Efficient Synthesis of Substituted Styrenes and Biaryls (or Heteroaryls) with Regioselective Reactions of *ortho*-, *meta*-, and *para*-Bromobenzyl Bromide

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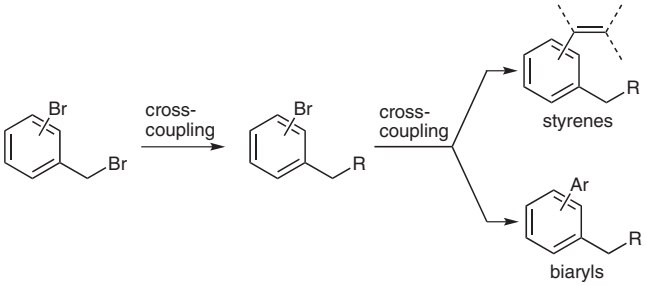
Abstract: Regio- and stereoselective reactions of *ortho*-, *meta*-, and *para*-bromobenzyl bromide under Stille and (or) Suzuki cross-coupling reactions are described that provided substituted styrene monomers and biaryls in two steps. By controlling the experimental conditions, the first coupling provided access to allylarene or diarylmethane intermediates, and the second reaction led to the desired styrenes and biaryls, substituted by a spacer arm in the *ortho*, *meta* or *para* position depending on the starting material.

Key words: Stille reaction, palladium, regioselectivity, organometallic reagents, biaryls

Styrenes and biaryls are useful building blocks for fine chemical synthesis.[1,2] Biaryl moieties with important physical or biological properties are widely represented in organic molecules.[3] As pharmacophores, they are found in many medicinally important compounds such as antibiotic, anti-inflammatory, antihypertensive, and anticancer drugs, among others. Di- or triaromatic rings are the backbone of some of the most efficient and selective ligands for asymmetric catalysis, especially when atropoisomerism is possible.[4]

Styrenes are of particular interest as monomers in the polymer industry,[5] conferring different properties on the polymers depending on the nature of the substituents present on the derivatives. The development of efficient, selective, and high-yielding methods for the preparation of these molecules will, therefore, continue well into the future.

In continuation of our previous studies on the different reactions of the two bromine atoms of bromobenzyl bromide[6] by cross-coupling reactions and recognizing that a chemoselective reaction could be valuable, we have developed an efficient and versatile method to synthesize a wide range of styrenes and biaryls very easily and selectively. We have investigated the selective substitution reaction under two successive Stille[7] and Suzuki[7g,8] cross-coupling reactions with *o*-, *m*-, and *p*-bromobenzyl bromides (Scheme 1).



Scheme 1 Preparation of styrene and biaryl compounds

The first coupling permitted regioselective access to allylarene or diarylmethane intermediates I and II, and the second reaction allowed the synthesis of styrenes and biaryls.

Synthesis of Intermediates I and II

Using 0.95 to 1 equivalents of an organometallic reagent and starting from *o*-, *m*- or *p*-bromobenzyl bromides, we were able to substitute benzylic bromide, rather than arylic bromide, regioselectively by Stille or Suzuki cross-coupling reactions in the presence of a palladium salt. The regioselective reaction of these two types of bromide has already been demonstrated by other reactions (e.g., nucleophilic or metallic substitution), however few reports have investigated this regioselectivity by cross-coupling catalysis.[6,9] We accessed bromo-substituted allylarenes **1a–j** (intermediates I) or brominated diarylmethanes **1k–r** (intermediates II) depending on the type of palladium catalysis and the organometallic reagent used.

The reaction conditions were classical (Table 1), but the temperature of the reaction should not exceed 80 °C, otherwise partial isomerization of the double bond of the allyl group occurred with the Stille reaction. The starting vinyltin compounds bearing a trialkylsilyl, trialkylgermyl, or triphenylgermyl, or a tributylstannyl group at the β position were obtained by hydrostannation of the corresponding alkynes.[10] For Suzuki cross-coupling, the temperature of the reaction depended on the boronic acid used. With some boronic acids, higher temperatures led to loss of regioselectivity.

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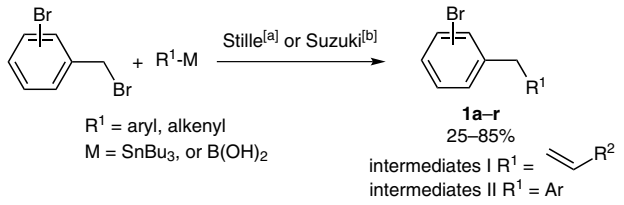
Table 1 Synthesis of Intermediates I **1a–j** and II **1k–r**[a,b]



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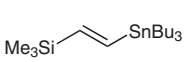
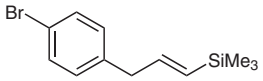
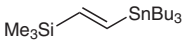
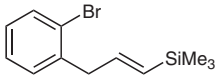
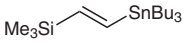
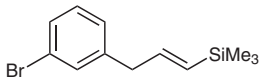
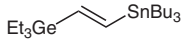
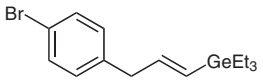
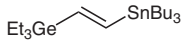
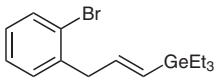
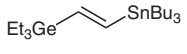
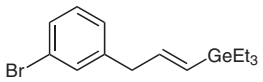
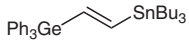
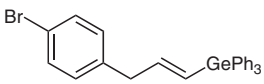
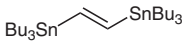
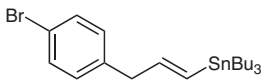
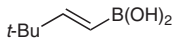
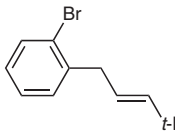
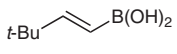
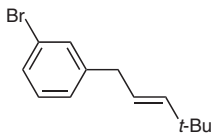
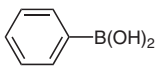
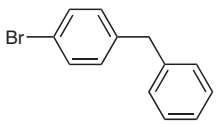
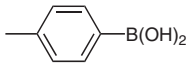
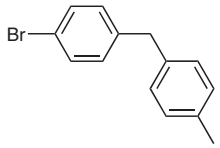
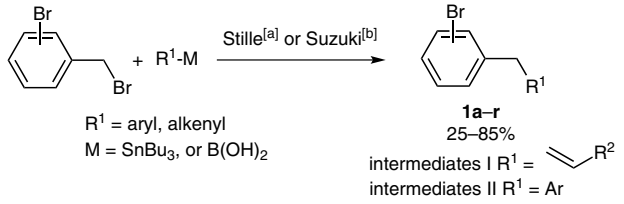
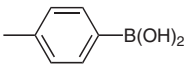
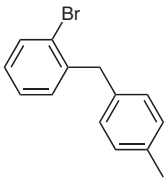
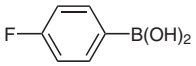
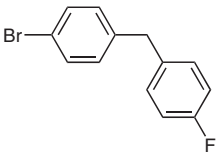
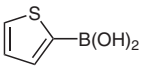
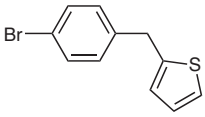
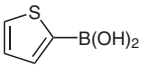
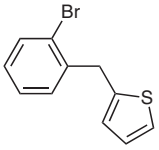
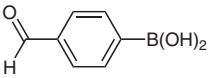
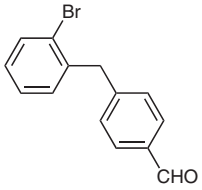
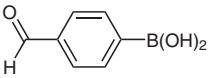
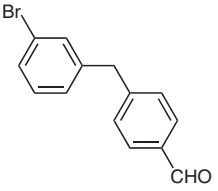
1			**1a**	78
2			**1b**	71
3			**1c**	72
4			**1d**	80
5			**1e**	67
6			**1f**	66
7			**1g**	67
8			**1h**[d]	25
9			**1i**	71
10			**1j**	69
11			**1k**[e]	84
12			**1l**[e]	83

Table 1 Synthesis of Intermediates I **1a–j** and II **1k–r**[a,b] (continued)



Entry	R-M reagent	Product		Yield[c] (%)
13			**1m**[e]	85
14			**1n**[f]	71
15			**1o**[f]	59
16			**1p**[f]	61
17			**1q**[g]	66
18			**1r**[g]	65

[a] Stille conditions: bromobenzyl bromide (12 mmol, 1 equiv), organotin (11.5 mmol, 0.95 equiv), $Pd(PPh_3)_4$ (3 mol%), toluene, 80 °C, 15 h.
[b] Suzuki conditions: bromobenzyl bromide (12 mmol, 1 equiv), boronic acid (12 mmol, 1 equiv), $Pd(PPh_3)_4$ (3 mol%), EtOH–toluene–H_2O, 1 M Na_2CO_3, 50 °C, 15 h.
[c] Yield of isolated product after chromatographic purification.
[d] 50% of double-coupling reaction was observed by GC.
[e] 80 °C.
[f] r.t., 24 h.
[g] 40 °C, 20 h.

As seen from the results in Table 1, these Stille and Suzuki cross-coupling reactions were completely regio- and stereoselective, and only the benzylic bromide was substituted. No bis-coupling products were obtained and no isomerization of allylic compounds occurred. The configuration of the double bond was conserved. We accessed diarylmethane **1k–r** or (*E*)-allylarenes **1a–j** very simply and in good yields, depending on the organometallic reagent used, substituted by an *o*-, *m*-, or *p*-bromo-substituted aryl group. It is noted that the reaction with (*E*)-1,2-bis(tributylstannyl)ethene (entry 8) provide a poor yield of **1h**, even when the reaction mixture was diluted and

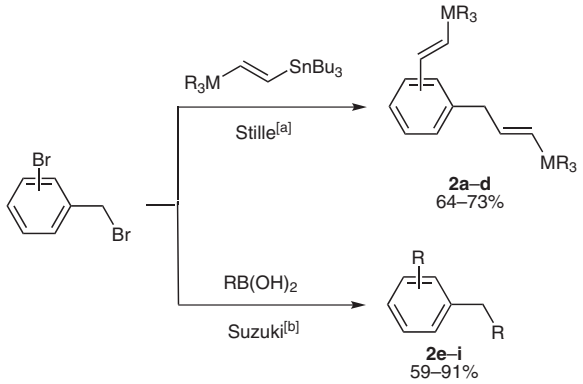
heated at only 70 °C. This was due to the inevitable formation of 50% of the product resulting from a double-coupling reaction.

Allylarenes **1a**–**h** bear 14th Group metals, this will be valuable in the synthesis of styrenes, because the polymers would have different properties after polymerization depending on the metal. Diarylmethanes are used in the synthesis of macrocycles, catenanes, and rotaxanes.[11] Moreover, they often appear in the constitution of natural products or advanced materials with important biological and medical properties.[12] The wide range of diarylmethanes thus synthesized could be of interest to modulate their pharmacological properties.

