Electronic Supplementary Information (ESI)

Cyclopalladated complex of corannulene with a pyridine pendant and its columnar self-assembly

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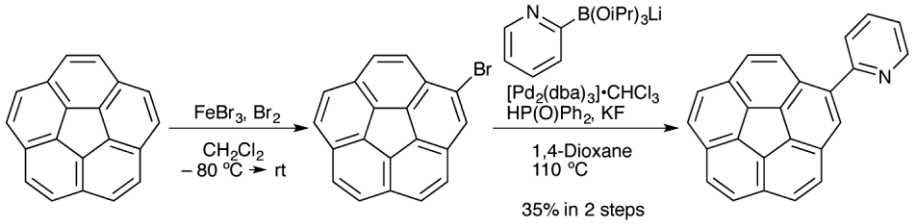
Materials and methods

All solvents, organic and inorganic reagents are commercially available, and were used without further purification. Corannulene[1] and lithium triisopropyl 2-pyridylborate[2] were synthesised according to the literature. Silica gel column chromatography was performed using Merck Silica Gel 60 (230-400 mesh).

NMR spectroscopic measurements were performed using AVANCE 500 spectrometers. NMR spectra are calibrated as below; $CDCl_3$: tetramethylsilane ($Si(C\mathit{H}_3)_4$) = 0 ppm for ^1H, $\mathit{C}DCl_3$ = 77.16 ppm for ^{13}C; CD_3CN: $CD_2\mathit{H}CN$ = 1.94 ppm for ^1H, $CD_3\mathit{C}N$ = 118.26 ppm for ^{13}C. Direct Analysis in Real Time (DART) mass spectra were recorded on a JMS-T100LP AccuTOF LC-plus. Electrospray ionization-time-of-flight (ESI-TOF) mass spectra were recorded on a Micromass LCT spectrometer. UV-vis spectroscopy was performed using a HITACHI U-3500 spectrophotometer. Melting points were measured using a Yanaco MP-500D apparatus. Single-crystal X-ray crystallographic analyses were performed using a Rigaku RAXIS-RAPID imaging plate diffractometer with MoKα radiation and a Bruker APEXII CCD detector with MoKα radiation, and obtained data were calculated using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97 or the SHELXL program suite.[3] X-ray structures were displayed using ORTEP-3. Molecular modeling was performed by a Spartan ’08 and was displayed using a Mercury program.

Synthesis of 2-pyridylcorannulene (1)

Scheme S1. Synthetic procedure of **1**.



Monobromocorannulene: Monobromocorannulene was synthesised according to the literature.[1g] Br_2 (10 mL, 200 μmol, 1.0 equiv.) was added dropwise to a solution of corannulene (49.9 mg, 199 μmol, 1.0 equiv.) and $FeBr_3$ (6.4 mg, 22 μmol, 0.1 equiv.) in dry CH_2Cl_2 (5.0 mL) under N_2 atmosphere at – 80 °C. The solution was allowed to warm to ambient temperature over several hours and quenched with a saturated aqueous solution of Na_2SO_3. The solution was diluted with CH_2Cl_2 (15 mL), washed with H_2O (15 mL × 3), dried with $MgSO_4$, filtered and evaporated to obtain a crude material as a pale yellow solid (61.7 mg). The obtained crude was used for the next reaction without further purification.

2-Pyridylcorannulene (1): Monobromocorannulene (60.7 mg, 184 μmol, 1.0 equiv.), lithium triisopropyl 2-pyridylborate (0.249 g, 0.911 mmol, 5.0 equiv.), $[Pd_2(dba)_3]\cdot CHCl_3$ (6.6 mg, 6.4 μmol, 3.5%), diphenylphosphine oxide (8.0 mg, 40 μmol, 22%, Pd/ligand = 1:3) and KF (0.107 g, 1.84 mmol, 10 equiv.) were dissolved in dry 1,4-dioxane (2.0 mL, degassed by bubbling N_2 for 30 min) under N_2 atmosphere. The reaction mixture was stirred at 110 °C for 42 h, and $[Pd_2(dba)_3]\cdot CHCl_3$ (6.7 mg, 6.5 μmol, 3.5%) and diphenylphosphine oxide (7.7 mg, 38 μmol, 21%, Pd/ligand = 1:3) were further added to the solution. After additional stirring for 10 h, the suspension was diluted with CH_2Cl_2, filtered under reduced pressure with a plug of silica and evaporated to obtain a crude material (0.125 g) as an orange-brown oil, which was purified by silica gel column chromatography with CH_2Cl_2:*n*-hexane = 1:10 –1:0 to obtain **1** as an orange oil (21.6 mg, 66.0 μmol, 35% in two steps).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.86 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H, ArH_m), 8.28 (s, 1H, ArH_i), 8.07 (d, J = 8.9 Hz, 1H, ArH_a), 7.95 (dt, J = 7.8, 1.1 Hz, 1H, ArH_j), 7.88 (td, J = 7.8, 1.7 Hz, 1H, ArH_k), 7.88 (d, J = 9.0 Hz, 1H, ArH_h), 7.82 (d, J = 7.8 Hz, 1H, ArH_g), 7.84-7.80 (m, 4H, Ar$H_{c\text{-}f}$), 7.80 (d, J = 9.0 Hz, 1H, ArH_b), 7.36 (ddd, 7.5, 4.8, 1.2 Hz, 1H, ArH_l).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 157.8 (C_y), 150.2 (C_m), 140.0 (C_n), 136.8 (C_k), 136.56, 136.51, 136.2, 135.9, 135.5, 131.23, 131.08, 131.05, 130.6, 129.2, 127.7, 127.49, 127.39, 127.38, 127.35, 127.27, 127.09, 124.7 (C_j), 122.4 (C_l) (Several signals are overlapped).

M.p.: 185-186 °C

UV-vis (CH_3CN, 293 K, 10 μM): λ_{max} = 255 nm (ε = 3.5 × 10^4 $M^{-1}cm^{-1}$) and 293 nm (ε = 2.8 × 10^4 $M^{-1}cm^{-1}$).

