene (0.175 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **29a** and **29b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 12:88 mixture of isomers (as determined by ^1H NMR of the crude mixture) in 79% (0.151 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-29a** was not isolated in pure form: ^1H NMR (300 MHz, $CDCl_3$): δ = 4.90 (s, 1 H), 4.55 (q, *J* = 7.0 Hz, 2 H) ppm. **(*E*)-29b**: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 5.3, 8.5 Hz, 2 H), 7.10 (t, *J* = 8.5 Hz, 2 H), 4.59 (s, 1 H), 3.98 (q, *J* = 7.0 Hz, 2 H), 1.42 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.4, 164.1 (d, *J* = 251.8 Hz), 130.1 (d, *J* = 8.6 Hz), 129.2, 118.6, 115.5 (d, *J* = 22.4 Hz), 69.8, 65.6, 14.0 ppm. $C_{11}H_{10}FNO$ (191.20): calcd. C 69.10, H 5.27; found C 69.24, H 5.38.

(*Z*)-3-Ethoxy-3-(*p*-tolyl)acrylonitrile (30a) and (*E*)-3-Ethoxy-3-(*p*-tolyl)acrylonitrile (30b, Table 4, Entry 2): The reaction of 4-bromotoluene (0.171 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **30a** and **30b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 35:65 mixture of isomers (as determined by ^1H NMR of the crude mixture) in 76% (0.142 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-30a**: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.5 Hz, 2 H), 7.18 (d, *J* = 8.5 Hz, 2 H), 4.90 (s, 1 H), 4.52 (q, *J* = 7.0 Hz, 2 H), 2.37 (s, 3 H), 1.44 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5, 141.5, 131.3, 129.3, 126.5, 117.9, 70.8, 68.0, 21.3, 15.9 ppm. **(*E*)-30b**: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.5 Hz, 2 H), 7.22 (d, *J* = 8.5 Hz, 2 H), 4.56 (s, 1 H), 3.96 (q, *J* = 7.0 Hz, 2 H), 2.38 (s, 3 H), 1.45 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.7, 141.4, 130.3, 129.0, 127.8, 119.0, 69.7, 65.3, 21.4, 14.1 ppm.

(*Z*)-3-(4-*tert*-Butylphenyl)-3-ethoxyacrylonitrile (31a) and (*E*)-3-(4-*tert*-Butylphenyl)-3-ethoxyacrylonitrile (31b, Table 4, Entry 3): The reaction of 1-bromo-4-(*tert*-butyl)benzene (0.175 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **31a** and **31b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 30:70 mixture of isomers (as determined by ^1H NMR of the crude mixture) in 82% (0.188 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-31a**: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.5 Hz, 2 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 4.91 (s, 1 H), 4.53 (q, *J* = 7.0 Hz, 2 H), 1.44 (t, *J* = 7.0 Hz, 3 H), 1.32 (s, 9 H) ppm. **(*E*)-31b:** ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.5 Hz, 2 H), 7.45 (d, *J* = 8.5 Hz, 2 H), 4.57 (s, 1 H), 3.97 (q, *J* = 7.0 Hz, 2 H), 1.44 (t, *J* = 7.0 Hz, 3 H), 1.34 (s, 9 H) ppm. These compounds were characterized by hydrolysis into the corresponding ketone **31c**.

(*Z*)-3-Ethoxy-3-(6-methoxynaphthalen-2-yl)acrylonitrile (32a) and (*E*)-3-Ethoxy-3-(6-methoxynaphthalen-2-yl)acrylonitrile (32b, Table 4, Entry 4): The reaction of 2-bromo-6-methoxynaphthalene (0.237 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex

