Supporting information

Highly Diastereo- and Enantioselective Synthesis of Multisubstituted Allylic Amino Acid Derivatives by Allylic Alkylation of a Chiral Glycine-Based Nickel Complex and Vinylethylene Carbonates

Chao Yu,[a] Yuyan Yu,[b] Longwu Sun,[b] Xinzhi Li,[b] Zhigang Liu,[c, d] Miaolin Ke*,[b] Fener Chen*[a, b, c, d]

[a] *College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China.*
[b] *Institute of Pharmaceutical Science and Technology, Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China.*
[c] *Engineering Center of Catalysis and Synthesis for Chiral Molecules, Department of Chemistry Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China.*
[d] *Shanghai Engineering Center of Industrial Asymmetric Catalysis for Chiral Drugs, Shanghai 200433, People's Republic of China.*

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General information: all reactions were accomplished in Schlenck tube and round flask. Column chromatograph was performed over silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a Bruker AM400 spectrometer, chemical shifts (in ppm) were referred to $CDCl_3$ (δ = 7.26 ppm). ^{13}C NMR spectrum were obtained by using the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.0 ppm). The following abbreviations have been using to illuminate the diversities: δ = chemical shifts, J = coupling constant, s = singlet, d= doublet, t = triplet, q = quartet, m =multiplet. HRMS were recorded on a Bruker micrOTOF spectrometer (ESI). Ee values were determined by Agilent high performance liquid chromatograph (HPLC). All anhydrous solvents were dried by standard treated method. Vinylethylene carbonates[1] and chiral Schiff base Ni(II) complex of glycine **6**[2] were synthesized according to known reference. All materials were obtained commercial suppliers, unless otherwise notice, and most stating material were purchased from Adamas, Bide and Energy Chemical. PE=petroleum ether, DCM=dichloromethane, MeOH=methanol, EA= ethyl acetate.

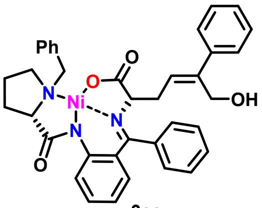
The method for the synthesis of racemic multisubstituted allylic amino acid derivatives (3aa-3al, 5aa-5ak, 6aa).

Under nitrogen atmosphere, *rac*-Gly-Ni-BPB (49.7 mg, 1 mmol), $Pd_2(dba)_3$•$CHCl_3$ (5.17 mg, 5 mmol %) and dppe (3.98mg, 10 mmol %) were placed in the Schleck tube. Then, the solution of vinylethylene carbonates **3** (0.12 mmol) in 1 mL of DCE were added sequentially. The mixture was stirred at 30 °C for 12 h. The crude production was purified by flash column chromatograph on silica gel to provide the pure product.

The method for the synthesis of chiral multisubstituted allylic amino acid derivatives (3aa-3al, 5aa-5ak, 6aa).

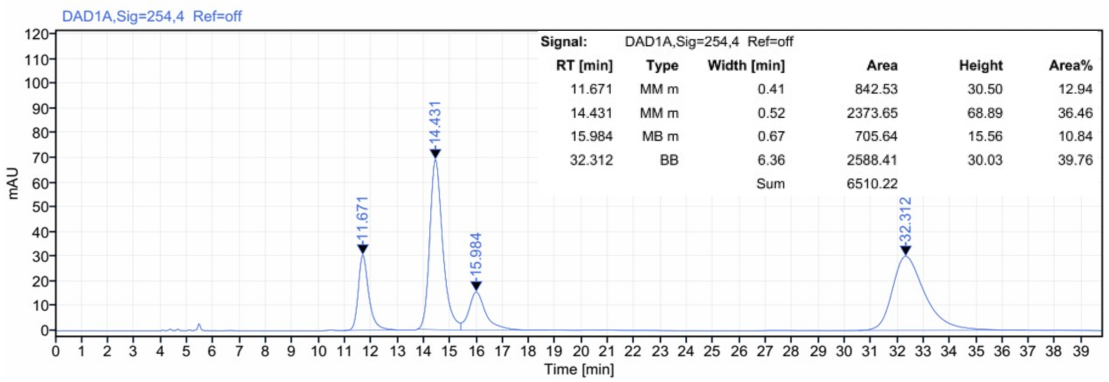
Method A: under nitrogen atmosphere, (*L, S*)-Gly-Ni-BPB **1a** or **1a′** (49.7 mg, 0.1 mmol), $Pd_2(dba)_3$•$CHCl_3$ (5.1 mg, 5 mmol %) and dppe (4.0 mg, 10 mmol %) were placed in the Schleck tube. Then, the solution of vinylethylene carbonates **2** or **4** (0.12 mmol) in 1.0 mL of DCE were added sequentially. The mixture was stirred at 30 °C for 12 h. The crude production was purified by flash column chromatograph on silica gel to provide the pure product.

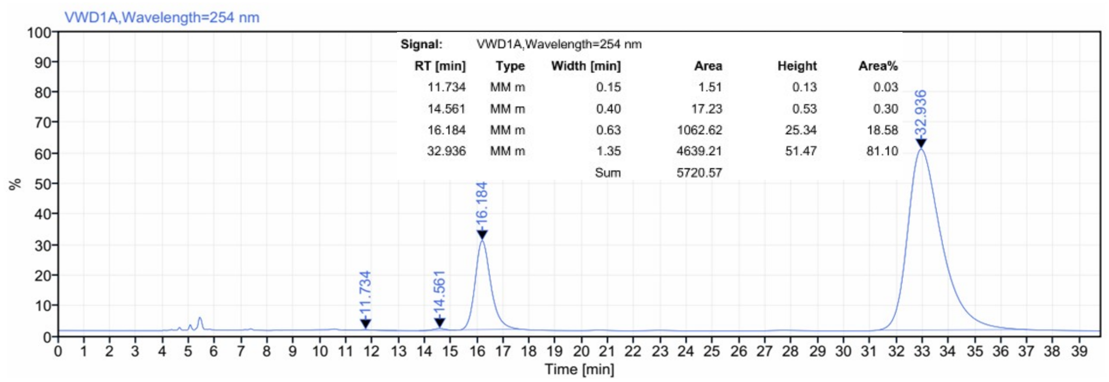
Characterization of multisubstituted allylic amino acid derivatives.

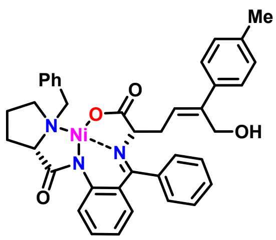


3aa

(*S*, *Z*)-2-Amino-6-hydroxy-5-phenylhex-4-enoic acid-Ni-(*S*)-BPB (**3aa**, 63.6 mg, 99% yield, EA/DCM=3:1, 99% ee, 19:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 99% isolated yield as red solid. [α]25 D= +2167 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 7.4 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.61 – 7.45 (m, 3H), 7.40 – 7.27 (m, 6H), 7.21 – 7.12 (m, 2H), 7.04 (d, J = 7.4 Hz, 1H), 6.86 – 6.78 (m, 1H), 6.71 – 6.63 (m, 2H), 4.49 (d, J = 12.4 Hz, 1H), 4.31 – 4.20 (m, 3H), 3.49 (d, J = 12.7 Hz, 1H), 3.35 – 3.26 (m, 2H), 2.81 – 2.69 (m, 1H), 2.57 – 2.37 (m, 3H), 2.31 – 2.05 (m, 3H), 1.97 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 144.2, 142.5, 141.8, 133.9, 133.4, 133.1, 132.5, 131.4, 129.9, 129.2, 129.1, 128.8, 128.8, 128.4, 127.7, 127.5, 126.9, 126.4, 123.8, 123.5, 120.7, 71.0, 70.5, 63.3, 59.7, 57.4, 33.3, 30.7, 22.8. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{37}H_{35}N_3NiO_4Na$ 666.1879; found: 666.1876. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 14.56 min (minor), 32.93 min (major).

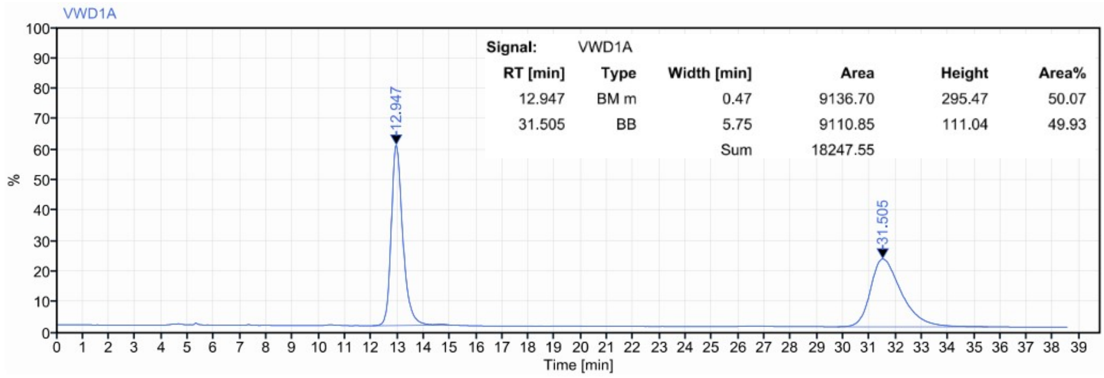


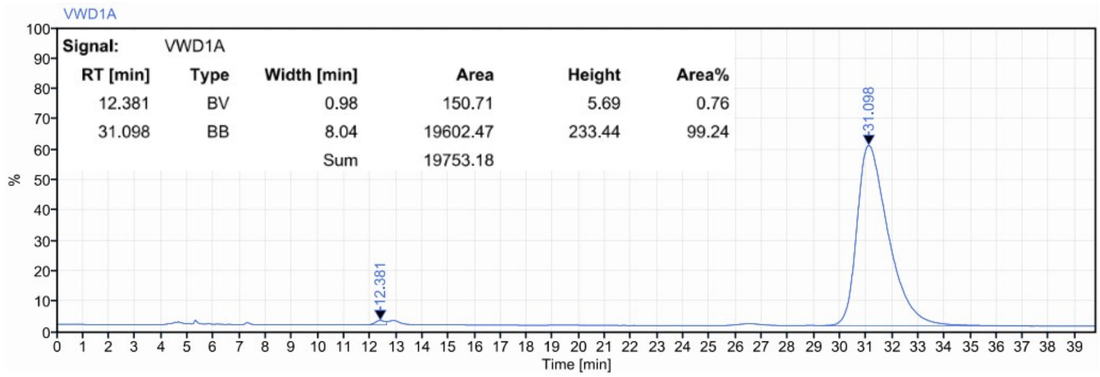


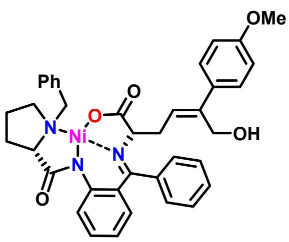


3ab

(*S*, *Z*)-2-Amino-6-hydroxy-5-(*p*-tolyl)hex-4-enoic acid-Ni-(*S*)-BPB (**3ab**, 58 mg, 88% yield, EA/DCM=3:1, 98% *ee*, >20:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 88% isolated yield as red solid. [α]25 D= +1300 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.6 Hz, 1H), 8.01 (d, J = 7.3 Hz, 2H), 7.60 – 7.52 (m, 4H), 7.51 – 7.46 (m, 1H), 7.35 – 7.27 (m, 3H), 7.21 – 7.14 (m, 4H), 7.04 (d, J = 7.4 Hz, 1H), 6.75 (q, J = 10.2, 6.4 Hz, 1H), 6.67 (d, J = 4.1 Hz, 2H), 4.54 – 4.42 (m, 1H), 4.31 – 4.18 (m, 3H), 3.50 (d, J = 12.7 Hz, 1H), 3.39 – 3.24 (m, 2H), 2.80 – 2.68 (m, 2H), 2.60 – 2.40 (m, 2H), 2.34 (s, 3H), 2.31 – 2.06 (m, 2H), 2.00 – 1.87 (m, 1H), 1.40 – 1.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 179.9, 171.5, 144.0, 142.6, 138.8, 137.3, 133.9, 133.4, 133.2, 132.5, 131.4, 129.9, 129.1, 129.1, 128.8, 128.8, 127.7, 127.0, 126.3, 123.5, 122.9, 120.7, 71.0, 70.5, 63.3, 59.7, 57.4, 33.4, 30.8, 22.9, 21.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{38}N_3NiO_4$ 658.2210; found: 658.2225. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 12.38 min (minor), 31.09 min (major).

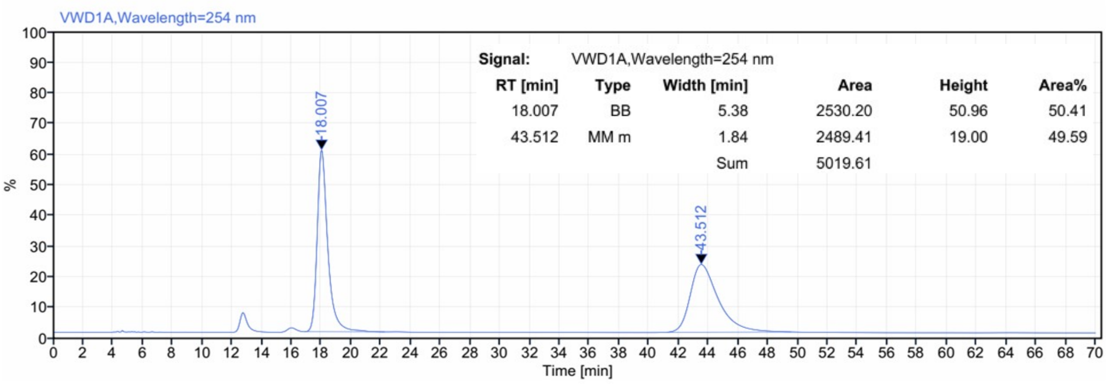


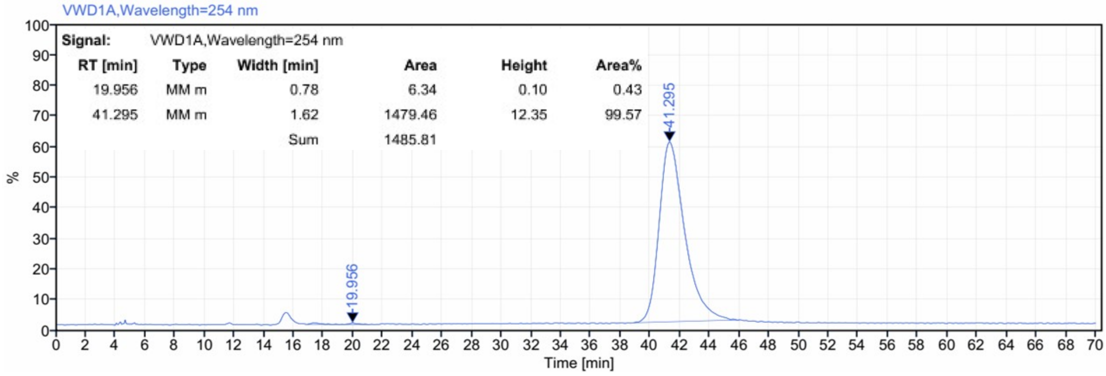


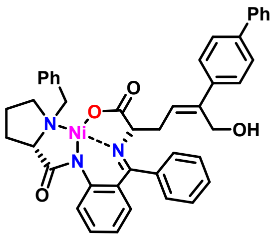


3ac

(*S*, *Z*)-2-Amino-6-hydroxy-5-(4-methoxyphenyl)hex-4-enoic acid-Ni-(*S*)-BPB (**3ac**, 66.7 mg, 99% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 99% isolated yield as red solid. [α]25 D= +1970 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.54 – 7.43 (m, 3H), 7.32 – 7.23 (m, 3H), 7.17 – 7.10 (m, 2H), 7.00 (d, J = 7.4 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.69 – 6.61 (m, 3H), 4.48 – 4.37 (m, 1H), 4.29 – 4.15 (m, 3H), 3.78 (s, 3H), 3.47 (d, J = 12.7 Hz, 1H), 3.34 – 3.23 (m, 2H), 2.81 – 2.64 (m, 2H), 2.64 – 2.47 (m, 1H), 2.48 – 2.34 (m, 1H), 2.32 – 2.06 (m, 2H), 1.96 – 1.85 (m, 1H), 1.42 – 1.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 171.5, 159.2, 143.5, 142.5, 134.3, 133.9, 133.4, 133.2, 132.4, 131.4, 129.9, 129.1, 129.0, 128.8, 128.8, 127.7, 127.6, 127.0, 126.3, 123.5, 122.0, 120.7, 113.7, 71.0, 70.5, 63.3, 59.7, 57.3, 55.3, 33.3, 30.8, 22.9. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{38}H_{38}N_3NiO_5$ 674.2159; found: 674.2166. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 19.95 min (minor), 41.29 min (major).

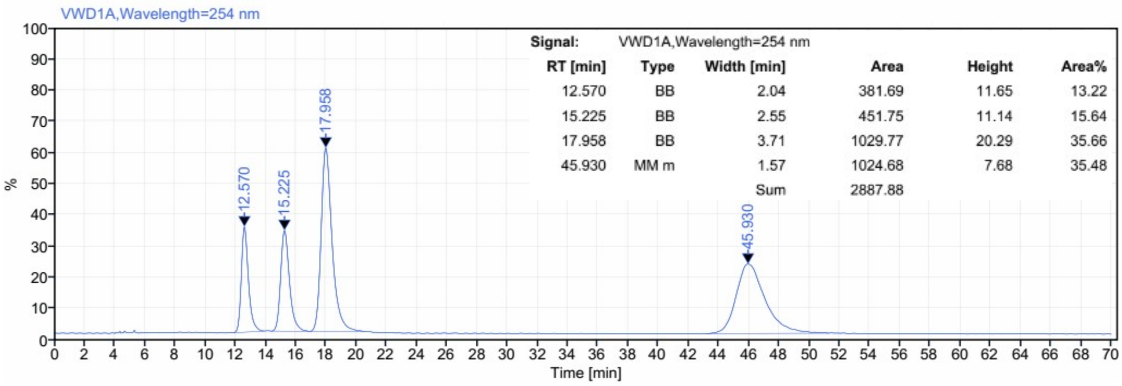


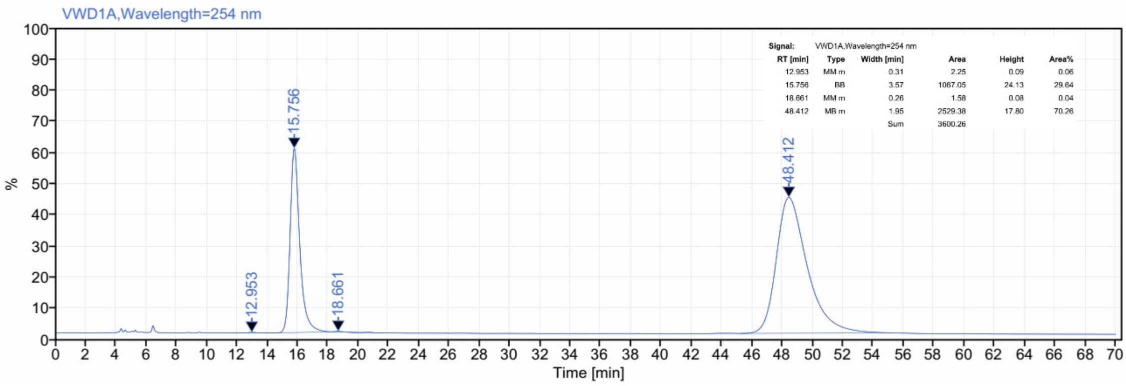


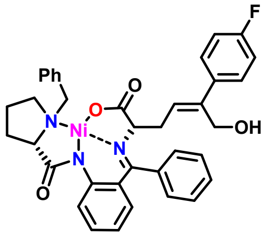


3ad

(*S*, *Z*)-5-([1,1'-Biphenyl]-4-yl)-2-amino-6-hydroxyhex-4-enoic acid-Ni-(*S*)-BPB (**3ad**, 69.8 mg, 97% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 97% isolated yield as red solid. [α]25 D= +1170 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.6 Hz, 1H), 8.05 – 7.97 (m, 2H), 7.83 – 7.75 (m, 2H), 7.65 – 7.49 (m, 7H), 7.48 – 7.41 (m, 2H), 7.39 – 7.28 (m, 4H), 7.22 – 7.13 (m, 2H), 7.09 – 7.03 (m, 1H), 6.89 (dd, J = 10.5, 6.2 Hz, 1H), 6.69 (d, J = 4.2 Hz, 2H), 4.53 (d, J = 12.4 Hz, 1H), 4.36 – 4.19 (m, 3H), 3.51 (d, J = 12.7 Hz, 1H), 3.37 – 3.24 (m, 2H), 2.84 – 2.73 (m, 1H), 2.59 – 2.40 (m, 2H), 2.35 – 2.23 (m, 1H), 2.18 – 2.00 (m, 2H), 1.97 – 1.87 (m, 1H), 1.37 – 1.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 180.0, 171.7, 143.8, 142.6, 140.8, 140.6, 140.4, 134.0, 133.5, 133.2, 132.6, 131.5, 130.0, 129.2, 129.1, 128.9, 128.8, 127.8, 127.3, 127.1, 127.0, 126.9, 126.9, 126.3, 123.9, 123.5, 120.8, 71.1, 70.5, 63.4, 59.7, 57.4, 33.4, 30.8, 22.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{43}H_{40}N_3NiO_4$ 720.2367; found: 720.2371. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 18.66 min (minor), 48.41 min (major).

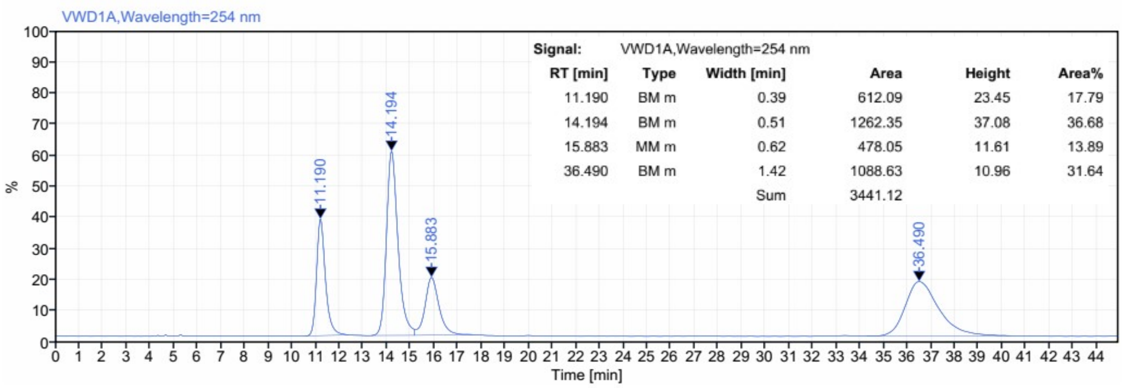


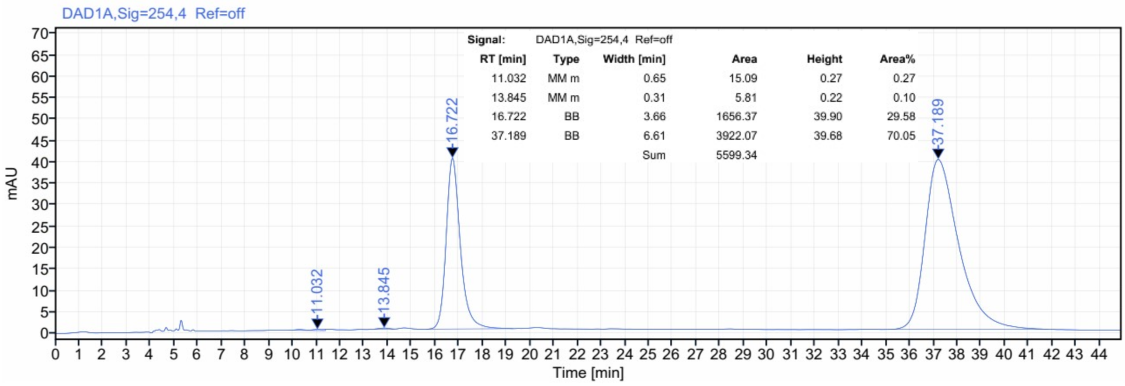


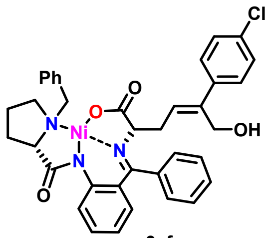


3ae

(S, Z)-2-Amino-5-(4-fluorophenyl)-6-hydroxyhex-4-enoic acid-Ni-(S)-BPB (**3ae**, 64.2 mg, 97% yield, EA/DCM=3:1, 99% *ee*, 16:1 *dr*, Z/E >20:1) was synthesized in method A afforded 97% isolated yield as red solid. [α]25 D= +1084 (c=0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7 Hz, 1H), 8.04 – 7.98 (m, 2H), 7.70 – 7.63 (m, 2H), 7.58 – 7.46 (m, 3H), 7.37 – 7.27 (m, 3H), 7.20 – 7.13 (m, 2H), 7.07 – 7.00 (m, 3H), 6.72 – 6.64 (m, 3H), 4.45 (d, J = 12.4 Hz, 1H), 4.27 – 4.17 (m, 3H), 3.52 (d, J = 12.7 Hz, 1H), 3.35 – 3.26 (m, 2H), 2.91 (s, 1H), 2.77 – 2.67 (m, 1H), 2.66 – 2.53 (m, 1H), 2.49 – 2.39 (m, 1H), 2.34 – 2.12 (m, 2H), 1.96 – 1.88 (m, 1H), 1.47 – 1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 180.0, 171.7, 162.4 (d, J = 246.9 Hz), 143.2, 142.5, 138.0 (d, J = 3.4 Hz), 133.9, 133.4, 133.2, 132.6, 131.4, 129.9, 129.2, 129.1, 128.9, 128.8, 128.2, 128.1, 127.7, 127.0, 126.3, 123.7, 122.1 (d, J = 277.8 Hz), 115.1 (d, J = 21.2 Hz), 71.0, 70.5, 63.4, 59.7, 57.2, 33.4, 30.7, 22.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{35}FN_3NiO_4$ 662.1960; found: 662.1975. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 13.84 min (minor), 37.18 min (major).

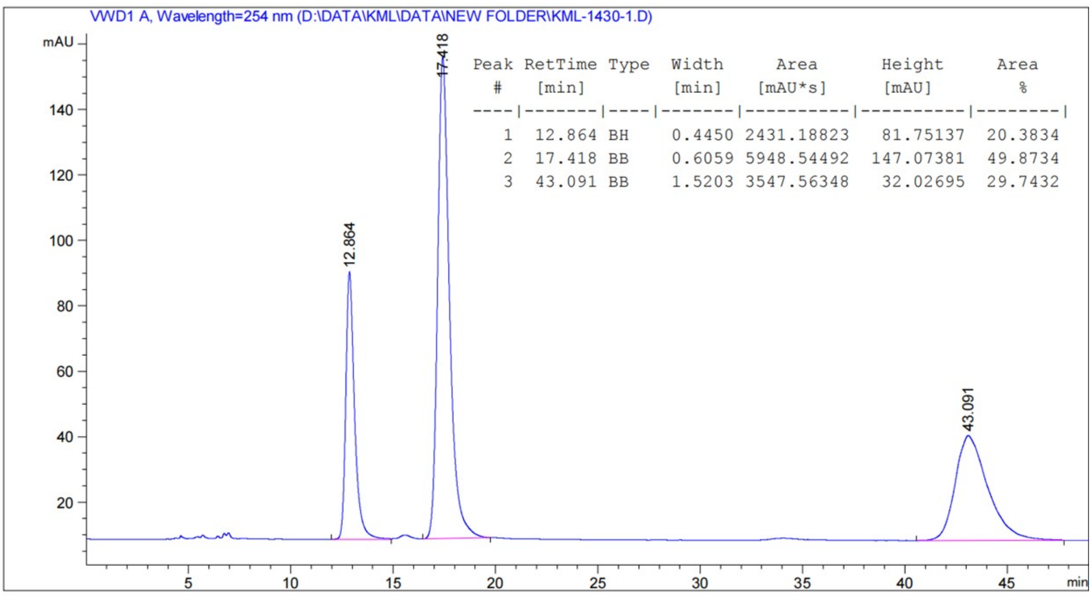


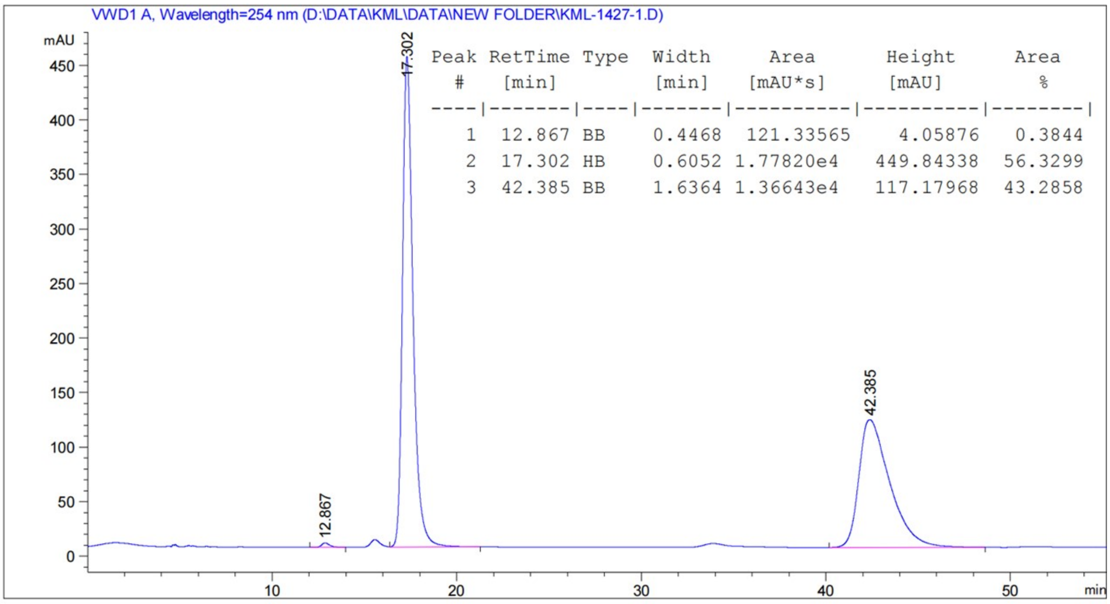


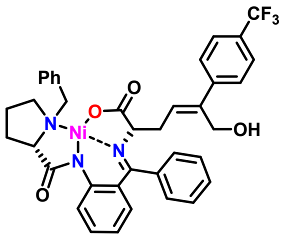


3af

(2*S*, *Z*)-2-Amino-5-(4-chlorocyclohexa-2,4-dien-1-yl)-6-hydroxyhex-4-enoic acid-Ni-(*S*)-BPB (**3af**, 65.8 mg, 97% yield, EA/DCM=3:1, 99% *ee*, 19:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 97% isolated yield as red solid. [α]25 D= +1138 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.7 Hz, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.53 – 7.47 (m, 1H), 7.37 – 7.27 (m, 5H), 7.21 – 7.13 (m, 2H), 7.02 (d, J = 7.4 Hz, 1H), 6.75 – 6.64 (m, 3H), 4.44 (d, J = 12.2 Hz, 1H), 4.30 – 4.13 (m, 3H), 3.52 (d, J = 12.7 Hz, 1H), 3.38 – 3.22 (m, 2H), 3.03 – 2.89 (m, 1H), 2.78 – 2.67 (m, 1H), 2.67 – 2.53 (m, 1H), 2.51 – 2.40 (m, 1H), 2.35 – 2.12 (m, 2H), 1.97 – 1.87 (m, 1H), 1.48 – 1.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 179.9, 171.7, 143.1, 142.5, 140.3, 133.9, 133.4, 133.3, 133.1, 132.5, 131.4, 129.9, 129.2, 129.0, 128.9, 128.8, 128.4, 127.8, 127.7, 126.9, 126.3, 124.3, 123.5, 120.8, 70.9, 70.4, 63.3, 59.5, 57.2, 33.4, 30.7, 22.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{37}H_{35}ClN_3NiO_4$ 678.1664; found: 678.1687. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 17.30 min (minor), 43.09 min (major).

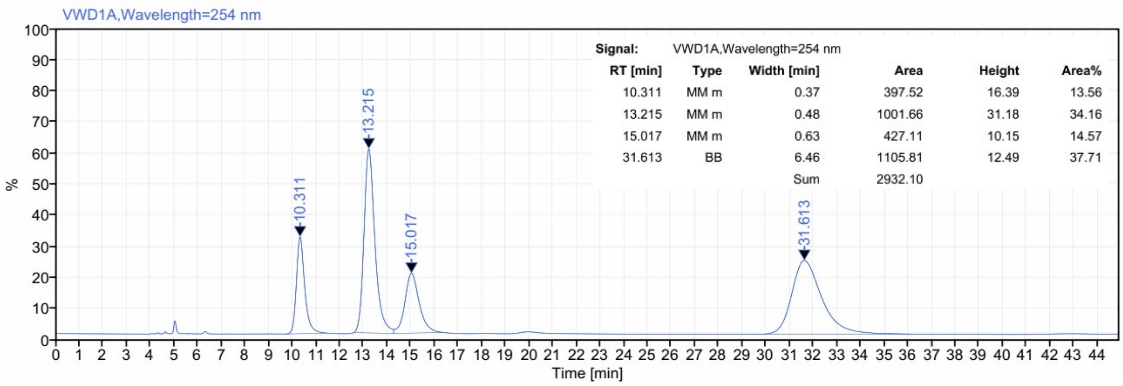


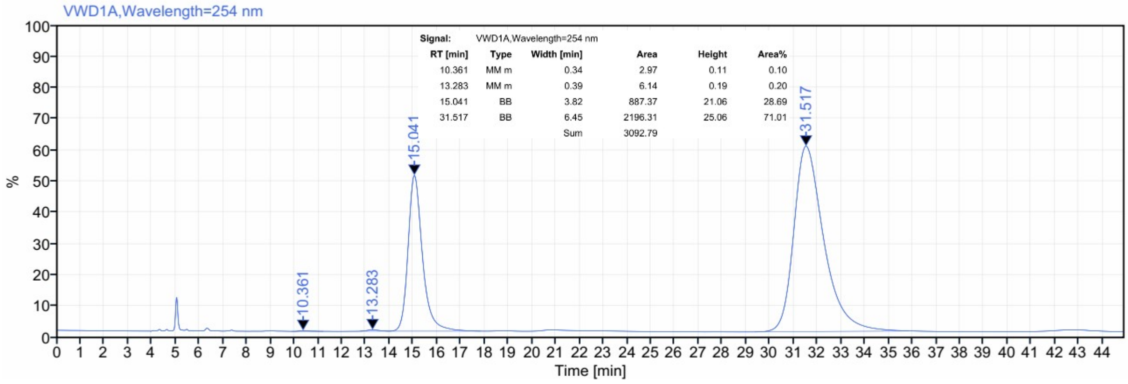


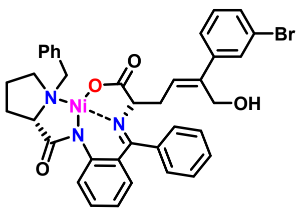


3ag

(*S*, *Z*)-2-Amino-6-hydroxy-5-(4-(trifluoromethyl)phenyl)hex-4-enoic acid-Ni-(*S*)-BPB (**3ag**, 68.2 mg, 96% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 96% isolated yield as red solid. [α]25 D= +900 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.7 Hz, 1H), 8.00 (d, J = 7.5 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.65 – 7.53 (m, 4H), 7.38 – 7.29 (m, 3H), 7.24 – 7.15 (m, 2H), 7.04 (d, J = 7.4 Hz, 1H), 6.82 – 6.75 (m, 1H), 6.72 – 6.63 (m, 2H), 4.48 (d, J = 12.5 Hz, 1H), 4.34 – 4.20 (m, 3H), 3.54 (d, J = 12.7 Hz, 1H), 3.36 – 3.20 (m, 2H), 2.83 – 2.67 (m, 1H), 2.59 – 2.41 (m, 2H), 2.34 – 2.08 (m, 3H), 1.98 – 1.87 (m, 1H), 1.40 – 1.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 179.9, 171.8, 145.5, 143.2, 142.6, 133.9, 133.5, 133.1, 132.7, 131.4, 130.0, 129.3, 129.1, 128.9, 128.9, 127.7, 127.0, 126.8, 126.0, 125.3 (q, J = 3.7 Hz), 124.2 (d, J = 271.8 Hz), 123.6, 120.8, 70.8, 70.4, 63.4, 59.5, 57.1, 33.5, 30.6, 22.9. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{38}H_{35}F_3N_3NiO_4$ 712.1928; found: 712.1930. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, 45min; t_R = 13.28 min (minor), 31.51 min (major).

