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Reaction of aryl di-, tri-, or tetrabromides with arylboronic acids or alkenes in the presence of a palladium-tetraphosphine catalyst

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Abstract

cis,cis,cis-1,2,3,4-Tetrakis(diphenylphosphinomethyl)cyclopentane/$\frac{1}{2}$[PdCl(C_3H_5)]$_2$ system catalyses the Suzuki and Heck reactions of aryl di-, tri-, or tetrabromides with a range of arylboronic acids or alkenes with moderate to high ratio substrate/catalyst in good yields. Aryl polybromides such as dibromobenzenes, 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene, dibromopyridines or a dibromothiophene have been successfully used. Convenient synthesis of a variety of di- and triarylated or vinylated compounds and even a 1,2,4,5-tetraarylated compound were prepared by use of this reaction.

Keywords: Tetraphosphine; Palladium; Suzuki-coupling; Heck-vinylation; Arylboronic acids; Alkenes; Aryl bromides

1. Introduction

The palladium-catalysed Heck vinylation and Suzuki cross-coupling reactions are two of the most powerful methods for the formation of C–C bonds [1–3]. The efficiency of several catalysts for the reaction of bromo- and iodobenzene derivatives has been studied in detail [4,5]. On the other hand, the reaction in the presence of dihalo-, trihalo- and tetrahalobenzene derivatives such as di-, tri-, tetrabromobenzenes, dibromopyridines or dibromothiophenes with thermally stable palladium catalysts has attracted less attention. A few ligands have been successfully employed for the reaction in the presence of polybromo- or polyiodobenzene derivatives. The most popular ones are triphenylphosphine and tri(*o*-tolyl)phosphine, but the palladium complexes formed with these ligands are generally not very efficient in terms of substrate/catalyst ratio [6–11]. The reaction also proceeds with $Pd(OAc)_2$ without added ligand [12]. In recent years, the ligand P(*t*-Bu)$_3$ has also been successfully tested with these substrates [13,14]. With this ligand good results have been reported by Crociani and co-workers [13] for Heck reaction on dibromobenzene derivatives. Hollow palladium spheres also efficiently catalyses Suzuki reaction in the presence of 1,4-diiodobenzene [15]. If monophosphine ligands have been successfully used for the reaction with these aryl polyhalides derivatives, to the best of our knowledge, the efficiency of tetraphosphine ligands has not been demonstrated.

The nature of the phosphine ligand on complexes has an important influence on the stability of the catalysts and on the rate of the reactions. 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) [16]. in which the four

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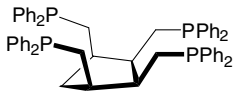


Tedicyp

Fig. 1.

diphenylphosphinoalkyl groups are stereospecifically bound to the same face of the cyclopentane ring.

We have reported that the complex formed by association of Tedicyp with $[PdCl(C_3H_5)]_2$ is an extremely efficient catalyst for allylic substitution [16], Sonogashira alkynylation [17], Heck vinylation reaction [18] and for the Suzuki cross-coupling of arylhalides with arylboronic acids [19]. Now, we wish to describe the results obtained with several aryl and heteroaryl polyhalides with a variety of alkenes and arylboronic acids using Tedicyp as ligand.

2. Experimental

2.1. General

All reactions under argon were run using vacuum lines in Schlenk tubes in oven-dried glassware. Xylene analytical grade (98%) and DMF (99%) were not distilled before use. Some of the aryl halides were distilled before use. Potassium carbonate (99+) was used without drying. 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 chromatography were performed on silica gel (230–400 mesh) eluting with ether/pentane mixtures.

2.2. Preparation of the Pd-Tedicyp catalyst [16]

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). 2.5 ml of anhydrous DMF were added, then the solution was stirred at room temperature for 10 min.

2.3. Catalytic procedure for Heck reactions

As a typical experiment, the reaction of aryl halide (1 mmol), alkene (4–6 mmol, see Tables 1 and 2) and K_2CO_3 (4–6 mmol, see Tables 1 and 2) at 130 °C during 20 h in dry DMF (3 ml) in the presence of *cis,cis,cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane/$\frac{1}{2}[PdCl(C_3H_5)]_2$ 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 with di- and tribromobenzene (Table 1)

2.4.1. n-Butyl (E,E)-4-(2-n-butoxycarbonylvinyl)cinnamate (**1a**): (Table 1, entry 1)

1,4-Dibromobenzene (0.236 g, 1 mmol), Pd complex (0.1 μmol) and *n*-butyl acrylate (0.512 g, 4 mmol). The residue was purified by column chromatography

Table 1
Palladium catalysed Heck reactions with di- or tribromobenzenes (Schemes 1 and 2)

Entry	Aryl bromide	Alkene	Ratio substrate/catalyst	Product	Ratio **a/b** or **a/b/c**[a]	Yield in product **a** (%)
1	1,4-Dibromobenzene	*n*-Butyl acrylate	10,000	**1a**	100/0	87
2	1,4-Dibromobenzene	*n*-Butyl acrylate	100,000	**1a**, **1b**	70/30	61[b]
3	1,4-Dibromobenzene	Styrene	10,000	**2a**	100/0	78
4	1,4-Dibromobenzene	Styrene	100,000	**2a**, **2b**	30/70	83[b]
5	1,4-Dibromobenzene	3-Methylstyrene	1000	**3a**	100/0	85
6	1,4-Dibromobenzene	3-Chlorostyrene	1000	**4a**	100/0	86
7	1,2-Dibromobenzene	*n*-Butyl acrylate	2500	**5a**	100/0	81
8	1,2-Dibromobenzene	Styrene	2000	**6a**	100/0	79
9	1,2-Dibromobenzene	Styrene	10,000	**6a**, **6b**	76/24	61[b,c]
10	1,2-Dibromobenzene	3-Methylstyrene	250	**7a**	100/0	82
11	1,2-Dibromobenzene	3-Chlorostyrene	250	**8a**	100/0	78
12	1,3-Dibromobenzene	*n*-Butyl acrylate	10,000	**9a**	100/0	88
13	1,3-Dibromobenzene	*n*-Butyl acrylate	100,000	**9a**, **9b**	20/80	47[b]
14	1,3-Dibromobenzene	Styrene	10,000	**10a**	100/0	84
15	1,3,5-Tribromobenzene	*n*-Butyl acrylate	100	**11a**	100/0/0	73[d]
16	1,3,5-Tribromobenzene	*n*-Butyl acrylate	250	**11b**, **11c**	0/64/36	100[b,c]

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp 1/2, aryl bromide (1 eq.), alkene (4 eq.), K_2CO_3 (4 eq.), DMF, 130 °C, 20 h, isolated yields.

[a] See Schemes 1 and 2.

[b] GC yield (mixture of mono-, di- and triaddition products).

[c] Alkene (6 eq.) and K_2CO_3 (6 eq.).

[d] Solvent NMP, 150 °C.

Table 2
Palladium catalysed Heck reactions with dibromopyridines or 3,4-dibromothiophene (Schemes 3 and 4)

Entry	Aryl bromide	Alkene	Ratio substrate/catalyst	Product	Ratio **a**/**b**[a]	Yield in product **a** (%)
1	3,5-Dibromopyridine	*n*-Butyl acrylate	1000	**12a**	100/0	76
2	3,5-Dibromopyridine	Styrene	500	**13a**	100/0	79
3	3,5-Dibromopyridine	3-Methylstyrene	100	**14a**	100/0	83
4	2,6-Dibromopyridine	*n*-Butyl acrylate	100	**15a**	100/0	62
5	2,6-Dibromopyridine	*n*-Butyl acrylate	250	**15a**, **15b**	70/30	54[b]
6	2,6-Dibromopyridine	Styrene	100	**16a**	100/0	78
7	2,6-Dibromopyridine	3-Methylstyrene	100	**17a**, **17b**	58/42	47
8	2,6-Dibromopyridine	3-Chlorostyrene	100	**18a**	100/0	77
9	3,4-Dibromothiophene	*n*-Butyl acrylate	25	**19a**	100/0	95[c]
10	3,4-Dibromothiophene	*n*-Butyl acrylate	250	**19a**, **19b**	18/82	65[c]
11	3,4-Dibromothiophene	Styrene	250	**20a**	100/0	82
12	3,4-Dibromothiophene	Styrene	1000	**20a**, **20b**	48/52	100[b]
13	3,4-Dibromothiophene	Styrene	5000	**20b**	0/100	20[b]
14	3,4-Dibromothiophene	3-Methylstyrene	250	**21a**	100/0	78
15	3,4-Dibromothiophene	3-Chlorostyrene	250	**22a**	100/0	80

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp 1/2, heteroaryl bromide (1 eq.), alkene (4 eq.), K_2CO_3 (4 eq.), NMP, 150 °C, 20 h, isolated yields.
[a] See Schemes 3 and 4.
[b] GC yield (mixture of mono- and diaddition products).
[c] Solvent DMF, 130 °C.

