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POLYMER-SUPPORTED PHOSPHINOOXATHIANE AS LIGANDS FOR PALLADIUM-CATALYZED ASYMMETRIC ALLYLATIONS

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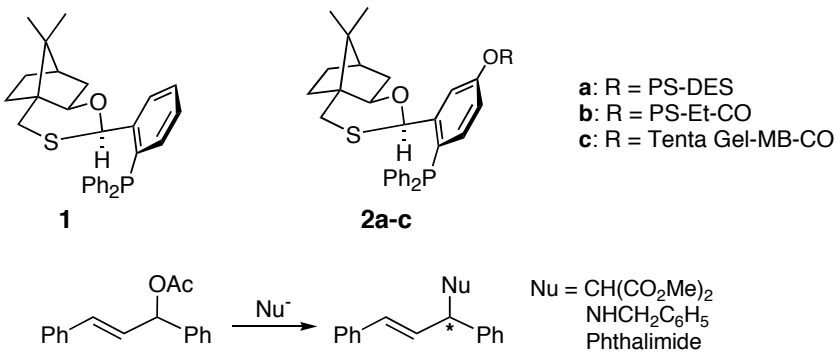
Abstract – New polymer-supported chiral ligands, PS-DES, PS-Et, and TentaGel supporting phosphinooxathianes were prepared and used in palladium-catalyzed asymmetric allylic alkylation and amination.

INTRODUCTION

More applications are being found for optically pure compounds, for economic, environmental, and social reasons. Of the various methods used to obtain single enantiomers, an asymmetric catalytic reaction is one of the most attractive from the atom-economic point of view.[1] In this field, palladium (Pd)-catalyzed allylic substitution reactions are effective tools for constructing carbon-carbon and carbon-heteroatom bonds, and several efficient chiral ligands have been explored for these reactions.[2] Recently, we reported



