

## On the nature of optical activity in chiral transition metal complexes: [Pd(Me)<sub>2</sub>(BINAP)] Supporting Information

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### Experimental Details

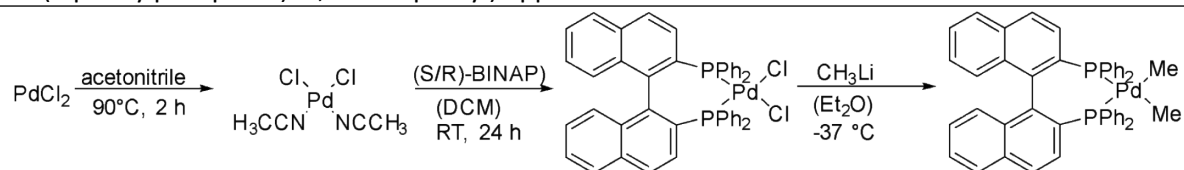
#### General

All procedures with water and air sensitive substrates were conducted under argon atmosphere (Schlenk, Glovebox). Chemicals were purchased from Sigma Aldrich. [PdCl<sub>2</sub>(BINAP)] was synthesized according to literature procedure.<sup>[1,2]</sup> Solvents were dried over molecular sieve Å4 and degassed via freeze pumping, afterwards stored under argon atmosphere. The liquid state <sup>1</sup>H-NMR and <sup>31</sup>P-NMR spectra were recorded on a 400 MHz Bruker Advance DRX400 spectrometer. Samples were dissolved in 0.4 mL of benzene-d<sub>6</sub> inside standard NMR tubes. All chemical shifts are given in δ-values (ppm). <sup>1</sup>H-NMR spectra of complexes were calibrated to the solvent signal benzene: 7.16 ppm. UV-VIS and CD spectroscopy were measured at room temperature on a J-815 spectrometer (Jasco) with 50 nm/min with two to three repetitions. Sample concentrations were 0.13 mg/mL for [Pd(Me)<sub>2</sub>(R/S-BINAP)]. The toluene solutions were placed into 1 mm quartz capillaries. The IR spectra were collected on a Bruker FT-IR spectrometer inside an argon-purged glove box with an attenuated total reflectance (ATR) setup.

#### PdMe<sub>2</sub>(BINAP) – (2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl)dimethylpalladium (II)

As the complexes were not described in the literature yet, we synthesized and structurally characterized the complexes (both enantiomers) for the first time. It was found that the PdMe<sub>2</sub>(BINAP) complex decomposes easily to the more stable Pd<sup>0</sup>(BINAP)<sub>2</sub> depending on synthesis route and reaction conditions. Finally, we decided for the synthesis pathway attaching the BINAP ligands directly to PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> by substitution of acetonitrile.<sup>[1,2]</sup> The PdCl<sub>2</sub>(BINAP) complex was subsequently methylated with methyl lithium resulting in PdMe<sub>2</sub>(BINAP) (Scheme S1). The final complex PdMe<sub>2</sub>(BINAP) was obtained with good purity for the S- and R-BINAP ligands with a yield of 36 %. After purification and re-crystallization, single crystals of PdMe<sub>2</sub>(S-BINAP) could be grown and isolated from the colourless solution and the structure of the complex was confirmed by X-ray diffraction (SC-XRD).

Scheme S1: Synthesis pathway from palladium chloride to PdMe<sub>2</sub>(BINAP) (BINAP = 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl) applied for both enantiomers R and S.



To a -35 °C cold solution of PdCl<sub>2</sub>(BINAP) (244 mg, 0.11 mmol) in diethyl ether (8 mL) a 1.6 M solution of methyl lithium (0.6 mL, 9.4 mmol) was added dropwise under continuous stirring. The reaction solution was kept at -5 °C until the complete discoloration of the solution could be observed. Afterwards, 5 mL of water was added to the reaction mixture, before it was cooled to -40 °C. The organic layer was separated and dried over MgSO<sub>4</sub>. The rest of the solvent was removed under vacuo,

so a light-pink solid was obtained. The solid was solved in 16 mL diethyl ether and stirred for one hour, then 18 mL pentane was added slowly to the solution and kept in the freezer overnight. A colourless precipitate was obtained, which was filtered and dried under vacuo. 85 mg (0.11 mmol, 36 % yield) of PdMe<sub>2</sub>(R-BINAP) or PdMe<sub>2</sub>(S-BINAP) was obtained and stored at -37 °C.

<sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) δ (ppm) = 1.10 (s, 6H, Pd(CH<sub>3</sub>)<sub>2</sub>), 6.34-6.42 (t, 4H, naphthyl-CH), 6.45-6.51 (m, 2H, PPh<sub>2</sub>), 6.63-6.69 (m, 4H, PPh<sub>2</sub>), 6.92-7.25 (m, 12H, PPh<sub>2</sub>), 7.48-7.759 (m, 6H, naphthyl-CH, PPh<sub>2</sub>), 7.89-7.97 (m, 4H, naphthyl-CH).

<sup>31</sup>P-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) δ (ppm) = 23.43 (s, 2P, 2P-BINAP).

CD: 300-334 nm, 334-433 nm.

UV-VIS: 300-400 nm.

IR: 3100 cm<sup>-1</sup> (Ph-H-stretch). 3000 cm<sup>-1</sup> (Me-H-stretch), 2900 cm<sup>-1</sup> (Me-H-stretch), 700 cm<sup>-1</sup> (P-Pd-P-bend).

### *X-ray Crystallographic Details*

Single crystals of PdMe<sub>2</sub>(R/S-BINAP) were grown from a toluene solution by slow evaporation and simultaneous diffusion of pentane into it under an argon atmosphere. Data were collected on a single crystal X-ray diffractometer equipped with a CCD detector (Bruker APEX II, κ-CCD), a fine-focus sealed tube with MoK<sub>α</sub> radiation (λ = 0.71073 Å) and a Triumph monochromator using the APEX2 software package (PdMe<sub>2</sub>(S-BINAP)) or a CMOS detector (Bruker Photon-100), a TXS rotating anode with MoK<sub>α</sub> radiation and a Helios optic using the APEX3 software package (PdMe<sub>2</sub>(R-BINAP)).<sup>[3]</sup> The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.<sup>[4]</sup> Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.<sup>[4]</sup> Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL in conjunction with SHELXLE.<sup>[5,6]</sup> Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and U<sub>iso</sub>(H) = 1.5·U<sub>eq</sub>(C). Non-methyl H atoms were placed in calculated positions and refined using a riding model with methylene, aromatic, and other C–H distances of 0.99 Å, 0.95 Å and 1.00 Å, respectively, and U<sub>iso</sub>(H) = 1.2·U<sub>eq</sub>(C). Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing Σw(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup> with the SHELXL weighting scheme.<sup>[5]</sup> Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.<sup>[7]</sup> Images of the crystal structure were generated with PLATON.<sup>[8]</sup> CCDC 2221766-2221767 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

Crystallographic Data PdMe<sub>2</sub>(S-BINAP) (CCDC 2221766)