DART mass *m/z*: 328.1 $[H\cdot\mathbf{1}]^+$, 655.2 $[H\cdot\mathbf{1}_2]^+$.

Elemental analysis: Anal. Calcd for $C_{25}H_{15.8}NO_{1.4}$ {**1**·1.4H_2O}: C 85.16; H 4.52; N 3.97. Found: C 85.14; H 4.59; N 3.86.

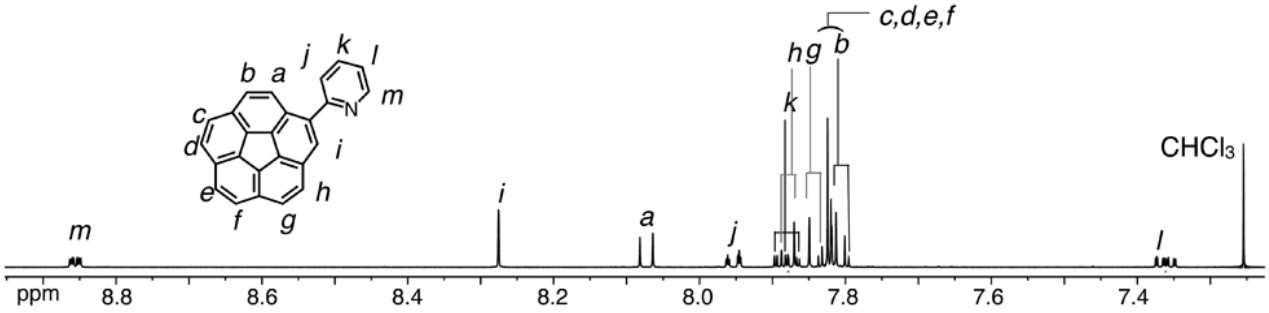


Figure S1. ^1H NMR spectrum (500 MHz, $CDCl_3$, 300 K) of **1**.

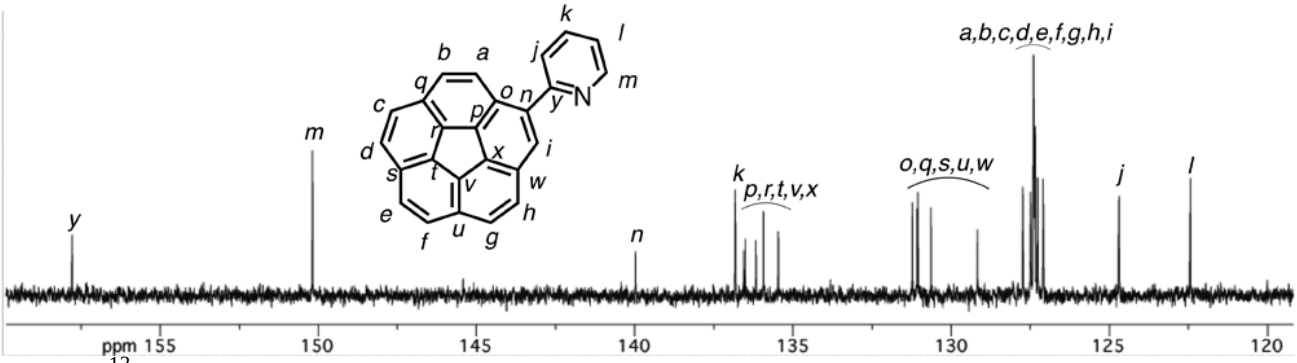


Figure S2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 300 K) of **1**.

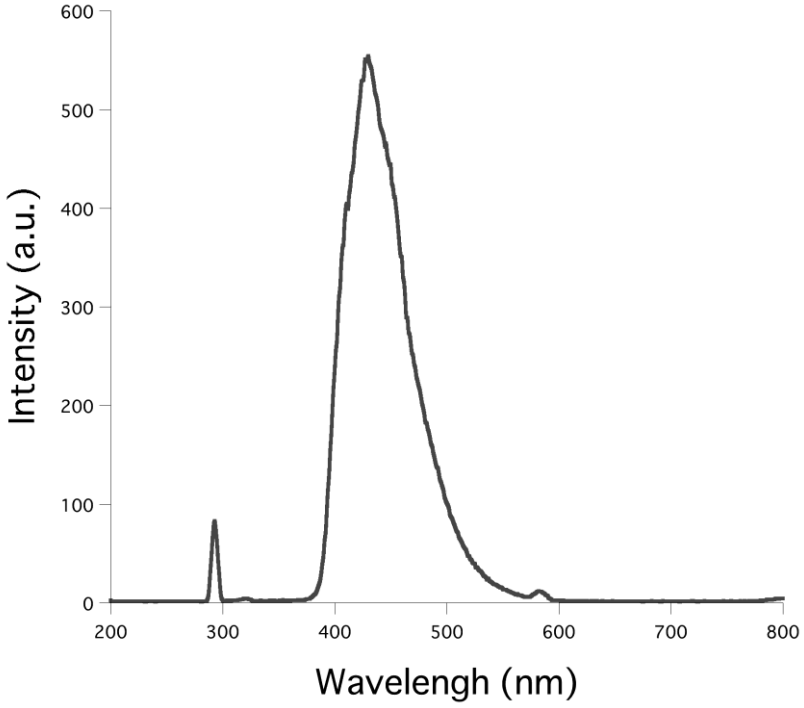


Figure S3. Fluorescence spectrum of **1** (CH_3CN, [**1**] = 10 μM, 293 K, λ_{ex} = 294 nm).

