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Polymer-supported chiral phosphinooxazolidine ligands for palladium-catalyzed asymmetric allylic alkylations and Diels–Alder reactions

Hiroto Nakano,* Kouichi Takahashi and Reiko Fujita

Tohoku Pharmaceutical University, 4-4-1 Komatsushima, Aoba-ku, Sendai 981-8558, Japan

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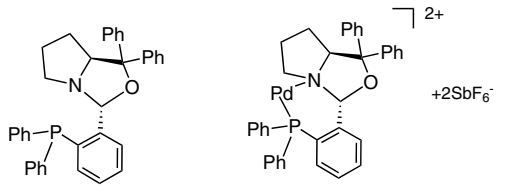
Abstract—Polymer-supported chiral phosphinooxazolidine (POZ) ligands **9a–c** and cationic palladium-POZ catalysts **16a–c** have been prepared. The former ligands were used in the Pd-catalyzed asymmetric allylic alkylation, while the latter catalysts were used in the Diels–Alder reaction to afford good to excellent enantioselectivities (Pd-catalyzed allylation: up to 99% ee, Diels–Alder reaction: up to 92% ee).

1. Introduction

An increasing number of applications are being found for enantiomerically pure compounds for economic, environmental and social reasons. Of the various methods used to obtain single enantiomers, a catalytic asymmetric reaction is one of the most attractive from an atom-economic perspective. Several efficient chiral ligands and catalysts have been investigated with regard to their use in these reactions.[1] We recently reported that chiral phosphinooxazolidine (POZ) **1** and cationic Pd-complex **2** are an effective ligand and catalyst, respectively, for asymmetric Pd-catalyzed allylic alkylations[2] and Diels–Alder reactions,[3] respectively (Fig. 1). Nevertheless, despite the huge amount of work on homogeneous chiral ligands and catalysts in these reactions, the use of heterogeneous ligands and catalysts has not been studied extensively.[4] In particular, only a few successful studies of the Diels–Alder reaction have been reported.[5,6] Furthermore, to the best of our knowledge, a polymer-supported N–P type ligand has never been used in the Diels–Alder reaction.

Herein, we report the synthesis of new N–P type polymer-supported chiral POZ ligands **9a–c** and their cationic Pd–POZ catalysts **16a–c**, and the applications of **9a–c** to Pd-catalyzed asymmetric allylic alkylation and of **16a–c** to the Diels–Alder reaction. Good to excellent enantioselectivities (allylic alkylation: up to 99% ee, Diels–Alder reaction: up to 92% ee) were observed in these reactions.



1 **2**

Figure 1. Chiral POZ ligand **1** and cationic Pd–POZ complex **2**.

2. Results and discussion

Polymer-supported POZ ligands **9a–c**, $PdCl_2$–POZ complexes **10a–c**, and their homogeneous analogues, **7a** and **7b** and **8a** and **8b**, were synthesized via the route shown in Scheme 1. Precursor **5** for linking to resins was synthesized via the condensation of (*S*)-(−)-1,1-diphenyl-2-pyrrolidinemethanol **3** with 2-diphenylphosphino-5-hydroxybenzaldehyde[5] **4** in 58% yield, and converted to $PdCl_2$-complex **6** by the reaction with $PdCl_2$. The stereochemical outcome of ligand **5** and $PdCl_2$-complex **6** were determined using NOE difference spectra (NOEDS) in ^1H NMR. NOE enhancement was not observed for the hydrogens at the 2- and 5-positions

* Corresponding author. Tel.: +81 22 234 4181; fax: +81 22 275 2013; e-mail: hnakano@tohoku-pharm.ac.jp

