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Montmorillonite Clay Catalyzed Tosylation of Alcohols and Selective Monotosylation of Diols with *p*-Toluenesulfonic Acid: An Enviro-Economic Route☆

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Abstract—An enviro-economic route for tosylation of alcohols and selective monotosylation of diols in good yield directly using *p*-toluenesulfonic acid together with metal-exchanged montmorillonite instead of *p*-toluenesulfonyl chloride or *p*-toluenesulfonic anhydride is described. The Fe^{3+}-montmorillonite clay is the most effective catalyst among metal-exchanged montmorillonites for such tosylation reactions. The activity follows the sequence $Fe^{3+}>Zn^{2+}>Cu^{2+}>Al^{3+}$-montmorillonite>K10 montmorillonite. Regioselective tosylation of diols to monotosylated derivatives is achieved with high purity. In diols having both primary and secondary hydroxy groups, tosylation occurred only at the primary hydroxy group. The solid catalyst displayed consistent activity for several cycles as exemplified in tosylation of cyclohexanol.

Introduction

Tosylation of alcohols is used extensively in organic synthesis.[1,2] Preparation of sulfonates generally relies on the use of the corresponding sulfonyl chloride or anhydride in the presence of pyridine,[3] triethylamine,[4] 1,4-diazabicyclo[2.2.2]octane (DABCO)[5] or aqueous base. Sulfonic acids are also used for synthesis of sulfonates but expensive alkylating agents such as trialkyl orthoformate, alkyl ethers, esters or 2-alkoxybenzothiazolium salt are employed instead of alcohol.[6] In recent years organic base adducts of sulfonyls such as aryl sulfonyl methylimidazolium salts and 1-phenylsulfonyl benzotriazole have also been employed for sulfonate synthesis.[7] The most widely used *p*-toluenesulfonyl chloride (TsCl) or anhydride is moisture-sensitive and too reactive. Further, undesirable conversion of the tosylates into their chlorides is liable to occur during tosylation when TsCl/pyridine is used.[8] Moreover, the bases or base adducts of sulfonyls which are employed in molar excess for the sulfonylation of alcohols generate significant amounts of by-products in the form of total dissolved salts. To the best of our knowledge, there is no report on the use of solid catalysts for the tosylation of alcohols.

In a molecule containing primary and secondary hydroxy groups, selective tosylation of a primary hydroxy group in the presence of a secondary hydroxy group is often required. The resulting hydroxy sulfonates are the precursors for epoxides en-route to the synthesis of a number of natural products and drugs.[9] It is important to realize a high regioselectivity in the initial sulfonylation step to obtain epoxides with high purity via cyclization of the product hydroxy sulfonates.

Thus, development of a new catalytic method, which can effectively overcome problems experienced in the sulfonylation reaction, should heighten the synthetic scope of the reaction. In this connection, the use of heterogeneous catalysts in the liquid-phase offers several advantages compared to their homogeneous counterparts, including the ease of recovery, recyclability, regioselectivity and enhanced stability.

The use of clays as catalysts and catalyst supports has received considerable attention recently.[10,11] Expandable layer lattice clays such as montmorillonites have magnetic field acidity (H_0) values between 1.5 and −3 and their acidities may be tuned further by metal ion exchange with the introduction of a large number of Lewis acidic sites. Wide use of solid acids for various organic transformations such as Friedel–Crafts reactions,[12] esterification[13] and condensation[14] reactions prompted us to initiate a systematic study on the tosylation reaction. We report here, a novel protocol for tosylation of alcohols and selective monotosylation of diols mediated by the metal-exchanged montmorillonite clay catalyst, employing *p*-toluenesulfonic acid (TsOH) as tosylating agent

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Keywords: tosylation; montmorillonite; diols.

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Table 1. Sulfonylation of cyclohexanol (**1h**) catalyzed by various metal-exchanged clays

Entry	Sulfonic acid	Catalyst (mmol)[a]	Solvent	Time (h)	Sulfonate	Isolated yield (%)	TOF(h^{-1})[b]	Specific activity (mmol/g/h)[c]
1	TsOH	K10 mont.	DCE[d]	12	**2h**	52	–	1.3
2	TsOH	Cu^{2+}-mont. (0.020)	DCE	12	**2h**	75	7.5	1.5
3	TsOH	Zn^{2+}-mont. (0.027)	DCE	12	**2h**	84	7.7	2.1
4	TsOH	Al^{3+}-mont. (0.034)	DCE	12	**2h**	60	4.6	1.5
5	TsOH	Fe^{3+}-mont. (0.075)	DCE	3	**2h**	86 (85)[e]	11.4	8.6
6	TsOH	Fe^{3+}-mont. (0.075)	Toluene	3	**2h**	32[f]	3.2	3.2
7	TsOH	Fe^{3+}-mont. (0.075)	*n*-Heptane	4	**2h**	86	8.6	6.4
8	TsOH	Fe^{3+}-mont. (0.075)	*n*-Hexane	6	**2h**	84	5.6	4.2
9	$PhSO_3H$	Fe^{3+}-mont. (0.075)	DCE	4	**5**	85	8.5	6.3
10	MsOH	Fe^{3+}-mont. (0.075)	DCE	4	**6**	82	8.2	6.1

