The Chemist
Journal of the American Institute of Chemists

Recent Advances and Perspectives in the Asymmetric Reformatsky Reaction

John Sarah, Salim Saranya, Sankuviruthiyil M. Ujwaldev and Gopinathan Anilkumar*
School of Chemical Sciences, Mahatma Gandhi University, Priyadarsini Hills P O., Kerala, India 686560
(E-mail: anilgi1@yahoo.com)

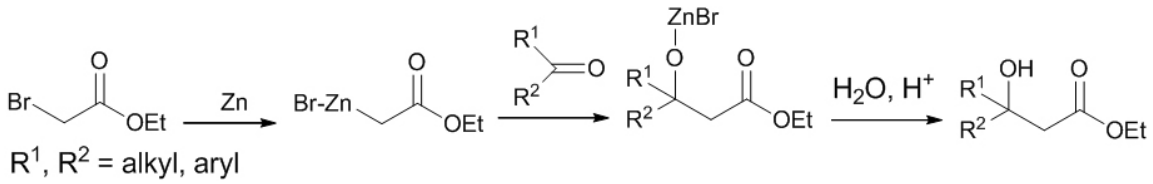
Abstract: Over the last five years much progress has been made in the catalytic asymmetric Reformatsky reaction. This reaction has been used since then in modern organic synthesis, especially in the synthesis of complex target molecules. In this review, both enantioselective and diastereoselective Reformatsky reactions were achieved using novel chiral ligands in combination with different metals such as Zn, Sm, Cr and Sn are described. Recent achievements in the total synthesis of natural products using diastereoselective Reformatsky reaction are also described and covers literature from 2013 to 2017.

Key Words: Reformatsky reaction, Asymmetric reaction, C-C bond formation, Metal-catalyzed reaction, Chiral auxiliary

INTRODUCTION

The classical Reformatsky reaction was discovered by Sergei Nikolayevich Reformatsky in 1887 [1]. It consists of a zinc-induced reaction between α-haloesters and aldehyde or ketone to produce β-hydroxy esters (Scheme 1), which are valuable precursors in natural product synthesis and pharmaceuticals. Generally, in this reaction, the enolate is formed by the oxidative addition of a metal or low-valent metal salt or complex into a carbon-halogen bond, activated by a vicinal carbonyl-derived group, followed by a reaction between enolate and appropriate electrophile [2]. It was reported that other metals like Sm, Cr, Sn, Ti, Co, In or Fe in low oxidation states are also suited for this reaction [3]. An aqueous metal-free electrochemical Reformatsky reaction is also known [4]. The solvents used are generally ethers such as Et_2O, THF, and 1,4-dioxane. The most important application is that this reaction takes place in neutral conditions, whereas the aldol reaction is a base or acid catalyzed reaction. The disadvantages are lower yield and stereoselectivity. Much progress has been made in this field to enhance the stereoselectivity by using chiral ligands. Furstner *et al.* introduced the catalytic redox cycle of this reaction [5]. Cozzi highlighted the possibility of catalytic enantioselective and diastereoselective Reformatsky reaction with different electrophiles [6]. A recent review describes the highly diastereoselective Reformatsky reactions using various chiral auxiliaries, either on the electrophile or on the nucleophile, in presence of different metals, which gave rise to high yield products [7]. In the same year, another review on highly enantioselective asymmetric Reformatsky reaction using chiral catalysts was also published [8].

The first example of an enantioselective Reformatsky reaction was reported in 1973 by using (-)-sparteine as the reagent [9]. In 1991, Soai reported an enantioselective Reformatsky reaction with the use of a chiral amino alcohol ligand (Table 1, entry 1), gave rise to the product with 91% yield and 75% enantiomeric excess (*ee*) [10]. This aroused great interest in the minds of organic chemists and led to the development of different chiral ligands for asymmetric Reformatsky reaction (Table1) [11].



Scheme 1. The classical Reformatsky reaction.

Table 1. Different chiral ligands used for asymmetric Reformatsky Reaction [12-18].

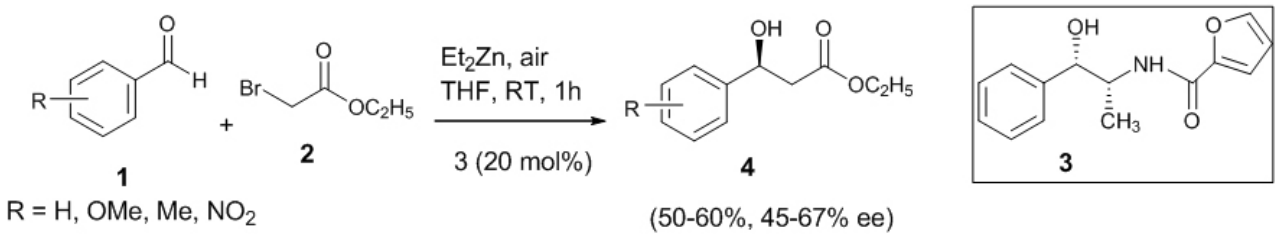
Entry	Chiral Ligand	ee (%)
1.	*S*-(+)-Diphenyl(1-methylpyrrolidin-2-yl)methanol[12]	75
2.	Trifluoromethylaminoalcohol[13]	90
3.	(-) DAIB[14]	93
4.	D-Glucosamine derived tertiary amino alcohol[15]	74
5.	Mn salen complex[16]	63
6.	Chiral indolinylmethanol[17]	81
7.	(*R*)-Binol[18]	85

ENANTIOSELECTIVE REFORMATSKY REACTION

Enantioselective Reformatsky reactions have been developed using chiral ligands for the formation of new C-C bonds.

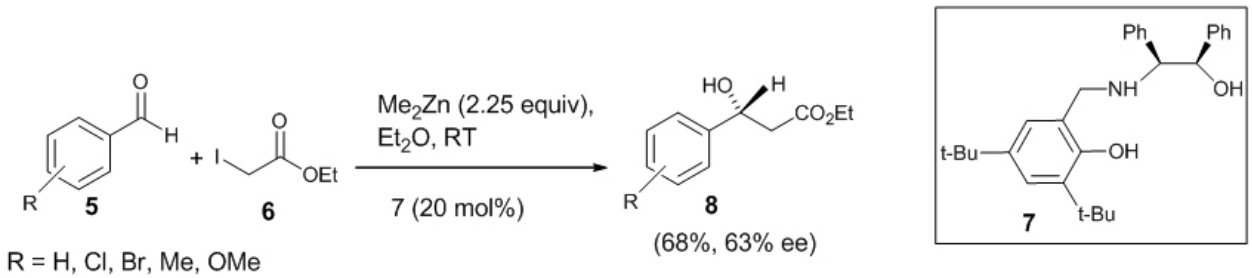
Asymmetric Reformatsky reaction involving aldehyde

A chiral amide ligand **3** was developed from (1*S*, 2*R*)-(+)-norephedrine and 2-furoic acid and applied in Reformatsky reaction which enhanced the enantioselectivity of the product. The asymmetric Reformatsky reaction was carried out between various substituted benzaldehydes **1** and α-bromomethyl acetate **2** in presence of chiral ligand **3** (10-30 mol%) mediated by Et_2Zn, which gave the corresponding β-hydroxy ester **4** in 50-60% yield and 45-67% *ee* (enantiomeric excess) (Scheme 2) [19]. Benzaldehydes with electron withdrawing group gave the product with good yield and enantioselectivity.



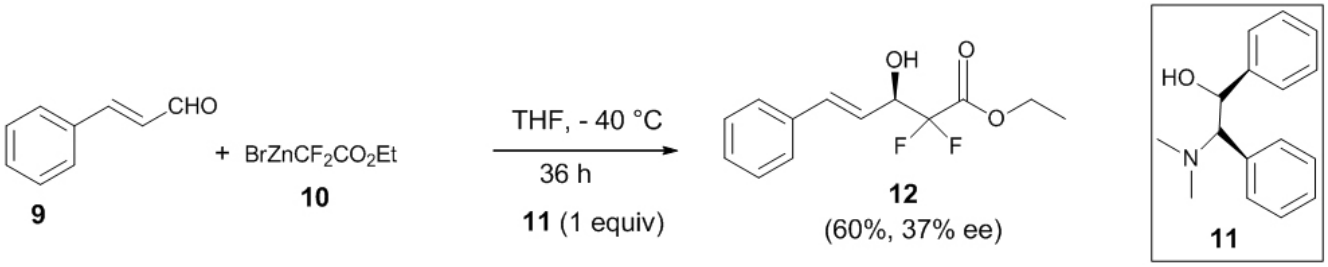
Scheme 2. Asymmetric Reformatsky reaction by chiral amide ligand.