Synthesis of 'Symmetrical' Dimetaled Styrenes and Biaryls

Using 2.2 or 2.5 equivalents of an organometallic reagent under the same conditions as described above, a clean double cross-coupling reaction occurred, providing 'symmetrical' dimetaled styrenes **2a**–**d** and biaryls **2e**–**i** in one step in good yields (Table 2). The products obtained were substituted in the *ortho*, *meta*, or *para* position according to the starting bromobenzyl bromide.

Table 2 Synthesis of Symmetrical Styrenes and Biaryls by Double Cross-Coupling[a,b]



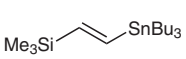
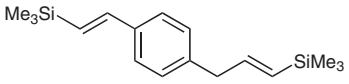
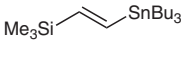
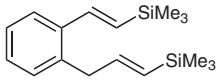
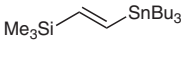
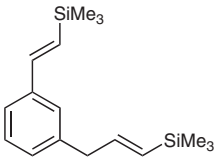
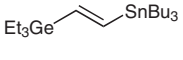
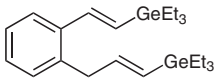
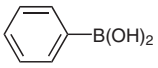
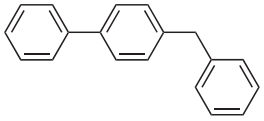
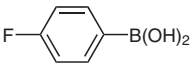
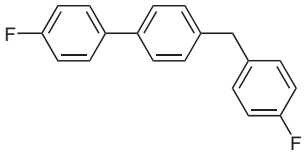
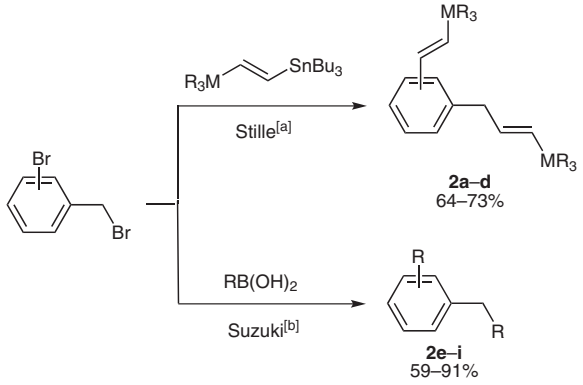
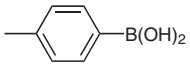
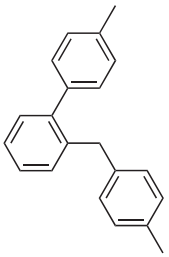
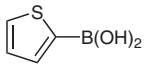
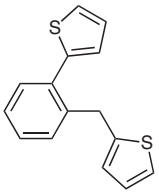
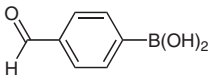
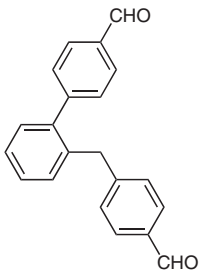
Entry	R-M reagent	Product		Yield[c] (%)
1			**2a**	73
2			**2b**	72
3			**2c**	70
4			**2d**[d]	64
5			**2e**	91
6			**2f**	79

Table 2 Synthesis of Symmetrical Styrenes and Biaryls by Double Cross-Coupling[a,b] (continued)



Entry	R-M reagent	Product		Yield[c] (%)
7			**2g**	87
8			**2h**[d]	59
9			**2i**[d]	71

[a] Stille conditions: bromobenzyl bromide (12 mmol, 1 equiv), organotin (30 mmol, 2.5 equiv), $Pd(PPh_3)_4$ (3 mol%), toluene, 80 °C, 18 h.
[b] Suzuki conditions: bromobenzyl bromide (12 mmol, 1 equiv), boronic acid (26.4 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (3 mol%), EtOH–toluene–H_2O, 1 M Na_2CO_3, 50 °C, 18 h.
[c] Yield of isolated product after chromatographic purification.
[d] 24 h.

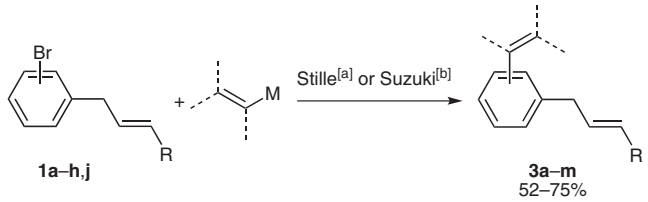
Synthesis of Substituted Styrenes (Types I and II): Cross-Coupling with Aryl Bromides

The synthesis of styrenes has been widely described in the literature, and several methods can be used, including palladium cross-coupling[13] such as Heck,[14] Hiyama,[15] Stille,[7,16] or Suzuki[17] reactions. A Stille or Suzuki reaction with vinylic reagents seemed to be the most efficient method by which to obtain the desired styrenes. These methods allowed us to synthesize various styrenes substituted with an allyl arm that could be metaled (type I styrenes) or with a diarylmethane (type II styrenes) depending on the intermediates.

The different type I styrenes were substituted by a three-carbon spacer between the phenyl group and a Group 14 metal. This type of monomer was required for polymerization in order to test the physical properties of the copolymers obtained, varying according to the nature of the metal. The polymers were tested in order to constitute one part of the target in the internal cavity of the laser megajoule (LMJ).[18] As can be seen in Table 2, vinyltin and vinylboronic acid reagents were good candidates for such

synthesis and proved their efficiency as tools for the transfer of a vinyl unit, with high tolerance of numerous functions both on the substrate and on the reagent.[19] The final styrenes **3a**–**m** were synthesized in large quantities to test the polymerization; conventional methods for the synthesis of vinyltin compounds by exchange between magnesium chloride and tributyltin are sometimes tedious. The organotins used in Stille cross-coupling were prepared by sonochemistry.[20] Stille and Suzuki palladium cross-coupling was performed on the arylic bromide of previously prepared (*E*)-allylarene intermediates I **1a**–**h**,**j** to obtain the desired styrenes **3a**–**m**. This Stille reaction was run in classical coupling arylic halide conditions with vinyltin in toluene at 90 °C for 18 hours, with a small excess of vinyltin for optimal reaction progress. The Suzuki cross-coupling reaction was performed with (*E*)-3,3-dimethylbut-2-enylboronic acid in slight excess at 80 °C for 18 hours. Metaled or bis-metaled new styrene monomers were obtained in good yields with a three carbon spacer in *ortho*, *meta*, or *para* position. The results are presented in Table 3.

Table 3 Synthesis of Type I Styrenes[a,b]



R = $SiMe_3$, $SnBu_3$, $GeEt_3$, $GePh_3$, *t*-Bu
M = $SnBu_3$, $B(OH)_2$

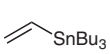
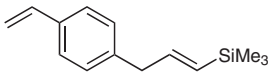
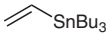
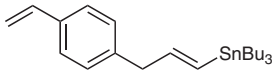
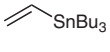
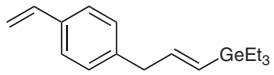
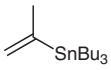
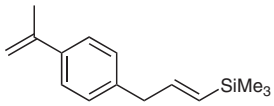
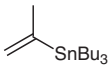
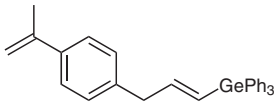
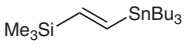
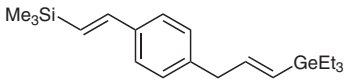
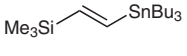
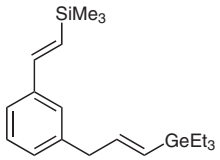
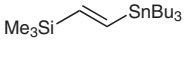
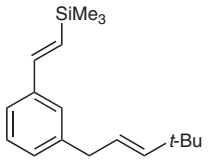
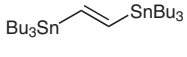
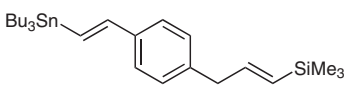
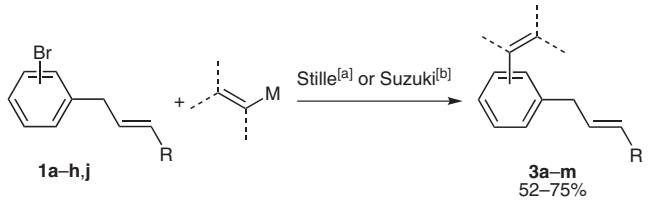
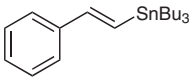
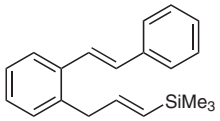
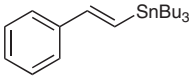
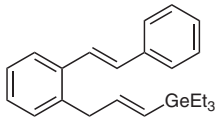
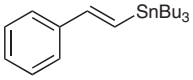
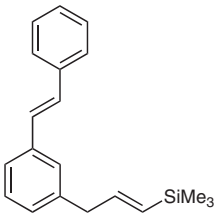
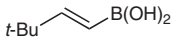
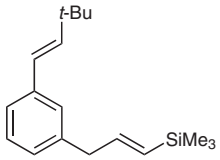
Entry	Intermediate I	R-M reagent	Product		Yield[c] (%)
1	**1a**			**3a**	75
2	**1h**			**3b**	64
3	**1d**			**3c**	71
4	**1a**			**3d**	69
5	**1g**			**3e**	60
6	**1d**			**3f**	64
7	**1f**			**3g**	70
8	**1j**			**3h**	73
9	**1a**			**3i**	52

Table 3 Synthesis of Type I Styrenes[a,b] (continued)



R = $SiMe_3$, $SnBu_3$, $GeEt_3$, $GePh_3$, *t*-Bu
M = $SnBu_3$, $B(OH)_2$

Entry	Intermediate I	R-M reagent	Product		Yield[c] (%)
10	**1b**			**3j**	65
11	**1e**			**3k**	62
12	**1c**			**3l**	63
13	**1c**			**3m**	74

[a] Stille conditions: intermediates **1a**–**h**,**j** (4 mmol, 1 equiv), organotin (5.2 mmol, 1.3 equiv), $Pd(PPh_3)_4$ (3 mol%), toluene, 90 °C, 18 h.
[b] Suzuki conditions: intermediate **1c** (4 mmol, 1 equiv), boronic acid (4.8 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (3 mol%), EtOH–toluene–H_2O, 1 M Na_2CO_3, 80 °C, 18 h.
[c] Yield of isolated product after chromatographic purification.

Another clean second substitution by the Stille or Suzuki-type reaction was also possible, providing diarylmethane-substituted type II styrenes. New substituted styrenes (metaled or unmetaled) with a one carbon spacer between the two aromatic groups were prepared by reaction of arylic bromides **1k**–**p**,**r**. Using the same conditions as previously used for the synthesis of type I styrenes, various arylstyrenes **4a**–**j** were also obtained in good yields, as presented in Table 4.