(ether/pentane: 1/4) to give **1a** in 87% (0.287 g) isolated yield. White solid, m.p. 73 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.66$ (d, $J = 16.0$ Hz, 2H, =C*H*), 7.53 (s, 4H, Ar), 6.47 (d, $J = 16{,}0$ Hz, 2H, =C*H*), 4.21 (t, $J = 6.4$ Hz, 4H, CH_2), 1.69 (m, 4H, CH_2), 1.42 (m, 4H, CH_2), 0.96 (t, $J = 7.3$ Hz, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.8$, 143.1, 132.1, 129.4, 119.0, 64.6, 30.7, 19.2, 13.7. MS (70 eV); *m*/*z* (%): 330 (100) [M^+]. Anal. Calc. for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.48; H, 7.69%. When a ratio substrate/catalyst of 100,000 was used (Table 1, entry 2), *n*-butyl 4-bromocinnamate **1b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.60$ (d, $J = 16.1$ Hz, 1H, =C*H*), 7.54 (d, $J = 8.5$ Hz, 2H, Ar), 7.38 (d, $J = 8.5$ Hz, 2H, Ar), 6.42 (d, $J = 16.1$ Hz, 1H, =C*H*), 4.20 (t, 2H, CH_2), 1.68 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 0.95 (t, 3H, Me).

2.4.2. (*E,E*)-1,4-distyrylbenzene (**2a**): (Table 1, entry 3)

1,4-Dibromobenzene (0.236 g, 1 mmol), Pd complex (0.1 μmol) and styrene (0.416 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/6) to give **2a** in 78% (0.220 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.55$–7.45 (m, 8H, Ar), 7.40–7.22 (m, 6H, Ar), 7.12 (m, 4 H, =C*H*). When a ratio substrate/catalyst of 100,000 was used (Table 1, entry 4), (*E*)-4-bromostilbene **2b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.54$–7.44 (m, 4H, Ar), 7.40–7.32 (m, 4H, Ar), 7.29 (t, $J = 7.5$ Hz, 1H, Ar), 7.10 (d, $J = 16.3$ Hz, 1H, =C*H*), 7.02 (d, $J = 16.3$ Hz, 1H, =C*H*).

2.4.3. (*E,E*)-1,4-bis(3-methylstyryl)benzene (**3a**): (Table 1, entry 5)

1,4-Dibromobenzene (0.236 g, 1 mmol), Pd complex (1 μmol) and 3-methylstyrene (0.472 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/6) to give **3a** in 85% (0.263 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$ (s, 4H, Ar), 7.35–7.20 (m, 6H, Ar), 7.09 (m, 4H, =C*H*), 7.07 (d, $J = 8.2$ Hz, 2H, Ar), 2.38 (s, 6H, Me).

2.4.4. (*E,E*)-1,4-bis(3-chlorostyryl)benzene (**4a**): (Table 1, entry 6)

1,4-Dibromobenzene (0.236 g, 1 mmol), Pd complex (1 μmol) and 3-chlorostyrene (0.554 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **4a** in 86% (0.301 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): 7.50 (m, 6H, Ar), 7.38 (dt, $J = 7.9$ and 1.7 Hz, 2H, Ar), 7.30 (m, 2 H, Ar), 7.22 (dt, $J = 7.9$ and 1.7 Hz, 2H, Ar), 7.12 (d, $J = 16.5$ Hz, 2H, Ar), 7.04 (d, $J = 16.5$ Hz, 2H, =C*H*).

2.4.5. *n*-Butyl (*E,E*)-2-(2-*n*-butoxycarbonylvinyl)cinnamate (**5a**): (Table 1, entry 7)

1,2-Dibromobenzene (0.236 g, 1 mmol), Pd complex (0.4 μmol) and *n*-butyl acrylate (0.512 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **5a** in 81% (0.267 g) isolated yield. White solid, m.p. 74 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.01$ (d, $J = 15.8$ Hz, 2H, =C*H*), 7.56 (dd, $J = 6.2$ and 2.4 Hz, 2H, Ar), 7.38 (m, 2H, Ar), 6.33 (d, $J = 15.8$ Hz, 2H, =C*H*), 4.21 (t, $J = 6.7$ Hz, 4H, CH_2), 1.68 (m, 4H, CH_2), 1.42 (m, 4H, CH_2), 0.95 (t, $J = 7.2$ Hz, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.6$, 143.2 (2c), 136.0 (2c), 128.3 (4c), 119.2 (2c), 64.0, 30.6, 19.1, 13.6. MS (70 eV); *m*/*z* (%): 330 (39) [M^+]. Anal. Calc. for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.39; H, 7.71%.

*2.4.6. (E,E)-1,2-distyrylbenzene (**6a**): (Table 1, entry 8)*

1,2-Dibromobenzene (0.236 g, 1 mmol), Pd complex (0.5 μmol) and styrene (0.416 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/6) to give **6a** in 79% (0.223 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.55 (m, 2H, Ar), 7.55–7.50 (m, 4H, Ar), 7.46 (d, J = 16.3 Hz, 2H, =C*H*), 7.40–7.33 (m, 4H, Ar), 7.31–7.26 (m, 4H, Ar), 7.01 (d, J = 16.3 Hz, 2H, =C*H*). When a ratio substrate/catalyst of 10,000 was used (Table 1, entry 9), (*E*)-2-bromostilbene **6b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (dd, J = 8.0 and 1.7 Hz, 1H, Ar), 7.62–7.54 (m, 3H, Ar), 7.47 (d, J = 16.3 Hz, 1H, =C*H*), 7.42–7.26 (m, 4H, Ar), 7.12 (td, J = 8.0 and 1.7 Hz, 1H, Ar), 7.05 (d, J = 16.3 Hz, 1H, =C*H*).

*2.4.7. (E,E)-1,2-bis(3-methylstyryl)benzene (**7a**): (Table 1, entry 10)*

1,2-Dibromobenzene (0.236 g, 1 mmol), Pd complex (4 μmol) and 3-methylstyrene (0.472 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/6) to give **7a** in 82% (0.254 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (dd, J = 5.7 and 3.5 Hz, 2H, Ar), 7.45 (d, J = 16.3 Hz, 2H, =C*H*), 7.38–7.26 (m, 8H, Ar), 7.11 (d, J = 7.4 Hz, 2H, Ar), 6.98 (d, J = 16.3 Hz, 2H, =C*H*), 2.39 (s, 6H, Me).

*2.4.8. (E,E)-1,2-bis(3-chlorostyryl)benzene (**8a**): (Table 1, entry 11)*

1,2-Dibromobenzene (0.236 g, 1 mmol), Pd complex (4 μmol) and 3-chlorostyrene (0.554 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **8a** in 78% (0.274 g) isolated yield. White solid, m.p. 61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (dd, J = 5.7 and 3.5 Hz, 2H, Ar), 7.52–7.48 (m, 2H, Ar), 7.45 (d, J = 16.3 Hz, 2H, =C*H*), 7.40–7.20 (m, 8H, Ar), 6.92 (d, J = 16.3, 2H, =C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.2, 135.7, 134.7, 130.2, 129.9, 128.1, 127.8, 127.7, 126.8, 126.6, 124.8. MS (70 eV); *m/z* (%): 350 (100) [M^+]. Anal. Calc. for $C_{22}H_{16}Cl_2$: C, 75.22; H, 4.59. Found: C, 74.98; H, 4.68%.

*2.4.9. n-Butyl (E,E)-3-(2-n-butoxycarbonylvinyl)cinnamate (**9a**): (Table 1, entry 12)*

1,3-Dibromobenzene (0.236 g, 1 mmol), Pd complex (0.1 μmol) and *n*-butyl acrylate (0.512 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **9a** in 88% (0.290 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, J = 16.0 Hz, 2H, =C*H*), 7.59 (s, 1H, Ar), 7.46 (d, J = 7.4 Hz, 2H, Ar), 7.33 (t, J = 7.4 Hz, 1H, Ar), 6.42 (d, J = 16.0 Hz, 2 H, =C*H*), 4.17 (t, J = 6.7 Hz, 4H, CH_2), 1.65 (m, 4H, CH_2), 1.40 (m, 4H, CH_2), 0.92 (t, J = 7.4 Hz, 6H, CH_3). When a ratio substrate/catalyst of 100,000 was used (Table 1, entry 13), *n*-butyl 3-bromocinnamate **9b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (s, 1H, Ar), 7.58 (d, J = 16.1 Hz, 1H, =C*H*), 7.49 (d, J = 7.9 Hz, 1 H, Ar), 7.43 (d, J = 7.9 Hz, 1H, Ar), 7.25 (t, J = 7.9 Hz, 1H, Ar), 6.43 (d, J = 16.1 Hz, 1H, =C*H*), 4.20 (t, J = 6.7 Hz, 2H, CH_2), 1.68 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 0.96 (t, J = 7.4 Hz, 3H, CH_3).

*2.4.10. (E,E)-1,3-distyrylbenzene (**10a**): (Table 1, entry 14)*

1,3-Dibromobenzene (0.236 g, 1 mmol), Pd complex (0.1 μmol) and styrene (0.416 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/6) to give **10a** in 84% (0.237 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (s, 1H, Ar), 7.57–7.52 (m, 4H, Ar), 7.46–7.33 (m, 7 H, Ar), 7.31–7.24 (m, 2H, Ar), 7.15 (s, 4H, =C*H*).

