

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

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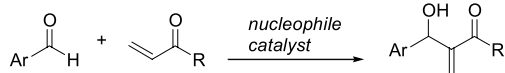
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Abstract—A series of polar group functionalized polystyrene-supported phosphine reagents were examined as catalysts in the aza-Morita–Baylis–Hillman reactions of *N*-tosyl arylimines and a variety of Michael acceptors with the aim of identifying the optimal polymer/solvent combination. For these reactions *JandaJel*-PPh₃ (1 mmol PPh₃/g loading) resin containing methoxy groups (*JJ*-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 *JJ*-OMe-PPh₃ using commercially available 4-methoxystyrene, and thus such polar polystyrene resins are easily accessible and should find utility as nucleophilic catalyst supports.

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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.¹ 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 mechanism² and improvements in its efficiency and reliability. Nowadays the use of improved catalysts,³ 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.⁴



Scheme 1. The Morita–Baylis–Hillman reaction.

We have had a long standing interest in the development of this reaction,⁵ and have reported on the use of not only

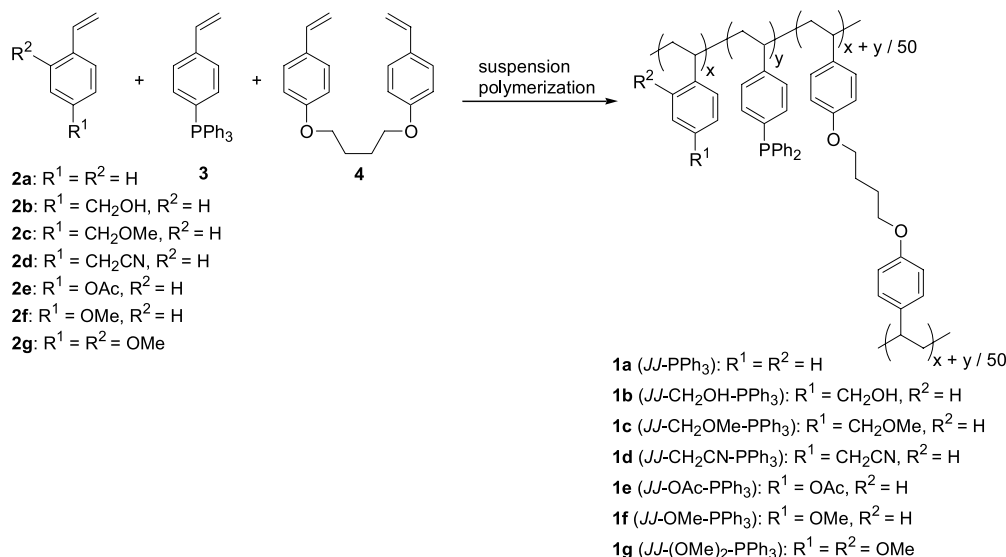
nucleophilic amine Lewis base catalysts, but phosphines as well, in aza-Morita–Baylis–Hillman (AMBH) reactions where the electrophile is a *N*-sulfonated imine rather than a simple, less electrophilic aldehyde.^{6,7} We have examined the scope of this reaction in terms of nucleophiles, electrophiles, and catalysts and have developed convenient methods for the synthesis of a large variety of β -amino carbonyl compounds.

Another area of research interest for us has been the development of polymer-supported reagents^{8,9} for use in solution-phase organic synthesis. We have recently reported both soluble and insoluble amine,¹⁰ arsine,¹¹ ketone,¹² nitroxyl,¹³ phosphine,¹⁴ sulfide,¹⁵ sulfonamide,¹⁶ and sulfoxide¹⁷ reagents that are useful in a wide range of synthetic transformations. In a bridging of our areas of interest, we have examined the use of a soluble poly(ethylene glycol)-supported phosphine,¹⁸ and insoluble polystyrene-supported DMAP^{18,19} and PPh₃ (*JandaJel*-PPh₃, **1a**, Scheme 2)^{20,21} reagents as nucleophilic catalysts in AMBH reactions²² and observed results similar to those obtained using the analogous small molecule catalysts.²³

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

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Scheme 2. Synthesis of Janda/Jel-Polar-PPh₃ reagents **1a–g**.

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 catalysts^{27,28} 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.

