# Synthesis of β-Dipyrrinyl Triphyrin(2.1.1) Ligand and Its Coordination Complexes

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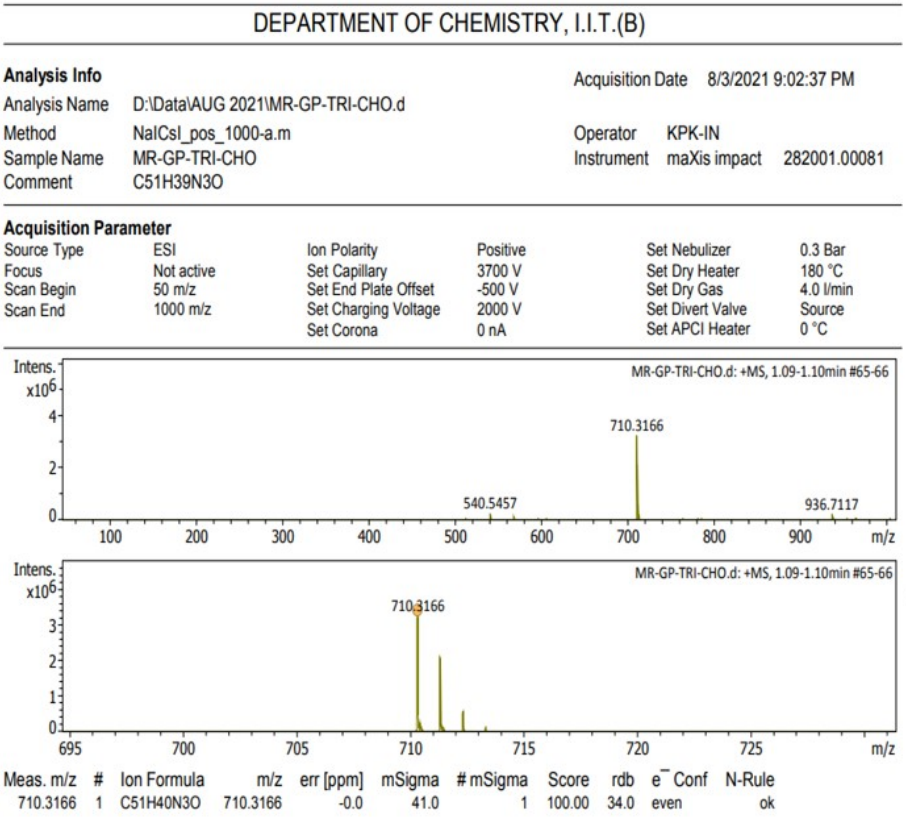
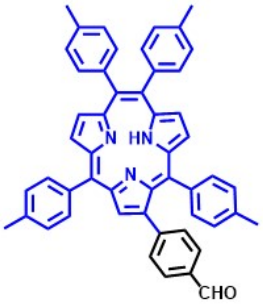



**Chemical Formula: $C_{51}H_{39}N_3O$**
**Exact Mass: 709.3093**
**Observed Mass: 710.3166 $[M+H]^+$**

**Figure S1.** HR mass spectrum of the compound **3.**

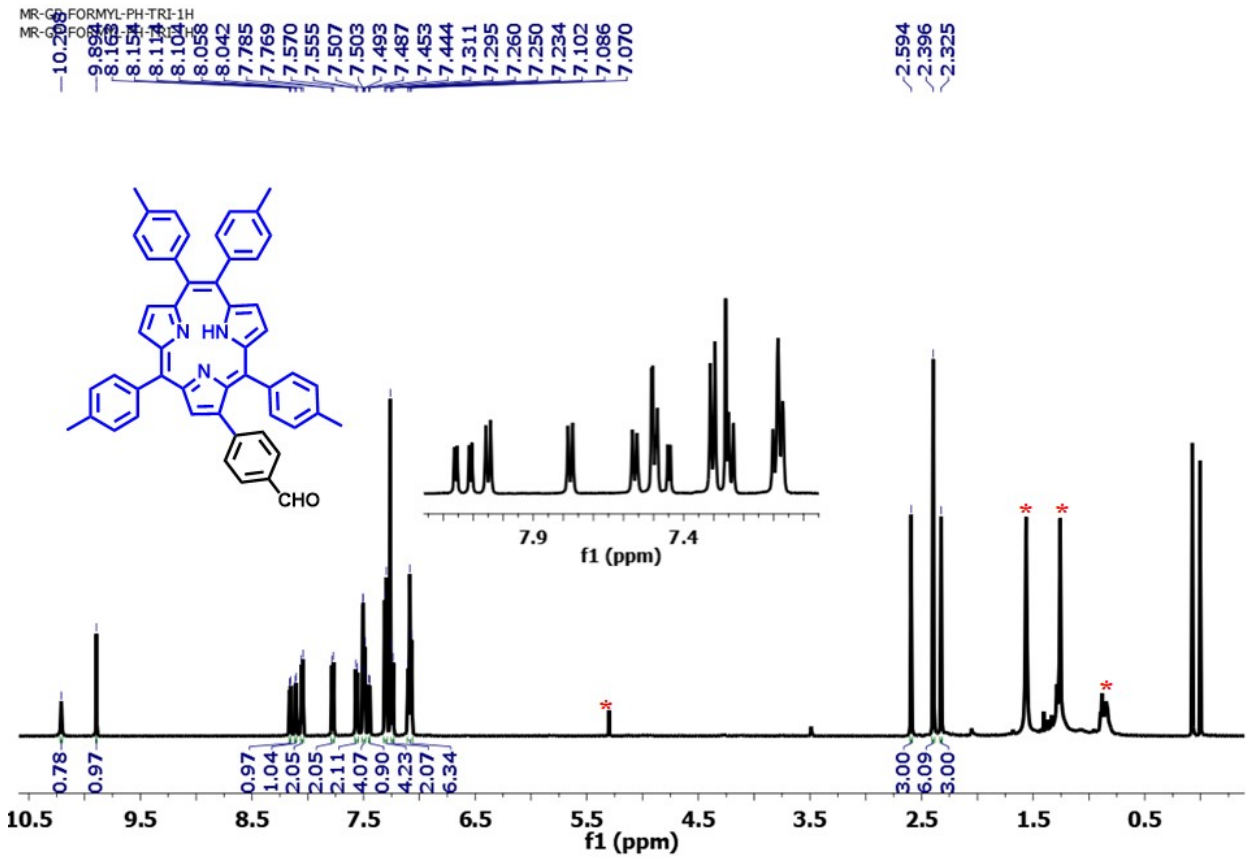



**Figure S2.** $^{1}H$ NMR spectrum of the compound **3** recorded in $CDCl_3$ in 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

