



<b>Title</b>	<b>A polystyrene-supported triflating reagent for the synthesis of aryl triflates</b>
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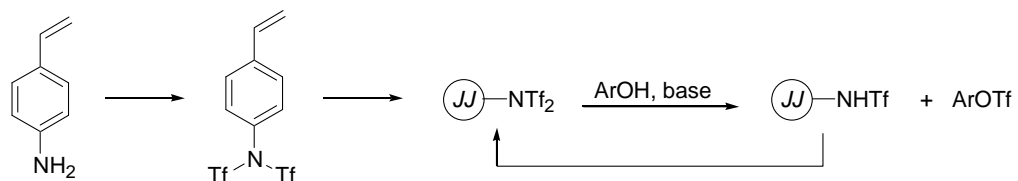
## Graphical Abstract

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### A polystyrene-supported triflating reagent for the synthesis of aryl triflates

Cecilia Wan Ying Chung and Patrick H. Toy\*

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# A polystyrene-supported triflating reagent for the synthesis of aryl triflates

Cecilia Wan Ying Chung and Patrick H. Toy\*

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**Abstract**—An insoluble polystyrene-supported triflating reagent has been prepared by suspension co-polymerization of *N*-(4-vinylphenyl)trifluoromethanesulphonimide, styrene and the JandaJel<sup>®</sup> cross-linker. This reagent, in the presence of triethylamine, allows for the efficient synthesis of aryl triflates from a wide range of phenols in a process that permits the desired product to be isolated from the reaction mixture in essentially pure form via several filtration and concentration operations. Adding to the utility of this reagent is its ability to be easily recovered, regenerated and reused. Both soluble and insoluble bifunctional polymers containing trialkylamine moieties in addition to triflimide groups were also prepared and examined as triflating reagents. Unfortunately these reagents afforded only modest yields of the desired products in representative reactions. © 2004 Elsevier Science. All rights reserved

## 1. Introduction

The use of polymer-supported reagents and catalysts in polymer-assisted organic synthesis has become commonplace since they can reduce product purification to simple filtration and concentration operations and are potentially easily recycled.<sup>1</sup> A vast array of such reagents and catalysts have been reported that use both insoluble<sup>2</sup> and soluble<sup>3</sup> polymers as their carriers and new ones are continually being developed in order to broaden the range of reactions in which they are applicable. In this regard, we have a long-standing interest in the development of both soluble and insoluble polymer-supported amine,<sup>4</sup> fluorinated ketone,<sup>5</sup> phosphine,<sup>6</sup> sulfide<sup>7</sup> and sulfoxide<sup>8</sup> reagents. Thus, in our research we have noticed that a missing tool from the polymeric reagent toolbox is a readily accessible and easy to use heterogeneous polymer-supported reagent that allows for the conversion of phenols to aryl triflates and isolation of the products via simple filtration and concentration operations.

Aryl triflates are versatile building blocks in organic synthesis since they participate in a variety of metal catalyzed carbonylation and coupling reactions.<sup>9,10</sup> Thus, methods and reagents for the synthesis of aryl (an enol) triflates are constantly being developed and refined.

Recent developments for their preparation include the use of triflic anhydride in an aqueous biphasic reaction system,<sup>11</sup> and the use of *N*-phenyltrifluoromethanesulphonimide (**1**)<sup>12</sup> (Figure 1) in conjunction with controlled microwave heating.<sup>13</sup> One drawback associated with the use of reagent **1** is that it and its by-products can be difficult to separate from the triflate product. Therefore both polar analog **2**, which not only aids in product purification but also accelerates its formation,<sup>14</sup> and soluble poly(ethylene glycol)-supported analog **3**,<sup>15</sup> which can facilitate product isolation, have been reported. While the former has seen widespread use, the latter has not. Perhaps one reason for the lack of use of **3** is that it requires a precipitation operation before it and its by-products can be removed by filtration, and thus, it is not very amenable to use in parallel synthesis or with automation equipment. Therefore an insoluble polymer-supported reagent that does not require a precipitation step prior to filtration might find broader acceptance and utilization. Herein we wish to report the synthesis and use of such a reagent.

