

## Supporting Information

### The Effect of Bromine Substitution on Blue Phosphorescent *trans*-(N-Heterocyclic Carbene)Pt(II) Acetylide Complexes

Amran Khan, Habtom B. Gobeze, Hadi D. Arman and Kirk S. Schanze \*

E-mail: kirk.schanze@utsa.edu

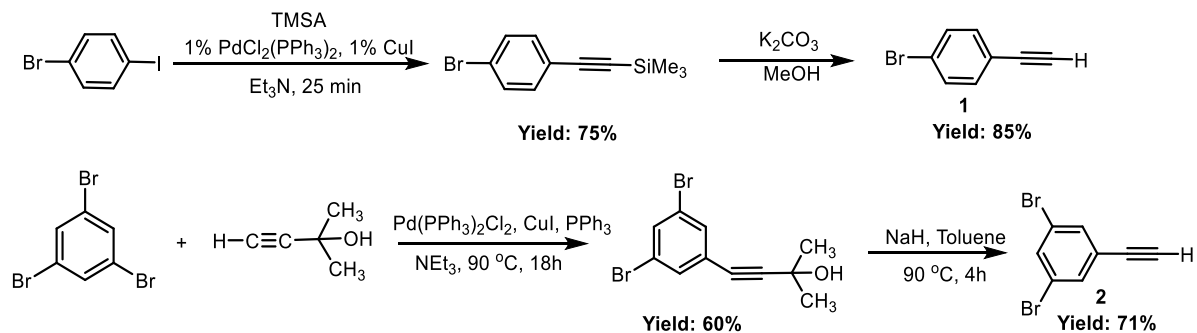
Department of Chemistry, The University of Texas at San Antonio, San Antonio, Texas 78249,  
USA

#### Experimental

All starting materials were purchased from either Sigma-Aldrich or Fisher Scientific and were used without further purification. Dry solvents were obtained from the MBraun-SPS-800 solvent purification system. The reactions were monitored by either silica or alumina gel TLC plates. Column chromatography was done by using a CombiFlash Rf+ (Teledyne-Isco) flash chromatography system.

<sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) NMR spectra were obtained from a Bruker 500 MHz Avance III HD spectrometer. The chemical shifts were reported in ppm relative to protonated solvent peaks in <sup>1</sup>H and <sup>13</sup>C NMR spectra. High-resolution mass spectrometry (HR-MS) was performed by the Mass Spectrometry Services at the University of Texas at San Antonio. HR-MS data was collected on a MaXis Plus quadrupole-time-of-flight mass spectrometer equipped with an electrospray ionization source (Bruker Daltonics) and operated in the positive ionization mode. Elemental analysis was carried out at Atlantic Microlab, Inc., GA-30071.

#### Synthesis



Scheme S1. Synthesis of compounds **1** and **2**

### Synthesis of 1-bromo-4-ethynyl benzene (1)

A Schlenk tube charged with 20 ml triethylamine and 2-bromo-4-iodo benzene (500 mg, 1.77 mmol). The solution was bubbled with nitrogen for 20 minutes before adding 1% CuI (3.4 mg, 0.017 mmol) and 1% PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (12.4 mg, 0.017 mmol). Following that, trimethylsilyl acetylene (174 mg, 1.77 mmol) was added. The reaction was then stirred for 25 min at room temperature. Upon completion, 20 ml of diethyl ether was added to the solution and filtered to separate solid materials. Solvents were removed in vacuo and purified by silica column chromatography (Ethyl Acetate/Hexane) to afford 343 mg of ((4-bromophenyl)ethynyl)trimethylsilane. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.49 (d, 2H), δ 7.36 (d, 2H), δ 0.28 (s, 9H).

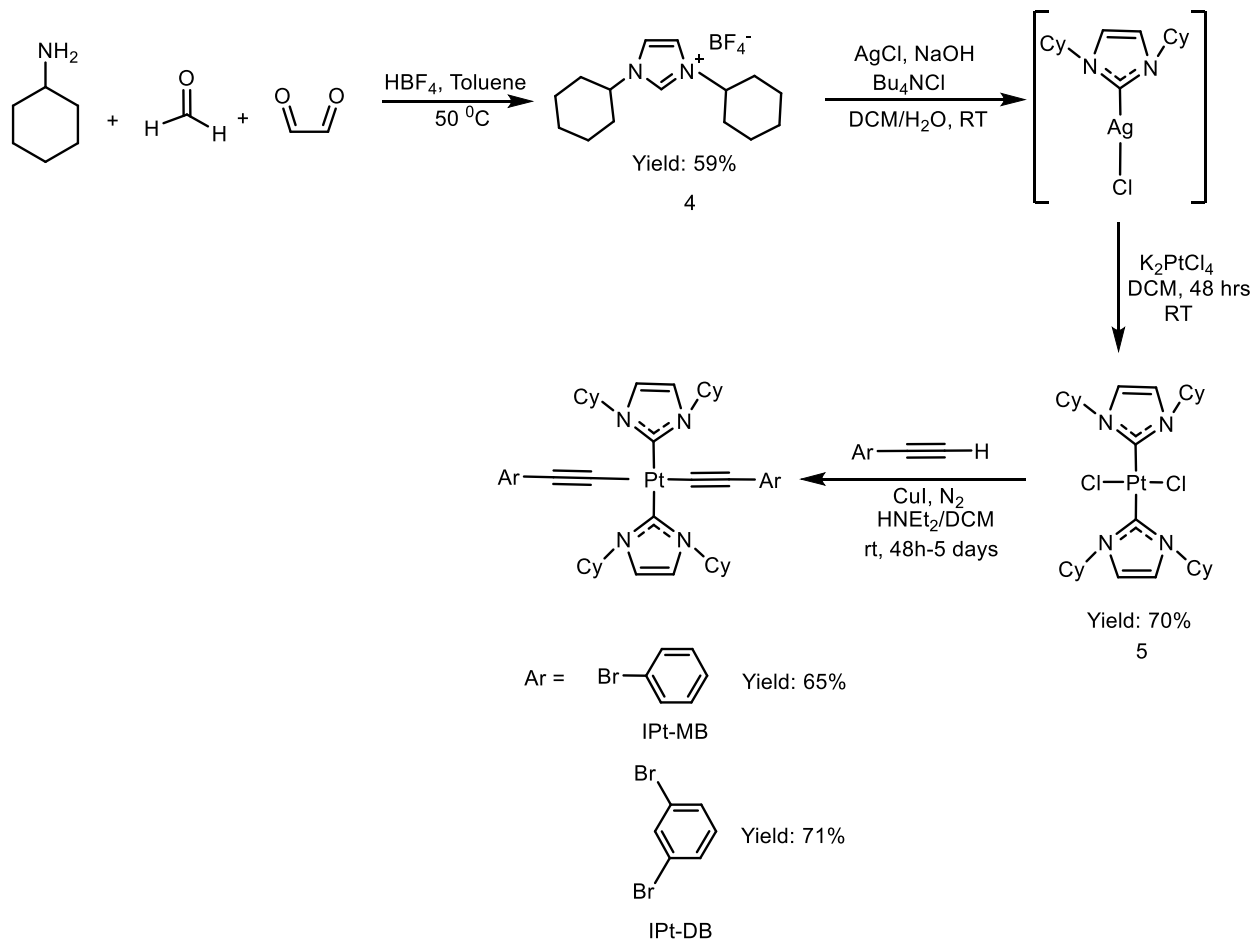
((4-bromophenyl)ethynyl)trimethylsilane (343 mg, 1.35 mmol) was dissolved in 20 mL methanol followed by the addition of potassium carbonate (225 mg, 1.63 mmol). The reaction mixture was stirred at room temperature overnight. After that, 20 ml dichloromethane was added, and extracted the organic layer with water (10 ml × 3 times). All the organic layers were collected and reduced in vacuo before being purified by silica column chromatography in hexane) to afford the final product **1** (Yield: 85%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.48 (d, 2H), δ 7.37 (d, 2H), δ 3.15 (s, 1H).

### Synthesis of 1,3-dibromo-5-ethynylbenzene (2)

2-methylbut-3-yn-2-ol (4 gm, 12.7 mmol) and 1,3,5-tribromo benzene (1.20 gm, 12.7 mmol) were added in degassed triethylamine (60 ml) solution. Subsequently, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (60 mg, 0.085 mmol), PPh<sub>3</sub> (100 mg, 0.381 mmol), and CuI (53 mg, 0.28 mmol) were added to the reaction mixture. The reaction mixture was then refluxed at 90 °C for 16 h. The progress of the reaction was monitored by TLC. After the reaction completion, the mixture was filtered, and triethylamine was removed by evaporation. A yellow oil of 4-(3,5-dibromophenyl)-2-methylbut-3-yn-2-ol (2.35 gm) was isolated by silica column chromatography using ethyl acetate/hexane (40/60). Yield: 60%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.68 (t, 3H), δ 7.56 (d, 2H), δ 2.13 (s, 1H), δ 1.61 (s, 6H).