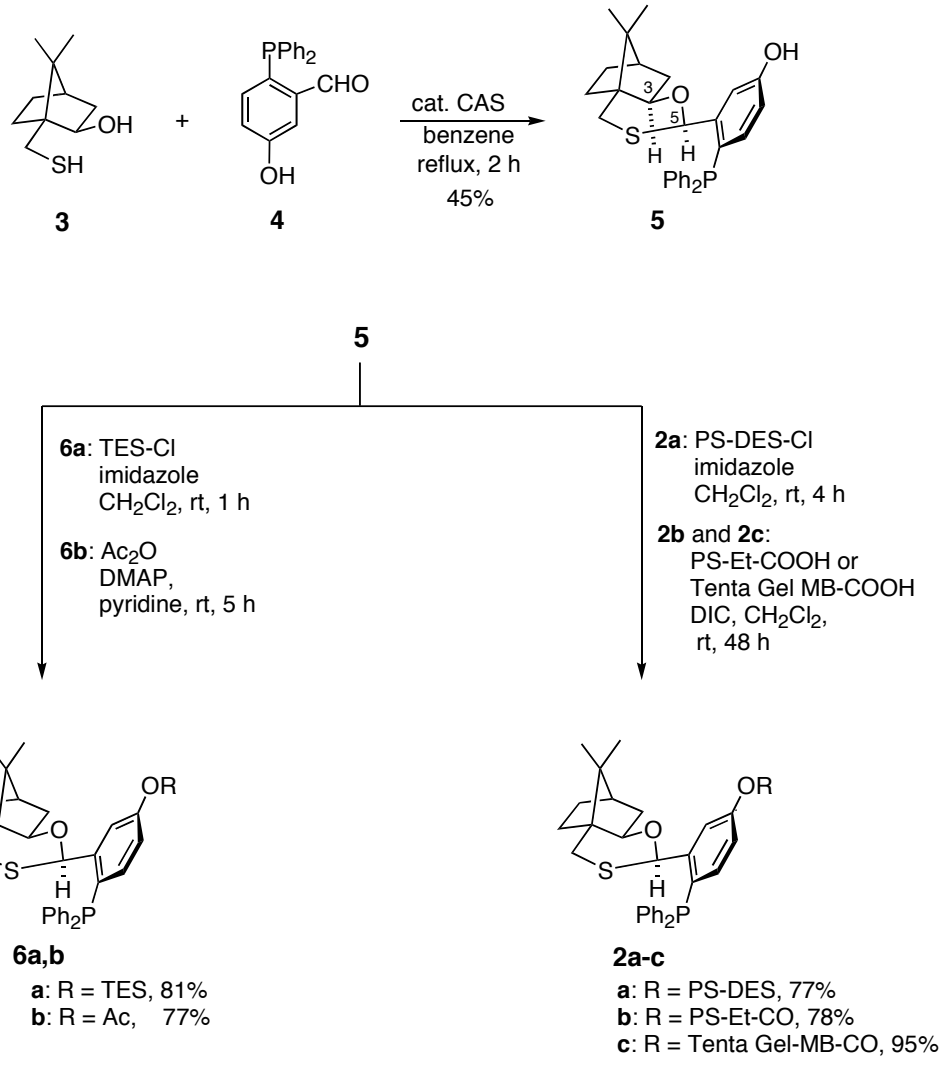
Scheme 1

Dedicated to Dr. Pierre Potier on the occasion of his 70th birthday.

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] Here, we present the easily prepared novel S-P type polymer-supported chiral POT ligands (**2a-c**) and apply these ligands to Pd-catalyzed asymmetric alkylation and amination (Scheme 1).

RESULTS AND DISCUSSION

The polymer-supported chiral ligands (**2a-c)** were synthesized easily as follows (Scheme 2). Homogeneous POT ligand (**5)** was prepared easily from the condensation reaction of commercially available (*S*)-mercaptoisoborneol (**3)** with 2-diphenylphosphino-4-hydroxybenzaldehyde (**4)**[5] in 45% yield. The stereochemical outcome of **5** was determined using NOE difference spectra (NOEDS). NOE enhancement was observed between the hydrogens at the 3- and 5-positions when either the 3- or 5-position was irradiated, respectively.[3]



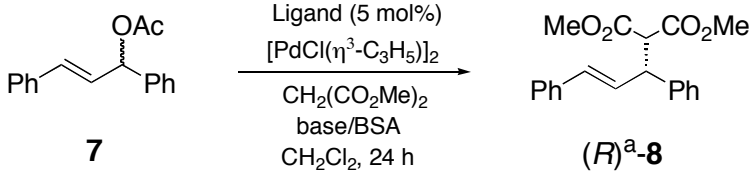
Scheme 2

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. By 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(ethylene glycol) linker. Chiral ligand (**5**) was linked *via* ester or ether bonds to PS-DES-Cl[6] resin, PS-Et-COOH[7] resin, or TentaGel-COOH[8] 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%[9] 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 78[9] and 95%[9] 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)[10] to give the allylation product (**8**) (Table 1).[11] First, the catalytic activities of the monomeric chiral ligands (**5**, **6a**, and **6b**) were tested as a control experiment. The reaction using ligand (**5**) with a hydroxy group gave the product (**8**) in 58% and 78% ee at room temperature or 39% and 92% ee at 0 °C (Entries 1 and 2). Similarly, the ligand (**6a**) with a triethylsilyloxy group and ligand (**6b**) with an acetoxy group at room temperature gave moderate yields and good enantioselectivities (**6a**: 81%, 79% ee, **6b**: 45%, 93% ee, Entries 3 and 5), respectively, but the reactions at 0 °C led to decrease of the chemical yields in spite of the enantioselectivities (**6a**: 25%, 87% ee, **6b**: 20%, 98% ee, Entries 4 and 6).

