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DIRECT AMIDATION/ESTERIFICATION OF CARBOXYLIC ACID CATALYZED BY TRIMETHYLSILYL TRIFLUOROMETHANESULFONATE SUPPORTED ON SILICA GEL

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ABSTRACT
The immense applications of Trimethylsilyl trifluoromethanesulfonate or (TMSOTf) or $(CH_3)_3SiO_3SCF_3$ in catalysis are not completely explored yet due to its corrosive and fuming properties. Immobilization of Trimethylsilyl trifluoromethanesulfonate supported on silica gel [TMSOTf.SiO_2 or $(CH_3)_3SiO_3SCF_3.SiO_2$] well solves these problems and affords efficient recovery and reusability with excellent yield, short reaction time, ease to handle and many more features for direct amidation/ esterification of carboxylic acids in organic synthesis.

KEYWORDS: Direct Amidation, Direct esterification, Trimethylsilyl trifluoromethanesulfonate supported on silica gel or (TMSOTf.SiO_2) or $(CH_3)_3SiO_3SCF_3.SiO_2$.

1. INTRODUCTION
We cannot overemphasize the dominance of amide and ester bonds as its formation accounts a vital role in drug discovery and development which makes them one of the most important functional groups in the chemistry known to chemists.[i,ii] In view of that, in last few decades lot of work has been carried out to devloped these chemistry.[iii–x] Still it is surprising that amidation reaction yet considered non-ideal and stated that development of amide formation has poor atom economy and need to develop novel methodologies to improve the condition.[xi ,xii] Currently much interest of researcher is for the development of direct amidation of carboxylic acids with amines.[xiii–xvii] An additional challenge for direct amidation from carboxylic acid is the environmental impact and scope which is not consistent.

Over the past 5 decades, variety of reagents such as lewis acids, heterogeneous silicon catalysts such as tetrachlorosilane[xviii,xix], dimethyldichlorosilane[xx], 9-silafluorenyl dichlorides[xxi], phenyltrichlorosilane[xxi], $PhSiH_3$[xxii], Et_2SiH_2[xxiii], $HSi(OCH(CF_3)_2)_3$[xxiv], $(EtO)_2MeSiH$[xxv], Poly(methylhydroxysilane)[xxvii], Hexamethyldisilazane[xxvii], Imidazolesilanes [xxviii], Tetrakis(pyridine-2-yloxy)silane[xxix], Tetrakis(1,1,1,3,3,3-hexafluoro-2-propoxy)silane[xxx], Tetramethyl orthosilicate [xxxi], Silicon tetraacetate [xxxii],

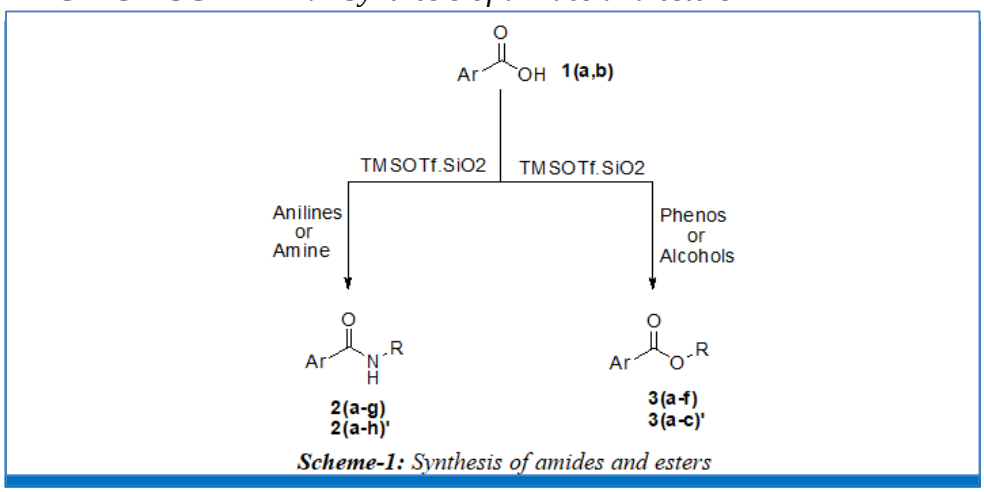
TMSOTf [xxxiii], metal triflates [xxxiv], and classical methods have been reported for direct amidation.