*2.4.11. n-Butyl (E,E,E)-3,5-bis(2-n-butoxycarbonylvinyl)cinnamate (**11a**): (Table 1, entry 15)*

1,3,5-Tribromobenzene (0.315 g, 1 mmol), Pd complex (0.01 mmol) and *n*-butyl acrylate (0.768 g, 6 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **11a** in 73% (0.333 g) isolated yield. White solid, m.p. 85 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 16.1 Hz, 3H, =C*H*), 7.63 (s, 3 H, Ar), 6.50 (d, J = 16.1 Hz, 3H, =C*H*), 4.22 (t, J = 6.8 Hz, 6H, CH_2), 1.66 (m, 6H, CH_2), 1.44 (m, 6H, CH_2), 0.96 (t, J = 7.4 Hz, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5, 142.7, 135.9, 128.5, 120.2, 64.6, 30.7, 19.2, 13.7. MS (70 eV); *m/z* (%): 456 (52) [M^+]. Anal. Calc. for $C_{27}H_{36}O_6$: C, 71.03; H, 7.95. Found: C, 70.98; H, 7.86%. When a ratio substrate/catalyst of 250 was used (Table 1, entry 16), *n*-butyl (*E,E*)-3-bromo-5-(2-*n*-butoxycarbonylvinyl)cinnamate **11b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (s, 2H, Ar), 7.57 (d, J = 16.1 Hz, 2H, =C*H*), 7.54 (s, 1H, Ar), 6.46 (d, J = 16.1 Hz, 2H, =C*H*), 4.21 (t, J = 6.5 Hz, 4H, CH_2), 1.66 (m, 4 H, CH_2), 1.44 (m, 4H, CH_2), 0.96 (t, J = 7.3 Hz, 6H, Me), and the *n*-butyl *E*-3,5-dibromocinnamate **11c** was observed by GC/MS.

2.5. Vinylation products with dibromopyridines and 3,4-dibromothiophene (Table 2)

*2.5.1. n-Butyl (E,E)-3-[5-(2-butoxycarbonylvinyl)pyridin-3-yl]acrylate (**12a**): (Table 2, entry 1)*

3,5-Dibromopyridine (0.237 g, 1 mmol), Pd complex (1 μmol) and *n*-butyl acrylate (0.512 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **12a** in 76% (0.251 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (d, J = 2.0 Hz, 2 H, Ar), 7.92 (t, J = 2.0 Hz, 1H, Ar), 7.64 (d, J = 16.1 Hz, 2H, =C*H*), 6.53 (d, J = 16.1 Hz, 2H, =C*H*), 4.20 (t, J = 6.4 Hz, 4H, CH_2), 1.67 (m, 4H, CH_2), 1.42 (m, 4H, CH_2), 0.93 (t, J = 7.5 Hz, 6H, Me).

*2.5.2. (E,E)-3,5-distyrylpyridine (**13a**): (Table 2, entry 2)*

3,5-Dibromopyridine (0.237 g, 1 mmol), Pd complex (2 μmol) and styrene (0.416 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **13a** in 79% (0.224 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.59$ (s, 2H, Ar), 7.95 (s, 1H, Ar), 7.54 (d, $J = 8.0$ Hz, 4H, Ar), 7.37 (t, $J = 7.8$ Hz, 4H, Ar), 7.27 (t, $J = 7.8$ Hz, 2H, Ar), 7.23 (d, $J = 16.5$ Hz, 2H, =C*H*), 7.08 (d, $J = 16.5$ Hz, 2H, =C*H*).

*2.5.3. (E,E)-3,5-bis(3-methylstyryl)pyridine (**14a**): (Table 2, entry 3)*

3,5-Dibromopyridine (0.237 g, 1 mmol), Pd complex (10 μmol) and 3-methylstyrene (0.472 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **14a** in 83% (0.258 g) isolated yield. White solid, m.p. 175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.59$ (s, 2H, Ar), 7.92 (s, 1H, Ar), 7.40–7.22 (m, 6H, Ar), 7.19 (d, $J = 16.5$ Hz, 2H, =C*H*), 7.12 (m, 2H, Ar), 7.07 (d, $J = 16.5$ Hz, 2H, =C*H*), 2.40 (s, 6H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.1$, 138.3, 136.5, 132.9, 131.0, 129.2, 129.0, 128.6, 127.3, 124.4, 123.8, 21.3. MS (70 eV); *m/z* (%): 311 (61) [M^+]. Anal. Calc. for $C_{23}H_{21}N$: C, 88.71; H, 6.80. Found: C, 88.79; H, 6.71%.

*2.5.4. n-Butyl (E,E)-3-[6-(2-butoxycarbonylvinyl)pyridin-2-yl]acrylate (**15a**): (Table 2, entry 4)*

2,6-Dibromopyridine (0.237 g, 1 mmol), Pd complex (10 μmol) and *n*-butyl acrylate (0.512 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **15a** in 62% (0.205 g) isolated yield. White solid, m.p. 86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.72$ (t, $J = 7.8$ Hz, 1H, Ar), 7.66 (d, $J = 15.6$ Hz, 2H, =C*H*), 7.36 (d, $J = 7.8$ Hz, 2H, Ar), 7.03 (d, $J = 15.6$ Hz, 2H, =C*H*), 4.23 (t, $J = 6.8$ Hz, 4H, CH_2), 1.70 (m, 4H, CH_2), 1.45 (m, 4H, CH_2), 0.96 (t, $J = 7.3$ Hz, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.7$, 153.0, 142.6, 137.5, 124.5, 123.2, 64.6, 30.7, 19.1, 13.7. MS (70 eV); *m/z* (%): 331 (26) [M^+]. Anal. Calc. for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60. Found: C, 68.67; H, 7.75%. When a ratio substrate/catalyst of 250 was used (Table 2, entry 5), *n*-butyl (*E*)-3-(6-bromopyridin-2-yl)acrylate **15b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$ (d, $J = 15.7$ Hz, 1H, =C*H*), 7.45 (t, $J = 7.8$ Hz, 1H, Ar), 7.32 (d, $J = 7.8$ Hz, 1H, Ar), 7.22 (d, $J = 7.8$ Hz, 1H, Ar), 6.83 (d, $J = 15.7$ Hz, 1H, =C*H*), 4.09 (t, $J = 6.8$ Hz, 2H, CH_2), 1.53 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 0.87 (t, $J = 7.3$ Hz, 3H, CH_3).

*2.5.5. (E,E)-2,6-distyrylpyridine (**16a**): (Table 2, entry 6)*

2,6-Dibromopyridine (0.237 g, 1 mmol), Pd complex (10 μmol) and styrene (0.416 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **16a** in 78% (0.221 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.71$ (d, $J = 16.1$ Hz, 2H, =C*H*), 7.64 (t, $J = 7.9$ Hz, 1H, Ar), 7.60 (d, $J = 7.2$ Hz, 4H, Ph), 7.42–7.25 (m, 8H, Ar), 7.21 (d, $J = 16.1$ Hz, 2H, =C*H*).

*2.5.6. (E,E)-2,6-bis(3-methylstyryl)pyridine (**17a**): (Table 2, entry 7)*

2,6-Dibromopyridine (0.237 g, 1 mmol), Pd complex (10 μmol) and 3-methylstyrene (0.472 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **17a** in 47% (0.146 g) isolated yield. White solid, m.p. 95 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.67$ (d, $J = 16.1$ Hz, 2H, =C*H*), 7.62 (t, $J = 7.9$ Hz, 1H, Ar), 7.45–7.40 (m, 4H, Ar), 7.31–7.23 (m, 4H, Ar), 7.19 (d, $J = 16.1$ Hz, 2H, =C*H*), 7.12 (d, $J = 7.5$ Hz, 2H, Ar), 2.39 (s, 6H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 155.4$, 138.2, 137.0, 136.6, 133.8, 129.1, 128.6 (2c), 127.8, 124.4, 120.2, 21.4. MS (70 eV); *m/z* (%): 311 (43) [M^+]. Anal. Calc. for $C_{23}H_{21}N$: C, 88.71; H, 6.80. Found: C, 88.47; H, 6.72%. (*E*)-2-bromo-6-(3-methylstyryl)pyridine **17b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.62$ (d, $J = 16.0$ Hz, 1H, =C*H*), 7.46 (t, $J = 7.5$ Hz, 1H, Ar), 7.40–7.33 (m, 2H, Ar), 7.32–7.27 (m, 2H, Ar), 7.26 (t, $J = 7.5$ Hz, 1H, Ar), 7.12 (d, $J = 7.5$ Hz, 1H, Ar), 7.06 (d, $J = 16.0$ Hz, 1H, =C*H*), 2.37 (s, 3H, Me).