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 enantioselectivity (80% ee)(Entry 7). Decreasing the temperature to 0 °C improved the enantioselectivity to 90% ee, but with a poor chemical yield (12%)(Entry 8). PS-Et-supported ligand (**2b**) also gave good enantioselectivities with poor yields at room temperature and 0 °C (rt: 16%, 85% ee, 0 °C: 16%, 93% ee, Entries 9 and 10). Whereas, the use of TentaGel-supported ligand (**2c**) brought about a slightly increase of chemical yield, but the enantioselectivities were a moderate at room temperature and 0 °C (Entries 11 and 12). Based on these results, PS-Et-supported POT ligand (**2b**) was more effective than the PS-DES- and TentaGel-supported POT ligands (**2a,c**) for obtaining good ee in this allylic alkylation, although a satisfactory chemical yield was not afforded.

Table 1: Asymmetric Pd-catalyzed allylic alkylation of acetate (**7**)



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

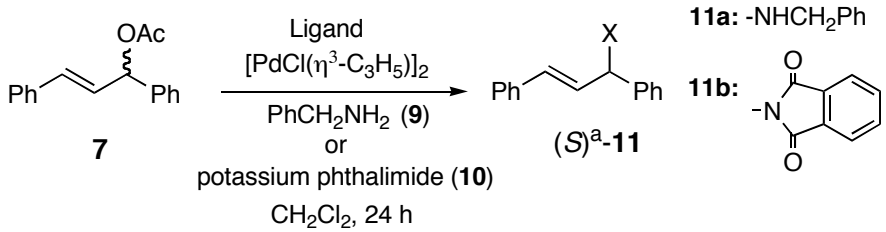
Entry[b]	Ligand	Temp. (°C)	Yield[c] (%)	E.e.[d] (%)
1	**5**	rt	58	78
2	**5**	0	39	92
3	**6a**	rt	81	79
4	**6a**	0	25	87
5	**6b**	rt	45	93
6	**6b**	0	20	98
7	**2a**	rt	39	80
8	**2a**	0	12	90
9	**2b**	rt	16	85
10	**2b**	0	16	93
11	**2c**	rt	58	47
12	**2c**	0	27	70

a) *R* configurations based on the specific rotation with literature data.[3] b) Molar ratio for entries 1-12 : $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (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.

Next, we examined the Pd-catalyzed allylic amination[12,13] of acetate (**7**) with benzylamine (**9**) acting as the nucleophile using the PS-Et-supported ligand (**2b**), which gave a good enantioselectivity in the allylic alkylation (Table 2). First, the catalytic activities of the monomeric chiral ligands (**5** and **6b**) 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 ligands (**5** and **6a**), 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**), the product (**11a**) was obtained in a good chemical yield (98%) and a moderate enantioselectivity (69% ee)(Entry 1). Furthermore, ligand (**6b**) also gave a good chemical yield (98%) and a comparatively good enantioselectivity (78% ee)(Entry 2). Next, the catalytic activity of polymer-supported chiral ligand (**2b**) was examined. The reaction at room

temperature afforded an excellent chemical yield (99%) and a moderate enantioselectivity (65% ee)(Entry 3). Cooling to 0 °C led to a slightly increase of the enantioselectivity (78% ee) with 99% yield (Entry 4). Furthermore, the same reaction was examined using potassium phthalimide (**10**) as a bulky, reactive nitrogen nucleophile. As the results, good enantioselectivities were obtained at both room temperature and 0 °C, but the chemical yields were poor (Entries 5 and 6). The reason, which gave a low yield, may be for the steric interaction of bulky nucleophile (**10**) and polymeric catalyst.

Table 2: Asymmetric Pd-catalyzed allylic amination of acetate (**7**)



Entry[b]	Nucleophile (equiv. to **7**)	Ligand (mol%)	Temp. (°C)	Yield[c] (%)	E.e.[d] (%)
1	**9** (10)	**5** (5)	0	98	69
2	**9** (10)	**6b** (5)	0	98	78
3	**9** (10)	**2b** (5)	rt	99	65
4	**9** (10)	**2b** (5)	0	99	78
5	**10** (3)	**2b** (5)	rt	26	89
6	**10** (3)	**2b** (5)	0	19	91

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

Finally, the recycle experiments were examined for the allylic amination with **7** using ligand (**2b**). After the first run giving 99% yield and 78% ee of the product (**11a**), the mixture was decanted off, and the solution of the reactants for the next cycle was then added without any further addition of a Pd source. These cycles were carried out three times. Consequently, **2b** was recycled with from 99% to 49% yields and 78% ee to 68% ee.

