Supporting Information

Novel Columnar Metallomesogens Based on Cationic Platinum(II) Complexes without Long Peripheral Chains

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Contents

1 General information

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All commercially available starting materials were used directly with no further purification. The solvents were carefully dried prior to use. NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on Varian INOVA-400 MHz and 100 MHz spectrometer. Mass spectra were recorded on Waters Q-TOF Premier. UV−Vis absorption spectra were measured at room temperature on Perkin Elmer Lambda 950 spectrophotometer. The photoluminescence (PL) spectra were measured on Horiba Fluorolog-4 spectrophotometer. The lifetimes of complexes were measured on Horiba Fluorolog-4 spectrophotometer. Thermal gravity analysis (TGA) were measured on TA Discovery TGA. Differential scanning calorimetry (DSC) were performed on TA Discovery DSC. Polarized optical microscopy (POM) were measured on Zeiss AxioCam MRc5 with a hot stage (Mettler FP80HT) and controller (LinkamScientific, T95-STD). X-ray diffraction (XRD) were measured on Rigaku SmartLab (Cu Kα).

2 General procedure for the synthesis of compounds and complexes

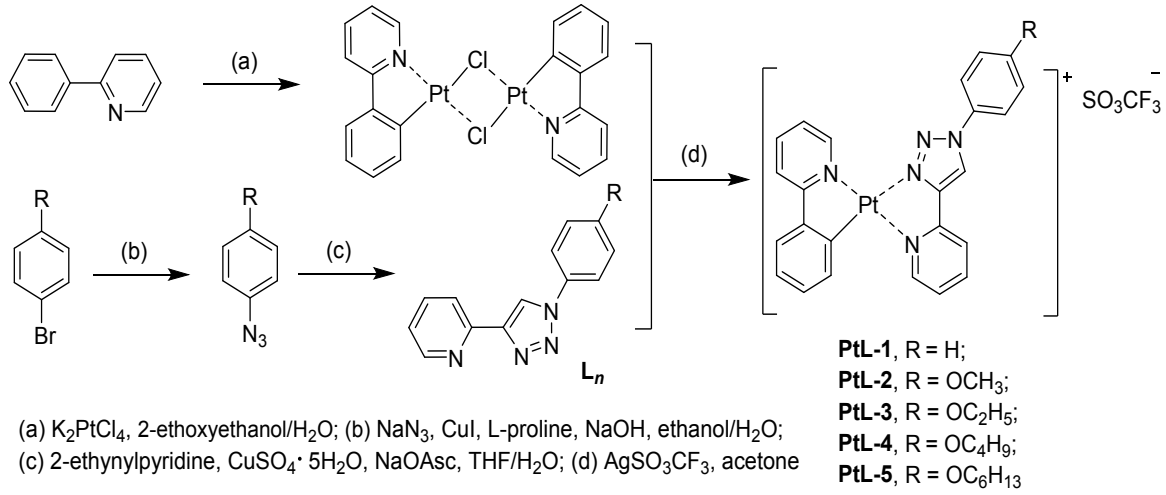
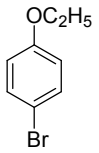


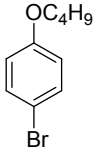
Figure S1.The synthesis routine of the complexes.

2.1. The synthesis of compounds



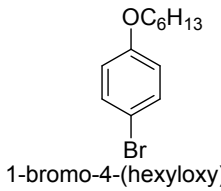
1-bromo-4-ethoxybenzene

1-bromo-4-ethoxybenzene(L_3-1): To a mixture of compound 4-bromophenol 5.16 g (0.03 mol), potassium carbonate 2.76 g (0.02 mol), bromoethane 3.78 g (0.035 mol) was added in ethanol 35 mL. The mixture was heated to 75 °C and stirred for 24 h. After cooling to room temperature, the mixture was evaporated to remove the solvent and extracted with dichloromethane and deionized water, the combined organic layer was dried with anhydrous magnesium sulfate overnight and filtered. The filtrate was evaporated to remove the solvent and the residual was purified on a silica column using petroleum ether (PE) as the eluent to give a white oily liquid 5.6 g (0.028 mol), Yield 95 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.43 - 7.30 (m, 2H), 6.83 - 6.69 (m, 2H), 3.97 (m, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H).



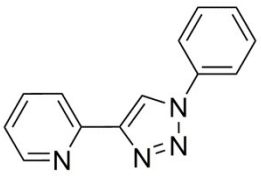
1-bromo-4-butoxybenzene

1-bromo-4-butoxybenzene (L_4-1)：According to L_3-1 method, also obtained white oily liquid 5.2 g (0.023 mol)，Yield 92 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.36 (m, J = 13.0, 11.1 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 3.89 (t, J = 6.5 Hz, 2H), 1.79 – 1.66 (m, 2H), 1.49 (m, J = 11.9, 6.1 Hz, 2H), 0.99 (m, J = 19.2, 12.1 Hz, 3H).



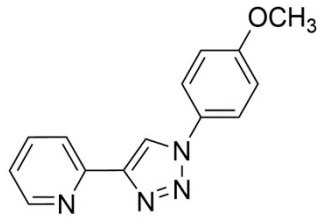
1-bromo-4-(hexyloxy)benzene

1-bromo-4-(hexyloxy)benzene (L_5-1)：According to L_3-1 method, also obtained white oily liquid 5.7 g (0.022mol), Yield 91 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 7.32 (t, J = 11.6 Hz, 2H), 6.73 (t, J = 11.7 Hz, 2H), 3.88 (t, J = 6.6 Hz, 2H), 1.79 - 1.63 (m, 2H), 1.47 - 1.22 (m, 6H), 0.90 (s, 3H).



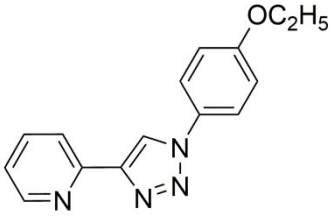
2-(1-phenyl-1*H*-1,2,3-triazol-4-yl)pyridine

2-(1-phenyl-1H-1,2,3-triazol-4-yl)pyridine (L_1)：A mixture of bromobenzene 6.28 g (0.04 mol), sodium azide 3.38 g (0.052 mol), copper (I) iodide 0.76 g (0.004 mol), L-Proline 1.38 g (0.012 mol), sodium hydroxide 0.48 g (0.012 mol), ethanol and deionized water (V : V = 10 : 3) was heated to 90 ^{o}C and stirred for 24 h under nitrogen atmosphere. After cooling to room temperature, the mixture was evaporated to remove the solvent and extracted with dichloromethane and deionized water, the combined organic layer was evaporated to remove the solvent and the residual was promptly purified on a neutral aluminium oxide column using PE as the eluent to give a yellow oily liquid 2.98 g (0.025 mol), Yield 62 %. The obtained compound was directly used in further reaction. To a mixture of azidobenzene 1.7 g (0.013 mol), 2-ethynylpyridine 1.5 g (0.014 mol), chalcanthite 0.5 g (0.02 mol), sodium ascorbate 0.77 g (0.039 mol), was added in tetrahydrofuran and deionized water (V: V = 7: 3). The mixure was stirred 24 h at room temperature under nitrogen atmosphere. The solvent was evaporated to remove and extracted with dichloromethane and deionized water, the combined organic layer was dried with anhydrous magnesium sulfate overnight and filtered. The filtrate was evaporated to remove the solvent and the residual was purified on a silica column using petroleum ether (PE) and ethyl acetate (EtOAc) (V : V = 2: 1) as the eluent to give a yellow solid 0.5 g (2.2 mmol), Yield 17 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 8.61 (d, J = 4.4 Hz, 1H), 8.53 (s, 1H), 8.25 (d, J = 7.9 Hz, 1H), 7.81 (td, J = 7.8, 1.6 Hz, 1H), 7.73 - 7.67 (m, 2H), 7.29 - 7.22 (m, 1H), 7.07 - 7.01 (m, 2H), 3.86 (d, J = 7.2 Hz, 3H).



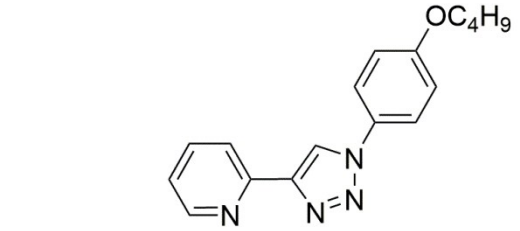
2-(1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)pyridine

2-(1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl) pyridine (L_2): According to L_1 method, obtained pale yellow solid 0.35 g (1.3 mmol), Yield 21 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 8.61 (d, J = 4.4 Hz, 1H), 8.53 (s, 1H), 8.25 (d, J = 7.9 Hz, 1H), 7.81 (td, J = 7.8, 1.6 Hz, 1H), 7.73 - 7.67 (m, 2H), 7.29 - 7.22 (m, 1H), 7.07 - 7.01 (m, 2H), 3.86 (d, J = 7.2 Hz, 3H).



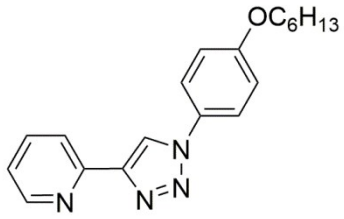
2-(1-(4-ethoxyphenyl)-1*H*-1,2,3-triazol-4-yl)pyridine

2-(1-(4-ethoxyphenyl)-1H-1,2,3-triazol-4-yl) pyridine (L_3): According to L_1 method, obtained pale yellow solid 0.35 g (1.3 mmol), Yield 21 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 8.61 (d, J = 4.6 Hz, 1H), 8.53 (s, 1H), 8.26 (d, J = 7.9 Hz, 1H), 7.87 - 7.77 (m, 1H), 7.74 - 7.65 (m, 2H), 7.30 - 7.23 (m, 1H), 7.04 (m, J = 7.1, 5.1 Hz, 2H), 4.09 (m, J = 7.1 Hz, 2H), 1.46 (t, J = 7.0 Hz, 3H).



2-(1-(4-butoxyphenyl)-1*H*-1,2,3-triazol-4-yl)pyridine

2-(1-(4-butoxyphenyl)-1H-1,2,3-triazol-4-yl) pyridine (L_4): According to L_1 method, obtained pale yellow solid 0.32 g (1.0 mmol), Yield 22 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 8.61 (d, J = 4.3 Hz, 1H), 8.52 (s, 1H), 8.25 (d, J = 7.9 Hz, 1H), 7.86 - 7.76 (m, 1H), 7.75 - 7.64 (m, 2H), 7.30 -7.25 (m, 1H), 7.03 (t, J = 6.1 Hz, 2H), 4.04 - 3.97 (m, 2H), 1.80 (m, J = 15.0, 6.5 Hz, 2H), 1.56 - 1.46 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).



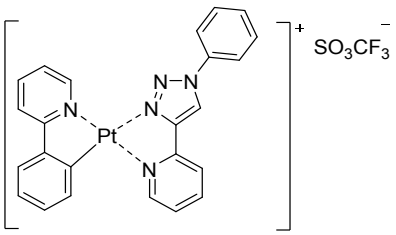
2-(1-(4-(hexyloxy)phenyl)-1*H*-1,2,3-triazol-4-yl)pyridine

2-(1-(4-(hexyloxy)phenyl)-1H-1,2,3-triazol-4-yl) pyridine (L_5): According to L_1 method, obtained pale yellow solid 0.46 g (1.4 mmol), Yield 26 %. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 8.61 (d, J = 4.5 Hz, 1H), 8.53 (s, 1H), 8.25 (d, J = 7.9 Hz, 1H), 7.86 - 7.77 (m, 1H), 7.69 (d, J = 9.0 Hz, 2H), 7.31 - 7.21 (m, 1H), 7.03 (d, J = 9.0 Hz, 2H), 4.04 - 3.94 (m, 2H), 1.87 - 1.75 (m, 2H), 1.54 - 1.27 (m, 6H), 0.91 (t, J = 6.9 Hz, 3H).

2.2. The synthesis of μ-chloro-bridged dimmer Platinum(II)

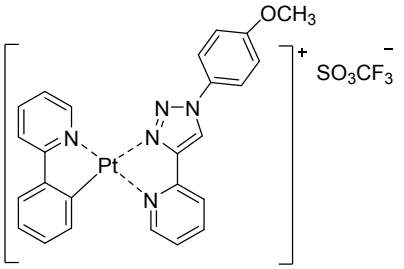
A mixture of 2-phenylpyridine 0.155 g (1 mmol), potassium tetrachloroplatinate(II) 0.242 g (0.58 mmol), was added in 2-ethoxyethanol and deionized water (*V: V* = 3: 1). The mixture was heated to 120 °C and stirred for 24 h under nitrogen atmosphere. The solvent was removed by reduced pressure distillation. After cooling to room temperature, immediately added anhydrous ethanol and filtered, obtained yellow solid 0.52 g (0.68 mmol), Yield 68 %. The μ-chloro-bridged dimmer platinum(II) was directly used in following process.

