

SUPPORTING INFORMATION

Photophysical properties of 4,4'-di-*tert*-butyl-2,2'-bipyridine supported 6-membered 2,2'-diphenyl-X platina-cycles (X = CH₂, NMe, O)

*Robert Robinson Jr., Alice Raphael Karikachery and Paul R. Sharp**

125 Chemistry, University of Missouri-Columbia, Columbia, MO 65211

SharpP@missouri.edu

Contents

Figure S1. Solid-state structure of Pt(^t Bu ₂ bpy) (2,2'-C ₆ H ₄ CH ₂ C ₆ H ₄) (4) (50% probability ellipsoid, hydrogen atoms omitted for clarity).	4
Figure S2. Dimeric unit in crystals of Pt(^t Bu ₂ bpy)Pt(2,2'-C ₆ H ₄ CH ₂ C ₆ H ₄) (4). Shortest bpy C...C contacts are shown. Hydrogen atoms omitted for clarity.	5
Figure S3. Dimeric unit in crystals of Pt(^t Bu ₂ bpy)Pt(2,2'-C ₆ H ₄ NMeC ₆ H ₄) (5). Shortest bpy C...C contacts are shown. Hydrogen atoms omitted for clarity.....	5
Figure S4. Dimeric unit in crystals of Pt(^t Bu ₂ bpy)Pt(2,2'-C ₆ H ₄ OC ₆ H ₄) (6). Shortest bpy C...C contacts are shown. Hydrogen atoms omitted for clarity.	6
Figure S6. Emission spectra of 5 and 6 in MeCN/ <i>n</i> -butyronitrile and 6 in benzene (77 K, λ _{ex} = 425 nm)	7
Figure S7. Drawing of DFT gas-phase optimized 4 (hydrogen atoms omitted for clarity).	8
Figure S8. Drawing of DFT gas-phase optimized 5 (hydrogen atoms omitted for clarity).	8
Figure S9. Drawing of DFT gas-phase optimized 6 (hydrogen atoms omitted for clarity).	9
Figure S10. Drawing of DFT optimized 7 in MeCN (hydrogen atoms omitted for clarity).	9
Figure S11. Drawing of DFT optimized 8 in MeCN (hydrogen atoms omitted for clarity).	10

Table S1. DFT coordinates for 4 (gas-phase).....	10
Table S2. DFT Coordinates for 5 (gas-phase).....	11
Table S3. DFT Coordinates for 6 (gas-phase).....	12
Table S4. DFT Coordinates for 7 in MeCN.	13
Table S5. DFT Coordinates for 8 in MeCN.	15
Figure S12. Drawing of triplet 4T (hydrogen atoms omitted for clarity).....	16
Figure S13. Drawing of triplet 5T (hydrogen atoms omitted for clarity).....	17
Figure S14. Drawing of triplet 6T (hydrogen atoms omitted for clarity).....	17
Table S7. Selected metrical parameters for DFT triplet structures 4T-6T , and 4T'-6T'	17
Table S8. DFT Coordinates for 4T	18
Table S9. DFT Coordinates for 5T	19
Table S10. DFT Coordinates for 6T	20
Figure S15. Drawing of triplet 4T' (hydrogen atoms omitted for clarity).....	22
Figure S16. Drawing of triplet 5T' (hydrogen atoms omitted for clarity).....	22
Figure S17. Drawing of triplet 6T' (hydrogen atoms omitted for clarity).....	23
Table S11. DFT Coordinates for non-planar triplet 4T'	23
Table S12. DFT Coordinates for non-planar triplet 5T'	24
Table S13. DFT Coordinates for non-planar triplet 6T'	25
Figure S18. Drawing of transition state 4TS	27
Figure S19. Drawing of transition state 5TS	27
Figure S20. Drawing of transition state 6TS	28
Table S14. DFT Coordinates for transition state 4TS connecting 4T and 4T'	28
Table S15. DFT Coordinates for transition state 5TS connecting 5T and 5T'	29

Table S16. DFT Coordinates for transition state 6TS connecting 6T and 6T'	30
Figure S21. Spin density plot for 4T (isoval = 0.004) (hydrogen atoms omitted for clarity). ^t Bu ₂ bpy on right.....	32
Figure S22. Spin density plot for 5T (isoval = 0.004) (hydrogen atoms omitted for clarity). ^t Bu ₂ bpy on right.....	33
Figure S23. Spin density plot for 4T' (isoval = 0.004) (hydrogen atoms omitted for clarity). ^t Bu ₂ bpy on right.....	34
Figure S24. Spin density plot for 5T' (isovalue = 0.004) (hydrogen atoms omitted for clarity). ^t Bu ₂ bpy on right.....	34
Figure S25. Spin density plot for 6T' (isovalue = 0.004) (hydrogen atoms omitted for clarity). ^t Bu ₂ bpy on right.....	35
Figure S26. Calculated UV-vis spectrum of 7 in MeCN (vertical green lines correspond to unbroadened oscillator strengths of calculated singlet-singlet transitions).	36
Figure S27. Calculated UV-vis spectrum of 8 in MeCN (vertical green lines correspond to unbroadened oscillator strengths of calculated singlet-singlet transitions).	37
Full references to Gaussian 03 and 09:	37

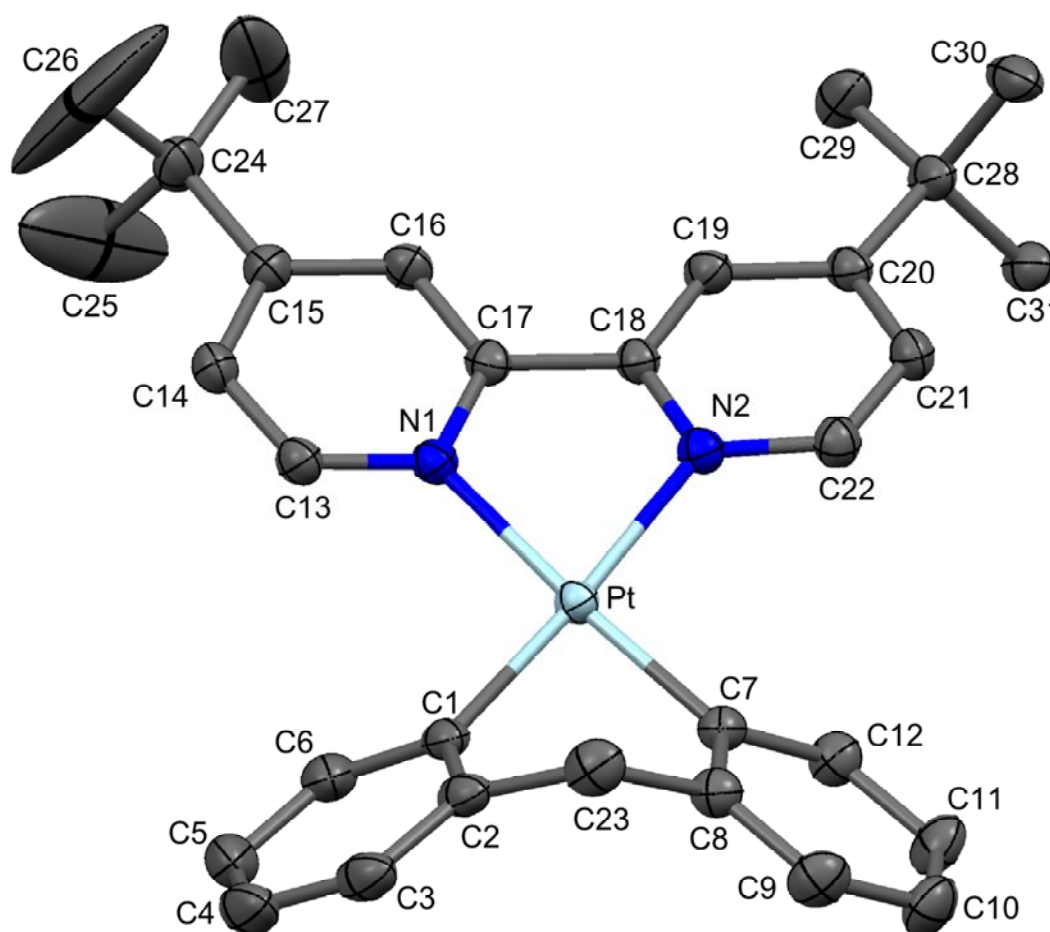


Figure S1. Solid-state structure of $\text{Pt}(\text{tBu}_2\text{bpy})$ ($2,2'\text{-C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4$) (**4**) (50% probability ellipsoid, hydrogen atoms omitted for clarity).

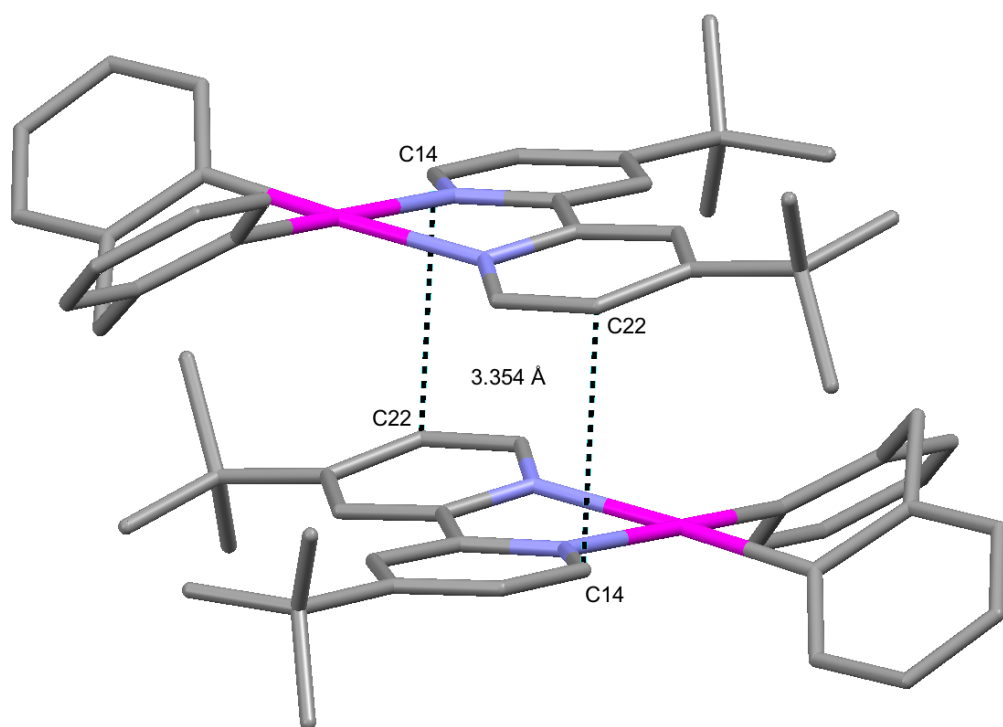


Figure S2. Dimeric unit in crystals of $\text{Pt}(\text{tBu}_2\text{bpy})\text{Pt}(2,2'\text{-C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)$ (**4**). Shortest bpy $\text{C}\cdots\text{C}$ contacts are shown. Hydrogen atoms omitted for clarity.

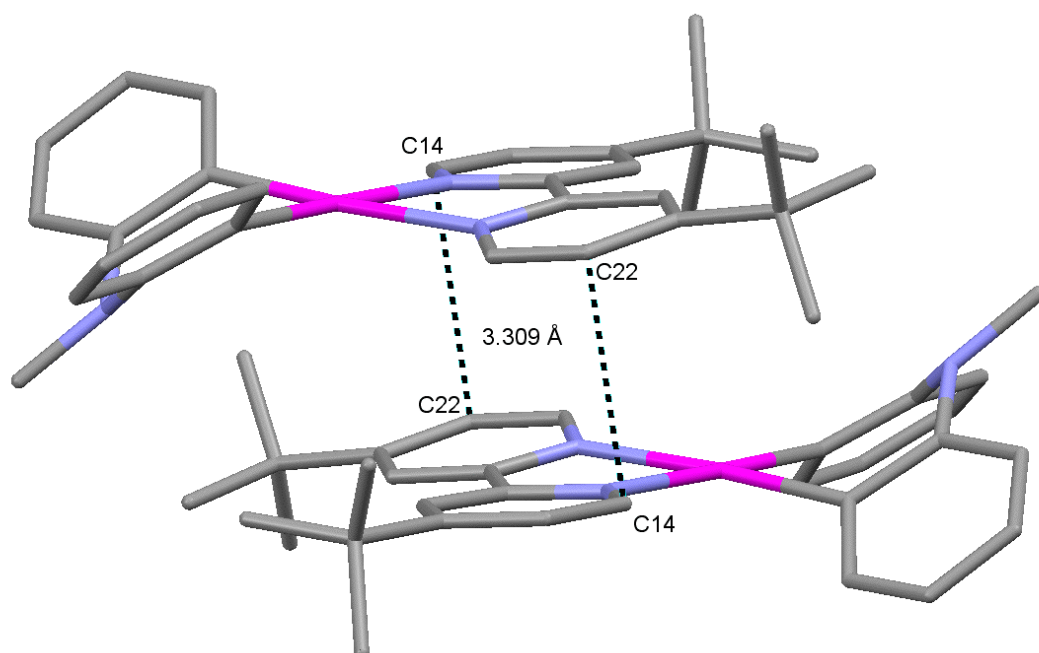


Figure S3. Dimeric unit in crystals of $\text{Pt}(\text{tBu}_2\text{bpy})\text{Pt}(2,2'\text{-C}_6\text{H}_4\text{NMeC}_6\text{H}_4)$ (**5**). Shortest bpy $\text{C}\cdots\text{C}$ contacts are shown. Hydrogen atoms omitted for clarity.

