Supporting Information for

Ultrafast Excited State Dynamics in *trans*-N-Heterocyclic Carbene Platinum(II) Acetylide Complexes

Silvano R. Valandro[a,†], Ru He[a,b,†], James D. Bullock[b], Hadi Arman and Kirk S. Schanze[a,*]

[a]Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249, United States

[b]Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

* Corresponding author e-mail: kirk.schanze@utsa.edu

[†]Equal contributions

Table of Contents

Experimental:

All starting chemicals used for the synthesis were purchased from commercial suppliers, reagent grade, and used without additional purification. K_2PtCl_4 was purchased from Strem Chemicals. Solvents were of reagent grade unless otherwise noted. $IPtCl_2$[1], IPtP[1], $BiPtCl_2$[2], BiPtP[2] and IPtP-2[3] were synthesized following the procedures described in other literatures.

1,3-di-tert-butyl-5-[2-(trimethylsilyl)ethynyl]benzene. 1-Bromo-3,5-di-tert-butylbenzene (0.5 g, 1.86 mmol) was dissolved in 30 mL triethylamine and degassed by N_2 for 30 mins. Then $Pd(PPh_3)_2Cl_2$ (130.4 mg, 0.186 mmol), CuI (35.4 mg, 0.186 mmol) and trimethylsilyl acetylene (0.912 g, 9.29 mmol) were added. The mixture was degassed for another 10 mins and stirred under reflux for 2 days. The solvents were removed under vacuum and DCM was added. The organic layer was washed with water 3 times and dried over $MgSO_4$ (anhydrous). The residue was purified by flash column chromatography with hexane to give the product as a pale yellow solid (0.45 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.37 (t, J = 1.9 Hz, 1H), 7.31 (d, J = 1.9 Hz, 2H), 1.31 (s, 18H), 0.26 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 150.83, 126.36, 123.13, 122.13, 106.56, 92.62, 34.94, 31.46, 0.25.

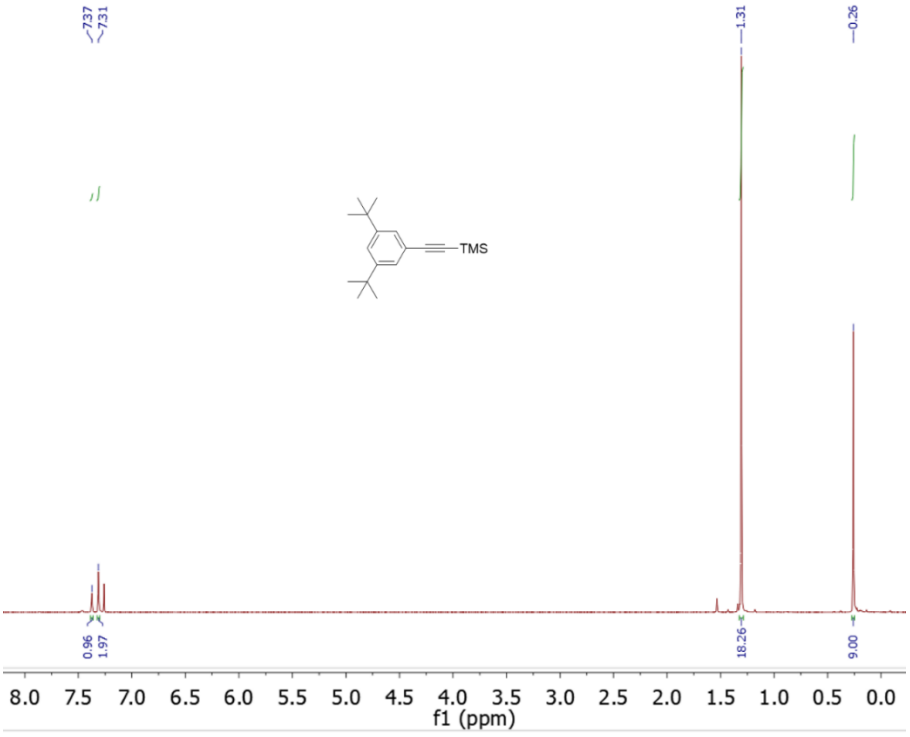

Figure S1. ^{1}H NMR spectrum of 1,3-di-tert-butyl-5-[2-(trimethylsilyl)ethynyl]benzene (500 MHz, $CDCl_3$)

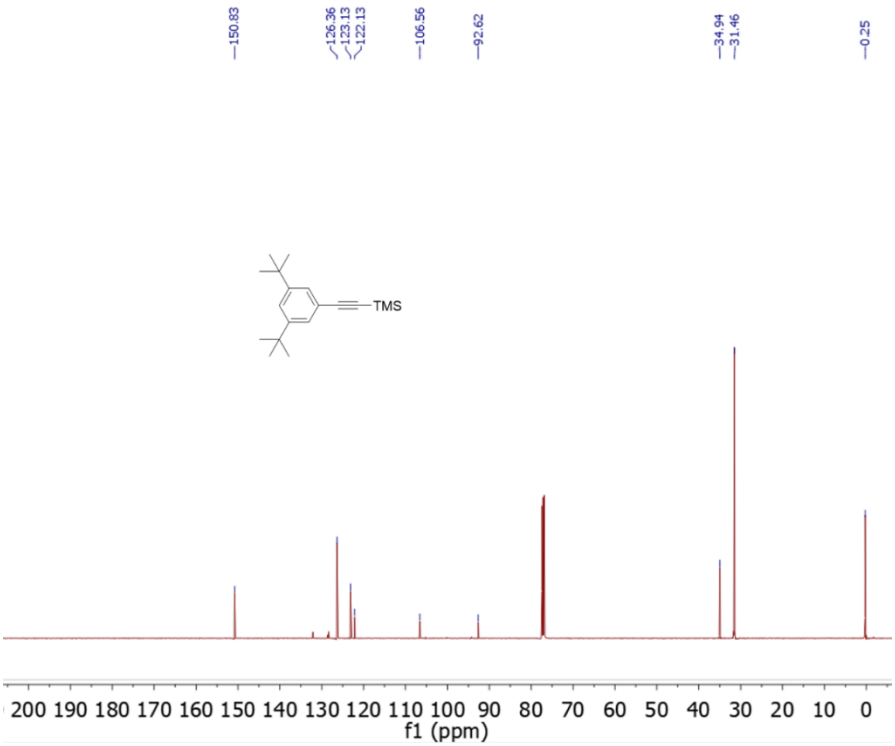

Figure S2. ^{13}C NMR spectrum of 1,3-di-tert-butyl-5-[2-(trimethylsilyl)ethynyl]benzene (125 MHz, $CDCl_3$)

