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Long-chain α-ω diols from renewable fatty acids via tandem olefin metathesis – ester hydrogenation

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Long chain α-ω diols were readily accessed from renewable fatty acid methyl esters following an ortogonal tandem self-metathesis-ester hydrogenation protocol. By adding a base and a bidentate ligand, the metathesis catalysts were transformed *in situ* into efficient ester hydrogenation catalysts. The selectivity of the hydrogenation reaction was tuned towards the exclusive formation of either the unsaturated or the saturated diol by modifying the ligand/catalyst ratio. Orthogonal tandem cross-metathesis-ester hydrogenation reaction was also applied to the synthesis of a fragrance compound.

Introduction

Fatty acids and fatty acid methyl esters (FAME) obtained via saponification or transesterification of fats and oils are attractive as renewable building blocks towards polymeric materials.[1-4] Typically, the natural acid/ester contains an additional functional group along the hydrocarbon chain, such as an olefinic bond, a hydroxyl group or an epoxide which allows its incorporation into polymers without requiring additional modifications. Alternatively, fatty acids/esters can be chemically or enzymatically converted to custom-tailored bifunctional monomers for the preparation of new materials with very specific properties. In fact, most of these chemical transformations are applied either to their isolated or conjugated carbon-carbon double bonds. In addition to Diels-Alder reactions, ozonolysis, epoxidation and carbonylation, olefin-metathesis has been widely used for such aim[5,6] starting as early as in the 70's.[7] In the last decades, the discovery of very active Ru-based metathesis catalysts[8-12] allowed to efficiently produce α-ω-bifunctional monomers from unsaturated fatty acid methyl esters either via self-metathesis at low catalyst loadings[13,14] or via cross-metathesis with electron-deficient olefins such as acrylate, acrylonitrile or acrolein[15-20] (Scheme 1). Subsequent modifications of the metathesis products were achieved *via* hydrogenation catalyzed by the Ru species generated in the metathesis step, i.e. in an orthogonal tandem catalysis protocol.[21-33] By placing the reaction mixture after metathesis under a pressurized H_2 atmosphere, the reduction of both the C=C double bonds and the aldehyde functionality was indeed accomplished.[16,34] Upon addition of a base, the residual Ru species were found to efficiently catalyze the reduction of nitrile groups to amines.[35] Therefore linear α-ω-aminoesters, useful for polyesters production, could be directly obtained from acrylonitrile and unsaturated fatty acid methyl esters *via* a tandem metathesis-hydrogenation protocol (Fig 1).[36]

Herein we report the first example of a tandem metathesis-ester hydrogenation for the selective formation of long chain diols directly from unsaturated fatty acid methyl esters. Upon addition of a bidentate ligand and a base, Grubbs metathesis catalysts are converted into efficient ester hydrogenation catalysts. The same protocol is applied to the Ru species generated *in situ* during the metathesis reaction, which ultimately results in the direct formation of aliphatic diols by a tandem process in which self-metathesis is followed by the hydrogenation of both, the ester and the olefinic C=C bond (Fig. 1). Furthermore, we demonstrate that unsaturated diols can also be selectively accessed by increasing the molar amount of the bidentate ligand in the tandem protocol, allowing to switch the selectivity of the hydrogenation towards the exclusive reduction of the ester functionality. Finally, the scope of this tandem reaction

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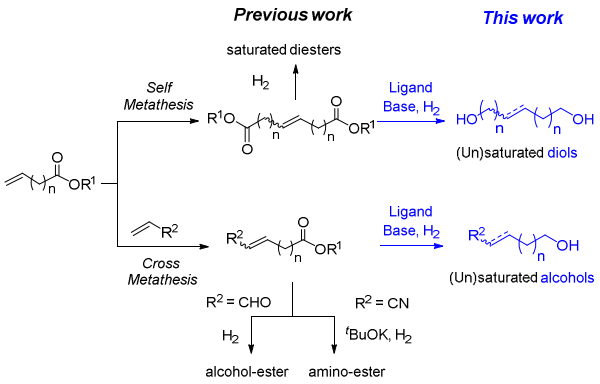


Fig. 1 Tandem metathesis-hydrogenation with unsaturated fatty acid methyl esters

is further expanded to a cross-methatesis and ester hydrogenation sequence highlighting its potential applications to the synthesis of an industrially relevant fragrance compound.

