ORIGINAL SCIENTIFIC PAPER

CROATICA CHEMICA ACTA

Croat. Chem. Acta **2023**, *96*(3), 141–152
Published online: December 23, 2023
DOI: 10.5562/cca4021

HKD 1926

Thia-Michael Addition in Diverse Organic Synthesis

Sachin A. Khiste,[1] Deepali S. Pakhare,[2] Vijaykumar S. More,[3] Guravaiah Chakibanda,[4] Mahendra N. Lokhande[4,*]

[1] Department of Chemistry, Vaishanvi Mahavidyalaya of Wadvani-431144, Maharashtra, India
[2] Department of Microbiology, Tuljaram Chaturchand College, Baramati-413102, Maharashtra, India
[3] Department of Chemistry, Kai. Rasika Mahavidyalaya Deoni-413519, Maharashtra, India
[4] Department of Chemistry, Aavvaiyar Government College for women, Karaikal, Pondicherry-609602 India
* Corresponding author's e-mail address: mnlok@dhtepdy.edu.in

RECEIVED: July 20, 2023 * REVISED: November 15, 2023 * ACCEPTED: December 6, 2023

Abstract: Thia-Michael addition reactions are significant for organic syntheses of important class of compounds to form C-S bond and its derivatives. It shows the prominent feature in medicinal field and material science. This review is focused on various methods towards thia-Michael adducts using Michael addition of sulfur containing electron rich species (Michael donor) on electron poor olefins (Michael acceptor). The C-S bond is ideal of making bioactive molecules generalized for the synthesis of various drug molecules and applied in field as insect sprays and polymer substances which are common for daily life. Due to the importance of C-S bond in recent years, novel methods for C-S bond formation were developed, which are more convenient with environment.

Keywords: Thia-Michael addition, catalyst, Michael donor, organo-sulfur compounds.

INTRODUCTION

MICHAEL reaction is the conjugate addition of a nucleophile or a carbanion to α,β-unsaturated carbonyl compound. It is the most practical way of forming C–C, C–N, C–O, and C–S bonds. Numerous varieties exist for regeoselective synthesis of nitro alkenes and substituted chalcones with "for example" 1,3-dicarbonyl compound to give an amazing value in natural combination, since these are dynamic and versatile structure blocks in the synthesis related to agricultural and pharmaceutical chemicals.[1] The thia-Michael expansion response has been entirely examined and demonstrated to be a helpful apparatus in synthetic union. The response's intensity has for quite some time been perceived C-S bond formation is the significant in the fields of therapeutic science, catalysis, drug improvement, and material examination. Various synthetic strategies including thia-Michael expansion of Thiol with electron-deficient alkenes have opened up plenty of opportunities for planning and blending a wide scope of organically significant organo-sulfur compounds. Regardless of its various expected manufactured applications, the thia-Michael expansion response has gotten no extraordinary attention. As an outcome, this article account on the improvement of the thia-Michael expansion response in natural union and arranges it into catalyzed and impetus free thia-Michael expansion processes.[2]

In organic chemistry, natural products and physiologically active compounds, such as calcium antagonist dilthiazem have sulfur-containing motifs. For sulfur nucleophiles and α,β-unsaturated alkenes from various accessibility, there is an extensive interest in making effective C–S security shaping responses from these basic beginning materials utilizing thia-Michael expansion. As a result, multiple efforts to design novel and simpler techniques for the Michael addition have resulted in the invention of several base and acid catalysts. C–S bonds are extremely essential functional units as they are needed for the development of a synthetic drug molecules through methodology development such as bioactive intermediate, surfactants, and polymers.

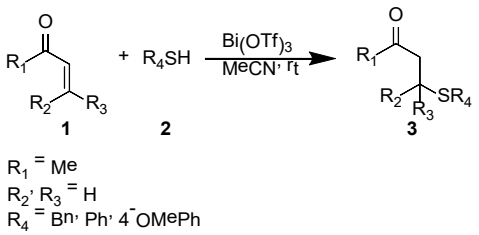
Organo sulphur compounds, on the other hand, have been used as therapeutic cures since the ancient Egyptians produced a sulphuric salve with antibacterial characteristics. Brimstone and treacle were commonly used as laxative and tonic for children in Europe. Patients with rheumatoid

arthritis were given “colloidal” sulphur on a regular basis in the early 1900s. Besides, 24.8 percent of medication (barring organic medications) incorporate this heteroatom. As a result, they've established themselves as a key participant in the sectors of drug delivery and medicines. The basic significance of organosulphur compounds in science and thus science has fuelled the advancement of proficient strategies for their manufacture.[3,4] The thia-Michael expansion response has demonstrated to be a solid and generally used technique for the union of organosulfur compounds. The thia-Michael expansion process is a stable, responsibly raised with high practical gathering functional group interconversion (FGI), high response rates, and symmetry to other reactions.[5–7] Accordingly, the response procedure's utility has been shown in the creation of an assortment of important mixtures for drug conveyance, polymer science, surfactant alterations, dendrimer blend and medicines. The thia-Michael expansion process is a sort of form expansion used in the course of last two decades,[8] in which sulfur-containing nucleophiles ("Michael donor") attack on the β-carbon of electron-deficient olefins ("Michael acceptors") to get particular thia-Michael adduct profoundly.

Indium halides, particularly indium(III) chloride and have arisen late as a strong Lewis acid for an assortment of substance changes. $InCl_3$ has been utilized in the Michael expansion of electron deficient alkenes to pyrroles, amines, silylenol ethers and indoles. $InCl_3$-catalyzed reaction namely chalcone derivatives to thiol is much solvent dependent reaction, so it does not go through the standard solvent such as CH_2Cl_2, THF, and H_2O.[9]

The heterocyclic scaffold 1,5-benzothiazepine is often found in medications with a wide range of pharmacological characteristics. Despite the fact that 1,5-benzothiazepines have sparked a lot of interest in the pharmaceutical area over the years and has resulted in a range of synthetic techniques, there is still a significant desire for new efficient pathways to these compounds in enantioenriched form. One of the most straightforward method for this motif is the sulfa-Michael addition of 2-aminothiophenols to α,β-unsaturated compounds, followed by cyclization.[10] The expansion of thiols to citral, in the presence of KF/Al_2O_3 at room temperature using recyclable glycerin is general, clean and basic method. The bactericide 3,7-dimethyl-3-(phenylthio) oct-6-enal was prepared from Cymbopogon citratus and thiophenol. The process was successfully used to treat with other electron-poor alkenes. The use of microwave irradiation in the solvent-free approach eased the operation and accelerated the reaction. The synergist framework and glycerin can be reused multiple times with practically identical action with no earlier treatment.[11]

M. Alam *et al*. proposed the Michael Addition reactions of thiols to electron deficient olefins is of much more



Scheme 1.

interest because there are number of derivatives occur in nature and possess a variety of biological activities. Recently, bismuth triflate has emerged as a powerful Lewis acid for various chemical transformations. Bismuth triflate used as an excellent catalyst for conjugate addition of thiol to α, β-unsaturated carbonyl compounds under mild conditions (Scheme 1). Encouraged by this result, the reaction under different conditions and the results were satisfactory. The best solvents for this reaction were found to be dichloromethane, dichloroethane, water, tetrahydrofuran and acetonitrile. Acetonitrile was worthier solvent in terms of yields than all the other solvents used. The use of 5 mol% of bismuth triflate was sufficient to carry out the reaction. An addition of thiols to α, β-unsaturated carbonyl compound was carried out at room temperature by using acetonitrile as a solvent and $Bi(OTf)_3$ as a catalyst, with a Michael adduct yield of 70–85 %. $Bi(OTf)_3$ as a catalyst and acetonitrile as a solvent was found to be useful for this transformation. In general, thiols reacted with electron deficient olefins under the present reaction conditions using $Bi(OTf)_3$ as a superior Lewis acid.[12]

