

# Trifluoromethanesulfonic Acid<sup>1</sup>



[1493-13-6]  $\text{CHF}_3\text{O}_3\text{S}$  (MW 150.09)  
 InChI = 1/CHF3O3S/c2-1(3,4)8(5,6)7/h(H,5,6,7)/f/h5H  
 InChIKey = ITMCEJHCFYSIIV-JSWHHWTPCD

(one of the strongest organic acids; catalyst for oligomerization/polymerization of alkenes and ethers; precursor for triflic anhydride and several metal triflates; acid catalyst in various reactions)

*Alternate Name:* triflic acid.

*Physical Data:* bp 162 °C/760 mmHg, 84 °C/43 mmHg, 54 °C/8 mmHg; *d* 1.696 g cm<sup>-3</sup>.

*Solubility:* sol water and in many polar organic solvents such as DMF, sulfolane, DMSO, dimethyl sulfone, acetonitrile; sol alcohols, ketones, ethers, and esters, but these generally are not suitable inert solvents (see below).

*Analysis of Reagent Purity:* IR;<sup>2</sup> <sup>19</sup>F NMR.<sup>3</sup>

*Preparative Methods:* best prepared by basic hydrolysis of  $\text{CF}_3\text{SO}_2\text{F}$  followed by acidification.<sup>2</sup>

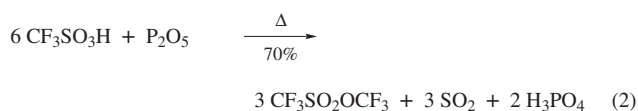
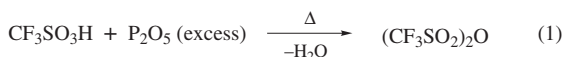
*Purification:* distilled with a small amount of  $\text{Tf}_2\text{O}$ .<sup>4</sup>

*Handling, Storage, and Precautions:* is a stable, hygroscopic liquid which fumes copiously on exposure to moist air. Transfer under dry nitrogen is recommended. Contact with cork, rubber, and plasticized materials will cause rapid discoloration of the acid and deterioration of the materials. Samples are best stored in sealed glass ampules or glass bottles with Kel-F<sup>TM</sup> or PTFE plastic screw cap linings. Use in a fume hood.

## Original Commentary

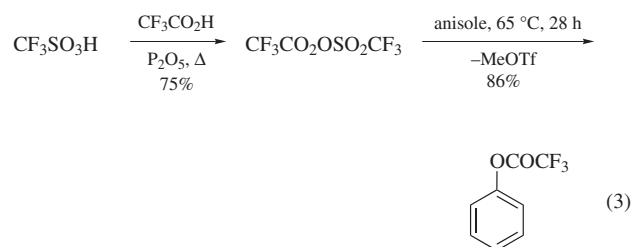
Lakshminarayanapuram R. Subramanian, Antonio García Martínez & Michael Hanack  
*Universität Tübingen, Tübingen, Germany*

**Reaction with  $\text{P}_2\text{O}_5$ .** Trifluoromethanesulfonic acid (TfOH) reacts with an excess of **Phosphorus(V) Oxide** to give **Trifluoromethanesulfonic Anhydride** (eq 1),<sup>5</sup> while treatment with a smaller amount of  $\text{P}_2\text{O}_5$  (TfOH: $\text{P}_2\text{O}_5$  = 6:1) and slower distillation leads to trifluoromethyl triflate (eq 2).<sup>6</sup>



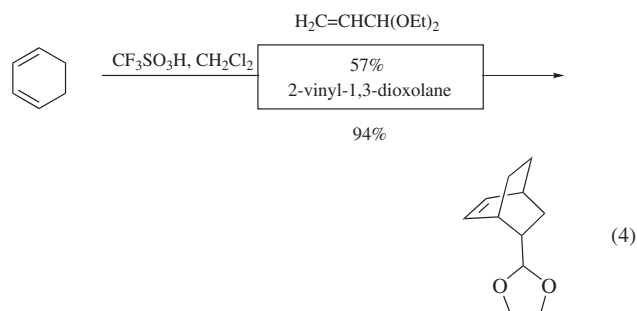
The synthetic utility of trifluoromethyl triflate as a trifluoromethanesulfonylating agent is severely limited, because the reagent is rapidly destroyed by a fluoride-ion chain reaction in the presence of other nucleophiles.<sup>7</sup>

Dehydration of a 2:1 mixture of  $\text{CF}_3\text{CO}_2\text{H}$  and TfOH with  $\text{P}_2\text{O}_5$  affords trifluoroacetyl triflate (eq 3),<sup>8</sup> which is a very reactive agent for trifluoroacetylations at O, N, C, or halogen centers (eq 3).<sup>8a</sup>

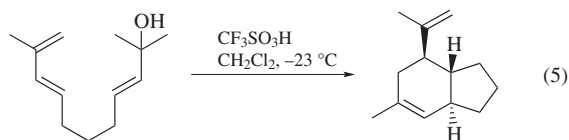


**Protonation and Related Reactions.** TfOH is one of the strongest monoprotic organic acids known. The acid, and its conjugate base ( $\text{CF}_3\text{SO}_3^-$ ), have extreme thermal stability, are resistant to oxidation and reduction, and are not a source of fluoride ions, even in the presence of strong nucleophiles. They do not lead to sulfonation as do **Sulfuric Acid**, **Fluorosulfuric Acid**, and **Chlorosulfonic Acid** in some reactions. TfOH is therefore effectively employed in protonation reactions.