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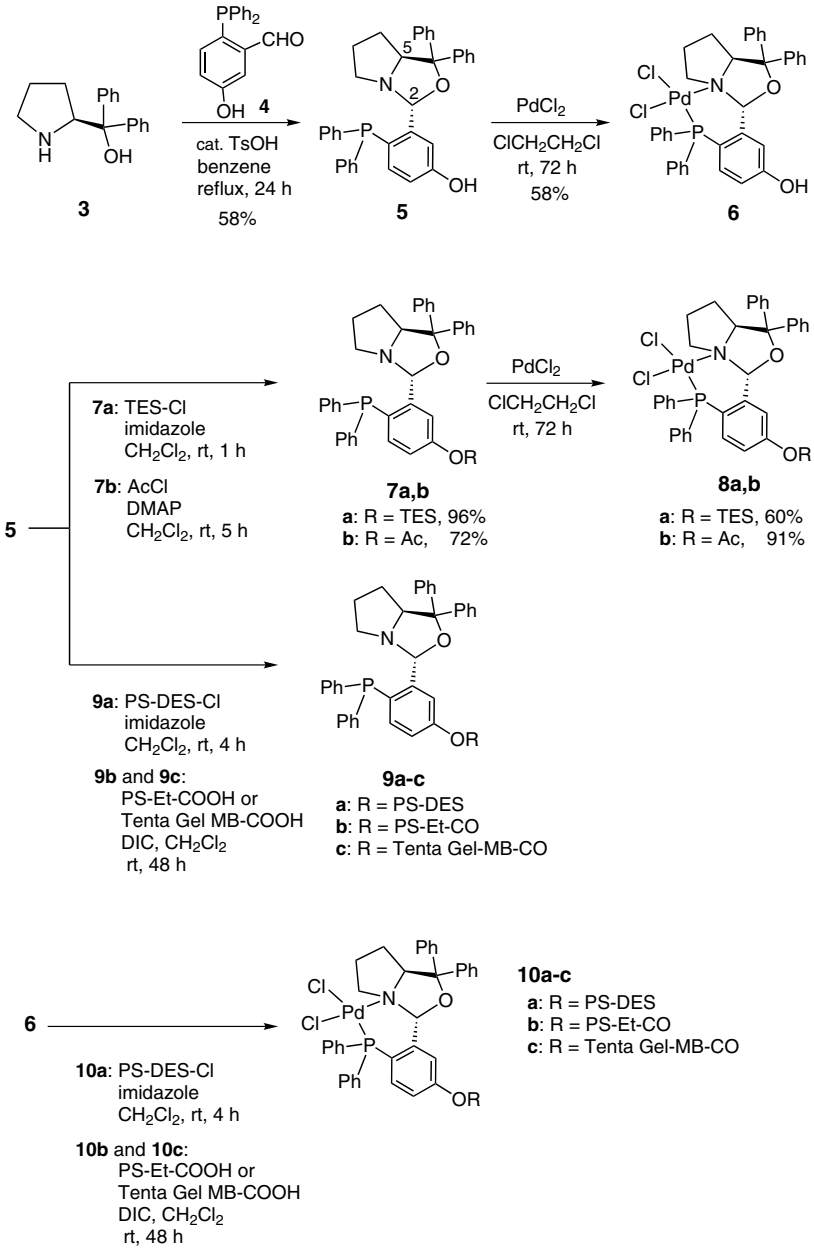
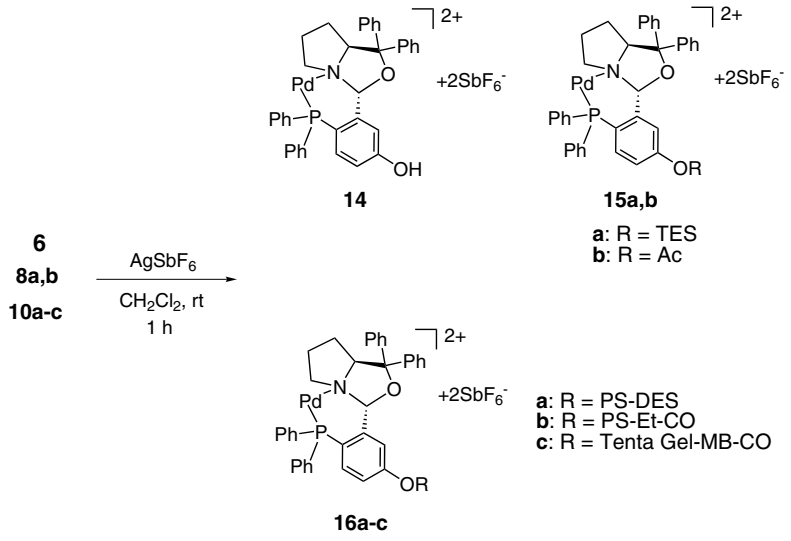


Scheme 1. Synthesis of monomeric and polymer-supported chiral POZ ligands and Pd–POZ complexes.

when these respective positions were irradiated (Scheme 2).

Polystyrene–diethylsilyl (PS–DES),[6] polystyrene–ethyl (PS–Et), and polystyrene–poly(ethylene glycol-OC_2H_4-$NHCO$-C_2H_5) (TentaGel) were used as resins. PS–DES and PS–Et were constituted from styrene and DVB (divinylbenzene) only and had a good solvent-swollen state in dichloromethane. In contrast, TentaGel is a graft-copolymer of gel-type polystyrene; catalysts bound to this support behave like homogeneous rather than heterogeneous catalysts in a wide range of solvents because of the long, flexible poly(ethylene glycol) linker. POZ ligand **5** and $PdCl_2$–POZ complex **6** were linked via ester and ether bond formation, respectively, to the PS–DES–Cl, PS–Et–COOH or TentaGel–COOH resins (Scheme 2). The reaction of POZ ligand **5** or $PdCl_2$-complex **6** with PS–DES–Cl in the presence of imidazole in dichloromethane for 4 h at room temperature gave the desired PS–DES-supported POZ ligand **9a** or $PdCl_2$–POZ complex **10a**. Furthermore, the reaction of **5** or **6** with PS–Et–COOH or TentaGel–COOH in the presence of diisopropylcarbodiimide (DIC) in dichloromethane for 48 h at room temperature gave the desired PS–Et- or TentaGel-supported ligands **9b** and **c** and PS–Et- or TentaGel-supported $PdCl_2$-complexes **10b** and **c**. In addition, to comparing the catalytic efficiency, homogeneous analogues **7a** and **7b** or **8a** and **8b** were also prepared by reacting ligand **5** or complex **6** with TES–Cl or AcCl.

