

Supporting Information for

Chiral Tectonics toward Square Planar Tetranuclear Pd(II) Complexes: Propagation of Axial Chirality through a Long Molecular Axis

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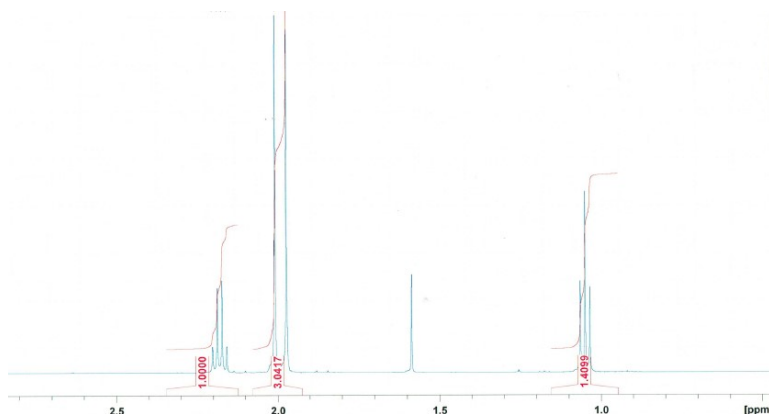
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S1. The ^1H NMR, ^{13}C NMR and mass analyses of Pd (II) complexes

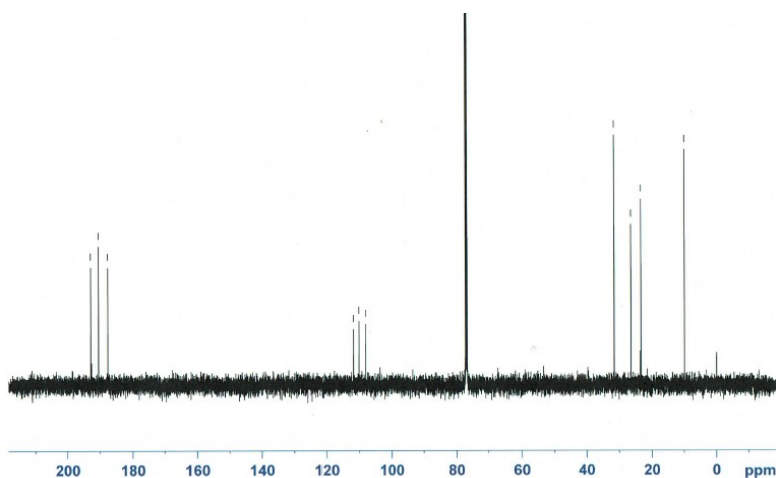
Tpret. ^1H NMR (500 MHz, CDCl_3): $\delta=2.25$ (8H, q, $J=7.5$ Hz, CH_2), 1.09 ppm (12H, t, $J=7.5$ Hz, CH_3); ^{13}C NMR (125 MHz, CDCl_3): $\delta=195.5$ (C_{CO}), 106.1 ($\text{C}_{1,2}$), 29.3 ($\text{C}_{\text{methylene}}$), 8.9 (C_{methyl}), ppm; LRMS (FAB^+ , 3-NBA) calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4$, found $m/z=255$ [$\text{M}+\text{H}$]

[(hfac)Pd(II)]₂(tpret) (1). ^1H NMR (500 MHz, CDCl_3): $\delta=6.21$ (2H, s, CH), 2.15 (8H, q, $J=7.5$ Hz, CH_2), 1.02 ppm (12H, t, $J=7.5$ Hz, CH_3).

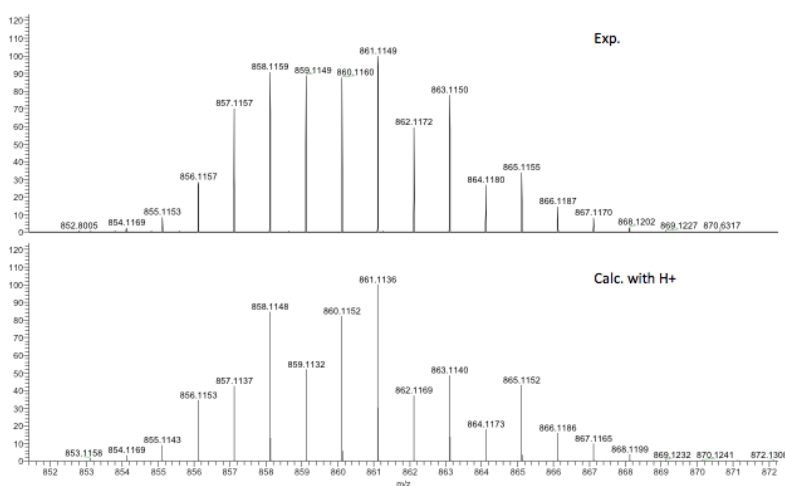
[(taetH)Pd(II)]₂(tpret)(2). ^1H NMR (500 MHz, CDCl_3): $\delta=2.17$ (8H, q, $J=7.4$ Hz, CH_2), 2.00 (12H, s, CH_3), 1.97 (12H, s, CH_3), 1.04 ppm (12H, t, $J=7.4$ Hz, CH_3); ^{13}C NMR (125 MHz, CDCl_3): $\delta=192.8$ (C_{CO}), 190.4 (C_{CO}), 187.6 (C_{CO}), 111.8 (C_{vinyl}), 110.1 (C_{vinyl}), 108.1 (C_{vinyl}), 31.5 ($\text{C}_{\text{methylene}}$), 26.3 (C_{methyl}), 23.2 (C_{methyl}), 9.85 (C_{methyl} in Et) ppm; HRMS (ESI^+ , $\text{CH}_3\text{CN}/\text{H}_2\text{O}$) calcd for $\text{C}_{34}\text{H}_{46}\text{O}_{12}^{106}\text{Pd}^{108}\text{Pd}+\text{H}$ 861.1146, found $m/z=861.1149$ [$\text{M}+\text{H}$]. The product isolated was analyzed by HPLC (SiO_2) and showed to be pure.



