Optimization of polystyrene-supported triphenylphosphine catalysts for aza-Morita–Baylis–Hillman reactions

Lin-Jing Zhao, a Cathy Kar-Wing Kwong, b Min Shi, a,* and Patrick H. Toy b,*

a School of Chemistry and Pharmaceutics, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People’s Republic of China

b Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, People’s Republic of China

Received 4 May 2005; revised 18 May 2005; accepted 18 May 2005

Available online 17 October 2005

Abstract—A series of polar group functionalized polystyrene-supported phosphine reagents were examined as catalysts in the aza-Morita–Baylis–Hillman reactions of N-tosyl arylimines and a variety of Michael acceptors with the aim of identifying the optimal polymer/solvent combination. For these reactions Janda/Jel-PPh3 (1 mmol PPh3/g loading) resin containing methoxy groups (JJA-OMe-PPh3) on the polystyrene backbone in THF solvent provided the highest yield of all the catalyst/solvent combinations examined. The methyl ether groups were incorporated into JJA-OMe-PPh3 using commercially available 4-methoxystyrene, and thus such polar polystyrene resins are easily accessible and should find utility as nucleophilic catalyst supports.

© 2005 Elsevier Ltd. All rights reserved.

1. Introduction

The Morita–Baylis–Hillman reaction (Scheme 1) is an important tool in organic synthesis that allows for the formation of carbon–carbon bonds in densely functionalized products under mild reaction conditions. While early versions of this reaction were marked by some irreproducible results and long reaction times, recent years have seen much advancement in the understanding of its mechanism and improvements in its efficiency and reliability. Nowadays the use of improved catalysts, including chiral ones, and activated electrophiles have greatly improved the utility and scope of this reaction and variations of it have seen increasing use in the synthesis of complex, biologically active compounds.

In this later report, we examined the relationship between resin loading level and catalyst efficiency and observed that a loading level of 1.5 mmol PPh3/g of resin was optimal. In order to further optimize catalyst efficiency by identifying the optimal polymer backbone, we sought to prepare a series of related polystyrene resins in which the non-phosphine bearing styrene aromatic rings were functionalized with polar groups. Herein we report the preparation of a variety

Keywords: Morita–Baylis–Hillman reaction; Polymer-supported reagents; Triphenylphosphine; Polystyrene.
of such triphenylphosphine resins, 1b–g, examination of their catalytic efficiency in AMBH reactions in a range of solvents and identification of the optimal polystyrene backbone for such catalyst.

2. Results and discussion

Various polar groups have been added to cross-linked polystyrene in order to increase resin polarity and compatibility with polar solvents such as DMF, MeOH and water. One of the most common and successful strategies for this is the introduction of long, polar poly(ethylene glycol) (PEG) grafts onto a polystyrene resin core and a variety of such polymers have been reported.24 Additionally, the use of short PEG chains25 and various ionic moieties26 have been added to polystyrene resins with the aim of increasing resin polarity, with varying degrees of success. Thus, we wanted to determine if adding additional polar functional groups onto the polymer backbone would provide better phosphine catalysts27,28 for AMBH reactions, with the idea of matching the polarity of the resin microenvironment29 with that of the transition states and intermediates of the reaction.

In keeping with our practice of using functional monomers to prepare the flexible cross-linker30 containing Janda/Jel resins,31 we selected styrene monomers 2b–g for incorporation into the new phosphine polymers 1b–g (Scheme 2). These monomers allow for the incorporation of alcohol, ether, ester, and nitrile functional groups. Styrenes 2c,33 and 2d34 were prepared according to literature procedures from 4-vinylbenzyl chloride and 2g was prepared from 2,4-dimethoxybenzaldehyde by a Wittig reaction.35 Monomers 2e and 2f are available commercially, while styryldiphenylphosphine (3)14a and cross-linker 431c were prepared as previously reported from 4-bromostyrene and 4-acetoxystyrene, respectively. With all of the required materials in hand, we prepared resins 1b–g by suspension polymerization (Scheme 2).36,37 The monomers were mixed such that for a 10 g batch of resin, 10 mmol of 3 was used and the balance of the monomer mixture was composed of 2b–g and 2 mol% 4 (Table 1). This was done in order to obtain resins with loading levels of 1.0 mmol PPh₃/g. We chose to use this lower loading for resins 1b–g, compared to a value of 1.5 mmol PPh₃/g for 1a, because this results in resins that contain between 3.3 and 5.4 functionalized styrene units per PPh₃ group and resin 1a has 3.3 styrene groups per PPh₃ group.14a Yields of the resins were good to excellent, and as in previous experiments,14a the observed P content was close to the theoretical value in all cases.

