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Assembly of a M_4L_4 "folded-cube" using a T-shaped, right-angled ligand

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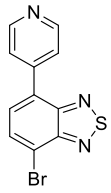
General Experimental Details

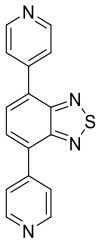
4,7-Dibromobenzo[c][1,2,5]thiadiazole[S1] and [Pt(**dppp**)$(OTf)_2$] were[S2] synthesized according to a literature method. Solvents were dried using an Innovative Technologies Solvent Purification System. Benzothiadiazole, PEPPSI™-IPr catalyst and 4-pyridineboronic acid were purchased from Sigma-Aldrich and used as received. ^{1}H, ^{19}F, ^{31}P and ^{13}C NMR spectra were recorded on an Avance 300 or 500 instrument. Column chromatography was performed using Silicycle Ultra-Pure Silica Gel (230–400 mesh). High resolution mass spectrometry (HR-MS) data for organic compounds were recorded on a Micromass LCT electrospray ionization (ESI) time-of-flight (ToF) mass spectrometer; solutions with concentrations of 0.001 M were prepared in methanol and injected for analysis at a rate of 5 µL/min using a syringe pump. Cold-spray ionization mass spectrometry (CSI-MS) experiments were performed on a MicroTOF II mass spectrometer from Brüker in positive ion mode using Cryospray: capillary voltage, 4500 V; End Plate Offset -500V; Capillary Exit voltage, 20-200 V; dry gas temperature, -20°C; Nebulizer gas temperature, -60°C; Nebulizer gas flow, 0.150 MPa; dry gas flow, 1.5 L/min; TOF voltage, 1957.1V. MS data were recorded in the full scan mode (from 50 to 8000 m/z). IR spectra were obtained using a Bruker Alpha FT-IR spectrometer equipped with a Platinum single reflection diamond ATR module. Elemental compositions were determined on a PerkinElmer 2400 Series II Elemental Analyzer.

Synthesis of 4-bromo-7-(pyridin-4-yl)benzothiadiazole

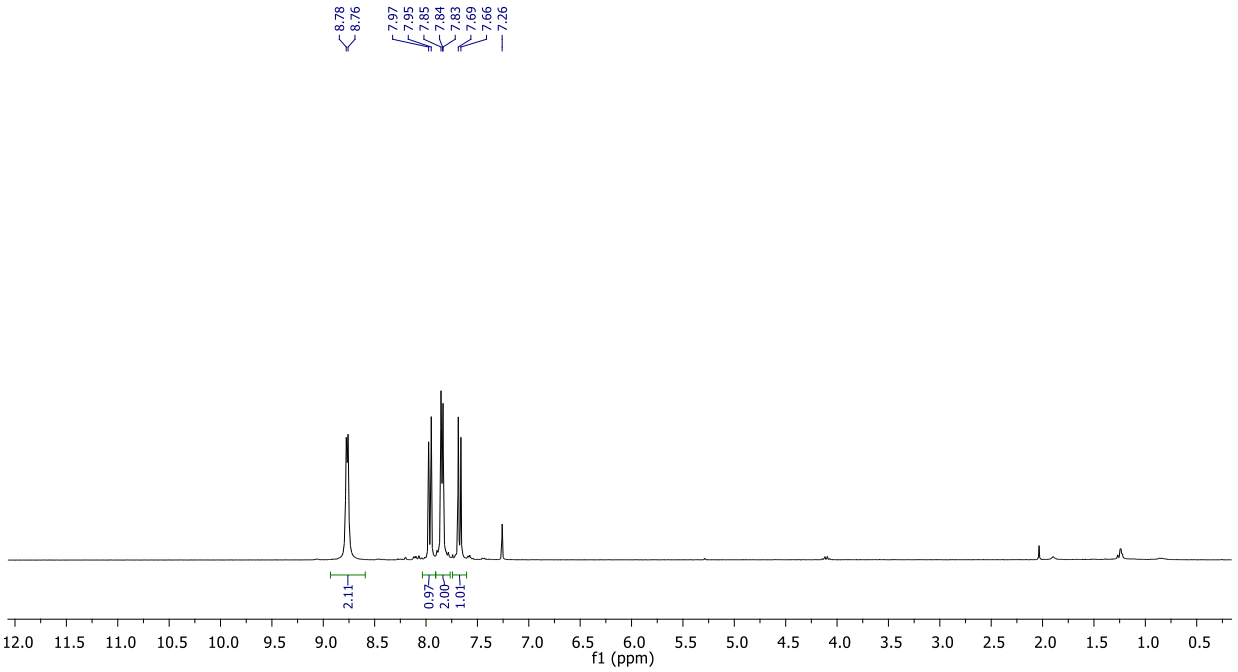


4-Pyridylboronic acid (0.420 g, 3.42 mmol), 4,7-dibromobenzothiadiazole (1.000 g, 3.40 mmol), PEPPSI^{TM}-IPr catalyst ([1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] (3-chloropyridyl) palladium(II)dichloride) (0.046 g, 0.07 mmol), and potassium carbonate (K_2CO_3) (2.35 g, 17.03 mmol) were added to a clean dry Schlenk flask (100 mL). The flask was evacuated and backfilled with N_2 three times. A 1,4-dioxane/water (1:1) mixture (60 mL) was added to the reaction mixture. The flask contents were refluxed (90 ^{o}C) under nitrogen for 24 h. The flask was allowed to cool to room temperature. Extraction with CH_2Cl_2 and drying over anhydrous $MgSO_4$ gave a greenish yellow solution. The solvent was removed using a rotary evaporator and the product collected. Column chromatography was performed using CH_2Cl_2/ethyl acetate (2:1) as eluent. After removal of the solvent the product was isolated as a greenish yellow solid. Yield 0.350 g, 35 %. MP: 178 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) = 8.77 (d, 2H, ^{3}J = 5.3 Hz), 7.96 (d, 1H, ^{3}J = 7.6 Hz), 7.84 (d, 2H, ^{3}J = 5.3 Hz), 7.67 (d, 1H, ^{3}J = 7.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.03, 152.56, 150.41, 143.91, 132.21, 130.99, 128.99, 123.54, 115.44. Elemental Analysis (%): Calcd. for $C_{11}H_6BrN_3S$: C, 45.22; H, 2.07; N, 14.38. Found: C, 45.41; H, 1.99; N, 14.16. IR (ATR) (ν/cm^{-1}) = 3032, 1596, 1584, 1545, 1528, 1474, 1408, 1328, 1301, 1264, 1213, 1154, 1089, 1068, 992, 933, 880, 845, 814, 785, 748, 669, 626, 614, 560, 545, 517, 503, 463.

