Supplementary Information

Heteroleptic enantiopure Pd(II)-complexes derived from halogen-substituted Schiff bases and 2-picolylamine: synthesis, experimental and computational characterization and investigation of the influence of chirality and halogen atoms on the anticancer activity

Nazanin Kordestani[a], Hadi Amiri Rudbari[a,*], Isabel Correia[b], Andreia Valente[c,*], Leonor Côrte-Real[c], Mohammad Khairul Islam[d], Nicola Micale[e], Jason D. Braun[f], David E. Herbert[f], Nikolay Tumanov[g], Johan Wouters[g], Mohammed Enamullah[d,*]

[a] *Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran.*

[b] *Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal*

[c] *Centro de Química Estrutural and Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.*

[d] *Department of Chemistry, Jahangirnagar University, Dhaka1342, Bangladesh.*

[e] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Viale Ferdinando Stagno D'Alcontres 31, I-98166 Messina, Italy.*

[f] *Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada.*

[g] *Department of Chemistry, Namur Institute of Structured Matter, University of Namur, 5000 Namur, Belgium.*

* Corresponding authors.

E-mail addresses: h.a.rudbari@sci.ui.ac.ir; hamiri1358@gmail.com (H. Amiri Rudbari), amvalente@fc.ul.pt (A. Valente); enamullah@juniv.edu (M. Enamullah).

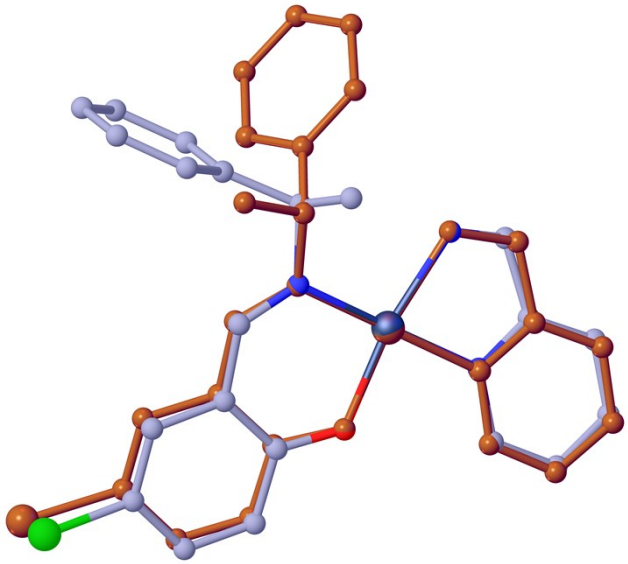
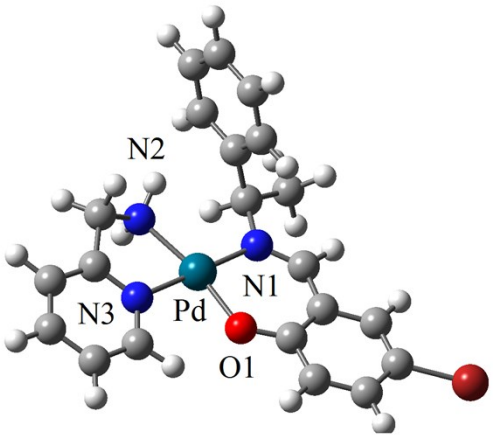
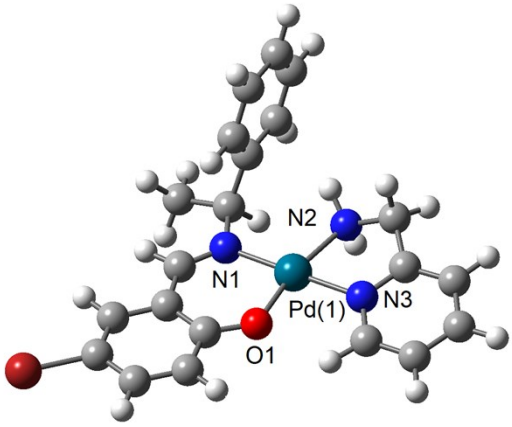


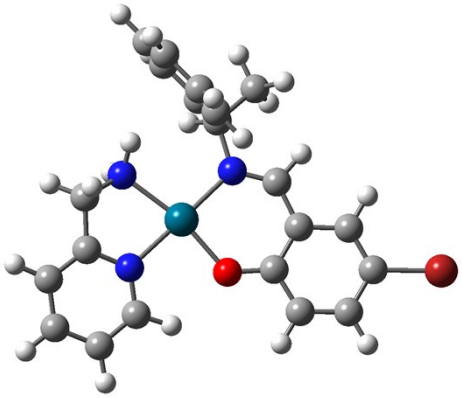
Fig. S1 Overlap of the cations [Pd(pic)*R*3]$^+$ and [Pd(pic)*R*2]$^+$, showing [Pd(pic)*R*3]$^+$ in brown color. H atoms have been omitted for clarity.



Λ–[Pd(pic)*R*3] (-1193.059926 a.u.)
B3LYP//SDD



Δ-[Pd(pic)*S*3] (-1193.059926 a.u.)
B3LYP//SDD



Λ–[Pd(pic)*R*3] (-1191.652683 a.u.)
B3LYP//LANL2DZ

Fig S2 DFT optimized structures (gas phase) for the enantiomeric pair Λ-[Pd(pic)*R*3] and Δ-[Pd(pic)*S*3].

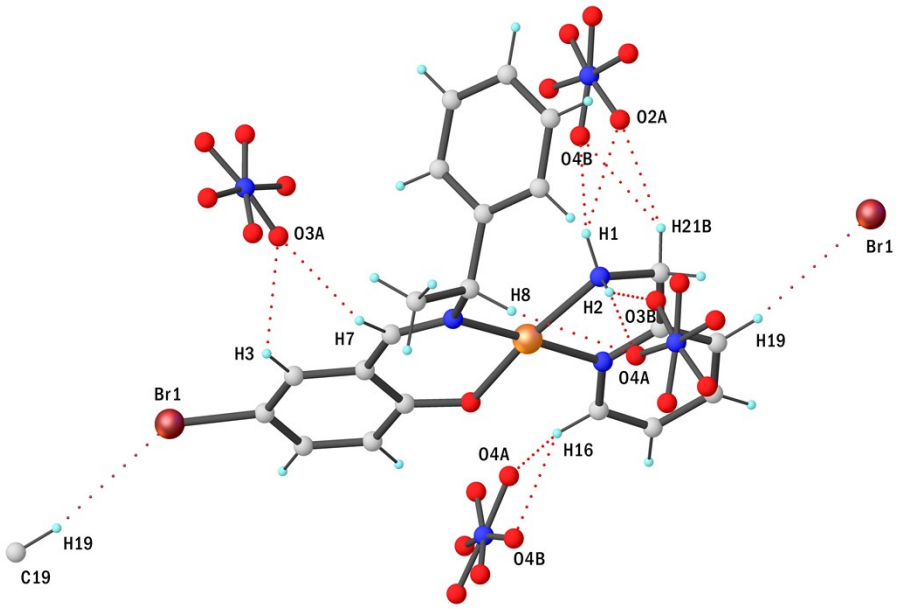


Fig. S3 A view of intermoleclar interactions in the crystal packing of [Pd(pic)*R*3]NO_3.