CONCLUSION

In summary, we prepared easily in two steps a new class of polymer-supported chiral POT ligands (**2a-c**) for heterogeneous asymmetric allylic substitution reactions. In particular, the PS-Et-based POT ligand

(**2b**) exhibited good activity and enantioselectivity for Pd-catalyzed allylic amination, and it was better than the monomeric POT for giving good enantioselectivity. Studies to optimize the reaction conditions for continuous processing, recycling, and application to other asymmetric reactions are in progress.

EXPERIMENTAL

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 (δ = 0) for ^{1}H-NMR and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C-NMR. MS were obtained by EI. The enantiomeric excess (ee) of the products were determined by chiral HPLC. Optical rotations were recorded at the sodium d line with a polarimetar 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,[6] 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.

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

A solution of (1*S*)-(-)-10-mercaptoisoborneol (**3**) (61 mg, 0.33 mmol), 2-diphenylphosphino-4-hydroxybenzaldehyde (**4**) (100 mg, 0.33 mmol) and DL-camphor-10-sulfonic acid (CSA, 15 mg, 0.06 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** (70 mg, 45 %) as a white solid. mp 88 °C. $[\alpha]_D^{20}$ = -80.0° (*c* 0.50, $CHCl_3$). IR (KBr) cm^{-1} = 696, 743, 1596, 2952, 3369. ^{1}H-NMR ($CDCl_3$) δ : 0.92 (3H, s), 0.95-1.05 (2H, m), 1.45-1.51 (4H, m), 1.60-1.78 (3H, m), 1.87-1.93 (1H, m), 2.70 (1H, d, *J* = 14.3 Hz), 3.22 (1H, d, *J* = 14.3 Hz), 3.65 (1H, dd, *J* = 3.0, 7.7 Hz), 5.67 (1H, br s), 6.42 (1H, *J* = 7.9 Hz), 6.66 (1H, dd, *J* = 2.6, 8.4 Hz), 6.83 (1H, dd, *J* = 4.1, 8.4 Hz), 7.19 (1H, t, *J* = 3.1 Hz), 7.25-7.30 (10H, m). ^{13}C-NMR ($CDCl_3$) δ : 20.42, 23.50, 27.21, 29.87, 34.27, 37.81, 41.92, 45.52, 46.76, 81.05, 85.68, 114.23, 116.11, 124.37, 128.25, 128.28, 128.33, 128.36, 128.38, 128.44, 133.17, 133.45, 133.73, 136.09, 137.10, 137.62, 145.87, 146.24, 157.08. MS *m*/*z* : 474 (M^+) ; HRMS : calcd for $C_{29}H_{31}O_2PS$ (M^+) : 474.1783, found : 474.1785. Anal. Calcd for $C_{29}H_{31}O_2PS$: C, 73.39; H, 6.58. Found : C, 73.46; H, 6.70.

(1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-5-(2-diphenylphosphino-4-triethylsilyloxy)phenyl-4-oxo-6-thiatricycloundecane (6a)

