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Polymer-supported chiral phosphinooxathiane ligands for palladium-catalyzed asymmetric allylations

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Abstract—Novel polymer-supported chiral ligands of PS–DES, PS–Et, and TentaGel supporting Pd-phosphinooxathianes were prepared and found to provide high levels of enantioselectivity (up to 99% ee) in palladium-catalyzed asymmetric allylic alkylations and aminations.

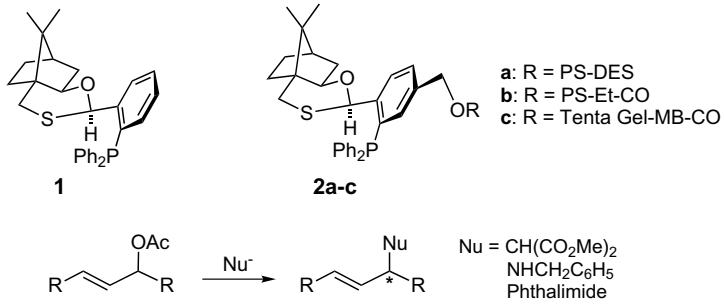
1. Introduction

More applications are being found for enantiomerically pure compounds, for economic, environmental, and social reasons. Of the various methods used to obtain single enantiomers, asymmetric catalytic reactions are amongst the most attractive from the atom-economic point of view.[1] In this field, palladium-catalyzed allylic substitution reactions are effective tools for constructing carbon–carbon and carbon–heteroatom bonds, with several efficient chiral ligands already being explored for these reactions.[2] Recently, we reported that an S–P type, chiral phosphinooxathiane (POT) ligand **1** is an effective ligand for such Pd-catalyzed reactions (Scheme 1).[3] Nevertheless, despite the huge amount of work on homogeneous catalysts in this reaction, the use of heterogeneous catalysts has not been studied extensively.[4] In particular, only a few successful studies of amination have been reported.[5,6] Furthermore, to the best of our knowledge, a polymer-supported S–P type ligand has never been used in this field.

Herein, we report the easily prepared novel S–P type polymer-supported POT ligands **2a**–**c** and apply these ligands to Pd-catalyzed asymmetric alkylations and aminations (Scheme 1). Excellent enantioselectivity (99% ee) was observed in the allylic amination.

2. Results and discussion

The polymer-supported chiral ligands **2a**–**c** were easily synthesized as follows (Scheme 2): Homogeneous POT ligand **5** was prepared from the condensation reaction



Scheme 1.

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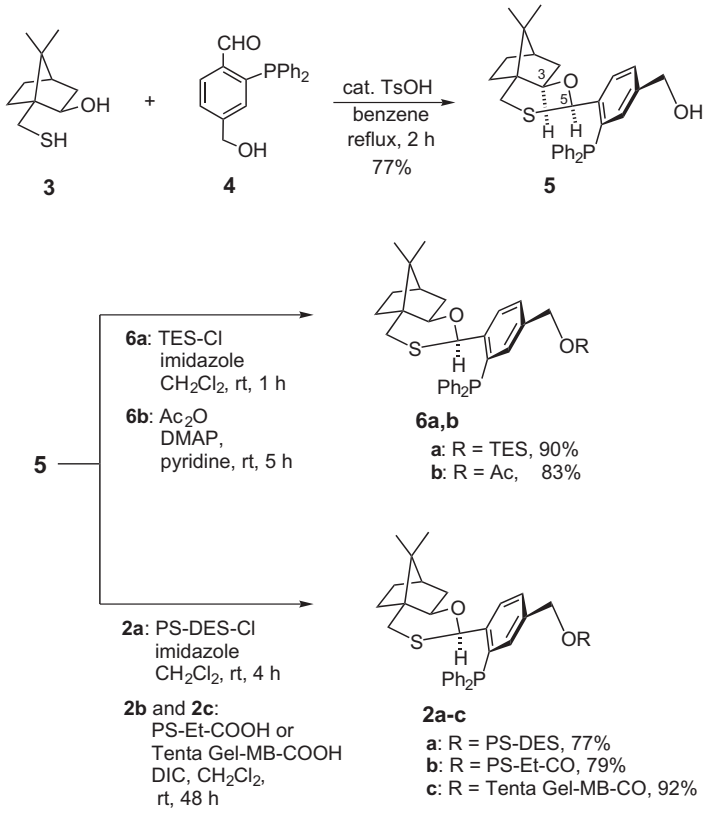


Scheme 2.