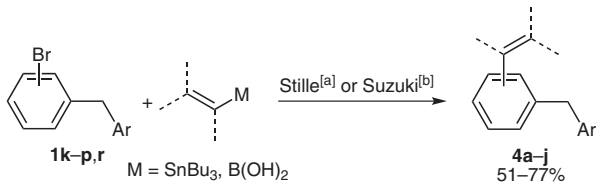
Synthesis of Substituted Biaryls: Cross-Coupling with Aryl Bromides

Cross-coupling catalysis, in particular the Suzuki reaction is the most versatile and often used reaction for the synthesis of biaryl-containing molecules.[21] We decided to use this coupling reaction on the two types of intermediates I and II in order to synthesize biaryls that were substituted with an allyl or a diarylmethane group, depending on the intermediate used. The reaction conditions were the same as previously described, various biaryls **5a**–**o** were also obtained very efficiently in good yields bearing either a diarylmethane or an allyl group in the *ortho*, *meta*, or *para* position, as shown in Table 5.

Double Coupling in One-Pot Reaction

In order to synthesize differently disubstituted styrenes and biaryls, we performed two one-pot cross-coupling reactions without isolating the intermediate. A Suzuki cross-coupling reaction was performed on two different boronic acids (Scheme 2) to test this strategy.

Table 4 Synthesis of Type II Styrenes



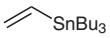
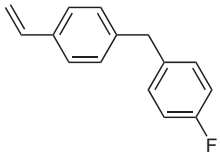
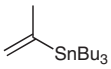
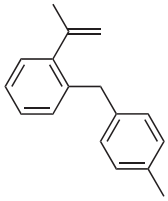
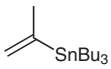
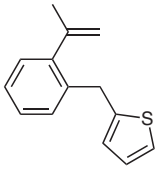
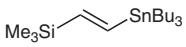
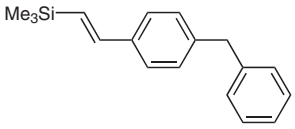
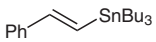
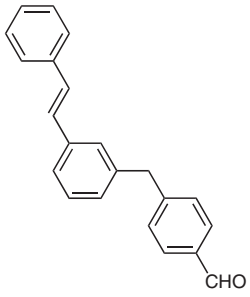
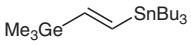
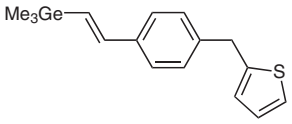
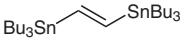
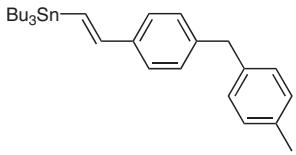
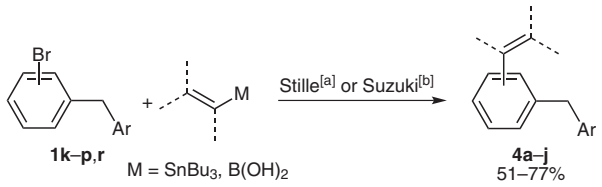
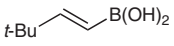
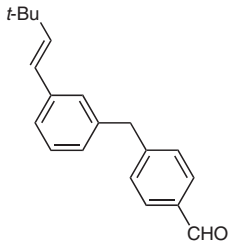
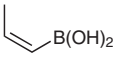
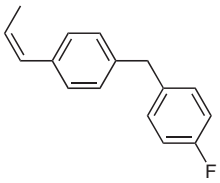
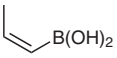
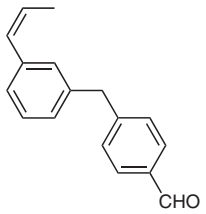
Entry	Intermediate II	R-M reagent	Product		Yield[c] (%)
1	**1n**			**4a**	72
2	**1m**			**4b**	67
3	**1p**			**4c**	63
4	**1k**			**4d**	77
5	**1r**			**4e**	64
6	**1o**			**4f**	58
7	**1l**			**4g**	51

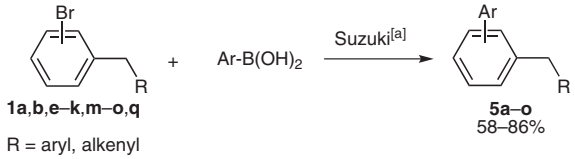
Table 4 Synthesis of Type II Styrenes (continued)



Entry	Intermediate II	R-M reagent	Product		Yield[c] (%)
8	**1r**			**4h**	76
9	**1n**			**4i**	70
10	**1r**			**4j**	75

[a] Stille conditions: intermediates **1l–p**,**r** (4 mmol, 1 equiv), organotin (5.2 mmol, 1.3 equiv), $Pd(PPh_3)_4$ (3 mol%), toluene, 90 °C, 18 h.
[b] Suzuki conditions: intermediates **1n**,**r** (4 mmol, 1 equiv), boronic acid (4.8 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (3 mol%), EtOH–toluene–H_2O, 1 M Na_2CO_3, 80 °C, 18 h.
[c] Yield of isolated product after chromatographic purification.

Table 5 Synthesis of Substituted Biaryls[a]



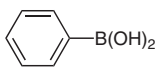
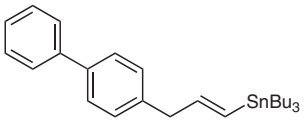
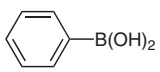
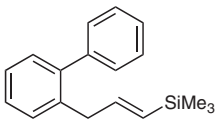
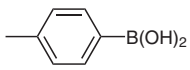
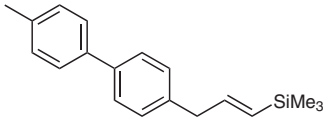
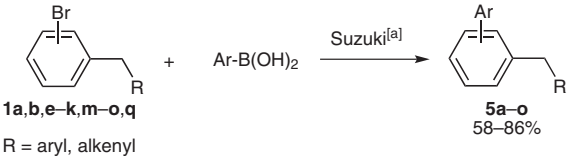
Entry	Intermediate	Boronic acids	Product		Yield[b] (%)
1	**1h**			**5a**	67
2	**1b**			**5b**	77
3	**1a**			**5c**	77

Table 5 Synthesis of Substituted Biaryls[a] (continued)



1a,**b**,**e–k**,**m–o**,**q**

R = aryl, alkenyl

5a–o
58–86%

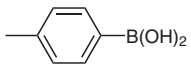
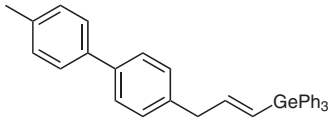
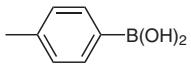
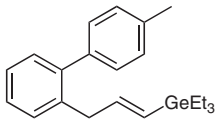
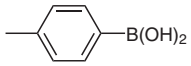
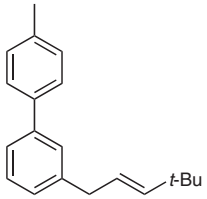
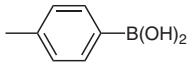
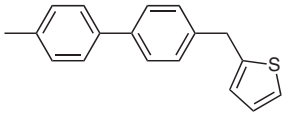
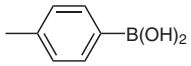
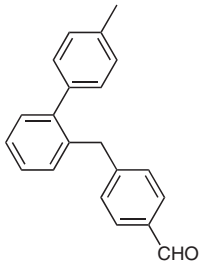
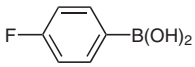
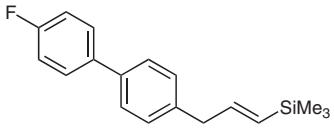
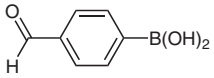
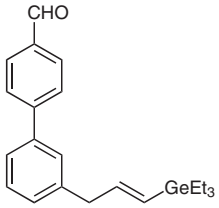
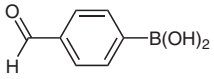
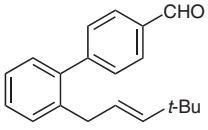
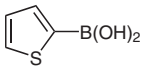
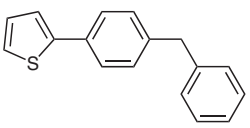
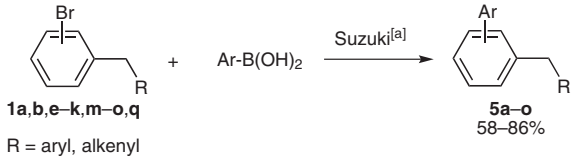
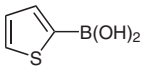
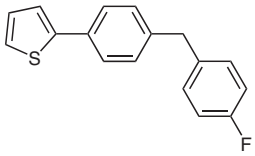
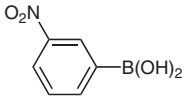
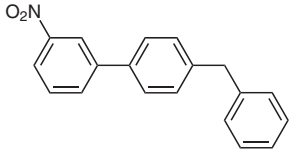
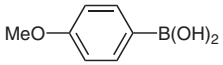
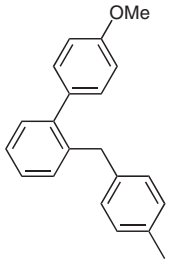
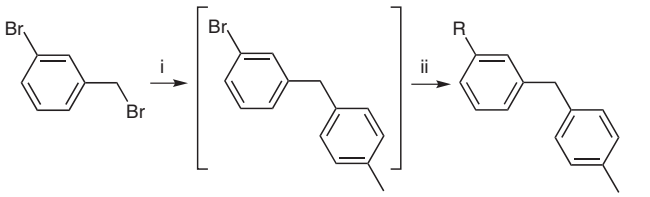
Entry	Intermediate	Boronic acids	Product		Yield[b] (%)
4	**1g**			**5d**	62
5	**1e**			**5e**	78
6	**1j**			**5f**	83
7	**1o**			**5g**	77
8	**1q**			**5h**	82
9	**1a**			**5i**	69
10	**1f**			**5j**	73
11	**1i**			**5k**	73
12	**1k**			**5l**	60

Table 5 Synthesis of Substituted Biaryls[a] (continued)



Entry	Intermediate	Boronic acids	Product		Yield[b] (%)
13	**1n**			**5m**	58
14	**1k**			**5n**	75
15	**1m**			**5o**	86

[a] Suzuki conditions: intermediates **1a**,**b**,**e**–**k**,**m**–**o**,**q** (4 mmol, 1 equiv), boronic acid (4.8 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (3 mol%), EtOH–toluene–H_2O, 1 M Na_2CO_3, 80 °C, 18 h.
[b] Yield of isolated product after chromatographic purification.



Scheme 2 Double cross-coupling. *Reagents and conditions*: (i) *p*-TolB$(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, EtOH–toluene–H_2O, 80 °C, 15 h; (ii) PhB$(OH)_2$ or (*E*)-*t*-BuCH=CHB$(OH)_2$, $Pd(PPh_3)_4$, 80 °C, 15 h.

