Supporting Information

Regulating the Polyethylene Microstructure by Increasing Steric Crowding in Naphthoxy Imine Ligated Ni(II) Complexes

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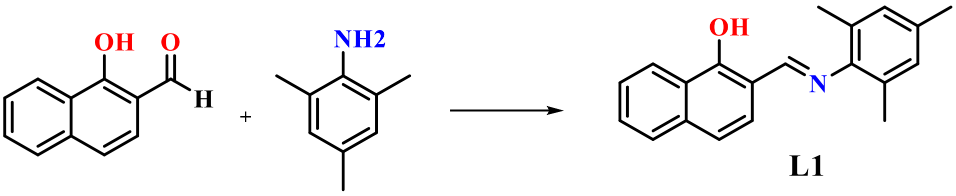
Contents

1. General methods and materials:

Unless noted otherwise, all manipulations were carried out under an inert atmosphere using standard Schlenk line techniques or an M-Braun glove box. Toluene, diethyl ether, 1,4 dioxane, and THF were distilled from sodium/benzophenone under an argon atmosphere. Acetonitrile, methylene chloride, and pyridine were distilled on calcium-hydride. Ethylene was supplied by Praxiar India Ltd., India. 1-Naphthol, and diisopropyl aniline were supplied by Loba Chemie and were used as received. 2, 4, 6 trimethyl aniline, $B(C_6F_5)_3$ and $[Ni(COD)_2]$ were supplied by Sigma Aldrich and were used as received. Sodium borohydride was supplied by Avara and was used as received. p-Anisidine and paraformaldehyde were supplied by Alfa Aeser and were used as received. $[NiCl(o\text{-}Tol)(PPh_3)_2]$[1], 1 hydroxy 2 napthaldehyde,[2] aniline derivative[3] were synthesized following known procedures. The insertion polymerization was run in a Büchi glasuster cyclone 075 high-pressure reactor equipped with an overhead mechanical stirrer, heating/cooling jacket, and pressure regulators.

Solution NMR spectra were recorded on a Bruker Avance 200, 400, and 500 MHz instruments. Chemical shifts are referenced to external reference TMS (^{1}H and ^{13}C). Coupling constants are given as absolute values. Multiplicities are given as follows s: singlet, d: doublet, t: triplet, m: multiplet. High-temperature NMR (HT-NMR) of the polymers was recorded in $C_2D_2Cl_4$ solvent at 80 °C. Mass spectra were recorded on Thermo Scientific Q-Exactive mass spectrometer, the column specification is Hypersil gold C18 column 150 × 4.6 mm diameter 8 µm particle size mobile phase used is 90 % methanol + 10 % water + 0.1 % formic acid. Differential Scanning Calorimeter (DSC) was carried out on DSC Q-10 equipment from TA instruments with a heating and cooling rate of 10 K min^{-1}, unless mentioned otherwise. High-temperature Gel Permeation Chromatography (HT-GPC) of the PE was recorded in 1,2,4-trichlorobenzene at 160 °C on a Viscotek GPC (HT-GPC module 350A) instrument equipped with triple detector system. The columns were calibrated with linear polystyrene standards and the reported molecular weights are with respect to polystyrene standards. Molecular weight measurements for Entry 3 and 7 were performed on GPC–IR5 + Visco + LS (GPC-IR-I Polymer Char) equipment at a flow rate 1 ml/ min on a column 3 × PL gel Olexis Mix-Bed columns (13 microns), 300 × 7.5mm + guard column. Weight-average molecular weight (Mw), number average molecular weight (Mn), and polydispersity index (PDI) of the synthesized PE were recorded using HT-GPC(160 °C).

2. Synthesis of Ligand L1:



Scheme S1: Synthesis of naphthoxy imine ligand **L1**.

In an oven-dried round bottom flask, 1-hydroxy 2-naphthaldehyde (0.010 mol, 1.8 g) and 2,4,6 trimethyl aniline (0.011mol, 1.55 g) were dissolved in 25 mL toluene. A catalytic amount of PTSA (5 mg) was added to the above solution and the resultant reaction mixture was refluxed for 6 hours. The color of the reaction mixture changed to yellowish; the reaction was monitored by TLC analysis. After completion of the reaction solvent was evaporated by using a rotatory evaporator and ligand was purified by silica gel column chromatography using pet ether (98%) and ethyl acetate (2%) as eluent (Yield: 2.9 g, < 99%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 14.66 (br. s., 1 H), 8.51 (d, *J* = 8.1 Hz, 1 H), 8.12 (br. s., 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.59 (t, *J* = 7.4 Hz, 1 H), 7.55 - 7.46 (m, 1 H), 7.15 (d, *J* = 8.8 Hz, 1 H), 7.08 (d, *J* = 8.8 Hz, 1 H), 6.97 (s, 2 H), 2.33 (s, 3 H), 2.30 (s, 6 H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 170.1, 163.4, 140.8, 136.9, 135.7, 130.2, 129.8, 129.4, 127.9, 127.6, 127.4, 125.4, 124.8, 116.7, 110.5, 20.9, 18.6. **ESI-MS** (positive mode): m/z = 290.1551 Da $[M+H]^+$ (observed); 290.1545 $[M+H]^+$ (calculated).

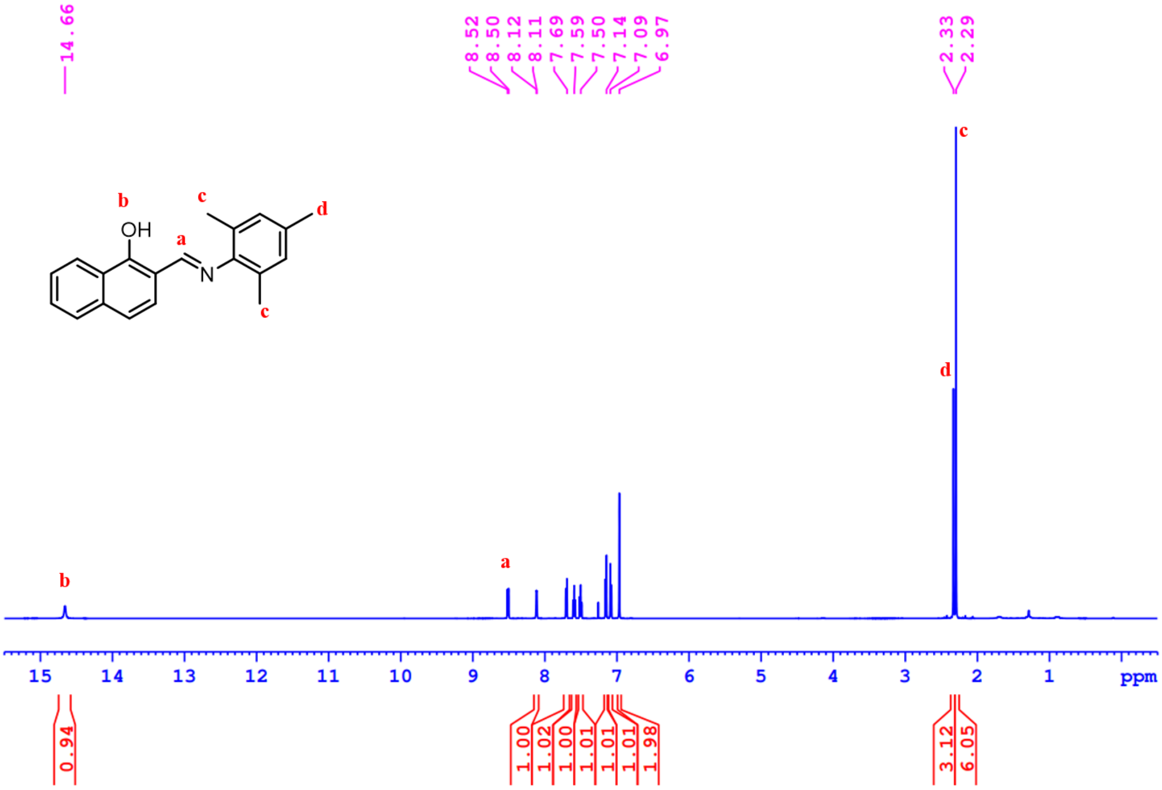


Figure S1: ^{1}H NMR spectrum of ligand L1 in $CDCl_3$.

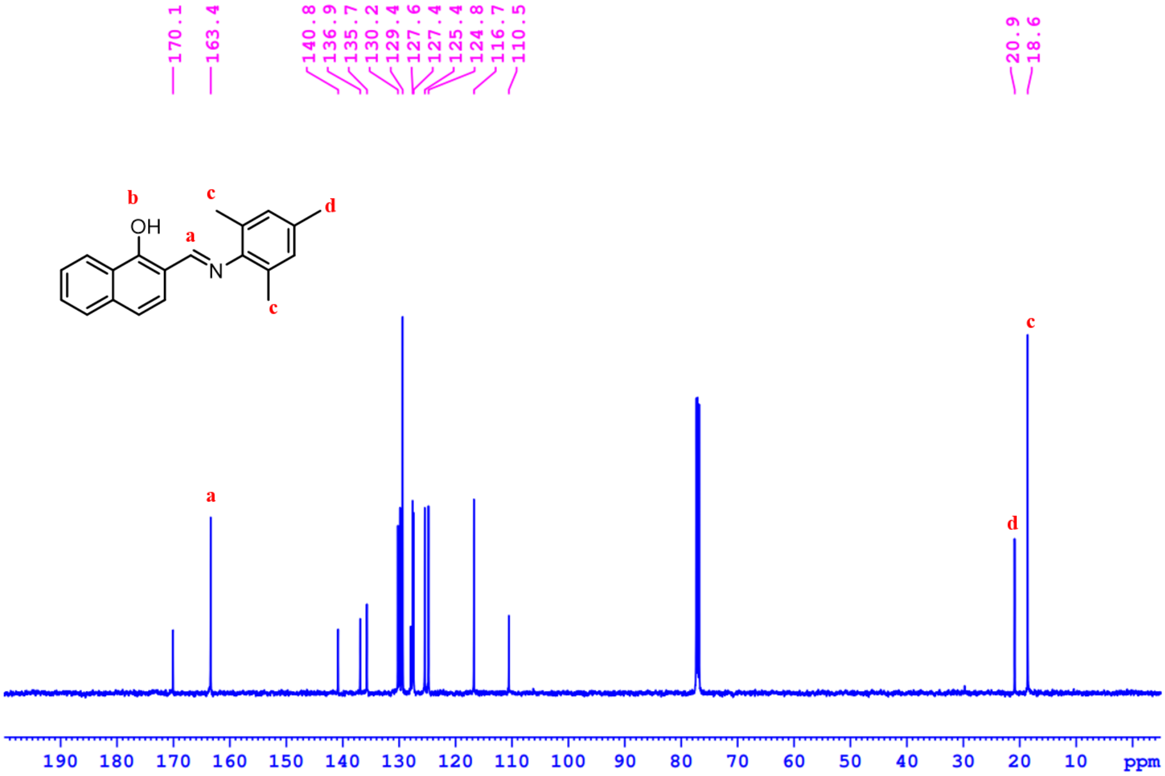


Figure S2: ^{13}C NMR spectrum of ligand L1 in $CDCl_3$.

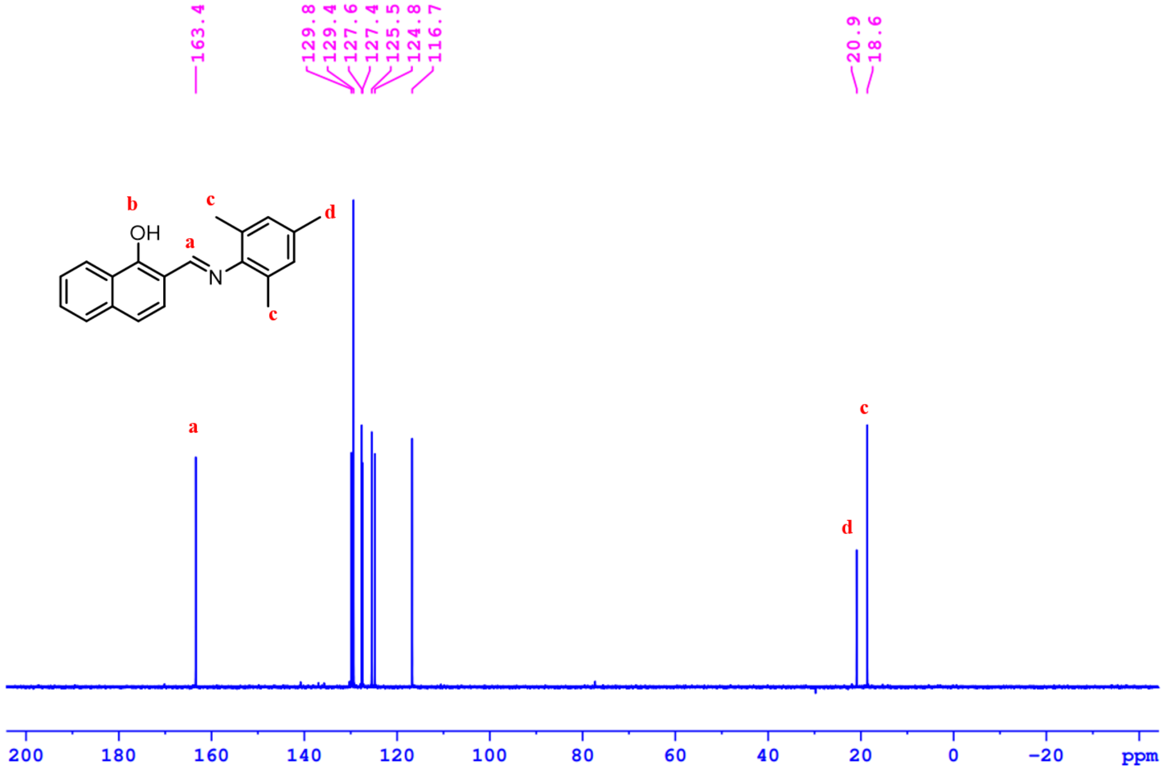


Figure S3: ^{13}C DEPT NMR spectrum of ligand in $CDCl_3$.

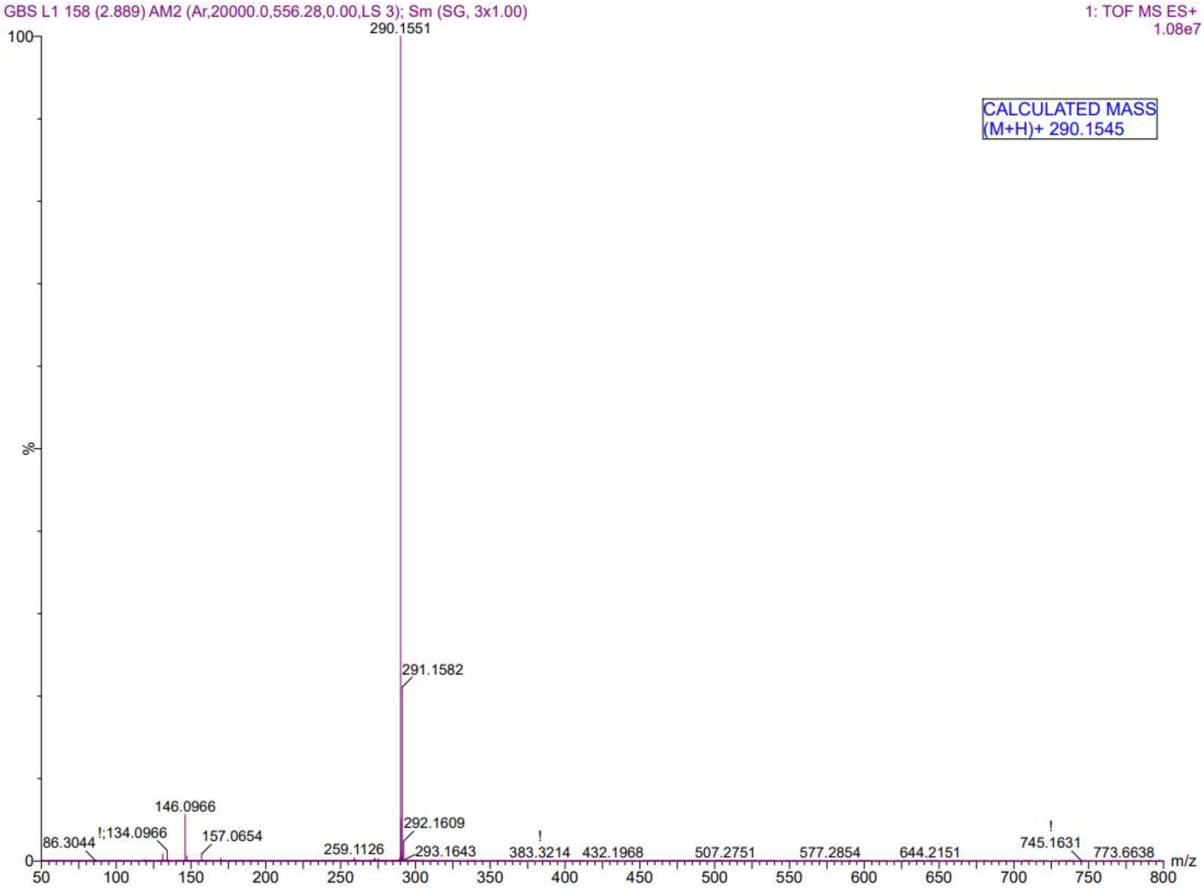
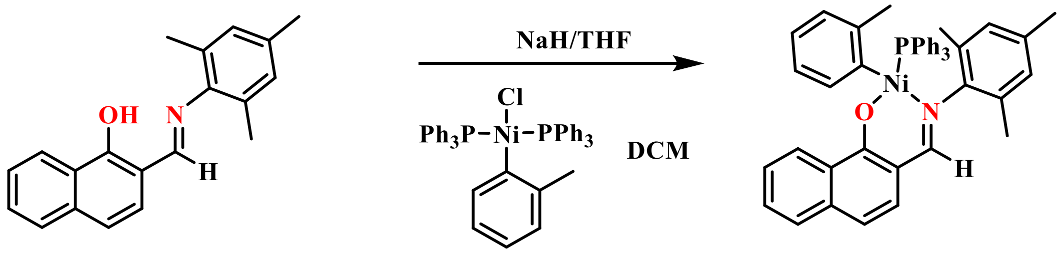


Figure S4: ESI-MS data of ligand L1.

3. Synthesis of Ni complex:

3.1 Synthesis of Ni1 complex:



Scheme S2: Synthesis of Ni1 complex.

In an oven-dried Schlenk flask, NaH (13.6 mg, 0.566 mmol) and ligand L1 (81.5 mg, 0.281 mmol) were taken. The flask was cooled to 0 °C and 5 mL THF was added. The reaction mixture was stirred at 0 °C for 2 hours after that solvent was evaporated. The obtained compound was dissolved in 5 mL DCM and transferred dropwise to another flask that contained [NiCl(*o*-Tol)(PPh_3)$_2$] (200 mg, 0.281 mmol) precursor at 0 °C. The mixture was stirred at the same temperature for 2 hours and DCM was evaporated. The resultant complex was purified by recrystallization in DCM and Hexane at 0 °C (Yield-184 mg, 93%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.5 Hz, 1 H), 7.55 - 7.43 (m, 7 H), 7.37 - 7.29 (m, 5 H), 7.23 - 7.19 (m, 5 H), 7.07 (d, *J* = 8.2 Hz, 1 H), 6.85 (d, *J* = 8.2 Hz, 1 H), 6.73 (t, *J* = 6.7 Hz, 1 H), 6.64 (d, *J* = 7.0 Hz, 1 H), 6.56 (br. s., 1 H), 6.50 (d, *J* = 7.6 Hz, 1 H), 6.39 (br. s., 1 H), 6.31 - 6.21 (m, 1 H), 6.01 (d, *J* = 6.7 Hz, 1 H), 5.99 - 5.92 (m, 1 H), 2.62 (br. s., 3 H), 2.48 (br. s., 3 H), 2.07 (br. s., 3 H), 2.02 (br. s., 3 H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 164.9, 164.8, 150.2, 143.2, 137.5, 137.1, 134.6, 134.5, 133.9, 133.8, 131.4, 131.0, 130.9, 129.9, 129.9, 129.7, 129.7, 128.8, 128.6, 128.6, 128.3, 128.1, 127.9, 127.9, 127.6, 126.7, 126.2, 126.0, 123.8, 121.8, 121.7, 113.6, 112.8, 26.4, 20.7, 19.7, 18.6. **^{31}P NMR (500 MHz, $CDCl_3$):** δ **=** 25.19. **ESI-MS** (positive mode): $C_{45}H_{40}NNaNiOP$ m/z = 722.15 Da [M+Na]$^+$ (observed); 722.20 [M+Na]$^+$ (calculated).

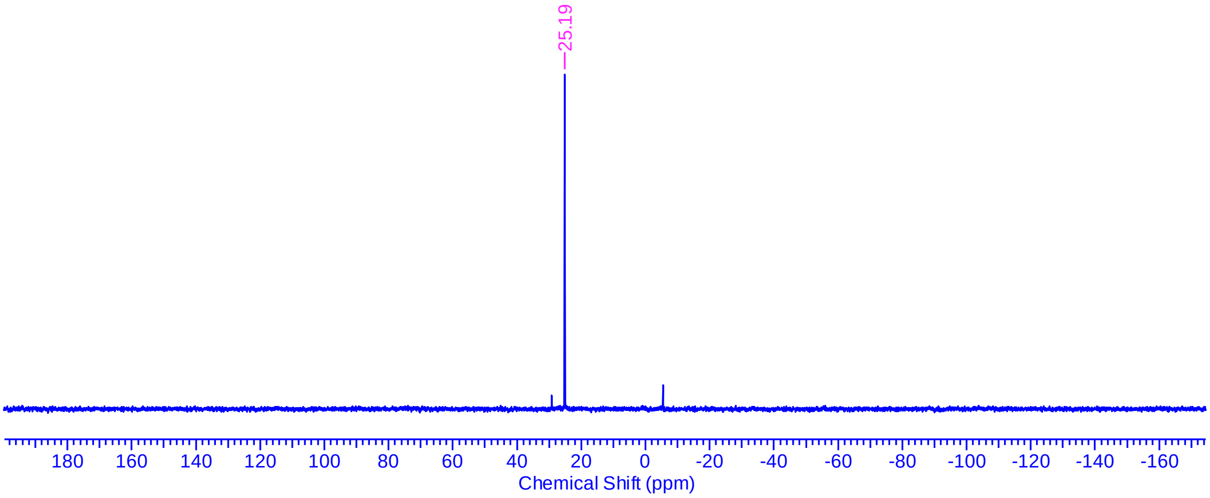


Figure S5: ^{31}P NMR spectrum of **Ni1** complex in $CDCl_3$.

