Exploration of New Biomass-Derived Solvents: Application to Carboxylation Reactions

Ashot Gevorgyan, Kathrin H. Hopmann, and Annette Bayer

A range of hitherto unexplored biomass-derived chemicals have been evaluated as new sustainable solvents for a large variety of CO₂-based carboxylation reactions. Known biomass-derived solvents (biosolvents) are also included in the study and the results are compared with commonly used solvents for the reactions. Biosolvents can be efficiently applied in a variety of carboxylation reactions, such as Cu-catalyzed carboxylation of organoboranes and organoboronates, metal-catalyzed hydrocarboxylation, borocarboxylation, and other related reactions. For many of these reactions, the use of biosolvents provides comparable or better yields than the commonly used solvents. The best biosolvents identified are the so far unexplored candidates isosorbide dimethyl ether, acetaldehyde diethyl acetal, rose oxide, and eucalyptol, alongside the known biosolvent 2-methyltetrahydrofuran. This strategy was used for the synthesis of the commercial drugs Fenoprofen and Flurbiprofen.

Introduction

The vast majority of known organic transformations require use of a solvent. Solvents are essential not only for running a reaction, but also for the separation and purification of target products. As a result, solvents usually constitute over 80% of all materials needed for the successful accomplishment of a typical synthetic transformation.[1] However, most commonly used organic solvents are derived from fossil resources, are not renewable, and have high toxicities. This can cause serious environmental and economic issues for large-scale chemical processes. One of the key directions of modern green chemistry is the minimization, elimination, or replacement of these solvents.[2] In this regard, so-called “solvent-free” reactions have significant potential.[3] However, most of them are not really solvent-free and require large amounts of organic solvents for the workup and purification. In most cases, the research tasks cannot be achieved without solvents. Nevertheless, undesirable solvents can be replaced by sustainable/renewable alternatives. For instance, liquids or chemicals with low melting points, available from renewable resources, can fill the gap.[4]

Particularly, many chemicals derived from biomass share common properties with organic solvents derived from fossil resources. Importantly, most biomass-derived chemicals fulfill many of the criteria for green solvents as proposed by Gu and Jerome, such as availability, renewability, low toxicity, biodegradability, and reasonable prices.[4]

The main biomass-derived solvents used in organic synthesis today are glycerol and its acetalts, several low-melting mixtures of carbohydrates, esters of lactic acid and gluconic acid, 2-methyltetrahydrofuran (2MeTHF), cyrene (Cyr), limonene (Lim), p-cymene (Cym), and γ-valerolactone (GVL; Figure 1).[2,4,5] The polar protic solvents like glycerol, carbohydrates as well as esters of lactic acid and gluconic acid are mainly used in condensation reactions and have found limited application in transformations involving organometallics.[4] The polar aprotic solvents (2MeTHF, GVL, Cyr, and Cym) solvents are far more popular and have been used for many classical transformations including transition metal (TM)-catalyzed cross-couplings[5,4,5] and several C–H activations.[5c–e,6] We should also highlight ethyl acetate (EtOAc), which is readily available from biomass and is often overlooked in the context of biomass-derived solvents.

In addition, some biomass-derived chemicals have been proposed as green solvents, such as isosorbide dimethyl ether (Me₂isos) and diethyl succinate (Et₂Suc), both derived from cellulose but, to our knowledge, have not been examined for this purpose.[7a,8] Further new and yet-unexplored candidates for biomass-derived solvents in organic synthesis may include acetaldehyde diethyl acetal (Acetal), which is readily available from ethanol, γ-terpinene (γ-Terp) and α-pinene (α-Pin) available from various coniferous plants, eucalyptol (Euc) from eucalyptus oil, and rose oxide (RoseOx) from rose oil (Figure 1). The availability of these solvents can be judged based on their prices, which are comparable with those of common organic
solvents and can decrease with further development of technologies in biorefinery (see the Supporting Information, Scheme S2). It should be emphasized that most of the solvents considered in the work here are quite safe and are used in large quantities in the food industry as flavor and fragrance ingredients. Low toxicity and biodegradability is particularly inherent to Acetal, Me$_2$Isos, Et$_2$Suc, Euc, RoseOx, and GVL. Unfortunately, information on overall environmental impacts and full life-cycle assessments (LCAs) of the solvents introduced here remain limited.

In the frame of our ongoing research program on C–C bond-forming reactions involving CO$_2$,[11] we became particularly interested to examine the use of biomass-derived solvents in a variety of carboxylative transformations (Scheme 1B). Utilization of CO$_2$,[12] and particularly development of C–C bond-forming reactions involving CO$_2$,[13] is a highly promising field of research that potentially can solve many global issues, such as replacement of depleting natural resources.[14] Previously reported carboxylations were typically performed in DMF, dioxane, toluene, and other related solvents,[12, 13] which are highly undesirable from the perspective of industry and green chemistry (Scheme 1A). To our knowledge, biomass-derived solvents have not been applied for any transformation involving CO$_2$.

