Supporting Information

Electronic Structure of Cobalt-Corrole-Pyridine Complexes: Noninnocent Five-coordinate Co(II) Corrole-Radical States

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Contents **Page Number**

A. ^{1}H NMR spectra S2
B. Mass spectra S10
C. EPR spectra S14
D. B3LYP/STO-TZP optimized coordinates S15

A. NMR spectra

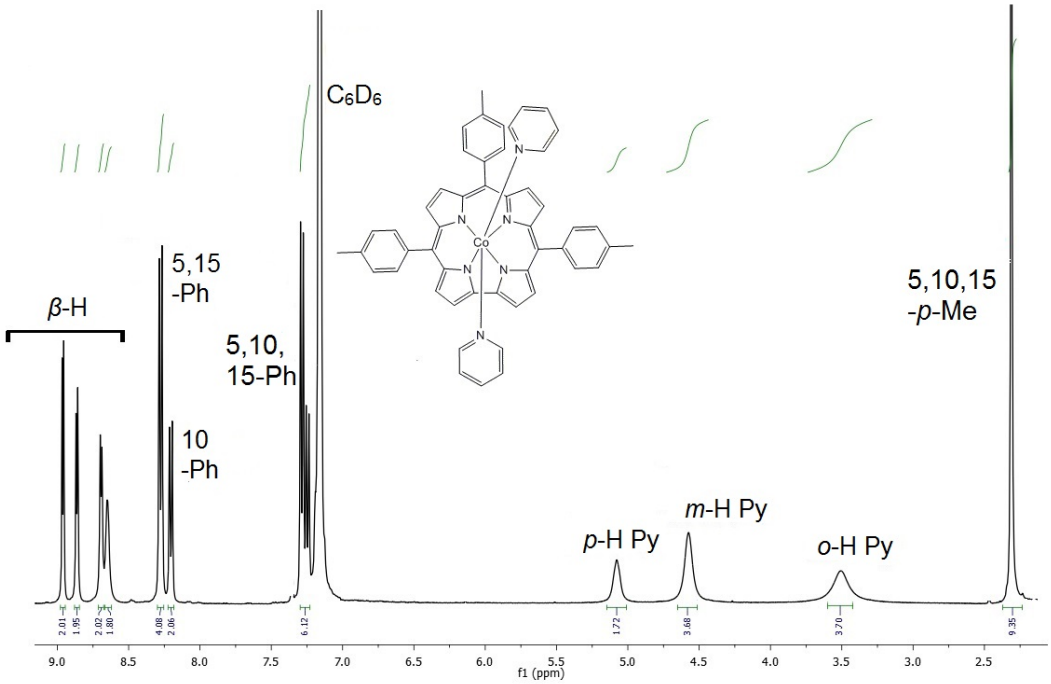


Figure. S1. ^{1}H NMR spectrum of Co[T*p*MePC](py)$_2$ in benzene-d_6.

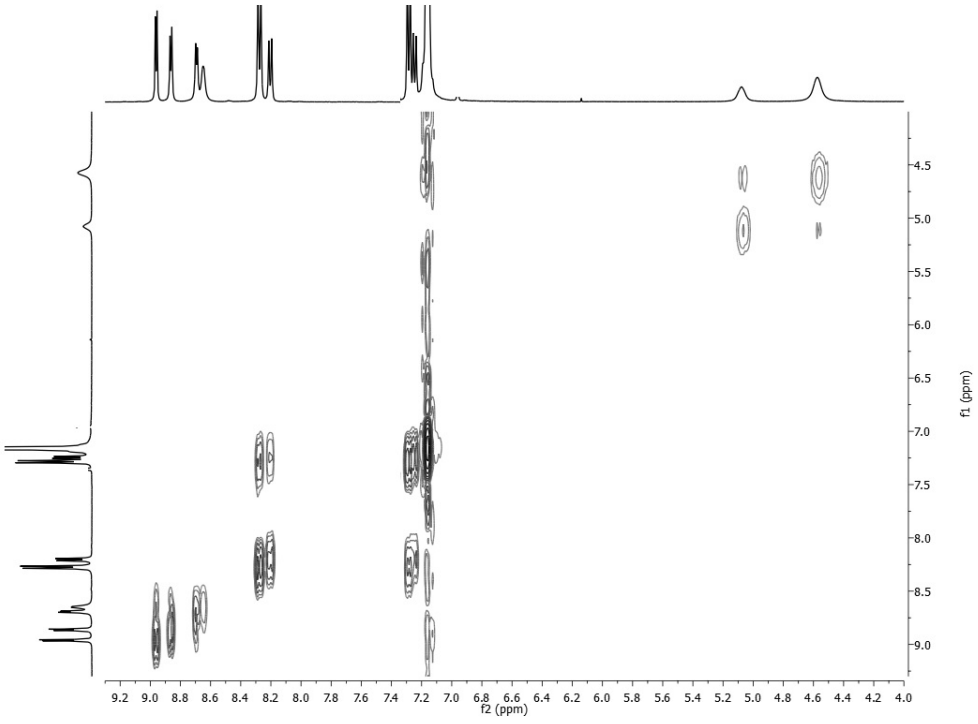


Figure. S2. ^{1}H-^{1}H gCOSY of Co[T*p*MePC](py)$_2$ in benzene-d_6.

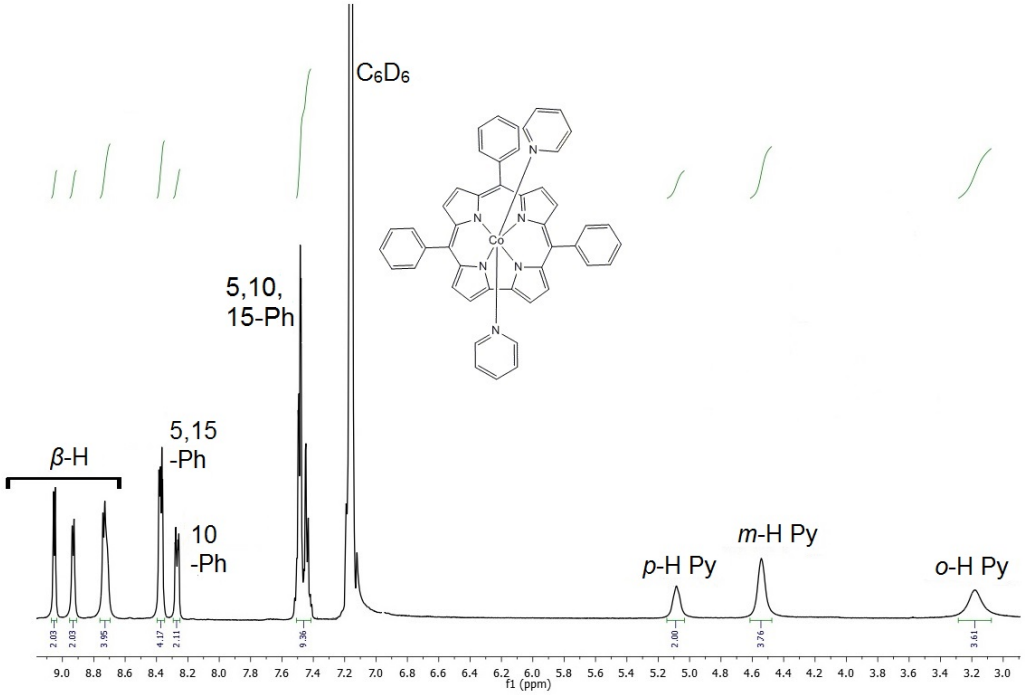


Figure. S3. ^{1}H NMR spectrum of Co[TPC](py)$_2$ in benzene-d_6.

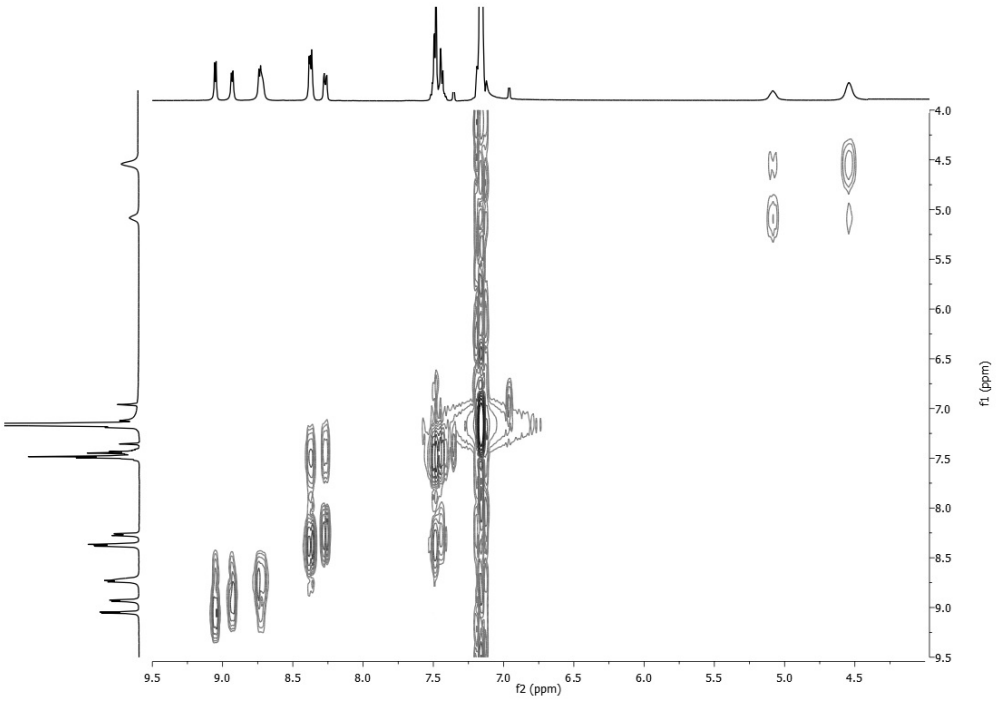


Figure. S4. ^{1}H-^{1}H gCOSY of Co[TPC](py)$_2$ in benzene-d_6.