2.3. The synthesis of complexes

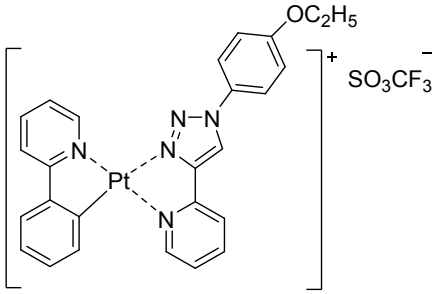


PtL-1: The μ-chloro-bridged dimmer platinum (II) 0.156 g (0.2 mmol), L_1 0.11 g (0.42 mmol) and silver trifluoromethanesulfonate 0.035 g (0.13 mmol) were dissolved in dry acetone (35 ml) under nitrogen atmosphere. The mixture was refluxed and stirred for 12 h, the bright yellow suspension was diluted with DCM, and filtered to remove the silver chloride precipitate. The filtrate was washed extensively with toluene and DCM. The resulted bright yellow solid was further washed with hot DCM, Pt-L1 was isolated as bright yellow solid 0.086 g (0.12 mmol), Yield 85 %. ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ: 9.91 (s, 1H), 9.86 (s, 1H), 9.45 (d, J = 5.8 Hz, 1H), 9.10 (d, J = 6.0 Hz, 1H), 8.89 (d, J = 5.7 Hz, 1H), 8.69 (d, J = 5.9 Hz, 1H), 8.44 - 8.34 (m, 2H), 8.21 (d, J = 6.3 Hz, 1H), 8.12 (m, J = 18.1, 10.3 Hz, 3H), 8.07 - 7.94 (m, 8H), 7.82 - 7.69 (m, 7H), 7.69 - 7.57 (m, 2H), 7.45 - 7.36 (m, 2H), 7.21 (s, 1H), 7.14 (m, J = 11.6, 7.8 Hz, 3H), 7.06 (m, J = 12.8, 7.2 Hz, 1H).^{13} C NMR(100 MHz, DMSO-d_6, TMS) δ: 166.05, 152.09, 151.02, 149.65, 148.88, 148.46, 146.24, 141.59, 140.98, 139.63, 137.78, 136.98, 135.88, 133.88, 132.66, 130.78, 130.34, 129.88, 129.27, 127.19, 126.97, 125.50, 125.34,

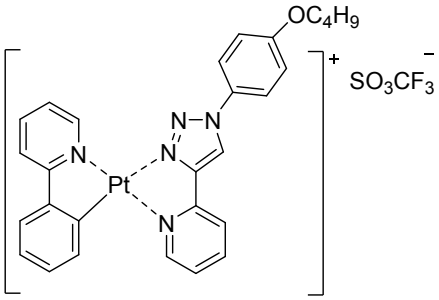
124.69, 124.39, 124.08, 123.22, 122.94, 122.41, 121.67, 120.91, 120.73, 120.58, 120.02. HRMS (ESI): 571.1215 [calcd for $(M\text{-}CF_3SO_3)^+$: 571.1210]. ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.78.



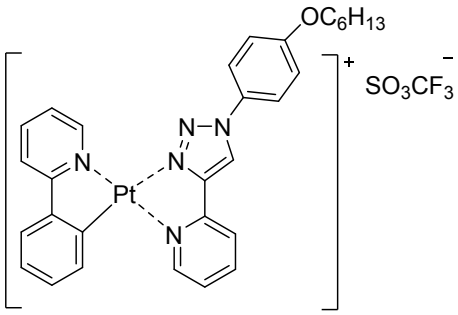
PtL-2: According to PtL-1 method, obtanied yellow solid 0.16 g (0.21 mmol), Yield 87 %. ^1H NMR (400 MHz, DMSO-d_6, TMS) δ: 9.25 (s, 1H), 9.20 (s, 1H), 8.75 (d, J = 5.5 Hz, 1H), 8.47 (d, J = 5.3 Hz, 1H), 8.23 (d, J = 5.2 Hz, 1H), 7.98 (m, J = 14.4, 7.7 Hz, 3H), 7.84 (d, J = 8.5 Hz, 1H), 7.68 m, J = 14.8, 7.2 Hz, 1H), 7.61 - 7.44 (m, 8H), 7.41 (d, J = 8.0 Hz, 1H), 7.29 (m, J = 12.8, 6.4 Hz, 2H), 7.18 - 7.04 (m, 6H), 7.00 (dd, J = 13.3, 7.0 Hz, 1H), 6.90 (t, J = 6.4 Hz, 1H), 6.80 (t, J = 7.2 Hz, 1H), 6.72 (m, J = 9.5, 4.2 Hz, 2H), 6.61 (d, J = 7.4 Hz, 1H), 6.55 (t, J = 7.3 Hz, 1H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6,TMS) δ: 166.00, 165.64, 160.87, 160.83, 151.41, 150.52, 150.05, 149.61, 149.04, 148.53, 147.90, 146.76, 145.80, 144.17, 141.13, 140.83, 140.72, 140.47, 139.47, 136.64, 133.43, 132.09, 129.50, 129.23, 128.80, 126.66, 126.54, 125.14, 124.81, 124.35, 123.60, 123.25, 122.56, 121.94, 121.70, 119.88, 119.60, 115.65, 115.53, 56.23. HRMS (ESI): 601.1312 [calcd for $(M\text{-}CF_3SO_3)^+$: 601.1316]. ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.78.



PtL-3: According to PtL-1 method, obtained orange solid 0.084 g (0.11 mmol), Yield 66.8 %. ^1H NMR (400 MHz, DMSO-d_6,TMS) δ: 9.56 (d, J = 14.9 Hz, 1H), 9.43 (d, J = 5.8 Hz, 1H), 9.20 – 9.12 (m, 1H), 8.86 (d, J = 5.5 Hz, 1H), 8.62 (d, J = 4.7 Hz, 1H), 8.24(m, 1H), 8.17 (d, J = 2.1 Hz, 1H), 8.12 – 8.04 (m, 4H), 7.98 – 7.84 (m, 4H), 7.83 – 7.76 (m, 2H), 7.75 – 7.70 (m, 2H), 7.57 (d, J = 7.0 Hz, 1H), 7.52 – 7.41 (m, 3H), 7.40 – 7.34 (m, 1H), 7.29 - 7.17 (m, 3H), 7.17 - 6.95 (m, 7H), 4.17 (m, J = 6.9 Hz, 2H), 4.07 (m, J = 6.9 Hz, 2H), 1.42 (t, 3H), 1.33 (t, 3H).^{13}C NMR(100 MHz, DMSO-d_6,TMS) δ: 165.44, 160.28, 159.06, 150.05, 149.66, 148.99, 144.90, 141.95, 140.66, 137.73, 133.89, 130.45, 130.23, 128.97, 125.34, 124.71, 124.01, 123.68, 123.22, 122.52, 122.35, 122.18, 121.55, 120.15, 119.93, 116.12, 116.00, 115.68, 64.31, 63.98, 15.02. HRMS (ESI): 615.1465 [calcd for $(M\text{-}CF_3SO_3)^+$: 615.1472]. ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.76.



PtL-4: According to PtL-1 method, obtained red solid 0.076 g (0.09 mmol), Yield 75 %. ^1H NMR (400 MHz, DMSO-d_6, TMS) δ: 9.56 (d, J = 14.9 Hz, 1H), 9.43 (d, J = 5.8 Hz, 2H), 9.32 (d, J = 2.1 Hz, 1H) 9.19 (s, 1H),9.07 (d, J = 1.3 Hz, 1H), 8.62 (d, J = 4.7 Hz, 1H), 8.33 (m, 1H), 8.18 (d, J = 1.1 Hz, 2H) 8.10 (s, 6H), 7.94 – 7.86 (m, 5H),7.75 (d, J = 2.1 Hz, 2H)7.47 (s, 1H)7.37 (s, 1H), 7.25 (t, J = 3.0 Hz, 1H), 7.14 – 7.09 (m, 8H), 4.10 (t, J = 3.1 Hz, 1H), 4.02 (t, J = 2.2 Hz, 3H), 1.77 – 1.68 (m, 4H), 1.47 - 1.36 (m, 4H), 0.90-0.97 (m, 6H). ^{13}C NMR(100 MHz, DMSO-d_6, TMS) δ: 165.46, 159.24, 150.05, 149.68, 144.92, 141.98, 140.67, 137.73, 133.91, 130.47, 125.36, 124.73, 123.24, 122.80, 122.20, 121.57, 119.94, 116.21, 116.10, 115.74, 68.34, 68.06, 31.09, 19.19, 19.16, 14.19, 14.15. HRMS (ESI): 643.1792 [calcd for $(M\text{-}CF_3SO_3)^+$: 643.1785]. ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.78.



PtL-5: According to PtL-1 method, obtained red solid 0.067 g (0.081 mmol), Yiled 78 %. ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ: 9.79 (d, J = 5.8 Hz, 1H), 9.49 (d, J = 23.0 Hz, 1H), 8.95 (d, J = 4.4 Hz, 1H), 8.52 (d, J = 7.6 Hz, 1H), 8.49 – 8.38 (m, 3H), 8.29 - 8.14 (m, 3H), 8.09 (d, J = 7.3 Hz, 1H), 7.81 (m, J = 8.5, 3.7 Hz, 1H), 7.74 - 7.64 (m, 1H), 7.53 - 7.37 (m, 4H), 4.32 (dt, J = 14.0, 6.7 Hz, 2H), 2.09 - 1.95 (m, 2H), 1.80 - 1.52 (m, 6H), 1.24 - 1.11 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6,TMS) δ: 165.47, 159.25, 150.09, 150.04, 149.70, 148.42, 144.95, 142.04, 140.65, 137.77, 133.93, 132.53, 130.49, 130.23, 125.41, 124.77, 123.71, 123.28, 122.23, 121.59, 120.17, 119.98, 115.75, 68.37, 31.44, 29.00, 25.61, 22.54, 14.40. HRMS (ESI): 672.2101 [calcd for $(M\text{-}CF_3SO_3)^+$: 671.2098]. ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.79.

3 POM of PtL-2

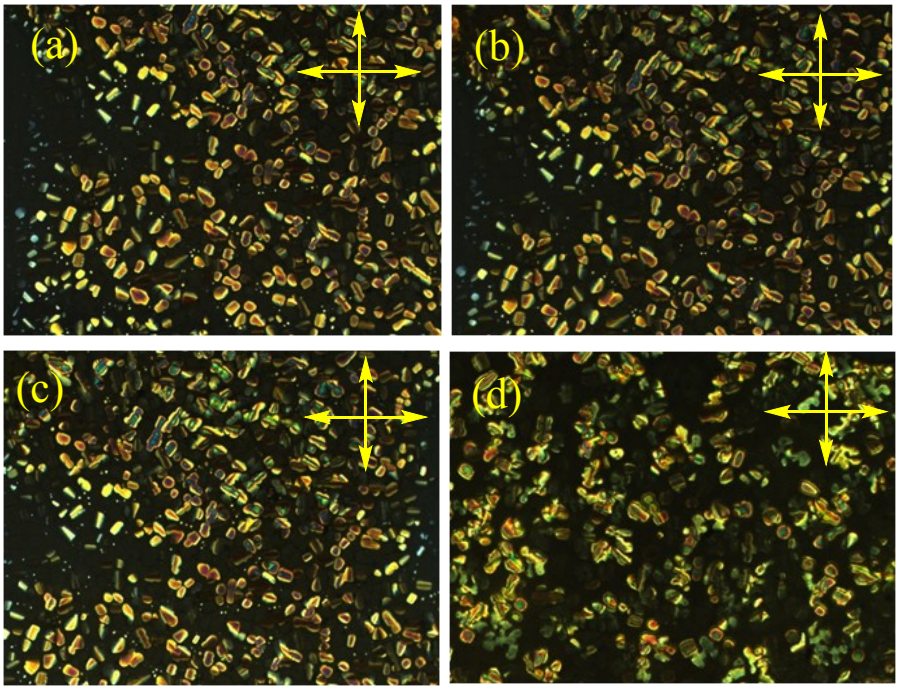


Figure S2. Optical polarizing microscopy images of PtL-2 cooling from the isotropic liquid (crossed polarizers are indicated by the yellow cross in the top right corner) at 25 (a), 87 (b), 110 (c), 236 °C (d)

4 TGA and the holding time TGA

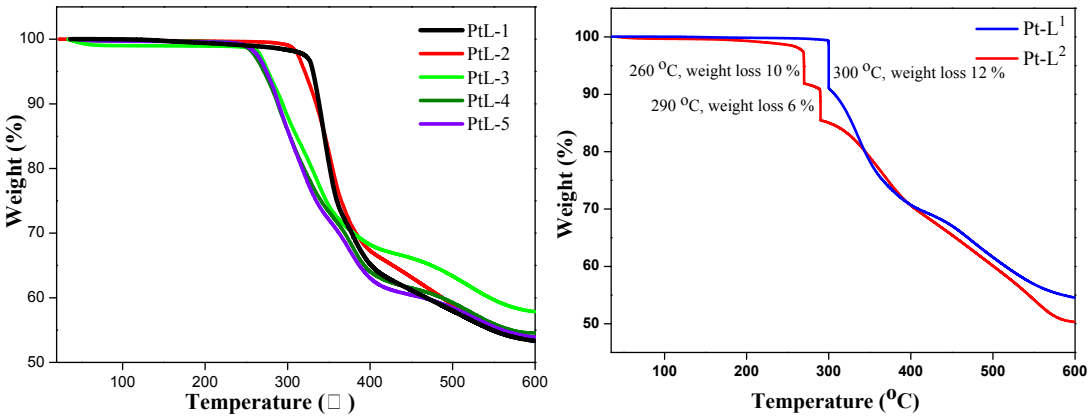


Figure S3. The TGA curves of complexes (left) and the holding time TGA analysis (right).