The main goal of the present study was to examine the suitability of a wide range of biomass-derived chemicals as solvents for carboxylation reactions, including the known solvents 2MeTHF, GVL, Cyr, EtOAc, Lim, and Cym, and the unexplored solvents Acetal, Me$_2$Isos, Et$_2$Suc, α-Terp, α-Pin, Euc, and RoseOx. We started out by screening the above listed biosolvents in two model reactions—carboxylations of organoboranes and organoboronates. The carboxylative transformation of organoboranes to carboxylic acids in biosolvents was proven to be useful in the preparation of two commercial drugs. Finally, some of the best solvents were evaluated in a wide range of carboxylation reactions using CO$_2$. Among others, these reactions included hydrocarboxylations, boro-carboxylation, and carbocarboxylation. The biomass-derived solvents were also successfully applied as extraction media during product isolation. Overall, biomass-derived solvents, and in particular some of the solvents tested for the first time in this study, have a high potential to replace common organic solvents in the near future.

Results and Discussion

As a starting point, we have examined the carboxylation of organoboranes, which can be easily generated in situ by hydroboration of the corresponding olefins with 9-BBN (9-borabicyclo[3.3.1]nonane dimer).[15] Analysis of the influence of various parameters on the outcome of the reaction were conducted on 4-methylstyrene 1a using 2MeTHF as a solvent, which already proved to be a suitable media for reactions involving organometallics (Table 1).[2, 4, 5] Careful ex-
amination of various parameters showed that the best yields of hydrocarbon hydroxylation can be achieved by using salts of copper combined with carbene ligands like IPrHCl, I tBuHBF$_4$, and IAdHCl (Table 1, entries 1–6). Thus, 2a was isolated in quantitative yield by using in situ-generated IPrCuI (5 mol %) catalyst precursor and CsF (3 equiv) as base when running the reaction at 120 °C for 24 h (Table 1, entry 1). Other catalysts and bases in general were less effective (see Tables S1–S4). Overall, our findings were in good agreement with previous reports performed in common solvents.$^{[15]}$ The optimal conditions for hydrocarboxylation of 1a were also tested for a model organoboronate, the phenylboronic acid pinacol ester 3a (Figure 2 and Table S5).$^{[16]}$ Gratifyingly, these conditions performed well for 3a, providing benzoic acid 4a isolated in 74% yield. Having these promising results in 2MeTHF in hand, we focused on the screening of other biosolvents (Figure 2).

Among the solvents analyzed for the hydrocarboxylation of 1a, the highest yields of 2a were obtained in the biomass-derived ethers 2MeTHF (98%), Euc (94%), Me$_2$Isos (92%), and Acetal (91%; Figure 2). In comparison, the best traditional solvents were THF (89%), dioxane (84%), and toluene (85%). Biomass-derived solvents possessing double bonds or other functional groups that could be reduced such as α-Pin, Lim, GVL, and Cyr were not good media for hydrocarboxylation of 1a. The reason could be that the functional groups present in the solvent interact with 9-BBN. However, comparable solvents such as RoseOx, γ-Terp, Et$_2$Suc, and EtOAc gave moderate yields of 2a (52, 32, 53, and 59%, respectively). In addition, we observed moderate yields of 2a in Cym (55%), whereas toluene gave good yields for the hydrocarboxylation of 1a (85%).

Similarly, screening of biomass-derived solvents for the carboxylation of 3a showed that the best yields of 4a can be achieved in biomass-derived ethers Me$_2$Isos (85%), 2MeTHF (74%), and RoseOx (73%; Figure 2). In addition, the reaction worked well in the ester EtOAc (71%). The traditional solvents THF (78%) and dioxane (76%) provided comparable yields. Moderate yields were obtained for several of the remaining solvents, such as Lim (43%), Acetal (51%), GVL (67%), and Et$_2$Suc (58%). In comparison, Acetal was one of the best solvents for the hydrocarboxylation of 1a, whereas the hydrocarboxylation did not work in Lim and GVL. Eventually, both carboxylation and hydrocarboxylation did not work in α-Pin and Cyr. In the case

![Figure 2. Screening of solvents for Cu-catalyzed carboxylation of phenylboronic acid pinacol ester 3a (blue) and hydrocarboxylation of 4-methylstyrene 1a (orange).](image-url)
of Cyr, we observed a massive polymerization of the solvent for both reactions.

Our analysis shows that biomass-derived solvents can provide excellent yields for the tested hydrocarboxylation and carboxylation reactions. Previously unexplored Me$_2$Jisos and Acetal are among the best solvents. The reactions worked particularly well in biomass-derived ethers, outperforming traditional organic solvents.

