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The Use of Porous Palladium(II)-polyimine in Cooperatively-catalyzed Highly Enantioselective Cascade Transformations

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Abstract: Porous organic polymers have prospects as functional substrates for catalysis, with quite different molecular properties from inorganic substrates. Here we disclose for the first time that porous palladium(II)-polyimines are excellent catalysts for cooperatively catalyzed and enantioselective cascade reactions. In synergy with a chiral amine co-catalyst, polysubstituted cyclopentenes and spirocyclic oxindoles, including the all-carbon quaternary stereocenter, were synthesized in high yields. High diastereo- and enantioselectivities were achieved for these dynamic kinetic asymmetric transformations (DYKAT) of enals with propargylic nucleophiles.

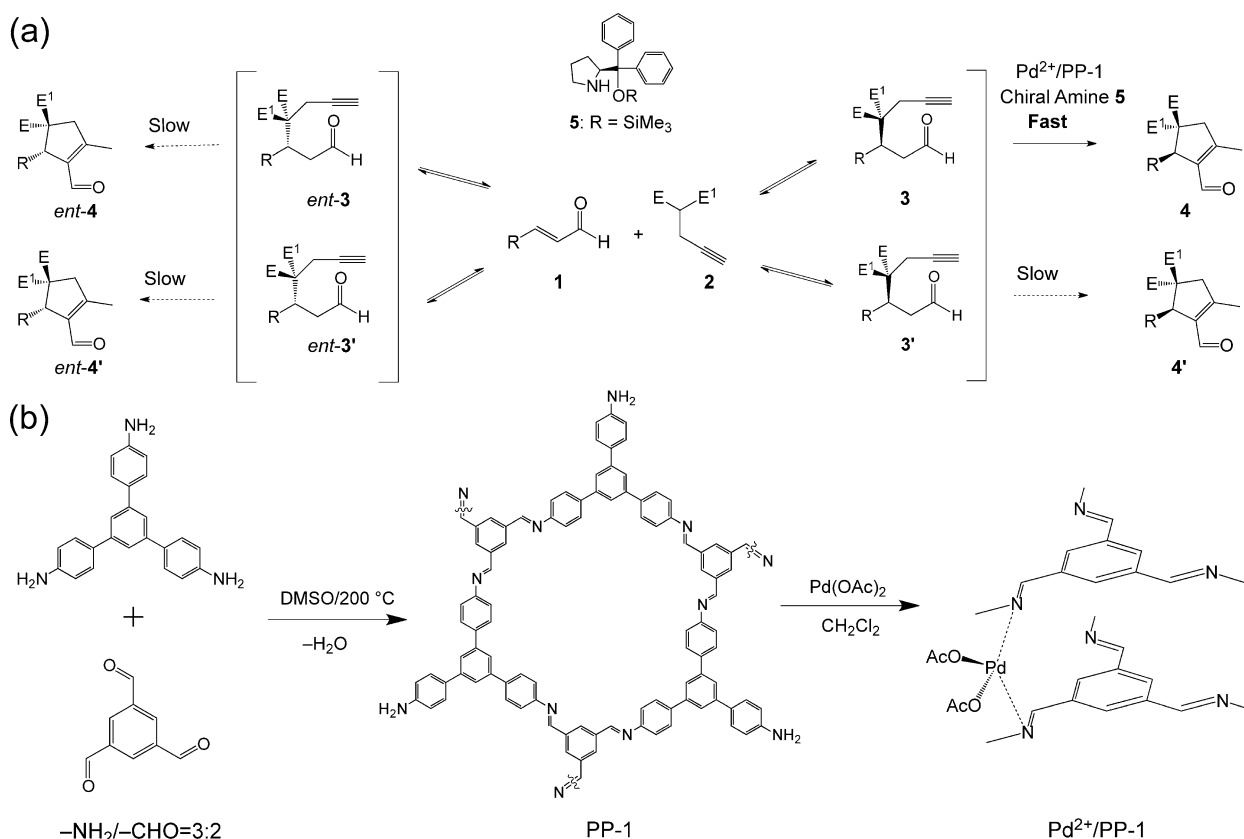
Keywords: cascade reaction; cooperative catalysis; enantioselective synthesis; heterogeneous catalysis; palladium; porous organic polymers