[a] Of exchanged cations.
[b] TOF (turnover frequency)=mmol sulfonate obtained per mmol of metal per hour.
[c] Specific activity=mmol of sulfonate obtained per gram of catalyst per hour.
[d] 1,2-Dichloroethane.
[e] Yield obtained with catalyst already used five times.
[f] Cyclohexyltoluenes were obtained in 65% yield (*ortho*/*para*=2:3) by ^{1}H NMR.

(Eq. (1)). This reaction generates water as the only by-product.

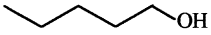
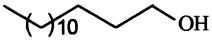
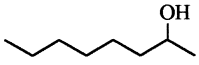
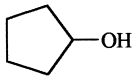
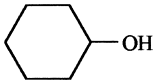
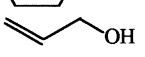
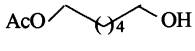
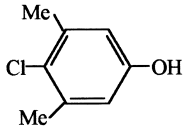
$$R\text{-}OH + R^1SO_3H \xrightarrow[\text{Clay, reflux}]{ClCH_2CH_2Cl} ROSO_2R^1 + H_2O \quad (1)$$

R^1 = *p*-tolyl, Ph, Me

Results and Discussion

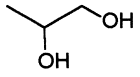
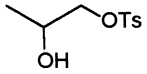
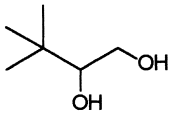
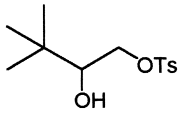
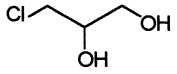
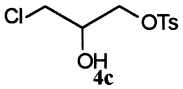
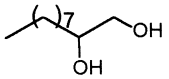
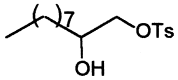
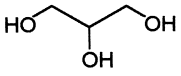
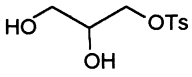
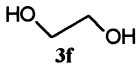
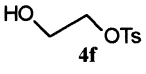
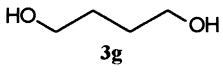
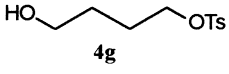
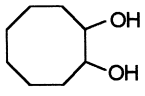
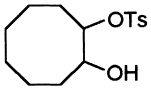
The reactions were conducted by stirring a mixture of alcohol, TsOH and clay catalyst in 1,2-dichloroethane at 80°C followed by a simple work-up procedure involving filtration of the solid catalyst and eventual evaporation of the solvent to obtain tosylated derivatives. This method-

Table 2. Tosylation of alcohols catalyzed by Fe^{3+}-montmorillonite clay

Alcohol		Time (h)	Tosylate	Isolated yield (%)	Specific activity (mmol /g / h)[a]
CH_3OH	**1a**	3	**2a**	82[b]	8.2
CH_3CH_2OH	**1b**	2	**2b**	78	11.7
	**1c**	2	**2c**	80	12.0
	**1d**	2	**2d**	84	12.6
$(CH_3)_2CHOH$	**1e**	5	**2e**	75	4.5
	**1f**	8	**2f**	82	3.0
	**1g**	4	**2g**	85	6.3
	**1h**	3	**2h**	86	8.6
	**1i**	2	**2i**	88	13.2
	**1j**	2	**2j**	89	13.3
	**1k**	24	**2k**	92	1.1

[a] Specific activity=mmol of sulfonate obtained per gram of catalyst per hour.
[b] Four equivalents of methanol were used.