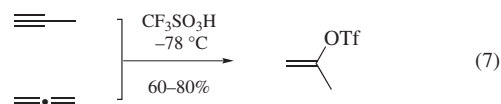
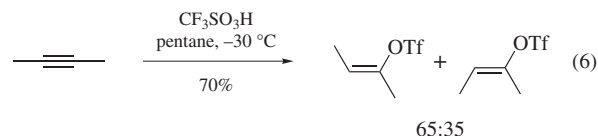
The strong protonating property of TfOH is used to generate allyl cations from suitable precursors in low-temperature ionic Diels–Alder reactions. 3,3-Diethoxypropene and 2-vinyl-1,3-dioxolane add to cyclohexa-1,3-diene in the presence of TfOH to give the corresponding Diels–Alder adducts, the latter in high yield (eq 4).<sup>9</sup>



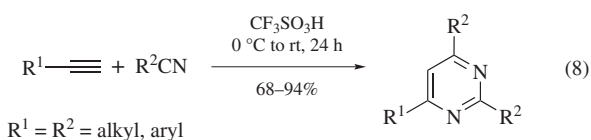
An intramolecular Diels–Alder reaction with high stereoselectivity occurs involving allyl cations by protonation of allyl alcohols (eq 5).<sup>10</sup>



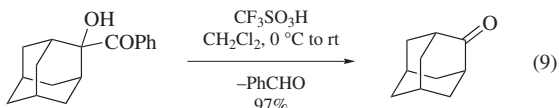
Alkynes and allenes are protonated with TfOH to give vinyl triflates (eqs 6 and 7),<sup>11</sup> which are precursors to vinyl cations.



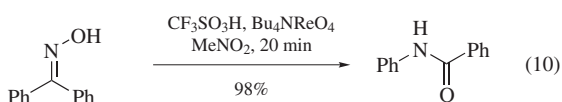
A convenient synthesis of pyrimidines is developed by protonation of alkynes with TfOH in the presence of nitriles (eq 8).<sup>12</sup>



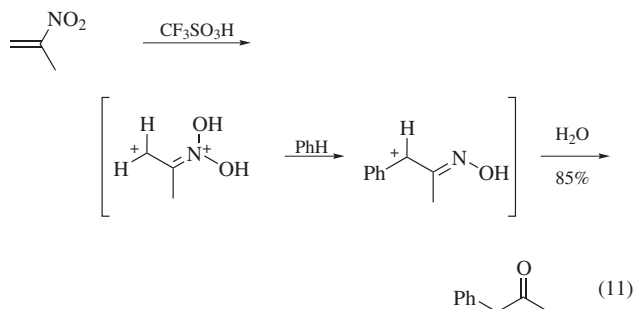
Triflic acid catalyzes the transformation of  $\alpha$ -hydroxy carbonyl compounds to ketones (eq 9).<sup>13</sup>



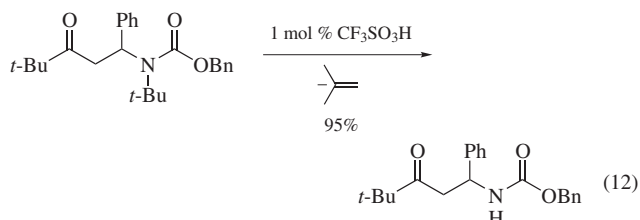
Oximes undergo Beckmann rearrangement with TfOH in the presence of  $\text{Bu}_4\text{NReO}_4$  to give amides in high yield (eq 10).<sup>14</sup>



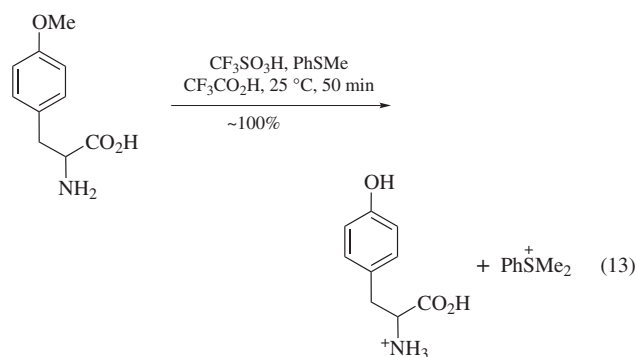
TfOH protonates nitroalkenes, even nitroethylene, to give *N,N*-dihydroxyiminium carbenium ions, which react with arenes to give arylated oximes. This overall process provides a route to  $\alpha$ -aryl methyl ketones from 2-nitropropene (eq 11)<sup>15</sup> and constitutes a versatile synthetic method for the preparation of  $\alpha$ -arylated ketones, otherwise difficult to synthesize by the conventional Friedel–Crafts reaction.



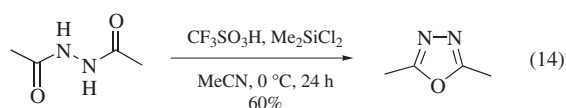
TfOH catalyzes the removal of *N-t*-butyl groups from *N*-substituted *N-t*-butylcarbamates to give carbamate-protected primary amines (eq 12).<sup>16</sup>



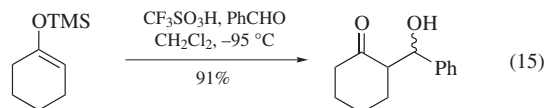
The methyl group attached to the phenolic oxygen of tyrosine is smoothly cleaved by TfOH in the presence of *Thioanisole* (eq 13).<sup>17</sup> This deblocking method was successfully applied to the synthesis of a new potent enkephalin derivative.



