

# Triphenylphosphine oxide supported on non-cross-linked maleimide–styrene copolymer: application as a novel Hendrickson reagent

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## Abstract

A new triphenylphosphine oxide reagent linked to a linear maleimide–styrene copolymer is synthesized. This phosphine-bound copolymer is converted to copolymer-supported triphenylphosphine ditriflate as a novel Hendrickson reagent by treatment with triflic anhydride. This reacts rapidly in various dehydration reactions such as anhydride, ester and amide formation. This linear and soluble support is also easily recovered and recycled several times without loss of efficiency.

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The Hendrickson reagent,<sup>1–5</sup> triphenylphosphonium anhydride trifluoromethane sulfonate, is a useful reagent for dehydration reactions such as ester, ether and amide formation in a manner analogous to the Mitsunobu reaction.<sup>6–9</sup> Indeed, an alkoxyphosphonium salt is the key intermediate in both reactions. The Hendrickson reagent has the following advantages over Mitsunobu reagents: (a) the recovered phosphine oxide can be readily recycled by treatment with trifluoromethanesulfonic (triflic) anhydride; (b) the use of azodicarboxylates is not required and (c) the alkylation of the hydrazinedicarboxylate and other side reactions do not occur.

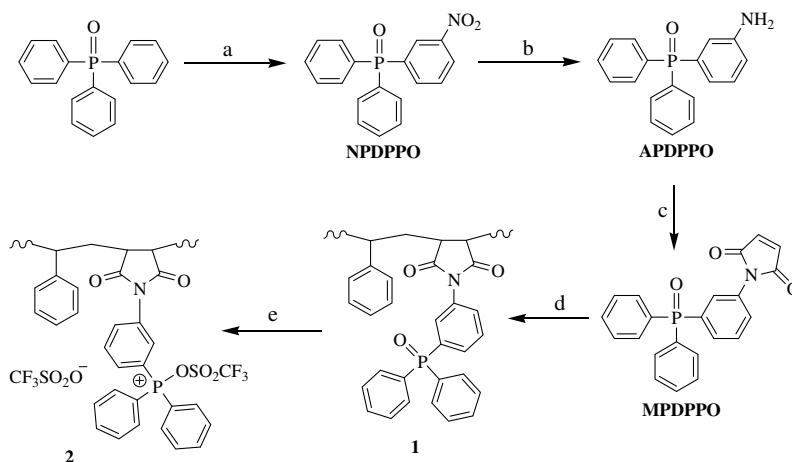
However, one of the main drawbacks of this reagent is the formation of a double stoichiometric amount of triphenylphosphine oxide. Also, the work-up of the reaction is sometimes problematic due to the difficulty in completely removing triphenylphosphine oxide from the reaction mixture.

Thus a method is required, which would allow easy removal of triphenylphosphine oxide. One possible solution is to use a polymer-bound reagent.

The use of polymeric supports in organic synthesis has become a common practice.<sup>10</sup> Insoluble supports such as lightly cross-linked polystyrene have generally been used for this purpose. However, despite the well-known advantages of insoluble supports, there are several shortcomings in the use of these resins because of the heterogeneous nature of the reaction conditions. Several laboratories have explored alternative methods to restore homogeneous reaction conditions resulting from a number of problems associated with insoluble polymer supports, including nonlinear kinetic behavior, unequal distribution and/or access to the chemical reaction, solvation problems associated with the nature of the support and synthetic difficulties in transferring standard organic reactions to the solid phase. Therefore, in recent years, the use of soluble polymer-supported reagents and catalysts has gained significant attention as an alternative to traditional solid-phase synthesis.<sup>11,12</sup>

In this Letter, we report the synthesis and application of triphenylphosphine oxide supported on non-cross-linked