The efficiencies of the polymer-supported ligands **9a–c** were examined with the Pd-catalyzed asymmetric allylic alkylation[7,8] of 1,3-diphenyl-2-propenyl acetate **11** with

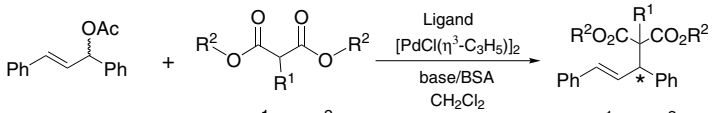


Scheme 2. Preparations of cationic POZ complexes.

dimethyl malonate **12a** in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and *N*,*O*-bis(trimethylsilyl)acetamide (BSA)[9] to give allylation product **13a** (Table 1). Initially, the activities of monomer ligands **5**, **7a**, and **7b** were tested as a controlled experiment. The reaction using ligand **5** with a hydroxy group gave product **13** in 97% yield and 58% enantiomeric excess (ee) (entry 1). Ligand **7a** with a triethylsilyloxy group afforded product **13a** in quantitative yield and good ee (89%) (entry 2). Furthermore, ligand **7b** with an acetoxy group gave an excellent ee (98%) with a reasonable chemical yield (93%) (entry 3).

With these results in hand, we investigated the efficiencies of the polymer-supported chiral POZ ligands **9a**–**c** in this reaction (Table 1). The use of PS–DES-supported ligand **9a** gave a poor chemical yield (25%) but a good ee (93%) (entry 4). PS–Et-supported ligand **9b** brought about high asymmetric induction (98%) in a moderate chemical yield (67%) (entry 5). Extending the reaction time from 6 to 12 h led to a substantial increase in the chemical yield to 99% (entry 6). However, decreasing the catalytic loading from 5 to 2 mol % led to a substantial decrease in the enantioselectivity to 77% ee (entry 7). Furthermore, TentaGel-supported ligand **9c** also afforded product **13a** in a satisfactory ee (96%) in a moderate chemical yield (78%) (entry 8). The superior ligand **9b** was also applied to the reaction with a bulkier diethyl methylmalonate **12b** as a nucleophile. However, the reaction gave product **13b** in only 51% ee, although

Table 1. Pd-catalyzed asymmetric allylic alkylation of acetate **11** with dialkylmalonates **12a**,**b**



Entry[a]	Ligand	Ligand (mol %)	Nucleophile	Temperature (°C)	Time (h)	Yield[b] (%)	% ee[c] (config)[d]
1	**5**	2	**12a**	rt	3	97	58 (*R*)
2	**7a**	2	**12a**	rt	3	99	89 (*R*)
3	**7b**	2	**12a**	rt	3	93	98 (*R*)
4	**9a**	5	**12a**	rt	6	25	93 (*R*)
5	**9b**	5	**12a**	rt	6	67	98 (*R*)
6	**9b**	5	**12a**	rt	12	99	99 (*R*)
7	**9b**	2	**12a**	rt	12	67	77 (*R*)
8	**9c**	5	**12a**	rt	6	78	96 (*R*)
9	**9b**	5	**12b**	rt	3	98	51 (*S*)
10	**9b**	5	**12b**	0	12	98	19 (*S*)

[a] Molar ratio for entries 1–10: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.001 equiv) for 1–3, 7 or $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.025 equiv) for 4–6, 8–10, dimethyl malonate (3 equiv), *N*,*O*-bis-(trimethylsilyl)acetoamide (BSA) (3 equiv), potassium acetate (0.02 equiv).
[b] Isolated yields.
[c] Determined by HPLC analysis using a DAICEL Chiralcel OD-H.
[d] *R* Configurations based on the specific rotation with literature data.[3]

the chemical yield was excellent (entry 9). Furthermore, the enantioselectivity at 0 °C was poor (19% ee) (entry 10).

From these results, PS–Et-supported POZ ligand **9b** was more effective than the PS–DES- and TentaGel-supported POZ ligands **9a** and **c** for this allylic alkylation, while **9b** gave a higher enantioselectivity than both the corresponding monomer ligand **7b** and the previously reported monomer ligand **1**.[2] Although it is unclear why ligand **9b** gave an excellent yield and enantioselectivity, it seemed to be dependent on the advantageous steric and electronic interactions of the nucleophile and π–allyl complex with its bulky polymeric backbone. In addition, low enantioselectivities using bulkier carbon nucleophiles (entries 9 and 10) might result from the interfering effects of the polymer backbone on ligand **9b** to the attack of bulkier carbon nucleophiles.

Finally, recycling experiments examined the allylic alkylation of **12a** with **11** using ligand **9b**. After the first run, which gave 99% yield and 99% ee of product **13a**, the mixture was decanted off, and the solution of reactants for the next cycle then added without any further addition of Pd. This process was repeated three times. Consequently, **9b** was recycled with 57% loss in activity (from 99% to 42% yield) and with 33% loss in enantioselectivity (from 99% to 66% ee).

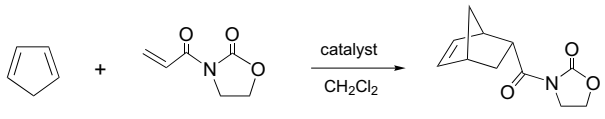
For application to other reactions, the catalytic activities of cationic polymer-supported Pd–POZ catalysts **16a–c** in the Diels–Alder reaction[10,11] were examined. Cationic catalysts **14**, **15a** and **15b**, and **16a–c**, with a hexafluoroantimonate counterion, were prepared by reacting **6**, **8a** and **8b**, and **10a–c**, respectively, with $AgSbF_6$ in dry CH_2Cl_2 at rt for 1 h under argon (Scheme 2).