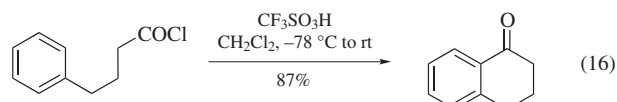
1,3,4-Oxadiazoles are prepared in good yields from silylated diacylhydrazines (formed in situ) by acid-catalyzed cyclization using TfOH (eq 14).<sup>18</sup>



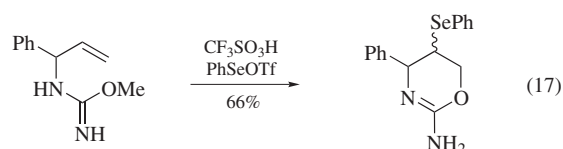
TfOH protonates naphthalene at room temperature to give a complex mixture of products.<sup>19</sup> TfOH promotes aldol reaction of silyl enol ethers with aldehydes and acetals, leading to new C–C bond formation (eq 15).<sup>20</sup> TfOH competes well with other reagents employed for the aldol reaction, while *Methanesulfonic Acid* does not afford any product.



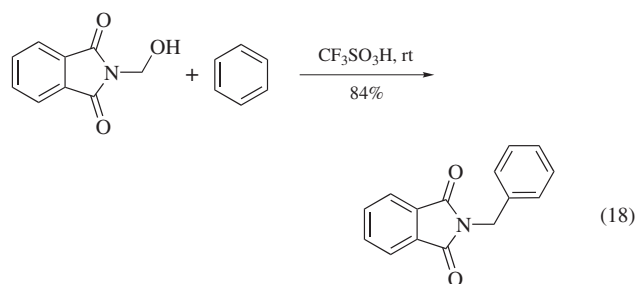
Cyclization of 3- and 4-arylalkanoic acids to bicyclic ketones is effected by TfOH via the corresponding acid chlorides (eq 16).<sup>21</sup>



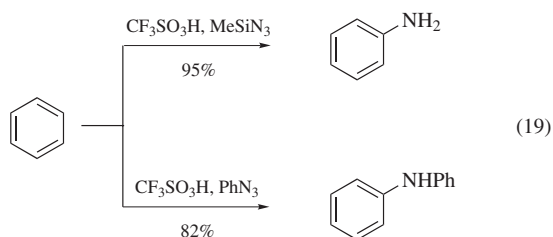
Allylic *O*-methylisoureas are cyclized with TfOH containing *Benzeneselenenyl Trifluoromethanesulfonate* to 5,6-dihydro-1,3-oxazines (eq 17).<sup>22</sup>



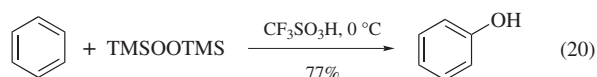
Tscherniac amidomethylation of aromatics with *N*-hydroxymethylphthalimide in TfOH proceeds smoothly at room temperature to give the corresponding  $\alpha$ -amido-methylated products (eq 18).<sup>23</sup>



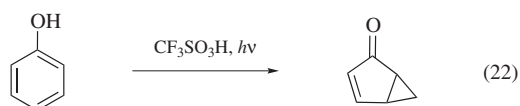
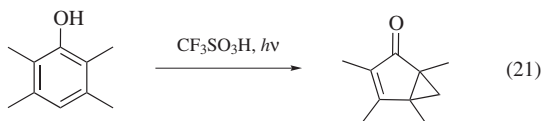
TfOH catalyzes the amination<sup>24</sup> and phenylation<sup>25</sup> of aromatics via the corresponding aminodiazonium ion generated from *Azidotrimethylsilane* and *Phenyl Azide* respectively (eq 19).



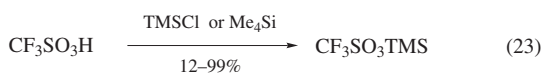
Electrophilic hydroxylation of aromatics is carried out by protonation of *Bis(trimethylsilyl) Peroxide* with TfOH in the presence of the substrate (eq 20).<sup>26</sup>



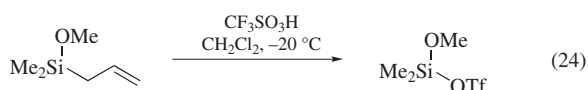
Phenol and 2,3,5,6-tetramethylphenol are protonated with TfOH under irradiation to afford rearranged products (eqs 21 and 22).<sup>27</sup>



**Other Applications.** TfOH is the starting material for the preparation of the electrophilic reagent *Trimethylsilyl Trifluoromethanesulfonate*. The latter is prepared by reacting TfOH with *Chlorotrimethylsilane*<sup>28</sup> or more conveniently with Me<sub>4</sub>Si (eq 23).<sup>29</sup>

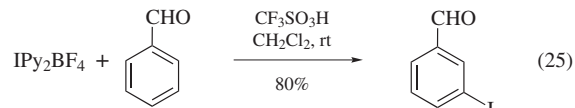


Functionalized silyl triflates can also be prepared using TfOH (eq 24).<sup>30</sup>

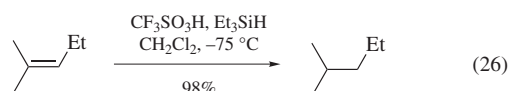


Reaction of aromatic compounds with *Bis(pyridine) iodonium(I) Tetrafluoroborate* in the presence of TfOH

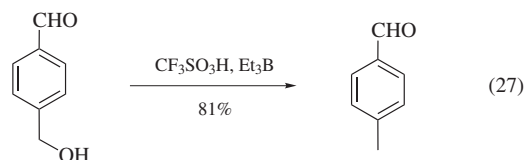
is an effective method to form the monoiodo compounds regioselectively (eq 25).<sup>31</sup>



