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PAPER

A facile and convenient sequential homobimetallic catalytic approach towards β-methylstyrenes. A one-pot Stille cross-coupling/isomerization strategy†

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An efficient one-pot synthetic approach towards β-methylstyrenes is reported. The transformation, based on sequential homobimetallic catalysis, involves a Stille cross-coupling reaction between aryl halides and allyltributylstannane, followed by an *in situ* palladium-catalyzed conjugative isomerization. The reaction was optimized, and the best results were obtained with 10 mol% $Pd(PPh_3)_2Cl_2$, 8.0 equiv. LiCl, and 0.5 equiv. PPh_3 in diglyme at 130 °C for 12 h. It was demonstrated that the reaction tolerates a wide variety of functional groups.

Introduction

Palladium-catalyzed cross-coupling reactions have become a highly significant field in modern arene chemistry, now being considered state of the art for C–C bond formation processes.[1]

The synthesis of β-methylstyrenes is of general interest because this motif is present in many natural products, such as the antibiotic agent fumimycin,[2a,b] the novel inhibitor of the enzymes lipoxygenase and aldose reductase nigerloxin,[2c,d] and the complex neolignan ratanhine, isolated from the medicinal plant *Ratanhiae radix*[2e,f] (Fig. 1).

The β-methylstyrene scaffold is also found in pharmaceutically and technologically relevant compounds[3] such as β-cathenin/tcf-4 inhibitors[3a] and the [1]benzothieno[3,2-*b*][1]-benzothiophene derivative OSC5, useful for building photoelectric converting elements.[3c] In addition, β-methylstyrenes have been employed as precursors of more complex molecules,[4] as substrates for testing the scope and limitations of new chemical reagents[5] and as dehydrogenation agents.[6]

β-Methylstyrenes are commonly accessed by conjugative migration of the double bond of allylbenzenes. This transformation has been performed by treatment of the latter with bases (KF/Al_2O_3 [7a] and K_2CO_3 [7b]) or transition metal complexes (from Ti[8a,b] and Fe[8c,d] to softer Lewis acid derivatives of Rh,[9a] Ru,[9b,c] Ir,[10a] Pd,[10b,c] Pt[11a] and Ni[11b,c]). It has also been shown that bulky palladium hydride complexes promote the selective conversion of terminal alkenes into 2-alkenes.[12]

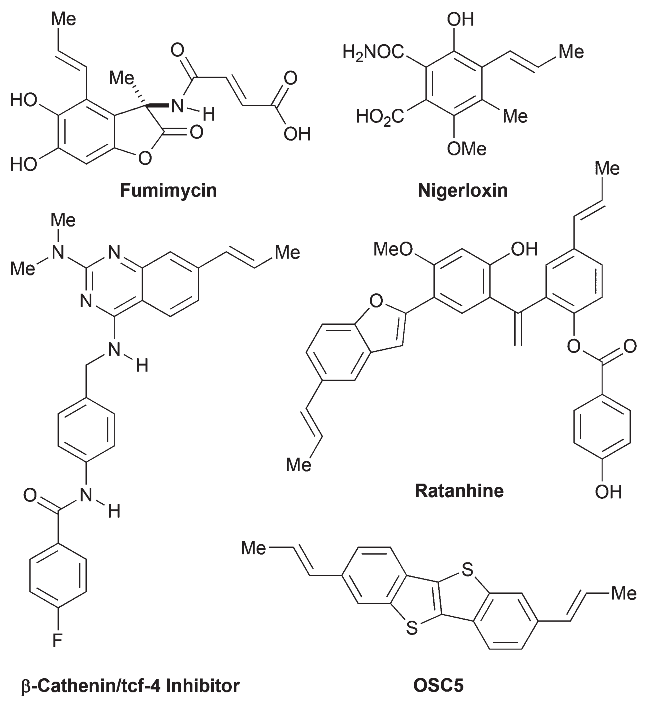

Fig. 1 Selected natural and synthetic β-methylstyrene derivatives.

In spite of the widespread use of β-methylstyrenes, rather few methods have been disclosed for their direct synthesis from easily available starting materials, and for employing C–C bond forming reactions to install the required three-carbon

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atom moiety, and many of them require special equipment, have scarce applicability or exhibit serious drawbacks.

These approaches include the cross-coupling reaction of aryllithium, arylmagnesium and arylmanganese compounds with vinyl halides,[13] vinyl boronates,[14] and allyl or vinyl sulfones;[15] however, they should be performed under conditions that are compatible with relatively few functional groups.

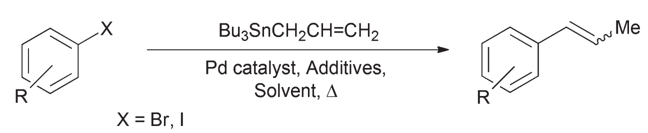
Other alternatives are the arylation of propyne involving a vinylborane cross-coupling/oxidation protocol under strongly basic conditions,[16] the iron-promoted arylation of propene with anilines[17a] and the electrochemically assisted nickel-catalyzed reaction of aryl halides with propene.[17b] A Heck-type arylation of allylsilanes, furnishing β-methylstyrenes as side/unexpected products,[18] and a nickel catalyzed cross-coupling of modified alkyl and alkenyl Grignard reagents with aryl- and heteroaryl nitriles have also been disclosed.[19] However, this group of transformations seems to have a rather narrow scope and some of them give relatively low yields of products.

