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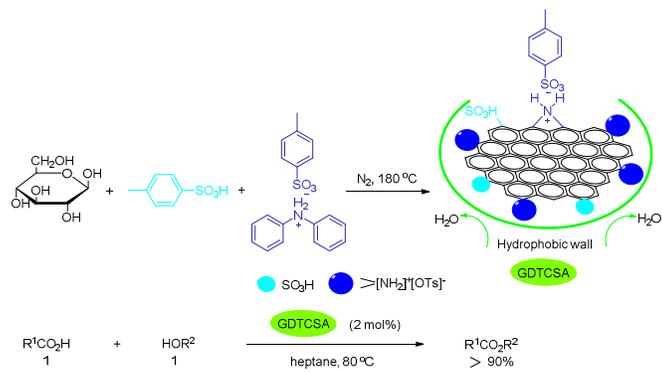
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A novel carbon material has been prepared conveniently, it can be catalyzed the esterification reaction with high reactivity and selectivity.



The Carbon Material Functionalized with NH_2^+ and SO_3H Groups Catalyzed Esterification with High Activity and Selectivity

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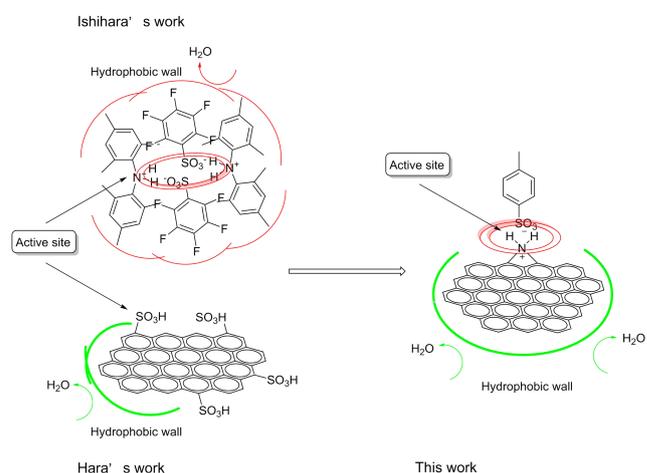
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A novel carbon-based solid acid has been conveniently prepared by heating the mixture of D-glucose, *p*-toluenesulfonic acid and diphenylammonium tosylate. Its structure has been measured by XRD, FT-IR, XPS, ^{13}C MAS NMR and EA to illustrate that the carbon material has been functionalized with NH_2^+ and SO_3H groups and has a strong “hydrophobic effect”. It can be used to catalyze the esterification reaction of carboxylic acids with equimolar amounts of sterically demanding and acid-sensitive alcohols with high reactivity (yield up to 90%) and selectivity (up to 95%) in heptane at 80 °C. And it could be easily recovered and reused more than ten times without loss of activity.

Generally, the esterification reaction between carboxylic acids and alcohols is catalyzed by Brønsted acids such as H_2SO_4 , *p*-toluenesulfonic acid, etc.^{1,2} Although these catalysts show good activity for esterification reaction, too strong acidity often leads to low selectivity for some acid-sensitive alcohols, such as secondary alcohol which can be converted to alkene in the presence of a strong acid.³ In 2000, Tanabe et al. developed a new type of esterification catalyst diphenylammonium triflate ($[\text{Ph}_2\text{NH}_2]^+[\text{OTf}]^-$),⁴ which has a weaker acidity and can be used to catalyze esterification of carboxylic acids with equimolar amounts of secondary alcohols in high yields. Subsequently, Ishihara’s group reported that bulky diarylammonium pentafluorobenzenesulfonates ($[\text{Ar}_2\text{NH}_2]^+[\text{O}_3\text{SC}_6\text{F}_5]^-$) were more efficient than $[\text{Ph}_2\text{NH}_2]^+[\text{OTf}]^-$ in catalytic activity and selectivity.^{3,5-7} They assumed that it is the dimeric cyclic ion pairs composed of two diarylammonium cations ($[\text{Ar}_2\text{NH}_2]^+$) and two pentafluorobenzenesulfonate anions ($[\text{O}_3\text{SC}_6\text{F}_5]^-$) which could form a “hydrophobic wall” to promote the esterification reactions. Also their steric hindrance could effectively suppress the

dehydrative elimination of secondary alcohols to produce alkenes (Scheme 1).⁶ In order to reuse these catalysts, several groups had tried to immobilize these types of ammonium salts on polymer, but complex synthetic process and unstability of polymer in high temperature limited the application.⁷⁻⁹