In the similar manner Esterification of carboxylic acids (and carboxylic esters) with alcohols have been recognized as one of the most important unit reactions in organic synthesis.[xxxv]

In both cases all reported methodologies and reagents are bearing drawbacks such as use of fancy and expensive reagents, toxicity, environmental challenges, harsh reaction condition, hazardous nature of catalysts, sensitive to moisture, less tolerability of functional groups, low yields, longer reaction time, commercial unavailability etc.

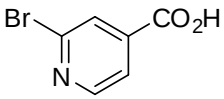
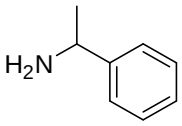
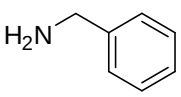
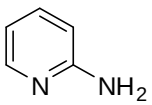
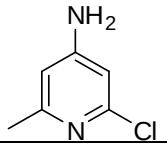
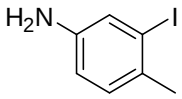
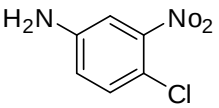
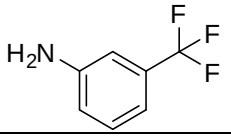
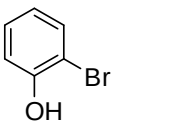
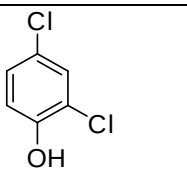
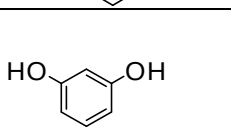
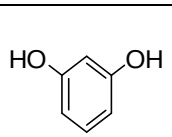
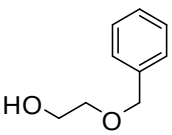
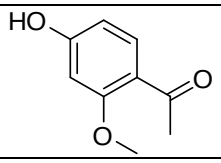
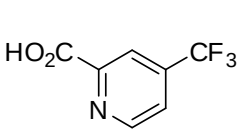
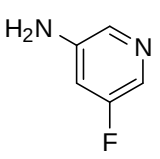
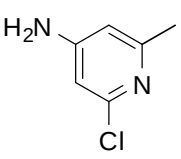
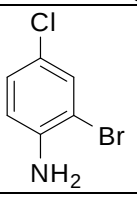
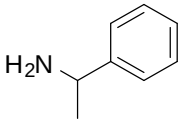
To overcome all above challenges and in a successive endeavor to explore more effective methods to bring to a halt, and the further applications we herein report direct amidation/ esterification of carboxylic acid using Trimethylsilyl trifluoromethanesulfonate supported on silica gel as a catalyst.

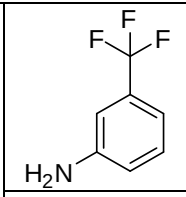
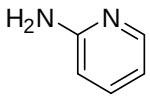
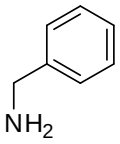
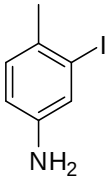
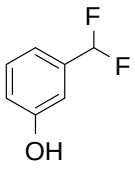
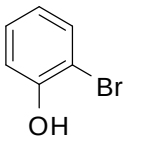
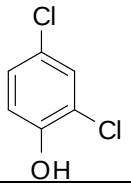
2. REACTION SCHEME: - *Synthesis of amides and esters*



Scheme-1: *Synthesis of amides and esters*

Where,

Ar	**R**			
				
				
				
				
				

3. RESULTS AND DISCUSSION

As an inclusive attempt to synthesize amides and esters, we had reported here a simplified process using $CH_3)_3SiO_3SCF_3.SiO_2$ with an efficient isolation techniques to obtain desired targets with moderate to good yield. Synthesis of amides obtained from carboxylic acid 1(a, b) and substituted amines/ anilines, TEA and $CH_3)_3SiO_3SCF_3.SiO_2$ in Dichloroethane as a solvent.