With these promising results in hand, we examined the substrate dependence of hydrocarboxylation of olefins in biomass-derived solvents (Scheme 2; for an overview of used starting materials, see Scheme S3). The solvents that showed the best performance for the hydrocarboxylation (2MeTHF, EuC, Acatel, and Me$_2$Jisos) were examined for the disubstituted styrene 1h, cyclohexene 1i, and stilbene 1p. In the case of 1h, Acetal was as efficient as 2MeTHF, providing 94% yield of 2h in both solvents, whereas EuC (88%) and Me$_2$Jisos (85%) gave slightly lower yields (Scheme 2). For cyclohexene 1i, the yields of 2i varied from 37–71% with best results in 2MeTHF (71%). However, when running the reaction in dioxane, the reaction in dioxane, the yield of 2i was slightly improved (73%). For trans-stilbene 1p, involving a benzylic organoboron intermediate, hydrocarboxylation in biomass-derived solvents was investigated by using our previously reported cesium-mediated conditions without Cu catalyst.\[11d\]

The best biosolvent was again 2MeTHF (81%) and reaction in dioxane gave comparable yields (83%); see also Table S6.

Having established that 2MeTHF is a suitable solvent for hydrocarboxylations, we continued to investigate the scope of this reaction (Scheme 2). Styrenes 1a–h and primary olefins 1i and 1j consistently provided moderate to excellent yields of the corresponding acids (2a–j, 73–98%). For these systems, the hydroboration step proceeded as an anti-Markovnikov addition, eventually leading to terminal carboxylic acids with excellent regioselectivity.\[15, 17\] Other regioisomers were not observed. Further studies showed that internal alkenes 1k–m are far less reactive than terminal olefins (2k–m, 52–71%). However, for these substrates the reactions proceeded with excellent regioselectivities owing to the steric control of the hydroboration step.\[15, 17\] The reduced reactivity of internal alkenes allowed us to conduct regioselective hydrocarboxylation on nonconjugated dienes possessing one internal and one terminal double bond, 1n and 1o. In this case, we used 0.7 equivalents of 9-BBN, which allowed us to prepare only the hydrocarboxylation product of the terminal double bond (2n, 58%; 2o, 73%). These observations may explain why the hydrocarboxylation of 1a worked in RoseOx and γ-Terp, which have internal double bonds (Figure 2). The Cu-free hydrocarboxylation of stilbenes and β-substituted styrenes 1p–s also worked well in 2MeTHF and the hydrocarboxylation products 2p–s were observed in good yields (48–82%) and excellent regioselectivity.

Next, we examined the substrate dependence of carboxylations of organoboronates in biomass-derived solvents (Scheme 3). The best solvents identified for organoboronates (Figure 2) were screened on several substrates. These studies indicated that depending on the substrate, the efficiency of the used solvent differs. For most aromatic systems, the best solvent was Me$_2$Jisos. However, for thiophene 4j, 2MeTHF performed slightly better (78% vs. 84%). For benzylicaric acid pinacol esters, 2MeTHF proved to be the best solvent, outperforming Me$_2$Jisos by 20% (4p, Scheme 3).

A range of differently substituted arylboronic acid pinacol esters 3a–j were then carboxylated in Me$_2$Jisos as the solvent. We found that the reaction works well for systems possessing electron-rich (4c, 98%; 4e, 71%) or -deficient (4d, 82%; 4f, 68%; 4g, 85%) aryl groups. Fused systems such as naphthalene 4h (81%) and heterocycles 4i (41%) and 4j (78%) were also successfully carboxylated. Analysis of other organoboronates revealed that the reaction has a general character and works equally well for alkenyl- (4k, 89%; 4l, 62%; 4m, 65%; 4n, 84%) and alkynylboronic acid pinacol esters (4o, 62%). The scope of the carboxylation of benzylicaric acid pinacol esters was evaluated in 2MeTHF as the solvent and a range of benzylic boronates were successfully transformed into the corresponding acids in good yields (4p, 87%; 4q, 82%; 4r, 60%; 4s, 53%).

The developed methodology for benzylicaric acid pinacol esters could be further applied for the synthesis of the commercial nonsteroidal anti-inflammatory drugs Fenoprofen (4r, 60%) and Flurbiprofen (4s, 53%). Notably, the starting materi-
These solvents on a range of other C

9a

were also observed in 2MeTHF (81 %), whereas Acetal in 78 % yield.

It is possible to apply bio-

to test different catalytic systems

Our studies showed that for Fe-

catalytic system based on CuCl and I CyHCl (1,3-dicyclohex-

alcohol ethers, initiating the reaction is performed at 150 °C for 36 h. This improvement allowed us to obtain 2b as a major product in 80 % yield by using 2MeTHF. Acetal and Euc also gave good yields of 2b but were less effective than 2MeTHF; whereas, the yield of the reaction in dioxane (84 %) was comparable with the yield observed in 2MeTHF. Overall, decarboxylative hydrocarboxylation was not described earlier.

