Supporting Information for

Fine-Tuning Nickel Phenoxyimine Olefin Polymerization Catalysts: Performance Boosting by Alkali Cations

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EXPERIMENTAL

Synthesis

Preparation of NaL0. Inside the glovebox, **HL1** (0.21 g, 0.67 mmol, 1.0 equiv.) was dissolved in 10 mL of THF. Solid NaH (60%, 0.04 g, 1 mmol, 1.5 equiv.) was added and the mixture was stirred at room temperature for 2 h. The solution was filtered through a pipet plug to remove a white solid. The yellow filtrate was dried under vacuum and then washed with pentane to give a light yellow solid (0.22 g, 0.66 mmol, 98%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 7.85 (s, 1H), 6.92 (s, 3H), 6.63 (s, 1H), 6.33 (s, 1H), 6.15 (s, 1H), 2.74 (s, 3H), 2.67 (s, 2H), 0.95 (s, 6H), 0.52 (s, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 167.35, 162.93, 152.00, 150.59, 138.51, 128.18, 123.51, 123.15, 121.10, 110.19, 109.15, 53.93, 28.19, 25.00, 21.83. ESI–MS(–) calc. for $C_{20}H_{25}NO_2$ $[M–H]^-$ = 310.18130, found 310.18100.

Preparation of aldehyde 1C. Solid 2,3-dihydroxybenzaldehyde (1.00 g, 7.25 mmol, 1.0 equiv.) was dissolved in 25 mL of DMSO in a Schlenk flask under nitrogen. Small aliquots of NaH (60%, 0.73 g, 18.1 mmol, 2.5 equiv.) were added and the mixture was stirred at room temperature with bromoethyl methoxyethyl ether (1.33 g, 7.25 mmol, 1.0 equiv.) and then stirred overnight. The reaction was quenched by the addition of HCl (aq) and was then extracted into 50 mL of Et_2O. The organic layer was separated, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (3:2, hexane:ethyl acetate) to afford a light yellow oil (0.58 g, 2.4 mmol, 33%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm)= 10.88 (s, 1H), 9.92 (s, 1H), 7.19 (dd, J_{HH}= 6.2Hz, J_{HH}= 1.6 Hz, 1H), 7.15 (dd, J_{HH}= 6.4 Hz, J_{HH}= 0.8Hz, 1H), 6.91(t, J_{HH}= 6.4 Hz, 1H), 4.21 (t, J_{HH}= 4.4 Hz, 2H), 3.88 (t, J_{HH}= 4.4 Hz, 2H), 3.71(m, 2H), 3.55 (m, 2H), 3.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 196.24, 152.15, 147.44, 125.11, 121.25, 120.79, 119.57, 71.96, 70.81, 69.65, 69.29, 59.08. FT-IR: 2876 (ν_{CHO}), 1654 (ν_{CO}) cm^{-1}. GC-MS calc. for $C_{12}H_{16}O_5$ $[M]^+$ = 240.1, found 240.1.

Preparation of HL2. Compound **1C** (0.45 g, 1.88 mmol, 1.0 equiv.) and 2,6-diisopropylaniline (0.33 g, 1.88 mmol, 1.0 equiv.) were dissolved in 5 mL of MeOH. The mixture was treated with 5 drops of acetic acid and then stirred under reflux for 8 h. The resulting clear yellow solution was evaporated to dryness to yield a yellow oil (0.55 g, 1.38 mmol, ~74%). This crude product was used in the preparation of **NaL2** without further purification. Pure **HL2** can be obtained by purification by silica gel column chromatography (1:1 hexane:ethyl acetate). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 13.43 (s, 1H), 8.29 (s, 1H), 7.18 (m, 3H), 7.08 (d, J_{HH}= 8.4Hz, 1H), 6.99 (d, J_{HH}= 6.6Hz, 1H), 6.88 (t, J_{HH}= 7.2 Hz, 1H), 4.28 (t, J_{HH}= 5.4 Hz, 2H), 3.96 (t, J_{HH}= 4.8 Hz, 2H), 3.76 (m, 2H), 3.60 (m, 2H), 3.39 (s, 3H), 3.00 (m, 2H), 1.16 (d, J_{HH}= 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 166.85, 151.81, 147.70, 146.10, 138.84, 125.63, 124.40, 123.35, 118.93, 118.66, 117.16, 72.06, 70.92, 69.83, 68.80, 59.19, 28.19, 23.65. FT-IR: 2960 (ν_{CNH}), 1620 (ν_{CN}) cm^{-1}.

Preparation of NaL2. Inside the glovebox, **HL2** (5.32 g, 13.3 mmol, 1.0 equiv.) was dissolved in 100 mL of THF. Solid NaH (60%, 1.07 g, 26.7 mmol, 2.0 equiv.) was added. The mixture was stirred at room temperature for 2 h and then filtered to remove the insoluble material. The yellow filtrate was collected and the solvent was removed under vacuum. The crude product was washed with pentane and then dried to yield a light yellow solid (4.03 g, 9.5 mmol, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.07 (s, 1H), 7.13 (d, J_{HH}= 6 Hz, 2H), 7.06 (t, J_{HH}= 6 Hz, 1H), 6.95 (d, J_{HH}= 5.2 Hz, 1H), 6.71 (d, J_{HH}= 6 Hz, 1H), 6.15 (t, J_{HH}= 6 Hz, 1H), 3.88 (s, 2H), 3.33-3.27 (m, 9H), 3.07 (m, 2H), 1.13 (d, J_{HH}= 4.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 166.39, 165.30, 152.00, 151.17, 139.18, 128.63, 123.28, 122.77, 122.09, 115.75, 106.76, 70.67, 68.10, 67.84, 66.94, 65.98, 58.93, 27.70, 24.15, 15.40. ESI–MS(–) calc. for $C_{24}H_{32}NO_4$ $[M–H]^-$ = 398.23370, found 398.23380.

Preparation of aldehyde 1D. Solid 2,3-dihydroxybenzaldehyde (2.3 g, 16 mmol, 1.0 equiv.) was dissolved in 50 mL of DMSO in a Schlenk flask under nitrogen. Small aliquots of NaH (60%, 1.6 g, 41 mmol, 2.5 equiv.) were added and the mixture was stirred at room temperature for 2 h. The resulting dark red solution was treated with triethylene glycol methyl *p*-tosyl ether (5.2 g, 16 mmol, 1.0 equiv.) and then stirred overnight. The reaction was quenched by the addition of HCl (aq) and was then extracted into 50 mL of Et_2O. The organic layer was separated, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (3:2, toluene:ethyl acetate) to afford a light yellow oil (2.6 g, 9.2 mmol, 55%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 10.88 (s, 1H), 9.95 (s, 1H), 7.21 (d, J_{HH}= 8.4 Hz, 1H), 7.17 (d, J_{HH}= 7.8 Hz, 1H), 6.92 (t, J_{HH}= 8.4 Hz, 1H), 4.21 (t, J_{HH}= 5.4 Hz, 2H), 3.89 (t, J_{HH}= 4.8 Hz, 2H), 3.73 (m, 2H), 3.67 (m, 2H), 3.64 (m, 2H), 3.55 (m, 2H), 3.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 195.29, 151.93, 147.32, 124.09, 121.59, 120.12, 119.37, 71.80, 70.66, 70.73, 70.29, 69.46, 68.83, 58.82. FT-IR: 2871 (ν_{CHO}), 1654 (ν_{CO}) cm^{-1}. GC-MS calc. for $C_{14}H_{20}O_6$ $[M]^+$ = 284.1, found 284.1.

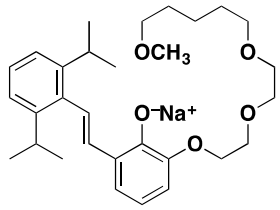
Preparation of HL3. Compound **1D** (0.71 g, 2.5 mmol, 1.0 equiv.) and 2,6-diisopropylaniline (0.44 g, 2.5 mmol, 1.0 equiv.) were dissolved in 10 mL of MeOH. The mixture was treated with 5 drops of acetic acid and then stirred under reflux for 8 h. The resulting clear yellow solution was evaporated to dryness to yield a yellow oil (1.0 g, 2.4 mmol, ~95%). This crude product was used in the preparation of **NaL3** without further purification. Pure **HL3** can be obtained by purification by silica gel column chromatography (1:1, hexane:ethyl acetate). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 13.42 (s, 1H), 8.29 (s, 1H), 7.17 (m, 3H), 7.07 (d, J_{HH}= 7.8 Hz, 1H), 6.99 (d, J_{HH}= 7.8 Hz, 1H), 6.88 (t, J_{HH}= 8.4 Hz, 1H), 4.26 (t, J_{HH}= 4.8 Hz, 2H), 3.94 (t, J_{HH}= 4.8 Hz, 2H), 3.77 (t, J_{HH}= 4.8 Hz, 2H), 3.69 (t, J_{HH}= 4.8 Hz 2H), 3.66 (t, J_{HH}= 3.6 Hz, 2H), 3.54 (t, J_{HH}= 4.8 Hz, 2H), 3.37 (s, 3H) 2.98 (m, 2H), 1.16 (d, J_{HH}= 7.2 Hz, 12H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 166.84, 151.85, 147.71, 146.09, 138.84, 125.63, 124.41, 123.34, 118.93, 118.65, 117.26, 72.03, 70.98, 70.75, 70.64, 69.81, 68.82, 59.13, 28.19, 23.64. FT-IR: 2960 (ν_{CHN}), 1619 (ν_{CN}) cm^{-1}.

Preparation of NaL3. Inside the glovebox, **HL3** (1.4 g, 3.1 mmol, 1.0 equiv.) was dissolved in 20 mL of THF. Solid NaH (60%, 0.19 g, 4.7 mmol, 1.5 equiv.) was added. The mixture was stirred at room temperature for 2 h and then filtered to remove the insoluble material. The yellow filtrate was collected and the solvent was removed under vacuum. The crude product was washed with pentane and then dried to yield a light yellow solid (1.08 g, 2.3 mmol, 74%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.76 (s, 1H), 7.68 (d, J_{HH}= 6.6 Hz, 1H), 7.06 (d, J_{HH}= 7.2 Hz, 2H), 6.97 (t, J_{HH}= 7.2 Hz, 1H), 6.64 (d J_{HH}= 7.8 Hz, 1H), 6.23 (t, J_{HH}= 7.8 Hz, 1H), 3.95 (t, J_{HH}= 4.2 Hz, 2H), 3.60 (s, 2H), 3.28-3.20 (m, 11H), 3.09 (m, 2H), 1.13 (d, J_{HH}= 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 165.02, 161.61, 152.03, 151.54, 138.28, 123,47, 122.58, 122.41, 120.46, 111.72, 107.83, 70.18, 69.31, 68.80, 68.50, 68.22, 65.65, 59.05, 27.78, 23.44. ESI–MS(–) calc for $C_{26}H_{36}NO_5$ $[M–H]^–$ = 442.25990, found 442.26030.

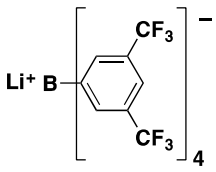
Preparation of aldehyde 1E. Solid 2,3-dihydroxybenzaldehyde (1.1 g, 8.3 mmol, 1.0 equiv.) was dissolved in 20 mL of DMSO in a Schlenk flask under nitrogen. Small aliquots of NaH (60%, 828 mg, 21 mmol, 2.5 equiv.) were added and the mixture was stirred at room temperature for 2 h. The resulting dark red solution was treated with tetraethylene glycol methyl *p*-tosyl ether (3.09 g, 8.3 mmol, 1.0 equiv.) and then stirred overnight. The reaction was quenched by the addition of HCl (aq) and was then extracted into 50 mL of Et_2O. The organic layer was separated, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (1:1 hexane:ethyl acetate to 1:4 hexane: ethyl acetate) to afford a light yellow oil (1.1 g, 3.2 mmol, 39%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm)= 10.82 (s, 1H), 9.91 (s, 1H), 7.17 (dd, J_{HH}= 7.5 Hz, J_{HH}= 1.0 Hz, 1H), 7.12 (dd, J_{HH}= 8.0 Hz, J_{HH}= 1.5 Hz, 1H), 6.88 (t, J_{HH}= 7.5 Hz, 1H), 4.17 (t, J_{HH}= 4.5 Hz, 2H), 3.84 (m, 2H), 3.69 (m, 2H), 3.64-3.58 (m, 8H), 3.49 (m, 2H), 3.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 196.11, 152.22, 147.50, 125.04, 121.32, 120.86, 119.55, 71.96, 70.91, 70.65, 70.56, 69.66, 69.32,59.09. FT-IR: 2873 (ν_{CHO}), 1655(ν_{CO}) cm^{-1}. GC-MS calc. for $C_{16}H_{24}O_7$ $[M]^+$ = 328.2, found 328.2.

Preparation of HL4. Compound **1E** (0.43 g, 1.3 mmol, 1.0 equiv.) and 2,6-diisopropylaniline (0.23 g, 1.3 mmol, 1.0 equiv.) were dissolved in 10 mL of MeOH. The mixture was treated with 5 drops of acetic acid and then stirred under reflux for 8 h. The resulting clear yellow solution was evaporated to dryness to yield a yellow oil (0.63 g, 1.3 mmol, 100%). This crude product was used in the preparation of **NaL4** without further purification. Pure **HL4** can be obtained by purification by silica gel column chromatography (1:1, hexane:ethyl acetate). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 13.38 (s, 1H), 8.27, (s, 1H), 7.14 (m, 3H), 7.05 (d, J_{HH}= 8.4 Hz, 1H), 6.97 (d, J_{HH}= 7.2 Hz, 1H), 6.85 (t, J_{HH}= 8.4 Hz, 1H), 4.24 (t, J_{HH}= 4.8 Hz, 2H), 3.92 (t, J_{HH}= 4.8 Hz, 2H), 3.75 (m, 2H), 3.67-3.60 (m, 8H), 3.50 (m, 2H), 3.32 (s, 3H), 2.97 (m, 2H), 1.13 (d, J_{HH}= 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 166.84, 151.83, 147.70, 146.12, 138.76, 125.63, 124.41, 123.32, 118.94, 118.68,117.30, 72.00, 70.97, 70.69, 70.58, 69.81, 68.85, 59.07, 28.18, 23.64. FT-IR: 2869 (ν_{CHN}), 1620(ν_{CN}) cm^{-1}.

Preparation of NaL4. Inside the glovebox, **HL4** (0.60 g, 1.2 mmol, 1.0 equiv.) was dissolved in 10 mL of THF. Solid NaH (60%, 74 mg, 1.8 mmol, 1.5 equiv.) was added. The mixture was stirred at room temperature for 2 h and then filtered to remove the insoluble material. The yellow filtrate was collected and the solvent was removed under vacuum. The crude product was washed with pentane and then dried to yield a light yellow solid (0.600 g, 1.18 mmol, 96%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.72 (s, 1H), 7.62 (s, 1H), 7.07 (d, J_{HH}= 7.8Hz, 2H), 6.97 (t, J_{HH}= 7.2Hz, 1H), 6.68 (d, J_{HH}= 6.6Hz, 1H), 6.20 (t, J_{HH}= 7.8Hz, 1H), 3.98 (s, 2H), 3.65 (s, 2H), 3.50 (s, 2H), 3.44 (s, 2H), 3.39-3.34 (m, 8H), 3.09 (m, 2H), 3.01 (s, 3H), 1.13 (d, J_{HH}= 6.6Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 165.40, 162.08, 152.16, 151.50, 138.30, 123.67, 122.85, 122.68, 122.46, 113.47, 107.82, 71.40, 69.69, 69.04, 69.02, 68.81, 68.62, 68.47, 66.46, 58.80, 27.81, 23.52, 22.56. ESI–MS(–) calc. for $C_{28}H_{40}NO_6$ $[M–H]^-$ = 486.28610, found 486.28650.



Preparation of LiBAr$^{F}_{4}$. A 20 mL solution of 3,5-bis(trifluoromethyl)bromobenzene (2.0 g, 6.8 mmol, 5 equiv.) in dry Et_2O was added slowly using an addition funnel to a Schlenk flask containing magnesium turnings (0.20 g, 8.2 mmol, 6.2 equiv.) in 15 mL of Et_2O. The mixture was stirred under reflux for 30 min to give a light brown solution. Solid $LiBF_4$ (0.13 g, 1.4 mmol, 1 equiv.) was added and the reaction was stirred at RT for an additional 48 h. About ~15 mL of 1,4-dioxane was added, which led to precipitation of a large amount of magnesium dihalide. The solvent was removed under vacuum and the reaction flask was brought inside the glovebox for further workup. Inside the glovebox, the product was extracted into Et_2O and the insoluble material was removed by filtration through a glass frit. The filtrate was evaporated to dryness and the resulting solid was re-dissolved in a minimal amount of Et_2O and then layered with pentane. Upon storing at -30°C overnight, a large amount of colorless crystals had formed. The crystals were isolated by filtration and dried to afford a white solid (0.74 g, 0.85 mmol, 63%). The NMR spectra of this material were identical to those reported previously.[1]



Metal Binding Study

The dilution-corrected spectra obtained from the addition of alkali salts (M^+) to solutions of the **NiL** complexes are shown in Figure S1. The program DynaFit[2] was used for non-linear regression fitting of the titration data based on absorbance changes observed at 340 nm. The data were fit to two different binding models, where one model assumes the formation of 1:1 **NiL**:M^+ species and the second assumes the formation of a mixture of 1:1 and 2:1 **NiL**:M^+ species. In almost in all cases, the latter model gave a better fit than the former based on statistical error analysis. The only exception is the titration data acquired from the addition of Na^+ to **NiL4**, which gave a better fit using a 1:1 rather than a 1:1/2:1 binding model. The Dynafit scripts for the two models used are provided below. Parameters that are allowed to vary in the fitting process are marked with "?" and all other parameters were held fixed.

A) 1:1 stoichiometry

```
[task]
  task = fit
  data = equilibria
[mechanism]
  Ni + M <==> NiM : K1 association
[constants]
  K1 = .01?
[concentrations]
  Ni = 100
[responses]
  Ni = 0.003 ?
  NiM = 0.001?
[data]
  variable M
  file./Experiments/data.txt
[output]
  directory ./Experiments/output/data
[end]
```

B) 1:1 and 2:1 stoichiometry

```
[task]
  task = fit
  data = equilibria
[mechanism]
  Ni + M <==> NiM : K1 association
  NiM + Ni <==> Ni2M : K2 association
[constants]
  K1 = .01?
  K2 = .01?
[concentrations]
  Ni = 100
[responses]
  Ni = 0.003 ?
  NiM = 0.001?
  Ni2M = 0.001?
[data]
  variable M
  file ./Experiments/data.txt
[output]
  directory ./Experiments/output/data
[end]
```

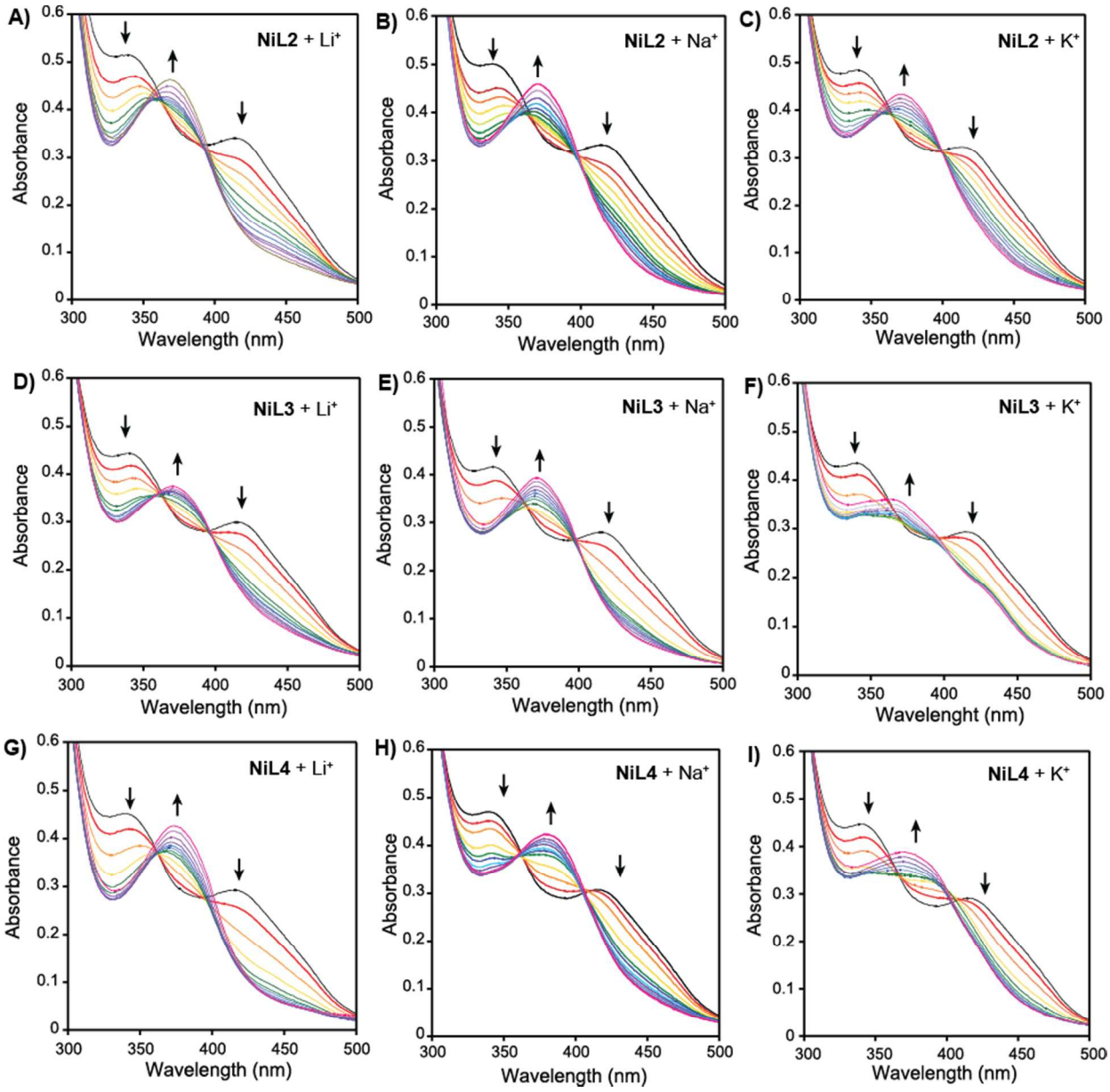


Figure S1. UV-vis spectral changes observed from the addition of $MBAr^F_4$ ($M^+ = Li^+$, Na^+, and K^+) to solutions of **NiL** (100 μM in Et_2O). Small aliquots containing 0.1 equiv. of M^+, relative to **NiL**, were added to **NiL** and the solutions were allowed to equilibrate for 20–30 min before recording the spectra. The titration plots are shown for the following: A) **NiL2**/Li^+, B) **NiL2**/Na^+, C) **NiL2**/K^+, D) **NiL3**/Li^+, E) **NiL3**/Na^+, F) **NiL3**/K^+, G) **NiL4**/Li^+, H) **NiL4**/Na^+, and I) **NiL2**/K^+. The data have been corrected for dilution.

