

# SYNLETT Spotlight 449

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

## Aluminum Trifluoromethanesulfonate

Compiled by Maretha du Plessis

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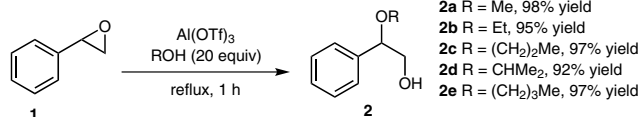
### Introduction

The synthesis of aluminum trifluoromethanesulfonate from aluminum trichloride and triflic acid was published by Olah et al.<sup>1,2</sup> in 1988. Aluminum triflate is a white solid with a high melting point<sup>2</sup> and acts as a strong, stable, oxophilic<sup>3–5</sup> Lewis acid that can easily be recycled and reused<sup>6</sup> due to its water-tolerant properties.<sup>7</sup> During initial investigations, aluminum trifluoromethanesulfonate was mainly used for Michael and Friedel–Crafts reactions, and

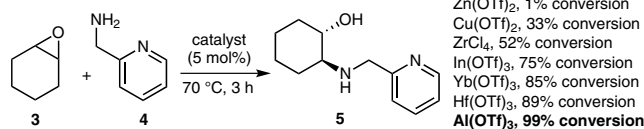
it also functioned as a Lewis acid catalyst for the protection of alcohols, phenols, and thiophenols<sup>8</sup> with a variety of different protecting groups (i.e., methyl, ethyl, isopropyl, *tert*-butyl, acetyl, tetrahydropyranyl and tetrahydrofuran).<sup>1,9,10</sup> Recently, the utilization of aluminum trifluoromethanesulfonate has been studied in much more diversity, for example as a co-catalyst in metal-catalyzed reactions,<sup>4,11</sup> in the nucleophilic opening of epoxides,<sup>5,12,13</sup> cyclization,<sup>14</sup> substitution,<sup>15</sup> and other reactions.

### Abstracts

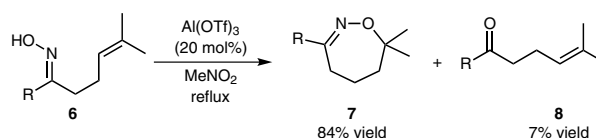
(A) Williams et al.<sup>12</sup> obtained excellent results (92–98% yield) in the ring opening of epoxides like styrene oxide with alcohols (ROH, R = C<sub>1</sub>–C<sub>4</sub>) and aluminum triflate to produce the monoethers of phenyl-substituted glycols. The ring opening of cyclohexene oxide also gave 83–89% yield utilizing only 0.002 mol% of triflate.



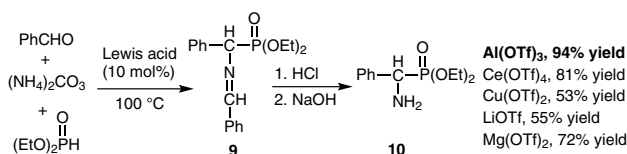
(B) Fringuelli et al.<sup>5</sup> and Williams et al.<sup>13</sup> extended the Al(OTf)<sub>3</sub>-catalysed ring opening of epoxides to include the use of amines instead of alcohols and were able to isolate the aminoalcohols in good yield (75–90%). The opening of cyclohexene oxide with 2-picolyamine could be effected with Al(OTf)<sub>3</sub> at concentrations of 5 mol% leading to the product being obtained in 99% yield under solvent-free conditions.



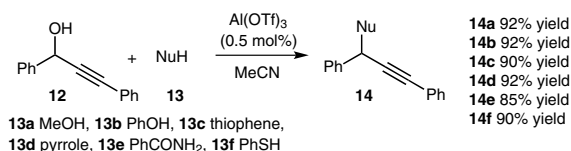
(C) Chaminade et al.<sup>14</sup> published the preparation of 1,2-oxaza heterocycles from unsaturated oximes through treatment of the substrate with different Lewis acid catalyst–solvent combinations. It was found that Al(OTf)<sub>3</sub> in nitromethane (MeNO<sub>2</sub>) gave the best result for this transformation.



