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# Non-cross-linked polystyrene-supported triphenylarsonium halides and their use in the arsa-Wittig reaction

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ABSTRACT

Non-cross-linked polystyrene-supported (carbomethoxymethyl)triphenylarsonium bromide (**1**) and benzyltriphenylarsonium iodide (**2**) were synthesized. They showed similar reactivities compared with the free arsonium salts in the arsa-Wittig reaction. The use of the polymer-supported reagents facilitated product purification and rendered the organoarsenic reagents easily separable and recyclable.



## 1. Introduction

Organoarsenic reagents have found various applications in organic synthesis. Triphenylarsine is an important ligand in Pd-mediated transformations.[1] Arsonium ylides[2] have been utilized in cyclopropanations,[3] epoxidations,[4] aziridinations,[5] aldehyde coupling reactions,[6] and the synthesis of vinyl halides[7] and heterocycles.[8] In particular, olefination by the reaction of arsonium ylides with aldehydes,[9] i.e., the arsa-Wittig reaction, offers synthetic advantages over the corresponding phosphonium counterparts (the phospha-Wittig reaction), including milder reaction conditions,[10] higher stereoselectivities[11] and/or yields,[12] and the possibility for catalysis,[13] due to the intrinsically higher nucleophilicity[14] of arsonium ylides.

However, despite the utility of arsines in organic synthesis, most practitioners consider that any advantages are far outweighed by their toxicity by creating problems in the handling, purification and disposal of these reagents. The development of reactions using a catalytic amount of arsine reduces the quantities used and subsequently needed to be separated from the product.[13] The use of polymer[13c,15] or silica[16] supports to immobilize arsenic reagents is another strategy, which provides additional benefits including simplification of reaction workup and product purification.[17] Finally, the ability to isolate and recycle the arsine increases the economy of the reaction and limits the actual amounts of arsines that need to be handled and stocked. In this connection, we have already described a controlled synthesis of non-cross-linked polystyrene (NCPS) triphenylarsine and its application as recyclable ligands in Suzuki[15a] and Stille[15c] coupling reactions.

On the other hand, the use of supported arsines for the synthesis and reactions of immobilized arsonium salts and ylides impart even greater benefits in handling, as stoichiometric amounts of arsines are used in arsa-Wittig reactions. The first examples have been reported by Tao and Hu, who prepared and isolated arsonium salts and ylides from the reaction of polystyrene-supported triphenylarsine and bromoacetophenones.[18] To further exploit the potential of arsonium ylides in organic synthesis but with the additional aims of mitigating the toxicity of arsines, streamlining product isolation, and obviating the problems associated with their disposal, we have synthesized two soluble and recyclable non-cross-linked polystyrene (NCPS) supported arsonium halides, which have been converted to arsonium ylides in situ and shown to undergo the arsa-Wittig reaction in the same pot.

## 2. Results and discussion

### 2.1. Synthesis of NCPS-arsonium halides 1, 2

The NCPS-triphenylarsine (**3**) used had been synthesized from a copolymerization of a 1:8 ratio of diphenylarsinated styrene and styrene and determined to have 0.87 g As/mmol by integration of the $^1$H NMR spectra, according to the methods described in our previous report.[15a] Treatment of **3** with over 20 equiv methyl bromoacetate in THF under reflux resulted in a very low yield of NCPS-(carbomethoxymethyl)triphenylarsonium bromide (**1**). Although

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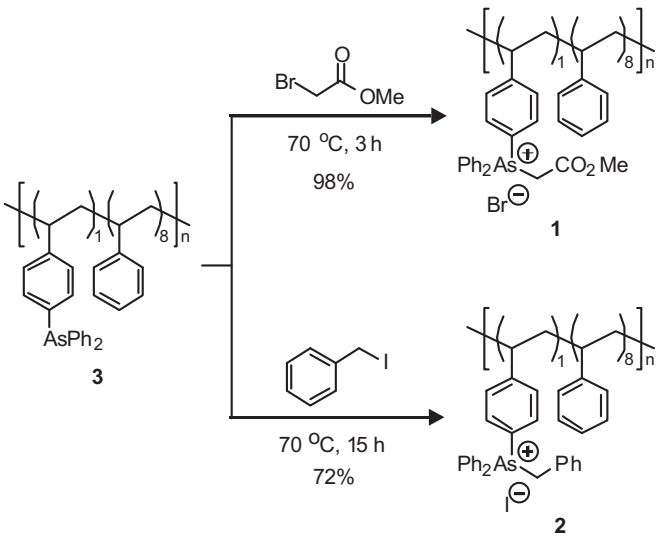
arsonium ylides are more reactive than their corresponding phosphonium counterparts, arsonium salts are more difficult to obtain due to the lower nucleophilicity of arsines.[19] Finally, heating **3** with neat methyl bromoacetate resulted in a homogeneous reaction mixture, and an excellent yield of **1** was obtained after polymer precipitation (Scheme 1).[20]




