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Recent Advances in the Synthesis of Carboxylic Acid Esters

Kouichi Matsumoto, Rina Yanagi and Yohei Oe

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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.

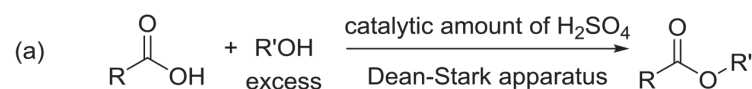
2. Synthesis of carboxylic acid esters using carboxylic acids as electrophiles

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].

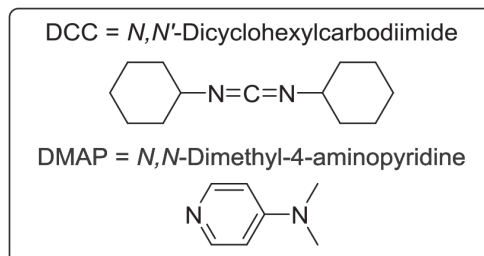
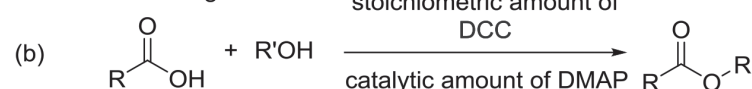
Besides the use of DCC, other condensation reagents are also developed. 2-Halo-pyridinium salts called Mukaiyama condensation reagent serve as effective reagents [9]. Mukaiyama et al. have extensively contributed this research area for the development of useful condensation reagents [10]. In addition, 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.

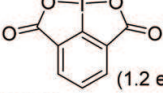
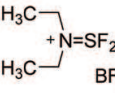
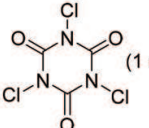
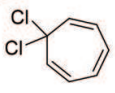
$\text{R}-\text{C}(=\text{O})\text{OH} + \text{R}'\text{OH} \xrightarrow[\text{Conditions}]{\text{Condensation reagents and}} \text{R}-\text{C}(=\text{O})\text{OR}'$		
Condensation reagents and Conditions		
Ref. 20 Polymer-bounded Ph_3P (or Ph_3P) (1.2 eq), and I_2 (1.2 eq); CH_3CN , microwave	Ref. 30 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_2PCI (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  (1.05 eq) 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).

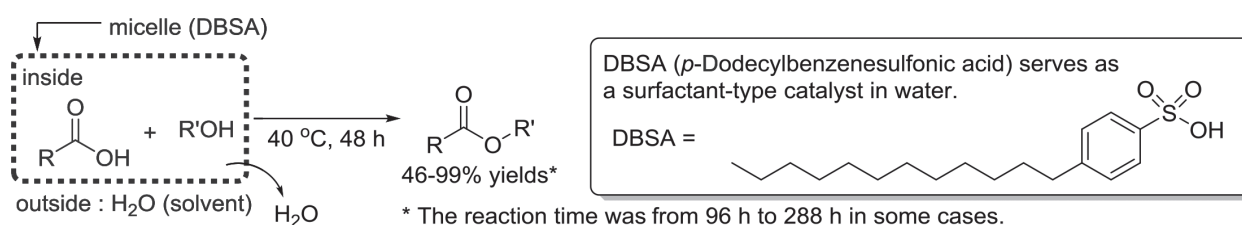
reagents. Basically, the amount of alcohols is not excess (**Table 1**). For examples, polymer-bounded Ph_3P (or Ph_3P)/ I_2 /microwave [20–23] and $\text{Ph}_3\text{P}/\text{I}_2/\text{Zn}(\text{OTf})_2$ condition [24] have been reported, because the combination of PPh_3 and I_2 in the presence of the base has been well known so far [25, 26]. In addition, the use of $\text{Ph}_2\text{PCI}/\text{I}_2$ /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.

