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ARTICLE

A Waste-Minimized Protocol for Copper-Catalyzed Ullmann-Type Reaction in a Biomass Derived Furfuryl Alcohol/Water Azeotrope

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We report the use of biomass-derived furfuryl alcohol as an effective bidentate ligand able to promote the Ullmann-type copper-catalyzed coupling of aryl halides with heteroaromatic or aliphatic amines. Furfuryl alcohol (FA) can be used in mixture with water to form the corresponding azeotrope (20%wt of FA) and therefore can be easily recovered and reused. This protocol is efficiently applicable to substrates with various electronic nature and affords the expected products (27 examples) in generally good to excellent yields. It has been also demonstrated that the protocol is both chemically and environmentally effective as the azeotropic mixture can be easily and almost quantitatively recovered at the end of the process.

Introduction

N-Arylation strategies are undoubtedly among the most useful reactions in organic chemistry. In fact, the aromatic amine moiety is almost ubiquitous in materials that find wide applications in different areas such as medicinal chemistry,[1] agrochemistry,[2] and material sciences.[3]A great number of catalytic protocols for the classical Ullmann reaction have been disclosed and copper-catalyzed *N*-arylations can be considered nowadays as a valid alternative to the palladium-catalyzed Buchwald–Hartwig protocols.[4] Copper-based methods offer advantages in terms of price and toxicity, although higher loadings, harsher reaction conditions and high-boiling aprotic solvents such as DMF, DMSO, toluene and butyronitrile are often required.[4] Progress towards highly chemically efficient and greener conditions has however recently been made, with protocols appearing in the literature using homeopathic copper loadings,[5] but also with examples of copper-catalyzed *N*-arylations in aqueous media,[6] generally employing phase transfer catalysts.

Although still not completely understood, the most widely accepted mechanism for this type of transformation involves a Cu(I)/Cu(III) catalytic cycle. This would involve the initial formation of a copper(I)-nucleophile species, promoted by the use of an inorganic base such as K_3PO_4 or K_2CO_3, that would then undergo an oxidative addition with the aryl halide. The generated copper(III)-intermediate would then afford the coupling product through a reductive elimination, which would also regenerate the Cu(I)-catalyst.[7]

Despite the great variety of reported methodologies and the above-mentioned recent advances, no specific effort has been reported for the definition of a protocol for the Ullmann-type coupling combining chemical efficiency and waste-minimization green chemistry restrictions. One of the most critical aspects that need to be addressed at this aim is the selection of the reaction medium, which is well known to be responsible for most of the waste generated in organic syntheses, particularly in pharmaceutical industries.[8] In this perspective, the shift from fossil-derived to biomass-derived[9] and most importantly recoverable solvents, would represent a significant improvement in terms of sustainability, particularly for large scale productions.

Following this line of thought, our research group has recently demonstrated that an accurate choice of solvent and reaction conditions can allow the access to chemically effective conditions and also the drastic reduction of waste, as proven by the E-factor calculation.[10-12] We have also proposed the use of γ-valerolactone (GVL), a chemical deriving from lignocellulosic biomass,[11] as an efficient and greener alternative to common polar aprotic solvents in several palladium-catalyzed reactions, including cross-couplings and C–H functionalizations.[12] Looking for other biomass-derived chemicals that could find potential application as reaction media in chemical processes, we identified furfuryl alcohol (FA) as a possible candidate. This chemical is produced from hemicellulose, and finds its main application in the synthesis of resins and as a precursor for the synthesis of other chemicals.[13]

FA is soluble in common organic solvents (e.g. ethyl acetate, chloroform, acetone), and is miscible with water. Very interestingly, although FA has a relatively high boiling point (171 °C), it forms an azeotrope with water (20 wt% of FA) that boils at 98.5 °C, a convenient temperature for distillation. Besides,