1,3-di-tert-butyl-5-ethynylbenzene. 1,3-Di-tert-butyl-5-[2-(trimethylsilyl)ethynyl]benzene (0.45 g, 1.57 mmol) and K_2CO_3 (1.3 g, 9.42 mmol) were added to 20 mL DCM and 20 mL methanol. The mixture was stirred at room temperature for 18 h. Solvents were removed under vacuum and the as-obtained solids were re-dissolved in DCM. After washing with water and dried over $MgSO_4$(anhydrous), the organic residue was purified by flash column chromatography with hexane and dried under vacuum to give white solid (0.188 g, 56%). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.42 (t, J = 1.8 Hz, 1H), 7.35 (d, J = 1.8 Hz, 2H), 3.02 (s, 1H), 1.31 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 151.01, 126.52, 123.41, 121.16, 85.00, 75.91, 34.94, 31.45.

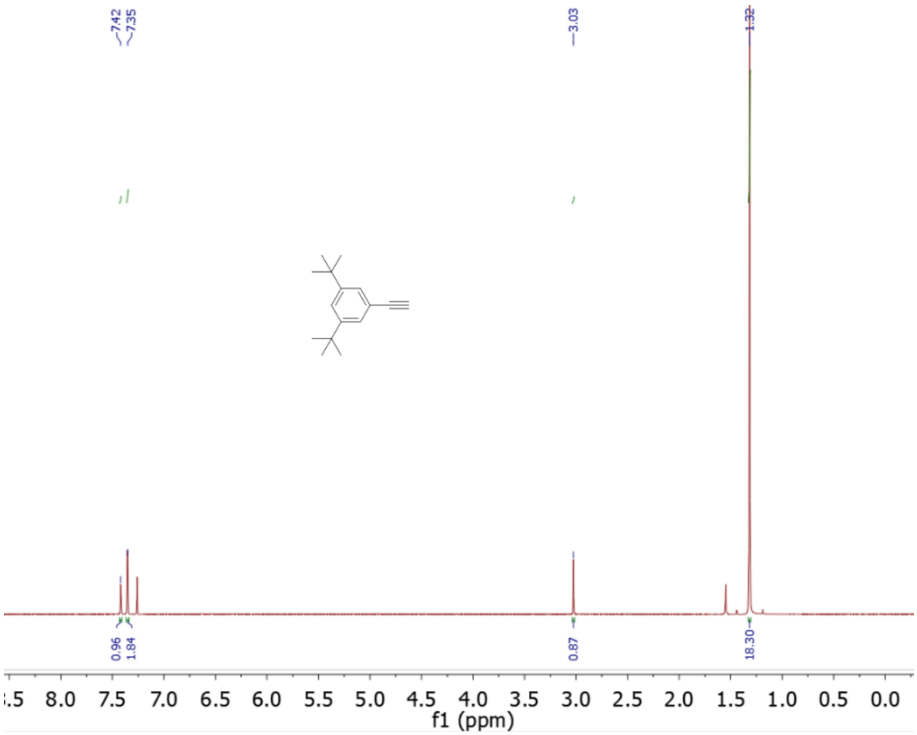

Figure S3. ^{1}H NMR spectrum of 1,3-di-tert-butyl-5-ethynylbenzene (500 MHz, $CDCl_3$)

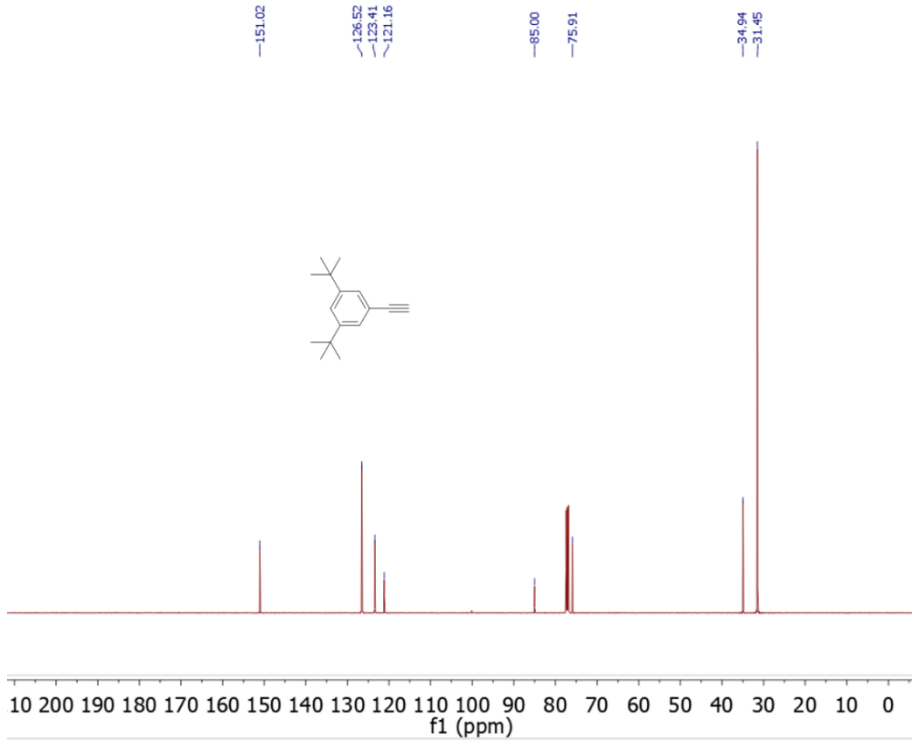

Figure S4. ^{13}C NMR spectrum of 1,3-di-tert-butyl-5-ethynylbenzene (125 MHz, $CDCl_3$)