4-(3,5-dibromophenyl)-2-methylbut-3-yn-2-ol (200 mg, 0.69 mmol) was added in 10 ml toluene. The solution was degassed under nitrogen for 15 min. A solution of sodium hydroxide (17 mg, 0.69 mmol) in 5 ml toluene was added to the reaction mixture by a cannula. The mixture was then heated to 90 °C and stirred for 3 h. After that, the reaction was cooled to room temperature

followed by the addition of 10% HCl and extracted with DCM. The organic portions were collected and reduced in vacuo followed by purification by silica column chromatography using hexane. Yield: 71% (128 mg).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.68 (t, 3H),  $\delta$  7.59 (d, 2H),  $\delta$  3.18 (s, 1H).



**Scheme S2.** Synthesis of compound IPT-MB and IPT-DB

### Synthesis of compound IPT-MB

A solution of **5** (50 mg, 0.069 mmol) in 7 ml dichloromethane and 3 ml diethylamine was purged under nitrogen for 30 min. Following that, 1-bromo-4-ethynylbenzene (75 mg, 0.41 mmol) and CuI (2 mg, 10 mol%) were added. The reaction mixture was then stirred at room temperature for 48 h. After that, the solvent was removed in vacuo and the pure product was isolated by column chromatography using hexane/ethylacetate (4/1). Yield: 45mg (65%).  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 500 MHz):  $\delta$  7.22 (d, 4H),  $\delta$  7.02 (s, 4H),  $\delta$  6.94 (d, 4H),  $\delta$  5.40 (s, 4H),  $\delta$  2.37 (bs, 8H),  $\delta$  1.92 (bs, 8H),  $\delta$  1.79 (d, 4H),  $\delta$  1.60 (m, 16H),  $\delta$  1.30 (m, 4H).

$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz):  $\delta$  25.46,  $\delta$  26.02,  $\delta$  33.57,  $\delta$  59.44,  $\delta$  104.21,  $\delta$  110.26,  $\delta$  116.35,  $\delta$  117.17,  $\delta$  128.59,  $\delta$  130.73,  $\delta$  132.40,  $\delta$  168.12.

HRMS (ESI, m/z):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{46}\text{H}_{56}\text{Br}_2\text{N}_4\text{Pt}$ , 1018.2592; (found): 1018.2590.

Anal. calcd for  $\text{C}_{46}\text{H}_{56}\text{Br}_2\text{N}_4\text{Pt}$ : C, 54.17, H, 5.53, N, 5.49. Found: C, 54.23, H, 5.52, N, 5.42.

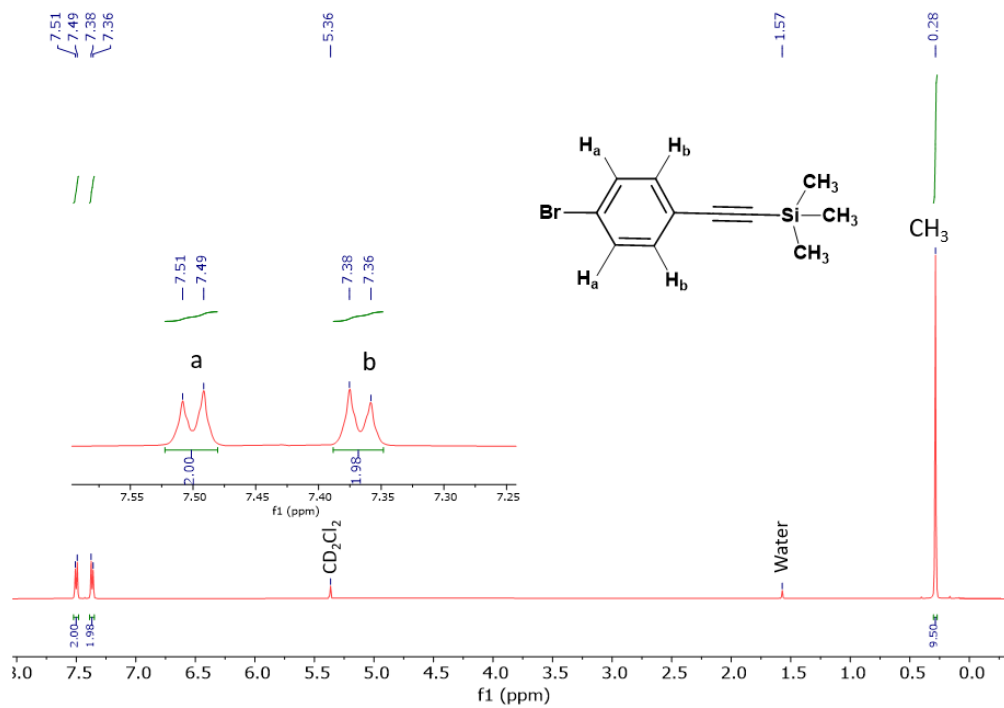
### Synthesis of compound IPT-DB

A solution of **6** (100 mg, 0.14 mmol) in 7 ml dichloromethane and 3 ml diethylamine was purged under nitrogen for 30 min. After that, 1,3-dibromo-5-ethynylbenzene (213 mg, 0.82 mmol) and CuI (3 mg, 10 mol%) were added. The reaction mixture was stirred for 5 days at room temperature. Upon completion, the solvent was removed in vacuo and purified by alumina column chromatography. First, hexane/ethyl acetate (2/1) was passed through the column to get starting materials and byproducts out. Then using dichloromethane as an eluent afforded the compound **7**. Yield: 106 mg (71%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.33 (t, 2H),  $\delta$  7.15 (d, 4H),  $\delta$  7.03 (s, 4H),  $\delta$  5.32 (s, 4H),  $\delta$  2.34 (bs, 8H),  $\delta$  1.99 (bs, 8H),  $\delta$  1.82 (d, 4H),  $\delta$  1.60 (m, 16H),  $\delta$  1.33 (m, 4H).

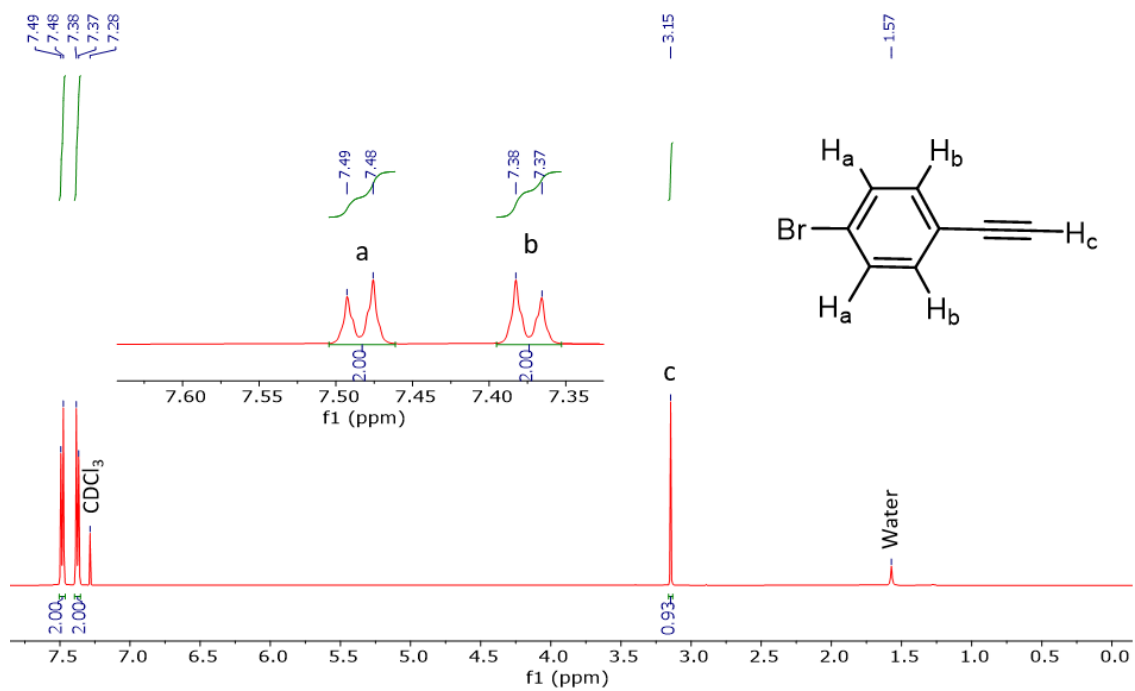
$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz):  $\delta$  25.48,  $\delta$  26.08,  $\delta$  33.66,  $\delta$  59.71,  $\delta$  103.19,  $\delta$  114.00,  $\delta$  116.61,  $\delta$  121.87,  $\delta$  129.43,  $\delta$  132.15,  $\delta$  132.70,  $\delta$  167.31.