Propenylations with the use of 1-propenyltributyltin,[20] allyl trifluoroborates,[21] vinylboronic acids (Suzuki-Miyaura cross-coupling)[22] and allyl/vinyl boronates have been reported as alternatives,[23] but these are comparatively expensive reagents.

The conversion of allyl benzenoids into their corresponding 1-propenyl derivatives has been occasionally observed as a secondary process during Pd-catalyzed cross-couplings[24] since the initial reports on Stille's reaction.[25] Significant amounts of the 1-propenyl derivatives (produced at the expense of their sought allyl congeners) were sometimes detected, especially when arenes carrying electron-withdrawing substituents were employed as starting materials.[26a] However, this outcome was qualified as a "very rare" and "unexpected" isomerization,[26b] and its usefulness as a synthetic transformation has surprisingly not been further explored.

During our recent synthesis of the structure originally assigned to the marine alkaloid aspergillitine,[27] we observed the conjugative migration of the double bond of a 7-allyl chromone intermediate to the related 1-propenyl derivative. Since this sequence took place in a completely atom-economical process and without addition of special reagents, and taking into account that tandem protocols are considered to be superior to stepwise procedures because they shorten the synthetic scheme, we considered optimizing the transformation towards the preparation of β-methylstyrenes.

Therefore, here we report a facile and convenient one-pot approach to the synthesis of β-methylstyrenes, as shown in Scheme 1, which involves a palladium-catalyzed Stille cross-coupling reaction of aryl halides with allyltributylstannane, followed by an *in situ* double bond conjugative migration. The transformation was optimized and its scope and limitations were studied.



Scheme 1 Proposed one-pot synthesis of β-methylstyrenes.

Results and discussion

The easy accessibility and comparative inexpensiveness of allyltributyltin are advantageous for its use as a three carbon atom source. In contrast, (*E*/*Z*)-propenyl tributylstannanes are costly and not readily available,[28] also being acid-sensitive and prone to proto-destannylation.[29]

In order to find the appropriate reaction conditions, the Pd-catalyzed model reaction of 2-bromoanisole (**1a**) with allyltributyltin, employing 8.0 equiv. LiCl and 0.5 equiv. PPh_3, was first used to evaluate the catalytic activity of several Pd sources. Compound **1a** was selected for optimization of the transformation because it has an *ortho* electron donating group, which may hinder the reaction by exerting both steric and electronic effects.

Among the catalysts tested, the results indicated that $Pd(PPh_3)_2Cl_2$ exhibited the best performance, furnishing 62% overall yield of a 35/65 mixture of 2-allylanisole (**2a**) and (*E*/*Z*)-1-methoxy-2-propenyl-benzene (**3a**, *E*/*Z* = 83/17) after 48 h at 130 °C in DMF (Table 1, entries 1–4). A good performance was also observed with the use of $Pd(PPh_3)_4$ as the catalyst, in DMF at 130 °C. This catalyst afforded the product in 60% yield; the corresponding allyl/propenyl derivative ratio was 2/98, with an *E*/*Z* relationship of 91/9 (entry 5).

Next, the effect of PPh_3, PBu_3 and Dppp and DavePhos as added phosphine ligands was examined, concluding that all of them were acceptable (entries 4 and 6–8), and that PPh_3 exhibited the best profile. Notably, DavePhos (0.5 equiv. regarding the amount of the Pd catalyst) gave a 71% combined yield of allyl/propenyl derivatives (ratio: 13/87) with an *E*/*Z* relationship of 85/15 (entry 6).

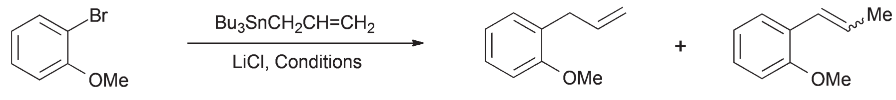
However, after analysis of these results it was concluded that the performances of $Pd(PPh_3)_4$ and DavePhos (entries 5 and 6) do not show highly significant differences; therefore, for price and convenience reasons their use was not further tested.

During the stage of solvent selection (entries 4 and 9–11), *N*,*N*-dimethylacetamide (DMA) and *N*-methyl pyrrolidone (NMP) allowed carrying out the transformation at higher temperatures; however, no meaningful improvements were observed.