5 DSC of PtL-1 and Pt-2

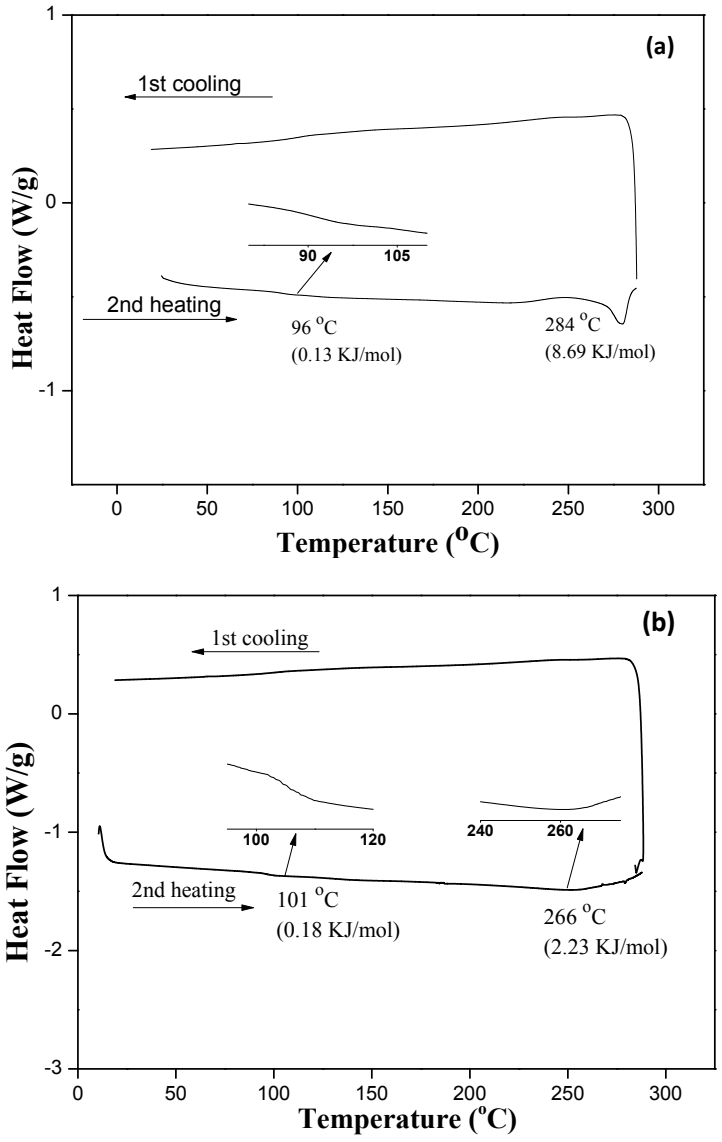


Figure S4. DSC thermograms of PtL-1(a) and PtL-2 (b)

6 PL spectra in solid state

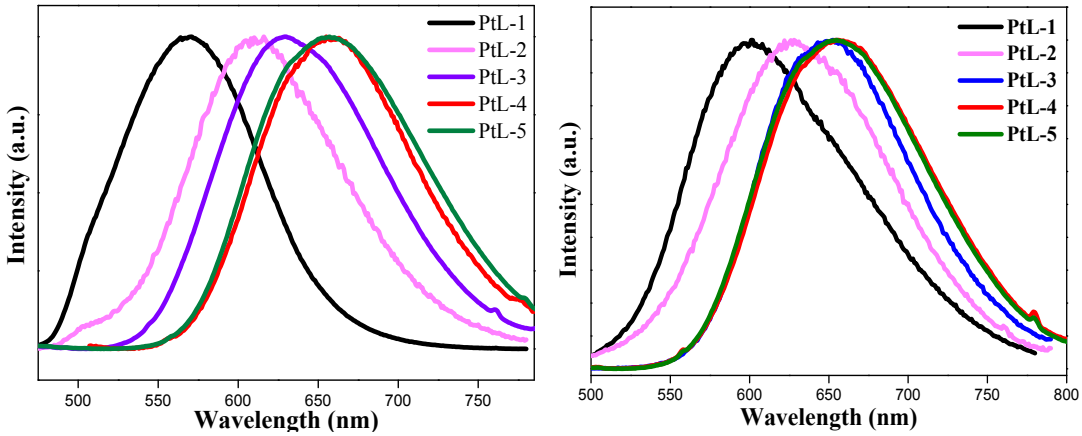


Figure S5. PL emission spectra of complexes in solid (left) and ground (right) state

Table S1. UV/Vis absorption, PL emission spectra and the quantum yields (φ_{em}) of complexes

Complexes	Absorption/nm ($\varepsilon/10^4$ L· mol^{-1} · cm^{-1})[a]	Emission/nm (298 K) [b]	Emission/nm (77 K) [c]	Solid emission /nm (grind)	φ_{em}[d]
PtL-1	290(0.65),382(0.15),402(0.015)	407(sh),432,458(sh), 581	407,432,495,525,565	569(602)	0.19
PtL-2	292(0.9),380(0.19),409(0.05)	409(sh),431,455(sh), 582	407,432,495,525,565	611(628)	0.18
PtL-3	292(0.91),380(0.19),409(0.05)	409(sh),431,455(sh), 582	407,432,496,528,565	630(648)	0.21
PtL-4	292(0.91),380(0.21),409(0.05)	406(sh),431,457(sh), 583	407,432,495,524,562	655(658)	0.23
PtL-5	292(0.9),380(0.19),409(0.05)	406(sh),431,457(sh), 582	407,432,495,524,562	657(658)	0.22

[a,b,c]Measured in MTHF solution 10^{-5} mol · L^{-1},[d] Photoluminescence quantum yields.

7 DFT calculations

Table S2. Energy, oscillator strength and assignment of calculated transition for PtL-1 and PtL-2

	Excited state	Energy / eV (nm)	Oscillator strength	Assignment
PtL-1	1	2.92(425.3)	0.0124	HOMO->LUMO(+92%)
	2	3.07(403.9)	0.0043	HOMO-1->LUMO(+93%) HOMO->LUMO(+5%)
	3	3.44(360.6)	0.0215	HOMO->LUMO+1(+84%)
	4	3.68(337.3)	0.0121	HOMO-3->LUMO(+59%) HOMO-2->LUMO(+28%)
	5	4.04(307.0)	0.0326	HOMO-5->LUMO(+92%)

PtL-2	1	2.97(417.2)	0.0267	HOMO->LUMO(+96%)
	2	3.18(390.1)	0.009	HOMO-2->LUMO(+92%) HOMO-1->LUMO(+6%)
	3	3.44(360.7)	0.0961	HOMO-1->LUMO(+75%) HOMO-4->LUMO(+10%)
	4	3.71(334.4)	0.0029	HOMO-2->LUMO+1(+85%) HOMO-1>LUMO+1(+6%)
	5	4.03(307.8)	0.0077	HOMO->LUMO+2(+81%)

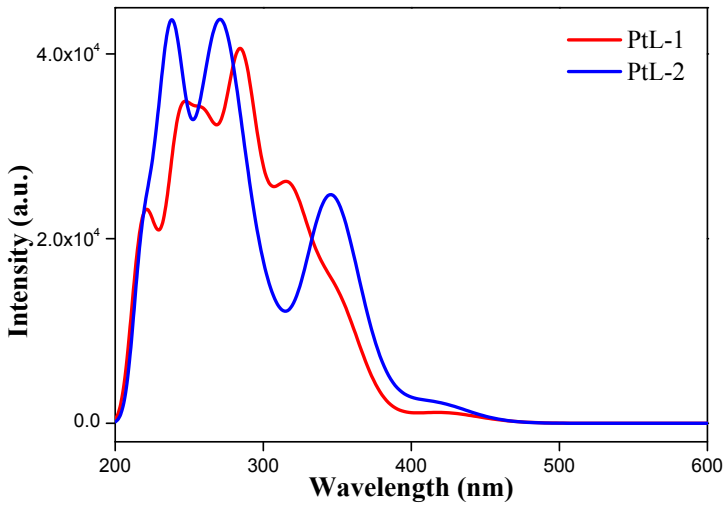
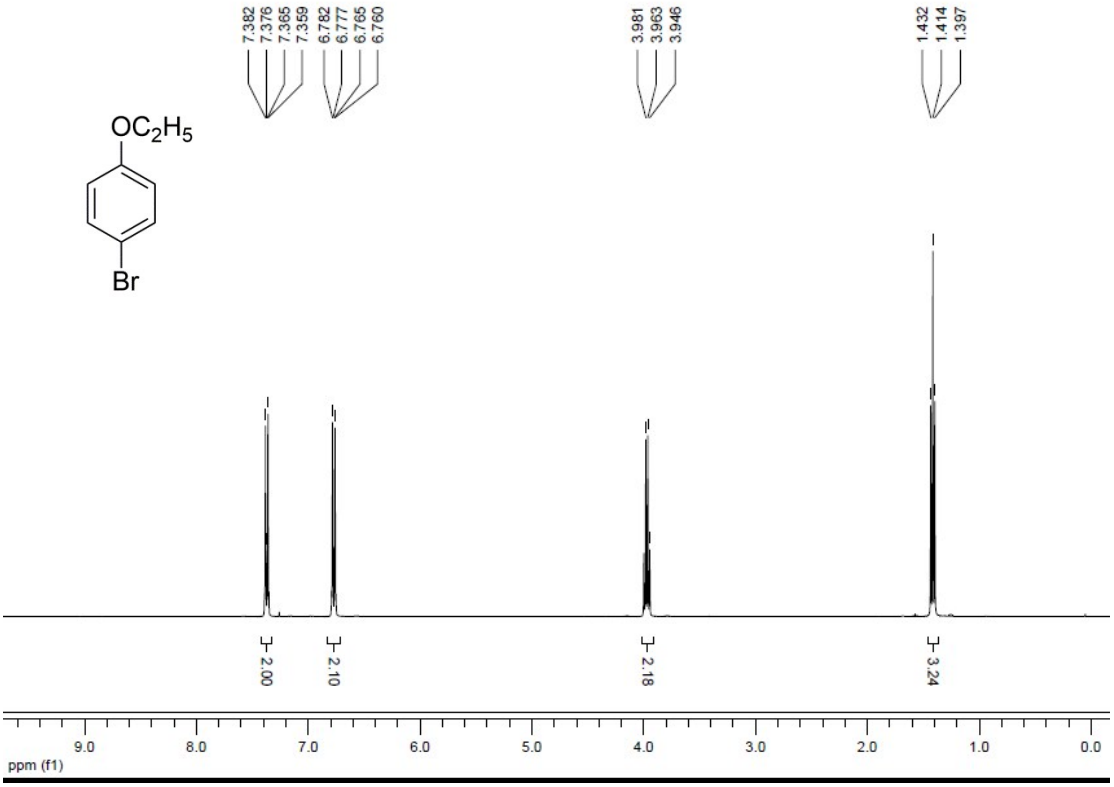


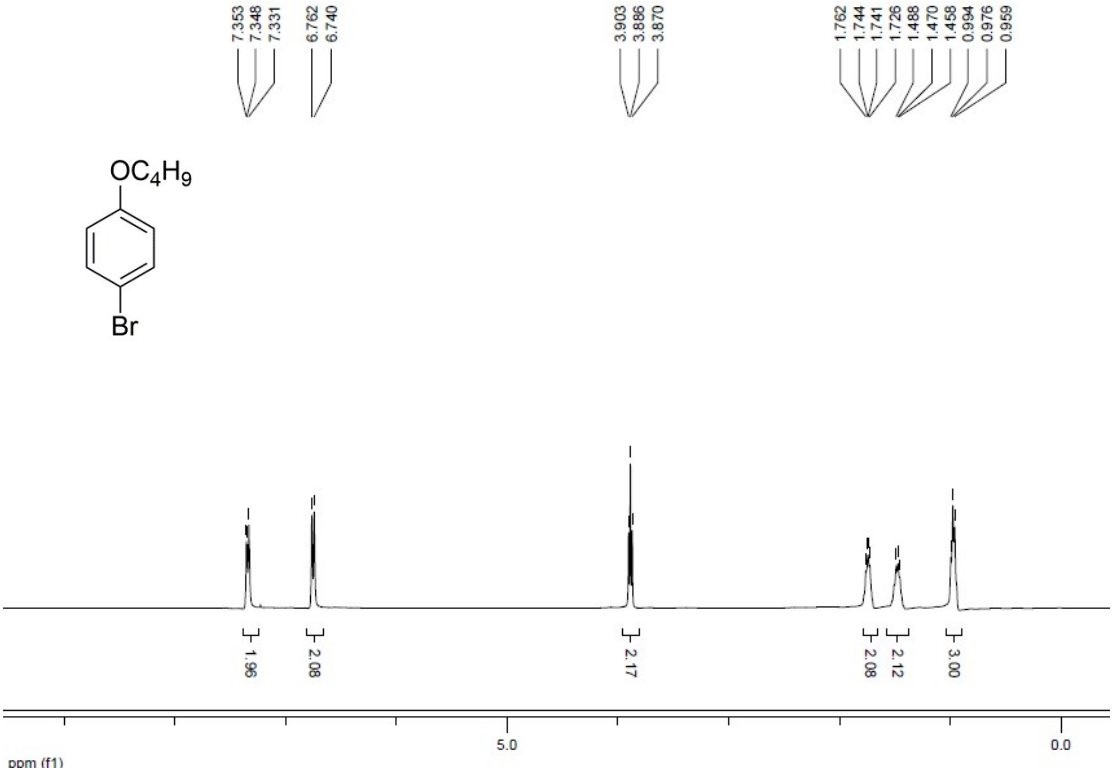
Figure S6. The theory UV-Vis absorption spectra

8 ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS

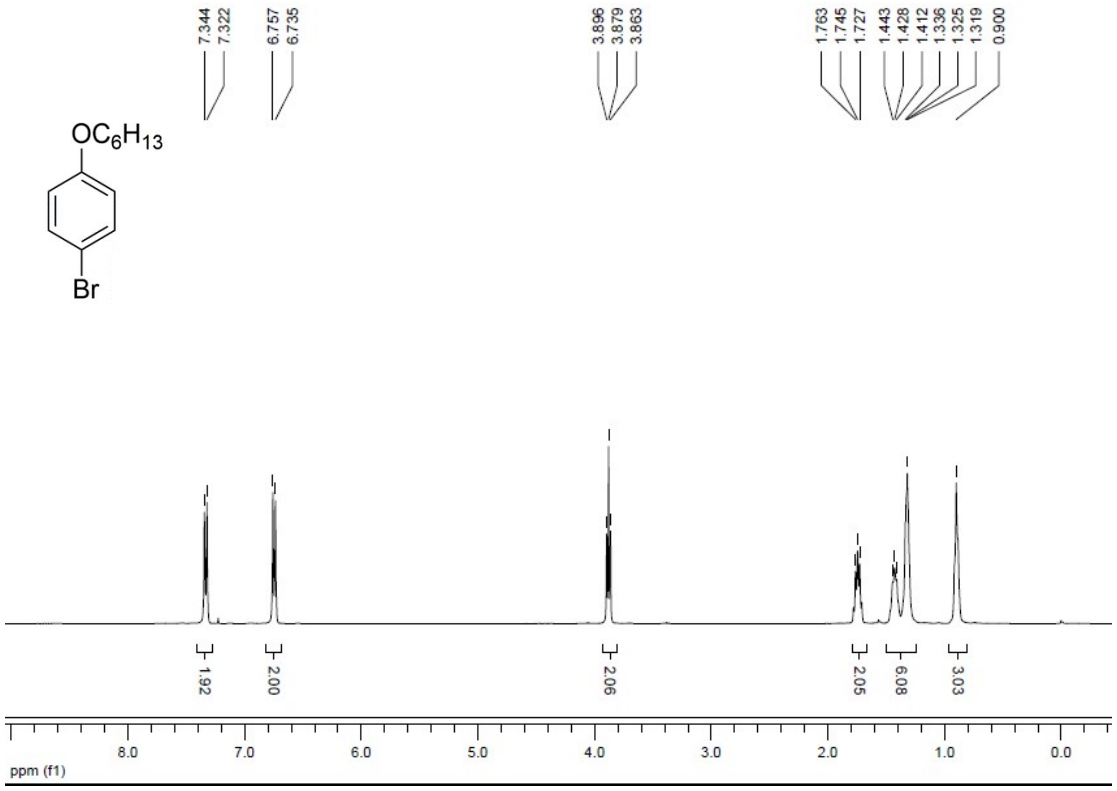
1-bromo-4-ethoxybenzene (L_3-1)



