**Electronic Supplementary Information for:**

# The Origin of *Exo*-Selectivity in Methyl Cyanoformate Addition onto the C=C Bond of Norbornene in Pd-Catalyzed Cyanoesterification

*Yasuhiro Okuda[1], Robert K. Szilagyi[2,3], Seiji Mori[3,]* Yasushi Nishihara[1,4]**

*[1]Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530, Japan*

*[2]Department of Chemistry and Biochemistry, Montana State University, Bozeman MT, 59717, U.S.A (current address: Department of Analytical Chemistry, University of Pannonia, Veszprem, 8200, Hungary)*

*[3]Faculty of Science, Ibaraki University, 2-1-1 Bunkyo, Mito 310-8512, Japan*

*[4]Japan Science and Technology Agency, ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

## **Corrections of translational entropy proposed by Whitesides** (Refs.10a and 10b)

Absolute values of experimental entropies in solution are larger than those by using Sacker-Tetrode equation, which is a conventional model for gas phase. Translational entropy in solution is proposed by Whitesides and his coworkers, as follows:

$$S_{\text{trans}}^{\text{corrected}} = R\ln\left[\left(\frac{10^{-15/2}V_{\text{free}}}{{N_A}^4[X]}\right)\left(\frac{2\pi MRTe^{5/3}}{h^2}\right)^{3/2}\right] = R\ln\left[\left(\frac{10^{-15/2}V_{\text{free}}}{{N_A}^4[X]}\right)\left(\frac{2\pi MRTe^{5/3}}{h^2}\right)^{3/2}\right] + R\ln V_{\text{free}}$$

$$= S_{\text{trans}} + R\ln V_{\text{free}}$$

$S_{\text{trans}}$ refers gas-phase translational entropy and is given by Sackur-Tetrode equation.
$e$: elementary electric charge, $1.60217657\times10^{-19}$ C
$h$: Planck's constant, $6.62606957\times10^{-34}$ m$^2$ kg s$^{-1}$
$R$: ideal gas constant, 8.3144621 J K$^{-1}$ mol$^{-1}$
$M$: molecular weight, g mol$^{-1}$
$N_A$: Avogadro's number, $6.0221413\times10^{-23}$ mol$^{-1}$
$V_{\text{free}}$, "free volume" is defined as "the volume occupied by the center of mass of one molecule of liquid moving randomly in a cage that is defined by its nearest neighbors" by a following equation

$$V_{\text{free}} = C_{\text{free}}\left\{\sqrt[3]{\left(\frac{10^{27}}{[X]N_A}\right)} - \sqrt[3]{V_{\text{mole}}}\right\}^3$$

Since density of toluene at 25 °C is 862.3 g dm$^{-3}$ from *CRC Handbook of Chemistry and Physics*, 91st Edition, Haynes, W. M. Ed. 2010, and $M$ for toluene is 92.14 g mol$^{-1}$, thus $[X]$ = 9.3585 (mol dm$^{-3}$). $V_{\text{mole}}$ = 144.5189 Å$^3$ by volume calculations by using Gaussian 09 program, $V_{\text{free}}$ is calculated as 0.4102 Å$^3$ when $C_{\text{free}}$ = 8. Then, $R\ln V_{\text{free}}$ for toluene is -50.464 J/mol K.

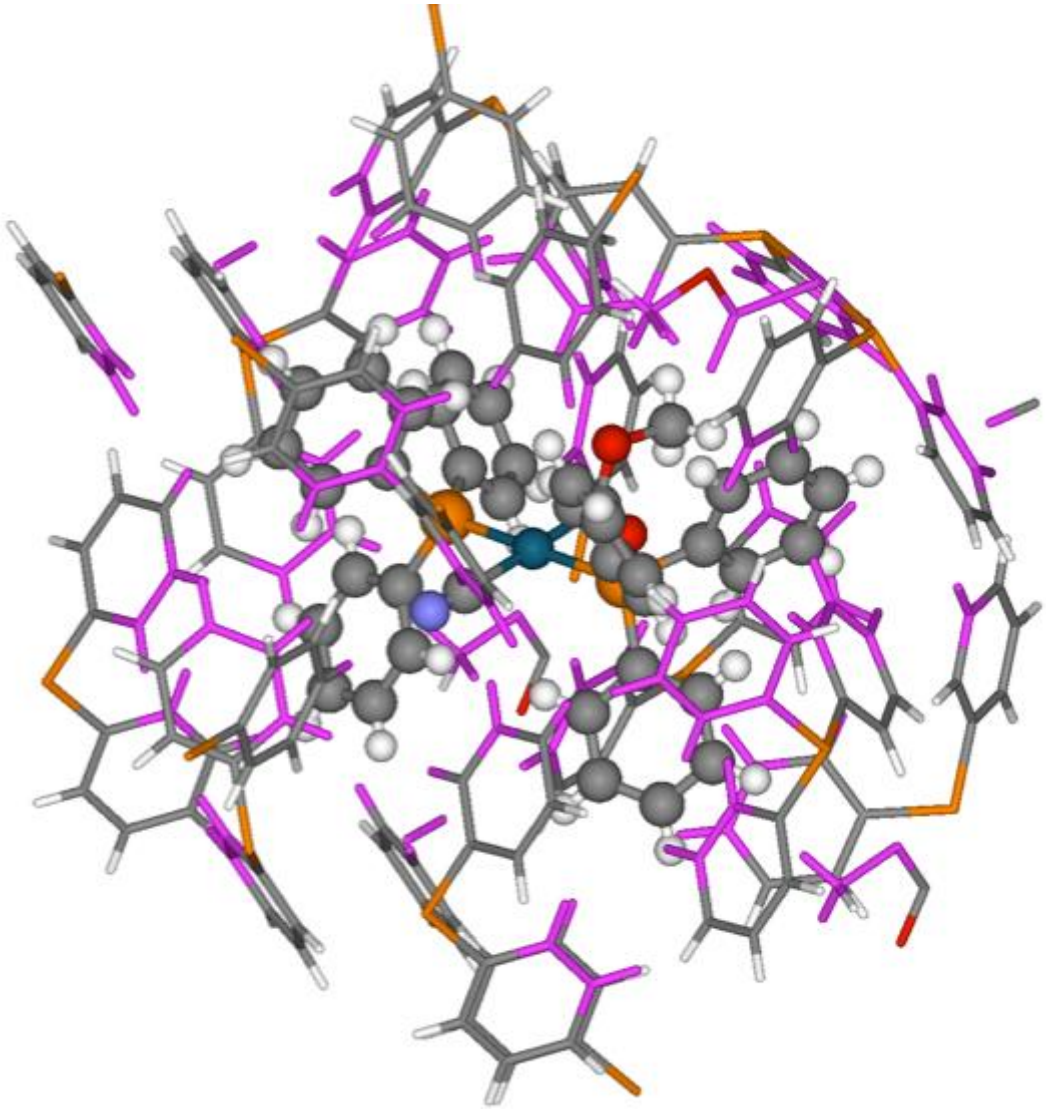


**Figure S1**: Network of crystal packing interactions of **2t2P** DAPRES (Ref. 3d) with 3.5 Å environment (see atomic positional coordinates on the next pages) around a central molecule (ball and stick presentation) highlighted with pink color

463
DAPRES 3x3x3
P 12.5766 26.9888 20.8284
C 12.0863 28.7238 20.5338
C 12.1001 29.6576 21.5783
C 11.7347 30.9711 21.3530
C 11.3821 31.3956 20.0890
C 11.4049 30.4927 19.0411
C 11.7453 29.1616 19.2571
H 12.3566 29.3794 22.4495
H 11.7350 31.5879 22.0763
H 11.1241 32.2985 19.9423
H 11.1822 30.7844 18.1641
H 11.7529 28.5434 18.5350
N 14.3426 46.6004 20.7337
C 14.4995 47.6422 20.8042
P 5.1443 38.6003 8.0568
C 6.0279 37.7032 9.3726
C 7.3766 37.4273 9.2964
C 8.0457 36.8245 10.3397
C 7.3637 36.5089 11.4928
C 6.0171 36.8015 11.5922
C 5.3530 37.3728 10.5234
H 7.8513 37.6654 8.5084
H 8.9713 36.6273 10.2611
H 7.8121 36.0723 12.2080
H 5.5606 36.6343 12.4079
H 4.4201 37.5469 10.5823
P 0.1506 38.6003 19.6108
C 0.6409 40.3353 19.9053
C 0.6271 41.2691 18.8608
C 0.9925 42.5826 19.0861
C 1.3451 43.0071 20.3501
C 1.3223 42.1042 21.3981
C 0.9819 40.7731 21.1820
C 0.9965 38.1849 18.0509
C 2.1851 38.8182 17.6881
C 2.7998 38.5307 16.4784
C 2.2382 37.6008 15.6280
C 1.0751 36.9415 15.9792
C 0.4513 37.2423 17.1878
C 1.0343 37.7032 20.9267
C 2.3830 37.4273 20.8504
C 3.0521 36.8245 21.8938
C 2.3700 36.5089 23.0469
C 1.0234 36.8015 23.1462
C 0.3593 37.3728 22.0775
H 0.3706 40.9909 17.9896
H 0.9922 43.1994 18.3628
H 1.6031 43.9100 20.4969
H 1.5450 42.3959 22.2750
H 0.9743 40.1549 21.9042
H 2.5756 39.4536 18.2773
H 3.6089 38.9682 16.2415
H 2.6486 37.4215 14.7903
H 0.7096 36.2790 15.4050
H -0.3574 36.8038 17.4293
H 2.8577 37.6654 20.0624
H 3.9777 36.6273 21.8152
H 2.8185 36.0723 23.7620
H 0.5670 36.6343 23.9619
H -0.5735 37.5469 22.1364
C 12.1468 36.6914 9.2987
C 12.3724 37.2002 10.5939
C 11.9913 36.4645 11.7019
C 11.4062 35.2239 11.5517
C 11.2095 34.7103 10.2739
C 11.5701 35.4506 9.1543
H 12.7843 38.0509 10.7002
H 12.1380 36.8154 12.5731
H 11.1255 34.7300 12.3131
H 10.8335 33.8452 10.1652
Pd 9.9596 38.1062 19.5527
P 12.2326 38.6003 19.6108
P 7.6741 37.7114 19.4323
O 9.6339 40.7886 18.5234
O 9.5149 40.6286 20.7164
N 10.4666 34.9889 19.7054
C 10.3097 36.0307 19.6349
C 9.6456 40.0968 19.5252
C 9.5024 42.1686 20.4518
C 12.7229 40.3353 19.9053
C 12.7091 41.2691 18.8608
C 13.0745 42.5826 19.0861
C 13.4271 43.0071 20.3501
C 13.4043 42.1042 21.3981
C 13.0639 40.7731 21.1820
C 13.0785 38.1849 18.0509
C 14.2671 38.8182 17.6881
C 14.8818 38.5307 16.4784
C 14.3202 37.6008 15.6280
C 13.1571 36.9415 15.9792
C 12.5333 37.2423 17.1878
C 13.1163 37.7032 20.9267
C 14.4650 37.4273 20.8504
C 15.1341 36.8245 21.8938
C 14.4520 36.5089 23.0469
C 13.1054 36.8015 23.1462
C 12.4413 37.3728 22.0775
C 6.5204 39.1310 19.4235
C 6.5888 40.0088 18.3455
C 5.6956 41.0548 18.2346
C 4.7320 41.2536 19.2005
C 4.6586 40.4090 20.2901
C 5.5544 39.3402 20.4091
C 7.1532 36.6914 20.8527
C 7.3787 37.2002 22.1479
C 6.9977 36.4645 23.2560
C 6.4126 35.2239 23.1058
C 6.2158 34.7103 21.8279
C 6.5764 35.4506 20.7083
C 7.1539 36.8066 17.9353
C 5.7941 36.7105 17.6292
C 5.3731 36.0509 16.4899
C 6.2982 35.4813 15.6326
C 7.6510 35.5637 15.9353
C 8.0745 36.2239 17.0746
H 10.3892 42.5074 20.4911
H 8.9736 42.5863 21.1219
H 9.1318 42.3518 19.5957
H 12.4526 40.9909 17.9896
H 13.0742 43.1994 18.3628
H 13.6851 43.9100 20.4969
H 13.6270 42.3959 22.2750
H 13.0563 40.1549 21.9042
H 14.6576 39.4536 18.2773
H 15.6910 38.9682 16.2415
H 14.7306 37.4215 14.7903
H 12.7916 36.2790 15.4050
H 11.7246 36.8038 17.4293
H 14.9397 37.6654 20.0624
H 16.0597 36.6273 21.8152
H 14.9005 36.0723 23.7620
H 12.6490 36.6343 23.9619
H 11.5085 37.5469 22.1364
H 7.2639 39.8785 17.6892
H 5.7341 41.6319 17.4801
H 4.1265 41.9825 19.1254
H 3.9966 40.5474 20.9579
H 5.5141 38.7476 21.1508
H 7.7907 38.0509 22.2542
H 7.1443 36.8154 24.1272
H 6.1318 34.7300 23.8672
H 5.8399 33.8452 21.7193
H 6.4257 35.1016 19.8383
H 5.1590 37.1150 18.2069
H 4.4447 35.9910 16.2981
H 6.0126 35.0273 14.8481
H 8.2893 35.1666 15.3530
H 9.0013 36.2836 17.2698
P 7.2390 38.6003 31.1648
C 8.0849 38.1849 29.6049
C 9.2735 38.8182 29.2421
C 9.8881 38.5307 28.0324
C 9.3266 37.6008 27.1820
C 8.1635 36.9415 27.5333
C 7.5397 37.2423 28.7418
H 9.6640 39.4536 29.8314
H 10.6973 38.9682 27.7956
H 9.7369 37.4215 26.3444
H 7.7979 36.2790 26.9591
H 6.7309 36.8038 28.9833
P 19.7561 37.7114 19.4323
C 18.6024 39.1310 19.4235
C 18.6708 40.0088 18.3455
C 17.7776 41.0548 18.2346
C 16.8140 41.2536 19.2005
C 16.7406 40.4090 20.2901
C 17.6364 39.3402 20.4091
C 19.2352 36.6914 20.8527
C 19.4607 37.2002 22.1479
C 19.0797 36.4645 23.2560
C 18.4946 35.2239 23.1058
C 18.2978 34.7103 21.8279
C 18.6584 35.4506 20.7083
C 19.2359 36.8066 17.9353
C 17.8761 36.7105 17.6292
C 17.4551 36.0509 16.4899
C 18.3802 35.4813 15.6326
C 19.7330 35.5637 15.9353
C 20.1565 36.2239 17.0746
H 19.3459 39.8785 17.6892
H 17.8161 41.6319 17.4801
H 16.2085 41.9825 19.1254
H 16.0786 40.5474 20.9579
H 17.5961 38.7476 21.1508
H 19.8727 38.0509 22.2542
H 19.2263 36.8154 24.1272
H 18.2138 34.7300 23.8672
H 17.9219 33.8452 21.7193
H 18.5077 35.1016 19.8383
H 17.2410 37.1150 18.2069
H 16.5267 35.9910 16.2981
H 18.0946 35.0273 14.8481
H 20.3713 35.1666 15.3530
H 21.0833 36.2836 17.2698
P 14.7624 37.7114 30.9863
C 14.2423 36.8066 29.4894
C 12.8825 36.7105 29.1832
C 12.4614 36.0509 28.0440
C 13.3865 35.4813 27.1867
C 14.7394 35.5637 27.4894
C 15.1628 36.2239 28.6286
H 12.2474 37.1150 29.7609
H 11.5331 35.9910 27.8522
H 13.1010 35.0273 26.4021
H 15.3777 35.1666 26.9071
H 16.0897 36.2836 28.8239
P 8.6885 42.6802 13.8338
P 4.1299 43.5691 13.6553
O 6.0897 40.4919 12.7464
O 5.9707 40.6519 14.9394
C 6.1014 41.1837 13.7482
C 5.9582 39.1119 14.6748
C 9.1787 40.9452 14.1283
C 9.1650 40.0114 13.0838
C 9.5303 38.6979 13.3091
C 9.8829 38.2734 14.5731
C 9.8601 39.1763 15.6211
C 9.5198 40.5074 15.4050
C 9.5721 43.5773 15.1497
C 10.9208 43.8532 15.0734
C 11.5899 44.4560 16.1167
C 10.9079 44.7716 17.2698
C 9.5613 44.4790 17.3692
C 8.8971 43.9077 16.3004
C 3.6090 44.5891 15.0757
C 3.8345 44.0803 16.3709
C 3.4535 44.8160 17.4790
C 2.8684 46.0565 17.3288
C 2.6716 46.5702 16.0509
C 3.0323 45.8299 14.9313
H 6.8450 38.7731 14.7141
H 5.4294 38.6942 15.3449