On the other hand, diglyme (entry 11) proved to be a superior solvent, furnishing a more efficient conversion of the allyl intermediate **2a** into the corresponding β-methylstyrene derivative **3a**. This solvent had been demonstrated to possess unique properties in previously reported Pd-catalyzed cross-couplings.[30]

Diglyme allowed shortening of the reaction time up to 12 h (entry 12), produced improvements in product yields, and eased the reaction work up. Attempts to further reduce the reaction time to 8 h or lower the temperature proved to be detrimental to the process performance, specifically diminishing

Table 1 Optimization of the reaction conditions



1a 2a 3a

Entry No.	Catalyst[a]	Ligand	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)	**2a**/**3a** (%)	*E*/*Z* (%)
1	$Pd(MeCN)_2Cl_2$	PPh_3	DMF	130	48	60	63/37	86/14
2	$Pd(OAc)_2$	PPh_3	DMF	130	48	93	71/29	80/20
3	$Pd_2(dba)_3$	PPh_3	DMF	130	48	30	34/64	86/14
4	$Pd(PPh_3)_2Cl_2$	PPh_3	DMF	130	48	62	35/65	83/17
5	$Pd(PPh_3)_4$	PPh_3	DMF	130	48	60	2/98	91/9
6	$Pd(PPh_3)_2Cl_2$	DavePhos	DMF	130	48	71	13/87	85/15
7	$Pd(PPh_3)_2Cl_2$	Dppp	DMF	130	48	68	63/37	81/19
8	$Pd(PPh_3)_2Cl_2$	PBu_3	DMF	130	48	55	58/42	86/14
9	$Pd(PPh_3)_2Cl_2$	PPh_3	DMA	140	48	56	14/86	84/16
10	$Pd(PPh_3)_2Cl_2$	PPh_3	NMP	160	24	43	93/7	91/9
11	$Pd(PPh_3)_2Cl_2$	PPh_3	Diglyme	130	48	36	0/100	92/8
12	$Pd(PPh_3)_2Cl_2$	PPh_3	Diglyme	130	12	59	4/96	100/0
13	$Pd(PPh_3)_2Cl_2$	PPh_3	Diglyme	130	8	65	63/37	90/10
14	$Pd(PPh_3)_2Cl_2$	PPh_3	Diglyme	110	12	65	17/83	90/10
15	$Pd(PPh_3)_2Cl_2$	PPh_3	Diglyme	90	12	76	51/49	90/10
16	$Pd(PPh_3)_2Cl_2$	PPh_3	Diglyme	90	4	80	100/0	—
17	$Pd(PPh_3)_2Cl_2$ (5%)	PPh_3	Diglyme	130	12	49	63/37	87/13
18[c]	$Pd(PPh_3)_2Cl_2$	PPh_3	Diglyme	130	12	49[d]	83/17	45/55

[a] Catalyst loading 10%. [b] Yields after isolation and purification. Prior to purification, the crude mixture was analyzed by GC-MS and ^1H NMR, confirming that the yields of the isolated product are a true reflection of the reaction outcome. [c] Without addition of LiCl. [d] Based on 55% of the recovered starting material.

the extent of the double bond conjugative migration stage (entries 13–15). Only 2-allylanisole (**2a**) was detected after heating for 4 h at 90 °C (entry 16).

It was also found that LiCl is critically important for obtaining a successful transformation (entry 18). On the other hand, the use of CsF in place of LiCl (DMF, 130 °C) slightly improved the reaction performance (58% yield, **2a**/**3a**: 6/94; *E*/*Z*: 91/9); however, the system proved to be incompatible with certain functional groups and study of its use was not further pursued.

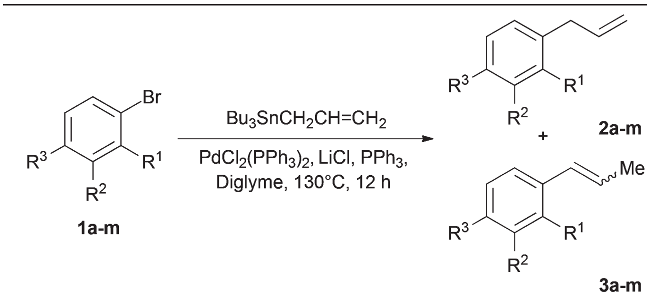
In order to demonstrate the efficiency and scope of the present method, the optimized catalytic system was applied to a representative set of aryl halides, containing various substituents and displaying different functionalization patterns. The results (Table 2) revealed that, in general, the transformation proceeded in good overall yield.

Taking into account that the process entails two consecutive reactions, even the lowest performances represent the result of individual transformations taking place in around 75% yield. Furthermore, the optimized conditions were compatible with several functional groups, including alkyl/aryl, ether, *N*,*N*-dimethylamino, ketone, ester, nitro and cyano moieties.

In addition, it was observed that the presence of functionalities *ortho* to the halide did not hinder the transformation and did not result in significantly lower yields of the corresponding β-methylstyrene products (entries 1 *vs.* 2 and 3 and 6 *vs.* 7).

However, a closer inspection revealed that the best results were obtained when the substrates carried electron withdrawing groups placed *para* to the halide (entries 4 and 5) and that compounds carrying electron withdrawing groups *ortho* to the halide exhibited better performances when compared with substrates having an electron releasing group at the same position (entries 1, 9 and 10).