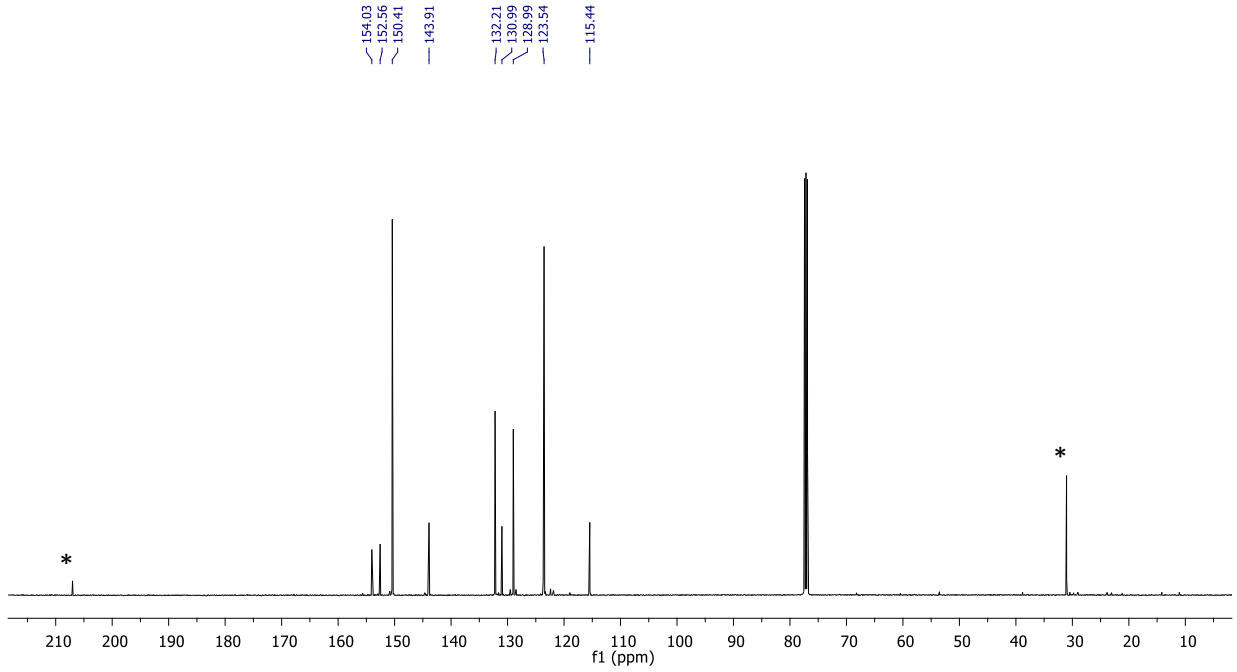
A brown coloured by-product was also isolated from the column chromatography by flushing the column with methanol, drying over anhydrous $MgSO_4$ and recrystallization from acetonitrile. This was identified as the di-substituted product shown below. The full characterization of this product will be reported in due course.



^{1}H NMR spectrum of 4-bromo-7-(pyridin-4-yl)benzothiadiazole; 500 MHz, $CDCl_3$

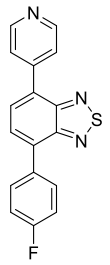


^{13}C NMR spectrum of 4-bromo-7-(pyridin-4-yl)benzothiadiazole; 126 MHz, $CDCl_3$



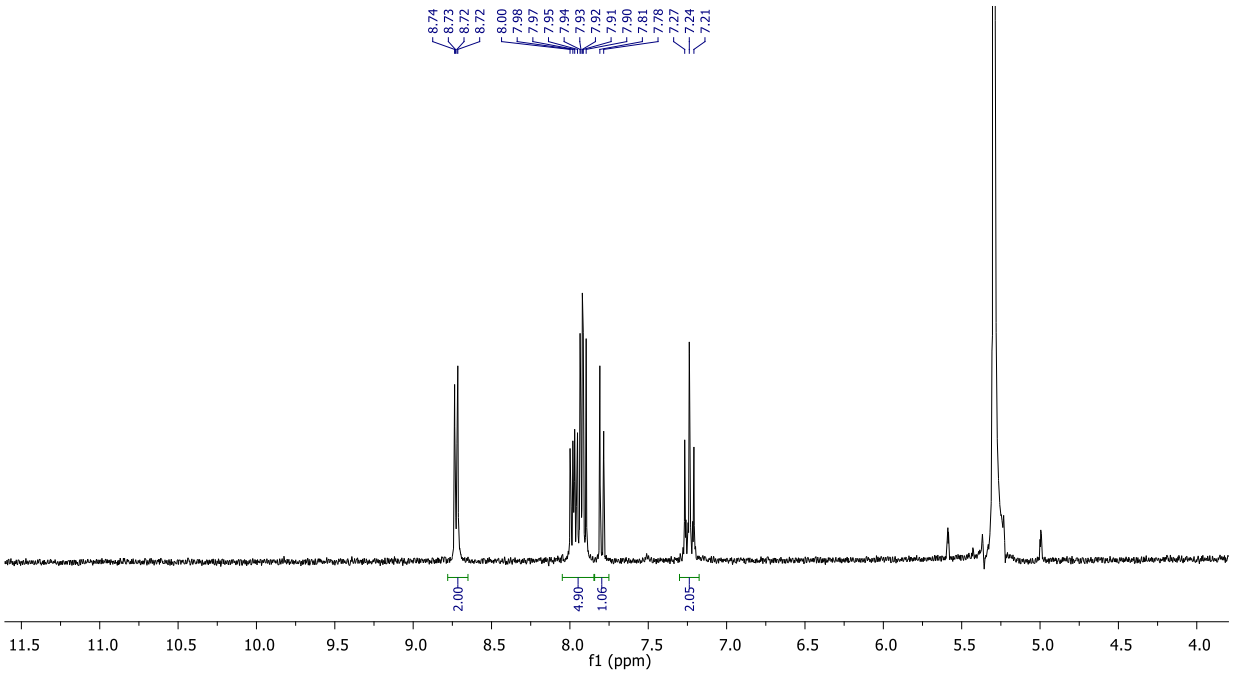
(*:acetone)

