Steel-Promoted Oxidation of Olefins in Supercritical Carbon Dioxide Using Dioxygen in the Presence of Aldehydes

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Abstract: Oxidation of olefins occurs effectively in supercritical carbon dioxide as the reaction medium with dioxygen as the primary oxidant and aldehydes as sacrificial co-oxidants. No catalyst is required, but the reaction is promoted by the stainless steel of the reactor walls. Depending on the substrate, vinylic oxidation or epoxidation can be the prevailing pathway. Epoxidation is particularly effective for substrates with internal double bonds and for long-chain terminal olefins.

Keywords: catalysis · epoxidation · oxygen · supercritical carbon dioxide · wall effect

Introduction

Supercritical carbon dioxide ($scCO_2$, $T_c = 30.9\,°C$, $p_c = 73.8$ bar) has recently received considerable attention as a reaction medium with unique properties for chemical synthesis and catalysis.[1, 2, 3] In contrast to many common organic solvents, $scCO_2$ is not toxic, not flammable, and its use is not associated with any immediate environmental hazards. The high miscibility with many reaction gases makes $scCO_2$ very attractive for processes involving gaseous reactants which often suffer from mass transport limitations. The possibility of tuning the density of $scCO_2$ by comparably small variations of pressure and temperature opens an additional range of fascinating applications in catalysis.[4, 5] The oxidation stability of CO_2 suggests $scCO_2$ as a particularly interesting reaction medium for the oxidation of organic substrates.[2b, 6]

One of the biggest challenges in oxidation catalysis is the selective oxidation of hydrocarbons with molecular oxygen.[7] In particular, the epoxidation of olefins is an important process for introducing functional groups in organic synthesis. Previous attempts to utilize dioxygen for epoxidation in $scCO_2$ led only to moderate yields of the desired products. Cyclohexene was oxidized with 8.9% conversion and a selectivity for epoxycyclohexane of 34% in $scCO_2$ using O_2 in the presence of a Fe-porphyrin catalyst.[8] Considerable amounts of by-products were formed from free-radical allylic oxidation, including cyclohex-2-enone, cyclohex-2-enol, and their epoxidation products such as 2,3-epoxycyclohexanone.

A common way of utilizing O_2 in transition metal catalyzed epoxidation chemistry is the addition of an aldehyde as sacrificial oxygen transfer agent (Mukaiyama conditions).[9] Typically, fairly elaborate transion metal complexes are used as homogeneous catalysts for these reactions in organic solvents.[9] There are, however, some reports on epoxidations using oxygen and aldehydes without deliberate addition of metal complexes. For example, cyclohexene was oxidized to epoxycyclohexane with 71% yield in CH_2Cl_2 using dioxygen under atmospheric pressure and heptanal in the presence of iron powder and acetic acid.[10a] The formation of soluble iron complexes under these conditions was suggested as a possible explanation for this observation. Other papers describe the epoxidation of simple olefins even in the absence of any metal source especially if chlorinated solvents are used.[10b,11]

Herein, we report that oxidation of olefins using O_2 in the presence of aldehydes occurs efficiently in $scCO_2$ as the reaction medium.[12] In particular, we found that addition of a metal catalyst was not required to achieve high reaction rates and selectivities for the epoxidation of internal double bonds. Extensive control experiments revealed that the presence of stainless steel (e. g. from the autoclave walls) promoted the epoxidation, presumably by initiating radical reaction pathways.

Results and Discussion

The reaction conditions for oxidation of olefins in $scCO_2$ were optimized on the basis of the epoxidation of *cis*-cyclooctene with molecular oxygen and aldehydes as sacrificial co-oxidants (Table 1). Reactions were carried out in a 100 mL stainless steel autoclave. Excellent results were obtained under the reaction conditions given in Table 1, entry 1 with nearly quantitative conversion of *cis*-cyclooctene and almost complete selectivity towards epoxycyclooctane. Decreasing the molecular ratio from *cis*-cyclooctene:O_2 to 1:1.6 (atmospheric pressure of O_2 in the autoclave, $V = 100$ mL) or