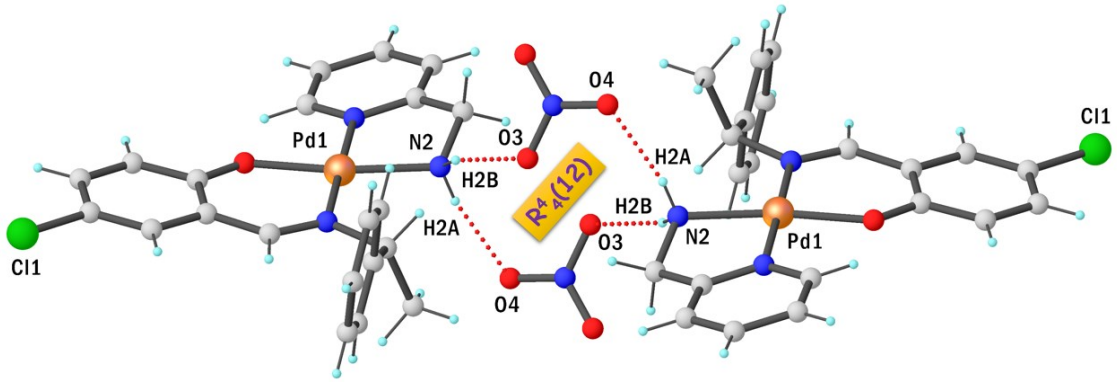


Fig. S4 Perspective view of $R^4_4(12)$ ring in [Pd(pic)*rac*2]NO_3.

Hirshfeld surface analyses

The results indicate that the highest contributions over the Hirshfeld surface are due to H atom with other atoms such as carbon (H···C), oxygen (H···O) and hydrogen (H···H) (Figs. S5 and S6). These three kind of contacts (H···H, H···C and O···H) overall are 74.8% and 72.8% of the total Hirshfeld surface area in [Pd(pic)*S*2]NO_3 and [Pd(pic)*R*3]NO_3, respectively (Fig. S6).

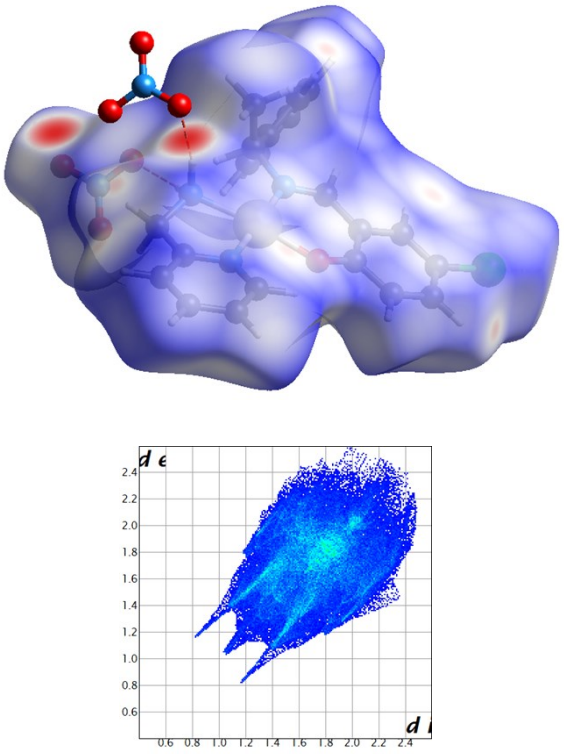
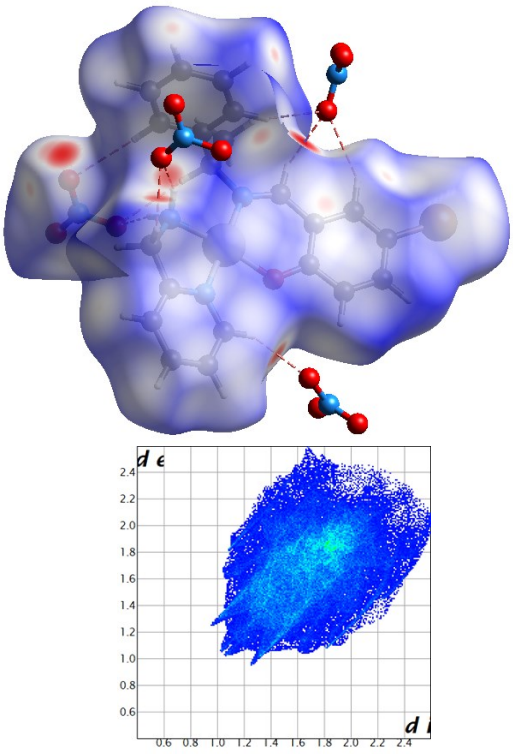
Between H···H, H···C and O···H interactions, FPs indicates that most of the contributions over the Hirshfeld surface are due to H···H contact (37.2 and 39.6% for [Pd(pic)*S*2]NO_3 and [Pd(pic)*R*3]NO_3, respectively) as the molecular surface is comprised of H atoms (Fig. S6). Large number of H-atoms over surface supported the C–H contact to be the third one after O···H interaction having 15.4 and 12.8% for [Pd(pic)*S*2]NO_3 and [Pd(pic)*R*3]NO_3, respectively (Fig. S5 and S6). Also, fingerprint plots indicate that chlorine and bromide intermolecular contacts (X···X, X···C, X···H and X···N) cover nearly 13% of the whole Hirshfeld surface (Figure. S6).

The H···H contacts are characterized by broader spikes in [Pd(pic)*R*3]NO_3 and sharper spikes in [Pd(pic)*S*2]NO_3 (Figs. S5). As shown in Fig. S5, the shortest H···H contacts in the fingerprint plots of both structures are at d_e+d_i = 2.1 Å. Furthermore, a subtle feature, splitting in the fingerprint plots of H···H, is evident in the fingerprint plot of [Pd(pic)*R*3]NO_3 complex. This splitting occurs when the shortest contact is between three atoms, rather than for a direct two-atom contact.

