We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Recent Advances in the Synthesis of Carboxylic Acid Esters

Kouichi Matsumoto, Rina Yanagi and Yohei Oe

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.74543>

Abstract

In this chapter, recent advances in the synthesis of carboxylic acid esters are summarized based on the utilization of carboxylic acids as electrophiles or nucleophiles in reactions. Condensation reagents or catalysts connect the carboxylic acids with the alcohols to afford the corresponding esters, together with the formation of 1 equiv. of H_2O , in which the carboxylic acids can be regarded as the electrophile. In contrast, the carboxylate ion intermediates derived from the carboxylic acids react with alkyl halides, carbocations, or their equivalents to produce the esters, in which the carboxylate ions from the carboxylic acids can be regarded as the nucleophile. This chapter mainly introduces the recent progress in this field of the formation of esters, based on the classification of the role of carboxylic acids in reactions.

Keywords: esterification, carboxylic acids, condensation reagents, catalysts, reaction media, reaction methods, S_N2 reactions, electrochemistry, transition metal catalysts, addition reactions

1. Introduction

In organic chemistry, the development of the efficient synthesis of carboxylic acid esters using carboxylic acids is still one of central research topics, because the organic material compounds, drug molecules, and natural products often contain ester unit as the functional group [1–3]. As for the view point of the synthesis of esters, the corresponding carboxylic acids are usually utilized as the key starting material and play an important role [1–3].

So far, many kinds of synthetic methods for the esters from carboxylic acids are well recognized and utilized, but a lot of researchers still have studied to investigate the new methods or aspects, because the synthesis of esters is also important from the point of view of green

chemistry and industry. In this chapter, recent advances in the synthesis of carboxylic acid esters are described. The reactions are classified into two categories, i.e., the reactions utilizing carboxylic acids as (1) electrophiles and (2) nucleophiles, in which the reactions are conducted by using various chemical reagents and catalysts as well as by using interesting reaction media and methods. Although many papers have appeared in this field, we herein have introduced important and selected examples because of the limitation of number of pages.

2. Synthesis of carboxylic acid esters using carboxylic acids as electrophiles

The typical and traditional method for the synthesis of carboxylic acid esters is the reaction of carboxylic acids with an excess amount of alcohols in the presence of a catalytic amount of H_2SO_4 by using Dean-Stark apparatus [1–3], in which H_2SO_4 catalyzes the addition of the alcohol to the carboxylic acid, and the H_2O thus generated is removed by Dean-Stark apparatus (**Scheme 1 (a)**). This reaction is called as Fischer esterification. However, there are some drawbacks. The excess amount of alcohols is used. The Dean-Stark apparatus is usually necessary. In addition, the substrates bearing the functional group which reacts with the acid cannot be utilized in this reaction. The alternative and reliable method to be developed is the use of DCC in the presence of a catalytic amount of DMAP (**Scheme 1 (b)**) [4]. DCC can serve as useful condensation reagents. The use of DCC as the condensation reagent realizes the decrease of the amount of alcohols. In addition, Mitsunobu reaction is also reliable method [5–8].

Besides the use of DCC, other condensation reagents are also developed. 2-Halo-pyridinium salts called Mukaiyama condensation reagent serve as effective reagents [9]. Mukaiyama et al. have extensively contributed this research area for the development of useful condensation reagents [10]. In addition, BOP ((benzotriazol-1-yloxy)-tris(dimethylamino)phosphonium hexafluorophosphate) [11, 12], CDI (carbonyldiimidazole) [13, 14], DMT-MM (4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride) [15–17], and so on [18, 19] are well established and used in the ester formation reactions.

As described above, many condensation reagents have been developed so far. However, there are still reports for this field. **Table 1** shows recent and selected reports of condensation reactions between carboxylic acids and alcohols using a stoichiometric amount of condensation

Fischer esterification

Condensation reagents

Scheme 1. Typical and traditional procedures for the synthesis of carboxylic acid esters and their chemical structures of reagents.

$\text{R}-\text{C}(=\text{O})\text{OH} + \text{R}'\text{OH} \xrightarrow[\text{Conditions}]{\text{Condensation reagents and}} \text{R}-\text{C}(=\text{O})\text{OR}'$		
Condensation reagents and Conditions		
Ref. 20 Polymer-bounded Ph_3P (or Ph_3P) (1.2 eq), and I_2 (1.2 eq); CH_3CN , microwave	Ref. 30 Ph_3P (1 eq), and $\text{Ph}-\text{N}_3$ (1 eq); microwave	Ref. 34 PPh_3 (2 eq), cat. $\text{Fe}(\text{Pc})$ (5 mol%) and cat. MPO (10 mol%) under air*; CH_3CN , reflux
Ref. 24 Ph_3P (2 eq), I_2 (2 eq) and $\text{Zn}(\text{OTf})_2$ (0.05 eq); CH_3CN , 60 °C	Ref. 31 (1.2 eq) PPh_3 (1 eq), and DMAP (1.2 eq); CHCl_3 , reflux	Ref. 35 PPh_3 (2 eq), flavin (10 mol%), azo compound (10 mol%) and MS4A under O_2 (1 atm) and hv; CH_3CN
Ref. 27 Ph_2PCl (0.5 eq), I_2 (0.5 eq) and imidazole (1.5 eq); CH_3CN , reflux	Ref. 32 PhIO (1.5 eq), PPh_3 (1.5 eq), and DMAP (0.1 eq); CH_2Cl_2 , reflux PhIO reacts with carboxylic acids to form hypervalent iodines.	Ref. 36 (XtalFluor-E) (1.1 eq) and Et_3N (1.5 eq); CH_2Cl_2
Ref. 28 Ph_3PBr_2 (5 eq) and K_2CO_3 (11 eq) (The excess amount of alcohols were used.)	Ref. 33 PPh_3 (1 eq) and (1 eq); CH_2Cl_2	Ref. 37 (TropCl2) (1.05 eq) and Et_3N (3 eq); CH_2Cl_2
Ref. 29 POCl_3 (1 eq), DMAP (0.3 eq), and Et_3N (2.4 eq); CH_2Cl_2		* Pc = phthalocyanine, MPO = 4-methoxypyridine

Table 1. Various condensation reagents and conditions used for the synthesis of carboxylic acid esters under the nearly equimolar carboxylic acids and alcohols (recent and selected examples).

reagents. Basically, the amount of alcohols is not excess (**Table 1**). For examples, polymer-bounded Ph_3P (or Ph_3P)/ I_2 /microwave [20–23] and $\text{Ph}_3\text{P}/\text{I}_2/\text{Zn}(\text{OTf})_2$ condition [24] have been reported, because the combination of PPh_3 and I_2 in the presence of the base has been well known so far [25, 26]. In addition, the use of $\text{Ph}_2\text{PCl}/\text{I}_2$ /imidazole [27], Ph_3PBr_2 [28], POCl_3 /DMAP/ Et_3N [29], or $\text{PPh}_3/\text{BnN}_3$ /microwave (Staudinger's phosphazene) [30] systems was found to be effective for the esterification. The hypervalent iodine reagents could be utilized in coupling reactions [31, 32]. The combination of PPh_3 and trichloroisocyanuric acid was also effective [33]. These reactions are based on the activation of PPh_3 . The catalytic activation of PPh_3 can be achieved by iron [34]. Photo-irradiated procedure in the presence of PPh_3 with a catalytic amount of flavin and azo compound under O_2 was developed [35]. XtalFluor-E and tropylium-based coupling reagents were found to be effective for the esterification [36, 37].

In the view point of green chemistry, the use of a catalytic amount of reagents is one of the attractive approaches, in which the ratio between carboxylic acids and alcohols is approximately equal. In 2000, Yamamoto et al. reported that 0.1 to 1.0 mol% hafnium (IV) salts in toluene at reflux condition catalyzed the condensation reaction of equimolar amount of carboxylic acids and alcohols (**Table 2**, entry 1) [38–47]. Since then, various types of catalysts have been found for the effective esterification reactions. Selected examples are summarized in **Table 2**. Diphenylammonium triflate (entry 2) [48], fluoroalkyldistannoxane (entry 3) [49], $\text{HClO}_4\text{-SiO}_2$ (entry 4) [50–52], Ti_4^{+} -mont (mont = montmorillonite, entry 5) [53], bulky diarylammonium arenesulfonates (entry 6) [54–58], $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (entry 7) [59], pentafluorophenylammonium triflate (entry 8) [60], TsOH or CSA (entry 9) [61], phosphorofluoric acid (entry 10) [62], N,N -diarylammonium pyrosulfates in H_2O (entry 11) [63, 64], TfOH in Solkane365mfc (entry 12) [65], 2-oleamido-5-nitro-pyridinium p -toluenesulfonate (entry 13) [66], zirconocene complex (entry 14) [67], and L-leucine as an organocatalyst (entry 15) [68] have been reported for the effective catalyst for the esterification using equal or nearly equal amount of carboxylic acids and alcohols.

