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Scope and limitations of the Heck–Matsuda-coupling of phenol diazonium salts and styrenes: a protecting-group economic synthesis of phenolic stilbenes†

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4-Phenol diazonium salts undergo Pd-catalyzed Heck reactions with various styrenes to 4′-hydroxy stilbenes. In almost all cases higher yields and fewer side products were observed, compared to the analogous 4-methoxy benzene diazonium salts. In contrast, the reaction fails completely with 2- and 3-phenol diazonium salts. For these substitution patterns the methoxy-substituted derivatives are superior.

Introduction

Numerous structurally diverse phenolic and polyphenolic stilbenes and stilbenoids have been isolated from plants.[1,2] They act mostly as phytoalexins to defend the plant against pathogenic fungi or bacterial infection. However, their activity as antioxidants, estrogenic activity or antiproliferative activity against numerous cancer cell lines has stimulated studies directed at the development of, *inter alia*, cardiovascular drugs[3] or cancer therapeutics.[4] Some representative examples are listed in Fig. 1. Resveratrol (**1**) is probably the most prominent stilbene, due to its occurrence in red wine and its alleged anti-aging effect.[5] Combretastatin B (**2**) is a member of the combretastatin family of natural products, which were isolated from the South African tree *Combretum caffrum*, an important source of remedies against numerous diseases in traditional folk medicine. Several combretastatins are antineoplastic agents and act by inhibiting or retarding tubulin polymerization.[6,7] The third example, hydroxystilbamidine isethionate (**3**) is an antiprotozoal drug which has been used for the treatment of leishmania[8] and later as a fluorescent dye for staining tissues in pathology.[9]

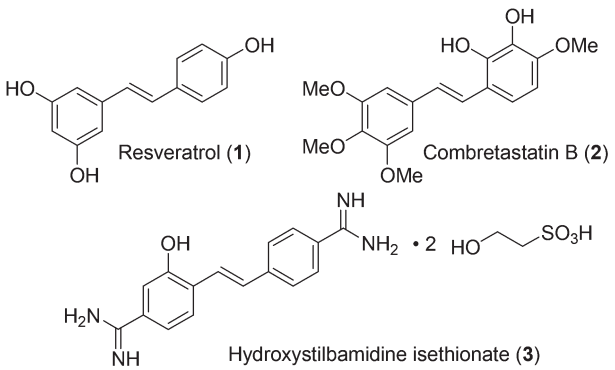

Fig. 1 Representative examples of bioactive stilbenes.

While traditional syntheses of stilbenes have mostly used eliminations or carbonyl condensation reactions,[10] an increasing number of examples for the successful application of transition metal catalyzed transformations have been reported over the past two decades,[11] such as Ru-catalyzed cross metathesis[12,13] and Pd-catalyzed Heck-[14–20] and cross coupling[14,17,19,21] reactions. Among these transformations, the Heck reaction of styrenes and aryl halides or -triflates is particularly important, but arene diazonium salts have been recognized as useful alternative arylating agents for styrenes[22–30] and olefins in general.[31–34] The Pd-catalyzed coupling of alkenes and arene diazonium salts is often referred to as the Heck–Matsuda-reaction.[31] Diazonium salts have also been used for the synthesis of stilbenes from styrenes *via* radical pathways.[35,36]

Our contributions to the field have been centered around the development of one-flask syntheses of alkoxy substituted arene diazonium tetrafluoroborates from acetanilides *via* deacetylation–diazotation sequences,[37–39] and their application in Heck–Matsuda reactions with cyclic enol ethers for the synthesis of centrolobines and related natural products.[40–42] In the course of these studies, we discovered that unprotected 4-phenol diazonium salts undergo Pd-catalyzed coupling reactions with dihydropyrans,[43] acrylates and acrylamides,[44] diarylalkynes,[45] and potassium organo-trifluoroborates[46] in remarkably high yields and efficiencies, which often exceed those observed for the analogous methoxy derivatives. In

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addition, the optimum reaction conditions for Pd-catalyzed coupling reactions using phenol diazonium salts often differ significantly from those using other arene diazonium salts.

Herein, we present a systematic comparative study of the Heck–Matsuda reaction of styrenes and phenol diazonium salts and their *O*-alkylated counterparts.

Results and discussion

Heck–Matsuda reactions of styrenes and 4-phenol *vs.* 4-methoxy benzene diazonium salts

Crucial parameters for a Heck–Matsuda coupling with arene diazonium salts are the precatalyst, the solvent, the presence or absence of a base, the stoichiometric ratio of reagents and of course the electronic nature of the coupling partners. From our own experience and from literature precedence we knew that Pd-catalyzed coupling reactions involving arene diazonium salts show only very little tolerance towards nucleophilic ligands.[47–49] Consequently, the number of useful Pd-precatalysts for these reactions is rather limited, and $Pd(OAc)_2$ is for economic reasons very often the precatalyst of choice (Table 1).

Commonly used solvents for these reactions are nitriles, in particular acetonitrile, and methanol. A few years ago, Correia *et al*. investigated the Pd-catalyzed Heck–Matsuda reaction of a di- and trimethoxy benzene diazonium salt and 4-methoxy styrene with a view to synthesis of resveratrol and its non-natural analogue DMU-212.[26] They found, in accordance with others,[50] that alcohols appear to be less suitable solvents and proposed benzonitrile and reaction temperatures of 80–90 °C as the best alternative. Some dispute exists about the role of added base in Heck–Matsuda reactions with diazonium salts. While it is commonly assumed that base-free conditions are preferable,[27] in the above cited work by Correia *et al*.[26] high yields were obtained in the presence of a base. For practical and economical reasons, it is desirable to use equimolar amounts of the coupling partners and a conveniently removable solvent. In spite of the discouraging literature reports[26,50] and considering our own positive experiences with methanol as a solvent in previous investigations,[44] we decided to start our study with this solvent, rather than nitriles. Thus, in all experiments, 2.5 mol% of $Pd(OAc)_2$, methanol, and an equimolar ratio of the appropriate styrene **4** and the 4-methoxybenzene diazonium salt **5a**[37] or 4-phenol diazonium salt **5b**[44] were used. All experiments were conducted in the presence of three equivalents of NaOAc and then repeated without added base, under otherwise identical conditions, to gather more information about the actual influence of a base.

As can be seen from the results listed in Table 1, for almost all examples higher yields were obtained with added base. While this result is in line with our previous observations for the Heck–Matsuda reactions of acrylates with 4-phenol diazonium salts, it is in marked contrast to the couplings of acrylates and 4-methoxy benzene diazonium salts. In these reactions the presence of a base was always found to be detrimental.[44] Furthermore, for all styrenes except **4a** and **4b**, the yields were better for phenol diazonium salt **5b** than for the 4-methoxy analogue **5a**. The stilbenes in entries 33 (R′=Me) and 34 (R′=H) are the natural products 3,5,4′-trimethoxy-*E*-stilbene (**6ja**)[51] and pterostilbene (**6jb**),[52] which have been isolated from a variety of plants. Compound **6ib** is a 3,5-diprotected resveratrol derivative, which was converted into resveratrol (**1**) by heating in methanol in the presence of diluted hydrochloric acid (Scheme 1).

Heck–Matsuda reactions of styrenes and 3-phenol *vs.* 3-methoxy benzene diazonium salts

In the next step, we investigated the analogous Heck–Matsuda reactions of styrenes **4a–d**, **f**, **g** with the regioisomeric 3-substituted diazonium salts **5c** (R=Me)[53] and **5d** (R=H)[54] under otherwise identical conditions. We expected a notable effect on the reactivity, because electronic stabilization of the diazonium moiety in **5c**, **d** through delocalization of the positive charge is no longer possible. Indeed, for both diazonium salts **5c**, **d** a dramatically decreased reactivity was observed. The results for the 3-phenol diazonium salt **5d** were particularly disappointing (Scheme 2). Under basic conditions, complex mixtures resulted with no identifiable major product. The desired stilbenes were observed in the NMR-spectra of the crude reaction mixtures only in trace amounts, if at all. Under base-free conditions, all experiments resulted in the formation of the same major product, 3-methoxy phenol (**7**). This illustrates that the Pd-catalyzed C–C-bond formation is obviously much slower than solvolysis of the diazonium salt **5d**.

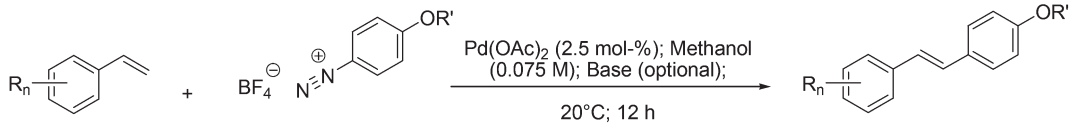
With the analogous 3-methoxy benzene diazonium salt **5c** the formation of stilbenes was observed in four cases if base-free conditions were used, although yields are mostly mediocre. In the presence of NaOAc complex mixtures with no detectable main product were formed with all styrenes, apart from **4g** bearing an electron withdrawing nitro group in the *para*-position. This alkene is also the most reactive one under base-free conditions and reacts with **5c** to the corresponding stilbene **6gc** in 87% yield (Table 2).

Heck–Matsuda reactions of styrenes and 2-phenol *vs.* 2-methoxy benzene diazonium salts

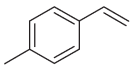
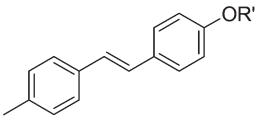
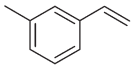
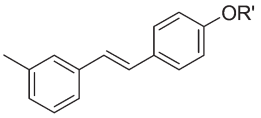
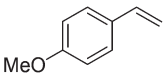
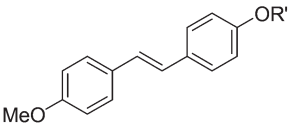
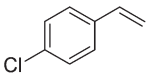
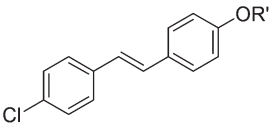
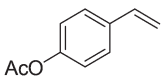
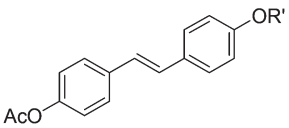
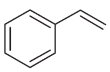
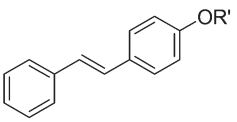
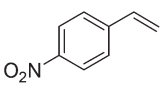
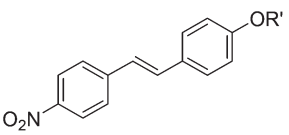
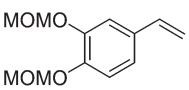
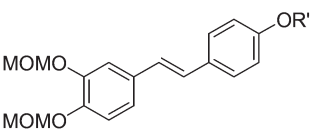
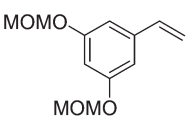
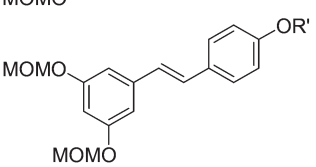
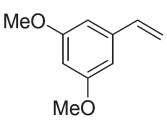
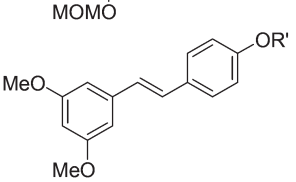
Originally, we investigated the diazotation of *ortho*-amino phenol (**8**) with $NaNO_2$ in aqueous HBF_4 for the synthesis of the 2-phenol diazonium salt required for this investigation. With a tetrafluoroborate counterion the salt did not precipitate readily in our hands and was found to be quite unstable. This is in line with observations previously published by Sefkow *et al*., who reported low yields of *ca*. 30% for this particular compound.[55] We thought that the easiest way to improve the stability might be to change the counterion, and therefore switched to PF_6^-. Adaptation of an earlier synthesis[56] led us to the isolation of **5f** as its hexafluorophosphate in gram quantities and in a useful yield of 67% (Scheme 3).

With useful quantities of a 2-phenol diazonium salt that was sufficiently stable to be isolated and handled at ambient temperature in hand, we tested the Heck–Matsuda arylation of the styrenes **4a–d**, **f**, **g** both under basic and base-free

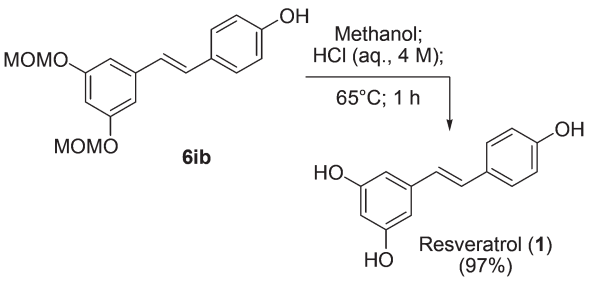
Table 1 Comparative Heck–Matsuda reactions of styrenes and 4-phenol *vs.* 4-methoxy benzene diazonium salts[a]



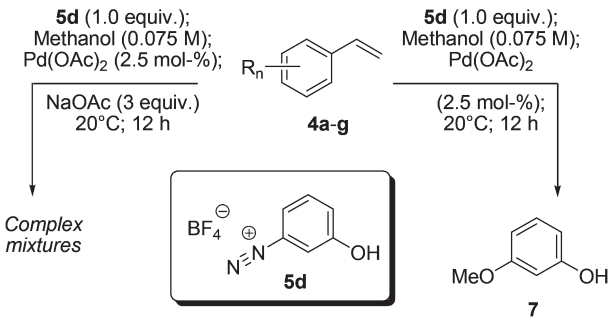
4 **5a** (R' = Me) **5b** (R' = H) **6**

Entry	Styrene	4	5	Base (equiv.)	Stilbene	R′	6	Yield[b]
1		**4a**	**5a**	NaOAc (3)		Me	**6aa**	80%
2				None				15%
3			**5b**	NaOAc (3)		H	**6ab**	72%
4				None				47%
5		**4b**	**5a**	NaOAc (3)		Me	**6ba**	89%
6				None				70%
7			**5b**	NaOAc (3)		H	**6bb**	78%
8				None				43%
9		**4c**	**5a**	NaOAc (3)		Me	**6ca**	46%
10				None				20%
11			**5b**	NaOAc (3)		H	**6cb**	83%
12				None				27%
13		**4d**	**5a**	NaOAc (3)		Me	**6da**	61%
14				None				56%
15			**5b**	NaOAc (3)		H	**6db**	98%
16				None				65%
17		**4e**	**5a**	NaOAc (3)		Me	**6ea**	38%
18				None				32%
19			**5b**	NaOAc (3)		H	**6eb**	95%
20				None				76%
21		**4f**	**5a**	NaOAc (3)		Me	**6fa**	75%
22				None				15%
23			**5b**	NaOAc (3)		H	**6fb**	>96%
24				None				45%
25		**4g**	**5a**	NaOAc (3)		Me	**6ga**	40%
26				None				64%
27			**5b**	NaOAc (3)		H	**6gb**	93%
28				None				68%
29		**4h**	**5a**	NaOAc (3)		Me	**6ha**	81%
30			**5b**	NaOAc (3)		H	**6hb**	97%
31		**4i**	**5a**	NaOAc (3)		Me	**6ia**	77%
32			**5b**	NaOAc (3)		H	**6ib**	93%
33		**4j**	**5a**	NaOAc (3)		Me	**6ja**	74%
34			**5b**	NaOAc (3)		H	**6jb**	89%

[a] Styrene and diazonium salts **5a** or **5b** were used in a 1 : 1 ratio. [b] Isolated yields of pure stilbenes **6.**

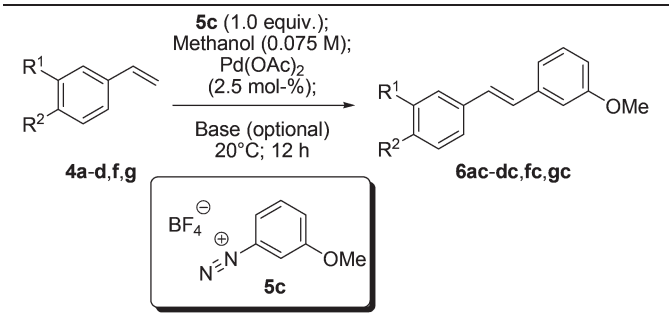


Scheme 1 Deprotection of the coupling product **6ib** to resveratrol.