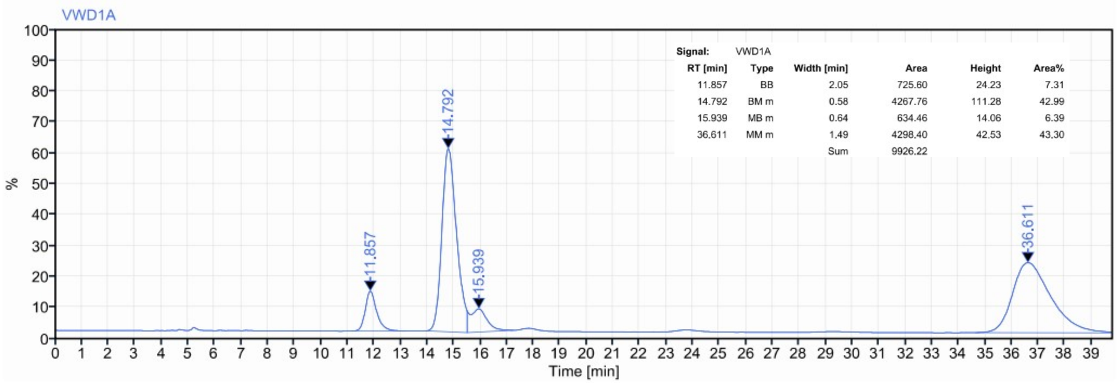


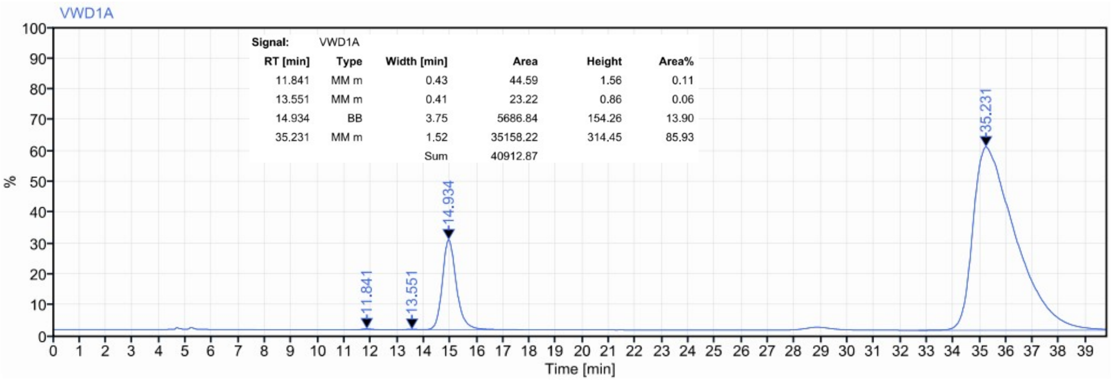


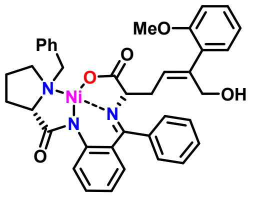


3ah

(S, Z)-2-Amino-5-(3-bromophenyl)-6-hydroxyhex-4-enoic acid-Ni-(S)-BPB (**3ah**, 69.2 mg, 96% yield, EA/DCM=3:1, 99% *ee*, 7:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 96% isolated yield as red solid. [α]25 D= +1095 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7 Hz, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.89 – 7.82 (m, 1H), 7.64 – 7.55 (m, 2H), 7.55 – 7.46 (m, 2H), 7.46 – 7.39 (m, 1H), 7.39 – 7.27 (m, 3H), 7.25 – 7.12 (m, 3H), 7.09 – 6.97 (m, 1H), 6.85 – 6.64 (m, 3H), 4.51 – 4.05 (m, 4H), 3.52 (d, J = 12.7 Hz, 1H), 3.38 – 3.19 (m, 2H), 3.05 – 2.93 (m, 1H), 2.77 – 1.87 (m, 6H), 1.51 – 1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 179.9, 171.7, 144.1, 143.0, 142.6, 133.9, 133.4, 133.2, 132.6, 131.4, 130.4, 123.0, 129.9, 129.4, 129.2, 129.1, 128.9, 128.8, 127.7, 126.9, 126.3, 125.2, 125.1, 123.5, 122.6, 120.7, 70.8, 70.5, 63.3, 59.5, 57.3, 33.4, 30.7, 22.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{37}H_{35}BrN_3NiO_4$ 722.1159; found: 722.1153. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 13.55 min (minor), 35.23 min (major).

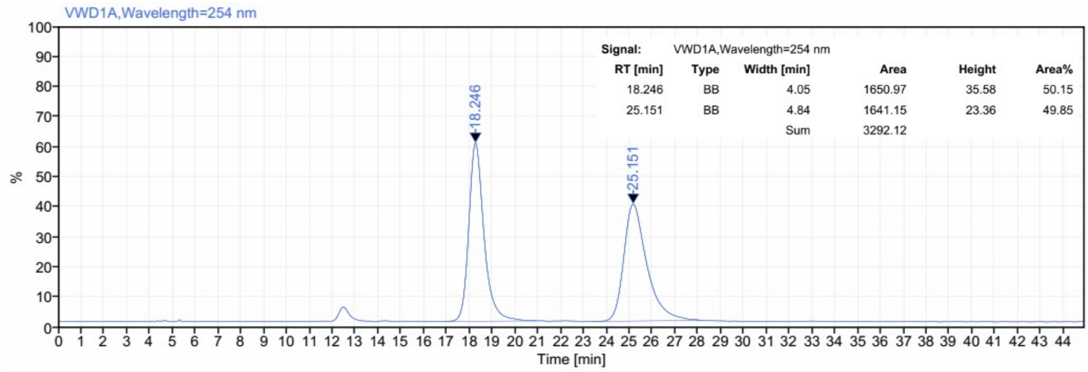


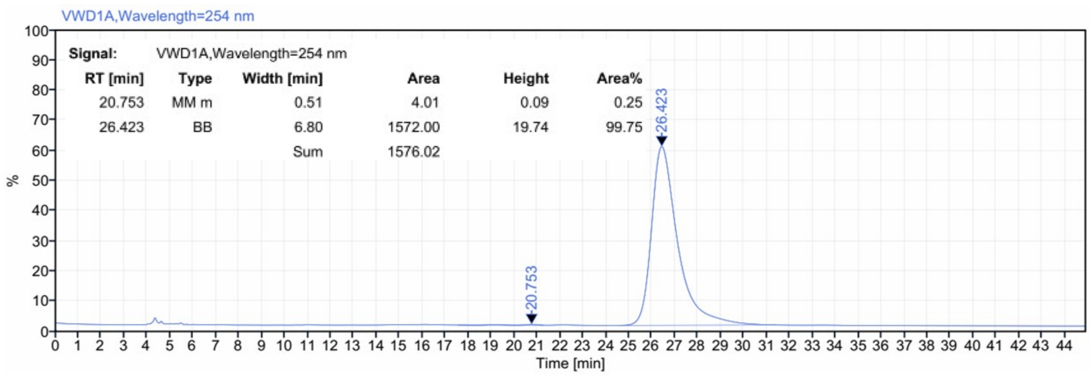


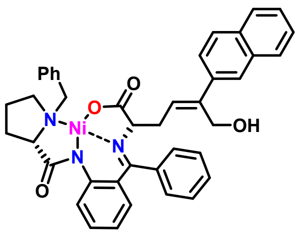


3ai

(*S*, *Z*)-2-Amino-6-hydroxy-5-(2-methoxyphenyl)hex-4-enoic acid-Ni-(*S*)-BPB (**3ai**, 66.7 mg, 99% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 99% isolated yield as red solid. [α]25 D= +1945 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.7 Hz, 1H), 8.02 (d, J = 7.2 Hz, 2H), 7.56 – 7.39 (m, 4H), 7.35 – 7.07 (m, 7H), 7.00 – 6.92 (m, 1H), 6.91 – 6.76 (m, 1H), 6.74 – 6.60 (m, 2H), 6.36 (q, J = 9.4, 6.4 Hz, 1H), 4.50 – 4.30 (m, 1H), 4.29 – 4.03 (m, 2H), 3.82 – 3.63 (m, 4H), 3.54 – 3.28 (m, 3H), 2.95 – 2.59 (m, 2H), 2.59 – 1.88 (m, 5H), 1.67 – 1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 179.2, 171.3, 156.1, 143.0, 142.3, 134.1, 133.4, 133.3, 132.1, 131.9, 131.5, 130.5, 129.6, 129.0, 128.8, 128.7, 128.2, 128.1, 127.1, 126.3, 123.2, 121.2, 120.5, 110.4, 70.1, 67.9, 63.1, 60.4, 57.0, 55.5, 33.5, 30.4, 22.9. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{38}H_{38}N_3NiO_5$ 674.2159; found: 674.2163. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 20.75 min (minor), 26.42 min (major).

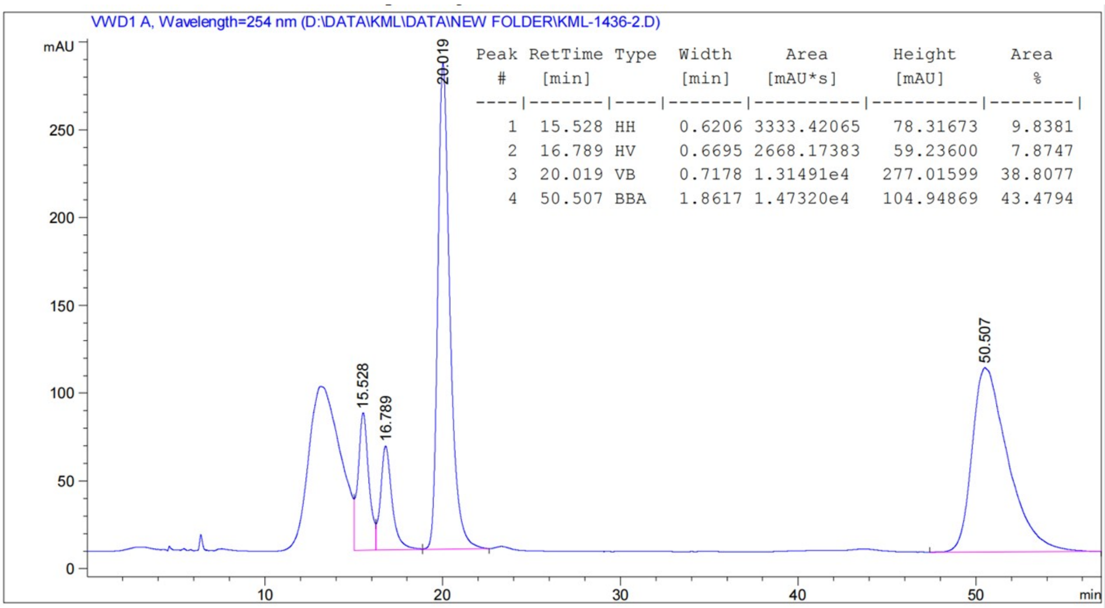


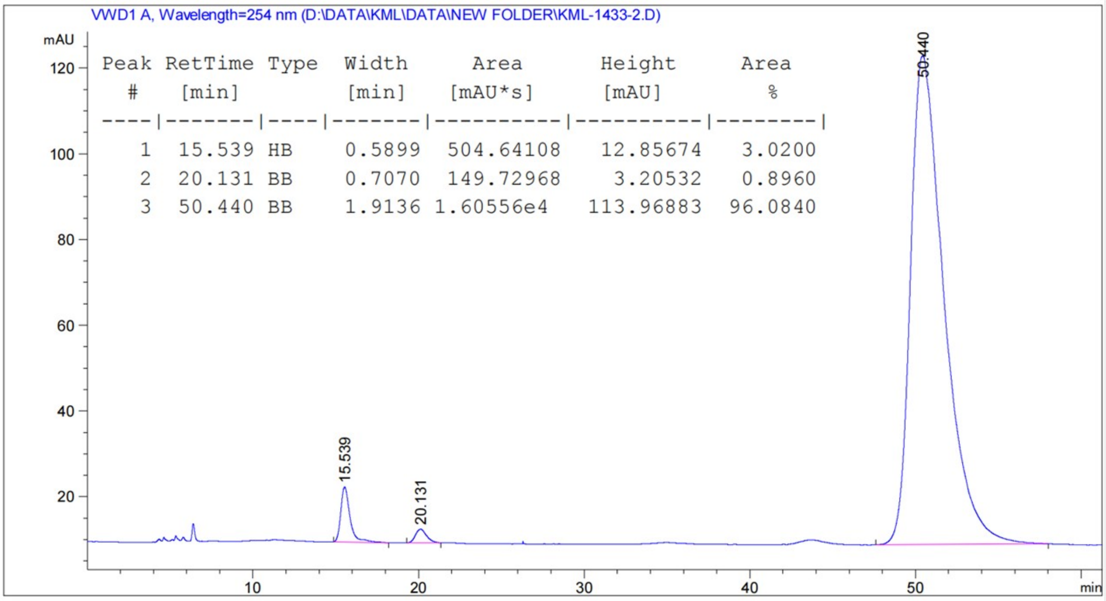




3aj

(*S*, *Z*)-2-Amino-6-hydroxy-5-(naphthalen-2-yl)hex-4-enoic acid-Ni-(*S*)-BPB (**3aj**, 68.7 mg, 99% yield, EA/DCM=3:1, 98% *ee*, >20:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 99% isolated yield as red solid. [α]25 D= +1191 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.15 (m, 2H), 8.03 – 7.94 (m, 2H), 7.89 – 7.78 (m, 4H), 7.60 – 7.42 (m, 5H), 7.35 – 7.28 (m, 3H), 7.20 – 7.14 (m, 2H), 7.11 – 7.05 (m, 1H), 6.96 (dd, *J* = 10.5, 6.3 Hz, 1H), 6.69 (d, *J* = 4.2 Hz, 2H), 4.59 (d, *J* = 12.4 Hz, 1H), 4.38 (d, *J* = 12.4 Hz, 1H), 4.33 – 4.27 (m, 1H), 4.20 (d, *J* = 12.7 Hz, 1H), 3.47 (d, *J* = 12.7 Hz, 1H), 3.32 – 3.17 (m, 2H), 2.88 – 2.76 (m, 1H), 2.55 – 2.42 (m, 1H), 2.42 – 2.10 (m, 3H), 1.99 – 1.78 (m, 2H), 1.13 – 0.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 180.0, 171.7, 144.2, 142.6, 139.0, 134.0, 133.5, 133.4, 133.1, 132.7, 132.5, 131.4, 130.0, 129.2, 129.1, 128.9, 128.8, 128.3, 128.0, 127.8, 127.4, 127.0, 126.4, 126.2, 125.9, 125.2, 124.7, 124.4, 123.5, 120.7, 71.1, 70.4, 63.3, 59.8, 57.2, 33.5, 30.6, 22.7. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{41}H_{37}N_3NiO_4Na$ 716.2035; found: 716.2029. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 20.13 min (minor), 50.44 min (major).





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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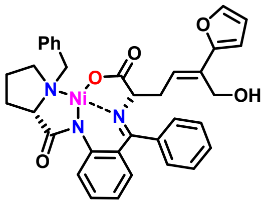
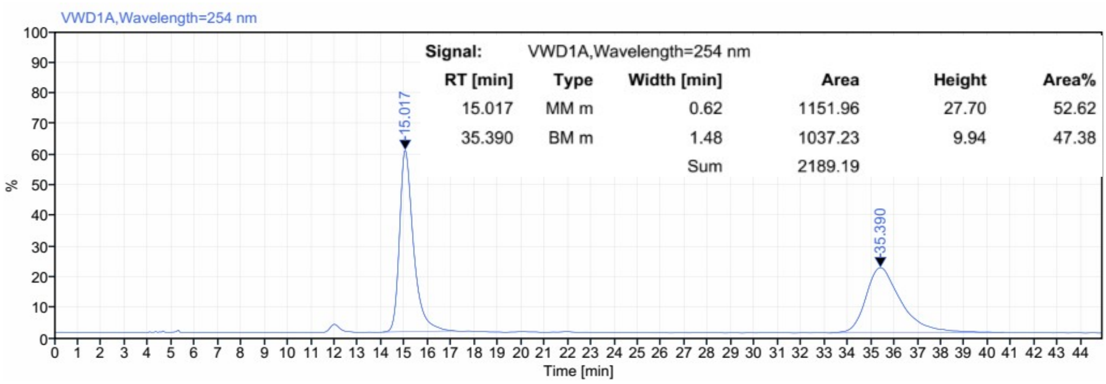
2	20.131	BB	0.7070	149.72968	3.20532	0.8960
3	50.440	BB	1.9136	1.60556e4	113.96883	96.0840



3ak

(S, E)-2-Amino-5-(furan-2-yl)-6-hydroxyhex-4-enoic acid-Ni-(S)-BPB (**3ak**, 62.8 mg, 99% yield, EA/DCM=3:1, 91% *ee*, >20:1 *dr*, *E/Z* >20:1) was synthesized in method A afforded 99% isolated yield as red solid. [α]25 D= +2215 (c=0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.6 Hz, 1H), 8.01 (d, J = 7.6 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.49 – 7.43 (m, 1H), 7.40 (s, 1H), 7.35 – 7.27 (m, 3H), 7.20 – 7.12 (m, 2H), 7.03 (d, J = 7.5 Hz, 1H), 6.94 – 6.86 (m, 1H), 6.68 – 6.62 (m, 2H), 6.55 – 6.50 (m, 1H), 6.46 – 6.40 (m, 1H), 4.45 – 4.35 (m, 1H), 4.31 – 4.17 (m, 3H), 3.54 (d, J = 12.7 Hz, 1H), 3.42 – 3.30 (m, 2H), 2.95 – 2.69 (m, 3H), 2.68 – 2.56 (m, 1H), 2.42 – 2.26 (m, 2H), 2.04 – 1.92 (m, 1H), 1.67 – 1.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 180.0, 171.7, 154.2, 142.6, 141.8, 134.2, 134.0, 133.4, 133.2, 132.4, 131.4, 129.9, 129.1, 129.0, 128.8, 128.8, 127.7, 126.8, 126.3, 123.5, 120.7, 119.9, 111.7, 107.2, 71.0, 70.5, 63.3, 57.6, 57.2, 32.0, 30.8, 22.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{35}H_{34}N_3NiO_5$ 634.1846; found: 634.1855. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 15.256 min (minor), 34.96 min (major).



RT [min]	Type	Width [min]	Area	Height	Area%
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35.390	BM m	1.48	1037.23	9.94	47.38
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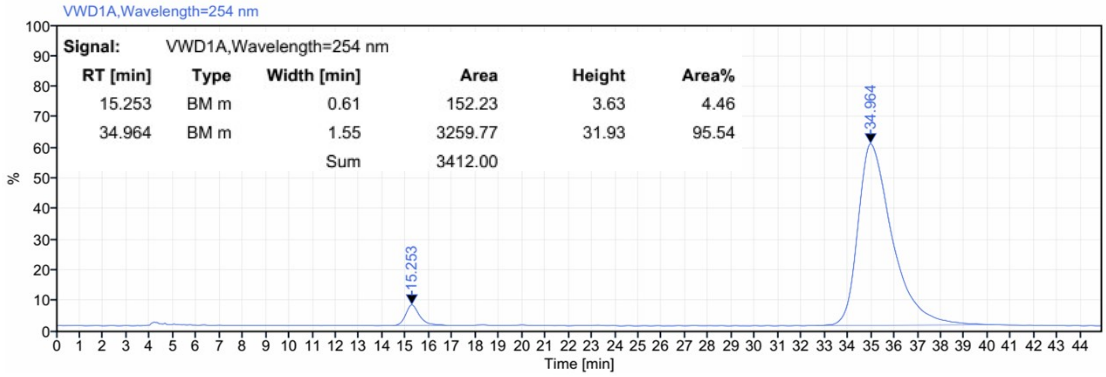
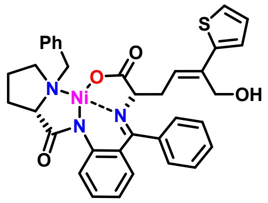
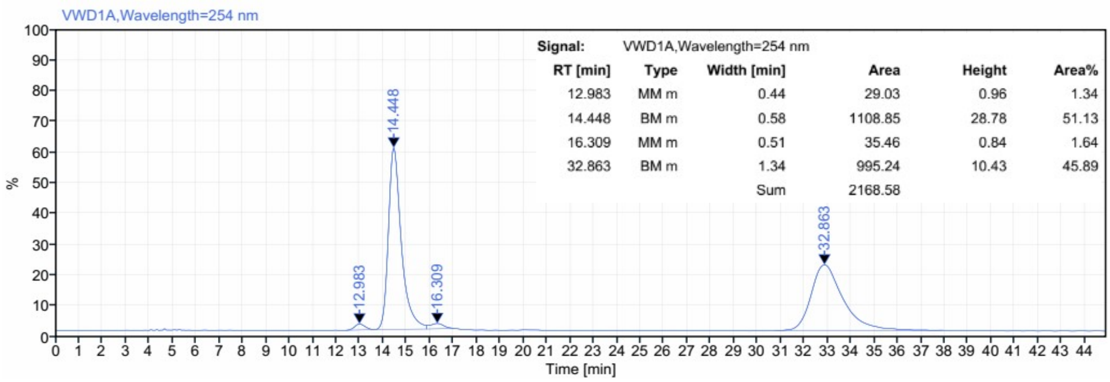
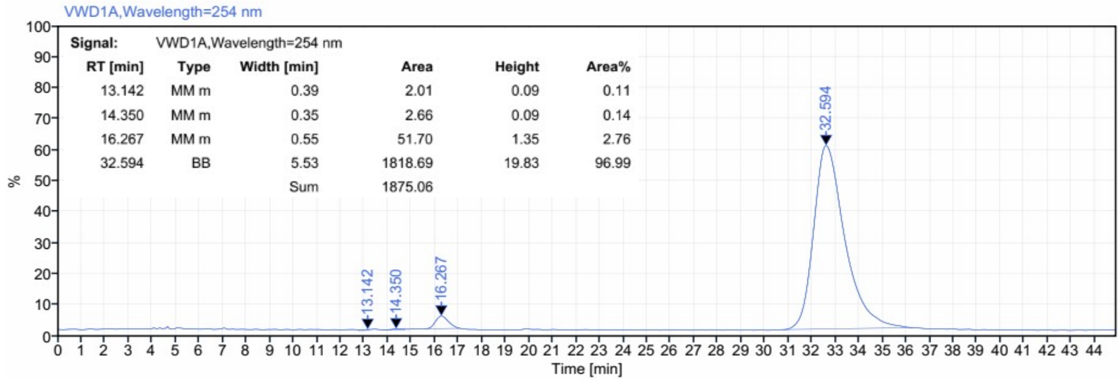


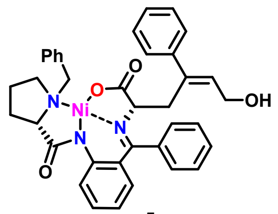


3al

(S, E)-2-amino-6-hydroxy-5-(thiophen-2-yl)hex-4-enoic acid-Ni-(S)-BPB (**3al**, 64.2 mg, 99% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *E/Z* >20:1) was synthesized in method A afforded 99% isolated yield as red solid. [α]25 D= +3297 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.6 Hz, 1H), 8.03 (d, J = 7.4 Hz, 2H), 7.59 – 7.45 (m, 3H), 7.36 – 7.27 (m, 4H), 7.21 – 7.13 (m, 3H), 7.07 – 6.98 (m, 2H), 6.67 (d, J = 4.3 Hz, 2H), 6.62 (dd, J = 10.2, 6.8 Hz, 1H), 4.51 – 4.41 (m, 1H), 4.36 – 4.25 (m, 2H), 4.24 – 4.16 (m, 1H), 3.50 (d, J = 12.7 Hz, 1H), 3.46 – 3.39 (m, 1H), 3.39 – 3.29 (m, 1H), 2.92 – 2.81 (m, 1H), 2.81 – 2.66 (m, 2H), 2.50 – 2.38 (m, 2H), 2.33 – 2.20 (m, 1H), 2.06 – 1.95 (m, 1H), 1.61 – 1.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 179.9, 171.6, 145.1, 142.5, 138.4, 133.9, 133.4, 133.2, 132.5, 131.4, 129.9, 129.1, 129.1, 128.8, 128.8, 127.6, 127.6, 126.9, 126.2, 124.6, 124.2, 123.5, 122.1, 120.7, 70.9, 70.4, 63.3, 59.7, 57.6, 33.0, 30.4, 23.0. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{35}H_{34}N_3NiO_4S$ 650.1618; found: 650.1614. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 14.35 min (minor), 32.59 min (major).

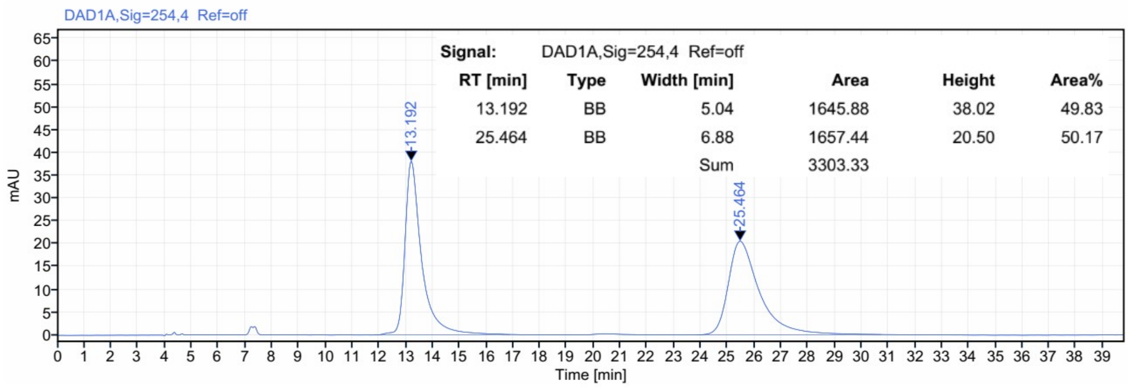


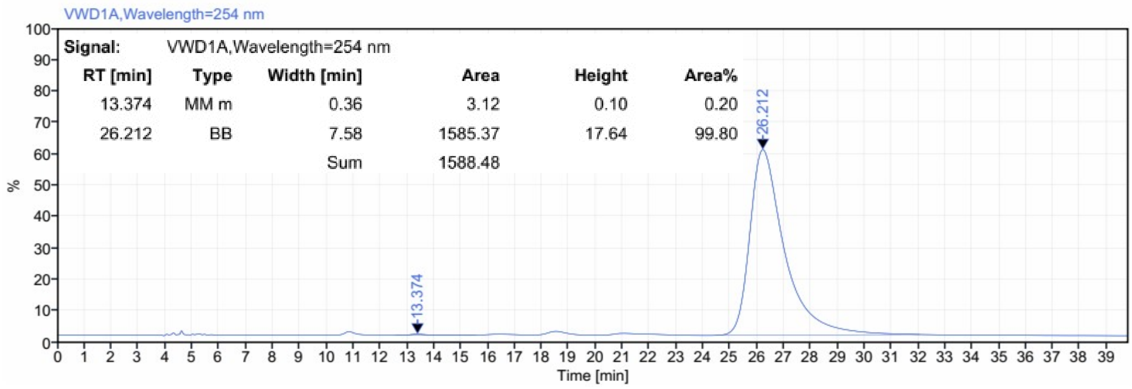


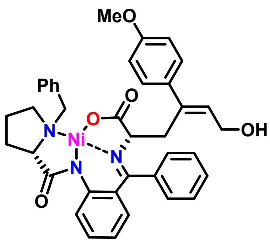


5aa

(S, E)-2-Amino-6-hydroxy-4-phenylhex-4-enoic acid-Ni-(S)-BPB (**5aa**, 63.7 mg, 99% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, E/Z >20:1) was synthesized in method A afforded 99% isolated yield as red solid. $[\alpha]25$ D= +2332 (c=0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.96 (m, 3H), 7.50 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 7.20 – 6.97 (m, 6H), 6.97 – 6.87 (m, 1H), 6.86 – 6.73 (m, 2H), 6.67 – 6.55 (m, 1H), 6.55 – 6.42 (m, 1H), 6.05 – 5.89 (m, 1H), 4.43 – 4.22 (m, 2H), 4.15 – 3.97 (m, 1H), 3.98 – 3.83 (m, 2H), 3.82 – 3.65 (m, 1H), 3.56 – 3.42 (m, 3H), 2.87 – 2.61 (m, 3H), 2.59 – 2.42 (m, 1H), 2.32 – 2.19 (m, 1H), 2.14 – 2.03 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 178.3, 170.3, 142.0, 140.9, 136.6, 133.4, 133.1, 133.0, 132.1, 131.4, 131.1, 129.8, 129.0, 128.9, 128.8, 128.0, 127.6, 127.3, 126.9, 126.4, 126.2, 123.7, 120.7, 70.1, 69.0, 63.2, 58.6, 57.5, 36.8, 30.6, 24.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{35}N_3NiO_4Na$ 666.1879; found: 666.1889. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 13.37 min (minor), 26.21 min (major).

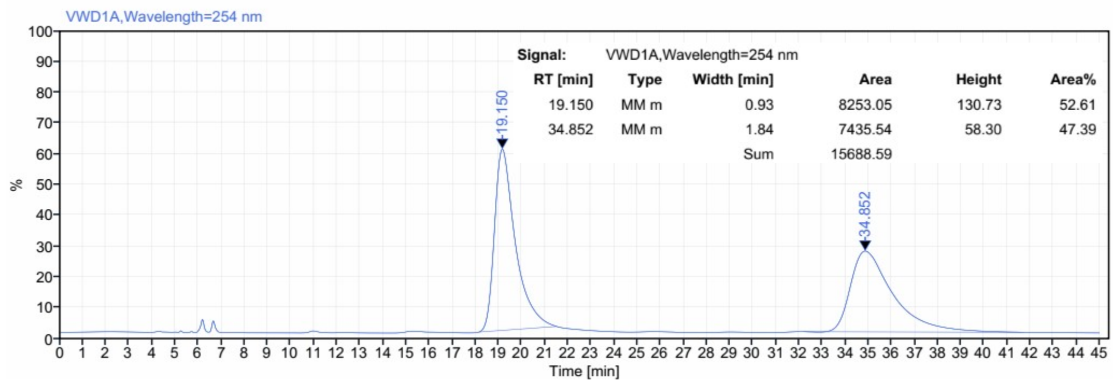


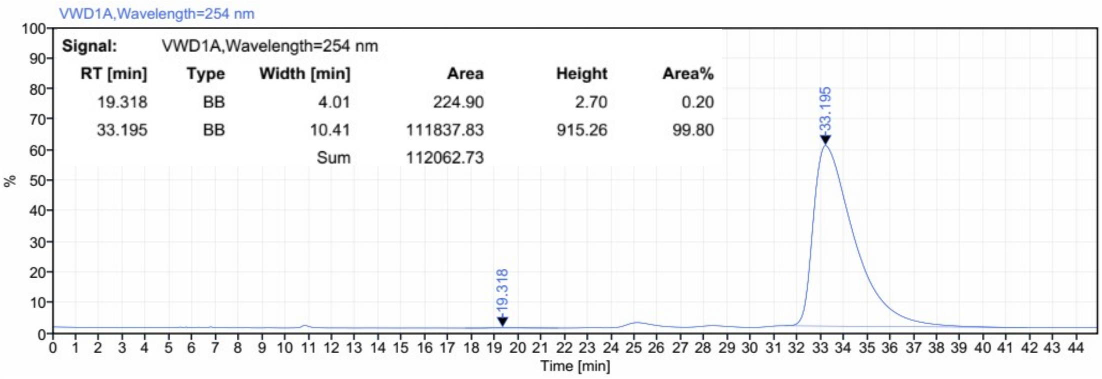


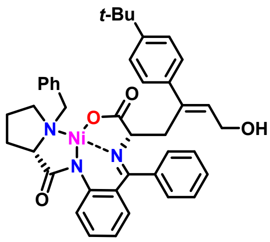


5ab

(*S*, *E*)-2-Amino-6-hydroxy-4-(4-methoxyphenyl)hex-4-enoic acid-Ni-(*S*)-BPB (**5ab**, 41 mg, 61% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *E/Z* >20:1) was synthesized in method A afforded 61% isolated yield as red solid. [*α*]25 D= +2571(c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.99 (m, 3H), 7.56 – 7.40 (m, 3H), 7.39 – 7.29 (m, 3H), 7.21 – 7.07 (m, 3H), 7.00 – 6.94 (m, 1H), 6.77 – 6.69 (m, 2H), 6.66 – 6.49 (m, 4H), 6.01 – 5.88 (m, 1H), 4.46 – 4.26 (m, 2H), 4.12 – 4.00 (m, 1H), 3.97 – 3.84 (m, 2H), 3.75 (s, 3H), 3.57 – 3.44 (m, 3H), 2.78 – 2.64 (m, 2H), 2.59 – 2.43 (m, 2H), 2.33 – 2.23 (m, 1H), 2.15 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 178.4, 170.2, 158.6, 142.0, 136.3, 133.3, 133.3, 133.1, 133.1, 132.1, 131.4, 129.7, 129.7, 129.1, 129.0, 128.9, 128.8, 127.7, 127.5, 127.3, 126.5, 123.7, 120.7, 113.4, 70.0, 63.1, 58.6, 57.5, 55.2, 36.8, 30.7, 24.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{38}H_{37}N_3NiO_5Na$ 696.1984; found: 696.1987. HPLC conditions: IA column, 254nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 19.31 min (minor), 33.19 min (major).

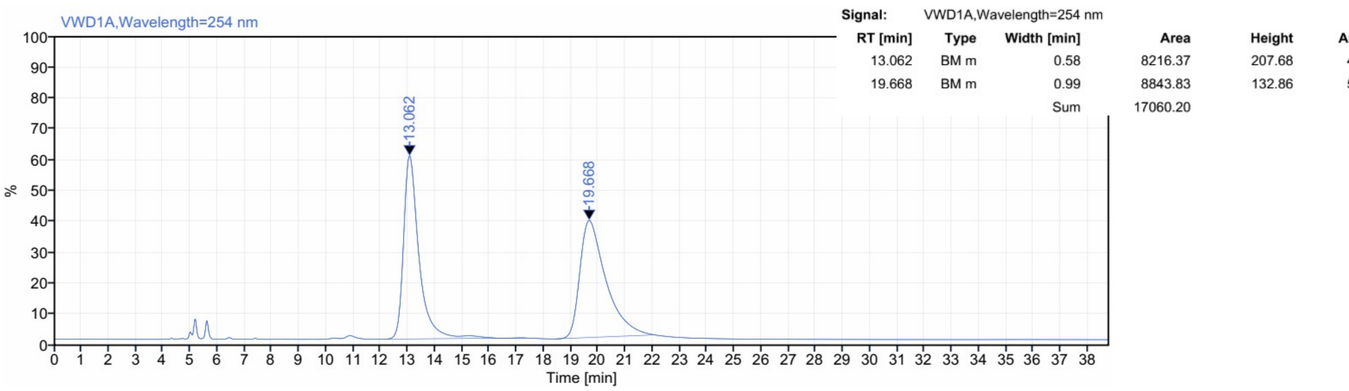


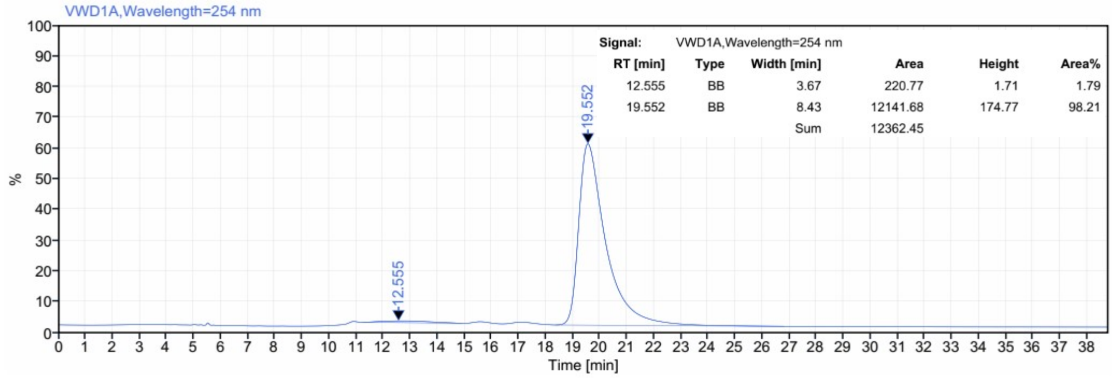




5ac

(S, E)-2-Amino-4-(4-(tert-butyl)phenyl)-6-hydroxyhex-4-enoic acid-Ni-(S)-BPB (**5ac**, 57.3 mg, 82% yield, EA/DCM=3:1, 96% *ee*, >20:1 *dr*, *E/Z* >20:1) was synthesized in method A afforded 82% isolated yield as red solid. [α]25 D= +2148 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 7.95 (m, 3H), 7.53 – 7.39 (m, 3H), 7.36 – 7.27 (m, 3H), 7.20 – 6.95 (m, 6H), 6.75 (d, J = 7.9 Hz, 2H), 6.66 – 6.59 (m, 1H), 6.54 – 6.47 (m, 1H), 6.08 – 5.93 (m, 1H), 4.45 – 4.29 (m, 2H), 4.13 – 4.03 (m, 1H), 3.98 – 3.83 (m, 2H), 3.59 – 3.44 (m, 3H), 2.82 – 2.65 (m, 2H), 2.60 – 2.41 (m, 2H), 2.33 – 2.21 (m, 1H), 2.15 – 2.05 (m, 1H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 178.4, 170.2, 149.6, 141.9, 137.8, 136.5, 133.3, 133.1, 133.0, 132.1, 131.4, 130.3, 129.7, 129.0, 128.8, 128.8, 127.7, 127.5, 126.5, 125.7, 125.0, 123.7, 120.7, 70.0, 69.1, 63.1, 58.6, 57.4, 36.8, 34.2, 31.2, 30.6, 24.2. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{41}H_{43}N_3NiO_4Na$ 722.2505; found: 722.2500. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 12.55 min (minor), 19.55 min (major).





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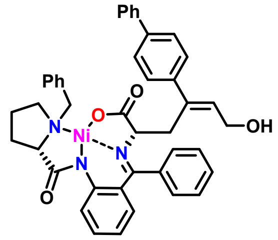
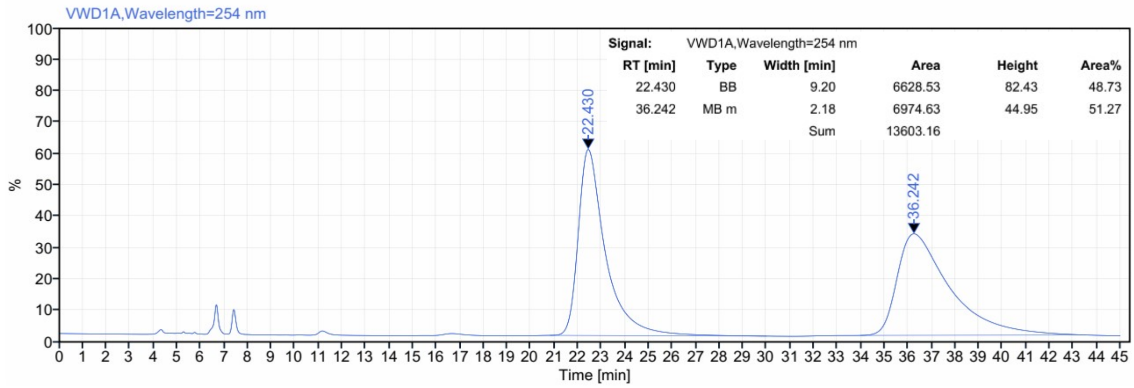


5ad

(*S*, *E*)-4-([1,1'-Biphenyl]-4-yl)-2-amino-6-hydroxyhex-4-enoic acid-Ni-(*S*)-BPB (**5ad**, 58.9 mg, 82% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *E/Z* >20:1) was synthesized in method A afforded 82% isolated yield as red solid. [*α*]25 D= +2041 (c=0.04, $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.00 (m, 3H), 7.57 – 7.52 (m, 2H), 7.49 – 7.42 (m, 4H), 7.39 – 7.31 (m, 4H), 7.30 – 7.26 (m, 2H), 7.22 – 7.09 (m, 3H), 7.03 – 6.95 (m, 1H), 6.89 (d, J = 7.9 Hz, 2H), 6.64 (t, J = 7.6 Hz, 1H), 6.58 – 6.50 (m, 1H), 6.11 – 6.02 (m, 1H), 4.46 – 4.32 (m, 2H), 4.16 – 4.07 (m, 1H), 4.04 – 3.89 (m, 2H), 3.87 – 3.74 (m, 1H), 3.60 – 3.47 (m, 3H), 2.84 – 2.69 (m, 2H), 2.62 – 2.48 (m, 2H), 2.37 – 2.23 (m, 1H), 2.17 – 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 178.4, 170.3, 142.0, 140.6, 139.8, 139.7, 136.3, 133.3, 133.2, 133.0, 132.2, 131.4, 131.0, 129.7, 129.1, 129.0, 128.8, 128.7, 127.6, 127.5, 127.2, 126.8, 126.6, 126.5, 123.8, 120.8, 70.1, 69.0, 63.1, 58.6, 57.5, 36.9, 30.7, 24.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{43}H_{39}N_3NiO_4Na$ 742.2192; found: 742.2193. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 22.18 min (minor), 34.57 min (major).