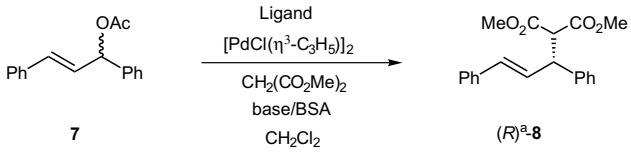
of (*S*)-mercaptoisoborneol **3** with 2-diphenylphosphino-4-hydroxymethylbenzaldehyde **4**[7] in 77% yield. The stereochemical outcome of **5** was determined using NOE difference spectra (NOEDS).[3] NOE enhancement was observed between the hydrogens at the 3- and 5-positions when either the 3- or 5-position was irradiated, respectively.

The resins polystyrene–diethylsilyl (PS–DES), polystyrene–ethyl (PS–Et), and polystyrene–poly(ethyleneglycol–OC_2H_4–NHCO–C_2H_5) (TentaGel) were selected. PS–DES and PS–Et are constituted from styrene and DVB (divinylbenzene) and have good solvent-swollen states in dichloromethane. In contrast, TentaGel is a graft-copolymer of gel-type polystyrene and the catalyst bound to this support behaves like a homogenous catalyst, rather than a heterogeneous one, in a wide range of solvents because of the long, flexible poly(ethyleneglycol) linker. Chiral ligand **5** was linked via ester or ether bonds to PS–DES–Cl resin, PS–Et–COOH resin, or TentaGel–COOH resin. The reaction of ligand **5** with PS–DES–Cl in the presence of imidazole in dichloromethane for 4 h at room temperature gave the desired PS–DES-supported POT ligand **2a** in 77%[8] yield. Furthermore, the reactions of **5** with PS–Et–COOH and TentaGel–COOH in the presence of diisopropylcarbodiimide (DIC) in dichloromethane for 48 h at room temperature gave the desired PS–Et- and TentaGel-supported POT ligands **2b** and **2c** in 79%[8] and 92%[8] yields, respectively. To compare the catalytic efficiency, homogeneous analogues **6a** and **6b** were also prepared by reacting ligand **5** with TES–Cl and Ac_2O, respectively.

The catalytic efficiency of the polymer-supported ligands was examined with the Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate **7** with dimethyl malonate in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and *N*,*O*-bis(trimethylsilyl)acetamide (BSA)[9] to give the allylation product **8** (Table 1). First, the catalytic activities of monomeric chiral ligands **5**, **6a**, and **6b** were tested as a control experiment. The reaction using ligand **5** with a hydroxy group gave product **8** in 76% yield and 93% enantiomeric excess (entry 1). Ligand **6a** with a triethylsilyloxy group and ligand **6b** with an acetoxy group both afforded product **8** in low chemical yields and moderate enantioselectivities (**6a**: 45%, 63% ee, **6b**: 39%, 68% ee, entries 2 and 3, respectively).

With these results in hand, we next investigated the catalytic efficiency of the polymer-supported chiral POT ligands **2a**–**c** (Table 1). The use of PS–DES-supported ligand **2a** gave a poor chemical yield (39%) and a good ee (88% ee, entry 4). Decreasing the temperature to 0 °C improved the enantioselectivity to 96% ee, but gave a poor chemical yield (22%, entry 5). PS–Et-supported ligand **2b** gave a poor chemical yield (20%) and moderate enantioselectivity (60% ee, entry 6). Furthermore, TentaGel-supported ligand **2c** afforded product **8** in poor chemical yield (12%) and enantioselectivity (39% ee, entry 7). This result can be explained based on the steric interaction of the nucleophile and the bulkier π-allyl complex, and the influence of the oxygen functional groups, coordinating to the Pd-moiety in the polymeric backborne on the chiral ligand **2c**. From these results, PS–DES-supported POT ligand **2a** was more effective