The first principal interaction in [Pd(pic)*S*2]NO_3 and [Pd(pic)*R*3]NO_3, results from classical N-H···O-NO_2 hydrogen bond. The dominant interactions between amine N–H and nitrate O atoms can be seen in the Hirshfeld surfaces as deep red spots (Fig. S5). In [Pd(pic)*S*2]NO_3 structure, a pair of equally deep red spots corresponds to both donor and acceptor of N–H···O hydrogen bonds. This is characteristic for the $R^4_4(12)$ dimer ring. Also, short C–H···O–NO_2 hydrogen bond can be seen in the Hirshfeld surfaces of [Pd(pic)*R*3]NO_3 as deep red spots (Fig. S5). It should be noted that we cannot see such interaction in the Hirshfeld surfaces of [Pd(pic)*S*2]NO_3. These interactions (X–H···O–NO_2; X = C or N) appear in 2D fingerprint plots as a pair of symmetric spikes extending towards the bottom left (the upper spike corresponds to the donor spike, the lower one is the acceptor spike) with d_i + d_e= 2.2 and 1.95 Å for [Pd(pic)*S*2]NO_3 and [Pd(pic)*R*3]NO_3, respectively.

Apart from the hydrogen bonding contacts, the structure of both complexes is stabilized through a C–H···π interaction that is visible on the d_e surface as well as in the fingerprint plot (Figs. S5 and S7). The 'bright-orange' spot and consequently a large depression on the d_e surface above the π–cloud of the aryl ring indicates the existence of a C–H···π interaction (Figs. S5 and S7). Moreover, these interactions manifest as two weak spikes (or pair of 'wings') besides H···Cl interactions in the fingerprint plot of [Pd(pic)*S*2]NO_3, while they are visible as two partly flat

spikes in the plot of [Pd(pic)*R*3]NO_3, where the left wing region ($d_i < d_e$) correspond to the points on the surface around the C–H donor and the right wing region ($d_e < d_i$) corresponds to the points surface as well as in the fingerprint plot. The interaction of the hydrogen with the halogen atom (H···Cl (or Br)) comprises a nearly high share of the Hirshfeld surface (~ 9% in both structures) and appear as wings on the top left (H…halogen) and bottom right (halogen···H) of the 2D fingerprint plots (Figs. S5 and S6). These contacts are due to C–H···halogen intermolecular interactions. π-stacking interactions (C···C contacts) appear in the central region of the plots and they comprise area fractions of 2.5% and 3.7% in [Pd(pic)*S*2]NO_3 and [Pd(pic)*R*3]NO_3 complexes, respectively.

[Pd(pic)*S*2]NO_3	**[Pd(pic)*R*3]NO_3**
	

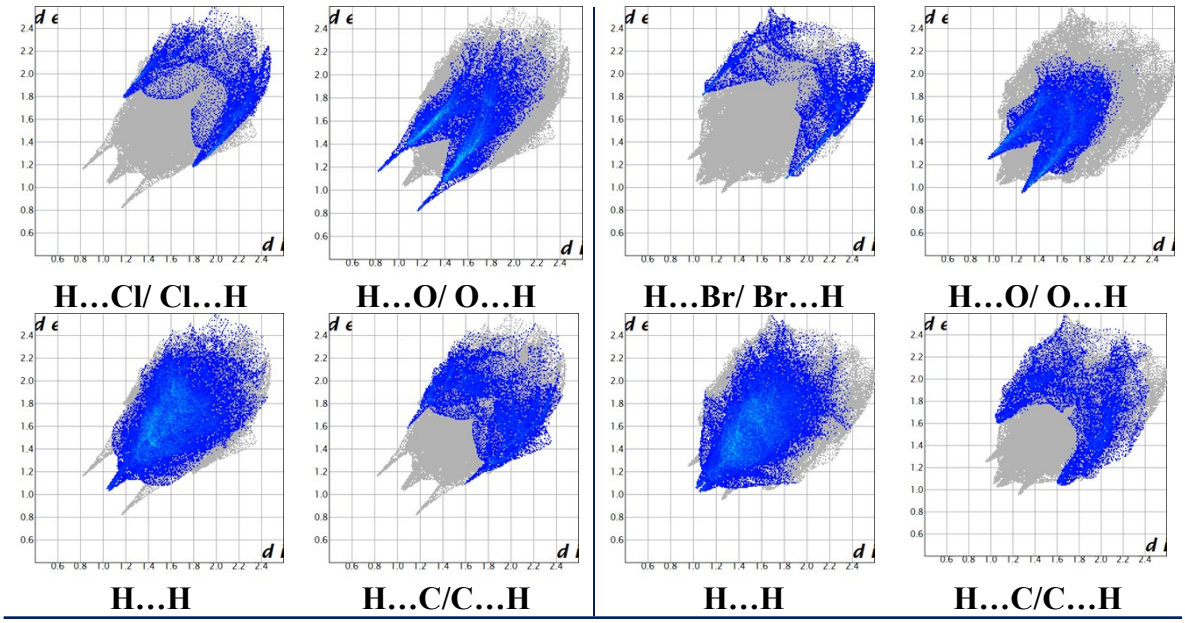


Fig. S5 The graphical illustration of Hirshfeld surfaces with d_{norm} properties and two-dimensional fingerprint plots for [Pd(pic)*S*2]NO_3 and [Pd(pic)*R*3]NO_3. The strongest intermolecular contacts are shown in red color, while weak contacts as blue color. The d_e (y-axis) and d_i (x-axis) values are the closest external and internal distances (Å) from given points on the Hirshfeld surfaces contacts.

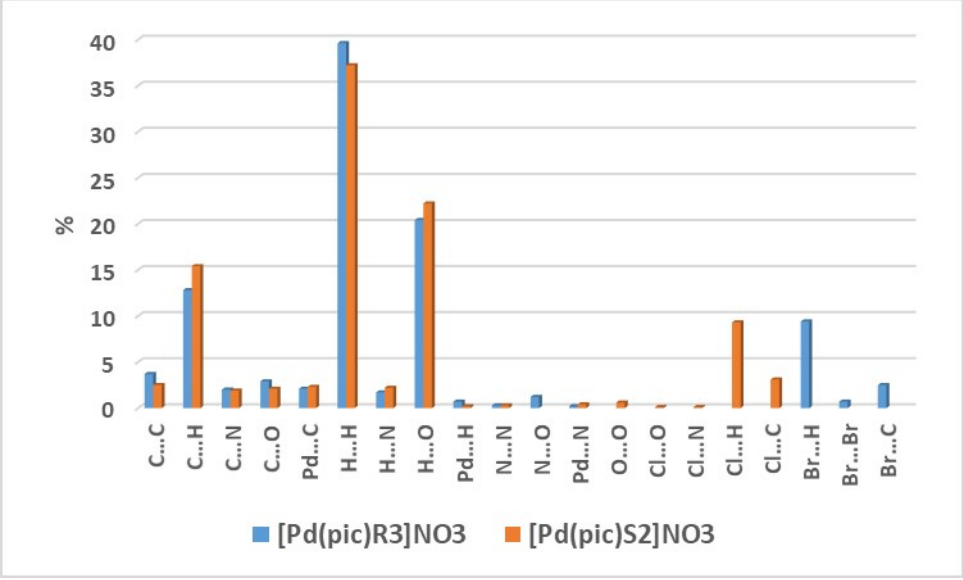


Fig. S6 Relative contributions to the Hirshfeld surfaces area for different intermolecular contacts in [Pd(pic)*S*2]NO_3 and [Pd(pic)*R*3]NO_3.

