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Olefin cross-metathesis/Suzuki–Miyaura reactions on vinylphenylboronic acid pinacol esters

Christine B. Baltus [a], Irina S. Chuckowree [a], Neil J. Press [b], Iain J. Day [c], Simon J. Coles [d], Graham J. Tizzard [d], John Spencer [a,c,*]

[a] School of Science at Medway, University of Greenwich, Chatham ME4 4TB, UK
[b] Novartis Pharmaceuticals UK, Horsham, Sussex RH12 5AB, UK
[c] Department of Chemistry, School of Life Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, UK
[d] EPSRC National Crystallography Service, School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

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ABSTRACT

A series of alkenyl phenylboronic acid pinacol esters has been synthesized via an olefin cross-metathesis reaction of vinylphenylboronic acid pinacol ester derivatives. After catalytic hydrogenation, the resulting boronates were coupled via a microwave-mediated Suzuki–Miyaura reaction to afford a library of biarylethyl aryl and biarylethyl cycloalkyl derivatives. A complementary reaction sequence involved an initial Suzuki–Miyaura coupling.

A number of diarylethane derivatives display biological activity. For example, **1a** is a potent *Helicobacter pylori* urease inhibitor[1] and **1b** is an estrogen receptor (ERβ) agonist (Fig. 1).[2] Relatively few examples of bioactive biarylethyl aryl compounds appear in the literature; **2a** is an interleukin-4 antagonist[3] and **2b** is an effective bombesin receptor subtype-3 (BRS-3) agonist for the treatment of obesity[4] (Fig. 1).

Retrosynthetic analysis reveals a cross-metathesis[5] reaction (CM) (Scheme 1) and a hydrogenation sequence with a supplementary Suzuki–Miyaura (SM) reaction to furnish **10** via the useful substituted ethylarylboronate synthon **8** (Scheme 1). We present herein our studies on a series of reactions leading to a library of biarylethyl arenes and precursors, with the crucial CM chemistry mediated by catalysts **6**.

Schmalz et al. previously investigated the synthesis of biologically important *trans*-stilbenes via Ru-catalyzed cross-metathesis reactions.[6] Indeed, olefin metathesis followed by hydrogenation reactions are vital in the synthesis of alkyl-bridges or chains,[7] or aliphatic rings or macrocycles,[8] and in diversity-oriented synthesis.[9]

Vinylphenylboronic acid pinacol esters **4** were readily synthesized in good yields from their boronic acid precursors **3** by reaction with pinacol, in the presence of magnesium sulfate ($MgSO_4$) as a desiccant. Initial CM reaction optimizations were attempted on **4a** (4-vinylphenylboronic acid pinacol ester) with styrene (**5a**) using a catalytic amount of Grubbs' catalysts, **6b** or **6c** (Table 1).

The ester **4a** and styrene (**5a**) are considered to be type I olefins which imply that they are able to undergo a rapid homodimerization and whose homodimers can participate in competing CM reactions. An excess of **5a** (up to 5 equiv) was used in order to obtain the cross-coupled product **7a** in good yield and to minimize homocoupling.[10] In our case, this still led to a large amount of *E*-stilbene (styrene homodimerization product) which, in most cases, was difficult to separate from the expected product, **7a**, by chromatography, probably also impacting on the final isolated yield of the latter. A number of pertinent observations can be made regarding this reaction:

(i) The reaction time appears to affect the yields obtained. When the reaction was stopped after 2.5 h a moderate yield of 55% was obtained (Table 1, entry 1) and better yields were obtained after 16 h or 24 h, that is, 58% and 60%, respectively (Table 1, entries 3 and 4). However, the best yield was obtained after 6 h reaction time (76%).
(ii) A decrease in the molar percentage of catalyst led to a decrease in the yields (e.g., 76% yield with 5 mol % of **6b**, Table 1, entry 2; 65% yield with 3 mol % of **6b**, entry 6; 52% yield with 1 mol % of **6b**, entry 9).

* Corresponding author.
E-mail address: j.spencer@sussex.ac.uk (J. Spencer).