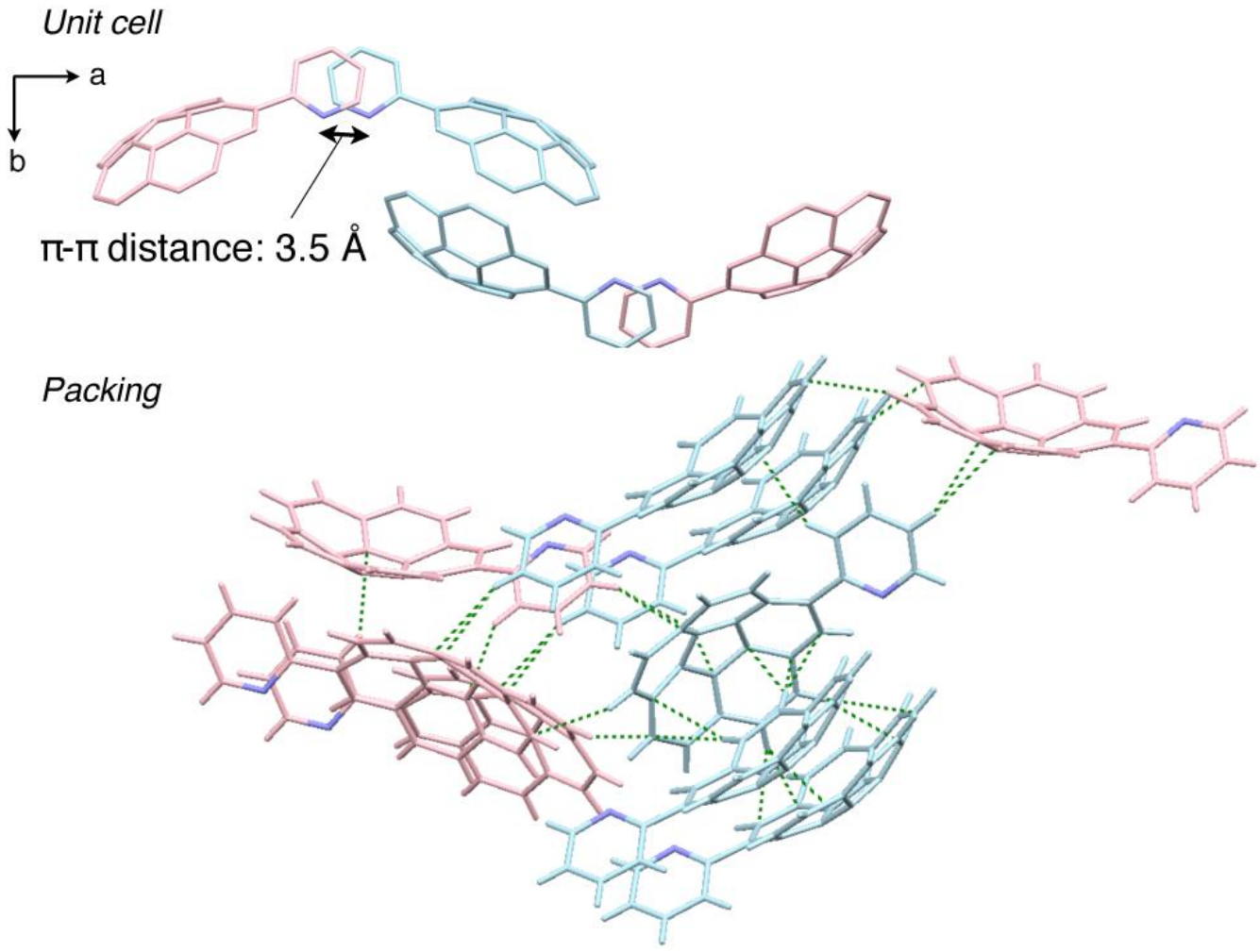
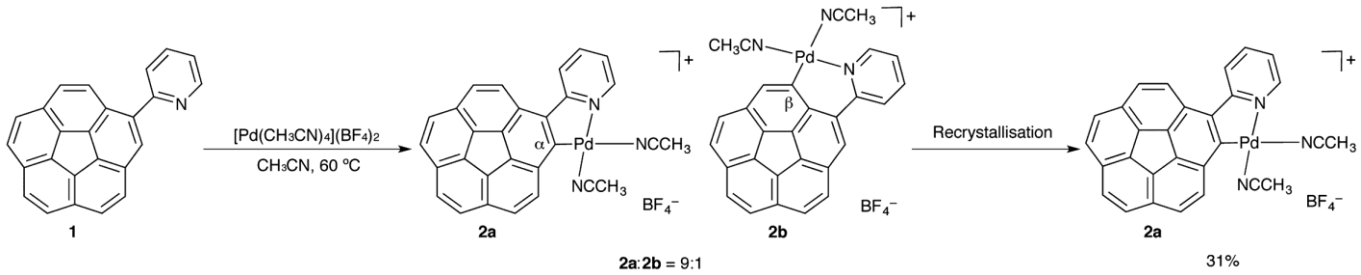


Figure S4. X-ray crystal structure of **1**.

Synthesis of cyclopalladated complex 2a

Scheme S2. Synthetic procedure of **2a**.



2-Pyridylcorannulenato-*N*,*C*$^{2'}$-bis(acetonitrile)palladium(II) tetrafluoroborate (2a): Ligand **1** (10.0 mg, 30.5 μmol, 1.0 equiv.) and $[Pd(CH_3CN)_4](BF_4)_2$ (13.5 mg, 30.5 μmol, 1.0 equiv.) were dissolved in CH_3CN (30 mL, degassed by bubbling N_2 for 1 h) under N_2 atmosphere. The solution was stirred at 90 °C under N_2 atmosphere for 37 h and evaporated to reduce the volume to 5~6 mL. After filtration, slow evaporation in a test tube produced yellow fine crystals (plate and needle) mainly on the wall. The solution and powder around the bottom of the tube were removed, and the remaining crystals on the wall were washed ($CHCl_3$ × 2) to obtain **2a** as a yellow crystal (5.71 mg, 9.49 μmol, 31%).

^{1}H NMR (500 MHz, CD_3CN): δ 8.68 (d, J = 8.3 Hz, 1H, Ar$H_{j'}$), 8.60-8.59 (m, 1H, Ar$H_{m'}$), 8.33 (d, J = 9.0 Hz, 1H, Ar$H_{a'}$), 8.22 (td, J = 7.9, 1.3 Hz, 1H, Ar$H_{k'}$), 8.11 (d, J = 8.9 Hz, 1H), 7.99-7.91 (m, 6H), 7.40 (td, J = 6.6, 1.3 Hz, 1H, Ar$H_{l'}$).