*2.5.7. (E,E)-2,6-di(3-chlorostyryl)pyridine (**18a**): (Table 2, entry 8)*

2,6-Dibromopyridine (0.237 g, 1 mmol), Pd complex (10 μmol) and 3-chlorostyrene (0.554 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **18a** in 77% (0.272 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.66$ (d, $J = 16.0$ Hz, 2H, =C*H*), 7.65 (t, $J = 7.5$ Hz, 1H, Ar), 7.58 (s, 2H, Ar), 7.46 (d, $J = 6.2$ Hz, 2H, Ar), 7.35-7.25 (m, 6H, Ar), 7.18 (d, $J = 16.0$ Hz, 2H, =C*H*).

*2.5.8. n-Butyl (E,E)-3-[4-(2-butoxycarbonylvinyl)thien-3-yl]acrylate (**19a**): (Table 2, entry 9)*

3,4-Dibromothiophene (0.242 g, 1 mmol), Pd complex (0.04 mmol) and *n*-butyl acrylate (0.512 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **19a** in 95% (0.319 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.73$ (d, $J = 15.8$ Hz, 2H, =C*H*); 7.56 (s, 2H, Ar), 6.29 (d, $J = 15.8$ Hz, 2H, =C*H*), 4.20 (t, $J = 6.6$ Hz, 4H, CH_2), 1.68 (m, 4H, CH_2), 1.42 (m, 4H, CH_2), 0.95 (t, $J = 7.4$ Hz, 6H, CH_3). When a ratio substrate/catalyst of 250 was used (Table 2, entry 10), *n*-butyl (*E*)-3-(4-bromothien-3-yl)acrylate **19b** was obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.67$ (d, $J = 16.3$ Hz, 1H, =C*H*), 7.58 (d, $J = 3.9$ Hz, 1H, Ar), 7.31 (d, $J = 3.9$ Hz, 1H, Ar), 6.43 (d, $J = 16.3$ Hz, 1H, =C*H*), 4.20 (t, $J = 6.6$ Hz, 2H,

CH_2), 1.69 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 0.95 (t, J = 7.4 Hz, 3H, CH_3).

2.5.9. (*E,E*)-3,4-distyrylthiophene (**20a**): (Table 2, entry 11)

3,4-Dibromothiophene (0.242 g, 1 mmol), Pd complex (4 μmol) and styrene (0.416 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **20a** in 82% (0.236 g) isolated yield. White solid, m.p. 190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.5 Hz, 4 H, Ar), 7.40 (s, 2H, Ar), 7.36 (t, J = 7.9 Hz, 4H, Ar), 7.26 (t, J = 7.5 Hz, 2H, Ar), 7.18 (d, J = 16.3 Hz, 2H, =C*H*), 6.97 (d, J = 16.3 Hz, 2H, =C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.6, 137.4, 130.7, 128.7, 127.7, 126.4, 121.7, 121.3. MS (70 eV); *m/z* (%): 288 (100) [M^+]. Anal. Calc. for $C_{20}H_{16}S$: C, 83.29; H, 5.59. Found: C, 83.02; H, 5.74%. When a ratio substrate/catalyst of 5000 was used (Table 2, entry 13), (*E*)-3-bromo-4-styrylthiophene **20b** was obtained selectively: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.2 Hz, 2H, Ar), 7.43 (dd, J = 3.4 and 0.5 Hz, 1H, Ar), 7.36 (t, J = 7.5 Hz, 2H, Ar), 7.31–7.25 (m, 2H, Ar), 7.12 (d, J = 16.3 Hz, 1H, =C*H*), 7.04 (d, J = 16.3 Hz, 1H, =C*H*).

2.5.10. (*E,E*)-3,4-bis(3-methylstyryl)thiophene (**21a**): (Table 2, entry 14)

3,4-Dibromothiophene (0.242 g, 1 mmol), Pd complex (4 μmol) and 3-methylstyrene (0.472 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **21a** in 78% (0.247 g) isolated yield. White solid, m.p. 55 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (s, 2H, Ar), 7.31–7.36 (m, 4H, Ar), 7.27 (t, J = 7.3 Hz, 2H, Ar), 7.19 (d, J = 16.3 Hz, 2H, =C*H*), 7.10 (d, J = 7.3 Hz, 2H, Ar), 6.96 (d, J = 16.3 Hz, 2H, =C*H*), 2.40 (s, 6 H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.6, 138.2, 137.3, 130.8, 128.6, 128.5, 127.1, 123.6, 121.5, 121.1, 21.4. MS (70 eV); *m/z* (%): 316 (100) [M^+]. Anal. Calc. for $C_{22}H_{20}S$: C, 83.50; H, 6.37. Found: C, 83.42; H, 6.49%.

2.5.11. (*E,E*)-3,4-bis(3-chlorostyryl)thiophene (**22a**): (Table 2, entry 15)

3,4-Dibromothiophene (0.242 g, 1 mmol), Pd complex (4 μmol) and 3-chlorostyrene (0.554 g, 4 mmol). The residue was purified by column chromatography (ether/pentane: 1/3) to give **21a** in 80% (0.286 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (s, 2H, Ar), 7.41 (s, 2H, Ar), 7.37 (d, J = 7.3 Hz, 2H, Ar), 7.28 (t, J = 7.3 Hz, 2H, Ar), 7.23 (d, J = 7.3 Hz, 2H, Ar), 7.16 (d, J = 16.1 Hz, 2H, =C*H*), 6.89 (d, J = 16.1 Hz, 2H, =C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.1, 138.0, 134.6, 129.9, 129.4, 127.6, 126.3, 124.6, 122.8, 121.9. MS (70 eV); *m/z* (%): 356 (34) [M^+]. Anal. Calc. for $C_{20}H_{14}Cl_2S$: C, 67.23; H, 3.95. Found: C, 66.97; H, 4.04%.

2.6. Catalytic procedure for Suzuki reactions

As a typical experiment, the reaction of aryl halide (1 mmol), arylboronic acid (3–6 mmol, see Tables 3 and 4) and K_2CO_3 (3–6 mmol, see Tables 3 and 4) at 130 °C during 20 h in dry xylene (3 ml) in the presence of *cis,-cis,cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclo-

Table 3
Palladium catalysed Suzuki cross-coupling reactions with di-, tri- or tetrabromobenzene (Schemes 5–7)

Entry	Aryl bromide	Arylboronic acid	Ratio substrate/catalyst	Product	Ratio **a/b**[a]	Yield in product **a** (%)
1	1,4-Dibromobenzene	Benzeneboronic acid	1000	**23a**	100/0	92
2	1,4-Dibromobenzene	Benzeneboronic acid	10,000	**23a**, **23b**	60/40	88[b]
3	1,4-Dibromobenzene	4-Fluorophenylboronic acid	1000	**24a**	100/0	95
4	1,4-Dibromobenzene	4-Fluorophenylboronic acid	10,000	**24a**, **24b**	97/3	100[b]
5	1,4-Dibromobenzene	2-Methylphenylboronic acid	250	**25a**	100/0	93
6	1,4-Dibromobenzene	2-Methylphenylboronic acid	1000	**25a**, **25b**	95/5	100[b]
8	1,2-Dibromobenzene	Benzeneboronic acid	250	**26a**	100/0	96
9	1,2-Dibromobenzene	Benzeneboronic acid	1000	**26a**, **26b**	89/11	100[b]
10	1,2-Dibromobenzene	Benzeneboronic acid	10,000	**26a**, **26b**	40/60	50[b]
11	1,2-Dibromobenzene	4-Fluorophenylboronic acid	250	**27a**	100/0	90
12	1,2-Dibromobenzene	2-Methylphenylboronic acid	250	**28a**	100/0	88
13	1,3-Dibromobenzene	Benzeneboronic acid	1000	**29a**	100/0	92
14	1,3,5-Tribromobenzene	Benzeneboronic acid	250	**30a**	100/0	94[c]
15	1,3,5-Tribromobenzene	Benzeneboronic acid	1000	**30a**, **30b**	97/3	83[b,c]
16	1,3,5-Tribromobenzene	4-Fluorophenylboronic acid	250	**31a**	100/0	85[c]
17	1,3,5-Tribromobenzene	2-Methylphenylboronic acid	250	**32a**, **32b**	71/29	66[c]
18	1,2,4,5-Tetrabromobenzene	Benzeneboronic acid	250	**33a**, **33b**	92/8	76[d]

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp 1/2, aryl bromide (1 eq.), arylboronic acid (3 eq.), K_2CO_3 (3 eq.), xylene, 130 °C, 20 h, isolated yields.
[a] See Schemes 5–7.
[b] GC yield (mixture of mono-, di- and triaddition products).
[c] Arylboronic acid (4.5 eq.) and K_2CO_3 (4.5 eq.).
[d] Benzeneboronic acid (6 eq.) and K_2CO_3 (6 eq.), traces of mono- and diaddition products were also observed by GC/MS.