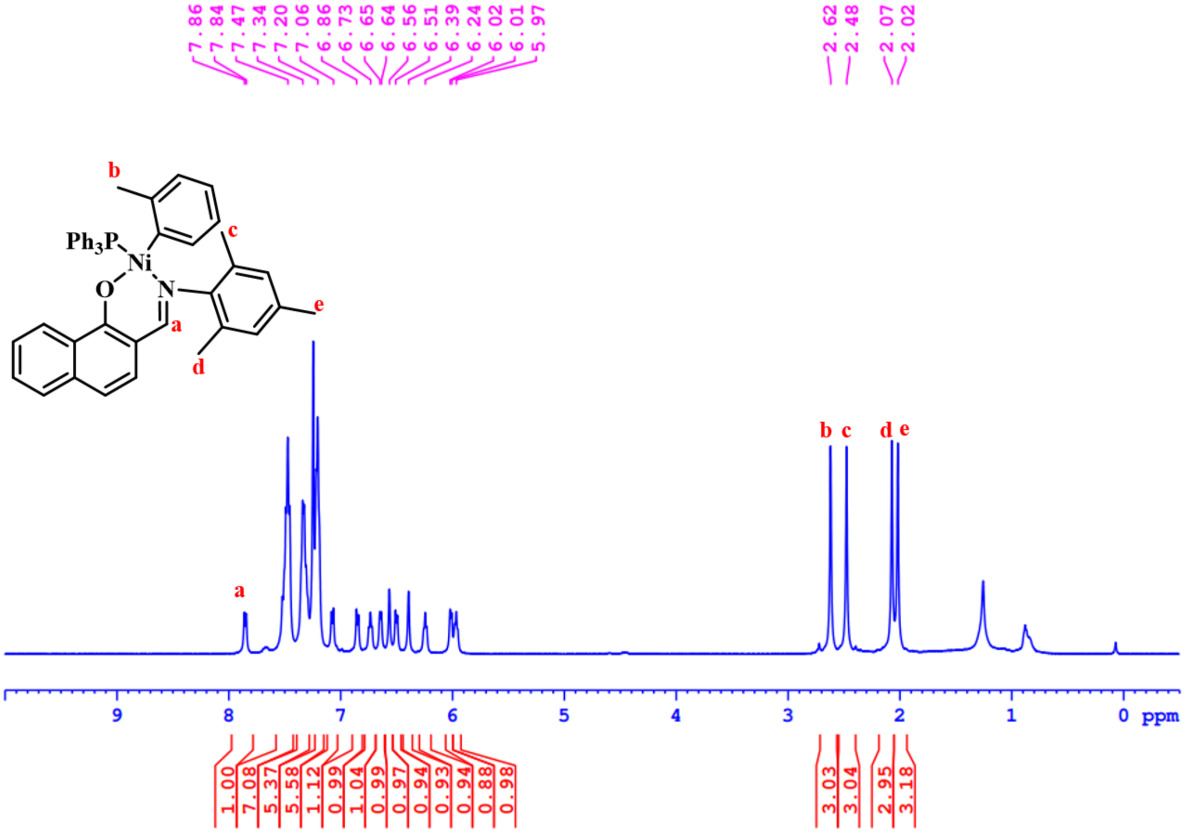


Figure S6: ^{1}H NMR spectrum of **Ni1** complex in CDCl$_3$.

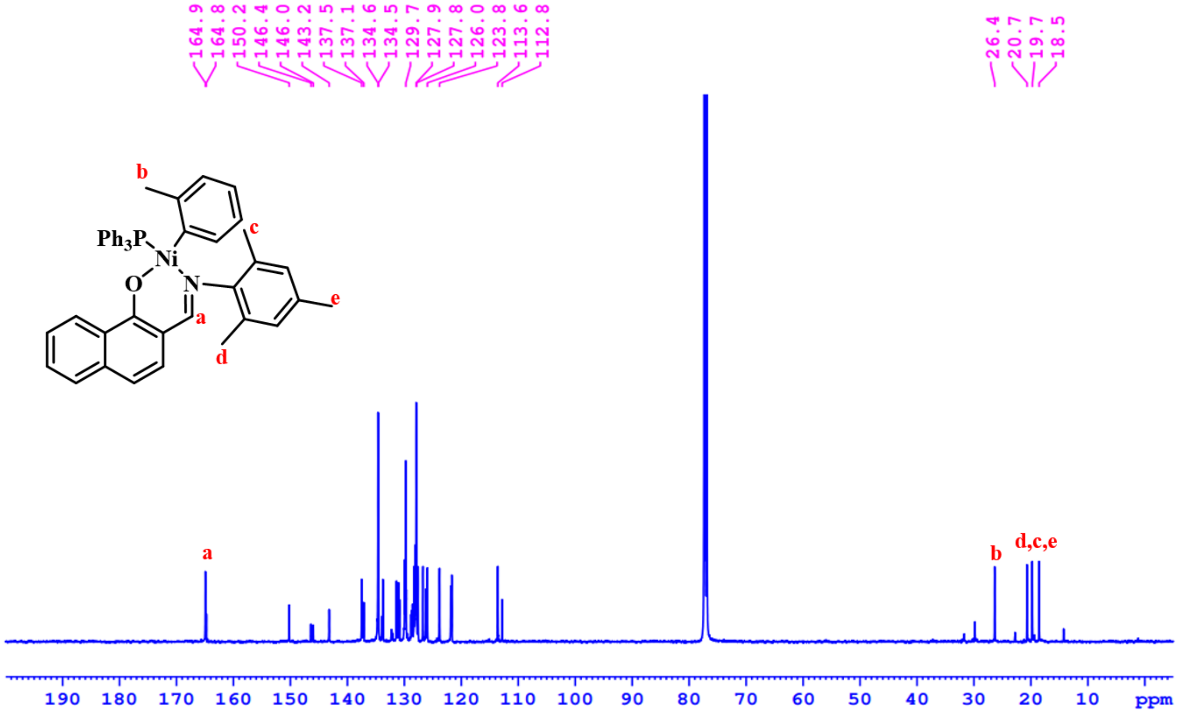


Figure S7: ^{13}C NMR spectrum of **Ni1** complex in CDCl$_3$.

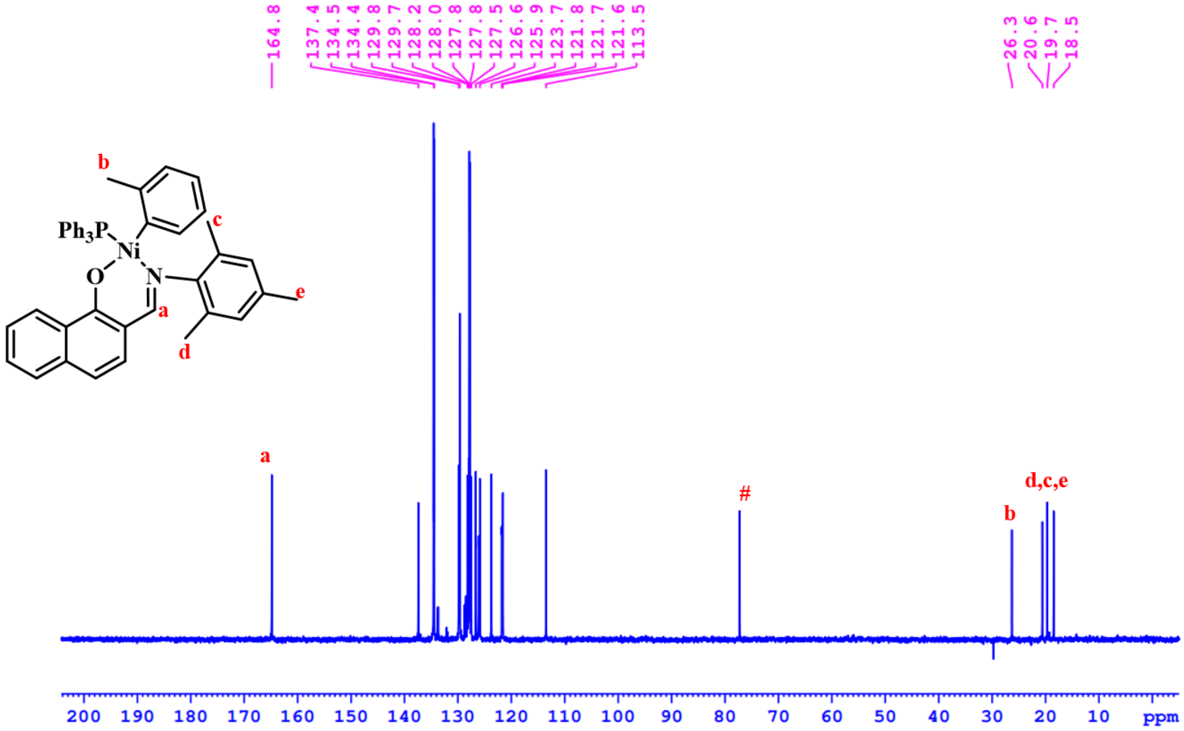


Figure S8: ^{13}C DEPT NMR spectrum of **Ni1** complex in CDCl$_3$.

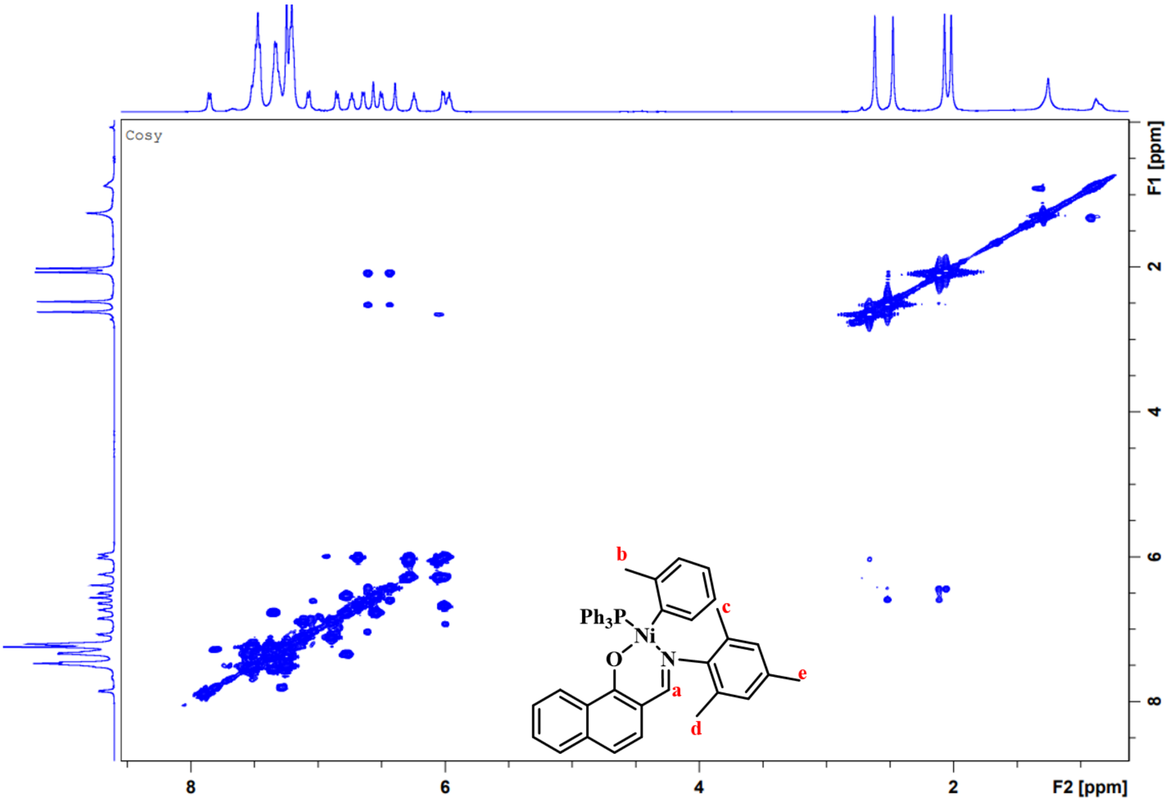


Figure S9: COSY NMR spectrum of **Ni1** complex in CDCl$_3$.

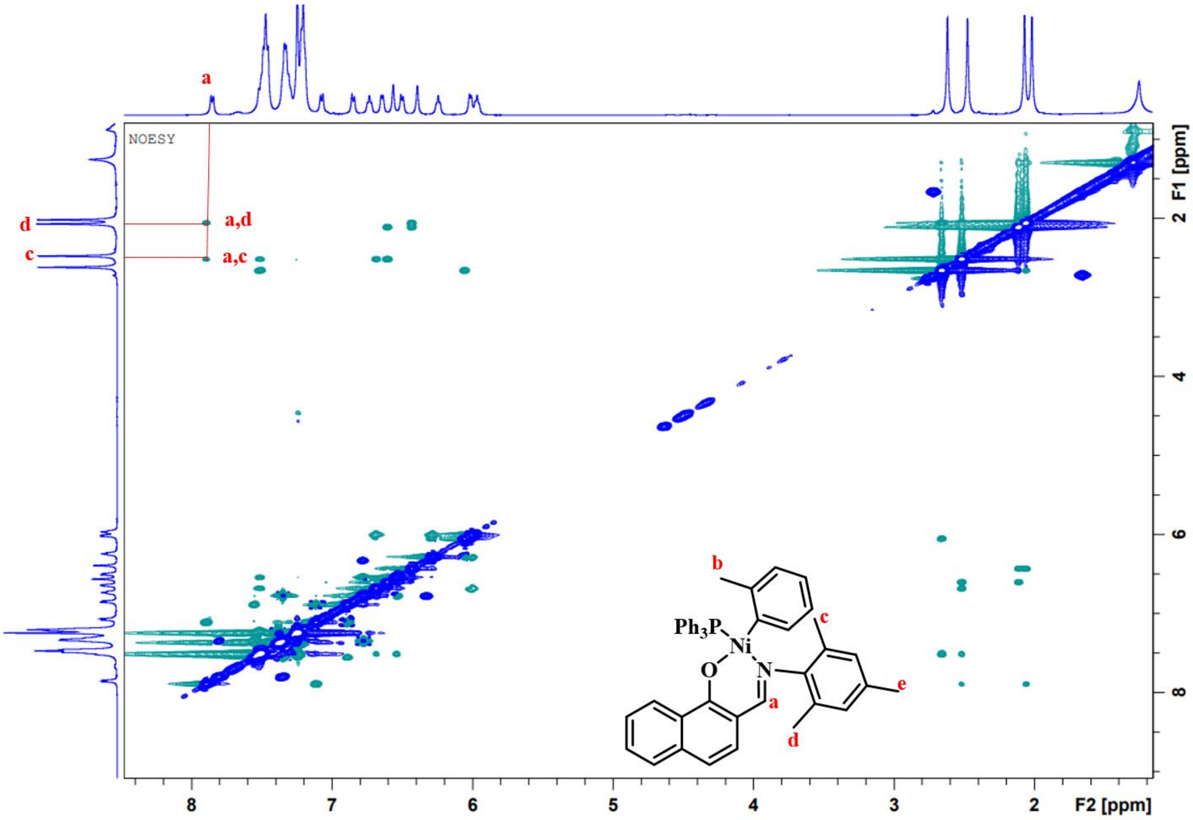


Figure S10: NOESY NMR spectrum of **Ni1** complex in $CDCl_3$.

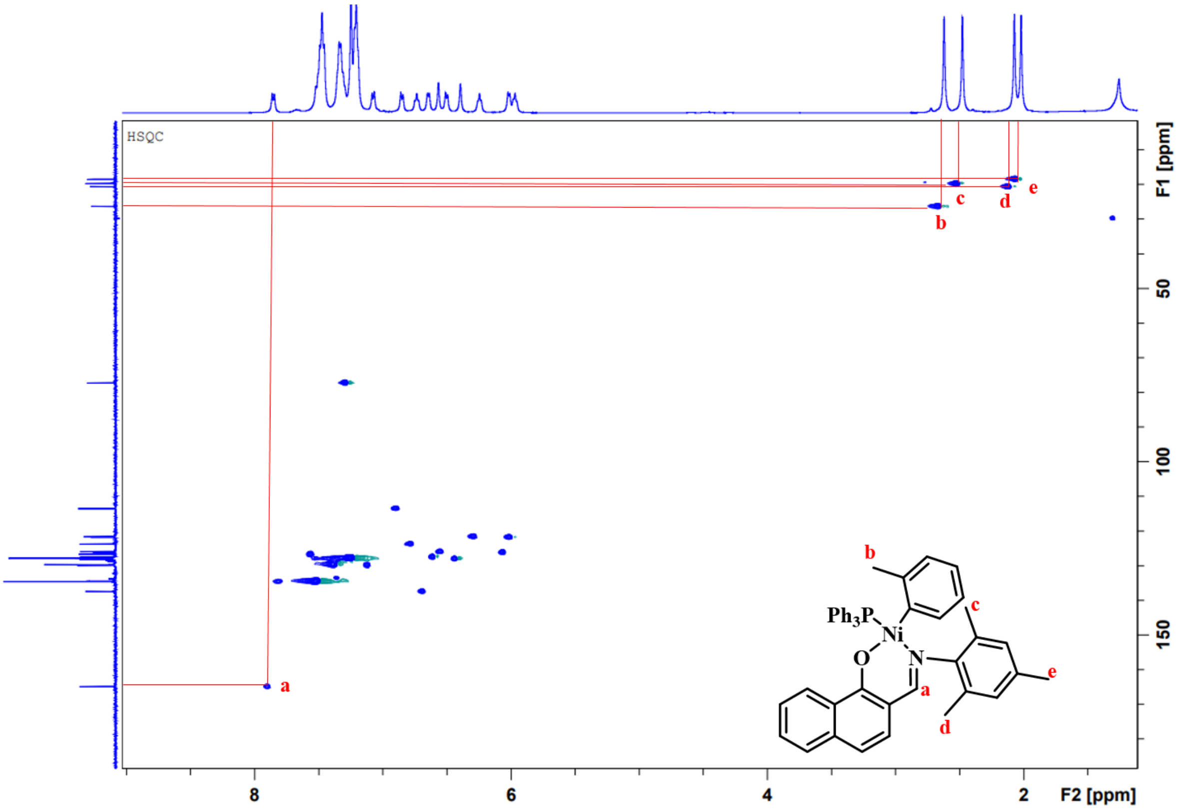


Figure S11: HSQC NMR spectrum of **Ni1** complex in $CDCl_3$.

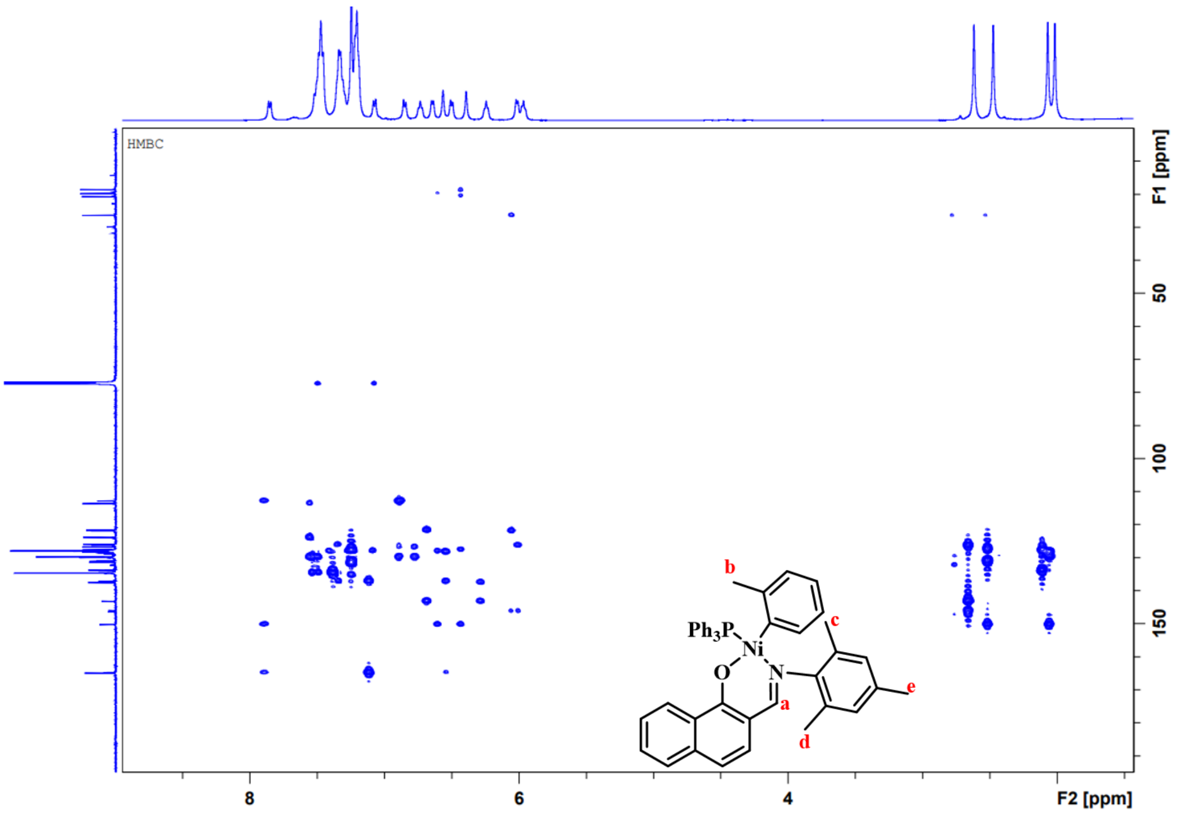


Figure S12: HMBC NMR spectrum of **Ni1** complex in $CDCl_3$.

