Synthesis of Polysubstituted Alkenes by Heck Vinylation or Suzuki Cross-Coupling Reactions in the Presence of a Tetraphosphane−Palladium Catalyst

Florian Berthiol,[a] Henri Doucet,*[a] and Maurice Santelli*[a]

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Through the use of $[PdCl(C_3H_5)]_2$/*cis*,*cis*,*cis*-1,2,3,4-tetrakis-[(diphenylphosphanyl)methyl]cyclopentane as a catalyst, a range of vinyl bromides undergo Suzuki cross-couplings with arylboronic acids in good yields. Furthermore, the catalyst can be used at low loadings, even for reactions of sterically hindered substrates. Mediated by this catalyst, stilbene and 1,1-diphenylethylene undergo Heck reactions with aryl halides to give triarylethylene derivatives.

Introduction

The Heck vinylation and Suzuki cross-coupling reactions are among the most widely used palladium-catalyzed methodologies in organic synthesis.[1−6] Several ligands have been successfully employed for these reactions. The most popular one is triphenylphosphane. Even though the catalyst formed by association of this ligand with palladium complexes is quite efficient in terms of the yield of coupled product, its efficiency in terms of the ratio of substrate to catalyst is generally low (1 to 10% of the catalyst must be used). In recent years, several more stable palladium catalysts have been successfully employed for Suzuki cross-coupling reactions of aryl halides with arylboronic acids[7−11] and for Heck vinylations of aryl halides with acrylates or styrene.[12−17] On the other hand, the Heck reaction with disubstituted ethylene derivatives[18] and the Suzuki reaction with vinyl halides derivatives[19−31] have attracted less attention and, with these substrates, relatively few results have been reported using thermally stable palladium catalysts. Moreover, to the best of our knowledge, the efficiency of tetraphosphane ligands for the synthesis of polysubstituted alkenes has not been reported.

Results and Discussion

The nature of the phosphane ligand has a huge influence on the stability of the catalysts and on the rates of catalyzed reactions. To find more stable and more efficient palladium catalysts, we have prepared the tetrapodal[32] phosphane ligand, *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphanylmethyl)-cyclopentane (Tedicyp)[33] in which four diphenylphosphanylalkyl groups are bound stereospecifically to the same face of a cyclopentane ring. Recently, we reported the first results using Tedicyp as an efficient ligand in allylic substitutions,[33] and Heck[34−37] and Suzuki[38−42] cross-couplings. For example, a TON of 9.8×10^7 was obtained for the coupling of 4-bromoacetophenone with benzeneboronic acid. To develop a general catalyst for cross-coupling reactions, we decided to apply this ligand for the preparation of polysubstituted alkenes by Suzuki cross-couplings of vinyl bromides with arylboronic acids and Heck vinylations of stilbene and 1,1-diphenylethylene with aryl halides.

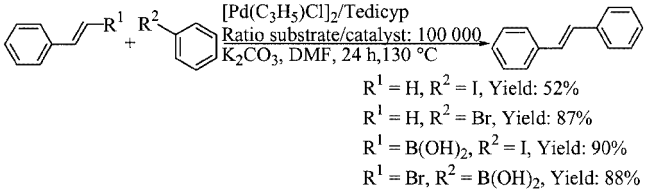
Tedicyp

First we tried to prepare bi-, tri- and tetraarylethylene derivatives by Heck or Suzuki reactions. For this study, based on previous results,[34] DMF was chosen as the solvent and potassium carbonate as the base. The reactions were generally performed at 80 or 130 °C under argon in the presence of $[Pd(C_3H_5)Cl]_2$/Tedicyp (ratio 1:2) as catalyst.

1,2-Biarylethylene derivatives can be prepared either by Heck or Suzuki reactions (Scheme 1). We have already reported the preparation of these compounds with $[Pd(C_3H_5)Cl]_2$/Tedicyp as the catalyst in Heck reactions.[36] Here, to determine the most efficient procedure, we have prepared these compounds by Suzuki reactions also. Quite similar reaction rates were observed using the Heck reaction, for the addition of iodobenzene or bromobenzene to styrene, or using the Suzuki reaction, for the coupling of β-bromostyrene with phenylboronic acid and for the coupling of *trans*-2-phenylvinylboronic acid with iodobenzene (Scheme 1). These results indicate that the Heck reaction

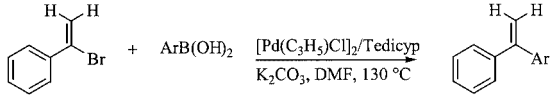
[a] Laboratoire de Synthèse Organique associé au CNRS, Faculté des Sciences de Saint Jérôme,
Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France
Fax: (internat.) +33-0491983865
E-mail: henri.doucet@univ.u-3mrs.fr
m.santelli@univ.u-3mrs.fr

seems to be the most efficient and economical procedure for the preparation of 1,2-biarylethylene derivatives.