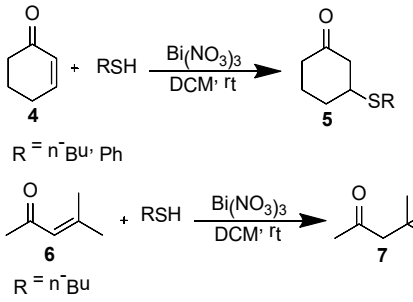
N. Srivatava *et al*. demonstrated the development of a bismuth nitrate-mediated Michael addition reaction of thiols with unsaturated ketones (Scheme 2). These methods are really very fascinating from a synthetic chemist’s point of view. Michael reactions of various organic compounds with moderate to low nucleophilicity have been successfully carried out in the presence of a catalytic amount of bismuth nitrate. The development of a reaction that uses catalytic quantities of minimally toxic, readily available, economic reagent should greatly contribute to the creation of environmentally benign processes. The thia-Michael addition of thiol to enones using $Bi(NO_3)_3$ as a catalyst at room temperature and dichloromethane as a solvent. This $Bi(NO_3)_3$ catalyst performed well with both aromatic and aliphatic thiols. However, it seemed to be more useful because it give high yields of products.[13] The best solvents for this reaction were found to be dichloromethane, tetrahydrofuran, diethyl ether, ethyl acetate, methanol, and acetonitrile. Among all the solvents, dichloromethane was best choice of solvents as it gave high yields than others. The addition of a small amount of dichloromethane solvent is helpful for the success of the

reaction. Even ordinary grade solvents and reagents that are undistilled or unpurified can be used with equal success. In addition, the applications of this type of compound are in the fine chemical and pharmaceutical fields, also shows variety of biological interest.

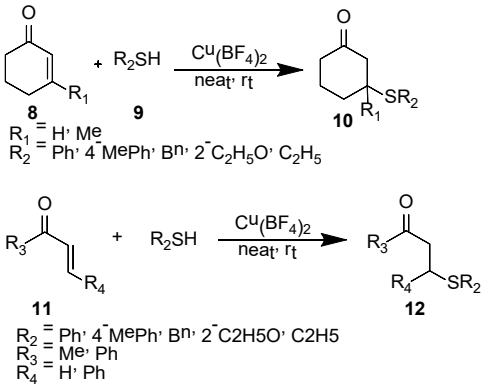
S. Garg *et al*. described a thia-Michael addition reaction between thiol and α,β-unsaturated carbonyl compounds utilizing copper tetraflouroborate as a catalyst at ambient temperature for 2 min-14 h, yielding the desired Michael adduct (Scheme 3). The recent trend for thia Michael addition reactions has demonstrated a great deal of interest in introducing various Lewis acid catalysts. The probable transition state or intermediate may be formed sterically hindered to afford desired product without any solvent. The most advantage of thia-Michael addition reaction with α,β-unsaturated carbonyl compounds with $Cu(BF_4)_2$ as a catalyst are use of commercially available, cheap catalyst, high yielding with short reaction time and easy to handle. However, using $Bi(OTf)_3$ as a catalyst, not showing any disadvantages during reaction. Furthermore, furnished the ideal items in amazing yields of thia-Michael adducts in short time of response time.[14]

In organic synthesis, C–S bond constitutes a key reaction with base catalyzed addition of thiols to α,β-unsaturated carbonyl compounds. Traditionally, these reactions are catalyzed by strong bases, also proceeds using different Lewis acids. Iron has enormous practical advantages as a catalyst due to its ample supply, low cost, lack of toxicity and environmental friendliness. The literature suggesting that the rate of the uncatalyzed reaction is not favourable when the reactions were conducted under different atmospheres also such as Ar, air and pure oxygen, no significant change was observed in the reaction mixture. Ferric mediated catalysts were efficient one in thia-Michael addition reactions. C. Chu et al. reported the thia-Michael addition between thiol and, α,β-unsaturated carbonyl compound employing ferric chloride as a catalyst at room temperature for 5–20 minutes generates Michael adduct (Scheme 4). The allyl, *n*-propyl thiols and cyclohexyl thiols gave good yields in addition with benzylthiol. In contrast to the other metal reagents, ferric chloride produced good yields of thia-Michael adducts in a short reaction time.[15] Moreover, using anhydrous $FeCl_3$, the reactions were clean, high yielding and the product is formed within a few minutes, so it was found to be superior one.

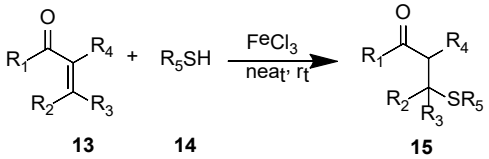
G. Khatik *et al*. investigated perchloric acid tethered on silica gel as a catalyst for thia-Michael addition of thiols to α,β-unsaturated ketone which gave high yield of corresponding β-sulfidocarbonyl compounds (Scheme 5). This reaction occurred under solvent free condition at room temperature. The catalytic effect of $HClO_4$–SiO_2 was treated with thiophenol under above mentioned conditions using 0.01–1mol% of $HClO_4$–SiO_2 affording the thia-Michael adduct in 85–99 % yields after 2–20 min.[16]



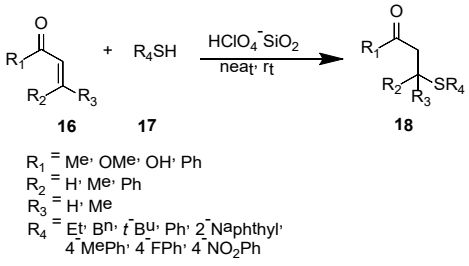
Scheme 2.



Scheme 3.



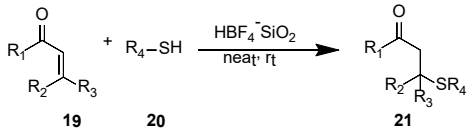
Scheme 4.



Scheme 5.

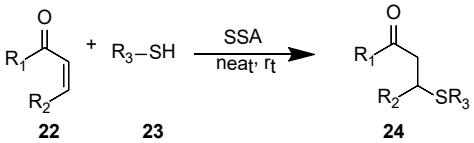
Sharma *et al*. investigated newer and better methodologies for thia-Michael addition reaction on α,β-unsaturated ketone. Also they work on maintenance of greenness in synthetic pathways and processes, that is, to prevent generation of waste, avoid use of auxiliary substances (e.g., solvents, additional reagents) and minimize energy requirements. They reported new, highly efficient and reusable HBF_4–SiO_2 as a heterogeneous catalyst (Scheme 6). The rate of the thia-Michael addition was influenced by the electronic and steric factors associated with the thiols and α,β-unsaturated carbonyl compounds. Excellent results were obtained in this addition reaction, also they made application in a one-pot synthesis of 2,3-dihydro-1,5-benzothiazepines. They used room temperature condition for electron donating and electron withdrawing substituents and HBF_4-SiO_2 as a catalyst under solvent free condition to give β-sulfidocarbonyls. The findings of their tests revealed that the steric hindrance around the β-position of α,β-unsaturated carbonyl complexes was needed for the desirable acceleration of the effective thia-Michael addition.[17]

D. Pore *et al*. presented the thia-Michael addition of α,β-unsaturated ketone and thiol using silica supported sulphuric acid (SSA) as a catalyst at room temperature under solvent free condition (Scheme 7). The silica supported sulphuric acid (SSA) acts as catalyst for sterically unhindered conjugated and electron deficient enone, but it is unsuitable for sterically hindered conjugated enone. The development of a simple but highly efficient method for the thia-Michael addition reaction is desirable. Short reaction time, high yields, cost effectiveness of catalyst and avoidance of anhydrous conditions made this protocol a useful alternative to existing methods.[18]



R_1 = OH, OMe, Me, Ph
R_2 = H, Me, Ph
R_3 = H, Me
R_4 = Et, Bn, Ph, 4-MePh, 4-FPh

Scheme 6.



