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Journal of Organometallic Chemistry 690 (2005) 3790–3802
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Selective synthesis of (*E*)-triethyl(2-arylethenyl)silane derivatives by reaction of aryl bromides with triethyl vinylsilane catalysed by a palladium–tetraphosphine complex

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Received 14 March 2005; received in revised form 4 May 2005; accepted 10 May 2005
Available online 20 June 2005

Abstract

Cis, cis, cis-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane / 0.5 $[PdCl(C_3H_5)]_2$ system catalyses the Heck reaction of vinylsilane derivatives with a range of aryl bromides with high ratio substrate/catalyst in good yields. The formation of mixtures of styrene, (*E*)-triethyl(2-arylethenyl)silane and triethyl(1-arylethenyl)silane derivatives was observed in some cases. Very high selectivities (up to 100%) in favour of the formation of (*E*)-triethyl(2-arylethenyl)silane derivatives were obtained in the presence of sodium acetate as base. With other bases such as potassium carbonate, the formation of large amounts of styrene derivatives was observed. The reaction tolerates several functions such as fluoro, trifluoromethyl, methoxy, dimethylamino, acetyl, formyl, benzoyl, carboxylate, nitro or nitrile. Moreover, turnover numbers up to 10,000 can be obtained for this reaction.

Keywords: Tetraphosphine; Palladium; Heck-vinylation; Vinyl silanes; Aryl bromides

1. Introduction

The palladium-catalysed Heck vinylation reaction is one of the most powerful methods for the formation of C–C bonds [1]. For a few years, some very efficient catalysts such as palladacycles have been described for Heck reaction [2]. The efficiency of these catalysts for the reaction of aryl halides with acrylates or styrenes has been studied in detail. On the other hand, the reaction in the presence of vinylsilane derivatives using these stable palladium catalysts has attracted less attention. Few ligands have been successfully employed for the reaction in the presence of these alkenes. The most popular one is triphenylphosphine but the palladium complexes formed with this ligand are generally not very efficient in terms of substrate/catalyst ratio, moreover, this catalyst was used in most cases with very reactive but expensive aryl iodides [3–9]. Tri-2-furylphosphine ligand in the presence of 2.5–5% $Pd_2(dba)_3$ also catalyses the reaction of aryl iodides with 2-pyridyldimethyl(vinyl)silane [10,11]. The reaction of aryl iodides and vinylsilanes also proceeds with $Pd(OAc)_2$ without added ligand in the presence of tetraalkylammonium halide salts [12–14]. If monophosphine ligands have been successfully used for the Heck reaction of vinylsilanes, to the best of our knowledge, the efficiency of tetraphosphine ligands has not been demonstrated. Moreover, the reactivity of aryl bromides with vinylsilanes has attracted much less attention than the reactivity of aryl

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doi:10.1016/j.jorganchem.2005.05.014

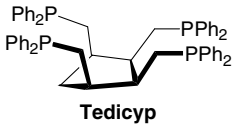


Fig. 1. Tedicyp.

iodides. Thus, an effective and selective method using high substrate/catalyst ratios for the reaction of vinylsilanes with aryl bromides are still subject to significant improvement.

In order to find more stable and more efficient palladium catalysts, we have prepared the new tetrapodal phosphine ligand, *cis,cis,cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl) cyclopentane or Tedicyp (Fig. 1) [15] in which the four diphenylphosphinoalkyl groups are stereospecifically bound to the same face of the cyclopentane ring.

We have already reported that the complex formed by association of Tedicyp with $[PdCl(C_3H_5)]_2$ is an extremely efficient catalyst for allylic substitution [15], Sonogashira reaction [16] Suzuki cross-coupling [17] and for Heck vinylation [18]. Now, we wish to report on the Heck vinylation of several aryl and heteroaryl bromides with vinylsilane derivatives using Tedicyp as ligand.

2. Experimental

2.1. General

All reactions were run under argon using vacuum lines in Schlenk tubes in oven-dried glassware. The solvents were not distilled before use. Commercial vinylsilane derivatives and aryl halides were used without purification. The reactions were followed by GC and NMR for high boiling point substrates and by GC for low boiling point substrates. ^1H (300 MHz) and ^{13}C (75 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shift (δ) are reported in ppm relative to $CDCl_3$. Flash chromatographies were performed on silica gel (230–400 mesh) eluting with ether/pentane mixtures.

2.2. Preparation of the Pd-tedicyp catalyst [15]

An over-dried 40-mL Schlenk tube equipped with a magnetic stirring bar, under argon atmosphere, was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4.2 mg, 11.6 μmol) and Tedicyp (20 mg, 23.2 μmol). About 2.5 mL of anhydrous DMF were added, then the solution was stirred at room temperature for 10 min. The appropriate amount of catalyst (see tables) was transferred to the mixture of aryl halide, alkene and base in DMF (see Section 2.3).

2.3. Catalytic procedure for Heck reactions

As a typical experiment, the reaction of aryl halide (1 mmol), alkene (2 mmol, see tables) and base (2 mmol, see tables) at 130 °C during 20 h in a solvent (2 mL, see tables) in the presence of *cis,cis,cis*-1,2,3,4-tetrakis-(diphenylphosphinomethyl)cyclopentane/1/2 $[PdCl(C_3H_5)]_2$ complex under argon affords the corresponding products after addition of water, extraction with ether or dichloromethane, separation, drying ($MgSO_4$), evaporation and chromatography on silica gel.

2.4. Vinylation products (Tables 1–4)

2.4.1. 4-(2-Triethylsilanyl-vinyl)acetophenone (**1a**)

(Table 2, entry 3) 4-Bromoacetophenone (0.199 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **1a** in 84% (0.219 g) isolated yield. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.87$ (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.3$ Hz, 2H), 6.88 (d, $J = 19.3$ Hz, 1H), 6.54 (d, $J = 19.3$ Hz, 1H), 2.55 (s, 3H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.63 (q, $J = 8.0$ Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 197.6$, 143.6, 142.8, 136.2, 130.2, 128.7, 126.3, 26.6, 7.3, 3.3. Anal. Calc. for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 74.00; H, 9.27%. Before purification **1b** was also observed: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.89$ (d, $J = 2.8$ Hz, 1H), 5.64 (d, $J = 2.8$ Hz, 1H). **1c** was also observed: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.75$ (dd, $J = 10.8$ and 17.6 Hz, 1H), 5.86 (d, $J = 17.6$ Hz, 1H), 5.37 (d, $J = 10.8$ Hz, 1H).

2.4.2. 4-(2-Triethylsilanyl-vinyl)benzaldehyde (**2a**)

(Table 2, entry 8) 4-Bromobenzaldehyde (0.185 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (0.1 μmol) gave **2a** in 87% (0.214 g) isolated yield. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.98$ (s, 1H), 7.83 (d, $J = 8.1$ Hz, 2H), 7.56 (d, $J = 8.1$ Hz, 2H), 6.93 (d, $J = 19.2$ Hz, 1H), 6.63 (d, $J = 19.2$ Hz, 1H), 0.95 (t, $J = 8.0$ Hz, 9H), 0.68 (q, $J = 8.0$ Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 191.8$, 144.1, 143.5, 135.6, 131.3, 130.1, 126.8, 7.3, 3.4. Anal. Calc. for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 73.28; H, 9.17%. Before purification **2b** was also observed: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.90$ (d, $J = 2.8$ Hz, 1H), 5.66 (d, $J = 2.8$ Hz, 1H). **2c** was also observed: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.77$ (dd, $J = 10.8$ and 17.6 Hz, 1H), 5.92 (d, $J = 17.6$ Hz, 1H), 5.43 (d, $J = 10.8$ Hz, 1H).