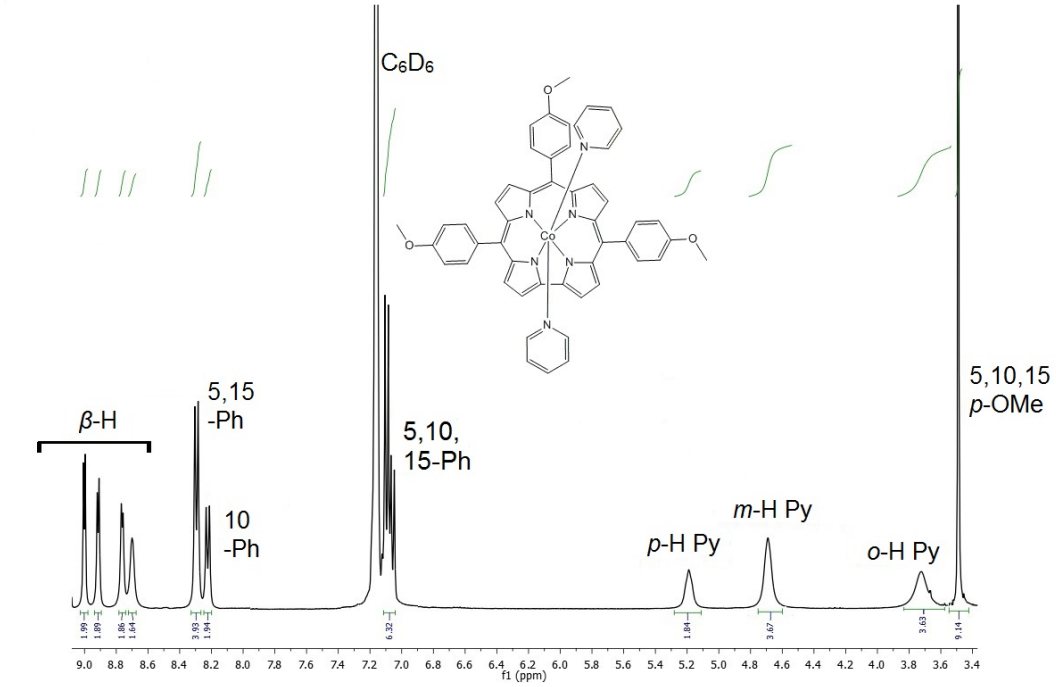


Figure. S5. ^{1}H NMR spectrum of Co[T*p*OMePC](py)$_2$ in benzene-d_6.

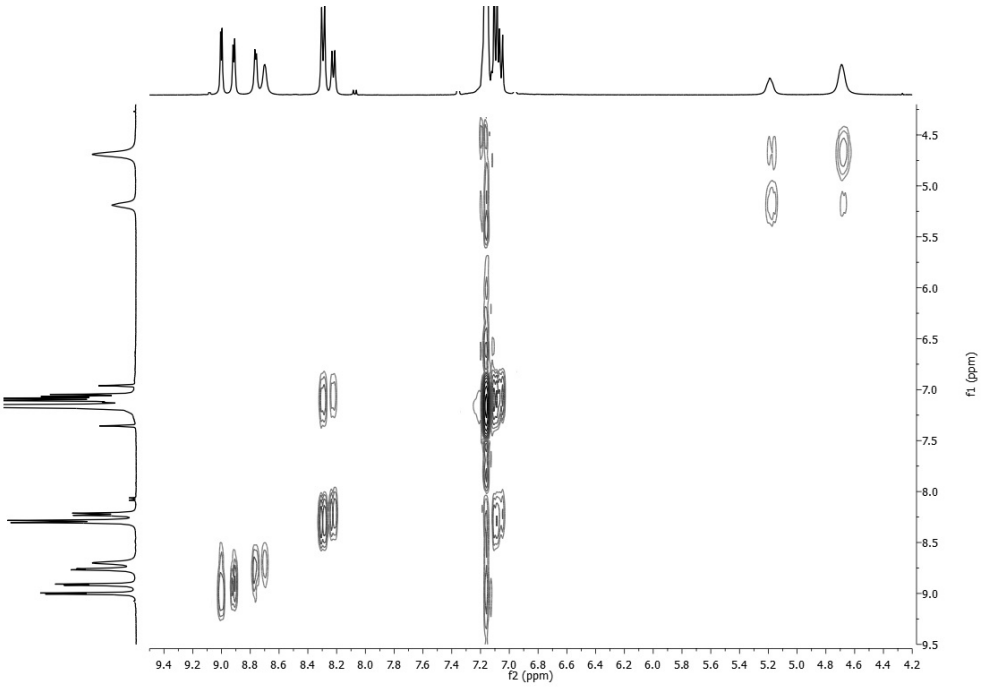


Figure. S6. ^{1}H-^{1}H gCOSY of Co[T*p*OMePC](py)$_2$ in benzene-d_6.

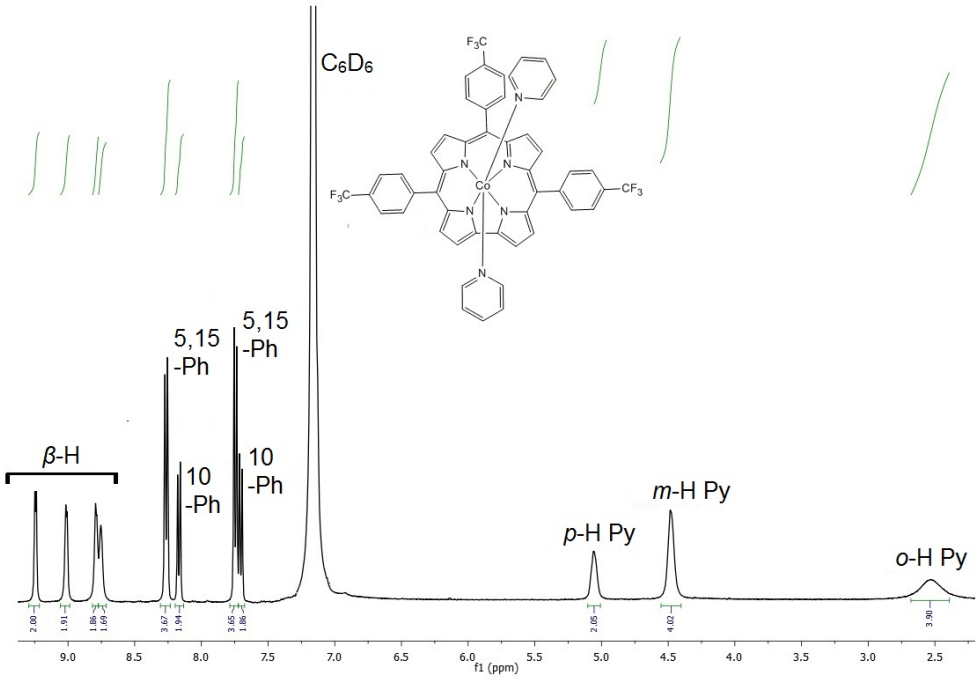


Figure. S7. ^{1}H NMR spectrum of Co[T*p*CF$_3$PC](py)$_2$ in benzene-d_6.

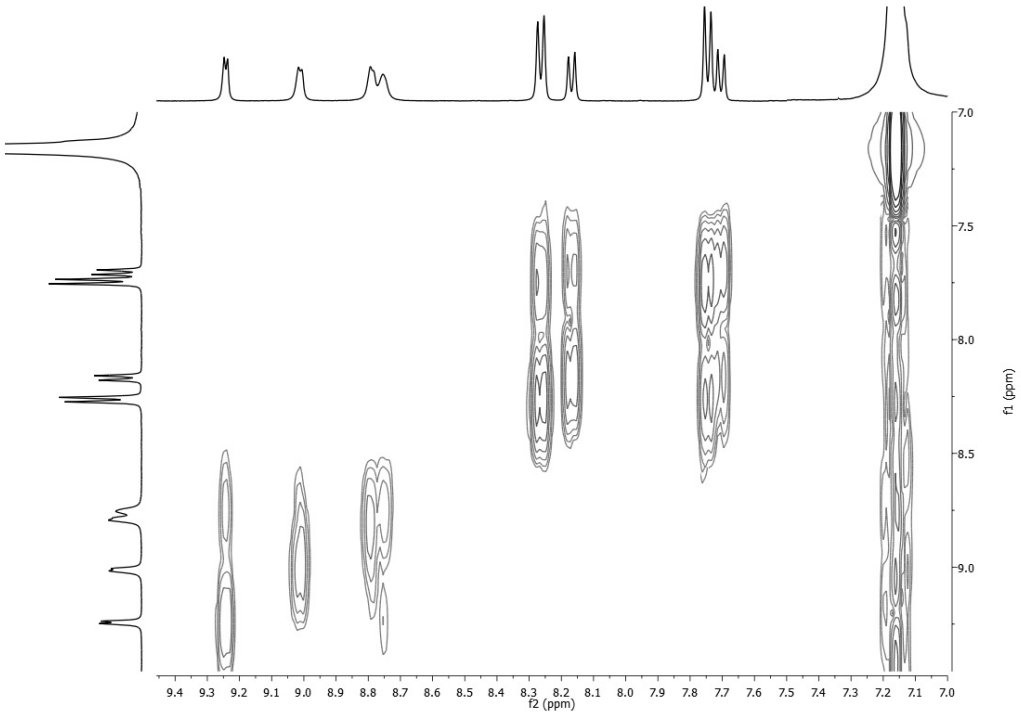


Figure. S8. ^{1}H-^{1}H gCOSY of Co[T*p*CF$_3$PC](py)$_2$ in benzene-d_6.

