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**supplementary information**

# Palladium(0) mediated C-H bond activation of N-(naphthyl)salicylaldimine and related ligands: Utilization of the resulting organopalladium complexes in catalytic C-C and C-N coupling reactions

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**Table S1** Selected bond distances and bond angles for $[Pd(L^2)(PPh_3)]$, $[Pd(L^3)(PPh_3)]$ and $[Pd(L^4)(PPh_3)]$

| $[Pd(L^2)(PPh_3)]$ | | | |
|---|---|---|---|
| Bond distances (Å) | | | |
| Pd1-O1 | 2.043(5) | O1-C1 | 1.290(8) |
| Pd1-N1 | 2.033(5) | N1-C7 | 1.298(8) |
| Pd1-C15 | 2.011(6) | N1-C8 | 1.431(8) |
| Pd1-P1 | 2.2671(17) | | |
| Bond angles (°) | | | |
| N1-Pd1-P1 | 174.59(14) | N1-Pd1-O1 | 90.78(19) |
| O1-Pd1-C15 | 173.7(2) | N1-Pd1-C15 | 83.0(2) |
| $[Pd(L^3)(PPh_3)]$ | | | |
| Bond distances (Å) | | | |
| Pd1-O1 | 2.0726(19) | O1-C1 | 1.300(3) |
| Pd1-N1 | 2.043(3) | N1-C7 | 1.284(3) |
| Pd1-C15 | 2.014(3) | N1-C8 | 1.417(4) |
| Pd1-P1 | 2.2672(8) | | |
| Bond angles (°) | | | |
| N1-Pd1-P1 | 177.48(7) | N1-Pd1-O1 | 90.53(9) |
| O1-Pd1-C15 | 173.00(10) | N1-Pd1-C15 | 82.52(11) |
| $[Pd(L^4)(PPh_3)]$ | | | |
| Bond distances (Å) | | | |
| Pd1-O1 | 2.052(3) | C1-O1 | 1.293(5) |
| Pd1-N1 | 2.033(3) | C11-N1 | 1.306(5) |
| Pd1-C19 | 1.986(4) | C12-N1 | 1.418(5) |
| Pd1-P1 | 2.2666(12) | | |
| Bond angles (°) | | | |
| N1-Pd1-P1 | 171.80(10) | O1-Pd1-N1 | 89.88(12) |
| O1-Pd1-C19 | 170.68(16) | N1-Pd1-C19 | 83.19(15) |

**Table S2** Computed parameters from TDDFT calculations on $[Pd(L^2)(PMe_3)]$ for electronic spectral properties in dichloromethane solution

| Transit-ion number | Nature of transition | CI value | E /eV | Oscillator strength, *f* | $\lambda_{theo}$ /nm | Assignment |
|---|---|---|---|---|---|---|
| 1 | H-1 → L<br>H → L | 0.16068<br>0.65154 | 2.8742 | 0.0898 | 431.37<br>(460)[a] | ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 2 | H-1 → L<br>H → L | 0.65111<br>-0.14199 | 3.1978 | 0.3491 | 387.72<br>(398)[a] | ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 3 | H-4 → L<br><br>H-3 → L<br>H → L+1 | 0.41488<br><br>-0.34370<br>-0.39425 | 4.0633 | 0.0462 | 305.14<br>(376)[a] | ILCT/LLCT/LMCT/<br>MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 4 | H-6 → L<br><br>H-5 → L<br>H-2 → L+2<br><br>H-1 → L+1<br>H-1 → L+2<br><br>H-1 → L+3<br>H → L+1 | -0.11448<br><br>0.13448<br>0.54934<br><br>-0.14866<br>0.15617<br><br>-0.11047<br>0.15539 | 4.3027 | 0.0306 | 288.15<br>(292)[a] | ILCT/LLCT/LMCT/<br>MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/<br>MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/<br>MLCT<br>ILCT/MLCT<br>ILCT/LMCT/MLCT |

[a] $\lambda_{exp}$ /nm is given in parenthesis.

**Table S3** Computed parameters from TDDFT calculations on $[Pd(L^3)(PMe_3)]$ for electronic spectral properties in dichloromethane solution

| Transit-ion number | Nature of transition | CI value | E /eV | Oscillator strength, *f* | $\lambda_{theo}$ /nm | Assignment |
|---|---|---|---|---|---|---|
| 1 | H-1 → L<br>H → L | -0.21232<br>0.63304 | 2.8451 | 0.0930 | 435.78<br>(468)[a] | ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 2 | H-1 → L<br>H → L | 0.63876<br>0.19719 | 3.1004 | 0.3279 | 399.90<br>(404)[a] | ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 3 | H-5 → L<br>H-4 → L<br>H-2 → L+2<br>H-1 → L+1<br>H-1 → L+3<br>H → L+1 | -0.10441<br>0.58467<br>-0.11661<br>-0.11062<br>0.19847<br>0.20351 | 4.0338 | 0.0233 | 307.36<br>(382)[a] | ILCT/LLCT/LMCT/MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 4 | H-6 → L<br>H-5 → L<br>H-2 → L+1<br>H-2 → L+2<br>H-1 → L+1<br>H-1 → L+2<br>H → L+1<br>H → L+2 | 0.15126<br>0.10114<br>-0.12250<br>0.49611<br>0.11233<br>0.22148<br>0.17511<br>0.19076 | 4.2281 | 0.0295 | 293.24<br>(294)[a] | ILCT/LLCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT |

[a] $\lambda_{exp}$ /nm is given in parenthesis.

**Table S4** Computed parameters from TDDFT calculations on $[Pd(L^4)(PMe_3)]$ for electronic spectral properties in dichloromethane solution

| Transit-ion number | Nature of transition | CI value | E /eV | Oscillator strength, *f* | $\lambda_{theo}$ /nm | Assignment |
|---|---|---|---|---|---|---|
| 1 | H-1 → L<br>H → L | 0.20797<br>0.62147 | 2.8034 | 0.2928 | 442.26<br>(480)[a] | ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 2 | H-1 → L<br>H → L | 0.64702<br>-0.20214 | 3.0472 | 0.2438 | 406.88<br>(454)[a] | ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 3 | H-4 → L<br>H-3 → L<br>H-2 → L<br>H → L+1 | 0.32491<br>0.52697<br>-0.23027<br>0.12642 | 3.7709 | 0.0801 | 328.79<br>(384)[a] | ILCT/LLCT/LMCT/MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 4 | H-7 → L<br>H-5 → L<br>H-1 → L+2<br>H-1 → L+3<br>H-1 → L+4<br>H → L+2<br>H → L+4 | -0.10317<br>0.49100<br>-0.22571<br>-0.15369<br>0.11033<br>0.31170<br>-0.13187 | 4.0458 | 0.0310 | 306.45<br>(318)[a] | ILCT/LLCT/LMCT/MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |

[a] $\lambda_{exp}$ /nm is given in parenthesis.