Initially 2-bromoisonicotinic acid, 1-phenylethanamine, TEA and $CH_3)_3SiO_3SCF_3.SiO_2$ was selected as reference substrates, for optimization of reaction condition. Different time, temperature and mole % of $CH_3)_3SiO_3SCF_3.SiO_2$ was screened as described in Table-1. As a result of optimization studies it is observed that, less yield obtained in absence of $CH_3)_3SiO_3SCF_3.SiO_2$ catalyst (Entry-1, Table-1**).** To determine the minimum requirement of catalyst for reaction, we screened mole equivalents of catalyst such as 0.5-1.5 (Entry-2-6, Table-1) and observed that 1.1 eq., $CH_3)_3SiO_3SCF_3.SiO_2$ is optimum requirement of reaction to get good result. During investigation of reaction time (Entry-7-9, Table-1); it is found that, 300 min. is sufficient time for completion of reaction. We also investigated reaction temperature (Entry-10-12, Table-1); and observed that at lower temperature yields are obtained less may be due to incomplete conversion of reaction while at higher temperature yield was comparable. The catalyst was recovered and recycled with standard optimized reaction condition using 2-bromoisonicotinic acid, 1-phenylethanamine, TEA and $CH_3)_3SiO_3SCF_3.SiO_2$ as a reference substrates summarized in Table-3. Comparative yields were obtained by using recycled catalyst up to three cycles (Entries-1-3, Table-3), while yield drop observed from next cycle i.e. from cycle 4 onwards.

To further extend the scope of $(CH_3)_3SiO_3SCF_3.SiO_2$ catalyst, a range of amides were prepared under the optimized reaction conditions by changing the substrate from simple aryl group to substituted amines, anilines and Benzylamine. The detailed results were summarized in Table -2.

Similar protocol used for the synthesis of esters and results were tabulated in Table -2.

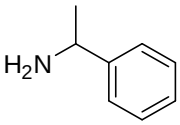
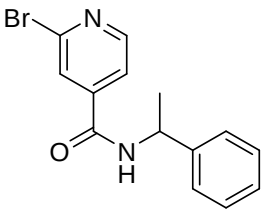
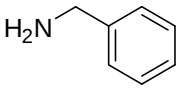
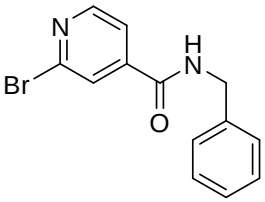
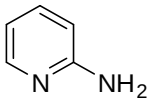
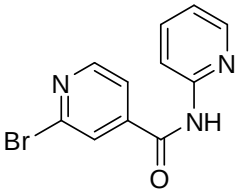
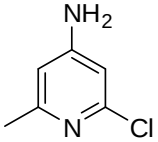
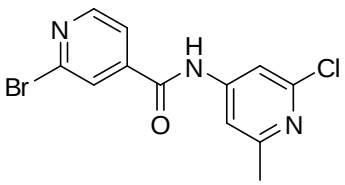
Table-1: *Optimization of reaction conditions for the synthesis of Amide.*

