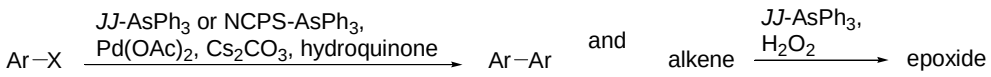
Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

Polystyrene-supported triphenylarsines: useful ligands in palladium-catalyzed aryl halide homocoupling reactions and a catalyst for alkene epoxidation using hydrogen peroxide

Leave this area blank for abstract info.

Helen Song He, Chuanxin Zhang, Chris Ka-Wo Ng and Patrick H. Toy*



Pergamon

TETRAHEDRON

Polystyrene-supported triphenylarsines: useful ligands in palladium-catalyzed aryl halide homocoupling reactions and a catalyst for alkene epoxidation using hydrogen peroxide

Helen Song He, Chuanxin Zhang, Chris Ka-Wo Ng and Patrick H. Toy*

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

Abstract—The utility of both soluble (non-cross-linked) and insoluble (cross-linked) polystyrene-supported triphenylarsine reagents were examined. These reagents were prepared by standard radical polymerization methodology and used in palladium-catalyzed homocoupling reactions of aryl halides. The insoluble reagent was also used as a catalyst precursor in heterogeneous alkene epoxidation reactions in which aqueous hydrogen peroxide was the stoichiometric oxidant. For the aryl halide homocoupling reactions, both reagents worked well and afforded similar results. Unhindered aryl iodides afforded the best yields in the shortest reaction times compared to aryl bromides. The epoxidation reactions of unfunctionalized alkenes were not very efficient. This was probably due to the hydrophobicity of the polystyrene matrix, which did not swell in the reaction medium. Thus, since a microporous, gel-type polystyrene matrix was used, the majority of the arsine groups were inaccessible to the reaction components and therefore incapable of participating in catalysis.

1. Introduction

The use of polymer-supported reagents and catalysts in polymer-assisted solution-phase organic synthesis has become commonplace since they can reduce product purification to simple filtration and concentration operations and are potentially easily recycled.[1] A large variety of such reagents and catalysts have been reported that utilize both insoluble[2] and soluble[3] polymers as their carriers and new ones are continually being developed in order to broaden their utility and increase their efficiency. We have a long-standing interest in the development of both soluble and insoluble polymer-supported amine,[4] fluorinated ketone,[5] nitroxyl radical,[6] phosphine,[7] sulfide,[8] sulfoxide,[9] and triflimide[10] reagents for use in solution-phase organic synthesis, especially in systems that simultaneously use multiple polymers.[4,6,7c] Herein we report an update on the further utilization of our previously reported polystyrene-supported triphenylarsine reagents that were previously found to be useful as ligands for palladium in a variety of Suzuki-Miyaura coupling reactions.[11]

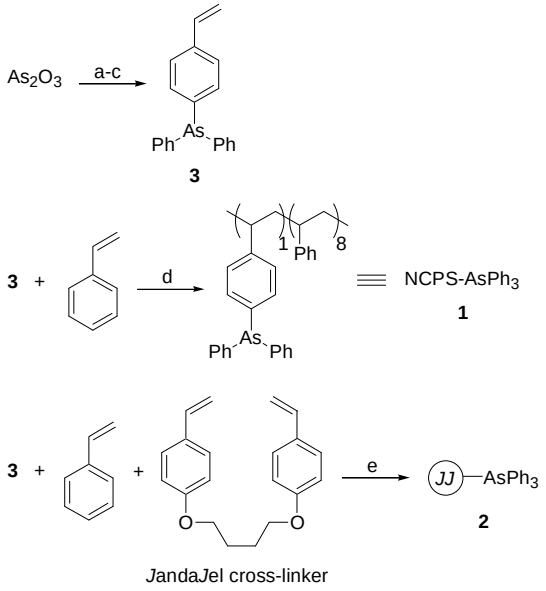
Triphenylarsine is an important reagent in organic synthesis that is complimentary to much more widely used triphenylphosphine.[12] It has been found to be useful as a ligand for palladium in a variety of palladium catalyzed cross-coupling reactions,[13] including the Suzuki-Miyaura coupling[14] of boronic acids with aryl and vinyl halides.[15] Furthermore, triphenylarsine is useful for the generation of arsonium ylides, which are more nucleophilic than the corresponding phosphonium ylides.[16] Due to the toxicity of organoarsenic compounds in general, they are prime candidates for immobilization onto a polymer support so that they can be easily recovered and reused. Indeed, early reports demonstrated that an arsenic acid functionalized polystyrene resin was useful in Baeyer-Villiger oxidation[17] and alkene epoxidation[18] reactions using aqueous hydrogen peroxide under conditions such that the polymers could be recovered and reused. Subsequently, a polystyrene-supported triphenylarsine oxide[19] was found to be an effective reagent for the preparation of carbodiimides.[20] Finally, prior to our recent report, the only other description of a supported arsine showed that a silica-supported alkyldiarylarsine was a good ligand for palladium in Heck coupling reactions.[21] In this current report we describe the