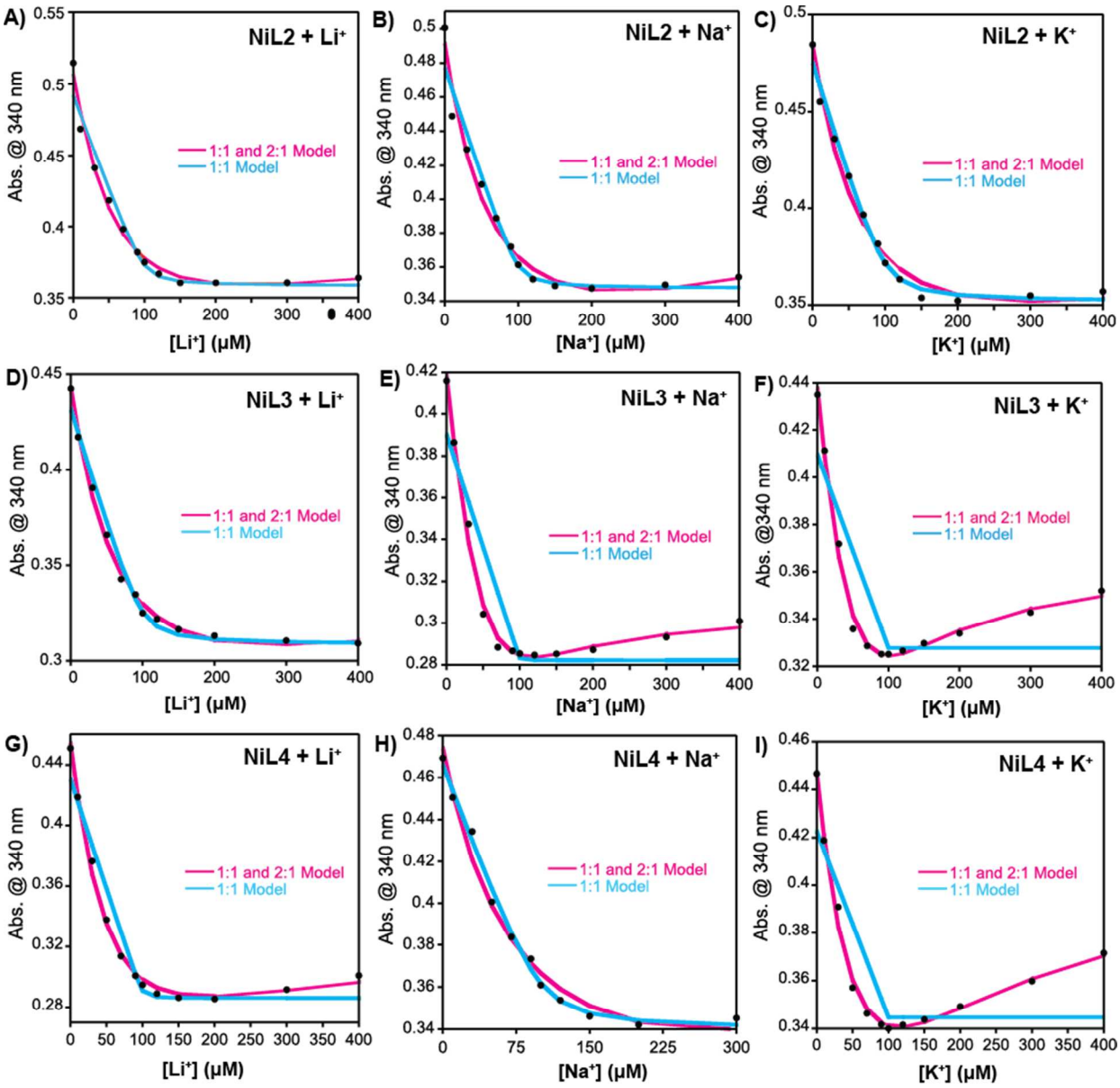


Figure S2. The single-wavelength absorption changes at 340 nm observed from the metal titration studies shown in Figure S1. The experimental data are shown as black dots. The data were fit to two metal binding models: the magenta trace represents a 1:1 and 2:1 **NiL**:M^+ model whereas the blue trace represents a 1:1 **NiL**:M^+ model. In almost all cases, except for **NiL4**/Na^+, the 1:1 and 2:1 model fits the data better than the 1:1 model. The binding constants K_{a1} and K_{a2} derived from data fitting are provided in Table 1. The single-wavelength titration plots are shown for: A) **NiL2**/Li^+, B) **NiL2**/Na^+, C) **NiL2**/K^+, D) **NiL3**/Li^+, E) **NiL3**/Na^+, F) **NiL3**/K^+, G) **NiL4**/Li^+, H) **NiL4**/Na^+, and I) **NiL2**/K^+.

X-ray Data Collection and Refinement

Single crystals suitable for X-ray diffraction studies were picked out of the crystallization vials and mounted onto Mitogen loops using Paratone oil. The crystals of **NiL2$_{Mes}$**, **NiNaL3,** and **NiKL4** were collected at a 6.0 cm detector distance (40 s/frame exposure time), whereas that of **Ni$_2$NaL2$_2$** was collected at a 9.0 cm detector distance (60 s/frame exposure time) to prevent diffraction spot overlap due to its large cell size (a = 12.0 Å, *b* = 59.9 Å, *c* = 17.3 Å). The structure of **NiL2$_{Mes}$** contains a pentane solvent molecule that is located on an inversion center, which was refined in Part -1 to suppress the generation of special position constraints and by using a site occupancy factor (sof) of 10.5000. Four of the CF_3 groups in the $BAr^F{}_4^-$ anion show significant rotational disorder and were refined separately as a two-part disorder using independent variables. The fluorine atoms of the disordered CF_3 groups were fixed to have equal atomic displacement parameters. The structure of **Ni$_2$NaL2$_2$** has several severely disordered phenyl rings, two of which are attached to P(1) of a triphenylphosphine ligand. These C_6H_5 groups [C(79)–C(84) and C(85)–C(90)] were modeled as two-part positional disorders. The phenyl group [C(73)–C(77)] that is coordinated to Ni(1) was refined using an AFIX 66 rigid group constraint and its carbon atoms were given equal atomic displacement parameters. The elongated ADPs of the C(73)–C(77) atoms suggest that this group is also disordered, but attempts to model the disorder did not give a stable structure refinement. Four of the CF_3 groups in the $BAr^F{}_4^-$ anion were also modeled as positional disorders using independent variables. The crystal structures of **NiNaL3** and **NiKL4** both contain $BAr^F{}_4^-$ anions with several disordered CF_3 units, which were also refined accordingly.

Table S1. Crystallographic table for **NiL2$_{Mes}$**, **NiNaL3**, **NiKL4**, and **Ni$_2$NaL2$_2$**

	NiL2$_{Mes}$·(C_5H_{12})	**NiNaL3**·(C_5H_{12})$_{0.5}$	**NiKL4**	**Ni$_2$NaL2$_2$**
Empirical Formula	$NiC_{51}H_{58}NO_4P$·(C_5H_{12})	$NiNaC_{82}H_{68}NO_5PBF_{24}$ ·(C_5H_{12})$_{0.5}$	$NiKC_{84}H_{72}NO_6PBF_{24}$	$Ni_2NaC_{128}H_{118}N_2O_8P_2BF_{24}$
Formula Weight	838.66	1762.93	1787.02	2481.40
Temperature (°C)	-150	-150	-150	-150
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal System,	Orthorhombic,	Triclinic,	Triclinic,	Monoclinic,
Space Group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Unit Cell Dimensions				
a (Å)	24.3130(12)	12.161(4)	11.539(3)	12.0736(10)
b (Å)	9.2770(5)	18.240(6)	19.626(4)	59.562(5)
c (Å)	19.2048(11)	18.943(6)	21.139(5)	17.2666(14)
α (°)		85.263(4)	62.823(2)	
β (°)		80.079(4)	78.790(3)	101.397(4)
γ (°)		86.325(4)	88.281(3)	
Volume (Å^3)	4331.7(4)	4119(2)	4167.9(15)	12172.1(17)
Z, Calculated Density (Mg/m^3)	4, 1.286	2, 1.421	2, 1.424	4, 1.354
Absorption Coefficient (mm^{-1})	0.531	0.366	0.408	0.433
F(000)	1784	1806	1828	5218
Theta Range for Data Collection (°)	1.98 to 30.56	1.86 to 25.00	1.11 to 26.37	0.68 to 24.71
Limiting Indices	$-34 \le h \le 34$ $-13 \le k \le 13$ $-23 \le l \le 27$	$-11 \le h \le 16$ $-21 \le k \le 24$ $-25 \le l \le 25$	$-14 \le h \le 11$ $-15 \le k \le 24$ $-26 \le l \le 26$	$-14 \le h \le 14$ $-68 \le k \le 69$ $-20 \le l \le 20$
Reflections Collected/ Unique	55608/ 12540 [R(int) = 0.0137]	24671/ 18618 [R(int) = 0.0162]	2270/ 16320 [R(int) = 0.0162]	58475/ 19956 [R(int) = 0.0569]
Max. and Min. Transmission	0.9151 and 0.8699	0.9678 and 0.9076	0.9451 and 0.9229	0.9662 and 0.9185
Data/ Restraints/ Parameters	12540/ 1/ 523	18618/ 155/ 1056	16320/ 120/1064	19956/ 120/ 1333
Goodness of Fit on F^2	1.028	1.031	1.037	1.053
Final R Indices	R_1= 0.0211	R_1= 0.0726	R_1 = 0.0517	R_1= 0.0897
[I > 2σ(I)]	wR_2 = 0.0576	wR_2 = 0.1796	wR_2 = 0.1288	wR_2 = 0.223
R Indices (All Data)*	R_1 = 0.0215	R_1 = 0.0905	R_1 = 0.0637	R_1 = 0.1364
	wR_2 = 0.0577	wR_2 = 0.1924	wR_2 = 0.1383	wR_2 = 0.2562
Largest Diff. Peak and Hole (e Å^{-3})	0.366 and -0.298	1.577 and -1.024	1.589 and -1.031	1.532 and -1.793

*$R_1 = \Sigma\,||F_o|-|F_o||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)_2]]^{1/2}$; GOF = $[\Sigma[w(F_o^2 - F_c^2)_2]/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

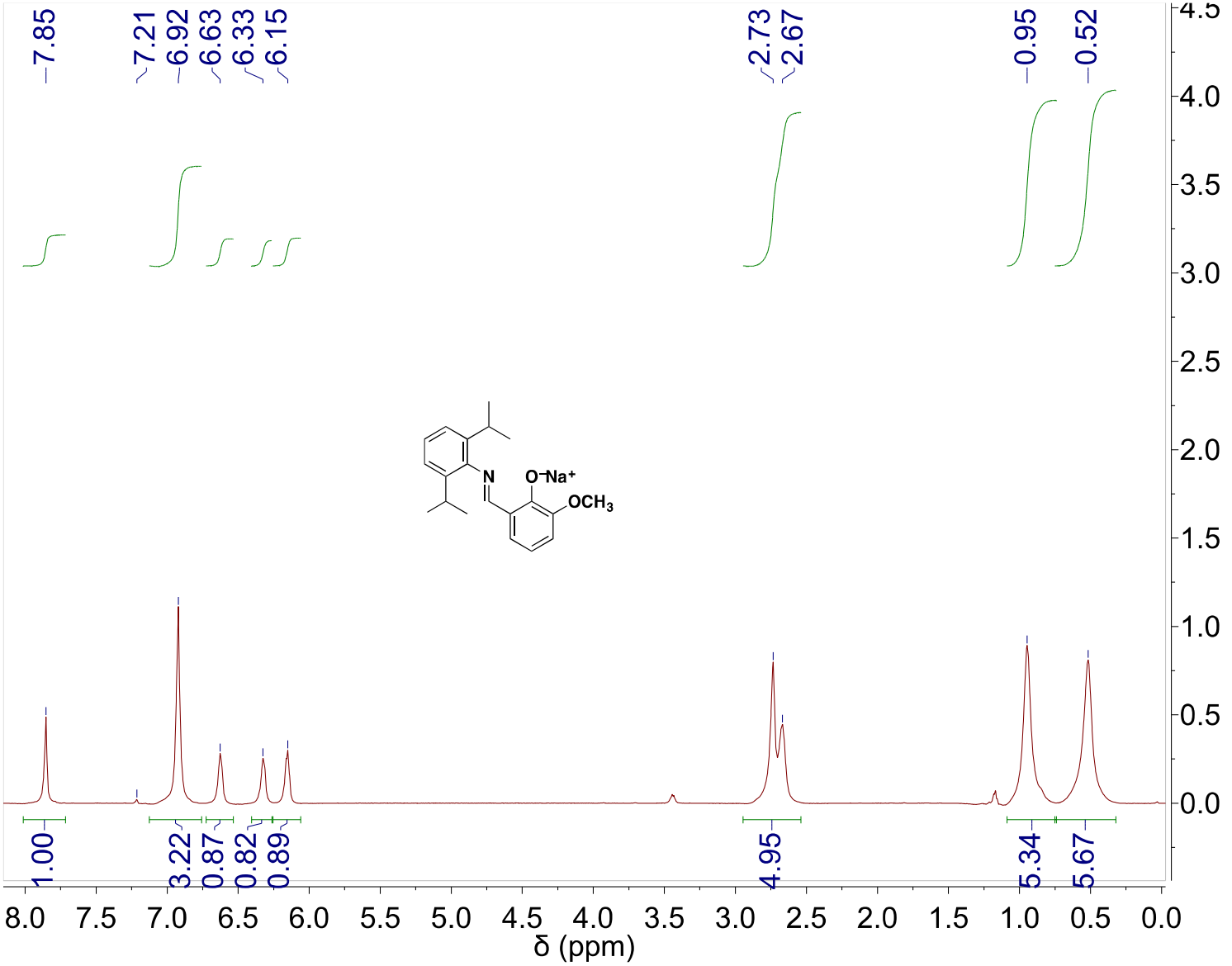


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **NaL0**.

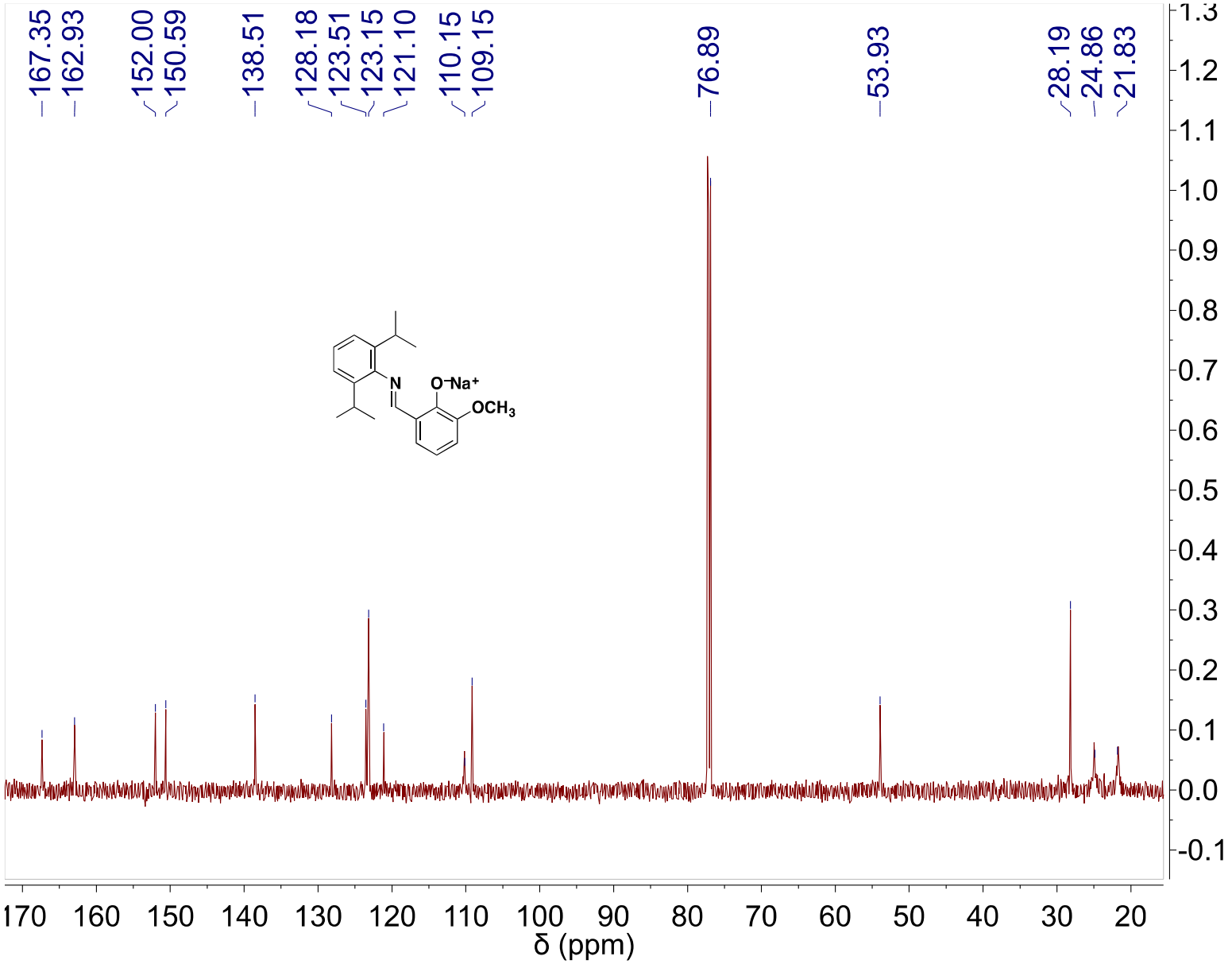


Figure S4. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **NaL0**.

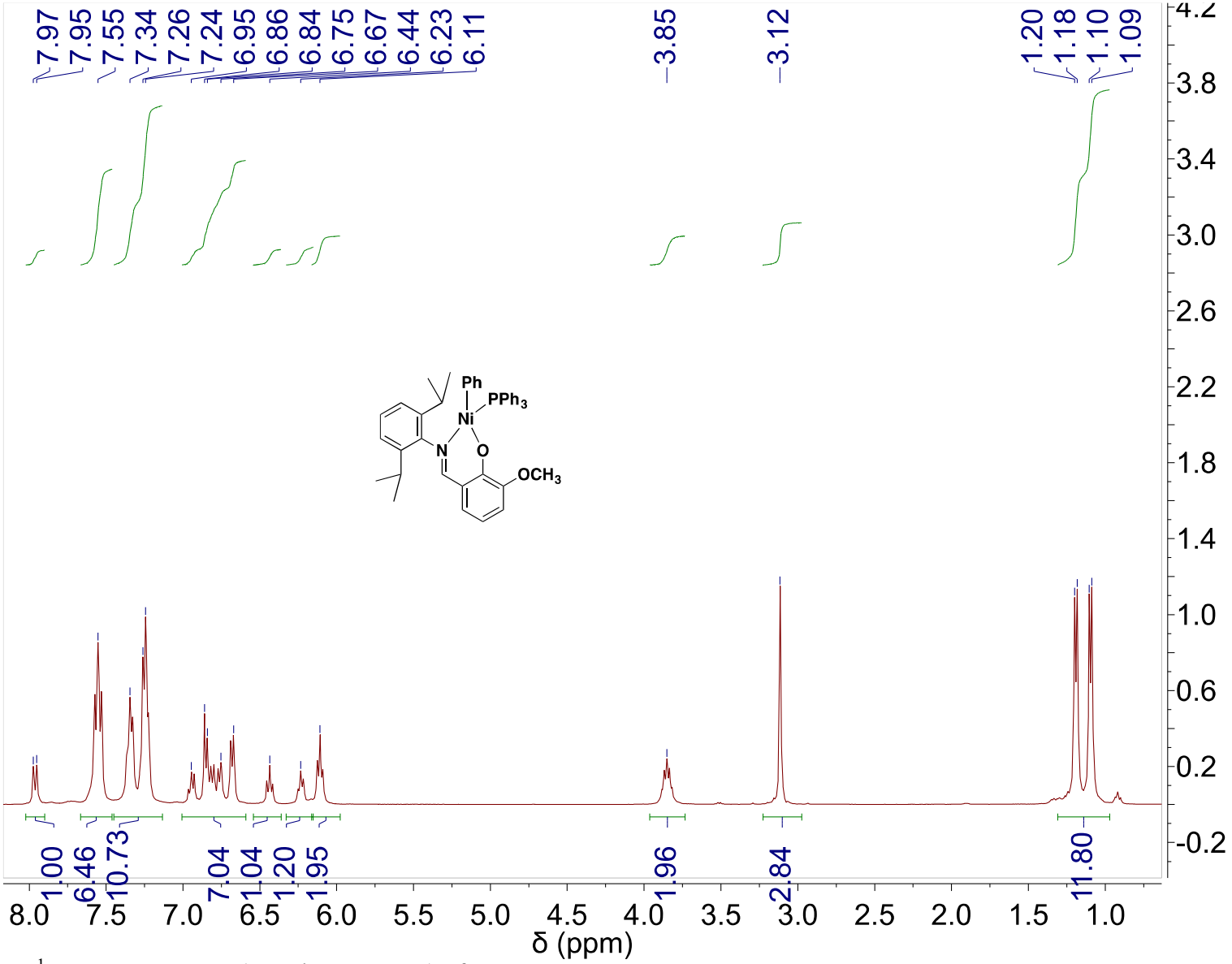


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **NiL0**.