Table 3. Selective monotosylation of diols and triol catalyzed by Fe^{3+}-montmorillonite

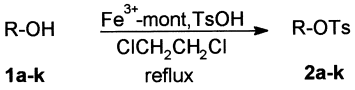
Entry	Substrate	Time (h)	Product [a]	Isolated yield (%)	Specific activity (mmol/g/h) [b]
1	 **3a**	4	 **4a**	76	5.7
2	 **3b**	3	 **4b**	94	9.4
3	 **3c**	4	 **4c**	82	6.1
4	 **3d**	4	 **4d**	85	6.3
5	 **3e**	6	 **4e**	50	2.5
6	 **3f**	5	 **4f**	84	5.0
7	 **3g**	4	 **4g**	78(75) [c]	5.8
8	 **3h**	4	 **4h**	82	6.1

[a] No secondary monotosylates by ^1H NMR (**4a**–**e**).
[b] Specific activity=mmol of sulfonate obtained per gram of catalyst per hour.
[c] The yield in parentheses refers to the ditosylated product with 2.2 equiv. of TsOH.

ology was extended to a larger scale (100 mmol scale) by removing azeotrope water with a Dean–Stark apparatus. Although azeotropic removal of water is not warranted for small scale operations (3 mmol), it is essential to remove water from larger scale reactions since the water formed inhibits the rate of reaction by blocking the acidic sites of montmorillonite. The tosylation reaction of cyclohexanol was optimized and a range of solvents was screened. Results indicate that heptane and hexane also afford similar yields to 1,2-dichloroethane at their reflux temperature but, with longer reaction timings. On the other hand, when toluene was used as solvent, the selectivity towards tosylated product is lowered due to a competing Friedel–Crafts alkylation reaction as described in Table 1, entry 6. The above tosylation reaction does not occur at room temperature. The tosylation occurs in the absence of catalyst too when conducted under identical conditions, but the yield is poor (18% for 12 h).

Results for the sulfonylation of cyclohexanol with various clay catalysts are summarized in Table 1. Fe^{3+}-montmorillonite showed better activity than the Zn^{2+}, Cu^{2+}, Al^{3+}-exchanged montmorillonites and the activity follows the sequence $Fe^{3+}>Zn^{2+}>Cu^{2+}>Al^{3+}$-montmorillonite>K10 montmorillonite. The catalytic activity in the tosylation of cyclohexanol was studied for five cycles and there was no loss in activity. The yields are 86, 85, 84, 85, 83, 85% from the fresh catalyst to the fifth recycle, respectively. The versatility of this method is also demonstrated in the sulfonylation of cyclohexanol with benzenesulfonic acid ($PhSO_3H$) and methanesulfonic acid (MsOH) which also afforded good yields (entries 9 and 10, Table 1).

As shown in Table 2, primary, secondary and allyl alcohols give tosylated products in good yields. Aliphatic alcohols are more easily tosylated than the aromatic alcohols. For example the time required for tosylation of 4-chloro-3,5-dimethylphenol (**1k**) is 24 h when compared to aliphatic alcohols (2–8 h). Primary alcohols such as ethanol, 1-pentanol and 1-tetradecanol are readily tosylated to the corresponding sulfonates in high yields within 2 h (**1b**–**d**). The reactions of secondary alcohols proceed slowly (3–8 h). However, aromatic alcohols such as phenol, 4-nitrophenol, 2,6-dimethylphenol, 2-*tert*-butyl-4-methylphenol and benzyl alcohols predominantly give rearranged or polymeric products under these conditions, except entry **1k** that yields tosylated product selectively upon prolonged reaction time.

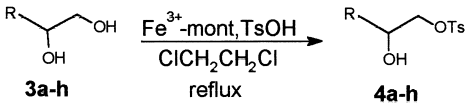


(2)

Aryl sulfonates are the best candidates for the McMurray coupling and Heck olefination, whilst alkyl sulfonates are useful for the preparation of formates,[15a] nitrites[15b] and intermediates for amines, which are chiral auxiliaries in asymmetric catalysis. Alkyl sulfonates, especially the cylohexyl sulfonate derivatives **2h** and **5** serve effectively as latent thermal catalysts for the cationic polymerization of isobutyl vinyl ether.[16]

Selective tosylation of diols

The difference in reaction rates between primary and secondary alcohols observed in Table 2 prompted us to examine the regioselective tosylation of alcohols. As shown in Table 3, diols are monotosylated selectively with one equivalent of TsOH. A significant feature is that diols, containing a primary and secondary hydroxy group underwent tosylation selectively at the primary hydroxy group in a ratio of more than 99:1 as determined by ^{1}H NMR. On the other hand the earlier method[17]using TsCl and pyridine offered a mixture of 1° OTs/2° OTs/ditosylate=7:1:1. Thus, the formation of secondary tosylate and ditosylate side products is always noticed in significant amounts. To enhance the regioselectivity, sterically more encumbered reagents such as 2,4,6-trimethylbenzenesulfonyl chloride and 2,4,6-triisopropyl-benzenesulfonyl chloride have also been employed. But the selectivities realized through this strategy are only 1° OTs/2° OTs/ditosylate=22:2:1.[17] Hence, the present solid acid, Fe^{3+}-montmorillonite induces very high selectivity in tosylation of a primary hydroxyl group in preference to the secondary hydroxy group to fulfil an important goal. This selective tosylation reaction assumes importance, since products of monotosylated derivatives are intermediates for drugs and pharmaceuticals. In the case of symmetrical diols, the reaction with one mole equivalent of TsOH provides selective monotosylation and with more than two molar quantities, ditosylation occurs. It is very significant that even triol is selectively tosylated as is evident in the tosylation of glycerol **3e**. Attempts to tosylate glucose derivatives were unsuccessful under these conditions. In the case of compound **3a**, the other metal-exchanged montmorillonites also give similar selectivities albeit lower yields. The higher yields obtained with Fe^{3+}-montmorillonite prompted us to opt for this as the catalyst for the other substrates.