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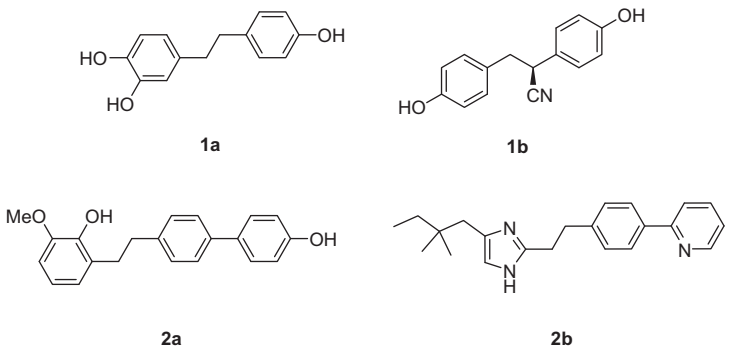
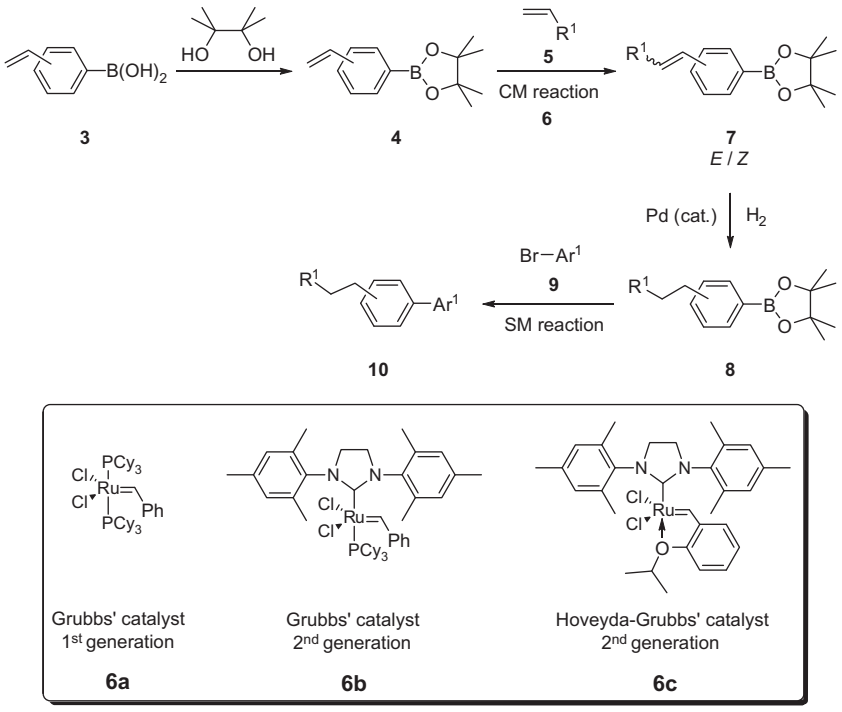


Figure 1. Biologically active diarylethanes and biarylethyl arenes.



Scheme 1. Synthesis of biarylethyl arenes or cycloalkanes via a CM/SM reaction sequence.

(iii) Product yields do not appear to be affected by the number of equivalents of **5a** used. Very similar yields were obtained when changing the number of equivalents (65%, 58%, and 63% yields obtained with 5, 2, and 1.6 equiv of **5a**, Table 1, entries 6–8, respectively).

(iv) With catalyst **6c** the expected product was formed in a moderate yield, 51% (Table 1, entry 11).

(v) The reaction was also attempted under microwave irradiation but gave lower yields (Table 1, entries 12 and 13).

Next, other 2-, 3-, and 4-substituted styrene derivatives **5** were selected as reaction partners with **4a**, using **6b** as the catalyst (3 mol %), in order to broaden the CM reaction scope (Table 2). The products **7** were obtained in poor to moderate yields (Table 2) although the 2-substituted styrene **5o** did not react, probably due to steric reasons. Crystals of the anisole-substituted product **7d** were grown and analyzed by X-ray crystallography (Fig. S1), which confirmed the presence of the olefin and boronate moieties, in the (*E*)-configuration.