In 2005, Hara’s group found a new carbon-based solid sulfonic acid, which was prepared by incompletely carbonizing glucose at high temperature (over 300 °C) to form a carbon-based material first, and then sulfonating it with large amount of concentrated sulfuric acid.¹⁰ The successive research optimized this preparation method,¹¹⁻¹⁶ including using aryl sulfonic acid as the resource of sulfonic acid group to avoid harsh reaction condition.¹⁷⁻¹⁹ This method is a convenient and efficient way to immobilize the sulfonic acid groups on the carbon-base material, and the recyclable catalyst showed good activity for esterification of simple carboxylic acids (such as acetic acid, oleic acid, etc) and alcohols (such as methanol, ethanol, etc).²⁰⁻²⁴ Strong hydrophobic polycyclic aromatic carbon sheets formed by incompletely carbonizing of organic matter is the key issue, which can prevent the produced water from gaining access to the active site of the catalysts and thus inhibits the inactivation of the catalyst by water (Scheme 1).^{24,25}



Scheme 1 Proposed strategy to improve the catalytic activity and selectivity by a synergistic effect of Ishihara’s and Hara’s catalyst.

Based on that, we assume using polycyclic aromatic carbon sheets in amorphous carbon to replace the bulky diarylamine and pentafluorophenyl groups as “hydrophobic wall”, and less bulky

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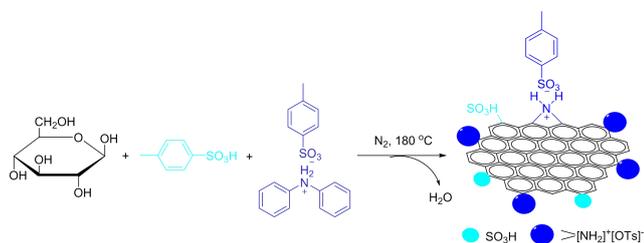
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† Electronic Supplementary Information (ESI) available: Experimental details, XRD pattern, SEM image, TGA pattern, FT-IR spectra, ^{13}C MAS NMR spectrum, ^1H NMR spectra, ^{13}C NMR spectra. See DOI: 10.1039/b000000x/

diphenylammonium tosylate ($[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$) as active site, the new carbon-based solid acid should have similar catalytic reactivity and selectivity as Ishihara's (Scheme 1). Moreover, the salt is embedded into the matrix of the carbon-based material, so it can be reused in catalytic esterification reaction.

Here, we report a novel carbon-based solid acid prepared by introducing $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ to the carbon-based material during the process of one-step incomplete carbonization of glucose and *p*-toluenesulfonic acid. This carbon-based solid acid showed high activity and selectivity in the catalytic ester condensation, and was recycled for ten times without losing the catalytic activity.



Scheme 2 Preparation of the GDTCSA.

The carbon-based solid acid can be readily prepared by heating the mixture of glucose, *p*-toluenesulfonic acid and $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ at 180 °C for 5 hours under a flow of nitrogen (Scheme 2). After cooled down to room temperature, the reaction product was washed with hot toluene to remove and recover unreacted raw materials, then the glucose-diphenylammonium tosylate-derived carbon solid acid (GDTCSA) was obtained as a black powder.