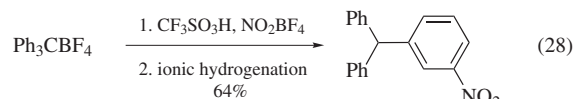
Ionic hydrogenation of alkenes with trialkylsilanes is possible in the presence of the strong acid TfOH, even at  $-75\text{ }^{\circ}\text{C}$  (eq 26).<sup>32</sup>



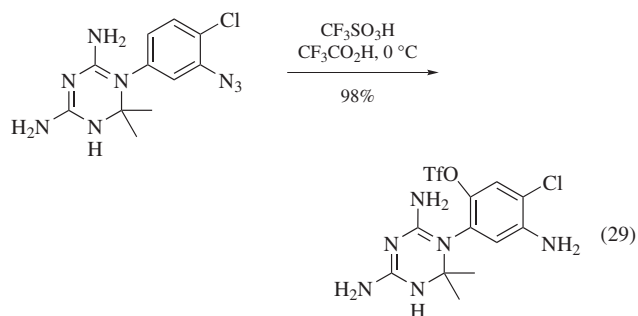
Hydroxycarbonyl compounds can be selectively reduced to carbonyl compounds by means of TfOH in the presence of trialkylboranes (eq 27).<sup>33</sup>



The triphenylmethyl cation is nitrated with *Nitronium Tetrafluoroborate* in the presence of TfOH (eq 28).<sup>34</sup>



Sterically hindered azidophenyltriazenes decompose in TfOH at  $0\text{ }^{\circ}\text{C}$  to give isomeric triflates (eq 29).<sup>35</sup>



Benzoyl triflate prepared from TfOH and *Benzoyl Chloride* is a mild and effective benzoylating agent for sterically hindered alcohols<sup>36</sup> and acylative ring expansion reactions.<sup>37</sup> The applications of TfOH in Koch–Haaf carboxylation,<sup>38</sup> Fries rearrangement,<sup>39</sup> and sequential chain extension in carbohydrates<sup>40</sup> are also documented. Recent applications of TfOH in cyclization reactions have been published.<sup>41–43</sup>

## First Update

G. K. Surya Prakash

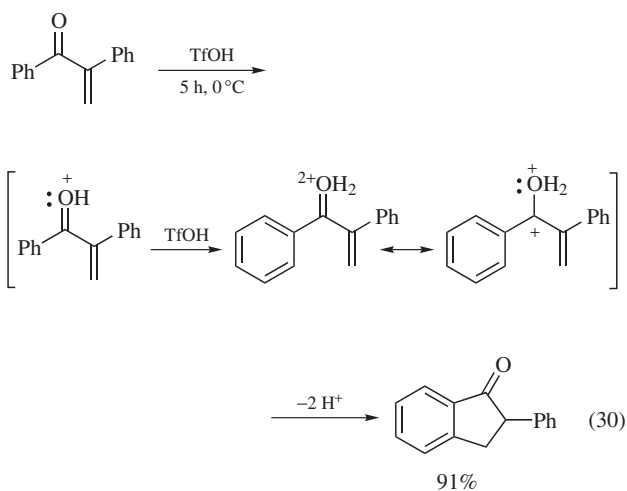
University of Southern California, Los Angeles, CA, USA

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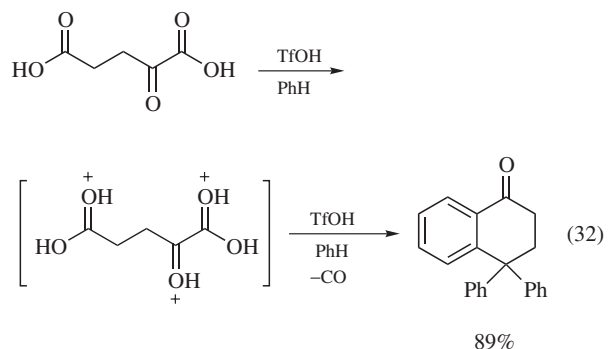
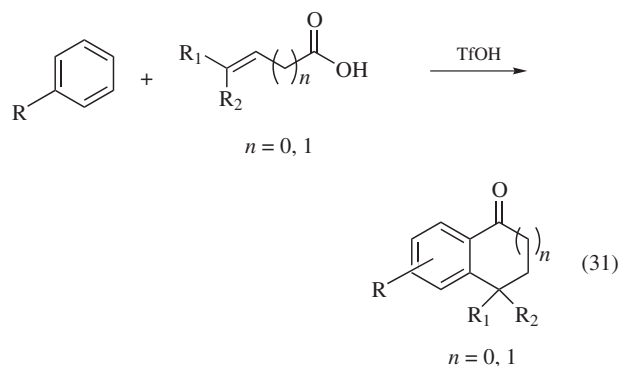
**Superelectrophilic Activation or Superelectrophilic Solvation.** Trifluoromethanesulfonic acid (triflic acid, TfOH) has been extensively employed as a superacid ( $H_o = -14.1$ ) in super-electrophilic activation (or superelectrophilic solvation), both concepts advanced by Olah.<sup>44,45</sup> Superelectrophilic activations may occur when a cationic electrophile reacts with a Bronsted or Lewis acid to give a dicationic (doubly electron-deficient) super-electrophile. However, it should be recognized that the activation may proceed through superelectrophilic solvation without necessarily forming limiting dicationic intermediates. The frequently used depiction of protosolvated species as their limiting dications is just for simplicity.<sup>45</sup>