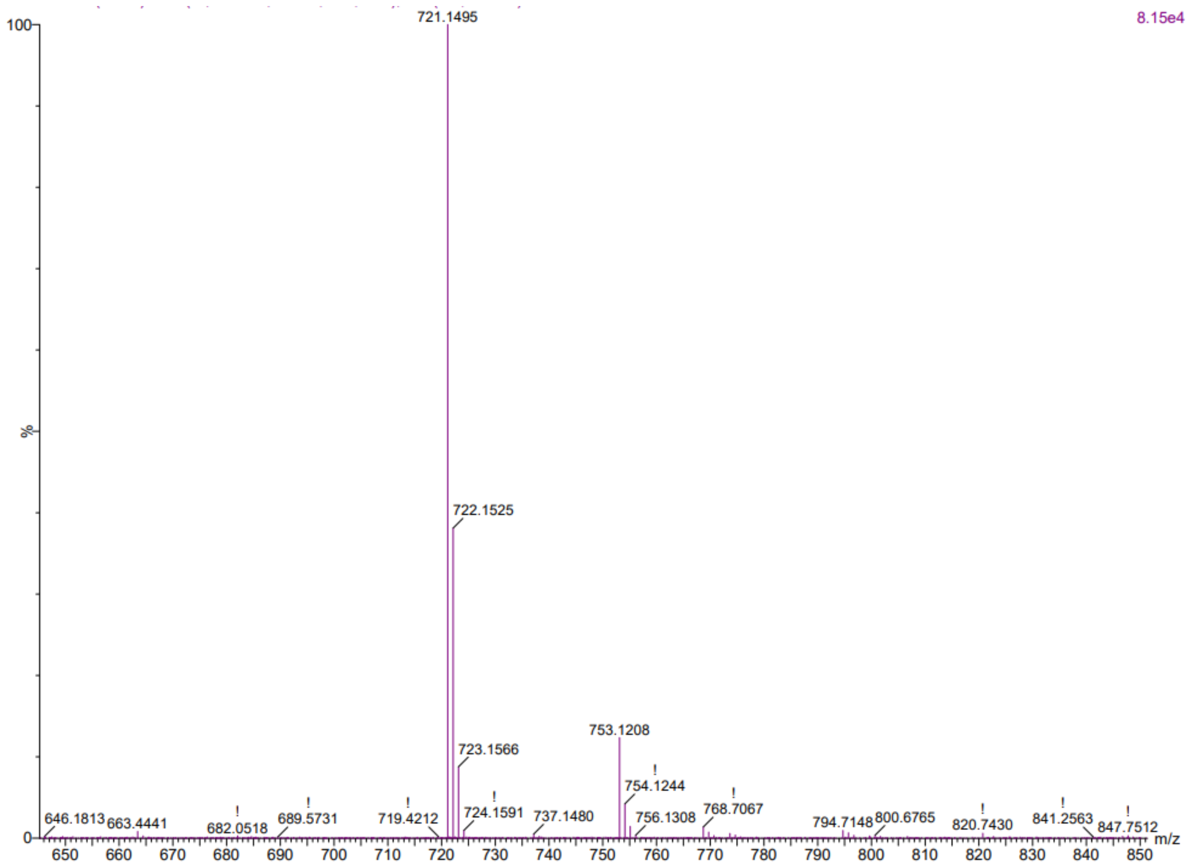


Figure S13: ESI-MS data of **Ni1**.

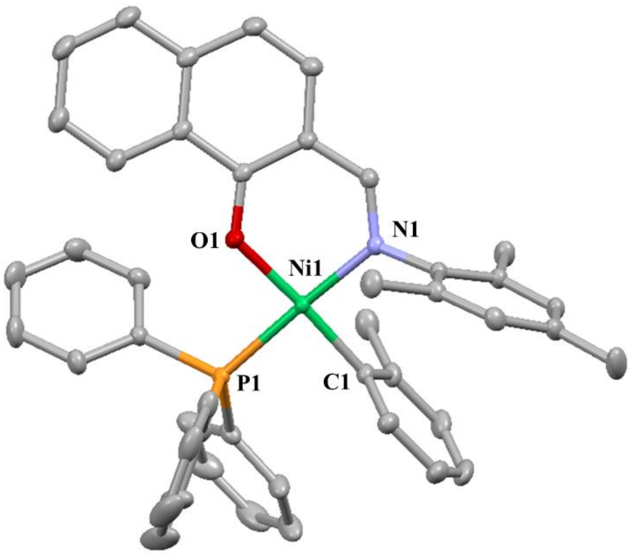
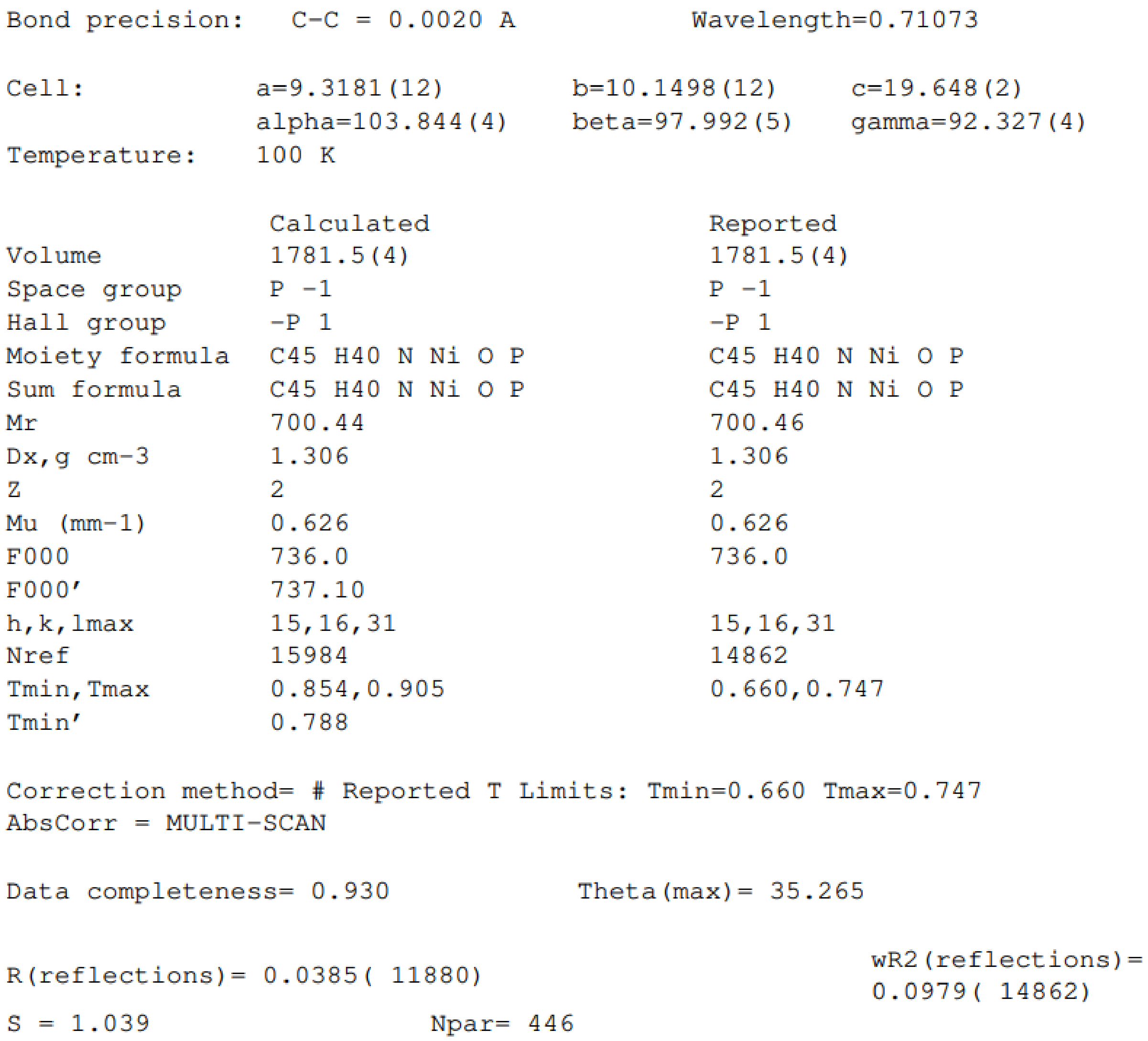


Figure S14: Molecular structure of **Ni1** complex.

Chart S1: Crystal data and structure refinement for Ni1.



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                  alpha=103.844(4)   beta=97.992(5)     gamma=92.327(4)
Temperature:      100 K

                   Calculated                  Reported
Volume             1781.5(4)                   1781.5(4)
Space group        P -1                        P -1
Hall group         -P 1                        -P 1
Moiety formula     C45 H40 N Ni O P            C45 H40 N Ni O P
Sum formula        C45 H40 N Ni O P            C45 H40 N Ni O P
Mr                 700.44                      700.46
Dx,g cm-3          1.306                       1.306
Z                  2                           2
Mu (mm-1)          0.626                       0.626
F000               736.0                       736.0
F000'              737.10
h,k,lmax           15,16,31                    15,16,31
Nref               15984                       14862
Tmin,Tmax          0.854,0.905                 0.660,0.747
Tmin'              0.788

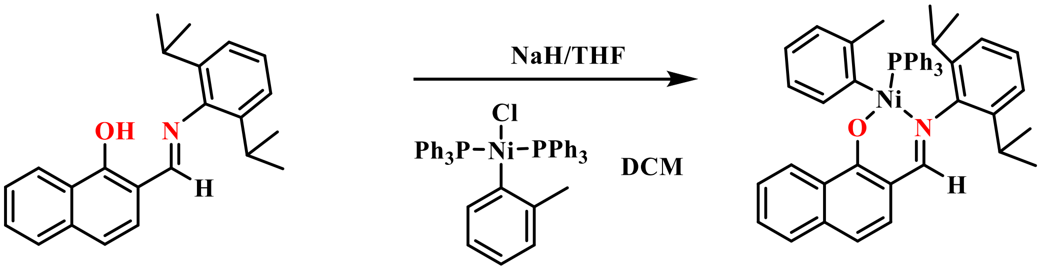
Correction method= # Reported T Limits: Tmin=0.660 Tmax=0.747
AbsCorr = MULTI-SCAN

Data completeness= 0.930             Theta(max)= 35.265

                                                      wR2(reflections)=
R(reflections)= 0.0385( 11880)                        0.0979( 14862)

