Journal of Fluorine Chemistry xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

# Taming of superacids: PVP-triflic acid as an effective solid triflic acid equivalent for Friedel–Crafts hydroxyalkylation and acylation

G.K. Surya Prakash *, Farzaneh Paknia, Aditya Kulkarni, Arjun Narayanan, Fang Wang, Golam Rasul, Thomas Mathew *, George A. Olah

*Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, United States*

ARTICLE INFO

*Article history:*
Received 23 June 2014
Accepted 28 August 2014
Available online xxx

*Keywords:*
Trifluoromethanesulfonic acid
PVP:triflic acid
Solid superacid
Hydroxyalkylation
Acylation

ABSTRACT

The application of poly(4-vinylpyridine) supported trifluoromethanesulfonic acid (PVP-TfOH, 1:10) as a convenient solid superacid catalyst system in Friedel–Crafts reactions is described. In the presence of PVP-TfOH, one pot solvent-free synthesis of a wide variety of diarylacetic acid derivatives was achieved by Friedel–Crafts hydroxyalkylation reaction of glyoxylic acid with arenes under mild conditions. Acylation of both activated and deactivated aromatic compounds with acetyl chloride was also achieved using PVP-TfOH complex under solvent-free conditions at room temperature. As the polymer supported triflic acid was found to be a very efficient and an easy-to-handle solid acid, it can be a useful addition to environmentally more adaptable strong acid catalyst systems.



## 1. Introduction

The Friedel–Crafts reaction is one of the most fundamental and useful reactions for C–C bond formation in organic chemistry [1]. The Friedel–Crafts reaction generally requires Lewis or Brønsted acid catalysts in large quantities, which quite often lead to many difficulties. Many of these catalysts are generally corrosive and difficult to recycle. Thus, there are still enormous demands for clean and eco-friendly Friedel–Crafts processes. Recently, considerable attention has been given towards the development of Friedel–Crafts reactions heterogenously catalyzed by solid acid catalysts such as zeolites, clays, Nafion-H, heteropolyacids (HPA), etc [2]. In which the acidity is an intrinsic property of the compounds and part of their chemical structure [3]. Nafion®-H (**1**), a perfluoroalkanesulfonic acid resin, has been found to be a viable solid acid catalyst with catalytic activity for many reactions giving high selectivity [4]. As the solid catalyst is can be easily recycled, the work-up of such reactions is usually very feasible. Therefore, large scale synthesis of many useful products can be achieved with significantly reduced cost. One major drawback of this catalyst is its inefficient swelling by aprotic organic solvents, which generally leads to low reaction rates. Polymer bound superacids that can be efficiently swollen by organic solvents are thus desired [5a]. Up to now, several polymer bound Lewis acids and Brønsted acids have been reported [5b]. It is believed that polystyrene bound super Brønsted acid **2** is a strong carbon acid among known solid acids [5]. Different types of polymer tethered Lewis acid catalysts namely "immobilized" or "microencapsulated" Lewis acids such as **3** have been documented [6a]. New polymer supported acid catalysts such as Cross-linked polystyrene-supported aluminum triflate {Ps–Al(OTf)$_3$} [6b], aluminum chloride immobilized on cross-linked polyvinyl alcohol microspheres [6c], and poly(vinylsulfonic acid)-grafted polystyrene [6c] have also been reported recently (Fig. 1).

Our group observed that PVP {poly(4-vinylpridine)} is an effective solid support for various gaseous and liquid acidic reagents. The preparation of a polymer supported hydrogen fluoride reagent, poly(4-vinylpyridinium) poly(hydrogen fluoride), was previously reported by Olah et al. Pyridinium poly(hydrogen fluoride) (PPHF, known as the Olah reagent) is an ionic liquid with a high dielectric constant and has been used as a fluorinating agent for alkenes, alkynes and alcohols [7]. Another Lewis acid complex, PVP-$SO_2$ was used as mild solid acid catalyst for three component Strecker synthesis of α-aminonitriles [8]. PVP-$H_2O_2$, a solid $H_2O_2$ equivalent, was exploited for *ipso*-hydroxylation of arylboronic acids to phenols, selective oxidation of sulfides to sulfoxides and conversion of ketones to *gem*-dihydroperoxides [9]. Trifluoromethanesulfonic acid (triflic acid) is a strong non-oxidizing Brønsted superacid, extensively utilized in acid catalyzed synthetic transformations. We have now immobilized triflic acid onto cross

* Corresponding authors at: Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, United States. Tel.: +1 213 740 5984; Fax: +1 213 740 6679.
*E-mail addresses:* gprakash@usc.edu (G.K. Surya Prakash), tmathew@usc.edu (T. Mathew).

http://dx.doi.org/10.1016/j.jfluchem.2014.08.020
0022-1139/

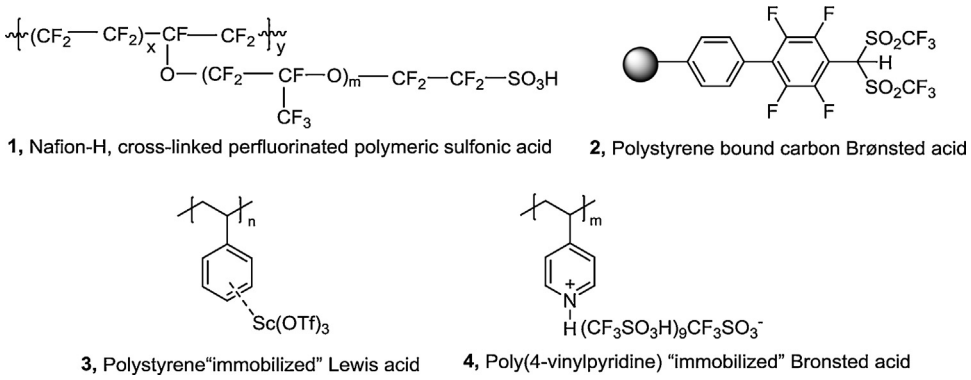



**Fig. 1.** Polymer-bound superacids.

linked poly(4-vinylpyridine) expecting the formation of a stable PVP-TfOH complex **4**, which represents a convenient solid form of triflic acid (Fig. 1).

In continuation of our studies on superacid catalyzed Friedel–Crafts reactions, we disclose the application of the new PVP-TfOH (1:10) complex, the "immobilized" superacid as an efficient catalyst for the hydroxyalkylation and acetylation of aromatic compounds at room temperature.

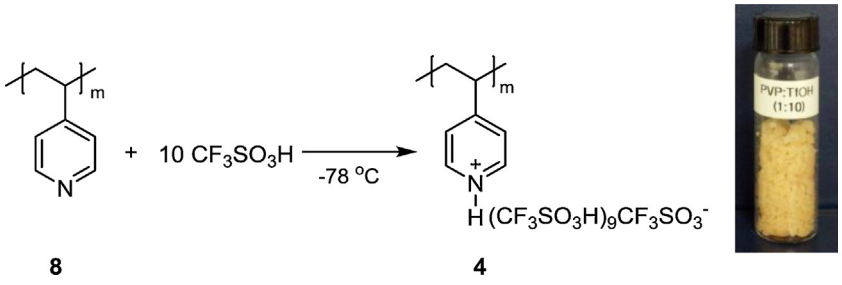
## 2. Results and discussion

### 2.1. Preparation and properties of poly(4-vinylpyridinium) poly(triflic acid)

Poly(4-vinylpyridinium) poly(triflic acid) in the solid form, was conveniently prepared from poly(4-vinylpyridine) and triflic acid. Commercially available 2% cross linked poly(4-vinylpyridine) was carefully added to triflic acid in small portions at −78 °C under nitrogen in the absence of solvents and mixed thoroughly until uniform complexation. A stable creamy white solid powder (slightly wet) was obtained when the loading ratio of the polymer and triflic acid reached to a 1:10 ratio (Scheme 1). The ratio 1:10 is more preferred for its use as a catalyst because the addition of more triflic acid resulted in a wet solid. The reagent PVP-TfOH (1:10) contains 93% triflic acid by weight and was found to be a very useful and efficient catalyst for the Friedel–Crafts reactions. However, a less acidic form was obtained in a drier solid form if the ratio is less than 1:10.

Poly(4-vinylpyridine) acts as a suitable solid phase reservoir for triflic acid, making the complex more convenient and safer for use. Although the light creamy colored polymer powder slightly fumes when exposed to air, it can be stored in well sealed Nalgene bottles in a refrigerator for months without the detectable loss of the catalytic activity. The surface morphology of the polymer samples was also determined through scanning electron microscope (Fig. 2).