We first performed the substitution of *m*-benzylic bromide by addition of one equivalent of *p*-tolylboronic acid. The reaction was followed by ^{1}H NMR to verify the disappearance of the boronic acid; after 15 hours we introduced the second boronic acid [phenyl- or (*E*)-3,3-dimethylbut-2-enylboronic acid]. The reaction was stirred for a further 15 hours, and we then isolated the differently disubstituted products (48% yield for styrene **6b** and 52% for biaryl **6a**). The symmetrical disubstituted product 4–6% was found with the first boronic acid. The yields were not as good as previously, but the products were obtained in one step which reduced the preparation time. This provided a very simple and efficient access to differently disubstituted styrenes and biaryls (heteroaryls).

In conclusion, we have developed a novel method to synthesize a wide range of differently disubstituted and/or functionalized styrenes and biaryls. They were obtained in good yields by a double cross-coupling reaction with very simple conditions. The first regio- and stereoselective coupling reaction allowed the substitution of only benzylic bromide using the Stille or Suzuki condition. The second cross-coupling reaction permitted clean substitution of the aryl bromide in good yields, providing a variety of styrenes and biaryls. A double one-pot Suzuki reaction is also possible, styrenes and biaryls also being obtained in only one step.

^{1}H NMR spectra were recorded on a Bruker AC 200 (200 MHz) using $CDCl_3$ as solvent. The results, reported using the residual proton resonance of $CDCl_3$ (δ = 7.26 ppm) as the internal reference. ^{13}C NMR spectra were recorded at 50.3 MHz on the same instrument using the $CDCl_3$ solvent peak at δ = 77.0 as reference. ^{19}F NMR were recorded at 188 MHz in $CDCl_3$ using C_6F_6 as an external reference (δ = –164.9 ppm). Mass spectra were obtained on a Hewlett Packard (engine 5989A) in GC–MS (70 eV) mode. The isotopic patterns are given for ^{120}Sn (isotopic abundance: 33%) in organostannyl fragments and for ^{74}Ge (isotopic abundance: 36.6%) in organogermyl fragments. This means that the reported abundances (values in brackets) for organostannyl or organogermyl fragments

are roughly only one-third of the correct value, taking into account the 10 isotopes of tin and the five isotopes of germanium compared with those of the organic fragment. IR spectra were recorded on a Perkin–Elmer 781 Infrared Spectrophotometer or on a Perkin-Elmer Spectrum-One. Standard column chromatography was performed on Merck silica gel (60 Å, 230–400 mesh silica gel) or on neutral alumina. DMF was dried by distillation over CaH_2, THF over Na/benzophenone, and toluene was dried by distillation over Na prior to use. Compound **1k** was commercially available, while the following are known compounds: **1a**,[6a] **1b**,[22] **1d**,[6a] **1g**,[6a] **1g**,[6a] **1h**,[6a] **1i**,[6a] **1l**,[23] **1m**,[24] **1n**,[25] **1o**,[26] **1p**,[27] **1q**,[6a] **2a**,[6a] **2e**,[6a] **2i**,[6a] **3a**,[6a] **3b**,[6a] **3c**,[6a] **3d**,[6a] **3e**,[6a] **3f**,[6a] **3i**,[6a] **4a**,[6a] **5m**.[6b]

Compounds 1a–h by Stille Reaction; General Procedure 1
A mixture of bromobenzyl bromide (3 g, 12 mmol, 1 equiv) and $Pd(PPh_3)_4$ (0.36 mmol, 3 mol%) in anhyd toluene (15 mL) was placed in a dry round-bottomed three-necked flask (50 mL) equipped with a condenser flushed with argon. Organotin compound (11.5 mmol, 0.95 equiv) was added after stirring for 15 min at r.t. The mixture was stirred at 80 °C for the recommended time. After cooling, the mixture was filtered through a Celite, and toluene was evaporated under reduced pressure. The residue was then treated with 1 M KF soln and EtOAc to eliminate the Bu_3SnF thus formed. The aqueous layer was extracted with Et_2O. The organic layer was washed with brine and dried ($MgSO_4$). After evaporation of the solvents, the crude product was purified by column chromatography (silica gel, 100% petroleum ether, previously neutralized with Et_3N).

(*E*)-3-(3-Bromophenyl)-1-(trimethylsilyl)prop-1-ene (1c)
Yellow oil; yield: 2.22 g (72%).

IR (NaCl): 3060, 1614, 1595, 1569 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 3.42 (dd, *J* = 6.1, 1.5 Hz, 2 H), 5.71 (dt, *J* = 18.4, 1.5 Hz, 1 H), 6.11 (dt, *J* = 18.4, 6.1 Hz, 1 H), 7.09–7.37 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.8 (3 C), 45.2, 122.9, 127.8, 129.5, 130.3, 132.2, 132.8, 142.8, 144.5.

MS (EI, 70 eV): *m*/*z* = 270 ($M^{+\bullet}$, 8), 268 ($M^{+\bullet}$, 8), 255 (54), 253 (52), 159 (13), 145 (11), 139 (14), 137 (14), 115 (22), 99 (22), 90 (12), 89 (13), 73 (100), 59 (86), 58 (14), 45 (22), 43 (25).

Anal. Calcd for $C_{12}H_{17}BrSi$: C, 53.53; H, 6.36. Found: C, 53.59; H, 6.30.

(*E*)-3-(2-Bromophenyl)-1-(triethylgermyl)prop-1-ene (1e)
Yellow oil; yield: 2.74 g (67%).

IR (NaCl): 3060, 1611, 1592, 1568 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.79–1.14 (m, 15 H), 3.65 (dd, *J* = 5.9, 1.2 Hz, 2 H), 5.85 (dt, *J* = 18.3, 1.2 Hz, 1 H), 6.11 (dt, *J* = 18.3, 5.9 Hz, 1 H), 7.07–7.31 (m, 3 H), 7.60 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 4.8 (3 C), 9.4 (3 C), 43.7, 125.2, 127.8, 128.1, 129.9, 130.9, 133.2, 140.1, 142.7.

MS (EI, 70 eV): *m*/*z* = 329 ($M^{+\bullet}$ – Et, 65), 327 ($M^{+\bullet}$ – Et, 98), 301 (28), 299 (41), 273 (11), 271 (15), 171 (14), 169 (14), 161 (34), 133 (15), 117 (71), 116 (38), 115 (100), 105 (26), 103 (51), 91 (22), 90 (29), 89 (45), 77 (13), 75 (24), 65 (12), 63 (23), 39 (17).

(*E*)-3-(3-Bromophenyl)-1-(triethylgermyl)prop-1-ene (1f)
Colorless oil; yield: 2.70 g (66%).

IR (NaCl): 1639, 1613 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.73–1.08 (m, 15 H), 3.45 (d, *J* = 6.0 Hz, 2 H), 5.81 (d, *J* = 18.3 Hz, 1 H), 6.03 (dt, *J* = 18.3, 6.0 Hz, 1 H), 7.03–7.35 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 4.8 (3 C), 9.4 (3 C), 43.3, 122.9, 127.7, 129.5, 130.0, 130.3, 132.2, 143.1, 143.8.

MS (EI, 70 eV): *m*/*z* = 329 ($M^{+\bullet}$ – Et, 66), 327 ($M^{+\bullet}$ – Et, 100), 301 (29), 299 (41), 273 (14), 271 (21), 116 (11), 115 (25), 105 (11), 103 (15).

Compounds 1i–r by Suzuki Reaction; General Procedure 2
An oven-dried Schlenk flask equipped with a condenser was evacuated and back-filled with argon and charged with EtOH (19 mL), H_2O (5.3 mL), toluene (23 mL), bromobenzyl bromide (3 g, 12 mmol, 1 equiv), and boronic acid (12 mmol, 1 equiv). The flask was evacuated and back-filled with argon and then 1 M Na_2CO_3 (13.5 mL) and $Pd(PPh_3)_4$ (0.36 mmol, 3 mol%) were added. The mixture was stirred at the desired temperature until completion of the reaction at the benzylic position. The soln was filtered through Celite and the solvents were evaporated under reduced pressure. The residue was extracted with Et_2O, washed with brine, and dried ($MgSO_4$). After purification by flash chromatography (silica gel) the products were characterized.

(*E*)-1-(3-Bromophenyl)-4,4-dimethylpent-2-ene (1j)
Colorless oil; yield: 2.09 g (69%).

IR (NaCl): 3059, 3024, 1668, 1593, 1568 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.03 (s, 9 H), 3.30 (d, *J* = 6.3 Hz, 2 H), 5.43 (dt, *J* = 15.4, 6.3 Hz, 1 H), 5.59 (d, *J* = 15.4 Hz, 1 H), 7.09–7.34 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.3 (3 C), 33.5, 39.3, 123.1, 123.1, 127.6, 129.6, 130.4, 132.1, 144.1, 144.4.

MS (EI, 70 eV): *m*/*z* = 254 ($M^{+\bullet}$, 5), 252 ($M^{+\bullet}$, 5), 239 (2), 237 (2), 211 (3), 209 (3), 115 (12), 83 (100), 70 (15), 57 (25), 41 (30), 39 (17).

Anal. Calcd for $C_{13}H_{17}Br$: C, 61.67; H, 6.77. Found: C, 61.75; H, 6.73.

4-(3-Bromobenzyl)benzaldehyde (1r)
White solid; yield: 2.14 g (65%); mp 33–35 °C.

IR (KBr): 3056, 2827, 2736, 1698, 1606, 1595, 1567 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.04 (s, 2 H), 7.10–7.41 (m, 6 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 10.0 (s, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 42.0, 123.2, 128.1, 130.0 (2 C), 130.1, 130.6 (2 C), 130.7, 132.4, 135.3, 142.6, 147.8, 192.2.

MS (EI, 70 eV): *m*/*z* = 276 ($M^{+\bullet}$, 39), 274 ($M^{+\bullet}$, 40), 247 (11), 245 (11), 195 (40), 167 (50), 166 (68), 165 (100), 152 (23), 91 (13), 90 (18), 89 (26), 82 (29), 63 (30), 51 (22), 50 (26), 39 (26).

Anal. Calcd for $C_{14}H_{11}BrO$: C, 61.11; H, 4.03. Found: C, 61.18; H, 4.10.

Compounds 2a–d by Stille Reaction; General Procedure
Using the conditions of general procedure 1, but organostannane (2.5 equiv) was used.

(1*E*)-1-(Trimethylsilyl)-3-{(*E*)-2-[2-(trimethylsilyl)vinyl]phenyl}prop-1-ene (2b)
Yellow oil; yield: 2.50 g (72%).

IR (NaCl): 3065, 3017, 1613, 1568 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.12 (s, 9 H), 0.24 (s, 9 H), 3.62 (dd, *J* = 5.7, 1.5 Hz, 2 H), 5.72 (dt, *J* = 18.5, 1.5 Hz, 1 H), 6.21 (dt, *J* = 18.5, 5.7 Hz, 1 H), 6.46 (d, *J* = 19 Hz, 1 H), 7.17–7.31 (m, 4 H), 7.61–7.66 (m, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.7 (6 C), 41.4, 126.0, 127.1, 128.4, 130.5, 131.7, 131.8, 137.4, 138.3, 141.8, 145.1.