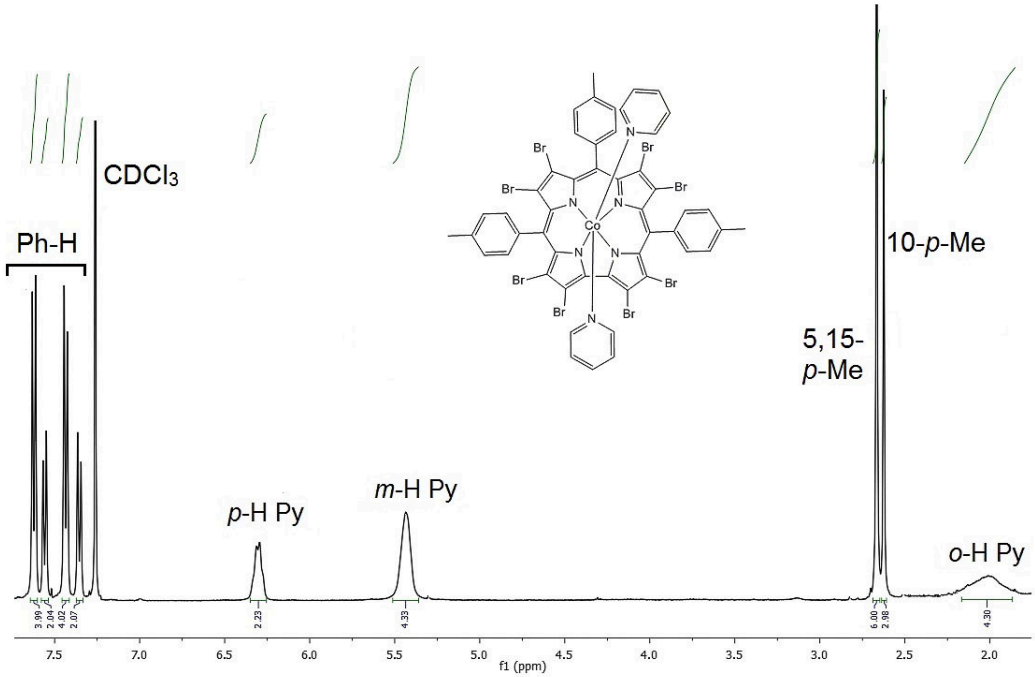


Figure. S9. ^{1}H NMR spectrum of Co[Br_8T*p*MePC](py)$_2$ in $CDCl_3$.

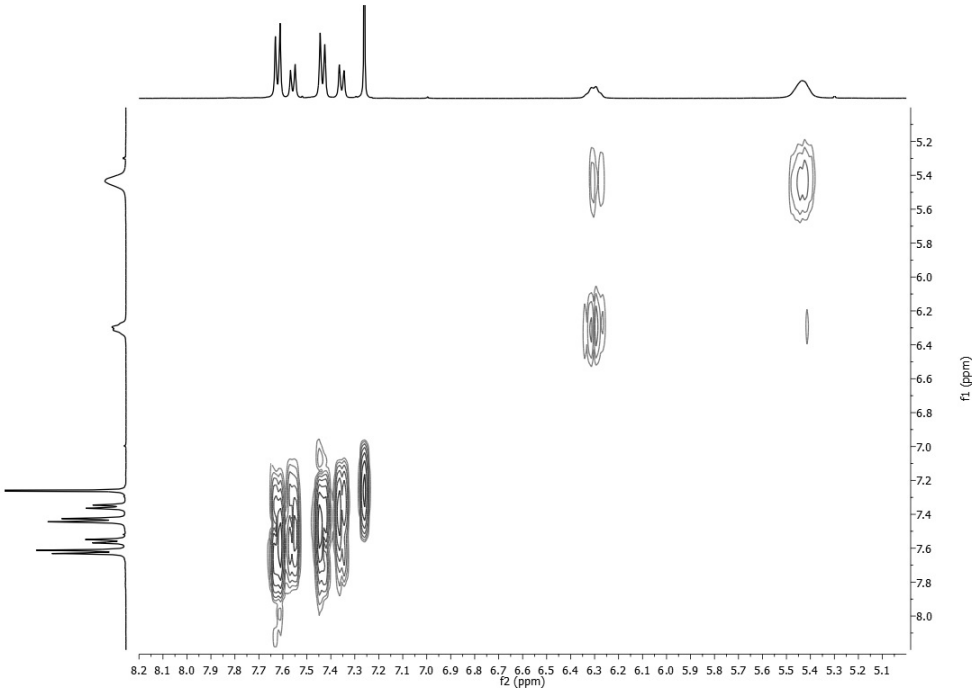


Figure. S10. ^{1}H-^{1}H gCOSY of Co[Br_8T*p*MePC](py)$_2$ in $CDCl_3$.

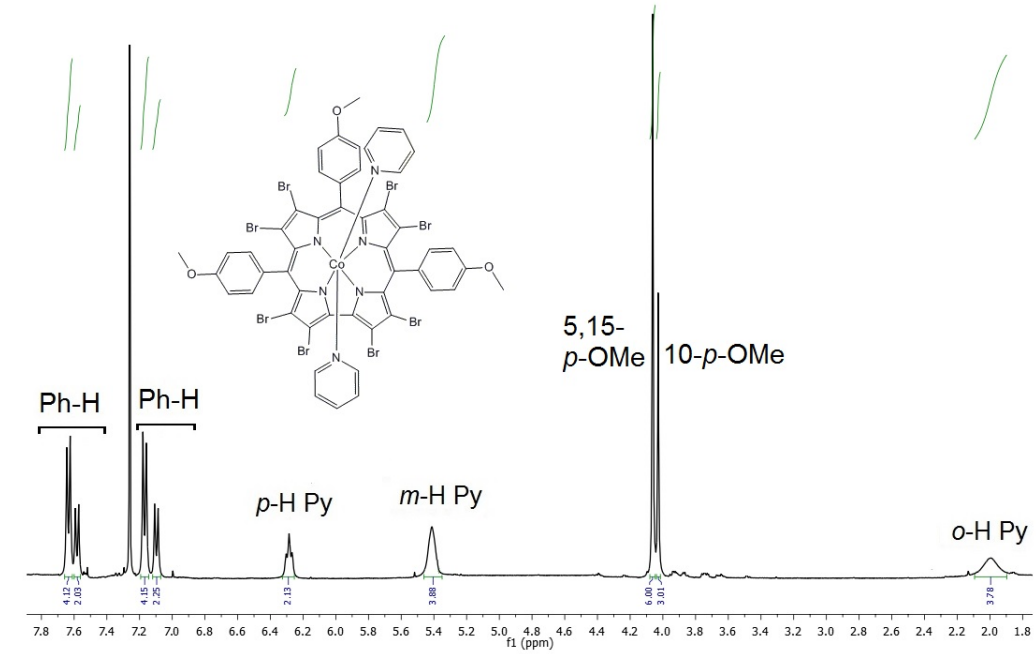


Figure. S11. ^{1}H NMR spectrum of Co[Br_8T*p*OMePC](py)$_2$ in $CDCl_3$.

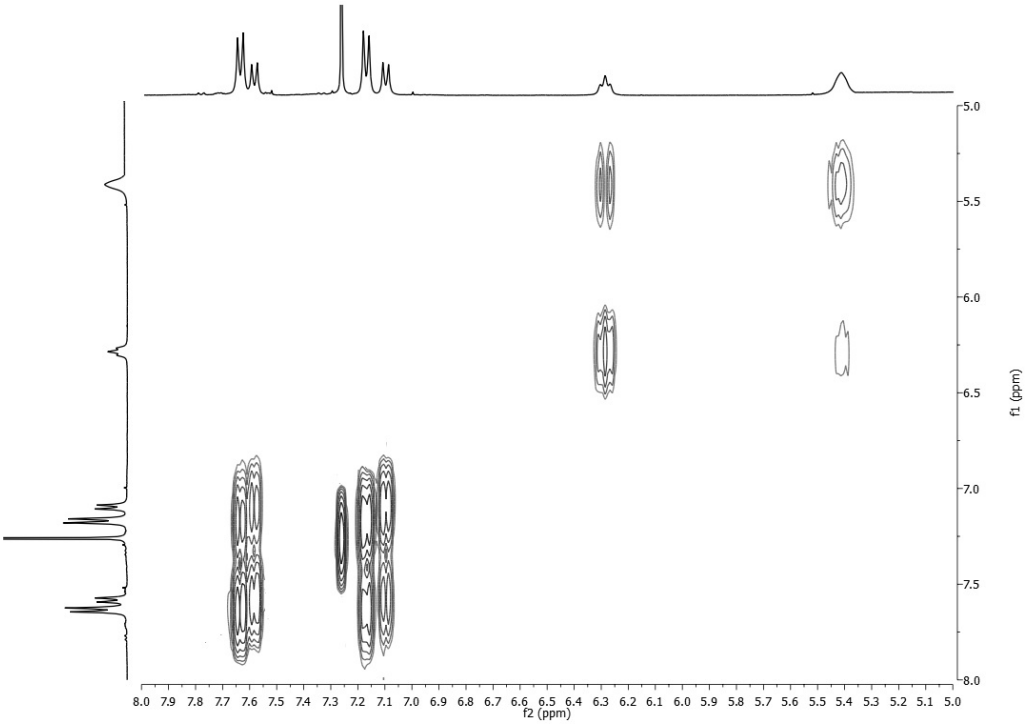


Figure. S12. ^{1}H-^{1}H gCOSY of Co[Br_8T*p*OMePC](py)$_2$ in $CDCl_3$.