In addition to the SEM characterization, we have also performed TGA analysis of PVP-TfOH (1:10). Initial weight loss of 87% at ~80–220 °C in the TGA diagram is probably due to the loss of loosely bound triflic acid molecules which are distant from the pyridinium center in the poly(triflic acid) chain. Additional 12% weight loss occurred at ~280–480 °C possibly due to the decomposition from




**Scheme 1.** Preparation of poly(4-vinylpyridinium) poly(triflic acid).

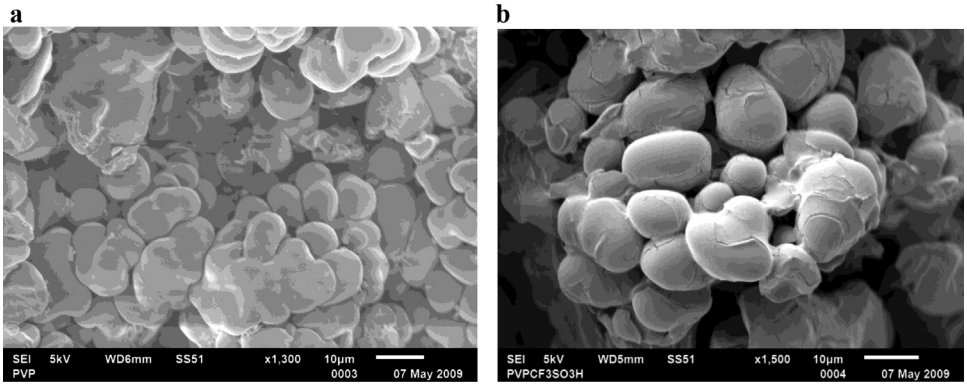



**Fig. 2.** (a) Surface morphology of 2% cross linked poly(4-vinyl pyridine). (b) Surface morphology of poly(4-vinylpyridinium) poly(triflic acid) (1:10).

Please cite this article in press as: G.K.S. Prakash, et al., J. Fluorine Chem. (2014), http://dx.doi.org/10.1016/j.jfluchem.2014.08.020

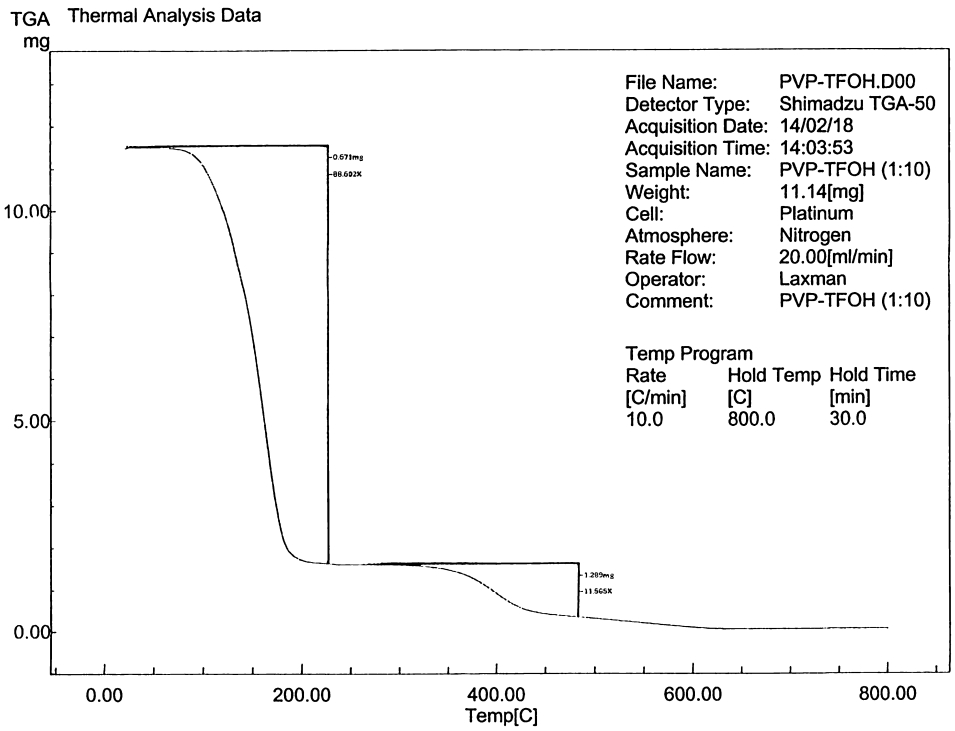



**Fig. 3.** TGA data of PVP-triflic acid.

molecules closer to cationic center and the 1:1 pyridinium salt form itself (Fig. 3). More than 99% of the polymer underwent decomposition above 500 °C. The TGA analysis clearly showed that the current solid polymeric triflic acid is much less volatile than liquid triflic acid and thus more convenient to handle.

The solid polymeric triflic acid is less volatile than liquid triflic acid and more convenient to handle, thus making the product separation easier by simple filtration of the reaction mixture followed by neutralization of the filtrate. Since the leaching of triflic acid is inevitable during the reaction, a complete recycling of the solid triflic acid reagent can be practically challenging. However, the regeneration PVP-TfOH can still be feasible and achieved by treating recovered solid PVP support with fresh triflic acid.

### *2.2. Synthesis of diarylacetic acid derivatives through Friedel–Crafts hydroxyalkylation reaction of arenes with glyoxylic acid using PVP-TfOH*

The acid catalyzed condensation of ketones and aldehydes with aromatic compounds is described in the literature as the hydroxyalkylation reaction. [1,10]. Our group [11] and others [12] have exploited hydroxyalkylation reaction for the synthesis of various biologically active heteroaryl compounds. With the present method, a wide variety of diarylacetic acid derivatives was synthesized by the Friedel–Crafts hydroxyalkylation reaction of glyoxylic acid using PVP-TfOH (1:10) as an acid catalyst (Scheme 2).

Diarylacetic acids have been used as valuable building blocks for the synthesis of many biologically active compounds such as **5–7** [13–16]. The compound **5** has shown anti-muscarinic, 5-$HT_{2A}$, and anti-dopaminergic activity [13]. α, α-Diphenylacetamide derivative (**6a**) has been shown to act as a local anesthetic with high selectivity for the type IIA sodium channels [14a–b], and antioxidant activity of acetamide **6b** has been studied [14c]. 2,2-Diphenylethylamine **7a** has also exhibited antidepressant activity [15a]. Modafinil analogue **7b** has also been synthesized and evaluated for biological activity [15b] (Fig. 4).

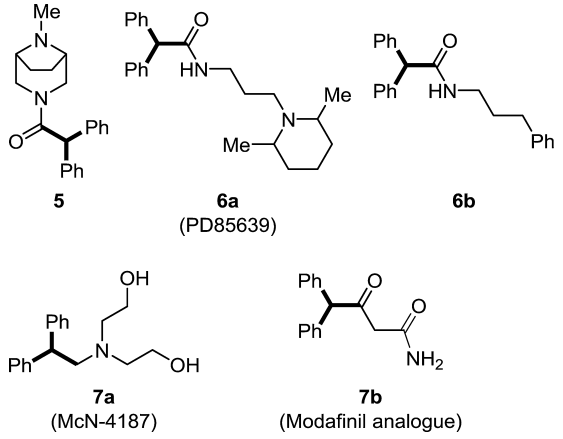
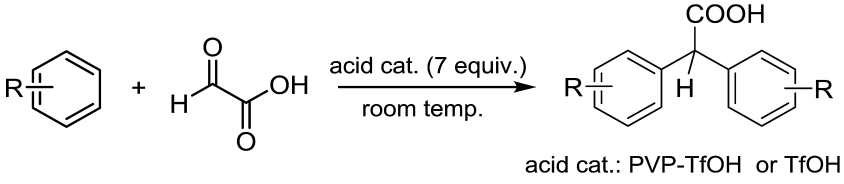
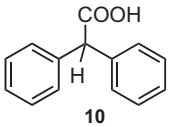
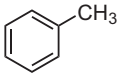
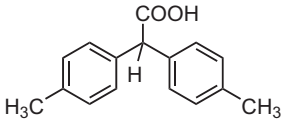
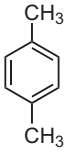
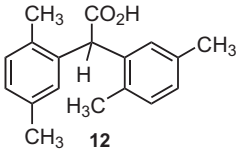
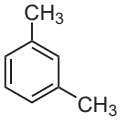
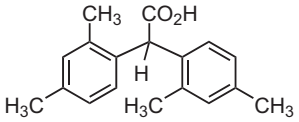
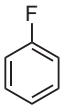
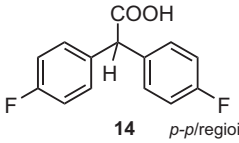
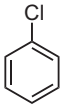
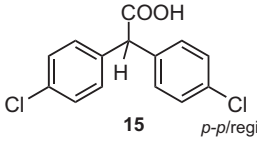
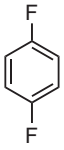
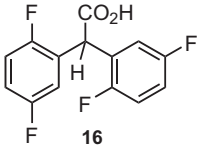
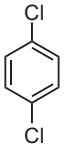
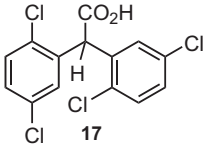



