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# Sc(OTf)₃ catalyzed carbon-carbon and carbon-heteroatom bond forming reactions: a review

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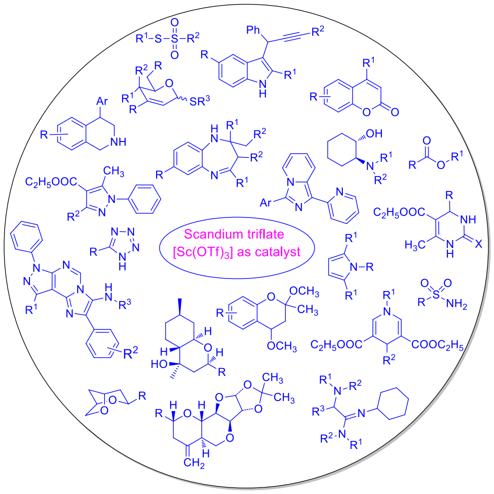
## Abstract

In recent years scandium(III) trifluoromethanesulfonate [$Sc(OTf)_3$] has emerged as an efficient, mild, commercially available, inexpensive, water tolerant Lewis acidic catalyst in the formation of both carbon-carbon and carbon-heteroatom bonds, and thereby the formation of various biologically promising organic compounds. The present review summarizes the latest developments on $Sc(OTf)_3$-catalyzed organic transformations especially carbon-carbon and carbon-heteroatom bond forming reactions reported during the last decade.



**Keywords:** Lewis acid catalysis, scandium triflate, heterocycles

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## 1. Introduction

Carbon-carbon and carbon-heteroatom bond-forming reactions are the important tools of organic synthesis to afford structurally varied bioactive organic compounds.[1-3] Catalysts play an obvious role in such reactions and thus they find wide application. But the screening of suitable catalysts plays a crucial role among the other significant parameters during such chemical praxis.

The last decade has seen a great development in the use of triflate salts as catalysts for organic transformations.[4] Among triflate salts, the applications of scandium(III) trifluoromethanesulfonate [$Sc(OTf)_3$, scandium triflate] as a Lewis acid catalyst have increased rapidly in the variety of organic transformations that can be effected.[5-17] The catalytic applicability of this mild catalyst is well documented in the literature, especially in cycloaddition reactions,[18] Diels-Alder,[19] Ugi,[20] and Michael reactions.[21] Though the majority of the developed methods are based upon the ability of scandium to activate C=X π-bonds toward nucleophilic additions, more recently it has been found that scandium(III) can also activate C-X σ-bonds.[22]

In 1993, Kobayashi *et al.*[23] first demonstrated the use of $Sc(OTf)_3$ as a promising Lewis acid catalyst in organic synthesis. $Sc(OTf)_3$ is now commercially available and can be prepared easily from scandium oxide ($Sc_2O_3$) and aqueous trifluoromethanesulfonic acid (TfOH).[7] In general, most of the traditional Lewis acids are deactivated in the presence of water, but $Sc(OTf)_3$ is stable in an aqueous environment and can efficiently catalyze organic transformations in aqueous media. Moreover, $Sc(OTf)_3$ is well tolerated and worked efficiently as a Lewis acid catalyst in several other organic solvents. As the size of the scandium ($Sc^{3+}$) ion is smaller than those of the rare-earth elements forming triflate salts, $Sc(OTf)_3$ is a much more efficient Lewis acid catalyst than its congeners. Because of all these benefits the use of this unique catalyst has increased rapidly in organic synthesis especially in carbon-carbon and carbon-heteroatom bond forming reactions.[24]

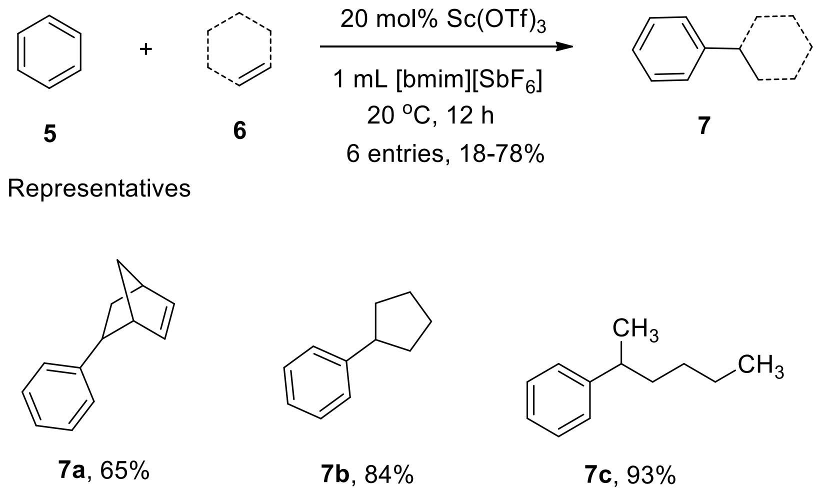
The present communication focuses on the catalytic application of $Sc(OTf)_3$ as a mild Lewis acid in organic synthesis, leading to carbon-carbon and carbon-heteroatom bond forming reactions, with up-to-date literature reported on this subject during the last decade.

The following Sections describe the catalytic applicability of scandium(III) triflate in organic synthesis.

## 2. Carbon-Carbon Bond-forming Reactions

### 2.1 Friedel-Crafts alkylation of aromatic compounds with alkenes

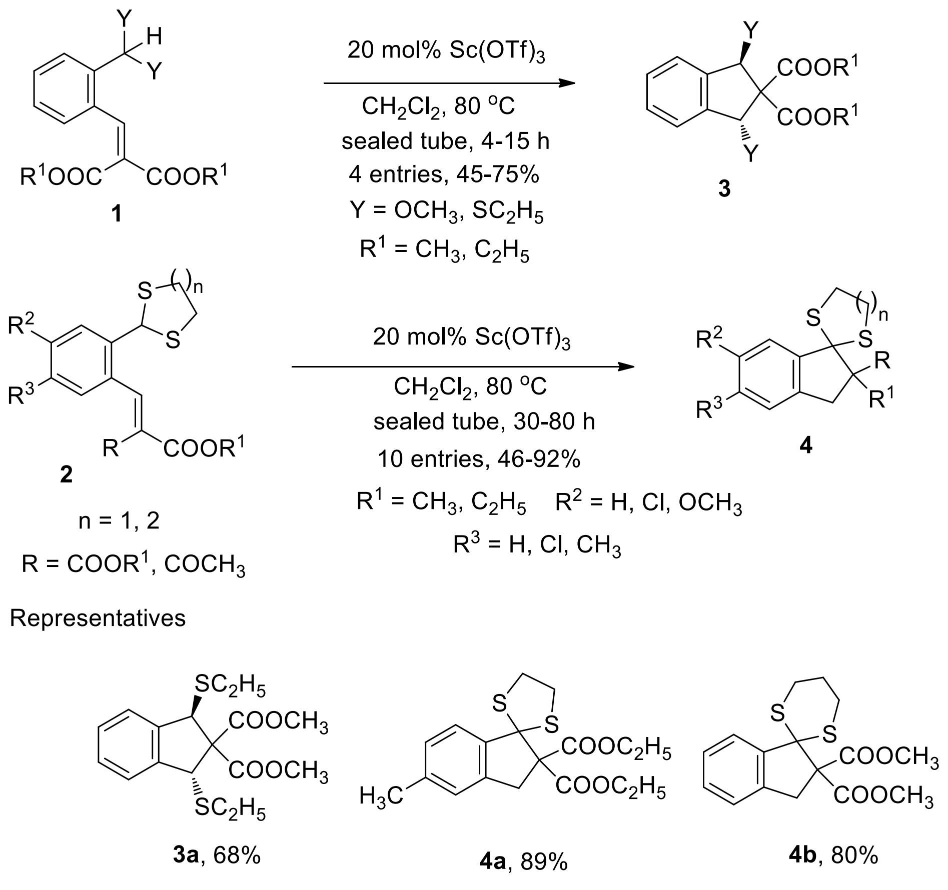
Scandium(III) triflate catalyzed Friedel-Crafts alkylation of aromatic compounds (**1**) with alkenes (**2**) to form the corresponding alkylated products (**3**) was demonstrated by Song *et al.*[25] (Scheme 1) in 1,3-dialkylimidazolium salts as hydrophobic ionic liquid solvents.



**Scheme 1.** Scandium(III) triflate catalyzed Friedel-Crafts alkylation.

### 2.2 Synthesis of 1,2-dihydroindane derivatives

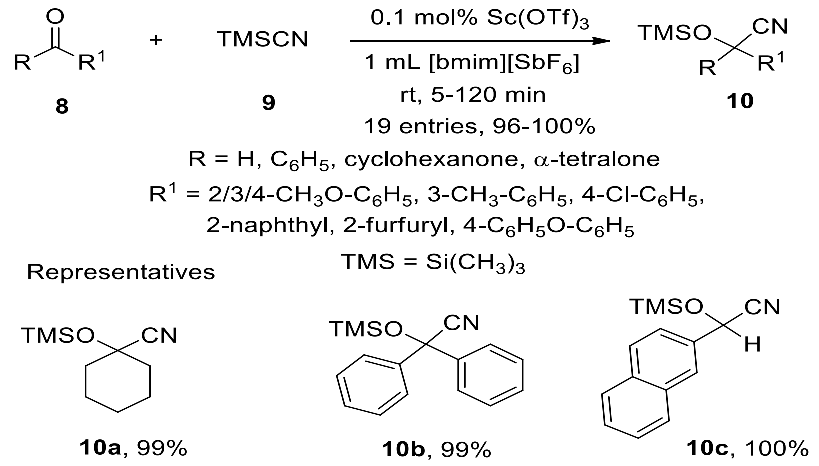
Alajarin *et al.*[26] designed a new carbon-carbon bond forming reaction leading to adjacent quaternary carbons to prepare 1,2-dihydroindane derivatives (**5**, **7**) in the presence of scandium(III) triflate as catalyst by the reaction of activated acetalic C-H bonds with benzylidenemalonate fragments (**4**, **6**) as electrophilic hydride acceptors. In this strategy both cyclic as well as acyclic acetal functions underwent smooth conversion to give the desired products (Scheme 2).