Porous polymers built from pure organic building blocks can display ultra-high surface areas and micropores (pores < 2 nm)^[1] due to cross-links or disordered interpenetrations among the polymer chains.^[2] Their covalent and often aromatic nature make them thermally and chemically stable.^[3] Only quite recently have such polymers started to be studied as functional and heterogeneous catalysts for single bond-forming transformations.^[4]

Porous polyimines are well suited as supports for catalysis as their imine groups can form complexes with metal ions. The imines are well suited for metal ions catalysts (Pd²⁺, Pt²⁺, Ru³⁺, Ir³⁺) that can be used

for coupling, cyclization and hydrogenation reactions.^[5] Ding et al. reported on a Pd²⁺ based catalyst that was heterogenized on a crystalline porous polyimine, which was effective for Suzuki–Miyaura coupling reactions.^[6] Amorphous porous polyimines, on the other hand, may have a larger potential to form complexes with noble metal ions than most crystalline polyimines. Their broad distributions of N...N distances and the significant amount of –NH₂ end groups will contribute to an enhanced tendency to form complexes with noble metal ions.^[7]

Porous organic substrates have only recently started being used for asymmetric catalysis, even though asymmetric synthesis of small molecules is of the utmost importance for life science research and the pharmaceutical industry.^[8] The application of cascade transformations is growing.^[9,10] It is an eco-friendly approach to create multiple C–C and C–hetero atom bonds in one-pot, which reduces the generation of waste and excess use of solvents in comparison to traditional organic step-by-step synthesis.^[11] The development of asymmetric versions for the generation of several contiguous stereocenters in a highly enantioselective fashion is still a major challenge. Particularly difficult is the synthesis of quaternary stereocenters.^[12] Consequently, it is relevant to investigate such eventual advantages for porous organic polymers as substrates for catalyzed asymmetric cascade transformations. Guided by our previous work on porous organic polymers,^[7d] we envisioned the synthesis of a Lewis acidic (Pd²⁺) based porous polyimine polymer that we could investigate as a catalyst for the dynamic kinetic asymmetric transformations (DYKAT) of enals **1** with propargylic nucleophiles **2** (E ≠ E')^[13,14] in cooperation with an amine catalyst^[13] (Scheme 1a). This reac-



Scheme 1. (a) Possible DYKAT between enals **1** and propargylic nucleophiles **2** in the presence of E and E¹ = electron withdrawing group.^[14] (b) Synthesis route of the porous polyimine (PP-1), and the catalyst Pd²⁺/PP-1. (An idealized structure of PP-1 only.)

tion proceeded *via* a reversible Michael/carbocyclization/isomerization cascade pathway, which could theoretically generate four possible stereoisomers of cyclopentenones **4** *via* Michael intermediates **3**. However, in cooperation with heterogeneous^[13] or homogeneous metal^[14]/chiral amine (**5**) catalyst systems a predominant stereoisomer of the corresponding poly-functionalized product **4** containing a quaternary stereocenter, can be assembled in high yield, diastereomeric ratio (dr) and enantiometric ratio (er).

Here, we show for the first time that porous Pd²⁺-polyimines are excellent co-catalysts for cooperatively catalyzed enantioselective cascade reactions. Our efforts began with the porous polyimine substrate, PP-1. It was synthesized through the condensation of 1,3,5-tris(4-aminophenyl)benzene and 1,3,5-benzenetricarboxaldehyde in refluxing DMSO (Scheme 1b), under dynamic equilibrium and the release of water. An unequal amine-to-aldehyde ratio of 3:2 was used, and the PP-1 displayed a narrow distribution of micropores and a broad distribution of mesopores. The catalyst Pd²⁺/PP-1 was formed by complexation of Pd²⁺ with the imine and possibly amine groups of PP-1. For the complexation, Pd(OAc)₂ was added to a suspension of PP-1 in CH₂Cl₂, and the Pd²⁺/PP-1 was re-

covered by a workup procedure (see experimental section).