**Table S5** Computed parameters from TDDFT calculations on [Pd($L^1$)(pic)] for electronic spectral properties in dichloromethane solution

| Transit-ion number | Nature of transition | CI value | E /eV | Oscillator strength, *f* | $\lambda_{theo}$ /nm | Assignment |
|---|---|---|---|---|---|---|
| 1 | H-1 → L<br>H → L | 0.48487<br>0.45859 | 2.8489 | 0.1062 | 435.30<br>(496)[a] | ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 2 | H-1 → L<br>H → L | -0.47762<br>0.46846 | 2.9857 | 0.3532 | 415.26<br>(412)[a] | ILCT/LMCT/MLCT<br>ILCT/LMCT/MLCT |
| 3 | H-1 → L<br>H → L+1 | 0.53868<br>-0.44699 | 3.8246 | 0.0197 | 324.17<br>(392)[a] | ILCT/LMCT/MLCT<br>LLCT/LMCT/MLCT |
| 4 | H-8 → L+4<br><br>H-5 → L+4<br><br>H-3 → L<br>H-3 → L+3<br><br>H-2 → L+2<br><br>H-2 → L+3<br><br>H-1 → L+5<br>H → L+5 | 0.10357<br><br>-0.23455<br><br>-0.14912<br>0.24240<br><br>0.13564<br><br>-0.11534<br><br>-0.33256<br>0.35304 | 4.6176 | 0.0586 | 268.50<br>(270)[a] | ILCT/LLCT/LMCT/<br>MLCT<br>ILCT/LLCT/LMCT/<br>MLCT<br>ILCT/LMCT/MLCT<br>ILCT/LLCT/LMCT/<br>MLCT<br>ILCT/LLCT/LMCT/<br>MLCT<br>ILCT/LLCT/LMCT/<br>MLCT<br>ILCT/LLCT/LMCT<br>ILCT/LLCT/LMCT |

[a] $\lambda_{exp}$ /nm is given in parenthesis.

**Table S6** Compositions of all molecular orbitals of $[Pd(L^2)(PMe_3)]$ associated with the electronic spectral transitions

| Molecular orbital | % Contribution of fragments | | |
|---|---|---|---|
| | Pd | $L^2$ | $PMe_3$ |
| L+3 | 0.2 | 99.8 | 0 |
| L+2 | 18.6 | 57.0 | 24.4 |
| L+1 | 11.4 | 88.6 | 0 |
| L | 8.6 | 91.4 | 0 |
| H | 16.8 | 83.2 | 0 |
| H-1 | 16.2 | 83.8 | 0 |
| H-2 | 55.7 | 29.8 | 14.5 |
| H-3 | 18.3 | 81.1 | 0.6 |
| H-4 | 19.2 | 75.3 | 5.5 |
| H-5 | 10.0 | 90.0 | 0 |
| H-6 | 21.7 | 69.4 | 8.9 |

**Table S7** Compositions of all molecular orbitals of [Pd($L^3$)($PMe_3$)] associated with the electronic spectral transitions

| Molecular orbital | % Contribution of fragments | | |
|---|---|---|---|
| | Pd | $L^3$ | $PMe_3$ |
| L+3 | 2.2 | 97.8 | 0 |
| L+2 | 16.8 | 59.1 | 24.1 |
| L+1 | 17.4 | 82.1 | 0.5 |
| L | 8.3 | 91.7 | 0 |
| H | 15.3 | 84.7 | 0 |
| H-1 | 14.8 | 85.2 | 0 |
| H-2 | 56.2 | 28.7 | 15.1 |
| H-4 | 10.6 | 89.4 | 0 |
| H-5 | 21.7 | 75.2 | 3.1 |
| H-6 | 18.9 | 77.5 | 3.6 |

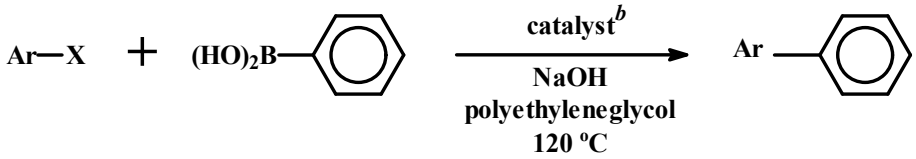
**Table S8** Compositions of all molecular orbitals of [Pd($L^4$)($PMe_3$)] associated with the electronic spectral transitions

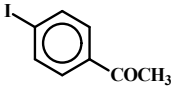
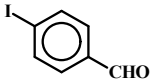
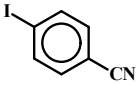
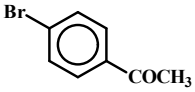
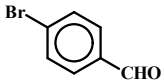
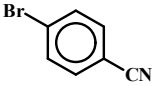
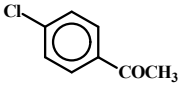
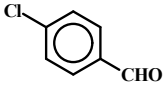
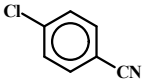
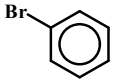
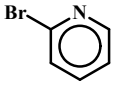
| Molecular orbital | % Contribution of fragments | | |
|---|---|---|---|
| | Pd | $L^4$ | $PMe_3$ |
| L+4 | 8.2 | 91.4 | 0.4 |
| L+3 | 15.9 | 66.8 | 17.3 |
| L+2 | 17.7 | 69.5 | 12.8 |
| L+1 | 6.8 | 93.2 | 0 |
| L | 7.6 | 92.4 | 0 |
| H | 10.4 | 89.6 | 0 |
| H-1 | 11.2 | 88.8 | 0 |
| H-2 | 30.6 | 55.0 | 14.4 |
| H-3 | 19.3 | 80.7 | 0 |
| H-4 | 13.4 | 64.0 | 22.6 |
| H-5 | 8.9 | 91.1 | 0 |
| H-7 | 26.2 | 58.0 | 15.8 |