(0.01 mmol) afforded **32a** and **32b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 27:73 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 84% (0.213 g) isolated yield (**32b** was a white solid with a m.p. of 105 °C). These isomers were separated by chromatography on silica gel. **(*Z*)-32a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (s, 1 H), 7.85 (m, 2 H), 7.53 (dd, J = 8.1 and 1.9 Hz, 1 H), 7.20–7.10 (m, 2 H), 5.05 (s, 1 H), 4.59 (q, J = 7.0 Hz, 2 H), 3.94 (s, 3 H), 1.49 (t, J = 7.0 Hz, 3 H) ppm. **(*E*)-32b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 7.85–7.75 (m, 3 H), 7.20–7.10 (m, 2 H), 4.64 (s, 1 H), 4.01 (q, J = 7.0 Hz, 2 H), 3.92 (s, 3 H), 1.48 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6, 159.0, 135.9, 130.4, 128.2, 127.9, 126.8, 124.9, 123.7, 119.5, 119.1, 105.5, 69.4, 65.5, 55.3, 14.2 ppm. $C_{16}H_{15}NO_2$ (253.30): calcd. C 75.87, H 5.97; found C 75.84, H 6.07.

(*Z*)-3-Ethoxy-3-phenylacrylonitrile (33a) and (*E*)-3-Ethoxy-3-phenylacrylonitrile (33b, Table 4, Entry 5): The reaction of iodobenzene (0.204 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **33a** and **33b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 40:60 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 80% (0.139 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-33a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.30 (m, 5 H), 4.94 (s, 1 H), 4.54 (q, J = 7.0 Hz, 2 H), 1.45 (t, J = 7.0 Hz, 3 H) ppm. **(*E*)-33b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.2 Hz, 2 H), (m, 3 H), 4.60 (s, 1 H), 3.99 (q, J = 7.0 Hz, 2 H), 1.46 (t, J = 7.0 Hz, 3 H) ppm. These compounds were characterized by hydrolysis into the corresponding ketone **33c**.

(*Z*)-3-Ethoxy-3-(4-methoxyphenyl)acrylonitrile (34a) and (*E*)-3-Ethoxy-3-(4-methoxyphenyl)acrylonitrile (34b, Table 4, Entry 7): The reaction of 4-bromoanisole (0.187 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **34a** and **34b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 24:76 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 85% (0.173 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-34a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (J = 8.5 Hz, 2 H), 6.88 (d, J = 8.5 Hz, 2 H), 4.86 (s, 1 H), 4.53 (q, J = 7.0 Hz, 2 H), 3.84 (s, 3 H), 1.44 (t, J = 7.0 Hz, 3 H) ppm. **(*E*)-34b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (J = 8.5 Hz, 2 H), 6.93 (d, J = 8.5 Hz, 2 H), 4.52 (s, 1 H), 3.98 (q, J = 7.0 Hz, 2 H), 3.84 (s, 3 H), 1.45 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2, 161.7, 129.6, 125.5, 119.2, 113.7, 68.4, 65.3, 55.4, 14.1 ppm. $C_{12}H_{13}NO_2$ (203.24): calcd. C 70.92, H 6.45; found C 71.10, H 6.45.

(*Z*)-3-Ethoxy-3-(*m*-tolyl)acrylonitrile (35a) and (*E*)-3-Ethoxy-3-(*m*-tolyl)acrylonitrile (35b, Table 4, Entry 8): The reaction of 3-bromotoluene (0.171 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **35a** and **35b**, after evaporation of the solvent and filtration of the crude material through silica gel, as an 11:89 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 81% (0.152 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-35a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.90 (s, 1 H) ppm. **(*E*)-35b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (m, 2 H), 7.32 (t, J = 7.3 Hz, 1 H), 7.28 (m, 1 H), 4.58 (s, 1 H), 3.98 (q, J = 7.0 Hz, 2 H), 2.39 (s, 3 H), 1.45 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.8, 138.1, 133.1, 131.7, 128.4, 128.3, 125.1, 118.8, 69.8, 65.4, 21.3, 14.1 ppm. $C_{12}H_{13}NO$ (187.24): calcd. C 76.98, H 7.00; found C 77.07, H 6.87.