Scheme 1

The Suzuki reaction between arylboronic acids and α-bromostyrene should be a powerful procedure for the synthesis of 1,1-biarylethylene derivatives (Scheme 2, Table 1). We have observed that it is indeed possible to efficiently cross-couple α-bromostyrene with arylboronic acids, under conditions very similar to those employed for the corresponding aryl bromides. This reaction can be performed with as little as 0.001% of catalyst. The $[Pd(C_3H_5)Cl]_2$/Tedicyp catalyst system is also tolerant of electronic variation in the arylboronic acid component. α-Bromostyrene reacts cleanly at 130 °C with electron-poor, electron-neutral, and electron-rich arylboronic acids, and a wide range of functions — such as methoxy, fluoro, trifluoromethyl, dimethylamino, nitro and acetyl groups — on the arylboronic acid are tolerated. A minor influence of these substituents on the reaction rate was observed. Moreover, the catalyst is also active for coupling of a heteroarylboronic acid (entry 15, Table 1).



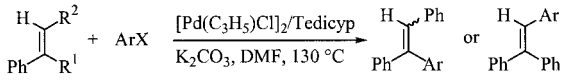
Scheme 2

Table 1. Suzuki reactions of α-bromostyrene (Scheme 2)

Entry[a]	$ArB(OH)_2$	Ratio Substrate/ catalyst	Product number	Yield [%]
1	$PhB(OH)_2$	100000	**1**	92
2	2-Me-$C_6H_4B(OH)_2$	100000	**2**	85
3	2-MeO-$C_6H_4B(OH)_2$	100000	**3**	88
4	4-MeO-$C_6H_4B(OH)_2$	100000	**4**	86
5	4-MeO-$C_6H_4B(OH)_2$	1000000	**4**	28[b]
6	1-naphthylboronic acid	100000	**5**	81
7	4-F-$C_6H_4B(OH)_2$	100000	**6**	83
8	2,4-F_2-$C_6H_3B(OH)_2$	100000	**7**	80
9	2-CF_3-$C_6H_4B(OH)_2$	10000	**8**	62
10	4-CF_3-$C_6H_4B(OH)_2$	100000	**9**	78
11	3,5-$(CF_3)_2$-$C_6H_3B(OH)_2$	10000	**10**	75
12	4-NMe_2-$C_6H_4B(OH)_2$	10000	**11**	91
13	3-NO_2-$C_6H_4B(OH)_2$	100000	**12**	86
14	4-MeCO-$C_6H_4B(OH)_2$	10000	**13**	95
15	thiophene-2-boronic acid	1000	**14**	77

[a] Conditions: catalyst (see ref.[33]), α-bromostyrene (1 equiv.), $ArB(OH)_2$ (2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h. [b] GC yield.

We also studied the synthesis of triarylalkenes by Heck vinylation of arylhalides with stilbene or 1,1-diphenylethylene (Scheme 3, Table 2). The addition of iodobenzene or 4-bromoanisole to *trans*-stilbene in the presence of 0.2% catalyst led to the corresponding coupled products in good yield. A mixture of the two stereoisomers [(*Z*) and (*E*)] was obtained for the reaction of 4-bromoanisole (entry 2, Table 2). Slower rates were observed for the reaction of arylhalides with 1,1-diphenylethylene, compared with those of *trans*-stilbene. The reactions were performed with 4-bromoanisole, iodobenzene, 4-fluorobromobenzene and 3- and 4-trifluoromethylbromobenzene (entries 3−7, Table 2). With all of these substrates, 0.4−1% catalyst must be used, which indicates that the rate-limiting step of the reaction is probably not the oxidative addition of the arylhalide. It is likely that a step after oxidative addition is turnover-limiting, presumably because of the steric demand of the olefin.



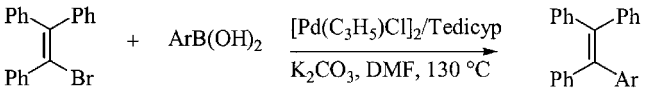
Scheme 3

Table 2. Heck reactions of stilbene and 1,1-diphenylethylene (Scheme 3)

Entry[a]	R^1	R^2	ArX	Ratio substrate/ catalyst	Product number	Yield [%]
1	H	Ph	PhI	500	**15**	78
2	H	Ph	4-MeO-C_6H_4Br	500	**16**	75[b]
3	Ph	H	3-CF_3-C_6H_4Br	100	**17**	69
4	Ph	H	4-CF_3-C_6H_4Br	100	**18**	51
5	Ph	H	PhI	100	**15**	63
6	Ph	H	4-MeO-C_6H_4Br	250	**19**	62
7	Ph	H	4-F-C_6H_4Br	250	**20**	70

[a] Conditions: catalyst (see ref.[33]), ArX (1 equiv.), alkene (1.3 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h. [b] Ratio *Z*/*E* is 39:61.