IPtP-*t*Bu. 1,3-Di-tert-butyl-5-ethynylbenzene (0.132 g, 0.616 mmol) was dissolved in a solvent mixture of 20 mL DCM and 10 mL $HNEt_2$. The solution was degassed by N_2 for 30 mins. Then $IPtCl_2$ (0.15 g, 0.205 mmol) and CuI (3.9 mg, 0.0205 mmol) were added. The reaction mixture was stirred at room temperature for 48 h. After removal of the solvents, 20 mL DCM was added and the organic layer was washed with water 3 times, dried over $MgSO_4$(anhydrous) and filtered. The filtrate was concentrated and poured into methanol to get a white precipitate. The as-obtained precipitate was filtered and washed with cold methanol and hexanes, then dried under vacuum resulting in a white solid (65 mg, 29%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (t, J = 1.8 Hz, 2H), 6.97 (d, J = 1.8 Hz, 4H), 6.85 (s, 4H), 5.52 (m, 4H), 2.48 (m, 8H), 1.91 (m, 8H), 1.75 (m, 4H), 1.64 – 1.45 (m, 16H), 1.29 – 1.24 (m, 4H), 1.22 (s, 36H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.44, 149.69, 128.78, 125.23, 118.39, 116.08, 106.72, 105.93, 59.21, 34.67, 33.93, 31.53, 26.22, 25.92. HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{62}H_{91}N_4Pt$, 1086.6886; (found) 1086.6873.

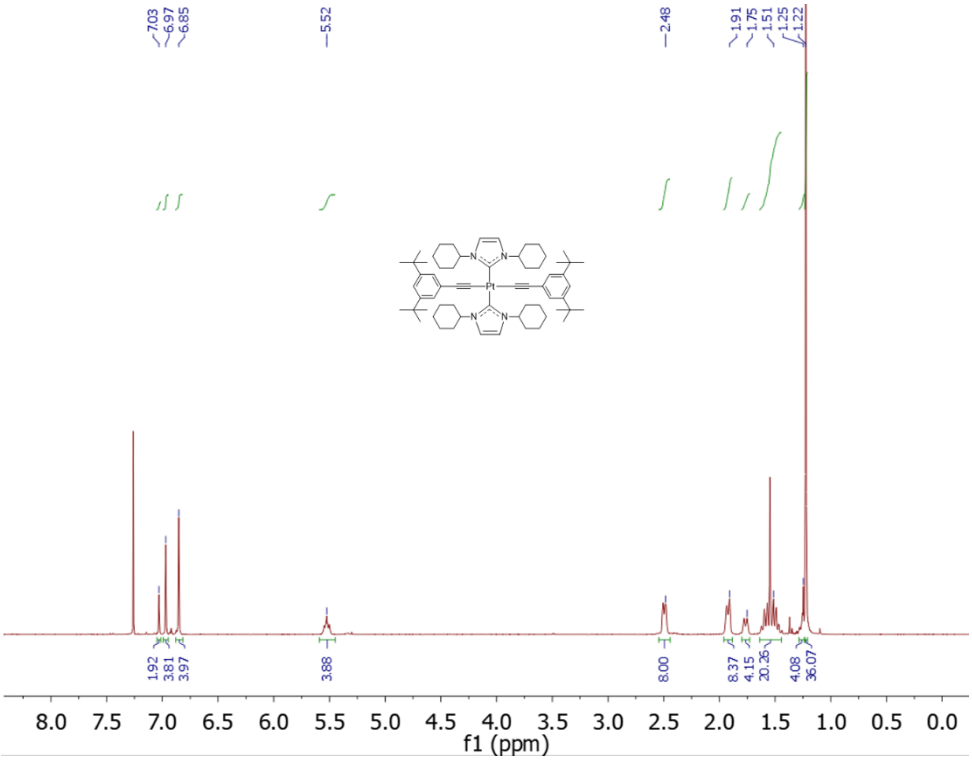

Figure S5. ^{1}H NMR spectrum of IPtP-*t*Bu (500 MHz, $CDCl_3$)

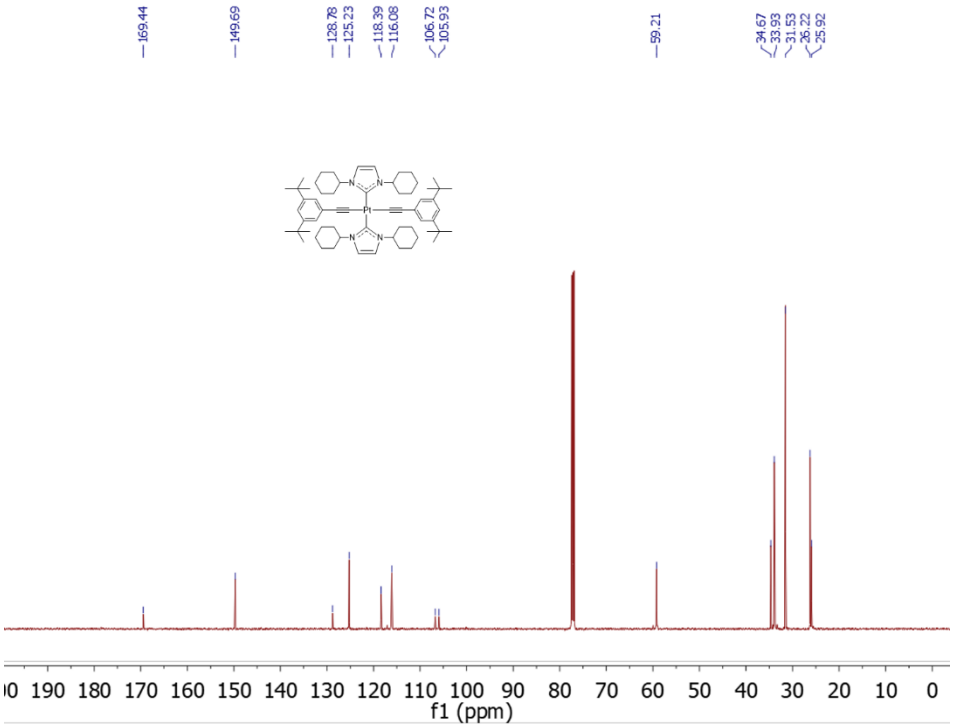

Figure S6. ^{13}C NMR spectrum of IPtP-*t*Bu (125 MHz, $CDCl_3$)