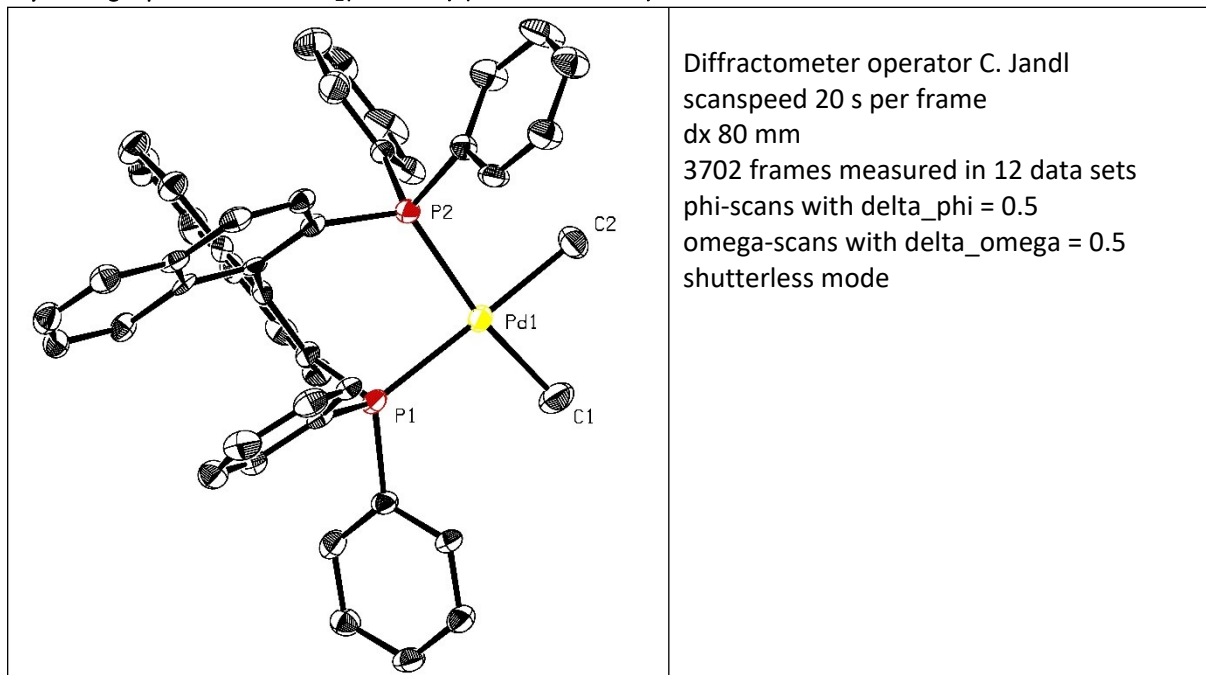


Table S1: Crystal Data PdMe<sub>2</sub>(S-BINAP)

<u>C<sub>46</sub>H<sub>38</sub>P<sub>2</sub>Pd</u>	
<u>M<sub>r</sub> = 759.10</u>	<u>D<sub>x</sub> = 1.413 Mg m<sup>-3</sup></u>
<u>Monoclinic, P2<sub>1</sub></u>	<u>Melting point: ? K</u>
<u>Hall symbol: P 2yb</u>	<u>Mo Kα radiation, λ = 0.71073 Å</u>
<u>a = 11.949 (4) Å</u>	<u>Cell parameters from 3674 reflections</u>
<u>b = 11.507 (4) Å</u>	<u>θ = 2.5–23.7°</u>
<u>c = 13.750 (4) Å</u>	<u>μ = 0.64 mm<sup>-1</sup></u>
<u>β = 109.32 (2)°</u>	<u>T = 100 K</u>
<u>V = 1784.1 (10) Å<sup>3</sup></u>	<u>Fragment, colourless</u>
<u>Z = 2</u>	<u>0.19 × 0.11 × 0.08 mm</u>
<u>F(000) = 780</u>	

Table S2: Data Collection PdMe<sub>2</sub>(S-BINAP)

<u>Radiation source: fine-focus sealed tube</u>	<u>5277 reflections with I &gt; 2σ(I)</u>
<u>Triumph monochromator</u>	<u>R<sub>int</sub> = 0.055</u>
<u>Detector resolution: 16 pixels mm<sup>-1</sup></u>	<u>θ<sub>max</sub> = 25.4°, θ<sub>min</sub> = 2.0°</u>
<u>phi- and ω-rotation scans</u>	<u>h = -14 14</u>
<u>Absorption correction: multi-scan</u>	<u>k = -13 13</u>
<u>SADABS 2016/2, Bruker</u>	
<u>T<sub>min</sub> = 0.615, T<sub>max</sub> = 0.745</u>	<u>l = -16 16</u>
<u>15060 measured reflections</u>	

Table S3: Refinement PdMe<sub>2</sub>(S-BINAP)

<u>Refinement on F<sup>2</sup></u>	<u>Hydrogen site location: inferred from neighbouring sites</u>
<u>Least-squares matrix: full</u>	<u>H-atom parameters constrained</u>
<u>R[F<sup>2</sup> &gt; 2σ(F<sup>2</sup>)] = 0.036</u>	<u>W = 1/[Σ<sup>2</sup>(FO<sup>2</sup>) + (0.023P)<sup>2</sup>] WHERE P = (FO<sup>2</sup> + 2FC<sup>2</sup>)/3</u>

$wR(F^2) = 0.069$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 0.99$	$\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$
6131 reflections	$\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$
444 parameters	Extinction correction: none
1 restraint	Extinction coefficient: -
0 constraints	Absolute structure: Flack, Parsons <sup>[9,10]</sup>
Primary atom site location: iterative	Absolute structure parameter: 0.02 (2)
Secondary atom site location: difference	
Fourier map	

Crystallographic Data PdMe<sub>2</sub>(R-BINAP) (CCDC 2221767)

