



Selective Ruthenium-Catalyzed Hydroaminomethylation of Unsaturated Oleochemicals

Kévin Cousin, Frédéric Hapiot, Eric Monflier

► To cite this version:

Kévin Cousin, Frédéric Hapiot, Eric Monflier. Selective Ruthenium-Catalyzed Hydroaminomethylation of Unsaturated Oleochemicals. *European Journal of Lipid Science and Technology*, 2020, 122 (1), pp.1900131. <10.1002/ejlt.201900131>. <hal-02439627>

HAL Id: hal-02439627

<https://hal.science/hal-02439627v1>

Submitted on 13 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Selective ruthenium-catalyzed hydroaminomethylation of unsaturated oleochemicals

Kévin Cousin¹, Frédéric Hapiot,¹ Eric Monflier*,¹

¹ Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), F-62300 Lens, France.

*Correspondance : Eric Monflier, Faculté des Sciences Jean Perrin, rue Jean Souvraz, SP18, 62307 Lens Cedex, France ; Fax: +33(0)321791755 ; Email: eric.monflier@univ-artois.fr

Running Title: hydroaminomethylation of oleochemicals

Keywords: ruthenium, hydroaminométhylation, triolein, methyl undecenoate, amines

Abbreviations: T, triolein; MO, methyl oleate; ML, methyl linoleate, MU, methyl undecenoate, VHOSO, very high oleic sunflower oil; HF, hydroformylation; HAM, hydroaminomethylation

Abstract

Rhodium-catalyzed hydroaminomethylation (HAM) was recently described as an innovative way to functionalize triglycerides. In our search to reduce production costs, we sought to replace rhodium by ruthenium whose price is currently more than 20 times lower. In this study, we proceeded to HAM of unsaturated oleochemicals using ruthenium precursors under phosphine-free conditions. The experimental conditions were optimized by changing the nature of the solvent, the reaction temperature, and the CO/H₂ pressure. While rhodium led to good catalytic activity and low chemoselectivity (mixture of hydroxyl and amino groups), ruthenium proved to be less active but more chemoselective as amino-substituted products were mainly formed. Of interest, HAM of methyl undecenoate (MU) occurred in a highly chemo- and regioselective fashion using acetonitrile as solvent.

Practical applications

Selective Ru-catalyzed hydroaminomethylation could be implemented on an industrial scale for the conversion of unsaturated oleochemicals into amines. This finding is of importance as the obtained amino-products can be used in many industrial areas such as surfactants, polymers, or lubricants.

1 Introduction

Hydroaminomethylation (HAM) has recently gained increasing interest within the field of green chemistry as the reaction provides biosourced amines (which may be used as monomers or quaternized to form surface active compounds) with high atom economy and low environmental impact.^{1,2} HAM is a homogeneously catalyzed reaction, employing transition metal catalysts, which consists in three consecutive reactions involving hydroformylation of carbon-carbon double bonds into aldehydes, condensation of amines, and hydrogenation of the resulting imines/enamines into amines. These tandem reactions occur under CO/H₂ pressure in a one-pot procedure, which is very appealing from a synthetic viewpoint. However, the economic viability of such reaction on an industrial scale is compromised by the high price of the rhodium catalyst and utilization of phosphines.^{3,4,5} Effective recyclability and low catalyst loading are thus required. To prevent

utilization of phosphines, alternatives emerged such as Rh/amine combinations.⁶ For example, we recently showed that phosphine-free HAM of triolein (T) and commercial oils resulted in the functionalization of fatty chains by amino and hydroxyl groups in various proportions depending on the applied experimental conditions.^{7,8} To overcome the pricing hurdle of rhodium catalysts, ruthenium-based approaches were developed. Ruthenium was envisaged as an interesting surrogate because it is currently more than 20 times cheaper than rhodium. Ruthenium-catalyzed HAM have already been described for petrosourced substrates.^{9,10,11,12,13,14,15,16,17} To our knowledge, nothing was reported so far on utilization of ruthenium catalysts in HAM of unsaturated oleochemicals. In the present study, we describe pros and cons of ruthenium as a metal catalyst in HAM of unsaturated fatty chains (Figure 1) and compare the observed catalytic performances to those obtained with rhodium.