Synthesis of 4-(4-flourophenyl)-7-(pyridin-4-yl)benzothiadiazole

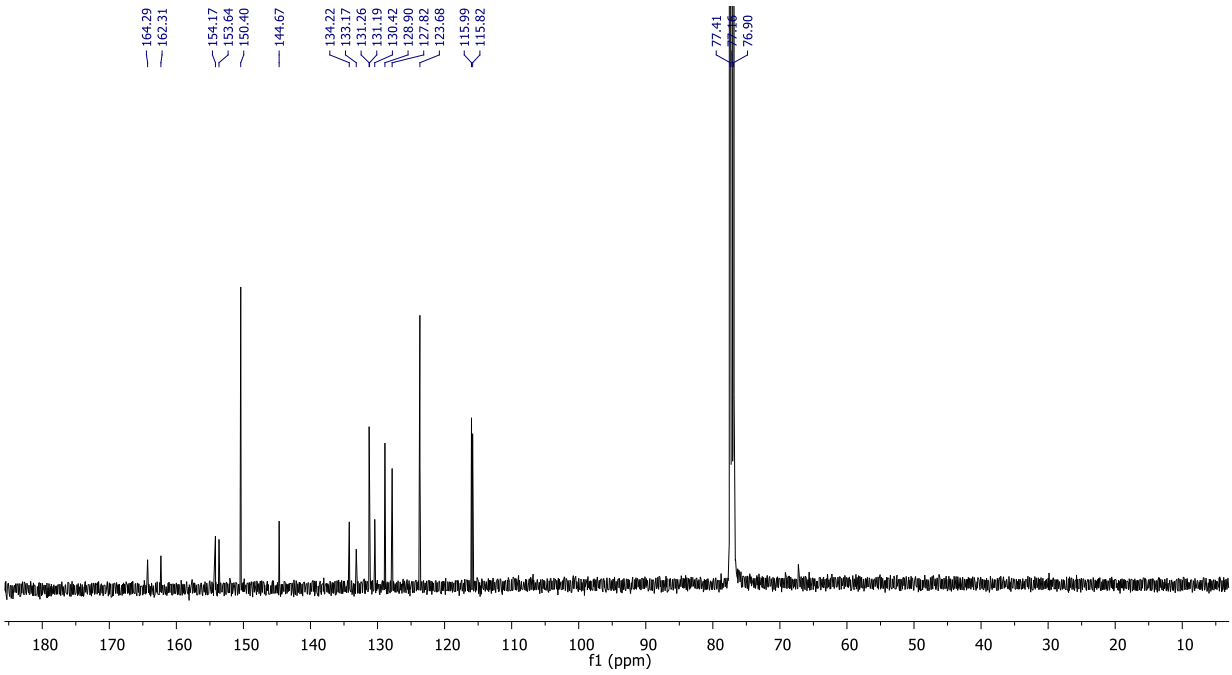


4-Fluorophenylboronic acid (0.166 g, 1.19 mmol), PEPPSI^{TM}-IPr catalyst ([1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II)dichloride) (0.016 g, 0.02 mmol), and potassium carbonate (K_2CO_3) (0.827 g, 5.99 mmol) were added to a Schlenk flask. The flask was evacuated and back-filled with nitrogen three times. 4-Bromo-7-(pyridin-4-yl) benzothiadiazole (0.350 g, 1.20 mmol) was dissolved in 1,4-dioxane (20 mL) and added to the solids. Then water (20 mL) was added. The mixture was refluxed under N_2 at 90 ^{o}C for 1 day. The product was extracted with $CHCl_3$. The solution was dried with $MgSO_4$, filtered and then solvent evaporated. The resulting solid was recrystallized from MeOH. Yield 0.368 g, 95 %. MP**:** 227 ^{o}C. IR (ATR) (v/cm^{-1}) = 3067, 3020, 2962, 1600, 1556, 1544, 1514, 1497, 1480, 1417, 1350, 1316, 1302, 1261, 1216, 1157, 1095, 1070, 1020, 1000, 957, 938, 889, 853, 811, 753, 719, 692, 670, 650, 632, 586, 550, 535, 516, 498, 481, 423. ^{1}H NMR (300 MHz, CD_2Cl_2) δ(ppm) = 8.73 (d, 2H, ^{3}J = 4.5 Hz), 7.98 (m, 2H), 7.93 (d, 2H, ^{3}J = 4.5 Hz), 7.90 (d, 1H, ^{3}J = 7.5 Hz), 7.79 (d, 1H, ^{3}J = 7.5 Hz), 7.24 (t, 2H, ^{3}J = 8.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.30 (d, $^{1}J_{F-C}$= 249 Hz), 154.20, 153.64, 150.40, 144.67, 134.22, 133.17, 131.23 (d, $^{3}J_{F-C}$ = 8.2 Hz), 130.42, 128.90, 127.82, 123.68, 115.90 (d, $^{2}J_{F-C}$ = 21 Hz). Elemental Analysis (%): Calcd for $C_{17}H_{10}FN_3S$: C, 66.44; H, 3.28; N, 13.67. Found: C, 67.48; H, 3.35; N, 13.06.

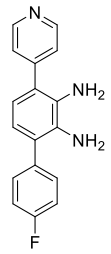
^{1}H NMR spectrum of 4-(4-flourophenyl)-7-(pyridin-4-yl)benzothiadiazole; 300 MHz, CD_2Cl_2



^{13}C NMR spectrum of 4-(4'-flourophenyl)-7-(pyridin-4-yl)benzothiadiazole; 126 MHz, $CDCl_3$

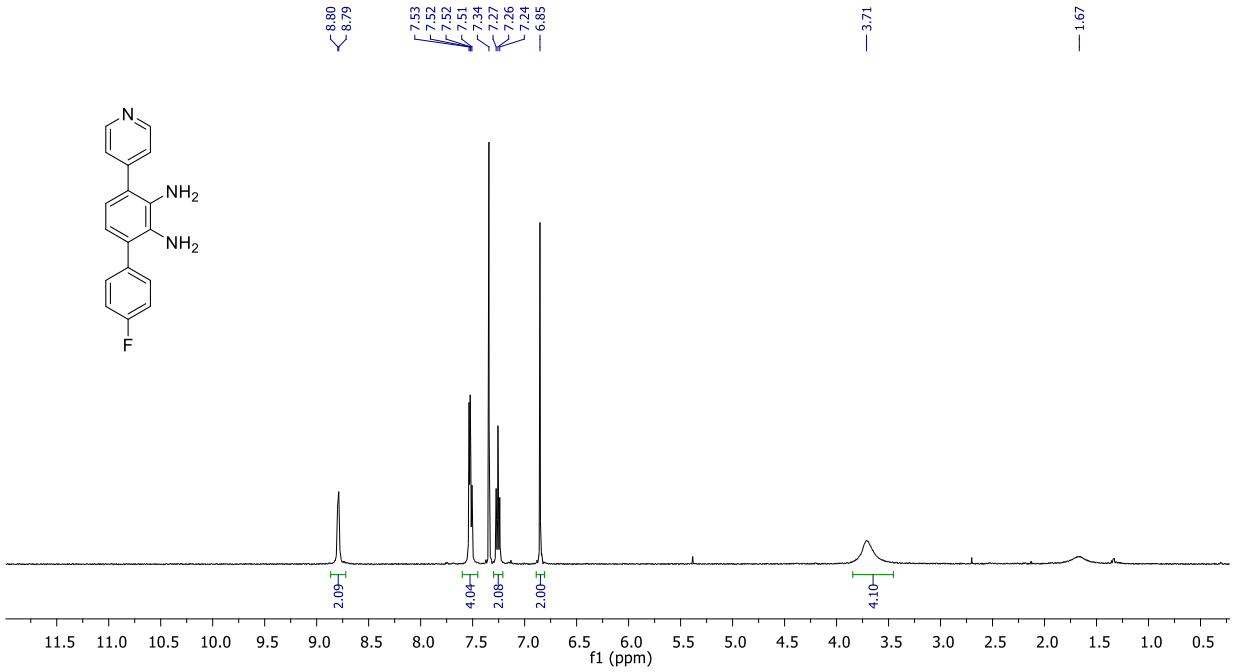


Synthesis of 3-(4'-flourophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine