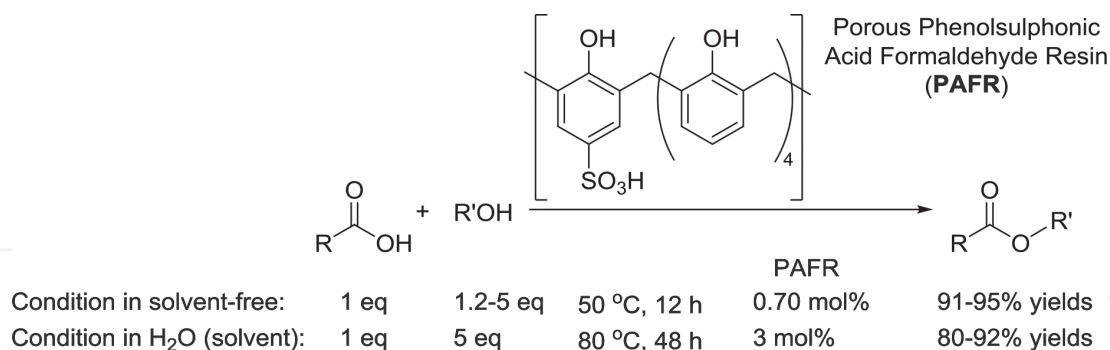
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{R}'\text{OH} \xrightarrow[\text{Solvent Conditions}]{\text{Catalyst (X mol\%)}} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$						
Entry	Authors	Published year	Catalyst (X mol%)	Solvent	Conditions	Ref.
1	H. Yamamoto 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.

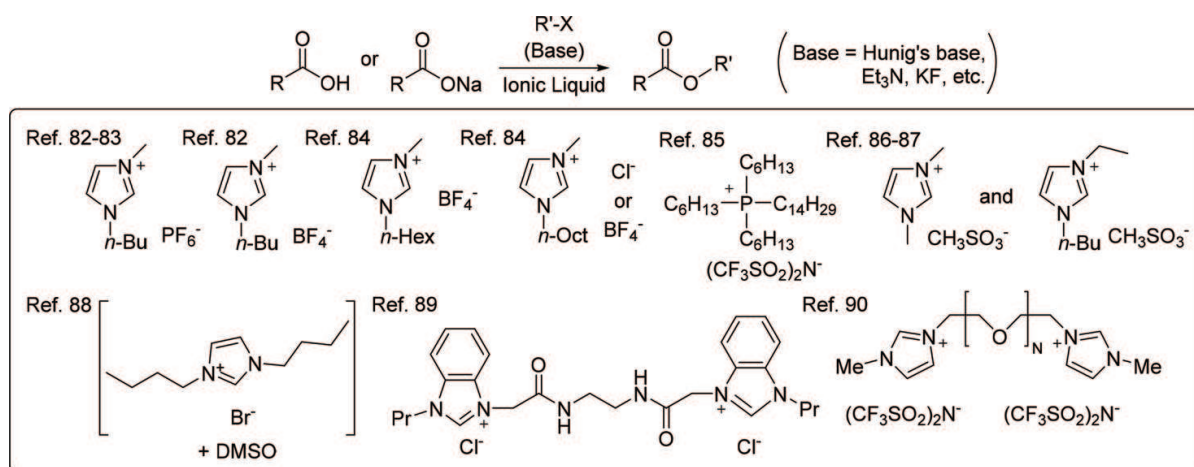
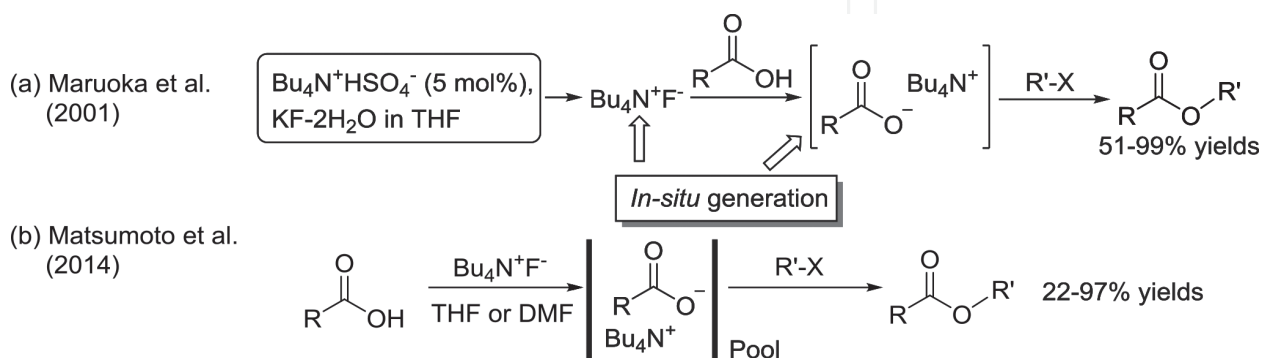