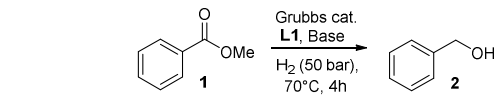
Results and discussion

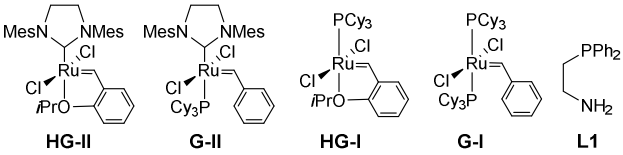
Ester hydrogenation with Ru metathesis catalysts

In recent years, several homogeneous catalysts have been developed for the selective hydrogenation of esters into alcohols.[37-57] In particular, the combination of Ru-based complexes with non-innocent ligands has been remarkably successful.[58-60] Such catalysts are operating via an outer-sphere mechanism where an hydride from the metal and a proton from the ligand are simultaneously delivered to the substrate. To start our investigations, we chose methyl benzoate (**1**) as a model substrate and Hoveyda-Grubbs II (**HG-II**) as the initial catalyst (Table 1). Formation of benzyl alcohol (**2**) was not observed when a THF solution of **1** was subjected to 50 bar of H_2 at 70°C in presence of 0.5 mol% of **HG-II** (entry 1). Similarly, no reaction took place when KOMe or ligand **L1** – previously used by Firmenich for ester hydrogenation[61]- were independently added to the reaction mixture (entries 2-3). To our delight, the quantitative formation of product **2** was finally accomplished when the reaction was performed in the presence of both additives (entry 4). Screening all other metathesis catalyst under these conditions also resulted in full conversion (entries 5-7) suggesting that the initial ligands of the Ru precursors have a limited role in controlling the hydrogenation activity of the newly formed Ru species. Unsurprisingly, MeOK could be replaced with ^{t}BuOK without affecting the outcome of the reaction (entry 8).

The catalyst described by Firmenich contains 2 equivalents of the P,N ligand **L1** per Ru.[61] In our initial screening, full conversion was achieved by adding only 1 equivalent of **L1** per Ru. However, it cannot be concluded that our active hydrogenation species is only monoligated. The active hydrogenation catalyst is indeed formed *in situ* from a mixture of Ru complexes. Among these, only a small fraction may be able to complex the ligand and thus a sufficient excess of ligand to form biligated complexes is warranted under our reaction conditions. Full conversion was also observed when the reaction was performed in the presence of 2 and 3 equivalents of **L1** per Ru catalyst (See the Supporting Information) albeit with a shorter

Table 1 Screening conditions for the hydrogenation of methyl benzoate with Grubbs metathesis catalyst [a]





Entry	Catalyst	Ligand	Base[b]	Conv. (%)[c]	Yield **2** (%)[c]
1	HG-II	-	-	N.R.	-
2	HG-II	-	MeOK	N.R.	-
3	HG-II	L1	-	N.R.	-
4	HG-II	L1	MeOK	>99	97[d]
5	G-II	L1	MeOK	>99	>99
6	HG-I	L1	MeOK	>99	>99
7	G-I	L1	MeOK	>99	>99
8[e]	G-I	L1	^{t}ButOK	>99	>99

[a]Conditions: 1 (1.275 mmol), Ru catalyst (0.5 mol%) and L1 (0.55 mol%) in THF (2.5 mL) under H_2 (50 bar) for 4 h at 70 °C. [b] 20 equivalents relative to Ru catalyst. [c]Determined by GC analyses using dodecane as internal standard. [d]Traces of benzaldehyde were observed. [e]Reaction run using **1** (1 mmol) in THF (2.0 mL).

induction period in comparison with the reactions run with only 1 equivalent of **L1** per Ru.