^{13}C NMR (125 MHz, CD_3CN): δ 165.78, 159.41, 152.04 ($C_{m'}$), 141.87, 141.56, 137.07, 135.48, 135.31, 135.19, 134.61, 134.18, 132.79, 132.13, 131.11, 129.94, 129.77, 129.08, 128.48, 128.29, 128.27, 128.02, 126.98, 125.36 ($C_{a'}$), 123.90 ($C_{j'}$), 123.49 ($C_{l'}$).

M.p.: > 360 °C (dec)

UV-vis (CH_3CN, 293 K, 9.9 μM): λ_{max} = 271 nm (ε = 2.0 × 10^4 M^{-1}cm^{-1}) and 306 mn (ε = 1.8 × 10^4 M^{-1}cm^{-1}).

HRMS (ESI) *m/z*: calcd for $C_{29}H_{18}N_3Pd$ {[Pd(H$_{-1}$**1**)$(CH_3CN)_2]^+$}: 514.0547; found: 514.0540.

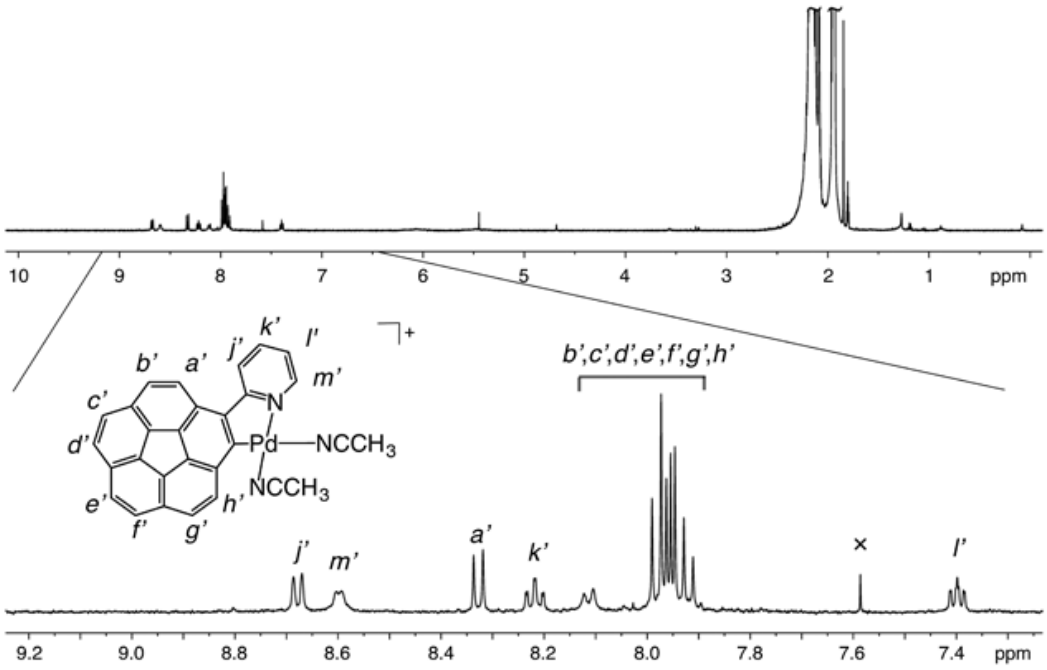


Figure S5. ^{1}H NMR spectrum (500 MHz, CD_3CN, 300 K) of **2a**.

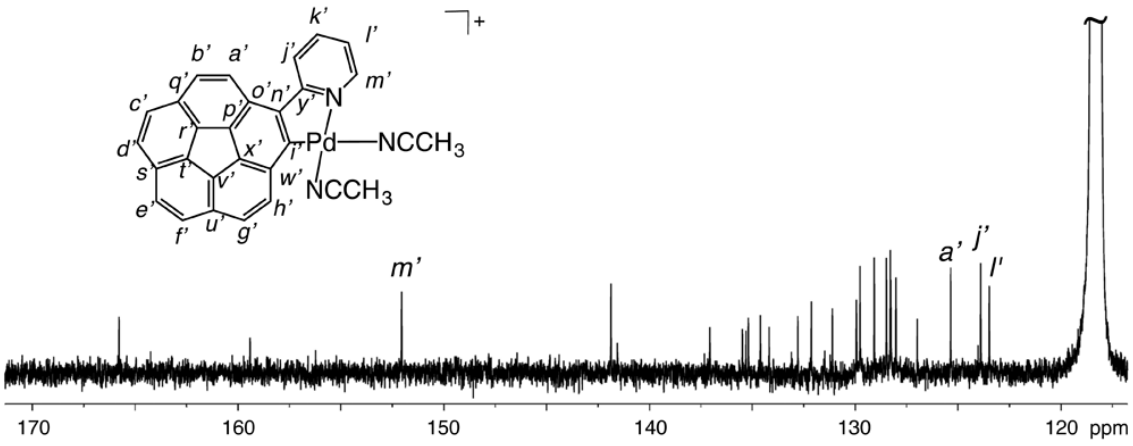


Figure S6. ^{13}C NMR spectrum (125 MHz, CD_3CN, 300 K) of **2a**.