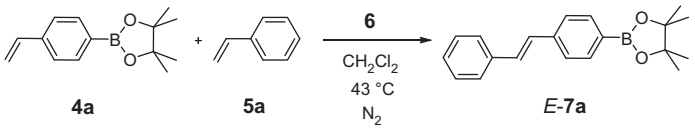
A few non-aromatic vinyl derivatives were reacted with **4a**. The cyclohexane derivative **7k** was obtained in a reasonable 58% yield (Table 2, entry 10), while none of the expected product was observed for the CM reaction with vinyl acetate **5l** (Table 2, entry 11), possibly due to the high volatility of this compound.

For the reactions leading to **7b** and **7g**, the expected products were obtained as mixtures with the homodimerization products of **5b** and **5g**, respectively, and could not be separated by chromatography. The yield could not be calculated by ^{1}H NMR spectroscopy due to overlapping signals (Table 2, entries 1 and 6). Hence, these products were used as mixtures for the next steps.

The CM reaction was also attempted with heterocyclic derivatives **5h–j**, but only the starting materials were observed after 6 h (Table 2, entries 7–9) in line with previous findings.[11,12] Although Schrock's catalyst has been shown to be successful for some of these substrates, we did not attempt to use it for these reactions.

Related symmetrical (*E*)-stilbenes have previously been prepared via the homocoupling of 1,3-dibenzylbenzotriazolium

Table 1
CM reaction of **4a** with **5a**



4a **5a** ***E*-7a**

Entry	**5a** (equiv)	**6** (mol %)	Time (h)	Yield[a] (%)
1	5	**6b** (5)	2.5	55
2	5	**6b** (5)	6	76[b]
3	5	**6b** (5)	16	58[b]
4	5	**6b** (5)	24	60[b]
5	5	**6b** (5)	16	42[b,c]
6	5	**6b** (3)	6	65
7	2	**6b** (3)	6	58
8	1.6	**6b** (3)	6	63
9	5	**6b** (1)	24	52[b]
10	2	**6b** (1)	24	65[b]
11	5	**6c** (3)	6	51
12	5	**6b** (5)	0.5	46[b,d]
13	5	**6b** (5)	2	26[b,d]

Only the *(E)-isomer* was observed by ^{1}H NMR.
[a] Isolated yields.
[b] Yield calculated by ^{1}H NMR spectroscopy; mixture of expected product + traces of starting material **4a**.
[c] Reaction achieved at room temperature.
[d] Reaction under microwave irradiation in a sealed vial at 40 °C (Power max.,300 W, in a CEM Explorer).
Power max is a special cooling feature which enables microwave irradiation with concomitant cooling.

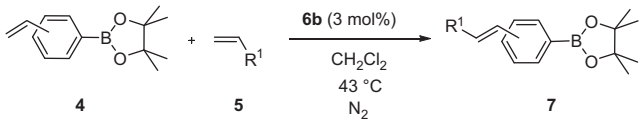
bromides[13] and styrylboronates **7** are also accessible via Wittig reactions.[14,15]

The homodimerization products **7m** and **7s**, from **4a** and **4b**, respectively, were deliberately synthesized, moreover in excellent yields, (Table 2, entries 12 and 18). Crystals of **7m** were grown and analyzed by X-ray diffraction (Fig. S1) and this confirmed its (*E*)-configuration. Compounds **7m** and **7s** promise to be useful synthons for the synthesis of symmetrical stilbenes (vide infra) as does the orthogonally-protected MIDA-analogue **7f**,[16] which is a potential precursor to unsymmetrical stilbenes (MIDA: methyliminodiacetic acid). ^{11}B NMR spectroscopic studies were able to distinguish the distinct boron [sp^2 (pinacol) or sp^3 (MIDA)] environments in the boron-containing metathesis products (Table 3 and Supplementary data).