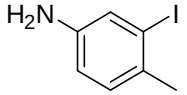
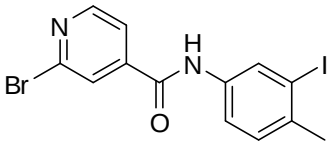
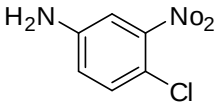
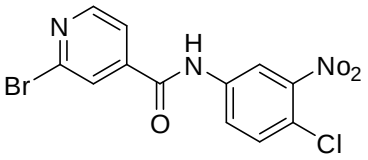
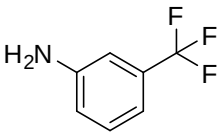
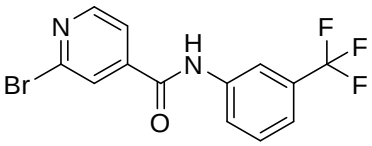
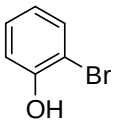
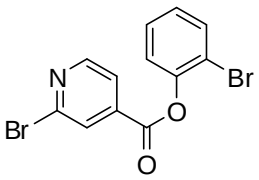
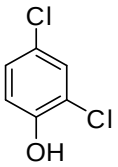
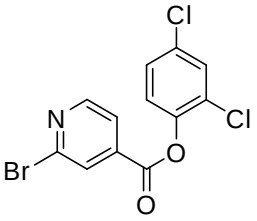
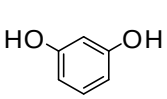
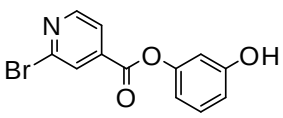
Entry	**$(CH_3)_3SiO_3SCF_3.SiO_2$ (Mole %)**	**Time (min.)**	**Temperature °C**	**Yield (%)**
1.	-	480	20-30	11
2.	1.5	300	20-30	80
3.	1.2	300	20-30	86
4.	**1.1**	300	20-30	93
5.	0.8	300	20-30	93

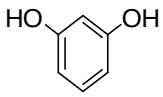
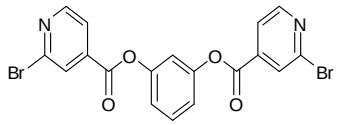
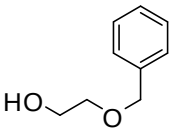
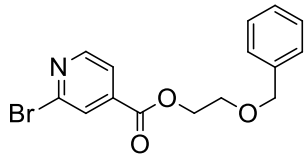
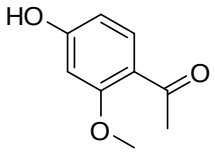
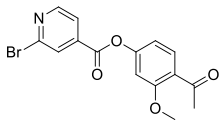
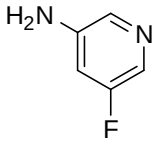
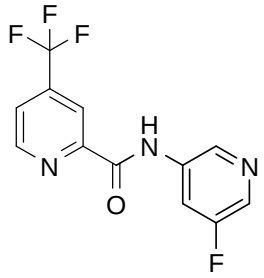
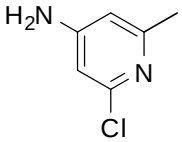
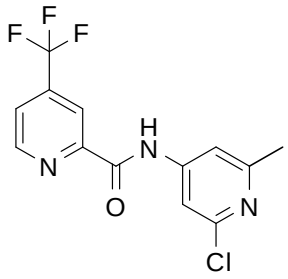
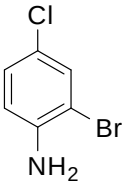
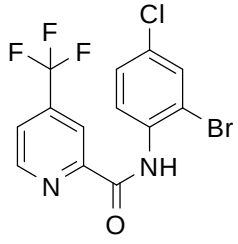
6.	0.5	300	20-30	84
7.	**1.1**	**300**	**20-30**	**93**
8.	1.1	240	20-30	62
9.	1.1	360	20-30	55
10.	1.1	300	50-60	93
11.	1.1	300	70-80	93
12.	1.1	300	10-15	82