| | | | |
|---|---|---|---|
| H | 5.5876 | 38.9287 | 13.8186 |
| H | 8.9084 | 40.2896 | 12.2126 |
| H | 9.5300 | 38.0811 | 12.5858 |
| H | 10.1409 | 37.3705 | 14.7199 |
| H | 10.0828 | 38.8846 | 16.4980 |
| H | 9.5121 | 41.1256 | 16.1271 |
| H | 11.3955 | 43.6151 | 14.2854 |
| H | 12.5155 | 44.6532 | 16.0382 |
| H | 11.3563 | 45.2082 | 17.9850 |
| H | 9.1048 | 44.6462 | 18.1849 |
| H | 7.9643 | 43.7336 | 16.3594 |
| H | 4.2465 | 43.2296 | 16.4772 |
| H | 3.6001 | 44.4651 | 18.3501 |
| H | 2.5877 | 46.5505 | 18.0902 |
| H | 2.2957 | 47.4353 | 15.9423 |
| H | 2.8815 | 46.1789 | 14.0613 |
| P | 3.6948 | 42.6802 | 25.3878 |
| C | 4.1850 | 40.9452 | 25.6823 |
| C | 4.1713 | 40.0114 | 24.6378 |
| C | 4.5367 | 38.6979 | 24.8631 |
| C | 4.8893 | 38.2734 | 26.1272 |
| C | 4.8665 | 39.1763 | 27.1751 |
| C | 4.5261 | 40.5074 | 26.9591 |
| C | 4.5407 | 43.0956 | 23.8279 |
| C | 5.7293 | 42.4623 | 23.4651 |
| C | 6.3440 | 42.7498 | 22.2554 |
| C | 5.7824 | 43.6797 | 21.4050 |
| C | 4.6193 | 44.3390 | 21.7563 |
| C | 3.9955 | 44.0382 | 22.9648 |
| H | 3.9147 | 40.2896 | 23.7667 |
| H | 4.5363 | 38.0811 | 24.1399 |
| H | 5.1472 | 37.3705 | 26.2739 |
| H | 5.0891 | 38.8846 | 28.0521 |
| H | 4.5185 | 41.1256 | 27.6812 |
| H | 6.1198 | 41.8269 | 24.0544 |
| H | 7.1531 | 42.3123 | 22.0185 |
| H | 6.1927 | 43.8590 | 20.5674 |
| H | 4.2537 | 45.0015 | 21.1820 |
| H | 3.1867 | 44.4767 | 23.2063 |
| P | 16.2119 | 43.5691 | 13.6553 |
| O | 18.1717 | 40.4919 | 12.7464 |
| O | 18.0527 | 40.6519 | 14.9394 |
| C | 18.1834 | 41.1837 | 13.7482 |
| C | 18.0402 | 39.1119 | 14.6748 |
| C | 15.0582 | 42.1495 | 13.6465 |
| C | 15.1266 | 41.2717 | 12.5685 |
| C | 14.2334 | 40.2257 | 12.4576 |
| C | 13.2698 | 40.0269 | 13.4235 |
| C | 13.1964 | 40.8716 | 14.5130 |
| C | 14.0922 | 41.9403 | 14.6320 |
| C | 15.6910 | 44.5891 | 15.0757 |
| C | 15.9165 | 44.0803 | 16.3709 |
| C | 15.5355 | 44.8160 | 17.4790 |
| C | 14.9504 | 46.0565 | 17.3288 |
| C | 14.7536 | 46.5702 | 16.0509 |
| C | 15.1143 | 45.8299 | 14.9313 |
| H | 18.9270 | 38.7731 | 14.7141 |
| H | 17.5114 | 38.6942 | 15.3449 |
| H | 17.6696 | 38.9287 | 13.8186 |
| H | 15.8017 | 41.4020 | 11.9122 |
| H | 14.2719 | 39.6486 | 11.7031 |
| H | 12.6643 | 39.2980 | 13.3484 |
| H | 12.5344 | 40.7331 | 15.1809 |
| H | 14.0519 | 42.5329 | 15.3738 |
| H | 16.3285 | 43.2296 | 16.4772 |
| H | 15.6821 | 44.4651 | 18.3501 |
| H | 14.6697 | 46.5505 | 18.0902 |
| H | 14.3777 | 47.4353 | 15.9423 |
| H | 14.9635 | 46.1789 | 14.0613 |
| Pd | 13.5038 | 43.1743 | 25.3297 |
| P | 15.7768 | 42.6802 | 25.3878 |
| P | 11.2182 | 43.5691 | 25.2093 |
| O | 13.1781 | 40.4919 | 24.3005 |
| O | 13.0591 | 40.6519 | 26.4934 |
| C | 13.1897 | 41.1837 | 25.3022 |
| C | 13.0466 | 39.1119 | 26.2288 |
| C | 16.2670 | 40.9452 | 25.6823 |
| C | 16.2533 | 40.0114 | 24.6378 |
| C | 16.6187 | 38.6979 | 24.8631 |
| C | 16.9713 | 38.2734 | 26.1272 |
| C | 16.9485 | 39.1763 | 27.1751 |
| C | 16.6081 | 40.5074 | 26.9591 |
| C | 16.6227 | 43.0956 | 23.8279 |
| C | 17.8113 | 42.4623 | 23.4651 |
| C | 18.4260 | 42.7498 | 22.2554 |
| C | 17.8644 | 43.6797 | 21.4050 |
| C | 16.7013 | 44.3390 | 21.7563 |
| C | 16.0775 | 44.0382 | 22.9648 |
| C | 10.0646 | 42.1495 | 25.2005 |
| C | 10.1330 | 41.2717 | 24.1225 |
| C | 9.2397 | 40.2257 | 24.0116 |
| C | 8.2761 | 40.0269 | 24.9775 |
| C | 8.2027 | 40.8716 | 26.0671 |
| C | 9.0985 | 41.9403 | 26.1861 |
| C | 10.6981 | 44.4739 | 23.7124 |
| C | 9.3383 | 44.5700 | 23.4062 |
| C | 8.9173 | 45.2296 | 22.2670 |
| C | 9.8424 | 45.7992 | 21.4096 |
| C | 11.1952 | 45.7168 | 21.7124 |
| C | 11.6186 | 45.0566 | 22.8516 |
| H | 13.9333 | 38.7731 | 26.2681 |
| H | 12.5177 | 38.6942 | 26.8990 |
| H | 12.6760 | 38.9287 | 25.3727 |
| H | 15.9967 | 40.2896 | 23.7667 |
| H | 16.6183 | 38.0811 | 24.1399 |
| H | 17.2292 | 37.3705 | 26.2739 |
| H | 17.1711 | 38.8846 | 28.0521 |
| H | 16.6005 | 41.1256 | 27.6812 |
| H | 18.2018 | 41.8269 | 24.0544 |
| H | 19.2351 | 42.3123 | 22.0185 |
| H | 18.2747 | 43.8590 | 20.5674 |
| H | 16.3357 | 45.0015 | 21.1820 |
| H | 15.2687 | 44.4767 | 23.2063 |
| H | 10.8081 | 41.4020 | 23.4663 |
| H | 9.2783 | 39.6486 | 23.2571 |
| H | 7.6707 | 39.2980 | 24.9024 |
| H | 7.5408 | 40.7331 | 26.7349 |
| H | 9.0582 | 42.5329 | 26.9279 |
| H | 8.7032 | 44.1655 | 23.9839 |
| H | 7.9889 | 45.2895 | 22.0752 |
| H | 9.5568 | 46.2533 | 20.6251 |
| H | 11.8335 | 46.1139 | 21.1300 |
| H | 12.5455 | 44.9969 | 23.0469 |
| P | 1.5090 | 31.9576 | 15.2298 |
| C | 2.0299 | 32.9776 | 13.8094 |
| C | 1.8043 | 32.4688 | 12.5142 |
| C | 2.1854 | 33.2045 | 11.4062 |
| C | 2.7704 | 34.4450 | 11.5564 |
| C | 2.9672 | 34.9587 | 12.8342 |
| C | 2.6066 | 34.2184 | 13.9538 |
| C | 2.0291 | 32.8624 | 16.7268 |
| C | 3.3889 | 32.9585 | 17.0330 |
| C | 3.8099 | 33.6181 | 18.1722 |
| C | 2.8848 | 34.1877 | 19.0295 |
| C | 1.5320 | 34.1053 | 18.7268 |
| C | 1.1086 | 33.4451 | 17.5876 |
| H | 1.3924 | 31.6181 | 12.4079 |
| H | 2.0387 | 32.8536 | 10.5350 |
| H | 3.0512 | 34.9390 | 10.7949 |
| H | 3.3432 | 35.8238 | 12.9428 |
| H | 2.7573 | 34.5674 | 14.8238 |
| H | 4.0240 | 32.5540 | 16.4553 |
| H | 4.7383 | 33.6780 | 18.3640 |
| H | 3.1704 | 34.6418 | 19.8140 |
| H | 0.8937 | 34.5024 | 19.3091 |
| H | 0.1817 | 33.3854 | 17.3923 |
| P | 9.0324 | 31.0687 | 15.0513 |
| P | 13.5910 | 31.9576 | 15.2298 |
| N | 10.7985 | 34.6801 | 14.9567 |
| C | 10.9553 | 33.6383 | 15.0272 |
| C | 8.1865 | 31.4841 | 16.6112 |
| C | 6.9979 | 30.8508 | 16.9740 |
| C | 6.3832 | 31.1383 | 18.1838 |
| C | 6.9448 | 32.0682 | 19.0341 |
| C | 8.1079 | 32.7275 | 18.6829 |
| C | 8.7317 | 32.4267 | 17.4743 |
| C | 8.1487 | 31.9658 | 13.7354 |
| C | 6.8000 | 32.2417 | 13.8117 |
| C | 6.1310 | 32.8445 | 12.7684 |
| C | 6.8130 | 33.1601 | 11.6153 |
| C | 8.1596 | 32.8675 | 11.5159 |
| C | 8.8237 | 32.2962 | 12.5847 |
| C | 14.1119 | 32.9776 | 13.8094 |
| C | 13.8863 | 32.4688 | 12.5142 |
| C | 14.2674 | 33.2045 | 11.4062 |
| C | 14.8524 | 34.4450 | 11.5564 |
| C | 15.0492 | 34.9587 | 12.8342 |
| C | 14.6886 | 34.2184 | 13.9538 |
| C | 14.1111 | 32.8624 | 16.7268 |
| C | 15.4709 | 32.9585 | 17.0330 |
| C | 15.8919 | 33.6181 | 18.1722 |
| C | 14.9668 | 34.1877 | 19.0295 |
| C | 13.6140 | 34.1053 | 18.7268 |
| C | 13.1906 | 33.4451 | 17.5876 |
| H | 6.6074 | 30.2154 | 16.3848 |
| H | 5.5741 | 30.7008 | 18.4206 |
| H | 6.5344 | 32.2475 | 19.8718 |
| H | 8.4735 | 33.3900 | 19.2571 |
| H | 9.5405 | 32.8652 | 17.2329 |
| H | 6.3254 | 32.0036 | 14.5997 |
| H | 5.2054 | 33.0417 | 12.8469 |
| H | 6.3646 | 33.5967 | 10.9001 |
| H | 8.6160 | 33.0347 | 10.7002 |
| H | 9.7565 | 32.1221 | 12.5257 |
| H | 13.4744 | 31.6181 | 12.4079 |
| H | 15.1332 | 34.9390 | 10.7949 |
| H | 15.4252 | 35.8238 | 12.9428 |
| H | 14.8393 | 34.5674 | 14.8238 |
| H | 16.1060 | 32.5540 | 16.4553 |
| H | 16.8203 | 33.6780 | 18.3640 |
| H | 15.2524 | 34.6418 | 19.8140 |
| H | 12.9757 | 34.5024 | 19.3091 |
| H | 12.2637 | 33.3854 | 17.3923 |
| P | 4.0387 | 31.0687 | 26.6054 |
| P | 8.5973 | 31.9576 | 26.7839 |
| N | 5.8048 | 34.6801 | 26.5108 |
| C | 5.9616 | 33.6383 | 26.5812 |
| C | 3.1551 | 31.9658 | 25.2895 |
| C | 1.8064 | 32.2417 | 25.3657 |
| C | 1.1373 | 32.8445 | 24.3224 |
| C | 1.8193 | 33.1601 | 23.1693 |
| C | 3.1659 | 32.8675 | 23.0700 |
| C | 3.8301 | 32.2962 | 24.1387 |
| C | 9.1182 | 32.9776 | 25.3634 |
| C | 8.8927 | 32.4688 | 24.0682 |
| C | 9.2737 | 33.2045 | 22.9602 |
| C | 9.8588 | 34.4450 | 23.1104 |
| C | 10.0556 | 34.9587 | 24.3883 |
| C | 9.6949 | 34.2184 | 25.5079 |
| H | 1.3317 | 32.0036 | 26.1537 |
| H | 0.2117 | 33.0417 | 24.4010 |
| H | 1.3709 | 33.5967 | 22.4541 |
| H | 3.6224 | 33.0347 | 22.2542 |
| H | 4.7629 | 32.1221 | 24.0798 |
| H | 8.4807 | 31.6181 | 23.9619 |
| H | 9.1271 | 32.8536 | 22.0890 |
| H | 10.1395 | 34.9390 | 22.3490 |
| H | 10.4315 | 35.8238 | 24.4969 |
| H | 9.8457 | 34.5674 | 26.3779 |
| P | 16.1207 | 31.0687 | 26.6054 |
| C | 15.2371 | 31.9658 | 25.2895 |
| C | 13.8884 | 32.2417 | 25.3657 |
| C | 13.2193 | 32.8445 | 24.3224 |
| C | 13.9013 | 33.1601 | 23.1693 |
| C | 15.2479 | 32.8675 | 23.0700 |
| C | 15.9121 | 32.2962 | 24.1387 |
| H | 13.4137 | 32.0036 | 26.1537 |
| H | 12.2937 | 33.0417 | 24.4010 |
| H | 13.4529 | 33.5967 | 22.4541 |
| H | 15.7044 | 33.0347 | 22.2542 |
| H | 16.8449 | 32.1221 | 24.0798 |