Next, catalytic hydrogenations were performed on compounds **7** to afford the reduced products **8** in very good yields (Table S1, Supplementary data). Crystals of **8b** were grown and analyzed by X-ray crystallography, which, along with its NMR spectra, confirmed that both the nitro group and vinylic bond had been reduced (Fig. S1).

The boronic esters **8** were then coupled with a range of aryl halides **9** in Suzuki–Miyaura (SM) reactions in the presence of tetrakis(triphenylphosphine)palladium(0) using microwave conditions. The corresponding biarylethyl arenes **10** were obtained in moderate to very good yields (Table 4). Crystals of **10e** were grown and analyzed by X-ray crystallography (Fig. S1). The symmetrical product **10f** is a very interesting compound (Table 4, entry 6) since it contains indole moieties, which are privileged scaffolds in medici-

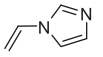
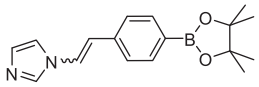
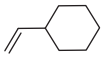
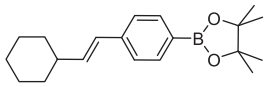
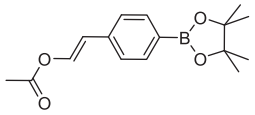
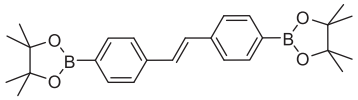
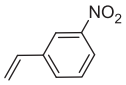
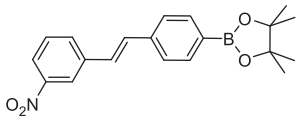
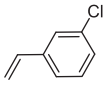
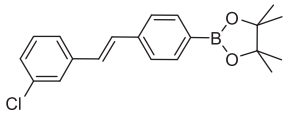
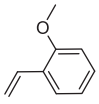
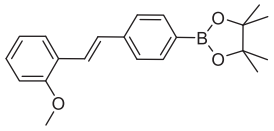
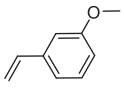
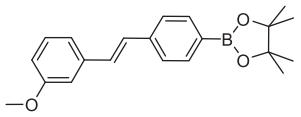
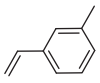
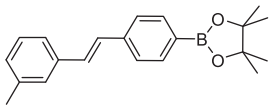
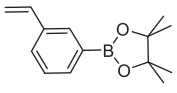
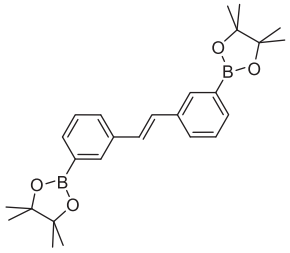
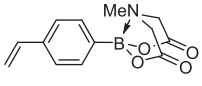
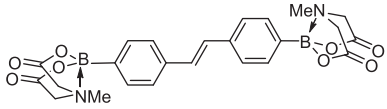
Table 2
CM reactions of **4**



4 **5** **7**

Entry	**4**	**5** (equiv)	Time (h)	Product (**7**)	Yield[a] (%)
1	**4a**	**5b** (3)	20	**7b**	[b]
2	**4a**	**5c** (3)	22	**7c**	22 (49)[c]
3	**4a**	**5d** (5)	6	**7d**	29[d]
4	**4a**	**5e** (3)	22	**7e**	45 (63)[c]
5	**4a**	**5f** (5)	16	**7f**	59
6	**4a**	**5g** (5)	6	**7g**	[b]
7	**4a**	**5h** (5)	6	**7h**	–
8	**4a**	**5i** (5)	6	**7i**	–

Table 2 (*Continued*)

Entry	**4**	**5** (equiv)	Time (h)	Product (**7**)	Yield[a] (%)
9	**4a**	 **5j** (5)	6	 **7j**	–
10	**4a**	 **5k** (5)	6	 **7k**	58
11	**4a**	 **5l** (5)	22	 **7l**	–
12	**4a**	–	22	 **7m**	89
13	**4a**	 **5m** (5)	22	 **7n**	34 (49)[c]
14	**4a**	 **5n** (5)	22	 **7o**	20 (39)[c]
15	**4a**	 **5o** (5)	22	 **7p**	–
16	**4a**	 **5p** (5)	22	 **7q**	68
17	**4a**	 **5q** (5)	22	 **7r**	36 (49)[c]
18	 **4b**	–	6	 **7s**	90
19	**4a**	 **5f** (5)	16	 **7t**	Variable[e]