^1H NMR (2)



^{13}C NMR (2)

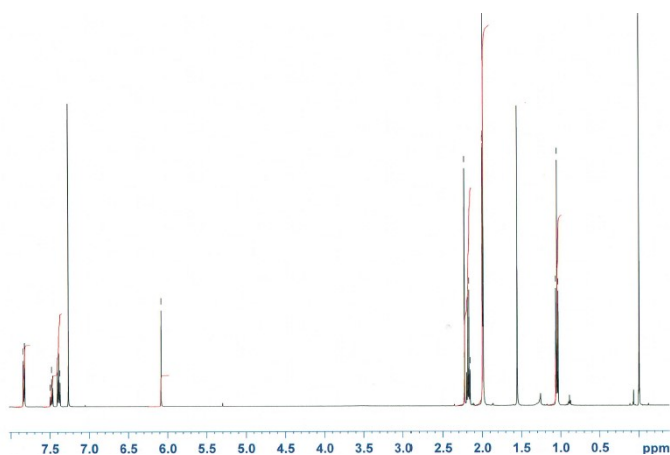


HRMS (2)

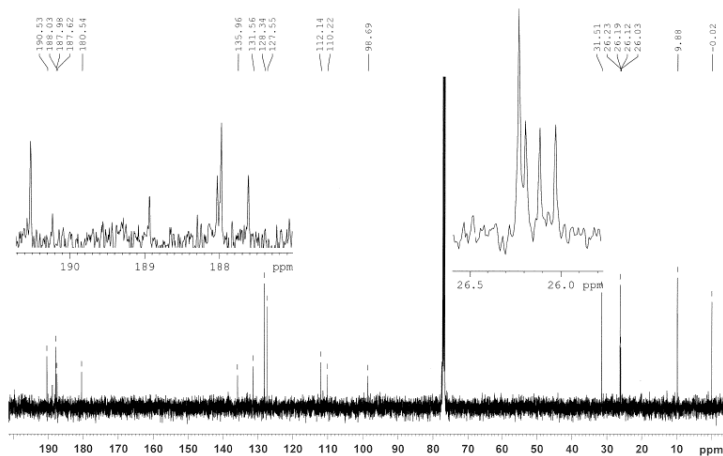
[[*hfac*Pd(II)(*taet*)Pd(II)]₂(*tpret*)] (4). ^1H NMR (500 MHz, CDCl_3): δ =6.25 (2H, s, CH), 2.17 (8H, q, J =7.5 Hz, CH_2), 2.02 (12H, s, CH_3), 1.96 (12H, s, CH), 1.04 (12H, t, J = 7.5 Hz, CH_3)

[[*bzac*Pd(II)(*taet*)Pd(II)]₂(*tpret*)] (5b). ^1H NMR (500 MHz, CDCl_3): δ =7.83 (4H, broad d, J =7.5 Hz, *o*-H), 7.47 (2H, broad t, J =7.5 Hz, *p*-H), 7.38 (4H, t, J =7.5 Hz, *m*-H), 6.06 (2H, s, CH), 2.20 (6H, s, CH_3), 2.15 (8H, q, J =7.5 Hz, CH_2), 1.973 (6H, s, CH_3), 1.969 (6H, s, CH_3), 1.96 (12H, s, CH_3), 1.02 ppm (12H, t, J =7.5 Hz, CH_3); ^{13}C NMR (125 MHz, CDCl_3): δ =190.5 (twice in integral ratio to signals of other carbonyl carbon atoms, C_{CO}), 188.9 (C_{CO}), 188.0 (C_{CO}), 187.9 (twice, C_{CO}), 187.6 (C_{CO}), 180.5 (C_{CO}),

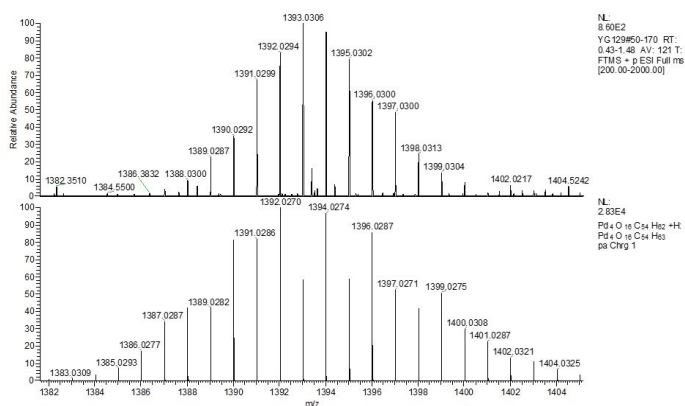
135.9 (C_{arom}), 131.5 (C_{arom}), 128.3 ($o\text{-}C_{\text{arom}}$), 127.5 ($m\text{-}C_{\text{arom}}$), 112.1 (twice, C_{vinyl}), 110.1 (C_{vinyl}), 98.6 (C_{vinyl}), 31.5 ($C_{\text{methylene}}$), 26.21 (twice, C_{methyl}), 26.17 (C_{methyl}), 26.09 (C_{methyl}), 26.01 (C_{methyl}), 9.9 (C_{methyl} in Et) ppm; HRMS (ESI⁺, CH₃CN/H₂O) calcd for C₅₄H₆₂O₁₆Pd₄+H⁺ 1391.0286, found m/z =1391.0299 [M+H⁺]. The product isolated was analyzed by HPLC (SiO₂) and showed to be pure.