This was followed by examination of the hydrocarboxylation of styrenes in biomass-derived solvents. Among others, these studies involved Fe-catalyzed hydrocarboxylation of 4-methyl-styrene 1a by using EtMgBr as a stoichiometric reductant (Scheme 4B). Notably, similar hydrocarboxylations were already reported in ether and THF.[18] Our studies showed that for Fe-catalyzed hydrocarboxylation of 1a, it is possible to apply biomass-derived solvents. The best results were obtained by using the Fe(acac)₃/TMEDA (tetramethylethylenediamine) system as the catalyst in 2MeTHF. In this case, the yield of 7a was 27 %, application of other biomass-derived ethers did not improve the outcome of the reaction; whereas the use of THF slightly enhanced the yield of hydrocarboxylation (27 % 2MeTHF vs. 39 % THF).[18] It should be emphasized that EtMgBr is now available as a 3.4 m solution in 2MeTHF, and this type of experiment can be conducted by applying exclusively biomass-derived solvents. The hydrocarboxylation of styrenes was also examined by using different Ni-based catalysts, which unfortunately were not successful (Scheme 5A-D).

Further, we have explored the hydrocarboxylation of acetylenes in biomass-derived solvents (Scheme 4C–E).[19] We employed diphenylacetylene 8a to test different catalytic systems based on Ni, Cu, and Fe. Promising results were observed when using the CuCl/IMesHCl/NaOEtBu catalytic system with triethoxysilane as a reducing agent (Scheme 4D). The best solvent proved to be Acetal (61 %), whereas the yields of the hydrocarboxylation product 9a were slightly lower in 2MeTHF (41 %) and Euc (43 %). The reaction performed in dioxane (solvent used in the original work) gave 9a in 57 % yield.[19] Hydrocarboxylation of 8a was also possible with the Ni(cod)/CsF catalytic system and using Et₂Zn as the reductant. In this case, the yield of 9a was only 21 % in 2MeTHF, whereas in MeCN (solvent used in the original work) the product was obtained in 49 % yield (Scheme 4C).[19] Among Fe-based catalytic systems, moderate yields of 9a were observed with FeCl₃ used in combination with 3.4 m EtMgBr in 2MeTHF (42 % in 2MeTHF, Scheme 4E). Similar conditions were tested in EtO (solvent used in the original work) where 9a was obtained in 14 % yield.[19]

Next, we examined other carboxylative transformations. Excellent results were observed for the Cu-catalyzed borocarboxylation of styrenes (Scheme 4F).[20] Particularly, we found that the catalytic system based on CuCl and ICyHCl (1,3-dicyclohexylimidazolium chloride), originally developed by Popp and co-workers,[20b] operates well in biomass-derived ethers, initiating efficient borocarboxylation of 1a. In this case, the best solvent was Euc (85 %), but good yields of borocarboxylation product 10a were also observed in 2MeTHF (81 %), whereas Acetal (44 %) was far less effective. For comparison, the borocarboxylation of 1a performed in THF (solvent used in the original work) gave 10a in 78 % yield.[20b]

We also explored the carbocarboxylation of olefins, which is known to proceed under the influence of a wide range of cata-

Scheme 3. Scope of Cu-catalyzed carboxylation of boronic acid pinacol esters. [a] Unless otherwise mentioned, the reaction was performed in Me₂Jsos.
lys based on both early and late transition metals.\[21\] Screening of several catalysts derived from Zr and Ti as well as reducing agents showed that carbocarboxylation of 4-methylstyrene 1a can be performed in biomass-derived solvents (Scheme 4G). The best results were observed when using \( \text{Cp}_2\text{ZrCl}_2 \) (zirconocene dichloride) as catalyst precursor combined with \( \text{EtMgBr} \) in Acetal (24\% yield). Application of other ethers as solvents did not improve the yield of 11a. Using THF under otherwise identical conditions gave 11a in comparable 28\% yield.\[21c\]

Similar to organoboronates, the carboxylation of organosilicon reagents can be performed in biomass-derived solvents (Scheme 4H).\[22\] The best results were observed with \( \text{CuBr} \) as catalyst precursor combined with EtMgBr in Acetal (24\%). Application of other ethers as solvents did not improve the yield of 4a. Using THF under otherwise identical conditions gave 4a in comparable 28\% yield.\[22\]

Finally, we examined TM-catalyzed direct C–H carboxylations.\[23, 24\] To date, direct C–H carboxylations have been performed on azoles possessing an acidic C–H bond, arenes with appropriate directing groups,\[23\] and terminal acetylenes.\[24\] Our studies on phenylacetylene 5a indicated that \( \text{Cs}_2\text{CO}_3 \) alone can initiate direct C–H carboxylation in 2MeTHF, albeit with only 20\% yield of the isolated product (Scheme 4I). The yield was improved to 31\% by switching to GVL. Further improvements were achieved by using the catalytic system developed for carboxylation of organoboranes and organoboronates. The best yields of 4o were observed in 2MeTHF and Acetal (76 and 63\%, respectively), whereas GVL turned out to be far less effective with the Cu catalyst (27\%). The best conditions were also tested with THF where 4o was obtained in 38\% yield. Unfortunately, all attempts to accomplish C–H carboxylation of azoles in biomass-derived solvents failed (Scheme S4 A,B).