Carboxonium ions are highly stabilized by strong oxygen participation and therefore are much less reactive compared to alkyl cations. However, under the superelectrophilic solvation by triflic acid, the Friedel–Crafts-type reactions still can occur via a protosolvated reactive intermediate. For example, 1-phenyl-2-propen-1-ones can be readily transformed into 1-indanones in good yields through triflic acid-catalyzed reaction (eq 30).<sup>46</sup>

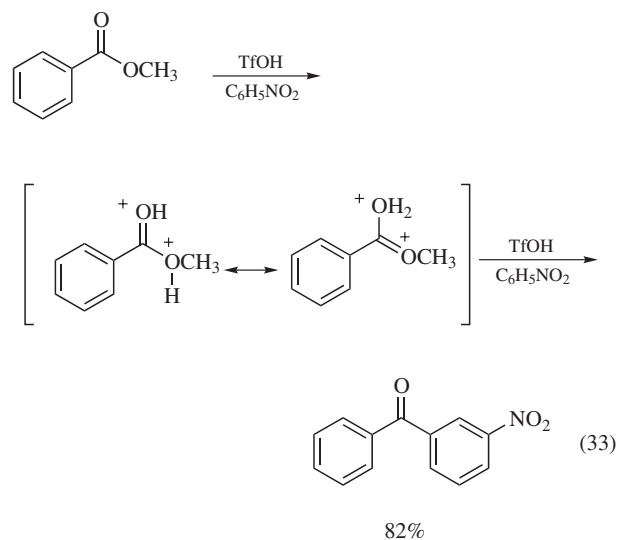


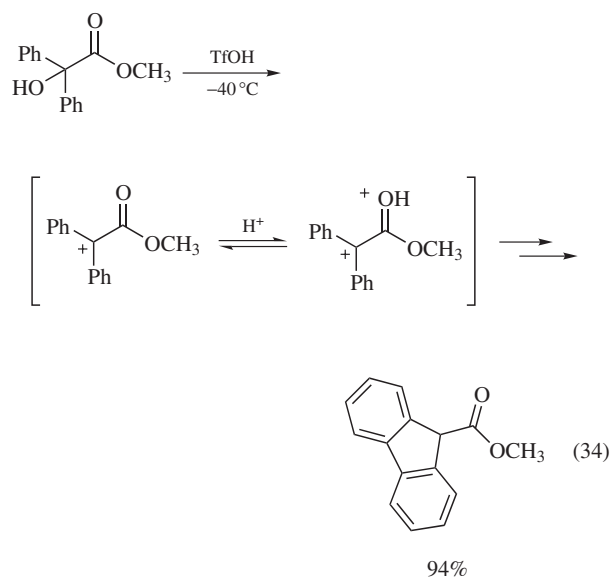
A one-pot synthesis of 1-indanones and 1-tetralones in good to excellent yields have been developed by reacting a series of alkenyl carboxylic acid derivatives with arenes in TfOH medium. The reaction involves dicationic intermediates involving intermolecular alkylation followed by intramolecular acylation (eq 31).<sup>47</sup> These reactions have been further investigated.<sup>48</sup>

Dicarboxylic acids can also form a variety of distonic superelectrophilic intermediates by TfOH-mediated protonation of the carboxylic acid group and ionization of adjacent functional groups.  $\alpha$ -Keto dicarboxylic acids in strongly acidic medium generate reactive multiply charged electrophilic species capable of condensing with arenes in high yields (eq 32).<sup>49</sup> The cascade of reactions also involve the loss of carbon monoxide.

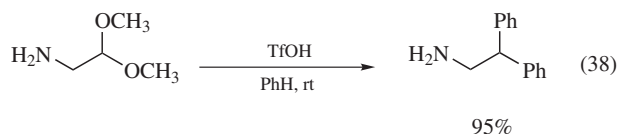
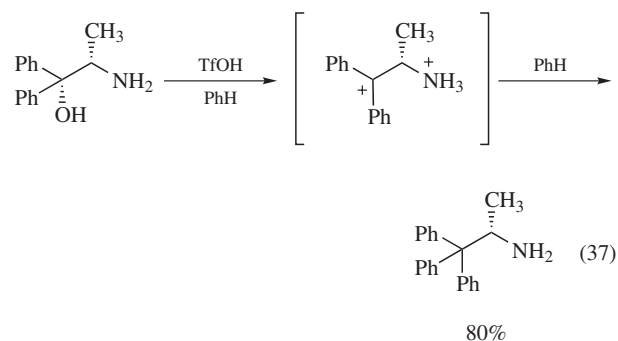
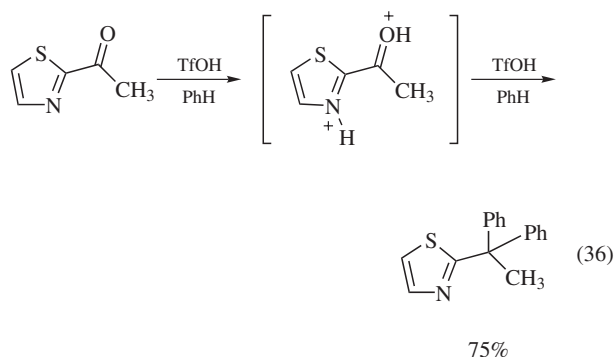
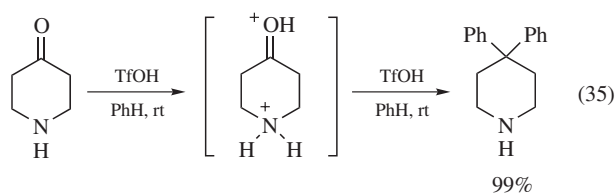