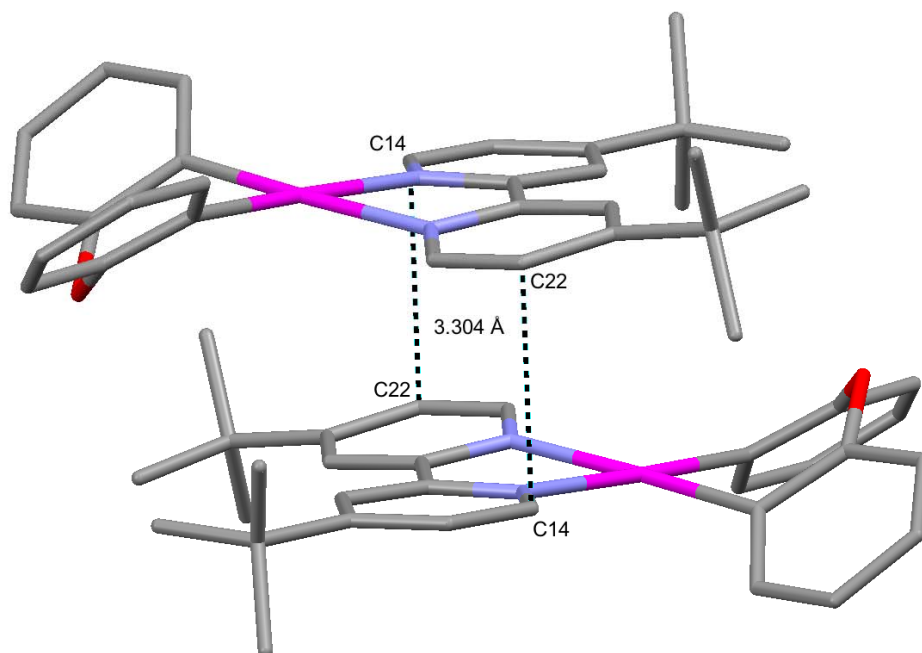


Figure S4. Dimeric unit in crystals of $\text{Pt}(\text{tBu}_2\text{bpy})\text{Pt}(2,2'\text{-C}_6\text{H}_4\text{OC}_6\text{H}_4)$ (**6**). Shortest bpy $\text{C}\cdots\text{C}$ contacts are shown. Hydrogen atoms omitted for clarity.

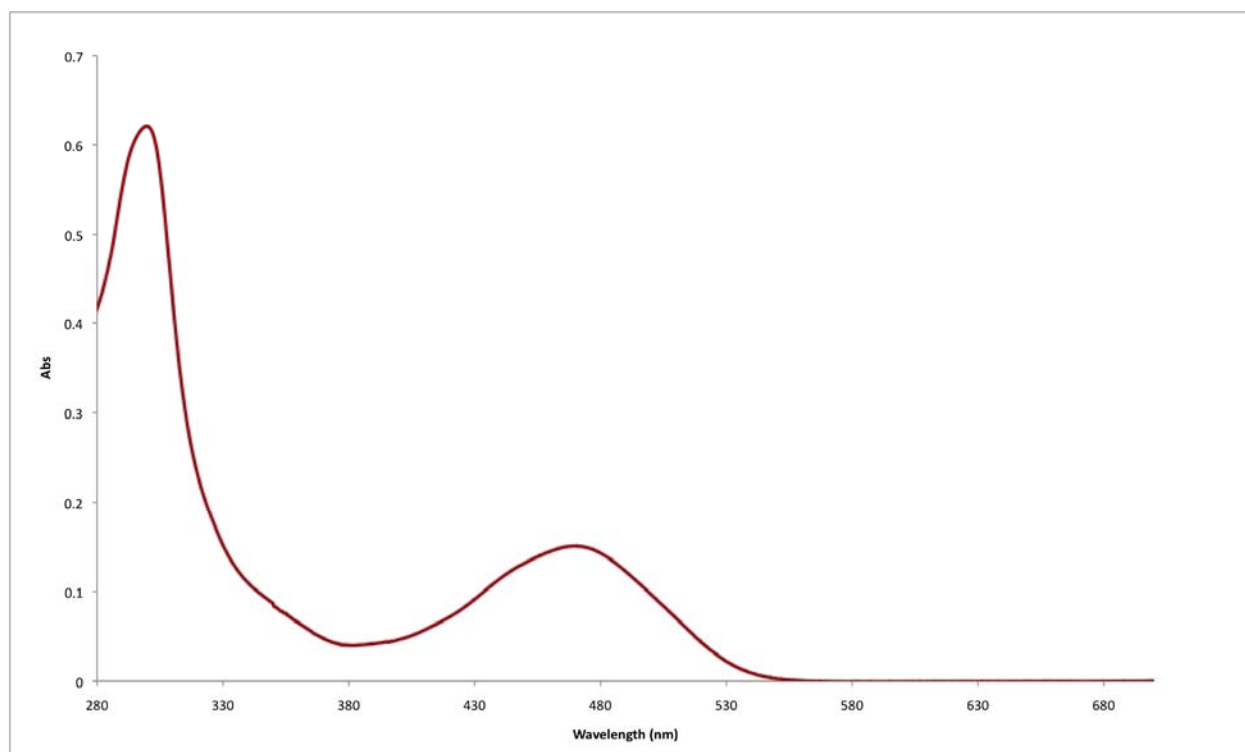


Figure S5. UV-vis spectrum of **6** in benzene.

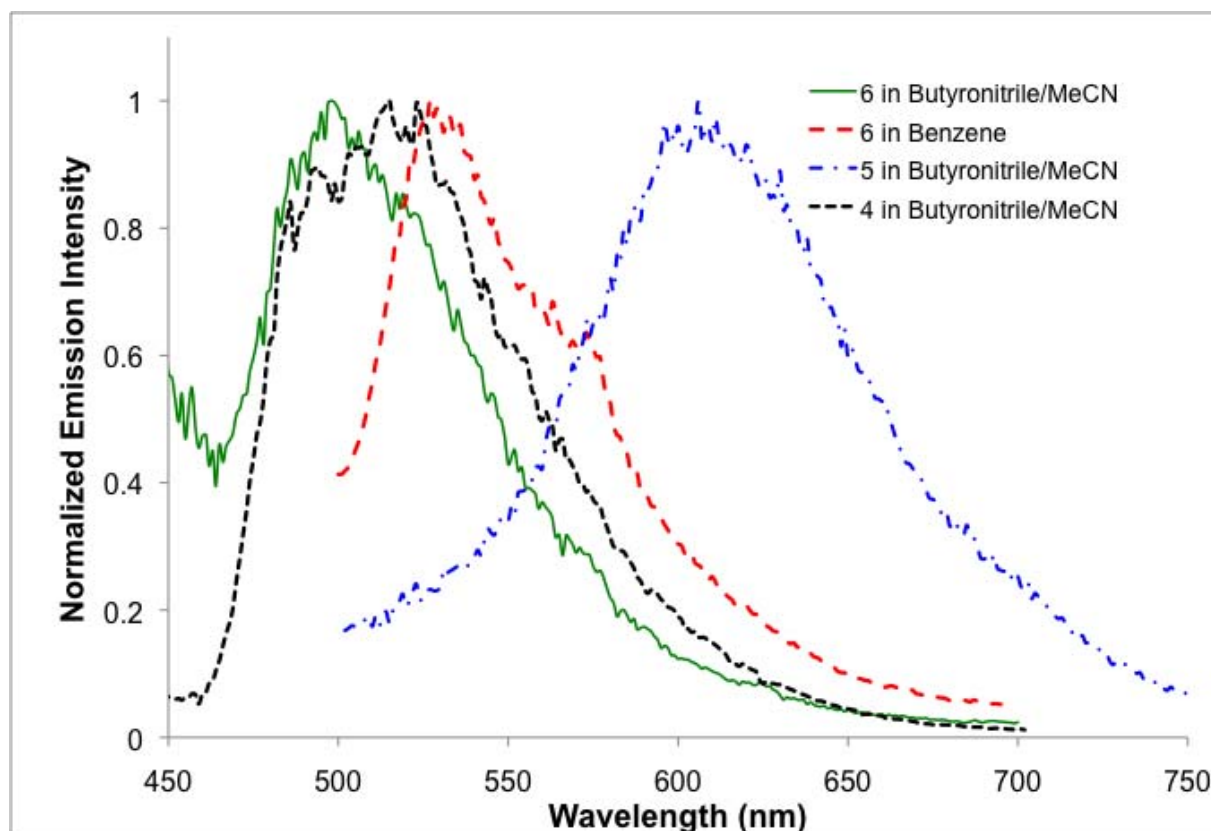


Figure S6. Emission spectra of **4-6** in n-butyronitrile/MeCN (80:20) and **6** in benzene (77 K, λ_{ex} = 425 nm).

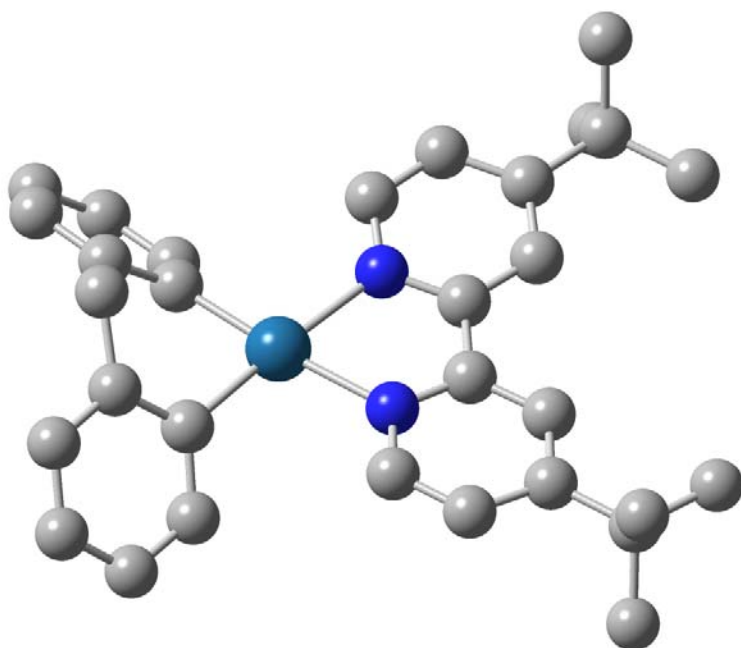


Figure S7. Drawing of DFT gas-phase optimized **4** (hydrogen atoms omitted for clarity).

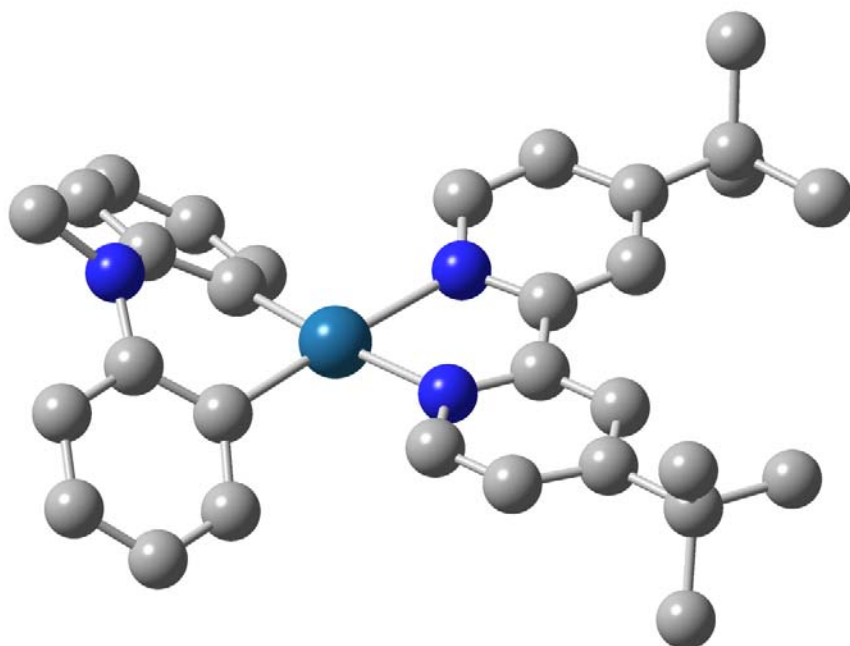


Figure S8. Drawing of DFT gas-phase optimized **5** (hydrogen atoms omitted for clarity).

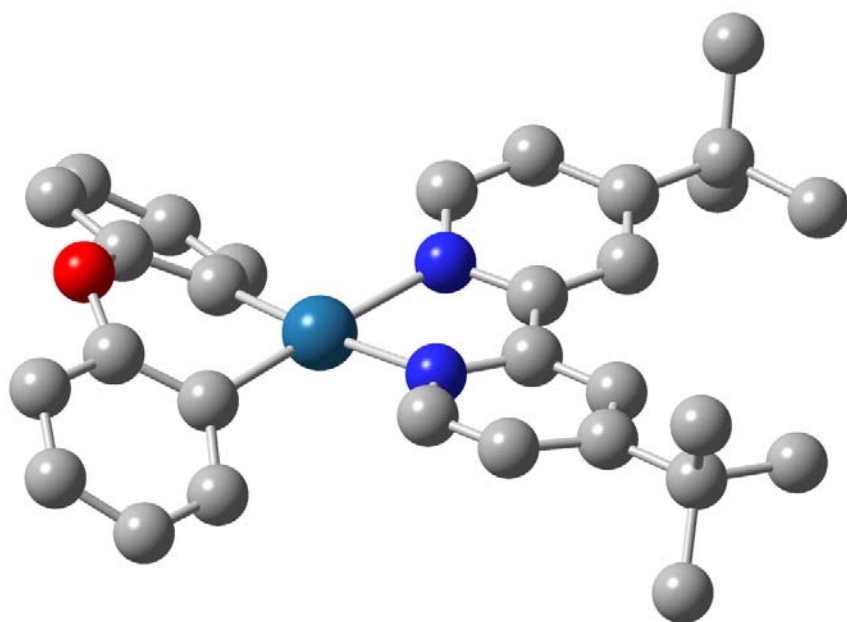


Figure S9. Drawing of DFT gas-phase optimized **6** (hydrogen atoms omitted for clarity).