Initially, the catalytic activities of the cationic monomer catalysts **14** and **15a** and **b** were tested as a control experiment in the reaction of cyclopentadiene **17** with acryloyl-1,3-oxazolidin-2-one **18** (Table 2). The Diels–Alder reactions were attempted at 0 °C using 10 mol % of the antimonate catalysts **14** and **15a** and **15b**. The reaction using catalyst **14** did not proceed (entry 1) at all. By contrast, catalysts **15a** and **15b** both showed good catalytic activity (entries 2 and 3); in particular, catalyst **15b** with an acetoxy group gave excellent enantioselectivity (98% ee) when the reaction temperature was reduced to −45 °C (entry 4).

Next, the Diels–Alder reactions using polymer-supported POZ catalysts **16a–c** were examined under the same reaction conditions as entries 2–4 (Table 2). The PS–DES- and TentaGel-supported catalysts, **16a** and **16c**, did not show effective catalytic activity (**16a**: 27% yield, 5% ee; **16c**: 34% yield, 0% ee) (entries 5 and 7). Conversely, PS–Et-supported catalyst **16b** gave comparatively good results (64% yield, 83% ee) (entry 6). We examined the effects of the molar ratio and reaction temperature on the reaction using the superior catalyst **16b**. The use of 5 mol % **16b** decreased both the chemical yield and ee (entry 8), while increasing **16b** to 20 mol % gave the best chemical yield (79%) and ee (92% ee) (entry 9). Unfortunately, with 20 mol % **16b**, decreasing the temperature to −30 °C led to a substantial decrease in the chemical yield along with a slight decrease in ee (86% ee) (entry 10).

The superior cationic antimonate catalyst **16b** was then tested using other dienes such as cyclohexadiene **20** or 2,3-dimethyl-1,3-butadiene **21**, and dienophiles, such as crotonyl-1,3-oxazaolidin-2-one **22a** or fumaroyl-1,3-oxazolidin-2-one **22b** (Table 3). The reactions were carried out with 20 mol % catalyst **16b** at 0 °C (Table 3). However, the reaction of diene **17** with dienophile **22a** was sluggish and only gave the Diels–Alder adduct **23a** in poor chemical yield and low enantioselectivity (entry 1). In contrast, the reaction with **22b** proceeded in

Table 2. Diels–Alder reactions with cationic POZ catalysts

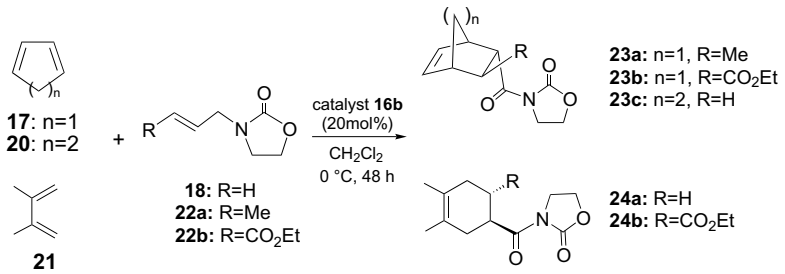


17 **18** **19**

Entry	Catalyst (mol %)	Temperature (°C)	Time (h)	Yield[a] (%)	*endo*/*exo*[b]	% ee[c]
1	**14** (10)	0	24	No reaction	—	—
2	**15a** (10)	0	3	99	93:3	90
3	**15b** (10)	0	3	97	93:7	93
4	**15b** (10)	−45	24	86	98:2	98
5	**16a** (10)	0	24	27	95:5	5
6	**16b** (10)	0	24	64	94:6	83
7	**16c** (10)	0	24	34	83:17	0
8	**16b** (5)	0	24	43	94:6	28
9	**16b** (20)	0	24	79	93:7	92
10	**16b** (20)	−30	48	29	97:3	86

[a] Isolated yields.
[b] *endo*/*exo* Ratio was determined by HPLC.
[c] Ee of *endo*-isomer was determined by chiral HPLC using a Daicel OD-H column.

Table 3. Substrate generality in the Diels–Alder reaction with cationic catalyst **16b**



Entry	Diene	Substrate	Yield (%)[a]	*endo*/*exo*[b]	% ee[c] (config)
1	**17**	**22a**	12	82:18	56 (*R*)
2	**17**	**22b**	99	67:33	17 (*S*)[d]
3	**20**	**18**	No reaction	—	—
4	**21**	**18**	11	—	35 (*R*)
5	**21**	**22b**	14	—	44 (*R*)

[a] Isolated yield.
[b] *endo*/*exo* Ratios were determined by HPLC or ^{1}H NMR.
[c] Ee of *endo*-isomers were determined by chiral HPLC.
[d] After conversion to the corresponding iodolactone (I_2, KI, $NaHCO_3$, yield 63%), the ee and absolute configuration were determined by comparison with known specific rotation.

excellent chemical yield, although the enantioselectivity was poor (entry 2). Furthermore, the reaction of relatively unreactive diene **20** with dienophile **18** did not proceed at all (entry 3). In addition, catalyst **16b** was applied to the reactions of acyclic diene **21** with dienophiles **18** and **22b**, although poor results were obtained for both the chemical yield and enantioselectivity (entries 4 and 5). Although it is unclear why catalyst **16b** gave good enantioselectivity, it seemed to be dependent on the advantageous steric and electronic interactions of diene **17** and the Pd–POZ complex with the bulky polymeric backbone of the coordinating dienophile. These results suggest that the linking of POZ on PS–Et resin was the most effective for giving good chemical yield and enantioselectivity, similar to the results of the allylic alkylation. However, this polymer-supported catalyst **16b** did not work as efficiently as either of the monomer catalysts **15b** and **2**[3] in the Diels–Alder reaction.