MS (EI, 70 eV): *m*/*z* = 288 ($M^{+\bullet}$, 10), 214 (12), 141 (10), 73 (100), 72 (14), 59 (39), 45 (17), 43 (12).

Anal. Calcd for $C_{17}H_{28}Si_2$: C, 70.76; H, 9.78. Found: C, 70.82; H, 9.72.

(1*E*)-1-(Trimethylsilyl)-3-{(*E*)-3-[2-(trimethylsilyl)vinyl]phenyl}prop-1-ene (2c)
Colorless oil; yield: 2.42 g (70%).

IR (NaCl): 3057, 3022, 1611, 1579 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 0.17 (s, 9 H), 3.45 (dd, *J* = 6.2, 1.5 Hz, 2 H), 5.71 (dt, *J* = 18.4, 1.5 Hz, 1 H), 6.16 (dt, *J* = 18.4, 6.2 Hz, 1 H), 6.48 (d, *J* = 19.1 Hz, 1 H), 6.88 (d, *J* = 19.1 Hz, 1 H), 7.07–7.30 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.8 (6 C), 43.6, 124.5, 127.2, 128.8, 129.0, 129.8, 132.0, 138.9, 140.7, 144.1, 145.5.

MS (EI, 70 eV): *m*/*z* = 288 ($M^{+\bullet}$, 26), 273 (31), 215 (17), 199 (10), 185 (13), 183 (23), 129 (11), 85 (18), 73 (100), 59 (66), 45 (18), 43 (10).

Anal. Calcd for $C_{17}H_{28}Si_2$: C, 70.76; H, 9.78. Found: C, 70.86; H, 9.83.

(1*E*)-1-(Triethylgermyl)-3-{(*E*)-2-[2-(triethylgermyl)vinyl]phenyl}prop-1-ene (2d)
Colorless oil; yield: 3.54 g (64%).

IR (NaCl): 3063, 1609, 1565 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.73–1.13 (m, 30 H), 3.56 (dd, *J* = 5.7, 1.4 Hz, 2 H), 5.72 (dt, *J* = 18.3, 1.4 Hz, 1 H), 6.06 (dt, *J* = 18.3, 5.7 Hz, 1 H), 6.50 (d, *J* = 18.8 Hz, 1 H), 7.10 (d, *J* = 18.8 Hz, 1 H), 7.12–7.24 (m, 3 H), 7.55 (d, *J* = 8.9 Hz, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 4.7 (3 C), 4.9 (3 C), 9.4 (3 C), 9.5 (3 C), 41.2, 126.1, 126.9, 128.0, 128.6, 130.0, 130.3, 137.3, 138.4, 141.7, 144.4.

MS (EI, 70 eV): *m*/*z* = 435 ($M^{+\bullet}$ – 29, 2), 303 (7), 302 (7), 301 (6), 273 (100), 245 (23), 217 (53), 161 (52), 133 (53), 105 (34), 103 (39).

Compounds 2e–i by Suzuki Reaction; General Procedure
Using the conditions of general procedure 2, but boronic acid (2.2 equiv) was used.

4-Fluoro-4′-(4-fluorobenzyl)biphenyl (2f)
White solid; yield: 2.65 g (79%); mp 64–66 °C.

IR (KBr): 3053, 1603, 1508 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.08 (s, 2 H), 7.04–7.35 (m, 8 H), 7.55–7.62 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 41.2, 115.8 (d, $^2J_{C-F}$ = 21 Hz), 116.1 (d, $^2J_{C-F}$ = 21 Hz), 127.6 (2 C), 129.0 (d, $^3J_{C-F}$ = 8 Hz), 129.8 (2 C), 130.9 (d, $^3J_{C-F}$ = 8 Hz), 137.2, 137.5, 138.7, 140.6, 162.0 (d, $^1J_{C-F}$ = 244 Hz), 162.9 (d, $^1J_{C-F}$ = 246 Hz).

^{19}F NMR (188 MHz, $CDCl_3$): δ = –116.4, –117.7.

MS (EI, 70 eV): *m*/*z* = 280 ($M^{+\bullet}$, 100), 279 (21), 185 (33), 184 (24), 183 (73), 170 (29), 165 (21), 133 (27), 109 (76), 107 (17), 83 (35), 75 (24), 63 (19), 57 (19), 39 (20).

Anal. Calcd for $C_{19}H_{14}F_2$: C, 81.41; H, 5.03. Found: C, 81.47; H, 5.08.

4′-Methyl-2-(4-methylbenzyl)biphenyl (2g)
Colorless oil; yield: 2.84 g (87%).

IR (NaCl): 3050, 3021, 1599, 1573, 1514 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 2.55 (s, 3 H), 4.11 (s, 2 H), 7.09 (d, *J* = 7.9 Hz, 2 H), 7.21 (d, *J* = 7.9 Hz, 2 H), 7.36–7.44 (m, 8 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6, 21.8, 39.1, 126.6, 127.9, 129.4 (4 C), 129.6 (2 C), 129.8 (2 C), 130.7, 130.8, 135.7, 137.0, 139.1 (2 C), 139.4, 142.7.

MS (EI, 70 eV): *m*/*z* = 272 ($M^{+\bullet}$, 100), 257 (35), 242 (10), 180 (26), 179 (46), 178 (16), 166 (12), 165 (51).

Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.75; H, 7.34.

2-[2-(Thiophen-2-yl)benzyl]thiophene (2h)
Colorless oil; yield: 1.81 g (59%).

IR (NaCl): 3104, 3067, 3018, 1599, 1532 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.26 (s, 2 H), 6.67 (dd, *J* = 3.4, 1.1 Hz, 1 H), 6.91 (dd, *J* = 5.1, 3.4 Hz, 1 H), 7.00 (dd, *J* = 3.5, 1.1 Hz, 1 H), 7.07 (dd, *J* = 5.1, 3.5 Hz, 1 H), 7.15 (dd, *J* = 5.1, 1.1 Hz, 1 H), 7.30–7.46 (m, 5 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 34.4, 124.4, 125.7, 126.1, 127.3 (3 C), 127.7, 128.8, 130.9, 131.8, 134.6, 139.0, 142.7, 144.9.

MS (EI, 70 eV): *m*/*z* = 256 ($M^{+\bullet}$, 100), 223 (88), 184 (26), 171 (28), 115 (10), 97 (17), 45 (22), 39 (10).

Anal. Calcd for $C_{15}H_{12}S_2$: C, 70.27; H, 4.72. Found: C, 70.38; H, 4.60.

Compounds 3a–l by Stille Reaction; General Procedure 3
A mixture of intermediate I **1a–h**,**j** (4 mmol, 1 equiv) and $Pd(PPh_3)_4$ (0.12 mmol, 3 mol%) in anhyd toluene (5 mL) was placed in a dry Schlenk equipped with a condenser flushed with argon. Organotin compound (5.2 mmol, 1.3 equiv) was added after stirring for 15 min at r.t. The mixture was stirred at 90 °C for 18 h. After cooling, the mixture was filtered through Celite, and toluene was evaporated under reduced pressure. The residue was then treated with 1 M KF soln and EtOAc to eliminate the Bu_3SnF thus formed. The aqueous layer was extracted with Et_2O. The organic layer was washed with brine and dried ($MgSO_4$). After evaporation of the solvents, the crude product was purified by column chromatography (silica gel, 100% petroleum ether, previously neutralized with Et_3N).

(1*E*)-1-(Triethylgermyl)-3-{3-[(*E*)-2-(trimethylsilyl)vinyl]phenyl}prop-1-ene (3g)
Colorless oil; yield: 1.05 g (70%).

IR (NaCl): 3055, 1608, 1578 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 9 H), 0.79–1.11 (m, 15 H), 3.50 (d, *J* = 6.1 Hz, 2 H), 5.82 (d, *J* = 18.2 Hz, 1 H), 6.09 (dt, *J* = 18.2, 6.2 Hz, 1 H), 6.49 (d, *J* = 19.2 Hz, 1 H), 6.90 (d, *J* = 19.2 Hz, 1 H), 7.10–7.30 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.8 (3 C), 4.8 (3 C), 9.4 (3 C), 43.7, 124.6, 127.0, 128.8, 129.0, 129.1, 129.7, 138.9, 140.9, 144.1, 144.8.

MS (EI, 70 eV): *m*/*z* = 376 ($M^{+\bullet}$, 6), 347 (100), 319 (18), 199 (14), 183 (26), 145 (11), 138 (20), 133 (12), 115 (13), 105 (23), 103 (24), 89 (10), 87 (15), 73 (67), 59 (52), 45 (13).

(2*E*)-4,4-Dimethyl-1-{3-[(*E*)-(trimethylsilyl)vinyl]phenyl}pent-2-ene (3h)
Yellow oil; yield: 0.79 g (73%).

IR (NaCl): 3029, 1607, 1599, 1579, 1534 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.20 (s, 9 H), 1.06 (s, 9 H), 3.36 (d, *J* = 5.8 Hz, 2 H), 5.42–5.66 (m, 2 H), 6.50 (d, *J* = 19.2 Hz, 1 H), 6.91 (d, *J* = 19.2 Hz, 1 H), 7.09–7.31 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.8 (3 C), 30.2 (3 C), 33.4, 39.5, 123.8, 124.4, 127.0, 128.6, 128.9, 129.7, 138.8, 141.9, 143.6, 144.2.

MS (EI, 70 eV): *m*/*z* = ($M^{+\bullet}$, 35), 257 (28), 142 (10), 141 (60), 99 (10), 97 (57), 83 (32), 73 (67), 69 (25), 59 (52), 57 (17), 55 (100), 45 (12), 43 (18), 41 (22).

Anal. Calcd for $C_{18}H_{28}Si$: C, 79.34; H, 10.36. Found: C, 79.45; H, 10.28.

(1*E*)-3-{2-[(*E*)-2-Phenylvinyl]phenyl}-1-(trimethylsilyl)prop-1-ene (3j)
Yellow oil; yield: 0.76 g (65%).

IR (NaCl): 3060, 3025, 1612, 1581 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.04 (s, 9 H), 3.61 (br dd, *J* = 5.7, 1.6 Hz, 2 H), 5.71 (dt, *J* = 18.5, 1.6 Hz, 1 H), 6.18 (dt, *J* = 18.5, 5.7 Hz, 1 H), 6.98 (d, *J* = 18.9 Hz, 1 H), 7.16–7.67 (m, 10 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.7 (3 C), 41.6, 126.2, 127.0 (2 C), 127.2 (2 C), 128.1, 128.2, 129.2 (2 C), 130.5, 130.7, 132.2, 137.2, 138.0, 138.3, 145.1.