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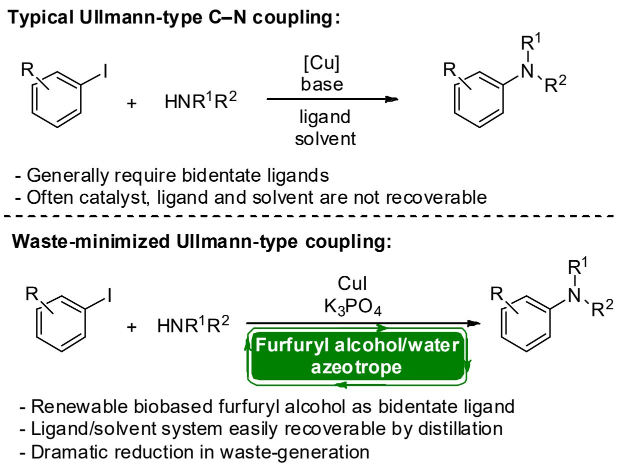
homogeneous mixtures of an organic solvent and water are often used as reaction media in several reactions, mainly to ensure dissolution of organic reactants as well as inorganic additives. For this reason, we are also developing sustainable protocols by exploiting the use of an azeotropic mixture as an effective tool to simplify the recovery and reuse of the reaction medium and reduce waste. We proved that this strategy is indeed applicable in a range of reactions,[14] and very recently we also reported the use of the FA/water az. as a recoverable and reusable reaction medium for the copper-catalyzed azide-alkyne cycloaddition (CuAAC). This resulted in a dramatic reduction in the amount of waste generated compared to commonly used literature protocols.[15]

Aiming at developing an efficient protocol for the Ullmann-type coupling of amines with aryl halides, we speculated that the use of an azeotropic mixture as reaction medium could be beneficial also in this case. The use of an azeotrope can in fact allow complete dissolution of the organic reactants as well as the required copper catalyst and inorganic base, and at the same time grants a simple recovery of the reaction medium. Furthermore, inspired by previous studies,[16] we hypothesized that *FA could act as a bidentate ligand for copper*, possibly resulting in an improved catalytic efficiency. In fact, most of the reported methodologies for Ullmann-type reactions make use of some sort of ligand, often *N*- or *O*-based, which result in higher product yields and faster reaction rates.[4,6,16] Specifically, for the use of FA, we have been inspired by the use of the closely related 1,2-ethanediol,[16h] or related moieties. Our reaction design based on use of the FA/water az., would thus allow the complete recovery of the reaction medium together with the ligand at the end of the reaction by simple distillation (Scheme 1).



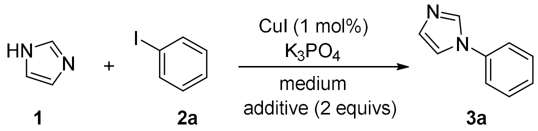
Scheme 1. Features of current work.

Results and discussion

To prove our strategy, we started the investigation by performing the model reaction between imidazole **1** and iodobenzene **2a** in different combinations of solvents and additives (Table 1). First, we used furfuryl alcohol as an additive (2 equivalents) in isopropanol, achieving higher conversion after 18 h compared to the reaction making use of 1,2-ethanediol as ligand (entry 1 vs 2). To our delight, we also found that by replacing isopropanol with water not only does the reaction proceeded to product **3a** satisfactorily, but also with slightly higher conversion (entry 3). 1,2-Ethanediol is also more effective as a ligand in water (entry 4) than in isopropanol.

Next, to test whether our strategy could allow for a waste minimized protocol for the Ullmann reaction, we performed the reaction using a FA/water ratio corresponding to the azeotropic mixture (20 wt% of FA) (entries 5 and 6). We found that the reaction proceeds slightly better, leading to complete conversion in 24 h and allowing isolation of the pure product **3a** in 87% yield (entry 6). We also ran the reaction with isopropanol replacing FA (entry 7). The significant drop in conversion to **3a** (23%) observed suggests that FA could have a more specific role as a copper ligand. Finally, we performed the model reaction in pure isopropanol and in water (entries 8 and 9, respectively). The reaction in water resulted in moderate conversion (54%), while the reaction in isopropanol only led to the formation of 7% of the coupling product **3a**, perhaps because of the low solubility of the inorganic base. Among representative inorganic bases, potassium phosphate resulted in the best results in the FA/water az. (see Supporting Information, SI). It is also worthy to notice that while most of the protocols using water as medium, propose the use of a phase transfer catalyst, in our case FA behaves as a ligand for copper but also lead to a homogeneous reaction mixture.