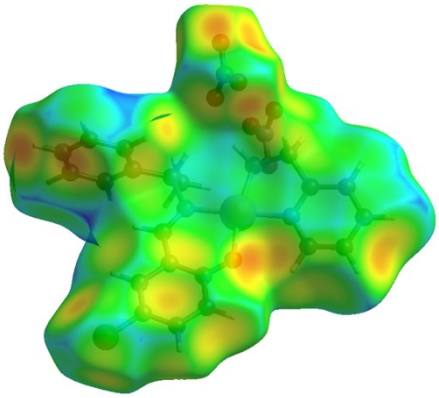
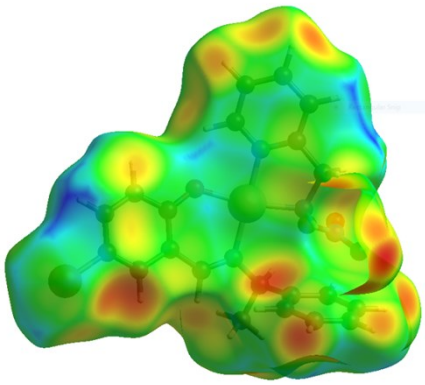
[Pd(pic)*S*2]NO_3	[Pd(pic)*R*3]NO_3
	

Fig. S7 Hirshfeld surface of [Pd(pic)*S*2]NO_3 and [Pd(pic)*R*3]NO_3 mapped with d_e

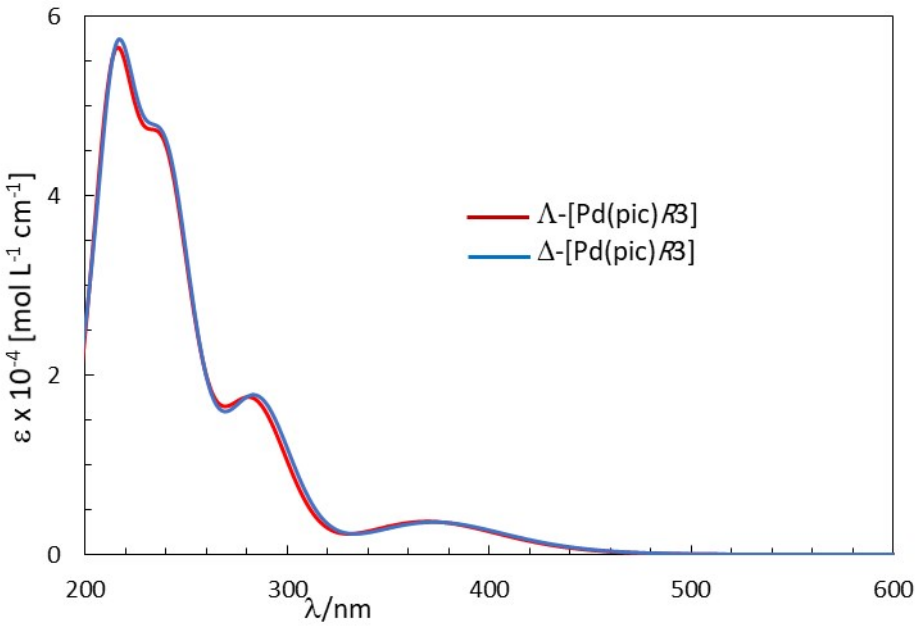


Fig. S8 Calculated UV-Vis. spectra for the diastereomeric pair [Λ-Pd(pic)*R*3] and [Δ-Pd(pic)*R*3], calculated at B3LYP/SDD with PCM in dichloromethane (Gaussian band shape with exponential half-width, σ = 0.33 eV).

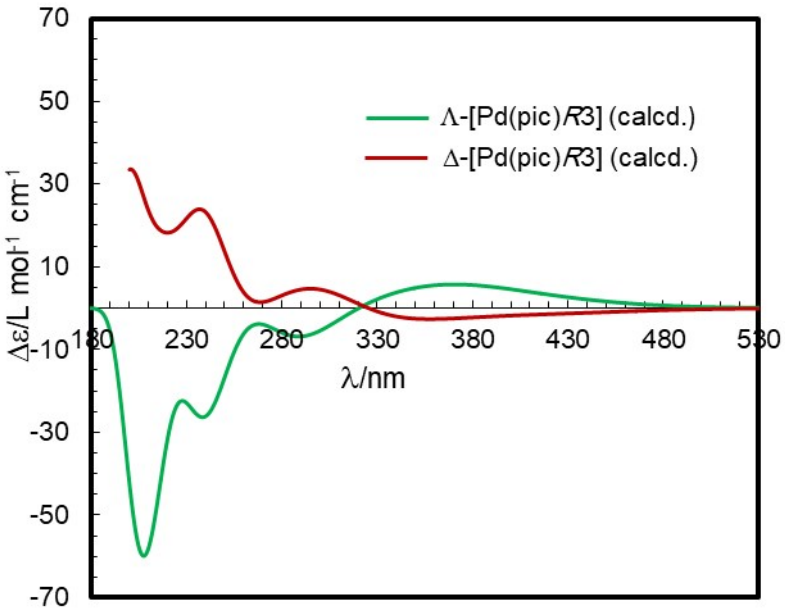


Fig. S9 Calculated ECD spectra for the diastereomeric pair [Λ-Pd(pic)*R*3] and [Δ-Pd(pic)*R*3], calculated at B3LYP/SDD with PCM in dichloromethane (Gaussian band shape with exponential half-width, σ = 0.33 eV).