Table 4
Palladium catalysed Suzuki cross-coupling reactions with dibromopyridines or 3,4-dibromothiophene (Schemes 8 and 9)

Entry	Aryl bromide	Arylboronic acid	Ratio substrate/catalyst	Product	Ratio **a**/**b**[a]	Yield in product **a** (%)
1	3,5-Dibromopyridine	Benzeneboronic acid	1000	**34a**	100/0	88
2	2,6-Dibromopyridine	Benzeneboronic acid	250	**35a**	100/0	82
3	2,6-Dibromopyridine	Benzeneboronic acid	1000	**35a**, **35b**	68/32	99[b]
4	2,5-Dibromopyridine	Benzeneboronic acid	1000	**36a**	100/0	85
5	2,5-Dibromopyridine	4-Fluorophenylboronic acid	100	**37a**	100/0	67
6	3,4-Dibromothiophene	Benzeneboronic acid	250	**38a**, **38b**	89/11	82

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/Tedicyp 1/2, heteroaryl bromide (1 eq.), arylboronic acid (4 eq.), K_2CO_3 (2 eq.), xylene, 130 °C, 20 h, isolated yields.
[a] See Schemes 8 and 9.
[b] GC yield (mixture of mono- and diaddition products).

pentane/$\frac{1}{2}[PdCl(C_3H_5)]_2$ complex under argon affords the corresponding products after evaporation and chromatography on silica gel.

2.7. Suzuki cross-coupling with di-, tri- and tetrabromobenzene (Table 3)

2.7.1. 1,4-Diphenylbenzene (**23a**): (Table 3, entry 1)

1,4-Dibromobenzene (0.236 g, 1 mmol), Pd complex (1 μmol) and phenylboronic acid (0.366 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **23a** in 92% (0.212 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.67$ (s, 4H, Ar), 7.63 (dd, $J = 7.8$ and 1.3 Hz, 4 H, Ar), 7.45 (dd, $J = 7.8$ and 7.0 Hz, 4H, Ar), 7.34 (t, $J = 7.0$ Hz, 2H, Ar). When a ratio substrate/catalyst of 10,000 was used (Table 3, entry 2), 4-bromobiphenyle **23b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.55$ (m, 4H, Ar), 7.44 (m, 4H, Ar), 7.36 (t, $J = 7.0$ Hz, 1H, Ar).

2.7.2. 1,4-Bis(4-fluorophenyl)benzene (**24a**): (Table 3, entry 3)

1,4-Dibromobenzene (0.236 g, 1 mmol), Pd complex (1 μmol) and 4-fluorophenylboronic acid (0.420 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **24a** in 95% (0.253 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.60$ (s, 4H, Ar), 7.56 (dd, $J = 8.8$ and 5.5 Hz, 4H, Ar), 7.13 (dd, $J = 8.8$ and 8.7 Hz, 4 H, Ar).

2.7.3. 1,4-Bis(2-methylphenyl)benzene (**25a**): (Table 3, entry 5)

1,4-Dibromobenzene (0.236 g, 1 mmol), Pd complex (4 μmol) and 2-methylphenylboronic acid (0.408 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **25a** in 93% (0.240 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$ (s, 4H, Ar), 7.18–7.27 (m, 8 H, Ar), 2.30 (s, 6H, CH_3). When a ratio substrate/catalyst of 1000 was used (Table 3, entry 6), 1-bromo-4-(2-methylphenyl)benzene **25b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.54$ (d, $J = 8.5$ Hz, 2H, Ar), 7.30–7.10 (m, 6H, Ar), 2.25 (s, 3H, CH_3).

2.7.4. 1,2-Diphenylbenzene (**26a**): (Table 3, entry 8)

1,2-Dibromobenzene (0.236 g, 1 mmol), Pd complex (4 μmol) and phenylboronic acid (0.366 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **26a** in 96% (0.221 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.42$ (m, 4H, Ar), 7.17–7.22 (m, 6H, Ar), 7.11–7.16 (m, 4 H, Ar). When a ratio substrate/catalyst of 10,000 was used (Table 3, entry 10), 2-bromo-biphenyle **26b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.61$ (d, $J = 7.3$ Hz, 1H), 7.37 (m, 4H, Ar), 7.33 (t, $J = 7.0$ Hz, 1 H, Ar), 7.27 (m, 2H, Ar), 7.11 (m, 1H, Ar).

2.7.5. 1,2-Bis(4-fluorophenyl)benzene (**27a**): (Table 3, entry 11)

1,2-Dibromobenzene (0.236 g, 1 mmol), Pd complex (4 μmol) and 4-fluorophenylboronic acid (0.420 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **27a** in 90% (0.240 g) isolated yield. White solid, m.p. 97 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$ (m, 4H, Ar), 7.06 (dd, $J = 8.8$ and 5.5 Hz, 4H, Ar), 6.91 (dd, $J = 8.8$ and 8.7 Hz, 4H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 161.8$ (d, $J = 245.9$ Hz), 139.5, 137.2, 131.3 (d, $J = 8.2$ Hz), 130.5, 127.7, 115.1, 114.9 (d, $J = 21.4$ Hz). MS (70 eV); *m/z* (%): 266 (100) [M^+]. Anal. Calc. for $C_{18}H_{12}F_2$: C, 81.19; H, 4.54. Found: C, 81.43; H, 4.47%.

2.7.6. 1,2-Bis(2-methylphenyl)benzene (**28a**): (Table 3, entry 12)

1,2-Dibromobenzene (0.236 g, 1 mmol), Pd complex (4 μmol) and 2-methylphenylboronic acid (0.408 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **28a** in 88% (0.227 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$–7.16 (m, 4H, Ar), 7.15–6.80 (m, 8H, Ar), 2.20–2.00 (m, 6H, Me).

*2.7.7. 1,3-Diphenylbenzene (**29a**): (Table 3, entry 13)*

1,3-Dibromobenzene (0.236 g, 1 mmol), Pd complex (1 μmol) and phenylboronic acid (0.366 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **29a** in 92% (0.211 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.79$ (t, $J = 1.9$ Hz, 1H), 7.63 (m, 2H), 7.61 (m, 2H), 7.56–7.52 (m, 2H), 7.50–7.39 (m, 5 H), 7.37–7.29 (m, 2H).

*2.7.8. 1,3,5-Triphenylbenzene (**30a**): (Table 3, entry 14)*

1,3,5-Tribromobenzene (0.315 g, 1 mmol), Pd complex (4 μmol) and phenylboronic acid (0.549 g, 4.5 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **30a** in 94% (0.288 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.78$ (s, 3H, Ar), 7.71 (d, $J = 7.1$ Hz, 6H, Ph), 7.44 (t, $J = 7.1$ Hz, 6H, Ph), 7.39 (t, $J = 7.1$ Hz, 3H, Ph). When a ratio substrate/catalyst of 1000 was used (Table 3, entry 15), 1-bromo-3,5-diphenylbenzene **30b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.70$ (m, 3H, Ar), 7.60 (d, $J = 7.2$ Hz, 4 H), 7.46 (t, $J = 7.2$ Hz, 4 H), 7.36 (t, $J = 7.2$ Hz, 2H).

*2.7.9. 1,3,5-Tris(4-fluorophenyl)benzene (**31a**): (Table 3, entry 16)*

1,3,5-Tribromobenzene (0.315 g, 1 mmol), Pd complex (4 μmol) and 4-fluorophenylboronic acid (0.630 g, 4.5 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **31a** in 85% (0.306 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.66$ (s, 3H, Ar), 7.61 (dd, $J = 8.7$ and 5.3 Hz, 6H, Ar), 7.16 (t, $J = 8.7$ Hz, 6H, Ar).

*2.7.10. 1,3,5-Tris(2-methylphenyl)benzene (**32a**): (Table 3, entry 17)*

1,3,5-Tribromobenzene (0.315 g, 1 mmol), Pd complex (4 μmol) and 2-methylphenylboronic acid (0.612 g, 4.5 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **32a** in 66% (0.230 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$–7.20 (m, 15H, Ph), 2.38 (s, 9 H, Me). 1-Bromo-3,5-*bis*(2-methylphenyl)benzene **32b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.45$ (s, 2H, Ar), 7.35–7.20 (m, 9H, Ar), 2.30 (s, 6H, Me).

*2.7.11. 1,2,4,5-Tetraphenylbenzene (**33a**): (Table 3, entry 18)*

1,2,4,5-Tetrabromobenzene (0.394 g, 1 mmol), Pd complex (4 μmol) and phenylboronic acid (0.732 g, 6 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **33a** in 76% (0.290 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.55$ (s, 2H), 7.24 (m, 20 H). Traces of the mono-, di- and triarylated compounds **33b**, **33c** and **33d** were also observed by GC and GC/MS.

2.8. Suzuki cross-coupling with dibromopyridines and 3,4-dibromothiophene (Table 4)

*2.8.1. 3,5-Diphenylpyridine (**34a**): (Table 4, entry 1)*

3,5-Dibromopyridine (0.237 g, 1 mmol), Pd complex (1 μmol) and phenylboronic acid (0.366 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **34a** in 88% (0.203 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.81$ (s, 2H, Ar), 8.04 (t, $J = 2.2$ Hz, 1H, Ar), 7.64 (d, $J = 8.5$ Hz, 4H, Ph), 7.52–7.39 (m, 6H, Ph).