These observations suggests that a higher concentration of ligand can accelerate the formation of the active hydrogenation species. In addition, ESI-MS analysis before and after hydrogenation revealed the presence of a large number of Ru species including both monomeric and dimeric ones (See the Supporting Information). In particular, the formation of Ru carbonyl hydride species upon addition of alkoxides to Grubbs metathesis catalysts is well-established.[62-66] In agreement with these studies, the $[Ru(CO)(H)(\mathbf{L1})(PCy_3)]^+$ fragment was identified by ESI-MS when **HG-I** was reacted with either 1 or 2 equivalents of **L1** in a pressurized H_2 atmosphere. When **HG-II** was used in combination with *t*BuOK as base and 2 equivalents of **L1**, a similar species bearing a N-heterocyclic carbene (NHC) instead of PCy_3, $[Ru(CO)(H)(\mathbf{L1})(NHC)]^+$ was present at the end of the reaction. The biligated species $[Ru(CO)(H)(\mathbf{L1})_2]^+$ was also detected. Although these may well be the catalytically active species, the large number of Ru complexes

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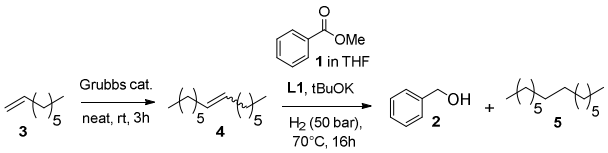
detected in the reaction mixture deterred us to explore this topic further.

Table 2 Reduction of methyl benzoate with Ru species formed during a metathesis reaction[a]



Entry	Catalyst	Metathesis of **3**[b]		Hydrogenation of **1** and **4**[b]		
		Conv. **3** (%)	Sel. **4** (%)	Conv.**1** (%)	Sel.**2** (%)	Conv. **4** (%)
1	G-I	78	100	100	100	<1
2	HG-I	96	33[c]	100	100	6
3	G-II	83	100	100	100	12
4	HG-II	98	52[c]	>99	100	3

[a]Conditions: Metathesis: **3** (3 mmol), Ru catalyst (0.0075 mmol, S/C = 400), neat at r.t. for 3 h. Hydrogenation: **1** (200 equiv/Ru), **L1** (2 equiv/Ru), ^{t}ButOK (20 equiv/Ru) in THF (V_{total} = 3.25 mL) under H2 (50 bar) for 16 h at 70 °C. [b]Determined by GC analysis with dodecane as internal standard. [c]Concomitant olefin isomerization and consecutive metathesis led to a range of lighter and heavier olefins.

Ester hydrogenation with Grubbs catalysts after metathesis

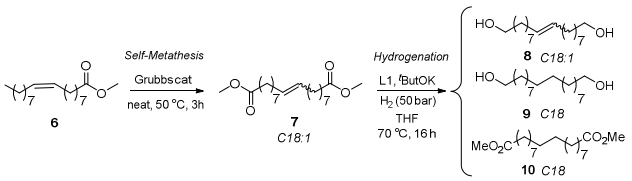
Having demonstrated that Grubbs metathesis catalysts can be converted into efficient ester hydrogenation catalysts, we next investigated whether the ester reduction could be accomplished by adding **L1** and a base to the mixture of Ru species formed during a metathesis reaction. For this purpose, the self-metathesis of 1-octene (**3**) was carried out with different catalysts under neat conditions at room temperature for 3h (Table 2).

Although the reaction conditions were not thoroughly optimized, modest to excellent yields of the expected metathesis product, 7-tetradecene (**4**) were obtained with all the metathesis catalysts tested. After addition of the ester model substrate **1**, ligand **L1** and ^{t}ButOK as base, the reaction mixtures were subjected to 50 bar of H_2 at 70°C for 16 h. To our delight, full conversion of **1** to benzyl alcohol **2** was obtained in all cases. Furthermore, the competitive reduction of the metathesis product **4** was barely observed under such reaction conditions. To the best of our knowledge, this is the first example of a modification of the chemoselectivity of the Ru species formed during a metathesis reaction *via* addition of an extra ligand.