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36.242	MB m	2.18	6974.63	44.95	51.27
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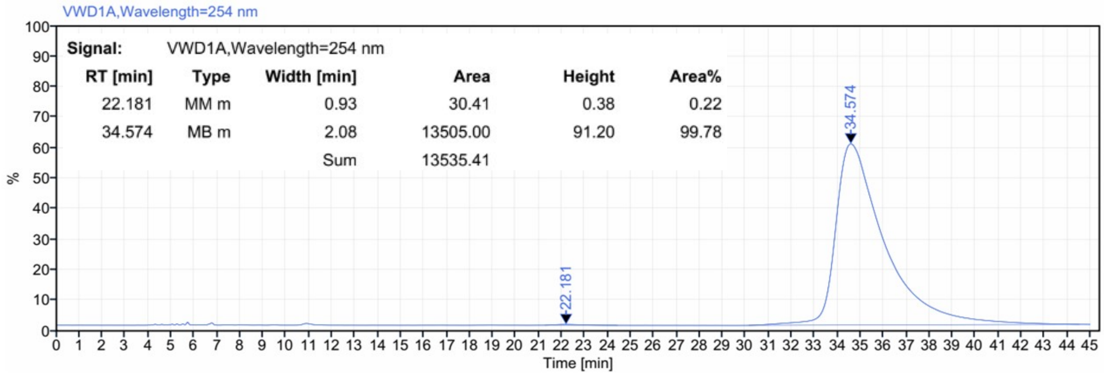
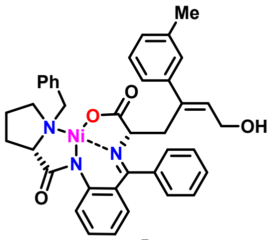
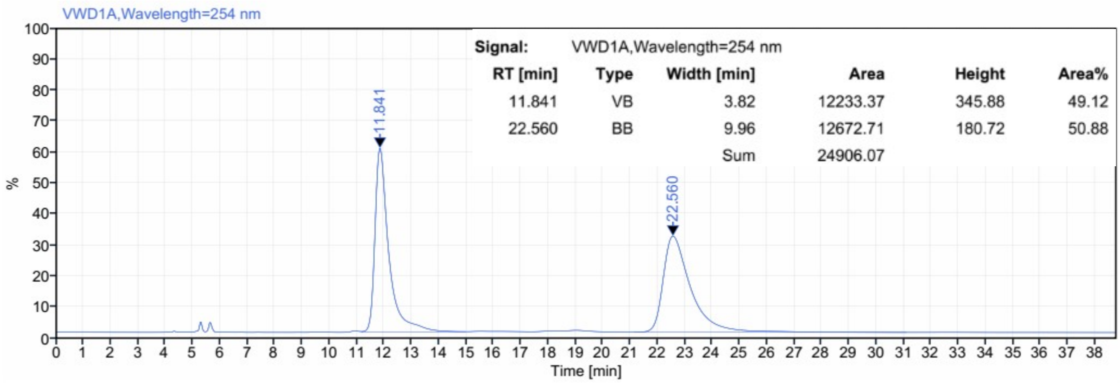
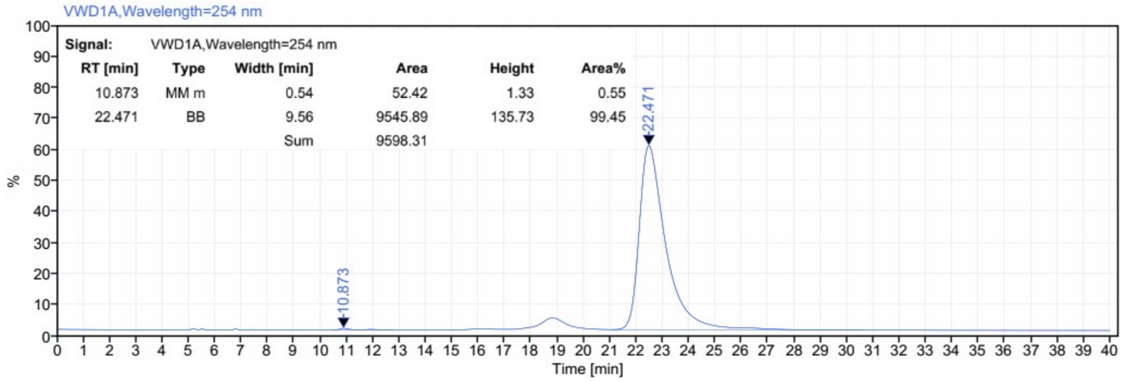


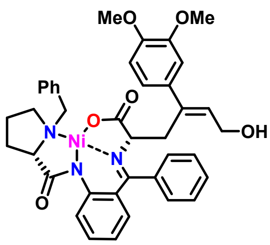


5ae

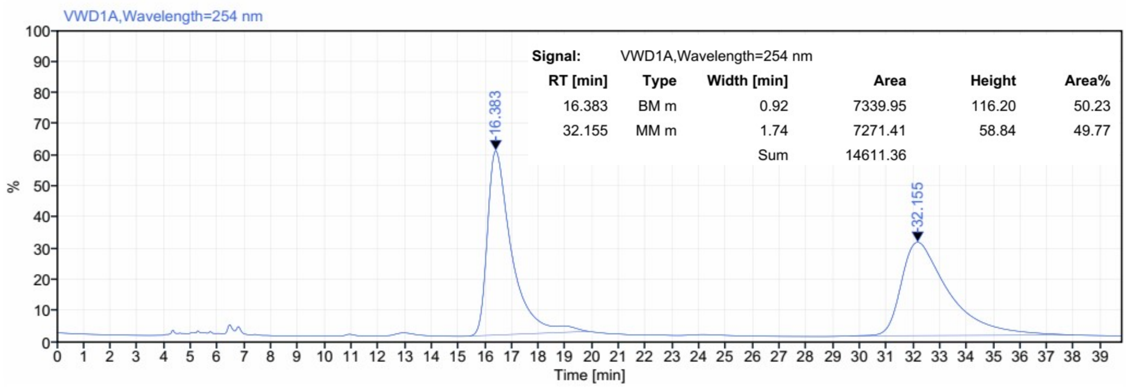
(*S*, *E*)-2-Amino-6-hydroxy-4-(*m*-tolyl)hex-4-enoic acid-Ni-(*S*)-BPB (**5ae**, 61.8 mg, 94% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *E/Z >20:1*) was synthesized in method A afforded 94% isolated yield as red solid. [*α*]25 D= +2761 (c=0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.00 (m, 3H), 7.54 – 7.37 (m, 3H), 7.36 – 7.29 (m, 3H), 7.20 – 7.08 (m, 3H), 6.96 – 6.86 (m, 4H), 6.66 – 6.60 (m, 1H), 6.56 – 6.46 (m, 2H), 5.98 – 5.91 (m, 1H), 4.41 (d, *J* = 12.6 Hz, 1H), 4.33 – 4.21 (m, 1H), 4.02 (dd, *J* = 12.3, 6.3 Hz, 1H), 3.93 – 3.83 (m, 2H), 3.56 – 3.44 (m, 3H), 2.79 – 2.46 (m, 4H), 2.29 – 2.19 (m, 4H), 2.16 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 178.5, 170.3, 142.0, 141.2, 137.4, 137.1, 133.3, 133.2, 132.9, 132.1, 131.4, 131.0, 129.7, 128.8, 128.8, 128.8, 127.9, 127.8, 127.5, 127.3, 126.4, 123.7, 123.1, 120.7, 70.1, 69.2, 63.1, 58.6, 57.4, 37.1, 30.6, 24.2, 21.4. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{38}H_{37}N_3NiO_4Na$ 680.2035; found: 680.2028. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 10.87 min (minor), 22.47 min (major).

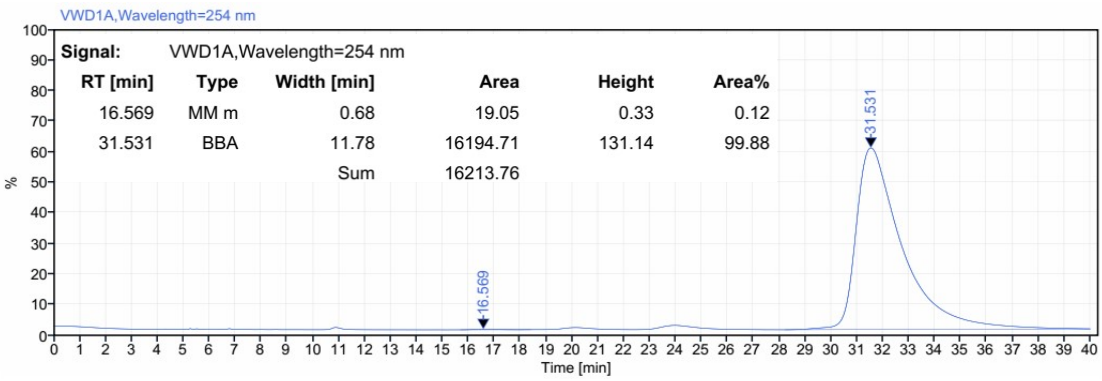


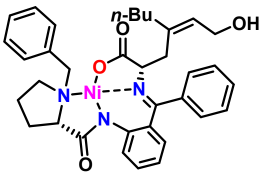



5af

(*S*, *E*)-2-Amino-4-(3,4-dimethoxyphenyl)-6-hydroxyhex-4-enoic acid-Ni-(*S*)-BPB (**5af**, 64 mg, 91% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *E/Z* >20:1) was synthesized in method A afforded 91% isolated yield as red solid. [*α*]25 D= +2812 (c=0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.09 – 7.99 (m, 3H), 7.52 – 7.36 (m, 3H), 7.34 – 7.28 (m, 3H), 7.19 – 7.07 (m, 3H), 6.95 – 6.88 (m, 1H), 6.68 – 6.59 (m, 2H), 6.54 – 6.49 (m, 1H), 6.45 (d, *J* = 8.3 Hz, 1H), 6.17 – 6.11 (m, 1H), 5.95 – 5.87 (m, 1H), 4.39 (d, *J* = 12.6 Hz, 1H), 4.31 – 4.23 (m, 1H), 4.07 – 3.98 (m, 1H), 3.95 – 3.86 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.53 – 3.45 (m, 3H), 2.75 – 2.45 (m, 4H), 2.29 – 2.20 (m, 1H), 2.14 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 180.4, 178.5, 170.2, 148.4, 148.2, 142.0, 136.6, 134.0, 133.3, 133.1, 132.9, 132.1, 131.4, 130.0, 129.6, 128.8, 128.8, 127.6, 127.4, 126.4, 123.7, 120.7, 118.2, 110.4, 110.3, 70.1, 69.1, 63.1, 58.5, 57.4, 55.8, 55.8, 37.4, 30.6, 24.2. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{39}H_{39}N_3NiO_6Na$ 726.2090; found: 726.2088. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 16.56 min (minor), 31.53 min (major).

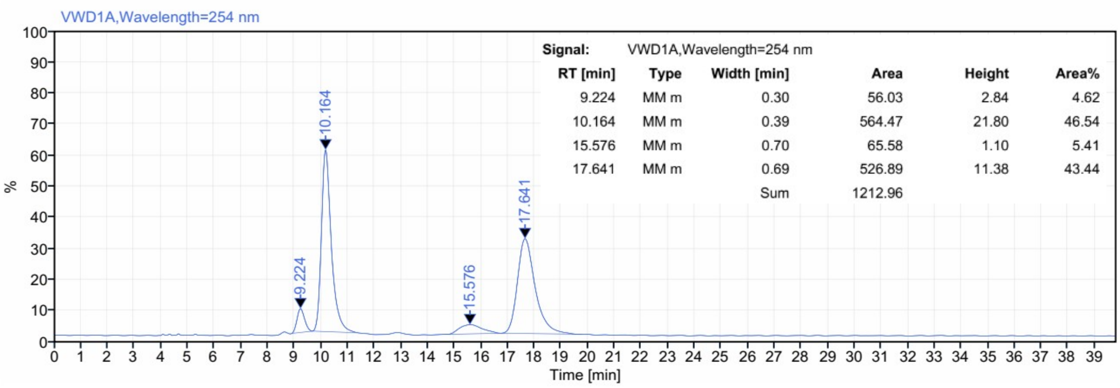


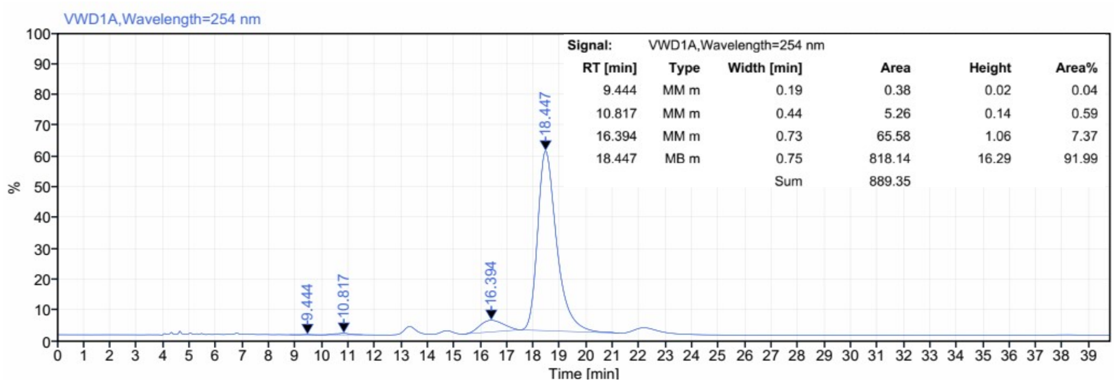


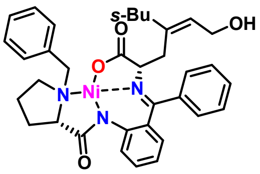


5ag

(S, Z)-2-Amino-4-(2-hydroxyethylidene)octanoic acid-Ni-(S)-BPB (**5ag**, 49.3 mg, 79% yield, EA/DCM=3:1, 99% *ee*, 13:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 79% isolated yield as red solid. [α]25 D= +2245 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 3H), 7.60-7.42 (m, 4H), 7.40 – 7.28 (m, 3H), 7.22 – 7.09 (m, 2H), 6.98 (d, J = 7.7 Hz, 1H), 6.71 – 6.58 (m, 2H), 5.65 – 5.41 (m, 1H), 4.43 (d, J = 12.5 Hz, 1H), 4.16 – 4.04 (m, 1H), 3.98 – 3.73 (m, 3H), 3.59 – 3.43 (m, 4H), 2.73 (dq, J = 14.3, 8.5, 6.8 Hz, 1H), 2.61 – 2.48 (m, 1H), 2.30 – 2.20 (m, 2H), 2.17 – 1.96 (m, 2H), 1.70 – 1.47 (m, 1H), 1.36 – 1.27 (m, 1H), 1.14 – 0.99 (m, 4H), 0.79 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 179.0, 170.1, 142.1, 136.9, 133.2, 133.2, 133.1, 132.2, 131.4, 129.9, 129.0, 129.0, 128.9, 128.5, 127.7, 127.5, 126.4, 123.8, 120.8, 70.1, 63.1, 58.4, 57.4, 37.2, 36.4, 30.7, 30.2, 24.1, 22.2, 13.8. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{35}H_{40}N_3NiO_4$ 624.2367; found: 624.2371. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 10.81 min (minor), 18.44 min (major).

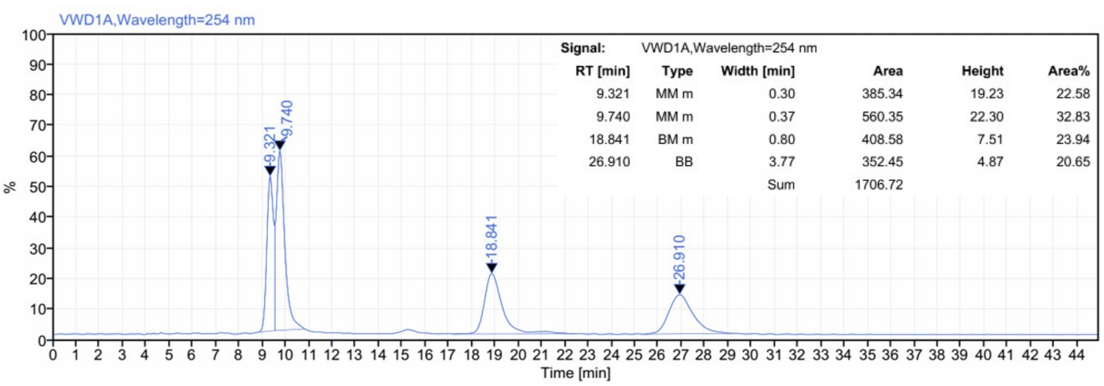


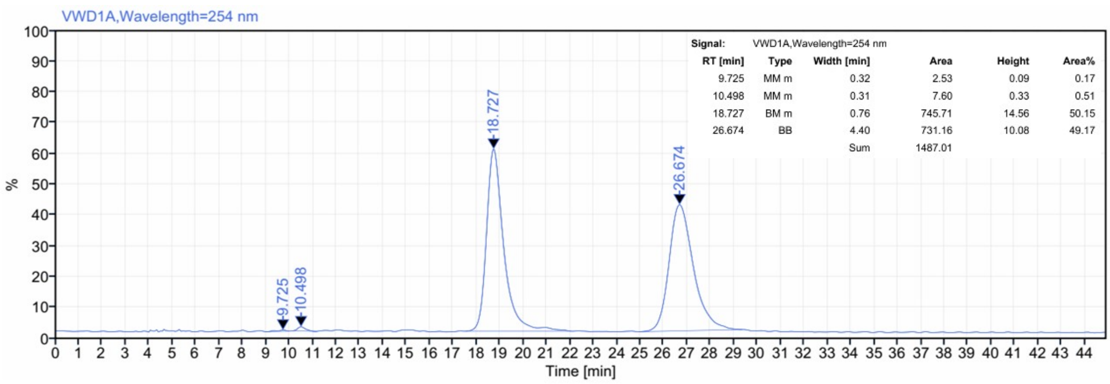


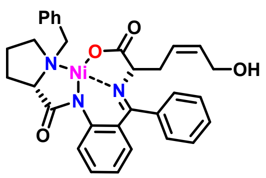


5ah

(2*S*, *E*)-2-Amino-4-(2-hydroxyethylidene)-5-methylheptanoic acid-Ni-(*S*)-BPB (**5ah**, 47.4 mg, 76% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *E/Z* >20:1) was synthesized in method A afforded 76% isolated yield as red solid. [α]25 D= +2317 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.00 (m, 3H), 7.59 – 7.41 (m, 4H), 7.40 – 7.28 (m, 3H), 7.22 – 7.09 (m, 2H), 6.99 (d, J = 7.3 Hz, 1H), 6.71 – 6.59 (m, 2H), 5.59 – 5.49 (m, 1H), 4.49 – 4.38 (m, 1H), 4.14 – 3.97 (m, 1H), 3.91 – 3.75 (m, 3H), 3.73 – 3.62 (m, 1H), 3.59 – 3.47 (m, 3H), 2.77 – 2.66 (m, 1H), 2.60 – 2.50 (m, 1H), 2.40 – 1.90 (m, 5H), 1.10 – 0.87 (m, 2H), 0.80 – 0.77 (m, 1H), 0.68 – 0.57 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 142.1, 141.6, 141.3, 133.4, 133.1, 132.2, 131.5, 129.8, 129.2, 128.9, 127.6, 127.5, 127.0, 126.6, 126.4, 123.9, 120.8, 70.2, 69.6, 63.2, 58.4, 57.5, 41.3, 37.3, 30.7, 27.6, 24.2, 20.2, 12.0. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{35}H_{40}N_3NiO_4$ 624.2367; found: 624.2376. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 9.72 min (minor), 26.67 min (major).

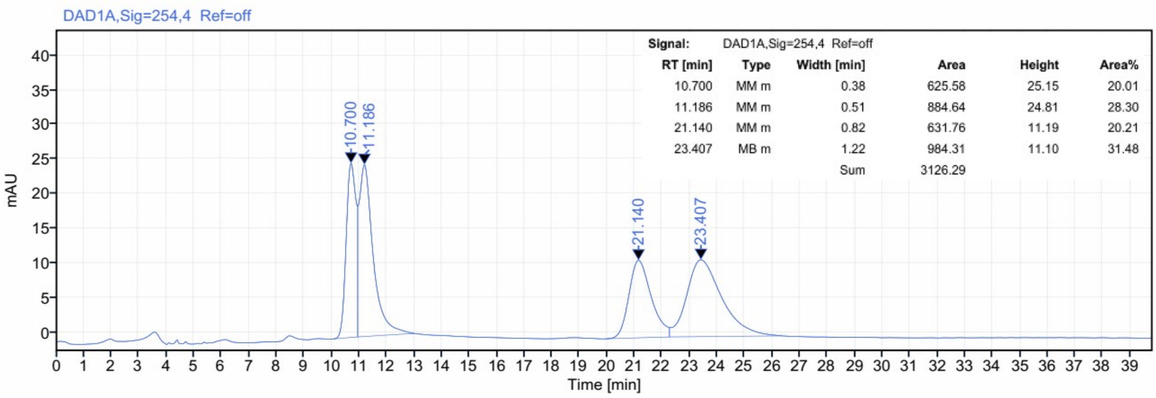


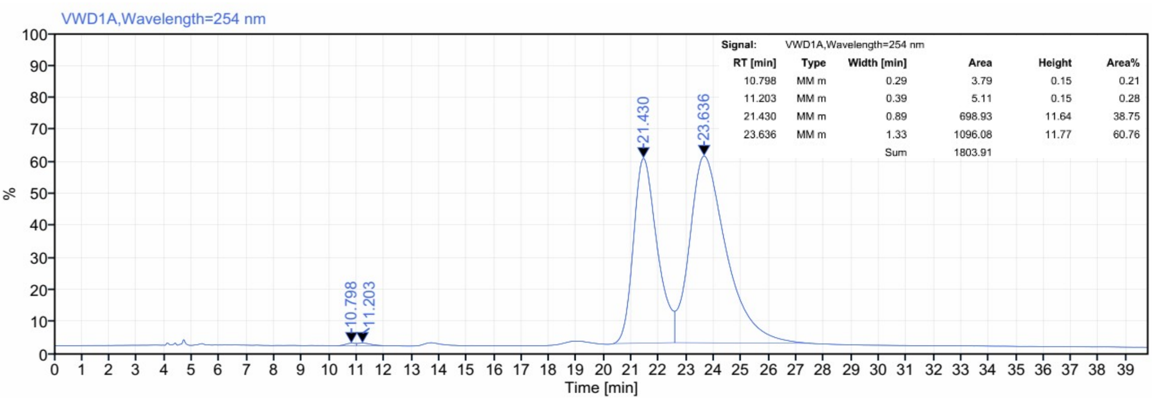


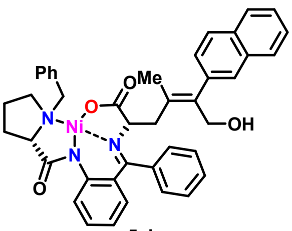


5ai

(*S*, *Z*)-2-Amino-6-hydroxyhex-4-enoic acid-Ni-(*S*)-BPB (**5ai**, 46.0 mg, 81% yield, EA/DCM=3:1, 99% *ee*, 2:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 81% isolated yield as red solid. [α]25 D= +2645 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.98 (m, 3H), 7.53 – 7.37 (m, 3H), 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 7.18 – 7.04 (m, 2H), 6.97 – 6.83 (m, 1H), 6.65 – 6.55 (m, 2H), 6.22 – 5.56 (m, 1H), 6.12 – 6.00 (m, 1H), 4.32 (t, J = 11.6 Hz, 1H), 4.16 – 4.07 (m, 1H), 4.05 – 3.88 (m, 2H), 3.58 – 3.35 (m, 4H), 2.88 (s, 1H), 2.77 – 2.64 (m, 1H), 2.59 – 2.34 (m, 3H), 2.14 – 1.96 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 180.2, 178.8, 170.6, 142.0, 134.0, 133.5, 133.1, 132.0, 131.3, 129.6, 128.9, 128.8, 128.6, 127.4, 126.8, 126.1, 124.8, 124.1, 123.4, 120.5, 70.1, 62.9, 62.5, 57.0, 37.4, 30.5, 23.4. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{31}H_{31}N_3NiO_4Na$ 590.1566; found: 590.1558. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 22.18 min (minor), 34.57 min (major).40 min; 99% *ee*(major).

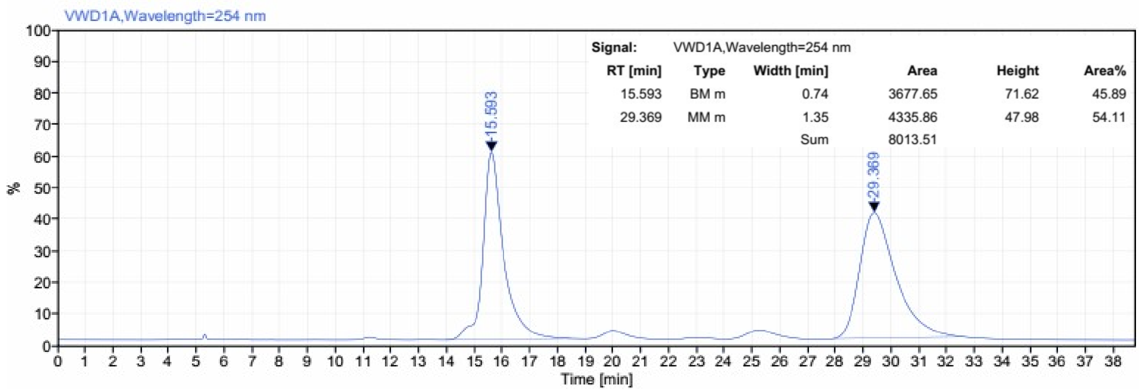


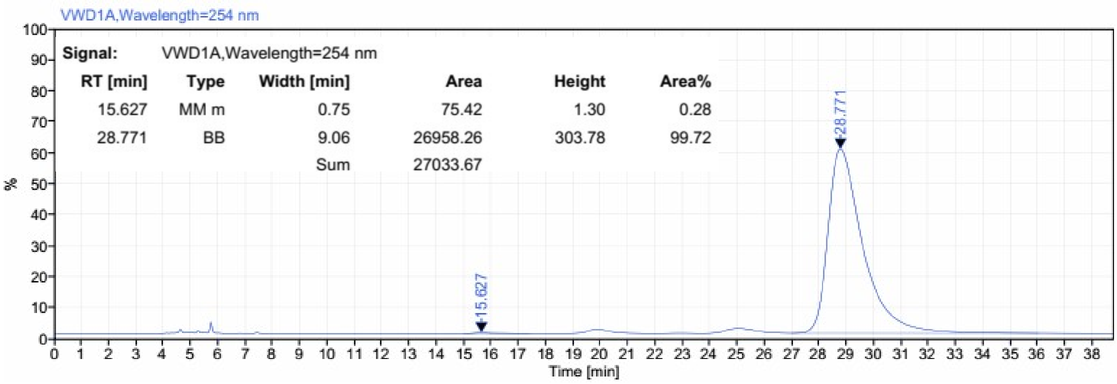


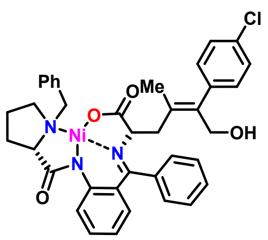


5aj

(*S*, *Z*)-2-Amino-6-hydroxy-4-methyl-5-(naphthalen-2-yl)hex-4-enoic acid-Ni-(*S*)-BPB (**5aj**, 50.2 mg, 71% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 71% isolated yield as red solid. [*α*]25 D= +1420 (c=0.04, $CHCl_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.16 – 8.01 (m, 3H), 7.82 – 7.72 (m, 3H), 7.61 – 7.49 (m, 2H), 7.48 – 7.35 (m, 6H), 7.34 – 7.27 (m, 2H), 7.24 – 7.13 (m, 2H), 7.04 – 6.98 (m, 1H), 6.77 – 6.62 (m, 2H), 4.47 (dd, *J* = 29.1, 12.3 Hz, 2H), 4.15 – 4.02 (m, 2H), 3.89 – 3.73 (m, 2H), 3.63 – 3.44 (m, 3H), 2.78 – 2.68 (m, 1H), 2.61 – 2.21 (m, 4H), 2.14 – 2.02 (m, 1H), 1.06 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 180.5, 179.2, 170.2, 142.1, 139.8, 139.0, 133.2, 133.2, 133.1, 132.2, 132.1, 131.5, 129.9 129.7, 129.0, 128.9, 128.9, 127.8, 127.6, 127.5, 127.4, 127.4, 127.2, 126.4, 125.7, 125.4, 123.9, 120.8, 70.0, 69.0, 63.0, 62.8, 57.4, 41.0, 30.6, 29.6, 24.1, 19.8. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{42}H_{39}N_3NiO_4Na$ 730.2192; found: 730.2192. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 15.62 min (minor), 28.77 min (major).

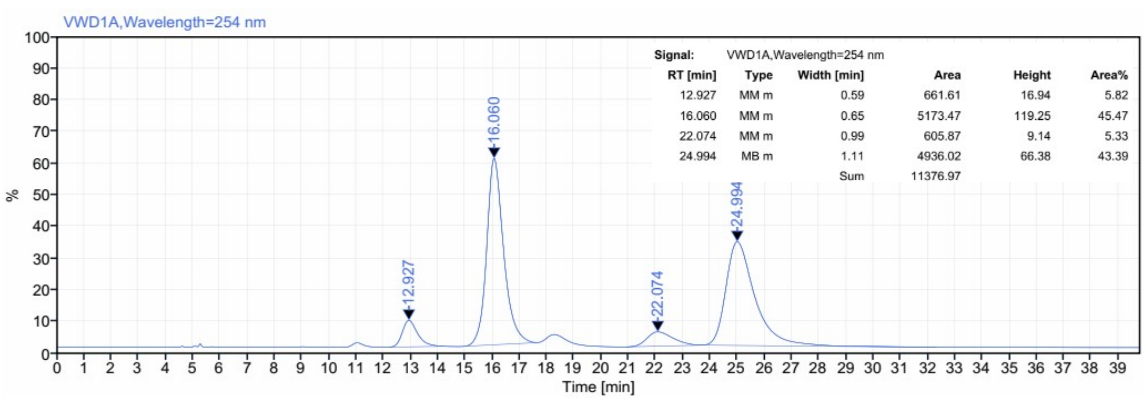


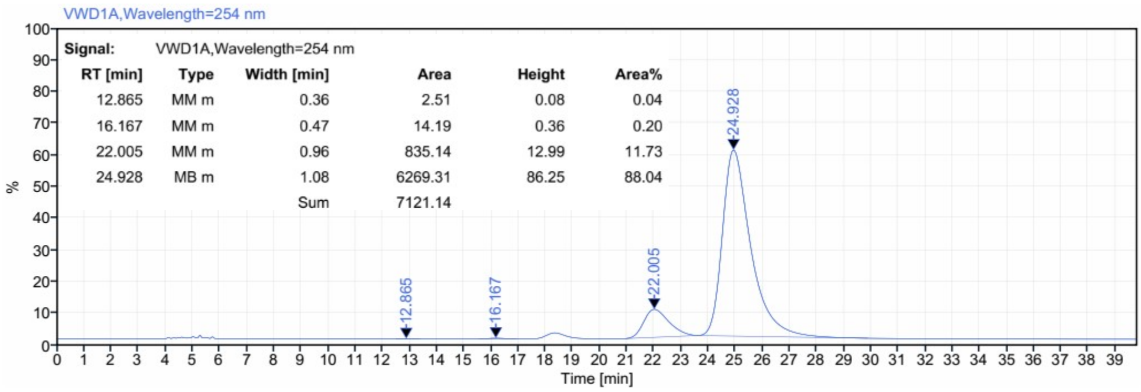




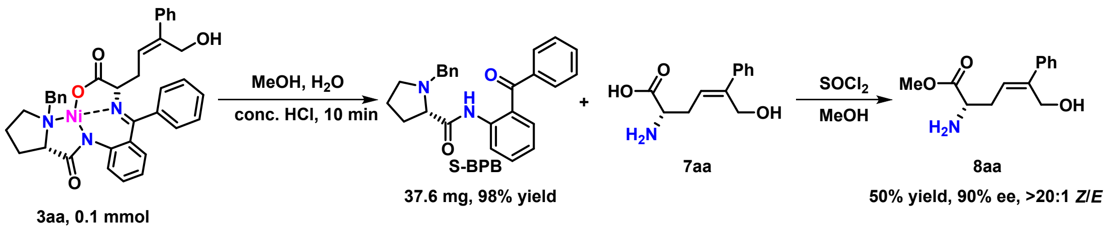
5ak

(*S*, *Z*)-2-Amino-5-(4-chlorophenyl)-6-hydroxy-4-methylhex-4-enoic acid-Ni-(*S*)-BPB (**5ak**, 53.2 mg, 77% yield, EA/DCM=3:1, 99% *ee*, >20:1 *dr*, *Z/E* >20:1) was synthesized in method A afforded 77% isolated yield as red solid. [*α*]25 D= +2401 (c=0.04, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.00 (m, 3H), 7.60 – 7.43 (m, 3H), 7.43 – 7.30 (m, 3H), 7.25 – 7.12 (m, 4H), 7.12 – 6.96 (m, 3H), 6.74 – 6.61 (m, 2H), 4.43 (t, *J* = 13.2 Hz, 2H), 4.07 – 3.87 (m, 2H), 3.84 – 3.69 (m, 2H), 3.64 – 3.46 (m, 3H), 2.83 – 2.68 (m, 1H), 2.64 – 2.46 (m, 1H), 2.37 – 2.23 (m, 2H), 2.15 – 1.93 (m, 2H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 179.2, 170.4, 142.2, 140.0, 139.0, 133.3, 133.2, 132.4, 131.6, 130.2, 130.0, 129.2, 129.1, 129.0, 129.0, 128.2, 127.7, 127.6, 126.4, 124.0, 120.9, 70.2, 69.0, 63.2, 62.8, 57.4, 40.9, 30.8, 24.2, 19.8. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{38}H_{36}N_3NiO_4Na$ 714.1646; found: 714.1644. HPLC conditions: IA column, 254 nm, 30 °C, flow rate: 0.7 mL/min, Hex:IPA = 55:45, t_R = 16.16 min (minor), 24.92 min (major).

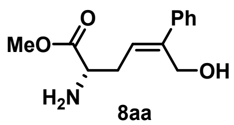




The method for the synthesis of 8aa.

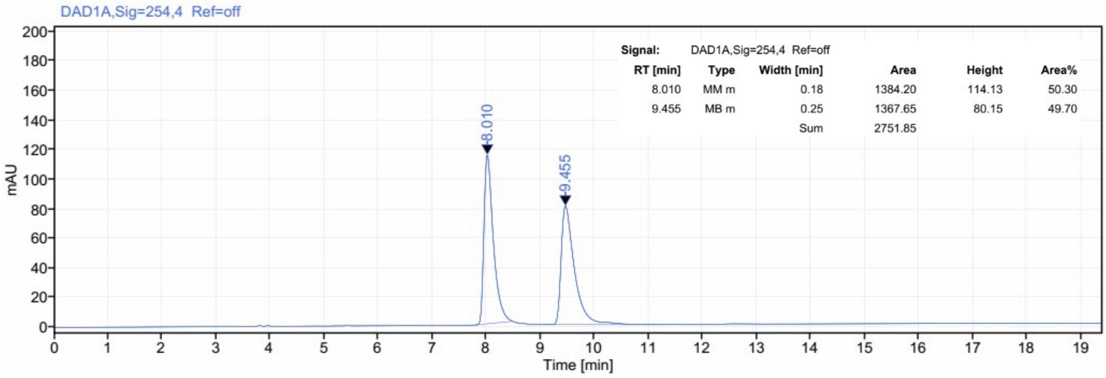


The compound **3aa** (64.3 mg, 0.1 mmol) were dissolved in 2.5 mL of MeOH and 1.2 mL of H_2O and stirred at room temperature. After adding conc. HCl (34 µL, 4.0 equiv.), the temperature was heated to 70 °C and stirred at the same temperature for 10 min. The mixture was cooled to room temperture and concentrated to provide the mixture. Then water (2 mL) was added to the mixture, and extracted with DCM (three times). The organic phase and the aqueous were concentrated to provide (S)-BPB (98% yield) and the crude product **7aa**, which was directly dissolved in 1 mL of dry MeOH and stirred at 0 °C. After adding $SOCl_2$ (24.0 mg, 2 equiv.), the temperature was heated to room temperature and stirred overnight. The crude product was purified by flash column chromatograph on silica gel to provide the pure product **8aa**.



