

Protection of hydroxy groups as trimethylsilyl ethers catalyzed by magnetically recyclable Schiff-base complexes of ruthenium using HMDS

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Abstract

In this study, a stable and effective magnetically recoverable nanocatalyst was prepared by coating Fe₃O₄ nanoparticles with SiO₂, followed by functionalization with N-(2-aminoethyl)-3-amino-propyltrimethoxysilane (AEPTMS) and production of Schiff base ligand to link Ru(OTf)₂ onto the surface. The nanocatalyst was characterized using various techniques such as FT-IR spectroscopy, SEM, TEM, and VSM to confirm its successful synthesis. The nanocatalyst was used for the trimethylsilylation of various alcohols (primary, secondary, and tertiary alcohols) using hexamethyldisilazane as a silylating agent in dichloromethane at room temperature. The reaction proceeded quickly with a protection time of only 90 seconds, which is a remarkable advantage of this nanocatalyst. The turnover frequency (TOF) values of the catalytic system were estimated to be 1869 h⁻¹. The use of this nanocatalyst offers many advantages, such as excellent yield, catalyst reusability, high acidity, and strong magnetic properties. These advantages make it a fascinating candidate for green chemistry principles. The simple reprocessing procedure and quick response times are also additional benefits of this nanocatalyst. Overall, this study provides a promising approach for the facile preparation of a stable and effective magnetically recoverable nanocatalyst that can be utilized for the trimethylsilylation of alcohols. The exceptional properties of this catalyst make it an attractive candidate for practical applications in the field of catalysis.

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Article info:

Received: 27 July 2023

Revised: 29 September 2023

Accepted: 20 November 2023

Keywords

Salen Ru(OTf)₂, protection, hydroxy compound, Nanocatalyst, Schiff base

1. INTRODUCTION

The protection of functional groups is a crucial step in multi-step syntheses of complex organic molecules (Wuts and Greene, 2006). Also this is an important process in synthetic organic and analytical chemistry (Sartori et al., 2004; Wan et al., 2007). To achieve this, various protective methods have been described in the literature, such as acetylation (Inoue et al., 2023), tetrahydropyranlation (Arnodo et al., 2023), methoxymethylation (van Melis et al., 2019), and trimethylacetylation (Changmai and Rokhum, 2020; Mehdigholami and Koohestanian, 2023). Among the various strategies for protecting hydroxyl groups, the conversion of alcohols to their corresponding silyl ethers is widely used and highly popular. 1,1,1,3,3,3-hexamethyldisilazane (HMDS) has become a versatile reagent for the trimethylsilyl (TMS) protection of alcohols and phenols. This commercially available and stable compound is convenient to handle and its workup is straightforward due to the production of ammonia as the only byproduct. However, its low silylation power poses a limitation to its application (Karimi and Golshani, 2000; Lalonde and Chan, 1985). As a result, various catalytic systems have been developed to activate HMDS. For example, Rahmzadeh et al. (2021) utilized ionic liquids, namely [H₂-DABCO][ClO₄] and [H₂-Bisim][ClO₄]₂, in

the role of catalysts to the protection of alcohols into their corresponding trimethylsilyl (TMS) derivatives. The experiment involved adding a mixture of alcohol (1 mmol) and HMDS (1.3 mmol) to either [H₂-Bisim][ClO₄]₂ (0.25 mmol) or [H₂-DABCO][ClO₄]₂ (0.75 mmol), and stirring the resulting mixture in an oil bath at 100 °C for 30 minutes. The limitations of this work include the high reaction temperature required, and the need for separation of the catalyst from the reaction mixture, which requires methods such as centrifugation. Yao et al. (2021) employed a Salamo-based Zn complex supported on Fe₃O₄ MNPs for the protection of alcohols. The reaction involved stirring a mixture of alcohols (1 mmol), HMDS (0.8 mmol), and Fe₃O₄@H₂L-Zn (6 mg) under solvent-free conditions at room temperature, with the progress of the reaction being monitored by TLC. The reaction time for alcohols such as 4-chlorobenzyl alcohol was 10 minutes with a 100% yield. Zolfigol et al. (2018), utilized a catalyst of nano-MCM-41@[(CH₂)₃-1-methylimidazole]Br₃ in CH₂Cl₂ and achieved a yield of 96% in 35 minutes. Another research conducted by Zareyee et al. (2011) employed a CMK-5-SO₃H catalyst in CH₂Cl₂ to protect TMS-alcohol, which resulted in a 90% yield after 30 minutes. Lastly, Abri and colleagues (Abri and Ranjdar, 2014), utilized NaHSO₄.SiO₂ as a nanocatalyst at room temperature and achieved a yield of 100% within just 7 minutes.



The stability, structural variability, facility of preparation, and variety of applications make metal Schiff base complexes important in coordination chemistry (Nag et al., 2004). The salophen and salen ligands, which contain N and O donor atoms, are particularly significant as their resulting metal complexes have extensive uses as catalysts in various organic reactions (Katsuki, 1995). Ruthenium complexes are known for their versatility as electron transfer compounds, with a wide range of application areas including oxidation catalysts, probes for biological macromolecules, and organic synthesis. Recent studies have focused their attention on the study of ruthenium complexes, particularly those containing Schiff bases (Buldu-run and Özdemir, 2020; Premkumar et al., 2019; Singh and Barman, 2021). These complexes are considered optimal for versatile catalytic processes due to the stability and resistance of the Schiff base ligands to various organic functionalities, air, and moisture (Chen and Han, 2022; Nagajothi and Maheswari, 2021). Moreover, these complexes exhibit an appropriate balance between the electronic and steric environments of the metal core. An additional advantage is that Schiff bases can be readily prepared in a one-step process by near quantitative condensation of an excess aldehyde with a common amino compound. Ruthenium complexes are known for their reactivity in organic synthesis, but their reusability and stability present practical limitations. To overcome these problems, various methods have been used, including the immobilization of the catalysts on different supports (Chołuj et al., 2020; Leckie and Mapolie, 2019; Skrodzki et al., 2021; Xia et al., 2021). This can be achieved by grafting the catalyst using covalent bonding or by simple adsorption in polymer matrices or porous inorganic materials. Another promising approach is the use of magnetic nanoparticles as supports (Kazemi and Shiri, 2022; Lv et al., 2020; Wang et al., 2022), which have attracted considerable attention due to their potential advantages. Particles have a large surface-to-volume ratio that enhances catalyst accessibility and activity, and their customizable shape and size allow easy and efficient separation from reaction mixtures using an external magnet without filtration or centrifugation steps or tedious processing (Al-Anazi, 2022; Bhole et al., 2022; Shalini et al., 2023). The ability to recover and reuse a catalyst is an important aspect of many catalytic processes (Kamalzare et al., 2021). In heterogeneous systems, the catalyst needs to be separated and recovered through centrifugation or filtration (Miceli et al., 2021). Nanoparticles have gained significant attention in catalysis due to their higher specific surface area compared to their bulk counterparts. However, recovering these tiny nanoparticles from the reaction media is not a simple process (Martin et al., 2021). To address this issue, the use of magnetic nanocatalysts has emerged as a viable solution. The paramagnetic character of the support allows for easy and efficient recovery of the magnetically supported catalysts with an external magnet, enabling them to be reused in subsequent cycles. Magnetic nanocatalysts have been employed in a wide range of reactions with desired activities, and their surface can be functionalized during catalyst preparation (Martin et al., 2021; Wang et al., 2020; You et al., 2021).