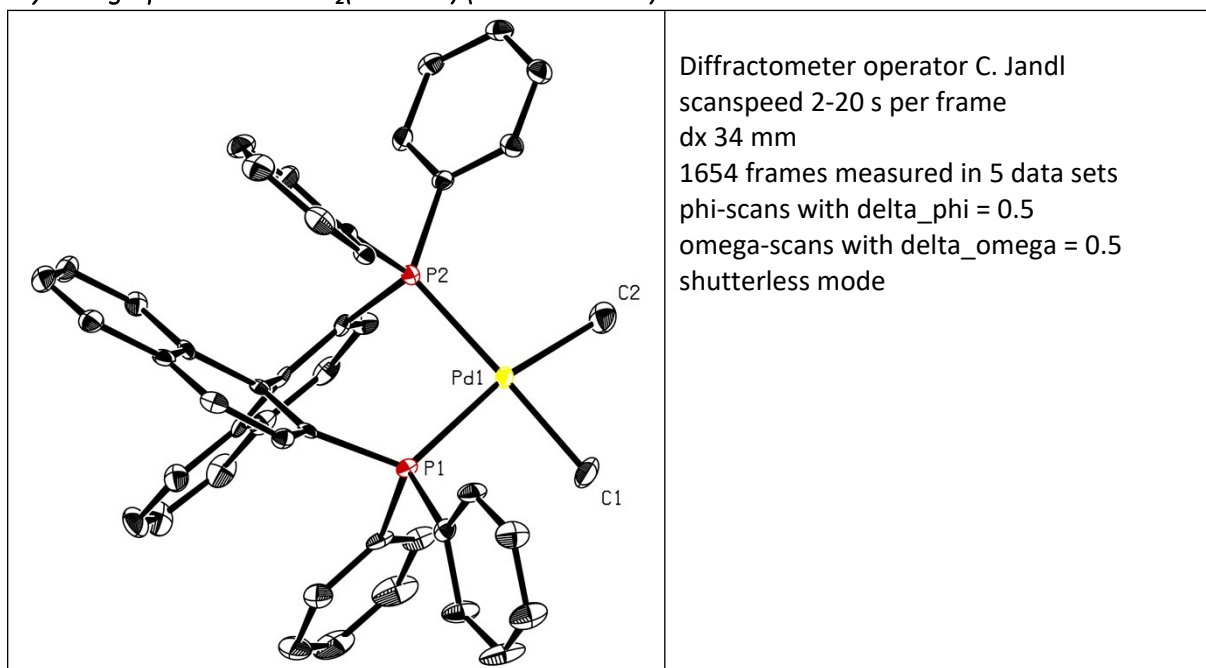


Table S4: Crystal Data PdMe<sub>2</sub>(R-BINAP)

$C_{46}H_{38}P_2Pd$	
$M_r = 759.10$	$D_x = 1.417 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Melting point: ? K
Hall symbol: $P 2_1 yb$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 11.8884 (6) \text{ \AA}$	Cell parameters from 9935 reflections
$b = 11.4981 (5) \text{ \AA}$	$\theta = 2.4\text{--}25.7^\circ$
$c = 13.7715 (7) \text{ \AA}$	$\mu = 0.65 \text{ mm}^{-1}$
$\beta = 109.110 (2)^\circ$	$T = 103 \text{ K}$
$V = 1778.74 (15) \text{ \AA}^3$	Fragment, colourless
$Z = 2$	$0.29 \times 0.05 \times 0.02 \text{ mm}$
$F(000) = 780$	

Table S5: Data Collection PdMe<sub>2</sub>(R-BINAP)

Bruker Photon CMOS diffractometer	6493 independent reflections
Radiation source: TXS rotating anode	5995 reflections with $I > 2\sigma(I)$
Helios optic monochromator	$R_{\text{int}} = 0.068$
Detector resolution: 16 pixels $\text{mm}^{-1}$	$\theta_{\max} = 25.4^\circ$ , $\theta_{\min} = 2.4^\circ$

<u>phi- and <math>\omega</math>-rotation scans</u>	$h = \underline{-14}$ <u>14</u>
Absorption correction: <u>multi-scan</u>	$k = \underline{-13}$ <u>13</u>
<u>SADABS 2016/2, Bruker</u>	
$T_{\min} = \underline{0.679}$ , $T_{\max} = \underline{0.745}$	$l = \underline{-16}$ <u>16</u>
<u>39950</u> measured reflections	

Table S6: Refinement PdMe <sub>2</sub> (R-BINAP)	
Refinement on $F^2$	Hydrogen site location: <u>inferred from neighbouring sites</u>
Least-squares matrix: <u>full</u>	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = \underline{0.027}$	$W = 1/[\Sigma^2(FO^2) + (0.0201P)^2 + 0.5977P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$wR(F^2) = \underline{0.053}$	$(\Delta/\sigma)_{\max} = \underline{0.001}$
$S = \underline{1.05}$	$\Delta\rho_{\max} = \underline{0.26} \text{ e } \text{Å}^{-3}$
<u>6493</u> reflections	$\Delta\rho_{\min} = \underline{-0.41} \text{ e } \text{Å}^{-3}$
<u>444</u> parameters	Extinction correction: <u>none</u>
<u>1</u> restraint	Extinction coefficient: <u>-</u>
<u>0</u> constraints	Absolute structure: <u>Flack, Parsons</u> <sup>[9,10]</sup>
Primary atom site location: <u>iterative</u>	Absolute structure parameter: <u>-0.034 (12)</u>
Secondary atom site location: <u>difference</u>	
Fourier map	