Although the synthesis of triarylethylene derivatives can be performed by Heck vinylation, the preparation of tetraarylethylenes from arylhalides and triarylethylenes was not possible with our catalyst. For example, iodobenzene, 1,1,2-triphenylethylene and potassium carbonate were recovered unchanged after their reaction in the presence of 1% catalyst for 20 hours at 130 °C. On the other hand, the synthesis of these tetraarylethylene derivatives was possible by Suzuki cross-coupling reactions (Scheme 4, Table 3). Bromotriphenylethylene reacts cleanly with electronically diverse arylboronic acids (entries 1 and 4, Table 3), and sterically hindered *ortho*-substituted arylboronic acids (entries 2 and 5, Table 3).



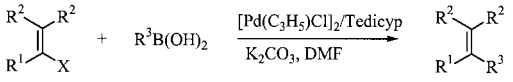
Scheme 4

Table 3. Suzuki reactions of bromotriphenylethylene (Scheme 4)

Entry[a]	$ArB(OH)_2$	Ratio substrate/catalyst	Product number	Yield [%]
1	4-F-$C_6H_4B(OH)_2$	10000	**21**	80
2	2-MeO-$C_6H_4B(OH)_2$	1000	**22**	82
3	2-MeO-$C_6H_4B(OH)_2$	10000	**22**	49[b]
4	4-MeO-$C_6H_4B(OH)_2$	10000	**23**	90
5	2-Me-$C_6H_4B(OH)_2$	10000	**24**	83

[a] Conditions: catalyst (see ref.[33]), bromotriphenylethylene (1 equiv.), $ArB(OH)_2$ (2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h. [b] GC yield.

Next, we studied the Suzuki cross-coupling reaction with a chloroalkene and four bromoalkenes (Scheme 5, Table 4). In the presence of a vinyl chloride (2-chloroprop-1-ene) we obtained the coupling products with 4-methoxybenzeneboronic acid and 1-naphthylboronic acid in good yield, but the presence of 4% catalyst was required (entries 1, 2, Table 4). The coupling products are also obtained selectively in good yields using 2-bromobut-1-ene, 1-bromo-2-methylprop-1-ene and 2-bromo-3-methylbut-2-ene. We observed almost no influence of the position of the alkyl substituent on the bromoalkene on the reaction rates. Arylboronic acids with *ortho* substituents are also efficiently coupled (entries 4, 6, 8−9, Table 4).



Scheme 5

2-Phenylacrylate derivatives are useful precursors for the synthesis of biologically active compounds, such as ibuprofen, ketoprofen and naproxen. We have observed that the cross-coupling of ethyl 2-bromoacrylate with arylboronic acids is a powerful method for the synthesis of these compounds (entries 16−26, Table 4). The reactions were performed in the presence of 0.4−0.01% catalyst at 80 °C. The functional group tolerance on the arylboronic acid is worthy of note.

Conclusion

We have established that the Tedicyp−palladium system is not limited to Suzuki reactions of aryl bromides; vinyl bromides are also efficiently coupled. This complex provides a convenient catalyst for the synthesis of polysubstituted ethylene derivatives. 1,1-Biarylethylene compounds have been prepared in good yield by the cross-coupling of arylboronic acids with α-bromostyrene. Tetraarylethylene compounds were obtained by reaction of arylboronic acids with 1,1,2-triphenylethylene. The reaction of bromoalkenes

Table 4. Suzuki reactions of 2-chloroprop-1-ene, 2-bromobut-1-ene, 1-bromo-2-methylprop-1-ene, 2-bromo-3-methylbut-2-ene and ethyl 2-bromoacrylate (Scheme 5)

Entry[a]	R^1	R^2	X	$R^3B(OH)_2$	Ratio substrate/catalyst	T [°C]	Product number	Yield [%]
1	Me	H	Cl	4-MeO-$C_6H_4B(OH)_2$	25	130[b]	**25**	65
2	Me	H	Cl	1-naphthylboronic acid	25	130[b]	**26**	54
3	Et	H	Br	4-MeO-$C_6H_4B(OH)_2$	10000	80	**27**	88
4	Et	H	Br	2-MeO-$C_6H_4B(OH)_2$	10000	80	**28**	93
5	Et	H	Br	4-F-$C_6H_4B(OH)_2$	10000	80	**29**	90
6	Et	H	Br	2-Me-$C_6H_4B(OH)_2$	10000	80	**30**	87
7	H	Me	Br	4-MeO-$C_6H_4B(OH)_2$	10000	80	**31**	81
8	H	Me	Br	2-MeO-$C_6H_4B(OH)_2$	1000	80	**32**	88
9	H	Me	Br	2-MeO-$C_6H_4B(OH)_2$	10000	80	**32**	68[c]
10	H	Me	Br	1-naphthylboronic acid	10000	80	**33**	80
11	Me	Me	Br	$PhB(OH)_2$	1000	100	**34**	84
12	Me	Me	Br	4-MeO-$PhB(OH)_2$	1000	100	**35**	92
13	Me	Me	Br	4-MeO-$PhB(OH)_2$	10000	100	**35**	44[c]
14	Me	Me	Br	4-F-$PhB(OH)_2$	1000	100	**36**	88
15	Me	Me	Br	4-F-$PhB(OH)_2$	10000	100	**36**	52[c]
16	CO_2Et	H	Br	$PhB(OH)_2$	1000	80	**37**	78
17	CO_2Et	H	Br	2-Me-$C_6H_4B(OH)_2$	1000	80	**38**	75
18	CO_2Et	H	Br	2-MeO-$C_6H_4B(OH)_2$	1000	80	**39**	75
19	CO_2Et	H	Br	4-MeO-$C_6H_4B(OH)_2$	1000	80	**40**	81
20	CO_2Et	H	Br	4-MeO-$C_6H_4B(OH)_2$	10000	80	**40**	62[c]
21	CO_2Et	H	Br	4-F-$C_6H_4B(OH)_2$	1000	80	**41**	82
22	CO_2Et	H	Br	4-F-$C_6H_4B(OH)_2$	10000	80	**41**	72[c]
23	CO_2Et	H	Br	1-naphthylboronic acid	250	80	**42**	84
24	CO_2Et	H	Br	6-methoxy-2-naphthylboronic acid	250	80	**43**	48
25	CO_2Et	H	Br	3,5-$(CF_3)_2$-$C_6H_3B(OH)_2$	1000	80	**44**	70
26	CO_2Et	H	Br	4-NMe_2-$C_6H_4B(OH)_2$	1000	80	**45**	76