We next screened resins 1b–g as catalysts in the AMBH reaction of 5a with methyl vinyl ketone (6) to form 7 under identical reaction conditions (1.0 equiv 5a, 1.5 equiv 6, 0.1 equiv catalyst, room temperature, 10 h) using various solvents to examine if any catalyst/solvent combination would provide a higher yield than obtained with 1a in THF (91%). The solvents chosen were acetonitrile (ACN), dichloromethane (DCM), DMF, DMSO, THF and toluene and the results of these reactions are summarized in Table 2. The only catalyst that afforded higher yield of 7 than 1a in

![Scheme 2. Synthesis of Janda/Jel-Polar-PPh₃ reagents 1a–g.](image-url)

<table>
<thead>
<tr>
<th>Table 1. Synthesis of resins 1b–g</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Resin</strong></td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>1b</td>
</tr>
<tr>
<td>1c</td>
</tr>
<tr>
<td>1d</td>
</tr>
<tr>
<td>1e</td>
</tr>
<tr>
<td>1f</td>
</tr>
<tr>
<td>1g</td>
</tr>
</tbody>
</table>
all solvents examined except for toluene, in which the yields were almost the same, was methyl ether group function-
alized and the highest obtained yield overall was with this catalyst in THF (97%). It is interesting to note the stark difference in performance between 1c and 1f, considering that they differ only by a methylene group. Resin 1c was less effective as a catalyst than 1f in all solvents except for DMF. Furthermore, the addition of a second methyl ether group, as in 1g, also decreased catalyst efficiency. It also was somewhat surprising that 1b, containing hydrogen bond donating hydroxyl groups, was the worst catalyst screened since such groups could stabilize intermediates of the AMBH reaction.2

In order to interpret the results in Table 2, we examined the swelling of resins 1b–g in the same set of solvents used to perform the reactions, since this factor has been shown by both fluorescence38 and NMR39 spectroscopy to be a key factor in determining substrate accessibility to the interior, and thus the functional groups, of the resins. The swelling data for 1b–g is summarized in Table 3. It is clear that there is a general correlation between the swelling of a resin in a particular solvent and yield obtained with that resin/solvent combination. All resins except 1b swell well in THF and afford high yields of 7 in this solvent. Resin 1b swells poorly in THF and affords the lowest yield of 7 in this solvent. On the other hand, the resins all swell very little or none at all in ACN and this proved to be one of the worst solvents for the reactions. A notable anomaly is the performance of 1d in DMSO. This resin exhibits the highest level of swelling in DMSO, yet affords only a modest yield of 7. Most importantly 1f clearly swells the most in the relatively non-polar solvent examined (DCM, THF and toluene) and affords the highest yields of 7 in them.

Since we previously examined 1a in AMBH reactions of a range of N-tosyl arylimines with only electrophile 6,20 we wanted to see if other Michael acceptors, such as acrolein (8) and phenyl acrylate (10), are also useful in this reaction system. The results of AMBH reactions catalyzed by 1f of 8 and 10 with a variety of electrophiles 5 are summarized in Tables 4 and 5, respectively. Gratifyingly, in reactions of 8 to form 9, complete disappearance of the electrophile 5 was observed within 3 h, except for when an electron-rich dimethylamino functionalized imine was used (Table 4, entry 5). Reactions of 10 catalyzed by 1f were much more sluggish by comparison and thus were allowed to proceed for 36 h. However, reasonable yields of 11 were obtained in all cases despite the long reaction times.

Table 2. Reactions of 5a with 6 using 1a–g as catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>ACN</th>
<th>DCM</th>
<th>DMF</th>
<th>DMSO</th>
<th>THF</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a&lt;sup&gt;b&lt;/sup&gt;</td>
<td>68</td>
<td>73</td>
<td>69</td>
<td>—</td>
<td>91</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>47</td>
<td>30</td>
<td>55</td>
<td>60</td>
<td>51</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>53</td>
<td>67</td>
<td>88</td>
<td>51</td>
<td>95</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>37</td>
<td>54</td>
<td>60</td>
<td>44</td>
<td>90</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>1e</td>
<td>43</td>
<td>53</td>
<td>76</td>
<td>63</td>
<td>96</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>1f</td>
<td>74</td>
<td>88</td>
<td>75</td>
<td>63</td>
<td>97</td>
<td>64</td>
</tr>
<tr>
<td>7</td>
<td>1g</td>
<td>42</td>
<td>55</td>
<td>64</td>
<td>58</td>
<td>92</td>
<td>32</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield.
<sup>b</sup> Results from Ref. 20.