* Corresponding author. Tel.: +852-2859-2167; fax: +852-2857-1586; e-mail: phtoy@hku.hk

application of our soluble and insoluble polystyrene-supported reagents in palladium-catalyzed homocoupling reactions of aryl halides and in organocatalytic alkene epoxidation reactions using aqueous H_2O_2.

2. Results and discussion

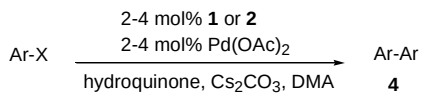
The soluble, non-cross-linked polystyrene reagent, NCPS-$AsPh_3$ (**1**), and the insoluble, cross-linked polystyrene reagent, *J*anda*J*el-$AsPh_3$ (*JJ*-$AsPh_3$, **2**),[22,23] were prepared as previously reported using functional monomer **3** for incorporation of the arsine groups (Scheme 1).[11] The *J*anda*J*el platform was chosen over other cross-linked polymers because it has been shown by EPR,[24] fluorescence,[25] and NMR[26] spectroscopy to provide better performance in terms of reagent/substrate accessibility to interior sites of the resin in solvents that it swells well in. Furthermore it has been used successfully as a synthesis platform in a variety of synthetic applications[27] and as a support for chiral catalysts.[28-31]

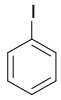
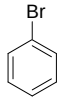
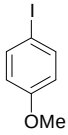
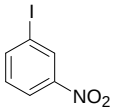
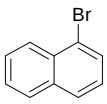
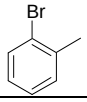


Scheme 1. Reaction conditions: (a) PhMgBr, THF, 0 °C to rt; (b) HCl; (c) *p*-BrMg-$C_6H_4CH{=}CH_2$, THF, 0 °C to rt; (d) AIBN, PhMe, 85 °C; (e) PhCl, H_2O, acacia gum, NaCl, AIBN, 85 °C.

Considering our previous success in using both **1** and **2** in Suzuki-Miyuara coupling reactions, we wanted to examine them in another palladium-catalyzed process. Since symmetrical biaryl compounds can be used to prepare useful chiral phosphine ligands,[32] and new methods for the homocoupling of aromatic compounds are continuously being developed,[33] we chose to study the reaction system reported by Rawal and co-workers in which they used a sterically crowded triarylarsine, tri-*o*-tolylarsine, as a ligand for palladium in the homocoupling of aryl bromides and iodides.[34] Thus, various aryl iodides and aryl bromides were examined in the homocoupling reactions using reagents **1** and **2** as ligands for palladium (Table 1).

Table 1. Homocoupling reactions of aryl halides



Entry	Ar-X	Product	Time (h)[c]	Yield (%)	
				1	**2**
1[a]		**4a**	16	90	88
2[b]		**4a**	40	92	95
3[a]		**4b**	16	80	92
4[a]		**4c**	16	60	74
5[b]		**4d**	60	65	40
6[b]		**4e**	60	21	11

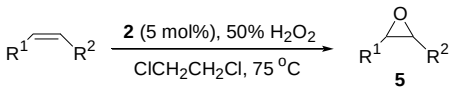
[a] 2 mol% $Pd(OAc)_2$, 2 mol% **1** or **2**, 0.5 equiv. hydroquinone, 1.0 equiv. Cs_2CO_3, 0.4 M, 75 °C; [b] 4 mol% $Pd(OAc)_2$, 4 mol% **1** or **2**, 0.5 equiv. hydroquinone, 1.0 equiv. Cs_2CO_3, 1.0 M, 100 °C; [c] Time for reactions using both **1** and **2**.