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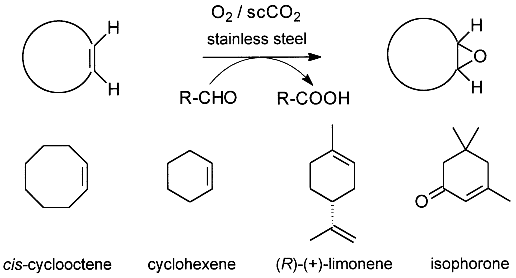
Table 1. Epoxidation of *cis*-cyclooctene in $scCO_2$ under various reaction conditions.[a]

Entry	S:A	T [°C]	t [h]	S:O_2	Conv. [%][b]	Sel. [%][c]
1	1:2	55	18	1:10	> 99	> 99
2	1:2	55	18	1:1.6	94	> 99
3	1:2	55	8	1:10	90	> 99
4	1:2[d]	55	18	1:10	100	99
5	1:1	55	18	1:10	2	> 95
6	1:2	25–28[e]	18	1:10	14	> 99

[a] S = *cis*-cyclooctene (2.5 mmol), A = 2-methyl-propionaldehyde. [b] Conversion of *cis*-cyclooctene as determined by GC. The GC values are corrected. Oxidation products have been characterized by GC/MS. [c] Selectivity = (GC area % of epoxycyclooctane)/(GC area % of all detected oxidation products of *cis*-cyclooctene). GC signals < 0.2 area % have been neglected. [d] A = 2,2-dimethyl-propionaldehyde. [e] In liquid CO_2.



Scheme 1. Steel-promoted epoxidation of cyclic olefins.

reducing the reaction time to 8 h led to somewhat lower conversion (entries 2 and 3). The molecular structure of the aldehyde had little influence on the epoxidation (entry 4). Two equivalents of aldehyde were sufficient to achieve quantitative conversion, but only trace amounts of the epoxide were formed with one equivalent of aldehyde (entry 5). The reaction rate was much lower in liquid CO_2 at lower reaction temperature (entry 6).

Conversion and selectivity for the epoxidation of various substrates in $scCO_2$ under standardized reaction conditions are listed in Table 2. The cyclic olefins *cis*-cyclooctene and cyclohexene were converted nearly quantitatively in $scCO_2$ with very high selectivities (Scheme 1). For *cis*-cyclooctene, the epoxidation occurred efficiently in six different stainless steel autoclaves that varied in manufacture and volume. Reaction temperatures between 46 and 55 °C were employed, but conversion was only slightly affected with somewhat lower conversion corresponding to lower reaction temperatures. In the case of cyclohexene, small amounts of cyclohex-2-enone (6 %) were formed as by-product. With (*R*)-(+)-limonene as the substrate, epoxides were detected as the only oxidation products at 30–51 % conversion in $scCO_2$. Epoxidation of the cyclic double bond was largely preferred over attack at the terminal position. Isophorone, an olefinic cyclic ketone, was oxidized with modest conversion and with comparably low selectivity for the epoxide in $scCO_2$. The main by-products were the cyclic 1,4-diketone and an acyclic carboxylic acid that was formed by oxidative cleavage of the double bond.

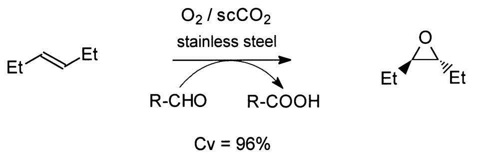
Table 2. Epoxidation of various olefins with dioxygen and 2-methyl-propionaldehyde in the presence of stainless steel.[a]

Entry	Olefin	Solvent	Conv. [%]	Epoxides	Sel. [%][b]	Runs
1	*cis*-cyclooctene	$scCO_2$	95–99.6	epoxycyclooctane	> 99	15[c]
2	*cis*-cyclooctene	toluene	50–84	epoxycyclooctane	> 99	4
3	cyclohexene	$scCO_2$	95	epoxycyclohexane	91	1
				2,3-epoxycyclohexane-1-one	3	
4	cyclohexene	CH_2Cl_2[e]	93	epoxycyclohexane	95	1
5	1-octene	$scCO_2$	23–46	1,2-epoxyoctane	70–87	5
				3,4-epoxyoctane	4–8	
6	1-octene	$scCO_2$[d]	26	1,2-epoxyoctane	94	1
				3,4-epoxyoctane	6	
7	1-octene	toluene	20–23	1,2-epoxyoctane	67–81	2
				3,4-epoxyoctane	1–7	
8	*trans*-3-hexene	$scCO_2$	96	*trans*-3,4-epoxyhexane	> 98	1
9	*trans*-3-hexene	toluene	69	*trans*-3,4-epoxyhexane	> 98	1
10	(*R*)-(+)-limonene	$scCO_2$	30–51	*cis*-1,2-epoxide	59–60	2
				trans-1,2-epoxide	30–32	
				8,9-epoxides[f]	9–10	
11	(*R*)-(+)-limonene	toluene	83	*cis*-1,2-epoxide	51	1
				trans-1,2-epoxide	32	
				8,9-epoxides[f]	6	
				1,2,8,9-diepoxides[f]	11	
12	isophorone	$scCO_2$	16	epoxyisophorone	30	1
13	isophorone	toluene	4	epoxyisophorone	19	1