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Scheme 1. Reagents and conditions: (a)  $\text{H}_2\text{SO}_4$ , fuming  $\text{HNO}_3$ ,  $-25\text{ }^\circ\text{C}$ ; (b) hydrazine hydrate, Pd/C; (c) (1) maleic anhydride, acetone,  $0\text{ }^\circ\text{C}$ , Ar, 4 h; (2)  $\text{CH}_3\text{COONa}$ ,  $\text{Ac}_2\text{O}$ ,  $60\text{ }^\circ\text{C}$ , Ar, 6 h; (d) styrene, AIBN,  $60\text{ }^\circ\text{C}$ , Ar; (e)  $(\text{CF}_3\text{SO}_2)_2\text{O}$ , DCM,  $\text{N}_2$ , 0.5 h.

maleimide–styrene copolymer **1** as a novel soluble support (Scheme 1). This copolymer has a reasonably high loading and should allow stoichiometric reactions to take place.

Copolymer **1** was synthesized in four steps from triphenylphosphine oxide.<sup>13</sup> 3-Nitrophenyldiphenylphosphine oxide (NPDPPPO) was synthesized by nitration of triphenylphosphine oxide. A subsequent reduction of NPDPPPO with hydrazine hydrate led to the 3-aminophenyldiphenylphosphine oxide (APDPPPO). In the next step, 3-maleimidophenyldiphenylphosphine oxide (MPDPPPO) was prepared by the reaction of APDPPPO with maleic anhydride. MPDPPPO was readily copolymerized with styrene in the presence of 2,2'-azobisisobutyronitrile (AIBN) as a radical initiator to provide copolymer **1**. Next, the phosphine oxide reagent **1** was treated with triflic anhydride in dry dichloromethane to produce a non-cross-linked polymer-supported triphenylphosphine ditriflate **2**.

It was imperative to employ a small excess of **1** to ensure that all of the triflic anhydride was consumed as excess triflic anhydride could react with the substrate to form its corresponding anhydride. Polymer-supported triphenylphosphine ditriflate **2** was subsequently used in a series of dehydration reactions. Removal of the triphenylphosphine

oxide byproduct was accomplished by a simple precipitation and filtration procedure.<sup>14</sup>

A preparative-scale procedure involved successive addition of 4-nitrobenzyl alcohol, 4-nitrobenzoic acid and diisopropylethylamine to a mixture of **2** in DCM to generate a homogeneous solution. Isolation of the product, 4-nitrobenzyl 4-nitrobenzoate, was accomplished by washing the reaction mixture with sodium hydrogen carbonate to remove the diisopropylethylammonium triflate. The polymeric triphenylphosphine oxide precipitated upon the addition of tetrahydrofuran (THF). Then, the polymer suspension was filtered and the filtrate was concentrated and purified by flash chromatography (1:1, DCM/hexane) to afford the product as a yellow solid in high yield (96%) (Table 1). Also, the  $^{31}\text{P}$  NMR spectrum of the crude product showed no signal, meaning that the polymeric triphenylphosphine oxide was precipitated and removed completely.

Treatment of **2** with 4-nitrobenzoic acid, benzylamine and diisopropylethylamine gave *N*-benzyl 4-nitrobenzamide in 97% yield. The filtered polymeric catalyst could be recovered several times and used without any loss in its reactivity.