**Scheme 2.** Scandium (III) triflate catalyzed synthesis of 1,2-dihydroindane derivatives.

### 2.3 Synthesis of α-(trimethylsilyloxy)nitriles

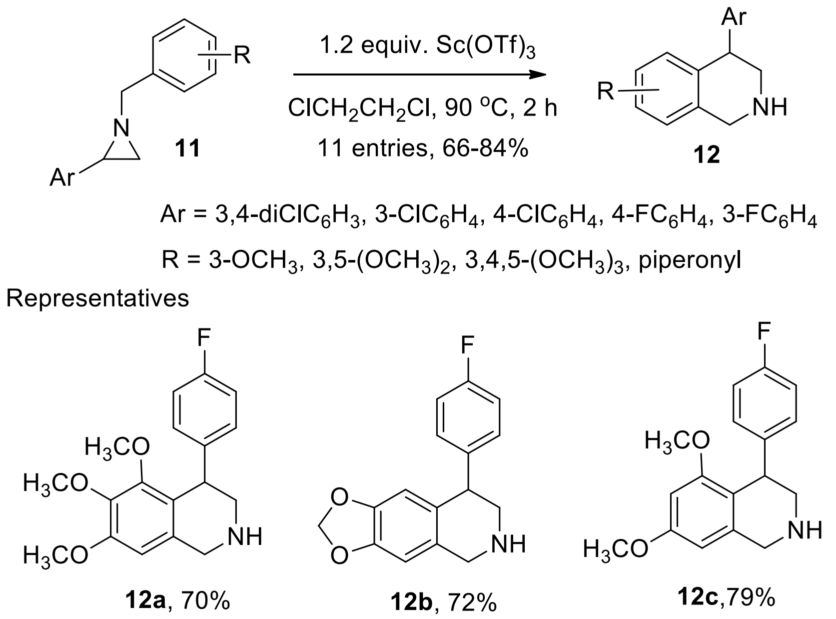
Park *et al.*[27] reported an environmentally benign, highly reactive Sc(OTf)$_3$ catalyzed cyanosilylation of carbonyl compounds (**8**) with trimethylsilyl cyanide (**9**) to prepare the corresponding α-(trimethylsilyloxy)carbonitriles (**10**) in [bmim][SbF$_6$] at room temperature (Scheme 3). They also successfully recovered and reused the ionic liquid containing Sc(OTf)$_3$ for several reaction cycles without any loss of catalytic activity.



**Scheme 3.** Sc(OTf)$_3$ catalyzed cyanosilylations of carbonyl compounds.

### 2.4 Synthesis of 4-substituted tetrahydroisoquinolines

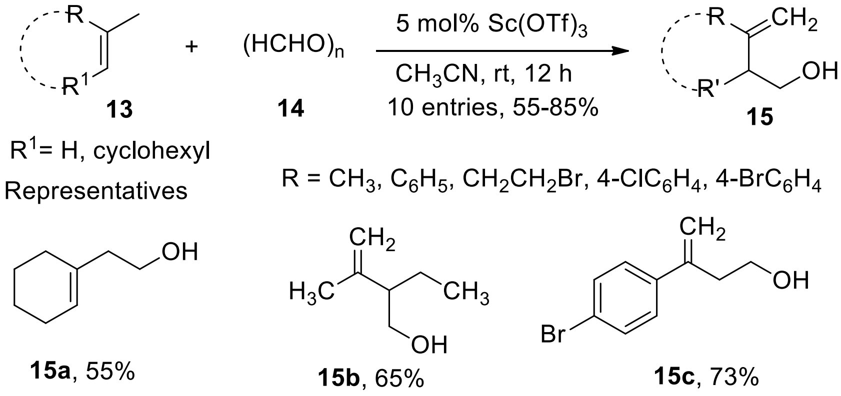
Tummanapalli *et al.*[28] demonstrated a novel, scandium(III) triflate catalyzed, facile, straight forward synthesis of 4-substituted tetrahydroisoquinolines (1**2**) *via* intramolecular ring expansion of aziridines (1**1**) in 1,2-dichloroethane at 90 °C (Scheme 4).



**Scheme 4.** Scandium(III) triflate catalyzed synthesis of 4-substituted tetrahydroisoquinolines.

### 2.5 Synthesis of primary homoallylic alcohols

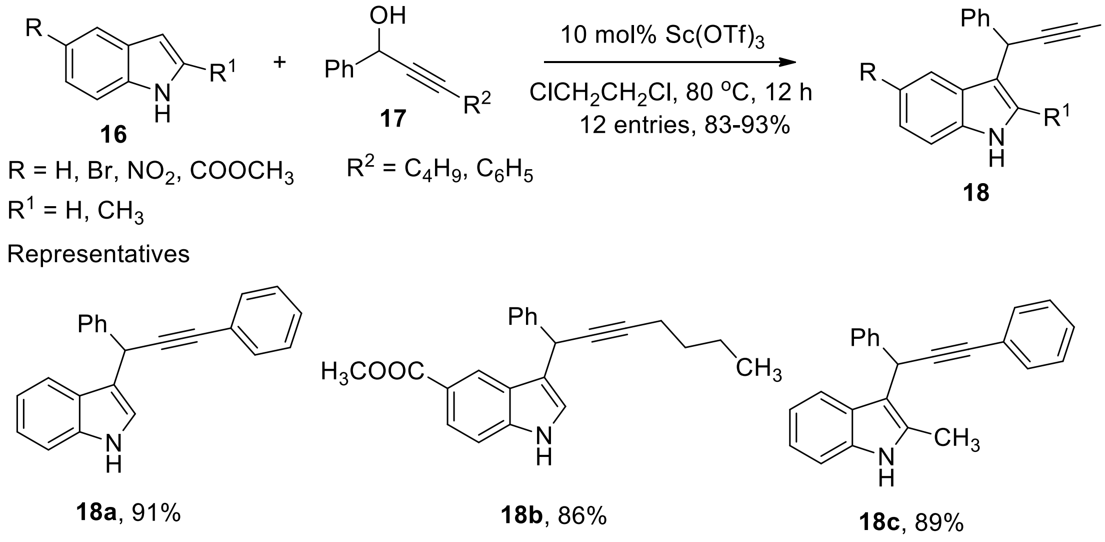
Sultana *et al.*[29] developed a simple protocol for the synthesis of primary homoallylic alcohols (**15**) from the reaction of alkenes (**13**) and paraformaldehyde (**14**) using scandium triflate as catalyst at room temperature (Scheme 5).



**Scheme 5.** Sc(OTf)$_3$-catalyzed synthesis of primary homoallylic alcohols.

### 2.6 Synthesis of 3-propargylated indoles

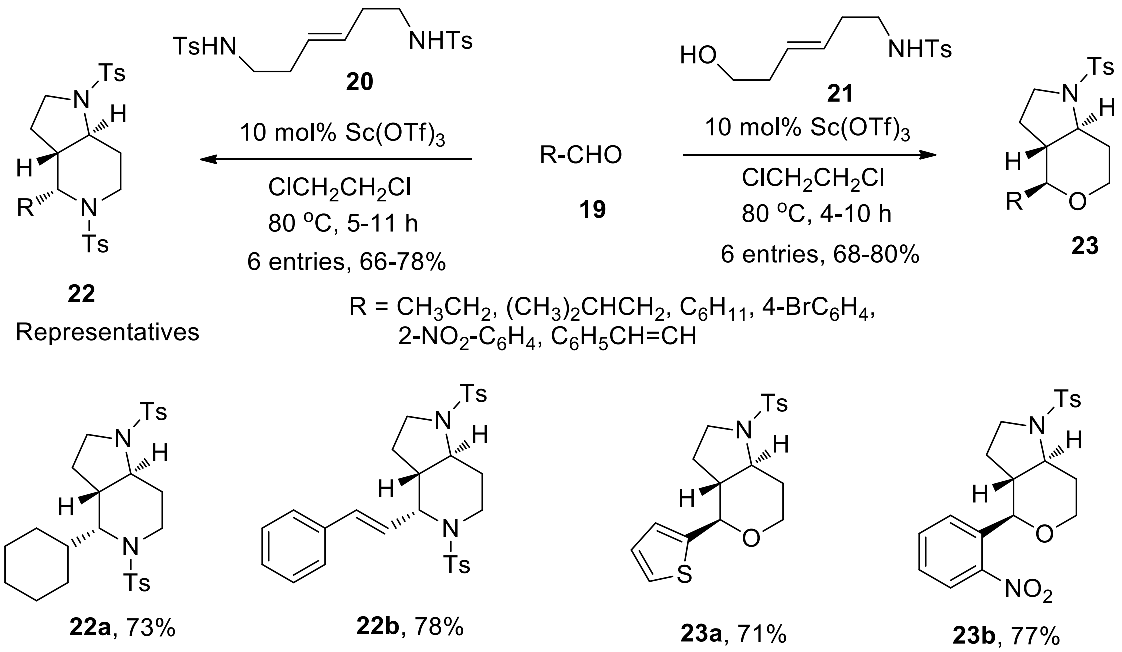
Yadav and his group (Scheme 6)[30] described a facile and efficient alkylation of indoles (16) with propargylic alcohols (17) to produce 3-propargylated indoles (18) in excellent yields using scandium triflate as catalyst in 1,2-dichloroethane at 80 °C.