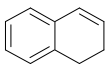
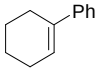
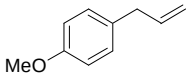
The reactions were performed according to the published procedure,[34] using $Pd(OAc)_2$, ligand, hydroquinone and Cs_2CO_3 in *N.N*-dimethylacetamide (DMA) at elevated temperature. In general aryl iodides reacted more readily than aryl bromides and aryl halides substituted at meta- or para-positions afforded good to excellent yields of the desired symmetrical biaryl compounds **4a-c** (Table 1, entries 1-4). When 1-bromonapthalene was the substrate, only moderate yields of **4d** were obtained after prolonged reaction times (Table 1, entry 5) and 2-bromotoluene afforded poor yield **4e** with both **1** and **2** (Table 1, entry 6). It was found that the product yields obtained from the reactions involving **2** were slightly higher than those with **1** (Table 1, entries 2-4). This was most likely due to the easier removal of **2** from the reaction mixture (filtration) compared to **1** (precipitation followed by filtration). On the other hand, in the cases where low yield was observed, **1** afforded higher yields than **2** (Table 1, entries 5-6), most likely due to its homogeneity.

To investigate other application of reagent **2**, a range of alkenes were studied in epoxidation reactions using H_2O_2

catalyzed by the oxide of **2** (Table 2). It has been previously shown that treatment of triphenylarsine with H_2O_2 affords triphenylarsine oxide, which is a good epoxidation reagent.[35] Thus, by using an excess of H_2O_2, triphenylarsine oxide can function as a catalyst. For the epoxidation reactions with **2**, 1,2-dichloroethane was chosen as solvent since appeared to swell **2** to a large degree and a control reaction in which **2** was omitted afforded only a small amount of the desired product **5a** (Table 2, entry 1). As seen from the Table 2, entry 2, addition of **2** greatly improved the conversion of cyclooctene to **5a**. While good yield can be obtained using **2**, it is a sluggish catalyst precursor compared to other homogeneous, electron-rich arsines.[35] Regardless, good isolated yield of **5b** could also be obtained from the epoxidation of cycloheptene (Table 2, entry 3). Unfortunately the epoxidation of substituted styrenes and a primary alkene afforded poor isolated yields of the desired products (Table 2, entries 4-6). In these reactions, the conversion rate of the alkene was slower than before and the products seemed to be moderately unstable to the reaction conditions since several unidentified, more highly polar products were observed in addition to the desired product.

Table 2. Epoxide reactions of alkenes



Entry	Alkene	Time (h)	Product	Yield (%)[b]
1[a]		8	**5a**	12[c]
2		8	**5a**	85 (98[c])
3		12	**5b**	80 (92[c])
4		24	**5c**	38
5		28	**5d**	47
6		30	**5e**	28

[a] No catalyst **2**. [b] Isolated yield. [c] Determined by GC.

3. Conclusions

In summary, we extended the use of our previously reported soluble and insoluble polystyrene-supported triphenylarsine reagents, **1** and **2** respectively, to the homocoupling of aryl halides to form symmetrical biaryl compounds and in epoxidation reactions using H_2O_2 as the stoichiometric oxidant. It was found that both reagents proved to be good ligands for Pd and the resulting complex showed good catalytic activity in the homocoupling reaction.

The performance of **2** as a catalyst precursor for epoxidation reactions was not very efficient. This could stem from the fact that polystyrene is hydrophobic and thus the H_2O_2 has a difficult time accessing the arsine groups attached to our gel-type, microporous polymer. Thus, only a small portion of the potential catalytic groups are actually active. Due to this limitation of **2**, we are currently examining the immobilization of electron-rich arsine groups to insoluble, hydrophilic and macroporous polymers with the aim of identifying better heterogeneous arsine catalysts for these expodiation reactions.

