Synthesis of New Fused Heterocyclic Aromatic Hydrocarbons via C-S and C-C bonds formation by C-H Bond Activation in the Presence of New Pd(II) Schiff's Base Complexes

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Analytical data

3,3'-(piperazine-1,4-diyl)bis(3-phenylpropanal) (PDBDP):

The purify the material by recrystallized from methanol to get pure product (1.21 g) in 74% yield. ^{1}H-NMR (400 MHz, $CDCl_3$), ∂ (ppm): 9.63 (m, 2H, C*H*=O), 7.65 – 7.27 (m, 10H, Ar-*H*s), 4.34 – 4.29 (m, 2H, Ar-C*H*-CH_2), 2.66 (s, 8H, piperzine-CH_2), 2.34 (d, 2H, -CH_2-CHO) and 2.15 (d, 2H, -CH_2-CHO); HRMS (FAB+) cald. For $C_{22}H_{26}N_2O_2$: 350.2 found: 351.2 (M^++1).

3,3'-(piperazine-1,4-diyl)bis(1,3-diphenylpropan-1-one) (PDBDPP)

The purify the material by recrystallized from methanol to get pure product (3.21 g) in 64% yield. ^{1}H-NMR (400 MHz, $CDCl_3$), ∂ (ppm): 8.15 – 7.53 (m, 20H, Ar-*H*s), 4.37 – 4.34 (m, 2H, Ar-C*H*-CH_2), 3.55 (d, 2H, -CH-CH_2^c-Ar), 3.15 (d, 2H, -CH-CH_2^b-Ar) and 2.79 (s, 8H, piperzine-CH_2); HRMS (FAB+) cald. For $C_{32}H_{34}N_2O_2$: 502.2 found: 502.2 (M^+).

2,15-Diphenyl-1,5,12,16-tetraaza-tricyclo[14.2.2.06,11]eicosa-4,6(11),7,9,12-pentaene (DPTTP)

The purify the material by recrystallized from methanol to get pure product (3.16 g) in 75% yield. ^{1}H-NMR (400 MHz, $CDCl_3$), ∂ (ppm): 8.93 (m, 2H, -C*H*=N-), 7.86 – 7.06 (m, 14H, Ar-*H*s), 3.56 (m, 2H, Ar-C*H*-CH_2), 2.68 (s, 8H, piperzine-CH_2), 1.98 (d, 2H, -CH_2-C=N) and 1.89 (d, 2H, -CH_2-C=N); HRMS (FAB+) cald. For $C_{28}H_{30}N_4$: 422.2 found: 422.2 (M^+).

2,4,13,15-Tetraphenyl-1,5,12,16-tetraaza-tricyclo[14.2.2.06,11]eicosa-4,6(11),7,9,12-pentaene (TPTTP)

The purify the material by recrystallized from ethanol to get pure product (3.9 g) in 68% yield. ^{1}H-NMR (400 MHz, $CDCl_3$), ∂ (ppm): 7.89 – 7.29 (m, 24H, Ar-*H*s), 4.04 – 3.97 (m, 2H,

Ar-C*H*-CH_2), 2.74 (s, 8H, piperzine-CH_2), 2.24 (d, 2H, -CH-CH_2-Ar), 1.99 (d, 2H, -CH-CH_2-Ar); HRMS (FAB+) cald. For $C_{40}H_{38}N_4$: 574.30 found: 574.30 (M^+).

Pd(DPTTP)Cl_2:

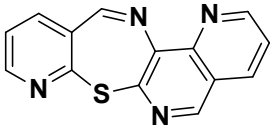
The purify the complex by recrystallized from 1,4-dioxane to get pure product in 63% yield. ^{1}H-NMR (400 MHz, $CDCl_3$), ∂ (ppm): 8.92 & 8.45 (d, 2H, ($C_6H_4N_2$)=), 8.73 (m, 2H, C*H*=O), 7.81 – 7.23 (m, 10H, Ar-*H*s), 4.89 (m, 2H, Ar-C*H*-CH_2), 3.45 (s, 8H, piperzine-CH_2), 3.21 (d, 2H, -CH_2-C=N) and 2.76 (d, 2H, -CH_2-C=N); HRMS (FAB+) cald. For $C_{28}H_{30}Cl_2N_4Pd$: 598.09 found: 598.09 (M^+).

Pd(TPTTP)Cl_2:

The purify the material by recrystallized from tetrahydrofuran to get pure product in 68% yield. ^{1}H-NMR (400 MHz, $CDCl_3$), ∂ (ppm): 9.07 & 8.30 (d, 2H, ($C_6H_4N_2$)=), 7.79 – 7.27 (m, 20H, Ar-*H*s), 4.79 – 4.72 (m, 2H, Ar-C*H*-CH_2), 3.77 (s, 8H, piperzine-CH_2), 2.31 (d, 2H, -CH-CH_2-Ar), 2.15 (d, 2H, -CH-CH_2-Ar); HRMS (FAB+) cald. For $C_{40}H_{38}Cl_2N_4Pd$: 752.08 found: 752.08 (M^+).

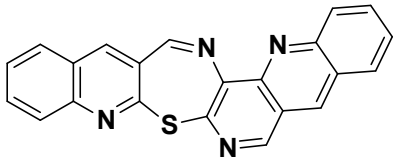
Synthesis of pyrido[3',2':6,7][1,4]thiazepino[2,3-h][1,6]naphthyridine and its derivatives

Pyrido[3',2':6,7][1,4]thiazepino[2,3-h][1,6]naphthyridine (compound 1a):



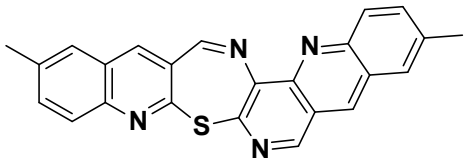
^{1}H-NMR (400 MHz, $CDCl_3$), δ ppm: 9.203 (s, 1H), 9.077 (d, 1H, J = 5.2 Hz), 8.679 (d, 1H, J = 6.0 Hz), 8.211 (d, 1H, J = 3.2 Hz), 7.977 (d, 1H, J = 4.4 Hz), 7.856 (s, 1H) and 7.796 – 7.664 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ ppm: 179.550, 160.880, 159.349, 155.476, 152.072, 150.129, 148.962, 137.503, 129.920, 124.803, 123.072, 122.081,121.857 and 120.223 HRMS (EI): cald. for $C_{14}H_8N_4S$: 264.047, found: 265.05 (M^+ + 1).

Benzo[b]quinolino[3',2':6,7][1,4]thiazepino[2,3-h][1,6]naphthyridine (compound 1b):



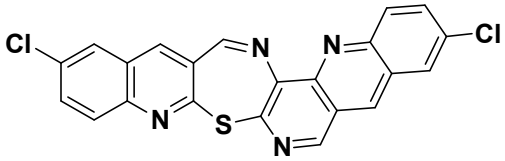
^{1}H-NMR (400 MHz, $CDCl_3$), δ ppm: 9.07 (s, 1H), 8.888 (s, 1H), 8.705 (s, 1H), 8.145 (d, 1H, J = 8 Hz), 8.092 (d, 1H, J = 7.2 Hz), 7.972 (d, 2H, J = 7.2 Hz), 7.838 (d, 2H, J = 6 Hz), 7.657 – 7.623 (m, 2H) and 7.577 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ ppm: 178.438, 162.166, 152.097, 148.477, 146.443, 144.620, 142.036, 137.524, 136.067, 133.624, 131.998, 128.929, 128.686, 126.951, 126.660, 124.815, 122.097, 120.228 and 118.816; HRMS (EI): cald. for $C_{22}H_{12}N_4S$: 364.078, found: 364.09 (M^+).

3,12-dimethylbenzo[b]quinolino[3',2':6,7][1,4]thiazepino[2,3-h][1,6]naphthyridine (compound 1c):



^{1}H-NMR (400 MHz, $CDCl_3$), δ ppm: 9.099 (s, 1H), 8.725 (s, 1H), 8.325 (s, 1H), 8.162 (m, 1H), 8.094 (d, 1H, J = 8 Hz), 7.977 (d, 1H, J = 7.2 Hz), 7.757 (d, 2H, J = 5.2 Hz), 7.569 (d, 2H, J = 4.8 Hz), 7.462 (s, 1H) and 2.799 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ ppm: 181.166, 162.076, 153.706, 149.794, 143.249, 138.474, 137.496, 136.166, 126.706, 126.662, 126.194, 124.803, 123.965, 122.089, 120.223 and 21.653; HRMS (EI): cald. for $C_{24}H_{16}N_4S$: 392.110, found: 392.11 (M^+).

3,12-dichlorobenzo[b]quinolino[3',2':6,7][1,4]thiazepino[2,3-h][1,6]naphthyridine (compound 1d):



^{1}H-NMR (400 MHz, $CDCl_3$), δ ppm: 9.240 (s, 1H), 8.890 (s, 1H), 8.728 (s, 1H), 8.265 (m, 1H), 8.145 (d, 1H, J = 8 Hz), 7.872 (d, 2H, J = 7.2 Hz), 7.657 (d, 2H, J = 5.2 Hz) and 7.444 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ ppm: 183.026, 154.983, 150.022, 144.107, 139.643, 138.881, 137.204, 136.034, 129.956, 129.783, 129.309, 128.891, 127.356, 125.438, 124.731, 123.643 and 121.803; HRMS (EI): cald. for $C_{22}H_{10}Cl_2N_4S$: 432.00, found: 432.00 (M^+).

Pyrido[3',2':6,7][1,4]thiazepino[2,3-c][2,6]naphthyridine (compound 1f):

^{1}H-NMR (400 MHz, $CDCl_3$), δ ppm: 9.431 (s, 1H), 9.165 (d, 1H, J = 5.2 Hz), 9.079 (d, 1H, J = 4.2 Hz), 8.601 (d, 1H, J = 5.6 Hz), 8.312 (d, 1H, J = 3.2 Hz), 7.906 (d, 1H, J = 4.8 Hz), 7.548 (s, 1H) and 7.492 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ ppm: 180.989, 161.280, 158.949, 154.716,

153.872, 151.924, 148.362, 138.003, 130.202, 125.612, 124.706, 123.316, 121.957 and 120.843 HRMS (EI): cald. for $C_{14}H_8N_4S$: 264.047, found: 265.05 ($M^+ + 1$).

Pyrido[3',2':6,7][1,4]thiazepino[3,2-f][1,7]naphthyridine (compound 1g):

^{1}H-NMR (400 MHz, $CDCl_3$), δ ppm: 9.125 (s, 1H), 8.872 (s, 1H), 8.655 (d, 1H, J = 2.8 Hz), 8.458 (d, 1H, J = 5.6 Hz), 8.265 (m, 1H), 8.145 (d, 1H, J = 8 Hz), 7.584 (s, 1H) and 7.458 (d, 1H, J = 4.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$), δ ppm: 180.103, 162.028, 159.349, 155.516, 154.063, 152.401, 147.992, 139.105, 131.814, 125.857, 125.212, 124.113, 122.361 and 121.013 HRMS (EI): cald. for $C_{14}H_8N_4S$: 264.047, found: 265.05 ($M^+ + 1$).

Pyrido[3,2-f]thieno[3',2':4,5]pyrido[2,3-b][1,4]thiazepine (compound 1h):

^{1}H-NMR (400 MHz, $CDCl_3$), δ ppm: 8.548 (d, 1H, J = 2.8 Hz), 8.262 (s, 1H), 7.912 (d, 1H, J = 2.8 Hz), 7.748 (s, 1H), 7.622 (m, 1H), 7.571 (d, 1H, J = 3.6 Hz) and 7.369 (d, 1H, J = 2.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$), δ ppm: 178.991, 159.889, 152.829, 150.211, 148.284, 138.302, 136.214, 132.655, 131.983, 126.326, 124.601, 122.845 and 121.421 HRMS (EI): cald. for $C_{13}H_7N_3S_2$: 269.08, found: 270.07 ($M^+ + 1$).

Pyrido[3',2':6,7][1,4]thiazepino[2,3-c]isoquinoline (compound 1i):

^{1}H-NMR (400 MHz, $CDCl_3$), δ ppm: 8.777 (d, 1H, J = 2.8 Hz), 8.551 (d, 1H, J = 2.8 Hz), 8.248 (d, 1H, J = 3.6 Hz), 8.045 (d, 1H, J = 2.8 Hz) and 7.657 – 7.532 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ ppm: 179.892, 163.236, 161.902, 153.009, 151.523, 137.985, 134.672, 133.095, 131.631, 130.356, 128.515, 124.824, 122.425 and 120.836 HRMS (EI): cald. for $C_{15}H_9N_3S$: 263.05, found: 263.05 (M^+).