A novel chiral tridentate β-amino alcohols **7** synthesized from a mixture of 2,5-di-tertbutyl salicylaldehyde and chiral (1*R*, 2*S*)-2-amino-1,2-diphenylmethanol was used as a catalyst for the asymmetric Reformatsky reaction [20]. Here, the reaction was carried out with variously substituted aldehydes **5** and ethyl iodoacetate **6** to obtain good enantioselectivity of the desired product **8** (Scheme 3). Both electron withdrawing and electron donating groups attached to the benzaldehyde gave enantioselectivity in the range 60-63% *ee*. It was found that 1-naphthaldehyde and 2-naphthaldehyde gave the best enantioselectivity with 81% and 80% *ee*, respectively.



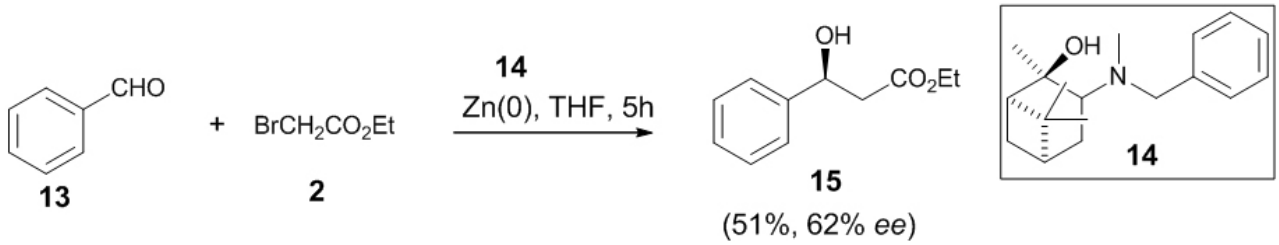
Scheme 3. Asymmetric Reformatsky reaction by chiral tridentate β-amino alcohol.

Wu *et al*. performed an asymmetric Reformatsky reaction between Cinnamaldehyde **9** and ethylbromodifluoroacetate **10** in the presence of the chiral ligand (1*S*, 2*R*)-N,N-dimethyl-2-amino-1,2-diphenylmethanol **11** to afford the desired product **12** in 37% *ee* (Scheme 4) [21].



Scheme 4. Enantioselective Reformatsky reaction mediated by chiral amino alcohol.

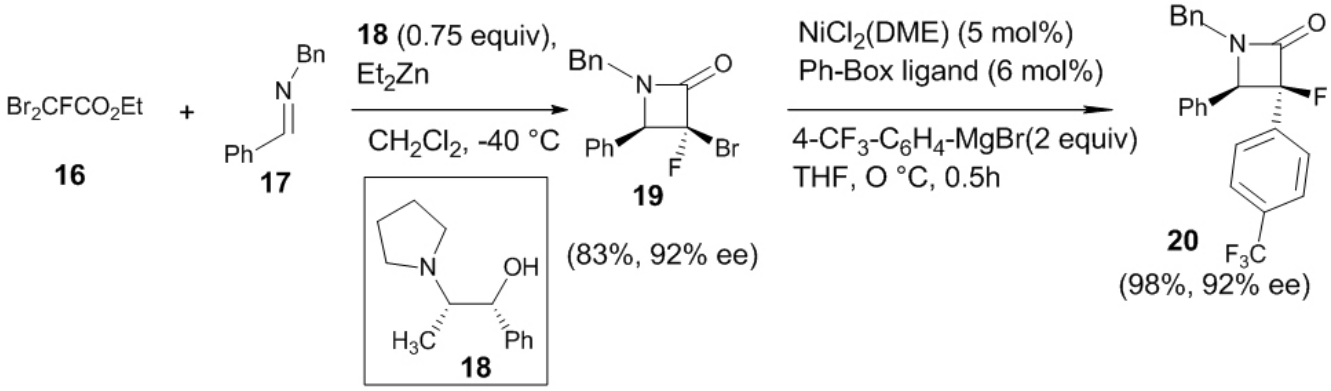
Morita *et al*. utilized the tertiary amino alcohol **14** obtained from α-pinene as a ligand for the asymmetric Reformatsky reaction between benzaldehyde **13** and 2-bromoethylacetate **2**, which yielded the corresponding β-hydroxy ester **15** in 51% yield and 62% *ee* (Scheme 5) [22].



Scheme 5. Reformatsky reaction using tertiary amino alcohol derived from α-pinene.

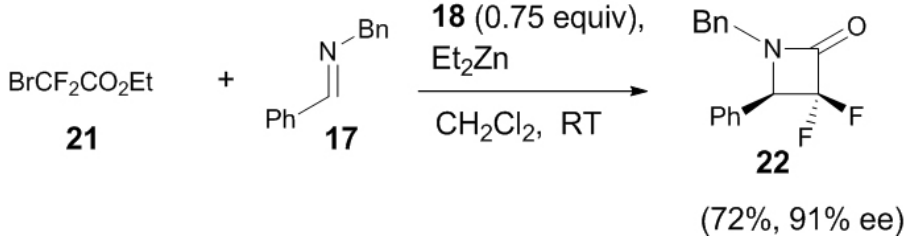
Asymmetric Imino-Reformatsky Reaction

The incorporation of fluorine atoms to β-lactams enhanced its antibiotic activity. In 2014, Ando *et. al*. reported the asymmetric Reformatsky reaction of dibromofluoroacetate **16** with imine **17** using stoichiometric amount of ligand **18** (1*R*,2*S*)1-phenyl-2-(1-pyrrolidinyl) propan-1-ol (0.75 equiv) in Et_2Zn (3.5 equiv.) at -40 °C producing α-bromo-α-fluoro β-lactam **19** with 83% yield and 92% *ee* (Scheme 6) [23]. The synthetic utility of the reaction was demonstrated by the aryl functionalization of **19** to α-aryl-α-fluoro-β-lactam **20** without any reduction in the optical purity.



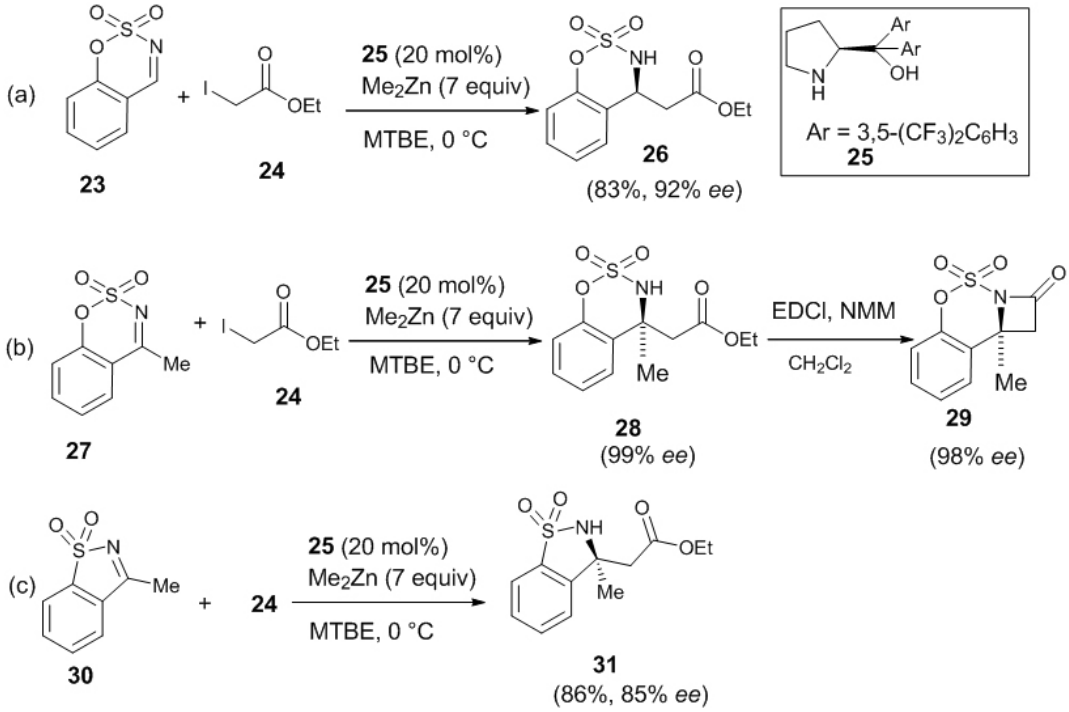
Scheme 6. Asymmetric Reformatsky reaction of dibromofluoroacetate with imine and its synthetic utility.