BiPtP-*t*Bu. $BiPtCl_2$ (0.15 g, 0.206 mmol) was dissolved in a solution mixture of 20 mL DCM and 10 mL $HNEt_2$. The solution was degassed by N_2 for 30 mins. Then 1,3-di-tert-butyl-5-ethynylbenzene (0.133 g, 0.619 mmol) and CuI (7.9 mg, 0.0414 mmol) were added, the mixture was degassed for another 5 mins and stirred at room temperature for 48 h. Solvents were removed by vacuum and DCM was added. The organic layer was washed with water for 3 times, dried over $MgSO_4$ (anhydrous) and filtered. The eluent was further purified by flash column chromatography with Hexane: DCM= 1: 1 and dried under vacuum to give white solid (0.138 g, 62%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm): 7.49 – 7.44 (m, 4H), 7.31 – 7.25 (m, 4H), 7.02 (t, J = 1.8 Hz, 2H), 6.85 (d, J = 1.8 Hz, 4H), 4.86 (t, J = 7.7 Hz, 8H), 2.28 (m, 8H), 1.61 (m, 8H), 1.16 (s, 36H), 1.04 (t, J = 7.4 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 182.08, 149.53, 134.74, 127.96, 125.10, 121.98, 118.80, 110.24, 106.68, 104.01, 48.23, 34.48, 31.49, 31.31, 20.73, 14.19. HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{62}H_{87}N_4Pt$, 1082.6573; (found) 1082.6563.

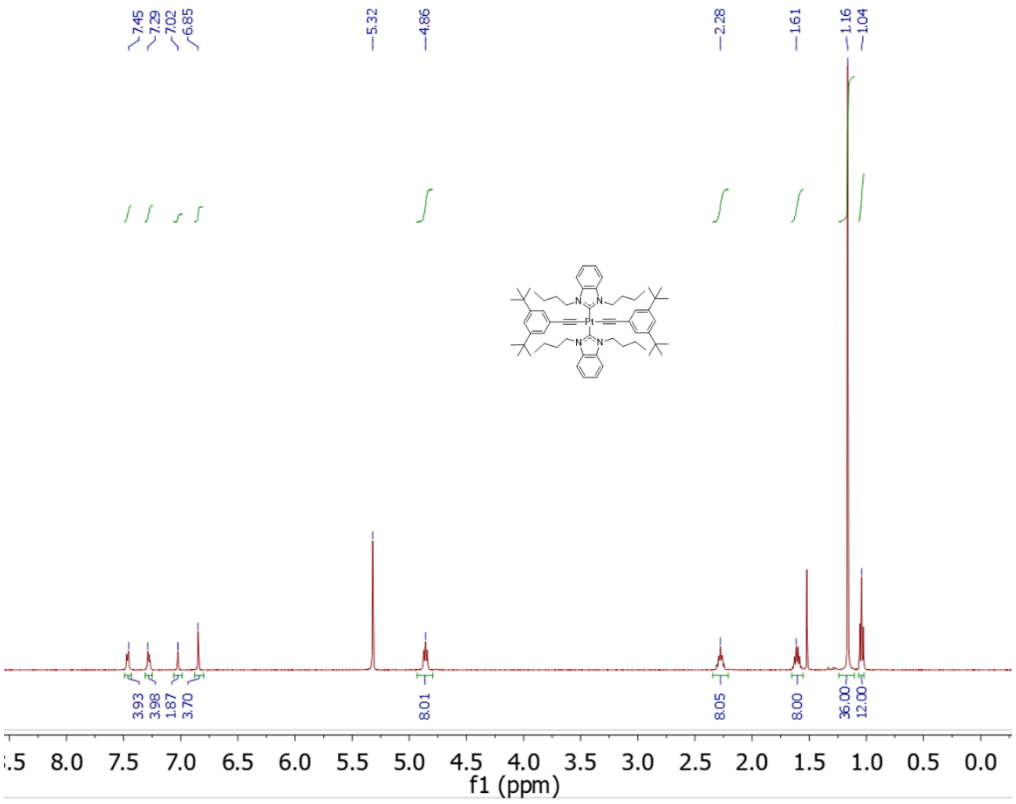

Figure S7. ^{1}H NMR spectrum of BiPtP-*t*Bu (500 MHz, CD_2Cl_2)