S = 1.039                     Npar= 446
```

3.2 Synthesis of Ni2 complex:



Scheme S3: Synthesis of **Ni2** complex.

In an oven-dried Schlenk flask, NaH (5.0 mg, 0.21 mmol) and ligand **L2** (35 mg, 0.10 mmol) were taken. The flask was cooled to 0 °C and 5 mL THF was added to that. The reaction mixture was stirred at 0 °C for 2 hours, after that solvent was evaporated. The resultant compound was dissolved in 5 mL DCM and was dropwise transferred to another flask that contained [NiCl(*o*-Tol)(PPh_3)$_2$] (74.8 mg, 0.10 mmol) precursor at 0 °C. The mixture was stirred at the same temperature for 2 hours and DCM was evaporated. The complex was purified by recrystallization in DCM and hexane at 0 °C (Yield- 54 mg, 73%).

^{1}H NMR (500 MHz, CDCl$_3$): δ **=** 7.92 (d, *J* = 8.5 Hz, 1 H), 7.50 (d, *J* = 8.5 Hz, 5 H), 7.35 - 7.30 (m, 7 H), 7.23 - 7.19 (m, 5 H), 7.08 - 7.02 (m, *J* = 8.5 Hz, 1 H), 7.00 - 6.96 (m, *J* = 7.6 Hz, 1 H), 6.90 (t, *J* = 7.8 Hz, 1 H), 6.87 - 6.82 (m, *J* = 8.5 Hz, 1 H), 6.73 (t, *J* = 7.5 Hz, 1 H), 6.67 - 6.62 (m, *J* = 7.3 Hz, 1 H), 6.47 (d, *J* = 7.9 Hz, 1 H), 6.42 - 6.36 (m, *J* = 7.3 Hz, 1 H), 6.22 - 6.13 (m, 1 H), 6.08 - 6.01 (m, *J* = 7.0 Hz, 1 H), 5.90 (t, *J* = 7.3 Hz, 1 H), 4.60 (td, *J* = 6.7, 13.4 Hz, 1 H), 3.01 (td, *J* = 6.6, 13.4 Hz, 1 H), 2.82 (s, 3 H), 1.51 (d, *J* = 6.7 Hz, 3 H), 1.03 (d, *J* = 6.7 Hz, 6 H), 0.80 (d, *J* = 6.7 Hz, 3 H). **^{13}C NMR (125 MHz, CDCl$_3$):** δ **=** 165.2, 164.8, 150.2, 145.7, 145.3, 142.6, 141.7, 140.4, 138.0, 137.1, 134.5, 134.4, 133.8, 133.7, 131.3, 130.9, 129.8, 129.7, 129.6, 128.7, 128.5, 128.5, 128.2, 127.9, 127.8, 126.8, 126.6, 125.9, 125.3, 123.7, 122.7, 122.0, 121.5, 113.7, 112.0, 29.1, 27.6, 26.0, 25.8, 22.7, 22.0. **^{31}P NMR (500 MHz, CDCl$_3$):** δ **=** 25.2.

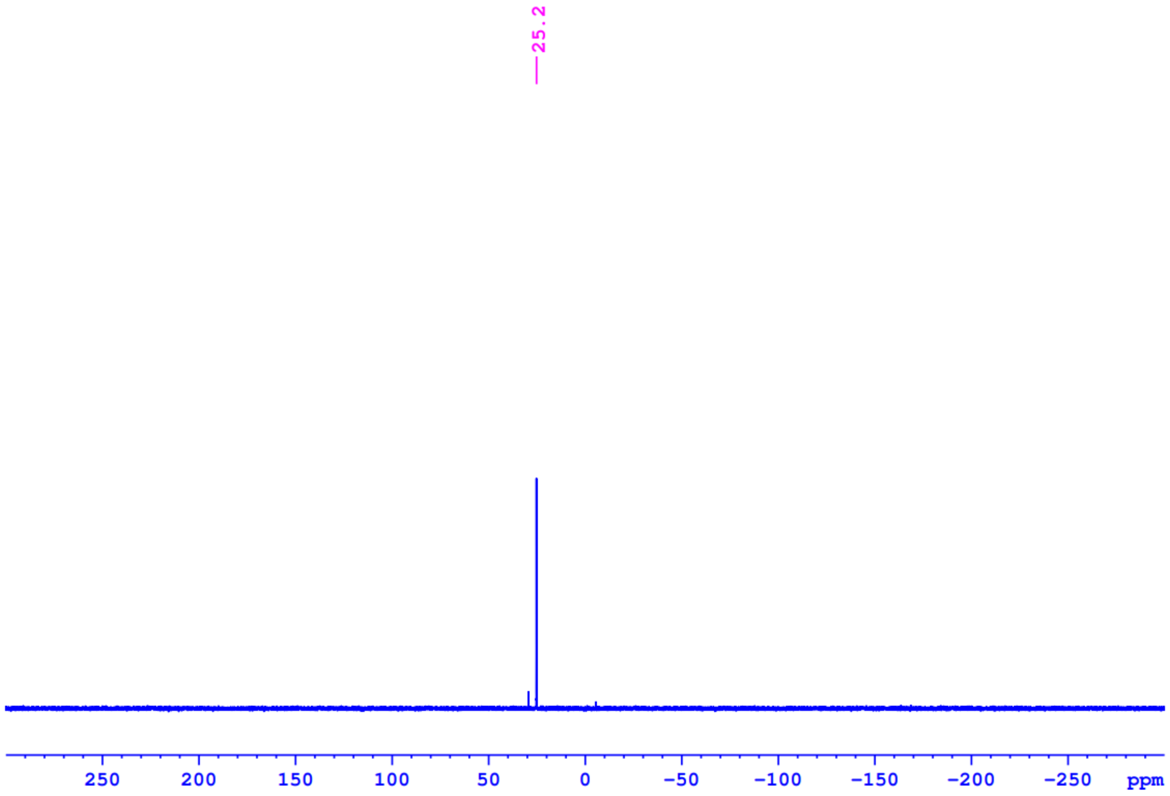


Figure S15: ^{31}P NMR spectrum of **Ni2** complex in CDCl$_3$.

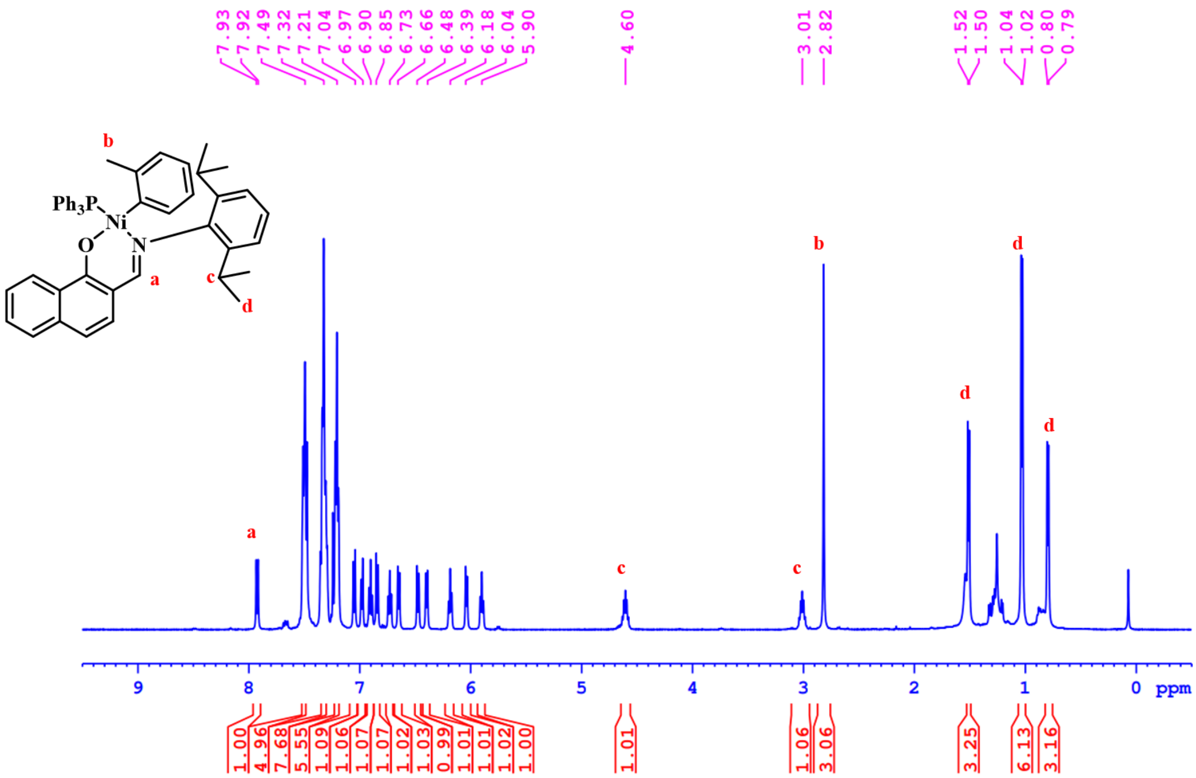


Figure S16: ^{1}H NMR spectrum of **Ni2** complex in CDCl$_3$.

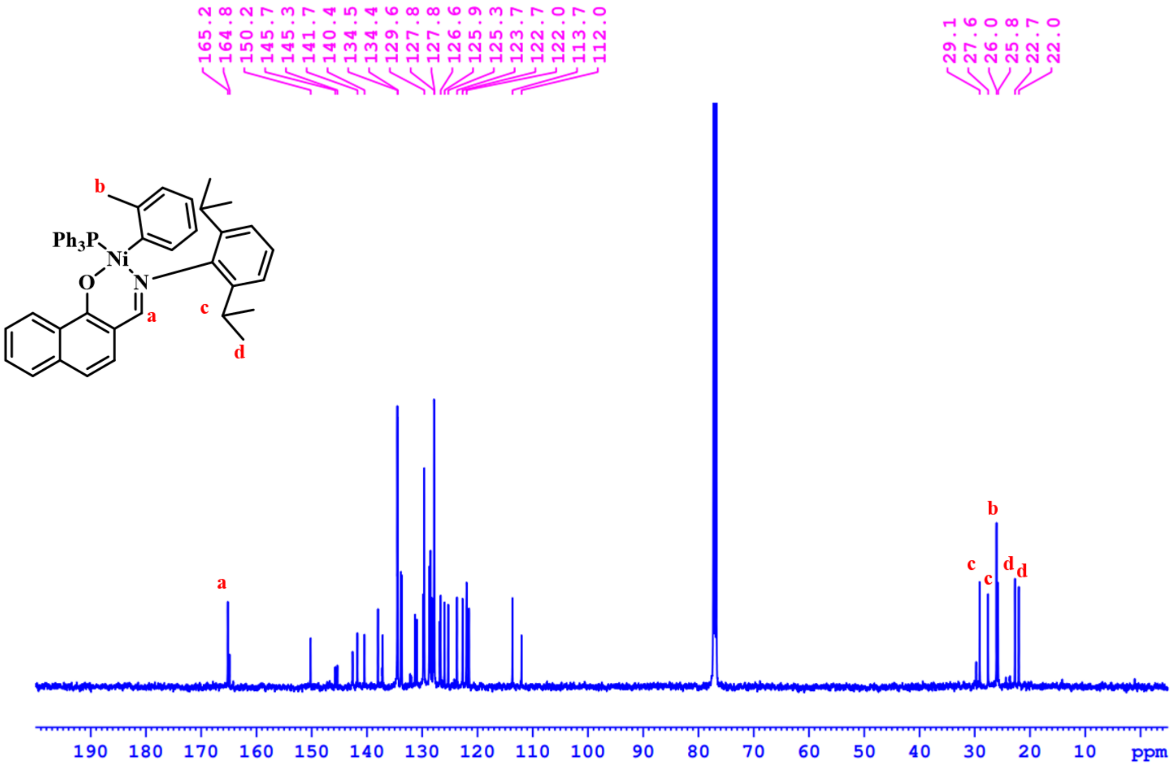


Figure S17: ^{13}C NMR spectrum of **Ni2** complex in CDCl$_3$.

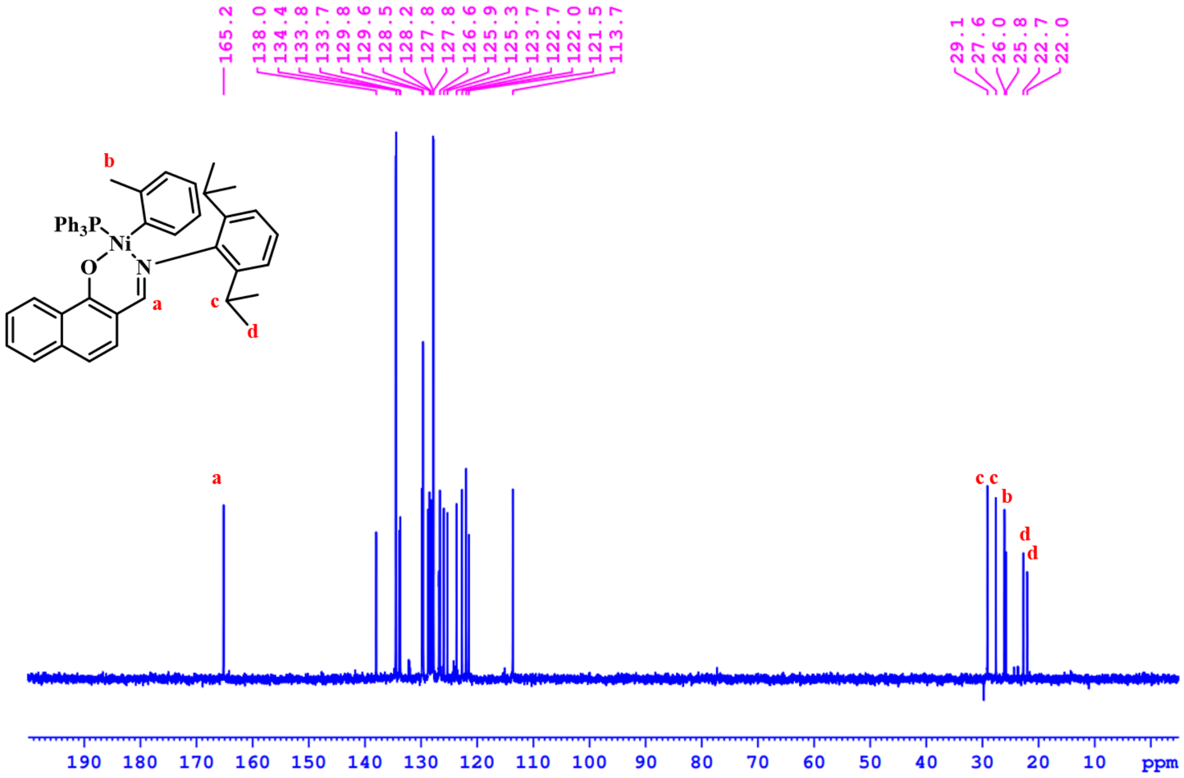


Figure S18: ^{13}C DEPT NMR spectrum of **Ni2** complex in CDCl$_3$.

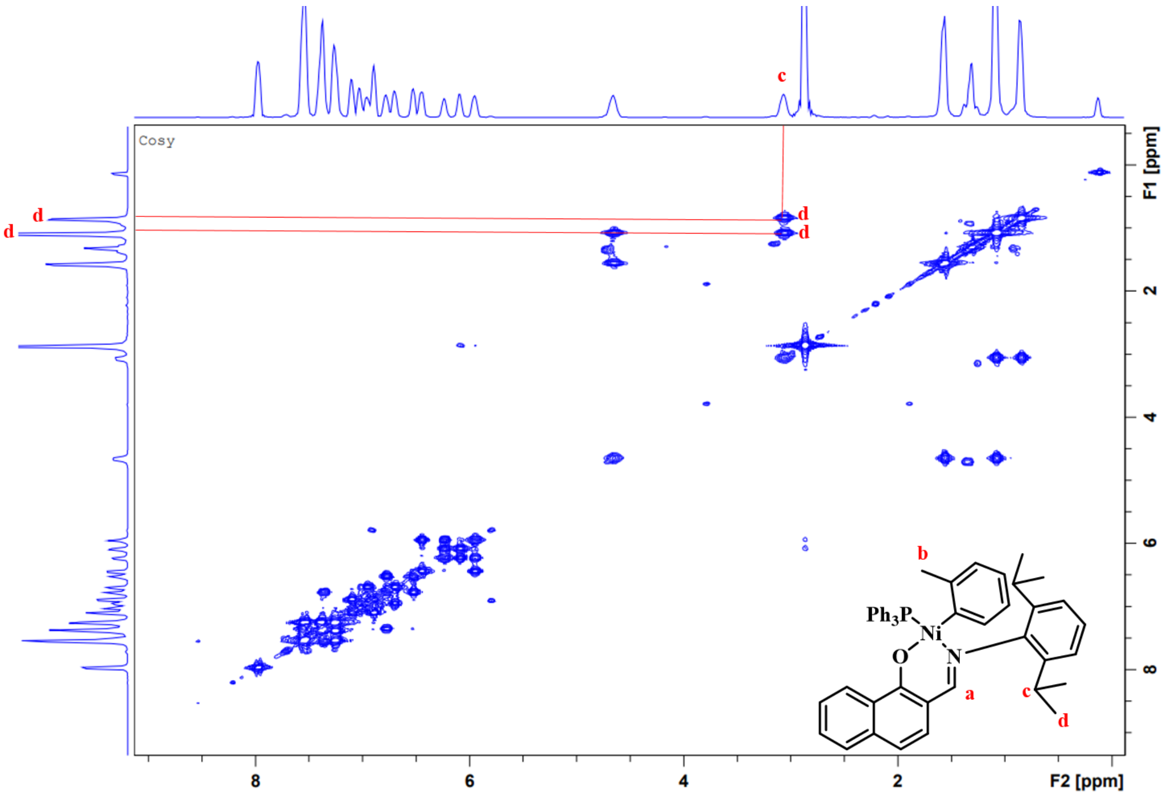


Figure S19: ^{1}H-^{1}H COSY NMR spectrum of **Ni2** complex in CDCl$_3$.

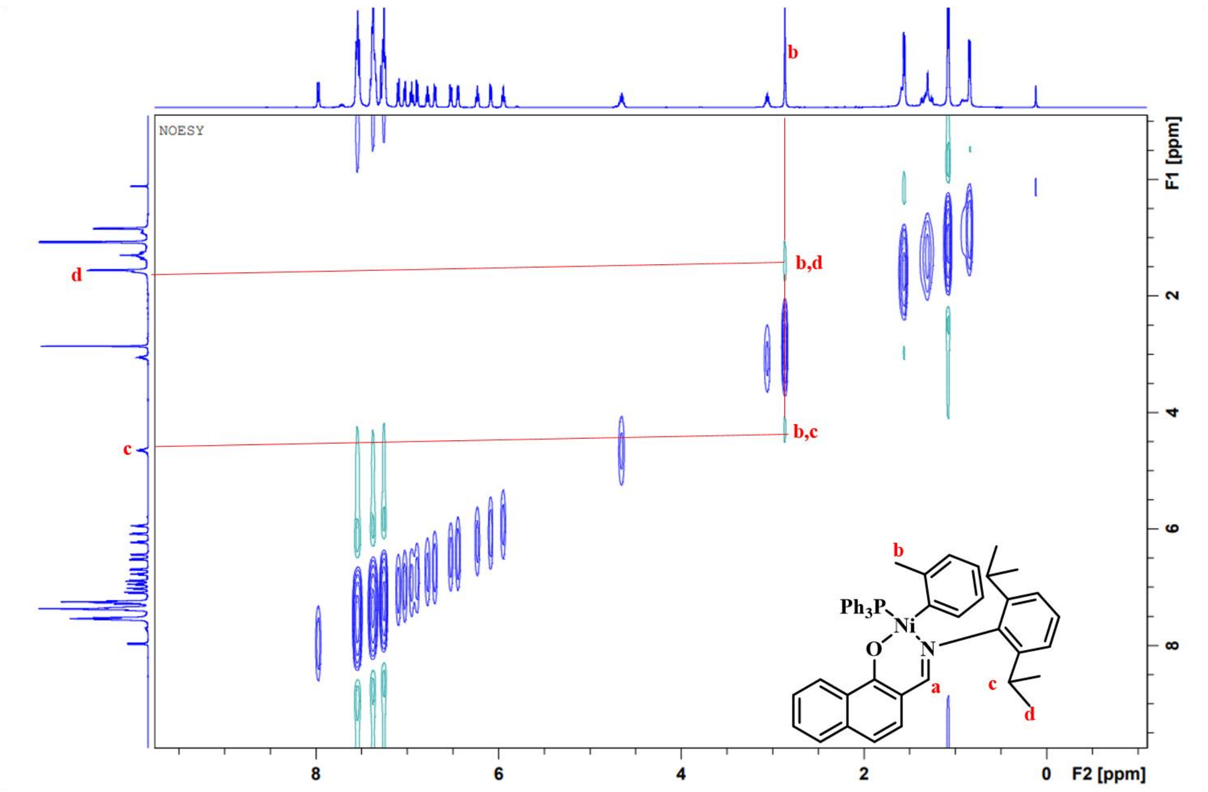


Figure S20: ^{1}H-^{1}H NOESY NMR spectrum of **Ni2** complex in $CDCl_3$.

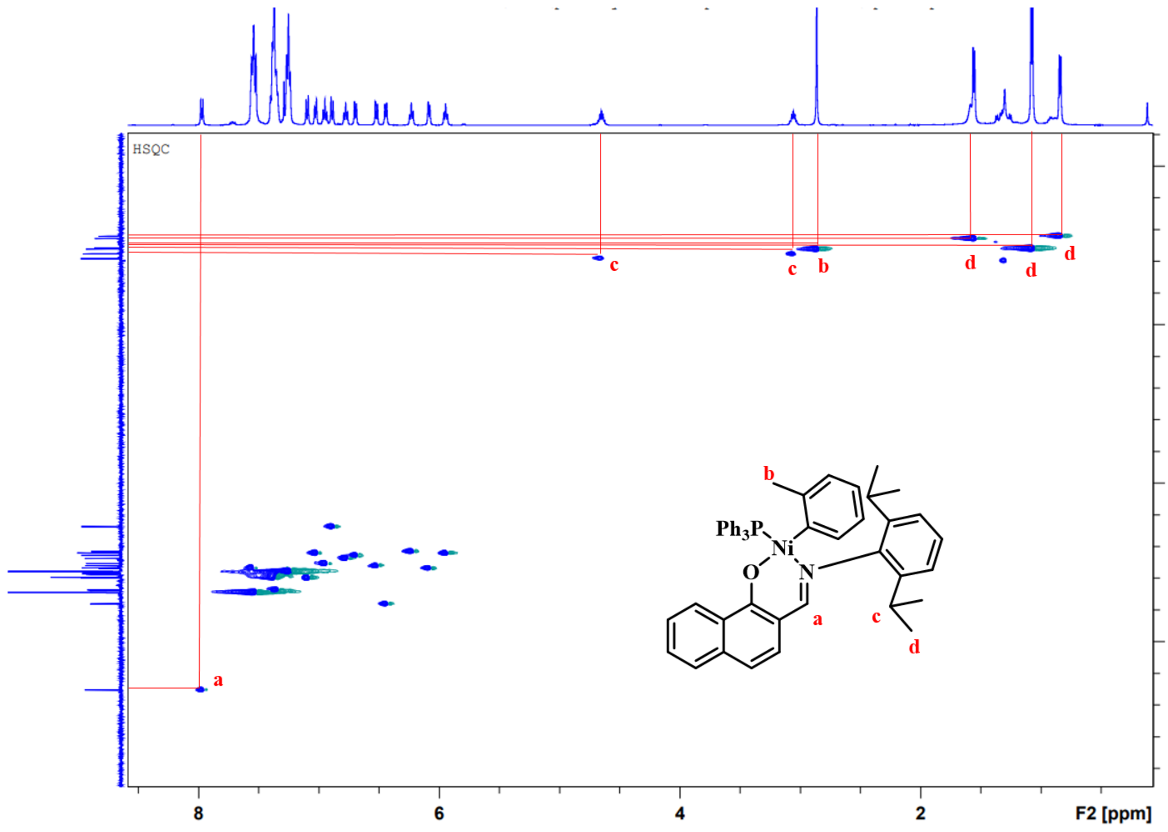


Figure S21: HSQC NMR spectrum of **Ni2** complex in $CDCl_3$.

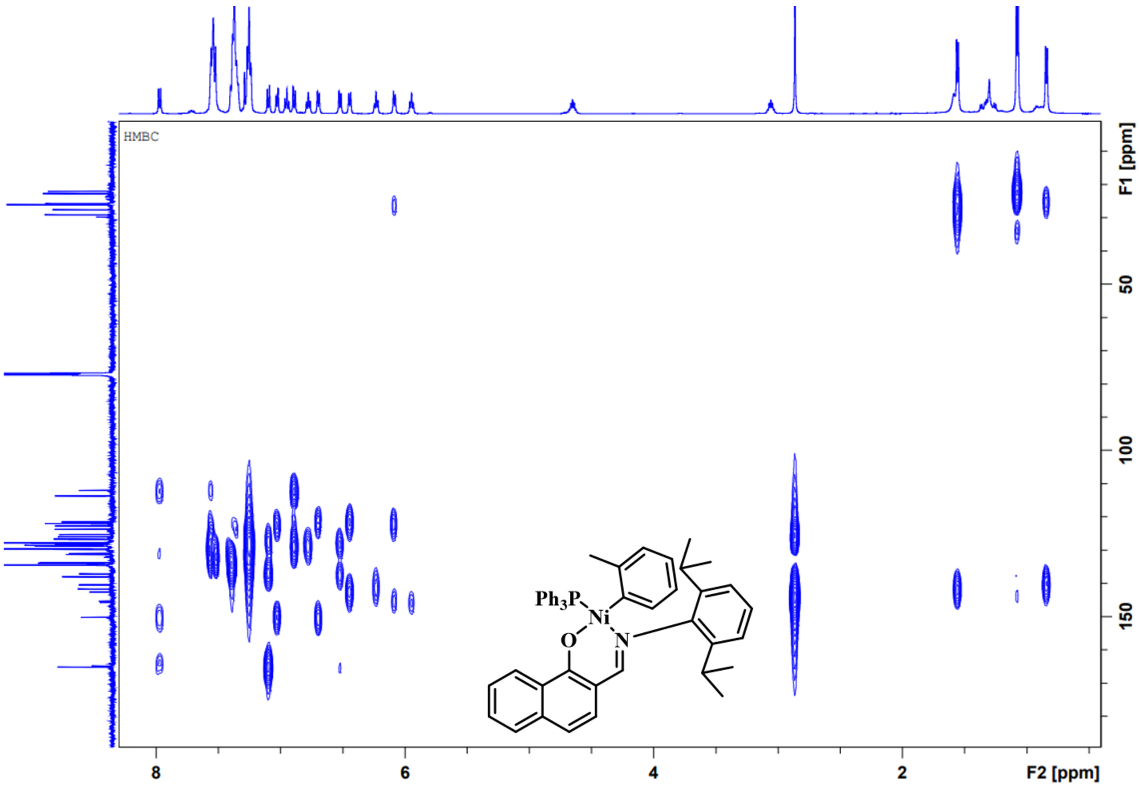


Figure S22: HMBC NMR spectrum of **Ni2** complex in $CDCl_3$.

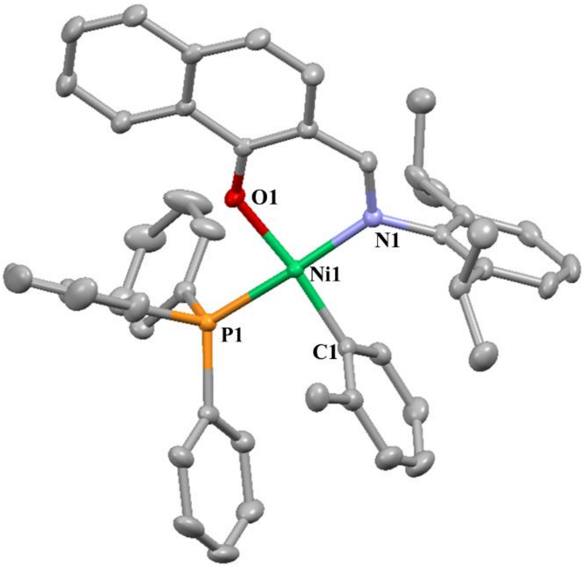


Figure S23: Molecular structure of **Ni2** complex.

Chart S2: Crystal data and structure refinement for Ni2.

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Bond precision:   C-C = 0.0034 A          Wavelength=0.71073

Cell:             a=11.4531(19)      b=13.695(2)       c=14.417(3)
                  alpha=77.010(6)    beta=66.853(5)    gamma=71.002(5)
Temperature:      100 K

                  Calculated                  Reported
Volume            1953.8(6)                   1953.8(6)
Space group       P -1                        P -1
Hall group        -P 1                        -P 1
Moiety formula    C48 H46 N Ni O P            C48 H46 N Ni O P
Sum formula       C48 H46 N Ni O P            C48 H46 N Ni O P
Mr                742.52                      742.54
Dx,g cm-3         1.262                       1.262
Z                 2                           2