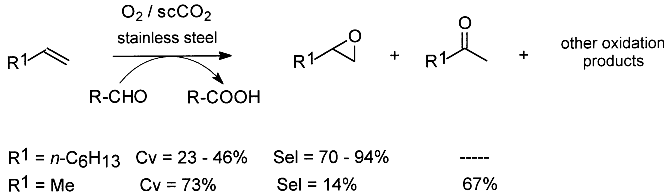
[a] Reaction conditions: see Experimental Section. Analysis by GC and GC/MS. For epoxycyclooctane the GC values are corrected, all other values are uncorrected. [b] Selectivity = (GC area % of the epoxide)/(GC area % of all detected oxidation products of the olefin), GC signals < 0.2 area % were neglected. Additional by-products for oxidation in toluene: benzaldehyde, benzyl alcohol, benzyl hydroperoxide, benzoic acid. [c] Six different stainless steel autoclaves were used. [d] 2,2-Dimethyl-propionaldehyde was used. [e] In absence of stainless steel. [f] Two isomers.

With linear olefins, epoxidation was nearly quantitative in the case of *trans*-3-hexene containing an internal double bond (Scheme 2) and *trans*-3,4-epoxyhexane was formed as the only stereoisomer. The terminal olefin 1-octene was epoxidized with moderate rate in $scCO_2$ (Scheme 3) and the selectivity towards the terminal epoxide was 70–87 %. Small amounts of heptanoic acid were detected and the 3,4-epoxide

Abstract in German: *Olefine können in überkritischem Kohlendioxid oxidiert werden, wenn Sauerstoff als primäres Oxidationsmittel und Aldehyde als Co-Oxidantien eingesetzt werden. Die Reaktion wird in Gegenwart des Edelstahls der Reaktorwände initiiert und erfordert keine zusätzlichen Katalysatoren. In Abhängigkeit vom Substrat findet bevorzugt vinylische Oxidation oder Epoxidierung statt. Die Epoxidierung ist besonders effektiv bei Substraten mit interner Doppelbindung und bei langkettigen endständigen Olefinen.*



Scheme 2. Steel-promoted epoxidation of *trans*-3-hexene. Cv = conversion.

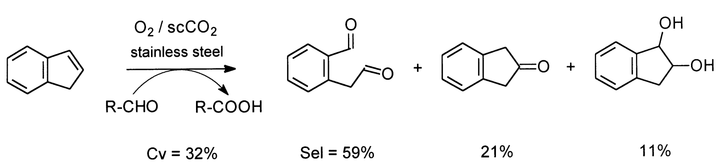


Scheme 3. Steel-promoted oxidation of terminal linear olefins. Cv = conversion; Sel = selectivity.

was formed, presumably resulting from isomerization of the olefin. However, a selectivity towards 1,2-epoxyoctane of up to 94% could be achieved when 2,2-dimethyl-propionaldehyde was used as the co-oxidant.

Conversion of propene was high under standard reaction conditions (Scheme 3), but vinylic oxidation was the prevailing pathway leading to acetone as the major product with 49% yield (relative to *n*-heptane as internal standard, see Experimental Section). Propylene oxide was formed in 10% yield and other oxidation products included isopropyl alcohol (6%), isopropyl formate (5%), acetaldehyde (2%), and traces of acetic acid.

The aromatic olefins styrene, *trans*-stilbene and indene were also treated with dioxygen under the same reaction conditions as above (see Table 1, entry 1). Indene was the only aromatic substrate that showed significant conversion (32%), leading to a mixture of oxidation products. Oxidative cleavage of the double bond gave 2-(2-oxoethyl)-benzaldehyde as the major component, but 1,2-indanediol and the vinylic oxidation product 2-indanone were also present in appreciable amounts (Scheme 4).