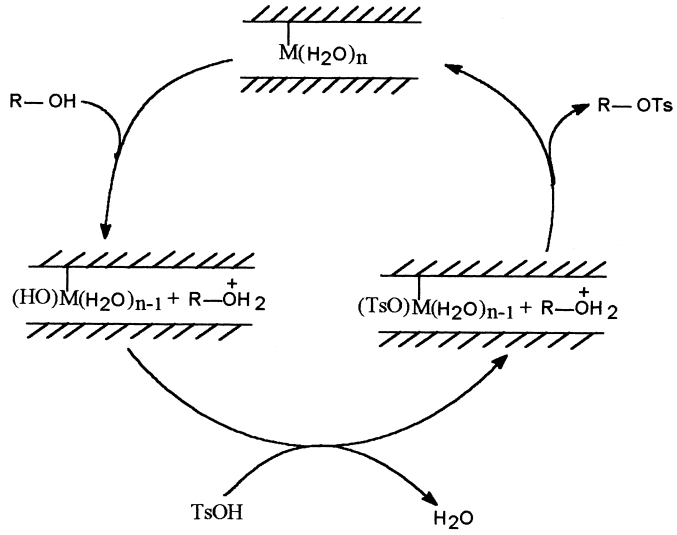
(3)

Hydroxy sulfonates are the precursors for epoxides en-route to the syntheses of number of natural products and drugs. It is important to realize a high regioselectivity in the initial sulfonylation step to obtain epoxides with high purity via cyclization of regiospecific hydroxy sulfonates. The synthesis of high purity monotosylates of 3-chloro-1,2-propanediol **4c**, an intermediate for a herbicide[18] and the bissulfonate of 1,4-butanediol (Table 3, note c), an antitumor drug (BUSULFAN),[19a] are possible by this environmentally friendly route. Further, the simple selective tosylation of diols described here also provides a very useful methodology for the synthesis of biologically active 1,2-amino alcohols, widely used as chiral auxiliaries and drug intermediates in the pharmaceutical industry.[19b]

Acid-treated montmorillonite, commercially known as montmorillonite K10, shows higher activity as a support than natural montmorillonite in the tosylation of alcohols. This is due to a highly mesoporous structure compatible for large reacting molecules and a high density of acidic sites. Therefore metal-exchanged montmorillonites are prepared using commercial K10 as a support. The activity of commercial K10 montmorillonite is lower than the metal-exchanged K10 montmorillonites in the tosylation of alcohols. This result indicates that the mere presence of a higher number of Bronsted acidic sites per unit volume are not adequate to afford optimum yields of tosylated product. In the hydrated montmorillonite, metal aquo-complexes generate protons to protonate approaching base[20a] and the number of protons generated is directly proportional to the ratio of ionic charge per ionic radius of exchanged metal ion. Accordingly, intercalated Fe^{3+} complex generates a higher number of protons than the other metal ions as is evident in the results of temperature-programmed desorption of ammonia gas (NH_3-TPD). Lewis acidic sites are also introduced by exchange of metal cations in montmorillonite K10. In fact this is indicated in our TPD studies in which out of a total of 1.029 mmol/g desorbed, 0.973 mmol/g desorbed at a higher temperature range (320–450°C) may be mostly due to Lewis acidic sites. These results are in conformity to the results of acidity measurements of Fe^{3+}-montmorillonte observed in IR studies.[20b] The higher activity of the Fe^{3+}-montmorillonite is therefore ascribed to the introduction of Lewis acidic sites through the exchange of iron in montmorillonite and also by the higher density of Bronsted acid sites as described.

A plausible mechanism for metal-exchanged clay-catalyzed tosylation is described (Scheme 1). The aquo-complex of metal-exchanged in montmorillonite protonates alcohol to form hydroxy metal aquo-complex, which in turn reacts with TsOH to form metal tosylate salt. The interaction of metal tosylate and protonated alcohol gives the tosylated product and regenerates the metal aquo-complex.