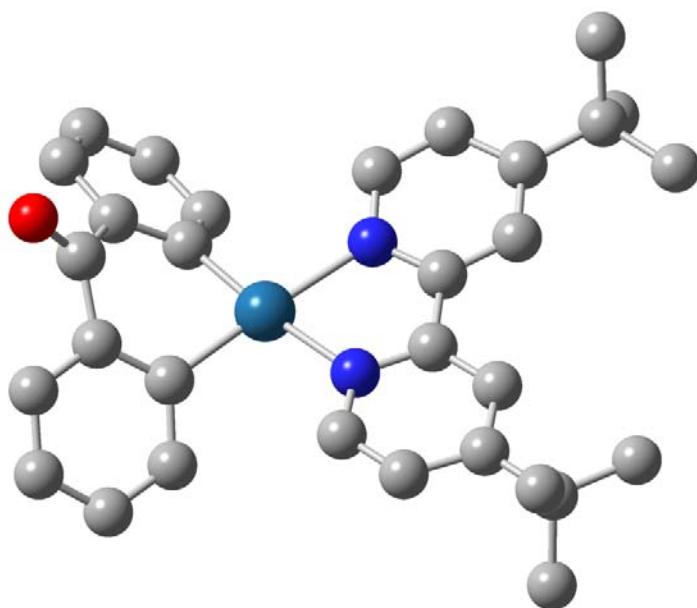


Figure S10. Drawing of DFT optimized **7** in MeCN (hydrogen atoms omitted for clarity).

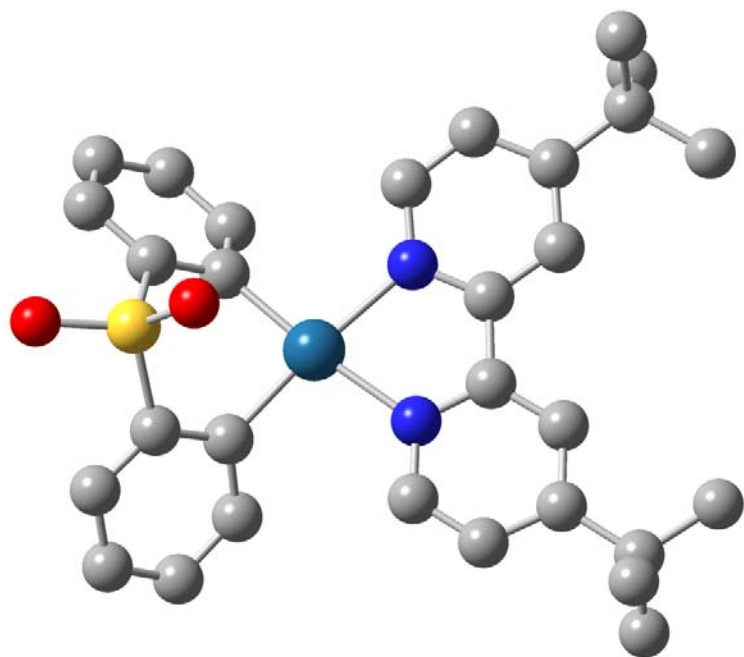


Figure S11. Drawing of DFT optimized **8** in MeCN (hydrogen atoms omitted for clarity).

Table S1. DFT coordinates for **4** (gas-phase).

Pt	-1.18719400	-0.00000700	-0.08017100
N	0.49533200	-1.32477000	0.02955300
N	0.49532100	1.32476700	0.02952800
C	-2.67844100	1.36925700	-0.15716500
C	2.90817100	1.52005600	-0.03228500
H	3.86761600	1.02435700	-0.09565700
C	-2.67844200	-1.36927600	-0.15709300
C	1.55731800	-3.49144000	0.16286900
H	1.41886200	-4.56361400	0.25548300
C	2.85055600	-2.92352800	0.05887500
C	-3.80340300	-1.24951100	0.70977900
C	1.73413800	-0.74045800	-0.03269800
C	-4.80913500	-2.23626400	0.71140100
H	-5.65834600	-2.13278000	1.38646900
C	2.90818100	-1.52004100	-0.03233600
H	3.86762000	-1.02433600	-0.09574400
C	-2.64709900	-2.47404200	-1.04546000
H	-1.83371600	-2.55905600	-1.76563500
C	-3.80340600	1.24953800	0.70970700
C	1.55728700	3.49144400	0.16288300
H	1.41882000	4.56361700	0.25548900
C	2.85053300	2.92354100	0.05894100
C	1.73413300	0.74046400	-0.03269200
C	4.10166400	-3.82353300	0.06048200
C	0.42210000	-2.67788100	0.14437800
H	-0.57538400	-3.09215300	0.21660000
C	0.42207600	2.67787800	0.14435000
H	-0.57541400	3.09214300	0.21653500
C	-4.80914100	2.23628800	0.71126700
H	-5.65835600	2.13284000	1.38633500
C	-3.66536300	-3.45167500	-1.05346600
H	-3.61813500	-4.28037700	-1.75856100

C	4.14595000	-4.63338200	1.39058300
H	4.21566900	-3.96405700	2.25760600
H	5.02186900	-5.29495400	1.39660100
H	3.25415200	-5.25822200	1.51844900
C	-2.64709000	2.47397800	-1.04558800
H	-1.83369800	2.55895700	-1.76575700
C	5.41433200	-3.01092500	-0.06162500
H	5.54522700	-2.31630700	0.77872100
H	5.45594400	-2.43922300	-0.99817400
H	6.27015900	-3.69686500	-0.05673000
C	4.10163400	3.82355600	0.06056600
C	-4.74496900	3.34347300	-0.15959100
H	-5.53385100	4.09312400	-0.15237000
C	4.02005400	-4.80956600	-1.14298000
H	4.89754100	-5.46905800	-1.14630800
H	3.99552500	-4.26641500	-2.09634600
H	3.12605100	-5.44237900	-1.09296300
C	-3.66535500	3.45160900	-1.05365300
H	-3.61812200	4.28027600	-1.75878900
C	-4.74496800	-3.34349600	-0.15939800
H	-5.53384700	-4.09314900	-0.15212900
C	5.41430600	3.01096400	-0.06159500
H	5.54524800	2.31635700	0.77875400
H	6.27012500	3.69691400	-0.05675000
H	5.45588300	2.43925100	-0.99813900
C	4.14593900	4.63335400	1.39069600
H	4.21568700	3.96399800	2.25769200
H	3.25413800	5.25818000	1.51860700
H	5.02185100	5.29493600	1.39671900
C	4.01999100	4.80963600	-1.14285700
H	4.89747100	5.46913700	-1.14617800
H	3.12598100	5.44243600	-1.09279600
H	3.99544700	4.26652100	-2.09624300
C	-3.94018000	0.00003800	1.57696300
H	-4.90614600	0.00005200	2.09845200
H	-3.15354000	0.00006200	2.34696400

Table S2. DFT Coordinates for 5 (gas-phase).

Pt	-1.06437900	-0.00001000	-0.17299200
N	-4.07768500	-0.00001400	1.05119500
N	0.61144400	1.32139200	0.03228100
N	0.61145000	-1.32141100	0.03227600
C	-2.54257000	1.35990100	-0.34164100
C	-2.38597500	2.53091000	-1.12463000
H	-1.50881500	2.61892400	-1.76395700
C	-3.32461600	3.58280900	-1.11637800
H	-3.16777900	4.46382200	-1.73579200
C	-4.46411000	3.47583900	-0.29985700
H	-5.19579800	4.28066100	-0.26222400
C	-4.68388400	2.30188700	0.44110700
H	-5.60129000	2.21089600	1.01521700
C	-3.75968000	1.22643900	0.39708200
C	-2.54258900	-1.35989800	-0.34168900
C	-2.38603000	-2.53085900	-1.12475600
H	-1.50888600	-2.61884800	-1.76410600
C	-3.32469200	-3.58274000	-1.11655700
H	-3.16788200	-4.46371800	-1.73602700
C	-4.46417600	-3.47579400	-0.30001800
H	-5.19588200	-4.28060200	-0.26242800
C	-4.68392300	-2.30187800	0.44100900

H	-5.60132800	-2.21089600	1.01512200
C	-3.75969800	-1.22644600	0.39703700
C	-5.09175600	-0.00002500	2.10753700
H	-6.12950600	-0.00000900	1.72807800
H	-4.96045300	0.88579900	2.73772100
H	-4.96046800	-0.88587700	2.73768700
C	0.54121000	2.67075500	0.19494100
H	-0.45457100	3.08500800	0.28178500
C	1.67603400	3.48294500	0.23756400
H	1.53753600	4.55156300	0.36505100
C	2.96981200	2.91904300	0.11063700
C	3.02685400	1.51906200	-0.01484500
H	3.98595500	1.02401500	-0.08855500
C	1.85252800	0.73905900	-0.03364700
C	1.85253200	-0.73907000	-0.03364500
C	3.02686300	-1.51906600	-0.01483000
H	3.98596200	-1.02401200	-0.08853500
C	2.96983100	-2.91904500	0.11066400
C	1.67605500	-3.48295300	0.23759300
H	1.53756400	-4.55157000	0.36509700
C	0.54122600	-2.67077100	0.19495700
H	-0.45455100	-3.08503000	0.28181100
C	4.22000600	3.81995600	0.12763300
C	5.53288100	3.01153900	-0.01814900
H	6.38824200	3.69802100	-0.00269000
H	5.57027300	2.46003400	-0.96687400
H	5.66817300	2.29901500	0.80637200
C	4.13209400	4.83177000	-1.05380300
H	3.23588000	5.45998500	-0.98727400
H	4.10602900	4.30912000	-2.01853700
H	5.00747900	5.49415100	-1.04579800
C	4.27006300	4.60080700	1.47461100
H	5.14580200	5.26253500	1.49128500
H	4.34374800	3.91262800	2.32644700
H	3.37858000	5.22226300	1.62005500
C	4.22003100	-3.81995000	0.12768300
C	5.53290100	-3.01152600	-0.01809900
H	5.57029800	-2.46003500	-0.96683300
H	6.38826600	-3.69800200	-0.00262100
H	5.66818000	-2.29898700	0.80641200
C	4.13213600	-4.83178000	-1.05374100
H	4.10607500	-4.30914300	-2.01848200
H	3.23592600	-5.46000100	-0.98721100
H	5.00752500	-5.49415400	-1.04571900
C	4.27008100	-4.60078200	1.47467100
H	5.14582400	-5.26250500	1.49136100
H	3.37860100	-5.22224200	1.62011600
H	4.34375500	-3.91259200	2.32649900

Table S3. DFT Coordinates for **6** (gas-phase).

Pt	-1.19727500	-0.00000200	-0.09291100
N	0.44744100	-1.32669700	0.11289500
N	0.44743500	1.32669500	0.11289600
O	-4.32000600	-0.00000200	0.96382300
C	-2.64467200	1.37910300	-0.22866400
C	2.88042300	1.52820700	-0.09429800
H	3.82974000	1.03704700	-0.26692100
C	-2.64467000	-1.37910900	-0.22865900
C	1.54037200	-3.47860300	0.36234100
H	1.42143000	-4.53688000	0.56749700
C	2.83409200	-2.90583800	0.09064700

C	-3.88710600	-1.22434800	0.45500800
C	1.70500000	-0.71533500	-0.03819500
C	-4.82243500	-2.27228300	0.62991600
H	-5.72211000	-2.08264200	1.20745200
C	2.88042900	-1.52820000	-0.09430000
H	3.82974400	-1.03703600	-0.26692200
C	-2.48921800	-2.62358300	-0.91198800
H	-1.60745700	-2.77168100	-1.52808200
C	-3.88710800	1.22434300	0.45500200
C	1.54035800	3.47860400	0.36234700
H	1.42141200	4.53688000	0.56750500
C	2.83408000	2.90584500	0.09065100
C	1.70499700	0.71533800	-0.03819500
C	4.07588500	-3.81492600	0.03810400
C	0.41323000	-2.67064000	0.35792100
H	-0.56376800	-3.09424900	0.55121600
C	0.41322000	2.67063700	0.35792600
H	-0.56378100	3.09424200	0.55122100
C	-4.82244000	2.27227600	0.62990400
H	-5.72211500	2.08263700	1.20744000
C	-3.42953600	-3.65510000	-0.80684700
H	-3.27059200	-4.58882000	-1.34161400
C	4.24319600	-4.53868400	1.40781100
H	4.39289700	-3.81258000	2.21713500
H	5.11485700	-5.20649500	1.37796400
H	3.36439400	-5.14450700	1.65843600
C	-2.48922200	2.62357300	-0.91199800
H	-1.60746000	2.77167100	-1.52809100
C	5.37642200	-3.02800700	-0.25744700
H	5.58855900	-2.28628400	0.52378000
H	5.32650800	-2.50921000	-1.22376700
H	6.22610000	-3.72162700	-0.29593800
C	4.07586900	3.81493800	0.03811100
C	-4.58901200	3.49477400	0.00063000
H	-5.30584300	4.30577500	0.09837800
C	3.88214400	-4.87923700	-1.08349900
H	4.74562300	-5.55748500	-1.11484800
H	3.78578000	-4.39798900	-2.06528000
H	2.98325200	-5.48430300	-0.91615200
C	-3.42954200	3.65508900	-0.80686400
H	-3.27059900	4.58880700	-1.34163400
C	-4.58900400	-3.49478300	0.00064700
H	-5.30583400	-4.30578500	0.09840000
C	5.37641000	3.02802400	-0.25744200
H	5.58855000	2.28630100	0.52378400
H	6.22608500	3.72164800	-0.29593100
H	5.32649900	2.50922900	-1.22376200
C	4.24317700	4.53869500	1.40781800
H	4.39288100	3.81259000	2.21714100
H	3.36437300	5.14451400	1.65844300
H	5.11483500	5.20650900	1.37797300
C	3.88212500	4.87925000	-1.08349200
H	4.74560100	5.55750100	-1.11483900
H	2.98323000	5.48431100	-0.91614400
H	3.78576400	4.39800200	-2.06527300

Table S4. DFT Coordinates for 7 in MeCN.