**Table S9** Compositions of all molecular orbitals of [Pd($L^1$)(pic)] associated with the electronic spectral transitions

| Molecular orbital | % Contribution of fragments | | |
|---|---|---|---|
| | Pd | $L^1$ | $PMe_3$ |
| L+5 | 0 | 96.4 | 3.6 |
| L+4 | 16.7 | 65.7 | 17.6 |
| L+3 | 12.5 | 65.8 | 21.7 |
| L+2 | 6.4 | 32.5 | 61.1 |
| L+1 | 9.6 | 1.1 | 89.3 |
| L | 8.5 | 91.5 | 0 |
| H | 15.9 | 84.1 | 0 |
| H-1 | 16.4 | 83.6 | 0 |
| H-2 | 60.4 | 31.3 | 8.3 |
| H-3 | 16.1 | 83.9 | 0 |
| H-5 | 19.4 | 69.3 | 11.3 |
| H-8 | 19.7 | 64.2 | 16.1 |

**Table S10** Suzuki cross-coupling of aryl halides with phenylboronic acids[a]



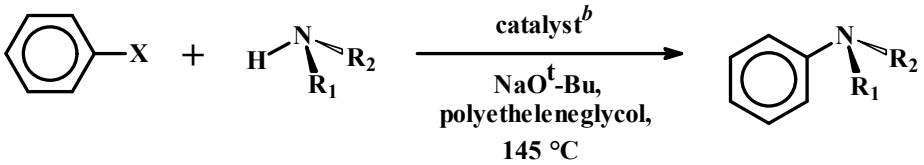

| Entry | Aryl halide | Time, (h) | Amt of cat., mol% | Yield[c], % | TON |
|---|---|---|---|---|---|
| 1 |  | 2 | 0.001 | 99 | 99 000 |
| 2 |  | 3 | 0.001 | 95 | 95 000 |
| 3 |  | 3 | 0.001 | 91 | 91 000 |
| 4 |  | 6 | 0.001 | 97 | 94 000 |
| 5 |  | 8 | 0.001 | 92 | 92 000 |
| 6 |  | 8 | 0.001 | 92 | 92 000 |
| 7 |  | 24 | 0.01 | 90 | 9 000 |
| 8 |  | 24 | 0.01 | 27 | 2700 |
| 9 |  | 24 | 0.01 | 12 | 1200 |
| 10 |  | 5 | 0.001 | 98 | 98 000 |
| 11 |  | 5 | 0.001 | 58 | 58 000 |

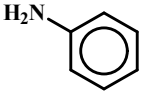
[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), NaOH (1.7 mmol), polyethyleneglycol (4 mL).

[b] $Pd(OAc)_2$ and $PPh_3$ in 1:2 mol ratio.

[c] Determined by GCMS.

**Table S11** C-N cross-coupling reaction of aryl halides with amines[a]




| Entry | X | Amine | Amt of cat., mol% | Time, h | Yield[c], % |
|---|---|---|---|---|---|
| 1 | I |  | 0.01 | 15 | N.O.[d] |
| 2 | I | | 0.01 | 15 | N.O.[d] |

[a] Reaction conditions: aryl halide (1.0 mmol), amines (1.0 mmol), $NaO^t$-Bu (1.7 mmol), Pd catalyst, polyetheleneglycol (4 mL).

[b] $Pd(OAc)_2$ and $PPh_3$ in 1:2 mol ratio.

[c] Determined by GCMS.

[d] Not observed.

**Table S12** Crystallographic data for $[Pd(L^2)(PPh_3)]$, $[Pd(L^3)(PPh_3)]$ and $[Pd(L^4)(PPh_3)]$

| Complex | $[Pd(L^2)(PPh_3)]$ | $[Pd(L^3)(PPh_3)]$ | $[Pd(L^4)(PPh_3)]$ |
|---|---|---|---|
| Empirical formula | $C_{35}H_{26}NOPPd$ | $C_{35}H_{25}NOPClPd$ | $C_{39}H_{28}NOPPd$ |
| Formula weight | 613.96 | 648.40 | 664.01 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ |
| $a$/Å | 14.3819(11) | 15.1395(5) | 8.9539(3) |
| $b$/Å | 11.8875(9) | 11.7820(4) | 14.4207(4) |
| $c$/Å | 17.6698(13) | 17.5381(6) | 23.0345(7) |
| $\alpha$/° | 90 | 90 | 90 |
| $\beta$/° | 112.090(4) | 115.068(2) | 91.811(2) |
| $\gamma$/° | 90 | 90 | 90 |
| $V$ /Å $^3$ | 2799.2(4) | 2833.66(17) | 2972.76(16) |
| $Z$ | 4 | 4 | 4 |
| $D_{calcd}$ /mg m$^{-3}$ | 1.457 | 1.520 | 1.484 |
| $F$(000) | 1248 | 1312 | 1352 |
| $\lambda$ /Å | 0.71073 | 0.71073 | 0.71073 |
| crystal size /mm$^3$ | 0.14 × 0.17 × 0.21 | 0.24 × 0.24 × 0.25 | 0.18 × 0.18 × 0.19 |
| Temp./K | 293 | 273 | 273 |
| $\mu$ /mm$^{-1}$ | 0.749 | 0.835 | 0.712 |
| Collected reflections | 42175 | 42565 | 24465 |
| $R_{int}$ | 0.140 | 0.046 | 0.060 |
| Independent reflections | 6506 | 5796 | 6072 |
| $R1^a$ | 0.0630 | 0.0327 | 0.0464 |
| $wR2^b$ | 0.1772 | 0.0852 | 0.1473 |
| $GOF^c$ | 1.02 | 1.09 | 0.77 |

[a] $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.
[b] $wR2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$.
[c] $GOF = [\Sigma(w(F_o^2-F_c^2)^2)/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