**Fig. 4.** Biologically important compounds prepared from diphenylacetic acids precursors.




**Scheme 2.** Synthesis of diarylacetic acid derivatives.

**Table 1**
Reaction of glyoxylic acid with arenes in the presence PVP-TfOH.

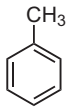
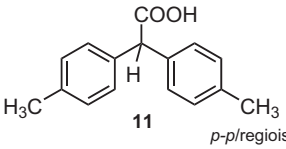
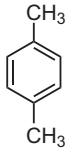
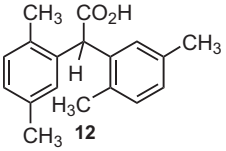
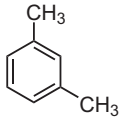
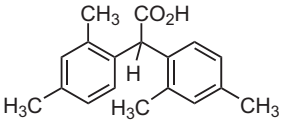
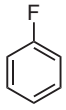
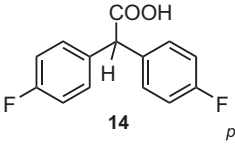
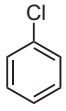
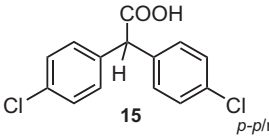
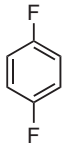
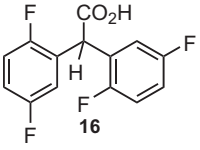
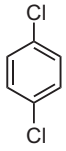
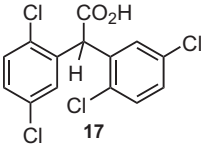
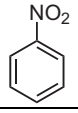
| Entry | Arenes | Time (h) | Products | Isolated yield (%) |
|---|---|---|---|---|
| 1 |  | 12 |  **10** | 79 |
| 2 |  | 7 |  **11** *p-p*/regioisomers = 7:3 | 92 |
| 3 |  | 4 |  **12** | 95 |
| 4 |  | 4 |  **13** *o,p-o,p*/regioisomers = 9:1 | 94 |
| 5 |  | 6 |  **14** *p-p*/regioisomers = 9:1 | 92 |
| 6 |  | 10 |  **15** *p-p*/regioisomers = 7:3 | 47 |
| 7 |  | 48 |  **16** | 38 |
| 8 |  | 72 |  **17** | 5 |

There are limited studies on the synthesis diarylacetic acids, which include, reduction of benzilic acid [17a], carboxylation of diarylmethanol with carbon monoxide in $H_2SO_4$ [17b], Friedel–Crafts reaction of methyl α-chloro-α-methoxyacetate with arenes in the presence of a Lewis acid [17c] and reaction of α-(*N*-methylanilino)acetonitrile with benzophenone to form α-cyano enamines followed by acidic hydrolysis [17d]. However, all these methods have shown drawbacks such as the utilization of toxic reagents, multistep procedures and poor yields. Reaction of glyoxylic acid with electron-rich aromatics in the presence of concentrated sulfuric acid, has also been reported [17e].

With the present method, the Friedel–Crafts hydroxyalkylation of various activated and deactivated aromatics with glyoxylic acid was carried out using poly(4-vinylpyridinium) poly(triflic acid) (1:10). Due to consumption of acid by coordination to the carboxyl group and formation of distonic superelectrophilic dicationic species, excess amount of acid catalyst is necessary. PVP-TfOH was found to be very efficient and the synthesis of various diarylacetic acid was achieved in a one pot process. To demonstrate the usefulness and effectiveness of PVP-TfOH as a solid acid catalyst, its catalytic activity in hydroxyalkylation reactions was compared with commercial TfOH. Tables 1 and 2 show that the catalytic activity of PVP-TfOH and TfOH is essentially comparable in most cases. Similar catalytic activity of TfOH and solid PVP-TfOH as acid catalysts is presumably due to the fact that a large amount of triflic acid is loosely bound in the polymeric chain by hydrogen bonding. Such property of PVP-TfOH allows the acid easily accessible for catalytic action.

The efficiency of hydroxyalkylation depends on the degree of activation of arenes. The reaction with electron-rich arenes afforded the final products in a short period of time with high yields (Entries 1–5, Table 1), whereas deactivated arenes generally led to low yields (Entries 6–8, Table 1). Hydroxyalkylation reaction

**Table 2**
Reaction of glyoxylic acid with arenes in the presence of triflic acid.

| Entry | Arenes | Time (h) | Products | Isolated yield (%) |
|---|---|---|---|---|
| 1 |  | 5 |  **11** *p-p*/regioisomers = 7:3 | 90 |
| 2 |  | 4 |  **12** | 95 |
| 3 |  | 4 |  **13** *o,p-o,p*/regioisomers = 9:1 | 93 |
| 4 |  | 6 |  **14** *p-p*/regioisomers = 9:1 | 90 |
| 5 |  | 7 |  **15** *p-p*/regioisomers = 7:3 | 81 |
| 6 |  | 24 |  **16** | 77 |
| 7 |  | 72 |  **17** | 40 |
| 8 |  | 24 | No reaction* | |

* The reaction was carried out at 80 °C.

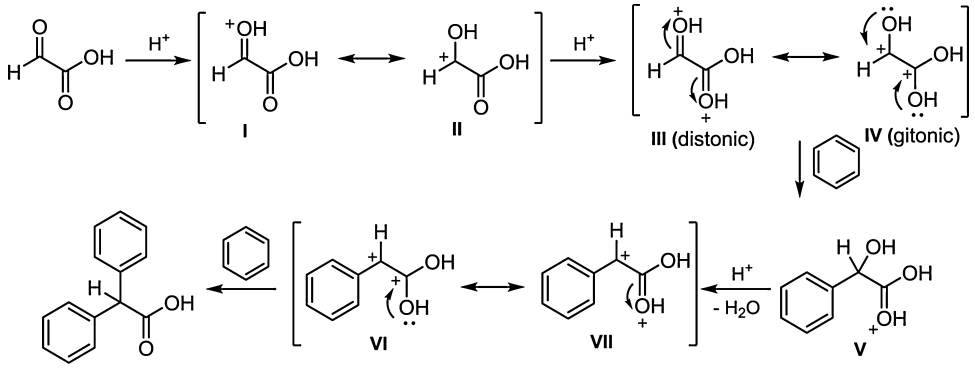
with highly deactivated arenes required longer period of time resulting in lower yields of the products. Reactions of chlorobenzene, difluorobenzene and dichlorobenzene with glyoxylic acid were carried out, respectively, in 7 h, 24 h and 72 h at room temperature, giving the final products in 81%, 38% and 5% yields, respectively (Tables 1 and 2). Condensation of mono-substituted arenes with glyoxylic acid gave rise to *para-para'* substituted diarylacetic acids as the major products along with other regioisomers.

### 2.3. The plausible mechanism for hydroxyalkylation

Since the initial proposal of superelectrophilic activation by Olah [18], there has been significant interest in the chemistry of superelectrophilic reactive intermediates. Superelectrophilic activation is proposed to occur in superacidic medium by protosolvation of electrophiles to give highly reactive superelectrophilic species. Based on spectroscopic evidence, Olah has previously suggested the formation of *O,O*-diprotonated diketones in superacid medium [19]. Later, superelectrophilic activation was studied by Shudo [20] and Klumpp [21] in the Friedel–Crafts hydroxyalkylation of 1,2-dicarbonyl compounds with arenes. They also proposed the formation of *O,O*-diprotonated 1,2-dicarbonyl species in superacidic solution. On the basis of these results, it seemed plausible that the glyoxylic acid might also serve as a superelectrophile in hydroxyalkyaltion reaction with arenes. In other words, the hydroxyalkylation reaction involves the protonation of both carbonyl groups [18–21] to produce superelectrophilic species with resonance structures III and IV. The electrophilic attack on arene results in hydroxycarboxylic acid (V). V can undergo further protonation to give dications resonance structures VI and VII, which reacts with second arene to form the corresponding *gem*-diaryl carboxylic acid product (Scheme 3).