Mu (mm-1)         0.575                       0.575
F000              784.0                       784.0
F000'             785.12
h,k,lmax          15,18,19                    15,18,19
Nref              9873                        9766
Tmin,Tmax         0.865,0.928                 0.684,0.746
Tmin'             0.827

Correction method= # Reported T Limits: Tmin=0.684 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.989            Theta(max)= 28.442

                                                      wR2(reflections)=
R(reflections)= 0.0509( 7919)                         0.0893( 9766)
S = 1.068                   Npar= 504
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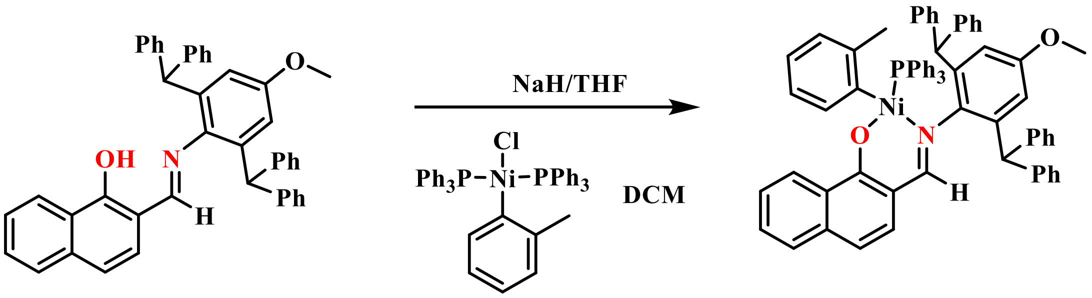
3.3 Synthesis of Ni3 complex:



Scheme S4: Synthesis of **Ni3** complex.

In an oven-dried Schlenk flask, NaH (33.8 mg, 1.40 mmol) and ligand **L3** (429 mg, 0.704 mmol) were taken. The flask was cooled to 0 °C and 25 mL THF was added to that. The reaction mixture was stirred at 0 °C for 1 hour, after that the solvent was evaporated. The resultant compound was dissolved in 20 mL DCM and was dropwise transferred to another flask that contained [NiCl(*o*-Tol)(PPh$_3$)$_2$] (500 mg, 0.704 mmol) precursor in 5 mL of DCM at 0 °C. The reaction mixture was stirred at the same temperature for 1 hour and DCM was evaporated. The resultant residue was purified by column chromatography using Pet Ether (98%)/ Ethyl acetate (2%) (Yield-620 mg, 86%).

^{1}H NMR (500 MHz, CDCl$_3$): δ **=** 7.66 (s, 1 H), 7.53 (t, *J* = 8.8 Hz, 6 H), 7.40 (d, *J* = 7.9 Hz, 1 H), 7.35 - 7.31 (m, 3 H), 7.26 (s, 3 H), 7.24 (d, *J* = 3.5 Hz, 3 H), 7.21 (d, *J* = 1.9 Hz, 2 H), 7.20 - 7.19 (m, 3 H), 7.19 - 7.17 (m, 4 H), 7.05 - 7.00 (m, 5 H), 6.75 (d, *J* = 7.3 Hz, 2 H), 6.72 - 6.62 (m, 3 H), 6.60 - 6.53 (m, 3 H), 6.49 (d, *J* = 2.8 Hz, 1 H), 6.43 (t, *J* = 7.3 Hz, 1 H), 6.38 (d, *J* = 8.5 Hz, 1 H), 6.24 - 6.17 (m, 3 H), 6.11 (t, *J* = 7.1 Hz, 1 H), 5.97 (d, *J* = 2.8 Hz, 1 H), 5.67 (d, *J* = 8.8 Hz, 1 H), 5.28 (d, *J* = 8.8 Hz, 1 H), 5.20 (s, 1 H), 3.43 (s, 3 H), 3.07 (s, 3 H). **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 168.5, 163.5, 155.8, 144.9, 143.7, 143.4, 143.3, 143.1, 139.7, 138.7, 138.6, 137.1, 134.4, 134.3, 131.3, 130.9, 130.5, 130.3, 130.2, 129.9, 129.6, 129.2, 128.5, 128.3, 128.0, 127.9, 127.7, 127.7, 127.4, 127.2, 126.4, 126.3, 126.2, 125.9, 125.8, 125.7, 123.3, 123.1, 121.8, 113.5, 113.3, 112.4, 112.1, 55.1, 53.5, 51.9, 26.5. **^{31}P NMR (500 MHz, CDCl$_3$):** δ = 22.8.

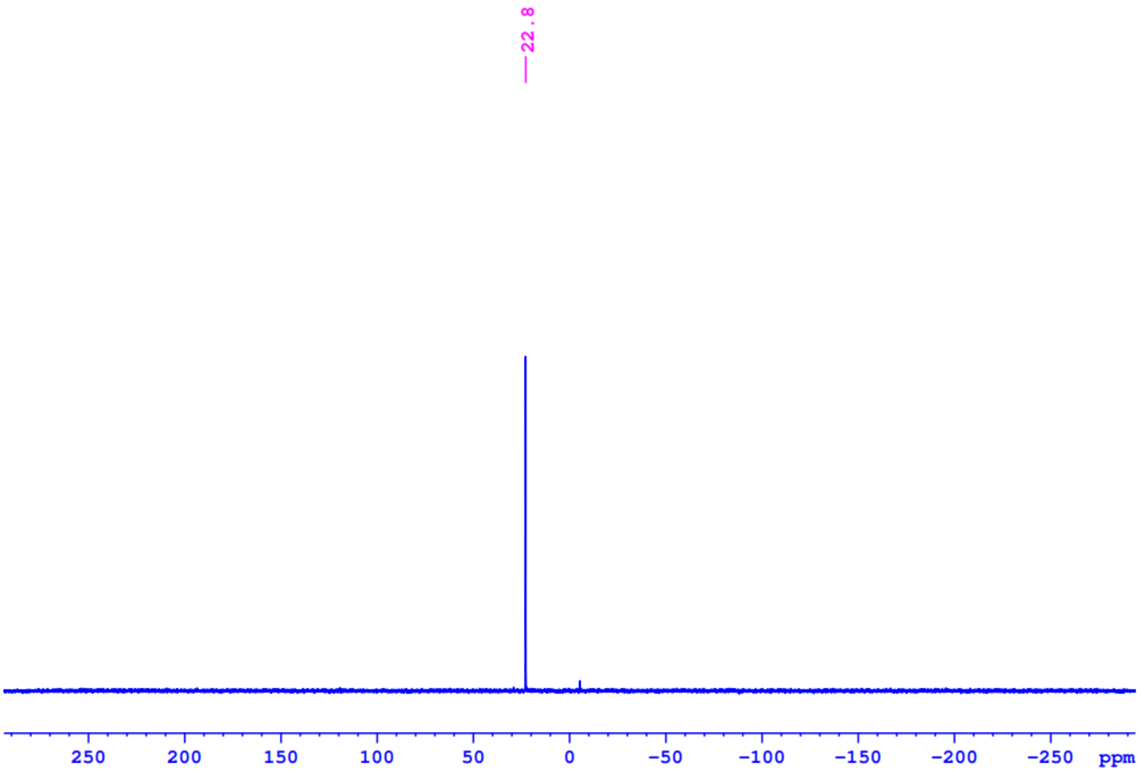


Figure S24: ^{31}P NMR spectrum of **Ni3** complex in CDCl$_3$.

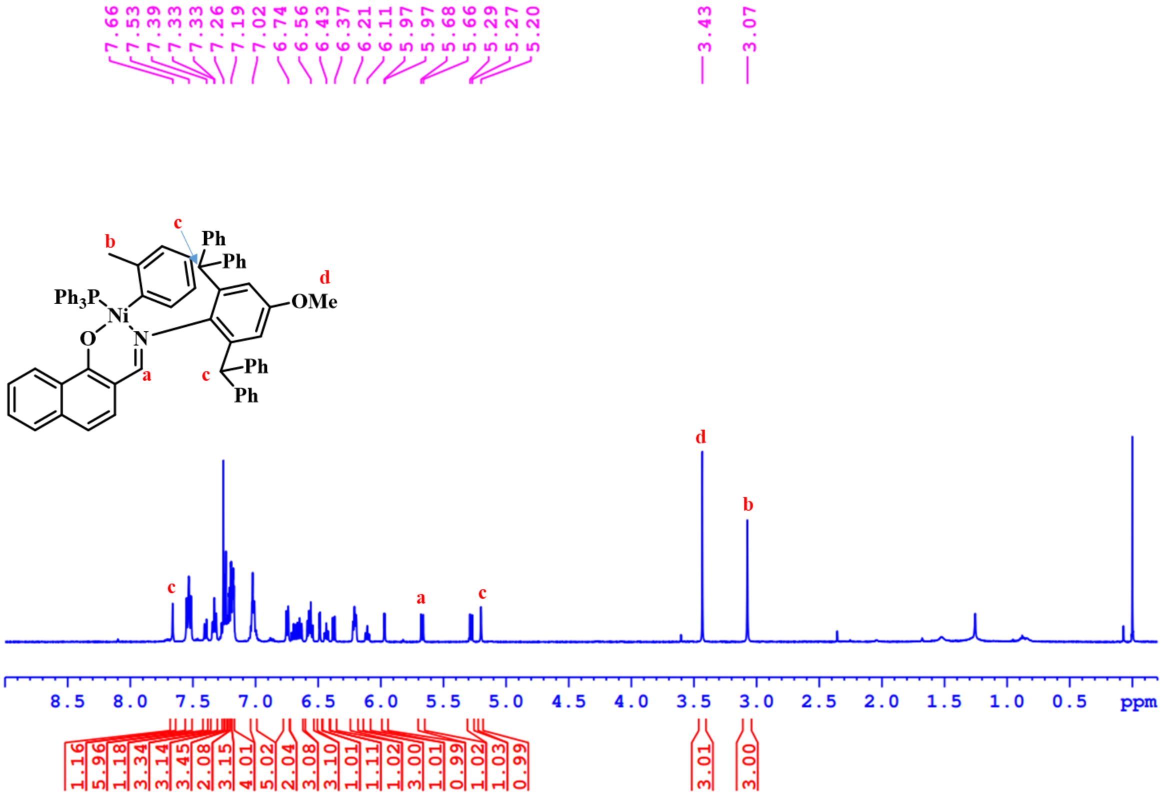


Figure S25: ^{1}H NMR spectrum of **Ni3** complex in $CDCl_3$.

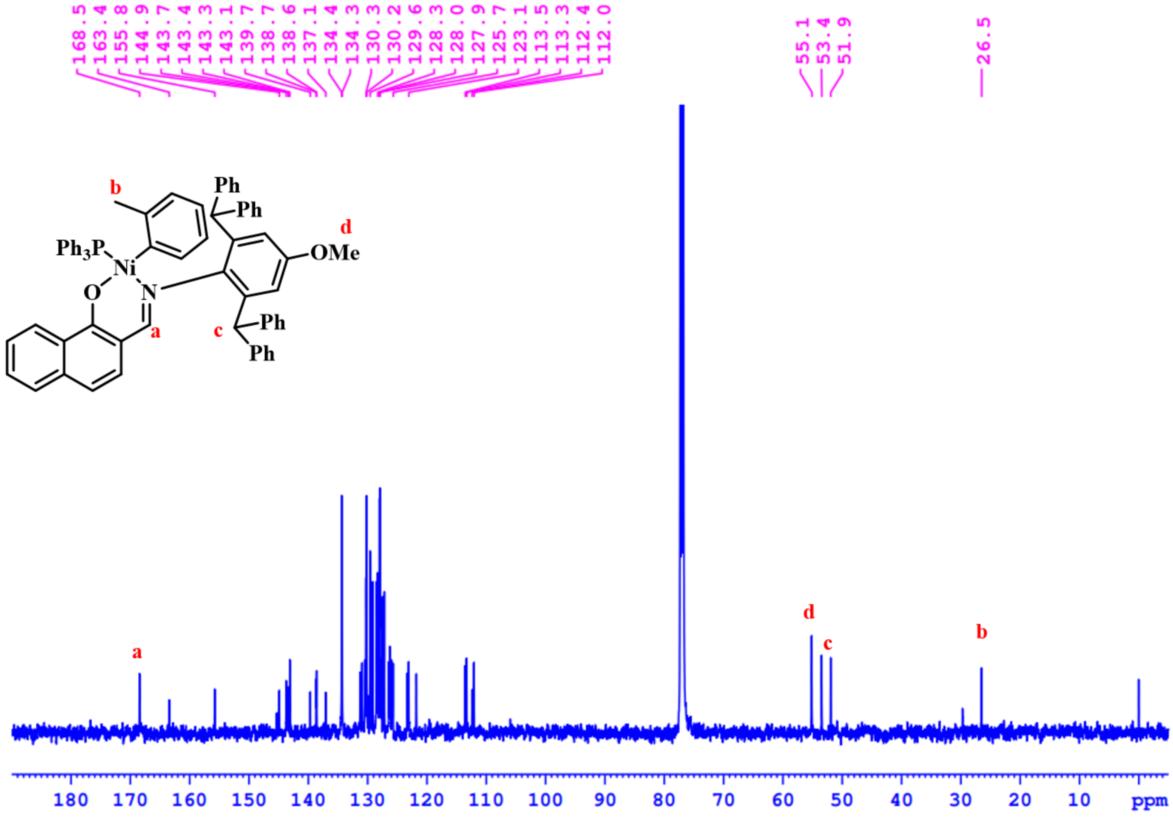


Figure S26: ^{13}C NMR spectrum of **Ni3** complex in $CDCl_3$.

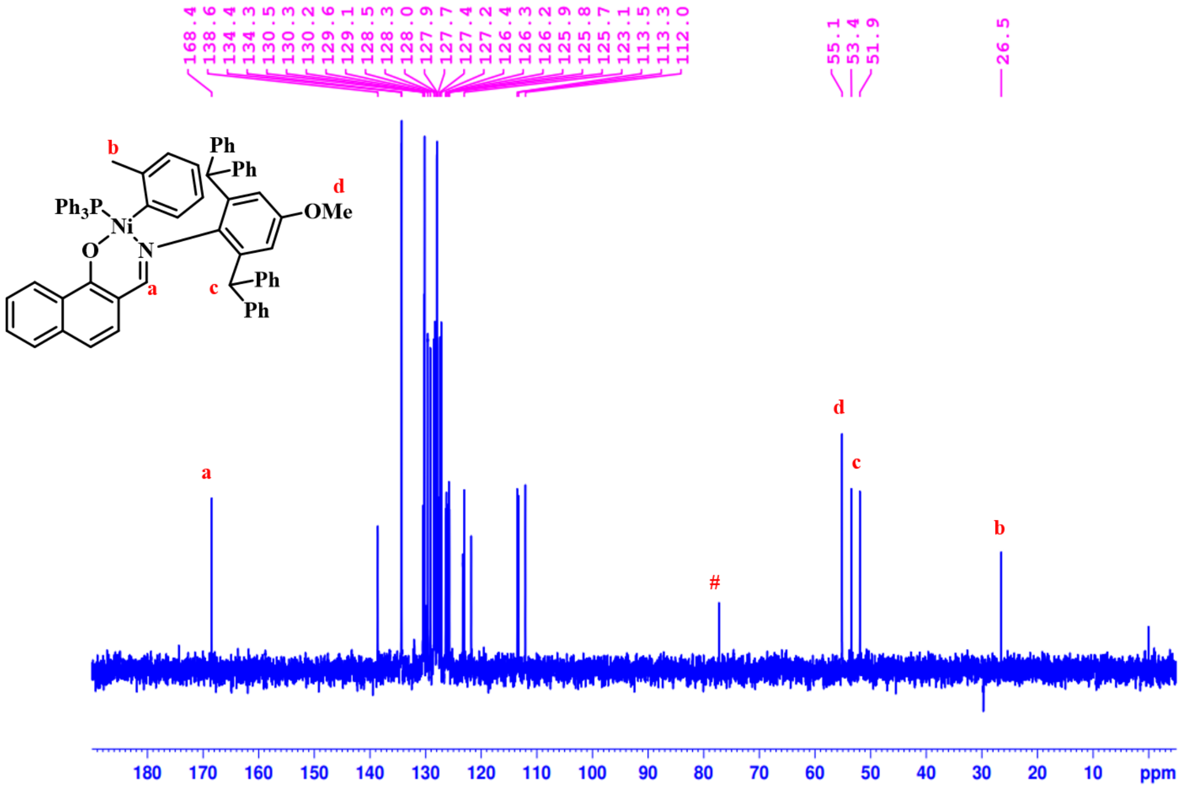


Figure S27: ^{13}C DEPT NMR spectrum of **Ni3** complex in CDCl$_3$.

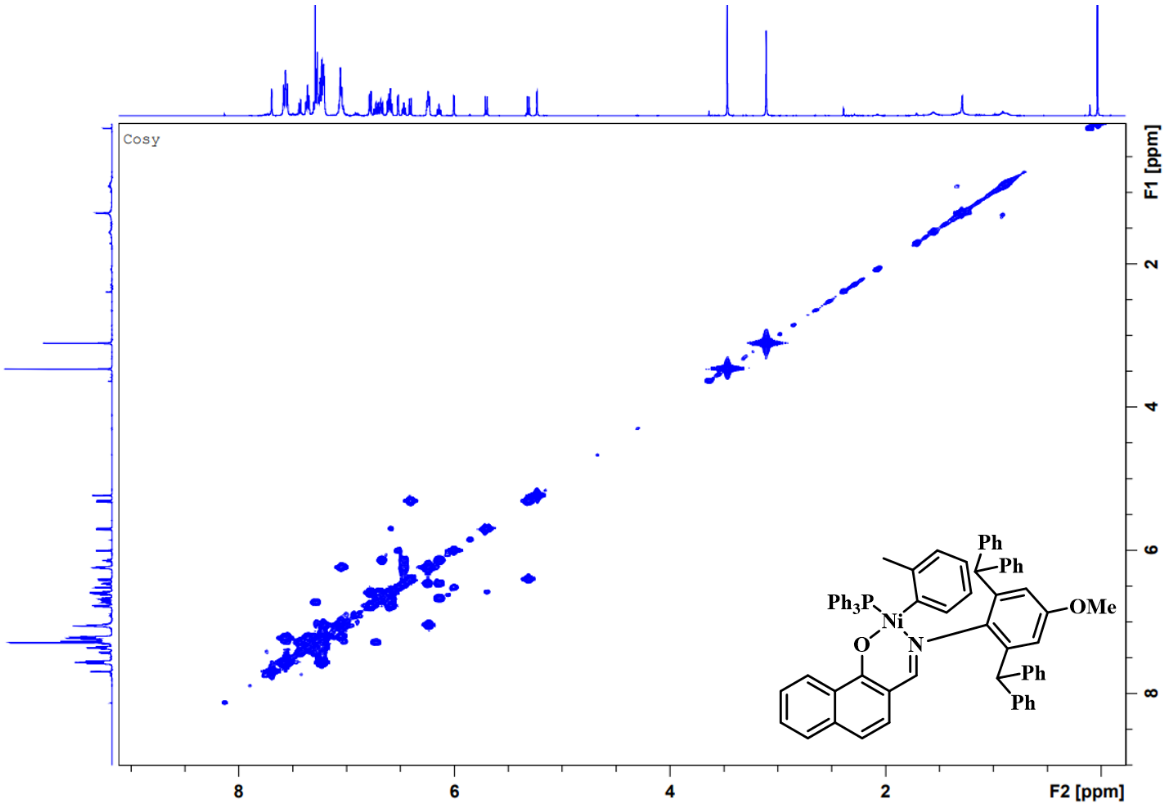


Figure S28: ^{1}H-^{1}H COSY NMR spectrum of **Ni3** complex in CDCl$_3$.

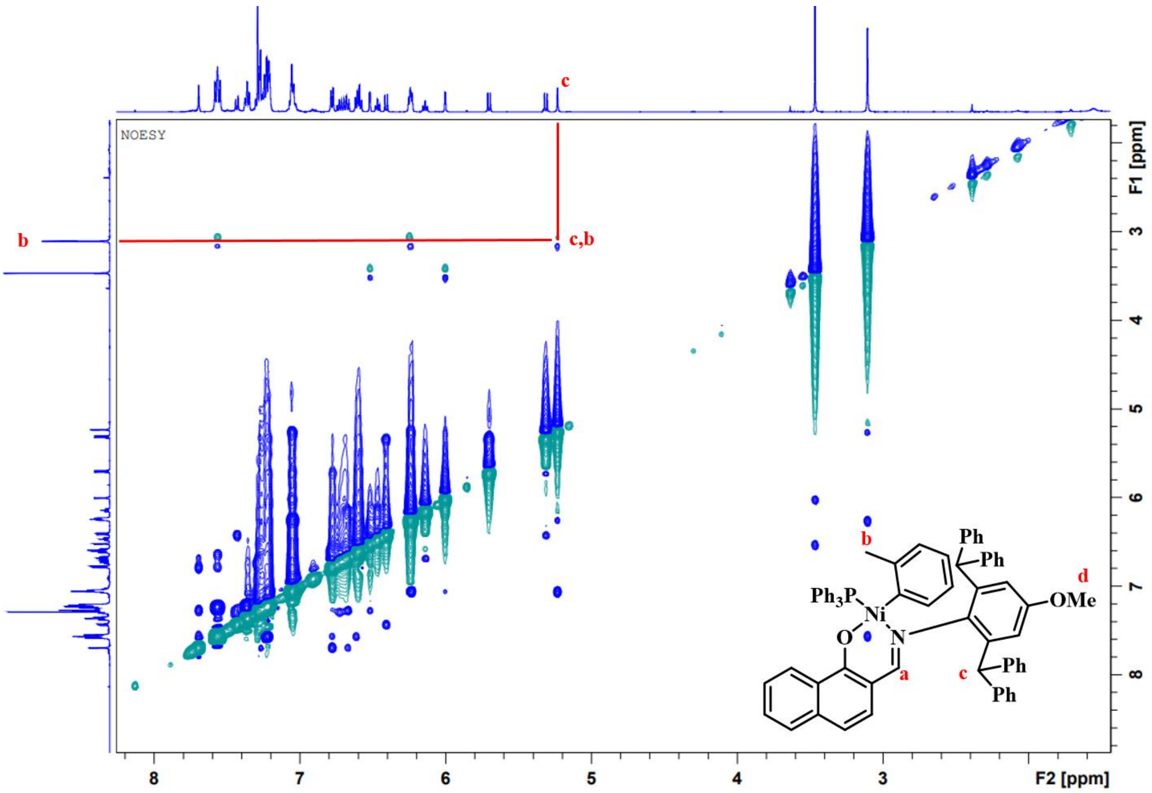


Figure S29: NOESY NMR of **Ni3** complex in $CDCl_3$.

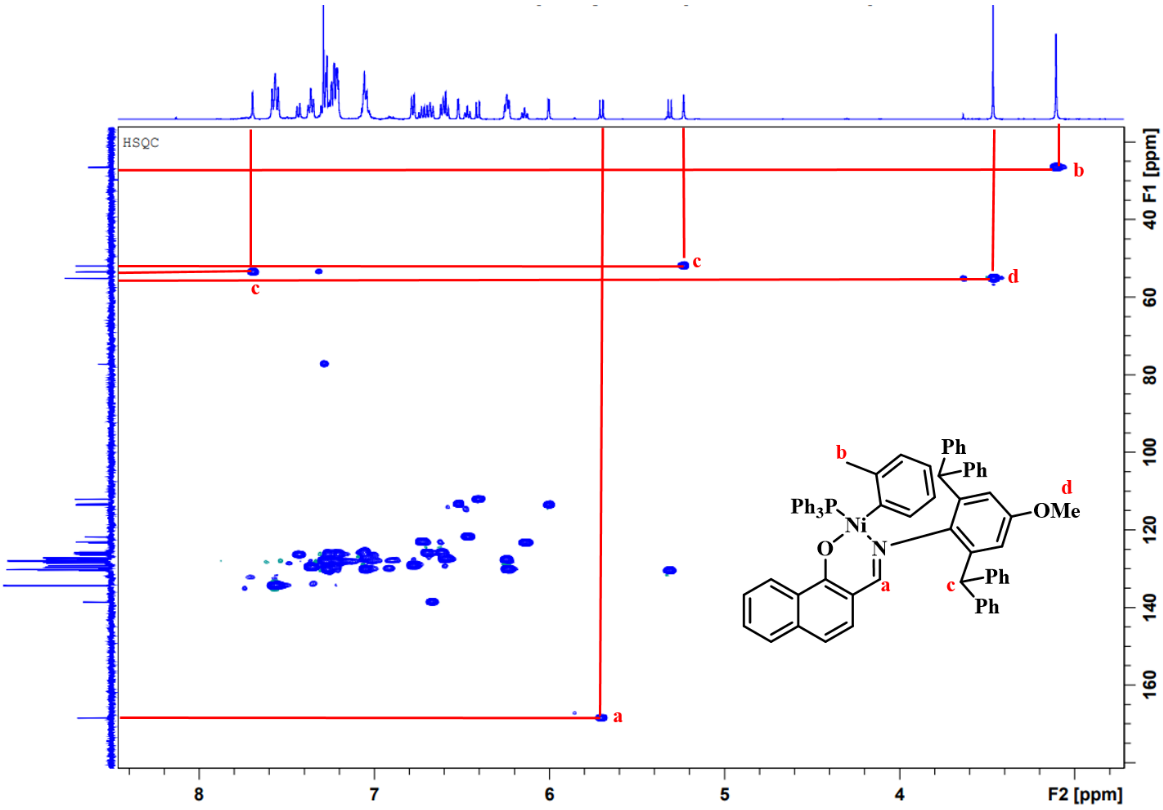


Figure S30: HSQC NMR spectrum of **Ni3** complex in $CDCl_3$.

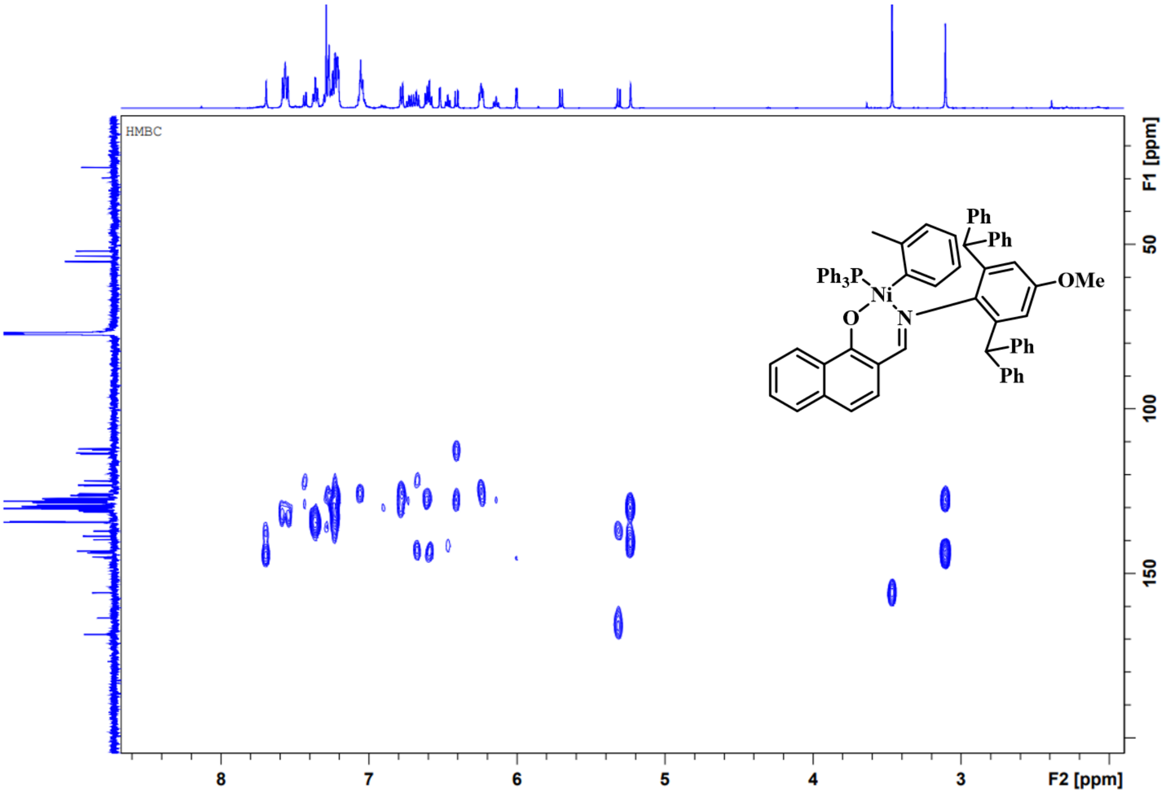


Figure S31: HMBC NMR spectrum of **Ni3** complex in $CDCl_3$.

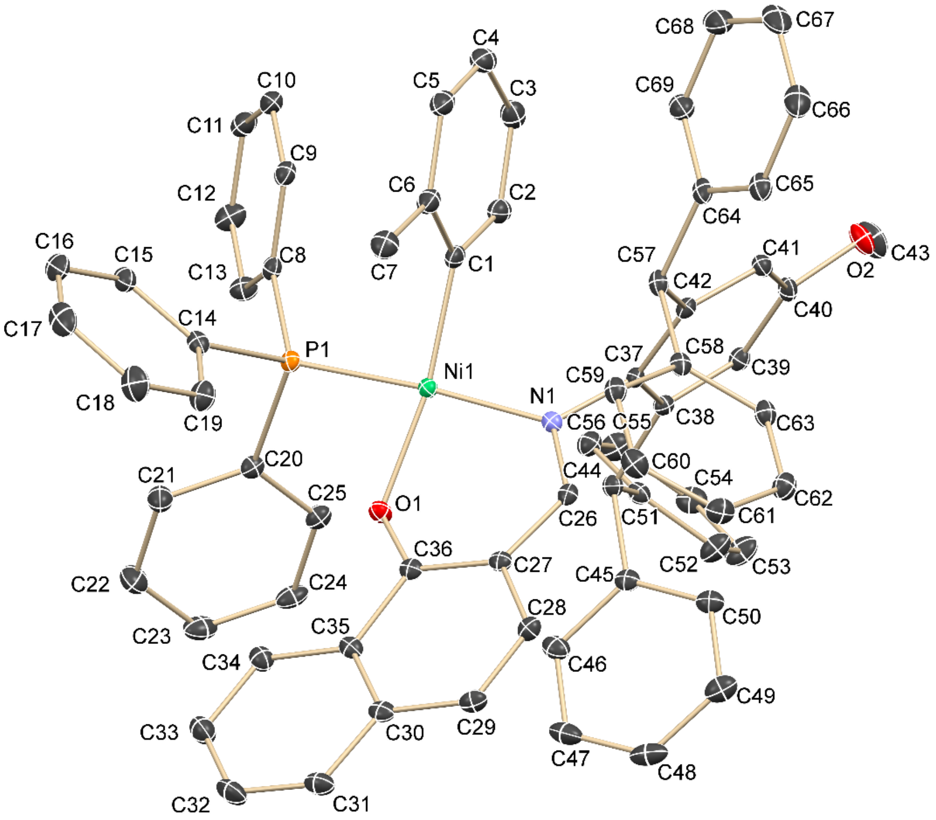
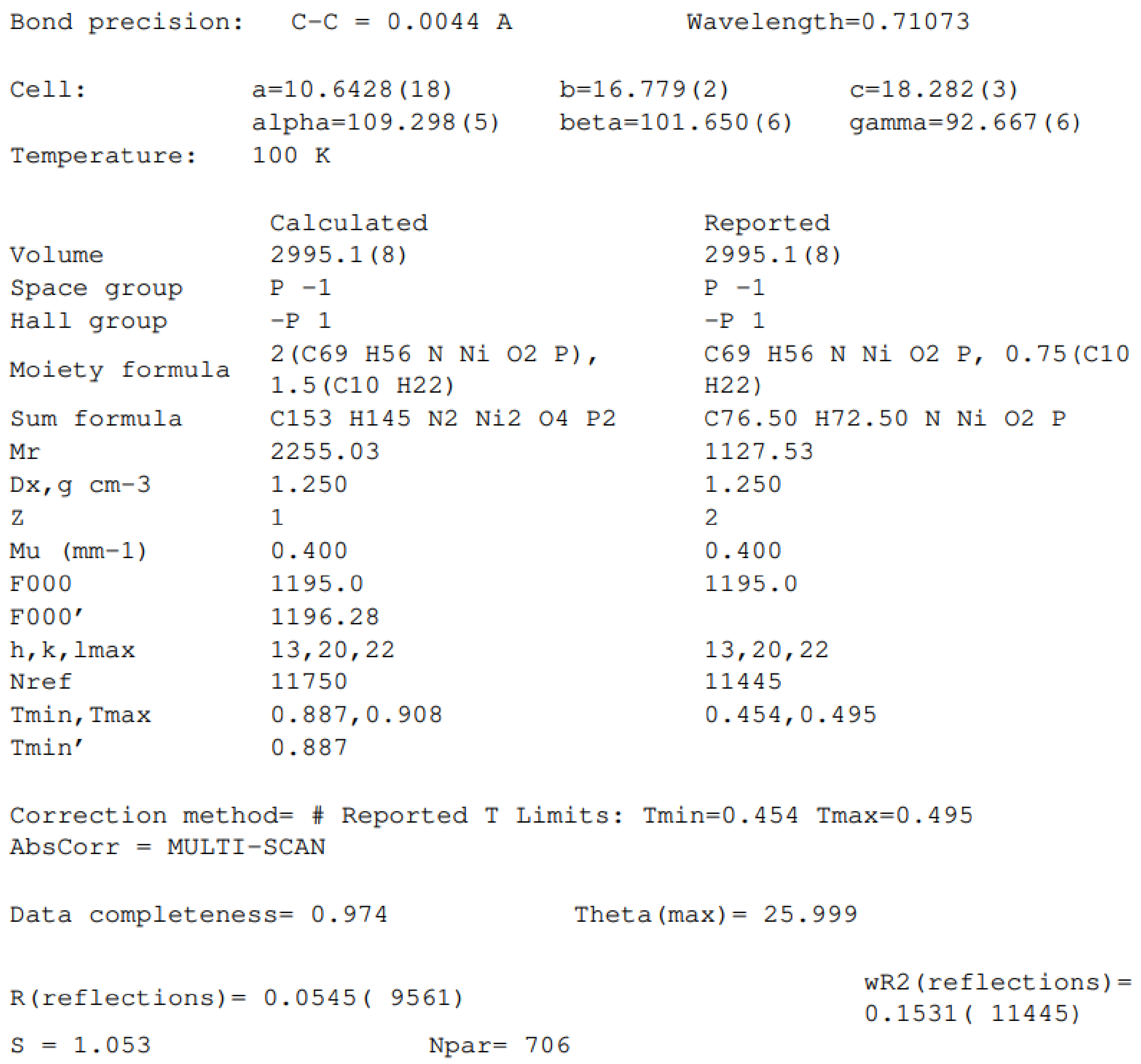


Figure S32: Molecular structure of **Ni3** complex.

Chart S3: Crystal data and structure refinement parameters for Ni3.