We conducted recycling experiments for the Diels–Alder reaction of diene **17** with dienophile **18** catalyzed using the PS–Et-supported Pd–POZ catalyst **16b**. After the first run, which gave 92% ee of Diels–Alder adduct **19**, the mixture was decanted, and a solution containing the reactants for the next cycle added. This process was carried out three times. Consequently, **15b** was recycled with approximately 30% losses in both activity (from 79% to 45% yield) and enantioselectivity (from 92% to 62% ee).

3. Conclusion

In conclusion, we have prepared six new chiral, polymer-supported POZ ligands **9a**–**c** and their cationic Pd–POZ catalysts **16a**–**c**, and applied them to heterogeneous Pd-catalyzed allylic alkylation and the Diels–Alder reaction, respectively. The PS–Et-supported POZ ligand **9b** and Pd–POZ catalyst with antimonate counterion **16b** had good activity and enantioselectivity (allylation with **9b**: 99% yield, 99% ee, Diels–Alder reaction with **16b**: 80% yield, 92% ee) in the reactions. In particular, **9b** gave a superior chemical yield and enantioselectivity than that of monomer **1**[2] in Pd-catalyzed allylic alkylation. Studies to optimize the reaction conditions for continuous processing, recycling, and application to other asymmetric reactions are currently in progress.

4. Experimental

4.1. General methods

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, and at 400 and 100 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 excess (ee) 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.

4.2. (2*R*,5*S*)-1-Aza-4,4-diphenyl-2-(5′-hydroxy-2′-diphenylphosphino)phenyl-3-oxobicyclo[3.3.0]octane 5

A solution of (*S*)-(−)-α,α-diphenyl-2-pyrrolidinemethanol **3** (41 mg, 0.16 mmol), 2-diphenylphosphanyl-5-hydroxybenzaldehyde **4** (50 mg, 0.16 mmol) and *p*-toluenesulfonic acid monohydrate (6 mg, 0.03 mmol) in

benzene (20 mL) was heated under reflux using a Dean-Stark trap. After 24 h, the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel (1:1 hexane–AcOEt) to give product **5** (50 mg, 58%) as colorless prism: mp 76 °C; $[\alpha]_D^{20} = +15.0$ (*c* 0.16, $CHCl_3$); IR (KBr) 698, 746, 1226, 1434, 1598 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.44–1.62 (m, 2H), 1.64–1.73 (m, 2H), 2.71–2.77 (m, 1H), 2.84–2.91 (m, 1H), 4.34 (t, $J = 6.9$ Hz, 1H), 6.36 (d, $J = 6.6$ Hz, 1H), 6.50 (dd, $J = 2.6$, 8.4 Hz, 1H), 6.73 (dd, $J = 4.3$, 8.4 Hz, 1H), 7.04–7.46 (m, 21H); ^{13}C NMR ($CDCl_3$): δ 24.62, 27.88, 50.72, 73.35, 88.97, 94.46, 114.98, 115.07, 116.06, 125.97, 126.15, 126.28, 126.39, 126.52, 126.71, 127.75, 127.85, 128.05, 128.24, 128.28, 128.34, 128.37, 128.49, 133.51, 133.65, 133.80, 133.93, 135.60, 137.66, 137.82, 137.97, 143.75, 146.57, 146.69, 147.02, 157.00; MS *m*/*z* 541 (M^+); HRMS calcd for $C_{36}H_{32}NO_2P$ (M^+) 541.2171. Found: 541.2188.

4.3. (2*R*,5*S*)-1-Aza-4,4-diphenyl-2-(2′-diphenylphosphino-5′-triethylsilyloxy)phenyl-3-oxobicyclo[3.3.0]octane 7a