Only the (*E*)-*isomer* was observed by ^{1}H NMR.
[b]Yield undetermined because the product is in a mixture with the homodimerization product of **5** and could not be separated by chromatography.
[c]Percentage yield in parentheses, calculated from the crude ^{1}H NMR.
[d]Yield calculated by ^{1}H NMR, a mixture of the expected product and traces of the homodimerization product of **5d** were obtained.
[e]By-product of entry 5.
[a] Isolated yields.

nal chemistry. Such analogues could be potential ligands for, for example, dimeric GPCRs (G-protein coupled receptors).[17]

A complementary route toward the synthesis of biarylethyl aryl and biarylethyl cycloalkyl derivatives was undertaken via an initial SM coupling, followed by a CM reaction. 4-Vinylphenylboronic acid (**3a**) was coupled with aryl halides **9** using McCluskey's conditions, with Pd(DIPHOS)$_2$ as the catalyst [DIPHOS = 1,2-*bis*(diphenylphosphino)ethane].[18] In our hands, the SM coupling under these conditions was effective for electron-rich and electron-poor aryl bromides (Table 5, entries 2 and 6), but no expected product was observed when using an *ortho*-substituted aryl bromide (Table 5, entry 5), although we did not investigate this extensively.

Table 3
^{11}B chemical shifts of homo- and cross-metathesis boron-containing stilbenes[a]

Compound	^{11}B chemical shift
4a	30.7[b]
5f	15.8[c]
7f	28.7, 10.4[c]
7m	30.8[b]
7t	14.1[b]

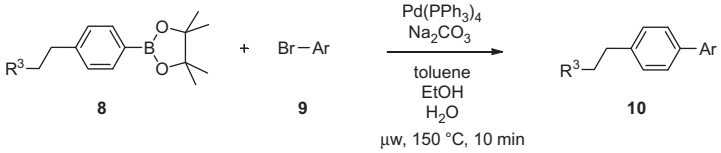
[a] Shifts are quoted at the peak center, relative to $BF_3{\cdot}Et_2O$, recorded on a Varian VNMRS 600 spectrometer at 192 MHz.
[b] Recorded in $CDCl_3$.
[c] Recorded in DMSO-d_6.

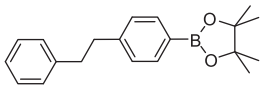
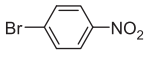
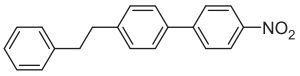
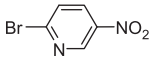
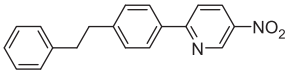
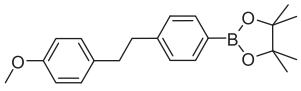
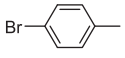
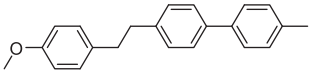
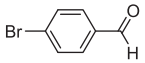
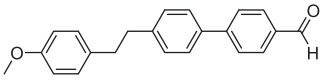
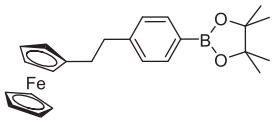
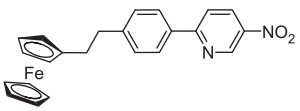
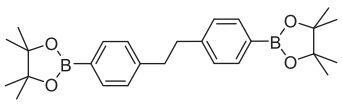
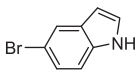
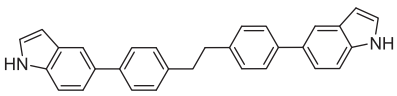
Three ruthenium-based catalysts were tested in the CM reaction of **11b**: **6a** was found to be inefficient (Table 6, entry 1), however, catalysts **6b** and **6c** were both suitable for this reaction since the expected product **12a** was obtained in moderate yields (e.g., 54% yield with **6b**, Table 6, entry 2 and 62% yield with **6c**, Table 6, entry 4). The CM reaction was also attempted on **11c** with olefin **5d**, catalyzed by **6b**, which gave the expected product **12b** in 75% yield (Table 6, entry 5). *E*/*Z* ratios were generally high.

