Organic & Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2021, **19**, 10343

Synthesis of 5,7-diarylindoles *via* Suzuki–Miyaura coupling in water†

Vijayaragavan Elumalai and Jørn H. Hansen *

Received 20th October 2021,
Accepted 16th November 2021

DOI: 10.1039/d1ob02058g

rsc.li/obc

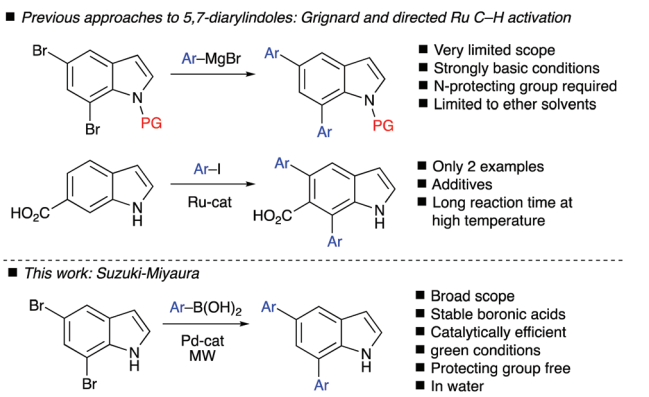
The synthesis of novel 5,7-diaryl and diheteroaryl indoles has been explored *via* efficient double Suzuki–Miyaura coupling. The method notably employs a low catalyst loading of $Pd(PPh_3)_4$ (1.5 mol%/coupling) and water as the reaction solvent to obtain 5,7-diarylated indoles without using *N*-protecting groups in up to 91% yield. The approach is also suitable for *N*-protected and 3-substituted indoles and constitutes an important green and convenient arylation strategy for the benzenoid ring of indoles. The synthesized diarylindoles are fluorescent.

Introduction

Indole is an essential nitrogen-containing heterocycle and a central scaffold in several natural products and other bioactive molecules.[1,2] Consequently, a range of synthetic methods and strategies have been described for the functionalization of indoles.[3] C2- and C3-functionalization of the pyrrole ring has been thoroughly investigated, and this has been extensively reviewed by Sandtorv.[3a] The innate high reactivity of the pyrrole ring has left functionalization on the benzenoid ring positions (C4–7) a challenging task.[4] Frost and co-workers[5] reported in 2017 a detailed review of site-selective functionalization on the benzenoid ring. In addition, a complete review of C4-indole functionalization has been recently assembled by Ackermann and Pilarski in 2018.[6] There is clearly a need for selective functionalization methods of the benzenoid ring in order to access sparsely explored parts of indole chemical space.

Diarylindoles are important precursors for the synthesis of biologically active compounds, pharmaceuticals and organic materials. 2,3-Diarylindoles have several important biological activities[7] and, thus, a range of methodologies have been described for the synthesis of such structures.[8] Other substitution patterns than 2,3-diaryl have not been extensively reported. 5,7-Bis(4-methoxyphenyl)indole has been previously described and was generated *via* a Kumada-coupling using 5,7-dibromoindole as the precursor (Scheme 1).[9] This approach has very limited scope, requires strongly basic and otherwise very specific reaction conditions (*e.g.* ether solvents). Poly(5,7-bis(2-thiophene)-indole), a polymer used in electrochromic devices, is synthesized from 5,7-bis(2-thiophene)-indole (BTI).[10a] Diarylindoles often exhibit fluorescent properties and are, arguably, useful building blocks in organic materials chemistry.[11] The potential for applications of novel diarylindoles both as bioactives and in materials chemistry, combined with the limited number of studies of these compounds, particularly in the 5,7-disubstituted series, became the impetus for developing a practical approach to the synthesis of novel compounds in this area of chemical space.

Synthetic approaches *via* transition metal-catalysed reactions are not abundant for double arylation and typically require *N*-protecting groups.[8,9] Several examples of multiple Suzuki–Miyaura couplings on indoles and related heterocycles exist,[10b–e] however, none in which 5,7-diarylindoles were generated. One approach was found involving a Ru-catalyzed C–H activation (Scheme 1),[8c] however, the scope was very narrow and this approach required a carboxylic acid directing group in the 6-position and prolonged reaction time at high temperature in order to generate the 5,7-diarylindoles. In this paper,



Scheme 1 Comparison of previous approaches and current work.