Table 1. Effect of Solvents and Additives in the Ullmann-Type Coupling of **1** with **2a**.[a]



Entry	Medium (1M)	Additive (2 eq.)	Conversion%[b]
1	*i*PrOH	1,2-Ethanediol	42
2	*i*PrOH	Furfuryl alcohol	89
3	H_2O	Furfuryl alcohol	92
4	H_2O	1,2-Ethanediol	91
5	FA/H_2O az.(20 wt% of FA)		95
6	FA/H_2O az.(20 wt% of FA)		100[c]
7	H_2O	*i*PrOH	23
8	*i*PrOH	-	7
9	H_2O	-	54

[a]Reaction conditions: Imidazole (1 eq.), iodobenzene (1 eq.), CuI (1 mol%), K_3PO_4 (2 eq.), additive (2 eq.), 150 °C, 18 h. [b]Determined by GC analysis. [c]24 h reaction time with 87% isolated yield of the pure product.

Intrigued by these results, we investigated the role of FA as bidentate ligand by performing the Ullmann reaction of **1** using related 1,2-diols/ether ligands (Scheme 2). Generally, all the tested bidentate diols and also their methyl ether gave comparable and very good results. This confirms the effectiveness of these easily accessible bidentate ligands and the beneficial effect of water as medium for the Ullmann-type reaction of imidazole **1**. FA and tetrahydro-FA showed a slightly

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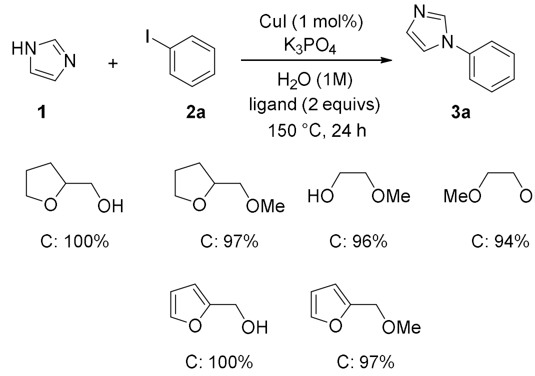
better efficiency allowing the complete disappearance of starting materials and the exclusive formation of the desired product **3a**. FA is however more functional in our strategy as it is the only one of these dioxygenated ligands able to form an azeotropic mixture with water, also in the optimal conditions for promoting the Ullmann-type process.

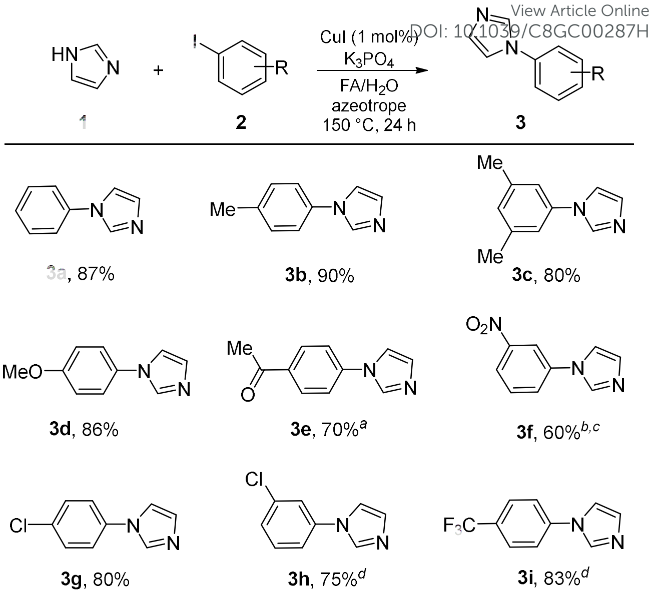


Scheme 2. Role of FA related ligands in the Ullmann-type coupling of **1**.