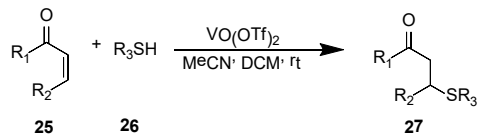
R_1 = Et R_2 = H
R_3 = Bn, cyclohexyl, n-Bu, Ph, 4-MePh, 4-ClPh

Scheme 7.

C. Chen *et al*. used a series of thiols as protic nucleophiles for Michael-type additions and $VO(OTf)_2$ as a catalyst (Scheme 8). They carried out reactions at ambient temperature with catalyst loading of less than 10 mol % with straight thiol or dithiol as nucleophiles. Herein, 5 mol% of $VO(OTf)_2$ was used for thia-Michael addition between thiol and α,β-unsaturated carbonyl compound by using 1 : 4 proportion of methyl cyanide and DCM as a solvent gave Michael adduct within 3–12 h. They used different thiophenols with different electron-donating and electron-withdrawing groups for addition reaction. The newly developed C–S bond formation protocols were carried out smoothly in good to high yields.[19]

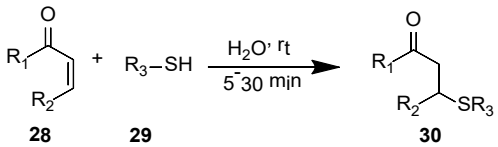
G. Khatik *et al*. developed the catalyst free thia-Michael addition response between α, β-unsaturated carbonyl emulsion and thiol at room temperature in aqueous medium gives the Michael adduct with yield of 80–95 % with only 5–30 min for completion (Scheme 9). The ester cleavage and *trans*esterification were not observed in this reaction. The hydrogen bond was formed between the carbonyl oxygen of α,β-unsaturated compound and water molecule which activated β-position towords Michael addition also simultaneously another hydrogen bond was also formed between thiol hydrogen and oxygen atom of water molecule and hence its nuclophilicity increases.[20]

R. Ghorbani *et al*. demonstrated the wet-TCT (2,4,6-trichloro-[1,3,5]-triazine or cyanaric chloride) or cyanaric chloride moderated thia-Michael addition reaction between α,β-unsaturated carbonyl compound and thiol. To study the effect of solvent and reaction conditions, they performed in the presence of 10 mol% of wet-TCT and acetonitrile for 5–15 min under pulverization–activation method at room temperature. It gave the Michael adduct with more than 75 % yield.[21]



R_1 = Ph R_2 = Me
R_3 = Bn, Ph, CH_2CH_2OH, 2-Naphth 4-ClPh, 4-MeOPh

Scheme 8.



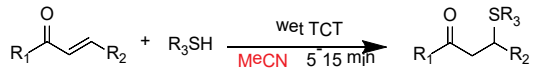
R_1 = H, Me, OMe
R_2 = H
R_3 = Ph, 4-NO_2Ph, Bn, 4-MePh

Scheme 9.

B. Movassagh *et al*. investigated the solvent free Michael addition of aromatic thiols on α,β- unsaturated carbonyl compound without any catalyst with good yield. (Scheme 11) The addition of thiols to α,β-unsaturated carbonyl compounds under solvent-free conditions in the absence of any catalyst. This economical, simple, efficient and environmentally benign process represents a suitable option to existing methods.[22]

B. Fetterly *et al*. identified azaphosphatrane nitrate as a useful catalyst for the thia Michael addition between Michael acceptors such as esters, cyclic and acyclic α,β-unsaturated carbonyl or nitriles and corresponding thiol in acetonitrile as a solvent at room temperature gave the Michael adduct in excellent yield, this reaction require 40–48 h for completion (Scheme 12). When bound to a solid support, this catalyst showed excellent catalytic activity at room temperature and it was also recyclable.[23]

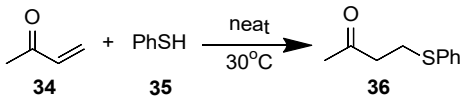
W. Guo *et al*. demonstrated odourless thia-Michael addition reaction between disulfide substrate and α,β-unsaturated ketone/ ester by using Ronglite/K_2CO_3 system



31 **32** **33**

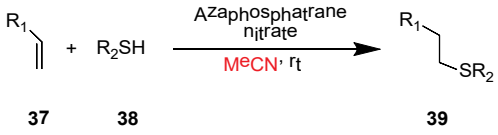
R_1, R_2 = H, Me, Ph
R_3 = Bn, Ph

Scheme 10.



34 **35** **36**

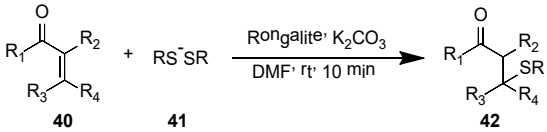
Scheme 11.



37 **38** **39**

R_1 = CN, COMe, COOMe
R_2 = n-Bu, Ph

Scheme 12.



40 **41** **42**

R_1 = Me, OMe R_2 = H, Me
R_3 = H, n-C_4H_9 R_4 = H, Ph

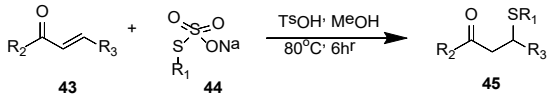
Scheme 13.

at room temperature and corresponding products β-sulfido carbonyl compounds were obtained within 10 min with 83-98% yield (Scheme 13).[24]

Y. Lin *et al*. described the less volatile and odourless Bunte Salts 44 as Michael donor (Scheme 14). The problems of high volatility safety and serious environment and unpleasant smell of thiols was minimized. The thia-Michael addition reaction of α,β-unsaturated ketone and Bunte salt in the presence of 20 mol% of p-TSA / MeOH at 80 °C for 6 h gave β-sulfido carbonyl compound in 69–93 % yield. Allyl, benzyl and cyclohexylbunte salts were successfully employed due to the steric hindered effect. Cyclohexylbunte salts gave lower yield about 46 % only.[25]

M. Bandini *et al*. proposed the reactions of substituted aromatic thiol compounds with electron deficient double bond in presence of $InBr_3$ as a catalyst in DCM at room temperature for 16–24 h which gave the desired β-substituted ketones (Scheme 15). The substituent present on aromatic ring of near double bond favoured the Micheal addition reaction while this approach failed to work with aliphatic and electron-deficient thiols, as well as sterically hindered, unsaturated systems. As a result, it exhibited a narrow substrate range.[26]

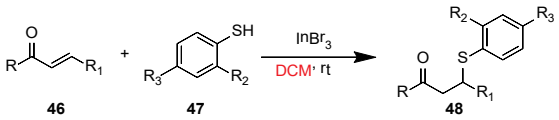
B. C. Ranu *et al*. investigated the use of $InCl_3$ for the Michael addition of chalcone and thiol in dry methanol which gave the high yields of corresponding adducts (Scheme 16). They found that the response goes productively in dry methanol.[9]



43 **44** **45**

R_1 = Allyl, Bn, CH_2COOEt, 4-MeBn, 4-NO_2Bn
R_2 = Me, Ph, OEt, $N(Me)_2$
R_3 = H,Ph, 2-thienyl, 4-BrPh, 4-MePh, 4-OMePh

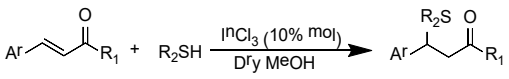
Scheme 14.



46 **47** **48**

R = Me, Ph
R_1 = Ph
R_2 = H, COOH
R_3 = H, Me

Scheme 15.



49 **50** **51**

R_1 = Me, Ar
R_2 = Ar, n-Bu

Scheme 16.

The reaction was most efficient with 10 mol% of $InCl_3$ as a catalyst using methanol as a solvent. The indium(III) chloride provided an efficient methodology for the Michael addition of thiols. This strategy was much efficient due to lower cost of indium(III) chloride also due to mild reaction conditions (room temperature), simple operation with high yields of adducts.