*2.8.2. 2,6-Diphenylpyridine (**35a**): (Table 4, entry 2)*

2,6-Dibromopyridine (0.237 g, 1 mmol), Pd complex (4 μmol) and phenylboronic acid (0.366 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **35a** in 82% (0.189 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.18$ (d, $J = 7.3$ Hz, 4H, Ph), 7.80 (t, $J = 8.5$ Hz, 1H, Ar), 7.69 (d, $J = 8.5$ Hz, 2H, Ar), 7.54 (dd, $J = 7.3$ and 7.3 Hz, 4H, Ph), 7.45 (t, $J = 7.3$ Hz, 2H, Ph). When a ratio substrate/catalyst of 1000 was used (Table 4, entry 3), 2-bromo-6-phenylpyridine **35b** was also obtained: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ ^{1}H NMR (300 MHz, $CDCl_3$): 8.00 (m, 2H, Ph), 7.60 (d, $J = 6.0$ Hz, 1H, Ar), 7.50 (t, $J = 6.0$ Hz, 1H, Ar), 7.39 (m, 3H, Ph), 7.30 (d, $J = 6.0$ Hz, 1H, Ar).

*2.8.3. 2,5-Diphenylpyridine (**36a**): (Table 4, entry 4)*

2,5-Dibromopyridine (0.237 g, 1 mmol), Pd complex (1 μmol) and phenylboronic acid (0.366 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **36a** in 85% (0.196 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.94$ (d, $J = 2.3$ Hz, 1H, Ar), 8.04 (d, $J = 7.0$ Hz, 2H, Ph), 7.95 (dd, $J = 8.3$ and 2.3 Hz, 1H, Ar), 7.80 (d, $J = 8.3$ Hz, 1H, Ar), 7.63 (d, $J = 7.7$ Hz, 2H, Ph), 7.52–7.38 (m, 6H, Ph).

*2.8.4. 2,5-Bis(4-fluorophenyl)pyridine (**37a**): (Table 4, entry 5)*

2,5-Dibromopyridine (0.237 g, 1 mmol), Pd complex (0.01 mmol) and 4-fluorophenylboronic acid (0.420 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **37a** in 67% (0.179 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.85$ (d, $J = 2.2$ Hz, 1H, Ar), 8.01 (dd, $J = 8.0$ and 5.5 Hz, 2H, Ar), 7.88 (dd, $J = 8.3$ and 2.2 Hz, 1H, Ar), 7.74 (d, $J = 8.3$ Hz, 1H, Ar), 7.56 (dd, $J = 7.8$ and 5.3 Hz, 2H, Ar), 7.17 (m, 4H, Ar).

*2.8.5. 3,4-Diphenylthiophene (**38a**): (Table 4, entry 6)*

3,4-Dibromothiophene (0.242 g, 1 mmol), Pd complex (4 μmol) and phenylboronic acid (0.366 g, 3 mmol). The residue was purified by column chromatography (ether/pentane: 1/4) to give **38a** in 82% (0.194 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$ (s, 2H, Ar),

7.30–7.19 (m, 10H, Ph). Traces of **38b** were also observed by GC and GC/MS.

2.9. CAS Registry No.

1b, 131061-14-8; **2a**, 1608-41-9; **2b**, 13041-70-8; **3a**, 131941-43-0; **4a**, 54842-62-5; **5a**, 501124-77-2; **6a**, 27164-48-3; **6b**, 54737-45-0; **7a**, 96585-71-6; **7b**, 226712-64-7; **9a**, 113236-22-9; **9b**, 423775-08-0; **10a**, 1725-76-4; **12a**, 477723-54-9; **13a**, 477723-55-0; **16a**, 125311-40-2; **18a**, 53925-20-5; **19a**, 9280144 (Beilstein Registry No.); **20b**, 75997-24-9; **23a**, 92-94-4; **23b**, 92-66-0; **24a**, 72864-01-8; **24b**, 398-21-0; **25a**, 53092-64-1; **25b**, 106475-19-8; **26a**, 84-15-1; **26b**, 2052-07-5; **28a**, 75896-77-4; **28b**, 251320-87-3; **29a**, 92-06-8; **30a**, 612-71-5; **30b**, 103068-20-8; **30c**, 16372-96-6; **31a**, 448-60-2; **32a**, 87226-88-8; **32b**, 247575-70-8; **33a**, 3383-32-2; **34a**, 92-07-9; **35a**, 3558-69-8; **35b**, 39774-26-0; **36a**, 15827-72-2; **37a**, 171820-18-1; **38a**, 16939-13-2; **38b**, 23062-41-1.

3. Results and discussion

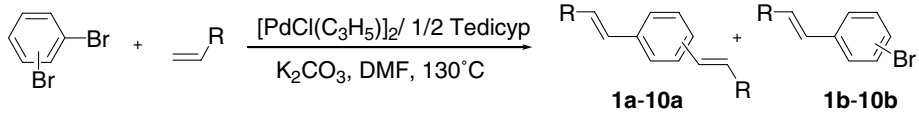
3.1. Heck vinylation products with di- and tribromobenzene

First, we have investigated the Heck vinylation reactions of 1,2-, 1,3- and 1,4-dibromobenzenes with *n*-butyl acrylate or styrene (Scheme 1, Table 1). For these reactions, DMF or NMP were chosen as the solvents and potassium carbonate as the base. The reactions were performed at 130 or 150 °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 an influence of the position of the bromide substituents on the aryl on the reaction rate. The reaction with 1,3- or 1,4-dibromobenzene can be performed with as little as 0.01% catalyst with *n*-butyl acrylate or styrene. In all cases the divinylation products were obtained selectively (Table 1, entries 1, 3, 12 and 14). When higher ratios subtrate/catalyst were used, mixtures of di- and monovinylated adducts were obtained (Table 1, entries 2, 4 and 13). As expected, lower turnover numbers (TONs) were obtained with 1,2-dibromobenzene and the diaddition products were obtained selectively when 0.05–0.04% catalyst were used (Table 1, entries 7 and 8). 1,2- and 1,4-dibromobenzene with 3-methyl or 3-chlorostyrene also led selectively to the divinylated adducts (Table 1, entries 5, 6, 10 and 11).

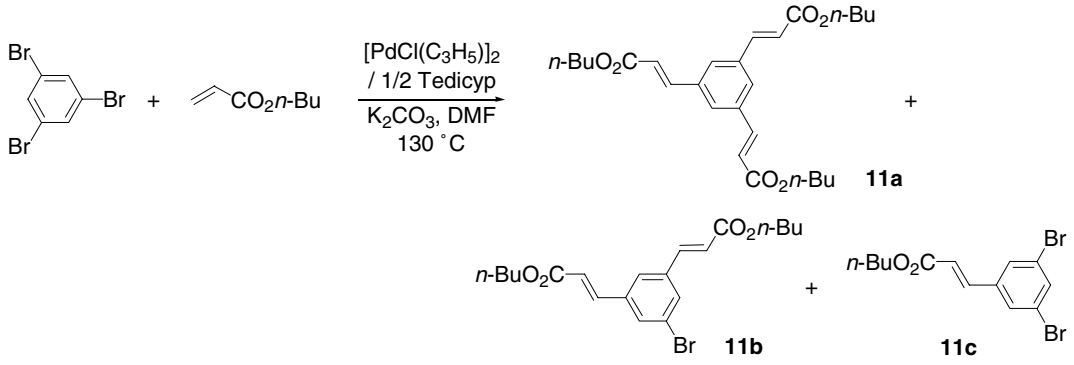
If the divinylations could be performed with high ratios substrates/catalyst, the trivinylation of 1,3,5-tribromobenzene was slower and 1% catalyst had to be used to obtain selectively the trisubstituted adduct **11a** (Scheme 2, Table 1, entries 15–16). We also reacted 1,2,4,5-tetrabromobenzene with *n*-butyl acrylate but a mixture of several products was observed including products arising from partially reduced polybromide. No significant pure product could be separated from this reaction mixture.

3.2. Heck vinylation products with dibromopyridines and 3,4-dibromothiophene

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



Scheme 1.



Scheme 2.

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 dibromopyridines on the rate of the coupling with *n*-butyl acrylate or styrene. 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) [3]. In fact, we observed higher TON's for the coupling of β,β′-disubstituted 3,5-dibromopyridine than with α,α′-disubstituted 2,6-dibromopyridine (Scheme 3, Table 2, entries 1–8). These results seem to indicate that with this α,α′-disubstituted dibromopyridine, a possible interaction between the nitrogen atom and the palladium complex has a decelerating effect on the reaction rate. With this substrate the oxidative addition is probably not the rate-limiting step of the reaction. Next, we tried to evaluate the influence of the substituents on the styrene on the rate of this reaction, so we investigated the coupling of 3-methyl- and 3-chlorostyrene with these dibromopyridines. Similar reaction rates were observed with all these substituted styrenes (Table 2, entries 3, 7 and 8).

Thiophenes are π-electron-excessive heterocycles. Oxidative addition to palladium should be slower with bromothiophenes, than with bromopyridines. 3,4-Dibromothiophene with *n*-butyl acrylate led to the divinylation adduct **19a** selectively with a very low TON of 25 (Scheme 4, Table 2, entry 9). In the presence of 0.4% catalyst the mono addition product can be obtained quite selectively (entry 10). An higher reaction rate was observed in the presence of styrene (Table 2, entry 11). The relatively low reactivity of this substrate may be explain both by a slow oxidative addition and also by steric factors due to two adjacent bromo groups.