Scheme 2 Attempted Heck–Matsuda reactions of **5d** and styrenes.

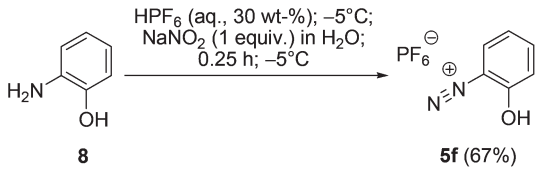
Table 2 Comparative Heck–Matsuda reactions of styrenes and 3-methoxy benzene diazonium salt **5c**



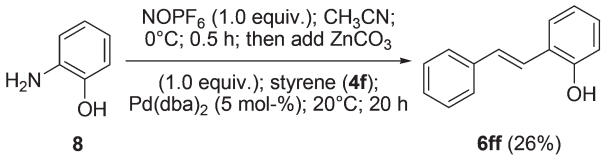
Entry	R^1	R^2	4	Base (equiv.)	6	Yield[a]
1	H	Me	**4a**	NaOAc (3)	**6ac**	—[b]
2	H	Me	**4a**	None	**6ac**	30%
3	Me	H	**4b**	NaOAc (3)	**6bc**	—[b]
4	Me	H	**4b**	None	**6bc**	<5%[c]
5	H	OMe	**4c**	NaOAc (3)	**6cc**	—[b]
6	H	OMe	**4c**	None	**6cc**	55%
7	H	Cl	**4d**	NaOAc (3)	**6dc**	—[b]
8	H	Cl	**4d**	None	**6dc**	46%
9	H	H	**4f**	NaOAc (3)	**6fc**	—[b]
10	H	H	**4f**	None	**6fc**	<5%[c]
11	H	NO_2	**4g**	NaOAc (3)	**6gc**	53%
12	H	NO_2	**4g**	None	**6gc**	87%

[a] Isolated yields of pure stilbenes **6**. [b] Complex mixture of products [c] Determined by GC-MS.

conditions as detailed above. In all cases the reactions failed completely: no coupling products could be detected and the starting styrenes **4** were recovered unchanged. This is so far surprising, as Sefkow *et al*. reported a Larock-type



Scheme 3 Synthesis of isolated **5f**.



Scheme 4 *In situ* diazotization–Heck–Matsuda arylation of styrene.

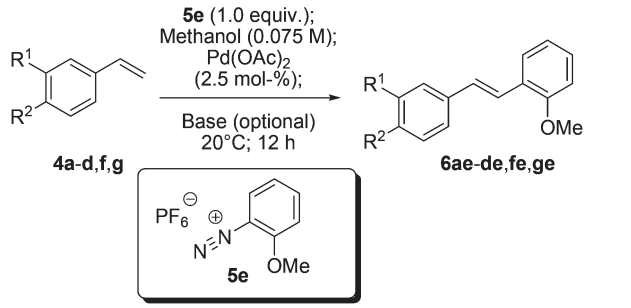
oxyarylation[57] leading to benzofurans when **5f** was reacted with anethole in the presence of $Pd_2(dba)_3$ in acetonitrile and with $ZnCO_3$ as a base.[55,58] These authors also developed a more convenient one-flask protocol, comprising an *in situ* diazotation of **8** with $NOPF_6$ and subsequent Pd-catalyzed oxyarylation of the transient diazonium salt **5f**. We investigated, for example, the possibility to adopt these *in situ* conditions for the synthesis of 2-hydroxy stilbenes. With $Pd_2(dba)_3{\cdot}CHCl_3$ [59] as a precatalyst the reaction led to a complex mixture, whereas the related precatalyst $Pd(dba)_2$ [59] catalyzed the formation of the desired stilbene **6ff**, albeit in low yield (Scheme 4).

We then investigated the Heck–Matsuda arylation of our test styrenes **4** with the 2-methoxy analogue **5e**,[60] using again the basic and base-free standard conditions. In almost all cases higher yields were obtained in the presence of the base, whereas only poor (Table 3, entries 2, 4, 6, 10) or at best mediocre yields (entry 8) were found with base-free conditions. A notable exception is again *para*-nitro styrene **4g**, which reacts with **5e** to the expected stilbene **6ge** in good yields in the presence of a base (entry 11) but in nearly quantitative yield under base-free conditions (entry 12).

From the results described so far it can be concluded that benzene diazonium salts substituted with a methoxy group in the *ortho*- or *para*-position perform significantly better in Heck–Matsuda reactions of styrenes than the *meta*-methoxy substituted analogue, which reacts only with the most reactive styrene, **4g**, in high yield. Another significant difference between *ortho*- (**5e**) and *para*- (**5a**) methoxy substituted diazonium salts, on the one hand, and the *meta*-substituted derivative **5c**, on the other, is the effect of added base. For the former two, basic conditions are advantageous, while the latter reacts with a complex mixture of products if a base is present. From the three phenol diazonium salts investigated, only the 4-phenol diazonium salt **5b** gives synthetically useful yields of coupling products **6ab–6jb**. In most cases, the yields obtained with **5b** exceed those obtained with the methoxy analogue **5a**, and again the presence of a base is in all cases beneficial.

Although we can not rationalize our results comprehensively, some reasonable interpretations can be made. The

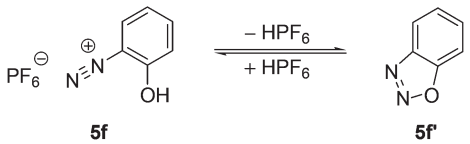
Table 3 Comparative Heck–Matsuda reactions of styrenes and 2-methoxy benzene diazonium salt **5e**



Entry	R^1	R^2	4	Base (equiv.)	6	Yield[a]
1	H	Me	**4a**	NaOAc (3)	**6ae**	79%
2	H	Me	**4a**	None	**6ae**	13%
3	Me	H	**4b**	NaOAc (3)	**6be**	82%
4	Me	H	**4b**	None	**6be**	12%
5	H	OMe	**4c**	NaOAc (3)	**6ce**	22%
6	H	OMe	**4c**	None	**6ce**	27%
7	H	Cl	**4d**	NaOAc (3)	**6de**	73%
8	H	Cl	**4d**	None	**6de**	42%
9	H	H	**4f**	NaOAc (3)	**6fe**	79%
10	H	H	**4f**	None	**6fe**	13%
11	H	NO_2	**4g**	NaOAc (3)	**6ge**	63%
12	H	NO_2	**4g**	None	**6ge**	97%

[a] Isolated yields of pure stilbenes **6**.

limited stability observed by us for the 3-methoxy benzene and 3-phenol diazonium salts **5c**, **d** is in line with a previous report by Gohier *et al.*,[53] who investigated the Lewis acid mediated ether cleavage of various methoxy substituted diazonium salts, *inter alia* **5c** to **5d**. These authors found that both **5c** and **5d** are significantly less stable than derivatives bearing an electron donating group in the 4-position. Most likely, this is also the key to understand the low yields in Heck–Matsuda reactions, because decomposition is significantly faster than the desired C–C-coupling reaction and is even further accelerated by the presence of a base. The increased stability of diazonium salts with electron donating groups in *ortho*- and *para*-position can be rationalized by the efficient delocalization of positive charge, and this might also explain why even better yields were obtained with the 4-phenol diazonium salt **5b**. These considerations can, however, not account for the complete failure of transformations involving the 2-phenol diazonium salt **5f**. We do not believe that its limited stability is the reason for the complete failure in all Heck–Matsuda reactions investigated, because we could synthesize this compound in multigram quantities and characterize it with all common spectroscopic techniques. Presumably, although we cannot provide any evidence for this hypothesis, the contrary might be the case: the literature precedence exists for the formation of benzo oxadiazole **5f′** from 2-diazo cyclohexadienone.[61] Under our conditions, **5f** might undergo partial deprotonation (in the absence of a base) or complete deprotonation in the presence of NaOAc. This would induce a cyclization to **5f′**, which might result in the deactivation of the arylating agent (Scheme 5).



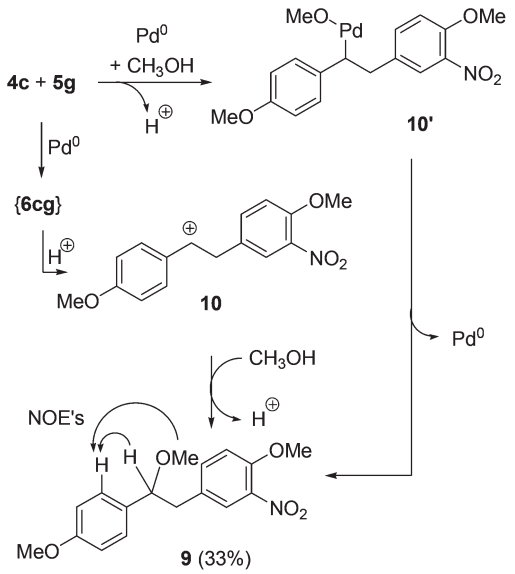
Scheme 5 2-Phenol diazonium salt *vs.* benzo oxadiazole.

Heck–Matsuda reactions of styrenes and nitro- and bromo 4-phenol diazonium salts

We then investigated the performance of nitro- and bromo-substituted 4-phenol and 4-methoxybenzene diazonium salts, because we thought that additional substituents might exert a significant influence on the reactivity of these diazonium salts in Matsuda–Heck reactions. As an additional bonus, these substituents allow for further functionalization of the aromatic core.

As for the parent diazonium salts **5a,b**, synthetically useful yields of stilbenes **6** were obtained with the 3-nitro substituted derivatives **5g,h** for almost all coupling partners **4** investigated in this study (Table 1). Notable exceptions are the reactions of **4a** and **4c**, bearing electron donating groups in the *para*-position. These styrenes react with the 4-methoxy-3-nitro benzene diazonium salt **5g** to complex mixtures of products. Only when **4c** was reacted with **5g** under base-free conditions, a defined major product could be isolated. This was identified as the methanol addition product **9**, with the methoxy group located adjacent to the 4-methoxy phenyl substituent. This assignment was established by 2D-NOESY spectra, which revealed strong interactions between the protons C*H*OCH_3 and the *ortho*-protons of the 4-methoxy phenyl substituent. The formation of methyl ether **9** might be the result of an acid catalyzed addition of methanol to the stilbene **6cg**, proceeding *via* the most stable carbenium ion **10** (Scheme 6). Such products have earlier been obtained by irradiation of stilbenes in alcohols[62] or if the photocatalytic reaction of arene diazonium salts and styrenes was conducted in methanol as a solvent.[36] In the latter case, the observation of methanol addition products points at the existence of carbenium ion intermediates analogous to **10′**, which are formed *via* oxidation of radicals. Although this mechanism is plausible and explains the regioselectivity well, it does not account for the complete absence of methanol addition products in all other examples investigated by us, where carbenium ion intermediates should be similarly stable.

Alternatively, product **9** could be formed directly from the Pd-σ-complex **10′** resulting from migratory insertion of the alkene into the Pd–aryl-σ-bond. This σ-complex **10′** would then undergo reductive elimination with C–O-bond formation (Scheme 6). This mechanism also explains the regioselectivity, because the location of the Pd is a consequence of the migratory insertion. Although precedence exists for the reductive elimination of alcohols from Pd(II)-intermediates, *e.g.* for the Pd(0)-catalyzed C–O-coupling of aryl halides and aliphatic alcohols, this step is normally assumed to be slow and require bulky ligands.[63] Other reactions involving Pd-catalyzed additions of



Scheme 6 Mechanistic rationale for the formation of side product **9**.

alcohols to alkenes rely on Pd in higher oxidation states which are not accessible under our reaction conditions.[64,65]

A singular and quite surprising lack of stereoselectivity was observed for stilbene **6bg**. Under basic as well as under base-free conditions 2 : 1 mixtures of *E*- and *Z*-diastereoisomers were obtained. The isomers could be separated and were identified by characteristic vicinal coupling constants of 12.2 Hz for *Z*-**6bg** and 16.6 Hz for *E*-**6bg**. For all Heck–Matsuda reactions with diazonium salt **5g** significantly higher yields were obtained under base-free conditions. In contrast, for the 4-phenol analogue **5h** the addition of a base is strongly preferable. Under these conditions very high yields of stilbenes were obtained with all styrenes tested in this investigation (Table 4).

A similar picture was observed for the 3-bromo-4-phenol diazonium salt **5i** and 3-bromo-4-methoxybenzene diazonium salt **5j** (Table 5). In the case of **5i** base-free conditions turned out to be superior for all styrenes except for **4f** (entries 17, 18), whereas the presence of a base is mandatory for the 4-phenol derivative **5j**. This diazonium salt reacts only with the most reactive styrene **4g** under base-free conditions to the stilbene **6gj**, albeit in a moderate yield of 40% (entry 24). The coupling fails completely for all other styrenes in the absence of a base, apart from **4d** which carries a moderately electron withdrawing chloro substituent in *para*-position and reacts with **5j** under base-free conditions in *ca.* 10% yield to the corresponding stilbene (entry 16). Under basic conditions, synthetically useful yields of stilbenes were obtained with all styrenes. Isolated yields vary between 60% for styrene **4c** (entry 11) bearing an electron donating group in the *para* position, and 93% for electron poor styrene **4g** (entry 23).

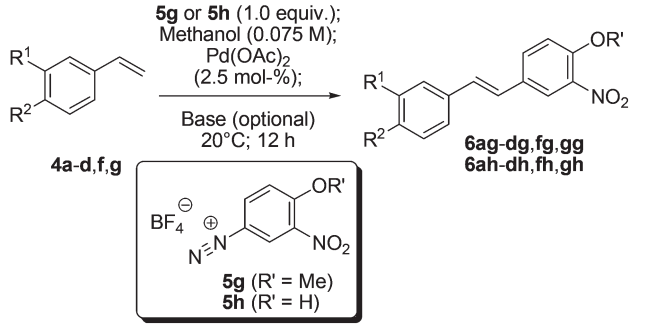
Heck–Matsuda reactions of styrenes and 3-alkenyl substituted diazonium salts

As outlined in the introduction, we have established acetanilides as useful alternative starting materials for the synthesis of arene diazonium salts, using a one-flask sequence.[37,44] In continuation of this work, we recently developed a synthesis of 2-alkenyl substituted diazonium salts such as **5k** and **5l**, which are accessible from **11a,b** in two steps, *via* oxidative Heck–Matsuda reaction and subsequent deacetylation–diazotation sequence (Scheme 7).[39]

We decided to test these two diazonium salts in Heck–Matsuda reactions with the styrenes **4** under our basic and base-free conditions. In the presence of NaOAc as a base, both **5k** and **5l** did not undergo noticeable conversion to the expected stilbenes **6**, but reacted mainly in a base-induced hydrodediazonation to the cinnamates **12a** and **12b**, respectively (Scheme 8).