B. Ranu *et al*. uses ionic liquid as solvent which is more convenient for thia-Michael addition reaction (Scheme 17). The double thia-Michael addition took place between thiol and conjugated terminal acetylenic ketone in the presence of ionic liquid, 1-methyl-3-butylimidazolium hydroxide [bmIm]OH at room temperature for 15–30 min and β-keo-1,3-dithiane were obtained with 95–98 % excellent yield. In this reaction, ionic liquid [bmIm]OH acted as both catalyst and solvent, so it provided ultimate facility to proceed thia Michael addition reaction.[27]

A. Khan *et al*. investigated the thia-Michael addition of thiols on α,β-unsaturated ketone, ester, amide, and nitrile at room temperature using $HClO_4$-/ SiO_2 as a catalyst and DCM as a solvent (Scheme 18). The advantage of this strategy is that there was aqueous preparation or chromatographic separation is not required, and the solid acid catalyst could be reused. Thus, a simple, efficient and greener protocol was employed for the thia-Michael reactions by using the $HClO_4$ / SiO_2 as a reusable catalyst.[28]

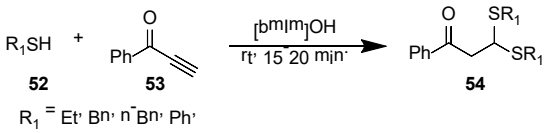
N. Azizi *et al*. investigated neat thia-Michael addition reaction at rt using LiOH (Scheme 19). The response of aryl, alkyl, aliphatic, and impeded thiols with chalcone, enone, and nitrostyrene gave the Michael adducts with huge benefits, like high transformations, short response time, mild response conditions, minimal expense, basic impetus, and high to quantitative yields with amazing chemoselectivity.[29]

Z. Shobeiri *et al*. used the LiF nano cube for thia-Michael expansion reaction of thiol on α,β-unsaturated carbonyl emulsion utilizing EtOH and room temperature condition which gave the β-aryl-mercapto ketone in 57–96 % yield, except for emulsion 4-phenyl-4-(p-tolylthio) butan-2-one, for which the yield was 25 % (Scheme 20). The reaction followed the acid catalysed reaction route; however, it was hampered by the protocol's limited substrate range.[30]

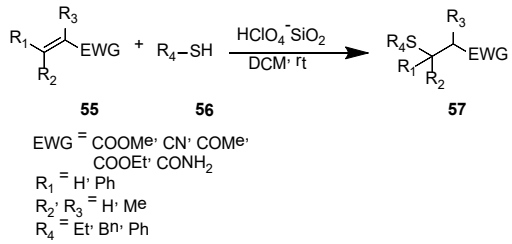
G. Perin *et al*. reported Diorganyl disulphide based thia-Michael addition reaction between electron deficient alkene and diorganyl disulphide compound in presence of $NaBH_4$ and PEG-400 system at room temperature under N_2 condition for about 30–90 min with 45–98 % yield (Scheme 21). In this reaction the cleavage S–S bond of diorganyl disulphide took place for the generation of thiol species in presence of $NaBH_4$.[31]

N. Azizi et al. reported multi-component thia-Michael addition reaction between organic halide, α,β-unsaturated carbonyl compound and derivative of thiourea using choline chloride urea based DES (deep eutectic solvent) at 60 °C for 20–100 min (Scheme 22). Choline chloride urea based DES gives high yield of product, also no need of column chromatography for purification. The cost effectiveness, biodegradability and high economy are the advantages of this reaction.

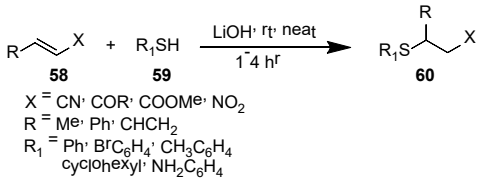
These reactions are economic and odourless alternative to other methods for C-S bond formation using a biodegradable and inexpensive DES. The reactions proceed under mild conditions and gave the products in good yields with complete atom economy with simple separation and purification.[32]



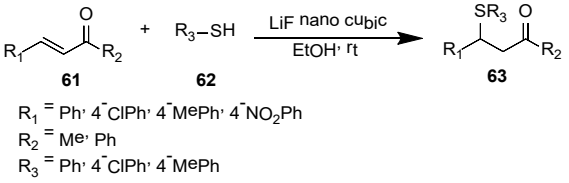
Scheme 17.



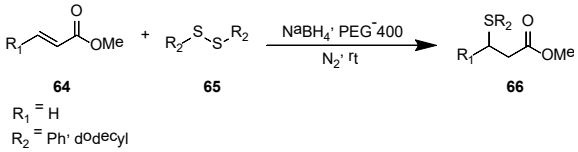
Scheme 18.



Scheme 19.



Scheme 20.

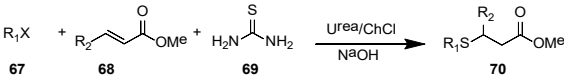


Scheme 21.

H. Firouzabadi *et al*. reported the high yield synthesis of dialkyl and diaryl sulfides via thia-Michael addition reaction of thiolate ion produced from dithiooxamide and halide compound with α,β-unsaturated compounds in the presence of $NaHCO_3$ with wet PEG-200 (Scheme 23). It is an eco-friendly and safe protocol for the synthesis of organosulfur compounds.[33]

E.J. Lenardae *et al*. developed the green Michael addition of thiols by using thiophenol and citral which is easily available from oil of lemon grass in the presence of KF/Al_2O_3 at room temperature or microwave (548W) under solvent free condition or KF / Al_2O_3 , glycerine at room temperature gave required products with good yields (Scheme 24).[34]

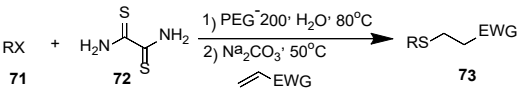
S. Shaw *et al*. investigated the enantio-specific and regio-specific conjugate addition of thiols to acyclic α, β, γ, δ-unsaturated dienones in presence of Fe (III) core catalyst which produced δ-thia-α,β-unsaturated ketones in excellent yields based on spectroscopic and chemical data (Scheme 25). A variety of α, β, γ, δ-unsaturated ketones were tested with different thiols to broaden the scope of the technique. With both aliphatic and aromatic thiols as Michael donor, as well as thioacetic acid, methyl, aryl, and heteroaryl ketones as Michael acceptors gave an excellent yields of the δ-sulfa-Michael product. Also, when an excess of thiol was employed, no further conjugate β-addition of a second molecule of thiol to δ-adduct was detected.[35]



67 68 69 70

R_1 = Me, Bn, cyclopentyl, allyl, 3-ClBn, 4-BrBn, 4-ClBn, 4-OMeBn
R_2 = H, X = Cl, Br, I

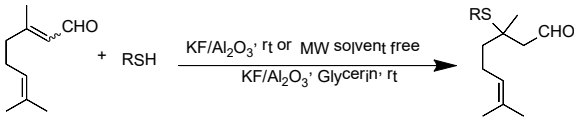
Scheme 22.



71 72 73

R = Me, allyl, i-Pr, t-Bu, n-octyl, n-decyl, cyclopentyl, 2-methylpropenyl, 4-BrBn, 4-MeBn, 4-NO2Bn
X = Cl, Br, I
EWG = methyl vinyl ketone, acrylonitrile, ethyl acrylate, acrylamide

Scheme 23.



74 75 76

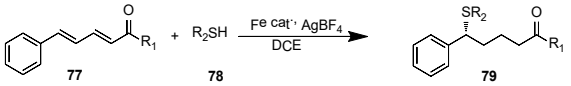
R = C_3H_7, Ph, 2-ClC_6H_4, 4-$CH_3OC_6H_4$, $C_{12}H_{25}$

Scheme 24.