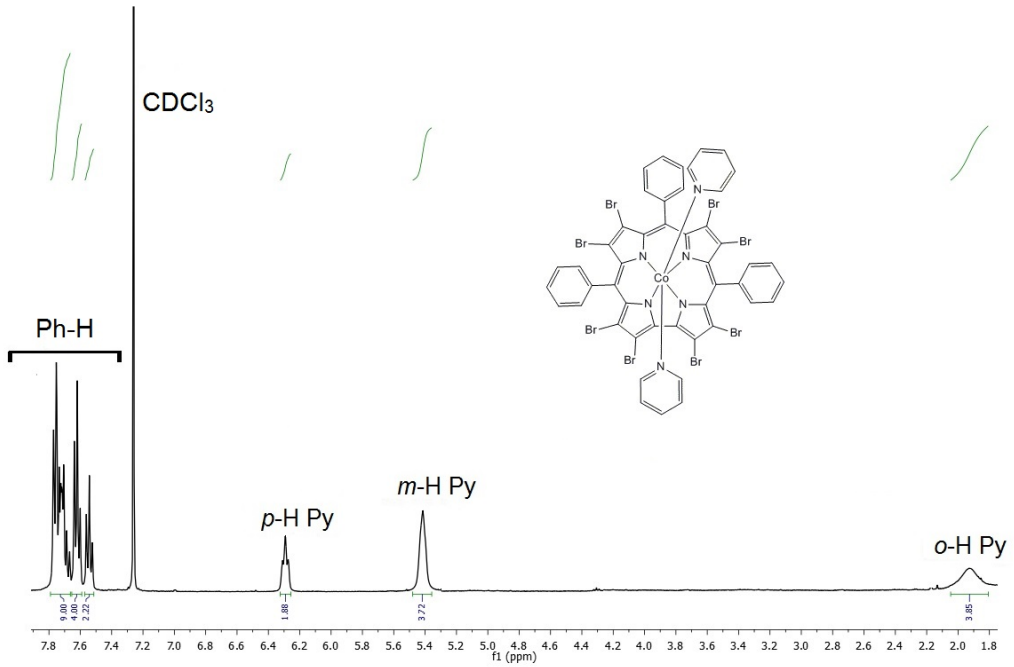


Figure. S13. ^{1}H NMR spectrum of Co[Br_8TPC](py)$_2$ in $CDCl_3$.

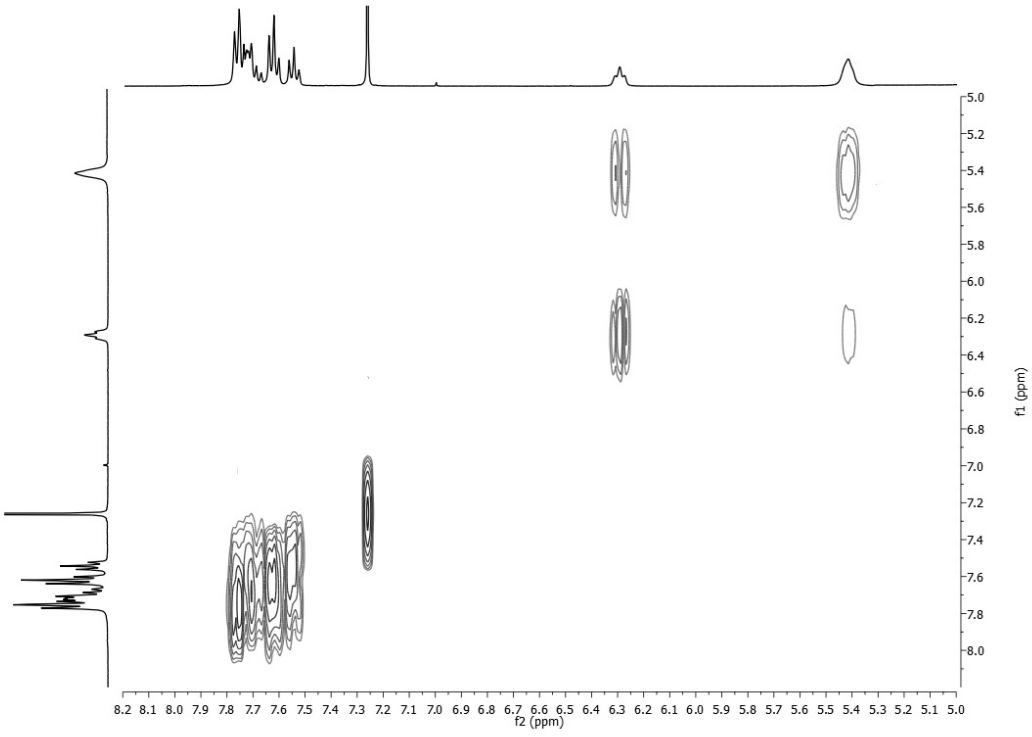


Figure. S14. ^{1}H-^{1}H gCOSY of Co[Br_8TPC](py)$_2$ in $CDCl_3$.

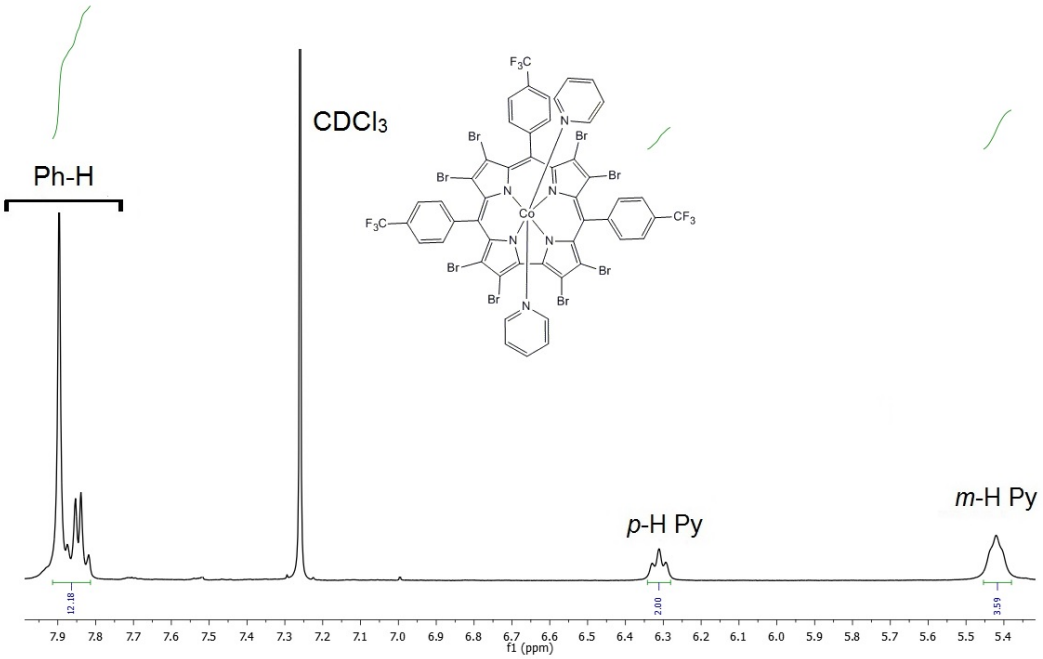


Figure. S15. ^{1}H NMR spectrum of Co[Br_8T*p*CF_3PC](py)$_2$ in $CDCl_3$.

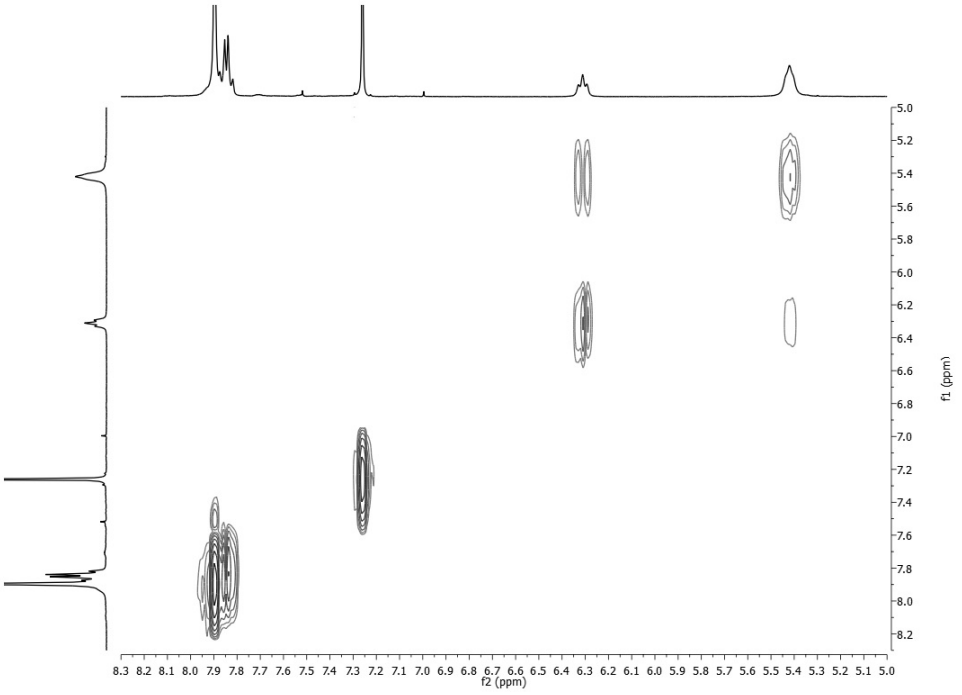


Figure. S16. ^{1}H-^{1}H gCOSY of Co[Br_8T*p*CF_3PC](py)$_2$ in $CDCl_3$.