To a solution of **5** (20 mg, 0.042 mmol) and imidazole (6 mg, 0.084 mmol) in CH_2Cl_2 (5 mL) was added TES-Cl (0.014 mL, 0.084 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, and the extract was dried with anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a column of silica gel with AcOEt : hexane = 1 : 10 to afford **6a** (20 mg, 81 %) as a colorless oil. $[\alpha]_D^{24}$ = -77.5° (*c* = 0.80, $CHCl_3$). IR (film) cm^{-1} = 758, 1216, 1593, 3020. ^{1}H-NMR ($CDCl_3$) δ : 0.67 (6H, q, *J* = 7.5 Hz), 0.85 (3H, s), 0.92 (9H, t, *J* = 7.8 Hz), 1.18 (2H, s), 1.36-1.44 (4H, m), 1.53-1.63 (3H, m), 1.79-1.87 (1H, m), 2.62 (1H, d, *J* = 14.2 Hz), 3.13 (1H, *J* = 14.3 Hz), 3.37 (1H, dd, *J* = 3.0, 7.9 Hz), 6.32 (1H, d, *J* = 7.9 Hz), 6.62 (1H, dd, *J* = 2.6, 8.4 Hz), 6.83 (1H, dd, *J* = 4.1, 8.4 Hz), 7.15-7.24 (11H, m). ^{13}C-NMR ($CDCl_3$) δ : 5.00, 6.60, 20.44, 23.31, 27.27, 29.84, 34.25, 37.94, 41.83, 45.58, 46.76, 80.72, 85.41, 118.56, 118.65, 120.36, 124.77, 124.94, 128.25, 128.34, 128.44, 133.29, 133.51, 133.57, 133.79, 135.54, 137.25, 137.68, 145.78, 146.15, 157.01. MS *m*/*z* : 588 (M^+) ; HRMS : calcd for $C_{35}H_{45}O_2PSSi$ (M^+) : 588.2670, found : 588.2656.

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

To a solution of **5** (25 mg, 0.053 mmol) and 4-dimethylaminopyridine (DMAP, 0.64 mg, 0.005 mmol) in pyridine (2 mL) was added acetic anhydride (0.025 mL, 0.26 mmol) at rt. The reaction mixture was stirred at rt for 5 h. The mixture was quenched with H_2O, extracted twice with $CHCl_3$. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a column of silica gel with AcOEt : hexane = 1 : 10 to afford **6b** (21 mg, 77 %) as a colorless oil. $[\alpha]_D^{25}$ = -85.0° (*c* = 0.40, $CHCl_3$). IR (film) cm^{-1} = 759, 1216, 1732, 3020. ^{1}H-NMR ($CDCl_3$) δ : 0.91 (3H, s), 0.95-1.06 (2H, m), 1.41-1.45 (4H, m), 1.58-1.73 (3H, m), 1.85-1.92 (1H, m), 2.29 (3H, s), 2.70 (1H, d, *J* = 14.2 Hz), 3.20 (1H, d, *J* = 14.3 Hz), 3.61 (1H, dd, *J* = 3.1, 7.9 Hz), 6.38 (1H, d, *J* = 7.6 Hz), 6.92-7.00 (2H, m), 7.25-7.34 (10H, m), 7.40-7.42 (1H, m). ^{13}C-NMR ($CDCl_3$) δ : 20.43, 21.23, 23.45, 27.23, 29.92, 34.26, 37.79, 41.83, 45.52, 46.75, 80.80, 85.64, 120.14, 121.76, 128.36, 128.38, 128.46, 128.48, 128.56, 128.68, 131.05, 131.28, 133.49, 133.84, 135.15, 136.43, 137.01, 145.75, 146.12, 151.75, 168.91. MS *m*/*z* : 516 (M^+) ; HRMS : calcd for $C_{31}H_{33}O_3PS$ (M^+) : 516.1888, found : 516.1887.

PS-DES-supported ligand (2a)

A mixture of **5** (100 mg, 0.21 mmol), chlorodiethylsilylpolystyrene (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 was washed with $CHCl_3$, MeOH, acetone and ether. The polymer was dried

under reduced pressure to give **2a** (128 mg, 77 %, 58 % conversion, 0.46 mmol/g of ligand in polymer).

PS-Et-supported ligand (2b)

A mixture of **5** (82 mg, 0.17 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 was washed with $CHCl_3$, MeOH, acetone and ether. The polymer was dried under reduced pressure to give **2b** (121 mg, 78 %, 38 % conversion, 0.37 mmol/g of ligand in polymer).