Chemical Synthesis and Analysis Division, Department of Chemistry, UiT The Arctic University of Norway, Hansine Hansens veg 54, 9037 Tromsø, Norway. E-mail: jorn.h.hansen@uit.no

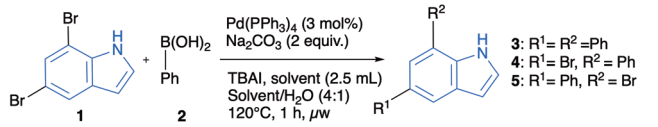
†Electronic supplementary information (ESI) available: Detailed experimental procedures, characterization and NMR-spectra. See DOI: 10.1039/d1ob02058g

we demonstrate a straightforward, protecting-group free and green approach to 5,7-diarylindoles employing a highly efficient Suzuki–Miyaura coupling in water to access a range of novel 5,7-disubstituted indoles.

Results and discussion

To obtain 5,7-diarylindoles we envisioned starting from commercially available 5,7-dibromoindole (**1**) which could undergo double cross-coupling with readily available arylboronic acids. Initially, classical conditions for the Suzuki–Miyaura coupling were explored, including palladium tetrakistriphenylphosphine as catalyst, DMF/water as solvent, sodium carbonate as base and *tert*-butylammonium iodide as an additive (Table 1).[12] The studies of coupling **1** with phenylboronic acid revealed that full conversion and excellent yield (95%) could be obtained at 120 °C with 3 equivalents of boronic acid present. Moreover, the reaction was completed efficiently in a microwave reactor after one hour employing only 3 mol% of palladium catalyst, effectively 1.5 mol% per functionalization event. A similar result was found for reaction under thermal heating in a sealed tube, but the microwave reaction was more convenient to conduct. Furthermore, the study also showed that protection of the indole nitrogen is not necessary in this chemistry. The double functionalization worked effectively in different solvent systems such as methanol, methanol/water, acetone/water, THF/water and ethanol/water (full conversion).

Table 1 Select entries from the optimization of conditions

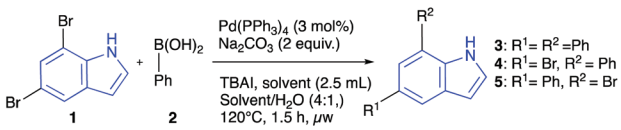


No.	Solvent	Deviation from conditions	Conversion (GC) **1** (%)	**3**[a,b] (%)	**4** + **5**[b] (%)
1	DMF/H_2O	TBAI (10 mol%)	>99	95 (80)[c]	nd
2	DMF	—	65	15	50
3	DMF/H_2O	150 °C, 10% Pd/S-Phos	>99	>99	nd
4	MeOH/H_2O	TBAI (10 mol%)	>99	>99	nd
5	MeOH	—	>99	>99	nd
6	Acetone/H_2O	TBAI (10 mol%)	>99	>99	nd
7	Acetone	—	71	10	61
8	MeCN/H_2O	TBAI (10 mol%)	93	46	47
9	**MeCN**	—	**81**	**15**	**66**
10	THF/H_2O	TBAI (10 mol%)	>99	>99	nd
11	THF	—	76	15	61
12	EtOH/H_2O	TBAI (10 mol%)	98	98	nd
13	**H_2O**	—	**96**	**96 (83)**[c]	**nd**

[a] General procedure: In a microwave vial, 5,7-dibromoindole **1** (1.0 mmol), phenylboronic acid **2** (3.0 mmol), Na_2CO_3 (2.0 mmol) and $Pd(PPh_3)_4$ (0.03 mmol, 3 mol%) were added. The vial was sealed, flushed with a stream of dry nitrogen and added the solvent (2.5 mL) or solvent/H_2O (4 : 1 ratio, 2.5 mL) *via* the septum. The vial was sonicated for 30 s and heated under microwave irradiation for 1 hour at 120 °C. [b] Conversion based on GC. nd = not detected. [c] Isolated yield.