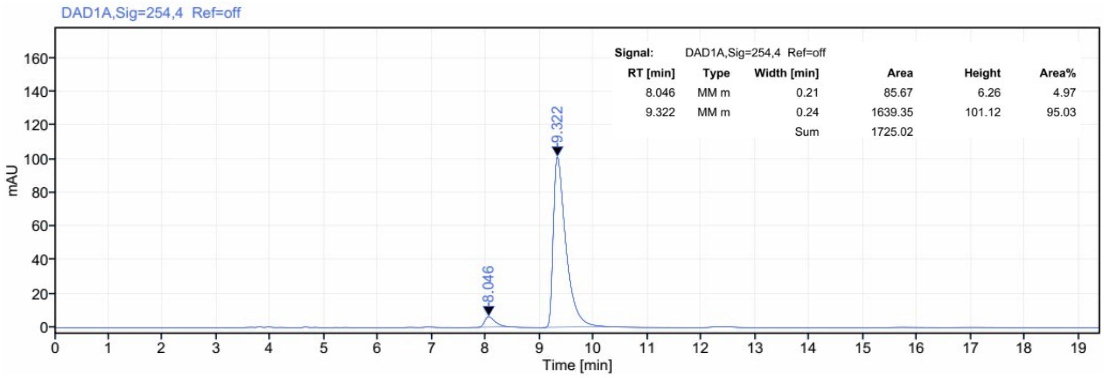
8aa

Methyl (*S*, *Z*)-2-amino-6-hydroxy-5-phenylhex-4-enoate (**8aa**, 11.7 mg, 50% yield, DCM/MeOH=30:1, 90% ee, *Z/E* >20:1) as colorless liquid. [α]25 D= -22.561 (c=0.16, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.31 – 7.27 (m, 1H), 5.83 (t, J = 8.5 Hz, 1H), 4.44 (dd, 2H), 3.80 (s, 3H), 3.65 – 3.58 (m, 1H), 2.90 (s, 3H), 2.81 – 2.72 (m, 1H), 2.67 – 2.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 145.0, 141.9, 128.3, 127.2, 126.0, 125.8, 59.4, 52.5, 52.1, 33.8. HPLC conditions: AD-H column, 254nm, 30 °C, flow rate: 0.8 mL/min, Hex:IPA = 70:30, t_R = 8.04 min (minor), 9.32 min (major).



Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%
8.010	MM m	0.18	1384.20	114.13	50.30
9.455	MB m	0.25	1367.65	80.15	49.70
		Sum	2751.85		

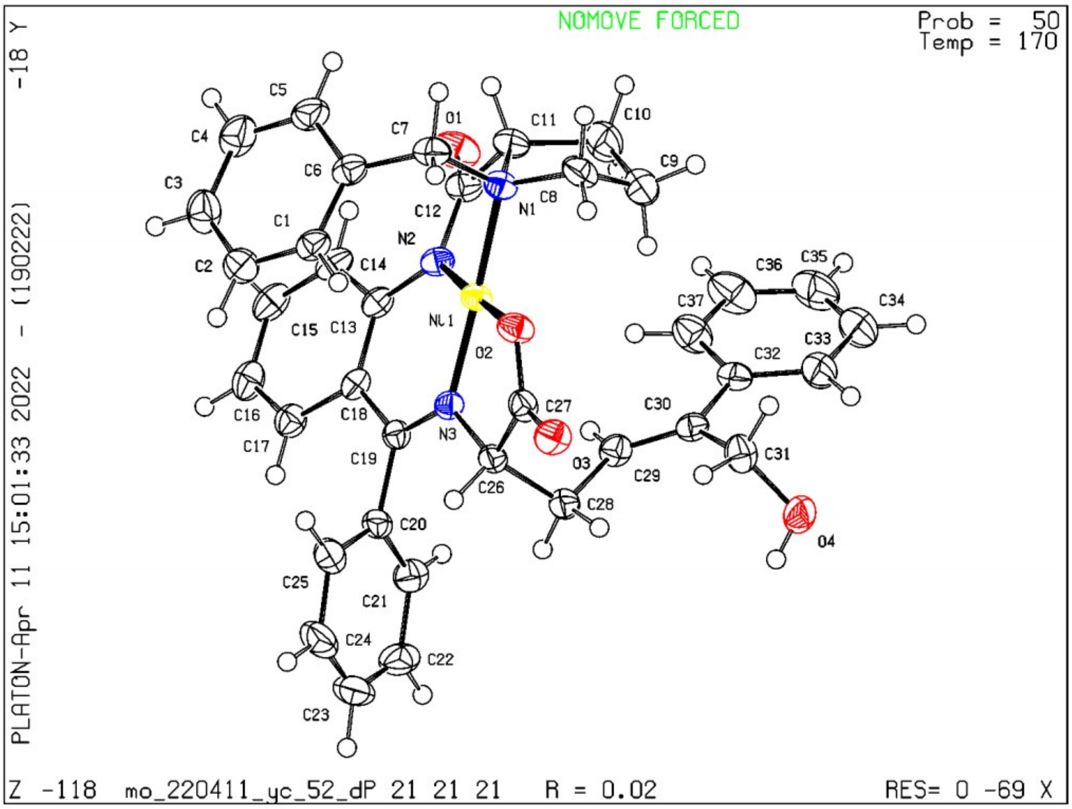


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%
8.046	MM m	0.21	85.67	6.26	4.97
9.322	MM m	0.24	1639.35	101.12	95.03
		Sum	1725.02		

Crystal data

Crystallographic datas for compound **3aa** and **3aa′** (CCDC- 2165884 and CCDC-2165885) have been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



The ellipsoid is shown at the 50% probability level

Datablock: compound 3aa

Bond precision:	C-C = 0.0036 A		Wavelength=0.71073
Cell:	a=10.3298(4)	b=13.1904(4)	c=22.5489(6)
	alpha=90	beta=90	gamma=90
Temperature:	170 K		

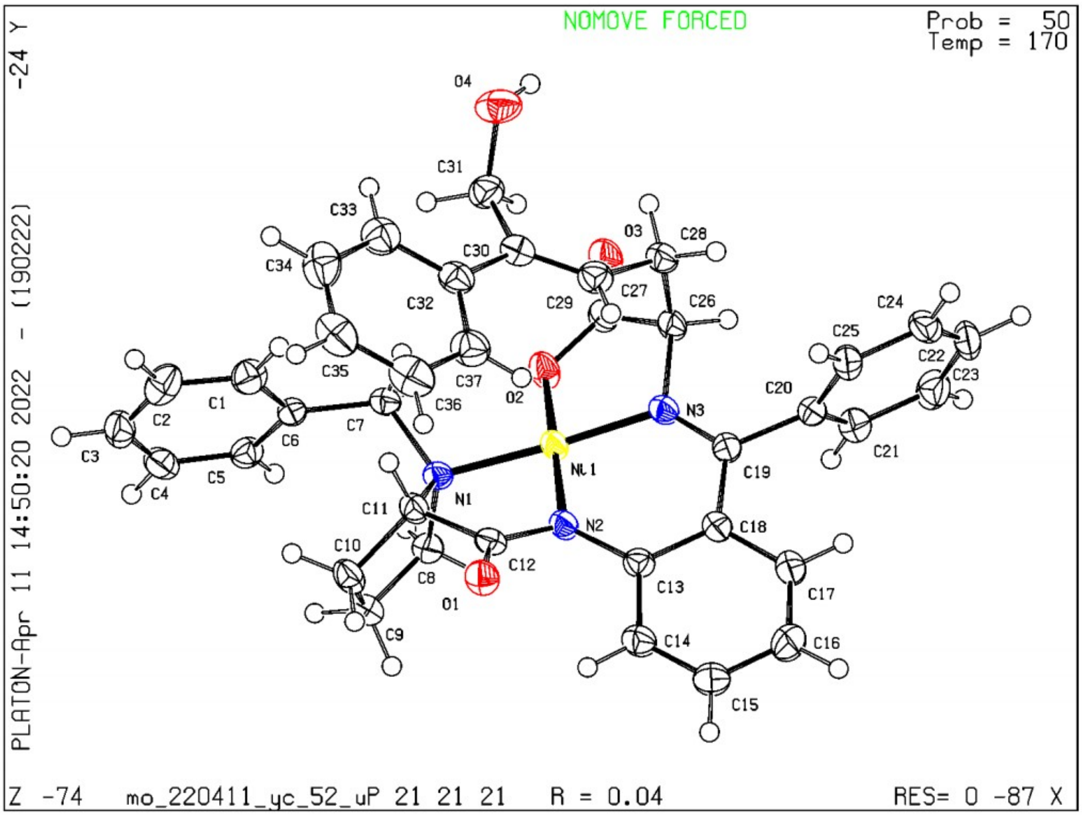
	Calculated	Reported
Volume	3072.38(17)	3072.38(17)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C37 H35 N3 Ni O4	C37 H35 N3 Ni O4
Sum formula	C37 H35 N3 Ni O4	C37 H35 N3 Ni O4
Mr	644.37	644.39
Dx,g cm-3	1.393	1.393
Z	4	4
Mu (mm-1)	0.678	0.678
F000	1352.0	1352.0
F000'	1353.85	
h,k,lmax	13,16,28	13,16,28
Nref	6793[3813]	6782
Tmin,Tmax	0.922,0.941	0.692,0.746
Tmin'	0.885	

Correction method= # Reported T Limits: Tmin=0.692 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.78/1.00   Theta(max)= 27.107

R(reflections)= 0.0247(6389)   wR2(reflections)= 0.0580(6782)

S = 1.033   Npar= 407



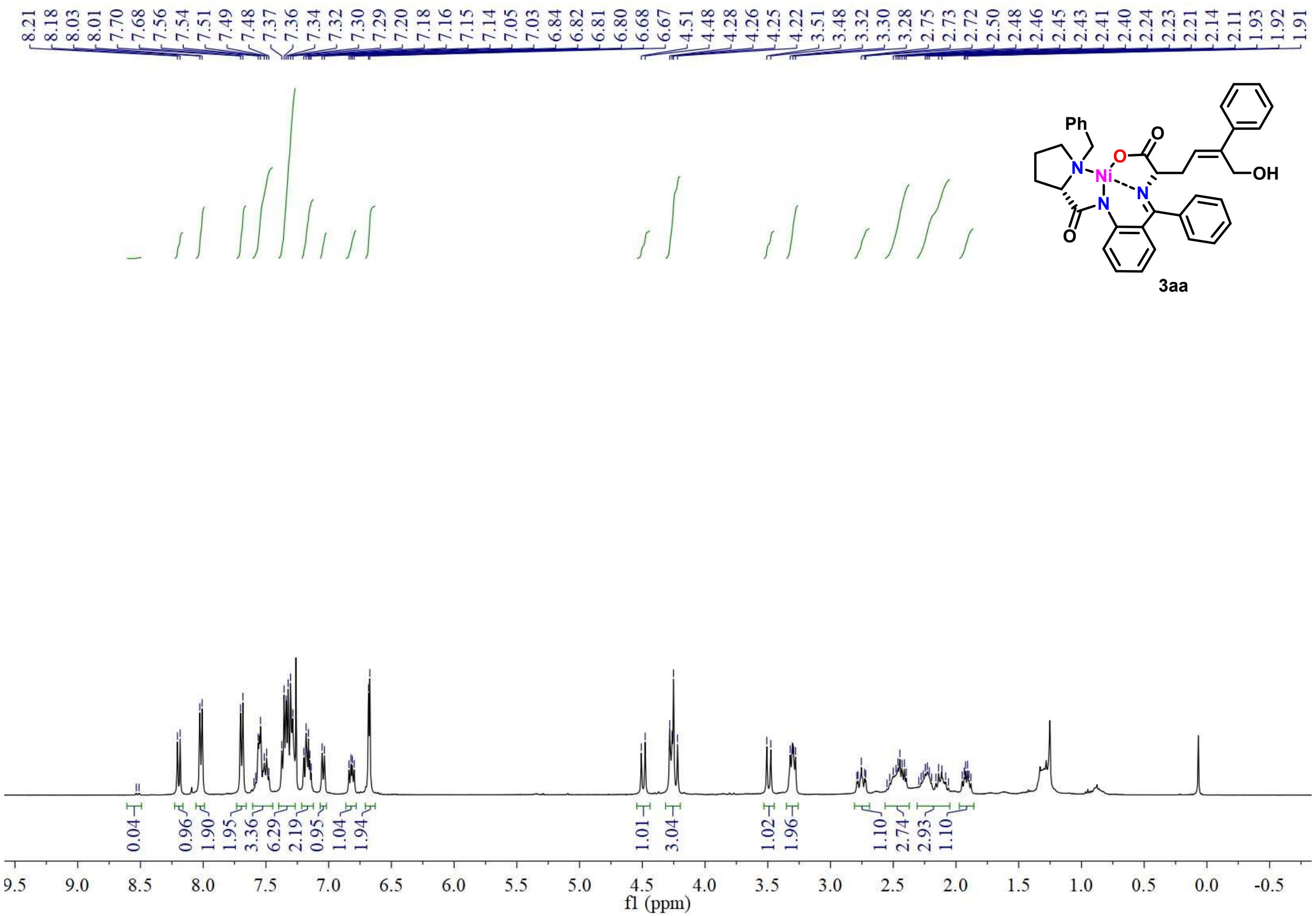
The ellipsoid is shown at the 50% probability level

Datablock: compound 3aa′

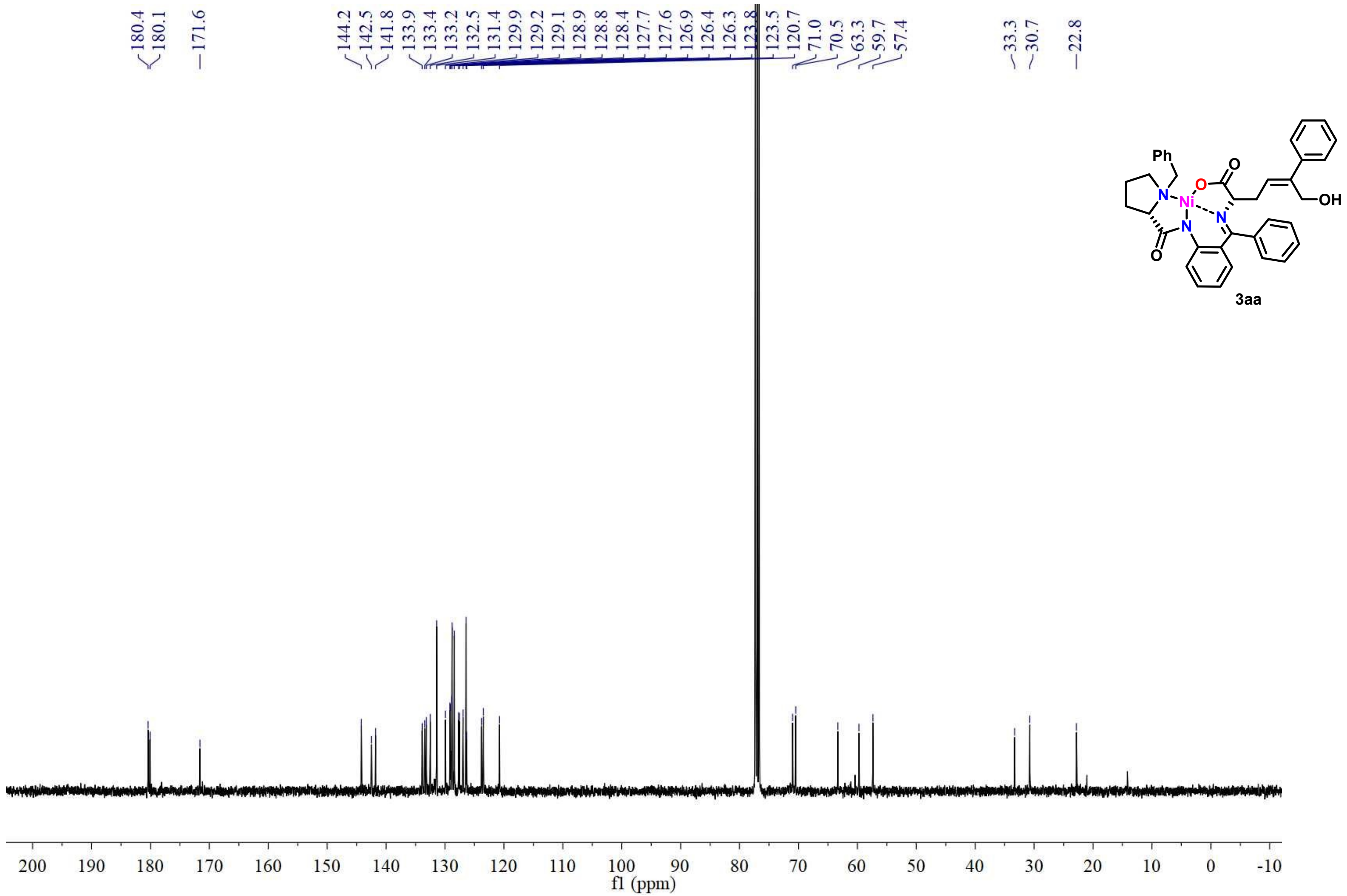
```
Bond precision:   C-C = 0.0058 A          Wavelength=0.71073

Cell:              a=9.4827(4)      b=9.7970(5)      c=32.8524(18)
                   alpha=90         beta=90          gamma=90
Temperature:       170 K

                 Calculated                  Reported
Volume           3052.1(3)                   3052.1(3)
Space group      P 21 21 21                  P 21 21 21
Hall group       P 2ac 2ab                   P 2ac 2ab
Moiety formula   C37 H35 N3 Ni O4            C37 H35 N3 Ni O4
Sum formula      C37 H35 N3 Ni O4            C37 H35 N3 Ni O4
Mr               644.37                      644.39
Dx,g cm-3        1.402                       1.402
Z                4                           4
Mu (mm-1)        0.682                       0.682
F000             1352.0                      1352.0
F000'            1353.85
h,k,lmax         12,12,42                    12,12,42
Nref             6786[ 3848]                 6763
Tmin,Tmax        0.952,0.973                 0.682,0.746
Tmin'            0.804

Correction method= # Reported T Limits: Tmin=0.682 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.76/1.00       Theta(max)= 27.152

                                                      wR2(reflections)=
R(reflections)= 0.0416( 5489)                         0.0794( 6763)
S = 1.023                   Npar= 407
```

Spectroscopic data of compounds

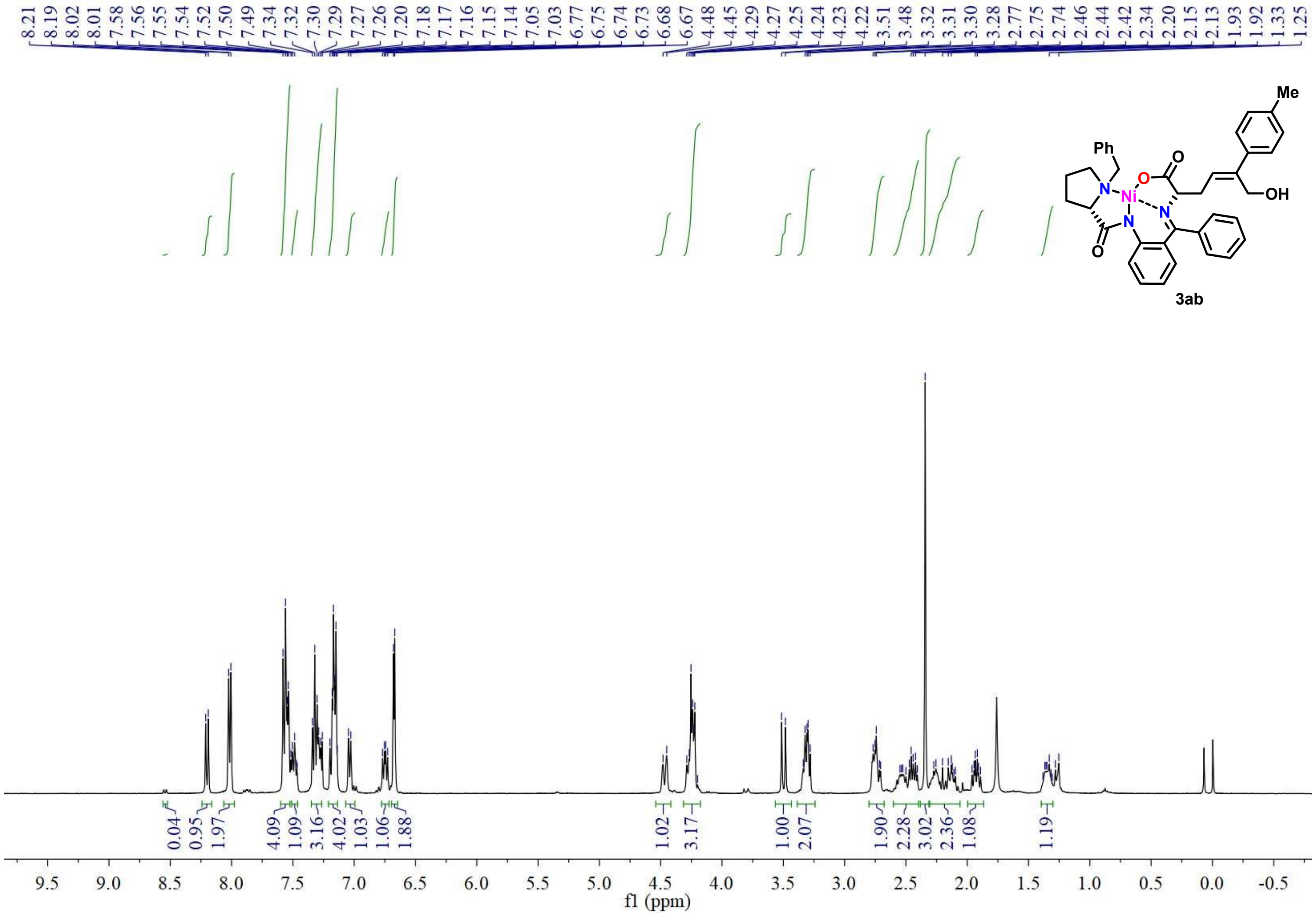
^{1}**H NMR** spectrum of **3aa** in $CDCl_3$



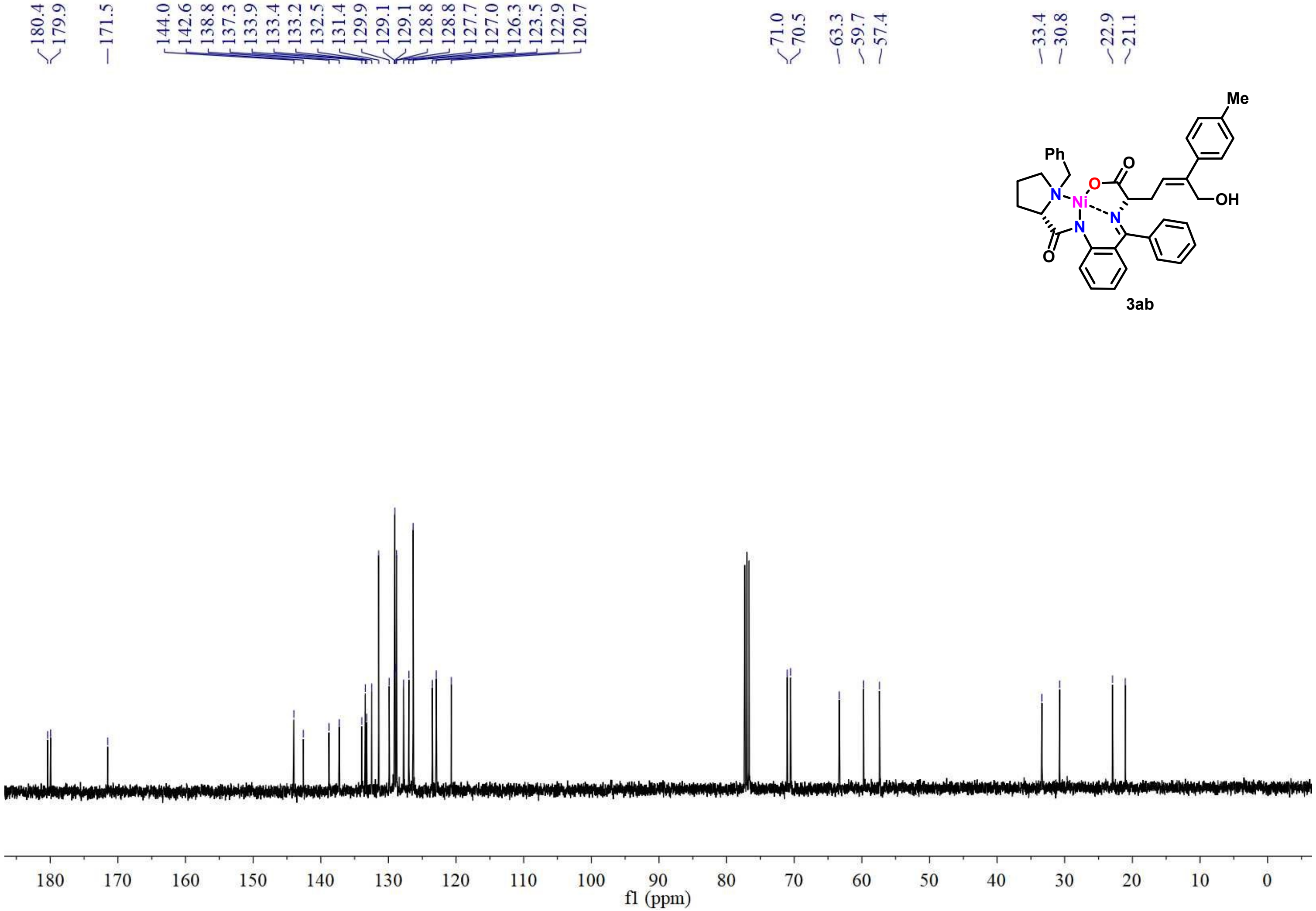
^{13}C NMR spectrum of **3aa** in $CDCl_3$



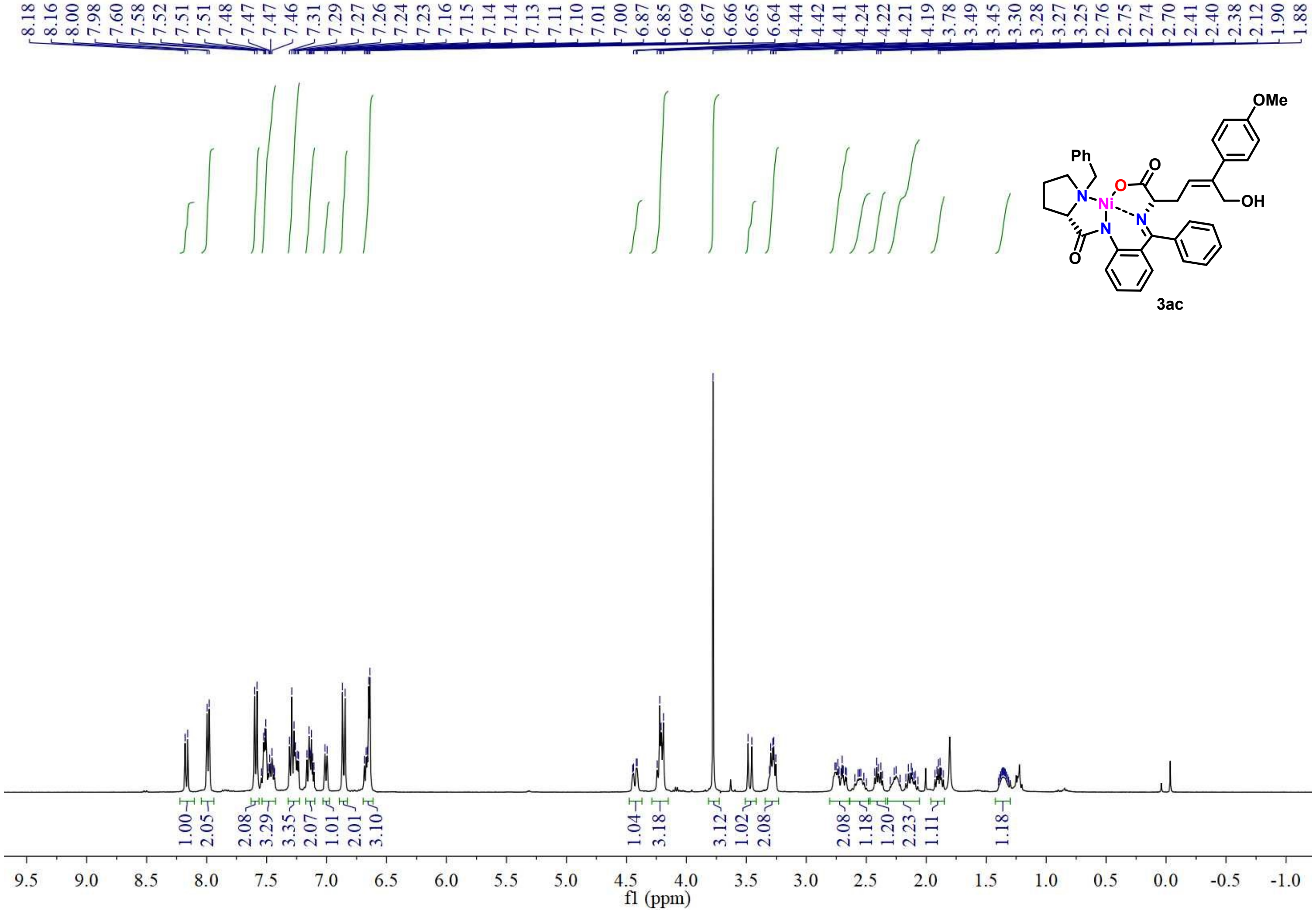
^{1}H NMR spectrum of **3ab** in $CDCl_3$



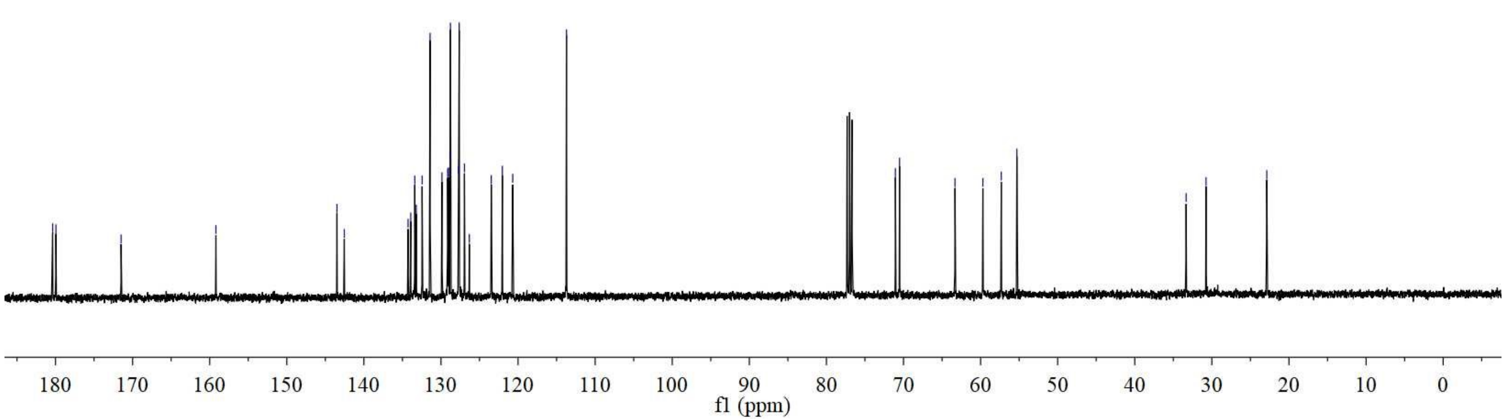
^{13}C NMR spectrum of **3ab** in $CDCl_3$

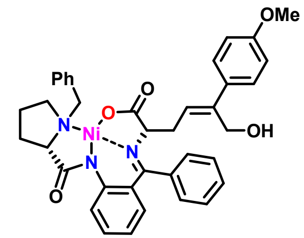


^{1}**H NMR** spectrum of **3ac** in $CDCl_3$



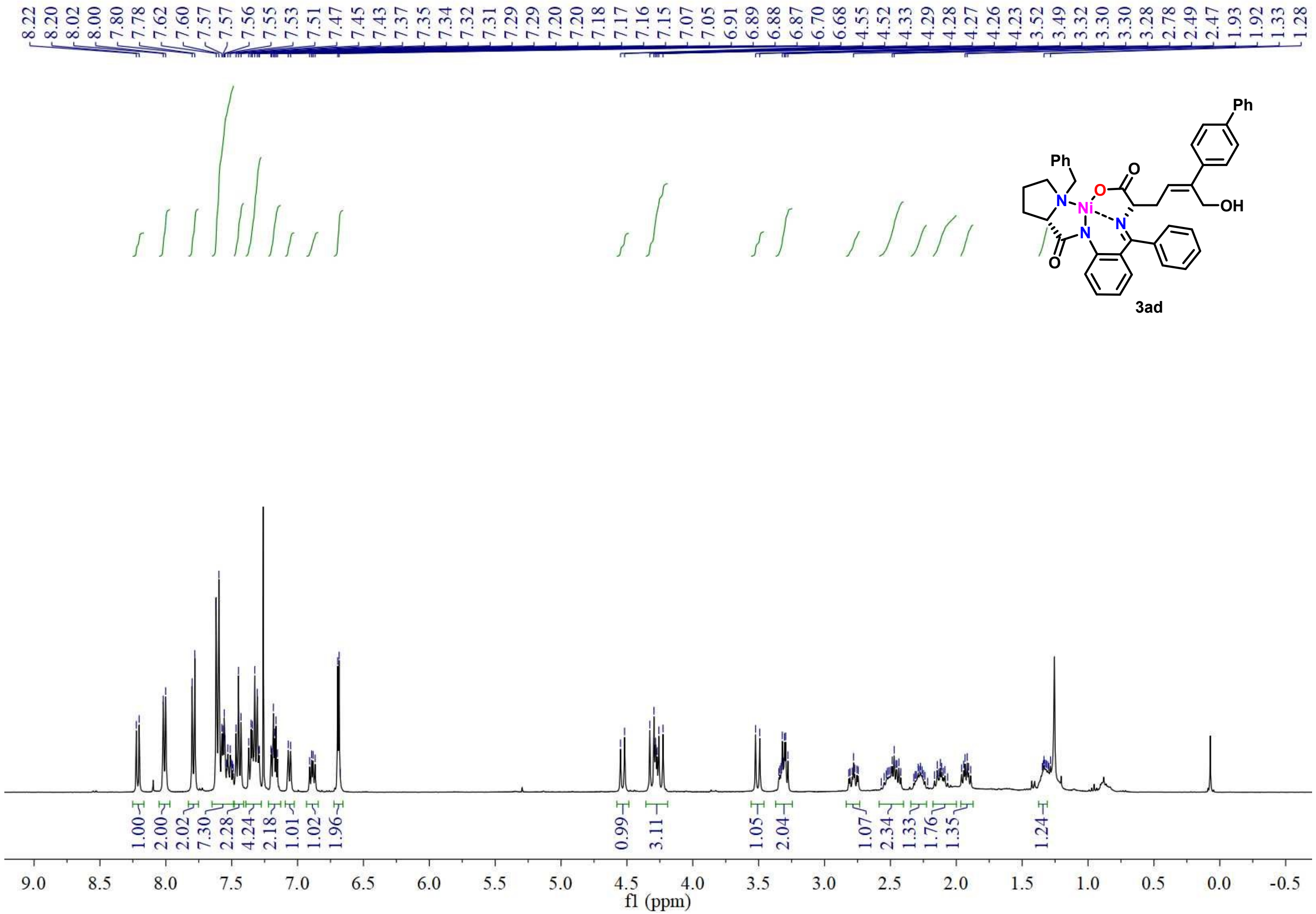
^{13}C **NMR** spectrum of **3ac** in $CDCl_3$