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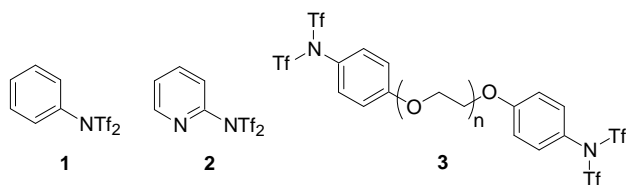
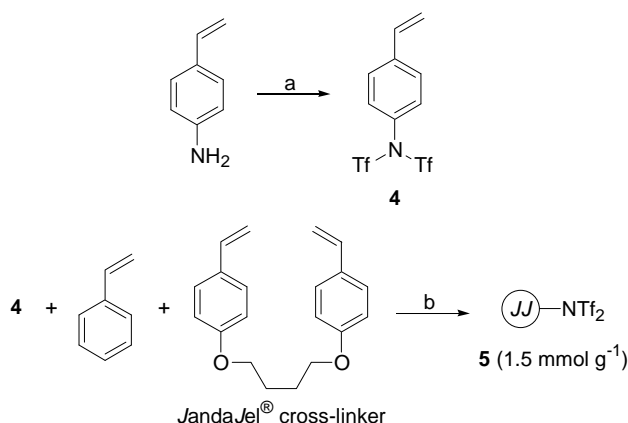


Figure 1. Current triflimide reagents.

## 2. Results and discussion

The preparation of a polymer-supported triflating reagent requires an aniline polymer as the base material and many preparations of such polymers have been reported. These methods include Schmidt rearrangement of a benzyl azide resin,<sup>16</sup> attachment of an aniline derivative to a preformed polymer,<sup>17</sup> and the incorporation of either 4-vinylaniline<sup>18</sup> or *N*-Boc-4-vinylaniline<sup>19</sup> in the polymerization process. While any of these methods could have provided us with a suitable polymeric starting material, we choose a more direct route by preparing a functional monomer<sup>20</sup> containing the desired triflimide functional group and incorporating it into the polymer during the polymerization process.

Thus functional monomer **4** was prepared in 90% yield by reaction of 4-vinylaniline with 2 equivalents of Tf<sub>2</sub>O in the presence of excess Et<sub>3</sub>N. After determining the stability of **4** to the polymerization reaction conditions, it was used to prepare an insoluble polystyrene reagent. Thus it was suspension co-polymerized<sup>21</sup> with styrene and the flexible JandaJel<sup>®</sup> cross-linker<sup>22,23</sup> to afford insoluble **5** (JandaJel<sup>®</sup>-NTf<sub>2</sub>) (Scheme 1). Elemental analysis was used to determine the loading level of **5** to be 1.6 mmol NTf<sub>2</sub> g<sup>-1</sup> based on the average analysis results for nitrogen and sulphur content.



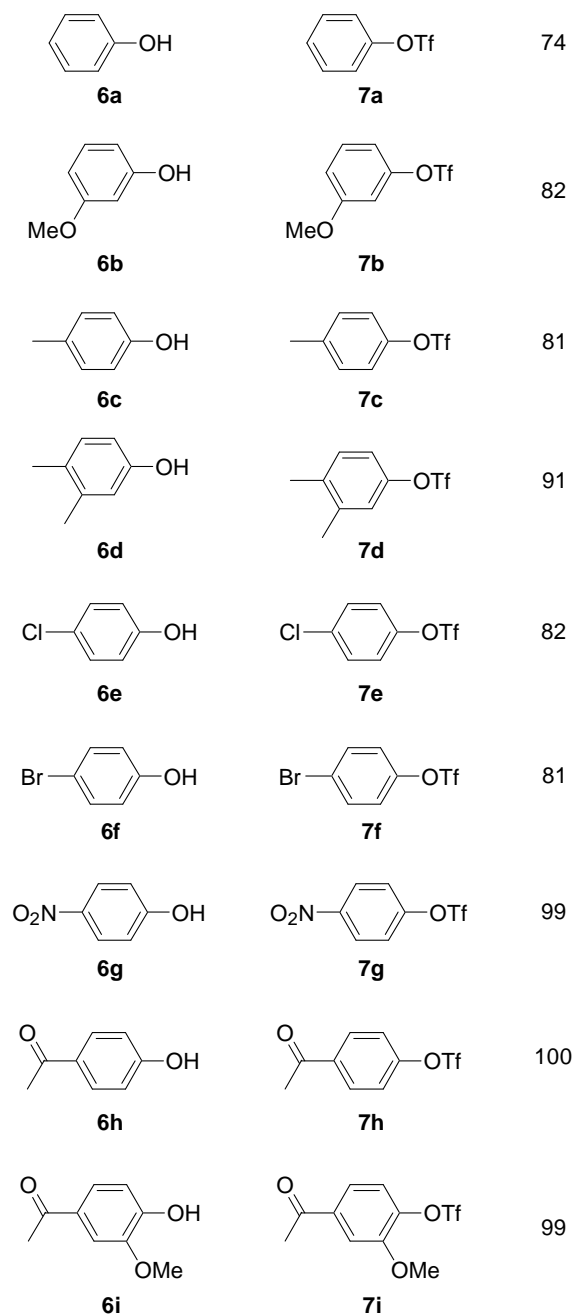
Scheme 1. Synthesis of reagents **5**. Reagents and conditions: (a) Et<sub>3</sub>N (3 eq), Tf<sub>2</sub>O (2 eq), anhydrous CH<sub>2</sub>Cl<sub>2</sub>, 0 °C. (b) PhCl, AIBN, water, acacia gum, NaCl, 85 °C.