D. Sureshkumar *et al*. demonstrated the thia-Michael addition reaction between derivatives of aziridines and electron deficient alkenes using $[BnEt_3N]_2MoS_4$ as sulphur source in presence of acetonitrile as a solvent at room temperature for 2–24 h (Scheme 26). The sulphur containing amino acid analog product with 50–85 % yield was obtained. This reaction was in situ synthesis of disulphide IV via nucleophilic addition reaction derivative with tetrathiomolybdate dianion followed by ring opening. They developed one pot Michael addition reaction using tetra thiomolybdate resulting in interesting high yield.[36]

S. Cheng *et al*. demonstrated the thia-Michael addition of thiol and *N*-anilino maleimides in the presence of dimethyl formamide and alumina, which gave 3-sulfanyl substituted 1-(arylamino)-pyrrrolidine-2,5-diones within 1 h (Scheme 27). The surface of alumina served as a Lewis acid, allowing thia-Michael addition. This scheme gave excellent return of substance from aliphatic, sterically blocked and electron deficient thiols. This method is flexible and may provide important leads as agricultural fungicides.[37]

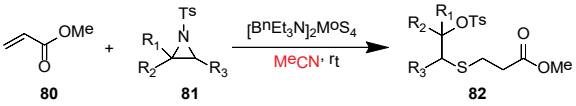
V. Kumar *et al*. reported the aqueous mediated simple and facile thia-Michael addition reaction between *N*-aryl maleimide and thiol at room temperature within 10–15 min and provided 80–96 % yields of corresponding Michael adducts (Scheme 28). Due to its operational simplicity, cost-effectiveness, less time consuming, and high yields, made this method more efficient.[38]



77 78 79

R_1 = Me, Ph, 2-furyl, 2-thienyl, 2-OMePh
R_2 = H, Me

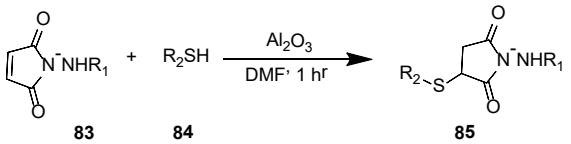
Scheme 25.



80 81 82

R_1, R_2 = H, Me, Et, i-Pr, Bn, i-Bu, t-Bu, 2-Bu, 2-indonyl, $(CH_2)_2SMe$
R_3 = H, Me, Et

Scheme 26.



83 84 85

R_1 = C_6H_5, BrC_6H_4, NCC_6H_4, $F_3CC_6H_4$, $F_2C_6H_3$, $ClFC_6H_3$
R_2 = C_6H_5, HOC_6H_4, $CH_3C_6H_4$, $CH_2OHC_6H_4$, $Cl_2C_6H_3$, $(OMe)_2C_6H_3$

Scheme 27.

G. Li *et al.* synthesized macromolecule of Michael adduct using the thiol-ene click Michael addition by using different types of catalyst like pentylamine (PAM), hexylamine (HA), trimethylamine (TEA), dimethylphenyl phosphine (DMPP) or tris(2-carboxyethyl) phosphine hydrochloride (TCEP) (Scheme 29). Using a wide range of monomers and oligomers, the best conditions for the thiol-ene reaction were explored using primary amines, tertiary amines, and phosphines at various temperatures and in various solvents. The TCEP was used to synthesize short oligomers with a terminal vinyl group. This approach has been used to make MMA and HEMA dimers (after separating them from higher adducts) as well as OEGMA oligomers. Different thiol-ene reactions with a wide range of thiol compounds and catalyst systems were employed to test the oligomers.[39]

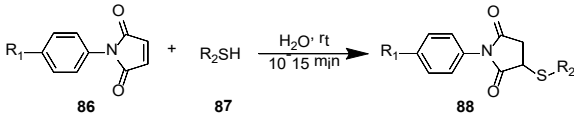
A. Khan *et al.* synthesised the 1-[(alkylthiol)(phenyl)methyl]-napthalene-2-ols 95 by using three component one pot synthesis using aldehyde, 2-napthol and thiol in presence of catalyst BDMS i.e. bromo dimethyl sulfonium bromide in acetonitrile at room temperature for 5–7 h in 21–81 % yield (Scheme 30).[40]

M. Abaee *et al.* synthesized β-aryl β-mercapto ketones using three component reactions of thiol, acetophenone and aldehyde in water / Et_2NH at room temperature for about 35 h in 90–98 % yield (Scheme 31). They employed all three amines i.e. primary, secondary and tertiary amines, out of these amines, secondary amines gave higher yields while primary and tertiary amines gave much lower yield, which is due to high solubility and basicity of secondary amine in water than tertiary and primary amine.[41]

S. Bruschi *et al.* developed the three component base catalysed thia-Michael addition using thiol, aldehyde and 3-methyl-4-nitro-5-styrylisoxazole in refluxed condition and isoxazole-sulphide hydrides were obtained (Scheme 32). In this thia-Michael addition, researcher observed 1,6-thia Michael addition reaction and not the 1,4-thia Michael addition reaction. This was probably due to the loss of aromaticity in isoxazole moiety for 1,4-thia Michael addition. They also used the different bases such as piperidine, pyridine, DBU, Et_3N and DMAP, among them piperidine required short reaction time with high yield of product. The advantages of this method were inexpensive and commercially available materials and excellent yields without chromatographic purification.[42]

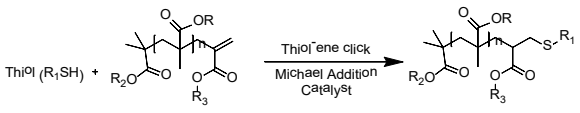
A. Kumar *et al*. reported the reaction proceeded via aldol condensation with related thia-Michael addition reaction. They constructed β-aryl-β-mercapto ketones catalyzed by zirconium chloride under solvent free condition with three components namely cyclic or acyclic enolizable ketones, aryl aldehyde and thiol at room temperature (Scheme 33).

This method provided an efficient multicomponent approach for the thia-Michael addition reaction. The



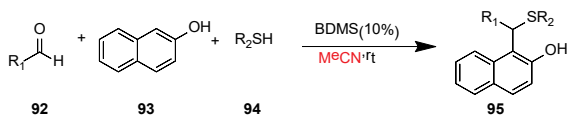
R_1 = 4-F, 4-Cl, 4-Br
R_2 = Ph, $(CH_2)_2OH$, 4-FPh, 4-ClPh, 4-BrPh

Scheme 28.



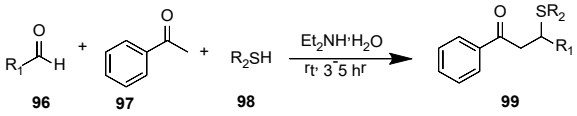
Thiol = propanethiol, cysteamine, dodecanethiol, benzyl mercaptan, thioglucose, thioglycerol, L-glutathione, mercaptopropionic acid, mercaptoethanol
R = H, Me
R_2, R_3 = H, Me, Et, Ph

Scheme 29.



R_1 = Ph, 2-ClPh, 2-Naphthyl, 2-NO_2Ph, 3-BrPh, 3-NO_2Ph, 4-ClPh, 4-BrPh, 4-NO_2Ph, 4-MePh

Scheme 30.

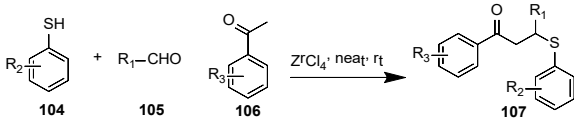


R_1 = Ph, 4-MePh, 4-OMePh, 4-NO_2Ph
R_2 = Bn, n-pentyl, n-octyl, Ph, 3-OMePh, 4-OMePh

Scheme 31.

Ar = Ph, 2,3-Cl_2Ph, 2,3-Cl_2Ph, 3,5-Cl_2Ph, 4-ClPh, 4-CNPh, 4-FPh, 4-MePh, 4-OMePh, 4-NO_2Ph

Scheme 32.