This study focuses on achieving a high yield synthesis of silyl ether substructures by protecting alcohols and phenols with silyl groups. To achieve this, salen-based-Ru catalytic complex-functionalized magnetically separable nanocomposite was used as a recyclable and reusable nanocatalyst. The synthesized nanocatalyst has shown improved efficiency for various catalytic applications. Notably, it has been found that the magnetic properties enable easy separation and efficient recovery with an external magnet. This has eliminated the need for more complicated and time-consuming separation methods, such as centrifugation or filtration. The magnetic nanocatalyst has proven to be a successful heterogeneous catalyst, which can be easily separated from the reaction mixture using a magnet.

2. EXPERIMENTAL INVESTIGATION

The study used chemical materials obtained from two reputable sources, Merck and Aldrich chemical companies, the purity of the substance used is approximately 96 to 100 percent and the resulting yields indicated the isolation of pure products.

2.1. Method

The products were characterized through spectral comparison. FT-IR spectra were obtained using a JASCO 6300 spectrophotometer, with potassium bromide pellets in the range of 400–4000 cm^{-1} . The experimental method utilized a Shimadzu GC-16A instrument $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CAA}$, equipped with a 2m column filled with either silicon DC-200 or Carbowax 20m. Transmission electron micrographs (TEM) of the magnetic nanoparticles were obtained using a Philips CM 120 TEM instrument. The SEM image acquisition was done using a scanning electron microscope (IROST) with an acceleration voltage of 15.00.

2.2. Synthesis method of silica-coated iron oxide nanoparticles

The co-precipitation method was utilized to synthesize magnetite (Fe_3O_4) particles. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (8.5 g, 31.45 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.0 g, 15.27 mmol) were dissolved in 38 mL of 0.4 M HCl under an argon atmosphere. Then, by addition of 375 mL of 28 wt% aqueous NH_4OH , a black precipitate was created, which was vigorously stirred for 30 minutes at room temperature. The black precipitate was collected using an external magnet positioned under the reaction flask, and the supernatant was decanted before washing the precipitate three times with deionized water. The sediment was then redispersed in 150 mL of deionized water, and a suspension of 50 mL of this solution with 20 mL of

2-propanol and PEG-400 (11.58 mL), NH₄OH (25 mL), deionized water (50 mL), TEOS (30 mL), and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane as a modifier was subjected to ultrasonic treatment for 20 minutes. The suspension was stirred under an argon gas atmosphere for 24 hours, and the resulting product was dried under vacuum. The nitrogen content of the product was determined to be 1.3% by CHN analysis.

2.3. Preparation method of Schiff complex synthesis

For the synthesis and immobilization of Schiff base, 500 mg of precipitate from the previous step and 5 mL of salicylaldehyde in acetonitrile (80 mL) were added and the mixture was stirred vigorously for 48 hours under reflux conditions at 80 °. The solid was collected with a magnet, washed thoroughly with acetone and ethanol, and dried in vacuum at room temperature for several hours.

2.4. Preparation Fe₃O₄@SiO₂/AEPTMS/Salen/Ru(Cl)₂

For the immobilization of RuCl₃·6H₂O on the magnetic Schiff base nanoparticles, 250 mg of RuCl₃·6H₂O and 500 mg of precipitate from the previous step and sodium acetate (20 mg) were stirred in 100 mL of acetonitrile for 48 hours under reflux.

The precipitate was collected with an external magnet, rinsed three times with ethanol and dried in vacuum.

2.5. Preparation Fe₃O₄@SiO₂/AEPTMS/Salen/Ru(OTf)₂

In the final step, the sediment obtained from the previous step was stirred with 0.6 mmol NaOTf to replace the Cl⁻ ligand with OTf⁻, for one hour in 20ml THF solvent at 60 °. Then, the precipitate was washed several times with acetone, and dried at room temperature. (Fig. 1)

3. RESULTS AND CHARACTERIZATION

The catalyst was analyzed using various techniques, including CHN analysis, ICP FT-IR spectroscopy, SEM and TEM imaging. The nitrogen content of the supported catalyst was found to be approximately 1.3 mmol g⁻¹ by CHN analysis, while the ruthenium content was determined to be 0.0214 mmol g⁻¹ of the supported catalyst by ICP analysis.

The FT-IR spectra of both the unfunctionalized and functionalized magnetic nanoparticles (Fig. 2) showed the presence of a Fe–O stretching vibration at approximately 590 cm⁻¹, indicating the presence of iron oxide on the surface of the nanoparticles. Additionally, there was an O–H stretching vibration due to physisorbed water and potentially surface