In the same year, Ando and co-workers also investigated a similar synthetic approach for the formation of α,α-difluoro-β-lactam from bromodifluoroacetate **21** with the same imine **17** and catalyst **18** at room temperature, which gave **22** in moderate yield (72%) and good enantioselectivity (91% *ee*) (Scheme 7) [24]. Imines which contain an electron withdrawing group as substituent in the aromatic ring, gave the corresponding products with high enantioselectivity in the range (94-99% *ee*) and moderate yield (45-74%), whereas electron donating group exhibited lower enantioselectivity (86-90% *ee*).



Scheme 7. Asymmetric Reformatsky reaction of bromodifluoroacetate with imine.

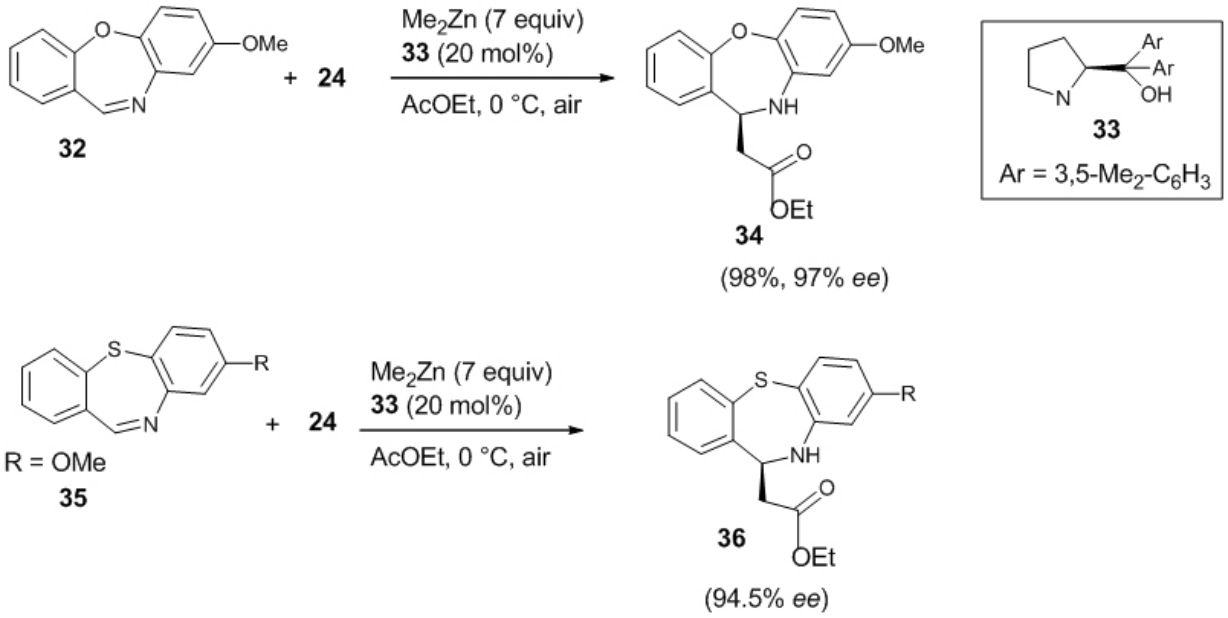
In 2016, De Munck *et al*. reported the first enantioselective aza-Reformatsky reaction of ethyliodoacetate with cyclic imines (aldimines and ketimines) forming chiral β-amino esters, which are valuable precursors for β-lactams, one of the most important classes of antibiotics [25]. Here, the reaction between cyclic benzo[*e*][1,2,3]-oxathiazine-2,2-dioxide **23** and ethyliodoacetate **24** in the presence of ligand, (*S*)-α,α-bis[3,5-bis(trifluoromethyl)phenyl]-2-pyrrolidinemethanol **25** (20 mol%**)** mediated by Me_2Zn afforded the product β-amino ester **26** in good yield (83%) and enantioselectivity (92%) [Scheme 8(a)]. When the amount of ligand was reduced to 10 mol%, the yield and enantioselectivity were reduced to 89% and 87%, respectively. Both electrons withdrawing and electron donating groups attached to the 6-position of the phenyl ring of the cyclic imine gave rise to high enantioselectivity (85-92% *ee*) and good yield (70-95%). Naphthyl ring substituted to the phenyl ring of cyclic imine gave excellent enantioselectivity (90-93% *ee*).



Scheme 8. Enantioselective aza-Reformatsky reaction between ethyliodoacetate and cyclic aldimines and ketimines.

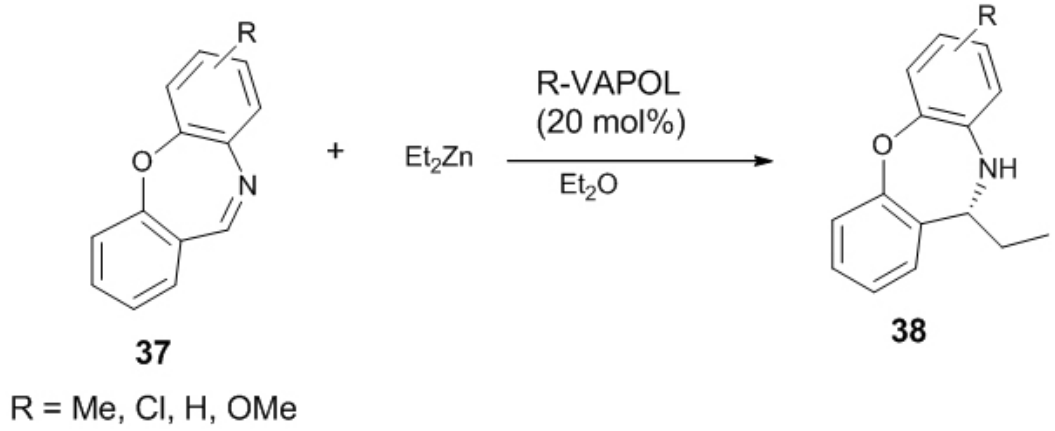
They also reported the enantioselective aza-Reformatsky reaction between cyclic ketimines like 4-methyl-benzo[*e*][1,2,3] oxathiazine-2,2-dioxide **27** and ethyliodoacetate **24** with the same ligand **25** and reaction condition as in aldimines [Scheme 8(b)]. The chiral β-amino ester **28** thus formed bears a quaternary stereocentre with excellent enantioselectivity (99% *ee*). Even when the amount of the ligand was reduced to 10 mol%, the enantioselectivity was 97% *ee*. The chiral β-amino ester can be used for the synthesis of β-lactam **29** without any reduction in the optical purity (98% *ee*). The reaction was extended successfully in the synthesis of chiral β-amino ester **31** (86%, 85% *ee*) from the five-membered cyclic N-sulfonyl ketimine **30** under the same reaction conditions [Scheme 8(c)].

Very recently, De Munck *et al*. published the enantioselective Reformatsky reaction between seven-membered cyclic imine like dibenzo [*b, f*] [1,4] oxazepine **32** and ethyliodoacetate **24** in the presence of ligand **33** (20 mol %) in Me_2Zn and air, and the corresponding β-amino ester **34** was obtained in 98% yield and 97% *ee* [26]. They also conducted similar Reformatsky reaction between dibenzo[*b,f*][1,4] thiazepine **35** and **24**, affording β-amino ester **36** in 95% yield and 94.5% *ee* (Scheme 9**)**.



Scheme 9. Reformatsky reaction between oxazepine/thiazepine derivatives with ethyliodoacetate.