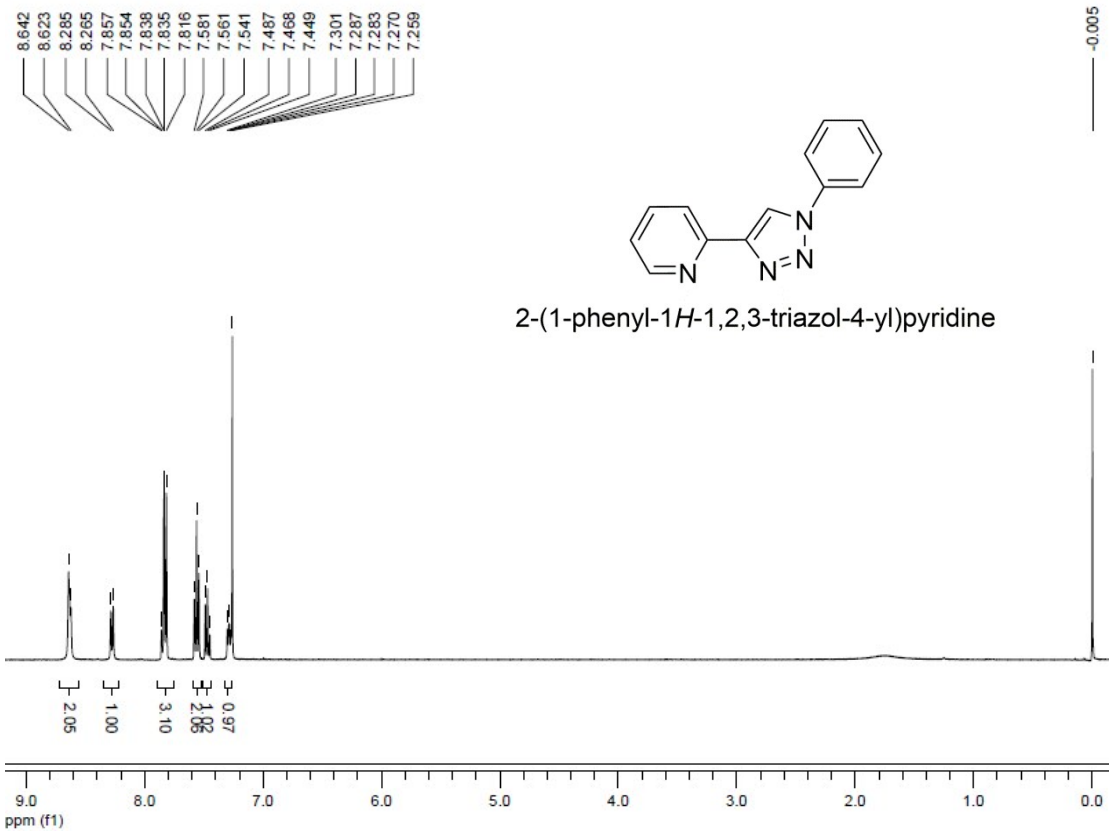
1-bromo-4-butoxybenzene (L_4-1)



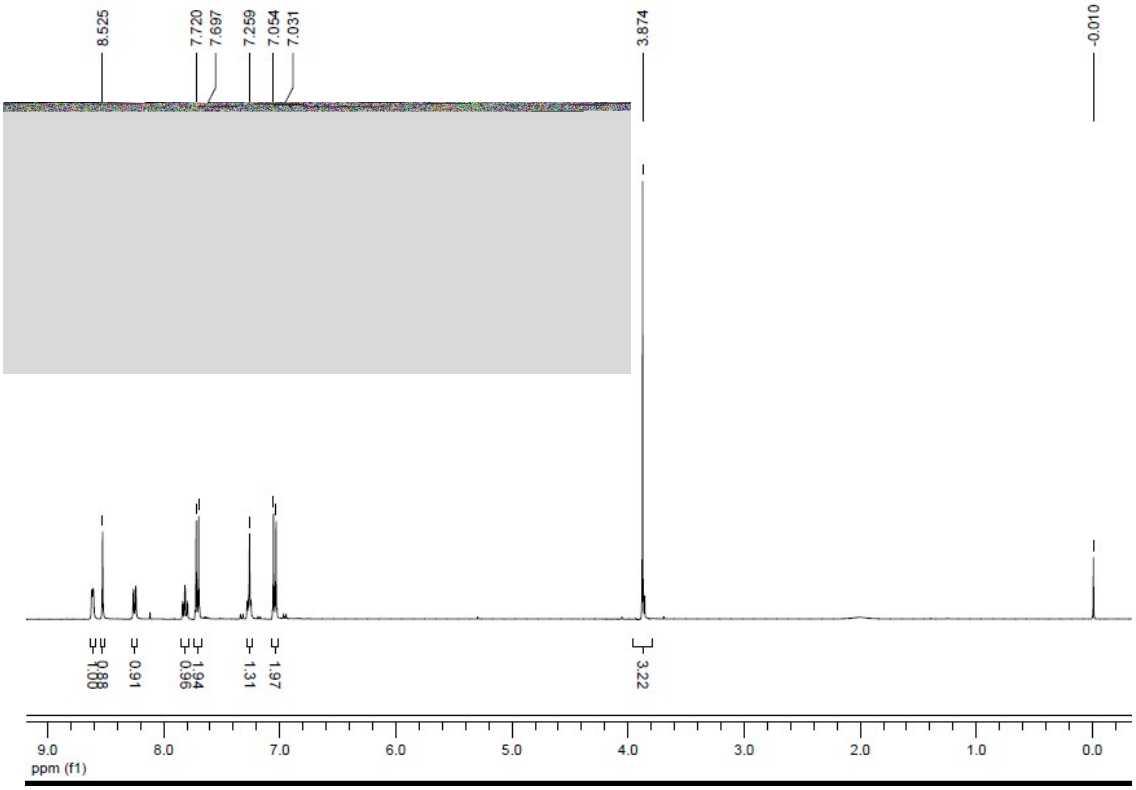
1-bromo-4-(hexyloxy)benzene (L_5-1)



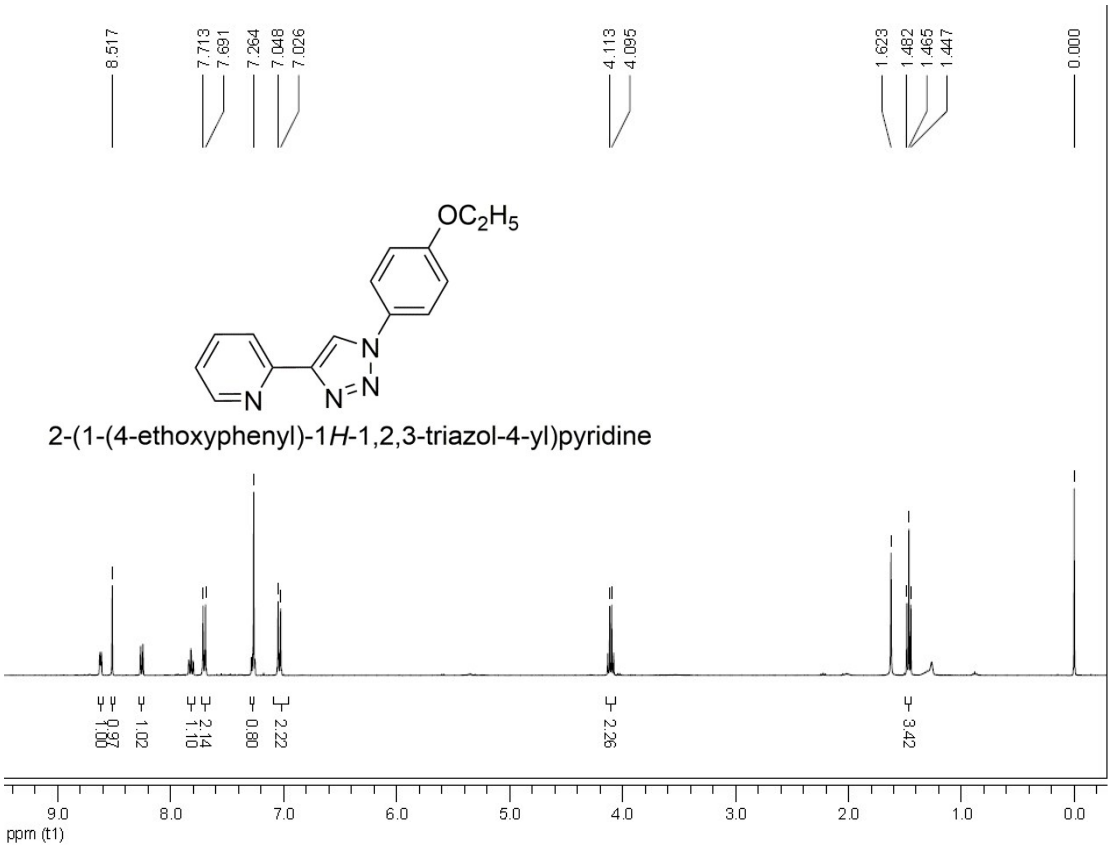
2-(1-phenyl-1H-1,2,3-triazol-4-yl)pyridine (L_1)



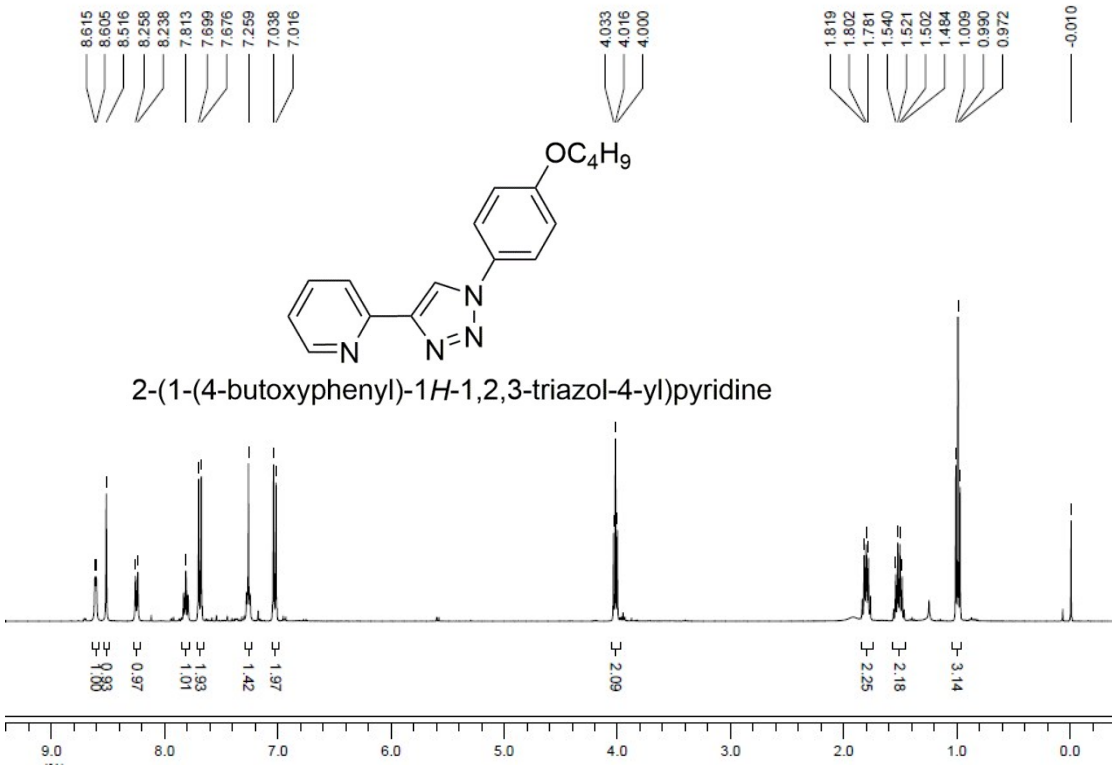
2-(1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl)pyridine (L_2)



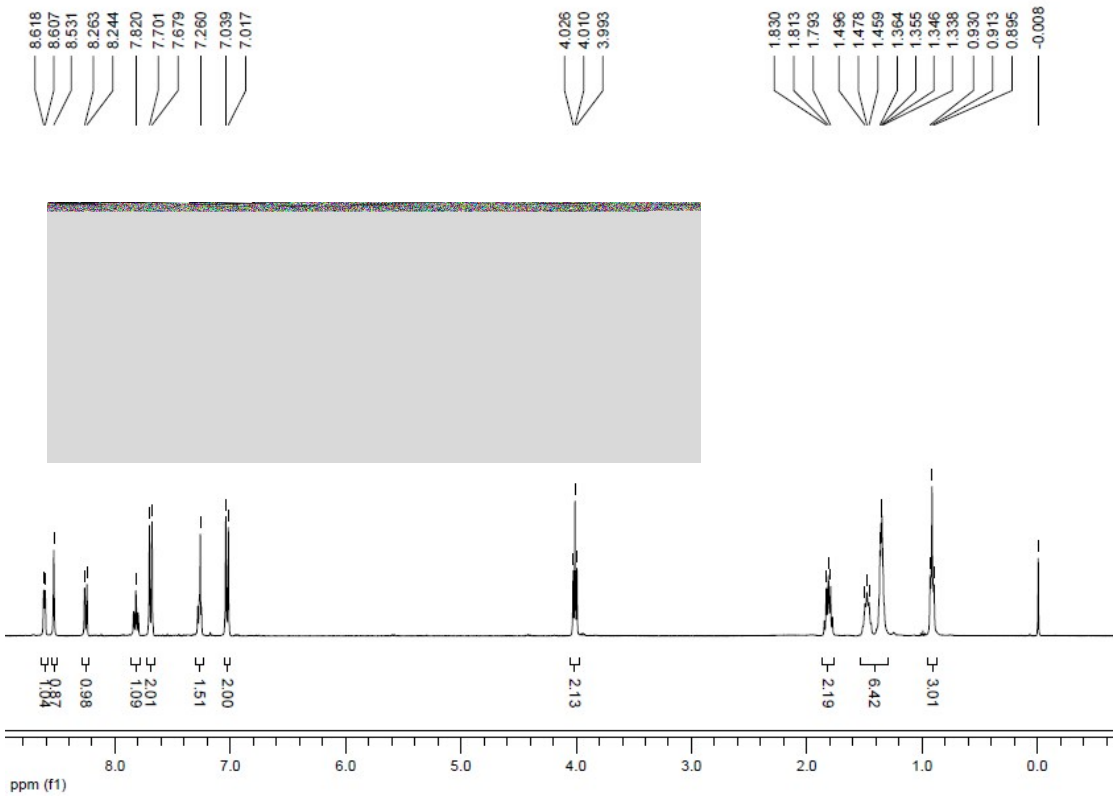
2-(1-(4-ethoxyphenyl)-1H-1,2,3-triazol-4-yl)pyridine (L_3)