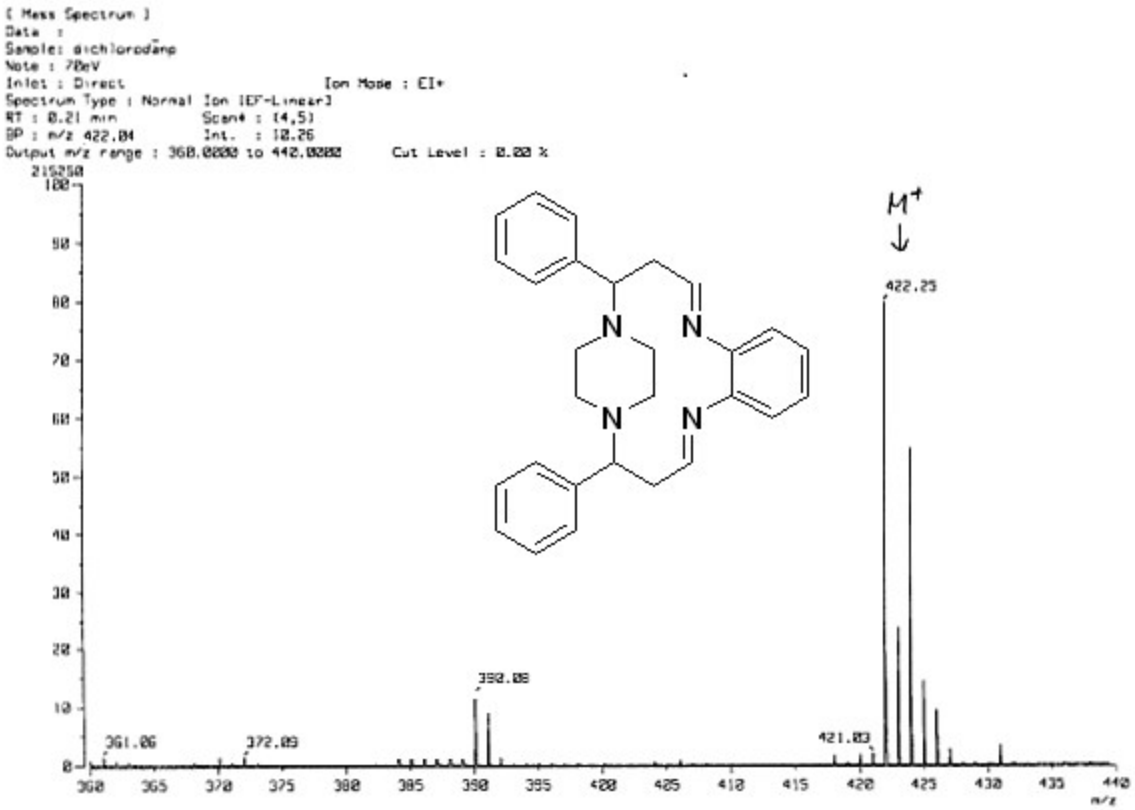


Fig. S1 Mass spectrum of DPTTP ligand

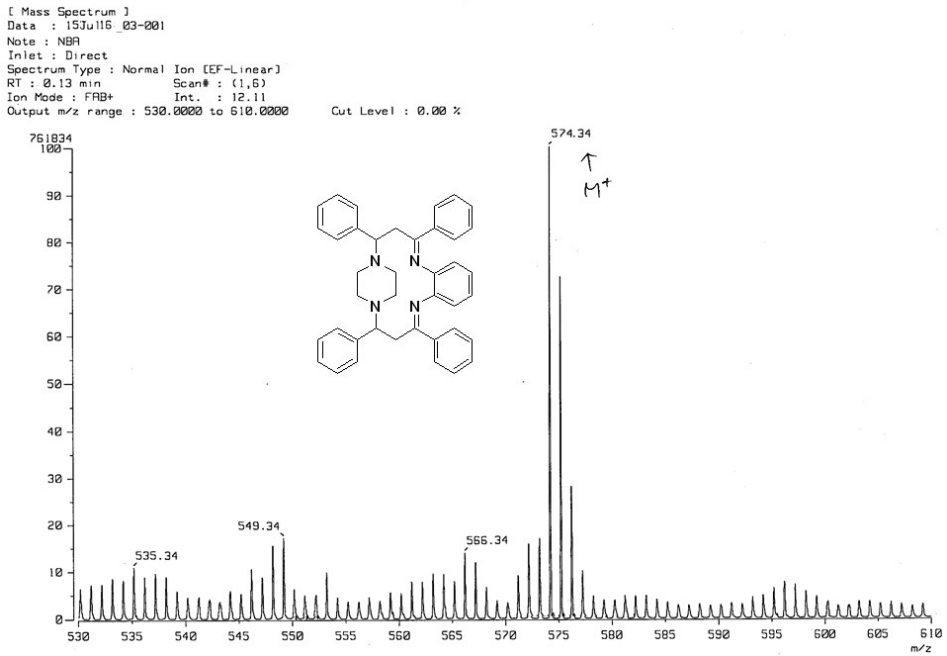


Fig. S2 Mass spectrum of TPTTP ligand

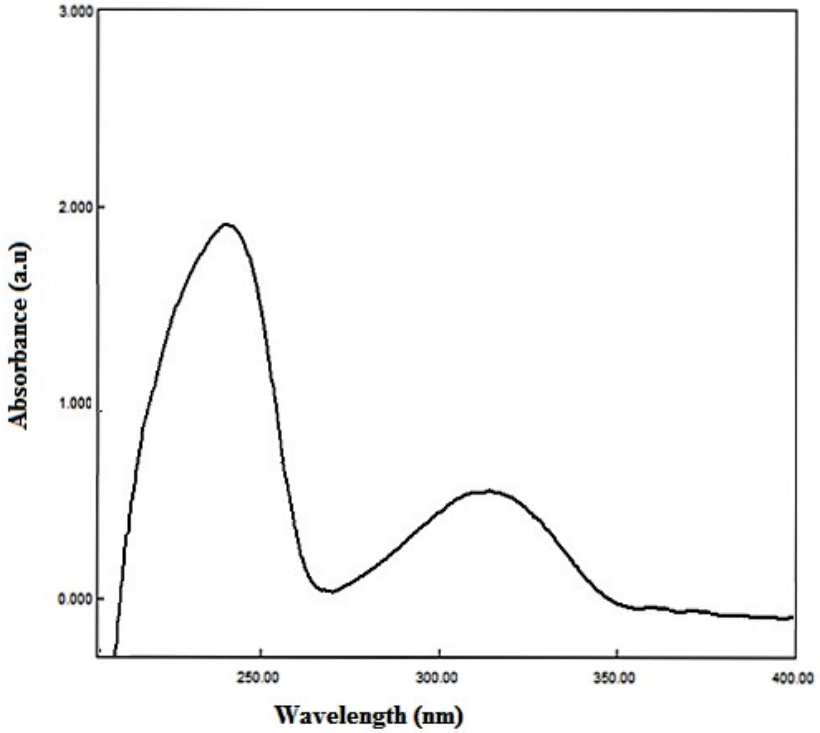


Fig. S3 UV spectrum of DPTTP ligand

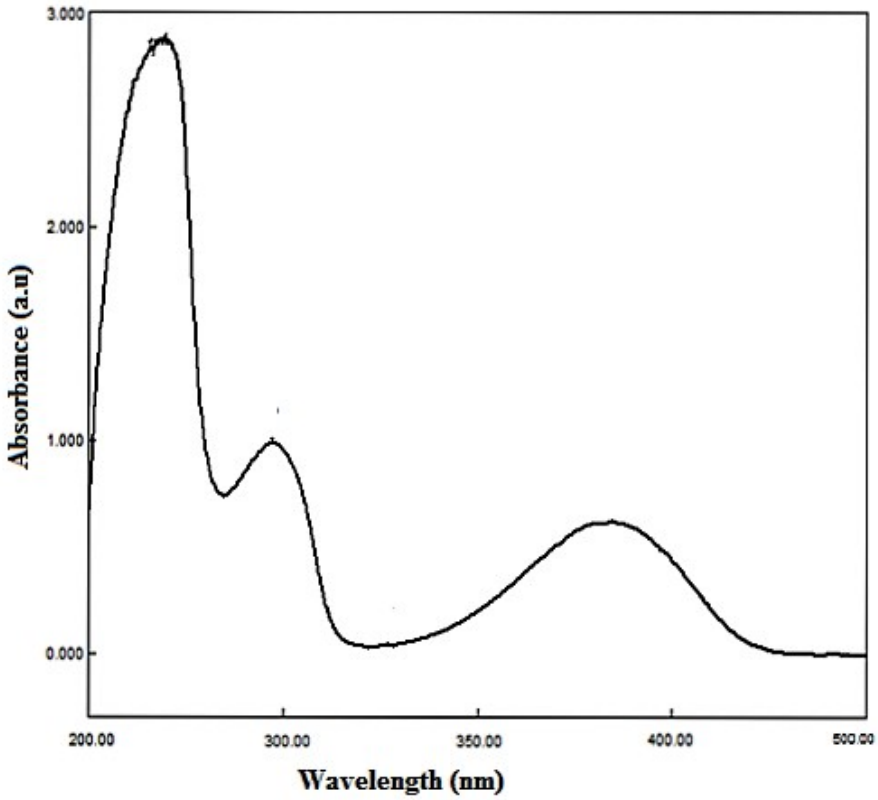


Fig. S4 UV spectrum of TPTTP ligand

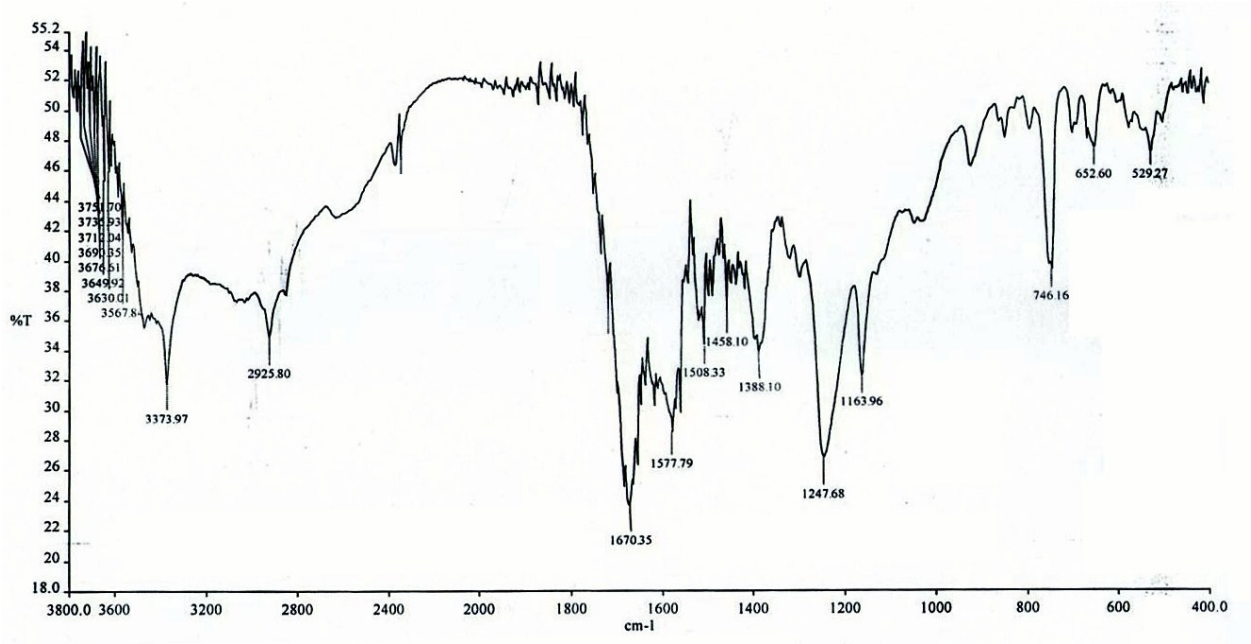


Fig. S5 IR spectrum of DPTTP ligand

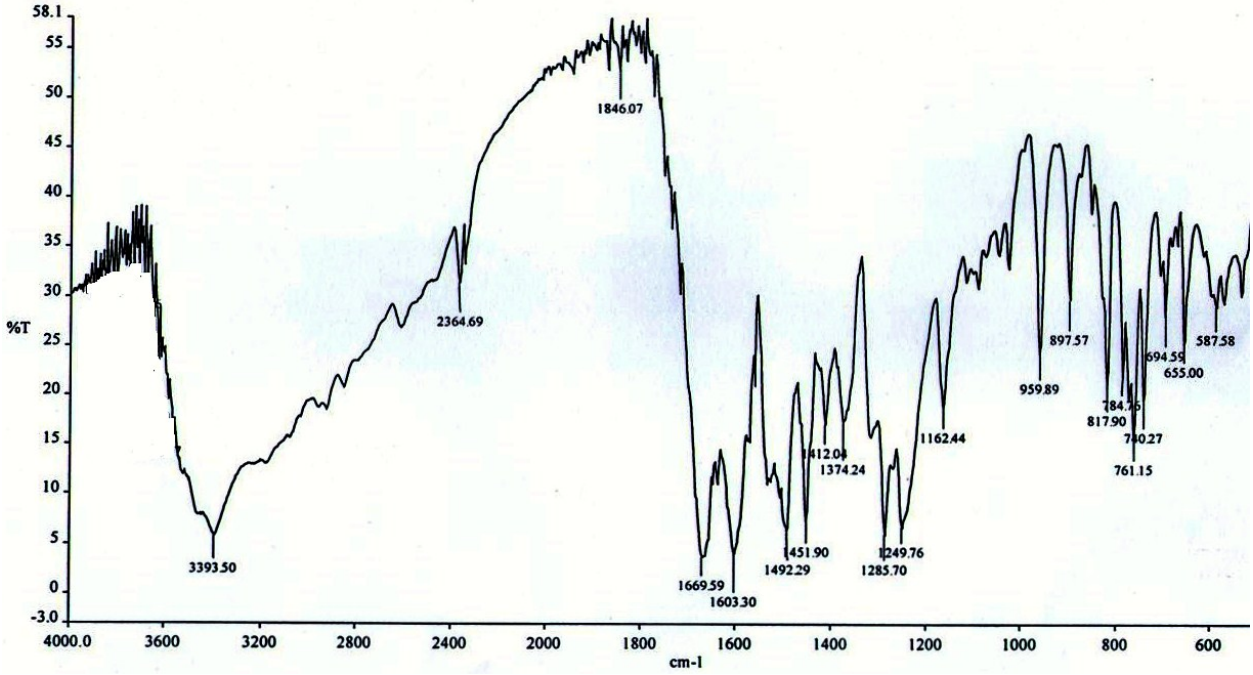


Fig. S6 IR spectrum of TPTTP ligand

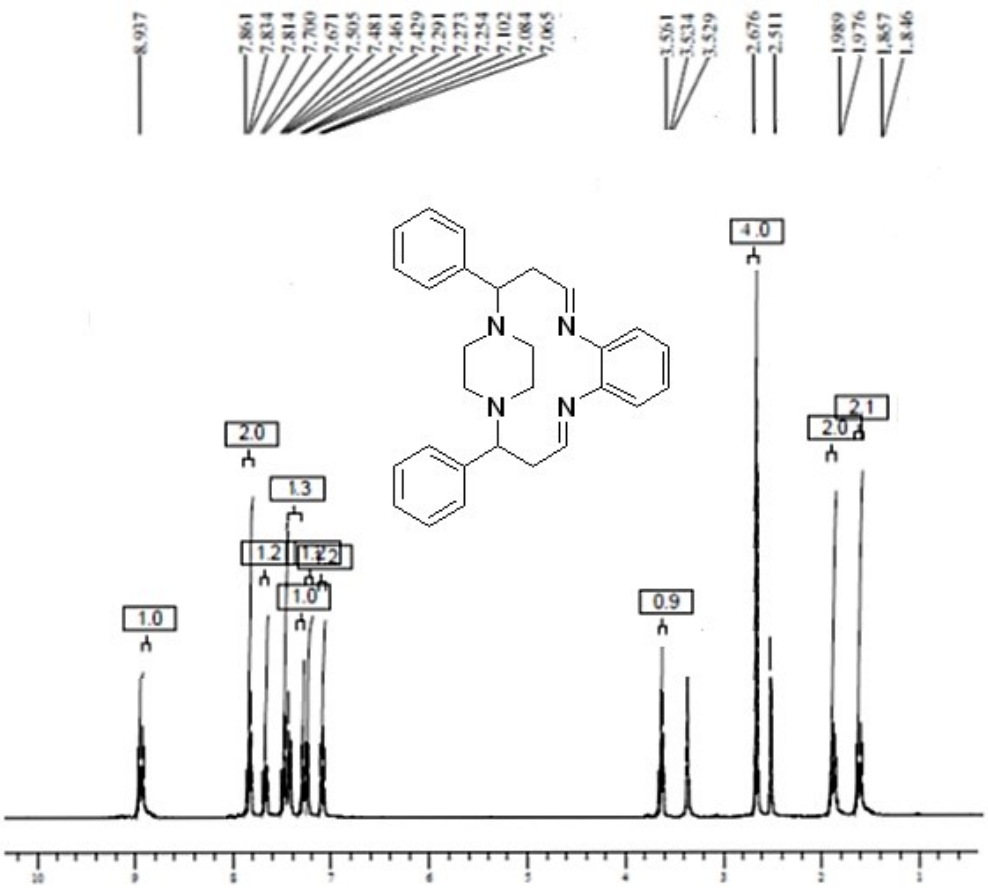


Fig. S7 ^{1}H-NMR Spectrum of DPTTP ligand

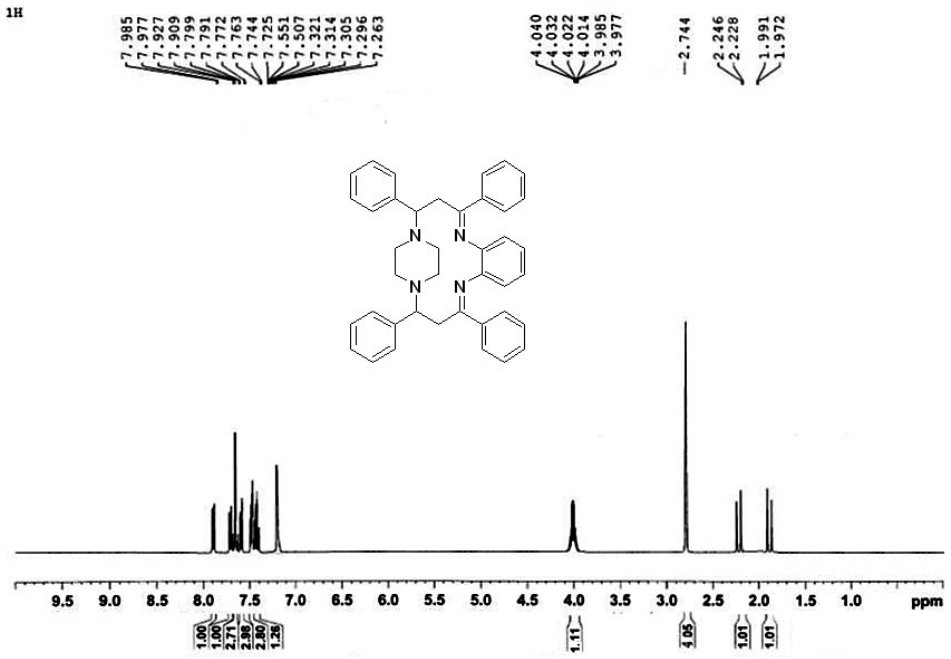


Fig. S8 ^{1}H-NMR spectrum of TPTTP ligand