```
Bond precision:    C-C = 0.0044 A           Wavelength=0.71073

Cell:            a=10.6428(18)       b=16.779(2)        c=18.282(3)
                 alpha=109.298(5)    beta=101.650(6)    gamma=92.667(6)
Temperature:     100 K

                  Calculated                  Reported
Volume            2995.1(8)                   2995.1(8)
Space group       P -1                        P -1
Hall group        -P 1                        -P 1
Moiety formula    2(C69 H56 N Ni O2 P),       C69 H56 N Ni O2 P, 0.75(C10
                  1.5(C10 H22)                H22)
Sum formula       C153 H145 N2 Ni2 O4 P2      C76.50 H72.50 N Ni O2 P
Mr                2255.03                     1127.53
Dx,g cm-3         1.250                       1.250
Z                 1                           2
Mu (mm-1)         0.400                       0.400
F000              1195.0                      1195.0
F000'             1196.28
h,k,lmax          13,20,22                    13,20,22
Nref              11750                       11445
Tmin,Tmax         0.887,0.908                 0.454,0.495
Tmin'             0.887

Correction method= # Reported T Limits: Tmin=0.454 Tmax=0.495
AbsCorr = MULTI-SCAN

Data completeness= 0.974             Theta(max)= 25.999

                                                      wR2(reflections)=
R(reflections)= 0.0545( 9561)                         0.1531( 11445)