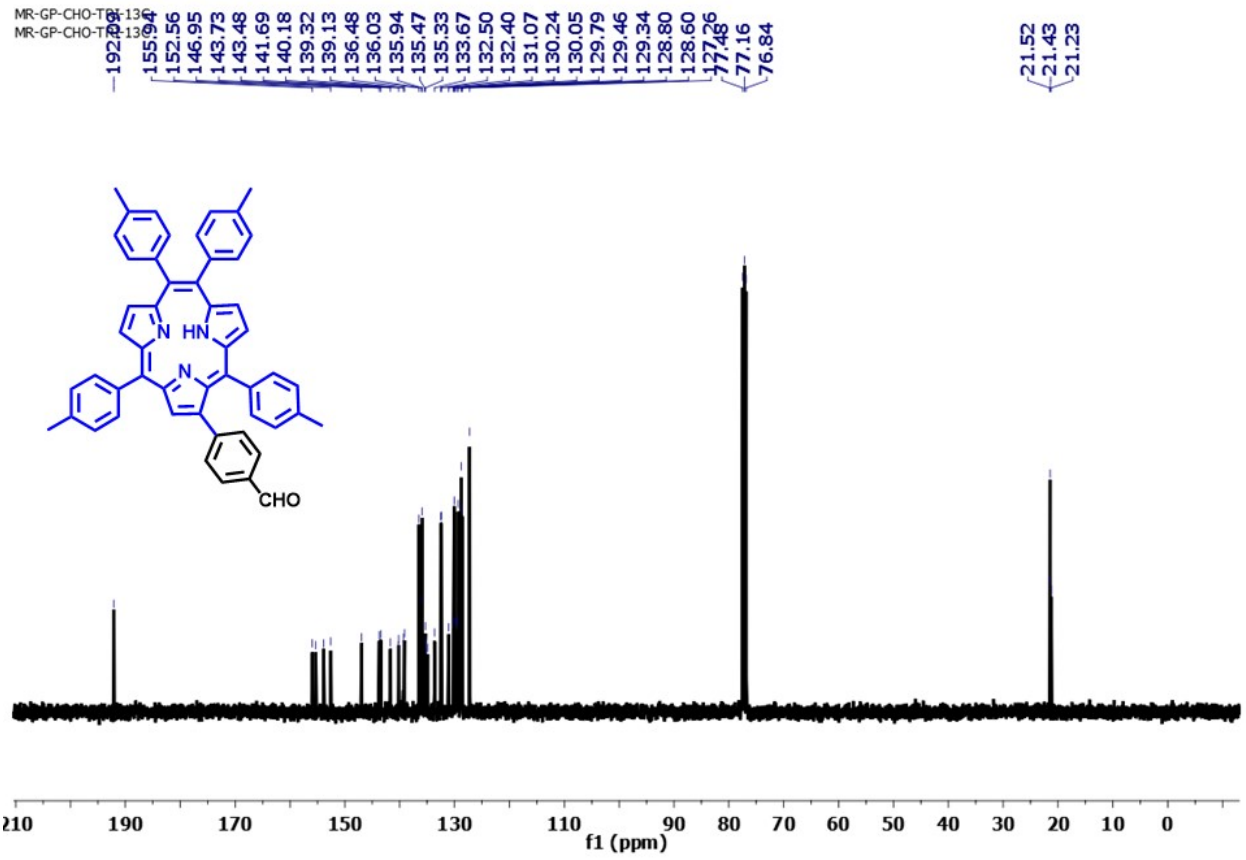



**Figure S3.** $^{13}C$ NMR spectrum of the compound **3** recorded in $CDCl_3$ in 101MHz instrument.

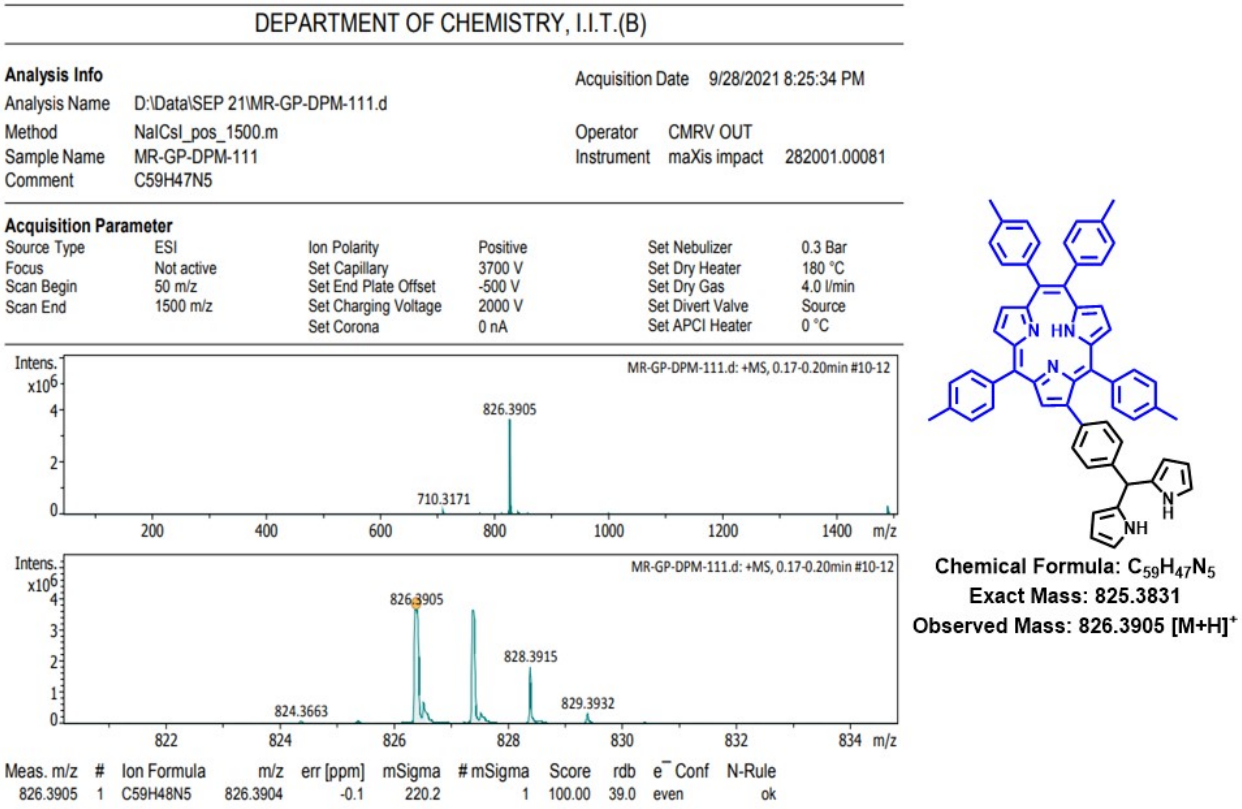



**Figure S4.** HR mass spectrum of the compound **4.**

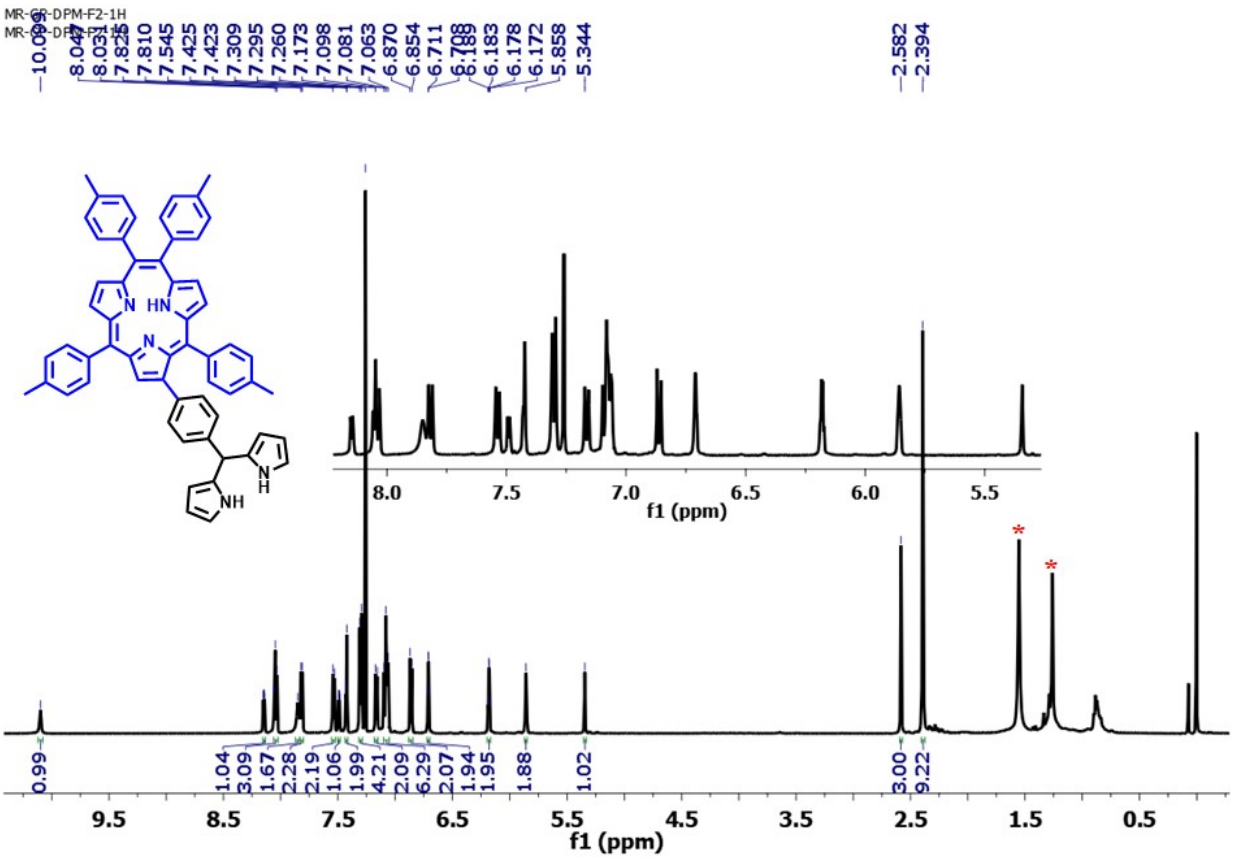



**Figure S5.** $^{1}H$ NMR spectrum of the compound **4** recorded in $CDCl_3$ in 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

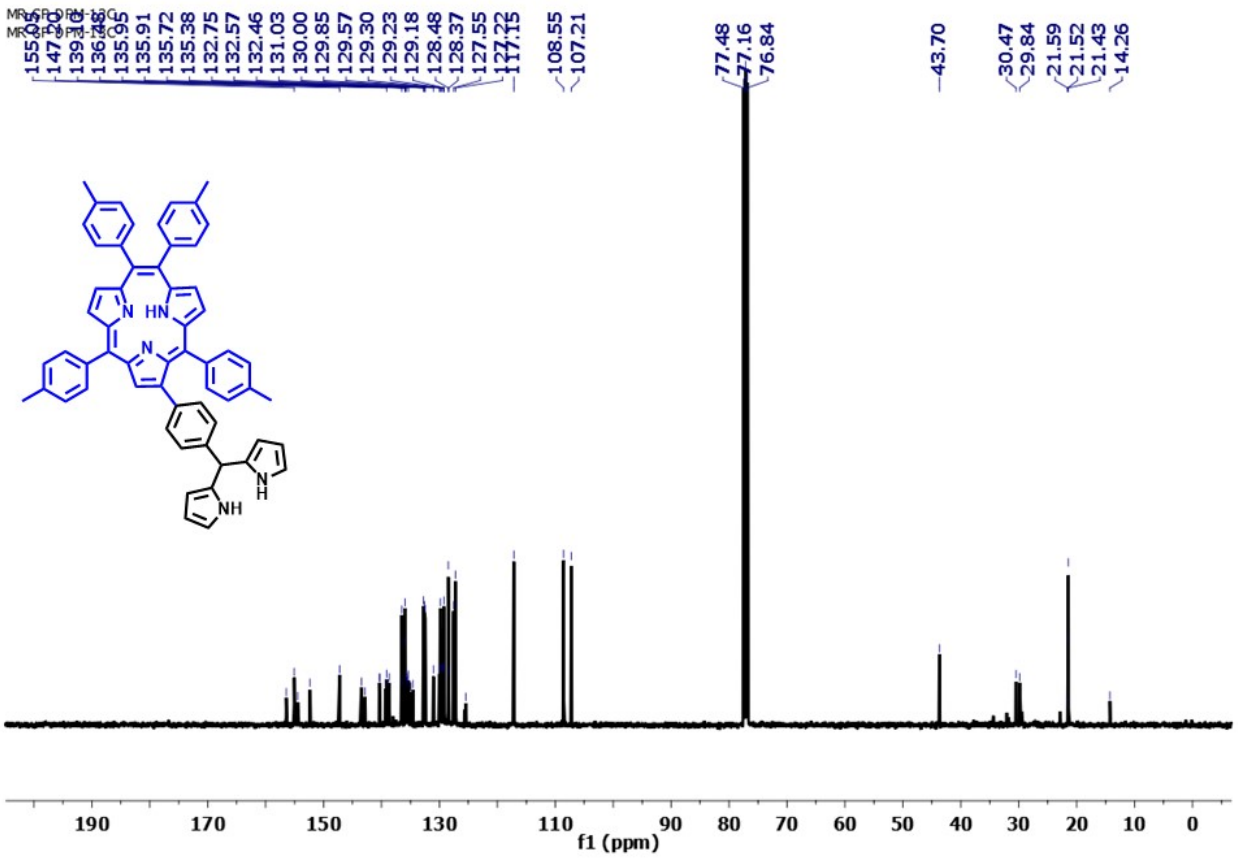
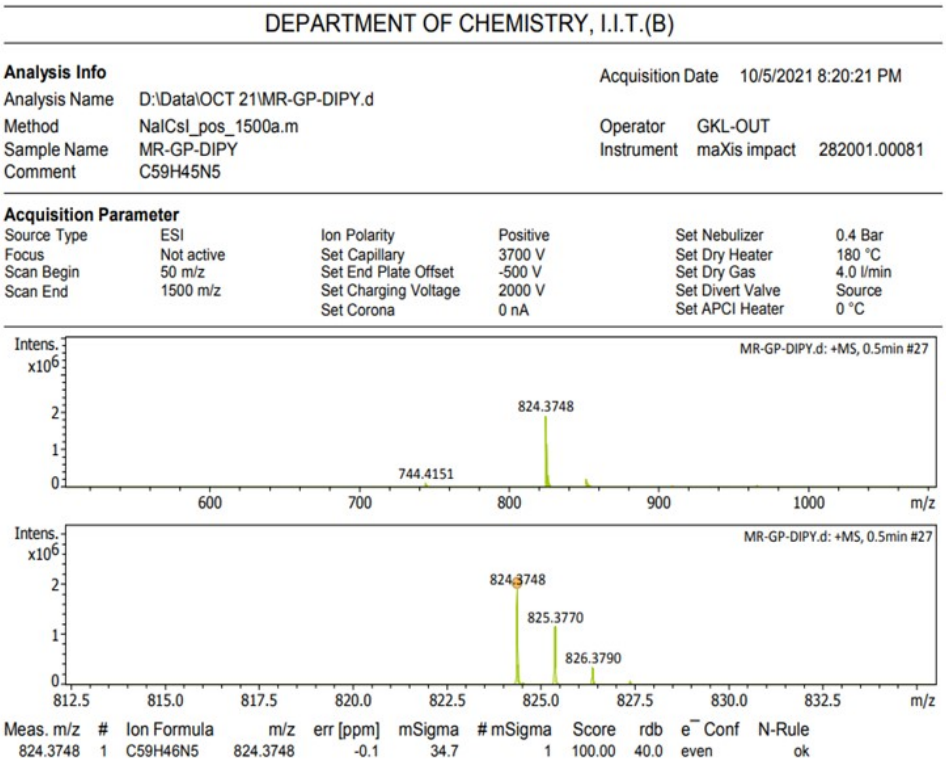
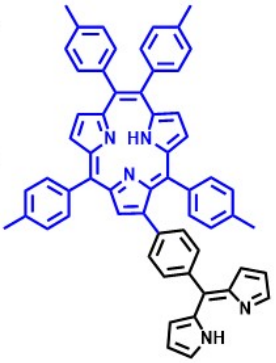