**Scheme 1.** Synthesis of **1** and **2**.

The degree of alkylation in **1** was determined by $^1$H NMR integration and analysis. The methylene group in free $[MeO_2C\text{-}CH_2AsPh_3]^+Br$ has a signal at 5.41 ppm,[20] and there is a corresponding broad peak at $\delta$ 5.2–5.6 ppm in the $^1$H NMR spectrum of **1**. From the ratio of the integration of the methylene protons to the aromatic protons, the loading of arsonium bromide was determined to be 0.76 mmol/g.[21]

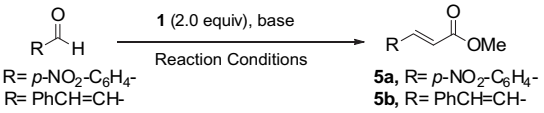
Attempts to synthesize **2** by treating **3** with neat benzyl bromide were unsuccessful, and unreacted **3** was largely recovered. When the more reactive benzyl iodide was used,[22] a good yield of **2** was obtained. As for the analysis of **1**, the loading of arsonium iodide on **2** was determined to be 0.72 mmol/g polymer, based on the integration of the methylene protons of the benzyl group ($\delta$=4.7–5.2 ppm) relative to the aromatic protons.[21]

## 2.2. Optimization of olefination reactions with 1

Previously, Tao and Hu have synthesized several polystyrene-supported aroylmethylarsonium salts and isolated the corresponding ylides. Subsequently aryl aldehydes were subjected to Wittig reactions with these supported-ylides to yield chalcones.[18] Our aim in this project was to generate the ylide from **1** and **2** in situ, to use the ylides directly in a one-pot reaction to streamline the operations of this arsa-Wittig reaction, and to recycle the polymer-supported arsine reagent to furnish a more environmentally and economically benign process overall.

We started our investigation of this one-pot arsa-Wittig reaction with **1** using aldehydes **4a** and **4b** as substrates. $K_2CO_3$ was first tried as base to generate the arsonium ylide from **1**. Although ylide formation and the subsequent Wittig reaction proceeded well, the use of $K_2CO_3$ necessitated an aqueous workup to isolate the product, resulting in additional operations, premature precipitation and a lower recovery of the polymer. On the other hand, $Et_3N$ proved to be equally effective as a base for generating the ylide, and the by-product $[Et_3HN]^+Br^-$ could be removed by filtration instead of by an aqueous workup, which facilitated a full recovery of the polymer after the reaction, as well as a nearly quantitative yield of Wittig product **4a** (Table 1, entry 3). The reaction did not go to completion with less than 2 equiv of **1** (Table 1, entry 1 vs 2). While the generation of the ylide occurred effectively at room temperature, the subsequent Wittig reaction proceeded at room temperature with the reactive aldehyde **4a**, but required higher temperatures when **4b** was substrate (Table 1, entries 2 and 5). Compared with heating, microwave irradiation did not promote the reaction effectively at 100 °C or 150 °C, with some decomposition of **4b** observed under these conditions.[23]

**Table 1**
Optimization of reaction conditions for olefination with **1**




**4a,** R= *p*-$NO_2$-$C_6H_4$-
**4b,** R= PhCH=CH-

**5a,** R= *p*-$NO_2$-$C_6H_4$-
**5b,** R= PhCH=CH-

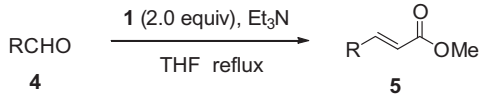
| Entry | RCHO | Base | Reaction conditions | Yield, % |
|---|---|---|---|---|
| 1 | **4a** | $K_2CO_3$ | THF, trace $H_2O$, rt, 2 h[a] | **5a**, 58 |
| 2 | **4a** | $K_2CO_3$ | THF, trace $H_2O$, rt, 15 min | **5a**, 95 |
| 3 | **4a** | $Et_3N$ | THF, rt, 15 min | **5a**, 98 |
| 4 | **4b** | $Et_3N$ | THF, rt, 4 h | **5b**, 69 |
| 5 | **4b** | $Et_3N$ | THF, reflux, 2h | **5b**, 89 |
| 6 | **4b** | $Et_3N$ | THF, reflux, 1 h | **5b**, 81 (10)[b] |
| 7 | **4b** | $Et_3N$ | THF, μW,[c] 25 min | **5b**, 34 (34)[b] |
| 8 | **4b** | $Et_3N$ | DMSO, μW at 150 °C,[c] 25 min | 0 |
| 9 | **4b** | $K_2CO_3$ | THF, trace MeOH, μW at 100 °C,[c] 25 min | 0 (100)[b] |