### 2.4. Friedel–Crafts acetylation of aromatics catalyzed by PVP-TfOH

The Friedel–Crafts acylation of aromatic compounds is the most important one step route for the synthesis of aromatic ketones [1].




**Scheme 3.** Plausible mechanism of superacid catalyzed Friedel–Crafts hydroxyalkylation reaction of glyoxylic acid with arenes through superelectrophilic activation.

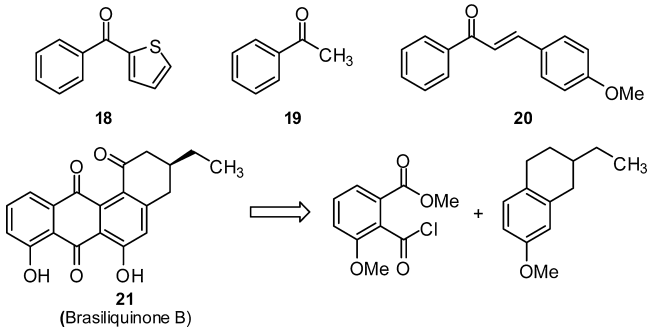



**Fig. 5.** A few important aromatic ketones.

Aromatic ketones, such as 2-benzoylthiophene **18**, have been used as photocatalysts [22]. Acetophenone **19** is a natural component of berries, seafood, beef, and nuts. Similar aromatic ketones have also been used as flavor ingredients. [23] Chalcone **20** and related compounds have been found to be very active against the human kidney carcinoma cells TK-10 and human colon adenocarcinoma cells HT-29 [24]. Aromatic ketones have also been used as precursors for the synthesis of a variety of pharmaceuticals, agrochemicals and natural products [25]. Brasiliquinone B **21** is a cytotoxic benz[*a*]anthraquinone, which belongs to a large group of antibiotics commonly called angucyclines (Fig. 5). The total synthesis of (±)-brasiliquinone B has been achieved based on Friedel–Crafts acylation [26].

In most cases of the Friedel–Crafts acylation, an aromatic compound undergoes electrophilic substitution reaction with a carboxylic acid derivative (e.g. acid anhydride, acyl chloride, or the acid itself) in the presence of a stoichiometric or excess amount of acid catalysts. Various acid catalysts have been used for the Friedel–Crafts acylation reactions such as methanesulfonic acid, [27a] triflic acid [27b–d], Nafion®-H [27e], gallium triflate [27f], scandium triflate [27g], zeolite [27h], heteropoly salt [27i], and zinc oxide [27j].

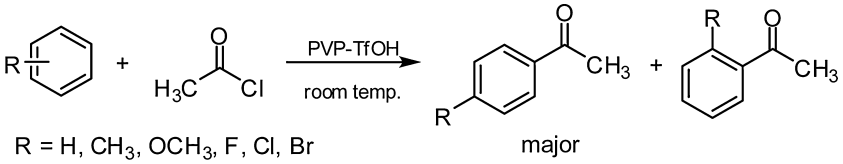
With PVP-TfOH (1:10), the reaction of acetyl chloride with various aromatics was carried out at room temperature to afford a variety of acetophenone derivatives in good yields (Scheme 4). All reactions were carried out using liquid arenes in excess, which also act as the solvent. The results are summarized in Table 3.

To compare the catalytic activity of supported acid catalyst with the acid, the acetylation of benzene was carried out in the presence of TfOH and PVP-TfOH. In both cases, in a period of three hours, the yield of acetophenone was found to be similar (40–41%) inidicating similar catalytic activity of PVP-TfOH to neat TfOH. The acetylation of toluene, *p*-xylene and *m*-xylene in the presence of PVP-TfOH gave the corresponding acetophenones in two hours at (60–73%) yield (Entry 2–4). The Friedel–Crafts acylation of mesitylene with acetyl chloride gave **23** in 69% yield (Entry 5). It is important to note that aromatic ether can act as a good donor to form a complex with acid catalyst, therefore diminishing the original activity of both aromatic ether and catalyst [28]. However, the acylation of anisole also underwent smoothly in 1.5 h to give a mixture of corresponding *ortho* and *para* regioisomers in 89% yield (Entry 6, Table 3). Furthermore, the reaction conditions are mild enough to avoid any dealkylation of the ether group during acylation of anisole [27j,29]. PVP-TfOH catalyzed acetylation of deactivated arenes such as chlorobenzene and bromobenzene gave rise to **26a,b** and **27a,b** in 25% and 20% yields, respectively (Entries 8 and 9, Table 3). The acylation of mono-substituted arenes occurred mainly at the *para* position in accordance with a typical electrophilic aromatic substitution reaction pathway. It should be noted that increase in reaction time did not result in higher yields but resulted in a mixture of unknown by-products. As observed in earlier studies, low yields for these acetylation reactions are probably due to ketene formation followed by polymerization (Scheme 5) [30].

### 2.5. The plausible mechanism for acetylation

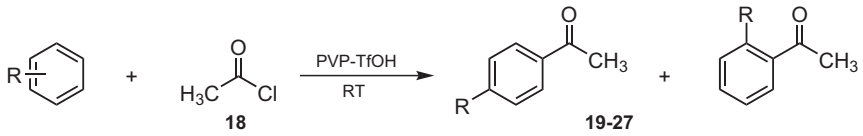
A possible mechanism of acylation involves the protonation of carbonyl group of acetyl chloride to form intermediates **I**. Further protonation of acetyl cation **I** give rise to superelectrophilic dicationic species **II**. The protonated acetyl cation may directly react with arenes to give acetylated product (Scheme 5). Possible formation of such activated intermediates in strong acids have been earlier explored by Olah [31] and Shudo [27b,32].

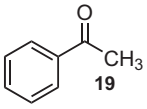
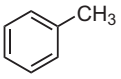
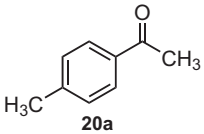
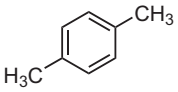
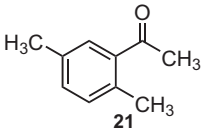
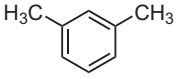
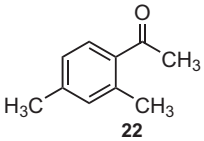
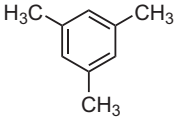
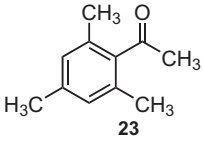
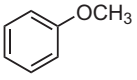
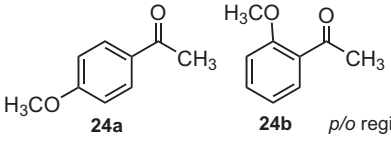
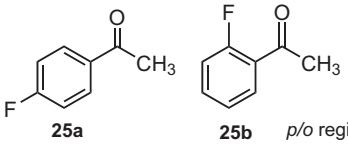
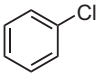
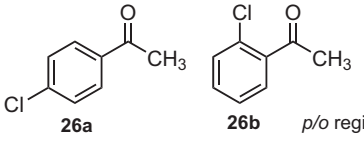
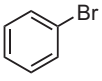
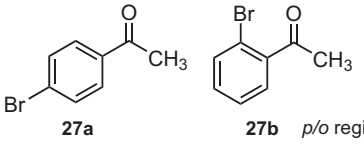
Fries rearrangement has also been successfully carried out using PVP-TfOH. Fries rearrangement, is a well-known method for the preparation of phenolic ketones through the arrangement of phenolic esters by acid catalysts or photocatalysts. Phenyl acetate was converted to *para* and *ortho* acetylated phenols in presence of PVP-TfOH in good yields with higher *para* selectivity (Scheme 6) though the yield is slightly diminished.