Later on, De Munck *et al*. extended their work and disclosed the first enantioselective addition of Et_2Zn to cyclic imines **37** in presence of (*R*)-VAPOL-Zn (II) complex as the catalyst [27]. The product **38** was obtained with moderate enantioselectivity (up to 70% *ee*) and good yield (up to 76%) (Scheme 10).



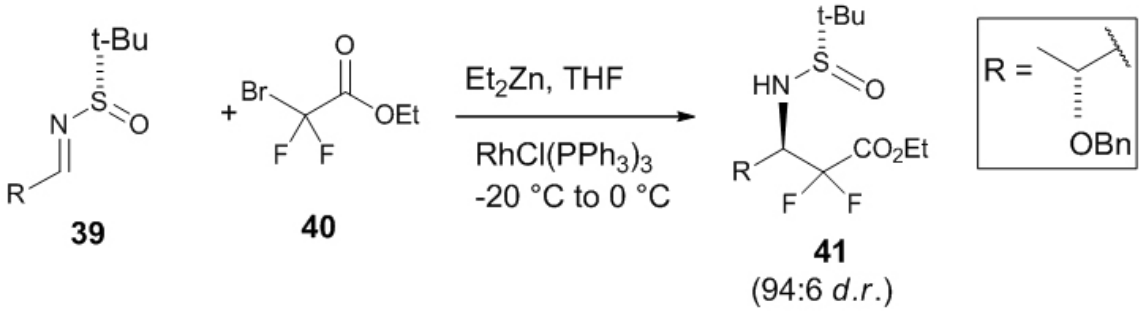
Scheme 10. Enantioselective Reformatsky reaction between cyclic imines and Et_2Zn.

DIASTEREOSELECTIVE REFORMATSKY REACTION

Diastereoselective Reformatsky reactions are widely used to perform the synthesis of cyclic and acyclic moieties using a large variety of chiral auxiliaries which control the stereochemistry of the desired products.

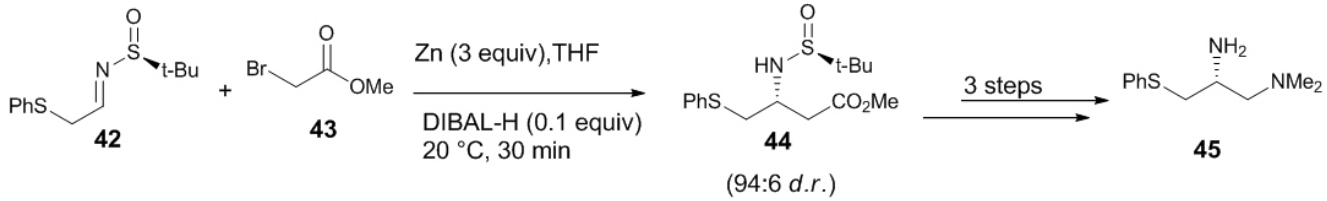
Reformatsky reaction on chiral imines

Reformatsky reaction between α-oxygenated sulfinylimine **39** and ethyl bromodifluoroacetate **40** has been reported using Honda-Reformatsky condition which afforded the desired product **41** with excellent diastereoselectivity (>94:6) (Scheme 11) [28]. The stereo induction of the product was determined by the configuration of the chiral auxiliary.



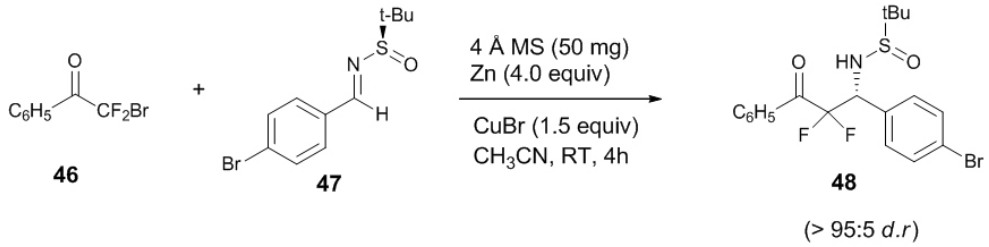
Scheme 11. Reformatsky reaction between α-oxygenated sulfinylimines and ethyl bromodifluoroacetate.

Laclef *et al.* reported a diastereoselective aza-Reformatsky reaction for the synthesis of the key fragment diamine present in anti-apoptotic Bcl-2/Bcl-xL protein inhibitors, used in anticancer therapy [29]. They performed a large-scale synthesis of the diamine with fewer purification processes. The Reformatsky reaction between sulfinimine **42** and excess of methylbromoacetate **43**, afforded the corresponding product **44** with a high diastereomeric ratio (>94:6) which was further transformed to give the diamine fragment **45** with 95% HPLC purity (Scheme 12).



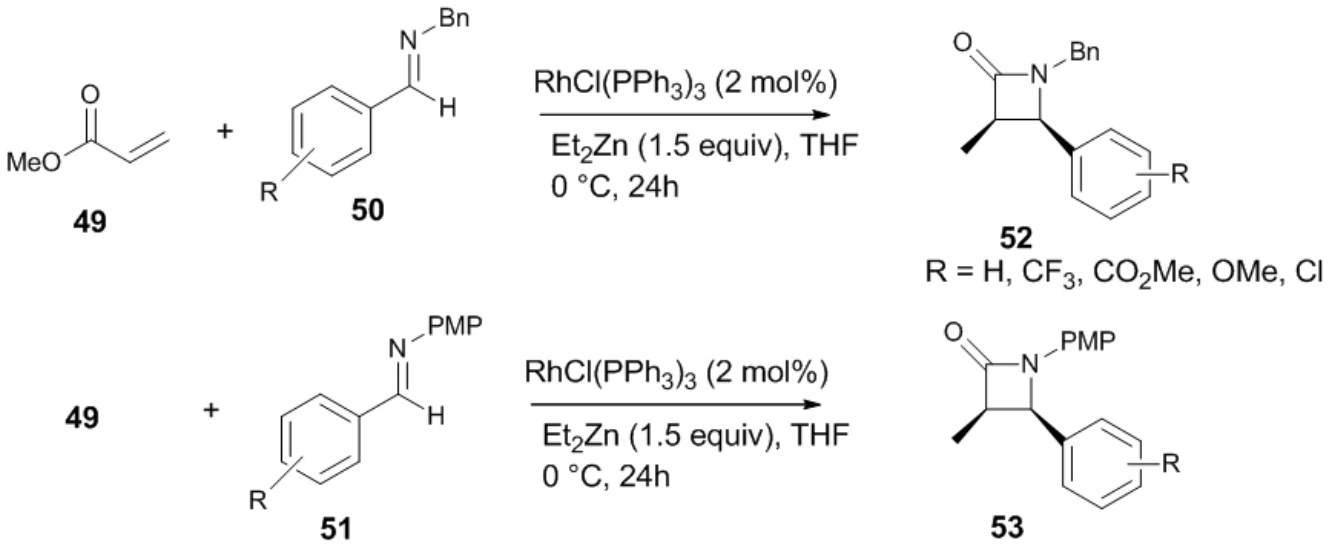
Scheme 12. Aza-Reformatsky reaction for the synthesis of diamine fragment of anti-apoptotic protein inhibitor.

An asymmetric Reformatsky reaction between bromodifluoromethyl phenyl ketone **46** and various substituted chiral ketimines **47** in presence of 4 Å molecular sieves (MS) was reported (Scheme 13) [30]. Both electron withdrawing and electron donating groups on the chiral ketimine afforded the product **48** with excellent diastereoselectivity (>95:5 *d.r.*) which has many synthetic applications.



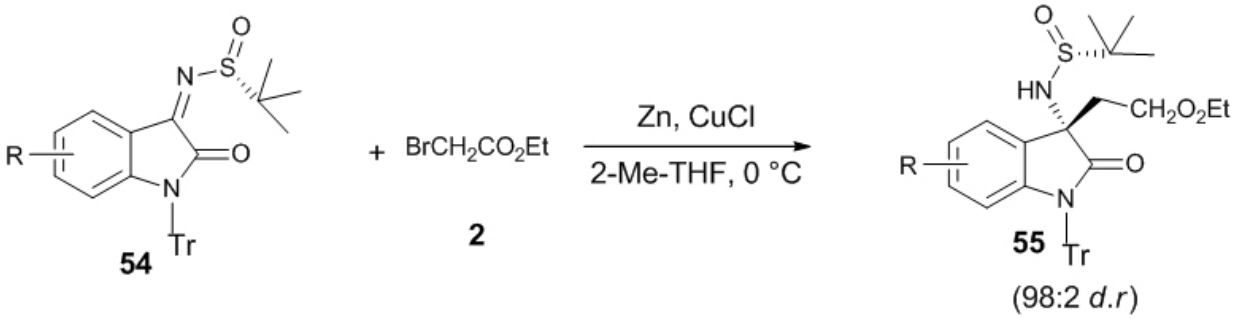
Scheme 13. Asymmetric Reformatsky reaction in presence of molecular sieves.