Next we examined the use of **5** in the preparation of a variety of aryl triflates derived from phenols (**6a-i**) substituted with both electron donating and withdrawing

substituents (Table 1). These reactions were performed in dichloromethane at room temperature using 2 equivalents of both **5** and Et<sub>3</sub>N. Upon the complete disappearance of **6a-i** according to TLC analysis (4-16 h), the reactions were filtered to remove the insoluble polymer, concentrated in vacuo and filtered through a short plug of silica gel. Finally, removal of the solvent afforded triflates **7a-i** in essentially pure form, as determined by <sup>1</sup>H NMR analysis. As can be seen in Table 1, all substrates were isolated in good to excellent yield.<sup>24</sup>

Table 1. Aryl triflate synthesis.

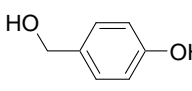
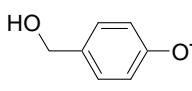
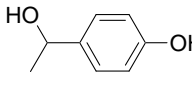
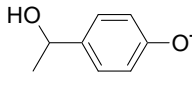
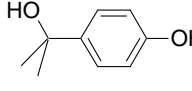
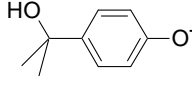
ArOH <b>6a-i</b>	$\xrightarrow{5, Et_3N}$	ArOTf + $\textcircled{JJ}$ -NHTf <b>7a-i</b> <b>8</b>
Phenol		Triflate      Yield (%)



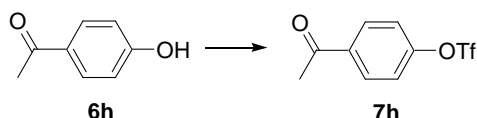
With our success in synthesizing aryl triflates containing carbonyl functional groups (**7h-i**), we were interested to see if aryl triflates containing aliphatic alcohols could also be prepared. Gratifyingly, diols **6j-l** afforded the corresponding monotriflates **7j-l** in moderate to good yield (Table 2) when the reactions were performed at 50 °C. The structures of **7j-k** were confirmed by their oxidation to the corresponding aldehyde and ketone (**7h**), respectively. It should be noted that these reactions were quite sluggish even at elevated temperature and 2-5 days and 4 equivalents of **5** were required for the complete consumption of the starting diol. Furthermore, the formation of **7j-l** was accompanied by numerous uncharacterized impurities and these products required

chromatographic purification. One possible explanation for the requirement of a larger excess of **5** for the synthesis of **7j-l** is that the isolated products may have been formed by hydrolysis of initially generated ditriflate molecules. Such a reaction pathway would also explain the complex crude product mixtures obtained for **7j-l**.

**Table 2.** Synthesis of aryl triflates containing aliphatic alcohol groups.

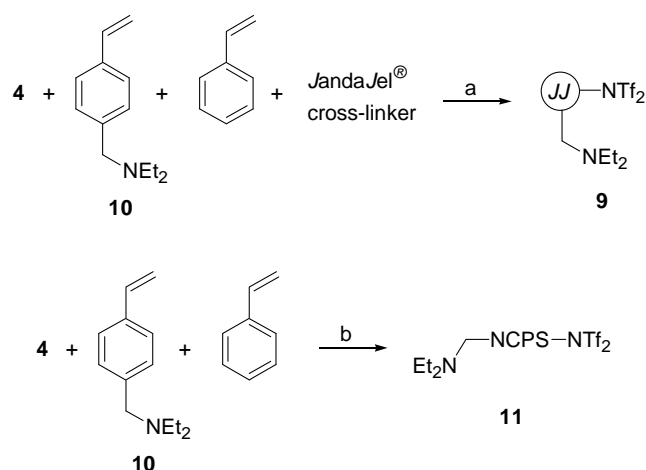
ArOH		$\xrightarrow{5, Et_3N}$	ArOTf + $\textcircled{JJ}$ -NHTf	
<b>6j-l</b>			<b>7j-l</b>	<b>8</b>
Phenol			Triflate	Yield (%)
				48
<b>6j</b>			<b>7j</b>	
				90
<b>6k</b>			<b>7k</b>	
				63
<b>6l</b>			<b>7l</b>	