**Scheme 4.** PVP-TfOH catalyzed acetylation of aromatics.

**Table 3**
Acetylation of aromatics with acetyl chloride in presence of PVP-TfOH (1:10).

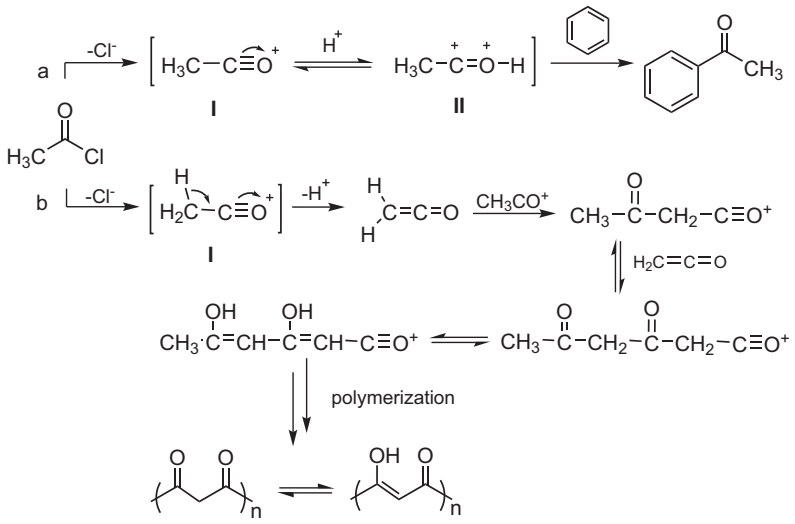



| Entry | Arenes | Time (h) | Products | Isolated yield (%) |
|---|---|---|---|---|
| 1 |  | 3.0 |  **19** | 40 |
| 2 |  | 1.0 |  **20a** **20b** *p/o* regioisomers = 8:2 | 60 |
| 3 |  | 2.0 |  **21** | 65 |
| 4 |  | 2.0 |  **22** | 73 |
| 5 |  | 6.0 |  **23** | 69 |
| 6 |  | 1.5 |  **24a** **24b** *p/o* regioisomers = 8:2 | 89 |
| 7 |  | 2.0 |  **25a** **25b** *p/o* regioisomers = 9:1 | 39 |
| 8 |  | 6.0 |  **26a** **26b** *p/o* regioisomers = 8:2 | 25 |
| 9 |  | 6.0 |  **27a** **27b** *p/o* regioisomers = 7:3 | 20 |

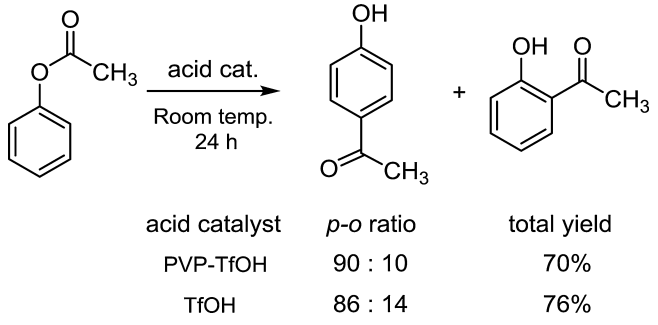
## 3. Theoretical study of mono- and diprotonation of glyoxylic acid

Geometry optimizations were performed at the MP2/cc-pVTZ level using the Gaussian 09 program [33]. Vibrational frequencies at the MP2/cc-pVTZ//MP2/cc-pVTZ level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) or transition state (NIMAG) = 1) and to evaluate zero point vibrational energies (ZPE), which were scaled by a factor of 0.95 [34]. Relative energies were computed at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. Computed energies are given in Table 4.

We have optimized the geometry of glyoxylic acid at the MP2/cc-pVTZ level (Fig. 6). The structure **28** with C–C bond length of 1.523 Å was found to be the lowest energy structure. Isomeric structure **29** was computed to be 1.2 kcal/mol less stable than structure **1** at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. O1-protonated **30** and O3-protonated **31** were found to be the viable minima for protonated glyoxylic acid at the MP2/cc-pVTZ level.




**Scheme 5.** Possible mechanism of PVP-TfOH catalyzed acetylation of arenes.




| acid catalyst | *p-o* ratio | total yield |
|---|---|---|
| PVP-TfOH | 90 : 10 | 70% |
| TfOH | 86 : 14 | 76% |

**Scheme 6.** Fries rearrangement of phenyl acetate.

Structure **30** was computed to be 2.9 kcal/mol more stable than structure **31** at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level. The C–C bond length of **32** (1.542 Å) was found to be significantly longer than that of **31** (1.513 Å) indicating differences in charge delocalization. The charge is localized (involving O1–C1–O2 atom) in **30**. On the other hand, the charge is delocalized (involving O3–C2–C1–O1 atom) in **31**. Diprotonated glyoxylic acid **32** was found to be the lowest energy structure at the MP2/cc-pVTZ level. Protonation of **28** to form **30** was calculated to be exothermic by 170.0 kcal/mol. Further protonation of **30** to form **32** was also found to be exothermic by 45.0 kcal/mol. Diprotonated glyoxylic acid **33** was also found to be a minimum. However, structure **33** is significantly less stable than structure **32** by 16.2 kcal/mol.

## 4. Experimental

Unless otherwise mentioned, all chemicals were purchased from commercial sources. PVP-TfOH was prepared by the method described below. $^{1}H$, $^{13}C$, and $^{19}F$ NMR spectra were recorded on varian NMR at 400 MHz. $^{1}H$ NMR chemical shifts were determined relative to internal tetramethylsilane at 0.0 ppm, $^{13}C$ NMR chemical shifts were determined relative to $^{13}C$ signal of $CDCl_3$ at 77.0 ppm. $^{19}F$ NMR chemical shifts were determined relative to internal $CFCl_3$ at 0.0 ppm. GC–MS spectra were recorded on a ThermoFinnigan Mass (EI) spectrometer. HRMS data were obtained from a high resolution Micromass GCT (GC–MS TOF) spectrometer at Mass Spectrometry Facility, Department of Chemistry, University of Arizona.

### *4.1. Typical procedure for the preparation of poly(4-vinylpyridinium) poly(triflic acid), PVP-TfOH (1:10)*

2% Cross linked poly(4-vinylpyridine) (10.7 g, 0.1 mol) was added under nitrogen to triflic acid (150 g, 1 mol) in a polyethylene bottle. Since the reaction between PVP and triflic acid is highly exothermic, triflic acid was added very slowly at −78 °C with frequent shaking. Then the bottle was gradually warmed to the room temperature and then stored in refrigerator. The resulting creme white solid was formed to 93% by weight triflic acid and 7% PVP (about 10 equivalent of triflic acid to each equivalent of vinylpyridine unit).

### *4.2. General procedure for the condensation reaction of glyoxylic acid with aromatics, using PVP-TfOH(1:10) as the solid acid catalyst*

The glyoxylic acid, 50% (0.6 g, 4 mmol), was mixed with arenes (5 mL) in a Nalgene® bottle and cooled to 0 °C. Then PVP-TfOH (4.5 g, 28 mmol, 7 equivalents) was added slowly. The reaction mixture was warmed up to room temperature and stirred over specific period of time (Table 1). The reaction progress was monitored by TLC (3:1 hexanes/ethyl acetate). After the reaction was complete, the mixture was poured over ice (25 g), neutralized with sodium bicarbonate, and extracted with diethyl ether (3 × 15 mL). The organic extracts were combined, washed with water and dried over anhydrous $Na_2SO_4$. The solvent was removed by vaccum evaporation and crude products were purified by column chromatography on silica gel (70–230 mesh) using hexane/ethyl acetate (85:15) as eluent. The products were characterized by spectral analysis and by comparing the spectral

**Table 4**
Total energies (-au), ZPE[a] and relative energies[b].

| Structure | Total energy | ZPE (kcal/mol) | Relative energy (kcal/mol) |
|---|---|---|---|
| **28** | −302.60282 | 26.1 | 215.0 |
| **29** | −302.60051 | 25.8 | 216.2 |
| **30** | −302.88508 | 33.2 | 45.0 |
| **31** | −302.88100 | 33.5 | 47.9 |
| **32** | −302.96810 | 40.3 | 0.0 |
| **33** | −302.94030 | 39.0 | 16.2 |

[a] Zero point vibrational energies (ZPE) at MP2/cc-pvtz//MP2/cc-pvtz level of theory scaled by a factor of 0.95.
[b] Relative energy at MP2/cc-pVTZ//MP2/cc-pVTZ level with ZPE correction.