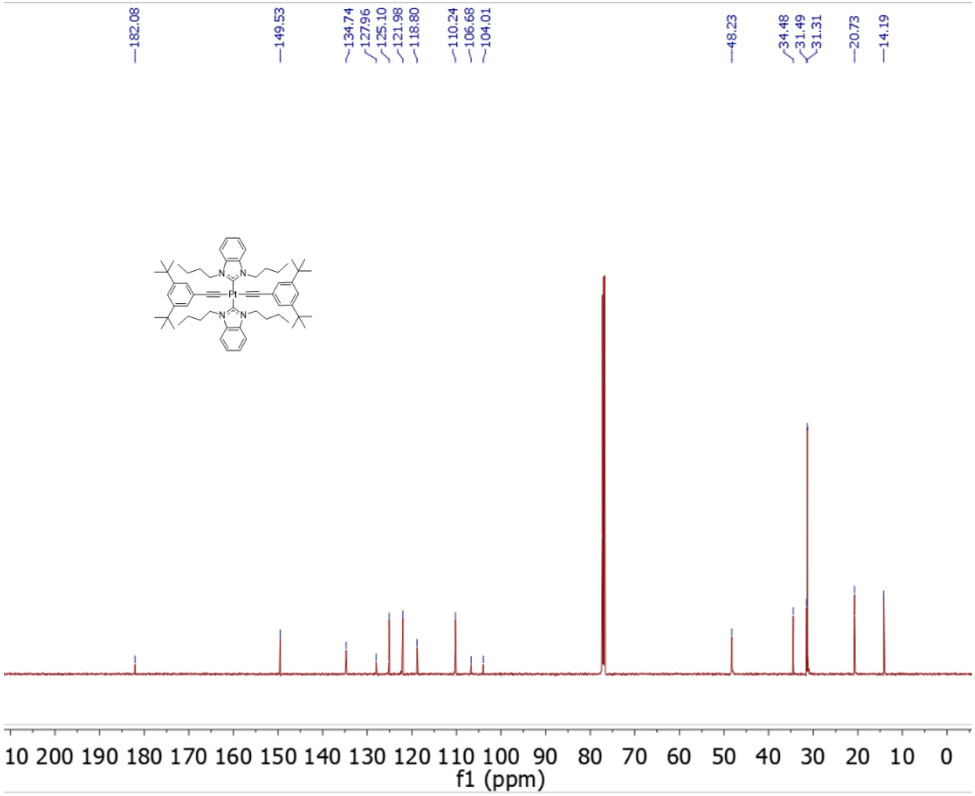

Figure S8. ^{13}C NMR spectrum of BiPtP-*t*Bu (125 MHz, $CDCl_3$)

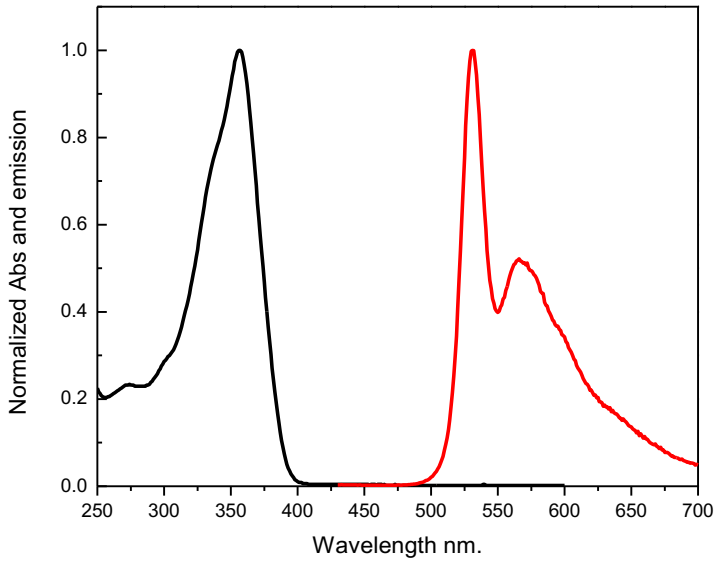

Figure S9. Normalized absorption and phosphorescence emission spectra of IPtP2 in THF at room temperature.

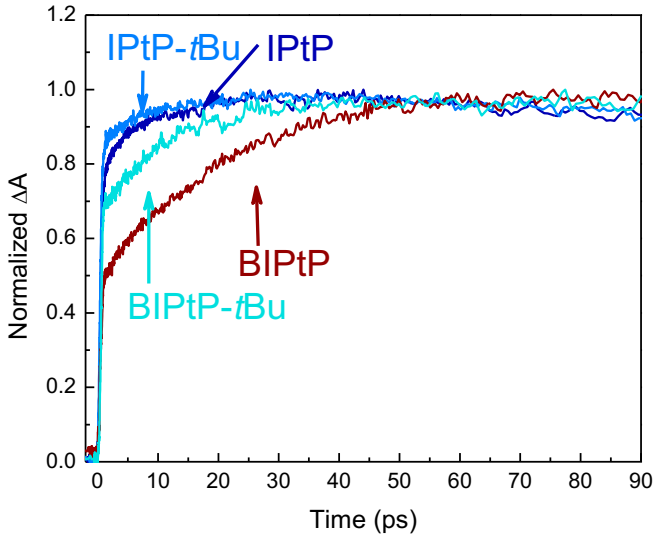

Figure S10. Normalized kinetic traces monitored at 600-620 nm for platinum acetylide carbenes in THF solution after 330 nm excitation.

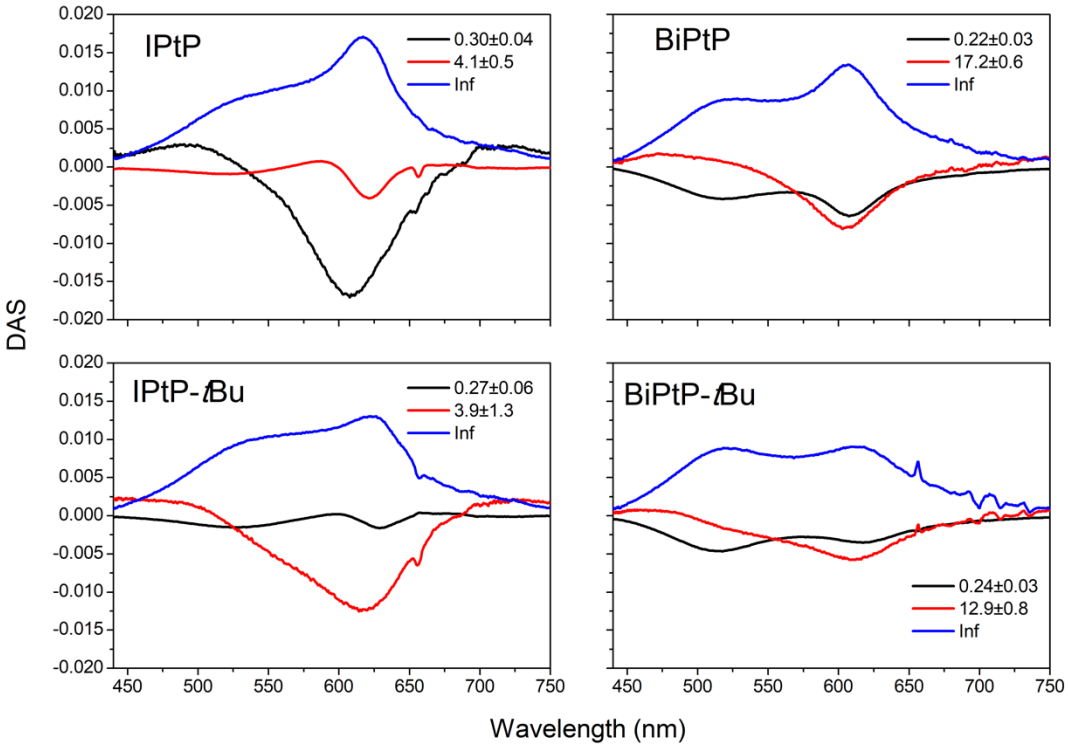

Figure S11. Decay associated spectral eigenvectors from global analysis of the transient absorption spectra of the Pt-complexes.