Having established that **5** is effective and efficient in converting a broad range of aryl alcohols into the corresponding triflates, we next examined its recyclability. Thus, we recovered the polymer (a mixture of **5** and **8**) at the end of the reactions and treated it with  $Tf_2O$  and  $Et_3N$ . As can be seen in Table 3, the same sample of **5** can be reused at least 3 times for the conversion of **6h** to **7h**, with only modest decrease in efficiency. Considering the small scale of the reactions performed, we consider the reported yields to be approximately equivalent. However, the reactions of the later cycles were somewhat sluggish compared to the initial reaction and required slightly longer reaction times. Nevertheless, it is important to note that the reactions were efficient in all cases and only the desired product was observed.

Table 3. Recycling of **5**.


Cycle	Yield (%)
1	100
2	88
3	95
4	92

Lastly, we examined the possibility of incorporating basic amine moieties into **5** so that the triflation reactions might be performed without the requirement for a base to be added and thereby possibly eliminate the need for the filtration through silica gel to obtain pure product. Thus bifunctional polymer **9**, which contains not only triflimide moieties, but also basic trialkylamine groups was prepared by the inclusion of monomer **10**<sup>4</sup> in a 3:2 ratio compared to **4**, in the polymerization process (Scheme 2). The loading levels of both the amine and triflimide functional groups were determined by elemental analysis to be 1.3 and 0.8 mmol g<sup>-1</sup>, respectively, based on nitrogen and sulfur content. To our knowledge only one other such bifunctional polymer has been reported in the literature and it contains both basic pyridine moieties and catalytic 4-dimethylaminopyridine groups and it was used in esterification reactions.<sup>25</sup> Unfortunately when **9** was used to convert **6h** to **7h**, only trace amounts (< 5%) of the desired product were observed by GC analysis, even after extended reaction times at elevated temperature.



Scheme 2. Synthesis of bifunctional polymers **9** and **11**. Reagents and conditions: (a) PhCl, AIBN, water, acacia gum, NaCl, 85 °C. (b) PhMe, AIBN, 85 °C.

In order to gain insight into the failure of **9** to be an efficient triflating reagent, we prepared the soluble, non-cross-linked polystyrene (NCPS) reagent **11** by copolymerization of **4**, **10**, and styrene (Scheme 2), since it would be easier to characterize spectroscopically and be a

homogeneous reagent. Analysis of **11** by IR, and <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy and comparison of this data with that of **4** indicated that the amine and triflimide groups are compatible with one other in the polystyrene matrix. Even when both **9** and **11** were subjected to the aqueous suspension polymerization reaction conditions, only minor signals indicating N-H bonds were observed in the IR spectra. Thus premature cleavage of the triflimide groups was probably not responsible for the poor results with **9**. Reaction of **6h** with **11** also only afforded low yield of **7h** (ca 8%), indicating that the heterogeneous nature of **9** was also not responsible for its inefficiency. Thus, some unknown interaction between the amine and triflimide functional groups must be responsible for the failure of the bifunctional polymers **9** and **11** to be useful triflating reagents.

### 3. Conclusions

We have prepared the new, insoluble polystyrene-supported triflimide reagent **5** and demonstrated its usefulness in the synthesis of a range of aryl triflates, including ones that contain aliphatic hydroxyl groups. This reagent is recyclable at least 3 times with no significant decrease in its efficiency. Finally, we report the synthesis of bifunctional polymeric reagents **9** and **11**. Unfortunately these are not as efficient as **5** is in the preparation of aryl triflates, which may be due to micro-environmental factors that arise from bringing the amine and triflimide moieties together in the same polymer matrix.<sup>25</sup>

Finally, we have attempted to use **5** in the synthesis of enol triflates from ketones, and in sample reactions the products formed required chromatographic purification, as is the case when **1** and **2** are used. Thus, considering the heterogeneity of **5** and the prolonged reaction times required compared to homogeneous small molecule reagents, we found no advantages to using **5** in enol triflate synthesis and therefore limited our study to the preparation of aryl triflates. Significantly, when **5** is used in such applications, the work-up and isolation of the aryl triflate product is simple, amenable to being performed in parallel in an automated fashion and can be completed in a matter of minutes. Thus it should be a useful tool in parallel synthesis, where the ability to simply isolate products with high purity is essential.