We then tested the influence of FA amount in the aqueous medium (see SI), finding that optimal results are obtained with a substrate/FA ratio of 1:2 (Table 1, entries 4-6). Finally, it is worth-considering that this ratio also corresponds to the use of 1M FA/water az. (20 wt% of FA in water), which represents our final target to access a protocol combining high chemical efficiency and minimal waste production.

To ultimately confirm the utility of the optimal reaction conditions and the essential advantage offered by the use of the FA/water azeotrope over previously reported protocols, we verified the possibility to recover both reaction medium and additive/ligand. On a representative 30 mmol scale, after completion of the reaction between imidazole (**1**) and iodobenzene (**2a**), distillation of the reaction medium allowed the recovery of 93% of the FA/water az., whose purity and composition was confirmed by ^{1}H NMR analysis.

Therefore, with our optimal reaction conditions based on the use of FA as a ligand in water, we extended the protocol to the reactions of imidazole (**1**) with a series of aryl iodides **2** using, otherwise, rather standard conditions, namely 1 mol % of CuI as catalyst and K_3PO_4 as base (Scheme 3). All the reactions proceeded efficiently at 150 °C in 12-24 h regardless of the electronic nature of the substituents, providing the coupling products **3** in generally good yields. The presence of a ketone functionality on the aryl iodide coupling partner was well tolerated (**3e**). Moreover, iodoarenes possessing a chloride substitution reacted selectively at the iodine position (**3g** and **3h**), thus allowing, in principle, for consecutive orthogonal functionalizations. The reaction of 1-iodo-3-nitrobenzene (**2f**) was not efficient in our standard reaction conditions, due to partial decomposition of the starting material. However, by reducing the temperature to 90 °C (but in longer reaction time), product **3f** was obtained with 60% yield.



Scheme 3. Substrate scope for imidazole arylation. Reaction conditions: imidazole (1 eq.), aryl iodide (1 eq.), CuI (1 mol%), K_3PO_4 (2 eq.), FA/H_2O azeotrope [1M], T = 150 °C, 24 h. All yields are isolated yields. ^{a}Reaction time 21 h. ^{b}Reaction time 40 h. ^{c}T = 90 °C. ^{d}Reaction time 12 h.

Next, we proceeded the investigation on the substrate scope by considering less explored and more challenging nitrogen-containing heterocycles, such as indole and carbazole (Scheme 4). To account for the reduced reactivity of these substrates compared to imidazole, the catalyst loading was increased to 5 mol%. In our reaction conditions, the *N*-arylation of indole occurred efficiently with isolated yields for the desired products **5a-h** ranging from 73% to 88%. Pleasingly, also in this case the reaction was insensitive to the electronic nature of the aryl iodide, and was tolerant to the presence of keto-groups (**5d**) or chloride substitutions (**5h**). As already observed for the arylation of imidazole, the presence of a nitro-group required lower temperatures and longer reaction time (**5f**). Carbazole also proved to be a competent substrate in our conditions, although leading to product **5i-n** in lower yields (40-65%) and longer reaction times (48-72 hours). Besides the expected reactivity limit, it is noteworthy that chloride functionalities on the aryl iodide remained untouched during the reaction.

Finally, we also tested our reaction conditions in few examples of *N*-arylation of primary alkyl amines with either simple iodobenzene or 4-iodoanisole (Table 2). The desired products **7** were isolated in yields ranging from 55% to 80%.

To complete the study, we also quantified the advantage obtainable in terms of waste produced, by calculating the E-factor (Kg of waste/Kg of product) associated with our protocol. Considering the recyclability of the recovered azeotrope (ca. 93%), we calculated a value as low as 9.7. It should be considered that for related processes most of the procedures reported in the literature are associated with much larger waste production, with E-factors usually in the order of hundreds (see SI for details). The recovered furfuryl alcohol/water azeotrope proved to pure and completely clean from any traces of products; it was reused expectedly giving identical results.