Table S1. Triplet conformation relaxation of platinum(II) acetylide complexes in different medias[a]

Solvent/matrix	IPtP	
	τ_1 / ps	τ_2 / ps
THF	0.27 ± 0.02 (0.85)	4.2 ±0.4 (0.15)
THF/TEGDME (4:1)	0.29 ± 0.03 (0.89)	4.6 ±0.6 (0.11)
THF/TEGDME (1:1)	0.26 ± 0.01 (0.89)	5.3 ±0.3 (0.11)
THF/TEGDME (1:4)	0.26 ±0.02 (0.91)	5.9 ± 0.4 (0.09)
TEGDME	0.26 ± 0.03 (0.91)	5.1 ±0.6 (0.09)
PMMA glass	0.34 ± 0.05 (0.88)	3.5 ±1.1 (0.12)

[a] Normalized amplitudes of the components are in parenthesis.

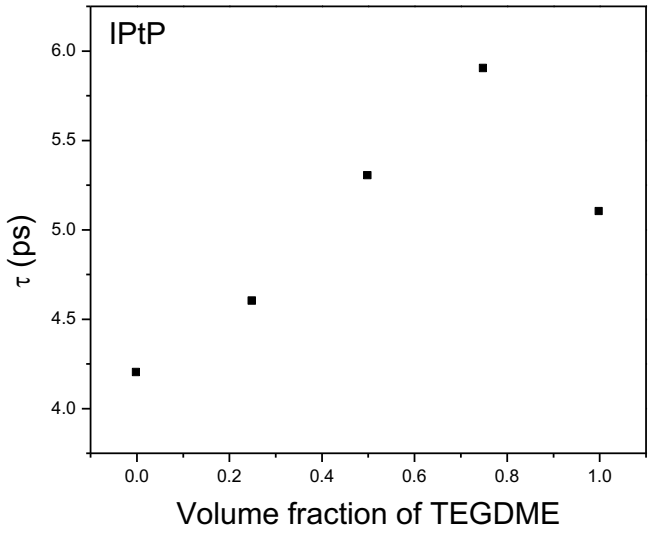

Figure S12. Plot of τ_2 as function of TEGDME fraction for IPtP. General trend is that the lifetime becomes longer as the viscosity increases.

Table S2: Crystallographic data and structure refinement for **IPtP-*t*Bu and BiPtP-*t*Bu**.

Identification code	**IPtP-*t*Bu**	**BiPtP-*t*Bu**
Empirical formula	$C_{62}H_{90}N_4Pt$	$C_{64}H_{90}Cl_4N_4Pt$ ($C_{62}H_{86}N_4Pt$ + $2CH_2Cl_2$)
Formula weight	1086.46	1252.28
Crystal system	monoclinic	monoclinic
Space group	*P2₁/c*	*P2₁/n*
a (Å)	16.0309(3)	9.4480(2)
b (Å)	13.1107(3)	31.9883(4)
c (Å)	27.7672(6)	10.2503(2)
α (°)	90	90
β (°)	98.701(2)	95.651(2)
γ (°)	90	90
Volume (Å^3)	5768.8(2)	3082.85(10)
Z	4	2
ρ (calc.)	1.251	1.349
λ	0.71073	0.71073
Temp. (K)	98(2)	100(2)
F(000)	2272.0	1296.0
μ (mm^{-1})	2.472	2.490
T_{min}, T_{max}	0.8894, 1.000	0.7786,1.000
$2\theta_{range}$ (°)	3.442 to 52	4.516 to 51.994
Reflections collected	110152	56826
Independent reflections	11317 [R_{int} = 0.0690, R_{sigma} = 0.0553]	6064 [R_{int} = 0.0367, R_{sigma} = 0.0187]
Completeness	99.9%	100%
Data / restraints / parameters	11317/0/586	6064/0/315
Observed data [I > 2σ(I)]	8643	5918
wR(F^2 all data)	0.1220	0.1093
R(*F* obsd data)	0.0495	0.0390
Goodness-of-fit on F^2	1.098	1.096
largest diff. peak and hole (e Å^{-3})	4.87/-0.93	1.47/-0.80