$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{R}'\text{OH} \xrightarrow[\text{Solvent Conditions}]{\text{Catalyst (X mol\%)}} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$						
Entry	Authors	Published year	Catalyst (X mol%)	Solvent	Conditions	Ref.
1	H. Yamamoto et al.	2000	hafnium(IV) salts (0.1 mol%-1.0 mol%)	toluene	reflux, 5-36 h	38
2	Y. Tanabe et al.	2000	diphenylammonium triflate (DPAT) (1 mol% - 10 mol%)	toluene	80 °C, 4-48 h	48
3	J. Otera et al.	2002	fluoroalkyldistannoxane (5 mol%)	FC-72	150 °C, 10-16 h	49
4	A. K. Chakraborti et al.	2003	HClO ₄ -SiO ₂ (1 mol%)	solvent-free	80 °C, 3.5-20 h	50
5	K. Kaneda et al.	2003	Ti ₄ ⁺ -mont (2 mol%)	solvent-free	110-150 °C, 3-6 h	53
6	K. Ishihara et al.	2005	bulky diarylammonium arenesulfonates (1 mol%-10 mol%)	heptane or solvent-free	r.t.-115 °C, 1-72 h	54
7	G. Bartoli et al.	2005	Zn(ClO ₄) ₂ ·6H ₂ O (5 mol%)	solvent-free	80-100 °C, 6-48 h	59
8	Y. Tanabe et al.	2006	pentafluorophenylammonium triflate (PFPAT) (1 mol%)	toluene	80 °C, 2-48 h	60
9	K. Ishihara et al.	2008	<i>p</i> -toluenesulfonic acid (TsOH) or 10-camphorsulfonic acid (CSA) (5 mol%)	solvent-free	60-80 °C, 3-48 h	61
10	T. Murai et al.	2009	phosphorofluoric acid (5 mol%)	solvent-free	100 °C, 6 h	62
11	K. Ishihara et al.	2012	<i>N,N</i> -diarylammonium pyrosulfates (5 mol%)	H ₂ O	60-80 °C, 6-47 h	63
12	N. Shibata et al.	2013	TfOH (0.2-1 mol%)	solkane365mfc	80 °C, 18-48 h	65
13	W. Wang et al.	2013	2-oleamido-5-nitro-pyridinium <i>p</i> -toluenesulfonate (1-10 mol%)	isooctane	r.t.-reflux, 5-144 h	66
14	R. Qiu et al.	2017	zirconocene complex (1 mol%)	solvent-free	80-100 °C, 12 h	67
15	U. Sharma et al.	2018	<i>L</i> -Leucine (5 mol%)	solvent-free	80 °C, 12-24 h	68

Table 2. Representative progresses for the synthesis of esters using equal or nearly equal amount of carboxylic acids and alcohols in the presence of the catalyst, since 2000 (selected examples).

Another approach for the esterification of carboxylic acids with alcohols (2 equiv.) was developed by Kobayashi and coworkers [69–71], in which *p*-dodecylbenzenesulfonic acid (DBSA) was used as a surfactant-type catalyst in water (**Scheme 2**). Because the micelles of DBSA are produced, the esterification reactions between carboxylic acid and alcohol proceed in the micelles. After the reaction, the micelle releases H₂O. The carboxylic acids and alcohols bearing the longer alkyl chains seem to be favored because of the increase of the hydrophobicity. Thus, the equilibrium between starting materials and the product lies in right side.

Scheme 2. The use of DBSA in H₂O solvent (Kobayashi [69, 70]). The reactions were conducted in the ratio of RCOOH (1 equiv.) and R'OH (2 equiv.).

Scheme 3. The use of PAFR as the condensation catalyst (Uozumi [72, 73]).

The use of resin was also reported by Uozumi et al., who designed and synthesized the porous phenolsulfonic acid formaldehyde resin (PAFR) from 4-hydroxybenzenesulfonic acid and formaldehyde (5 equiv.) in H₂O (**Scheme 3**). The solid resin was allowed to react with RCOOH and R'OH to give the corresponding esters in good yields [72, 73]. The merit of the resin is that it can be recovered by the simple filtration and reused without the significant loss of the catalytic activity. Other type of solid catalysts bearing SO₃H unit are also reported. For examples, polystyrene-supported sulfonic acid catalyst [74], SBA-15-functionalized propyl-sulfonic acid catalyst [75], *p*-sulonic acid calix[*n*]arenes catalyst [76], β-cyclodextrin-derived carbonaceous catalyst [77], and sulfonated hyperbranched poly(aryleneoxindole) acid catalyst [78] are developed and utilized for the esterification.

As for the promising reaction tool for the esterification, the use of the flow chemistry has emerged. For example, Uozumi et al. applied the PAFR to the flow method [72, 73]. Fukuyama et al. demonstrated Fisher esterification by the flow system, in which silica bearing terminal -SO₃H group was used [79, 80].

3. Synthesis of carboxylic acid esters using carboxylic acids as nucleophiles

3.1. Nucleophilic reactions of carboxylate ion intermediates

3.1.1. The use of bases and ionic liquids

Because the acidity of carboxylic acids is relatively high, it is easy to generate and accumulate the carboxylate ion intermediates by the deprotonation of carboxylic acids. S_N2 reaction of carboxylate ions with alkyl halides is one of the most popular approaches, when carboxylate ions can be used as the nucleophiles. It was found that CsF or KF is the effective base toward carboxylic acids by Clark and Miller [81]. Since then, various reactions have been reported in these fields. Recent examples of this chemistry utilize the combination of bases (such as Huning's base, Et₃N and KF) and various ionic liquids (such as imidazolium salts and phosphonium salts), summarized in **Figure 1** [82–90]. The counteranions of carboxylate ions are bulky cations such as imidazolium salts and phosphonium salts, which seem to increase the reactivity of the carboxylate ions toward electrophiles.

Figure 1. Recent and selected examples for nucleophilic reactions using carboxylate ion intermediates in various ionic liquids.

It has been well known so far that F^- source such as KF and CsF can serve as good base toward carboxylic acids, described above [81]. Because of this reason, Bu_4NF is also the attractive reagent for the deprotonation of carboxylic acid. In 2001, Maruoka et al. reported in situ generation of Bu_4NF from the combination of a catalytic amount of Bu_4NHSO_4 (5 mol%) and $\text{KF}\cdot\text{H}_2\text{O}$ (5 equiv.), which takes the proton of carboxylic acids to generate reactive carboxylate ion intermediates, whose counteraction is presumably bulky Bu_4N^+ (**Scheme 4 (a)**) [91]. In addition, Matsumoto et al. also reported the reactions of carboxylic acids with a stoichiometric amount of Bu_4NF cleanly generated and accumulated reactive carboxylate ion intermediates, which reacted with various alkyl halides to give the corresponding esters in moderate to good yields (**Scheme 4 (b)**) [92].

The use of good affinity of F^- and metals such as Si and Sn was also developed in order to generate and accumulate highly reactive carboxylate ion intermediates. For example, the reaction of silyl-protected carboxylic acids with Ph_3CF in the presence of a small amount of SiF_4 produced the corresponding esters, in which SiF_4 might activate both silyl-protected carboxylic acids (substrates) and $\text{Ph}_3\text{C}-\text{F}$ to generate carboxylate ions and Ph_3C^+ , respectively (**Scheme 5 (a)**, Noyori et al.) [93]. The combination of silyl-protected carboxylic acids and Bu_4NF was also reported by Maruoka et al. (**Scheme 5 (b)**) [94]. Nozaki et al. reported the use of Sn in 1992. The intermediate bearing $\text{COO}-\text{Sn}$ bond reacted with alkyl halides in the presence of CsF, as shown in **Scheme 5 (c)** [95].

Scheme 4. Nucleophilic reactions of carboxylate ion intermediates by using Bu_4NF as the base. (a) in situ generation of a catalytic amount of Bu_4NF (Maruoka [91]). (b) the use of a stoichiometric amount of Bu_4NF (Matsumoto [94]).

Scheme 5. The use of affinity of F[−] and metals such as Si and Sn to generate carboxylate ion intermediates.

3.1.2. The use of electrochemical reduction methods

Electrochemistry is a clean technique, and basically the electron serves as the reagent instead of chemical reagents [96–99]. Therefore, electrochemistry in organic synthesis does not generate the waste derived from reagents, and is recognized as one of the powerful tools for green chemistry. The pioneering work for the esterification of carboxylic acids and alkyl halides using electrochemistry was developed by Nonaka et al. (**Scheme 6**) [100, 101]. The solution containing carboxylic acids underwent electrochemical reduction to generate highly reactive carboxylate ions, which reacted with alkyl halides to produce the corresponding esters. Matsumoto et al. investigated the detailed reaction condition, the scope and limitations, and the mechanism of the electroreductive esterification reaction (**Scheme 6**) [102].

The use of electro-generated base (EGB) [97] is also effective to generate reactive carboxylate ion intermediates, developed by Shono et al. (**Scheme 7**) [103]. 2-Pyrrolidone was electrochemically reduced and 2-pyrrolidone anion was generated and accumulated as the base in the solution phase, which reacted with carboxylic acids to generate carboxylate ions bearing the quaternary ammonium cation. The reaction was applicable to the formation of macrolides.

3.1.3. The use of electrophile equivalents

Some substrates were found to be effective as the electrophile equivalents, when carboxylic acids served as the nucleophile (**Figure 2**). For example, One of the interesting examples is the use of 2-benzyloxy-1-methylpyridinium triflate reported by Dudley (**Figure 2 (a)**) [104]. The benzyl cation was gradually generated, which was allowed to react with carboxylic acids. The in situ version was also established by Albiniak et al. [105]. Cu-mediated coupling reactions using aryl

Scheme 6. Electrochemical reduction condition to generate carboxylate ion intermediates followed by esterification. * The electro-reductive esterification of carboxylic acids in the presence of alkyl halides was also examined.

Scheme 7. Electrochemical preparation of EGB (electro-generated base) and its utilization for the esterification (Shono and Kashimura [103]).