Tandem self-metathesis - ester hydrogenation of unsaturated fatty acid methyl esters

Encouraged by this initial results, we investigated whether this protocol could be applied to the tandem self-metathesis-ester hydrogenation of unsaturated fatty acid methyl esters. Bearing both an ester moiety and an olefinic bond prone to undergo metathesis,[6] this class of renewable compounds were perfectly fitted for our protocol. Moreover, a tandem self-metathesis–ester hydrogenation reaction would directly convert them into fatty alcohols (as saturated or unsaturated mono- or diols) that constitute an important class of industrial chemicals with applications in polymers, surfactants, oil additives and cosmetics.[67] Methyl oleate (**6**) was selected as a representative example of an unsaturated fatty acid ester (Table 3). This fatty ester bearing an internal olefinic bond can be obtained from many natural oils and upon self-metathesis it gives rise to the unsaturated C18:1 diester and 9-octadecene as primary products (Scheme in Table 3). The desired C18:1 diester (**7**) was obtained with moderate yields and high chemoselectivity when (**6**) was subjected to metathesis in the presence of **G-I** or **HG-I** for 3 h at 50 °C (entries 1 and 2). However, extensive isomerization of the C=C bond within the starting material and the primary product took place with the second generation of catalysts (entries 3 and 4), resulting in a wide distribution of diester products (See ESI S13).[68] Such a difference in the chemoselectivity of the reaction between the first and second generation of metathesis catalysts is indeed to be expected since olefin isomerization reactions tend to be less important with the first generation catalysts.[69-72]

Table 3 Tandem self-metathesis-ester hydrogenation of methyl oleate [a]



Entry	Catalyst	Metathesis of **6**[b]		Hydrogenation of **7**[b]		
		Conv. **6** (%)	Sel. **7** (%)[c]	Conv.**7** (%)	Sel.**8** (%)	Sel. **9** (%)
1	G-I	40	96	100	64	36
2	HG-I	55	86	100	52	48
3	G-II	89	9	Not determined		
4	HG-II	96	8	Not determined		
5	G-I[d]	40	96	100	0	100
6	G-I[e]	41	96	100	0	100
7	G-I[f]	40	98	100	0	100
8	G-I[g]	40	96	100	99	1

[a]Conditions: Metathesis: **7** (1.5 mmol), Ru catalyst (0.0075 mmol, S/C = 200), neat at 50 °C for 3 h. Hydrogenation: **L1** (2.0 equiv/Ru), ^{t}ButOK (40 equiv/Ru) in THF (V_{total} = 2.00 mL) under H2 (50 bar) for 16 h at 70 °C. [b]Determined by GC analysis with dodecane as internal standard. [c]The other products formed are a range of lighter and heavier olefins due to concomitant olefin isomerization and consecutive metathesis. [d]Reaction run with **L1** (1.25 equiv/Ru). [e]Reaction run with **L1** (1.5 equiv/Ru). [f]Reaction run with **L1** (1.75 equiv/Ru). [g]Reaction run with **L1** (2.5 equiv/Ru).

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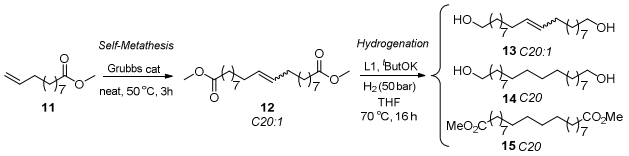
After hydrogenation according to our tandem protocol, full conversion of the primary self-metathesis product C18:1 (**7**) was achieved with the first generation of metathesis catalysts. Interestingly, the unsaturated C18:1 (**8**) and the saturated C18 (**9**) diols were obtained in almost equimolar amounts under the initial reaction conditions. The undesired C=C bond reduction C18 ester (**10**) was not observed (Entries 1 and 2). Inspired by our earlier observation of larger amounts of **L1** being able to accelerate the hydrogenation reaction and considering that several Ru species coexists at the start of/during the hydrogenation, we envisioned that variations in the **L1**/Ru molecular ratio would be reflected in significant modifications in the chemoselectivity of the hydrogenation reaction. Indeed, the chemoselective formation of the saturated diol **9** was observed for **L1**/Ru ratios between 1.0 to 1.75 (entries 5-7) whereas the unsaturated diol **8** was obtained in excellent yields upon increasing the **L1**/Ru ratio to 2.5 (entry 8). In a similar fashion, the unreacted methyl oleate was completely reduced to octadecanol and the 9-octadecene resulting from the metathesis reaction was fully reduced to octadecane at **L1**/Ru ratios lower than 1.75 (See the Supporting Information). In contrast, 9-octadecene was not reduced and 9-octadecen-1-ol was generated from the unreacted methyl oleate when the **L1**/Ru ratio was set at 2.5. In agreement with previous reports on the use of metathesis catalysts for reducing olefinic bonds,[21-32] the formation of the saturated product **10** took place exclusively in the absence of **L1** or partially when setting **L1**/Ru ratios lower than 1.0. There are only a limited number of homogeneous catalysts capable of promoting the selective reduction of ester functionalities in the presence of olefinic bonds.[50, 61, 73] Our **L1**/Ru catalytic system is, to the best of our knowledge, the first catalyst reported in the literature that allows to control the chemoselectivity of the reduction towards the desired saturated or unsaturated form. These experimental observations suggest the coexistence of several Ru species active in hydrogenation. The formation of the saturated diol **8** at lower **L1**/Ru ratios can be attributed to biligated Ru-**L1** complexes responsible of the ester reduction and other Ru species capable of reducing the olefinic C=C bonds. By increasing the **L1**/Ru ratio to 2.5, the formation of biligated Ru-$(\mathbf{L1})_2$ complexes becomes predominant switching the selectivity of the reaction towards the exclusive formation of the unsaturated diol **9**. We also demonstrated that **G-I** treated with an excess of ligand **L1** and a base is no more active in metathesis and therefore can achieve the chemoselective hydrogenation of methyl oleate to the corresponding unsaturated alcohol (See ESI Table S5).