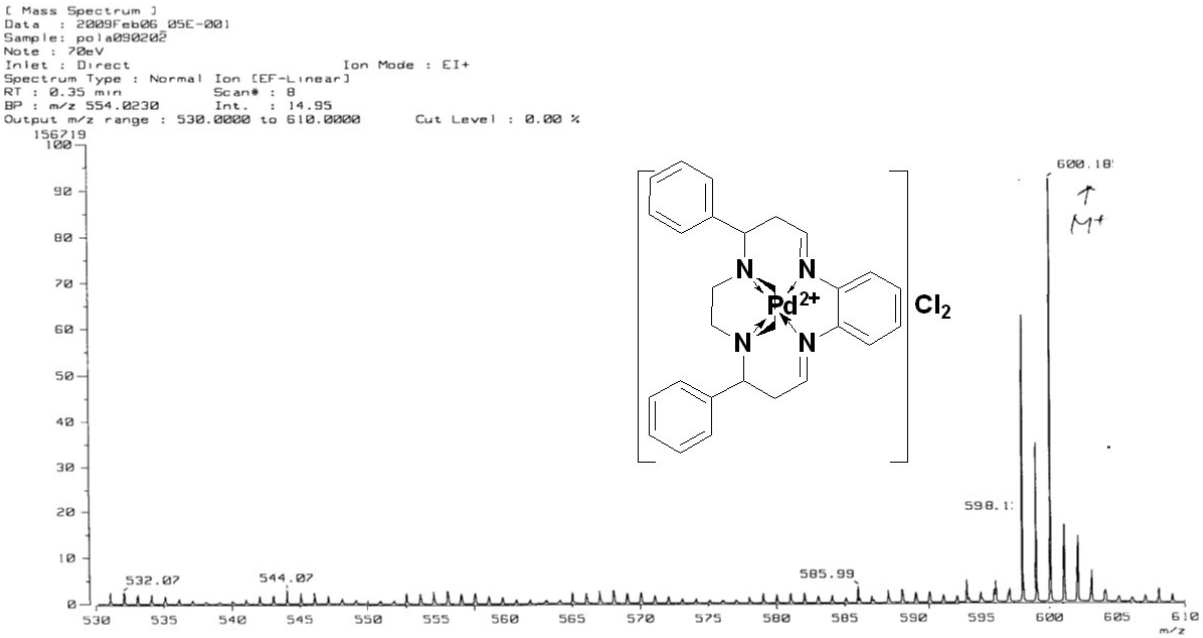


Fig. S9 Mass spectrum of Pd(DPTTP)Cl_2

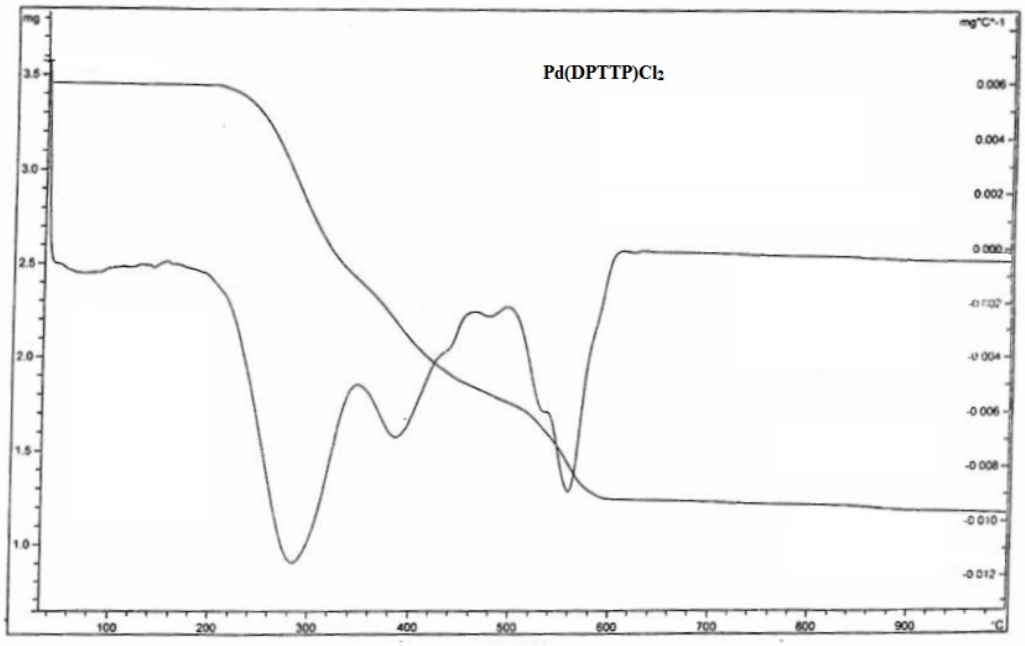


Fig. S10 Thermogram of Pd(DPTTP)Cl_2

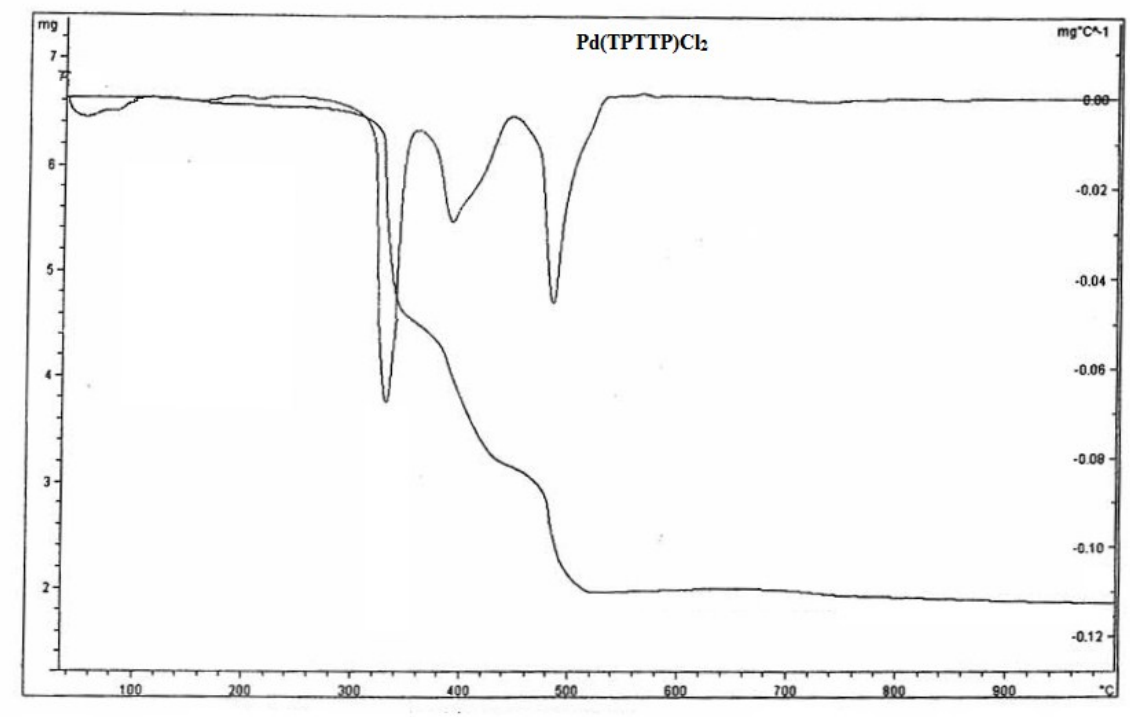


Fig. S11 Thermogram of Pd(TPTTP)Cl_2

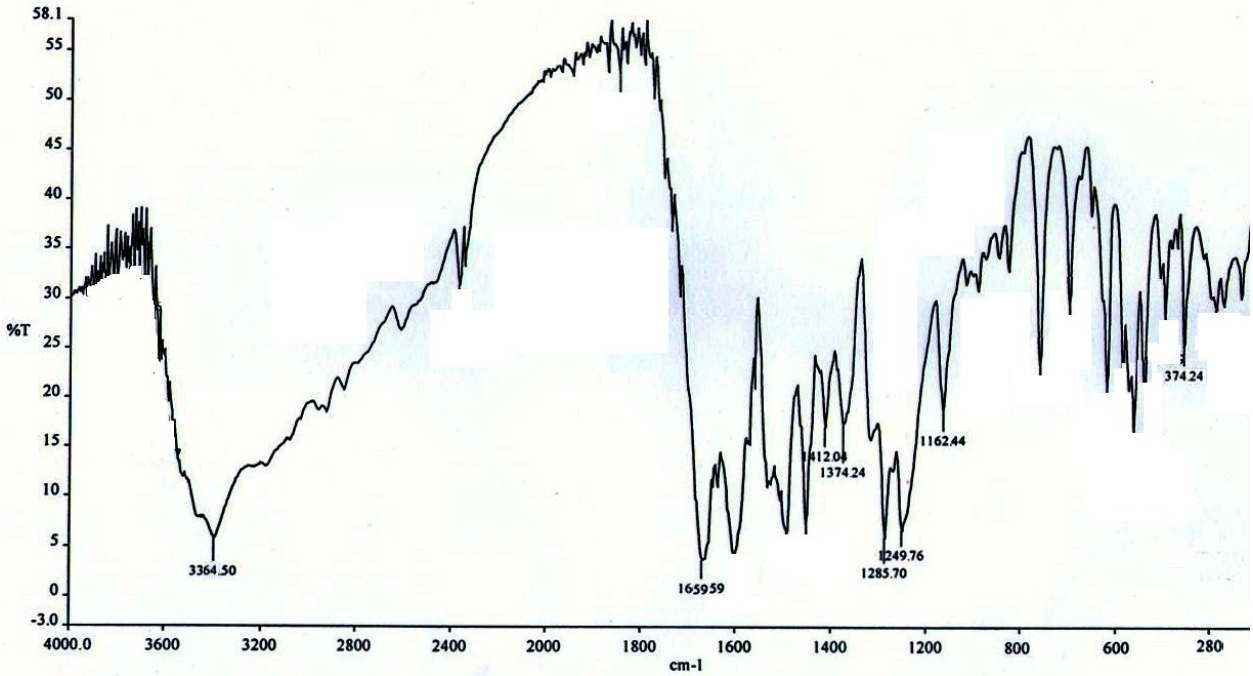


Fig. S12 IR spectrum of Pd(TPTTP)Cl_2

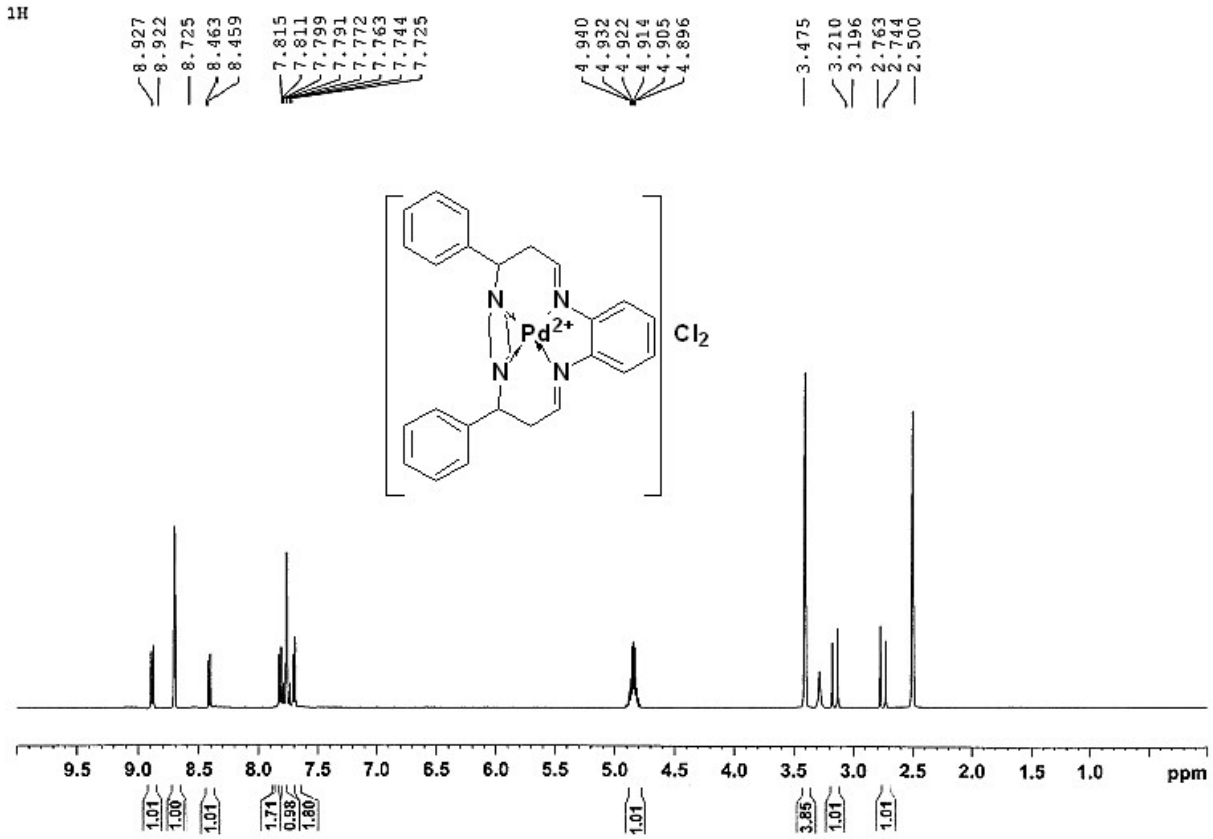


Fig. S13 ^{1}H-NMR spectrum of Pd(DPTTP)Cl_2 complex

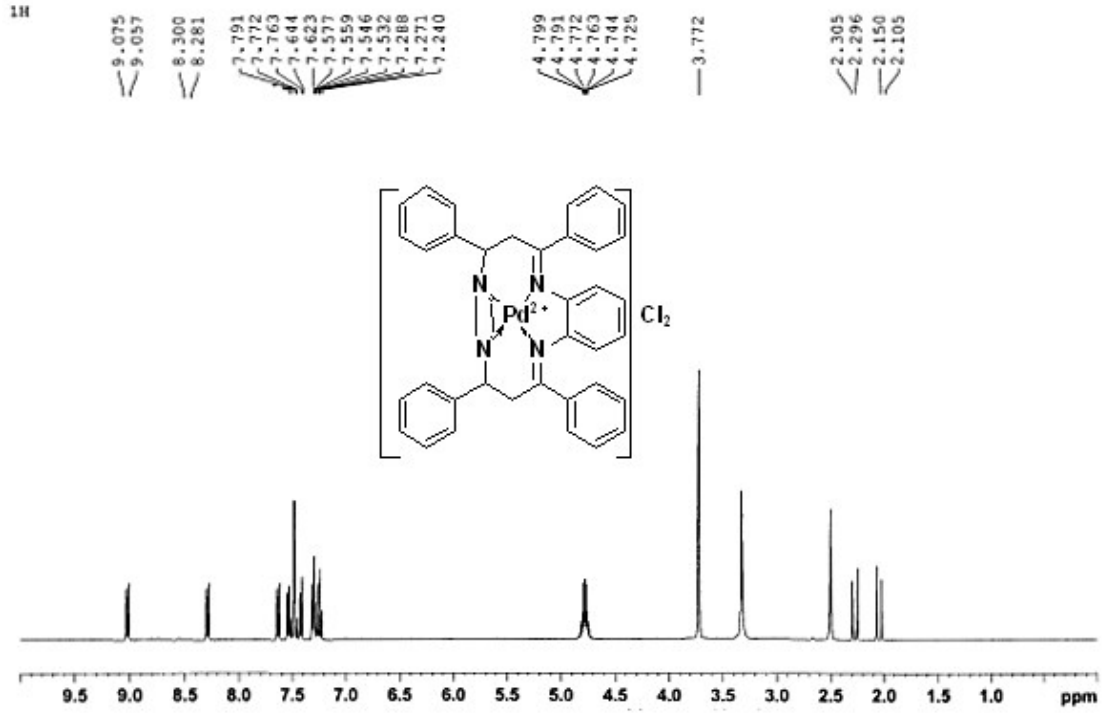


Fig. S14 ^{1}H-NMR spectrum of Pd(TPTTP)Cl_2

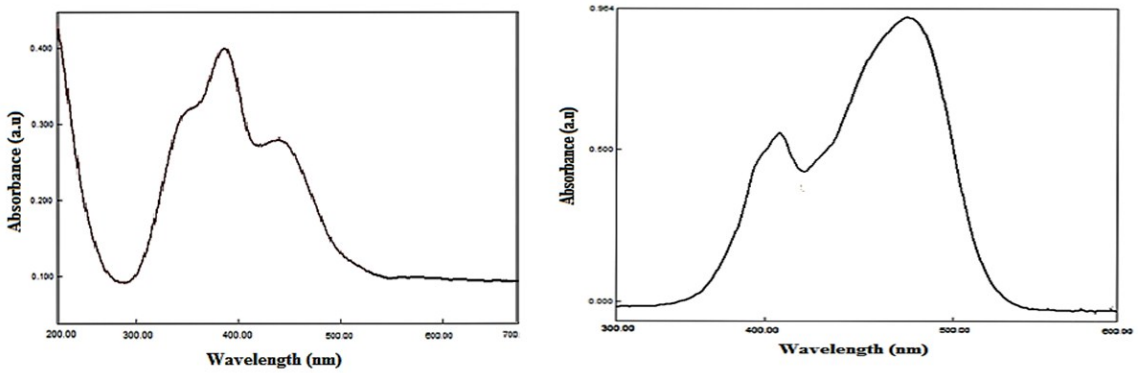


Fig. S15 UV-Visible spectra of $Pd(DPTTP)Cl_2$ and $Pd(TPTTP)Cl_2$

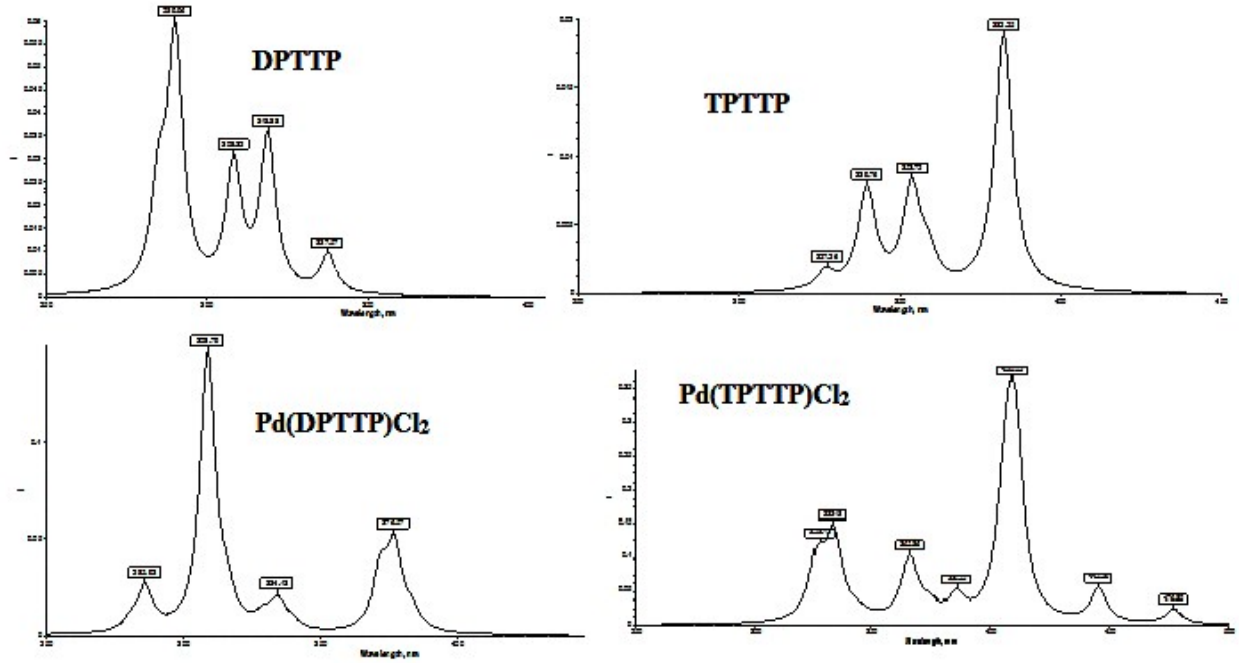