The X-ray diffraction (XRD) pattern of sample GDTCSA exhibits two diffraction peaks at 2θ angle of 20° and 45° (see supplementary information), which is typical of amorphous carbon consisting of disordered polycyclic aromatic carbon sheets²⁶ with a flat structure. The absorption spectrum of Fourier transform infrared spectroscopy (FT-IR) for the GDTCSA at 1040 cm^{-1} , 1167 cm^{-1} and 1495 cm^{-1} , 1507 cm^{-1} confirms the existence of $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ ⁷ and SO_3H groups²³ (see supplementary information). The X-ray photoelectron spectroscopy (XPS) spectra of the GDTCSA reveal a single S 2p peak at 168 eV and a single N 1s peak at 401 eV (Fig. 1), which are attributable to sulfur in the SO_3H groups²⁷ and nitrogen in the diphenylammonium (Ph_2NH_2^+)²⁸ respectively. The ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectrum of the GDTCSA is shown in Fig. 2. The peak at 20 ppm is assigned to CH_3 groups on the polycyclic aromatic rings; 130 ppm is the signal peak of polycyclic aromatic carbon atoms. There are three peaks at 139, 140 and 141 ppm, which are attributable to polycyclic aromatic carbon sheets with SO_3H groups,²⁹ $[\text{Ph}_2\text{NH}_2]^+$ ⁷ and *p*-toluenesulfonate anions (TsO^-).⁸ In addition, the GDTCSA also contains phenolic OH (150 ppm) and COOH (180 ppm) groups. These results show that the carbon-based material is a polycyclic aromatic plane structure loaded with active Brønsted acids of $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ and SO_3H groups.

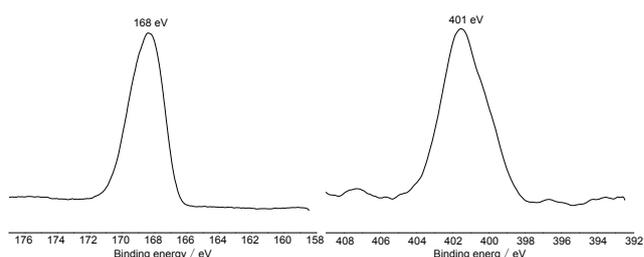


Fig. 1 XPS spectra of the GDTCSA.

Table 1 summarizes the structural parameters of the GDTCSA, including the nominal composition, the acid amount of $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ and SO_3H groups. The nominal composition of the GDTCSA suggests that the sulfur component is more than nitrogen, which indicates that sulfur not only existed in the forms of *p*-TsOH to form a salt with diphenylamine, but there is also about 1/4 sulfur attached to the polycyclic aromatic carbon sheets in the forms of SO_3H groups. And the amount of GDTCSA as a catalyst for the esterification reaction is based on the acid amount of $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ and SO_3H groups. GDTCSA was treated with dilute aqueous NaOH (Scheme 3). The reactant was filtered, the filtered aqueous phase was concentrated and then recrystallized by EtOH to give a white solid (w.t. 32%), which was confirmed as sodium *p*-toluene sulfonate by ^1H NMR analysis and melt point measurement.³⁰ For black filter residue GDCSA (w.t. 67%), the absorption spectrum of FT-IR (see supplementary information) and the component (Table 1) show that TsO^- was lost from GDTCSA, but diphenylamine groups were still immobilized on the matrix of the carbon-based material, and there were also small number of SO_3H groups connected with it.

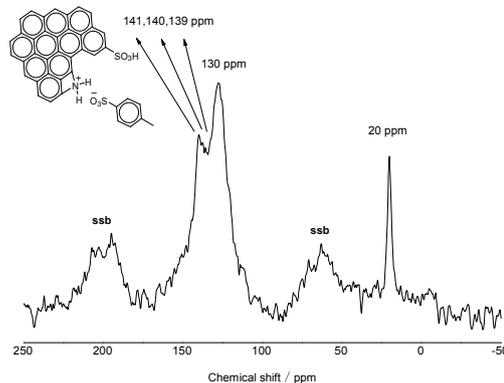


Fig. 2 ^{13}C MAS NMR spectrum of the GDTCSA.

