ScienSage

Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

CELLULOSE SULPHURIC ACID (CSA) AS A BIODEGRADABLE, RECYCLABLE CATALYST FOR AN EFFICIENT FORMATION OF CARBON-SULPHUR BOND: EXPLORED THROUGH THE TRANSTHIOACETALIZATION OF ACETALS AND ACYLALS

Kailas R. Kadam

Padmashri Vikhe Patil College of Arts' Science and Commerce, Pravaranagar, Loni(kd), Rahata, Ahmednagar, Maharashtra, India

**Corresponding author: kailasshkadam@gmail.com*

ABSTRACT

Cellulose sulphuric acid (CSA) as a degradable, bio-polymeric acid was synthesized and its utility as an efficient, reusable catalyst was investigated for the transthioacetalization of O, O-acetals, S, O-acetals and acylals. Acetals and acylals of a diverse range of aldehydes as well as ketones were observed to undergo the conversion smoothly at room temperature in acetonitrile. High yields, very short reaction times, reusability of catalyst, environmental benign conditions are the salient features of the present protocol. Structures of the synthesized compounds were confirmed by their analytical studies such as ^{1}H NMR, ^{13}C NMR, Mass, FTIR and qualitative analysis.

Keywords: Cellulose sulphuric acid (CSA); Transthioacetalization; Carbon-sulphur bond; Biodegradable catalyst

1. INTRODUCTION

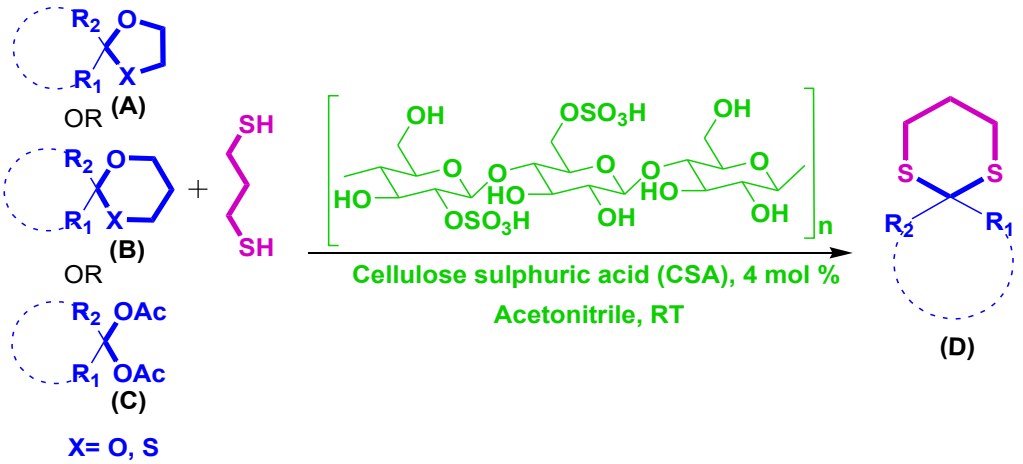
Carbon-sulphur bond is recognized as one of the widely distributed bonds among the natural products, synthetic drugs, agrochemicals and functional materials as well [1]. Many of the sulphur heterocycles are found to show a diverse range of pharmaceutical activities such as analgesic, antibiotic, antimicrobial, anti-inflammatory, antipsychotic, anti-diabetic, anticancer, anti-Alzheimer's, anti-Parkinson's, and anti-HIV [2]. This demonstrates the remarkable significance of the carbon–sulphur bond formation reactions in synthetic chemistry. However the C-S bond formation reactions are less focused as compared to the C-N, C-O and C-halogens bond formation reactions, which may due to the hurdles associated with sulphur precursors viz: susceptibility to oxidative dimerization [3], nucleophilic reactivity [4], metal catalyst poisoning ability [5] and hateful odor [6]. Conventional approaches of the carbon-sulphur bond formation mainly involved the addition of neucleophilic sulphur to unsaturation site, strained ring opening by sulphur nucleophile, nucleophilic substitution reactions and catalytic cross coupling reactions [7]. Recently, many inorganic reagents such as sulphur powder, sodium sulphide, sodium thiosulphate, sodium bi-sulphide, sodium tetra-sulphide, potassium thioacetate, potassium thiocyanate have been largely employed as the source of sulphur in organic synthesis [8]. Majority of reported carbon-sulphur bond formation processes took place through the monosulphenylation of substrates while the difunctionalization was rarely observed [9]. So here are the opportunities to expand the scope of difunctionalization reaction for the carbon-sulphur bond formation process. Therefore, it becomes highly anticipated to develop an expedient and efficient protocol for the C-S bond formation through the difunctionalization reaction. Dithioacetalization is a carbonyl protection procedure, a double addition-elimination route of thiol or dithiol to the carbonyl carbon has reported as a versatile method of C-S bond formation [10]. Due to the superior properties such as the ease of formation, inherent stability towards acidic or basic conditions [11] as well as the ability to revert the polarity of the carbonyl group [12], the 1,2-dithianes, or 1,3-dithianes became the preferred candidates for the dithioacetalization over the mono-thiols [11]. In addition to these, 1,2-dithianes, 1,3-dithianes and 1,3-dithiolanes can be directly reduced to their parent hydrocarbons by reductive desulphurization reaction [13]. Therefore, the dithioacetalization using 1,2-dithianes or 1,3-dithianes arose as a widely studying protocol for the protection of carbonyl group and in other sense the carbon-sulphur bond formation reaction as well [14]. Among the reported protocols, the condensation of a carbonyl compound with 1, 2 or 1, 3-dithiol is the most practical and direct apporch while the transthioacetalisation of acetals and acylals is an indirect but significant approach