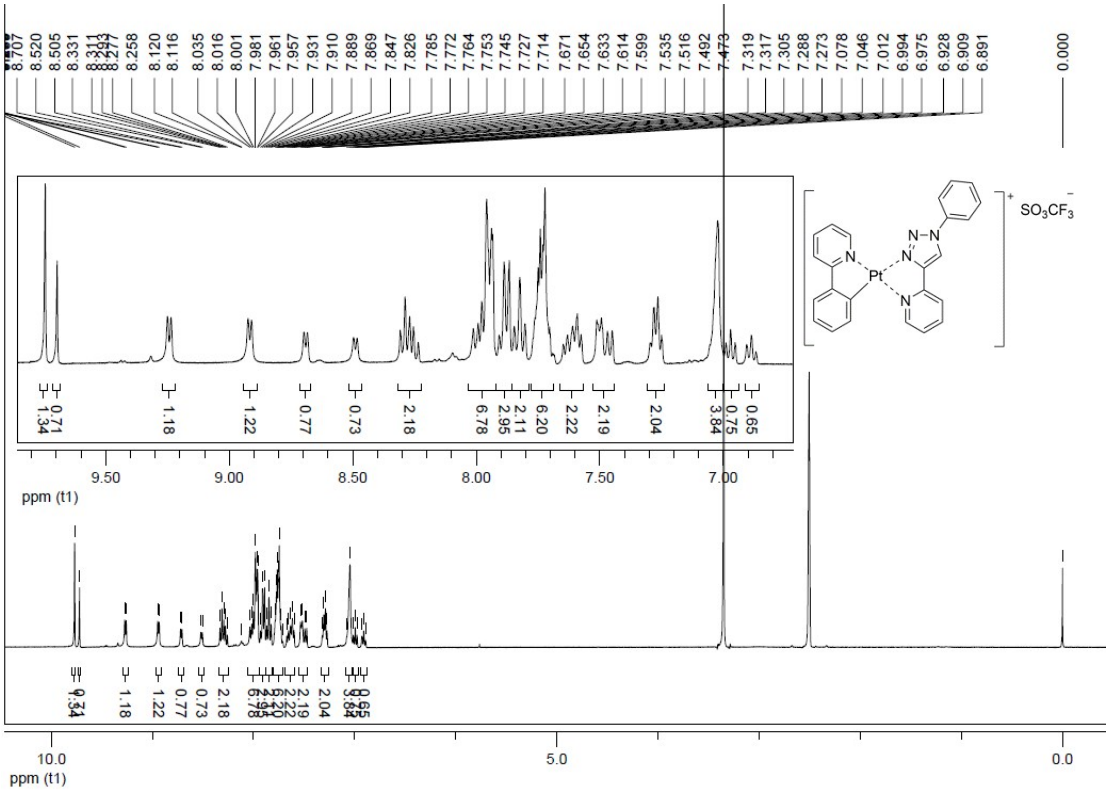
2-(1-(4-butoxyphenyl)-1H-1,2,3-triazol-4-yl)pyridine (L_4)



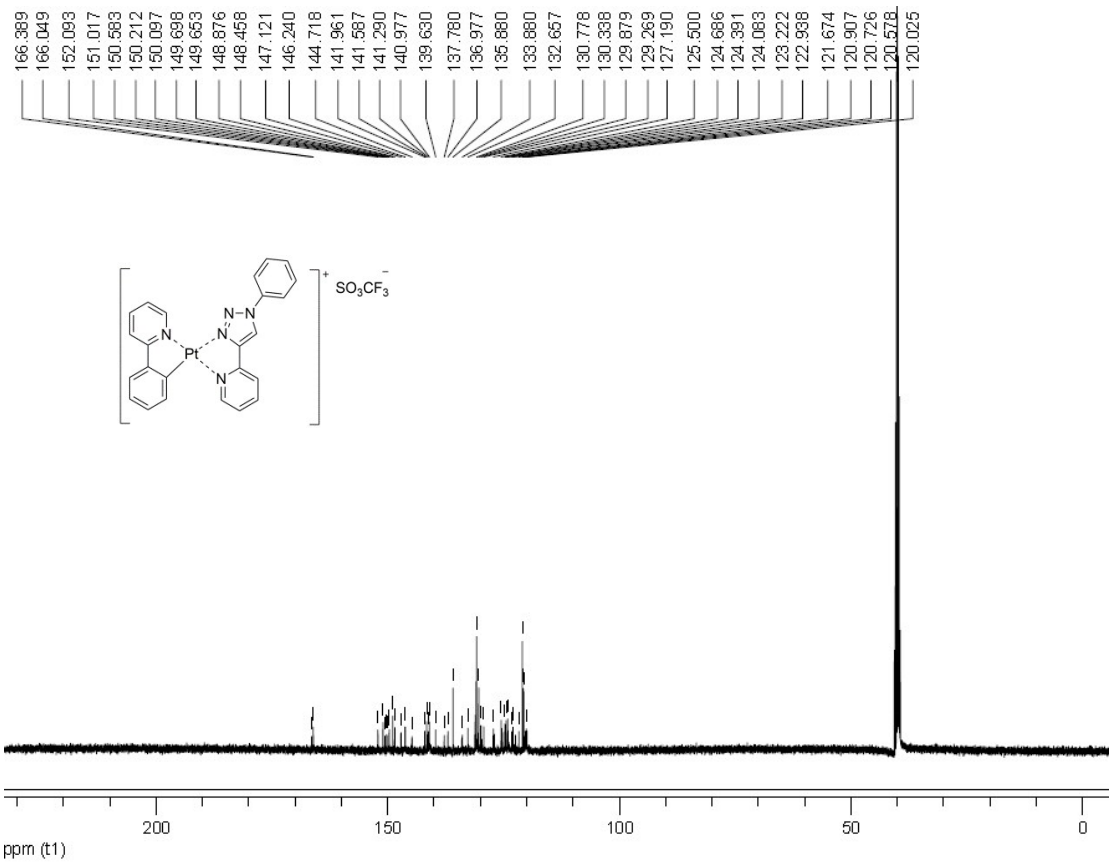
2-(1-(4-(hexyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridine (L_5)



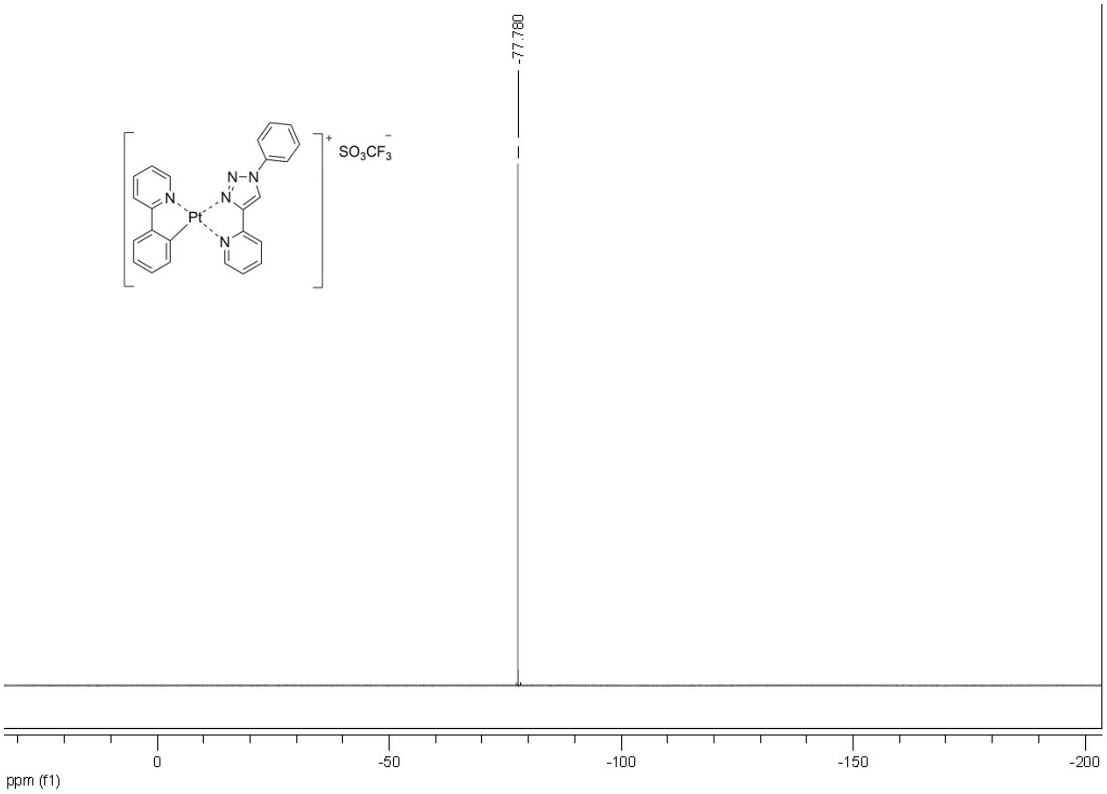
PtL-1: ^{1}H NMR (400 MHz, DMSO-d_6, TMS)



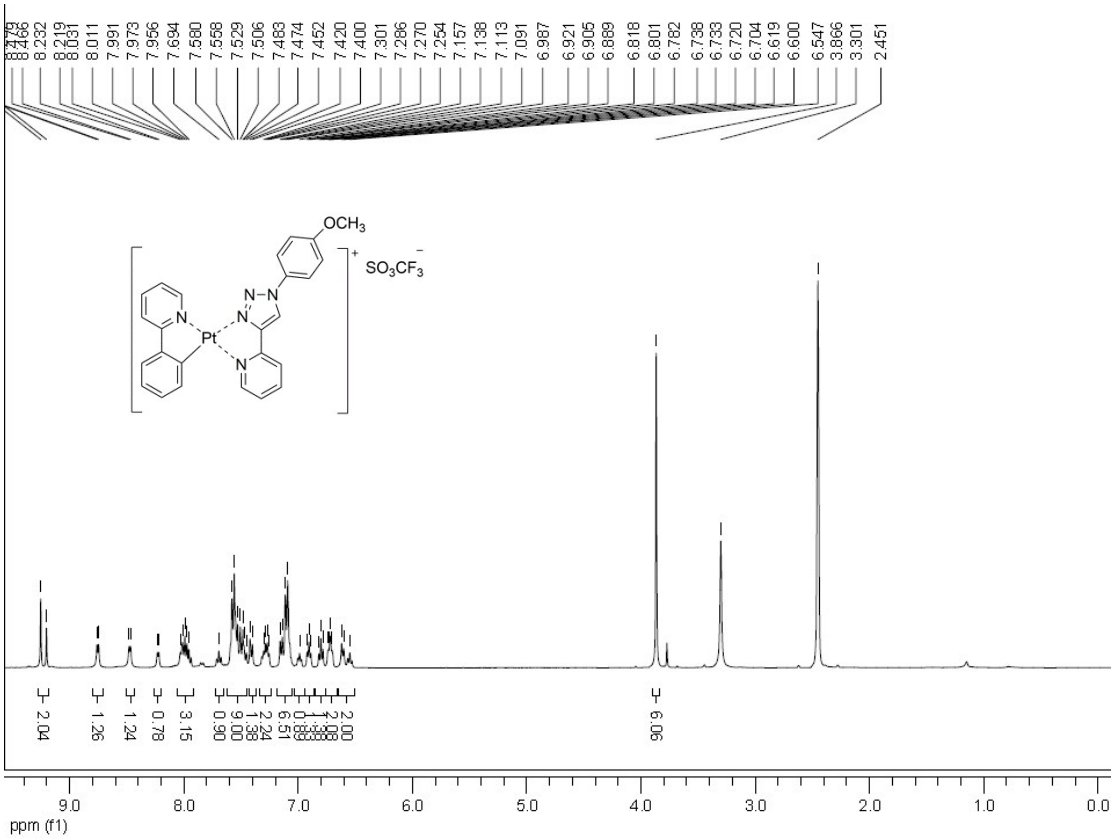
PtL-1: ^{13}C NMR (101 MHz, DMSO-d_6, TMS)