The reaction in pure methanol without adding TBAI was just as effective as the binary systems, suggesting that this additive was not necessary in the polar solvent system and that binary solvent mixtures were not necessary either to achieve an efficient transformation. These observations led to testing pure water (without TBAI) as the solvent, which yielded essentially full conversion and 83% isolated yield of the 5,7-diphenylindole **3**. Another interesting observation from the survey arose from monitoring the formation of mono-coupled products (**4** + **5** combined). When using acetonitrile as solvent, it appeared that mono-coupling was the favoured product (4.4 : 1 ratio). A similar selectivity was observed in THF and suggested the possibility of a solvent-controlled mono-coupling, a phenomenon that has not been studied systematically to our knowledge. To investigate this, a survey of solvents and catalysts was conducted in which only 1.5 equivalents of boronic acid was employed, and otherwise keeping the reaction conditions the same as before (Table 2). It was found that **4** (5-bromo-7-phenylindole) is the predominant species when the conversion is below *ca.* 50% in acetonitrile or THF. All three species **3**–**5** are detectable at higher conversions and only the doubly coupled product **3** is detectable when using water or methanol as solvents. 30% isolated yield of **4** was obtained at 54% conversion of **1** with negligible amounts of **5** and **3** present. Although not a great synthetic result, it is interesting and may be one of few direct routes to this disubstituted indole. In summary, our survey of the reaction variables led to a set of green and mild conditions for double Suzuki–Miyaura couplings of 5,7-dibromoindole **1** including low catalyst

Table 2 Selectivity between mono- and double coupling products



No.	Solvent	Pd-Catalyst	Conversion (GC) **1** (%)	**4**[a,b] (%)	**5**[b] (%)	**3**[b] (%)
1	**MeCN**	**$Pd(PPh_3)_4$**	**54**	**53(30%)**[c]	**nd**	**1**
2	MeCN/H_2O	$Pd(PPh_3)_4$	87	40	23	23
3	H_2O	$Pd(PPh_3)_4$	>99	nd	nd	99
4	MeOH/H_2O	$Pd(PPh_3)_4$	>99	Traces	Traces	99
5	THF	$Pd(PPh_3)_4$	49	38	8	2
6	MeCN	$Pd(PPh_3)_2CI_2$	51	50	nd	1
7	MeCN	$Pd_2(dba)_3$	Traces	Traces	Traces	nd
8[d]	MeCN	$Pd(PPh_3)_4$	41	35	4	1
9[e]	MeCN	$Pd(PPh_3)_4$	Traces	Traces	Traces	nd
10[f]	MeCN	$Pd(PPh_3)_4$	63	41	15	6

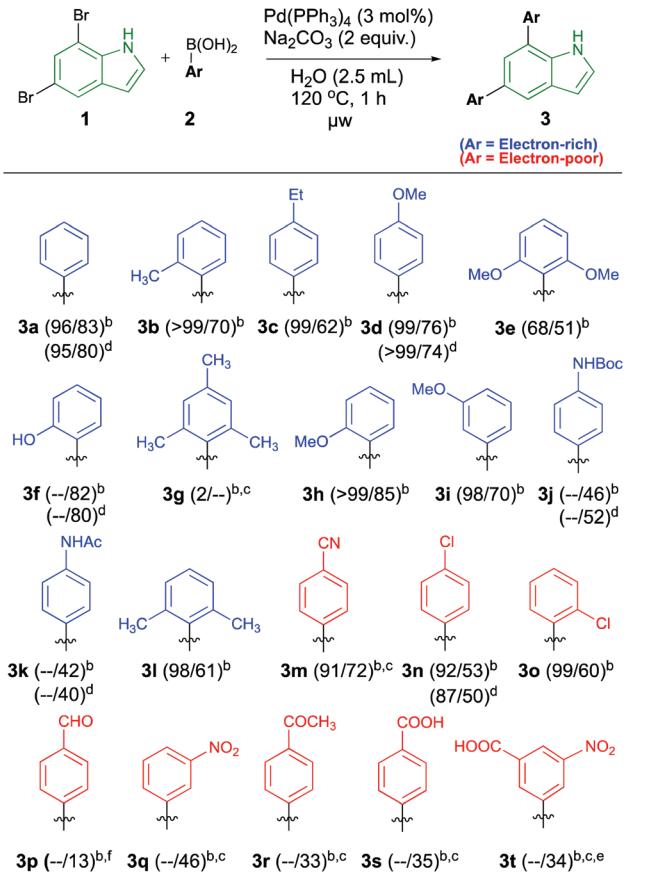
[a] General procedure: In a microwave vial, 5,7-dibromoindole **1** (1 mmol), phenylboronic acid **2** (1.5 mmol), Na_2CO_3 (2 mmol), and Pd-catalyst (0.03 mmol, 3 mol%) were added. The vial was sealed and flushed with stream of dry nitrogen and added the solvent (2.5 ml)/solvent/H_2O (4 : 1 ratio, 2.5 ml) *via* the septum. The vial was sonicated for 30 s and heated under microwave irradiation for 1.5 hours at 120 °C. [b] Conversion based on GC. [c] Isolated yield. nd-not detected. [d] Ligand S-phos (6 mol%) was used. [e] Reaction performed at ambient temperature. [f] 2 equivalents of boronic acid was used.