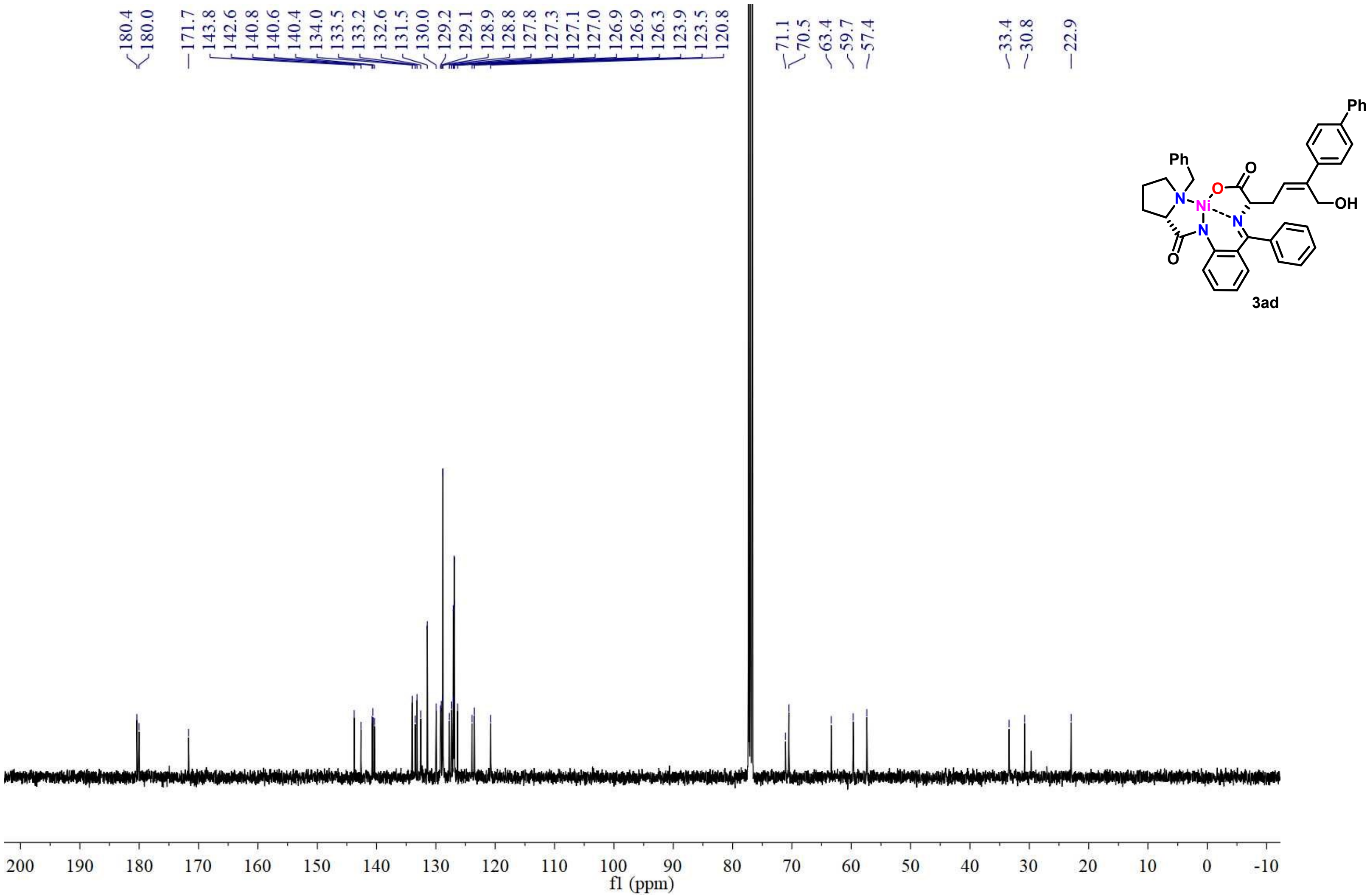


3ac

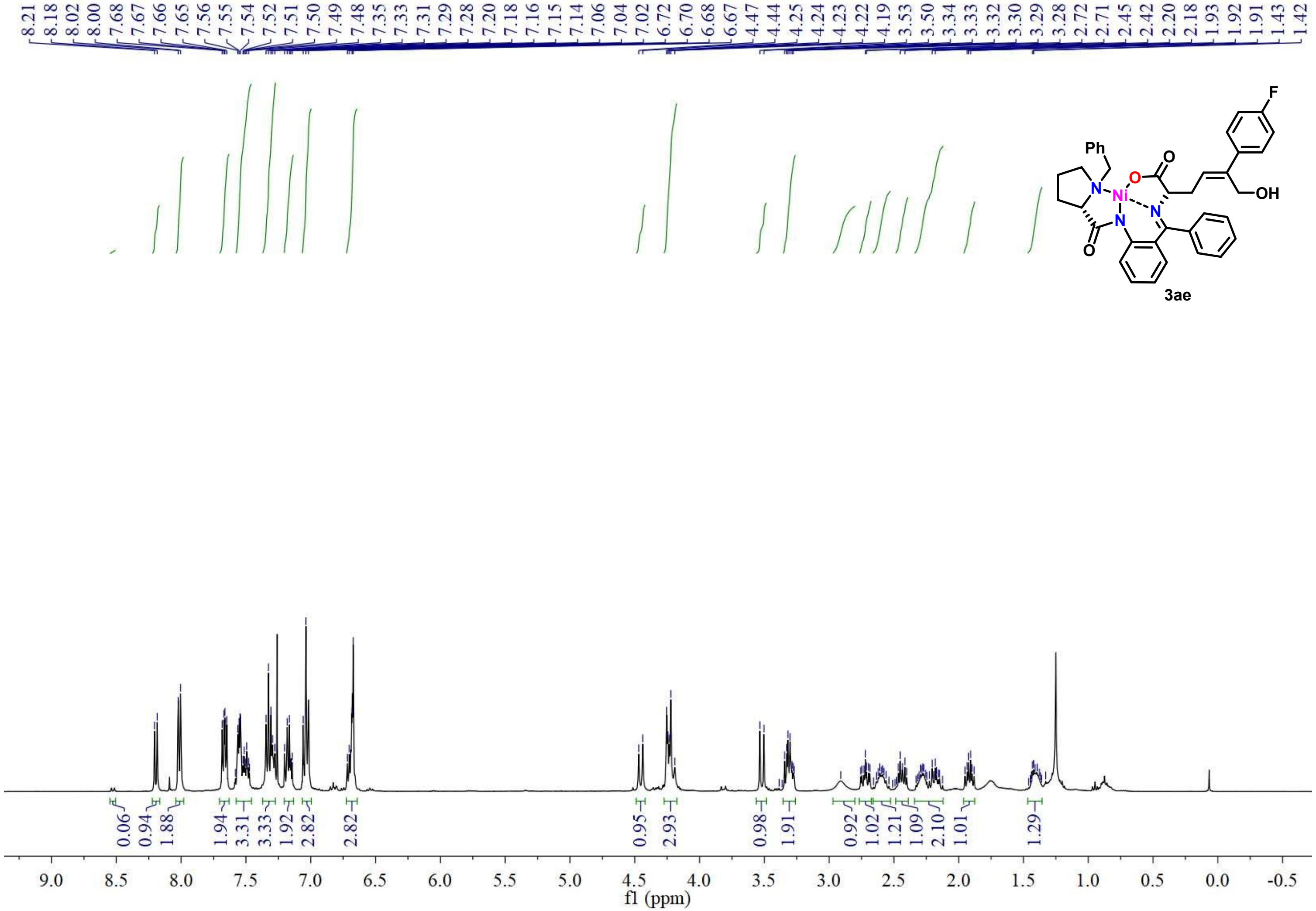
^{1}**H NMR** spectrum of **3ad** in $CDCl_3$



^{13}C NMR spectrum of **3ad** in $CDCl_3$

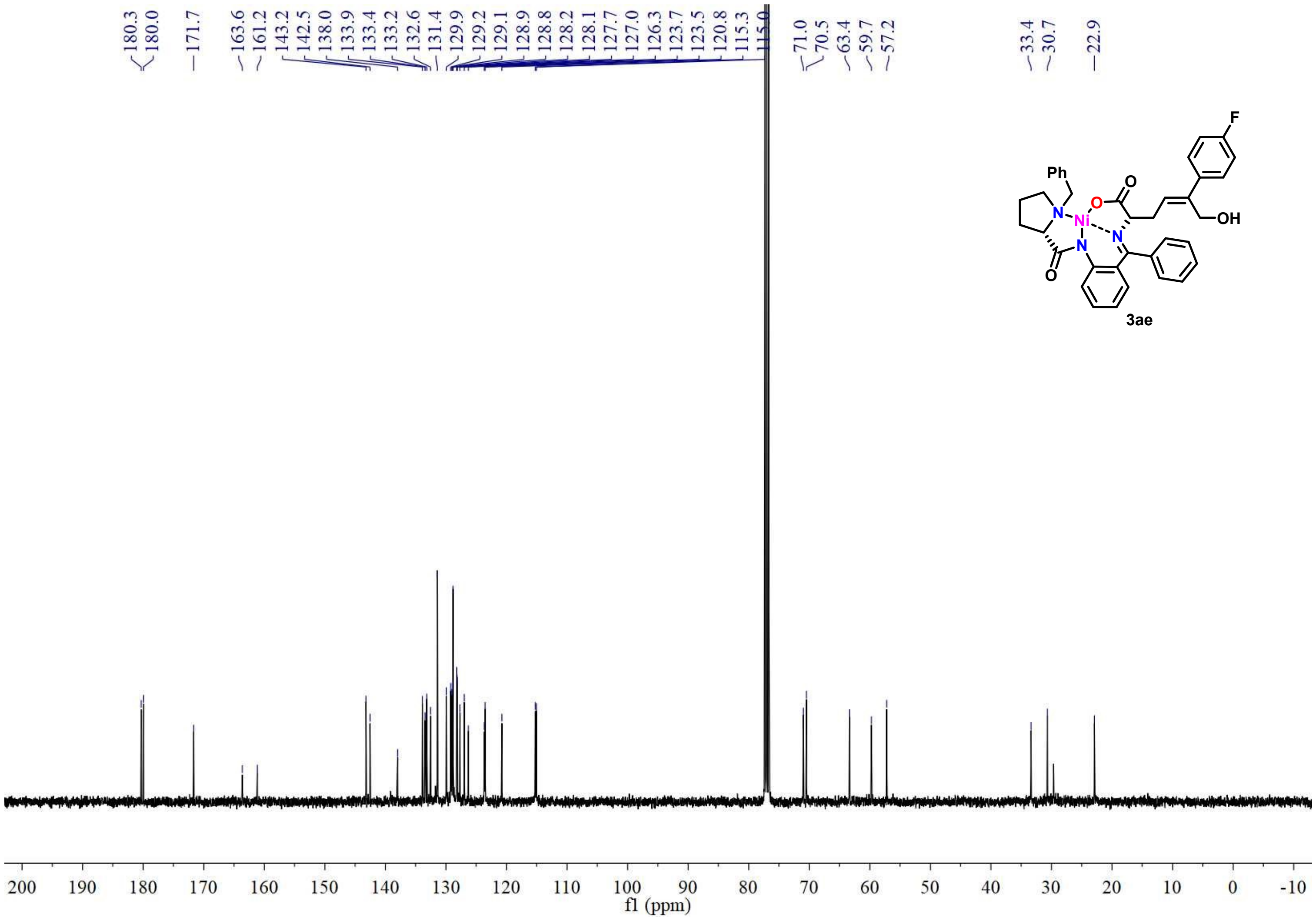


^{1}H NMR spectrum of **3ae** in $CDCl_3$

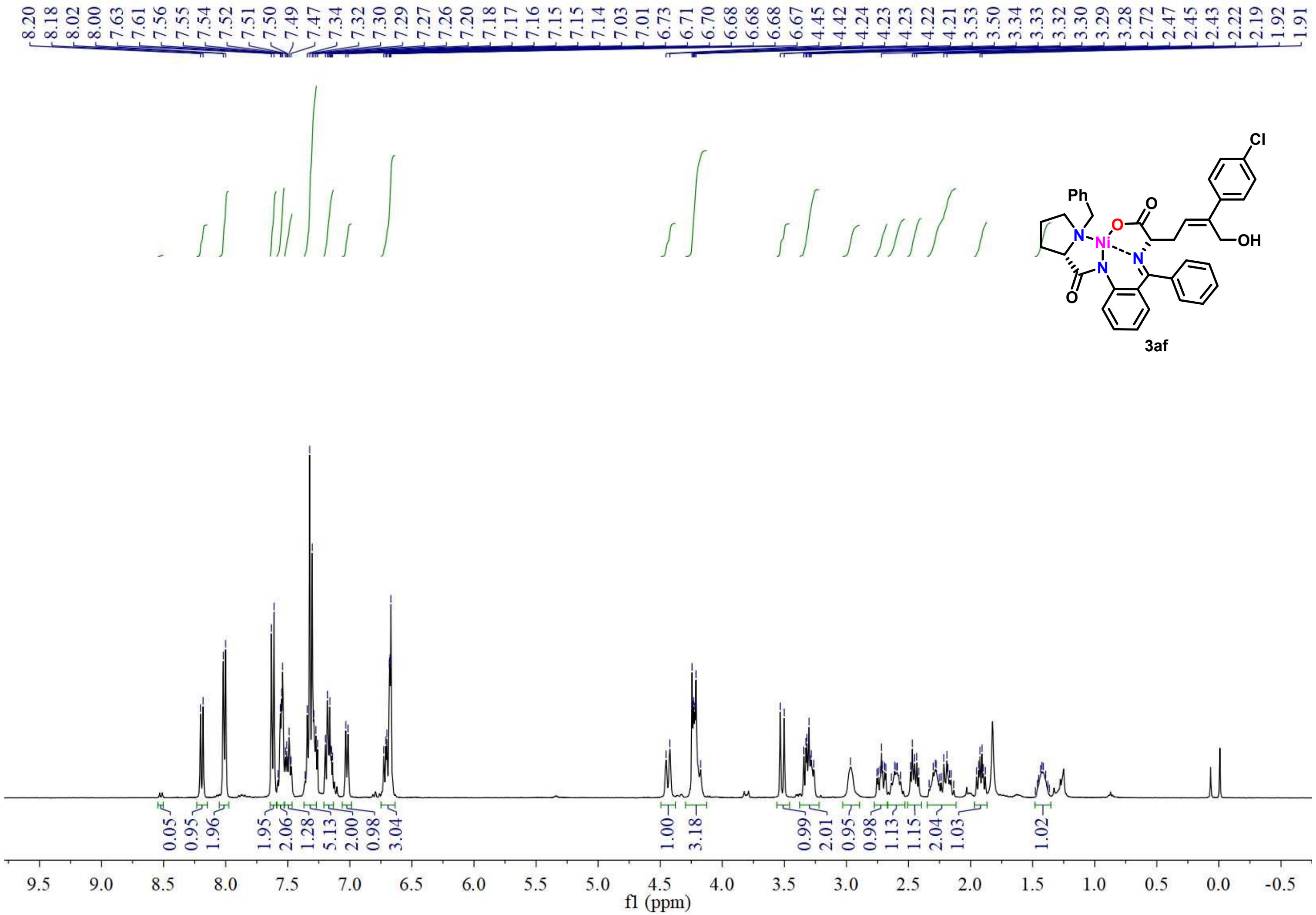


3ae

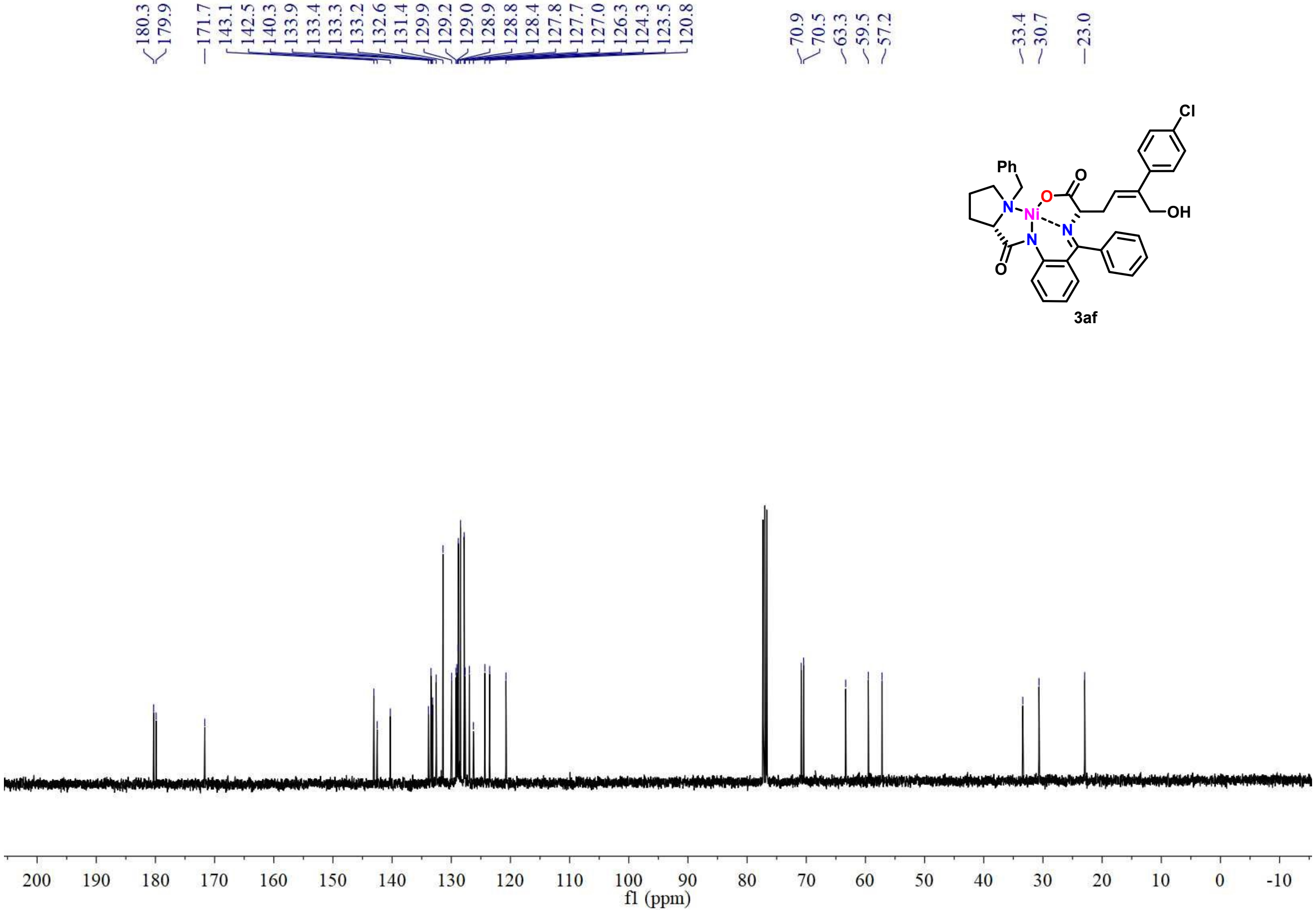
^{13}C NMR spectrum of **3ae** in $CDCl_3$



^{1}H NMR spectrum of **3af** in $CDCl_3$

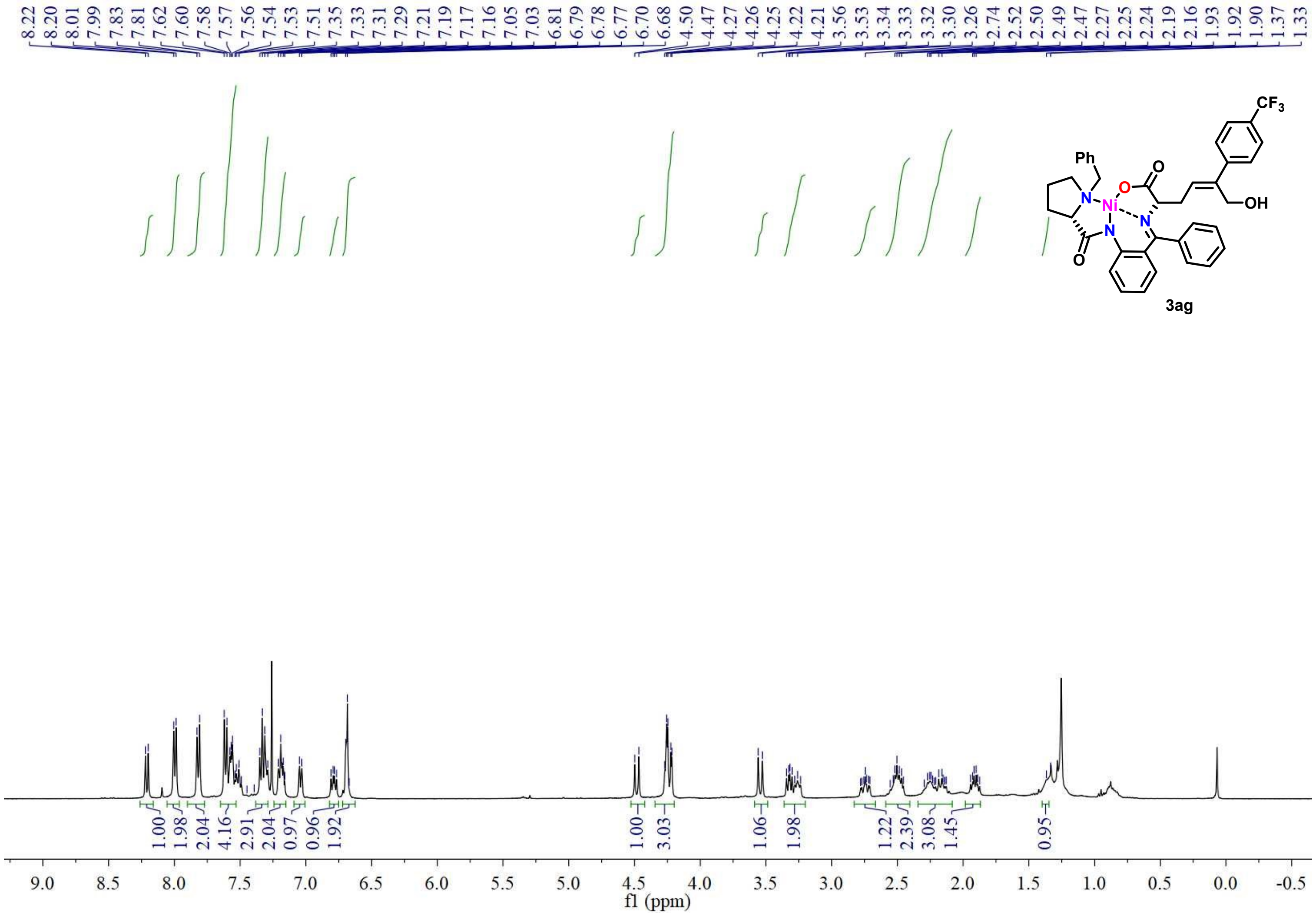


[13]C NMR spectrum of **3af** in $CDCl_3$

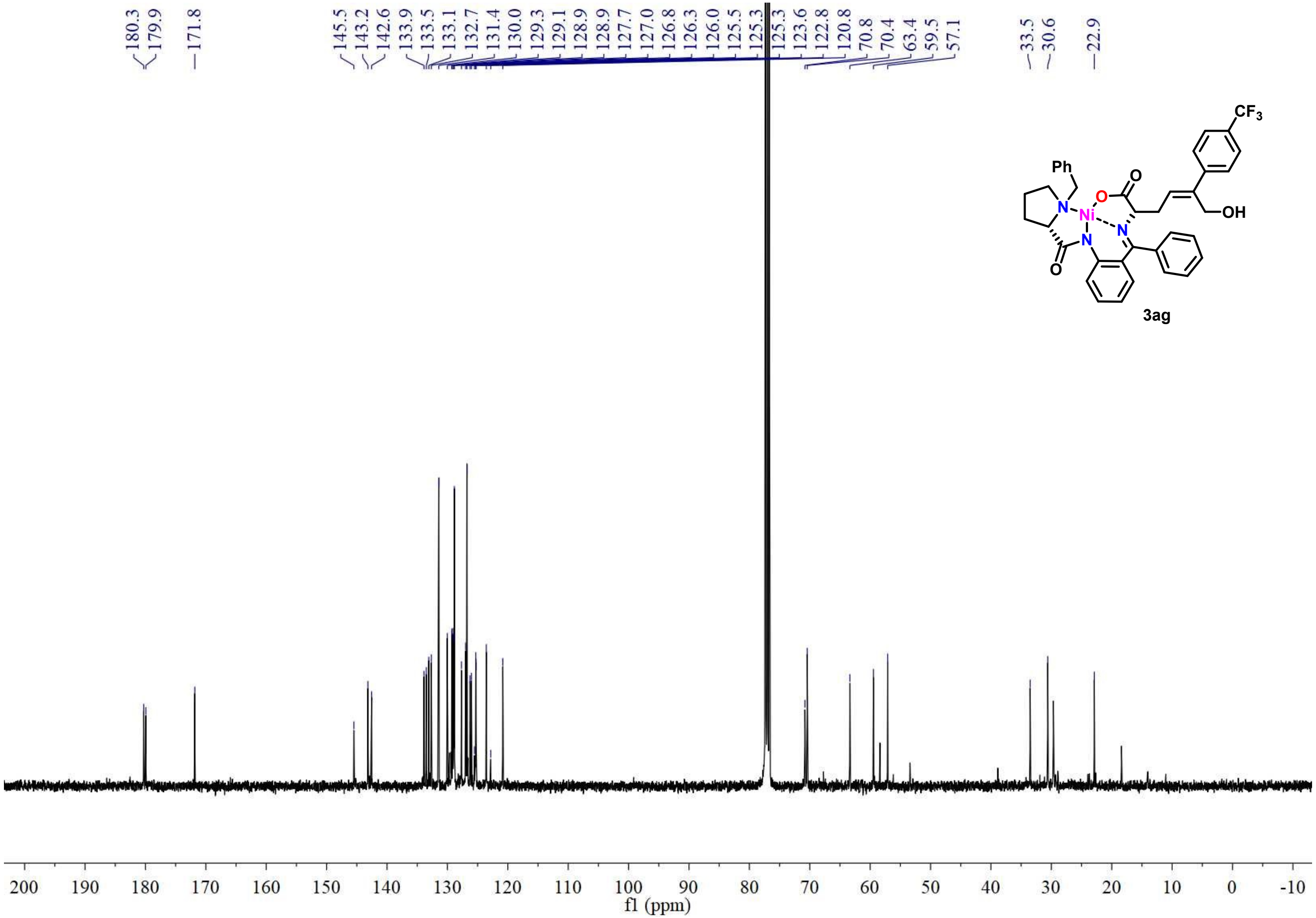


3af

^{1}H NMR spectrum of **3ag** in $CDCl_3$

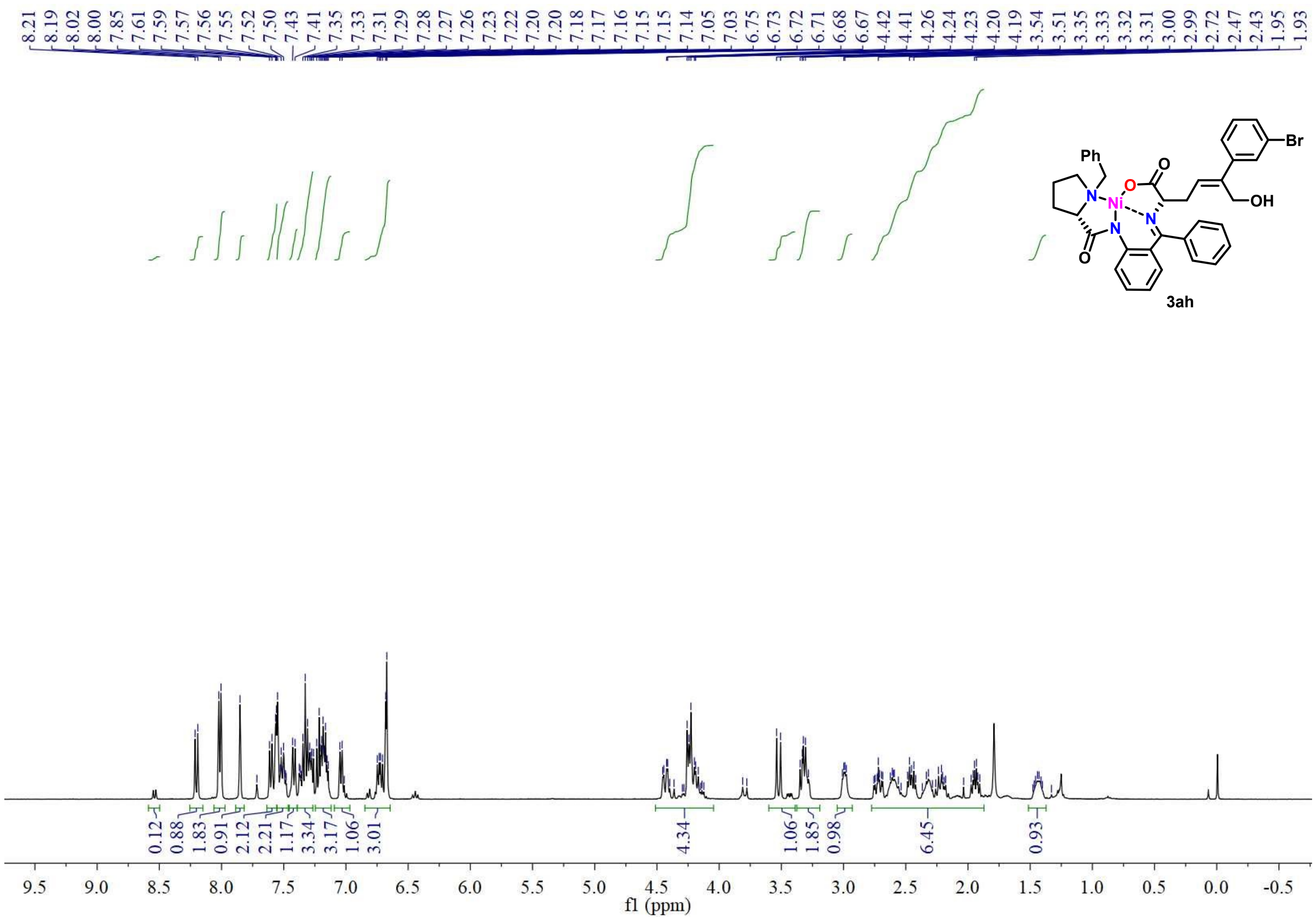


^{13}C NMR spectrum of **3ag** in $CDCl_3$

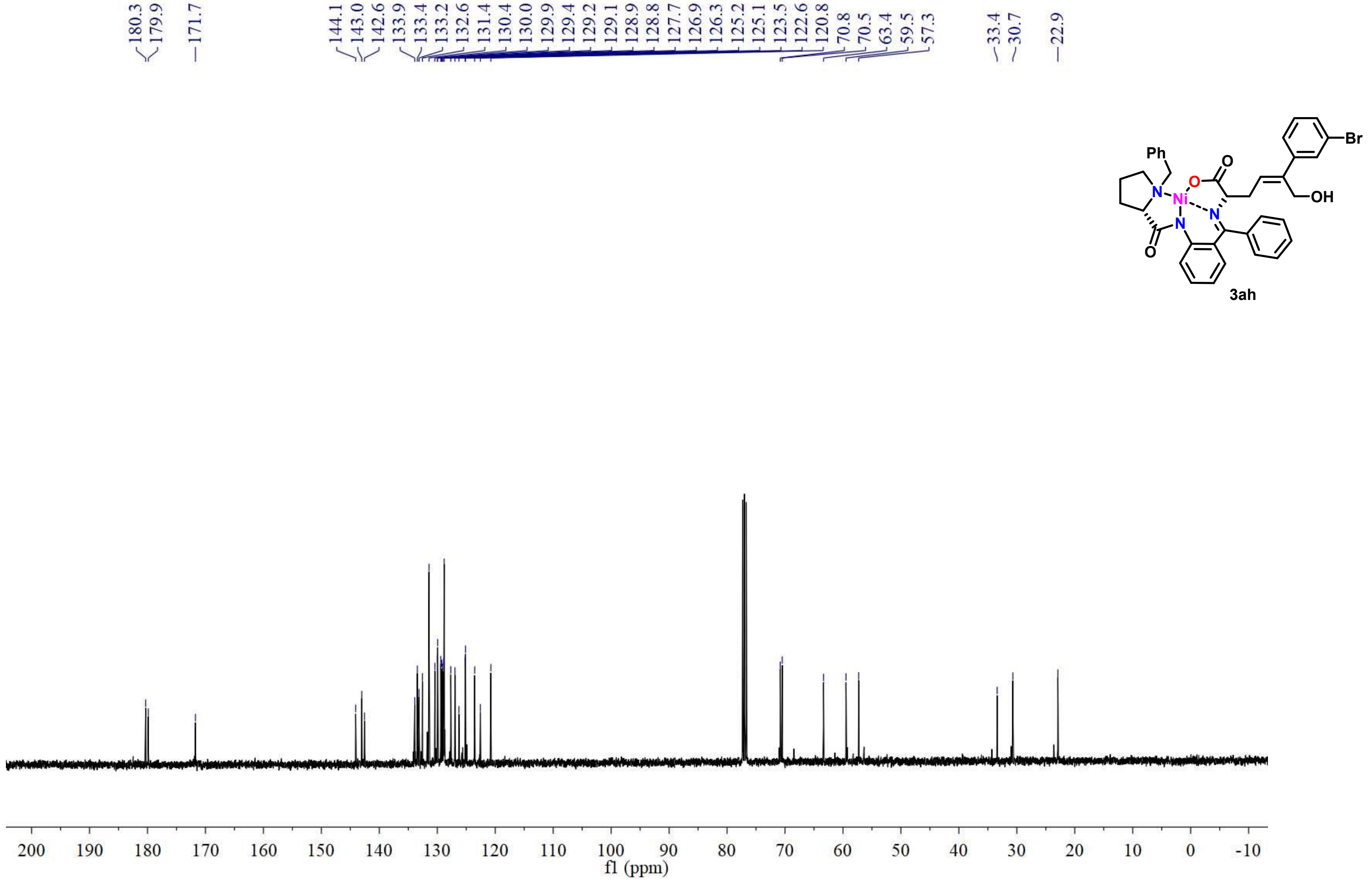


3ag

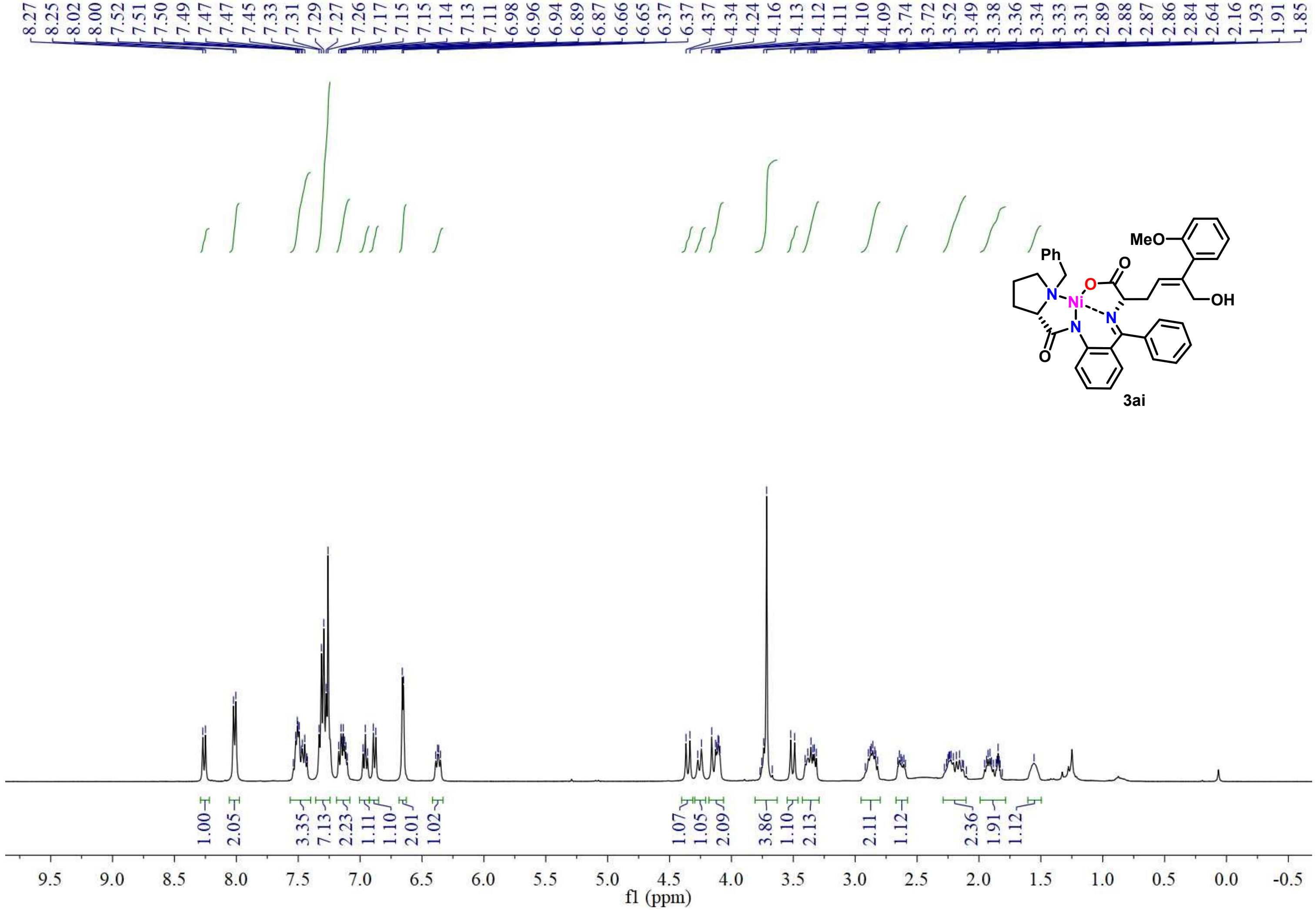
^{1}H NMR spectrum of **3ah** in $CDCl_3$