**Figure S6.** $^{13}C$ NMR spectrum of the compound **4** recorded in $CDCl_3$ in 101 MHz instrument.




**Chemical Formula: $C_{59}H_{45}N_5$**
**Exact Mass: 823.3675**
**Observed Mass: 824. $[M+H]^+$**

**Figure S7.** HR mass spectrum of the compound **5.**

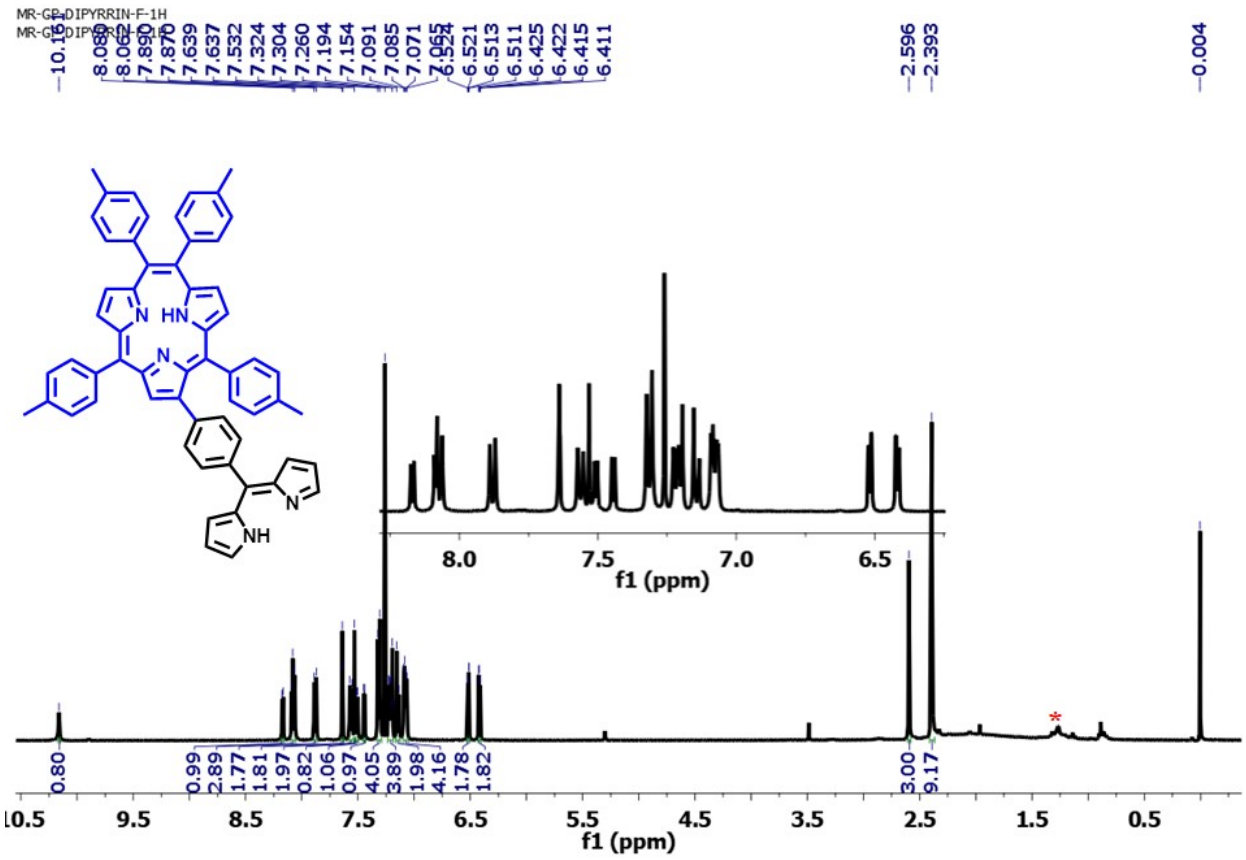
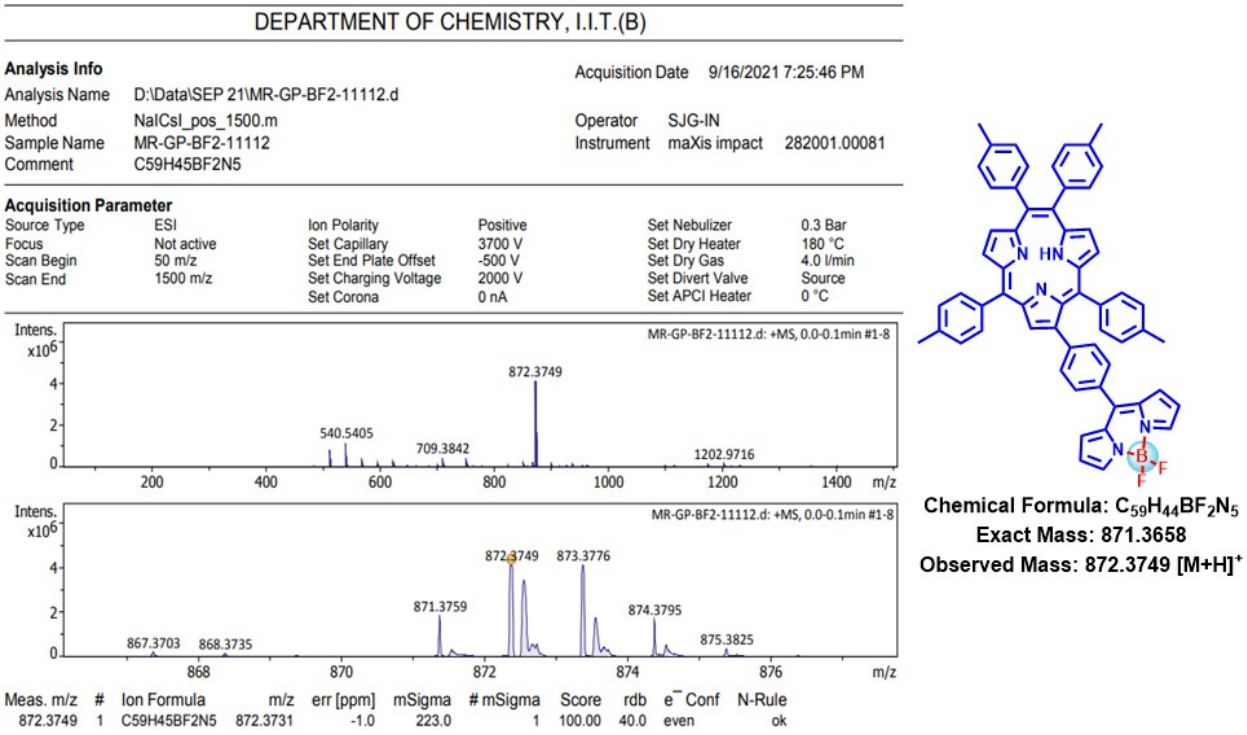



**Figure S8.** $^{1}H$ NMR spectrum of the compound **5** recorded in $CDCl_3$ in 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.






**Chemical Formula: $C_{59}H_{44}BF_2N_5$**
**Exact Mass: 871.3658**
**Observed Mass: 872.3749 $[M+H]^+$**

**Figure S9.** HR mass spectrum of the compound **6.**

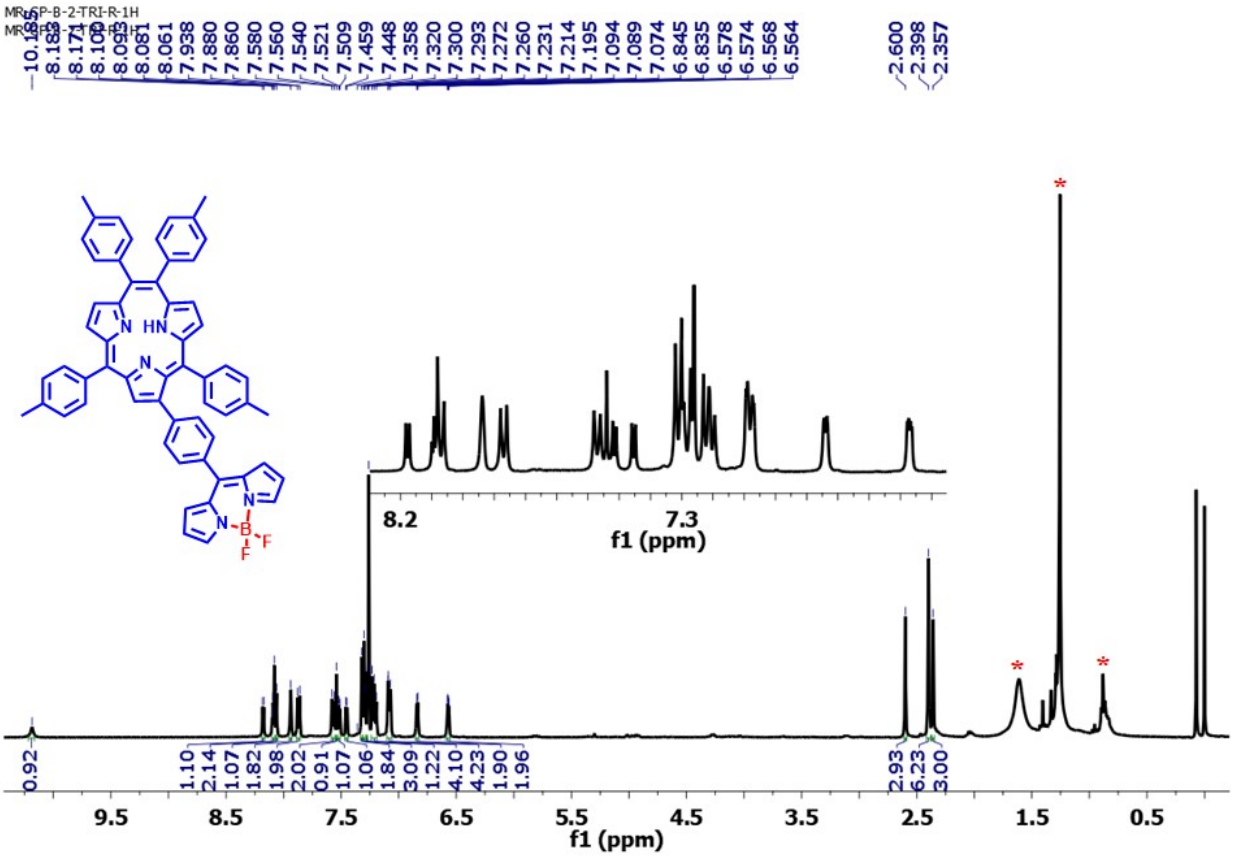



**Figure S10.** $^{1}H$ NMR spectrum of the compound **6** recorded in $CDCl_3$ in 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