### Computational Methods

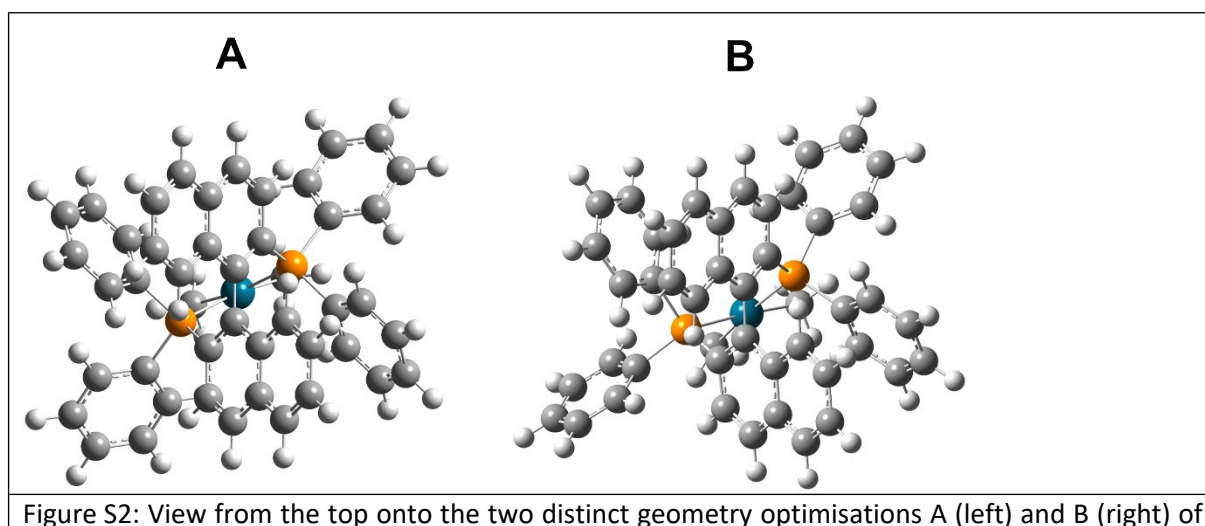
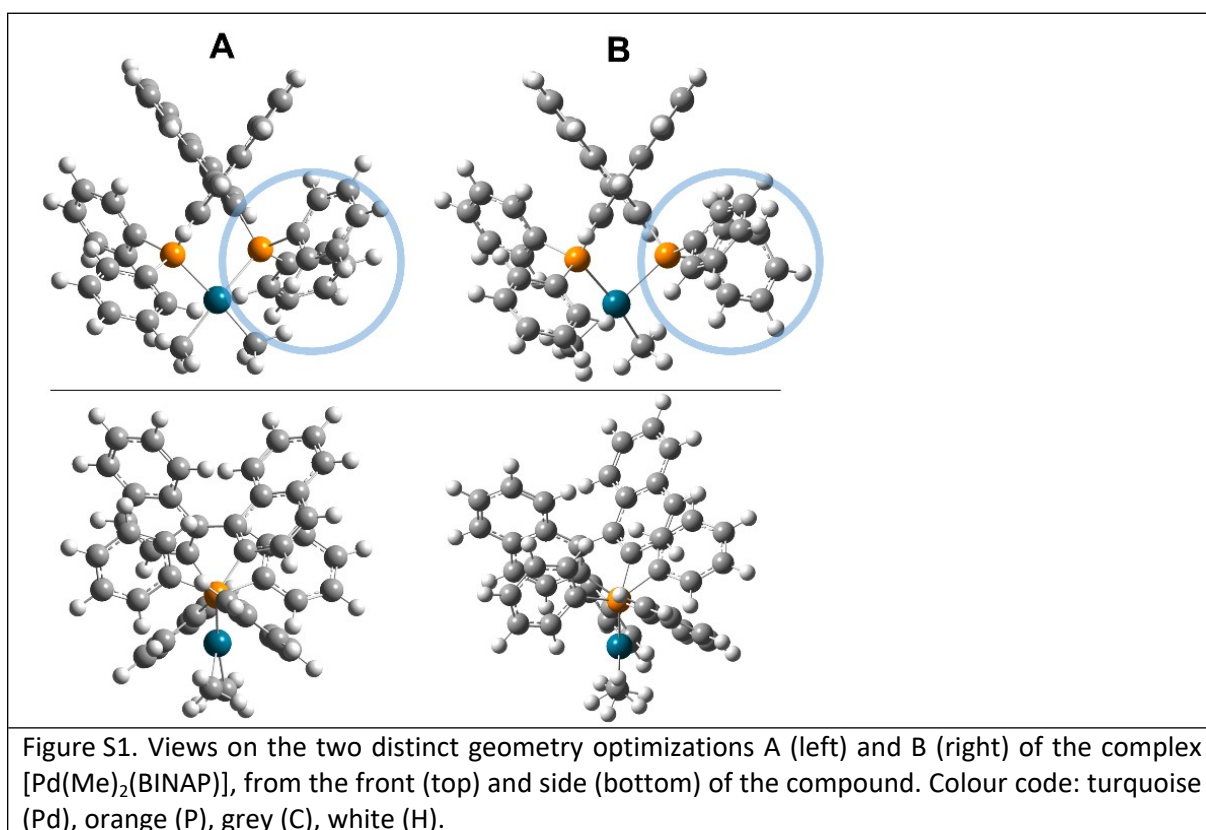
All calculations were obtained by the Gaussian<sup>®</sup>16 program.<sup>[11]</sup> The DFT functional B3LYP was used for all calculations, where two basis sets were considered. The carbon, hydrogen, oxygen, phosphorus, and silicon atoms were calculated with the basis set of 6-311++g\*. The metal centre Pd was calculated with the basis set LanL2DZ split valence. For this study, the obtained molecules were geometry optimized and afterwards a frequency calculation took place. For the calculation of absorption and CD spectra, the TD-SCF method was used, and 40 single-excited-states were calculated. All calculations were obtained at a FUJITSU CELSIUS Workstation with an Intel<sup>®</sup> Xeon<sup>®</sup> E-2136 CPU with 3.31 GHz and 64 GB RAM. The system runs on Windows 10 Pro for workstations. Geometry optimization and excited states can be found in Table S9-Table S14.

### Structural aspects of the DFT calculations

As already mentioned, the two structures origin from two distinct DFT optimizations. They converge in different minima of the energy hypersurface and, thus, are of different structural parameters. Table S7 compares zero-point energy, enthalpy, and Gibb's free energy of the two optimized structures. It becomes evident that both optimizations lead to indistinguishable local minima in the hypersurface from an energetic point of view. Figure S1 shows the two optimized geometries in a comparing manner. At first glance, structure A and structure B are very similar in geometry (Figure S1), in addition to their energetic properties (Table S7).

Table S7. Energetic minima by DFT for two distinct geometry optimizations of [Pd(Me) <sub>2</sub> (BINAP)]		
Energetic property (kJ/mol)	Structure A	Structure B
<b>Zero-point energy</b>	-2584.99	-2584.99
<b>Enthalpy</b>	-2584.94	-2584.94
<b>Gibbs' free energy</b>	-2585.07	-2585.06

At a closer look, however, the phenyl groups located at the phosphorous atoms are oriented in a different manner, as seen most obviously in the right part of the representations (highlighted in the top part of Figure S1). Furthermore, it becomes clear from the side view of the complexes in the bottom part of Figure S1 that the atoms of the BINAP ligand are evenly distributed (non-evenly distributed) across the Pd-P-P plane for structure A (B), additionally witnessed by the dihedral angles around the coordination sphere, i.e. Pd centre, coordinating P, and C atoms of BINAP that bind to coordinating P. An additional view on the top of the molecule can be found in Figure S2. The close to square-planar coordination sphere of Pd is not impeded by this for both structures. To this end, small changes in the geometry then lead to variations in the electronic structure and thus modify all electronic transitions. Importantly, the calculated rotatory strengths are much more affected than the oscillator strengths.<sup>[12]</sup>



the complex [PdMe<sub>2</sub>BINAP].

### Occurrence of molecular orbitals

Table S8: Occurrence of molecular orbitals for calculated structures A (left) and B (right), full set

MO number A	Occurrence A (%)	MO number B	Occurrence B (%)
172	3.1	171	1.3
173	6.3	172	4.2
174	0.2	173	2.6
175	7.5	174	2.5
176	7.7	175	10.2
177	5.5	176	12.1
178	9.6	177	4.6
179	19.1	178	5.8
180	21.8	179	17.8
181	19.4	180	15.8
182	21.8	181	23.1
183	21.1	182	28.9
184	17.8	183	18.7
185	9.5	184	12.8
186	6.1	185	12.2
187	4.6	186	5.1
188	4.2	187	6.9
189	4.4	188	2.1
190	0.0	189	2.2
191	0.2	190	1.3
192	0.2	191	0.1
193	1.2	192	2.9
194	0.1	193	0.2
195	2.1	194	1.4
196	3.2	195	2.6
197	0.1	196	0.4
198	1.2	197	0.0
199	0.4	198	0.8
205	1.6	201	0.3
206	0.2	203	0.8
		205	0.3