Table 2 One pot synthesis of β-methylstyrenes **3a–m**



Entry	R_1	R_2	R_3	Yield (%)	Prod.	**2**/**3**	*E*/*Z*
1	OMe	H	H	59	**2a**/**3a**	4/96	100/0
2	H	OMe	H	65	**2b**/**3b**	4/96	92/8
3	H	H	OMe	62	**2c**/**3c**	3/97	95/5
4	H	H	CN	92	**2d**/**3d**	0/100	95/5
5	H	H	COMe	96	**2e**/**3e**	0/100	94/6
6	H	H	Me	76	**2f**/**3f**	0/100	100/0
7	Me	H	H	72	**2 g**/**3g**	0/100	94/6
8	NO_2	H	OMe	56	**2h**/**3h**	0/100	90/10
9	CO_2Et	H	H	77[a]	**2i**/**3i**	0/100	100/0
10	CO_2Et	H	H	72	**2i**/**3i**	0/100	93/7
11	Ph	H	H	76	**2j**/**3j**	6/94	89/11
12	H	H	NMe_2	59	**2k**/**3k**	0/100	89/11
13	1-Bromonaphthalene			76	**2l**/**3l**	9/91	100/0
14	9-Bromophenanthrene			59	**2m**/**3m**	12/88	100/0

[a] The iodo derivative was employed.

Although the exact details of the reaction mechanism of this transformation are still uncertain, a mechanistic picture can be proposed based on several observations made during this study. Firstly, the formation of the isomerized product should take place through the intermediacy of an allylbenzenoid species, resulting from an initial Stille cross-coupling reaction. These compounds were chromatographically detected and spectroscopically identified. In addition, 1-propenyl stannane should be ruled out as a reactant, since in the absence of aryl halides, the starting allylstannane proved to be remarkably stable under the optimized reaction conditions, not isomerizing to the related 1-propenyl stannane.[31]

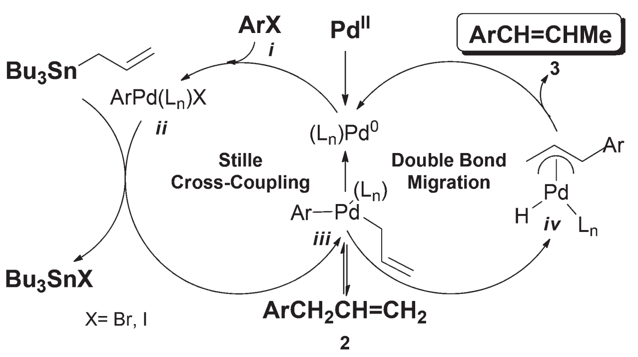
That the double bond migration requires the presence of a Pd catalyst and is not a merely thermal process was also assessed with a control experiment employing 4-allylanisole. It was observed that no conjugative isomerization took place under the standard conditions in the absence of the catalyst.

These observations enabled us to speculate that an initial Stille cross-coupling reaction takes place between the aryl derivative (***i***) and the allylstannane (Scheme 2). It is known that the Stille reaction is promoted by a Pd^0 species, which can be formed *in situ* by partial reduction of the Pd^{II} catalyst by PPh_3 or by the stannane itself.[32]

After the well-established steps of oxidative addition of the substrate to the Pd complex (***ii***) and transmetallation with transfer of the allyl moiety to the Pd complex (***iii***), the latter may undergo reductive elimination to the allyl derivative (**2**), with either regeneration of the Pd^0 catalyst, or formation of an η^3-allyl hydride (***iv***).

The subsequent double-bond conjugative migration to yield the isomerized alkene product **3** should involve a β-hydride elimination.[33] Alternatively, the intermediate ***iv*** should give back the starting olefin (**2**) if the H returns to the same site it left.[34a]

The intermediacy of the allyl derivatives **2** in this transformation was unequivocally demonstrated with control experiments run with **2c**. As expected, when **2c** was exposed to $Pd(PPh_3)_2Cl_2$ and LiCl in diglyme, in the presence of PPh_3, the reaction met with failure, due to the reduction of the Pd by the phosphine.[32b] However, omission of PPh_3 provided 78% yield of **3c**, when **2c** was submitted to the optimized reaction conditions.



Scheme 2 Proposed reaction mechanism.

Taking into account that the palladium source is added in catalytic amounts and that complete conversion of the starting material into the allyl derivative **2** has been clearly observed at the earliest stages of the transformation, it should be concluded that the allylarene derivative **2** could also be a source of intermediate (***iii***), acting as a proxy towards **3**.

Observation of **2** as the first reaction product and its conversion into **3** under higher temperature conditions can be regarded as a result of a process in which the allyl derivative **2** is the kinetically controlled product of a sequence, in which it is driven towards the thermodynamic, most stable product **3** when heated for a longer time.

Precipitation of the palladium metal has been associated with the isomerization of allyl moieties;[34b] in our case, however, it was observed that the addition of PPh_3 avoids precipitation of palladium black,[34c] while ensuring good overall yields.

On the other hand, LiCl may participate in the mechanism as a source of chloride ligand, stabilizing the Pd intermediates and making the cross-coupling stage more efficient. It has been demonstrated that LiCl is a powerful reaction rate accelerant, turning the Pd catalyst more active towards transmetalation and more prone to oxidative addition. Furthermore, LiCl enhances the polarity of the solvent, enhancing the leaving ability of anionic ligands. As an additive, it has been found necessary when the transformation is run in ethereal solvents.[35a,b]

Interestingly, the presence of Bu_3SnCl was detected during GC-MS monitoring of the reactions (M^+ = 326, with its characteristic isotopic cluster).