MS (EI, 70 eV): *m*/*z* = 292 ($M^{+\bullet}$, 11), 218 (26), 129 (18), 116 (16), 91 (10), 73 (100), 59 (24), 45 (13).

Anal. Calcd for $C_{20}H_{24}Si$: C, 82.13; H, 8.27. Found: C, 82.19; H, 8.30.

(1*E*)-3-{2-[(*E*)-2-Phenylvinyl]phenyl}-1-(triethylgermyl)prop-1-ene (3k)
Colorless oil; yield: 0.94 g (62%).

IR (NaCl): 3026, 1609, 1589 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.69–1.03 (m, 15 H), 3.62 (dd, *J* = 5.6, 1.4 Hz, 2 H), 5.78 (dt, *J* = 18.4, 1.4 Hz, 1 H), 6.09 (dt, *J* = 18.4, 5.6 Hz, 1 H), 6.99 (d, *J* = 16.2 Hz, 1 H), 7.13–7.66 (m, 10 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 4.9 (3 C), 9.5 (3 C), 41.7, 126.2, 127.1 (2 C), 127.2 (2 C), 128.1, 128.2, 129.2 (3 C), 130.5, 130.6, 137.2, 138.2, 138.3, 144.5.

MS (EI, 70 eV): *m*/*z* = 380 ($M^{+\bullet}$, 9), 351 (49), 235 (28), 218 (65), 217 (100), 202 (19), 203 (20), 161 (23), 133 (28), 129 (46), 115 (23), 105 (33), 103 (37), 91 (76), 77 (10).

(1*E*)-3-{3-[(*E*)-2-Phenylvinyl]phenyl}-1-(trimethylsilyl)prop-1-ene (3l)
White solid; yield: 0.73 g (63%); mp 57–59 °C.

IR (KBr): 3081, 3030, 1613, 1601, 1582 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.09 (s, 9 H), 3.49 (d, *J* = 6.1 Hz, 2 H), 5.75 (dt, *J* = 18.4, 1.5 Hz, 1 H), 6.19 (dt, *J* = 18.4, 6.2 Hz, 1 H), 7.11–7.13 (m, 2 H), 7.30–7.42 (m, 7 H), 7.54 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.6 (3 C), 43.7, 124.8, 127.0 (2 C), 127.5, 128.1, 128.7, 129.2 (2 C), 129.3 (3 C), 132.2, 137.9, 138.0, 140.9, 145.5.

MS (EI, 70 eV): *m*/*z* = 292 ($M^{+\bullet}$, 100), 277 (29), 218 (22), 202 (10), 179 (13), 178 (17), 135 (14), 73 (99), 59 (55), 45 (14).

Anal. Calcd for $C_{20}H_{24}Si$: C, 82.13; H, 8.27. Found: C, 82.05; H, 8.25.

Compound 3m by Suzuki Reaction; General Procedure 4
An oven-dried Schlenk flask equipped with a condenser was evacuated and back-filled with argon and charged with EtOH (6.3 mL), H_2O (1.8 mL), toluene (7.7 mL), intermediate I **1c** (4 mmol, 1 equiv), and boronic acid (4.8 mmol, 1.2 equiv). The flask was evacuated and back-filled with argon and then 1 M Na_2CO_3 (4.5 mL) and $Pd(PPh_3)_4$ (0.12 mmol, 3 mol%) were added. The mixture was stirred at 80 °C for 18 h. The soln was filtered through a Celite path and the solvents were evaporated under reduced. The residue was extracted with Et_2O, washed with brine, and dried ($MgSO_4$). After purification by flash chromatography (silica gel) the products were characterized.

(1*E*)-3,3-Dimethyl-1-{3-[(*E*)-3-(trimethylsilyl)prop-2-enyl]phenyl}but-1-ene (3m)
Colorless oil; yield: 0.80 g (74%).

IR (NaCl): 3026, 1613, 1602, 1582, 1363 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 1.14 (s, 9 H), 3.45 (d, *J* = 6.2 Hz, 2 H), 5.72 (d, *J* = 18.4 Hz, 1 H), 6.17 (dt, *J* = 18.4, 6.2 Hz, 1 H), 6.27–6.29 (m, 2 H), 7.01–7.28 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.4 (3 C), 30.3 (3 C), 34.0, 43.9, 124.5, 125.4, 127.2, 127.9, 129.2, 132.0, 138.7, 140.7, 142.2, 144.5.

MS (EI, 70 eV): *m*/*z* = 272 ($M^{+\bullet}$, 27), 257 (13), 159 (25), 85 (19), 73 (100), 59 (54), 45 (11).

Anal. Calcd for $C_{18}H_{28}Si$: C, 79.34; H, 10.36. Found: C, 79.38; H, 10.41.

Compounds 4a–g by Stille Reaction; General Procedure
Using the conditions for general procedure 3, but using intermediates II **1k–p**,**r**.

2-{[2-(4-Methylbenzyl)]phenyl}propene (4b)
Colorless oil; yield: 0.59 g (67%).

IR (NaCl): 3049, 3019, 1640, 1599, 1514 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.99 (t, *J* = 1.2 Hz, 3 H), 2.33 (s, 3 H), 4.02 (s, 2 H), 4.85–4.87 (m, 1 H), 5.18–5.21 (m, 1 H), 7.01–7.23 (m, 8 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.5, 25.7, 38.7, 115.6, 126.4, 127.4, 128.6, 129.3 (2 C), 129.5 (2 C), 130.6, 135.7, 138.0, 139.0, 144.4, 145.9.

MS (EI, 70 eV): *m*/*z* = 222 ($M^{+\bullet}$, 21), 208 (18), 207 (100), 193 (16), 192 (89), 191 (14), 178 (10), 129 (10), 115 (16), 91 (8).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.79; H, 8.19.

2-(2-Isopropenylbenzyl)thiophene (4c)
Colorless oil; yield: 0.54 g (63%).

IR (NaCl): 3069, 3011, 1640, 1601, 1533 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 4.31 (s, 2 H), 4.99 (br s, 1 H), 5.33 (br s, 1 H), 6.83 (dd, *J* = 3.4, 1.1 Hz, 1 H), 7.00 (dd, *J* = 5.1, 3.4 Hz, 1 H), 7.20–7.34 (m, 5 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 25.8, 33.6, 115.9, 124.2, 125.6, 127.0, 127.2, 127.6, 128.7, 130.4, 137.3, 144.1, 144.4, 145.5.

MS (EI, 70 eV): *m*/*z* = 214 ($M^{+\bullet}$, 42), 199 (15), 185 (100), 165 (22), 152 (10), 129 (13), 115 (28), 97 (12), 45 (11), 39 (13).

Anal. Calcd for $C_{14}H_{14}S$: C, 78.46; H, 6.58. Found: C, 78.34; H, 6.63.

(*E*)-[2-(4-Benzylphenyl)vinyl]trimethylsilane (4d)
Yellow oil; yield: 0.82 g (77%).

IR (NaCl): 3026, 1605, 1565, 1509 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.28 (s, 9 H), 4.07 (s, 2 H), 6.55 (d, *J* = 19.1 Hz, 1 H), 6.98 (d, *J* = 19.1 Hz, 1 H), 7.24–7.43 (m, 8 H), 7.48 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –6.6 (3 C), 42.2, 126.6, 127.0 (2 C), 129.0 (2 C), 129.3, 129.4 (2 C), 129.7 (2 C), 136.9, 141.5, 141.6, 143.9.

MS (EI, 70 eV): *m*/*z* = 266 ($M^{+\bullet}$, 9), 175 (12), 135 (21), 91 (100), 59 (30), 45 (10).

Anal. Calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. Found: C, 81.03; H, 8.38.

4-{3-[(1*E*)-2-Phenylvinyl]benzyl}benzaldehyde (4e)
White solid; yield: 0.76 g (64%); mp 72–74 °C.

IR (KBr): 3054, 1701, 1601, 1574, 1167 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.10 (s, 2 H), 7.10–7.14 (m, 2 H), 7.30–7.57 (m, 11 H), 7.86 (d, *J* = 8.20 Hz, 2 H), 10.01 (s, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 42.5, 125.1, 127.0 (2 C), 127.7, 128.2, 128.8, 128.9, 129.1 (2 C), 129.4, 129.5, 130.0 (2 C), 130.5 (2 C), 135.2, 137.6, 138.2, 140.6, 148.7, 192.1.

MS (EI, 70 eV): *m*/*z* = 298 ($M^{+\bullet}$, 100), 191 (13), 189 (10), 180 (13), 179 (89), 178 (40), 165 (15), 152 (10), 115 (10), 91 (35), 77 (11), 51 (10), 39 (10).

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.48; H, 6.01.

2-{4-[(*E*)-2-(Trimethylgermyl)vinyl]benzyl}thiophene (4f)
Colorless oil; yield: 0.73 g (58%).

IR (NaCl): 3078, 3047, 1604, 1565, 1509 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.39 (s, 9 H), 4.21 (s, 2 H), 6.73 (d, *J* = 19 Hz, 1 H), 6.87 (dd, *J* = 3.4, 1.2 Hz, 1 H), 6.91 (d, *J* = 19 Hz, 1 H), 7.00 (dd, *J* = 5.1, 3.4 Hz, 1 H), 7.22 (dd, *J* = 5.1, 1.2 Hz, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.46 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –1.12 (3 C), 36.3, 124.5, 125.7, 127 (2 C), 127.3, 129.4 (2 C), 131.2, 137.1, 140.5, 142.4, 144.6.

MS (EI, 70 eV): *m*/*z* = 318 ($M^{+\bullet}$, 8), 303 ($M^{+\bullet}$ – 15, 7), 115 (6), 97 (100).

1-(4-Methylbenzyl)-4-[(1*E*)-2-(tributylstannyl)vinyl]benzene (4g)
Yellow oil; yield: 1.01 g (51%).

IR (NaCl): 1607, 1593, 1508 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.2 Hz, 9 H), 1.29–1.60 (m, 18 H), 2.33 (s, 3 H), 3.94 (s, 2 H), 6.82–8.84 (m, 2 H), 7.09–7.37 (m, 8 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 10.2 ($^1J_{Sn\text{-}C}$ = 328–344 Hz, 3 C), 14.4 (3 C), 21.6, 27.9 ($^3J_{Sn\text{-}C}$ = 54 Hz, 3 C), 29.6 ($^2J_{Sn\text{-}C}$ = 21 Hz, 3 C), 41.8, 126.7 (2 C), 129.0, 129.4 (2 C), 129.6 (2 C), 129.7 (2 C), 136.0, 137.3, 138.6, 141.4, 146.5.

MS (EI, 70 eV): *m*/*z* = 441 ($M^{+\bullet}$ – 57, 90), 385 (31), 325 (26), 191 (26), 179 (20), 177 (20), 165 (12), 163 (14), 121 (25), 105 (100), 91 (20), 57 (18), 41 (46), 39 (15).

Compounds 4h–j by Suzuki Reaction; General Procedure
Using the conditions for general procedure 4, but using intermediates II **1n**,**r**.