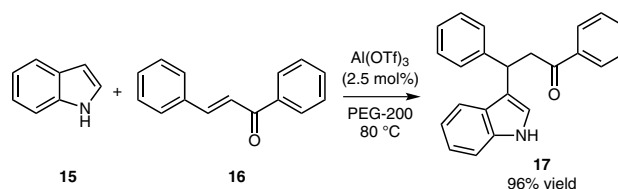
(D) Since naturally occurring 1-amino acids display a variety of biological activities and also act as plant-growth regulators and herbicides, Sobhani et al.<sup>16</sup> studied the synthesis of 1-amino-phosphonates and found that Al(OTf)<sub>3</sub> could be applied as a catalyst in a one-pot synthesis of primary diethyl 1-aminophosphonates under solvent-free conditions.



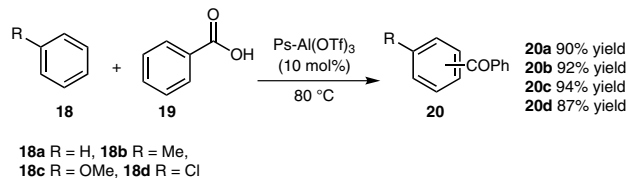
(E) Gohain et al.<sup>15</sup> showed Al(OTf)<sub>3</sub> to be a highly efficient and relatively inexpensive catalyst for the direct nucleophilic substitution of propargylic alcohols forming carbon–carbon and carbon–heteroatom bonds.



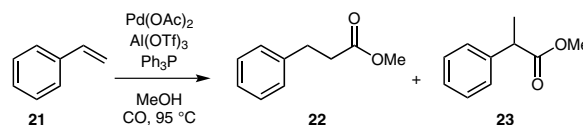
(F) Gohain et al.<sup>17</sup> reported a 'green' Friedel–Crafts, Michael-type addition of indole to  $\alpha,\beta$ -unsaturated ketones catalyzed by  $\text{Al}(\text{OTf})_3$  in the recyclable solvent polyethylene glycol.



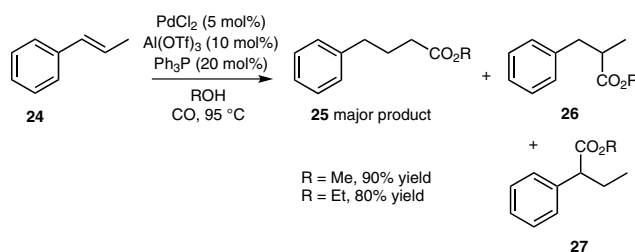
(G) Parvanak-Boroujeni and co-workers utilized polystyrene-supported aluminum triflate in the acylation of a range of aromatic substrates with benzoic acid and were able to obtain the corresponding benzophenones in excellent yields.<sup>18</sup>



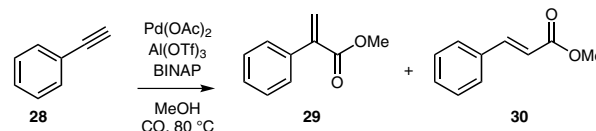
(H) Williams and co-workers discovered that aluminum triflate could be used as a highly active non-protic co-catalyst for the palladium-catalysed methoxycarbonylation of alkenes.<sup>4</sup> High conversions of up to 98% were obtained for the methoxycarbonylation of styrene with  $I/b$  ratios of up to 3:1. One of the main advantages of the Lewis acid co-catalyst is that it does not lead to phosphonium salt formation and depletion of the ligand, resulting in palladium 'fall-out' during these reactions.



(I) During the author's M.Sc. project, the utilization of  $\text{Al}(\text{OTf})_3$  as co-catalyst in alkoxycarbonylation was extended to include alkyl-substituted styrene substrates. In this regard,  $\text{PdCl}_2$  was found to be more reactive than  $\text{Pd}(\text{OAc})_2$ , and *trans*- $\beta$ -methylstyrene could be transformed into its respective methyl and ethyl esters with up to 95% conversion, with the major products being linear in this instance.<sup>19</sup>



(J) The Williams group<sup>11</sup> found that the alkoxycarbonylation reaction could be extended to include alkynes when a bidentate ligand is utilized in the process. High conversions (100%) with very high  $b/I$  ratios (99:1) were obtained.



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