

Bench-Stable Nickel Precatalysts with Heck-type Activation

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I. Materials, Methods, and General Considerations

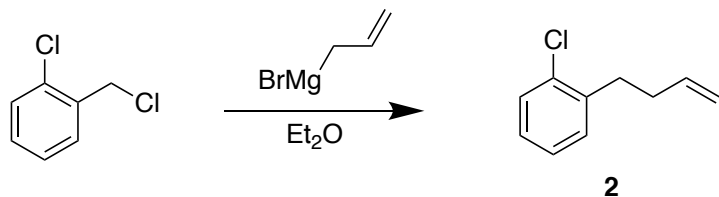
Reactions were carried out under N₂ using standard glovebox and Schlenk techniques at ambient temperature (23–27 °C) under Ar unless otherwise noted. Diethyl ether (Et₂O), tetrahydrofuran (THF), dimethylformamide (DMF), and dichloromethane (DCM) were degassed by sparging with nitrogen and dried via passage through a column of activated alumina on a Glass Contour solvent purification system. Methanol (>99.8%) and pentane were used as received. Complexes (PPh₃)₂NiBr₂, (PPh₃)₂NiCl₂, and (PPh₃)₂Ni(*o*-tolyl)Cl were prepared according to previously published procedures.⁴ Metal catalyst Bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)₂) was purchased from Strem Chemicals (Newburyport, MA) and stored at –30 °C in a glovebox freezer. Flash chromatography was performed on a Biotage Isolera with accelerated chromatographic isolation (ACI) system.

Purity was determined by ³¹P, ¹H and ¹³C NMR. NMR spectra were obtained in CD₂Cl₂, C₆D₆, or toluene-*d*₈ purchased from Cambridge Isotope Laboratories and used as received. Norell 5mm NMR tubes with standard septa caps were used. ¹H NMR Spectra were obtained at 400 MHz, ¹³C spectra were obtained at 101 MHz with ¹H decoupling, and ³¹P spectra were obtained at 126 MHz with ¹H decoupling. ¹H chemical shifts are reported in parts per million relative to TMS (δ = 0.00 ppm) and were referenced to the residual solvent peak. ³¹P chemical shifts are reported in parts per million relative to 85% phosphoric acid (δ = 0.00 ppm). The following designations are used to describe multiplicities: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet). For ¹H NMR yields, nitromethane (1 equiv) was used as an internal standard added post reaction, added after dilution with CDCl₃. Unless otherwise noted, NMR spectra were collected at room temperature (23–27 °C).

Gas chromatography (GC) analyses were performed on an Agilent 7890A GC system with an autosampler and (5%-phenyl)-methylpolysiloxane column coupled to a flame ionization detector. Gas chromatography/ mass spectroscopy (GC/MS) analyses were performed on an Agilent 5975C with a triple-axis detector using an autosampler and (5%-phenyl)-methylpolysiloxane column coupled to a quadrupole MSD. Dodecane (1 equiv) was used as an internal standard for determination of yields. Authentic samples of compounds **9** and **10** were synthesized via a previously published method and used to make a calibration curve used to determine yield.¹

Melting points were collected on eletrothermal apparatus using glass capillaries. The meting points were determined open to air on recrystallized material. Infrared spectroscopy (IR) spectra were collected using an Agilent Cary 630 FT-IR spectrometer equipped with an ATR accessory. Peaks from the fingerprint region were omitted from the report for clarity. Elemental analyses (EA) were obtained for the complexes that did not successfully crystallize. EA was performed at Atlantic Microlabs, Inc. High-Resolution Mass Spectroscopy (HRMS) was obtained on a Bruker Daltonics APEXIV 4.7 Tesla FT-ICR-MS outfitted with either an electrospray ionization (ESI) or an IonSense DART ion source. X-Ray diffraction was performed on a Bruker APEX.

II. Synthesis and Characterization of the Aryl Precursors.



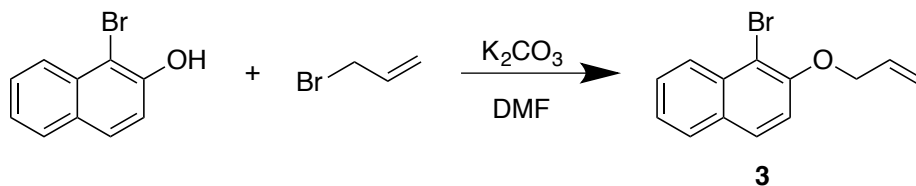
Procedure adapted from Bigi, M. A.; White, M. C. *J. Am. Chem. Soc.* **2013**, *135*, 7831-7834.