4. Experimental

4.1. General

All reagents were obtained from the Aldrich, Lancaster or Acros chemical companies and were used without further purification. All moisture sensitive reactions were carried out in dried glassware under a N_2 atmosphere. Merck silica gel 60 (230-400 mesh) was used for chromatography. Thin layer chromatography analysis was performed using glass plates coated with silica gel 60 F_{254}. Gas chromatographic analyses were performed using a Thermo Finnigan Focus chromatograph equipped with an RTX-5 column. 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. MS data was recorded on a Finnigan MAT 96 mass spectrometer.

4.2. General procedure for biaryl synthesis using 1.

To a mixture of aryl halide (1.5 mmol), hydroquinone (0.083 g, 0.75 mmol), and Cs_2CO_3 (0.49 g, 1.5 mmol) was added a pre-stirred DMA solution (3.8 mL or 1.5 mL) of $Pd(OAc)_2$ (0.007 g, 0.03 mmol or 0.013 g, 0.06 mmol) and **1** (0.038 g, 0.03 mmol or 0.076 g, 0.06 mmol, loading = 0.8 $AsPh_3$ mmol/g) in a 8 mL vial. The reaction mixture darkened immediately upon addition of the catalyst solution to the solid reagents. The vial was placed in a shaking reaction block and heated at 75 °C or 100 °C for the indicated time. The reaction mixture was cooled to room temperature, quenched with 1 N HCl (20 mL), diluted with water (20 mL), and extracted with EtOAc (2 × 40 mL). The organic layers were combined and washed sequentially with 10% NaOH (3 × 30 mL), and brine (2 × 30 mL), dried over $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (100% hexane) to afford the desired product.

4.3. General procedure for biaryl synthesis using 2.

To a mixture of aryl halide (1.5 mmol), hydroquinone (0.083 g, 0.8 mmol), and Cs_2CO_3 (0.49 g, 1.5 mmol) was added a pre-stirred DMA solution (3.8 mL or 1.5 mL) of $Pd(OAc)_2$ (0.007 g, 0.03 mmol or 0.013 g, 0.06 mmol) and **2** (0.021 g, 0.03 mmol or 0.042 g, 0.06 mmol, loading =

1.44 $AsPh_3$ mmol/g) in a 8 mL vial. The reaction mixture darkened immediately upon addition of the catalyst solution to the solid reagents. The vial was placed in a shaking reaction block and heated at 75 °C or 100 °C for the indicated time. The reaction mixture was cooled to room temperature and the polymer was filtrated off and washed with water and EtOAc. The filtrate was extracted with EtOAc (2 × 40 mL). The organic layers were combined and washed sequentially with 1 N HCl (3 × 30 mL), 10% NaOH (3 × 30 mL), and brine (2 × 30 mL), dried over $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (100% hexane) to afford the desired product.

4.3.1. Characterization data for Biphenyl (4a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.44 (d, *J* = 6.3 Hz, 4H), 7.58-7.61 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.2 (2C), 127.3 (2C), 128.8 (2C), 141.3 (2C). EI-MS: calcd. for $C_{12}H_{10}$, 154.08; found, 154 (M+).

4.3.2. Characterization data for 4,4'-Dimethoxybiphenyl (4b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 6H), 6.94 (d, *J* = 8.8 Hz, 4H), 7.46 (d, *J* = 8.8, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.4 (2C), 114.2 (4C), 127.8 (4C), 133.5 (2C), 158.7 (2C). HR EI-MS: calcd. for $C_{14}H_{14}O_2$, 214.0994; found, 214.0988.

4.3.3. Characterization data for 3,3'-Dinitrobiphenyl (4c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (t, *J* = 8.0 Hz, 2H), 7.94-7.97 (m, 2H), 8.27 (d, *J* = 1.2 Hz, 2H), 8.48 (t, *J* = 2.0 Hz, 2H). ^{13}C NMR (75 MHz, DMSO) δ 122.3 (2C), 123.7 (2C), 131.2 (2C), 134.2 (2C), 139.9 (2C), 148.9 (2C). HR EI-MS: calcd. for $C_{12}H_8N_2O_4$, 244.0484; found, 244.0489.