¹H NMR (5b)

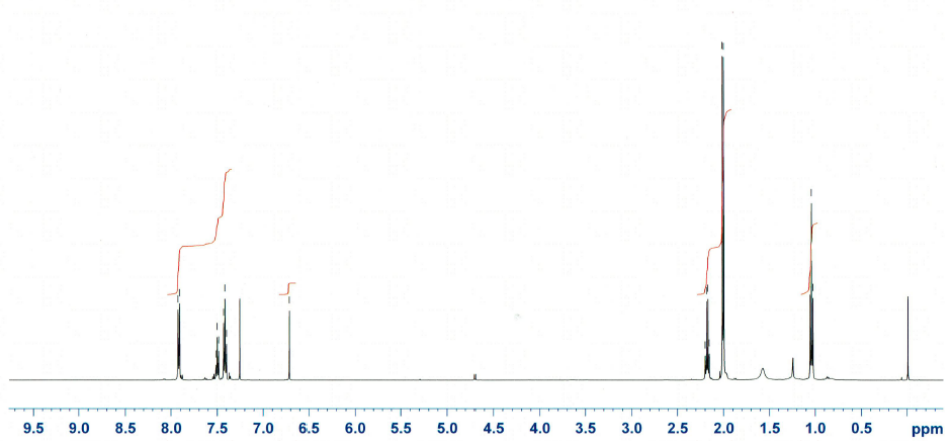


¹³C NMR (5b)

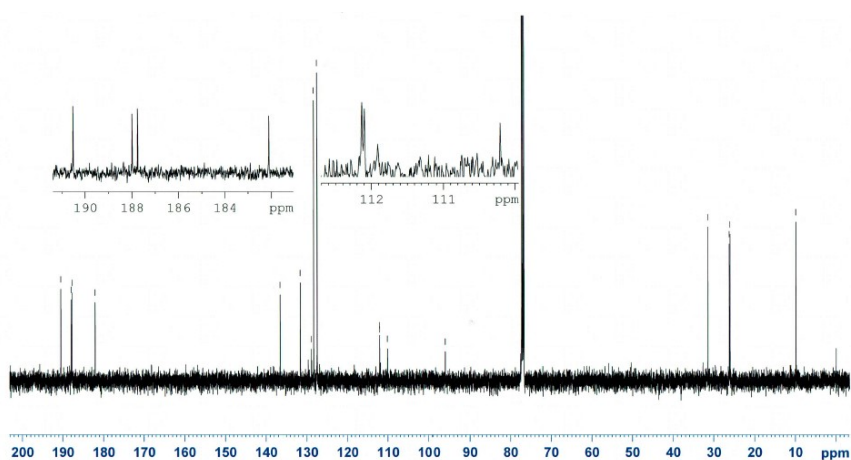


HRMS (5b)

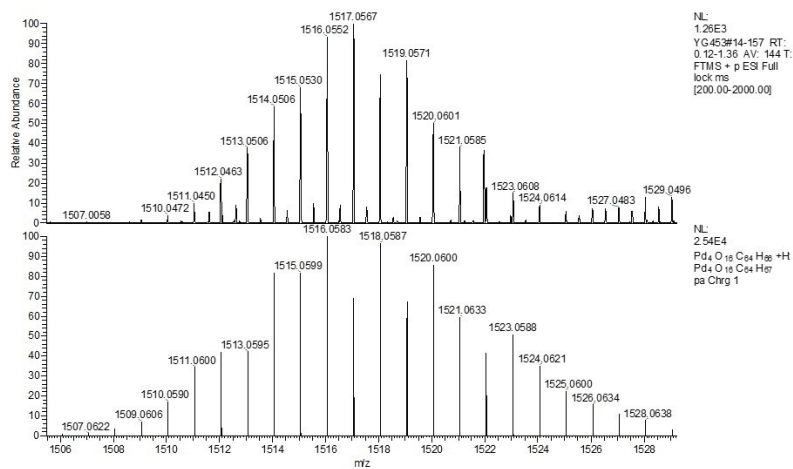
[[{(dbm)Pd(II)(taet)Pd(II)}₂(tpret)] (5a). ¹H NMR(400 MHz, CDCl₃): δ=7.93 (8H, broad d, *J*=8.0 Hz, *o*-H), 7.51 (4H, broad t, *J*=8.0 Hz, *p*-H), 7.42 (8H, broad t, *J*=8.0 Hz, *m*-H), 6.72 (2H, s, CH), 2.18 (8H, q, *J*=8.0 Hz, CH₂), 2.02 (12H, s, CH₃), 2.01 (12H, s, CH₃), 1.05 ppm (12H, t, *J*=8.0 Hz, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ=190.5 (C_{CO}), 188.0 (C_{CO}), 187.8 (C_{CO}), 182.1 (C_{CO}), 136.6 (C_{arom}), 131.6 (C_{arom}), 128.4 (*o*-C_{arom}), 127.6 (*m*-C_{arom}), 112.14 (twice, C_{vinyl}), 112.10 (C_{vinyl}), 110.2 (C_{vinyl}), 31.5 (C_{methylene}), 26.3 (C_{methyl}), 26.0 (C_{methyl}), 9.9 (C_{methyl}) ppm; HRMS (ESI⁺, CH₃CN/H₂O) calcd for C₆₄H₆₆O₁₆Pd₄+H⁺ 1515.0568, found *m/z*=1515.0530 [M+H⁺]. The product isolated was analyzed by HPLC (SiO₂) and showed to be pure.