2.4.3. 4-(2-Triethylsilanyl-vinyl)toluene (**3a**)

(Table 2, entry 22) 4-Bromotoluene (0.171 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex

Table 1
Influence of the solvent, base and vinylsilane derivative on the selectivity of the reaction (Scheme 1)

Entry	Aryl bromide	Ratio substrate/catalyst	Solvent	Base	Vinylsilane	Product	Ratio **a/b/c**[a]	Yield (%)
1	4-Bromoacetophenone	1000	DMF	K_2CO_3	Vinyltriethylsilane	**1a–c**	27/5/68	88
2	4-Bromoacetophenone	250	Xylene	K_2CO_3	Vinyltriethylsilane	**1a–c**	58/4/38	50
3	4-Bromoacetophenone	250	NMP	K_2CO_3	Vinyltriethylsilane	**1a–c**	69/3/28	87
4	4-Bromoacetophenone	250	DMAC	K_2CO_3	Vinyltriethylsilane	**1a–c**	31/3/66	100
5	4-Bromoacetophenone	250	Ethylene glycol	K_2CO_3	Vinyltriethylsilane	–	–	0
6	4-Bromobenzaldehyde	1000	DMF	K_2CO_3	Vinyltriethylsilane	**2a–c**	66/4/30	100
7	4-Bromotoluene	250	DMF	K_2CO_3	Vinyltriethylsilane	**3a–c**	75/6/19	100
8	4-Bromoanisole	1000	DMF	K_2CO_3	Vinyltriethylsilane	**4a–c**	42/9/49	97
9	1-Bromonaphthalene	250	DMF	K_2CO_3	Vinyltriethylsilane	**5a–c**	65/1/34	100
10	4-*t*Butylbromobenzene	1000	DMF	K_2CO_3	Vinyltriethylsilane	**6a–c**	46/8/46	95
11	4-*t*Butylbromobenzene	250	DMF	Na_2CO_3	Vinyltriethylsilane	**6a–c**	49/7/44	100
12	4-*t*Butylbromobenzene	250	DMF	$NaHCO_3$	Vinyltriethylsilane	**6a–c**	49/8/43	100
13	4-*t*Butylbromobenzene	250	DMF	Cs_2CO_3	Vinyltriethylsilane	**6a–c**	72/4/24	100
14	4-*t*Butylbromobenzene	250	DMF	KF	Vinyltriethylsilane	**6a–c**	61/11/28	100
15	4-*t*Butylbromobenzene	1000	DMF	AcONa	Vinyltriethylsilane	**6a–c**	91/6/3	100
16	4-*t*Butylbromobenzene	250	DMF	AcONa	Vinyltriethylsilane	**6a–c**	89/7/4	100[b]
17	4-*t*Butylbromobenzene	1000	DMF	AcONa	Vinyltriethylsilane	**6a–c**	93/6/1	84[b]
18	4-*t*Butylbromobenzene	250	DMF	AcONa	Vinyltriethylsilane	**6a–c**	93/5/2	80[c]
19	4-*t*Butylbromobenzene	1000	DMF	AcONa	Dimethylphenylvinylsilane	**7a,b**	93/7/0	75 (67)
20	4-Bromoacetophenone	1000	DMF	AcONa	Dimethylphenylvinylsilane	**8a–c**	86/12/2	100 (83)
21	4-Bromobenzophenone	1000	DMF	AcONa	Dimethylphenylvinylsilane	**9a–c**	85/13/2	100 (81)
22	1-Bromonaphthalene	250	DMF	AcONa	Dimethylphenylvinylsilane	**10a,b**	94/6/0	98 (80)
23	4-Bromoacetophenone	250	DMF	AcONa	Vinyltriphenylsilane	–	–	0
24	4-*t*Butylbromobenzene	1000	DMF	AcONa	Vinyltriphenylsilane	–	–	0

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp 1/2, aryl bromide (1 eq.), vinylsilane derivative (2 eq.), base (2 eq.), 130 °C, 20 h, GC and NMR yields, yields in parenthesis are isolated yields of product **a**.
[a] See Scheme 1.
[b] Reaction temperature 100 °C.
[c] Reaction temperature 80 °C.

(1 μmol) gave **3a** in 90% (0.209 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 6.85 (d, J = 19.2 Hz, 1H), 6.35 (d, J = 19.2 Hz, 1H), 2.33 (s, 3H), 0.96 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). Before purification **3b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.86 (d, J = 2.8 Hz, 1H), 5.66 (d, J = 2.8 Hz, 1H). **3c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.73 (d, J = 17.6 Hz, 1H), 5.20 (d, J = 10.8 Hz, 1H).

2.4.4. 4-(2-Triethylsilanyl-vinyl)anisole (*4a*)

(Table 2, entry 26) 4-Bromoanisole (0.187 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **4a** in 86% (0.214 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 19.2 Hz, 1H), 6.24 (d, J = 19.2 Hz, 1H), 3.81 (s, 3H), 0.98 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 144.2, 131.6, 127.5, 123.0, 113.9, 55.3, 7.4, 3.6. Before purification **4b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.85 (d, J = 2.8 Hz, 1H), 5.51 (d, J = 2.8 Hz, 1H). **4c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.67 (dd, J = 10.8 and 17.6 Hz, 1H), 5.60 (d, J = 17.6 Hz, 1H), 5.12 (d, J = 10.8 Hz, 1H).

2.4.5. Triethyl-[2-(naphthalen-1-yl)-vinyl]silane (*5a*)

(Table 3, entry 15) 1-Bromonaphthalene (0.207 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **5a** in 88% (0.236 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.73–7.62 (m, 2H), 7.55–7.41 (m, 3H), 6.48 (d, J = 19.2 Hz, 1H), 1.01 (t, J = 8.0 Hz, 9H), 0.73 (q, J = 8.0 Hz, 6H). Before purification **5b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.92 (d, J = 2.8 Hz, 1H), 5.84 (d, J = 2.8 Hz, 1H). **5c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.78 (d, J = 17.6 Hz, 1H), 5.47 (d, J = 10.8 Hz, 1H).

2.4.6. 4-(2-Triethylsilanyl-vinyl)-tert-butylphenyl (*6a*)

(Table 2, entry 24) 4-*t* Butylbromobenzene (0.213 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **6a** in 86% (0.236 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (m, 4H), 6.89 (d, J = 19.2 Hz, 1H), 6.38 (d, J = 19.2 Hz, 1H), 1.32 (s,

Table 2
Palladium catalysed Heck reactions with vinyltriethylsilane and *para*-substituted aryl bromides (Scheme 1)