HRMS (ESI, m/z):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{46}\text{H}_{54}\text{Br}_4\text{N}_4\text{Pt}$ , 1174.0803; (found): 1174.0800

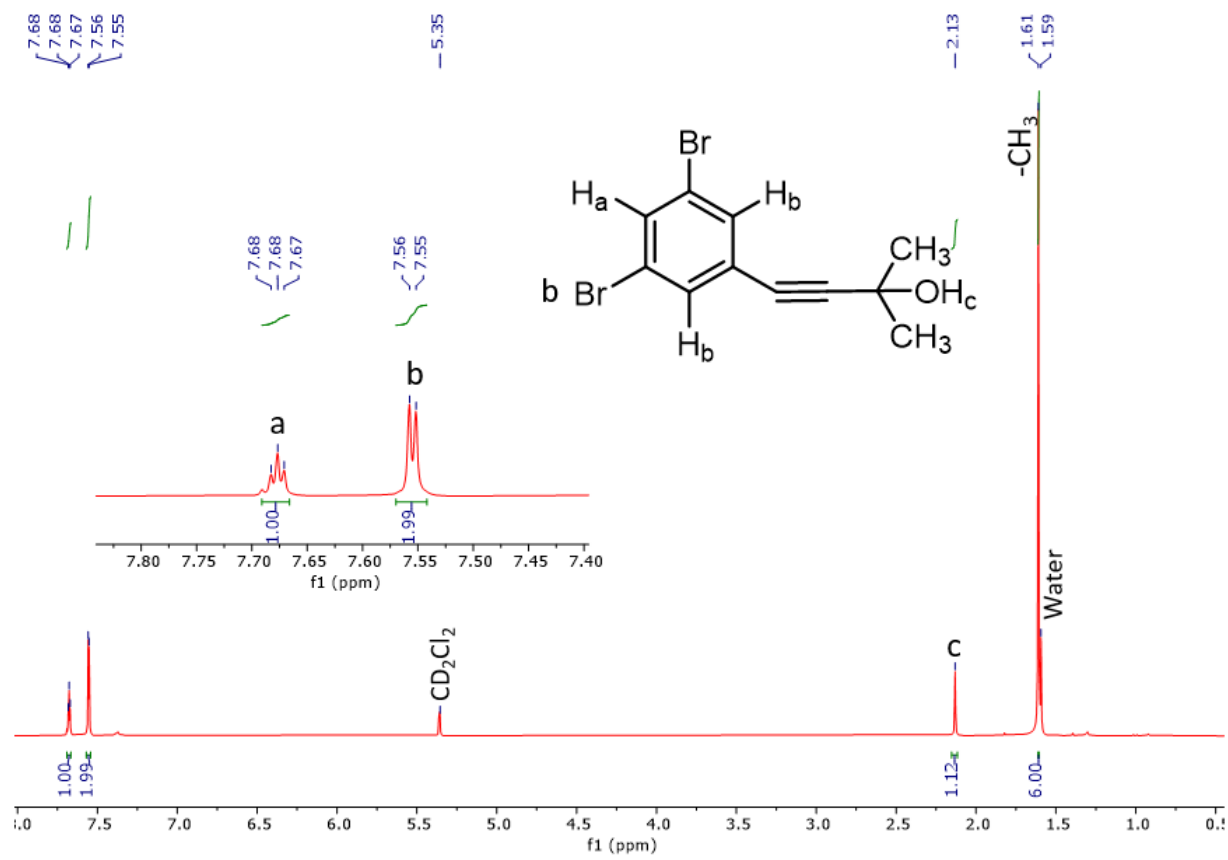
Anal. calcd for  $\text{C}_{46}\text{H}_{54}\text{Br}_4\text{N}_4\text{Pt}$ : C, 46.92, H, 4.62, N, 4.76. Found: C, 46.95, H, 4.56, N, 4.68.



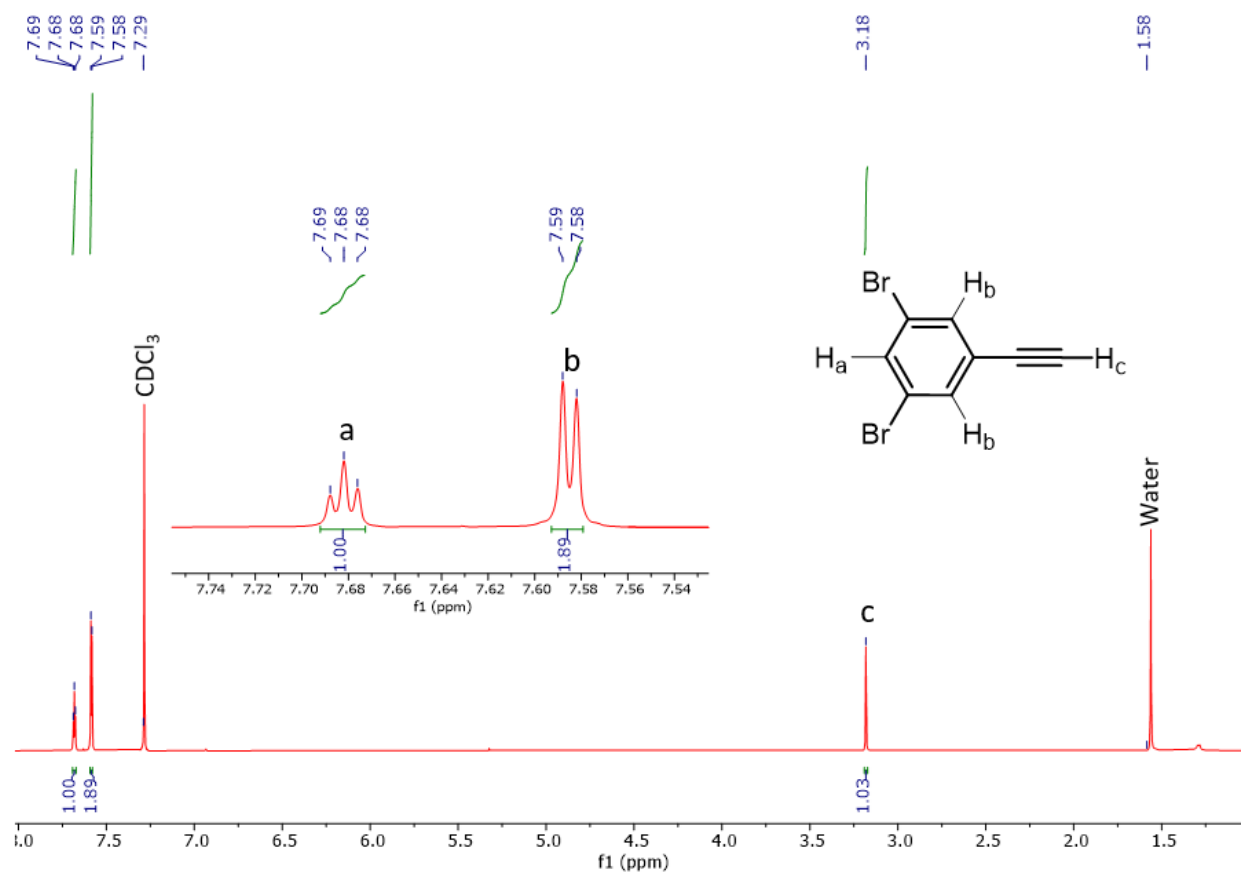
**Figure S1.**  $^1\text{H}$  NMR of (4-bromophenyl)ethynyl trimethylsilane