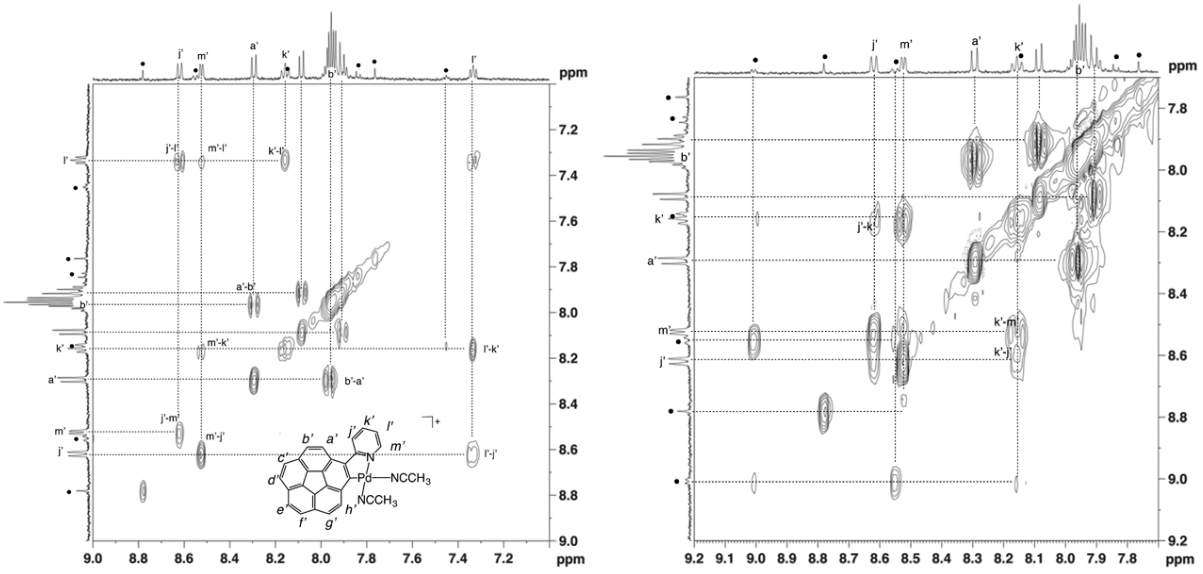


Figure S7. ^{1}H-^{1}H TOCSY (500 MHz, CD_3CN, 300 K) of a mixture of **2a** and **2b**.

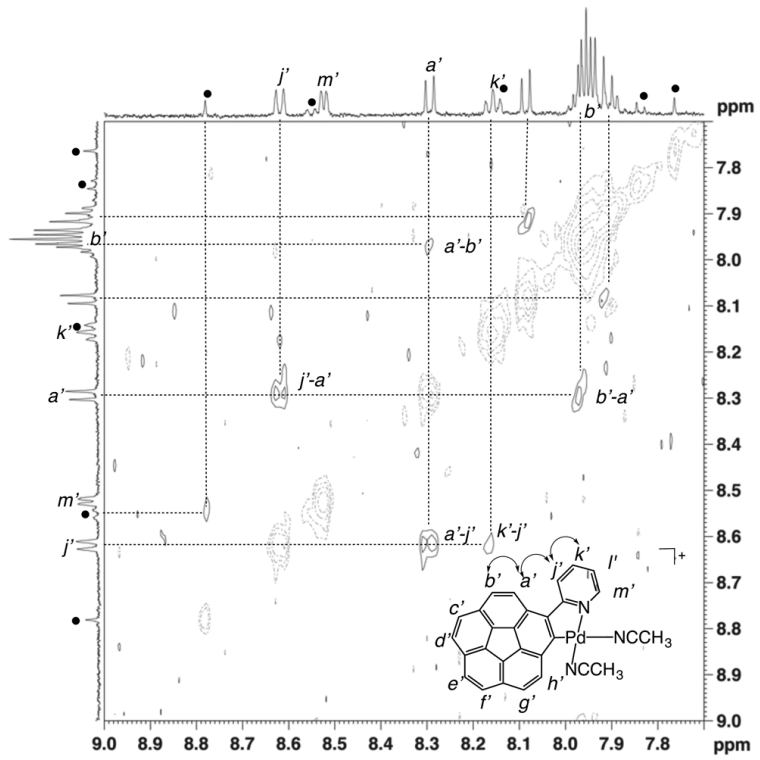


Figure S8. ^{1}H-^{1}H NOESY (500 MHz, CD_3CN, 300 K) of a mixture of **2a** and **2b**.

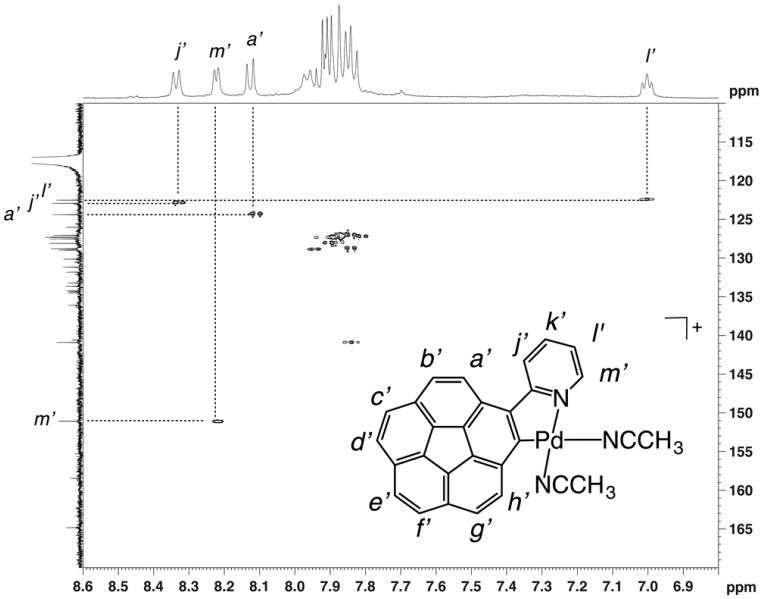


Figure S9. HMQC (^{1}H: 500 MHz, ^{13}C:126 MHz, CD_3CN, 300 K) of a mixture of **2a** and **2b**.