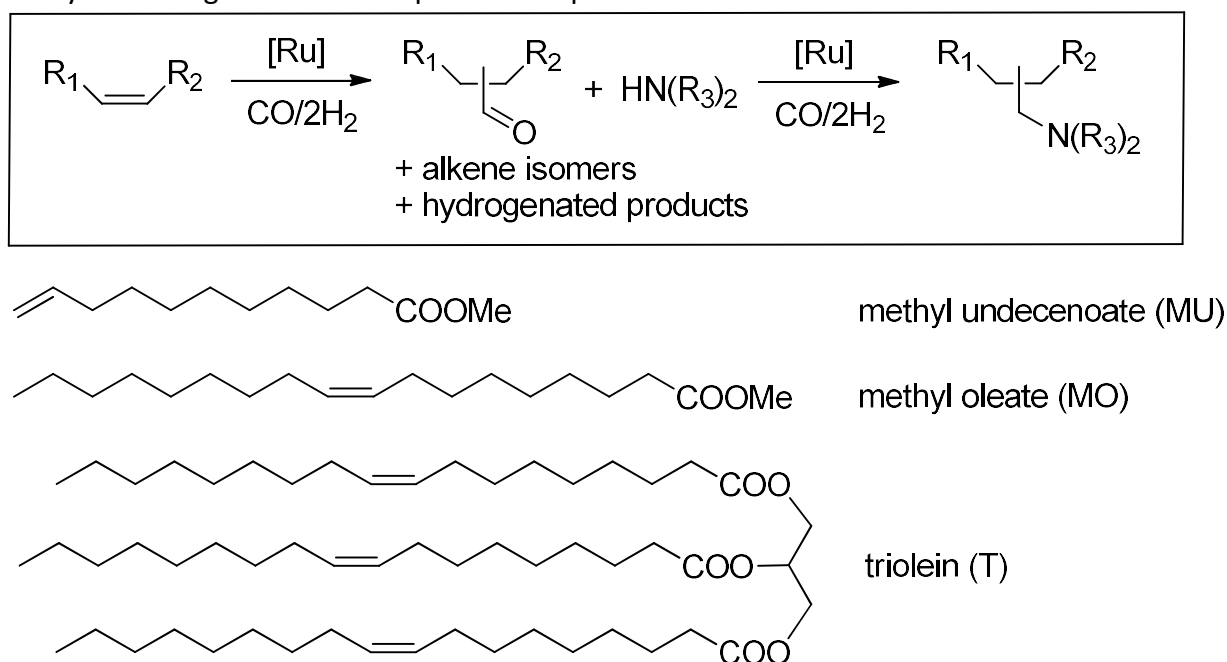


Figure 1. Ru-catalyzed hydroaminomethylation of unsaturated oleochemicals.

2 Materials and methods

2.1 Reagents and solvents

Triolein (T, 97% C18:1), methyl oleate (MO), methyl linoleate (ML), methyl undecenoate (MU), Ru₃CO₁₂, amines, and solvents were received from Aldrich (France) in their highest purity. VHOSO (Very High

Oleic Sunflower Oil, 86% C18:1, 6% C18:2, 4% C18:3, 3% C18:0, 1% C20:0) was a gift from Novance (Venette, France). T, MO, ML, MU and VHOSO were deperoxidized over basic alumina before use. Syngas (CO/H₂ = 1/1) and hydrogen were supplied from Air Liquide (France). CDCl₃ (99.50% isotopic purity) was purchased from Eurisotop.

2.2 General procedure of HAM experiments

All hydroaminomethylation experiments were carried out in laboratory reactors equipped with a mechanical stirrer, pressure regulators and a safety rupture valve from Parr Instrument Company (USA). In a typical experiment, triolein (1 mL, 1 mmol), $\text{Ru}_3\text{CO}_{12}$ (3.2 mg, 0.015 mmol), and HNBu_2 (3 mmol) were dissolved in toluene (6 mL). The solution was then poured into the stainless-steel autoclave. After it had been heated to reaction temperature, the reactor was pressurized under CO and H_2 pressures and the solution was stirred at 1500 rpm. After 18 h, the reactor was cooled down to RT and depressurized. The crude reaction mixture was filtered on Celite®545 to remove the ruthenium catalyst and the products were analyzed.