Triflic acid-catalyzed Friedel–Crafts acylation reactions of aromatics with methyl benzoate give benzophenone products in good to excellent yields (eq 33).<sup>50</sup> To explain the high level of electrophilic reactivity of this system, protosolvated species are proposed as possible intermediates (eq 32). In the triflic acid-catalyzed cyclization of some ethylene dications, protonation of the ester group is thought to be a key activation step. Reaction of  $\alpha$ -(methoxycarbonyl)diphenylmethanol with TfOH gives the fluorene product in 94% yield (eq 34).<sup>51</sup>

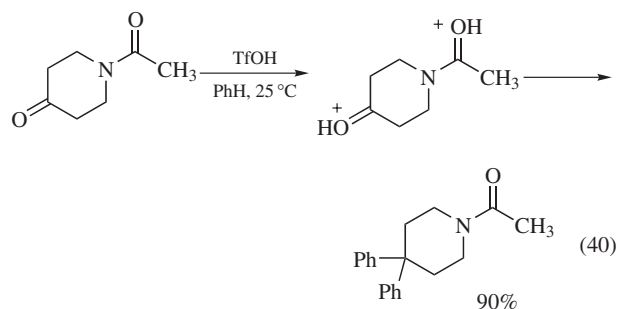
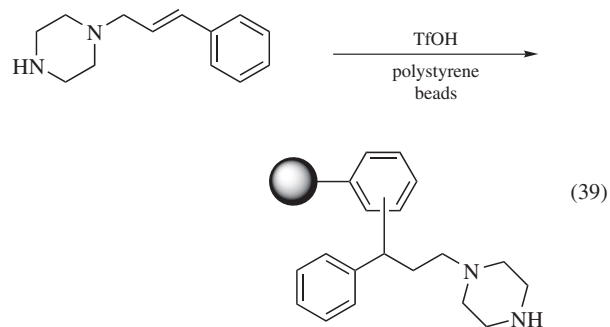


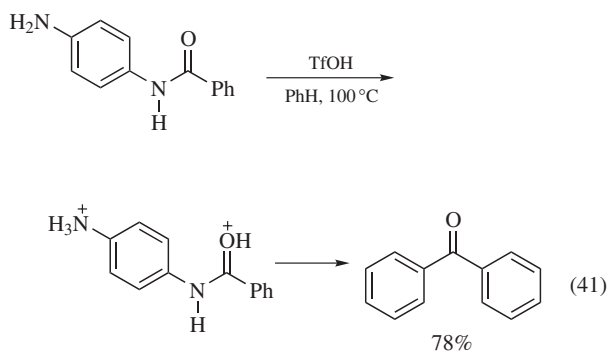


The same concept was applied in the synthesis of aryl-substituted piperidines by the TfOH-catalyzed reaction of piperidones with benzene (eq 35).<sup>52</sup> In the TfOH-catalyzed reactions, acetyl-substituted heteroaromatic compounds, such as pyridines, thiazoles, quinolines, and pyrazines can condense with benzene in good yields via the dicationic intermediates (eq 36).<sup>53</sup> Amino alcohols have also been found to ionize cleanly to the dicationic intermediates, which were directly observed by low-temperature <sup>13</sup>C NMR.<sup>54</sup> Amino alcohols can react with benzene in triflic acid by electrophilic aromatic substitution with 70~99% yields (eq 37).<sup>54</sup> Similarly, amino acetals can react with benzene in triflic acid medium to give 1-(3,3-diphenylpropyl)amines or 1-(2,2-diphenylethyl)amines in 50~99% yield (eq 38).<sup>55</sup>

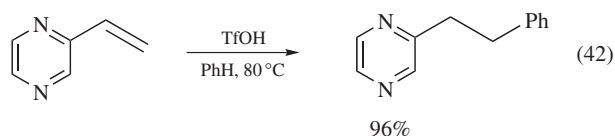


Klumpff and co-workers reported the triflic acid-catalyzed reactions of olefinic amines with benzene to give addition products in 75~99% yields.<sup>56</sup> Remarkably, the chemistry was also used to conveniently prepare functionalized polystyrene beads having pendant amine groups (eq 39).<sup>56</sup> In the triflic acid medium, amides are also able to form reactive, dicationic electrophiles.<sup>57</sup> It has been shown that protonated amide increases the reactivity of an adjacent electrophilic group (eq 40), and the protonated amide itself shows enhanced reactivity for Friedel-Crafts acylation arising from an adjacent cationic charge (eq 41).<sup>57</sup> Similar types of TfOH-catalyzed Friedel-Crafts acylation of aromatics with  $\beta$ -lactams have been reported.<sup>58</sup> TfOH-mediated activation of  $\alpha,\beta$ -unsaturated amides for condensation with arenes have been disclosed by Koltunov co-workers.<sup>59</sup> Klumpff and co-workers have also demonstrated the triflic acid-catalyzed superelectrophilic reactions of 2-oxazolines with benzene to give the corresponding amide products.<sup>60</sup> When aminoalkynes and related heterocycles reacted with benzene in triflic acid, diarylated products were obtained in generally good yields (69~99%) via dicationic intermediates.<sup>61</sup> Triflic acid also promotes reactions of pyrazolecarboxaldehydes with arenes.<sup>62</sup>