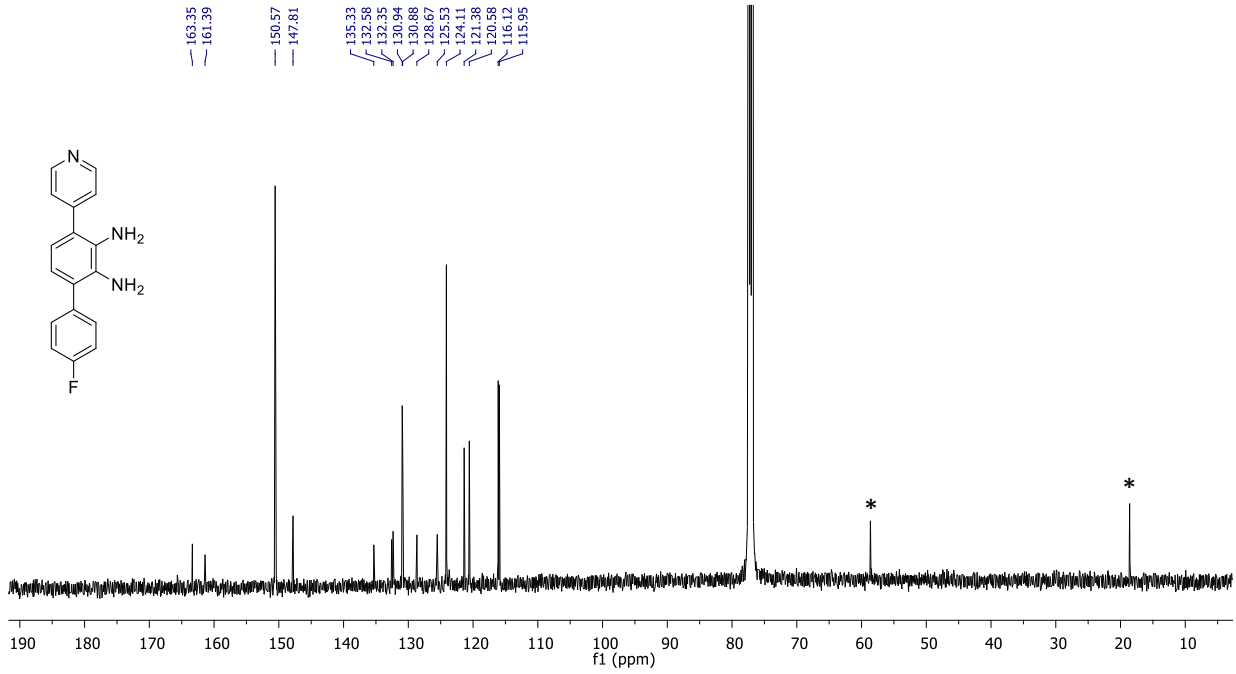


4-(4-Flourophenyl-7-(pyridin-4-yl)benzothiadiazole (0.348 g, 1.13 mmol) was dissolved in EtOH (45 mL) and THF (15 mL) and transferred to a Schlenk flask. Cobalt(II) chloride hexahydrate (0.006 g, 0.02 mmol) and sodium borohydride ($NaBH_4$) (0.065 g, 1.70 mmol) were then added and the resulting mixture refluxed (70 ^oC) for 1 h. The reaction progress was monitored by running TLC using CH_2Cl_2/ethyl acetate (2:1). More $NaBH_4$ (0.065 g, 1.70 mmol) was added every 1 h until the reaction was complete (4 h). The reaction mixture was then cooled to room temperature. The resulting solution was extracted with CH_2Cl_2 and filtered under N_2 and the solvent removed using a rotary evaporator. The resulting white solid was stored under N_2 until being used in the next step. Yield 0.300 g, 95 %. MP**:** 238 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ(ppm) = 8.79 (d, 2H, ^3J = 3.0 Hz), 7.53 (d, 2H, ^3J = 3.0 Hz), 7.52 (m, 2H), 7.26 (t, 1H, $^3J_{F-H}$ = 5.4 Hz, $^3J_{H-H}$ = 5.4 Hz,), 6.85(s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.37 (d, $^1J_{F-C}$= 247 Hz), 161.39, 150.57, 147.81, 135.33, 132.58, 132.35, 130.91 (d, $^3J_{F-C}$ = 7.6 Hz), 128.67, 125.53, 124.11, 121.38, 120.58, 116.03 (d, $^2J_{F-C}$ = 21 Hz). HR-MS (ESI): Calcd for [**M** + H]$^+$, $[C_{17}H_{15}FN_3]^+$, *m*/*z* = 280.1250, found *m*/*z* = 280.1279. IR (ATR) (v/cm^{-1}) = 3311, 2960, 2923, 2863, 2296, 2225, 1617, 1593, 1474, 1437, 1409, 1378, 1345, 1320, 1260, 1207, 1112, 991, 879, 864, 824, 808, 793, 748, 692, 648, 581, 520.

^{1}H NMR spectrum of 3-(4'-flourophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine; 300 MHz, $CDCl_3$

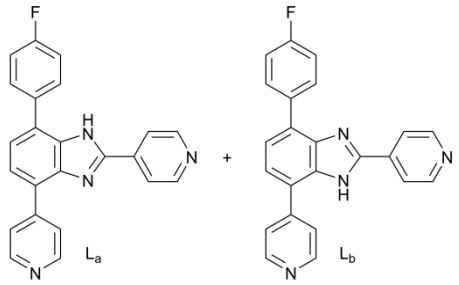


^{13}C NMR spectrum of 3-(4'-flourophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine; 126 MHz, $CDCl_3$



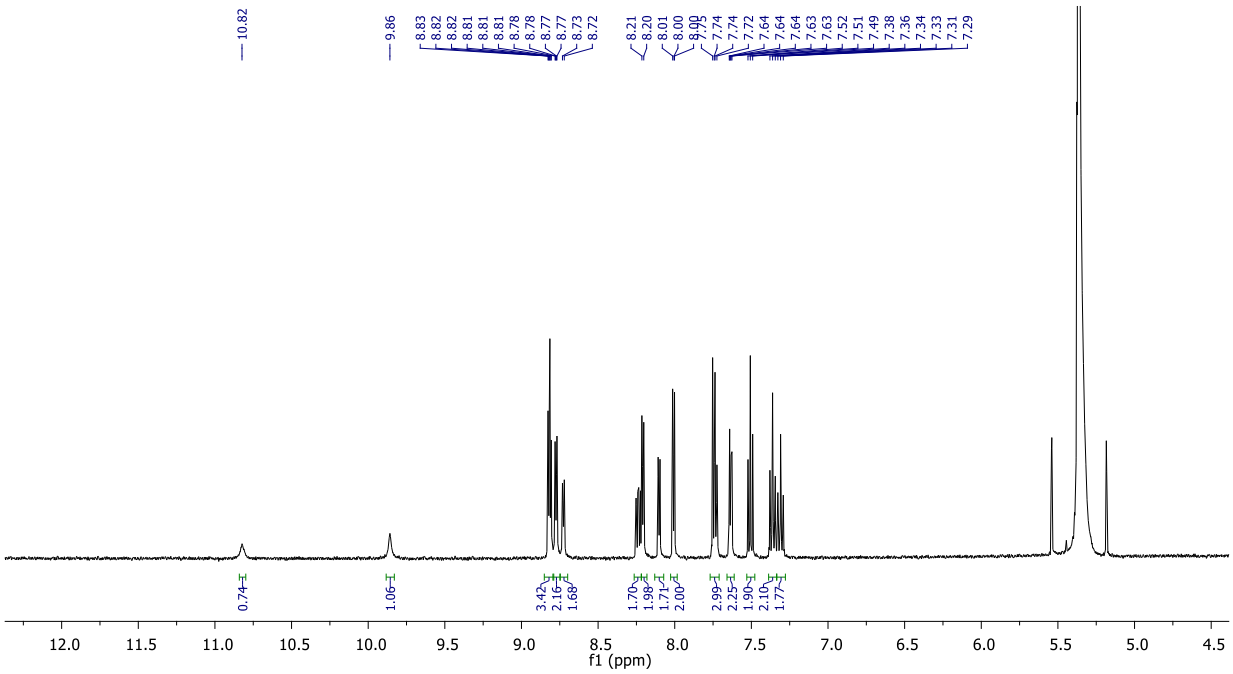
(*ethanol)