Fig. S16 Calculated absoprion spectra of Ligands and metal complexes

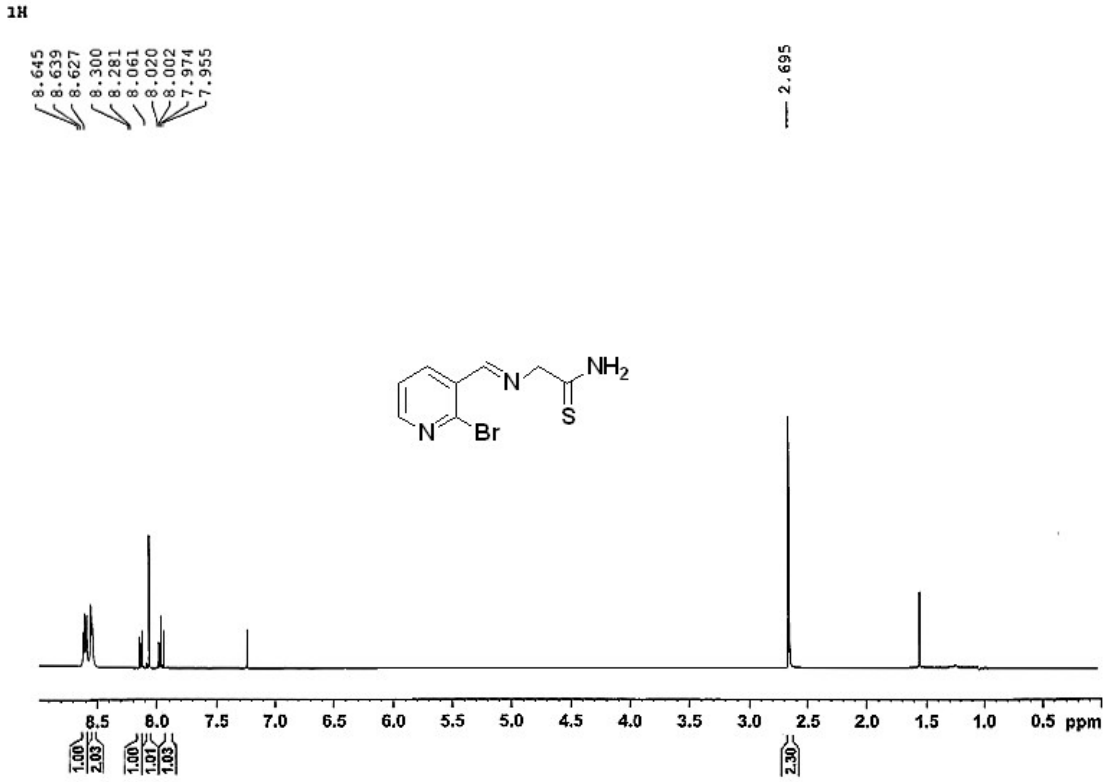


Fig. S17 ^{1}H-NMR spectrum of compound 5

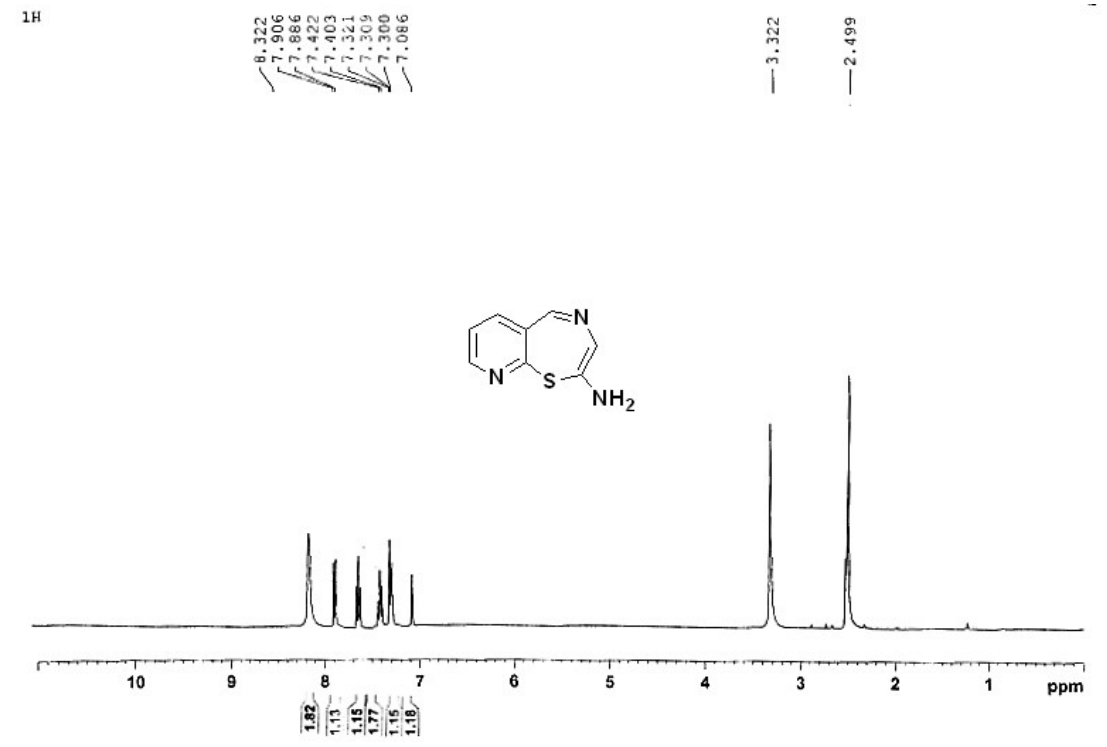


Fig. S18 ^{1}H-NMR spectrum of compound 6

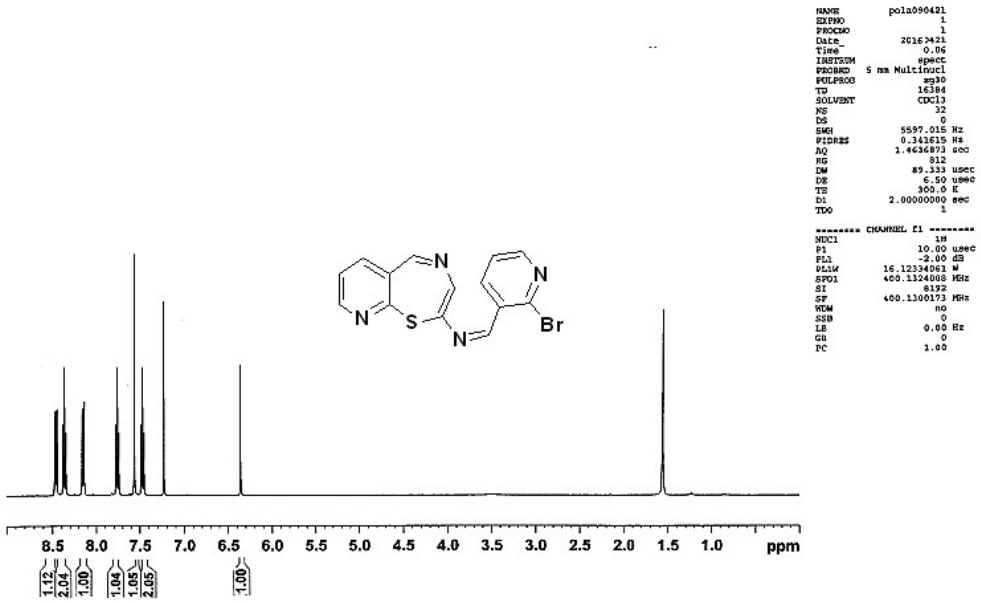


Fig. S19 ^{1}H-NMR spectrum of compound 7

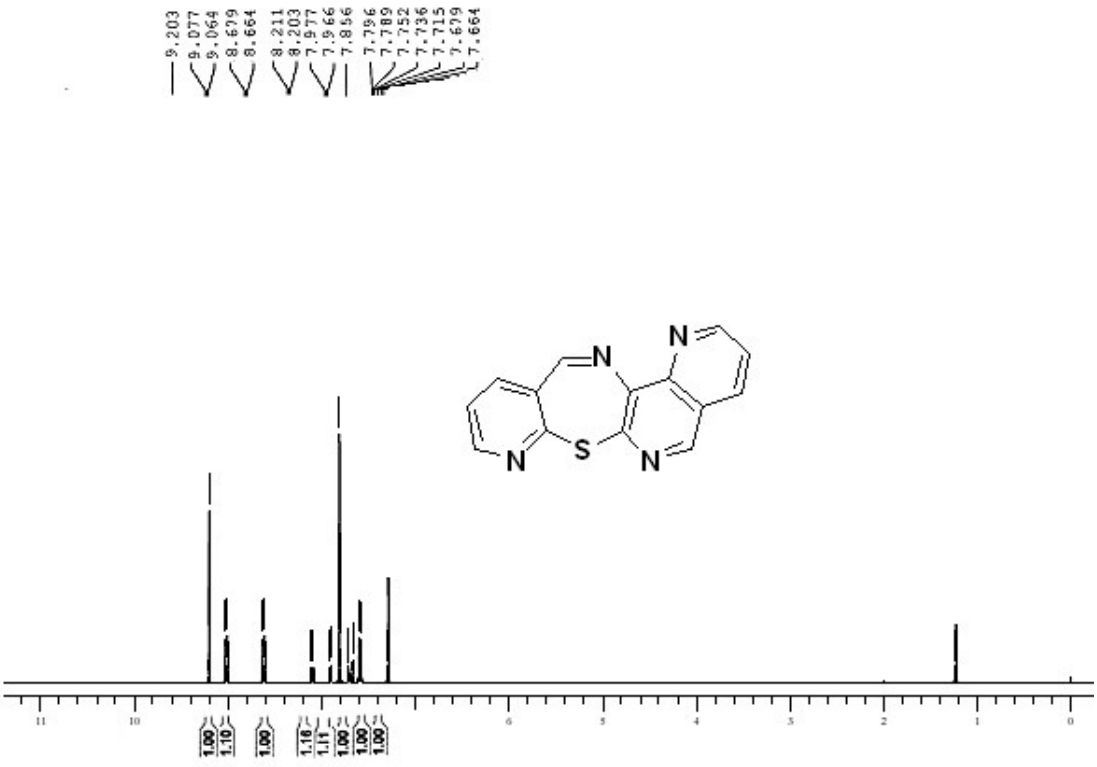


Fig. S20 ^{1}H-NMR spectrum of compound 1a

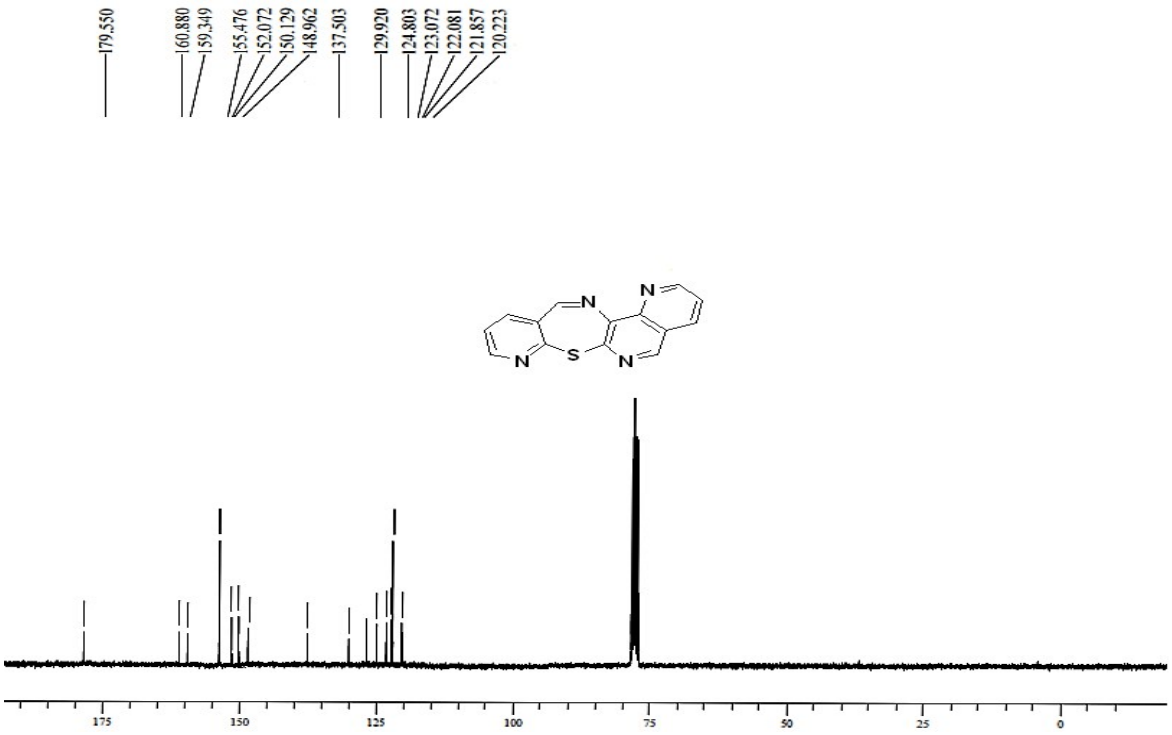


Fig. S21 ^{13}C-NMR spectrum of compound 1a

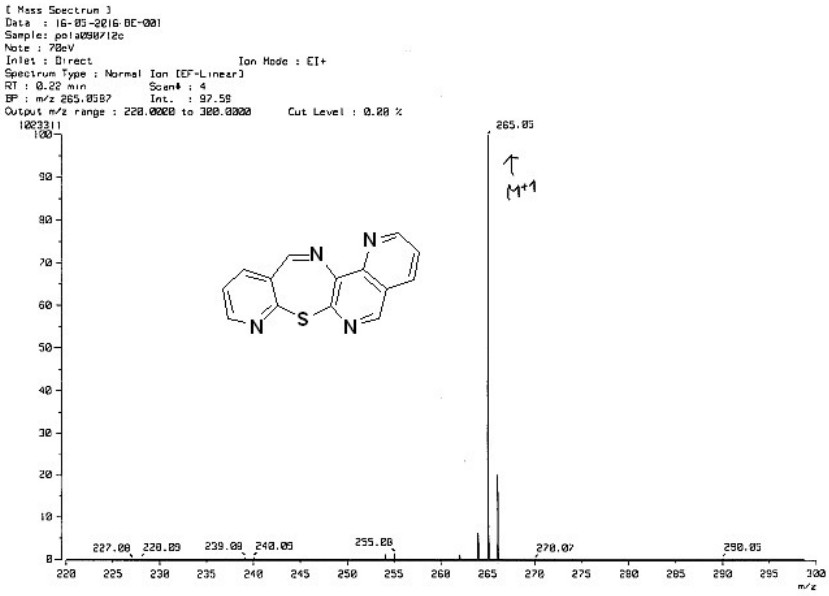


Fig. S22 Mass spectrum of compound 1a

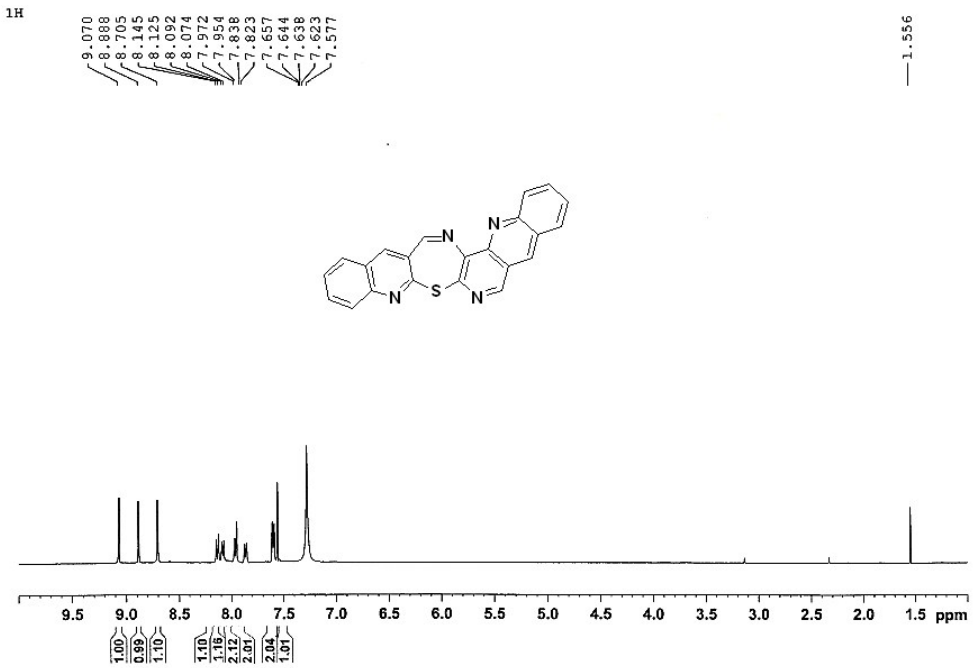


Fig. S23 ^{1}H-NMR spectrum of compound 1b

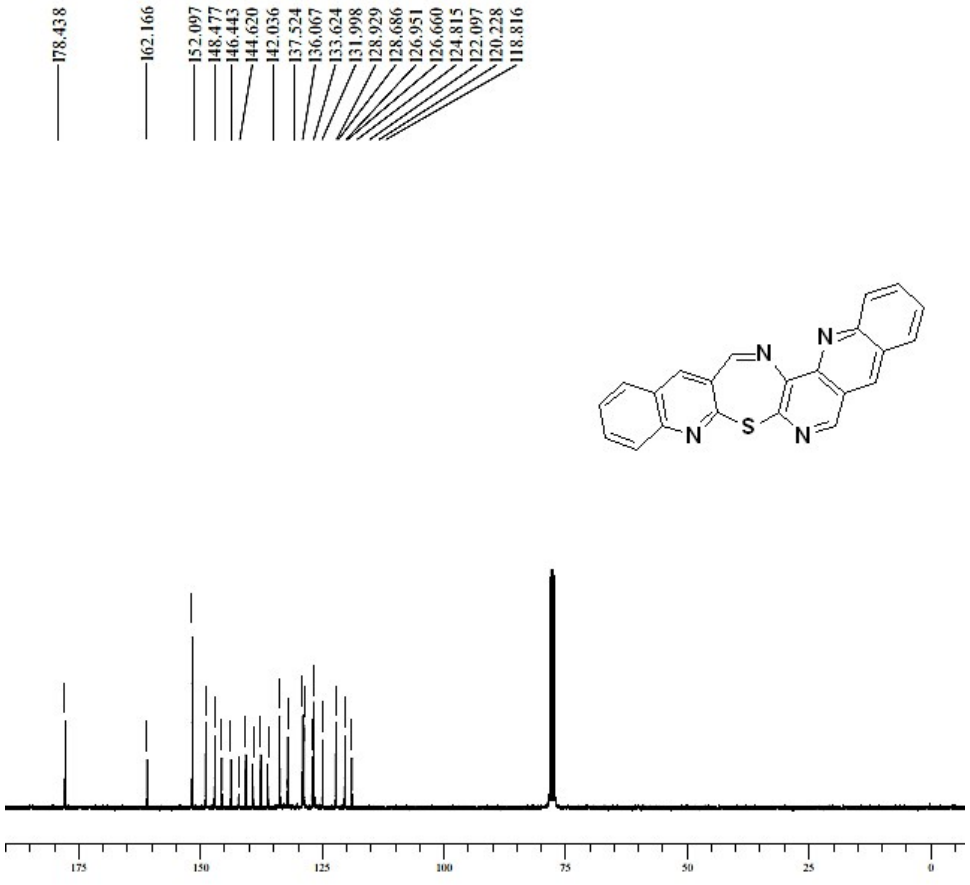