### Occupied and unoccupied orbital representations of structure A and B

**A**

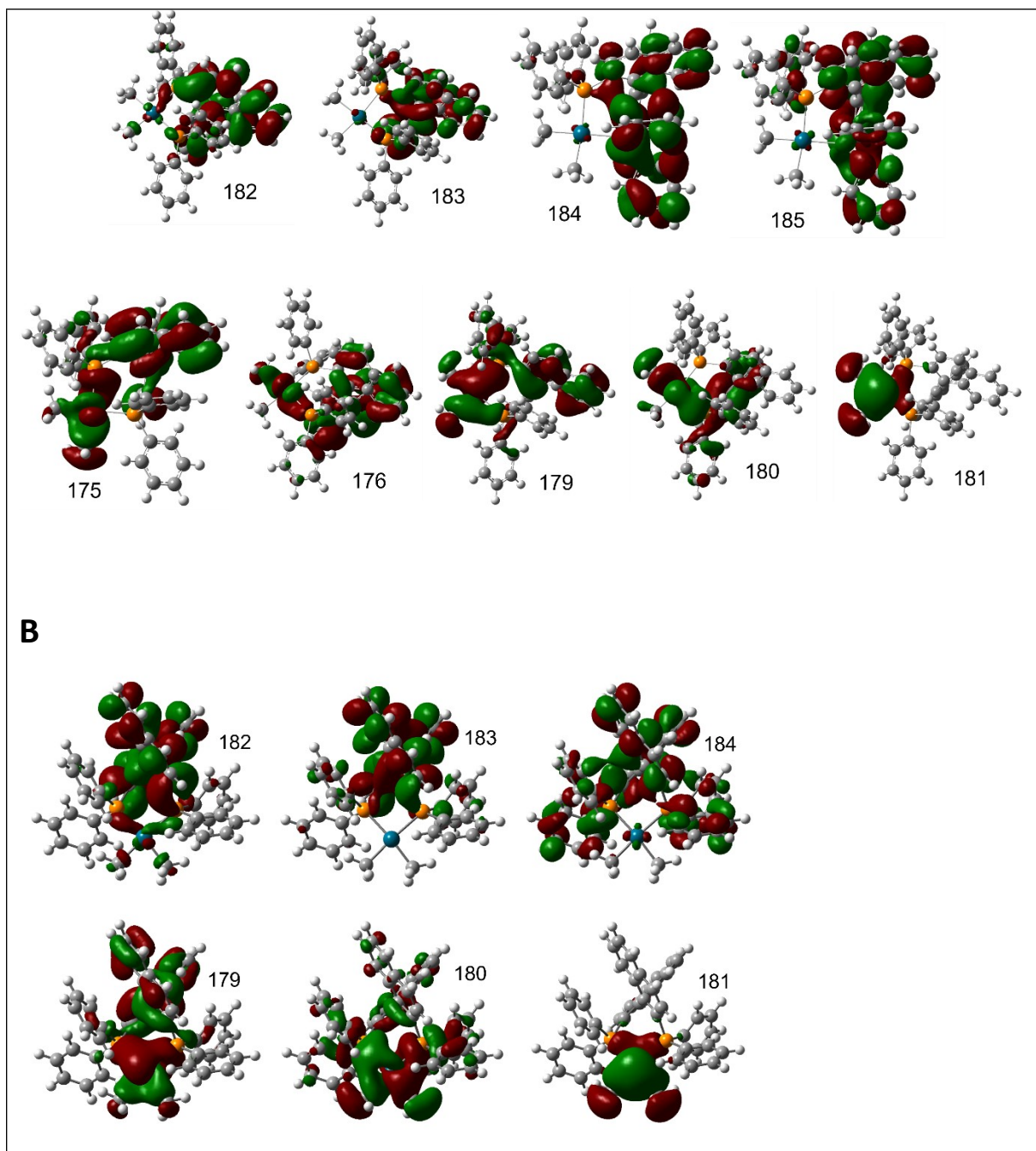


Figure S3: Unoccupied (top) and occupied (bottom) molecular orbital representations for the main contributions of selected CD-active electronic transitions of optimised structure A and B of the complex [PdMe<sub>2</sub>BINAP] (iso value 0.02). Colour code: turquoise (Pd), orange (P), grey (C), white (H).

Calculations for structure A

Table S9: Through DFT obtained zero-point energy (E), enthalpy (H) and Gibbs free energy (G) of structure A in kJ/mol

E	H	G
-2584.99	-2584.94	-2585.07

Table S10: Through DFT obtained geometry of structure A

Center	Atomic	Coordinates (Angstroms)
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Number	Number	X	Y	Z
1	6	-0.979817	-4.675577	-3.382094
2	6	-0.030475	-3.766416	-3.777054
3	6	0.40497	-2.738218	-2.90036
4	6	-0.153805	-2.636473	-1.588218
5	6	-1.137394	-3.597289	-1.218541
6	6	-1.536085	-4.585787	-2.086077
7	1	1.840083	-1.886457	-4.275887
8	1	-1.30273	-5.461299	-4.057655
9	1	0.407496	-3.822138	-4.769489
10	6	1.398106	-1.810211	-3.286458
11	6	0.287782	-1.594682	-0.696287
12	1	-1.579052	-3.552494	-0.231697
13	1	-2.285487	-5.305702	-1.772022
14	6	1.26842	-0.694629	-1.118014
15	6	1.812523	-0.828885	-2.426564
16	1	2.581291	-0.143179	-2.754504
17	6	-0.286893	-1.595274	0.695121
18	6	0.156153	-2.636816	1.586657
19	6	-1.268688	-0.696646	1.117269
20	6	-0.40241	-2.739843	2.898789
21	6	-1.812529	-0.832213	2.425802
22	6	1.540895	-4.584614	2.083596
23	6	0.034395	-3.767848	3.775027
24	6	-1.396768	-1.813321	3.285286
25	1	-2.582233	-0.147724	2.754077
26	6	0.984844	-4.675653	3.37961
27	1	2.291188	-5.303445	1.769187
28	1	-0.403433	-3.824531	4.767471
29	1	-1.838621	-1.890551	4.274694
30	1	1.308793	-5.461253	4.054817
31	6	3.240233	1.453974	-1.043133
32	6	4.56162	1.136796	-0.70959
33	6	3.010743	2.325118	-2.11798
34	6	5.625324	1.662826	-1.443529
35	1	4.77305	0.488066	0.131387
36	6	4.071476	2.839725	-2.858053

Center	Atomic	Coordinates (Angstroms)		
37	1	1.994075	2.612677	-2.363246
38	6	5.384158	2.509191	-2.522806
39	1	6.644018	1.410635	-1.165512
40	1	3.872658	3.512933	-3.685976
41	1	6.212889	2.919248	-3.09143
42	15	1.758416	0.814267	-0.125218
43	6	2.478103	0.197116	1.455358
44	6	3.238402	-0.974095	1.56028
45	6	2.291757	0.98975	2.595343
46	6	3.806048	-1.341662	2.777931
47	1	3.383784	-1.606236	0.691103
48	6	2.865028	0.624001	3.811873
49	1	1.696135	1.894036	2.523143
50	6	3.6235	-0.54137	3.90505
51	1	4.385121	-2.256909	2.847713
52	1	2.714307	1.24818	4.687015
53	1	4.066773	-0.828903	4.853294
54	15	-1.760129	0.81312	0.126409
55	6	-3.245834	1.447315	1.041958
56	6	-4.565539	1.126866	0.704815
57	6	-3.02141	2.317388	2.118738
58	6	-5.63247	1.648592	1.437115
59	1	-4.77316	0.478908	-0.137696
60	6	-4.085374	2.827737	2.857143
61	1	-2.006174	2.60747	2.366867
62	6	-5.396291	2.493925	2.518313
63	1	-6.649772	1.39386	1.156328
64	1	-3.890434	3.500207	3.686585
65	1	-6.227538	2.900663	3.085648
66	6	-2.474706	0.198536	-1.457465
67	6	-3.231662	-0.974349	-1.567595
68	6	-2.288189	0.995214	-2.594611
69	6	-3.795742	-1.339712	-2.787563
70	1	-3.37717	-1.609548	-0.700687
71	6	-2.85797	0.631714	-3.813452