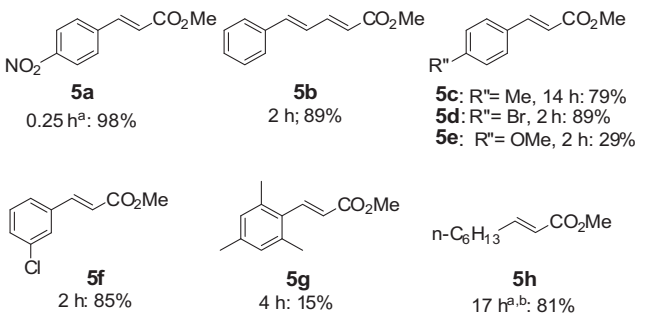
[a] Compound **1** (1.1 equiv) was used.
[b] Recovered **4b**.
[c] μW=250 W.

## 2.3. One-pot ylide generation-arsa-Wittig reactions with 1

The one-pot ylide generation-olefination reactions of various **4** were then investigated (Table 2). Except for **4a** and **4h**, all arsa-Wittig reactions were conducted with **4** in the presence of 2 equiv of **1**, 2 equiv of $Et_3N$, and heated in refluxing THF for the shown reaction times. Good yields of olefins **5** were generally obtained in this one-pot reaction. As expected, the more electrophilic and less sterically demanding aldehydes completed reactions in comparatively less time and with higher yields. The electron-rich anisaldehyde (**4e**), and the sterically hindered mesitaldehyde (**4g**) reacted to give poor yields of the corresponding enoate products **5e** and **5g**. No olefination of cyclopentanone was observed under these reaction conditions.[24]

**Table 2**
Olefinations of **4** with **1**




[a]Reaction at room temperature.
[b]$K_2CO_3$ used as base.

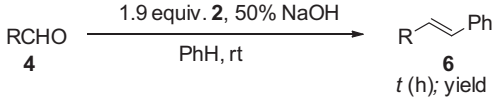
On the other hand, the one-pot reaction with the highly electrophilic **4a** proceeded efficiently even at room temperature. In the case of **4h**, reaction under the typical conditions with $Et_3N$ in refluxing THF yielded about 14% self-aldol as a side-product. However, when the reaction was conducted at room temperature and with $K_2CO_3$ as base, a good yield of **5h** was obtained. The yield of this reaction was comparable to that reported for hexanal, $[MeO_2CCH_2AsPh_3]^+Br^-$, and $K_2CO_3$ (82% yield).[25] Therefore, the reactivity of **1** in ylide formation and in the ensuing arsa-Wittig reaction was similar to that of the free arsonium bromide.

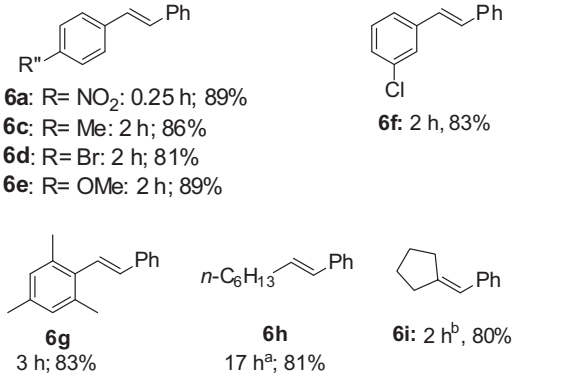
### 2.4. One-pot ylide generation-arsa-Wittig reactions with 2

We next proceeded to study the reactions of **2**, which would typify that of semi-stabilized arsa-Wittig reagents. Reactions of benzyltriphenylarsonium ylides with aldehydes have been reported to yield epoxides and olefins, the latter being favored in non-polar solvents.[26]