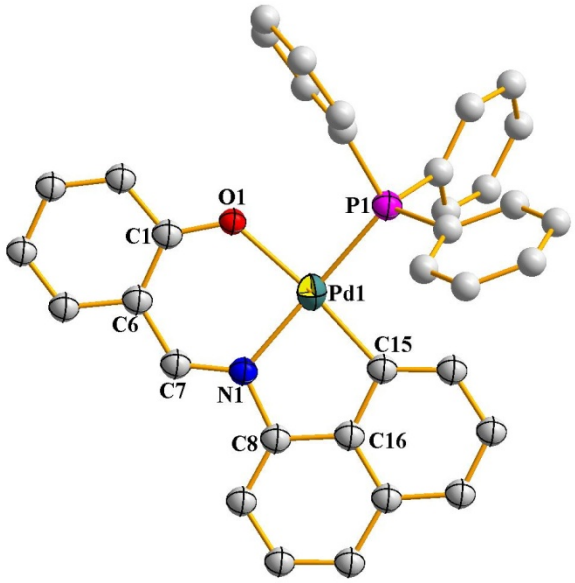



**Fig. S1** Structure of complex [Pd($L^2$)($PPh_3$)].

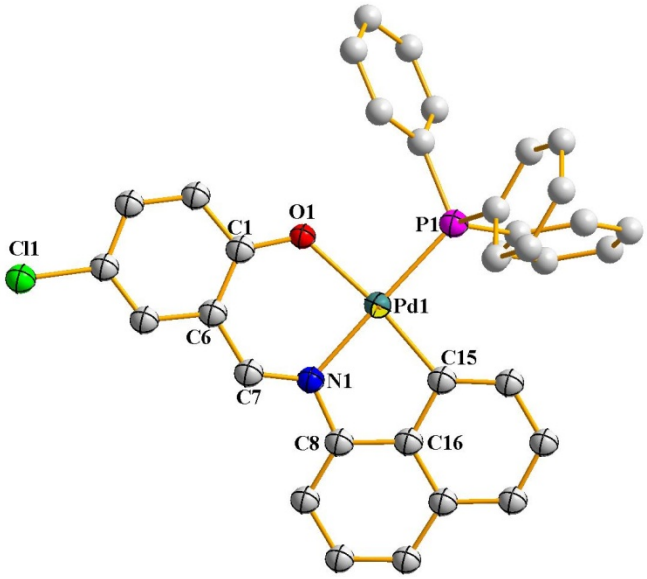



**Fig. S2** Structure of complex [Pd($L^3$)($PPh_3$)].

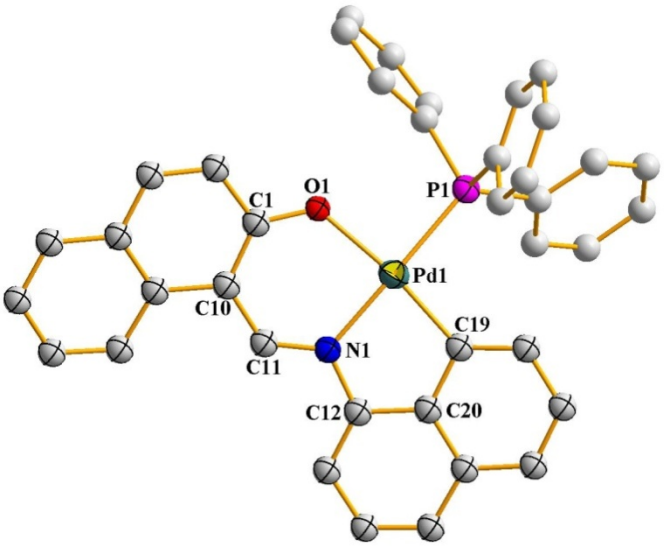
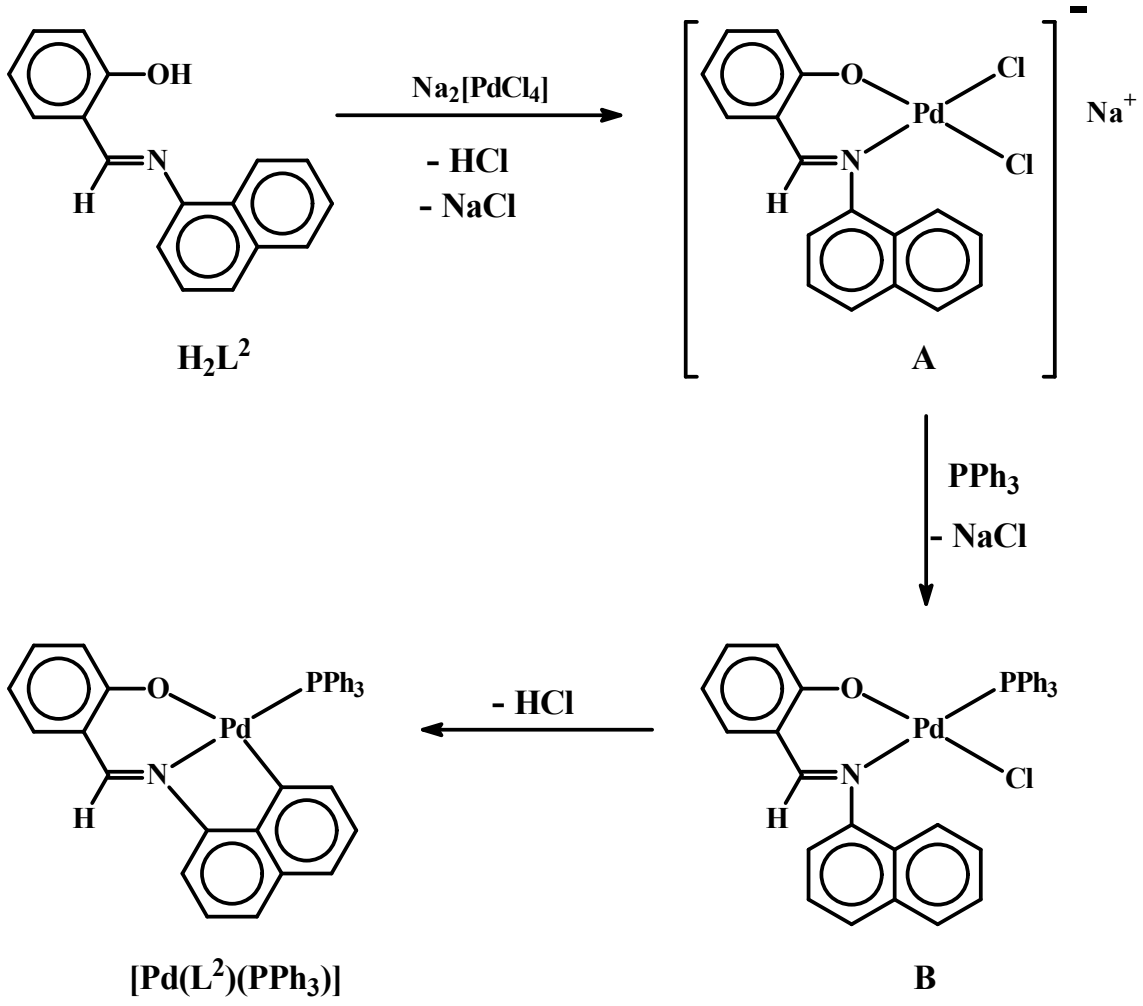
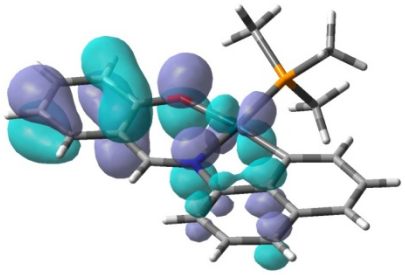