**Figure S2.**  $^1\text{H}$  NMR of 1-bromo-4-ethynylbenzene (1)

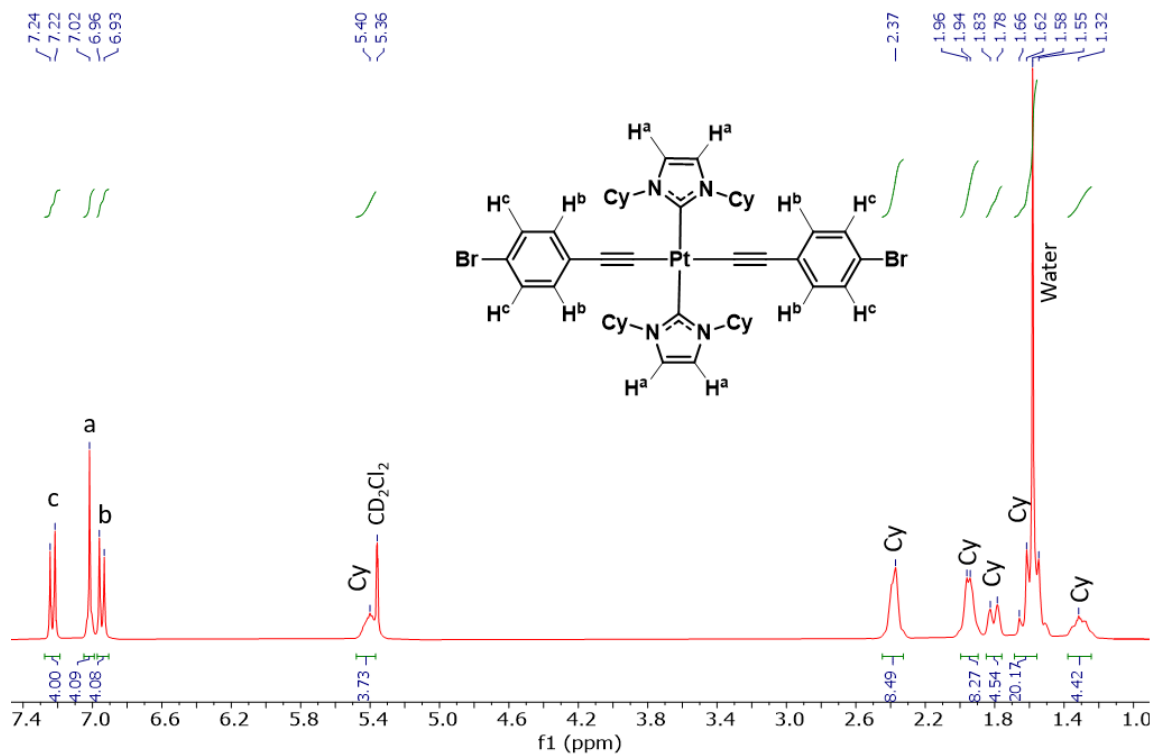


**Figure S3.**  $^1\text{H}$  NMR of 4-(3,5-dibromophenyl)-2-methylbut-3-yn-2-ol

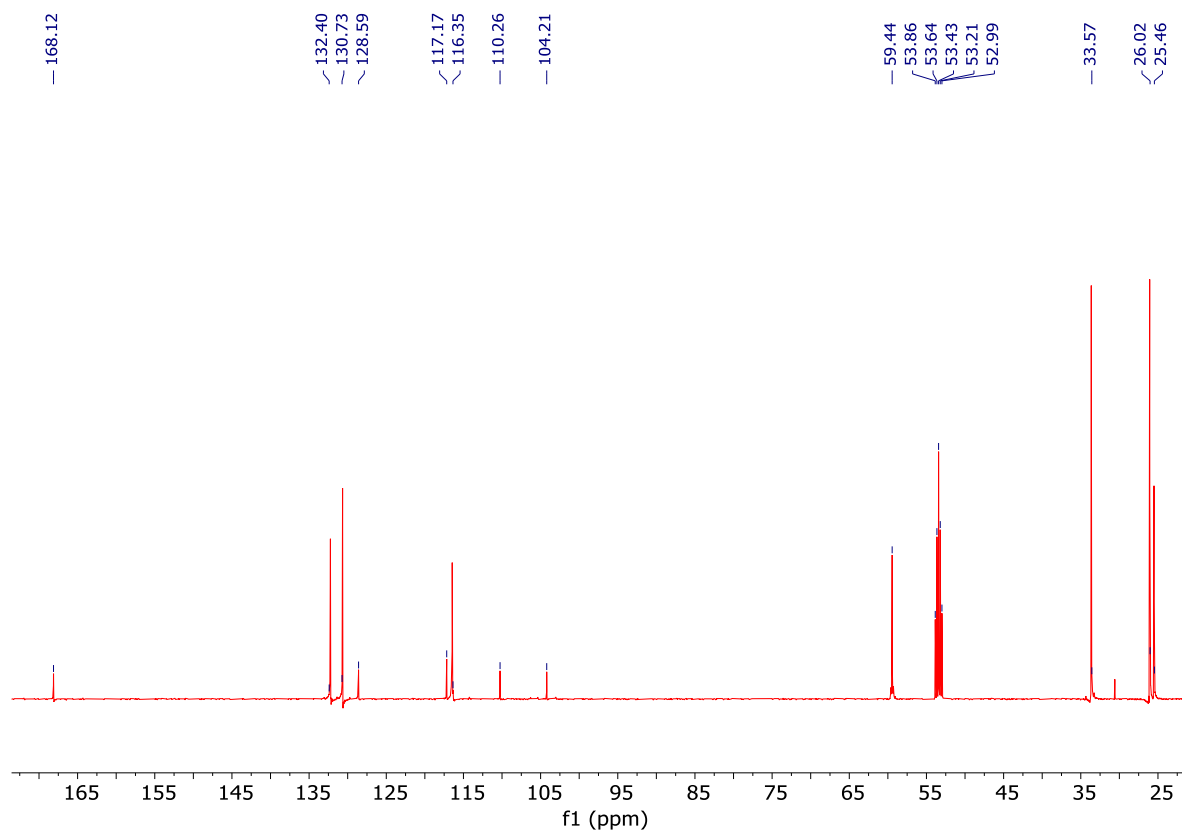