Entry	Aryl bromide	Ratio substrate/catalyst	Product	Ratio **a/b/c**[a]	Yield (%)
1	Iodobenzene	1000	**11a,b**	92/8/0	100 (87)
2	Iodobenzene	10000	**11a,b**	91/9/0	95
3	4-Bromoacetophenone	1000	**1a–c**	88/6/6	100 (84)
4	4-Bromoacetophenone	10,000	**1a–c**	90/4/6	92
5	4-Bromobenzophenone	1000	**12a–c**	90/8/2	100
6	4-Bromobenzophenone	10,000	**12a–c**	90/6/4	100 (83)
7	4-Bromobenzaldehyde	1000	**2a–c**	95/3/2	100
8	4-Bromobenzaldehyde	10,000	**2a–c**	94/4/2	100 (87)
9	Methyl 4-bromobenzoate	1000	**13a,b**	96/4/0	100 (90)
10	Methyl 4-bromobenzoate	10,000	**13a–c**	92/6/2	91
11	4-Trifluoromethylbromobenzene	1000	**14a,b**	95/5/0	100
12	4-Trifluoromethylbromobenzene	10,000	**14a,b**	95/5/0	100 (89)
13	4-Bromobenzonitrile	1000	**15a–c**	91/5/4	100
14	4-Bromobenzonitrile	10,000	**15a,b**	94/6/0	100 (89)
15	4-Bromonitrobenzene	250	**16a,b**	92/8/0	100
16	4-Bromonitrobenzene	1000	**16a–c**	90/2/8	100 (81)
17	3,5-*bis* (Trifluoromethyl)bromobenzene	1000	**17a,b**	98/2/0	100
18	3,5-*bis* (Trifluoromethyl)bromobenzene	10,000	**17a,b**	98/2/0	100 (91)
19	4-Fluorobromobenzene	1000	**18a,b**	95/5/0	100 (86)
20	4-Fluorobromobenzene	10,000	**18a,b**	96/4/0	75
21	Bromobenzene	1000	**11a,b**	96/4/0	100
22	4-Bromotoluene	1000	**3a–c**	96/3/1	99 (90)
23	4-Bromotoluene	10,000	**3a,b**	94/6/0	83
24	4-*t*Butylbromobenzene	1000	**6a–c**	91/6/3	100 (86)
25	4-*t*Butylbromobenzene	10,000	**6a–c**	90/6/4	56
26	4-Bromoanisole	1000	**4a–c**	92/4/4	100 (86)
27	4-Bromoanisole	10,000	**4a–c**	83/5/12	74
28	2-Bromo-6-methoxynaphthalene	1000	**19a–c**	87/7/6	100 (81)
29	2-Bromo-6-methoxynaphthalene	10,000	**19a–c**	96/4/0	78
30	4-Dimethylaminobromobenzene	1000	**20a–c**	84/5/11	100 (76)

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp 1/2, aryl halide (1 eq.), vinyltriethylsilane (2 eq.), AcONa (2 eq.), DMF, 130 °C, 20 h, GC and NMR yields, yields in parenthesis are isolated yields of product **a**.
[a] See Scheme 1.

9H), 0.99 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.0, 144.6, 135.8, 126.0, 125.4, 124.8, 34.6, 31.3, 7.4, 3.5. Anal. Calc. for $C_{18}H_{30}Si$: C, 78.75; H, 11.02. Found: C, 78.60; H, 11.21%. Before purification **6b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90 (d, J = 2.8 Hz, 1H), 5.55 (d, J = 2.8 Hz, 1H). **6c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.71 (d, J = 17.6 Hz, 1H), 5.19 (d, J = 10.8 Hz, 1H).

2.4.7. *[2-(4-tert-Butyl-phenyl)-vinyl]-dimethylphenyl-silane (**7a**)*

(Table 1, entry 19) 4-*t*Butylbromobenzene (0.213 g, 1 mmol), dimethylphenylvinylsilane (0.324 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **7a** in 67% (0.197 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (m, 3H), 7.45–7.32 (m, 6H), 6.95 (d, J = 19.2 Hz, 1H), 6.56 (d, J = 19.2 Hz, 1H), 1.33 (s, 9H), 0.44 (s, 6H). Before purification **7b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.04 (d, J = 2.8 Hz, 1H), 5.66 (d, J = 2.8 Hz, 1H).

2.4.8. *[2-(4-Acetylphenyl)vinyl]dimethylphenylsilane (**8a**)*

(Table 1, entry 20) 4-Bromoacetophenone (0.199 g, 1 mmol), dimethylphenylvinylsilane (0.324 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **8a** in 83% (0.233 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.4 Hz, 2H), 7.58 (m, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.39 (m, 3H), 6.97 (d, J = 19.2 Hz, 1H), 6.75 (d, J = 19.2 Hz, 1H), 2.59 (s, 3H), 0.46 (s, 6H). Before purification **8b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.02 (d, J = 2.8 Hz, 1H), 5.76 (d, J = 2.8 Hz, 1H). **8c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.88 (d, J = 17.6 Hz, 1H), 5.40 (d, J = 10.8 Hz, 1H).

2.4.9. *[2-(4-Benzoylphenyl)vinyl]dimethylphenylsilane (**9a**)*

(Table 1, entry 21) 4-Bromobenzophenone (0.261 g, 1 mmol), dimethylphenylvinylsilane (0.324 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **9a** in 81% (0.277 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (m, 4H),

Table 3
Palladium catalysed Heck reactions with vinyltriethylsilane and *meta*- or *ortho*-substituted aryl bromides (Scheme 1)

Entry	Aryl bromide	Ratio substrate/catalyst	Product	Ratio **a/b/c**[a]	Yield (%)
1	3-Trifluoromethylbromobenzene	1000	**21a,b**	94/6/0	100
2	3-Trifluoromethylbromobenzene	10,000	**21a,b**	95/5/0	100 (92)
3	3-Bromobenzaldehyde	1000	**22a,b**	98/2/0	100 (91)
4	3-Bromobenzaldehyde	10,000	**22a,b**	94/6/0	100
5	2-Bromoacetophenone	100	**23a,b**	86/14/0	66 (52)
6	Methyl 2-bromobenzoate	250	**24a–c**	94/2/4	94
7	Methyl 2-bromobenzoate	1000	**24a,c**	97/0/3	90 (84)
8	2-Trifluoromethylbromobenzene	1000	**25a**	100/0/0	100 (92)
9	2-Bromobenzonitrile	100	**26a,b**	98/2/0	80 (72)
10	2-Bromobenzonitrile	250	**26a,b**	98/2/0	49
11	2-Bromonitrobenzene	100	**27a,b**	95/5/0	85 (79)
12	2-Bromonitrobenzene	250	**27a,b**	97/3/0	23
13	2-Fluorobromobenzene	1000	**28a,b**	97/3/0	100 (91)
14	2-Fluorobromobenzene	10,000	**28a,b**	98/2/0	67
15	1-Bromonaphthalene	1000	**5a–c**	95/2/3	100 (88)
16	1-Bromonaphthalene	10,000	**5a,b**	96/4/0	50
17	2-Bromotoluene	250	**29a**	100/0/0	100 (93)
18	2-Bromotoluene	1000	**29a**	100/0/0	74
19	2-Bromoanisole	100	**30a–c**	90/6/4	64 (54)
20	2-Bromoanisole	250	**30a–c**	93/2/5	31
21	9-Bromoanthracene	100	**31a,c**	59/0/41	63 (37)
22	2,4,6-Trimethylbromobenzene	250	**32a,c**	95/0/5	65 (57)
23	2,4,6-Trimethylbromobenzene	1000	**32a,c**	98/0/2	41

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp 1/2, aryl bromide (1 eq.), vinyltriethylsilane (2 eq.), AcONa (2 eq.), DMF, 130 °C, 20 h, GC and NMR yields, yields in parenthesis are isolated yields of product **a**.
[a] See Scheme 1.