**Scheme 6.** Scandium(III) triflate catalyzed alkylation of indoles with propargyl alcohols.

### 2.7 Synthesis of octahydro-1*H*-pyrrolo[3,2-*c*]pyridines and octahydropyrano[4,3-*b*]pyrroles

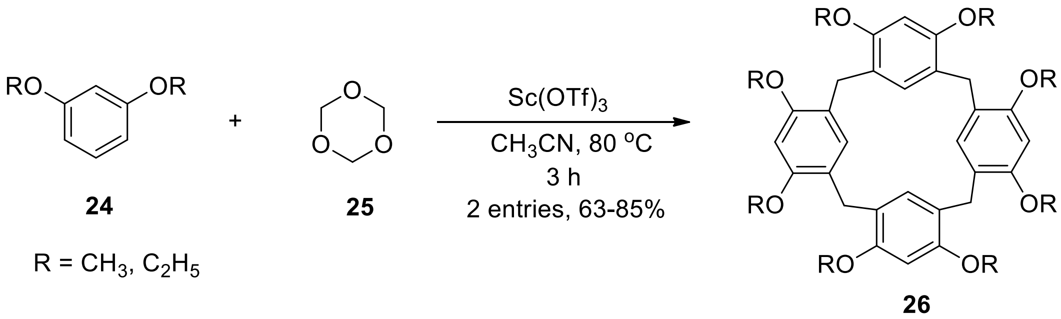
Reddy *et al*. (Scheme 7)[31] developed a new method for the synthesis of octahydro-1*H*-pyrrolo[3,2-*c*]pyridines (**22**) and octahydropyrano[4,3-*b*]pyrroles (**23**) selectively by means of intramolecular aza-Prins and Prins cyclization of aldehydes (**19**) and *bis*-homoallyl (**20**) and heteroallyl (**21**) derivatives respectively.



**Scheme 7.** Synthesis of octahydropyrrolo[3,2-*c*]pyridines and octahydropyrano[4,3-*b*]pyrroles.

## 2.8 Synthesis of resorcin[4]arene octaalkyl ethers

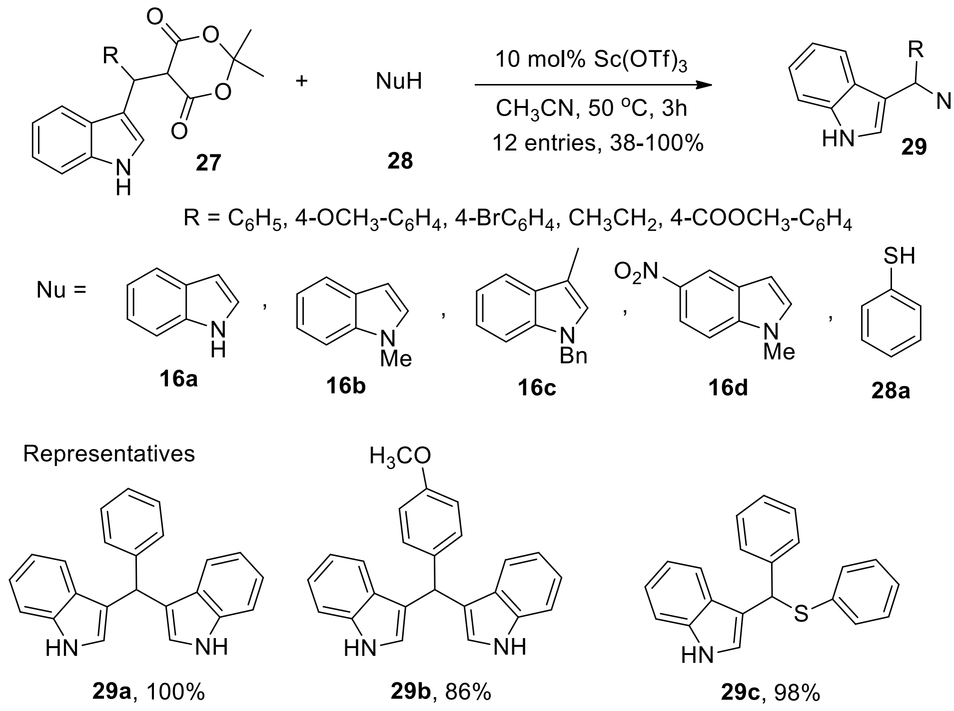
Morikawa *et al.*[32] demonstrated a simple and straightforward cyclocondensation of 1,3-dialkoxybenzenes (**24**) with 1,3,5-trioxane (**25**) to produce resorcin[4]arene octaalkyl ethers (**26**) in good yields using catalytic amount of $Sc(OTf)_3$ in acetonitrile at 80 °C (Scheme 8).



**Scheme 8.** Scandium(III) triflate catalyzed synthesis of resorcin[4]arene octaalkyl ethers.

## 2.9 Synthesis of indolemethane derivatives

Kerr and his group[33] developed an expedient and efficient method for the synthesis of indolemethane derivatives (**29**) from the reaction of indolylmethyl Meldrum's acids (**27**) with a variety of nucleophiles (**28**) *via* the nucleophilic displacement of the Meldrum's acid moiety in the presence of catalytic scandium triflate at 50 °C in acetonitrile as solvent (Scheme 9).

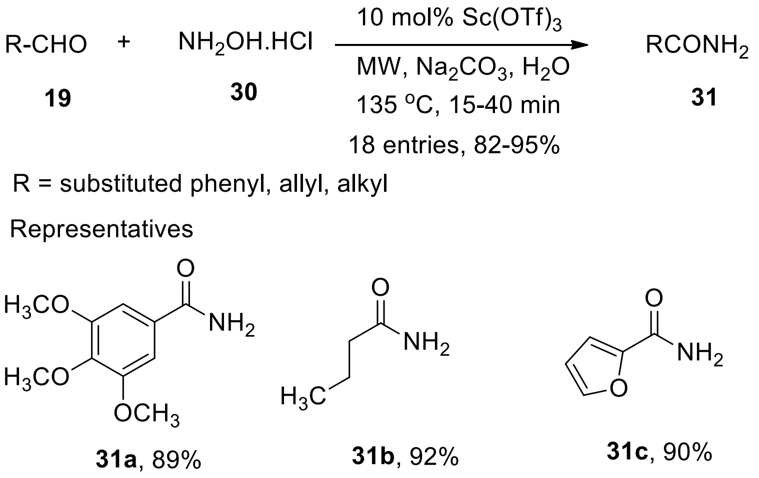


**Scheme 9.** Scandium(III) triflate catalyzed synthesis of indolemethane derivatives.

## 3. Carbon-Nitrogen Bond-forming Reactions

### 3.1 Synthesis of primary amides

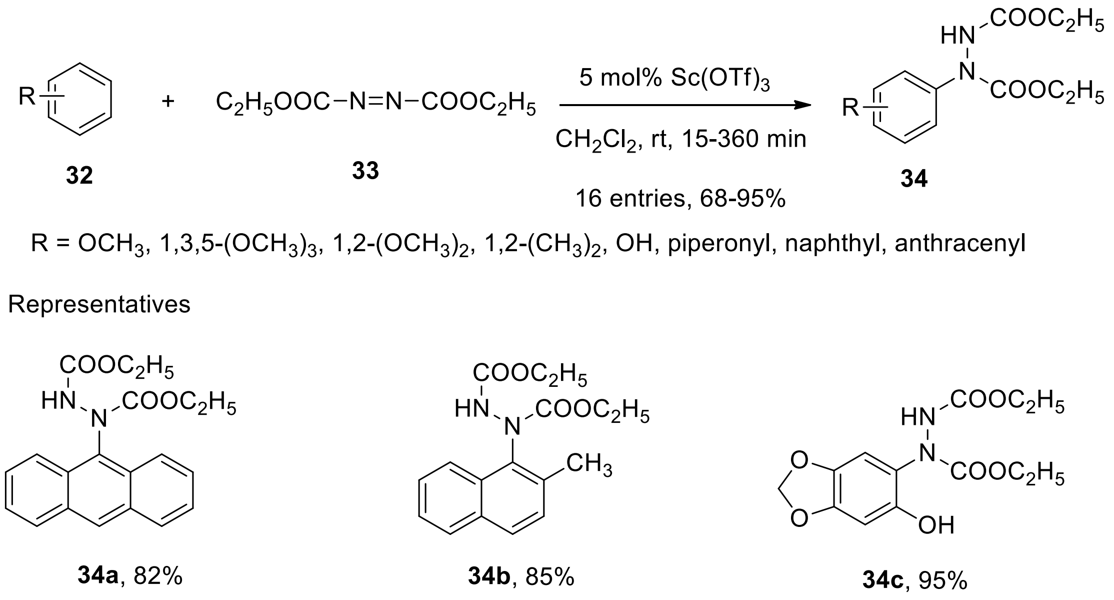
Allam *et al.*[34] described a versatile microwave-assisted synthetic protocol for the one-pot synthesis of primary amides (**31**) from aldehydes (**19**) and hydroxylamine hydrochloride (**30**) using scandium(III) triflate as a catalyst in water (Scheme 10).



**Scheme 10.** Scandium(III) triflate catalyzed synthesis of primary amides.

### 3.2 Synthesis of aryl hydrazides

Yadav *et al.*[35] reported a Sc(OTf)$_3$ catalyzed electrophilic amination of arenes (**32**) with diethyl azodicarboxylate (**33**) in dichloromethane at ambient temperature to afford the corresponding arylhydrazides (**34**) in high yields with high regioselectivity (Scheme 11).



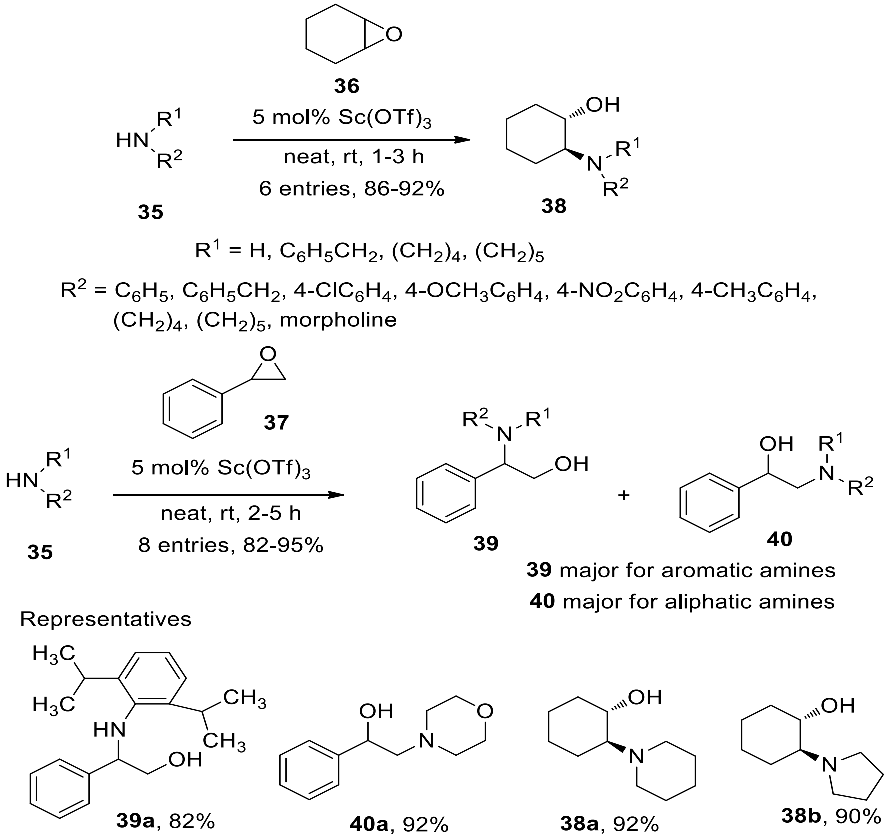
**Scheme 11.** Sc(OTf)$_3$ catalyzed electrophilic amination of arenes.