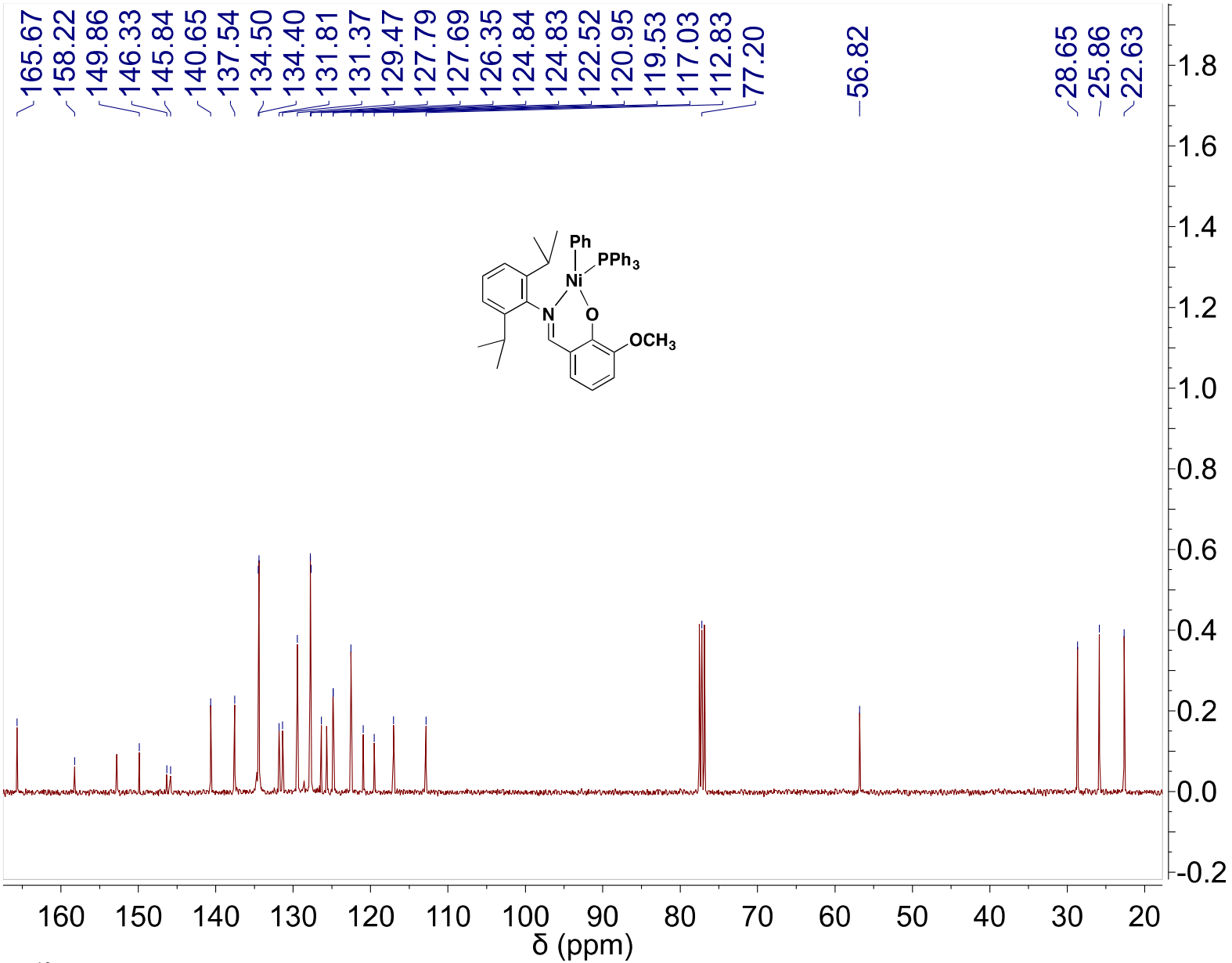


Figure S6. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **NiL0**.

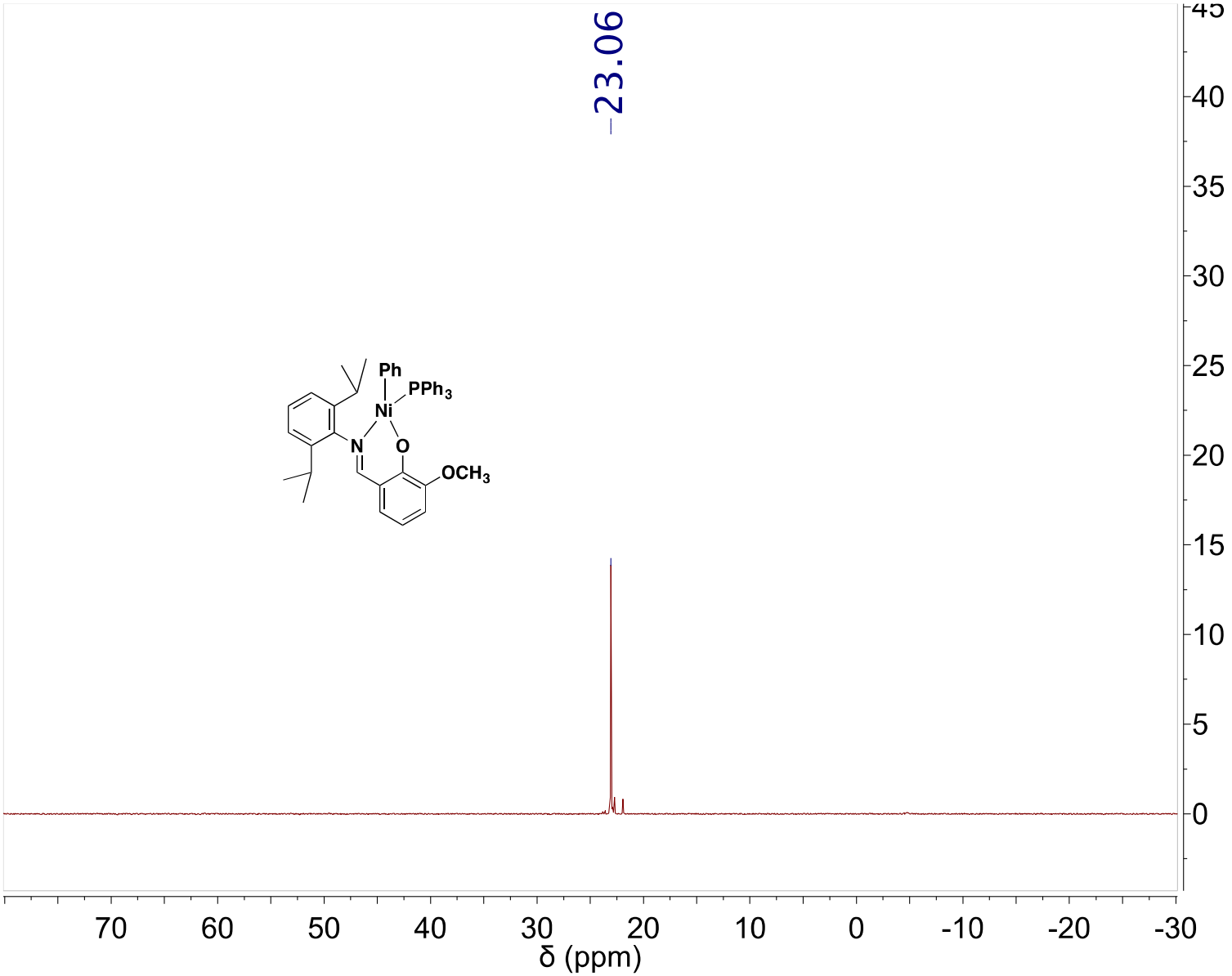


Figure S7. ^{31}P NMR spectrum ($CDCl_3$, 162 MHz) of **NiL0**.

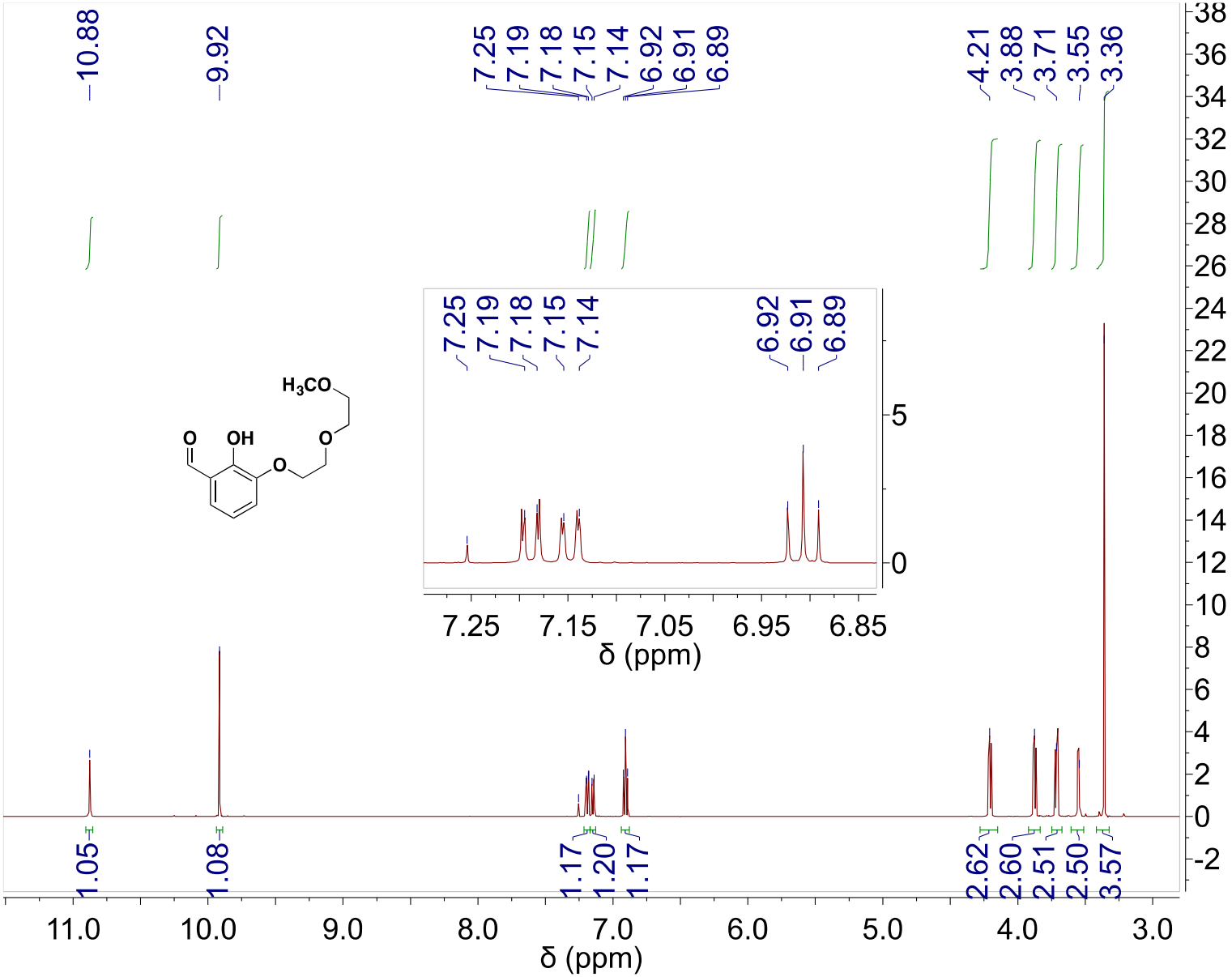


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of aldehyde **1C**.

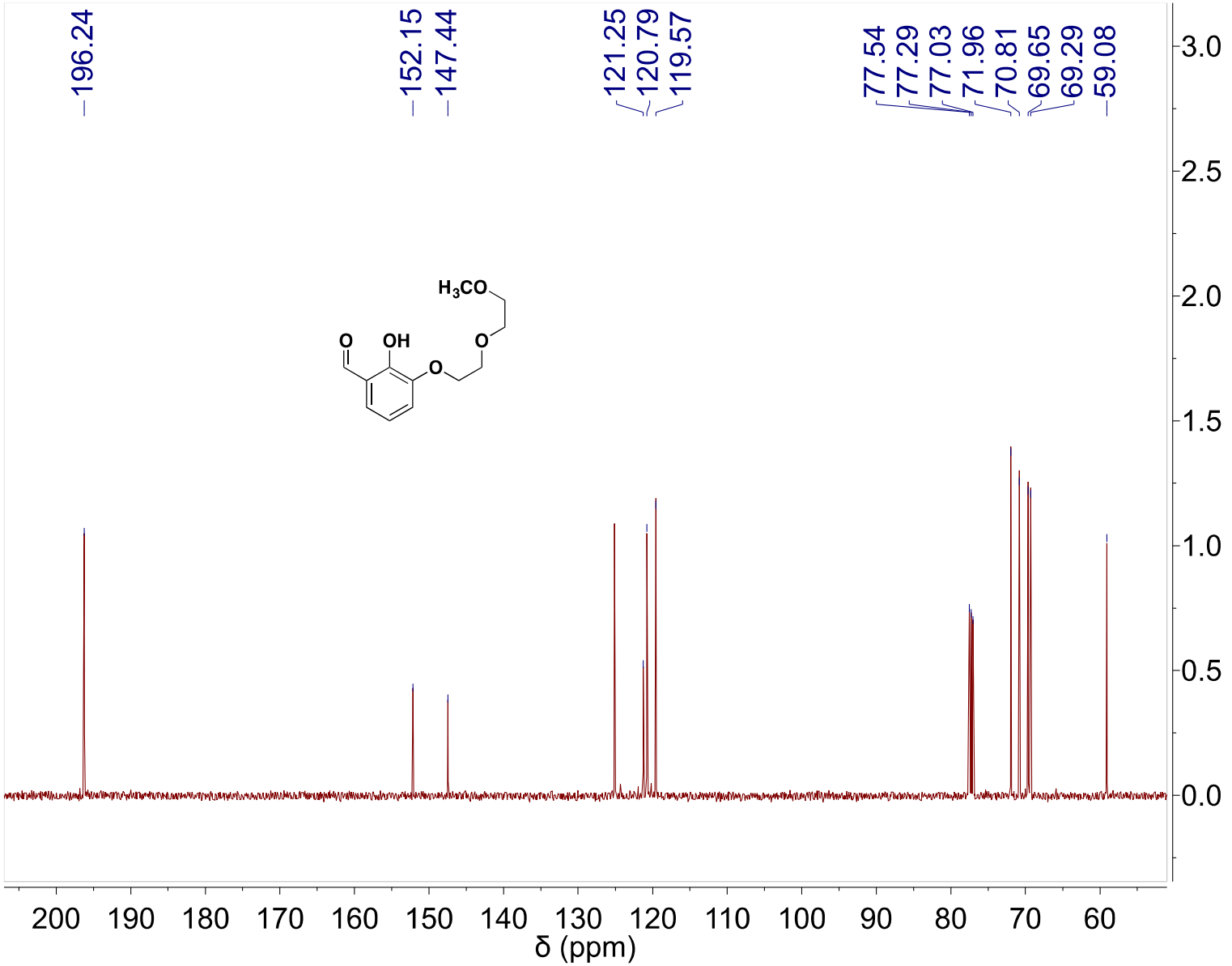


Figure S9. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of aldehyde **1C**.

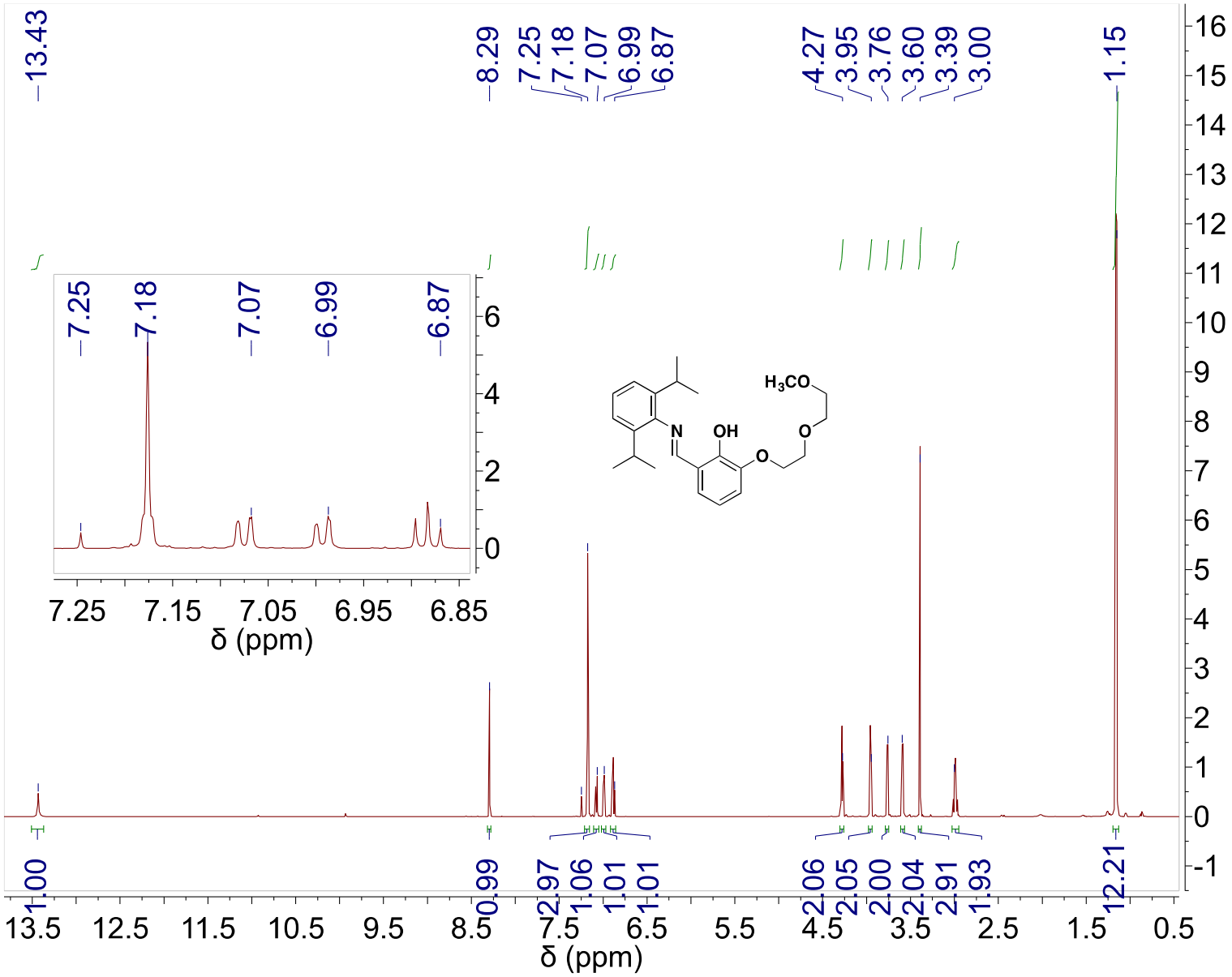


Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **HL2**.