Table 4
Palladium catalysed Heck reactions with vinyltriethylsilane and heteroaryl bromides (Scheme 1)

Entry	Aryl bromide	Ratio substrate/catalyst	Product	Ratio **a/b/c**[a]	Yield (%)
1	3-Bromopyridine	1000	**33a–c**	94/4/2	100 (86)
2	3-Bromopyridine	10,000	**33a,b**	95/5/0	100
3	4-Bromopyridine hydrochloride	250	**34a–c**	96/3/1	100 (92)[b]
4	4-Bromopyridine hydrochloride	1000	**34a,b**	97/3/0	100[b]
5	3-Bromoquinoline	1000	**35a,b**	91/9/0	100 (85)
6	3-Bromoquinoline	10,000	**35a–c**	87/7/6	56
7	4-Bromoisoquinoline	250	**36a–c**	93/2/5	100 (84)
8	4-Bromoisoquinoline	1000	**36a–c**	93/2/5	100
9	2-Bromothiophene	100	**37a,b**	94/6/0	100 (85)
10	2-Bromothiophene	250	**37a,b**	94/6/0	10
11	3-Bromothiophene	100	**38a–c**	92/7/1	100 (87)
12	3-Bromothiophene	250	**38a,b**	95/5/0	56

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp 1/2, aryl bromide (1 eq.), vinyltriethylsilane (2 eq.), AcONa (2 eq.), DMF, 130 °C, 20 h, GC and NMR yields, yields in parenthesis are isolated yields of product **a**.
[a] See Scheme 1.
[b] AcONa 3 eq.

7.64–7.35 (m, 10H), 7.02 (d, J = 19.2 Hz, 1H), 6.78 (d, J = 19.2 Hz, 1H), 0.50 (s, 6H). Before purification **9b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.07 (d, J = 2.8 Hz, 1H), 5.79 (d, J = 2.8 Hz, 1H). **9c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90 (d, J = 17.6 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H).

2.4.10. Dimethyl-[(2-naphthalen-1-yl)-vinyl]-phenylsilane (*10a*)

(Table 1, entry 22) 1-Bromonaphthalene (0.207 g, 1 mmol), dimethylphenylvinylsilane (0.324 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (4 μmol) gave **10a** in 80% (0.231 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.5 Hz, 1H), 7.90–7.35 (m, 12H), 6.67 (d, J = 19.2 Hz, 1H), 0.51 (s, 6H). Before purification **10c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.93 (d, J = 17.6 Hz, 1H), 5.87 (d, J = 10.8 Hz, 1H).

2.4.11. Triethylstyrylsilane (*11a*)

(Table 2, entry 1) Iodobenzene (0.204 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **11a** in 87% (0.190 g) isolated yield. ^{1}H

NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.3 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.25 (m, 1H), 6.90 (d, J = 19.3 Hz, 1H), 6.42 (d, J = 19.3 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). Before purification **11b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.86 (d, J = 2.8 Hz, 1 H), 5.57 (d, J = 2.8 Hz, 1H).

*2.4.12. 4-(2-Triethylsilanyl-vinyl)-benzophenone (**12a**)*

(Table 2, entry 6) 4-Bromobenzophenone (0.261 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (0.1 μmol) gave **12a** in 83% (0.267 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (m, 4H), 7.62–7.40 (m, 5H), 6.95 (d, J = 19.2 Hz, 1H), 6.60 (d, J = 19.2 Hz, 1H), 0.97 (t, J = 8.0 Hz, 9H), 0.70 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.3, 143.8, 142.4, 138.0, 136.8, 132.4, 130.7, 130.1, 130.0, 128.4, 126.2, 7.5, 3.5. Anal. Calc. for $C_{21}H_{26}OSi$: C, 78.21; H, 8.13. Found: C, 78.02; H, 8.28%. Before purification **12b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.93 (d, J = 2.8 Hz, 1H), 5.66 (d, J = 2.8 Hz, 1H). **12c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.94 (d, J = 17.6 Hz, 1H), 5.40 (d, J = 10.8 Hz, 1H).

*2.4.13. 4-(2-Triethylsilanyl-vinyl)-benzoic acid methyl ester (**13a**)*

(Table 2, entry 9) Methyl 4-bromobenzoate (0.215 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **13a** in 90% (0.249 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 7.5 Hz, 2H), 7.47 (d, J = 7.5 Hz, 2H), 6.91 (d, J = 19.2 Hz, 1H), 6.56 (d, J = 19.2 Hz, 1H), 3.90 (s, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.9, 143.7, 142.7, 129.9, 129.8, 129.2, 126.2, 52.0, 7.3, 3.4. Anal. Calc. for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75. Found: C, 69.32; H, 8.49%. Before purification **13b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.88 (d, J = 2.8 Hz, 1H), 5.62 (d, J = 2.8 Hz, 1H). **13c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.74 (dd, J = 10.8 and 17.6 Hz, 1H), 5.84 (d, J = 17.6 Hz, 1H), 5.36 (d, J = 10.8 Hz, 1H).

*2.4.14. Triethyl-[2-(4-trifluoromethyl-phenyl)-vinyl]-silane (**14a**)*

(Table 2, entry 12) 4-Trifluoromethylbromobenzene (0.225 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (0.1 μmol) gave **14a** in 89% (0.255 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 19.2 Hz, 1H), 6.55 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.68 (q, J = 8.0 Hz, 6H). Before purification **14b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.88 (d, J = 2.8 Hz, 1H), 5.65 (d, J = 2.8 Hz, 1H).

*2.4.15. 4-(2-Triethylsilanyl-vinyl)-benzonitrile (**15a**)*

(Table 2, entry 14) 4-Bromobenzonitrile (0.182 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (0.1 μmol) gave **15a** in 89% (0.217 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 19.0 Hz, 1H), 6.59 (d, J = 19.0 Hz, 1H), 0.98 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8, 142.5, 132.3, 131.5, 126.7, 118.9, 110.9, 7.3, 3.3. Anal. Calc. for $C_{15}H_{21}NSi$: C, 74.01; H, 8.70. Found: C, 74.12; H, 8.49%. Before purification **15b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.87 (d, J = 2.8 Hz, 1H), 5.65 (d, J = 2.8 Hz, 1H). **15c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90 (d, J = 17.6 Hz, 1H), 5.46 (d, J = 10.8 Hz, 1H).

*2.4.16. 4-(2-Triethylsilanyl-vinyl)-nitrobenzene (**16a**)*

(Table 2, entry 16) 4-Bromonitrobenzene (0.202 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **16a** in 81% (0.213 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 19.2 Hz, 1H), 6.66 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.68 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.1, 144.4, 142.4, 132.9, 126.8, 123.9, 7.3, 3.3. Anal. Calc. for $C_{14}H_{21}NO_2Si$: C, 63.84; H, 8.04. Found: C, 64.02;H, 8.31%. Before purification **16b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.91 (d, J = 2.8 Hz, 1H), 5.69 (d, J = 2.8 Hz, 1H). **16c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.93 (d, J = 17.6 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H).

*2.4.17. [2-(3,5-Bis-trifluoromethyl-phenyl)-vinyl]-triethylsilane (**17a**)*

(Table 2, entry 18) 3,5-Bis(trifluoromethyl)bromobenzene (0.293 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (0.1 μmol) gave **17a** in 91% (0.322 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (s, 2H), 7.73 (s, 1H), 6.92 (d, J = 19.2 Hz, 1H), 6.61 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.68 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.6, 140.2, 131.7 (q, J = 33.2 Hz), 131.6, 126.1, 123.2 (q, J = 273.0 Hz), 121.1 (q, J = 4.0 Hz), 7.3, 3.3. Anal. Calc. for $C_{16}H_{20}F_6Si$: C, 54.22; H, 5.69. Found: C, 54.21; H, 5.79%. Before purification **17b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.93 (d, J = 2.8 Hz, 1H), 5.72 (d, J = 2.8 Hz, 1H).