Under base-free conditions, complex mixtures of products were obtained with **5l**. These contained, apart from cinnamate **12b** and trace amounts of the desired stilbenes, several unidentified products. In contrast, the methoxy substituted diazonium salt **5k** underwent Heck–Matsuda reactions with most

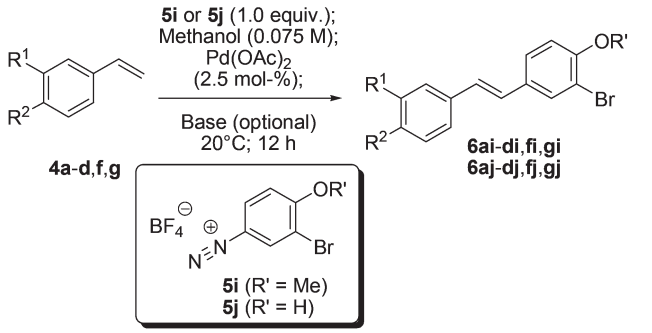
Table 4 Comparative Heck–Matsuda reactions of styrenes and 3-nitro-4-phenol *vs.* 3-nitro-4-methoxy benzene diazonium salts



Entry	R^1	R^2	4	R′	5	Base (equiv.)	6	Yield[a]
1	H	Me	**4a**	Me	**5g**	NaOAc (3)	**6ag**	—[b]
2	H	Me	**4a**	Me	**5g**	None	**6ag**	—[b]
3	H	Me	**4a**	H	**5h**	NaOAc (3)	**6ah**	99%
4	H	Me	**4a**	H	**5h**	None	**6ah**	16%
5	Me	H	**4b**	Me	**5g**	NaOAc (3)	**6bg**	46%[c]
6	Me	H	**4b**	Me	**5g**	None	**6bg**	79%[c]
7	Me	H	**4b**	H	**5h**	NaOAc (3)	**6bh**	95%
8	Me	H	**4b**	H	**5h**	None	**6bh**	34%
9	H	OMe	**4c**	Me	**5g**	NaOAc (3)	**6cg**	—[b]
10	H	OMe	**4c**	Me	**5g**	None	**6cg**	—[d]
11	H	OMe	**4c**	H	**5h**	NaOAc (3)	**6ch**	92%
12	H	OMe	**4c**	H	**5h**	None	**6ch**	35%
13	H	Cl	**4d**	Me	**5g**	NaOAc (3)	**6dg**	14%
14	H	Cl	**4d**	Me	**5g**	None	**6dg**	60%
15	H	Cl	**4d**	H	**5h**	NaOAc (3)	**6dh**	91%
16	H	Cl	**4d**	H	**5h**	None	**6dh**	86%
17	H	H	**4f**	Me	**5g**	NaOAc (3)	**6fg**	42%
18	H	H	**4f**	Me	**5g**	None	**6fg**	99%
19	H	H	**4f**	H	**5h**	NaOAc (3)	**6fh**	77%
20	H	H	**4f**	H	**5h**	None	**6fh**	37%
21	H	NO_2	**4g**	Me	**5g**	NaOAc (3)	**6gg**	9%
22	H	NO_2	**4g**	Me	**5g**	None	**6gg**	88%
23	H	NO_2	**4g**	H	**5h**	NaOAc (3)	**6gh**	98%
24	H	NO_2	**4g**	H	**5h**	None	**6gh**	85%

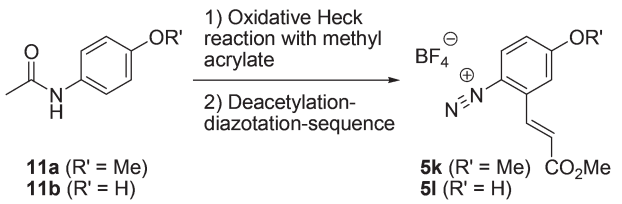
[a] Isolated yields of pure stilbenes **6**. [b] Complex mixture of products. [c] Mixture of *E*- and *Z*-**6bg** in a 2 : 1 ratio. [d] Mixture of products; **9** identified as a major side product and isolated in 33% yield.

Table 5 Comparative Heck–Matsuda reactions of styrenes and 3-bromo-4-phenol *vs.* 3-bromo-4-methoxy benzene diazonium salts

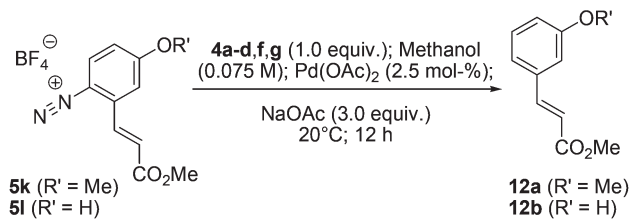


Entry	R^1	R^2	4	R′	5	Base (equiv.)	6	Yield[a]
1	H	Me	**4a**	Me	**5i**	NaOAc (3)	**6ai**	55%
2	H	Me	**4a**	Me	**5i**	None	**6ai**	80%
3	H	Me	**4a**	H	**5j**	NaOAc (3)	**6aj**	83%
4	H	Me	**4a**	H	**5j**	None	**6aj**	<5%
5	Me	H	**4b**	Me	**5i**	NaOAc (3)	**6bi**	57%
6	Me	H	**4b**	Me	**5i**	None	**6bi**	76%
7	Me	H	**4b**	H	**5j**	NaOAc (3)	**6bj**	81%
8	Me	H	**4b**	H	**5j**	None	**6bj**	<5%
9	H	OMe	**4c**	Me	**5i**	NaOAc (3)	**6ci**	48%
10	H	OMe	**4c**	Me	**5i**	None	**6ci**	79%
11	H	OMe	**4c**	H	**5j**	NaOAc (3)	**6cj**	60%
12	H	OMe	**4c**	H	**5j**	None	**6cj**	<5%
13	H	Cl	**4d**	Me	**5i**	NaOAc (3)	**6di**	35%
14	H	Cl	**4d**	Me	**5i**	None	**6di**	43%
15	H	Cl	**4d**	H	**5j**	NaOAc (3)	**6dj**	77%
16	H	Cl	**4d**	H	**5j**	None	**6dj**	9%
17	H	H	**4f**	Me	**5i**	NaOAc (3)	**6fi**	48%
18	H	H	**4f**	Me	**5i**	None	**6fi**	41%
19	H	H	**4f**	H	**5j**	NaOAc (3)	**6fj**	66%
20	H	H	**4f**	H	**5j**	None	**6fj**	<5%
21	H	NO_2	**4g**	Me	**5i**	NaOAc (3)	**6gi**	36%
22	H	NO_2	**4g**	Me	**5i**	None	**6gi**	94%
23	H	NO_2	**4g**	H	**5j**	NaOAc (3)	**6gj**	93%
24	H	NO_2	**4g**	H	**5j**	None	**6gj**	40%

[a] Isolated yields of pure stilbenes **6**.

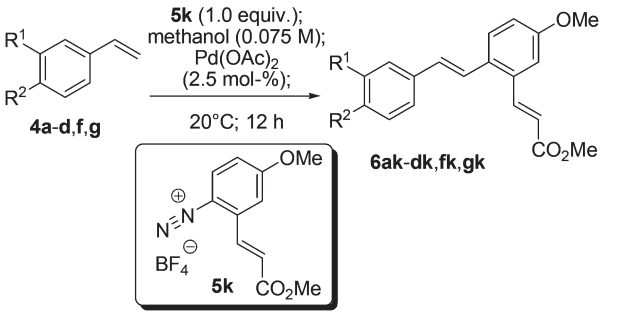


Scheme 7 Two-step synthesis of 2-alkenyl diazonium salts **5k,l**.[39]



Scheme 8 Hydrodediazonation of **5k,l** under basic conditions.

Table 6 Heck–Matsuda reactions of styrenes and 2-alkenyl diazonium salt **5k** under base-free conditions



Entry	4	R^1	R^2	6	Yield[a]
1	**4a**	H	Me	**6ak**	45%
2	**4b**	Me	H	**6bk**	70%
3	**4c**	H	OMe	**6ck**	14%
4	**4d**	H	Cl	**6dk**	75%
5	**4f**	H	H	**6fk**	86%
6	**4g**	H	NO_2	**6gk**	83%

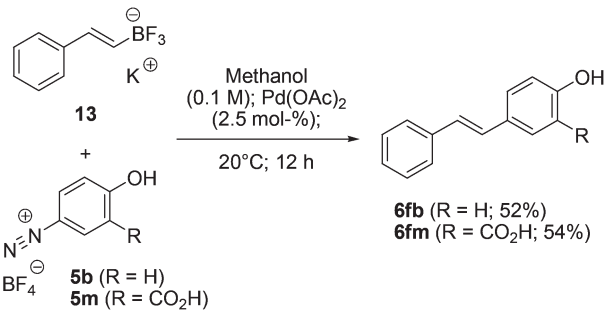
[a] Isolated yields of pure stilbenes **6**.

styrenes in acceptable or good yields in the absence of a base, with the electron rich styrene **4c** again being the least reactive coupling partner (Table 6).

Stilbenes *via* Suzuki coupling with phenol diazonium salts

Cross coupling reactions provide an alternative access to stilbenes, for example by using a Suzuki coupling of a styrenyl boron compound in combination with a diazonium salt. We[46] and others[66–72] have previously investigated Suzuki coupling reactions of arene diazonium salts, in particular for the synthesis of biaryls. In these investigations, potassium organotrifluoroborates turned out to be particularly reactive nucleophilic coupling partners, which have a remarkably low tendency towards undesired oxidative homocoupling.[73–76]

In the course of this study we tested the commercially available potassium styrenyl trifluoroborate (**13**) as a coupling reagent in a Suzuki coupling with 4-phenol diazonium salts for two examples (Scheme 9). The combination of **13** and **5b** gave **6fb** in 52% yield, which is significantly lower than the yield obtained for the same stilbene *via* Heck–Matsuda reaction of **4f**



Scheme 9 Stilbenes *via* Suzuki coupling with phenol diazonium salts.

and **5b** (compare with Table 1, entries 23 and 24). A comparable yield of 54% of **6fm** was obtained from **13** and diazonium salt **5m**. Remarkably, this coupling proceeds without any protecting groups for the phenol or the carboxylic acid.

Conclusions

In summary, we showed that numerous phenolic stilbenes are accessible from styrenes and electron rich arene diazonium salts through Heck–Matsuda coupling in methanol, using moderate amounts of $Pd(OAc)_2$ as a precatalyst. We could demonstrate that the location of the electron donating group at the aromatic core of the diazonium cation has a significant influence on the reactivity. While 3-methoxy benzene diazonium salts are least reactive and give only moderate yields of coupling products, significantly higher yields were observed for 2-methoxy- and 4-methoxy substituted derivatives. For phenol diazonium salts, however, only the *para*-phenol derivatives react to give useful yields of stilbenes. In these cases isolated yields were almost always higher than those for the *O*-alkylated counterparts. The presence or absence of a base was discovered as another crucial factor. While the addition of NaOAc as a base is beneficial for the more reactive diazonium salts, it was found to be detrimental for less reactive ones. The synthesis of stilbenes *via* Suzuki coupling of styrenyl trifluoroborates and 4-phenol diazonium salts is also in principle possible, but proceeds in lower yields and is economically disadvantageous.

Experimental

General remarks

All experiments were conducted in dry reaction vessels under an atmosphere of dry nitrogen. Solvents were purified by standard procedures. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ ($CHCl_3$ (δ = 7.24 ppm) used for calibration), in DMSO-d_6 (DMSO-d_5 (δ = 2.50 ppm) used for calibration), in acetone-d_6 (acetone-d_5 (δ = 2.05 ppm) used for calibration), or in methanol-d_4 (CHD_2OD (δ = 3.31 ppm) used for calibration). Coupling constants (J) are given in Hz. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ ($CDCl_3$ (δ = 77.0 ppm) used for calibration), in DMSO-d_6 (DMSO-d_6 (δ = 39.5 ppm) used for calibration), in acetone-d_6 (acetone-d_6 (δ = 29.9 ppm) used for calibration), or in methanol-d_4 (methanol-d_4 (δ = 49.9 ppm) used for calibration). The number of coupled protons was analyzed by APT-experiments and is denoted by a number in parentheses following the chemical shift value. IR spectra were recorded neatly on NaCl or KBr plates, or as KBr-discs. Wavenumbers (ν) are given in cm^{-1}. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70 eV.

General procedure for Heck–Matsuda reactions of styrenes under basic conditions

To a solution of the appropriate styrene **4** (0.75 mmol) in anhydrous methanol (10 mL) was added the corresponding arene diazonium salt **5** (0.75 mmol) and NaOAc (185 mg, 2.25 mmol), followed by $Pd(OAc)_2$ (4.2 mg, 2.5 mol%). The solution was stirred for 12 h at ambient temperature. The reaction was quenched by the addition of water (20 mL) and extracted with MTBE (60 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica, using hexane–MTBE (5 : 1) mixtures as the eluent, to furnish the desired stilbenes **6**.

General procedure for Heck–Matsuda reactions of styrenes under base-free conditions

To a solution of the appropriate styrene **4** (0.75 mmol) in anhydrous methanol (10 mL) was added the corresponding arene diazonium salt **5** (0.75 mmol), followed by $Pd(OAc)_2$ (4.2 mg, 2.5 mol%). The solution was stirred for 12 h at ambient temperature. Work-up of the reaction mixture and purification of the products were accomplished as stated above for the procedure under basic reaction conditions.

Analytical data for coupling products of 5a,b

(*E*)-1-Methoxy-4-(4-methylstyryl)benzene (6aa). Following the general procedures, **6aa** was obtained from **5a** (166 mg, 0.75 mmol) and **4a** (89 mg, 0.75 mmol) as a colourless solid. Yield of **6aa** using basic conditions: 135 mg (0.60 mmol, 80%). Yield of **6aa** using base free conditions: 25 mg (0.11 mmol, 15%). Mp 159–165 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.52 (d, J = 8.7, 2H), 7.45 (d, J = 8.0, 2H), 7.17 (d, J = 8.0, 2H), 7.13 (d, J = 16.5, 1H), 7.04 (d, J = 16.5, 1H), 6.94 (d, J = 8.7, 2H), 3.77 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.7 (0), 136.4 (0), 134.5 (0), 129.7 (0), 129.2 (1), 127.5 (1), 127.0 (1), 126.0 (1), 126.0 (1), 114.1 (1), 55.0 (3), 20.7 (3); MS (ESI) m/z 165 (28%), 209 (25%), 224 ([M]$^+$, 100%); HRMS (ESI) calcd for $C_{16}H_{16}O$ [M]$^+$: 224.1201, found: 224.1198.

(*E*)-4-(4-Methylstyryl)phenol (6ab). Following the general procedures, **6ab** was obtained from **5b** (156 mg, 0.75 mmol) and **4a** (89 mg, 0.75 mmol) as a colourless solid. Yield of **6ab** using basic conditions: 113 mg (0.54 mmol, 72%). Yield of **6ab** using base free conditions: 75 mg (0.35 mmol, 47%). Mp 198–205 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.60 (s, 1H), 7.49–7.38 (m, 4H), 7.15 (d, J = 8.1, 2H), 7.11 (d, J = 16.4, 1H), 7.00 (d, J = 16.4, 1H), 6.85 (d, J = 8.6, 2H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6) δ 158.1 (0), 137.5 (0), 136.1 (0), 130.2 (0), 130.1 (1), 128.6 (1), 128.4 (1), 127.0 (1), 126.4 (1), 116.4 (1), 21.2 (3); MS (ESI) m/z 165 (18%), 195 (24%), 210 ([M]$^+$, 100%); HRMS (ESI) calcd for $C_{15}H_{14}O$ [M]$^+$: 210.1045, found: 210.1063.

(*E*)-1-(4-Methoxystyryl)-3-methylbenzene (6ba). Following the general procedures, **6ba** was obtained from **5a** (166 mg, 0.75 mmol) and **4b** (89 mg, 0.75 mmol) as a colourless solid. Yield of **6ba** using basic conditions: 150 mg (0.67 mmol, 89%). Yield of **6ba** using base free conditions: 118 mg (0.52 mmol, 70%). Mp 106–109 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 7.53 (d, J = 8.7, 2H), 7.41–7.31 (m, 2H), 7.24 (d, J = 7.6, 1H), 7.18 (d, J = 16.4, 1H), 7.06 (d, J = 7.6, 1H), 7.05 (d, J = 16.4, 1H), 6.94 (d, J = 8.7, 2H), 3.81 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz,

acetone-d_6) δ 160.4 (0), 138.9 (0), 138.7 (0), 131.1 (0), 129.4 (1), 128.9 (1), 128.8 (1), 128.6 (1), 127.8 (1), 127.4 (1), 124.3 (1), 115.0 (1), 55.6 (3), 21.5 (3); MS (ESI) *m*/*z* 165 (31%), 209 (23%), 224 ([M]$^+$, 100%); HRMS (ESI) calcd for $C_{16}H_{16}O$ [M]$^+$: 224.1201, found: 224.1208.

(*E*)-4-(3-Methylstyryl)phenol (6bb). Following the general procedures, **6bb** was obtained from **5b** (156 mg, 0.75 mmol) and **4b** (89 mg, 0.75 mmol) as a colourless solid. Yield of **6bb** using basic conditions: 123 mg (0.59 mmol, 78%). Yield of **6bb** using base free conditions: 69 mg (0.32 mmol, 43%). Mp 129–134 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.62 (s, 1H), 7.44 (d, *J* = 8.6, 2H), 7.38–7.30 (m, 2H), 7.21 (dd, *J* = 7.6, 7.6, 1H), 7.15 (d, *J* = 16.4, 1H), 7.04 (d, *J* = 7.0, 1H), 7.00 (d, *J* = 16.4, 1H), 6.86 (d, *J* = 8.6, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6) δ 158.2 (0), 138.8 (0), 130.0 (0), 129.4 (1), 129.2 (1), 128.0 (0), 128.7 (1), 128.6 (1), 127.7 (1), 126.6 (1), 124.2 (1), 116.5 (1), 21.5 (3); MS (ESI) *m*/*z* 165 (20%), 195 (26%), 210 ([M]$^+$, 100%); HRMS (ESI) calcd for $C_{15}H_{14}O$ [M]$^+$: 210.1045, found: 210.1062.

