Electronic Supplementary Information

Decoding Ligand Influence in Porphyrin-Nickel Photocatalysts for Degradation of Rhodamine B

*Nur Jalal Mondal[1, 5], Tanmi Kundu[1], Bitupan Mohan[1, 5], Eman Ali Sk[2], Mritunjoy Prasad Ghosh[1], Ijaz Ullah Muzaddadi[3], Suvankar Deka[4, 5], Horsita Kalita[4, 5], Biswajit Choudhury[4, 5], Devasish Chowdhury[1, 5, *]*

[1]Material Nanochemistry Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Paschim Boragaon, Garchuk, Guwahati-781035, Assam, India

[2]Department of Chemistry, Indian Institute of Technology, Guwahati, Assam, India

[3]Department of Chemistry, North Eastern Regional Institute of Science and Technology (NERIST), Itanagar, Papum Pare (District), 791109, Nirjuli, Arunachal Pradesh, India

[4]Materials and Energy Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology (IASST), Paschim Boragaon, Vigyan Path, Assam-781035, India

[5]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, Uttar Pradesh, India.

[*]Corresponding author Email: devasish@iasst.gov.in

Characterization techniques

Surface morphology of the porphyrin nanocatalysts was investigated using FESEM microscopy (FESEM, JEOL-JSM 5600). For collecting absorption spectra and dye degradation data, ultraviolet–visible (UV–Vis) spectroscopy (UV-2550, Shimadzu, USA) was employed. To elucidate the photocatalytic activity exhibited by the catalyst, their photoluminescence (PL) spectra were obtained using an enhanced-performance benchtop modular photoluminescence spectrophotometer (Model: QM08075–21-C, Make: Horiba instruments). The proton (^{1}H), carbon (^{13}C) and fluorine ^{19}F NMR spectra were recorded on a Bruker spectrometer operating at 600 MHz, (151 MHz, 125 MHz) and 565 MHz, respectively, at IIT, Guwahati. TMS is used as an internal reference; chemical shifts (δ scale) are reported in parts per million (ppm). ^{1}H NMR spectra are reported in the order of multiplicity, coupling constant (J value) in Hertz (Hz), and the number of protons; signals were characterised as s (singlet), and d (doublet). All NMR experiments were conducted at 298.15 K. All the samples were prepared in $CDCl_3$, stirred thoroughly, sonicated, and allowed to equilibrate overnight at room temperature before measurement. NMR data were processed using MestReNova (14.3.3). HRMS spectra were recorded on an ESI mass analyzer. Elemental analysis was done using CHNSO Analyser (Model: FLASH Smart, Thermo). The crystal structure was determined using a single-crystal XRD diffractometer. Complete crystallographic data of compounds (CCDC no. 2482202) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk).

X-ray crystallographic data of compound 5,10,15,20-Tetraphenyl Ni (II) porphyrin (Ni-L_1)

Entry	Identification Code	Ni-L_1
01	Empirical formula	C_{44} H_{28} N_4 Ni, C_{44} H_{30} N_4
02	Formula weight	1286.11
03	Temperature	298 K
04	Wavelength	0.71073
05	Radiation type	Mo k\α
06	Radiation system	Fine-focus sealed tube
07	Crystal system	Tetragonal I
08	Space group	I 21 21 21
09	Cell length (Å)	(a)=15.0803(11), (b)=13.8787(10), (c)=15.0818(11)
10	Cell angle (°)	(α)=90, (β)=90, (γ)=90
11	Cell volume (Å^3)	3156.5(4)
12	Density	1.353
13	Absorption correction	Multi-scan
14	Reflection number	4888 [2704]
15	Cell formula units Z	2
16	CCDC no	2482202

Table T1: Crystal data and structure refinement for compound ATK-ES-5-P

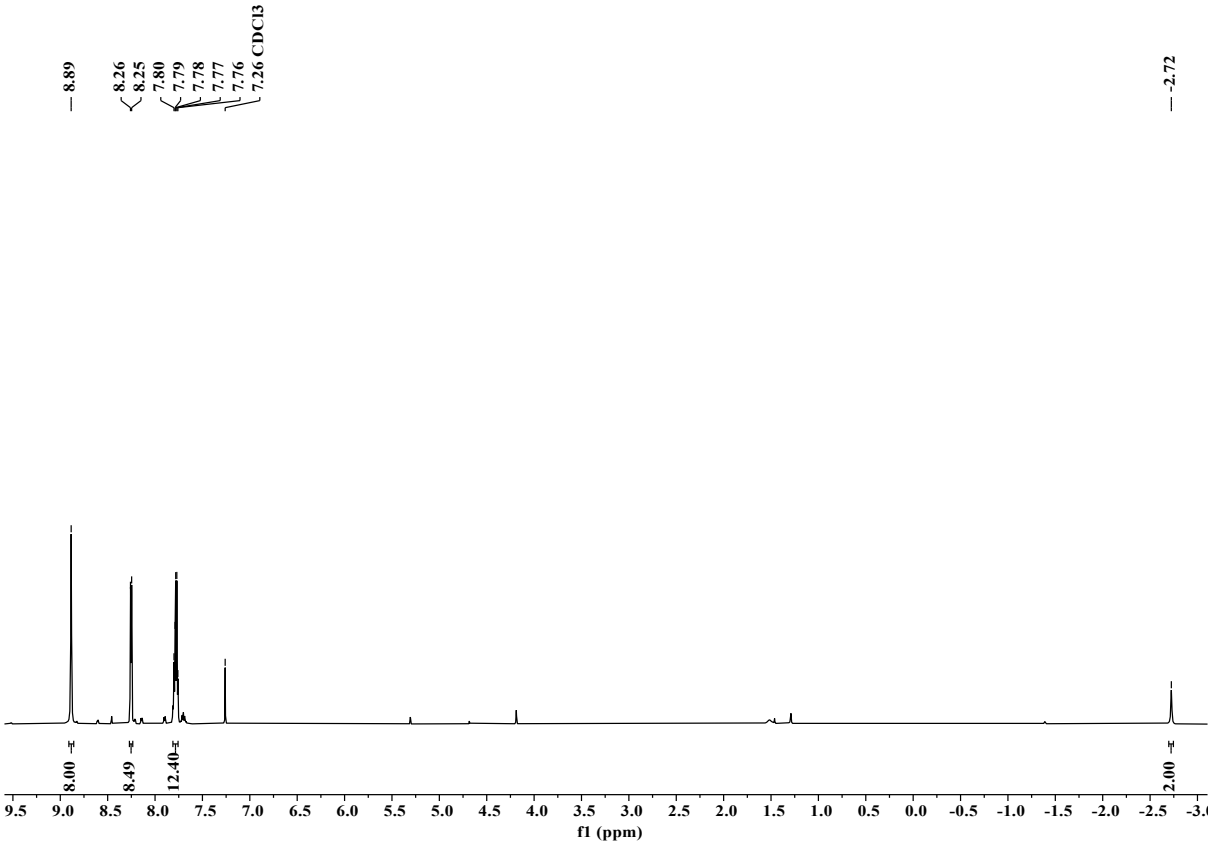

Figure S1.1. A. ^{1}H spectrum of L_1 recorded in $CDCl_3$ at room temperature

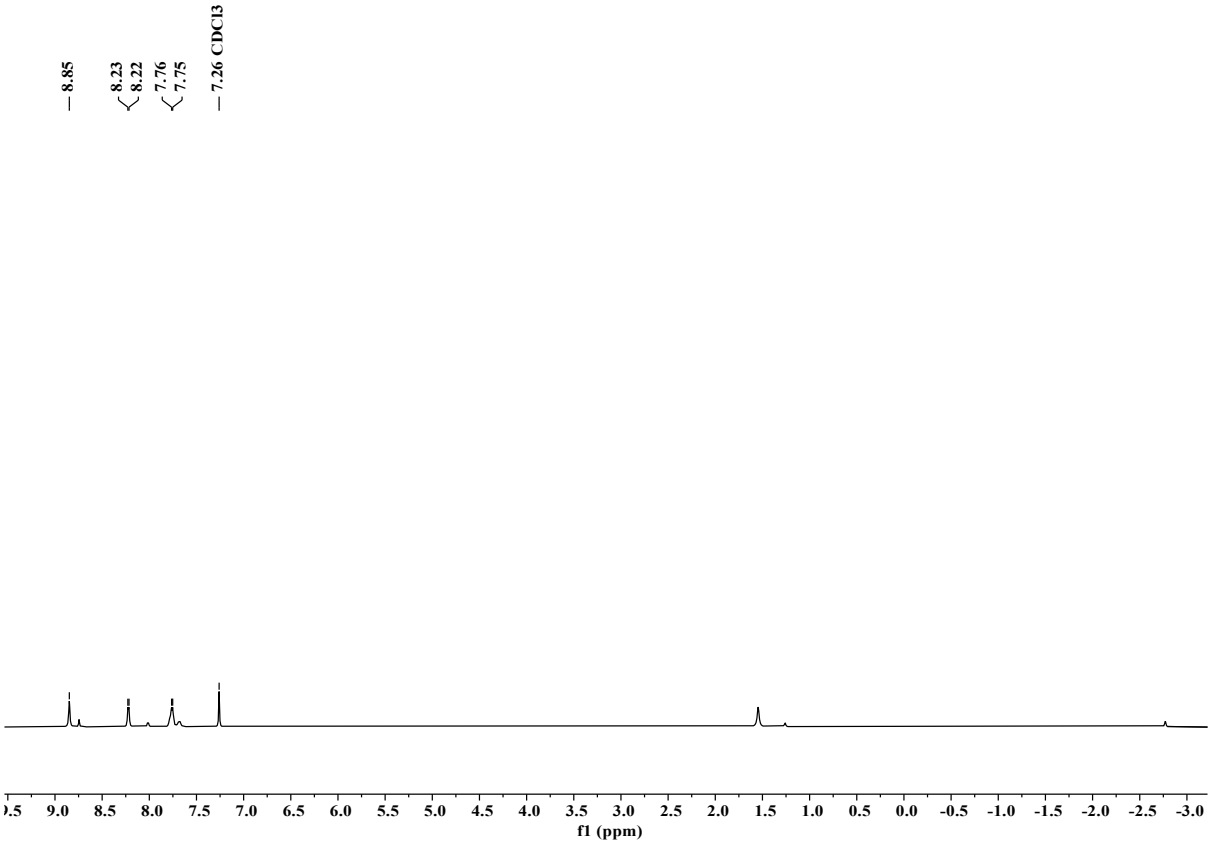

Figure S1.1. B. ^{1}H spectrum of Ni-L_1 recorded in $CDCl_3$ at room temperature