2.3 Products analysis

After evaporation of toluene, an aliquot of the organic phase was dissolved in 500 μL CDCl_3 and analyzed at RT by NMR spectrometry using a Bruker DRX300 spectrometer operating at 300 MHz for ^1H nuclei and 75 MHz for ^{13}C nuclei. Conversions and selectivities were determined by ^1H NMR by comparing the integrations of signals (see supporting information).

Conversions and selectivities were also confirmed by GC-MS for MU. The GC-MS analyses were performed using a Shimadzu QP2010 gas chromatograph with a split/splitless injection port and coupled with mass spectrometer. The separation was performed with a silica capillary column Zebron ZB-SemiVolatils (5% polysilarylene-95% dimethylsiloxane, 30×0.25 mm, internal diameter 0.25 μm) (see supporting information).

Crude reaction mixtures were also purified on a silica column (heptane/ethyl acetate 90/10 v/v) and the isolated products were fully characterized by NMR spectroscopy (see supporting information).

3 Results

In an initial exploratory study to assess the performances of ruthenium in HAM of biosourced substrates, we chose T as a model substrate and $\text{Ru}_3\text{CO}_{12}$ as a ruthenium precursor as its efficacy was recently proven in HAM of petrosourced substrates.^{15,16} Reaction conditions were similar to previous studies on rhodium catalysts.⁷ The first set of experiments concerned the amine nature (Table

1). Indeed, during the course of the HAM reaction, amines may act as both reactants and ruthenium ligands. It is thus of importance to define the ideal amine structure capable of i) coordinating to ruthenium to form hydroformylating and hydrogenating catalysts, and ii) condensing with aldehydes to form imine/enamine intermediates. To reach T-grafted tertiary amines, we made use of secondary amines.

Insert Table 1

Acyclic secondary amines led to moderate conversions (Table 1, entries 1-3) and high selectivity in amino-derivatives (amine selectivity up to 94%) while pyrrolidine gave lower conversion (entry 4) and higher proportion of aldehydes (*S. Ald* = 10%). Diethanolamine, for its part, was dissolved in THF as it was insoluble in toluene. It was basically inactive under such experimental conditions.

A set of batch experiments was then carried out to optimize the experimental conditions using dibutylamine, the best secondary amine of Table 1 in terms of catalytic performances. Changing the nature of the solvent greatly affected the catalytic activity. The conversion dropped to 18% with THF (Table 1, entry 6) and to 6% with isopropanol (entry 7), suggesting that the solvent has an influence on the catalytic performances. Conversely, the selectivity in amino-derivatives were slightly higher (96% and 97% with THF and isopropanol, respectively, vs 94% with toluene). Only hydrogenated products were detected as side-products whatever the solvent. Under otherwise identical conditions, no reaction took place using *N*-methyl-2-pyrrolidone (NMP) as a solvent (entry 8). Logically, reducing the catalyst loading by a factor 2 halved the conversion without altering the selectivities (Table 2, entry 3).

Insert Table 2.

As expected, variations of the reaction temperature greatly influenced both the conversion and selectivities. At 90 °C, the conversion is only 6%, indicative of the higher activation energy required with ruthenium compared to rhodium. Raising the temperature to 120 °C speeded up the catalytic activity as 31% C=C were converted over 18 h at 120 °C. No aldehydes or alcohols were identified

irrespective of the temperature. The proportion of amino-derivatives was high (up to 98%) but slightly decreased when increasing the temperature, to the benefit of small amounts of hydrogenated products.

Insert Table 3

Attempts to enhance the performance of the Ru-catalyst through variation of the CO/H₂ pressure from 40 to 100 bar resulted in a significant increase in the conversion from 9 to 29%, respectively, in line with previous results from the literature (Table 3).¹¹ However, contrary to what was observed when increasing the reaction temperature, the proportion of amino-derivatives slightly increased at the expense of the percentage of hydrogenated products. The best results were obtained at 100 bar of CO/H₂ (entry 4). The pressure ratio of CO and H₂ was varied to 1/2 while keeping the total pressure at 100 bar (entry 5). The slight increase in conversion (31%) was compensated by a significant decrease of amine selectivity. Under such experimental conditions, less amino-derivatives were formed to the benefit of hydrogenated products.