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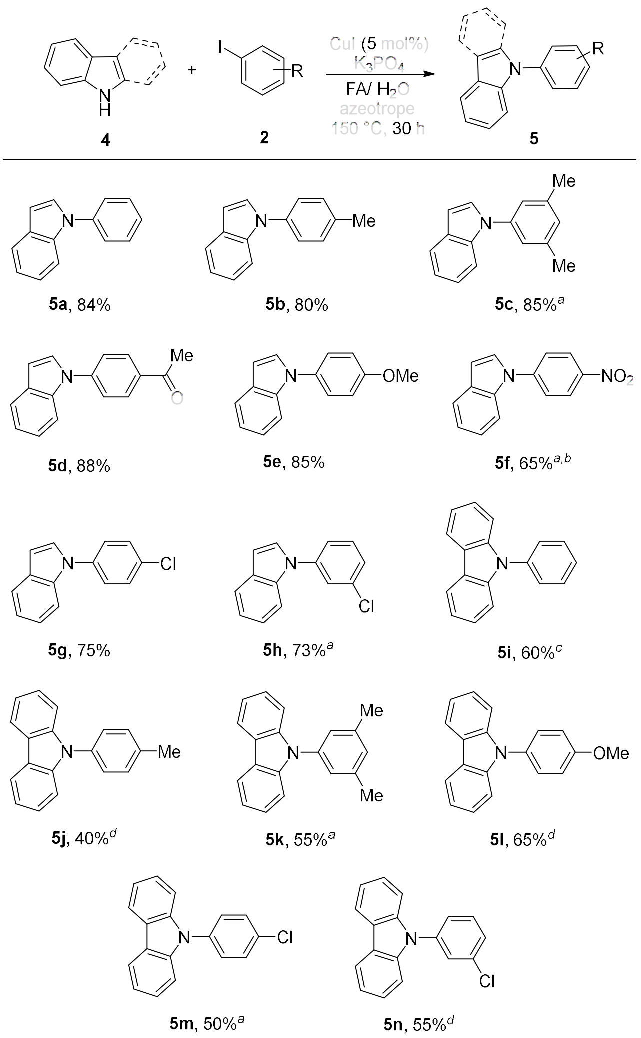
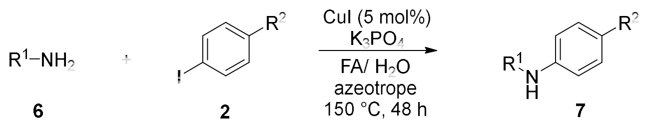


Scheme 4. Substrate scope for indole and carbazole arylation. Reaction conditions: indole or carbazole (1 eq.), aryl iodide (1 eq.), CuI (5mol%), K_3PO_4 (2 eq.), FA/H_2O azeotrope [1M], T = 150 °C, 30 h. All yields are isolated yields. [a]Reaction time 48 h. [b]T = 90 °C. [c]Reaction time 12 h. [d]Reaction time 72 h.

Table 2. Substrate scope for alkylamines arylation[a]



Entry	R¹	R²	Yield %[b]
1	*n*Hex	H	75[c] (**7a**)
2	*n*Oct	H	55 (**7b**)
3	*n*Hex	OMe	80 (**7c**)
4	*n*Oct	OMe	75 (**7d**)

[a]Reaction conditions: imidazole (1 eq.), aryl iodide (1 eq.), CuI (5 mol%), K_3PO_4 (2 eq.), FA/H_2O azeotrope [1M], T = 150 °C, 48 h. [b]All yields are isolated yields. [c]Reaction conducted with 2 eq. of **2**.