[a] Conditions: catalyst (see ref.[33]), RBr (1 equiv.), $ArB(OH)_2$ (2 equiv.), K_2CO_3 (2 equiv.), DMF, 20 h. [b] 2-Chloropropene (2 equiv.), $ArB(OH)_2$ (1 equiv.), reaction performed in an autoclave. [c] GC yield.

and ethyl 2-bromoacrylate with arylboronic acids also led to the coupling adducts in good yields. In the presence of this catalyst some of the reactions can be performed with as little as 0.001 mol % catalyst. To date, only a few other ligands have good reactivity at such a low loading. We have also observed that 1,1,2-triarylethylene derivatives can be prepared by Heck reactions of arylhalides with 1,1-diphenylethylene and stilbene.

Experimental Section

General Remarks: All reactions were run under argon in Schlenk tubes using vacuum lines. In order to avoid contamination with palladium residues, the reactions were performed in brand-new Pyrex chromatography tubes inserted in Schlenk tubes; dry DMF was added in the Schlenk tube for the conduction of the temperature of the oil bath to the Pyrex tubes. Analytical grade DMF (99.8%) was not distilled before use. Some of the aryl halides were distilled before use. Potassium carbonate (99+%) was used without drying. The reactions were monitored by both GC and NMR spectroscopy for substrates with high boiling points, and by GC for substrates with low boiling points. GC/MS was performed with a Varian Saturn 2100T spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using $CDCl_3$ solutions in a Bruker 300 MHz spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ (δ = 7.25 ppm). Flash chromatography was performed on silica gel (230−400 mesh).

General Procedure for the Coupling of Arylboronic Acids with Bromoalkenes: The reaction of the bromoalkene (10 mmol), K_2CO_3 (2.76 g, 20 mmol) and the arylboronic acid (20 mmol) in the presence of the Tedicyp−palladium complex, at the appropriate temperature (see Table 1, and Table 3−4) for 20 h in anhydrous DMF (10 mL) under argon, affords the corresponding coupling product after addition of water, extraction with dichloromethane, separation, drying ($MgSO_4$), evaporation and filtration through silica gel.

1-(2-Methylphenyl)-1-phenylethylene (2):[43] ^{1}H NMR: δ = 2.12 (s, 3 H, Me), 5.26 (d, J = 1.2 Hz, 1 H, =CH*H*), 5.83 (d, J = 1.2 Hz, 1 H, =C*H*H), 7.30 (m, 9 H, Ar) ppm.

1-(2-Methoxyphenyl)-1-phenylethylene (3):[44] ^{1}H NMR: δ = 3.63 (s, 3 H, OMe), 5.32 (d, J = 1.3 Hz, 1 H, =CH*H*), 5.73 (d, J = 1.3 Hz, 1 H, =C*H*H), 6.90 (d, J = 8.2 Hz, 1 H, Ar), 6.98 (t, J = 8.2 Hz, 1 H, Ar), 7.35−7.15 (m, 7 H, Ar and Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4, 111.1, 115.2, 120.5, 126.2, 127.2, 127.9, 128.9, 131.0, 131.1, 141.0, 146.9, 157.0 ppm. MS (EI, 70 eV): m/z (%) = 210 (100) [M$^+$].

1-(4-Methoxyphenyl)-1-phenylethylene (4):[45] ^{1}H NMR: δ = 3.82 (s, 3 H, OMe), 5.35 (d, J = 1.3 Hz, 1 H, =CH*H*), 5.40 (d, J = 1.3 Hz, 1 H, =C*H*H), 6.86 (d, J = 9.0 Hz, 2 H, Ar), 7.27 (d, J = 9.0 Hz, 2 H, Ar), 7.33 (m, 5 H, Ph) ppm.