loading and water as the reaction solvent, but also demonstrated that a variety of solvent choices are available as long as a protic co-solvent is also added. This feature is useful in cases where the solubility of reaction components needs to be modified.

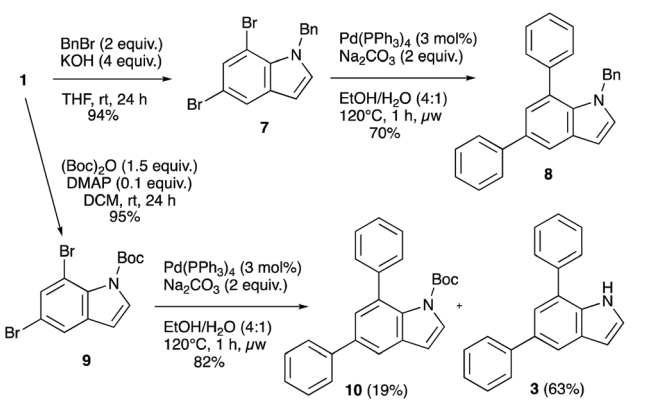
The scope of electron-rich arylboronic acids was studied first (Scheme 2 in blue). These are well-tolerated and afforded moderate to excellent yields in most cases. Some of the reactions were also conducted in DMF/water or EtOH/water for comparison, and these all yielded similar results as in pure water. In the *para*-substituted series, both ethyl (**3c**) and methoxy (**3d**) afforded good 62% and 76% isolated yields of **3c**. Boc- and acetyl protected amino groups yielded 46% and 42% yields of **3j** and **3k**, respectively. It appears that the good π-donating methoxy group is generally increasing the yields, because also *meta* and *ortho*-methoxy substituted products **3i** and **3h** were formed in good yields of 70% and 85% respectively. The latter further shows that the reaction is relatively insensitive to steric clash with the *ortho*-substituent of the boronic acid. This notion was further challenged with *ortho*-methyl and *ortho*-hydroxy substituents affording **3b** and **3f** in 70% and 82% yields, respectively. The good yield of the latter further supports that good π-donation is an important factor to increase the yield. The introduction of substituents in both *ortho*-positions led to somewhat diminished yields. *ortho*-Dimethyl and dimethoxy patterns still afforded products **3l** and **3e** in 61% and 51% yields, respectively. Attempts to introduce mesityl groups did not result in any practically important product formation of **3g** under these reaction conditions.

In the series of electron-withdrawing groups, generally lower to moderate yields were observed. The *para* and *ortho*-chlorosubstituted products **3n** and **3o** were formed in 53% and 60% yields, respectively, under the standard reaction conditions. The remaining electron-withdrawing systems **3p–3t** were formed in rather low 13–46% yields, thus demonstrating that such groups have a detrimental effect on the yield. Some improvement could be observed when increasing reaction times and temperatures. For example, the conversion was improved from 31% to 91% with an isolated yield of 72% of the *para*-cyano substituted product **3m**, suggesting that high yields are also possible in this series. Overall, the examples demonstrate tolerance towards halides, carboxy-, cyano- and nitro-groups and that *ortho*, *para* and *meta*-substituent patterns can be used in this chemistry.