Table 1  
Dehydration reactions with phosphine polymer **2**

Entry <sup>a,b</sup>	Substrate	Nucleophile	Product	Yield <sup>c</sup> (%)	Mp $^\circ\text{C}$ (lit. mp $^\circ\text{C}$ )
1	4- $\text{NO}_2$ - $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	4- $\text{NO}_2$ - $\text{C}_6\text{H}_4\text{COOH}$	4-Nitrobenzyl 4-nitrobenzoate	96	167–168 (168) <sup>17</sup>
2	4- $\text{NO}_2$ - $\text{C}_6\text{H}_4\text{COOH}$	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	<i>N</i> -Benzyl 4-nitrobenzamide	97	142 (141–143) <sup>18</sup>
3	4- $\text{CH}_3$ - $\text{C}_6\text{H}_4\text{COOH}$	4- $\text{CH}_3$ - $\text{C}_6\text{H}_4\text{COOH}$	4-Toluic anhydride	94	93–95 (93) <sup>3</sup>
4	4- $\text{Cl}$ - $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	$\text{CH}_3$ - $\text{C}(\text{O})$ -SH	4-Chlorobenzyl thioacetate	92	Oil <sup>5</sup>
5	4- $\text{NO}_2$ - $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	4-MeO- $\text{C}_6\text{H}_4\text{OH}$	<i>o</i> -(4-Nitrobenzyl)-4-methoxyphenol	90	87 (88) <sup>19</sup>
6	<i>meso</i> - $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}(\text{OH})\text{C}_6\text{H}_5$	—	( <i>E</i> )-Stilbene oxide	87	64–65 (65–67) <sup>20</sup>
7	4- $\text{Cl}$ - $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	$\text{NaN}_3$ <sup>c</sup>	4-Chlorobenzyl azide	90	Oil <sup>5</sup>
8	Cyclohexanol	4- $\text{NO}_2$ - $\text{C}_6\text{H}_4\text{COOH}$ <sup>d</sup>	Cyclohexyl 4-nitrobenzoate	83	47–49 (48) <sup>21</sup>

<sup>a</sup> Reaction conditions: **2** (1.35 equiv), triflic anhydride (1.0 equiv), nucleophile (1.0 equiv), diisopropylethylamine (3.5 equiv), DCM (10 mL).

<sup>b</sup> Reaction times: entries 1, 4 (2 h, rt); entries 2, 3, 5–7 (overnight, rt); entry 8 (overnight, reflux).

<sup>c</sup> Added as a 0.5 M solution in DMSO.

<sup>d</sup> Active ester generated using DMAP (1.0 equiv).

<sup>e</sup> Isolated yield.

In a similar fashion, 4-toluic anhydride was formed in high yield (94%), from the reaction of 2 equiv of 4-toluic acid with **2** and diisopropylethylamine in DCM. Treatment of **2** with 4-chlorobenzyl alcohol, thioacetic acid and diisopropylethylamine in DCM produced 4-chlorobenzyl thioacetate, which was purified by flash chromatography (1:1, DCM/hexane). Addition of 4-methoxyphenol and diisopropylethylamine to a mixture of 4-nitrobenzyl alcohol and **2** in DCM gave *o*-(4-nitrobenzyl)-4-methoxyphenol in high yield (90%). In another reaction, (*E*)-stilbene oxide was synthesized by the treatment of **2** with *meso*-hydrobenzoin in the presence of diisopropylethylamine (87% yield). We also synthesized 4-chlorobenzyl azide from its corresponding alcohol (4-chlorobenzyl alcohol) using a 0.5 M solution of NaN<sub>3</sub> in DMSO<sup>15</sup> and diisopropylethylamine, in high yield (90%) (1:1, DCM/hexane).

An additional advantage of polymeric reagent **2** is that after the reaction, it is obtained as a triphenylphosphine oxide copolymer, which is readily reconverted to **2** by treatment with triflic anhydride. The recovered copolymer can be recycled at least four times without the loss of its efficiency.

In conclusion, we have generated a soluble triphenylphosphine oxide supported on non-cross-linked maleimide–styrene copolymer **1** as a stoichiometric reagent for several chemical reactions. Copolymer **1** reacts rapidly with triflic anhydride and produces polymer-supported triphenylphosphine ditriflate **2** as a novel dehydrating reagent.

The use of new polymeric reagent **2** offers considerable advantages over triphenylphosphonium anhydride triflate as the main by-product, triphenylphosphine oxide, remains attached to the polymer-support and is removed by simple filtration after precipitation, so no chromatography is necessary to remove this side-product. Furthermore, an excess of the reagent can be used without subsequent problems during purification. On comparison with the heterogeneous reaction,<sup>16</sup> product yields are equivalent but reaction times are shorter.