### 3.3 Synthesis of β-amino alcohols

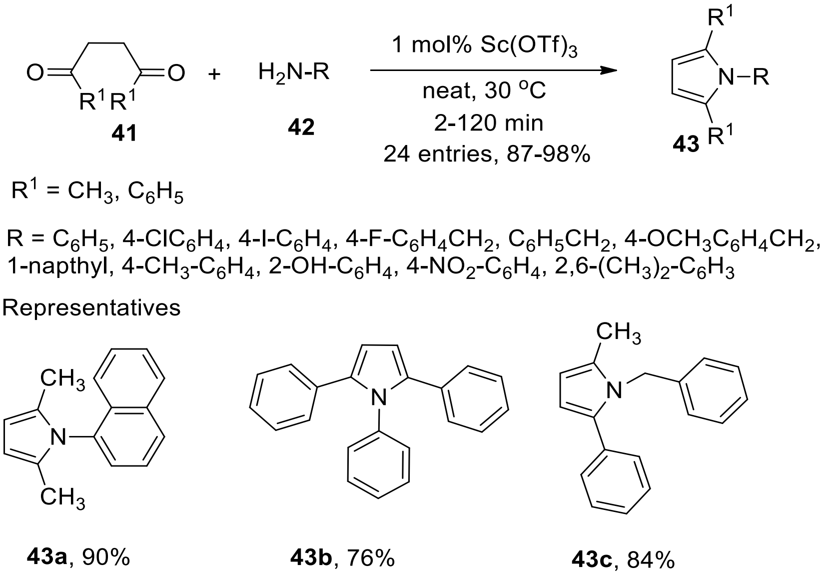
Placzek *et al.*[36] reported a simple, straight forward, efficient method for the synthesis of β-amino alcohols (**38**, **39**, **40**) *via* ring opening of epoxides (**36**, **37**) with amines (**35**) in the presence of a catalytic amount of Sc(OTf)$_3$ at room temperature under solvent-free conditions (Scheme 12).

### 3.4 Synthesis of N-substituted pyrroles

Chen *et al.*[37] developed a simple and efficient method for the synthesis of *N*-substituted pyrroles (**43**) by the Paal-Knorr condensation of various amines (**42**) with 1,4-diketones (**41**) using a catalytic amount of Sc(OTf)$_3$ under neat conditions at ambient temperature (Scheme 13). They also successfully recovered and reused the catalyst without significant loss in catalytic activity.



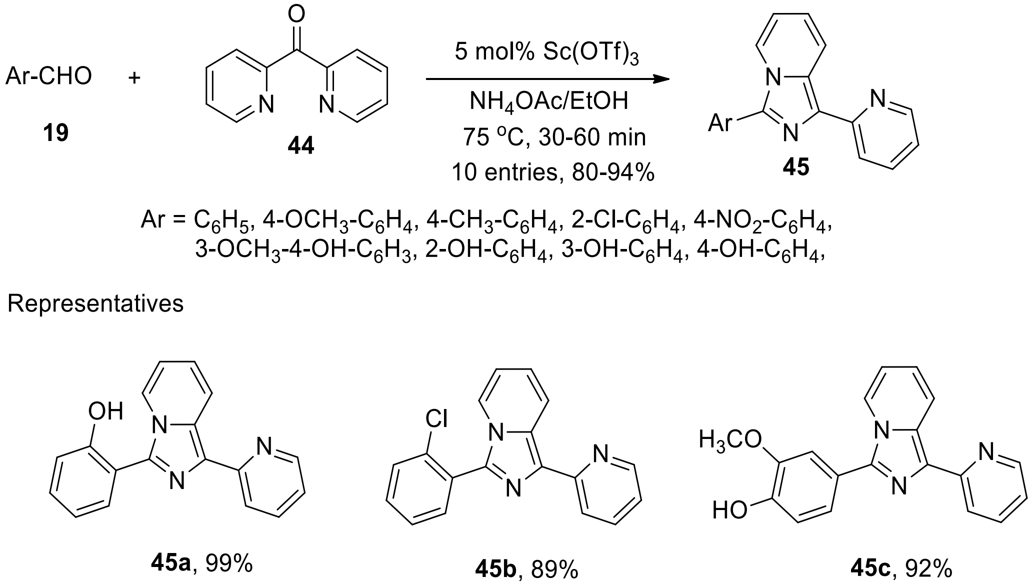
**Scheme 12.** Scandium(III) triflate catalyzed synthesis of β-amino alcohols.



**Scheme 13.** Scandium(III) triflate catalyzed synthesis of *N*-substituted pyrroles.

### 3.5 Synthesis of 1-pyridylimidazo-[1,5-a]-pyridines

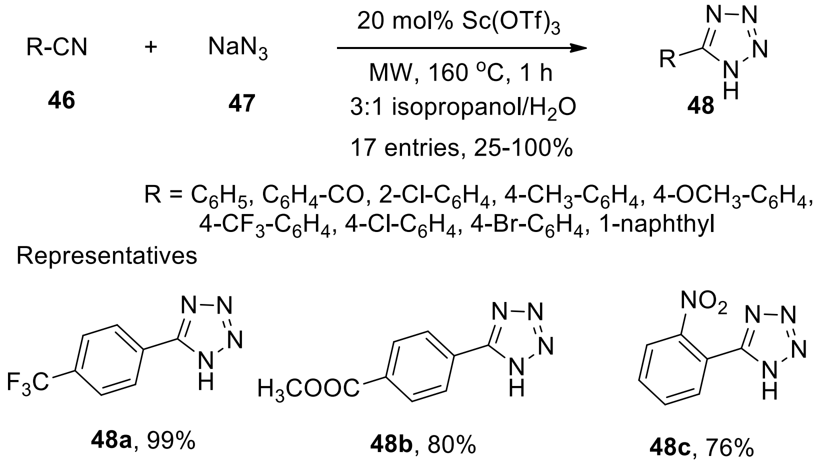
Kottawar et *al*. (Scheme 14)[38] described a facile, mild and highly efficient protocol for the synthesis of 1-(2-pyridyl)imidazo[1,5-*a*]pyridines (**45**) from the reaction of various aromatic aldehydes (**19**) with di-2-pyridyl ketone (**44**) in presence of ammonium acetate in ethanol using scandium(III) triflate as catalyst.



**Scheme 14.** Scandium(III) triflate catalyzed synthesis of 1-pyridylimidazo[1,5-*a*]pyridines.

### 3.6 Synthesis of 5-substituted 1*H*-tetrazoles

Several 5-substituted 1*H*-tetrazoles (**48**) were synthesized by Coca *et al.*[39] (Scheme 15) *via* the [2+3] cycloaddition of sodium azide (**47**) with aryl nitriles, aliphatic nitriles, and vinyl nitriles (**46**) under the influence of microwave irradiation of 1 h at 160 °C in a 3:1 isopropanol / water mixture using scandium(III) triflate as catalyst.