Regardless of their electrophilicity, **4** reacted with 1.9–2.0 equiv of **2** in a biphasic reaction in the presence of 50% aqueous NaOH and benzene, to give excellent yields of olefins, with ≤5% of epoxides observed in crude $^1H$ NMR of the product mixture obtained under these conditions (Table 3). Olefination of both the electron-rich **4e** and the sterically demanding **4g** proceeded smoothly to give **6e** and **6g**, respectively. It is noteworthy that *E*-alkenes were exclusively formed in the reactions of all aldehydes, highlighting the stereoselectivity offered by arsoranes, in contrast to the usual formation of a mixture of *E*/*Z* isomers in the phospha-Wittig reaction of semi-stabilized ylides.[27] Whereas the benzylidenation of cyclopentanone by $Ph_3P{=}CHPh$ proceeds poorly, cyclopentanone was effectively olefinated using **2** in 80% yield with heating.

**Table 3**
Benzylidenation of **4** with **2**



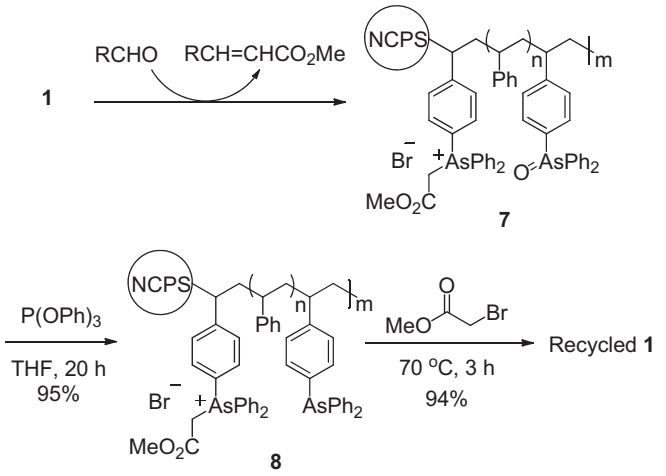

[a] $K_2CO_3$ used as base.
[b] Reaction conducted at 70 °C.

Comparing the results of benzylidenation of **4a**, **4d**, and **4e** using **2** and the corresponding unbound ylide, in which **6a**, **6d**, and **6e** were reported to be obtained in similar yields of 95%, 81% and 91%, respectively,[26] it can be seen that the immobilization of the arsonium salt on the polystyrene support again did not adversely affect its reactivity in this reaction.

In workup of this reaction, after separation of the aqueous phase, the polymer could be obtained by precipitation from the organic layer, with a recovery of about 90%.

### 2.5. Recycling of 1

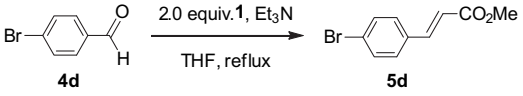
Finally we investigated the feasibility of recycling **1** for reaction. In the arsa-Wittig reaction, after **1** reacts with an aldehyde, the used polymer is represented by **7** in which the arsine residues have undergone reaction have become oxidized (Scheme 2). Polymer **7** was readily isolated as described previously, and was treated with triphenyl phosphite to reduce the arsine oxide back to the arsine.[28] Polymer **8** thus obtained was converted back to **1** by reaction with methyl bromoacetate as in the original preparation of **1** (Scheme 2).




**Scheme 2.** Reconstitution of **1**.

The reactivity of **1** obtained from this protocol was examined over several cycles with aldehyde **4d** (Table 4). Recycled **1** was shown to be efficient for the olefination reaction, albeit there was a slight reduction in the yields. Each reaction was complete in 2 h, and the efficiency of **1** was maintained over at least three subsequent cycles, showing that a sub-stoichiometric use of arsine was possible in a large scale arsa-Wittig reaction by recycling of **1**.

**Table 4**
Efficiency of recycled **1**




| Cycle | Reaction time (h) | Yield, % |
|---|---|---|
| 1 (Freshly prepared) | 2 | 89 |
| 2 | 2 | 79 |
| 3 | 2 | 81 |
| 4 | 2 | 83 |

## 3. Conclusion

From non-cross-linked polystyrene-supported triphenylarsine **3**, we have successfully synthesized two recyclable, NCPS-triphenylarsonium halides, **1** and **2**. Arsa-Wittig reactions using these reagents were executed in one-pot efficiently and with a similar reactivity compared with the free arsonium salts. The arsine residues in **1** and **2** are anchored to the polymer support, thus mitigating the toxicity of the organoarsenic reagents. This streamlines product isolation by using extraction and filtrations, rather than by chromatography as operations, and makes recovery of the arsines practical, preventing the bulk loss of the arsines to the wastes. Finally, **1** was demonstrated to be recyclable, and therefore

a sub-stoichiometric use of arsines in these Wittig reactions is possible by recycling the reagent. These properties and applications of **1**, **2**, and **3** should make reactions involving stoichiometric amounts of arsines more practicable.