Figure 2. Selected examples for the use of electrophile equivalents.

trialkoxysilanes [106] or arylboronic acids [107] were developed by Cheng et al. (**Figure 2 (b)**). Diaryliodonium salts were found to be good electrophiles for the esterification (**Figure 2 (c)**) [108]. Meier et al. reported the use of diphenyl carbonate as the electrophile to produce phenyl esters (**Figure 2 (d)**) [109, 110]. Kunishima et al. found that 2,4,6-tris(benzyloxy)-1,3,5-triazine (TriBOT) serves as the benzyl cation equivalent via S_N2 mechanism in the presence of a catalytic amount of TfOH at room temperature (**Figure 2 (e)**) [111]. The reaction at high temperature also proceeded without TfOH. Thus, *O*-benzylation of carboxylic acids took place smoothly. This methodology was extended to the use of 2,4,6-tris(tert-butoxy)-1,3,5-triazine (TriAT-*t*Bu), in which carboxylic acids can react with the *tert*-butyl cation via S_N1 mechanism to afford the corresponding esters (**Figure 2 (e)**) [112, 113]. The reactions of the diphenylmethyl trichloroacetimidate with carboxylic acids were also investigated by Chisholm et al. [114, 115].

Recently, dimethyl sulfoxide (DMSO) was utilized for the source of CH_3 - unit in the reaction with carboxylic acids to give the methyl esters shown in **Scheme 8**. The generation of methyl radical was indicated [116].

Scheme 8. Methyl esterification of carboxylic acids using DMSO (Guo [116]).

In situ generation of benzyl bromide from toluene derivatives by using $\text{NaBrO}_3/\text{NaHSO}_3$, followed by the nucleophilic reactions of the carboxylic acids could be achieved by Khan et al. (**Scheme 9**) [117]. Although aliphatic carboxylic acids were not suitable, the aromatic carboxylic acids can be converted to the corresponding esters.

Scheme 9. In situ formation of benzyl bromide as the electrophile equivalent (Khan [117]).

3.2. The use of the functionalization of C–H bonds

Recently, the esterification of carboxylic acids and suitable substrates via the functionalization of C–H bond has been extensively studied. For example, Zhang et al. found that the reaction of carboxylic acids and toluene in the presence $\text{Pd}(\text{OAc})_2$ (10 mol%), $\text{CF}_3\text{SO}_3\text{H}$ (10 mol%) and *N,N*-dimethylacetamide (1 equiv.) under O_2 (1 atm) afforded the corresponding esters via benzylic C–H bond activation (**Scheme 10**) [118]. Other interesting examples of this approach have been extensively studied [119–125].

Scheme 10. Esterification of carboxylic acids and toluene catalyzed by $\text{Pd}(\text{OAc})_2$ (Zhang [118]).

3.3. The use of metal catalysts

The addition of carboxylic acids onto C–C multiple bonds proceeds with high atom efficiency to afford the corresponding enol or alkyl esters. Hg salts have been used as the catalysts for these reactions for a long time; however, the use of these toxic salts should be avoided from the view point of green chemistry. Ruthenium complexes have been paid much attention for the alternative catalyst for the addition of carboxylic acids onto C–C multiple bonds. These ruthenium-catalyzed addition reactions of carboxylic acids to alkynes and several catalytic formation of alkyl esters by the addition of carboxylic acids to alkenes are summarized in this section.

3.3.1. The addition of carboxylic acids onto alkynes

The addition reaction of carboxylic acids onto alkynes with ruthenium catalysts through the Markovnikov's rule was well investigated by Mitsudo and Dixneuf, independently [126–128]. In 1987, Mitsudo and coworkers reported that the reaction of carboxylic acids including *N*-protected α -amino acids with alkynes were performed in the presence of $\text{Ru}(\eta^5\text{-cod})_2$, phosphine ligands and maleic anhydride in toluene to afford the corresponding enol esters in 31–99% yields (**Scheme 11**) [126]. This reaction proceeds with the high regioselectivity (>89% selectivity).

Scheme 11. Markovnikov addition (Mitsudo [126]).

On the other hand, Dixneuf and coworkers developed the simpler catalytic system for the Markovnikov addition. Thus, (*p*-cymene) $\text{RuCl}_2(\text{PPh}_3)_2$ catalyzed the addition of carboxylic acids to the alkynes to give the corresponding adducts in high yields (78–92%), as shown in **Scheme 12** [127, 128]. They also found the highly selective *anti*-Markovnikov addition by the use of $\text{Ru}(\eta^3\text{-methallyl})_2(\text{diphosphine})$ (diphosphine = dppb or dppe) to obtain the *Z*-enol esters in high yields with regio- and *Z*-selectivities (**Scheme 13**) [129–132].

Scheme 12. Markovnikov addition (Dixneuf [127, 128]).

The reaction mechanisms for both regioselective additions were proposed by Dixneuf et al. (**Scheme 14**), and the formation of vinylidene complex is crucial for the *anti*-Markovnikov addition. Thus, the Markovnikov adducts are formed through the activation of alkynes by the formation of π -complex with ruthenium catalyst, followed by the nucleophilic attack of the carboxylate ion onto the internal carbon atom of alkynes and the protonolysis of Ru–C δ -bond [128]. On the other hand, the *anti*-Markovnikov adducts are afforded by the vinylidene complex formation between the ruthenium catalyst and alkynes, followed by the nucleophilic attack of the carboxylate ion to the terminal carbon of alkynes and the protonolysis of the resulting intermediate [129].

Scheme 13. Anti-Markovnikov addition of carboxylic acids onto terminal alkynes (Dixneuf [129–132]).

a) Formation of Markovnikov Adducts

b) Formation of anti-Markovnikov Adducts

Scheme 14. Reaction mechanisms of the present enol ester formations.

Two simple catalytic systems, in which the regioselectivity is easily controlled by the use of the same or similar catalyst, have been reported [133, 134]. Goossen et al. found that the reaction of carboxylic acids and alkenes with $RuCl_2(p\text{-cymene})$ /phosphine catalyst in the presence of K_2CO_3 gave the corresponding Markovnikov adducts in good to excellent yields, whereas the use of DMAP instead of K_2CO_3 afforded the *anti*-Markovnikov (*Z*) esters in high yields (**Scheme 15**) [133]. The reactions with $RuClH(CO)(PCy)_3$ catalyst showed the interesting solvent-controlled regioselectivity (**Scheme 16**) [134]. Thus, the reaction of benzoic acid with aryl acetylene in the presence of $RuClH(CO)(PCy)_3$ as a catalyst in CH_2Cl_2 gave the Markovnikov adducts in high yields. On the other hand, the use of THF as a solvent instead of CH_2Cl_2 led to the inverse of the selectivity to afford the corresponding *anti*-Markovnikov (*Z*) esters in high

Method I Markovnikov selective

Reaction Conditions: $[\text{RuCl}_2(p\text{-cymene})]_2/2(\text{Fur})_3\text{P}$ (0.8 mol% Ru), toluene
 Na_2CO_3 (1.6 mol%) 50°C, 16 h

Method II anti-Markovnikov selective

Reaction Conditions: $[\text{RuCl}_2(p\text{-cymene})]_2/2(p\text{-ClC}_6\text{H}_4)_3\text{P}$ (1 mol% Ru), toluene
 DMAP (4 mol%) 60°C, 16 h

Scheme 15. Regioselective addition (Goossen [133]).

Scheme 16. Solvent-controlled selective additions (Yi [134]).

yields together with the high selectivity. It is considered that the use of THF accelerated the formation of vinylidene complex intermediates. Unfortunately, this interesting effect was not observed in the reaction of aliphatic alkynes.

The stereoselective formation of *anti*-Markovnikov (*E*) esters is so far limited [135–137]. Verpoort [135], Leong [136] and Fan [137] and their coworkers showed the (*E*)-selective formation of enol esters with their own ruthenium catalyst (**Scheme 17**), independently. However, the *E/Z* ratios were dependent on the alkyne and/or substrates of carboxylic acids. The ruthenium catalyst showed the *E*-selectivity, though the selectivity was also strongly dependent on the substrates of alkynes. Similar selectivity was obtained when $\text{Re(CO)}_5\text{Br}$ was used as a catalyst, though the *E/Z* ratios were moderate (**Scheme 18**) [138].

Two examples for the regio- and *E*-selective addition of carboxylic acids onto “internal” alkynes have been reported (**Scheme 19**). Lang et al. found that the reaction of the carboxylic acid with

Scheme 17. Ruthenium catalysts for *E*-selective additions.

Scheme 18. Rhenium catalysis for additions of carboxylic acids onto alkynes (Hua [138]).

Scheme 19. Regio- and stereoselective additions to unsymmetrical internal alkynes.

symmetrical internal alkynes in the presence of $[\text{Ru}(\text{CO})_2\{(\text{p-CF}_3\text{C}_6\text{H}_4)_3\text{P}\}(\text{O}_2\text{CPh})_2]/\text{B}(\text{C}_6\text{F}_5)_3$ catalyst afforded the corresponding *E*-enol esters in up to 99% yield with the extremely high *E*-selectivity [139]. This catalytic system also achieved the regio- and stereoselective addition of carboxylic acids to unsymmetrical internal alkynes, in which the *E*/*Z* ratio reached up to 72:28. Kawatsura and Itoh reported the reaction with alkynes having trifluoromethyl and aryl group [140]. The reaction proceeded with high regioselectivity and stereoselectivity to provide the corresponding (*E*)-enol esters including trifluoromethyl group in up to 92% yield.

3.3.2. The addition of carboxylic acids onto alkenes

In 2004, Oe et al. reported the first transition metal-catalyzed addition of carboxylic acids onto alkenes. Thus, the reaction of benzoic acids with norbornene was carried out in the presence of $[\text{Cp}^*\text{RuCl}_2]_2/\text{AgOTf}/\text{Dppb}$ catalyst in toluene at 85 °C to obtain the corresponding norbornyl benzoates in good to high yields (**Scheme 20**) [141]. After that, several metal catalysts for the addition of carboxylic acids to alkenes have been reported and are summarized in **Table 3**.

