Silver-Triggered Activity of a Heterogeneous Palladium Catalyst in Oxidative Carbonylation Reactions

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Supporting Information

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General information

Unless otherwise noted, all reagents were used as received from commercial suppliers. Reactions were monitored using thin-layer chromatography (SiO₂). TLC plates were visualized with UV light (254 nm) or KMnO₄ stain. Flash chromatography was carried out with 60Å (particle size 35-70 μm) normal flash silica gel. NMR spectra were recorded at 400 MHz (¹H) and at 100 MHz (¹³C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in CDCl₃ (H = 7.26 and C = 77.0 ppm) as internal standard, and coupling constants (J) are given in Hz. HRMS were recorded using ESI-TOF techniques. The enantiomeric excess of compounds was determined by chiral GC using racemic compounds as references. The morphology and Pd loading of the heterogeneous palladium catalysts were determined by TEM (JEOL2010) and ICP-OES (Thermo ICAP 6000). XPS measurements were performed on a Thermo ESCALAB 250 configured with a monochromated AlKα (1486.8 eV) 150 W X-ray source, 0.5 mm circular spot size and a flood gun to counter charging effects.
**Preparation of Pd-AmP-CNC**

*Crystalline nanocellulose (CNC) foam preparation:* The CNC was prepared according to modified Shoseyov and Paltiel method. Microcrystalline cellulose (Avicel) was hydrolyzed in 63 wt% H$_2$SO$_4$. After stirring with a mechanical stirrer for 1h at 40-50 °C, the resulting suspension was cooled to 15 °C and centrifugated. The resulting supernatant was removed and the precipitate was resuspended in deionized water. This was repeated for 5 times. After the final wash, the CNC was resuspended in deionized water to reach a consistency of 3% and neutralized with 0.1 M NaOH, which was followed by sonication. Next, the CNC (3% consistency) was converted to a solid foam by lyophyilization.

*Amino-functionalized crystalline nanocellulose foam (AmP-CNC):* In an oven dried flask, CNC foam (1 equiv., 1g), tartaric acid (148 mg, 5% mol% to silane) was dispersed in dry toluene (40 mL). Next, 3-aminopropyltrimethoxysilane (3 equiv., 3.4 mL) was added and the mixture was stirred at 82 °C for 48 h. The crude AmP-CNC was removed and washed using soxholated extraction with acetone. After 16h, the AmP-CNC foam was dried under vacuum.

*Pd immobilized on amino-functionalized crystalline nanocellulose (Pd-AmP-CNC):* AmP-CNC (1.0 g) was suspended in pH-adjusted H$_2$O solution by the use of 0.1 N LiOH (pH 8; 30 ml) and was allowed to stir at room temperature for 10 min. Li$_2$PdCl$_4$ (100 mg) was added and the resulting suspension was left to stir over night. The suspension was then centrifuged, and the separated solid was washed with H$_2$O (3-4 times) and dried under vacuum for 24 h. The amount of Pd(II) loaded on AmP-CNC was determined to be 4.61 wt.% by ICP-OES. The Pd-Amp-CNC was characterized by its TEM and XPS (see Figures S1 and S2)
Characterizations of Pd-AmP-CNC

Figure S1. Transmission Electron Microscope (TEM) images.

Figure S2. X-ray photoelectron spectroscopy (XPS) spectrum.
**Determination of Cl/Pd molar ratios in Pd-AmP-CNC**

The Pd amounts in Pd-AmP-CNC were determined by inductively coupled plasma mass spectrometry (ICP-MS).

The Cl⁻ amounts in Pd-AmP-CNC were determined by the Mohr titration method: 30 mL deionized water, 0.01 M AgNO₃, 5% K₂CrO₄. The standard curve was determined by titration using 0.01 M NaCl solution.

The experiments for determination of Cl/Pd molar ratios in Pd-AmP-CNC were repeated for 5 times, and the Cl/Pd molar ratios value were the average values. The Cl/Pd molar ratios before and after treatment by AgOTf were determined to be 2.1/1 and 0.03/1, respectively.
**General procedure for the preparation of allene amides 1**

*For the preparation of allene amides 1a−1f, 1i−1k, 1m−1n, and 1fa, see ref. [2]. For the preparation of allene amide 1h, see ref. [3].*

**Preparation of allene amide 1g**

![Reaction Diagram](image.png)

To a solution of allene amide 1f (340 mg, 1.0 mmol) in dry Et₂O (5 mL) was added LiAlH₄ (48.0 mg, 1.2 mmol) at 0 °C under Ar atmosphere. The mixture was stirred for 2 h at 0 °C, then diluted with Et₂O (10 mL) and carefully quenched with H₂O (5 mL). The organic layer was separated, and the aqueous layer was extracted with Et₂O (2 × 30 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated in vacuo.

The residue was dissolved in DCM (10 mL) and then Et₃N (0.3 mL, 1.5 mmol), 4-dimethylaminopyridine (DMAP, 12.5 mg, 0.1 mmol), and TsCl (210 mg, 1.1 mmol) was added at room temperature. The mixture was stirred for 2 h and concentrated. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 2/1) to afford 1g (412 mg, 0.92 mmol, 92% yield).

*5-Methyl-3-(((4-methylphenyl)sulfonamido)methyl)-hexa-3,4-dien-1-yl-4-methyl-benzenesulfonate (1g):*

![5-Methyl-3-(((4-methylphenyl)sulfonamido)methyl)-hexa-3,4-dien-1-yl-4-methyl-benzenesulfonate](image.png)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.78-7.68 (m, 4H), 7.37-7.27 (m, 4H), 4.48 (t, J = 6.4 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 3.38 (d, J = 6.4 Hz, 2H), 2.43 (d, J = 9.6 Hz, 6H), 2.24 (t, J = 6.4 Hz, 2H), 1.60 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 198.0, 144.8, 143.5, 136.8, 133.1, 129.8, 129.7, 127.8, 127.0, 101.7, 94.2, 68.3, 45.1, 29.9, 21.6, 21.5, 20.5; HRMS (ESI): calc. for C₂₂H₂₇NNaO₅S₂ [M+Na]⁺: 472.1223;
For the preparation of allene amide 1l, 1o and 1p, see below:

Using the general procedure as described in ref. [2]:

For 1l, using 4-methylcyclohexan-1-one as the ketone in the step of S1→S2.

For 1o, using BocNHs instead of BocNHTs in the step of S3→1.

For 1p, using BocNHMs instead of BocNHTs in the step of S3→1.