(*Z*)-3-Ethoxy-3-(2-fluorophenyl)acrylonitrile (36a) and (*E*)-3-Ethoxy-3-(2-fluorophenyl)acrylonitrile (36b, Table 4, Entry 9): The reaction of 1-bromo-2-fluorobenzene (0.175 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **36a** and **36b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 26:74 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 78% (0.149 g) isolated yield (**36b** was a white solid with a m.p. = 180 °C). These isomers were separated by chromatography on silica gel. **(*Z*)-36a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (t, J = 7.5 Hz, 1 H), 7.40 (t, J = 7.5 Hz, 1 H), 7.19 (t, J = 7.5 Hz, 1 H), 7.12 (m, 1 H), 4.95 (s, 1 H), 4.34 (q, J = 7.0 Hz, 2 H), 1.40 (t, J = 7.0 Hz, 3 H) ppm. **(*E*)-36b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (t, J = 7.5 Hz, 1 H), 7.43 (t, J = 7.5 Hz, 1 H), 7.19 (t, J = 7.5 Hz, 1 H), 7.13 (m, 1 H), 4.75 (s, 1 H), 4.00 (q, J = 7.0 Hz, 2 H), 1.43 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.8, 159.8 (d, J = 248.5 Hz), 132.4 (d, J = 8.6 Hz), 130.4 (d, J = 2.3 Hz), 124.1 (d, J = 3.4 Hz), 121.8 (d, J = 12.0 Hz), 117.5, 116.3 (d, J = 21.3 Hz), 74.0, 65.9, 14.0 ppm. $C_{11}H_{10}FNO$ (191.20): calcd. C 69.10, H 5.27; found C 69.02, H 5.31.

(*Z*)-3-Ethoxy-3-(naphthalen-1-yl)acrylonitrile (37a) and (*E*)-3-Ethoxy-3-(naphthalen-1-yl)acrylonitrile (37b, Table 4, Entry 10): The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **37a** and **37b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 75:25 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 81% (0.181 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-37a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.3 Hz, 1 H), 7.85 (m, 2 H), 7.64 (d, J = 7.0 Hz, 1 H), 7.60–7.47 (m, 3 H), 4.90 (s, 1 H), 4.07 (q, J = 7.0 Hz, 2 H), 1.43 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.0, 133.6, 131.0, 130.9, 130.4, 128.5, 127.7, 126.9, 126.3, 124.9, 124.6, 117.8, 74.2, 65.8, 14.1 ppm. $C_{15}H_{13}NO$ (223.27): calcd. C 80.69, H 5.87; found C 80.48, H 5.97. **(*E*)-37b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.85 (m, 3 H), 7.62–7.45 (m, 4 H), 4.71 (s, 1 H), 3.93 (q, J = 7.0 Hz, 2 H), 1.25 (t, J = 7.0 Hz, 3 H) ppm.

(*Z*)-3-Ethoxy-3-(*o*-tolyl)acrylonitrile (38a) and (*E*)-3-Ethoxy-3-(*o*-tolyl)acrylonitrile (38b, Table 4, Entry 11): The reaction of 2-bromotoluene (0.171 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **38a** and **38b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 77:23 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 77% (0.144 g) isolated yield (**38b** was a white solid with a m.p. 149 °C). These isomers were separated by chromatography on silica gel. **(*Z*)-38a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.20 (m, 4 H), 4.70 (s, 1 H), 3.98 (q, J = 7.0 Hz, 2 H), 2.34 (s, 3 H), 1.43 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.8, 136.2, 133.3, 130.6, 130.3, 129.0, 125.8, 117.9, 72.8, 65.5, 19.3, 14.0 ppm. $C_{12}H_{13}NO$ (187.24): calcd. C 76.98, H 7.00; found C 76.81, H 6.82. **(*E*)-38b** was not isolated in pure form: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.51 (s, 1 H) ppm.