## 4. Experimental

### 4.1. General experimental

Benzyl iodide was synthesized according to the literature,[22] and washed with 10% $Na_2S_2O_3$ to remove $I_2$ before use. Other reagents were purchased from Aldrich, Lancaster, Acros or Merck and used without further purification. Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh ASTM). $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard at ambient temperature on Bruker Avance DPX300, AV400 or DRX500 spectrometers, operating at 300 MHz, 400 MHz or 500 MHz for $^1H$ NMR, and 75 MHz, 100 MHz or 125 MHz for $^{13}C$ NMR. IR spectra were recorded on a Bio-Rad FT-IR spectrometer. All products were known compounds, and their spectral properties were identical to those reported in the literature.

### 4.2. Synthesis of 1 and 2

*4.2.1. Synthesis of NCPS-(carbomethoxymethyl)triphenylarsonium bromide (**1**).* NCPS-triphenylarsine (**3**) (2.0 g, 1.7 mmol) was dissolved in 5.0 mL methyl bromoacetate. The reaction mixture was heated in a 70 °C oil bath for 3 h under argon. Excess methyl bromoacetate in the reaction mixture was removed by vacuum distillation until a pale brown residue was left. THF (5.0 mL) was added to dissolve the residue, and this solution was poured into 150 mL hexane for polymer precipitation. The precipitated polymer was collected by suction filtration using filter paper on a Buchner funnel, washed with 3×15 mL hexane, and dried in vacuo over $P_2O_5$ to afford **1** as a white solid (2.243 g, 1.72 mmol, 98%). $^1H$ NMR (300 MHz, $CDCl_3$): 0.82–2.38 (br m, 26H), 3.73–3.95 (br m, 3H), 5.20–5.58 (br m, 2H), 6.20–7.25 (br m, 38.5H), 7.52–7.91 (br m, 14H) ppm; IR ($CHCl_3$): 3063, 3030, 3009, 2958, 2930, 1733, 1602, 1494, 1454, 1441, 1304, 1215, 1085, 845, 782, 767, 754, 732 $cm^{-1}$.

*4.2.2. Synthesis of NCPS-benzyltriphenylarsonium iodide (**2**).* NCPS-triphenylarsine (**3**) (2.0 g, 1.7 mmol) was dissolved in 4.0 mL benzyl iodide.[22] The reaction mixture was heated in a 70 °C oil bath for 15 h under argon. $CH_2Cl_2$ (30 mL) was added to the reaction mixture, and the organics were washed with 3×15 mL 10% aqueous sodium thiosulfate solution. The bulk of the $CH_2Cl_2$ was removed under reduced pressure, and the residue was poured into 150 mL hexane for polymer precipitation. The precipitated polymer was collected by suction filtration using filter paper on a Buchner funnel, washed with 3×15 mL hexane, and dried in vacuo over $P_2O_5$ to afford **2** as a white solid (1.71 g, 1.27 mmol, 72%). $^1H$ NMR (400 MHz, $CDCl_3$): 1.20–2.13 (br m, ~26H) 4.71–5.17 (br m, ~2H), 6.28–7.20 (br m, ~43H), 7.40–7.80 (br m, ~14H) ppm; IR ($CHCl_3$): 3083, 3062, 3029, 3010, 2929, 2852, 1602, 1494, 1454, 1441, 1235, 1220, 1210, 1186, 1084, 909, 825 $cm^{-1}$.

### 4.3. Typical procedure for olefinations of 4 using 1

To a solution of **4b** (0.0283 g, 0.214 mmol) in 2.0 mL THF were added **1** (0.564 g, 0.428 mmol) and $Et_3N$ (0.06 mL, 0.43 mmol). The reaction mixture was heated in a 70 °C oil bath for 2 h. The white solids $[Et_3NH]^+Br^-$ were removed by suction filtration. This filtrate was concentrated and poured into 60 mL of 20% ether/hexane. The precipitated polymer **7** was collected by suction filtration on a Buchner funnel, and washed with 3×10 mL 20% ether/hexane and set aside. The filtrates and washings were combined and concentrated in vacuo, and the residue was purified by silica gel chromatography to afford **5b** (35.8 mg, 0.190 mmol) in 89% yield as a white solid. (*E*)-5-Phenylpenta-2,4-dienoic acid, methyl ester (**5b**):[29] $^1H$ NMR (300 MHz, $CDCl_3$): 3.77 (s, 3H), 6.00 (d, 1H, *J*=15.4 Hz), 6.81–6.94 (m, 2H), 7.27–7.52 (m, 6H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$): 51.7, 121.0, 126.3, 127.3, 128.9, 129.2, 136.1, 140.7, 145.0, 167.6 ppm.