4-Methyl-N-(3-(4-methylcyclohexylidene)-2-phenyl-allyl)benzenesulfonamide (1l)

(40% starting from S1), colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78-7.74 (m, 2H), 7.32-7.17 (m, 7H), 4.60 (t, J = 6.4 Hz, 1H), 3.94 (d, J = 6.4 Hz, 2H), 2.42 (s, 3H), 2.29-2.23 (m, 2H), 2.13-2.04 (m, 2H), 1.88-1.83 (m, 2H), 1.56-1.50 (m, 1H), 1.20-1.10 (m, 2H), 0.96 (d, J = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.7, 143.4, 136.7, 135.2, 129.7, 128.6, 127.2, 126.9, 125.6, 109.6, 100.1, 42.8, 36.0, 32.1, 30.8, 22.1, 21.5; HRMS (ESI): calc. for C$_{23}$H$_{27}$NNaO$_2$S [M+Na]$^+$: 404.1655; found: 404.1644.

N-(4-methyl-2-phenyl-penta-2,3-dien-1-yl)-4-nitrobenzenesulfonylamine (1o)

(54% starting from S1), colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31-8.26 (m, 2H), 8.03-7.98 (m, 2H), 7.29-7.24 (m, 2H), 7.23-7.14 (m, 3H), 5.06 (t, J = 6.4 Hz, 1H),

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4.04 (d, J = 6.4 Hz, 2H), 1.76 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 200.6, 149.9, 145.8, 134.8, 128.6, 128.2, 127.3, 127.1, 125.7, 124.2, 102.7, 100.0, 43.2, 20.2; HRMS (ESI): calc. for C$_{18}$H$_{18}$N$_2$NaO$_4$S [M+Na]$^+$: 381.0879; found: 381.0871.

$N$-(4-methyl-2-phenyl-penta-2,3-dien-1-yl)methanesulfonamide ($1p$) (48% starting from S1), colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.41-7.29 (m, 4H), 7.27-7.21 (m, 1H), 4.45-4.44 (m, 1H), 4.15 (d, J = 6.4 Hz, 2H), 2.96 (s, 3H), 1.86 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 200.3, 135.1, 128.7, 127.2, 125.9, 102.9, 101.1, 43.1, 40.8, 20.4; HRMS (ESI): calc. for C$_{13}$H$_{17}$NNaO$_2$S [M+Na]$^+$: 274.0872; found: 274.0881.
**Initial experiments**

- Ethyl 2-(5,5-dimethyl-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)acetate (3fa)

  - Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31-7.20 (m, 2H), 6.74-6.64 (m, 3H), 5.81-5.68 (m, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 4.14 (d, $J = 0.8$ Hz, 2H), 3.20 (d, $J = 0.8$ Hz, 2H), 1.53 (s, 6H), 1.29 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.4, 145.5, 136.7, 129.0, 127.7, 115.1, 112.6, 67.0, 60.9, 57.8, 34.8, 25.2, 14.2; HRMS (ESI): calc. for C$_{16}$H$_{21}$NNaO$_2$ [M+Na]$^+$: 282.1465; found: 282.1471.

- Ethyl 2-(5,5-dimethyl-1-tosyl-2,5-dihydro-1H-pyrrol-3-yl)acetate (3f)

  - Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76-7.68 (m, 2H), 7.33-7.23 (m, 2H), 5.36-5.34 (m, 1H), 4.15-4.04 (m, 4H), 3.02 (d, $J = 0.8$ Hz, 2H), 2.38 (s, 3H), 1.49 (s, 6H), 1.20 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.7, 142.8, 137.9, 134.5, 129.3, 127.4, 127.2, 71.5, 60.9, 56.6, 34.4, 27.7, 21.4, 14.0; HRMS (ESI): calc. for C$_{17}$H$_{23}$NNaO$_4$S [M+Na]$^+$: 360.1240; found: 360.1238.
## Optimization of reaction conditions

Table S1. Optimization of reaction conditions in oxidative carbonylation of 1a.\(^a\)

| Entry | Catalyst | Oxidant | Solvent | Additive | Yield of 2a\(^b\) | Recovery of 1a |
|-------|----------|---------|---------|----------|-------------------|----------------|
| 1     | Pd(TFA)\(_2\) | BQ      | CHCl\(_3\) | none     | 0                 | 92             |
| 2     | Pd(OAc)\(_2\) | BQ      | CHCl\(_3\) | none     | 0                 | 94             |
| 3     | PdCl\(_2\)    | BQ      | CHCl\(_3\) | none     | 0                 | 90             |
| 4     | Pd(PhH)\(_2\)Cl\(_2\) | BQ | CHCl\(_3\) | none     | 0                 | 95             |
| 5     | Pd(TFA)\(_2\) | 2-Methyl-BQ | CHCl\(_3\) | none     | 0                 | 90             |
| 6     | Pd(TFA)\(_2\) | Tetrafluoro-BQ | CHCl\(_3\) | none     | 0                 | 84             |
| 7     | Pd(TFA)\(_2\) | 2,6-Dimethyl-BQ | CHCl\(_3\) | none     | 0                 | 92             |
| 8     | Pd(TFA)\(_2\) | 2,6-Dimethoxy-BQ | CHCl\(_3\) | none     | 0                 | 91             |
| 9     | Pd(TFA)\(_2\) | BQ      | THF     | none     | 0                 | 94             |
| 10    | Pd(TFA)\(_2\) | BQ      | Toluene | none     | 0                 | 96             |
| 11    | Pd(TFA)\(_2\) | BQ      | Acetone | none     | 0                 | 93             |
| 12    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | none     | 0                 | 94             |
| 13    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | AgOTf    | 95                | 0              |
| 14    | Pd(TFA)\(_2\) | BQ      | CHCl\(_3\) | AgOTf    | 18                | 0              |
| 15    | Li\(_2\)PdCl\(_4\) | BQ | CHCl\(_3\) | AgOTf    | 23                | 0              |
| 16    | none          | BQ      | CHCl\(_3\) | AgOTf    | 0                 | 35             |
| 17    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | Cu(OTf)\(_2\) | 0             | 29             |
| 18    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | Fe(OTf)\(_3\) | 0             | 40             |
| 19    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | Zn(OTf)\(_2\) | 0             | 0              |
| 20    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | AgNO\(_3\) | 0                 | 90             |
| 21    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | AgTFA    | 25                | 0              |
| 22    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | AgOAc    | 0                 | 91             |
| 23    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | AgPF\(_6\) | 91                | 0              |
| 24    | Pd-AmP-CNC    | BQ      | CHCl\(_3\) | AgSbF\(_6\) | 94                | 0              |
| 25\(^c\) | Pd-AmP-CNC | BQ      | CHCl\(_3\) | AgOTf    | 94                | 0              |
| 26\(^c\) | Pd-AmP-MCF | BQ      | CHCl\(_3\) | AgOTf    | 90                | 0              |