Conclusions

In conclusion, we demonstrated that the furfuryl alcohol/water azeotrope can be efficiently used as a recoverable reaction medium and activating system for the Ullmann-type copper-catalyzed coupling of aryl halides with heteroaromatic or aliphatic amines. The protocol is efficiently applicable to substrates with various electronic nature and affords the expected products in generally good yields. Importantly, our results suggest that furfuryl alcohol does not merely act as a co-solvent, but instead facilitates the reaction in a more specific fashion, arguably acting as a ligand for copper. We also demonstrated that our protocol is both chemically and environmentally effective as the azeotropic mixture can be easily and almost quantitatively recovered at the end of the process, which contributes to a dramatic reduction in waste-generation compared to established literature procedures.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (a) J. Magano and J. R. Dunetz, *Chem. Rev.*, 2011, **111**, 2177; (b) A. Ribecai, S. Bacchi, M. Delpogetto, S. Guelfi, A. M. Manzo, A. Perboni, P. Stabile, P. Westerduin, M. Hourdin, S. Rossi, S. Provera and L. Turco, *Org. Process Res. Dev.*, 2010, **14**, 895; (c) S. Bhattacharya and P. Chaudhuri, *Curr. Med. Chem.*, 2008, **15**, 1762; (d) Y.-M. Pu, Y.-Y. Ku, T. Grieme, L. A. Black, A. V. Bhatia and M. Cowart, *Org. Process Res. Dev.*, 2007, **11**, 1004; (e) A. Ghosh, J. E. Sieser, S. Caron, M. Couturier, K. Dupont-Gaudet and M. Girardin, *J. Org. Chem.*, 2006, **71**, 1258.

2 J.-M. Dupret, A. Cocaign, C. Mougin, F. Rodrigues-Lima, F. Busi, J. Dairou, M. Martins and P. Silar, in *Pesticides in the Modern World Pests Control and Pesticides Exposure and Toxicity Assessment*, ed. M. Stoytcheva, INTECH Open Access Publisher, 2011, pp. 601–614.

3 G. D'Aprano, M. Leclerc, G. Zotti and G. Schiavon, *Chem. Mater.*, 1995, **7**, 33.

4 For selected reviews, see: (a) C. Sambiagio, S. P. Marsden, A. J. Blacker and P. C. McGowan, *Chem. Soc. Rev.*, 2014, **43**, 3525; (b) F. Monnier and M. Taillefer, *Angew. Chem. Int. Ed.*, 2009, **48**, 6954; (c) G. Evano, N. Blanchard and M. Toumi, *Chem. Rev.*, 2008, **108**, 3054; (d) I. P. Beletskaya and A. V. Cheprakov, *Coord. Chem. Rev.*, 2004, **248**, 2337; (e) S. V. Ley and A. W. Thomas, *Angew. Chem. Int. Ed.*, 2003, **42**, 5400.

View Article Online
DOI: 10.1039/C8GC00287H

5 (a) J. Gao, S. Bhunia, K. Wang, L. Gan, S. Xia and D. Ma, *Org. Lett.*, 2017, **19**, 2809; (b) P.-F. Larsson, A. Correa, M. Carril, P.-O. Norrby and C. Bolm, *Angew. Chem. Int. Ed.*, 2009, **48**, 5691; (c) S. L. Buchwald and C. Bolm, *Angew. Chem. Int. Ed.*, 2009, **48**, 5586; (d) R. A. Altmann and S. L. Buchwald, *Org. Lett.*, 2006, **13**, 2779.

6 (a) Y. Liu, N. Gu, P. Liu, J. Xie, B. Dai and Y. Liu, *App. Organometal. Chem.*, 2015, **29**, 468; (b) Y. Wong, Y. Zhang, B. Yang, A. Zhang and Q. Yao, *Org. Biomol. Chem.*, 2015, **13**, 4101; (c) R. Lv, Y. Wang, C. Zhou, L. Li and R. Wang, *ChemCatChem*, 2013, **5**, 2978; (d) J. Engel-Andreasen, B. Shimpukade and T. Ulven, *Green Chem.*, 2013, **15**, 336; (e) D. Wang, F. Zhang, D. Kuang, J. Yu and J. Li, *Green Chem.*, 2012, **14**, 1268; (f) J. S. Peng, M. Ye, C. J. Zong, F. Y. Hu, L. T. Feng, X. Y. Wang, Y. F. Wang and C. X. Chen, *J. Org. Chem.*, 2011, **76**, 716; (g) X. Li, D. Yang, Y. Jiang and H. Fu, *Green Chem.*, 2010, **12**, 1097; (h) K. Swapna, S. N. Murthy and Y. V. D. Nageswar, *Eur. J. Org. Chem.*, 2010, 6678; (i) H.-J. Xu, F.-Y. Zheng, Y.-F. Liang, Z.-Y. Cai, Y.-S. Feng and D.-Q. Che, *Tetrahedron Lett.*, 2010, **51**, 669; (j) L. Liang, Z. Li and X. Zhou, *Org. Lett.*, 2009, **11**, 3294; (k) Y. Wang, Z. Wu, L. Wang, Z. Li and X. Zhou, *Chem. Eur. J.*, 2009, **15**, 8971.