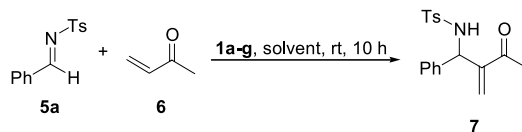
In keeping with our practice of using functional monomers to prepare the flexible cross-linker³⁰ containing Janda/Jel resins,³¹ we selected styrene monomers **2b–g** for incorporation into the new phosphine polymers **1b–g** (Scheme 2). These monomers allow for the incorporation of alcohol, ether, ester, and nitrile functional groups. Styrenes **2b**,³²

2c,³³ and **2d**³⁴ 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 **4**^{31c} 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

Table 1. Synthesis of resins **1b–g**

Resin	2 (mmol)	3 (mmol)	4 (mmol)	Yield (%)	P content (%)	
					Theor	Obsd
1b	53	10	1.3	90	3.10	3.06
1c	46	10	1.1	69	3.10	3.09
1d	42	10	1.0	93	3.10	3.31
1e	42	10	1.0	88	3.10	3.03
1f	54	10	1.2	91	3.10	3.15
1g	42	10	1.0	86	3.10	2.95

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

Entry	Catalyst	Yield (%) ^a					
		ACN	DCM	DMF	DMSO	THF	Toluene
1	1a ^b	68	73	69	—	91	66
2	1b	47	30	55	60	51	34
3	1c	53	67	88	51	95	60
4	1d	37	54	60	44	90	42
5	1e	43	53	76	63	96	35
6	1f	74	88	75	63	97	64
7	1g	42	55	64	58	92	32

^a Isolated yield.^b Results from Ref. 20.**Table 3.** Resin swelling in various solvents^a

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

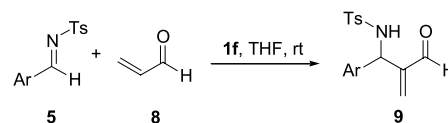
^a Data is given in mL/g.^b Data is taken from Ref. 20.

all solvents examined except for toluene, in which the yields were almost the same, was methyl ether group functionalized **1f** 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 4. AMBH reaction of **8** catalyzed by **1f**

Entry	Ar–	Time (h)	Yield (%) ^a
1	Ph–	3	75
2	4-Me–C ₆ H ₄ –	3	54
3	4-Et–C ₆ H ₄ –	3	75
4	4-MeO–C ₆ H ₄ –	3	36
5	4-NMe ₂ –C ₆ H ₄ –	24	No reaction

^a Isolated yield of **9** from reaction of **5** (1.0 equiv), **8** (2.0 equiv) and **1f** (0.1 equiv).

Table 5. AMBH reaction of **10** catalyzed by **1f**

Entry	Ar–	Yield (%) ^a
1	Ph–	81
2	4-Me–C ₆ H ₄ –	58
3	4-Et–C ₆ H ₄ –	50
4	4-F–C ₆ H ₄ –	63
5	4-Cl–C ₆ H ₄ –	74
6	4-Br–C ₆ H ₄ –	45
7	2,3-Cl ₂ –C ₆ H ₃ –	68
8	4-NO ₂ –C ₆ H ₄ –	67
9	3-NO ₂ –C ₆ H ₄ –	70

^a Isolated yield of **11** from reaction of **5** (1.0 equiv), **10** (1.2 equiv) and **1f** (0.1 equiv).

3. Conclusions

In summary, we have examined a range of polar polystyrene resins as supports for PPh₃ 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-methoxystyrene 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** and **6** to form **7**. Furthermore the scope of the reaction system was extended to the use of acrolein and phenyl acrylate as Michael acceptors with a wide range of *N*-tosyl arylimines. We believe that the enhanced performance of **1f** compared to **1a** is a result of its increased polarity since AMBH reactions are known to involve polar transition states and reaction intermediates.

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 a orange oil (37.1 g, 99%). ¹H NMR (CDCl₃, TMS, 300 MHz): δ 2.09 (s, 3H), 5.08 (s, 2H), 5.26 (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), 7.31 (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 C₉H₁₀O, 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 heated to reflux for 24 h. After cooling to room temperature, it was then filtered and concentrated in vacuo. The crude product was diluted with diethyl ether (100 mL) and then washed with water (3×100 mL). The organic layer was dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (5% EtOAc/hexane) to afford as **2c** 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, 137.79. 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 (100 mL). The organic layer was sequentially washed with water (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 3.74 (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 C₁₀H₉N, 143.0735; found, 143.0735.

4.1.4. 2,4-Dimethoxystyrene (2g). A solution of 2,4-dimethoxybenzaldehyde (10.0 g, 6.0 mmol), methyltriphenylphosphonium bromide (25.8 g, 7.2 mmol), K_2CO_3 (40.0 g, 30.0 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 ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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 $C_{10}H_{12}O_2$, 164.0837; found, 164.0836.

4.2. General procedure for Janda/Jel-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 N_2 for 2 h.³⁷ 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 × 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-acetoxystyrene]-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 **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/Jel-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 μ L, 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 CH_2Cl_2 (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 μ L,

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 (**1f**) catalyzed AMBH reactions of *N*-sulfonated imines (**5**) with phenyl acrylate (**10**)

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 **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.^{6f}

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