Methyl undecenoate (**11**) which can be obtained by pyrolysis (via a retro-Alder-ene reaction) of methyl ricinoleate, was also subjected to our tandem protocol (Table 4). Due to its terminal C=C bond, the self-metathesis of **11** forms a C20 diester as primary product (See scheme in Table 4). The unsaturated diester C20:1;OMe (**12**) was generated with good to excellent yields when **11** was subjected to the metathesis catalysts for 3 h at 50 °C. Again, significant isomerization occurred with the second generation of catalysts resulting in the formation of lighter and heavier diesters ranging from C16 to C21 (entries 3 and 4). Full conversion of **12** was achieved after hydrogenation with the chemoselectivity being again determined by the **L1**/Ru ratio. Thus, the saturated C20 diol (**14**) was exclusively obtained when setting **L1**/Ru ratios between 1.0 and 1.75 (entries 5 and 6) whilst the unsaturated C20:1 diol (**13**) was generated at a higher **L1**/Ru ratio of 2.5 (entry 7).

Tandem cross-metathesis-ester hydrogenation

To further expand the scope of our tandem protocol we finally investigated the cross metathesis of styrene and ethyl 3-methylpent-4-enoate (**17**), followed by its subsequent hydrogenation in an attempt to synthesize 3-methyl-5-phenyl-1-pentanol (**21**), a well-established fragrance compound commercialized under various trade names such as Mefrosol, Phenoxaflor and Rosaphen[74,75] (Table 5). The second generation of metathesis catalysts were more efficient than the first generation catalysts for the formation of the desired cross-metathesis product (**18**) (Entries 1-4).[76]

Table 4 Tandem self-metathesis-ester hydrogenation of methyl undecenoate [a]



Entry	Catalyst	Metathesis of **11** [b]		Hydrogenation of **12** [b]		
		Conv. **11** (%)	Sel. **12** (%) [c]	Conv.**12** (%)	Sel.**13** (%)	Sel. **14** (%)
1	G-I	89	97	100	95	4
2	HG-I	80	95	100	96	4
3	G-II	96	46	100 [d]	93	4
4	HG-II	93	31	100	94	3
5	G-I [e]	89	97	100	0	100
6	G-I [f]	65 [g]	97	100	0	100
7	G-I [h]	89	97	100	99	1

[a]Reaction conditions: Metathesis: **11** (1.5 mmol), Ru catalyst (0.0075 mmol, S/C = 200), neat at 50 °C for 3 h. Hydrogenation: **L1** (2.0 equiv/Ru), [t]ButOK (40 equiv/Ru) in THF (V_{total} = 2.00 mL) under H2 (50 bar) for 16 h at 70 °C. [b]Determined by GC analysis with dodecane as internal standard. [c]The other products formed are a range of lighter and heavier olefins due to concomitant olefin isomerization and consecutive metathesis. [d]Compound **10** was detected with 1% selectivity. [e]Reaction run with **L1** (1.25 equiv/Ru). [f]Reaction run with **L1** (1.5 equiv/Ru). [g]Metathesis reaction run at r.t. [h]Reaction run with **L1** (2.5 equiv/Ru).