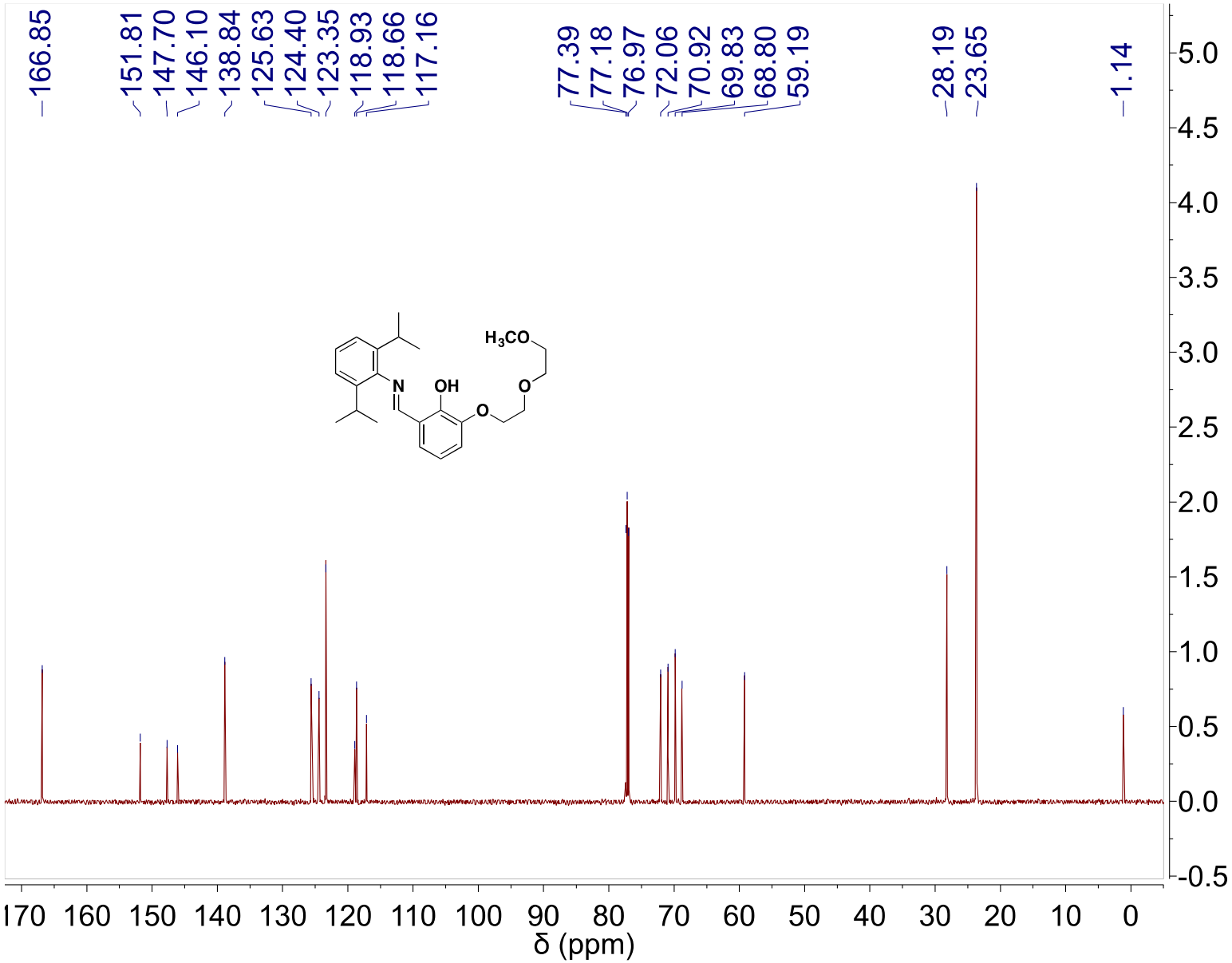


Figure S11. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **HL2.**

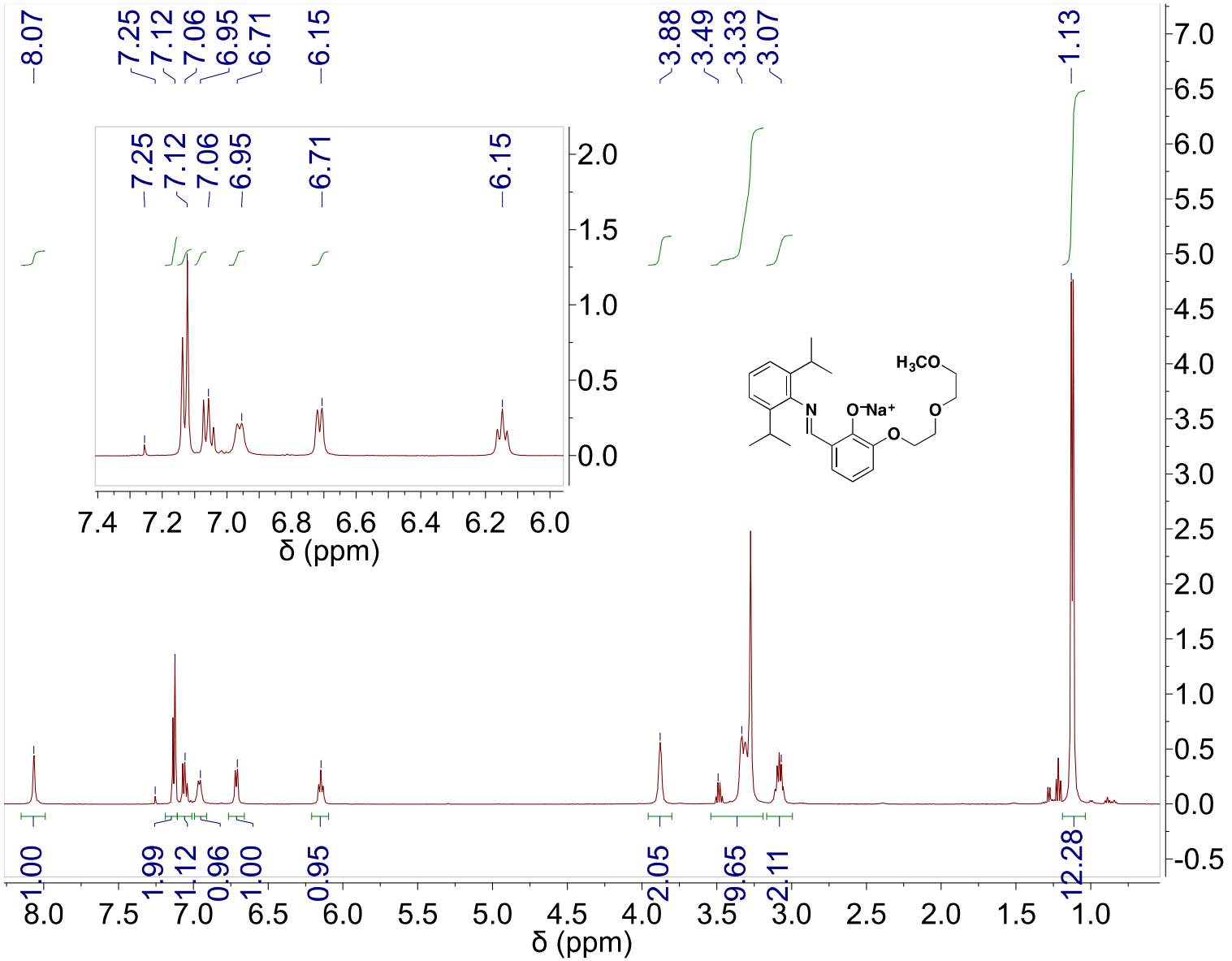


Figure S12. ^{1}H NMR ($CDCl_3$, 400 MHZ) of **NaL2**.

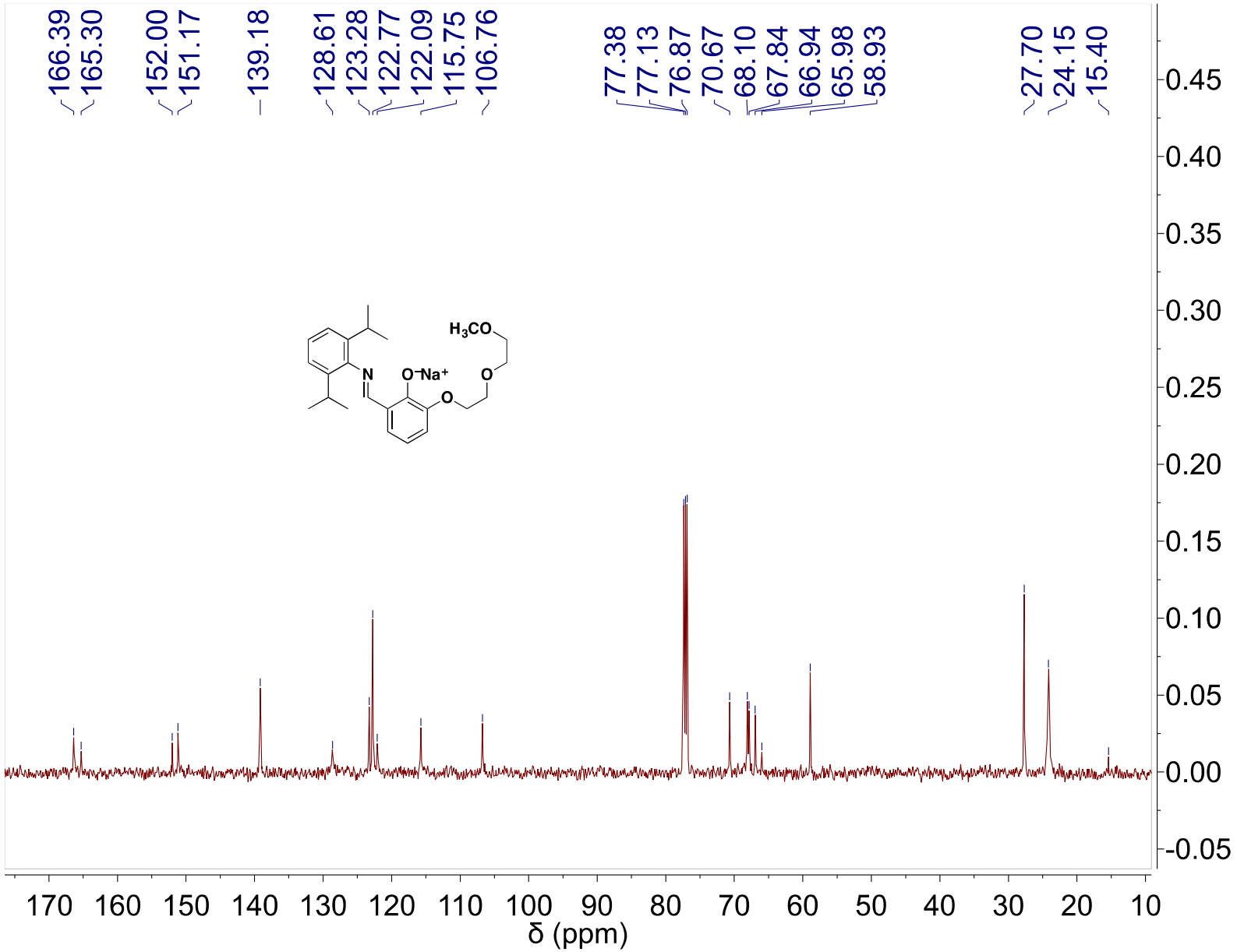


Figure S13. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **NaL2**.

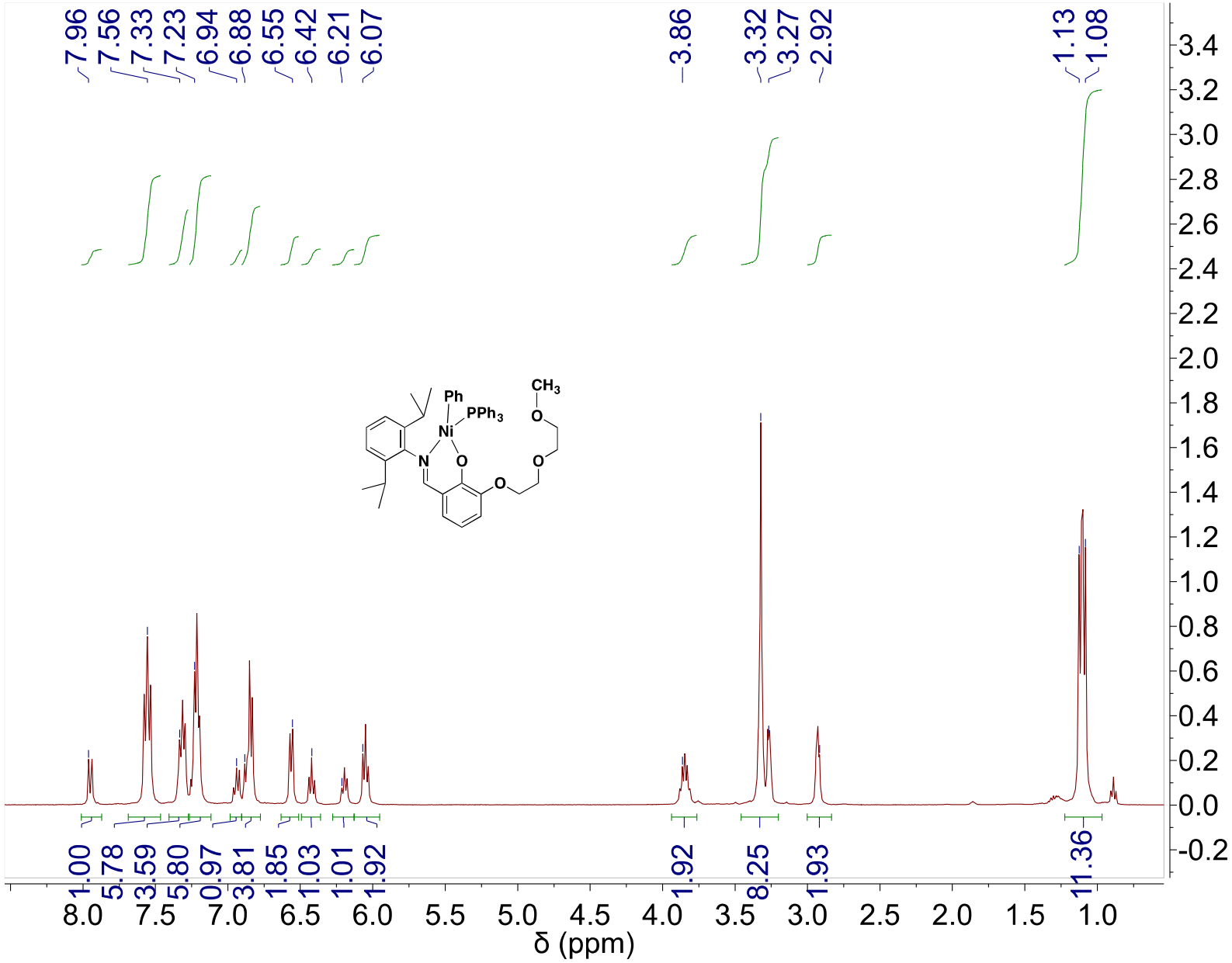


Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **NiL2**.

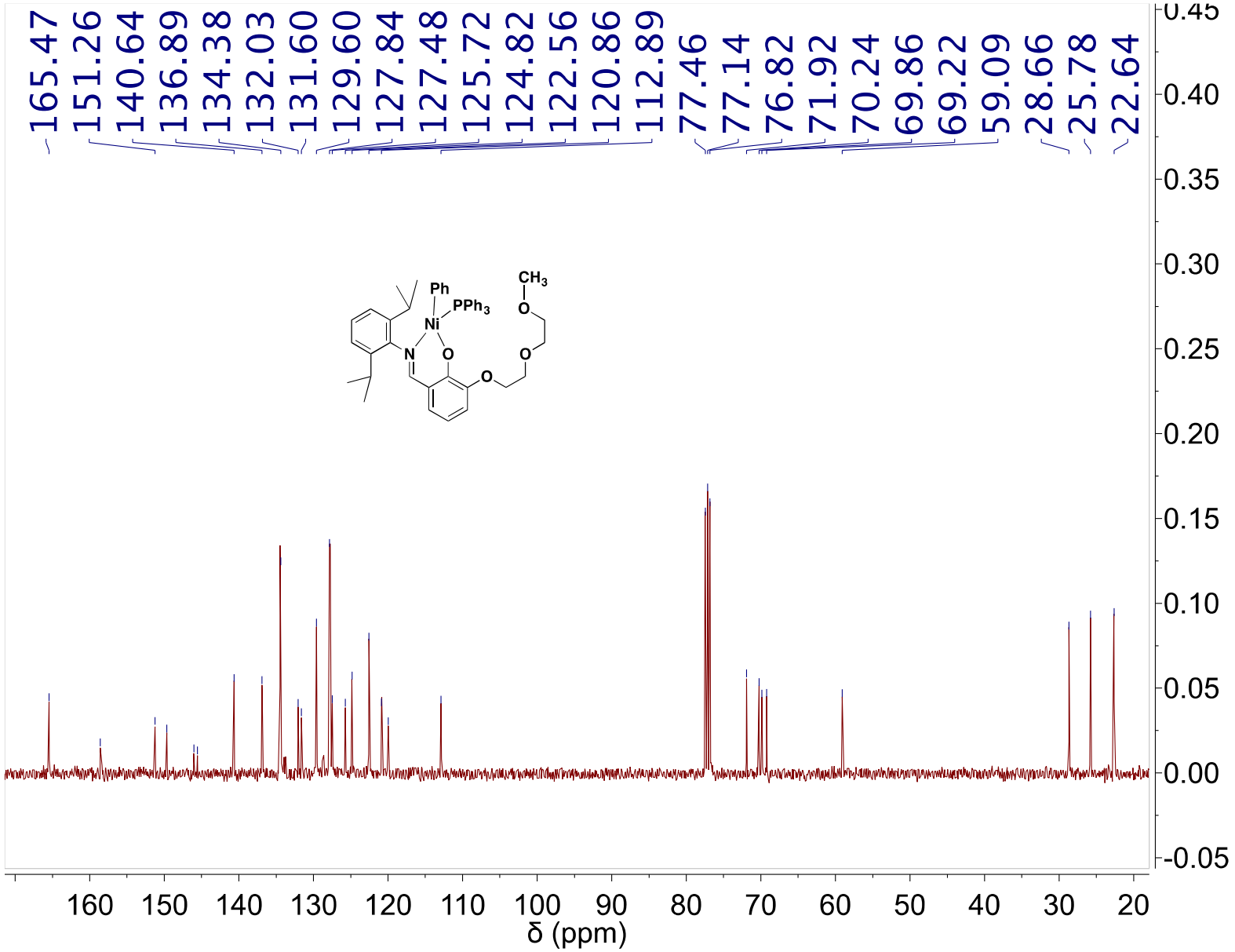


Figure S15. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **NiL2**.

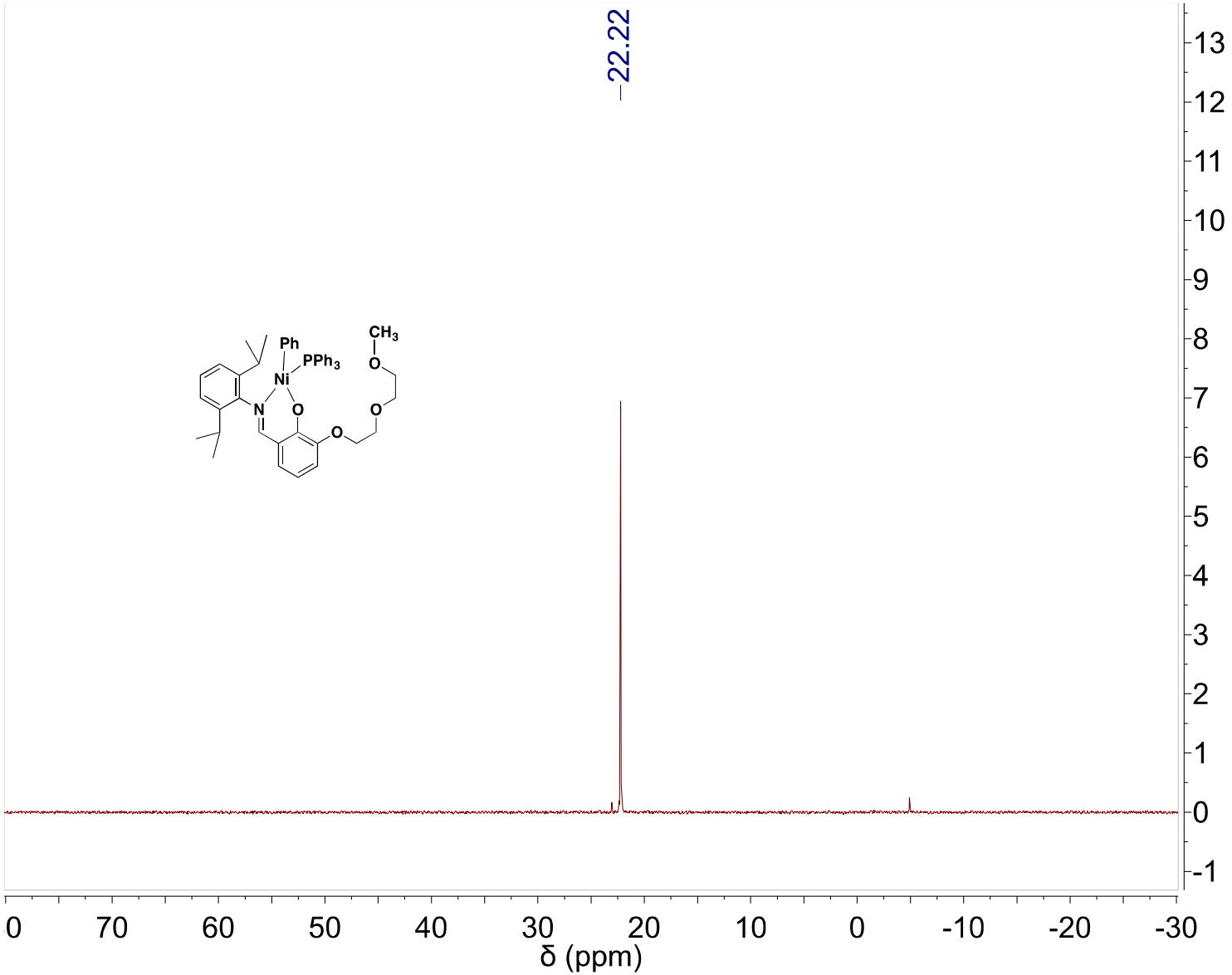


Figure S16. ^{31}P NMR spectrum ($CDCl_3$, 162 MHz) of **NiL2**.