(*E*)-1,2-Bis(4-methoxyphenyl)ethene (6ca). Following the general procedures, **6ca** was obtained from **5a** (166 mg, 0.75 mmol) and **4c** (101 mg, 0.75 mmol) as a colourless solid. Yield of **6ca** using basic conditions: 84 mg (0.34 mmol, 46%). Yield of **6ca** using base free conditions: 37 mg (0.15 mmol, 20%). Mp 208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8, 4H), 6.91 (s, 2H), 6.81 (d, *J* = 8.8, 4H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0 (0), 130.5 (0), 127.4 (1), 126.2 (2), 114.1 (1), 55.3 (3); MS (ESI) *m*/*z* 165 (20%), 225 (49%), 240 ([M]$^+$, 100%); HRMS (ESI) calcd for $C_{16}H_{16}O_2$ [M]$^+$: 240.1150, found: 240.1154.

(*E*)-4-(4-Methoxystyryl)phenol (6cb). Following the general procedures, **6cb** was obtained from **5b** (156 mg, 0.75 mmol) and **4c** (101 mg, 0.75 mmol) as a colourless solid. Yield of **6cb** using basic conditions: 141 mg (0.62 mmol, 83%). Yield of **6cb** using base free conditions: 46 mg (0.20 mmol, 27%). Mp 198–205 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.57 (s, 1H), 7.47 (d, *J* = 8.8, 2H), 7.40 (d, *J* = 8.7, 2H), 7.03–6.98 (m, 2H), 6.91 (d, *J* = 8.8, 2H), 6.83 (d, *J* = 8.7, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6) δ 160.0 (0), 158.0 (0), 131.6 (0), 130.3 (0), 128.4 (1), 128.2 (1), 127.2 (1), 126.2 (1), 116.4 (1), 115.0 (1), 55.6 (3). MS (ESI) *m*/*z* 137 (79%), 211 (36%), 226 ([M]$^+$, 100%); HRMS (ESI) calcd for $C_{15}H_{14}O_2$ [M]$^+$: 226.0994, found: 226.0986.

(*E*)-1-Chloro-4-(4-methoxystyryl)benzene (6da). Following the general procedures, **6da** was obtained from **5a** (166 mg, 0.75 mmol) and **4d** (104 mg, 0.75 mmol) as a colourless solid. Yield of **6da** using basic conditions: 109 mg (0.48 mmol, 61%). Yield of **6da** using base free conditions: 102 mg (0.42 mmol, 56%). Mp 180–182 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 7.57 (d, *J* = 8.5, 2H), 7.54 (d, *J* = 8.7, 2H), 7.37 (d, *J* = 8.5, 2H), 7.22 (d, *J* = 16.4, 1H), 7.08 (d, *J* = 16.4, 1H), 6.94 (d, *J* = 8.7, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6) δ 159.7 (0), 136.7 (0), 132.0 (0), 129.8 (0), 129.1 (1), 128.6 (1), 127.8 (1), 127.6 (1), 124.8 (1), 114.1 (1), 54.7 (3); MS (ESI) *m*/*z* 165 (51%), 229 (18%), 244 ([M]$^+$, 100%); HRMS (ESI) calcd for $C_{15}H_{13}OCl$ [M]$^+$: 244.0655, found: 244.0634.

(*E*)-4-(4-Chlorostyryl)phenol (6db). Following the general procedures, **6db** was obtained from **5b** (156 mg, 0.75 mmol) and **4d** (104 mg, 0.75 mmol) as a colourless solid. Yield of **6db** using basic conditions: 170 mg (0.74 mmol, 98%). Yield of **6db** using base free conditions: 113 mg (0.49 mmol, 65%). Mp 181–187 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.67 (s, 1H), 7.55 (d, *J* = 8.6, 2H), 7.45 (d, *J* = 8.6, 2H), 7.35 (d, *J* = 8.6, 2H), 7.18 (d, *J* = 16.4, 1H), 7.02 (d, *J* = 16.4, 1H), 6.86 (d, *J* = 8.6, 2H); ^{13}C NMR (75 MHz, acetone-d_6) δ 158.5 (0), 137.8 (0), 132.8 (0), 130.3 (1), 129.7 (0), 129.5 (1), 128.9 (1), 128.5 (1), 125.0 (1), 116.5 (1); MS (ESI) *m*/*z* 137 (23%), 194 (28%), 230 ([M]$^+$, 100%); HRMS (ESI) calcd for $C_{14}H_{11}OCl$ [M]$^+$: 230.0498, found: 230.0490.

(*E*)-1-Acetyloxy-4-(4-methoxystyryl)benzene (6ea). Following the general procedures, **6ea** was obtained from **5a** (166 mg, 0.75 mmol) and **4e** (121 mg, 0.75 mmol) as a colourless solid. Yield of **6ea** using basic conditions: 81 mg (0.30 mmol, 38%). Yield of **6ea** using base free conditions: 64 mg (0.24 mmol, 32%). Mp 168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7, 2H), 7.43 (d, *J* = 8.7, 2H), 7.06 (d, *J* = 8.7, 2H), 7.00 (d, *J* = 16.5, 1H), 6.93 (d, *J* = 16.5, 1H), 6.89 (d, *J* = 8.7, 2H), 3.81 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6 (0), 159.6 (0), 150.0 (0), 135.7 (0), 130.2 (0), 128.7 (1), 127.9 (1), 127.3 (1), 125.8 (1), 121.9 (1), 114.4 (1), 55.5 (3), 21.3 (3); IR (KBr-disc) ν/cm^{-1} 3444 (m), 1753 (s), 1602 (s), 1512 (s); MS (ESI) *m*/*z* 227 (100%), 239 (11%), 269 ([M + H]$^+$, 22%). HRMS (ESI) calcd for $C_{17}H_{17}O_3$ [M + H]$^+$: 269.1178, found: 269.1164; Anal. calcd for $C_{17}H_{16}O_3$: C, 76.1%; H, 6.0%. Found: C, 75.6%; H, 5.6%.

(*E*)-1-Acetyloxy-4-(4-hydroxystyryl)benzene (6eb). Following the general procedures, **6eb** was obtained from **5b** (156 mg, 0.75 mmol) and **4e** (121 mg, 0.75 mmol) as a colourless solid. Yield of **6eb** using basic conditions: 181 mg (0.72 mmol, 95%). Yield of **6eb** using base free conditions: 145 mg (0.57 mmol, 76%). Mp 206–209 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.49 (s, 1H), 7.57 (d, *J* = 8.7, 2H), 7.45 (d, *J* = 8.7, 2H), 7.14 (d, *J* = 16.5, 1H), 7.09 (d, *J* = 8.7, 2H), 7.04 (d, *J* = 16.5, 1H), 6.85 (d, *J* = 8.7, 2H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6) δ 169.7 (0), 158.3 (0), 151.0 (0), 136.5 (0), 130.0 (0), 129.6 (1), 128.8 (1), 127.8 (1), 125.6 (1), 122.9 (1), 116.5 (1), 21.1 (3); IR (KBr-disc) ν/cm^{-1} 3456 (s), 1740 (s), 1605 (s), 1513 (s); MS (ESI) *m*/*z* 99 (100%), 213 (23%), 255 ([M + H]$^+$, 11%); HRMS (ESI) calcd for $C_{16}H_{15}O_3$ [M + H]$^+$: 255.1021, found: 255.1021; Anal. calcd for $C_{16}H_{14}O_3$: C, 75.6%; H, 5.6%. Found: C, 75.7%; H, 5.3%.

(*E*)-1-Methoxy-4-styrylbenzene (6fa). Following the general procedures, **6fa** was obtained from **5a** (100 mg, 0.45 mmol) and **4f** (47 mg, 0.45 mmol) as a colourless solid. Yield of **6fa** using basic conditions: 71 mg (0.34 mmol, 75%). Yield of **6fa** using base free conditions: 14 mg (0.07 mmol, 15%). Mp 126–130 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 7.53–7.46 (m, 2H), 7.46 (d, *J* = 8.5, 2H), 7.33 (dd, *J* = 7.5, 7.5, 2H), 7.21 (tt, *J* = 7.5, 2.1 Hz, 1H), 7.06 (d, *J* = 16.3, 1H), 6.96 (d, *J* = 16.3, 1H), 6.89 (d, *J* = 8.5, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 137.9, 130.8, 128.9, 128.4, 127.9, 127.4, 126.9, 126.5, 114.4, 55.6; MS (ESI) *m*/*z* 210 ([M]$^+$, 100%), 165 (33%), 152 (21%); HRMS (ESI) calcd for $C_{15}H_{14}O$ [M]$^+$: 210.1045, found: 210.1034.

(*E*)-4-Styrylphenol (6fb). Following the general procedures, **6fb** was obtained from **5b** (100 mg, 0.48 mmol) and **4f** (50 mg, 0.48 mmol) as a colourless solid. Yield of **6fb** using basic conditions: 93 mg (0.47 mmol, >96%). Yield of **6fb** using base free conditions: 42 mg (0.21 mmol, 45%). Mp 183–184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 7.5, 2H), 7.39 (d, J = 8.5, 2H), 7.33 (dd, J = 7.5, 7.5, 2H), 7.21 (tt, J = 7.5, 2.1 Hz, 1H), 7.04 (d, J = 16.3, 1H), 6.94 (d, J = 16.3, 1H), 6.81 (d, J = 8.5, 2H), 4.83 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 137.5, 130.4, 128.6, 128.1, 127.9, 127.2, 126.8, 126.3, 115.6; MS (ESI) m/z 196 ($[M]^+$, 100%), 165 (36%), 152 (20%); HRMS (ESI) calcd for $C_{14}H_{12}O$ $[M]^+$: 196.0888, found: 196.0878.

(*E*)-1-Methoxy-4-(4-nitrostyryl)benzene (6ga). Following the general procedures, **6ga** was obtained from **5a** (100 mg, 0.45 mmol) and **4g** (67 mg, 0.45 mmol) as a colourless solid. Yield of **6ga** using basic conditions: 45 mg (0.18 mmol, 40%). Yield of **6ga** using base free conditions: 73 mg (0.29 mmol, 64%). Mp 128–131 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.21 (d, J = 8.8, 2H), 7.81 (d, J = 8.8, 2H), 7.62 (d, J = 8.8, 2H), 7.48 (d, J = 16.5, 2H), 7.25 (d, J = 16.5, 1H), 6.99 (d, J = 8.8, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.3, 146.5, 144.3, 132.9, 128.9, 128.4, 126.5, 124.1, 124.1, 114.4, 55.4; MS (EI) m/z 165 (87%), 225 (10%), 255 ($[M + H]^+$, 100%); HRMS (ESI) calcd for $C_{14}H_{12}NO_3$ $[M + H]^+$: 255.0895, found: 255.0897.

(*E*)-4-(4-Nitrostyryl)phenol (6gb). Following the general procedures, **6gb** was obtained from **5b** (100 mg, 0.48 mmol) and **4g** (72 mg, 0.48 mmol) as a colourless solid. Yield of **6gb** using basic conditions: 108 mg (0.45 mmol, 93%). Yield of **6gb** using base free conditions: 83 mg (0.34 mmol, 72%). Mp 207–209 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.98 (s, 1H), 8.01 (d, J = 8.5, 2H), 7.43 (d, J = 8.5, 2H), 7.25 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 16.3, 1H), 6.80 (d, J = 16.3, 1H), 6.71 (d, J = 8.5, 2H); ^{13}C NMR (75 MHz, acetone-d_6) δ 158.3, 146.0, 144.5, 133.4, 128.4, 127.5, 126.3, 123.9, 122.9, 115.9; MS (ESI) m/z 241 ($[M]^+$, 100%), 165 (74%), 152 (23%); HRMS (ESI) calcd for $C_{14}H_{11}O_3N$ $[M]^+$: 241.0739, found: 241.0737.

(*E*)-1,2-Bis(methoxymethoxy)-4-(4-methoxystyryl)benzene (6ha). Following the general procedures, **6ha** was obtained from **5a** (166 mg, 0.75 mmol) and **4h** (168 mg, 0.75 mmol) as a colourless solid. Yield of **6ha** using basic conditions: 200 mg (0.61 mmol, 81%). Mp 74–76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.8, 2H), 7.32 (d, J = 1.9, 1H), 7.13 (d, J = 8.4, 1H), 7.08 (dd, J = 8.4, 1.9, 1H), 6.96 (d, J = 16.2, 1H), 6.89 (d, J = 16.2, 1H), 6.89 (d, J = 8.8, 2H), 5.28 (s, 2H), 5.24 (s, 2H), 3.83 (s, 3H), 3.55 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2 (0), 147.5 (0), 146.7 (0), 132.6 (0), 130.3 (0), 127.6 (1), 127.2 (1), 126.1 (1), 120.8 (1), 116.9 (1), 114.4 (1), 114.1 (1), 95.6 (2), 95.5 (2), 56.2 (3), 56.2 (3), 55.3 (3); IR (KBr-disc) ν 2946 (w), 2834 (w), 1601 (m), 1510 (s), 1278 (m), 1248 (s), 1230 (m), 1205 (m), 1151 (s), 1123 (s), 1076 (s); MS (EI) m/z 254 (100%), 330 ($[M]^+$, 53%); HRMS (EI) calcd for $C_{19}H_{22}O_5$ $[M]^+$: 330.1467, found: 330.1455; Anal. calcd for $C_{19}H_{22}O_5$: C, 69.1; H, 6.7. Found: C, 69.0; H, 6.0.

(*E*)-4-(3,4-Bis(methoxymethoxy)styryl)phenol (6hb). Following the general procedures, **6hb** was obtained from **5b** (156 mg, 0.75 mmol) and **4h** (168 mg, 0.75 mmol) as a colourless solid. Yield of **6hb** using basic conditions: 230 mg (0.73 mmol, 97%). Mp 85–86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 8.6, 2H), 7.30 (d, J = 1.9, 1H), 7.13 (d, J = 8.4, 1H), 7.06 (dd, J = 8.4, 1.9, 1H), 6.92 (dd, J = 16.3, 1H), 6.85 (d, J = 16.3, 1H), 6.78 (d, J = 8.6, 2H), 5.63 (s, 1H), 5.29 (s, 2H), 5.25 (s, 2H), 3.56 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2 (0), 147.4 (0), 146.5 (0), 132.7 (0), 130.2 (0), 127.7 (1), 127.2 (1), 125.9 (1), 120.8 (1), 116.9 (1), 115.6 (1), 114.3 (1), 95.5 (2), 95.4 (2), 56.2 (3), 56.2 (3); IR (KBr-disc) ν 3386 (m), 2955 (w), 2827 (w), 1608 (m), 1514 (s), 1441 (m), 1265 (s), 1200 (m), 1152 (s), 1126 (m), 1074 (s); MS (ESI) m/z 339 ($[M + Na]^+$, 100%); HRMS (ESI) calcd for $C_{18}H_{20}O_5Na$ $[M + Na]^+$: 339.1208, found: 339.1212; Anal. calcd for $C_{18}H_{20}O_5$: C, 68.3; H, 6.4. Found: C, 67.6; H, 6.3.