Center	Atomic	Coordinates (Angstroms)		
72	1	-1.695219	1.900924	-2.518401
73	6	-3.613043	-0.53544	-3.91182
74	1	-4.372136	-2.25633	-2.861367
75	1	-2.707178	1.259038	-4.68633
76	1	-4.053561	-0.82124	-4.86187
77	6	1.140942	-3.59622	1.216526
78	1	1.582426	-3.550455	0.229654
79	46	-0.001132	2.492559	0.00498
80	6	-1.361555	4.092195	-0.134667
81	1	-1.42691	4.604403	0.828481
82	1	-0.996428	4.803277	-0.878243
83	1	-2.361423	3.756782	-0.419291
84	6	1.36073	4.090362	0.152657
85	1	2.36021	3.752834	0.436214
86	1	1.42703	4.606452	-0.808346
87	1	0.996092	4.798699	0.899079

Table S11: Calculated excited states of structure A, their crossings, rotatory strengths, energies in eV and nm, and their oscillator strength

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f
1	181 → 182	0.70176	2.7716	447.34	0.0017
2	181 → 183	0.70382	2.9913	414.48	0.0003
3	179 → 182 180 → 182	0.63842 0.25397	3.4176	362.78	0.0115
4	179 → 182 180 → 182 181 → 184	-0.25641 0.63246 -0.11077	3.4183	362.7	0.0295
5	180 → 182 181 → 184 181 → 186	0.10882 0.64691 0.23640	3.5261	351.62	0.0107
6	181 → 185	0.69823	3.538	350.44	0.0002
7	180 → 183	0.69048	3.6023	344.18	0.0152
8	178 → 182 179 → 183 181 → 186	-0.25553 0.62709 -0.15707	3.6474	339.93	0.0033
9	179 → 183 181 → 184 181 → 186	0.13737 -0.23506 0.64166	3.6974	335.33	0.0041

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f
<b>10</b>	177 → 182 181 → 187 181 → 189	-0.15711 0.65031 -0.19162	3.7543	330.25	0.0041
<b>11</b>	175 → 182 177 → 182 178 → 183 181 → 187	0.18398 0.63184 -0.10371 0.17372	3.7837	327.68	0.0089
<b>12</b>	176 → 182 177 → 183 178 → 182 179 → 183 181 → 188	-0.27932 -0.11608 0.54462 0.18944 -0.17760	3.8155	324.94	0.0265
<b>13</b>	175 → 182 177 → 182 178 → 183 181 → 187 181 → 189	0.29105 -0.14434 0.12797 0.13479 0.55243	3.8666	320.66	0.0071
<b>14</b>	178 → 182 181 → 188	0.15432 0.66745	3.8952	318.3	0.0145
<b>15</b>	175 → 182 178 → 183 181 → 189	0.43618 0.41521 -0.30850	3.9655	312.66	0.0008
<b>16</b>	176 → 182 177 → 183 178 → 182 179 → 183	0.57615 -0.27850 0.20032 0.13394	3.9698	312.32	0.0101
<b>17</b>	181 → 190	0.69468	3.9903	310.72	0.0015
<b>18</b>	175 → 182 177 → 182 178 → 183 180 → 184 181 → 189	-0.36101 0.15545 0.51727 0.13448 0.12348	4.0522	305.97	0.0526
<b>19</b>	176 → 182 177 → 183 178 → 182 179 → 184	0.15584 0.60340 0.20102 -0.13515	4.0645	305.04	0.0004
<b>20</b>	181 → 191 181 → 192	0.68084 0.13184	4.0936	302.87	0.0034
<b>21</b>	176 → 183 179 → 185 180 → 184	0.45339 0.12426 0.46226	4.14	299.48	0.0158
<b>22</b>	175 → 183 177 → 183 179 → 184 180 → 185	0.36574 0.13770 0.33958 0.42276	4.1534	298.51	0.0177

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f
<b>23</b>	175 → 183 179 → 184 179 → 186 180 → 185 181 → 192	-0.35173 -0.14456 0.16905 0.48675 0.18134	4.1679	297.47	0
<b>24</b>	174 → 182 176 → 183 179 → 185 180 → 184 180 → 186 181 → 193	0.51450 -0.20748 0.10993 0.15649 0.12872 -0.30859	4.176	296.9	0.001
<b>25</b>	174 → 182 176 → 183 179 → 185 180 → 184 180 → 186 181 → 193	0.43203 0.29218 -0.15436 -0.14902 -0.18177 0.29528	4.1796	296.64	0.0029
<b>26</b>	176 → 183 179 → 185 180 → 184 180 → 186 181 → 193	-0.26822 0.13011 0.31402 0.14458 0.50774	4.1882	296.03	0.0146
<b>27</b>	180 → 185 181 → 191 181 → 192 181 → 194	-0.19427 -0.11277 0.60529 0.26711	4.2009	295.14	0.0004
<b>28</b>	176 → 183 179 → 185 180 → 184	0.13370 0.60788 -0.26685	4.2595	291.08	0.0282
<b>29</b>	173 → 182 175 → 183 179 → 184 180 → 185	-0.15629 -0.42312 0.47962 -0.11434	4.2803	289.66	0.0848
<b>30</b>	176 → 183 179 → 185 180 → 184 180 → 186	0.16483 -0.20621 -0.13874 0.59440	4.3254	286.64	0.0545
<b>31</b>	173 → 182 175 → 183 177 → 184 179 → 184 179 → 186 180 → 185 180 → 187	0.20888 0.17266 -0.17102 0.19146 0.52250 -0.14026 0.14628	4.3416	285.57	0.0001

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f
<b>32</b>	172 → 182	-0.22535	4.3611	284.3	0.0242
	173 → 183	-0.14947			
	176 → 183	0.16186			
	178 → 184	0.16125			
	179 → 187	0.33353			
	179 → 189	0.20842			
	180 → 184	0.13097			
	180 → 186	-0.18932			
	181 → 196	0.15801			
	181 → 198	0.12841			
	181 → 205	0.11575			
	<b>33</b>	179 → 184			
179 → 186		-0.21696			
180 → 187		0.61867			
181 → 194		-0.14024			
<b>34</b>	180 → 187	0.14524	4.4112	281.07	0.0016
	181 → 192	-0.24503			
	181 → 194	0.59785			
	181 → 197	0.18741			
<b>35</b>	179 → 187	-0.30104	4.4178	280.64	0.0038
	179 → 189	0.15025			
	181 → 195	0.20754			
	181 → 196	0.39885			
	181 → 198	0.25208			
	181 → 205	0.11460			
	181 → 206	0.13708			
<b>36</b>	179 → 187	0.24105	4.4564	278.22	0.0093
	179 → 189	-0.24127			
	180 → 188	-0.15534			
	181 → 193	-0.10813			
	181 → 195	0.42792			
	181 → 196	0.14850			
	181 → 199	-0.22733			
	181 → 205	-0.18285			
<b>37</b>	172 → 183	0.11492	4.4796	276.78	0.0002
	173 → 182	0.31778			
	177 → 184	-0.20913			
	178 → 187	-0.15654			
	179 → 184	0.12141			
	179 → 186	-0.30194			
	179 → 188	0.17805			
	180 → 189	0.30206			
<b>38</b>	174 → 183	0.69	4.5023	275.38	0.0005