Synthesis of L_a/L_b

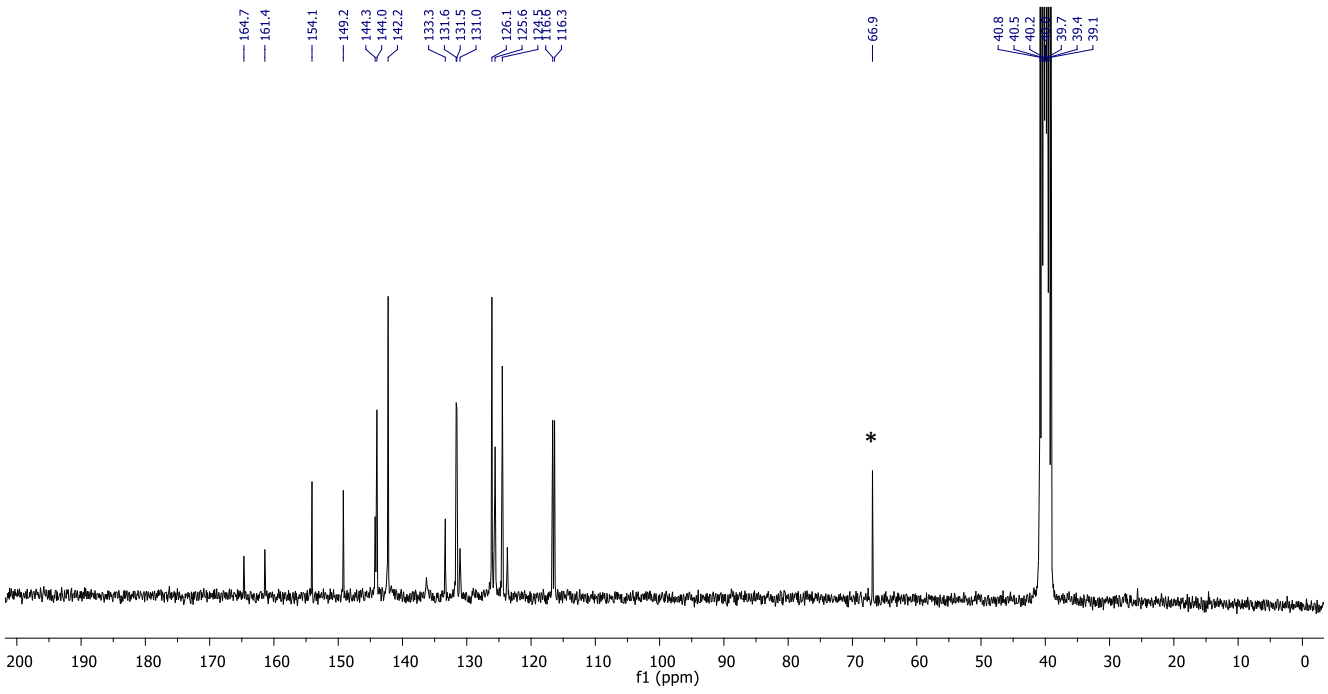


4-Pyridinecarboxaldehyde (0.115 g, 1.07 mmol) was weighed into in a small vial, diluted with chloroform (10 mL) and added to 3-(4-flourophenyl-6-(pyridin-4-yl)benzene-1,2-diamine (0.300 g, 1.07 mmol) under N_2 in a round bottom flask. Zirconium tetrachloride ($ZrCl_4$) (0.0025 g, 0.01 mmol) was added and the mixture was stirred overnight at room temperature. The solvent was then removed using a rotary evaporator. The resulting solid was dissolved in THF, the solution filtered and the THF evaporated using a rotary evaporator. The resulting pale yellow product was recrystallized twice from acetonitrile. Yield 0.195 g, 48%. MP: 292 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ(ppm) = 10.82 (s, 1H), 9.86 (s, 1H), 8.83 (d, 2H, ^3J = 6.5 Hz), 8.81 (d, 2H, ^3J = 6.5 Hz), 8.77 (d, 2H, ^3J = 6.5 Hz), 8.72 (d, 2H, ^3J = 6.5 Hz), 8.24 (d, 1H, ^3J = 8.5 Hz), 8.23 (d, 1H, ^3J = 8.5 Hz), 8.21 (d, 2H, ^3J = 6.0 Hz), 8.10 (d, 2H, ^3J = 6.0 Hz), 8.01 (d, 2H, ^3J = 6.5 Hz), 7.74 (d, 1H, ^3J = 8.0 Hz), 7.73 (d, 2H, ^3J = 8.0 Hz), 7.64 (d, 1H, ^3J = 8.0 Hz), 7.63 (d, 2H, ^3J = 6.4 Hz), 7.51 (d, 1H, ^3J = 8.0 Hz), 7.40 (d, 1H, ^3J = 8.0Hz), 7.36 (m, 2H), 7.31 (m, 2H). ^{13}C NMR (75 MHz, 0.5%HBF_4 in DMSO-d_6) δ = 164.7 (d, $^1J_{F\text{-}C}$= 248 Hz), 154.1, 149.2, 144.3, 144.0, 142.2, 136.3, 133.3, 131.5 (d, $^3J_{F\text{-}C}$= 8 Hz), 131.0, 126.1, 125.6, 125.6, 124.5, 124.5, 123.7, 116.1 (d, $^2J_{F\text{-}C}$= 23 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2) δ (ppm) = −115.25, −115.81. HR-MS (ESI): Calcd for [**M** + H]$^+$, $[C_{23}H_{16}FN_4]^+$, *m*/*z* = 367.1359, found *m*/*z* = 367.1367. IR (ATR) (v/cm^{-1}) = 3060, 3043, 2961, 1933, 1852, 1594, 1559, 1539, 1522, 1506, 1491, 1477, 1437, 1420, 1405, 1378, 1364, 1327, 1302, 1256, 1226, 1220, 1215, 1157, 1092, 1068, 1011, 999, 991, 861, 930, 870, 845, 831, 811, 801, 740, 731, 703, 695, 668, 651, 642, 614, 603, 583, 553, 528, 504, 447, 429.

^{1}H NMR spectrum of L_a/L_b: 500 MHz, CD_2Cl_2



^{13}C NMR spectrum of L_a/L_b; 75 MHz, 0.5%HBF_4 in DMSO-d_6

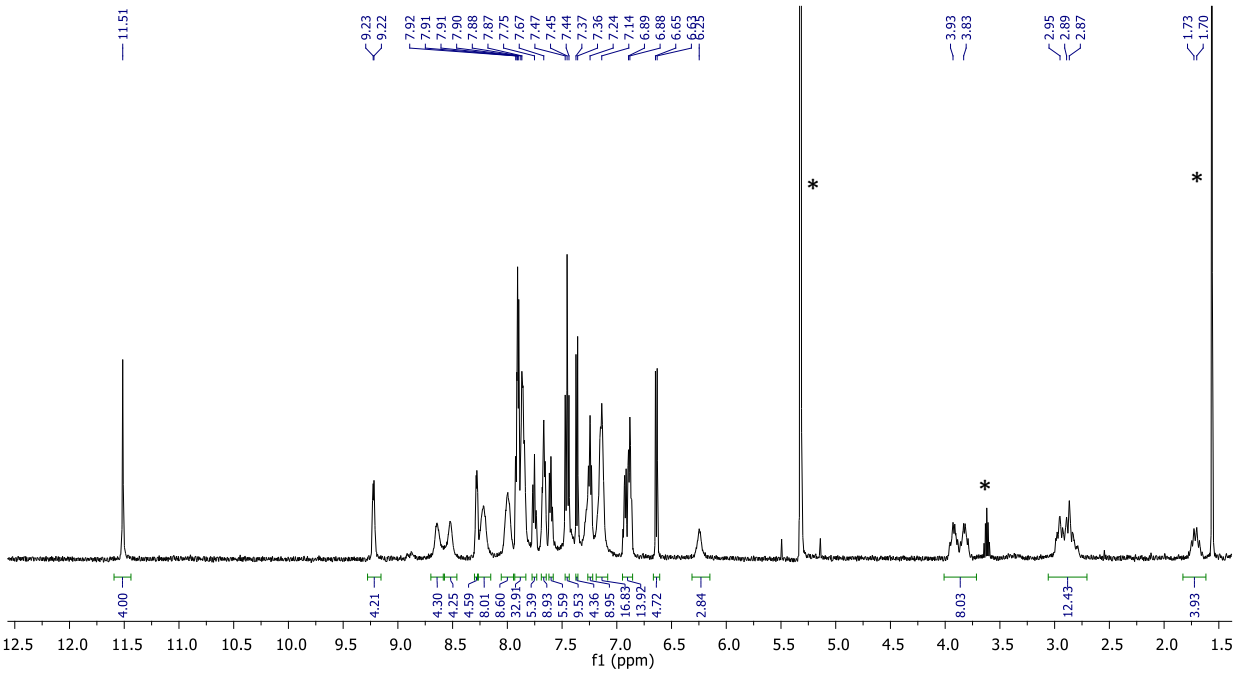


(*1,4-dioxane)