Table 1. Asymmetric Pd-catalyzed allylic alkylation of acetate **7**



7 (*R*)[a]-**8**

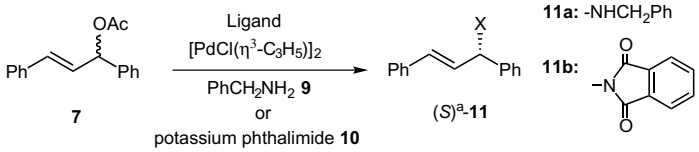
Entry[b]	Ligand	Ligand (mol %)	Temp (°C)	Time (h)	Yield[c] (%)	Ee[d] (%)
1	**5**	5	0	24	76	93
2	**6a**	5	0	24	45	63
3	**6b**	5	0	24	39	68
4	**2a**	5	rt	24	39	88
5	**2a**	5	0	24	22	96
6	**2b**	5	0	24	20	60
7	**2c**	5	0	48	12	39

[a](*R*)-Configurations based on the specific rotation with literature data.[3]
[b] Molar ratio for entries 1–7: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.025 equiv), dimethyl malonate (3 equiv), *N*,*O*-bis-(trimethylsilyl)acetoamide (BSA) (3 equiv), potassium acetate (0.02 equiv).
[c] Isolated yields.
[d] Determined by HPLC analysis using a DAICEL Chiralcel OD-H.

than the PS–Et- or TentaGel-supported POT ligands **2b** and **2c** for this allylic alkylation, and gave a higher enantioselectivity than ligand **5** and the corresponding monomeric **6a**. Although a clear explanation is not available as to why ligand **2a** gave good enantioselectivity, it seems to be dependant on the advantageous steric and electronic interactions of the nucleophile and the π-allyl complex having the bulky polymeric backbone. In addition, low chemical yields (entries 4–6) might be explained by the interfering effects of polymer backbone on ligands **2a** and **2b** to the attack of carbon nucleophile.

Next, we examined the Pd-catalyzed allylic amination of acetate **7** with benzylamine **9** acting as the nucleophile using the PS–DES-supported ligand **2a**, which resulted in an efficient allylic alkylation (Table 2). First, the catalytic activities of the monomeric chiral ligands **5** and **6a** in this reaction were tested as a control experiment. The reaction was carried out in dichloromethane using a catalyst generated by mixing 2.5 mol % $[PdCl(\eta^3\text{-}C_3H_5)]_2$ with 5 mol % chiral ligand **5**, **6a**, and **6b**, respectively, to give the aminated product **11a**. When the reaction was carried out at 0 °C using chiral ligand **5** and 10 equiv of benzylamine **9** with substrate **7**, product **11a** was obtained in good chemical yield (94%) and enantioselectivity (84% ee, entry 1). Furthermore, the use of ligands **6a** and **6b** also gave good enantioselectivities and chemical yields (entry 2: 72%, 83% ee, entry 3: 79%, 87% ee). Next, the catalytic activity of polymer-supported chiral ligand **2a** was examined. The reaction at room temperature afforded an excellent chemical yield (99%) and a moderate ee (68%, entry 4). Conversely, the reaction at 0 °C under the same conditions as entries 1 and 2 using monomers **5** and **6a** gave a good chemical yield (90%) and an excellent enantioselectivity (99% ee, entry 5). However, changing the catalyst

Table 2. Asymmetric Pd-catalyzed allylic amination of acetate **7**



7 (*S*)[a]-**11**

Entry[b]	Nucleophile	Ligand (mol %)	Nucleophile (equiv to **7**)	Temp (°C)	Yield[c] (%)	Ee[d] (%)
1	**9**	**5** (**5**)	10	0	94	84
2	**9**	**6a** (**5**)	10	0	72	83
3	**9**	**6b** (**5**)	10	0	79	87
4	**9**	**2a** (**5**)	10	rt	99	68
5	**9**	**2a** (**5**)	10	0	90	99
6	**9**	**2a** (**2**)	10	0	34	79
7	**9**	**2b** (**5**)	10	0	62	78
8	**9**	**2c** (**5**)	10	0	17	13
9	**10**	**2a** (**5**)	3	rt	44	88
10	**10**	**2a** (**5**)	3	0	35	90