4.3.4. Characterization data for 1,1'-Binaphthyl (4d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.47-7.50 (m, 4H), 7.55-7.59 (m, 2H), 7.95 (dd, *J* = 8.1 Hz, 1.3 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.4 (2C), 125.8 (2C), 126.0 (2C), 126.6 (2C), 127.9 (2C), 128.0 (2C), 128.2 (2C), 132.9 (2C), 133.6 (2C), 138.5 (2C). HR EI-MS: calcd. for $C_{20}H_{14}$, 254.1096; found, 254.1086.

4.3.5. Characterization data for 2,2'-Dimethylbiphenyl (4e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 6H), 7.09 (d, *J* = 6.7 Hz, 2H), 7.20-7.26 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8 (2C), 125.5 (2C), 127.1 (2C), 129.3 (2C), 129.8 (2C), 135.8 (2C), 141.6 (2C). HR EI-MS: calcd. for $C_{14}H_{14}$, 182.1096; found, 182.1094.

4.4. General procedure for alkene epoxidation using 2.

A solution of the alkene (1.0 mmol) was added to a mixture of **2** (0.035 g, 0.05 mmol) and 50% H_2O_2 (0.5 mL, 8.7 mmol) in 1,2-dichloroethane (2 mL). The reaction mixture was stirred at 75 ˚C and monitored by TLC and GC analysis. After the complete disappearance of the alkene, the suspension was filtered and the resin was washed by diethyl ether (2 × 10 mL). The combined organic layer was concentrated and the crude residue was filtered through a plug of silica gel with diethyl ether to provide the essentially pure epoxide product after solvent removal. Reactions were also performed where the yields were determined by GC analysis by comparison to an internal standard.

4.4.1. Characterization data for *cis*-cyclooctene epoxide (5a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26-1.63 (m, 10H), 2.12-2.18 (m, 2H), 2.87-2.94 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.5, 26.2, 26.4, 55.5. This data matches that of a commercially available sample.

4.4.2. Characterization data for cycloheptene epoxide (5b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20-1.59 (m, 6H), 1.89-1.94 (m, 4H), 3.08 (t, *J* = 2.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5, 29.0, 31.0, 56.1. EI-MS calcd. for $C_7H_{12}O$, 112.09; found, 112 (M+).

4.4.3. Characterization data for 1,2-dihydronaphthalene epoxide (5c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69-1.80 (m, 1H), 2.36-2.39 (m, 1H), 2.43-2.57 (m, 1H), 2.72-2.79 (m, 1H), 3.71 (t, *J* = 3.1 Hz, 1H), 3.83 (d, *J* = 4.2 Hz, 1H), 7.08 (d, *J* = 7.1 Hz, 1H), 7.19-7.25 (m, 2H), 7.37 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 24.4, 52.8, 55.1, 126.1, 128.4, 129.5, 132.6, 136.7. HR EI-MS: calcd. for $C_{10}H_{10}O$, 146.0732; found, 146.0736.

4.4.4. Characterization data for 1-phenylcyclohexene epoxide (5d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26-1.59 (m, 4H), 1.95-2.00 (m, 2H), 2.12-2.13 (m, 1H), 2.23-2.27 (m, 1H), 3.06 (s, 1H), 7.08-7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, 20.1, 28.9, 60.2, 61.9, 125.3, 127.2, 128.3, 142.5. EI-MS: calcd. for $C_{12}H_{14}O$, 174.10; found, 174 (M+).

4.4.5. Characterization data for 2-(4-methoxybenzyl)-oxirane epoxide (5e): ^{1}H NMR (300 MHz, $CDCl_3$) δ. 2.51 (dd, *J* = 5.0, 2.6 Hz, 1H), 2.73-2.83 (m, 3H), 3.09-3.11 (m, 1H), 3.77 (s, 3H), 6.82-6.87 (m, 2H), 7.15 (dd, *J* = 6.9 Hz, 2.0 Hz, 2H). HR EI-MS: calcd. for $C_{10}H_{12}O_2$, 164.0837; found, 164.0839.

Acknowledgments

This research was supported financially by the University of Hong Kong, and the Research Grants Council of the Hong Kong Special Administrative Region, P. R. of China (Project No. HKU 7112/02P). We thank Prof. Kin Shing Chan (Chinese University of Hong Kong) for helpful discussions.