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f
39	172 → 182	-0.13798	4.5228	274.13	0.0354
	173 → 183	-0.11421			
	178 → 184	0.24166			
	179 → 187	-0.24380			
	180 → 188	0.43863			
	181 → 195	0.22131			
	181 → 196	-0.14507			
40	172 → 182	0.10961	4.5480	272.61	0.0106
	178 → 184	-0.25295			
	178 → 186	0.12321			
	179 → 187	0.32911			
	180 → 188	0.48808			

### Calculations for structure B

Table S12: Through DFT obtained zero-point energy (E), enthalpy (H) and Gibbs free energy (G) of structure B in kJ/mol

E	H	G
-2584.99	-2584.94	-2585.06

Table S13: Through DFT obtained geometry of structure B

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	2.90052	1.767532	1.116753
2	6	4.24766	1.42724	1.284403
3	6	2.417965	2.925823	1.740723
4	6	5.085065	2.214429	2.074761
5	1	4.655978	0.553943	0.790289
6	6	3.250773	3.705973	2.538793
7	1	-3.373393	3.162858	-0.948103
8	6	4.587983	3.350401	2.710071
9	1	6.129229	1.939778	2.188198
10	1	2.859506	4.601268	3.01161
11	1	5.241664	3.963225	3.322752
12	15	1.700506	0.791221	0.091911
13	6	2.786816	-0.177871	-1.044328
14	6	2.894641	0.243728	-2.375258
15	6	3.530777	-1.287331	-0.621488

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
16	6	3.745154	-0.419017	-3.258559
17	1	2.309096	1.090507	-2.714152
18	6	4.37877	-1.949204	-1.506185
19	1	3.441758	-1.644412	0.399094
20	6	4.49096	-1.513467	-2.825838
21	1	3.819832	-0.080557	-4.287174
22	1	4.945558	-2.810459	-1.16666
23	1	5.151149	-2.030616	-3.515116
24	15	-1.737302	0.845411	-0.497125
25	6	-2.221132	0.677611	1.283973
26	6	-1.734664	1.633536	2.181621
27	6	-3.159964	-0.258332	1.736636
28	6	-2.169626	1.650965	3.506825
29	1	-1.021068	2.37344	1.834556
30	6	-3.58835	-0.246606	3.060029
31	1	-3.566897	-0.997092	1.055623
32	6	-3.096297	0.710623	3.948375
33	1	-1.785008	2.401715	4.190049
34	1	-4.310497	-0.982941	3.397991
35	1	-3.438578	0.723564	4.978455
36	6	-3.441966	1.024832	-1.210358
37	6	-4.252623	-0.050227	-1.600357
38	6	-3.980608	2.317481	-1.247332
39	6	-5.561939	0.16471	-2.02583
40	1	-3.866256	-1.062804	-1.580017
41	6	-5.292686	2.530613	-1.666205
42	1	1.390294	3.231513	1.574467
43	6	-6.086434	1.455888	-2.060075
44	1	-6.173485	-0.680148	-2.327625
45	1	-5.690037	3.54036	-1.690036
46	1	-7.106472	1.621982	-2.391859
47	6	1.059871	-0.483897	1.304742
48	6	0.123844	-1.450768	0.932653
49	6	1.454182	-0.390665	2.667947
50	6	-0.437588	-2.3209	1.927879



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
51	6	0.938966	-1.223952	3.625675
52	1	2.182066	0.354332	2.960307
53	6	-0.023361	-2.203976	3.291338
54	1	1.265696	-1.132352	4.657657
55	6	-0.279406	-1.65145	-0.501363
56	6	-1.131677	-0.775988	-1.167894
57	6	0.249736	-2.797403	-1.198729
58	6	-1.389023	-0.973288	-2.557387
59	6	-0.072601	-3.002371	-2.576672
60	6	-0.884918	-2.047741	-3.235232
61	1	-1.995861	-0.252755	-3.091976
62	1	-1.103812	-2.176237	-4.29137
63	6	-0.584498	-3.062735	4.272507
64	1	-0.25597	-2.959944	5.302728
65	6	-1.417985	-3.303909	1.615521
66	1	-1.752433	-3.410768	0.591193
67	6	-1.946624	-4.119131	2.587666
68	1	-2.692898	-4.860957	2.32094
69	6	-1.525722	-4.002578	3.932311
70	1	-1.948327	-4.654821	4.689965
71	6	1.08937	-3.758094	-0.570338
72	1	1.360072	-3.628529	0.469228
73	6	0.432048	-4.139651	-3.257602
74	1	0.174991	-4.27495	-4.304261
75	6	1.227159	-5.05455	-2.611593
76	1	1.604131	-5.924297	-3.14016
77	6	1.557842	-4.855882	-1.253385
78	1	2.190894	-5.575421	-0.743562
79	46	0.130737	2.313882	-1.050692
80	6	-0.98274	3.716124	-2.14087
81	1	-0.357033	4.296763	-2.817473
82	1	-1.759749	3.211116	-2.719629
83	1	-1.453771	4.4026	-1.428821
84	6	1.725066	3.554173	-1.644322
85	1	1.794419	3.562361	-2.734965

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
86	1	1.510516	4.571241	-1.307747
87	1	2.686318	3.245256	-1.228369

Table S14: Calculated excited states of structure B, their crossings, rotatory strengths, energies in eV and nm, and their oscillator strength

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f
1	181 → 182	0.69589	2.797	443.28	0.0047
2	181 → 183	0.69685	3.0474	406.85	0.0012
3	179 → 182 180 → 182	-0.23818 0.64914	3.438	360.63	0.0105
4	181 → 184	0.68646	3.4531	359.05	0.0008
5	179 → 182 181 → 185 181 → 186	0.29924 0.42322 0.45688	3.5293	351.3	0.0027
6	179 → 182 180 → 182 180 → 183 181 → 185 181 → 186	-0.45411 -0.18169 -0.10290 -0.12496 0.46691	3.5516	349.1	0.0177
7	179 → 182 180 → 182 180 → 183 181 → 184 181 → 185 181 → 186	-0.28818 -0.13474 -0.13539 0.12675 0.53001 -0.24269	3.5749	346.82	0.0233
8	176 → 182 178 → 182 179 → 182 180 → 183 181 → 187	0.22846 0.10984 -0.14518 0.59590 -0.10534	3.7214	333.17	0.0422
9	177 → 182 178 → 182 179 → 183 180 → 183	0.11816 -0.17108 0.64439 0.10828	3.7564	330.06	0.009
10	177 → 182 177 → 183 178 → 182 179 → 182 179 → 183 180 → 183 181 → 187 181 → 188	0.47791 -0.10294 -0.20288 -0.10266 -0.15052 -0.10020 -0.26874 -0.21735	3.8115	325.29	0.0013