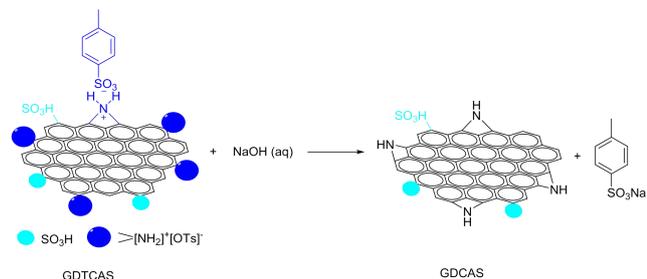
Table 1 Structural Parameters of the GDTCSA and the GDCSA.

catalsysis	composition ^a	acid amount ^b (mmol·g ⁻¹)
GDTCSA	$\text{CH}_{0.89}\text{O}_{0.2}\text{N}_{0.03}\text{S}_{0.04}$	2.43
GDCSA	$\text{CH}_{0.88}\text{O}_{0.17}\text{N}_{0.03}\text{S}_{0.01}$	0.61

^a The nominal sample composition was determined by elemental analysis. ^b The acid amount of $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ and SO_3H groups was estimated by sulfur elemental analysis.

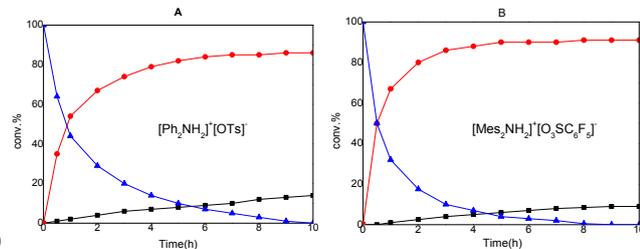
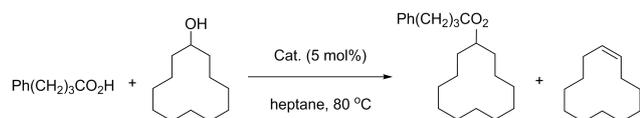
These results illustrate that *p*-toluenesulfonic acid participated in the process of incompletely carbonized glucose and provided the SO_3H groups for the polycyclic aromatic carbon sheets of flat structure. Meanwhile, most of the $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ were introduced to the carbonaceous material and the diphenylamine

groups were embedded in the carbon sheets to provide the NH_2^+ groups.

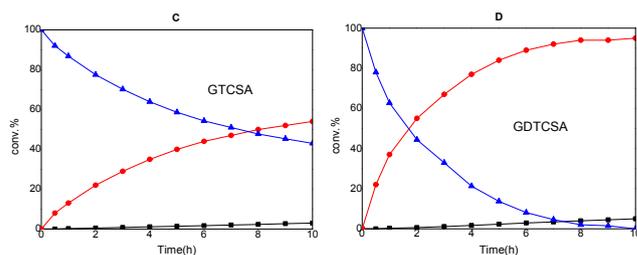


Scheme 3 GDTCSA was reacted with dilute aqueous NaOH.

5 According to the Ishihara's method,^{3,7} 4-phenylbutyric acid was condensed with an equimolar amount of cyclododecanol in heating heptane using 5 mol% $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$,⁸ dimesitylammonium pentafluorobenzenesulfonate ($[\text{Mes}_2\text{NH}_2]^+[\text{O}_3\text{SC}_6\text{F}_5]^-$),³¹ the glucose-TsOH-derived carbon solid acid (GTCSA)¹⁷ and GDTCSA as catalyst respectively to examine their catalytic activities and selectivities in this reaction by ¹H NMR analysis (Fig. 3). First, homogeneous catalyst $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ was used, cyclododecyl 4-phenylbutyrate (graph A red line) and cyclododecene (graph A black line) were produced at 80 °C, and latter conversion was up to 15%, while bulky homogeneous catalyst $[\text{Mes}_2\text{NH}_2]^+[\text{O}_3\text{SC}_6\text{F}_5]^-$ showed higher catalytic activity (graph B red line) and selectivity (graph B black line) than $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$, these results were similar to the Ishihara's report.^{3,7} The dehydration rate from cyclododecanol to cyclododecene decreased to 3% (graph C black line), but the esterification rate also decreased to 54% (graph C red line) even at heptane reflux (98 °C) with the heterogeneous catalyst GTCSA. When the novel carbon-based solid acid GDTCSA was used, the catalytic rate was slower initially than the two homogeneous catalysts indicated above. This might be due to physical diffusion barriers of heterogeneous catalyst.³²⁻³³ As the reaction carried on, both external and internal diffusion limitations did not affect the overall reaction rate,³² so the maximum conversion of the ester increased to more than 95% (graph D red line) and the cyclododecene was suppressed to less than 5% (graph D black line) at 80 °C. These experimental results showed that GDTCSA immobilized with both NH_2^+ and SO_3H groups was more active than GTCSA contained only SO_3H groups in the catalytic condensation reaction. And strong "hydrophobic effect" due to polycyclic aromatic carbon sheets of the carbon solid acid could effectively suppress the dehydrative elimination of secondary alcohol to produce alkene by comparison between GDTCSA and less bulky $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$.