[15]. It is worthy to note that almost all the transthioacetalization protocols work equi-smoothly for the chemoselective thioacetalization of aldehydes [16]. The literature survey revealed that thioacetal and transthioacetal preparations are the catalytic reactions and were reported to catalyze by Liwice acids [17], Braonsted acids [18], ionic liquids [19], microwave and UV-visible irradiations [20, 21]. Though, the protocols from literature worked well for the transthioacetalization but many of them carry one or more serious drawbacks such as environmental distraction, cumbersome procedures of preparing catalyst, moderate yields, prolonged reaction time, expensive and corrosive reagents, harsh reaction conditions, and tedious work-up procedures.

In recent days, some solid supported reagents such as SiO_2-$SOCl_2$ [22], SiO_2-$ZrCl_4$ [23], SiO_2-$HClO_4$ [24]. SiO_2-$FeCl_3$ [25], SiO_2-$Cu(OTf)_2$ [26], were found to catalyse the thioacetalization protection. Along with their own merits, all these supported reagents have the active catalytic part physisorbed on some suitable solid support (silica). Physisorption is a reversible phenomenon, which can easily revert by small change in temperature and pressure (Le Chatelier's principle), so the functioning of these catalysts at elevated temperature get restricted. Hence a convenient, facile and environmentally friendly route for the carbon-sulphur bond synthesis through the transthioacetalization is needed to be explored more.

The need of development of renewable and environmentally benign protocols for the organic synthesis has attracted the attention of the researchers, in this regard, the natural polymers such as gelatin, alginate, chistosan, cellulose and starch are the pretty candidates to explore as the recyclable, biodegradable catalyst supports [27]. Among the natural polymers, Cellulose and starch have been studied widely than any other polymers due to their anticipated properties such as the most natural abundance, renewable, biodegradable, readily available, safe to handle and high adsorption coefficient [28]. These advanced properties make it a potential alternative to the conventional inorganic supports in catalytic applications. The literature survey revealed that the cellulose sulphuric acid (CSA) has been employed as a biodegradable catalyst for many more biologically important transformations [29], but yet its' catalytic potential for the trans-thioacetalization of O,O- and S,O-acetals or acylals needs to be explored.

With this background and in continuing with our research to develop greener and convenient routes for the important organic transformations [30-33], herewith we wish to report our study on the use of cellulose sulphuric acid (CSA) as a biodegradable, recyclable, environmentally friendly catalyst for the transthioacetalization of O,O-acetals, / S, O-acetals or acylals (Scheme 1). A diverse range of acetals as well as acylals smoothly underwent the thioacetalization reaction to yield the corresponding products in good to excellent yields.