Scheme 4. Steel-promoted oxidation of indene. Cv = conversion; Sel = selectivity.

From these investigations, one can conclude that $scCO_2$ is an interesting medium for oxidation processes utilizing molecular oxygen in the presence of aldehydes as the co-oxidant. In particular, the epoxidation of internal double bonds occurs with high rates and selectivities even in the absence of any additional catalyst. To further assess the potential of $scCO_2$ as a solvent for this type of oxidation reactions, we compared its performance to that with conventional liquid organic solvents. In a standard glass flask, the epoxidation of cyclohexene occurred also efficiently in CH_2Cl_2 with 95% selectivity under atmospheric pressure of O_2 and in the presence of three equivalents of 2-methyl-propionaldehyde (Table 2, entry 4).[10b]

In sharp contrast, virtually no conversion occurred when toluene was used as a solvent for the oxidation of cyclic olefins in standard glassware. Whereas chlorinated solvents such as CH_2Cl_2 are known to initiate radical oxygen transfer reactions,[11] neither toluene nor CO_2 are expected to enable similar pathways. To account for the obvious discrepancy between the lack of oxidation in toluene and the highly effective conversion in $scCO_2$, we speculated that the stainless steel of the reactor walls played a crucial role in promoting the oxidation in the supercritical medium.[13, 14] The results summarized in Figure 1 strongly support this hypothesis.

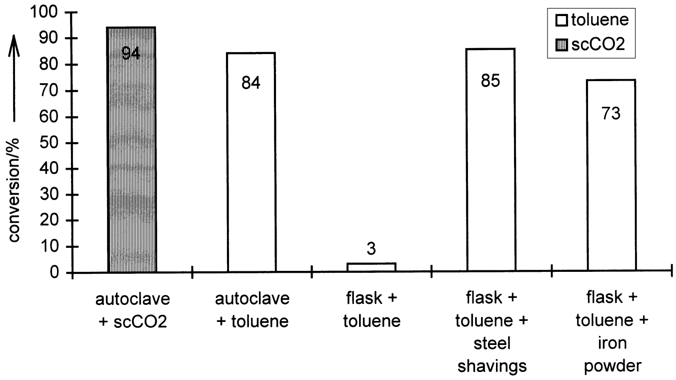


Figure 1. Epoxidation of *cis*-cyclooctene in $scCO_2$ and in toluene using a partial pressure of O_2 of 1 bar.

In a stainless steel autoclave, *cis*-cyclooctene was converted to epoxycyclooctane with 94% conversion and >99% selectivity after 18 h at 55 °C in $scCO_2$ ($d = 0.75$ g mL^{-1}) under a partial pressure of O_2 of 1 bar using two equivalents of 2-methyl-propionaldehyde. Epoxidation was also initiated in toluene by using the same stainless steel autoclave under otherwise identical reaction conditions, but conversion was less efficient than in $scCO_2$. Most significantly, only 3% conversion occurred in toluene in the absence of steel after 18 h in a borosilicate glass flask, but O_2 consumption started immediately upon addition of steel shavings and 85% conversion of the olefin to the epoxide was detected after further stirring for 18 h. This experiment unambiguously demonstrates the promoting effect of steel. The surface and composition of the steel had no significant influence on the reaction rate. Substitution of the steel shavings with iron powder was also possible, but resulted in slightly lower conversion of the olefin.

As seen from Table 2, the steel-promoted epoxidation occurred generally more efficiently in $scCO_2$ than in toluene under otherwise identical reaction conditions. In the case of *cis*-cyclooctene (entry 1/2), 1-octene (entry 5/7), and *trans*-3-hexene (entry 8/9), the selectivities of the desired epoxides were very similar in both solvents, but conversion was significantly lower in toluene than in $scCO_2$. Practically no oxidation of isophorone occurred in toluene as compared to 16% conversion in $scCO_2$ (entry 12/13). (*R*)-(+)-limonene was the only substrate for which conversion was higher in toluene than in $scCO_2$ (entry 10/11), but two isomeric diepoxides were formed as additional products.