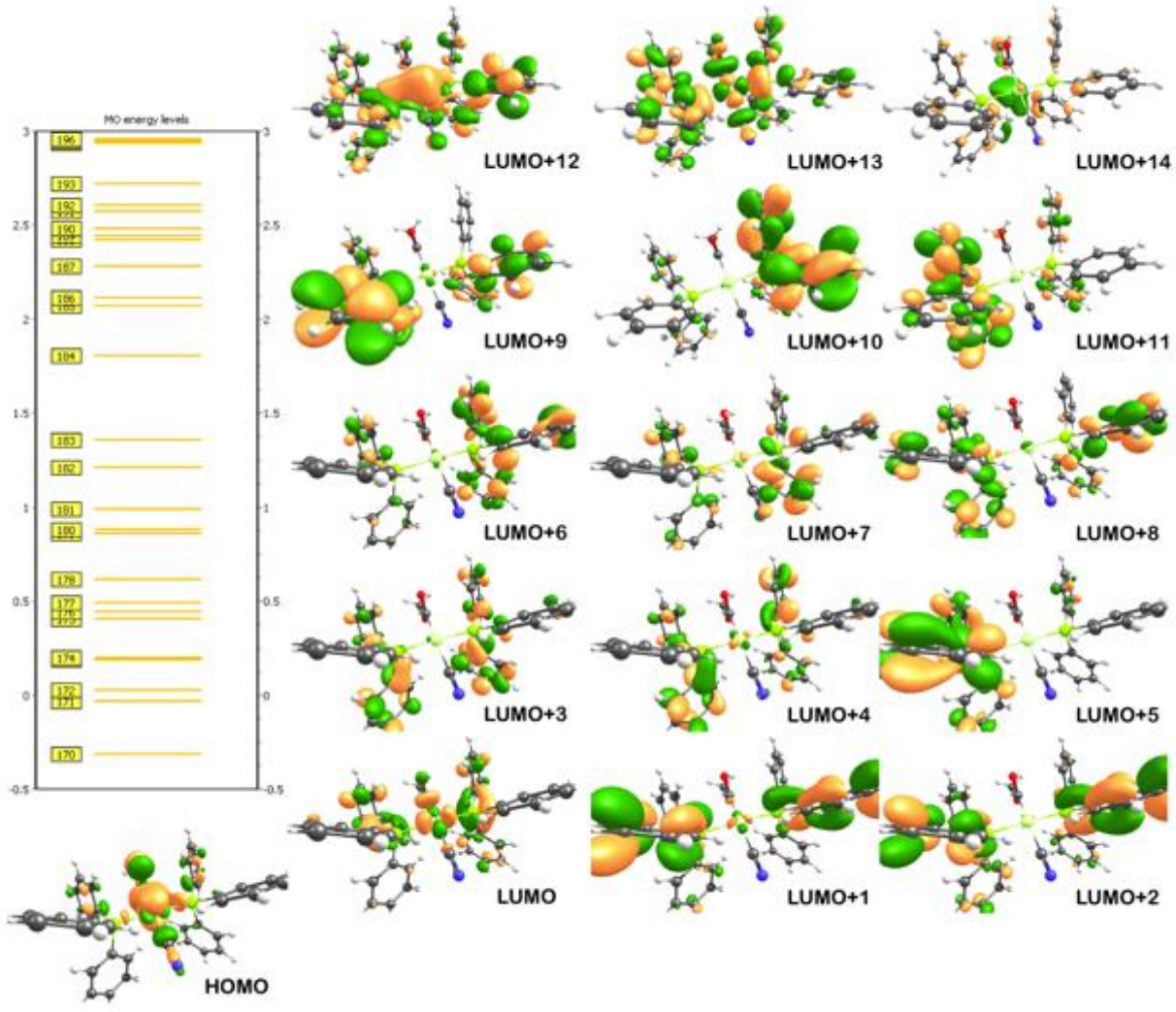



**Figure S2**: Molecular orbital analysis of complex **2t2P** from BHandHLYP/def2TZVP/PCM(toluene) calculation

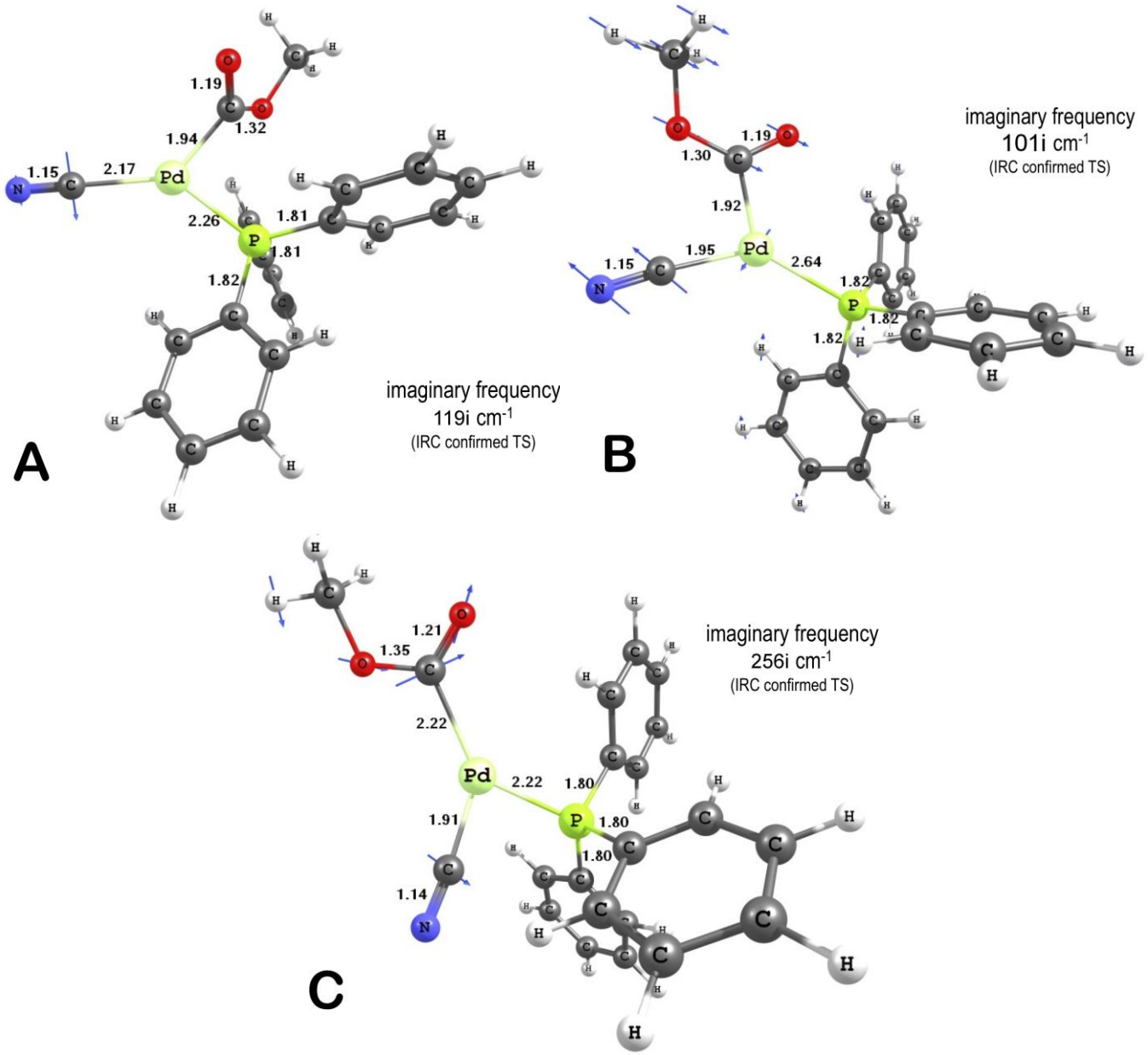



**Figure S3**: Scaled displacement vectors of normal mode displacements with imaginary frequencies for isomerization transition states **trans-cisNP** (A), **cisOP-cisNP** (B), **trans-cisOP** (C) (see atomic coordinates on following pages)

## trans-cisNP

```
44
2cNP_TS, electronic energy = -1485.20882949 a.u.
C       1.914601862     1.660434345     0.372539000
O       2.485341896     2.076664155     1.327665052
O       2.496944827     1.174737311    -0.704778017
C       3.929895827     1.161888121    -0.705244983
H       4.213824793     0.739413104    -1.655583000
H       4.311000965     2.167945052    -0.605786948
H       4.293163724     0.550154035     0.108270000
Pd     -0.002345207     1.924760879     0.317248983
P      -0.184629879    -0.308191138    -0.003806017
C      -1.759794931    -0.769974069     0.771923983
C      -2.908379914    -0.088328104     0.382547896
C      -1.855524965    -1.754924983     1.742985069
C      -4.125669931    -0.390939017     0.951559931
H      -2.856031914     0.683207776    -0.364340242
C      -3.078535983    -2.054604931     2.311877052
H      -0.983228965    -2.293783965     2.059465121
C      -4.212791965    -1.374711931     1.918968000
H      -5.003709914     0.146602983     0.644454862
H      -3.140493000    -2.820553879     3.063146104
H      -5.162219965    -1.606844879     2.365907000
C      -0.378455931    -0.758159086    -1.748872017
C      -1.129212965    -1.871042069    -2.107513035
C       0.213682035     0.008901948    -2.740990000
C      -1.272592017    -2.215945017    -3.434904035
H      -1.611549948    -2.464840086    -1.353085035
C       0.067280000    -0.339158017    -4.069075017
H       0.785244069     0.877794931    -2.477661000
C      -0.673274035    -1.450729983    -4.417222017
H      -1.858129035    -3.076677000    -3.701536052
H       0.525084983     0.265267000    -4.830434000
H      -0.791536069    -1.716129948    -5.452037035
C       1.060320086    -1.418383121     0.704621000
C       1.523207086    -1.160439069     1.988950983
C       1.555089069    -2.513599138     0.014412017
C       2.450797069    -1.993745052     2.576764017
H       1.165496086    -0.303108035     2.530089948
C       2.490900052    -3.342374121     0.603041052
H       1.220161052    -2.722785155    -0.983543965
```

| | | | |
|---|---|---|---|
| C | 2.936378052 | -3.086842086 | 1.883822052 |
| H | 2.800103069 | -1.784054035 | 3.570978000 |
| H | 2.870562052 | -4.186629138 | 0.057161069 |
| H | 3.664387052 | -3.732671086 | 2.339938069 |
| C | -1.313600016 | 3.650786794 | 0.271234121 |
| N | -2.004143603 | 4.565956345 | 0.219513052 |