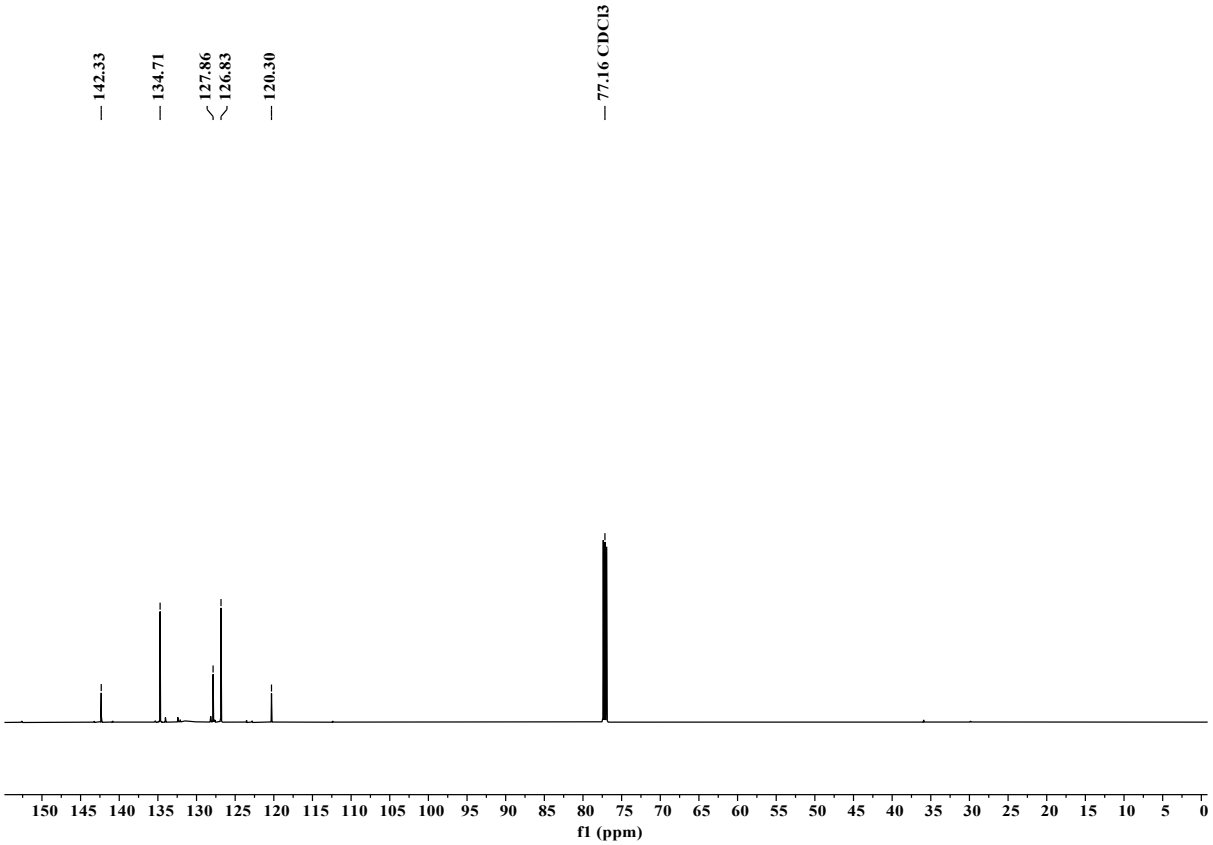

Figure S1.1. C. ^{13}C spectrum of L_1 recorded in $CDCl_3$ at room temperature

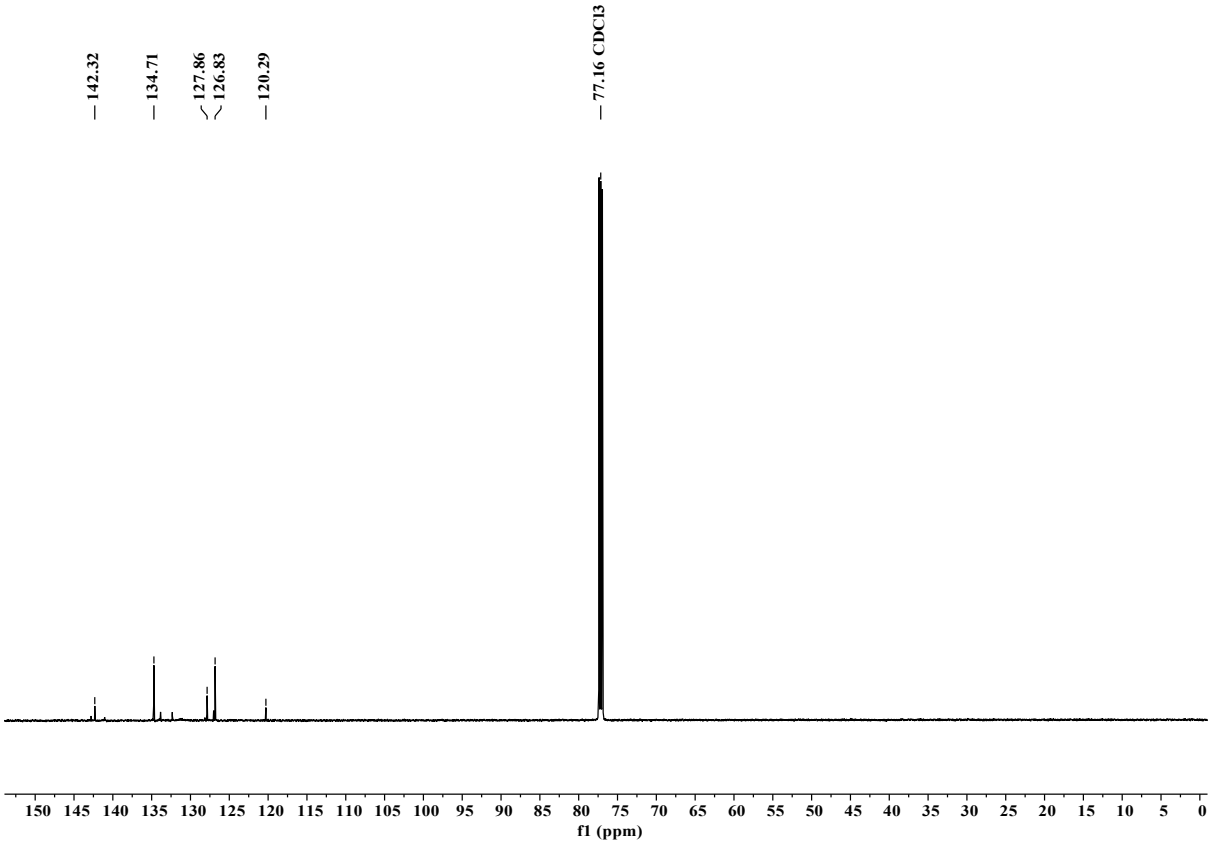

Figure S1.1. D. ^{13}C spectrum of Ni-L_1 recorded in $CDCl_3$ at room temperature