More examples of related biarylethyl aryl analogues were obtained through reduction of the nitro group in **10b**, affording aminopyridine **13a**, which was subsequently functionalized by reaction with isovaleryl chloride to give **15a** (Scheme 2). Both the olefin and nitro group in compound **12b** were reduced by catalytic hydrogenation to afford the aryl product **13b** in 75% yield (Scheme 2).

In conclusion, we have demonstrated that 3- and 4-vinylphenylboronic acid pinacol esters are able to undergo CM reactions allowing the synthesis of ethylenic phenylboronic acid pinacol ester derivatives. The latter can be reduced, coupled via an SM reaction and functionalized leading to a library of highly substituted biarylethyl aryl and biarylethyl cycloalkyl compounds. A complementary and equally useful approach, employing an initial SM coupling, was also achieved. This highlights the synthetic potential of arylboronic esters, in furnishing libraries of compounds with drug-like properties or synthetically challenging architectures.[19,20] Compounds **7m**/**8f**, and regiosiomers, for example, **7s**, as well as the orthogonally protected boronic ester **7f**, may have applications as linkers or staplers in, for example, supramolecular chemistry or as synthons in organic synthesis and medicinal chemistry, and this is actively being pursued.[21,22] Moreover, although somewhat limited commercially, vinylaryl boronic acids should be readily syn-

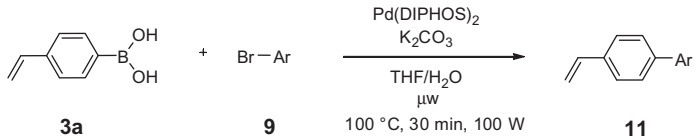
Table 4
SM reactions of compounds **8**



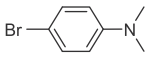
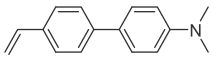
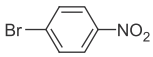
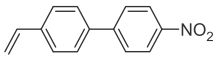
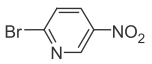
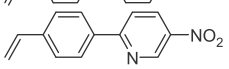
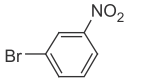
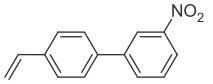
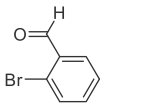
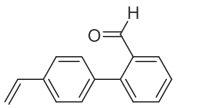
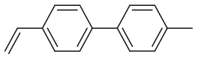
Entry	**8**	**9**	Product (**10**)		Yield[a] (%)
1	 **8a**	 **9a**		**10a**	99
2	**8a**	 **9b**		**10b**	89
3	 **8c**	 **9c**		**10c**	75
4	**8c**	 **9d**		**10d**	54
5	 **8d**	**9b**		**10e**	41[b]
6	 **8f**	 **9e**		**10f**	77

Conditions: **9** (1.1 equiv), $Pd(PPh_3)_4$ (3 mol %), Na_2CO_3 (3 equiv), toluene/ethanol/water 1:1:1, microwave irradiation (Power max., 300 W, CEM Explorer), 150 °C, 10 min. Power max is a special cooling feature which enables microwave irradiation with concomitant cooling.
[a] Isolated yields.
[b] Yield over 3 steps.