(*Z*)-3-Ethoxy-3-(2,4,6-trimethylphenyl)acrylonitrile (39a) and (*E*)-3-Ethoxy-3-(2,4,6-trimethylphenyl)acrylonitrile (39b, Table 4, Entry 12): The reaction of 1-bromo-2,4,6-trimethylbenzene (0.195 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) af-

forded **39a** and **39b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 66:34 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 73% (0.157 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-39a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.88 (s, 2 H), 4.76 (s, 1 H), 3.96 (q, J = 7.0 Hz, 2 H), 2.25 (m, 9 H), 1.42 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.2, 139.5, 135.7, 130.5, 128.5, 117.6, 73.9, 65.5, 21.1, 19.0, 14.0 ppm. $C_{14}H_{17}NO$ (215.29): calcd. C 78.10, H 7.96; found C 78.00, H 7.82. **(*E*)-39b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.88 (s, 2 H), 4.33 (s, 1 H), 3.82 (q, J = 7.0 Hz, 2 H), 2.25 (m, 9 H), 1.26 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3, 139.6, 136.0, 129.8, 128.4, 116.7, 75.0, 65.7, 21.1, 19.7, 15.1 ppm.

(*Z*)-3-(2,6-Diethyl-4-methylphenyl)-3-ethoxyacrylonitrile (40a) and (*E*)-3-(2,6-Diethyl-4-methylphenyl)-3-ethoxyacrylonitrile (40b, Table 4, Entry 13): The reaction of 1-bromo-2,6-diethyl-4-methylbenzene (0.219 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **40a** and **40b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 65:35 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 74% (0.180 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-40a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94 (s, 2 H), 4.78 (s, 1 H), 3.97 (q, J = 7.0 Hz, 2 H), 2.57 (q, J = 7.0 Hz, 4 H), 2.32 (s, 3 H), 1.39 (t, J = 7.0 Hz, 3 H), 1.21 (t, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.2, 141.8, 139.8, 129.5, 126.9, 117.8, 74.3, 65.3, 26.0, 21.4, 15.5, 14.1 ppm. $C_{16}H_{21}NO$ (243.34): calcd. C 78.97, H 8.70; found C 79.11, H 8.87. **(*E*)-40b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93 (s, 2 H), 4.36 (s, 1 H), 3.84 (q, J = 7.0 Hz, 2 H), 2.54 (q, J = 7.0 Hz, 4 H), 2.32 (s, 3 H), 1.27 (t, J = 7.0 Hz, 3 H), 1.18 (t, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2, 142.0, 140.0, 128.8, 126.8, 116.7, 74.9, 65.9, 26.1, 21.3, 15.4, 15.1 ppm.

(*Z*)-3-Ethoxy-3-(2,4,6-triisopropylphenyl)acrylonitrile (41a) and (*E*)-3-Ethoxy-3-(2,4,6-triisopropylphenyl)acrylonitrile (41b, Table 4, Entry 14): The reaction of 1-bromo-2,4,6-triisopropylbenzene (0.283 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **41a** and **41b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 93:7 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 76% (0.227 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-41a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03 (s, 2 H), 4.80 (s, 1 H), 3.98 (q, J = 7.0 Hz, 2 H), 2.90 (m, 3 H), 1.38 (t, J = 7.0 Hz, 3 H), 1.25 (m, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.4, 150.6, 146.3, 128.7, 121.2, 117.9, 74.5, 65.3, 31.0, 24.6, 24.0, 23.9, 14.7 ppm. $C_{20}H_{29}NO$ (299.45): calcd. C 80.22, H 9.76; found C 80.14, H 9.87. **(*E*)-41b** was not isolated in pure form: ^{1}H NMR (300 MHz, $CDCl_3$): 4.37 (s, 1 H), 3.87 (q, J = 7.0 Hz, 2 H).