*2.4.18. 4-(2-Triethylsilanyl-vinyl)-fluorobenzene (**18a**)*

(Table 2, entry 19) 4-Fluorobromobenzene (0.175 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **18a** in 86% (0.203 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (dd, J = 5.5 and 8.7 Hz, 2H), 7.00 (t, J = 8.7 Hz, 2H), 6.84 (d, J = 19.2 Hz, 1H), 6.32 (d, J = 19.2 Hz, 1H), 0.97 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9 (d, J = 244.4 Hz), 143.9, 135.1, 128.1 (d, J = 8.2 Hz), 126.1, 115.7 (d, J = 21.9 Hz), 7.8, 3.9. Anal. Calc. for $C_{14}H_{21}FSi$: C, 71.13; H, 8.95. Found: C, 71.29; H, 9.14%. Before purification **18b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.83 (d, J = 2.8 Hz, 1H), 5.55 (d, J = 2.8 Hz, 1H).

*2.4.19. Triethyl-[2-(6-methoxy-naphthalen-2-yl)-vinyl]silane (**19a**)*

(Table 2, entry 28) 2-Bromo-6-methoxynaphthalene (0.237 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **19a** in 81% (0.242 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.63 (m, 4H), 7.12 (m, 2H), 7.02 (d, J = 19.2 Hz, 1H), 6.47 (d, J = 19.2 Hz, 1H), 3.91 (s, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.69 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.8, 144.9, 134.4, 134.0, 129.6, 129.0, 126.9, 126.3, 125.0, 123.9, 118.9, 105.8, 55.2, 7.4, 3.6. Anal. Calc. for $C_{19}H_{26}OSi$: C, 76.45; H, 8.78. Found: C, 76.22; H, 8.77%. Before purification **19b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.96 (d, J = 2.8 Hz, 1H), 5.62 (d, J = 2.8 Hz, 1H). **19c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.81 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.8 Hz, 1H).

*2.4.20. Dimethyl-[4-(2-triethylsilanyl-vinyl)-phenyl]-amine (**20a**)*

(Table 2, entry 30) 4-Bromo-*N,N*-dimethylaniline (0.200 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **20a** in 76% (0.199 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 19.2 Hz, 1H), 6.67 (d, J = 8.6 Hz, 2H), 6.14 (d, J = 19.2 Hz, 1H), 2.96 (s, 6H), 0.97 (t, J = 8.0 Hz, 9H), 0.63 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.3, 144.7, 127.5, 127.4, 120.0, 112.3, 40.5, 7.4, 3.6. Anal. Calc. for $C_{16}H_{27}NSi$: C, 73.49; H, 10.41. Found: C, 73.37; H, 10.67%. Before purification **20b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.85 (d, J = 2.8 Hz, 1H), 5.44 (d, J = 2.8 Hz, 1H). **20c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.53 (d, J = 17.6 Hz, 1H), 5.02 (d, J = 10.8 Hz, 1 H).

*2.4.21. Triethyl-[2-(3-trifluoromethyl-phenyl)-vinyl]-silane (**21a**)*

(Table 3, entry 2) 3-Trifluoromethylbromobenzene (0.225 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (0.1 μmol) gave **21a** in 92% (0.263 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (s, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.52–7.35 (m, 2H), 6.90 (d, J = 19.2 Hz, 1H), 6.52 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.2, 139.2, 130.9 (q, J = 32.1 Hz), 129.4, 128.8, 128.7, 124.3 (q, J = 4.0 Hz), 124.1 (q, J = 272.5 Hz), 123.0 (q, J = 3.4 Hz), 7.3, 3.4. Anal. Calc. for $C_{15}H_{21}F_3Si$: C, 62.90; H, 7.39. Found: C, 63.06; H, 7.24%. Before purification **21b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.89 (d, J = 2.8 Hz, 1H), 5.64 (d, J = 2.8 Hz, 1H).

*2.4.22. 3-(2-Triethylsilanyl-vinyl)benzaldehyde (**22a**)*

(Table 3, entry 3) 3-Bromobenzaldehyde (0.185 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **22a** in 91% (0.224 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.0 (s, 1H), 7.94 (s, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 19.2 Hz, 1H), 6.55 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.4, 143.2, 139.4, 136.6, 132.2, 129.2, 129.0, 128.7, 127.2, 7.3, 3.4. Anal. Calc. for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 73.31; H, 8.87%. Before purification **22b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.92 (d, J = 2.8 Hz, 1H), 5.66 (d, J = 2.8 Hz, 1H).

*2.4.23. 2-(2-Triethylsilanyl-vinyl)acetophenone (**23a**)*

(Table 3, entry 5) 2-Bromoacetophenone (0.199 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (10 μmol) gave **23a** in 52% (0.135 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (m, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 19.2 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 6.31 (d, J = 19.2 Hz, 1H), 2.57 (s, 3H), 1.00 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.3, 143.7, 138.9, 137.5, 131.4, 130.2, 128.4, 127.5, 127.3, 29.9, 7.3, 3.5. Anal. Calc. for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.50; H, 9.47%. Before purification **23b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.64 (d, J = 2.8 Hz, 1H), 5.62 (d, J = 2.8 Hz, 1H).

*2.4.24. 2-(2-Triethylsilanyl-vinyl)-benzoic acid methyl ester (**24a**)*

(Table 3, entry 7) Methyl 2-bromobenzoate (0.215 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium

acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **24a** in 84% (0.232 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 19.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 6.32 (d, J = 19.2 Hz, 1H), 3.89 (s, 3H), 0.99 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 143.7, 140.5, 131.9, 130.2, 129.6, 128.4, 127.3, 127.2, 52.0, 7.4, 3.5. Anal. Calc. for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75. Found: C, 69.78; H, 8.45%. Before purification **24b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.60 (d, J = 2.8 Hz, 1H), 5.56 (d, J = 2.8 Hz, 1H). **24c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.63 (d, J = 17.6 Hz, 1H), 5.34 (d, J = 10.8 Hz, 1H).

2.4.25. Triethyl-[2-(2-trifluoromethyl-phenyl)-vinyl]-silane (*25a*)

(Table 3, entry 8) 2-Trifluoromethylbromobenzene (0.225 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **25a** in 92% (0.263 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 19.2 Hz, 1H), 6.42 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.68 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.6 (d, J = 2.3 Hz), 138.1 (d, J = 1.7 Hz), 131.8, 131.7 127.3, 127.1, 127.0 (q, J = 29.8 Hz), 125.5, (q, J = 5.7 Hz), 124.4 (q, J = 273.6 Hz), 7.3, 3.4. Anal. Calc. for $C_{15}H_{21}F_3Si$: C, 62.90; H, 7.39. Found: C, 62.76; H, 7.51%.

2.4.26. 2-(2-Triethylsilanyl-vinyl)-benzonitrile (*26a*)

(Table 3, entry 9) 2-Bromobenzonitrile (0.182 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (10 μmol) gave **26a** in 72% (0.175 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 19.2 Hz, 1H), 6.65 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.70 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.5, 140.1, 133.1, 132.9, 132.6, 127.8, 125.4, 117.8, 111.0, 7.3, 3.3. Anal. Calc. for $C_{15}H_{21}NSi$: C, 74.01; H, 8.70. Found: C, 73.81; H, 8.57%. Before purification **26b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.92 (d, J = 2.8 Hz, 1H), 5.85 (d, J = 2.8 Hz, 1H).

2.4.27. 2-(2-Triethylsilanyl-vinyl)-nitrobenzene (*27a*)

(Table 3, entry 11) 2-Bromonitrobenzene (0.202 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (10 μmol) gave **27a** in 79% (0.208 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 19.2 Hz, 1H), 6.43 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.7, 139.8, 134.6, 133.1, 132.9, 128.5, 128.1, 124.2, 7.3, 3.3. Anal. Calc. for $C_{14}H_{21}NO_2Si$: C, 63.84; H, 8.04. Found: C, 63.59; H, 8.05%. Before purification **27b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.68 (d, J = 2.8 Hz, 1H), 5.62 (d, J = 2.8 Hz, 1H).