*4.3.1. (E)-3-(4-Nitrophenyl)acrylic acid, methyl ester (**5a**)[30].* Following the typical procedure, but stirring at room temperature for 15 min, the reaction of **4a** (37.8 mg, 0.250 mmol) yielded **5a** (51.3 mg, 0.248 mmol, 98% yield) as a white solid; $^1H$ NMR (400 MHz, $CDCl_3$): 3.83 (s, 3H), 6.56 (d, 1H, *J*=16.1 Hz), 7.66 (d, 2H, *J*=8.7 Hz), 7.71 (d, 1H, *J*=16.1 Hz), 8.24 (d, 2H, *J*=8.8 Hz) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): 52.2, 122.2, 124.3, 128.8, 140.6, 142.0, 148.6, 166.6 ppm.

*4.3.2. (E)-3-(p-Tolyl)acrylic acid methyl ester (**5c**)[31].* Following the typical procedure, the reaction of **4c** (37.5 mg, 0.229 mmol) yielded **5c** (32.0 mg, 0.182 mmol, 79% yield) as a white solid; $^1H$ NMR (300 MHz, $CDCl_3$): 2.37 (s, 3H), 3.80 (s, 3H), 6.40 (d, 1H, *J*=16.0 Hz), 7.19 (d, 2H, *J*=8.0 Hz), 7.42 (d, 2H, *J*=8.1 Hz), 7.67 (d, 1H, *J*=16.0 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$): 21.6, 51.8, 116.9, 128.2, 129.8, 131.8, 140.9, 145.0, 167.8 ppm.

*4.3.3. (E)-3-(4-Bromophenyl)acrylic acid methyl ester (**5d**)[32].* Following the typical procedure, the reaction of **4d** (25.7 mg, 0.194 mmol) yielded **5d** (43 mg, 0.178 mmol, 89%) as a white solid; $^1H$ NMR (300 MHz, $CDCl_3$): 3.80 (s, 3H), 6.42 (d, 1H, *J*=16.0 Hz), 7.37 (d, 2H, *J*=8.5 Hz), 7.51 (d, 2H, *J*=8.5 Hz), 7.61 (d, 1H, *J*=16.0 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$): 52.0, 118.7, 124.7, 129.6, 132.3, 133.4, 143.6, 167.3 ppm.

*4.3.4. (E)-3-(4-Methoxyphenyl)acrylic acid methyl ester (**5e**)[33].* Following the typical procedure, the reaction of **4e** (28.0 mg, 0.205 mmol) yielded **5e** (11.4 mg, 0.059 mmol, 29%) as a white solid; $^1H$ NMR (300 MHz, $CDCl_3$): 3.79 (s, 3H), 3.84 (s, 3H), 6.31 (d, 1H, *J*=16.0 Hz), 6.90 (d, 2H, *J*=8.8 Hz), 7.47 (d, 2H, *J*=8.7 Hz), 7.65 (d, 1H, *J*=16.0 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$): 51.7, 55.5, 114.5, 115.5, 127.3, 129.9, 144.7, 161.6, 167.9 ppm.

*4.3.5. (E)-3-(3-Chlorophenyl)acrylic acid methyl ester (**5f**)[34].* Following the typical procedure, the reaction of **4f** (36.0 mg, 0.256 mmol) yielded **5f** (42.8 mg, 0.218 mmol, 85%) as a white solid; $^1H$ NMR (400 MHz, $CDCl_3$): 3.80 (s, 3H), 6.43 (d, 1H, *J*=16.0 Hz), 7.28–7.40 (m, 3H), 7.41–7.52 (m, 1H), 7.61 (d, 1H, *J*=16.0 Hz) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): 51.9, 119.4, 126.4, 127.9, 130.2, 130.3, 135.0, 136.3, 143.3, 167.1 ppm.