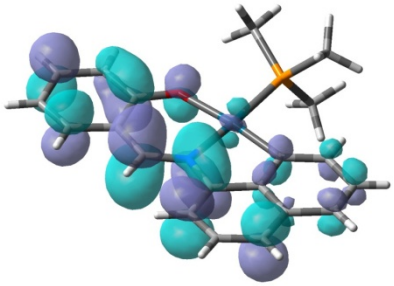
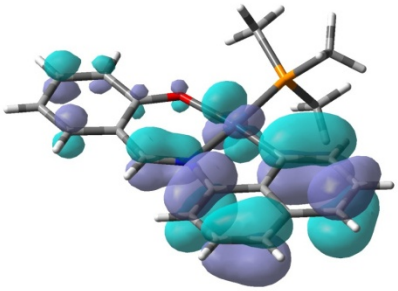
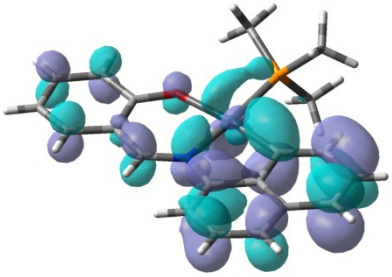
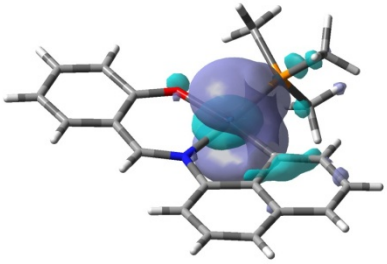
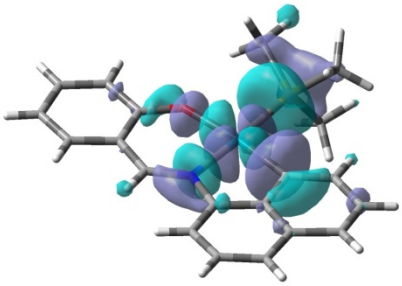
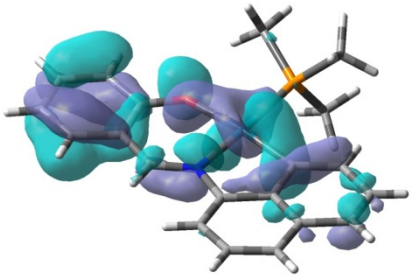
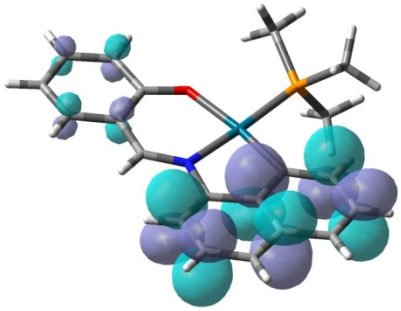