Fig. S24 ^{13}C-NMR spectrum of compound 1b

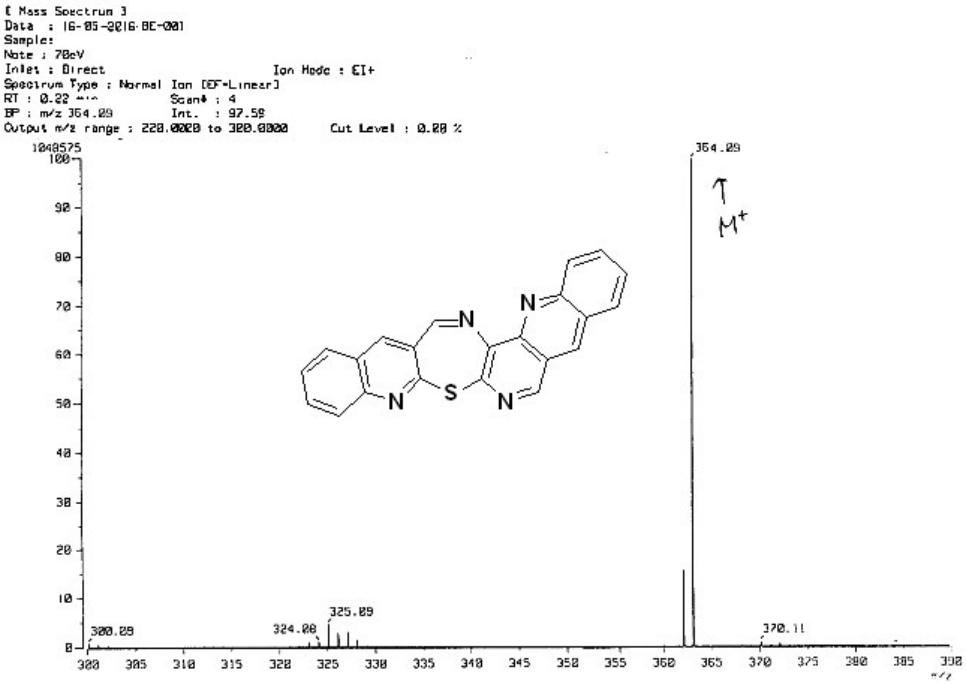


Fig. S25 Mass spectrum of compound 1b

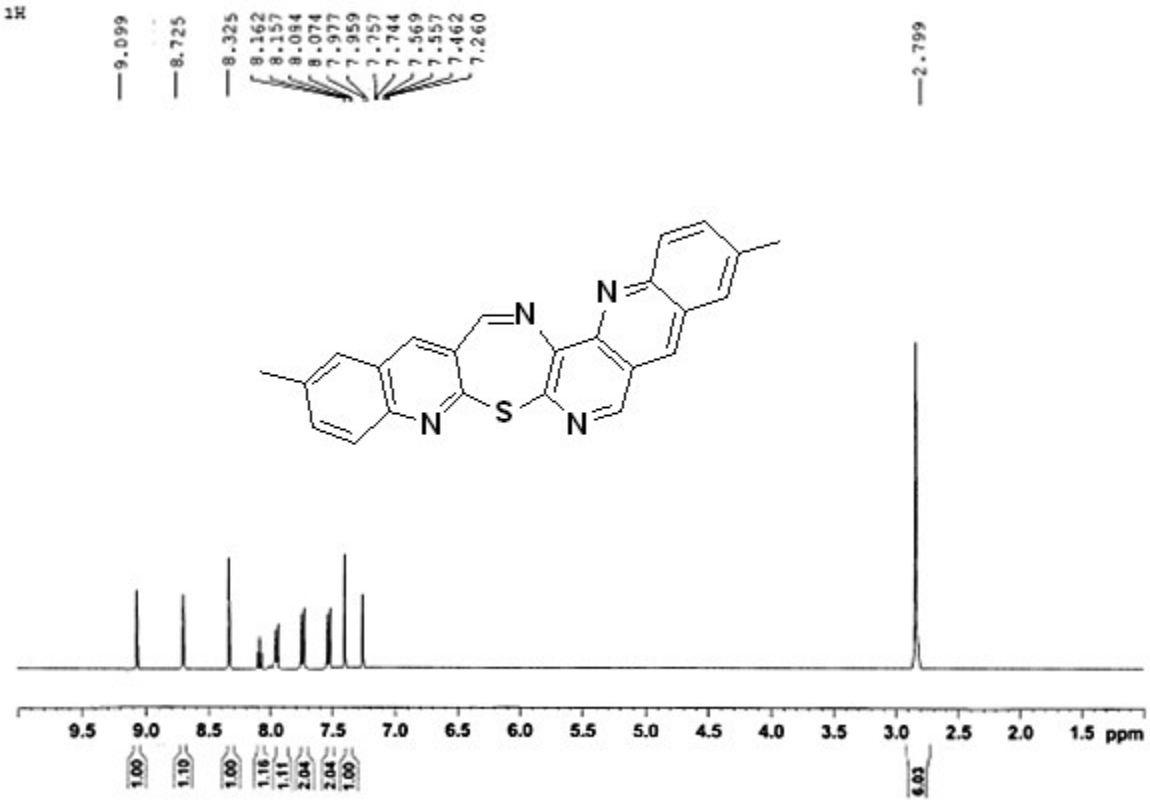


Fig. S26 ^{1}H-NMR spectrum of compound 1c

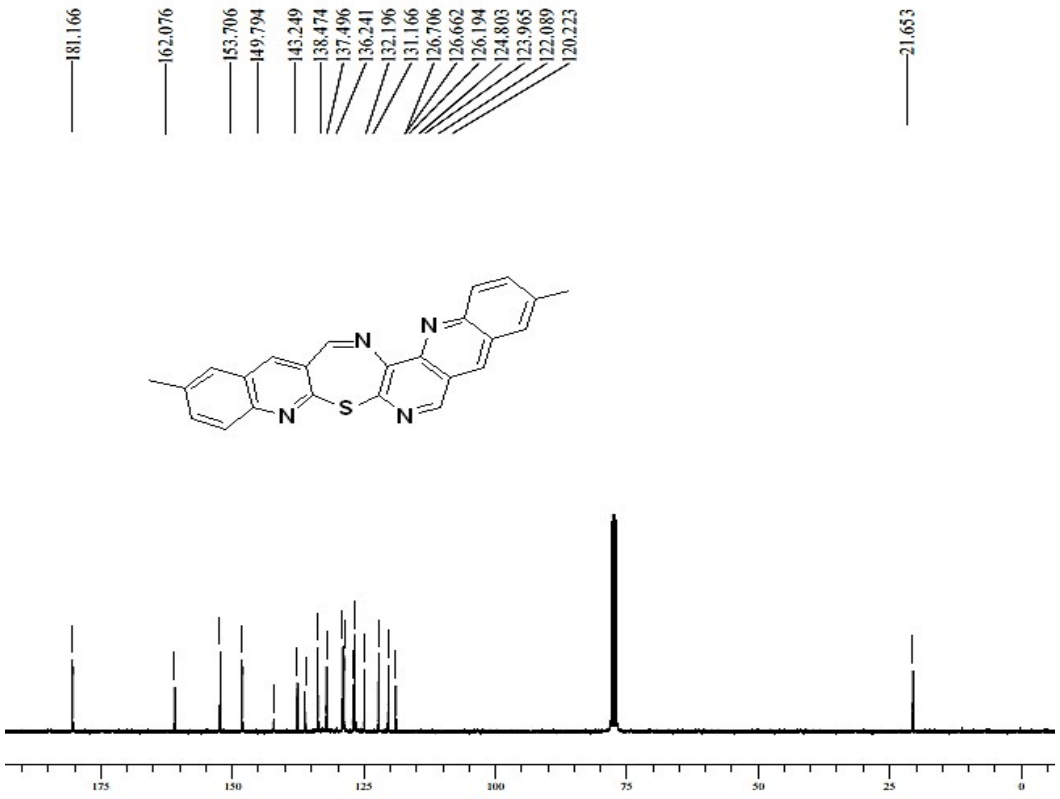


Fig. S27 ^{13}C-NMR spectrum of compound 1c

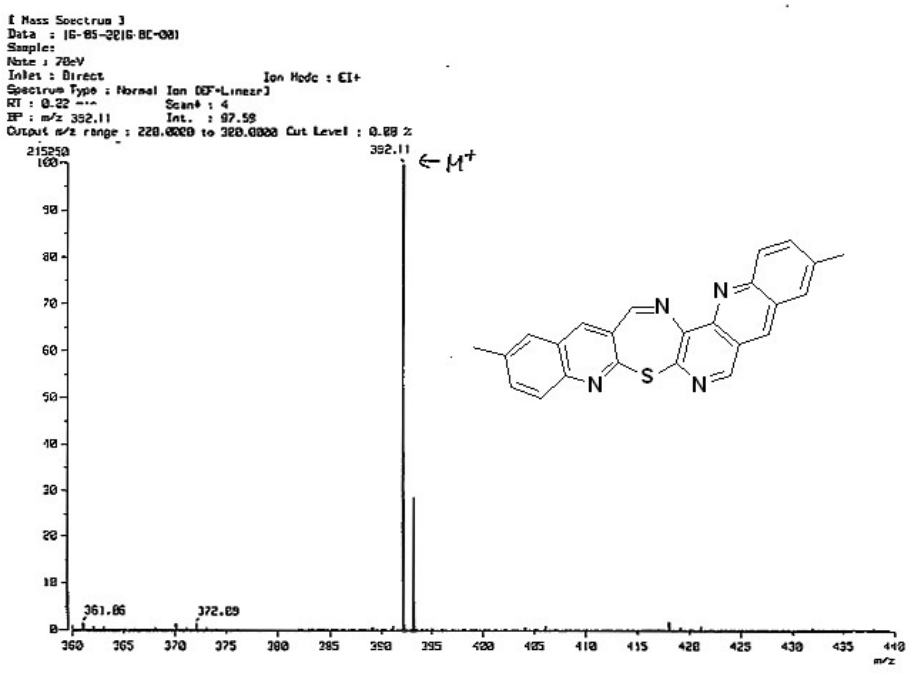


Fig. S28 Mass spectrum of compound 1c

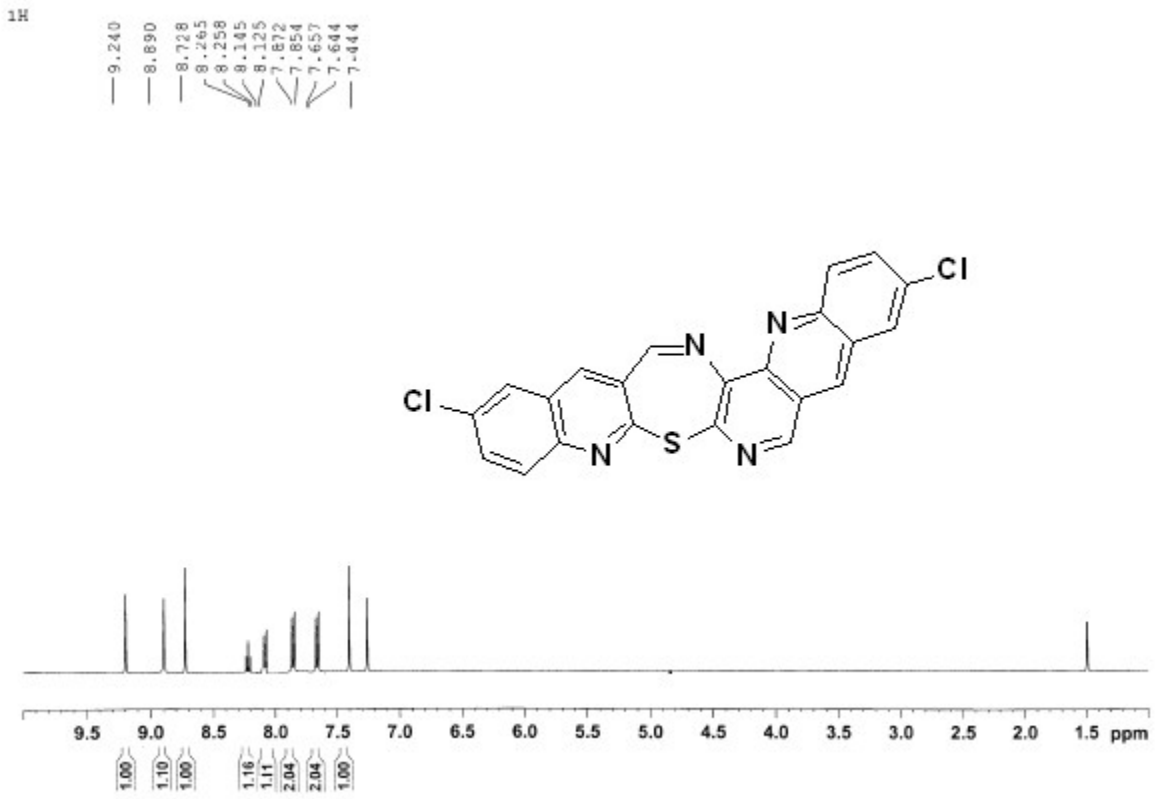


Fig. S29 ^{1}H-NMR spectrum of compound 1d

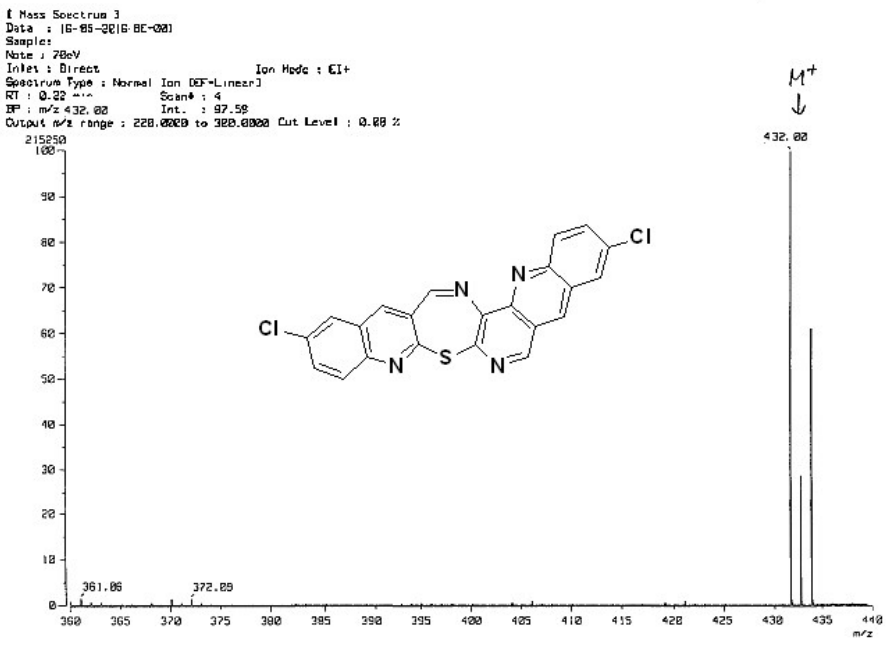


Fig. S30 Mass spectrum compound 1d

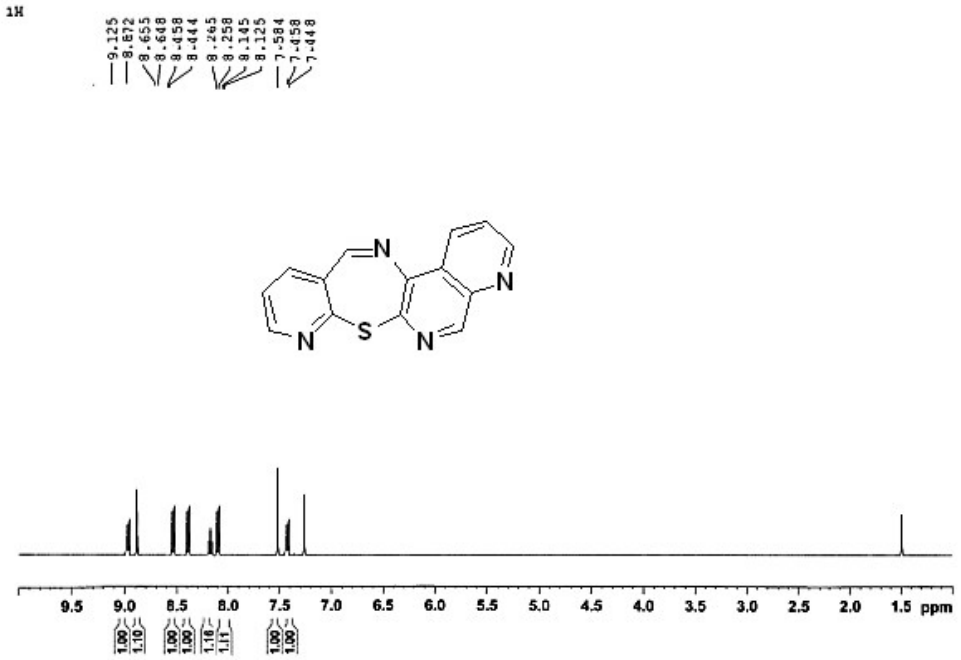


Fig. S31 ^{1}H-NMR spectrum of compound 1f

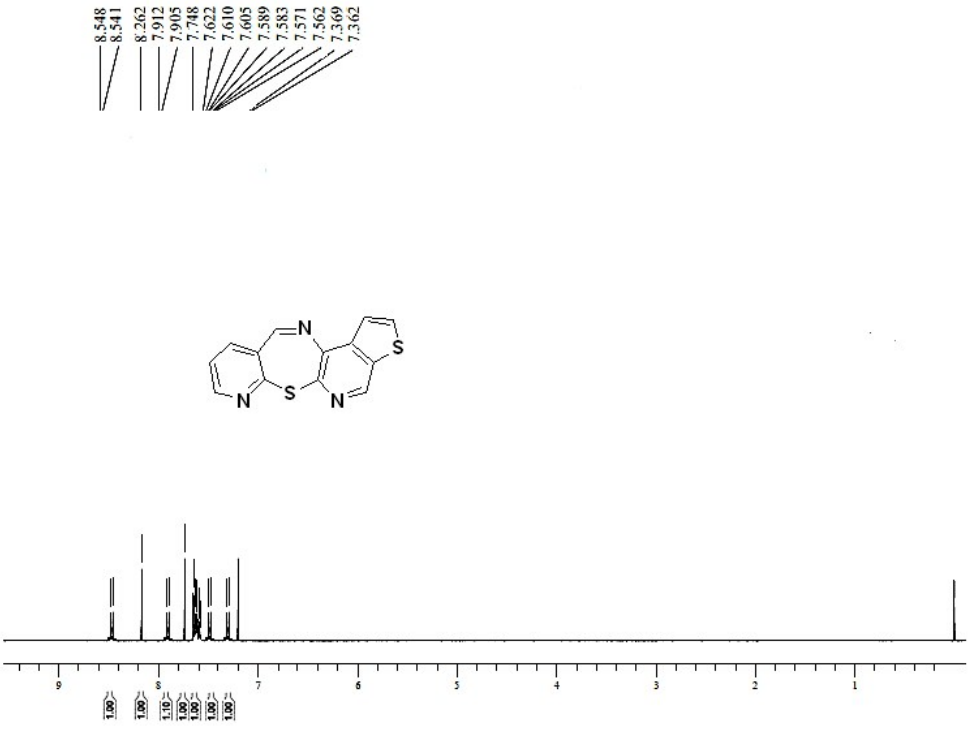