[a]*S*-Configurations based on the specific rotation with literature data.[3]
[b] Molar ratio for entries 1–10: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (entries 1–5, 7–10: 0.025 equiv, entry 6: 0.01 equiv).
[c] Isolated yields.
[d] Determined by HPLC analysis using a DAICEL Chiralcel OD-H column.

loading to 2 mol % led to a substantial decrease in both chemical yield (34%) and enantioselectivity (79% ee, entry 6). The catalytic activities of chiral ligands **2b** and **2c** were also tested in the reaction under the same conditions as entry 5. However, satisfying results were not obtained for chemical yields and enantioselectivities (entry 7: 62%, 78% ee, entry 8: 17%, 13% ee). Furthermore, the same reaction was examined using potassium phthalimide **10** as a bulky, reactive nitrogen nucleophile. The reaction at room temperature gave product **11b** in good enantioselectivity (88% ee), but with a low chemical yield (44%, entry 9). It seems that the low chemical yield was given by the steric interaction of both the bulky nucleophile **10** and the π-allyl complex. Cooling to 0 °C led to a slight decrease in the chemical yield (35%) and a slight increase in enantioselectivity (90% ee, entry 10). From these results, benzylamine **9** is better than potassium phthalimide **10** as a nucleophile for this amination. Furthermore, the polymer-supported POT ligand **2a** showed higher asymmetric catalytic activity than ligand **5** and the corresponding monomeric POT **6a** in terms of the chemical yield and enantioselectivity. For reasons that are unclear, this might be explained based on the strong nucleophilicity of benzylamine **9** overcoming the steric influence of the bulky polymeric backbone of the ligand on nucleophile, and the advantageous steric and electronic interactions of nucleophile and π-allyl complex.

Finally, recycling experiments were examined for the allylic amination with **9** using ligand **2a**. After the first run which gave 90% yield and 99% ee for product **11a**, the mixture was decanted, and the solution of the reactants for the next cycle then added without any further addition of a Pd source. These cycles were carried out three times. Consequently, **2a** was recycled with 89% to 59% yields and 99% ee to 79% ee.

3. Conclusion

In summary, we have easily prepared in two steps a novel class of polymer-supported chiral POT ligands **2a**–**2c** for heterogeneous asymmetric allylic substitution reactions. In particular, the PS–DES-based POT ligand **2a** exhibited excellent activity and enantioselectivity for Pd-catalyzed allylic amination. We found that polymer-supported POT is better than the monomeric POT for giving excellent enantioselectivity. This is the first reported use of a polymer-supported S–P type chiral ligand in a catalytic asymmetric reaction. Studies to optimize the reaction conditions for continuous processing, recycling, and application to other asymmetric reactions are in progress.

4. Experimental

4.1. General

Melting points are uncorrected. IR spectra were recorded as KBr pellets (solids) or thin films (liquids). The ^{1}H and ^{13}C NMR spectra were recorded at 270 and 67.5 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. Mass spectra were obtained by EI. The enantiomeric excesses of the products were determined by chiral HPLC. Optical rotations were recorded at the sodium D line with a polarimeter at room temperature. Commercially available compounds were used without further purification. Solvents were dried according to standard procedures. Chromatography refers to flash chromatography on silica gel (230–400 mesh), unless otherwise noted. PS–DES–Cl,[10] was prepared from the reaction of 1,3-dichloro-5,5′-dimethylhydantoin with diethylsilylbutyl polystyrene (Fluka, 200–400 mesh, 1.5 mmol/g, cross-linked with 1% divinylbenzene), carboxyethylpolystylene (Aldrich, 100–200 mesh, 0.8–1.5 mmol/g, cross-linked with 1% divinylbenzene), and TentaGel MB–COOH (Fluka, 140–170 mm, 0.40 mmol/g) were used. Due to poor resolutions in the ^{13}C NMR of **2a**, **2b**, and **2c**, those carbon signals spectrum were not able to be assigned.