## cisOP-cisNP

44
2cNPiso_TS, electronic energy = -1485.17323031 a.u.

| | | | |
|---|---|---|---|
| C | -3.479618275 | -0.354092257 | 0.034484303 |
| O | -3.849687660 | 0.669276688 | 0.559601027 |
| O | -4.407375431 | -1.214686642 | -0.447423395 |
| C | -5.773589156 | -0.862581816 | -0.286413697 |
| H | -6.344683312 | -1.675056541 | -0.711454605 |
| H | -6.023407367 | -0.741669633 | 0.760024000 |
| H | -6.001029000 | 0.060666275 | -0.804308092 |
| Pd | -1.338070000 | -0.921402147 | -0.148842605 |
| P | 0.650700670 | 0.049012514 | 0.005332303 |
| C | 0.198290395 | 1.752571514 | -0.374586000 |
| C | -0.914310908 | 2.309788211 | 0.249477697 |
| C | 0.910978303 | 2.502959908 | -1.301519395 |
| C | -1.295188000 | 3.601949211 | -0.044046000 |
| H | -1.503626119 | 1.744100000 | 0.948410578 |
| C | 0.527782303 | 3.797285908 | -1.583492000 |
| H | 1.763489303 | 2.082619605 | -1.799710092 |
| C | -0.573655697 | 4.347000908 | -0.955981303 |
| H | -2.161767303 | 4.018316514 | 0.434621395 |
| H | 1.087451303 | 4.374036605 | -2.296671303 |
| H | -0.873483697 | 5.353776908 | -1.183312605 |
| C | 1.309407184 | 0.012171000 | 1.683860000 |
| C | 1.651687092 | 1.190983000 | 2.332228697 |
| C | 1.504926395 | -1.204937000 | 2.326231000 |
| C | 2.184582000 | 1.151791000 | 3.605161395 |
| H | 1.504522486 | 2.139089000 | 1.851492000 |
| C | 2.040804000 | -1.236047000 | 3.595424697 |
| H | 1.239516395 | -2.124369303 | 1.839722303 |
| C | 2.379217000 | -0.059409000 | 4.237016395 |
| H | 2.444207000 | 2.069204000 | 4.100522092 |
| H | 2.186905303 | -2.180871000 | 4.085464395 |
| H | 2.790061605 | -0.087817000 | 5.229744395 |
| C | 1.965147578 | -0.420810000 | -1.130413000 |
| C | 1.640023789 | -0.827220000 | -2.417047303 |
| C | 3.295615578 | -0.342785000 | -0.749951395 |
| C | 2.636568395 | -1.141910697 | -3.314324697 |
| H | 0.610689092 | -0.911424000 | -2.714689908 |
| C | 4.290992184 | -0.663655697 | -1.651782092 |
| H | 3.559828275 | -0.040904000 | 0.246047605 |
| C | 3.962769092 | -1.060908697 | -2.931879092 |
| H | 2.378560697 | -1.462147697 | -4.306757000 |
| H | 5.320558184 | -0.608009395 | -1.349704486 |
| H | 4.738652697 | -1.316256395 | -3.630319789 |
| C | -0.269900404 | -2.508897578 | -0.201601605 |
| N | 0.282226330 | -3.511467514 | -0.222120303 |

## trans-cisOP

```
44
2cOP_TS, electronic energy = -1485.20838409 a.u.
C       3.355638173    -0.562963636     0.044325921
O       2.983084332    -1.697561636     0.044540841
O       4.584756332    -0.149831636     0.044903000
C       5.601849332    -1.161247556     0.044656921
H       6.536447332    -0.625192477     0.047213921
H       5.510853411    -1.776991636     0.928048921
H       5.513863411    -1.773265556    -0.841656079
Pd      1.806729762     0.566918907     0.043058079
P      -0.768443603    -0.015704271     0.005052000
C      -1.781434285     1.433424206    -0.417717841
C      -1.274086206     2.332012206    -1.347003841
C      -3.022694285     1.679353364     0.149525159
C      -2.000879047     3.444890285    -1.715455762
H      -0.302817206     2.167078047    -1.779723841
C      -3.745964126     2.798415444    -0.213978841
H      -3.425742444     1.003350444     0.880461079
C      -3.238393047     3.679966444    -1.147825841
H      -1.594839967     4.133374285    -2.433623762
H      -4.704912126     2.981721523     0.235593159
H      -3.800852967     4.552597523    -1.426070841
C      -1.210025000    -1.286988874    -1.217300079
C      -2.351150079    -1.217096636    -2.002053000
C      -0.352195000    -2.369602794    -1.366565397
C      -2.634620238    -2.217048397    -2.912077159
H      -3.019190000    -0.380982556    -1.910961682
C      -0.642323159    -3.371542636    -2.269389556
H       0.549585079    -2.428641874    -0.782655556
C      -1.783874238    -3.296345397    -3.044391397
H      -3.520256238    -2.150083238    -3.517476079
H       0.028564762    -4.204528636    -2.374502794
H      -2.005314397    -4.072690238    -3.754073556
C      -1.435519841    -0.617483794     1.585466079
C      -0.971180841    -0.026795556     2.753763921
C      -2.375349079    -1.632985556     1.672972159
C      -1.450498000    -0.430242159     3.982307000
H      -0.229796603     0.751434206     2.705178841
C      -2.847836238    -2.042980159     2.904865238
H      -2.738336079    -2.111320636     0.782447238
C      -2.389685238    -1.441201921     4.059592159
H      -1.084159000     0.037401000     4.877867921
H      -3.573658397    -2.833848921     2.959828397
H      -2.757504397    -1.762327603     5.017133159
C       2.906443463     2.178964000     0.031828921
N       3.479293622     3.170617921     0.023100921
```