Synthetic Scheme 1

2. MATERIAL AND METHODS

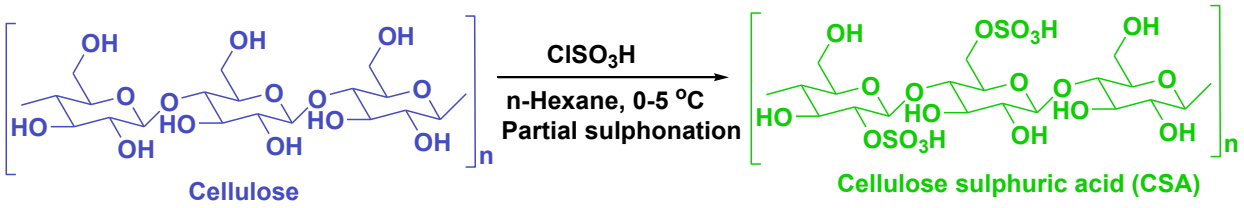
2.1. Material and experimental

All the chemicals used were purchased from the Loba or Merck chemical companies and used without further purification. ^{1}HNMR and ^{13}CNMR spectrums were recorded on BrukerAvance-II FT-NMR (400 MHz). The MASS spectrums were obtained from Waters micromass Q-Tof Micro mass spectrometer. The silica quoted aluminium plates were purchased from Merk Company were used to carry out thin layer chromatographic

checks. The melting points were observed in open capillary tubes by gradual heating in paraffin oil. The chemical structures were drawn using chem draw 0.8version software of Cambridge softwares.

2.2. Preparation of cellulose sulphuric acid (CSA)

Cellulose sulphuric acid (CSA) has been prepared according to the literature procedure [34], to a cold, stirring suspension of cellulose (5 g) in n-hexane (20 ml), 1 g of chlorosulphonic acid (9 mmol) was added dropwise (Scheme 2) over 30 minutes, the evolved HCl gas was neutralized by a scavenger assembly arranged along. After the completion of the addition the suspension was further stirred for 2 hrs at room temperature. The resulting suspension was filtered, washed with acetonitrile (3 x 10 ml) to remove any trace of unreacted chlorosulphonic acid, dried at room temperature, which produced the stable non-hygroscopic white power of cellulose sulphuric acid (CSA, 5.25 g).



Synthetic Scheme 2

2.3. General procedure for the transthioacetalization

A mixture of acetal or acylal (2 mmol) and propane-1,3-dithiol (2.2 mmol) and cellulose sulphuric acid (55 mg / 4.12 mol %) stirred together in dry acetonitrile at room temperature for a specific time as mentioned in table 2. The progress of the reaction was monitored by the TLC using n-hexane and ethyl acetate as the mobile phase. After completion of the reaction the insoluble catalyst was recovered by simple filtration. The solvent form the filtrate was removed under reduced pressure and so obtained crude product was purified by the suitable purification technique. The structures of the products were confirmed by the spectroscopic and analytical data. Spectroscopic characterizations of some of the representative compounds were done and the related data is given along.

3. RESULT AND DISCUSSION

In the preliminary phase of study, the synthesis of cellulose sulphuric acid (CSA) was achieved through the reported procedure [34]. The acid equivalents of the synthesized CSA was determined by a simple acid-base titration method and 1.5 milli bquivalents of acid per gram of the sample was observed with the CSA. In extension with our recent research on the CSA catalytic protection of carbonyl group, herein we explored the potential of the catalyst for the trans-thioacetalization of O,O-acetals, S,O- acetals and acylals. The precursors required for the study were already present with us as a part of our earlier study. To select the convenient solvent for the trans-thioacetalization reaction, a model reaction between 2-phenyl-1,3-dioxane (B 1), propane-1,3-dithiol with excess amount of CSA (100 mg) as a catalyst is carried out at room temperature in different solvents as noted in table 1.