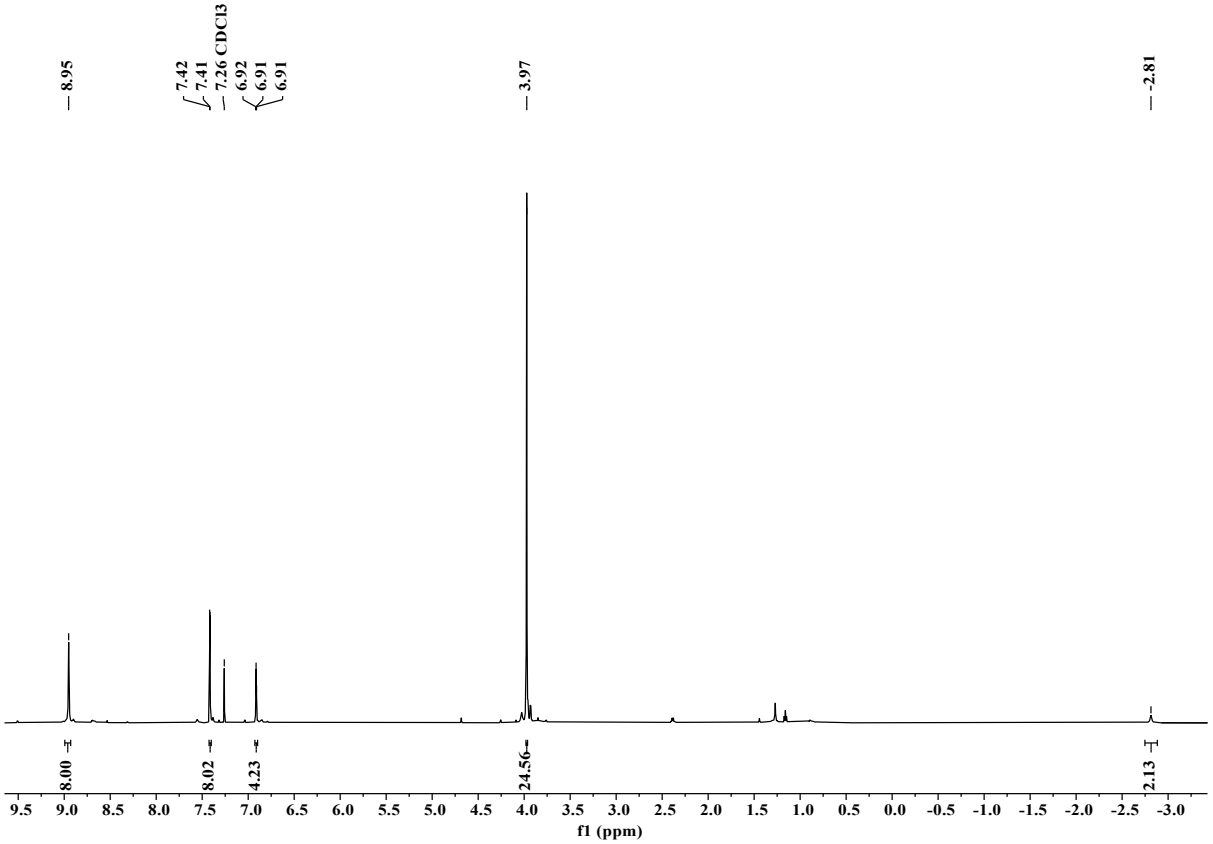

Figure S1.2. A. ^{1}H spectrum of L_2 recorded in $CDCl_3$ at room temperature

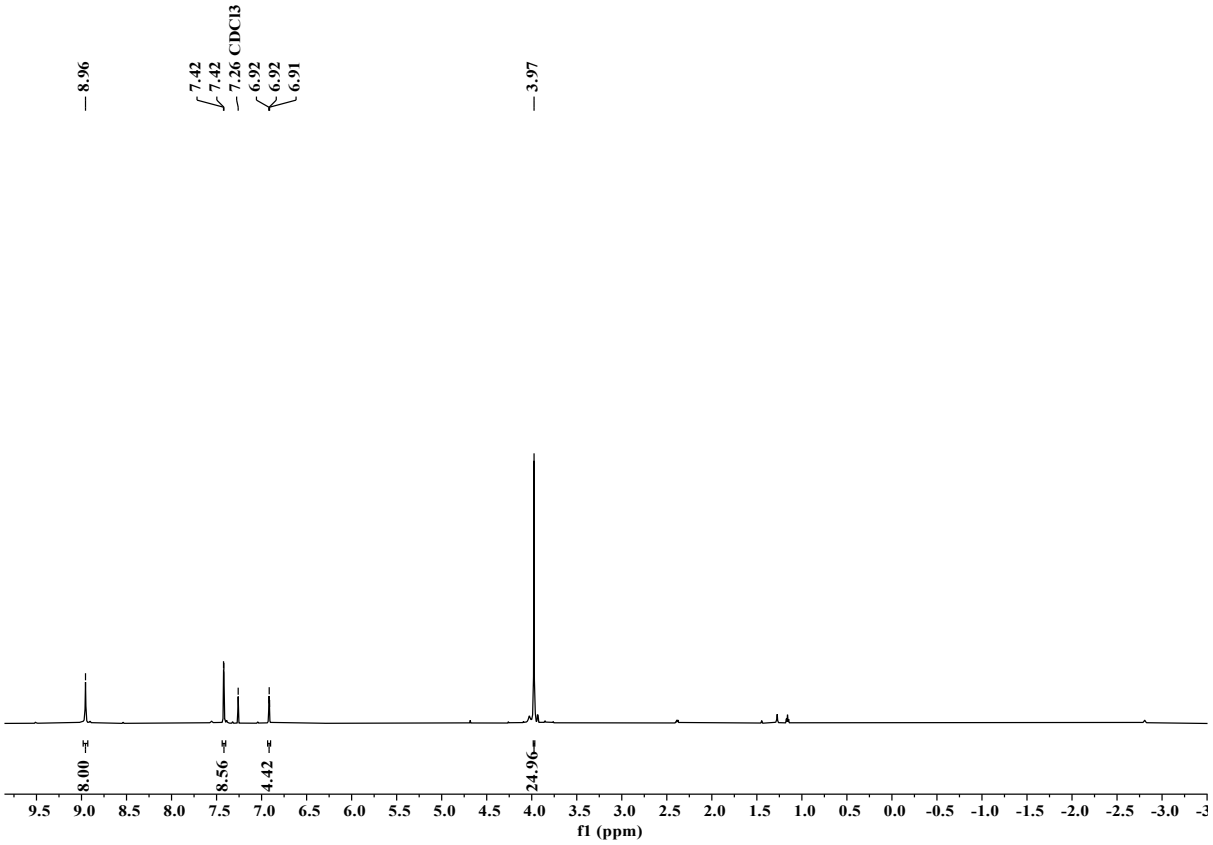

Figure S1.2. B. ^{1}H spectrum of Ni-L_2 recorded in $CDCl_3$ at room temperature