The molecular conformations of PP-1 and Pd²⁺/PP-1 were studied by solid state nuclear magnetic resonance (NMR), infrared (IR), and X-ray photoelectron (XPS) spectroscopy (Figure 1). The solid state ¹³C{¹H} CPMAS NMR spectrum of PP-1 displays characteristic peaks for carbon atoms in imine and free aldehyde groups at chemical shifts of 163 and 192 ppm. The signals at 128 and 138 ppm belong to secondary and tertiary aromatic carbon atoms, respectively, while those at 16 ppm were assigned to -S-R based decomposition products of DMSO^[15] (additional signatures of the decomposition products appear to be convoluted with the side band intensities at ~35 ppm). The decomposition products of DMSO are also detected by an IR band at ~1035 cm⁻¹, see Figure 1a–b. The IR spectrum shows a strong band for the imine stretching (C=N) band at a frequency of 1669 cm⁻¹. A high-resolution XPS spectrum of Pd²⁺/PP-1 shows the characteristic doublet in the Pd 3d region. The peak at 337.9 eV corresponded to 3d_{5/2} and belongs to Pd²⁺. Similar 3d_{5/2} XPS bands were observed for Pd²⁺ in Pd/COF-LZU1 (337.7 eV) and a model complex of Pd/Phen (337.8 eV).^[6] In contrast, for free Pd(OAc)₂ that

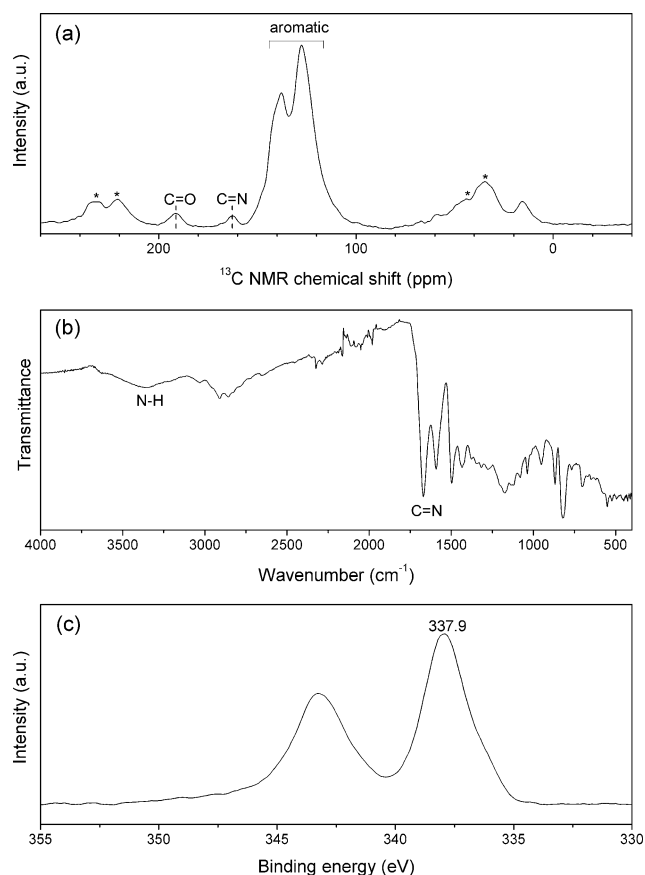


Figure 1. (a) Solid state $^{13}\text{C}\{^1\text{H}\}$ nuclear magnetic resonance spectrum of the porous polyimine (PP-1), side bands denoted by (*); (b) infrared spectrum of PP-1; (c) high-resolution X-ray photoelectron spectrum (Pd 3d) of the catalyst $\text{Pd}^{2+}/\text{PP-1}$.