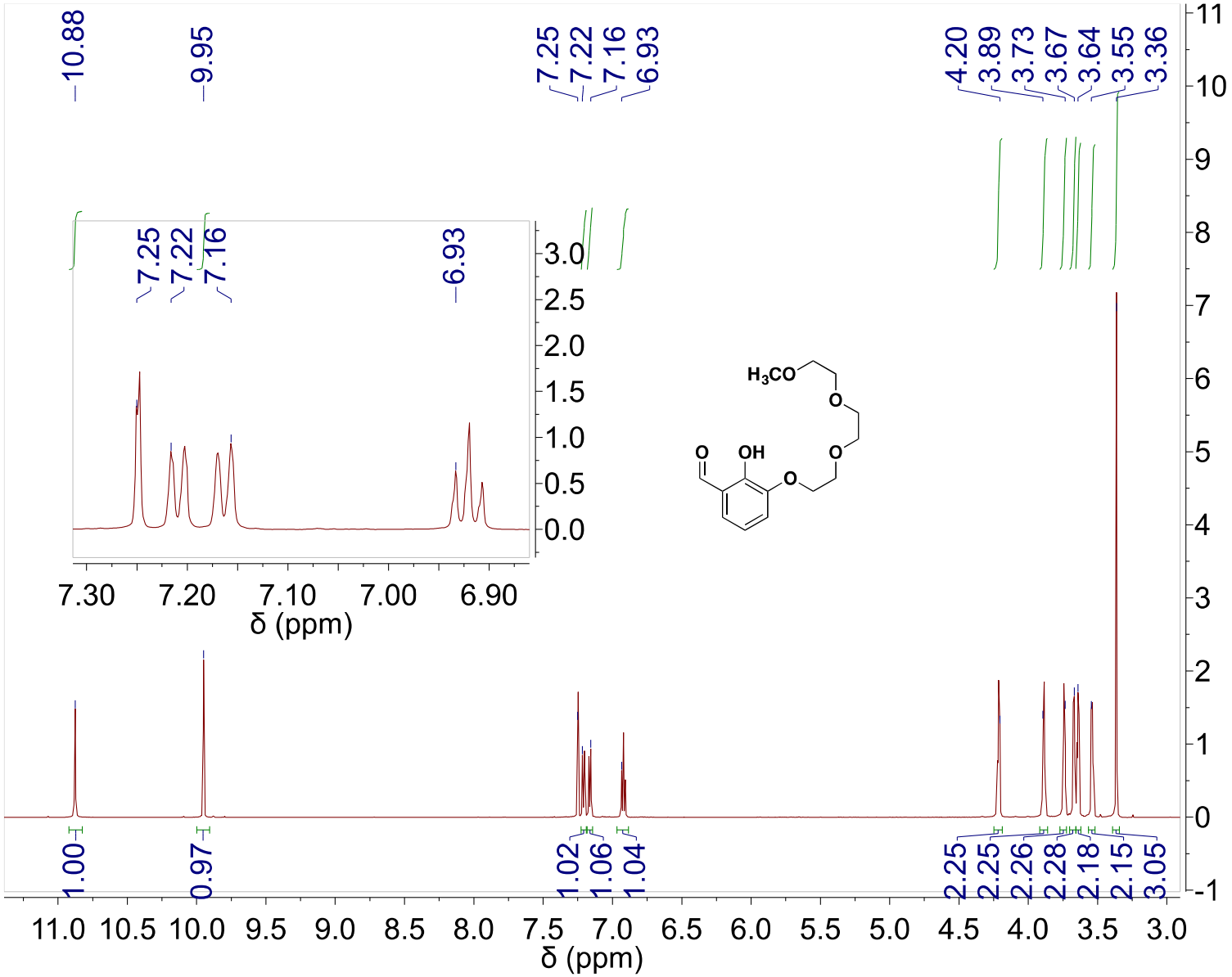


Figure S17. ^{1}H NMR ($CDCl_3$, 600 MHz) of aldehyde **1D**.

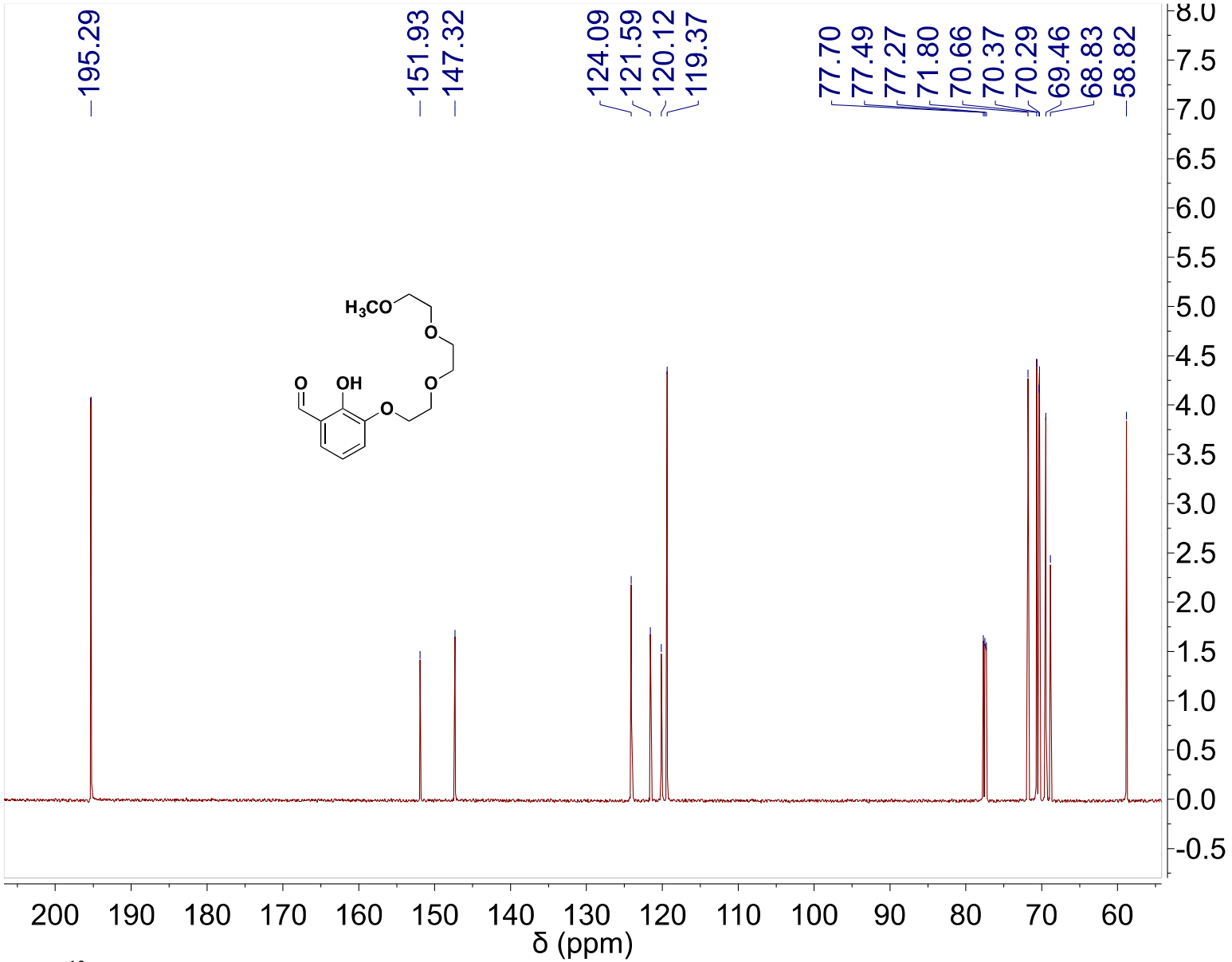


Figure S18. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of aldehyde **1D**.

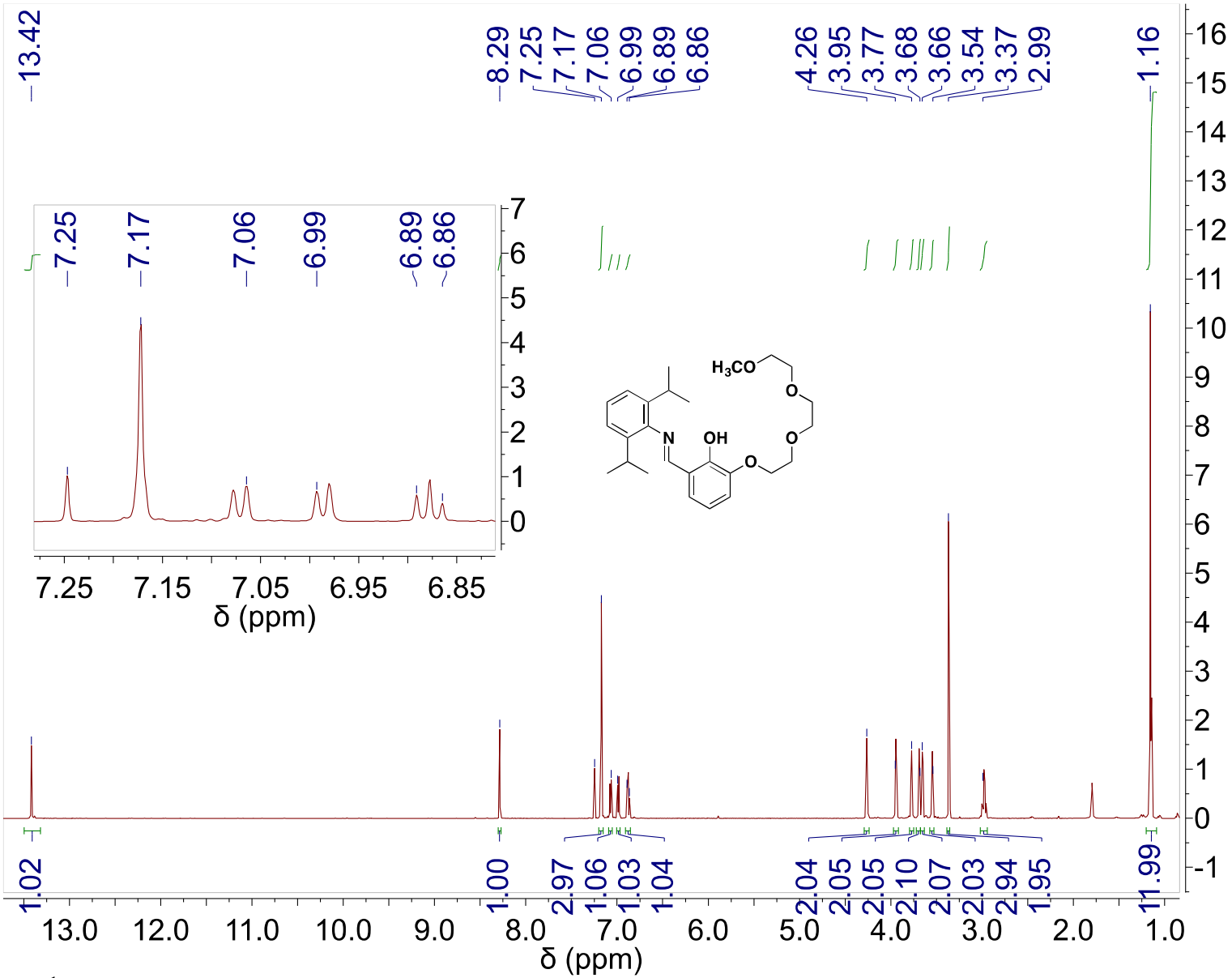


Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 600 HMz) of **HL3**.

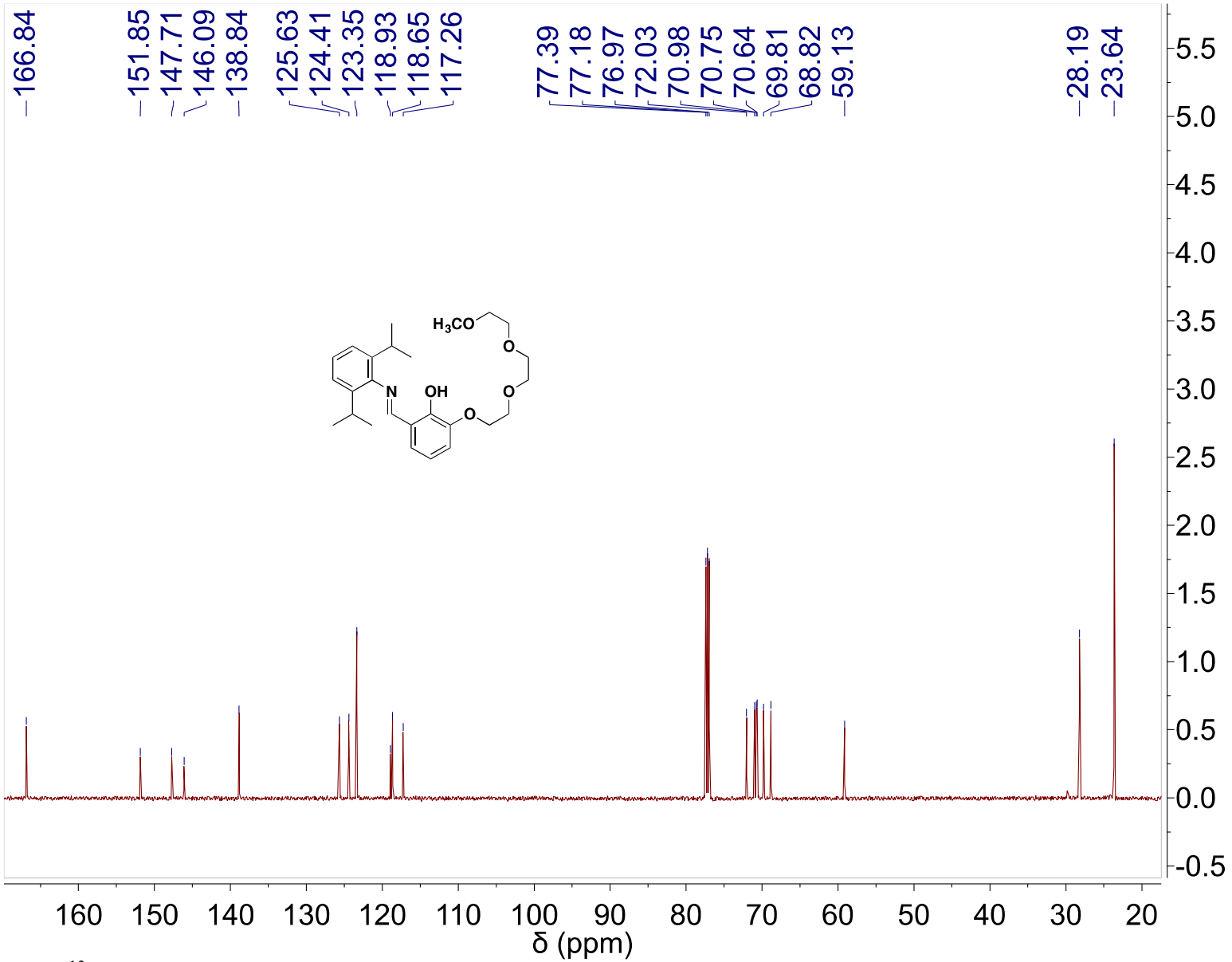


Figure S20. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **HL3**.

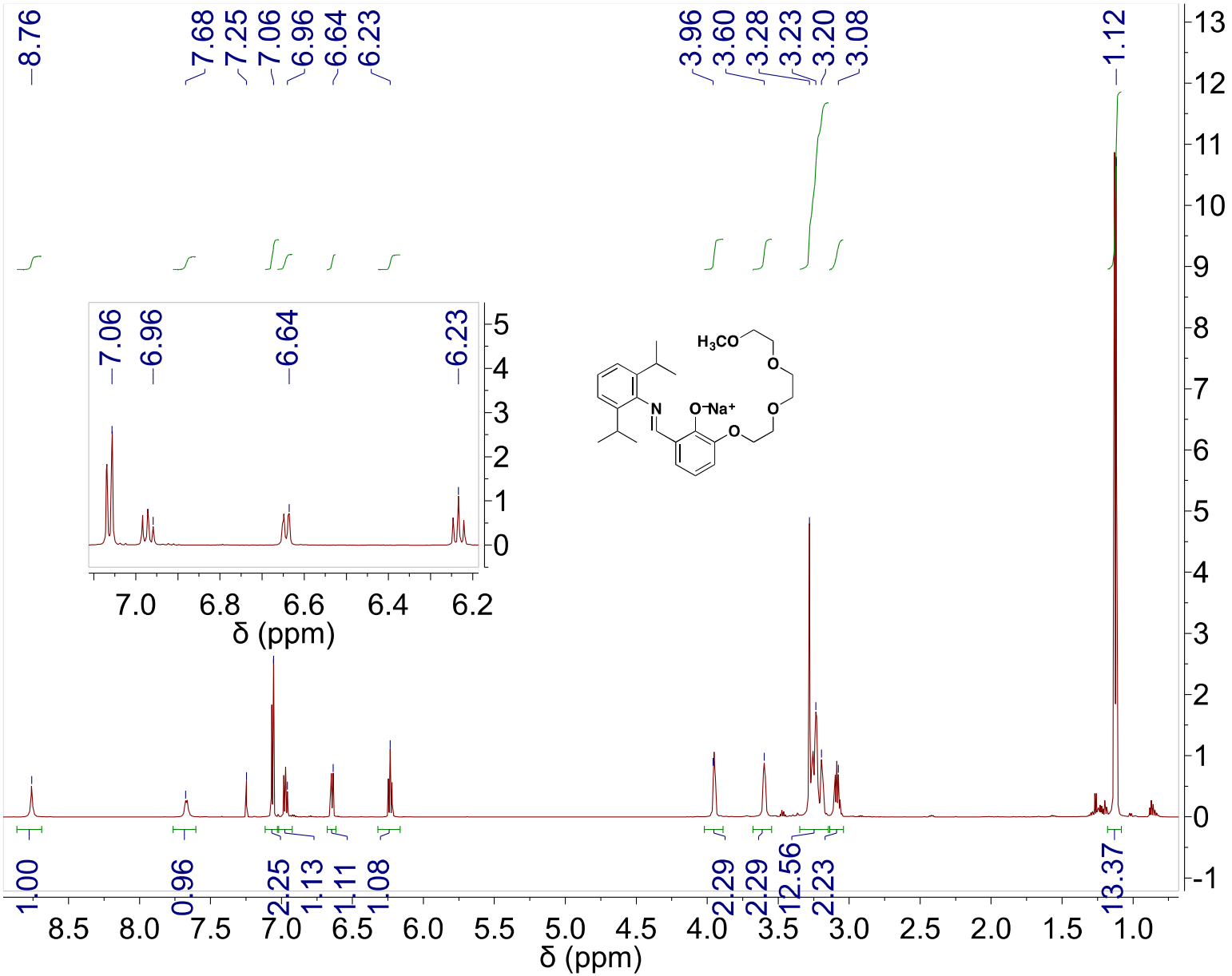


Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **NaL3**.

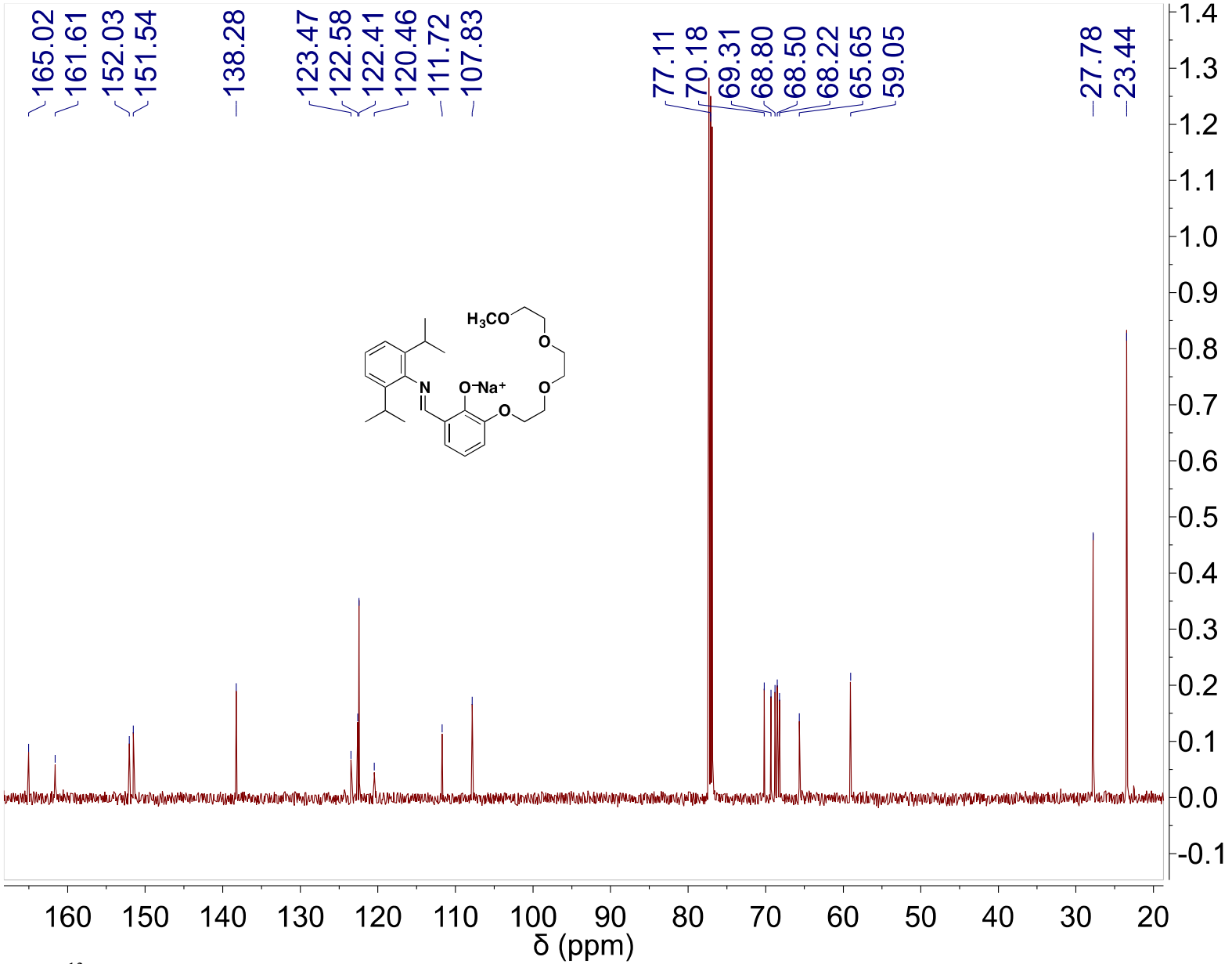


Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **NaL3**.