Norbornene is a generally good substrate due to the strain of the C–C double bond, therefore the reported catalyst afforded the corresponding esters in high yields (**Table 3**) [142–145]. In 2005, He et al. reported the Au catalyst, where the four alkenes including unstrained 1-octene were transformed into the corresponding esters in 75–95% yields (entry 1) [142]. Hii et al. showed the catalytic activity of $\text{Cu}(\text{OTf})_2$, though only norbornene was used as an alkene substrate (entry 2) [143]. In these cases, the addition of phenols onto alkenes was also catalyzed under the similar reaction conditions. With only norbornene, $\text{In}(\text{OTf})_3$ was also found as a good catalyst under the solvent-free reaction condition (entry 3) [144]. An ubiquitous iron catalysis has been reported by Sakakura et al., where the unstable ester such as acrylates can be synthesized under the solvent-free reaction conditions (entry 4) [145]. Modified ruthenium(II) catalysis including xantphos ligand improved the scope of substrates of alkenes compared to that with ruthenium(III) catalyst to afford the corresponding esters in up to 99% yield by Oe et al. (entry 5) [146].

Scheme 20. Ruthenium-catalyzed additions of carboxylic acids to norbornene (Oe [141]).

$\text{R}^1\text{C}(=\text{O})\text{OH} + \text{CH}_2=\text{CH-R}^2 \xrightarrow[\text{Conditions}]{\text{Catalyst (X mol\%)}} \text{R}^1\text{C}(=\text{O})\text{OCH}_2\text{CH(R}^2\text{)}$					
Entry	Authors	Published year	Catalyst (X mol%) & Conditions	Alkenes (yield, %)	Ref.
1	C. He et al.	2005	catalyst: Ph_3PAuOTf (5 mol%) conditions: in toluene, 85 °C	norbornene (>95%) and 4 alkenes	142
2	K. K. Hii et al.	2005	catalyst: $\text{Cu}(\text{OTf})_2$ (5 mol%) conditions: in dioxane, 80 °C	norbornene (80-98%)	143
3	W. Chen et al.	2007	catalyst: $\text{In}(\text{OTf})_3$ (5 mol%) conditions: neat, 80 °C, 2 h	norbornene (80-92%)	144
4	T. Sakakura et al.	2008	catalyst: $\text{Fe}(\text{OTf})_3$ (2 mol%) conditions: in Bu_2O , 80 °C, 18 h	norbornene (98-99%) cyclohexene (70-88%) 1-octene (78%)	145
5	Y. Oe et al.	2015	catalyst: $\text{RuCl}_2(\text{xan})\{\text{P}(\text{OPh})_3\}_3$ (5 mol%) AgOTf (10 mol%) conditions: in toluene, 80 °C	4-allylanisole (>99%) and 4 alkenes	146

Table 3. Recent reported catalysts and generality of alkene substrates.

Hartwig and He found that TfOH itself showed the catalytic activity for the present addition reactions (**Scheme 21**) [147, 148]. Interestingly, the relatively large amount of catalyst and/or higher reaction temperature decreased the chemical yield of the product. It might be due to the polymerization of substrates of alkenes. Accompanied with the importance of triflate in the metal-catalyzed reaction described above, these metal catalysts might act as a TfOH source.

Recently, an organocatalytic addition under the LED light irradiation conditions have been reported by Nicewicz et al. (**Scheme 22**) [149]. The reaction of carboxylic acids and internal and/or cyclic alkenes proceeds nicely under mild conditions to afford the corresponding esters in up to 99% yield regio-selectively.

Scheme 21. TfOH-catalyzed reactions.

Scheme 22. The additions of carboxylic acids onto alkenes in the presence of the organocatalyst under the LED irradiation (Nicewicz [149]).

4. Conclusion

In this chapter, the recent progress of the esterification reactions using carboxylic acids as the starting material was overviewed, together with some basic and pioneering works. Various reagents, catalysts, synthetic media, and methods have been developed so far, and the quality of this field seems to be obviously increased. Because the topic of the efficient synthesis of esters is still an important task, it is expected that more innovative approach is discovered in near future.

Author details

Kouichi Matsumoto^{1*#}, Rina Yanagi¹ and Yohei Oe²

*Address all correspondence to: kmatsumo@chem.kindai.ac.jp

1 Department of Chemistry, School of Science and Engineering, Kindai University, Higashi-osaka, Osaka, Japan

2 Department of Biomedical Information, Faculty of Life and Medical Sciences, Doshisha University, Kyotanabe, Kyoto, Japan

#This book chapter is dedicated to K. M.'s wife, Yuko Matsumoto

References

- [1] Otera J, Nishikido J. Esterification: Methods, Reactions, and Applications, 2nd ed. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2009. DOI: 10.1002/9783527627622
- [2] Siengalewicz P, Mulzer J, Rinner U. Synthesis of Esters and Lactones. In: Knochel P, Molander GA, editors. Comprehensive Organic Synthesis. 2nd ed; 2014;6:355-410. DOI: 10.1016/B978-0-08-097742-3.00612-1
- [3] Li JJ, Corey EJ, editors. Carboxylic Acid Derivatives Synthesis, in Name Reactions for Functional Group Transformations. Hoboken, NJ, USA: John Wiley & Sons, Inc; 2007. DOI: 10.1002/9780470176511.ch6
- [4] Neises B, Steglich W. Simple method for the esterification of carboxylic acids. *Angewandte Chemie International Edition England*. 1978;17:522-524. DOI: 10.1002/anie.197805221. DIC (*N,N'*-diisopropylcarbodiimide) is also recognized as a useful reagent for the alteration of DCC
- [5] Mitsunobu O, Yamada M. Preparation of esters of carboxylic and phosphoric acid via quaternary phosphonium salts. *Bulletin Chemical Society of Japan*. 1967;40:2380-2382. DOI: 10.1246/bcsj.40.2380
- [6] Hirose D, Gazvoda M, Kosmrlj J, Taniguchi T. Advances and mechanistic insight on the catalytic Mitsunobu reaction using recyclable azo reagents. *Chemical Science*. 2016;7:5148-5159. DOI: 10.1039/C6SC00308G. Recent reports of catalytic versions of Mitsunobu reaction
- [7] Hirose D, Taniguchi T, Ishibashi H. Recyclable Mitsunobu reagents: Catalytic Mitsunobu reactions with an iron catalyst and atmospheric oxygen. *Angewandte Chemie, International Edition*. 2013;52:4613-4617. DOI: 10.1002/anie.201300153. Recent reports of catalytic versions of Mitsunobu reaction

- [8] But TYS, Toy PH. Organocatalytic Mitsunobu reactions. *Journal of the American Chemical Society*. 2006;**128**:9636-9637. DOI: 10.1021/ja063141v. Recent reports of catalytic versions of Mitsunobu reaction
- [9] Mukaiyama T, Usui M, Shimada E, Saigo K. Convenient method for the synthesis of carboxylic esters. *Chemistry Letters*. 1975:1045-1048. DOI: 10.1246/cl.1975.1045
- [10] Funasaka S, Mukaiyama T. A versatile, practical, and inexpensive reagent, pyridine-3-carboxylic anhydride (3-PCA), for condensation reactions. *Bulletin Chemical Society of Japan*. 2008;**81**:148-159. DOI: 10.1246/bcsj.81.148, and references therein
- [11] Castro B, Dormoy J, Evin G, Selve C. Reactifs de couplage peptidique I (1) - l'hexafluorophosphate de benzotriazolyl *N*-oxytrisdimethylamino phosphonium (B.O.P.). *Tetrahedron Letters*. 1975;**16**:1219. DOI: 10.1016/S0040-4039(00)72100-9
- [12] Kim MH, Patel DV. BOP as a reagent for mild and efficient preparation of esters. *Tetrahedron Letters*. 1994;**31**:5603-5606. DOI: 10.1016/S0040-4039(00)77257-1
- [13] Paul R, Anderson GW. *N,N'*-Carbonyldiimidazole, a new peptide-forming reagent. *Journal of the American Chemical Society*. 1960;**82**:4596-4600. DOI: 10.1021/ja01502a038
- [14] For example of reviews, Armstrong A, Li W. *N,N'*-Carbonyldiimidazole. *e-EROS Encyclopedia of Reagents for Organic Synthesis*. 2007. DOI: 10.1002/9780470842898.rc024.pub2
- [15] Kunishima M, Kawachi C, Iwasaki F, Terao K, Tani S. Synthesis and characterization of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride. *Tetrahedron Letters*. 1999;**40**:5327-5330. DOI: 10.1016/S0040-4039(99)00968-5
- [16] Kunishima M, Morita J, Kawachi C, Iwasaki F, Terao K, Tani S. Esterification of carboxylic acids with alcohols by 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM). *Synlett*. 1999:1255-1256. DOI: 10.1055/s-1999-2828
- [17] Kunishima M, Kawachi C, Morita J, Terao K, Iwasaki F, Tani S. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride: An efficient condensing agent leading to the formation of amides and esters. *Tetrahedron*. 1999;**55**:13159-13170. DOI: 10.1016/S0040-4020(99)00809-1
- [18] Valeur E, Bradley M. One of the excellent reviews for condensation reagents including uronium based coupling reagents. *Chemical Society Reviews*. 2009;**38**:606-631. DOI: 10.1039/b701677h
- [19] The following catalog was referred for making this paragraph. Condensation reagents catalog for organic synthesis, 2nd ed, Wako Pure Chemical Industries (written in Japanese), and references therein
- [20] Pathak G, Das D, Rokhum L. A microwave-assisted highly practical chemoselective esterification and amidation of carboxylic acids. *RSC Advances*. 2016;**6**:93729-93740. DOI: 10.1039/C6RA22558F