¹H NMR (5a)



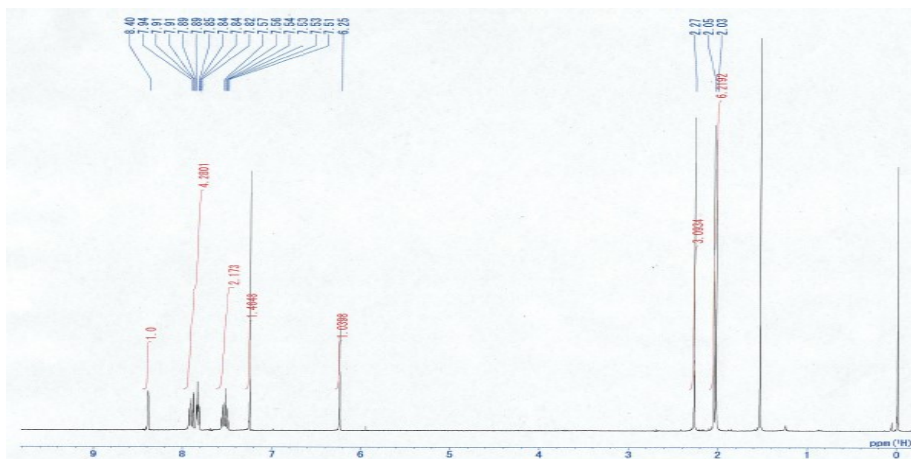
^{13}C NMR (**5a**)



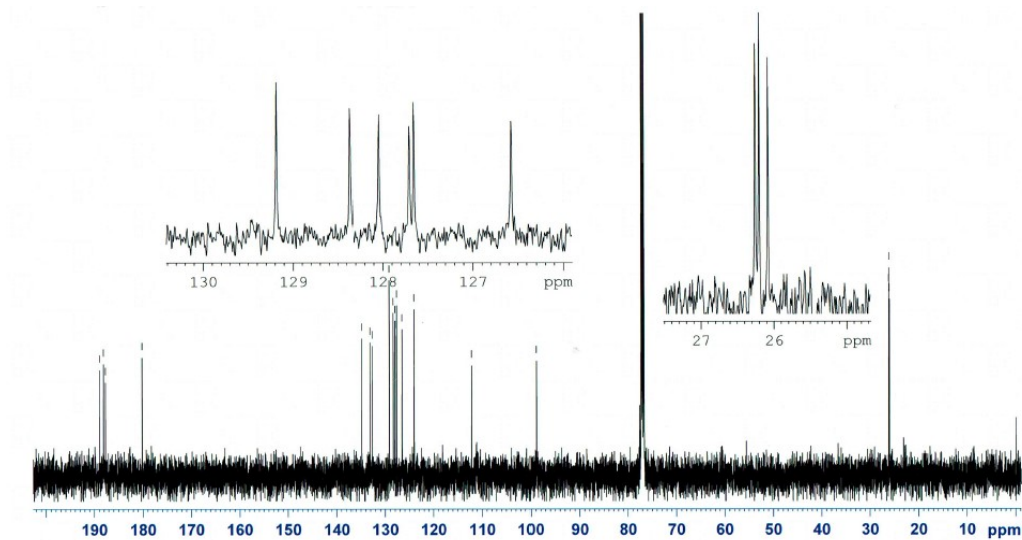
HRMS (**5a**)

[[*(npac)Pd(II)*]₂(*taet*)] (7b**).** ^1H NMR (500 MHz, CDCl_3): δ =8.38 (2H, s, aromatic H₁), 7.91-7.81 (8H, aromatic H_{3,4,5,8}), 7.53 (2H, broad t, J =8.0 Hz, aromatic H₆), 7.49 (2H, broad t, J =8.0 Hz, aromatic H₇), 6.23 (2H, s, CH), 2.26 (6H, s, CH₃), 2.03 (6H, s, CH₃), 2.01 ppm (6H, s, CH₃); ^{13}C NMR (125 MHz, CDCl_3): δ =188.9 (C_{CO}), 188.1 (C_{CO}), 187.7 (C_{CO}), 180.2 (C_{CO}), 134.8 (C_{arom}), 133.1 (C_{arom}), 132.6 (C_{arom}), 129.2 (C_{arom}),