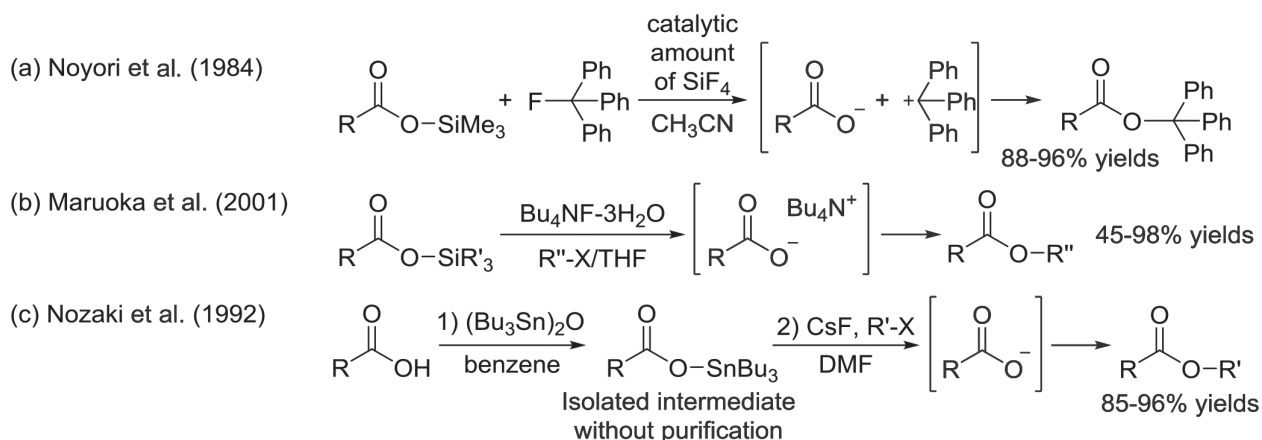
Figure 1. Recent and selected examples for nucleophilic reactions using carboxylate ion intermediates in various ionic liquids.

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.

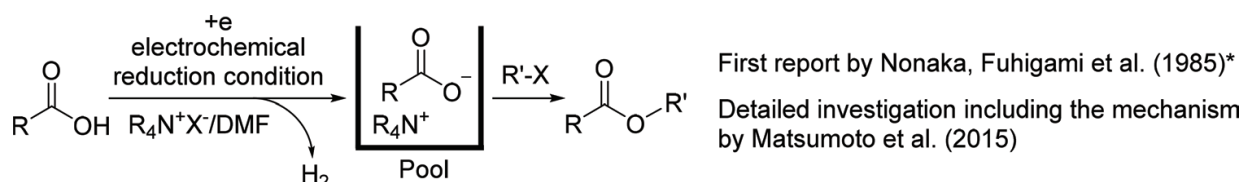
3.1.2. The use of electrochemical reduction methods

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].

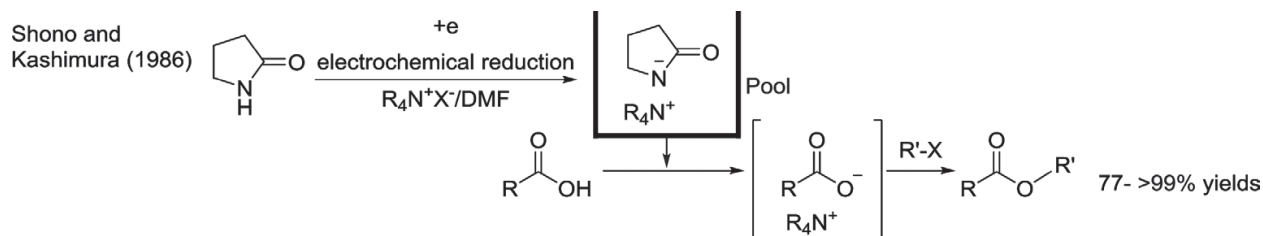
The use of electro-generated base (EGB) [97] is also effective to generate reactive carboxylate ion intermediates, developed by Shono et al. (**Scheme 7**) [103]. 2-Pyrrolidone was electrochemically reduced and 2-pyrrolidone anion was generated and accumulated as the base in the solution phase, which 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]).