Pt	1.11427509	-0.00109700	-0.21947102
N	-0.57101304	1.33179310	-0.01946700
N	-0.57295905	-1.33243710	-0.01690300
C	2.58346420	-1.37978110	-0.32620802

C	-2.98663123	-1.51054611	-0.00291500
H	-3.94391430	-1.00980708	-0.04126400
C	2.58426720	1.37676110	-0.33050403
C	-1.64309012	3.49339127	0.17345201
H	-1.49974511	4.56627635	0.27793202
C	-2.93416522	2.91769622	0.10054201
C	3.73122929	1.27309610	0.51264304
C	-1.80847314	0.74125805	-0.04504700
C	4.67137836	2.33079918	0.61158005
H	5.51804540	2.22480417	1.28861510
C	-2.98439523	1.51346912	-0.00166400
H	-3.94245030	1.01407708	-0.03798100
C	2.48784219	2.54484619	-1.13631909
H	1.65403612	2.65238420	-1.82989714
C	3.73014229	-1.27400410	0.51713204
C	-1.64843013	-3.49231127	0.17489401
H	-1.50699411	-4.56548735	0.27945602
C	-2.93853322	-2.91477822	0.09930101
C	-1.80953814	-0.74008705	-0.04451100
C	-4.19174132	3.80480129	0.14731501
C	-0.50611804	2.68417120	0.10993301
H	0.48349004	3.11658424	0.16528901
C	-0.51009804	-2.68485521	0.11295801
H	0.47880704	-3.11862724	0.17023001
C	4.66932436	-2.33219618	0.62010005
H	5.51576444	-2.22469117	1.29717910
C	3.44988326	3.57287427	-1.07763408
H	3.34811025	4.44533534	-1.72443213
C	-4.19329932	4.61220935	1.48001711
H	-4.22740032	3.94038530	2.34757118
H	-5.07635339	5.26299940	1.51531312
H	-3.30413225	5.24718140	1.57379712
C	2.48674619	-2.54997220	-1.12877109
H	1.65366013	-2.65871621	-1.82304714
C	-5.50060441	2.98186223	0.06825101
H	-5.59676041	2.28364318	0.91054107
H	-5.57182944	2.41365418	-0.86885707
H	-6.35907950	3.66327228	0.10629701
C	-4.19726232	-3.80034929	0.14194401
C	4.53375434	-3.48570727	-0.16827701
H	5.26862640	-4.28763833	-0.10406101
C	-4.15413232	4.79364537	-1.05669808
H	-5.03772738	5.44408240	-1.02759108
H	-4.15852532	4.25172032	-2.01142516
H	-3.26418525	5.43412540	-1.03094808
C	3.44791226	-3.57864027	-1.06606208
H	3.34600526	-4.45295934	-1.71032613
C	4.53639335	3.48181027	-0.18048001
H	5.27202540	4.28328633	-0.11936801
C	-5.50493440	-2.97550523	0.06301100
H	-5.60095843	-2.27869417	0.90648607
H	-6.36437249	-3.65582028	0.09891501
H	-5.57446543	-2.40549618	-0.87312907
C	-4.20213432	-4.61184335	1.47210811
H	-4.23759632	-3.94270430	2.34167518
H	-3.31363425	-5.24774540	1.56575312
H	-5.08570439	-5.26213540	1.50352411
C	-4.15864532	-4.78578236	-1.06492208
H	-5.04321038	-5.43504839	-1.03946308
H	-3.26961325	-5.42752042	-1.03914408
H	-4.16031032	-4.24107232	-2.01807016
C	4.06453031	0.00068900	1.22547609

O 4.75837036 0.00228000 2.28998918

Table S5. DFT Coordinates for **8** in MeCN.

Pt	0.88199000	-0.00132200	-0.29592100
N	-0.76661500	1.33108000	-0.07843800
N	-0.76911200	-1.33133500	-0.08046400
C	2.32630400	-1.40984200	-0.49842400
C	-3.17888700	-1.51312200	0.01278500
H	-4.13788600	-1.01418400	0.01420900
C	2.32820700	1.40394300	-0.50813300
C	-1.82385500	3.49646900	0.12022400
H	-1.67484800	4.57026000	0.20558600
C	-3.11781100	2.92283000	0.10059200
C	3.48994500	1.44312700	0.28639700
C	-2.00527600	0.74172800	-0.06042600
C	4.49810500	2.41684300	0.23639100
H	5.36360600	2.36336700	0.89450600
C	-3.17607700	1.51747200	0.01425000
H	-4.13618500	1.02064700	0.01378500
C	2.24782500	2.45397600	-1.46963200
H	1.40283400	2.48319300	-2.15691700
C	3.48504100	-1.44633900	0.30074100
C	-1.83094100	-3.49511500	0.11208200
H	-1.68357700	-4.56946600	0.19170800
C	-3.12375000	-2.91883400	0.09572100
C	-2.00661800	-0.73958600	-0.06166200
C	-4.37063400	3.81377200	0.18223900
C	-0.69093800	2.68452900	0.02870900
H	0.30096200	3.11587400	0.04161400
C	-0.69640800	-2.68516100	0.02322000
H	0.29453500	-3.11858600	0.03498800
C	4.48938300	-2.42445100	0.26316700
H	5.35256500	-2.36942200	0.92384500
C	3.23939500	3.45013400	-1.56895600
H	3.13863200	4.23237000	-2.32201400
C	-4.31804600	4.64133900	1.50155800
H	-4.31432600	3.98305800	2.38001200
H	-5.20038600	5.29098800	1.56360500
H	-3.42741600	5.27938000	1.54804900
C	2.24665600	-2.46649800	-1.45271700
H	1.40442600	-2.49811000	-2.14336600
C	-5.68330600	2.99335500	0.16649100
H	-5.74734200	2.30690800	1.02144800
H	-5.79337000	2.41271500	-0.75919500
H	-6.53802200	3.67756500	0.22913000
C	-4.37886400	-3.80703200	0.17443000
C	4.35247100	-3.46152100	-0.67735800
H	5.10907300	-4.24209000	-0.74457700
C	-4.37641600	4.78430200	-1.03731600
H	-5.25652300	5.43789300	-0.98416200
H	-4.41894900	4.22826800	-1.98290300
H	-3.48446100	5.42217900	-1.05484900
C	3.23524300	-3.46672700	-1.54025900
H	3.13515100	-4.25410900	-2.28801500
C	4.36088400	3.44703100	-0.71158400
H	5.12002700	4.22426100	-0.78827000
C	-5.68908100	-2.98251100	0.17098300
H	-5.74484800	-2.29877700	1.02864400
H	-6.54537900	-3.66438400	0.23756000
H	-5.80408100	-2.39855700	-0.75199700

C	-4.32549800	-4.64670100	1.48603600
H	-4.31886200	-3.99647600	2.37042600
H	-3.43638600	-5.28730600	1.52540300
H	-5.20903100	-5.29510500	1.54375300
C	-4.39241200	-4.76576300	-1.05431300
H	-5.27431100	-5.41717600	-1.00403000
H	-3.50243200	-5.40610100	-1.08163400
H	-4.43693100	-4.20043900	-1.99427400
S	3.76420500	0.00396800	1.46063200
O	5.34705300	0.00262100	1.92637900
O	2.71587800	0.01398700	2.73618800

Table S6. Calculated HOMO/LUMO energies (eV).

Complex	Gas phase		MeCN	
	HOMO	LUMO	HOMO	LUMO
4	-5.020	-2.421	-5.612	-2.375
5	-4.124	-2.337	-4.779	-2.364
6	-4.822	-2.492	-5.551	-2.425

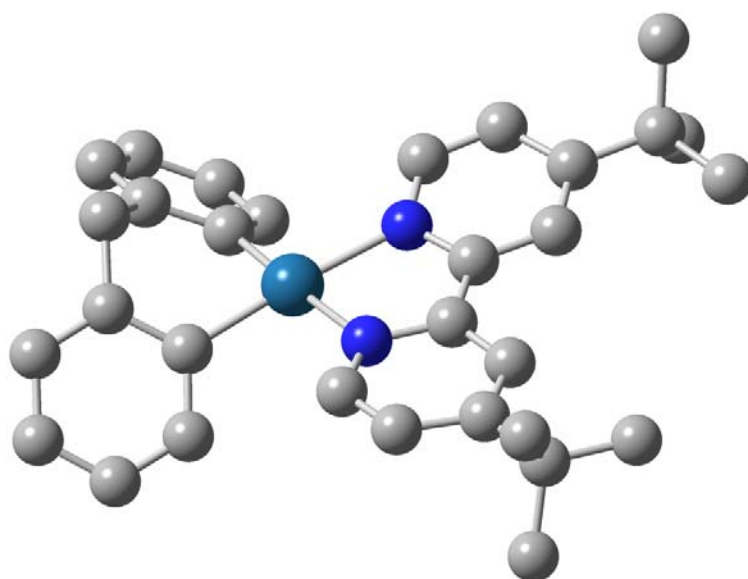


Figure S12. Drawing of triplet **4T** (hydrogen atoms omitted for clarity).

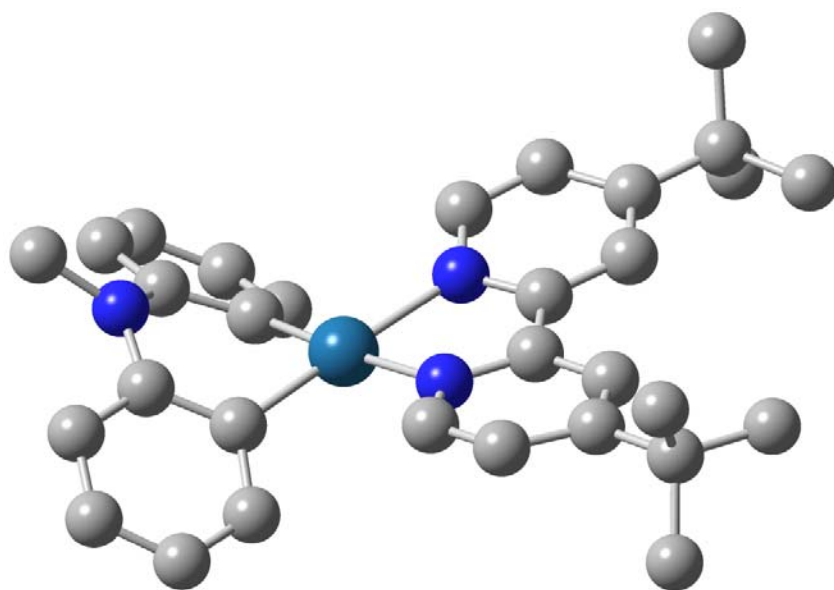


Figure S13. Drawing of triplet **5T** (hydrogen atoms omitted for clarity).

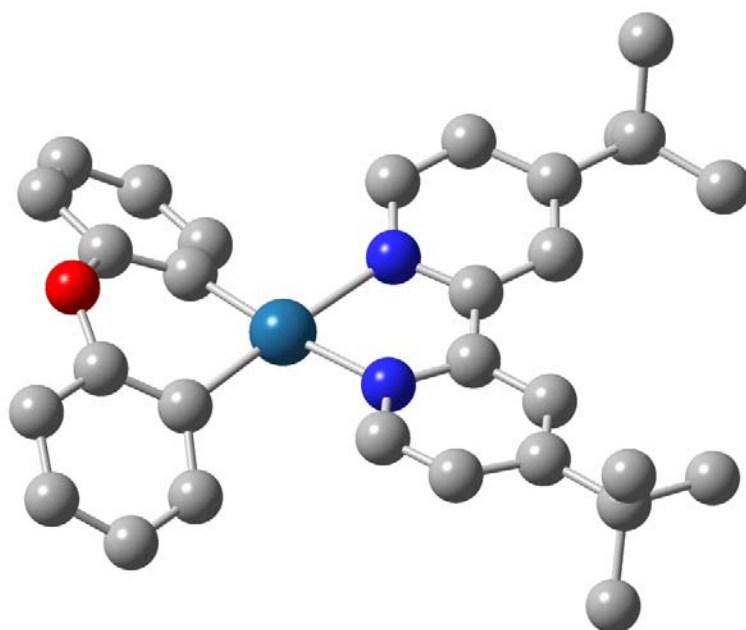


Figure S14. Drawing of triplet **6T** (hydrogen atoms omitted for clarity).

Table S7. Selected metrical parameters for DFT triplet structures **4T-6T**, and **4T'-6T'**.

	4T	5T	6T	4T'	5T'	6T'
Complex number	(X=CH ₂)	(X=NMe)	(X=O)	(X=CH ₂)	(X=NMe)	(X=O)

Pt-C	2.022	1.998	2.004	2.040	2.005	2.020
				2.035 ^a	1.999 ^a	2.009 ^a
Pt-N	2.107	2.127	2.123	2.132	2.125	2.135
				2.130 ^b	2.143 ^b	2.103 ^b
X-C	1.523	1.416	1.395	1.525	1.412	1.398
				1.519	1.411	
C-Pt-C	85.46	85.62	86.98	90.89	89.34	90.37
N-Pt-N	78.61	77.34	77.35	76.62	76.89	77.19
C-X-C	107.70	121.56	122.76	115.49	124.68	125.77

^a Carbon atom out of the Pt, C, N, N plane. ^b N atom "trans" to the out of plane C atom.

Table S8. DFT Coordinates for **4T**.