Another aspect of relevance to the synthetic utility of the double coupling approach would be compatibility with some commonly employed protecting groups at nitrogen. The chemistry is nicely compatible with a free N–H, which is a major strength, but protecting groups are sometimes desired in synthesis for various reasons. We therefore employed benzyl- and Boc-protected model indoles in order to demonstrate that these are also tolerated in the arylation chemistry (Scheme 3), and the benzyl-protected 5,7-dibromoindole **7** underwent a clean transformation to the diarylindole **8** in 70% isolated yield. The *N*-Boc protected system **9** also underwent double arylation with a very good overall yield of 82%, but was mostly deprotected under the reaction conditions (63% free NH



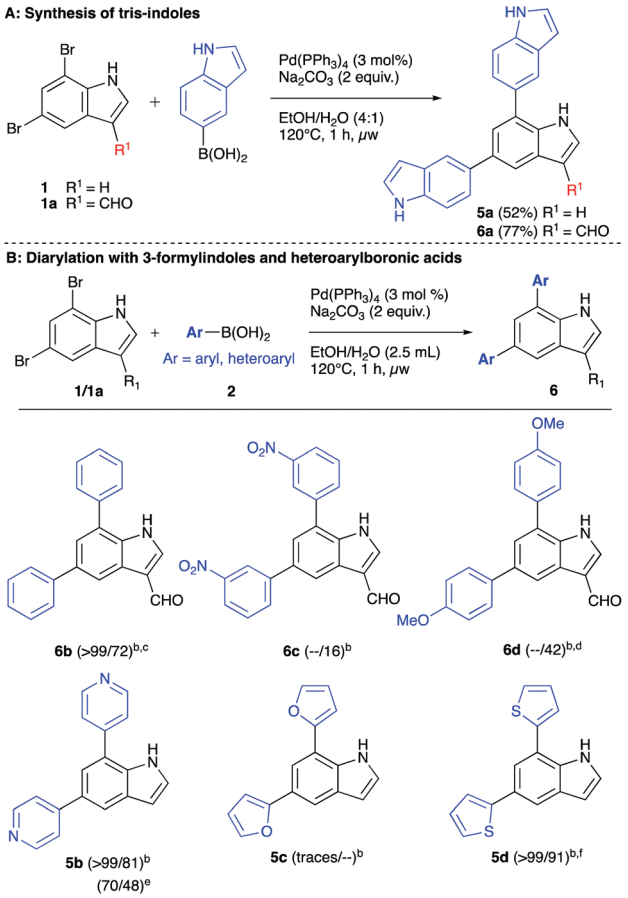
Scheme 2 Scope of arylboronic acids in the indole double arylation. [a] Reaction procedure: In a microwave vial, 5,7-dibromoindole **1** (1 mmol), arylboronic acid **2** (3 mmol), Na_2CO_3 (2 mmol), and $Pd(PPh_3)_4$ (0.03 mmol, 3 mol%) were added. The vial was sealed and flushed with stream of dry nitrogen and added H_2O (2.5 ml) *via* the septum. The vial was sonicated for 30 s and heated under microwave irradiation for 1 hour at 120 °C. [b] Conversion based on GC/isolated yield. [c] Reaction was performed at 140 °C for 90 min. [d] In DMF/H_2O 4 : 1. [e] Mixture (both mono and bis-coupling) of products were observed. [f] Reaction was performed in EtOH/H_2O at 120 °C for 1 hour.



Scheme 3 Double arylation with some common *N*-protecting groups.

product). This lability of the Boc-group under thermal conditions is not unexpected and may allow for simultaneous diarylation/deprotection if the conditions are optimized further. These examples demonstrate that the diarylation chemistry is compatible with *N*-protecting groups.