The influence of diglyme as the reaction solvent may stem from its ability to exchange with the Pd-ligands at various stages of the cycle, also stabilizing the resulting intermediates. It has been found that diglyme has an accelerating effect on some Pd-catalyzed C–C bond forming processes. The ether-O-donor atoms may act initially by blocking the soft metal centers; in this way, at a later stage these are more rapidly substituted by the substrates, since Pd^{II} has a low affinity for neutral O-ligands. Similarly, these solvent properties may offer a more rapid product decomplexation step, favoring the whole process.[35c]

Globally observed, the transformation may be regarded as a novel case of sequential homobimetallic catalysis.[36] This is a recent concept designed to describe a condition where a transition metal catalyst, with the metal in a certain oxidation state, catalyzes a given reaction to yield a product, which *in situ* undergoes a subsequent transformation, catalyzed by another complex of the same metal, but in a different oxidation state.[37]

In the current case, the Pd^0-catalyzed Stille cross-coupling reaction is concatenated with a Pd^{II}-catalyzed conjugative migration process, leading to the resulting β-methylstyrenes. It is noteworthy that examples of this new but highly useful paradigm of reactions in tandem are scarce.

Conclusions

In conclusion, we have developed a facile and convenient alternative for the synthesis of β-methylstyrenes through an efficient sequential homobimetallic palladium catalyzed one-pot process.

The transformation entails two steps in tandem, namely a Stille cross-coupling reaction, followed by an *in situ* Pd-assisted double bond conjugative isomerization.

In light of its operational simplicity, tolerance to a wide range of functional groups, good overall yields and satisfactory regioselectivity, it is expected that this strategy will find wide applications in organic synthesis of complex molecules, including natural products.

Experimental section

General information

The reactions were carried out under an anhydrous argon atmosphere, employing oven-dried glassware. Dry DMF, NMP and DMA were prepared by distillation from anhydrous BaO; xylenes and diglyme were distilled from Na°/benzophenone ketyl. Anhydrous solvents were stored in dry Young's ampoules. The other reagents were used as received.

In the conventional purification procedure, the crude material was submitted to flash column chromatography with silica gel 60 H (particle size 63–200 μm). Elution was carried out with mixtures of hexane–Et_2O, under positive pressure of N_2 and employing gradient of solvent polarity techniques.

All new compounds gave single spots when run on TLC plates of Kieselgel 60 GF_{254}, employing different hexane–Et_2O and hexane–EtOAc solvent systems. Chromatographic spots were detected by exposure of the plates to UV light (254 nm), followed by spraying with the ethanolic *p*-anisaldehyde/sulfuric acid reagent and careful heating.

Apparatus

The IR spectra were recorded with a Shimadzu Prestige 21 spectrophotometer of thin films held between NaCl cells.

The ^{1}H and ^{13}C NMR spectra were acquired at 300.13 and 75.48 MHz, respectively, on a Bruker Avance 300 spectrometer. The resonances of $CHCl_3$ in $CDCl_3$ (δ 7.26 and 77.0 for ^{1}H and ^{13}C NMR, respectively) were used as internal standards. Chemical shifts are reported in parts per million in the δ scale and the magnitudes of the coupling constants (J) are given in hertz. DEPT 135 and DEPT 90 experiments aided the interpretation of the fully decoupled ^{13}C NMR spectra. In special cases, 2D-NMR experiments (COSY, HSQC and HMBC) were also employed.

The GC-MS experiments were carried out with a Shimadzu QP2010 *plus* instrument equipped with an AOC-20i autosampler. The chromatographic runs were performed in the split injection mode (ratio: 50), on a SPB-1 column (28.5 m × 0.25 mm × 0.25 μm), with a helium flow of 1.05 mL min^{-1}. The oven temperature program was as follows: T_{Init} = 50 °C (3 min); then ΔT = 5 °C min^{-1} up to T_1 = 180 °C; then ΔT = 20 °C min^{-1} up to T_{End} = 310 °C.

Low resolution mass spectra were obtained under the following conditions: $T_{\text{Interface}}$ = 300 °C; $T_{\text{Ion source}}$ = 230 °C; solvent cut time = 8 min; ionization voltage = 70 eV. The mass spectra were compared against the NIST08 library. Diphenyl ether (Aldrich 99.5%) was employed as the internal standard for interpretation, comparison and quantitative purposes. The quality of the results was assessed against simultaneous ^{1}H NMR analysis of a small sample (1–2 mg) of the reaction.

The high resolution mass spectra were obtained on a Bruker MicroTOF-Q II instrument. Detection of the ions was performed with electrospray ionization in positive ion mode.

General procedure for the preparation of β-methylstyrenes. Allyltributyltin (1.2 equiv.) was added to a degassed solution of the aryl halide (1 equiv.), anhydrous LiCl (8 equiv.), Ph_3P (0.5 equiv.) and $Pd(Ph_3P)_2Cl_2$ (0.1 equiv.) in anhydrous diglyme (final concentration *ca.* 0.15 M). The mixture was heated at 130 °C for 14 h under an argon atmosphere until complete consumption of the starting material as ascertained by GC analysis. The reaction was left to reach room temperature, when it was diluted with Et_2O (10 mL) and treated with a saturated solution of KF (5 mL). The mixture was stirred for 30 min in order to quench the organotin-derivatives. The organic phase was successively washed with brine (2 × 5 mL) and H_2O (2 × 5 mL). The organics were filtered through a short pad of a 1 : 1 mixture of Florisil and Celite and dried over Na_2SO_4 prior to concentration under reduced pressure. Column chromatography of the residue gave the corresponding propenyl derivatives.