(*E*)-4-[3-(3,3-Dimethylbut-1-enyl)benzyl]benzaldehyde (4h)
Yellow oil; yield: 0.84 g (76%).

IR (NaCl): 1704, 1602, 1576 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.16 (s, 9 H), 4.06 (s, 2 H), 6.30–6.32 (br s, 2 H), 7.01–7.06 (m, 1 H), 7.23–7.30 (m, 3 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 7.83 (d, *J* = 8.1 Hz, 2 H), 10 (s, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.1 (3 C), 33.9, 42.5, 124.6, 124.9, 127.3, 127.9, 129.3, 130.0 (2 C), 130.5 (2 C), 135.1, 138.9, 140.3, 142.5, 148.9, 192.4.

MS (EI, 70 eV): *m*/*z* = 278 ($M^{+\bullet}$, 52), 263 (21), 165 (11), 159 (46), 144 (18), 143 (20), 129 (17), 128 (15), 120 (19), 119 (92), 117 (17), 115 (12), 91 (100), 89 (13), 65 (10), 41 (21), 39 (11).

Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.38; H, 8.06.

(*Z*)-1-[4-(4-Fluorobenzyl)phenyl]prop-1-ene (4i)
Yellow oil; yield: 0.63 g (70%).

IR (NaCl): 3041, 1630, 1602, 1570, 1510 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.98 (dd, *J* = 7.2, 1.8 Hz, 3 H), 4.01 (s, 2 H), 5.85 (dq, *J* = 11.6, 1.8 Hz, 1 H), 6.50 (dq, *J* = 11.6, 1.8 Hz, 1 H), 7.01–7.31 (m, 6 H), 7.52 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.2, 41.3, 115.7 (d, $^2J_{C\text{-}F}$ = 21 Hz, 2 C), 125.8, 128.7 (2 C), 129.5 (2 C), 130.1, 130.8 (d, $^3J_{C\text{-}F}$ = 7.5 Hz, 2 C), 136.2, 137.3, 139.6, 162.0 (d, $^1J_{C\text{-}F}$ = 243 Hz).

MS (EI, 70 eV): *m*/*z* = ($M^{+\bullet}$, 100), 211 (47), 197 (30), 196 (23), 185 (13), 183 (21), 165 (11), 133 (11), 117 (54), 115 (34), 109 (39), 99 (21), 98 (14), 91 (18), 83 (14), 39 (13).

Anal. Calcd for $C_{16}H_{15}F$: C, 84.92; H, 6.68. Found: C, 84.84; H, 6.75.

4-[(*Z*)-3-(Prop-1-enyl)benzyl]benzaldehyde (4j)
Yellow oil; yield: 0.70 g (75%).

^1H NMR (200 MHz, $CDCl_3$): δ = 1.87 (dd, *J* = 7.1, 1.8 Hz, 3 H), 4.07 (s, 2 H), 5.79 (dq, *J* = 11.6, 7.1 Hz, 1 H), 6.41 (dq, *J* = 11.6, 1.8 Hz, 1 H), 7.03–7.40 (m, 6 H), 7.82 (d, *J* = 8.1 Hz, 2 H), 9.99 (s, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.1, 42.5, 127.5 (3 C), 128.9, 130.0 (3 C), 130.1, 130.5 (2 C), 135.2, 138.5, 140.1, 148.8, 192.3.

MS (EI, 70 eV): *m*/*z* = 236 ($M^{+\bullet}$, 100), 207 (11), 179 (24), 178 (25), 166 (10), 165 (28), 129 (12), 120 (69), 118 (11), 117 (87), 115 (43), 91 (43), 90 (14), 89 (26), 76 (10), 65 (13), 63 (10), 39 (15).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.45; H, 6.80.

Substituted Biaryls 5; General Procedure
Using the conditions for general procedure 4, but using intermediates I or II **1a**,**b**,**e–k**,**m–o**,**q**.

4-[(2*E*)-3-(Tributylstannyl)prop-2-enyl]biphenyl (5a)
Colorless oil; yield: 1.30 g (67%).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.1 Hz, 9 H), 1.28–1.61 (m, 18 H), 3.56 (d, $^3J_{1H}$ = 5.8 Hz, 2 H), 6.00–6.15 (m, 2 H), 7.23–7.66 (m, 9 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 9.9 ($^1J_{Sn\text{-}C}$ = 345–389 Hz, 3 C), 14.2 (3 C), 27.8 ($^3J_{Sn\text{-}C}$ = 54 Hz, 3 C), 29.6 ($^2J_{Sn\text{-}C}$ = 21 Hz, 3 C), 44.6, 127.5 (2 C), 127.6 (2 C), 128.7, 129.2 (2 C), 129.5 (2 C), 130.2, 139.5, 139.9, 141.6, 145.1.

^{119}Sn NMR (74.2 MHz, $CDCl_3$): δ = –47.2.

MS (EI, 70 eV): *m*/*z* = 427 ($M^{+\bullet}$ – 57, 100), 371 (47), 315 (51), 193 (16), 178 (10), 167 (16), 157 (18), 41 (10).

2-[(2*E*)-3-(Trimethylsilyl)prop-2-enyl]biphenyl (5b)
Colorless oil; yield: 0.82 g (77%).

IR (NaCl): 3060, 3023, 1613, 1583, 1501 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.03 (s, 9 H), 3.41 (dd, *J* = 5.9, 1.6 Hz, 2 H), 5.50 (dt, *J* = 18.5, 1.6 Hz, 1 H), 6.06 (dt, *J* = 18.5, 5.9 Hz, 1 H), 7.25–7.44 (m, 9 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.6 (3 C), 41.2, 126.7, 127.4, 128.0, 128.5 (2 C), 129.8 (2 C), 130.5, 130.6, 131.9, 137.8, 142.2, 142.7, 145.9.

MS (EI, 70 eV): *m*/*z* = 266 ($M^{+\bullet}$, 23), 251 (28), 233 (29), 192 (43), 191 (21), 179 (18), 165 (27), 73 (100), 59 (45), 58 (12), 45 (16), 43 (15).

Anal. Calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. Found: C, 81.18; H, 8.34.

4-Methyl-4′-[(2*E*)-3-(trimethylsilyl)prop-2-enyl]biphenyl (5c)
Yellow oil; yield: 0.86 g (77%).

IR (NaCl): 3024, 1609, 1561 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.21 (s, 9 H), 2.50 (s, 3 H), 3.59 (d, *J* = 6.2 Hz, 2 H), 5.87 (d, *J* = 18.4 Hz, 1 H), 6.30 (dt, *J* = 18.4, 6.2 Hz, 1 H), 7.34 (d, *J* = 7.9 Hz, 4 H), 7.60 (d, *J* = 7.9 Hz, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.64 (3 C), 21.6, 43.4, 127.4 (2 C), 127.5 (2 C), 129.6 (2 C), 130.0 (2 C), 132.1, 137.2, 138.7, 139.3, 139.4, 145.6.

MS (EI, 70 eV): *m*/*z* = 280 ($M^{+\bullet}$, 12), 265 (4), 73 (100), 59 (45), 45 (13).

Anal. Calcd for $C_{19}H_{24}Si$: C, 81.36; H, 8.62. Found: C, 81.23; H, 8.68.

4-Methyl-4′-[(2*E*)-3-(triphenylgermyl)prop-2-enyl]biphenyl (5d)
White solid; yield: 1.25 g (62%); mp 96–98 °C.

IR (KBr): 3068, 3048, 1607, 1584, 1570 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 3.70 (d, *J* = 6.0 Hz, 2 H), 6.39–6.42 (m, 2 H), 7.30–7.63 (m, 23 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6, 43.2, 126.1, 127.3 (2 C), 127.5 (2 C), 128.7 (6 C), 129.5 (3 C), 129.6 (2 C), 130.0 (2 C), 137.6 (6 C), 137.1 (3 C), 137.3, 138.6, 138.8, 139.5, 148.9.

MS (EI, 70 eV): *m*/*z* = 512 ($M^{+\bullet}$, 8), 435 (11), 331 (36), 305 (55), 284 (29), 229 (69), 228 (100), 207 (24), 206 (24), 205 (17), 192 (46), 191 (29), 181 (27), 165 (43), 151 (74), 115 (33), 91 (38), 78 (12), 77 (15), 51 (18), 39 (10).

4′-Methyl-2-[(2*E*)-3-(triethylgermyl)prop-2-enyl]biphenyl (5e)
Yellow oil; yield: 1.14 g (78%).

IR (NaCl): 3058, 3021, 1611, 1586, 1516 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.77–1.15 (m, 15 H), 2.49 (s, 3 H), 3.53 (dd, *J* = 5.9, 1.5 Hz, 2 H), 5.71 (dt, *J* = 18.3, 1.5 Hz, 1 H), 6.09 (dt, *J* = 18.3, 5.9 Hz, 1 H), 7.30–7.39 (m, 8 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 4.8 (3 C), 9.4 (3 C), 21.7, 41.2, 126.5, 127.7, 128.7, 129.1 (2 C), 129.6 (2 C), 130.3, 130.6, 136.9, 137.9, 139.3, 142.5, 145.3.

MS (EI, 70 eV): *m*/*z* = 368 ($M^{+\bullet}$, 9), 339 (100), 311 (19), 283 (5), 281 (13), 207 (21), 206 (13), 205 (42), 192 (23), 191 (21), 179 (22), 178 (22), 165 (39), 133 (10), 105 (10), 103 (12).

3-[(*E*)-4,4-Dimethylpent-2-enyl]-4′-methylbiphenyl (5f)
Yellow oil; yield: 0.87 g (83%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.11 (s, 9 H), 2.46 (s, 3 H), 3.46 (d, *J* = 5.6 Hz, 2 H), 5.53–5.73 (m, 2 H), 7.20–7.58 (m, 8 H)

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6, 30.2 (3 C), 33.4, 39.6, 123.8, 125.1, 127.5 (2 C), 127.6 (2 C), 129.1, 129.9 (2 C), 137.4, 139.0, 141.7, 142.2, 143.8.

MS (EI, 70 eV): *m*/*z* = 264 ($M^{+\bullet}$, 67), 221 (11), 208 (22), 207 (21), 194 (44), 193 (27), 192 (18), 191 (10), 182 (10), 179 (35), 178 (18), 166 (12), 165 (29), 83 (100), 57 (42), 55 (41), 43 (11), 41 (39), 39 (14).

Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.79; H, 9.18.

2-[(4′-Methylbiphenyl-4-yl)methyl]thiophene (5g)
White solid; yield: 0.81 g (77%); mp 54–56 °C.

IR (KBr): 1647, 1597, 1514 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 4.21 (s, 2 H), 6.86 (dd, *J* = 3.2, 1.1 Hz, 1 H), 6.96 (dd, *J* = 5.1, 3.2 Hz, 1 H), 7.18 (dd, *J* = 5.1, 3.2 Hz, 1 H), 7.23–7.34 (m, 4 H), 7.48–7.56 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.8, 36.3, 124.6, 125.9, 127.5 (2 C), 127.7, 129.6 (2 C), 130.1 (2 C), 137.5, 138.6, 139.8, 140.0, 144.6.