4.2. 2-Diphenylphosphino-4-hydroxymethylbenzaldehyde 4

A solution of 2-bromo-4-hydroxymethylbenzaldehyde (830 mg, 3.86 mmol), diphenylphosphine (0.87 mL, 4.98 mmol), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), and Et_3N (0.69 mL, 4.98 mmol) in toluene (20 mL) was heated under reflux for 24 h. Then the reaction mixture was filtered, and the filtrate washed with saturated NH_4Cl solution and brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed on a column of silica gel with AcOEt–hexane = 1:1 to afford **4** (603 mg, 49%); Yellow solid. Mp 115 °C. IR (KBr) cm^{-1} = 699, 1688, 3451. ^{1}H NMR ($CDCl_3$) δ: 2.13 (1H, br s), 4.58 (2H, s), 6.91 (1H, dd, J = 1.1, 4.7 Hz), 7.24–7.36 (10H, m), 7.50 (1H, d, J = 6.8 Hz), 7.95 (1H, dd, J = 3.7, 7.8 Hz), 10.45 (1H, d, J = 5.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 64.42, 126.93, 128.65, 128.75, 128.86, 129.14, 129.43, 130.97, 131.03, 131.63, 133.85, 134.16, 135.84, 135.98, 137.52, 137.73, 141.22, 141.61, 146.80, 191.34. MS m/z: 320 (M^+); HRMS: calcd for $C_{30}H_{33}O_2PS$ (M^+): 320.0966, found: 320.0955.

4.3. (1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-5-(2-diphenylphosphino-4-hydroxymethyl)-phenyl-4-oxo-6-thiatricyclo undecane 5

A solution of (1*S*)-(−)-10-mercaptoisoborneol **3** (99 mg, 0.53 mmol), 2-diphenylphosphino-4-hydroxymethylbenzaldehyde **4** (170 mg, 0.53 mmol), and *p*-TsOH·H_2O (9 mg, 0.05 mmol) in benzene (20 mL) was heated under reflux for 2 h. Then the solvent was evaporated under reduced pressure. The residue was chromatographed on a column of silica gel with AcOEt–hexane = 1:1 to afford **5** (200 mg, 77%); White solid. Mp 65 °C. $[\alpha]_D^{23} = -63.8$ (c 2.13, $CHCl_3$). IR (KBr) cm^{-1} = 694, 746, 1722, 2952, 3401. ^{1}H NMR ($CDCl_3$) δ: 0.87–0.93 (4H, m), 0.98–1.04 (1H, m), 1.42–1.49 (4H, m), 1.60 (1H, dd, J = 7.9, 13.5 Hz), 1.64–1.72 (2H, m), 1.84–1.90 (2H, m), 2.70 (1H, d, J = 14.1 Hz), 3.18 (1H, d, J = 14.4 Hz), 3.57 (1H, dd, J = 3.1, 7.9 Hz), 4.45 (2H,

s), 6.37 (1H, d, $J = 7.8$ Hz), 6.89 (1H, dd, $J = 1.6$, 4.3 Hz), 7.26–7.32 (10H, m), 7.37 (1H, dd, $J = 1.7$, 8.1 Hz), 7.71 (1H, dd, $J = 4.1$, 8.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 20.45, 23.39, 27.25, 29.95, 34.29, 37.85, 41.81, 45.53, 46.74, 64.83, 80.94, 85.62, 127.68, 128.25, 128.38, 128.45, 128.56, 128.71, 131.98, 133.54, 133.91, 134.19, 134.34, 136.35, 136.45, 136.90, 141.06, 141.07, 143.40, 143.64. ^{31}P NMR (CD_3COCD_3) δ: −17.63 (s). MS *m/z*: 488 (M^+); HRMS: calcd for $C_{30}H_{33}O_2PS$ (M^+): 488.1939, found: 488.1929.