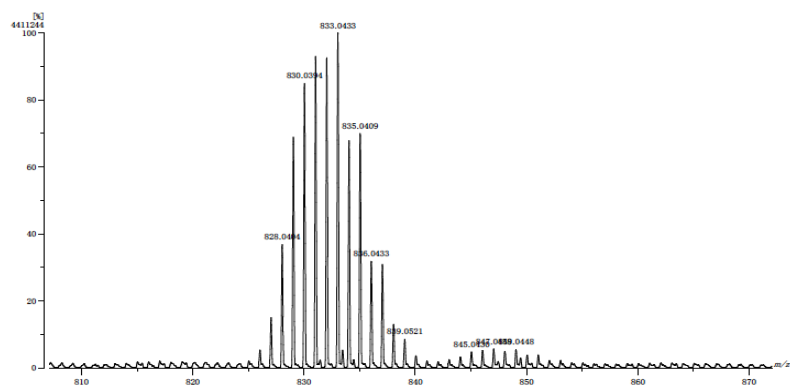
128.3 (C_{arom}), 128.0 (C_{arom}), 127.7 (C_{arom}), 127.6 (C_{arom}), 126.5 (C_{arom}). 124.1 (C_{arom}), 112.2 (C_{vinyl}), 98.9 (C_{vinyl}), 26.2 (C_{methyl}), 26.1 (C_{methyl}), 26.0 (C_{methyl}) ppm; HRMS (FAB⁺, 3-NBA) calcd for C₃₈H₃₄O₈Pd₂+H⁺ 833.0406, found *m/z*=833.0433 [M+H]. The product isolated was analyzed by HPLC (SiO₂) and showed to be pure.



¹H NMR (7b)

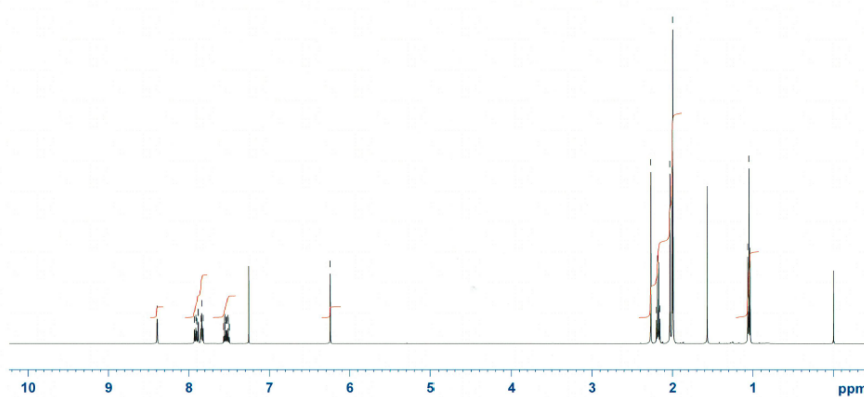


¹³C NMR (7b)

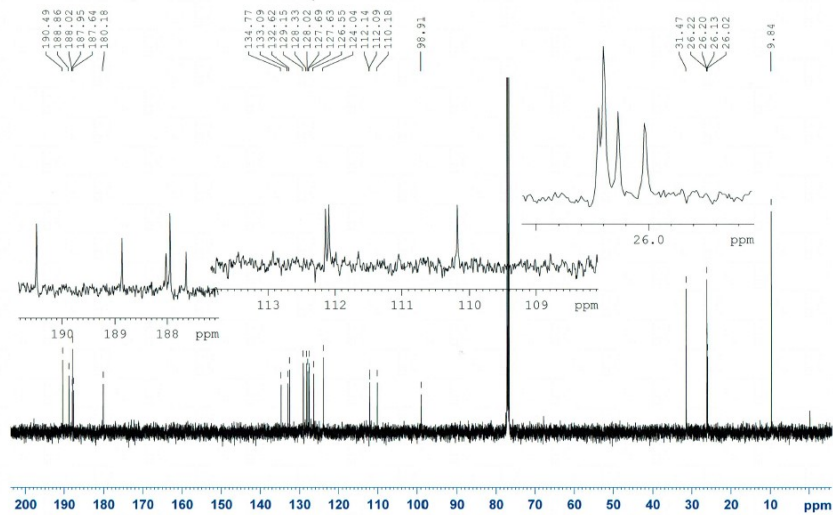


HRMS (7b)

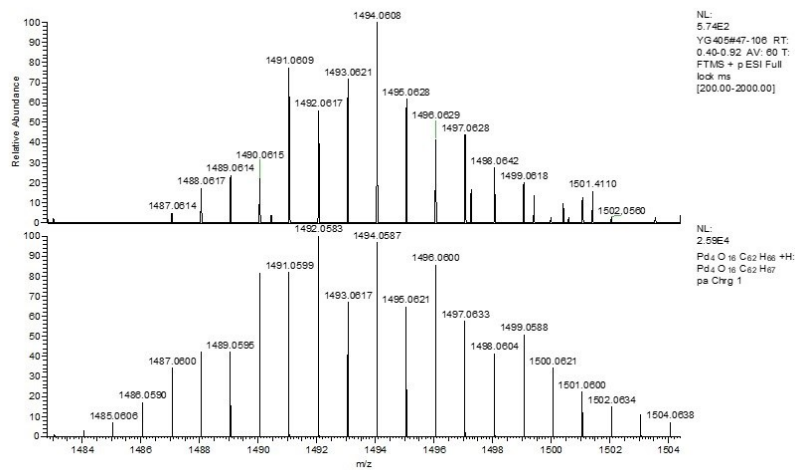
[{(npac)Pd(II)(taet)Pd(II)}₂(tpret)] (5c). ¹H NMR(400 MHz, CDCl₃): δ=8.40 (2H, s, aromatic H₁), 7.94-7.80 (8H, aromatic H_{3,4,5,8}), 7.56 (2H, broad t, *J*=8.0 Hz, aromatic H₆), 7.52 (2H, broad t, *J*=8.0 Hz, aromatic H₇), 6.25 (2H, s, CH), 2.28 (6H, s, CH₃), 2.18 (8H, q, *J*=8.0 Hz, CH₂), 2.04 (6H, s, CH₃), 2.01 (6H, s, CH₃), 2.00 (12H, s, CH₃), 1.05 ppm (12H, t, *J*=8.0 Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ=190.5 (twice, C_{CO}), 188.9 (C_{CO}), 188.05 (C_{CO}), 187.98 (twice, C_{CO}), 187.67 (C_{CO}), 180.2 (C_{CO}), 134.8 (C_{arom}), 133.1 (C_{arom}), 132.7 (C_{arom}), 129.1 (C_{arom}), 128.4 (C_{arom}), 128.1 (C_{arom}), 127.7 (C_{arom}), 127.6 (C_{arom}), 126.6 (C_{arom}), 124.1 (C_{arom}), 112.2 (C_{vinyl}), 112.1 (C_{vinyl}), 110.2 (C_{vinyl}), 99.0 (C_{vinyl}), 31.5 (C_{methylene}), 26.26 (twice, C_{methyl}), 26.24 (C_{methyl}), 26.18 (C_{methyl}), 26.06 (C_{methyl}), 9.9 (C_{methyl} in Et) ppm; HRMS (ESI⁺, CH₃CN/H₂O) calcd for C₆₂H₆₆O₁₆Pd₄+H⁺ 1491.0568, found *m/z*=1491.0599 [M+H]. The product isolated was analyzed by HPLC (SiO₂) and showed to be pure.