Manipulations of selective tosylation of diols may be based



Scheme 1. A plausible mechanism for metal-exchanged clay catalyzed tosylation of alcohol.

upon steric effects, which render one hydroxyl group more reactive than the other[21a] and in fact, this has recently been shown with chelated Sn complexes.[21b,c] The high selectivity towards primary alcohol is achieved by the design and use of partially disrupted lamellar clay material. It is attributed to the effective steric crowding in the mesoporous system of the solid acid that renders relatively uncrowded primary alcohol as the primary target in preference to the branched secondary alcohol of the same molecule. When the primary alcohol is at the end of the molecule, it is more accessible to the acidic sites present in the montmorillonite mesopores. It is striking to note that the steric effects induced by the catalyst are more pronounced in the present case than with the more sterically crowded sulfonylating reagents. It should also be noted that chelation of the diol by Fe^{3+} followed by selective sulfonylation of primary alcohol cannot be ruled out.

Conclusions

In summary, a simple methodology for the sulfonylation of alcohols with cheap *p*-toluenesulfonic acid as tosylating agent, rather than tosyl chloride or tosyl anhydride is described. This shorter process is catalyzed by a small amount of reusable Fe^{3+}-montmorillonite as catalyst. This present methodology, in which the only by-product is water, offers superior enviro-economical viability over presently practiced tosylations conducted with stoichiometric quantities of TsCl/pyridine as it generates large amounts of salt effluents. The higher activity of Fe^{3+}-montmorillonite is due to a compatible mixture of a large number of Lewis and Bronsted acid sites per unit volume. Less toxic and environmentally friendly solvents such as heptane and hexane also offer good yields. Steric crowding of the supported catalyst influences higher selectivity towards a primary alcohol group. Hence, with the significant features of high atom economy and a near zero emission of effluents our methodology is not only economic, but also meets with the stringent requirements of environmental laws.

Experimental

Infrared spectra were recorded on Nicolet 740 FTIR either as film or KBr pellets. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200 MHz instrument for solutions in $CDCl_3$ with TMS as an internal standard. Mass spectra were recorded on VG micromass 7070H and Fennigan Mat 1020 mass spectrometer. Thin layer chromatography was performed on silica gel 60 F_{254} plates procured from E-Merck. Column chromatography was performed using silica gel 60 (230–400 mesh). *p*-Toluenesulfonic acid, benzenesulfonic acid, methanesulfonic acid and 1,2-dichloroethane (Spectrochem, India) were used without further purification. Starting materials purchased from Aldrich or Fluka were used as received. All reactions were run in flame-dried glassware under a nitrogen atmosphere.

Preparation of catalysts

K10 montmorillonite purchased from Fluka was used as such. The chemical composition of this starting material (main elements) is SiO_2, 67.6; Al_2O_3, 14.6; Fe_2O_3, 2.9; MgO, 1.8. Metal-exchanged montmorillonite:[22] to 1 L of 1 M aqueous metal chloride solution, 80 g of K10 montmorillonite was added. Stirring was maintained for 16–30 h in order to saturate the exchange capacity of K10 montmorillonite. The clay suspension was centrifuged and the supernatant solution was discarded. The clay catalyst was washed each time with fresh distilled water until free of chloride ions as indicated by $AgNO_3$ test. The catalyst was dried overnight in an oven at 120°C and finely ground in a mortar.

The metal content of each Fe^{3+}, Zn^{2+}, Cu^{2+}, Al^{3+}-exchanged montmorillonite catalysts were analyzed according to Vogel's procedure[23] and found to be 6.3, 1.79, 1.28 and 7.82% respectively. The maximum acid strengths for K10 montmorillonite with Hammett indicators in benzene are known ($-8.2 \geq H_0$).[24] It is difficult to judge color changes of Hammett indicators for Fe^{3+} and

Cu^{2+}-montmorillonites since these two are colored. Hence, the amount of acid sites (Bronsted and Lewis acid sites) of Fe^{3+}, Zn^{2+}, Cu^{2+}, Al^{3+}-exchanged montmorillonite and K10 was estimated by the temperature-programmed desorption of ammonia gas (NH_3-TPD) analyses and found to be 1.029, 0.547, 0.35, 0.524, 0.047 mmol/g, respectively. For example a glass vessel containing clay catalyst (ca. 80–90 mg) was evacuated at 250°C for 2 h. After it had been cooled to 100°C, ammonia gas was introduced into the glass vessel for 1.5 h. After subsequent evacuation at 100°C for 2 h, the amount of adsorbed ammonia gas was desorbed by stepwise TPD in the range of 120–450°C and the amount of desorbed ammonia was measured using the TCD signal. Specific surface areas are calculated from BET nitrogen isotherms determined at −196°C (Micromeritics ASAP 2000) on samples degassed at 250°C for 12 h before the experiment.