*4.3.6. (E)-3-(2,4,6-Trimethylphenyl)acrylic acid methyl ester (**5g**)[35].* Following the typical procedure, the reaction of **4g** (34.8 mg, 0.235 mmol) yielded **5g** (7.2 mg, 0.035 mmol, 15%) as a white solid; $^1H$ NMR (500 MHz, $CDCl_3$): 2.28 (s, 3H), 2.33 (s, 6H), 3.81 (s, 3H), 6.06 (d, 1H, *J*=16.4 Hz), 6.89 (s, 2H), 7.85 (d, 1H, *J*=16.4 Hz) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): 21.2, 21.2, 51.8, 123.0, 129.3, 131.1, 137.0, 138.5, 143.6, 167.6 ppm.

*4.3.7. (E)-Non-2-enoic acid methyl ester (**5h**)[36].* Following the typical procedure, but using $K_2CO_3$ as base and a solvent mixture of THF (2.0 mL) and water (0.23 mL), the reaction of **4h** (43.5 mg, 0.381 mmol) at room temperature yielded **5i** (52.6 mg, 0.309 mmol, 81%) as a colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): 0.83–0.88 (m, 3H), 1.22–1.45 (m, 8H), 2.14–2.20 (m, 2H), 3.70 (s, 3H), 5.79 (dt, 1H, *J*=15.6, 1.6 Hz), 6.95(dt, 1H, *J*=15.6, 7.0 Hz) ppm;

$^{13}$C NMR (100 MHz, $CDCl_3$): 14.1, 22.6, 28.1, 28.9, 31.7, 32.3, 51.4, 120.9, 149.9, 167.3 ppm.

### 4.4. Typical procedure for olefinations of 4 using 2

*4.4.1. (E)-4-Nitrostilbene (**6a**)*[37]. Polymer **2** (0.54 g, 0.39 mmol) and **4a** (30.2 mg, 0.200 mmol) were dissolved in 2.0 mL benzene. Aqueous 50% NaOH was added and the reaction mixture was stirred at room temperature. After 0.25 h, 10.0 mL benzene was added and the aqueous layer was separated and discarded. The organic layer was washed with 2×10 mL $H_2O$, and concentrated in vacuo. THF (1.0 mL) was added to dissolve the residue, which was then poured into 60 mL of 20% ether/hexane. The polymer was collected by suction filtration on filter paper using a Buchner funnel, and washed with 3×10 mL 20% ether/hexane. The filtrate and washings were combined, concentrated in vacuo, and the residue was purified by silica gel chromatography to afford **6a** as a pale yellow solid (40.1 mg, 0.178 mmol, 89%); $^1$H NMR (500 MHz, $CDCl_3$): 7.15 (d, 1H, $J$=16.3 Hz), 7.25–7.30 (m, 1H), 7.32–7.35 (m, 1H), 7.38–7.42 (m, 2H), 7.55 (d, 2H, $J$=7.3 Hz), 7.64 (d, 2H, $J$=8.8 Hz), 8.21–8.24 (m, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): 124.2, 126.3, 126.9, 127.0, 128.9, 128.9, 133.4, 136.2, 143.9, 146.8 ppm.

*4.4.2. (E)-4-Methylstilbene (**6c**)*[38]. Following the typical procedure, the reaction of **4c** (36.1 mg, 0.300 mmol) yielded **6c** (50.0 mg, 0.257 mmol, 86%) as a white solid; $^1$H NMR (500 MHz, $CDCl_3$): 2.37 (s, 3H), 7.07–7.09 (m, 2H), 7.17 (d, 2H, $J$=8.0 Hz), 7.23–7.25 (m, 1H), 7.33–7.37 (m, 2H), 7.42 (d, 2H, $J$=8.1 Hz), 7.49–7.52 (m, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): 21.4, 126.5, 126.6, 127.5, 127.9, 128.8, 128.8, 129.5, 134.7, 137.7, 137.7 ppm.

*4.4.3. (E)-4-Bromostilbene (**6d**)*[39]. Following the typical procedure, the reaction of **4d** (29.8 mg, 0.161 mmol) yielded **6d** (33.8 mg, 0.130 mmol, 81%) as a white solid; $^1$H NMR (500 MHz, $CDCl_3$): 7.03 (d, 1H, $J$=16.3 Hz), 7.10 (d, 1H, $J$=16.4 Hz), 7.26–7.30 (m, 1H), 7.34–73.39 (m, 4H), 7.46–7.53 (m, 4H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): 121.3, 126.6, 127.4, 127.9, 128.0, 128.8, 129.5, 131.8, 136.3, 137.0 ppm.