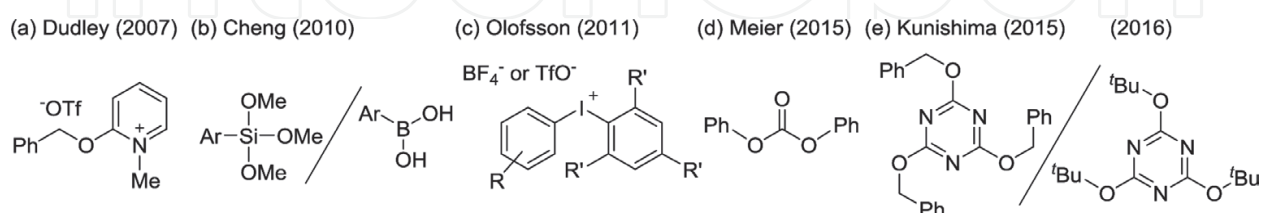
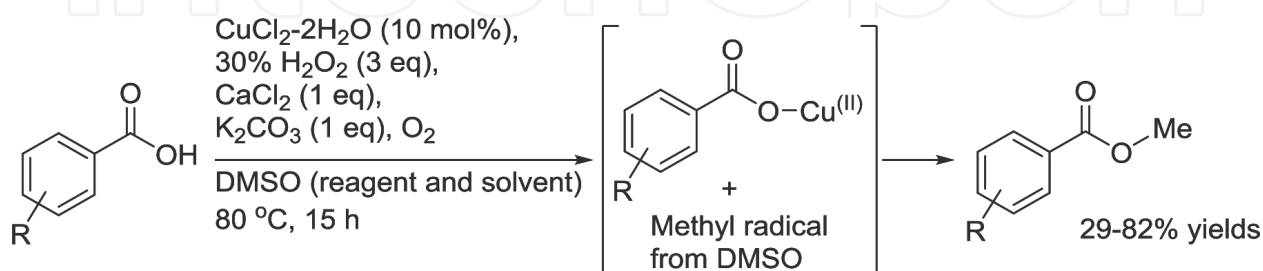


Figure 2. Selected examples for the use of electrophile equivalents.

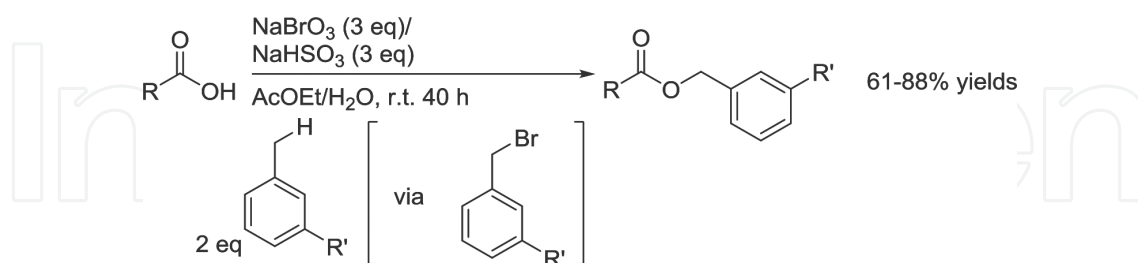
trialkoxysilanes [106] or arylboronic acids [107] were developed by Cheng et al. (**Figure 2 (b)**). Diaryliodonium salts were found to be good electrophiles for the esterification (**Figure 2 (c)**) [108]. Meier et al. reported the use of diphenyl carbonate as the electrophile to produce phenyl esters (**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]).

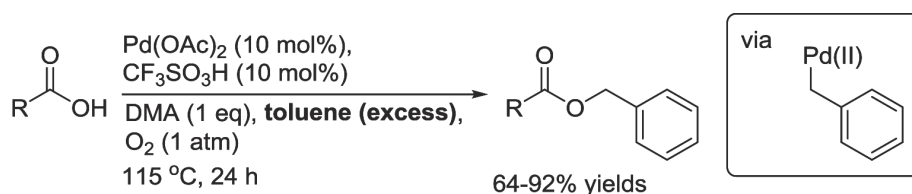
In situ generation of benzyl bromide from toluene derivatives by using $\text{NaBrO}_3/\text{NaHSO}_3$, followed by the nucleophilic reactions of the carboxylic acids could be achieved by Khan et al. (**Scheme 9**) [117]. Although aliphatic carboxylic acids were not suitable, the aromatic carboxylic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