Tosylation of cyclohexanol: general procedure

To a solution of cyclohexanol (0.3 g, 3 mmol) and *p*-toluenesulfonic acid (0.57 g, 3 mmol) in 1,2-dichloroethane (20 mL), Fe^{3+}-montmorillonite (0.1 g, 0.075 mmol of exchanged Fe) was added and refluxed in a two-necked flask equipped with a Dean–Stark apparatus. The reaction was complete in 3 h (monitored by TLC). The reaction mixture was filtered and washed with 1,2-dichloroethane (10 mL) to remove the catalyst. The solvent was removed under reduced pressure and the product was column chromatographed (2% ethyl acetate/petroleum ether) on a silica gel column to afford cyclohexyl tosylate (0.655 g, 86% yield).

For compounds **2a**–**2c**, and **2e** the reaction mixture was filtered and extracted with water to remove the unreacted tosic acid, then evaporation of solvent gave chromatographically pure products. The products have been characterized by their spectral (IR, ^1H and ^{13}C NMR and mass) data and melting points.

Methyl *p*-toluenesulfonate (2a).[26] Thick oil; IR (film) 1178, 1351 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.45 (3H, s, CH_3), 3.72 (3H, s, OCH_3), 7.32 (2H, d, *m*-H, *J*=9.0 Hz), 7.78 (2H, d, *o*-H, *J*=9.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 144.45, 132.12, 129.53, 127.58 (Ar carbons), 95.76 (CH_3O), 21.10 (CH_3); MS (EI) *m*/*z* 186 (M^+, 20), 155 (27), 91 (100), 65 (42).

Ethyl *p*-toluenesulfonate (2b).[26] Thick oil; IR (film) 1179, 1351 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.30 (3H, t, *J*=6.8 Hz, CH_3), 2.44 (3H, s, CH_3), 4.08 (2H, q, *J*=7.1 Hz, OCH_2), 7.32 (2H, d, *m*-H, *J*=9.0 Hz), 7.78 (2H, d, *o*-H, *J*=9.0 Hz); MS (EI) *m*/*z* 200 (M^+, 12), 155 (28), 107 (15), 91 (100), 65 (75), 39 (42).

1-Pentyl *p*-toluenesulfonate (2c).[27] Thick oil; IR (film) 1175, 1351 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (3H, t, *J*=7.1 Hz, CH_3), 1.27 (4H, m, alkane), 1.67 (2H, m, CH_2), 2.44 (3H, s, CH_3), 4.02 (2H, t, *J*=6.9 Hz, CH_2O–), 7.32 (2H, d, *m*-H, *J*=8.1 Hz), 7.78 (2H, d, *o*-H, *J*=8.1 Hz).

1-Tetradecyl *p*-toluenesulfonate (2d).[3c] Semisolid; IR (film) 1170, 1351 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (3H, t, *J*=7.2 Hz, CH_3), 1.24 (22H, brs, alkane), 1.62 (2H, m, CH_2), 2.44 (3H, s, CH_3), 4.02 (2H, t, *J*=6.9 Hz, CH_2O–), 7.32 (2H, d, *m*-H, *J*=8.1 Hz), 7.78 (2H, d, *o*-H, *J*=8.1 Hz).

2-Propyl *p*-toluenesulfonate (2e).[26] Thick oil; IR (film) 1170, 1351 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20 (6H, d, *J*=6.9 Hz, $CHMe_2$), 2.45 (3H, s, CH_3), 4.63 (1H, h, *J*=6.9 Hz, CHO–), 7.32 (2H, d, *m*-H, *J*=8.1 Hz), 7.78 (2H, d, *o*-H, *J*=8.1 Hz); MS (EI) *m*/*z* 214 (M^+, 2), 172 (62), 107 (33), 91 (100), 65 (31).

2-Octyl *p*-toluenesulfonate (2f).[26] Thick oil; IR (film) 1173, 1352 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.84 (3H, t, *J*=7.2 Hz, CH_3), 1.18 (3H, d, $CHCH_3$) 1.23 (8H, m, alkane) 2.45 (3H, s, CH_3), 4.53 (1H, m, CHO–), 7.32 (2H, d, *m*-H, *J*=8.1 Hz), 7.79 (2H, d, *o*-H, *J*=8.1 Hz).