- [21] Choi MKW, He HS, Toy PH. Direct radical polymerization of 4-styryldiphenylphosphine: Preparation of cross-linked and non-cross-linked Triphenylphosphine-containing polystyrene polymers. *The Journal of Organic Chemistry*. 2003;**68**:9831-9834. DOI: 10.1021/jo035226+. See also, the polymer-supported PPh_3 mediated esterification
- [22] Jaita S, Phakhodee W, Pattarawarapan M. Ultrasound-assisted methyl esterification of carboxylic acids catalyzed by polymer-supported triphenylphosphine. *Synlett*. 2015;**26**: 2006-2008. DOI: 10.1055/s-0034-1381117. See also, the polymer-supported PPh_3 mediated esterification
- [23] Pathak G, Rokhum L. Selective monoesterification of symmetrical diols using resin-bound triphenylphosphine. *ACS Combinatorial Science*. 2015;**17**:483-487. DOI: 10.1021/acscombsci.5b00086. See also, the polymer-supported PPh_3 mediated esterification
- [24] Mamidi N, Manna D. $\text{Zn}(\text{OTf})_2$ -promoted chemoselective esterification of hydroxyl group bearing carboxylic acids. *The Journal of Organic Chemistry*. 2013;**78**:2386-2396. DOI: 10.1021/jo302502r
- [25] Garegg PJ, Samuelsson B. Novel reagent system for converting a hydroxy group into an iodo group in carbohydrates with inversion of configuration. *Journal of the Chemical Society, Chemical Communications*. 1979:978-980. DOI: 10.1039/c39790000978
- [26] Morcillo SP, de Cienfuegos LA, Mota AJ, Justicia J, Robles R. Mild method for the selective esterification of carboxylic acids based on the Garegg-Samuelsson reaction. *The Journal of Organic Chemistry*. 2011;**76**:2277-2281. DOI: 10.1021/jo102395c
- [27] Nowrouzi N, Mehranpour AM, Rad JA. A simple and convenient method for preparation of carboxylic acid alkyl esters, phenolic and thioesters using chlorodiphenylphosphine/ I_2 and imidazole reagent system. *Tetrahedron*. 2010;**66**:9596-9601. DOI: 10.1016/j.tet.2010.10.022
- [28] Salome C, Kohn H. Triphenylphosphine dibromide: A simple one-pot esterification reagent. *Tetrahedron*. 2009;**65**:456-460. DOI: 10.1016/j.tet.2008.10.062
- [29] Chen H, Xu X, Liu L, Tang G, Zhao Y. Phosphorus oxychloride as an efficient coupling reagent for the synthesis of esters, amides and peptides under mild conditions. *RSC Advances*. 2013;**3**:16247-16250. DOI: 10.1039/c3ra42887g
- [30] Dinesh M, Ranganathan R, Archana S, Sathishkumar M, Roshan B, Mohamed S, Ponnuswamy A. Staudinger's phosphazene as an efficient esterifying reagent. *Synthetic Communication*. 2016;**46**:1454-1460. DOI: 10.1080/00397911.2016.1211705
- [31] Tian J, Gao W, Zhou D, Zhang C. Recyclable hypervalent iodine(III) reagent iodosodilactone as an efficient coupling reagent for direct esterification, amidation, and peptide coupling. *Organic Letters*. 2012;**14**:3020-3023. DOI: 10.1021/ol301085v
- [32] Boulogeorgou MA, Triantakoustanti VV, Gallos Jn K. The system $\text{PhIO}/\text{Ph}_3\text{P}$ as an efficient reagent for mild and direct coupling of alcohols with carboxylic acids. *ARKIVOC* 2015:244-251. DOI: 10.3998/ark.5550190.p008.997

- [33] Rodrigues RC, Barros IMA, Lima ELS. Mild one-pot conversion of carboxylic acids to amides or esters with Ph_3P /trichloroisocyanuric acid. *Tetrahedron Letters*. 2005;**46**:5945-5947. DOI: 10.1016/j.tetlet.2005.06.127
- [34] Taniguchi T, Hirose D, Ishibashi H. Esterification via iron-catalyzed activation of triphenylphosphine with air. *ACS Catalysis*. 2011;**1**:1469-1474. DOI: 10.1021/cs2003824
- [35] Marz M, Chudoba J, Kohout M, Cibulka R. Photocatalytic esterification under Mitsunobu reaction conditions mediated by flavin and visible light. *Organic & Biomolecular Chemistry*. 2017;**15**:1970-1975. DOI: 10.1039/C6OB02770A
- [36] Vandamme M, Bouchard L, Gilbert A, Keita M, Paquin J. Direct esterification of carboxylic acids with perfluorinated alcohols mediated by XtalFluor-E. *Organic Letters*. 2016;**18**:6468-6471. DOI: 10.1021/acs.orglett.6b03365
- [37] Nguyen TV, Lyons DJM. A novel aromatic carbocation-based coupling reagent for esterification and amidation reactions. *Chemical Communications*. 2015;**51**:3131-3134. DOI: 10.1039/C4CC09539A
- [38] Ishihara K, Ohara S, Yamamoto H. Direct condensation of carboxylic acids with alcohols catalyzed by hafnium(IV) salts. *Science*. 2000;**290**:1140-1142. DOI: 10.1126/science.290.5494.1140
- [39] Ishihara K, Nakayama M, Ohara S, Yamamoto H. A green method for the selective esterification of primary alcohols in the presence of secondary alcohols or aromatic alcohols. *Synlett*. 2001, 1117-1120. DOI: 10.1055/s-2001-15156
- [40] Ishihara K, Nakayama M, Ohara S, Yamamoto H. Direct ester condensation from a 1:1 mixture of carboxylic acids and alcohols catalyzed by hafnium(IV) or zirconium(IV) salts. *Tetrahedron*. 2002;**58**:8179-8188. DOI: 10.1016/S0040-4020(02)00966-3
- [41] Nakayama M, Sato A, Ishihara K, Yamamoto H. Water-tolerant and reusable catalysts for direct ester condensation between equimolar amounts of carboxylic acids and alcohols. *Advanced Synthesis and Catalysis*. 2004;**346**:1275-1279. DOI: 10.1002/adsc.200404149
- [42] Mantri, K, Nakamura R, Komura K, Sugi Y. Esterification of long chain aliphatic acids with long chain alcohols catalyzed by multi-valent metal salts. *Chemistry Letters*. 2015;**34**:1502-1503. DOI 10.1246/cl.2005.1502
- [43] Mantri K, Komura K, Sugi Y. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ catalysts for the esterification of long chain aliphatic carboxylic acids and alcohols. The enhancement of catalytic performance by supporting on ordered mesoporous silica. *Green Chemistry*. 2005;**7**:677-682. DOI: 10.1039/b504369g
- [44] Chen C, Munot YS. Direct atom-efficient esterification between carboxylic acids and alcohols catalyzed by amphoteric, water-tolerant $\text{TiO}(\text{acac})_2$. *The Journal of Organic Chemistry* 2005;**70**:8625-8627. DOI: 10.1021/jo051337s
- [45] Sato A, Nakamura Y, Maki T, Ishihara K, Yamamoto H. Zr(IV)-Fe(III), -Ga(III), and -Sn(IV) binary metal complexes as synergistic and reusable esterification catalysts. *Advanced Synthesis and Catalysis*. 2005;**347**:1337-1340. DOI: 10.1002/adsc.200505083

- [46] Mantri K, Komura K, Sugi Y. Efficient esterification of long chain aliphatic carboxylic acids with alcohols over $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ catalyst. *Synthesis*. 2005;1939-1944. DOI: 10.1055/s-2005-869951
- [47] Nakamura Y, Maki T, Wang X, Ishihara K, Yamamoto H. Iron(III)-zirconium(IV) combined salt immobilized on *N*-(polystyrylbutyl) pyridinium triflylimide as a reusable catalyst for a dehydrative esterification reaction. *Advanced Synthesis and Catalysis*. 2006;**348**:1505-1510. DOI: 10.1002/adsc.200606126
- [48] Wakasugi K, Misaki T, Yamada K, Tanabe Y. Diphenylammonium triflate (DPAT): Efficient catalyst for esterification of carboxylic acids and for transesterification of carboxylic esters with nearly equimolar amounts of alcohols. *Tetrahedron Letters*. 2000;**41**: 5249-5252. DOI: 10.1016/S0040-4039(00)00821-2
- [49] Xiang J, Orita A, Otera J. Fluorous biphasic esterification directed towards ultimate atom efficiency. *Angewandte Chemie, International Edition*. 2002;**41**:4117-4119. DOI: 10.1002/1521-3773(20021104)41:21<4117::AID-ANIE4117>3.0.CO;2-4
- [50] Chakraborti AK, Gulhane R. Perchloric acid adsorbed on silica gel as a new, highly efficient, and versatile catalyst for acetylation of phenols, thiols, alcohols, and amines. *Chemical Communication*. 2003;1896-1897. DOI: 10.1039/B304178F
- [51] Chakraborti AK, Singh B, Chankeshwara SV, Patel AR. Protic acid immobilized on solid support as an extremely efficient recyclable catalyst system for a direct and atom economical esterification of carboxylic acids with alcohols. *Journal of Organic Chemistry*. 2009;**74**:5967-5974. DOI: 10.1021/jo900614s
- [52] Chakraborti AK, Chankeshwara SV, Singh B. Indian patent. 2764/DEL/2007 (Dec 28, 2007)
- [53] Kawabata T, Mizugaki T, Ebitani K, Kaneda K. Highly efficient esterification of carboxylic acids with alcohols by montmorillonite-enwrapped titanium as a heterogeneous acid catalyst. *Tetrahedron Letters*. 2003;**44**:9205-9208. DOI: 10.1016/j.tetlet.2003.10.024
- [54] Ishihara K, Nakagawa S, Sakakura A. Bulky diarylammonium arenesulfonates as selective esterification catalysts. *Journal of American Chemical Society*. 2005;**127**:4168-4169. DOI: 10.1021/ja050223v
- [55] Sakakura A, Nakagawa S, Ishihara K. Bulky diarylammonium arenesulfonates as mild and extremely active dehydrative ester condensation catalysts. *Tetrahedron*. 2006;**62**:422-433. DOI: 10.1016/j.tet.2005.09.059. See also
- [56] Sakakura A, Watanabe H, Nakagawa S, Ishihara K. Unusual rate acceleration in Brønsted acid catalyzed dehydration reactions: Local hydrophobic environment in aggregated *N*-(2,6-diphenylphenyl)-*N*-mesitylammonium pentafluorobenzenesulfonates. *Chemistry, an Asian Journal*. 2007;**2**:477-483. DOI: 10.1002/asia.200600380
- [57] Sakakura A, Nakagawa S, Ishihara K. Direct ester condensation catalyzed by bulky diarylammonium pentafluorobenzenesulfonates. *Nature Protocols*. 2007;**2**:1746-1751. DOI: 10.1038/nprot.2007.254