Fig. S32 ^{1}H-NMR spectrum of compound 1g

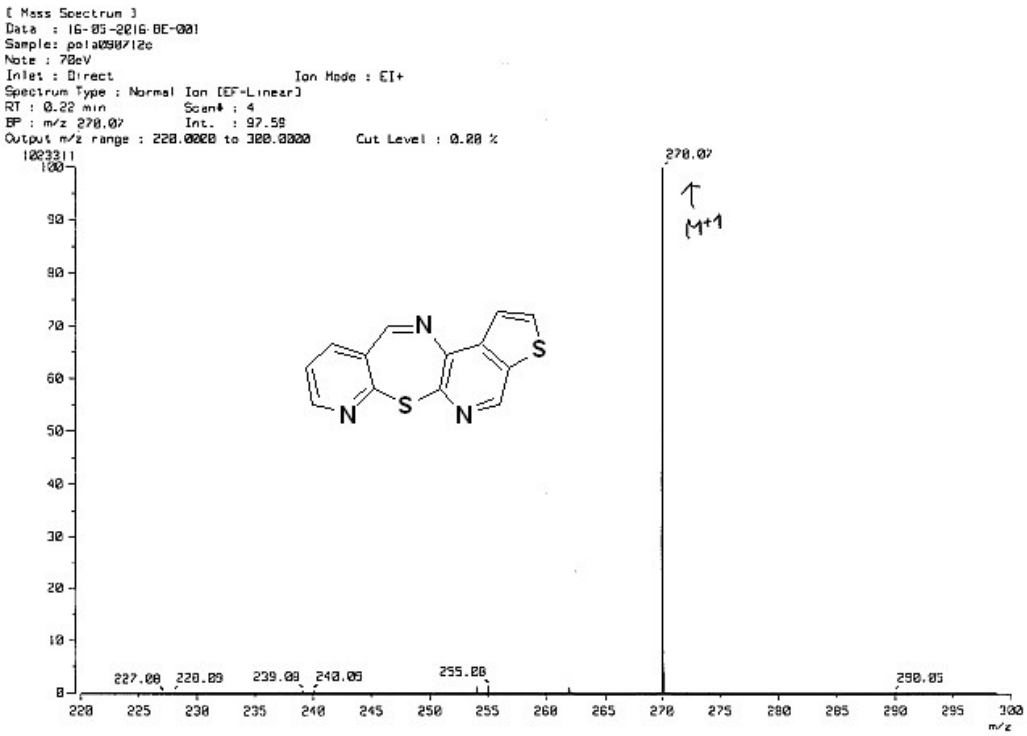


Fig. S33 Mass spectrum of compound 1g

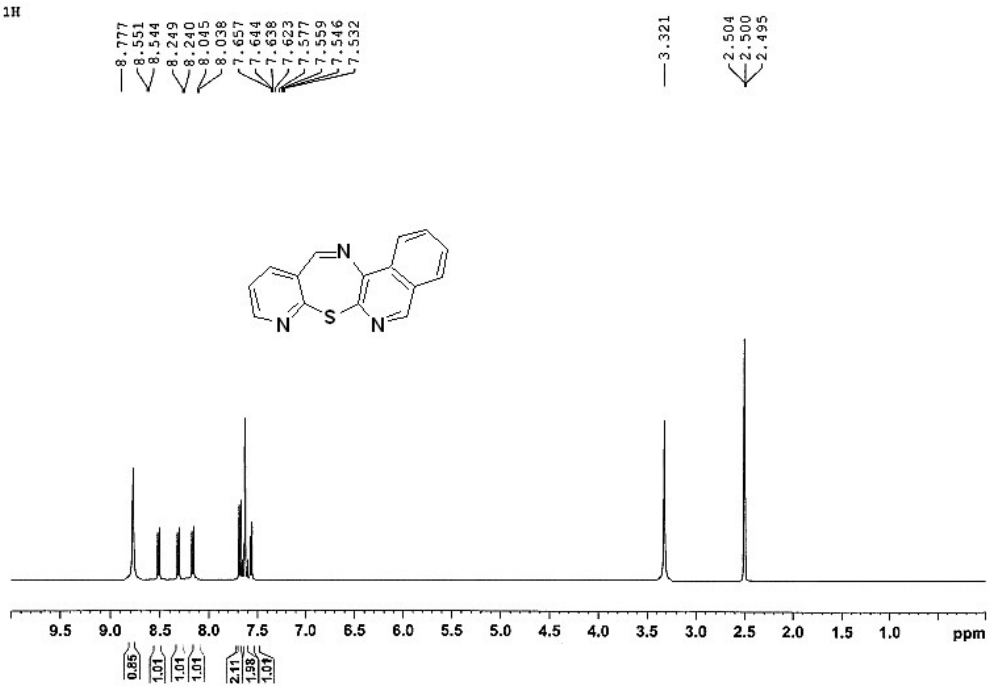


Fig. S34 ^{1}H-NMR spectrum of compound 1h

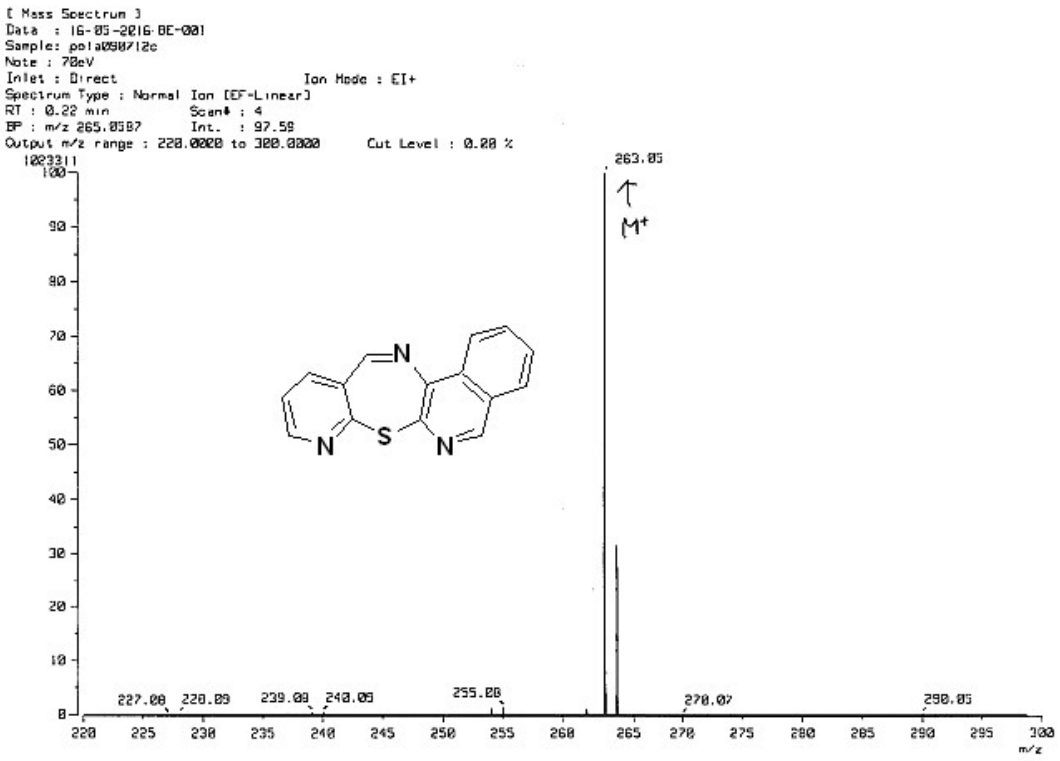


Fig. S35 Mass spectrum of compound 1h

Table S1: Absorption energies (λ nm), Oscillator strength (*f*), Transitions and Weight in % of ligands calculated at TD-B3LYP/6-31G (d, p) level of theory for B3LYP/6-31G (d, p) optimized geometries.

Name	State	λ_{abs}	*f*	Transition	% Ci
L1	S1	338	0.008	H-2 -> L	8
				H -> L	88
	S2	319	0.033	H-2 -> L	80
				H-1 -> L	5
				H -> L	8
	S3	308	0.027	H-2 -> L	3