B. Mass spectra

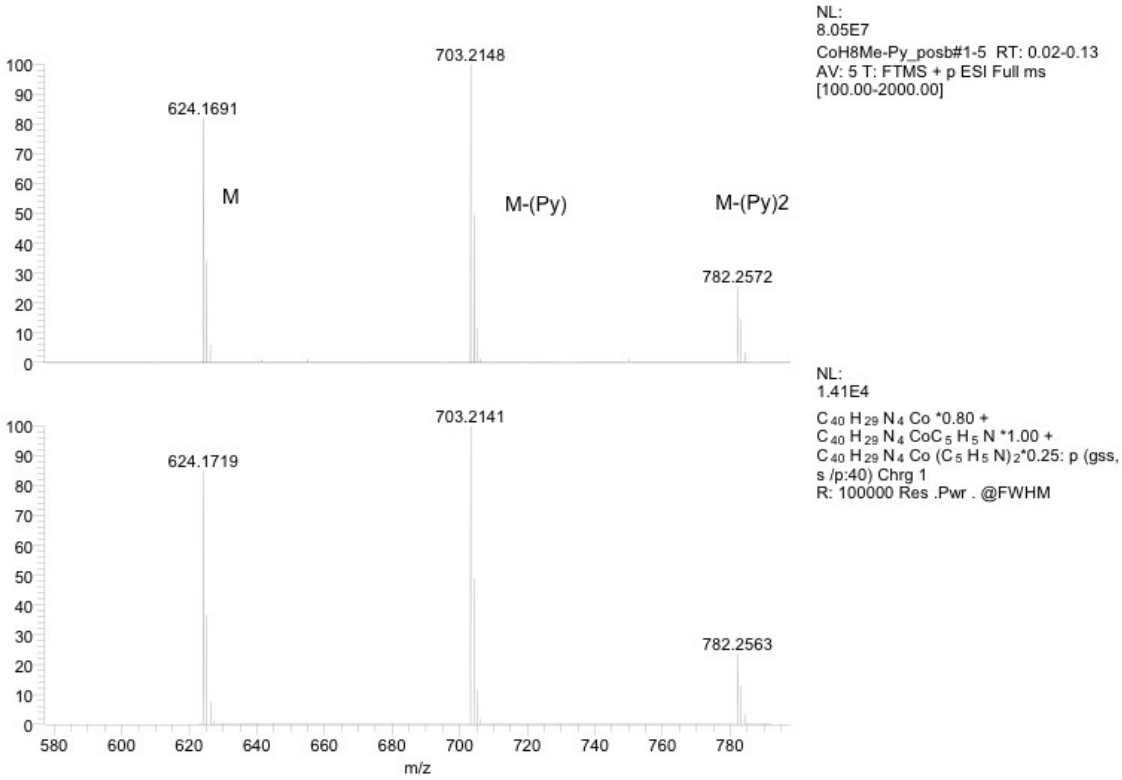


Figure S17. Positive-mode ESI mass spectrum of Co[T*p*MePC](py)$_2$.

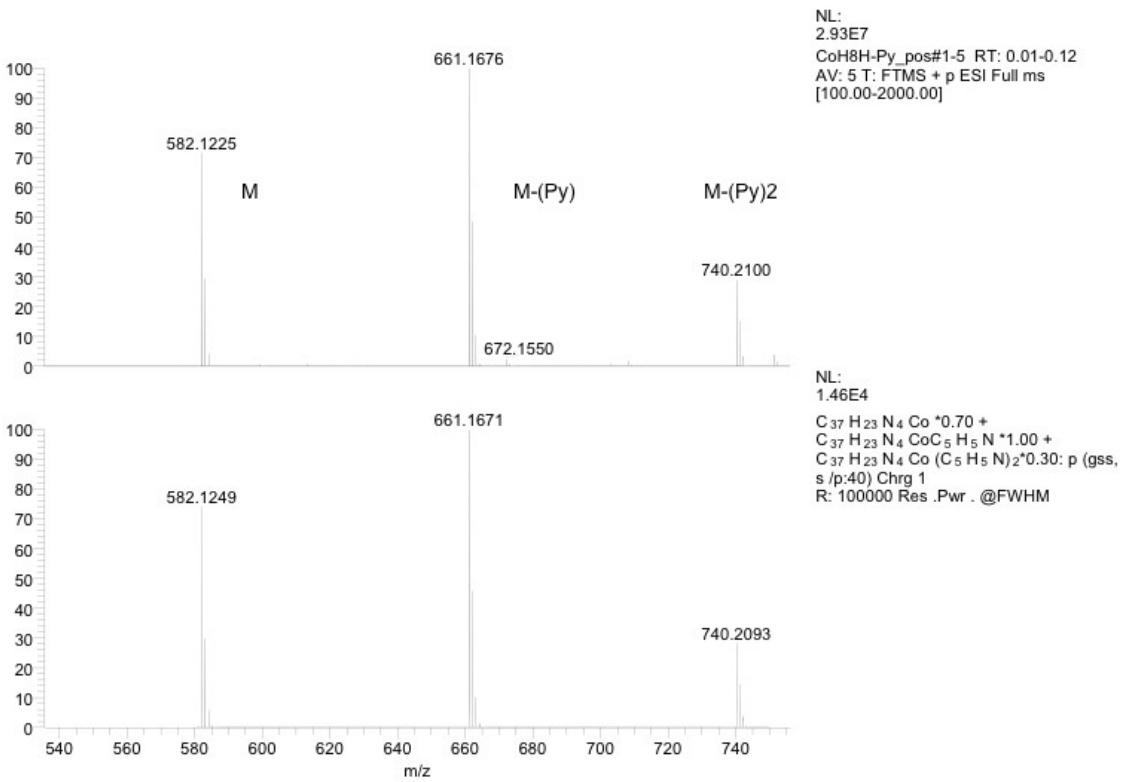


Figure S18. Positive-mode ESI mass spectrum of Co[TPC](py)$_2$.

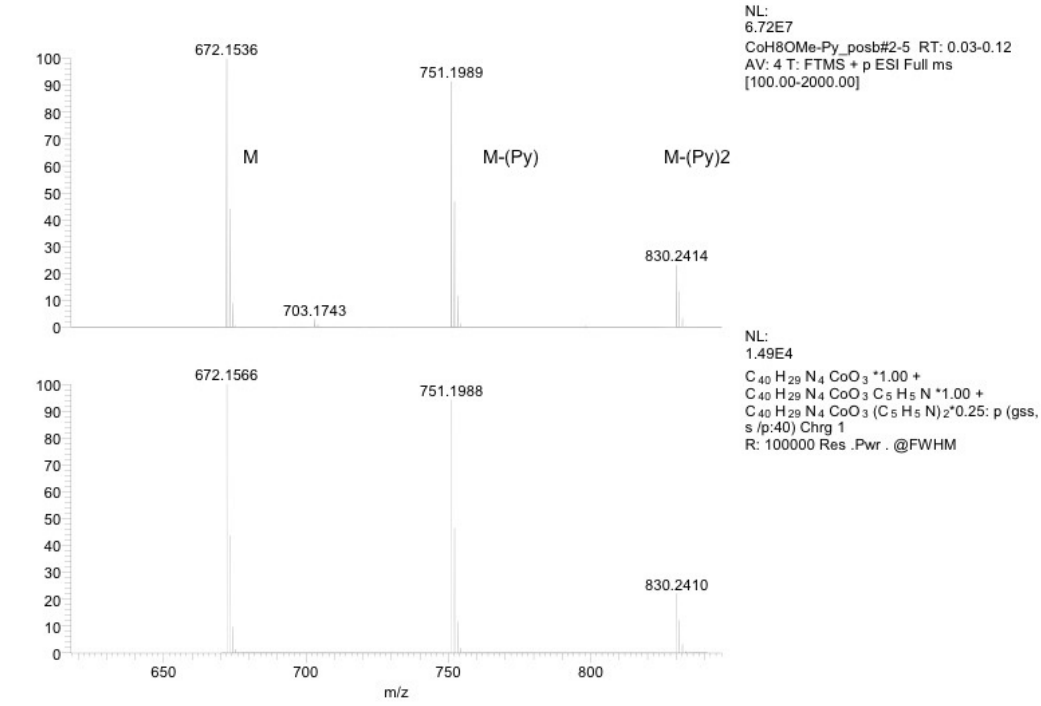


Figure S19. Positive-mode ESI mass spectrum of Co[T*p*OMePC](py)$_2$.