- [58] Ishihara K. Dehydrative condensation catalyses. *Tetrahedron*. 2009;**65**:1085-1109. DOI: 10.1016/j.tet.2008.11.004. Review of esterification
- [59] Bartoli G, Boeglin J, Bosco M, Locatelli M, Massaccesi M, Melchiorre P, Sambri L. Highly efficient solvent-free condensation of carboxylic acids with alcohols catalyzed by zinc perchlorate hexahydrate, $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. *Advanced Synthesis and Catalysis*. 2005;**347**:33-38. DOI: 10.1002/adsc.200404171
- [60] Funatomi T, Wakasugi K, Misaki T, Tanabe Y. Pentafluorophenylammonium triflate (PFPAT): An efficient, practical, and cost-effective catalyst for esterification, thioesterification, transesterification, and macrolactone formation. *Green Chemistry*. 2006;**8**:1022-1027. DOI: 10.1039/b609181b
- [61] Sakakura A, Koshikari Y, Ishihara K. Open-air and solvent-free ester condensation catalyzed by sulfonic acids. *Tetrahedron Letters*. 2008;**49**:5017-5020. DOI: 10.1016/j.tetlet.2008.06.058
- [62] Murai T, Tanaka N, Higashijima S, Miura H. Phosphorofluoridic acid-catalyzed condensation reaction of carboxylic acids with 1-arylkyl alcohols leading to esters under solvent-free conditions. *Chemistry Letters*. 2009;**38**:668-669. DOI: 10.1246/cl.2009.668
- [63] Sakakura A, Koshikari Y, Akakura M, Ishihara K. Hydrophobic *N,N*-diarylammonium pyrosulfates as dehydrative condensation catalysts under aqueous conditions. *Organic Letters*. 2012;**14**:30-33. DOI: 10.1021/ol2027366
- [64] Igarashi T, Yagyu D, Naitoa T, Okumura Y, Nakajo T, Mori Y, Kobayashi S. Dehydrative esterification of carboxylic acids with alcohols catalyzed by diarylammonium *p*-dodecylbenzenesulfonates in water. *Applied Catalysis B-Environment*. 2012;**119-120**:304-307. DOI: 10.1016/j.apcatb.2012.03.001
- [65] Xu X, Azuma A, Taniguchi M, Tokunaga E, Shibata N. Efficient direct ester condensation between equimolar amounts of carboxylic acids and alcohols catalyzed by trifluoromethanesulfonic acid (TfOH) in Solkane365mfc. *RSC Advances*. 2013;**3**:3848-3852. DOI: 10.1039/c3ra00132f
- [66] Wang W, Liu H, Xu S, Gao Y. Esterification catalysis by pyridinium *p*-toluenesulfonate revisited-modification with a lipid chain for improved activities and selectivities. *Synthetic Communication*. 2013;**43**:2906-2912. DOI: 10.1080/00397911.2012.749990
- [67] Tang Z, Jiang Q, Peng L, Xu X, Li J, Qiu R, Au C. Zirconocene-catalyzed direct (trans) esterification of acyl acids (esters) and alcohols in a strict 1 : 1 ratio under solvent-free conditions. *Green Chemistry*. 2017;**19**:5396-5402. DOI: 10.1039/C7GC02174G
- [68] Kumar M, Thakur K, Sharma S, Nayal OS, Kumar N, Singh B, Sharma U. Solvent-free, L-leucine-catalyzed direct dehydrative esterification of carboxylic acids with alcohols: Direct synthesis of 3-alkoxy 1(3 H)-isobenzofuranone. *Asian Journal of Organic Chemistry*. 2018;**7**:227-231. DOI: 10.1002/ajoc.201700523

- [69] Manabe K, Sun X, Kobayashi S. Dehydration reactions in water. Surfactant-type Brønsted acid-catalyzed direct esterification of carboxylic acids with alcohols in an emulsion system. *Journal of the American Chemical Society*. 2001;**123**:10101-10102. DOI: 10.1021/ja016338q
- [70] Manabe K, Iimura S, Sun X, Kobayashi S. Dehydration reactions in water. Brønsted acid-surfactant-combined catalyst for ester, ether, thioether, and dithioacetal formation in water. *Journal of American Chemical Society*. 2002;**124**:11971-11978. DOI: 10.1021/ja026241j
- [71] Jing L, Li X J, Han Y C, Chu Y. The esterification in cyclohexane/DBSA/water micro-emulsion system. *Colloids and Surface A. Physicochemical and Engineering Aspects*. 2008;**326**:37-41. DOI: 10.1016/j.colsurfa.2008.05.008
- [72] Baek H, Minakawa M, Yamada YMA, Han JW, Uozumi Y. In-water and neat batch and continuous-flow direct esterification and transesterification by a porous polymeric acid catalyst. *Scientific Reports*. 2016;**6**:25925. DOI: 10.1038/srep25925
- [73] Minakawa M, Baek H, Yamada YMA, Han JW, Uozumi Y. Direct dehydrative esterification of alcohols and carboxylic acids with a macroporous polymeric acid catalyst. *Organic Letters*. 2013;**15**:5798-5801. DOI: 10.1021/ol4028495
- [74] Manabe K, Kobayashi S. Dehydrative esterification of carboxylic acids with alcohols catalyzed by polymer-supported sulfonic acids in water. *Advanced Synthesis and Catalysis*. 2002;**344**:270-273. DOI:10.1002/1615-4169(200206)344:3/4<270::AID-ADSC270>3.0.CO;2-7
- [75] Karimi B, Vafaezadeh M. SBA-15-functionalized sulfonic acid confined acidic ionic liquid: A powerful and water-tolerant catalyst for solvent-free esterifications. *Chemical Communications*. 2012;**48**:3327-3329. DOI: 10.1039/c2cc17702a
- [76] Fernandes SA, Natalino R, Gazolla PAR, da Silva MJ, Jham GN. *p*-sulfonic acid calix[*n*]arenes as homogeneous and recyclable organocatalysts for esterification reactions. *Tetrahedron Letters*. 2012;**53**:1630-1633. DOI: 10.1016/j.tetlet.2012.01.078
- [77] Thombal RS, Jadhav AR, Jadhav VH. Biomass derived β -cyclodextrin-SO₃H as a solid acid catalyst for esterification of carboxylic acids with alcohols. *RSC Advances*. 2015;**5**:12981-12986. DOI: 10.1039/C4RA16699J
- [78] Verheyen T, Smet M, De Borggraeve WM. Water tolerant and reusable sulfonated hyper-branched poly(aryleneoxindole) acid catalyst for solvent-free esterification. *Chemistry Select*. 2017;**2**:9822-9828. DOI: 10.1002/slct.201701636
- [79] Furuta A, Fukuyama T, Ryu I. Efficient flow Fischer esterification of carboxylic acids with alcohols using sulfonic acid-functionalized silica as supported catalyst. *Bulletin Chemical Society of Japan*. 2017;**90**:607-612. DOI: 10.1246/bcsj.20170025
- [80] Audubert C, Lebel H. Mild esterification of carboxylic acids via continuous flow diazotization of amines. *Organic Letters*. 2017;**19**:4407-4410. DOI: 10.1021/acs.orglett.7b02231. See also another example using micro reactor. This reaction is categorized into 3.1 Nucleophilic reaction of carboxylate ion intermediate