For isolation and purification of the obtained carboxylic acids, we mainly used acid–base extraction techniques. Analysis of different renewable solvents for extraction showed that \( \text{Et}_2\text{O} \), which is readily available from ethanol, but is not popular in industry owing to its volatility and flammability, can be replaced by renewable 2MeTHF, Acetal, diethoxymethane, and dimethoxymethane without any noticeable drop in yields. Column chromatography, with mixtures of heptane/EtOAc or \( \text{Et}_2\text{O}/\text{pentane}/\text{HCO}_2\text{H} \) as eluent, was only necessary for the pu-
rification of the products of decarboxylative hydrocarboxyla-
tion of phenylacetylene (Scheme 4A).

Conclusions
We have shown that a variety of CO₂-based carboxylations can be performed in biomass-derived solvents, including a range of previously unknown solvents. The studied media included polar aprotic biomass-derived ethers (2MeTHF, Acetal, Me₂Jsos, Cyr, Euc, RoseOx) and esters (GVL, Et₅Suc, ETOAc), as well as nonpolar aprotic unsaturated terpenes and their derivatives (γ-Terp, α-Pin, Lim, Cym). Initial studies on Cu-catalyzed carboxylation of in situ-generated organoboranes and -boronates revealed that most of the biosolvents are suitable for carboxyla-
tive transformations, with biomass-derived ethers showing the best efficiency. Our methodology was successfully applied to organoboranes generated from styrenes and internal alkenes, as well as for carboxylation of aryl-, alkenyl-, alkynyl-, and benzylboronic acid pinacol esters. On the basis of the latter, we have synthesized the commercial drugs Fenoprofen and Flurbiprofen.

Biomass-derived solvents were further applied for the hydro-
carboxylation of acetylenes and styrenes, using catalysts based on Cu, Ni, or Fe. We observed moderate to good yields and ex-
cellent regioselectivities. Very good results were obtained for the Cu-catalyzed borocarboxylation of styrenes and C–H car-
boxylation of phenylacetylene. Biomass-derived ethers can also be used for the Cu-catalyzed carboxylation of triethoxysilane and the Zr-catalyzed carboxylation of styrenes. Most of the reactions were examined in traditional organic sol-
vents as a comparison. These studies revealed that there is no advantage in using traditional solvents for the reactions de-
scribed herein. In most cases, the yields obtained in traditional solvents were comparable with those in biosolvents, whereas in some cases, biomass-derived solvents performed even better. Biomass-derived ethers showed the best performance, with 2MeTHF generally being superior. However, it is not a uni-
versal solvent. In several cases, excellent results were instead observed when using Me₂Jsos, Acetal, RoseOx, or Euc solvents. We believe that the biomass-derived solvents introduced herein will find broad applications in many processes currently based on traditional organic solvents.

Experimental Section
General experimental procedure for Cu-catalyzed carboxyla-
tion of organoboronates (Scheme 3)
Inside of a glovebox, a 45 mL pressure tube was charged with the appropriate organoboronate (0.8 mmol), CsF (3 equiv), and corre-
sponding dry solvent (2 mL). This was followed by addition of a previously prepared solution of the catalyst (mixture of Cul (5 mol%), IPHCl (6 mol%), and NaOrBu (6 mol%) in an appropriate dry solvent (2 mL) was stirred at 20 °C for 30 min). The pressure tube was closed with the cap and removed from the glovebox. Af-

and removed from the glovebox. Afterwards, CO₂ (120 mL) was added via a syringe, which was followed by stirring of the reaction mixture at 120 °C for 24 h. Next, the reaction mixture was diluted with Et₂O (30 mL) and transferred into a 500 mL separating funnel. The resulting mixture was extracted with saturated NaHCO₃ solution (3 × 30 mL). The resulting basic solution was washed with Et₂O (15 mL), acidified (50–55 mL 6 mol% HCl), and extracted with Et₂O (3 × 30 mL). The resulting solution of Et₂O was distilled to dryness to give the corresponding acid.