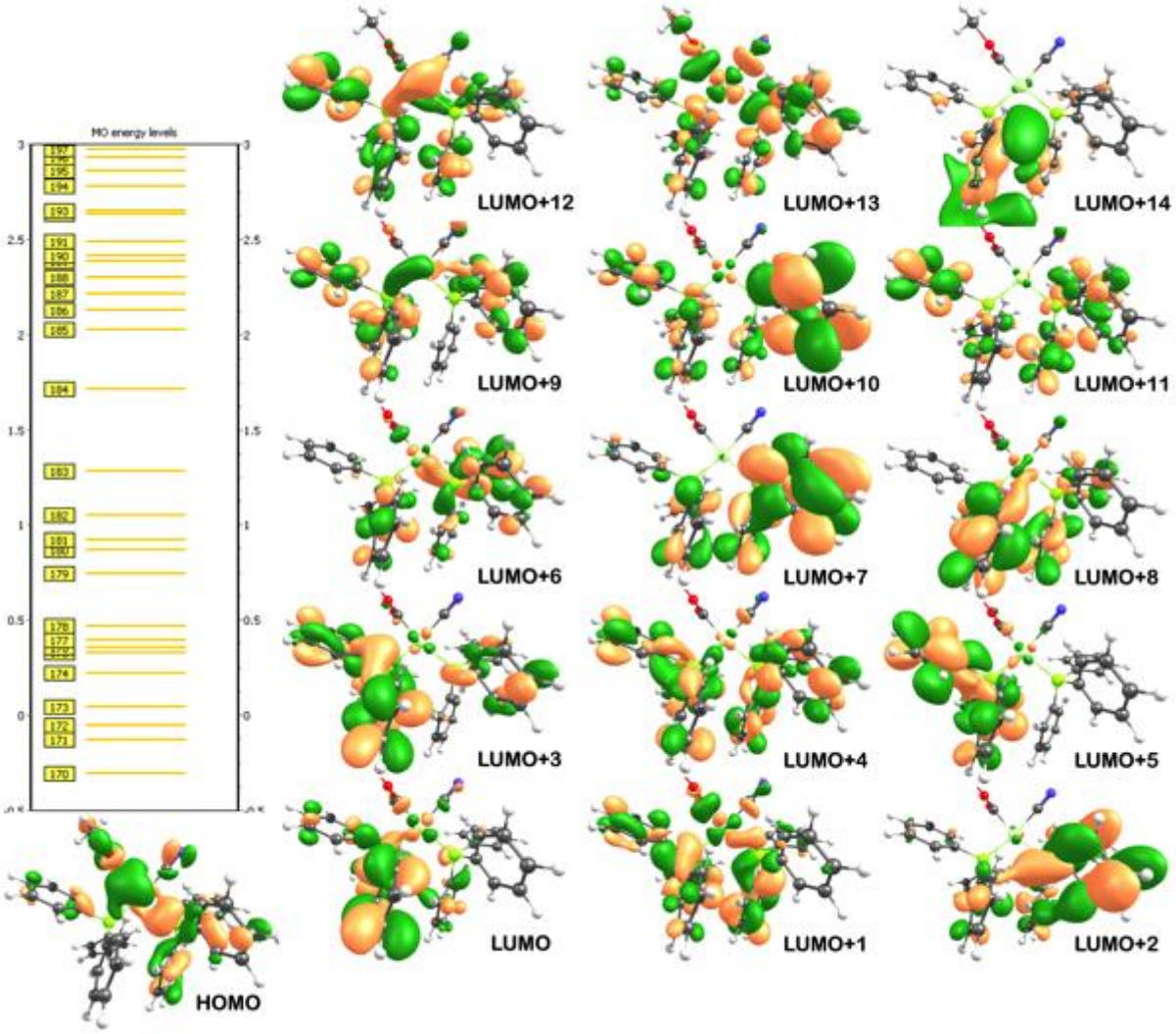



**Figure S4**: Molecular orbital analysis of complex **2c2P** from BHandHLYP/def2TZVP/PCM(toluene) calculation

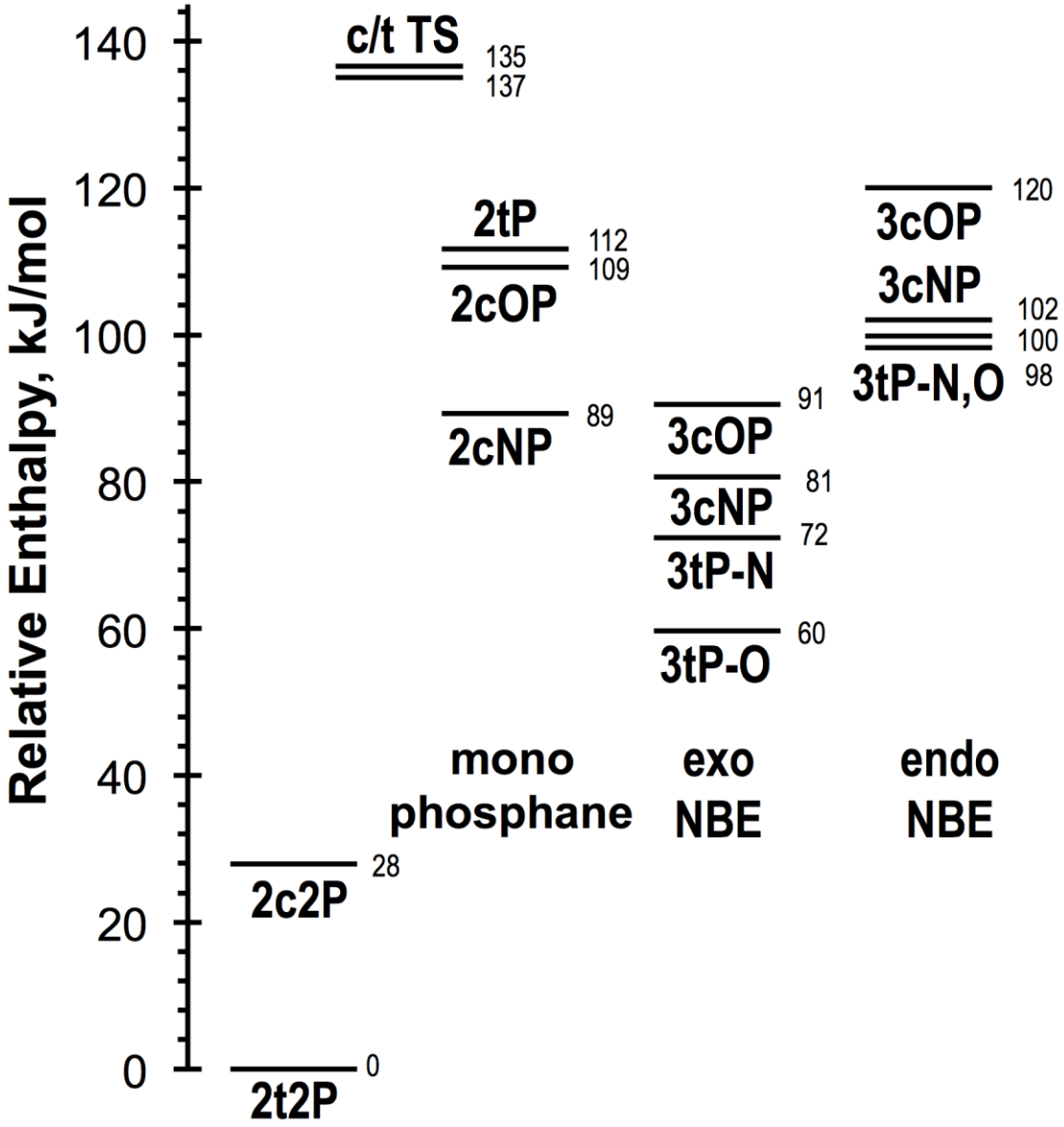
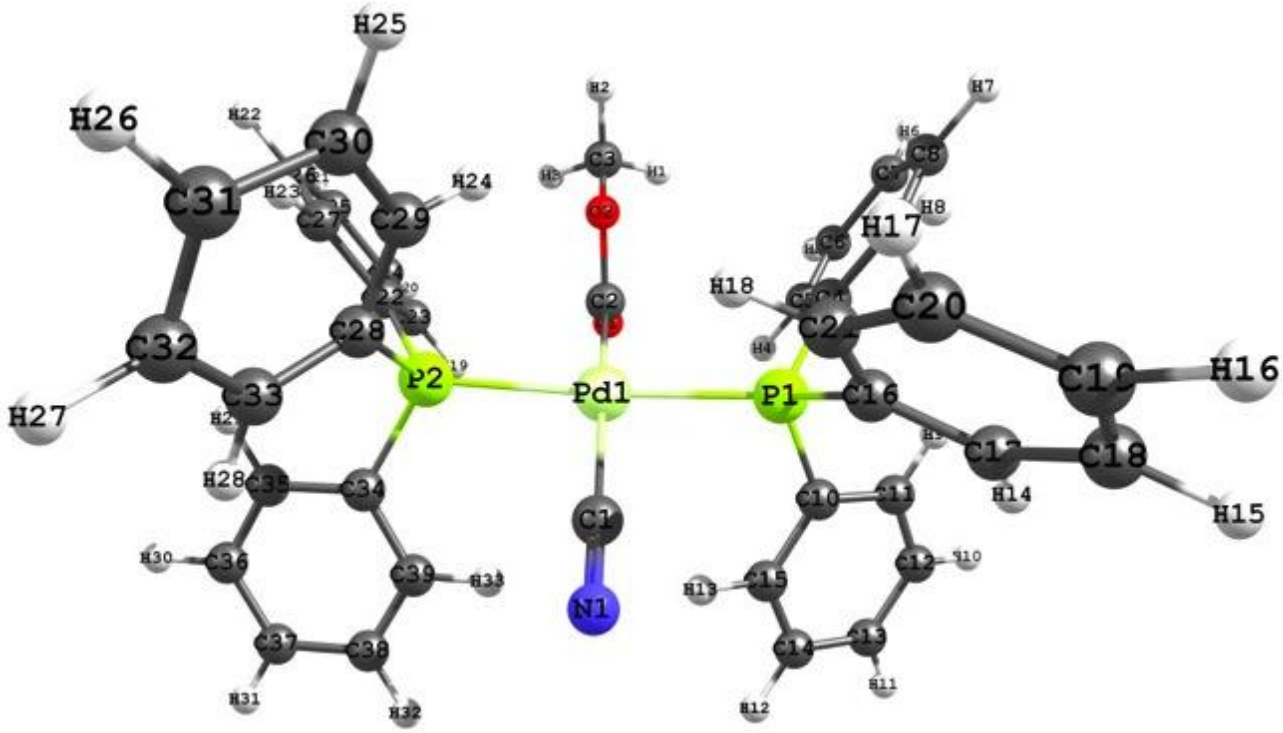
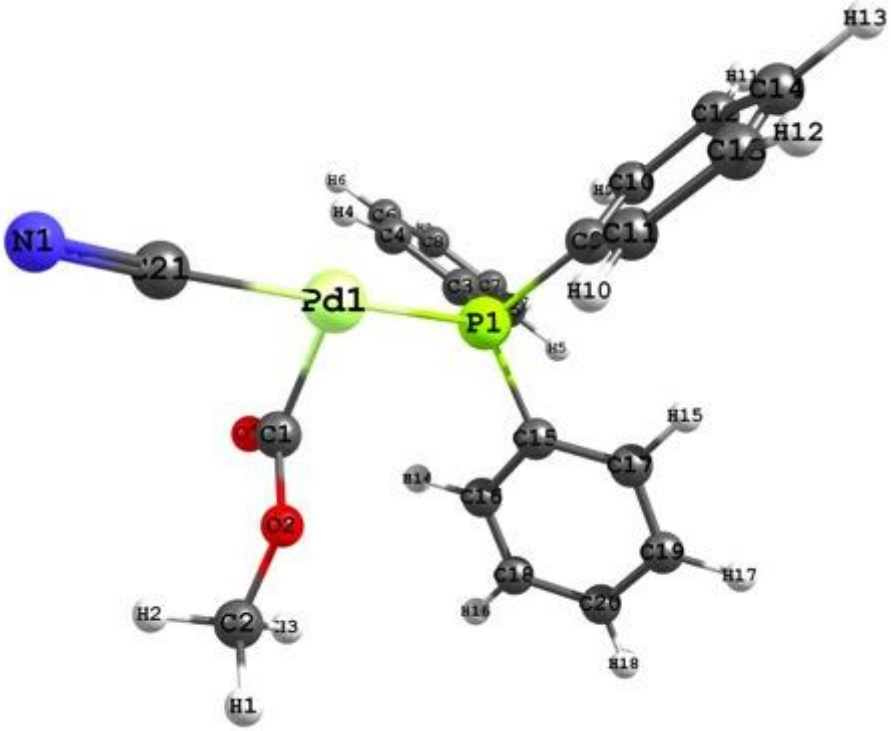



**Figure S5:** Relative enthalpy surface of norbornene complexes (**3**) of the 14 electron $Pd^{II}$ complexes (**2**) calculated at BHandHLYP/def2TZVP/PCM(toluene) level ('N', and 'O' suffixes refer to the position of the norbornene methylene bridge *versus* $CN^-$, and $COOMe^-$ ligands

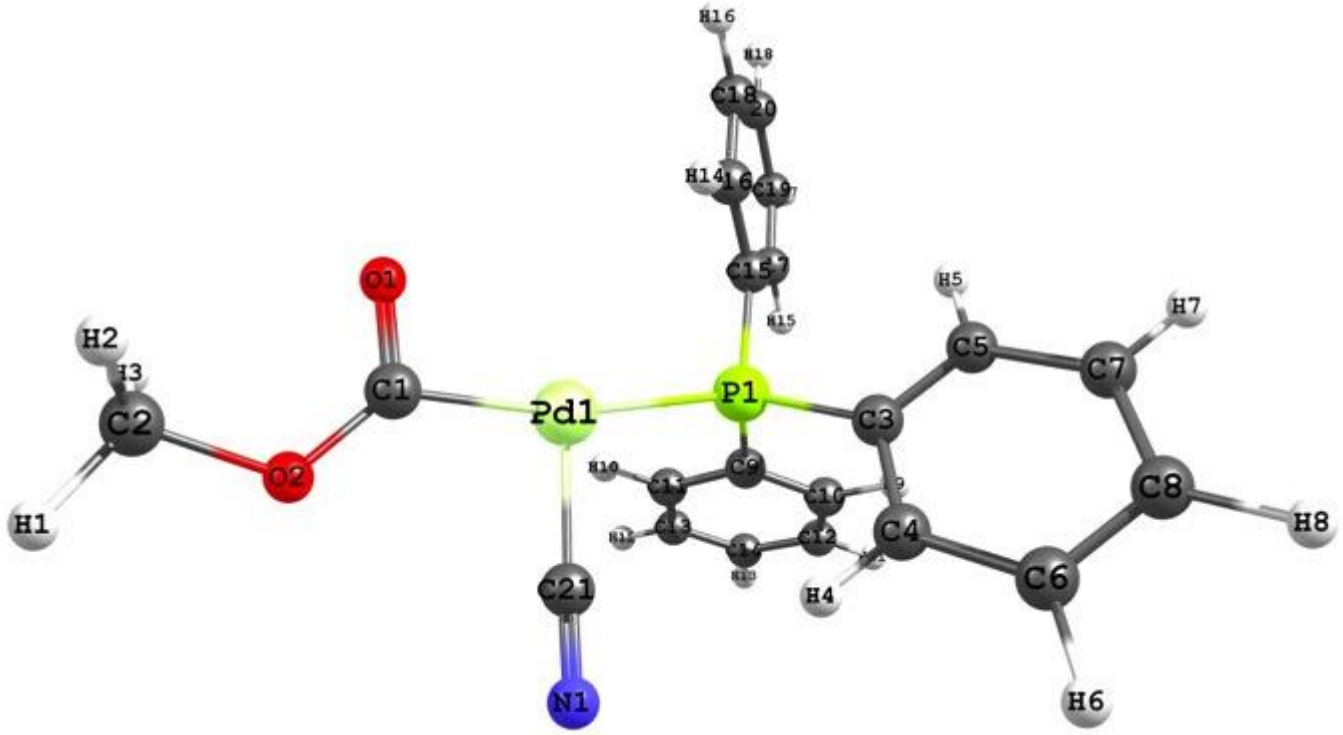
Compilation of calculated molecular structures at the BHandHLYP(PCM)/def2TZVP level without truncation.



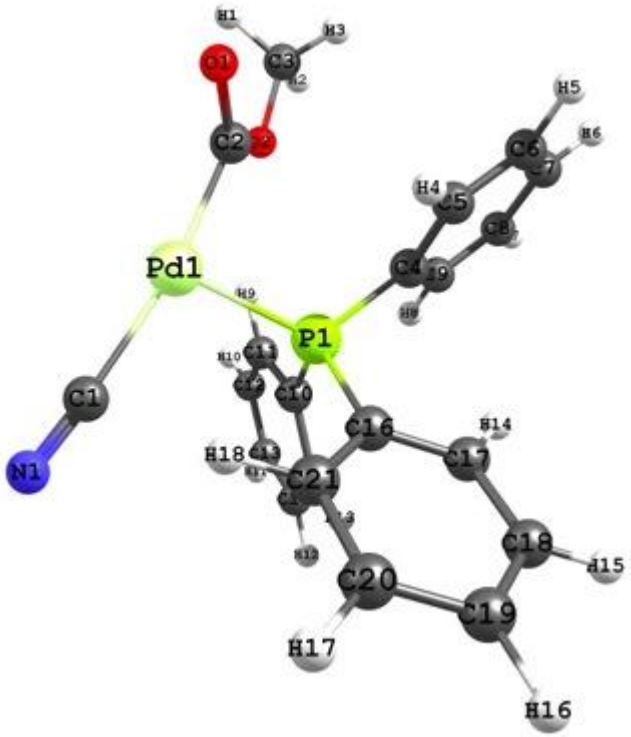

**2t2P**



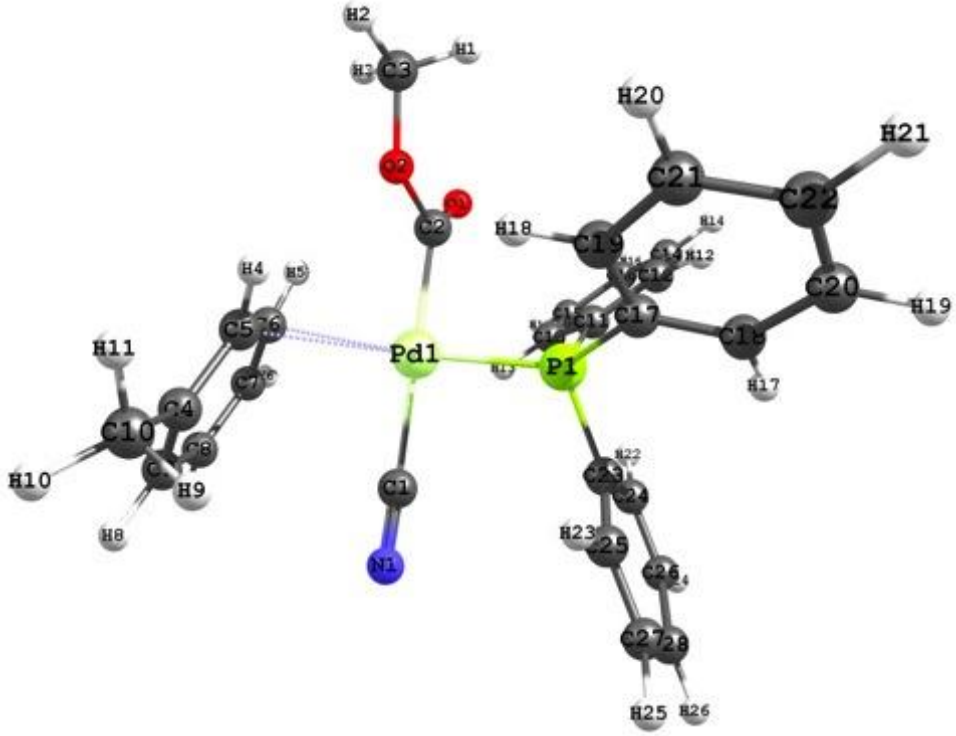

**2cNP**


H16
H18
C18
C20
H14
C16
C19
C15
C17
H15
O1
H2
H3
C1
Pd1
P1
C3
H5
C5
H7
C7
C2
O2
C9
C8
H8
H10
C10
C4
H1
C13
C12
C6
H4
C21
H6
N1