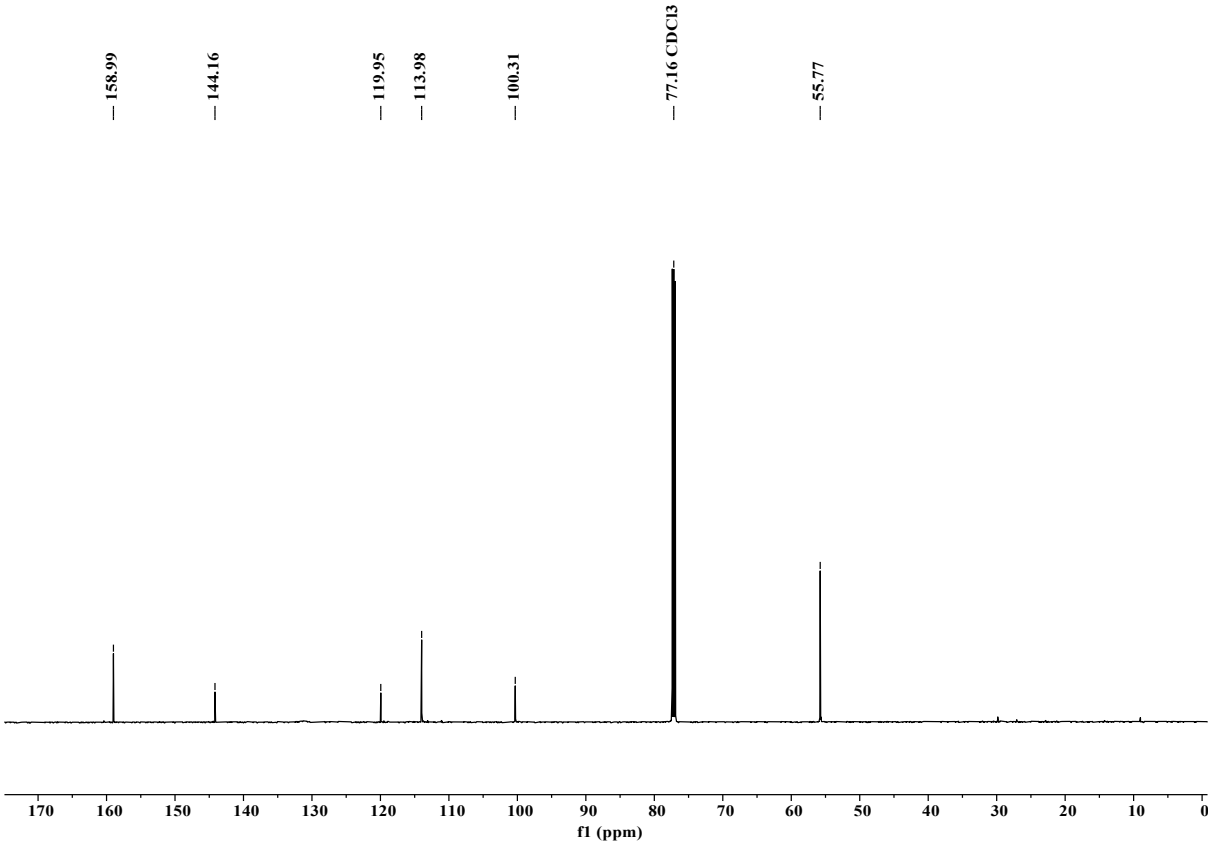

Figure S1.2. C. ^{13}C spectrum of L_2 recorded in $CDCl_3$ at room temperature

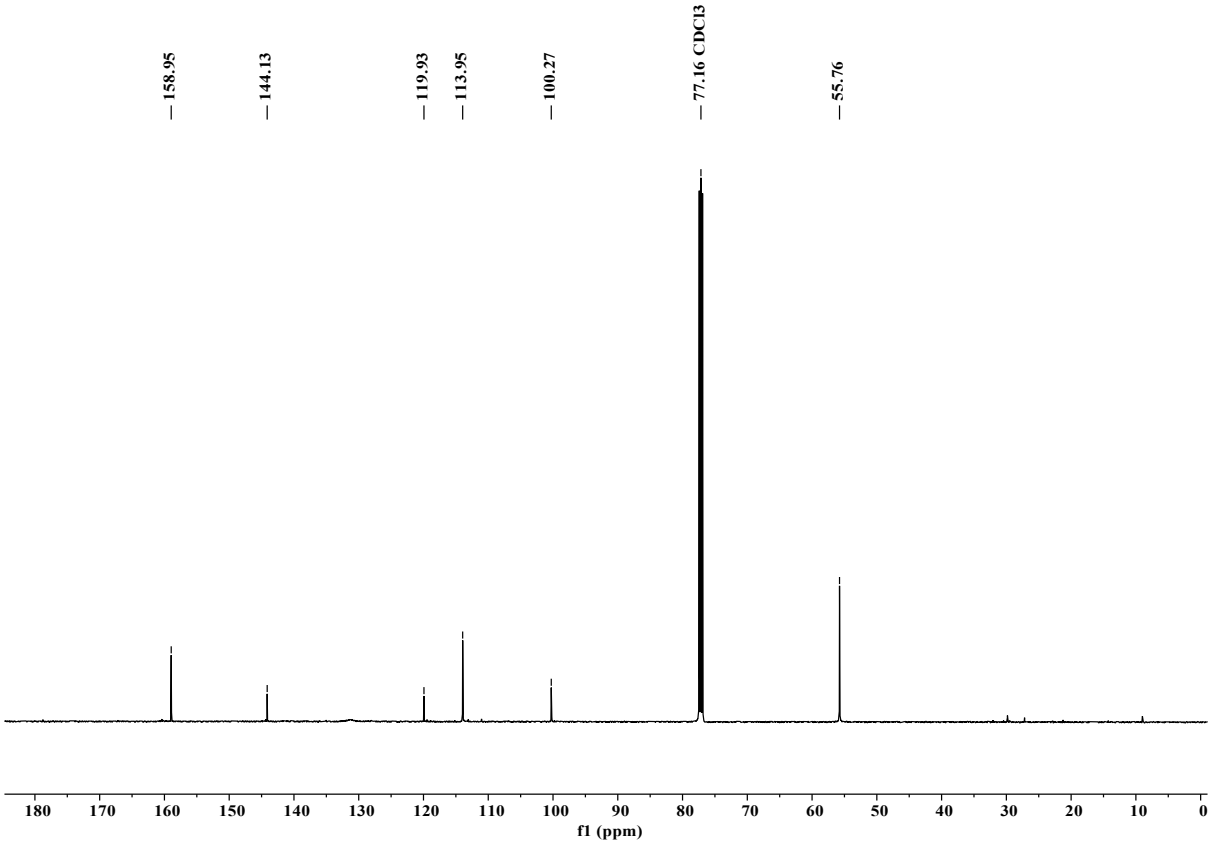

Figure S1.2. D. ^{13}C spectrum of Ni-L_2 recorded in $CDCl_3$ at room temperature

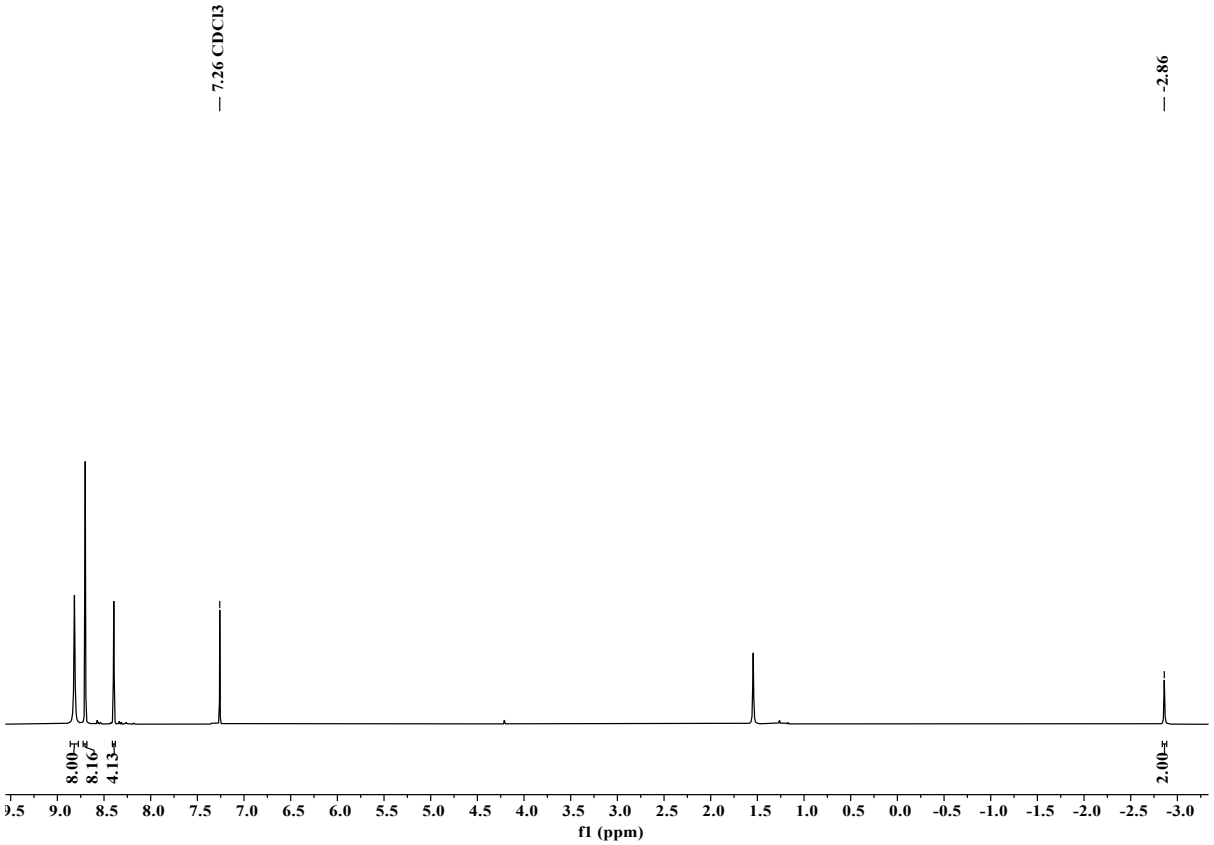

Figure S1.3. A. ^{1}H spectrum of L_3 recorded in $CDCl_3$ at room temperature

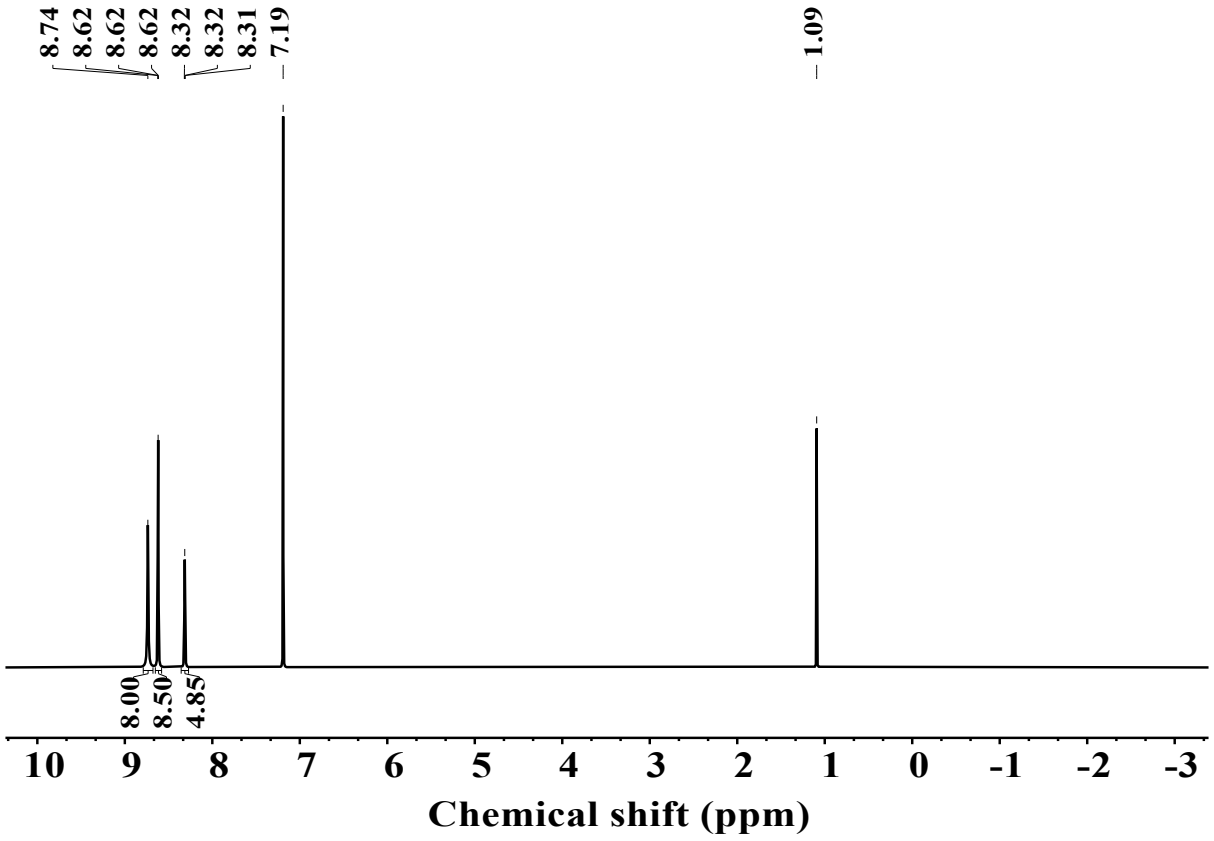

Figure S1.3. B. ^{1}H spectrum of Ni-L_3 recorded in $CDCl_3$ at room temperature