It was observed that the trans-thioacetalization reaction took shortest reaction time in acetonitrile (Table 1, entry **5**) while longest in distilled water (Table 1, entry **1**), the obtained results are summarized in table 1. The solvents methanol and ethanol took comparable reaction time but less than that of acetonitrile. Rest of the solvents under study took longer to offer the considerable yields. After the selection of the solvent for the transformation, we shifted our attention on the optimization of the amount of the catalyst, for this study we employed different amounts of catalysts from 10 mg to 100 mg for the above model reaction at room temperature in acetonitrile, the obtained results are given in table 1. It was observed that the 55 mg (4.12 mol%) of CSA is sufficient to produce the optimized yield in shortest reaction time (Table 1, entry **19**). There were enhancement in yields and lowering in reaction time when the amounts of catalyst increased from 10 mg to 55 mg while further increase in amount of catalyst could not brought any positive effects.(Table 1, entry **11 -16**). The reuse profile of the CSA catalyst was examined with the above model reaction under optimized conditions. It was observed that the catalyst has produced comparable yields of the product with a minor extended reaction times after each cycle of reuse (Fig.1).

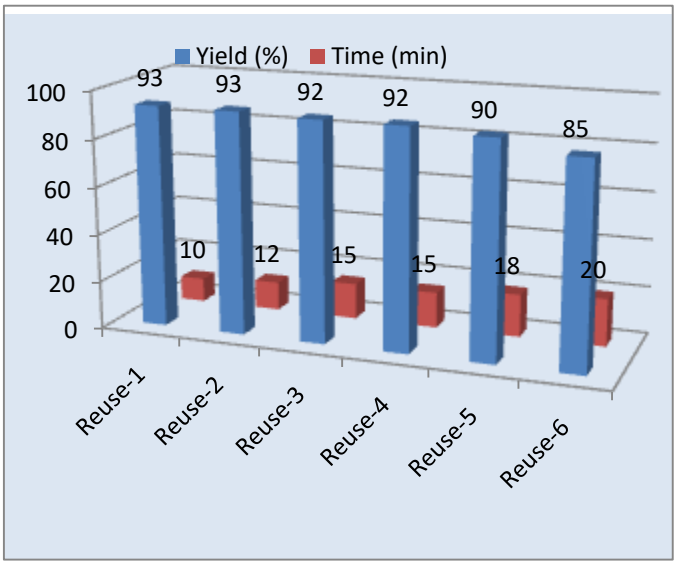


Fig. 1: Catalytic reusability study of cellulose sulphuric acid (CSA)