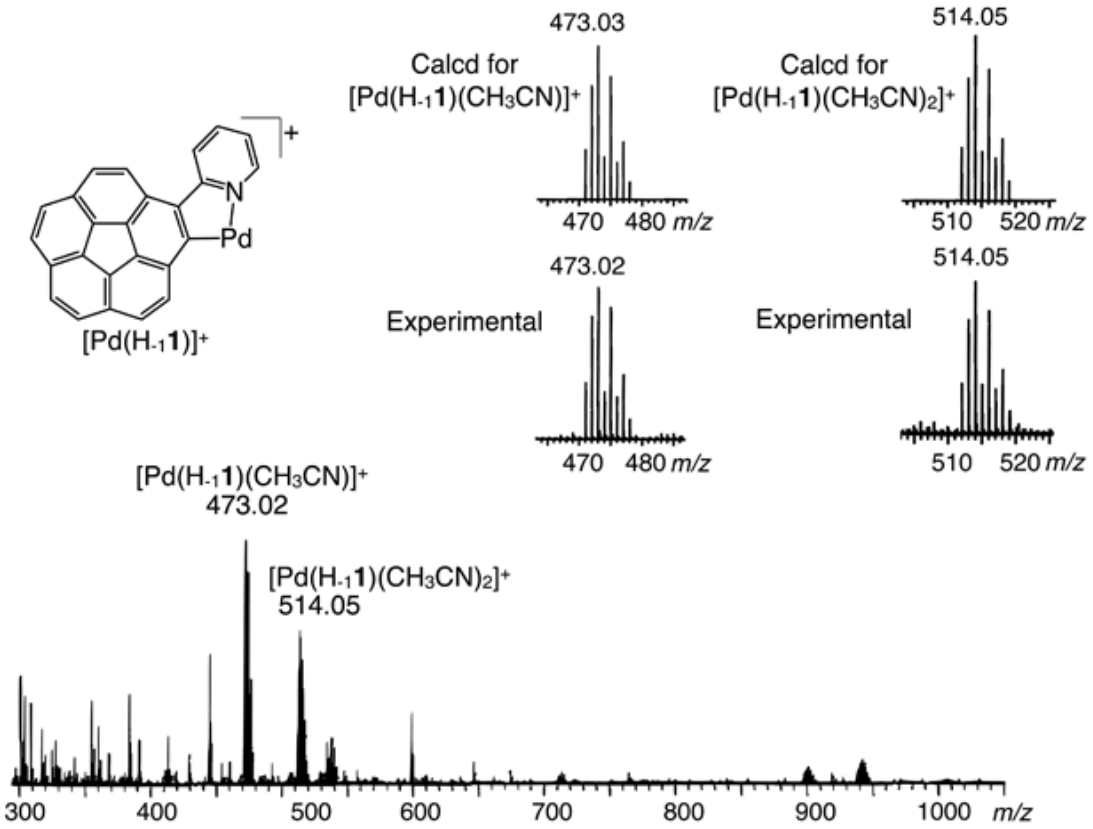


Figure S10. ESI-TOF mass spectrum (positive, CH_3CN) of a mixture of **2a** and **2b**.

Formation of 2a and 2b

A 1.0 mM solution (A) of ligand **1** (1.02 mg, 3.12 μmol) in CD_3CN (3.05 mL) and a 20 mM solution (B) of $[Pd(CH_3CN)_4](BF_4)_2$ (4.49 mg, 10.1 μmol) in CD_3CN (0.5 mL) were prepared. To a solution (A) (0.4 mL) was added a solution (B) (20 μL, 1.0 equiv.) and heated at 60 ºC for ^{1}H NMR measurement.

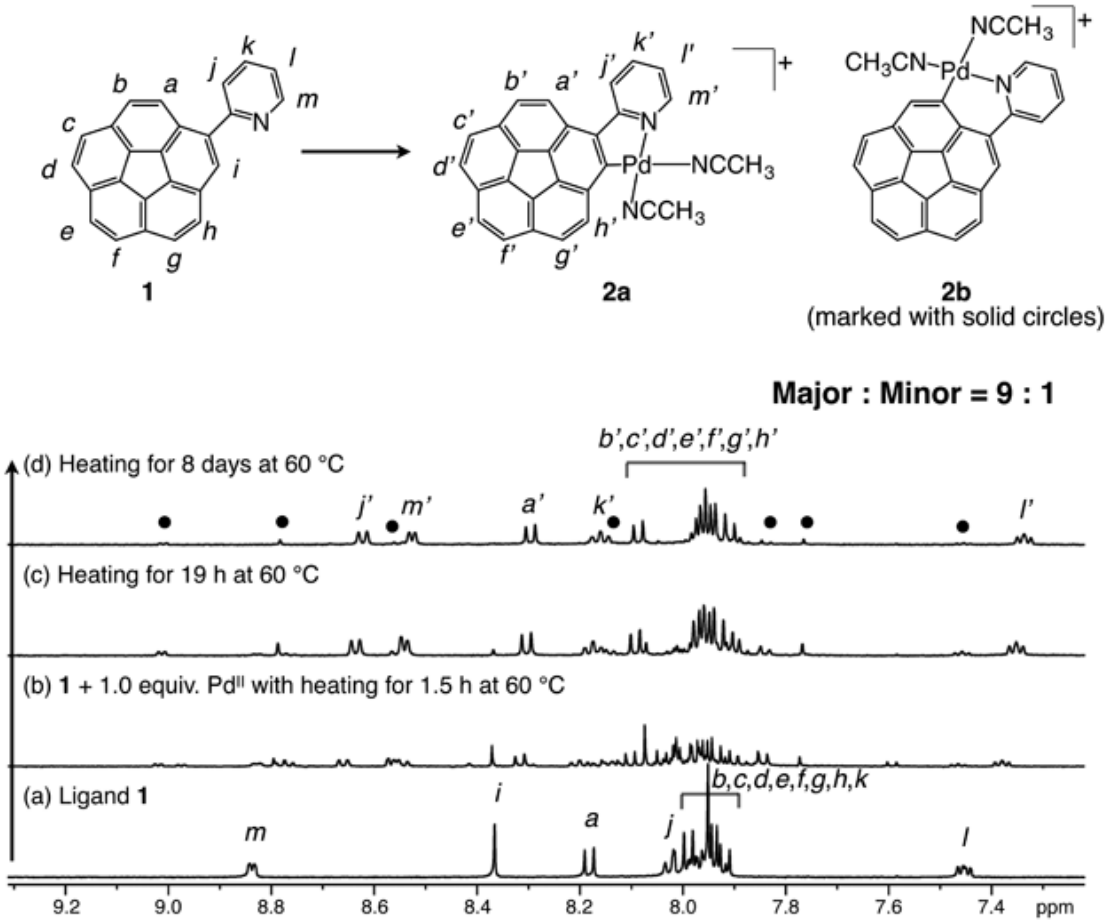


Figure S11. ^{1}H NMR spectrum (500 MHz, CD_3CN, 300 K) for the formation of **2a** and **2b**.