**Figure S4.**  $^1\text{H}$  NMR of 1,3-dibromo-5-ethynylbenzene (**2**)

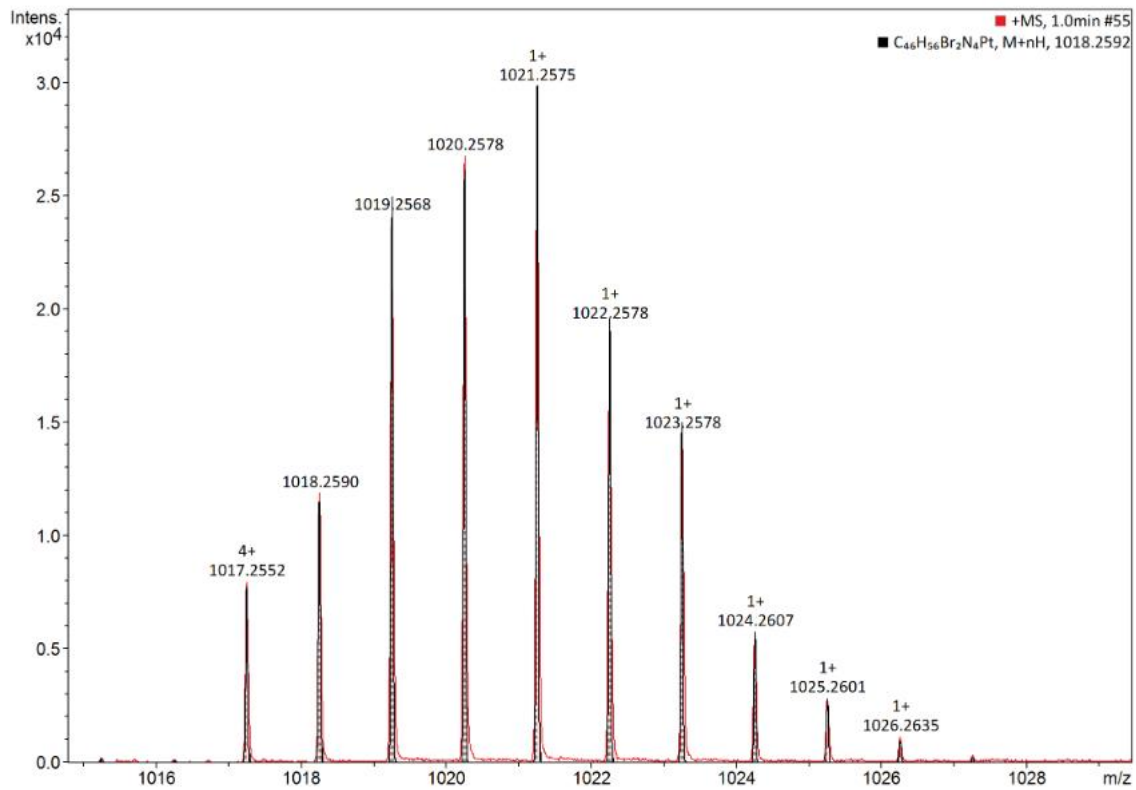




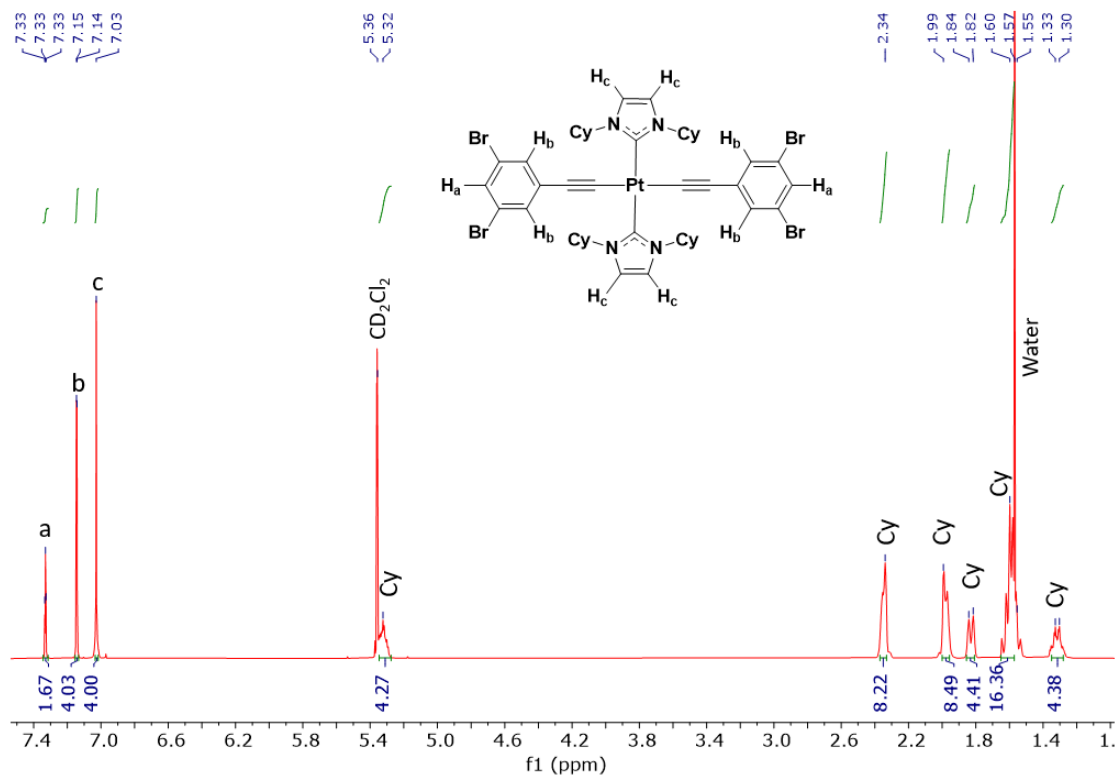
**Figure S5.** <sup>1</sup>H NMR of IPT-MB; Cy: Cyclohexyl



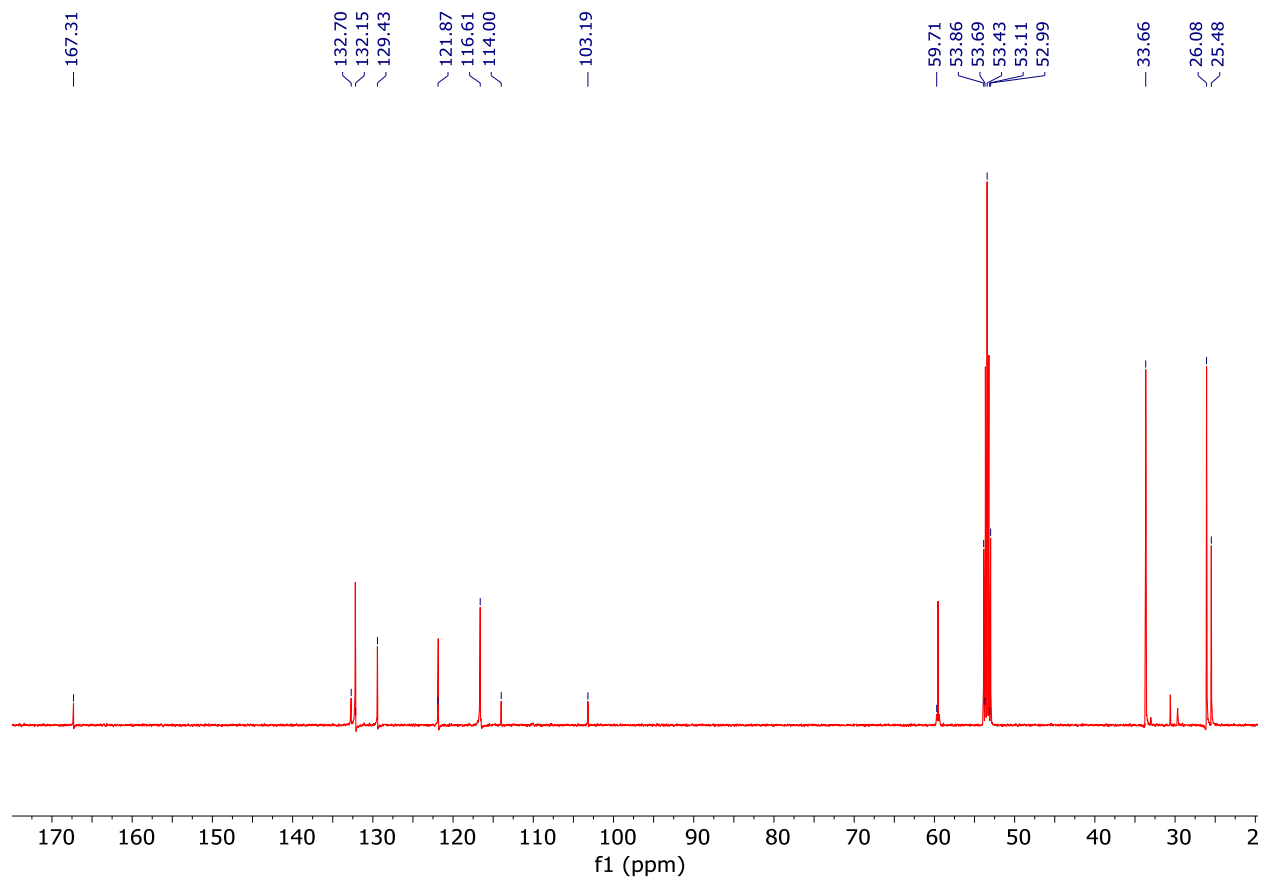
**Figure S6.**  $^{13}\text{C}$  NMR of IPT-MB