\(^a\) The reaction was conducted by using 0.2 mmol of 1a, 1 atm of CO, 5 mol% of catalyst, 1.1 equiv. of oxidant, 10 mol% of additive (if any), and 1.0 mL of solvent at room temperature for 12 h.\(^b\) Determined by NMR using anisole as the internal standard. \(^c\) 0.5 mol% of Pd catalyst and 1.0 mol% of AgOTf was used. Reaction time: 30 min.
**Typical procedure for the formation of pyrrolidones 2**

*Preparation of 4-phenyl-3-(prop-1-en-2-yl)-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2a):*

![Chemical structure of 2a]

To a solution of Pd-AmP-CNC (2.3 mg, 0.001 mmol), AgOTf (0.51 mg, 0.002 mmol) and BQ (23.8 mg, 0.22 mmol) in CHCl₃ (1.0 mL) was added allene amide 1a (65.4 mg, 0.2 mmol). The tube was closed with a septum, evacuated and filled with carbon monoxide gas using a balloon. The procedure was repeated three times. The reaction was stirred at room temperature for 30 min and then evaporated. The residue was purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford 2a (65.5 mg, 93%), colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.04-8.01 (m, 2H), 7.52-7.45 (m, 2H), 7.43-7.39 (m, 3H), 7.36-7.26 (m, 2H), 5.32-5.29 (m, 1H), 5.16-5.15 (m, 1H), 4.69 (s, 2H), 2.44 (s, 3H), 1.83 (t, J = 1.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.7, 149.7, 145.1, 135.5, 134.8, 133.2, 132.0, 130.3, 129.8, 128.9, 128.2, 127.5, 120.1, 51.1, 21.7, 21.6; HRMS (ESI): calc. for C₂₀H₁₉N₉NaO₃ [M+Na]⁺: 376.0978; found: 376.0971.

The general method from above was used for the preparation of the following compounds:

*4-Benzyl-3-(prop-1-en-2-yl)-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2b)*

![Chemical structure of 2b]

84% isolated yield, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.94-7.91 (m, 2H), 7.36-7.23 (m, 5H), 7.13-7.09 (m, 2H), 5.29-5.27 (m, 1H), 5.04-5.02 (m, 1H), 4.18 (s, 2H), 3.79 (s, 2H), 2.42 (s, 3H), 2.00 (t, J = 1.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 153.5, 145.0, 136.5, 135.3, 134.9, 129.7, 128.6, 128.1, 127.3, 118.9, 100.0, 51.6, 34.8, 21.9, 21.7; HRMS (ESI): calc. for C₂₁H₂₁N₉NaO₃ [M+Na]⁺: 390.1134; found: 390.1135.
4-Butyl-3-(prop-1-en-2-yl)-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2c)

90% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98-7.95 (m, 2H), 7.34-7.25 (m, 2H), 5.22-5.19 (m, 1H), 4.91-4.89 (m, 1H), 4.31 (s, 2H), 2.48-2.39 (m, 5H), 1.93 (t, $J = 1.2$ Hz, 3H), 1.50-1.45 (m, 2H), 1.44-1.31 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.9, 155.7, 144.9, 135.6, 135.4, 134.0, 129.7, 128.1, 118.4, 51.7, 30.4, 28.3, 22.6, 21.8, 21.7, 13.7; HRMS (ESI): calc. for C$_{14}$H$_{23}$NNaO$_3$S [M+Na]$^+$: 356.1291; found: 356.1281.

4-Isopropyl-3-(prop-1-en-2-yl)-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2d)

85% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00-7.95 (m, 2H), 7.35-7.25 (m, 2H), 5.21-5.18 (m, 1H), 4.87-4.85 (m, 1H), 4.33 (s, 2H), 3.17-3.09 (m, 1H), 2.43 (s, 3H), 1.92 (t, $J = 1.2$ Hz, 3H), 1.13 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.9, 160.9, 144.9, 135.6, 135.5, 132.9, 129.7, 128.1, 118.2, 48.6, 27.6, 21.9, 21.7, 21.6; HRMS (ESI): calc. for C$_{17}$H$_{21}$NNaO$_3$S [M+Na]$^+$: 342.1134; found: 342.1140.

4-Cyclopentyl-3-(prop-1-en-2-yl)-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2e)

90% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99-7.96 (m, 2H), 7.35-7.25 (m, 2H), 5.20-5.17 (m, 1H), 4.87-4.85 (m, 1H), 4.34 (s, 2H), 3.17-3.10 (m, 1H), 2.43 (s, 3H), 1.92 (t, $J = 1.2$ Hz, 3H), 1.90-1.84 (m, 5H), 1.79-1.62 (m, 4H),
1.51-1.40 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.9, 159.0, 144.9, 135.7, 135.6, 133.9, 129.7, 128.1, 118.2, 49.2, 39.0, 32.7, 25.8, 21.9, 21.7; HRMS (ESI): calc. for C$_{19}$H$_{23}$NNaO$_5$S [M+Na]$^+$: 368.1291; found: 368.1285.

Ethyl 2-(5-oxo-4-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrol-3-yl)acetate (2f)

88% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99-7.95 (m, 2H), 7.35-7.25 (m, 2H), 5.25-5.22 (m, 1H), 4.93-4.91 (m, 1H), 4.48 (s, 2H), 4.18 (q, $J = 7.2$ Hz, 2H), 3.48 (s, 2H), 3.48 (s, 2H), 2.43 (s, 3H), 1.94 (t, $J = 1.2$ Hz, 3H), 1.27 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.5, 167.1, 146.2, 145.1, 137.1, 135.3, 135.1, 129.8, 128.1, 119.3, 61.7, 52.2, 34.3, 21.7, 21.4, 14.1; HRMS (ESI): calc. for C$_{18}$H$_{21}$NNaO$_5$S [M+Na]$^+$: 386.1033; found: 386.1043.

2-(5-Oxo-4-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrol-3-yl)ethyl-4-methylbenzenesulfonate (2g)

97% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96-7.91 (m, 2H), 7.76-7.70 (m, 2H), 7.36-7.25 (m, 4H), 5.17-5.14 (m, 1H), 4.83-4.80 (m, 1H), 4.23 (s, 2H), 4.14 (t, $J = 6.4$ Hz, 2H), 2.80 (t, $J = 6.4$ Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H), 1.84 (t, $J = 1.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.0, 149.4, 145.4, 145.1, 136.8, 135.2, 135.0, 132.2, 130.1, 129.7, 128.0, 127.7, 119.0, 67.0, 51.8, 28.0, 21.7, 21.6, 21.5; HRMS (ESI): calc. for C$_{23}$H$_{25}$NNaO$_6$S$_2$ [M+Na]$^+$: 498.1016; found: 498.1021.