(*E*)-1,3-Bis(methoxymethoxy)-5-(4-methoxystyryl)-benzene (6ia). Following the general procedures, **6ia** was obtained from **5a** (166 mg, 0.75 mmol) and **4i** (168 mg, 0.75 mmol) as a colourless solid. Yield of **6ia** using basic conditions: 190 mg (0.58 mmol, 77%). Mp 84–86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 8.8, 2H), 7.07 (d, J = 16.2, 1H), 6.92 (d, J = 8.8, 2H), 6.92 (d, J = 16.2, 1H), 6.88 (d, J = 2.0, 2H), 6.66 (t, J = 2.0, 1H), 5.22 (s, 4H), 3.85 (s, 3H), 3.53 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4 (0), 158.5 (0), 139.9 (0), 129.9 (0), 128.9 (1), 127.8 (1), 126.3 (1), 114.1 (1), 107.6 (1), 104.0 (1), 94.5 (2), 56.0 (3), 55.3 (3); IR (KBr-disc) ν 2953 (w), 2834 (w), 1588 (m), 1510 (m), 1439 (w), 1295 (w), 1250 (m), 1140 (s), 1080 (m), 1022 (s); MS (EI) m/z 299 (96%), 331 ($[M + H]^+$, 100%); HRMS (ESI) calcd for $C_{19}H_{23}O_5$ $[M + H]^+$: 331.1545, found: 331.1548; Anal. calcd for $C_{19}H_{22}O_5$: C, 69.1; H, 6.7. Found: C, 68.9; H, 6.5.

(*E*)-4-(3,5-Bis(methoxymethoxy)styryl)phenol (6ib). Following the general procedures, **6ib** was obtained from **5b** (156 mg, 0.75 mmol) and **4i** (168 mg, 0.75 mmol) as a colourless oil. Yield of **6ib** using basic conditions: 220 mg (0.70 mmol, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 8.6, 2H), 7.00 (d, J = 16.2, 1H), 6.85 (d, J = 2.2, 2H), 6.84 (d, J = 16.2, 1H), 6.80 (d, J = 8.6, 2H), 6.65 (t, J = 2.2, 1H), 6.21 (s, 1H), 5.21 (s, 4H), 3.52 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3 (0), 155.7 (0), 140.0 (0), 129.7 (0), 129.0 (1), 128.0 (1), 126.0 (1), 115.6 (1), 107.7 (1), 104.0 (1), 94.4 (2), 56.0 (3); IR (neat) ν 3384 (m), 2954 (w), 2828 (w), 1586 (s), 1513 (s), 1437 (m), 1295 (m), 1276 (m), 1214 (m), 1138 (s), 1074 (s); MS (EI) m/z 137 (100%), 316 ($[M]^+$, 53%); HRMS (EI) calcd for $C_{18}H_{20}O_5$ $[M]^+$: 316.1311, found: 316.1305; Anal. calcd for $C_{18}H_{20}O_5$: C, 68.3; H, 6.4. Found: C, 68.3; H, 6.3.

Resveratroltrimethylether (6ja). Following the general procedures, **6ja** was obtained from **5a** (100 mg, 0.48 mmol) and **4j** (79 mg, 0.48 mmol) as a colourless solid. Yield of **6ja** using basic conditions: 89 mg (0.33 mmol, 74%). Mp 55–58 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.7, 2H), 7.03 (d, J = 16.3, 1H), 6.89 (d, J = 16.3, 1H), 6.88 (d, J = 8.7, 2H), 6.64 (d, J = 2.2, 2H), 6.36 (t, J = 2.2, 1H), 3.83 (s, 6H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 159.6, 139.9, 130.2, 128.9, 128.0, 126.8, 114.4, 104.6, 99.9, 55.6, 55.5; MS (EI) m/z 270 ($[M]^+$, 100%), 239 (18%), 152 (15%); HRMS (EI) calcd for $C_{17}H_{18}O_3$ $[M]^+$: 270.1256, found: 270.1266.

Pterostilbene (6jb). Following the general procedures, **6jb** was obtained from **5b** (100 mg, 0.48 mmol) and **4j** (79 mg, 0.48 mmol) as a colourless oil. Yield of **6jb** using basic conditions: 110 mg (0.43 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 8.5, 2H), 7.01 (d, J = 16.3, 1H), 6.87 (d, J = 16.3, 1H), 6.82 (d, J = 8.5, 2H), 6.63 (d, J = 2.2, 2H), 6.36 (t, J = 2.2, 1H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 155.8, 139.7, 129.8, 128.9, 127.9, 126.4, 115.7, 104.4, 99.6, 55.4; MS (EI) m/z 256 ([M]$^+$, 100%), 181 (24%), 115 (22%); HRMS (EI) calcd for $C_{16}H_{16}O_3$ [M]$^+$: 256.1099, found: 256.1092.

Synthesis of resveratrol (1) from 6ib

To a solution of **6ib** (114 mg, 0.36 mmol) in MeOH (5 mL) was added aqueous HCl (4 M; 230 μL). The solution was heated for 1 h and stirred at ambient temperature for 2 h. The reaction was diluted with DCM (10 mL) and washed with saturated aqueous $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with DCM (50 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica using hexane–MTBE (1 : 1) mixtures as an eluent to furnish **1** (80 mg, 0.35 mmol, 97%) as a colourless solid. ^{1}H NMR (300 MHz, methanol-d_4) δ 7.35 (d, J = 8.6, 2H), 6.96 (d, J = 16.3, 1H), 6.79 (d, J = 16.3, 1H), 6.77 (d, J = 8.6, 2H), 6.46 (d, J = 2.2, 2H), 6.17 (t, J = 2.2, 1H); ^{13}C NMR (75 MHz, methanol-d_4) δ 159.7 (0), 158.4 (0), 141.5 (0), 130.6 (0), 129.5 (1), 128.9 (1), 127.1 (1), 116.6 (1), 105.9 (1), 102.8 (1); MS (ESI) m/z 229 ([M + H]$^+$, 100%); HRMS (ESI) calcd for $C_{14}H_{13}O_3$ [M + H]$^+$: 229.0865, found: 229.0850.

Analytical data for coupling products of 5c

(*E*)-1-Methoxy-3-(4-methylstyryl)benzene (6ac). Following the general procedure, **6ac** was obtained from **5c** (100 mg, 0.45 mmol) and **4a** (53 mg, 0.45 mmol) as a colourless solid. Yield of **6ac** using basic conditions: 30 mg (0.13 mmol, 30%). Mp 70 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0, 2H), 7.26 (dd, J = 8.0, 8.0, 1H), 7.16 (d, J = 8.0, 2H), 7.08 (d, J = 7.8 Hz, 1H), 7.06–6.97 (m, 3H), 6.80 (ddd, J = 8.0, 2.5, 0.8, 1H), 3.84 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 138.9, 137.6, 134.5, 129.6, 129.4, 128.9, 127.6, 126.5, 119.1, 113.1, 111.6, 55.3, 21.3; MS (ESI) m/z 224 ([M]$^+$, 34%), 178 (20%), 165 (37%), 105 (100%); HRMS (ESI) calcd for $C_{16}H_{16}O$ [M]$^+$: 224.1213, found: 224.1201.

(*E*)-1-Methoxy-3-(4-methoxystyryl)benzene (6cc). Following the general procedures, **6cc** was obtained from **5c** (100 mg, 0.45 mmol) and **4c** (60 mg, 0.45 mmol) as a colourless solid. Yield of **6cc** using basic conditions: 60 mg (0.25 mmol, 55%). Mp 108–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 8.7, 2H), 7.28 (dd, J = 7.9, 7.9, 1H), 7.12 (d, J = 7.9, 1H), 7.09 (d, J = 16.3, 1H), 7.05 (m, 1H), 7.03 (d, J = 16.3, 1H), 6.93 (d, J = 8.7, 2H), 6.78 (ddd, J = 7.9, 1.7, 0.7, 1H), 3.82 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 159.4, 139.1, 130.1, 129.6, 128.5, 127.8, 126.5, 119.0, 114.1, 112.9, 111.5, 55.3, 55.2; IR (KBr-disc) ν 1520 (m), 1510 (m), 1281 (m), 1246 (s), 687 (w); MS (EI) m/z 153 (18%), 165 (28%), 240 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{16}H_{16}O_2$ [M]$^+$: 240.1150, found: 240.1160; Anal. calcd for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 79.5; H, 6.7.

(*E*)-1-Methoxy-3-(4-chlorostyryl)benzene (6dc). Following the general procedures, **6dc** was obtained from **5c** (100 mg, 0.45 mmol) and **4d** (62 mg, 0.45 mmol) as a colourless solid. Yield of **6dc** using basic conditions: 50 mg (0.20 mmol, 46%). Mp 67–69 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.6, 2H), 7.32 (d, J = 8.6, 2H), 7.26 (d, J = 8.0, 1H), 7.09 (dt, J = 8.0, 0.9, 1H), 7.06–7.03 (m, 3H), 6.78 (ddd, J = 8.0, 2.5, 0.8, 1H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 138.5, 135.8, 133.2, 129.7, 129.3, 127.7, 127.7, 119.3, 113.5, 111.9, 55.3; IR (KBr-disc) ν 1719 (w), 1491 (s), 1270 (s), 1154 (m), 962 (m); MS (EI) m/z 165 (95%), 194 (46%), 244 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{13}OCl$ [M]$^+$: 244.0642, found: 244.0646; Anal. calcd for $C_{15}H_{13}OCl$: C, 73.6; H, 5.4. Found: C, 73.6; H, 5.2.

(*E*)-1-Methoxy-3-(4-nitrostyryl)benzene (6gc). Following the general procedures, **6gc** was obtained from **5c** (166 mg, 0.75 mmol) and **4g** (112 mg, 0.75 mmol) as a colourless solid. Yield of **6gc** using basic conditions: 101 mg (0.40 mmol, 53%). Yield of **6gc** using base free conditions: 166 mg (0.65 mmol, 87%). Mp 85–87 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 8.8, 2H), 7.62 (d, J = 8.8, 2H), 7.32 (dd, J = 7.9, 7.9, 1H), 7.24 (d, J = 16.3, 1H), 7.14 (d, J = 7.9, 1H), 7.13 (d, J = 16.3, 1H), 7.08 (m, 1H), 6.89 (ddd, J = 7.9, 2.5, 0.7, 1H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2 (0), 147.1 (0), 143.9 (0), 137.8 (0), 133.4 (1), 130.0 (1), 127.0 (1), 126.7 (1), 124.2 (1), 119.8 (1), 114.6 (1), 112.5 (1), 55.4 (3); IR (KBr-disc) ν 2959 (m), 1721 (m), 1593 (s), 1335 (s), 1152 (m); MS (EI): m/z 165 (54%), 208 (17%), 255 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{13}O_3N$ [M]$^+$: 255.0895, found: 255.0899; Anal. calcd for $C_{15}H_{13}O_3N$: C, 70.6; H, 5.1. Found: C, 70.8; H, 5.1.

Synthesis of (*E*)-2-styrylphenol (6ff) *via in situ* diazotation

A solution of **8** (109 mg, 1.00 mmol) in acetonitrile (8.0 mL) was cooled to 0 °C. $NOPF_6$ (175 mg, 1.00 mmol) was added, followed after 0.5 h by $ZnCO_3$ (250 mg, 2.00 mmol), $Pd(dba)_2$ (29 mg, 5 mol%) and styrene (137 μL, 1.2 mmol). The mixture was stirred at ambient temperature for 20 h. After this time, an aqueous solution of $NaHCO_3$ (10%, 25 mL) was added. The aqueous layer was extracted with ethyl acetate (60 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica, using hexane–MTBE (5 : 1) as the eluent, to afford **6ff** (50 mg, 0.26 mmol, 26%) as a colourless solid. Mp 138–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6, 1H), 7.52 (d, J = 7.3, 2H), 7.38 (d, J = 16.4, 1H), 7.34 (dd, J = 7.3, 7.3, 2H), 7.25 (t, J = 7.3, 1H), 7.14 (ddd, J = 7.6, 7.6, 1.7, 1H), 7.11 (d, J = 16.4, 1H), 6.94 (dd, J = 7.6, 7.6, 1H), 6.80 (dd, J = 7.6, 1.0, 1H), 5.18 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 137.9, 130.4, 128.9, 128.9, 127.8, 127.5, 126.8, 124.9, 123.3, 121.3, 116.2; MS (EI) m/z 152 (22%), 165 (39%), 196 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{14}H_{12}O$ [M]$^+$: 196.0888, found: 196.0881.

Analytical data for coupling products of 5e

(*E*)-1-Methoxy-2-(4-methylstyryl)benzene (6ae). Following the general procedures, **6ae** was obtained from **5e** (210 mg,

0.75 mmol) and **4a** (89 mg, 0.75 mmol) as a colourless solid. Yield of **6ae** using basic conditions: 131 mg (0.59 mmol, 79%). Yield of **6ae** using base free conditions: 23 mg (0.10 mmol, 13%). Mp 78–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.7, 1.2, 1H), 7.52–7.45 (m, 3H), 7.28 (dd, J = 8.0, 8.0, 1H), 7.20 (d, J = 7.9, 2H), 7.13 (d, J = 16.5, 1H), 7.01 (dd, J = 8.0, 8.0, 1H), 6.94 (d, J = 8.0, 1H), 3.92 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1 (0), 137.3 (0), 135.4 (0), 129.4 (1), 129.2 (1), 128.5 (1), 126.9 (0), 126.6 (1), 126.5 (1), 122.7 (1), 120.9 (1), 111.2 (1), 55.7 (3), 21.3 (3); MS (EI) m/z 118 (22%), 165 (42%), 224 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{16}H_{16}O$ [M]$^+$: 224.1201, found: 224.1213; Anal. calcd for $C_{16}H_{16}O$: C, 85.7; H, 7.2. Found: C, 85.5; H, 7.2.

(*E*)-1-Methoxy-2-(3-methylstyryl)benzene (6be). Following the general procedures, **6be** was obtained from **5e** (210 mg, 0.75 mmol) and **4b** (89 mg, 0.75 mmol) as a colourless oil. Yield of **6be** using basic conditions: 136 mg (0.61 mmol, 82%). Yield of **6be** using base free conditions: 20 mg (0.09 mmol, 12%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.8, 1.6, 1H), 7.50 (d, J = 16.5, 1H), 7.40–7.33 (m, 2H), 7.30–7.23 (m, 2H), 7.11 (d, J = 16.5, 1H), 7.03 (d, J = 7.3, 1H), 6.98 (dd, J = 7.6, 7.6, 1H), 6.92 (d, J = 7.8, 1H), 3.91 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1 (0), 138.2 (0), 138.1 (0), 129.4 (1), 128.7 (1), 128.6 (1), 128.3 (1), 127.4 (1), 126.8 (0), 126.6 (1), 123.9 (1), 123.5 (1), 120.9 (1), 111.2 (1), 55.7 (3), 21.5 (3); MS (EI) m/z 118 (12%), 165 (34%), 224 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{16}H_{16}O$ [M]$^+$: 224.1201, found: 224.1214; Anal. calcd for $C_{16}H_{16}O$: C, 85.7; H, 7.2. Found: C, 85.3; H, 7.2.

(*E*)-1-Methoxy-2-(4-methoxystyryl)benzene (6ce). Following the general procedures, **6ce** was obtained from **5e** (210 mg, 0.75 mmol) and **4c** (101 mg, 0.75 mmol) as a colourless solid. Yield of **6ce** using basic conditions: 42 mg (0.17 mmol, 22%). Yield of **6ce** using base free conditions: 51 mg (0.20 mmol, 27%). Mp 93–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.7, 1.4, 1H), 7.49 (d, J = 8.7, 2H), 7.37 (d, J = 16.5, 1H), 7.23 (dd, J = 7.7, 1.7, 1H), 7.08 (d, J = 16.5, 1H), 6.98 (dd, J = 7.7, 7.7, 1H), 6.93–6.88 (m, 3H), 3.90 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3 (0), 156.9 (0), 131.0 (0), 128.8 (1), 128.3 (1), 127.9 (1), 127.0 (0), 126.3 (1), 121.6 (1), 120.9 (1), 114.2 (1), 111.1 (1), 55.7 (3), 55.4 (3); MS (EI) m/z 134 (25%), 165 (20%), 240 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{16}H_{16}O_2$ [M]$^+$: 240.1150, found: 240.1140; Anal. calcd for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 79.6; H, 6.5.