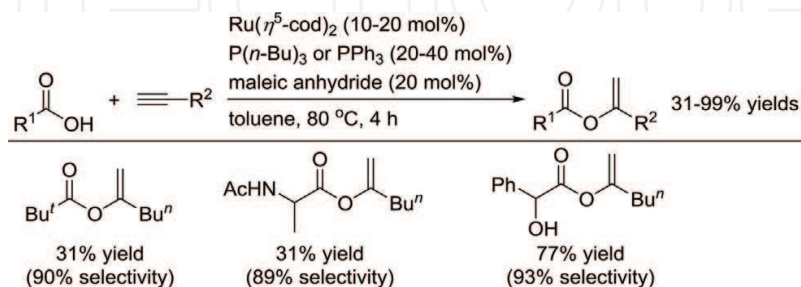
Scheme 10. Esterification of carboxylic acids and toluene catalyzed by $\text{Pd}(\text{OAc})_2$ (Zhang [118]).

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.

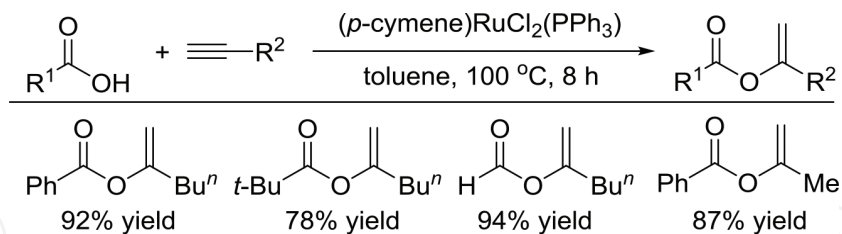
3.3.1. The addition of carboxylic acids onto alkynes

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).



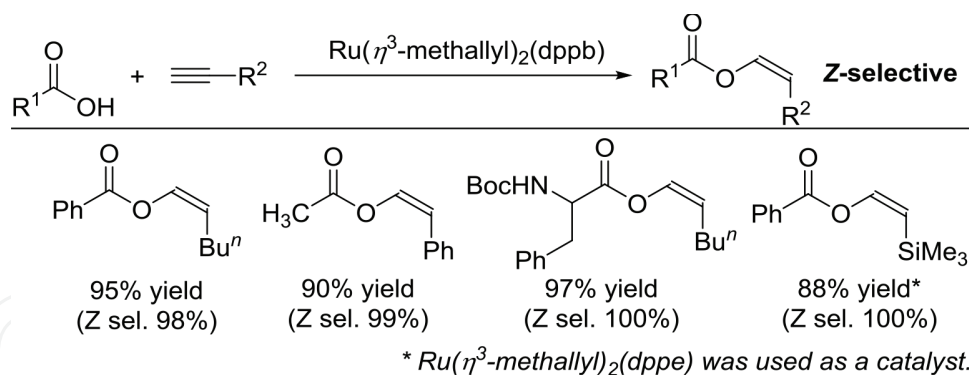
Scheme 11. Markovnikov addition (Mitsudo [126]).

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].



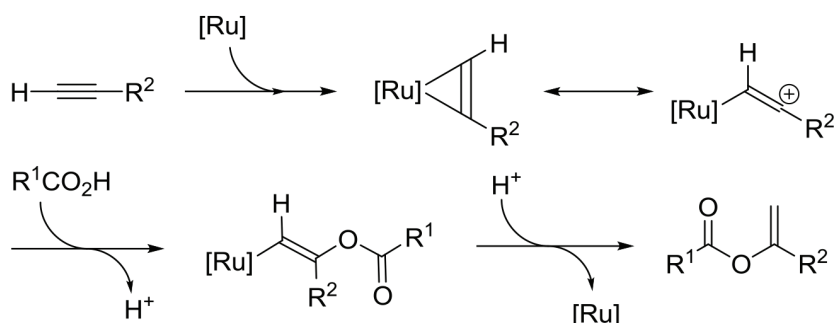
Scheme 12. Markovnikov addition (Dixneuf [127, 128]).

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].