- [81] Clark JH, Miller JM. Hydrogen bonding in organic synthesis. V. Potassium fluoride in carboxylic acids as an alternative to crown ether with acid salts in the preparation of phenacyl esters. *Tetrahedron Letters*. 1977;**18**:599. DOI: 10.1016/S0040-4039(01)92703-0. See also, the introduction of ref. 56
- [82] Cardellini F, Brinchi L, Germani R, Tiecco M. Convenient esterification of carboxylic acids by S_N2 reaction promoted by a Protic ionic-liquid system formed in situ in solvent-free conditions. *Synthetic Communications*. 2014;**44**:3248-3256. DOI: 10.1080/00397911.2014.933353
- [83] Gok Y, Alici B, Cetinkaya E, Ozdemir I, Ozeroglu O. Ionic liquids as solvent for efficient esterification of carboxylic acids with alkyl halides. *Turkish Journal of Chemistry*. 2010;**34**:187-191. DOI: 10.3906/kim-0904-39
- [84] Judeh ZMA, Shen H, Chi BC, Feng L, Selvasothi S. A facile and efficient nucleophilic displacement reaction at room temperature in ionic liquids. *Tetrahedron Letters*. 2002;**43**:9381-9384. DOI: 10.1016/S0040-4039(02)02327-4
- [85] McNulty J, Cheekoori S, Nair J, Larichev V, Capretta A, Robertson A. A mild esterification process in phosphonium salt ionic liquid. *Tetrahedron Letters*. 2005;**46**:3641-3644. DOI: 10.1016/j.tetlet.2005.03.169
- [86] Brinchi L, Germani R, Savelli G. Ionic liquids as reaction media for esterification of carboxylate sodium salts with alkyl halides. *Tetrahedron Letters*. 2003;**44**:2027-2029. DOI: 10.1016/S0040-4039(03)00179-5
- [87] Brinchi L, Germani R, Savelli G. Efficient esterification of carboxylic acids with alkyl halides catalyzed by fluoride ions in ionic liquids. *Tetrahedron Letters*. 2003;**44**:6583-6585. DOI: 10.1016/S0040-4039(03)01693-9
- [88] Dighe S, Bhattad R, Kulkarni R, Jain K, Srinivasan K. A rapid and facile esterification of Na-carboxylates with alkyl halides promoted by the synergy of the combined use of DMSO and an ionic liquid under ambient conditions. *Synthetic Communications*. 2010;**40**:3522-3527. DOI: 10.1080/00397910903457357
- [89] Muskawar PN, Thenmozhi K, Gajbhiye M, Bhagat PR. Facile esterification of carboxylic acid using amide functionalized benzimidazolium dicationic ionic liquids. *Applied Catalysis A*. 2014;**482**:214-220. DOI: 10.1016/j.apcata.2014.06.004
- [90] Jadhav A H, Lee K, Koo S, Seo J G. Esterification of carboxylic acids with alkyl halides using imidazolium based dicationic ionic liquids containing bis-trifluoromethane sulfonimide anions at room temperature. *RSC Advances*. 2015;**5**:26197-26208. DOI: 10.1039/C5RA00802F
- [91] Ooi T, Sugimoto H, Doda K, Maruoka K. Esterification of carboxylic acids catalyzed by in situ generated tetraalkylammonium fluorides. *Tetrahedron Letters*. 2001;**42**:9245-9248. DOI: 10.1016/S0040-4039(01)02035-4

- [92] Matsumoto K, Shimazaki H, Miyamoto Y, Shimada K, Haga F, Yamada Y, Miyazawa H, Nishiwaki K, Kashimura S. Simple and convenient synthesis of esters from carboxylic acids and alkyl halides using tetrabutylammonium fluoride. *Journal of Oleo Science*. 2014;**63**:539-544. DOI: 10.5650/jos.ess13199
- [93] Hashimoto S, Hayashi M, Noyori R. An easy preparation of triphenylmethyl carboxylates. *Bulletin of the Chemical Society of Japan*. 1984;**57**:1431-1432. DOI: 10.1246/bcsj.57.1431
- [94] Ooi T, Sugimoto H, Maruoka K. Facile conversion of trialkylsilyl esters to alkyl esters mediated by tetrabutylammonium fluoride trihydrate. *Heterocycles*. 2001;**54**:593-596
- [95] Sato T, Otera J, Nozaki H. Cesium fluoride-promoted esterification of carboxylic acids. A practical alternative to the diazomethane method and direct conversion of organotin carboxylates. *The Journal of Organic Chemistry*. 1992;**57**:2166-2169. DOI: 10.1021/jo00033a048
- [96] Selected reviews of electro-organic chemistry, Yoshida J, Kataoka K, Horcajada R, Nagaki A. Modern strategies in electroorganic synthesis. *Chemical Reviews*. 2008;**108**:2265-2299. DOI: 10.1021/cr0680843. chemrev.7b00475, and references therein
- [97] Selected reviews of electro-organic chemistry, Frontana-Urbe BA, Little RD, Ibanez JG, Palma A, Vasquez-Medrano R. Organic electrosynthesis: A promising green methodology in organic chemistry. *Green Chemistry*. 2010;**12**:2099-2119. DOI: 10.1039/c0gc00382d. chemrev.7b00475, and references therein
- [98] Selected reviews of electro-organic chemistry, Sperry JB, Wright DL. The application of cathodic reductions and anodic oxidations in the synthesis of complex molecules. *Chemical Society Reviews*. 2006;**35**:605-621. DOI: 10.1039/b512308a. chemrev.7b00475, and references therein
- [99] Selected reviews of electro-organic chemistry, Yoshida J, Shimizu A, Hayashi R. Electrogenated cationic reactive intermediates: The pool method and further advances. *Chemical Review*. in press. DOI: 10.1021/acs.chemrev.7b00475, and references therein
- [100] Awata T, Baizer M, Nonaka T, Fuchigami T. Cathodic esterification of carboxylic acids. *Chemical Letters*. 1985;**3**:371-374. DOI: 10.1246/cl.1985.371
- [101] Fuchigami T, Awata T, Nonaka T, Baizer MM. Esterification, etherification, and aldol condensation using cathodically generated organic olate anions. *Bulletin Chemical Society Japan*. 1986;**59**:2873-2879. DOI: 10.1246/bcsj.59.2873
- [102] Miyamoto Y, Yamada Y, Shimazaki H, Shimada K, Nokami T, Nishiwaki K, Kashimura S, Matsumoto K. Esterification of carboxylic acids with alkyl halides using electroreduction *Electrochemistry* 2015;**83**:161-164. DOI: 10.5796/electrochemistry.83.161
- [103] Shono T, Ishige O, Uyama H, Kashimura S. Electroorganic chemistry. 91. A novel base useful for synthesis of esters and macrolides. *The Journal of Organic Chemistry* 1986;**51**:546-549. DOI: 10.1021/jo00354a030

- [104] Tummatorn J, Albiniak PA, Dudley GB. Synthesis of benzyl esters using 2-benzyloxy-1-methylpyridinium triflate. *The Journal of Organic Chemistry*. 2007;**72**:8962-8964. DOI: 10.1021/jo7018625
- [105] Strayer TA, Culy CC, Bunner MH, Frank AR, Albiniak PA. In situ synthesis of 2-allyloxy-1-methylpyridinium triflate for the allylation of carboxylic acids. *Tetrahedron Letters*. 2015;**56**:6807-6809. DOI: 10.1016/j.tetlet.2015.10.085
- [106] Luo F, Pan C, Qian P, Cheng J. Copper(II)-catalyzed esterification of arenecarboxylic acids with aryl- and vinyl-substituted trimethoxysilanes. *Synthesis*. 2010:2005-2010. DOI: 10.1055/s-0029-1218759
- [107] Zhang L, Zhang G, Zhang M, Cheng J. Cu(OTf)₂-mediated Chan-lam reaction of carboxylic acids to access phenolic esters. *The Journal of Organic Chemistry* 2010;**75**:7472-7474. DOI: 10.1021/jo101558s
- [108] Petersen TB, Khan R, Olofsson B. Metal-free synthesis of aryl esters from carboxylic acids and diaryliodonium salts. *Organic Letters*. 2011;**13**:3462-3465. DOI: 10.1021/ol2012082
- [109] Kreye O, Meier MAR. Base catalyzed sustainable synthesis of phenyl esters from carboxylic acids using diphenyl carbonate. *RSC advances*. 2015;**5**:53155-53160. DOI: 10.1039/C5RA10206E
- [110] Shieh W, Dell S, Repic O. *Tetrahedron Letters* 2002;**43**:5607-5609. DOI: 10.1016/S0040-4039(02)01116-4
- [111] Yamada K, Yoshida S, Fujita H, Kitamura M, Kunishima M. O-benzylation of carboxylic acids using 2,4,6-Tris(benzyloxy)-1,3,5-triazine (TriBOT) under acidic or thermal conditions. *European Journal of Organic Chemistry*. 2015:7997-8002. DOI: 10.1002/ejoc.201501172
- [112] Kunishima M, Fujita H, Yamada K. PCT Int. Appl. WO 2013 073681 A1, 2013
- [113] Yamada K, Hayakawa N, Fujita H, Kitamura M, Kunishima M. Development of a triazine-based *tert*-Butylating reagent, TriAT-*t*Bu. *European Journal of Organic Chemistry*. 2016:4093-4098. DOI: 10.1002/ejoc.201600663
- [114] Adhikari AA, Shah JP, Howard KT, Russo CM, Wallach DR, Linaburg MR, Chisholm JD. Convenient formation of diphenylmethyl esters using diphenylmethyl trichloroacetimidate. *Synlett*. 2014;**25**:283-287. DOI: 10.1055/s-0033-1340293
- [115] Shah JP, Russo CM, Howard KT, Chisholm JD. Spontaneous formation of PMB esters using 4-methoxybenzyl-2,2,2-trichloroacetimidate. *Tetrahedron Letters*. 2014;**55**:1740-1742. DOI: 10.1016/j.tetlet.2014.01.097
- [116] Jia J, Jiang Q, Zhao A, Xu B, Liu Q, Luo W, Guo C. Copper-catalyzed O-methylation of carboxylic acids using DMSO as a methyl source. *Synthesis*. 2016;**48**:421-428. DOI: 10.1055/s-0035-1560967