(*E*)-1-(4-Chlorostyryl)-2-methoxybenzene (6de). Following the general procedures, **6de** was obtained from **5e** (210 mg, 0.75 mmol) and **4d** (104 mg, 0.75 mmol) as a colourless solid. Yield of **6de** using basic conditions: 133 mg (0.55 mmol, 73%). Yield of **6de** using base free conditions: 77 mg (0.31 mmol, 42%). Mp 86–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.6, 1.6, 1H), 7.48 (d, J = 16.5, 1H), 7.47 (d, J = 8.5, 2H), 7.33 (d, J = 8.5, 2H), 7.27 (dd, J = 7.6, 1.6, 1H), 7.07 (d, J = 16.5, 1H), 6.98 (dd, J = 7.6, 7.6, 1H), 6.92 (dd, J = 7.6, 0.7, 1H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0 (0), 136.6 (0), 132.9 (0), 129.0 (1), 128.8 (1), 127.8 (1), 127.8 (1), 126.5 (1), 126.1 (0), 124.2 (1), 120.8 (1), 111.0 (1), 55.6 (3); MS (EI) m/z 138 (22%), 165 (58%), 244 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{13}OCl$ [M]$^+$: 244.0655, found: 244.0648; Anal. calcd for $C_{15}H_{13}OCl$: C, 73.6; H, 5.3. Found: C, 73.3; H, 5.3.

(*E*)-1-Methoxy-2-styrylbenzene (6fe). Following the general procedures, **6fe** was obtained from **5e** (210 mg, 0.75 mmol) and **4f** (78 mg, 0.75 mmol) as a colourless solid. Yield of **6fe** using basic conditions: 125 mg (0.59 mmol, 79%). Yield of **6fe** using base free conditions: 20 mg (0.10 mmol, 13%). Mp 57–61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.5, 1.6, 1H), 7.56 (d, J = 7.5, 2H), 7.53 (d, J = 16.5, 1H), 7.37 (dd, J = 7.5, 7.5, 2H), 7.30–7.23 (m, 2H), 7.14 (d, J = 16.5, 1H), 7.00 (dd, J = 7.5, 7.5, 1H), 6.92 (d, J = 7.5, 1H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0 (0), 138.1 (0), 129.2 (1), 128.7 (1), 128.7 (1), 127.4 (1), 126.6 (0), 126.5 (1), 126.5 (1), 123.6 (1), 120.8 (1), 111.0 (1), 55.6 (3); MS (EI) m/z 152 (19%), 165 (36%), 210 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{14}O$ [M]$^+$: 210.1045, found: 210.1043.

(*E*)-1-Methoxy-2-(4-nitrostyryl)benzene (6ge). Following the general procedures, **6ge** was obtained from **5e** (210 mg, 0.75 mmol) and **4g** (112 mg, 0.75 mmol) as a colourless solid. Yield of **6ge** using basic conditions: 121 mg (0.47 mmol, 63%). Yield of **6ge** using base free conditions: 185 mg (0.72 mmol, 97%). Mp 123–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8, 2H), 7.65 (d, J = 16.5, 1H), 7.64 (d, J = 8.8, 2H), 7.60 (dd, J = 8.0, 1.5, 1H), 7.32 (ddd, J = 8.4, 8.4, 1.6, 1H), 7.16 (d, J = 16.5, 1H), 7.00 (dd, J = 8.0, 8.0, 1H), 6.94 (d, J = 8.4, 1H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5 (0), 146.7 (0), 144.7 (0), 130.1 (1), 128.5 (1), 127.1 (1), 126.9 (1), 126.8 (1), 125.4 (0), 124.1 (1), 121.0 (1), 111.3 (1), 55.7 (3); MS (EI) m/z 119 (25%), 165 (70%), 255 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{13}O_3N$ [M]$^+$: 255.0895, found: 255.0881; Anal. calcd for $C_{15}H_{13}O_3N$: C, 70.6; H, 5.1; N, 5.5. Found: C, 70.2; H, 5.0; N, 5.6.

Analytical data for coupling products of 5g,h

(*E*)-4-(4-Methylstyryl)-2-nitrophenol (6ah). Following the general procedures, **6ah** was obtained from **5h** (190 mg, 0.75 mmol) and **4a** (89 mg, 0.75 mmol) as a yellow solid. Yield of **6ah** using basic conditions: 190 mg (0.75 mmol, 99%). Yield of **6ah** using base free conditions: 32 mg (0.12 mmol, 16%). Mp 119–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.58 (s, 1H), 8.15 (d, J = 2.0, 1H), 7.74 (dd, J = 8.8, 2.0, 1H), 7.39 (d, J = 8.0, 2H), 7.18 (d, J = 8.0, 2H), 7.14 (d, J = 8.8, 1H), 7.03 (d, J = 16.3, 1H), 6.95 (d, J = 16.3, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3 (0), 138.2 (0), 135.1 (1), 133.8 (0), 133.8 (0), 130.7 (0), 129.8 (1), 129.6 (1), 126.6 (1), 124.7 (1), 122.2 (1), 120.3 (1), 21.3 (3); MS (EI) m/z 115 (20%), 165 (75%), 255 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{13}O_3N$ [M]$^+$: 255.0895, found: 255.0887; IR (KBr-disc) ν 3211 (m), 1625 (m), 1532 (s), 1315 (s), 1177 (m); Anal. calcd for $C_{15}H_{13}O_3N$: C, 70.6; H, 5.1; N, 5.5. Found: C, 70.5; H, 5.1; N, 5.6.

(*E*,*Z*)-1-Methoxy-4-(3-methylstyryl)-2-nitrobenzene (*E*-6bg and *Z*-6bg). Following the general procedures, (*E*, *Z*)-**6bg** were obtained from **5g** (200 mg, 0.75 mmol) and **4b** (89 mg, 0.75 mmol) as yellow solids in an *E* : *Z*-ratio of 2 : 1. Combined yield of (*E*,*Z*)-**6bg** using basic conditions: 94 mg (0.35 mmol, 46%). Yield of (*E*,*Z*)-**6bg** using base free conditions: 124 mg (0.52 mmol, 79%). NMR-data for (*E*)-**6bg**: ^{1}H NMR (300 MHz,

$CDCl_3$) δ 7.99 (d, J = 2.3, 1H), 7.64 (dd, J = 8.7, 2.3, 1H), 7.35–7.21 (m, 3H), 7.11 (d, J = 7.1, 1H), 7.07 (d, J = 8.8, 1H), 7.03 (d, J = 16.6, 1H), 6.98 (d, J = 16.6, 1H), 3.97 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2 (0), 146.0 (0), 138.4 (0), 136.7 (0), 131.8 (1), 130.7 (0), 129.9 (1), 129.0 (1), 128.8 (1), 127.4 (1), 125.6 (1), 123.9 (1), 123.2 (1), 114.0 (1), 56.8 (3), 21.5 (3). NMR-data for (*Z*)-**6bg**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 2.1, 1H), 7.39 (dd, J = 8.7, 2.2, 1H), 7.15 (dd, J = 7.6, 7.6, 1H), 7.09–6.98 (m, 3H), 6.90 (d, J = 8.7, 1H), 6.64 (d, J = 12.1, 1H), 6.46 (d, J = 12.1, 1H), 3.92 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8 (0), 138.3 (0), 136.5 (0), 134.5 (1), 131.7 (1), 130.0 (0), 129.4 (1), 128.5 (1), 128.4 (1), 127.1 (1), 125.9 (1), 125.7 (1), 114.8 (0), 113.3 (1), 56.6 (3), 21.4 (3). MS (EI) m/z 165 (32%), 178 (65%), 269 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{16}H_{15}O_3N$ [M]$^+$: 269.1052, found: 269.1049; IR ν 1617 (m), 1529 (s), 1320 (s), 1277 (m), 962 (w); Anal. calcd for $C_{16}H_{15}O_3N$: C, 71.4; H, 5.6; N, 5.2. Found: C, 71.4; H, 5.6; N, 5.5.

(*E*)-4-(3-Methylstyryl)-2-nitrophenol (6bh). Following the general procedures, **6bh** was obtained from **5h** (190 mg, 0.75 mmol) and **4b** (89 mg, 0.75 mmol) as a red solid. Yield of **6bh** using basic conditions: 181 mg (0.71 mmol, 95%). Yield of **6bh** using base free conditions: 66 mg (0.25 mmol, 34%). Mp 131–132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.19 (d, J = 2.1, 1H), 7.78 (dd, J = 8.8, 2.1, 1H), 7.38–7.24 (m, 3H), 7.18 (d, J = 8.8, 1H), 7.12 (d, J = 7.1, 1H), 7.07 (d, J = 16.5, 1H), 7.01 (d, J = 16.6, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4 (0), 138.5 (0), 136.6 (0), 135.1 (1), 133.8 (0), 130.6 (0), 130.0 (1), 129.1 (1), 128.8 (1), 127.3 (1), 125.5 (1), 123.9 (1), 122.4 (1), 120.4 (1), 21.5 (3); MS (EI) m/z 115 (25%), 165 (100%), 255 ([M]$^+$, 93%); HRMS (EI) calcd for $C_{15}H_{13}O_3N$ [M]$^+$: 255.0895, found: 255.0887; IR (KBr-disc) ν 3199 (m), 1626 (m), 1526 (s), 1323 (m), 1176 (s); Anal. calcd for $C_{15}H_{13}O_3N$: C, 70.6; H, 5.1; N, 5.5. Found: C, 70.4; H, 5.2; N, 5.6.

1-Methoxy-4-(2-methoxy-2-(4-methoxyphenyl)-ethyl)-2-nitrobenzene (9). Following the general procedure using base-free conditions, the methanol adduct **9** rather than the expected product **6cg** was obtained from **5g** (200 mg, 0.75 mmol) and **4c** (101 mg, 0.75 mmol) as a colourless solid. Yield of **6cg** using base free conditions: 78 mg (0.24 mmol, 33%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 2.1, 1H), 7.22 (dd, J = 8.6, 2.2, 1H), 7.12 (d, J = 8.6, 2H), 6.93 (d, J = 8.6, 1H), 6.86 (d, J = 8.7, 2H), 4.23 (dd, J = 7.4, 5.7, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 3.15 (s, 3H), 3.04 (dd, J = 13.9, 7.6, 1H), 2.85 (dd, J = 13.9, 5.6, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4 (0), 151.5 (0), 139.3 (0), 135.5 (1), 132.9 (0), 131.2 (0), 127.9 (1), 126.4 (1), 114.0 (1), 113.2 (1), 84.0 (1), 56.6 (3), 56.6 (3), 55.3 (3), 43.3 (2); MS (EI) m/z 150 (100%), 134 (15%), 90 (5%); HRMS (EI) calcd for $C_{17}H_{19}O_5N$ [M]$^+$: 317.1258, found: 317.1259.

(*E*)-4-(4-Methoxystyryl)-2-nitrophenol (6ch). Following the general procedures, **6ch** was obtained from **5h** (190 mg, 0.75 mmol) and **4c** (101 mg, 0.75 mmol) as a yellow solid. Yield of **6ch** using basic conditions: 188 mg (0.69 mmol, 92%). Yield of **6ch** using base free conditions: 71 mg (0.26 mmol, 35%). Mp 119–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.57 (s, 1H), 8.15 (d, J = 2.0, 1H), 7.74 (dd, J = 8.8, 2.1, 1H), 7.44 (d, J = 8.7, 2H), 7.14 (d, J = 8.7, 1H), 7.02 (d, J = 16.3, 1H), 6.91 (d, J = 16.3, 2H), 6.89 (d, J = 8.7, 1H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8 (0), 154.2 (0), 135.0 (1), 133.8 (0), 130.9 (0), 129.5 (1), 127.9 (1), 123.6 (1), 122.0 (1), 120.3 (1), 114.4 (1), 55.4 (3), one signal was not observed due to low intensity; MS (EI) m/z 152 (20%), 181 (10%), 271 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{13}O_4N$ [M]$^+$: 271.0845, found: 271.0845; IR (KBr-disc) ν 3253 (w), 1623 (m), 1533 (s), 1249 (s), 1175 (s); Anal. calcd for $C_{15}H_{13}O_4N$: C, 66.4; H, 4.8; N, 5.2. Found: C, 66.2; H, 4.6; N, 5.4.

(*E*)-4-(4-Chlorostyryl)-1-methoxy-2-nitrobenzene (6dg). Following the general procedures, **6dg** was obtained from **5g** (200 mg, 0.75 mmol) and **4d** (104 mg, 0.75 mmol) as a yellow solid. Yield of **6dg** using basic conditions: 31 mg (0.10 mmol, 14%). Yield of **6dg** using base free conditions: 130 mg (0.45 mmol, 60%). Mp 127–129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 2.2, 1H), 7.63 (dd, J = 8.7, 2.2, 1H), 7.41 (d, J = 8.4, 2H), 7.32 (d, J = 8.6, 2H), 7.07 (d, J = 8.7, 1H), 7.00 (d, J = 16.5, 1 H), 6.94 (d, J = 16.5, 1H), 3.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4 (0), 140.1 (0), 135.3 (0), 133.8 (0), 131.9 (1), 130.2 (0), 129.1 (1), 128.4 (1), 127.8 (1), 126.5 (1), 123.3 (1), 114.0 (1), 56.8 (3); MS (EI) m/z 165 (25%), 178 (52%), 289 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{12}O_3NCl$ [M]$^+$: 289.0506, found: 289.0503; IR (KBr-disc) ν 1616 (m), 1527 (s), 1353 (m), 1274 (s), 1016 (m); Anal. calcd for $C_{15}H_{12}O_3NCl$: C, 62.2; H, 4.2; N, 4.8. Found: C, 62.3; H, 4.2; N, 4.7.

(*E*)-4-(4-Chlorostyryl)-2-nitrophenol (6dh). Following the general procedures, **6dh** was obtained from **5h** (190 mg, 0.75 mmol) and **4d** (104 mg, 0.75 mmol) as a yellow solid. Yield of **6dh** using basic conditions: 188 mg (0.68 mmol, 91%). Yield of **6dh** using base free conditions: 178 mg (0.64 mmol, 86%). Mp 150–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.16 (d, J = 2.1, 1H), 7.74 (dd, J = 8.8, 2.1, 1H), 7.42 (d, J = 8.6, 2H), 7.33 (d, J = 8.5, 2H), 7.16 (d, J = 8.7, 1H), 7.01 (d, J = 16.8, 1H), 6.95 (d, J = 16.8, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6 (0), 135.2 (0), 135.1 (1), 133.9 (0), 133.8 (0), 130.1 (0), 129.1 (1), 128.5 (1), 127.8 (1), 126.3 (1), 122.5 (1), 120.5 (1); MS (EI) m/z 139 (20%), 165 (97%), 275 ([M]$^+$, 100%); HRMS (EI): calcd for $C_{14}H_{10}O_3NCl$ [M]$^+$: 275.0349, found: 275.0338; IR (KBr-disc) ν 3241 (m), 1624 (m), 1530 (s), 1310 (s), 1175 (s); Anal. calcd for $C_{14}H_{10}O_3NCl$: C, 61.0; H, 3.7; N, 5.1. Found: C, 60.8; H, 3.5; N, 5.0.

(*E*)-1-Methoxy-2-nitro-4-styrylbenzene (6fg). Following the general procedures, **6fg** was obtained from **5g** (200 mg, 0.75 mmol) and **4f** (78 mg, 0.75 mmol) as a yellow solid. Yield of **6fg** using basic conditions: 81 mg (0.31 mmol, 42%). Yield of **6fg** using base free conditions: 190 mg (0.74 mmol, 99%). Mp 118–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, J = 2.2, 1H), 7.65 (dd, J = 8.7, 2.3, 1H), 7.50 (d, J = 7.1, 2H), 7.37 (dd, J = 7.2, 7.1, 2H), 7.30 (t, J = 7.2, 1H), 7.07 (d, J = 8.8, 1H), 7.05 (d, J = 16.4, 1H), 6.99 (d, J = 16.4, 1H), 3.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2 (0), 139.9 (0), 136.8 (0), 131.8 (1), 130.5 (0), 129.7 (1), 128.9 (1), 128.1 (1), 126.6 (1), 125.8 (1), 123.2 (1), 114.0 (1), 56.8 (3); MS (EI) m/z 165 (45%), 178 (78%), 255 ([M]$^+$, 93%); HRMS (EI) calcd for $C_{15}H_{13}O_3N$ [M]$^+$: 255.0895, found: 255.0895; IR (KBr-disc) ν 1525 (s), 1354 (m),

1273 (s), 1183 (m), 962 (s); Anal. calcd for $C_{15}H_{13}O_3N$: C, 70.6; H, 5.1; N, 5.5. Found: C, 70.4; H, 5.1; N, 5.6.