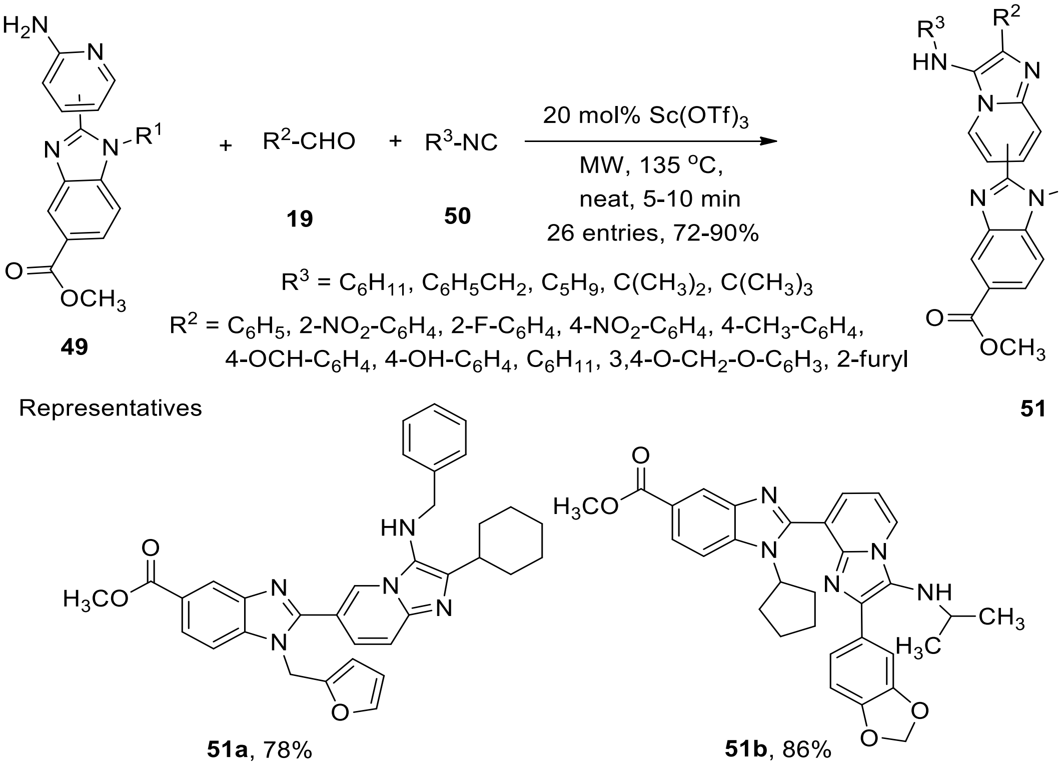


**Scheme 15.** Scandium(III) triflate catalyzed synthesis of 5-substituted 1*H*-tetrazoles.

## 4. Simultaneous Carbon-Carbon and Carbon-Nitrogen Bond-forming Reactions

### 4.1 Synthesis of benzimidazolyl imidazo[1,2-*a*]pyridines

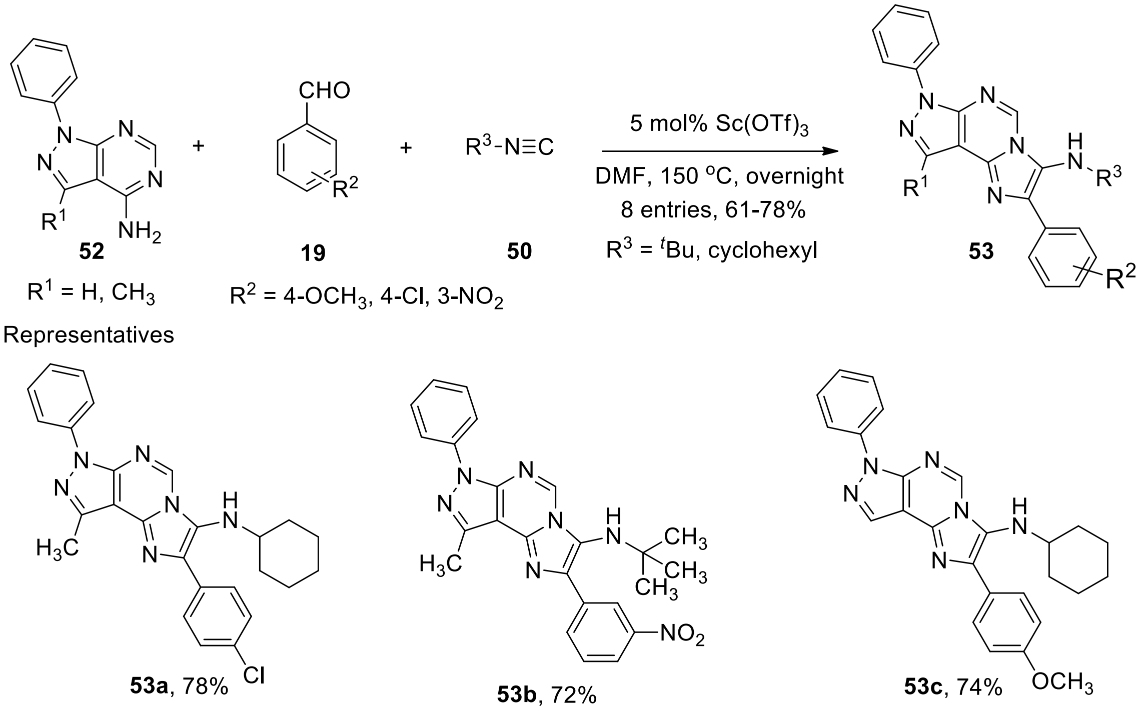
Maiti *et al.*[40] developed a microwave irradiated novel environmentally benign, one-pot three-component reaction protocol for the synthesis of biologically interesting benzimidazolyl-imidazo[1,2-*a*]pyridines (**51**) employing variously substituted benzimidazole-linked amino pyridines (**49**), aldehydes (**19**), and isocyanides (**50**) in presence of catalytic amount of scandium(III) triflate under solvent-free conditions (Scheme 16).



**Scheme 16.** Synthesis of benzimidazolyl imidazo[1,2-*a*]pyridines.

### 4.2 Synthesis of imidazo[1,2-*c*]pyrazolo[3,4-*e*]pyrimidines

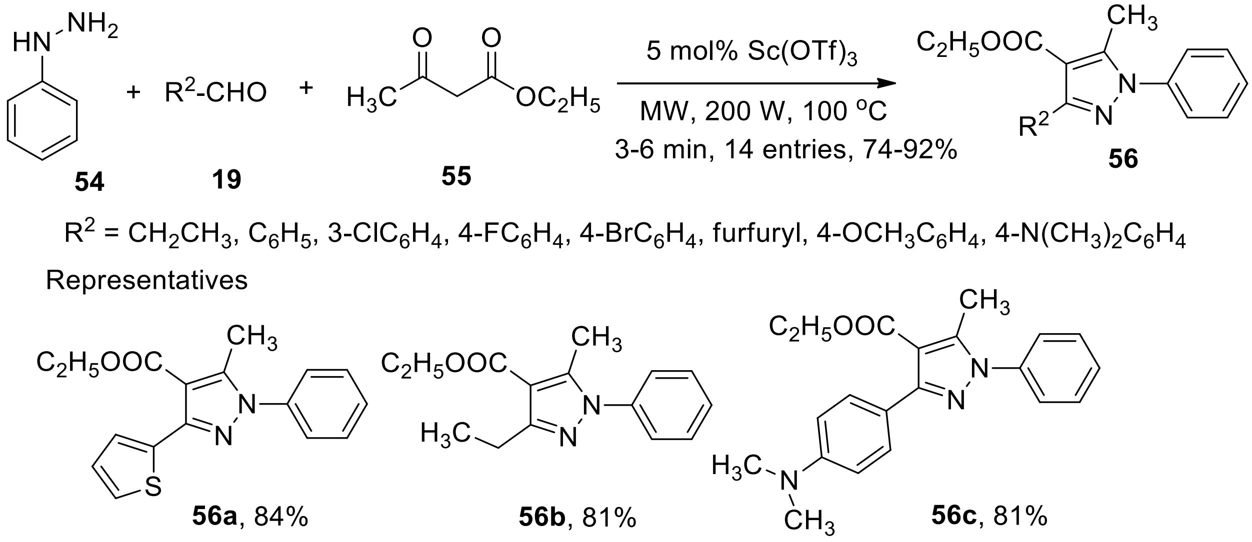
A facile, one-pot three-component scandium triflate catalyzed condensation reaction between aminopyrazolo[3,4-*d*]pyrimidine (**52**), aldehyde (**19**), and isocyanide (**50**) was developed by Agrebi *et al.*[41] for the synthesis of a series of fluorescent imidazo[1,2-*c*]pyrazolo[3,4-*e*]pyrimidines (**53**) in good to excellent yields at 150 °C (Scheme 17).



**Scheme 17.** Synthesis of imidazo[1,2-*c*]pyrazolo[4,3-*e*]pyrimidines.

### 4.3 Synthesis of functionalized pyrazoles

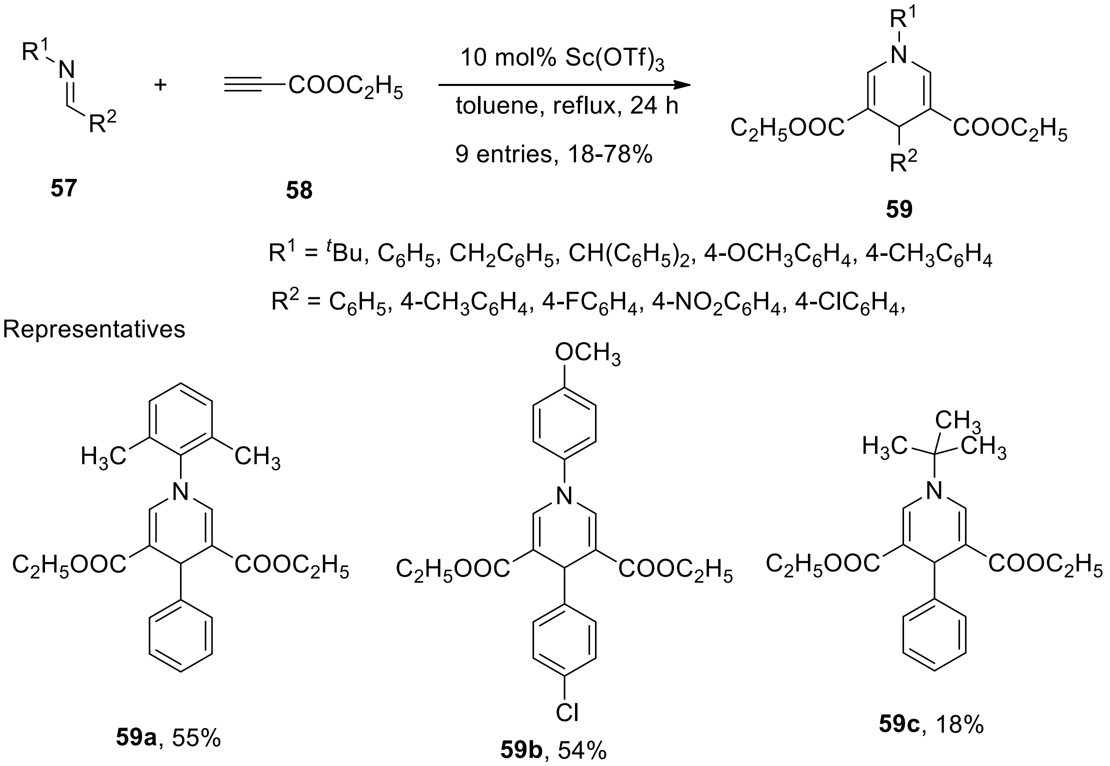
Kumari *et al.*[42] reported an efficient, facile, straight forward, microwave irradiated rapid, and environmentally benign scandium triflate catalyzed synthesis of functionalized pyrazoles (**56**) by the reaction of phenyl hydrazine (**54**), aldehydes (**19**) and ethyl acetoacetate (**55**) under neat conditions (Scheme 18).