Finally, we employed some heterocyclic boronic acids in this chemistry under the standard reaction conditions as well as 3-substituted indole **1a** (Scheme 4). The system employing the indolyl boronic acid is particularly interesting, as it constitutes a synthesis of tris-indoles (Scheme 4A). The parent indole **1** afforded the tris-indole **5a** in 52% yield. If a 3-formyl substituted indole was employed in the chemistry, the corresponding tris-indole **6a** was formed in 77% yield. Employing the 3-formyl substituted indole further afforded 16–72% yields



Scheme 4 Tris-indole formation and diarylation with 3-formylindoles and heteroarylboronic acids. [a] Reaction procedure: In a microwave vial, 5,7-dibromoindole-3-carbaldehyde **1** (1 mmol), arylboronic acid **2** (3 mmol), Na_2CO_3 (2 mmol) and $Pd(PPh_3)_4$ (0.03 mmol, 3 mol%) were added. The vial was sealed and flushed with stream of dry nitrogen and added EtOH/H_2O (4 : 1 ratio, 2.5 ml) *via* the septum. The vial was sonicated for 30 s and heated under microwave irradiation for 1 hour at 120 °C. [b] Conversion based on GC/isolated yield. [c] Only traces of product was observed when H_2O (100%) was used as a solvent. [d] Obtained an unseparable mixture of *ca.* 10% mono-functionalized indole and **6d**. Yield of **6** was estimated from NMR-ratio of the two components in the isolated material. [e] In DMF/H_2O 4 : 1. [f] 50% conversion was obtained in water as solvent.

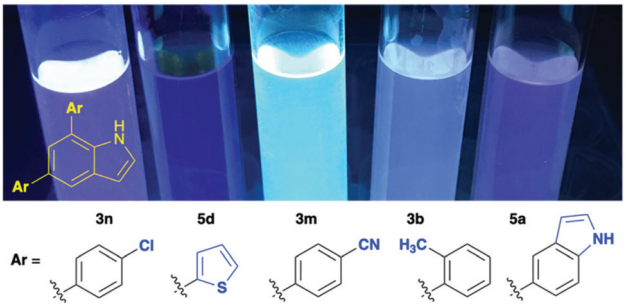


Fig. 1 Fluorescence of 5,7-diarylindoles dissolved in MeOH and irradiated with a UV-lamp (365 nm).

of **6b–d** (Scheme 4B). Concerning heteroaromatic boronic acids, 4-pyridyl boronic acid afforded full conversion and 81% isolated yield of **5b** (Scheme 4B). Surprisingly, the furanyl boronic acid only produced trace amounts of product, whereas 2-thiophenyl boronic acid afforded the expected product **5d** in excellent chemical yield of 91%. In these reactions, some ethanol was required in the solvent mixture to improve the solubility of the boronic acids.

The 5,7-diarylindoles generated in this study are fluorescent. As such, they are of interest for organic materials science and as potential fluorescent probes in molecular imaging. Although the fluorescent properties of these compounds are not central to this study, we decided to visually ascertain to what extent the differences in structure of the introduced aryl substituents influenced the fluorescence. Solutions of five compounds (**3n**, **5d**, **3m**, **3b** and **5a**) in methanol were irradiated with a simple hand-held UV-lamp (365 nm) and a broad spectrum of fluorescence intensities are evident (Fig. 1). Notably, the novel compound **3m** appears to be particularly bright, likely since it is a push–pull electronic system. A more detailed study of these properties will be disclosed in the near future.

Conclusions

In conclusion, we have disclosed a practical and green Suzuki–Miyaura coupling approach for the synthesis of 5,7-diarylindoles in moderate to excellent yields. Some selectivity for mono-coupling at the 7-position can be achieved in acetonitrile and THF. The functionalization proceeds readily in about 1 hour with only 1.5 mol% catalyst loading per coupling in water or water/ethanol solvent mixtures under microwave heating conditions. We have also demonstrated its synthetic utility in the synthesis of tris-indoles and that the chemistry is compatible with some common protecting groups at nitrogen and a formyl group in the indole 3-position. This approach should be a preferred method for the synthesis of 5,7-diarylindoles. The 5,7-diarylindoles display interesting fluorescence properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge funding for this research project by the Research Council of Norway (grant no. 275043 CasCat).