^{13}C NMR spectrum of **3ah** in $CDCl_3$

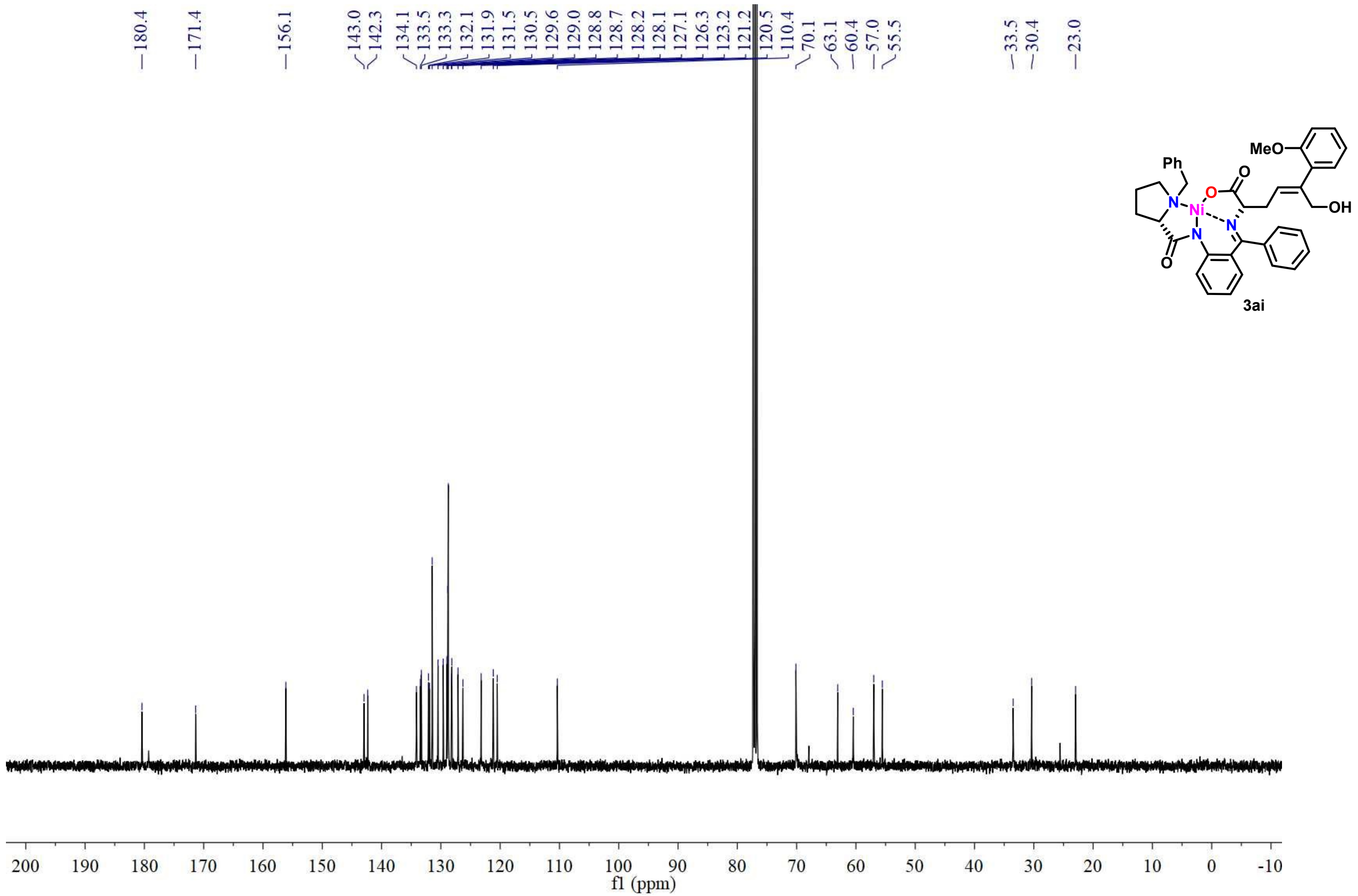


^{1}H NMR spectrum of **3ai** in $CDCl_3$

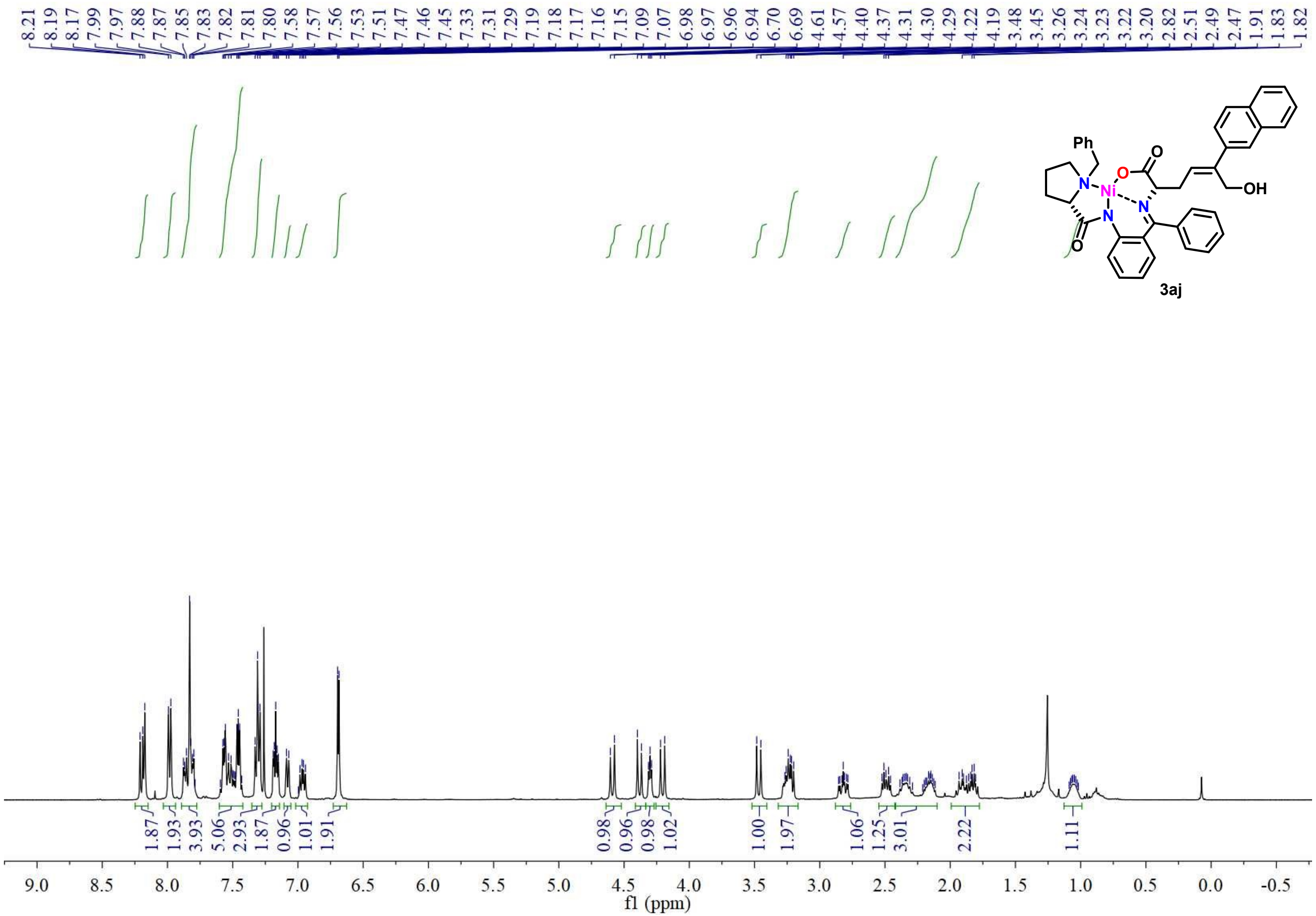


3ai

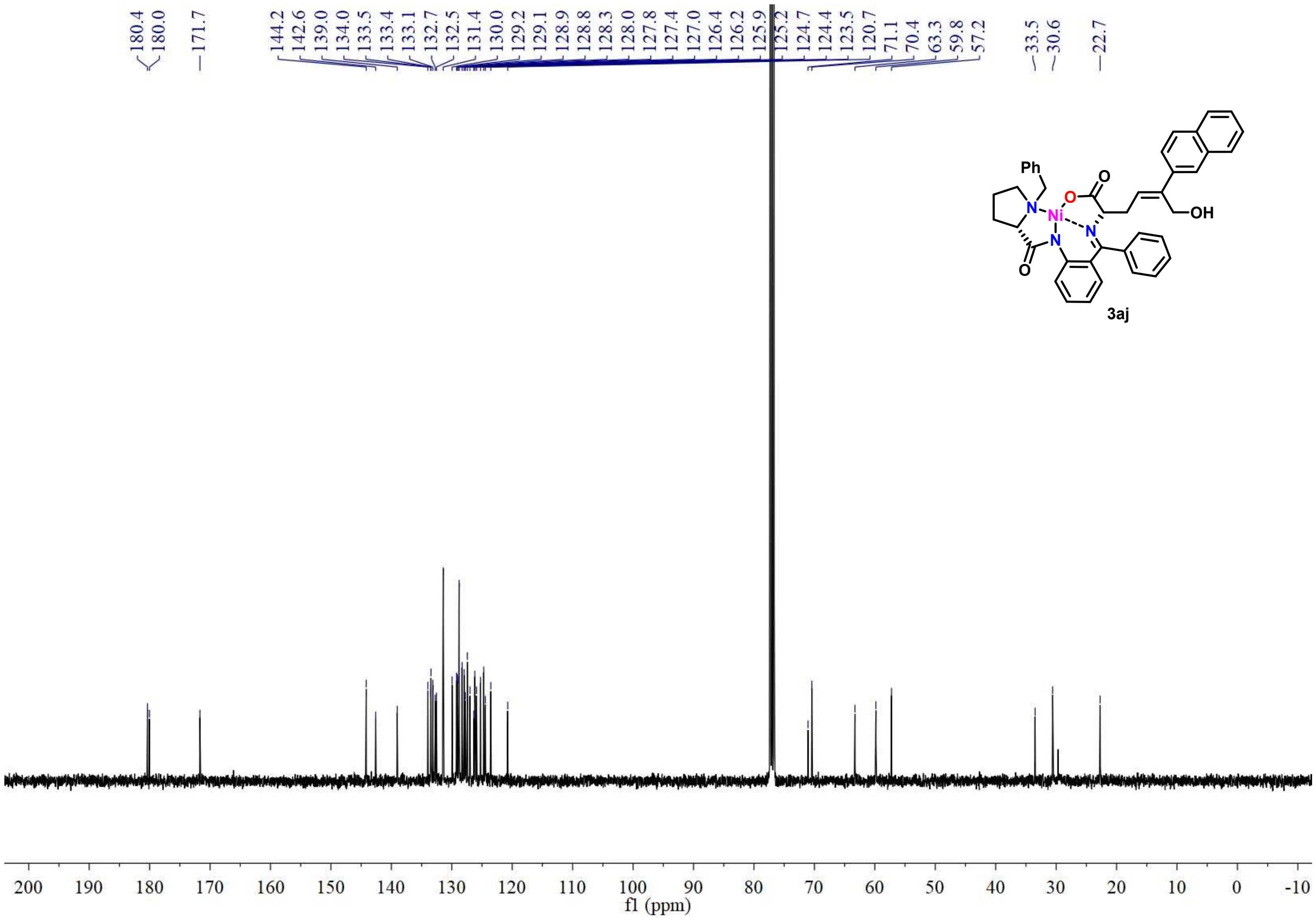
^{13}C NMR spectrum of **3ai** in $CDCl_3$



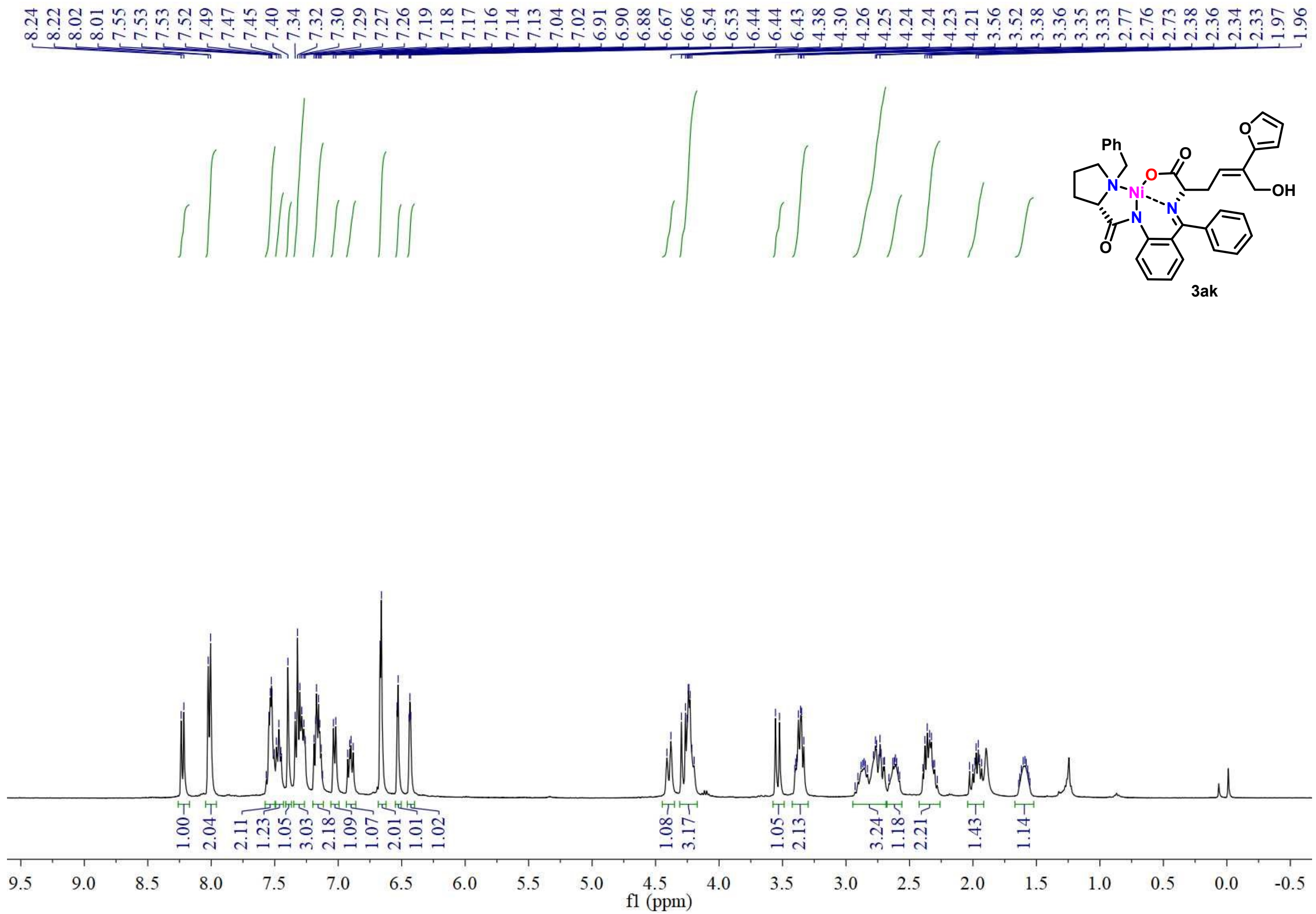
^{1}H NMR spectrum of **3aj** in $CDCl_3$



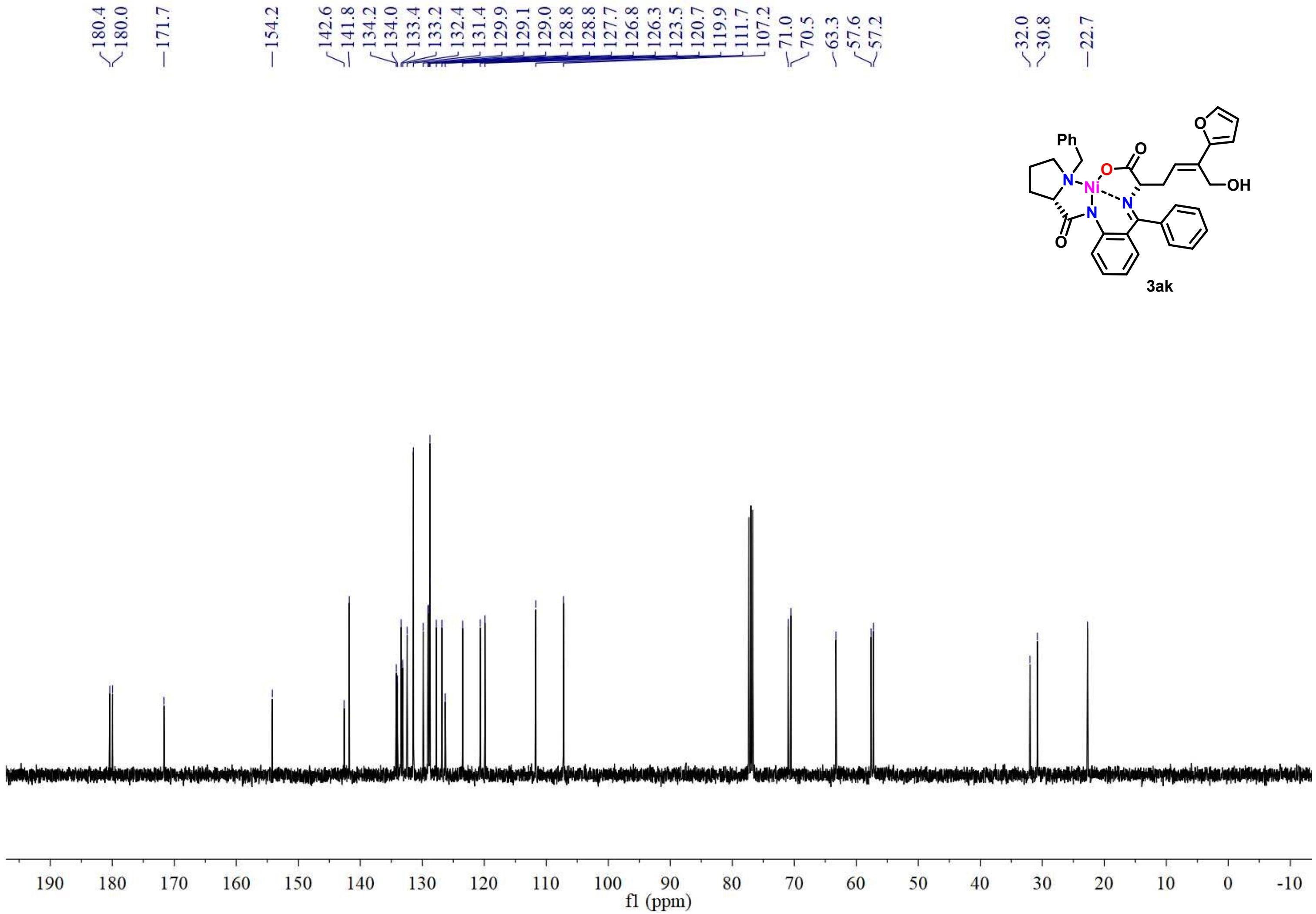
^{13}C NMR spectrum of **3aj** in $CDCl_3$



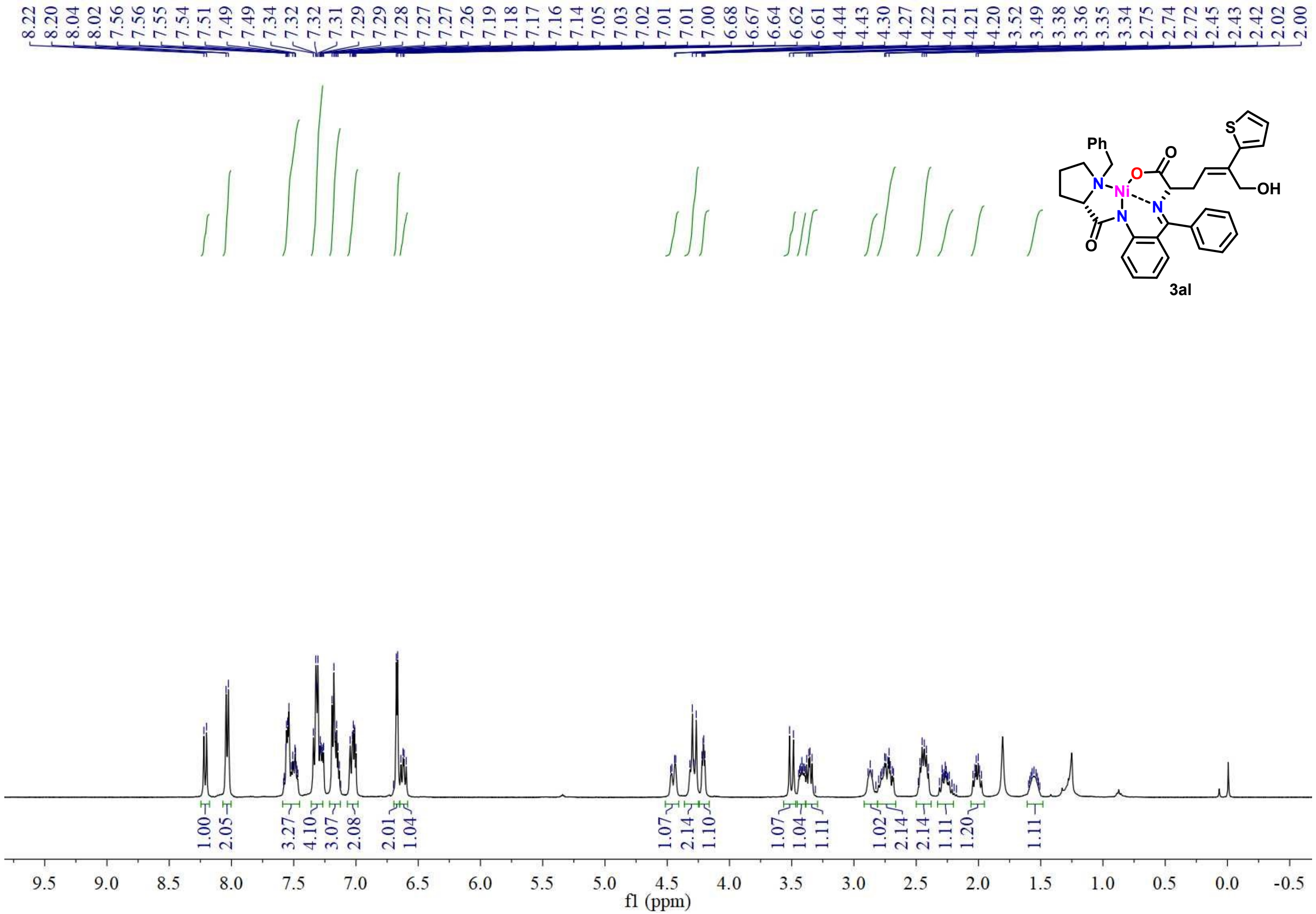
^{1}H NMR spectrum of **3ak** in $CDCl_3$



^{13}C NMR spectrum of **3ak** in $CDCl_3$

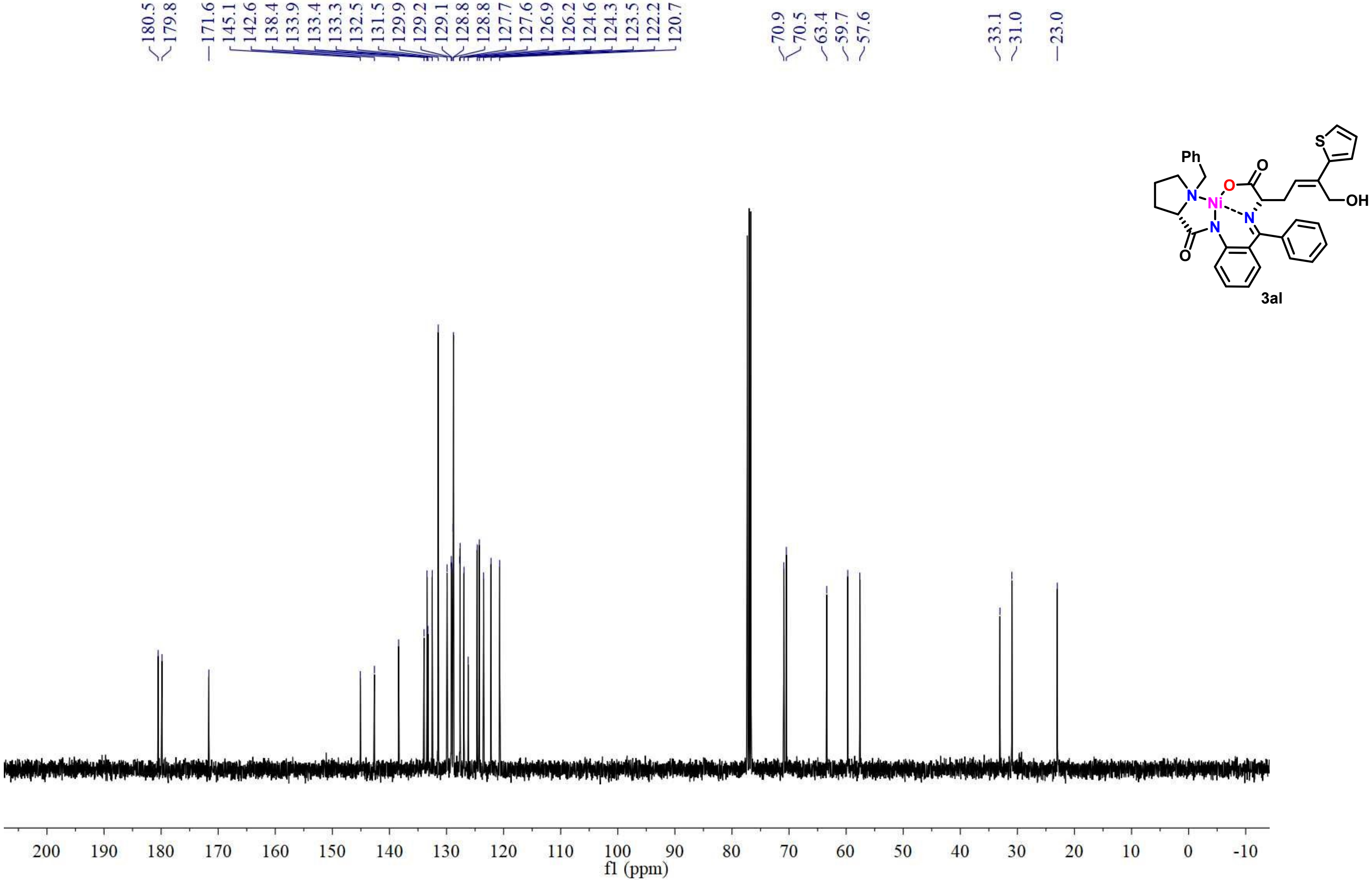


^{1}H NMR spectrum of **3al** in $CDCl_3$



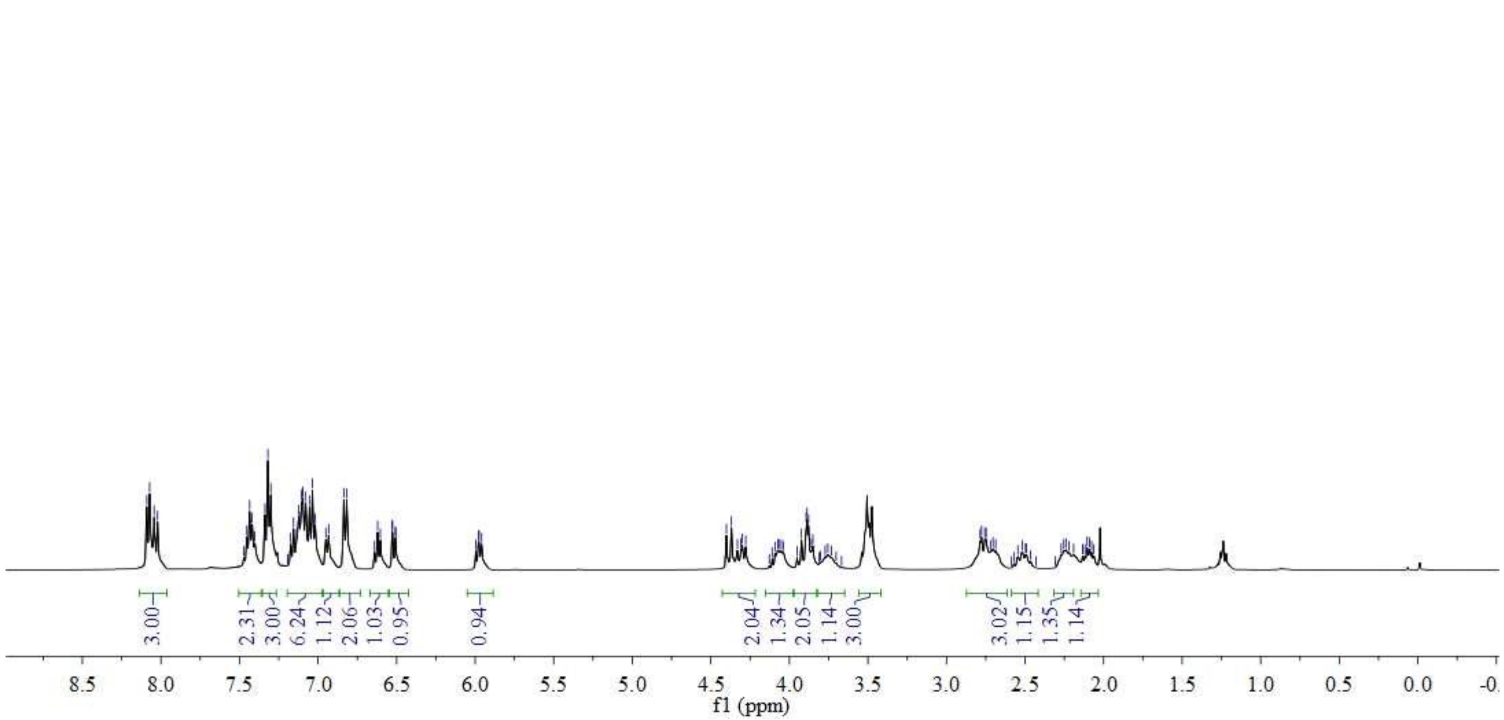
3al

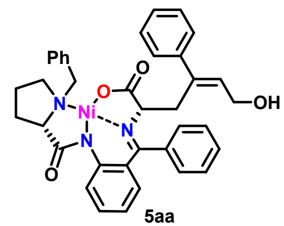
^{13}C NMR spectrum of **3al** in $CDCl_3$