4-Butyl-3-(prop-1-en-2-yl)-1-tosyl-5-vinyl-1,5-dihydro-2H-pyrrol-2-one (2h)
94% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.97-7.94 (m, 2H), 7.32-7.25 (m, 2H), 5.60 (d, $J = 16.8$ Hz, 1H), 5.48 (d, $J = 9.6$ Hz, 1H), 5.35 (ddd, $J = 16.8$, 9.6, 8.8 Hz, 1H), 5.22-5.20 (m, 1H), 5.07 (d, $J = 8.8$ Hz, 1H), 4.92-4.90 (m, 1H), 2.56-2.50 (m, 1H), 2.42 (s, 3H), 2.19-2.11 (m, 1H), 1.94 (t, $J = 1.2$ Hz, 3H), 1.40-1.27 (m, 4H), 0.91 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.6, 158.2, 144.7, 136.5, 135.4, 133.7, 133.1, 129.5, 128.2, 121.8, 118.6, 65.8, 30.2, 26.7, 22.6, 21.9, 21.7, 13.7; HRMS (ESI): calc. for C$_{20}$H$_{25}$NNaO$_3$S [M+Na]$^+$: 382.1447; found: 382.1456.

5-Methyl-4-phenyl-3-(prop-1-en-2-yl)-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2i)

96% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05-8.01 (m, 2H), 7.44-7.39 (m, 3H), 7.36-7.25 (m, 4H), 5.27-5.24 (m, 1H), 5.23-5.11 (m, 2H), 2.44 (s, 3H), 1.73 (t, $J = 1.2$ Hz, 3H), 1.47 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.5, 157.0, 144.8, 136.2, 134.3, 131.9, 131.8, 129.9, 128.8, 128.3, 128.2, 120.3, 59.0, 21.7, 21.6, 19.8; HRMS (ESI): calc. for C$_{21}$H$_{27}$NNaO$_3$S [M+Na]$^+$: 390.1134; found: 390.1141.

4-Butyl-5-phenyl-3-(prop-1-en-2-yl)-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2j)

71% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.32 (m, 3H), 7.31-7.29 (m, 2H), 7.28-7.05 (m, 4H), 5.60 (s, 1H), 5.27-5.24 (m, 1H), 4.97-4.95 (m, 1H), 2.48-2.42 (m, 1H), 2.35 (s, 3H), 2.00 (t, $J = 1.2$ Hz, 3H), 1.90-1.74 (m, 1H), 1.33-1.19 (m, 4H), 0.84 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.0, 159.5, 144.3, 136.0, 135.5, 134.7, 133.4, 129.0, 128.8, 128.7, 128.0, 127.9, 118.6, 66.3, 30.2, 26.8, 22.5, 22.0, 21.6, 13.6; HRMS (ESI): calc. for C$_{24}$H$_{27}$NNaO$_3$S
[M+Na]⁺: 432.1604; found: 432.1600.

4-Phenyl-3-(1-phenylvinyl)-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2k)

92% isolated yield, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.05-8.02 (m, 2H), 7.46-7.42 (m, 2H), 7.37-7.31 (m, 2H), 7.30-7.16 (m, 8H), 5.89-5.88 (m, 1H), 5.42-5.41 (m, 1H), 4.85 (s, 2H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 151.6, 145.1, 138.7, 137.6, 135.4, 131.7, 131.2, 130.5, 129.8, 128.7, 128.4, 128.2, 128.1, 127.6, 126.2, 119.5, 51.1, 21.7; HRMS (ESI): calc. for C₂₅H₂₁NNaO₃S [M+Na]⁺: 438.1134; found: 438.1129.

3-(4-Methylcyclohex-1-en-1-yl)-4-phenyl-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2l)

94% isolated yield, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.04-7.99 (m, 2H), 7.49-7.44 (m, 2H), 7.42-7.38 (m, 3H), 7.36-7.31 (m, 2H), 5.83-5.81 (m, 1H), 4.73-4.61 (m, 2H), 2.43 (s, 3H), 2.23-2.18 (m, 1H), 2.09-2.05 (m, 1H), 1.99-1.87 (m, 1H), 1.76-1.65 (m, 3H), 1.29-1.22 (m, 1H), 0.95 (d, J = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 148.7, 145.0, 135.5, 133.6, 132.4, 131.2, 130.1, 129.7, 128.8, 128.2, 127.9, 127.4, 50.9, 34.0, 30.7, 27.7, 27.0, 21.7, 21.6; HRMS (ESI): calc. for C₂₅H₂₅NNaO₃S [M+Na]⁺: 430.1447; found: 430.1454.

3-(Cyclohept-1-en-1-yl)-4-phenyl-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2m)

84% isolated yield, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.03-7.99 (m, 2H),
7.49-7.45 (m, 2H), 7.42-7.38 (m, 3H), 7.36-7.33 (m, 2H), 5.98 (t, J = 6.8 Hz, 1H),
4.65 (s, 2H), 2.44 (s, 3H), 2.22-2.15 (m, 4H), 1.77-1.68 (m, 2H), 1.57-1.49 (m, 4H);
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.2, 147.7, 144.9, 137.0, 135.6, 135.4, 134.0, 132.5,
130.0, 129.8, 128.7, 128.2, 127.5, 128.0, 127.9, 118.6, 66.3, 30.2, 26.8, 22.5, 22.0, 21.6, 13.6; HRMS (ESI): calc. for C\(_{25}\)H\(_{27}\)NNaO\(_3\)S [M+Na]\(^+\): 444.1604; found: 444.1600.

\((E)-3-(cyclooct-1-en-1-yl)-4-phenyl-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (2n)\)

87% isolated yield, colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02-7.98 (m, 2H),
7.52-7.45 (m, 2H), 7.42-7.32 (m, 5H), 5.80 (t, J = 5.2 Hz, 1H), 4.67 (s, 2H), 2.43 (s,
3H), 2.24-2.17 (m, 4H), 1.56-1.47 (m, 6H), 1.38-1.29 (m, 2H); \(^{13}\)C NMR (100 MHz,
CDCl\(_3\)) \(\delta\) 168.0, 159.5, 144.3, 136.0, 135.5, 134.7, 133.4, 129.0, 128.7, 128.0,
127.9, 118.6, 66.3, 30.2, 26.8, 22.5, 22.0, 21.6, 13.6; HRMS (ESI): calc. for C\(_{25}\)H\(_{27}\)NNaO\(_3\)S [M+Na]\(^+\): 444.1604; found: 444.1600.