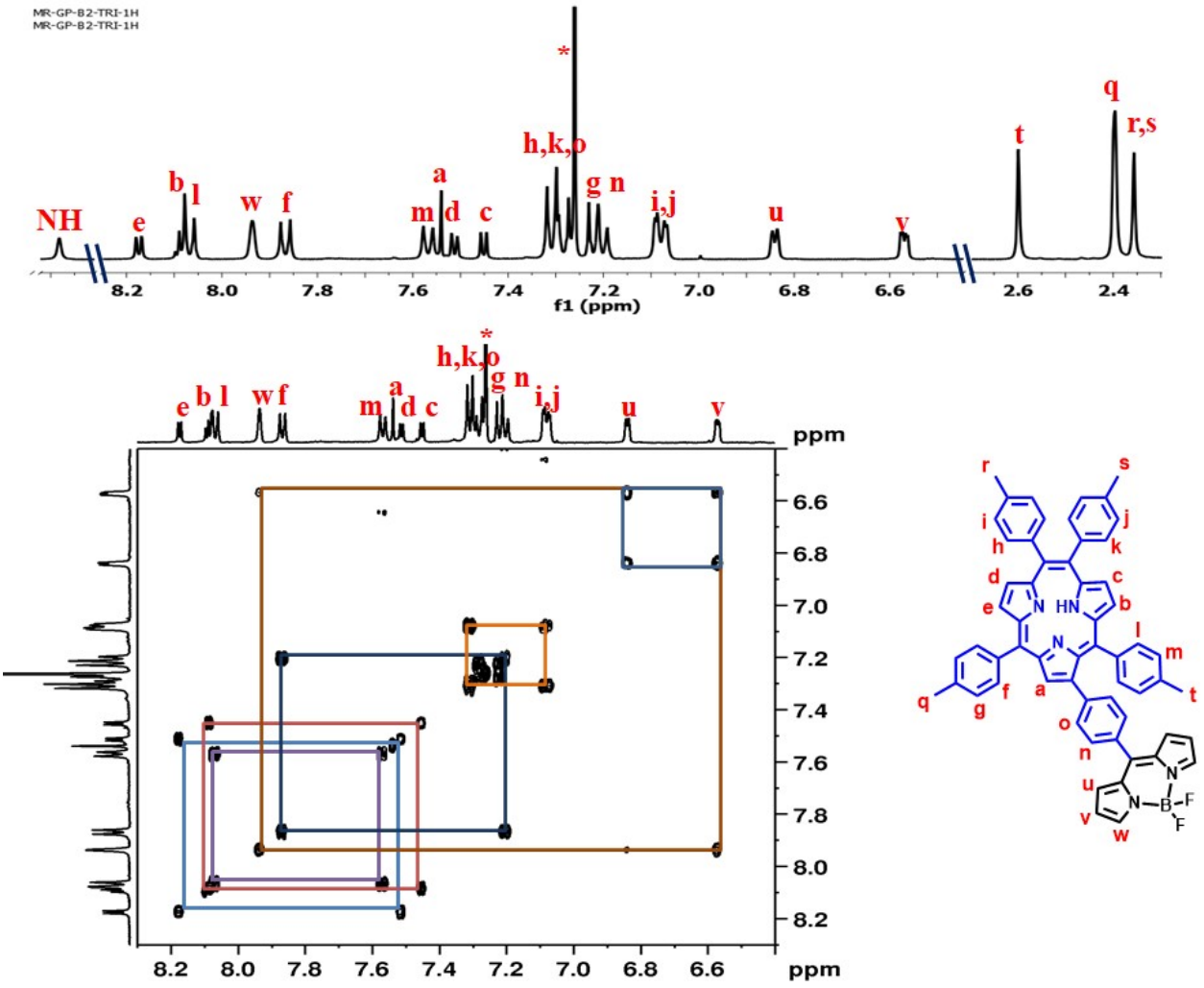



**Figure S11.** $^{1}$H-$^{1}$H COSY of Compound **6** recorded in $CDCl_3$.

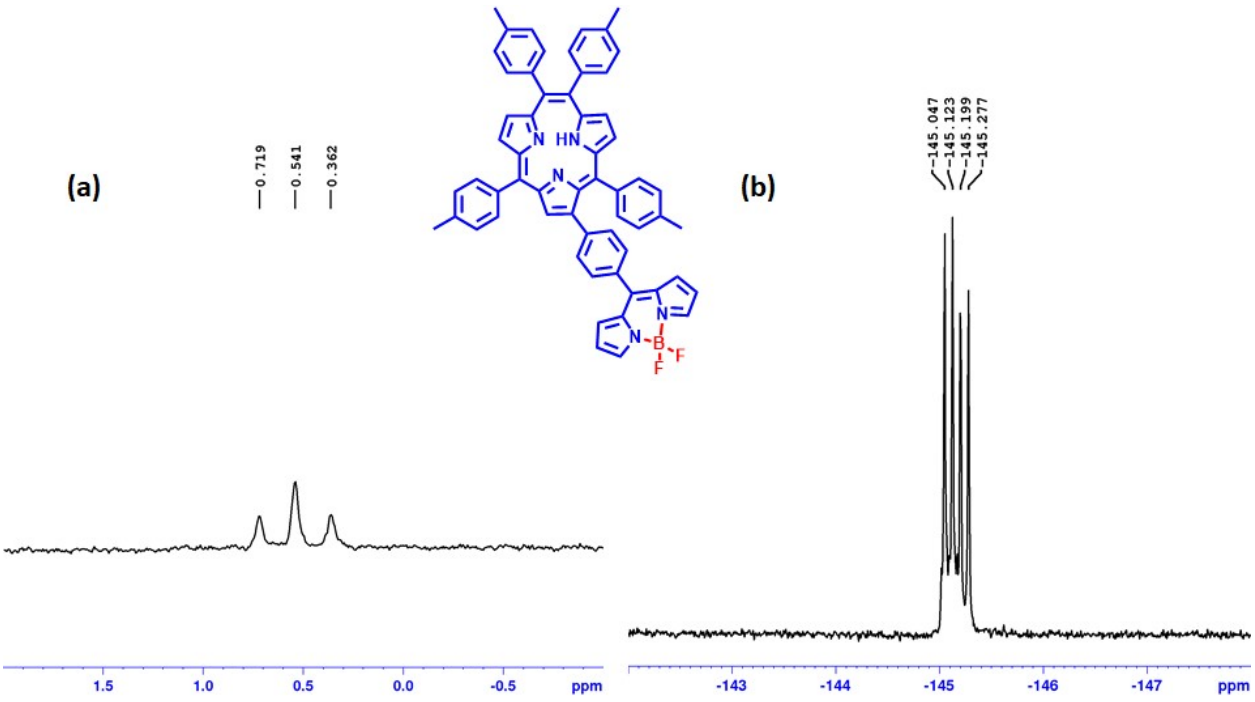



**Figure. S12.** $^{11}B$ NMR spectrum **(a)** and $^{19}F$ spectrum **(b)** of the compound **6** recorded in $CDCl_3$.

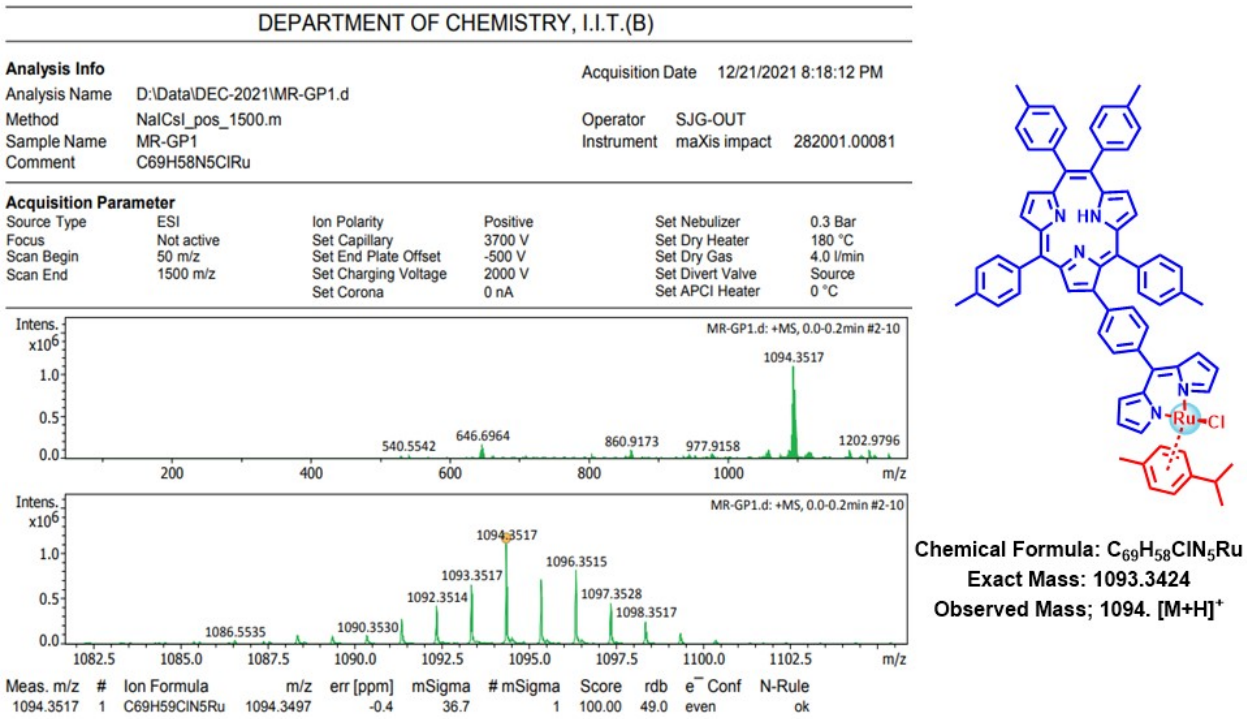



**Figure S13.** HR mass spectrum of the compound **7.**

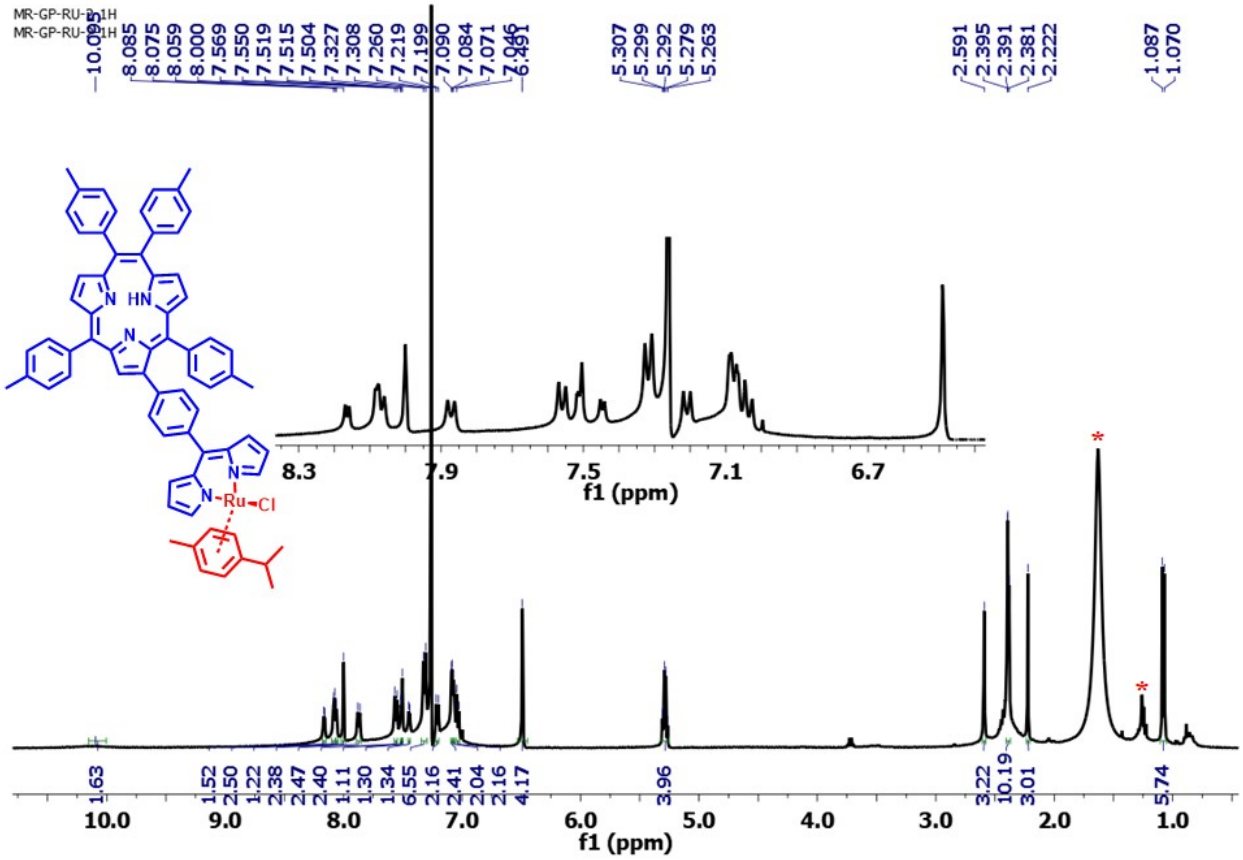
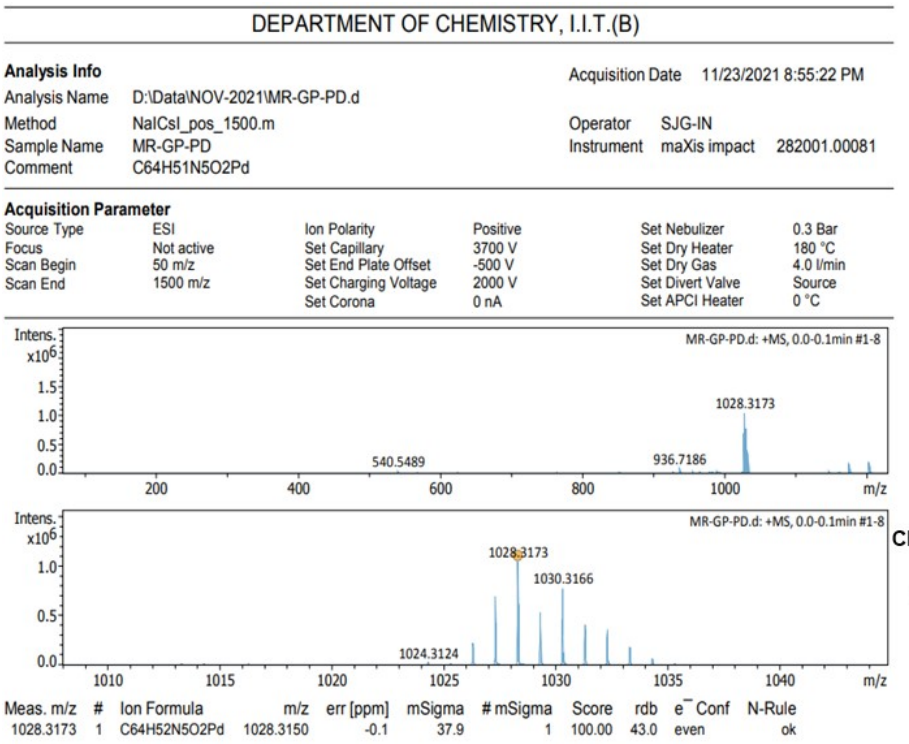
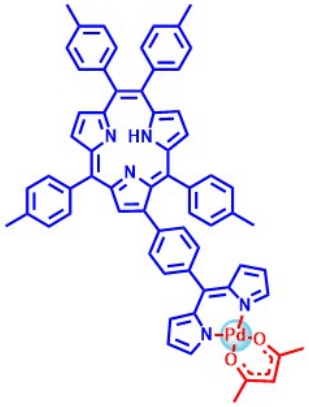



**Figure S14.** $^{1}H$ NMR spectrum of the compound **7** recorded in $CDCl_3$ in 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



**Chemical Formula: $C_{64}H_{51}N_5O_2Pd$**
**Exact Mass: 1027.3078**
**Observed Mass: 1028. $[M+H]^+$**

**Figure S15.** HR mass spectrum of the compound **8.**

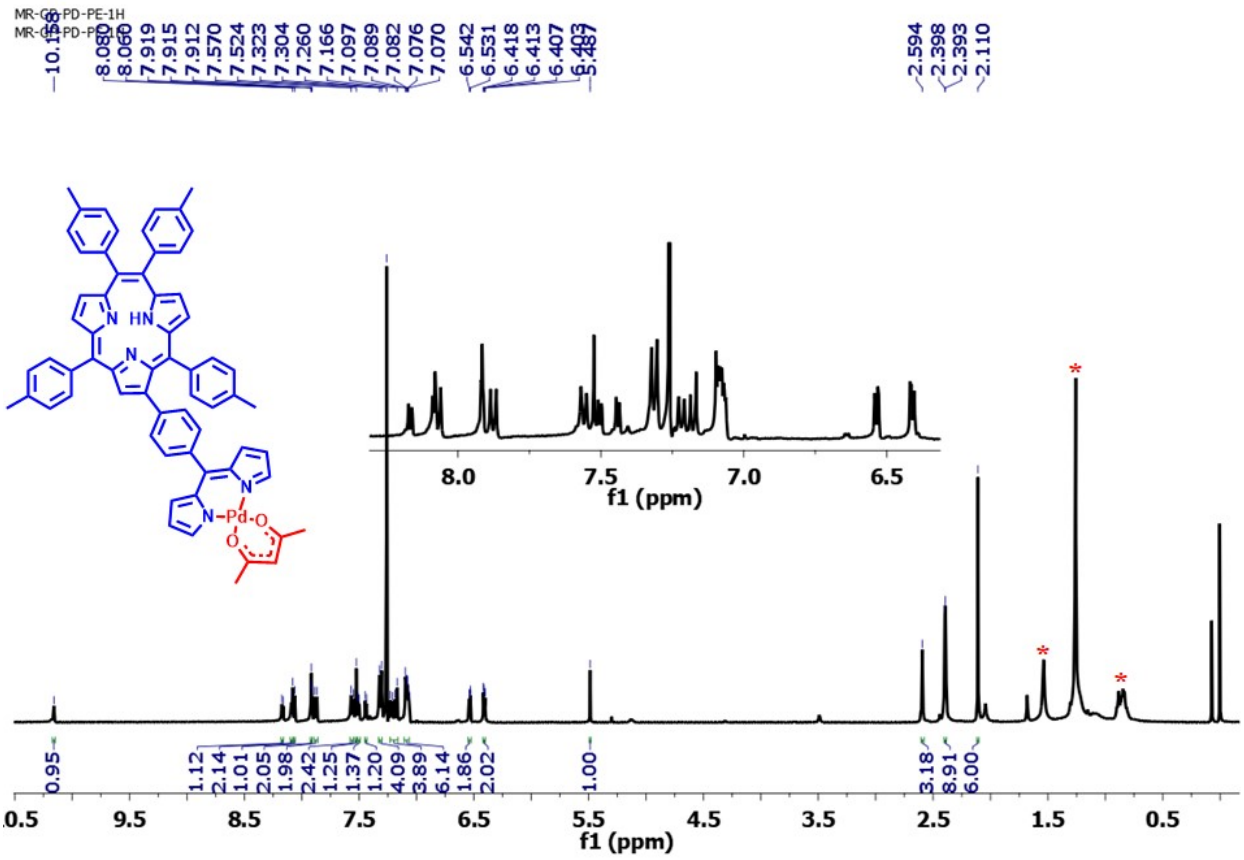



**Figure S16.** $^{1}H$ NMR spectrum of the compound **8** recorded in $CDCl_3$ in 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