To a solution of **5** (30 mg, 0.06 mmol) and imidazole (8 mg, 0.11 mmol) in CH_2Cl_2 (3 mL) was added chlorotriethylsilane (0.02 mL, 0.11 mmol) at room temperature. The reaction was carried out at room temperature for 1 h. Then the reaction mixture was quenched with water and extracted twice with ether. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a column of silica gel (1:10 AcOEt–hexane) to give the product **7a** (35 mg, 96%) as colorless oil: $[\alpha]_D^{20} = -65.0$ (*c* 0.20, $CHCl_3$); IR (NaCl) 698, 749, 1292, 1469, 1592, 2957 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.58 (q, $J = 8.1$ Hz, 6H), 0.89 (t, $J = 8.1$ Hz, 9H), 1.31–1.38 (m, 1H), 1.48–1.55 (m, 1H), 1.67 (dd, $J = 6.2$, 13.2 Hz, 2H), 2.68–2.72 (m, 1H), 2.90–2.95 (m, 1H), 4.22–4.29 (m, 1H), 6.38 (d, $J = 6.2$ Hz, 1H), 6.64 (dd, $J = 2.2$, 8.4 Hz, 1H), 6.76 (dd, $J = 4.4$, 8.4 Hz, 1H), 7.12–7.15 (m, 2H), 7.17–7.20 (m, 5H), 7.21–7.28 (m, 4H), 7.29–7.32 (m, 5H), 7.34–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 4.90, 6.61, 24.30, 27.70, 50.56, 73.18, 89.01, 94.90, 118.95, 119.90, 126.25, 126.35, 126.49, 126.58, 126.65, 126.81, 126.88, 126.97, 127.69, 127.86, 128.25, 128.34, 128.47, 131.92, 131.99, 133.66, 133.79, 133.88, 134.01, 135.34, 137.91, 137.98, 138.08, 138.14, 144.30, 146.88, 147.53, 156.63; MS *m*/*z* 655 (M^+); HRMS calcd for $C_{42}H_{46}NO_2PSi$ (M^+) 655.3035. Found: 655.3078.

4.4. (2*R*,5*S*)-2-(5′-Acetoxy-2′-diphenylphosphino)phenyl-1-aza-4,4-diphenyl-3-oxobicyclo-[3.3.0]octane 7b

To a mixture of **5** (70 mg, 0.13 mmol), DMAP (8 mg, 0.06 mmol) and Et_3N (0.04 mL, 0.26 mmol) in CH_2Cl_2 (5 mL) was added acetylchloride (0.02 mL, 0.26 mmol) at 0 °C. The reaction was carried out at room temperature for 5 h. Then the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted twice with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The residue was chromatographed on a column of silica gel (1:10 AcOEt–hexane) to give product **7b** (54 mg, 72%) as colorless oil: $[\alpha]_D^{20} = -52.0$ (*c* 1.00, $CHCl_3$); IR (NaCl) 699, 735, 1216, 1733, 2931 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.45–1.69 (m, 4H), 2.20 (s, 3H), 2.69–2.78 (m, 1H), 2.93–3.02 (m, 1H), 4.27 (t, $J = 6.7$ Hz, 1H), 6.34 (d, $J = 5.8$ Hz, 1H), 6.90 (s, 2H), 7.05–7.24 (m, 10H), 7.28–7.36 (m, 10H), 7.50–7.70 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 21.11, 24.52, 27.82, 50.92, 73.29, 89.16, 94.72, 120.83, 121.34, 125.09, 126.28, 126.44, 126.66, 127.74, 128.38, 128.43, 128.48, 128.54, 128.80, 131.65, 131.89, 133.21, 133.68, 133.81, 133.94, 134.05, 134.08, 134.18, 135.06, 135.31, 137.04, 137.56, 144.04, 146.76, 147.67, 151.36, 169.02; MS *m*/*z* 583 (M^+); HRMS calcd for $C_{38}H_{34}NO_3P$ (M^+) 583.2277. Found: 583.2244.

4.5. Dichloro[(2*R*,5*S*)-1-aza-4,4-diphenyl-2-(2′-diphenylphosphino-5′-hydroxy)-phenyl-3-oxobicyclo-[3.3.0]octane]palladium 6

A suspension of POZ ligand **5** (30 mg, 0.06 mmol) and $PdCl_2$ (10 mg, 0.06 mmol) in 1,2-dichloroethane (5 mL) was stirred at room temperature for 72 h. Then the solvent was evaporated under reduced pressure. The residue was chromatographed on a column of silica gel (1:1 AcOEt–$CHCl_3$) to give complex **6** (23 mg, 58%) as a yellow prism: mp 229 °C; $[\alpha]_D^{20} = -95.0$ (*c* 0.20, DMSO); IR (KBr) 692, 1438, 1600 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.41–1.56 (m, 1H), 1.88–1.93 (m, 1H), 2.07–2.10 (m, 1H), 2.23–2.44 (m, 1H), 2.88–2.99 (m, 1H), 4.03 (t, $J = 9.7$ Hz, 1H), 4.97 (s, 1H), 6.54–6.28 (m, 1H), 6.66 (t, $J = 9.1$ Hz, 1H), 6.91–7.03 (m, 3H), 7.08–7.56 (m, 19H), 10.76 (br s, 1H); ^{13}C NMR (DMSO-d_6): 27.31, 28.21, 54.48, 78.69, 87.79, 92.45, 109.02, 109.79, 118.70, 118.34, 121.64, 121.77, 124.86, 125.55, 126.71, 127.53, 127.90, 128.10, 128.26, 128.51, 128.69, 128.84, 129.17, 130.42, 130.85, 130.95, 133.05, 133.21, 134.26, 135.01, 137.06, 139.28, 139.53, 143.32, 143.46, 160.84; MS *m*/*z* 646 ($[M-1H2Cl]^+$); HRMS calcd for $C_{36}H_{31}NO_2PPd$ ($[M-1H2Cl]^+$) 646.1128. Found: 646.1235 (FAB with *p*-nitrobenzylalcohol added).