\(1-((4-Nitrophenyl)sulfonyl)-4-phenyl-3-(prop-1-en-2-yl)-1,5-dihydro-2H-pyrrol-2-one (2o)\)

79% isolated yield, colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.43-8.32 (m, 4H),
7.51-7.42 (m, 5H), 5.35-5.32 (m, 1H), 5.18-5.16 (m, 1H), 4.73 (s, 2H), 1.83 (t, J = 1.2
Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.7, 150.9, 150.5, 143.6, 134.5, 132.8,
131.6, 130.7, 129.7, 129.0, 127.5, 124.3, 120.5, 51.1, 21.5; HRMS (ESI): calc. for C\(_{19}\)H\(_{16}\)N\(_2\)NaO\(_3\)S [M+Na]\(^+\): 407.0672; found: 407.0680.

\(1-(Methylsulfonyl)-4-phenyl-3-(prop-1-en-2-yl)-1,5-dihydro-2H-pyrrol-2-one (2o)\)
71% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53-7.49 (m, 2H), 7.46-7.41 (m, 3H), 5.39-5.37 (m, 1H), 5.25-5.24 (m, 1H), 4.68 (s, 2H), 3.40 (s, 3H), 1.90 (t, $J = 1.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.8, 134.8, 133.0, 131.8, 130.5, 129.0, 127.5, 120.3, 116.1, 50.4, 41.1, 21.6; HRMS (ESI): calc. for C$_{14}$H$_{15}$NNaO$_3$S [M+Na]$^+$: 300.0665; found: 300.0672.
Typical procedure for the formation of polycyclic compounds 4

Preparation of 5-methyl-2,8a-diphenyl-7-tosyl-3a,4,7,8,8a,8b-hexahydropyrrolo-[3,4-e]isoindole-1,3,6(2H)-trione (4a):

To a solution of Pd-AmP-CNC (2.3 mg, 0.001 mmol), AgOTf (0.51 mg, 0.002 mmol) and BQ (23.8 mg, 0.22 mmol) in CHCl₃ (1.0 mL) was added allene amide 1a (65.4 mg, 0.2 mmol). The tube was closed with a septum, evacuated and filled with carbon monoxide gas using a balloon. The procedure was repeated three times. The reaction was stirred at room temperature for 30 min. After finished, the mixture was filtrated and washed by CHCl₃ for two times. The obtained solution was evaporated and then diluted in the reaction tube by toluene (0.5 mL), followed by the addition of N-Phenylmaleimide (69.2 mg, 0.4 mmol). The tube was closed with a septum and the reaction mixture was stirred at 120°C for 24 h. After that, the mixture was concentrated and the residue was purified via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1) to afford 4a (65.5 mg, 74%), colorless oil.

1H NMR (400 MHz, CDCl₃) δ 7.91-7.87 (m, 2H), 7.43-7.31 (m, 6H), 7.23-7.11 (m, 4H), 7.00-6.94 (m, 2H), 5.38 (d, J = 5.6 Hz, 1H), 4.04 (d, J = 8.4 Hz, 1H), 3.92 (d, J = 10.8 Hz, 1H), 3.23-3.16 (m, 1H), 2.61-2.55 (m, 1H), 2.41 (s, 3H), 2.32 (s, 3H), 2.20-2.13 (m, 1H); 13C NMR (100 MHz, CDCl₃) δ 177.1, 175.4, 164.0, 152.2, 144.8, 142.6, 135.2, 131.2, 129.6, 129.4, 129.1, 128.9, 128.8, 128.3, 127.9, 126.3, 125.1, 55.3, 46.5, 46.0, 39.0, 33.9, 21.7, 19.4; HRMS (ESI): calc. for C₃₀H₂₆N₂NaO₅S [M+Na]⁺: 549.1455; found: 549.1444.

The general method from above was used for the preparation of the following compounds:

2-(5-Methyl-1,3,6-trioxo-2-phenyl-7-tosyl-2,3,3a,4,6,7,8,8b-octahydropyrrolo[3,4-e]-isoindol-8a(1H)-yl)ethyl 4-methylbenzenesulfonate (4g)
70% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92-7.89 (m, 2H), 7.79-7.75 (m, 2H), 7.43-7.38 (m, 5H), 7.28-7.25 (m, 2H), 6.99-6.94 (m, 2H), 4.82 (d, $J$ = 11.2 Hz, 1H), 4.17-3.99 (m, 2H), 3.78 (d, $J$ = 11.2 Hz, 1H), 3.44-3.38 (m, 2H), 2.80-2.72 (m, 2H), 2.48 (s, 3H), 2.41 (s, 3H), 2.20 (s, 3H), 2.17-1.97 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.0, 175.0, 163.5, 151.6, 145.5, 145.1, 134.9, 132.2, 131.1, 130.2, 129.6, 129.1, 128.9, 128.2, 127.9, 126.8, 126.2, 65.9, 51.1, 45.7, 39.9, 38.7, 37.3, 32.6, 21.8, 21.7, 19.5; HRMS (ESI): calc. for C$_{33}$H$_{32}$N$_2$NaO$_8$S$_2$ [M+Na]$^+$: 671.1492; found: 671.1499.

5,8-Dimethyl-2,8a-diphenyl-7-tosyl-3a,4,7,8a,8b-hexahydropyrrolo[3,4-e]isoindole-1,3,6(2H)-trione (4i)

68% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01-7.96 (m, 2H), 7.43-7.30 (m, 7H), 7.25-7.23 (m, 1H), 7.22-7.14 (m, 2H), 6.95-6.91 (m, 2H), 5.88 (q, $J$ = 6.4 Hz, 1H), 4.17 (d, $J$ = 8.0 Hz, 1H), 3.15-3.09 (m, 1H), 2.52-2.46 (m, 1H), 2.40 (s, 3H), 2.26 (s, 3H), 1.97-1.89 (m, 1H), 1.03 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.2, 175.2, 164.4, 151.4, 144.4, 138.4, 135.7, 131.3, 130.1, 129.2, 129.1, 129.0, 128.9, 128.8, 128.0, 126.5, 58.7, 50.9, 46.4, 38.7, 34.9, 21.7, 21.6, 19.6; HRMS (ESI): calc. for C$_{31}$H$_{28}$N$_2$NaO$_5$S [M+Na]$^+$: 563.1611; found: 563.1610.

2,3b-Diphenyl-5-tosyl-3b,4,5,7,8,9,10,11,11a,11b-decahydro-1H-cyclohepta[e]-pyrrolo[3,4-g]isoindole-1,3,6(2H,3aH)-trione (4m)
72% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93-7.89 (m, 2H), 7.43-7.26 (m, 8H), 7.23-7.20 (m, 2H), 6.89-6.85 (m, 2H), 5.34 (d, $J = 10.4$ Hz, 1H), 4.34-4.28 (m, 1H), 4.08 (d, $J = 8.0$ Hz, 1H), 3.81 (d, $J = 10.4$ Hz, 1H), 3.14-3.09 (m, 1H), 2.40 (s, 3H), 2.27-2.23 (m, 1H), 2.06-1.81 (m, 3H), 1.78-1.69 (m, 3H), 1.33-1.15 (m, 2H), 0.82-0.77 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.2, 174.8, 164.1, 162.1, 144.7, 142.6, 135.2, 131.2, 129.9, 129.3, 129.0, 128.7, 128.5, 128.0, 127.9, 126.4, 124.2, 55.2, 47.4, 46.5, 44.8, 44.6, 30.5, 29.9, 28.7, 28.3, 27.6, 21.7; HRMS (ESI): calc. for C$_{34}$H$_{32}$N$_2$NaO$_5$S [M+Na]$^+$: 603.1924; found: 603.1920.