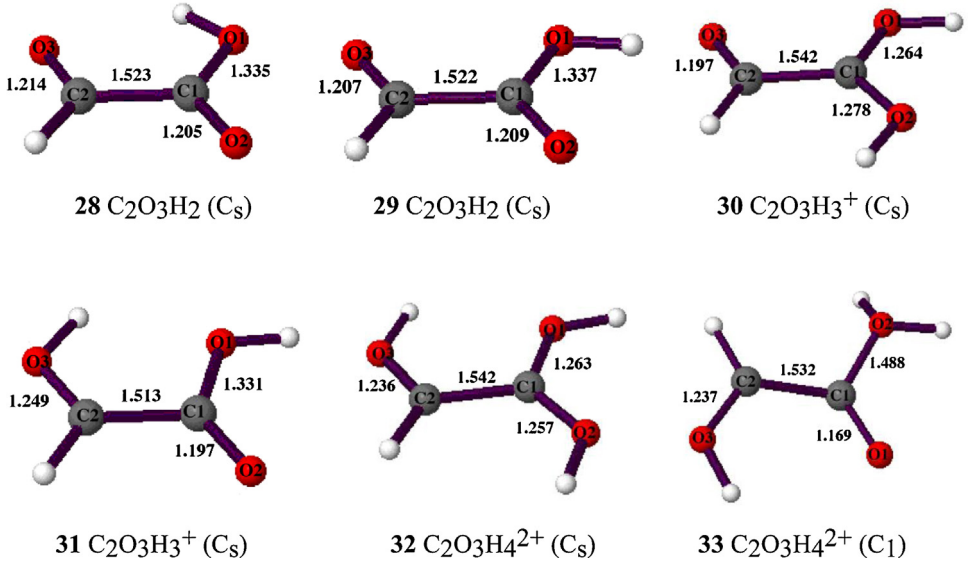



**Fig. 6.** MP2/cc-pVTZ calculated structures of **28**–**33**.

data with those of the authentic samples (in the case of known compounds). Some of the reactions were also repeated in presence of TfOH (7 equivalents, Table 2). Since dichlorobenzene is a solid aromatic compound, it was dissolved in dichloromethane and the solution was used in the reaction.

### 4.3. General procedure for the PVP-TfOH catalyzed reactions of acetyl chloride with arenes

Acetyl chloride (20 mmol, 1.57 g) was added to arene (50 mmol) in a Nalgene® bottle. The solution was cooled to 0 °C and then PVP-TfOH (1:10) complex (4.81 g, 30 mmol) was added slowly. The mixture was stirred at 0 °C and gradually allowed to warm up to room temperature and continued for specific period of time (Table 3). Reaction of benzene (50 mmol) with acetylchloride (20 mmol, 1.57 g) was repeated in presence of pure TfOH (30 mmol) for comparison. Progress of the reactions was monitored by TLC (4:1 hexane/ethyl acetate). After the reaction was complete the reaction mixture was carefully filtered into ice water, neutralized with solution of sodium bicarbonate, and extracted with diethyl ether (3 × 15 mL). The organic extracts were combined, washed with water and dried over anhydrous $Na_2SO_4$. The solvent was removed by vacuum evaporation and crude products were purified with column chromatography using silica gel and hexane/ethyl acetate (85:15) as eluent. All products were characterized by comparing the spectral data with those of the authentic samples.

*2,2-Diphenylacetic acid* (**10**) [35,36]: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.04 (s, 1*H*), 7.25–7.33 (m, 10*H*), 11.37 (brs, 1*H*); GC–MS (EI), *m/z*, 212.00 ($M^+$).

*2,2-Bis(methylphenyl)acetic acids* (**11**) [37–39]: A mixture with para–para isomer as a major product along with other regioisomers. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.28 (s, 6*H*), 2.30 (s, 6*H*), 4.96 (s, 1*H*), 5.18 (s,1*H*), 7.11 (d, *J* = 7.63 Hz, 7*H*), 7.17–7.21 (m, 8*H*), 7.26–7.29 (m, 1*H*) 11.30 (brs, 2*H*); $^{13}$C NMR (100.5 MHz, $CDCl_3$): $\delta$ 19.78, 21.01, 53.28, 56.25, 126.22, 127.47, 128.04, 128.45, 128.80, 129.29, 130.67, 134.20 135.09, 136.40 137.08, 179.26, 179.30; GC–MS (EI), *m/z*, 239.55 ($M^+$).

*2,2-Bis(2′,5′-dimethylphenyl)acetic acid* (**12**) [38,39]: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.21 (s, 6*H*), 2.26 (s, 6*H*), 5.27 (s,1*H*), 6.91 (s, 2*H*), 7.00 (dd, *J* = 7.7 Hz, *J* = 1.1 Hz, 2*H*), 7.07 (d, *J* = 7.8 Hz, 2*H*), 10.82 (br, 1*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 19.1, 21.2, 50.8, 128.2, 128.9, 130.4, 133.3, 135.5, 135.6, 178.9; GC–MS (EI), *m/z*, 268.25 ($M^+$).

*2,2-Bis(2′,4′-dimethylphenyl)acetic acid* (**13**) [38,39]: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.22 (s, 6*H*), 2.29 (s, 6*H*), 5.24 (s,1*H*), 6.97–7.00 (m, 6*H*), 10.79 (br, 1*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 19.5, 21.0, 50.1, 126.9, 128.1, 131.4, 132.9, 136.2, 137.0, 179.2; GC–MS (EI), *m/z*, 268.05 ($M^+$).

*2,2-Bis(4′-fluorophenyl)acetic acid* (**14**) [37,40]: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.00 (s, 1*H*), 7.00–7.04 (m, 4*H*), 7.25–7.29 (m, 4*H*), 10.36 (br, 1*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.3, 115.7 (d, $^2J_{C-F}$ = 21.4 Hz), 130.2 (d, $^3J_{C-F}$ = 7.6 Hz), 133.4 (d, $^4J_{C-F}$ = 3.1 Hz), 162.2 (d, $^1J_{C-F}$ = 247.2 Hz), 178.5; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ −115.0 (m); GC–MS (EI), *m/z*, 248.05 ($M^+$).

*2,2-Bis(chlorophenyl)acetic acids* (**15**) [37,40]: A mixture was obtained with para–para isomer as a major product along with other regioisomers. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.97 (s, 1*H*), 5.48 (s, 1*H*), 7.22–7.25 (m, 7*H*), 7.29–7.33 (m, 9*H*), 10.86 (brs, 2*H*); $^{13}$C NMR (100.5 MHz, $CDCl_3$): $\delta$ 55.33, 55.82, 127.33, 129.20, 129.32, 129.95, 130.07, 130.159, 130.61, 134.01, 134.50, 135.00, 135.59, 136.06, 177.97, 178.26; GC–MS (EI), *m/z*, 280.20 ($M^+$).

*2,2-Bis(2′,5′-difluorophenyl)acetic acid* (**16**): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.50 (s, 1*H*), 6.95–7.10 (m, 6*H*), 10.10 (br, 1*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 43.3, 116.2–117.0 (m),124.9 (dd, $^2J_{C-F}$ = 17.9 Hz, $^3J_{C-F}$ = 8.0 Hz),156.44 (dd, $^1J_{C-F}$ = 243.4 Hz, $^4J_{C-F}$ = 2.7 Hz), 158.6 (dd, $^1J_{C-F}$ = 243.4 Hz, $^4J_{C-F}$ = 2.3 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ −118.0 (m), −122.4 (m); GC–MS (EI), *m/z*, 284.15 ($M^+$); HRMS (ESI), *m/z* calcd for $C_{13}H_7F_4$ ($M^+$—45) 239.0484, observed 239.0476.

*2,2-Bis(2′,5′-dichlorophenyl)acetic acid* (**17**): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.80 (s, 1*H*), 7.12 (d, *J* = 2.3 Hz, 2*H*), 7.28 (dd, *J* = 8.5 Hz, *J* = 2.4 Hz, 2*H*), 7.38 (d, *J* = 8.5 Hz, 2*H*), 9.37 (br, 1*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 51.2, 129.6, 129.7, 131.1, 133.0, 133.2, 135.5, 175.9; GC–MS (EI), *m/z*, 305.95 ($M^+$—44); HRMS (ESI), *m/z* calcd for $C_{13}H_8Cl_4$ (M—44) 303.9380, observed 303.9369.