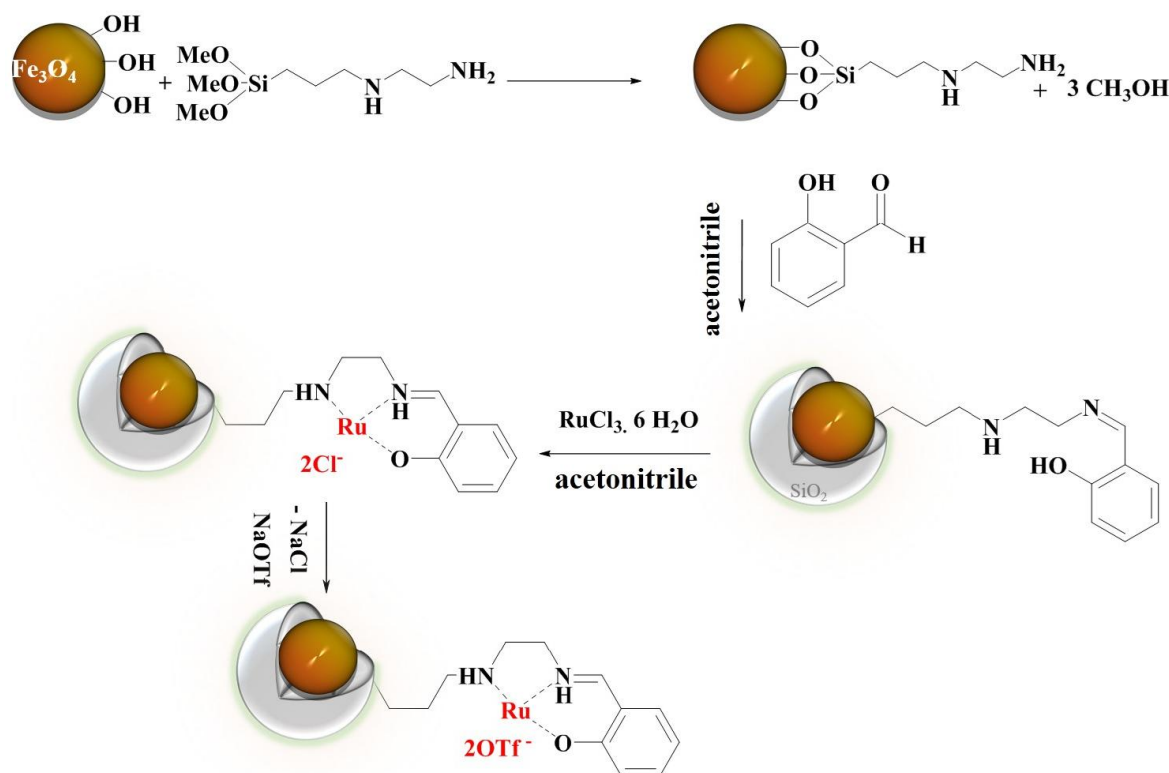


Figure 1. Scheme of synthesis of Fe₃O₄/SiO₂/AEPTMS/Salen/Ru(OTf)₂.

hydroxyls near 3434.6 cm^{-1} in the functionalized nanoparticles. In the case of the amine-functionalized nanoparticles, the immobilized Schiff base, and the immobilized ruthenium catalyst, the appearance of peaks near 1038 cm^{-1} indicated the presence of Si-O stretching vibrations. Moreover, the immobilized ligand and the catalyst showed the appearance of peaks near 2943.8 cm^{-1} and 2878.2 cm^{-1} due to $-\text{CH}_2$ vibrations. The sharp band at 1616 cm^{-1} was assigned to the $-\text{C}=\text{N}$ stretching vibration of the imine group of the ligand, indicating the formation of the Schiff base (Koc and Ucan, 2007). These features suggest that the functionalization process was successful and that the ligand and catalyst were successfully immobilized onto the surface of the magnetic nanoparticles.

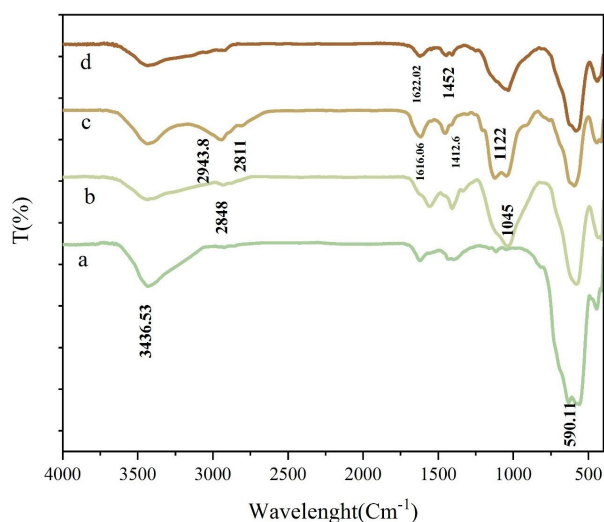


Figure 2. FT-IR spectrum related to a) Fe_3O_4 , b) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{AEAPTMS}$, c) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Salen}$, d) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Salen}/\text{Ru}(\text{OTf})_2$.

SEM analysis was used to investigate the morphology and size of the samples. The SEM images showed that the samples had a uniform morphology and were composed of spherical particles with an average size of 27 nm. The particles were well-dispersed and showed no significant agglomeration (Fig. 3).

TEM was utilized to investigate the core-shell structure of the sample (Fig. 4). The TEM image revealed that the sample had a core-shell structure. The TEM analysis demonstrated the effectiveness of the synthesis method used to produce a core-shell structure with well-defined boundaries, which is important for improving the performance of the sample in various applications. The particle size measured by TEM is consistent with that obtained by SEM.

In addition, according to the results of energy dispersive X-ray (EDX) analysis, $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{AEAPTMS}/\text{Salen}/\text{Ru}(\text{OTf})_2$ nanoparticles (Fig. 5), confirm the presence of elements of Fe, O, Si, N, C, Ru and F in this material.

The high saturation magnetization of the nanoparticles, which quantifies their maximum magnetic strength, was

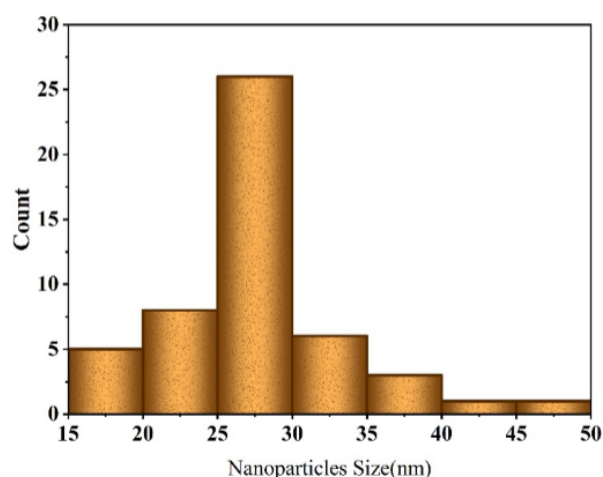
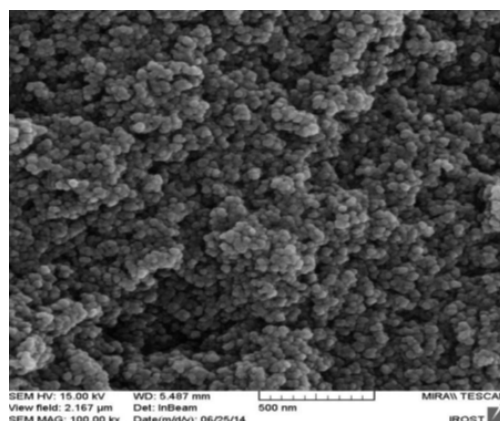


Figure 3. SEM images of a) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{AEPTMS}/\text{Salen}/\text{Ru}(\text{OTf})_2$ catalyst nanoparticles, b) histogram related to SEM electron microscope image of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{AEPTMS}/\text{Salen}/\text{Ru}(\text{OTf})_2$ catalyst nanoparticles.