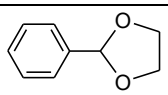
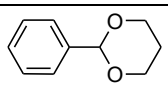
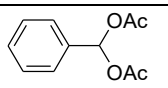
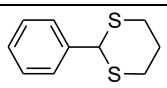
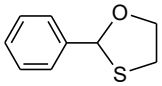
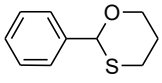
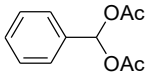
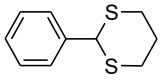
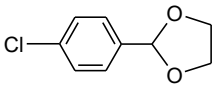
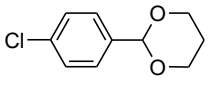
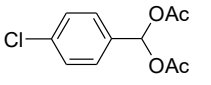
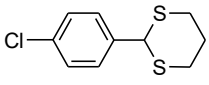
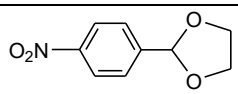
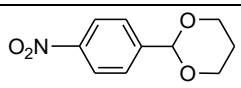
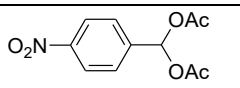
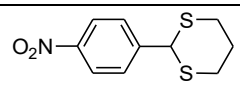
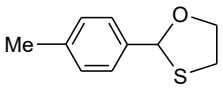
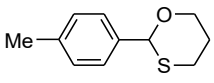
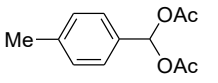
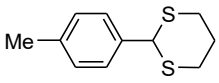
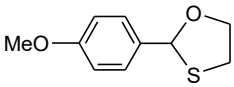
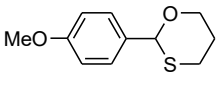
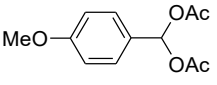
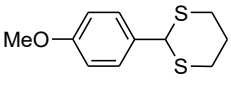
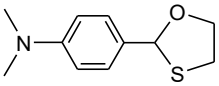
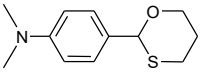
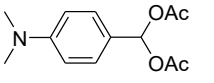
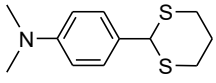
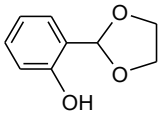
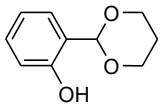
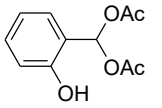
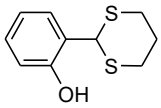
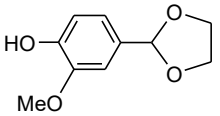
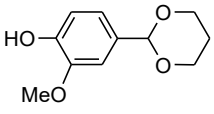
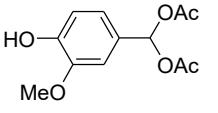
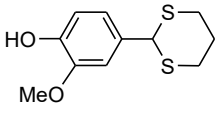
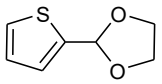
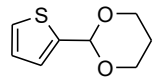
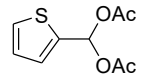
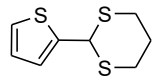
The generality of developed catalytic protocol was examined by employing it for the trans-thioacetalization of dioxolane, oxathiolane, dioxane, oxathiane and diacylals of aldehydes as well as ketones under the optimized conditions of solvent and catalyst. For this study the acetal, semithioacetal and acylal of benzaldehyde have been used as the model candidates. Among the model candidates, the six membered S, O-acetal (Table 2, **B2**) took the longest reaction time while the open chain acylal (Table 2, **C1**) took the shortest to produce the corresponding thioacetals (Table 2, **D1**). Among the six membered O,O-acetal (Table 2, **B1**) and five membered S,O-acetal (Table 2, **A2**) of benzaldehyde, later took little more reaction time than earlier. As expected, the electronic as well as the steric effect of substituents placed on aromatic ring have shown their effect on reaction coordinates. Substrates having electron withdrawing substituents (Table 2, entry **4**) required shorter reaction times while those having electron donating substituents (Table 2, entry **7**) took longer times to produce comparable yields. Steric effect of substituent also reflected well in terms of longer reaction time and reduced yields (Table 2, entry **8**).

Table 1: Optimization of reaction conditions for CSA catalyzed trans-thioacetalization of 2-phenyl-1.3-dioxane by propane-1,3-dithiol and comparison with reported catalyst.

Sr. No.	Catalyst	Reaction conditions	Catalyst amount (mg)	Time (min)	Yields* (%)
1.	CSA	Distilled water, RT	100 mg	6 hrs	<20
2.	CSA	MeOH, RT	100 mg	15	94
3.	CSA	EtOH, RT	100 mg	15	92
4.	CSA	DCE, RT	100 mg	30	85
5.	CSA	CH_3CN, RT	100 mg	8	94
6.	CSA	Dioxane, RT	100 mg	55	70
7.	CSA	THF, RT	100 mg	55	60
8.	CSA	DMF, RT	100 mg	65	55
9.	CSA	DMSO, RT	100 mg	80	45
10.	CSA	CH_3CN, RT	--------	6 hrs	trace
11.	CSA	CH_3CN, RT	10 mg	150	90
12.	CSA	CH_3CN, RT	20 mg	60	90
13.	CSA	CH_3CN, RT	30 mg	40	92
14.	CSA	CH_3CN, RT	40 mg	25	92
15.	CSA	CH_3CN, RT	50 mg	10	92
16.	CSA	CH_3CN, RT	60 mg	8	94
17.	CSA	CH_3CN, RT	70 mg	8	94
18.	CSA	CH_3CN, RT	100 mg	8	94
19.	CSA	CH_3CN, RT	55 mg (4.12 mol %)	8	94
20.	CSA	CH_3CN, RT	55 mg	8	94