2.4.28. 2-(2-Triethylsilanyl-vinyl)-fluorobenzene (*28a*)

(Table 3, entry 13) 2-Fluorobromobenzene (0.175 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **28a** in 91% (0.215 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (t, J = 7.8 Hz, 1H), 7.19 (m, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.10 (d, J = 19.2 Hz, 1H), 7.01 (t, J = 7.7 Hz, 1H), 6.48 (d, J = 19.2 Hz, 1H), 0.98 (t, J = 8.0 Hz, 9H), 0.68 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1 (d, J = 249.0 Hz), 136.4 (d, J = 4.6 Hz), 129.1, 129.0, 126.6 (d, J = 3.4 Hz), 126.3 (d, J = 11.5 Hz), 123.9 (d, J = 3.5 Hz), 115.7 (d, J = 21.8 Hz), 7.4, 3.4. Anal. Calc. for $C_{14}H_{21}FSi$: C, 71.13; H, 8.95. Found: C, 71.29; H, 8.84%. Before purification **28b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.84 (d, J = 2.8 Hz, 1H), 5.70 (d, J = 2.8 Hz, 1H).

2.4.29. 2-(2-Triethylsilanyl-vinyl)toluene (*29a*)

(Table 3, entry 17) 2-Bromotoluene (0.171 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (4 μmol) gave **29a** in 93% (0.216 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.5 Hz, 1H), 7.18–7.08 (m, 4H), 6.28 (d, J = 19.2 Hz, 1H), 2.36 (s, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H).

2.4.30. 4-(2-Triethylsilanyl-vinyl)anisole (*30a*)

(Table 3, entry 19) 2-Bromoanisole (0.187 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (10 μmol) gave **30a** in 54% (0.134 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 19.2 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H), 6.38 (d, J = 19.2 Hz, 1H), 3.84 (s, 3H), 0.98 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 139.0, 128.9, 127.7, 126.1, 126.0, 120.6, 111.0, 55.5, 7.4, 3.6. Anal. Calc. for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74. Found: C, 72.41; H, 9.87%. Before purification **30b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.76 (d, J = 2.8 Hz, 1H), 5.59 (d, J = 2.8 Hz, 1H). **30c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.72 (d, J = 17.6 Hz, 1H), 5.24 (d, J = 11.7 Hz, 1H).

*2.4.31. (2-Anthracen-9-yl-vinyl)-triethylsilane (**31a**)*

(Table 3, entry 21) 9-Bromoanthracene (0.257 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (10 μmol) gave **31a** in 37% (0.118 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 8.31–8.22 (m, 2H), 8.00 (m, 2H), 7.70 (d, J = 19.2 Hz, 1H), 7.50–7.40 (m, 4H), 6.28 (d, J = 19.2 Hz, 1H), 1.13 (t, J = 8.0 Hz, 9H), 0.85 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.9, 137.3, 135.9, 131.4, 128.7, 128.6, 126.0, 125.9, 125.3, 125.1, 7.6, 3.6. Anal. Calc. for $C_{22}H_{26}Si$: C, 82.96;H, 8.23. Found: C, 82.70; H, 8.27%. Before purification **31c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.01 (d, J = 11.6 Hz, 1H), 5.64 (d, J = 17.7 Hz, 1H).

*2.4.32. Triethyl-[2-(2,4,6-trimethyl-phenyl)-vinyl]silane (**32a**)*

(Table 3, entry 22) 2-Bromomesitylene (0.199 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (4 μmol) gave **32a** in 57% (0.148 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.92–6.85 (m, 3H), 5.84 (d, J = 19.2 Hz, 1H), 2.39 (s, 3H), 2.28 (s, 6H), 1.02 (t, J = 8.0 Hz, 9H), 0.69 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.8, 137.0, 135.9, 135.1, 131.9, 128.5, 20.9, 20.7, 7.4, 3.5. Anal. Calc. for $C_{17}H_{28}Si$: C, 78.38; H, 10.83. Found: C, 78.57; H, 10.70%. Before purification **32c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.70 (dd, J = 10.8 and 17.6 Hz, 1H), 5.54 (d, J = 10.8 Hz, 1H), 5.25 (d, J = 17.6 Hz, 1H).

*2.4.33. 3-(2-Triethylsilanyl-vinyl)pyridine (**33a**)*

(Table 4, entry 1) 3-Bromopyridine (0.158 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **33a** in 86% (0.189 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 8.45 (m, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.25 (m, 1H), 6.85 (d, J = 19.2 Hz, 1H), 6.51 (d, J = 19.2 Hz, 1H), 0.96 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.7, 148.5, 141.1, 133.8, 132.6, 129.4, 123.4, 7.3, 3.3. Anal. Calc. for $C_{13}H_{21}NSi$: C, 71.17;H, 9.65. Found: C, 70.97; H, 9.79%. Before purification **33b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.89 (d, J = 2.8 Hz, 1H), 5.66 (d, J = 2.8 Hz, 1H). **33c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.83 (d, J = 17.6 Hz, 1H), 5.34 (d, J = 10.8 Hz, 1H).

*2.4.34. 4-(2-Triethylsilanyl-vinyl)pyridine (**34a**)*

(Table 4, entry 3) 4-Bromopyridine hydrochloride (0.195 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.246 g, 3 mmol), DMF (2 mL) and Pd complex (4 μmol) gave **34a** in 92% (0.202 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35 (d, J = 6.1 Hz, 2H), 7.13 (d, J = 6.1 Hz, 2H), 6.65 (d, J = 19.2 Hz, 1H), 6.53 (d, J = 19.2 Hz, 1H), 0.76 (t, J = 8.0 Hz, 9H), 0.50 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.6, 145.6, 142.1, 133.0, 120.8, 7.3, 3.2. Anal. Calc. for $C_{13}H_{21}NSi$: C, 71.17; H, 9.65. Found: C, 71.38; H, 9.62%. Before purification **34b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.75 (d, J = 2.8 Hz, 1H), 5.50 (d, J = 2.8 Hz, 1H). **34c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.80 (d, J = 17.6 Hz, 1H), 5.31 (d, J = 10.8 Hz, 1H).

*2.4.35. 3-(2-Triethylsilanyl-vinyl)quinoline (**35a**)*

(Table 4, entry 5) 3-Bromoquinoline (0.208 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (1 μmol) gave **35a** in 85% (0.229 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.03 (s, 1H), 8.07 (m, 2H), 7.79 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 19.2 Hz, 1H), 6.68 (d, J = 19.2 Hz, 1H), 1.00 (t, J = 8.0 Hz, 9H), 0.71 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4, 147.6, 141.4, 132.3, 131.1, 129.6, 129.2, 129.1, 128.0, 127.9, 126.8, 7.3, 3.4. Anal. Calc. for $C_{17}H_{23}NSi$: C, 75.78; H, 8.60. Found: C, 75.88; H, 8.73%. Before purification **35b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.02 (d, J = 2.8 Hz, 1H), 5.77 (d, J = 2.8 Hz, 1H). **35c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.97 (d, J = 17.6 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H).

*2.4.36. 4-(2-Triethylsilanyl-vinyl)isoquinoline (**36a**)*

(Table 4, entry 7) 4-Bromoisoquinoline (0.208 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (4 μmol) gave **36a** in 84% (0.226 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.15 (s, 1H), 8.64 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.73 (t, J = 7.8 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.51 (d, J = 19.3 Hz, 1H), 6.56 (d, J = 19.3 Hz, 1H), 1.04 (t, J = 8.0 Hz, 9H), 0.73 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.9, 140.6, 139.0, 133.3, 133.0, 131.6, 130.4, 130.2, 128.0, 127.0, 122.8, 7.4, 3.4. Anal. Calc. for $C_{17}H_{23}NSi$: C, 75.78; H, 8.60. Found: C, 75.99; H, 8.55%. Before purification **36b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.99 (d, J = 2.8 Hz, 1H), 5.92 (d, J = 2.8 Hz, 1H). **36c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.86 (d, J = 17.6 Hz, 1H), 5.57 (d, J = 10.8 Hz, 1H).