In the cases of Me₂Jsos, GVL and Et₅Suc, the basic solution was washed with either CH₃Cl or Et₂O (3 × 15 mL), and the final Et₂O solution was washed with distilled water (3 × 15 mL) before evapo-
ration. Other renewable solvents such as 2MeTHF, Acetal, diethoxy-
methane, or dimethoxymethane can replace Et₂O without any no-
ticeable difference (the difference was in the range ±3%). Similarly, the saturated solution of NaHCO₃ can be replaced by a 2 mol solu-
tion of KOH.

Abbreviations
2MeTHF = 2-methylenetetrahydrofuran; 9-BBN = 9-borabicyclo[3.3.1] nonane; Rpin = boric acid pinacol ester; Acetal = acetaldehyde di-
ethyl acetal; Cyr = cycrene; Cym = p-cymene; DMF = dimethylforma-
mide; DMA = dimethylacetamide; Euc = eucalyptol; Et₅Suc = diethyl succinate; ETOAc = ethyl acetate; GVL = γ-valerolactone; IPHCl = 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride; IBuBF₃ = 1,3-
di-tert-butylimidazolium tetrafluoroborate; IAdHCl = 1,3-bis(1-adam-
mantyl)imidazolium chloride; IMesHCl = 1,3-bis(2,4,6-trimethylphe-
nyl)imidazolium chloride; ICyHCl = 1,3-dicyclohexylimidazolium chloride; Lim = (R)-(+)limonene; LCA = life-cycle assessment; Me₂Jsos = isosorbide dimethyl ether; α-Pin = α-pinene; RoseOx = (+)-rose oxide; γ-Terp = γ-terpine; THF = tetrahydrofuran; TMEDA = tetramethylethylenediamine.
Acknowledgements

We gratefully acknowledge financial support from NordForsk (Grant No. 85378) and the Tromsø Research Foundation (Grant No. TF52016KHH).

Conflict of interest

The authors declare no conflict of interest.

Keywords: biomass valorization · carbon dioxide · carboxylation · organic synthesis · solvents

[1] For a general discussion on this topic, see: a) D. J. C. Constable, C. Jimenez-Gonzalez, R. K. Henderson, Org. Process Res. Dev. 2007, 11, 133–137; b) P. Pollet, E. A. Davey, E. E. Urena-Benavides, C. A. Ecketta, C. L. Liotta, Green Chem. 2014, 16, 1034–1055; c) D. H. Clark, T. J. Farmer, L. Herrero-Davila, J. Sherwood, Green Chem. 2016, 18, 3914–3934.

[2] For a general overview of green solvents, see: C. J. Clarke, W.-C. Tu, O. Levers, A. Brohl, J. P. Hallett, Chem. Rev. 2018, 118, 747–800.

[3] For selected reviews on solvent-free organic synthesis, see: a) K. Tanaka, F. Toda, Chem. Rev. 2000, 100, 1025–1074; b) E. Boldyrev, Chem. Soc. Rev. 2013, 42, 7719–7738; c) A. Sarker, S. Santra, S. K. Kundu, A. Hajra, G. V. Zyrayan, O. N. Chupakhin, V. N. Charushin, A. Magee, Green Chem. 2016, 18, 4475–4452; d) D. T. Loos, T. Frisic, Chem. Commun. 2016, 52, 7760–7781; e) J. Andersen, J. Mack, Green Chem. 2018, 20, 1435–1443; f) J. Colberg, J. G. Hernandez, Angew. Chem. Int. Ed. 2019, 58, 3285–3299; Angew. Chem. 2019, 137, 3320–3335.

[4] For a general discussion of criteria that should be fulfilled by green solvents, see: Y. Gu, F. Jerome, Chem. Soc. Rev. 2013, 42, 9550–9570.

[5] For recent reviews on applications of biomass-derived solvents, see: a) V. Pace, P. Hoyos, L. Castoldi, P. D. de Maria, A. R. Alcantara, ChemSusChem 2012, 5, 1369–1379; b) J. Hulsbosch, D. E. De Vos, K. Binnemans, R. Ameloot, ACS Sustainable Chem. Eng. 2016, 4, 2917–2931; c) S. Santoro, F. Forlin, L. Luciani, L. Ackermann, L. Vaccaro, Green Chem. 2017, 19, 1601–1612; d) S. Santoro, A. Marrocchi, D. Lanari, L. Ackermann, L. Vaccaro, Chem. Eur. J. 2018, 24, 13383–13390; e) P. Gandeepan, N. Kaplaneris, S. Santoro, L. Vaccaro, L. Ackermann, ACS Sustainable Chem. Eng. 2019, 7, 8023–8040.