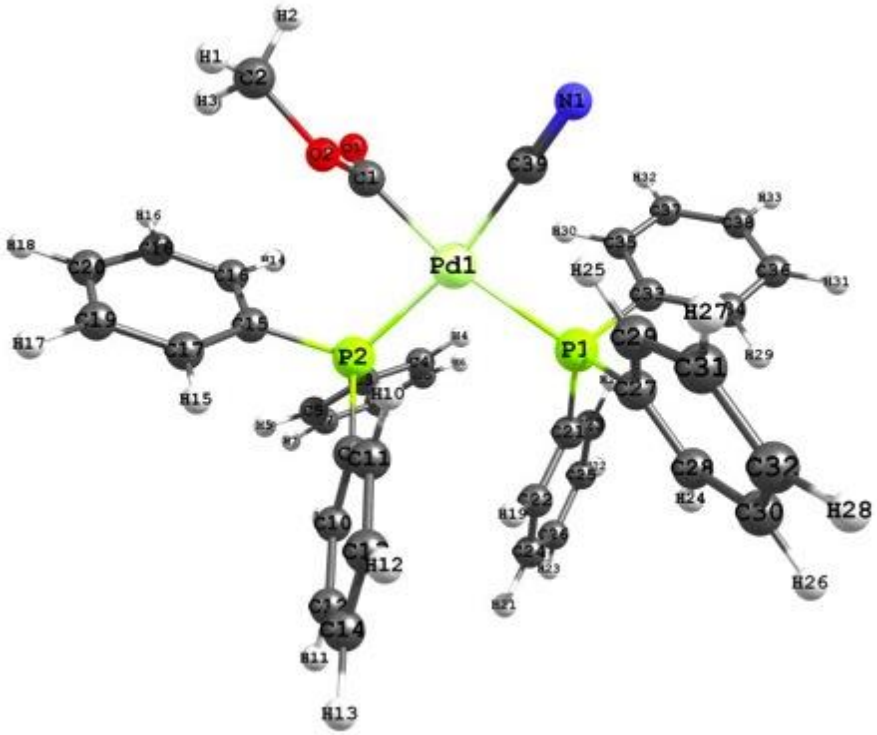
**2cOP**


H1
H3
O1
C3
C2
H5
C6
H6
C7
H4
C5
C8
C4
Pd1
H9
P1
C11
H10
C1
C10
C16
H14
H18
C17
N1
C21
C18
H15
C20
C19
H17
H16

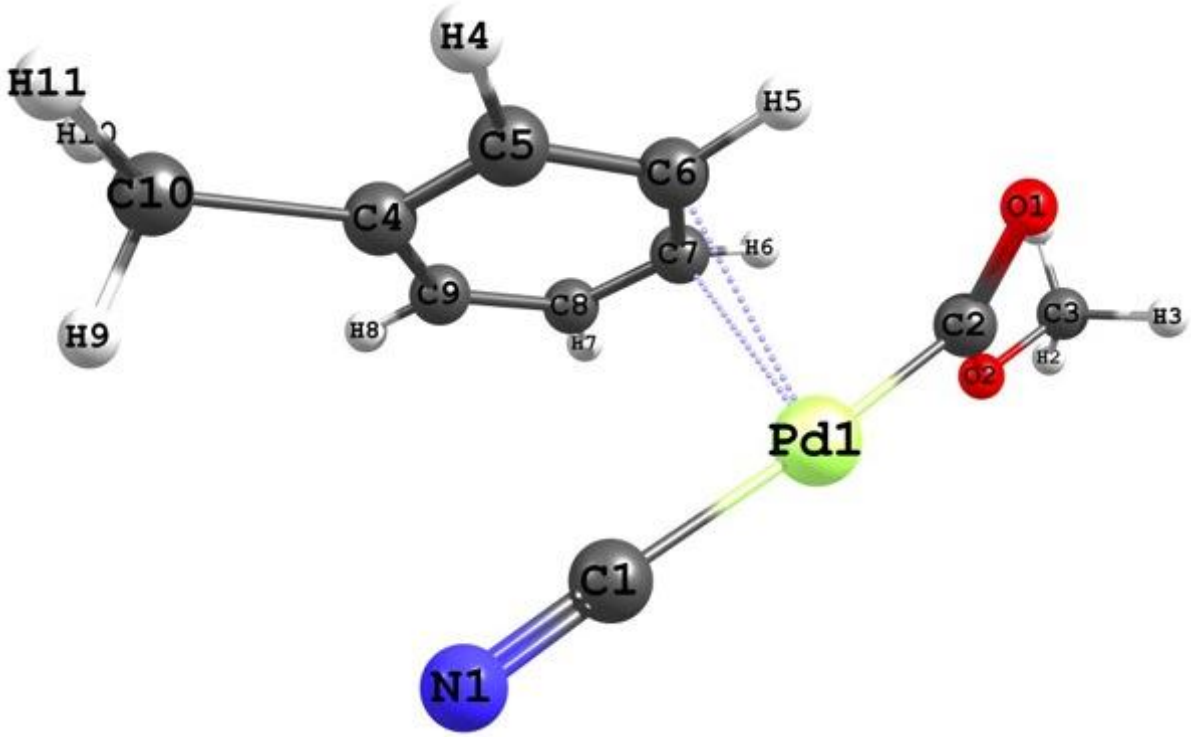
**2tP**


H2
H1
C3
O2
C2
H20
H21
C21
C22
H18
C19
C20
H19
C17
C18
H17
H4
C5
Pd1
P1
H11
C4
C10
C8
H10
H9
H8
C1
N1
H22
C23
H23
C25
C26
C27
C28
H25
H26

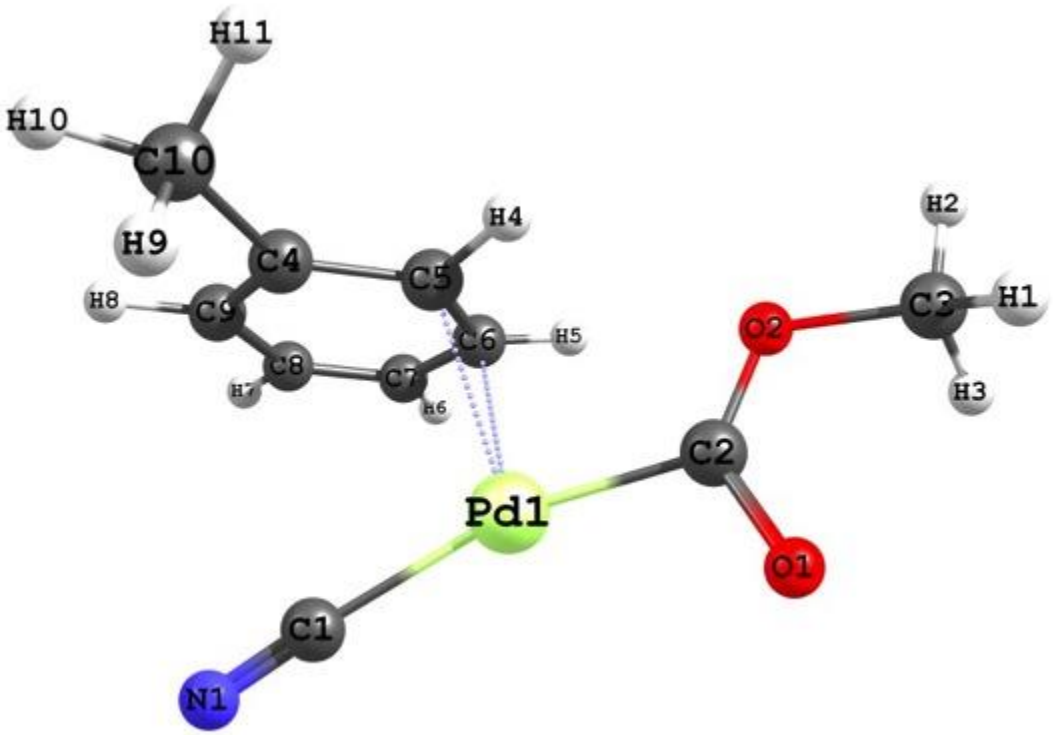
**2tPT**


H2
H1
C2
H3
O2
O1
C1
N1
C30
Pd1
H16
H18
H14
H17
H15
P2
P1
H10
H12
H32
H33
H30
H25
H27
H29
C31
C32
C30
H28
H24
H26
H13

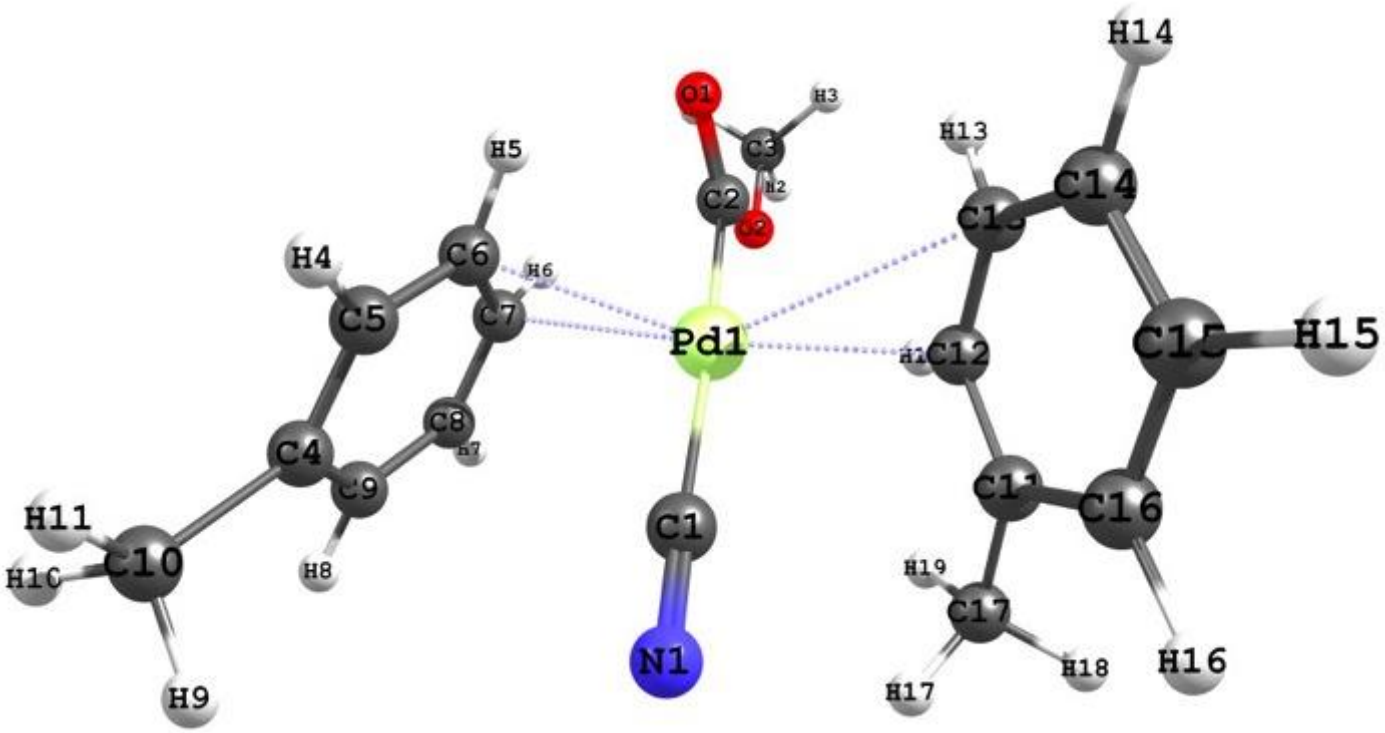
**2c2P**


H4
H11
H5
C5
C6
C10
C4
O1
C7
H6
C9
C8
C2
C3
H3
H9
H8
H7
O2
H2
Pd1
C1
N1

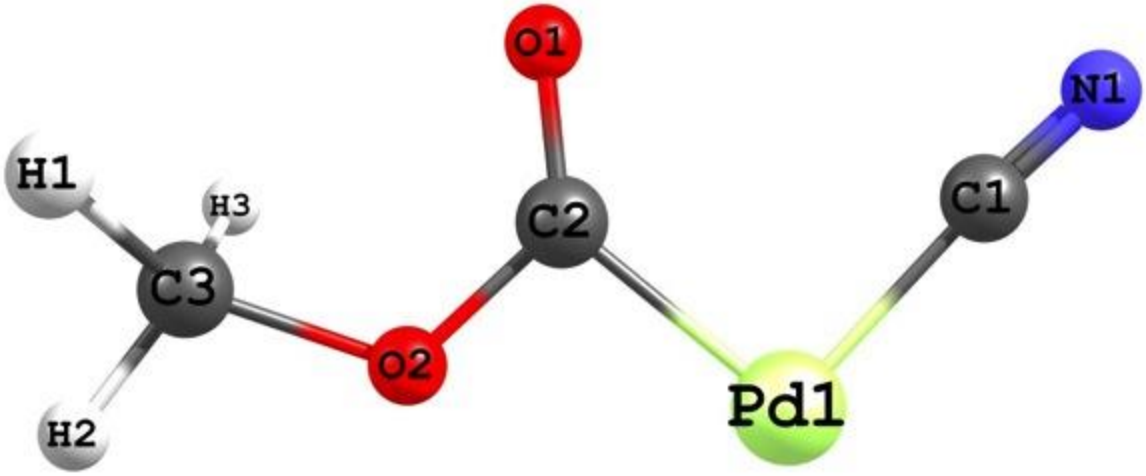
**2tT-O**


H11
H10
C10
H2
H9
H4
C4
C5
H8
C9
H1
O2
C3
C6
H5
C8
C7
H7
H6
H3
C2
Pd1
O1
C1
N1

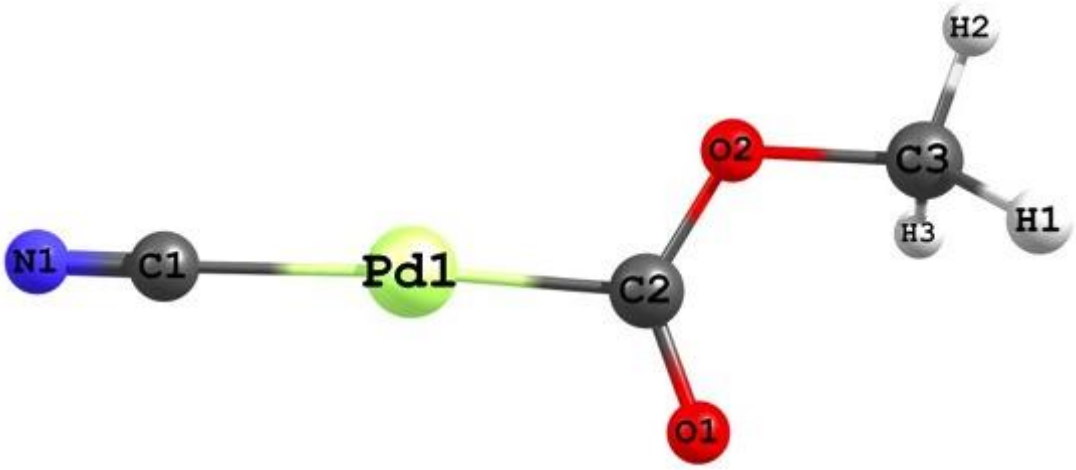
**2tT-OMe**


H14
O1
H3
H13
H5
C3
C2
H2
O2
C14
H4
C6
H6
C5
C7
Pd1
C12
H15
C8
C4
H7
C9
C11
C16
H11
C1
C10
H19
H1C
H8
C17
N1
H16
H18
H17
H9