S = 1.053                  Npar= 706
```

Table S1: Nickel complexes and their CCDC number.

Complex	CCDC No.
Ni1	2285806
Ni2	2285654
Ni3	2225186

4. Percent buried volume data:

Percent buried volume data (%Vbur) were generated by SambVca 2.1 web application.[4]

More details for %Vbur calculation and steric maps are as under:

1) The nickel atom (Ni) defines the center of the xyz coordinate system.

2) $Ni(PPh_3)$(*o*-Tolyl) fragment was excluded.

3) Bondi radii was scaled by 1.17.

4) Mesh spacing for numerical integration was 0.10.

5) Sphere radius was set to 3.5 Å.

6) H atoms were excluded.

For all compounds positive x-plane was defined as imine nitrogen and negative z plane was defined as the oxygen of the naphthoxy ligand.

5. Ethylene polymerization:

The polymerization reaction was performed in a Buchi high-pressure metal reactor, which was connected to ethylene gas line. Initially, the reactor was dried at 90 °C under vacuum for 1 hour. The reactor temperature was maintained at the desired polymerization temperature and the reactor was purged with ethylene gas. To that, 100 mL of anhydrous toluene was added under positive ethylene gas flow. Further, toluene was stirred under the ethylene pressure for 30 minutes to dissolve ethylene in toluene. Excess ethylene was vented and the desired amount of catalyst and cocatalyst was injected into the reactor using the syringe. The reactor was pressurized with rapid stirring and the desired pressure was maintained throughout the polymerization. After the completion of polymerization, excess ethylene was vented and polymerization was quenched by adding acidic methanol. The polymer was filtered by using Whatman filter paper, polymer was dried under a high vacuum to yield polyethylene. Table S2 summarizes important runs using Ni-catalyst.

Table S2. Ethylene polymerization by using a Ni catalysts.

Entry No	**Cat.**	**Temp. (°C)**	**Pressure (bar)**	**Time (minute)**	**yield (g)**	**TOF X10^4**	**Tm**	**% of cryst.**	**Mn**	**Mw**	**PDI**
1.	Ni1	60	20	20	0.003	-	97.5	16.8	-	-	-
2.	Ni1	70	20	20	0.026	0.028	94.4	27.8	-	-	-
3.	Ni1	80	20	20	0.185	0.204	83.1	11.7	3900	7900	2
4.	Ni1	90	20	20	0.124	0.135	75.93	12.8	-	-	-

5.	Ni2	60	20	20	0.014	0.015	107.0	49.0	-	-	-
6.	Ni2	70	20	20	0.528	0.578	101.7	32.3	-	-	-
7.	Ni2	80	20	20	1.210	1.325	94.6	24.9	6600	13200	2
8.	Ni2	90	20	20	2.423	2.65	80.5	10.4	-	-	-
9	Ni3	60	20	20	0.420	0.46	114.4	63.4	-	-	-
10	Ni3	70	20	20	1.748	1.95	106.3	55.1	39000	100000	2.5
11	Ni3	70	20	10	0.767	1.66	107.3	32.1	-	-	-
12	Ni3	70	20	30	2.265	1.65	107.6	47.7	-	-	-
13	Ni3	80	20	20	3.236	3.54	96.3	28.5	61000	160000	2.6
14	Ni3	90	20	20	2.235	2.4	81.4	11.5	70000	113000	1.6
15	Ni3	80	25	20	2.862	3.13	99.6	36.5	114000	270000	2.3
16	Ni3	80	15	20	3.186	3.49	89.1	23.5	-	-	-
17	Ni3	80	10	20	1.611	1.76	78.3	13.9	48000	114600	2.3
18[a]	Ni3	70	20	90	2.260	0.38	94.5	31.2	75000	150000	1.9
19[b]	Ni3	80	20	20	3.053	3.37	-	-	-	-	-
20[b]	Pd1	80	20	90	0.298	525	-	-	-	-	-

Reaction conditions: Toluene: 100 mL, Catalyst: 9.79 µmol., Cocatalyst: [Ni(COD)$_2$] 2 equivalent, Ethylene: 10-25 bar, TOF: in (mol of PE/mol of Ni h^{-1}), (-): Not Determined. The reported yield is after reprecipitating the polyethylene in acidic methanol and drying in high vacuum for 4 hours. Branches per 1000 carbon atoms was calculated using ^{1}H NMR spectroscopy (calculation for entry 13, figure S35 is shown below). [a]Catalyst: 15 mg, Cocatalyst: ($(C_6F_5)_3B$) 2 equivalent, [b]Cocatalyst: ($(C_6F_5)_3B$) 1 equivalent, [c]Taken from the Ref. 5, Tm and % of crystallinity was calculated from DSC, Mn/Mw/PDI: HT-GPC in TCB at 160 °C against polystyrene-standard.

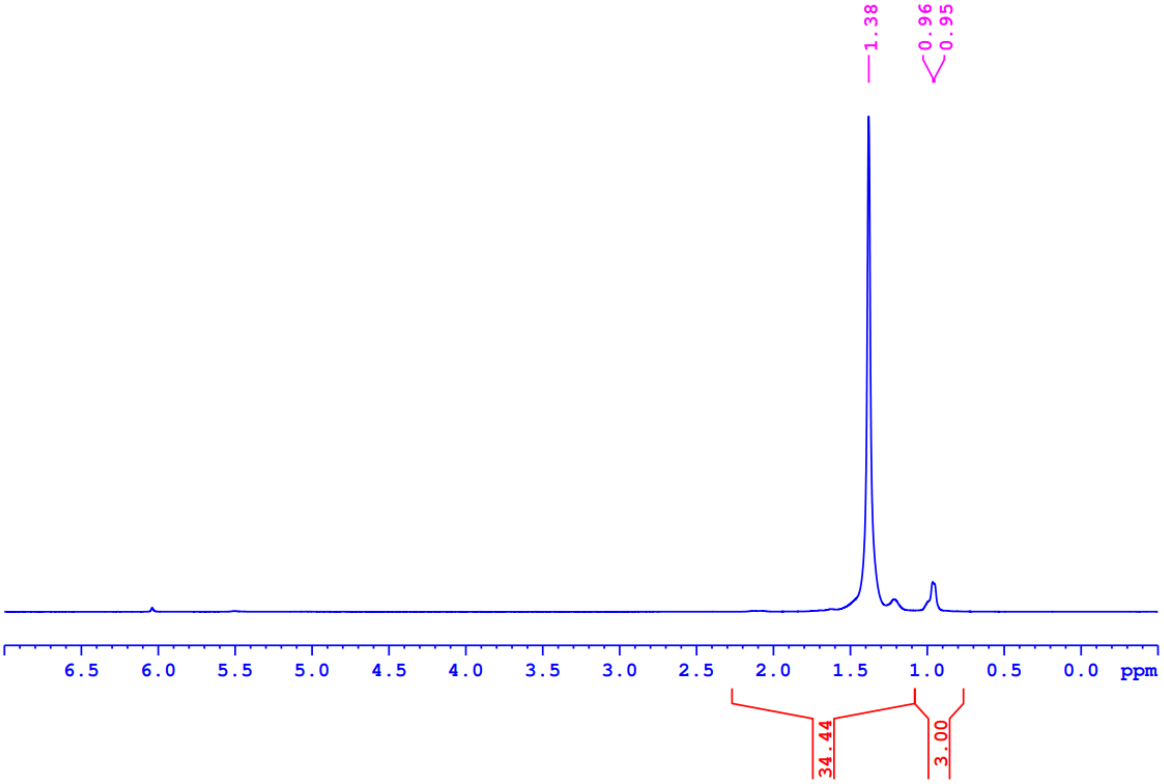


Figure S33: ^{1}H NMR spectrum of polyethylene in $C_2D_2Cl_4$ at 80 °C (entry no. 3).

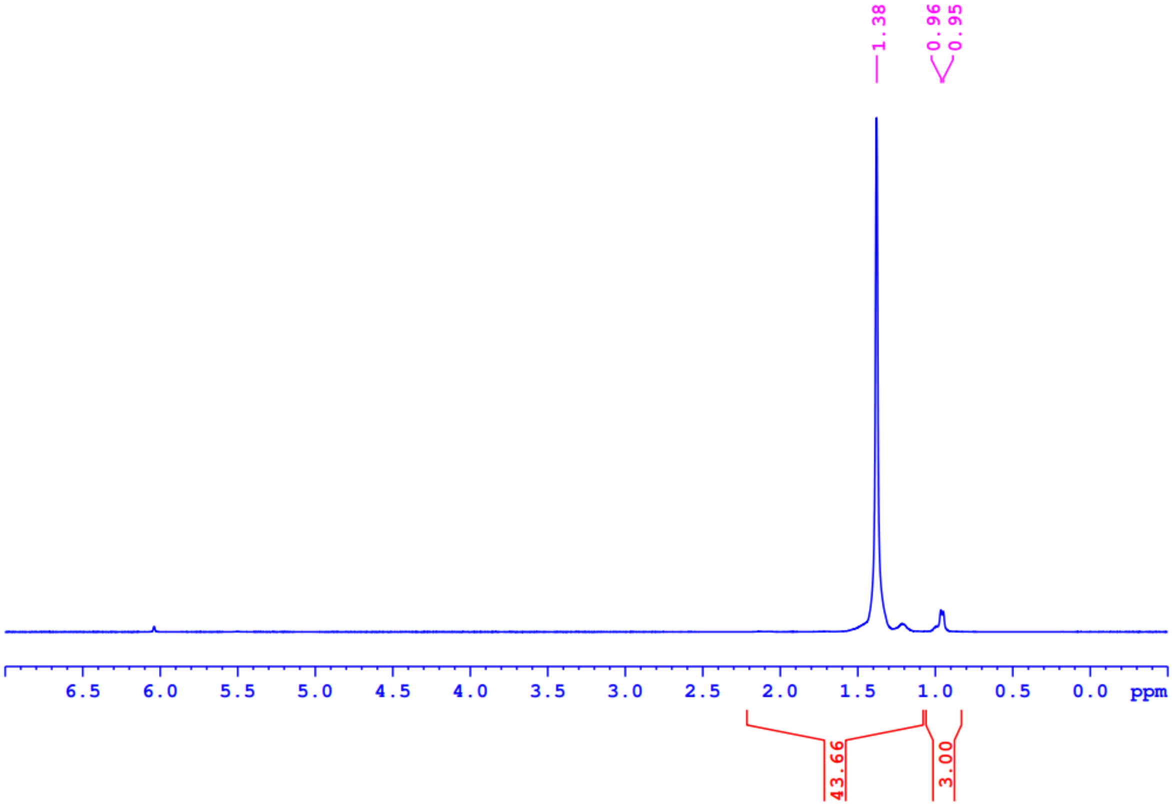


Figure S34: ^{1}H NMR spectrum of polyethylene in $C_2D_2Cl_4$ at 80 °C (entry no.7).

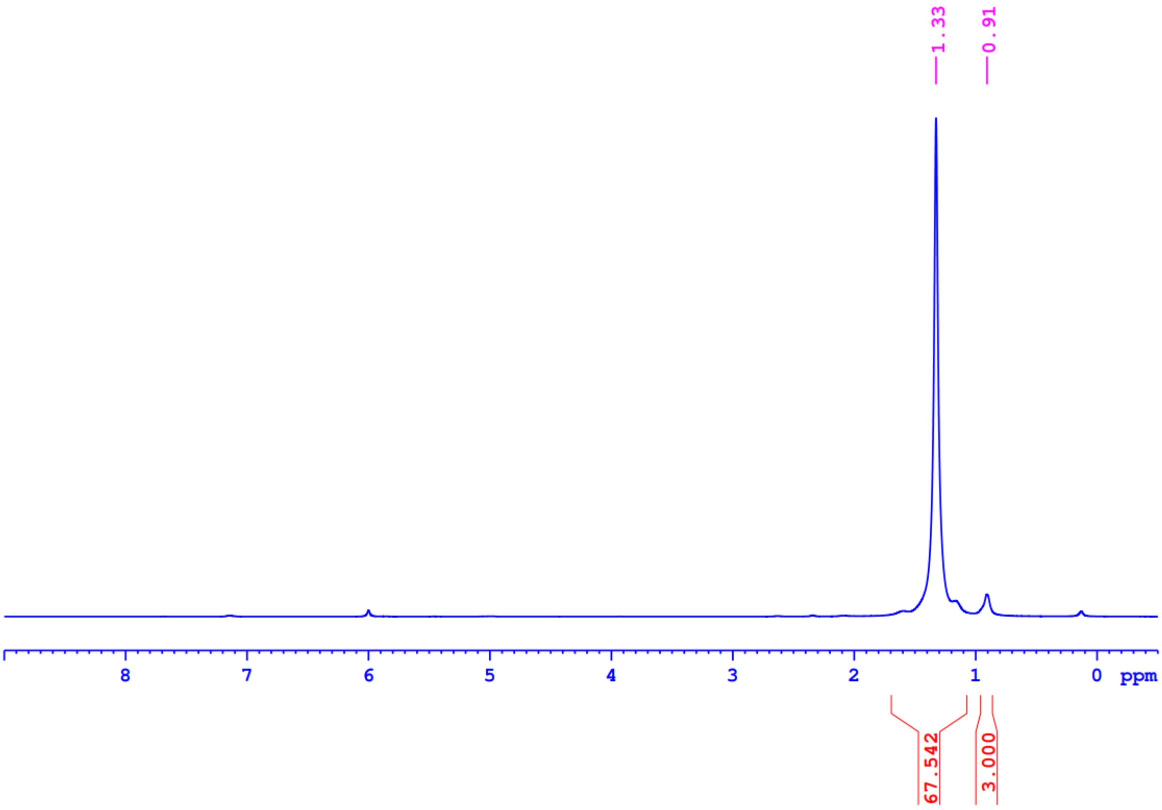


Figure S35: ^{1}H NMR spectrum of polyethylene in $C_2D_2Cl_4$ at 80 °C (entry no. 13).

Calculation of Me groups/1000C:[6]