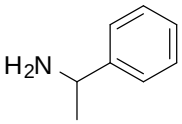
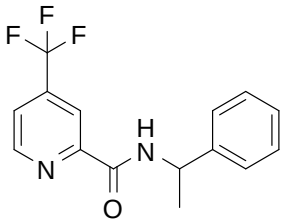
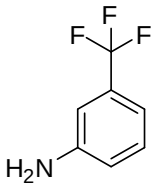
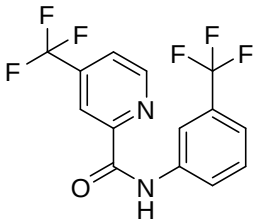
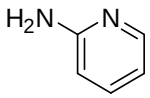
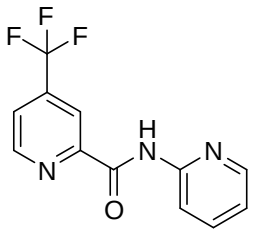
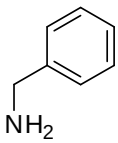
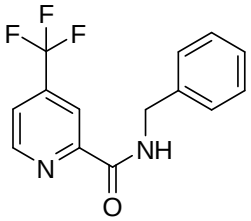
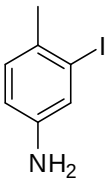
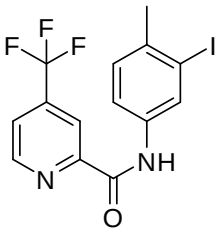
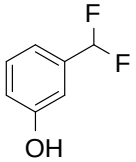
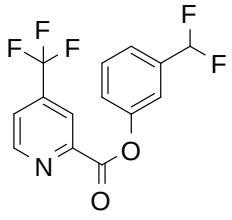
** Reaction conditions: Carboxylic acid(1.0 eq), $(CH_3)_3SiO_3SCF_3.SiO_2$ (1.1 eq), amines (1.05 eq), TEA (2.0 eq), and solvent DCM (10.0 rel vol.) was maintained at 20-30°C for 300.0 min.*

Table-2: Substitution pattern of amides and esters

Amine/anilines/benzylamines Phenols/alcohols	**Products**	**Spectroscopic data**
	 2a	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 9.19-9.21(1H,d), 8.54-8.58(1H,d), 8.07(1H,s), 7.94(1H,d), 7.22-7.41(5H,m),1.35-1.36(3H,d)
	 2b	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 9.41-9.43(1H,s),8.55-8.59(1H,d), 8.05(1H.s), 7.81-7.92(1H,d), 7.20-7.38(5H,m), 4.50-4.52(2H,d).
	 2c	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.59-8.61(1H,d), 8.41-8.43(1H,d), 8.16-8.19(1H,d), 8.04(1H,s), 7.85-7.95(2H,m), 7.20-7.24(1H,t), 6.42-6.48(1H,t).
	 2d	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 10.37(1H,s), 8.65-8.67(1H,d), 8.31(1H,s), 8.00(1H,s), 7.86-7.87(1Hd), 7.82(1H,s),2.29(3H,s).

	 2e	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 10.56(1H,s), 8.60-8.64(1H,d), 8.30(1H,d),8.123(1H,s), 7.85-7.90(1H,d), 7.69-7.72(1H,d), 7.32-7.35(1H,d),2.29(3H,s).
	 2f	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.85(1H,d), 8.64-8.70(1H,d), 8.43(1H,s), 8.08-8.12(1H,d), 7.55(2H,s), 6.51(1H,d).
	 2g	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.66-8.68(1H,d),8.11(1H,s), 8.02-8.05(2H,d),7.85-7.91(2H,m), 7.74(1H,d), 7.71-7.72(1H,d).
	 3a	^{1}H-NMR, 300 MHz, DMSO-d6: δ = 8.30-8.38(1H,d), 7.93-8.00(1H,d), 7.79(1H,d), 7.54-7.65(1H,d), 7.24-7.36(1H,d), 6.93-6.97(1H,m),6.62-6.64(1H,d).
	 3b	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.63-8.65(1H,d), 7.83-7.87(2H,m), 7.43(1H,d), 7.18-7.21(1H,m), 6.96(1H,d).
	 3c	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 9.23(1H,s), 8.33-8.37(1H,d), 7.15-7.24(2H,s), 6.72-6.77(1H,t),6.18-6.23(3H,d), 3.07(1H,s).