## 4. Experimental

### 4.1. General

All reagents were obtained from the Aldrich, Lancaster or Acros chemical companies and were used without further purification. All moisture sensitive reactions were carried out in dried glassware under a N<sub>2</sub> atmosphere. Tetrahydrofuran was distilled under a N<sub>2</sub> atmosphere over sodium and benzophenone. Dichloromethane was distilled under a N<sub>2</sub> atmosphere over calcium hydride. Merck silica gel 60 (230-400 mesh) was used for chromatography. Thin

layer chromatography analysis was performed using glass plates coated with silica gel 60 F<sub>254</sub>. Gas chromatographic analyses were performed using an RTX-5 column with a Thermo Finnigan Focus chromatograph. NMR spectra were recorded using either a Bruker DRX 300 or an AV400 spectrometer. Chemical shift data is expressed in ppm with reference to TMS. HR EI-MS data was recorded on a Finnigan MAT 96 mass spectrometer.

#### 4.1.1. *N*-(4-vinylphenyl)trifluoromethanesulfonimide (**4**).

To a solution of 4-aminostyrene (5.40 g, 45.2 mmol) and Et<sub>3</sub>N (18.8 mL, 135.5 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at -78 °C was added triflic anhydride (15.2 mL, 90.3 mmol). The reaction mixture was stirred at this temperature for 1 h and then warmed to rt and stirred for 1 h more. At this time, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (400 mL) and then washed sequentially with saturated aqueous NaHCO<sub>3</sub> (150 mL) and brine (150 mL). The organic phase was dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (5% EtOAc/hexanes) to afford **4** as white solid (15.58 g, 90%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 5.43 (d, 1H, *J* = 10.9 Hz), 5.85 (d, 1H, *J* = 17.6 Hz), 6.73 (dd, 1H, *J* = 17.6, 10.9 Hz), 7.35 (d, 2H, *J* = 8.5 Hz), 7.51 (d, 2H, *J* = 8.6 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 113.3, 113.3-123.3 (*J*<sub>CF</sub> = 323.2 Hz), 127.9, 131.1, 131.5, 135.3, 141.8. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -71.1. IR (KBr, cm<sup>-1</sup>): 3073, 1633, 1507, 1122, 741, 661. HR EI-MS: calcd for C<sub>10</sub>H<sub>7</sub>NS<sub>2</sub>O<sub>4</sub>F<sub>6</sub>, 382.9720; found 382.9713.

The stability of **4** to the suspension polymerization conditions was examined by placing it in the acacia solution described below. This was heated to 85 °C for 20 h. At this time, TLC analysis indicated only the presence of unchanged **4**. No more highly polar compounds were observed.

**4.1.2. JandaJel<sup>®</sup>-NTf<sub>2</sub> (**5**).** A solution of acacia gum (6.0 g) and NaCl (3.8 g) in warm deionized water (45 °C, 150 mL) was placed in a 150 mL flanged reaction vessel equipped with a mechanical stirrer and deoxygenated by purging with N<sub>2</sub> for 2 h.<sup>26</sup> A solution of **4** (5.74 g, 15.0 mmol), styrene (4.26 g, 41.0 mmol), 1,4-bis(4-vinylphenoxy)butane<sup>22d</sup> (0.33 g, 1.1 mmol), and AIBN (0.2 g, 1.3 mmol) in chlorobenzene (10 mL) was injected into the rapidly stirred aqueous solution. The resulting suspension was heated at 85 °C for 20 h. At this time the crude polymer was collected and washed with hot water (3 x 100 mL) and then placed in a Soxhlet extractor and washed with THF for 24 h. The beads were then washed sequentially with diethyl ether (250 mL), and hexane (250 mL), and then dried in vacuo for 24 h to afford **5** (8.5 g, 85%). IR (KBr, cm<sup>-1</sup>): 3068, 3029, 1603, 1501, 1128, 760, 701. Elemental analysis was used to determine the nitrogen content (2.3%) and the sulfur content (9.6%), and thus the loading level of **5** was 1.6 mmol g<sup>-1</sup>.