Me groups/1000C $= (2 * I_{Me} / 3 * I_{tot}) * 1000$ …(*for figure S35, Entry 13*)

$= (2 * 3 / 3 * 70.5) * 1000$

$= 28.3 \sim$ **28**

Determination of percentage crystallinity:

%Crystallinity: The crystallinity of the resultant polyethylene was calculated from the melting enthalpy measured by DSC and relative to the theoretical value 293 J/g for 100% crystalline polyethylene (Table S3).

The term ΔHm° is a reference value and represents the heat of melting, if the polymer were 100% crystalline. This reference heat of melting has been established for each of the commonly used polymers and some of these are listed below.

Table S3. Melting enthalpy for 100% crystalline polymers.

Polymer	**ΔHm° (J/g)**
Nylon 6	230.1
PET	140
Nylon 6, 6	255.8
Polypropylene	207.1
Polyethylene	293

The DSC software directly provides melting enthalpy values to make the assessment of the percent crystallinity more convenient and easier. Crystallinity for one of the polyethylene samples is determined using the following method.

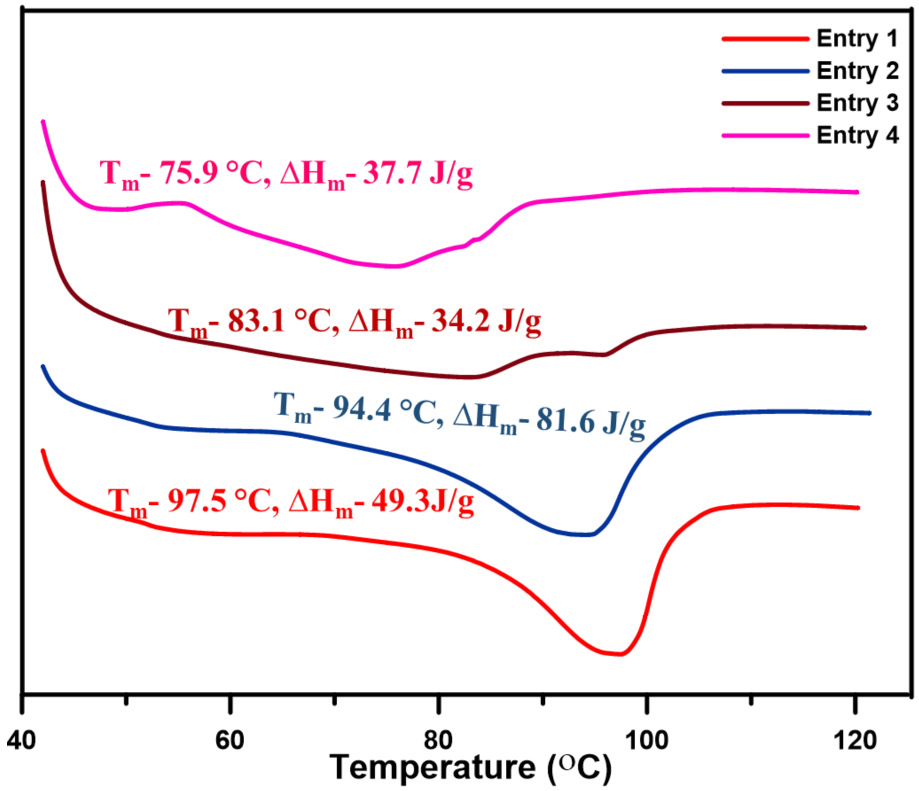
% Crystallinity = ΔHm /ΔHm° (J/g) ×100

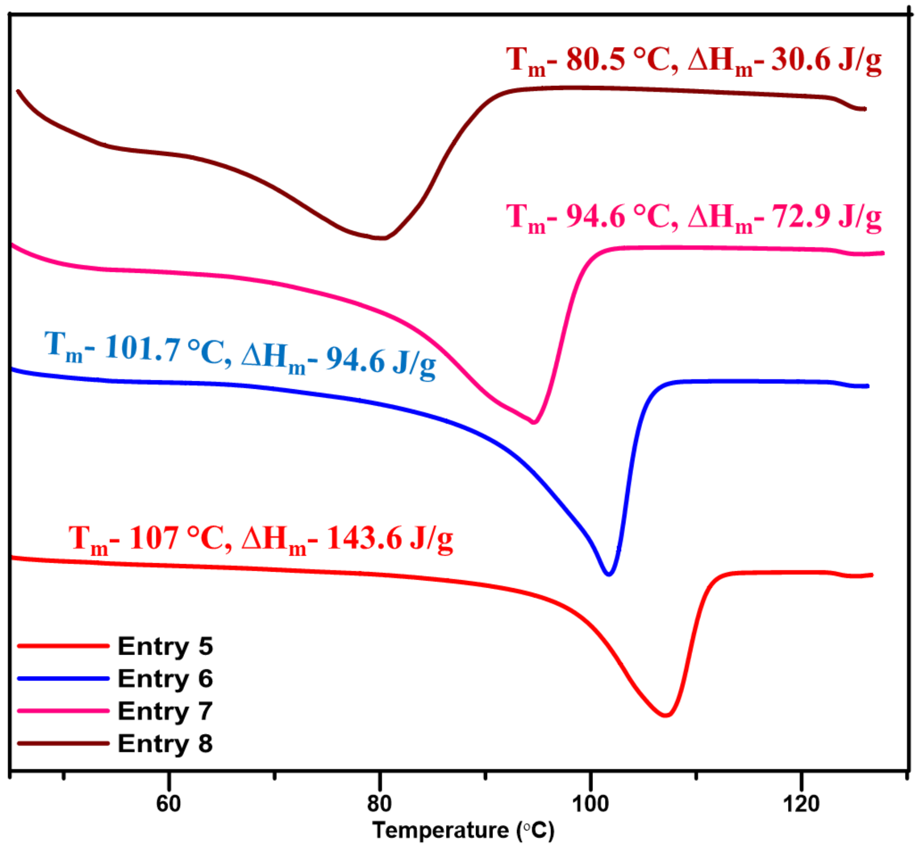
Therefore, ΔHm = 49.32 J/g …(*for entry 1*.)

ΔHm° = 293 J/g

% Crystallinity = 49.32 /293 ×100 = **16.8%**

6. DSC data:


Entry 1
Entry 2
Entry 3
Entry 4
T$_m$- 75.9 °C, ΔH$_m$- 37.7 J/g
T$_m$- 83.1 °C, ΔH$_m$- 34.2 J/g
T$_m$- 94.4 °C, ΔH$_m$- 81.6 J/g
T$_m$- 97.5 °C, ΔH$_m$- 49.3J/g
40
60
80
100
120
Temperature (°C)


T$_m$- 80.5 °C, ΔH$_m$- 30.6 J/g
T$_m$- 94.6 °C, ΔH$_m$- 72.9 J/g
T$_m$- 101.7 °C, ΔH$_m$- 94.6 J/g
T$_m$- 107 °C, ΔH$_m$- 143.6 J/g
Entry 5
Entry 6
Entry 7
Entry 8
60
80
100
120
Temperature (°C)

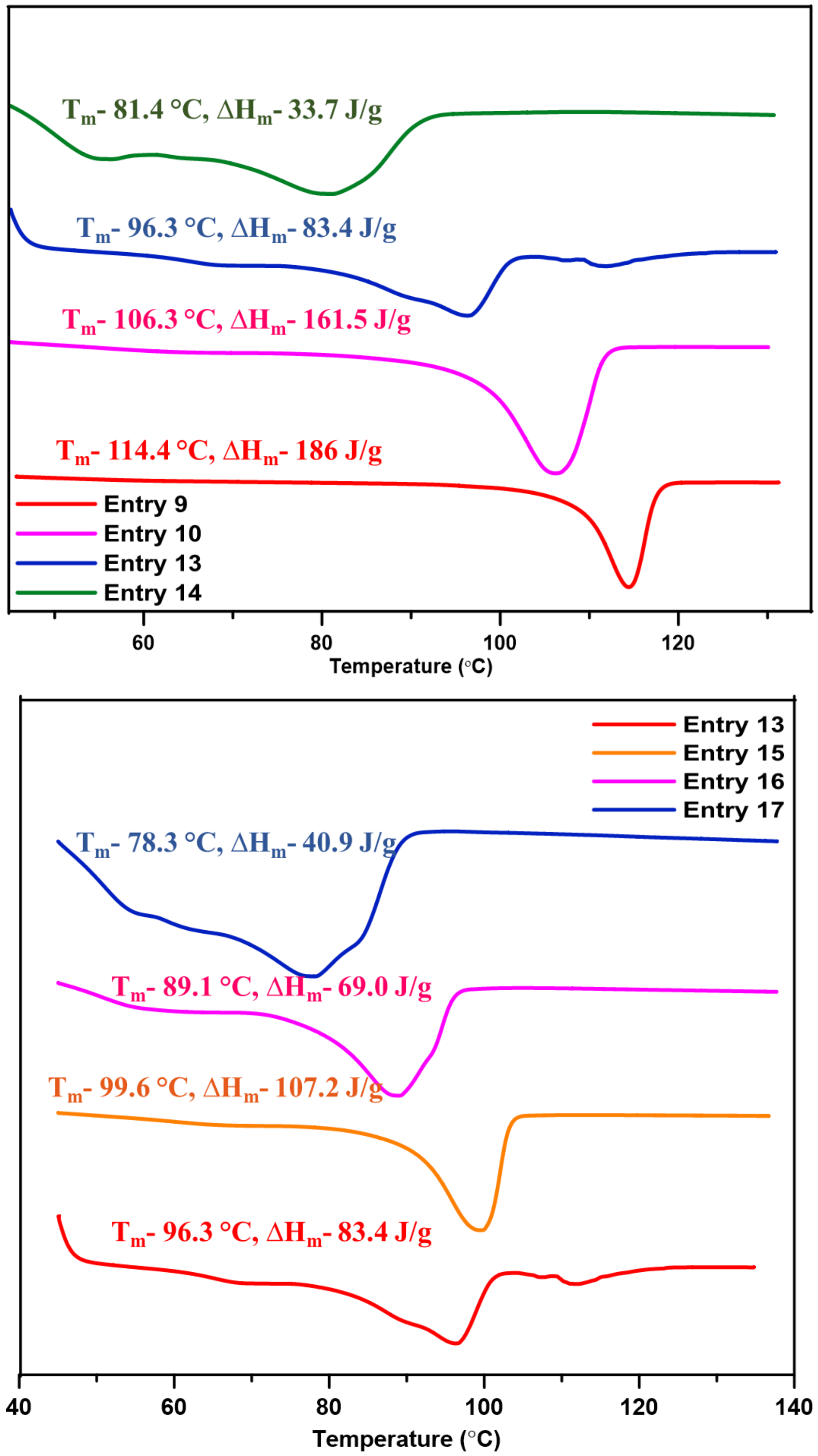
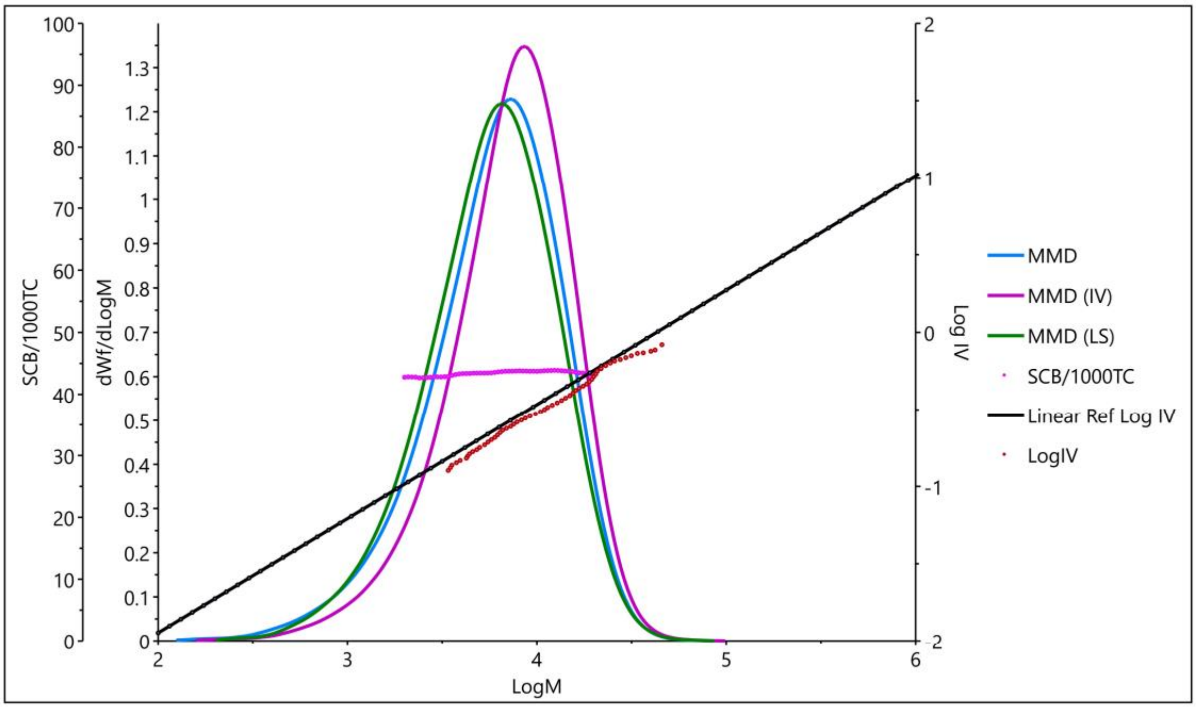
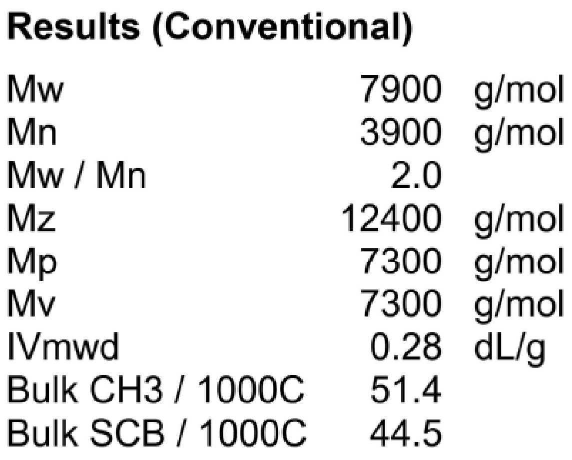


Figure S36: DSC thermogram of polyethylene for Table S2.

7a. HT-GPC chromatogram :

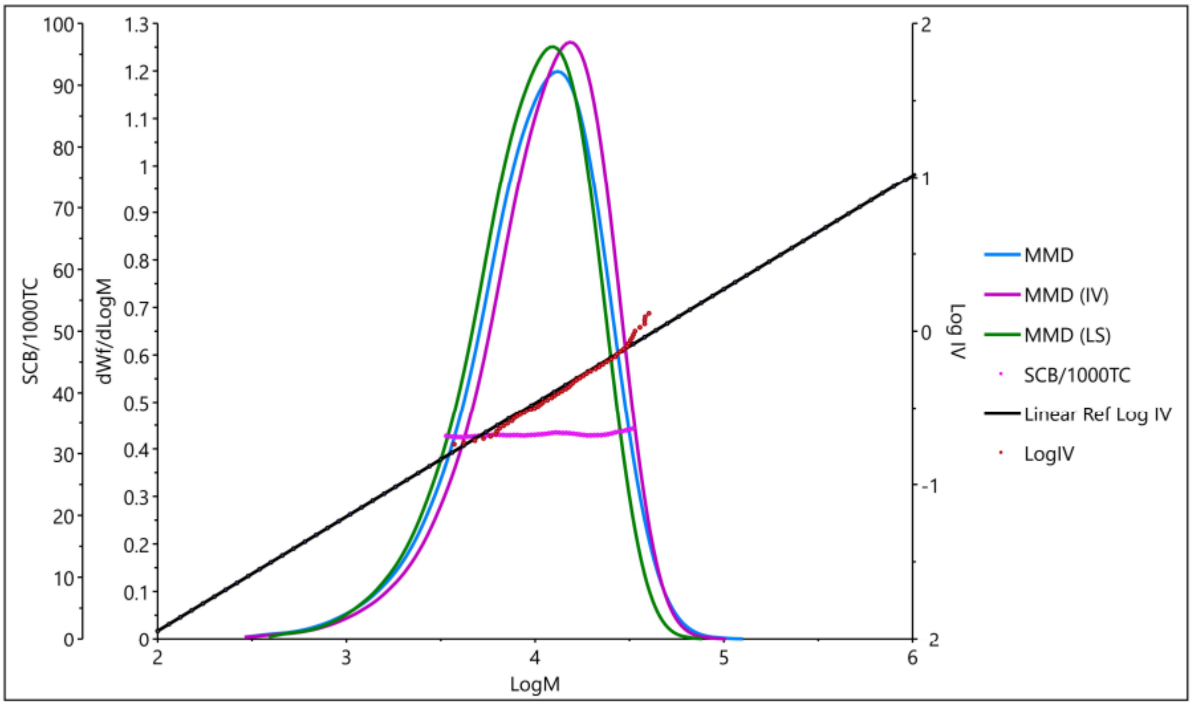




Results (Conventional)

Mw	7900	g/mol
Mn	3900	g/mol
Mw / Mn	2.0	
Mz	12400	g/mol
Mp	7300	g/mol
Mv	7300	g/mol
IVmwd	0.28	dL/g
Bulk CH3 / 1000C	51.4	
Bulk SCB / 1000C	44.5	

Figure S37: HT-GPC chromatogram of polyethylene for Table S2, entry 3.



Results (Conventional)

Mw	13200	g/mol
Mn	6600	g/mol
Mw / Mn	2.0	
Mz	20600	g/mol
Mp	13100	g/mol
Mv	12300	g/mol
IVmwd	0.41	dL/g
Bulk CH3 / 1000C	38.6	
Bulk SCB / 1000C	34.5	

Figure S38: HT-GPC chromatogram of polyethylene for Table S2, entry 7.

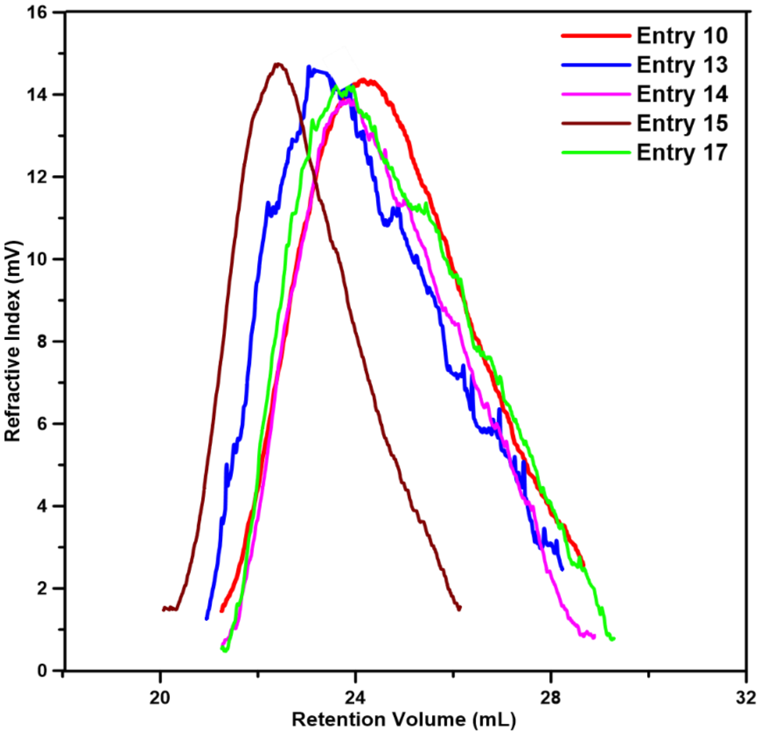


Figure S39: HT-GPC chromatogram of polyethylene for Table S2.

7b. ^{13}C NMR data:

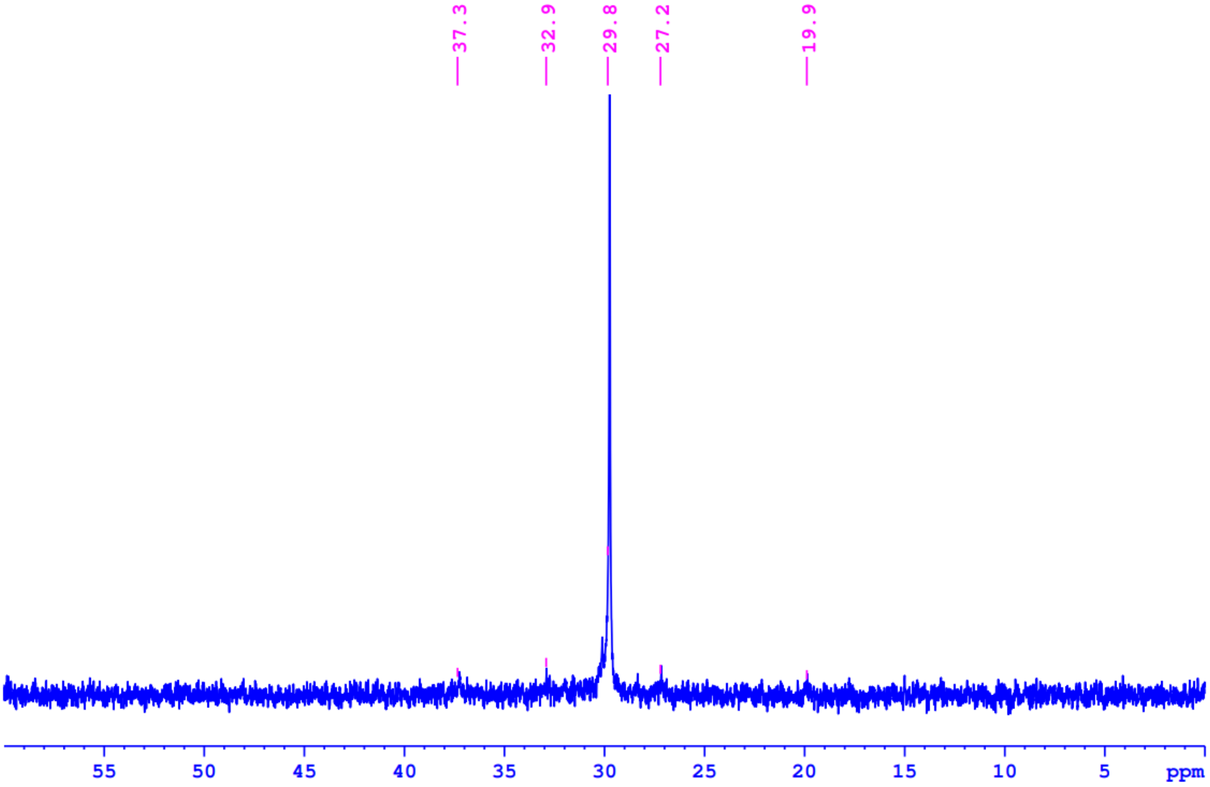


Figure S40: ^{13}C NMR spectrum of polyethylene in $C_2D_2Cl_4$ at 80 °C (entry no. 9).

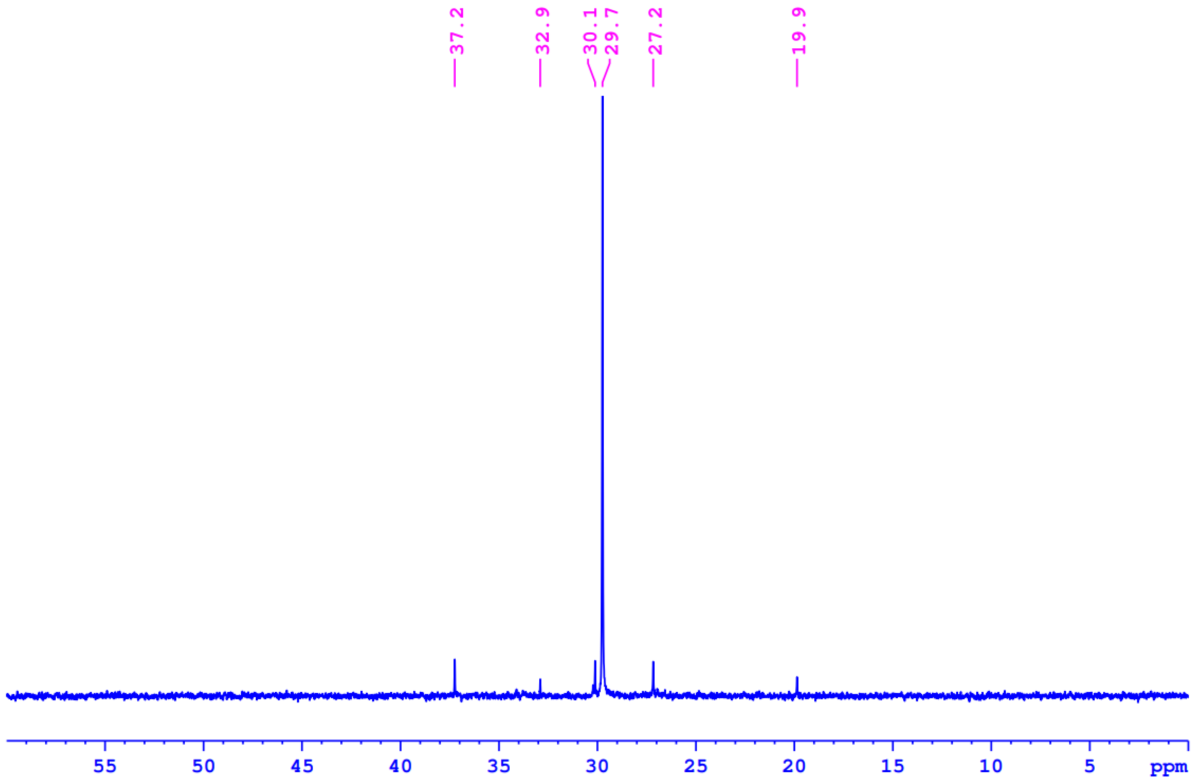


Figure S41: ^{13}C NMR spectrum of polyethylene in $C_2D_2Cl_4$ at 80 °C (entry no. 13).

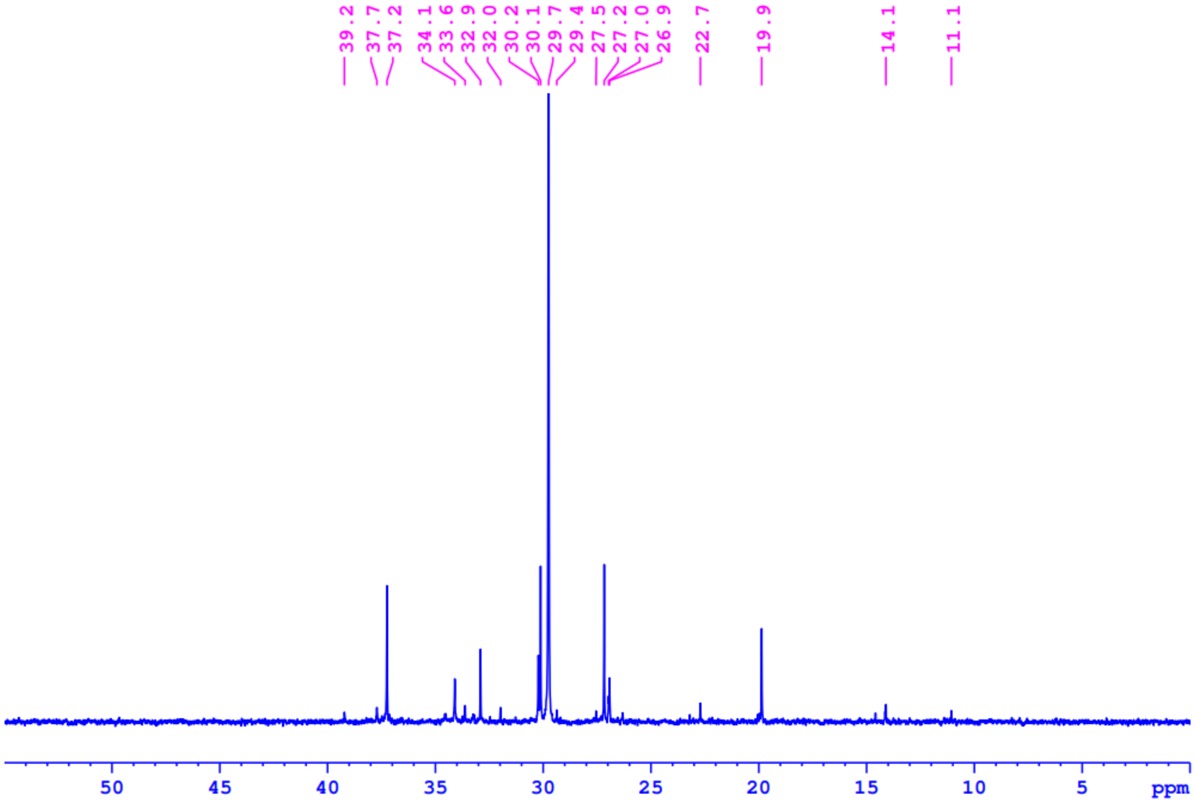


Figure S42: ^{13}C NMR spectrum of polyethylene in $C_2D_2Cl_4$ at 80 °C (entry no. 17).

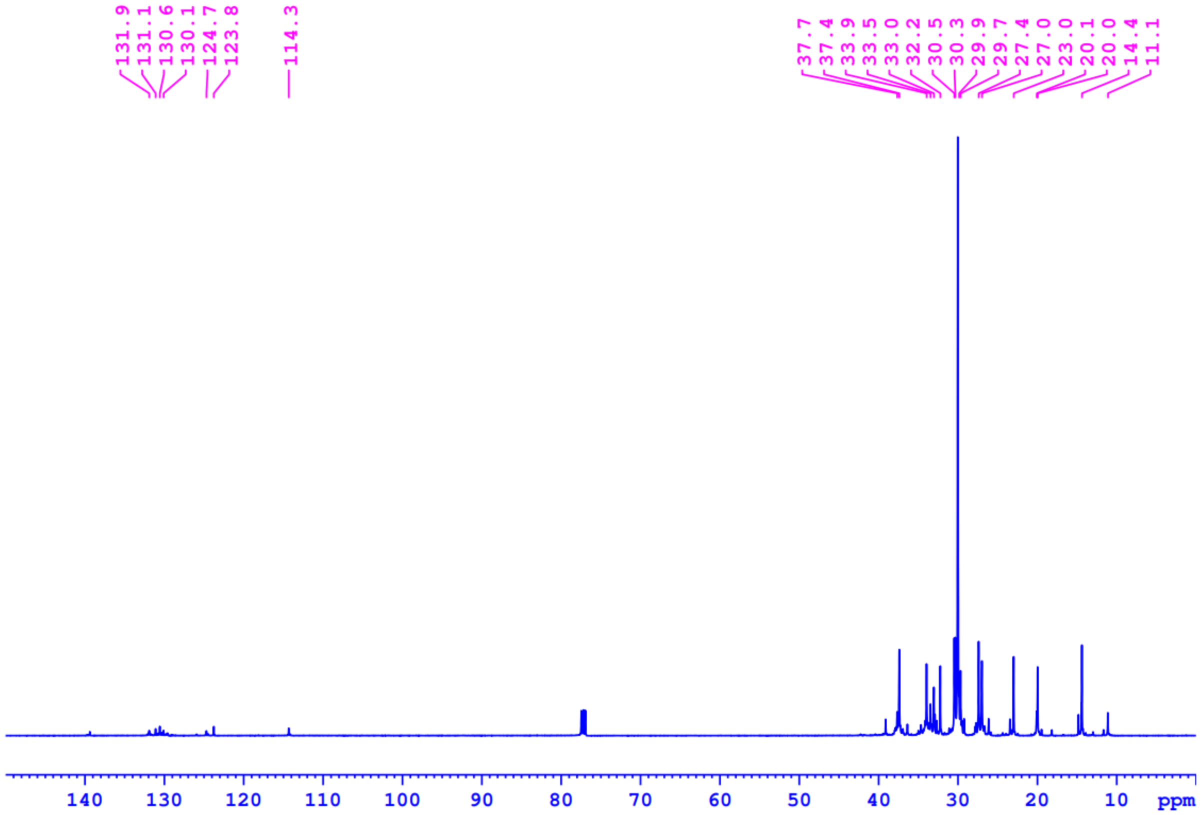


Figure S43: Quantitative ^{13}C NMR of ethylene oligomer in $CDCl_3$ obtained from Pd catalyst.

7c. Melting temperature versus branching/1000C:

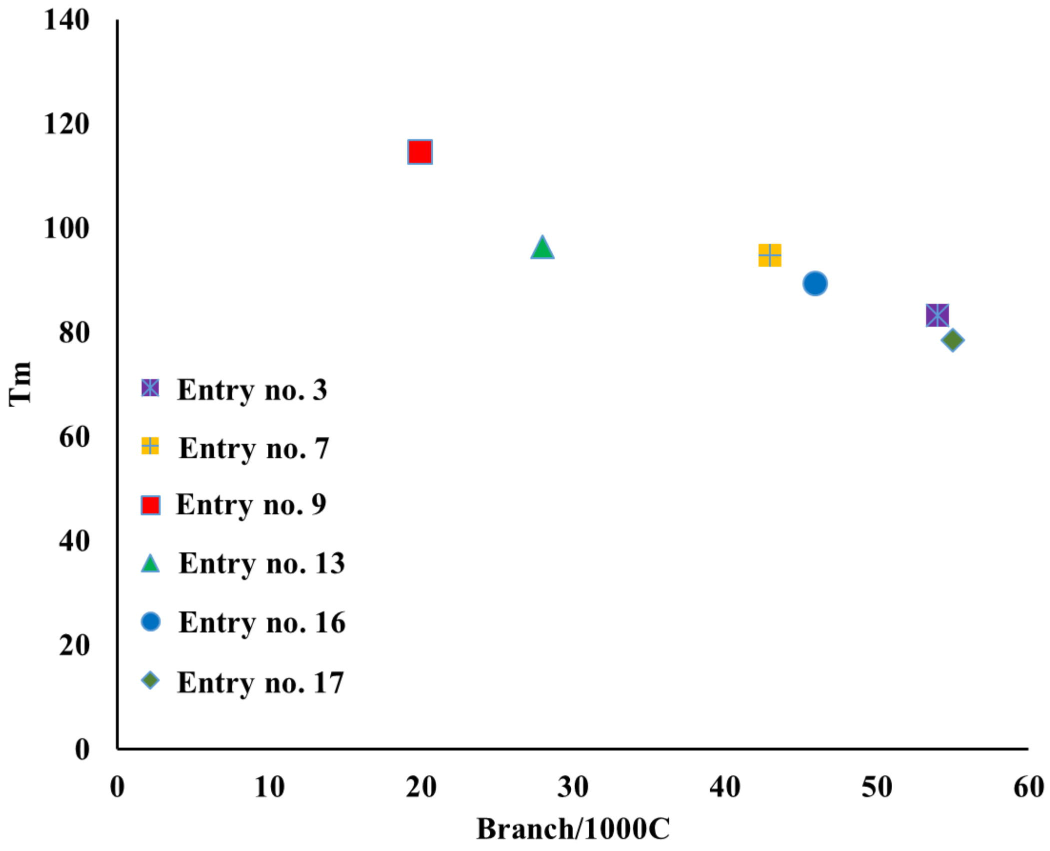


Figure S44: Plot of melting temperature versus branching.

Table S4. Determination of number of branches per 1000 carbon atoms.

Entry No.[a]	**Branch/1000C**[b]	**T_m**
3	54	83.1
7	43	94.6
9	20	114.4
13	28	96.3
16	46	89.1
17	55	78.3

[a] entry numbers are based on the table 1, [b] Branches per 1000 carbons calculated by ^{1}H NMR.

8. WAXS data:

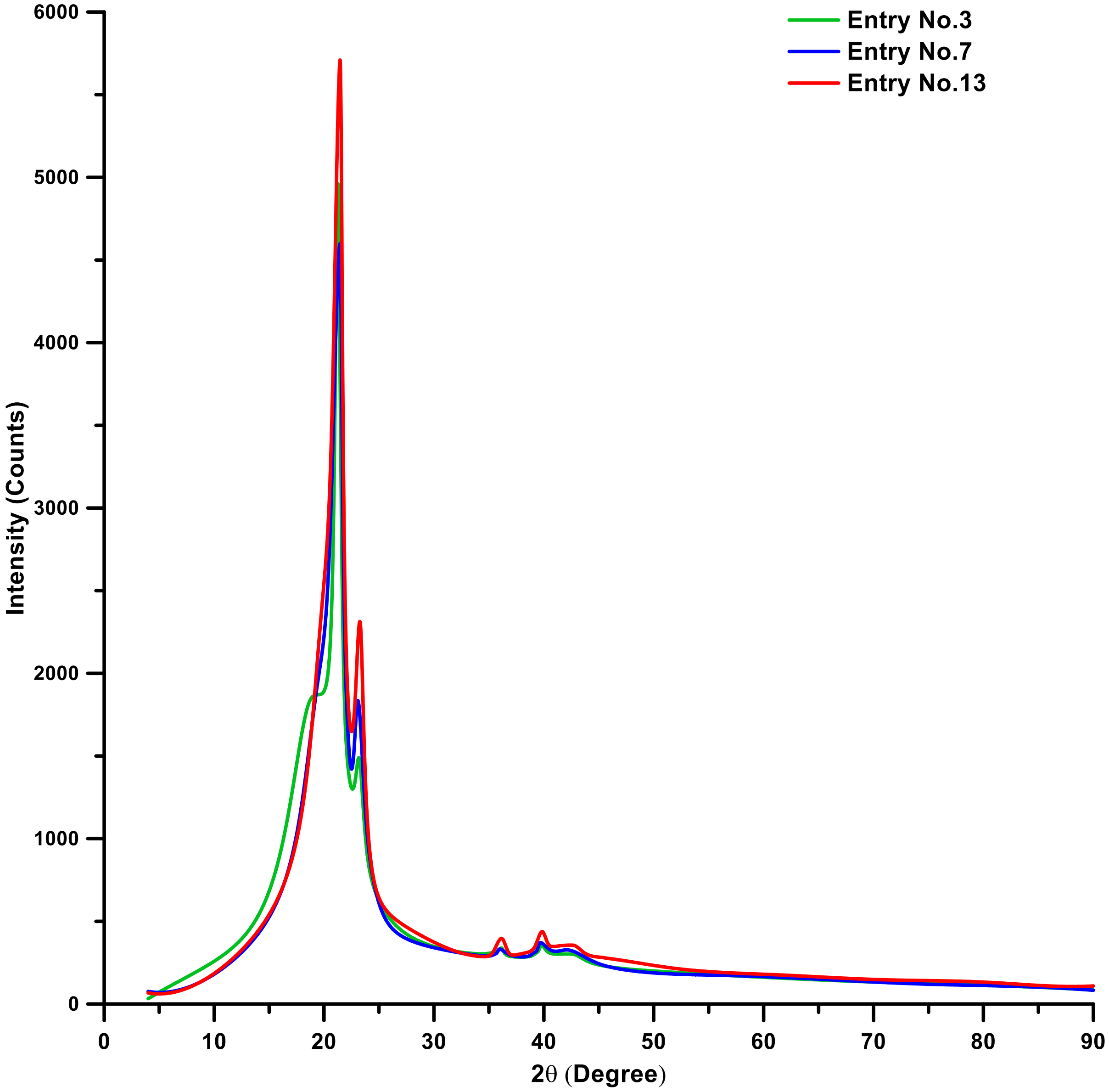


Figure S45: WAXS graph of polyethylene for Table S2

The % of crystallinity of the samples were calculated by X- ray graph by using an following formula.

Crystallinity (%) = Area of crystalline peaks/ (Area of crystalline + Area of amorphous peaks) x 100

Ni1= 10262.13/32341.27

Ni2= 16908.01/31782.14

Ni3= 18998.96/35773.57

Sr. No	Cat. Used for PE synthesis	Entry No.	Branch/1000C	Crystallinity (%) by X-ray
1	Ni1	Entry no. 3	54	31.7
2	Ni2	Entry no. 7	43	53.1
3	Ni3	Entry no. 13	28	53.1

8. References:

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