R_1 = Ph, naphthyl, 2,6-diClPh, 3-ClPh, 3-NO_2Ph, 4-OMePh
R_2 = H, 4-Cl, 4-Me
R_3 = H, 4-OH, 4-OMe

Scheme 33.

reaction was versatile and also offered several advantages, such as high yields, shorter reaction times, cleaner reaction profiles and simple experimental and work-up procedures.[43]

M. Sani *et al*. synthesised γ-trifluoro methyl-γ-sulfonehydroxamates which is a significant class of biologically active nitrogenous compounds. They firstly obtained thia-Michael adduct of diastereomers 110 by reacting 4-methoxy benzene thiol 109 with 3,3,3-trifluorocrotonoyl Michael acceptors 108 under Et_3N/DCM system at room temperature in 15-30 min. The required diastereomer was separated using flash chromatography technique, which was further used for next sequences and final product γ-trifluoromethyl γ-sulfone hydroxamate 111 was synthesized as shown in Scheme 34. The *R*-enantiomer of compound 111 was the most potent inhibitor of MMP-3 i.e. stromelysin-1 with IC_{50} = 3.2 nM.[44]

Z. Xia *et al*. blended both 1,4 and 1,2-thia-Michael expansion response between α,β-unsaturated *N*-acylbenzotriazoles and thiophenol in SiO_2 (Scheme 35). Under THF/Water (9 : 1 proportion) and low temperature gave 1,4-expansion and water assumed the principle part for acquiring specific 1,4-expansion. On the orther side, the particular 1,2-expansion happened by involving zinc chloride and triethyl amine under reflux condition in THF. $ZnCl_2$ offered chelation of nitrogen and oxygen of benzotriazole and carbonyl, triethyl amine deprotonated thiols which gave more nucleophilic thiolate ion. The combination of both these factors favoured 1,2-addition and α,β-unsaturated thioesters were obtained.[45]

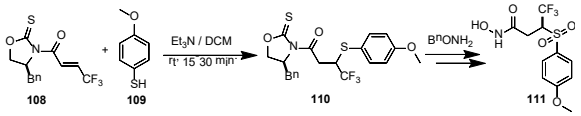
I. Yavari *et al*. reported PPh_3 mediated synthesis of alkyl 3,4-dihydro-2H-1,3-thiazine by thia-Michael addition reaction between *N*,*N*'-substituted thiourea and alkyl acetylene dicarboxylate at 50°C for 1-3 hrs (Scheme 36). In this reaction, Zwitter ion produced by the reaction of dialkyl acetylene dicarboxylate and PPh_3, was trapped by *N*,*N*'-substituted thiourea through thia-Michael addition reaction. Finally the intramolecular cyclization took place by elimination of PPh_3 and alkyl 3,4-dihydro-2H-1,3-thiazines were obtained in 83–90 % yield.[46]

A. Malik *et al*. demonstrated thia-Michael addition reaction by using molecular iodine as a catalyst for the synthesis of thiochromane analog using thiophenol cinnamylidene acetophenone under refluxed condition in DCM for 2.5–3.5 h (Scheme 37). The synthesised thiochromane is present in number of medicinally related molecule which showed anti-inflammatory, anti-bacterial, anti-cancer, anti-hyperplasia, anti-psychotic activity.[47]

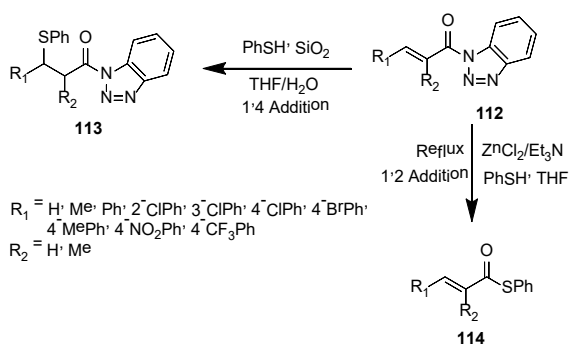
A. Ali *et al*. synthesized 1,3-thiazines which is class of compounds that have desired applicability from agrochemical science to pharmaceutical as pesticides, herbicides as well as antifungal, antitubercular, anticonvulsant, bacteriostatic, antitumour, analgesic, anti-inflammatory, and Na^+/H^+ exchange system inhibitor.

The thia *N*-aroyl substituted thiourea 121 underwent thia-Michael addition reaction with dimethyl but-2-ynedioate 122 under refluxed condition in acetic acid which acted as both solvent and catalyst resulted in 1,3-thiazines 123 in excellent yield (Scheme 38). They also used ethyl propiolate and (E)-1,4-diphenyl-but-2-ene-1,4-dione for thia-Michael addition reaction which gave corresponding 1,3-thiazines.[48]

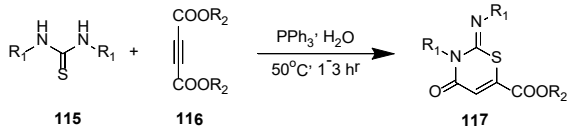
P. Sasmal *et al*. explored intra-molecular thia-Michael addition between electron deficient alkynes and



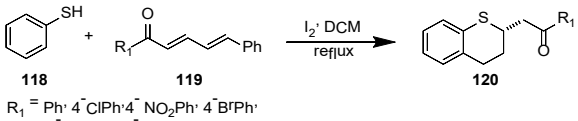
Scheme 34.



Scheme 35.



Scheme 36.



Scheme 37.

Scheme 38.

isothiocyanates in Et_3N at room temperature for 12–24 h and cyclized product of 2-aminothiazoles were obtained with 65–90 % yield (Scheme 39). This reaction started through in-situ generation of *N*,*N*'-substituted thiourea intermediate followed by aromatization in consecutive manner and intermolecular thia-Michal addition. This is very mild, simple, highly efficient method for the synthesis of substituted 2-aminothiazoles.[49]

G. Kumar Verma *et al*. demonstrated the thia-Michel addition reaction between carbon atom of sp-hybridized electron deficient alkynes compound 127 and β-ketothioamide 128 which gave the acyclic α-oxoketene-N,S-acetal intermediate. Then intra molecular amide formation took place by removal of alcohol which gave the product 1,3-thiazolidin-4-one 129 with 71–92 % yield within 3-10 min in presence of DMP as a catalyst at room temperature (Scheme 40). In this reaction, two new C-N and C-S bond were produced in a single step which made this reaction high atom economy.[50]

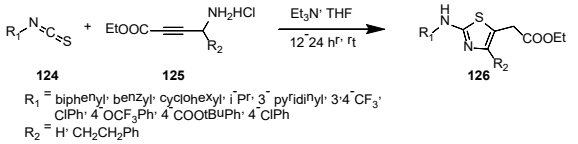
Y. Xiang *et al*. synthesised chiral dihydro thiophene by using thia-Michael addition between 1,4-dithiane-2,5-diol and α,β- unsaturated aldehyde in presence of Pepsin and acetonitrile/ buffer solvent system at 30 °C for about 96–168 h which gave the asymmetric dihydo thiophene with 53–84 % ee purity[51] (Scheme 41).