Table 3. Resin swelling in various solvents<sup>a</sup>

<table>
<thead>
<tr>
<th>Resin</th>
<th>ACN</th>
<th>DCM</th>
<th>DMF</th>
<th>DMSO</th>
<th>THF</th>
<th>Toluene</th>
<th>Dry vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.6</td>
<td>6.6</td>
<td>4.4</td>
<td>—</td>
<td>6.2</td>
<td>5.4</td>
<td>1.6</td>
</tr>
<tr>
<td>1b</td>
<td>2.2</td>
<td>3.6</td>
<td>6.7</td>
<td>6.8</td>
<td>5.3</td>
<td>2.3</td>
<td>1.9</td>
</tr>
<tr>
<td>1c</td>
<td>3.1</td>
<td>10.3</td>
<td>7.5</td>
<td>3.9</td>
<td>9.8</td>
<td>9.0</td>
<td>1.8</td>
</tr>
<tr>
<td>1d</td>
<td>3.9</td>
<td>7.6</td>
<td>8.3</td>
<td>8.1</td>
<td>7.3</td>
<td>3.3</td>
<td>1.6</td>
</tr>
<tr>
<td>1e</td>
<td>3.4</td>
<td>8.0</td>
<td>6.4</td>
<td>5.4</td>
<td>6.3</td>
<td>5.3</td>
<td>1.5</td>
</tr>
<tr>
<td>1f</td>
<td>2.4</td>
<td>11.3</td>
<td>7.0</td>
<td>4.2</td>
<td>12.9</td>
<td>12.3</td>
<td>1.7</td>
</tr>
<tr>
<td>1g</td>
<td>2.6</td>
<td>8.4</td>
<td>7.4</td>
<td>4.0</td>
<td>7.8</td>
<td>7.4</td>
<td>1.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> Data is given in mL/g.
<sup>b</sup> Data is taken from Ref. 20.

Table 4. AMBH reaction of 8 catalyzed by 1f

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar–</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph–</td>
<td>3</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>4-Me–C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;–</td>
<td>3</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td>4-Et–C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;–</td>
<td>3</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>4-OMe–C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;–</td>
<td>3</td>
<td>36</td>
</tr>
<tr>
<td>5</td>
<td>4-NMe&lt;sub&gt;2&lt;/sub&gt;–C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;–</td>
<td>24 No reaction</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield of 9 from reaction of 5 (1.0 equiv), 8 (2.0 equiv) and 1f (0.1 equiv).
3. Conclusions

In summary, we have examined a range of polar polystyrene resins as supports for PPPh₃ groups in which the supported phosphine was used as a nucleophilic catalyst in AMBH reactions. To our knowledge, this is the first such comparative study and it was observed that incorporation of 4-methoxyxystrene into the polymer afforded the best support in terms of catalyst efficiency in THF solvent. Thus, resin 1f was found to be the best heterogeneous polymer-supported catalyst examined to date for the prototypical AMBH reaction of 5.

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 N₂ atmosphere. Tetrahydrofuran was distilled under a N₂ atmosphere over sodium and benzophenone. Dichloromethane was distilled under a N₂ 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 F₂₅₄. 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. 4-Vinylbenzyl alcohol (2b). A solution of 4-vinylbenzyl chloride (32.0 g, 213 mmol), sodium acetate (23.0 g, 280 mmol), Bu₄NI (7.9 g, 21.3 mmol) in dry THF (300 mL) was heated to reflux for 48 h. After cooling to room temperature, this was diluted with water (200 mL), extracted with CHCl₃ (3 × 300 mL). The organic layers were dried over Na₂SO₄, filtered and concentrated in vacuo to afford 4-vinylbenzyl acetate as an orange oil (37.1 g, 99%). 1H NMR (CDCl₃, TMS, 300 MHz): δ 5.77 (dd, 1H, J = 17.6, 0.9 Hz), 6.71 (1H, dd, J = 17.6, 10.9 Hz), 7.29 (d, 2H, J = 8.1 Hz), 7.40 (d, 2H, J = 8.1 Hz). 13C NMR (CDCl₃, TMS, 75 MHz): δ 20.71, 65.83, 114.15, 126.26 (2C), 128.37 (2C), 135.44, 136.23, 137.41, 170.52. HR EI-MS: calcd for C₁₁H₁₂O₂, 176.0837; found, 176.0837.