Insert Table 4

After a clearly positive effect of temperature and pressure was established, the study was then further extended to Ru-catalyzed HAM of other unsaturated oleochemicals. Converting MO was slightly easier than T, and a better selectivity in amino-derivatives was obtained as well (Table 4, entry 1).

Conversely, the presence of a multiple C=C bonds on the fatty alkyl chains turned out to have a deleterious influence on both the conversion and selectivity. For example, conversions lower than 5% were measured for ML and VHOSO, suggesting that the presence of at least two C=C might inhibit the Ru-catalyst. As already stated for Rh-catalyst,⁷ C=C double bonds probably isomerize to form a π -allyl Ru-complex displaying reduced catalytic activity towards internal alkenes. However, no conclusive statement can be made at this stage.

HAM of MU was regarded with great attention, as it contains a terminal alkene that would behave very differently from the other studied substrates. Increasing the reaction time from 6 to 36 h

improved the amine selectivity from 47 to 96% while the proportion of alkene isomers dropped from 47 to 0% (Table 4, entries 4-6). However, the l/b ratio slightly decreased. A nearly stoichiometric proportion of linear and branched amino derivatives was obtained over 36 h. Lowering the reaction temperature to 80 °C resulted in both a poor 14% conversion over 6 h, and an increase in the selectivity in linear products, which is expected due to the lower energy barrier for the hydroformylation of the terminal position (entry 7). Conversely, increasing the temperature to 120 °C resulted in substantial proportions of alkenes isomers (up to 60%, entry 9). Similar effects were observed by lowering the pressure of CO/H₂ (1/1) (entry 10). Changing the CO/H₂ from 1/1 to 1/2 gave the highest alkene isomers proportion found in this study (80%, entry 11). As confirmed by GC-MS, alkenes isomers showed their carbon-carbon double bond in 2- or 3-position. Utilization of THF instead of toluene as a solvent resulted in a lower conversion (from 100 to 74%) and chemoselectivity (from 47 to 40%) while the l/b ratio was improved from 62/38 to 75/25. The effect was even more pronounced when MU was subjected to HAM in CH₃CN. The conversion dropped to 41% but the l/b ratio raised 96/4, the highest value found herein (entry 13). Over 18 h in CH₃CN, the conversion reached 74% and the proportion of amino derivatives was significantly improved to 38% without affecting the regioselectivity (entry 14). Over 66 h, both the conversion and the chemoselectivity were increased (entry 15). The proportion of isomers decreased to 30% while the percentage of hydrogenated products remained constant. Similar results were obtained over 18 h at 140 °C (entry 16). Satisfyingly, isomers were no longer detected when the reaction proceeded over 66 h at 140 °C (entry 17). Amino-derivatives represented 96% of the final mixture, alongside 4% of hydrogenated products. Additionally, the regioselectivity remained constant with a l/b of 96/4. A further increase in reaction temperature to 160 °C did not alter the relative proportion of products but substantially altered the regioselectivity (entry 18).

4 Discussion

Generally speaking, we notice a lower catalytic activity of the Ru/amine combination by comparison with the Rh/amine couple in HAM of internal C=C bonds.⁷ For example, under 80 bar CO/H₂ (1/1) at 110 °C in toluene with HNBu₂ as amine, the turn-over frequency (TOF) is of 0.88 h⁻¹ in HAM of T using Ru-catalyst while we obtained TOF of 3.7 h⁻¹ with Rh-catalyst in our previous study.⁷ Amongst the studied amines, acyclic ones are the more appropriate, probably because of their σ -donating ability towards ruthenium and the flexibility of their structure to fit the ruthenium coordination sphere. Both electronic and steric effects can be distinguished using pyrrolidine and diethanolamine as reactants and potential Ru-ligands. In the presence of pyrrolidine, the presence of aldehyde intermediates (aldehyde selectivity = 10%) shows that the conversion of C=C bonds is incomplete within 18 h. Pyrrolidine being more rigid than acyclic amines, the bulky pyrrolidine-coordinated Ru-catalyst probably experiences more difficulty to reach bulky internal C=C bonds. This assumption is supported by previous studies by Beller et al.¹³ They showed that pyrrolidine is more appropriate for HAM of terminal alkenes than internal C=C bonds. As an indirect proof of the lower reactivity of internal C=C bonds, the less hindered terminal C=C bond of MU is converted over 6 h (Table 4, entry 4). The ineffectiveness of diethanolamine in combination with ruthenium clearly informs that inductive effects also affect the amine coordination towards the Ru center. Compared with acyclic amines, the lower σ -donating ability of the diethanolamine nitrogen is undoubtedly responsible for the lack of reactivity of the Ru-catalyst, and the subsequent absence of aldehydes.