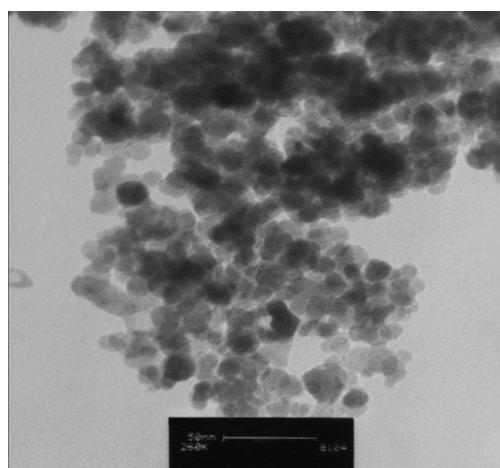


Figure 4. TEM image of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{AEPTMS}/\text{Fe}(\text{OTf})_3$ nanoparticles on a scale of 50 nm.

demonstrated in the magnetization curves obtained from VSM analysis (Fig. 6). The saturation magnetization values for Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{AEPTMS}/\text{Salen}/\text{Ru}(\text{OTf})_2$ nanoparticles were 69.4845 emu, 43.4457

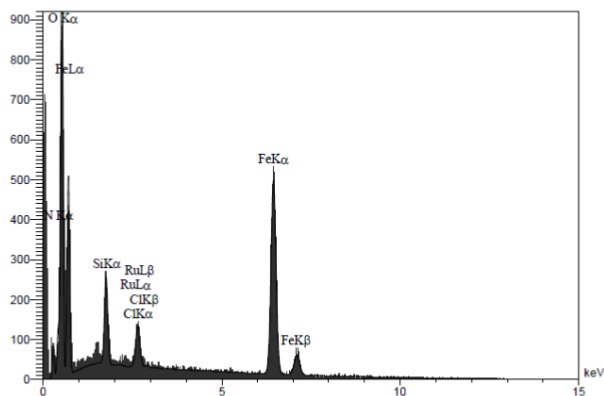


Figure 5. The results of EDX analysis of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{AEPTMS}/\text{Salen Ru}(\text{OTf})_2$ catalyst nanoparticles.

emu/g, and 37.5647 emu/g, respectively. Despite the silica coating reducing the saturation magnetization, the nanoparticles still had sufficient levels of magnetization for magnetic separation using an ordinary magnet. The absence of a hysteresis loop in the magnetization curve confirmed that the synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{AEPTMS}/\text{Salen}/\text{Ru}(\text{OTf})_2$ nanoparticles were superparamagnetic and could be easily separated from the mixture with an external magnetic field.

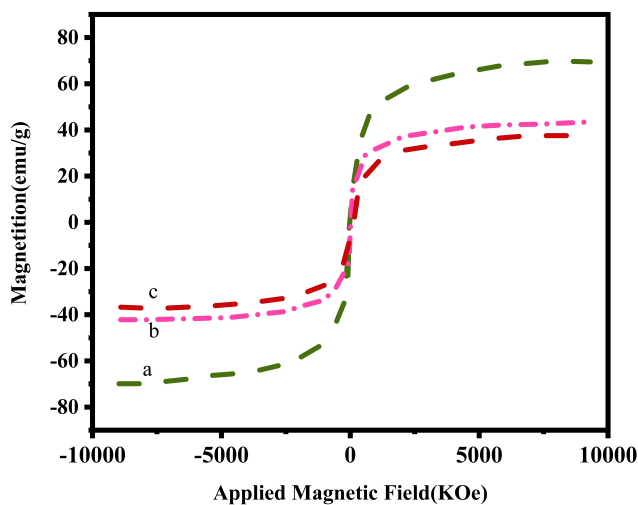


Figure 6. VSM diagrams related to a) Fe_3O_4 b) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ c) $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{AEPTMS}/\text{Salen Ru}(\text{OTf})_2$.

4. RESULTS AND DISCUSSION

At the beginning of the investigation, 4-chloro benzyl alcohol (1.0 mmol) was reacted with HMDS (1.0 mmol) as a model to evaluate the suitability of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{AEPTMS}/\text{Salen Ru}(\text{OTf})_2$ (50 mg) as a catalyst in different solvents (Table 1). It was found that CH_2Cl_2 was the most efficient and rapid solvent for the silylation of alcohols (Table 1, entry 1).

The amount of catalyst was also screened, and it was observed that the reaction did not significant yield in the absence of

Table 1. The impact of solvents on the protection of alcohols and phenols with HMDS in the presence of a $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{AEPTMS}/\text{Salen}/\text{Ru}(\text{OTf})_2$.

Yield (%) ^b	Solvent	Entry
100	CH_2Cl_2	1
56	CHCl_3	2
82	CH_3CN	3
34	THF	4
61	CH_3COCH_3	5

a) Reaction conditions: 4-chlorobenzyl alcohol (1 mmol), hexamethyl disilazane (1 mmol), catalyst (0.214 mmol), and solvent (1 mL) were reacted for 1.5 minutes.

b) The yield was determined by GC analysis based on 4-chlorobenzyl alcohol.

catalyst. (Table 2, entry 1). The highest yield of TMS ether was obtained with 45 mg of nanocatalyst. After 1.5 minute (Table 2, entry 4), and increasing the amount of the catalyst did not significantly improve the yield (Table 2, entry 5).

Table 2. The effect of amount of the Catalyst on the protection of alcohols and phenols using HMDS.

Yield (%) ^b	Catalyst mg (mmol) ^a	Entry
8	0 (0.000)	1
85	20 (0.012)	2
94	30 (0.017)	3
100	45 (0.0214)	4
100	50 (0.0245)	5

a) Reaction conditions: 4-chlorobenzyl alcohol (1 mmol), hexamethyldisilazane (1 mmol), catalyst, and dichloromethane (1 mL) for a duration of 1.5 minutes.

b) The yield was determined by GC analysis based on 4-chlorobenzyl alcohol.

Lowering the amount of HMDS to 0.6 mmol in the same reaction also produced the highest yield of TMS ether with 1 mmol of HMDS (Table 3, entry 2). Therefore, the best

Table 3. The effect of amount of HMDS on the protection of alcohols and phenols in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{AEPTMS}/\text{Salen}/\text{Ru}(\text{OTf})_2$ catalyst.

Yield (%) ^b	HMDS mg (mmol) ^a	Entry
79	80 (0.5)	1
100	96 (0.6)	2
100	160 (1)	3

a) Reaction conditions: 4-chlorobenzyl alcohol (1 mmol), catalyst, and dichloromethane (1 mL) for a duration of 1.5 minutes.

b) The yield was determined by GC analysis based on 4-chlorobenzyl alcohol.

results were obtained in the presence of 45 mg of the nano catalyst within 0.6 mmol HMDS in 1 mL CH₂Cl₂ at ambient temperature.