Table 5
SM couplings of **3a**

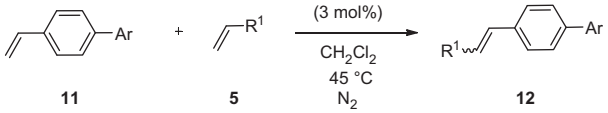


3a **9** **11**

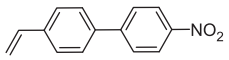
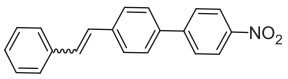
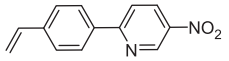
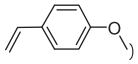
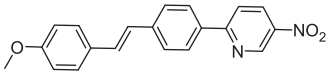
Entry	**9**		Product (**11**)		Yield (%)[a]
1		**9f**		**11a**	63
2		**9a**		**11b**	98
3		**9b**		**11c**	67
4		**9g**		**11d**	63
5		**9h**		**11e**	–
6		**9c**		**11f**	67

Conditions: ArBr (1 equiv), Pd(DIPHOS)$_2$ (1 mol %), K_2CO_3 (2.4 equiv), THF/H_2O 1:1 [5 mL for 1 mmol of ArB(OH)$_2$], CEM Explorer microwave irradiation (100 W), 100 °C, 30 min.
[a] Isolated yields.

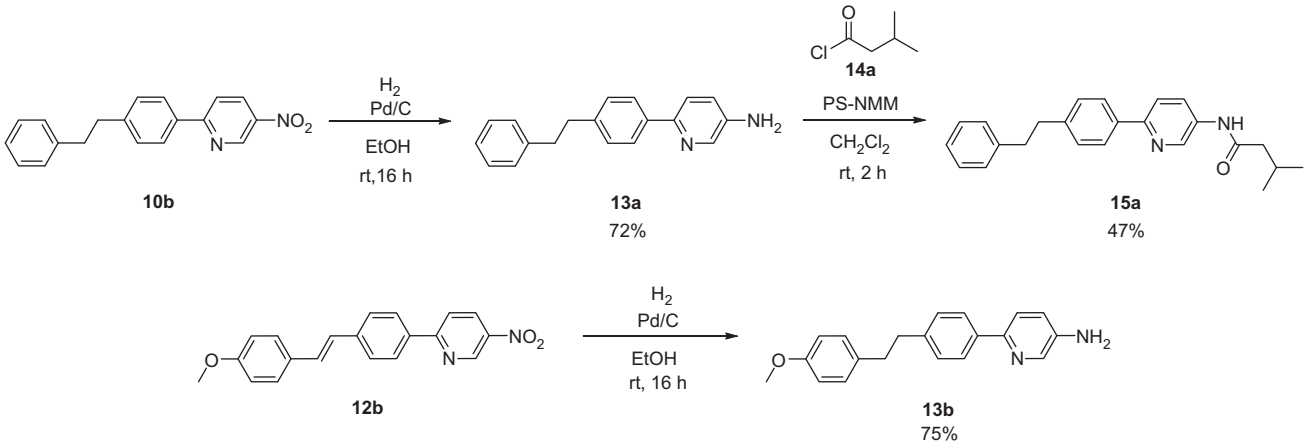
Table 6
CM reactions on compounds **11b**, **c**



11 **5** **12**

Entry	**11**	**5** (equiv)	**6**	Time (h)	Product (**12**)	*E*/*Z* ratio[a]	Yield[b] (%)
1	 **11b**	 **5a** (3)	**6a**	6	 **12a**	–	–
2	**11b**	**5a** (3)	**6b**	6	**12a**	100:0	54
3	**11b**	**5a** (1.5)	**6c**	6	**12a**	95:5	37
4	**11b**	**5a** (3)	**6c**	6	**12a**	95:5	62
5	 **11c**	 **5d** (5)	**6b**	16	 **12b**	100:0	75

[a] Calculated by ^{1}H NMR spectroscopy.
[b] Isolated yields.



Scheme 2. Hydrogenation of compounds **10b** and **12b** (PS-NMM = polymer supported *N*-methylmorpholine base).

thesized from their vinylaryl halide precursors in a single step.[23] The solid state structures presented in the *Supplementary* data (Fig. S1) have been deposited at the Cambridge Crystallographic Centre.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.12.081.

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