Pt	-1.17024200	-0.00003100	0.03943000
N	0.45641400	-1.33439300	0.14502500
N	0.45637900	1.33436000	0.14503500
C	-2.64635200	1.37194400	-0.12555300
C	2.89673200	1.52597500	-0.07015800
H	3.84671300	1.02987400	-0.22196100
C	-2.64636300	-1.37198600	-0.12560300
C	1.54961700	-3.49317300	0.29379600
H	1.43230100	-4.56032200	0.44710000
C	2.84836800	-2.90642000	0.06050300
C	-3.87355500	-1.23009200	0.60321800
C	1.71811900	-0.71226700	0.00584900
C	-4.89796500	-2.18720600	0.47422600
H	-5.81723400	-2.07002900	1.04557900
C	2.89677300	-1.52594000	-0.07016500
H	3.84674000	-1.02981300	-0.22197000
C	-2.52515200	-2.49737000	-0.99459300
H	-1.62457800	-2.61343400	-1.59253900
C	-3.87354100	1.23003800	0.60326800
C	1.54951800	3.49317400	0.29378000
H	1.43217100	4.56032100	0.44706800
C	2.84828700	2.90645400	0.06050000
C	1.71810000	0.71226800	0.00585400
C	4.08939300	-3.81440400	-0.01645200
C	0.42076100	-2.68949200	0.32159700
H	-0.55909000	-3.11923700	0.48716600
C	0.42068400	2.68946200	0.32158400
H	-0.55918300	3.11918000	0.48712800
C	-4.89793100	2.18718100	0.47433300
H	-5.81720200	2.06999200	1.04568100
C	-3.55837400	-3.43629100	-1.13405200
H	-3.44582600	-4.27186200	-1.82167000
C	4.24248300	-4.59173300	1.32529300
H	4.38437800	-3.89835800	2.16419900
H	5.11443300	-5.25790500	1.27750300
H	3.36167300	-5.20722900	1.54333100
C	-2.52509800	2.49739700	-0.99444400

H	-1.62450300	2.61349700	-1.59235400
C	5.39318400	-3.01765900	-0.26789400
H	5.59805400	-2.30721100	0.54372000
H	5.35352000	-2.46200200	-1.21399300
H	6.24269400	-3.71008400	-0.32474700
C	4.08928700	3.81447200	-0.01644700
C	-4.74785100	3.29177000	-0.38542400
H	-5.54514000	4.02624100	-0.47625600
C	3.90539900	-4.83247800	-1.18175900
H	4.76917900	-5.50900600	-1.23177300
H	3.81884100	-4.31235500	-2.14442500
H	3.00531300	-5.44426100	-1.04838600
C	-3.55829800	3.43635100	-1.13384400
H	-3.44572000	4.27197700	-1.82139200
C	-4.74791400	-3.29174200	-0.38560400
H	-5.54522200	-4.02618600	-0.47648500
C	5.39312500	3.01774600	-0.26770900
H	5.59797900	2.30741600	0.54401100
H	6.24261000	3.71019900	-0.32460500
H	5.35353500	2.46196100	-1.21373600
C	4.24224200	4.59193300	1.32523700
H	4.38410900	3.89864400	2.16421900
H	3.36138400	5.20740400	1.54315300
H	5.11416200	5.25814400	1.27744900
C	3.90535400	4.83243000	-1.18186400
H	4.76912200	5.50897300	-1.23188000
H	3.00524600	5.44420600	-1.04861700
H	3.81888000	4.31221300	-2.14448700
C	-4.06267300	-0.00004500	1.48147200
H	-5.05755800	-0.00004900	1.94252300
H	-3.32058200	-0.00006700	2.29178600

Table S9. DFT Coordinates for 5T.

Pt	1.06366100	0.00000000	-0.17683800
N	4.14064300	0.00000000	0.94182800
N	-0.58113900	-1.32914700	0.05229000
N	-0.58113900	1.32914600	0.05229000
C	2.51899700	-1.35804800	-0.35401800
C	2.35031500	-2.55079300	-1.11619100
H	1.46175200	-2.64478800	-1.73366700
C	3.27526300	-3.60073900	-1.08687300
H	3.10627100	-4.49435400	-1.68355900
C	4.42944900	-3.50207800	-0.27004000
H	5.14536200	-4.31916600	-0.22839600
C	4.66977500	-2.33163200	0.44873700
H	5.59059100	-2.24623600	1.01626400
C	3.75811500	-1.23594600	0.36528500
C	2.51899600	1.35804700	-0.35401600
C	2.35031400	2.55079400	-1.11618900
H	1.46175100	2.64479000	-1.73366500
C	3.27526200	3.60074100	-1.08686800
H	3.10626900	4.49435700	-1.68355300
C	4.42944700	3.50207900	-0.27003400
H	5.14535900	4.31916800	-0.22838800
C	4.66977400	2.33163200	0.44874100
H	5.59058900	2.24623700	1.01626800
C	3.75811400	1.23594500	0.36528600
C	5.15790200	0.00000000	2.01523500
H	6.18371800	0.00000000	1.62079600
H	5.01814900	-0.88447900	2.63976600
H	5.01814900	0.88447700	2.63976700

C	-0.53601000	-2.67711400	0.25877400
H	0.45052000	-3.10526100	0.38419100
C	-1.66240400	-3.48739200	0.30516200
H	-1.53304400	-4.55099500	0.47414800
C	-2.96798600	-2.90780100	0.12143900
C	-3.02200000	-1.52747500	-0.03447200
H	-3.97842100	-1.03268000	-0.14794600
C	-1.84289000	-0.71532100	-0.03013000
C	-1.84289000	0.71532100	-0.03013000
C	-3.02200000	1.52747400	-0.03447200
H	-3.97842100	1.03268000	-0.14794600
C	-2.96798600	2.90780000	0.12143900
C	-1.66240400	3.48739200	0.30516200
H	-1.53304500	4.55099500	0.47414700
C	-0.53601000	2.67711300	0.25877400
H	0.45052100	3.10526100	0.38419000
C	-4.21269800	-3.81517500	0.12052200
C	-5.52710100	-3.02105100	-0.07993300
H	-6.37972000	-3.71244600	-0.07723700
H	-5.53558600	-2.48576500	-1.03843400
H	-5.68751900	-2.29220200	0.72535100
C	-4.08841000	-4.85280700	-1.03514100
H	-3.18302600	-5.46331500	-0.93520100
H	-4.04666500	-4.34763900	-2.00878400
H	-4.95466800	-5.52857400	-1.03349800
C	-4.30208600	-4.57040500	1.48024900
H	-5.17354700	-5.23941700	1.48529900
H	-4.40568400	-3.86264600	2.31282700
H	-3.40936300	-5.17910500	1.66675800
C	-4.21269700	3.81517400	0.12052100
C	-5.52710100	3.02105100	-0.07993300
H	-5.53558600	2.48576400	-1.03843200
H	-6.37972000	3.71244600	-0.07723700
H	-5.68751900	2.29220300	0.72535200
C	-4.08841000	4.85280500	-1.03514400
H	-4.04666500	4.34763500	-2.00878600
H	-3.18302500	5.46331200	-0.93520500
H	-4.95466700	5.52857200	-1.03350100
C	-4.30208500	4.57040800	1.48024700
H	-5.17354500	5.23942000	1.48529600
H	-3.40936100	5.17910700	1.66675400
H	-4.40568300	3.86265000	2.31282600

Table S10. DFT Coordinates for 6T.

Pt	-1.19727500	-0.00000200	-0.09291100
N	0.44744100	-1.32669700	0.11289500
N	0.44743500	1.32669500	0.11289600
O	-4.32000600	-0.00000200	0.96382300
C	-2.64467200	1.37910300	-0.22866400
C	2.88042300	1.52820700	-0.09429800
H	3.82974000	1.03704700	-0.26692100
C	-2.64467000	-1.37910900	-0.22865900
C	1.54037200	-3.47860300	0.36234100
H	1.42143000	-4.53688000	0.56749700
C	2.83409200	-2.90583800	0.09064700
C	-3.88710600	-1.22434800	0.45500800
C	1.70500000	-0.71533500	-0.03819500
C	-4.82243500	-2.27228300	0.62991600
H	-5.72211000	-2.08264200	1.20745200
C	2.88042900	-1.52820000	-0.09430000
H	3.82974400	-1.03703600	-0.26692200
C	-2.48921800	-2.62358300	-0.91198800

H	-1.60745700	-2.77168100	-1.52808200
C	-3.88710800	1.22434300	0.45500200
C	1.54035800	3.47860400	0.36234700
H	1.42141200	4.53688000	0.56750500
C	2.83408000	2.90584500	0.09065100
C	1.70499700	0.71533800	-0.03819500
C	4.07588500	-3.81492600	0.03810400
C	0.41323000	-2.67064000	0.35792100
H	-0.56376800	-3.09424900	0.55121600
C	0.41322000	2.67063700	0.35792600
H	-0.56378100	3.09424200	0.55122100
C	-4.82244000	2.27227600	0.62990400
H	-5.72211500	2.08263700	1.20744000
C	-3.42953600	-3.65510000	-0.80684700
H	-3.27059200	-4.58882000	-1.34161400
C	4.24319600	-4.53868400	1.40781100
H	4.39289700	-3.81258000	2.21713500
H	5.11485700	-5.20649500	1.37796400
H	3.36439400	-5.14450700	1.65843600
C	-2.48922200	2.62357300	-0.91199800
H	-1.60746000	2.77167100	-1.52809100
C	5.37642200	-3.02800700	-0.25744700
H	5.58855900	-2.28628400	0.52378000
H	5.32650800	-2.50921000	-1.22376700
H	6.22610000	-3.72162700	-0.29593800
C	4.07586900	3.81493800	0.03811100
C	-4.58901200	3.49477400	0.00063000
H	-5.30584300	4.30577500	0.09837800
C	3.88214400	-4.87923700	-1.08349900
H	4.74562300	-5.55748500	-1.11484800
H	3.78578000	-4.39798900	-2.06528000
H	2.98325200	-5.48430300	-0.91615200
C	-3.42954200	3.65508900	-0.80686400
H	-3.27059900	4.58880700	-1.34163400
C	-4.58900400	-3.49478300	0.00064700
H	-5.30583400	-4.30578500	0.09840000
C	5.37641000	3.02802400	-0.25744200
H	5.58855000	2.28630100	0.52378400
H	6.22608500	3.72164800	-0.29593100
H	5.32649900	2.50922900	-1.22376200
C	4.24317700	4.53869500	1.40781800
H	4.39288100	3.81259000	2.21714100
H	3.36437300	5.14451400	1.65844300
H	5.11483500	5.20650900	1.37797300
C	3.88212500	4.87925000	-1.08349200
H	4.74560100	5.55750100	-1.11483900
H	2.98323000	5.48431100	-0.91614400
H	3.78576400	4.39800200	-2.06527300

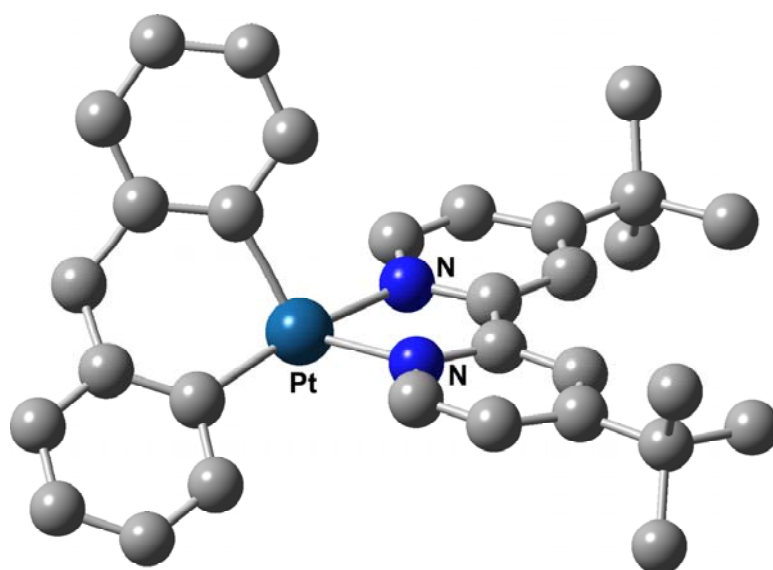


Figure S15. Drawing of triplet 4T' (hydrogen atoms omitted for clarity).

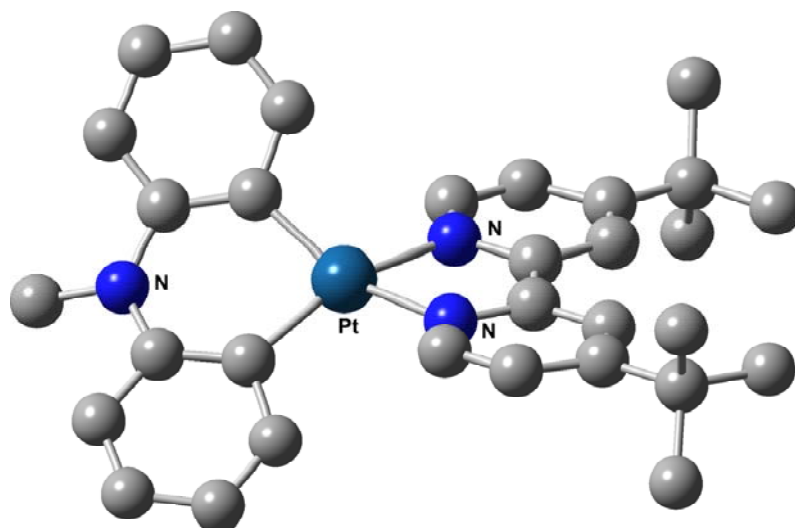


Figure S16. Drawing of triplet 5T' (hydrogen atoms omitted for clarity).

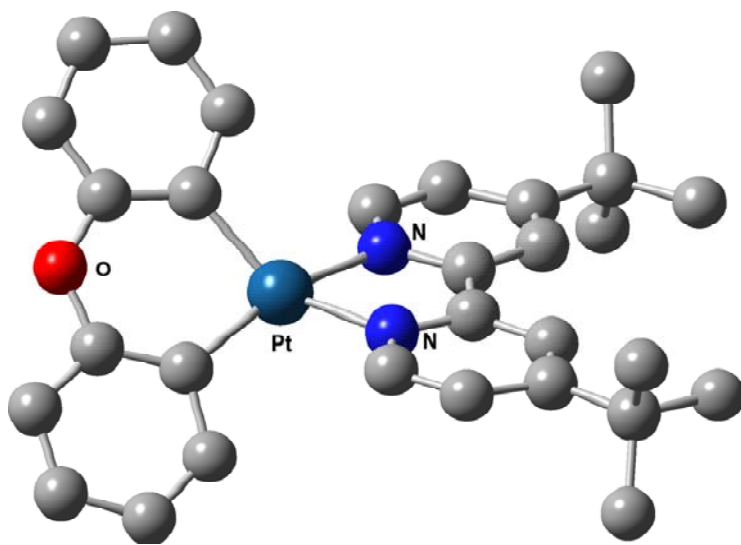


Figure S17. Drawing of triplet **6T'** (hydrogen atoms omitted for clarity).

Table S11. DFT Coordinates for non-planar triplet **4T'**.