**Fig. S3** Structure of complex [Pd($L^4$)($PPh_3$)].




**Scheme S1** Probable steps behind formation of the $[Pd(L)(PPh_3)]$ complexes.

| HOMO (H) | LUMO (L) |
|---|---|
|  |  |
| H-1 | L+1 |
|  |  |
| H-2 | L+2 |
|  |  |
| H-3 | L+3 |
|  |  |

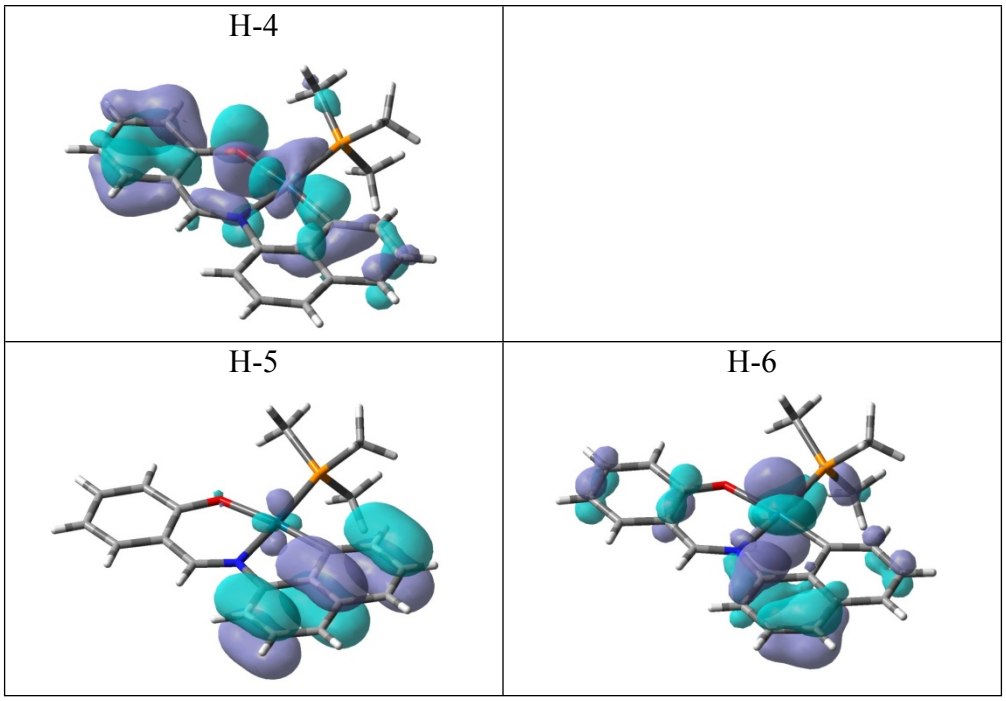
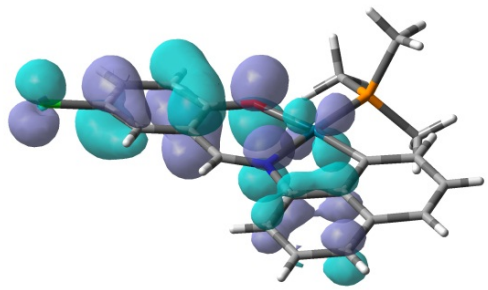
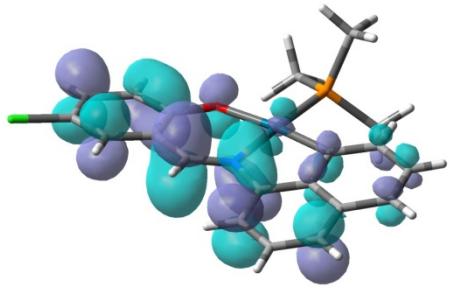
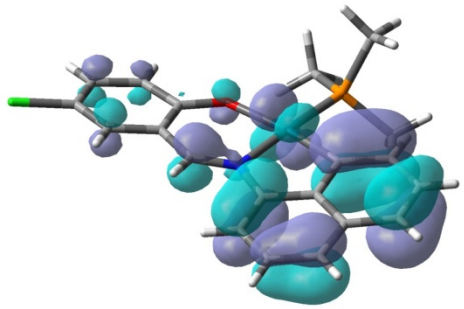
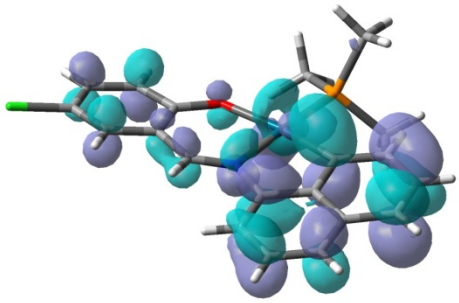
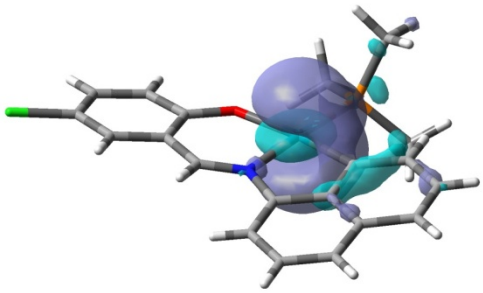
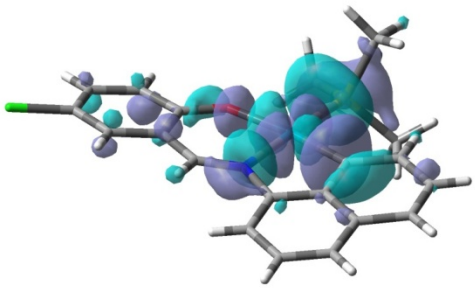
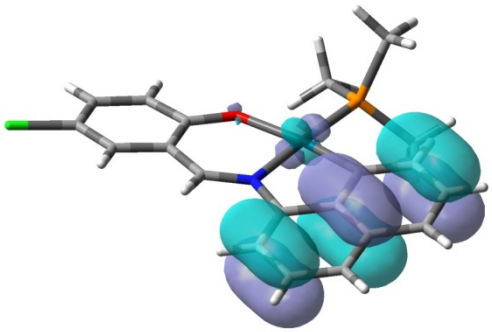
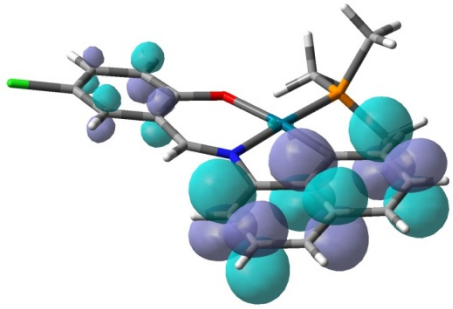



**Fig. S4** Contour plots of all molecular orbitals of [Pd($L^2$)($PMe_3$)] associated with the electronic spectral transitions (See Table S2).