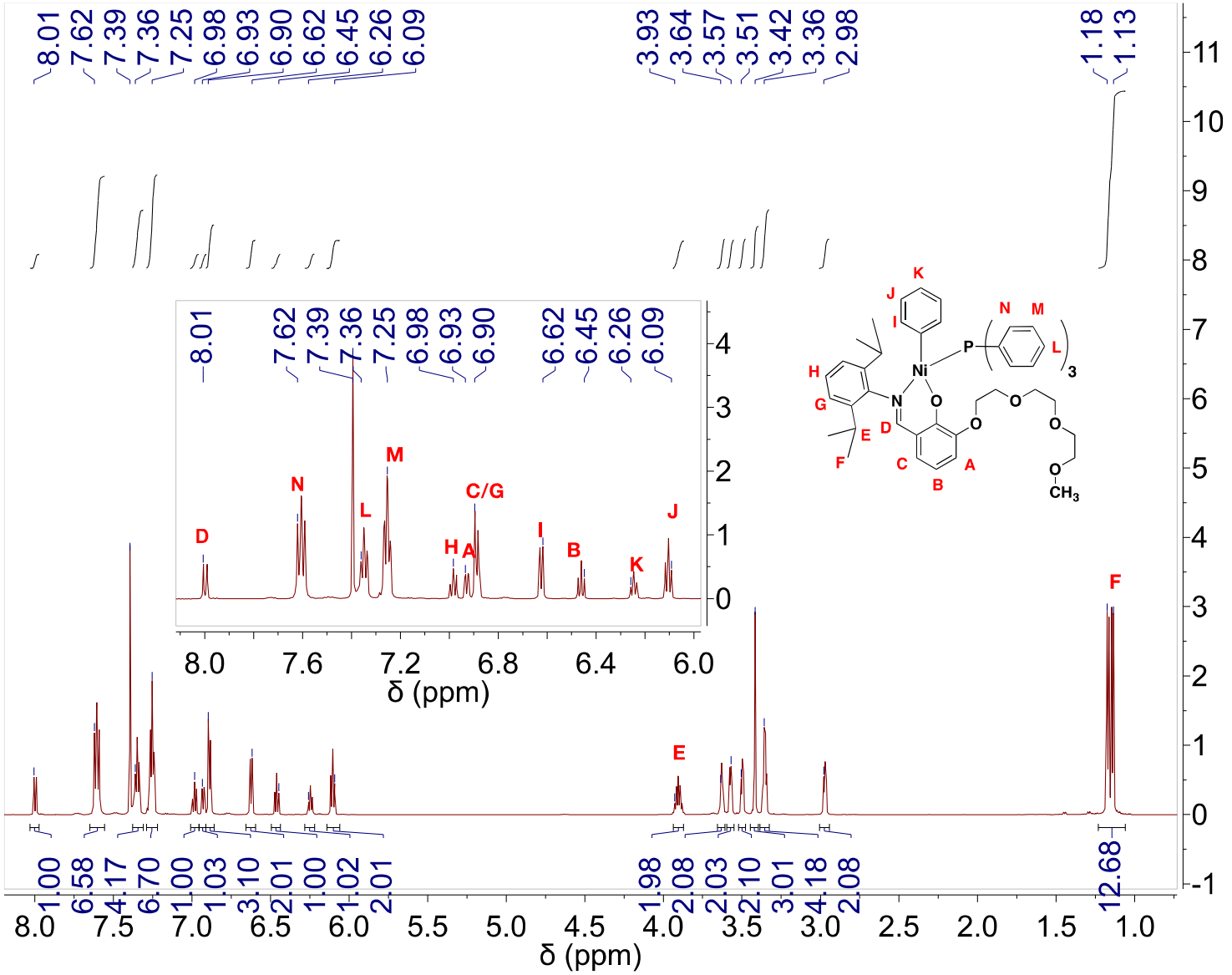


Figure S23. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **NiL3**. Spectral assignments were aided by the COSY data (Figure S26).

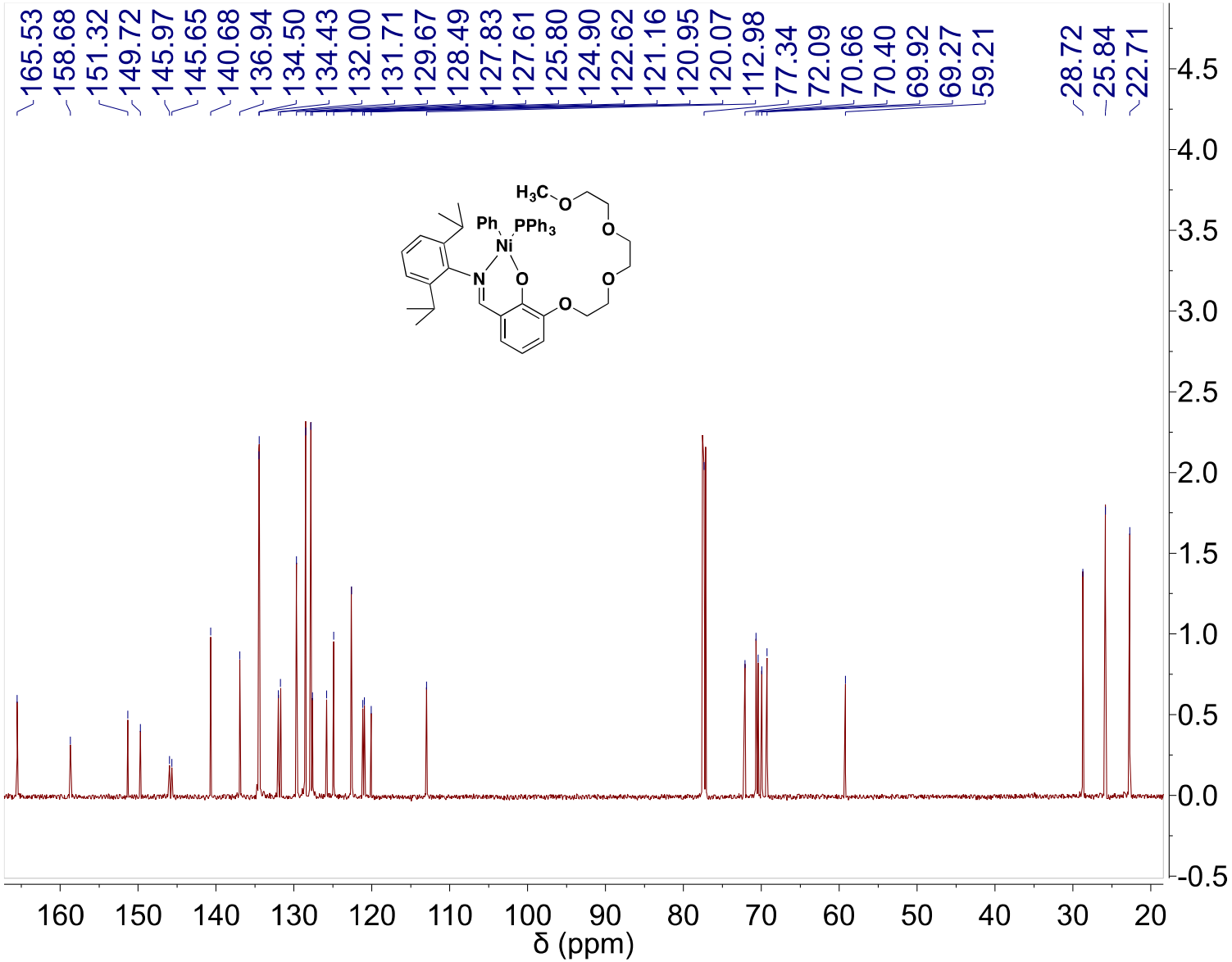


Figure S24. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **NiL3**.

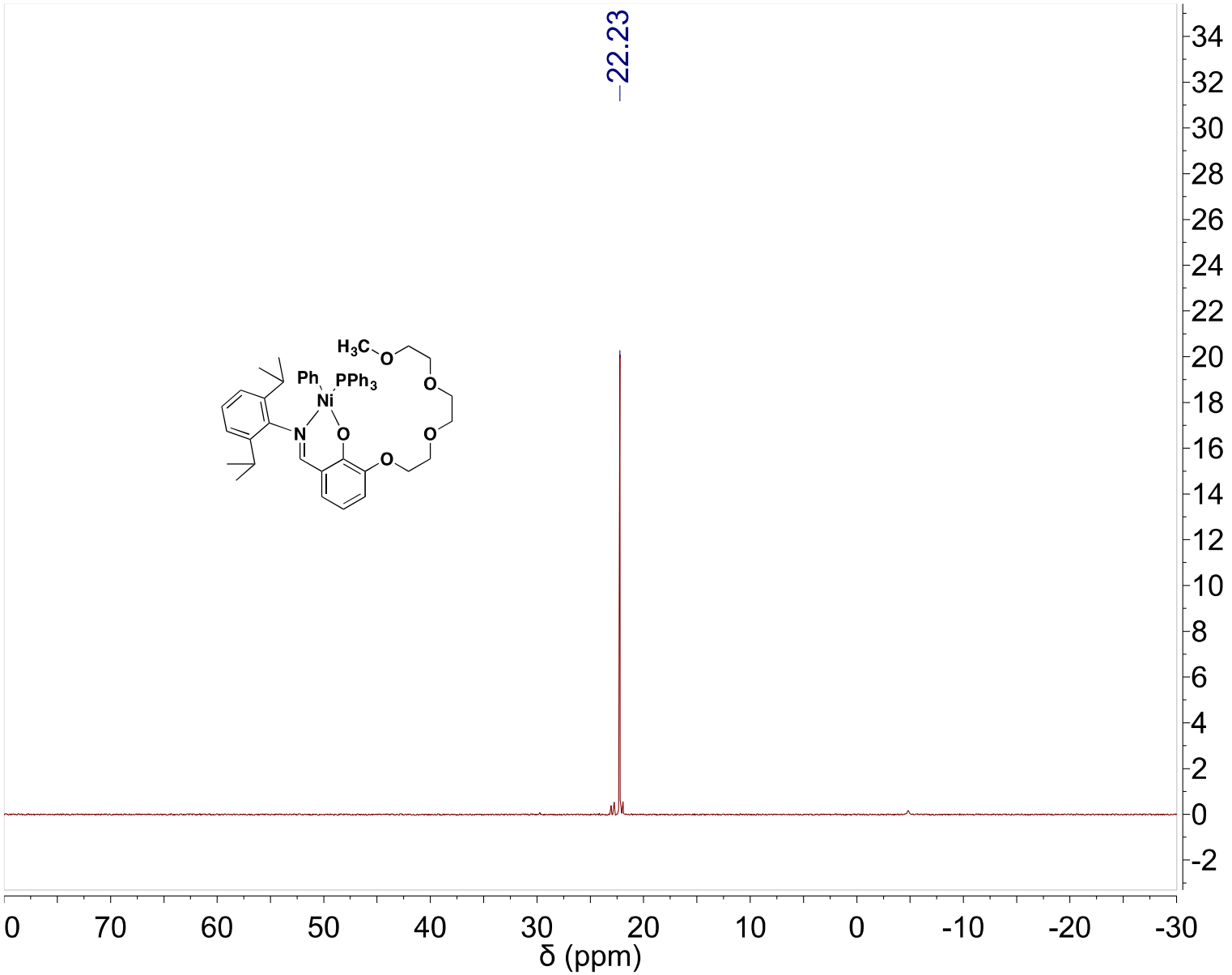


Figure S25. ^{31}P NMR spectrum ($CDCl_3$, 243 MHz) of **NiL3**.

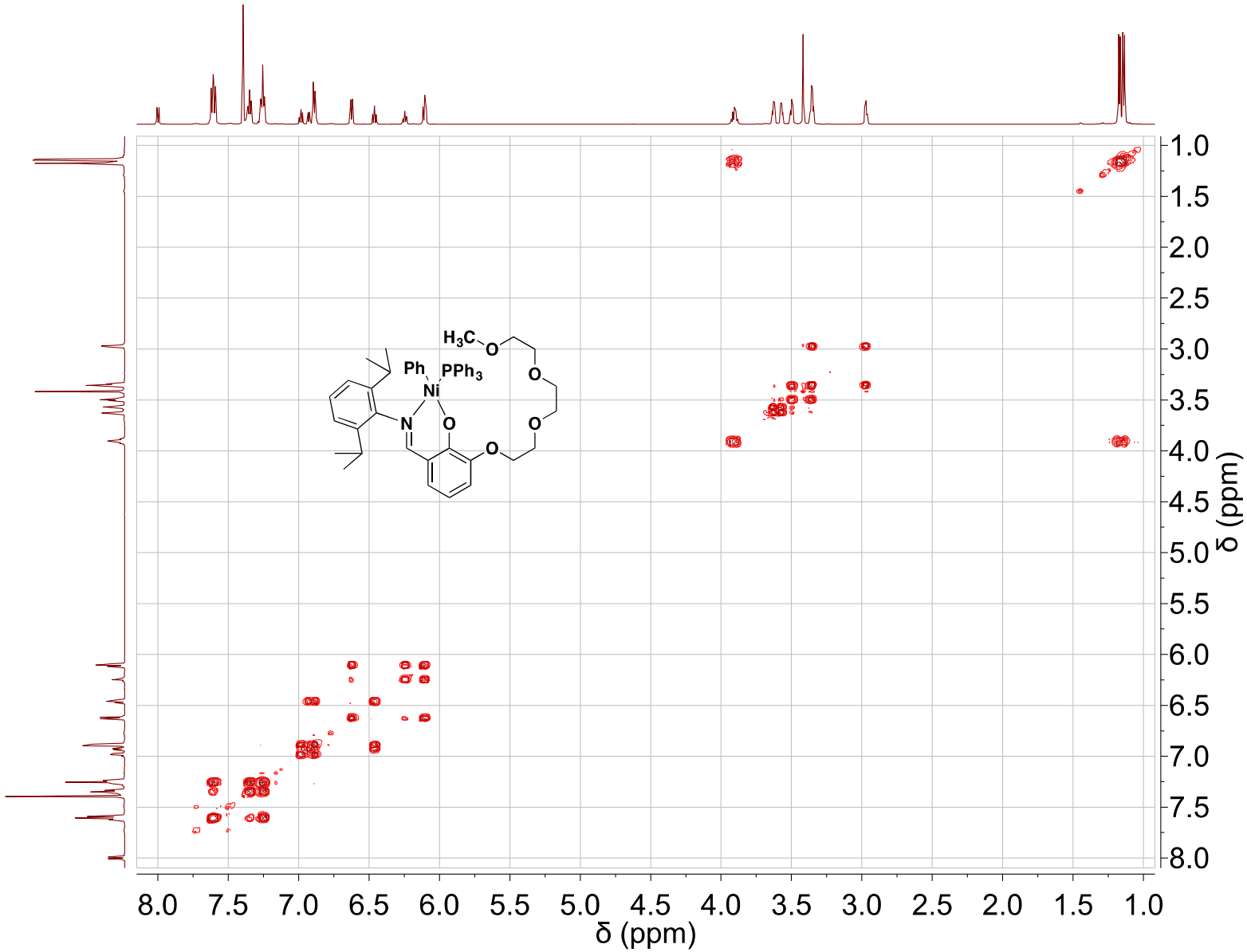


Figure S26. DFQ-COSY spectrum ($CDCl_3$, 600 MHz) of **NiL3**.

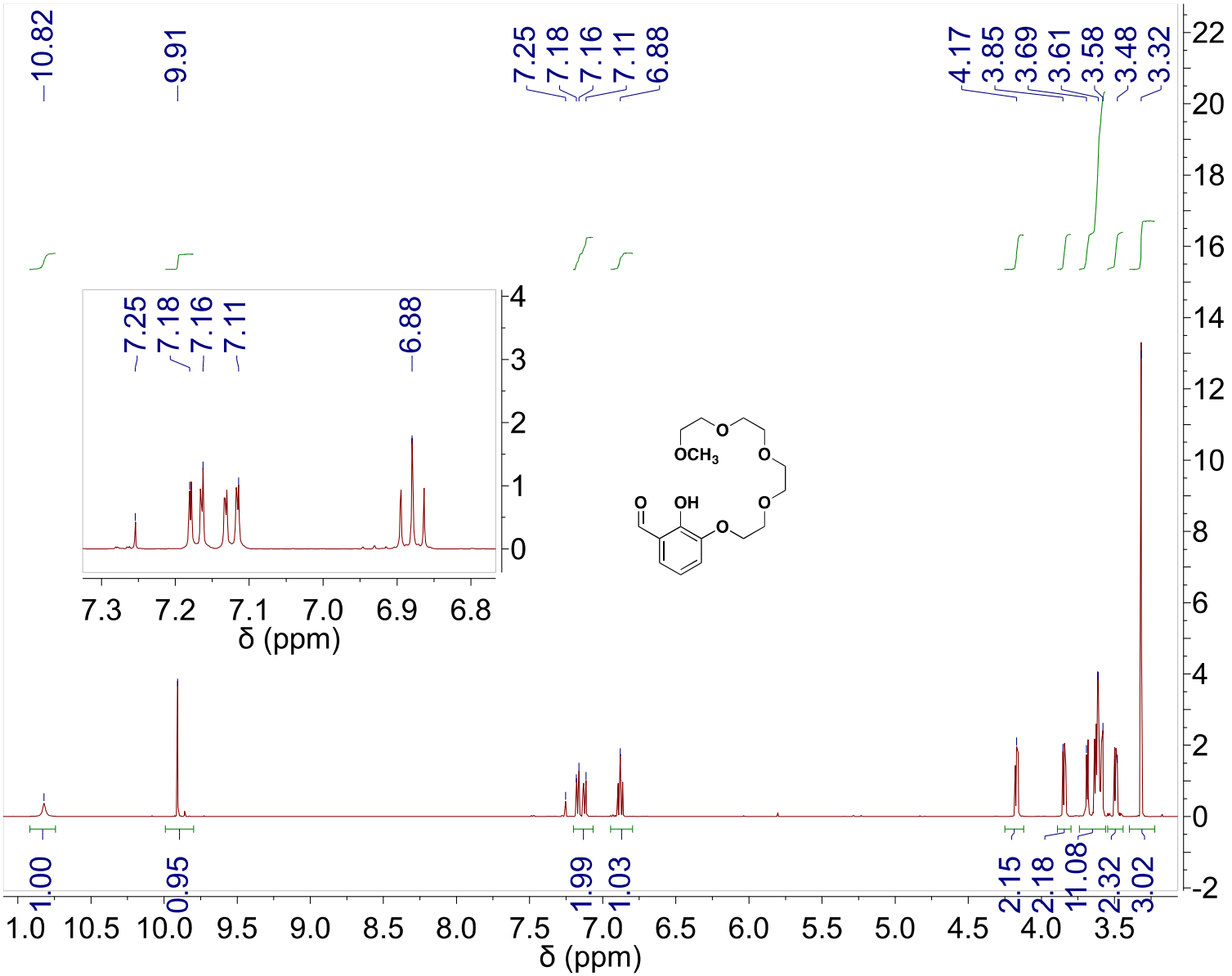


Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of aldehyde **1E**.

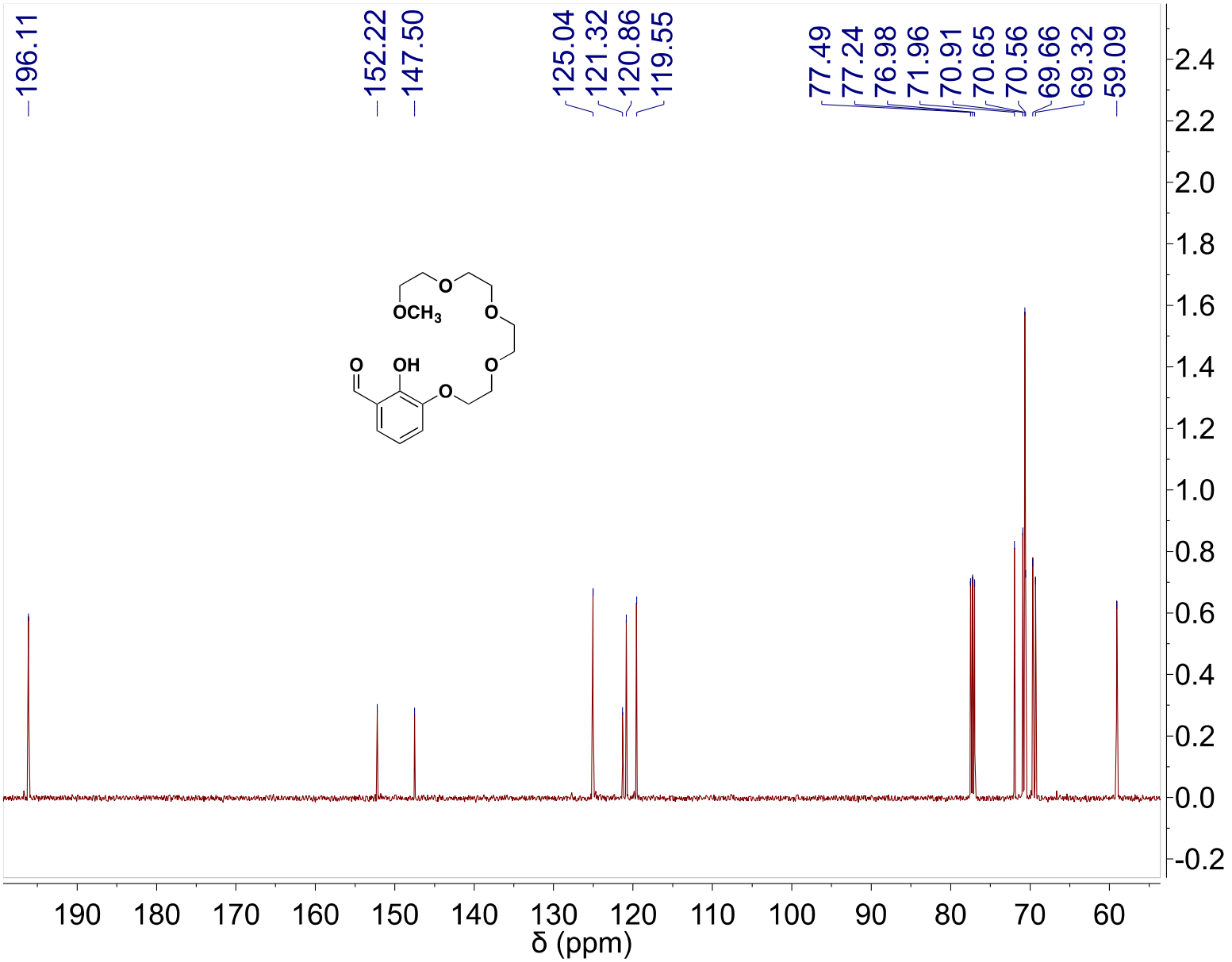


Figure S28. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of aldehyde **1E**.