band was detected at 338.4 eV. A shoulder peak at 336.0 eV indicates the existence of small relative amount of Pd^0 (9.8 wt %) in $\text{Pd}^{2+}/\text{PP-1}$ (Figure S2), which is quite common in such catalysts.^[16]

The porosities of the PP-1 and $\text{Pd}^{2+}/\text{PP-1}$ were studied by N_2 sorption experiments. Both compositions showed both (ultra)micro- and mesopores, which is indicative of highly cross-linked and tight interpenetrated structures. The PP-1 had a specific surface area of $256 \text{ m}^2 \text{ g}^{-1}$, which was reduced to $92 \text{ m}^2 \text{ g}^{-1}$ for the $\text{Pd}^{2+}/\text{PP-1}$. The large reduction indicated a change in the polymer conformation as the $\text{Pd}^{2+}/\text{PP-1}$ contained 2.3 wt % Pd. The adsorption and desorption isotherms of N_2 on PP-1 and $\text{Pd}^{2+}/\text{PP-1}$, in Figure 2 show distinct N_2 uptake at low partial pressures belonging to micropores. The desorption isotherms display a step at a partial pressure of $P/P_0 = \sim 0.45\text{--}0.5$, indicative of partially blocked mesopores. This cavitation based unloading occurred at lower relative pressures (0.31–0.36) for Ar (Figure S1, SI).^[17] The corresponding pore size distribution shows micropores in PP-1 with pore size centered at 0.7 nm and 1.3 nm, and broadly

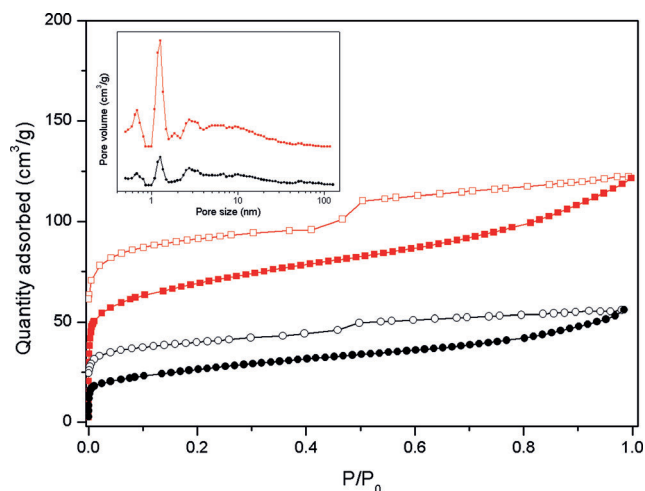


Figure 2. Nitrogen adsorption (solid) and desorption (empty) isotherms of the porous polyimine PP-1 (squares) and the catalyst $\text{Pd}^{2+}/\text{PP-1}$ (circles) at 77 K. Inset shows pore size distribution of PP-1 (upper line) and $\text{Pd}^{2+}/\text{PP-1}$ (lower line) analyzed on the N_2 adsorption isotherms with DFT method.

distributed mesopores. The large hystereses in between adsorption and desorption in Figure 2 correspond to “swelling”.^[18] It is still being investigated if such “swelling” relates to the degree of cross-linking, a somewhat elastic expansion of the polymer, or a restricted access to small pores.^[19] Both swelling of the polymer and the presence of mesopores can help to accommodate relatively large catalysts, reactants and products, and can contribute to the rapid mass transport of reactants and products.