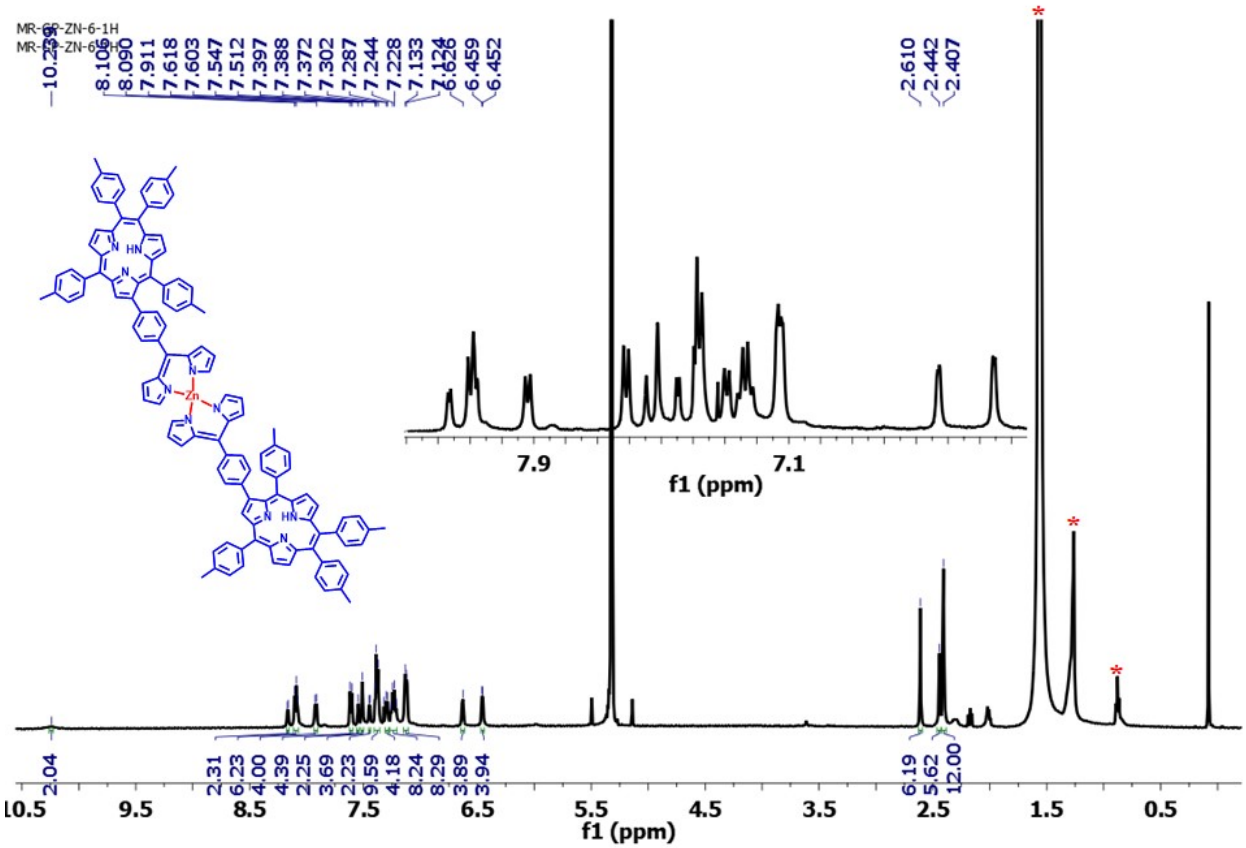



**Figure S17.** $^{1}$H NMR spectrum of the compound **9** recorded in $CD_2Cl_2$ in 500 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

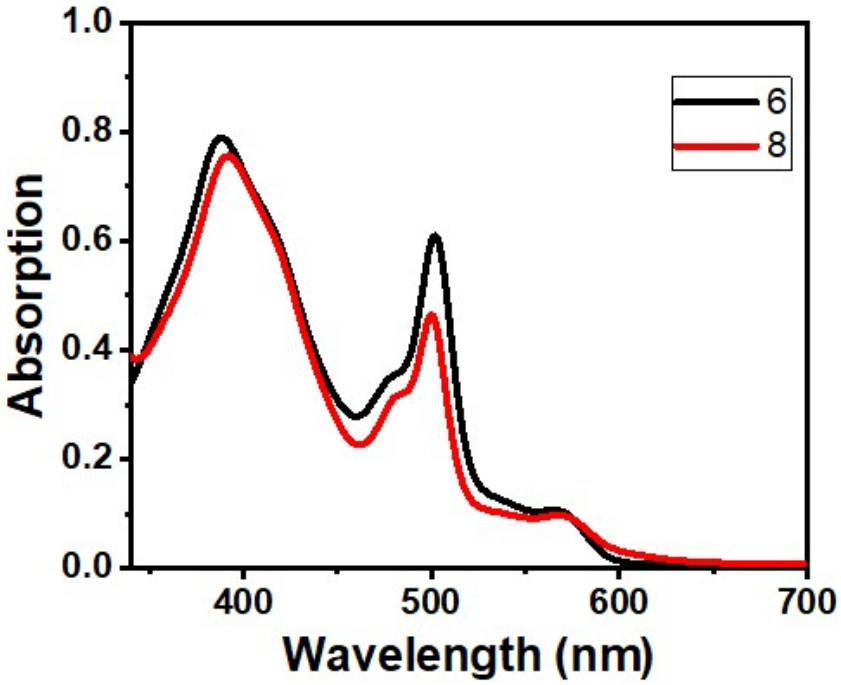



**Figure S18.** Comparison of absorption spectra of compounds **6** and **8** ($1 \times 10^{-5}$ M) recorded in $CHCl_3$.

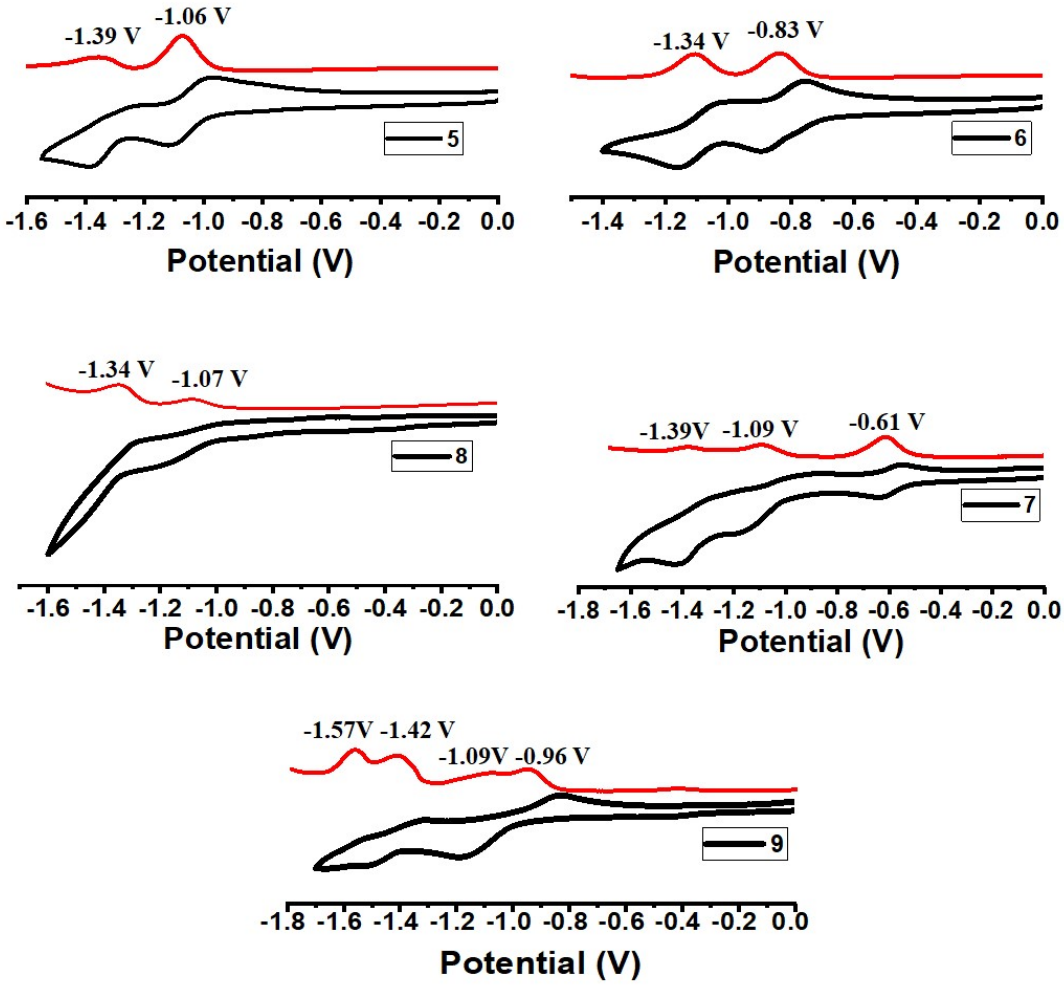



**Figure S19.** Reduction waves of the Cyclic Voltammogram (black line) along with differential pulse voltammogram (red line) of compound **5**, **6**, **7**, **8** and **9** recorded in dry dichloromethane with 0.1M TBAP as supporting electrolyte and saturated calomel electrode (SCE) as the reference electrode at a scan rate of 50 mV/s.

**Table S1.** $S_0$ optimized geometry of the compound **5** at B3LYP/6-31g (d,p) level of theory
# Sum of imaginary frequencies = 0
# Total Energy (hartree) = -2549.180243