Rhodium enolate based Reformatsky reaction in presence of Wilkinson catalyst and Zn has also been developed [31]. Here, the reaction was conducted on α,β-unsaturated esters **49** and various imines like N-benzyl substituted imines **50** and N-*para*-methoxy phenyl imines **51** resulting in *syn* β-lactam **52** and **53** as the products (Scheme 14). Both electron withdrawing and electron donating groups in the benzene ring produced the *syn* β-lactams in better yields. This method can be used for the one-pot synthesis of spiro β-lactams from ketimines.



Scheme 14. Synthesis of *syn* β-lactams using Wilkinson catalyst and Et_2Zn.

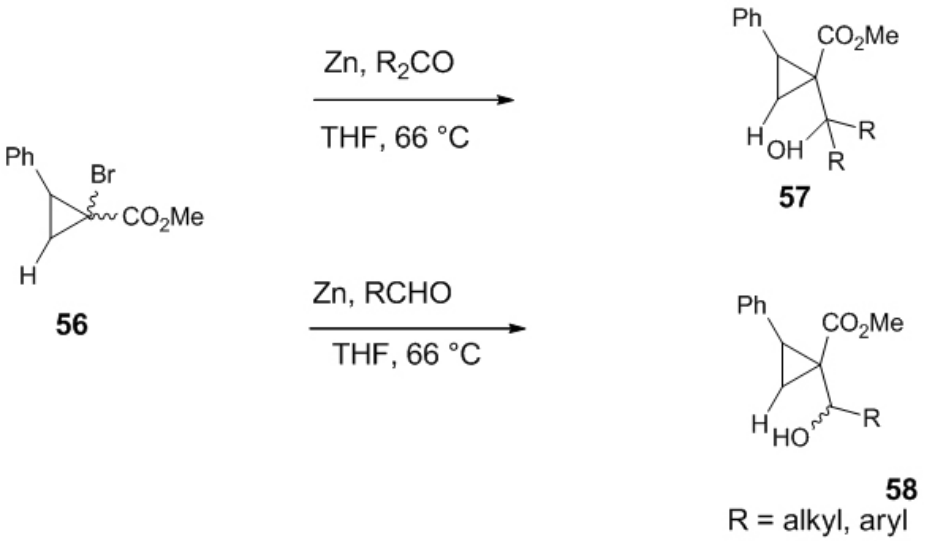
A highly efficient diastereoselective asymmetric Reformatsky reaction between isatin-derived chiral N-sulfinyl ketimines **54** and ethyl bromoacetate **2** in presence of the solvent 2-methyltetrahydrofuran and mediated by Zn-CuCl has been developed in which optically pure 2-oxoindolinyl β3,3-amino acid ester **55** was obtained with excellent diastereoselectivity (98:2 *d.r*) (Scheme 15) [32]. The reaction was performed with different ketimines and concluded that both electrons withdrawing and electron donating groups in the benzene ring of the ketimine gave rise to better yield and excellent diastereoselectivity. The β-amino acid so obtained was used for the synthesis of gastrin/cholecytokinin-B receptor antagonist AG-041R.



Scheme 15. Synthesis of β-amino acid ester from isatin-derived chiral N-sulfinyl ketimines.

Reformatsky reaction involving chiral auxiliary on cyclopropane ring

Nishii *et al*. developed a Reformatsky reaction between α-bromocyclopropanecarboxylate **56** and ketones, in presence of zinc affording *trans* adducts **57** (99:1 *d.r*) in high yield [33]. When the same reaction was carried out in presence of aldehydes, the product **58** was obtained with excellent *trans* selectivity at the α-position (99:1 *d.r*) and moderate diastereoselectivity at the β-position (62:38 *d.r*) (Scheme 16).



Scheme 16. Synthesis of *trans* adducts from α-bromocyclopropanecarboxylates by Reformatsky reaction.

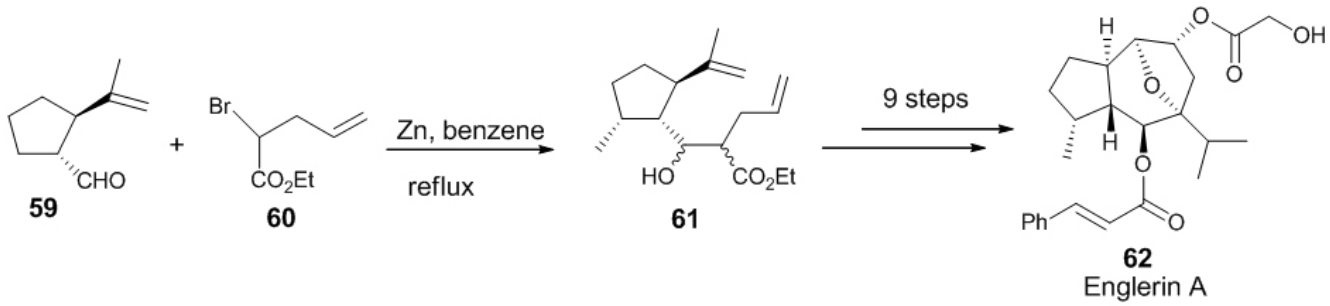
APPLICATIONS OF REFORMATSKY REACTION IN THE TOTAL SYNTHESIS OF NATURAL PRODUCTS

Reformatsky reaction has been applied in a large number of total synthesis of natural products. We have categorized the reactions based on the metal complex used.

Zinc-mediated Reformatsky reaction

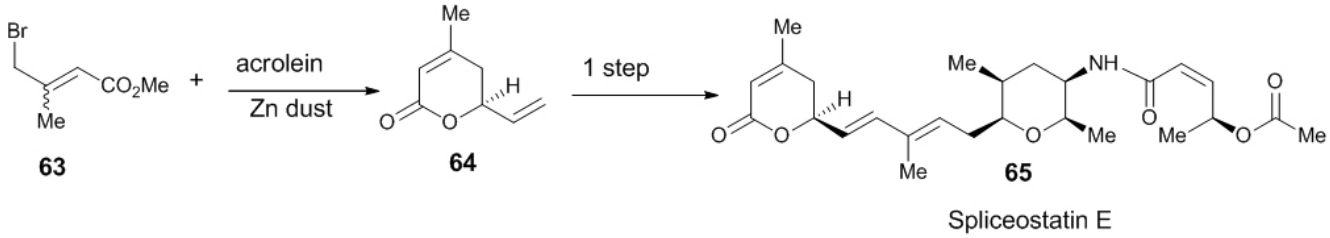
Different Zn complexes will show different reactivities, for example, the weak nucleophilic Me_2Zn was found to be less reactive than Et_2Zn [34]. Zinc reacts slowly with halo compound due to the formation of the oxide coating on Zinc. This problem was solved to some extent by using activated Zn like Rieke-Zn [35] or Cu-Zn alloy [36]. Later, Knochel developed a practical method for the activation of Zn. It was reported that for the synthesis of β-hydroxyesters, ZnCl2 or SnCl2 reduced with sodium in liquid ammonia was used. Some additives in combination with zinc are also used for this reaction which includes tantalum, vanadium binuclear complex, Hg2Cl2, triethyl boron, cerium (III) salts, etc.

A short synthetic route for the natural product, (-)-Englerin A (active against renal cancer cell lines) **62** was reported with 12 steps in 16% yield [37]. The first step in the construction of the hydroazulene framework was a zinc-mediated reaction between photocitral A **59** and bromoester **60** under mild conditions, affording the product **61** in good yield as a diastereomeric mixture (Scheme 17).