TentaGel-supported ligand (2c)

A mixture of **5** (28 mg, 0.06 mmol), TentaGel MB-COOH (100 mg, 0.04 mmol) and DIC (0.01 mL, 0.6 mmol) in CH_2Cl_2 (2 mL) was stirred at rt for 48 h. The reaction mixture was filtered and the polymer was washed with $CHCl_3$, MeOH, acetone and ether. The polymer was dried under reduced pressure to give **2c** (113 mg, 95 %, 68 % conversion, 0.24 mmol/g of ligand in polymer).

General procedure for the Pd-catalyzed allylic alkylation using chiral 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 were 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 mixture was quenched with saturated NH_4Cl solution and extracted twice with ether. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated. The residue was purified by preparative TLC (hexane : AcOEt = 2 : 1) to afford **8**.

General procedure for the Pd-catalyzed allylic amination using chiral 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 1,3-diphenyl-2-propenyl acetate (**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 mixture was quenched with saturated NH_4Cl solution and extracted twice with ether. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated. The residue was purified by preparative TLC (hexane : AcOEt = 2 : 1) to afford **11**.

General procedure for the Pd-catalyzed allylic alkylation using polymer-supported ligand (2b).

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) were stirred for 1 h at rt under argon. To this mixture at the desired reaction temperature were 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 mixture was filtered, quenched with saturated NH_4Cl solution and extracted twice with ether. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated. The residue was purified by preparative TLC (hexane : AcOEt = 2 : 1) to afford **8**.

General procedure for the Pd-catalyzed allylic amination using polymer-supported ligand (2b).

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 1,3-diphenyl-2-propenyl acetate (**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 mixture was filtered, quenched with saturated NH_4Cl solution and extracted twice with ether. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated. The residue was purified by preparative TLC (hexane : AcOEt = 2 : 1) to afford **11**.

Recycling experiments of the Pd-catalyzed allylic amination using polymer-supported ligand (2b).

After the reaction, the mixture was decanted off by using a cannula, and the solution of the reactants for the next cycle was added to the ligand (**2b**).

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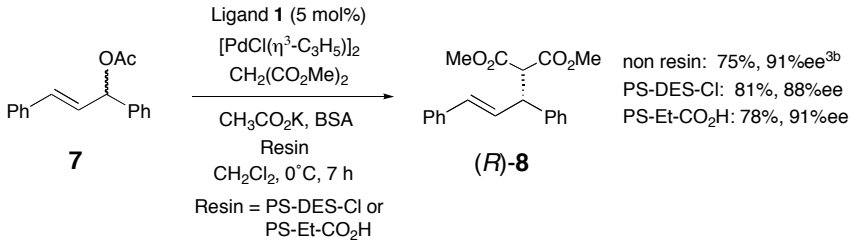
11. The polymer-supported ligands (**2a**: 77% and **2b**: 78%) were used without the end capping of the unreacted resins (PS-DES-Cl and PS-Et-COOH). In order to investigate the influence of the unreacted PS-DES-Cl and PS-Et-COOH resins to the Pd-catalyzed allylic alkylation, the reactions using the monomeric POT ligand **1**[3b] in the presence of the resins were carried out, and they hardly affected the chemical yield and enantioselectivity in the reactions.



12. For some recent successful publications on polymer-supported chiral ligands in Pd-catalyzed allylic amination: (a) C. E. Song, J. W. Yang, E. J. Roh, S.-g. Lee, J. H. Ahn, and H. Han, *Angew. Chem., Int. Ed.,* 2002, **41**, 4691; (b) B. M. Trost, Z. Pan, J. Zambrano, and C. Kujat, *Angew. Chem., Int. Ed.,* 2002, **41**, 4691; (c) Y. Uozumi, H. Tanaka, and K. Shibatomi, *Org. Lett.,* **2004**, 6, 281.
13. Reviews on allylic amination: (a) M. Johannsen and K. A. Jorgensen, *Chem. Rev.,* **1998**, 98, 1689. (b) A. Heumann, '*Transition Metals for Organic Synthesis*,' ed. by M. Beller and C. Bolm, Wiley-VCH, Weinheim, 1998, p. 251.