| Atom | X | V | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| C | 0.668 | 0.08557 | 0.89629 | C | 3.46858 | -3.0193 | 2.3931 |
| C | 1.84833 | 0.92805 | 0.58232 | C | 3.62896 | -4.1567 | 1.58706 |
| C | 1.36259 | 2.21481 | 0.53746 | C | 2.73731 | -4.3345 | 0.52159 |
| C | -0.0703 | 2.13911 | 0.78454 | C | 1.71063 | -3.424 | 0.27904 |
| N | -0.4098 | 0.87187 | 1.05874 | H | 2.33833 | -1.2367 | 2.79562 |
| H | 1.92218 | 3.09549 | 0.25221 | H | 4.14897 | -2.8537 | 3.22459 |
| C | -1.0948 | 3.11372 | 0.57696 | H | 2.85051 | -5.1964 | -0.131 |
| C | 0.44069 | -1.325 | 0.88959 | H | 1.04681 | -3.5754 | -0.5661 |
| C | -3.09 | -1.7714 | 0.22848 | C | -1.2752 | 5.42139 | -0.4164 |
| C | -2.7177 | -3.1439 | 0.47465 | C | -0.9272 | 6.76906 | -0.4322 |
| C | -1.3776 | -3.1665 | 0.7753 | C | -0.0364 | 7.30163 | 0.50917 |
| C | -0.88 | -1.8175 | 0.6957 | C | 0.49464 | 6.43268 | 1.47257 |
| N | -1.9602 | -1.0377 | 0.35507 | C | 0.15498 | 5.08356 | 1.49242 |
| H | -3.3886 | -3.988 | 0.44294 | C | -0.7435 | 4.54805 | 0.55027 |
| H | -0.7904 | -4.0319 | 1.0432 | H | -1.9472 | 5.02907 | -1.1724 |
| C | -4.4027 | -1.2564 | -0.0659 | H | -1.3485 | 7.41857 | -1.1955 |
| C | -4.848 | 0.0779 | -0.1513 | H | 1.17858 | 6.8211 | 2.2232 |
| C | -2.4304 | 2.69085 | 0.35214 | H | 0.56386 | 4.43497 | 2.26063 |
| C | -3.6484 | 3.49011 | 0.41309 | C | 4.30888 | 1.22235 | 0.8763 |
| C | -4.6907 | 2.63266 | 0.21945 | C | 3.23828 | 0.56059 | 0.25161 |
| C | -4.1072 | 1.3046 | 0.0262 | C | 3.54323 | -0.3943 | -0.7335 |
| N | -2.7702 | 1.39175 | 0.09527 | C | 5.93077 | -0.0207 | -0.4428 |
| H | -1.993 | 0.02214 | 0.28185 | C | 5.62868 | 0.94017 | 0.53619 |
| H | -3.7016 | 4.54683 | 0.63367 | H | 4.09688 | 1.95369 | 1.65035 |
| H | -5.7446 | 2.86846 | 0.23153 | H | 2.73657 | -0.9011 | -1.252 |
| C | -6.3128 | 0.31295 | -0.4146 | H | 6.43932 | 1.44868 | 1.04766 |
| C | -6.729 | 0.86299 | -1.6346 | C | 0.36242 | 8.75684 | 0.46942 |
| C | -8.0766 | 1.12396 | -1.8809 | H | 0.55884 | 9.14584 | 1.47305 |
| C | -9.0537 | 0.85846 | -0.9144 | H | -0.4166 | 9.37352 | 0.01185 |
| C | -8.6323 | 0.32675 | 0.3117 | H | 1.27801 | 8.89948 | -0.1184 |
| C | -7.2883 | 0.05566 | 0.55815 | C | 4.7184 | -5.1614 | 1.8761 |
| H | -5.9882 | 1.08988 | -2.3959 | H | 4.50194 | -5.7259 | 2.79126 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -8.3718 | 1.54643 | -2.8384 | H | 5.68701 | -4.6719 | 2.02206 |
| H | -9.3671 | 0.12507 | 1.08749 | H | 4.82241 | -5.8826 | 1.06092 |
| H | -6.9893 | -0.3518 | 1.51856 | C | 4.8607 | -0.6843 | -1.069 |
| C | -10.516 | 1.11668 | -1.189 | H | 5.06883 | -1.4134 | -1.8451 |
| H | -11.043 | 1.43817 | -0.2851 | C | 7.34071 | -0.3262 | -0.7999 |
| H | -10.65 | 1.88917 | -1.9518 | C | 7.75283 | -1.7007 | -0.744 |
| H | -11.018 | 0.21063 | -1.5508 | C | 7.06786 | -2.8538 | -0.3157 |
| C | -5.9243 | -3.1041 | 0.77357 | N | 9.02244 | -2.1083 | -1.112 |
| C | -5.4165 | -2.3505 | -0.2931 | C | 7.94722 | -3.9423 | -0.4391 |
| C | -5.8428 | -2.6724 | -1.5882 | H | 6.05137 | -2.8787 | 0.04717 |
| C | -6.7527 | -3.7052 | -1.8057 | C | 9.15292 | -3.4412 | -0.9294 |
| C | -7.2695 | -4.4543 | -0.7408 | H | 9.70797 | -1.3951 | -1.3881 |
| C | -6.8352 | -4.1366 | 0.55184 | H | 7.74178 | -4.9764 | -0.2026 |
| H | -5.6003 | -2.8802 | 1.78611 | H | 10.0791 | -3.9504 | -1.1545 |
| H | -5.4547 | -2.1095 | -2.4316 | C | 8.20122 | 0.70532 | -1.1642 |
| H | -7.0635 | -3.9359 | -2.8218 | C | 7.88505 | 2.10418 | -1.374 |
| H | -7.2139 | -4.7046 | 1.39823 | N | 9.56137 | 0.49036 | -1.4457 |
| C | -8.2808 | -5.5507 | -0.9773 | C | 9.04965 | 2.7085 | -1.7656 |
| H | -9.3029 | -5.1517 | -0.99 | H | 6.91037 | 2.55706 | -1.2655 |
| H | -8.1162 | -6.0477 | -1.9382 | C | 10.0448 | 1.66589 | -1.7913 |
| H | -8.239 | -6.3107 | -0.1914 | H | 9.20454 | 3.74905 | -2.0188 |
| C | 1.54194 | -2.2926 | 1.09508 | H | 11.0903 | 1.78151 | -2.0616 |
| C | 2.45075 | -2.1036 | 2.15255 | | | | |

**Table S2.** $S_0$ optimized geometry of the compound **6** at B3LYP/6-31g (d,p) level of theory
# Sum of imaginary frequencies = 0
# Total Energy (hartree) = -2773.312036

| Atom | X | Y | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| C | 0.107401 | 0.176725 | 0.991249 | C | 3.189447 | -3.93465 | 1.871256 |
| C | 1.26815 | 1.046795 | 0.683875 | C | 2.337295 | -4.17415 | 0.785812 |
| C | 0.748286 | 2.319668 | 0.610278 | C | 1.284449 | -3.31026 | 0.48825 |
| C | -0.68524 | 2.206739 | 0.832526 | H | 1.74976 | -1.03972 | 2.966017 |
| N | -0.99406 | 0.934401 | 1.121564 | H | 3.605812 | -2.57385 | 3.491594 |
| H | 1.287139 | 3.211252 | 0.31883 | H | 2.500664 | -5.04928 | 0.162057 |
| C | -1.73268 | 3.148133 | 0.587843 | H | 0.65157 | -3.50958 | -0.37058 |
| C | -0.07681 | -1.24098 | 1.005863 | C | -1.9599 | 5.440238 | -0.43235 |
| C | -3.57029 | -1.80114 | 0.249562 | C | -1.65212 | 6.797351 | -0.45327 |
| C | -3.16512 | -3.15889 | 0.526035 | C | -0.79814 | 7.364726 | 0.502235 |
| C | -1.83504 | -3.13771 | 0.867082 | C | -0.26239 | 6.520669 | 1.484747 |
| C | -1.37488 | -1.77558 | 0.782272 | C | -0.56204 | 5.162061 | 1.509958 |
| N | -2.46708 | -1.03251 | 0.398119 | C | -1.42355 | 4.591717 | 0.553916 |
| H | -3.80982 | -4.02276 | 0.486288 | H | -2.60342 | 5.021285 | -1.19883 |
| H | -1.23153 | -3.98181 | 1.165102 | H | -2.07606 | 7.427336 | -1.23132 |
| C | -4.88863 | -1.32993 | -0.08943 | H | 0.392631 | 6.936188 | 2.246515 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -5.37067 | -0.01056 | -0.20273 | H | -0.15177 | 4.533082 | 2.293596 |
| C | -3.04816 | 2.681307 | 0.334942 | C | 3.719039 | 1.415707 | 0.984921 |
| C | -4.29138 | 3.44258 | 0.355589 | C | 2.668675 | 0.707693 | 0.374936 |
| C | -5.30099 | 2.550965 | 0.144849 | C | 3.003668 | -0.2722 | -0.57612 |
| C | -4.67183 | 1.239846 | -0.01855 | C | 5.377979 | 0.154736 | -0.26678 |
| N | -3.34036 | 1.369063 | 0.084225 | C | 5.047383 | 1.150882 | 0.668363 |
| H | -2.52964 | 0.024852 | 0.308672 | H | 3.483668 | 2.16791 | 1.731497 |
| H | -4.38315 | 4.499307 | 0.562949 | H | 2.213067 | -0.80879 | -1.08852 |
| H | -6.36168 | 2.753604 | 0.12723 | H | 5.841017 | 1.691657 | 1.173361 |
| C | -6.83349 | 0.17781 | -0.50977 | C | -0.44327 | 8.831053 | 0.456976 |
| C | -7.23047 | 0.708791 | -1.74457 | H | -0.24225 | 9.225533 | 1.457377 |
| C | -8.57758 | 0.927387 | -2.03112 | H | -1.24753 | 9.424432 | 0.012303 |
| C | -9.57385 | 0.637056 | -1.09149 | H | 0.457608 | 9.000771 | -0.14614 |
| C | -9.17235 | 0.124872 | 0.149401 | C | 4.316792 | -4.87954 | 2.212236 |
| C | -7.82846 | -0.10421 | 0.436073 | H | 4.195618 | -5.29177 | 3.220522 |
| H | -6.47522 | 0.954365 | -2.48567 | H | 5.286752 | -4.37006 | 2.18947 |
| H | -8.85746 | 1.335889 | -2.99916 | H | 4.361279 | -5.71867 | 1.512707 |
| H | -9.92281 | -0.09494 | 0.904909 | C | 4.329059 | -0.54912 | -0.88603 |
| H | -7.54533 | -0.49743 | 1.407199 | H | 4.560397 | -1.2928 | -1.64111 |
| C | -11.0347 | 0.84894 | -1.4104 | C | 6.790982 | -0.14589 | -0.58311 |
| H | -11.6016 | 1.137013 | -0.51977 | C | 7.258317 | -1.47491 | -0.54836 |
| H | -11.1712 | 1.628624 | -2.16555 | C | 6.597035 | -2.69009 | -0.22479 |
| H | -11.4924 | -0.06792 | -1.80278 | N | 8.584353 | -1.77854 | -0.85118 |
| C | -6.37712 | -3.2158 | 0.72462 | C | 7.530202 | -3.71169 | -0.35558 |
| C | -5.86162 | -2.45663 | -0.33438 | H | 5.562011 | -2.7807 | 0.069507 |
| C | -6.23913 | -2.80356 | -1.63818 | C | 8.743 | -3.10561 | -0.73645 |
| C | -7.10988 | -3.86606 | -1.87177 | H | 7.374092 | -4.76912 | -0.19706 |
| C | -7.63472 | -4.62095 | -0.81487 | H | 9.707521 | -3.55949 | -0.91789 |
| C | -7.24885 | -4.27814 | 0.486649 | C | 7.672337 | 0.895154 | -0.93332 |
| H | -6.09074 | -2.9726 | 1.744023 | C | 7.433724 | 2.274922 | -1.17551 |
| H | -5.84387 | -2.23653 | -2.47553 | N | 9.015175 | 0.641454 | -1.20526 |
| H | -7.38312 | -4.11576 | -2.89419 | C | 8.638784 | 2.835608 | -1.57855 |
| H | -7.63496 | -4.84973 | 1.32722 | H | 6.477792 | 2.768587 | -1.08445 |
| C | -8.6044 | -5.75031 | -1.07005 | C | 9.586177 | 1.793162 | -1.58789 |
| H | -9.63658 | -5.382 | -1.12439 | H | 8.826727 | 3.863772 | -1.85253 |
| H | -8.39159 | -6.25533 | -2.01724 | H | 10.6327 | 1.821992 | -1.85829 |
| H | -8.56804 | -6.49775 | -0.27202 | B | 9.73713 | -0.74323 | -1.09023 |
| C | 1.048997 | -2.16562 | 1.26778 | F | 10.40418 | -1.02777 | -2.26663 |
| C | 1.916619 | -1.91585 | 2.347703 | F | 10.5967 | -0.74562 | -0.00553 |
| C | 2.959952 | -2.78484 | 2.642977 | | | | |