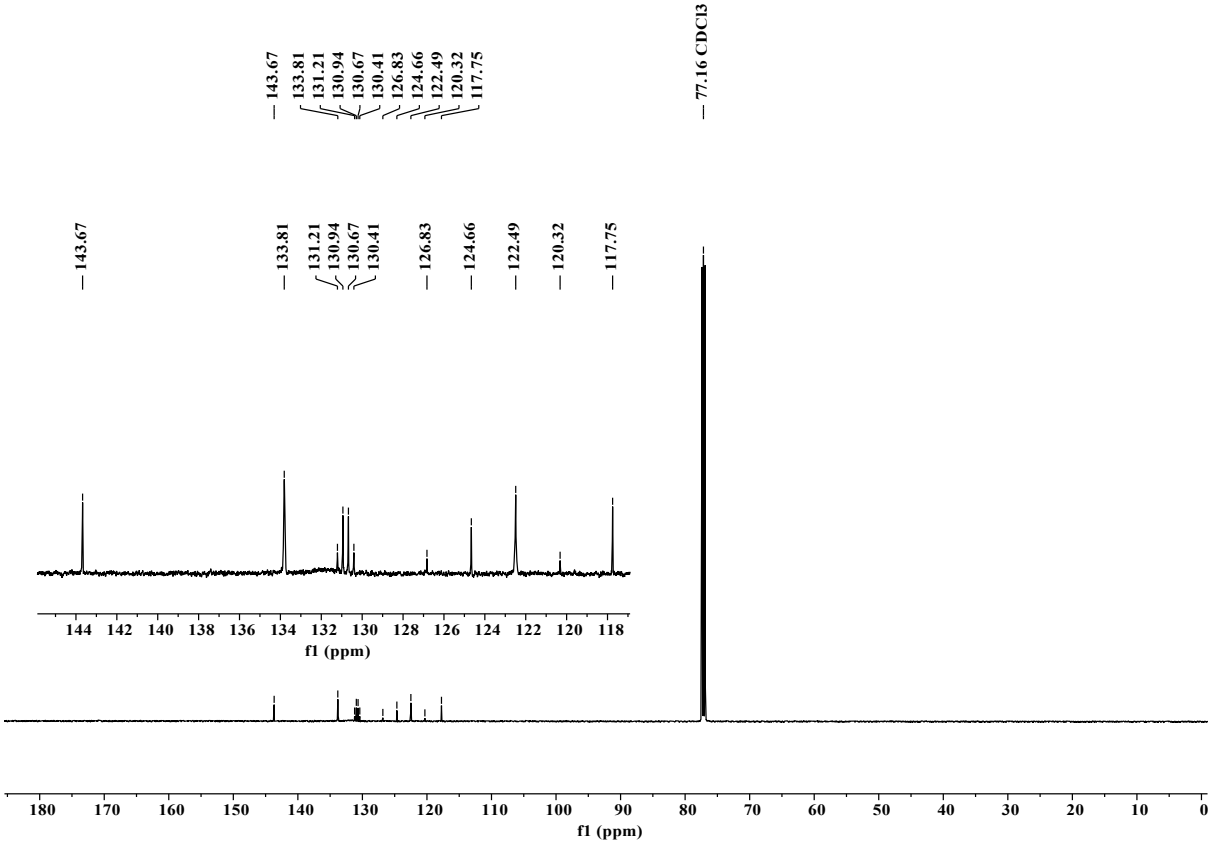

Figure S1.3. C. ^{13}C spectrum of L_3 recorded in $CDCl_3$ at room temperature

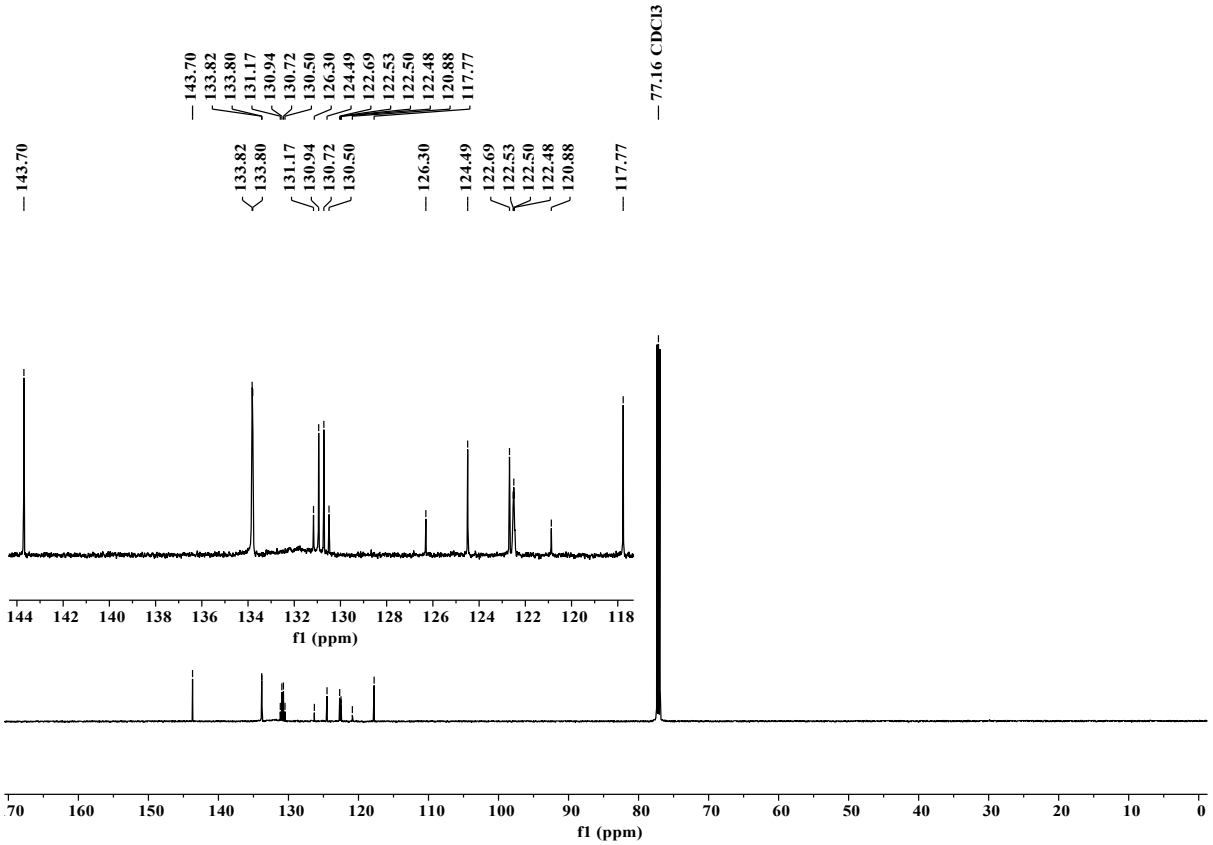

Figure S1.3. D. ^{13}C spectrum of Ni-L_3 recorded in $CDCl_3$ at room temperature