1-(1-Phenylvinyl)naphthalene (5):[46] ^{1}H NMR: δ = 5.39 (s, J = 1.3 Hz, 1 H, =CH*H*), 5.98 (d, J = 1.3 Hz, 1 H, =C*H*H), 7.15−7.26 (m, 3 H, Ar), 7.27−7.35 (m, 3 H, Ar), 7.40−7.52 (m, 3 H, Ar), 7.75 (d, J = 8.5 Hz, 1 H, Ar), 7.86 (m, 2 H, Ar) ppm.

1-(4-Fluorophenyl)-1-phenylethylene (6):[47] ^{1}H NMR: δ = 5.34 (d, J = 1.1 Hz, 1 H, =CH*H*), 5.36 (d, J = 1.1 Hz, 1 H, =C*H*H), 6.93 (t, J = 8.8 Hz, 2 H, Ar), 7.23 (dd, J = 5.4, 8.8 Hz, 2 H, Ar), 7.26 (m, 5 H, Ph) ppm.

1-(2,4-Difluorophenyl)-1-phenylethylene (7): ^{1}H NMR: δ = 5.39 (d, J = 1.7 Hz, 1 H, =CH*H*), 5.72 (d, J = 1.7 Hz, 1 H, =C*H*H), 6.91−6.77 (m, 2 H, Ar), 7.15−7.35 (m, 6 H, Ar and Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 103.7, 104.1, 104.4, 110.9, 111.0, 111.1, 111.2, 117.1, 125.3, 125.4, 125.5, 125.6, 126.7, 127.9, 128.3, 132.0, 132.1, 132.2, 140.3, 143.3, 158.5, 158.6, 160.8, 160.9, 161.8, 161.9, 164.1, 164.2 ppm. $C_{14}H_{10}F_2$ (216.2): calcd. C 77.77, H 4.66; found C 77.49, H 4.57. MS (EI, 70 eV): m/z (%) = 216 (100) [M$^+$].

1-Phenyl-1-(2-trifluoromethylphenyl)ethylene (8):[48] ^{1}H NMR: δ = 5.21 (s, 1 H, =CH*H*), 5.86 (s, 1 H, =C*H*H), 7.15−7.30 (m, 6 H, Ar and Ph), 7.43 (t, J = 7.3 Hz, 1 H, Ar), 7.52 (t, J = 7.3 Hz, 1 H, Ar), 7.70 (d, J = 8.1 Hz, 1 H, Ar) ppm.

1-Phenyl-1-(4-trifluoromethylphenyl)ethylene (9):[49] ^{1}H NMR: δ = 5.50 (s, 1 H, =CH*H*), 5.55 (s, 1 H, =C*H*H), 7.30−7.40 (m, 5 H, Ph), 7.44 (d, J = 8.7 Hz, 2 H, Ar), 7.56 (d, J = 8.7 Hz, 2 H, Ar) ppm.

1-Phenyl-1-[3,5-bis(trifluoromethyl)phenyl]ethylene (10): ^{1}H NMR: δ = 5.55 (s, 1 H, =CH*H*), 5.64 (s, 1 H, =C*H*H), 7.27 (m, 2 H, Ph), 7.37 (m, 3 H, Ph), 7.77 (s, 2 H, Ar), 7.82 (s, 1 H, Ar) ppm. $C_{16}H_{10}F_6$ (316.2): calcd. C 60.77, H 3.19; found C 60.58, H 3.28. MS (EI, 70 eV): = m/z (%) = 316 (100) [M$^+$].

1-(4-*N*,*N*-Dimethylaminophenyl)-1-phenylethylene (11):[50] ^{1}H NMR: δ = 2.96 (s, 6 H, Me), 5.24 (d, J = 1.3 Hz, 1 H, =CH*H*), 5.37 (d, J = 1.3 Hz, 1 H, =C*H*H), 6.67 (d, J = 8.8 Hz, 2 H, Ar), 7.23 (d, J = 8.8 Hz, 2 H, Ar), 7.25−7.40 (m, 5 H, Ph) ppm.

1-(3-Nitrophenyl)-1-phenylethylene (12):[51] ^{1}H NMR: δ = 5.56 (d, J = 0.6 Hz, 1 H, =CH*H*), 5.60 (d, J = 0.6 Hz, 1 H, =C*H*H), 7.28−7.38 (m, 5 H, Ph), 7.49 (t, J = 8.0 Hz, 1 H, Ar), 7.64 (dt, J = 8.0, 1.6 Hz, 1 H, Ar), 8.17 (ddd, J = 8.0, 2.3, 1.1 Hz, 1 H, Ar), 8.22 (t, J = 1.9 Hz, 1 H, Ar) ppm.

1-(4-Acetylphenyl)-1-phenylethylene (13):[45] ^{1}H NMR: δ = 2.61 (s, 3 H, Me), 5.54 (d, J = 1.0 Hz, 1 H, =CH*H*), 5.55 (d, J = 1.0 Hz, 1 H, =C*H*H), 7.26−7.38 (m, 5 H, Ph), 7.42 (d, J = 8.7 Hz, 2 H, Ar), 7.92 (d, J = 8.7 Hz, 2 H, Ar) ppm.