*4.4.4. (E)-4-Methoxystilbene (**6e**)*[40]. Following the typical procedure, the reaction of **4e** (39.5 mg, 0.290 mmol) yielded **6e** (54.6 mg, 0.260 mmol, 89%) as a white solid; $^1$H NMR (300 MHz, $CDCl_3$): 3.84 (s, 3H), 6.89–7.11 (m, 4H), 7.20–7.26 (m, 1H), 7.32–7.38 (m, 2H), 7.44–7.51 (m, 4H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): 55.5, 114.3, 126.4, 126.8, 127.4, 127.9, 128.4, 128.8, 130.3, 137.8, 159.4 ppm.

*4.4.5. (E)-3-Chlorostilbene (**6f**)*[41]. Following the typical procedure, the reaction of **4f** (32.8 mg, 0.233 mmol) yielded **6f** (41.7 mg, 0.194 mmol, 83%) as a white solid; $^1$H NMR (300 MHz, $CDCl_3$): 7.03 (d, 1H, $J$=16.3 Hz), 7.12 (d, 1H, $J$=16.3 Hz), 7.20–7.25 (m, 1H), 7.26–7.40 (m, 5H), 7.50–7.53 (m, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): 124.9, 126.5, 126.8, 127.4, 127.6, 128.2, 128.9, 130.0, 130.3, 134.8, 137.0, 139.4 ppm.

*4.4.6. (E)-2,4,6-Trimethylstilbene (**6g**)*[42]. Following the typical procedure, the reaction of **4g** (32.3 mg, 0.218 mmol) yielded **6g** (40.2 mg, 0.181 mmol, 83%) as a white solid; $^1$H NMR (300 MHz, $CDCl_3$): 2.35 (s, 3H), 2.40 (s, 6H), 6.64 (d, 1H, $J$=16.6 Hz), 6.96 (s, 2H), 7.15 (d, 1H, $J$=16.6 Hz), 7.29–7.35 (m, 1H), 7.39–7.44 (m, 2H), 7.55 (d, 2H, $J$=7.4 Hz) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): 21.1, 21.1, 126.4, 127.1, 127.6, 128.8, 128.9, 133.8, 134.1, 136.3, 136.4, 137.9 ppm.

*4.4.7. (E)-Hept-1-enylbenzene (**6h**)*[43]. Following the typical procedure, but using $K_2CO_3$ as base in water, the reaction of **4h** (33.6 mg, 0.294 mmol) yielded **6h** (52.2 mg, 0.277 mmol, 81%) as a colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): 0.88–0.93 (m, 3H), 1.31–1.54 (m, 8H), 2.18–2.26 (m, 2H), 6.24 (dt, 1H, $J$=15.8, 6.8 Hz), 6.39 (d, 1H, $J$=15.9 Hz), 7.16–7.23 (m, 1H), 7.26–7.38 (m, 4H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): 14.3, 22.8, 29.1, 29.5, 31.9, 33.2, 126.1, 126.9, 128.6, 129.8, 131.4, 138.1 ppm.

*4.4.8. Cyclopentylidenemethylbenzene (**6i**)*[44]. Following the typical procedure, but with heating in a 70 °C oil bath, the reaction of **4i** (37.0 mg, 0.440 mmol) yielded **6i** (56.4 mg, 0.356 mmol, 80%) as a colorless oil; $^1$H NMR (500 MHz, $CDCl_3$): 1.63–1.70 (m, 2H), 1.75–1.81 (m, 2H), 2.47–2.51 (m, 2H), 2.53–2.57 (m, 2H), 6.35–6.37 (m, 1H), 7.13–7.17 (m, 1H), 7.29–7.33 (m, 4H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): 25.6, 27.2, 31.2, 36.0, 120.8, 125.6, 127.9, 128.2, 138.9, 147.2 ppm.

### 4.5. Recycling of 1

*4.5.1. Reduction of* **7**. Polymer **7** (1.02 g, ≈0.80 mmol) was dissolved in 4.0 mL THF and treated with triphenyl phosphite (0.4960 g, 1.60 mmol). The reaction mixture was stirred at room temperature for 20 h, then poured into 20% ether/hexane. The precipitated polymer was collected by suction filtration, and washed with 3×15 mL 20% ether/hexane, dried in vacuo over $P_2O_5$ to afford **8** (0.921 g, ≈0.76 mmol, 95%).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## Supplementary data

$^1$H NMR spectra of polymers **1** and **2**, and the calculations of their arsonium salt loadings. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.09.005.

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