(*E*)-2-Nitro-4-styrylphenol (6fh). Following the general procedures, **6fh** was obtained from **5h** (190 mg, 0.75 mmol) and **4f** (78 mg, 0.75 mmol) as a yellow solid. Yield of **6fh** using basic conditions: 140 mg (0.58 mmol, 77%). Yield of **6fh** using base free conditions: 67 mg (0.28 mmol, 37%). Mp 105–107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.17 (d, J = 2.2, 1H), 7.76 (dd, J = 8.8, 2.2, 1H), 7.50 (d, J = 7.3, 2H), 7.38 (dd, J = 7.2, 7.2, 2H), 7.30 (t, J = 7.2, 1H), 7.16 (d, J = 8.7, 1H), 7.07 (d, J = 16.4, 1H), 7.00 (d, J = 16.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7 (0), 136.9 (0), 135.4 (1), 134.1 (0), 130.8 (0), 130.2 (1), 129.1 (1), 128.5 (1), 126.9 (1), 126.0 (1), 122.7 (1), 120.6 (1); MS (EI) m/z 152 (13%), 165 (50%), 241 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{14}H_{11}O_3N$ [M]$^+$: 241.0739, found: 241.0727; Anal. calcd for $C_{14}H_{11}O_3N$: C, 69.7; H, 4.6; N, 5.8. Found: C, 69.7; H, 4.4; N, 6.1.

(*E*,*Z*)-1-Methoxy-2-nitro-4-(4-nitrostyryl)benzene (6gg). Following the general procedures, **6gg** was obtained from **5g** (200 mg, 0.75 mmol) and **4g** (112 mg, 0.75 mmol) as a yellow solid in an $E:Z$ ratio of 10 : 1. Yield of **6gg** using basic conditions: 20 mg (0.07 mmol, 9%). Yield of **6gg** using base free conditions: 198 mg (0.66 mmol, 88%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.23 (d, J = 8.9, 2H), 8.20 (d, J = 2.2, 1H), 7.95 (dd, J = 8.8, 2.2, 1H), 7.83 (d, J = 8.9, 2H), 7.54 (d, J = 16.5, 1H), 7.44 (d, J = 16.5, 1H), 7.41 (d, J = 8.8, 1H), 3.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7 (0), 146.2 (0), 143.6 (0), 139.5 (0), 132.5 (1), 130.6 (1), 129.1 (0), 127.1 (1), 126.7 (1), 123.9 (1), 122.8 (1), 114.6 (1), 56.8 (3); MS (EI) m/z 165 (40%), 178 (22%), 300 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{12}O_5N_2$ [M]$^+$: 300.0746, found: 300.0759; IR (KBr-disc) ν 1614 (w), 1524 (s), 1333 (s), 1269 (s), 1014 (m); Anal. calcd for $C_{15}H_{12}O_5N_2$: C, 60.0; H, 4.0; N, 9.3. Found: C, 59.7; H, 3.8; N, 9.5. Selected ^{1}H NMR data of *Z*-**6gg** (obtained from the mixture): ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.15 (d, J = 8.9, 2H), 7.75 (d, J = 2.2, 1H), 7.25 (d, J = 8.8, 1H), 6.83 (d, J = 12.3, 1H), 6.78 (d, J = 12.3, 1H), 3.90 (s, 3H).

(*E*)-2-Nitro-4-(4-nitrostyryl)phenol (6gh). Following the general procedures, **6gh** was obtained from **5h** (190 mg, 0.75 mmol) and **4g** (112 mg, 0.75 mmol) as a yellow solid. Yield of **6gh** using basic conditions: 210 mg (0.73 mmol, 98%). Yield of **6gh** using base free conditions: 183 mg (0.64 mmol, 85%). Mp 220–223 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.26 (d, J = 2.2, 1H), 8.24 (d, J = 8.9, 1H), 7.81 (dd, J = 8.8, 2.2, 1H), 7.64 (d, J = 8.8, 2H), 7.24 (d, J = 8.8, 1H), 7.20 (d, J = 16.3, 1H), 7.11 (d, J = 16.3, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3 (0), 147.3 (0), 143.1 (0), 135.4 (1), 133.9 (0), 130.3 (1), 129.3 (0), 127.4 (1), 127.1 (1), 124.4 (1), 123.3 (1), 120.8 (1); MS (EI) m/z 69 (86%), 165 (73%), 286 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{14}H_{10}N_2O_5$ [M]$^+$: 286.0590, found: 286.0578; IR (KBr-disc) ν 1624 (s), 1531 (s), 1504 (s), 1337 (s); Anal. calcd for $C_{14}H_{10}N_2O_5$: C, 58.7; H, 3.5; N, 9.8. Found C, 58.4; H, 3.3; N, 9.9.

Analytical data for coupling products of 5i,j

(*E*)-2-Bromo-1-methoxy-4-(4-methylstyryl)benzene (6ai). Following the general procedures, **6ai** was obtained from **5i** (226 mg, 0.75 mmol) and **4a** (89 mg, 0.75 mmol) as a colourless solid. Yield of **6ai** using basic conditions: 125 mg (0.41 mmol, 55%). Yield of **6ai** using base free conditions: 181 mg (0.60 mmol, 80%). Mp 156–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 2.2, 1H), 7.38 (d, J = 8.3, 2H), 7.37 (d, J = 8.6, 1H), 7.17 (d, J = 7.9, 2H), 6.97 (d, J = 16.7, 1H), 6.92 (d, J = 16.7, 1H), 6.88 (d, J = 8.5, 1H), 3.91 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4 (0), 137.6 (0), 134.6 (0), 132.1 (0), 131.1 (1), 129.5 (1), 128.1 (1), 126.8 (1), 126.4 (1), 125.9 (1), 112.3 (0), 112.2 (1), 56.5 (3), 21.3 (3); MS (EI): m/z 165 (58%), 287 (27%), 302 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{16}H_{15}OBr$ [M]$^+$: 302.0306, found: 302.0319; IR (KBr-disc) ν 1511 (s), 1280 (m), 1053 (m), 967 (m), 815 (s); Anal. calcd for $C_{16}H_{15}OBr$: C, 63.4; H, 5.0. Found: C, 63.4; H, 4.9.

(*E*)-2-Bromo-4-(4-methylstyryl)phenol (6aj). Following the general procedures, **6aj** was obtained from **5j** (215 mg, 0.75 mmol) and **4a** (89 mg, 0.75 mmol) as a colourless solid. Yield of **6aj** using basic conditions: 181 mg (0.62 mmol, 83%). Mp 110–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 2.1, 1H), 7.39 (d, J = 7.9, 2H), 7.36 (dd, J = 8.4, 2.1, 1H), 7.18 (d, J = 7.9, 2H), 7.02 (d, J = 8.4, 1H), 6.96 (d, J = 16.7, 1H), 6.91 (d, J = 16.7, 1H), 5.54 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7 (0), 137.6 (0), 134.5 (0), 132.2 (0), 129.8 (1), 129.5 (1), 128.1 (1), 127.3 (1), 126.4 (1), 125.9 (1), 116.3 (1), 110.7 (0), 21.3 (3); MS (EI) m/z 165 (37%), 194 (63%), 288 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{13}OBr$ [M]$^+$: 288.0147, found: 288.0144; IR (KBr-disc) ν 3407 (s), 1512 (m), 1294 (m), 1038 (m), 966 (w); Anal. calcd for $C_{15}H_{13}OBr$: C, 62.3; H, 4.5. Found: C, 62.6; H, 4.6.

(*E*)-2-Bromo-1-methoxy-4-(3-methylstyryl)benzene (6bi). Following the general procedures, **6bi** was obtained from **5i** (226 mg, 0.75 mmol) and **4b** (89 mg, 0.75 mmol) as a colourless solid. Yield of **6bi** using basic conditions: 130 mg (0.43 mmol, 57%). Yield of **6bi** using base free conditions: 173 mg (0.57 mmol, 76%). Mp 104–105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 2.2, 1H), 7.39 (dd, J = 8.5, 2.2, 1H), 7.34–7.21 (m, 3H), 7.08 (d, J = 7.1, 1H), 6.99 (d, J = 16.4, 1H), 6.94 (d, J = 16.4, 1H), 6.88 (d, J = 8.5, 1H), 3.91 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5 (0), 138.3 (0), 137.3 (0), 131.9 (0), 131.1 (1), 128.7 (1), 128.5 (1), 128.3 (1), 127.2 (1), 126.9 (1), 126.7 (1), 123.7 (1), 112.3 (0), 112.2 (1), 56.4 (3), 21.5 (3); MS (EI) m/z 165 (80%), 287 (20%), 302 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{16}H_{15}OBr$ [M]$^+$: 302.0306, found: 302.0300; IR (KBr-disc) ν 1596 (m), 1496 (s), 1259 (s), 1051 (m), 960 (m); Anal. calcd for $C_{16}H_{15}OBr$: C, 63.4; H, 5.0. Found: C, 63.5; H, 5.2.

(*E*)-2-Bromo-4-(3-methylstyryl)phenol (6bj). Following the general procedures, **6bj** was obtained from **5j** (215 mg, 0.75 mmol) and **4b** (89 mg, 0.75 mmol) as a colourless solid. Yield of **6bj** using basic conditions: 176 mg (0.61 mmol, 81%). Mp 93–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 2.1, 1H), 7.37 (dd, J = 8.5, 2.1, 1H), 7.34–7.21 (m, 3H), 7.09 (d, J = 7.0, 1H), 7.02 (d, J = 8.5, 1H), 6.96 (d, J = 16.4, 1H), 6.93 (d, J = 16.4, 1H), 5.54 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8 (0), 138.3 (0), 137.2 (0), 132.1 (0), 129.9 (1), 128.7 (1), 128.6 (1), 128.3 (1), 127.4 (1), 127.2 (1), 126.7 (1), 123.7 (1), 116.3 (1), 110.8 (0), 21.5 (3); MS (EI) m/z 73 (100%), 165 (43%),

288 ([M]$^+$, 64%); HRMS (EI) calcd for $C_{15}H_{13}OBr$ [M]$^+$: 288.0147, found: 288.0144; IR (KBr-disc) ν 3099 (m), 1597 (m), 1493 (s), 1280 (m), 1176 (m); Anal. calcd for $C_{15}H_{13}OBr$: C, 62.3; H, 4.5. Found: C, 62.2; H, 4.4.

(*E*)-2-Bromo-1-methoxy-4-(4-methoxystyryl)benzene (6ci). Following the general procedures, **6ci** was obtained from **5i** (226 mg, 0.75 mmol) and **4c** (101 mg, 0.75 mmol) as a colourless solid. Yield of **6ci** using basic conditions: 115 mg (0.36 mmol, 48%). Yield of **6ai** using base free conditions: 190 mg (0.59 mmol, 79%). Mp 154–155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 2.1, 1H), 7.42 (d, J = 8.7, 2H), 7.35 (dd, J = 8.5, 2.1, 1H), 6.97–6.80 (m, 5H), 3.90 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5 (0), 155.2 (0), 132.2 (0), 130.9 (1), 130.2 (0), 127.7 (1), 126.6 (1), 124.8 (1), 114.3 (1), 112.3 (0), 112.2 (1), 56.4 (3), 55.4 (3); MS (EI) *m*/*z* 196 (28%), 303 (42%), 318 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{16}H_{15}O_2Br$ [M]$^+$: 318.0255, found: 318.0253; IR (KBr-disc) ν 2939 (w), 1600 (m), 1508 (s), 1256 (s), 1177 (s); Anal. calcd for $C_{16}H_{15}O_2Br$: C, 60.2; H, 4.7. Found: C, 60.1; H, 4.5.

(*E*)-2-Bromo-4-(4-methoxystyryl)phenol (6cj). Following the general procedures, **6cj** was obtained from **5j** (215 mg, 0.75 mmol) and **4c** (101 mg, 0.75 mmol) as a colourless solid. Yield of **6cj** using basic conditions: 138 mg (0.45 mmol, 60%). Mp 121–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 2.0, 1H), 7.42 (d, J = 8.7, 2H), 7.34 (dd, J = 8.5, 2.0, 1H), 7.00 (d, J = 8.4, 1H), 6.92 (d, J = 16.3, 1H), 6.90 (d, J = 8.7, 2H), 6.83 (d, J = 16.3, 1H), 5.50 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5 (0), 151.5 (0), 132.3 (0), 130.1 (0), 129.6 (1), 127.8 (1), 127.7 (1), 127.2 (1), 124.8 (1), 116.3 (1), 114.3 (1), 110.7 (0), 55.4 (3); MS (EI) *m*/*z* 152 (52%), 182 (100%), 304 ([M]$^+$, 98%); HRMS (EI) calcd for $C_{15}H_{13}O_2Br$ [M]$^+$: 304.0099, found: 304.0089; IR (KBr-disc) ν 3299 (m), 2837 (w), 1511 (s), 1250 (s), 1178 (m); Anal. calcd for $C_{15}H_{13}O_2Br$: C, 59.0; H, 4.3. Found: C, 59.1; H, 4.2.

(*E*)-2-Bromo-4-(4-chlorostyryl)-1-methoxybenzene (6di). Following the general procedures, **6di** was obtained from **5i** (226 mg, 0.75 mmol) and **4d** (104 mg, 0.75 mmol) as a colourless solid. Yield of **6di** using basic conditions: 85 mg (0.26 mmol, 35%). Yield of **6di** using base free conditions: 105 mg (0.32 mmol, 43%). Mp 104–106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 2.1, 1H), 7.39 (d, J = 8.6, 2H), 7.35 (dd, J = 8.5, 2.1, 1H), 7.31 (d, J = 8.6, 2H), 6.94 (d, J = 16.4, 1H), 6.89 (d, J = 16.4, 1H), 6.87 (d, J = 8.5, 1H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7 (0), 135.8 (0), 133.3 (0), 131.4 (0), 131.2 (1), 128.9 (1), 127.6 (1), 127.5 (1), 127.0 (1), 126.8 (1), 112.3 (0), 112.1 (1), 56.4 (3); MS (EI) *m*/*z* 165 (75%), 309 (30%), 324 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{12}OBrCl$ [M]$^+$: 321.9760, found: 321.9769; IR (KBr-disc) ν 1497 (s), 1262 (m), 1053 (m), 963 (w), 817 (m); Anal. calcd for $C_{15}H_{12}OBrCl$: C, 55.7; H, 3.7. Found: C, 55.7; H, 3.5.

(*E*)-2-Bromo-4-(4-chlorostyryl)phenol (6dj). Following the general procedures, **6dj** was obtained from **5j** (215 mg, 0.75 mmol) and **4d** (104 mg, 0.75 mmol) as a colourless solid. Yield of **6dj** using basic conditions: 178 mg (0.58 mmol, 77%). Mp 103–107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 2.1, 1H), 7.43–7.29 (m, 5H), 7.01 (d, J = 8.4, 1H), 6.94 (d, J = 16.3, 1H), 6.88 (d, J = 16.3, 1H), 5.57 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1 (0), 135.8 (0), 133.3 (0), 131.6 (0), 130.0 (1), 129.0 (1), 127.6 (1), 127.5 (1), 127.5 (1), 126.8 (1), 116.4 (1), 110.8 (0); MS (EI) *m*/*z* 165 (65%), 194 (85%), 310 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{14}H_{10}OBrCl$ [M]$^+$: 307.9604, found: 307.9624; IR (KBr-disc) ν 3497 (m), 1496 (s), 1179 (m), 959 (m), 819 (m).

(*E*)-2-Bromo-1-methoxy-4-styrylbenzene (6fi). Following the general procedures, **6fi** was obtained from **5i** (226 mg, 0.75 mmol) and **4f** (78 mg, 0.75 mmol) as a colourless solid. Yield of **6fi** using basic conditions: 105 mg (0.36 mmol, 48%). Yield of **6fi** using base free conditions: 89 mg (0.31 mmol, 41%). Mp 138–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 2.2, 1H), 7.50 (d, J = 7.3, 2H), 7.40 (dd, J = 8.5, 2.5, 1H), 7.36 (dd, J = 7.3, 7.3, 2H), 7.26 (tt, J = 7.3, 1.3, 1H), 7.01 (d, J = 16.3, 1H), 6.96 (d, J = 16.5, 1H), 6.88 (d, J = 8.5, 1H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5 (0), 137.3 (0), 131.8 (0), 131.1 (1), 128.8 (1), 128.1 (1), 127.7 (1), 126.9 (1), 126.9 (1), 126.5 (1), 112.3 (0), 112.1 (1), 56.4 (3); MS (EI) *m*/*z* 165 (78%), 273 (22%), 288 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{13}OBr$ [M]$^+$: 288.0150, found: 288.0153; IR (KBr-disc) ν 1592 (m), 1499 (s), 1266 (m), 1050 (m), 966 (m); Anal. calcd for $C_{15}H_{13}OBr$: C, 62.3; H, 4.5. Found: C, 62.6; H, 4.8.