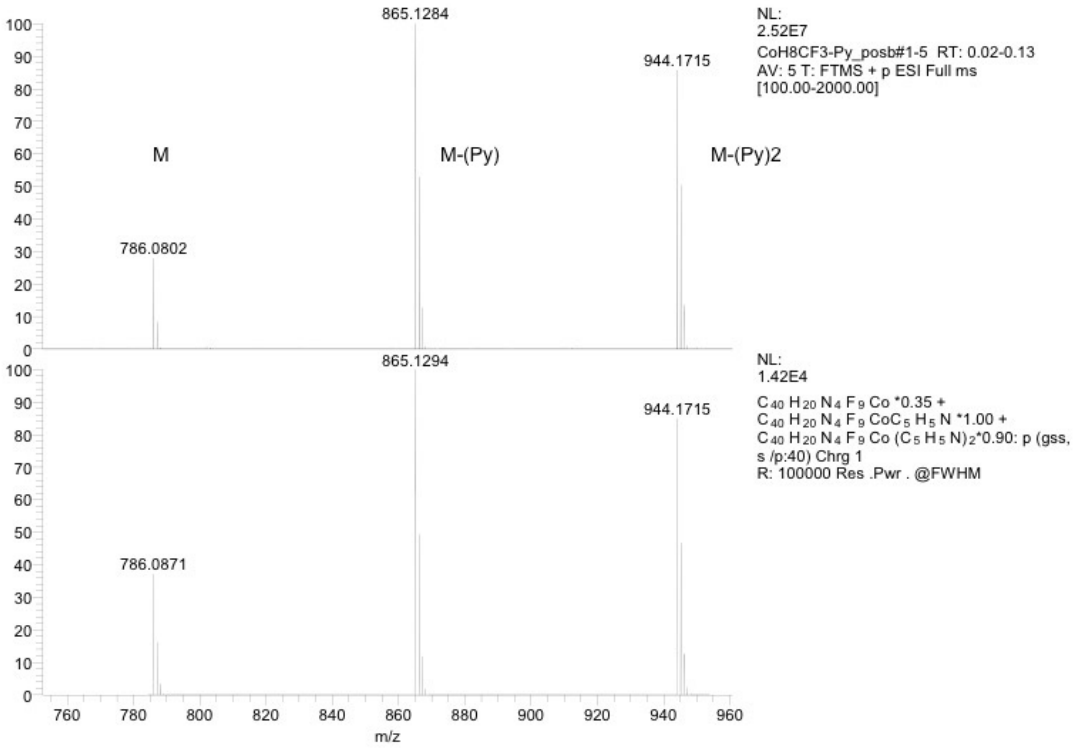


Figure S20. Positive-mode ESI mass spectrum of Co[T*p*CF$_3$PC](py)$_2$.

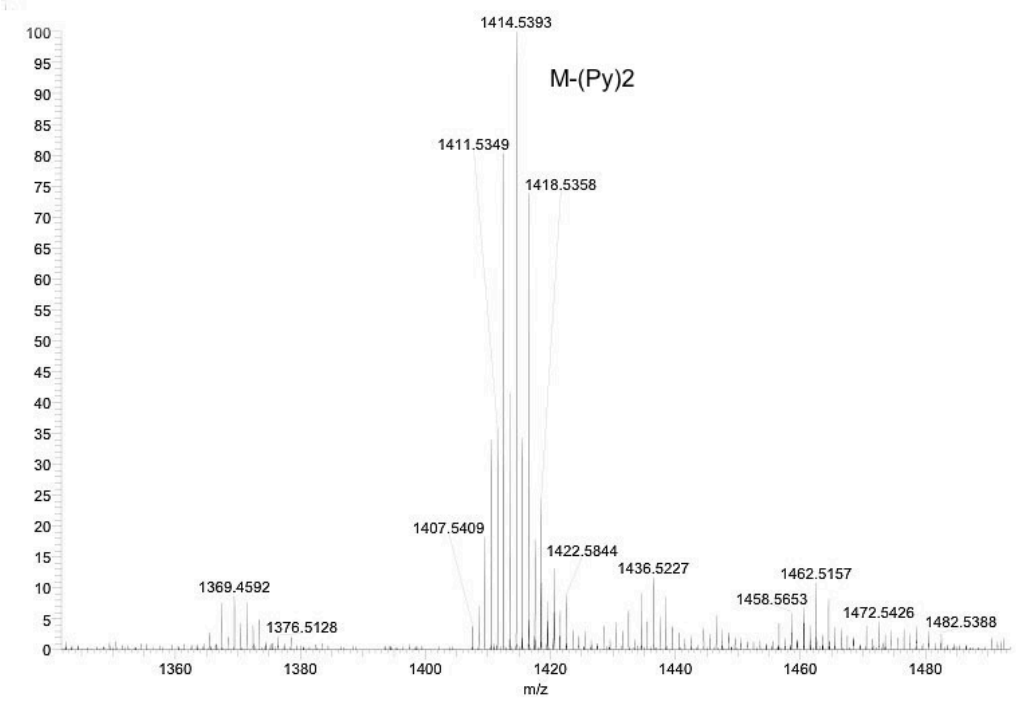


Figure S21. Positive-mode ESI mass spectrum of Co[Br_8T*p*MePC](py)$_2$.

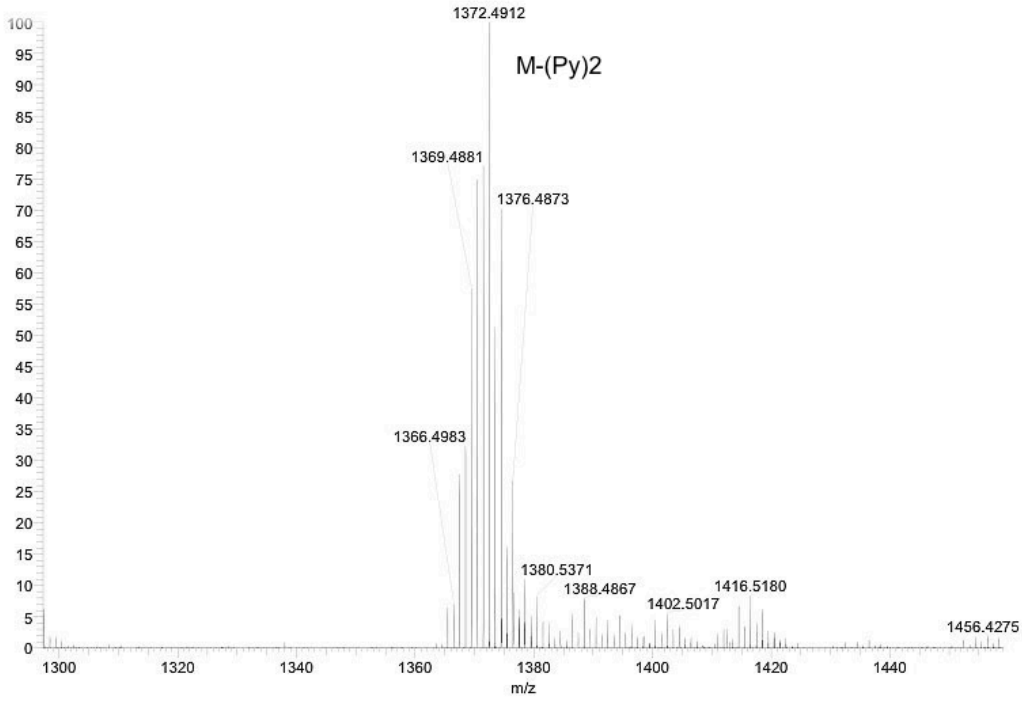


Figure S22. Positive-mode ESI mass spectrum of Co[Br_8TPC](py)$_2$.

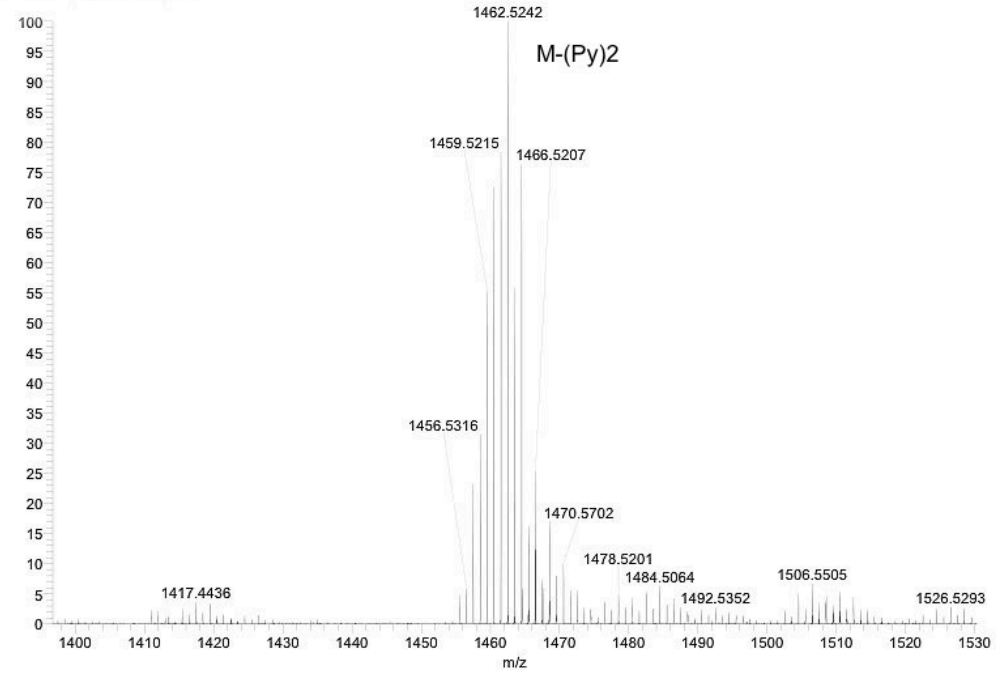


Figure S23. Positive-mode ESI mass spectrum of Co[Br_8T*p*OMePC](py)$_2$.