We are currently testing copolymer **1** in other phosphine-mediated processes, and the results will be reported in due course.

## Acknowledgement

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## Supplementary data

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3-nitrophenyldiphenylphosphine oxide, 3-aminophenyldiphenylphosphine oxide and 3-maleimidophenyldiphenylphosphine oxide and the <sup>31</sup>P NMR spectrum of polymer-supported triphenylphosphine oxide are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.02.001.

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- Procedure for the synthesis of 3-nitrophenyldiphenylphosphine oxide (NPDPPPO): Triphenylphosphine oxide (27.8 g, 0.1 mol) was charged into a 500 mL round-bottomed flask equipped with an overhead mechanical stirrer and an addition funnel and 100 mL of 98% sulfuric acid was added. The reaction system was cooled to –25 °C. Then a solution of 4.1 mL (0.1 mol) of fuming nitric acid in 25 mL of sulfuric acid was cooled to 0 °C and transferred to the addition funnel. The acid mixture was slowly added dropwise and the bath temperature was maintained at –25 °C. The reaction was allowed to continue for 2 h at –10 °C, 3 h at –5 °C, 3 h at 0 °C and 3 h at room temperature, respectively, once the addition had been completed. The reaction mixture was poured slowly onto ice. The precipitate produced was dissolved in chloroform, washed with aqueous sodium bicarbonate solution and water until the solution turned neutral. The solvent was removed, and the resulting crude product was recrystallized from cyclohexane. 3-Nitrophenyldiphenylphosphine oxide (NPDPPPO) was obtained as white crystals in a yield of 75%, mp = 91 °C. IR (KBr) ( $\nu_{\max}$ , cm<sup>-1</sup>): 879 (C–NO<sub>2</sub>), 1190 (P=O), 1348 and 1523 (Ph–NO<sub>2</sub>) and 1438 (P–Ph). <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta$  7.50 (1H, ddd, <sup>3</sup>J<sub>HH</sub> = 8.2 and 8.1 Hz, <sup>4</sup>J<sub>PH</sub> = 2.9 Hz, CH<sub>meta</sub> to NO<sub>2</sub>), 7.56 (4H, ddd, 4CH<sub>arom,meta</sub> to P=O), 7.64 (2H, ddd, 2CH<sub>arom,para</sub> to P=O), 7.70–7.73 (4H, ddd, 4CH<sub>arom,ortho</sub> to P=O), 8.11–8.15 (1H, dddd, <sup>3</sup>J<sub>PH</sub> = 11.0 Hz, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>4</sup>J<sub>HH</sub> = 1.03 and 1.01 Hz, CH<sub>para</sub> to NO<sub>2</sub>), 8.42–8.44 (1H, ddd, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 and 1.07 Hz, CH<sub>ortho</sub> to NO<sub>2</sub>), 8.50–8.53 (1H, ddd, <sup>3</sup>J<sub>PH</sub> = 11.96 Hz, <sup>4</sup>J<sub>HH</sub> = 1.75 and 1.6 Hz, CH<sub>ortho</sub> to NO<sub>2</sub> and P=O). <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): 127.11–127.20 (1C, d, <sup>3</sup>J<sub>PC</sub> = 11.8 Hz, C<sub>meta</sub> to NO<sub>2</sub>), 128.87–128.97 (1C, d, <sup>2</sup>J<sub>PC</sub> = 12.3 Hz, C<sub>para</sub> to NO<sub>2</sub>), 129.28–129.38 (4C, d, <sup>2</sup>J<sub>PC</sub> = 12.44 Hz, C<sub>arom,ortho</sub> to P=O), 130.25–130.35 (1C, d, <sup>2</sup>J<sub>PC</sub> = 11.94 Hz, C<sub>ortho</sub> to NO<sub>2</sub> and P=O), 131.15–131.99 (2C, d, <sup>1</sup>J<sub>PC</sub> = 105.59 Hz, 2C<sub>ipso</sub>), 132.33–132.35 (1C, d, <sup>4</sup>J<sub>PC</sub> = 2.64 Hz, C<sub>ortho</sub> to NO<sub>2</sub>), 132.40–132.48 (4C, d, <sup>3</sup>J<sub>PC</sub> = 10.18 Hz, C<sub>arom,meta</sub> to P=O), 133.05–133.07 (2C, d, <sup>4</sup>J<sub>PC</sub> = 2.76 Hz, C<sub>arom,para</sub> to P=O), 135.96–136.76 (1C, d, <sup>1</sup>J<sub>PC</sub> = 100.8 Hz, C<sub>ipso</sub>), 138.15–138.22 (1C, d, <sup>3</sup>J<sub>PC</sub> = 9.17 Hz, C–NO<sub>2</sub>).
- Procedure for the synthesis of 3-aminophenyldiphenylphosphine oxide (APDPPPO): NPDPPPO (32.3 g, 0.1 mol) was charged into a 500 mL round-bottomed flask equipped with an addition funnel and a reflux condenser. Ethanol (350 mL) and 1.4 g of palladium on activated carbon (10%) were added. The mixture was warmed to about 50 °C and while being mechanically stirred, a solution of hydrazine hydrate (20.5 mL) in ethanol (20 mL) was added dropwise over 1.5 h while maintaining the temperature at about 50 °C. Then, the reaction mixture was refluxed for 3 h. The completion of the reduction was demonstrated by TLC. The reaction mixture was filtered and the solvent was evaporated. The solid residue was recrystallized from 2-propanol. 3-Aminophenyldiphenylphosphine