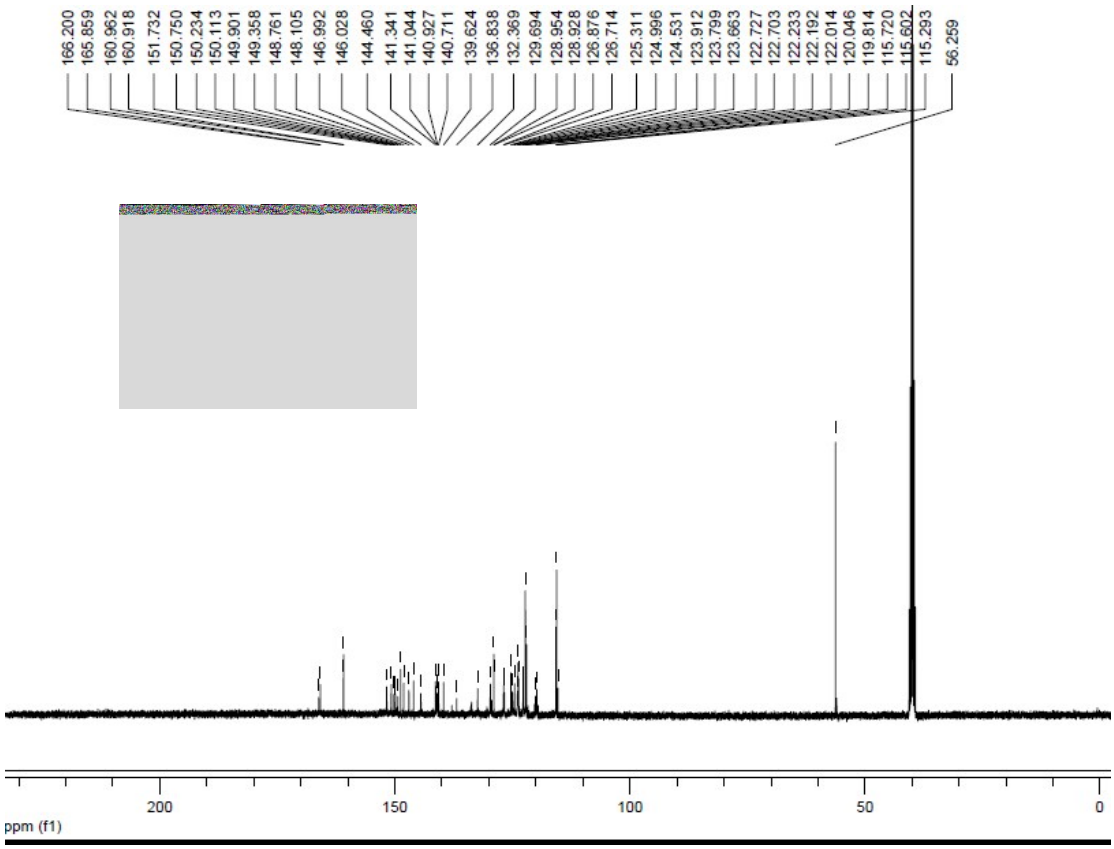
PtL-1: ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.780



PtL-2: ^{1}H NMR (400 MHz, DMSO-d_6, TMS)

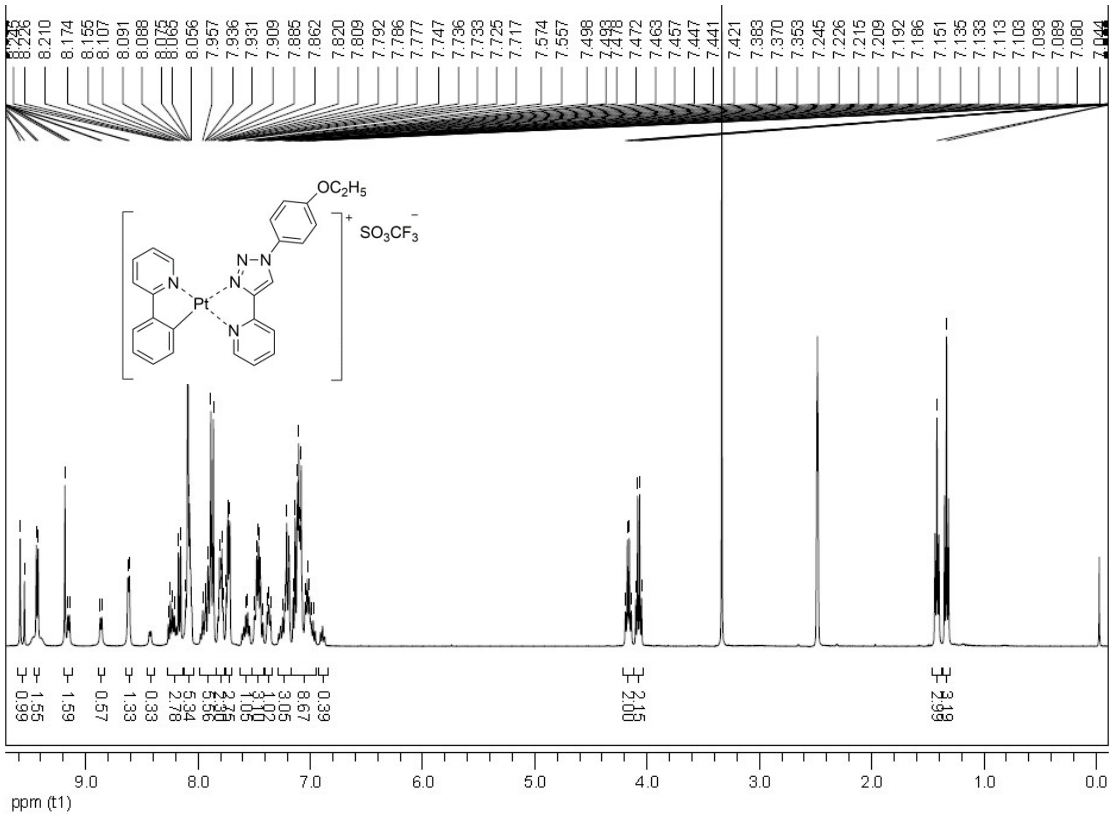


PtL-2: ^{13}C NMR (101 MHz, DMSO-d_6, TMS)

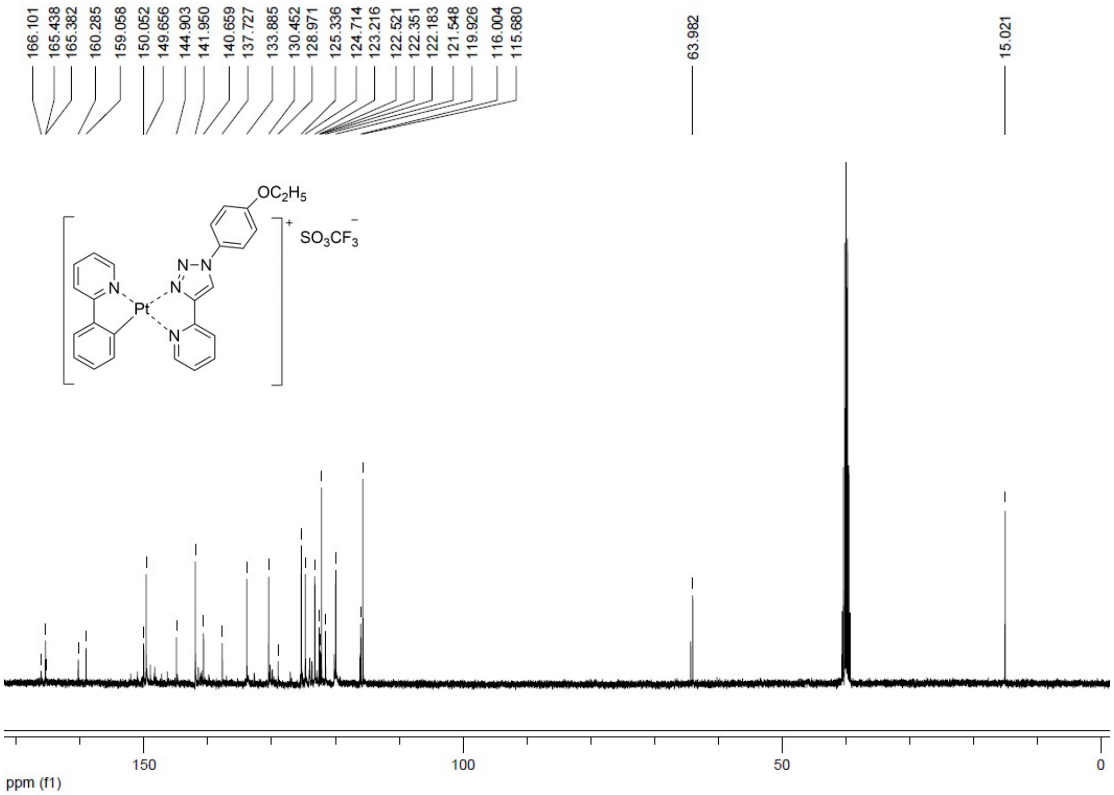


PtL-2: ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.780

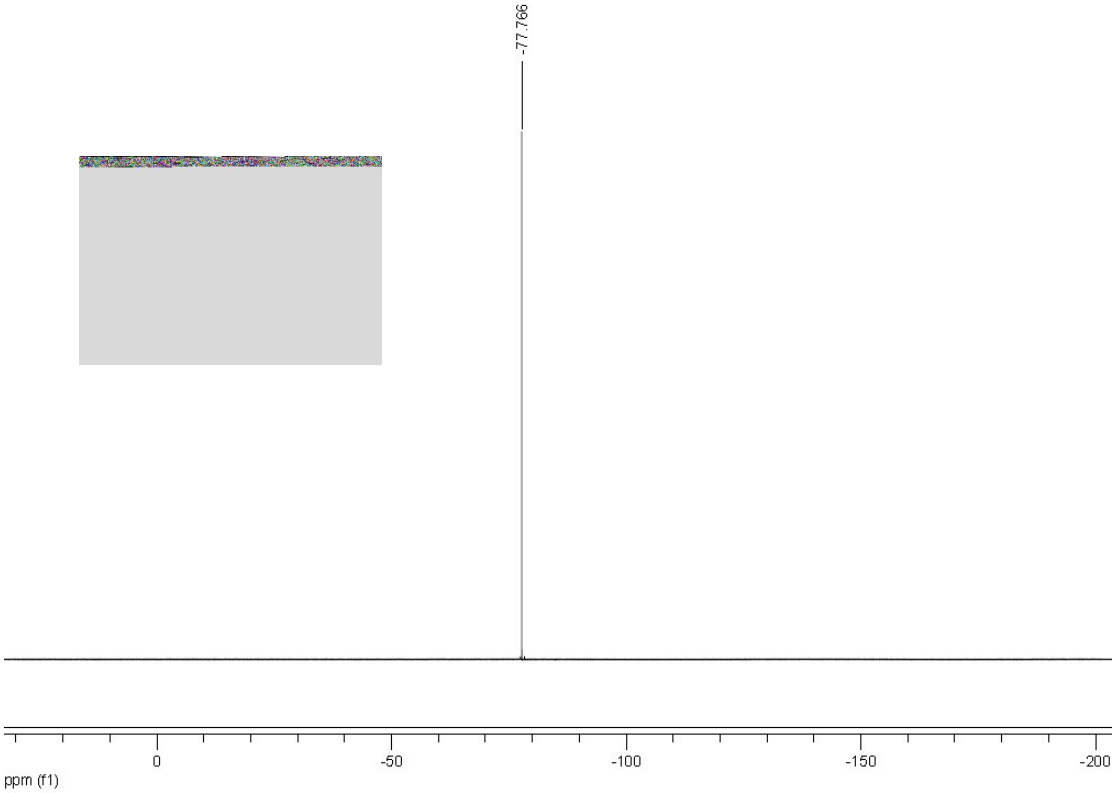
PtL-3: ^{1}H NMR (400 MHz, DMSO-d_6, TMS)



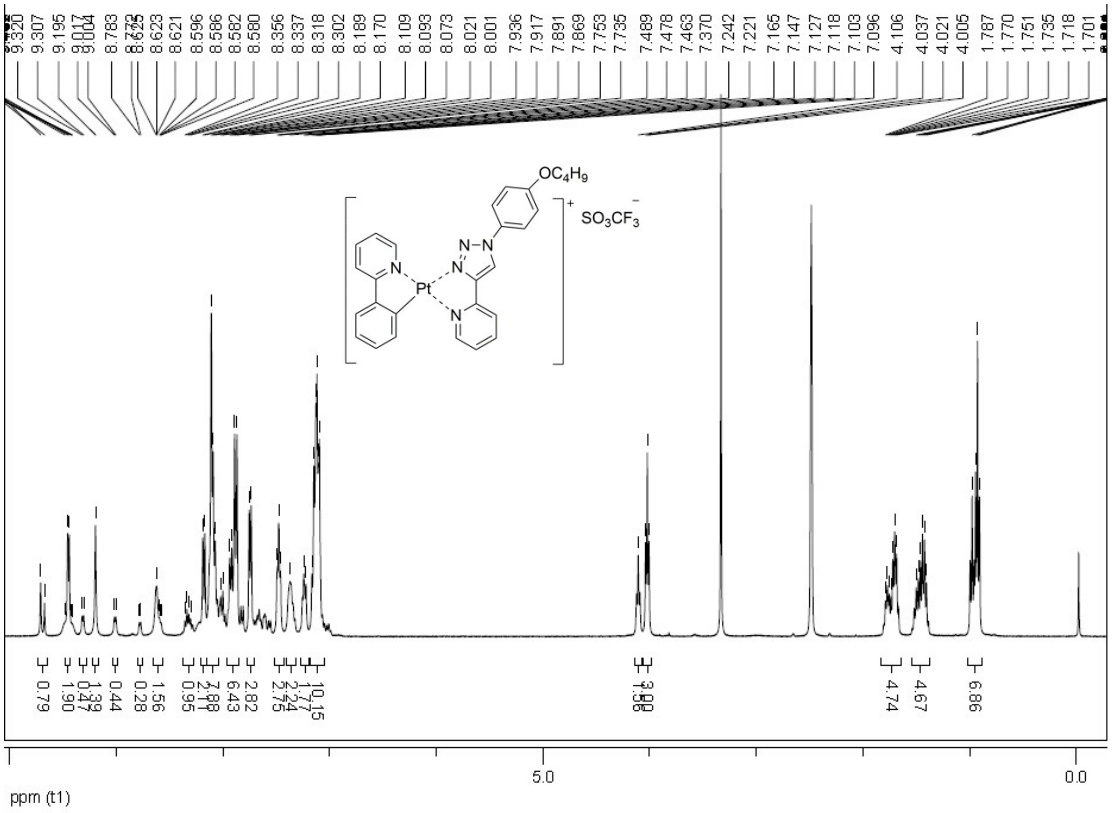
PtL-3: ^{13}C NMR (101 MHz, DMSO-d_6, TMS)