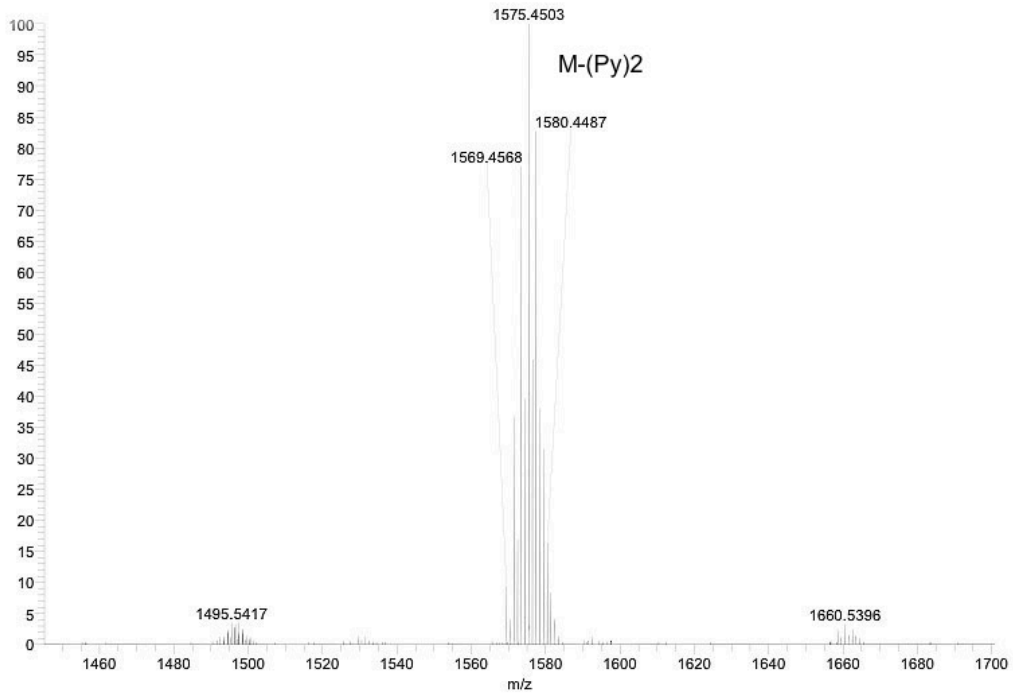


Figure S24. Positive-mode ESI mass spectrum of Co[Br_8T*p*CF_3PC](py)$_2$.

C. EPR spectra

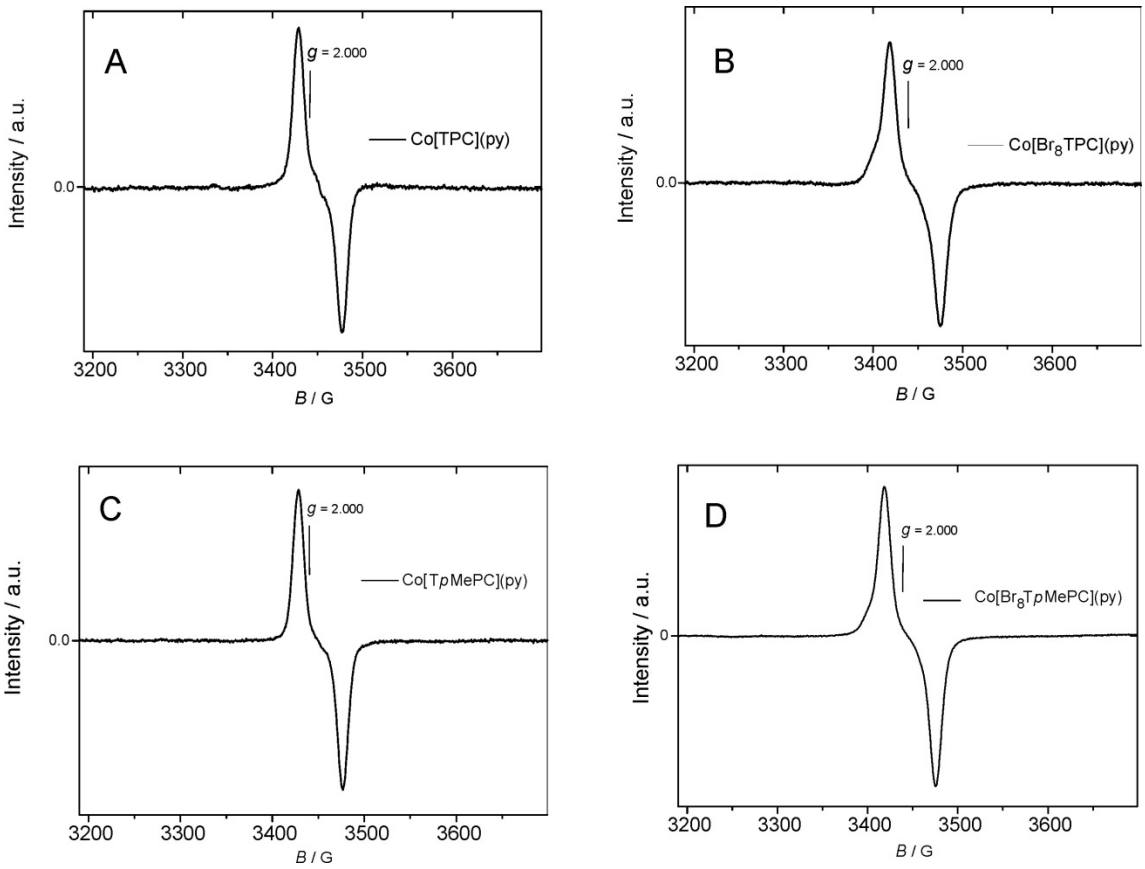


Figure. S25. Room temperature X-band EPR spectra (in 2:1 CH_2Cl_2:toluene) of Co[TPC](py) (**A**), Co[Br_8TPC](py) (**B**), Co[T*p*MePC](py) (**C**), and Co[Br_8T*p*MePC](py) (**D**). Microwave power 1 mW, concentration range 5-25 μM.

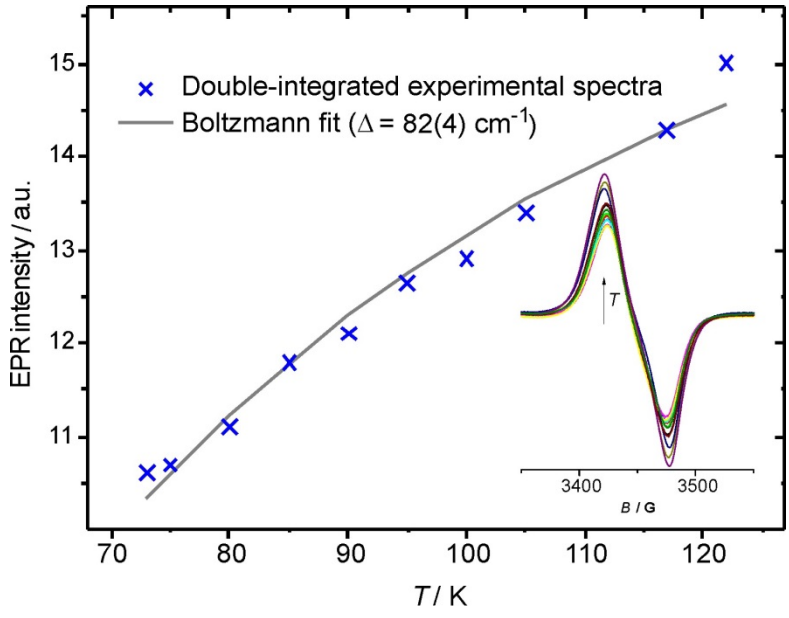


Figure. S26. Temperature variation of EPR signal intensity in a frozen 2:1 CH_2Cl_2:toluene solution of Co[Br_8T*p*MePC](py) and corresponding Boltzmann fit, assuming a triply degenerate excited state and $I(T = 0) = 0$.

D. B3LYP-D3/STO-TZP optimized coordinates

1. Co[TPC](py); M_S = 0 (broken-symmetry)

C	0.451307000	0.572187000	5.595344000
C	0.451307000	0.572187000	-5.595344000
C	0.574268000	0.574772000	6.979959000
C	0.574268000	0.574772000	-6.979959000
C	0.774203000	2.483275000	1.151487000
C	0.774203000	2.483275000	-1.151487000
C	0.845647000	-0.487002000	3.353774000
C	0.845647000	-0.487002000	-3.353774000
C	0.872972000	3.866212000	1.195553000
C	0.872972000	3.866212000	-1.195553000
C	0.922189000	4.573122000	0.000000000
C	0.959088000	-0.486234000	4.833804000
C	0.959088000	-0.486234000	-4.833804000
C	1.203464000	-0.484326000	7.628226000
C	1.203464000	-0.484326000	-7.628226000
C	1.590769000	-1.544376000	5.496997000
C	1.590769000	-1.544376000	-5.496997000
C	1.709309000	-1.544377000	6.881977000
C	1.709309000	-1.544377000	-6.881977000
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C	3.212987000	-0.652118000	-0.717626000
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C	3.409378000	-0.643375000	-2.964705000
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C	4.145536000	-0.699464000	-1.799736000
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C	-0.452902000	-0.418680000	-2.767047000
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C	-1.707689000	-0.425848000	-3.472137000
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C	-2.077159000	-0.343933000	-1.249903000
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C	-2.705400000	-0.374972000	-2.540534000
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C	-4.213339000	-0.246117000	0.000000000
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C	-4.973200000	-1.416303000	0.000000000
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C	-6.363143000	-1.354498000	0.000000000
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Co	0.561261000	-0.273285000	0.000000000
H	0.181895000	1.406347000	7.552547000
H	0.181895000	1.406347000	-7.552547000
H	0.734152000	1.890019000	2.054577000
H	0.734152000	1.890019000	-2.054577000
H	0.912088000	4.371351000	2.151379000