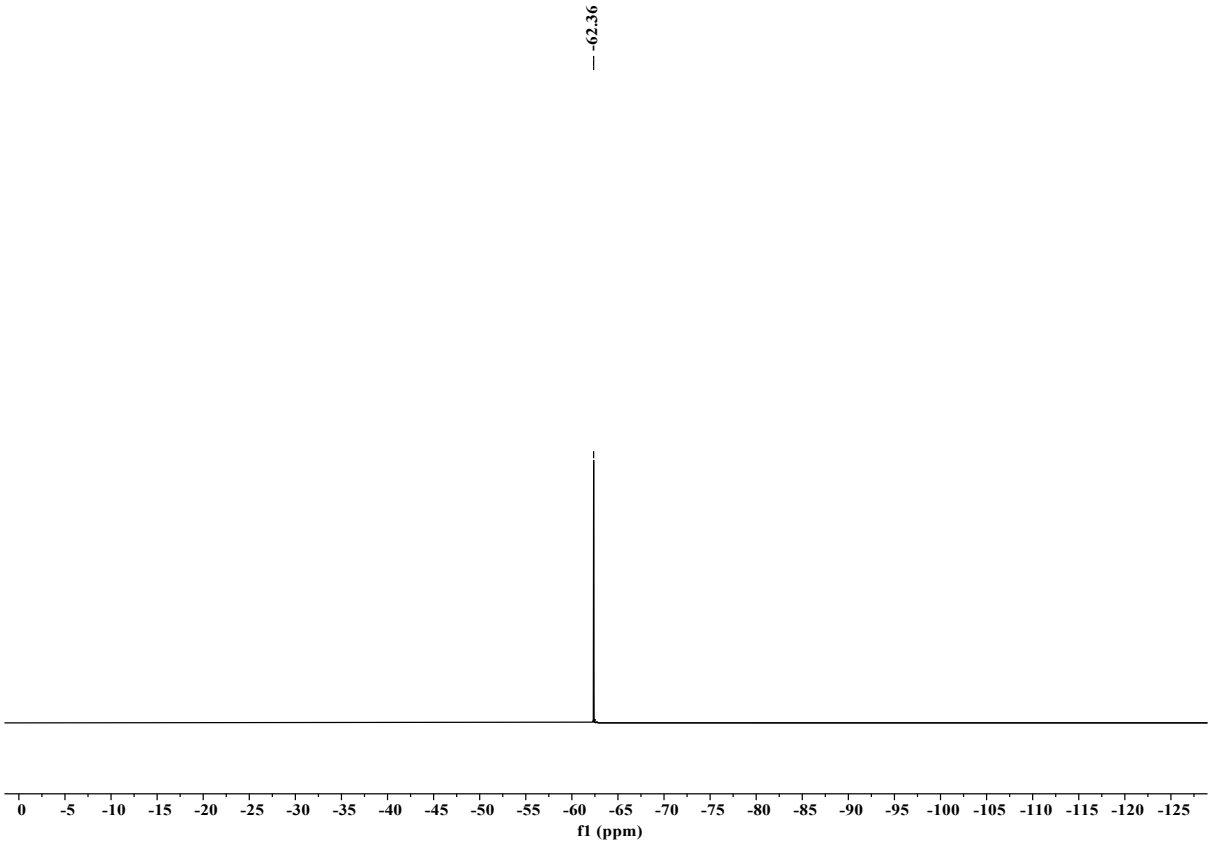

Figure S1.3. E. ^{19}F spectrum of L_3 recorded in $CDCl_3$ at room temperature

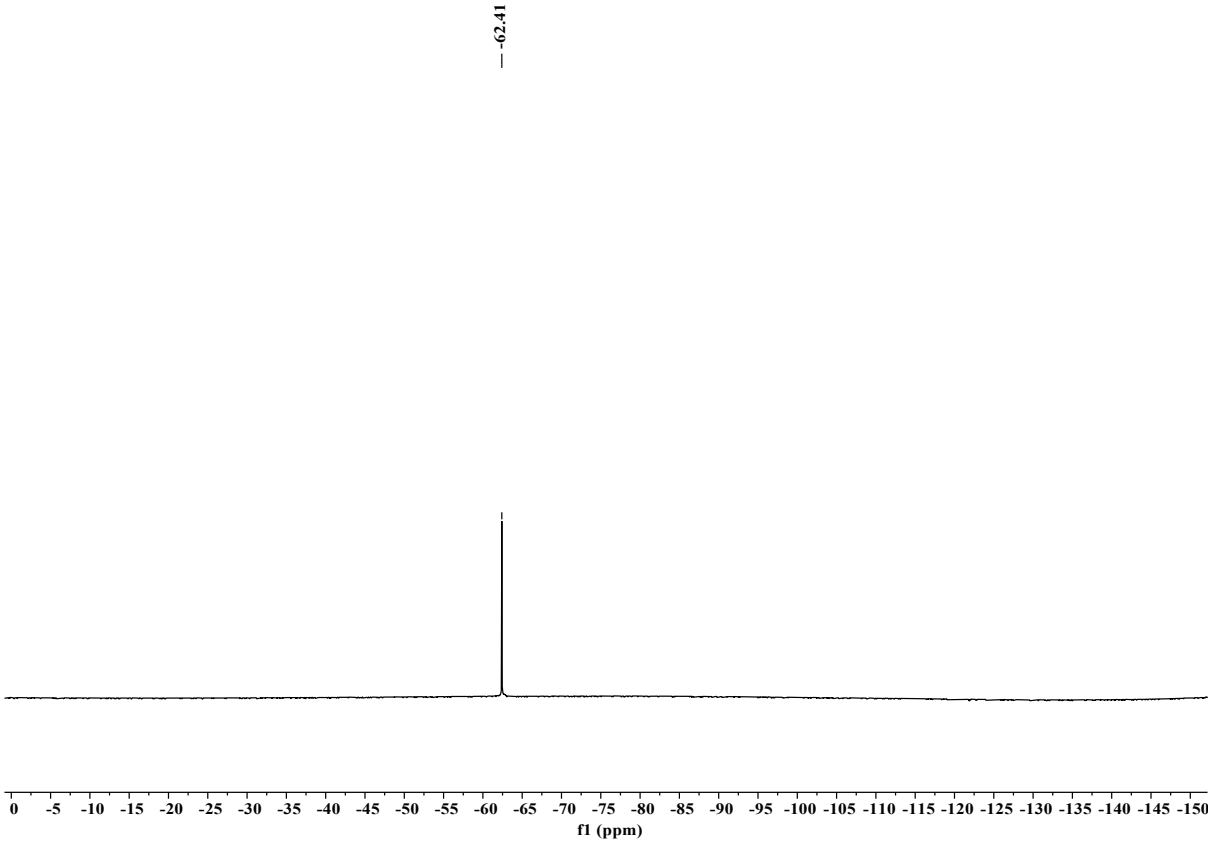

Figure S1.3. F. ^{19}F spectrum of Ni-L_3 recorded in $CDCl_3$ at room temperature

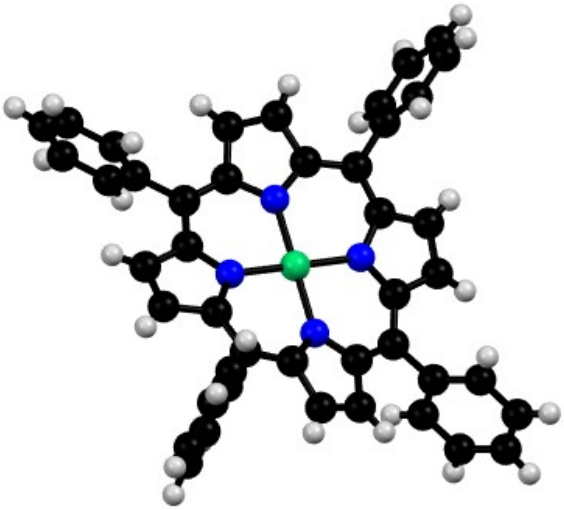

Figure S2: ORTEP Diagram (50 % probability) of compound 5,10,15,20-Tetraphenyl Ni (II) porphyrin (Ni-L_1)

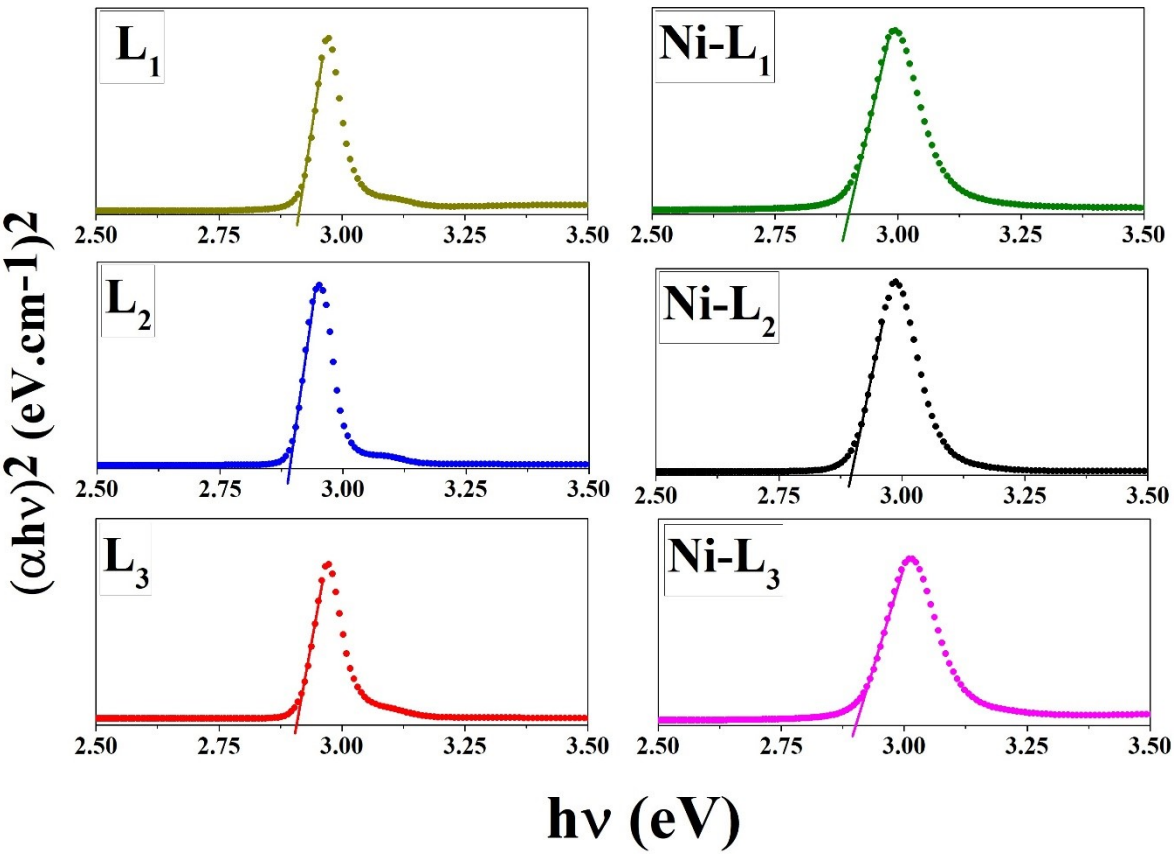

Figure S3: Tauc plot obtained at 300 K for the entire sample.