## 5. Conclusions

A novel solid superacidic system, poly(4-vinylpyridinium) poly(triflic acid) (PVP-TfOH) was developed by immobilization of triflic acid on poly(4-vinylpyridine). Being much safer to handle, the polymer supported triflic acid was found to be very convenient and effective solid acid catalyst for Friedel–Crafts hydroxyalkylation and acetylation reactions. One pot solvent-free synthesis of wide variety of diarylacetic acids in high yields can be achieved by

Please cite this article in press as: G.K.S. Prakash, et al., J. Fluorine Chem. (2014), http://dx.doi.org/10.1016/j.jfluchem.2014.08.020

Friedel–Crafts hydroxyalkylation of arenes with glyoxilic acid by using the polymer supported triflic acid complex as a convenient solid triflic acid equivalent. Furthermore, an efficient solvent free procedure for Friedel–Crafts acylation of aromatic compounds using PVP-TfOH is also described. The advantages of this protocol include easy handling and use of a solid acid catalyst, mild reaction conditions, short reaction time and eliminating the need for solvents. Poly(triflic acid) complex may find wide application as a convenient solid superacid system for many organic transformations. Taming of superacids such as triflic acid is attained by immobilization on poly(4-vinylpyridine) thus significantly reducing the volatility and making the catalyst more environment friendly and essentially making a step closer towards a green protocol.

## Statement of significance

The solid poly(4-vinylpyridine)-triflic acid (1:10) complex acts as an effective solid equivalent of superacidic triflic acid without significant loss of its catalytic activity. Both Friedel–Crafts hydroxyalkylation and acetylation reactions are shown to be effectively catalyzed by PVP-TfOH system. Application of this complex in organic reactions allows storage and handling safer and make the reactions more convenient compared to liquid triflic acid. Therefore, the complex will find wide applications as a solid reservoir of triflic acid in superacid catalysis.

## Acknowledgement

Financial support of our work by the Loker Hydrocarbon Research Institute is gratefully acknowledged.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.08.020.

## References

[1] (a) G.A. Olah, Friedel–Crafts and Related Reactions, vol. 2, Part I Ed., John Wiley & Sons, New York, NY, 1964;
(b) G.A. Olah, Friedel–Crafts Chemistry, Wiley Interscience, New York, NY, 1973.
[2] (a) G. Sartori, R. Maggi, Chem. Rev. 106 (2006) 1077–1104;
(b) I.V. Kozhevnikov, Appl. Catal., A: Gen. 256 (2003) 3–18;
(c) T. Okayasu, K. Saito, H. Nishide, M.T.W. Hearn, Green Chem. 12 (2010) 1981–1989;
(d) S.K. Jana, Catal. Surv. Asia 2 (2006) 98–109;
(e) K. Omata, Appl. Catal., A: Gen. 407 (2011) 112–117;
(f) K.-I. Shimizua, A. Satsumav, Energy Environ. Sci. 4 (2011) 3140–3153.
[3] G.A. Olah, G.K.S. Prakash, A. Molnár, J. Sommer, Superacid Chemistry, John Wiley & Sons, Inc., Hoboken, NJ, 2009.
[4] (a) G.A. Olah, R. Malhotra, S.C. Narang, J.A. Olah, Synthesis (1978) 672–673;
(b) G.A. Olah, P.S. Iyer, G.K.S. Prakash, Synthesis (1986) 513–531;
(c) G.K.S. Prakash, T. Mathew, S. Krishnaraj, E.R. Marinez, G.A. Olah, Appl. Catal., A: Gen. 181 (1999) 283–288;
(d) M. Hachoumy, T. Mathew, E.C. Tongco, Y.D. Vankar, G.K.S. Prakash, G.A. Olah, Synlett (1999) 363–365;
(e) G.A. Olah, T. Mathew, M. Farnia, G.K.S. Prakash, Synlett (1999) 1067–1068;
(f) G.A. Olah, T. Mathew, G.K.S. Prakash, Chem. Commun. (2001) 1696–1697;
(g) G.K.S. Prakash, H. Vaghoo, C. Panja, A. Molnár, T. Mathew, G.A. Olah, Synthesis (2008) 897–902;
(h) G.K.S. Prakash, G. Fogassy, G.A. Olah, Catal. Lett. 138 (2010) 155–159;
(i) G.K.S. Prakash, K.E. Glinton, C. Panja, L. Gurung, P.T. Battamack, B. Török, T. Mathew, G.A. Olah, Tetrahedron Lett. 53 (2012) 607–611.
[5] (a) K. Ishihara, A. Hasegawa, H. Yamamoto, Angew. Chem. Int. Ed. Engl. 40 (2001) 4077–4079;
(b) Y. Yin, G. Zhao, G.L. Li, Tetrahedron 61 (2005) 12042–12052 (and references therein).
[6] (a) S. Kobayashi, S. Nagayama, J. Am. Chem. Soc. 120 (1998) 2985–2986;
(b) K.P. Boroujeni, K. Parvanak, J. Serb. Chem. Soc. 76 (2011) 155–163;
(c) Z. Wang, B. Gao, J. Mol. Catal. A: Chem. 330 (2010) 35–40;
(d) T. Okayasu, K. Saito, H. Nishide, M. Hearn, Green Chem. 12 (2010) 1981–1989.
[7] (a) G.A. Olah, X.-Y. Li, Q. Wang, G.K.S. Prakash, Synthesis (1993) 693–699;
(b) G.A. Olah, X.-Y. Li, Synlett (1990) 267–268;
(c) G.A. Olah, T. Mathew, A. Goeppert, B. Török, I. Bucsi, X.-Y. Li, Q. Wang, E.R. Marinez, P. Batamack, R. Aniszfeld, G.K.S. Prakash, J. Am. Chem. Soc. 127 (2005) 5964–5969.
[8] G.A. Olah, T. Mathew, C. Panja, K. Smith, G.K.S. Prakash, Catal. Lett. 114 (2007) 1–7.
[9] (a) G.K.S. Prakash, S. Chacko, C. Panja, T.E. Thomas, L. Gurung, G. Rasul, T. Mathew, G.A. Olah, Adv. Synth. Catal. 351 (2009) 1567–1574;
(b) G.K.S. Prakash, S. Chacko, C. Panja, T. Mathew, G.A. Olah, Abstracts of Papers, 230th ACS National Meeting, Aug. 28–Sept. 1, 2005, Washington, DC, United States, 2005;
(c) G.K.S. Prakash, A. Shakhmin, K.E. Glinton, S. Rao, T. Mathew, G.A. Olah, Green Chem. 16 (2014), http://dx.doi.org/10.1039/c4gc00586d.
[10] J. March, Advanced Organic Chemistry, fourth ed., Wiley, New York, NY, 1992.
[11] G.K.S. Prakash, F. Paknia, S. Chacko, T. Mathew, G.A. Olah, Heterocycles 76 (2008) 783–799.
[12] (a) D.A. Klumpp, Y. Zhang, D. Do, R. Kartika, Appl. Catal., A: Gen. 336 (2008) 128–132;
(b) D.A. Klumpp, M. Garza, A. Jones, S. Mendoza, J. Org. Chem. 64 (1999) 6702–6705;
(c) D.A. Klumpp, P.J. Kindelin, A. Li, Tetrahedron Lett. 46 (2005) 2931–2935;
(d) D.A. Klumpp, M. Garza, G.V. Sanchez, S. Lau, S. Leon, J. Org. Chem. 65 (2000) 8997–9000;
(e) A.S. Gothelf, T. Hansen, K.A. Jorgensen, J. Chem. Soc., Perkin Trans. 1 (2001) 854–860;
(f) M. Abid, B. Torok, Adv. Synth. Catal. 347 (2005) 1797–1803;
(g) J. Zhang, P.G. Blazecka, T.T. Curran, Tetrahedron Lett. 48 (2007) 2611–2615.
[13] R.K. Singh, S. Jain, N. Sinha, A. Mehta, F. Naqvi, A.K. Agarwal, N. Anand, Tetrahedron Lett. 48 (2007) 545–548.
[14] (a) I. Roufos, S.J. Hays, D.J. Dooley, R.D. Schwarz, G.W. Campbell, A.W. Probert, J. Med. Chem. 37 (1994) 268–274 (and the references therein);
(b) I. Roufos, S. Hays, R.D. Schwarz, J. Med. Chem. 39 (1996) 1514–1520;
(c) G. Autore, A. Caruso, S. Marzocco, B. Nicolaus, C. Palladino, A. Pinto, A. Popolo, M.S. Sinicropi, G. Tommonaro, C. Saturnino, Molecules 15 (2010) 2028–2038.
[15] (a) B.E. Maryanoff, S.O. Nortey, J.F. Gardocki, J. Med. Chem. 27 (1984) 1067–1071;
(b) C. De Risi, L. Ferraro, G.P. Pollini, S. Tanganelli, F. Valente, A.C. Veronese, Bioorg. Med. Chem. 16 (2008) 9904–9910.
[16] (a) F. Picard, E. Baston, W. Reichert, R.W. Hartmann, Bioorg. Med. Chem. 8 (2000) 1479–1487;
(b) F. Picard, S. Barassin, A. Mokhtarian, R.W. Hartmann, J. Med. Chem. 45 (2002) 3406–3417;
(c) J. Charton, S. Girault-Mizzi, M.A. Debreu-Fontaine, F. Foufelle, I. Hainault, J.G. Bizot-Espiard, D.H. Caignard, C. Sergheraert, Bioorg. Med. Chem. 14 (2006) 4490–4518;
(d) R.S. Dothager, K.S. Putt, B.J. Allen, B.J. Leslie, V. Nesterenko, P.J. Hergenrother, J. Am. Chem. Soc. 127 (2005) 8686–8696;
(e) M. Graffner-Nordberg, K. Kolmodin, J. Aqvist, S.F. Queener, A. Hallberg, Eur. J. Pharm. Sci. 22 (2004) 43–54;
(f) C. Kaiser, C.J. Spagnuolo, T.C. Adams, V.H. Audia, A.C. Dupont, H. Hatoum, V.C. Lowe, J.C. Prosser, B.L. Sturm, L. Noronha-Blob, J. Med. Chem. 35 (1992) 4415–4424.
[17] (a) P. Strazzolini, A.G. Giumanini, G. Verardo, Synth. Commun. 17 (1987) 1919–1928 (and references therein);
(b) Y. Takahashi, N. Yoneda, H. Nagai, Chem. Lett. (1985) 1733–1734;
(c) M.J. Earle, R.A. Fairhurst, H. Heaney, Tetrahedron Lett. 32 (1991) 6171–6174;
(d) K. Takahashi, K. Shibasaki, K. Ogura, H. Iida, J. Org. Chem. 48 (1983) 3566–3569;
(e) J. Tang, R. Zhang, J. Shen, Synth. Met. 155 (2005) 100–104.
[18] (a) R.R. Naredla, D.A. Klumpp, Chem. Rev. 113 (2013) 6905–6948;
(b) G.A. Olah, D.A. Klumpp, Superelectrophiles and Their Chemistry, Wiley-Interscience, Hoboken, NJ, 2008;
(c) G.A. Olah, D.A. Klumpp, Acc. Chem. Res. 37 (2004) 211–220.
[19] G.A. Olah, M. Calin, J. Am. Chem. Soc. 90 (1968) 4672–4675.
[20] T. Yamazaki, S.-i. Saito, T. Ohwada, K. Shudo, Tetrahedron Lett. 36 (1995) 5749–5752.
[21] D.A. Klumpp, S. Lau, M. Garza, B. Schick, K. Kantardjieff, J. Org. Chem. 64 (1999) 7635–7637.
[22] J. Perez-Prieto, R.E. Galian, M.C. Morant-Minana, ChemPhysChem 7 (2006) 2077–2080.
[23] T.B. Adams, M.M. McGowen, M.C. Williams, S.M. Cohen, V.J. Feron, J.I. Goodman, L.J. Marnett, I.C. Munro, P.S. Portoghese, R.L. Smith, W.J. Waddell, Food Chem. Toxicol. 45 (2007) 171–180.
[24] M. Cabrera, M. Simoens, G. Falchi, M.L. Lavaggi, O.E. Piro, E.E. Castellano, A. Vidal, A. Azqueta, A. Monge, A.L. Cerain, G. Sagrera, G. Seoane, H. Cerecettoa, M. Gonzaleza, Bioorg. Med. Chem. 15 (2007) 3356–3367.
[25] (a) K. Nakamura, R. Yamanaka, T. Matsuda, T. Harada, Tetrahedron: Asymmetry 14 (2003) 2659–2681;
(b) E.B. Kurbanoglu, K. Zilbeyaz, N.I. Kurbanogluc, M. Taskin, Tetrahedron: Asymmetry 18 (2007) 1529–1532.
[26] M.L. Patil, H.B. Borate, D.E. Ponde, V.H. Deshpande, Tetrahedron 58 (2002) 6615–6620.
[27] (a) V. Premasagar, V.A. Palaniswamy, E.J. Eisenbraun, J. Org. Chem. 46 (1981) 2974–2976;