**Isolated Yields*

Table 2: CSA catalyzed trans-thioacetalization of O,O-acetals, S,O-acetals and acylals under optimized condition

Entry	Substrate (A)	Substrate (B)	Substrate (C)	Product (D)	Yield (%) Time (min)		
					A	B	C
1.					95 7	94 8	95 5
2.					94 10	94 12	95 5
3.					95 7	94 7	95 5
4.					94 7	95 5	95 5
5.					90 12	92 12	92 8
6.					90 15	90 20	90 15
7.					86 20	86 25	85 20
8.					85 20	80 35	80 35
9.					88 15	85 20	88 18
10.					94 8	93 8	94 8
11.					94 10	90 12	94 10
12.					88 12	90 15	90 15
13.					86 25	85 30	88 25

4. SPECTROSCOPIC DATA OF REPRESENTATIVE COMPOUNDS

4.1. Spectroscopic data of 2-Phenyl-1,3-dithiane (D1)

FTIR (KBr, ν): 2926, 2897, 1643, 1515, 1458, 1415, 1279, 1237, 1176, 1023, 904, 885, 838, 729, 696, 677, 598, 507 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.43 (m, 2H), 7.37-7.27 (m, 3H), 5.16 (s, 1H), 3.15-2.86 (m, 4H), 2.22-1.83 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.3, 32.3, 51.6, 127.9, 128.6, 128.9, 139.2 ppm; MS-EI (70 eV, m/z): 196.22, 153.12, 131.22, 122.13, 121.11, 105.13.

4.2. Spectroscopic data of 2-(1,3-Dithian-2-yl)phenol (D7)

FTIR (KBr, ν): 3026, 2932, 2885, 1706, 1588, 1455, 1272, 1224, 1176, 1065, 1033, 888, 836, 789, 755, 695, 676, 598, 495 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30-7.26 (m, 1H), 7.22-7.15 (m, 1H), 6.90-6.86 (m, 2H), 6.44 (s, 1H), 5.40 (s, 1H), 3.10-3.02 (m, 2H), 2.96-2.86 (m, 2H), 2.22-2.12 (m, 1H), 1.96-1.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.10, 31.82, 47.53, 117.56, 120.94, 123.78, 129.39, 130.34, 154.66 ppm; MS-EI (70 eV, m/z): 212.0, 163.1, 135.0, 121.0, 90.0.

4.3. Spectroscopic data of 4-(1,3-Dithian-2-yl)-2-methoxyphenol (D8)

FTIR (KBr, ν): 3375, 2935, 2891, 1645, 1601, 1518, 1466, 1429, 1275, 1179, 1035, 946, 875, 766 and 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.01 (d, 1H), 6.96 (dd, 1H), 6.86 (d, 1H), 5.12 (s, 1H), 4.51 (s, 1H), 3.91 (s, 3H), 3.11-2.89 (m, 4H), 2.24-1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.12, 32.33, 51.33, 56.10, 110.22, 114.46, 120.86, 131.05, 145.88, 146.62. ppm; MS-EI (70 eV, m/z): 242.52, 200.15, 168.11, 148.41, 121.11, 84.20, 74.10.

4.4. Spectroscopic data of 3-(1,3-Dithian-2-yl)-indole (D11)

FTIR (KBr, ν): 3032, 2967, 2876, 1654, 1534, 1476, 1265, 1223, 1184, 1036, 910, 876, 843, 746, 689, 656, 589, 523 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 1H), 7.46 (d, 1H), 6.73 (d, 4H), 5.12 (s, 1H), 2.59 (t, 2H), 2.42 (t, 2H), 1.65 (t, 1H), 1.45 (t, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.68, 125.23, 122.88, 122.23, 119.55, 119.38, 113.82, 111.38, 42.71, 31.94, 25.18 ppm; MS-EI (70 eV, m/z): 235, 161, 120, 105.