4.6. Dichloro[(2*R*,5*S*)-1-aza-4,4-diphenyl-2-(2′-diphenylphosphino-5′-triethylsilyloxy)-phenyl-3-oxobicyclo[3.3.0]octane]palladium 8a

A suspension of **7a** (30 mg, 0.05 mmol) and $PdCl_2$ (8 mg, 0.05 mmol) in 1,2-dichloroethane (5 mL) was stirred at room temperature for 72 h. Then the solvent was evaporated under reduced pressure. The residue was chromatographed on a column of silica gel (AcOEt only) to give the product **8a** (23 mg, 60%) as yellow prism: mp 213 °C; $[\alpha]_D^{20} = -235.55$ (*c* 0.90, DMSO); IR (KBr) 689, 1437, 1600, 2345 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.82 (q, $J = 8.1$ Hz, 6H), 0.85–0.94 (m, 1H), 1.05 (t, $J = 8.1$ Hz, 9H), 1.39–1.46 (m, 1H), 1.86–1.91 (m, 1H), 2.06–2.08 (m, 1H), 2.60–2.65 (m, 1H), 2.90 (dt, $J = 8.1$, 12.5 Hz, 1H), 4.43 (dt, $J = 3.7$, 11.2 Hz, 1H), 4.79 (d, $J = 1.5$ Hz, 1H), 6.69–6.72 (m, 1H), 6.86 (dd, $J = 7.7$, 10.6 Hz, 1H), 6.91 (ddd, $J = 0.7$, 1.8, 8.4 Hz, 1H), 7.00 (t, $J = 7.7$ Hz, 2H), 7.03–7.04 (m, 1H), 7.08 (t, $J = 7.3$ Hz, 3H), 7.11–7.14 (m, 2H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.24–7.36 (m, 7H), 7.38 (dd, $J = 1.5$, 7.3 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 5.07, 6.60, 26.96, 28.83, 54.99, 77.37, 89.15, 94.46, 133.68, 114.01, 122.16, 122.22, 124.89, 125.39, 125.46, 126.58, 127.05, 127.30, 127.99,

128.07, 128.42, 128.49, 128.57, 128.60, 130.56, 130.58, 130.69, 132.50, 132.69, 133.31, 133.92, 137.66, 137.68, 139.29, 139.40, 142.13, 143.59, 158.92; MS *m/z* 761 ($[M-2Cl]^+$); HRMS calcd for $C_{42}H_{46}NO_2PSiPd$ ($[M-2Cl]^+$) 761.2069. Found: 761.2272 (FAB with *p*-nitrobenzylalcohol added).

4.7. Dichloro[(2*R*,5*S*)-2-(5′-acetoxy-2′-diphenylphosphino)phenyl-1-aza-4,4-diphenyl-3-oxobicyclo-[3.3.0]octane]palladium 8b

A suspension of **7b** (50 mg, 0.09 mmol) and $PdCl_2$ (15 mg, 0.09 mmol) in 1,2-dichloroethane (5 mL) was stirred at room temperature for 72 h. Then the solvent was evaporated under reduced pressure. The residue was chromatographed on a column of silica gel (AcOEt only) to give product **8b** (59 mg, 91%) as yellow prism: mp 214 °C; $[\alpha]_D^{20} = -260.9$ (*c* 0.46, DMSO); IR (KBr) 690, 1437, 1763, 2983 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.32–1.48 (m, 1H), 1.81–1.91 (m, 1H), 2.05–2.13 (m, 1H), 2.37 (s, 3H), 2.556–2.67 (m, 1H), 2.93 (dt, $J = 7.9$, 16.0 Hz, 1H), 4.41 (dt, $J = 3.3$, 9.1 Hz, 1H), 4.89 (s, 1H), 6.83–6.91 (m, 2H), 6.97–7.19 (m, 9H), 7.22–7.36 (m, 7H), 7.39–7.44 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 21.12, 26.93, 28.71, 54.92, 77.31, 89.16, 93.99, 120.04, 120.72, 124.67, 124.91, 125.04, 125.42, 126.44, 126.56, 126.68, 127.00, 127.22, 127.96, 128.15, 128.37, 128.46, 128.62, 130.67, 130.80, 131.74, 132.76, 133.11, 133.26, 133.37, 133.84, 137.30, 138.85, 139.09, 141.89, 143.23, 152.98, 168.43; MS *m/z* 689 ($[M-2Cl]^+$); HRMS calcd for $C_{38}H_{34}NO_3PPd$ ($[M-2Cl]^+$) 689.1311. Found: 689.1375 (FAB with *p*-nitrobenzylalcohol added).

4.8. PS–DES-supported POZ ligand 9a and Pd–POZ complex 10a

A mixture of POZ ligand **5** or Pd–POZ complex **6** (0.21 mmol), chlorodiethylsilyl polystyrene (PS–DES–Cl, 100 mg, 0.14 mmol) and imidazole (33 mg, 0.49 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature 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 PS–DES-supported POZ ligand **9a** (100 mg) or PS–DES-supported Pd–POZ **10a** (121 mg). Elemental analysis of **9a**: Found: C, 82.74; H, 8.40; N, 0.16, containing 0.16% N, corresponding to 0.11 mmol ligand/g of polymer. Elemental analysis of **10a**: Found: C, 81.40; H, 8.39; N, 0.79, containing 0.79% N, corresponding to 0.56 mmol complex/g of polymer.