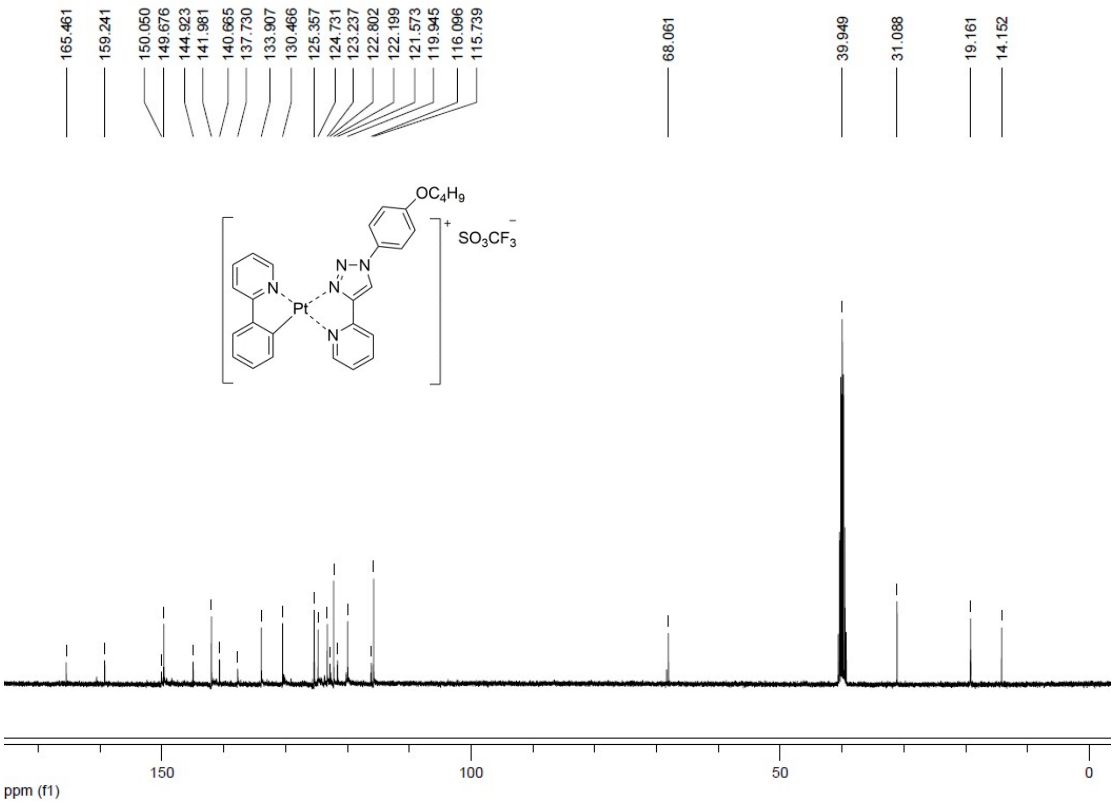
PtL-3: ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.766



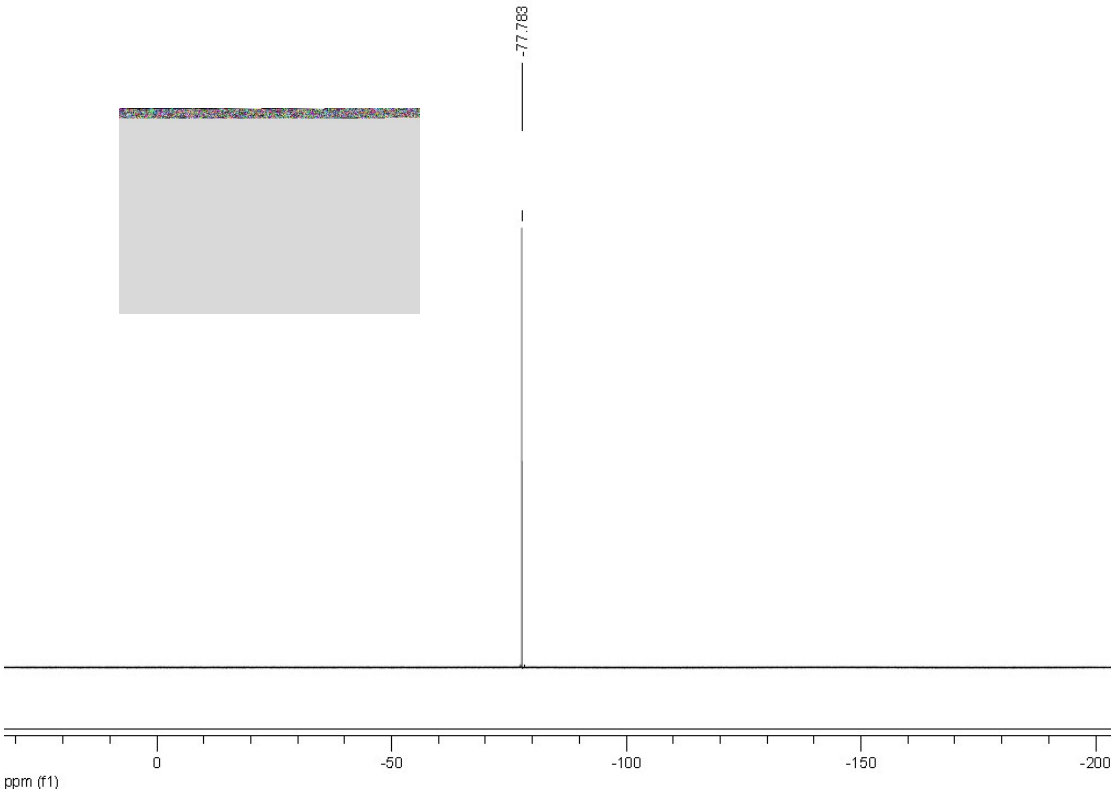
PtL-4: ^{1}H NMR (400 MHz, DMSO-d_6,TMS)



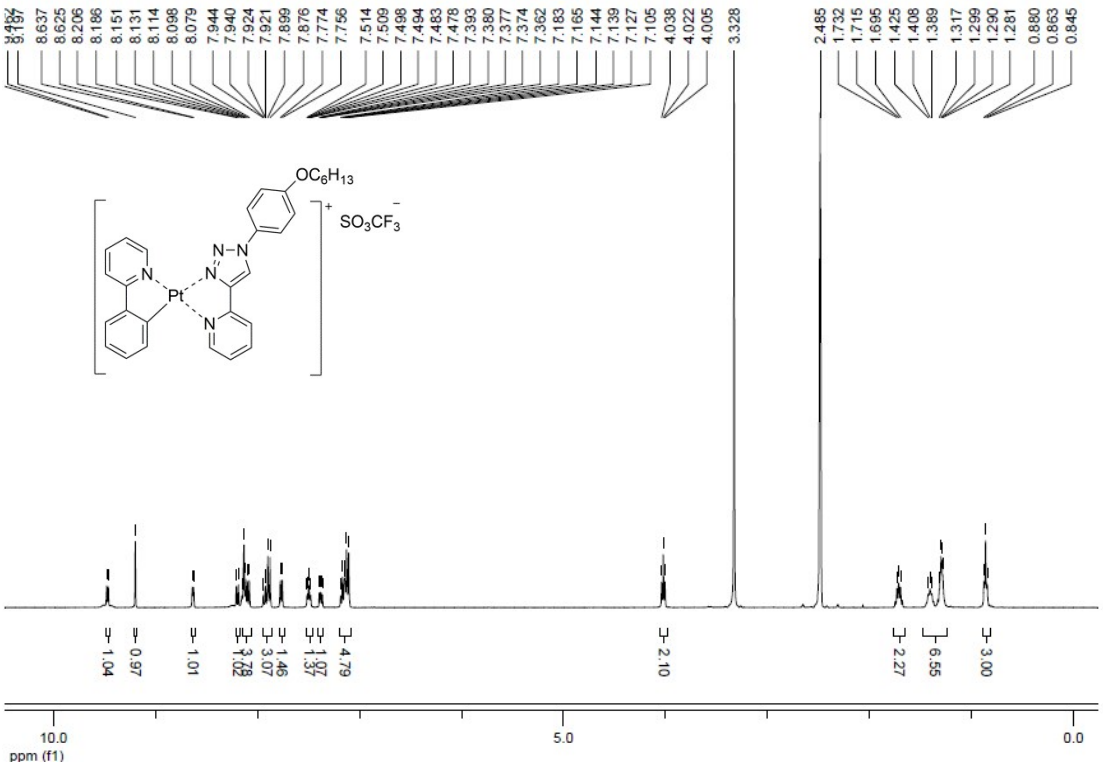
PtL-4: ^{13}C NMR (101 MHz, DMSO-d_6, TMS)



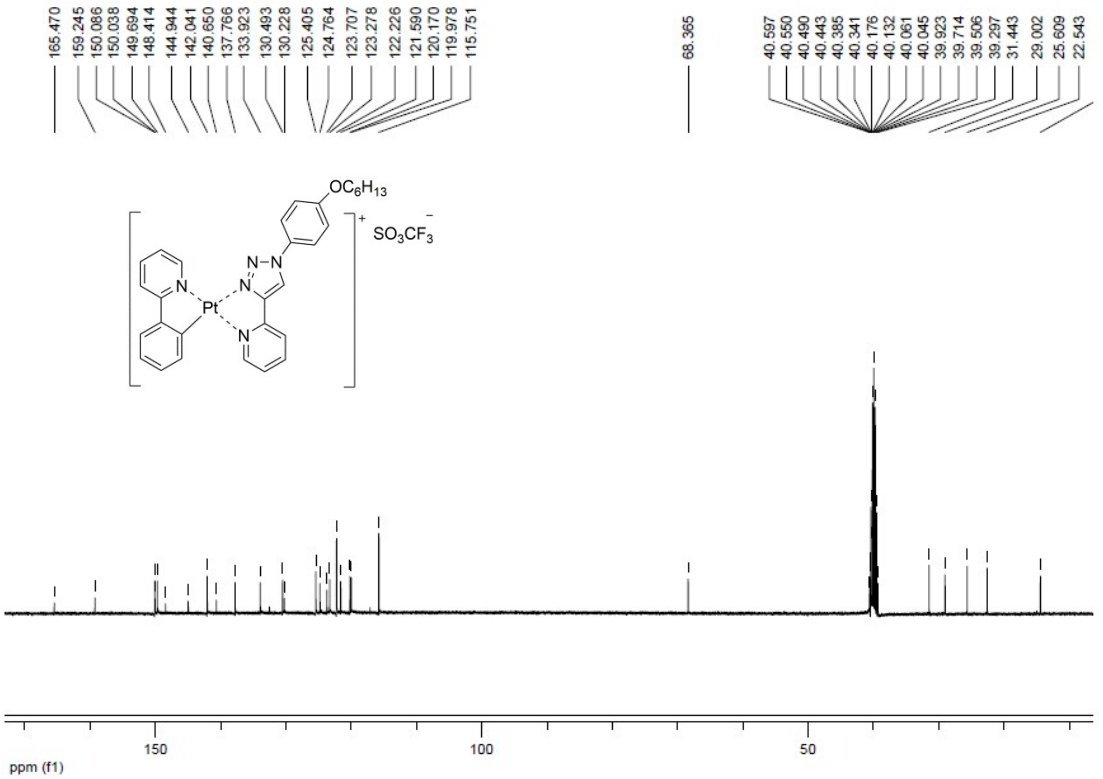
PtL-4: ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.783



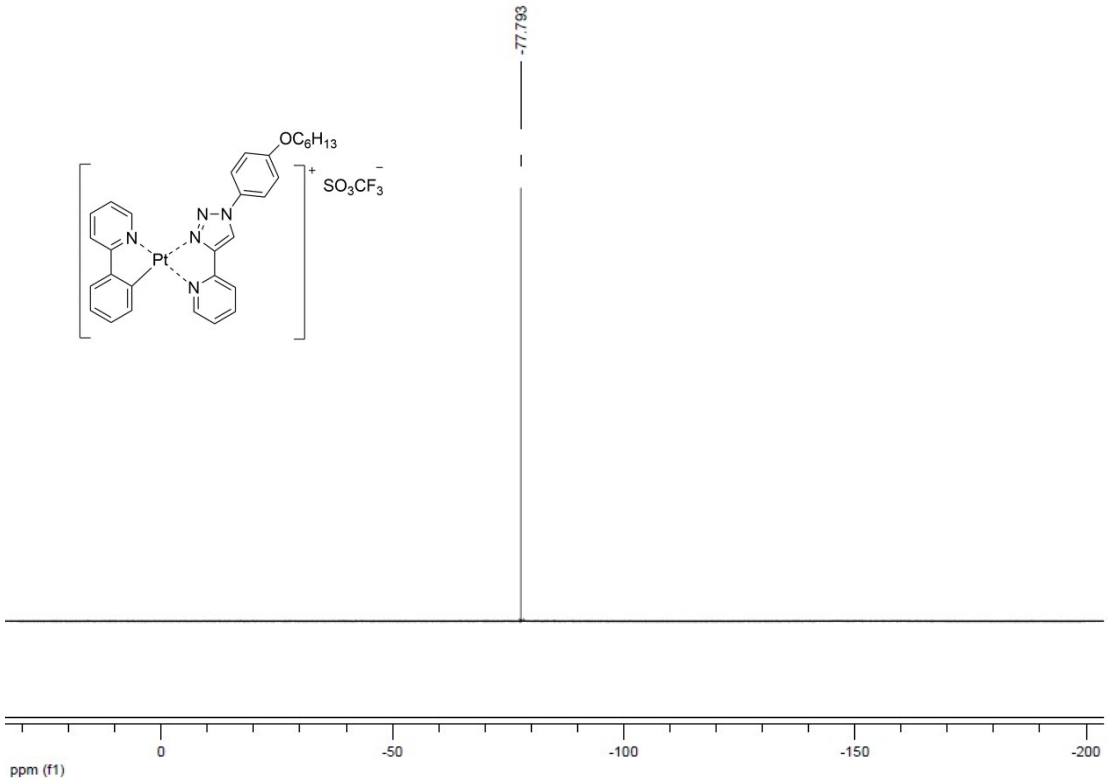
PtL-5: ^{1}H NMR (400 MHz, DMSO-d_6,TMS)