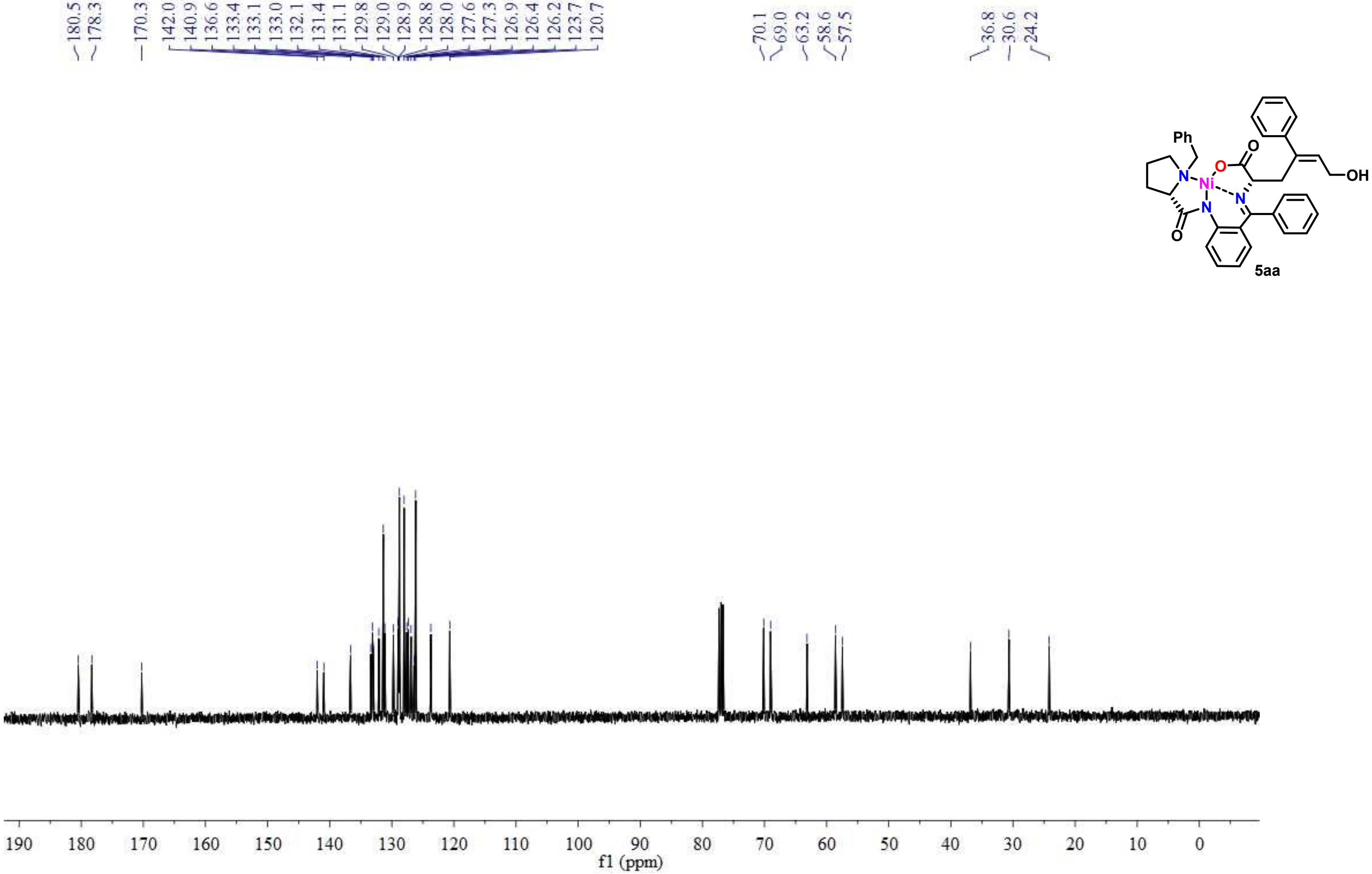
3al

^{1}**H NMR** spectrum of **5aa** in $CDCl_3$



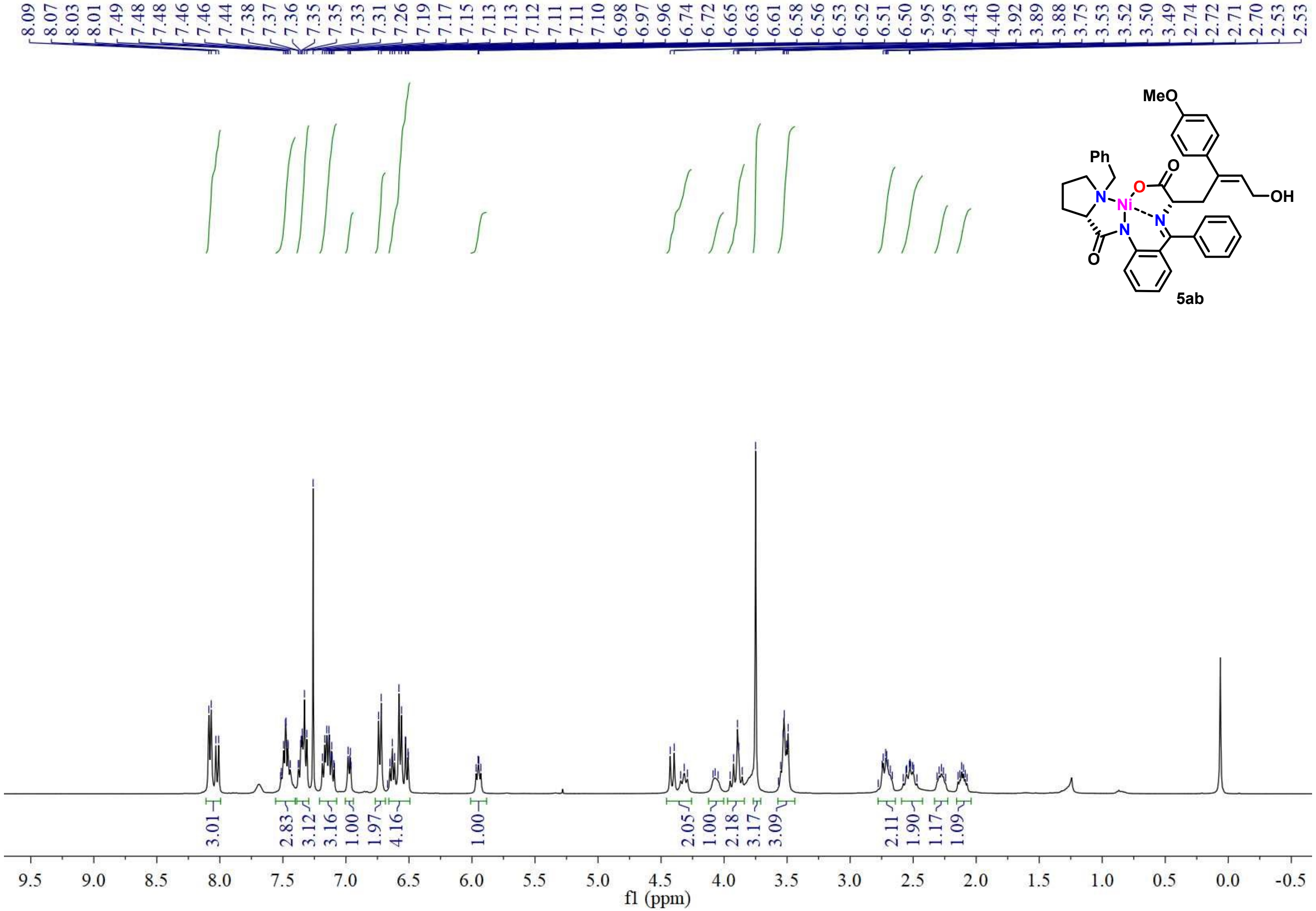


^{13}C NMR spectrum of **5aa** in $CDCl_3$

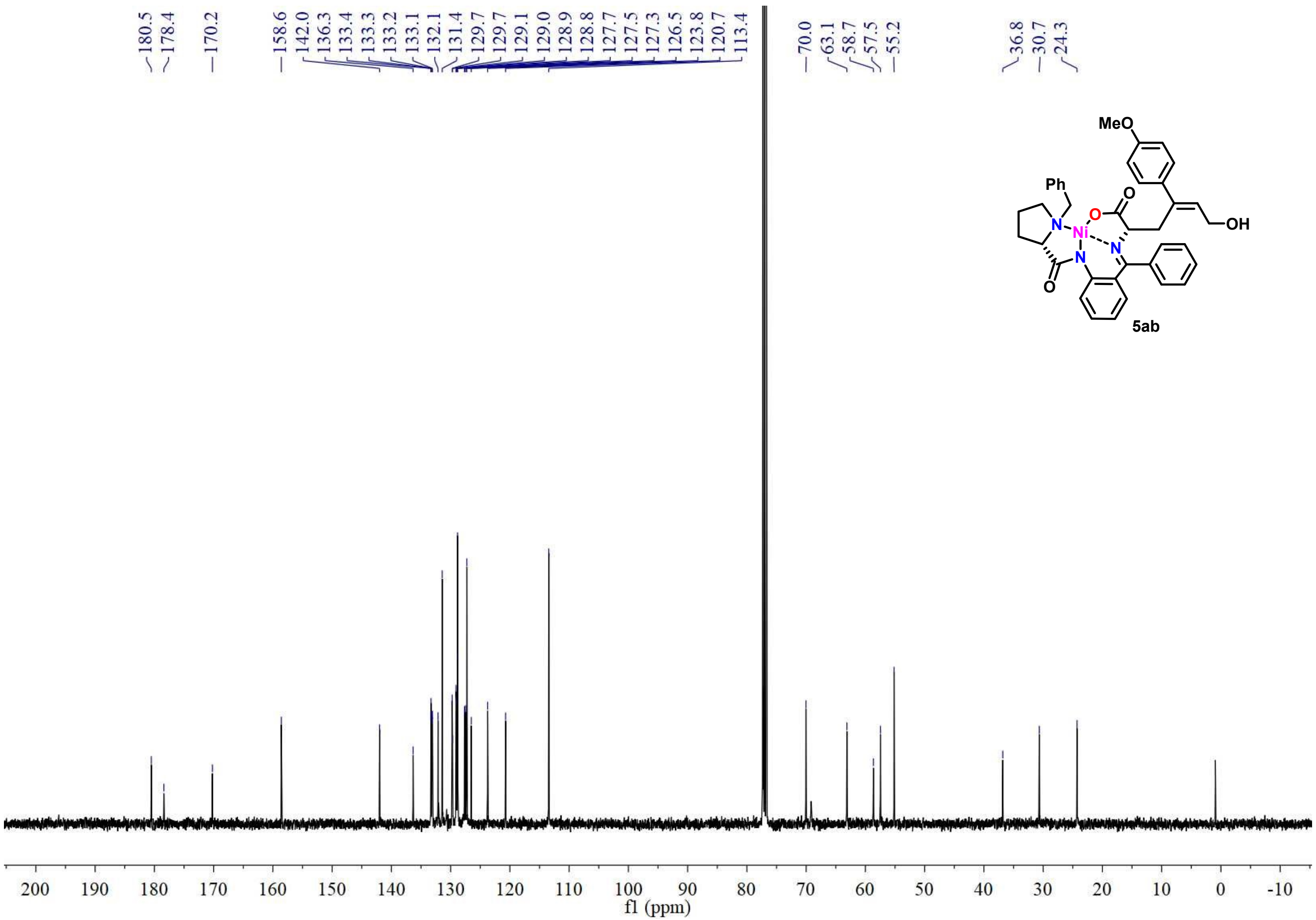


5aa

^{1}H NMR spectrum of **5ab** in $CDCl_3$

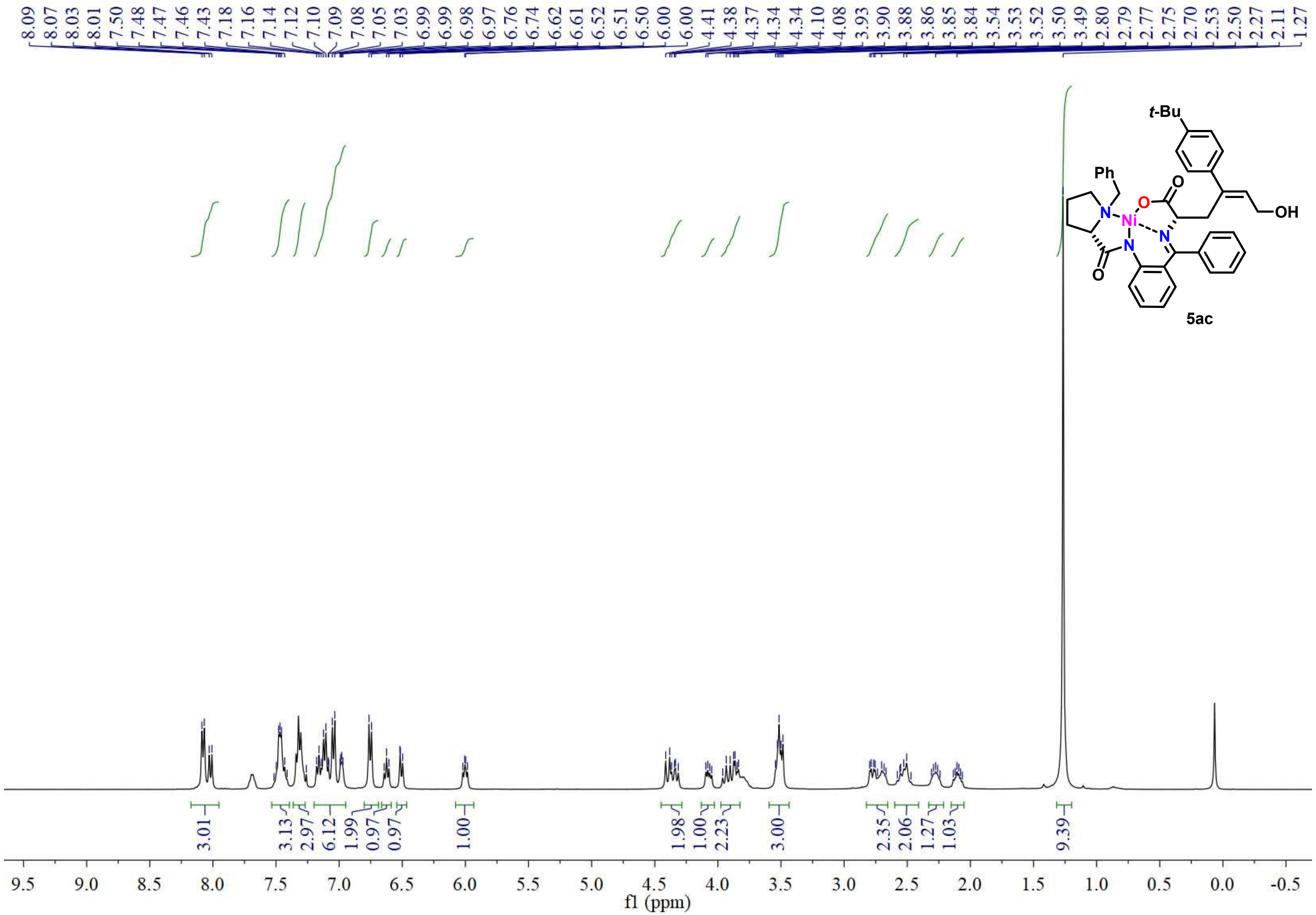


^{13}C NMR spectrum of **5ab** in $CDCl_3$

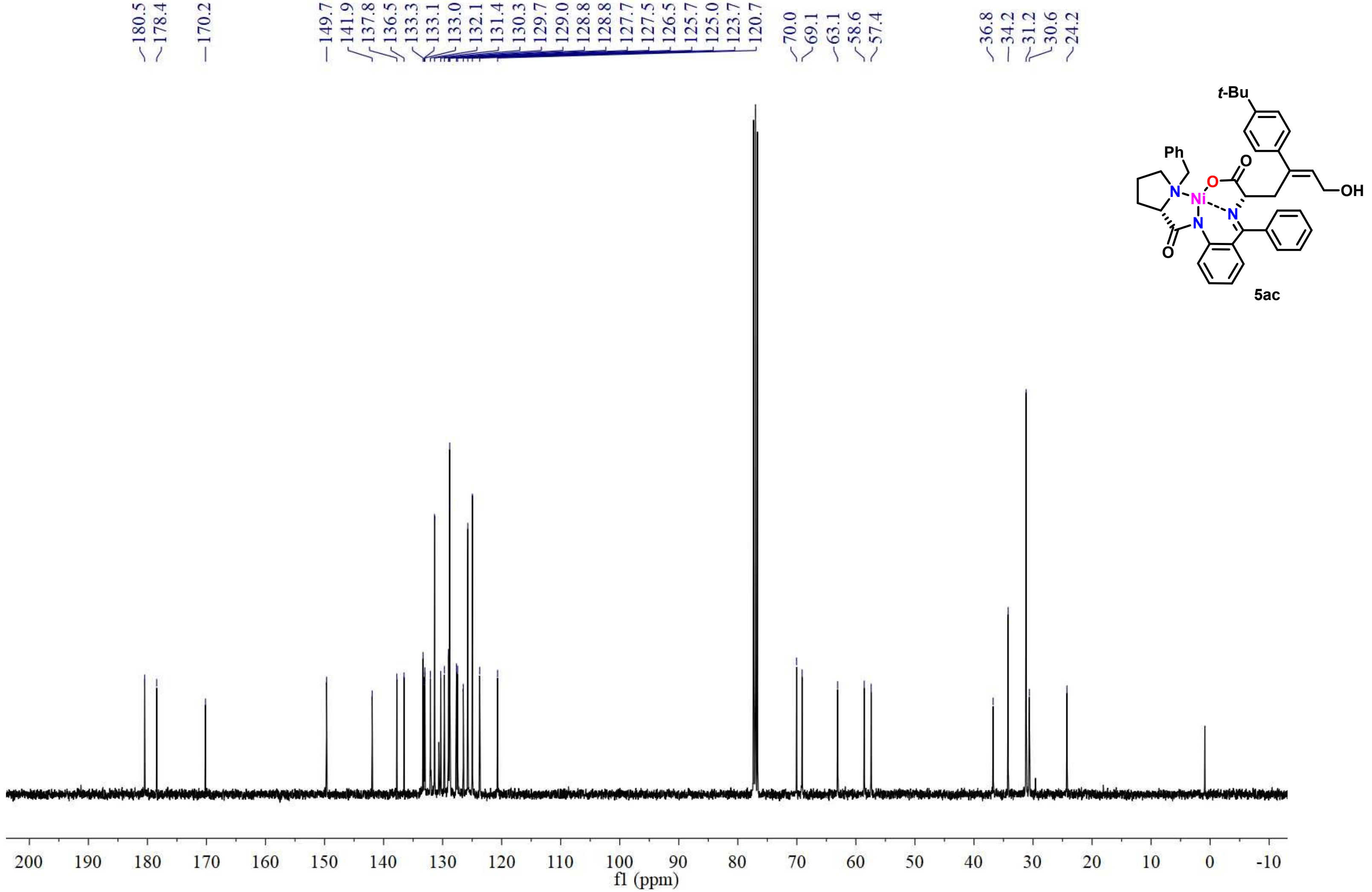


5ab

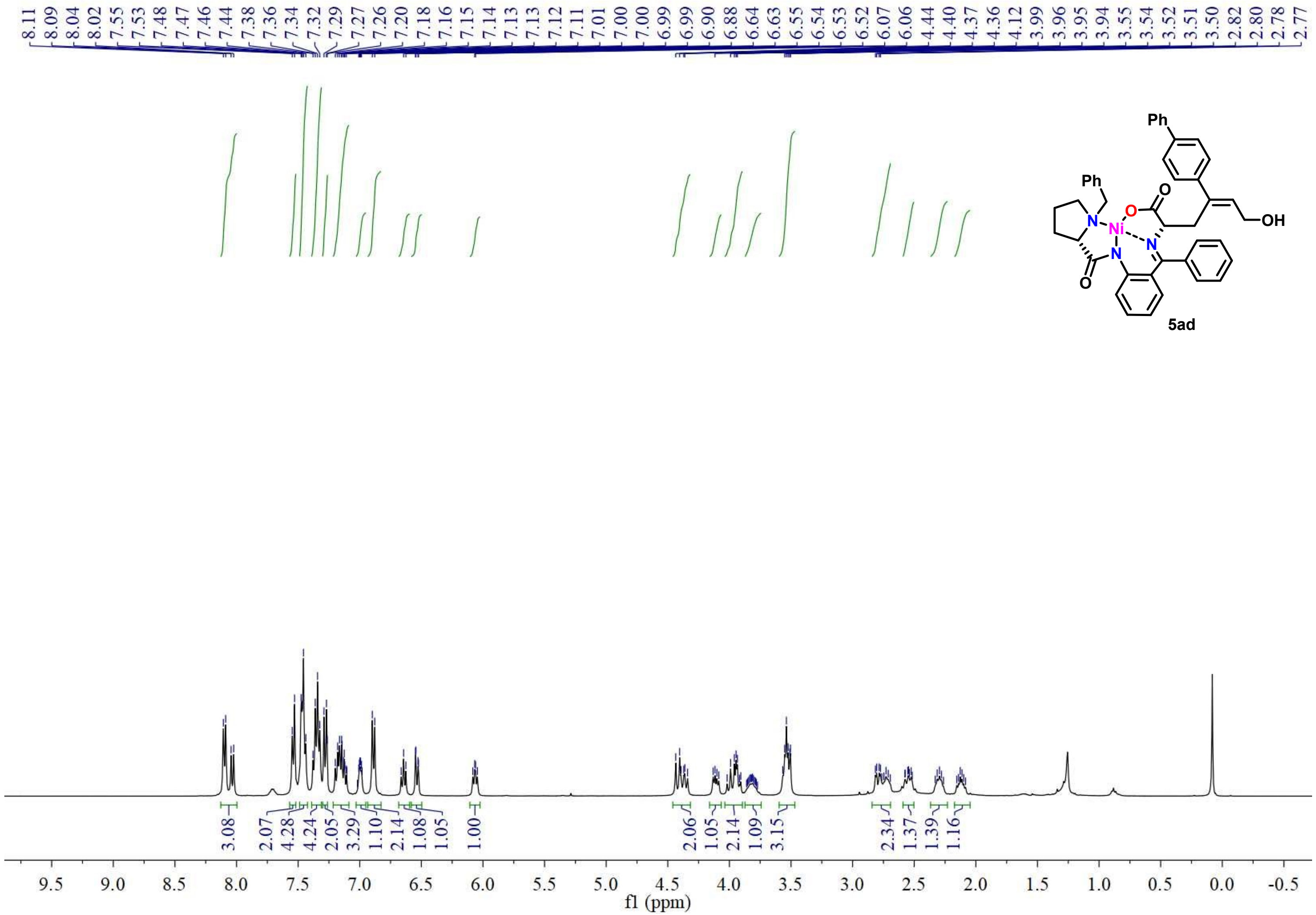
[1]H NMR spectrum of **5ac** in $CDCl_3$



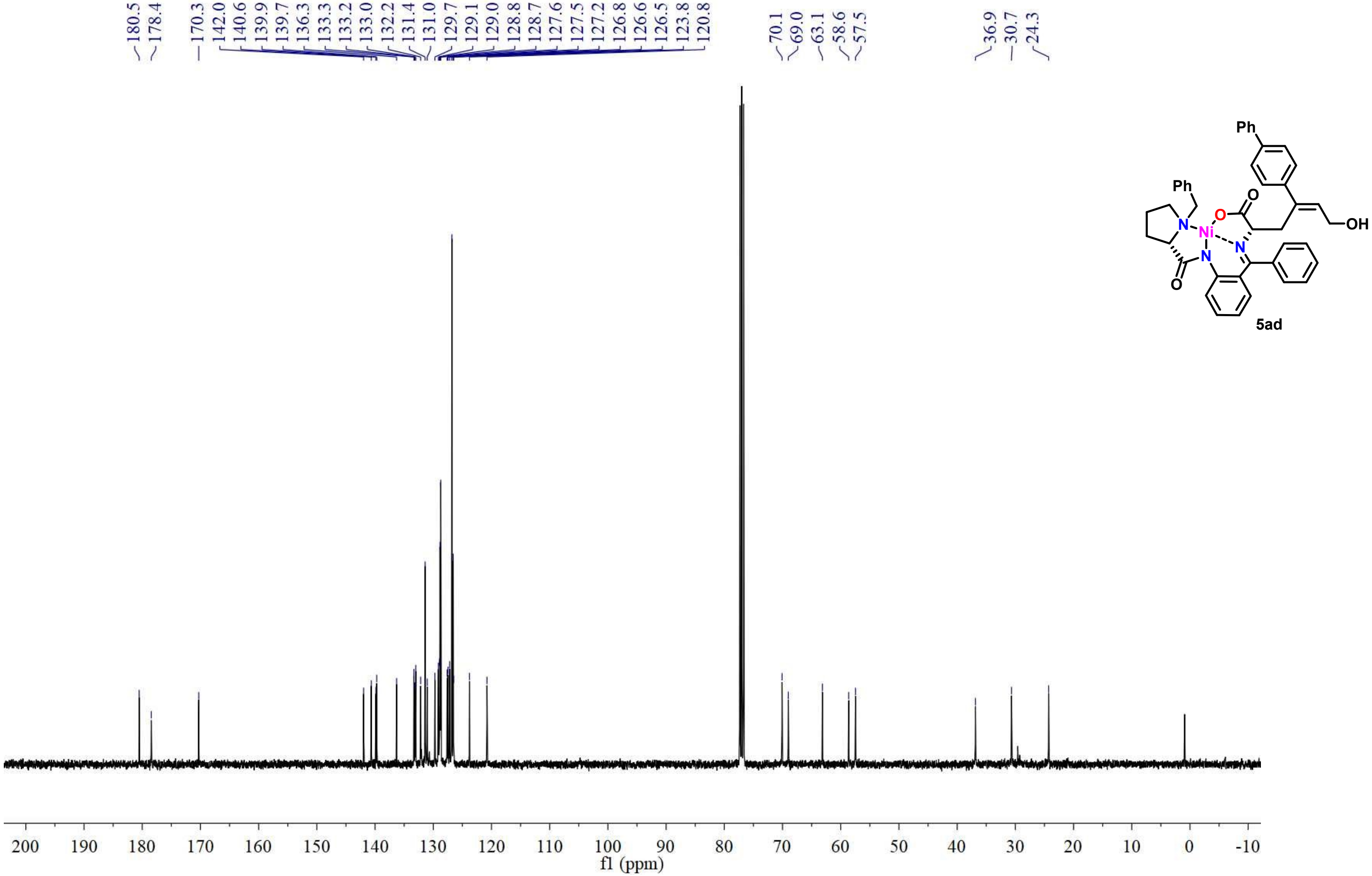
^{13}**C NMR** spectrum of **5ac** in $CDCl_3$



^{1}H NMR spectrum of **5ad** in $CDCl_3$

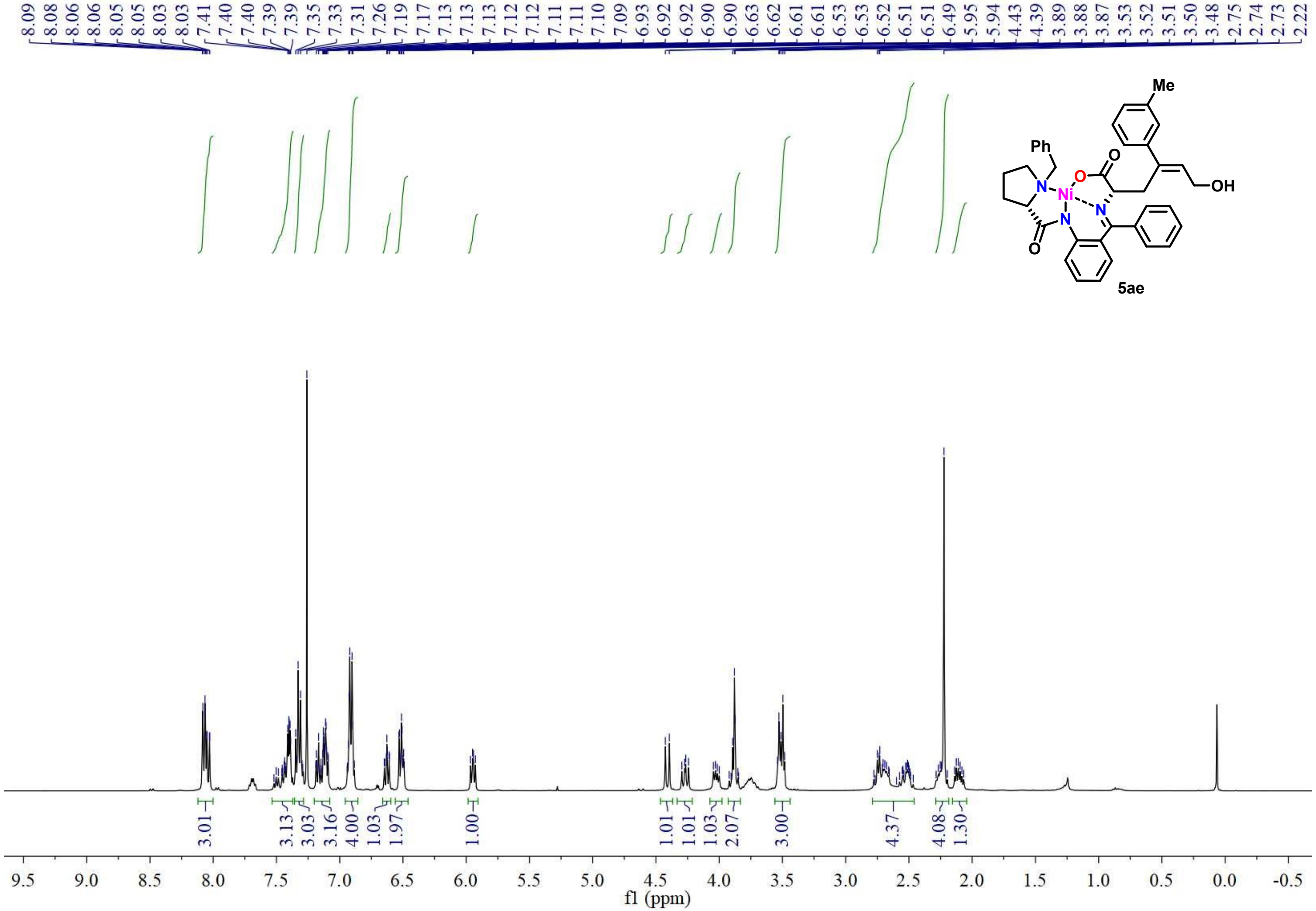


^{13}C NMR spectrum of **5ad** in $CDCl_3$

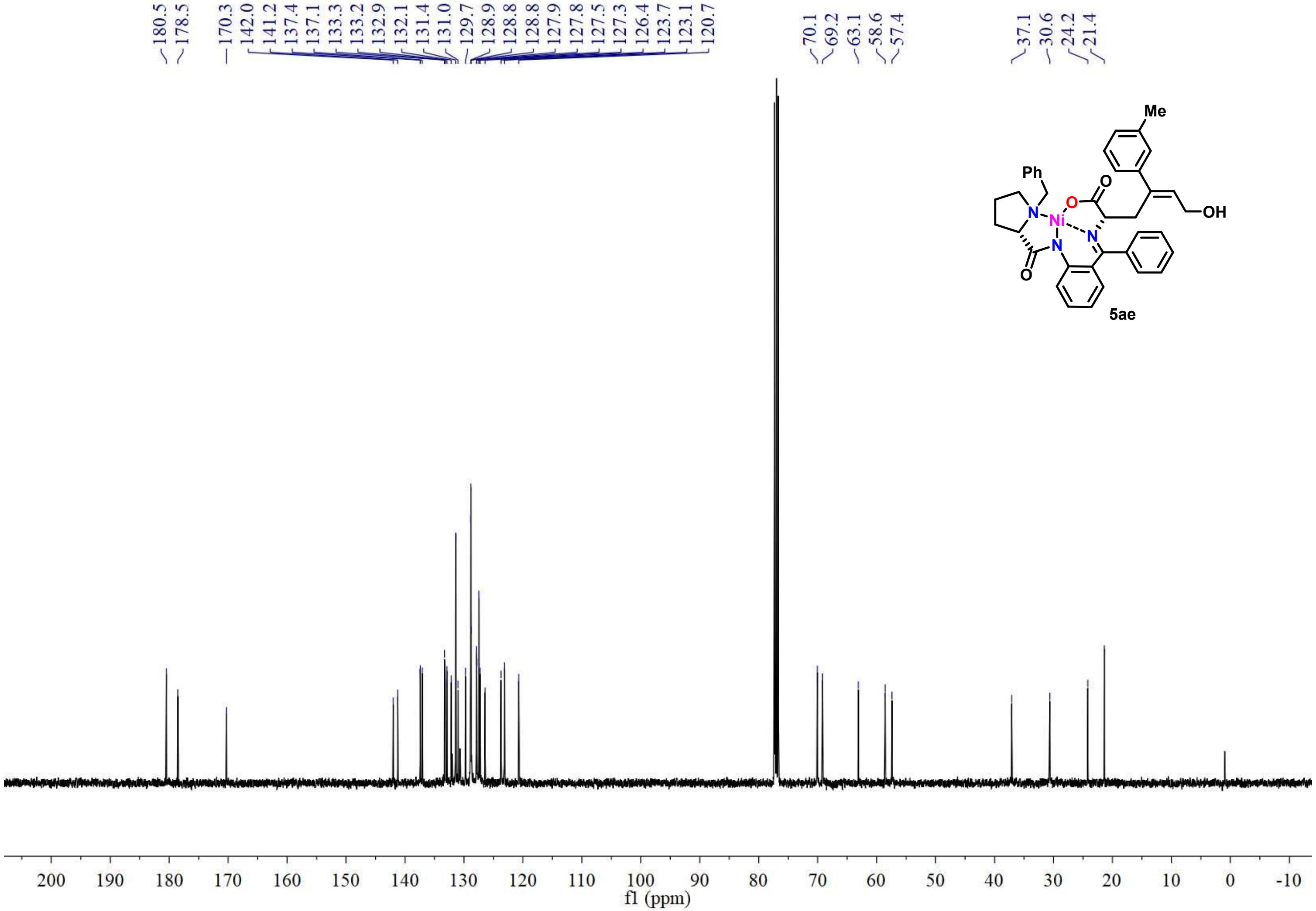


5ad

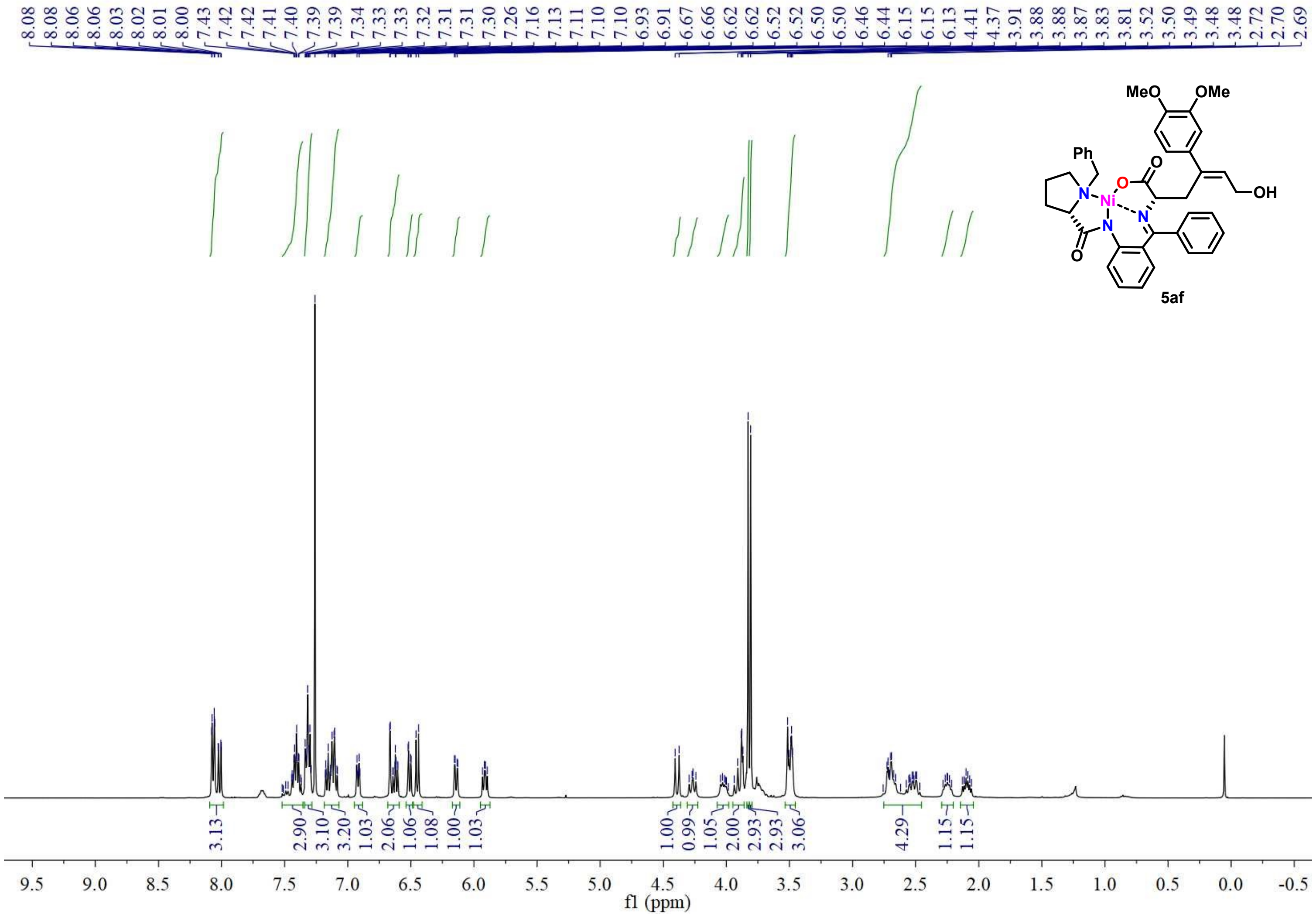
^{1}H NMR spectrum of **5ae** in $CDCl_3$



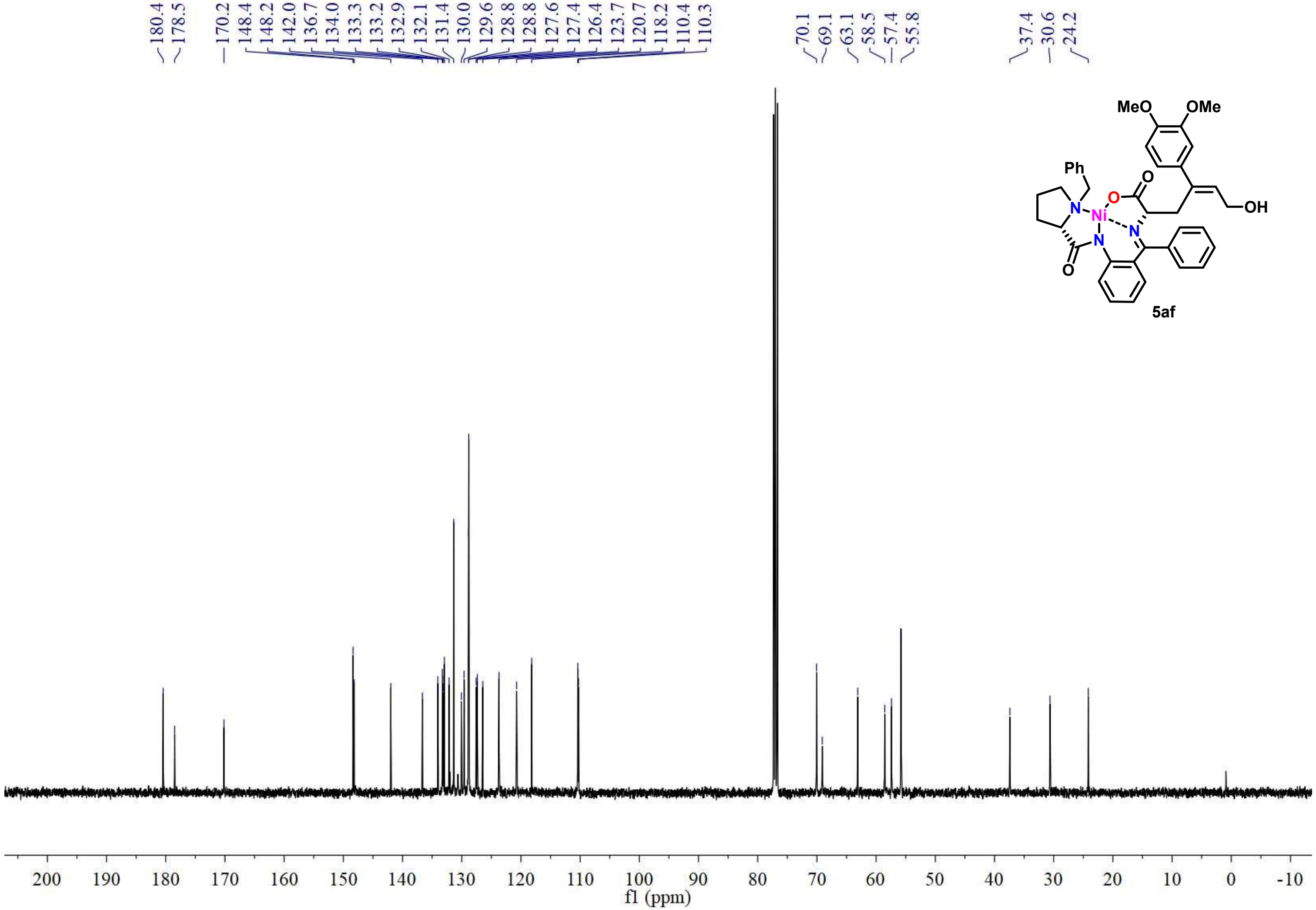
^{13}C NMR spectrum of **5ae** in $CDCl_3$



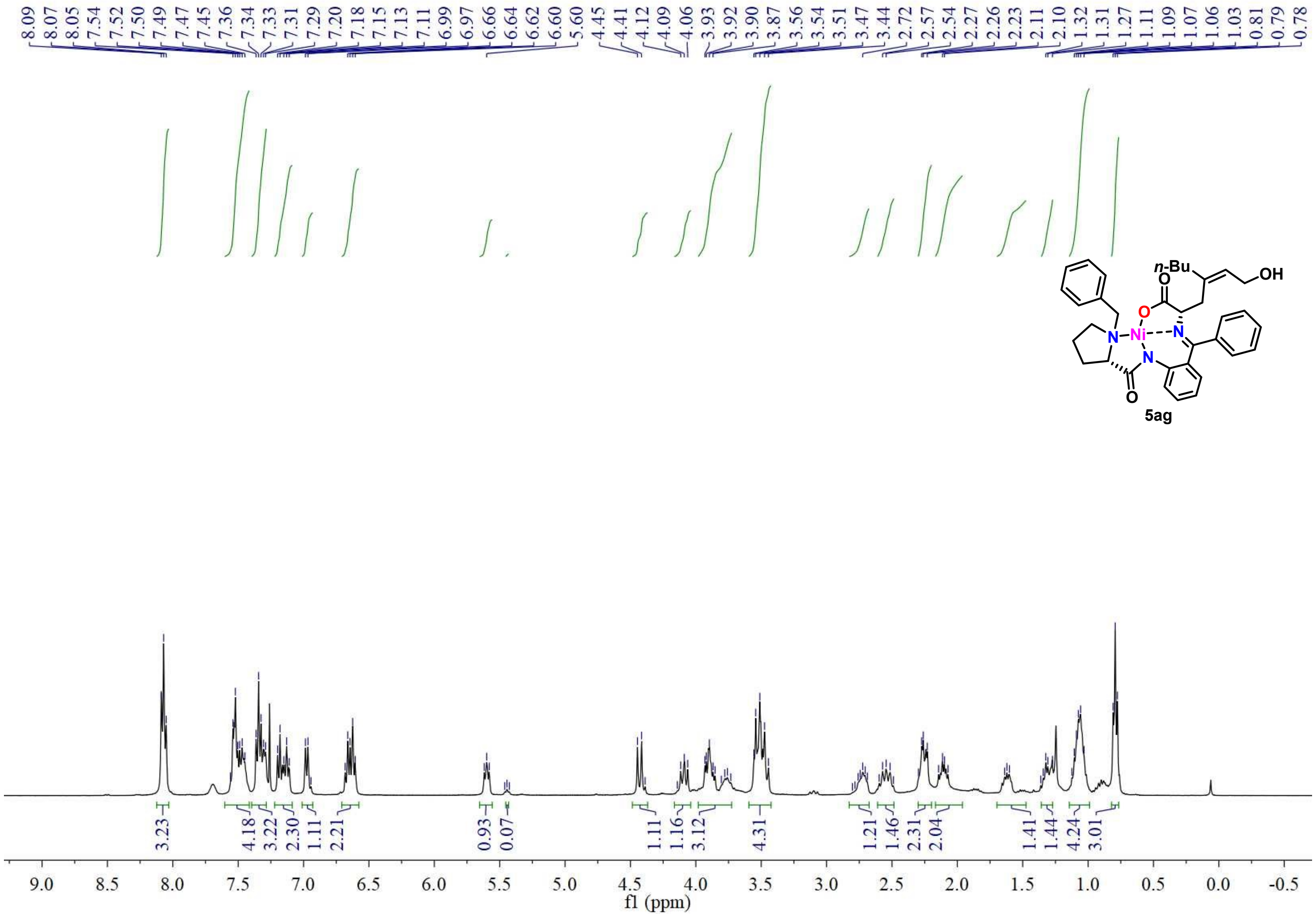
^{1}H NMR spectrum of **5af** in $CDCl_3$



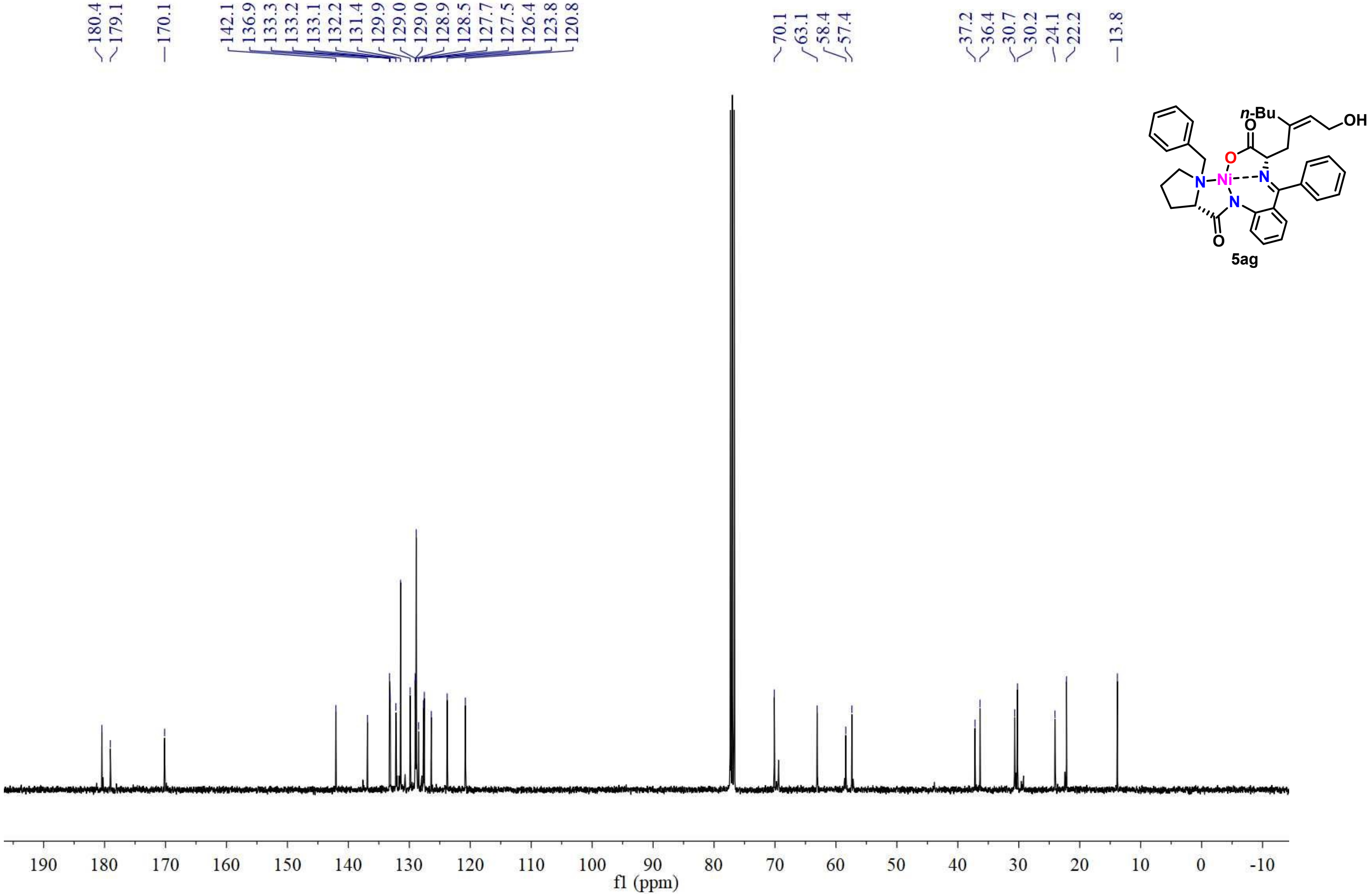
^{13}C NMR spectrum of **5af** in $CDCl_3$