(*Z*)-3-Ethoxy-3-(pyridin-3-yl)acrylonitrile (42a) and (*E*)-3-Ethoxy-3-(pyridin-3-yl)acrylonitrile (42b, Table 4, Entry 15): The reaction of 3-bromopyridine (0.158 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **42a** and **42b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 9:91 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 78% (0.136 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-42a** was not isolated in pure form: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.98 (s, 1 H) ppm. **(*E*)-42b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.95 (s, 1 H), 8.68 (d, J = 4.1 Hz, 1 H), 8.11 (dt, J = 8.1 and 1.6 Hz, 1 H), 7.36 (dd, J = 8.1 and 4.1 Hz, 1 H), 4.70 (s, 1 H), 4.01 (q, J = 7.0 Hz, 2 H), 1.45 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9, 151.6, 148.8, 135.7, 129.1, 123.0, 117.9, 71.4, 65.9, 14.0 ppm. $C_{10}H_{10}N_2O$ (174.20): calcd. C 68.95, H 5.79; found C 68.84, H 5.84.

(*Z*)-3-Ethoxy-3-(quinolin-3-yl)acrylonitrile (43a) and (*E*)-3-Ethoxy-3-(quinolin-3-yl)acrylonitrile (43b, Table 4, Entry 16): The reaction of 3-bromoquinoline (0.208 g, 1 mmol), 3-ethoxyacrylonitrile (0.194 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **43a** and **43b**, after evaporation of the solvent and filtration of the crude material through silica gel, as a 10:90 mixture of isomers (as determined by ^{1}H NMR of the crude mixture) in 80% (0.179 g) isolated yield as an oil. These isomers were separated by chromatography on silica gel. **(*Z*)-43a** was not isolated in pure form: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.17 (s, 1 H) ppm. **(*E*)-43b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.17 (d, J = 2.3 Hz, 1 H), 8.63 (d, J = 2.1 Hz, 1 H), 8.12 (d, J = 8.5 Hz, 1 H), 7.90 (d, J = 8.1 Hz, 1 H), 7.79 (td, J = 7.0 and 1.5 Hz, 1 H), 7.60 (td, J = 7.0 and 1.2 Hz, 1 H), 4.77 (s, 1 H), 4.07 (q, J = 7.0 Hz, 2 H), 1.51 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.0, 148.7, 148.4, 136.1, 131.1, 129.3, 128.7, 127.4, 126.7, 126.2, 118.1, 71.5, 66.0, 14.1 ppm. $C_{14}H_{12}N_2O$ (224.26): calcd. C 74.98, H 5.39; found C 75.07, H 5.18.

Methyl 3-(4-*tert*-Butylphenyl)-3-oxopropionate (44c, Table 5, Entry 1): The reaction of 1-bromo-4-(*tert*-butyl)benzene (0.213 g, 1 mmol), methyl (*E*)-3-methoxyacrylate (0.232 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **44a** and **44b** as a mixture of isomers. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **44c** in 62% (0.145 g) isolated yield.

Methyl 3-(4-Methoxyphenyl)-3-oxopropionate (45c, Table 5, Entry 2): The reaction of 4-bromoanisole (0.187 g, 1 mmol), methyl (*E*)-3-methoxyacrylate (0.232 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **45a** and **45b** as a mixture of isomers. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **45c** in 60% (0.125 g) isolated yield.

Methyl 3-Methoxy-3-(*o*-tolyl)acrylate (46c): The reaction of 2-bromotoluene (0.171 g, 1 mmol), methyl (*E*)-3-methoxyacrylate (0.232 g, 2 mmol) and $NaHCO_3$ (0.168 g, 2 mmol) with the palladium complex (0.01 mmol) afforded **46a** and **46b** as a mixture of isomers. This inseparable mixture of isomers was hydrolysed into the corresponding ketone to give **46c** in 56% (0.108 g) isolated yield.

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Supporting Information (see also the footnote on the first page of this article): ^{1}H NMR of compounds **2–5**, **7–10**, **15c–26c** and **44c–46c**.

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