	 3d	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.33-8.37(1H,d),7.86(1H,s), 7.15-7.24(2H,s), 6.72-6.77(2H,t),6.18-6.23(4H,d).
	 3e	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.62-8.65(1H,d), 7.81-7.86(2H,d), 7.24-7.34(5H,m),4.48-4.56(2H,d), 3.77-3.80(2H,t), 3.45-3.60(2H,m).
	 3f	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.82-8.86(1H,d), 8.02-8.07(1H,d), 7.64-7.69(1H,d), 7.48-7.53(1H,d), 7.44-7.45(1H,d), 6.85-6.88(1H,d), 3.83(3H,s), 2.50-2.51(3H,m).
	 2a’	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 9.02-9.07(1H,d), 8.38(1H,s), 7.79-7.80(1H,d),7.64-7.65(1H,d),6.70-6.75(1H,m),5.70(2H,s).
	 2b’	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 9.02-9.09(1H,d), 8.39(1H,s), 8.15-8.18(1H,d), 8.07-8.09(1H,d),7.68(1H,s), 6.50(1H,s), 1.97(3H,s).
	 2c’	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 9.03-9.07(1H,d), 8.38(1H,s), 8.26-8.29(1H,d), 7.71(1H,s), 7.40(1H,s), 7.09-7.12(1H,d), 6.78-6.80(1H,d).

	 2d′	^{1}H-NMR, 300 MHz, DMSO-d6: δ=9.29-9.31(1H,d), 8.96-8.98(1H,d),8.24(1H,s), 8.00-8.02(1H,d), 7.17-7.49(5H,m), 1.23-1.32(3H,d).
	 2e′	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.38(1H,s), 8.44(1H,s), 8.11(1H,d),7.17-7.23(1H,t), 6.75-6.85(4H,m).
	 2f′	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 9.04-9.05(1H,d), 8.39(1H,d),8.26-8.29(1H,d),7.88-7.93(2H,m),7.32-7.38(1H,t), 6.42-6.48(2H,m).
	 2g′	^{1}H-NMR, 300 MHz, DMSO-d6: δ 9.55-9.59(1H,t), 8.95-8.97(1H,d), 8.26(1H,s), 8.01-8.03(1H,d), 7.21-7.47(5H,m),4.53-4.55(2H,d).
	 2h′	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 9.02-9.04(1H,d), 8.50(1H,d),8.34(1H,s), 8.25-8.27(1H,d), 8.08-8.10(1H,d), 7.83-7.86(1H,d), 7.31-7.34(1H,d), 2.35(3H,s).
	 3a′	^{1}H-NMR, 300 MHz, DMSO-d6: δ=7.42-7.55(2H,dd), 7.30(1H,s),7.06-7.09(4H,m), 1.86-1.89(1H,s).

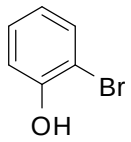
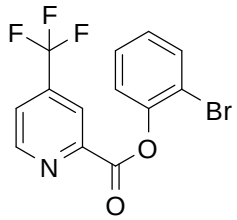
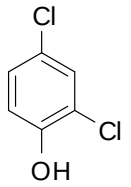
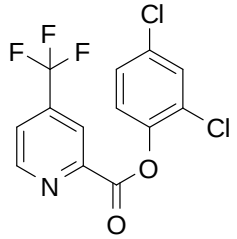
	 3b′	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.95-8.98(1H,d), 8.36(1H,d), 7.69-7.02(1H,d),7.46-7.47(1H,d), 7.18-7.44(1H,m), 6.98-7.03(1H,d),6.77-6.82(1H,t).
	 3c′	^{1}H-NMR, 300 MHz, DMSO-d6: δ= 8.93-8.98(1H,d), 8.36(1H,s), 7.73-7.74(1H,d), 7.43(1H,d), 7.18-7.21(1H,d), 6.96-6.99(1H,d).