R. Rios *et al*. developed the thia-Michael addition reaction of α,β-unsaturated cyclic ketone and mercapto benzaldehyde in DMF using chiral Pyrrolidine, (S)-Pyrrolidin-2-yl methanol as a catalyst for 24 h and tricyclic tetrahydro thioxanethenone were obtained in 74–78 % yield (Scheme 42). Apart from limitations such as moderate enantioselectivity and limited substrate scope, R. Rios and co-workers developed the first chiral catalyst for the synthesis of tricyclic tetrahydro thioxanethenone.[52]

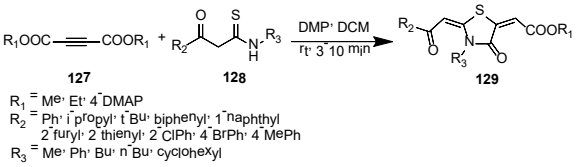
O. Brun *et al*. developed green synthesis of cysteine based cyclopent-4-ene-1,3-dione (CPSs) peptides via thia-Michael addition reaction between cyclopet-4-ene-1,3-diones and various cysteines under mild condition (Scheme 43). This reaction underwent thia-Michael addition and intra molecular cyclization which resulted into bicyclic nonadienone adduct, which is having more importance in bio-conjugation.[53]

L. Hua *et al*. investigated the thia-Michael addition reaction for the synthesis of 2-Amino-3,1-benzothiazines by using o-aminocinnamate and isothiocyanates in presence of $Yb(OTf)_3$ as a catalyst (Scheme 44). Even in the presence of water, product 2-Amino-3,1-benzothiazines were formed in good yields. $Yb(OTf)_3$ catalyzed thia-Michael expansion could be clarified based on Hard-Soft-Acid-Base (HSAB) hypothesis.[54]

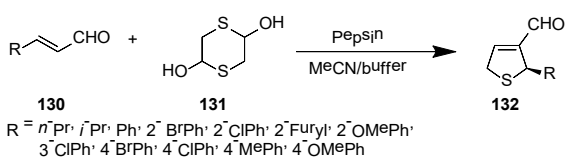
V. Corti *et al*. resulted the two step organocatalytic asymmetric sulfa-michael reaction of *trans* chalcones 142 with 2-amino thiophenols 143 catalysed by a cinchona-alkaloid-based sulfonamide inorganic catalyst which gave the Michael adduct 144 which on reductive amination gave 2,3,4,5-tetra hydro-1,5-benzothiazepines 145 (Scheme 45).



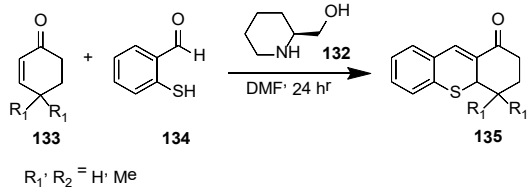
Scheme 39.



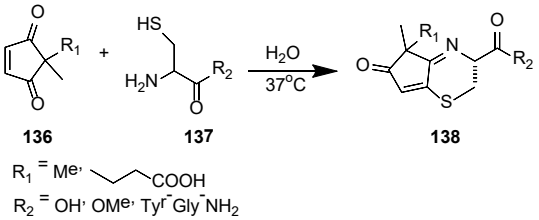
Scheme 40.



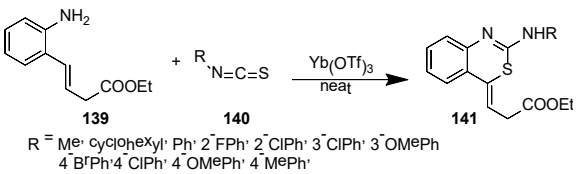
Scheme 41.



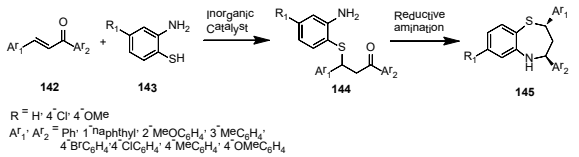
Scheme 42.



Scheme 43.



Scheme 44.



Scheme 45.

In medicinal chemistry, 1,5-benzothiazepine frameworks are important. This two-step protocol was used to synthesize different *trans* enantioenriched 2,3,4,5-tetrahydro-1,5-benzothiazepines with moderate to good yields.[10]

Lokhande *et al*. demonstrated the Michael addition of substituted 2-aminobenzoxazole and 2-aminobenzothiazole 147 on substituted chalcones 146 in good to excellent yields (Scheme 45). All compounds were studied against MCF-7 cell line for their anticancer activity also docking studies were done.[55]

CONCLUSIONS

C–C, C–N, C–S bond formation reactions are incredibly attractive due to their diverse applications in various fields of chemistry. C-S bond formation via thia-Michael addition has received inimitable attention for its remarkable contribution in every aspect of chemistry. Owing to the diversity of thia-Michael addition product and its application in medicinal chemistry, material science and catalysis plentiful methods were developed which includes catalyst free and solvent free reactions. Varity of methods were focused and discussed in this review with wide range of structures including macromolecules, biologically active molecules and natural products which were synthesized through thia-Michael addition.

Acknowledgment. MNL thanks to all authors for their contribution in this review and DSP would like to thank DST (Kiran) for Women Scientist-A research fellowship.

REFERENCES

[1] S. A. Khiste, M. N. Lokh e, P. Vibhute, R. G. Shinde, D. S. Wankhede, *Current Pharma Research*. **2019**, *411*, 90–97. https://doi.org/10.25166/jcprd6.101744065

[2] P. Wadhwa, A. Kharb a, A. Sharma, *Asian Journal of Organic Chemistry* **2018**, *7*, 634–661. https://doi.org/10.1002/ajoc.201700609

[3] a) T. Kondo, T. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205–3220. https://doi.org/10.1021/cr9902749
b) N. Azizi, A.K. Amiri, H. Ghafuri, M. Bolourtchian, *Green Chemistry Letters Reviews* **2009**, *2*, 43–46. https://doi.org/10.1080/17518250902998103

[4] A. M. Alswieleh, N. Cheng, I. Canton, B. Ustbas, X. Xue, V. Ladmiral, V. Xia, R. E. Ducker, O. E. Zubir, M. L. Cartron, C. N. Hunter, G. J. Leggett, S. P. Armes, *J. Am. Chem. Soc.* **2014**, *136*, 9404–9413. https://doi.org/10.1021/ja503400r

[5] W. Xi, C. Wang, C. J. Kloxin, C. N. Bowman, *ACS Macro Lett.* **2012**, *1*, 811–814. https://doi.org/10.1021/mz3001918

[6] E. A. Ilardi, E. Vitaku, J. T. Njardarson, *J. Med. Chem.* **2014**, *57*, 2832–2842. https://doi.org/10.1021/jm401375q

[7] G. Liu, J. T. Link, Z. H. Pei, E. B. Reilly, S. Leitza, B. Nguyen, K. C. Marsh, G. F. Okasinski, T. W. Geldern, M. Ormes, K. Fowler, M. Gallatin, *J. Med. Chem.* **2000**, *43*, 4025–4040. https://doi.org/10.1021/jm0002782

[8] K. L. Dunbar, D. H. Scharf, A. Litomska, C. Hertweck, *Chem. Rev.* **2017**, *117*, 5521–5577. https://doi.org/10.1021/acs.chemrev.6b00697

[9] B. C. Ranu, S. S. Dey, S. Samanta, *Arkivoc,* **2005**, *3*, 44–50.

[10] V. Corti, P. C. Gonzalez, J. Febvay, L. Caruana, A. Mazzanti, M. Fochi, L. Bernardi, *Eur.J.org.Chem.* **2016**, *10*, 6473–6477. https://doi.org/10.1021/acscatal.6b01962

[11] E. J. Lenardão, D. O. Trecha, P. C. Ferreira, R. G. Jacob, G. Perin, J. *Braz. Chem. Soc.***2009**, *20*, 93–99. https://doi.org/10.1590/S0103-50532009000100016

[12] M. Alam, R. Varala, S. Adapa, *Tetrahedron Lett*. **2003**, *44*, 5115–5119. https://doi.org/10.1016/S0040-4039(03)01089-X

[13] N. Srivatava, B. Banik *J. Org. chem*. **2003**, *68*, 2109–2114. https://doi.org/10.1021/jo026550s

[14] S. Garg, R. Kumar, A. Chakraborti, *Tetrahedron Lett.* **2005**, *46*, 1721–1724. https://doi.org/10.1016/j.tetlet.2005.01.051

[15] C. Chu, W. Huang, P. Wu, C. Lu, C. Yau, J. Liu, *Tetrahedron Lett.* **2006**, *47*, 7375–7380. https://doi.org/10.1016/j.tetlet.2006.07.151

[16] G. Khatik, G. Sharma, R. Kumar, A. Chakraborti, *Tetrahedron*. **2007**, *63*, 1200–1210. https://doi.org/10.1016/j.tet.2006.11.050