Concentration-depedent aggregation of 2a and 2b

The reaction mixture prepared according to the above-mentioned method was heated at 60 ºC for 10 days. The resulting 1.0 mM solution in CD_3CN was found to include cyclopalladated complexes, **2a** and **2b**, by ^1H NMR spectroscopy. The solution was diluted with CD_3CN to prepare 0.5 and 0.1 mM solutions for ^1H NMR study.

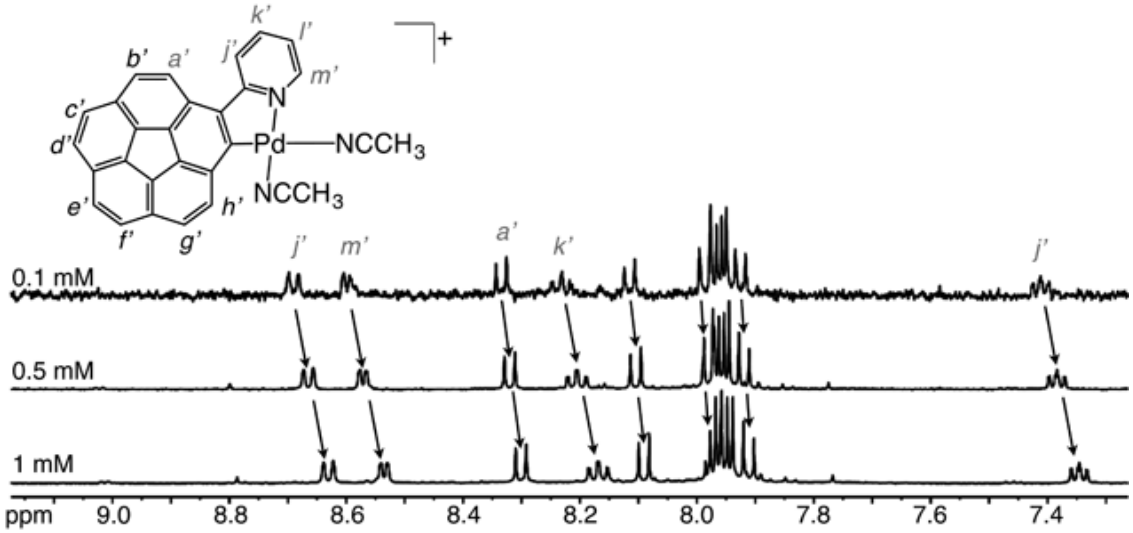
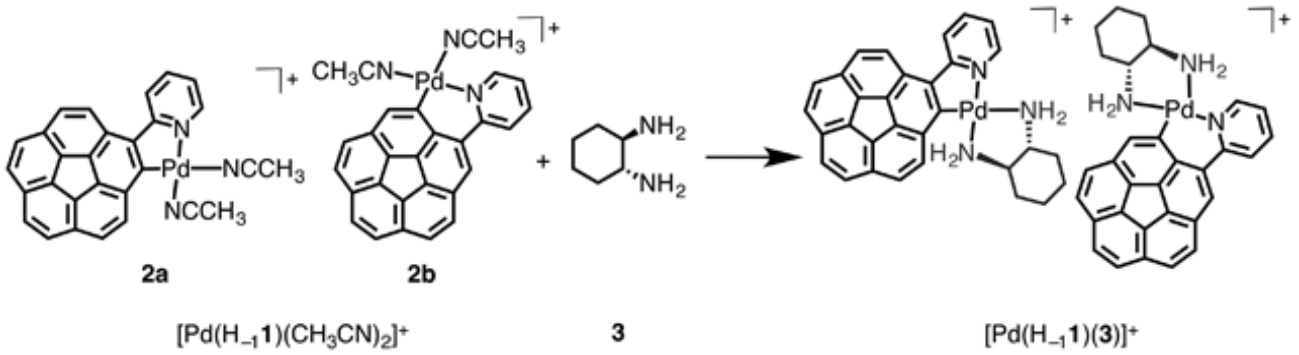


Figure S12. ^1H NMR spectra (500 MHz, CD_3CN, 300 K) of solutions containing a mixture of **2a** and **2b** at various concentrations.

Reaction of a mixture of 2a and 2b with 1*R*,2*R*-(–)-diaminochclohexane (3)

Scheme S3. Reaction of a mixture of **2a** and **2b** with **3**.



Ligand **1** (7.5 mg, 22.9 μmol) and $[Pd(CH_3CN)_4](BF_4)_2$ (10.5 mg, 23.6 μmol, 1.0 equiv.) were dissolved in CH_3CN (20 mL) and heated at 90 °C for 4 days. The reaction mixture was evaporated and the residue was redissolved in CH_3CN (20 mL) to prepare a 1.1 mM solution of cyclopalladated complexes (**2a** and **2b**). A part of the solution (0.4 mL) was taken up and evaporated and redissolved in CD_3CN (0.4 mL) to prepare a 1.1 mM solution in CD_3CN for ^1H NMR measurement. Meanwhile, 1*R*,2*R*-(–)-diaminocyclohexane (**3**) (1.32 mg, 11.6 μmol) was dissolved in CD_3CN (1.16 mL) to prepare a 10 mM solution. ^1H NMR spectra of cyclopalladated complex before and after addition of 10 mM ligand **3** solution (40 μL, 1.0 equiv.) were measured.