4.5. Spectroscopic data of 2-Methyl-2-phenyl-1,3-dithiane (D12)

FTIR (KBr, ν): 3034, 2926, 1648, 1560, 1277, 1172, 1028, 906, 884, 696, 599, 502 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.43 (m, 2H), 7.37-7.27 (m, 3H), 3.15-2.86 (m, 4H), 2.22-1.83 (m, 2H), 1.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.21, 25.33, 32.38, 51.65, 127.96, 128.64, 128.95, 139.28 ppm; MS-EI (70 eV, m/z): 210.22, 1673.12, 131.22, 122.13, 121.11, 105.13.

4.6. Spectroscopic data of Compound (D13*)*

FTIR (KBr, ν): 2926, 2858, 1648, 1440, 1275, 1247, 1018, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.92-2.72 (m, 4H), 2.14 (d, 2H), 2.04-1.75 (m, 2H), 1.70-1.60 (m, 1H), 1.30-1.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.22, 25.71, 36.35, 26.62, 27.05, 27.82, 46.46, 54.28 MS-EI (70 eV, m/z): 216.12, 133.02, 109.10.

5. CONCLUSION

In summary, the synthesis of cellulose sulphuric acid (CSA) as a polymer supported acid has been achieved and its utility as a recyclable catalyst for the transthioacetalization of O,O-acetals, S,O- acetals and acylals were studied. Cellulose sulphuric acid (CSA) was observed as an efficient, recyclable, biodegradable, non-toxic, solid acid catalyst for the efficient and convenient synthesis of transthioacetalization.

6. ACKNOWLEDGEMENT

The author is thankful to the Head and Professor, department of chemistry, Institute of Science, Nagpur (India) for the fruitful discussions during the work. We acknowledge the financial support provided by BCUD, Savitribai Phule Pune University, Pune (India) in terms of research grants. We also acknowledge the SAIF, Panjab University, Chandigarh (India) for providing the necessary characterization facility.

6. REFERENCES

1. (a) Ilardi EA,Vitaku E,Njardarson JT.*J Med Chem,*2014; **57:** 2832-2842; b) Dunbar KL , Scharf DH, Litomska A, Hertweck C. *Chem Rev,* 2017; **117:**5521-5577.
2. (a) Vardanyan RS, Hruby VJ. Synthesis of essential drugs. Amsterdam: Elsevier; 2006. (b) Dewick PM, Medicinal natural products. 2nd ed. West Sussex (England): John Wiley & Sons; 2002.
3. WangL, HeW, Yu Z. *ChemSoc Rev,* 2013; **42:**599-621.
4. Xu X, Liu J, Zhang J, Wang Y, Peng Y. *OrgLett,* 2013; **15:**550-553.
5. Hegedus LL, McCabe RW. Catalyst poisoning. New York: Marcel Dekker;1984.
6. Kondo T, Mitsudo TA. *Chem Rev,* 2000; **100:**3205-3220.
7. Beletskaya IP, Ananikov VP. *Chem Rev,* 2011; **111:**1596-1636.
8. Liu H, Jiang X. *Chem Asian J,* 2013; **8:**2546-2563.