Cyclopentyl *p*-toluenesulfonate (2g).[25] Thick oil; IR (film) 1172, 1354 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.54–1.78 (8H, m, $-[CH_2]_4-$), 2.43 (3H, s, CH_3), 4.94 (1H, m, CHO–), 7.32 (2H, d, *m*-H, *J*=8.1 Hz), 7.78 (2H, d, *o*-H, *J*=8.1 Hz); MS (EI) *m*/*z* 240 (M^+, 2), 172 (61), 107 (33), 91 (100), 65 (34).

Cyclohexyl *p*-toluenesulfonate (2h).[25] Thick oil; IR (film) 1170, 1351 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.30–1.78 (10H, m, $-[CH_2]_5-$), 2.44 (3H, s, CH_3), 4.49 (1H, m, CHO–), 7.32 (2H, d, *m*-H, *J*=8.8 Hz), 7.79 (2H, d, *o*-H, *J*=8.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 143.99, 134.32, 129.38, 127.11 (Ar carbons), 81.12 (CHO), 31.90, 24.46, 22.92, 21.11 (alkane); MS (EI) *m*/*z* 254 (M^+, 2), 173 (100), 155 (46), 91 (31), 82 (31), 67 (22), 65 (7).

Allyl *p*-toluenesulfonate (2i).[27] Thick oil; IR (film) 1175, 1361 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.44 (3H, s, CH_3), 4.51 (2H, d, *J*=5.1 Hz, CH_2O–), 5.27 (2H, dd, *J*=1.8, 13.9 Hz, $=CH_2$), 5.82 (1H, m, =CH–), 7.32 (2H, d, *m*-H, *J*=8.1 Hz), 7.78 (2H, d, *o*-H, *J*=8.1 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 145.2, 133.1, 129.8, 128.0 (Ar carbons), 120.3, 71.2, 21.9 (aliphatic carbons); MS (EI) *m*/*z* 121 (M^+-CH_3Ph, 100), 91 (12), 77 (9).

6-Acetyloxyhexyl *p*-toluenesulfonate (2j). Liquid; IR (film) 1176, 1359 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.38 (4H, m), 1.67 (4H, m), 2.06 (3H, s, CH_3), 2.45 (3H, s, CH_3), 3.93–4.1 (4H, 2t, *J*=7.1 and 6.9 Hz, 2×CH_2O–), 7.32 (2H, d, *m*-H, *J*=8.1 Hz), 7.78 (2H, d, *o*-H, *J*=8.1 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 170.4(CO), 144.3, 132.1, 129.7, 127.9 (Ar carbons), 96.1, 64.0, 28.8, 28.4, 25.3, 25.1, 21.6, 20.8; Anal. Calcd for $C_{15}H_{22}O_5S$: C, 57.30; H, 7.04; S, 10.19. Found: C, 57.24; H, 7.05; S, 10.16.

4-Chloro-3,5-dimethylphenyl *p*-toluenesulfonate (2k). The reaction mixture was filtered to remove the catalyst and work-up procedure was carried with aqueous NaOH solution. The organic layer was then dried (Na_2SO_4) and concentrated to give the product as a white solid: mp 96–98°C (Lit.[28] mp 95°C); IR (KBr) 1179, 1360 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 2.31 (6H, s, *m*-CH_3), 2.47 (3H, s, CH_3), 6.72 (2H, s), 7.32 (2H, d, *m*-H, *J*=9.0 Hz), 7.73 (2H, d, *o*-H, *J*=9.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 147.2, 145.6,

137.6, 133.3, 132.8, 129.9, 128.7, 122.1 (Ar carbons), 21.8, 20.7 (CH_3); MS (EI) *m*/*z* 310 (M^+, 13) 155 (45), 127 (7), 91 (100), 65 (27).

2-Hydroxypropyl *p*-toluenesulfonate (4a). The crude product was purified by silica gel column in EtOAc/hexane 1:4. Mp 48–49°C (Lit.[18] mp 49.5–50°C); IR (KBr) 1175, 1352 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.16 (3H, d, J=6.0 Hz, CH_3), 2.21 (1H, brs, OH), 2.44 (3H, s, CH_3), 3.82 (1H, m, CH–), 4.04 (2H, m, CH_2O–), 7.32 (2H, d, *m*-H, J=8.1 Hz), 7.79 (2H, d, *o*-H, J=8.1 Hz); MS (EI) *m*/*z* 200 (M^+-CH_3, 13), 156 (34), 91 (100), 57 (48), 43 (39).