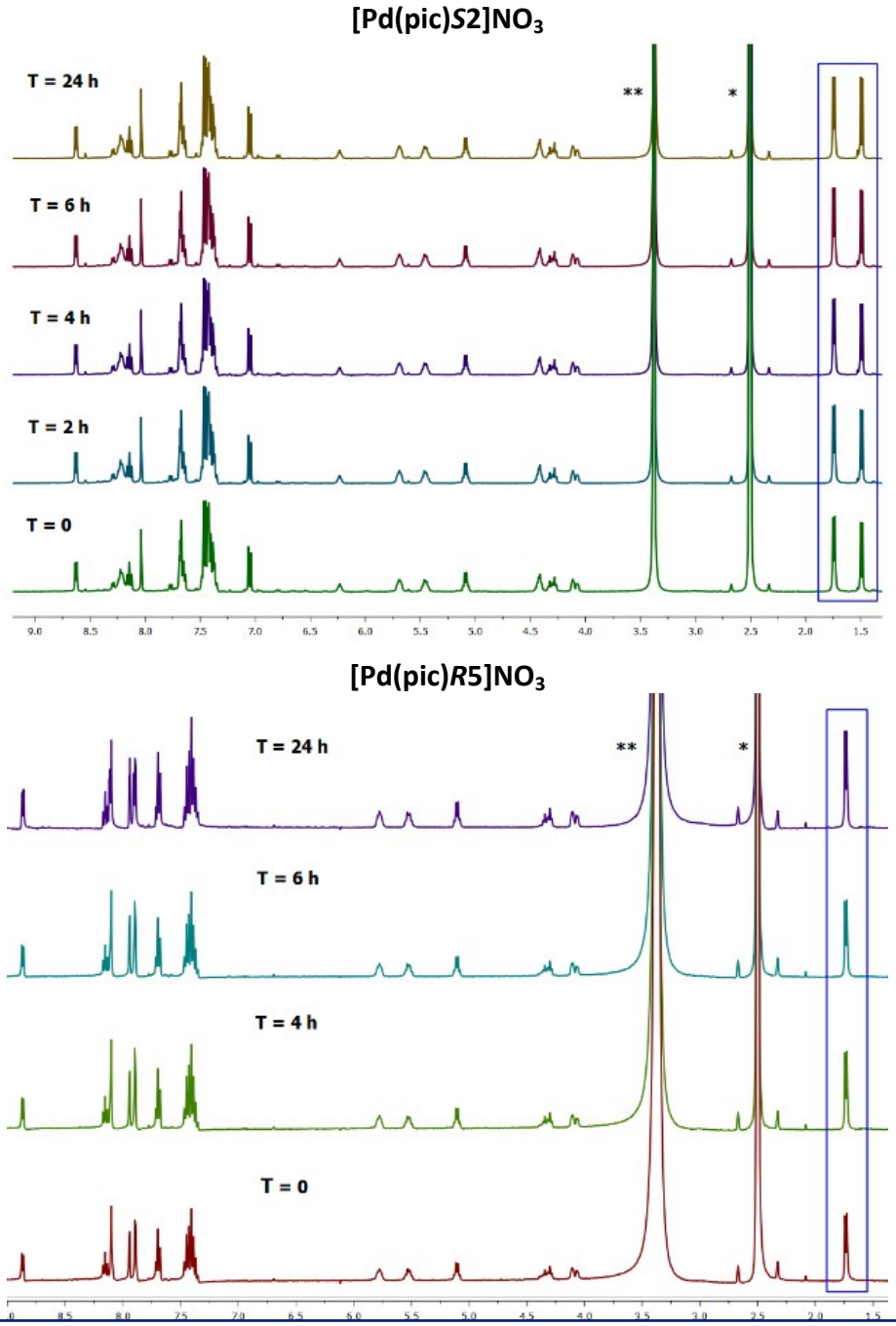


Fig S10. VT ^{1}H NMR of **[Pd(pic)*S*2]NO_3** (up) and **[Pd(pic)*R*5]NO_3** (down) in DMSO-d_6 solution. The hydrogen of the methyl group is indicated in the rectangular box. (* peak for dmso-d_6 and ** peak for water in dmso-d_6).

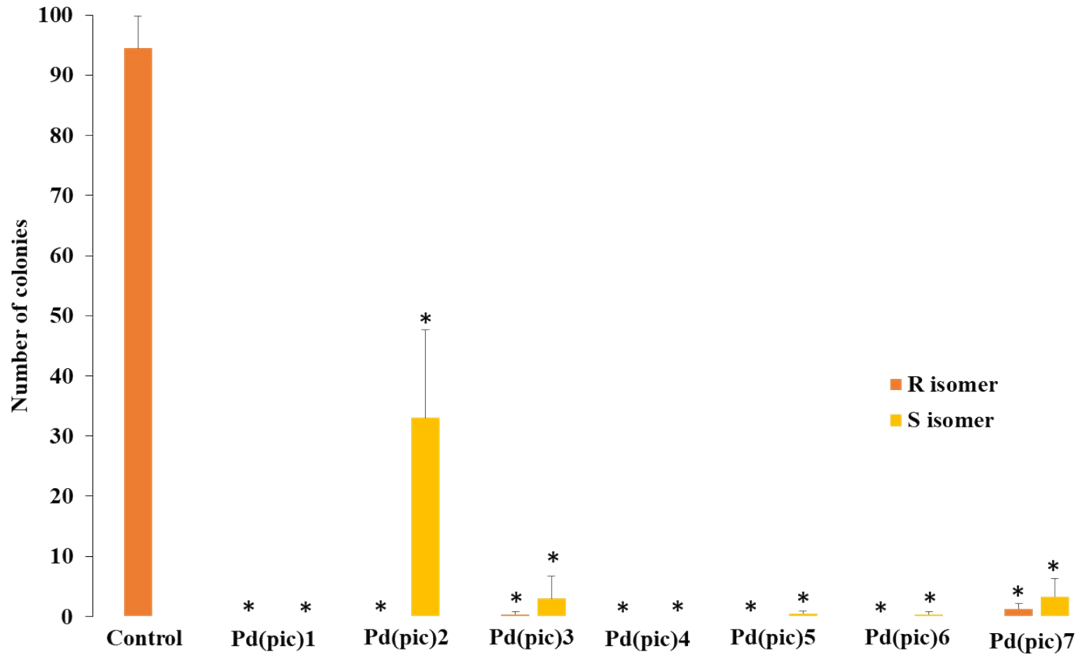


Fig. S11 Colony formation assay of MDA-MB-231 cell line after exposure with the Pd(II) compounds. Analysis of the clonogenic ability, after 24 h of incubation with IC_{50}. Values represent mean ± S.D. of at least two independent experiments. Statistical analysis was performed by one-way ANOVA with Dunnett's multiple comparisons test. *P ≤ 0.0001 compared with control.

Table S1 Classical and non-classical hydrogen bonds for [Pd(pic)*R*3]NO_3 and [Pd(pic)*rac*2]NO_3.

	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
[Pd(pic)*R*3]NO_3					
	C(3)—H(3)…O(3A)$^{\#1}$	0.95	2.62	3.333(5)	132.0
	C(7)—H(7)…O(3A)$^{\#1}$	0.95	2.32	3.034(5)	131.8
	C(8)—H(8)…O(4A)$^{\#2}$	1.00	2.63	3.599(6)	163.7
	C(16)—H(16)…O(1)	0.95	2.25	2.815(3)	117.4
	C(16)—H(16)…O(4A)$^{\#3}$	0.95	2.41	3.096(6)	128.4
	C(16)—H(16)…O(4B)$^{\#3}$	0.95	2.56	3.325(16)	138.2
	C(19)—H(19)…Br(1)$^{\#4}$	0.95	3.05	3.977(3)	166.4
	C(21)—H(21B)…O(2A)$^{\#5}$	0.99	2.41	3.139(7)	129.6
	C(21)—H(21B)…O(4B)$^{\#5}$	0.99	2.44	3.138(13)	126.9
	N(2)—H(2)…O(4A)$^{\#2}$	0.80	2.13	2.920(6)	166.4
	N(2)—H(2)…O(3B)$^{\#2}$	0.80	2.17	2.932(10)	159.4
	N(2)—H(1)…O(2A)$^{\#5}$	0.90	2.44	3.175(7)	139.1
	N(2)—H(1)…O(4B)$^{\#5}$	0.90	2.25	2.997(12)	140.0
[Pd(pic)*rac*2]NO_3					
	N(2)—H(2A)…O(4)	0.83	2.15	2.9776(1)	169
	N(2)—H(2B)…O(3)	0.87	2.11	2.9317(1)	156
	C(8)—H(8)…O(3)	0.98	2.48	3.4179(1)	161
	C(8)—H(8)…N(2)	0.98	2.60	3.1291(1)	114 (Intra)
	C(16)—H(16)…O(1)	0.93	2.34	2.8719(1)	116 (Intra)
	C(16)—H(16)…O(2)	0.93	2.57	3.2043(1)	126
	C(21)—H(21A)…O(1)	0.97	2.56	3.3197(1)	136