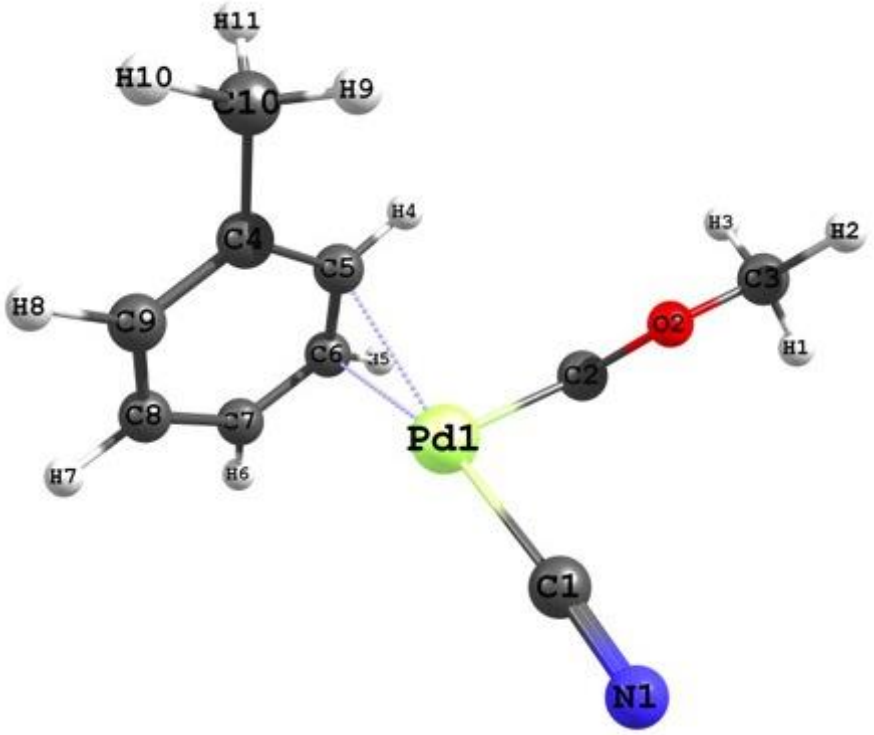
**2t2T**


O1
N1
H1
H3
C2
C1
C3
O2
H2
Pd1

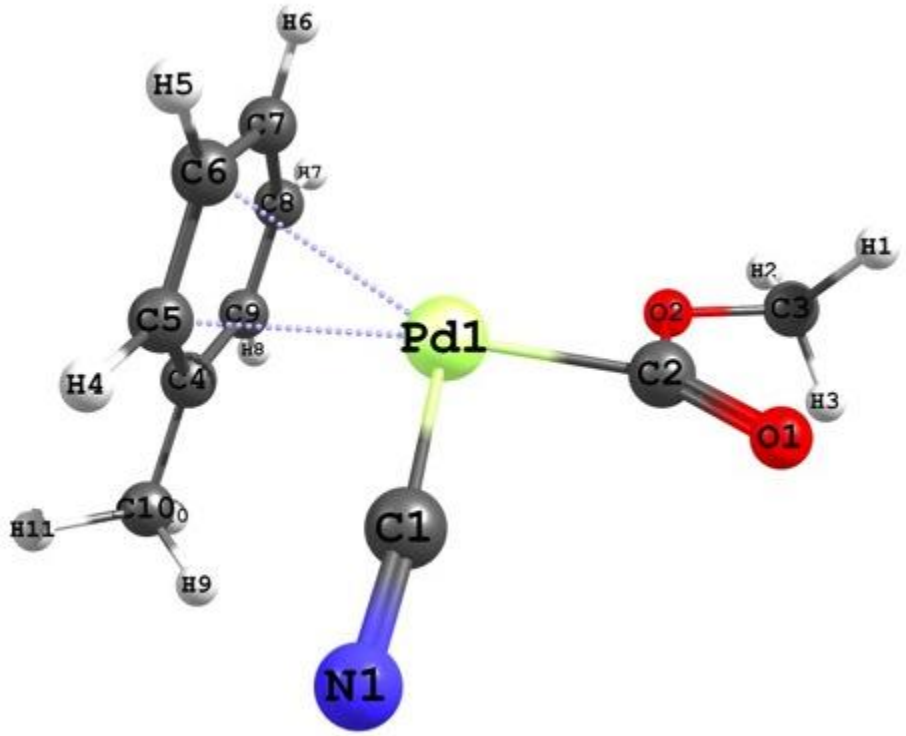
**2c**


H2
O2
C3
H3
H1
N1
C1
Pd1
C2
O1

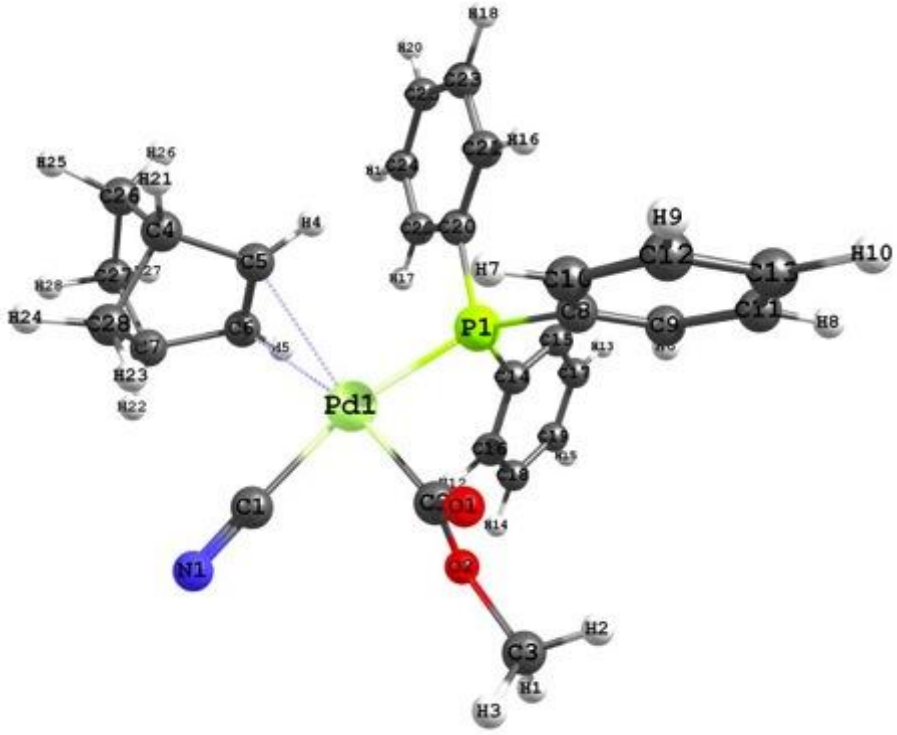
**2t**


H11
H10
C10
H9
C4
H4
C5
H3
H2
C3
H8
C9
O2
C6
H5
H1
C2
C8
C7
Pd1
H7
H6
C1
N1

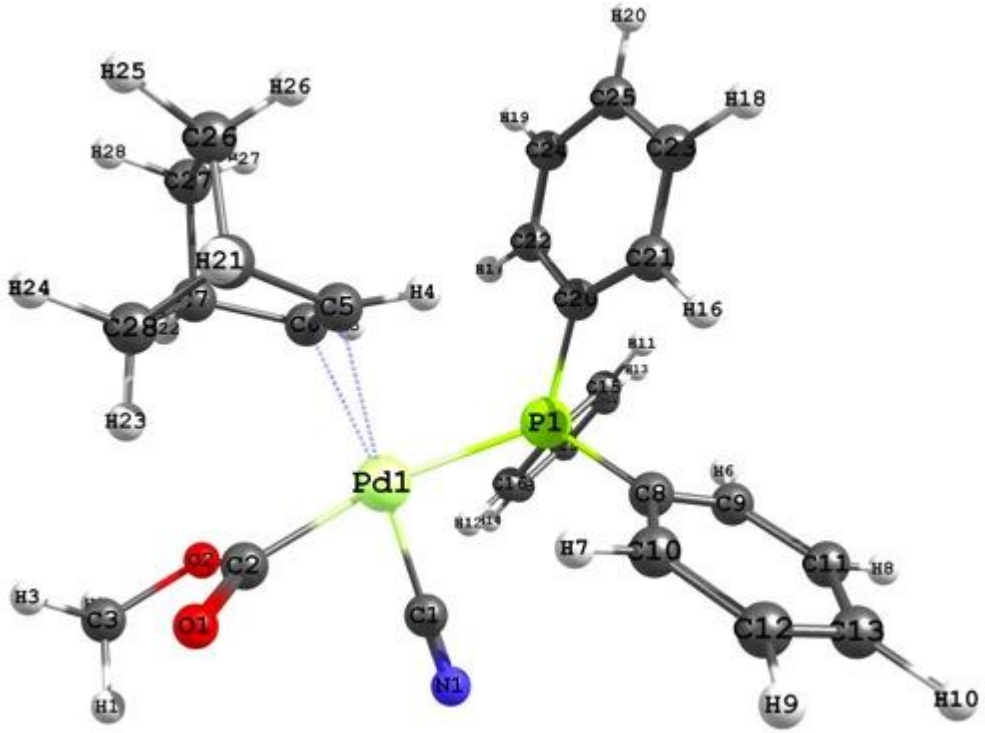
**2cNT**


H6
H5
C7
C6
H7
C8
H1
H2
C5
C9
O2
C3
Pd1
H8
C4
C2
H4
H3
O1
C10
H11
C1
H9
N1

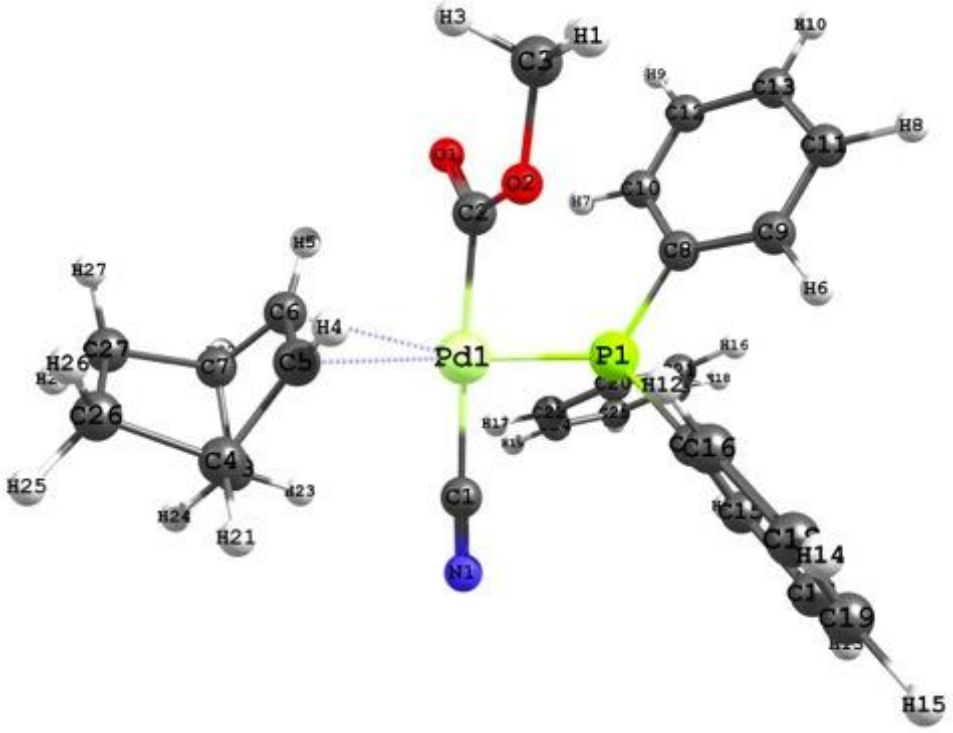
**2cOT**



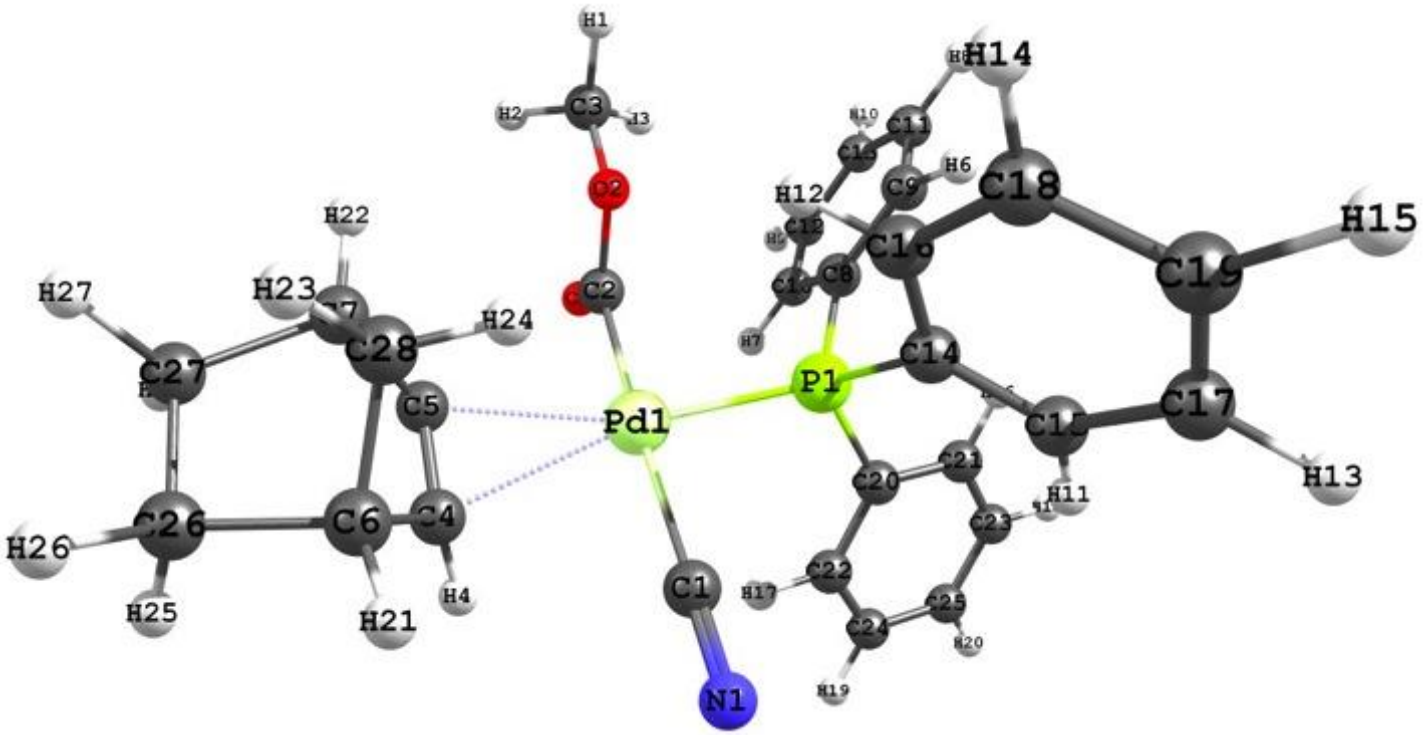

**exo-3cNP**



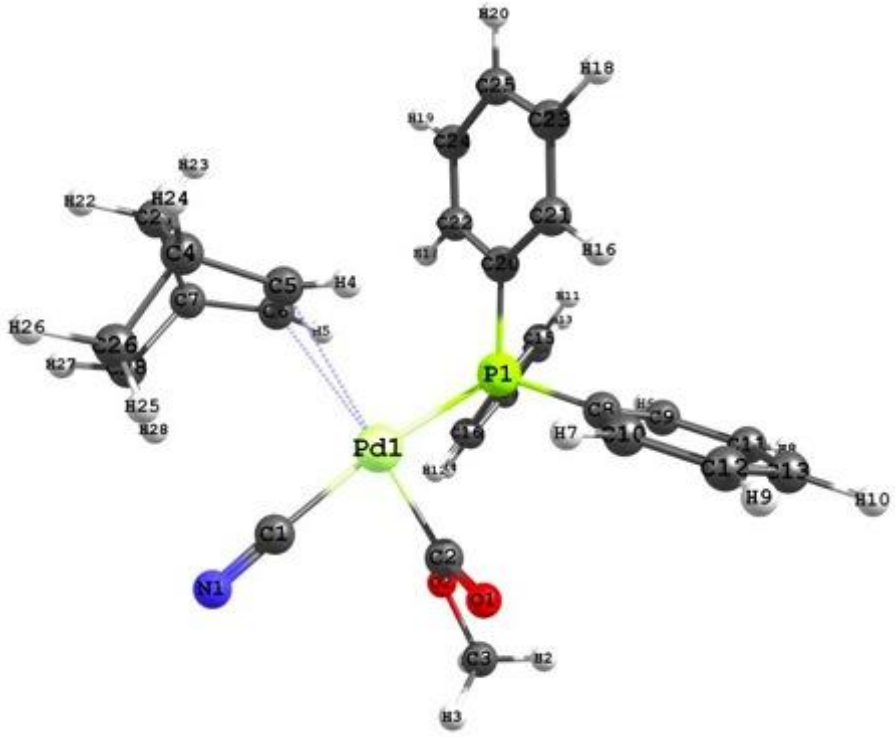