| HOMO (H) | LUMO (L) |
|---|---|
|  |  |
| H-1 | L+1 |
|  |  |
| H-2 | L+2 |
|  |  |
| H-4 | L+3 |
|  |  |

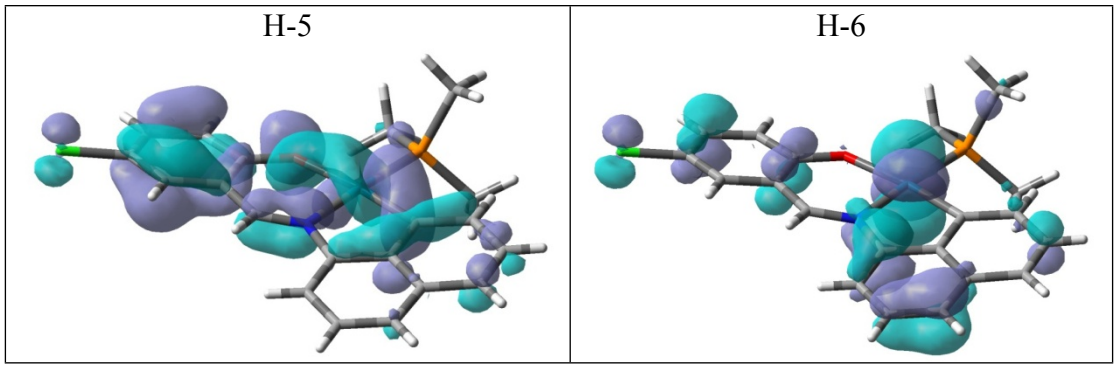
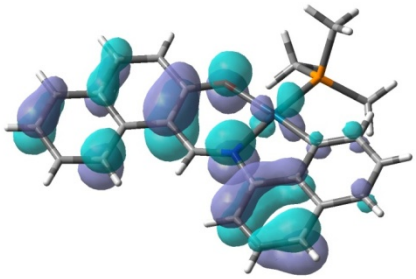
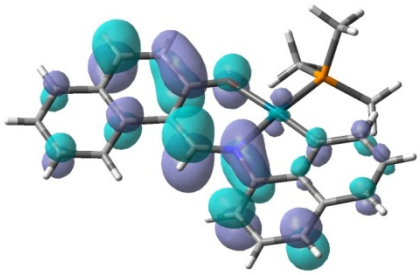
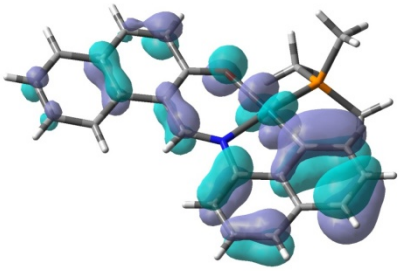
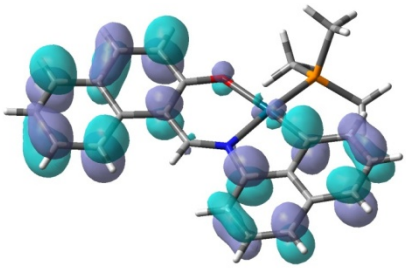
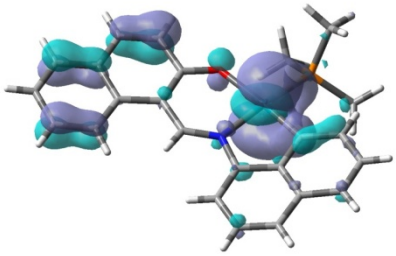
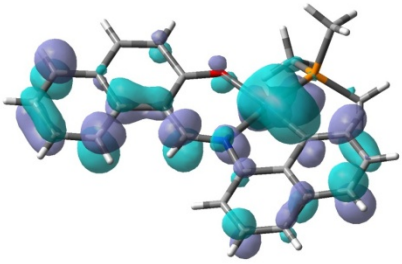
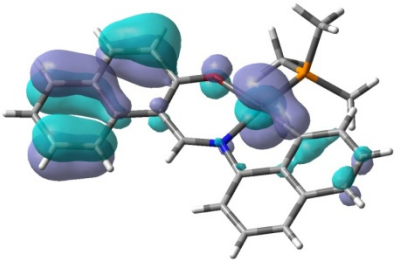
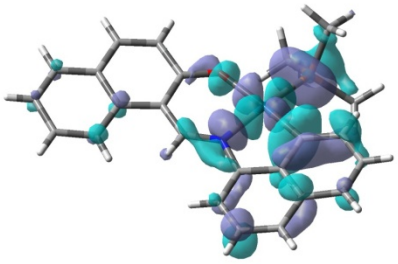
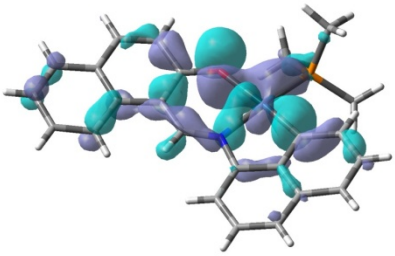
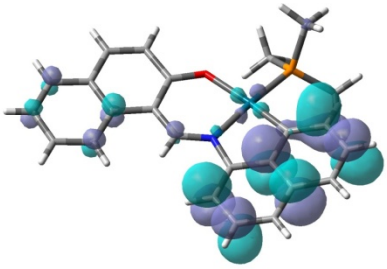



**Fig. S5** Contour plots of all molecular orbitals of [Pd($L^3$)($PMe_3$)] associated with the electronic spectral transitions (See Table S3).

| HOMO (H) | LUMO (L) |
|---|---|
|  |  |
| H-1 | L+1 |
|  |  |
| H-2 | L+2 |
|  |  |
| H-3 | L+3 |
|  |  |
| H-4 | L+4 |
|  |  |