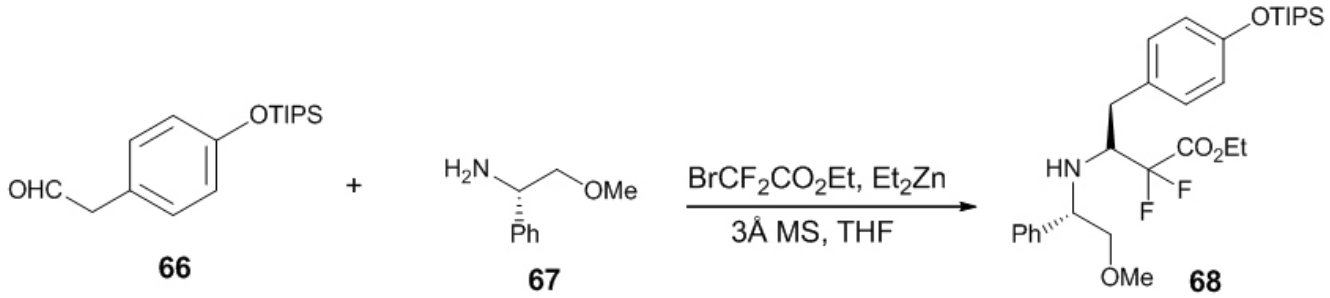
Scheme 17. Zinc-mediated Reformatsky reaction for the total synthesis of (-)Englerin A.

Ghosh *et al*. performed zinc-mediated reaction for the formation of racemic dihydropyranone from methyl-3-bromomethylcrotonate **63** and acrolein as one of the steps in the synthesis of Spliceostatin E **65**, which has potent antitumor activity (Scheme 18) [38]. The racemic mixture was resolved by chiral HPLC and the (*S*)-dihydropyranone **64** was used for the synthesis.



Scheme 18. Synthesis of (*S*)-dihydropyranone by Reformatsky reaction for the eventual synthesis of Spliceostatin E.

The synthesis of Tyr[1]-ψ [(Z) CF=CH]-Gly[2] Leu-enkephalin fluorinated peptidomimetics have been reported using Reformatsky reaction [39]. In the key step, fluorine was incorporated through a diastereoselective Reformatsky-Honda reaction between TIPS protected phenyl acetaldehyde **66** and chiral amine **67** using molecular sieves, and the desired product **68** was obtained in good yield **(**Scheme 19**)**.

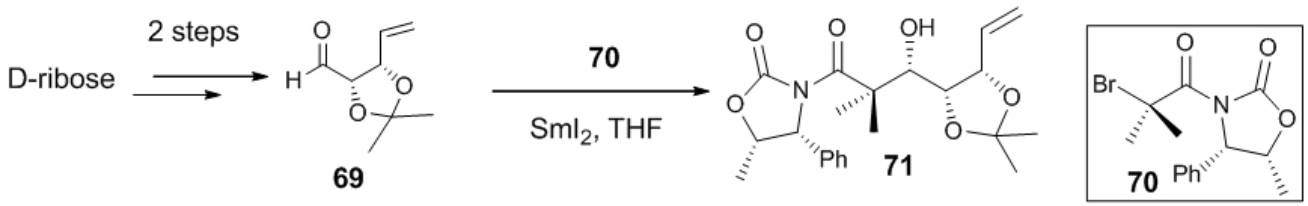


Scheme 19. Incorporation of fluorine through Reformatsky-Honda reaction.

Samarium-mediated Reformatsky reaction

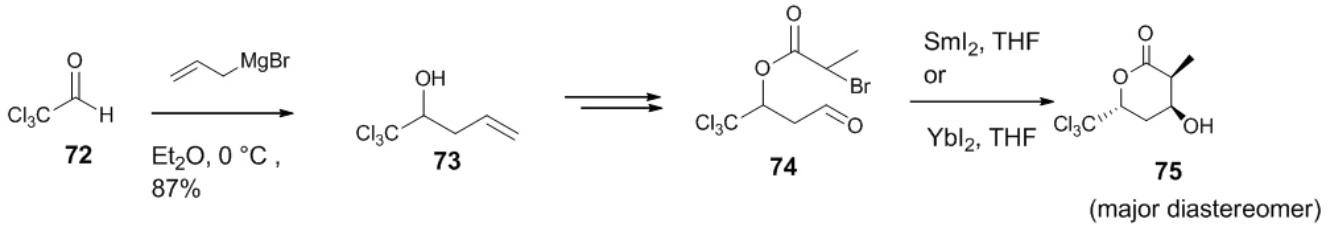
High diastereoselective products can be obtained by using a one-electron reducing agent, Samarium diiodide, due to its moderate oxidation potential and high oxophilicity. Samarium-mediated Reformatsky reaction proceeds through an intramolecular reaction yielding medium to largely sized carbocycles [1(b)]. Metallic Samarium can be used in combination with Cadmium (II) chloride or Bismuth (III) Chloride to produce β-hydroxy ketones in moderate to good yields from α-bromoacetophenone and aldehydes in THF-H2O.

The key step for the synthesis of the eastern fragment of PI-3- a jatrophane diterpene used in the treatment of cancerous conditions, swellings and warts was a diastereoselective SmI_2-mediated Reformatsky reaction [40]. Here, D-ribose was converted to an unsaturated aldehyde **69** which was further reacted with bromoacyl oxazolidinone **70** to afford the oxazolidinone product **71** as a single diastereomer with *S*-configured hydroxyl group (Scheme 20).



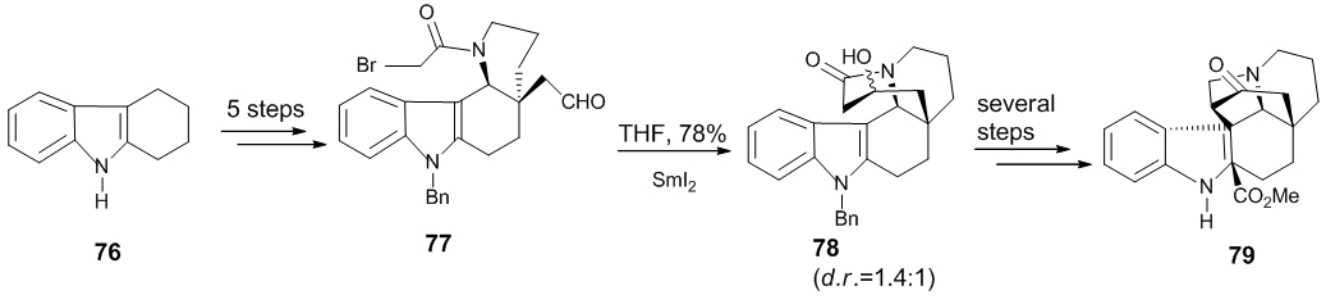
Scheme 20. SmI_2-mediated Reformatsky reaction in the total synthesis of the eastern part of PI-3.

The importance of substituted lactones in the synthesis of natural products encouraged Schulze *et al*. to synthesize substituted valerolactones by the intramolecular SmI_2/YI_2-mediated Reformatsky reaction [41]. The synthesis involved the preparation of intermediate **73** from allyl magnesium bromide and chloral **72**, which was further transformed into the ester **74** and underwent an intramolecular Reformatsky reaction to produce four diastereomeric products, out of which the major product **75** was the 4,6-anti-configured diastereomer as determined by NMR (Scheme 21).



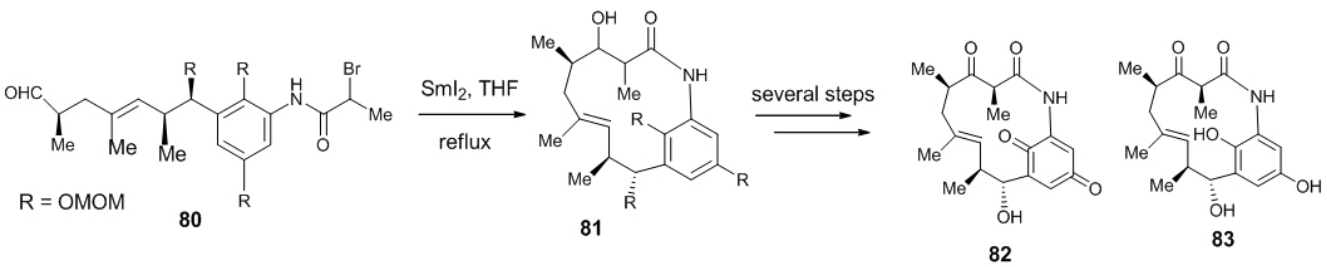
Scheme 21. Synthesis of β-hydroxy-δ-trichloromethyl-δ-valerolactone by Reformatsky reaction.