4.1. Typical Process for Trimethylsilylation hydroxyl compound with HMDS catalyzed by Fe₃O₄@SiO₂/AEPTMS/Salen Ru(OTf)₂

The present study expands the general procedure for trimethylsilylation hydroxyl compound with HMDS catalyzed by Fe₃O₄@SiO₂/AEPTMS/Salen Ru(OTf)₂ (Fig. 7). Initially, a mixture of alcohol or phenol (1 mmol) and HMDS (0.6mmol per OH group) in CH₂Cl₂ (1 mL) was prepared. Subsequently, 45 mg of catalyst (0.0214 mmol Ru) was added to the mixture and stirred at room temperature. The progress of the reaction was monitored by GC. Upon completion of the reaction, Et₂O (10 mL) was introduced, and the catalyst was separated by a magnet. The filtrates were meticulously washed with brine, dried, and concentrated under reduced pressure to afford the crude product (Table 4).

The evaluation of the catalytic performance was conducted through the utilization of turnover frequency (TOF) values, which are indicated as (TOF) = TON divided by the time of the reaction. The turnover number (TON) is represented as the number of moles of reactant consumed per mole of catalyst. The determination of TOF was carried out using Equations (1) and (2) (Gonzalez-Carrillo et al., 2020).

$$\text{TON} = \text{mole product obtained} / \text{mole catalyst} \quad (1)$$

$$\text{TOF}(h - 1) = \text{TON} / \text{reaction time (h)} \quad (2)$$

Under the optimized conditions, a wide range of primary and secondary alcohols were successfully trimethylsilylated with HMDS in the presence of catalyst. Electron-withdrawing substituents on benzylic alcohols required longer reaction times for completion, while benzylic alcohols bearing electron-donating substituents were completed in shorter reaction times. Steric hindrance caused by ortho substituents on benzylic alcohols did not affect the reaction time, except for 2-nitrobenzyl alcohol. It was found that intramolecular hydrogen bonding between the hydroxyl and nitro groups in

2-nitrobenzyl alcohol reduced the acidity of the alcohol and therefore required a longer reaction time for silylation.

These results suggest that the Fe₃O₄@SiO₂/AEPTMS/Salen Ru(OTf)₂ catalyst is an effective catalyst for the silylation of alcohols with HMDS, and that the reaction conditions can be optimized for different substrates to achieve high yields. In the case of linear, secondary, and tertiary alcohols, the reaction times were longer compared to benzylic alcohols. The trimethylsilylation of phenols was also investigated, and the corresponding TMS ethers were produced in high yields.

Table 4 shows the TOFs for some alcohols and phenols, which demonstrate the high catalytic activity of the catalyst in these reactions. Overall, these findings suggest that the Fe₃O₄@SiO₂/AEPTMS/Salen/Ru (OTf)₂ /HMDS system is an efficient and selective catalyst for the trimethylsilylation of alcohols and phenols, and has potential applications in organic synthesis.

Figure 8 illustrates a suggested mechanism for trimethylsilylation reactions that utilizes a Lewis acid-base interaction strategy. Specifically, the nitrogen atom of hexamethyldisilazane acts as a base and is connected to Ruthenium, which functions as a Lewis acid, resulting in the formation of an active intermediate. The intermediate undergoes an attack by an oxygen group, resulting in the formation of silyl ether compounds and the release of the catalyst for the next reaction cycle. The release of ammonia gas, detectable using litmus paper, serves as evidence for this mechanism.

4.2. Catalyst recycling

The study evaluated the recyclability of the catalyst by conducting experiments using 4-chlorobenzyl alcohol as a model substrate. The experiments involved using an external magnet to separate the catalyst from the reaction mixture, followed by washing the solid twice with 1, 2-dichloroethane. The catalyst was then reused for the next run with a fresh substrate dissolved in the same solvent. The study found that the catalyst could be consecutively reused up to ten times without any significant decrease in its catalytic activity. This demonstrates the potential for the catalyst to be used repeatedly, which could lead to cost savings and reduce the environmental impact of

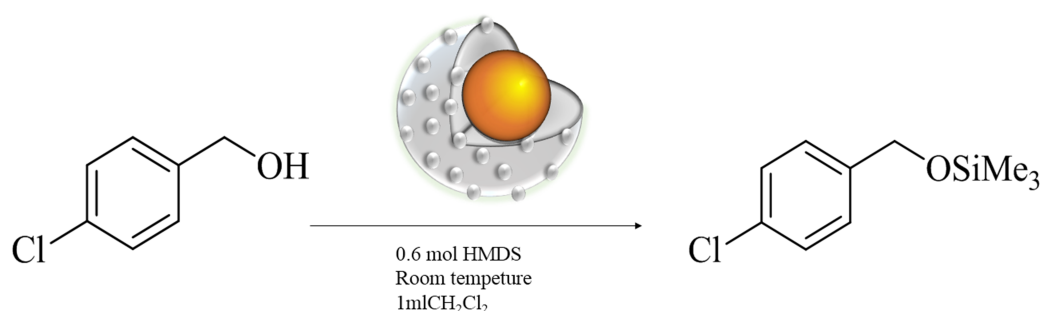
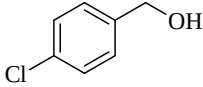
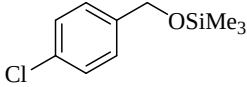
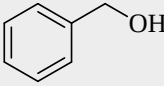
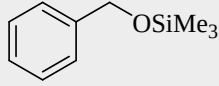
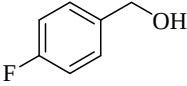
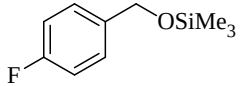
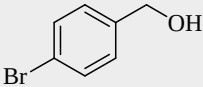
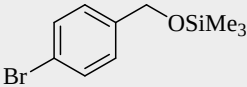
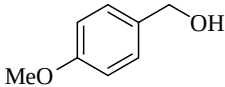
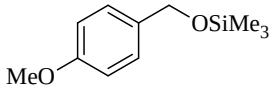
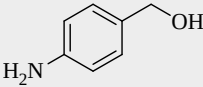
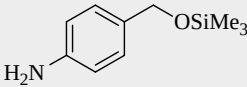
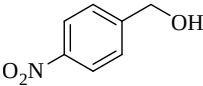
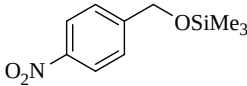
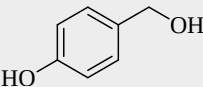
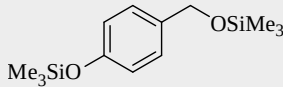
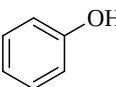
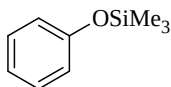
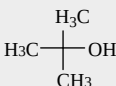
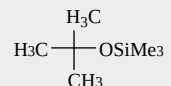
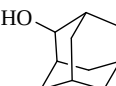
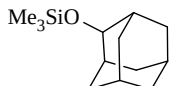
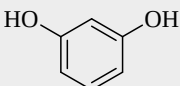
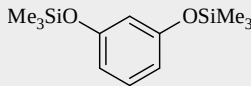
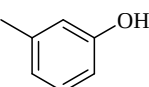
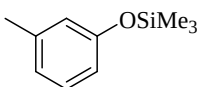
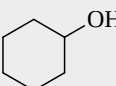
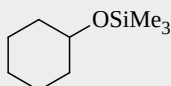
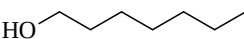
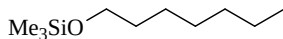