$$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

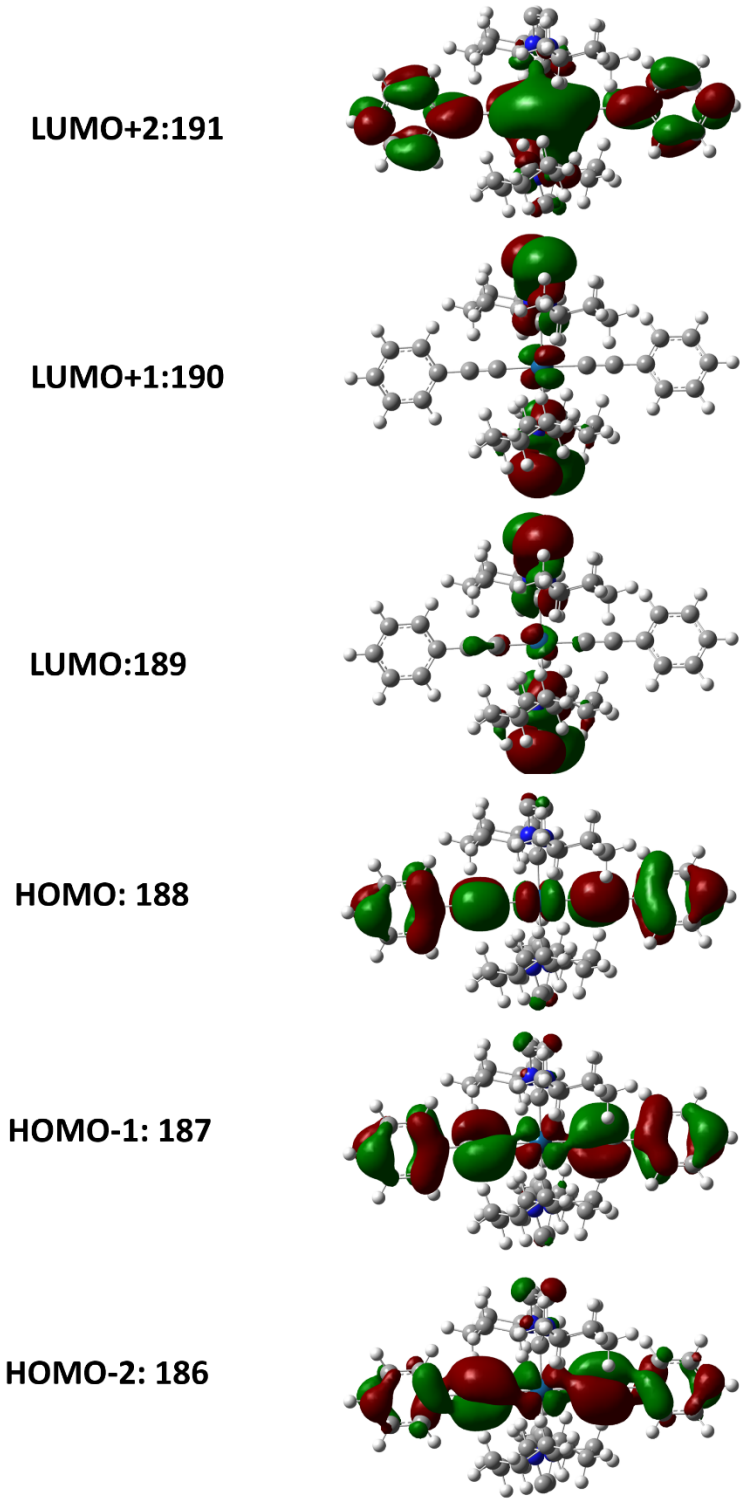

Figure S13: Frontier molecular orbitals (HOMOs and LUMOs) of IPtP.

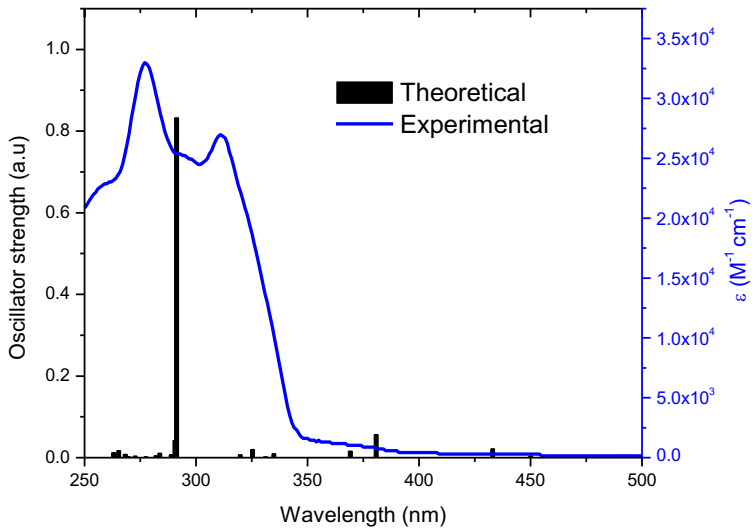

Figure S14. Experimental and TDDFT absorption UV-vis spectra for IPtP.

Table S3. Table of transitions for IPtP.

Excited State	Excitation transitions		Energy (eV)	Wavelength (nm)	Oscillator strengths (*f*)
1	177 ->189	-0.16106	2.4667	502.63	0.0107
	178 ->190	0.14903			
	184 ->189	0.21783			
	184 ->190	0.35125			
	185 ->189	-0.24397			
	185 ->190	-0.27395			
	186 ->190	0.32308			
	187 ->190	-0.10591			
2	177 ->189	0.13975	2.5202	491.96	0.0058
	178 ->190	-0.13698			
	184 ->189	-0.23403			
	184 ->190	0.47857			
	185 ->189	-0.25221			
	185 ->190	0.12680			
	186 ->190	-0.24565			
3	160 ->189	0.10578	2.5364	488.82	0.0010
	162 ->189	0.10216			
	162 ->190	0.10084			
	173 ->189	-0.18283			
	173 ->190	-0.11373			
	175 ->189	0.20613			
	175 ->190	0.19904			

	177 ->189	0.22524			
	177 ->190	0.29701			
	178 ->189	-0.27903			
	178 ->190	-0.16559			
	184 ->189	0.11918			
	185 ->189	-0.11516			
	185 ->190	-0.16239			
4	159 ->189	0.13615	2.5874	479.18	0.0039
	159 ->190	-0.12979			
	160 ->189	0.10387			
	160 ->190	-0.10214			
	173 ->189	0.19185			
	173 ->190	-0.17040			
	175 ->189	0.36020			
	175 ->190	-0.34124			
	177 ->189	-0.20323			
	177 ->190	0.19671			
5	173 ->190	-0.23374	2.7547	450.08	0.0038
	175 ->189	0.14741			
	177 ->189	0.17683			
	177 ->190	-0.17266			
	178 ->189	0.28624			
	178 ->190	-0.14035			
	179 ->189	-0.13662			
	184 ->190	0.12487			
	185 ->189	0.37522			
	185 ->190	-0.24573			
6	173 ->189	-0.29228	2.8628	433.09	0.0217
	173 ->190	-0.18419			
	175 ->189	0.10579			
	175 ->190	0.14988			
	177 ->189	-0.10302			
	178 ->190	0.23419			
	179 ->190	-0.10538			
	184 ->190	0.12939			
	185 ->189	0.11121			
	185 ->190	0.43384			
7	176 ->189	0.37186	3.2562	380.76	0.0565
	176 ->190	-0.17031			
	180 ->189	0.33605			
	180 ->190	-0.16836			
	181 ->189	0.25193			
	181 ->190	-0.32500			
8	176 ->189	0.18283	3.3583	369.19	0.0159
	176 ->190	0.24629			
	180 ->189	0.28950			