*2.4.37. Triethyl-(2-thiophen-2-yl-vinyl)silane (**37a**)*

(Table 4, entry 9) 2-Bromothiophene (0.163 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (10 μmol) gave **37a** in 85% (0.191 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (m, 1H), 7.00–6.92

(m, 3H), 6.15 (d, J = 19.2 Hz, 1H), 0.96 (t, J = 8.0 Hz, 9H), 0.63 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.5, 137.3, 127.4, 125.8, 125.4, 124.6, 7.3, 3.4. Anal. Calc. for $C_{12}H_{20}SSi$: C, 64.22; H, 8.98. Found: C, 63.97; H, 9.10%. Before purification **37b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.09 (d, J = 2.8 Hz, 1H), 6.45 (d, J = 2.8 Hz, 1H).

*2.4.38. Triethyl-(2-thiophen-3-yl-vinyl)silane (**38a**)*

(Table 4, entry 11) 3-Bromothiophene (0.163 g, 1 mmol), vinyltriethylsilane (0.284 g, 2 mmol), sodium acetate (0.164 g, 2 mmol), DMF (2 mL) and Pd complex (10 μmol) gave **38a** in 87% (0.195 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 2H), 7.17 (m, 1H), 6.87 (d, J = 19.2 Hz, 1H), 6.18 (d, J = 19.2 Hz, 1H), 0.97 (t, J = 8.0 Hz, 9H), 0.64 (q, J = 8.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.3, 138.6, 125.8, 125.6, 124.9, 122.3, 7.4, 3.4. Anal. Calc. for $C_{12}H_{20}SSi$: C, 64.22; H, 8.98. Found: C, 64.00; H, 8.87%. Before purification **38b** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.01 (d, J = 2.8 Hz, 1H), 5.52 (d, J = 2.8 Hz, 1H). **38c** was also observed: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.42 (d, J = 17.6 Hz, 1H), 5.32 (d, J = 10.8 Hz, 1H).

2.8. CAS Registry Nos.: **3a**, 327999-88-2; **4a**, 327999-89-3; **5a**, 644998-08-3; **11a**, 21209-32-5; **14a**, 724785-95-9; **29a**, 327999-87-1.

3. Results and discussion

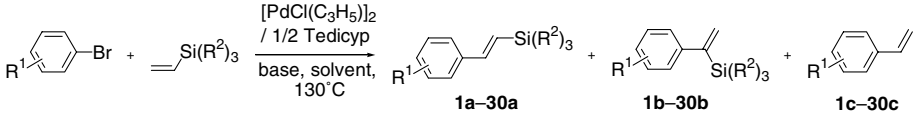
3.1. Influence of the reactions conditions on the selectivity

First, we have investigated the influence of the base, solvent and substituents on the vinylsilane derivative on the selectivity of the reaction with our catalyst (Scheme 1, Table 1). The reactions were performed at 130 °C, under argon, in the presence of a ratio 1/2 of $[Pd(C_3H_5)Cl]_2$/tedicyp as catalyst. The results presented in the Table 1 disclose a strong influence of the reaction conditions on the selectivity of the reaction. The first experiments were performed using 4-bromoacetophenone, vinyltriethylsilane, potassium carbonate as base with a few solvents. In the presence of DMF, xylene, NMP or DMAC the (*E*)-triethyl(2-arylethenyl)silane products **a** were obtained, but the reaction was not selective and the formation of large amounts of styrene derivatives **c** was also observed (Table 1, entries 1–4). When ethylene glycol was used as solvent, no vinylation product was observed (Table 1, entry 5). Next, in order to improve the selectivity of the reaction in favour of the formation of (*E*)-triethyl(2-arylethenyl)silane derivatives **a** we performed a few coupling reactions using electron-rich, electron-poor or sterically hindered arylbromides. In all cases, mixtures of (*E*)-triethyl(2-arylethenyl)silane **a**, triethyl(1-arylethenyl)silane **b** and styrene derivatives **c** were obtained (Table 1, entries 6–10). Then, we studied the influence of the base for the coupling of 4-*t* butylbromobenzene with vinyltriethylsilane. Disappointing low selectivities were also obtained using sodium carbonate, sodium hydrogen carbonate, cesium carbonate or potassium fluoride (Table 1, entries 11–14). On the other hand, a much higher selectivity in favour of the formation of (*E*)-4-(2-triethylsilanyl-vinyl)-tert-butylphenyl **6a** was observed using sodium acetate as base (Table 1, entry 15). With this base, using lower reaction temperatures (100 and 80 °C) high selectivities in favour or isomer **6a** were also obtained, but lower reactions rates were observed (Table1, entries 16–18). Finally, the selectivity using two other vinylsilanes derivatives was studied. Dimethylphenylvinylsilane with four aryl bromides using sodium acetate as base gave the (*E*)-dimethylphenyl(2-arylethenyl)silane derivatives **7a**–**10a** with 86–93% selectivities in the presence of 0.4–0.1% catalyst. Vinyltriphenylsilane using similar reaction conditions gave no vinylation product (Table 1, entries 19–24).

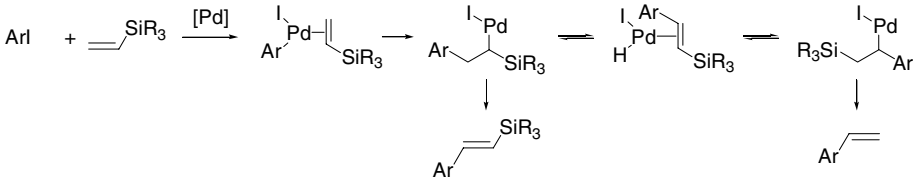
Hallberg et al. have explained the formation of styrene derivatives for this reaction by desilylation during the catalytic cycle [5]. After ordinary Heck arylation on the terminal or internal carbon, an elimination–readdition of HPdI followed by desilylation would occur (Scheme 2). They had observed that in the presence of silver nitrate this desilylation was suppressed. They assumed that a silver-mediated abstraction of iodide from the arylpalladium iodide takes place. This intermediate would form a π alkene–palladium complex from which the aryl is transferred to the terminal position which is not prone to desilylation. Then, the (arylethenyl)silane would be formed after irreversible elimination of a PdH species.

Jeffery [13] had observed that high selectivities in favour of the formation of (*E*)-dimethylphenyl(2-arylethenyl)silane derivatives **a** could also be obtained using tetra-*n*-butylammonium acetate as base or in the presence of a mixture of tetra-*n*-butylammonium acetate and potassium acetate instead of silver nitrate.

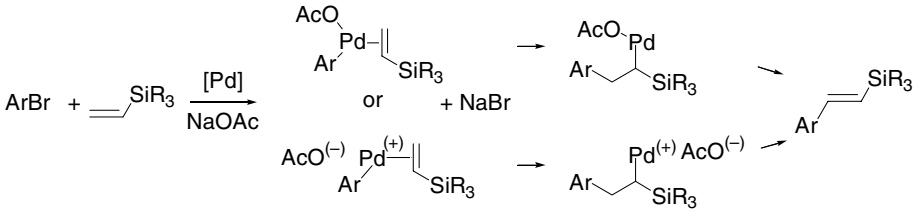
We believe that with our tetraphosphine/palladium catalyst in the presence of sodium acetate abstraction of bromide from the arylpalladium bromide intermediate to form an arylpalladium acetate and sodium



Scheme 1.