The mesopores of $\text{Pd}^{2+}/\text{PP-1}$ were visible by transmission electron microscopy (TEM) (Figure 3), and display the character of intraparticle based and disordered mesopores, which are quite different compared with those in ordered mesoporous materials.^[20] In general, disordered mesopores are difficult to detect by TEM, with some previously reported TEM images not clearly displaying the mesopores;^[3c] here, the contrast variations in the images agree well with the pore sizes deduced from the N_2 adsorption data.

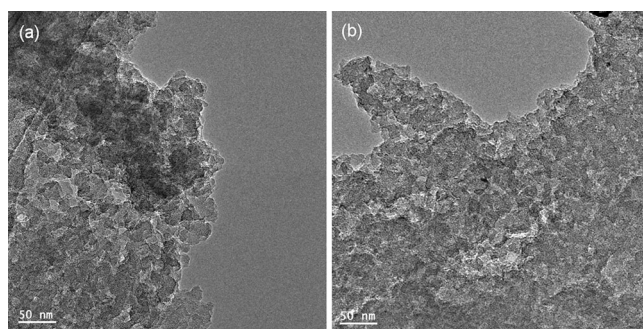


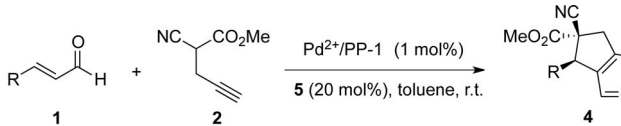
Figure 3. Transmission electron microscopy images of (a) PP-1 and (b) $\text{Pd}^{2+}/\text{PP-1}$.

After establishing the synthesis and characterization of $\text{Pd}^{2+}/\text{PP-1}$ in detail, we began to investigate if it could act as a catalyst for the synthesis of various carbocycles (Scheme 1a). Thus, a catalyst system of $\text{Pd}^{2+}/\text{PP-1}$ and chiral amine-based co-catalyst **5** was tested for the DYKAT reactions between enals **1** and propargylic nucleophile **2** that if successful could give the corresponding carbocycles **4** with an all-carbon stereocenter *via* Michael intermediates **3**. An initial screening of the conditions (Table S1, SI), revealed that highly enantioselective cascade reactions were possible using dynamic cascade catalysis in toluene with the catalytic system ($\text{Pd}^{2+}/\text{PP-1}$ /chiral amine). The co-catalytic reaction converted cinnamic aldehyde **1a** to **4a** in an 85 % yield with a diastereomeric ratio (dr) of 95:5 and an enantiometric ratio (er) of 97.5:2.5. To form **4** both the $\text{Pd}^{2+}/\text{PP-1}$ and the chiral amine **5** had to be present, demonstrating the synergy achieved by the two catalysts for the cascade sequence.

The catalytic system $\text{Pd}^{2+}/\text{PP-1}$ /chiral amine was further investigated for the dynamic cascade reactions for a set of enals **1** in toluene (Table 1). These Michael–carbocyclization reactions were highly enantioselective. The corresponding cyclopentenones **4** were isolated in high yields with up to 97:3 dr and 99.5:0.5 er. Moreover, having electron-donating or electron-withdrawing groups on the β -aryl-substituted **1** did not affect the efficiency or stereoselectivity of the reactions. The spirocyclic oxindole structural motif **7**, with an all carbon quaternary stereocenter, is a valuable structural motif present in several natural products and pharmaceuticals.^[21] With the $\text{Pd}^{2+}/\text{PP-1}$, we achieved similar (or better), as compared with amine-modified silica supported Pd^{2+} ,^[13] enantioselective formation of such spirocyclic oxindoles **7** (up to > 99.5:0.5 er) by the conjugate/carbocyclization cascade transformation between enals **1** and **6** (Scheme 2).