[6] For recent examples on applications of biomass-derived solvents, see: a) J. Xu, W. Huang, R. Bai, Y. Queneau, F. Jerome, Y. Gu, Green Chem. 2019, 21, 2061–2069; b) B. He, L.-S. Zheng, P. Phansavath, V. Ratoevola-manana-Vidal, ChemSusChem 2019, 12, 3032–3036; c) Y.-T. Xu, C.-Y. Li, X.-B. Huang, W.-X. Gao, Y.-B. Zhou, M.-C. Liu, H.-Y. Wu, Green Chem. 2019, 21, 4971–4975; d) C. Wu, H.-J. Xiao, S.-W. Wang, M.-S. Tang, Z.-L. Tang, W. Xia, W.-F. Li, Z. Cao, W.-M. He, ACS Sustainable Chem. Eng. 2017, 5, 2169–2175; e) S. Planer, A. Jana, K. Grela, ChemSusChem 2016, 12, 4665–4661; f) F. J. Yao, N. Liu, L. Yin, J. Xing, T. Liu, X. Dou, Green Chem. 2019, 21, 4946–4950; g) W.-H. Bao, Z. Wang, X. Tang, Y.-F. Zhang, J.-X. Tan, Q. Zhu, Z. Cao, Y.-W. Lin, W.-M. He, Chin. Chem. Lett. 2019, 30, 2259–2262; h) S. Nejrotta, M. Iannicelli, S. S. Jamil, D. Arndo, M. Blan-tetti, G. Prandi, Green Chem. 2020, 22, 110–117.

[7] For selected guides on choosing green solvents, see: a) K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Penny, M. Stefaniak, Green Chem. 2008, 10, 31–36; b) R. K. Henderson, C. Jimenez-Gonzalez, D. J. C. Constable, S. R. Alston, G. G. A. Inglis, G. Fisher, J. Sherwood, S. P. Binks, A. D. Curzon, Green Chem. 2011, 13, 854–862; c) D. Prat, O. Pandigh, H.-W. Flemming, S. Letuestu, V. Ducandas, P. Isnard, E. Guirmon, T. Senac, S. Ruisseau, P. Cruciani, P. Hosek, Adv. Synth. Catal. 2013, 355, 4195–4198; d) P. Crivellini, B. He, L.-S. Zheng, P. Phansavath, V. Ratoevolamanana-Vidal, ChemSusChem 2019, 12, 3032–3036; e) Y.-T. Xu, C.-Y. Li, X.-B. Huang, W.-X. Gao, Y.-B. Zhou, M.-C. Liu, H.-Y. Wu, Green Chem. 2019, 21, 4971–4975; f) C. Wu, H.-J. Xiao, S.-W. Wang, M.-S. Tang, Z.-L. Tang, W. Xia, W.-F. Li, Z. Cao, W.-M. He, ACS Sustainable Chem. Eng. 2017, 5, 2169–2175; e) S. Planer, A. Jana, K. Grela, ChemSusChem 2016, 12, 4665–4661; f) F. J. Yao, N. Liu, L. Yin, J. Xing, T. Liu, X. Dou, Green Chem. 2019, 21, 4946–4950; g) W.-H. Bao, Z. Wang, X. Tang, Y.-F. Zhang, J.-X. Tan, Q. Zhu, Z. Cao, Y.-W. Lin, W.-M. He, Chin. Chem. Lett. 2019, 30, 2259–2262; h) S. Nejrotta, M. Iannicelli, S. S. Jamil, D. Arndo, M. Blan-tetti, G. Prandi, Green Chem. 2020, 22, 110–117.