7 (a) E. Sperotto, G. P. M. van Klink, G. van Koten and J. G. de Vries, *Dalton Trans.*, 2010, **39**, 10338; (b) G. J. Sherborne, S. Adomeit, R. Menzel, J. Rabeah, A. Brückner, M. R. Fielding, C. E. Willans and B. N. Nguyen, *Chem. Sci.*, 2017, **8**, 7203.

8 (a) C. Jimenez-Gonzalez, C. S. Ponder, Q. B. Broxterman and J. B. Manley, *Org. Process Res. Dev.*, 2011, **15**, 912; (b) C. Jiménez-González, A. D. Curzons, D. J. C. Constable and V. L. Cunningham, *Int. J. Life Cycle Assess.*, 2004, **9**, 114.

9 (a) S. Santoro, F. Ferlin, L. Luciani, L. Ackermann and L. Vaccaro, *Green Chem.*, 2017, **19**, 1601; (b) A. G. Corrêa, M. W. Paixão and R. S. Schwab, *Curr. Org. Synth.*, 2015, **12**, 675; (c) Y. Gu, and F. Jérôme, *Chem. Soc. Rev.*, 2013, **42**, 9550; (d) P. G. Jessop, *Green Chem.*, 2011, **13**, 1391; (e) I. T. Horváth, *Green Chem.*, 2008, **10**, 1024; (f) C. Capello, U. Fischer and K. Hungerbühler, *Green Chem.*, 2007, **9**, 927.

10 For selected examples see: (a) F. Fringuelli, D. Lanari, F. Pizzo and L. Vaccaro, *Green Chem.*, 2010, **12**, 1301; (b) R. Girotti, A. Marrocchi, L. Minuti, O. Piermatti, F. Pizzo and L. Vaccaro, *J. Org. Chem.*, 2006, **71**, 70; (c) S. Bonollo, F. Fringuelli, F. Pizzo and L. Vaccaro, *Synlett*, 2007, 2683; (d) L. Castrica, F. Fringuelli, L. Gregoli, F. Pizzo and L. Vaccaro, *J. Org. Chem.*, 2006, **71**, 9536; (e) F. Fringuelli, F. Pizzo and L. Vaccaro, *J. Org. Chem.*, 2001, **66**, 3554; (f) F. Fringuelli, F. Pizzo and L. Vaccaro, *Synlett*, 2000, 311.

11 (a) A. M. Raspolli Galletti, C. Antonetti, V. De Luise and M. Martinelli, *Green Chem.*, 2012, **14**, 688; (b) S. W. Fitzpatrick, *World Patent*, WO96/40609, 1996.

12 (a) F. Ferlin, S. Santoro, L. Ackermann and L. Vaccaro, *Green Chem.*, 2017, **19**, 2510; (b) D. Rasina, A. Kahler-Quesada, S. Ziarelli, S. Warratz, H. Cao, S. Santoro, L. Ackermann and L. Vaccaro, *Green Chem.*, 2016, **18**, 5025; (c) X. Tian, F. Yang, D. Rasina, M. Bauer, S. Warratz, F. Ferlin, L. Vaccaro, and L. Ackermann, *Chem. Commun.*, 2016, **52**, 9777; (d) G. Strappaveccia, E. Ismalaj, C. Petrucci, D. Lanari, A. Marrocchi, M. Drees, A. Facchetti and L. Vaccaro, *Green Chem.*, 2015, **17**, 365; (e) G. Strappaveccia, L. Luciani, E. Bartollini, A. Marrocchi, F. Pizzo and L. Vaccaro, *Green Chem.*, 2015, **17**, 1071; (f) E. Ismalaj, G. Strappaveccia, E. Ballerini, F. Elisei, O. Piermatti, D. Gelman and L. Vaccaro, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2461.