The cascade reactions with $\text{Pd}^{2+}/\text{PP-1}$ were significantly faster than with Pd^{2+} supported on aminopropyl-modified silica of the mesocellular foam type, as determined by $^1\text{H-NMR}$.^[13a] The products **4** also showed slightly higher dr and er. The absolute stereochemistry of the cyclopentenones **4** and the spirocyclic oxindoles **7** was determined by comparing them with the literature.^[14a,22] Performing the reactions with a chiral amine **5** provided carbocycles (1*R*,2*R*)-**4** (*R* = aryl) with an *R* configuration at C-1 and C-2, while the intermediate Michael adducts **3** were nearly racemic in the presence of the $\text{Pd}^{2+}/\text{PP-1}$ co-catalyst. Thus, the co-catalytic reactions proceed *via* the DYKAT mechanism.^[23] An important aspect in heterogeneous catalysis is the recovery of the solid catalyst. The $\text{Pd}^{2+}/\text{PP-1}$ catalyst showed excellent recyclability with respect to the yield of product **4a**, and the enantioselectivity of the cascade sequence was not significantly affected (Table S2, SI, 2.2 mol % of $\text{Pd}^{2+}/\text{PP-1}$

Table 1. Scope of use of a heterogeneous $\text{Pd}^{2+}/\text{PP-1}$ /chiral amine catalyst to react enals with propargylic nucleophiles into carbocycles.



Entry	R	Prod.	Time [h]	Yield [%] ^[a]	d.r. ^[b]	er [%] ^[c]
1		4a	24	85	19:1	97.5:2.5
2		4b	23	73	10:1	99:1
3		4c	24	77	15:1	99.5:0.5
4		4d	23	72	13:1	98.5:1.5
5		4e	21	79	12:1	96:4
6		4f	24	67	19:1	96:4
7		4g	24	88	23:1	98:2
8		4h	24	85	28:1	99.5:0.5
9		4i	24	87	27:1	98:2
10 ^[d]		4j	24	71	19:1	95:5
11	<i>n</i> -Bu	4k	21	84	6:1	98.5:1.5

^[a] Isolated yield of pure compound **4**.

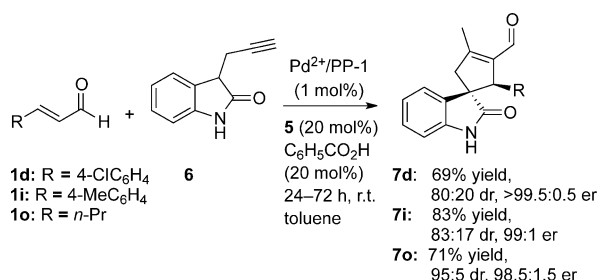
^[b] Determined by $^1\text{H-NMR}$.

^[c] Determined by chiral-phase HPLC analysis.

^[d] Reaction performed at 4 °C.

1 was used for the recycling experiments). No Pd^{2+} leaching was observed as determined by elemental analysis. (The elemental analysis was performed on the filtrate after hot filtration and after completion of the reaction. It showed very low Pd contents of 7.5 and 15.1 ppm in the filtrates, respectively. The background Pd content was 9 ppm as determined for a sample where no $\text{Pd}^{2+}/\text{PP-1}$ catalyst was added).

In summary, we showed for the first time that porous organic polymers can successively be applied to heterogeneous catalysis for asymmetric cascade reactions. First, the Lewis acidic catalyst $\text{Pd}^{2+}/\text{PP-1}$ was synthesized directly by complexation. Next, $\text{Pd}^{2+}/\text{PP-1}$



Scheme 2. Cascade synthesis of spirocyclic oxindoles **7**.