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catalytic activity: $[\text{Mes}_2\text{NH}_2]^+[\text{O}_3\text{SC}_6\text{F}_5]^- \geq [\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^- \geq \text{GDTCSA} > \text{GTCSA}$
selectivity: $\text{GTCSA} \geq \text{GDTCSA} \geq [\text{Mes}_2\text{NH}_2]^+[\text{O}_3\text{SC}_6\text{F}_5]^- > [\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$

15 Fig. 3 Esterification of 4-phenylbutyric acid with cyclododecanol catalyzed by various catalysts $[\text{Ph}_2\text{NH}_2]^+[\text{OTs}]^-$ (graph A), $[\text{Mes}_2\text{NH}_2]^+[\text{O}_3\text{SC}_6\text{F}_5]^-$ (graph B), GTCSA (graph C), GDTCSA (graph D). The ratio of cyclododecanol (blue line), cyclododecyl 4-phenylbutyrate (red line) and cyclododecene (black line) in the reaction mixture over time was evaluated by ¹H NMR analysis.

50 To explore the generality and scope of the selective esterification catalyzed by GDTCSA (2 mol%) in heptane at 80 °C, the condensation was examined with an equimolar mixture of various structurally diverse carboxylic acids and alcohols (Table 2). Straight-chain carboxylic acids and alcohols were easily condensed to produce the corresponding esters (entries 1-6). Sterically demanding pivalic acid and 3-cyclopentene-1-carboxylic acid were apt to be condensed to obtain the corresponding esters (entries 7-9). Benzoic acid and α , β -unsaturated carboxylic acids were also transformed into the relevant esters (entries 10-12). Allylic alcohol and propargylic alcohol were similarly converted into the appropriate esters (entries 13-14). In particular, GDTCSA could be used for acid-sensitive and sterically demanding alcohols such as cyclododecanol, cyclohexanol and menthol to give the desired esters in good yields with high selectivity (entries 15-20). The citric acid and glycerol could be also esterified completely with the corresponding alcohol and carboxylic acid respectively (entries 21-22).

70 Table 2 Esterification reaction between an equimolar mixture of carboxylic acids and alcohols catalyzed by GDTCSA.^a

R ¹ CO ₂ H		+	HOR ²	GDTCSA (2 mol%)		R ¹ CO ₂ R ²
				heptane, 80 °C		
Entry	R ¹ CO ₂ R ²	Time (h)	Yield (%) ^b	Entry	R ¹ CO ₂ R ²	Time (h) Yield (%) ^b
1	PhCH ₂ CO ₂ C ₁₂ H ₂₅	1	94	13	PhCH ₂ CO ₂	3 97
2	PhCH ₂ CO ₂ Bn	1	99	14	PhCH ₂ CO ₂	24 90
3	Ph(CH ₂) ₃ CO ₂ C ₆ H ₁₃	1	99	15	PhCH ₂ CO ₂ C ₁₂ H ₂₅ ^c	10 97 (98)
4	Ph(CH ₂) ₃ CO ₂ C ₆ H ₁₇	1	98	16	Ph(CH ₂) ₃ CO ₂ C ₁₂ H ₂₅ ^d	10 95 (98)
5	C ₁₁ H ₂₃ CO ₂ C ₆ H ₁₃	4	93	17	PhCH ₂ CO ₂ C ₆ H ₁₁ ^d	7 97 (99)
6	C ₁₇ H ₃₃ CO ₂ C ₆ H ₁₃	7	94	18	C ₁₁ H ₂₃ CO ₂ C ₆ H ₁₁ ^d	11 91 (99)
7	<i>t</i> -BuCO ₂ C ₆ H ₁₃	6	94	19	PhCH ₂ CO ₂ C ₁₀ H ₁₉ ^e	8 92 ^f (99)
8	<i>t</i> -BuCO ₂ C ₆ H ₁₇	6	94	20	Ph(CH ₂) ₃ CO ₂ C ₁₀ H ₁₉ ^e	10 94 ^g (99)
9	CO ₂ C ₆ H ₁₃	5	96			
10	PhCO ₂ C ₆ H ₁₃	24	93	21	HO	24 95
11	Ph CO ₂ C ₆ H ₁₃	24	95	22		18 93
12	CO ₂ C ₆ H ₁₃	24	92			