Synthesis of $[Pt(dppp)(L)]_4[OTf]_8$

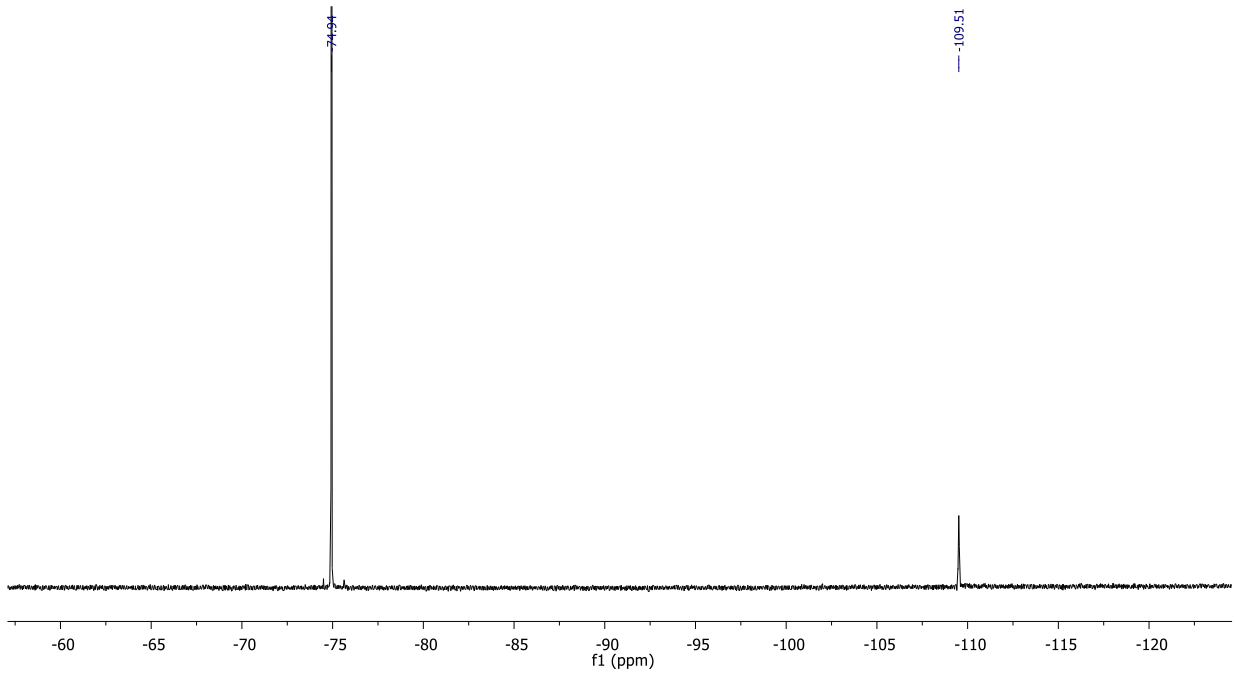
L (0.050 g, 0.136 mmol) and [Pt(**dppp**)$(OTf)_2$] (0.147 g, 0.162 mmol) were dissolved in a MeOH/$MeNO_2$ mixture (1:1, 30 mL). The mixture was stirred overnight at 70 °C, cooled to RT and filtered. The volume of the solution was then reduced to about 10 mL and *iso*-propylether added until a yellow precipitate formed. This yellow solid was collected using vacuum filtration and dissolved in a mixture *iso*-propylether/CH_2Cl_2 mixture (1:1). Slow evaporation of this solution resulted in the formation of colourless crystals; yield 65%. Repeating the reaction by scaling down to a mass of 0.010 g of ligand (**L**) and stirring for only 2 h gave a similar result. ^{1}H NMR (500 MHz, CD_2Cl_2) δ(ppm) = 11.51 (s, 4H), 9.22 (dd, 4H, J = 6.0 Hz, 2.0 Hz), 8.65 (m, 4H), 8.52 (m, 4H), 8.29 (m, 4H), 8.22 (m, 8H), 7.80 (m, 8H), 7.87–7.92 (m, 32H), 7.75 (t, 4H, ^3J = 7.5 Hz), 7.66 (m, 8H), 7.60 (t, 4H, ^3J = 7.5 Hz), 7.45 (t, 4H, ^3J = 8.5 Hz), 7.36 (d, 4H, ^3J = 7.5 Hz), 7.24 (t, 8H, ^3J = 6.0 Hz), 7.14 (m, 16H), 6.90 (m, 12H), 6.64 (d, 4H, ^3J = 8.0 Hz), 6.25 (m, 4H), 3.93 (m, 4H), 3.83 (m, 4H), 2.89 (m, 12H), 1.72 (m, 4H). ^{31}P NMR (202 MHz, CD_2Cl_2) δ(ppm) = −13.24 (d, $^2J_{P\text{-}P}$ = 30.8 Hz), −15.70 (d, $^2J_{P\text{-}P}$ = 30.8 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2) δ(ppm) = −74.9 (CF_3), −109.5 (phenyl-*F*). CSI-MS calcd for [**M** − 3 OTf]$^{3+}$, $[C_{205}H_{164}F_{19}N_{16}O_{15}P_8Pt_4S_5]^{3+}$, m/z = 1546.9127, found m/z = 1546.9210.

^{1}H NMR spectrum of $[Pt(dppp)(L)]_4[OTf]_8$; 500 MHz, CD_2Cl_2

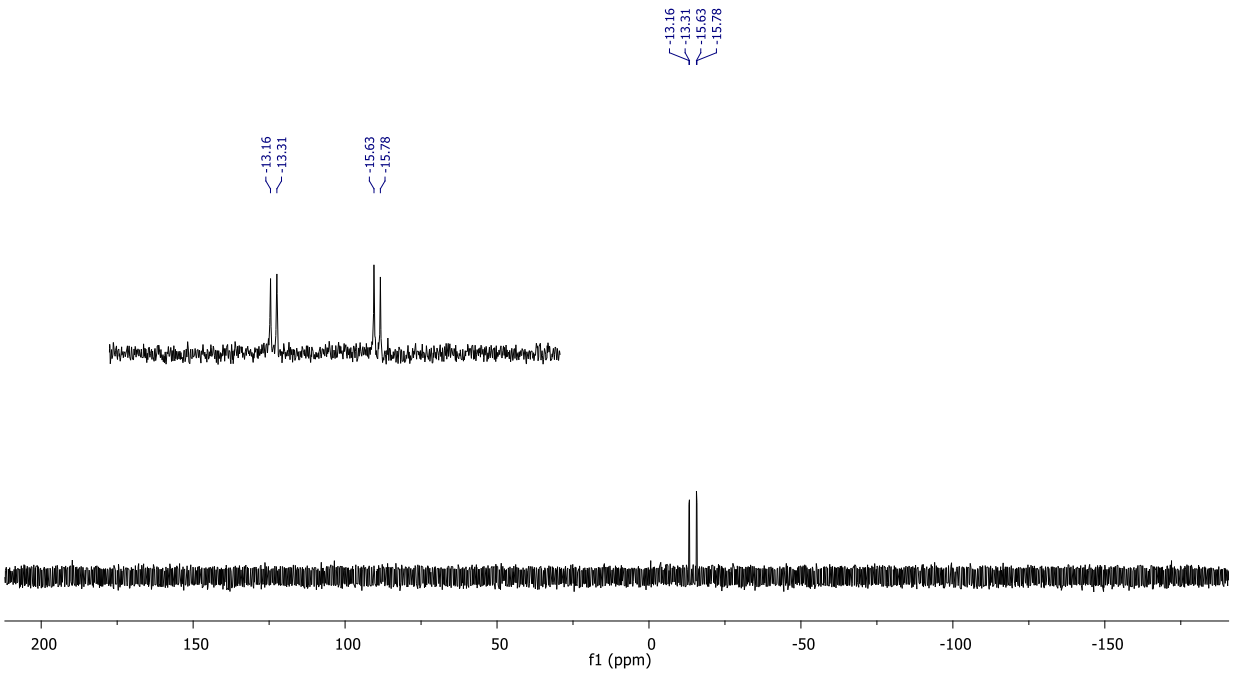


(*solvent)