For the more volatile compounds **3f** and **3g**, the work-up was carried out as follows: the reaction was diluted with a 1 : 1 mixture of pentane and hexane (10 mL) and transferred to a separation flask. The organics were sequentially treated with a saturated solution of KF (5 mL) for 15 min, brine (5 mL) and H_2O (2 × 5 mL). The organic phase was then filtered through a short pad of Celite and silica gel (1 : 1, w/w), and washed with pentane (10 mL). The liquids were dried over Na_2SO_4 and concentrated under a slow stream of nitrogen.

(*E*)-1-Methoxy-2-(prop-1-enyl)benzene (3a).[38a,b] Yield = 59%; E/Z = 100 : 0; colourless oil. IR (Film, ν): 2924, 2852, 1463, 1456, 1437, 1244, 1119, 750, 721 and 694 cm^{-1}. ^{1}H NMR (δ): 1.90 (dd, J = 1.4 and 6.6, 3H), 3.84 (s, 3H), 6.22 (dq, J = 6.6 and 16.0, 1H), 6.72 (dd, J = 1.4 and 16.0, 1H), 6.85 (d, J = 8.2, 1H), 6.90 (t, J = 7.6, 1H), 7.18 (dt, J = 1.5 and 7.6, 1H) and 7.39 (dd, J = 1.5, 7.6, 1H). ^{13}C NMR (δ): 18.9, 55.4, 110.7, 120.6, 125.6, 126.4, 126.6, 127.7, 133.2 and 156.2. EI-MS (m/z, %): 148 (M$^+$, 100), 147 (10), 133 (22), 119 (55), 117 (33), 115 (46), 105 (69), 103 (26), 91 (83), 79 (26) and 77 (34).

(*E*)-1-Methoxy-3-(prop-1-enyl)benzene (3b).[38c,d] Yield = 65%; E/Z = 92 : 8; colourless oil. IR (Film, ν): 2922, 2851, 1599, 1578, 1489, 1464, 1454, 1435, 1288, 1263, 1252, 1155, 1047, 964, 768 and 648 cm^{-1}. ^{1}H NMR (δ): 1.88 (dd, J = 1.2 and 6.4, 3H), 3.81 (s, 3H), 6.23 (dq, J = 6.4 and 15.7, 1H), 6.38 (d, J = 15.7, 1H), 6.75 (dd, J = 2.0 and 7.9, 1H), 6.87 (t, J = 2.1, 2H), 6.93 (dd, J = 1.9 and 7.7, 1H) and 7.20 (t, J = 7.8, 1H). ^{13}C NMR (δ): 18.4, 55.2, 111.2, 112.3, 118.5, 121.0, 126.1, 129.4, 139.4 and 159.8. EI-MS (m/z, %): 148 (M^+, 36), 147 (16), 117 (64), 116 (25), 115 (45), 105 (63), 103 (38), 92 (14), 91 (94), 89 (26), 79 (69), 78 (48) and 77 (100).

(*E*)-1-Methoxy-4-(prop-1-enyl)benzene (3c).[39a,d] Yield = 62%; E/Z = 95 : 5; colourless oil. IR (Film, ν): 2924, 2851, 1732, 1607, 1512, 1456, 1377, 1174 and 1034 cm^{-1}. ^{1}H NMR (δ): 1.85 (dd, J = 1.6 and 6.6, 3H), 3.80 (s, 3H), 6.09 (dq, J = 6.6, 15.8, 1H), 6.35 (dd, J = 1.5 and 15.8, 1H), 6.83 (d, J = 8.8, 2H) and 7.26 (d, J = 8.8, 2H). ^{13}C NMR (δ): 18.4, 55.3, 113.9, 123.5, 126.9, 130.3, 130.8 and 158.6. EI-MS (m/z, %): 148 (M^+, 16), 119 (42), 115 (43), 105 (79), 103 (30), 91 (100), 79 (42), 78 (23) and 77 (56).

(*E*)-4-(Prop-1-enyl)benzonitrile (3d).[39e,f] Yield = 92%; E/Z = 95 : 5; colourless oil. IR (Film, ν): 3059, 2986, 2930, 2230, 1701, 1609, 1504, 1408, 1379, 1202, 1119, 1107, 1018, 843 and 820 cm^{-1}. ^{1}H NMR (δ): 1.92 (d, J = 5.9, 3H), 6.31–6.44 (m, 2H), 7.38 (d, J = 8.3, 2H) and 7.55 (d, J = 8.3, 2H). ^{13}C NMR (δ): 18.6, 109.9, 119.9, 126.3 (2C), 129.8, 130.2, 132.3 (2C) and 142.4. EI-MS (m/z, %): 143 (M^+, 100), 142 (72), 140 (16), 117 (15), 116 (85), 115 (79), 89 (26) and 76 (13).