The higher reaction rates in $scCO_2$ than in toluene may be partly due to the fact that $scCO_2$ and dioxygen are completely miscible, whereas in toluene the availability of dioxygen is limited. The higher diffusivity of $scCO_2$ compared to toluene may also play an important role. A further benefit of CO_2 as compared to toluene is the above-mentioned inertness towards oxidation, allowing the partial pressure of O_2 to be raised to several bars. Generally, in organic solvents, only low pressures of dioxygen can be used because explosion limits have to be considered. In the present case, significant amounts of by-products from the oxidation of toluene as solvent (i. e. benzaldehyde, benzyl alcohol, benzyl hydroperoxide, benzoic acid) were observed even under atmospheric pressure of O_2.

The promoting effect of steel in the epoxidation of internal olefins can be related to the formation of acylperoxy radicals from the reaction of the aldehyde and dioxygen. Monitoring the epoxidation of *cis*-cyclooctene in $scCO_2$ by online GC/MS reveals a significant induction period, which can be reasonably associated with this process (Figure 2).[15] Once the acylperoxy radicals are present in sufficient concentration, the subsequent oxidation of the olefin can occur in a non-catalytic radical pathway (Scheme 5).

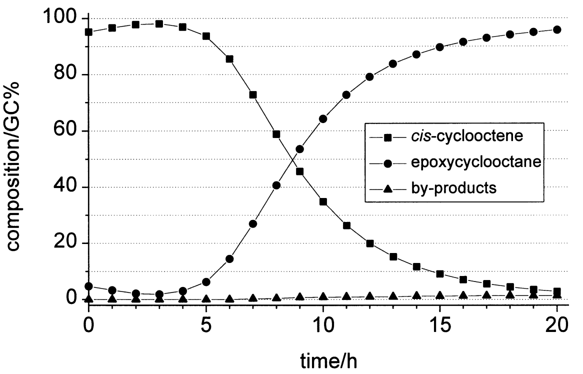
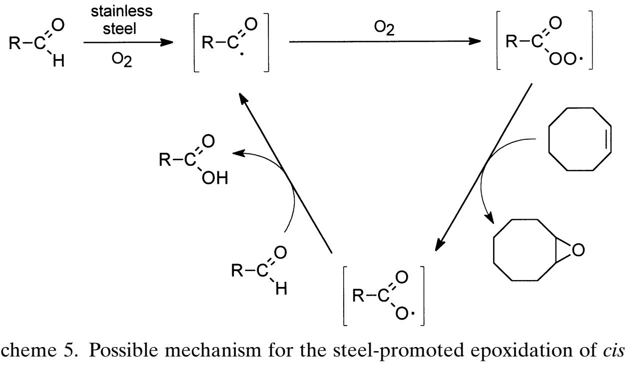


Figure 2. Reaction profile for a typical steel-promoted epoxidation of *cis*-cyclooctene in $scCO_2$.



Scheme 5. Possible mechanism for the steel-promoted epoxidation of *cis*-cyclooctene.

Consistent with this picture, the amount of typical by-products arising from direct free-radical oxidation with O_2 is very small under our conditions. Furthermore, the epoxidation of *cis*-cyclooctene continues, if a toluene solution is filtered from the steel shavings after initiation. However, oxidation stops immediately if *p-tert*-butylcatechol is added as a radical scavenger to either the filtrate or the steel-containing mixture. The sequence shown in Scheme 5 is consistent with these experimental results. However, we note that our data do not necessarily exclude a pathway involving the formation of soluble metal species that may contribute to the oxygen transfer.[11c] For $scCO_2$, we consider such a scenario less likely based on the weak solvent power of this medium for metal ions. [16]

Conclusion

In conclusion, $scCO_2$ provides an interesting reaction medium for the oxidation of olefins using dioxygen in the presence of aldehydes as the co-oxidant. Depending on the substrate, either vinylic oxidation or epoxidation occurs with high rates and selectivities. Epoxidation is particularly efficient in the case of linear or cyclic substrates containing internal double bonds. No additional catalyst is required to achieve high reaction rates and selectivities. However, the epoxidation is promoted through the presence of stainless steel from the reactor wall, which seems to facilitate the initial formation of acylperoxy radicals.

Experimental Section

Safety warning: The use of compressed gases and especially O_2 in the presence of organic substrates requires appropriate safety precautions and must only be carried out using suitable equipment.