Table-3 Recycle study of catalyst recovered from spent

Entry	$(CH_3)_3SiO_3SCF_3.SiO_2$ (5.0 Mole %)	Time (min.)	Temperature °C	Yield (%)
1	Cycle-1	300	20-30	92
2	Cycle-2	300	20-30	92
3	Cycle-3	300	20-30	91
4	Cycle-4	300	20-30	89
5	Cycle-5	300	20-30	85

1. EXPERIMENTAL SECTION

All Solvents, chemicals and reagents were purchased from resources like Sigma-Aldrich, finar and Spectrochem etc utilized as such from the suppliers. Wherever necessary, anhydrous solvents were used. Thin layer chromatography (TLC) analysis was done by utilizing Merk silica gel 60 F254 aluminum plates and visualized under UV light. Melting points were obtained by using (SMP 30) apparatus. The ^{1}H-NMR spectra were recorded using $CDCl_3$ or DMSO-d_6 as a solvent on Bruker 300 MHz instrument using TMS as the internal standard. Isolated compounds are purified using re-crystallization technique. Synthesized products were reported and identified by melting points, MASS and 1H-NMR values with reported values.

1.1 General Procedure for Synthesis of Amides from Carboxylic Acids (Scheme 1)

To a solution of the carboxylic acid (1.0 eq) in CH_2Cl_2 (10 volume) at 20-30°C was added $CH_3)_3SiO_3SCF_3.SiO_2$ (1.1 eq) followed by Et3N (2.0eq). The reaction mixture was stirred for an additional 30 minutes at the same temperature before the addition of amine/anilines (1.05eq). Progress of the reaction was monitored by TLC. After completion of reaction, catalyst filtered out and filtrate mL of the reaction mass was diluted with CH_2Cl_2 (5vol) and washed with 1 M aq., HCl (10 vol), followed by aq., $NaHCO_3$ (10 vol) and then brine (10 vol). The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated

under reduced pressure to furnish the desired product. If required, further purification was carried out using flash column chromatography, eluting with EtOAc–hexane.
Synthesized molecules physical properties as well as spectroscopic data (NMR, Mass and IR) confirmed with reported literature values.

1.2 General Procedure for Synthesis of esters from Carboxylic Acids (Scheme 1)

To a solution of the carboxylic acid (1.0 eq) in CH_2Cl_2 (10 volume) at 20-30°C was added $CH_3)_3SiO_3SCF_3.SiO_2$ (1.1 eq) followed by Et3N (2.0eq). The reaction mixture was stirred for an additional 30 minutes at the same temperature before the addition of alcohols/phenols (1.05eq). Progress of the reaction was monitored by TLC. After completion of reaction, catalyst filtered out and filtrate mL of the reaction mass was diluted with CH_2Cl_2 (5vol) and washed with 1 M aq., HCl (10 vol), followed by aq., $NaHCO_3$ (10 vol) and then brine (10 vol). The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure to furnish the desired product. If required, further purification was carried out using flash column chromatography, eluting with EtOAc–hexane.
Synthesized molecules physical properties as well as spectroscopic data (NMR, Mass and IR) confirmed with reported literature values.

2. CONCLUSION

An efficient and mild methodology has been developed for the synthesis of amides and esters using $CH_3)_3SiO_3SCF_3.SiO_2$ the heterogeneous catalyst. The catalyst could be reused after a simple work-up and used several times without noticeable reduction in the catalytic activity. Moderate to good yields, relatively short reaction times, simple operation and easy work-up are some advantages of this protocol. This improved reaction condition allows the preparation of a wide variety of amides and esters in moderate to good yields and excellent purity under mild reaction conditions. We believe the applicability of $CH_3)_3SiO_3SCF_3.SiO_2$ with the mentioned advantages makes our method superior among other reported methods to synthesize amides and esters.

5. ACKNOWLEDGEMENT

Authors sincerely thank to Department of chemistry, Mansarovar Global University, Sehore, (M.P.), India, for their support.

6. REFERENCE

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