1 was shown to be an excellent heterogeneous catalyst for the DYKATs between enals and propargylic nucleophiles together with a chiral amine co-catalyst. The Pd²⁺/PP-1/chiral amine system provided an excellent catalysis platform for the synthesis of highly functionalized carbocycles and spirocyclic oxindoles, including the all-carbon quaternary center, in high yield with up to 97:3 dr and 99.5:0.5 er. It also exhibited a higher reactivity in comparison to systems based on amine-modified mesocellular silica particles. These results indicate that metal-bound polyimine based porous polymers (e. g. Pd²⁺/PP-1 and Pd/COF-LZU1^[6]) should be widely useful catalysts and co-catalysts for various cascade transformations involving C–C bond formation. We expect that mesoporosity, and the ability for the porous polymer to swell will be important properties for the use of nanoporous polymers as a functional catalyst. Here they could serve as a modular bridge between heterogeneous and homogeneous catalysis. In particular, applications towards integrated heterogeneous metal/chiral amine multiple relay catalysis could be expected.^[13b]

Experimental Section

Synthesis of PP-1

1,3,5-Tris(4-aminophenyl)benzene (0.375 mmol, 132 mg) was dissolved in 5 mL of dimethyl sulfoxide (DMSO) and formed a yellow solution. A colorless solution of 1,3,5-benzenetricarboxaldehyde (0.25 mmol, 41 mg) in 5 mL of DMSO were prepared, which was added drop-wise to the amine solution at a temperature of 50 °C. A pale yellow solution formed. This solution was heated at a temperature of 120 °C for 12 h and subsequently refluxed at a temperature of 200 °C under stirring for another 3 days. Yellow precipitates formed at 120 °C, which turned brown during the reflux. The brown precipitates were filtered off, and repeatedly washed with methanol or tetrahydrofuran until the filtrates were colorless. The resulting precipitates were dried at a temperature of 200 °C under a N₂ atmosphere.

Synthesis of Pd²⁺/PP-1

The coarse particles of PP-1 were ground with a mortar for 20 min into a fine powder. Pd(OAc)₂ (100 mg) was added to

a suspension of PP-1 (100 mg) in CH₂Cl₂ (12 mL) under nitrogen, and the reacting mixture was stirred for 24 h. Next, the reaction mixture was transferred to a centrifuge vial (45 mL) and centrifuged 3 times with CH₂Cl₂ (40 mL). The solid was purified by Soxhlex extraction with CH₂Cl₂ at a temperature of 70 °C for 24 h and subsequently dried under dynamic vacuum conditions.

General procedure for the combined transition metal/chiral amine catalytic enantioselective reaction using methyl propargylcyanoacetate

An oven-dried microwave vial equipped with a magnetic stir bar was charged with methyl propargylcyanoacetate (16.1 mg, 0.12 mmol, 1.2 equiv) and Pd²⁺/PP-1 (5 mg, 1.1 mol % or 2.5 mg, 0.55 mol %), followed by addition of toluene (0.100 mL) and the resulting mixture was stirred at room temperature for 5 min. In parallel to the above procedure, an oven-dried vial was charged with the aldehyde (0.1 mmol, 1.0 equiv), organocatalyst (6.5 mg, 0.02 mmol, 20 mol %) and followed by addition of toluene (0.150 mL), after stirring at room temperature for additional 5 min, the resulting mixture was transferred to the vial containing the mixture of palladium catalyst and methyl propargylcyanoacetate *via* a syringe. (Total volume of toluene = 0.250 mL, final concentration = 0.8 M to aldehyde). The reaction was stirred for the time shown in the table. The conversions and diastereomeric ratios were monitored by ¹H NMR analysis of the crude mixture. Upon completion, the mixture was directly subjected to flash chromatography on silica (pentane/EtOAc) affording the pure products.