To a EtOH solution (150 mL) of 4-vinylbenzyl acetate (37.1 g, 211 mmol) was added 6 N NaOH (50 mL). The reaction mixture was refluxed for 3 h. After cooling to room temperature, it was diluted with water (200 mL), extracted with CHCl₃ (3 × 300 mL). The organic layers were purified by distillation (100 °C, 20 mmHg) to afford 2b as a colourless liquid (17.0 g, 60%). 1H NMR (CDCl₃, TMS, 400 MHz): δ 4.64 (s, 2H), 5.24 (dd, 1H, J = 10.9, 0.9 Hz), 5.75 (dd, 1H, J = 17.6, 0.9 Hz), 6.71 (1H, dd, J = 17.6, 10.9 Hz), 7.29 (d, 2H, J = 8.1 Hz), 7.39 (d, 2H, J = 8.1 Hz). 13C NMR (CDCl₃, TMS, 75 MHz): δ 65.22, 114.03, 126.54 (2C), 127.36 (2C), 136.61, 137.13, 140.68. HR EI-MS: calcd for C₁₀H₁₀O, 134.0732; found, 134.0732.

4.1.2. 4-Vinylbenzyl methyl ether (2c). To a MeOH solution (100 mL) of 4-vinylbenzyl chloride (10.0 g, 6.6 mmol) sodium methoxide (7.1 g, 13.1 mmol) was added. The reaction mixture was stirred at room temperature for 16 h and then filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (5% EtOAc/hexane) to afford 2c as a colourless liquid (8.8 g, 91%). 1H NMR (CDCl₃, TMS, 300 MHz): δ 3.39 (s, 3H), 4.45 (s, 2H), 5.24 (dd, 1H, J = 10.9, 0.9 Hz), 5.74 (dd, 1H, J = 17.6, 0.9 Hz), 6.71 (1H, dd, J = 17.6, 10.9 Hz), 7.29 (d, 2H, J = 8.1 Hz), 7.39 (d, 2H, J = 8.1 Hz). 13C NMR (CDCl₃, TMS, 75 MHz): δ 58.07, 74.42, 113.80, 126.25 (2C), 127.94 (2C), 136.55, 137.01, 140.79. HR EI-MS: calcd for C₁₀H₁₂O, 148.0888; found, 148.0813.

4.1.3. 4-Vinylphenylacetonitrile (2d). To an anhydrous CH₃CN solution (55 mL) of 18-crown-6 (0.7 g, 2.8 mmol), 4-vinylbenzyl chloride (10.0 g, 70.0 mmol) and powdered KCN (6.4 g, 100 mmol) were added. The reaction mixture was stirred at room temperature for 16 h and then concentrated in vacuo. The residue was diluted with water (100 mL) and extracted with diethyl ether (50 mL), brine (50 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (10% EtOAc/hexane) to afford 2d as a yellow liquid (8.9 g, 95%). 1H NMR (CDCl₃, TMS, 300 MHz): δ 3.34 (s, 2H), 5.29 (dd, 1H, J = 10.9, 0.9 Hz), 5.77 (dd, 1H, J = 17.6, 0.9 Hz), 6.70 (1H, dd, J = 17.6, 10.9 Hz), 7.28 (d, 2H, J = 8.1 Hz), 7.42 (d, 2H, J = 8.1 Hz). 13C NMR (CDCl₃, TMS, 75 MHz): δ 23.72, 114.64, 117.77, 126.81 (2C), 128.59 (2C), 129.18, 135.87, 137.37. HR EI-MS: calcd for C₁₉H₁₆N, 280.0983; found, 280.0985.
4.1.4. 2,4-Dimethoxystyrene (2g). A solution of 2,4-dimethoxybenzaldehyde (10.0 g, 60 mmol), methyltriphenylphosphonium bromide (25.8 g, 72 mmol), K2CO3 (40.0 g, 300 mmol), 18-crown-6 (0.2 g, 0.1 mmol) in dry THF (180 mL) was heated to reflux for 24 h. After cooling to room temperature, it was then filtered through Celite and concentrated in vacuo. The crude product was purified by silica gel chromatography (20% EtOAc/hexane) to afford 2g as a colourless liquid (7.8 g, 78%). 1H NMR (CDCl3, TMS, 400 MHz): δ 3.72 (s, 3H), 3.73 (s, 3H), 5.06 (dd, 1H, J = 11.2, 1.6 Hz), 5.54 (dd, 1H, J = 17.8, 1.6 Hz), 6.35 (d, 1H, J = 2.3 Hz), 6.39 (dd, 1H, J = 8.4, 2.3 Hz), 6.87 (1H, dd, J = 17.8, 11.2 Hz), 7.30 (d, 1H, J = 8.4 Hz). 13C NMR (CDCl3, TMS, 75 MHz): δ 55.34, 55.41, 98.34, 104.68, 112.24, 119.84, 127.23, 131.23, 157.82, 160.55. HR EI-MS: calcd for C10H12O2, 164.0837; found, 164.0836.