¹H NMR (5c)



^{13}C NMR (5c)



HRMS (5c)

S2. HPLC chromatographic resolution of Pd(II) complexes

The chromatograms are shown below when Pd(II) complexes were resolved on a chiral HPLC column:

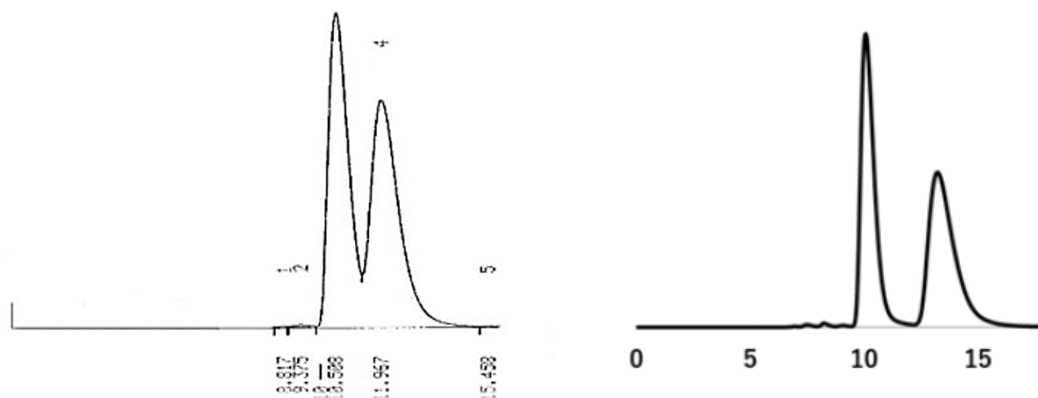


Figure S1. The HPLC chromatogram when $[\{(bzac)Pd(II)(taet)Pd(II)\}_2(tpret)]$ (**5b**) and $[\{(npac)Pd(II)(taet)Pd(II)\}_2(tpret)]$ (**5c**) was eluted on a 4 mm (i.d.) \times 25 cm column (IC Daicel, Japan) at a flow rate of 0.5 ml/min. The eluent was dichloromethane with 0.07% methanol. The monitoring wavelength was 400 nm.