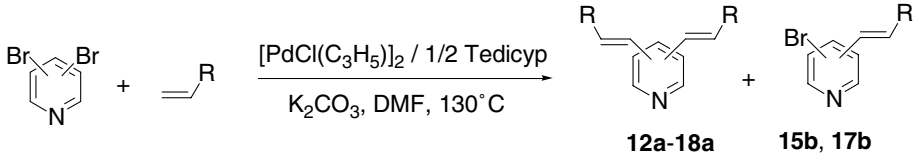
3.3. Suzuki cross-coupling with di-, tri- and tetrabromobenzene

The palladium-catalysed cross-coupling reaction between aryl halides and arylboronic acids provides a very efficient method for the preparation of polyaryls derivatives. Organoboron reagents exhibit greater functional group compatibility than organozinc or Grignard reagents. Moreover, the innocuous nature of boronic acids, which are generally nontoxic and thermally, air-, and moisture-stable, is a practical advantage of the Suzuki reaction, relative to many other cross-coupling processes.

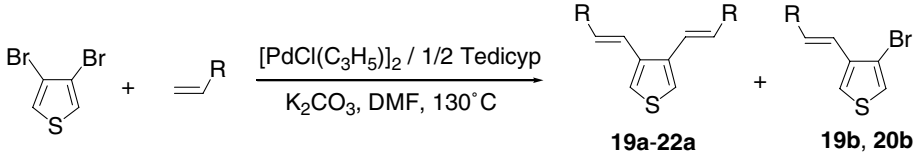
For this study, xylene was chosen as the solvent and potassium carbonate as the base. The reactions were performed at 130 °C, under argon, in the presence of a ratio 1/2 of $[Pd(C_3H_5)Cl]_2$/tedicyp as catalyst.

We observed that 1,3- or 1,4-dibromobenzene with arylboronic acids led to the diarylation adducts in the presence of 0.1% catalyst (Scheme 5, Table 3, entries 1, 3, 6 and 13). Similar TONs were observed in the presence of 4-fluorophenylboronic acid or 2-methylboronic acid (Table 3, entries 4–6). Lower TONs were obtained with 1,2-dibromobenzene (entries 8–12).

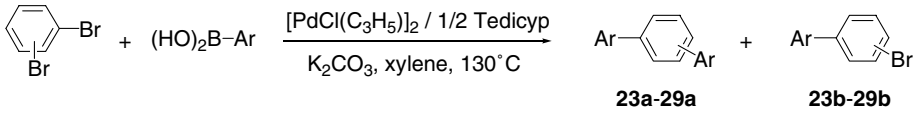
We also reacted 1,3,5-tribromobenzene with benzeneboronic acid, 4-fluorophenylboronic acid and 2-methylphenylboronic acid (Scheme 6, Table 3, entries 14–17). The triarylated products were obtained in all cases, but higher reactions rates were observed with benzeneboronic acid and 4-fluorophenylboronic acid. With benzeneboronic acid the triaddition products **30a** was obtained in 97% selectively in the presence of 0.1% catalyst. In order to present a more simple procedure, we



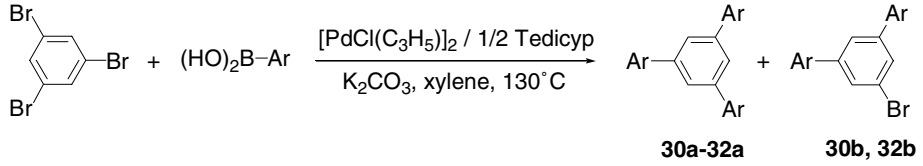
Scheme 3.



Scheme 4.



Scheme 5.



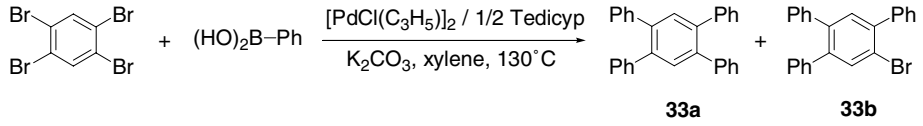
Scheme 6.

also performed the same reaction using 1% of $[Pd(C_3H_5)Cl]_2$ as catalyst in absence of ligand. Under these conditions the triaddition product **30a** was obtained in a satisfactory yield (58%) but the presence 18% of the diaddition product **30b** and of 19% of product **29a** arising from partial debromation of tribromobenzene was also observed.

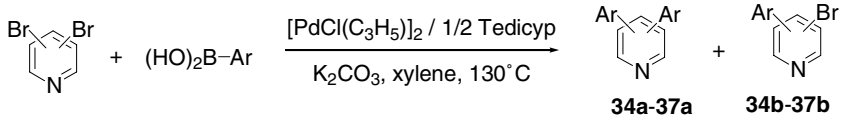
The 1,2,4,5-tetrabromobenzene also did undergo the normal arylation with benzeneboronic acid to give 1,2,4,5-tetraphenylbenzene **33a** in 92% selectivity and 76% yield (Scheme 7, Table 3, entry 18).

3.4. Suzuki cross-coupling with dibromopyridines and 3,4-dibromothiophene

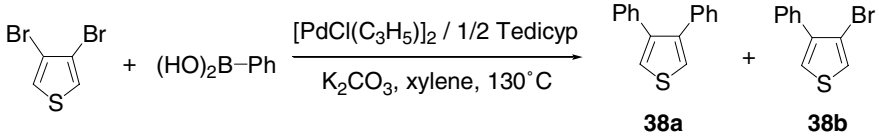
Next, we studied the reactivity of dibromopyridines and a dibromothiophene for Suzuki reaction (Table 4). First, we studied the influence of position of the bromo substituent on pyridines on the rate of the coupling with benzeneboronic acid. The reactivity of three dibromopyridines was studied: 3,5-, 2,6- and 2,5-dibromopyridines. A similar reactivity was observed than for Heck reaction and slightly better results were obtained for the coupling of β,β′-disubstituted 3,5-dibromopyridine than with α,α′-disubstituted 2,6-dibromopyridine (Scheme 8, Table 4, entries 1–3). The α,β′-disubstituted 2,5-dibromopyridine also led selectively to the diarylated adducts **36a** and **37a** in the presence of 1–0.1% catalyst (Table 4, entries 4 and 5). Finally, we examined the reactivity of 3,4-dibromothiophene with phenylboronic acid. The corresponding diarylated compound **38a** was obtained in 89% selectivity and 82% yield when 0.4% catalyst was used (Scheme 9, Table 4, entry 6).



Scheme 7.



Scheme 8.



Scheme 9.

4. Conclusion

The Tedicyp-palladium complex provides a convenient catalyst for the reaction of several aryl or heteroaryl polybromides with arylboronic acids or with alkenes. In the presence of this catalyst 1,2-, 1,3- or 1,4-dibromobenzene derivatives led to the expected disubstitution products in good yield. The position of the halide on the aromatic has an effect on the reaction rate and faster reactions were generally observed with 1,3- or 1,4-dibromobenzene than with 1,2-dibromobenzene. With some substrates, the reaction can be performed with as little as 0.001% catalyst. In the presence of 1,3,5-tribromobenzene the trivinylation and the triarylation products were also selectively obtained. To date, only a few other ligands have achieved this objective; most of the other ligands were used with more reactive but more expensive aryliodides. On the other hand, if the selective tetraarylation of 1,2,4,5-tetrabromobenzene was possible, the tetravinylation led to a mixture of products. 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.

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References

[1] (a) For reviews on the palladium-catalysed Heck reaction see: R.F. Heck, Vinyl substitution with organopalladium intermediates, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 4, Pergamon, Oxford, 1991;
(b) A. de Meijere, F.E. Meyer, Angew. Chem. Int. Ed. Eng. 33 (1994) 2379;
(c) J.-L. Malleron, J.-C. Fiaud, J.-Y. Legros, Handbook of Palladium-Catalyzed Organic Reactions, Academic Press, London, 1997;
(d) M.T. Reetz, Transition Metal Catalyzed Reactions, in: S.G. Davies, S.-I. Murahashi (Eds.), Blackwell Science, Oxford, 1999;
(e) I. Beletskaya, A. Cheprakov, Chem. Rev. 100 (2000) 3009;
(f) N. Withcombe, K.K. Hii (Mimi), S. Gibson, Tetrahedron 57 (2001) 7449.

[2] (a) For reviews on the Suzuki cross-coupling of aryl bromides with arylboronic acids: N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457;
(b) A. Suzuki, Metal-catalysed Cross-coupling Reaction, in: F. Diederich, P.J. Stang (Eds.), Wiley, New York, 1998;
(c) A. Suzuki, J. Organomet. Chem. 576 (1999) 147;
(d) S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633;
(e) A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4177.

[3] For examples of palladium-catalysed Heck and Suzuki reactions with heteroaromatic compounds: J.J. Li, G.W. Gribble, Palladium in Heterocyclic Chemistry, Pergamon, Amsterdam, 2000.