An indole alkaloid, Methyl N-decarbomethoxychanofruticosinate **79**, used in the treatment of pharyngitis, tonsillitis, rheumatoid arthritis, etc., has been synthesized using Reformatsky reaction [42]. The commercially available 1, 2, 3, 4-tetrahydro-4-oxocarbazole **76** was transformed to aldehyde **77**. In order to create a seven-membered ring, an intramolecular SmI_2-mediated Reformatsky reaction was performed to give **78**, which underwent several steps to afford the product as a mixture of two diastereomers in good yield (Scheme 22).



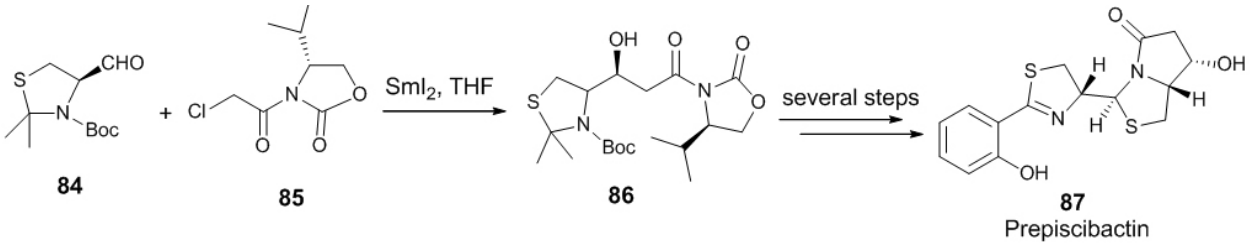
Scheme 22. Synthesis of indole alkaloid using SmI_2-mediated Reformatsky reaction.

One of the key steps in the total synthesis of Ansamacrolactams (+)-Q-1047H-A-A **82** and (+)-Q-1047H-R-A **83** (class of macrolactam bacterial metabolites, used for the synthesis of some natural products) was the SmI_2-mediated intramolecular Reformatsky reaction for the formation of macrolactam ring **81** from the intermediate **80** (Scheme 23) [43].



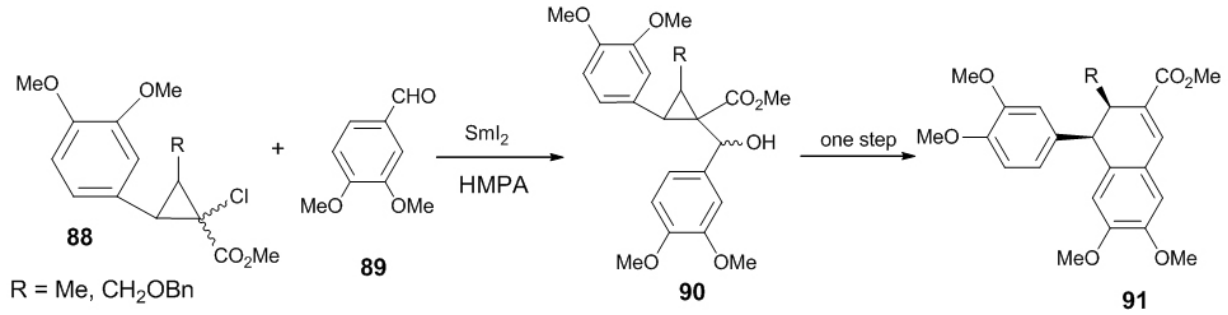
Scheme 23. SmI_2-mediated intramolecular Reformatsky reaction for the synthesis of ansamacrolactams.

The first total synthesis of Prepiscibactin **87**, the key intermediate for the biosynthesis of piscibactin (siderophore seen in bacterium *Photobacterium damselae*) was realized by SmI_2-mediated Reformatsky reaction [44]. The key step in the synthesis was a SmI_2-mediated Reformatsky reaction between thiazolidinic aldehyde **84** and α-chloroacetyl-2-oxazolidinone **85** affording the *syn*-selective product **86** with 99% *d.r.* (Scheme 24).



Scheme 24. Total synthesis of Prepiscibactin utilizing SmI_2-mediated Reformatsky reaction.

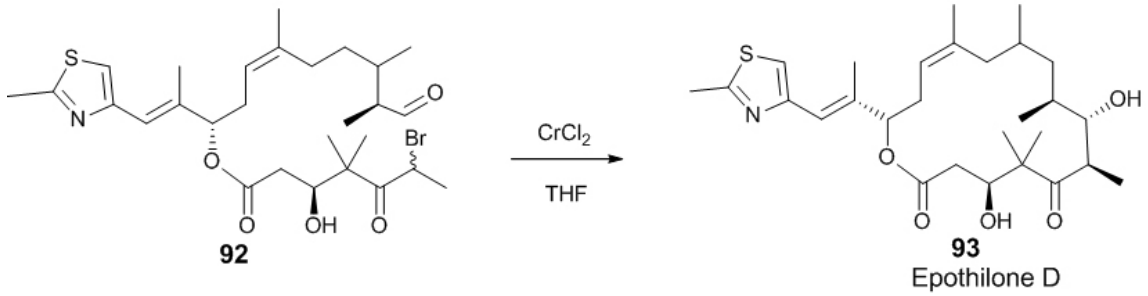
Nishii *et al*. reported the total synthesis of Cyclogalgravin and its dicarboxyl analog due to its biological importance such as antineoplastic cytotoxicity and apoptosis-inducing activities [45]. One of the key steps in this synthesis was a SmI_2-mediated Reformatsky reaction between α-chloroester **88** and veratraldehyde **89**. An excellent *trans* selective product **90** (*trans*/*cis* = 99/1) was obtained in good yields which on ring expansion gave Cyclogalgravin **91** (Scheme 25).



Scheme 25. Total synthesis of Cyclogalgravin and its dicarboxyl analog using SmI_2-mediated Reformatsky reaction.

Chromium-mediated Reformatsky reaction

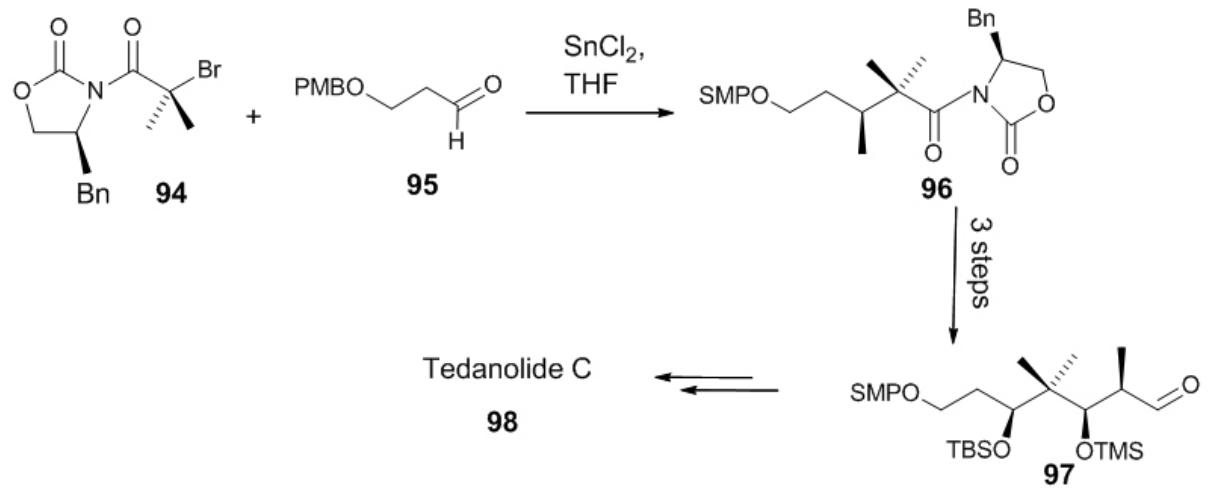
Chromium is rarely used in the Reformatsky reaction. A chromium-mediated Reformatsky reaction is a powerful tool for the formation of the asymmetric C-C bond due to its unusual stereospecificity and chemoselectivity in macroaldolization. In this reaction, when aldehydes are used as electrophiles, diastereoselective *syn* products are obtained whereas *anti* products are obtained with chiral auxiliaries. A chromium-mediated Reformatsky reaction was used in the total synthesis of Epothilone D **93** [46]. The required *syn* selective C6-C7 bond of this compound was prepared from the precursor **92** in presence of $CrCl_2$. (Scheme 26).