MS (EI, 70 eV): *m*/*z* = 264 ($M^{+\bullet}$, 100), 249 (18), 231 (22), 215 (22), 165 (49), 152 (21), 131 (19), 115 (20), 97 (92), 91 (19), 89 (18), 85 (15), 77 (12), 65 (22), 63 (26), 57 (12), 53 (28), 51 (23), 45 (67), 39 (57).

Anal. Calcd for $C_{18}H_{16}S$: C, 81.77; H, 6.10. Found: C, 81.71; H, 6.18.

4-[(4′-Methylbiphenyl-2-yl)methyl]benzaldehyde (5h)
Yellow oil; yield: 0.93 g (82%).

IR (NaCl): 3056, 3023, 1698, 1607, 1575, 1516 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 4.11 (s, 2 H), 7.17–7.43 (m, 10 H), 7.78 (d, *J* = 8.0 Hz, 2 H), 10.0 (s, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6, 39.8, 127.1, 127.9, 129.3, 129.5, 129.9, 130.2, 130.7, 130.9, 134.8, 137.2, 137.5, 138.8, 142.8, 149.4, 192.5.

MS (EI, 70 eV): *m*/*z* = 286 ($M^{+\bullet}$, 93), 271 (12), 241 (12), 239 (13), 215 (12), 180 (32), 179 (75), 178 (26), 166 (22), 165 (100), 152 (13), 115 (13), 107 (27), 91 (19), 79 (13), 65 (11), 51 (14), 39 (17).

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.37. Found: C, 88.15; H, 6.39.

(*E*)-[3-(4′-Fluorobiphenyl-4-yl)prop-1-enyl]trimethylsilane (5i)
White solid; yield: 0.78 g (69%); mp 34–36 °C

IR (KBr): 3029, 1606 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.15 (s, 9 H), 3.55 (d, *J* = 6.1 Hz, 2 H), 5.82 (dt, *J* = 18.4, 1.5 Hz, 1 H), 6.26 (dt, *J* = 18.4, 6.1 Hz, 1 H), 7.17 (dd, J_{H-F} = 8.7 Hz, 2 H), 7.31 (d, *J* = 8.3 Hz, 2 H), 7.51–7.63 (m, 4 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –0.7 (3 C), 43.3, 116.0 (d, $^2J_{C-F}$ = 21 Hz, 2 C), 127.5 (2 C), 129.0 (d, $^3J_{C-F}$ = 8 Hz, 2 C), 129.7 (2 C), 132.2, 137.6, 138.5, 139.6, 145.4, 162.8 (d, $^1J_{C-F}$ = 245 Hz).

^{19}F NMR (188 MHz, $CDCl_3$): δ = –116.5.

MS (EI, 70 eV): *m*/*z* = 284 ($M^{+\bullet}$, 12), 192 (12), 191 (16), 73 (100), 59 (64), 58 (12), 45 (23), 43 (19).

Anal. Calcd for $C_{18}H_{21}FSi$: C, 76.01; H, 7.44. Found: C, 76.15; H, 7.48.

3′-[(*E*)-3-(Triethylgermyl)prop-2-enyl]biphenyl-4-carbaldehyde (5j)
Colorless oil; yield: 1.11 g (73%).

IR: 3058, 3027, 1703, 1604, 1567 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.78–1.09 (m, 15 H), 3.57 (d, *J* = 6.0 Hz, 2 H), 5.86 (dt, *J* = 18.3, 1.2 Hz, 1 H), 6.11 (dt, *J* = 18.3, 6.0 Hz, 1 H), 7.24–7.52 (m, 4 H), 7.76 (d, *J* = 8.2 Hz, 2 H), 7.96 (d, *J* = 8.2 Hz, 2 H), 10.07 (s, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 4.8 (3 C), 9.3 (3 C), 43.7, 125.5, 128.1 (3 C), 129.3, 129.5, 129.6, 130.6 (2 C), 135.6, 140.2, 141.6, 144.4, 147.8, 192.3.

MS (EI, 70 eV): *m*/*z* = 382 ($M^{+\bullet}$, 3), 353 (100), 325 (31), 297 (13), 219 (27), 207 (86), 205 (30), 191 (16), 189 (19), 178 (30), 165 (38), 152 (22), 148 (18), 147 (14), 133 (19), 115 (10), 105 (28), 103 (33), 77 (11), 75 (14).

(*E*)-2′-(4,4-Dimethylpent-2-enyl)biphenyl-4-carbaldehyde (5k)
White solid; yield: 0.81 g (73%); mp 54–56 °C.

IR (KBr): 3057, 3024, 1704, 1607, 1564, 1510, 1265 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (s, 9 H), 3.29 (d, *J* = 4.9 Hz, 2 H), 5.33–5.38 (m, 2 H), 7.22–7.39 (m, 4 H), 7.52 (d, *J* = 8.2 Hz, 2 H), 7.94 (d, *J* = 8.2 Hz, 2 H), 10.09 (s, 1 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.0 (3 C), 33.3, 37.0, 123.7, 126.6, 128.6, 129.9 (2 C), 130.1, 130.3, 130.5 (2 C), 135.5, 138.7, 141.1, 143.7, 148.7, 192.3.

MS (EI, 70 eV): *m*/*z* = 278 ($M^{+\bullet}$, 16), 207 (20), 193 (27), 179 (58), 178 (32), 165 (51), 152 (14), 83 (100), 57 (12), 55 (47), 43 (14), 41 (60), 39 (17).

Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.24; H, 7.92.

2-(4-Benzylphenyl)thiophene (5l)
White solid; yield: 0.60 g (60%); mp 68–70 °C.

IR (KBr): 3107, 3063, 3025, 1600, 1535, 1501 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.06 (s, 2 H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 1 H), 7.25–7.37 (m, 9 H), 7.55–7.65 (m, 2 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 42.1, 123.3, 125.0, 126.6, 126.7, 128.5, 129.0, 129.4, 129.9, 132.8, 141.0, 141.4, 144.8.

MS (EI, 70 eV): *m*/*z* = 250 ($M^{+\bullet}$, 100), 217 (16), 216 (10), 215 (23), 202 (13), 173 (23), 171 (12), 165 (21), 115 (17), 91 (19), 89 (17), 77 (12), 65 (22), 63 (22), 51 (77), 45 (31), 39 (35).

Anal. Calcd for $C_{17}H_{14}S$: C, 81.56; H, 5.64. Found: C, 81.62; H, 5.65.

4′-Benzyl-3-nitrobiphenyl (5n)
White solid; yield: 0.86 g (75%); mp 57–59 °C.

IR (KBr): 3084, 3061, 3027, 1602, 1583, 1531, 1515 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.09 (s, 2 H), 7.24–7.38 (m, 7 H), 7.56–7.65 (m, 3 H), 7.89–8.46 (m, 3 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 42.0, 122.2, 122.3, 126.8, 127.7 (2 C), 129.1 (2 C), 129.4 (2 C), 130.2 (3 C), 133.3, 136.9, 141.1, 142.3, 143.1, 149.2.

MS (EI, 70 eV): *m*/*z* = ($M^{+\bullet}$, 100), 254 (14), 242 (38), 241 (21), 167 (19), 165 (34), 152 (16), 120 (13), 91 (78), 65 (18).

Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.75; H, 5.18; N, 4.88.

4′-Methoxy-2-(4-methylbenzyl)biphenyl (5o)
Yellow oil; yield: 1.00 g (86%).

IR (NaCl): 3019, 3008, 1612, 1578, 1514 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 3.86 (s, 3 H), 3.94 (s, 2 H), 6.88–6.94 (m, 4 H), 7.05 (d, *J* = 7.9 Hz, 2 H), 7.17–7.28 (m, 6 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6, 39.1, 55.8, 114.0 (2 C), 126.6, 127.8, 129.3 (2 C), 129.5 (2 C), 130.8 (2 C), 130.9 (2 C), 134.6, 135.7, 139.1, 139.2, 142.4, 159.2.

MS (EI, 70 eV): *m*/*z* = 288 ($M^{+\bullet}$, 100), 273 (16), 257 (11), 256 (11), 195 (25), 181 (11), 165 (24), 152 (13).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.39; H, 6.91.

1-Substituted-3-(4-methylbenzyl)benzenes 6a,b by Double Coupling in One Pot; General Procedure
An oven-dried Schlenk flask equipped with a condenser was evacuated and back-filled with argon and charged with EtOH (19 mL), H_2O (5.3 mL), toluene (23 mL), *m*-bromobenzyl bromide (3 g, 12 mmol, 1 equiv), and boronic acid (12 mmol, 1 equiv). The flask was evacuated and back-filled with argon and then 1 M Na_2CO_3 (13.5 mL) and $Pd(PPh_3)_4$ (0.36 mmol, 3 mol%) were added. The mixture was stirred at 80 °C until completion of reaction (15 h). The second boronic acid (18 mmol, 1.5 equiv) and $Pd(PPh_3)_4$ (0.36 mmol, 3 mol%) were then introduced. The mixture was stirred at 80 °C for 15 h. The soln was filtered through a Celite path and the solvents were evaporated under reduced. The residue was extracted with Et_2O, washed with brine, and dried ($MgSO_4$). After purification by flash chromatography (silica gel) the products were characterized.

3-(4-Methylbenzyl)biphenyl (6a)
White oil; yield: 1.61 g (52%).

IR (NaCl): 3028, 1600, 1575, 1514 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 4.14 (s, 2 H), 7.25–7.72 (m, 13 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6, 42.2, 125.5, 127.8 (3 C), 128.1, 128.4, 129.2 (2 C), 129.4 (3 C), 130.0 (2 C), 136.1, 138.5, 141.8, 141.9, 142.4.

MS (EI, 70 eV): *m*/*z* = 258 ($M^{+\bullet}$, 100), 257 (11), 243 (54), 211 (12), 166 (16), 165 (37), 104 (10), 91 (11).

Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.21; H, 7.04.

(*E*)-1-(3,3-Dimethylbut-1-enyl)-3-(4-methylbenzyl)benzene (6b)
Colorless oil; yield: 1.52 g (48%).

IR (NaCl): 3023, 1648, 1602, 1583, 1514 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.26 (s, 9 H), 2.45 (s, 3 H), 4.06 (s, 2 H), 6.39–6.40 (br s, 2 H), 7.22–7.34 (m, 8 H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6, 30.2 (3 C), 33.9, 42.0, 124.2, 125.2, 127.4, 128.0, 129.1, 129.3 (2 C), 129.7 (2 C), 136.0, 138.7 (2 C), 142.0, 142.2.

MS (EI, 70 eV): *m*/*z* = 264 ($M^{+\bullet}$, 27), 159 (26), 105 (100).

Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.92; H, 9.18.

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