2,3b-Diphenyl-5-tosyl-3a,3b,4,5,7,8,9,10,11,12,12a,12b-dodecahydrocycloocta[e]-pyrrolo[3,4-g]isoindole-1,3,6(2H)-trione (4n)

76% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95-7.91 (m, 2H), 7.42-7.28 (m, 8H), 7.23-7.16 (m, 2H), 6.82-6.77 (m, 2H), 5.38 (d, $J = 10.8$ Hz, 1H), 4.07 (d, $J = 7.6$ Hz, 1H), 3.82 (d, $J = 8.0$ Hz, 1H), 3.57-3.51 (m, 1H), 3.15-3.10 (m, 1H), 2.38 (s, 3H), 2.12-1.96 (m, 3H), 1.89-1.70 (m, 4H), 1.61-1.55 (m, 1H), 1.38-1.34 (m, 1H), 1.25-1.20 (m, 1H), 1.10-0.90 (m, 1H), 0.77-0.67 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.2, 174.9, 163.6, 162.3, 144.6, 142.6, 135.2, 131.2, 129.8, 129.3, 129.0, 128.9, 128.6, 128.0, 126.4, 124.3, 55.3, 46.8, 46.4, 45.5, 43.7, 31.2, 30.8, 26.8, 26.6, 26.1, 25.4, 21.7; HRMS (ESI): calc. for C$_{35}$H$_{34}$N$_2$NaO$_5$S [M+Na]$^+$: 617.2081; found: 617.2077.

5-Methyl-7-((4-nitrophenyl)sulfonyl)-2,8a-diphenyl-3a,4,7,8,8a,8b-hexahydropyrrolo-
**[3,4-e]isoindole-1,3,6(2H)-trione (4o)**

80% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20-8.19 (m, 4H), 7.44-7.33 (m, 6H), 7.25-7.22 (m, 2H), 6.89-6.85 (m, 2H), 5.41 (d, $J$ = 10.8 Hz, 1H), 4.05 (d, $J$ = 8.4 Hz, 1H), 3.93 (d, $J$ = 10.8 Hz, 1H), 3.22-3.17 (m, 1H), 2.63-2.56 (m, 1H), 2.32 (s, 3H), 2.21-2.15 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.8, 175.5, 163.9, 153.9, 150.6, 143.2, 142.1, 131.0, 129.9, 129.8, 129.2, 129.1, 128.3, 128.2, 126.1, 125.0, 123.8, 55.4, 46.4, 46.0, 38.6, 34.3, 19.6; HRMS (ESI): calc. for C$_{29}$H$_{23}$N$_3$NaO$_7$S $[M+Na]^+$: 580.1149; found: 580.1140.

**5-Methyl-7-(methylsulfonyl)-2,8a-diphenyl-3a,4,7,8,8a,8b-hexahydropyrrolo[3,4-e]-isoindole-1,3,6(2H)-trione (4p)**

77% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51-7.45 (m, 5H), 7.43-7.42 (m, 1H), 7.30-7.22 (m, 2H), 7.17-7.13 (m, 2H), 5.28 (d, $J$ = 10.4 Hz, 1H), 4.11 (d, $J$ = 8.4 Hz, 1H), 3.80 (d, $J$ = 10.4 Hz, 1H), 3.25-3.17 (m, 4H), 2.63-2.57 (m, 1H), 2.44 (s, 3H), 2.29-2.21 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.2, 175.9, 165.1, 152.3, 141.9, 131.2, 129.8, 129.3, 129.2, 129.1, 128.1, 126.3, 124.9, 55.0, 47.0, 45.6, 40.0, 38.7, 34.5, 19.4; HRMS (ESI): calc. for C$_{24}$H$_{22}$N$_2$NaO$_5$S $[M+Na]^+$: 473.1142; found: 473.1144.
Enantiodivergent syntheses of pyrrolidones 2

**Enzymatic KR:** To a solution of 1i-ol (376 mg, 2.0 mmol) in toluene (1.0 mL) was added isopropenyl acetate (300.0 mg, 3.0 mmol), Na₂CO₃ (210 mg, 2.0 mmol) and *Candida antarctica* lipase B (CalB, 10.0 mg). The mixture was stirred at room temperature for 5 h and then purified via column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 10/1) to afford (S)-1i-ol (185 mg, 49%) and (R)-1i-OAc (210 mg, 46%). (R)-1i-OAc was hydrolyzed in MeOH with K₂CO₃ to give (R)-1i-ol (171 mg).

**Mitsunobu Reaction:** (S)-1i-ol (185 mg, 0.96 mmol) or (R)-1i-ol (170 mg, 0.90 mmol), BocNHTs (323 mg, 1.2 mmol) and PPh₃ (389 mg, 1.5 mmol) were dissolved in THF (5.0 mL), and then DEAD (651 mg, 1.5 mmol, 40% in toluene) was added at 0 °C. The mixture was stirred for 5 h at room temperature, and then concentrated in vacuo. DMSO (2.0 mL) was added, and the mixture was stirred at 180 °C for 10 min. After that, the mixture was cooled to room temperature and H₂O (10 mL) was added. The residue was extracted with Et₂O (2 × 30 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 5/1) to afford product (R)-1i (306 mg, 0.89 mmol, 94% ee) or (S)-1i (245 mg, 0.71 mmol, 92% ee).