**Scheme 18.** Scandium triflate catalyzed synthesis of functionalized pyrazoles.

### 4.4 Synthesis of *N*-substituted 1,4-dihydropyridine derivatives

Kikuchi *et al.*[43] developed a facile and straight forward method for the synthesis of *N*-substituted 1,4-dihydropyridine derivatives (59) from the reaction of imines (**57**) with ethyl propiolate (**58**) using catalytic amount of scandium(III) triflate in toluene or benzotrifluoride under reflux conditions (Scheme 19).



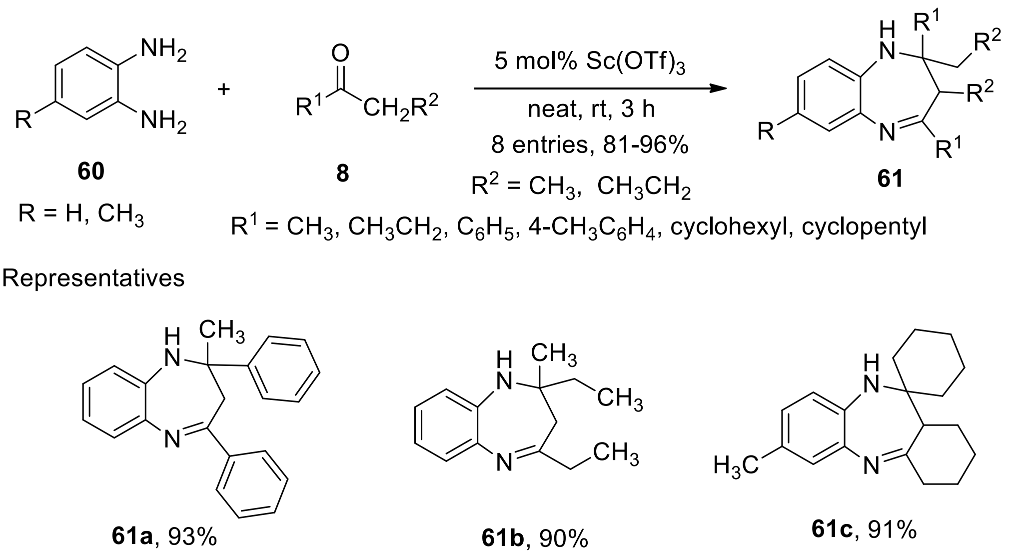
**Scheme 19.** Scandium(III) triflate catalyzed synthesis of 1,4-dihydropyridines.

### 4.5 Synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines

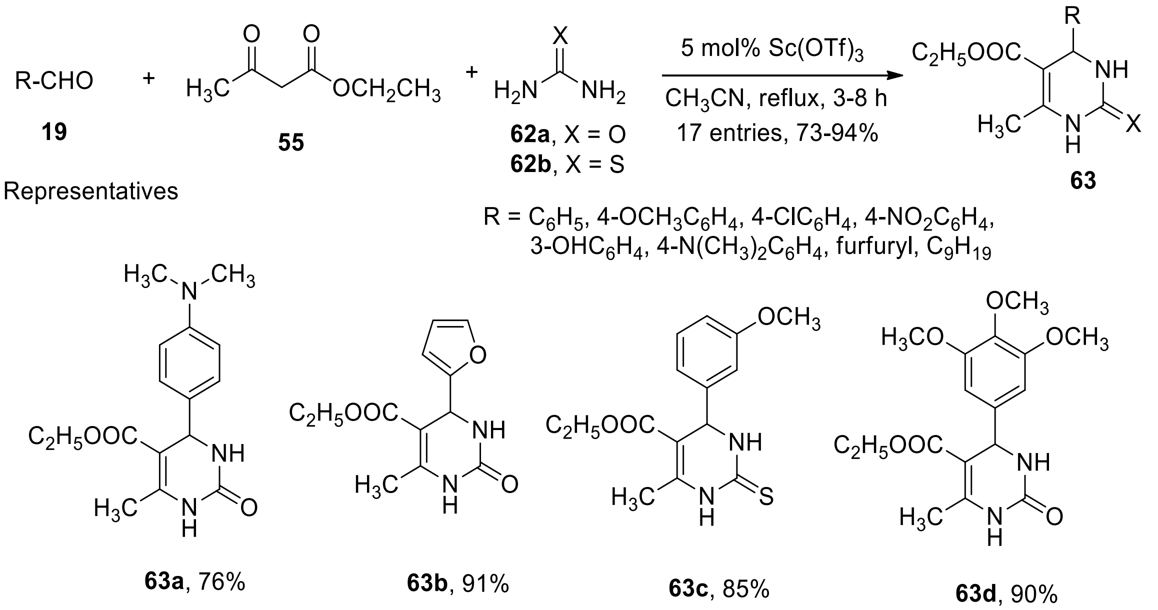
De *et al.*[44] demonstrated a mild, simple and efficient method for the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines (**61**) with good yields from the reaction of *o*-phenylenediamines (**60**) and ketones (**8**) in the presence of a catalytic amount of Sc(OTf)$_3$ under neat conditions at room temperature (Scheme 20).

### 4.6 Synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones

De and his group[45] developed another scandium(III) triflate catalyzed protocol for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones (**63**) *via* the three component Biginelli reaction of aldehyde (**19**), β-ketoester (**55**), and urea (**62a**) or thiourea (**62a)** in acetonitrile under reflux conditions (Scheme 21).



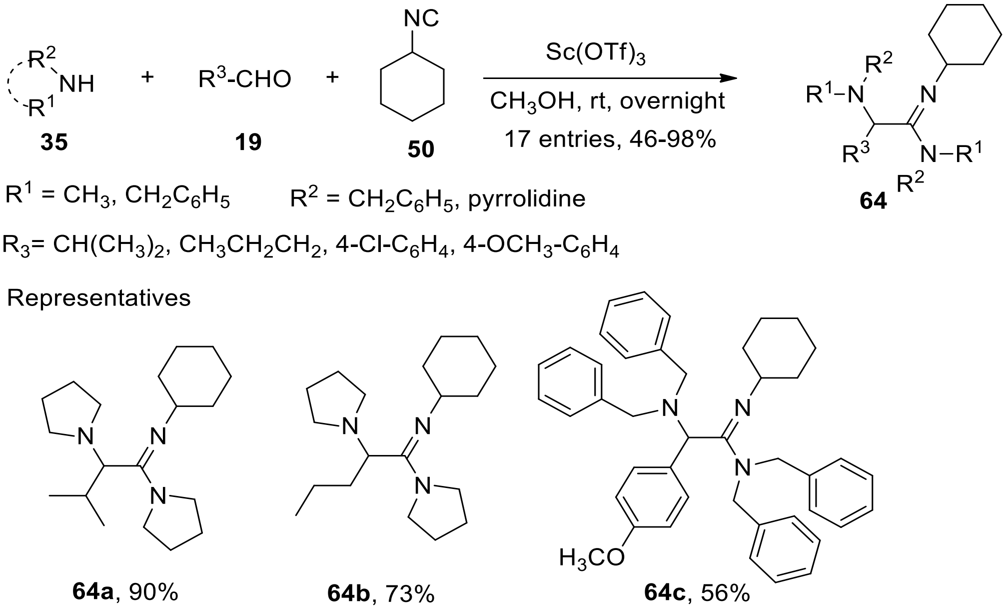
**Scheme 20.** Scandium(III) triflate catalyzed synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines.



**Scheme 21.** Scandium(III) triflate catalyzed synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones.

### 4.7 Synthesis of α-amino amidines

α-Amino amidines (**64**) were synthesized by Keung *et al.*[46] *via* a simple, efficient and straightforward three-component reaction of amines (**35**), aldehydes (**19**), and isonitrile (**50**) using scandium(III) triflate as catalyst in methanol at room temperature (Scheme 22).

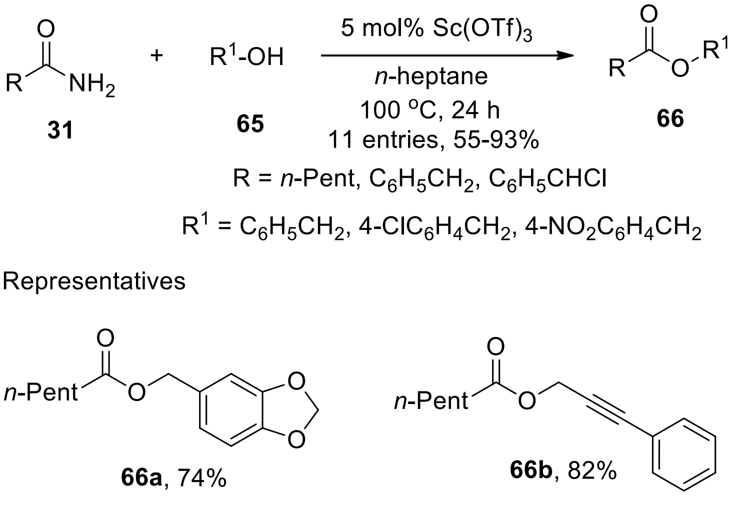


**Scheme 22.** Scandium(III) triflate catalyzed synthesis of α-amino amidines.

## 5. Carbon-Oxygen Bond-forming Reactions

### 5.1 Synthesis of esters

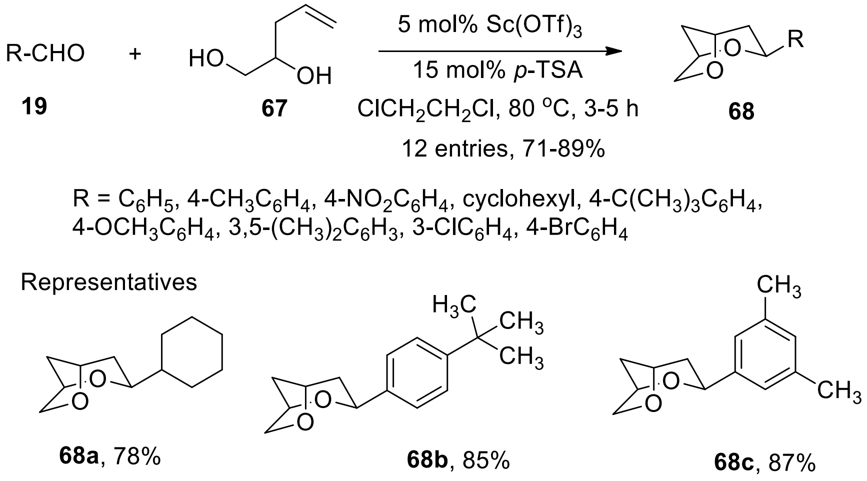
Atkinson *et al.*[47] demonstrated a scandium(III) triflate catalyzed protocol for the synthesis of esters (**66**) from the reaction of various primary amides (**31**) and alcohols (**65**) in *n*-heptane at 100 °C (Scheme 23).