oxide (APDPPO) was obtained as white crystals in 87% yield, mp = 166 °C. IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3441 and 3309 (NH<sub>2</sub>), 1436 (P–Ph), 1180 (P=O). <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta$  3.89 (2H, s, NH<sub>2</sub>), 6.82–6.84 (1H, ddd, <sup>3</sup>J<sub>HH</sub> = 8.01 Hz, <sup>4</sup>J<sub>HH</sub> = 1.23 and 1.18 Hz, CH<sub>ortho</sub> to NH<sub>2</sub>), 6.90–6.94 (1H, dddd, <sup>3</sup>J<sub>PH</sub> = 11.85 Hz, <sup>3</sup>J<sub>HH</sub> = 7.54 Hz, <sup>4</sup>J<sub>HH</sub> = 1.01 and 0.98 Hz, CH<sub>para</sub> to NH<sub>2</sub>), 7.06–7.09 (1H, ddd, <sup>3</sup>J<sub>PH</sub> = 13.19 Hz, <sup>4</sup>J<sub>HH</sub> = 1.78 and 1.7 Hz, CH<sub>ortho</sub> to NH<sub>2</sub> and P=O), 7.20–7.22 (1H, ddd, <sup>3</sup>J<sub>HH</sub> = 8.01 and 7.74 Hz, <sup>4</sup>J<sub>PH</sub> = 3.69 Hz, CH<sub>meta</sub> to NH<sub>2</sub>), 7.44–7.48 (4H, ddd, 4CH<sub>arom,meta</sub> to P=O), 7.53–7.55 (2H, ddd, 2CH<sub>arom,para</sub> to P=O), 7.67–7.72 (4H, ddd, 4CH<sub>arom,ortho</sub> to P=O). <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): 118.43–118.52 (1C, d, <sup>3</sup>J<sub>PC</sub> = 10.68 Hz, C<sub>meta</sub> to NH<sub>2</sub>), 118.77–118.79 (1C, d, <sup>4</sup>J<sub>PC</sub> = 2.76 Hz, C<sub>ortho</sub> to NH<sub>2</sub>), 122.22–122.30 (1C, d, <sup>3</sup>J<sub>PC</sub> = 10.06 Hz, C–NH<sub>2</sub>), 128.79–128.88 (4C, d, <sup>2</sup>J<sub>PC</sub> = 12.07 Hz, C<sub>arom,ortho</sub> to P=O), 129.74–129.86 (1C, d, <sup>2</sup>J<sub>PC</sub> = 14.08 Hz, C<sub>para</sub> to NH<sub>2</sub>), 132.23–132.25 (2C, d, <sup>4</sup>J<sub>PC</sub> = 2.64 Hz, C<sub>arom,para</sub> to P=O), 132.48–132.56 (4C, d, <sup>3</sup>J<sub>PC</sub> = 9.93 Hz, C<sub>arom,meta</sub> to P=O), 132.72–133.54 (2C, d, <sup>1</sup>J<sub>PC</sub> = 103.83 Hz, C<sub>ipso</sub>), 133.23–134.05 (1C, d, <sup>1</sup>J<sub>PC</sub> = 103.58 Hz, C<sub>ipso</sub>), 147.13–147.24 (1C, d, <sup>2</sup>J<sub>PC</sub> = 14.2 Hz, C<sub>ortho</sub> to NO<sub>2</sub> and P=O). MS (70 eV):  $m/z$  (%) = 292 (M<sup>+</sup>–1, 35), 277 (100), 214 (5), 199 (22), 183 (21), 167 (4), 152 (14), 77 (24), 65 (5), 51 (16). Procedure for the synthesis of 3-maleimidophenyldiphenylphosphine oxide (MPDPPO): Maleic anhydride (10.8 g) was