Symmetry transformations used to generate equivalent atoms: #1: -x+3/2,-y+1,z-1/2; #2: x-1/2,-y+1/2,-z+1; #3: x,y,z-1; #4: x,y-1,z; #5: x+1/2,-y+1/2,-z+1

Table S2 Excited states, excitation energy (eV), wavelength (nm) and osilator strenth (f) and MOs contributions for [Λ-Pd(pic)*R*3], calculated at B3LYP/SDD with PCM in dichloromethane.

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      2.8349 eV  437.35 nm  f=0.0002  <S**2>=0.000
      95 ->102        -0.22816
     100 ->102         0.65595
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1193.34963573
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      3.0626 eV  404.83 nm  f=0.0168  <S**2>=0.000
      96 ->102         0.13743
      99 ->102         0.57965
     100 ->101        -0.35011

 Excited State   3:      Singlet-A      3.3208 eV  373.35 nm  f=0.0513  <S**2>=0.000
      99 ->102         0.33486
     100 ->101         0.60119

 Excited State   4:      Singlet-A      3.5587 eV  348.39 nm  f=0.0004  <S**2>=0.000
      93 ->102         0.22564
      94 ->102         0.26243
      97 ->102         0.49066
      98 ->102        -0.32794
```

```
Excited State   5:      Singlet-A      3.5968 eV  344.71 nm  f=0.0269  <S**2>=0.000
    100 ->103         0.69207

Excited State   6:      Singlet-A      3.8604 eV  321.17 nm  f=0.0019  <S**2>=0.000
     89 ->102        -0.15985
     91 ->102        -0.19424
     92 ->102         0.15686
     99 ->101         0.60295

Excited State   7:      Singlet-A      3.8690 eV  320.45 nm  f=0.0021  <S**2>=0.000
     89 ->102         0.33197
     91 ->102         0.38032
     92 ->102        -0.30726
     99 ->101         0.31512

Excited State   8:      Singlet-A      4.0867 eV  303.39 nm  f=0.0005  <S**2>=0.000
     90 ->102         0.27041
     95 ->102         0.55894
    100 ->102         0.24017

Excited State   9:      Singlet-A      4.2184 eV  293.92 nm  f=0.0016  <S**2>=0.000
     96 ->103         0.11961
     99 ->103         0.67673

Excited State  10:      Singlet-A      4.2396 eV  292.45 nm  f=0.0001  <S**2>=0.000
    100 ->104         0.69760

Excited State  11:      Singlet-A      4.3508 eV  284.97 nm  f=0.2885  <S**2>=0.000
     95 ->101        -0.10103
     97 ->101        -0.36072
     98 ->101         0.55885
    100 ->108         0.10057

Excited State  12:      Singlet-A      4.3554 eV  284.67 nm  f=0.0136  <S**2>=0.000
     97 ->101         0.56462
     98 ->101         0.38597

Excited State  13:      Singlet-A      4.4274 eV  280.04 nm  f=0.0098  <S**2>=0.000
     97 ->102         0.33793
     98 ->102         0.58817
     99 ->102         0.10380

Excited State  14:      Singlet-A      4.5321 eV  273.57 nm  f=0.0011  <S**2>=0.000
     95 ->101         0.16642
     96 ->101         0.66468

Excited State  15:      Singlet-A      4.6249 eV  268.08 nm  f=0.0043  <S**2>=0.000
     95 ->102        -0.10972
     96 ->102         0.66666
     99 ->102        -0.14097

Excited State  16:      Singlet-A      4.6411 eV  267.15 nm  f=0.0313  <S**2>=0.000
     95 ->101         0.57722
     96 ->101        -0.17759
     97 ->103         0.21995
     98 ->103        -0.21429

Excited State  17:      Singlet-A      4.6531 eV  266.46 nm  f=0.0000  <S**2>=0.000
    100 ->106        -0.12215
    100 ->107         0.67865

Excited State  18:      Singlet-A      4.7409 eV  261.52 nm  f=0.0389  <S**2>=0.000
     95 ->101         0.28463
     97 ->102         0.10010
     97 ->103        -0.33740
     98 ->103         0.46767
    100 ->108         0.16175

Excited State  19:      Singlet-A      4.8109 eV  257.72 nm  f=0.0048  <S**2>=0.000
    100 ->105         0.69435
```

```
Excited State  20:      Singlet-A      4.8170 eV  257.39 nm  f=0.0114  <S**2>=0.000
     93 ->102         0.12990
     94 ->102         0.16174
     97 ->102        -0.17055
     97 ->103         0.45723
     98 ->103         0.44114

Excited State  21:      Singlet-A      4.8396 eV  256.19 nm  f=0.0068  <S**2>=0.000
     93 ->102         0.33033
     94 ->102         0.42639
     97 ->102        -0.27241
     97 ->103        -0.27354
     98 ->102         0.12680

Excited State  22:      Singlet-A      4.8797 eV  254.08 nm  f=0.0029  <S**2>=0.000
     91 ->101        -0.44049
     92 ->101         0.44727
     93 ->101         0.12302
     94 ->101        -0.23913

Excited State  23:      Singlet-A      4.8917 eV  253.46 nm  f=0.0010  <S**2>=0.000
    100 ->106         0.69056
    100 ->107         0.12249

Excited State  24:      Singlet-A      4.9454 eV  250.71 nm  f=0.0002  <S**2>=0.000
     96 ->103        -0.10096
     96 ->104         0.10423
     99 ->104         0.68556

Excited State  25:      Singlet-A      4.9567 eV  250.13 nm  f=0.0433  <S**2>=0.000
     95 ->103         0.22877
     96 ->103         0.57511
     99 ->104         0.10572
    100 ->108        -0.21755

Excited State  26:      Singlet-A      4.9809 eV  248.92 nm  f=0.1092  <S**2>=0.000
     93 ->101         0.26911
     94 ->101         0.28600
     96 ->103         0.29208
    100 ->108         0.44298