9. Bao Y, Yang X, Zhou Q, Yang F. *Org Lett,* 2018; **20:** 1966-1969.
10. Kamble VT, Bundgar BP, Muley DB, Joshi NS. *J MolCatal A: Chem,* 2007; **268:**70-75.
11. Greene TW, Wuts PGM. Protective groups in organic synthesis, 3rd ed. New York: John Wiley and Sons; 1999.
12. (a) Seebach D. *Angew ChemInt Ed Engl*, 1969; **8:**639-649; (b) Seebach D. *Angew Chem Int Ed Engl*, 1979; **18:**239-258; (c) Bulman Page PC, Van Niel MB, Prodger J. *Tetrahedron,* 1989;**45:**7643-7677; (d) Corey EJ, Seebach D. *Angew Chem Int Ed Engl,* 1965; **4:**1075-1077.
13. Olsen RK, Currier Jr JO. *The chemistry of the thiolgroup ed. S Patai*.New York: John Wiley & Sons; 1974, Part 2, P. 519.
14. (a) Ralls JW, Dobson RM, Reigel B. *J Am ChemSoc,*1949; **71:**3320-3325. (b) Nishino K, Minato K, Miyazaki T, Ogiwara Y, Sakai N. *J Org Chem,*2017; **82:**3659-3665.
15. Hu PF, Dong B, Zhou ZP, Chen WD, Zeng BB. *Chemistry Select,* 2019; **4:**10798-10804.
16. (a) Bandgar BP, Joshi NS, Bettigeri SV. *Monatsh Chem,* 2007; **138:**67-71. (b) Fahid F, Pourmousavi S. *J Sulfur Chem,* 2015; **36:**16-29.
17. (a) Firouzabadi H, Iranpoor N, Karimi B. *Synthesis,*1999; **1:**58-60. (b) Besra RC, Rudrawar S, Chakraborti AK. *Tetrahedron Lett,* 2005;**46:**6213-6217. (c) Lai JS, Du WB, Tian LX, Zhao CG, She XG, Tang SC. *Org Lett,* 2014;**16:**4396-4399.
18. Yan OY, Dong DW, Zheng CB, Yu HF, Liu Q, Fu ZO. *Synthesis,* 2006; **22:**3801-3804. (b) Rudrawar S, Besra RC, Chakraborti AK. *Synthesis,* 2006; **16:**2767-2771.
19. (a) Hajipour AR, Hosseini P, Ruoho AE. *Phosphorus, Sulfur Silicon Relat Elem,* 2008;**183:**2502-2508. (b) Hajipour AD, Azizi G, Ruoho AE. *Synlett,* 2009; **12:**1974-1978. (c) Bao SH, Chen L, Ji YJ, Yang JG. *Chin J Chem,* 2010; **28:** 2119-2122.
20. (a) Bez G, Gogoi D. *Tetrahedron Lett,* 2006; **47:**5155-5157. (b) Gupta N, Kad GL, Singh J. *CatalCommun,* 2007; **8:**1323-1328. (c) Zarei A, Hajipour AR, Khazdooz L, Mirjalili BF, Zahmatkesh SJ. *J MolCatal A: Chem,* 2009; **301:**39-46.
21. (a) Xing ZM, Yang MY, Sun HY, Wang ZM, Chen P, Liu L, et al. *Green Chem,* 2018; **20:**5117-5122. (b) Chaiseeda K, Chavasiri W. *Phosphorus, Sulfur Silicon Relat Elem,* 2017; **192:**1034-1039.
22. Kamitori Y, Hojo M, Masuda R, Kimura T, Yoshida TJ. *Org Chem,* 1986; **51:**1427-1431.
23. Patney HK, Margan S. *Tetrahedron Lett,* 1996; **37:**4621-4622.
24. Rudrawar S, Besra RC, Chakraborti AK. *Synthesis*, 2006; **16:** 2767-2771.
25. Patney HK. *Tetrahedron Lett*, 1991; **32:**2259-2260.
26. Anand RV, Saravanan P, Singh VK. *Synlett,* 1999; **3:**415-416.
27. Breslow R. *AccChem Res,* 1980; **13:**170-177.
28. Klemm D, Heublein B, Fink HP, Bohn A. *Angew Chem Int Ed*, 2005; **44:**3358-3393.
29. (a) Murthy Y, Rajack A, Taraka RM, Praveen C, Aruna Lakshmi K. *Bioorg Med Chem Lett,* 2012; **22:**6016-6023. (b) Alinezhad H, Haghighi AH, Salehian FA. *Chin Chem Lett,* 2010; **21:**183-186. (c) Nemati F, Elhampour A. *ScientiaIranica,* 2012; **19:**1594-1596.
30. Kamble VT, Tayade RA, Davane BS, Kadam KR. *Aust J Chem,* 2007; **60:**590-594.
31. Kamble VT, Kadam KR, Joshi NS, Muley DB. *Catal Commun,* 2007; **8:**498-502.
32. Waghmare AS, Patil TD, Kadam KR, Pandit SS. *Iran J Catal,* 2015; **5:**1-8.
33. Kadam KR. *J. Sulfur Chem*, 2020; **41:**530-541.
34. Safari J, Banitaba SH, Khalili SD. *J MolCatal A: Chem,* 2011; **335:**46-50.