Pt	1.22436500	-0.25465600	-0.43821700
N	-0.64541600	-1.27857600	-0.48250800
N	-0.18064100	1.26191800	0.07542300
C	2.12486300	-1.32614700	1.03889500
C	1.31469000	-1.72181300	2.12822900
H	0.26535200	-1.44237500	2.15410000
C	1.85788000	-2.46944100	3.18925100
H	1.22385400	-2.76451000	4.02240400
C	3.21953000	-2.82519400	3.16728100
H	3.65117700	-3.39904300	3.98419800
C	4.02334000	-2.42298100	2.08638200
H	5.07837200	-2.69223600	2.07170900
C	3.49819700	-1.66462900	1.01417500
C	2.96411100	0.73934200	-0.82140100
C	2.89797600	2.02590200	-1.41791200
H	1.93006500	2.48680500	-1.60470900
C	4.05581300	2.72486600	-1.80858600
H	3.96809000	3.70909800	-2.26467400
C	5.32107100	2.14521500	-1.60617100
H	6.22560600	2.67753600	-1.89201500
C	5.40387200	0.86215400	-1.03592100
H	6.38115800	0.40180900	-0.89463900
C	4.24610200	0.15161500	-0.64960900
C	-0.79496500	-2.61369400	-0.72261100
H	0.12338300	-3.17264500	-0.87124900
C	-2.03392200	-3.23574700	-0.78072200
H	-2.07413900	-4.29996500	-0.98601800
C	-3.23165300	-2.46931500	-0.57014600
C	-3.07307900	-1.10990800	-0.30770800
H	-3.93993900	-0.48733000	-0.12421800
C	-1.78221500	-0.50187800	-0.25860100
C	-1.53163900	0.88847900	0.00552200
C	-2.53503700	1.88325900	0.20488900
H	-3.57108700	1.58825500	0.09191300
C	-2.21643800	3.19590400	0.54317300
C	-0.81651300	3.50788600	0.69051000

H	-0.48929800	4.49662000	0.99351100
C	0.14225600	2.54053100	0.44984700
H	1.19978100	2.75018800	0.55539200
C	-4.60387200	-3.16744600	-0.63241600
C	-5.77783200	-2.19007400	-0.37953100
H	-6.72855800	-2.73513000	-0.43471400
H	-5.81017600	-1.39011400	-1.13083400
H	-5.71678700	-1.73017800	0.61559000
C	-4.79098900	-3.80298600	-2.04247400
H	-4.00331100	-4.53131000	-2.26883400
H	-4.77161600	-3.03275200	-2.82416400
H	-5.75626300	-4.32396200	-2.09661100
C	-4.65925300	-4.28779800	0.44882400
H	-5.62581900	-4.80731500	0.40440200
H	-4.54152200	-3.86605600	1.45531900
H	-3.86992600	-5.03481200	0.30351300
C	-3.26841900	4.29738900	0.76971100
C	-4.71616600	3.78365400	0.57445000
H	-4.88205300	3.41172500	-0.44519700
H	-5.42370400	4.60455900	0.74660900
H	-4.96194800	2.98090700	1.28214600
C	-3.02089700	5.45751200	-0.24081500
H	-3.12169500	5.10324000	-1.27480100
H	-2.01832600	5.88728700	-0.12915700
H	-3.75173300	6.26135200	-0.07967500
C	-3.13558500	4.84435000	2.22268700
H	-3.86475700	5.64805000	2.39137900
H	-2.13649900	5.25278100	2.41552700
H	-3.32195700	4.05073000	2.95759300
C	4.40944000	-1.27510200	-0.13739600
H	5.45344000	-1.44169000	0.15528800
H	4.21878200	-1.96321700	-0.97939100

Table S12. DFT Coordinates for non-planar triplet 5T'.

Pt	-1.06867700	-0.07390300	0.05079800
N	0.66310600	-1.32750800	0.19382600
N	0.53944400	1.30398500	-0.12342100
C	-2.47945400	-1.32955900	-0.62245300
C	-2.00201300	-2.49927500	-1.29931100
H	-0.93154800	-2.64197100	-1.38176800
C	-2.83854400	-3.45874100	-1.87076200
H	-2.41369700	-4.33633700	-2.35230100
C	-4.24196600	-3.28351000	-1.80582600
H	-4.91535300	-4.04008500	-2.20098500
C	-4.75661900	-2.12146200	-1.24210900
H	-5.83344000	-2.00371000	-1.19997400
C	-3.89989700	-1.11093000	-0.69269500
C	-2.50317500	1.10824400	0.78727900
C	-2.04319900	2.06125100	1.74990700
H	-0.97866800	2.10557100	1.95951300
C	-2.89613600	2.93105100	2.43283100
H	-2.49224300	3.64535400	3.14628200
C	-4.28960200	2.86298500	2.19660100
H	-4.97462000	3.51166500	2.73705800
C	-4.78844700	1.92789100	1.29375800
H	-5.86388000	1.84434300	1.18303100
C	-3.91728300	1.03740300	0.58661500
C	0.66690500	-2.64545200	0.55504900
H	-0.30616000	-3.09667500	0.71282300
C	1.82583100	-3.38794800	0.72625300
H	1.74039600	-4.42753700	1.02327700

C	3.11019200	-2.77091600	0.51185900
C	3.10956400	-1.41774600	0.19001000
H	4.04681300	-0.89646300	0.04052100
C	1.89685600	-0.66822300	0.06763800
C	1.82858000	0.74844700	-0.13067600
C	2.95739100	1.60199700	-0.33985400
H	3.94376600	1.15595700	-0.31344100
C	2.81676900	2.96424900	-0.58306200
C	1.47323600	3.48553800	-0.61345800
H	1.27720200	4.53241800	-0.81833800
C	0.39988700	2.63883500	-0.38055300
H	-0.61745700	3.01287800	-0.39427700
C	4.39313400	-3.60946800	0.66524300
C	5.67722600	-2.78309900	0.40760100
H	6.55911300	-3.42594500	0.52497400
H	5.77532400	-1.95210300	1.11851200
H	5.69839700	-2.37224300	-0.61035500
C	4.46309900	-4.18156000	2.11293800
H	3.59750600	-4.81412500	2.34268800
H	4.49206500	-3.37056400	2.85190800
H	5.36817200	-4.79200800	2.23495600
C	4.35939000	-4.79010300	-0.35097600
H	5.25533800	-5.41509400	-0.23538600
H	4.33110600	-4.41610500	-1.38257100
H	3.48053700	-5.42827400	-0.20071600
C	4.00680900	3.91162200	-0.82526500
C	5.37032500	3.18043600	-0.75953500
H	5.53783900	2.72257300	0.22421100
H	6.18256100	3.89729300	-0.93543800
H	5.44742600	2.39667600	-1.52449700
C	4.00069900	5.03218800	0.25728700
H	4.11529100	4.60465300	1.26176400
H	3.06688100	5.60677600	0.24201000
H	4.83007100	5.73125700	0.08353700
C	3.86780600	4.55955700	-2.23548400
H	4.69917900	5.25433400	-2.41665300
H	2.93165400	5.12171900	-2.33417500
H	3.88273700	3.79206400	-3.01999600
N	-4.51076500	0.09142100	-0.27759400
C	-5.86655900	0.39565100	-0.79697400
H	-6.66284000	-0.01714800	-0.16204000
H	-5.99107600	1.47728300	-0.86378500
H	-5.96892400	-0.01341500	-1.80357500

Table S13. DFT Coordinates for non-planar triplet **6T'**.

Pt	1.20409100	-0.12363500	-0.17560900
N	-0.56735200	-1.30990800	-0.28737000
N	-0.32100100	1.28241600	0.16836200
C	2.47410200	-1.37725100	0.74720700
C	1.90526300	-2.43140500	1.53187800
H	0.82572900	-2.51136500	1.59289600
C	2.68980400	-3.35273400	2.22940200
H	2.21438400	-4.14822200	2.79793300
C	4.10366600	-3.24338500	2.20083000
H	4.72165300	-3.95558800	2.74178300
C	4.69652600	-2.19765000	1.49588100
H	5.77286900	-2.05587100	1.47591500
C	3.88925100	-1.26083200	0.80252900
C	2.74981000	1.04733500	-0.74053200
C	2.44181100	2.15805600	-1.58333400
H	1.40207300	2.35864200	-1.82961800
C	3.43011200	2.99687900	-2.11645300

H	3.14557100	3.83459100	-2.74897300
C	4.79454000	2.75201900	-1.83189600
H	5.56818400	3.39860500	-2.23804300
C	5.13999400	1.65873600	-1.03479600
H	6.17429300	1.41836800	-0.80685900
C	4.12423200	0.82248400	-0.51574300
C	-0.61261300	-2.63627600	-0.60766300
H	0.34647900	-3.12048600	-0.75661100
C	-1.79899800	-3.34187200	-0.74652700
H	-1.75304800	-4.39170300	-1.01419000
C	-3.05772200	-2.67562800	-0.54037600
C	-3.00958500	-1.31849500	-0.23306700
H	-3.92684600	-0.76609500	-0.07223100
C	-1.77052300	-0.61435700	-0.12500000
C	-1.63929400	0.79310800	0.11086300
C	-2.72453300	1.70364100	0.29139100
H	-3.73167300	1.31733800	0.19463300
C	-2.52022100	3.04663500	0.59243100
C	-1.15055900	3.48823800	0.71050500
H	-0.90909200	4.51224800	0.97377700
C	-0.11445400	2.59920200	0.49088900
H	0.92053700	2.91034800	0.56767000
C	-4.37028800	-3.47106600	-0.67384100
C	-5.62295200	-2.59593900	-0.42300900
H	-6.52701700	-3.20900300	-0.52855000
H	-5.69558000	-1.77197200	-1.14510000
H	-5.62680000	-2.17137800	0.58954900
C	-4.46682400	-4.06193400	-2.11238600
H	-3.62533200	-4.72795100	-2.33698700
H	-4.47258500	-3.26216600	-2.86400100
H	-5.39290400	-4.64239900	-2.22009100
C	-4.37241200	-4.63558800	0.36113600
H	-5.29262200	-5.22670100	0.26158800
H	-4.32241900	-4.24735300	1.38658700
H	-3.52100400	-5.31094900	0.21527200
C	-3.66396700	4.05440300	0.80728700
C	-5.06210900	3.40865900	0.64722000
H	-5.20652600	2.99614400	-0.36004800
H	-5.83873000	4.16667900	0.80966400
H	-5.22488800	2.60557400	1.37811800
C	-3.53387900	5.20585300	-0.23464500
H	-3.61706400	4.81763200	-1.25794100
H	-2.57156600	5.72421100	-0.14890300
H	-4.33016800	5.94676400	-0.08162500
C	-3.56078200	4.64819000	2.24442000
H	-4.36073200	5.38282100	2.40745600
H	-2.60213600	5.15443300	2.40835100
H	-3.65809400	3.85934400	3.00127800
O	4.63626100	-0.25783600	0.20877900

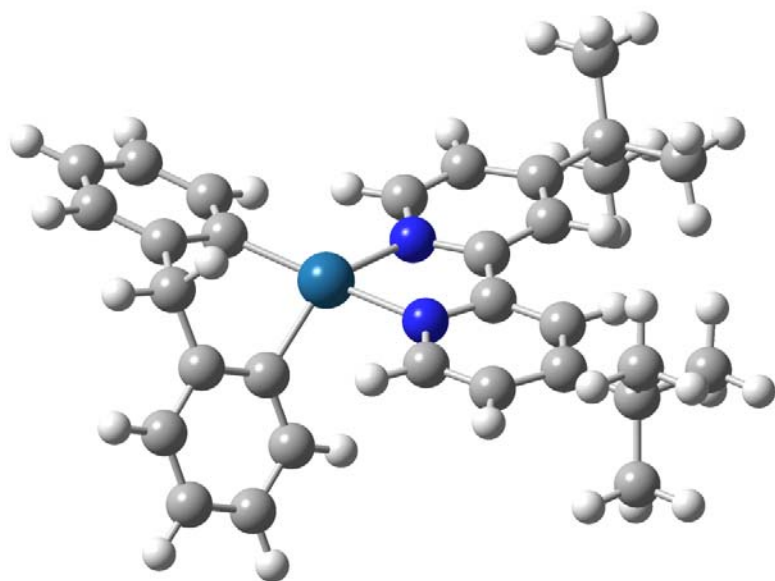


Figure S18. Drawing of transition state 4TS.

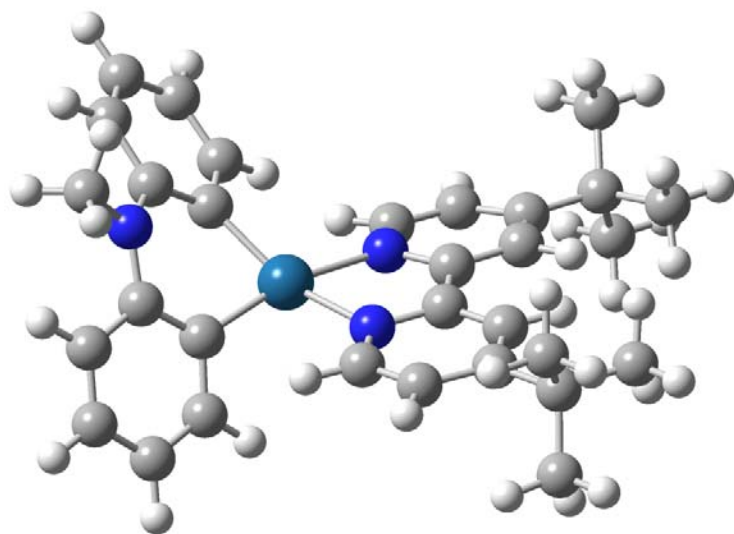


Figure S19. Drawing of transition state 5TS.

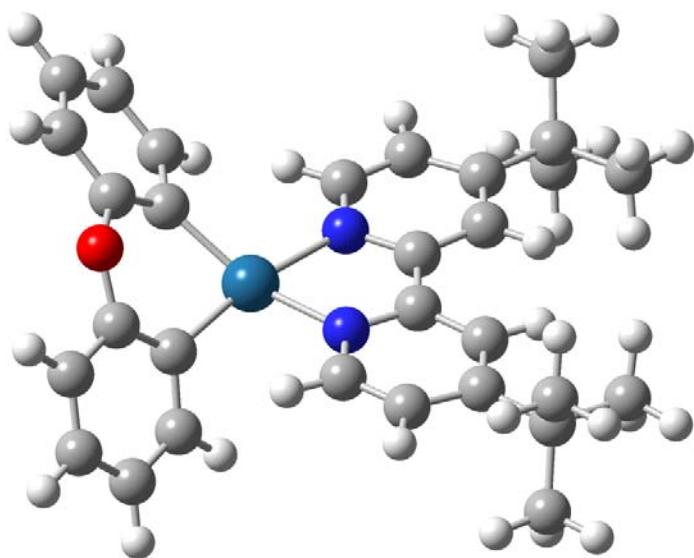


Figure S20. Drawing of transition state **6TS**.