Excited State  27:      Singlet-A      5.0435 eV  245.83 nm  f=0.0055  <S**2>=0.000
     90 ->103         0.10259
     93 ->101         0.15031
     93 ->103        -0.14828
     95 ->103         0.57610
     96 ->103        -0.21213
     97 ->104        -0.12877

Excited State  28:      Singlet-A      5.0614 eV  244.96 nm  f=0.0259  <S**2>=0.000
     92 ->102        -0.10346
     93 ->101         0.13258
     93 ->102         0.52165
     94 ->102        -0.41427

Excited State  29:      Singlet-A      5.1151 eV  242.39 nm  f=0.0083  <S**2>=0.000
     92 ->101         0.12045
     93 ->101        -0.17647
     93 ->103         0.22873
     94 ->101         0.28442
     94 ->103        -0.22857
     94 ->104         0.12935
     95 ->103         0.22905
     97 ->104         0.30992
     98 ->104        -0.22590

Excited State  30:      Singlet-A      5.1875 eV  239.00 nm  f=0.5760  <S**2>=0.000
     93 ->101        -0.31086
     94 ->101        -0.34687
     97 ->101         0.12627
    100 ->108         0.37615
```

```
Excited State  31:      Singlet-A      5.2416 eV  236.54 nm  f=0.0004  <S**2>=0.000
     91 ->101         0.49812
     92 ->101         0.48042

Excited State  32:      Singlet-A      5.2540 eV  235.98 nm  f=0.0332  <S**2>=0.000
    100 ->109         0.66092

Excited State  33:      Singlet-A      5.2739 eV  235.09 nm  f=0.0141  <S**2>=0.000
     89 ->101         0.11215
     91 ->101         0.14927
     92 ->101        -0.15045
     93 ->101         0.44427
     93 ->103         0.18487
     94 ->101        -0.30231
     94 ->103        -0.16754
     97 ->104         0.19709
     98 ->104        -0.18223

Excited State  34:      Singlet-A      5.2984 eV  234.00 nm  f=0.0075  <S**2>=0.000
     96 ->105         0.23524
     96 ->106         0.30115
     97 ->105        -0.23608
     97 ->106         0.17195
     98 ->104         0.10585
     98 ->105        -0.24629
     98 ->106         0.26585
     99 ->105        -0.25133
    100 ->109         0.16162

Excited State  35:      Singlet-A      5.3534 eV  231.60 nm  f=0.0047  <S**2>=0.000
     91 ->103         0.47367
     92 ->103        -0.43153
     94 ->103         0.15803

Excited State  36:      Singlet-A      5.4366 eV  228.05 nm  f=0.0151  <S**2>=0.000
     90 ->101        -0.14500
     94 ->103        -0.20111
     97 ->104         0.22559
     98 ->104         0.58341

Excited State  37:      Singlet-A      5.4489 eV  227.54 nm  f=0.1044  <S**2>=0.000
     89 ->101         0.10962
     89 ->102        -0.22719
     90 ->101         0.44024
     92 ->102        -0.14067
     93 ->103        -0.29994
     94 ->103        -0.23716
     97 ->104         0.12900

Excited State  38:      Singlet-A      5.4620 eV  226.99 nm  f=0.0525  <S**2>=0.000
     89 ->101         0.16609
     90 ->101         0.33643
     93 ->103         0.32322
     94 ->103         0.39514
     97 ->104         0.13771
     98 ->104         0.16429

Excited State  39:      Singlet-A      5.5207 eV  224.58 nm  f=0.0221  <S**2>=0.000
     88 ->104        -0.10296
     89 ->101         0.44014
     92 ->103        -0.10106
     93 ->103         0.15820
     94 ->103        -0.21031
     97 ->104        -0.38166

Excited State  40:      Singlet-A      5.5476 eV  223.49 nm  f=0.0107  <S**2>=0.000
     89 ->101         0.47166
     90 ->101        -0.22102
     93 ->103        -0.25034
     94 ->103         0.16097
```

```
     95 ->104        -0.10802
     97 ->104         0.26808

Excited State  41:      Singlet-A      5.5887 eV  221.85 nm  f=0.0021  <S**2>=0.000
     83 ->102         0.10097
     89 ->102        -0.11631
     90 ->102         0.59520
     95 ->102        -0.29508

Excited State  42:      Singlet-A      5.5961 eV  221.56 nm  f=0.0018  <S**2>=0.000
     96 ->104         0.66359
     99 ->105         0.15377

Excited State  43:      Singlet-A      5.6144 eV  220.83 nm  f=0.0248  <S**2>=0.000
     96 ->104        -0.16440
     96 ->105         0.15383
     97 ->105        -0.10738
     98 ->105        -0.14655
     99 ->105         0.52173
    100 ->110        -0.29623

Excited State  44:      Singlet-A      5.6168 eV  220.74 nm  f=0.0193  <S**2>=0.000
     89 ->102         0.13072
     90 ->101         0.13375
     92 ->102         0.24959
     99 ->105         0.31768
    100 ->110         0.47620

Excited State  45:      Singlet-A      5.6464 eV  219.58 nm  f=0.0393  <S**2>=0.000
     91 ->102         0.42425
     92 ->102         0.47341
    100 ->110        -0.27402

Excited State  46:      Singlet-A      5.6809 eV  218.25 nm  f=0.0307  <S**2>=0.000
     96 ->106         0.15910
     99 ->106         0.66946

Excited State  47:      Singlet-A      5.7489 eV  215.66 nm  f=0.2302  <S**2>=0.000
     89 ->102        -0.18792
     90 ->101        -0.11249
     90 ->104         0.10317
     91 ->102         0.14249
     95 ->104         0.57036
    100 ->110         0.10506
    100 ->111        -0.17832

Excited State  48:      Singlet-A      5.7755 eV  214.67 nm  f=0.2145  <S**2>=0.000
     89 ->102         0.15209
     95 ->104         0.22470
     99 ->108         0.51434
    100 ->111         0.26117

Excited State  49:      Singlet-A      5.7832 eV  214.39 nm  f=0.3134  <S**2>=0.000
     89 ->102        -0.17150
     91 ->102         0.10311
     95 ->104        -0.21524
     98 ->108        -0.11011
     99 ->108         0.44783
     99 ->109         0.10266
    100 ->111        -0.34501

Excited State  50:      Singlet-A      5.8328 eV  212.56 nm  f=0.0221  <S**2>=0.000
     89 ->102        -0.21098
     91 ->102         0.13326
     97 ->105         0.19171
     98 ->105        -0.22058
    100 ->110         0.16159
    100 ->111         0.40053
    100 ->112         0.29044

Excited State  51:      Singlet-A      5.8385 eV  212.36 nm  f=0.0076  <S**2>=0.000
```