Scheme 26. Chromium-mediated Reformatsky reaction used in the synthesis of Epothilone D.

Tin-mediated Reformatsky reaction

Tedanolide C **98** is a marine natural product isolated from a Papua New Guinea sponge which showed excellent potency towards colorectal cancer cell line and is also a protein synthesis inhibitor. The starting material **97** for the synthesis of a C1-C11 fragment of Tedanolide C was synthesized from oxazolidinone **94** with an aldehyde **95**, by a tin-mediated Reformatsky reaction which gave rise to a product **96** with 56% yield and >98:2 *d.r.* (Scheme 27) [47].



Scheme 27. Tin-mediated Reformatsky reaction for the synthesis of Tedanolide C.

CONCLUSIONS

Asymmetric Reformatsky reaction facilitates the formation of a C-C bond between a halide and an aldehyde which leads to the formation of a chiral alcohol. This review covers the asymmetric Reformatsky reaction using different transition metals and various chiral ligands. Both enantioselective and diastereoselective Reformatsky reactions are discussed. In addition to Zinc, other transition metals such as Sm-, Sn-, and Cr-mediated Reformatsky reactions have also evolved, affording the products in excellent yields due to their improved reactivity. The incorporation of fluorine into β-lactam has become a major research interest due to the enhanced antibiotic activity. Much progress has been observed in the intramolecular Reformatsky reaction using SmI_2, which was also included in this review.

REFERENCES

1. (a) Reformatsky S. *Ber. Dtsch. Chem. Ges.*, 1887, 20, 1210. (b) Ocampo R, Dolbier Jr WR. *Tetrahedron*, 2004, 60, 9325.
2. Furstner A in Encyclopedia of Reagents for Organic Synthesis, ed. Paquette, LA, Wiley, New York, 1995, p 2402.
3. Orsini F, Sello G. *Curr. Org. Synth.*, 2004, 1, 111.
4. Areias MCC, Bieber LW, Navarro M, Diniz FB. *J. Electroanal. Chem.*, 2003, 558, 125.
5. (a) Furstner A, Hupperts A. *J. Am. Chem. Soc.*, 1995, 117, 4468. (b) Furstner A, Shi N. *J. Am. Chem. Soc.*, 1996, 118, 12349.
6. Cozzi PG. *Angew. Chem., Int. Ed.*, 2007, 46, 2568.
7. Choppin S, Ferreiro-Medeiros L, Barbarotto M, Colobert F. *Chem. Soc. Rev.*, 2013, 42, 937.
8. Fernandez-Ibanez MA, Macia B, Alonso DA, Pastor IM. *Eur. J. Org. Chem.*, 2013, 7028.
9. (a) Guette M, Guette JP, Capillon J. *Tetrahedron Lett.*, 1971, 12, 2863. (b) Guette M, Capillon J, Guette JP. *Tetrahedron*, 1973, 29, 3659.
10. Soai K, Kawase Y. *Tetrahedron Asymmetry*, 1991, 2, 781.
11. Baba A, Yasuda M, Nishimoto Y in Comprehensive Organic Synthesis II, Elsevier, Japan, 2014, vol 2, p 523.
12. Andres JM, Martin Y, Pedrosa R, Perez-Eneabo A. *Tetrahedron*, 1997, 53, 3787.
13. Fujiwara Y, Katagiri T, Uneyama K. *Tetrahedron Lett.*, 2003, 44, 6161.

14. Kloetzing R, Thaler T, Knochel P. *Org. Lett*., 2006, 8, 1125.
15. Emmerson DPG, Herms WP, Davis BG. *Tetrahedron Asymmetry*, 2005, 16, 213.
16. Cozzi PG, AML. *Synthesis*, 2007, 17, 2746.
17. Lin N, Chen M.-M, Luo R-S, Deng Y-Q, Lu DG. *Tetrahedron Asymmetry*, 2010, 21, 2186.
18. Fernandez-Ibanez MA, Macia B, Minnaard AJ, Feringa BL. *Org. Lett*., 2008, 10, 4041.
19. Ananthi N, Velmathi S. *J. Chem. Sci*., 2014, 126, 151.
20. Yan Li, Bin He. *Synth, Commun*., 2014, 44, 1938.
21. Fang C, Lin Y, Zhang H, Wu F. *Adv. Mater. Res.,* 2014, 881-883, 154.
22. Morito CM, de Farias FMC, Valverde AL, Ribeiro CMR. *SOP Transactions on Org. Chem*., 2015, 2, 22.
23. Tarui A, Nishimura H, Ikebata T, Tahira A, Sato K, Omote M, Minami H, Miwa Y, Ando A. *Org. Lett*., 2014, 16, 2080.
24. Tarui A, Ikebata T, Sato K, Omote M, Ando A. *Org. Biomol. Chem*., 2014, 12, 6484.
25. Munck LD, Vila C, Munoz MC, Pedro JR. *Chem. Eur. J*., 2016, 22, 17590.
26. Munck LD, Sukowski V, Vila C, Munoz MC, Pedro JR. *Org. Chem. Front*., 2017, 4, 1624.
27. Munck LD, Sukowski V, Vila C, Pedro, JR. *Tetrahedron Lett*., 2017, 58, 3358.
28. Fontenelle CQ, Conroy M, Light M, Poisson T, Pannecoucke X, Linclau B. *J. Org. Chem*., 2014, 79, 4186.
29. Laclef S, Taillier C, Penloup C, Viger A, Briere J-F, Hardouin C, Levacher V. *RSC Adv*., 2014, 4, 39817.
30. Cao CR, Jiang M, Liu J-T. *Eur. J. Org. Chem*., 2015, 1144.
31. Isoda M, Sato K, Funakoshi M, Omura K, Tarui A, Omote M, Ando A. *J. Org. Chem*., 2015, 80, 8398.
32. Su L, Xu M-H. *Synthesis*, 2016, 48, 2595.
33. Sakuma D, Yamada K, Sasazawa K, Nishii Y. *Chem. Lett*., 2015, 44, 818.
34. Adrian JC Jr, Snapper ML. *J. Org. Chem*., 2003, 68, 2143.
35. Rieke RD, Uhm SJ. *Synthesis*, 1975, 452.
36. Santaniello E, Manzocchi A. *Synthesis*, 1977, 698.
37. Zahel M, Keberg A, Metz P. *Angew. Chem., Int. Ed*., 2013, 52, 1.
38. Ghosh AK, Veitschegger AM, Sheri VR, Effenberger KA, Prichard BE, Jurica MS. *Org. Lett*., 2014, 16, 6200.
39. Karad SN, Pal M, Crowley RS, Prisinzano TE, Altman RA. *ChemMedChem*., 2017, 12, 571.
40. Furst R, Lentsch C, Rinner U. *Eur. J. Org. Chem*., 2013, 2293.
41. Schulze TM, Grunenberg J, Schulz S. *Tetrehedron Lett.*, 2013, 54, 921.
42. Wei Y, Zhao D, Ma D. *Angew. Chem., Int. Ed*., 2013, 52, 12988.
43. Yang S, Xi Y, Zhu R, Wang L, Chen J, Yang Z, *Org. Lett*., 2013, 15, 812.
44. Segade Y, Montaos MA, Rodriguez J, Jimenez C. *Org. Lett*., 2014, 16, 5820.
45. Sakuma D, Ito J, Sakai R, Taguchi R, Nishii Y. *Chem. Lett*., 2014, 43, 610.
46. Wessjohann LA, Scheid GO, Eichelberger U, Umbreen S. *J. Org. Chem*., 2013, 78, 10588.
47. Geist JG, Barth R, Roush WR. *Org. Lett*., 2013, 15, 58.