Note that, apart for pyrrolidine, no aldehyde intermediates are detected over the course of the HAM reaction, indicative of their fast conversion into enamines by condensation with amines (see Figure S24, Supporting Information). Enamines then undergo fast hydrogenation to give saturated amino-derivatives. We conclude that the hydroformylation step seems to be rate-determining in the Ru-catalyzed HAM process (Table 1), as already observed throughout the literature.^{10,13}

Increases in both conversion and selectivity in amino-derivatives are observed in HAM of T on increasing the CO/H₂ pressure (Table 3). Of interest, the selectivity in amino derivatives reaches 95% upon operating at 100 bar of CO/H₂. This trend agrees well with those obtained in former studies on HAM of terminal alkenes.¹²

The effect of the reaction temperature is typical of what is usually observed for HAM reaction of internal C=C bonds (Table 2). Rising the temperature leads to higher catalytic activity but lower selectivity.^{1,7} Herein, the proportion of amino-derivatives decreases to the benefit of unwanted hydrogenated products. However, the effect of increasing the temperature is less pronounced with terminal alkenes such as MU as the selectivities remain rather constant up to 160 °C (Table 4, entry 17). Only the regioselectivity is slightly affected.

The nature of the solvent also greatly affect the catalytic performances of the Ru-catalyzed HAM reaction. Regarding the coordination capability of the solvents, polar solvents such as THF, isopropanol, or NMP lead to low conversions, suggesting that they modify the ruthenium coordination sphere to such an extent that the coordination of the substrate is rendered difficult. The effect is amplified in CH₃CN as this solvent can strongly coordinate ruthenium. The resulting Ru-catalyst is then more prone to react with the terminal position, as exemplified by the high I/b of 96/4 reported in Table 4 (entry 13). This observation is in line with results reported by Keim et al. who showed that more strongly coordinating polar solvents favor high selectivities.¹⁰

The crucial role played by the bulkiness of both the Ru-catalyst and the substrate is also revealed upon HAM of MU. Indeed, the results from Table 4 show that isomers are formed alongside the expected amino-derivatives. However, the proportion of isomers is clearly reduced over time while the proportion of branched amino-derivative increases (entries 13-15 and entries 16-17). The effect is especially spectacular in CH₃CN at 140 °C over 66 h as internal isomers are fully converted into amino-derivatives with high chemo- and regioselectivities (Table 4, entry 17). This clearly indicates internal C=C are less reactive than terminal ones because of the lower accessibility towards the catalyst. As the isomerization process continues over the course of

the reaction, internal C=C bonds isomerize into terminal ones, which then undergo HAM to yield amino derivatives.

5 Conclusions

To summarize, we investigated Ru-catalyzed HAM of unsaturated oleochemicals with a cost-cutting goal in mind. Throughout this study, we show that one of the main advantage of ruthenium over rhodium lies in the high selectivity in amino-derivatives and the absence of hydroxylated products. While alcohols are formed in non-negligible proportions upon Rh-catalyzed HAM of unsaturated oleochemicals such as triglycerides, no alcohol is detected with $\text{Ru}_3\text{CO}_{12}$ as a catalytic precursor. Note that upon Ru-catalyzed HAM of terminal alkene such as MU, alkene isomers may be formed in non-negligible proportion. However,

increasing the temperature and reaction time suffices to reduce their proportion. Interestingly, utilization of CH_3CN as a solvent leads to both high conversion and selectivities.

This work was performed, in partnership with the SAS PIVERT, within the frame of the French Institute for the Energy Transition (Institut pour la Transition Energétique (ITE) P.I.V.E.R.T. (www.institut-pivert.com) selected as an Investment for the Future ("Investissements d'Avenir"). This work was supported, as part of the Investments for the Future, by the French Government under the reference ANR-001-01.