Scheme 2.



Scheme 3.

bromide takes place (Scheme 3). Then, the arylpalladium acetate would lead to an $ArCH_2CH(SiR_3)$(PdOAc) intermediate. This complex would give the (arylethenyl)silane rather than to be involved in an elimination–readdition process of HPdOAc.

In order to determine the scope and limitations of the reaction with triethylvinylsilane and aryl bromides in the presence of sodium acetate and the tedicyp/palladium complex; the reaction was applied to several *para*-substituted aryl bromides (Table 2), *meta*- and *ortho*-substituted aryl bomides (Table 3) and heteroaryl bromides (Table 4).

3.2. Reaction with para-substituted aryl bromides

Several reactions were performed using *para*-substituted aryl bromides and vinyltriethylsilane with sodium acetate as base in DMF. We observed that in most cases the reaction proceeds very smoothly with high selectivities in favour of the formation of (*E*)-dimethylphenyl(2-arylethenyl)silane derivatives **a**, moreover, a wide variety of functional groups are tolerated (Table 2). Similar reaction rates were obtained with electron-rich and electron-poor aryl bromide. For example, turnover numbers of 7500–10,000 can be achieved with this catalyst for activated substrates such as 4-bromoacetophenone, 4-bromobenzaldehyde, 4-bromobenzophenone, 4-bromobenzonitrile and 4-fluorobromobenzene (Table 2, entries 3–20). With the deactivated aryl bromides: 4-*t* butylbromobenzene, 4-bromoanisole and 4-dimethylaminobromobenzene TONs of 5600, 7400 and 1000 were obtained, respectively (Table 2, entries 24–27 and 30). This observation seems to indicate that the oxidative addition of the aryl bromide to the palladium complex is generally not the rate-limiting step of this reaction. Similar selectivities in favour of the formation of (*E*)-triethyl(2-arylethenyl)silane derivatives **a** were observed with electron-poor (88–98%) and with electron-rich aryl bromides (84–96%).

3.3. Reaction with meta- and ortho-substituted aryl bromides

The influence of *meta* or *ortho* substituents on the aryl bromide on the reaction rate is reported in the Table 3. As expected very similar TONs were obtained with the *meta*-substituted aryl bromides 3-trifluoromethylbromobenzene and 3-bromobenzaldehyde than with the *para*-substituted substrates (Table 3, entries 1–4). *ortho*-Substituents on the aryl bromides generally have a more important effect on the reactions rates of Heck reactions [18b]. However, with vinyltriethylsilane high TONs were obtained in some cases with *ortho*-substituted aryl bromides. We observed that the coupling of methyl 2-bromobenzoate, 2-trifluoromethylbromobenzene, 2-fluorobromobenzene, 1-bromonaphthalene or 2-bromotoluene proceeds in the presence of 0.1–0.01% catalyst (Table 3, entries 6–8 and 13–18). On the other hand, 2-bromoacetophenone, 2-bromobenzonitrile, 2-bromonitrobenzene or 2-bromoanisole also gave the expected adducts, but in the presence of 1–0.4% catalyst (Table 3, entries 5, 9–12, 19 and 20). In all cases very high selectivities in favour of the formation of (*E*)-triethyl(2-arylethenyl)silane derivatives **a** were observed (86–100%).

Next, we tried to evaluate the difference of reaction rate between mono- and di-*ortho*-substituted aryl bromides, and we observed that even very hindered aryl bromides could be coupled efficiently with vinyltriethylsilane (Table 3, entries 21–23). For example, with 2,4,6-trimethylbromobenzene the expected (*E*)-triethyl(2-mesitylethenyl)silane **32a** was obtained in 57%

yield and 95% selectivity in the presence of 0.4% catalyst. A much lower selectivity in favour of the formation of (*E*)-triethyl(2-anthracenylethenyl)silane **31a** was observed with 9-bromoanthracene. With this substrate the formation of a large amount of 9-vinylanthracene **31c** was also obtained. These two sterically congested di-*ortho*-substituted aryl bromides gave no traces of branched isomers **b**.

3.4. Reaction with heteroaryl bromides

Palladium chemistry involving heterocycles has its unique characteristics stemming from the heterocycles' inherently different structural and electronic properties in comparison to the corresponding carbocyclic aryl compounds. Pyridines are π-electron deficient. Thiophenes are π-electron excessive. If the oxidative addition of the aryl halides to the palladium complex is the rate-limiting step of the reaction with this catalyst, the reactions should be slower with thiophenes than with pyridines. Furthermore, palladium(II) possesses strong thiophilicity. This is reflected in the poisoning effects of the sulphur atom on some palladium-catalysed reactions. This poisoning effect has also been observed in the presence of nitrogen atom. For this reason, the position of the halide on a heteroaromatic ring has an effect on the reactions rates.

First, we studied the influence of position of the bromo substituent on bromopyridines or bromoquinolines on the rate of the coupling with vinyltriethylsilane. Due to the electronegativity of the nitrogen atom, the α position of bromopyridines should be the most susceptible to the oxidative addition to Pd(0). In fact, we observed better results for the coupling of 3- and 4-bromopyridine than with 2-bromopyridine (Table 4, entries 1–4). The reaction of 2-bromopyridine with 1% catalyst gave no coupling product. These results seem to indicate that with the α-substituted 2-bromopyridine, a possible interaction between the nitrogen atom and the palladium complex has a deleterious effect on the reaction. On the other hand, 3-bromopyridine, 3-bromoquinoline, 4-bromopyridine hydrochloride and 4-bromoisoquinoline gave the expected vinylation adducts in good yields with as little as 0.1–0.01% catalyst. The selectivities in favour of the *E* isomers **a** are very high (91–97%). Traces of the styrene derivatives **c** were also observed for some reactions with these substrates.

Thiophenes are π-electron-excessive heterocycles. Oxidative addition to palladium should be slower with bromothiophenes, than with bromopyridines. 2-Bromo and 3-bromothiophenes with vinyltriethylsilane led to the vinylation *E* adducts **37a** and **38a** with high selectivities (92–95%) but with very low TONs of 100 and 140 (Table 4, entries 9–12). With these substrates the oxidative addition is probably the rate-limiting step of the reaction, but a poisoning effects of the sulphur atom is also possible.

4. Conclusion

The Tedicyp–palladium complex provides a convenient catalyst for the reaction of several aryl or heteroaryl bromides with vinylsilanes. In the presence of this catalyst, the (*E*)-triethyl(2-arylethenyl)silane adducts **a** were obtained selectively in good yields when sodium acetate was used as base. With several substrates, the reaction can be performed with as little as 0.01% catalyst. In general, traces of triethyl(1-arylethenyl)vinylsilanes **b** and desilylation products **c** were also observed. With other bases such as potassium, sodium or cesium carbonates, the formation of large amounts of the styrene derivatives was observed. This procedure avoids the use of expensive silver nitrate or the addition of stoechiometric amounts of ammonium salts as additives. A wide range of functions such as methoxy, fluoro, acetyl, formyl, benzoyl, carboxylate, nitro, dimethylamino or nitrile on the aryl bromide are tolerated. To date, only a few other ligands have achieved this objective; most of the other ligands were used with more reactive but more expensive aryl iodides. These results represent economically attractive procedures and due to the high price of palladium, the practical advantage of such low catalyst loading reactions can become increasingly important for industrial processes.

Acknowledgements

We thank the CNRS and the "Conseil Général des Bouches-du-Rhône, Fr" for providing financial support.

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