Figure 7. Protection of alcohol with HMDS by Fe₃O₄@SiO₂/AEPTMS/SalenRu(OTf)₂ catalyst nanoparticles.

Table 4. Trimethylsilylation of alcohols and phenols with HMDS catalyzed by $\text{Fe}_3\text{O}_4\text{@AEAPTMS}/\text{SalenRu}(\text{OTf})_2$ at room temperature.

Tof (h^{-1})	Yield ^b (%)	Time (min)	TMS-ether	Hydroxy compound	Entry
1869	100	1.5			1
1869	100	1.5			2
1869	100	1.5			3
1869	100	1.5			4
1869	100	1.5			5
1869	100	1.5			6
700.7	100	4			7
869	93	3			8 ^c
1812	97	2			9
1475	96	2			10
887.7	95	3			11
869	93	3			12 ^c
934.5	100	3			13
869	93	3			14
887	95	3			15

a) Reaction conditions: alcohol or phenol (1 mmol), HMDS (0.6 mmol), catalyst (45 mg, 0.0214 mmol Ru), CH_2Cl_2 (1 mL).

b) GC yield.

c) Reaction was performed with 0.6 mmol of HMDS per OH group.

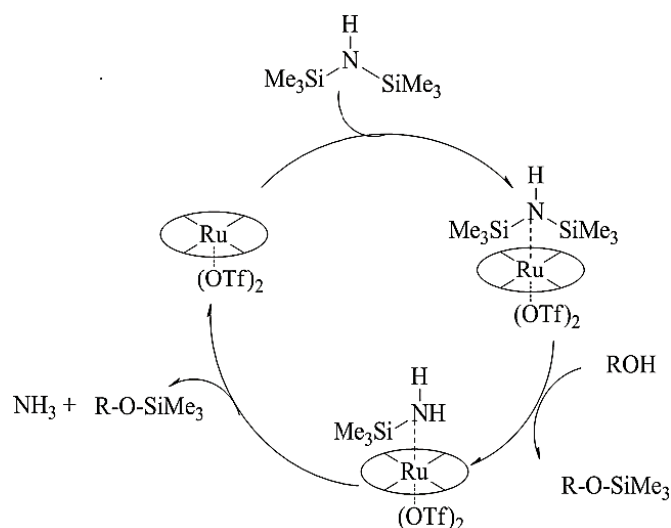


Figure 8. Proposal mechanism for TMS-alcohol with $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{AEAPTMS}/\text{Salen Ru}(\text{OTf})_2$.

the reaction. The diagram in Fig. 9 illustrates the number of catalyst cycles with minimal decrease in efficiency, as demonstrated by the slight decrease in efficiency over ten cycles.

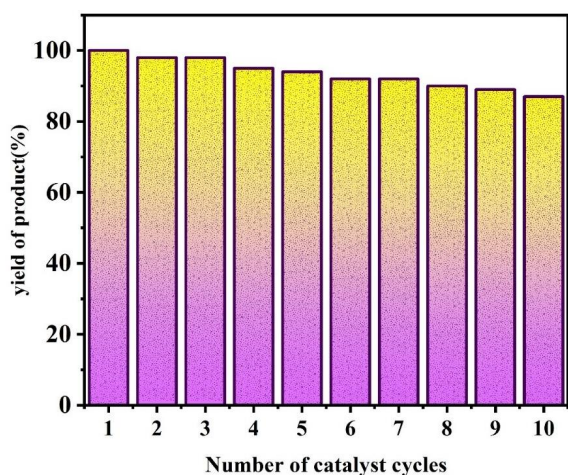


Figure 9. Diagram of correlation between catalyst recovery cycles and product efficiency.

5. CONCLUSIONS

A newly developed $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{AEAPTMS}/\text{Salen Ru}(\text{OTf})_2$ nanocatalyst with heterogeneous properties was created and analyzed through various techniques such as FT-IR spectra investigated for both the unfunctionalized and functionalized magnetic nanoparticles, SEM, TEM analysis were used to investigate the morphology and size of the samples and VSM was demonstrated for the measured magnetization of the nanoparticles. The catalyst was tested for its ability to silylation alcohols and phenols using HMDS in dichloromethane at room temperature. The results showed that primary, secondary, and tertiary alcohols as well as phenols could be protected

with high yields and fast reaction times. This method is advantageous due to its low-cost processing, simple synthesis of the nanocatalyst, easy work-up procedure, Furthermore, the catalyst can be easily separated from the product using magnetic separation, and it can be reused multiple times with only a minimal decrease in activity. In summary, this protocol offers significant benefits including environmentally-friendly reaction conditions, facile separation using an external magnetic field, catalyst recyclability, and satisfactory reaction times and product yields.