[4] (a) For examples of efficient catalysts for Heck reaction: W.A. Herrmann, C. Brossmer, K. Öfele, C. Reisinger, T. Riermeier, M. Beller, H. Fisher, Angew. Chem. Int. Ed. 34 (1995) 1844;
(b) M. Ohff, A. Ohff, M. Boom, D. Milstein, J. Am. Chem. Soc. 119 (1997) 11687;
(c) D. Albisson, R. Bedford, P.N. Scully, Tetrahedron Lett. 39 (1998) 9793;
(d) D. Bergbreiter, P. Osburn, Y.-S. Liu, J. Am. Chem. Soc. 121 (1999) 9531;
(e) C. Gürtler, S. Buchwald, Chem. Eur. J. 5 (1999) 3107;
(f) S. Gibson, D. Foster, D. Eastham, R. Tooze, D. Cole-Hamilton, Chem. Commun. (2001) 779;
(g) A. Littke, G. Fu, J. Am. Chem. Soc. 123 (2001) 6989.

[5] (a) For examples of efficient catalysts for Suzuki cross-coupling reaction: M. Beller, H. Fischer, A. Herrmann, K. Öfele, C. Brossmer, Angew. Chem. Int. Ed. Eng. 34 (1995) 1848;
(b) D.A. Albisson, R.B. Bedford, S.E. Lawrence, P.N. Scully, Chem. Commun. (1998) 2095;
(c) J. Wolfe, R. Singer, B. Yang, S. Buchwald, J. Am. Chem. Soc. 121 (1999) 9550;
(d) H. Weissman, D. Milstein, Chem. Commun. (1999) 1901;
(e) J. Wolfe, S. Buchwald, Angew. Chem. Int. Ed. Eng. 38 (1999) 2413;
(f) A. Zapf, M. Beller, Chem. Eur. J. 6 (2000) 1830;
(g) D. Mc Guiness, K. Cavell, Organometallics 19 (2000) 741;
(h) R. Bedford, S. Welch, Chem. Commun. (2001) 129.

[6] (a) For examples of Heck reactions with dibromo or diiodobenzene derivatives: K.N. Dack, R.P. Dickinson, C.J. Long, J. Steele Bioorg. Med. Chem. Lett. 8 (1998) 2061;
(b) S. Bräse, J. Rümper, K. Voigt, S. Albecq, G. Thureau, R. Villard, B. Waegell, A. de Meijere, Eur. J. Org. Chem. (1998) 671;
(c) R. Klopsch, S. Koch, A.D. Schlüter, Eur. J. Org. Chem. (1998) 1275.

[7] For examples of Heck reactions with tribromo or triiodobenzene derivatives: S.D. Bull, S.G. Davies, A.D. Smith, J. Chem. Soc., Perkin Trans. 1 (2001) 2931.

[8] For examples of Heck reaction with tetraiodobenzene derivatives: W. Tao, S. Nesbitt, R.F. Heck, J. Org. Chem. 55 (1990) 63.

[9] (a) For examples of Suzuki cross-coupling reaction with dibromo or diiodobenzene derivatives: N. Miyaura, T. Yanagi, A. Suzuki, Synth. Commun. 11 (1981) 513;
(b) C.M. Unrau, M.G. Campbell, V. Snieckus, Tetrahedron Lett. 33 (1992) 2773;
(c) K. Manabe, K. Okamura, T. Date, K. Koga, J. Org. Chem. 58 (1993) 6692;
(d) P. Galda, M. Rehahn, Synthesis (1996) 614;
(e) M.B. Goldfinger, K.B. Crawford, T.M. Swager, J. Am. Chem. Soc. 119 (1997) 4578;
(f) A.J. Blake, P.A. Cooke, K.J. Doyle, S. Gair, N.S. Simpkins, Tetrahedron Lett. 39 (1998) 9093;
(g) F.C. Krebs, M. Jorgensen, M. Larsen, J. Org. Chem. 64 (1999) 8758;
(h) M. Albrecht, M. Schneider, Synthesis (2000) 1557;
(i) L.-Z. Gong, Q.-S. Hu, L. Pu, J. Org. Chem. 66 (2001) 2358;
(j) V. Percec, T.K. Bera, B.B. De, Y. Sanai, J. Smith, M.N. Holerca, B. Barboiu, R.B. Grubbs, J.M.J. Fréchet, J. Org. Chem. 66 (2001) 2104;
(k) F.C. Krebs, M. Jorgensen, J. Org. Chem. 66 (2001) 6169;
(l) A.N. Cammidge, H. Gopee, Chem. Commun. (2002) 966.

[10] (a) For examples of Suzuki cross-coupling reaction with tribromo or triiodobenzene derivatives: T.M. Miller, T.X. Neenan, R.

Zayas, H.E. Bair, J. Am. Chem. Soc. 114 (1992) 1018;
(b) Y. Miura, H. Oka, M. Momoki, Synthesis (1995) 1419;
(c) S. Grilli, L. Lunazzi, A. Mazzanti, M. Pinamonti, J. Org. Chem. 67 (2002) 5733;
(d) G.J. Capitosti, C.D. Guerrero, D.E. Binkley Jr., C.S. Rajesh, D.A. Modarelli, J. Org. Chem. 68 (2003) 247.

[11] (a) For examples of Suzuki cross-coupling reaction with heteroarylhalides: Y. Miura, S. Kurokawa, M. Nakatsuji, K. Ando, Y. Teki, J. Org. Chem. 63 (1998) 8295;
(b) D. Brugier, F. Outurquin, C. Paulmier, Tetrahedron 56 (2000) 2985;
(c) R. Pereira, B. Iglesias, A.R. de Lera, Tetrahedron 57 (2001) 7871;
(d) J.E. Baldwin, R.M. Adlington, A. Conte, N.R. Irlapati, R. Marquez, G.J. Pritchard, Org. Lett. 4 (2002) 2125;
(e) F. Bracher, J. Daab, Eur. J. Org. Chem. (2002) 2288;
(f) G.M. Chapman, S.P. Stanforth, B. Tarbit, M.D. Watson, J. Chem. Soc., Perkin Trans. 1 (2002) 581.

[12] (a) B. Basu, P. Das, M.M.H. Bhuiyan, S. Jha, Tetrahedron Lett. 44 (2003) 3817;
(b) S. Merlet, M. Birau, Z.Y. Wang, Org. Lett. 4 (2002) 2157.

[13] A. Ceccon, L. Crociani, S. Santi, A. Venzo, A. Biffis, G. Boccaletti, Tetrahedron Lett. 43 (2002) 8475.

[14] J.V. Mello, N.S. Finney, Org. Lett. 4 (2001) 4263.

[15] S.-W. Kim, M. Kim, W.Y. Lee, T. Hyeon, J. Am. Chem. Soc. 124 (2002) 7642.

[16] D. Laurenti, M. Feuerstein, G. Pèpe, H. Doucet, M. Santelli, J. Org. Chem. 66 (2001) 1633.

[17] M. Feuerstein, F. Berthiol, H. Doucet, M. Santelli, Org. Biomol. Chem. 1 (2003) 2235.

[18] (a) M. Feuerstein, H. Doucet, M. Santelli, J. Org. Chem. 66 (2001) 5923;
(b) M. Feuerstein, H. Doucet, M. Santelli, Synlett (2001) 1980;
(c) M. Feuerstein, H. Doucet, M. Santelli, Tetrahedron Lett. 43 (2002) 2191;
(d) F. Berthiol, M. Feuerstein, H. Doucet, M. Santelli, Tetrahedron Lett. 43 (2002) 5625;
(e) F. Berthiol, H. Doucet, M. Santelli, Tetrahedron Lett. 44 (2003) 1221;
(f) F. Berthiol, H. Doucet, M. Santelli, Synlett (2003) 841;
(g) I. Kondolff, H. Doucet, M. Santelli, Tetrahedron Lett. 44 (2003) 8487.

[19] (a) M. Feuerstein, D. Laurenti, C. Bougeant, H. Doucet, M. Santelli, Chem. Commun. (2001) 325;
(b) M. Feuerstein, D. Laurenti, H. Doucet, M. Santelli, Synthesis (2001) 2320;
(c) M. Feuerstein, H. Doucet, M. Santelli, Tetrahedron Lett. 42 (2001) 5659;
(d) M. Feuerstein, H. Doucet, M. Santelli, Tetrahedron Lett. 42 (2001) 6667;
(e) M. Feuerstein, H. Doucet, M. Santelli, Synlett (2001) 1458;
(f) M. Feuerstein, F. Berthiol, H. Doucet, M. Santelli, Synlett (2002) 1807;
(g) F. Berthiol, H. Doucet, M. Santelli, Eur. J. Org. Chem. (2003) 1091;
(h) L. Chahen, H. Doucet, M. Santelli, Synlett (2003) 1668;
(i) M. Feuerstein, H. Doucet, M. Santelli, J. Organomet. Chem. 687 (2003) 327;
(j) E. Peyroux, F. Berthiol, H. Doucet, M. Santelli, Eur. J. Org. Chem. (2004) 1075.