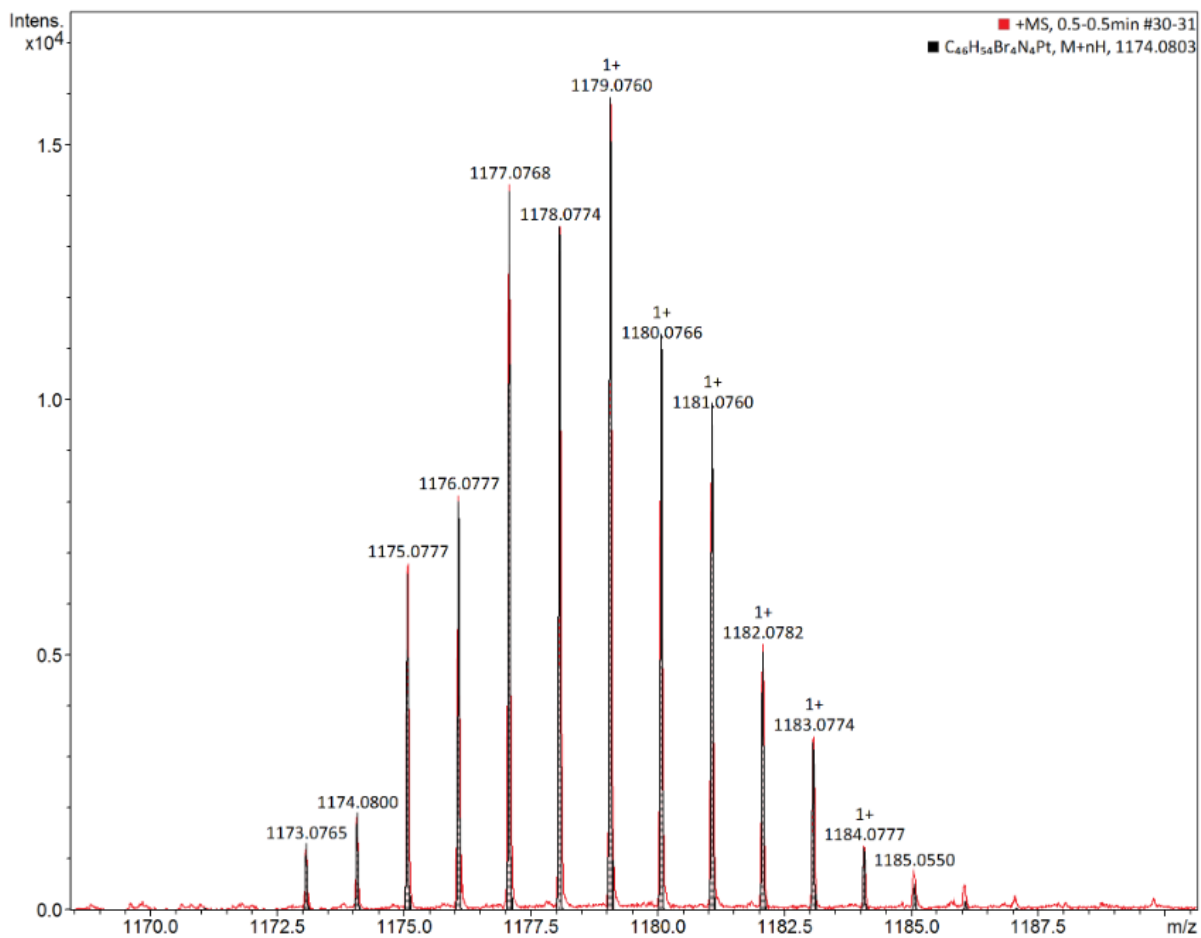
**Figure S7.** ESI-MS of IPT-MB



**Figure S8.** <sup>1</sup>H NMR of IPT-DB; Cy: Cyclohexane



**Figure S9.** <sup>13</sup>C NMR of IPT-DB



**Figure S10.** ESI-MS of IPt-DB

## X-ray Crystallography of Compounds IPt-MB and IPt-DB

Single crystals of compounds 1(MB) were prepared by slow evaporation of a solution of hexane and dichloromethane. A suitable colorless plate-like crystal with dimensions, 0.138 x 0.059 x 0.037 mm, was mounted in paratone oil onto a nylon loop. Single crystals of compounds 2(DB) were prepared by slow evaporation of a solution of hexane and dichloromethane. A suitable colorless plank-like crystal with dimensions, 0.194 x 0.050 x 0.043 mm, was mounted in paratone oil onto a nylon loop. All data were collected at 100.0(1) K, using a XtaLAB Synergy/ Dualflex, HyPix fitted with CuK $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Data collection and unit cell refinement were performed using *CrysAlisPro* software.<sup>[1]</sup> The total number of data were measured in the  $8.8^\circ < 2\theta < 153.0^\circ$  and  $6.2^\circ < 2\theta < 153.5^\circ$  for compounds 1 and 2 respectively, using  $\omega$  scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.713, 1.000 for compound (1) and 0.989, 0.997 for compound (2)), were accomplished with *CrysAlisPro*<sup>[1]</sup> and *SCALE3 ABSPACK*<sup>[2]</sup>, respectively. All structures, using Olex2<sup>[3]</sup>, were solved with the ShelXT<sup>[4]</sup> structure solution program using direct methods and refined (on  $F^2$ ) with the ShelXL<sup>[5]</sup> refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms, for compounds 1 and 2, were refined with anisotropic displacement parameters. All hydrogen atom positions, for compounds 1 and 2, were determined by geometry and refined by a riding model.

**Table S1:** Crystallographic data and structure refinement for **IPt-MB** and **IPt-DB**

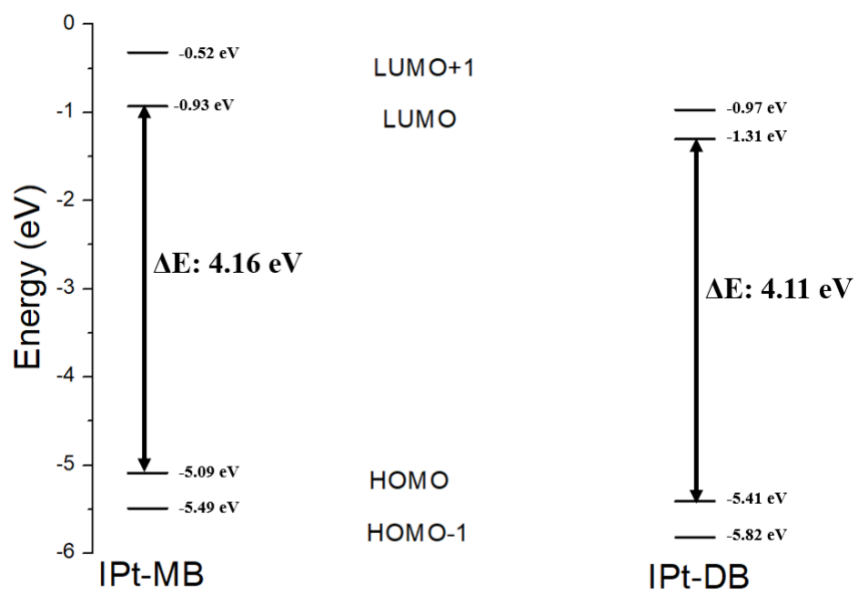
<b>Identification code</b>	<b>IPt-MB</b>	<b>IPt-DB</b>
CCDC	2263726	2263727
Empirical formula	C <sub>46</sub> H <sub>56</sub> Br <sub>2</sub> N <sub>4</sub> Pt	C <sub>46</sub> H <sub>54</sub> Br <sub>4</sub> N <sub>4</sub> Pt
Formula weight	1189.71	1177.66
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/n</i>	<i>Cc</i>
<i>a</i> (Å)	12.18770(10)	22.6051(12)
<i>b</i> (Å)	13.2995(2)	28.2889(3)
<i>c</i> (Å)	15.2041(2)	12.9480(7)
$\alpha$ (°)	90	90
$\beta$ (°)	95.8340(10)	148.017(13)
$\gamma$ (°)	90	90
Volume (Å <sup>3</sup> )	2451.67(5)	4385.6(16)
Z	2	4
$\rho$ (calc.)	1.612	1.784
$\lambda$	1.54184	1.54184
Temp. (K)	100.0(1)	100.0(1)
F(000)	1184	2281.774
$\mu$ (mm <sup>-1</sup> )	9.545	10.530
T <sub>min</sub> , T <sub>max</sub>	0.713, 1.000	0.989, 0.997
2 $\theta$ <sub>range</sub> (°)	8.8 to 153.0	6.2 to 153.5
Reflections collected	23592	14040
Independent reflections	4967 [R(int) = 0.0458]	14040 [R(int) = ]