Table S14. DFT Coordinates for transition state **4TS** connecting **4T** and **4T'**.

Pt	-1.19237400	-0.15130100	-0.17610000
N	0.43270300	1.22297300	-0.26681900
N	0.49037600	-1.38993000	0.15916800
C	-2.41167900	1.16819400	0.77430800
C	-2.04260800	1.77036800	1.99165500
H	-1.13329500	1.45908600	2.49924300
C	-2.85175400	2.77884000	2.55226000
H	-2.56607700	3.24011200	3.49489400
C	-4.02624400	3.18430900	1.88961600
H	-4.65461500	3.96205100	2.31766000
C	-4.39549200	2.56841800	0.67861200
H	-5.31150000	2.87209600	0.17420700
C	-3.60753300	1.54376900	0.11198500
C	-2.87662200	-1.33196800	-0.37763200
C	-2.99688700	-2.70566800	-0.06648200
H	-2.18808600	-3.23540900	0.42205200
C	-4.16807400	-3.44047200	-0.34264800
H	-4.21505100	-4.49686100	-0.08505800
C	-5.26907400	-2.80699800	-0.93989200
H	-6.17628500	-3.36368100	-1.16358800
C	-5.19108700	-1.43007500	-1.22095400
H	-6.05080400	-0.92073900	-1.65439500
C	-4.02525500	-0.69238800	-0.93700300
C	0.30310700	2.56671800	-0.45874400
H	-0.71120300	2.93911000	-0.54899000
C	1.39168700	3.42501400	-0.53583400
H	1.21133000	4.48167900	-0.69979900
C	2.84949800	1.53494900	-0.18917300
H	3.82897700	1.09206000	-0.06078900
C	1.70616000	0.67886200	-0.13161100
C	1.74309700	-0.74042900	0.04579000
C	2.94014900	-1.51673900	0.09352800
H	3.87999000	-0.99609400	-0.04187100
C	1.63551800	-3.50652400	0.46613900
H	1.53667700	-4.57086300	0.64953800
C	0.48745200	-2.74525500	0.38665500

H	-0.48055200	-3.20710300	0.49728000
C	-4.03308700	0.82012700	-1.16039600
H	-5.03369300	1.15087700	-1.46252800
H	-3.35238700	1.08358100	-1.98594300
C	2.93133600	-2.89017300	0.30452000
C	2.72420900	2.90673500	-0.39352700
C	3.92650100	3.86825300	-0.46149500
C	4.20122400	-3.75597800	0.36849400
C	3.80067700	4.92500000	0.67629400
H	3.81708100	4.44192000	1.66175700
H	4.63742100	5.63467500	0.62688700
H	2.86874300	5.49733200	0.59822800
C	5.28151200	3.13657600	-0.29848300
H	5.43970700	2.39215800	-1.08989400
H	6.10121500	3.86371500	-0.35834200
H	5.35729000	2.63207400	0.67370900
C	3.92507500	4.59313200	-1.84037200
H	3.00034900	5.15955000	-2.00195300
H	4.76539600	5.29794400	-1.89649400
H	4.02549000	3.87195200	-2.66167200
C	5.49476300	-2.92402300	0.18872100
H	6.36877200	-3.58479400	0.24935100
H	5.52465600	-2.42436400	-0.78851000
H	5.60025700	-2.16214500	0.97241400
C	4.14723300	-4.82814000	-0.76125800
H	5.03724300	-5.47019600	-0.71596100
H	3.26366300	-5.47132600	-0.67056000
H	4.11592700	-4.35235500	-1.74985800
C	4.26738900	-4.47018800	1.75193800
H	4.32473300	-3.73782000	2.56747200
H	3.38816600	-5.10119400	1.92834600
H	5.15693100	-5.11230700	1.80249700

Table S15. DFT Coordinates for transition state **5TS** connecting **5T** and **5T'**.

Pt	1.06120100	-0.30427000	-0.39063200
N	-0.35328300	1.25495400	-0.18549900
N	-0.84887200	-1.35412700	-0.37709300
C	2.64093200	0.82441400	-0.84917900
C	2.54237500	1.66543600	-1.99531900
H	1.64933200	1.59823000	-2.61236200
C	3.53933700	2.58837800	-2.33405000
H	3.42432800	3.21973000	-3.21198500
C	4.69429900	2.70134100	-1.52284800
H	5.47658800	3.41266200	-1.77618900
C	4.84525100	1.87104900	-0.41131600
H	5.76124100	1.93111000	0.16781000
C	3.84258800	0.90852100	-0.08935500
C	2.38034700	-1.69324400	0.24202900
C	2.08069200	-3.08846700	0.26059500
H	1.21212600	-3.43956500	-0.27393700
C	2.84571600	-4.04348500	0.93337100
H	2.56682200	-5.09377200	0.88909100
C	3.97988100	-3.63698900	1.67502100
H	4.58401700	-4.36555800	2.20991700
C	4.33382700	-2.29202800	1.69241200
H	5.22972000	-2.00159200	2.22946600
C	3.58023200	-1.31733700	0.96581700
C	-0.03511100	2.58104300	-0.06719200
H	1.00286600	2.83663600	-0.23835900
C	-0.96037200	3.56436200	0.24335500
H	-0.62220000	4.59245200	0.31593400
C	-2.66247900	1.86043500	0.35701500

H	-3.68320300	1.53578200	0.51417000
C	-1.68198300	0.86410700	0.04563900
C	-1.95093700	-0.53512200	-0.06991500
C	-3.25912600	-1.10904700	0.03267400
H	-4.07307100	-0.46460500	0.33944000
C	-2.38042700	-3.21541500	-0.71806700
H	-2.49023000	-4.24649600	-1.03661400
C	-1.11712500	-2.64012800	-0.74531300
H	-0.27993100	-3.22312700	-1.10290400
C	-3.50708500	-2.44252300	-0.26968700
C	-2.34037100	3.20775000	0.46333400
C	-3.36689700	4.30605900	0.79697800
C	-4.89676500	-3.09868000	-0.16956000
C	-3.41844900	5.33088100	-0.37570400
H	-3.74192200	4.84317100	-1.30435400
H	-4.12785100	6.13734900	-0.14469600
H	-2.43814500	5.78623800	-0.55972200
C	-4.79284300	3.74166600	1.01166600
H	-4.82505600	3.02724400	1.84471900
H	-5.48267600	4.56163700	1.24941000
H	-5.17039000	3.24044700	0.11076700
C	-2.93018900	5.03923800	2.10058000
H	-1.93692900	5.49217000	1.99845400
H	-3.64300700	5.83953000	2.34181900
H	-2.89570400	4.34152800	2.94720600
C	-5.98490200	-2.11137500	0.31936700
H	-6.95130400	-2.62809700	0.38251100
H	-5.75386100	-1.71471300	1.31668500
H	-6.10534100	-1.26565000	-0.37047700
C	-4.82829500	-4.28831000	0.83413600
H	-5.80537700	-4.78636500	0.89998500
H	-4.08773600	-5.03566200	0.52505400
H	-4.55199200	-3.93701000	1.83664200
C	-5.31732100	-3.63432900	-1.57087700
H	-5.37692000	-2.81543700	-2.29928800
H	-4.60418200	-4.37360000	-1.95453600
H	-6.30271900	-4.11632600	-1.51203900
N	4.07947100	0.00405000	0.97186800
C	5.02111700	0.41371500	2.03623800
H	4.72808000	-0.05479600	2.97827200
H	6.06081500	0.13761300	1.80965100
H	4.96343100	1.49625200	2.16373700

Table S16. DFT Coordinates for transition state **6TS** connecting **6T** and **6T'**.

Pt	1.19713000	-0.28596100	-0.33612900
N	-0.21675900	1.21846400	-0.01528700
N	-0.69772900	-1.38622300	-0.28803800
C	2.75732700	0.92751200	-0.68406200
C	2.70307000	1.87606900	-1.74404600
H	1.86215100	1.85022500	-2.43335700
C	3.68901200	2.86208800	-1.90040900
H	3.61489200	3.57774700	-2.71584400
C	4.77344000	2.93595300	-0.99140400
H	5.53235100	3.70600500	-1.10455200
C	4.87991300	1.99463700	0.03862900
H	5.71364200	1.99452700	0.73443100
C	3.89491900	0.99011300	0.14752400
C	2.54456000	-1.67620700	0.25536500
C	2.37881300	-3.09075800	0.14269200
H	1.61787600	-3.48041000	-0.51785800
C	3.19850800	-4.01139100	0.80165000
H	3.04105300	-5.07730900	0.65484600
C	4.23453200	-3.55903400	1.65744800

H	4.85380800	-4.26988400	2.19836800
C	4.47770300	-2.19011900	1.76543800
H	5.29061300	-1.79608900	2.36763400
C	3.67946500	-1.27838700	1.03686900
C	0.09894100	2.53733000	0.21175300
H	1.15185400	2.78422200	0.19390000
C	-0.85179800	3.51356000	0.43576700
H	-0.51887600	4.53160900	0.60490600
C	-2.57221100	1.83265300	0.23729500
H	-3.60825800	1.51944500	0.23347600
C	-1.56782400	0.83206300	0.04553500
C	-1.82173300	-0.56756100	-0.08641700
C	-3.13168300	-1.14244500	-0.04784000
H	-3.96836000	-0.48323400	0.14401600
C	-2.18689800	-3.30164300	-0.49783200
H	-2.26029600	-4.36766800	-0.68414000
C	-0.92879500	-2.71303500	-0.50006300
H	-0.06401400	-3.32907200	-0.68705900
C	-3.35091800	-2.50063600	-0.24694900
C	-2.25584700	3.17076600	0.43513700
C	-3.30636800	4.27350100	0.65454000
C	-4.74376200	-3.15634200	-0.21264100
C	-3.16431800	5.34635600	-0.46684800
H	-3.34883200	4.90500800	-1.45473000
H	-3.89054900	6.15530100	-0.30975600
H	-2.16225400	5.79111200	-0.47958100
C	-4.75578000	3.72910300	0.62542700
H	-4.92854300	2.98950200	1.41835500
H	-5.46163800	4.55460600	0.78274200
H	-4.99698000	3.26587200	-0.34038600
C	-3.06352200	4.94390300	2.04025300
H	-2.05970800	5.37884200	2.11259000
H	-3.79190300	5.74989300	2.20192300
H	-3.17231200	4.21306000	2.85179700
C	-5.87222100	-2.13610500	0.07533500
H	-6.84040700	-2.65256500	0.09089800
H	-5.73979900	-1.64920900	1.05040400
H	-5.92381300	-1.35792400	-0.69747700
C	-4.77044700	-4.24252800	0.90382400
H	-5.75202600	-4.73483000	0.92938000
H	-4.01060800	-5.01536800	0.73769700
H	-4.58423200	-3.79491800	1.88854000
C	-5.02857800	-3.82695700	-1.58969800
H	-5.03365700	-3.08019100	-2.39411600
H	-4.27360500	-4.58247000	-1.83770800
H	-6.00866400	-4.32246700	-1.57351300
O	4.14016600	0.03388900	1.14023100

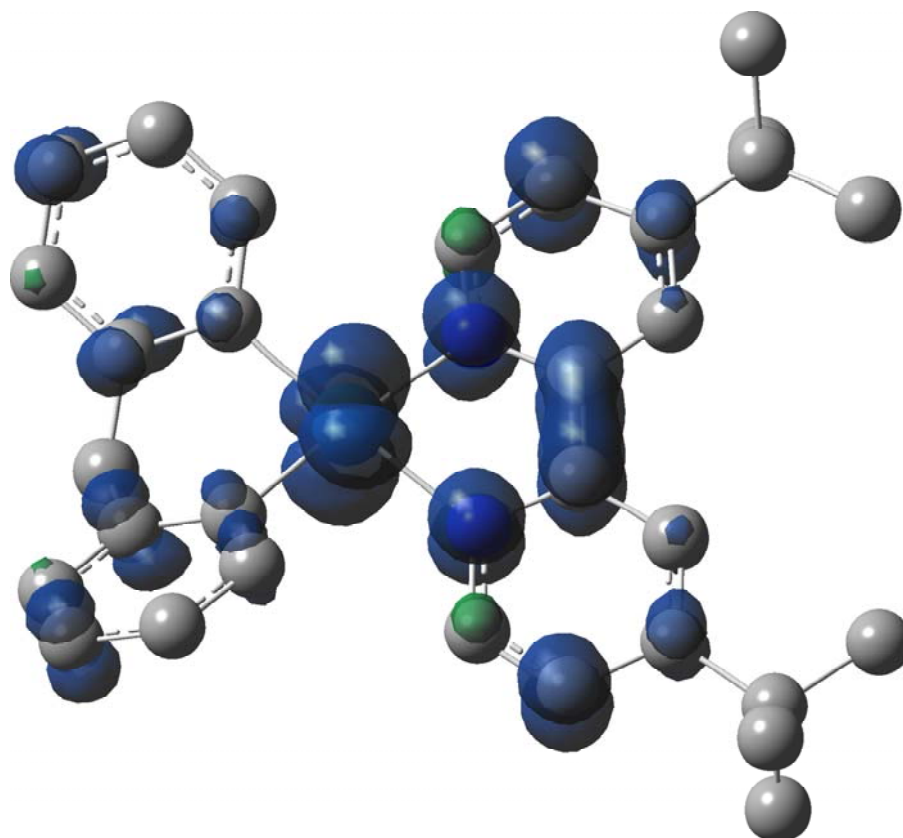


Figure S21. Spin density plot for **4T** (isoval = 0.004) (hydrogen atoms omitted for clarity).

^tBu₂bpy on right.