**Pd-catalyzed oxidative carbonylation:** (R)-1i or (S)-1i (65.4 mg, 0.2 mmol) was transformed to (R)-2i (68.9 mg, 0.188 mmol, 94% ee) or (S)-2i (67.5 mg, 0.184 mmol, 92% ee) under the standard reaction conditions for the oxidative carbonylation.
HPLC for 1i: Chiralpak IA column, i-PrOH/i-hexane (10/90), flow rate 1.0 mL/min, $t_R$: 6.8 min for (R)-isomer and 8.9 min for (S)-isomer.
HPLC for \(2i\): Chiralpak IF column, \(i\)-PrOH/\(i\)-hexane (10/90), flow rate 1.0 mL/min, \(t_R\): 21.8 min for (S)-isomer and 22.8 min for (R)-isomer.

| Peak | RetTime | Type | Width (min) | Area (mAU*s) | Height (mAU) | Area (%) |
|------|---------|------|-------------|--------------|--------------|----------|
| 1    | 21.767  | MM   | 0.4607      | 1372.41602   | 49.64817    | 50.3393  |
| 2    | 22.847  | MM   | 0.4887      | 1353.91455   | 46.17705    | 49.6607  |

| Peak | RetTime | Type | Width (min) | Area (mAU*s) | Height (mAU) | Area (%) |
|------|---------|------|-------------|--------------|--------------|----------|
| 1    | 21.879  | BV   | 0.4414      | 271.63379    | 9.62172     | 2.9856   |
| 2    | 22.833  | VB   | 0.4899      | 8826.61621   | 278.42908   | 97.0144  |

| Peak | RetTime | Type | Width (min) | Area (mAU*s) | Height (mAU) | Area (%) |
|------|---------|------|-------------|--------------|--------------|----------|
| 1    | 21.972  | MM   | 0.5094      | 1.34477e4    | 439.95609    | 95.7084  |
| 2    | 23.242  | MM   | 0.5315      | 602.99664    | 18.90721    | 4.2916   |
Recycling experiments and hot filtration test of Pd-AmP-CNC

Recycling experiments:

\[
\begin{align*}
\text{Ph}\underbrace{\begin{array}{c}
\text{NHTs} \\
\hline
\text{1a}
\end{array}}_{\text{1 atm}} + \text{CO} & \xrightarrow{\text{1 atm}} \text{Pd-AmP-CNC (0.5 mol\%)} \\
\text{BQ (1.1 equiv.)} & \text{AgOTf (1 mol\%)} \\
\text{CDCl}_3, \text{ rt, 30 min} & \xrightarrow{\text{30 min}} \text{Ph}\underbrace{\begin{array}{c}
\text{NHTs} \\
\hline
\text{2a}
\end{array}}_{\text{NHTs}}
\end{align*}
\]

To a solution of Pd-AmP-CNC (5.75 mg, 0.0025 mmol), AgOTf (1.28 mg, 0.005 mmol) and BQ (59.4 mg, 0.55 mmol) in CDCl$_3$ (2.5 mL) was added allene amide 1a (164 mg, 0.5 mmol). The tube was closed with a septum, evacuated and filled with carbon monoxide gas using a balloon. The procedure was repeated three times. The reaction was stirred at room temperature for 30 min and then centrifuged for 5 min at 5000 rpm. The catalyst was washed with CDCl$_3$ (2 × 2 mL) before being used in the next run or for characterizations, and the supernatant was combined for the determination of yield by NMR using anisole as the internal standard.

Figure S3. TEM images of Pd-AmP-CNC after the 1$^{\text{st}}$ and 9$^{\text{th}}$ run.

Figure S4. Deconvoluted Pd3d XPS spectr$\text{a}$ of Pd-AmP-CNC after the 1$^{\text{st}}$ and 9$^{\text{th}}$ run.
TEM and XPS after the 1st and 9th run showed that the Pd-AmP-CNC had not undergone any significant change and showed the same nanoparticle size and about the same ratio Pd(II)/Pd(0) (Figures S3 and S4)

**Hot filtration test:**

To a solution of Pd-AmP-CNC (2.3 mg, 0.001 mmol), AgOTf (0.51 mg, 0.002 mmol) and BQ (23.8 mg, 0.22 mmol) in CDCl$_3$ (1.0 mL) was added allene amide 1a (65.4 mg, 0.2 mmol). The tube was closed with a septum, evacuated and filled with carbon monoxide gas using a balloon. The procedure was repeated three times. The reaction was stirred at room temperature for 5 min and then centrifuged for 5 min at 5000 rpm. The yield of 2a was determined to be 47% by NMR using anisole as the internal standard. The supernatant was transferred to another clean reaction tube, closed with a septum, evacuated and filled with carbon monoxide gas using a balloon. The procedure was repeated three times and the mixture was stirred at room temperature for another 30 min. Analysis of the reaction mixture showed that the yield of 2a was unchanged (still 47% yield as determined by NMR).
Kinetic isotope effect studies

1. Determination of intermolecular competition KIE

To a solution of Pd-AmP-CNC (2.3 mg, 0.001 mmol), AgOTf (0.51 mg, 0.002 mmol) and BQ (23.8 mg, 0.22 mmol) in CDCl₃ (1.0 mL) was added allene amide 1a (32.7 mg, 0.1 mmol), 1a-d₆ (33.3 mg, 0.1 mmol). The tube was closed with a septum, cooled to 0°C, evacuated and filled with carbon monoxide gas using a balloon. The procedure was repeated three times. The reaction was stirred at 0°C for 20 min. The yields of 2a and 2a-d₆ were determined by ¹H NMR measurements using anisole as the internal standard (22 μL, 0.2 mmol).

Figure S5. ¹H NMR spectrum of the reaction of 1a and 1a-d₆ for 20 min (see above).
As shown in the $^1$H NMR spectrum in Figure S5, the combined yield of 2a and 2a-$d_5$ was 6% (0.12/2), and the yield of 2a was 5%, thus the yield of 2a-$d_5$ was 1%. Therefore, the ratio of 2a and 2a-$d_5$ was determined as 5:1. Furthermore, the combined recovery of 1a and 1a-$d_6$ was 92% (1.83/2), so the reaction conversion was 8%. Finally, the isotope effect value calculated from the product ratio and conversion of the reaction is 5.4 according to Sih’s equation.[4]

2. Determination of parallel KIE

![Chemical structure](image)

To a solution of Pd-AmP-CNC (2.3 mg, 0.001 mmol), AgOTf (0.51 mg, 0.002 mmol) and BQ (23.8 mg, 0.22 mmol) in CDCl$_3$ (1.0 mL) was added allene amide 1a (65.4 mg, 0.2 mmol), or allene 1a-$d_6$ (66.6 mg, 0.2 mmol). The tube was closed with a septum, cooled to 0°C, evacuated and filled with carbon monoxide gas using a balloon. The procedure was repeated three times. The reaction was stirred at 0°C. The yields were determined by $^1$H NMR measurements using anisole as the internal standard (see Table S2 and S3, respectively).

Table S2. For 1a:

| Time/min | 0  | 5  | 15 | 25 | 35 | 45  | 55 |
|----------|----|----|----|----|----|-----|----|
| Yield of 2a/% | 0  | 2.5 | 5.4 | 8.0 | 10.0 | 13.2 | 15.4 |

Due to the nature of the experiment, plots to determine the KIE were taken for 1a (Figure S6).
Figure S6. Linear function fit for reaction rate of 1a.