Notes and references

1 For some examples of natural products containing the indole moiety, see: (*a*) N.-Y. Ji, X.-M. Li, L.-P. Ding and B.-G. Wang, *Helv. Chim. Acta*, 2007, **90**, 385–391; (*b*) S. R. Walker, E. J. Carter, B. C. Huff and J. C. Morris, *Chem. Rev.*, 2009, **109**, 3080–3098; (*c*) R. J. Melander, M. L. Minvielle and C. Melander, *Tetrahedron*, 2014, **70**, 6363–6372.

2 (*a*) D. A. Horton, G. T. Bourne and M. L. Smythe, *Chem. Rev.*, 2000, **103**, 893–930; (*b*) M. Z. Zhang, Q. Chen and G. F. Yang, *Eur. J. Med. Chem.*, 2015, **89**, 421–424; (*c*) V. Sharma, P. Kumar and D. Pathak, *J. Heterocycl. Chem.*, 2010, **47**, 491–502; (*d*) S. Biswal, U. Sahoo, S. Sethy, H. K. S. Kumar and M. Banerjee, *Asian J. Pharm. Clin. Res.*, 2012, **5**, 1–6; (*e*) A. W. Woodward and B. Bartel, *Ann. Bot.*, 2005, **95**, 707–735; (*f*) C. V. Galliford and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2007, **46**, 8748–8758; (*g*) B. Trost and M. K. Brennan, *Synthesis*, 2009, 3003–3025; (*h*) A. J. Kochanowska-Karamyan and M. T. Hamann, *Chem. Rev.*, 2010, **110**, 4489–4497; (*i*) R. D. Taylor, M. MacCoss and A. D. G. Lawson, *J. Med. Chem.*, 2014, **57**, 5845–5859.

3 For a review, see: (*a*) A. H. Sandtorv, *Adv. Synth. Catal.*, 2015, **357**, 2403–2435. For key seminal publications, see: (*b*) X. Wang, B. S. Lane and D. Sames, *J. Am. Chem. Soc.*, 2005, **127**, 4996–4997; (*c*) D. R. Stuart, E. Villemure and K. Fagnou, *J. Am. Chem. Soc.*, 2007, **129**, 12072–12073; (*d*) N. P. Grimster, C. Guantlett, C. R. A. Godfrey and M. J. Gaunt, *Angew. Chem., Int. Ed.*, 2005, **44**, 3125–3129; (*e*) R. J. Phipps, N. P. Grimster and M. J. Gaunt, *J. Am. Chem. Soc.*, 2008, **130**, 8172–8174; (*f*) N. R. Deprez, D. Kalyani, A. Krause and M. S. Sanford, *J. Am. Chem. Soc.*, 2006, **128**, 4972–4973; (*g*) N. Lebrasseur and I. Larrosa, *J. Am. Chem. Soc.*, 2008, **130**, 2926–2927; (*h*) M. Bandini and A. Eichholzer, *Angew. Chem., Int. Ed.*, 2009, **48**, 9608–9644.

4 (*a*) A. K. Pitts, F. O'Hara, R. H. Snell and M. J. Gaunt, *Angew. Chem., Int. Ed.*, 2015, **54**, 5451; (*b*) A. D. Yamaguchi, K. M. Chepiga, J. Yamaguchi, K. Itami and H. M. Davies, *J. Am. Chem. Soc.*, 2015, **137**, 644; (*c*) An approach using stoichiometric Pd is reported: J. Liang, W. Hu, P. Ta and Y. Jia, *J. Org. Chem.*, 2013, **78**, 5810; (*d*) P. Tao, J. Liang and Y. Jia, *Eur. J. Org. Chem.*, 2014, 5735.