dissolved in 100 mL of acetone and charged into a 500 mL round-bottomed flask under an argon atmosphere and stirred in an ice bath. A solution of APDPPO (29.3 g, 0.1 mol) in 500 mL of acetone was then added dropwise over 2 h. The reaction solution was stirred in an ice bath for another 5 h. Then, 20.4 mL of acetic anhydride and 2.87 g of sodium acetate were added, the reaction temperature was raised to 60 °C and maintained at this temperature for 6 h. After being cooled to room temperature, the reaction mixture was extracted with chloroform, washed with water until the solution turned neutral, then the solvent was evaporated. The crude product was purified by column chromatography (ethyl acetate) and dried. 3-Maleimidophenyldiphenylphosphine oxide (MPDPPO) was obtained as a yellowish solid in a 79% yield. IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3057 (–C=C–H), 1720 (C=O), 1555, 1480 (–C<sub>6</sub>H<sub>5</sub>), 1433 (P–Ph), 1188 (–P=O), 831 (C=C). <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta$  6.86 (2H, s, CH=), 7.61 (1H, ddd, <sup>3</sup>J<sub>HH</sub> = 8.1 and 8.0 Hz, <sup>4</sup>J<sub>PH</sub> = 3.23 Hz, CH<sub>meta</sub> to N(COCH)<sub>2</sub>), 7.66–7.70 (2H, m, CH<sub>ortho and para</sub> to N(COCH)<sub>2</sub>), 7.76 (1H, ddd, <sup>3</sup>J<sub>PH</sub> = 12.09 Hz, <sup>4</sup>J<sub>HH</sub> = 1.76 and 1.68 Hz, CH<sub>ortho</sub> to NH<sub>2</sub> and N(COCH)<sub>2</sub>), 7.51 (4H, ddd, 4CH<sub>arom,meta</sub> to P=O), 7.58–7.60 (2H, ddd, 2CH<sub>arom,para</sub> to P=O), 7.73 (4H, ddd, 4CH<sub>arom,ortho</sub> to P=O). <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>):  $\delta$  129.02–129.12 (4C, d, <sup>2</sup>J<sub>PC</sub> = 12.19 Hz, C<sub>arom,ortho</sub> to P=O),  $\delta$  129.06–129.15 (1C, d, <sup>2</sup>J<sub>PC</sub> = 11.94 Hz, C<sub>para</sub> to N(COCH)<sub>2</sub>),  $\delta$  129.59–129.61 (1C, d, <sup>4</sup>J<sub>PC</sub> = 2.64 Hz, C<sub>ortho</sub> to N(COCH)<sub>2</sub>), 129.70–129.79 (1C, d, <sup>3</sup>J<sub>PC</sub> = 11.31 Hz, C<sub>meta</sub> to N(COCH)<sub>2</sub>), 130.21–130.30 (1C, d, <sup>2</sup>J<sub>PC</sub> = 12.82 Hz, C<sub>ortho</sub> to N(COCH)<sub>2</sub> and P=O), 131.64–131.72 (1C, d, <sup>3</sup>J<sub>PC</sub> = 9.05 Hz, C–N(COCH)<sub>2</sub>), 131.86–