[8] For selected guides on choosing green solvents, see: a) K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Penny, M. Stefaniak, Green Chem. 2008, 10, 31–36; b) R. K. Henderson, C. Jimenez-Gonzalez, D. J. C. Constable, S. R. Alston, G. G. A. Inglis, G. Fisher, J. Sherwood, S. P. Binks, A. D. Curzon, Green Chem. 2011, 13, 854–862; c) D. Prat, O. Pandigh, H.-W. Flemming, S. Letuestu, V. Ducandas, P. Isnard, E. Guirmon, T. Senac, S. Ruisseau, P. Cruciani, P. Hosek, Adv. Synth. Catal. 2013, 355, 4195–4198; d) P. Crivellini, B. He, L.-S. Zheng, P. Phansavath, V. Ratoevolamanana-Vidal, ChemSusChem 2019, 12, 3032–3036; e) Y.-T. Xu, C.-Y. Li, X.-B. Huang, W.-X. Gao, Y.-B. Zhou, M.-C. Liu, H.-Y. Wu, Green Chem. 2019, 21, 4971–4975; f) C. Wu, H.-J. Xiao, S.-W. Wang, M.-S. Tang, Z.-L. Tang, W. Xia, W.-F. Li, Z. Cao, W.-M. He, ACS Sustainable Chem. Eng. 2017, 5, 2169–2175; e) S. Planer, A. Jana, K. Grela, ChemSusChem 2016, 12, 4665–4661; f) F. J. Yao, N. Liu, L. Yin, J. Xing, T. Liu, X. Dou, Green Chem. 2019, 21, 4946–4950; g) W.-H. Bao, Z. Wang, X. Tang, Y.-F. Zhang, J.-X. Tan, Q. Zhu, Z. Cao, Y.-W. Lin, W.-M. He, Chin. Chem. Lett. 2019, 30, 2259–2262; h) S. Nejrotta, M. Iannicelli, S. S. Jamil, D. Arndo, M. Blan-tetti, G. Prandi, Green Chem. 2020, 22, 110–117.
[19] For selected examples of TM-catalyzed hydrocarboxylation of acetylenes, see: a) T. Fujihara, T. Xu, K. Sembra, J. Terao, Y. Tsuji, Angew. Chem. Int. Ed. 2011, 50, 523–527; b) S. Li, W. Yuan, S. Ma, Angew. Chem. Int. Ed. 2011, 50, 2578–2582; c) X. Wang, M. Nakajima, R. Martin, J. Am. Chem. Soc. 2015, 137, 8924–8927; d) K. Nogi, T. Fujihara, J. Terao, Y. Tsuji, J. Am. Chem. Soc. 2016, 138, 5547–5550; e) R. Santhoshkumar, Y.-C. Hong, C.-Z. Luo, Y.-C. Wu, C.-H. Hung, K.-Y. Hwang, A.-P. Tu, C.-H. Cheng, ChemCatChem 2016, 8, 2210–2213; f) P. Shao, S. Wang, G. Du, C. Xi, RSC Adv. 2017, 7, 3534–3539; g) J. Hou, A. Ee, W. Feng, J.-H. Xu, Y. Zhao, J. Wu, J. Am. Chem. Soc. 2018, 140, 5257–5263.

[20] For selected examples of TM-catalyzed borocarboxylation, see: a) L. Zhang, J. Cheng, B. Cary, Z. Hou, J. Am. Chem. Soc. 2012, 134, 14314–14317; b) T. W. Butcher, E. J. McClain, T. G. Hamilton, T. M. Perrone, K. M. Kroner, G. C. Donohoe, N. G. Alkhmedov, J. L. Petersen, B. V. Popp, Org. Lett. 2016, 18, 6428–6431; c) X. Li, Y.-B. Wu, G. Lu, Catal. Sci. Technol. 2017, 7, 5049–5054; d) S. Lin, Z. Lin, Organometallics 2019, 38, 240–247.

[21] For selected examples of TM-catalyzed carbocarboxylation, see: a) M. Takimoto, M. Mori, J. Am. Chem. Soc. 2002, 124, 10008–10009; b) K. Shimizu, M. Takimoto, Y. Sato, M. Mori, Org. Lett. 2005, 7, 195–197; c) P. Shao, S. Wang, C. Chen, C. Xi, Chem. Commun. 2015, 51, 6640–6642; d) M. Takimoto, S. S. Gholap, Z. Hou, Chem. Eur. J. 2015, 21, 15218–15223; e) L. Dian, D. S. Müller, I. Marek, Angew. Chem. Int. Ed. 2017, 56, 6783–6787; Angew. Chem. 2017, 129, 6887–6891; f) V. R. Yatham, Y. Shen, R. Martín, Angew. Chem. Int. Ed. 2017, 56, 10915–10919; Angew. Chem. 2017, 129, 11055–11059.

[22] For selected examples of carboxylation of organosilicon reagents, see: a) G. E. Greco, B. L. Gleason, T. A. Lowery, M. J. Kier, L. B. Hollander, S. A. Gibbs, A. D. Worthy, Org. Lett. 2007, 9, 3817–3820; b) M. Yonemoto-Kobayashi, K. Inamoto, Y. Kondo, Chem. Lett. 2014, 43, 477–479; c) K. Sekine, Y. Sadamitsu, T. Yamada, Org. Lett. 2015, 17, 5706–5709; d) X. Frogneux, N. von Wolff, P. Thurfy, G. Lefèvre, T. Cantat, Chem. Eur. J. 2016, 22, 2930–2934; e) T. V. Q. Nguyen, J. A. Rodriguez-Santamaría, W.-J. Yoo, S. Kobayashi, Green Chem. 2017, 19, 2501–2505; f) T. V. Q. Nguyen, W.-J. Yoo, S. Kobayashi, Asian J. Org. Chem. 2018, 7, 116–118.

[23] For a review on C–H carboxylation of arenes, see: J. Luo, I. Larrosa, ChemSusChem 2017, 10, 3317–3332.

[24] For a review on C–H carboxylation of terminal acetylenes, see: F. Mancolinho, M. Arndt, K. Goodlen, L. J. Goodlen, ACS Catal. 2012, 2, 2014–2021.

Manuscript received: November 25, 2019
Revised manuscript received: January 5, 2020
Accepted manuscript online: January 7, 2020
Version of record online: February 11, 2020