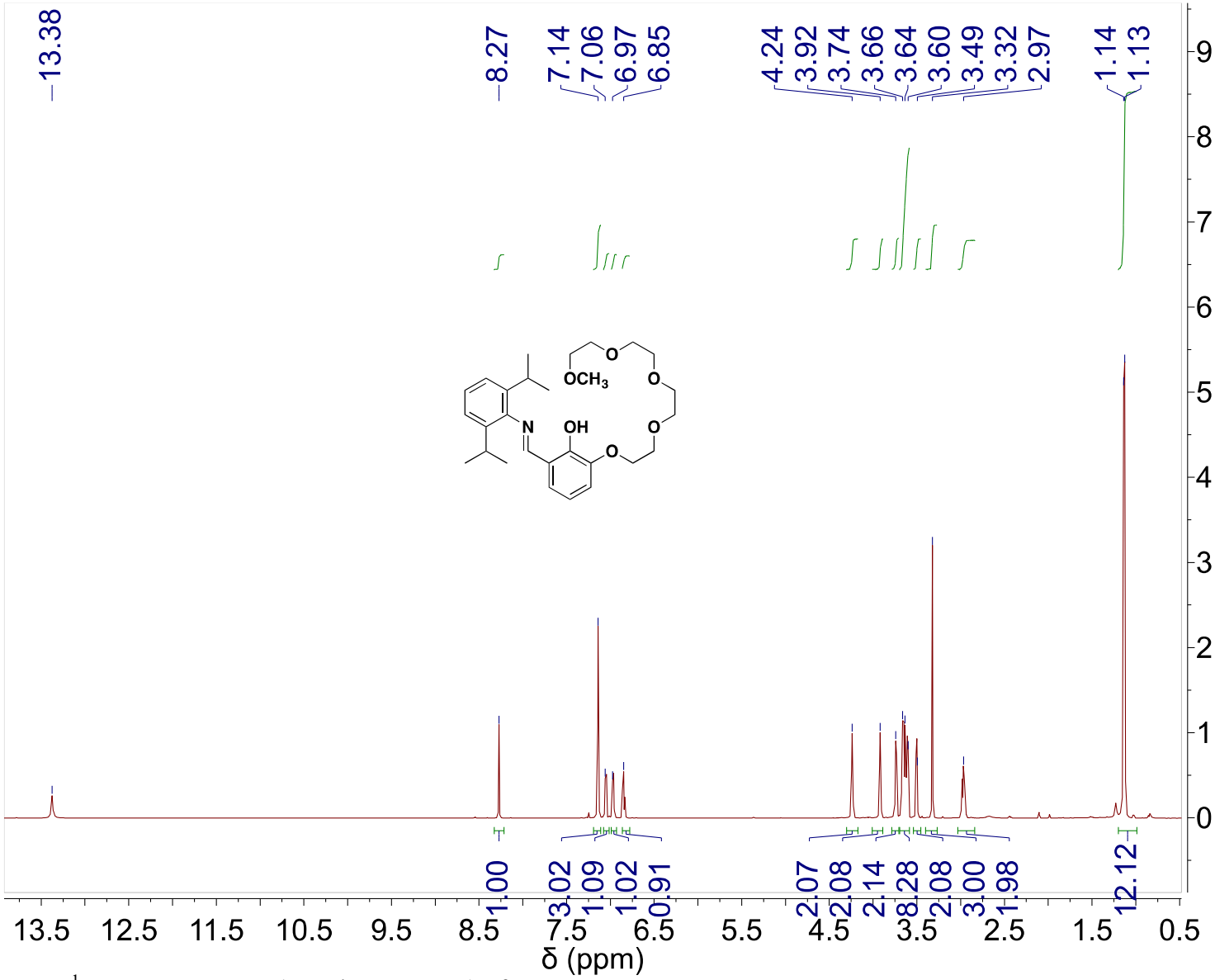


Figure S29. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **HL4**.

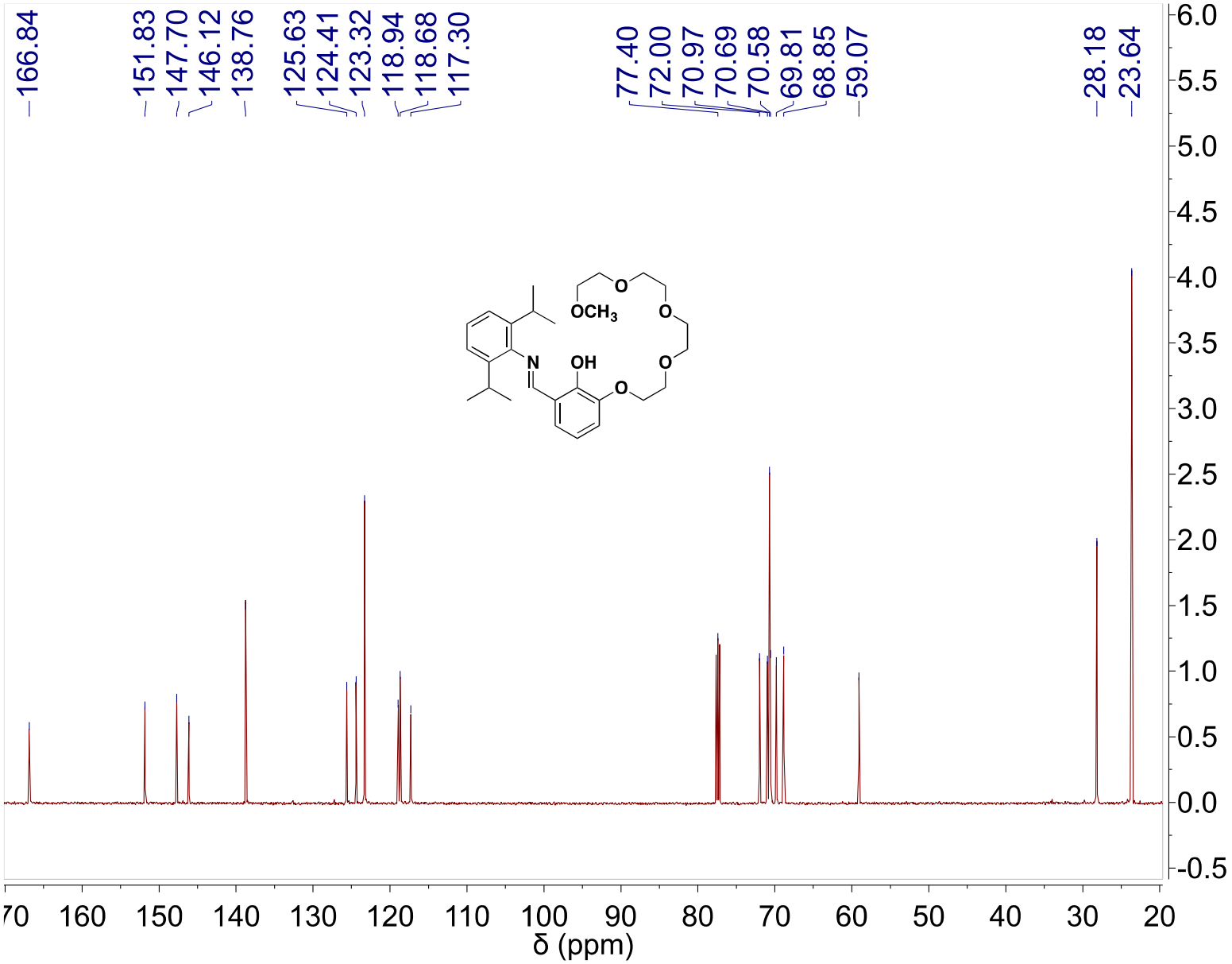


Figure S30. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of **HL4**.

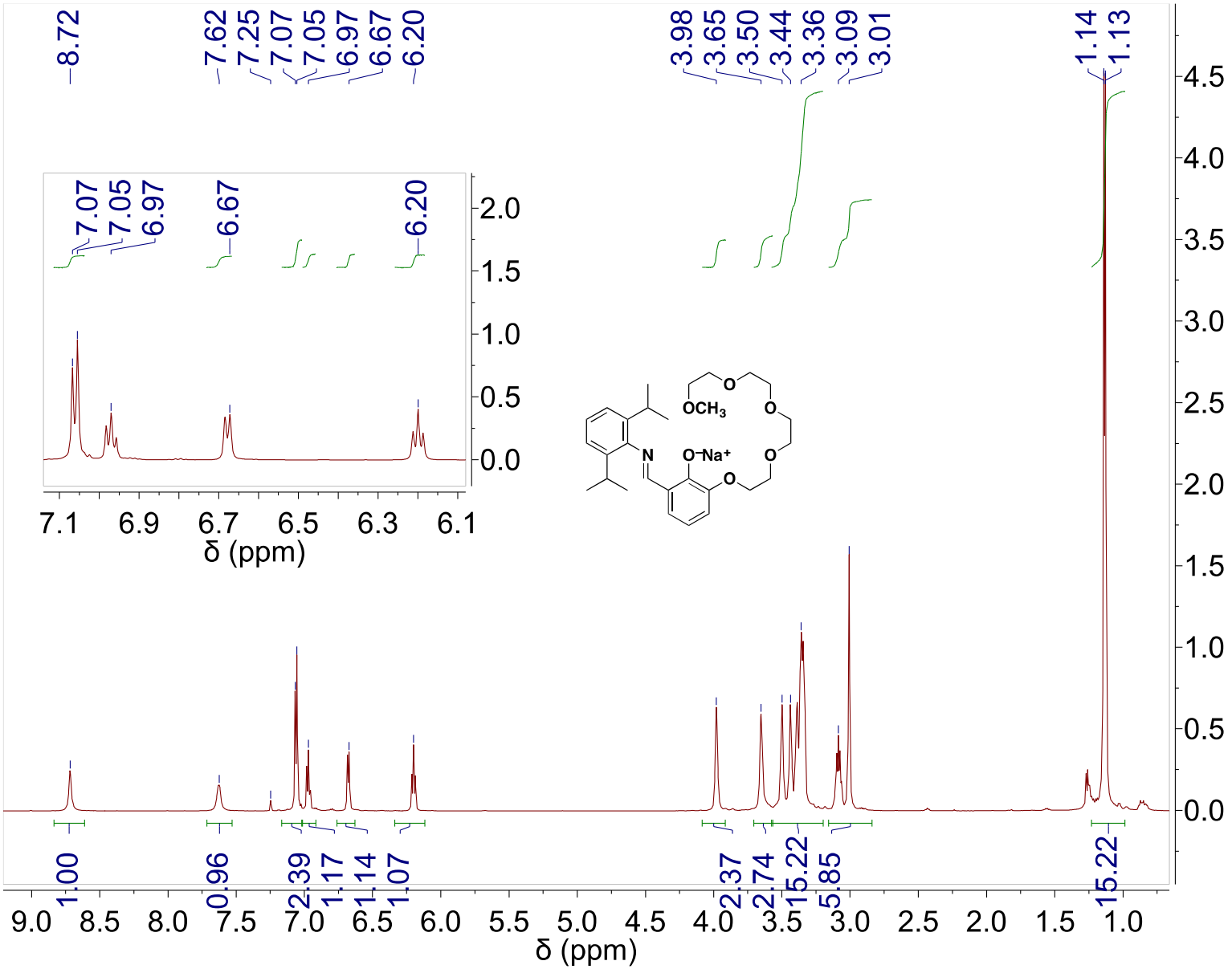


Figure S31. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **NaL4**.

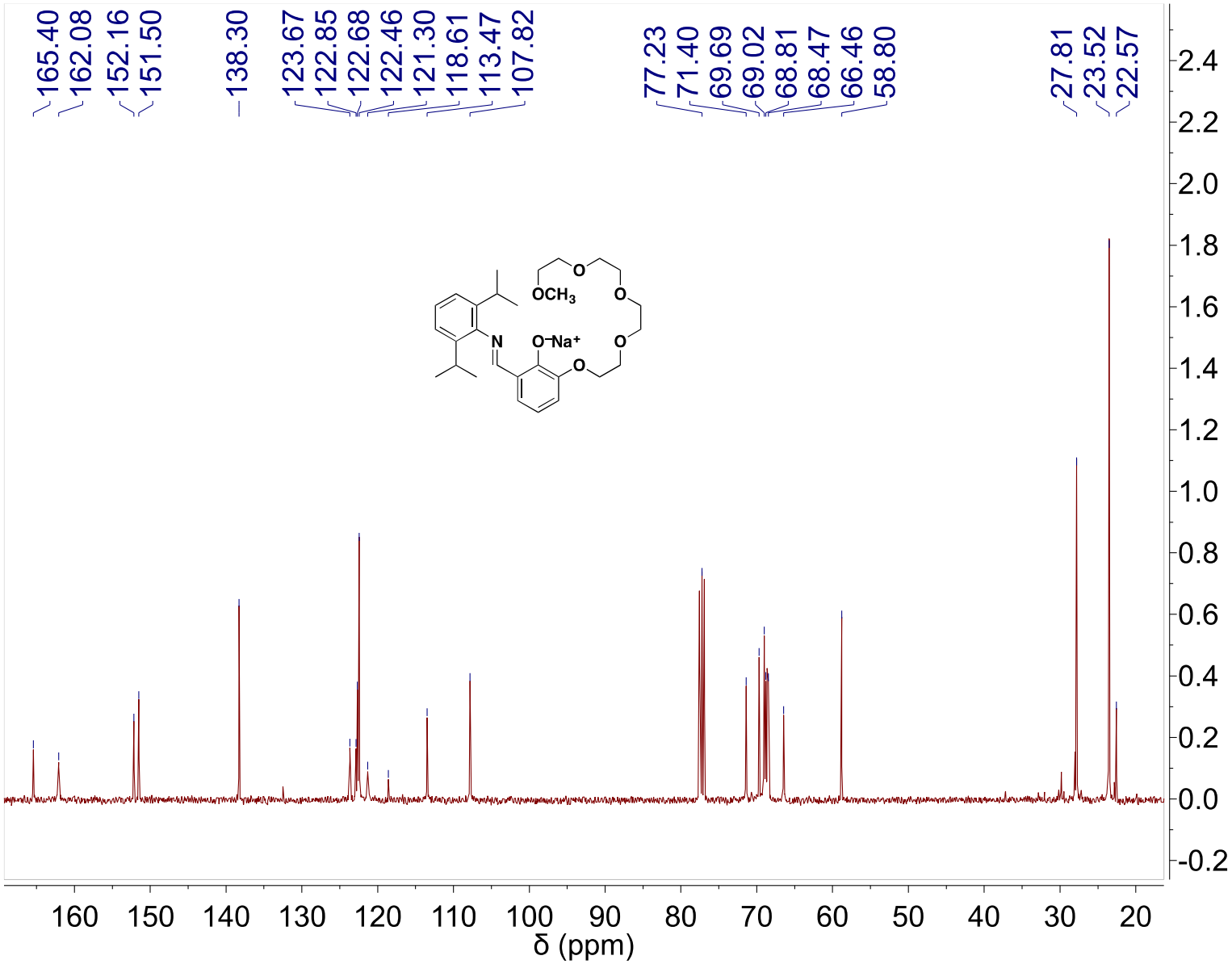


Figure S32. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **NaL4**.

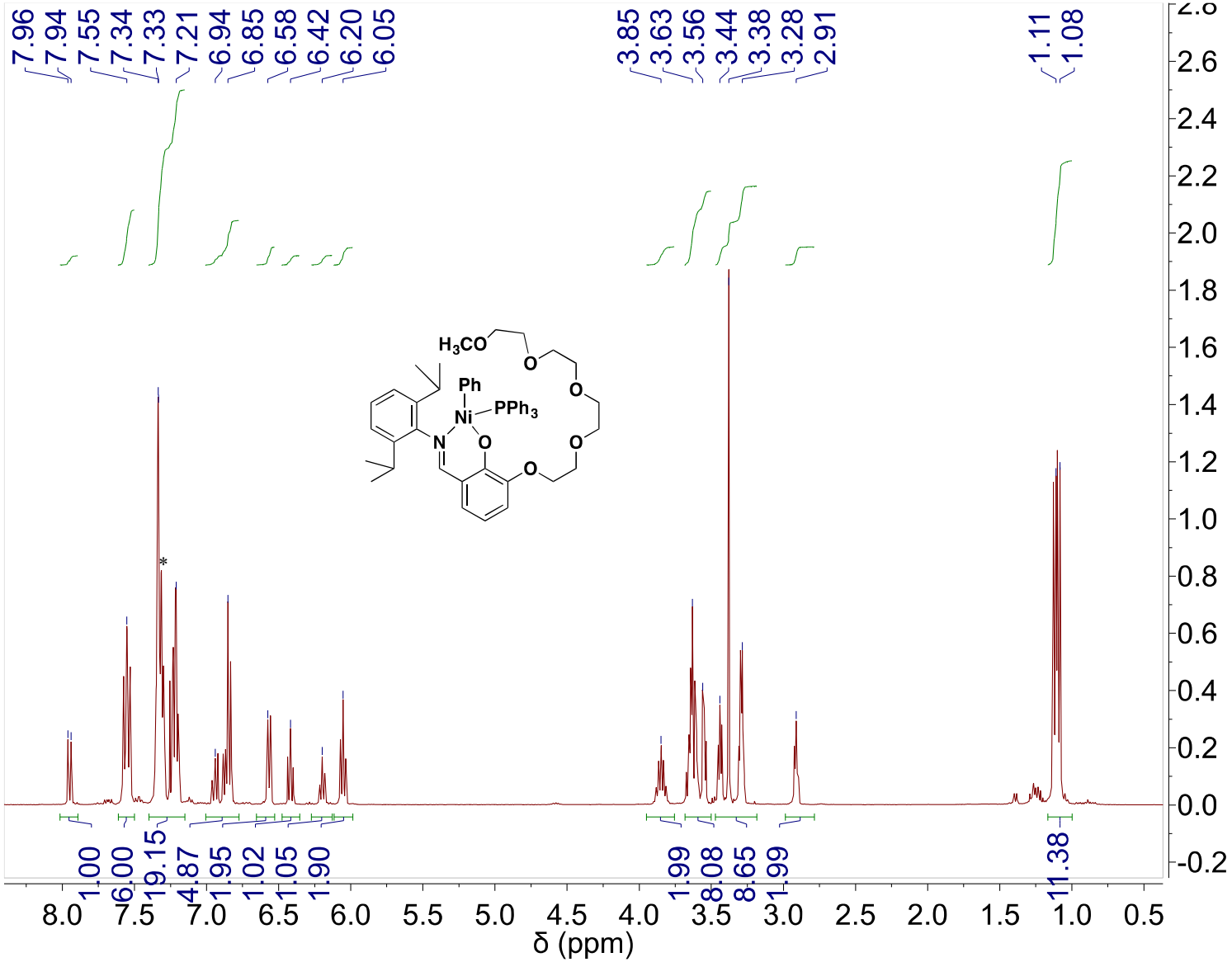


Figure S33. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **NiL4**. Signals arising from a PPh_3 impurity are marked with (*).

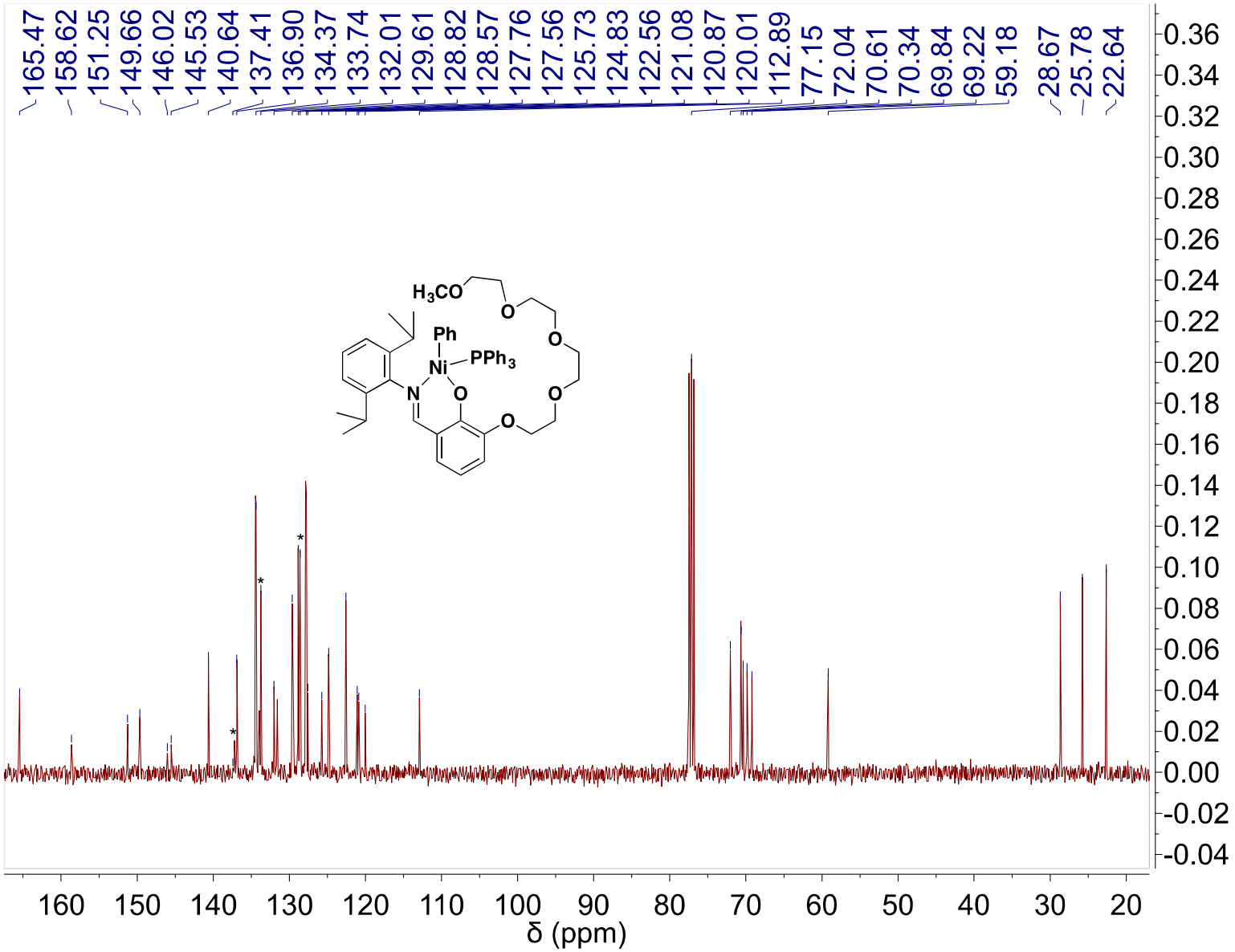


Figure S34. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **NiL4**. Signals arising from a PPh_3 impurity are marked with (*).