S3. ECD spectra of dinuclear Pd(II) complexes

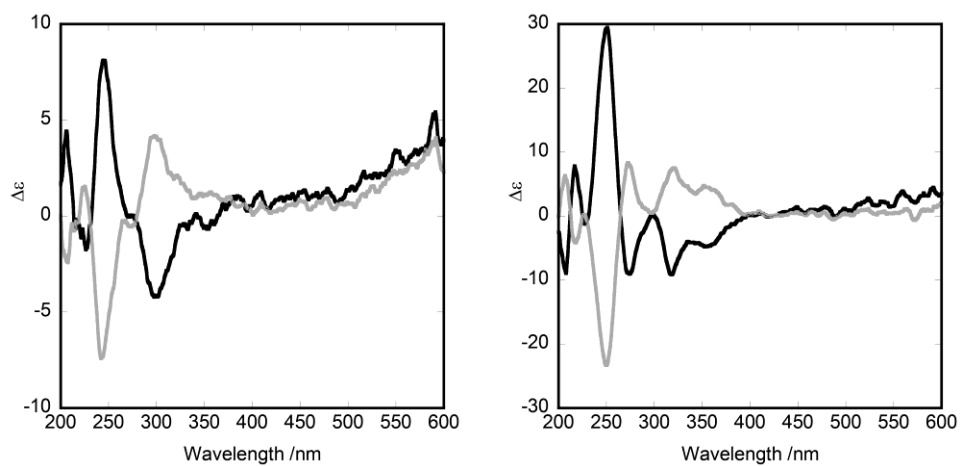
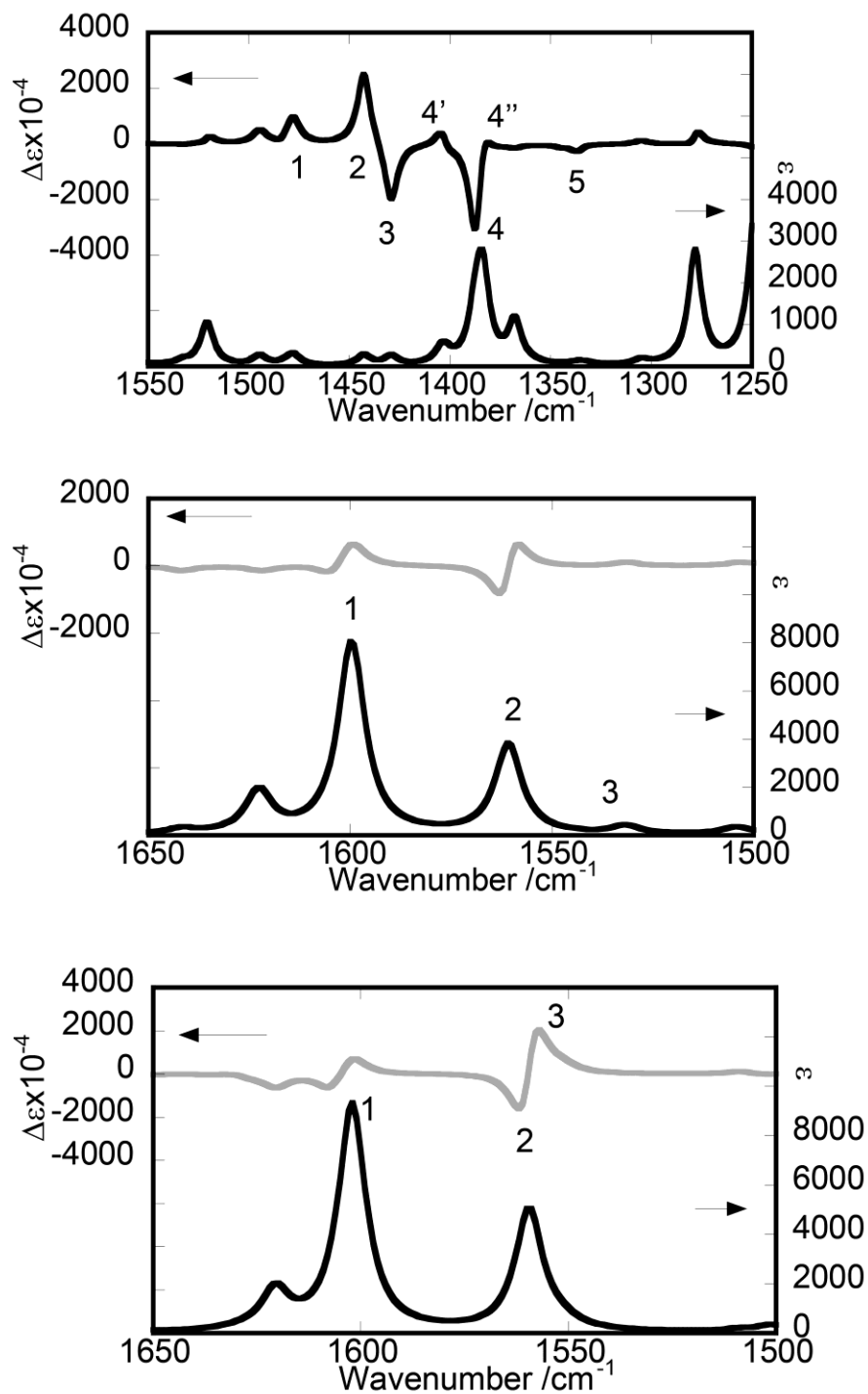


Figure S2. The ECD spectra of $[\{(bzac)Pd(II)\}_2(taet)]$ (**7a**) (left) and $[\{(npac)Pd(II)\}_2(taet)]$ (**7b**) (right) resolved on a chiral column. The solid and grey lines indicated the less and more retaining fractions, respectively. The solvent was acetonitrile.

S4. DFT calculation of IR and VCD



The IR and VCD spectra of Pd(II) complexes were calculated.

Figure S3. Calculated IR and VCD spectra:

[{(hfac)Pd(II)}₂(dabe)] (**6**) (upper) [(bzac)Pd(II)]₂(taet) (**7a**) (middle) and [(npac)Pd(II)]₂(taet) (**7b**) (lower)

Table S1 (a) Assignment of VCD [(hfac)Pd(II)]₂(dabe) (**6**)

No	Ligand	assignment	VCD signal sign and wavenumber (cm ⁻¹) (experiment) (less retaining fraction)	VCD signal sign and wavenumber (cm ⁻¹) (calculation)(S-form)
1	dabe(CH ₃)	C-H bending	+ 1444	+ 1478(in plane)
2	dabe	C-C-C (C-O)	+ 1416	+ 1443 (out of phase)
3	dabe	C-C-C (C-O)	- 1400	- 1430 (in-phase)
4'	dabe(CH ₃)	C-H bending	+ 1341	+ 1403(out of plane)
4	dabe	C-C-C	- 1327	- 1387 (out of phase)
4''	dabe	C-C-C	+ 1314	+ 1384 (in phase)
5	dabe(benzyl)	C-H(benzyl)	- 1302	- 1337

Table S1 (b) Assignment of VCD [$\{(bzac)Pd(II)\}_2(taet)$] (**7a**)

No	Ligand	assignment	VCD signal sign and wavenumber (cm ⁻¹) (experiment) (more retaining fraction)	VCD signal sign and wavenumber (cm ⁻¹) High/Low (calculation) (<i>S</i> -form)
1	bzac and taet	C=O stretching	+ 1541	+/- 1604, 1599
2	bzac	C-C-C, C-H	-/+ 1522, 1510	-/+ 1560 couplet
3	bzac	C-H (benzyl)	+ 1488	-/+ 1531 couplet