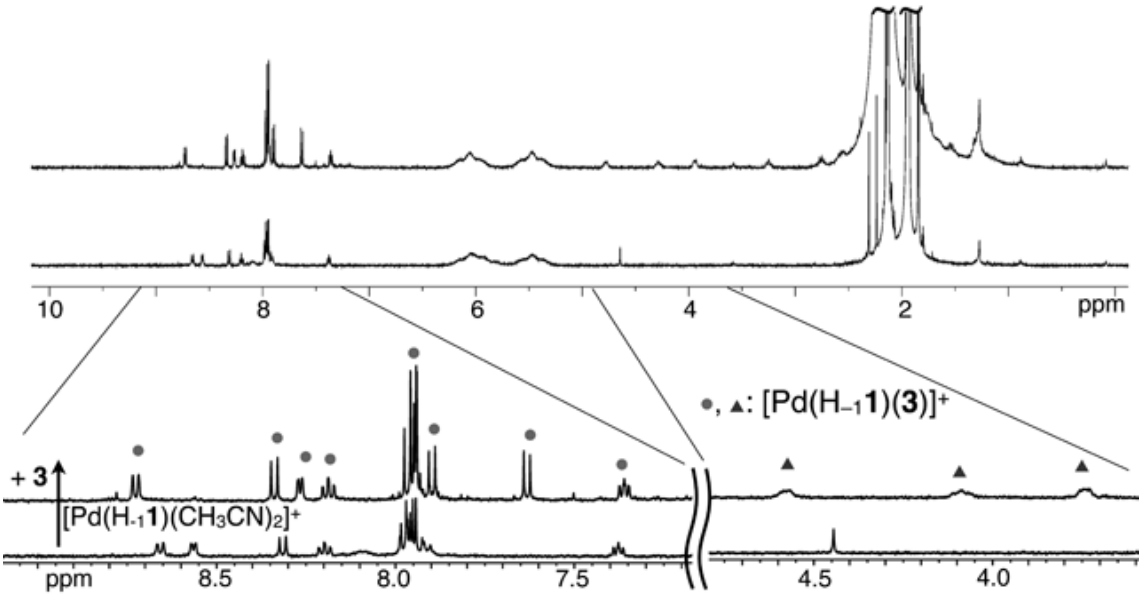


Figure S13. ^1H NMR spectra (500 MHz, CD_3CN, 300 K) of reaction of **2a** and **2b** with **3**.

Preliminary single-crystal X-ray analysis of 2a (needle)

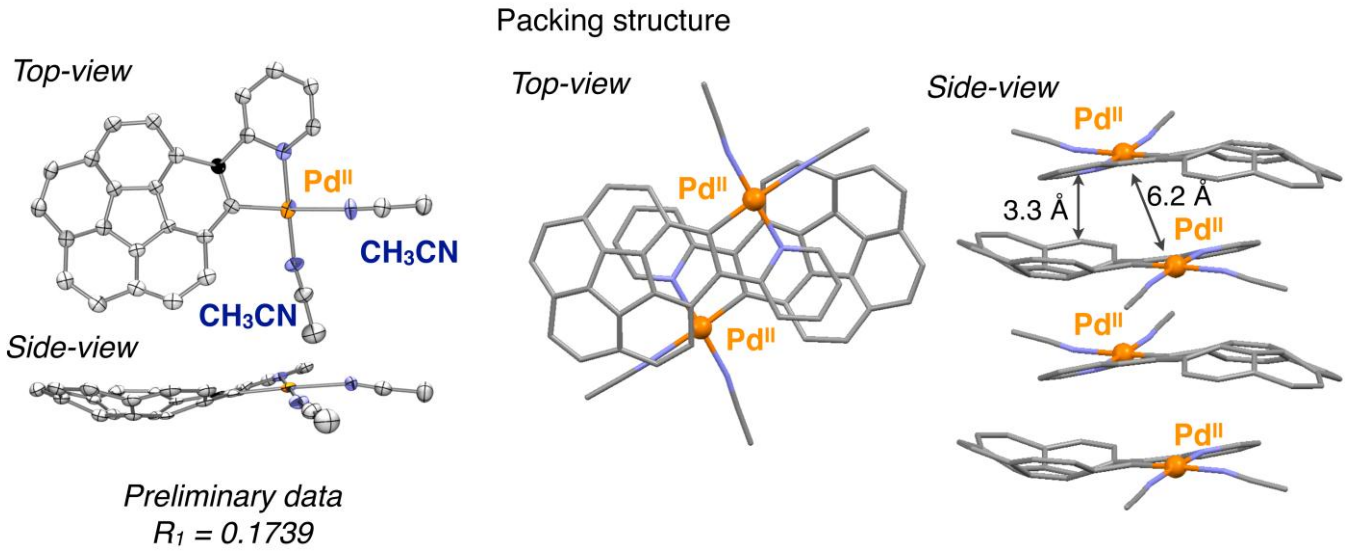


Figure S14. Preliminary single-crystal X-ray analysis of **2a** (needle).

References

1. (a) A. M. Butterfield, B. Gilomen and Jay S. Siegel, *Org. Process Res. Dev.*, 2012, **16**, 664-676; (b) A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldridge and Jay S. Siegel, *J. Am. Chem. Soc.*, 1992, **114**, 1921-1923; (c) J. Christoffers and A. Mann, *Eur. J. Org. Chem.*, 1999, 2511-2514; (d) J. W.-Modcydlarz, P. Cannone and L. C. Leitch, *Synthesis*, 1974, **8**, 566-568; (e) C. S. Jones, E. Elliott and J. S. Siegel, *Synlett*, 2004, **No.1**, 187-191; (f) O. Guillermet, E. Niemi, S. Nagarajan, X. Bouju, D. Martrou, A. Gourdon and S. Gauthier, *Angew. Chem. Int. Ed.*, 2009, **48**, 1970-1973; (g) T. J. Seiers, E. L. Elliott, G. H. Grube and J. S. Siegel, *J. Am. Chem. Soc.*, 1999, **121**, 7804-7813; (h) A. Sygula and P. W. Rabideau, *J. Am. Chem. Soc.*, 2000, **122**, 6323-6324.
2. K. L. Billingsley and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2008, **47**, 4695-4698.
3. (a) G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997. (b) G. M. Sheldrick, SADABS, Program for scaling and correction of area detector data, University of Göttingen (Germany), **1996**.