The authors have declared no conflict of interest.

Table 1. Ruthenium-catalyzed HAM of triolein using various amines and solvent^a

Entry	Amine	Conv. (%)	S. Ald (%)	S. Amine (%)	S. Hydro (%)
1	HNEt ₂	37	0	86	14
2	HNBu ₂	45	0	94	6
3	HNHex ₂	45	0	90	10
4	pyrrolidine	25	10	80	10
5	HN(CH ₂ CH ₂ OH) ₂ ^b	0	0	0	0
6	HNBu ₂ ^b	18	0	96	4
7	HNBu ₂ ^c	6	0	97	3
8	HNBu ₂ ^d	0	0	0	0

^aTriolein (1 mL, 1 mmol), Ru₃CO₁₂ (6.4 mg, 0.030 mmol), amine (3 mmol), toluene (6 mL), 110 °C, 100 bar CO/H₂ (1/1), 18 h.

^bIn THF.

^cin isopropanol.

^dIn NMP.

Table 2. Influence of the temperature in ruthenium-catalyzed HAM of triolein^a

Entry	Temperature (°C)	Conv. (%)	S. Amine (%)	S. Hydro (%)
1	90	6	98	2
2	100	10	97	3
3	110	24	94	6
4	120	31	92	8

^aTriolein (1 mL, 1 mmol), Ru₃CO₁₂ (3.2 mg, 0.015 mmol), HNBu₂ (3 mmol), toluene (6 mL), 80 bar CO/H₂ (1/1), 18 h.

Table 3. Influence of the CO and H₂ pressures in ruthenium-catalyzed HAM of triolein^a

Entry	Pressure (bar)	CO/H ₂	Conv. (%)	S. Amine (%)	S. Hydro (%)
1	40	1/1	9	90	10
2	60	1/1	16	92	8
3	80	1/1	24	94	6
4	100	1/1	29	95	5
5	100	1/2	31	86	14

^aTriolein (1 mL, 1 mmol), Ru₃CO₁₂ (3.2 mg, 0.015 mmol), HNBu₂ (3 mmol), toluene (6 mL), 110 °C, 18 h.

Table 4. Ruthenium-catalyzed HAM of other unsaturated oleochemicals.^a

Entry	Substrate	Temp. (°C)	Reaction time (h)	Conv. (%)	<i>S. Amine</i> (%) (l/b)	<i>S. Hydro</i> (%)	<i>S. Iso</i> (%)
1	MO	110	18	52	97	3	-
2	ML	110	18	<5	-	-	-
3	VHOSO	110	18	<5	-	-	-
4	MU	110	6	100	47 (62/38)	5	47
5	MU	110	18	100	70 (57/43)	3	27
6	MU	110	36	100	96 (53/47)	4	0
7	MU	80	6	14	67 (86/14)	4	29
8	MU	100	6	52	54 (73/27)	6	40
9	MU	120	6	100	38 (73/27)	2	60
10 ^b	MU	110	6	79	21 (77/23)	6	63
11 ^c	MU	110	6	97	18 (67/33)	2	80
12 ^d	MU	110	6	74	40 (75/25)	3	57
13 ^e	MU	110	6	41	29 (96/4)	2	69
14 ^e	MU	110	18	74	38 (96/4)	6	56
15 ^e	MU	110	66	100	67 (96/4)	3	30
16 ^e	MU	140	18	100	64 (96/4)	2	34
17 ^e	MU	140	66	100	96 (95/5)	4	0
18 ^e	MU	160	18	100	64 (89/11)	6	30

^aC=C bonds (3 mmol), Ru₃CO₁₂ (6.4 mg, 0.030 mmol), HNBu₂ (3 mmol), toluene (6 mL), pressure of CO/H₂ (1/1) = 100 bar.

^bpressure of CO/H₂ (1/1) = 80 bar

^cpressure of CO/H₂ (1/2) = 100 bar

^din THF.

^ein CH₃CN.