2-Hydroxy-3,3-dimethylbutyl *p*-toluenesulfonate (4b). Mp 45–46°C (Lit.[29a] mp 45–46°C); IR (KBr) 1179, 1351, 3546 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (9H, s, $-CMe_3$), 2.45 (3H, s, CH_3), 2.64 (1H, brs, OH), 3.52 (1H, dd, J=2.3, 9.3 Hz, CH_2OTs), 3.93 (1H, t, J=9.3 Hz, $-CH_2CH$–), 4.22 (1H, dd, J=2.3, 9.3 Hz, CH_2OTs), 7.34 (2H, d, *m*-H, J=8.1 Hz), 7.80 (2H, d, *o*-H, J=8.1 Hz).

2-Hydroxy-3-chloropropyl *p*-toluenesulfonate (4c).[18] Thick oil; IR (film) 1178, 1351 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.43 (3H, s, CH_3), 2.65 (1H, brs, OH), 3.56 (2H, d, J=5.3 Hz, CH_2Cl), 4.02 (1H, m, CH), 4.09 (2H, d, J=5.0 Hz, CH_2O), 7.34 (2H, d, *m*-H, J=8.1 Hz), 7.78 (2H, d, *o*-H, J=8.1 Hz); MS (EI) *m*/*z* 155 ($M^+-C_3H_6ClO_2$, 65), 91 (100), 65 (28), 43 (46).

2-Hydroxydecyl *p*-toluenesulfonate (4d). Mp 39–41°C (Lit.[29b] mp 39–41°C); IR (film) 1173, 1358 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.9 (3H, t, J=6.4 Hz, CH_3), 1.1–1.7 (14H, m), 2.12 (1H, brs, OH), 2.46 (3H, s, CH_3), 3.70–4.02 (3H, m, $-CH_2CH$–), 7.38 (2H, d, *m*-H, J=8.6 Hz), 7.81 (2H, d, *o*-H, J=8.6 Hz).

2,3-Dihydroxypropyl *p*-toluenesulfonate (4e). The crude product was purified by silica gel column in EtOAc/hexane 1:1. mp 51–53°C (Lit.[29c] mp 54°C); IR (KBr) 1175, 1356, 3365 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.40 (3H, s, CH_3), 3.5–3.95 (5H, m, 3-H_2, 2-H and 2×OH), 4.09 (2H, d, J=5.0 Hz, 1-H_2), 7.38 (2H, d, *m*-H, J=8.1 Hz), 7.8 (2H, d, *o*-H, J=8.1 Hz).); ^{13}C NMR (200 MHz, $CDCl_3$) δ 145.7, 132.7, 130.5, 120.5, 71.3, 70.1, 63.3, 22.1.

2-Hydroxyethyl *p*-toluenesulfonate (4f).[6c] Thick oil; IR (film) 1179, 1351, 3400 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.44 (3H, s, CH_3), 3.78 (2H, t, J=5.1 Hz, CH_2OH), 4.12 (2H, t, J=5.1 Hz, CH_2O), 7.32 (2H, d, *m*-H, J=8.1 Hz), 7.79 (2H, d, *o*-H, J=8.1 Hz); MS (EI) *m*/*z* 216 (M^+, 2), 155 (33), 121 (100), 91 (73), 65 (19).

4-Hydroxybutyl *p*-toluenesulfonate (4g).[30] Thick oil; IR (film) 1187, 1351 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.54 (2H, m, CH_2), 1.67 (2H, m, CH_2), 2.44 (3H, s, CH_3), 3.31 (2H, t, J=6.5 Hz, CH_2OH), 4.01 (2H, t, J=5.8 Hz, CH_2O), 7.32 (2H, d, *m*-H, J=8.1 Hz), 7.79 (2H, d, *o*-H, J=8.1 Hz).

2-Hydroxycyclooctyl *p*-toluenesulfonate (4h).[31] Thick oil; IR (film) 1171, 1350 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.27–2.06 (12H, m, alkane), 2.43 (3H, s, CH_3), 3.73 (1H, m, CHOH), 4.46 (1H, m, CHOTs), 7.32 (2H, d, *m*-H, J=8.1 Hz), 7.79 (2H, d, *o*-H, J=8.1 Hz).

Cyclohexyl benzenesulfonate (5).[32] Thick oil; IR (film) 1170, 1351 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.34–1.80 (10H, m, $-[CH_2]_5$–), 4.53 (1H, m, CHO–), 7.56 (3H, m, Ar-H), 7.91 (2H, d, J=7.5 Hz, Ar-H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 133.27, 129.13, 128.99, 127.35 (Ar carbons), 81.81 (CHO), 32.17, 24.68, 23.18 (alkane).

Cyclohexyl methanesulfonate (6).[33] Thick oil; IR (film) 1175, 1354 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.32–1.98 (10H, m, $-[CH_2]_5$–), 2.97 (3H, s, CH_3), 4.78 (1H, m, CHO–).

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