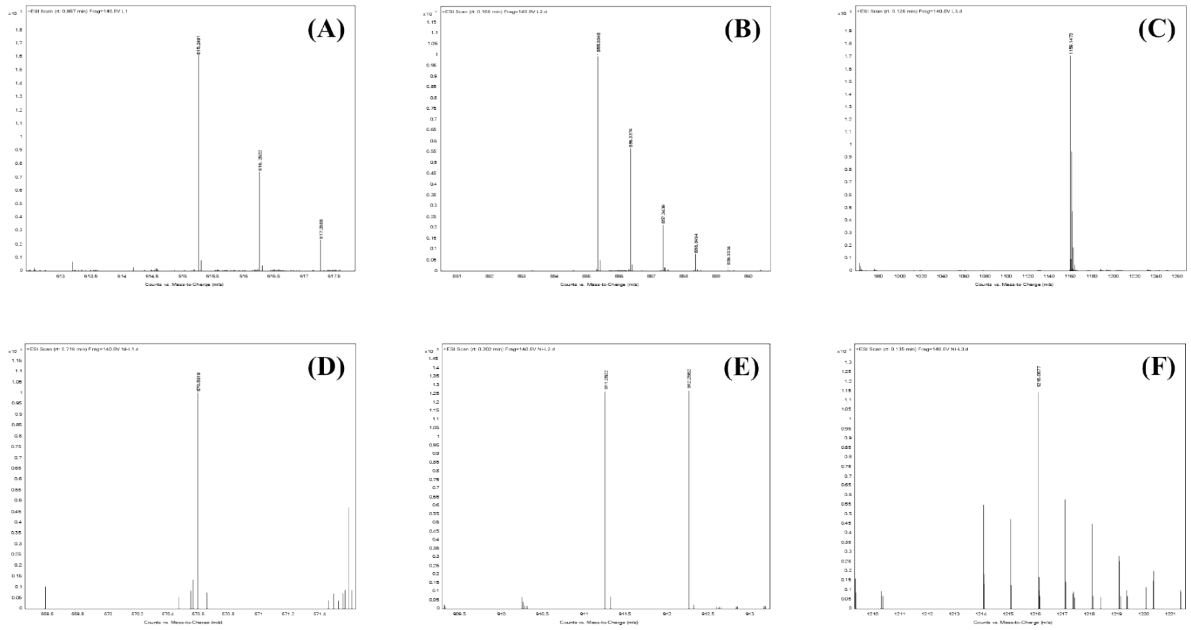

Figure S4: High-resolution mass spectrum (HRMS) in (A) L_1, (B) L_2, and (C) L_3 and (D) Ni-L_1, (E) Ni-L_2 and (F) Ni-L_3, respectively

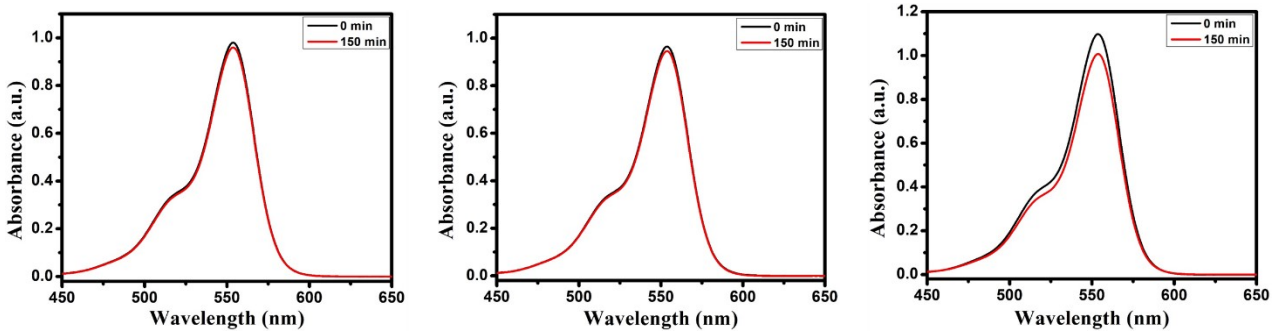

Figure S5: Control experiments: RhB dye degradation in the dark, using only light, and using only the catalyst, respectively (from left to right)

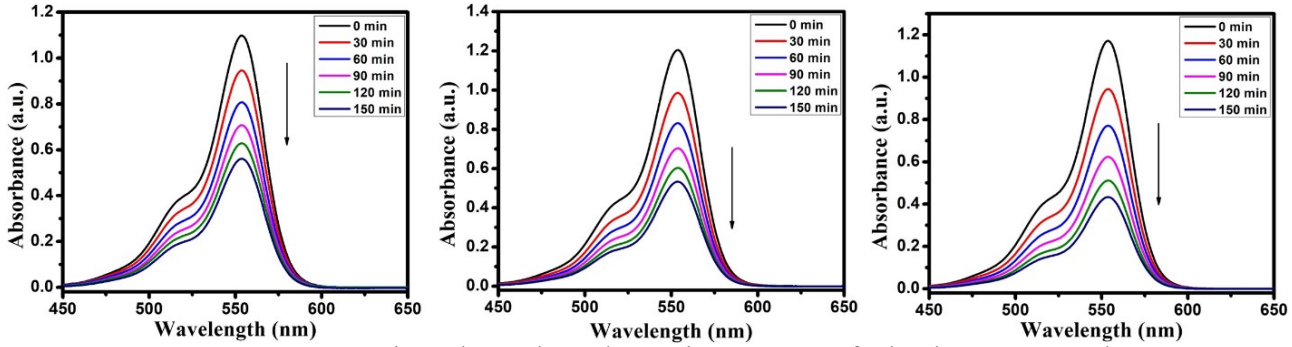

Figure S6: Time-dependent absorption spectra of RhB by L_1, L_2, and L_3

Parameters	L_1	L_2	Ni-L_2	Ni-L_3

R1	3.912	4.612	4.082	3.772
R2	6.271	2.23E+01	11.72	8.61
R3	47.26	23.28	80.41	43.78
Yo4	5.28E-06	5.11E-03	6.32E-06	4.47E-04
a5	7.83E-01	6.20E-01	7.63E-01	5.74E-01
Yo6	4.24E-02	3.87E-06	9.94E-03	1.19E-03
a7	3.27E-01	7.57E-01	6.05E-01	8.34E-01
R8	4.46E+04	5.73E+03	5.20E+03	4.38E+03
Yo9	6.45E-04	2.16E-03	3.23E-03	9.11E-04
a10	9.33E-01	9.36E-01	9.62E-01	7.74E-01
Goodness of Fit	1.60E-05	2.84E-04	1.72E-04	6.07E-04

Table T2. Fitted parameters of Nyquist Plot

Sample	**E_{CB} (V)**	**$E_{VB} \approx E_{fb}$ (V)**
L_1 (2.91 eV)	-2.05	0.86
L_2 (2.90 eV)	-2.10	0.80
Ni-L_2 (2.90 eV)	-2.06	0.84
Sample	**$E_{CB} \approx E_{fb}$ (V)**	**E_{VB} (V)**
Ni-L_3 (2.91 eV)	+0.02	2.93

Table T3. Conduction band and Valence band edge potentials of L_1, L_2, Ni-L_2 and Ni-L_3 obtained from Mott-Schottky analysis performed in 1 M KCl.