13 (a) G. Li, N. Li, M. Zheng, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Green Chem.*, 2016, **18**, 3607; (b) A. Gandini, in *Biopolymers–New Materials for Sustainable Films and Coatings*, ed. D. Plackett, John Wiley & Sons, Ltd, 2011, pp. 179–209; (c) J.-P. Lange, W. D. van de Graaf and R. J. Haan, *ChemSusChem*, 2009, **2**, 437; (d) A. Gandini and M. N. Belgacem, in *Monomers, Polymers and Composites from Renewable Resources*; Elsevier: Amsterdam, 2008, pp. 115–152; (e) A. Gandini and M. N. Belgacem, *Prog. Polym. Sci.*, 1997, **22**, 1203.

14 (a) V. Kozell, M. McLaughlin, G. Strappaveccia, S. Santoro, L. A. Bivona, C. Aprile, M. Gruttadauria and L. Vaccaro, *ACS Sustainable Chem. Eng.*, 2016, **4**, 7209; (b) M. Nocchetti, C. Petrucci, F. Costantino, O. Piermatti and L. Vaccaro, *Chem. Commun.*, 2015, **51**, 15990; (c) C. Petrucci, G. Strappaveccia, F. Giacalone, M. Gruttadauria, F. Pizzo and L. Vaccaro, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2813; (d) C. Pavia, E. Ballerini, L. A. Bivona, F. Giacalone, C. Aprile, L. Vaccaro and M. Gruttadauria, *Adv. Synth. Catal.*, 2013, **355**, 2007.

15 D. Rasina, A. Lombi, S. Santoro, F. Ferlin and L. Vaccaro, *Green Chem.*, 2016, **18**, 6380.

16 For selected examples, see: (a) R. A. Altman and S. L. Buchwald, *Nat. Protoc.*, 2007, **2**, 2474; (b) R. A. Altman and S. L. Buchwald, *Org. Lett.*, 2006, **8**, 2779; (c) L. Liu, M. Frohn, N. Xi, C. Dominguez, R. Hungate and P. J. Reider, *J. Org. Chem.*, 2005, **70**, 10135; (d) T. Jerphagnon, G. P. M. van Klink, J. G. de Vries and G. van Koten, *Org. Lett.*, 2005, **7**, 5241; (e) E. Alcalde, I. Dinarès, S. Rodríguez and C. Garcia de Miguel, *Eur. J. Org. Chem.*, 2005, 1637; (f) H. Zhang, Q. Cai and D. Ma, *J. Org. Chem.*, 2005, **70**, 5164; (g) H.-J. Cristau, P. P. Cellier, J.-F. Spindler and M. Taillefer, *Chem. Eur. J.*, 2004, **10**, 5607; (h) F. Y. Kwong, A. Klapars and S. L. Buchwald, *Org. Lett.*, 2002, **4**, 581.

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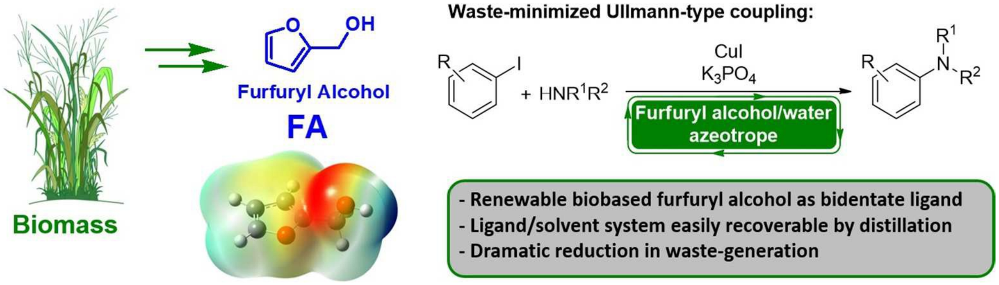

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