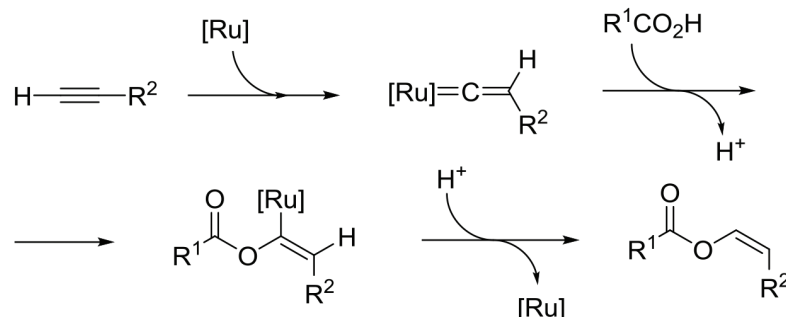


Scheme 13. Anti-Markovnikov addition of carboxylic acids onto terminal alkynes (Dixneuf [129–132]).

a) Formation of Markovnikov Adducts

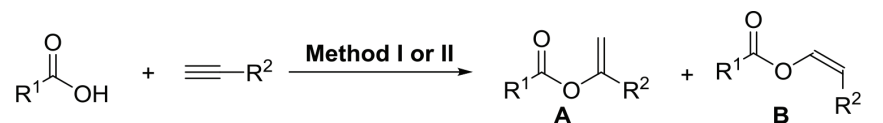


b) Formation of anti-Markovnikov Adducts

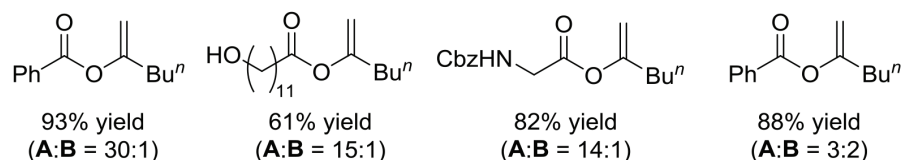


Scheme 14. Reaction mechanisms of the present enol ester formations.

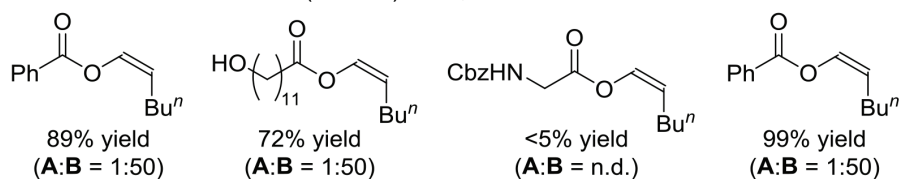
Two simple catalytic systems, in which the regioselectivity is easily controlled by the use of the same or similar catalyst, have been reported [133, 134]. Goossen et al. found that the reaction of carboxylic acids and alkenes with $RuCl_2(p\text{-cymene})$ /phosphine catalyst in the presence of K_2CO_3 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

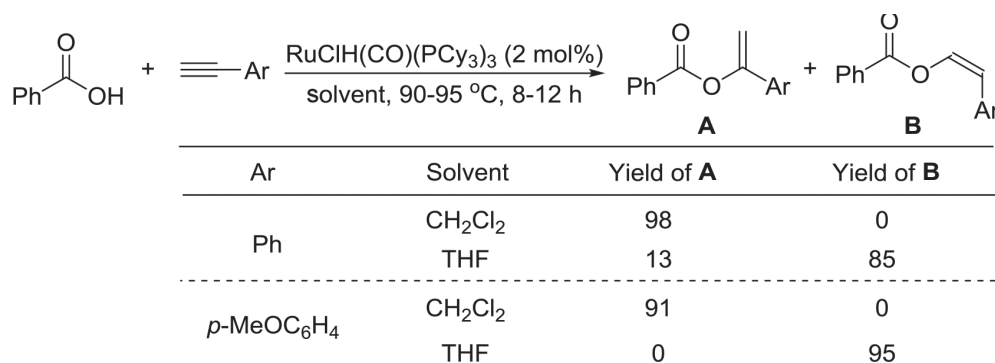
Reaction Conditions: $[\text{RuCl}_2(p\text{-cymene})]_2/2(\text{Fur})_3\text{P}$ (0.8 mol% Ru), toluene
 Na_2CO_3 (1.6 mol%) 50°C, 16 h