```
     94 ->107         0.10645
     97 ->105         0.25185
     97 ->106         0.12138
     97 ->107        -0.30354
     98 ->105        -0.26699
     98 ->106        -0.16178
     98 ->107         0.37710
    100 ->112        -0.13337

Excited State  52:      Singlet-A      5.8586 eV  211.63 nm  f=0.0048  <S**2>=0.000
     97 ->105         0.35335
     97 ->107         0.26549
     98 ->105        -0.34142
     98 ->107        -0.33167
    100 ->112        -0.11143

Excited State  53:      Singlet-A      5.8996 eV  210.16 nm  f=0.0001  <S**2>=0.000
     89 ->103         0.10907
     91 ->103         0.46006
     92 ->103         0.50479

Excited State  54:      Singlet-A      5.9244 eV  209.28 nm  f=0.0050  <S**2>=0.000
     97 ->105         0.10713
     97 ->106        -0.45840
     97 ->107        -0.12203
     98 ->106         0.46382
     98 ->107         0.14499

Excited State  55:      Singlet-A      5.9552 eV  208.19 nm  f=0.0275  <S**2>=0.000
     89 ->102         0.12434
     97 ->108         0.22823
     98 ->108        -0.23800
    100 ->108         0.10586
    100 ->110        -0.19070
    100 ->112         0.50394

Excited State  56:      Singlet-A      5.9872 eV  207.08 nm  f=0.0038  <S**2>=0.000
     87 ->101        -0.10338
     88 ->102        -0.13626
     89 ->103         0.57167
     90 ->103         0.27220
     91 ->103        -0.11419

Excited State  57:      Singlet-A      5.9896 eV  207.00 nm  f=0.0411  <S**2>=0.000
     87 ->101         0.36330
     96 ->105        -0.28309
     96 ->106         0.17240
     97 ->105        -0.25549
     97 ->106        -0.27445
     98 ->105        -0.18929
     98 ->106        -0.16296

Excited State  58:      Singlet-A      5.9942 eV  206.84 nm  f=0.0070  <S**2>=0.000
     87 ->101         0.55013
     96 ->105         0.19339
     96 ->106        -0.10759
     97 ->105         0.15066
     97 ->106         0.16780
     98 ->105         0.12178
     98 ->106         0.10983
    100 ->112        -0.10651

Excited State  59:      Singlet-A      6.0109 eV  206.27 nm  f=0.0367  <S**2>=0.000
     88 ->102        -0.10251
     89 ->103         0.17405
     90 ->103        -0.27249
     99 ->107         0.39601
     99 ->109        -0.36885

Excited State  60:      Singlet-A      6.0393 eV  205.30 nm  f=0.0068  <S**2>=0.000
     89 ->103        -0.15728
```

```
     90 ->103         0.42710
     94 ->104         0.17058
     99 ->107         0.44974

Excited State  61:      Singlet-A      6.0646 eV  204.44 nm  f=0.0082  <S**2>=0.000
     90 ->103        -0.16012
     91 ->104         0.46102
     92 ->104        -0.43566
     93 ->104        -0.17743
     94 ->104         0.14146

Excited State  62:      Singlet-A      6.0693 eV  204.28 nm  f=0.0185  <S**2>=0.000
     88 ->102         0.16896
     89 ->103         0.10116
     90 ->103        -0.20485
     94 ->104        -0.15163
     99 ->107         0.32961
     99 ->109         0.47674

Excited State  63:      Singlet-A      6.0859 eV  203.72 nm  f=0.0013  <S**2>=0.000
     87 ->103        -0.15653
     88 ->102         0.58160
     88 ->103         0.12005
     89 ->103         0.12973
     99 ->109        -0.19751

Excited State  64:      Singlet-A      6.1514 eV  201.55 nm  f=0.0540  <S**2>=0.000
     88 ->102         0.10394
     88 ->104         0.10565
     89 ->103         0.17692
     90 ->103        -0.15908
     93 ->103        -0.11071
     93 ->104         0.32139
     94 ->104         0.45996
     97 ->108         0.11916
     98 ->108        -0.11085

Excited State  65:      Singlet-A      6.1755 eV  200.77 nm  f=0.0422  <S**2>=0.000
     87 ->102         0.24021
     88 ->101         0.14780
     88 ->103        -0.12277
     97 ->108        -0.22738
     98 ->108         0.28916
    100 ->111        -0.20123
    100 ->112         0.22601
    100 ->113         0.27846

Excited State  66:      Singlet-A      6.2229 eV  199.24 nm  f=0.0016  <S**2>=0.000
     97 ->108         0.47586
     98 ->108         0.46357
    100 ->113        -0.10189

Excited State  67:      Singlet-A      6.2317 eV  198.96 nm  f=0.0234  <S**2>=0.000
     87 ->102         0.12927
     88 ->101         0.12253
     90 ->107        -0.16073
     93 ->104        -0.14959
     95 ->107         0.42096
     96 ->107         0.10566
     97 ->107        -0.16993
     98 ->107        -0.17074
    100 ->113        -0.32159

Excited State  68:      Singlet-A      6.2327 eV  198.93 nm  f=0.0436  <S**2>=0.000
     87 ->102        -0.18113
     88 ->101        -0.14959
     88 ->103         0.13527
     90 ->107        -0.12013
     93 ->104         0.20511
     95 ->107         0.30559
     97 ->107        -0.12693
```

```
     97 ->108         0.11271
     98 ->107        -0.11730
     98 ->108         0.12107
     98 ->109         0.10473
    100 ->113         0.38144

Excited State  69:      Singlet-A      6.2551 eV  198.21 nm  f=0.0464  <S**2>=0.000
     87 ->102         0.13099
     88 ->101         0.15533
     88 ->103        -0.10766
     93 ->104        -0.20293
     97 ->108         0.20241
     97 ->109        -0.12149
     98 ->108        -0.12796
     98 ->109         0.41097
    100 ->111         0.10498
    100 ->113         0.23365

Excited State  70:      Singlet-A      6.2728 eV  197.65 nm  f=0.0057  <S**2>=0.000
     87 ->103         0.40520
     93 ->104        -0.16079
     97 ->109         0.32938
     98 ->109        -0.22693
    100 ->113         0.17203

Excited State  71:      Singlet-A      6.2838 eV  197.31 nm  f=0.0113  <S**2>=0.000
     93 ->104         0.13071
     95 ->107        -0.21028
     96 ->106        -0.12837
     97 ->107        -0.22090
     97 ->109         0.41465
     98 ->107        -0.15137
     98 ->109         0.25147
    100 ->113        -0.12965

Excited State  72:      Singlet-A      6.2903 eV  197.10 nm  f=0.0198  <S**2>=0.000
     87 ->102        -0.15283
     87 ->103         0.40612
     88 ->102         0.15304
     95 ->105        -0.18606
     97 ->109        -0.19104
     98 ->109         0.26695
     99 ->110        -0.10833
    100 ->113        -0.20821
SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 NState=   72 LETran=    1306.
```