5 J. A. Leitch, Y. Bhonoah and C. G. Frost, *ACS Catal.*, 2017, **7**, 5618.

6 J. Kalepu, P. Gandeepan, L. Ackermann and L. T. Pilarski, *Chem. Sci.*, 2018, **9**, 4203–4216.

7 (*a*) J. Szmuszkovicz, E. M. Glenn, R. V. Heinzelman, J. B. Hester, Jr. and G. A. Youngdale, *J. Med. Chem.*, 1966, **9**, 527–536; (*b*) B. F. McAdam, F. Catella-Lawson, I. A. Mardini, S. Kapoor, J. A. Lawson and G. A. FitzGerald, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, **96**, 272–277; (*c*) H. El-Diwani, S. S. Nakkady, O. H. Hishmat, O. A. El-Shabrawy and S. S. Mahmoud, *Pharmazie*, 1992, **47**, 178–181; (*d*) H. I. El-Diwani, N. A. M. M. Shmeiss and N. M. Saleh, *Pol. J. Chem.*, 1995, **69**, 470–475; (*e*) N. A. M. M. Shmeiss, M. M. F. Ismail, H. I. El-Diwani, A. B. Hassan and S. A. Nada, *Modell. Meas. Control, C*, 1997, **55**, 11–36; (*f*) R. L. Jones, Y.-M. Qian, H. Wise, H. N. C. Wong, W.-L. Lam, H.-W. Chan, A. P. C. Yim and J. K. S. Ho, *J. Cardiovasc. Pharmacol.*, 1997, **29**, 525–535; (*g*) O. H. Hishmat, M. Y. Ebeid, S. S. Nakkady, M. M. Fathy and S. S. Mahmoud, *Bull. Chim. Farm.*, 1999, **138**, 259–266.

8 (*a*) Y. Liu and G. W. Gribble, *Tetrahedron Lett.*, 2000, **41**, 8717–8721; (*b*) M. F. Ibad, D. S. Zinad, M. Hussain, A. Ali, A. Villinger and P. Langer, *Tetrahedron*, 2013, **69**, 7492–7504; (*c*) M. Simonetti, D. M. Cannas, A. Panigrahi, S. Kujawa, M. Kryjewski, P. Xie and I. Larrosa, *Chem. – Eur. J.*, 2017, **23**, 549–553.

9 S. Ishikawa and K. Manabe, *Tetrahedron*, 2011, **67**, 10156–10163.

10 (*a*) X. Yang, C. Liu, J. Guo, L. Wang and G. Nie, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 2356–2364; (*b*) J. Pang, S. Yuan, J. Qin, M. Wu, C. T. Lollar, J. Li, N. Huang, B. Li, P. Zhang and H.-C. Zhou, *J. Am. Chem. Soc.*, 2018, **140**, 12328–12332; (*c*) S. T. Handy, T. Wilson and A. Muth, *J. Org. Chem.*, 2007, **72**, 8496–8500; (*d*) S. C. Anderson and S. T. Handy, *Synthesis*, 2010, 2721–2724; (*e*) N. Bisballe, M. Hedidi, C. S. Demmer, F. Chevallier, T. Roisnel, V. Dorcet, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis, G. Bentabed-Ababsa, L. Bunch and F. Mongin, *Eur. J. Org. Chem.*, 2018, 3904–3913.

11 M. Miyasaka, A. Fukushima, T. Satoh, K. Hirano and M. Miura, *Chem. – Eur. J.*, 2009, **15**, 3674–3677.

12 (*a*) N. Miyaura, T. Yanagi and A. Suzuki, *Synth. Commun.*, 1981, **11**, 513–519; (*b*) P. R. Eastwood, *Tetrahedron Lett.*, 2000, **41**, 3705–3708; (*c*) A. F. Littke, S. Dai and G. C. Fu, *J. Am. Chem. Soc.*, 2000, **122**, 4020–4028; (*d*) R. R. González, L. Liguori, A. Martinez Carrillo and H.-R. Bjørsvik, *J. Org. Chem.*, 2005, **70**, 9591–9594; (*e*) I. Hoffmann, B. Blumenröder, S. O. N. Thumann, S. Dommer and J. Schatz, *Green Chem.*, 2015, **17**, 3844; (*f*) V. Elumalai, A. H. Sandtorv and H.-R. Bjørsvik, *Eur. J. Org. Chem.*, 2016, 1344–1354; (*g*) V. Elumalai and H.-R. Bjørsvik, *ChemistrySelect*, 2017, **2**, 9387.