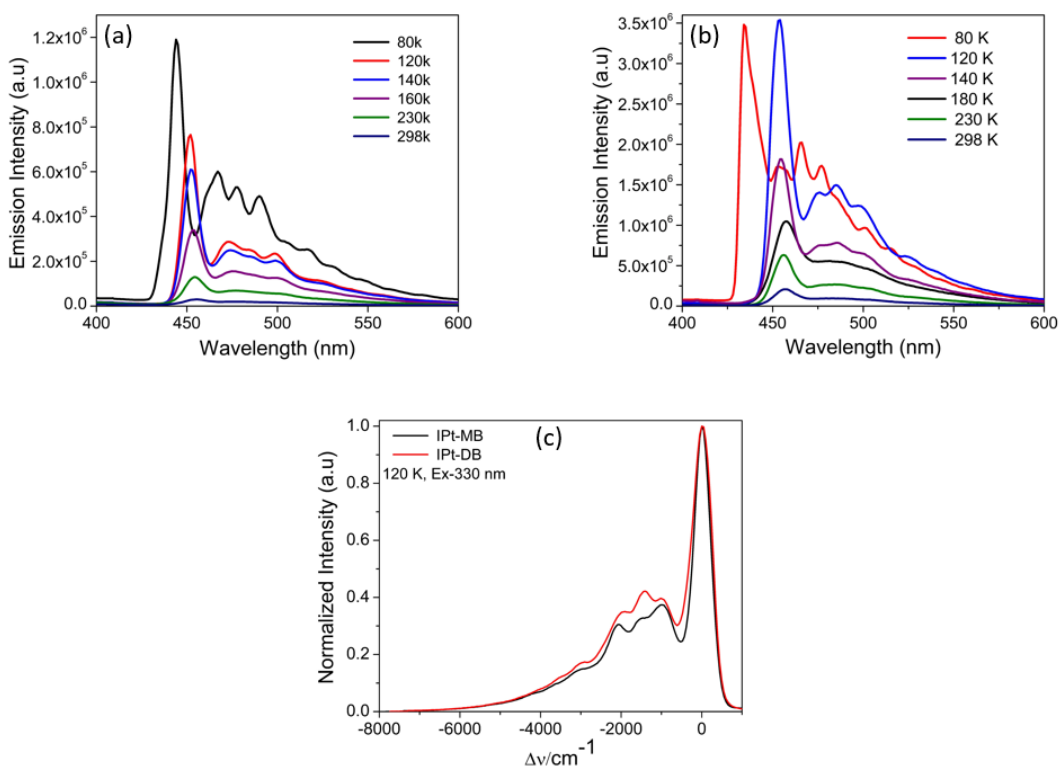
Completeness	99.9%	99.9%
Data / restraints / parameters	4967 / 0 / 268	14040 / 2 / 497
Observed data [I > 2σ(I)]	4574	13964
wR(F <sup>2</sup> all data)	0.0984	0.1055
R(F obsd data)	0.0348	0.0399
Goodness-of-fit on F <sup>2</sup>	1.08	1.05
largest diff. peak and hole (e Å <sup>-3</sup> )	2.10 / -2.03	3.32 / -1.25

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

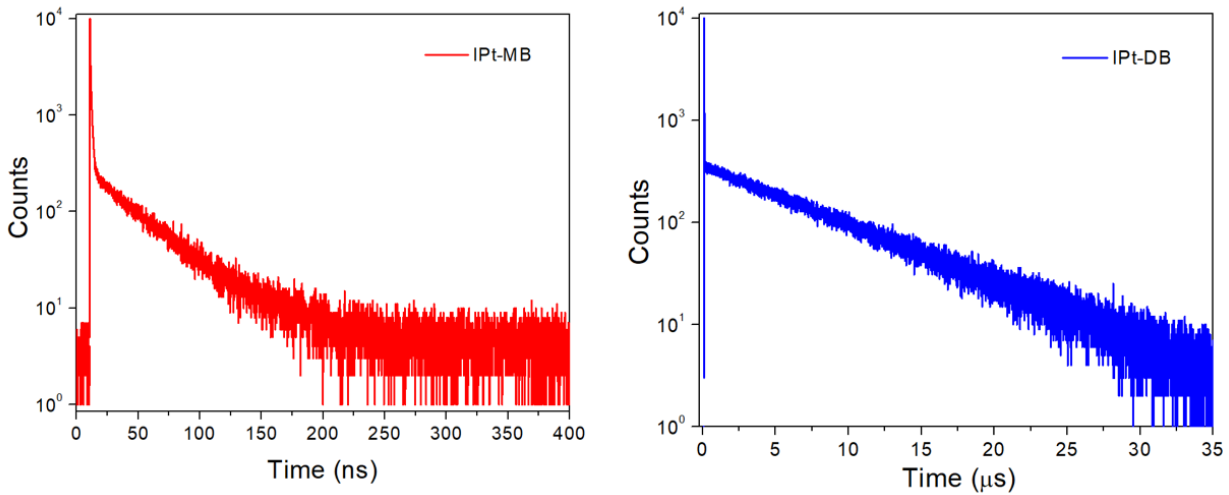
$$R_1 = \Sigma ||F_O| - |F_C|| / \Sigma |F_O|$$



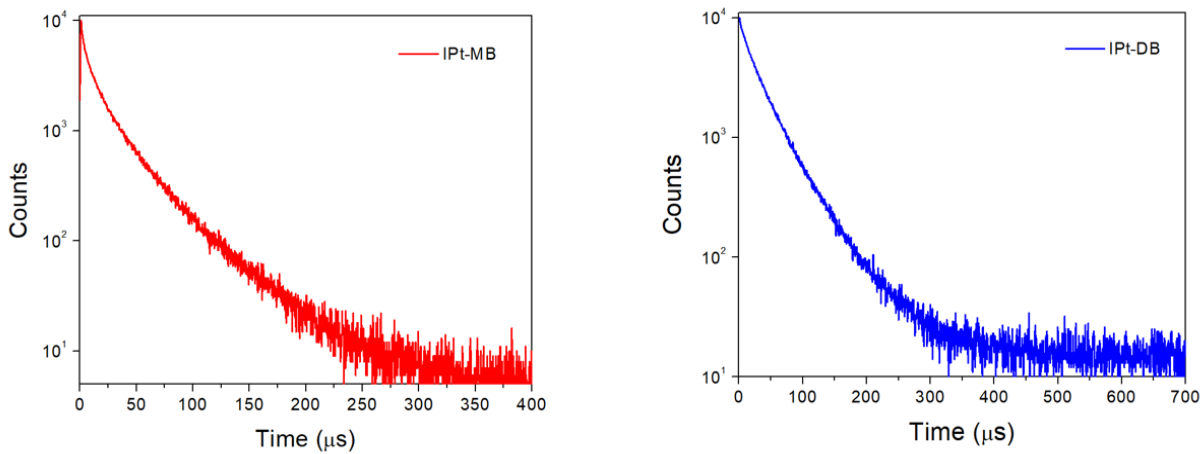
**Figure S11.** DFT optimized HOMO-LUMO energy level of IPt-MB and IPt-DB



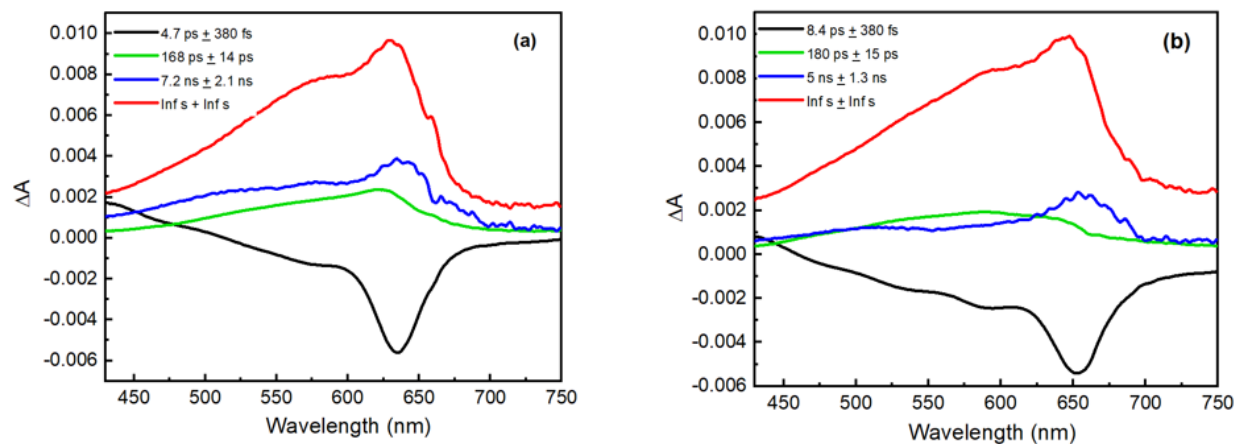
**Figure S12.** Temperature-dependent emission of a) IPt-MB (6) b) IPt-DB (7); Ex 330 nm c) Emission at for both complexes at 120 K with plotted on energy scale ( $\text{cm}^{-1}$ ), with 0-0 band peak set to 0 and the remainder of the spectrum plotted in energy relative to the 0-0 band ( $\Delta\nu$ ).



**Figure S13.** Emission decay of IPT-MB (left) and IPT-DB (right) in THF solution.



**Figure S14.** Time-dependent emission decay of IPT-MB (Left) and IPT-DB (Right) in PMMA



**Figure S15.** Global analysis of the femtosecond transient absorption data for IPT-MB (a) and IPT-DB (b) in THF with excitation at 330 nm (100  $\mu$ J per pulse). Plots show the unnormalized decay associated spectra obtained from the global analysis. Negative amplitude reflects an increase in absorption with time (rise) and positive amplitude reflects a decrease in absorption with time (decay). The absolute value of the amplitudes reflects the contribution of the spectral components to the time-evolving spectra. Time constants associated with each spectral component are shown in the legend. “Inf” decay time means that the component does not decay on the 7 ns timescale of the experiment.