All liquid starting materials and solvents were dried and distilled under argon prior to use. Dioxygen (Messer Griesheim, 4.8) and CO_2 (Messer Griesheim, 4.5) were used as received.

Oxidation of olefins in $scCO_2$: A 100-mL stainless steel autoclave (austenitic steel, material number 1.4571) equipped with thick-wall glass windows, PTFE-stir bar, two thermocouples for the inner temperature and the temperature of the electrically heated wall, pressure transducer, and needle and ball valves was charged with the olefin (2.50 mmol) and the aldehyde (5.00 mmol) under argon. The reactor was filled with CO_2 (75 g, $d = 0.75\ g\,mL^{-1}$) using a compressor. Dioxygen was introduced from a pressurized vessel whereby the amount of O_2 (ca. 25.0 mmol) was estimated from the pressure drop in the reservoir. The partial pressures of O_2 in the mixture under reaction conditions were additionally controled by means of a calibration curve. A colorless homogeneous supercritical phase was formed upon heating to 55 °C under stirring ($p^0_{tot} \approx 190$ bar). After 18 h the reactor was vented through a cryo trap (−78 °C, acetone/dry ice). To collect all products, the reactor and the cryo trap were washed with an organic solvent and the combined solutions were analyzed by GC and GC/MS. The reaction products were additionally characterized by ^1H and ^{13}C NMR spectroscopy in the case of the substrates *trans*-3-hexene and indene.

Monitoring the epoxidation by online GC/MS: A typical reaction mixture containing *cis*-cyclooctene as the substrate was prepared as described above in a stainless steel autoclave ($V = 100$ mL). The reactor was connected to a HP GC 6890 gas chromatograph including a HP MSD 5973 mass detector and a 30-m HP-5MS column using an automatic sampling valve system described in detail elsewhere.[17] GC/MS spectra were automatically recorded at 1 h intervals.

Epoxidation of *cis*-cyclooctene under atmosheric pressure of O_2 in $scCO_2$: *cis*-Cyclooctene (2.50 mmol) and 2-methyl-propionaldehyde (5.00 mmol) were placed in the above-described 100-mL stainless steel autoclave under an O_2 atmosphere (100 mL = 1.6 equivalents). The reactor was filled with CO_2 (75 g, $d = 0.75\ g\,mL^{-1}$) using a compressor, stirred for 18 h at 55 °C ($p^0_{tot} \approx 190$ bar) and the contents worked-up as described above.

Oxidation of propene in $scCO_2$: 2-Methyl-propionaldehyde (8.20 mmol) was placed in the 100-mL stainless steel autoclave under a propene atmosphere (100 mL = 4.10 mmol). The reactor was filled with CO_2 (75 g, $d = 0.75$ g mL^{-1}) using a compressor. Then dioxygen (ca. 40.0 mmol) was introduced from a pressurized vessel as described above. After stirring the mixture for 18 h at 55 °C ($p^0_{tot} \approx 190$ bar) the reactor was vented through a cryo trap filled with 70 mL of dry and degassed toluene at −50 °C. The reactor was washed with toluene and the combined toluene solutions were analyzed by GC and GC/MS. The yield of oxidation products was determined using *n*-heptane as an internal standard and are based on corrected GC values for all oxidation products.

Oxidation of olefins in toluene: A 100-mL two-necked round-bottom flask or the 100-mL stainless steel autoclave described above was charged with dry and degassed toluene (70 mL), the olefin (2.50 mmol), and 2-methyl-propionaldehyde (5.00 mmol) under argon. The reaction compartment was purged with O_2 and a gas burette filled with dioxygen was connected. The reaction mixture was agitated with a magnetic stir bar for 18 h at 55 °C. After cooling to ambient temperature the solution was analyzed by GC and GC/MS.

Epoxidation of cyclohexene in CH_2Cl_2:[10b] A 50-mL two-necked pear-shaped flask was charged with dry and degassed CH_2Cl_2 (10 mL), cyclohexene (2.00 mmol), and 2-methyl-propionaldehyde (6.00 mmol) under argon. The reaction compartment was purged with O_2 and a gas burette filled with dioxygen was connected. The reaction mixture was agitated with a magnetic stir bar for 15 h at ambient temperature (23–24 °C). Then the solution was analyzed by GC and GC/MS.

Acknowledgement

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