[17] G. Sharma, R. Kumar, A. Chakraborti, *Tetrahedron Lett*. **2008**, *49*, 4272–4275. https://doi.org/10.1016/j.tetlet.2008.04.144

[18] D. Pore, M. Soudagar, U. Desai, T. Thopate, P. Wadagaonkar, *Tetrahedron Lett.* **2006**, *47*, 9325–9328. https://doi.org/10.1016/j.tetlet.2006.10.114

[19] C. Chen, Y. Lin, C. Liu, *Tetrahedron* **2009**, *65*, 10470–10476. https://doi.org/10.1016/j.tet.2009.10.012

[20] G. Khatik, A. Chakraborti, R. Kumar, *Org. Lett.* **2006**, *8*, 2433–2436. https://doi.org/10.1021/ol060846t

[21] R. Ghorbani, H. Vein, *Mol. Divers*. **2010**, *14*, 385–392. https://doi.org/10.1007/s11030-009-9184-2

[22] Movassagh, P. Shaygan, *Arkivoc*. **2006**, *12*, 130–137. https://doi.org/10.3998/ark.5550190.0007.c15

[23] B. Fetterly, N. Jana, J. Verkade, *Tetrahedron*. **2006**, *62*, 440–456. https://doi.org/10.1016/j.tet.2005.09.117

[24] W. Guo, J. Chen, G. Lu, W. Gao, H. Wu, J. Ding, *Tetrahedron* **2010**, *66***,** 2297–2300. https://doi.org/10.1016/j.tet.2010.02.001

[25] Y.Lin, G. Lu, C. Cai, W. Yi, *RSC Adv*. **2015**, *5*, 27107–27111. https://doi.org/10.1039/C5RA01381J

[26] M. Bini, P. Cozzi, M. Gialomini, P. Melchiore, A. Umani-ronchi, *J.Org. chem*. **2002**, *67*, 3700–3704. https://doi.org/10.1021/jo0163243

[27] B. C. Ranu, R. Jana, S. Banetjee, *Tetrahedron*. 2007**,** *63*, 776–782. https://doi.org/10.1016/j.tet.2006.10.077

[28] A. Khan, S. Ghosh, L. Choudhury, *Eur. J. Org. Chem.* **2006**, *9*, 2226–2231. https://doi.org/10.1002/ejoc.200600006

[29] N. Azizi, A. Amiri, H. Ghafuri, M. Bolurtchain, *Green Chemistry Letters Reviews* **2009**, *2*, 43–46. https://doi.org/10.1080/17518250902998103

[30] Z. Shobeiri, M. Pourayoubi, M. Necas, V. Divjakovic, M. Babiak, *J. Iran. Chem. Soc.* **2015**, *12*, 245–255. http://dx.doi.org/10.1007/s13738-014-0479-6

[31] G. Perin, T. Peglow, E. Borges, J. Lenardo, *Tetrahedron Lett.* **2014**, *55*, 5652–5655. http://dx.doi.org/10.1016/j.tetlet.2014.08.101

[32] N. Azizi, A. Rahimzade, Z. Yadollahy, *Tetrahedron Lett*. **2014**, *55*, 1722–1725. https://doi.org/10.1016/j.tetlet.2014.01.104

[33] H. Firouzabadi, A. Samadi, F. Gorginpour, N. Iranpoor, *Eur. J. Org. chem.* **2015**, *51*, 2914–2920. https://doi.org/10.1002/ejoc.201500156

[34] E. Lenardao, D. Trecha, P. Ferreira, R. Jacob, G. Perin. *J. Braz. Chem. Soc.* **2009**, *20*, 93–99. https://doi.org/10.1590/S0103-50532009000100016

[35] S. Shaw, J. White,*Org. Lett.* **2015**, *17*, 4564–4567. https://doi.org/10.1021/acs.orglett.5b02280

[36] D. Sureshkumar, S. Ch. rasakaran, T. Gunasundari, *Tetrahedron* **2015**, *71*, 7267–7281. http://dx.doi.org/10.1016/j.tet.2015.04.003

[37] S. Cheng, D. Comer, *Tetrahedron Lett*. **2002**, *43*, 1179–1181. https://doi.org/10.1016/S0040-4039(01)02401-7

[38] V. Kumar, V. Nair, S. Bhattarai, R. Mitra, *Synthetic commun.* **2011**, *1*, 392–404. https://dx.doi.org/10.1080/00397911.2010.502999

G. Li, R. Rev, A. Soeriyadi, G. Rees, C. Boyer, Z. Tong, T. Davis, C. Becer, D. Haddleton, *Polym. Chem.* **2010**, *1*, 1196–1204. https://doi.org/10.1039/C0PY00100G

[39] A. Khan, S. Ali, A. Dar, M. Lal, *Tetrahedron Let.* **2011**, *52*, 5157–5160. http://dx.doi.org/10.1016/j.tetlet.2011.07.113

[40] M. Abaee, S. Navidipoor, S. Cherghi, S. Forghani, M. Mojtahedi, *Tetrahedron Lett.* **2012**, *53*, 4405–4408. https://doi.org/10.1016/j.tetlet.2012.06.040

[41] S. Bruschi, M. Adamo, M. Moccia, *Tetrahedron Lett.* **2011**, 52, 3602–3604. http://dx.doi.org/10.1016/j.tetlet.2011.05.007

[42] A. Kumar, Akanksha, *Tetrahedron Lett.* **2007**, *48*, 8730–8734. https://doi.org/10.1016/j.tetlet.2007.10.023

[43] M. Sani, F. Pecker, G. C iani, M. Z a, L. Mulpezi, *Tetrahedron Let.* **2005**, *46*, 2393–2396. https://doi.org/10.1016/j.tetlet.2005.02.063

[44] Z. Xia, X. Lu, W. Wang, *Tetrahedron Lett.* **2011**, *52*, 4906–4910. https://doi.org/10.1016/j.tetlet.2011.07.057

[45] I. Yavari, Z. Hossani, M. Namatpour, *Monatsh chem.* **2010**, *141*, 229–232. http://dx.doi.org/10.1007/s00706-009-0247-y

[46] A. Malik, R. Pal, T. M al, A. Patra, D. Ghosal, *Synlett*, **2012**, *23*, 2459–2462. http://dx.doi.org/10.1055/s-0032-1317319

[47] A. Ali, E. Ahmed, K. Mokadam, *J. Heterocyclic chem.* **2011**, *44*, 1431–1438. https://doi.org/10.1002/jhet.5570440630

[48] P. Sasmal, J. Iqbal, S. Sridhar, *Tetrahedron Lett.* **2006**, *47*, 8661–8665. https://doi.org/10.1016/j.tetlet.2006.09.157

[49] G. Kumar Verma, A. Nagaraju, K. Raghuvanshib, G. Shukla, A. Srivastava, M. Singh, *RSC Adv.* **2014**, *4*, 11640–11647. https://doi.org/10.1039/C4RA00131A

[50] Y. Xiang, Y. Zhang, J. Song, Z. Guan, Y. He, D. Yang, *J. Org. chem.* **2016**, *81*, 6042–6048. https://doi.org/10.1021/acs.joc.6b01132

[51] R. Rios, I. Ibrahem, A.Cordva,H. Sunden, G. Zhao, *Tetrahedron Lett.* **2006**, *47*, 8679–8682. http://dx.doi.org/10.1002/chin.200713145

[52] O. Brun, A. Grus, J. Agramunt, C. Rovira, L. Raich, E. Pedrosa, *Org. Lett.* **2016**, *18*, 4836–4839. https://doi.org/10.1021/acs.orglett.6b02301

[53] L. Hua, Z. Yao, F. Xu, Q. Shen, *RSC Adv.* **2014**, *4*, 3113–3120. https://doi.org/10.1039/C3RA44829K

[54] R. A.Gayake, M. M. Kodape, S. A. Khiste, V. B. Jagrut, M. N. Lokhe, *Zeichen Journal* **2022**, *8*, 31–44. http://doi.org/15.10089.ZJ.2020.V08I07.285311.2934