Table S1 (c) Assignment of VCD [$\{(\text{npac})\text{Pd}(\text{II})\}_2(\text{taet})$] (**7b**)

No	Ligand	assignment	VCD signal sign and wavenumber (cm^{-1}) (experiment) (more retaining fraction)	VCD signal sign and wavenumber (cm^{-1}) High/Low (calculation)(S-form)
1	npac and taet	C=O stretching	+ 1542	-/+ 1607, 1602
2,2'	npac	C-C-C, C-H	-/+ 1521, 1511	-/+ 1560 couplet
3	npac	C-H (naphthyl)	+ 1503	-/+ 1551 couplet

S5. The crystal data and the table of selected bond lengths and torsion angles

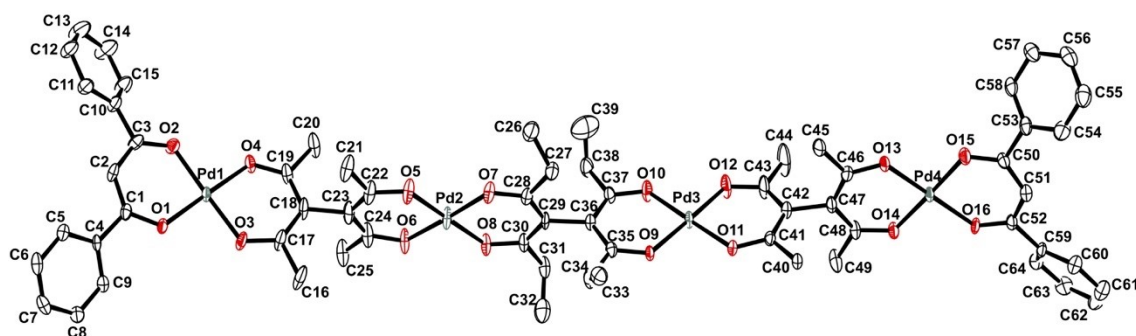


Figure S5-1. An ORTEP drawing of $[\{(\text{dbm})\text{Pd}(\text{II})(\text{taet})\text{Pd}(\text{II})\}_2(\text{tpret})]$ (**5a**) with a numbering scheme of atoms. The thermal ellipsoids are scaled to the 50% probability level. Disordered phenyl group atoms with lower occupancy, hydrogen atoms, and solvent molecules are omitted for clarity.

Table S5-1. Selected bond distances (Å) and torsion angles (deg) of $[\{(\text{dbm})\text{Pd}(\text{II})(\text{taet})\text{Pd}(\text{II})\}_2(\text{tpret})]$

Distances (Å)			
Pd1 – O1	1.970(2)	Pd1 – O2	1.968(3)
Pd1 – O3	1.963(3)	Pd1 – O4	1.973(2)
Pd2 – O5	1.971(3)	Pd2 – O6	1.968(3)
Pd2 – O7	1.957(4)	Pd2 – O8	1.970(3)
Pd3 – O9	1.981(2)	Pd3 – O10	1.966(3)
Pd3 – O11	1.969(3)	Pd3 – O12	1.960(3)
Pd4 – O13	1.961(3)	Pd4 – O14	1.965(3)
Pd4 – O15	1.970(3)	Pd4 – O16	1.990(2)

Torsion angles (deg)

C19 – C18 – C23 – C22	82.4(6)	C28 – C29 – C36 – C35	85.3(5)
C43 – C42 – C47 – C46	85.2(5)		

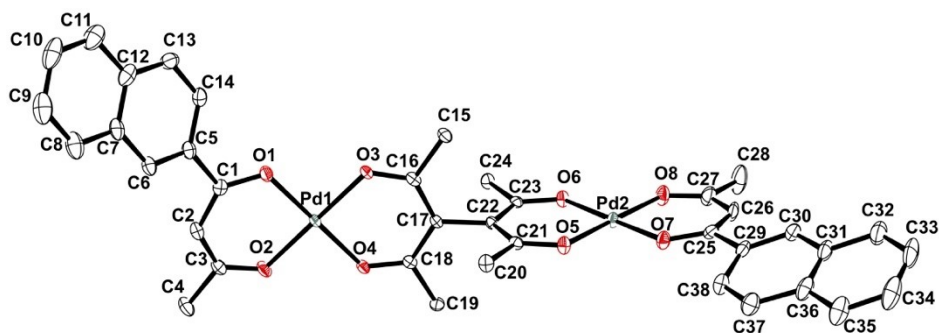


Figure S5-2. An ORTEP drawing of [$\{(\text{npac})\text{Pd}(\text{II})\}_2(\text{taet})$] (**7b**) with a numbering scheme of atoms. The thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms, and solvent molecules are omitted for clarity.

Table S5-2. Selected bond distances (Å) and torsion angle (deg) of [$\{(\text{npac})\text{Pd}(\text{II})\}_2(\text{taet})$]

Distances (Å)			
Pd1 – O1	1.992(3)	Pd1 – O2	1.982(2)
Pd1 – O3	1.963(2)	Pd1 – O4	1.973(2)
Pd2 – O5	1.963(2)	Pd2 – O6	1.973(2)
Pd2 – O7	1.977(3)	Pd2 – O8	1.999(3)

Torsion angle (deg)	
C16 – C17 – C22 – C21	86.3(3)