(*E*)-1-[4-(Prop-1-enyl)phenyl]ethanone (3e).[40a,b] Yield = 96%; E/Z = 94 : 6; colourless oil. IR (Film, ν): 2914, 1674, 1603, 1409, 1360, 1267, 1180, 958, 852, 789 and 590 cm^{-1}. ^{1}H NMR (δ): 1.91 (d, J = 5.2, 3H), 2.57 (s, 3H), 6.32–6.47 (m, 2H), 7.39 (d, J = 8.4, 2H) and 7.88 (d, J = 8.4, 2H). ^{13}C NMR (δ): 18.7, 26.5, 125.8 (2C), 128.7 (2C) 129.1, 130.3, 135.4, 142.6 and 197.6. EI-MS (m/z, %): 160 (M^+, 33), 146 (10), 145 (100), 117 (25), 116 (12), 115 (59) and 91 (30).

(*E*)-1-Methyl-4-(prop-1-enyl)benzene (3f).[23,39f,40c,d] Yield = 76%; E/Z = 100 : 0; colourless oil. IR (Film, ν): 3023, 2921, 1638, 1551, 1432, 1110, 1015, 990, 962, 802 and 776 cm^{-1}. ^{1}H NMR (δ): 1.89 (dd, J = 1.2 and 6.5, 3H), 2.34 (s, 3H), 6.20 (dq, J = 6.5 and 15.8, 1H), 6.39 (d, J = 15.8, 1H), 7.24 (d, J = 8.3, 2H) and 7.37 (d, J = 8.3, 2H). ^{13}C NMR (δ): 18.5, 21.1, 124.6, 125.7 (2C), 129.2 (2C), 130.9, 135.2 and 136.4. EI-MS (m/z, %): 132 (M^+, 62), 117 (100), 115 (45), 105 (9), 91 (32) and 77 (10).

(*E*)-1-Methyl-2-(prop-1-enyl)benzene (3g).[39d] Yield = 72%; E/Z = 94 : 6; colourless oil. IR (Film, ν): 3023, 2921, 1638, 1551, 1432, 1110, 1015, 990, 962, 802 and 776 cm^{-1}. ^{1}H NMR (δ): 1.89 (dd, J = 1.2 and 6.5, 3H), 2.34 (s, 3H), 6.20 (dq, J = 6.5 and 15.8, 1H), 6.39 (d, J = 15.8, 1H), 7.04 (d, J = 7.6, 1H), 7.12 (t, J = 7.6, 1H), 7.24 (d, J = 8.3, 1H) and 7.35 (t, J = 7.6, 1H). ^{13}C NMR (δ): 18.5, 21.1, 124.6, 125.7 (2C), 129.2 (2C), 130.9, 135.2 and 136.4. EI-MS (m/z, %): 132 (M^+, 62), 131 (14), 117 (100), 116 (15),115 (51), 91 (34), 93 (28) and 91 (56).

(*E*)-4-Methoxy-2-nitro-1-(prop-1-enyl)benzene (3h). Yield = 56%; E/Z = 90 : 10; yellowish oil. IR (Film, ν): 2914, 1674, 1651, 1602, 1409, 1360, 1267, 1180, 958, 852 and 789 cm^{-1}. ^{1}H NMR (δ): 1.91 (dd, J = 0.9 and 6.6, 3H), 3.85 (s, 3H), 6.13 (dq, J = 6.6 and 15.9, 1H), 6.78 (d, J = 15.9, 1H), 7.08 (dd, J = 2.6 and 8.7, 1H), 7.38 (d, J = 2.6, 1H) and 7.47 (d, J = 8.7 Hz, 1H). ^{13}C NMR (δ): 18.3, 55.5, 108.2, 108.7, 119.6, 125.6, 129.1, 129.2, 147.8 and 158.4. EI-MS (m/z, %): 193 (M^+, 24), 176 (10), 151 (58), 150 (100), 133 (20), 122 (47), 121 (21), 115 (29), 107 (22), 106 (30), 105 (31), 104 (20), 103 (59), 94 (36), 93 (28), 91 (56) and 77 (92). HRMS (ESI-TOF, m/z) Found: 216.06311; $C_{10}H_{11}NNaO_3^+$ requires 216.0637.

(*E*)-Ethyl 2-(prop-1-enyl)benzoate (3i)

Procedure A. From the aryl iodide. Yield = 77%; E/Z = 100 : 0; colourless oil. IR (Film, ν): 2980, 1714, 1479, 1444, 1279, 1246, 1132, 1099, 1072 and 964 cm^{-1}. ^{1}H NMR (δ): 1.39 (t, J = 7.1, 3H), 1.92 (dd, J = 1.7 and 6.6, 3H), 4.36 (q, J = 7.1, 2H), 6.14 (dq, J = 7.1 and 15.7, 1H), 7.14 (dd, J = 1.5 and 15.7, 1H), 7.25 (dt, J = 0.9 and 7.2, 1H), 7.42 (dt, J = 1.2 and 7.5, 1H), 7.51 (d, J = 7.9, 1H), 7.83 (dd, J = 1.2 and 7.9, 1H). ^{13}C NMR (δ): 14.3, 18.8, 60.9, 126.4, 127.1, 128.4, 129.5, 129.7, 130.1, 131.8, 139.5 and 167.7. EI-MS (m/z, %): 190 (M^+, 49), 175 (46), 147 (86), 145 (47), 144 (24), 117 (67), 116 (45), 115 (100) and 91 (37). HRMS (ESI-TOF, m/z) Found: 191.1067; $C_{12}H_{15}O_2^+$ $[M + H]^+$ requires 191.1072.