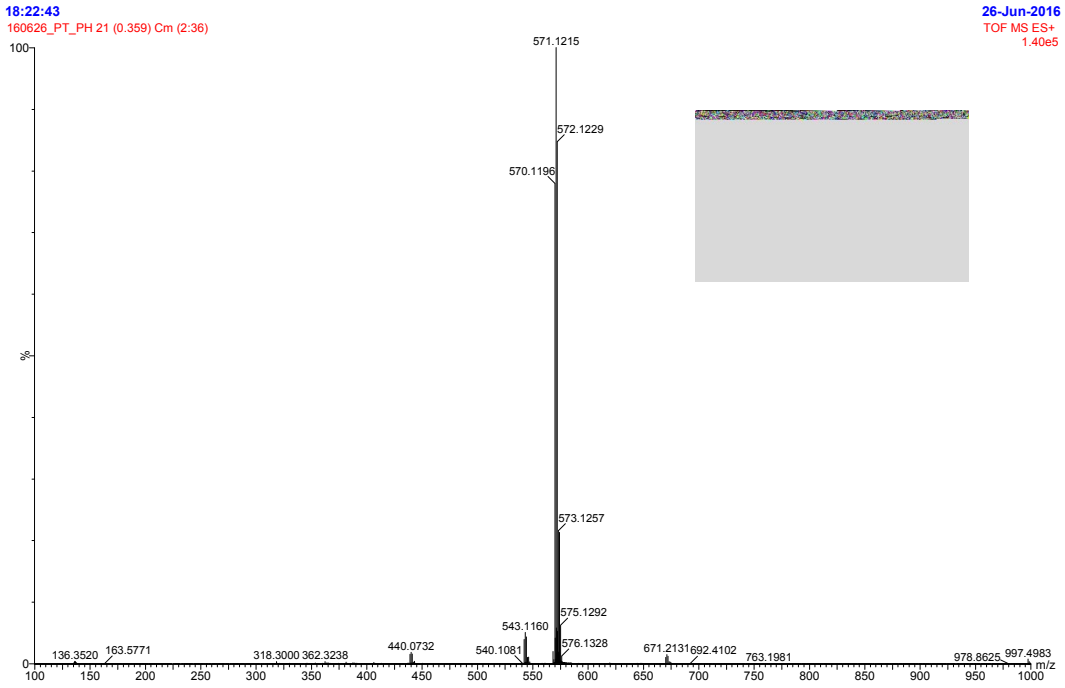
PtL-5: ^{13}C NMR (101 MHz, DMSO-d_6,TMS)



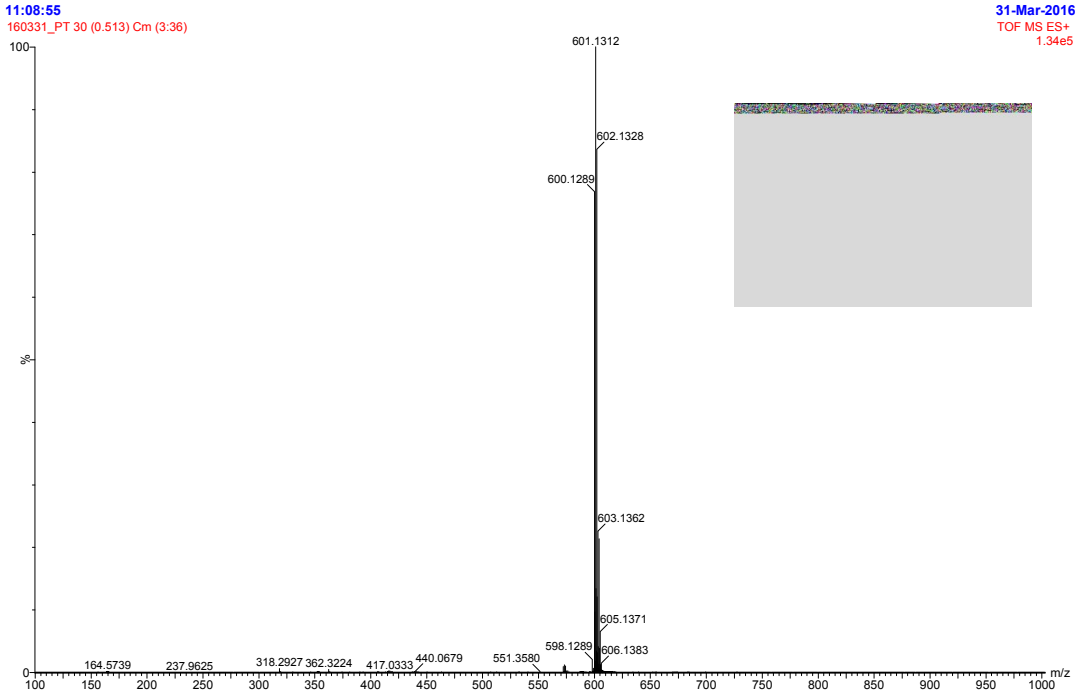
PtL-5: ^{19}F NMR (376 MHz, DMSO-d_6, ppm): -77.793.



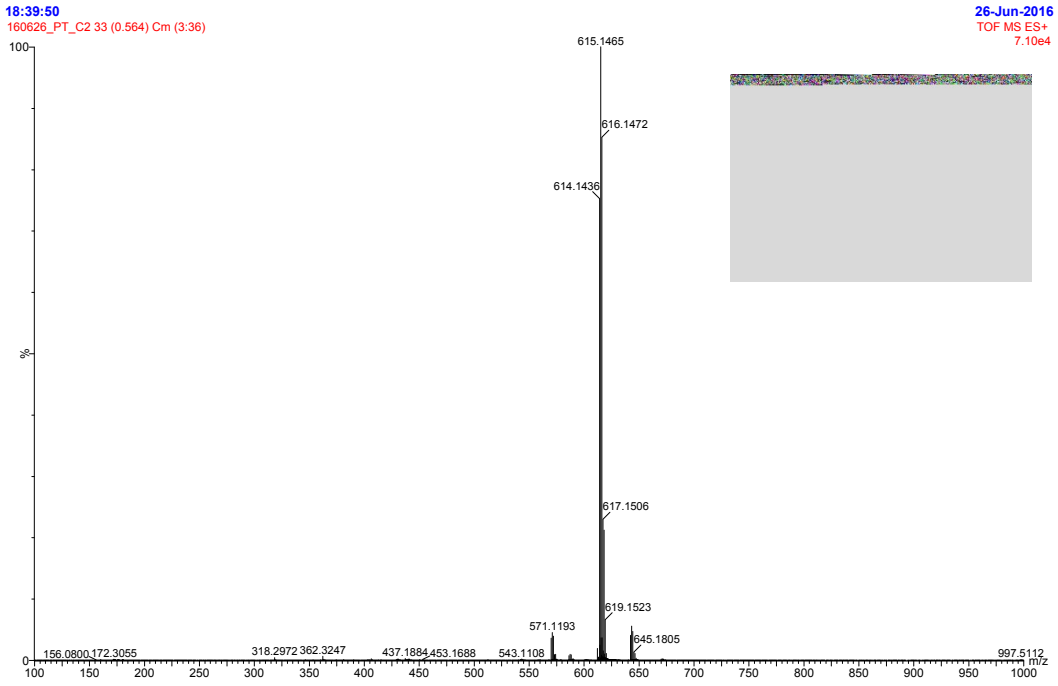
PtL-1: HRMS (ESI): 571.1215 [calcd for $(M\text{-}CF_3SO_3)^+$: 571.1210].



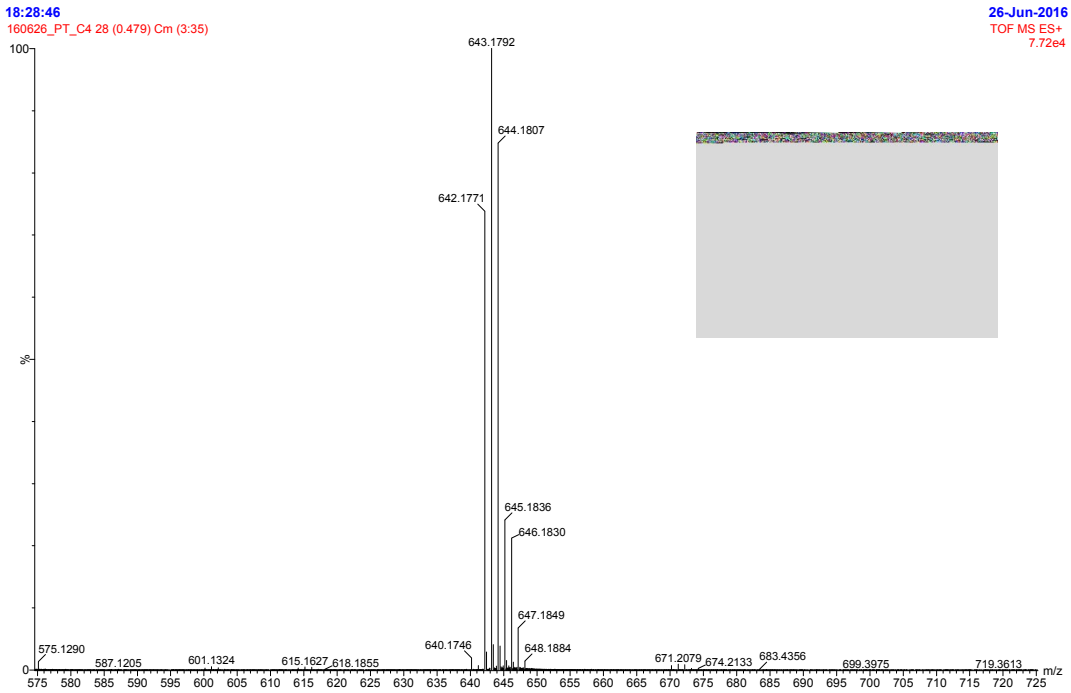
PtL-2: HRMS (ESI): 601.1312 [calcd for $(M\text{-}CF_3SO_3)^+$: 601.1316].



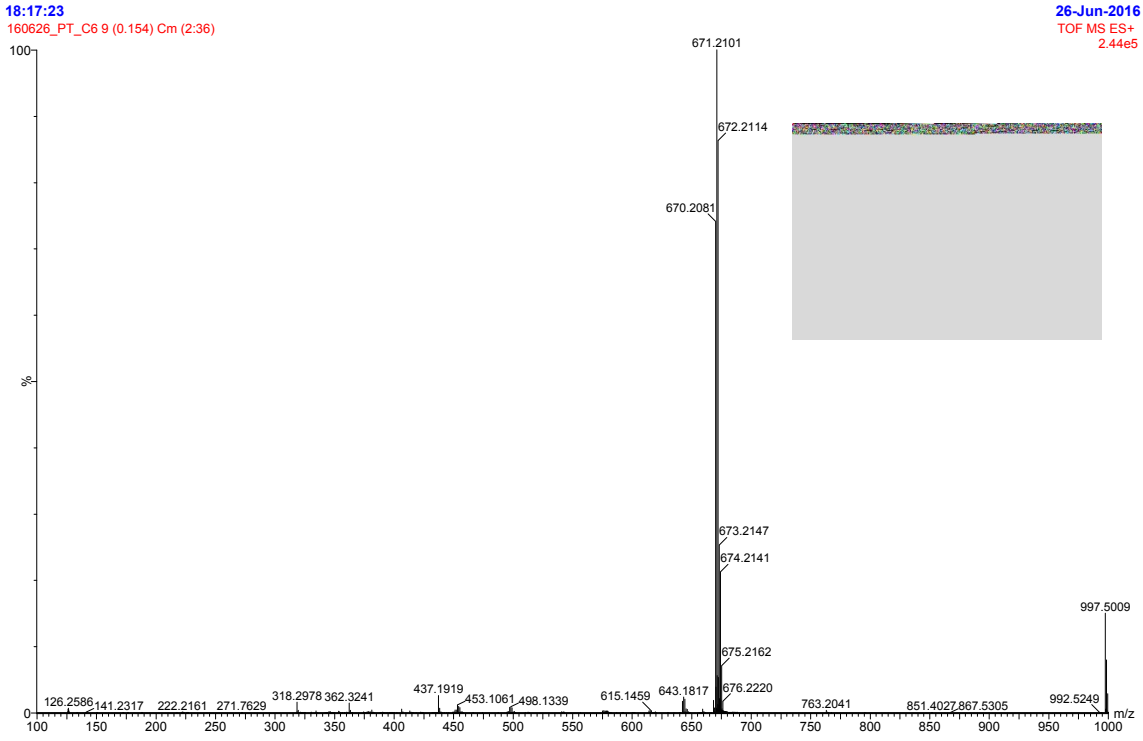
PtL-3: HRMS (ESI): 615.1465 [calcd for $(M\text{-}CF_3SO_3)^+$: 615.1472].



PtL-4: HRMS (ESI): 643.1792 [calcd for $(M\text{-}CF_3SO_3)^+$: 643.1785].



PtL-5: HRMS (ESI): 672.2101 [calcd for $(M\text{-}CF_3SO_3)^+$: 671.2098].



7 References

[1] D. Demus, J. Goodby,G. W. Gray,H.-W. Spiess, V. Vill. Handbook of Liquid Crystals; Wiley-VCH: Weinheim, 1998; Vols. 1 - 3.

[2] J.L.Serrano,Ed. Metallomesogens. Synthesis,Properties, and Applications; VCH: New York, 1996.

[3] Sajoto, T.; Djurovich, P. I.; Tamayo, A. B.; Oxgaard, J.; Goddard, W. A.; Thompson, M. E. *J. Am. Chem. Soc*. 2009, 131, 9813 - 9822.

[4] A. B. Tamayo, B. D. Alleyne, P. I. Jurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E.Thompson, *J. Am. Chem. Soc*.2003, 125, 7377 - 7387.

[5] E.Turner, N. Bakken, J. Li.Inorg. Chem. 2013, 52, 7344 - 7351.

[6] Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.*2001, 40, 2004 - 2021.

[7]Finn, M. G.; Kolb, H. C.; Fokin, V. V.; Sharpless, K. B. *Prog. Chem*. 2008, 20, 1 - 4.

[8] Kim, S. J; Kang, S. H.; Park, K.-M.; Kim, H.; Zin, W.-C.; Choi, M.-G.; Kim, K. *Chem. Mater.* 1998, 10, 1889.

[9] a) M.B. Smith and J. Michl. *Chem. Rev*. 2010, 110, 6891–6936; b) Takao Itoh. *Chem. Rev.* 2012, 112, 4541 - 4568.

[10] M. Krikorian, S. Liu, and T. M. Swager. *J. Am. Chem. Soc*. 2014, 136, 2952 - 2955.