4.4. (1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-5-(2-diphenylphosphino-4-triethylsilyloxy-methyl)phenyl-4-oxo-6-thiatricyclo undecane 6a

To a solution of **5** (65 mg, 0.13 mmol) and imidazole (18 mg, 0.27 mmol) in CH_2Cl_2 (5 mL) was added TES–Cl (0.05 mL, 0.27 mmol) at rt. The reaction mixture was stirred at rt for 1 h. Then the reaction mixture was quenched with H_2O, extracted twice with ether, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed on a column of silica gel with AcOEt–hexane = 1:10 to afford **6a** (72 mg, 90%); Colorless oil. $[\alpha]_D^{21} = -84.8$ (*c* 1.05, $CHCl_3$). IR (film) cm^{-1} = 759, 1216, 3019. ^{1}H NMR ($CDCl_3$) δ: 0.48 (6H, q, $J = 8.0$ Hz), 0.84 (9H, t, $J = 7.9$ Hz), 0.91 (3H, s), 0.94–1.05 (2H, m), 1.43–1.56 (4H, m), 1.59–1.69 (3H, m), 1.84–1.89 (1H, m), 2.70 (1H, d, $J = 14.2$ Hz), 3.19 (1H, d, $J = 14.2$ Hz), 3.59 (1H, dd, $J = 2.9$, 7.8 Hz), 4.56 (2H, s), 6.38 (1H, d, $J = 7.7$ Hz), 6.94 (1H, d, $J = 3.0$ Hz), 7.26–7.32 (11H, m), 7.67 (1H, dd, $J = 4.3$, 7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 4.42, 5.39, 5.81, 6.59, 6.74, 7.29, 20.47, 23.41, 27.28, 29.98, 34.33, 37.88, 41.84, 45.58, 46.78, 65.00, 81.00, 85.65, 127.28, 127.44, 127.75, 128.36, 128.43, 128.51, 128.64, 131.35, 132.05, 134.56, 133.74, 133.86, 134.19, 136.43, 136.78, 141.27, 142.86, 143.63. MS *m/z*: 602 (M^+); HRMS: calcd for $C_{36}H_{47}O_2PSSi$ (M^+): 602.2803, found: 602.2789.

4.5. (1*R*,3*R*,5*R*,8*S*)-5-(4-Acetoxymethyl-2-diphenylphosphino)phenyl-11,11-dimethyl-4-oxo-6-thiatricyclo undecane 6b

To a solution of **5** (50 mg, 0.10 mmol) and Et_3N (0.03 mL, 0.20 mmol) in CH_2Cl_2 (5 mL) was added Ac_2O (0.01 mL, 0.15 mmol) at rt. The reaction mixture was stirred for 5 h at rt. The mixture was quenched with H_2O and extracted twice with $CHCl_3$. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed on a column of silica gel with AcOEt–hexane = 1:10 to afford **6b** (45 mg, 83%); Colorless oil. $[\alpha]_D^{20} = -73.0$ (*c* 1.00, $CHCl_3$). IR (film) cm^{-1} = 756, 1216, 1249, 1733, 3021. ^{1}H NMR ($CDCl_3$) δ: 0.86–0.88 (1H, m), 0.92 (3H, s), 0.95–1.06 (1H, m), 1.42 (1H, s), 1.45 (3H, s), 1.59–1.72 (3H, m), 1.83–1.89 (1H, m), 1.97 (3H, s), 2.71 (1H, d, $J = 14.2$ Hz), 3.18 (1H, d, $J = 14.2$ Hz), 3.55 (1H, dd, $J = 3.0$, 8.0 Hz), 4.93 (2H, s), 6.34 (1H, d, $J = 7.3$ Hz), 6.84 (1H, dd, $J = 1.5$, 4.3 Hz), 7.27–7.37 (10H, m), 7.47–7.57 (1H, m), 7.71 (1H, dd, $J = 4.2$, 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 20.42, 23.36, 27.23, 29.69, 29.95, 34.29, 37.23, 41.83, 45.54, 46.74, 65.59, 81.35, 85.38, 127.67, 128.39, 128.49, 128.54, 128.62, 128.78, 128.88, 131.98, 132.12, 132.74, 133.43, 133.72, 133.84, 134.12, 134.43, 136.18, 143.72, 144.67, 17.60. MS *m/z*: 530 (M^+); HRMS: calcd for $C_{32}H_{35}O_2PS$ (M^+): 530.2045, found: 530.2072.