H	0.912088000	4.371351000	-2.151379000
H	0.999260000	5.653454000	0.000000000
H	1.297094000	-0.483867000	8.707119000
H	1.297094000	-0.483867000	-8.707119000
H	1.976369000	-2.373070000	4.917586000
H	1.976369000	-2.373070000	-4.917586000
H	2.192748000	-2.376448000	7.379045000
H	2.192748000	-2.376448000	-7.379045000
H	3.789958000	-0.653837000	3.972734000
H	3.789958000	-0.653837000	-3.972734000
H	5.218725000	-0.768285000	1.714362000
H	5.218725000	-0.768285000	-1.714362000
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H	-0.036546000	1.398064000	-5.093385000
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H	-1.820209000	-0.487019000	-4.541693000
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H	-3.768842000	-0.376484000	-2.715443000
H	-4.278230000	1.897002000	0.000000000
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H	-6.942648000	-2.269727000	0.000000000
H	-8.089400000	-0.072169000	0.000000000
N	0.722212000	1.803150000	0.000000000
N	1.964544000	-0.577045000	1.226796000
N	1.964544000	-0.577045000	-1.226796000
N	-0.715232000	-0.380673000	1.418432000
N	-0.715232000	-0.380673000	-1.418432000

2. Co[TPC](py); M_S = 1; ^{3}A′′

C	0.462347000	0.622236000	5.584915000
C	0.462347000	0.622236000	-5.584915000
C	0.590923000	0.653001000	6.969351000
C	0.590923000	0.653001000	-6.969351000
C	0.825368000	-0.487029000	3.362154000
C	0.825368000	-0.487029000	-3.362154000
C	0.832920000	2.530544000	1.152878000
C	0.832920000	2.530544000	-1.152878000
C	0.931576000	3.913951000	1.197304000
C	0.931576000	3.913951000	-1.197304000
C	0.950469000	-0.458359000	4.841779000
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C	0.980038000	4.618230000	0.000000000
C	1.214184000	-0.397019000	7.636931000
C	1.214184000	-0.397019000	-7.636931000
C	1.573568000	-1.508028000	5.526036000
C	1.573568000	-1.508028000	-5.526036000
C	1.704777000	-1.477717000	6.909698000
C	1.704777000	-1.477717000	-6.909698000
C	1.996104000	-0.593766000	2.583368000

C	1.996104000	-0.593766000	-2.583368000
C	3.211101000	-0.701874000	0.702366000
C	3.211101000	-0.701874000	-0.702366000
C	3.383974000	-0.677905000	2.945781000
C	3.383974000	-0.677905000	-2.945781000
C	4.127658000	-0.751362000	1.783295000
C	4.127658000	-0.751362000	-1.783295000
C	-0.447243000	-0.422121000	2.773210000
C	-0.447243000	-0.422121000	-2.773210000
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C	-2.081752000	-0.367664000	-1.236312000
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C	-2.700323000	-0.379117000	-2.529802000
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C	-4.229794000	-0.282101000	0.000000000
C	-4.894589000	0.945227000	0.000000000
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C	-6.284970000	0.999075000	0.000000000
C	-6.375056000	-1.405751000	0.000000000
C	-7.028524000	-0.177235000	0.000000000
Co	0.556008000	-0.325412000	0.000000000
H	0.208849000	1.500300000	7.525905000
H	0.208849000	1.500300000	-7.525905000
H	0.791704000	1.933015000	2.054274000
H	0.791704000	1.933015000	-2.054274000
H	0.970208000	4.421528000	2.151792000
H	0.970208000	4.421528000	-2.151792000
H	1.056085000	5.698744000	0.000000000
H	1.315280000	-0.374389000	8.714920000
H	1.315280000	-0.374389000	-8.714920000
H	1.944521000	-2.355641000	4.964059000
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H	2.183194000	-2.303917000	7.421681000
H	2.183194000	-2.303917000	-7.421681000
H	3.761651000	-0.682754000	3.955166000
H	3.761651000	-0.682754000	-3.955166000
H	5.200302000	-0.830294000	1.704029000
H	5.200302000	-0.830294000	-1.704029000
H	-0.018018000	1.443219000	5.067494000
H	-0.018018000	1.443219000	-5.067494000
H	-1.821052000	-0.456337000	4.534823000
H	-1.821052000	-0.456337000	-4.534823000
H	-3.764319000	-0.376350000	2.703252000
H	-3.764319000	-0.376350000	-2.703252000
H	-4.313583000	1.859410000	0.000000000
H	-4.473689000	-2.411248000	0.000000000
H	-6.787323000	1.959207000	0.000000000
H	-6.947809000	-2.325407000	0.000000000
H	-8.111117000	-0.136622000	0.000000000
N	0.781585000	1.855569000	0.000000000

N	1.936643000	-0.608152000	1.226704000
N	1.936643000	-0.608152000	-1.226704000
N	-0.716358000	-0.399378000	1.406224000
N	-0.716358000	-0.399378000	-1.406224000

3. Co[TPC](py); M_S = 1; ; ^{3}A′

C	0.431808000	0.602627000	5.590012000
C	0.431808000	0.602627000	-5.590012000
C	0.555350000	0.630711000	6.974178000
C	0.555350000	0.630711000	-6.974178000
C	0.822389000	-0.496984000	3.366313000
C	0.822389000	-0.496984000	-3.366313000
C	0.826126000	2.523999000	1.153211000
C	0.826126000	2.523999000	-1.153211000
C	0.943370000	-0.466188000	4.845327000
C	0.943370000	-0.466188000	-4.845327000
C	0.986535000	3.901288000	1.197671000
C	0.986535000	3.901288000	-1.197671000
C	1.066653000	4.602220000	0.000000000
C	1.194325000	-0.411170000	7.640243000
C	1.194325000	-0.411170000	-7.640243000
C	1.586878000	-1.505394000	5.527023000
C	1.586878000	-1.505394000	-5.527023000
C	1.709466000	-1.478965000	6.911248000
C	1.709466000	-1.478965000	-6.911248000
C	2.002078000	-0.596841000	2.594676000
C	2.002078000	-0.596841000	-2.594676000
C	3.205556000	-0.692368000	0.714305000
C	3.205556000	-0.692368000	-0.714305000
C	3.381128000	-0.625893000	2.957993000
C	3.381128000	-0.625893000	-2.957993000
C	4.127123000	-0.691768000	1.784514000
C	4.127123000	-0.691768000	-1.784514000
C	-0.449011000	-0.434050000	2.776264000
C	-0.449011000	-0.434050000	-2.776264000
C	-1.710810000	-0.430794000	3.464645000
C	-1.710810000	-0.430794000	-3.464645000
C	-2.079672000	-0.354151000	1.237201000
C	-2.079672000	-0.354151000	-1.237201000
C	-2.702310000	-0.378733000	2.531238000
C	-2.702310000	-0.378733000	-2.531238000
C	-2.733426000	-0.319195000	0.000000000
C	-4.225792000	-0.272083000	0.000000000
C	-4.896092000	0.952010000	0.000000000
C	-4.973716000	-1.450615000	0.000000000
C	-6.286991000	0.998452000	0.000000000
C	-6.364615000	-1.407110000	0.000000000
C	-7.024183000	-0.181808000	0.000000000
Co	0.551095000	-0.320438000	0.000000000
H	0.156726000	1.468796000	7.532552000

H	0.156726000	1.468796000	-7.532552000
H	0.757564000	1.927606000	2.053640000
H	0.757564000	1.927606000	-2.053640000
H	1.047491000	4.407220000	2.152276000
H	1.047491000	4.407220000	-2.152276000
H	1.191680000	5.678168000	0.000000000
H	1.289694000	-0.391166000	8.718822000
H	1.289694000	-0.391166000	-8.718822000
H	1.979764000	-2.340810000	4.961930000
H	1.979764000	-2.340810000	-4.961930000
H	2.202485000	-2.297143000	7.422108000
H	2.202485000	-2.297143000	-7.422108000
H	3.762564000	-0.602821000	3.965678000
H	3.762564000	-0.602821000	-3.965678000
H	5.201877000	-0.730630000	1.702379000
H	5.201877000	-0.730630000	-1.702379000
H	-0.061986000	1.416092000	5.073524000
H	-0.061986000	1.416092000	-5.073524000
H	-1.828158000	-0.488230000	4.534106000
H	-1.828158000	-0.488230000	-4.534106000
H	-3.766408000	-0.374177000	2.701953000
H	-3.766408000	-0.374177000	-2.701953000
H	-4.319978000	1.869212000	0.000000000
H	-4.458051000	-2.402849000	0.000000000
H	-6.794455000	1.955781000	0.000000000
H	-6.932626000	-2.329616000	0.000000000
H	-8.106999000	-0.146796000	0.000000000
N	0.745272000	1.851967000	0.000000000
N	1.943847000	-0.646454000	1.234409000
N	1.943847000	-0.646454000	-1.234409000
N	-0.714993000	-0.391883000	1.406856000
N	-0.714993000	-0.391883000	-1.406856000