**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]).

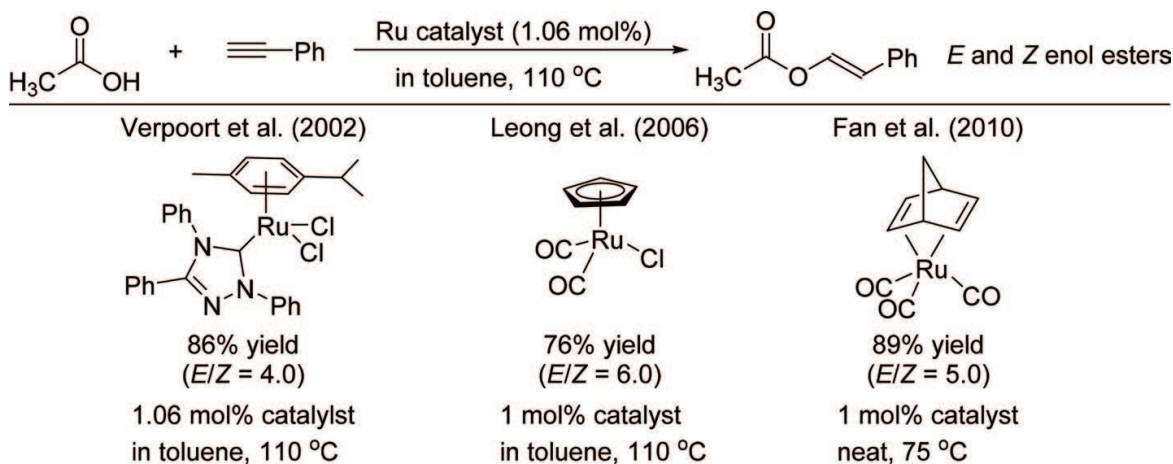


Scheme 16. Solvent-controlled selective additions (Yi [134]).

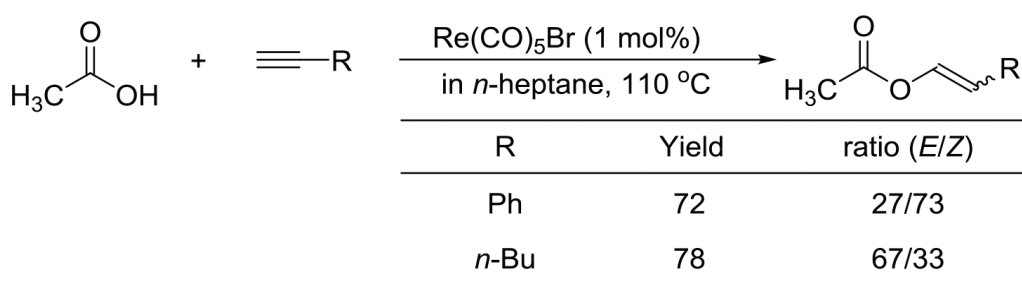
yields together with the high selectivity. It is considered that the use of THF accelerated the formation of vinylidene complex intermediates. Unfortunately, this interesting effect was not observed in the reaction of aliphatic alkynes.

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 $\text{Re}(\text{CO})_5\text{Br}$ was used as a catalyst, though the *E/Z* ratios were moderate (**Scheme 18**) [138].

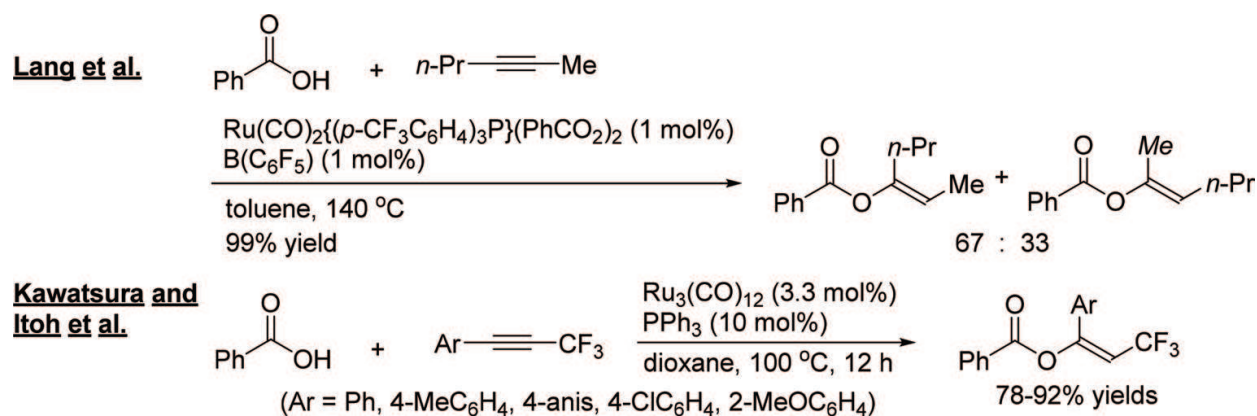
Two examples for the regio- and *E*-selective addition of carboxylic acids onto “internal” alkynes have been reported (**Scheme 19**). Lang et al. found that the reaction of the carboxylic acid with