(*E*)-2-Bromo-4-styrylphenol (6fj). Following the general procedures, **6fj** was obtained from **5j** (215 mg, 0.75 mmol) and **4f** (78 mg, 0.75 mmol) as a colourless solid. Yield of **6fj** using basic conditions: 137 mg (0.50 mmol, 66%). Mp 116–119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, J = 2.1, 1H), 7.48 (d, J = 7.3, 2H), 7.39–7.33 (m, 3H), 7.26 (tt, J = 7.3, 1.3, 1H), 7.02 (d, J = 8.4, 1H), 7.02–6.93 (m, 2H), 5.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9 (0), 137.3 (0), 132.0 (0), 129.9 (1), 128.8 (1), 128.2 (1), 127.7 (1), 127.5 (1), 126.9 (1), 126.5 (1), 116.4 (1), 110.8 (0); MS (EI) *m*/*z* 165 (58%), 194 (47%), 274 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{14}H_{11}OBr$ [M]$^+$: 273.9993, found: 273.9999; IR (KBr-disc) ν 3305 (s), 1594 (m), 1660 (m), 1424 (m), 963 (s); Anal. calcd for $C_{14}H_{11}OBr$: C, 61.1; H, 4.0. Found: C, 61.0; H, 4.4.

(*E*)-2-Bromo-1-methoxy-4-(4-nitrostyryl)benzene (6gi). Following the general procedures, **6gi** was obtained from **5i** (226 mg, 0.75 mmol) and **4g** (112 mg, 0.75 mmol) as a yellow solid. Yield of **6gi** using basic conditions: 91 mg (0.27 mmol, 36%). Yield of **6gi** using base free conditions: 243 mg (0.70 mmol, 94%). Mp 145–148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, J = 8.8, 2H), 7.75 (d, J = 2.1, 1H), 7.57 (d, J = 8.7, 2H), 7.42 (dd, J = 8.6, 2.1, 1H), 7.12 (d, J = 16.3, 1H), 6.98 (d, J = 16.3, 1H), 6.90 (d, J = 8.6, 1H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4 (0), 146.9 (0), 143.8 (0), 131.6 (1), 131.5 (1), 130.5 (0), 127.7 (1), 126.8 (1), 125.5 (1), 124.2 (1), 112.5 (0), 112.1 (1), 56.5 (3); MS (EI) *m*/*z* 165 (78%), 318 (10%), 333 ([M]$^+$, 100%); HRMS (EI) calcd for $C_{15}H_{12}O_3NBr$ [M]$^+$: 333.0001, found: 333.0009; IR (KBr-disc) ν 1589 (m), 1498 (s), 1336 (s), 1264 (m), 961 (w); Anal. calcd for $C_{15}H_{12}O_3NBr$: C, 53.9; H, 3.6; N, 4.2. Found: C, 53.8; H, 3.3; N, 4.4.

(*E*)-2-Bromo-4-(4-nitrostyryl)phenol (6gj). Following the general procedures, **6gj** was obtained from **5j** (215 mg, 0.75 mmol) and **4g** (112 mg, 0.75 mmol) as a yellow solid.

Yield of **6gj** using basic conditions: 224 mg (0.70 mmol, 93%). Yield of **6gj** using base free conditions: 96 mg (0.30 mmol, 40%). Mp 202–203 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 9.37 (s, 1H), 8.22 (d, J = 8.9, 2H), 7.84 (d, J = 2.1, 1H), 7.81 (d, J = 8.8, 2H), 7.52 (dd, J = 8.5, 2.1, 1H), 7.42 (d, J = 16.4, 1H), 7.27 (d, J = 16.4, 1H), 7.05 (d, J = 8.4, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 155.5 (0), 147.5 (0), 145.3 (0), 132.7 (1), 132.6 (1), 131.1 (0), 128.6 (1), 127.8 (1), 125.8 (1), 124.8 (1), 117.6 (1), 111.0 (0); MS (EI) m/z 165 (100%), 194 (40%), 319 ([M]$^+$, 43%); HRMS (EI) calcd for $C_{14}H_{10}NO_3Br$ [M]$^+$: 318.9844, found: 318.9840; IR (KBr-disc) ν 3445 (s), 1588 (s), 1496 (s), 1341 (s); Anal. calcd for $C_{14}H_{10}NO_3Br$: C, 52.5; H, 3.1; N, 4.4. Found C, 52.4; H, 2.9; N, 4.6.

Analytical data for coupling products of 5k

(*E*)-Methyl-3-(5-methoxy-2-((*E*)-4-methylstyryl)-phenyl)-acrylate (6ak). Following the general procedures, **6ak** was obtained from **5k** (100 mg, 0.33 mmol) and **4a** (39 mg, 0.33 mmol) as a yellow oil. Yield of **6ak** using base free conditions: 45 mg (0.15 mmol, 45%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03 (d, J = 15.8, 1H), 7.62 (d, J = 8.7, 1H), 7.49 (d, J = 8.1, 2H), 7.40 (d, J = 16.1, 1H), 7.26 (d, J = 2.6, 1H), 7.19 (d, J = 8.0, 2H), 7.03 (dd, J = 8.8, 2.6, 1H), 6.94 (d, J = 16.1, 1H), 6.60 (d, J = 15.8, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.5, 158.7, 141.6, 137.1, 134.3, 133.0, 130.6, 130.1, 129.2, 128.2, 126.4, 123.7, 120.0, 117.2, 111.2, 55.3, 51.4, 20.8; MS (EI) m/z 105 (100%), 234 (44%), 249 (73%), 308 ([M]$^+$, 44%); HRMS (EI) calcd for $C_{20}H_{20}O_3$ [M]$^+$: 308.1412, found: 308.1421; IR (KBr-disc) ν 2950 (w), 1719 (m), 1603 (m), 1169 (m), 752 (s).

(*E*)-Methyl-3-(5-methoxy-2-((*E*)-3-methylstyryl)-phenyl)-acrylate (6bk). Following the general procedures, **6bk** was obtained from **5k** (100 mg, 0.33 mmol) and **4b** (39 mg, 0.33 mmol) as a yellow oil. Yield of **6bk** using base free conditions: 71 mg (0.23 mmol, 70%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.69 (d, J = 15.8, 1H), 8.12 (d, J = 8.7, 1H), 7.92–7.78 (m, 4H), 7.67 (d, J = 7.7, 1H), 7.62 (d, J = 2.6, 1H), 7.53 (dd, J = 8.7, 2.6, 1H), 7.44 (d, J = 16.0, 1H), 6.95 (d, J = 16.0, 1H), 4.41 (s, 3H), 4.40 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.4, 159.7, 142.5, 138.7, 137.9, 134.0, 131.8, 131.0, 129.5, 129.3, 127.9, 125.5, 124.6, 120.9, 118.1, 112.2, 56.3, 52.4, 21.9; MS (EI) m/z 234 (44%), 249 (100%), 308 ([M]$^+$, 71%); HRMS (EI) calcd for $C_{20}H_{20}O_3$ [M]$^+$: 308.1412, found: 308.1425. IR (KBr-disc) ν 2947 (w), 1712 (m), 1493 (m), 1166 (s); Anal. calcd for $C_{20}H_{20}O_3$: C, 77.9; H, 6.5. Found: C, 77.4; H, 6.6.

(*E*)-Methyl-3-(5-methoxy-2-((*E*)-4-methoxystyryl)-phenyl)-acrylate (6ck). Following the general procedures, **6ck** was obtained from **5k** (100 mg, 0.33 mmol) and **4c** (44 mg, 0.33 mmol) as a yellow oil. Yield of **6ck** using base free conditions: 15 mg (0.05 mmol, 14%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.13 (d, J = 15.8, 1H), 7.55 (d, J = 8.7, 1H), 7.47 (d, J = 8.6, 2H), 7.24 (d, J = 16.0, 1H), 7.05 (d, J = 2.6, 1H), 6.97 (dd, J = 8.6, 2.7, 1H), 6.93 (d, J = 8.7, 1H), 6.86 (d, J = 16.0, 1H), 6.38 (d, J = 15.8, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.2, 159.5, 158.9, 142.4, 133.7, 130.9, 130.5, 130.3, 128.1, 127.8, 122.9, 119.9, 116.7, 114.2, 111.4, 55.4, 55.3, 51.7; MS (EI) m/z 324 ([M]$^+$, 11%), 262 (22%), 231 (27%), 49 (100%); HRMS (EI) calcd for $C_{20}H_{12}O_4^+$ [M]$^+$: 324.1362, found: 324.1366; IR (KBr-disc) ν 2954 (w), 1716 (m), 1512 (m), 1251 (s), 1172 (s).

(*E*)-Methyl-3-(5-methoxy-2-((*E*)-4-chlorostyryl)-phenyl)-acrylate (6dk). Following the general procedures, **6dk** was obtained from **5k** (100 mg, 0.33 mmol) and **4d** (45 mg, 0.33 mmol) as a yellow solid. Yield of **6dk** using base free conditions: 80 mg (0.25 mmol, 75%). Mp 216–218 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03 (d, J = 15.8, 1H), 7.65–7.57 (m, 3H), 7.48 (d, J = 16.2, 1H), 7.42 (d, J = 8.5, 2H), 7.26 (d, J = 2.6, 1H), 7.03 (dd, J = 8.7, 2.6, 1H), 6.97 (d, J = 16.1, 1H), 6.60 (d, J = 15.8, 1H), 3.82 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.5, 159.0, 141.5, 136.0, 133.3, 131.9, 129.7, 129.2, 128.6, 128.3, 128.2, 125.6, 120.2, 117.2, 111.3, 55.3, 51.5; MS (EI) m/z 59 (100%), 189 (64%), 269 (74%), 328 ([M]$^+$, 46%); HRMS (EI) calcd for $C_{19}H_{17}O_3Cl$ [M]$^+$: 328.0866, found: 328.0877; IR (KBr-disc) ν 2949 (w), 1714 (s), 1495 (s), 1318 (m), 1171 (s); Anal. calcd for $C_{19}H_{17}ClO_3$: C, 69.4; H, 5.2. Found: C, 69.3; H, 5.2.

(*E*)-Methyl-3-(5-methoxy-2-(*E*)-styrylphenyl)acrylate (6fk). Following the general procedures, **6fk** was obtained from **5k** (100 mg, 0.33 mmol) and **4f** (34 mg, 0.33 mmol) as a yellow oil. Yield of **6fk** using base free conditions: 83 mg (0.28 mmol, 86%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.04 (d, J = 15.8, 1H), 7.65 (d, J = 8.7, 1H), 7.61 (d, J = 7.3, 2H), 7.47 (d, J = 16.2, 1H), 7.39 (dd, J = 7.4, 7.4, 2H), 7.33–7.25 (m, 2H), 7.05 (dd, J = 8.7, 2.6, 1H), 6.98 (d, J = 16.1, 1H), 6.61 (d, J = 15.8, 1H), 3.83 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.4, 159.8, 142.5, 137.9, 134.1, 131.6, 130.9, 129.6, 129.3, 128.6, 127.4, 125.7, 121.0, 118.1, 112.2, 56.3, 52.4; MS (EI) m/z 294 ([M]$^+$, 79%), 235 (100%), 220 (38%), 191 (26%); HRMS (EI) calcd for $C_{19}H_{18}O_3$ [M]$^+$: calcd 294.1256, found: 294.1251; IR (KBr-disc) ν 2947 (w), 1710 (m), 1316 (m), 1166 (s); Anal. calcd for $C_{19}H_{18}O_3$: C, 77.5; H, 6.2. Found: C, 77.0; H, 6.2.

(*E*)-Methyl-3-(5-methoxy-2-((*E*)-4-nitrostyryl)-phenyl)-acrylate (6gk). Following the general procedures, **6gk** was obtained from **5k** (100 mg, 0.33 mmol) and **4g** (49 mg, 0.33 mmol) as a yellow solid. Yield of **6gk** using base free conditions: 91 mg (0.27 mmol, 83%). Mp 142–145 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.23 (d, J = 8.9, 2H), 8.09 (d, J = 15.8, 1H), 7.89 (d, J = 8.9, 2H), 7.76 (d, J = 16.2, 2H), 7.73 (d, J = 8.8, 1H), 7.30 (d, J = 2.6, 1H), 7.17 (d, J = 16.1, 1H), 7.08 (dd, J = 8.8, 2.6, 1H), 6.63 (d, J = 15.8, 1H), 3.85 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.4, 159.6, 146.2, 144.0, 141.3, 134.1, 129.5, 129.1, 128.6, 128.2, 127.4, 124.0, 120.8, 117.2, 111.5, 55.5, 51.6; MS (EI) m/z 59 (100%), 189 (79%), 280 (87%), 339 ([M]$^+$, 36%); HRMS (EI) calcd for $C_{19}H_{17}O_5N$ [M]$^+$: 339.1107, found; 339.1114; IR (KBr-disc) ν 2953 (w), 1716 (m), 1515 (m), 1339 (s); Anal. calcd for $C_{19}H_{17}O_5N$: C, 67.2; H, 5.1; N, 4.1. Found C, 66.8; H, 5.3; N, 4.0.

General procedure and analytical data for Suzuki coupling products of phenol diazonium salts

To a solution of the corresponding phenol diazonium salt **5** (0.5 mmol) in methanol (5.0 mL) was added $Pd(OAc)_2$ (3 mg, 2.5 mol%) and organotrifluoroborate **13** (101 mg, 0.5 mmol). The suspension was stirred for 12 h at ambient temperature. After this time, activated charcoal was added to absorb the

Pd-residues, all volatiles were evaporated and the residue was mixed with MTBE (20 mL). The mixture was immersed in an ultrasonic bath for 5 min, filtered through celite, and all volatiles were evaporated *in vacuo*. The residue was purified by chromatography on silica, using hexane–MTBE mixtures as the eluent.

(*E*)-4-Styrylphenol (6fb). Following the general procedure, **6fb** was obtained from **5b** (104 mg, 0.50 mmol) as a colourless solid. Yield of **6fb** using base free conditions: 51 mg (0.26 mmol, 52%). Mp 186–187 °C. All other analytical data are identical to those reported above for **6fb**.

(*E*)-2-Hydroxy-5-styrylbenzoic acid (6fm). Following the general procedure, **6fm** was obtained from **5m** (126 mg, 0.50 mmol) as a colourless solid. Yield of **6fb** using base free conditions: 65 mg (0.27 mmol, 54%). Mp 221–223 °C. ^{1}H NMR (300 MHz, methanol-d_4) δ 7.99 (d, J = 2.3, 1H), 7.70 (dd, J = 8.7, 2.3, 1H), 7.50 (d, J = 7.5, 2H), 7.31 (dd, J = 7.5, 7.5, 2H), 7.21 (t, J = 7.5, 1H), 7.09 (d, J = 16.4, 1H), 7.01 (d, J = 16.4, 1H), 6.93 (d, J = 8.6, 1H); ^{13}C NMR (75 MHz, methanol-d_4) δ 173.5 (0), 162.8 (0), 139.0 (0), 134.3 (1), 130.4 (0), 129.8 (1), 129.8 (1), 128.5 (1), 127.5 (1), 118.8 (1), 114.2 (0), two signals could not be located due to signal overlap; IR (KBr-disc) ν 2917 (w), 1675 (w), 1448 (w), 1300 (w), 1218 (m); MS (EI) m/z 240 ([M]$^+$, 60%), 222 (100%), 165 (80%), 131 (37%); HRMS (EI) calcd for $C_{15}H_{12}O_3$ [M]$^+$: 240.0794, found: 240.0794; Anal. calcd for $C_{15}H_{12}O_3$: C, 75.0; H, 5.0. Found: C, 75.0; H, 4.8.

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Notes and references

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