--

References

- ¹ Crozet, D., Urrutigoñy, M., Kalck, P. Recent Advances in Amine Synthesis by Catalytic Hydroaminomethylation of Alkenes. *ChemCatChem* 2011, 3, 1102–1118.
- ² Kalck, P., Urrutigoñy, M. Tandem Hydroaminomethylation Reaction to Synthesize Amines from Alkenes. *Chem. Rev.* 2018, 118, 3833–3861.
- ³ Behr, A., Vorholt, A.J., Hydroformylation and related reactions of renewable resources, in Top. Organometal. Chem.; Meier, M.A.R., Weckhuysen, B.M., Bruijninx, P.C.A., Eds.; Springer-Verlag: Berlin, Germany, 2012; Vol. 39, pp 103–128.
- ⁴ de Oliveira Dias, A., Gutiérrez, M.G.P., Villarreal, J.A.A., Carmo, R.L.L., Oliveira, K.C.B., Santos, A.G., dos Santos, E.N., Gusevskaya, E.V., Sustainable route to biomass-based amines: rhodium catalyzed hydroaminomethylation in green solvents, *Applied Catal. A: Gen.* 2019, 574, 97–104.
- ⁵ Chen, C., Dong, X.-Q., Zhang, X. Recent progress in rhodium-catalyzed hydroaminomethylation. *Org. Chem. Front.* 2016, 3, 1359–1370.
- ⁶ Behr, A., Fiene, M., Buss, C., Eilbracht, P. Hydroaminomethylation of fatty acids with primary and secondary amines - a new route to interesting surfactant substrates. *Eur. J. Lipid Sci. Technol.* 2000, 102, 467–471.
- ⁷ Vanbésien, T., Monflier, E., Hapiot, F., A hydroaminomethylation/hydrohydroxymethylation sequence for the one pot synthesis of aminohydroxytriglycerides. *Green Chem.* 2017, 19, 1940–1948.
- ⁸ Hapiot, F., Monflier, E., Vanbésien, T., Aminoalcools gras et procédé de préparation de ceux-ci. French Patent FR3032708, 2015.
- ⁹ Jachimowicz, F., Raksis, J.W., Scope and Pathway of Catalytic Aminomethylation of Olefins. *J. Org. Chem.* 1982, 47, 445–441.
- ¹⁰ Schaffrath, H., Keim, W., Regio control in ruthenium catalysed aminomethylation. *J. Mol. Catal. A: Chem.* 1999, 140, 107–113.
- ¹¹ Srivastava, V.K., Eilbracht, P., Ruthenium carbonyl-complex catalyzed hydroaminomethylation of olefins with carbon dioxide and amines. *Catal. Commun.* 2009, 10, 1791–1795.
- ¹² Wu, L., Fleischer, I., Jackstell, R., Beller, M., Efficient and Regioselective Ruthenium-catalyzed Hydroaminomethylation of Olefins. *J. Am. Chem. Soc.* 2013, 135, 3989–3996.
- ¹³ Güllak, S., Wu, L., Liu, Q., Franke, R., Jackstell, R., Beller, M. Phosphine- and Hydrogen-Free: Highly Regioselective Ruthenium-Catalyzed Hydroaminomethylation of Olefins. *Angew. Chem. Int. Ed.* 2014, 53, 7320–7323.
- ¹⁴ Wu, L., Fleischer, I., Zhang, M., Liu, Q., Franke, R., Jackstell, R., Beller, M., Using Aqueous Ammonia in Hydroaminomethylation Reactions: Ruthenium-Catalyzed Synthesis of Tertiary Amines. *ChemSusChem* 2014, 7, 3260–3263.
- ¹⁵ Liu, J., Kubis, C., Franke, R., Jackstell, R., Beller, M., From Internal Olefins to Linear Amines: Ruthenium-catalyzed Domino Water-gas Shift/Hydroaminomethylation Sequence. *ACS Catal.* 2016, 6, 907–912.
- ¹⁶ Ali, M., Gual, A., Ebeling, G., Dupont, J., Carbon Dioxide Transformation in Imidazolium Salts: Hydroaminomethylation Catalyzed by Ru-Complexes. *ChemSusChem* 2016, 9, 2129–2134.
- ¹⁷ Oda, S., Franke, J., Krische, M.J., Diene hydroaminomethylation via ruthenium-catalyzed C–C bond forming transfer hydrogenation: beyond carbonylation. *Chem. Sci.* 2016, 7, 136–141.