**Table S3.** $S_0$ optimized geometry of the compound **7** at B3LYP/6-31g (d,p) and LANL2DZ level of theory

# Sum of imaginary frequencies = 0

# Total Energy (hartree) = -3492.202984

| Atom | X | Y | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| Ru | -8.0148 | -0.1195 | -0.649 | C | 8.4789 | -3.2752 | 0.5447 |
| Cl | -8.928 | 2.0465 | -0.0188 | H | 8.7654 | -2.6228 | 1.3634 |
| N | 4.3276 | -0.9502 | 0.4391 | C | -7.1873 | -0.3052 | 2.2698 |
| N | 5.5635 | 1.302 | 0.1802 | H | -8.2261 | -0.513 | 2.4861 |
| H | 4.8161 | 0.5657 | 0.338 | C | 9.1528 | -4.4796 | 0.3538 |
| N | 3.2452 | 1.2553 | 1.3058 | H | 9.9601 | -4.751 | 1.0302 |
| N | -6.5121 | 0.9217 | -1.6383 | C | -5.4302 | 2.0297 | -3.3041 |
| N | -6.7992 | 0.0282 | 1.0323 | H | -5.2793 | 2.5478 | -4.2412 |
| C | 5.4344 | 2.6646 | 0.3075 | C | -0.7764 | -3.3334 | 1.5481 |
| C | 3.229 | -1.5177 | 1.0322 | H | -1.1085 | -4.2258 | 1.023 |
| C | 5.3024 | -1.8666 | 0.3851 | C | 0.3851 | -2.6863 | 1.1294 |
| C | 3.0712 | 2.5513 | 0.9755 | H | 0.9374 | -3.0675 | 0.2762 |
| C | 2.0481 | -0.7992 | 1.3383 | C | -4.5033 | 1.7927 | -2.3083 |
| C | 4.0843 | 4.7851 | 0.4475 | H | -3.4669 | 2.0958 | -2.2842 |
| C | 0.8312 | -1.5178 | 1.7707 | C | -6.6534 | 1.4797 | -2.8446 |
| C | 7.3056 | -0.4032 | -0.3217 | H | -7.6164 | 1.4924 | -3.3366 |
| C | 3.5304 | -2.9131 | 1.3353 | C | -2.2516 | 0.2672 | -0.4479 |
| H | 2.8712 | -3.6084 | 1.8353 | H | -2.577 | -0.4778 | -1.1677 |
| C | 6.8305 | 0.9462 | -0.1388 | C | 11.3833 | -0.4952 | -1.8268 |
| C | 4.206 | 3.3208 | 0.6054 | C | 10.2944 | -0.7985 | -2.656 |
| C | 6.7344 | 3.2134 | 0.04 | H | 10.4711 | -1.0558 | -3.6979 |
| H | 6.9872 | 4.2629 | 0.0779 | C | -7.8784 | -1.9089 | -2.022 |
| C | 8.724 | -0.4531 | -0.832 | H | -7.0225 | -2.1382 | -2.6448 |
| C | 4.6167 | 5.4664 | -0.6627 | C | 8.8075 | -5.3487 | -0.6905 |
| H | 5.1178 | 4.9025 | -1.4427 | C | -6.0924 | -0.3094 | 3.1673 |
| C | 1.6514 | 2.827 | 0.8068 | H | -6.1378 | -0.5351 | 4.224 |
| H | 1.2071 | 3.764 | 0.4982 | C | -1.0781 | -1.6889 | 3.2723 |
| C | -0.4435 | 1.41 | 0.7135 | H | -1.6381 | -1.2975 | 4.1183 |
| C | 4.8157 | -3.1323 | 0.9395 | C | -1.5326 | -2.8465 | 2.6214 |
| H | 5.3872 | -4.0437 | 1.0384 | C | -7.9479 | -2.412 | -0.7045 |
| C | 4.4699 | 6.8449 | -0.7932 | C | -8.9101 | -1.0646 | -2.5557 |
| H | 4.8778 | 7.3432 | -1.6692 | H | -8.8062 | -0.6834 | -3.5658 |
| C | 3.3911 | 5.5418 | 1.411 | C | 3.6642 | 9.0982 | 0.0456 |
| H | 2.9771 | 5.0384 | 2.279 | H | 3.6734 | 9.4129 | -1.0022 |
| C | 6.6488 | -1.6254 | -0.0879 | H | 4.4964 | 9.6094 | 0.5462 |
| C | 2.0613 | 0.6369 | 1.2505 | H | 2.7391 | 9.4623 | 0.5025 |
| C | 7.4266 | -2.8973 | -0.3013 | C | -9.9954 | -0.6498 | -1.7692 |
| C | 7.5853 | 2.1693 | -0.2441 | C | -9.0755 | -1.9999 | 0.0925 |
| H | 8.6336 | 2.2362 | -0.4901 | H | -9.1264 | -2.3159 | 1.1292 |
| C | 7.0653 | -3.7752 | -1.3332 | C | -6.9224 | -3.3596 | -0.1062 |
| H | 6.2398 | -3.5135 | -1.9893 | H | -6.8051 | -3.0621 | 0.9438 |
| C | 3.7917 | 7.5995 | 0.1741 | C | -5.5397 | -3.2809 | -0.7665 |
| C | -1.4069 | 2.1895 | 1.375 | H | -5.5578 | -3.6575 | -1.7955 |
| H | -1.0799 | 2.9424 | 2.0864 | H | -4.8284 | -3.8984 | -0.2098 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 8.989 | -0.7758 | -2.1706 | H | -5.1616 | -2.2552 | -0.7773 |
| H | 8.1628 | -1.0156 | -2.8333 | C | -7.4685 | -4.8029 | -0.1311 |
| C | 0.0741 | -1.0339 | 2.855 | H | -8.4361 | -4.88 | 0.3752 |
| H | 0.4085 | -0.1418 | 3.3748 | H | -6.7715 | -5.4825 | 0.37 |
| C | 11.1164 | -0.1691 | -0.4921 | H | -7.5997 | -5.1526 | -1.1612 |
| H | 11.9414 | 0.0664 | 0.1761 | C | 9.5678 | -6.6344 | -0.9155 |
| C | 3.252 | 6.92 | 1.2751 | H | 8.964 | -7.3677 | -1.4582 |
| H | 2.7181 | 7.4799 | 2.0391 | H | 9.8801 | -7.0867 | 0.0311 |
| C | -0.8933 | 0.4528 | -0.2116 | H | 10.4766 | -6.4596 | -1.5053 |
| H | -0.1685 | -0.1466 | -0.7527 | C | -2.8068 | -3.5251 | 3.0625 |
| C | -3.212 | 1.0223 | 0.2429 | H | -3.6713 | -2.8645 | 2.9241 |
| C | -5.1834 | 1.1051 | -1.2531 | H | -2.7708 | -3.7891 | 4.1258 |
| C | -2.7686 | 1.9946 | 1.1516 | H | -2.9882 | -4.443 | 2.496 |
| H | -3.4974 | 2.6007 | 1.6808 | C | 12.7945 | -0.5011 | -2.3662 |
| C | -4.6682 | 0.7823 | 0.011 | H | 12.9914 | 0.3889 | -2.977 |
| C | 0.9962 | 1.6264 | 0.9543 | H | 12.9762 | -1.3735 | -3.0027 |
| C | 9.8096 | -0.1443 | -0.002 | H | 13.5317 | -0.5137 | -1.5583 |
| H | 9.6298 | 0.1111 | 1.0388 | C | 10.0502 | -1.1254 | -0.4066 |
| C | -5.4295 | 0.2886 | 1.0864 | H | -0.8356 | -0.7627 | 0.2468 |
| C | 7.749 | -4.9755 | -1.5273 | C | -1.0427 | 0.3018 | -2.2737 |
| H | 7.4508 | -5.6343 | -2.3396 | H | -1.0699 | 1.1894 | -1.6327 |
| C | -4.9822 | 0.0495 | 2.4231 | H | -12.031 | -0.1719 | -2.2578 |
| H | -3.9655 | 0.164 | 2.7686 | H | -0.8304 | 0.6203 | -3.2971 |

**Table S4.** $S_0$ optimized geometry of the compound **8** at B3LYP/6-31g (d,p) and LANL2DZ level of theory

# Sum of imaginary frequencies = 1

# Total Energy (hartree) = -3020.547334

| Atom | X | Y | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| C | 7.055117 | -0.1282 | -0.35867 | C | -5.66394 | -1.07575 | 0.173245 |
| C | 6.53875 | -1.4333 | -0.22792 | N | -6.991 | -1.44213 | -0.04771 |
| C | 7.45924 | -2.5875 | -0.53805 | Pd | -8.53788 | -0.26283 | -0.60577 |
| C | 5.227818 | -1.8662 | 0.183796 | O | -9.79783 | -1.87933 | -0.50727 |
| C | 6.406937 | 1.141266 | -0.12751 | O | -10.082 | 0.968818 | -1.15769 |
| C | 8.50397 | 0.018293 | -0.7445 | C | -11.2927 | 0.590927 | -1.30764 |
| C | 7.761988 | -2.92403 | -1.86454 | C | -11.0499 | -1.83791 | -0.75506 |
| C | 8.590339 | -4.00581 | -2.15701 | C | -11.7946 | -0.70855 | -1.13139 |
| C | 9.142012 | -4.79481 | -1.13866 | C | -12.2394 | 1.699407 | -1.71899 |
| C | 8.835782 | -4.45895 | 0.18573 | C | -11.7529 | -3.17212 | -0.61277 |
| C | 8.006612 | -3.37667 | 0.482557 | H | 7.348117 | -2.32802 | -2.67243 |
| C | 8.850117 | 0.546658 | -1.9958 | H | 8.811826 | -4.24169 | -3.19533 |
| C | 10.18669 | 0.720042 | -2.35633 | H | 9.254066 | -5.04901 | 0.997877 |
| C | 11.22287 | 0.389635 | -1.47483 | H | 7.785615 | -3.13623 | 1.51892 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 10.87353 | -0.1265 | -0.21928 | H | 8.063909 | 0.818377 | -2.69465 |
| C | 9.540303 | -0.31012 | 0.140886 | H | 10.42694 | 1.120673 | -3.33843 |
| N | 4.15993 | -1.06417 | 0.402653 | H | 11.65721 | -0.38919 | 0.487606 |
| C | 3.068813 | -1.7759 | 0.844856 | H | 9.298216 | -0.7114 | 1.119943 |
| C | 3.489395 | -3.15259 | 0.893343 | H | 4.25124 | -0.00756 | 0.316435 |
| C | 4.796375 | -3.21295 | 0.47417 | H | 2.87722 | -3.9799 | 1.219987 |
| C | 7.08375 | 2.431832 | 0.005224 | H | 5.409839 | -4.09643 | 0.390845 |
| C | 6.114812 | 3.35216 | 0.278149 | H | 8.147376 | 2.603184 | -0.07344 |
| C | 4.849991 | 2.628467 | 0.326138 | H | 6.250451 | 4.404711 | 0.483683 |
| N | 5.087737 | 1.309879 | 0.05331 | H | 0.535187 | 3.291995 | 0.576988 |
| C | 3.565535 | 3.133727 | 0.657126 | H | 10.6453 | -5.79031 | -2.33809 |
| C | 1.801996 | -1.20386 | 1.148133 | H | 10.67292 | -6.23757 | -0.62503 |
| C | 2.50573 | 2.223539 | 0.958721 | H | 9.414031 | -6.87201 | -1.68705 |
| C | 1.064056 | 2.382274 | 0.828265 | H | 12.80162 | 0.634128 | -2.93615 |
| C | 0.509417 | 1.126435 | 0.928012 | H | 13.04476 | 1.559763 | -1.453 |
| C | 1.660507 | 0.218295 | 1.154807 | H | 13.31145 | -0.18336 | -1.45038 |
| N | 2.792174 | 0.93997 | 1.218446 | H | 0.094823 | -0.96123 | 3.208899 |
| C | 3.30107 | 4.586743 | 0.646437 | H | -1.7714 | -2.44567 | 3.832672 |
| C | 0.666457 | -2.09703 | 1.468899 | H | -0.93184 | -4.92841 | 0.430693 |
| C | 10.01698 | -5.98289 | -1.46275 | H | 0.927565 | -3.43863 | -0.19944 |
| C | 12.66966 | 0.608059 | -1.85046 | H | 2.11315 | 4.556069 | 2.445361 |
| C | -0.13025 | -1.82972 | 2.598033 | H | 1.633701 | 6.97421 | 2.431316 |
| C | -1.17996 | -2.67117 | 2.948618 | H | 3.929127 | 7.408162 | -1.17154 |
| C | -1.48498 | -3.80954 | 2.18618 | H | 4.388675 | 4.987878 | -1.17202 |
| C | -0.70478 | -4.06499 | 1.050968 | H | -3.52178 | -4.17673 | 2.8221 |
| C | 0.353299 | -3.22933 | 0.697566 | H | -2.8378 | -5.45526 | 1.804335 |
| C | 2.506904 | 5.17781 | 1.647423 | H | -2.34273 | -5.30244 | 3.493705 |
| C | 2.243638 | 6.544616 | 1.640241 | H | 1.535293 | 9.098847 | 1.122957 |
| C | 2.755356 | 7.377934 | 0.635732 | H | 2.477649 | 9.27633 | -0.36668 |
| C | 3.536682 | 6.78913 | -0.36833 | H | 3.272029 | 9.399405 | 1.203679 |
| C | 3.80669 | 5.423483 | -0.36642 | H | -0.62345 | -0.6676 | -0.8044 |
| C | -2.60727 | -4.73408 | 2.593496 | H | -3.0231 | -1.0348 | -1.22085 |
| C | 2.492109 | 8.864413 | 0.646884 | H | -3.99406 | 1.94451 | 1.715709 |
| C | -0.92136 | 0.838681 | 0.71019 | H | -1.5869 | 2.296739 | 2.148537 |
| C | -1.35652 | -0.10458 | -0.23655 | H | -8.65262 | 2.733556 | -1.38598 |
| C | -2.71168 | -0.31154 | -0.47386 | H | -8.07768 | -3.22597 | 0.174514 |
| C | -3.68724 | 0.425376 | 0.218523 | H | -4.37902 | 2.942614 | -0.73492 |
| C | -3.25677 | 1.373425 | 1.160296 | H | -6.50504 | 4.415171 | -1.51559 |
| C | -1.9001 | 1.572021 | 1.402759 | H | -5.70868 | -4.28726 | 1.020166 |
| C | -5.14085 | 0.213246 | -0.03996 | H | -3.92694 | -2.25514 | 0.934296 |
| C | -7.62163 | 2.525247 | -1.1395 | H | -12.8539 | -0.85345 | -1.30226 |
| C | -7.11845 | -2.73753 | 0.267007 | H | -12.208 | 2.498012 | -0.97085 |
| N | -7.26506 | 1.305651 | -0.71705 | H | -11.9015 | 2.130745 | -2.66688 |
| C | -5.8912 | 1.318939 | -0.47963 | H | -13.2679 | 1.351773 | -1.83017 |
| C | -5.41007 | 2.627869 | -0.79508 | H | -11.6137 | -3.54791 | 0.406082 |
| C | -6.49756 | 3.380766 | -1.20043 | H | -12.8207 | -3.10742 | -0.82826 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -5.88368 | -3.26718 | 0.706693 | H | -11.2923 | -3.89785 | -1.29096 |
| C | -4.97075 | -2.22751 | 0.658672 | | | | |