**Scheme 23.** Scandium(III) triflate catalyzed synthesis of ester using primary amides.

### 5.2 Synthesis of 2,6-dioxabicyclo[3.2.1]octane derivatives.

Reddy *et al.* (Scheme 24)[48] demonstrated an efficient straight forward strategy for the synthesis of aryl and alkyl substituted 2,6-dioxabicyclo[3.2.1]octane derivatives (**68**) *via* an intramolecular Prins cyclization of aldehydes (**19**) with pent-4-ene-1,2-diol (**67**) in the presence of 5 mol% scandium triflate and 15 mol% *p*-toluenesulfonic acid in dichloroethane at 80 °C.



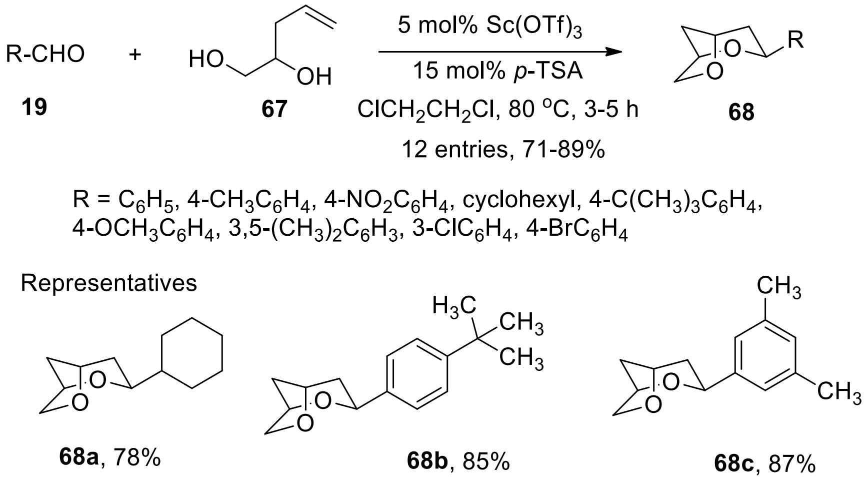
**Scheme 24.** Scandium(III) triflate catalyzed synthesis of 2,6-dioxabicyclo[3.2.1]octanes.

## 5.3 Synthesis of sugar fused pyranopyran derivatives

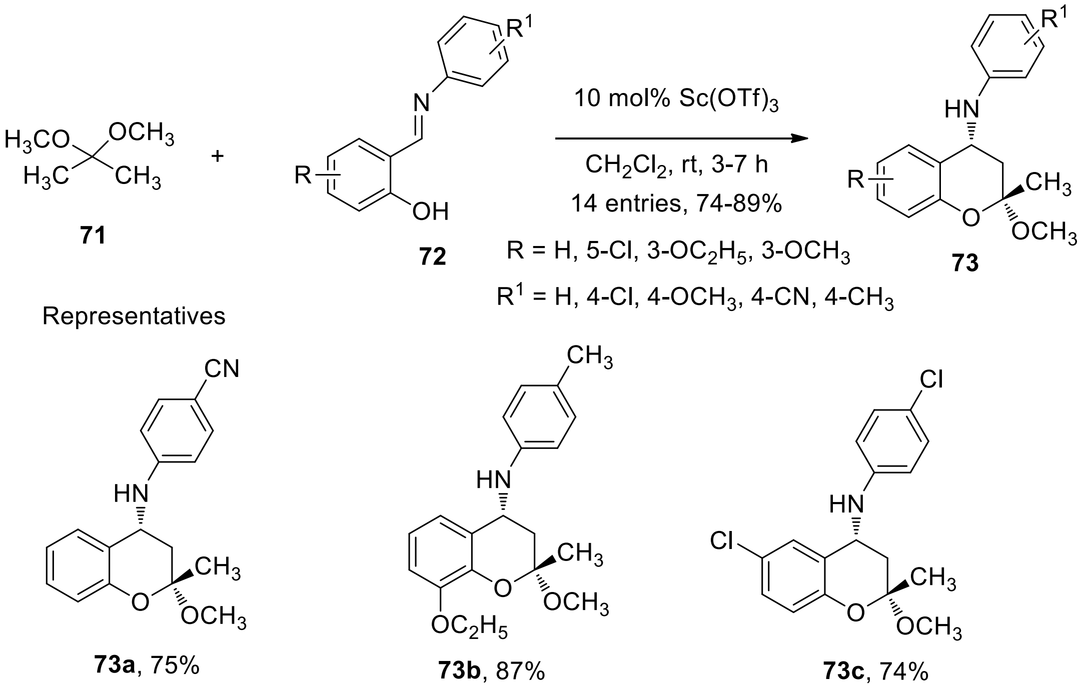
Tandem ene-Prins cyclization between an aldehyde (**19**) and *O*-prenyl derivative of a sugar aldehyde (**69**) was successfully coupled by Reddy *et al*. (Scheme 25)[49] using a catalytic amount of scandium triflate (10 mol %) at ambient temperature in dichloromethane to produce a novel series of sugar fused pyranopyran derivatives (**70**) in good to excellent yields with high enantioselectivity.

## 5.4 Synthesis of 3,4-dihydro-4-amino-2-methoxy-2-methyl-2*H*-1-benzopyrans

Yadav and his group (Scheme 26)[50] demonstrated a simple, facile and efficient protocol for the diastereoselective synthesis of 3,4-dihydro-4-amino-2-methoxy-2-methyl-2*H*-1-benzopyrans (**73**) with good yields from the reaction of 2,2-dimethoxypropane (**71**) with a variety of *o*-hydroxybenzaldimines (**72**) in the presence of a catalytic amount of scandium triflate at ambient temperature.



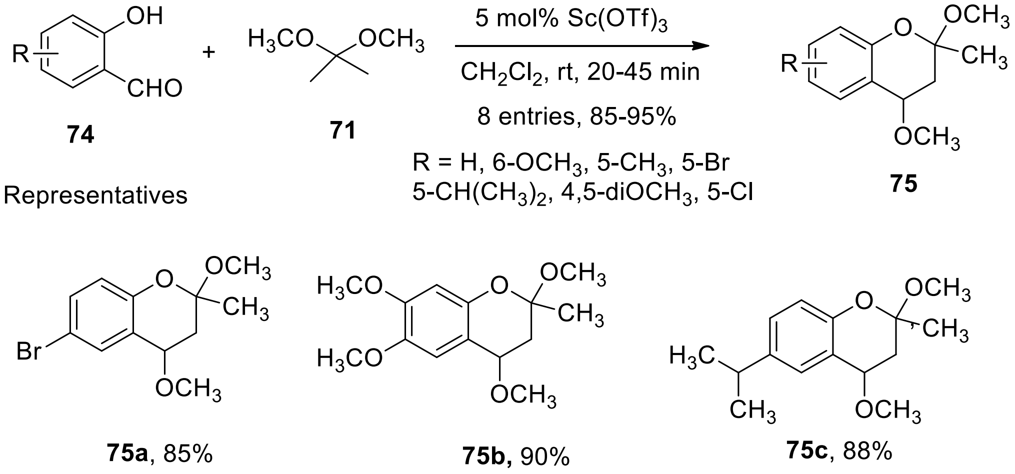
**Scheme 25.** Synthesis of sugar fused pyranopyran derivatives.



**Scheme 26.** Synthesis of 3,4-dihydro-4-amino-2*H*-1-benzopyrans.

### 5.5 Synthesis of 2,4-dimethoxy-2-methyl chromans

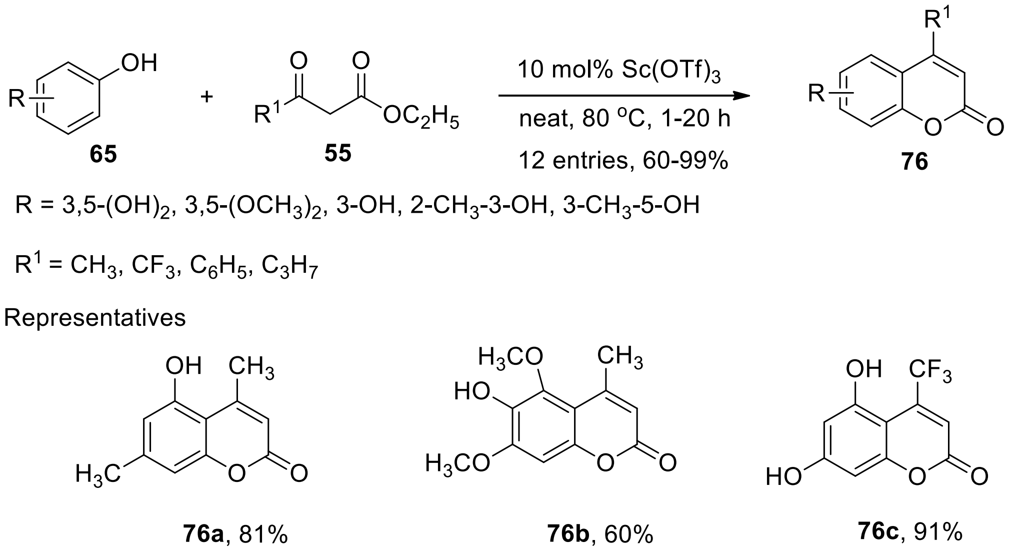
Yadav and his group (Scheme 27)[51] also reported a novel facile, straight forward, efficient procedure for the synthesis of a new class of 2,4-dimethoxy-2-methyl chromans (**75**) in high yields *via* an unusual cyclocondensation of *o*-hydroxybenzaldehydes (**74**) with 2,2-dimethoxypropane (**71**) using a catalytic amount of scandium triflate at room temperature.