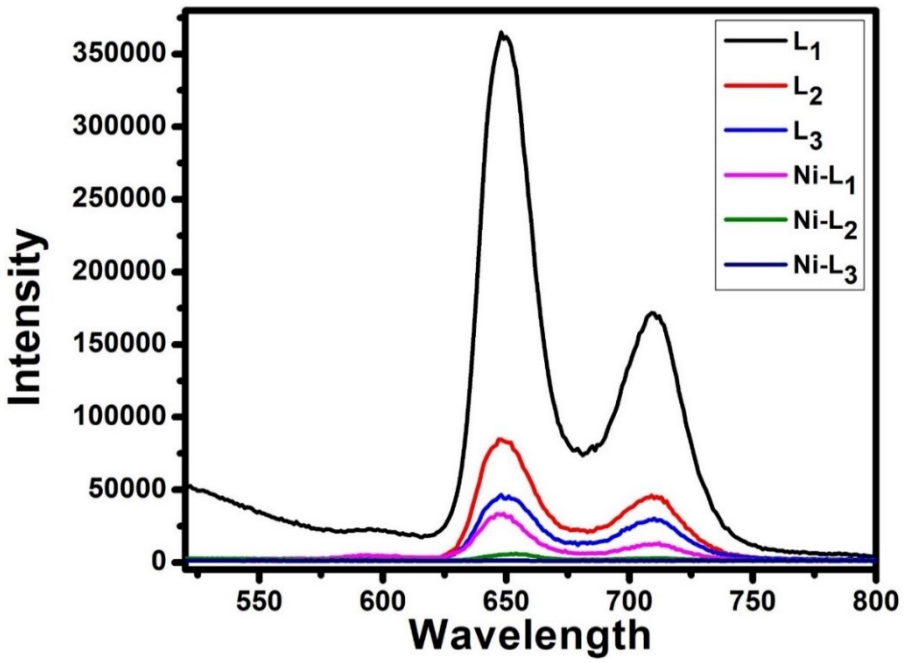

Figure S7: Photoluminescence spectra of L_1, L_2, L_3, Ni-L_1, Ni-L_2, and Ni-L_3 excited at 420 nm

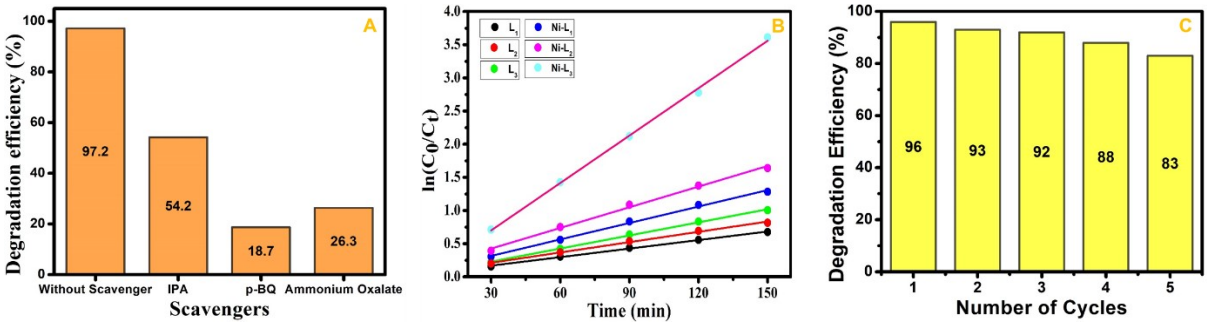

Figure S8: (A) Effect of radical intermediate trapping (B) agents First-order degradation rate kinetics and (C) Reusability test on the removal efficiency of RhB upon visible light irradiation

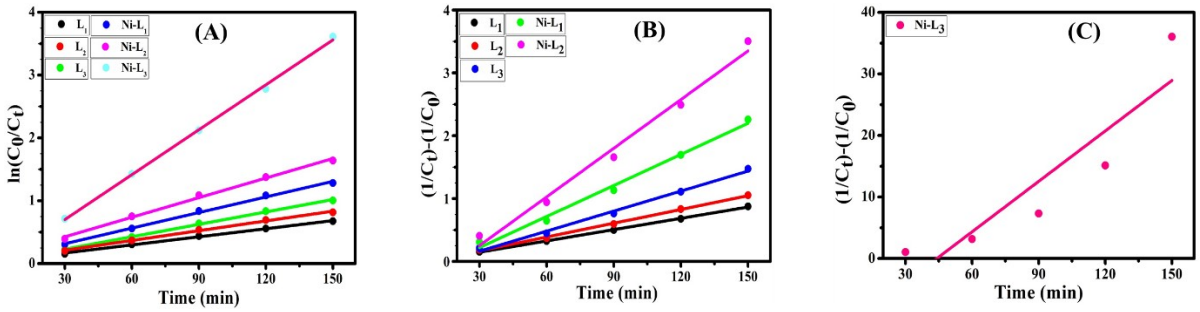

Figure S9: (A) First-order degradation rate kinetics and (B, C) Rate constant of 2nd order kinetics

Table T4. DFT calculation data for Ni-L_3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.320329	2.439741	0.345382
2	6	0	3.229311	-1.413940	-0.772278
3	6	0	-0.988062	-2.377943	0.486933
4	6	0	-2.636020	0.624282	-1.115240
5	6	0	-1.746237	1.295854	-0.367830

6	6	0	-2.085467	2.348027	0.387325
7	6	0	-0.935813	2.826480	0.847851
8	6	0	0.036167	2.031412	0.364426
9	7	0	-0.483032	1.051606	-0.289004
10	6	0	2.040905	1.636333	-0.447294
11	6	0	3.105584	1.945729	-1.200914
12	6	0	3.615628	0.777788	-1.573271
13	6	0	2.862305	-0.129445	-0.935177
14	7	0	1.804804	0.380061	-0.394773
15	6	0	2.211159	-2.023752	-0.158825
16	6	0	2.335252	-3.015154	0.740917
17	6	0	1.118949	-3.211752	1.254799
18	6	0	0.339891	-2.346972	0.591601
19	7	0	1.001545	-1.624095	-0.220631
20	6	0	-1.163709	-2.452264	-0.852227
21	6	0	-1.592853	-2.296108	-2.121278
22	6	0	-2.373709	-1.294352	-2.485089
23	6	0	-2.110132	-0.565892	-1.415891
24	7	0	-1.202972	-1.107324	-0.697266
25	28	0	0.337860	-0.268164	-1.297255
26	6	0	1.664182	3.660158	0.819439
27	6	0	-3.837717	1.054857	-1.565585
28	6	0	-1.843130	-2.963295	1.355280
29	6	0	4.426349	-2.008328	-0.987318
30	6	0	1.399744	3.939470	2.112605
31	6	0	1.724022	5.107494	2.694813
32	6	0	2.387500	6.012071	1.955393
33	6	0	2.654361	5.800234	0.655724
34	6	0	2.307279	4.614762	0.123331
35	6	0	-4.825494	0.183753	-1.855628
36	6	0	-6.034601	0.563062	-2.306065
37	6	0	-6.272292	1.879146	-2.434321

38	6	0	-5.315057	2.792356	-2.200752
39	6	0	-4.123858	2.358309	-1.752003
40	6	0	-3.042239	-3.420814	0.945617
41	6	0	-3.941592	-3.949840	1.793761
42	6	0	-3.596868	-4.064350	3.087660
43	6	0	-2.412109	-3.626465	3.547260
44	6	0	-1.573835	-3.042889	2.672243
45	6	0	5.607318	-1.361422	-0.958694
46	6	0	6.786547	-1.971275	-1.174928
47	6	0	6.775520	-3.281911	-1.468947
48	6	0	5.634891	-3.991582	-1.467805
49	6	0	4.484543	-3.331372	-1.244852
50	6	0	-2.089871	-3.664625	5.025684
51	9	0	-3.173727	-3.649532	5.785913
52	9	0	-1.318866	-2.658735	5.408991
53	9	0	-1.435816	-4.783877	5.297539
54	6	0	-5.259153	-4.489525	1.281045
55	9	0	-5.158709	-4.985597	0.057310
56	9	0	-6.142308	-3.503549	1.231598
57	9	0	-5.766077	-5.435087	2.056486
58	6	0	-7.135958	-0.453103	-2.522700
59	9	0	-7.024699	-1.504493	-1.725136
60	9	0	-7.073680	-0.899050	-3.768205
61	9	0	-8.345359	0.056125	-2.347715
62	6	0	-5.596583	4.273749	-2.331456
63	9	0	-6.881650	4.566862	-2.209040
64	9	0	-5.210610	4.686790	-3.529167
65	9	0	-4.935015	4.993463	-1.437793
66	6	0	1.478808	5.335427	4.170875
67	9	0	1.505913	4.213321	4.873116
68	9	0	0.277132	5.868573	4.332260
69	9	0	2.353533	6.168049	4.713341

70	6	0	3.420405	6.818348	-0.161503
71	9	0	4.173916	7.613412	0.581892
72	9	0	2.562616	7.587009	-0.815268
73	9	0	4.205877	6.252378	-1.065058
74	6	0	8.074963	-1.176944	-1.187509
75	9	0	7.897614	0.064330	-1.614138
76	9	0	9.012898	-1.728843	-1.941185
77	9	0	8.553407	-1.102174	0.045180
78	6	0	5.629168	-5.458149	-1.843467
79	9	0	6.661695	-5.799066	-2.598586
80	9	0	4.528231	-5.815894	-2.486486
81	9	0	5.691180	-6.188011	-0.739981
82	1	0	-3.069141	2.798035	0.566646
83	1	0	-0.889743	3.771155	1.401379
84	1	0	3.583619	2.899041	-1.435390
85	1	0	4.534792	0.660044	-2.156876
86	1	0	3.238839	-3.553654	1.053211
87	1	0	0.849546	-3.997264	1.970208
88	1	0	-1.501722	-3.166014	-2.793385
89	1	0	-2.989924	-1.139303	-3.374714
90	1	0	0.935723	3.166714	2.749938
91	1	0	2.705434	6.957374	2.422230
92	1	0	2.507613	4.483545	-0.947352
93	1	0	-4.684703	-0.893833	-1.675841
94	1	0	-7.269738	2.216063	-2.756953
95	1	0	-3.351864	3.127296	-1.596590
96	1	0	-3.333991	-3.351870	-0.114768
97	1	0	-4.311722	-4.514523	3.794152
98	1	0	-0.644563	-2.607814	3.072218
99	1	0	5.659264	-0.299555	-0.679760
100	1	0	7.725595	-3.791232	-1.693564
101	1	0	3.554392	-3.917200	-1.329478