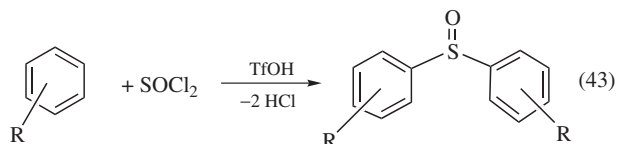


In TfOH medium, vinylpyrazine undergoes anti-Markovnikow addition involving superelectrophilic intermediates. Arylation of such an electrophile with benzene gave 2-phenylethylpyrazine in high yield (eq 42).<sup>63</sup>



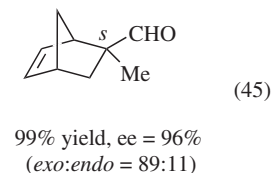
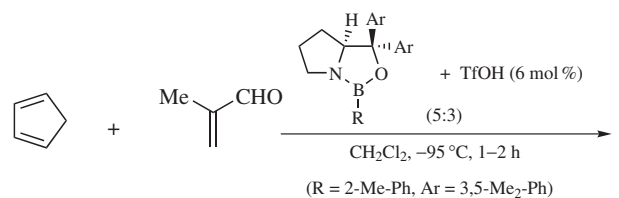
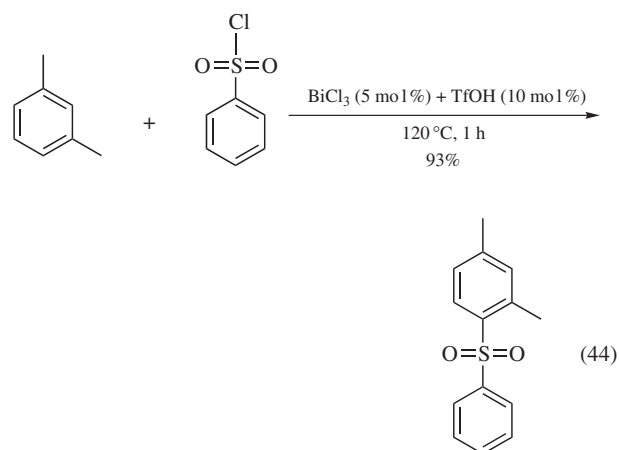
Ethyl trifluoropyruvate has been activated in TfOH medium for the hydroxyalkylation of arenes to give valuable Mosher's acid derivatives in good to excellent yields.<sup>64</sup> Even Selectfluor<sup>®</sup> has been activated in TfOH to effect electrophilic fluorination of arenes including fluorobenzene and chlorobenzene.<sup>65</sup>

A novel, mild method for the preparation of diaryl sulfoxides from arenes and thionyl chloride has been developed in TfOH medium. Under the nonoxidative reaction conditions only sulfoxides are produced without any contamination from the corresponding sulfones (eq 43).<sup>66</sup>

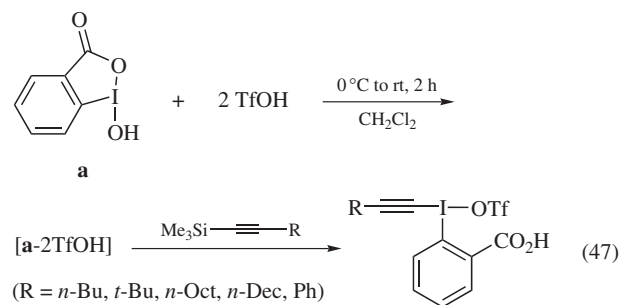
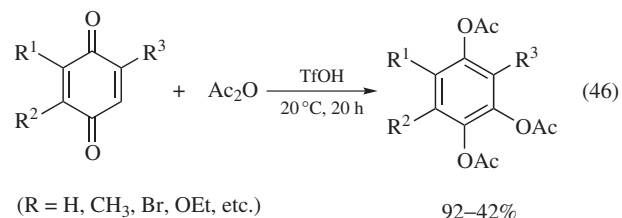


**Other Protonation and Acid-catalyzed Reactions.** The catalytic activity of triflic acid can be dramatically increased by the addition of a catalytic amount of bismuth(III) chloride. For example, triflic acid or BiCl<sub>3</sub> by itself poorly catalyzes the sulfonylation of arenes using arenesulfonyl chlorides. However, the BiCl<sub>3</sub>-triflic acid combination catalysts can efficiently catalyze the sulfonylation reactions (eq 44).<sup>67</sup> Similar synergistic effects between TfOH and bismuth(III) or antimony(III) chlorides have been observed in methanesulfonylation of arenes.<sup>68</sup>

Corey et al. have shown the asymmetric Diels-Alder reactions catalyzed by a triflic acid activated chiral oxazaborolidine (eq 45).<sup>69</sup> Triflic acid has also been found to be an efficient catalyst (1 mol %) for the hetero-Diels-Alder reaction between aromatic aldehydes and unactivated dienes.<sup>70</sup>