(1-Phenylvinyl)-2-thiophene (14):[52] ^{1}H NMR: δ = 5.25 (s, 1 H, =CH*H*), 5.59 (s, 1 H, =C*H*H), 6.90 (d, J = 3.4 Hz, 1 H, Ar), 6.97 (dd, J = 5.1, 3.4 Hz, 1 H, Ar), 7.22 (d, J = 5.1 Hz, 1 H, Ar), 7.32−7.39 (m, 3 H, Ph), 7.40−7.48 (m, 2 H, Ph) ppm.

1-(4-Fluorophenyl)-1,2,2-triphenylethylene (21): ^{1}H NMR: δ = 6.81 (t, J = 8.7 Hz, 2 H, Ar), 6.90−7.20 (m, 17 H, Ar) ppm. $C_{26}H_{19}F$ (350.4): calcd. C 89.11, H 5.46; found C 88.99, H 5.27. MS (EI, 70 eV): m/z (%) = 350 (100) [M$^+$].

1-(2-Methoxyphenyl)-1,2,2-triphenylethylene (22):[53] ^{1}H NMR: δ = 3.44 (s, 3 H, OMe), 6.72 (m, 2 H, Ar), 7.00−7.15 (m, 17 H, Ph) ppm.

1-(4-Methoxyphenyl)-1,2,2-triphenylethylene (23):[54] ^{1}H NMR: δ = 3.74 (s, 3 H, OMe), 6.64 (d, J = 8.9 Hz, 2 H, Ar), 6.96 (d, J = 8.9 Hz, 2 H, Ar), 7.00−7.15 (m, 15 H, Ph) ppm.

1-(2-Methylphenyl)-1,2,2-triphenylethylene (24):[55] ^{1}H NMR: δ = 2.09 (s, 3 H, Me), 6.90−7.20 (m, 19 H) ppm.

2-(4-Methoxyphenyl)propene (25):[56] ^{1}H NMR: δ = 2.07 (s, 3 H, Me), 3.75 (s, 3 H, OMe), 4.93 (s, 1 H, =CH_2), 5.23 (s, 1 H, =CH_2), 6.80 (d, J = 8.5 Hz, 2 H, Ar), 7.32 (d, J = 8.5 Hz, 2 H, Ar) ppm.

2-(1-Naphthyl)propene (26):[57] ^{1}H NMR: δ = 2.16 (s, 3 H, Me), 5.05 (s, 1 H, =CH_2), 5.40 (s, 1 H, =CH_2), 7.10−8.00 (m, 7 H, Ar) ppm.

2-(4-Methoxyphenyl)but-1-ene (27):[58] ^{1}H NMR: δ = 1.11 (t, *J* = 7.4 Hz, 3 H, Me), 2.48 (q, *J* = 7.4 Hz, 2 H, CH_2), 3.80 (s, 3 H, OMe), 4.98 (s, 1 H, =C*H*H), 5.21 (s, 1 H, =CH*H*), 6.85 (d, *J* = 8.8 Hz, 2 H, Ar), 7.37 (d, *J* = 8.8 Hz, 2 H, Ar) ppm.

2-(2-Methoxyphenyl)but-1-ene (28):[59] ^{1}H NMR: δ = 1.11 (t, *J* = 7.4 Hz, 3 H, Me), 2.57 (q, *J* = 7.4 Hz, 2 H, CH_2), 3.90 (s, 3 H, OMe), 5.10 (d, *J* = 1.5 Hz, 1 H, =C*H*H), 5.24 (d, *J* = 1.5 Hz, 1 H, =CH*H*), 7.00 (m, 2 H, Ar), 7.23 (dd, *J* = 7.5, 1.9 Hz, 1 H, Ar), 7.35 (m, 1 H, Ar) ppm.

2-(4-Fluorophenyl)but-1-ene (29):[60] ^{1}H NMR: δ = 1.09 (t, *J* = 7.4 Hz, 3 H, Me), 2.48 (q, *J* = 7.4 Hz, 2 H, CH_2), 5.04 (s, 1 H, =C*H*H), 5.22 (s, 1 H, =CH*H*), 7.00 (t, *J* = 8.5 Hz, 2 H, Ar), 7.36 (dd, *J* = 5.5, 8.5 Hz, 2 H, Ar) ppm.

2-(2-Methylphenyl)but-1-ene (30):[61] ^{1}H NMR: δ = 1.02 (t, *J* = 7.4 Hz, 3 H, Me), 2.31 (q, *J* = 7.4 Hz, 2 H, CH_2), 2.27 (s, 3 H, Me), 4.83 (s, 1 H, =C*H*H), 5.15 (s, 1 H, =CH*H*), 7.00−7.30 (m, 4 H, Ar) ppm.