References

1. (a) Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815-4195. (b) Clapham, B.; Reger, T. S.; Janda, K. D. *Tetrahedron* **2001**, *57*, 4637-4662. (c) Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.* **2003**, *103*, 3401-3429. (d) Bräse, S.; Lauterwasser, F.; Ziegert, R. E. *Adv. Synth. Catal.* **2003**,

345, 869-929. (e) Bhattacharyya, S. *Curr. Opin. Drug Dis. Dev.* **2004**, *7*, 752-764.
2. (a) Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217-3273. (b) McNamara, C. A.; Dixon, M. J.; Bradley, M. *Chem. Rev.* **2002**, *102*, 3275-3299. (c) Fan, Q.-H.; Li, Y.-M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385-3465.
3. (a) Toy, P. H.; Janda, K. D. *Acc. Chem. Res.* **2000**, *33*, 546-554. (b) Dickerson, T. J.; Reed, N. N.; Janda, K. D. *Chem. Rev*. **2002**, *102*, 3325-3343. (c) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345-3383.
4. Toy, P. H.; Reger, T. S.; Janda, K. D. *Org. Lett.* **2000**, *2*, 2205-2207.
5. Kan, J. T. W.; Toy, P. H. *Tetrahedron Lett.* **2004**, *45*, 6357-6359.
6. But, T. Y. S.; Tashino, Y.; Togo, H.; Toy, P. H. *Org. Biomol. Chem.* **2005**, *3*, 970-971.
7. (a) Choi, M. K. W.; He, H. S.; Toy, P. H. *J. Org. Chem.* **2003**, *68*, 9831-9834. (b) Zhao, L.-J.; He, H. S.; Shi, M.; Toy, P. H. *J. Comb. Chem.* **2004**, *6*, 680-683. (c) Harned, A. M.; He, H. S.; Toy, P. H.; Flynn, D. L.; Hanson, P. R. *J. Am. Chem. Soc.* **2005**, *127*, 52-53.
8. Choi, M. K. W.; Toy, P. H. *Tetrahedron* **2004**, *60*, 2875-2879.
9. Choi, M. K. W.; Toy, P. H. *Tetrahedron* **2003**, *59*, 7171-7176.
10. Chung, C. W. Y.; Toy, P. H. *Tetrahedron* **2005**, *61*, 709-715.
11. Lau, K. C. Y.; He, H. S.; Chiu, P.; Toy, P. H. *J. Comb. Chem.* **2004**, *6*, 955-960.
12. Huang, Y.-Z.; Shi, L.-L.; Zhou, Z.-L. Triphenylarsine. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A, Ed.; Wiley: 1995; pp 5339-5342.
13. Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585-9595
14. (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457-2483. (b) Bellina, F.; Carpita, A.; Rossi, R. *Synthesis* **2004**, 2419-2440.
15. (a) Faust, R.; Göbelt, B. *J. Prakt. Chem.* **1998**, *340*, 90-93. (b) Yao, M.-L.; Deng, M.-Z. *J. Org. Chem.* **2000**, *65*, 5034-5036. (c) Bellina, F.; Anselmi, C.; Rossi, R. *Tetrahedron Lett.* **2001**, *42*, 3851-3854. (d) Bellina, F.; Anselmi, C.; Viel, S.; Mannina, L.; Rossi, R. *Tetrahedron* **2001**, *57*, 9997-10007.
16. (a) Huang, Y. Z.; Shen, Y. C. *Adv. Organomet. Chem.* **1982**, *20*, 115-157. (b) Lloyd, D.; Gosney, I.; Ormiston, R. A. *Chem. Soc. Rev.* **1987**, *16*, 45-74. (c) He., H. S.; Chung, C. W. Y.; But, T. Y. S.; Toy, P. H. *Tetrahedron* **2005**, *61*, 1385-1405.
17. Jacobson, S. E.; Mares, F.; Zambri, P. M. *J. Am. Chem. Soc.* **1979**, *101*, 6938-6946.
18. Jacobson, S. E.; Mares, F.; Zambri, P. M. *J. Am. Chem. Soc.* **1979**, *101*, 6946-6950.