	180 ->190	0.46567			
	181 ->189	-0.28161			
9	183 ->189	0.69838	3.4850	355.76	0.0001
10	182 ->189	0.69643	3.4869	355.57	0.0001
11	182 ->190	-0.28026	3.6564	339.08	0.0001
	183 ->190	0.63899			
12	182 ->190	0.64005	3.6585	338.90	0.0000
	183 ->190	0.28627			
13	170 ->189	0.10878	3.7022	334.90	0.0094
	176 ->189	0.46034			
	178 ->189	0.13371			
	179 ->189	0.27967			
	180 ->189	-0.20305			
	181 ->190	0.31034			
14	170 ->189	0.16599	3.7438	331.17	0.0021
	176 ->189	-0.25938			
	178 ->189	0.19790			
	179 ->189	0.50821			
	180 ->189	0.10312			
	181 ->190	-0.20365			
15	176 ->190	0.57876	3.8105	325.37	0.0200
	177 ->190	0.10177			
	180 ->190	-0.14082			
	181 ->189	0.28851			
16	170 ->190	0.20854	3.8766	319.83	0.0069
	178 ->190	0.21224			
	179 ->190	0.58642			
17	186 ->194	-0.11054	4.2560	291.31	0.8325
	187 ->194	0.12420			
	188 ->191	0.63354			
18	167 ->189	0.10192	4.2667	290.59	0.0423
	171 ->190	0.14925			
	172 ->189	0.45041			
	172 ->190	-0.35849			
	174 ->189	0.11823			
	188 ->191	0.13062			
19	171 ->189	0.48224	4.2921	288.86	0.0071
	171 ->190	0.37588			
	172 ->190	0.17691			
20	150 ->189	0.10788	4.3689	283.79	0.0105
	151 ->189	0.17253			
	153 ->189	-0.22901			
	166 ->189	-0.10446			
	173 ->190	0.22245			
	177 ->190	0.34413			
	178 ->189	0.35505			

	179 ->189	-0.11523			
21	151 ->190	0.15210	4.3963	282.02	0.0045
	153 ->190	-0.19812			
	173 ->189	0.21647			
	177 ->189	0.35362			
	178 ->190	0.41723			
	179 ->190	-0.10888			
22	167 ->190	0.12939	4.4676	277.43	0.0020
	168 ->189	0.11484			
	169 ->189	-0.15494			
	174 ->189	0.60177			
23	167 ->189	-0.10251	4.5179	274.43	0.0001
	168 ->189	0.10324			
	169 ->189	-0.20160			
	170 ->189	-0.13276			
	174 ->190	-0.14096			
	185 ->194	0.16687			
	186 ->191	0.29722			
	187 ->191	0.43895			
24	167 ->189	-0.18274	4.5458	272.68	0.0040
	168 ->189	0.14171			
	168 ->190	-0.16815			
	169 ->189	0.39857			
	169 ->190	0.36605			
	170 ->189	0.13519			
	170 ->190	0.12933			
	174 ->190	-0.14594			
25	167 ->189	-0.13060	4.5664	271.51	0.0005
	168 ->189	0.30269			
	168 ->190	-0.25482			
	169 ->189	-0.14442			
	170 ->189	-0.14670			
	172 ->189	0.10680			
	174 ->189	-0.21728			
	174 ->190	-0.22741			
	185 ->194	-0.11238			
	186 ->191	-0.21598			
	187 ->191	-0.22153			
26	165 ->189	-0.11087	4.5998	269.54	0.0027
	167 ->189	0.20479			
	168 ->189	0.30232			
	168 ->190	-0.25146			
	169 ->190	-0.14905			
	170 ->189	0.31393			
	173 ->189	-0.12395			
	174 ->190	0.16316			

27	165 ->189	-0.12645	4.6218	268.26	0.0079
	165 ->190	-0.14261			
	167 ->189	-0.22660			
	168 ->189	-0.17654			
	168 ->190	0.12117			
	169 ->189	-0.21665			
	170 ->189	0.24036			
	170 ->190	0.22249			
	173 ->189	-0.17201			
	174 ->190	-0.22367			
28	156 ->189	-0.11768	4.6724	265.35	0.0172
	166 ->190	-0.11067			
	167 ->189	-0.30220			
	167 ->190	-0.36333			
	169 ->190	-0.12481			
	171 ->189	0.11433			
	174 ->190	0.36627			
29	159 ->189	-0.14116	4.6791	264.98	0.0031
	159 ->190	0.19585			
	160 ->189	-0.18911			
	162 ->190	-0.10703			
	164 ->189	0.17565			
	164 ->190	-0.13608			
	165 ->190	-0.12332			
	166 ->189	0.25468			
	166 ->190	-0.18698			
	167 ->189	-0.10223			
	167 ->190	0.10606			
	170 ->190	0.15207			
	173 ->189	0.11095			
	175 ->189	0.25823			
	177 ->189	-0.14110			
	188 ->192	-0.11159			
30	162 ->190	0.11205	4.7143	262.99	0.0119
	167 ->189	-0.12761			
	167 ->190	0.18474			
	169 ->189	-0.12117			
	169 ->190	0.22151			
	170 ->190	0.17371			
	172 ->189	0.13865			
	172 ->190	-0.12247			
	174 ->189	-0.14042			
	174 ->190	0.36372			
	175 ->189	-0.19732			

References:

[1] Bullock J D, Salehi A, Zeman IV C J, et al. In Search of Deeper Blues: Trans-N-Heterocyclic Carbene Platinum Phenylacetylide as a Dopant for Phosphorescent OLEDs[J]. *ACS Appl. Mater. Interfaces*, **2017**, 9(47): 41111-41114.

[2] Bullock J D, Valandro S R, Sulicz A N, et al. Blue Phosphorescent trans-N-Heterocyclic Carbene Platinum Acetylides: Dependence on Energy Gap and Conformation[J]. *J. Phys. Chem. A*, **2019**, 123(42): 9069-9078.

[3] Winkel R W, Dubinina G G, Abboud K A, et al. Photophysical properties of trans-platinum acetylide complexes featuring N-heterocyclic carbene ligands[J]. *Dalton Trans.*, **2014**, 43(47): 17712-17720.