**4.1.3. JandaJel<sup>®</sup>-(CH<sub>2</sub>NEt<sub>2</sub>)NTf<sub>2</sub> (**9**).** A solution of acacia gum (6.0 g) and NaCl (3.8 g) in warm deionized water (45 °C, 150 mL) was placed in a 150 mL flanged reaction vessel equipped with a mechanical stirrer and

deoxygenated by purging with N<sub>2</sub> for 2 h. A solution of **4** (3.83 g, 10.0 mmol), **10**<sup>4</sup> (2.84 g, 15 mmol), styrene (3.33 g, 32.0 mmol), 1,4-bis(4-vinylphenoxy)butane<sup>22d</sup> (0.34 g, 1.1 mmol), and AIBN (0.2 g, 1.3 mmol) in chlorobenzene (10 mL) was injected into the rapidly stirred aqueous solution. The resulting suspension was heated at 85 °C for 20 h. At this time the crude polymer was collected and washed with hot water (3 x 100 mL) and then placed in a Soxhlet extractor and washed with THF for 24 h. The beads were then washed sequentially with diethyl ether (250 mL), and hexane (250 mL), and then dried in vacuo for 24 h to afford **9** (5.4 g, 54%). IR (KBr, cm<sup>-1</sup>): 3498, 3027, 1606, 1510, 1145, 761, 700. Elemental analysis was used to determine the nitrogen content (2.9%) and the sulfur content (5.0%), and thus the loading levels of the amine and triflimide groups in **9** were 1.3, and 0.8 mmol g<sup>-1</sup>, respectively.

**4.1.4. NCPS-(CH<sub>2</sub>NEt<sub>2</sub>)NTf<sub>2</sub> (**11**).** To a solution of styrene (1.67 g, 16.0 mmol), diethyl(4-vinylbenzyl)amine (1.42 g, 7.5 mmol) and **4** (1.79 g, 5.0 mmol) in toluene (20 mL) was added AIBN (0.024 g, 0.14 mmol). The mixture was purged with N<sub>2</sub> for 30 min and the solution was stirred at 85 °C for 24 h. The solution was concentrated in vacuo and the residue was taken up in 2 mL of THF. This solution was added dropwise to a vigorously stirred cold Et<sub>2</sub>O (0 °C, 200 mL). The white precipitate was filtered and dried to afford **11** as a white powder (1.6 g, 32%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 1.02-1.60 (br, 10H), 1.63-2.41 (br, 36H), 2.82-3.32 (br, 4H), 3.81-4.38 (br, 1H), 6.12-7.75 (br, 20H). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -71.1. IR (KBr, cm<sup>-1</sup>): 3504, 3028, 1603, 1506, 1129, 762, 702.

## 4.2. General procedure for aryl triflate synthesis using **5**.

Reagent **5** (0.47 g, 0.75 mmol) and Et<sub>3</sub>N (0.1 mL, 0.75 mmol) were added to a solution of **6** (0.375 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The reaction mixture was shaken at rt until TLC analysis indicated the complete disappearance of **6** (4-16 h). At this time, the resin was filtered off and the filtrate was concentrated in vacuo. The resulting residue was then filtered through a plug of silica gel using CH<sub>2</sub>Cl<sub>2</sub>. Removal of the solvent afforded **7** that was determined to be essentially pure by <sup>1</sup>H NMR.

The syntheses of **7j-l** were performed at 50 °C and required 4, 5, and 2 d, respectively, for the complete disappearance of starting material. These products were purified by silica gel chromatography.

**4.2.1. Characterization data for **7a**:**<sup>11</sup> Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.25-7.29 (m, 2H), 7.34-7.49 (m, 3H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 112.8-125.6 (*J*<sub>CF</sub> = 318.7 Hz), 121.7, 128.8, 130.7, 150.1. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -72.9. HR EI-MS: calcd for C<sub>7</sub>H<sub>5</sub>SO<sub>3</sub>F<sub>3</sub>, 225.9911; found 225.9913.