19. (a) Smith, C. P.; Temme, G. H. *J. Org. Chem.* **1983**, *48*, 4681-4685. (b) Steiner, U. B.; Caseri, W. R.; Suter, U. W. *Langmuir* **1998**, *14*, 347-351.
20. (a) Lim, A. R.; Kim, J. H.; Novak, B. M. *Polymer* **2000**, *41*, 2431-2438. (b) Lim, A. R.; Chang, J. H.; Kim, J. H.; Novak, B. M. *Solid State Commun.* **2000**, *115*, 23-28.
21. Cai, M. ; Huang, Y.; Zhao, H.; Song, C. *React. Funct. Polym.* **2004**, *59*, 81-86.
22. (a) Toy, P. H.; Janda, K. D. *Tetrahedron Lett.* **1999**, *40*, 6329-6332. (b) Garibay, P.; Toy, P. H.; Hoeg-Jensen, T.; Janda, K. D. *Synlett* **1999**, 1438-1440. (c) Toy, P. H.; Reger, T. S.; Janda, K. D. *Aldrichimica Acta* **2000**, *33*, 87-93. (d) Toy, P. H.; Reger, T. S.; Garibay, P.; Garno, J. C.; Malikayil, J. A.; Liu, G.-Y.; Janda, K. D. *J. Comb. Chem.* **2001**, *3*, 117-124. (e) Choi, M. K. W.; Toy, P. H. *Tetrahedron* **2004**, *60*, 2903-2907.
23. JandaJel® is a registered trademark of the Aldrich Chemical Co.
24. Vaino, A. R.; Goodin, D. B.; Janda, K. D. *J. Comb. Chem.* **2000**, *2*, 330-336.
25. Walsh, D. P.; Pang, C.; Parikh, P. B.; Kim, Y.-S.; Chang, Y.-T. *J. Comb. Chem.* **2002**, *4*, 204-208.
26. Gambs, C.; Dickerson, T. J.; Mahajan, S.; Pasternack, L. B.; Janda, K. D. *J. Org. Chem.* **2003**, *68*, 3673-3678.
27. (a) Lee, S.-H.; Clapham, B.; Koch, G.; Zimmermann, J.; Janda, K. D. *J. Comb. Chem.* **2003**, *5*, 188-196. (b) Fujimori, T.; Wirsching, P.; Janda, K. D. *J. Comb. Chem.* **2003**, *5*, 625-631. (c) Lee, S.-H.; Matsushita, H.; Koch, G.; Zimmermann, J.; Clapham, B.; Janda, K. D. *J. Comb. Chem.* **2004**, *6*, 822-827.
28. (a) Reger, T. S.; Janda, K. D. *J. Am. Chem. Soc.* **2000**, *122*, 6929-6934. (b) Clapham, B.; Cho, C.-W.; Janda, K. D. *J. Org. Chem.* **2001**, *66*, 868-873.
29. (a) Nogami, H.; Matsunaga, S.; Kanai, M.; Shibasaki, M. *Tetrahedron Lett.* **2001**, *42*, 279-283. (b) Takamura, M.; Funabashi, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, *123*, 6801-6808.
30. Selkälä, S. A.; Tois, J.; Pihko, P. M.; Koskinen, A. M. P. *Adv. Synth. Catal.* **2002**, *344*, 941-945.
31. Song, C. E.; Yang, J. W.; Roh, E. J.; Lee, S.-G.; Ahn, J. H.; Han, H. *Angew. Chem. Int. Ed.* **2002**, *41*, 3852-3854.
32. (a) Alexakis, A.; Polet, D.; Rosset, S.; March, S. *J. Org. Chem.* **2004**, *69*, 5660-5667. (b) Alexakis, A.; Polet, D.; Benhaim, C.; Rosset, S. *Tetrahedron: Asymmetry* **2004**, *15*, 2199-2203.
33. (a) Punna, S.; Díaz, D. D.; Finn, M. G. *Synlett* **2004**, 2351-2354. (b) Seganish, W. M.; Mowery, M. E.; Riggleman, S.; DeShong, P. *Tetrahedron* **2005**, *61*, 2117-2121. (c) Nagano, T.; Hayashi, T. *Org. Lett.* **2005**, *7*, 491-493.
34. Hennings, D. D.; Iwama, T.; Rawal, V. H. *Org. Lett.* **1999**, *1*, 1205-1208.
35. van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *Tetrahedron Lett.* **1999**, *40*, 5239-5242.