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f
<b>11</b>	176 → 182 177 → 182 178 → 182 181 → 188	-0.20448 0.23790 0.54082 -0.23172	3.819	324.65	0.0041
<b>12</b>	176 → 182 178 → 182 181 → 187 181 → 188	0.13178 -0.19310 0.54183 -0.35083	3.8244	324.2	0.0069
<b>13</b>	175 → 182 177 → 182 181 → 187 181 → 188 181 → 189	-0.16438 0.37444 0.28150 0.43785 0.11467	3.8456	322.41	0.0038
<b>14</b>	175 → 182 176 → 182 178 → 182 180 → 183 181 → 189	0.33018 0.50939 0.15238 -0.23456 0.10419	3.9426	314.48	0.0157
<b>15</b>	175 → 182 176 → 182 181 → 188 181 → 189	0.17527 -0.19611 -0.14121 0.60253	3.9729	312.07	0.0035
<b>16</b>	175 → 182 175 → 183 176 → 182 178 → 182 179 → 183 181 → 188 181 → 189 181 → 190	0.46709 -0.10954 -0.23153 -0.16011 -0.12117 0.15268 -0.22401 -0.18452	3.9908	310.67	0.0187
<b>17</b>	175 → 182 181 → 188 181 → 189 181 → 190	0.11615 -0.10032 -0.18238 0.61959	4.0618	305.24	0.0111
<b>18</b>	176 → 183 177 → 183 178 → 182 178 → 183 180 → 185	-0.16066 -0.19518 0.10354 0.58336 0.15207	4.0949	302.78	0.0023
<b>19</b>	177 → 183 178 → 183 180 → 184 180 → 185	0.47249 0.25516 -0.33232 -0.19394	4.1002	302.39	0.0027

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f
<b>20</b>	176 → 183 178 → 183 180 → 184 180 → 185 180 → 187	0.33291 0.21537 0.43693 -0.30357 -0.10273	4.1177	301.1	0.0139
<b>21</b>	175 → 183 176 → 183 177 → 183 180 → 184 180 → 185	-0.11278 -0.30516 0.42197 0.38595 0.14614	4.12	300.93	0.0061
<b>22</b>	181 → 191	0.67244	4.1302	300.19	0.0006
<b>23</b>	172 → 182 175 → 183 176 → 183 177 → 183 179 → 184 179 → 185 180 → 185	0.13714 0.41145 -0.27547 -0.13041 0.25826 0.19213 -0.12319	4.1529	298.54	0.0224
<b>24</b>	176 → 183 181 → 190 181 → 191 181 → 192 181 → 193	0.11524 -0.15320 -0.12003 0.53580 0.30831	4.1868	296.13	0.0025
<b>25</b>	174 → 182 175 → 182 175 → 183 176 → 183 179 → 184 181 → 192	0.13582 -0.14835 -0.22217 0.12954 0.56834 -0.13129	4.2302	293.09	0.0396
<b>26</b>	174 → 182 174 → 183 175 → 183	0.62394 -0.11208 0.23233	4.2398	292.43	0.008
<b>27</b>	172 → 182 174 → 182 175 → 183 176 → 183 179 → 185 179 → 186 180 → 185	-0.16528 -0.14606 0.21480 0.11740 -0.23059 0.48784 0.14924	4.2824	289.52	0.0055
<b>28</b>	172 → 182 175 → 183 179 → 184 179 → 185 179 → 186	0.14270 -0.21305 -0.13844 0.42743 0.40686	4.2891	289.07	0.0278

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f				
<b>29</b>	175 → 183	0.17750	4.2985	288.44	0.059				
	176 → 183	0.23640							
	179 → 185	0.10833							
	179 → 186	-0.20823							
	180 → 185	0.37771							
	181 → 192	-0.12095							
	181 → 194	0.30968							
<b>30</b>	176 → 183	-0.13536	4.3092	287.72	0.0218				
	179 → 185	-0.10915							
	179 → 186	0.10942							
	180 → 185	-0.19782							
	181 → 194	0.61055							
<b>31</b>	180 → 185	0.19025	4.3203	286.98	0.0124				
	180 → 186	0.53456							
	180 → 187	-0.13808							
	181 → 192	0.12143							
	181 → 195	0.11496							
	181 → 198	0.13021							
	181 → 203	-0.11856							
<b>32</b>	179 → 185	-0.10021	4.3359	285.95	0.0064				
	180 → 185	-0.11575							
	180 → 186	0.39821							
	180 → 187	0.13168							
	181 → 192	-0.15876							
	181 → 194	-0.11443							
	181 → 195	-0.20539							
	181 → 196	0.12084							
	181 → 198	-0.20294							
	181 → 201	-0.14753							
	181 → 203	0.18010							
	181 → 205	0.10439							
	<b>33</b>	172 → 182				0.19071	4.3946	282.13	0.0188
		173 → 182				0.44281			
175 → 184		-0.11647							
177 → 184		-0.11557							
179 → 184		-0.11885							
179 → 185		-0.28610							
179 → 187		-0.12830							
<b>34</b>	173 → 182	0.10222	4.411	281.08	0.0019				
	181 → 192	-0.30463							
	181 → 193	0.56601							
	181 → 196	-0.13314							
	181 → 197	0.15769							

Excited State	Crossing	Rotary strength	Energy [eV]	Wavelength [nm]	Oscillator strength f
<b>35</b>	172 → 182 173 → 182 178 → 184 179 → 185 179 → 187	-0.25878 0.47961 -0.21126 0.19002 0.14281	4.4544	278.34	0.0109
<b>36</b>	171 → 182 173 → 182 176 → 183 176 → 185 177 → 184 178 → 184 180 → 187 181 → 195	-0.14989 -0.16713 0.10088 0.10605 -0.18581 -0.30963 0.33983 0.12210	4.4643	277.72	0.0294
<b>37</b>	172 → 182 176 → 184 177 → 184 178 → 184 180 → 187 181 → 195	-0.13499 -0.17858 0.24794 0.44039 0.23057 0.15151	4.4879	276.27	0.0141
<b>38</b>	178 → 184 181 → 193 181 → 195 181 → 196	-0.10631 0.10395 0.31472 0.54491	4.5079	275.04	0.001
<b>39</b>	175 → 184 176 → 184 177 → 184 178 → 184 179 → 187	-0.15446 0.11688 0.53654 -0.23787 -0.10221	4.5166	274.51	0.0001
<b>40</b>	174 → 182 174 → 183 179 → 187	0.13035 0.63671 -0.16811	4.5535	272.28	0.0059

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