**4.2.2. Characterization data for **7b**:**<sup>27</sup> Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 3.82 (s, 3H), 6.80 (t, 1H, *J* = 2.3 Hz), 6.85-6.94 (m, 2H), 7.33 (t, 1H, *J* = 8.3 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 55.7, 107.5, 113.3, 114.2, 114.0-123.5 (*J*<sub>CF</sub> = 319.0 Hz), 130.6, 150.3, 160.9. <sup>19</sup>F-

NMR (376 MHz, CDCl<sub>3</sub>) δ -72.9. HR EI-MS: calcd for C<sub>8</sub>H<sub>7</sub>SO<sub>4</sub>F<sub>3</sub>, 256.0017; found 256.0019

**4.2.3. Characterization data for 7c:**<sup>11</sup> Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 2.37 (s, 3H), 7.15 (d, 2H, *J* = 8.6 Hz), 7.23 (d, 2H, *J* = 8.7 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 20.9, 114.0-123.6 (*J*<sub>CF</sub> = 318.8 Hz), 121.0, 130.7, 138.5, 147.6. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -72.9. HR EI-MS: calcd for C<sub>8</sub>H<sub>7</sub>SO<sub>3</sub>F<sub>3</sub>, 240.0068; found 240.0071.

**4.2.4. Characterization data for 7d:**<sup>28</sup> Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 2.26 (s, 3H), 2.28 (s, 3H), 6.99 (dd, 1H, *J* = 8.3, 2.6 Hz), 7.03 (d, 1H, *J* = 2.4 Hz), 7.17 (d, 1H, *J* = 8.3 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 19.6, 20.2, 112.8-125.6 (*J*<sub>CF</sub> = 318.7 Hz), 118.7, 122.4, 131.3, 137.5, 139.5, 148.0. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -73.0. HR EI-MS: calcd for C<sub>9</sub>H<sub>9</sub>SO<sub>3</sub>F<sub>3</sub>, 254.0224; found 254.0226.

**4.2.5. Characterization data for 7e:**<sup>10c</sup> Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.23 (d, 2H, *J* = 9.0 Hz), 7.43 (d, 2H, *J* = 9.0 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 112.7-125.5 (*J*<sub>CF</sub> = 318.9 Hz), 123.1, 130.8, 134.7, 148.3. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -72.8. HR EI-MS: calcd for C<sub>7</sub>H<sub>4</sub>SClO<sub>3</sub>F<sub>3</sub>, 259.9522; found 259.9526.

**4.2.6. Characterization data for 7f:**<sup>11</sup> Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16 (d, 2H, *J* = 8.8 Hz), 7.56 (d, 2H, *J* = 8.9 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 117.5-123.9 (*J*<sub>CF</sub> = 318.9 Hz), 122.4, 123.4, 133.8, 148.9. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -72.8. HREI-MS: calcd for C<sub>7</sub>H<sub>4</sub>SBrF<sub>3</sub>O<sub>3</sub>, 303.9017; found 303.9014.

**4.2.7. Characterization data for 7g:**<sup>11</sup> Yellow solid (mp 52-56 °C). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.49 (d, 2H, *J* = 8.9 Hz), 8.37 (d, 2H, *J* = 8.9 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 112.7-125.4 (*J*<sub>CF</sub> = 318.9 Hz), 122.9, 126.4, 147.5, 153.5. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -73.0. HR EI-MS: calcd for C<sub>7</sub>H<sub>4</sub>NSF<sub>3</sub>O<sub>5</sub>, 270.9762; found 270.9760.

**4.2.8. Characterization data for 7h:**<sup>30</sup> Yellow oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 2.63 (s, 3H), 7.39 (d, 2H, *J* = 8.8 Hz), 8.07 (d, 2H, *J* = 8.9 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 27.0, 112.7-125.4 (*J*<sub>CF</sub> = 318.8 Hz), 122.0, 130.9, 137.3, 152.8, 196.4. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -72.8. HR EI-MS: calcd for C<sub>9</sub>H<sub>7</sub>SO<sub>4</sub>F<sub>3</sub>, 268.0017; found 268.0015.

**4.2.9. Characterization data for 7i:**<sup>321</sup> White solid (mp 100-104 °C). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 2.62 (s, 3H), 3.98 (s, 3H), 7.32 (d, 1H, *J* = 8.4 Hz), 7.57 (dd, 1H, *J* = 8.4, 2.0 Hz), 7.65 (d, 1H, *J* = 1.9 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 26.5, 56.4, 112.3, 114.0-123.5 (*J*<sub>CF</sub> = 318.5 Hz), 122.6, 122.5, 137.8, 141.9, 151.7, 196.3. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -73.8. HR EI-MS: calcd for C<sub>10</sub>H<sub>9</sub>SO<sub>5</sub>F<sub>3</sub>, 298.0123; found 298.0116.