1-(4-Methoxyphenyl)-2-methylprop-1-ene (31):[62] ^{1}H NMR: δ = 1.84 (s, 3 H, Me), 1.87 (s, 3 H, Me), 3.80 (s, 3 H, OMe), 6.20 (s, 1 H, =CH), 6.85 (d, *J* = 8.8 Hz, 2 H, Ar), 7.15 (d, *J* = 8.8 Hz, 2 H, Ar) ppm.

1-(2-Methoxyphenyl)-2-methylprop-1-ene (32):[63] ^{1}H NMR: δ = 1.80 (s, 3 H, Me), 1.92 (s, 3 H, Me), 3.82 (s, 3 H, OMe), 6.30 (s, 1 H, =CH), 6.85 (d, *J* = 8.7 Hz, 1 H, Ar), 6.91 (t, *J* = 7.5 Hz, 1 H, Ar), 7.17 (m, 2 H, Ar) ppm.

2-Methyl-1-naphthylprop-1-ene (33):[64] ^{1}H NMR: δ = 1.74 (s, 3 H, Me), 2.04 (s, 3 H, Me), 6.68 (s, 1 H, =CH), 7.30 (d, *J* = 7.0 Hz, 1 H, Ar), 7.48−8.05 (m, 6 H, Ar) ppm.

3-Methyl-2-phenylbut-2-ene (34):[65] ^{1}H NMR: δ = 1.48 (s, 3 H, Me), 1.70 (s, 3 H, Me), 1.85 (s, 3 H, Me), 7.00 (d, *J* = 6.8 Hz, 2 H, Ar), 7.10−7.25 (m, 3 H, Ar) ppm.

2-(4-Methoxyphenyl)-3-methylbut-2-ene (35):[66] ^{1}H NMR: δ = 1.60 (s, 3 H, Me), 1.79 (s, 3 H, Me), 1.94 (s, 3 H, Me), 3.80 (s, 3 H, OMe), 6.84 (d, *J* = 8.7 Hz, 2 H, Ar), 7.04 (d, *J* = 8.7 Hz, 2 H, Ar) ppm.

2-(4-Fluorophenyl)-3-methylbut-2-ene (36):[67] ^{1}H NMR: δ = 1.57 (s, 3 H, Me), 1.79 (s, 3 H, Me), 1.93 (s, 3 H, Me), 6.92−7.10 (m, 4 H, Ar) ppm.

Ethyl 2-Phenylacrylate (37):[68] ^{1}H NMR: δ = 1.32 (t, *J* = 7.1 Hz, 3 H, Me), 4.27 (q, *J* = 7.1 Hz, 2 H, CH_2), 5.88 (s, 1 H, =C*H*H), 6.34 (s, 1 H, =CH*H*), 7.26−7.50 (m, 5 H, Ph) ppm.

Ethyl 2-(2-Methylphenyl)acrylate (38):[68] ^{1}H NMR: δ = 1.29 (t, *J* = 7.1 Hz, 3 H, Me), 2.21 (s, 3 H, Me), 4.25 (q, *J* = 7.1 Hz, 2 H, CH_2), 5.70 (s, 1 H, =C*H*H), 6.50 (s, 1 H, =CH*H*), 7.00−7.35 (m, 4 H, Ar) ppm.

Ethyl 2-(2-Methoxyphenyl)acrylate (39):[69] ^{1}H NMR: δ = 1.25 (t, *J* = 7.0 Hz, 3 H, Me), 3.78 (s, 3 H, MeO), 4.25 (q, *J* = 7.0 Hz, 2 H, CH_2), 5.72 (d, *J* = 1.5 Hz, 1 H, =C*H*H), 6.26 (d, *J* = 1.5 Hz, 1 H, =CH*H*), 6.87 (d, *J* = 8.3 Hz, 1 H, Ar), 6.65 (t, *J* = 7.5 Hz, 1 H, Ar), 7.22 (d, *J* = 7.5 Hz, 1 H, Ar), 7.32 (t, *J* = 7.3 Hz, 1 H, Ar) ppm.

Ethyl 2-(4-Methoxyphenyl)acrylate (40):[68] ^{1}H NMR: δ = 1.30 (t, *J* = 7.0 Hz, 3 H, Me), 3.81 (s, 3 H, MeO), 4.27 (q, *J* = 7.0 Hz, 2 H, CH_2), 5.82 (s, 1 H, =C*H*H), 6.26 (s, 1 H, =CH*H*), 6.87 (d, *J* = 8.5 Hz, 2 H, Ar), 7.36 (d, *J* = 8.5 Hz, 2 H, Ar) ppm.

Ethyl 2-(4-Fluorophenyl)acrylate (41):[70] ^{1}H NMR: δ = 1.32 (t, *J* = 7.0 Hz, 3 H, Me), 4.28 (q, *J* = 7.0 Hz, 2 H, CH_2), 5.85 (s, 1 H, =C*H*H), 6.34 (s, 1 H, =CH*H*), 7.02 (t, *J* = 8.6 Hz, 2 H, Ar), 7.38 (dd, *J* = 8.6, 5.5 Hz, 2 H, Ar) ppm.