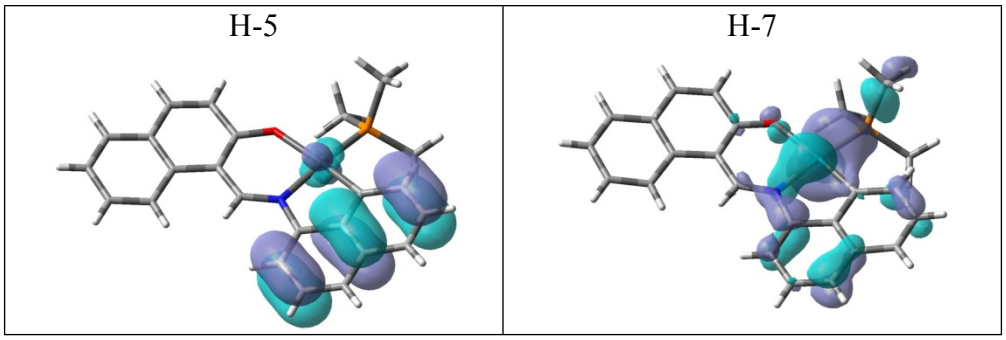
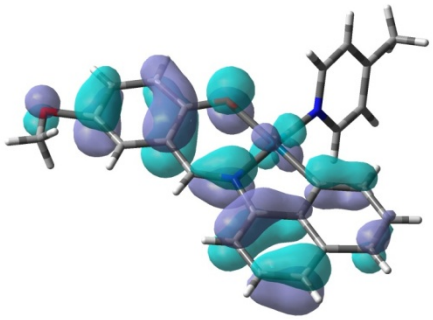
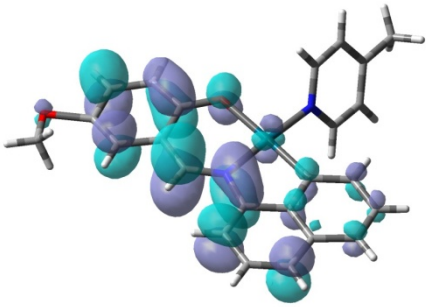
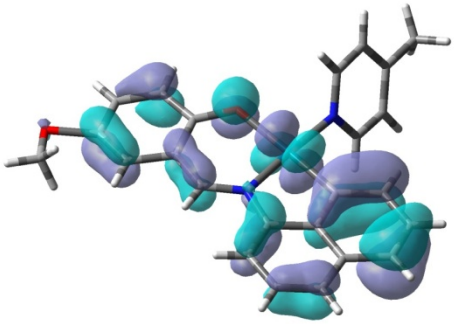
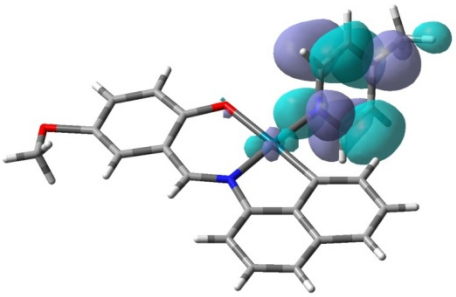
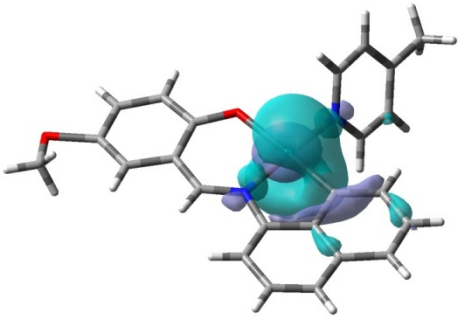
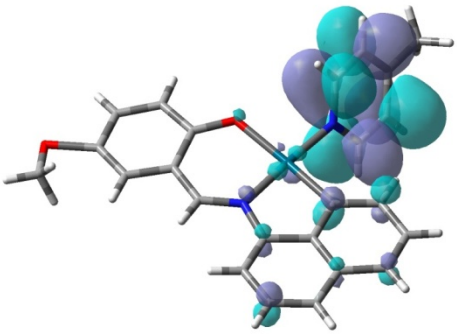
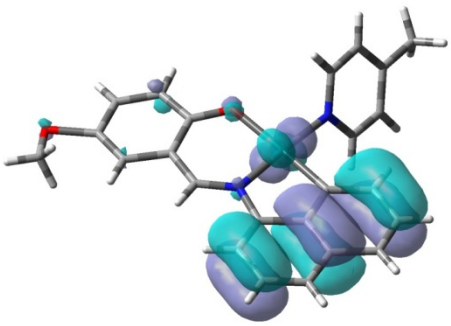
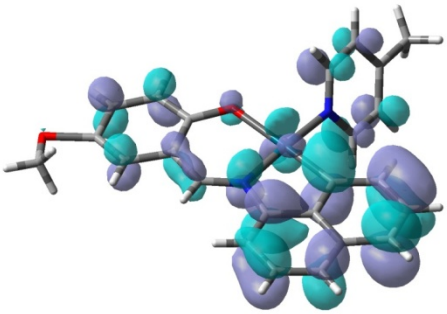



**Fig. S6** Contour plots of all molecular orbitals of [Pd($L^4$)($PMe_3$)] associated with the electronic spectral transitions (See Table S4).

| | |
|---|---|
| HOMO (H)  | LUMO (L)  |
| H-1  | L+1  |
| H-2  | L+2  |
| H-3  | L+3  |

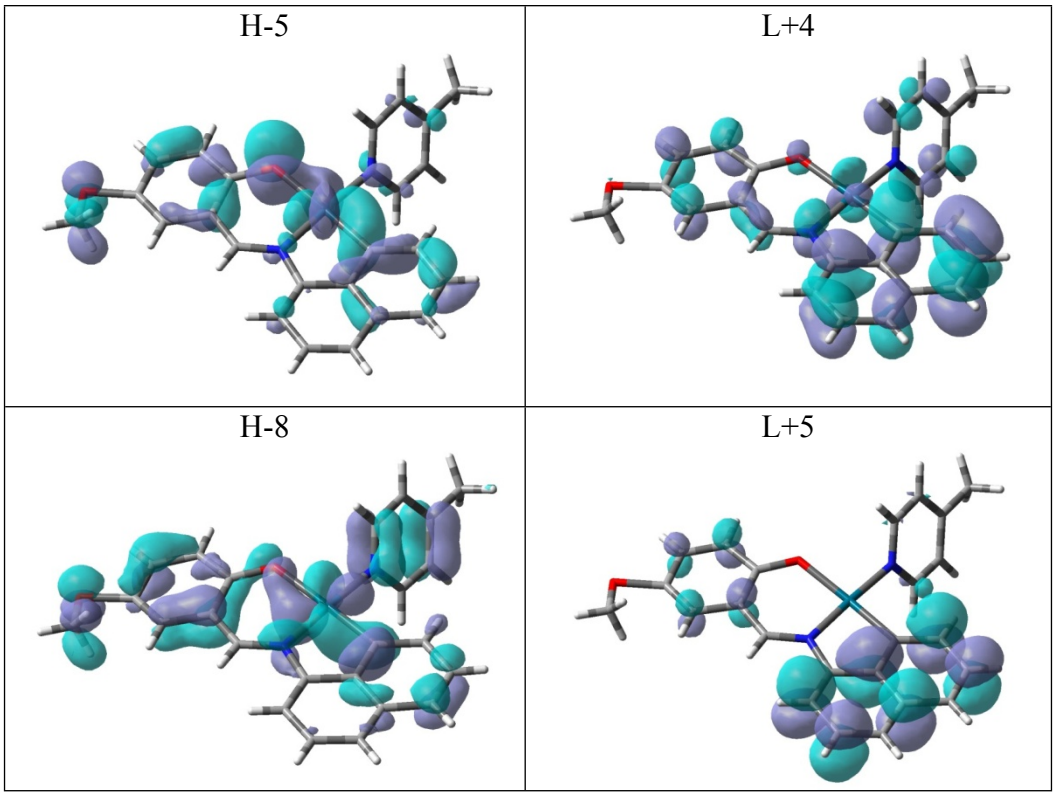



**Fig. S7** Contour plots of all molecular orbitals of [Pd($L^1$)(pic)] associated with the electronic spectral transitions (See Table S5).