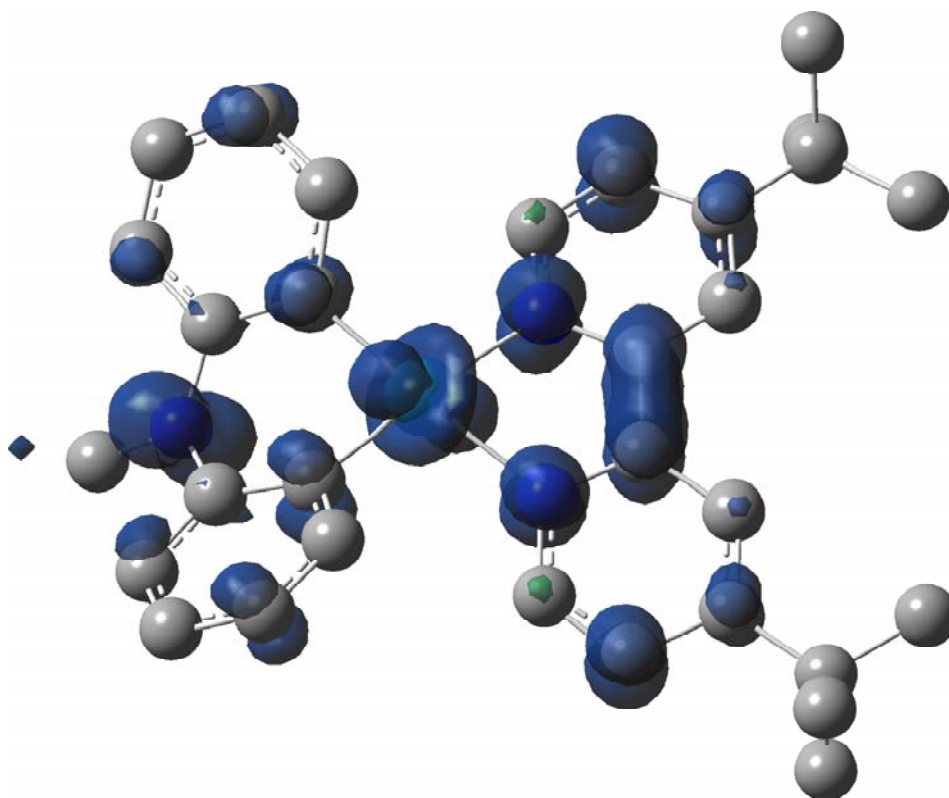


Figure S22. Spin density plot for 5T (isoval = 0.004) (hydrogen atoms omitted for clarity).

^tBu₂bpy on right.

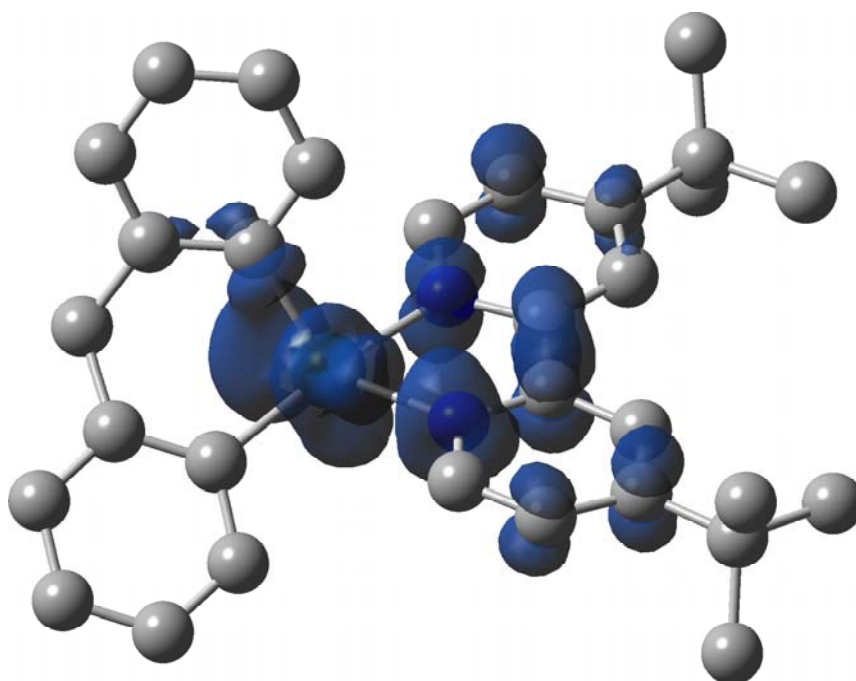


Figure S23. Spin density plot for **4T'** (isoval = 0.004) (hydrogen atoms omitted for clarity).

^tBu₂bpy on right.

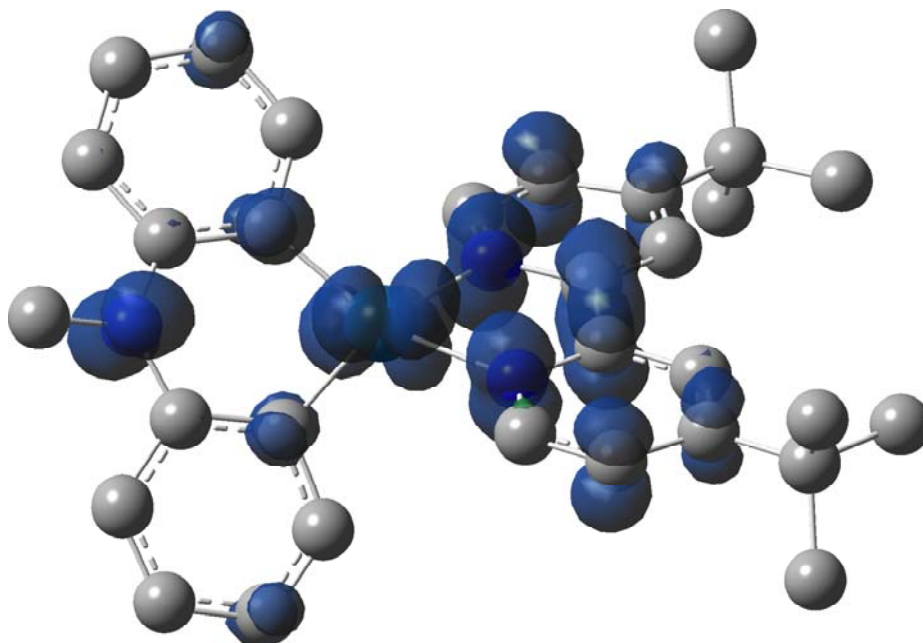


Figure S24. Spin density plot for **5T'** (isovalue = 0.004) (hydrogen atoms omitted for clarity).

^tBu₂bpy on right.

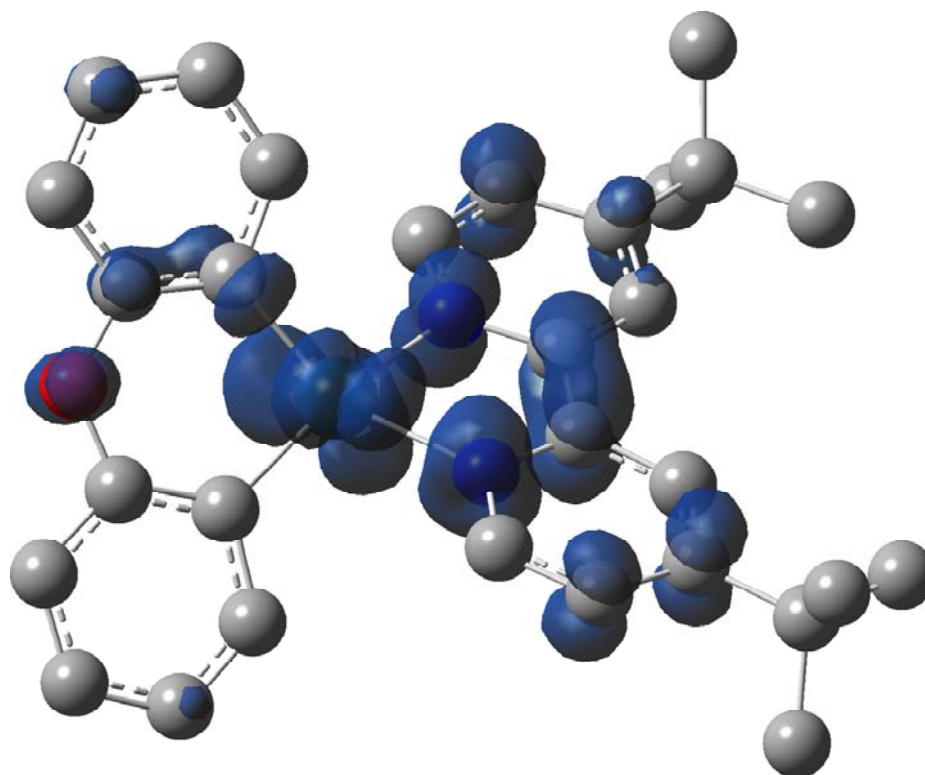


Figure S25. Spin density plot for **6T'** (isovalue = 0.004) (hydrogen atoms omitted for clarity).

^tBu₂bpy on right.

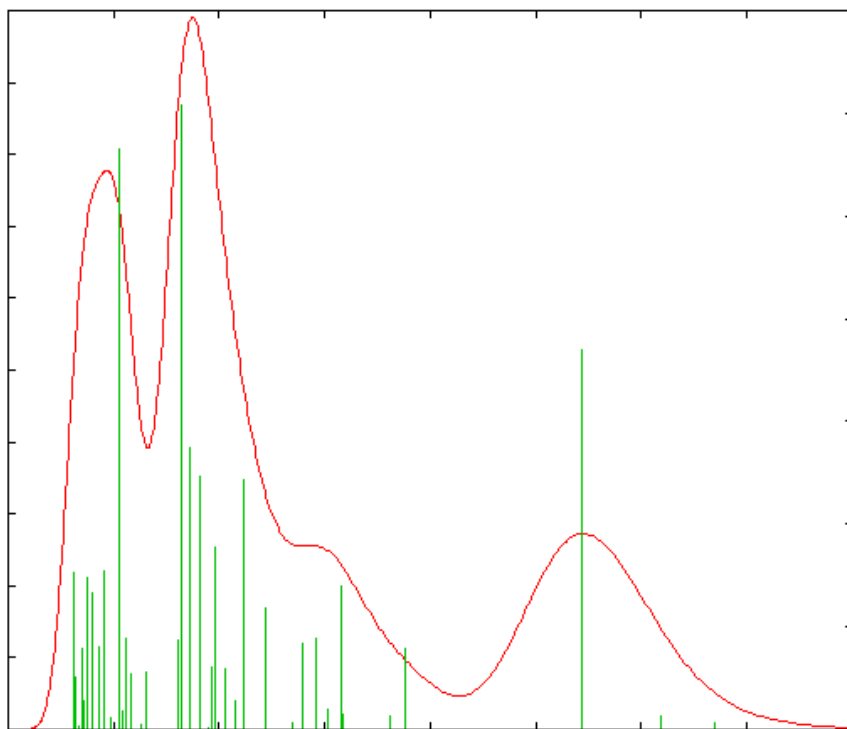


Figure S26. Calculated UV-vis spectrum of **7** in MeCN (vertical green lines correspond to unbroadened oscillator strengths of calculated singlet-singlet transitions).

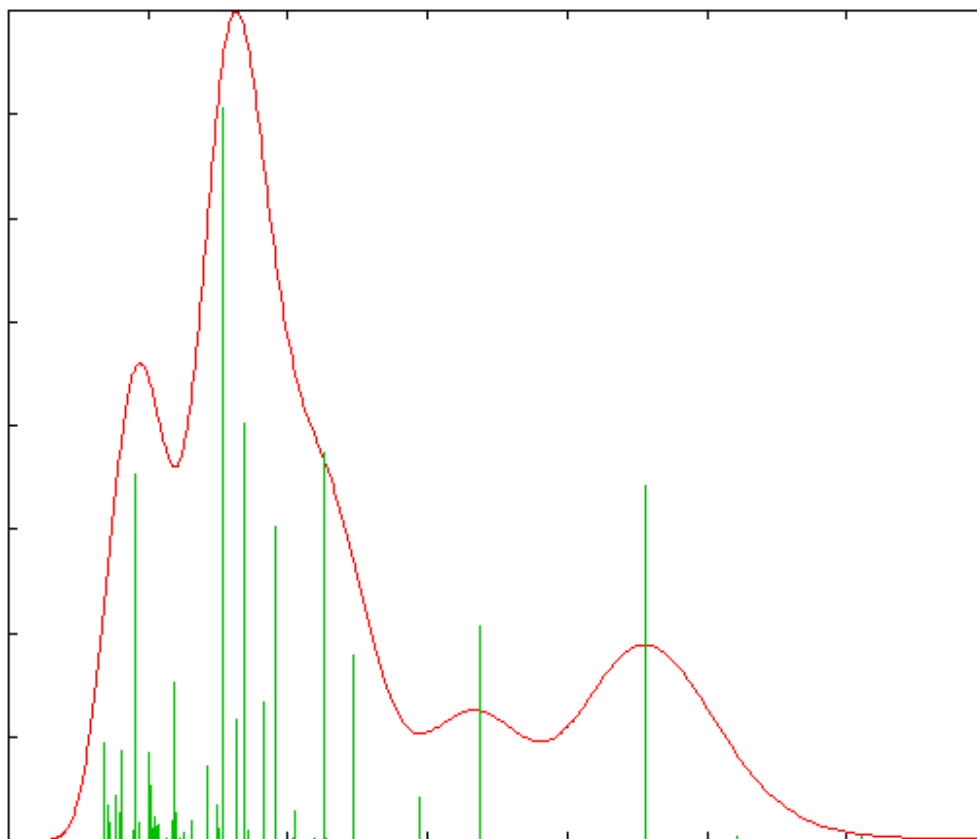


Figure S27. Calculated UV-vis spectrum of **8** in MeCN (vertical green lines correspond to unbroadened oscillator strengths of calculated singlet-singlet transitions).

Full references to Gaussian 03 and 09:

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; J. A. Montgomery, J.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.;

Pople, J. A. *Gaussian 03*, Gaussian, Inc.: Pittsburgh PA,, 2003.

2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision B.01* Gaussian, Inc., Wallingford CT: 2009.