In the initial set of conditions, **G-II** showed a higher activity than **HG-II** in the consecutive hydrogenation (Entry 3) although the unsaturated alcohol (**20**) was obtained as the main product. As already demonstrated, varying **L1**/Ru ratio had a large impact on the chemoselectivity. In absence of ligand **L1**, the saturated ester (**19**) was obtained selectively (Entry 5) at 90°C while the

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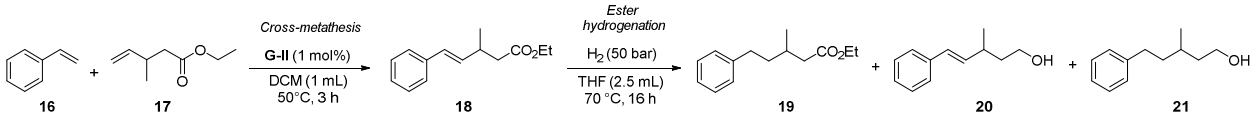
unsaturated alcohol (20) was the main product when the **L1**/Ru ratio was set at 3 (Entry 8). By increasing further the hydrogenation temperature to 110 °C, the desired saturated alcohol (21) was obtained with a very good yield at a **L1**/Ru ratio of 2.5 (Entry 11). At such a temperature, the chemoselective ester hydrogenation catalyst which is the

Table 5 Tandem cross-metathesis-ester hydrogenation[a]



Entry	Catalyst	Metathesis of **17**[b]				Hydrogenation of **18**[b]			
		Conv. **17** (%)	Sel. **18** (%)	**L1** (eq Ru)	T (°C)	Conv. **18** (%)	Sel. **19** (%)	Sel.**20** (%)	Sel. **21** (%)
1	G-I	45	93	2	70	93	-	29	71
2	HG-I	39	81	2	70	100	-	27	73
3	G-II	86	94	2	70	100	3	87	13
4	HG-II	86	93	2	70	49	5	42	53
5	G-II	84	87	0	90	66	100	-	-
6	G-II	81	86	1	90	100	-	45	45
7	G-II	81	87	2	90	100	-	85	15
8	G-II	82	86	3	90	99	-	99	1
9	G-II	87	86	1	110	100	56	3	41
10	G-II	89	86	2	110	98	8	8	84
11	G-II	89	86	2.5	110	100	-	12	88
12	G-II	81	87	3	110	100	-	39	61

[a]Conditions: Metathesis: **16** (7.5 mmol), **17** (1.5 mmol), Ru catalyst (0.015 mmol, S/C = 100 rel.to **17**), DCM (1 mL) at 50 °C for 3 h. Hydrogenation: : **L1** (2.0 equiv/Ru), ^{t}ButOK (20 equiv/Ru) in THF (V_{total} = 2.00 mL) under H_2 (50 bar) for 16 h at 70 °C. [b]Determined by GC analysis with dodecane as internal standard.

predominant species at such a high **L1**/Ru ratio is possibly decomposing partially into Ru species (eventually Ru nanoparticles) able to hydrogenate the C-C double bonds.

Conclusions

In summary, we have disclosed a new protocol for transforming Grubbs metathesis catalyst into efficient ester hydrogenation catalysts via the addition of a bidentate P,N ligand and a base. This simple protocol allows to perform an orthogonal tandem self- or cross-metathesis followed by a selective ester hydrogenation from which valuable saturated or unsaturated diols or alcohols can be obtained by simply adjusting the equivalents of ligand and the hydrogenation temperature. Such a process is intrinsically sustainable since two catalytic reactions are performed with one single load of catalyst. Additionally, the ester hydrogenation does not rely on the use of the traditional catalysts for this transformation, i.e. copper chromites[38] that contain toxic chromium and operate under much harsher operating conditions (T>250°C, P>200bar). Further improvement in terms of catalyst loadings would be needed before implementation at scale for bulk chemicals. However, this protocol may already be efficient for the production of high value fine chemicals.

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