4.2. General procedure for Janda/el-Polar-PPh3 synthesis (Procedure A)

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 N2 for 2 h.23 A solution of polar styrene monomer 2a–g, 3 (1.0 mmol/g of total monomer), 4 (2.0 mol%), and AIBN (0.2 g) 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 further washed with THF for one day. The beads were recovered, washed sequentially with methanol, diethyl ether and hexanes, and dried in vacuo. Elemental analysis was used to determine phosphine content, and thus the PPh3 loading level.

4.2.1. Poly(4-styryldiphenylphosphine-co-[4-vinylbenzyl alcohol]-co-1,4-bis[4-vinylphenoxy]butane) (JJ-CH2OH-PPh3, 1b). This was prepared by procedure A using of 2b (7.1 g, 53.0 mmol), 3 (2.9 g, 10.0 mmol), 4 (0.4 g, 1.3 mmol), and AIBN (0.2 g) in chlorobenzene (10 mL) to afford 1b (9.0 g, 90%). Elemental analysis was used to determine the phosphine content (3.1%), and thus a loading level of 1.0 mmol PPh3/g.

4.2.2. Poly(4-styryldiphenylphosphine-co-[4-vinylbenzyl methyl ether]-co-1,4-bis[4-vinylphenoxy]butane) (JJ-CH2OMe-PPh3, 1c). This was prepared by procedure A using of 2c (7.0 g, 46.0 mmol), 3 (2.9 g, 10.0 mmol), 4 (0.4 g, 1.1 mmol), and AIBN (0.2 g) in chlorobenzene (10 mL) to afford 1c (6.9 g, 69%). Elemental analysis was used to determine the phosphine content (3.1%), and thus a loading level of 1.0 mmol PPh3/g.

4.2.3. Poly(4-styryldiphenylphosphine-co-[4-vinylphenylacetonitrile]-co-1,4-bis[4-vinylphenoxy]butane) (JJ-CH2CN-PPh3, 1d). This was prepared by procedure A using of 2d (6.8 g, 42.0 mmol), 3 (2.9 g, 10.0 mmol), 4 (0.3 g, 1.1 mmol), and AIBN (0.2 g) in chlorobenzene (10 mL) to afford 1d (9.3 g, 93%). Elemental analysis was used to determine the phosphine content (3.3%), and thus a loading level of 1.0 mmol PPh3/g.

4.2.4. Poly(4-styryldiphenylphosphine-co-[4-acetoxy-styrene]-co-1,4-bis[4-vinylphenoxy]butane) (JJ-CH2OAc-PPh3, 1e). This was prepared by procedure A using of 2e (6.8 g, 42.0 mmol), 3 (2.9 g, 10.0 mmol), 4 (0.3 g, 1.0 mmol), and AIBN (0.2 g) in chlorobenzene (10 mL) to afford 1e (8.8 g, 88%). Elemental analysis was used to determine the phosphine content (3.0%), and thus a loading level of 1.0 mmol PPh3/g.

4.2.5. Poly(4-styryldiphenylphosphine-co-[4-methoxystyrene]-co-1,4-bis[4-vinylphenoxy]butane) (JJ-(OMe)-PPh3, 1f). This was prepared by procedure A using of 2f (7.1 g, 54.0 mmol), 3 (2.9 g, 10.0 mmol), 4 (0.4 g, 1.2 mmol), and AIBN (0.2 g) in chlorobenzene (10 mL) to afford 1f (9.1 g, 91%). Elemental analysis was used to determine the phosphine content (3.2%), and thus a loading level of 1.0 mmol PPh3/g.