Methyl (1*R*,2*R*)-1-cyano-3-formyl-4-methyl-2-phenyl-cyclopent-3-enecarboxylate (4a): oil; ¹H NMR (400 MHz, CDCl₃): δ 9.92 (s, 1H), 7.38–7.32 (m, 3H), 7.17–7.15 (m, 2H), 4.72 (bs, 1H), 3.89 (s, 3H), 3.41 (d, *J* = 14.8 Hz, 1H), 3.26 (dt, *J* = 12.4 Hz, *J'* = 1.2 Hz, 1H), 2.33 (d, *J* = 0.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): 186.2, 168.8, 157.8, 136.8, 136.6, 129.1, 128.7, 128.0, 117.4, 58.4, 54.4, 51.7, 47.9, 14.3; HRMS (ESI): calcd for [M + Na] (C₁₆H₁₅NO₃) requires *m/z* 292.0944, found 292.0946; [α]_D²⁵ = –68.2 (*c* = 1.0 CHCl₃). The enantiomeric excess was determined by HPLC analysis in comparison with authentic racemic material (ODH-column, *n*-hexane/*i*PrOH = 85/15, λ = 210 nm, 1.0 mL min^{–1}) *t*_r (major enantiomer) = 16.01 min, *t*_r (minor enantiomer) = 24.4 min.

General procedure for the combined transition metal/chiral amine catalytic enantioselective reaction using propargyloxindole

An oven-dried microwave vial equipped with a magnetic stir bar was charged with propargyloxindole (20.5 mg, 0.12 mmol, 1.2 equiv), PhCO₂H (2.4 mg, 0.02 mmol, 20 mol %) and Pd²⁺/PP-1 (5 mg, 1.1 mol %), followed by addition of toluene (0.100 mL) and the resulting mixture was stirred at room temperature for 5 min. In parallel to the above procedure, an oven-dried vial was charged with the aldehyde (0.1 mmol, 1.0 equiv), organocatalyst (6.5 mg, 0.02 mmol, 20 mol %) and followed by addition of toluene (0.150 mL), after stirring at room temperature for additional 5 min, the resulting mixture was transferred to the vial containing the mixture of palladium catalyst and propargylcyanoacetate *via* a syringe. (Total volume of toluene =

0.250 mL, final concentration = 0.8 M to aldehyde). The reaction was stirred for the time shown in the table. The conversions and diastereomeric ratio were monitored by ^1H NMR analysis of the crude mixture. Upon completion, the mixture was directly subjected to flash chromatography on silica (pentane/EtOAc) affording the pure products.

(1R,2R)-2-(4-chlorophenyl)-4-methyl-2'-oxospiro[cyclopent[3]ene-1,3'-indoline]-3-carbaldehyde (7d): Yellow oil; IR (neat): ν_{max} 3017 (w), 2923 (w), 1707 (m), 1666 (m), 1620 (m), 1489 (m), 1471 (m), 1378 (w), 1335 (m), 1215 (w), 1090 (w), 1015 (w), 843 (w), 746 (s), 667 (m), 592 (w), 569 (w), 524 (w), 492 (w) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 10.08 (s, 1H), 8.05 (br s, 1H), 7.10–7.01 (m, 3H), 6.80–6.72 (m, 3H), 6.69 (t, $J=7.6$ Hz, 1H), 6.33 (d, $J=7.6$ Hz, 1H), 4.61 (br s, 1H), 3.09 (d, $J=18.9$ Hz, 1H), 2.94 (d, $J=18.8$ Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125.8 MHz, CDCl_3): 187.1, 182.2, 161.6, 140.2, 137.5, 136.6, 132.9, 130.4, 129.5, 128.4, 128.3, 125.0, 122.2, 109.6, 57.9, 56.5, 48.9, 14.9; HRMS (ESI): calcd for $[\text{M}+\text{Na}]$ ($\text{C}_{20}\text{H}_{16}\text{ClNO}_2$) requires m/z 360.0762, found 360.0772; $[\alpha]_{\text{D}}^{25} = -99.8$ ($c=1$, CHCl_3). The enantiomeric excess was determined by HPLC analysis in comparison with authentic racemic material (ODH-column, n -hexane/ i PrOH = 80/20, $\lambda=210$ nm, 1.0 mL min^{-1}) t_{r} (major enantiomer) = 27.4 min, t_{r} (minor enantiomer) = 18.7 min.

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8 The Use of Porous Palladium(II)-polyimine in Cooperatively-catalyzed Highly Enantioselective Cascade Transformations

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