REFERENCES

- Abri A., Ranjdar S., 2014. Preparation of nano silica supported sodium hydrogen sulfate: As an efficient catalyst for the trimethyl, triethyl and t-butyl dimethyl silylations of aliphatic and aromatic alcohols in solution and under solvent-free conditions. *J. Chinese Chem. Soc.*, 61, 929–934. DOI: [10.1002/jccs.201300586](https://doi.org/10.1002/jccs.201300586).
- Al-Anazi A., 2022. Iron-based magnetic nanomaterials in environmental and energy applications: a short review. *Curr. Opin. Chem. Eng.*, 36, 100794. DOI: [10.1016/j.coche.2022.100794](https://doi.org/10.1016/j.coche.2022.100794).
- Arnodo D., De Nardo E., Ghinato S., Baldino, S., Blangetti, M., Prandi, C., 2023. A mild, efficient and sustainable tetrahydropyranlation of alcohols promoted by acidic natural deep eutectic solvents. *ChemSusChem*, 16, e202202066. DOI: [10.1002/cssc.202202066](https://doi.org/10.1002/cssc.202202066).
- Bhole R., Gonsalves D., Murugesan G., Narasimhan M.K., Srinivasan N.R., Dave N., Varadavenkatesan T., Vinayagam R., Govarthanam M., Selvaraj R., 2022. Superparamagnetic spherical magnetite nanoparticles: synthesis, characterization and catalytic potential. *Appl. Nanosci.*, 13, 6003–6014. DOI: [10.1007/s13204-022-02532-4](https://doi.org/10.1007/s13204-022-02532-4).
- Buldurun K., Özdemir M., 2020. Ruthenium (II) complexes with pyridine-based Schiff base ligands: Synthesis, structural characterization and catalytic hydrogenation of ketones. *J. Mol. Struct.*, 1202, 127266. DOI: [10.1016/j.molstruc.2019.127266](https://doi.org/10.1016/j.molstruc.2019.127266).
- Changmai B., Rokhum L., 2020. Nanostructured catalysts in the protection and deprotection of hydroxyl and thiol groups, In: Sudarsanam P., Singh L. (Eds.), *Advanced heterogeneous catalysts Volume 1: Applications at the nano-scale*. ACS Symposium Series 1359. American Chemical Society, Washington, DC, 129–150. DOI: [10.1021/bk-2020-1359.ch004](https://doi.org/10.1021/bk-2020-1359.ch004).
- Chen D., Han C., 2022. An alkoxo-bridged dinuclear ruthenium-schiff base complex: Synthesis, structure and catalytic reactivity. *Inorg. Chem. Commun.*, 142, 109595. DOI: [10.1016/j.inoche.2022.109595](https://doi.org/10.1016/j.inoche.2022.109595).
- Chołuj A., Nogaś W., Patrzalek M., Krzesiński P., Chmielewski M.J., Kajetanowicz A., Grela K., 2020. Preparation of ruthenium olefin metathesis catalysts immobilized on MOF, SBA-15, and 13X for probing heterogeneous boomerang effect. *Catalysts*, 10, 438. DOI: [10.3390/catal10040438](https://doi.org/10.3390/catal10040438).
- Gonzalez-Carrillo G., Gonzalez J., Emparan-Legaspi M.J., Lino-Lopez G.J., Aguayo-Villarreal I.A., Ceballos-Magaña S.G., Martinez-Martinez F.J., Muñiz-Valencia R., 2020. Propylsulfonic acid grafted on mesoporous siliceous FDU-5 material: A high