Table S3. For 1a-d₆:

| Time/min | 0  | 10 | 30 | 50 | 70 | 90 | 110 |
|----------|----|----|----|----|----|----|-----|
| Yield of 2a-d₆/% | 0  | 1.0 | 2.5 | 4.0 | 5.3 | 6.5 | 7.8 |

Due to the nature of the experiment, plots to determine the KIE were taken for 1a-d₆ (Figures S7).

Figure S7. Linear function fit for reaction rate of 1a-d₆.

Finally, the parallel KIE value is determined to be $k_d/k_D = (0.2709)/(0.0699) = 3.9$. 
**Crystal structure determination of 4m**

Single crystal X-ray diffraction data for suitable crystals of compounds 4m were collected using Cu Kα radiation on a Bruker D8 VENTURE diffractometer equipped with a PHOTON II CPAD detector. The datasets were reduced and absorption corrections applied using the Bruker APEX3 suite. The crystal structures were solved and refined by SHELXT and SHELXL respectively.\(^5\) The crystal structures were refined using full-matrix least-squares based on $F^2$, with all non-hydrogen atoms anisotropically defined. For both compounds, all non-hydrogen atoms were located in the initial structure solution. All hydrogen atom positions for 4m were placed by means of a riding model. A summary of the crystallographic data and refinement parameters are provided in Table S4. CCDC (1916248) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/structures.

**Table S4. Crystallographic data and refinement parameters**

| Identification code | 4m                           |
|---------------------|-------------------------------|
| Empirical formula   | \(C_{35}H_{32}Cl_3N_2O_5S\)  |
| Formula weight      | 701.05 g mol\(^{-1}\)        |
| Temperature         | 296(2) K                      |
| Wavelength          | 1.54178 Å                     |
| Crystal system      | Triclinic                     |
| Space group         | \(P\overline{1}\) (No. 2)    |
| Unit cell dimensions| \(a = 7.8374(3)\) Å          |
|                     | \(b = 13.7006(5)\) Å         |
|                     | \(c = 16.5460(6)\) Å         |
|                     | \(\alpha = 102.471(2)\)°   |
|                     | \(\beta = 102.543(2)\)°     |
|                     | \(\gamma = 93.064(2)\)°     |
| Property                          | Value                  |
|----------------------------------|------------------------|
| Volume                           | $1683.9(1) \text{ Å}^3$ |
| $Z$                              | 2                      |
| Density (calc.)                  | 1.383 g cm$^{-3}$      |
| Absorption coefficient           | 3.412 mm$^{-1}$        |
| $F(000)$                         | 728                    |
| Crystal size                     | 0.60 × 0.08 × 0.04 mm$^3$ |
| $\theta$ range for data collection | 2.814 to 69.054°      |
| Index ranges                     | $-9 \leq h \leq 9$    |
|                                  | $-16 \leq k \leq 16$  |
|                                  | $-19 \leq l \leq 19$  |
| Reflections collected            | 62766                  |
| Independent reflections          | 6205                   |
| [R(int) = 0.1954]                |                        |
| Absorption correction            | Multi-scan             |
| Min. and max. transmission       | 0.5003 and 0.7531      |
| Data / restr. / param.           | 6205/0/416             |
| Goodness-of-fit on $F^2$         | 1.018                  |
| Final R indices [$I > 2\sigma(I)$]| $R1 = 0.0944,$        |
|                                  | $wR2 = 0.2296$         |
| Largest diff. peak and hole      | 0.443 and -0.823 e Å$^{-3}$ |
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$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
\[ \text{Ph} \quad \text{NHTs} \]

\[ 1I \]

$^1\text{H NMR (400 MHZ, CDCl}_3\text{)}$

\[ \text{Ph} \quad \text{NHTs} \]

\[ 1I \]

$^{13}\text{C NMR (100 MHZ, CDCl}_3\text{)}$
Ph\rightleftharpoons\text{HNNs}

10

$^1$H NMR (400 MHz, CDCl$_3$)

Ph\rightleftharpoons\text{HNNs}

10

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHZ, CDCl$_3$)

$^{13}C$ NMR (100 MHZ, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
**$^1$H NMR (400 MHz, CDCl$_3$)**

![$^1$H NMR spectrum](image)

**$^{13}$C NMR (100 MHz, CDCl$_3$)**

![$^{13}$C NMR spectrum](image)
$^1$H NMR (400 MHZ, CDCl$_3$)

$^{13}$C NMR (100 MHZ, CDCl$_3$)
\[ \text{NTs} \]

\[ 2d \]

\[ ^1H \text{ NMR (400 MHZ, CDCl}_3) \]

\[ \text{NTs} \]

\[ 2d \]

\[ ^13C \text{ NMR (100 MHZ, CDCl}_3) \]
$\text{NTs}$

$\text{2e}$

$^1\text{H NMR (400 MHz, CDCl}_3)$

$\text{NTs}$

$\text{2e}$

$^{13}\text{C NMR (100 MHz, CDCl}_3)$
ML06.84-1-H.10.5d

**$^{1}H$ NMR (400 MHZ, CDCl$_3$)**

![NMR spectrum of compound 2f](image)

ML06.84-1-C.10.5d

**$^{13}C$ NMR (100 MHZ, CDCl$_3$)**

![NMR spectrum of compound 2f](image)
$^{1}$H NMR (400 MHZ, CDCl$_3$)

$^{13}$C NMR (100 MHZ, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHZ, CDCl$_3$)

$^{13}C$ NMR (100 MHZ, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{Ph}\text{NTs}$

$\text{2I}$

$^1\text{H NMR (400 MHZ, CDCl}_3$}

$\text{NTs}$

$\text{2I}$

$^{13}\text{C NMR (100 MHZ, CDCl}_3$}
$2m$

$^1$H NMR (400 MHZ, CDCl$_3$)

$^1$C NMR (100 MHZ, CDCl$_3$)
$^1$H NMR (400 MHZ, CDCl$_3$)

$^{13}$C NMR (100 MHZ, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
2p

$^1$H NMR (400 MHZ, CDCl$_3$)

2p

$^{13}$C NMR (100 MHZ, CDCl$_3$)
$^{1}H$ NMR (400 MHZ, CDCl₃)

$^{13}C$ NMR (100 MHZ, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
\( ^1\text{H NMR (400 MHz, CDCl3)} \)

\( ^{13}\text{C NMR (100 MHz, CDCl3)} \)
$^{1}$H NMR (400 MHZ, CDCl3)

$^{13}$C NMR (100 MHZ, CDCl3)
$^{1}$H NMR (400 MHz, CDCl3)

$^{13}$C NMR (100 MHz, CDCl3)
$^{1}H$ NMR (400 MHz, CDCl3)

$^{13}$C NMR (100 MHz, CDCl3)
$^1$H NMR (400 MHZ, CDCl3)

$^{13}$C NMR (100 MHZ, CDCl3)