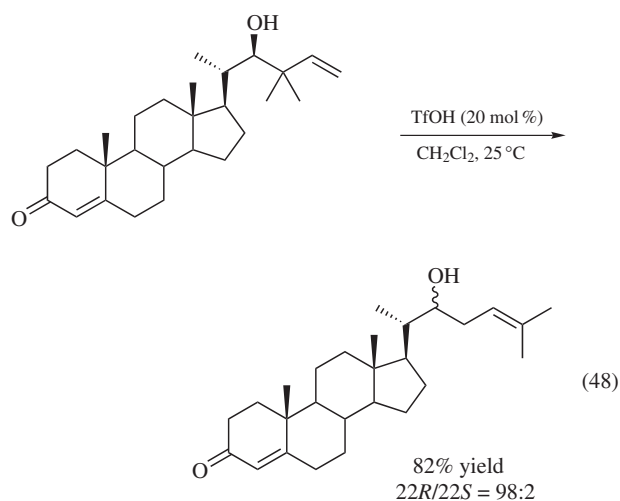


The synthetic scope of the Thiele-Winter reaction of quinines with acetic anhydride can be increased by the use of triflic acid (eq 46).<sup>71</sup> Reaction of cyclopropylacetylsilanes with triflic acid in aprotic solvent affords the corresponding cyclobutanone or 2-silyl-4,5-dihydrofuran derivatives.<sup>72</sup> Triflic acid can react with *o*-iodosylbenzoic acid to form a hypervalent iodine reagent, which reacts with 1-trimethylsilylalkynes to afford alkynyliodonium triflates bearing a carboxy group in high yields (eq 47).<sup>73</sup> Reaction of (diacetoxyiodo)benzene [PhI(OAc)<sub>2</sub>] with excess triflic acid results in oligomerization of PhI(OAc)<sub>2</sub>.<sup>74</sup>

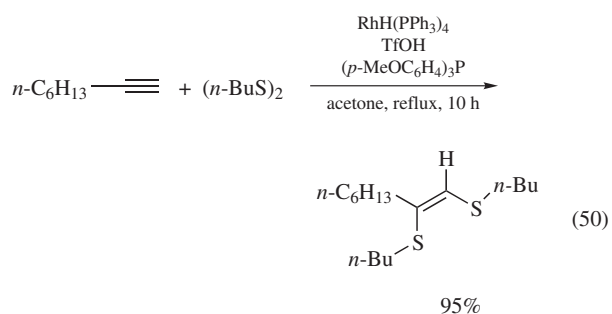
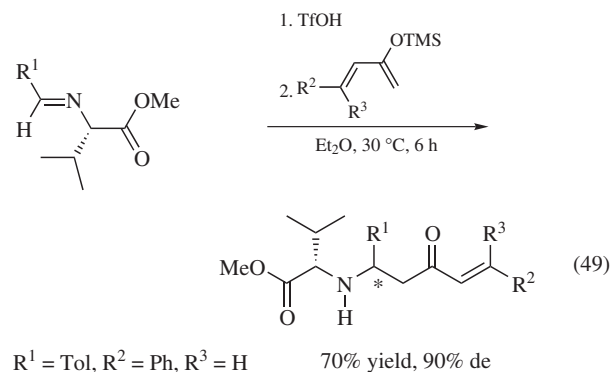


Olah et al. reported the triflic acid-catalyzed isobutene-isobutylene alkylation, modified with trifluoroacetic acid (TFA) or water. They found that the best alkylation conditions were at an acid strength of about  $H_0 = -10.7$ , giving a calculated research octane number (RON) of 89.1 (TfOH/TFA) and 91.3 (TfOH/H<sub>2</sub>O).<sup>75</sup> Triflic acid-modified zeolites can be used for the gas phase synthesis of methyl *tert*-butyl ether (MTBE), and the mechanism of activity enhancement by triflic acid modification appears to be related to the formation of extra-lattice Al rather than the direct presence of triflic acid.<sup>76</sup> A thermally stable solid catalyst prepared from amorphous silica gel and triflic acid has also been reported.<sup>77,78</sup> The obtained material was found to be an active catalyst in the alkylation of isobutylene with *n*-butenes to yield high-octane gasoline components.<sup>77</sup> A similar study has been carried out with triflic acid-functionalized mesoporous Zr-TMS catalysts.<sup>79,80</sup> Triflic acid-catalyzed carbonylation,<sup>81</sup> direct coupling reactions,<sup>82</sup> and formylation<sup>83</sup> of toluene have also been reported. Triflic acid also promotes transalkylation<sup>84</sup> and adamantylation of arenes in ionic liquids.<sup>85</sup> Triflic acid-mediated reactions of methylenecyclopropanes with nitriles have also been investigated to provide [3 + 2] cycloaddition products as well as Ritter products.<sup>86</sup> Triflic acid also catalyzes cyclization of unsaturated alcohols to cyclic ethers.<sup>87</sup>

Loh et al. found a triflic acid-catalyzed 2-oxonia Cope rearrangement, which was used in the stereocontrolled synthesis of linear 22*R*-homoallylic sterols (eq 48).<sup>88</sup> Interestingly, poor stereoselectivity was observed when In(OTf)<sub>3</sub> was employed as the catalyst for this reaction. Stereoselective Mannich-type reaction of chiral aldimines with 2-silyloxybutadienes in the presence of triflic acid gives the corresponding products with 70–92% de in 62–74% chemical yield, which are not obtained by general Lewis acid-promoted methods (eq 49).<sup>89</sup>



Triflic acid was also used in the synthesis of dixanthenes and poly(dixanthenes) by cyclization of 2-aryloxybenzotrioles at room temperature.<sup>90</sup> Addition of dialkyl disulfides to terminal alkynes is catalyzed by a rhodium-phosphine complex and triflic acid giving (*Z*)-bis(alkylthio)olefins stereoselectively (eq 50).<sup>91</sup>



Marko and co-workers have reported the role of triflic acid in the metal triflate-catalyzed acylation of alcohols with carboxylic anhydrides.<sup>92</sup> Their mechanistic insights demonstrate that triflic acid is generated under the acylation reaction conditions, and that two competing catalytic cycles are operating at the same time: a rapid one involving triflic acid and a slower one involving the metal triflates. A straightforward synthesis of aziridines is reported by treating electron rich alkyl- or aryl azide with electron deficient olefin and TfOH in cold acetonitrile.<sup>93</sup>

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