**Scheme 27.** Synthesis of 2,4-dimethoxy-2-methyldihydrobenzopyrans.

### 5.6 Synthesis of coumarins

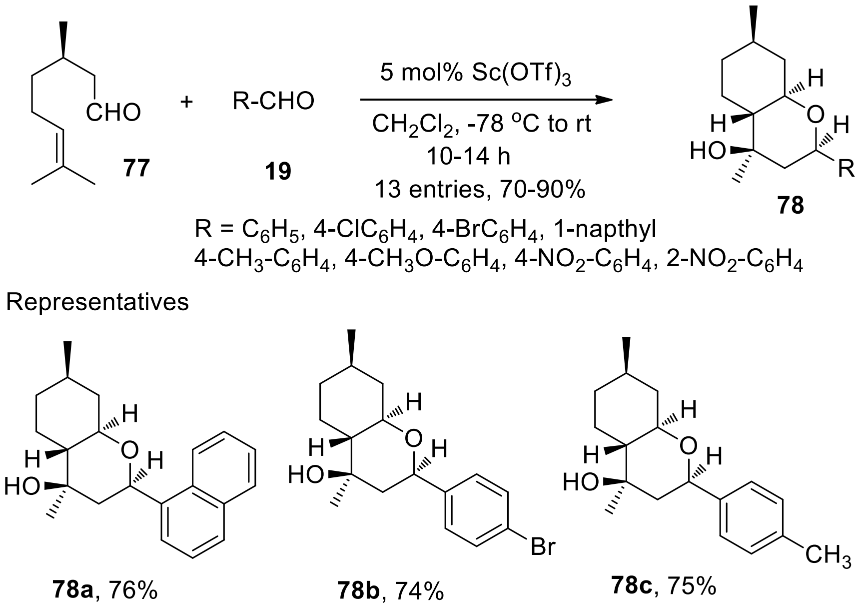
Jung *et al.*[52] demonstrated the application of scandium(III) triflate as an efficient catalyst for the synthesis of coumarins (**76**) *via* the Pechmann condensation of a variety of phenols (**65**) and β-ketoesters (**55**) under neat conditions at 80 °C (Scheme 28).



**Scheme 28.** Scandium(III) triflate catalyzed synthesis of coumarins.

### 5.7 Synthesis of octahydro-2*H*-chromen-4-ols

Yadav *et al*. (Scheme 29)[53] demonstrated a tandem ene-Prins cyclization between (R)-citronellal (**77**) and aldehydes (**19**) using Sc(OTf)$_3$ as a catalyst at ambient temperature to furnish octahydro-2*H*-chromen-4-ols (**78**) in good to excellent yields with high cis-selectivity.

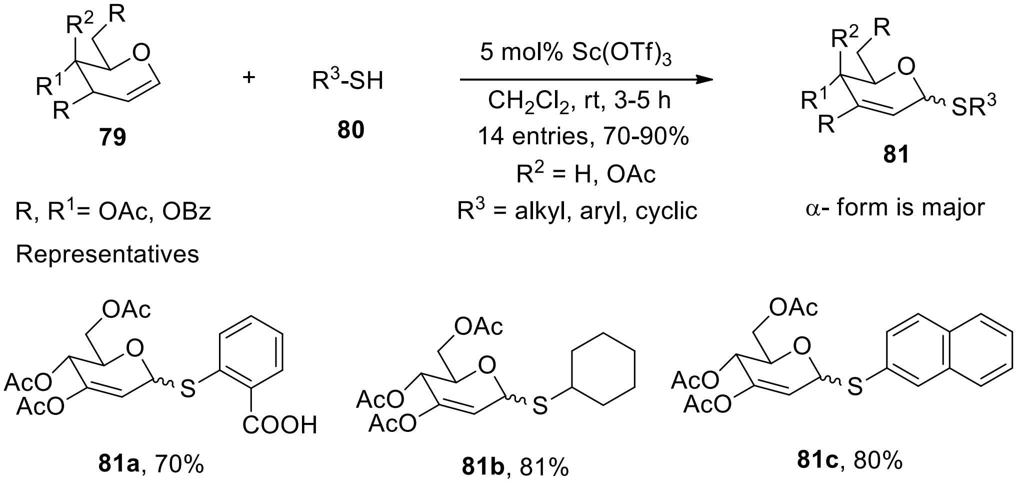


**Scheme 29.** Scandium(III) triflate catalyzed synthesis of octahydro-2*H*-chromen-4-ols.

## 6. Carbon-Sulfur Bond-forming Reactions

### 6.1 Synthesis of 2,3-unsaturated thioglycosides

Another scandium(III) triflate catalyzed method was developed by Yadav *et al*. (Scheme 30)[54] for the selective synthesis of 2,3-unsaturated thioglycosides (**81**) with good yields *via* the thioglycosidation of 3,4,6-tri-*O*-acetyl or benzoyl-D-glycals (**79**) with various thiols (**80**) in dichloromethane at room temperature.

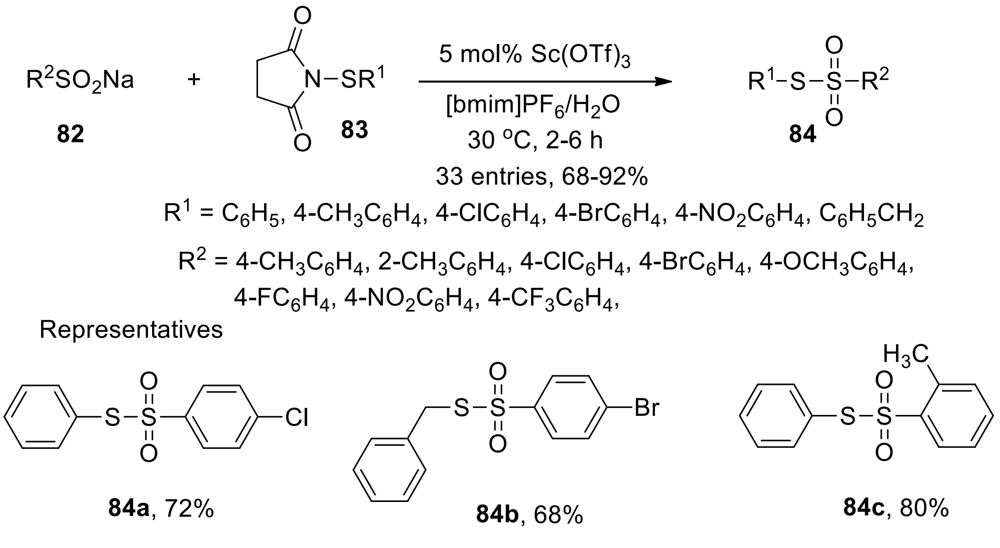


**Scheme 30.** Scandium(III) triflate catalyzed synthesis of 2,3-unsaturated thioglycopyranosides

## 7. Sulfur-Sulfur Bond-forming Reactions

### 7.1 Synthesis of thiosulfonates

Sc(OTf)$_3$-catalyzed sulfenylation of sodium sulfinates (**82**) with *N*-(organothio)succinimides (**83**) in ionic liquids and water mixture as cosolvent was demonstrated by Liang *et al*. (Scheme 31)[55] to afford thiosulfonates (**84**) in moderate to excellent yields at ambient temperature. They also successfully recovered and reused the ionic liquid containing Sc(OTf)$_3$ for several reaction cycles without any significant loss of catalytic activity.

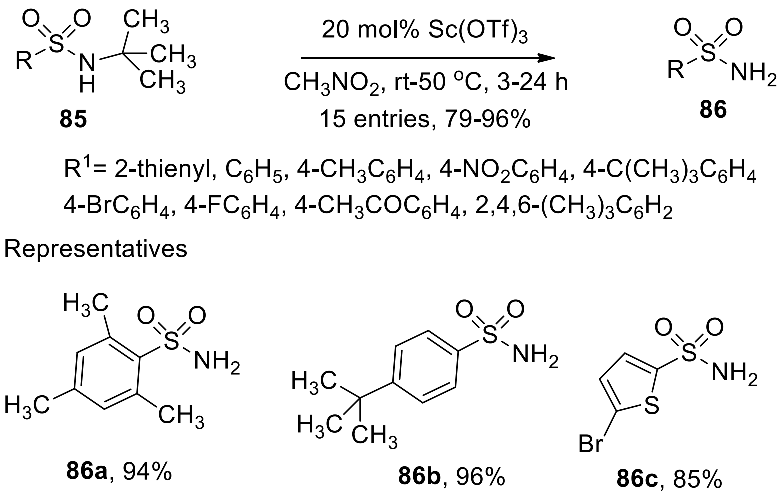


**Scheme 31.** Scandium(III) triflate catalyzed synthesis of thiosulfonates.

## 8. Other Reactions

### 8.1. Deprotection of tert-butyl aryl sulfonamides

Mahalingam *et al*.[56] developed a mild and high-yielding method for removal of a variety of *tert*-butyl protecting group from the *N*-substituted aryl sulfonamides (85) to form the corresponding sulfonamides (86) utilizing $Sc(OTf)_3$ as catalyst in nitomethane at ambient temperature (Scheme 32).



**Scheme 32.** Scandium(III) triflate catalyzed deprotection of *tert*-butyl aryl sulphonamides.

## 9. Conclusions

The present review offers an up-to-date literature on the latest developments of $Sc(OTf)_3$-catalyzed organic transformations specially carbon-carbon and carbon-heteroatom bond forming reactions reported during the last decade. Therefore the present review will surely make some impacts on the on-going developments of triflate salts catalyzed organic transformations as it is one of the thrusting areas for today's organic methodologists worldwide.

## 10. Acknowledgements

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This paper is dedicated to **Prof. (Dr.) Goutam Brahmachari** who is pictured above.