**exo-3cOP**



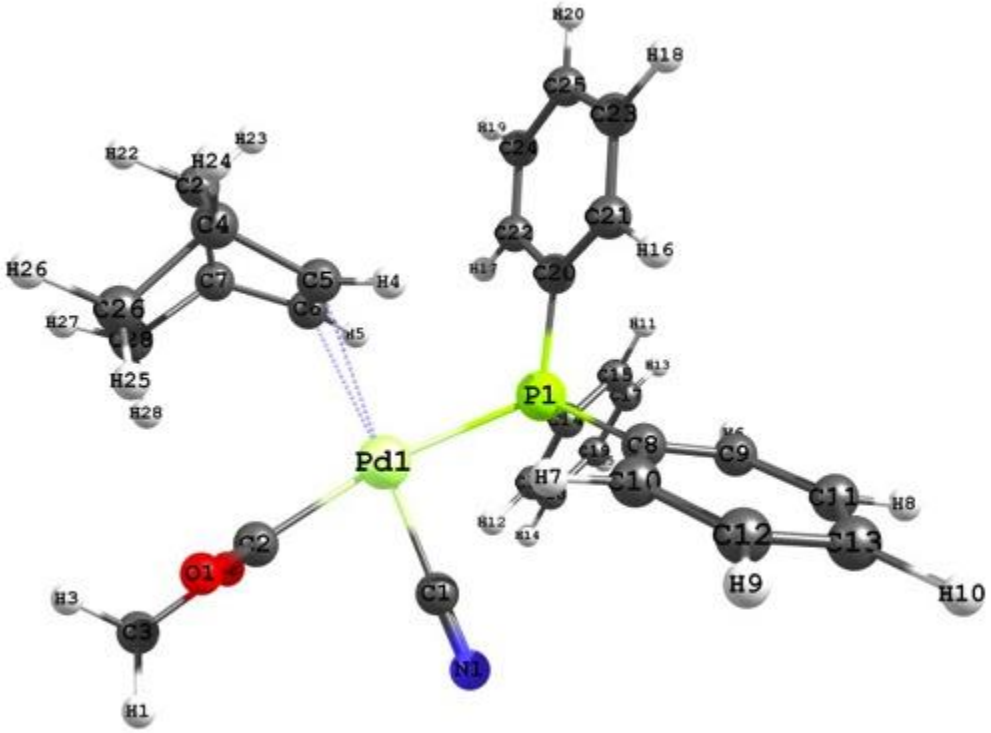

**exo-3tP-N**



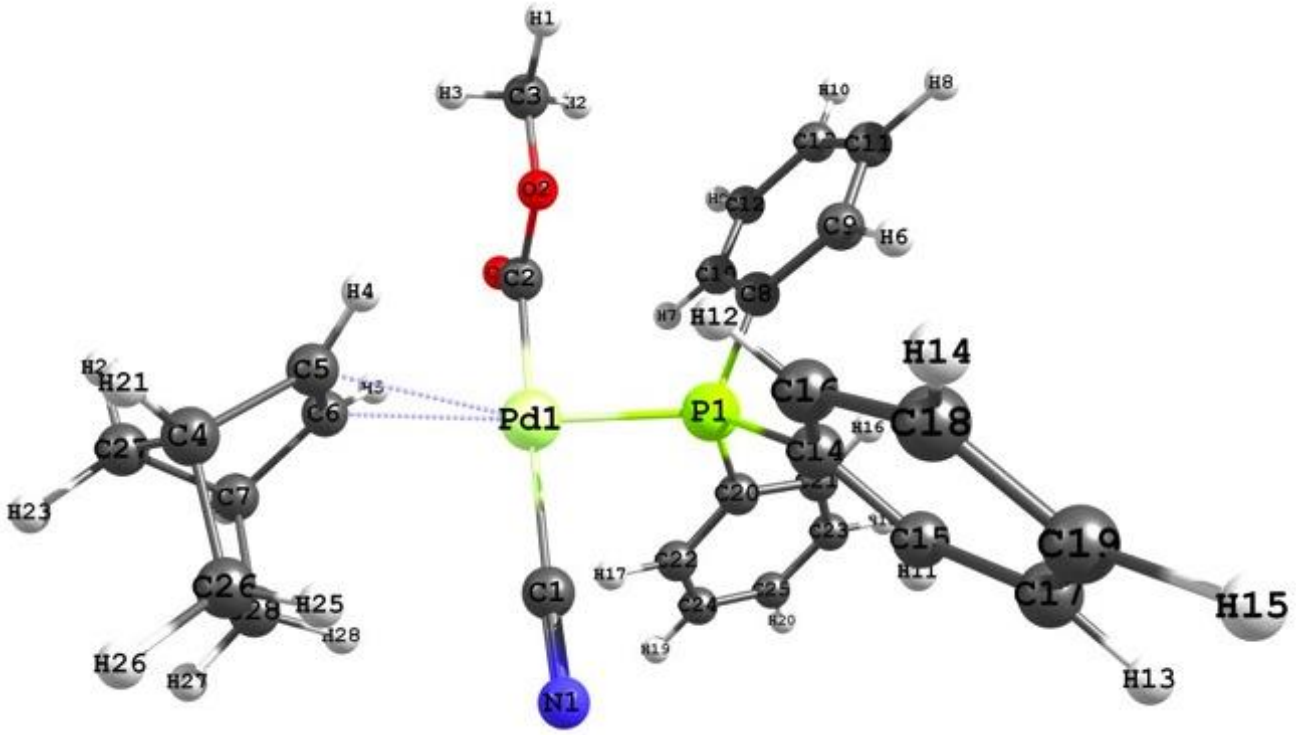

**exo-3tP-O**



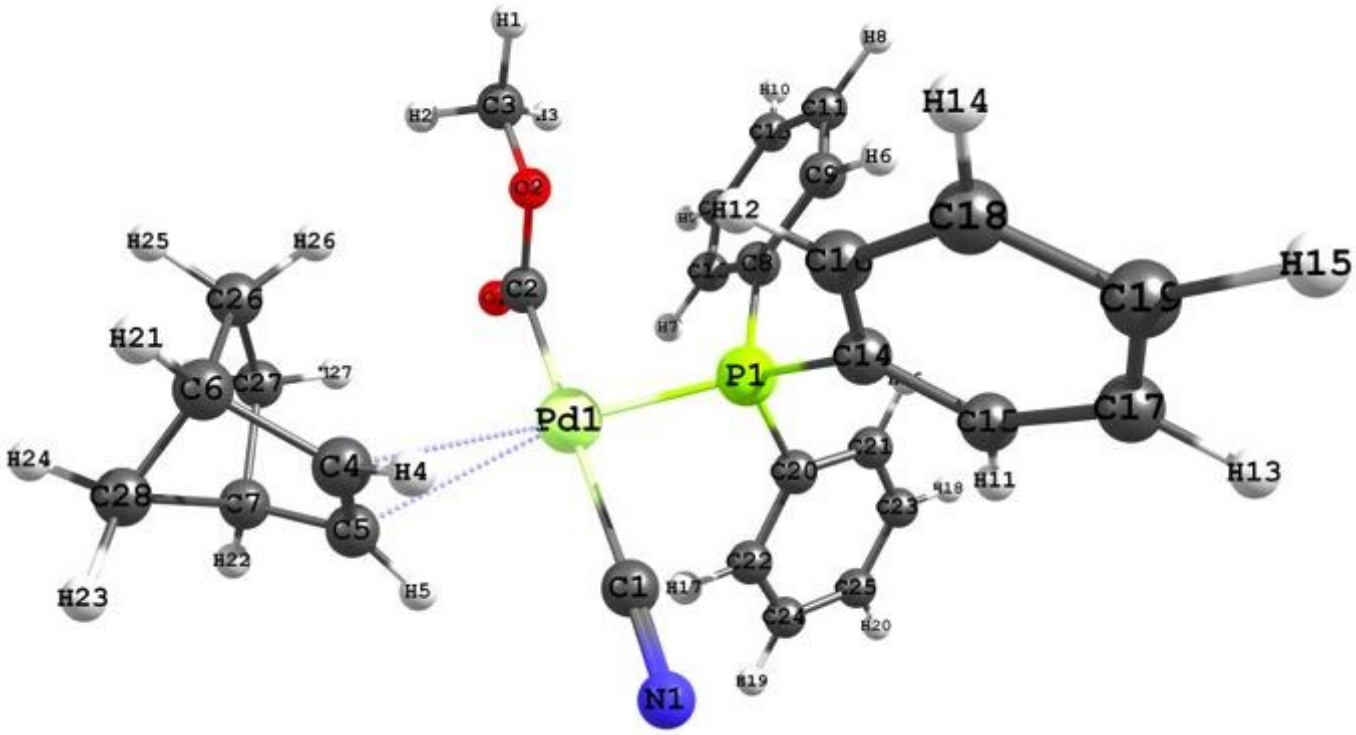

**endo-3cNP**




**endo-3cOP**




**endo-3tP-N**




**endo-3tP-O**

The supplemental file *filename.xyz* contains the computed Cartesian coordinates of all of the molecules reported in this study. This file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as **Mercury** (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis. Electronic energies computed at the BHandHLYP(PCM)/def2TZVP level are shown in the title line of each file.