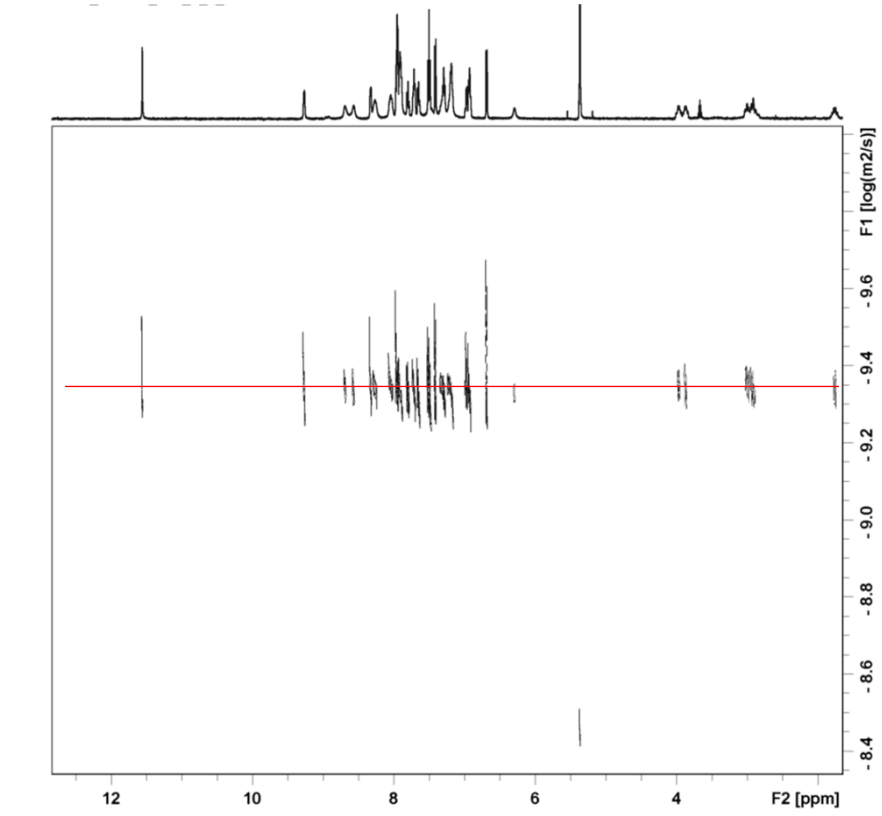
^{19}F NMR spectrum of $[Pt(dppp)(L)]_4[OTf]_8$; 470 MHz, CD_2Cl_2



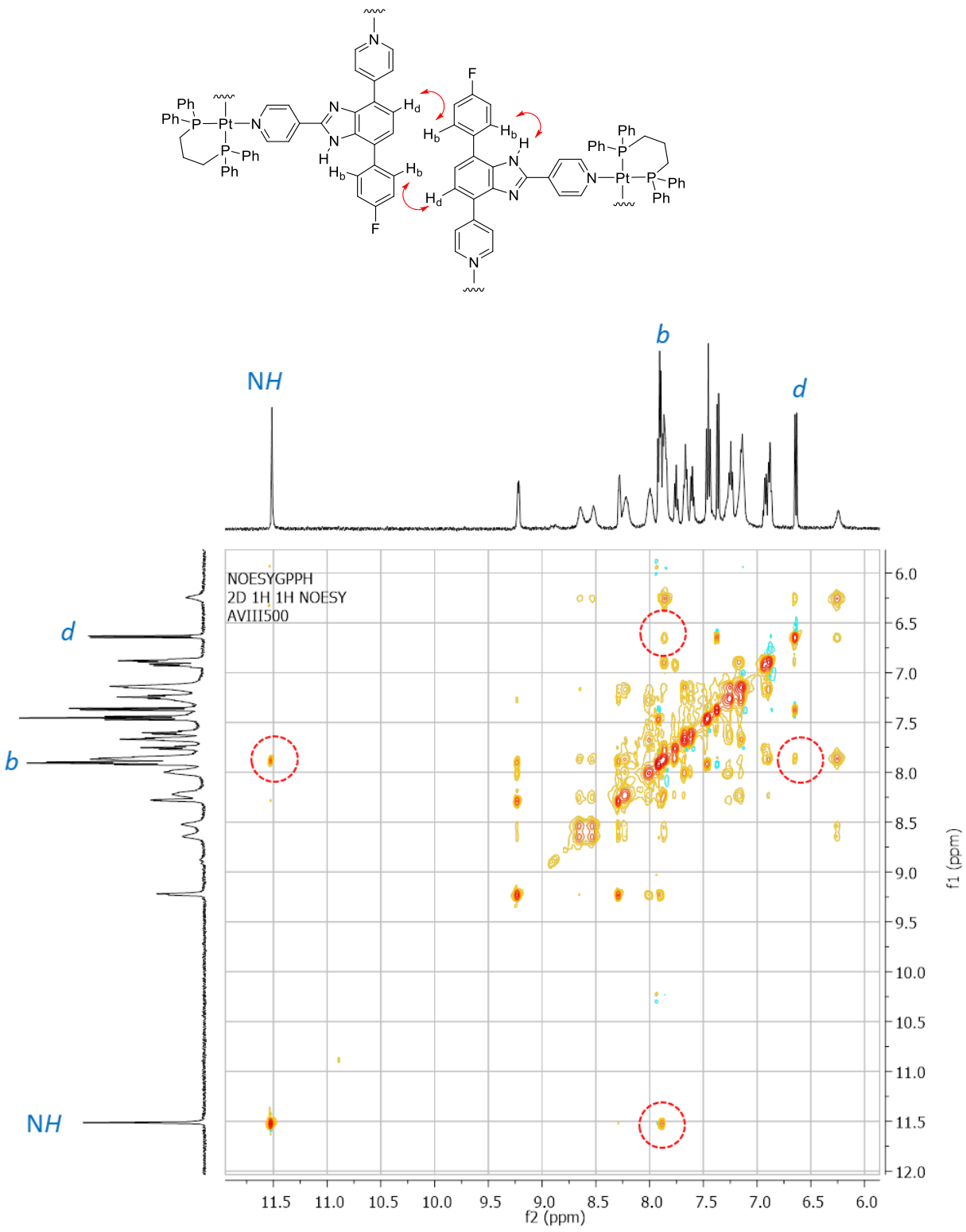
^{31}P NMR spectrum of $[Pt(dppp)(L)]_4[OTf]_8$; 202 MHz, CD_2Cl_2



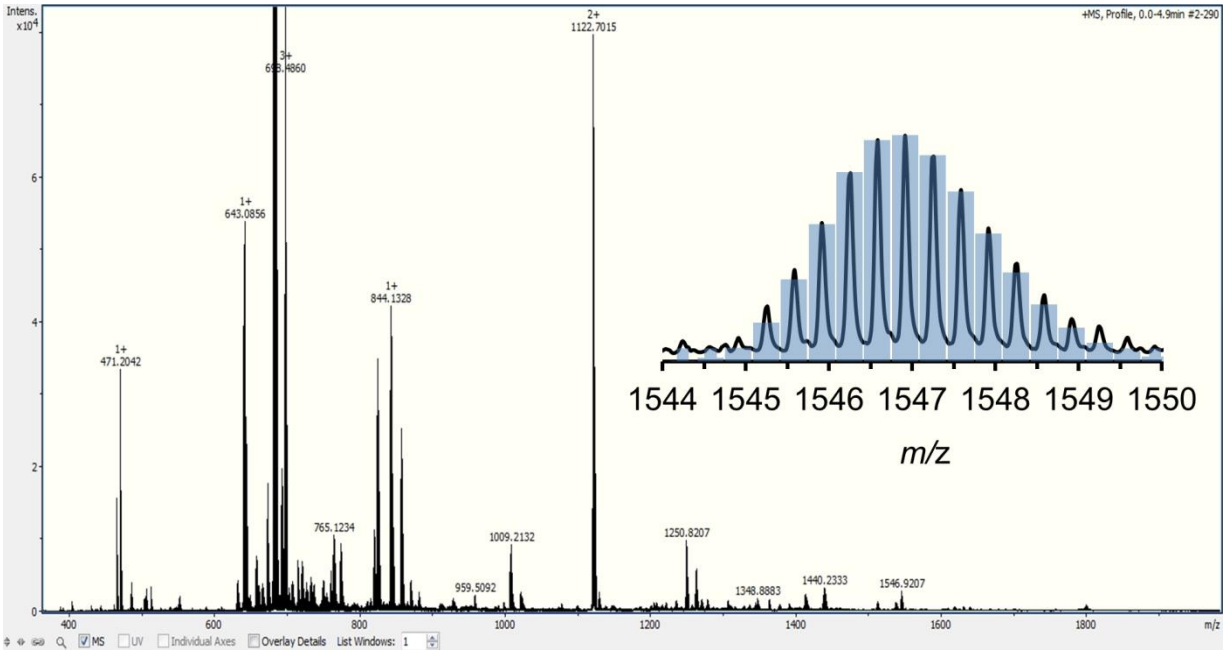
2D DOSY spectrum of $[Pt(dppp)(L)]_4[OTf]_8$; (500 MHz, CD_2Cl_2 , 298 K).