^{1}H NMR spectrum of **5ag** in $CDCl_3$

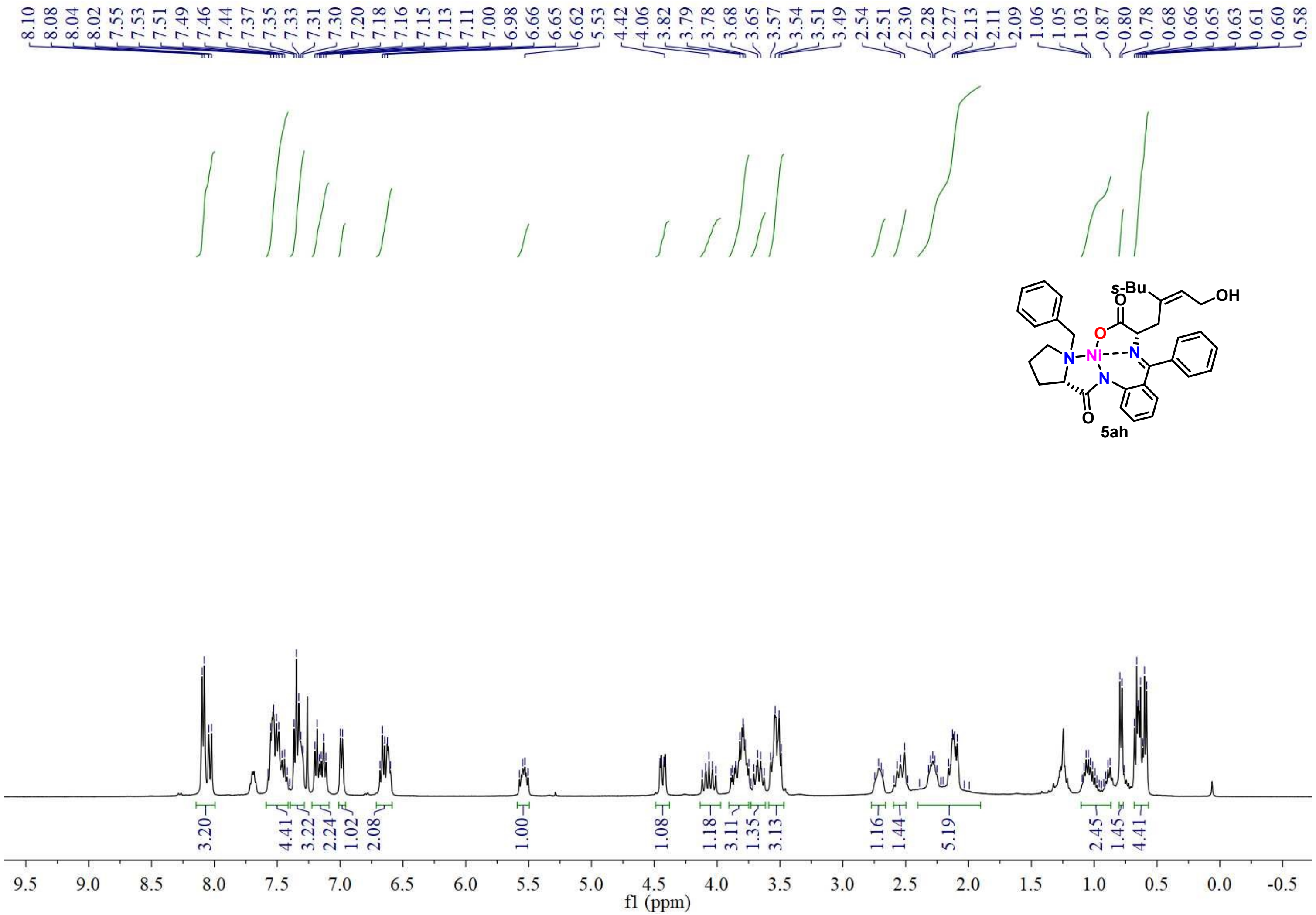


^{13}**C NMR** spectrum of **5ag** in $CDCl_3$

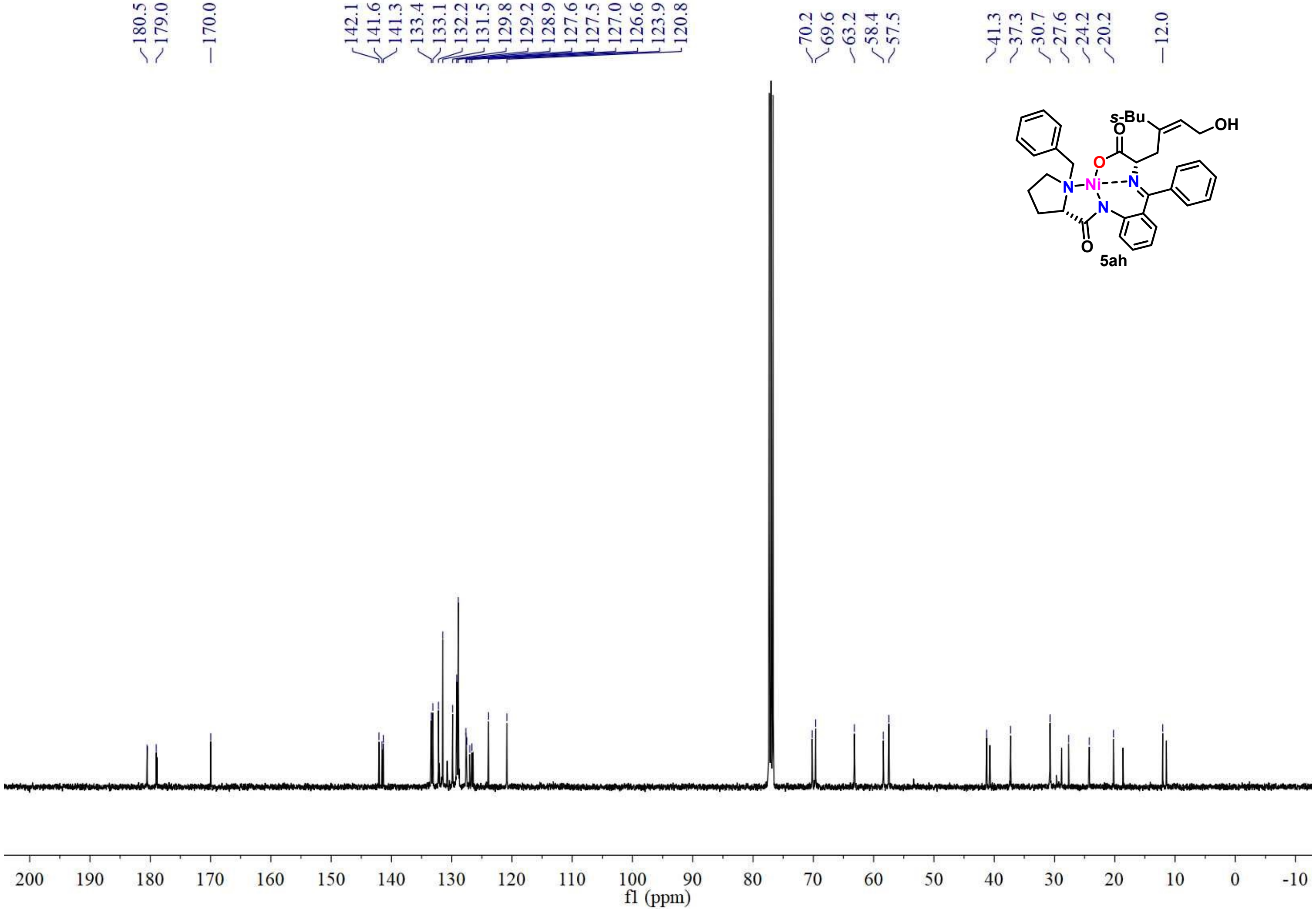


5ag

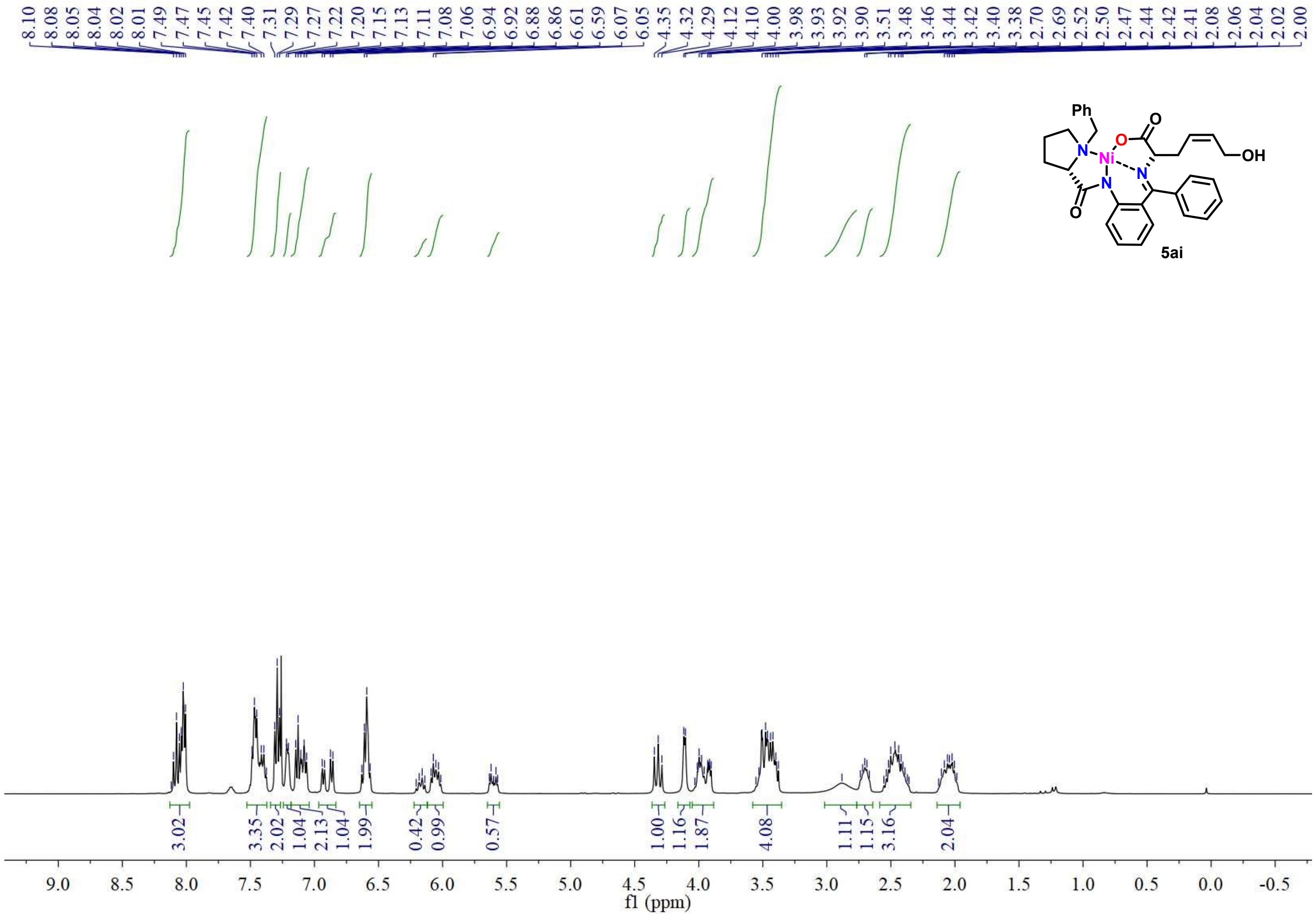
^{1}H NMR spectrum of **5ah** in $CDCl_3$



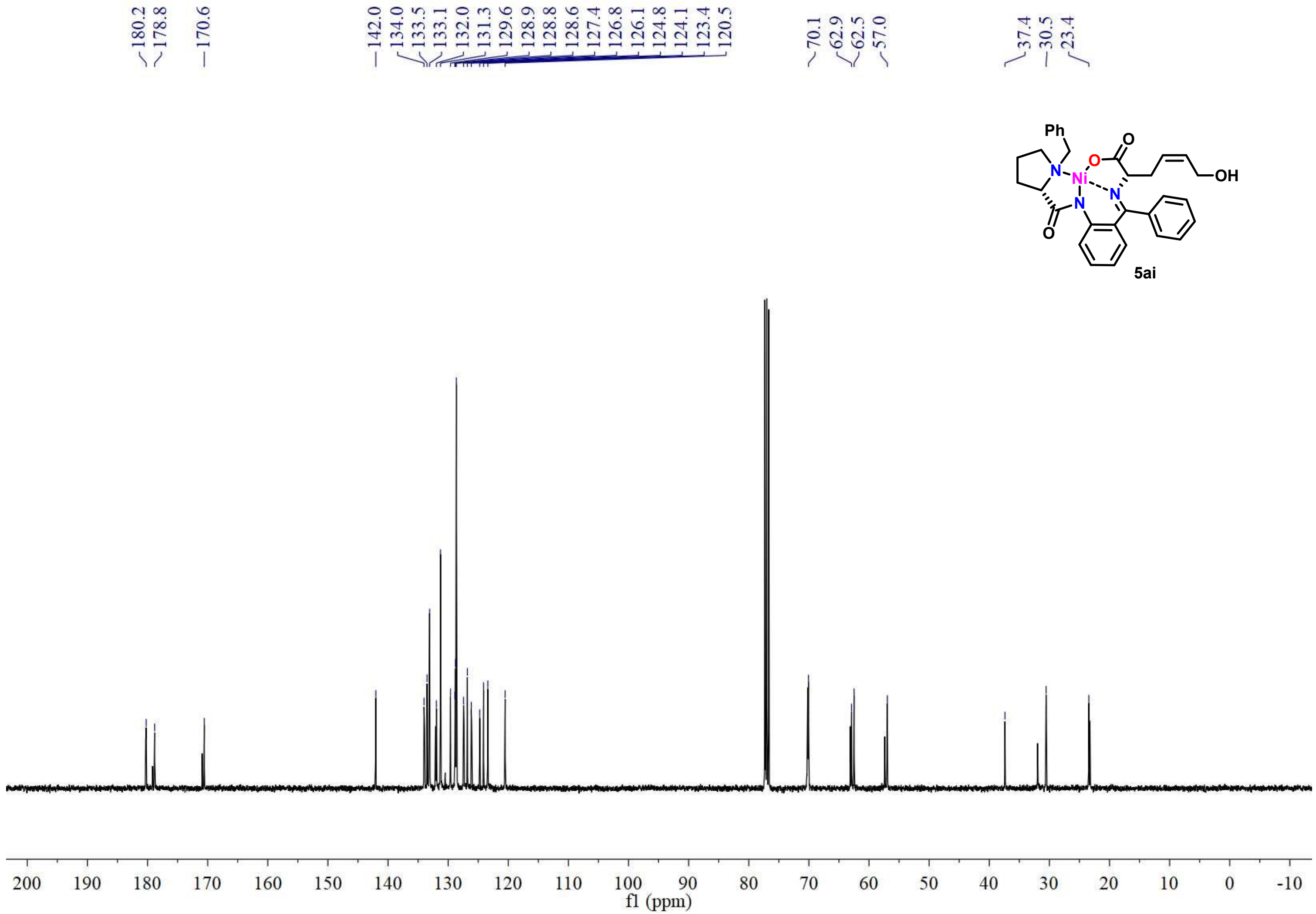
^{13}**C NMR** spectrum of **5ah** in $CDCl_3$



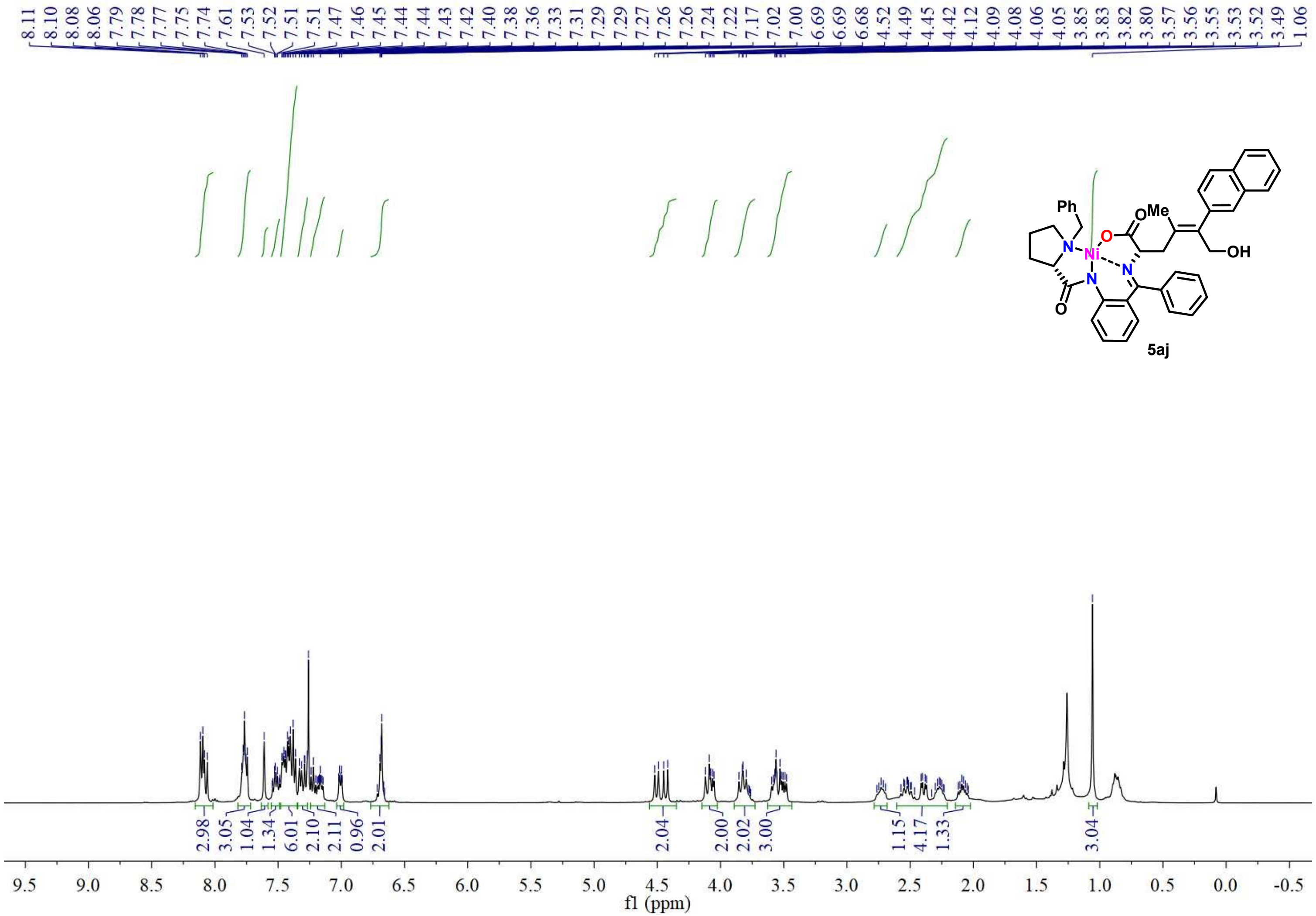
^{1}H NMR spectrum of **5ai** in $CDCl_3$



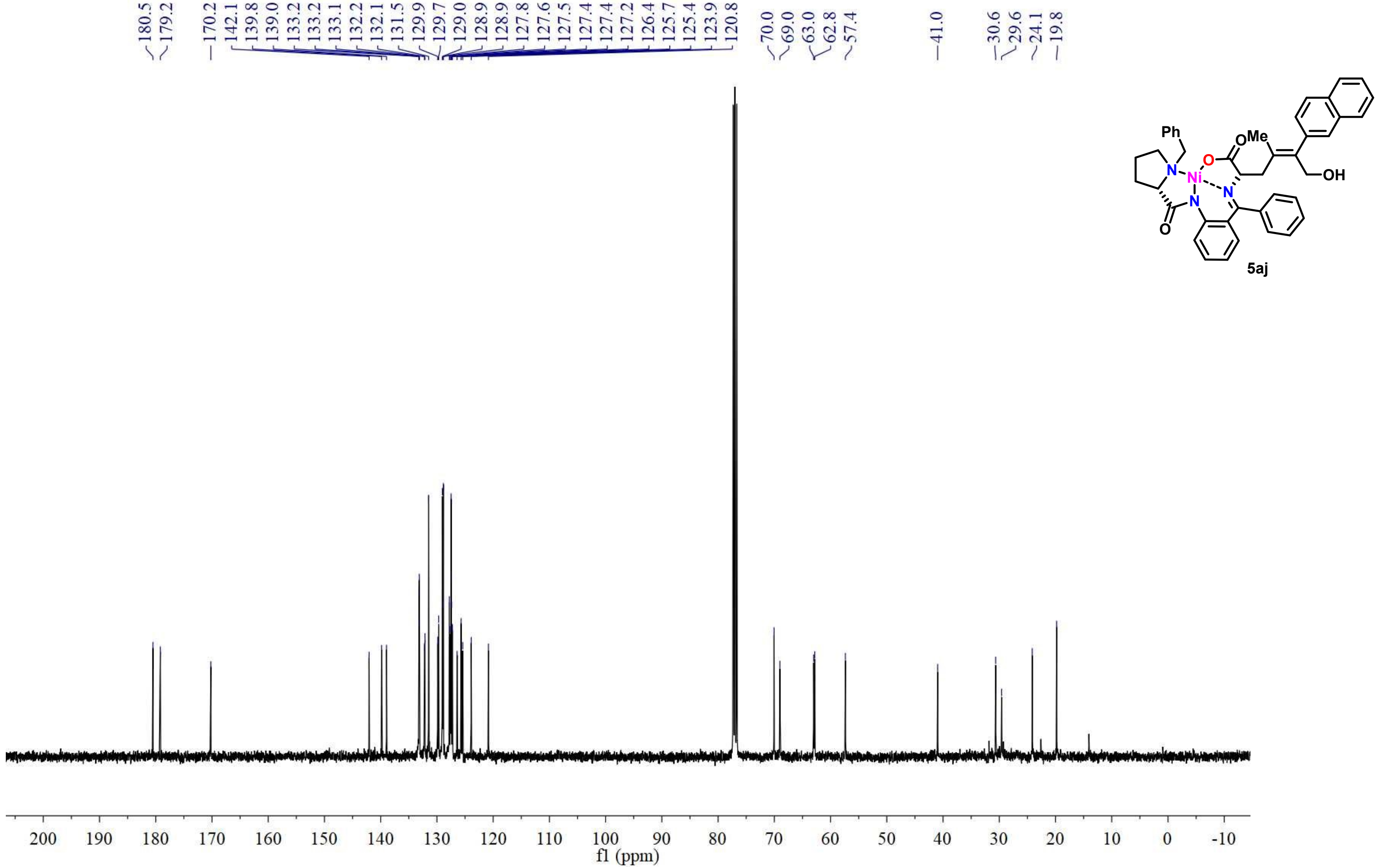
^{13}C NMR spectrum of **5ai** in $CDCl_3$



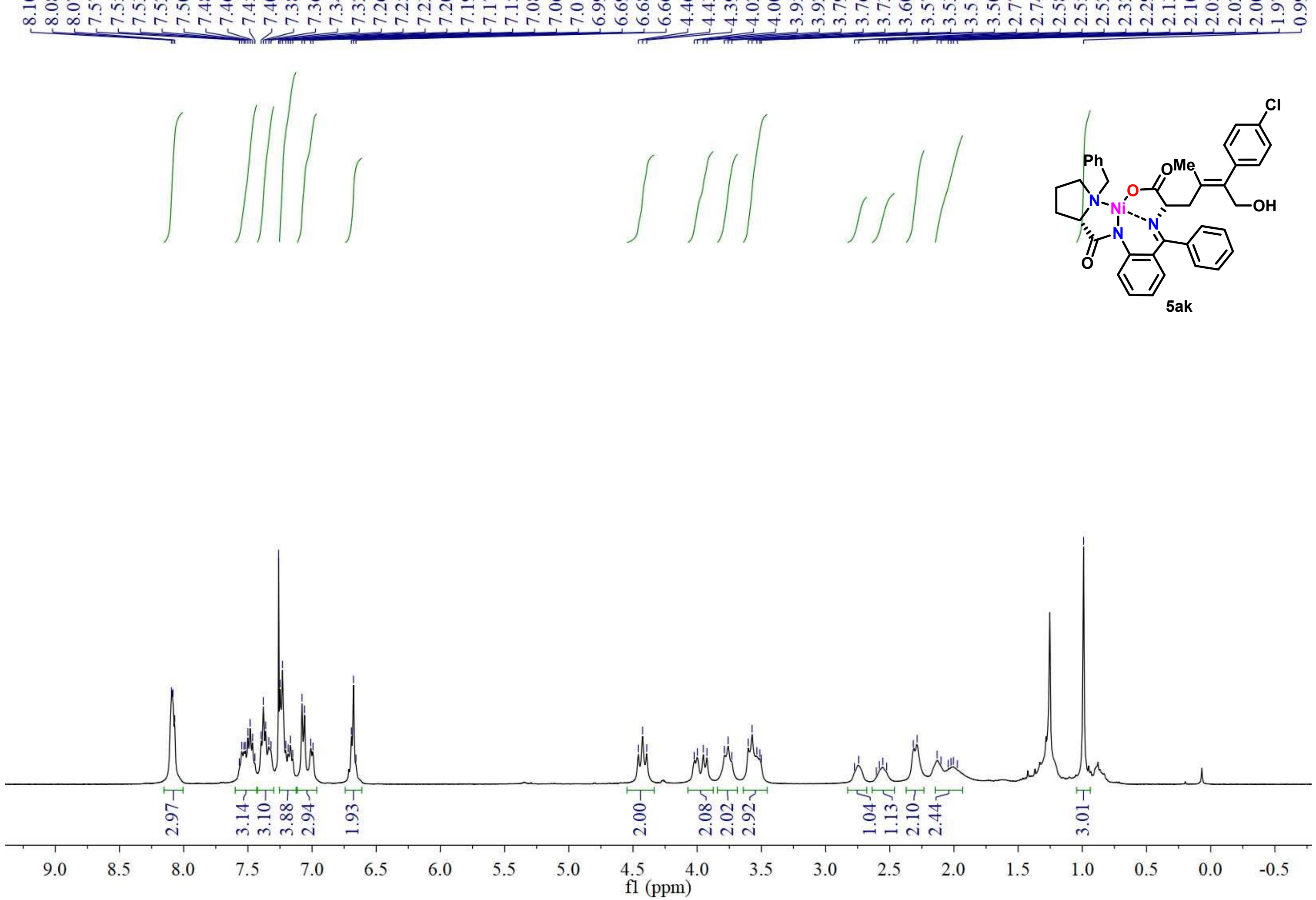
¹H NMR spectrum of **5aj** in $CDCl_3$



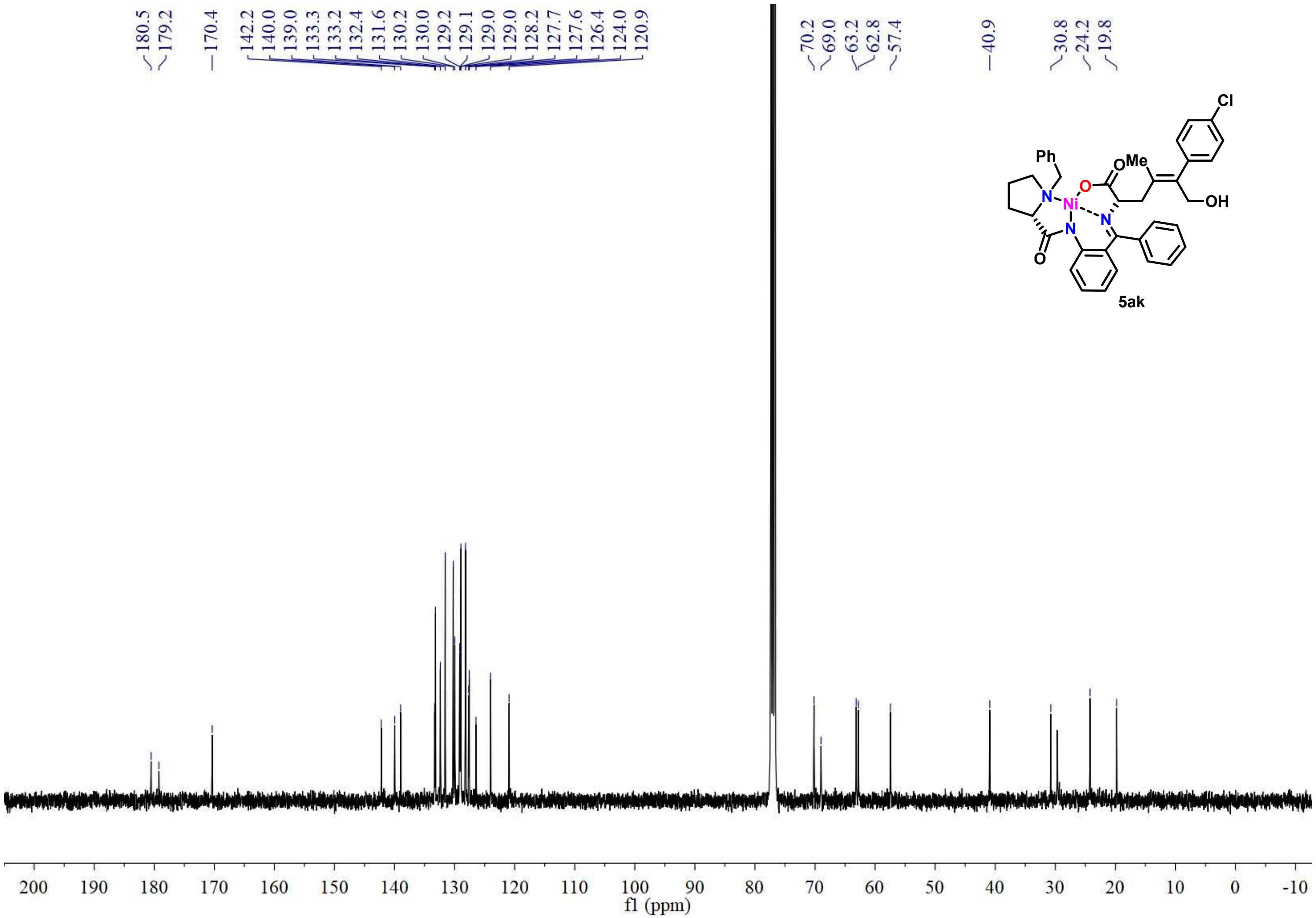
^{13}C NMR spectrum of **5aj** in $CDCl_3$



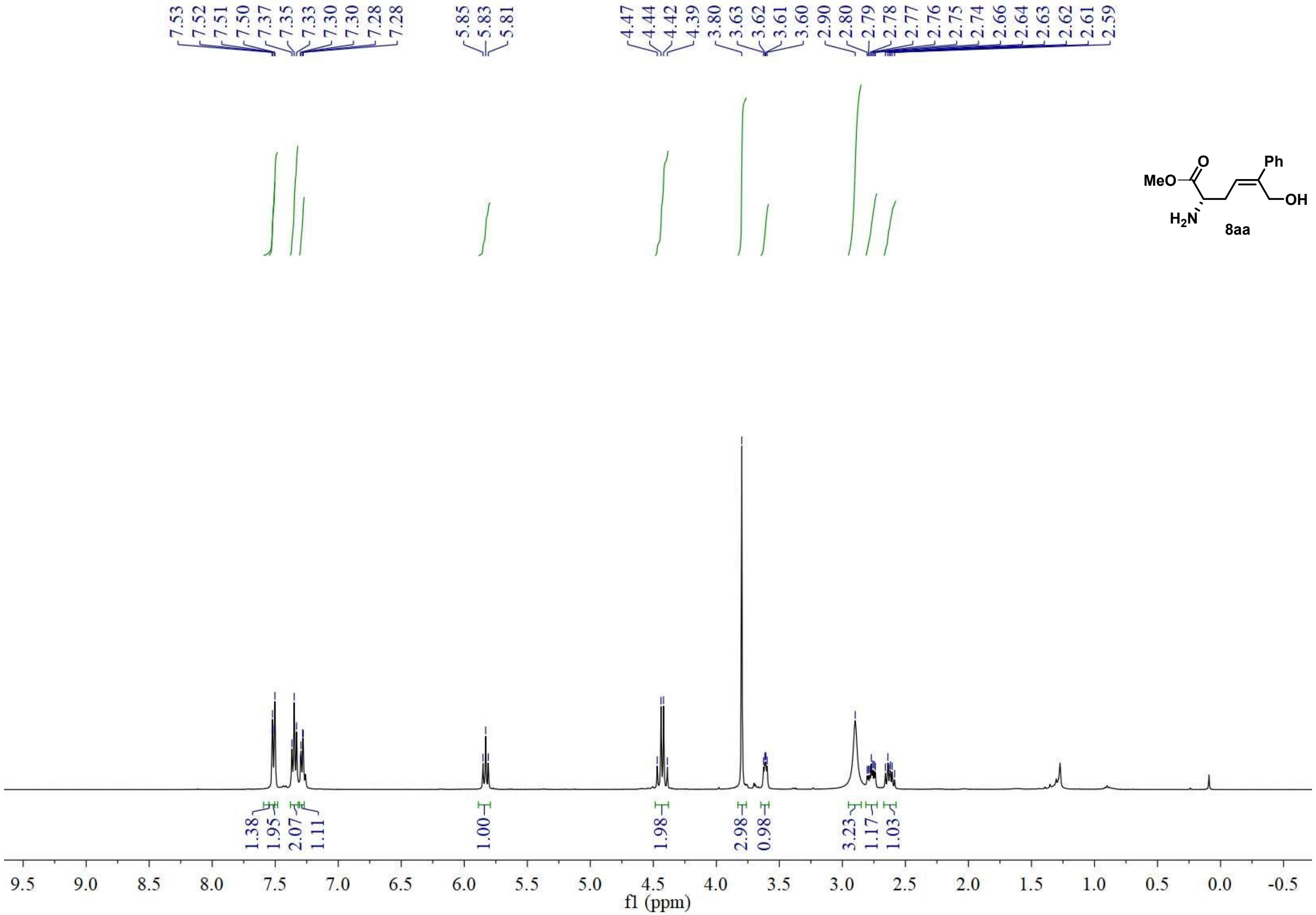
^{1}H NMR spectrum of **5ak** in $CDCl_3$



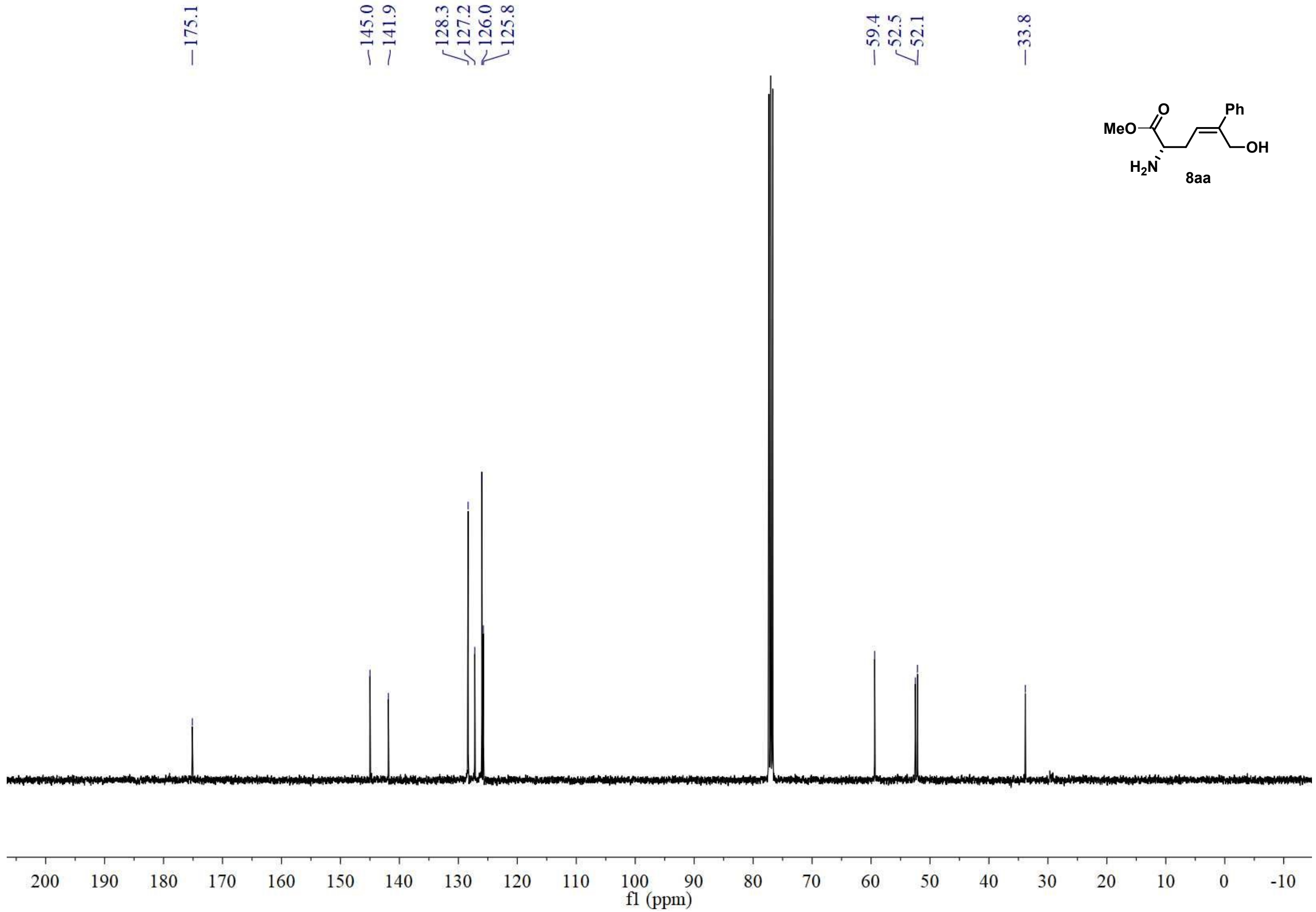
^{13}C NMR spectrum of **5ak** in $CDCl_3$



^{1}H NMR spectrum of **8aa** in $CDCl_3$



[13]C NMR spectrum of **8aa** in $CDCl_3$



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