**Table S5.** $S_0$ optimized geometry of the compound **9** at B3LYP/6-31g (d,p) and LANL2DZ level of theory

# Total Energy (hartree) = -5162.521603

| Atom | X | Y | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| C | 10.34134 | -0.28142 | -0.80079 | C | -9.15497 | -1.0547 | -0.36816 |
| C | 9.221735 | 0.564007 | -1.28949 | C | -9.8214 | -2.22252 | -0.67855 |
| C | 9.807731 | 1.735128 | -1.72613 | C | -11.2416 | -1.93423 | -0.64864 |
| C | 11.23693 | 1.617241 | -1.51709 | N | -11.4063 | -0.64621 | -0.24288 |
| N | 11.48203 | 0.40565 | -0.94807 | H | -9.3582 | -3.13755 | -1.02587 |
| H | 9.282795 | 2.578173 | -2.15659 | C | -12.4479 | -2.60038 | -0.98232 |
| C | 12.38799 | 2.419283 | -1.71537 | C | -10.2031 | 1.309259 | 0.37462 |
| C | 10.44407 | -1.60355 | -0.23981 | C | -13.6813 | 2.350824 | 0.541776 |
| C | 13.89837 | -1.99196 | 0.833152 | C | -13.031 | 3.616154 | 0.803548 |
| C | 13.43164 | -3.35009 | 0.989358 | C | -11.6708 | 3.415293 | 0.815005 |
| C | 12.10015 | -3.39554 | 0.650886 | C | -11.4201 | 2.026105 | 0.522435 |
| C | 11.68373 | -2.06732 | 0.274897 | N | -12.6622 | 1.455355 | 0.387246 |
| N | 12.79959 | -1.28004 | 0.435854 | H | -13.5453 | 4.553409 | 0.956471 |
| H | 14.05194 | -4.18275 | 1.287337 | H | -10.9088 | 4.159913 | 0.99388 |
| H | 11.46806 | -4.27157 | 0.628587 | C | -15.0741 | 2.020086 | 0.558903 |
| C | 15.1883 | -1.43308 | 1.094573 | C | -15.5599 | 0.724574 | 0.200155 |
| C | 15.53977 | -0.11309 | 0.665017 | C | -13.4775 | -1.61787 | -1.31381 |
| C | 13.59632 | 1.597674 | -1.66597 | C | -13.2418 | -0.51173 | -2.24385 |
| C | 13.75281 | 0.351009 | -2.41397 | C | -14.137 | 0.455706 | -1.9099 |
| C | 14.65211 | -0.3927 | -1.71623 | C | -14.86 | -0.06196 | -0.76787 |
| C | 14.99219 | 0.397905 | -0.55101 | N | -14.5382 | -1.38203 | -0.51795 |
| N | 14.44189 | 1.663614 | -0.61985 | H | -12.6884 | 0.45008 | 0.172308 |
| H | 12.75207 | -0.32179 | 0.075983 | H | -12.4952 | -0.50145 | -3.02808 |
| H | 13.23626 | 0.101244 | -3.33209 | H | -14.2691 | 1.434635 | -2.35188 |
| H | 15.02325 | -1.38476 | -1.93801 | C | -16.7148 | 0.106908 | 0.889691 |
| C | 16.37495 | 0.780863 | 1.4947 | C | -16.97 | 0.309486 | 2.258682 |
| C | 16.33685 | 0.746972 | 2.901863 | C | -18.0413 | -0.3149 | 2.888029 |
| C | 17.1069 | 1.620282 | 3.661011 | C | -18.9068 | -1.16303 | 2.181398 |
| C | 17.95106 | 2.562269 | 3.053212 | C | -18.6484 | -1.37511 | 0.820651 |
| C | 17.98283 | 2.605172 | 1.653354 | C | -17.5742 | -0.75764 | 0.187191 |
| C | 17.21049 | 1.736427 | 0.887899 | H | -16.3073 | 0.943673 | 2.837533 |
| H | 15.67954 | 0.042809 | 3.400836 | H | -18.2048 | -0.14996 | 3.950855 |
| H | 17.04624 | 1.578808 | 4.746493 | H | -19.2975 | -2.03531 | 0.249525 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 18.62212 | 3.330822 | 1.155336 | H | -17.3917 | -0.9408 | -0.86684 |
| H | 17.24982 | 1.791315 | -0.195 | C | -20.0898 | -1.81007 | 2.861535 |
| C | 18.80922 | 3.485504 | 3.884859 | H | -20.3642 | -2.75332 | 2.377239 |
| H | 19.10982 | 4.372906 | 3.318111 | H | -19.8815 | -2.01778 | 3.916809 |
| H | 18.28172 | 3.820228 | 4.785214 | H | -20.9736 | -1.15802 | 2.828273 |
| H | 19.72783 | 2.983021 | 4.217728 | C | -17.2013 | 3.328701 | 0.36571 |
| C | 17.49134 | -2.31931 | 1.529539 | C | -16.0167 | 3.053772 | 1.073048 |
| C | 16.13757 | -2.23893 | 1.908132 | C | -15.7779 | 3.787803 | 2.247932 |
| C | 15.74166 | -2.95272 | 3.05293 | C | -16.6783 | 4.757923 | 2.68682 |
| C | 16.6561 | -3.71574 | 3.778506 | C | -17.8509 | 5.037182 | 1.973989 |
| C | 18.00085 | -3.79522 | 3.397523 | C | -18.096 | 4.298385 | 0.807149 |
| C | 18.3991 | -3.08119 | 2.256916 | H | -17.4137 | 2.772806 | -0.543 |
| H | 17.8235 | -1.78346 | 0.645088 | H | -14.8911 | 3.577073 | 2.838752 |
| H | 14.71079 | -2.89244 | 3.389707 | H | -16.47 | 5.299824 | 3.606914 |
| H | 16.31888 | -4.2516 | 4.66319 | H | -19.0014 | 4.487932 | 0.234324 |
| H | 19.4361 | -3.12917 | 1.931128 | C | -18.8123 | 6.108232 | 2.432498 |
| C | 18.99819 | -4.60131 | 4.195842 | H | -19.854 | 5.807806 | 2.272555 |
| H | 19.64405 | -3.95035 | 4.800254 | H | -18.6845 | 6.333208 | 3.496462 |
| H | 18.49789 | -5.29413 | 4.880216 | H | -18.6586 | 7.04482 | 1.879423 |
| H | 19.65531 | -5.18692 | 3.542356 | C | -8.93744 | 2.015188 | 0.715794 |
| C | 9.320506 | -2.57153 | -0.28192 | C | -8.52595 | 3.169445 | 0.032975 |
| C | 8.659934 | -2.85042 | -1.4903 | C | -7.33812 | 3.818582 | 0.374832 |
| C | 7.646088 | -3.80378 | -1.54847 | C | -6.52527 | 3.346632 | 1.411789 |
| C | 7.245877 | -4.51162 | -0.40618 | C | -6.94709 | 2.199951 | 2.102163 |
| C | 7.892974 | -4.22128 | 0.803089 | C | -8.12539 | 1.543284 | 1.761175 |
| C | 8.913499 | -3.2748 | 0.865997 | H | -9.12847 | 3.546796 | -0.78894 |
| H | 8.958819 | -2.32596 | -2.39282 | H | -7.0347 | 4.702674 | -0.18156 |
| H | 7.161198 | -4.00795 | -2.50042 | H | -6.34167 | 1.817131 | 2.921154 |
| H | 7.591843 | -4.74209 | 1.709496 | H | -8.42919 | 0.656833 | 2.31031 |
| H | 9.392226 | -3.06034 | 1.817409 | C | -13.8249 | -4.60458 | -1.48502 |
| C | 13.54989 | 4.534676 | -2.28858 | C | -14.069 | -5.9692 | -1.39496 |
| C | 13.59532 | 5.921877 | -2.36531 | C | -13.1981 | -6.81982 | -0.69715 |
| C | 12.51615 | 6.709055 | -1.93872 | C | -12.0725 | -6.24793 | -0.08345 |
| C | 11.38757 | 6.052281 | -1.42136 | C | -11.8276 | -4.8823 | -0.15506 |
| C | 11.33773 | 4.667583 | -1.32941 | C | -12.6944 | -4.02619 | -0.86913 |
| C | 12.41657 | 3.871113 | -1.77362 | H | -14.5022 | -3.96619 | -2.0433 |
| H | 14.38971 | 3.942877 | -2.63877 | H | -14.9467 | -6.38776 | -1.88253 |
| H | 14.48071 | 6.405553 | -2.77153 | H | -11.3884 | -6.8843 | 0.473763 |
| H | 10.5432 | 6.64071 | -1.06876 | H | -10.9741 | -4.46071 | 0.366358 |
| H | 10.47295 | 4.190771 | -0.88001 | C | -7.11109 | 0.110653 | -1.25205 |
| C | 6.976142 | 0.677459 | -2.38314 | C | -7.68972 | -0.89154 | -0.45508 |
| C | 7.762605 | 0.343032 | -1.26681 | C | -6.83083 | -1.78255 | 0.20946 |
| C | 7.10219 | -0.11317 | -0.11287 | C | -4.87422 | -0.65488 | -0.68829 |
| C | 4.932364 | 0.116206 | -1.19068 | C | -5.72943 | 0.222364 | -1.37331 |
| C | 5.587887 | 0.572572 | -2.3451 | H | -7.75269 | 0.804687 | -1.7853 |
| H | 7.46446 | 1.014221 | -3.29344 | H | -7.25774 | -2.56661 | 0.828872 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 7.680782 | -0.36053 | 0.771265 | H | -5.30337 | 1.00369 | -1.99571 |
| H | 5.002297 | 0.834045 | -3.22147 | C | -13.4813 | -8.29791 | -0.58057 |
| C | 12.57424 | 8.216128 | -2.00069 | H | -12.558 | -8.87723 | -0.47293 |
| H | 11.61002 | 8.644068 | -2.29779 | H | -14.0192 | -8.67361 | -1.45767 |
| H | 13.33255 | 8.559318 | -2.71192 | H | -14.1045 | -8.51319 | 0.298344 |
| H | 12.82755 | 8.64284 | -1.02059 | C | -5.23453 | 4.038633 | 1.782798 |
| C | 6.174311 | -5.57416 | -0.47989 | H | -5.28198 | 4.455462 | 2.797204 |
| H | 6.614645 | -6.57435 | -0.59151 | H | -5.01055 | 4.861263 | 1.096316 |
| H | 5.508974 | -5.41374 | -1.33452 | H | -4.38927 | 3.339877 | 1.760415 |
| H | 5.562449 | -5.58985 | 0.42881 | C | -5.44633 | -1.66029 | 0.104689 |
| C | 5.716073 | -0.23136 | -0.07793 | H | -4.79991 | -2.35101 | 0.638469 |
| H | 5.228412 | -0.57563 | 0.829102 | C | -3.38794 | -0.51111 | -0.79272 |
| C | 3.441218 | 0.011935 | -1.14451 | C | -2.71608 | -0.11623 | 0.385796 |
| C | 2.904251 | -1.2778 | -0.93003 | C | -3.32491 | 0.242372 | 1.629596 |
| C | 3.638185 | -2.50332 | -0.84511 | N | -1.33105 | 0.026558 | 0.51841 |
| N | 1.543478 | -1.5723 | -0.78858 | C | -2.30598 | 0.592021 | 2.500671 |
| C | 2.719545 | -3.51976 | -0.64444 | H | -4.38726 | 0.246193 | 1.827183 |
| H | 4.710641 | -2.60075 | -0.93432 | C | -1.1031 | 0.442573 | 1.771559 |
| C | 1.449936 | -2.89784 | -0.61818 | H | -2.39573 | 0.914521 | 3.529671 |
| H | 2.916992 | -4.57776 | -0.53361 | H | -0.09147 | 0.625554 | 2.116937 |
| H | 0.482711 | -3.37014 | -0.48486 | C | -2.81593 | -0.77514 | -2.05543 |
| C | 2.721421 | 1.21643 | -1.31937 | C | -3.50602 | -1.2309 | -3.22318 |
| C | 3.274477 | 2.530937 | -1.43769 | N | -1.45764 | -0.64998 | -2.37016 |
| N | 1.327159 | 1.32326 | -1.37916 | C | -2.56642 | -1.36716 | -4.22998 |
| C | 2.217049 | 3.413168 | -1.57894 | H | -4.5654 | -1.43452 | -3.28515 |
| H | 4.326453 | 2.774234 | -1.40508 | C | -1.32615 | -1.00062 | -3.65639 |
| C | 1.044853 | 2.624024 | -1.53597 | H | -2.73077 | -1.69128 | -5.24908 |
| H | 2.263313 | 4.488174 | -1.69261 | H | -0.35335 | -0.98499 | -4.13576 |
| H | 0.016288 | 2.960165 | -1.61003 | Zn | 0.019994 | -0.2151 | -1.01155 |
| C | -10.2113 | -0.05931 | -0.05778 | | | | |

**Table S6:** Comparison of energy levels using B3LYP/LANL2DZ and def2-TZVP basis sets.

| Compound | B3LYP/LANL2DZ | | | def2-TZVP | | |
|---|---|---|---|---|---|---|
| | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | ΔE (eV) | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | ΔE (eV) |
| 7 | -5.1040 | -2.3584 | 2.74 | -5.3936 | -2.6669 | 2.72 |
| 8 | -5.1928 | -2.3865 | 2.80 | -5.4981 | -2.6923 | 2.80 |
| 9 | -4.7760 | -2.4640 | 2.31 | -5.0711 | -2.7826 | 2.28 |