2D ^{1}H-^{1}H NOESY NMR spectrum of complex [Pt(dppp)(L)]$_4$[OTf]$_8$; 500 MHz, CD_2Cl_2



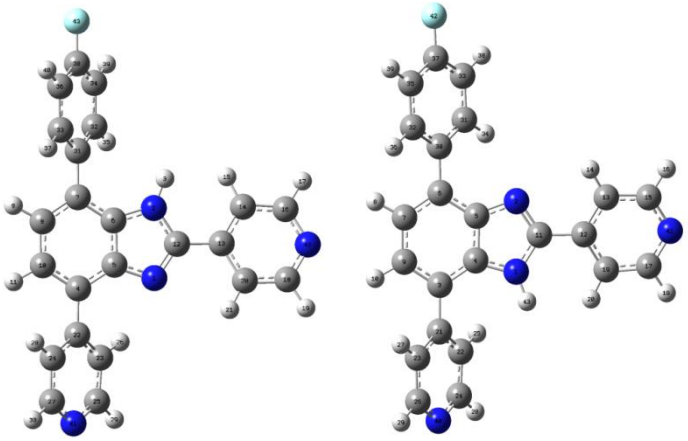
CryoSpray-Ionization-MS Data for $[Pt(dppp)(L)]_4[OTf]_8$



DFT Calculations

All calculations were performed using the Gaussian 09 software package[S3] For compounds $\mathbf{L_a}$, $\mathbf{L_b}$, DFT calculations were performed at the B3LYP level of theory, using the basis set of 6-31+G(d,p). The same level of theory and basis set were also used for calculating the ^{1}H, ^{13}C, ^{15}N, and ^{19}F -NMR shielding constants by applying the Gauge Independent Atomic Orbitals (GIAO) method. The effect of solvent was accounted for using the default model provided by Gaussian 09, with chloroform as the solvent. Single point energies for compounds $\mathbf{L_a}$, $\mathbf{L_b}$ were obtained from the optimized structures as Self-Consistent Field (SCF) solutions. Raw data are summarized below.

$\mathbf{L_a}$ $\mathbf{L_b}$



	$\mathbf{L_a}$	$\mathbf{L_b}$
E (KJ/mol)	-3162707.438	-3162707.317
ΔE (KJ/mol)	0.123	

Details of Single-Crystal X-ray Diffraction Experiments

Crystals were frozen in paratone oil inside a cryoloop under a cold stream of N_2. Reflection data were collected on either a Bruker APEX (Pt cluster) or Venture D8 (L1 ligand) diffractometer using MoKα and CuKα radiation respectively. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined using full-matrix least-squares methods against $|F^2|$ data. When practical, non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in idealized positions and refined using a riding model. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL program library[S4] and figures drawn with CrystalMaker[S5] software. Details can be obtained from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk for CCDC accession numbers 1025103 and 1025105. Details pertinent to individual experiments are provided in the paragraphs and Tables below.

Crystals of $\mathbf{L_a}$ were of good quality. The unit cell contained two molecules of the ligand ($C_{68}H_{70}N_4$) and two chloroform ($CHCl_3$) solvent molecules. There was no evidence of any anions should the material have been inadvertently isolated as the protonated form. The structure was solved in the triclinic space group P-1 (#2) with Z = 2. All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were placed in idealized positions and refined using a riding model. A summary of the crystal data, solution and refinement parameters are presented in Table S-1.

Table S-1 X-ray Data for $L_a \cdot (CHCl_3)$

Empirical formula	$C_{24}H_{16}Cl_3FN_4$
Formula weight	485.78
Crystal system	triclinic
Space group	P-1
a/Å	9.0898(3)
b/Å	10.2902(3)
c/Å	13.0414(4)
α/°	80.2999(11)

β/°	89.0859(11)
γ/°	64.1607(10)
Volume/Å^3	1079.91(6)
Z	2
Reflections collected	15092
Independent reflections	4246 [R_{int} = 0.0436]
Data/restraints/parameters	4246/0/288
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)][a]	R_1 = 0.0537, wR_2 = 0.1510
Final R indexes [all data][b]	R_1 = 0.0579, wR_2 = 0.1578

[a] $R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$; [b] $R_2w = [\Sigma[w(F_o^2 - F_c^2)^2] \, / \, \Sigma[w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

Crystals of [Pt(**dppp**)(**L**)]$_4$[OTf]$_8$ were initially of good quality and size, but were very susceptible to rapid loss of CH_2Cl_2 solvent and therefore degradation in crystal quality. Numerous attempts were made to transfer the crystals from the mother liquor to the diffractometer cold stream with minimal loss of solvent and crystallinity; the data set used for this solution represents our best efforts in this regard. Attempts to grow X-ray quality crystals from other solvents were unsuccessful. The structure was solved in the triclinic space group P-1 (#2) with Z = 2 for a formula of [Pt(**dppp**)(**L**)(CH_2Cl_2)]$_4$[OTf]$_8$·34(CH_2Cl_2). The majority of the non-hydrogen atoms of the cluster and anions were easily located. A number peaks due to solvent were input as carbon atoms in order to help phasing and allow location and preliminary refinement of the cluster, however none of these atoms could be modelled as actual solvent molecules and were ultimately removed from the model and taken into account using SQUEEZE.[S6] The poor quality of the data only allowed full anisotropic refinement of the Pt, P, S, F, O and N atoms; all the C atoms were refined isotropically except for the triflate C-atoms which were refined anisotropically to be consistent with the rest of the atoms of the anion model. All aromatic rings were input as idealized hexagons using AFIX 66. The F-atoms of **L** were constrained with DFIX (C-F) and FLAT to be in the plane of the attached phenyl ring. The P-C bonds of the **dppp** ligand were constrained with DFIX (P-C) and all triflate anions were input as rigid groups using DFIX (S-O, S-C and C-F) SADI, DELU and SIMU restraints. The 38 molecules of CH_2Cl_2 per asymmetric unit were treated

as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON[S6]. All the hydrogen atoms were placed in idealized positions and refined using a riding model. A summary of the crystal data, solution and refinement parameters are presented in Table S-2.

NOTE: Although, the data set is of poor quality and the model overly restrained, the solution is certainly good enough to provide reliable atom connectivity and therefore verify the product as the described M_4L_4 cluster.

Table S-1 X-ray Data for $[Pt(dppp)(L)(CH_2Cl_2)]_4[OTf]_8 \cdot 34(CH_2Cl_2)$

Empirical formula	$C_{246}H_{240}Cl_{76}F_{28}N_{16}O_{24}P_8Pt_4S_8$
Formula weight	8315.33
Crystal system	triclinic
Space group	P-1
a/Å	23.492(8)
b/Å	23.764(8)
c/Å	27.348(10)
α/°	80.079(4)
β/°	79.153(4)
γ/°	88.711(4)
Volume/Å^3	14769(9)
Z	2
Reflections collected	106206
Independent reflections	36047 [R_{int} = 0.1500]
Data/restraints/parameters	36047/1940/1282
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)][a]	R_1 = 0.1646, wR_2 = 0.3757
Final R indexes [all data][b]	R_1 = 0.2296, wR_2 = 0.4121

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; [b] $R_2w = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

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