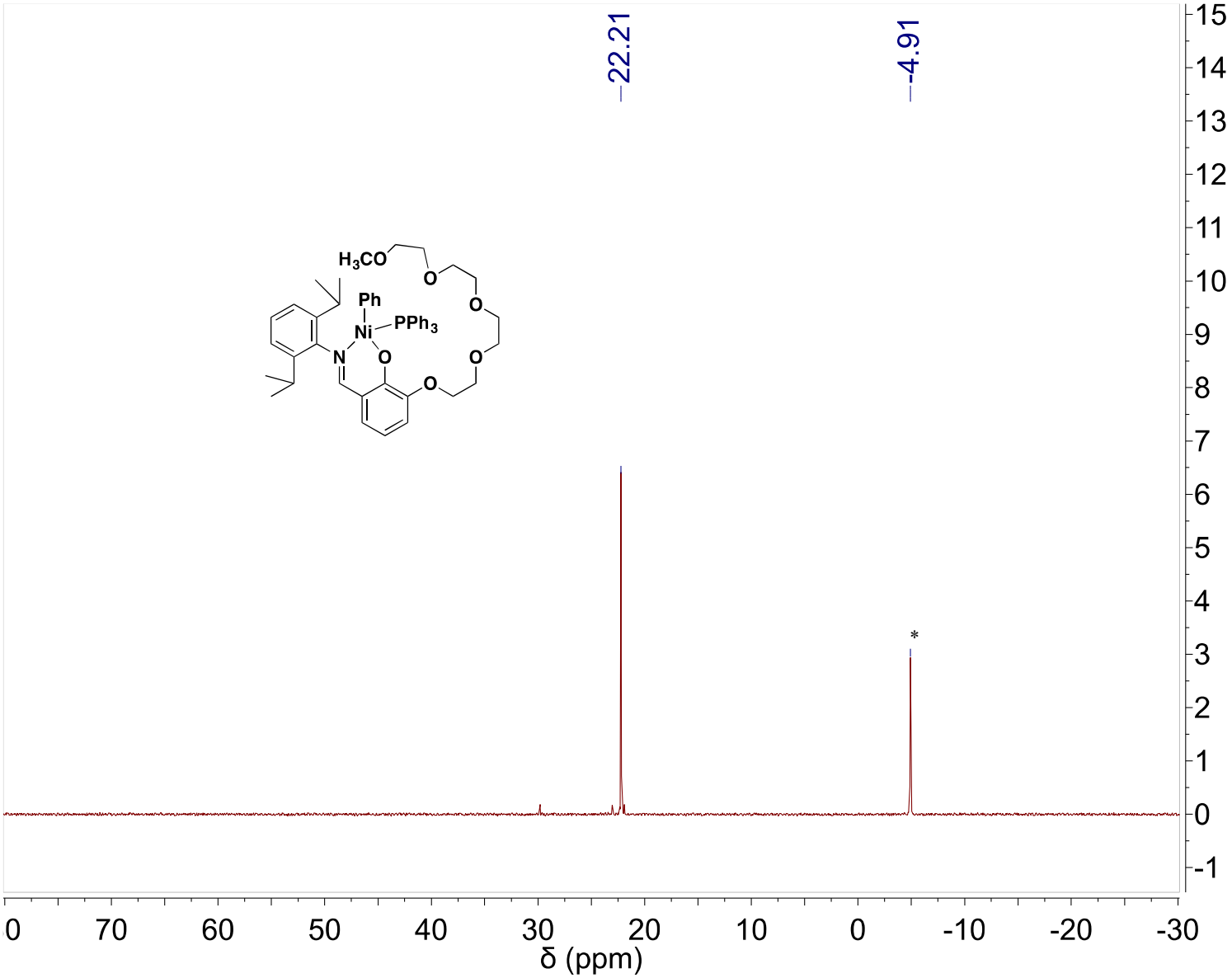


Figure S35. ^{31}P NMR spectrum ($CDCl_3$, 162 MHz) of **NiL4**. The peak marked with (*) comes free PPh_3 impurity.

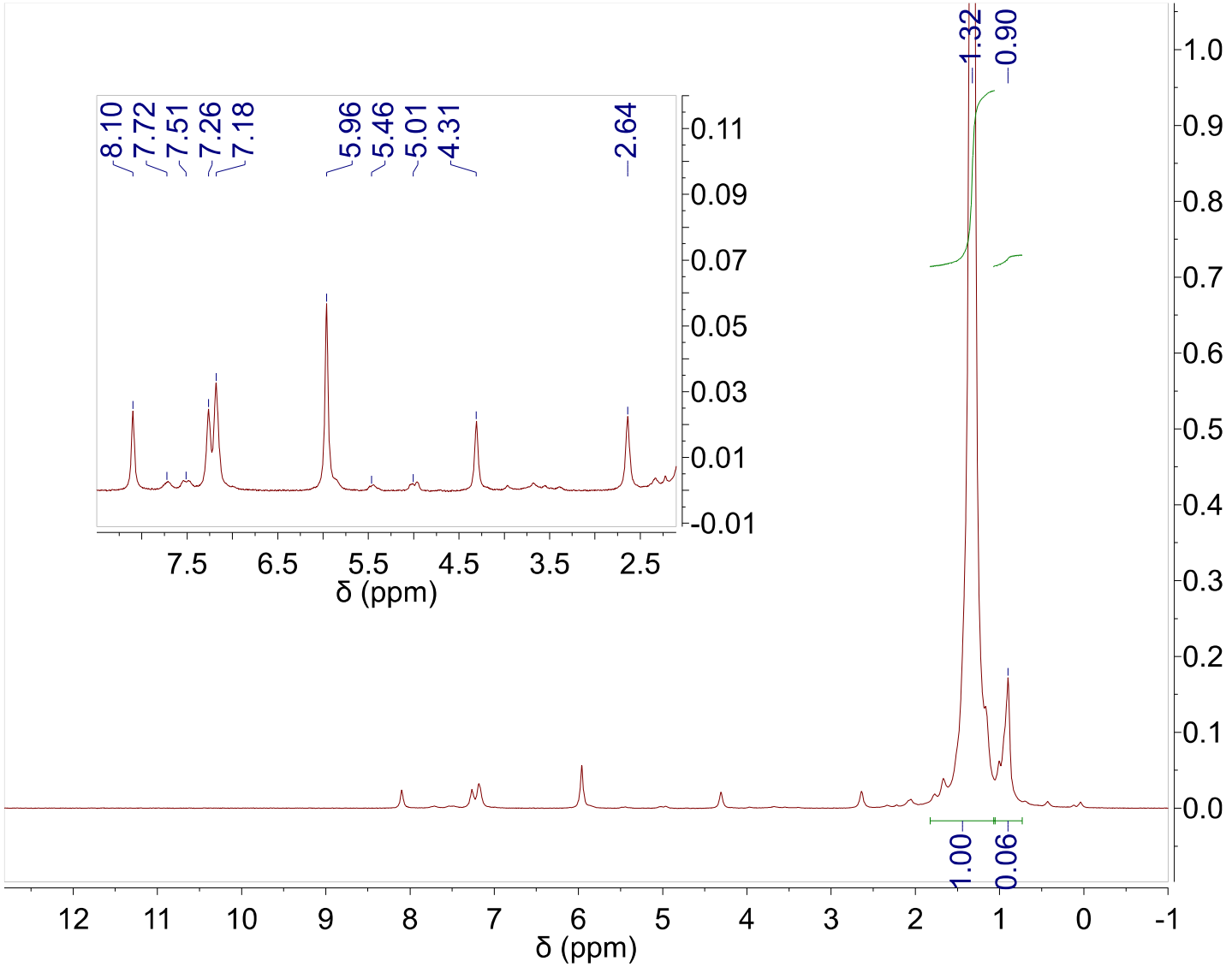


Figure S36. [1]H NMR spectrum (TCE-d_2, 600 MHz) of the solid polyethylene obtained from the reaction of **NiL3**/Ni(COD)$_2$ in the presence of ethylene. Spectral assignments were based on the chemical shift valves reported in the literature.[3]

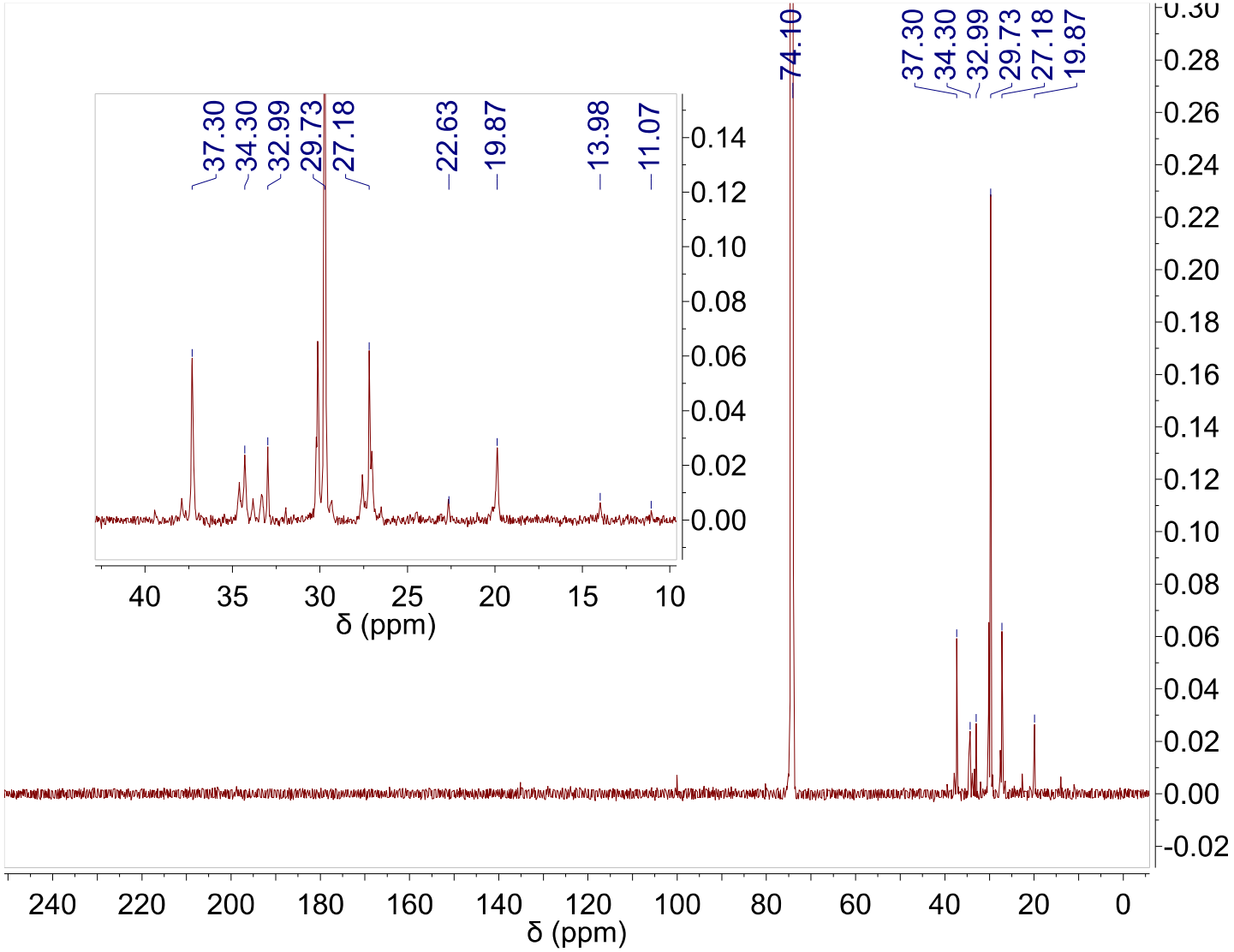


Figure S37. ^{13}C NMR spectrum (TCE-d_2, 150 MHz) of the solid polyethylene obtained from the reaction of **NiL3**/Ni(COD)$_2$ in the presence of ethylene. Spectral assignments were based on the chemical shift valves reported in the literature.[4,5]

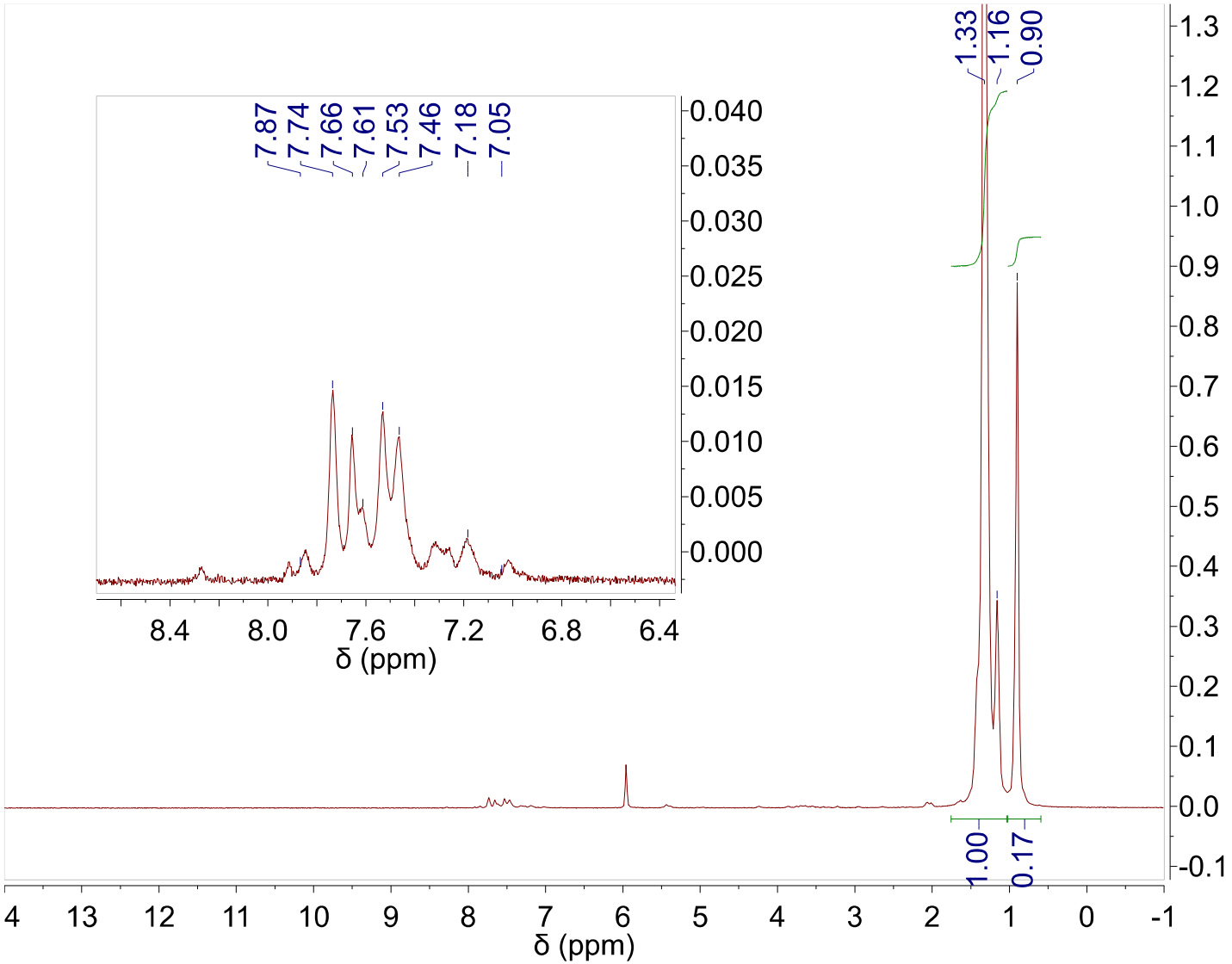


Figure S38. ^{1}H NMR spectrum (TCE-d_2, 600 MHz) of the amorphous polyethylene obtained from the reaction of **NiL3**/NaBAr$^{F}_{4}$/Ni(COD)$_2$ in the presence of ethylene. Spectral assignments were based on the chemical shift valves reported in the literature.[3]

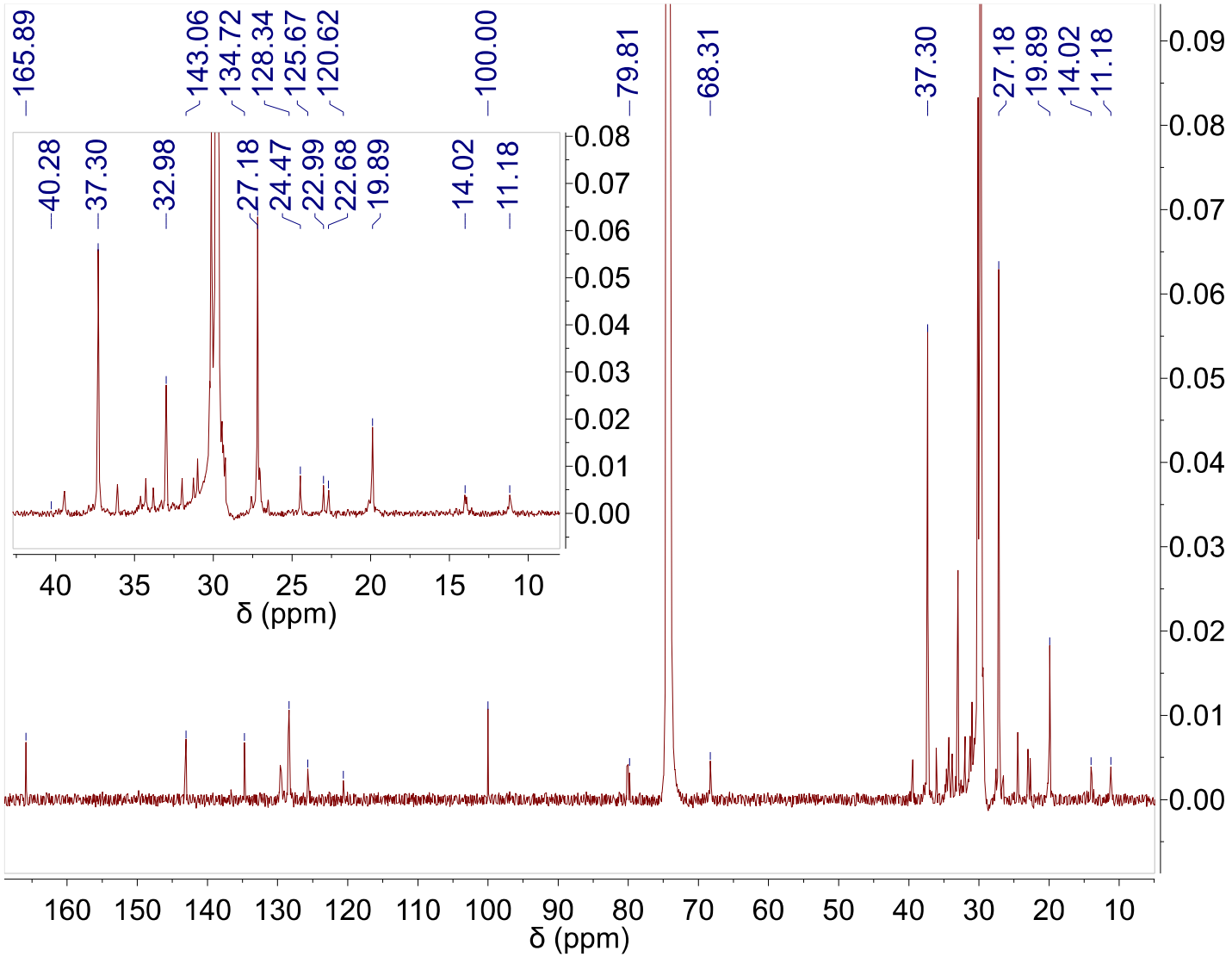


Figure S39. ^{13}C NMR spectrum (TCE-d_2, 150 MHz) of the amorphous polyethylene obtained from the reaction of **NiL3**/$NaBAr^F{}_4$/$Ni(COD)_2$ in the presence of ethylene. Spectral assignments were based on the chemical shift valves reported in the literature.[4,5]

References

(1) Kita, M. R.; Miller, A. J. M. *J. Am. Chem. Soc.* **2014**, *136*, 14519.
(2) Kuzmic, P. *Anal. Biochem.* **1996**, *237*, 260.
(3) Hansen, E. W.; Blom, R.; Bade, O. M. *Polym.* **1997**, *38*, 4295.
(4) Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620.
(5) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *33*, 6945.