- TOF catalyst for the synthesis of coumarins via Pechmann condensation. *Microporous Mesoporous Mater.*, 307, 110458. DOI: [10.1016/j.micromeso.2020.110458](https://doi.org/10.1016/j.micromeso.2020.110458).
- Inoue H., Tachibana T., Bito T., Arima J., 2023. Acetylation of amines and alcohols catalyzed by acetylcholinesterase from *Pseudomonas aeruginosa* PAO1. *Enzyme Microb. Technol.*, 165, 110208. DOI: [10.1016/j.enzmictec.2023.110208](https://doi.org/10.1016/j.enzmictec.2023.110208)
- Kamalzare M., Ahghari M.R., Bayat M., Maleki A., 2021. Fe₃O₄@chitosan-tannic acid bionanocomposite as a novel nanocatalyst for the synthesis of pyranopyrazoles. *Sci. Rep.*, 11, 20021. DOI: [10.1038/s41598-021-99121-2](https://doi.org/10.1038/s41598-021-99121-2).
- Karimi B., Golshani B., 2000. Mild and highly efficient method for the silylation of alcohols using hexamethyldisilazane catalyzed by iodine under nearly neutral reaction conditions. *J. Org. Chem.*, 65, 7228–7230. DOI: [10.1021/jo005519s](https://doi.org/10.1021/jo005519s).
- Katsuki T., 1995. Catalytic asymmetric oxidations using optically active (salen)manganese(III) complexes as catalysts. *Coord. Chem. Rev.*, 140, 189–214. DOI: [10.1016/0010-8545\(94\)01124-T](https://doi.org/10.1016/0010-8545(94)01124-T).
- Kazemi M., Shiri L., 2022. Ionic liquid immobilized on magnetic nanoparticles: A nice and efficient catalytic strategy in synthesis of heterocycles. *J. Synth. Chem.*, 1, 1–7. DOI: [10.22034/jsc.2022.149201](https://doi.org/10.22034/jsc.2022.149201).
- Koc Z.E., Ucan H.I., 2007. Complexes of iron(III) salen and saloph Schiff bases with bridging 2,4,6-*tris*(2,5-dicarboxy phenylimino-4-formylphenoxy)-1,3,5-triazine and 2,4,6-*tris*(4-carboxyphenylimino-4'-formylphenoxy)-1,3,5-triazine. *Transit. Met. Chem.*, 32, 597–602. DOI: [10.1007/s11243-007-0213-7](https://doi.org/10.1007/s11243-007-0213-7).
- Lalonde M., Chan T.H., 1985. Use of organosilicon reagents as protective groups in organic synthesis. *Synthesis*, 1985, 817–845. DOI: [10.1055/s-1985-31361](https://doi.org/10.1055/s-1985-31361).
- Leckie L., Mapolie S.F., 2019. Triazole complexes of ruthenium immobilized on mesoporous silica as recyclable catalysts for octane oxidation. *Catal. Commun.*, 131, 105803. DOI: [10.1016/j.catcom.2019.105803](https://doi.org/10.1016/j.catcom.2019.105803).
- Lv B., Lei C., Ren F., Wang M., Hu, F., Meng S., Yang Y., Yang Z., Lei Z., 2020. Asymmetric hydrogenation of acetophenone catalyzed by chirally modified ruthenium nanoparticles supported on carbon nanotubes. *ChemistrySelect*, 5, 11803–11810. DOI: [10.1002/slct.202003232](https://doi.org/10.1002/slct.202003232).
- Martin J.S., Zeng X., Chen X., Miller C., Han C., Lin Y., Yamamoto N., Wang X., Yazdi S., Yan Y., Beard M.C., Yan Y., 2021. A nanocrystal catalyst incorporating a surface bound transition metal to induce photocatalytic sequential electron transfer events. *J. Am. Chem. Soc.*, 143, 11361–11369. DOI: [10.1021/jacs.1c00503](https://doi.org/10.1021/jacs.1c00503).
- Mehdigholami S., Koohestanian E., 2023. Fe₃O₄@SiO₂/AEPTMS/Fe(OTf)₃: An efficient superparamagnetic nanocatalyst for the protecting of alcohols. *J. Part. Sci. Technol.*, 9, 1–9. DOI: [10.22104/jpst.2023.6188.1224](https://doi.org/10.22104/jpst.2023.6188.1224).
- Miceli M., Frontera P., Macario A., Malara A., 2021. Recovery/reuse of heterogeneous supported spent catalysts. *Catalysts*, 11, 591. DOI: [10.3390/catal11050591](https://doi.org/10.3390/catal11050591).
- Nag S., Gupta P., Butcher R.J., Bhattacharya S., 2004. Unprecedented migration of a methyl group in 2-(2',6'-dimethylphenylazo)-4-methylphenol mediated by ruthenium. *Inorg. Chem.* 43, 4814–4816. DOI: [10.1021/ic049494h](https://doi.org/10.1021/ic049494h).
- Nagajothi D., Maheswari J., 2021. Synthesis, characterization and antimicrobial activity of Schiff base ligand metal complexes. *GIS Sci. J.*, 8(1), 1314–1326.
- Premkumar M., Vijayan P., Venkatachalam G., 2019. Half-sandwich Ruthenium(II) Schiff base complexes: Synthesis, characterization and effective catalysts for one-pot conversion of aldehydes to amides. *J. Organomet. Chem.*, 902, 120964. DOI: [10.1016/j.jorganchem.2019.120964](https://doi.org/10.1016/j.jorganchem.2019.120964).
- Rahmanzadeh A., Daneshvar N., Shirini F., Tajik H., 2021. Comparison of the efficiency of two dicationic ionic liquids catalysts based on perchloric acid for the protection of alcohols. *J. Iran. Chem. Soc.*, 18, 3295–3302. DOI: [10.1007/s13738-021-02267-z](https://doi.org/10.1007/s13738-021-02267-z).
- Sartori G., Ballini R., Bigi F., Bosica G., Maggi R., Righi P., 2004. Protection (and deprotection) of functional groups in organic synthesis by heterogeneous catalysis. *Chem. Rev.*, 104, 199–250. DOI: [10.1021/cr0200769](https://doi.org/10.1021/cr0200769).
- Shalini P., Deepanraj B., Vijayalakshmi S., Ranjitha J., 2023. Synthesis and characterisation of lipase immobilised magnetic nanoparticles and its role as a catalyst in biodiesel production. *Mater. Today Proc.*, 80, 2725–2730. DOI: [10.1016/j.matpr.2021.07.027](https://doi.org/10.1016/j.matpr.2021.07.027).
- Singh A., Barman P., 2021. Recent advances in Schiff base ruthenium metal complexes: Synthesis and applications. *Top. Curr. Chem.*, 379, 1–71. DOI: [10.1007/s41061-021-00342-w](https://doi.org/10.1007/s41061-021-00342-w).
- Skrodzki M., Patroniak V., Pawluć P., 2021. Schiff base cobalt(II) complex-catalyzed highly Markovnikov-selective hydrosilylation of alkynes. *Org. Lett.*, 23, 663–667. DOI: [10.1021/acs.orglett.0c03721](https://doi.org/10.1021/acs.orglett.0c03721).
- van Melis C.G.W., Penny M.R., Garcia A.D., Petti A., Dobbs A.P., Hilton S.T., Lam K., 2019. Supporting-electrolyte-free electrochemical methoxymethylation of alcohols using a 3D-printed electrosynthesis continuous flow cell system. *ChemElectroChem*, 6, 4144–4148. DOI: [10.1002/celec.201900815](https://doi.org/10.1002/celec.201900815).
- Wan P.J., Dowd M.K., Thomas A.E., Butler B.H., 2007. Trimethylsilyl derivatization/gas chromatography as a method to determine the free fatty acid content of vegetable oils. *J. Am. Oil Chem. Soc.*, 84, 701–708. DOI: [10.1007/s11746-007-1101-1](https://doi.org/10.1007/s11746-007-1101-1).
- Wang A., Sudarsanam P., Xu Y., Zhang H., Li H., Yang S., 2020. Functionalized magnetic nanosized materials for efficient biodiesel synthesis via acid–base/enzyme catalysis. *Green Chem.*, 22, 2977–3012. DOI: [10.1039/D0GC00924E](https://doi.org/10.1039/D0GC00924E).
- Wang C., Karmakar B., Awwad N.S., Ibrahim H.A., El-kott A.F., Abdel-Daim M.M., Oyouni A.A.A., Al-Amer O., Batiha G.E.-S., 2022. Bio-supported of Cu nanoparticles on the surface of Fe₃O₄ magnetic nanoparticles mediated by *Hibiscus sabdariffa* extract: Evaluation of its catalytic activity for synthesis of pyrano[3,2-c]chromenes and study of its anti-colon cancer properties. *Arab. J. Chem.*, 15, 103809. DOI: [10.1016/j.arabjc.2022.103809](https://doi.org/10.1016/j.arabjc.2022.103809).
- Wuts P.G.M., Greene T.W., 2006. *Greene's protective groups in organic synthesis*. John Wiley & Sons, Inc., 24–222. DOI: [10.1002/0470053488](https://doi.org/10.1002/0470053488).
- Xia S.-P., Ding G.-R., Zhang R., Han L.-J., Xu B.-H., Zhang S.-J., 2021. Ruthenium complex immobilized on supported ionic-liquid-phase (SILP) for alkoxycarbonylation of olefins with CO₂. *Green Chem.*, 23, 3073–3080. DOI: [10.1039/D0GC04386A](https://doi.org/10.1039/D0GC04386A).

- Yao H., Wang Y., Razi M.K., 2021. An asymmetric Salamo-based Zn complex supported on Fe₃O₄ MNPs: a novel heterogeneous nanocatalyst for the silyl protection and deprotection of alcohols under mild conditions. *RSC Adv.*, 11, 12614–12625. DOI: [10.1039/D1RA01185E](https://doi.org/10.1039/D1RA01185E).
- You J., Wang L., Zhao Y., Bao W., 2021. A review of amino-functionalized magnetic nanoparticles for water treatment: Features and prospects. *J. Cleaner Prod.*, 281, 124668. DOI: [10.1016/j.jclepro.2020.124668](https://doi.org/10.1016/j.jclepro.2020.124668).
- Zareyee D., Ghandali M.S., Khalilzadeh M.A., 2011. Sulfonated ordered nanoporous carbon (CMK-5-SO₃H) as an efficient and highly recyclable catalyst for the silylation of alcohols and phenols with hexamethyldisilazane (HMDS). *Catal. Lett.*, 141, 1521–1525. DOI: [10.1007/s10562-011-0621-3](https://doi.org/10.1007/s10562-011-0621-3).
- Zolfigol M.A., Sajjadifar S., Ghorbani-Choghamarani A., Tami F., 2018. Application of a novel nano-immobilization of ionic liquid on an MCM-41 system for trimethylsilylation of alcohols and phenols with hexamethyldisilazane. *Res. Chem. Intermed.*, 44, 7093–7106. DOI: [10.1007/s11164-018-3544-4](https://doi.org/10.1007/s11164-018-3544-4).