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



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



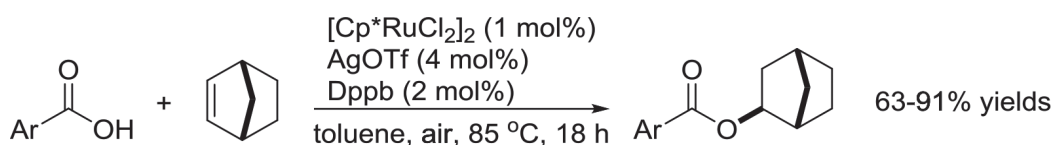
Scheme 19. Regio- and stereoselective additions to unsymmetrical internal alkynes.

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].



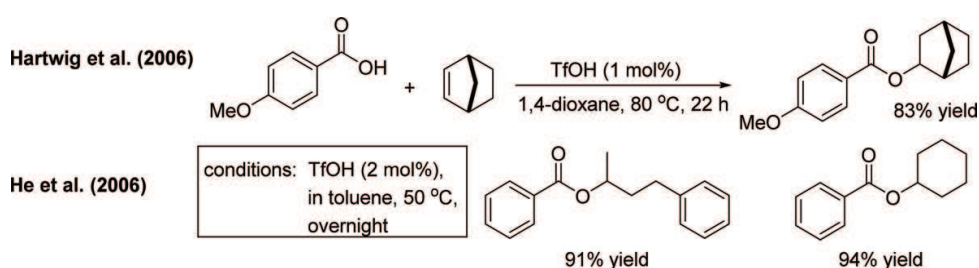
Scheme 20. Ruthenium-catalyzed additions of carboxylic acids to norbornene (Oe [141]).

$\text{R}^1\text{C}(=\text{O})\text{OH} + \text{CH}_2=\text{CH-R}^2 \xrightarrow[\text{Conditions}]{\text{Catalyst (X mol\%)}} \text{R}^1\text{C}(=\text{O})\text{OCH}_2\text{CH(R}^2\text{)}$					
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

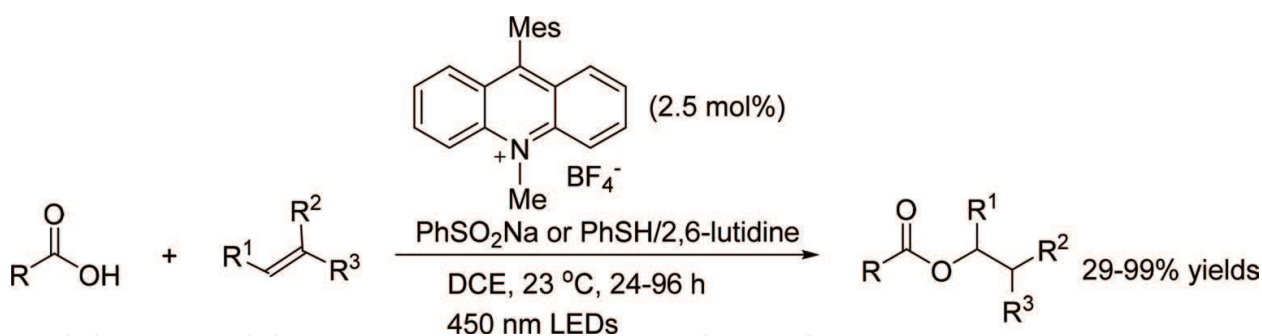
Table 3. Recent reported catalysts and generality of alkene substrates.

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

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