**4.2.10. Characterization data for 7j:** Yellow oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 2.10 (br, 1H), 4.70 (s, 2H), 7.25 (dd, 2H, *J* = 6.8, 2.2 Hz), 7.43 (d, 2H, *J* = 8.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 64.0, 114.0-123.5 (*J*<sub>CF</sub> = 318.8 Hz), 121.4, 128.5, 141.4, 148.8. <sup>19</sup>F-NMR (376 MHz,

CDCl<sub>3</sub>) δ -72.9. HR EI-MS: calcd for C<sub>8</sub>H<sub>7</sub>SO<sub>4</sub>F<sub>3</sub>, 256.0017; found 256.0019.

For structural proof, **7j** was oxidized to the corresponding aldehyde using PDC (2.5 equiv) in CH<sub>2</sub>Cl<sub>2</sub> at rt for 2 h (83% yield). Characterization data for this aldehyde: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.47 (d, 2H, *J* = 8.6 Hz), 8.01 (d 2H, *J* = 8.6 Hz), 10.05 (s, 1H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ 114.9-122.5 (*J*<sub>CF</sub> = 318.9 Hz), 122.3, 131.8, 136.0, 153.2, 190.1. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -72.7. HR EI-MS: calcd for C<sub>8</sub>H<sub>5</sub>SO<sub>4</sub>F<sub>3</sub>, 253.9861; found 253.9860.

**4.2.11. Characterization data for 7k:** Yellow oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 1.49 (d, 3H, *J* = 6.5 Hz), 2.07 (br, 1H), 4.93 (q, 1H, *J* = 6.5 Hz), 7.24 (dd, 2H, *J* = 6.8, 2.0 Hz), 7.45 (dd, 2H, *J* = 6.8, 1.7 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 25.3, 69.4, 114.0-123.5 (*J*<sub>CF</sub> = 318.8 Hz), 121.3, 127.2, 146.3, 148.6. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -73.0. HR EI-MS: calcd for C<sub>9</sub>H<sub>9</sub>SO<sub>4</sub>F<sub>3</sub>, 270.0174; found 270.0168.

For structural proof **7k** was oxidized to **7h** using PDC (2.5 equiv) in CH<sub>2</sub>Cl<sub>2</sub> at rt for 3 h (87% yield). Characterization data for this product agreed with that which was previously observed.

**4.2.12. Characterization data for 7l:** White solid (mp 32-35 °C). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 1.57 (s, 6H), 7.22 (d, 2H, *J* = 8.9 Hz), 7.56 (d, 2H, *J* = 8.9 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 32.1, 72.6, 112.8-125.5 (*J*<sub>CF</sub> = 318.7 Hz), 121.3, 126.9, 148.6, 150.0. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -72.9. HR EI-MS: calcd for C<sub>10</sub>H<sub>11</sub>SO<sub>4</sub>F<sub>3</sub>, 284.0330; found 284.0363.

### 4.3. Procedure for regeneration and reuse of polymer 5.

The polymeric reagent recovered from the aryl triflate synthesis reactions (a mixture of **5** and **8**) was treated with triflic anhydride (3 equiv) and Et<sub>3</sub>N (3 equiv) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> at -78 °C for 1 h and then warmed to room temperature and stirred for 18 h more. The polymer **5** was filtered and washed as before.

The same sample of **5** was used 4 times to prepare **7h**. For each triflation cycle, the reaction was monitored by TLC analysis and the product was purified and characterized as before.

### 4.4. Use of polymers 9 and 11 for aryl triflate synthesis.

Reagent **9** (2 equiv of -NTf<sub>2</sub>, 3 equiv of -CH<sub>2</sub>NEt<sub>2</sub>) was used in CH<sub>2</sub>Cl<sub>2</sub>, DMF, 1,4-dioxane at rt (70 °C for the later two solvents) for the conversion of **6h** to **7h**. Samples of the reaction solutions were intermittently analyzed by gas chromatography to determine the extent of reaction. After up to 5 d, **7h** was formed in less than 5% yield under all reaction conditions.

Reagent **11** (2 equiv of -NTf<sub>2</sub>, 3 equiv of -CH<sub>2</sub>NEt<sub>2</sub>) was used in CH<sub>2</sub>Cl<sub>2</sub> at rt. After 3 d, analysis by gas



chromatography indicated that **7h** was formed in only 8% yield.

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