## DFT Computational results

### IPt-MB

#### Cartesian coordinates:

Pt	-0.002365	0.004574	0.001149
C	-0.255297	4.242643	-0.632040
C	0.340561	4.241136	0.602857
C	0.019083	2.053531	-0.005912
N	0.505591	2.897225	0.970230
N	-0.449300	2.899738	-0.988728
C	-1.033341	2.454390	-2.262430
H	-1.563071	1.514908	-2.097406
H	-0.248778	2.303744	-3.013183
H	-1.739926	3.209889	-2.620797
C	1.079866	2.450062	2.247665
H	0.294240	2.338271	3.004135
H	1.814906	3.184772	2.591827
H	1.575123	1.490185	2.093689
C	0.237063	-4.237280	-0.610691
C	-0.330851	-4.227885	0.637297
C	-0.023703	-2.044270	0.007382
N	-0.487916	-2.881662	0.999621
N	0.422641	-2.896672	-0.980269
C	0.977802	-2.459144	-2.269518
H	1.515884	-1.521580	-2.121301
H	0.175995	-2.307568	-3.001606
H	1.671706	-3.219618	-2.641835
C	-1.033446	-2.425791	2.286588
H	-1.749896	-3.165146	2.658777
H	-1.544126	-1.473598	2.134962
H	-0.229398	-2.295678	3.020377
C	-2.027486	0.025470	0.022887

C	2.022720	-0.016562	-0.020679
C	-3.268950	0.038130	0.036138
C	3.264176	-0.029428	-0.034094
H	0.515339	-5.060003	-1.248465
H	-0.626490	-5.041063	1.279488
H	-0.547794	5.061316	-1.268671
H	0.650652	5.058347	1.233010
C	-4.702523	0.052652	0.051424
C	-5.454484	-1.020683	-0.499959
C	-5.420747	1.140860	0.618412
C	-6.859490	-1.011966	-0.488937
H	-4.926093	-1.862174	-0.939754
C	-6.825563	1.160569	0.637191
H	-4.866254	1.971407	1.046726
C	-7.531269	0.081271	0.081433
H	-7.416655	-1.840072	-0.915976
H	-7.356678	1.999688	1.075774
C	4.697745	-0.043831	-0.049283
C	5.437688	1.028591	-0.618425
C	5.428003	-1.130920	0.504324
C	6.842613	1.020073	-0.637141
H	4.899960	1.869218	-1.048447
C	6.832904	-1.150426	0.493372
H	4.882847	-1.960723	0.945863
C	7.526503	-0.072044	-0.079151
H	7.390476	1.847474	-1.077380
H	7.373328	-1.988676	0.922133
Br	9.494922	-0.091654	-0.099915
Br	-9.499683	0.101178	0.102317

**Table S2.** TD-DFT Calculated Transitions for **IPt-MB**

<b>Excited State</b>	<b>Excitation transitions</b>	<b>Oscillator strength (<i>f</i>)</b>	<b>Energy (eV)</b>	<b>Wavelength (nm)</b>
1	120→121	1.0024	3.6442	340.23
	116→122			
2	118→121	0.0000	3.8475	322.24
	119→121			
	120→122			
	119→121			
3	119→129	0.0000	4.1757	296.92
	120→122			
	118→126			
4	119→126	0.0000	4.1975	295.37
	120→123			
	113→121			
5	119→125	0.0077	4.2210	293.73
	120→124			
	120→125			
	112→121			
6	119→124	0.0053	4.2213	293.71
	120→124			
	120→125			
	116→121			
7	118→122	0.2902	4.2321	292.96
	119→122			
	120→129			
	118→123			
8	119→123	0.0009	4.2345	292.79
	120→126			
	120→128			

9	120→126	0.0003	4.3429	285.49
	120→128			
10	119→126	0.0000	4.4088	281.22
	120→127			
11	119→122	0.2094	4.4294	279.91
	120→129			
12	116→122	0.0000	4.5338	273.47
	118→121			
	119→121			
	119→129			
13	117→121	0.0181	4.5402	273.08
14	116→125	0.0011	4.6200	268.36
	112→124			
	119→125			
	120→125			
15	116→124	0.0014	4.6212	268.29
	119→124			
	119→125			
	120→124			



## Ipt-DB

### Cartesian coordinates:

Pt	-0.002359	0.004658	0.000727
C	-0.250336	4.243633	-0.637874
C	0.325099	4.243140	0.606410
C	0.016660	2.055610	-0.007024
N	0.485808	2.899400	0.976913
N	-0.436546	2.900277	-0.997664
C	-0.997145	2.456574	-2.282420
H	-1.475558	1.486442	-2.141225
H	-0.206443	2.367156	-3.036545
H	-1.744504	3.180589	-2.622557
C	1.037837	2.455576	2.265303
H	0.246670	2.393844	3.021734
H	1.803786	3.164176	2.596466
H	1.491623	1.472415	2.133421
C	0.231888	-4.238835	-0.612294
C	-0.315043	-4.229195	0.644757
C	-0.021281	-2.046259	0.008285
N	-0.467711	-2.882772	1.008843
N	0.409492	-2.898156	-0.986142
C	0.940453	-2.463781	-2.286582
H	1.424173	-1.493878	-2.162949

H	0.132286	-2.377247	-3.022295
H	1.677904	-3.191698	-2.639744
C	-0.990375	-2.429171	2.306072
H	-1.741156	-3.140695	2.664514
H	-1.456031	-1.451387	2.175375
H	-0.180645	-2.352291	3.041138
C	-2.024509	0.023369	0.023020
C	2.019767	-0.014235	-0.021589
C	-3.265810	0.035014	0.036787
C	3.261063	-0.026091	-0.035378
H	0.500395	-5.061761	-1.253980
H	-0.598734	-5.042312	1.292387
H	-0.533322	5.061864	-1.279348
H	0.623563	5.060945	1.241382
C	-4.696251	0.048783	0.052683
C	-5.440330	-1.059453	-0.441276
C	-5.407636	1.171082	0.562810
C	-6.837792	-1.021934	-0.415332
H	-4.911770	-1.920683	-0.834398
C	-6.805791	1.160596	0.567871
H	-4.853942	2.021848	0.943935
C	-7.558350	0.076453	0.084434
C	4.691499	-0.039784	-0.051221

C	5.424317	1.067034	-0.564810
C	5.414157	-1.160563	0.446249
C	6.822014	1.029641	-0.569798
H	4.887065	1.927084	-0.948623
C	6.812078	-1.150022	0.420209
H	4.869153	-2.010213	0.842105
C	7.553605	-0.067263	-0.082974
H	-8.641483	0.086924	0.096441
H	8.636739	-0.077661	-0.094999
Br	-7.844131	-2.565027	-1.103714
Br	-7.766588	2.722709	1.278085
Br	7.812663	2.570755	-1.284863
Br	7.788565	-2.710036	1.113436

**Table S3.** TD-DFT Calculated Transitions for **IPt-DB**

Excited State	Excitation transitions	Oscillator strength ( <i>f</i> )	Energy (eV)	Wavelength (nm)
1	126→127	1.1598	3.2743	378.66
	122→130			
2	124→127	0.0000	3.4569	358.65
	125→127			
3	124→129	0.0000	3.7520	330.45
	126→128			
4	124→128	0.0001	3.7544	330.23
	126→129			

5	122→127 125→130	0.0088	3.9370	314.92
6	124→127 126→130	0.0000	3.9955	310.31
7	119→130	0.0002	4.0586	305.48
8	119→127 120→130 124→131 126→132	0.0107	4.0627	305.18
9	124→127 125→127 125→133 126→130	0.0000	4.2433	292.19
10	126→133	0.1418	4.2767	289.90
11	123→127	0.0197	4.2887	289.09
12	126→137	0.0000	4.3799	283.08
13	122→127 125→130	0.0239	4.4408	279.19
14	122→128 125→129 126→134	0.0030	4.4555	278.28
15	122→129 125→128	0.0001	4.4556	278.26

## References for Supporting Information

---

[<sup>1</sup>] CrysAlisPro 1.171.40.63a (Rigaku Oxford Diffraction, 2019)

[<sup>2</sup>] SCALE3 ABSPACK -An Oxford Diffraction program(1.0.4,gui:1.0.3) (C) 2005 Oxford Diffraction Ltd.

[<sup>3</sup>] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, 42, 339.

[<sup>4</sup>] G. M. Sheldrick, *Acta Cryst.* **2015**, A71, 3.

[<sup>5</sup>] G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112.