^a Unless otherwise noted, a solution of carboxylic acid (2 mmol) and alcohol (2 mmol) in heptane (4 mL) was heated at 80 °C in the presence of GDTCSA (2 mol%). ^b Isolated yield of ester and selectivity is shown in parentheses. ^c Cyclododecanol (C₁₂H₂₅OH) was used. ^d Cyclohexanol (C₆H₁₁OH) was used. ^e (-)-Menthol (C₁₀H₁₉OH) was used. ^f [α]_D²⁵ - 65.8 ° (c 1.38, CH₂Cl₂). ^g [α]_D²⁵ - 59.2 ° (c 1.38, CH₂Cl₂).

The reusability of the carbonaceous material GDTCSA was measured. After the reaction, the ‘used’ catalyst was recovered by centrifugation and reused. It was confirmed that the activity and selectivity remained unchanged, even after the GDTCSA had been recycled for ten times (Table 3).

Table 3 The cycle experiment of catalytic activity.^a



run	1	2	3	4	5	6	7	8	9	10
conv.(%)	99	99	99	98	98	98	98	98	97	97

^a The conversion of hexanyl 4-phenylbutyrate based on hexanol over time was evaluated by ¹H NMR analysis.

Conclusions

Using polycyclic aromatic carbon sheets formed by incompletely carbonized glucose as ‘hydrophobic wall’, along with simple and inexpensive diphenylammonium tosylate as active site, the novel carbon-based material functionalized with NH₂⁺ and SO₃H groups has been achieved with one step synthesis by heating the mixture of D-glucose, *p*-toluenesulfonic acid and diphenylammonium tosylate together. And its structure has been illustrated by a series of tests such as XRD, FT-IR, XPS, ¹³C MAS NMR and EA. It not only could be used to catalyze the ester condensation reaction of carboxylic acids with equimolar amounts of sterically demanding and acid-sensitive alcohols with high reactivity and selectivity under mild conditions, but also could be easily recovered and reused more than ten times without loss of activity, which indicated that the novel material hold great potential for the green chemical processes.

Experimental Section

In a typical synthesis, 3.6 g glucose (20.0 mmol) and 1.9 g *p*-toluenesulfonic acid monohydrate (10.0 mmol) were mixed in toluene, then 3.41 g diphenylammonium tosylate⁸ (10.0 mmol) prepared in advance was added to the mixture, under a flow of nitrogen, the water formed during the reaction and the toluene were distilled off while heating to 180 °C slowly, after reacting for 5 hours, the product was washed with hot toluene for 5 × 25 mL (toluene and 1.3 g *p*-toluene-sulfonic acid were recovered) to get a black powder GDTCSA (5.7 g), the nominal sample composition was determined by elemental analysis to be CH_{0.89}O_{0.2}N_{0.03}S_{0.04}, the acid amount of SO₃H groups and [Ph₂NH₂]⁺[OTs]⁻ is 2.43 mmol · g⁻¹. (See Scheme 2)

The reaction mixture, carboxylic acid (2.0 mmol), alcohol (2.0 mmol), 2 mol% of GDTCSA (2.43 mmol NH₂⁺ and SO₃H · g⁻¹; 16 mg, 0.04 mmol), and heptane (4 mL), was stirred at 80 °C. Then separation of GDTCSA by filtration and evaporation of heptane in vacuo gave the crude material, which was purified by column chromatography to give the desired colorless oil carboxylic ester.

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