132.70 (2C, d, <sup>1</sup>J<sub>PC</sub> = 104.83 Hz, C<sub>ipso</sub>), 132.77–133.65 (1C, d, <sup>1</sup>J<sub>PC</sub> = 110.61 Hz, C<sub>ipso</sub>), 132.49–132.57 (4C, d, <sup>3</sup>J<sub>PC</sub> = 10.06 Hz, C<sub>arom,meta</sub> to P=O), 132.61–132.63 (2C, d, <sup>4</sup>J<sub>PC</sub> = 2.64 Hz, C<sub>arom,para</sub> to P=O), 134.72 (2C, s, HC=CH), 169.39 (2C, s, C=O). MS (70 eV):  $m/z$  (%) = 372 (M<sup>+</sup>–1, 33), 344 (7), 277 (100), 199 (39), 183 (32), 152 (22), 77 (40), 51 (26), 43 (22).

Preparation of copolymer 1: Copolymer 1 was prepared by the radical copolymerization of 3-maleimidophenyldiphenylphosphine oxide (MPDPPO) with styrene. The reaction was carried out in a round-bottomed flask at 60 °C in dry dioxane under an argon atmosphere. MPDPPO and styrene monomer were reacted in a 1:1 molar ratio with 2 mol % of AIBN initiator with respect to the combined monomers. The copolymer was obtained by precipitation from *n*-hexane. The resulting copolymer was purified by reprecipitation from dichloromethane into *n*-hexane and dried in vacuo. The composition of the copolymer was calculated from elemental analysis of phosphorus. The percentage of phosphorus content in the copolymer was about 5.6%. IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 1710 (–C=O), 1555, 1483 (–C<sub>6</sub>H<sub>5</sub>), 1433 (P–Ph), 1182 (–P=O). <sup>1</sup>H NMR spectrum of P(MPDPPO/St) exhibited aromatic protons at around 7.0–7.6 ppm in a very broad fashion. <sup>31</sup>P NMR (202.4 MHz, CDCl<sub>3</sub>): 28.50 (1P, s, P=O).

- Representative experimental procedure for the synthesis of 4-nitrobenzyl 4-nitrobenzoate: Triflic anhydride (0.13 mL, 0.75 mmol) was added to a solution of polymer-supported triphenylphosphine oxide 1 (0.55 g, 1 mmol, 1.8 mmol/g) in dry dichloromethane (15 mL) under a nitrogen atmosphere. A brown precipitate was generated immediately, which was stirred for 30 min. It was important to distil the triflic anhydride from a small amount of P<sub>2</sub>O<sub>5</sub> prior to use. 4-Nitrobenzyl alcohol (0.113 g, 0.74 mmol) was added and the solution stirred at room temperature for 30 min. 4-Nitrobenzoic acid (0.124 g, 0.74 mmol) and diisopropylethylamine (0.44 mL) were then added to afford a yellow solution. After stirring for 2 h at room temperature, the mixture was washed with saturated aqueous NaHCO<sub>3</sub> and water. The solution was then poured into THF to precipitate the copolymer. Then, the suspension was filtered and the filtrate was concentrated and purified by flash chromatography (1:1, DCM/hexane) to give the product as a yellow solid in high yield (96%). Mp 167–168 °C (lit.,<sup>17</sup> 168 °C).
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