				H-1 -> L	86
				H -> L+1	8
	S4	290	0.054	H-3 -> L	4
				H-2 -> L+1	35
				H-2 -> L+3	5
				H-1 -> L	3
				H -> L+1	44
	S5	285	0.020	H-3 -> L	3
				H-2 -> L+1	34
				H-2 -> L+3	4
				H-1 -> L	5

				H -> L+1	46
L2	S1	382	0.019	H-1 -> L	51
				H -> L	45
	S2	359	0.002	H-2 -> L+1	2
				H-1 -> L	40
				H -> L	47
				H -> L+1	5
	S3	354	0.007	H-3 -> L	2
				H-1 -> L	3
				H-1 -> L+1	49
				H -> L	5
				H -> L+1	37
	S4	340	0.007	H-2 -> L	49
				H-1 -> L+1	23
				H -> L+1	24
	S5	327	0.001	H-2 -> L	48
				H-1 -> L	2
				H-1 -> L+1	21
				H -> L+1	26

Table S2: Absorption energies (λ nm), Oscillator strength (*f*), Transitions and Weight in % of metal complexes calculated at TD-B3LYP/6-31G (d, p) level of theory for B3LYP/6-31G (d, p) optimized geometries.

Name	**State**	**λ_{abs}**	***f***	**Transition**	**% Ci**
L1-Pd	S1	384	0.008	H-3 -> L	4
				H-2 -> L+1	82
				H -> L+1	12
	S2	381	0.002	H-3 -> L+1	30
				H-2 -> L	52
				H -> L	14
	S3	378	0.002	H-3 -> L+1	10
				H-1 -> L+1	15
				H-1 -> L+2	2
				H -> L	71
	S4	377	0.038	H-3 -> L+1	56
				H-2 -> L	38
	S5	372	0.030	H-3 -> L	91
				H-2 -> L+1	4
				H-2 -> L+2	3
L2-Pd	S1	477	0.023	H -> L	93
	S2	445	0.051	H-5 -> L	5
				H-1 -> L	90
	S3	411	0.011	H-4 -> L	22
				H-2 -> L	75
	S4	411	0.154	H-10 -> L	4
				H-5 -> L	31

				H-3 -> L	26
				H -> L+1	34
	S5	409	0.023	H-4 -> L	74
				H-2 -> L	23