Ethyl 2-(1-Naphthyl)acrylate (42):[71] ^{1}H NMR: δ = 1.19 (t, *J* = 7.0 Hz, 3 H, Me), 4.20 (q, *J* = 7.0 Hz, 2 H, CH_2), 5.87 (s, 1 H, =C*H*H), 6.69 (s, 1 H, =CH*H*), 7.35 (dd, *J* = 7.0, 1.1 Hz, 1 H, Ar), 7.45 (m, 3 H, Ar), 7.72 (m, 1 H, Ar), 7.84 (m, 2 H, Ar) ppm.

Ethyl 2-(6-Methoxy-2-naphthyl)acrylate (43):[72] ^{1}H NMR: δ = 1.30 (t, *J* = 7.0 Hz, 3 H, Me), 3.95 (s, 3 H, OMe), 4.32 (q, *J* = 7.0 Hz, 2 H, CH_2), 5.97 (s, 1 H, =C*H*H), 6.36 (s, 1 H, =CH*H*), 7.12 (m, 2 H, Ar), 7.49 (dd, *J* = 8.4, 1.7 Hz, 1 H, Ar), 7.71 (m, 2 H, Ar), 7.83 (s, 1 H, Ar) ppm.

Ethyl 2-[3,5-Bis(trifluoromethyl)phenyl]acrylate (44): ^{1}H NMR: δ = 1.32 (t, *J* = 7.0 Hz, 3 H, Me), 4.31 (q, *J* = 7.0 Hz, 2 H, CH_2), 6.03 (s, 1 H, =C*H*H), 6.57 (s, 1 H, =CH*H*), 7.84 (s, 1 H, Ar), 7.88 (s, 2 H, Ar) ppm. $C_{13}H_{10}F_6O_2$ (312.2): calcd. C 50.01, H 3.23; found C 50.18, H 3.10.

Ethyl 2-(4-*N*,*N*-Dimethylaminophenyl)acrylate (45): ^{1}H NMR: δ = 1.32 (t, *J* = 7.0 Hz, 3 H, Me), 2.96 (s, 6 H, NMe_2), 4.28 (q, *J* = 7.0 Hz, 2 H, CH_2), 5.76 (s, 1 H, =C*H*H), 6.12 (s, 1 H, =CH*H*), 6.68 (d, *J* = 8.7 Hz, 2 H, Ar), 7.32 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. $C_{13}H_{17}NO_2$ (219.3): calcd. C 71.21, H 7.81; found C 70.98, H 7.62.

General Procedure for the Coupling of Aryl Bromides and Alkenes: The reaction of the aryl bromide (10 mmol), K_2CO_3 (2.76 g, 20 mmol) and the alkene (13 mmol) in the presence of the Tedicyp-palladium complex, at 130 °C for 20 h in anhydrous DMF (10 mL) under argon, affords the corresponding addition product after addition of water, extraction with dichloromethane, separation, drying ($MgSO_4$), evaporation and filtration through silica gel.

1-(4-Methoxyphenyl)-1,2-diphenylethylene (16):[73] ^{1}H NMR, (*Z*) isomer: δ = 3.84 (s, 3 H, OMe), 6.83−7.36 (m, 15 H) ppm; (*E*) isomer: δ = 3.82 (s, 3 H, OMe), 6.83−7.36 (m, 15 H) ppm.

1,1-Diphenyl-2-(3-trifluoromethylphenyl)ethylene (17):[74] ^{1}H NMR: δ = 6.89 (s, 1 H, =CH), 7.05−7.32 (m, 14 H, Ar) ppm. MS (EI, 70 eV): *m*/*z* (%) = 324 (100) [M^+].

1,1-Diphenyl-2-(4-trifluoromethylphenyl)ethylene (18): ^{1}H NMR: δ = 6.98 (s, 1 H, =CH), 7.11 (d, *J* = 8.3 Hz, 2 H, Ar), 7.15−7.40 (m, 12 H, Ar) ppm. $C_{21}H_{15}F_3$ (324.3): calcd. C 77.77, H 4.66; found C 77.89, H 4.87. MS (EI, 70 eV): *m*/*z* (%) = 324 (100) [M^+].

1,1-Diphenyl-2-(4-methoxyphenyl)ethylene (19):[75] ^{1}H NMR: δ = 3.74 (s, 3 H, OMe), 6.66 (d, *J* = 8.7 Hz, 2 H, Ar), 6.94 (m, 3 H, = CH and Ar), 7.17−7.35 (m, 10 H, Ar) ppm.

1,1-Diphenyl-2-(4-fluorophenyl)ethylene (20):[76] ^{1}H NMR: δ = 6.81 (t, *J* = 8.8 Hz, 2 H, Ar), 6.91 (s, 1 H, =CH), 6.97 (dd, *J* = 5.7, 8.8 Hz, 2 H, Ar), 7.17 (m, 2 H, Ph), 7.25−7.35 (m, 8 H, Ph) ppm.

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