- [117] Khan KM, Maharvi GM, Hayat S, Zia-Ullah CMI, Rahman A-U. An expedient esterification of aromatic carboxylic acids using sodium bromate and sodium hydrogen sulfite. *Tetrahedron*. 2003;**59**:5549-5554. DOI: 10.1016/S0040-4020(03)00812-3
- [118] Liu H, Shi G, Pan S, Jiang Y, Zhang Y. Palladium-catalyzed benzylation of carboxylic acids with toluene via benzylic C-H activation. *Organic Letters*. 2013;**15**:4098-4101. DOI: 10.1021/ol401687f
- [119] Selected recent examples of this chemistry. Lu B, Zhu F, Sun H, Shen Q. Esterification of the primary benzylic C-H bonds with carboxylic acids catalyzed by ionic iron(III) complexes containing an imidazolium cation. *Organic Letters*. 2017;**19**:1132-1135. DOI: 10.1021/acs.orglett.7b00148/C7RA02788E, and references therein
- [120] Selected recent examples of this chemistry. Zheng Y, Mao J, Rong G, Xu X. A NCS mediated oxidative C-H bond functionalization: Direct esterification between a C(sp³)-H bond and carboxylic acids. *Chemical Communications*. 2015;**51**:8837-8840. DOI: 10.1039/C5CC02424B/C7RA02788E, and references therein
- [121] Selected recent examples of this chemistry. Ren T, Xu B, Mahmood S, Sun M, Zhang S. Cobalt-catalyzed oxidative esterification of allylic/benzylic C(sp₃)-H bonds. *Tetrahedron*. 2017;**73**:2943-2948. DOI: 10.1016/j.tet.2017.04.002/C7RA02788E, and references therein
- [122] Selected recent examples of this chemistry. Lu B, Zhu F, Wang D, Sun H, Shen Q. Iron-catalyzed esterification of allylic sp³ C-H bonds with carboxylic acids: Facile access to allylic esters. *Tetrahedron Letters*. 2017;**58**:2490-2494. DOI: 10.1016/j.tetlet.2017.05.039/C7RA02788E, and references therein
- [123] Selected recent examples of this chemistry. Dick AR, Hull KL, Sanford MS. A highly selective catalytic method for the oxidative functionalization of C-H bonds. *Journal of the American Chemical Society*. 2004;**126**:2300-2301. DOI: 10.1021/ja031543m/C7RA02788E, and references therein
- [124] Selected recent examples of this chemistry. Chen X, Hao X, Goodhue C E, Yu J. Cu(II)-catalyzed functionalizations of aryl C-H bonds using O₂ as an oxidant. *Journal of the American Chemical Society*. 2006;**128**:6790-6791. DOI: 10.1021/ja061715q/C7RA02788E, and references therein
- [125] Selected recent examples of this chemistry. Mou F, Sun Y, Jin W, Zhang Y, Wang B, Liu Z, Guo L, Huang J, Liu C. Reusable ionic liquid-catalyzed oxidative esterification of carboxylic acids with benzylic hydrocarbons via benzylic Csp³-H bond activation under metal-free conditions. *RSC Advances*. 2017;**7**:23041-23045. DOI: 10.1039/C7RA02788E, and references therein
- [126] Mitsudo T, Hori Y, Yamakawa Y, Watanabe Y. Ruthenium-catalyzed selective addition of carboxylic acids to alkynes. A novel synthesis of enol esters. *The Journal of Organic Chemistry*. 1987;**52**:2230-2239. DOI: 10.1021/jo00387a024

- [127] Ruppin C, Dixneuf HP. Synthesis of enol esters from terminal alkynes catalyzed by ruthenium complexes. *Tetrahedron Letters*. 1986;**52**:6323-6324. DOI: 10.1016/S0040-4039(00)87798-9
- [128] Bruneau C, Neveux M, Kabouche Z, Ruppin C, Dixneuf HP. Ruthenium-catalysed additions to alkynes: Synthesis of activated esters and their use in acylation reactions. *Synlett*. 1991:755-763. DOI: 10.1055/s-1991-20866
- [129] Bruneau C, Dixneuf HP. Metal vinylidenes and allenylidenes in catalysis: Applications in Anti-Markovnikov additions to terminal alkynes and alkene metathesis. *Angewandte Chemie International Edition*. 2006;**45**:2176-2203. DOI: 10.1002/anie.200501391, and references therein
- [130] Dixneuf HP, Bruneau C, Dérien S. Smart ruthenium catalysts for the selective catalytic transformation of alkynes. *Pure and Applied Chemistry*. 1998;**70**:1065-1070. DOI: 10.1351/pac199870051065
- [131] Doucet H, Martin-Veca B, Bruneau C, Dixneuf HP. General synthesis of (Z)-Alk-1-en-1-yl esters via ruthenium-catalyzed *anti*-Markovnikov *trans*-addition of carboxylic acids to terminal alkynes. *The Journal of Organic Chemistry*. 1995;**60**:7247-7255. DOI: 10.1021/jo00127a033
- [132] Doucet H, Höfer J, Bruneau C, Dixneuf HP. Stereoselective synthesis of Z-enol esters catalysed by [bis(diphenylphosphino)alkane]bis(2-methylpropenyl)ruthenium complexes. *Journal of the Chemical Society, Chemical Communications*. 1993:850-851. DOI: 10.1039/C39930000850
- [133] Goossen JL, Paetzold J, Koley D. Regiocontrolled Ru-catalyzed addition of carboxylic acids to alkynes: Practical protocols for the synthesis of vinyl esters. *Chemical Communication*. 2003:706-707. DOI: 10.1039/B211277A
- [134] Yi SC, Gao R. Scope and mechanistic investigations on the solvent-controlled regio- and stereoselective formation of enol esters from the ruthenium-catalyzed coupling reaction of terminal alkynes and carboxylic acids. *Organometallics* 2009;**28**:6585-6592. DOI: 10.1021/om9007357
- [135] Melis K, Samulkiwicz P, Rynkowski J, Verpoort F. Ruthenium-catalyzed selective *anti*-Markovnikov *trans* addition of carboxylic acids and tail-to-tail dimerization of terminal alkynes. *Tetrahedron Letters*. 2002;**43**:2713-2716. DOI: 10.1016/S0040-4039(02)00366-0
- [136] Ye S, Leong KW. Regio- and stereoselective addition of carboxylic acids to phenylacetylene catalyzed by cyclopentadienyl ruthenium complexes. *Journal of Organometallic Chemistry*. 2006;**691**:1117-1120. DOI: 10.1016/j.jorganchem.2005.11.023
- [137] Tan TS, Fan YW. Ligand-controlled regio- and stereoselective addition of carboxylic acids onto terminal alkynes catalyzed by carbonylruthenium(0) complexes. *European Journal of Organic Chemistry*. 2010:4631-4635. DOI: 10.1002/ejic.201000579

- [138] Hua R, Tian X. $\text{Re}(\text{CO})_5\text{Br}$ -catalyzed addition of carboxylic acids to terminal alkynes: A high *anti*-Markovnikov and recoverable homogeneous catalyst. *The Journal of Organic Chemistry*. 2004;**69**:5782-5784. DOI: 10.1021/jo049455n
- [139] Jeschke J, Engelhardt BT, Lang H. Ruthenium-catalyzed hydrocarboxylation of internal alkynes. *European Journal of Organic Chemistry*. 2016:1548-1554. DOI: 10.1002/ejoc.201501583
- [140] Kawatsura M, Namioka J, Kajita K, Yamamoto M, Tsuji H, Itoh T. Ruthenium-catalyzed regio- and stereoselective addition of carboxylic acids to aryl and trifluoromethyl group substituted unsymmetrical internal alkynes. *Organic Letters*. 2011;**13**:3285-3287. DOI: 10.1021/ol201238
- [141] Oe Y, Ohta T, Ito Y. Ruthenium catalyzed addition reaction of carboxylic acid across olefins without β -hydride elimination. *Chemical Communications*. 2004:1620-1621. DOI: 10.1039/B404229H
- [142] Yang C, He C, Gold(I)-catalyzed intermolecular addition of phenols and carboxylic acids to olefins. *Journal of the American Chemical Society*. 2005;**127**:6966-6967. DOI: 10.1021/ja050392f
- [143] Taylor GJ, Whittall N, Hii KK. Copper(II)-catalysed addition of O–H bonds to norbornene. *Chemical Communications*. 2005:5103-5105. DOI: 10.1039/B509933A
- [144] Chen W, Lu J. $\text{In}(\text{OTf})_3$ -catalyzed intermolecular addition of carboxylic acids and phenols to norbornene under solvent-free conditions. *Catalysis Communications*. 2007;**8**:1298-1300. DOI: 10.1016/j.catcom.2006.11.031
- [145] Choi J, Kohno K, Masuda D, Yasuda H, Sakakura T. Iron-catalysed green synthesis of carboxylic esters by the intermolecular addition of carboxylic acids to alkenes. *Chemical Communications*. 2008:777-779. DOI: 10.1039/B713951A
- [146] Higashi S, Takenaka H, Ito Y, Oe Y, Ohta T. Synthesis of $\text{RuCl}_2(\text{xantphos})\text{L}$ ($\text{L} = \text{PPh}_3$, $\text{P}(\text{O}i\text{Pr})_3$, DMSO) complexes, and their catalytic activity for the addition of carboxylic acids onto olefins. *Journal of Organometallic Chemistry*. 2015;**791**:46-50. DOI: 10.1016/j.jorganchem.2015.04.016
- [147] Rosenfeld C D, Shekhar S, Takemiya A, Utsunomiya M, Hartwig JF. Hydroamination and hydroalkoxylation catalyzed by triflic acid. Parallels to reactions initiated with metal triflates. *Organic Letters*. 2006;**8**:4179-4182. DOI: 10.1021/ol061174+
- [148] Li Z, Zhang J, Brouwer C, Yang C, Reich WN, He C. Brønsted acid catalyzed addition of phenols, carboxylic acids, and tosylamides to simple olefins. Brønsted acid catalyzed addition of phenols, carboxylic acids, and tosylamides to simple olefins. *Organic Letters*. 2006;**8**:4175-4178. DOI: 10.1021/ol0610035
- [149] Perkowski JA, Nicewicz AD. Direct catalytic *anti*-Markovnikov addition of carboxylic acids to alkenes. *Journal of the American Chemical Society*. 2013;**135**:10334-10337. DOI: 10.1021/ja4057294