4.2.6. Poly(4-styryldiphenylphosphine-co-[2,4-dimethoxystyrene]-co-1,4-bis[4-vinylphenoxy]butane) (JJ-(OMe)2-PPh3, 1g). This was prepared by procedure A using of 2g (6.8 g, 42.0 mmol), 3 (2.9 g, 10.0 mmol), 4 (0.3 g, 1.0 mmol), and AIBN (0.2 g) in chlorobenzene (10 mL) to afford 1g (8.6 g, 86%). Elemental analysis was used to determine the phosphine content (3.0%), and thus a loading level of 1.0 mmol PPh3/g.

4.3. Resin swelling measurements

The Janda/el-Polar-PPh3 resin (50.0 mg) was placed in a syringe (1 mL) equipped with a polypropylene frit and the dry volume was measured. Solvents were injected into the syringe until resins were soaked thoroughly. After equilibrating for 1 h, the volume of the swollen resin was measured and the measured volume was normalized to mL/g.

4.4. General procedure for the JJ-Polar-PPh3 catalyzed AMBH reactions of N-sulfonated imine (5) with methyl vinyl ketone (6)

The JJ-Polar-PPh3 (0.05 mmol) was added to dry THF (1.0 mL) under an argon atmosphere and the suspension was stirred for 1 h at room temperature (swelling time). At this time, the N-sulfonated imine (5, 0.5 mmol) and 6 (63 μL, 0.75 mmol, 1.5 equiv) were added to the suspension. The reaction mixture was stirred at room temperature for the indicated time or until TLC analysis indicated the disappearance of 5. The reaction mixture was then diluted with CH2Cl2 (7.0 mL) and the catalyst was filtered off and recovered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (25% EtOAc/petroleum ether) to afford the desired product 7. Characterization data for 7 was consistent with the previously reported data.6f

4.5. General procedure for the JJ-OMe-PPh3 (1f) catalyzed AMBH reactions of N-sulfonated imines (5) with acrolein (8)

JJ-OMe-PPh3 (1f, 0.05 mmol) was added to dry THF (1.0 mL) under an argon atmosphere and the suspension was stirred for 1 h at room temperature (swelling time). At this time, the N-sulfonated imine (5, 0.5 mmol) and 8 (67 μL,
56 mg, 1.0 mmol, 2.0 equiv) were added to the suspension. The reaction mixture was stirred at room temperature for the indicated time or until TLC analysis indicated the disappearance of 5. The reaction mixture was then diluted with CH2Cl2 (7.0 mL) and the catalyst was filtered off and recovered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (20% EtOAc/petroleum ether) to afford the desired product 9. Characterization data for these products was consistent with previously reported data.6m

4.6. General procedure for the JJ-OMe-PPh3 (If) catalyzed AMBH reactions of N-sulfonated imines (5) with phenyl acrylate (10)

JJ-OMe-PPh3 (If, 0.05 mmol) was added to dry THF (1.0 mL) under an argon atmosphere and the suspension was stirred for 1 h at room temperature (swelling time). At this time, the N-sulfonated imine 5 (0.5 mmol) and 10 (89 mg, 0.6 mmol, 1.2 equiv) were added to the suspension. The reaction mixture was stirred at room temperature for the indicated time. The reaction mixture was then diluted with CH2Cl2 (7.0 mL) and the catalyst was filtered off and recovered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (12.5% EtOAc/petroleum ether) to afford the desired product 11. Characterization data for these products was consistent with previously reported data.6n

Acknowledgements

This research was supported financially by the University of Hong Kong, the Research Grants Council of the Hong Kong Special Administrative Region, People’s Republic of China (Project No. HKU 7027/03P), the State Key Project of Basic Research (Project 973, no. G2000048007), the Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China (Nos. 20025206, 203900502, and 20272069).

References and notes


19. For an additional report using polymer-supported DMAP that was published concurrently with our report, see: Corma, A.; Garcia, H.; Leyva, A. Chem. Commun. 2003, 2806–2807.
21. JandaJel® is a registered trademark of the Aldrich Chemical Co.
28. For a report of a phosphine functionalized non-cross-linked polystyrene polymer containing tert-butyl groups that has unique solubility properties, see: Bergbreiter, D. E.; Li, C. Org. Lett. 2003, 5, 2445–2447.