4.6. PS–DES-supported ligand 2a

A mixture of **5** (103 mg, 0.21 mmol), chlorodiethylsilyl polystyrene (PS–DES–Cl, 100 mg, 0.14 mmol), and imidazole (33 mg, 0.49 mmol) in CH_2Cl_2 (1 mL) was stirred at rt for 4 h. The reaction mixture was filtered and the polymer washed with $CHCl_3$, MeOH, acetone, and ether. The polymer was dried under reduced pressure to give **2a** (130 mg, 77%, 43% conversion, 0.47 mmol/g of ligand in polymer). ^{31}P NMR (CD_3COCD_3) δ: −17.64 (s).

4.7. PS–Et-supported ligand 2b

A mixture of **5** (112 mg, 0.23 mmol), carboxyethylpolystyrene (PS–Et–COOH, 100 mg, 0.12 mmol), and diisopropylcarbodiimide (DIC, 0.04 mL, 0.23 mmol) in CH_2Cl_2 (2 mL) was stirred at rt for 48 h. The reaction mixture was filtered and the polymer washed with $CHCl_3$, MeOH, acetone, and ether. The polymer was dried under reduced pressure to give **2b** (124 mg, 79%, 43% conversion, 0.40 mmol/g of ligand in polymer). ^{31}P NMR (CD_3COCD_3) δ: −18.05 (s).

4.8. TentaGel-supported ligand 2c

A mixture of **5** (30 mg, 0.06 mmol), TentaGel MB–COOH (100 mg, 0.04 mmol), and DIC (0.01 mL, 0.8 mmol) in CH_2Cl_2 (2 mL) was stirred at rt for 48 h. The reaction mixture was filtered and the polymer washed with $CHCl_3$, MeOH, acetone, and ether. The polymer was dried under reduced pressure to give **2c** (107 mg, 92%, 36% conversion, 0.13 mmol/g of ligand in polymer). ^{31}P NMR (CD_3COCD_3) δ: −17.93 (s).

4.9. General procedure for the Pd-catalyzed allylic alkylation using polymer-supported ligand

A mixture of polymer-supported ligand (0.01 mmol, 5 mol %), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2 mg, 0.005 mmol, 2.5 mol %), 1,3-diphenyl-2-propenyl acetate **7** (50 mg, 0.2 mmol), and KOAc (0.4 mg, 0.004 mmol, 2 mol %) in CH_2Cl_2 (1 mL) was stirred for 1 h at rt under argon. To this mixture at the desired reaction temperature was added dimethyl malonate (0.07 mL, 0.59 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (0.15 mL, 0.59 mmol). After 24 h, the reaction mixture was quenched with saturated NH_4Cl solution and filtered. The filtrate was extracted twice with ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by preparative TLC (hexane–AcOEt = 2:1) to afford **8**.

4.10. General procedure for the Pd-catalyzed allylic amination using polymer-supported ligand

A mixture of polymer-supported ligand (0.01 mmol, 5 mol %), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2 mg, 0.005 mmol,

2.5 mol %), and **7** (50 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) was stirred for 1 h at rt under argon. To this mixture at the desired reaction temperature was added benzylamine **9** (0.22 mL, 1.98 mmol) or potassium phthalimide **10** (110 mg, 0.60 mmol). After 24 h, the reaction mixture was quenched with saturated NH_4Cl solution and filtered. The filtrate was extracted twice with ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by preparative TLC (hexane–AcOEt = 2:1) to afford **11**.

4.11. Recycling experiments with polymer-supported POT ligand 2a

After reaction, the mixture was decanted off by using a cannula, and the solution of the reactants added to the polymer-supported **2a** for the next cycles. This procedure was recycled three times.

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