Procedure B. From the aryl bromide. Yield = 72%; E/Z = 93 : 7; colourless oil. IR, NMR and EI-MS spectra fully agree with those of **3i** obtained according to Procedure A.

(*E*)-2-(Prop-1-enyl)-biphenyl (3j).[41] Yield = 76%; E/Z = 89 : 11; colourless oil. IR (Film, ν): 3061, 3040, 2928, 2914, 2851, 1584, 1487, 1236, 1163, 1072, 1022, 962, 866, 785, 748 and 691 cm^{-1}. ^{1}H NMR (δ): 2.01 (dd, J = 1.7 and 6.6, 3H), 6.26 (dq, J = 6.6 and 15.4, 1H), 7.15 (dd, J = 1.8 and 15.4, 1H) and 7.16–8.16 (m, 9H). ^{13}C NMR (δ): 19.0, 123.5, 124.0, 125.6, 125.7, 125.8, 127.2, 128.2, 128.3, 128.4, 128.6, 131.1, 133.6, 135.8 and 158.3. EI-MS (m/z, %): 194 (M^+, 34), 179 (100), 178 (54), 165 (16), 152 (7) 115 (6), 89 (18), 83 (12) and 76 (9).

(*E*)-Dimethyl-(4-propenyl-phenyl)-amine (3k).[23,40c,d] Yield = 57%; E/Z = 89/11; yellow-pale oil. IR (Film, ν): 2924, 1732, 1861, 1611, 1520, 1487, 1350, 1234 and 1165 cm^{-1}. ^{1}H NMR (δ): 1.85 (dd, J = 1.4 and 6.6, 3H), 2.94 (s, 6H), 6.03 (dq, J = 6.6 and 15.2, 1H), 6.32 (dd, J = 1.4 and 15.2, 1H), 6.68 (d, J = 8.8, 2H) and 7.23 (t, J = 8.8, 2H). ^{13}C NMR (δ): 18.4, 40.7 (2C), 116.7, 121.4 (2C), 123.2 (2C), 126.8, 130.7 (2C) and 149.6. EI-MS (m/z, %): 161 (M^+, 100), 160 (76), 145 (15), 144 (10), 134 (19), 118 (12), 117 (33), 115 (32), 91 (29) and 77 (19).

(*E*)-1-(Prop-1-enyl)naphthalene (3l).[42a,b] Yield = 68%; E/Z = 81 : 19; colourless oil. IR (Film, ν): 3061, 3040, 2928, 2914, 2851, 1584, 1487, 1236, 1163, 1072, 1022, 962, 866, 785, 748 and 691 cm^{-1}. ^{1}H NMR (δ): 1.83 (dd, J = 1.6 and 6.5, 3H), 6.20 (dq, J = 6.5 and 15.7, 1H), 6.42 (d, J = 15.7, 1H), 7.24 (d, J = 8.3, 2H), 7.37 (d, J = 8.3, 2H), 7.48 (dt, J = 1.4 and 8.3, 1H), 7.60 (d, J = 7.0, 1H) and 7.63 (dt, J = 1.5 and 8.1, 1H). ^{13}C NMR (δ): 18.7, 125.8, 126.5, 126.7, 126.8, 127.2, 127.3, 127.4, 128.8, 130.2, 136.0, 140.2 and 141.3. EI-MS (m/z, %): 168 (M^+, 50), 167 (27), 165 (27), 154 (13), 153 (100), 152 (36), 83 (17) and 82 (14).

(*E*)-9-(Prop-1-enyl)phenanthrene (3m).[42c,d] Yield = 69%; E/Z = 88 : 12; colourless oil. IR (Film, ν): 3057, 3018, 2924, 2851, 1597, 1493, 1450, 1433, 1242, 962, 812, 744, 735, 723 and 618 cm^{-1}. ^{1}H NMR (δ): 2.04 (dd, J = 1.7 and 6.6, 3H), 6.33 (dq, J = 6.6 and 16.1, 1H), 7.13 (d, J = 16.1, 1H), 7.37 (d, J = 8.3, 2H), 7.75 (s, 1H), 7.76 (d, J = 5.7, 1H), 7.85–7.92 (m, 2H), 8.18 (dd, J = 0.9 and 8.3, 1H) and 8.64–8.74 (m, 4H). ^{13}C NMR (δ): 18.9, 122.5, 122.7, 123.0, 124.3, 124.8, 126.9, 128.4, 128.6, 128.7, 129.3, 129.9, 130.3, 130.8, 132.0, 132.1 and 134.7. EI-MS (m/z, %): 218 (M^+, 58), 217 (24), 215 (19), 204 (17), 203 (100), 202 (49), 109 (12), 108 (34), 107 (19), 101 (36), 100 (10), 95 (32) and 94 (10).

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