4.9. PS–Et-supported POZ ligand 9b and Pd–POZ complex 10b

A mixture of **5** or **6** (0.17 mmol), carboxyethylpolystyrene (PS–Et–COOH, 100 mg, 0.11 mmol) and diisopropylcarbodiimide (DIC, 0.04 mL, 0.23 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature 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 PS–Et-supported POZ ligand **9b** (123 mg) or PS–Et-supported Pd–POZ **10b** (159 mg). Elemental analysis of **9b**: Found: C, 85.25; H, 7.42; N, 1.10, containing 1.10% N, corresponding to 0.78 mmol ligand/g of polymer. Elemental analysis of **10b**: Found: C, 82.89; H, 7.48; N, 1.07, containing 1.07% N, corresponding to 0.76 mmol complex/g of polymer.

4.10. TentaGel-supported POZ ligand 9c and Pd–POZ complex 10c

A mixture of **5** or **6** (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 room temperature 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 TentaGel-supported POZ ligand **9c** (128 mg) or TentaGel-supported Pd–POZ **10c** (124 mg). Elemental analysis of **9c**: Found: C, 69.13; H, 8.30; N, 1.03, containing 1.03% N, corresponding to 0.37 mmol ligand/g of polymer. Elemental analysis of **10c**: Found: C, 66.15; H, 7.76; N, 0.98, containing 0.98% N, corresponding to 0.35 mmol complex/g of polymer.

4.11. General procedure for the Pd-catalyzed allylic alkylation using nonsupported ligand

A mixture of nonsupported ligand (0.004 mmol, 2 mol %) and $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.7 mg, 0.002 mmol, 1 mol %) in CH_2Cl_2 (1 mL) was stirred at room temperature under argon for 1 h. The resulting yellow solution was added to a mixture of 1,3-diphenyl-2-propenyl acetate **11** (50 mg, 0.2 mmol) and KOAc (0.4 mg, 0.004 mmol, 2 mol %) in CH_2Cl_2 (1 mL) via a cannula, followed by the addition of malonate **12a** (0.07 mL, 0.59 mmol) and BSA (0.15 mL, 0.59 mmol). The reaction was carried out at room temperature after 3 h. The reaction mixture was quenched with saturated NH_4Cl solution and extracted twice with ether. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by preparative TLC on silica gel (2:1 hexane–AcOEt) to give the alkylated product **13a**.

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

A mixture of polymer-supported ligand (0.01 mmol, 5 mol %), $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2 mg, 0.005 mmol, 2.5 mol %), 1,3-diphenyl-2-propenyl acetate **11** (50 mg, 0.2 mmol) and KOAc (0.4 mg, 0.004 mmol, 2 mol %) in CH_2Cl_2 (1 mL) was stirred at room temperature under argon for 1 h. To this mixture, cooled to the desired reaction temperature, was added malonate **12a** or **12b** (0.59 mmol) and BSA (0.15 mL, 0.59 mmol). The reaction was then carried out at the same temperature. After a certain time had elapsed, the mixture was quenched with saturated NH_4Cl solution, filtered, and extracted twice with ether. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by preparative TLC on silica gel (2:1 hexane–AcOEt) to give alkylated product **13a** or **13b**.

4.13. General procedure for the Diels–Alder reaction using nonsupported Pd–POZ complex

A suspension of nonsupported Pd–POZ complex (0.034 mmol) and $AgSbF_6$ (30 mg, 0.089 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature under argon for 1 h. The suspension was cooled to the desired reaction temperature and to which were added cyclopentadiene **17** (0.057 mL, 0.84 mmol) and CH_2Cl_2 (1 mL) solution of *N*-acryloyloxazolidinone **18** (25 mg, 0.18 mmol). The reaction was carried out at the same temperature. After a certain time had elapsed, the reaction mixture was quenched with saturated NH_4Cl solution and extracted twice with ether. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by preparative TLC on silica gel (1:1 hexane–AcOEt) to give Diels–Alder adduct **19**.

4.14. General procedure for the Diels–Alder reaction using polymer-supported Pd–POZ complex

A suspension of polymer-supported Pd–POZ complex (0.034 mmol) and $AgSbF_6$ (30 mg, 0.089 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature under argon for 1 h. The suspension was cooled to the desired reaction temperature and to which were added diene **17**, **20**, or **21** (0.84 mmol) and CH_2Cl_2 (1 mL) solution of dienophile **18**, **22a**, or **22b** (0.18 mmol). The reaction was carried out at the same temperature. After a certain time had elapsed, the reaction mixture was filtered, quenched with saturated NH_4Cl solution and extracted twice with ether. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by preparative TLC on silica gel (1:1 hexane–AcOEt) to give Diels–Alder adduct **19**, **23a**–**c**, **24a**, or **24b**.

4.15. Recycling experiments with supported ligand and catalyst

After allylic alkylation or Diels–Alder reaction, the reaction mixture was decanted off by using a cannula, and the solution of the reactants (allylic alkylation: acetate, malonate, and BSA, Diels–Alder reaction: diene and dienophile) for the next cycle added to the polymer.

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