(b) Y. Sato, M. Yato, T. Ohwada, S. Saito, K. Shudo, J. Am. Chem. Soc. 117 (1995) 3037–3043;
(c) F. Effenberger, G. Epple, Angew. Chem. Int. Ed. 11 (1972) 299–300;
(d) F. Effenberger, G. Epple, Angew. Chem. Int. Ed. 11 (1972) 300–301;
(e) T. Yamato, C. Hideshima, G.K.S. Prakash, G.A. Olah, J. Org. Chem. 56 (1991) 3955–3957;
(f) G.K.S. Prakash, P. Yan, B. Török, I. Bucsi, M. Tanaka, G.A. Olah, Catal. Lett. 85 (2003) 1–6;
(g) Y. Matsushita, K. Sugamoto, T. Matsui, Tetrahedron Lett. 45 (2004) 4723–4727;
(h) B. Chiche, A. Finiels, C. Gauthier, P. Geneste, J. Graille, D. Pioch, J. Org. Chem. 51 (1986) 2128–2130;
(i) K. Shimizu, K. Niimi, A. Satsuma, Catal. Commun. 9 (2008) 980–983;
(j) M.H. Sarvari, H. Sharghi, J. Org. Chem. 69 (2004) 6953–6956.
[28] G. Sartori, R. Maggi, Chem. Rev. 106 (2006) 1077–1104.
[29] G.P. Schiemenz, U. Schmidt, Liebigs Ann. Chem. (1976) 1514–1519.
[30] (a) G.A. Olah, R. Malhotra, S.C. Narang, J.A. Olah, Synthesis (1978) 672–673;
(b) G.A. Olah, E. Zadok, R. Edler, D.H. Adamson, W. Kasha, G.K.S. Prakash, J. Am. Chem. Soc. 111 (1989) 9123–9125.
[31] (a) G.A. Olah, A. Germain, H.C. Lin, D. Forsyth, J. Am. Chem. Soc. 97 (1975) 2928–2929;
(b) G.A. Olah, Angew. Chem. Int. Ed. 32 (1993) 767–788.
[32] T. Ohwada, N. Yamagata, K. Shudo, J. Am. Chem. Soc. 113 (1991) 1364–1373.
[33] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, et al., Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.
[34] J.B. Foresman, A. Frisch, Exploring Chemistry with Electronic Structure Methods, Gaussian Inc., Pittsburgh, 1996, pp. 1–64.
[35] J.E. Miline, T. Storz, J.T. Colyer, O.R. Thiel, M.D. Seran, R.D. Larsen, J.A. Murry, J. Org. Chem. 76 (2011) 9519–9524.
[36] C. Schnabel, K. Sterz, H. Mueller, J. Rehbein, M. Wiese, M. Hiersemann, J. Org. Chem. 76 (2011) 512–522.
[37] J.R. Coats, J.W. Williams, C. Chang, A.H. Lee, R.L. Metcalf, Environ. Toxicol. Chem. 8 (1989) 45–52.
[38] Y. Iwakura, F. Toda, M. Kosugi, Y. Torii, J. Org. Chem. 36 (1970) 3990–3992.
[39] (a) R.C. Fuson, M.L. Ward, J. Am. Chem. Soc. 68 (1946) 521–522;
(b) G. Werber, F. Buccheri, Gaz. Chim. Ital. 96 (1966) 465–474.
[40] Y. Takahashi, N. Yoneda, H. Nagai, Chem. Lett. 11 (1985) 1733–1734.

Please cite this article in press as: G.K.S. Prakash, et al., J. Fluorine Chem. (2014), http://dx.doi.org/10.1016/j.jfluchem.2014.08.020