1-(but-3-en-1-yl)-2-chloride (2): Under Ar, in an oven-dried round bottom flask charged with a stir bar, *o*-chlorobenzylchloride (3.38 g, 1 equiv, 21 mmol) was dissolved in dry Et₂O (30 mL). The solution was cooled to 0 °C in an ice bath and 1M allylmagnesium bromide (1.2 equiv, 25.2 mmol) was added dropwise via syringe. The solution was warmed to room temperature and stirred for 20 h. The reaction was quenched with 10 mL of NH₄Cl at 0 °C. After which, 5 mL of Et₂O was added. The organic layer was collected and washed with 2 x 25 mL H₂O. The organic layer was then dried with Na₂SO₄, filtered, and concentrated under vacuum. The product **2** (2.95 g, 84% yield) was purified via automated flash chromatography in 100% hexanes to give a yellow oil. R_f = 0.65 in 100% hexanes

¹H NMR (400 MHz, CDCl₃, δ): 7.38 (d, *J* = 7.7 Hz, 1H), 7.12–7.24 (m, 3H), 5.86–5.98 (m, 1H), 5.01–5.15 (m, 2H), 2.87 (td, *J* = 7.6 Hz, 2H), 2.42 (q, *J* = 7.6 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃, δ): 139.5, 137.9, 134.1, 130.6, 129.6, 127.5, 126.8, 115.3, 33.8, 33.2.

HRMS-DART (*m/z*): Predicted: [M+H]⁺: 167.0622 *m/z* Found: [M+H]⁺: 167.0625 *m/z*.



Procedure adapted from Amiratu, R.; Catarzi, F.; Menichetti, S.; Pedulli, G. F.; Viglianisi. *J. Am. Chem. Soc.* **2008**, *130*, 237–244.

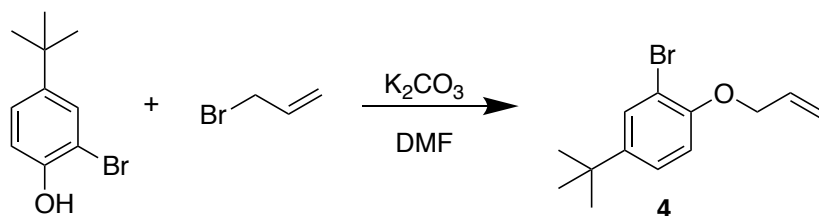
2-(allyloxy)-1-bromonaphthalene (3): Under Ar, in an oven-dried round bottom flask charged with a stir bar, DMF (25 mL) was added to 1-bromo-2-naphthol (5.58 g, 1 equiv, 25 mmol) and K₂CO₃ (6.00 g, 4 equiv, 100 mmol). Allyl bromide (12.1 g, 8.65 mL, 4 equiv) was added via syringe and the reaction was stirred for 24 h at room temperature. Then H₂O was added until the salt was dissolved and the desired product was extracted with 3 x 25 mL of DCM. The organic layer was dried over Na₂SO₄, filtered, and concentrated. The desired product **3** (4.82 g, 73% yield) was isolated as a white solid via automated flash chromatography followed by crystallization from hexanes. R_f = 0.4 in

10% EtOAc/Hexanes.

^1H NMR (400 MHz, CDCl_3 , δ): 8.24 (d, $J = 8.9$ Hz, 1H), 7.78 (d, $J = 8.9$ Hz, 2H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.41 (t, $J = 7.3$ Hz, 1H), 7.24 (d, $J = 8.9$ Hz, 1H), 6.07–6.19 (m, 1H), 5.53 (dq, $J = 1.5$ Hz, 1H), 5.33 (dq, $J = 1.5$ Hz, 1H), 4.76 (d, $J = 5.0$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3 , δ): 153.0, 133.3, 133.0, 130.1, 128.9, 128.1, 127.8, 126.3, 124.6, 118.0, 115.4, 109.8, 70.7.

Consistent with previously reported characterization data.²



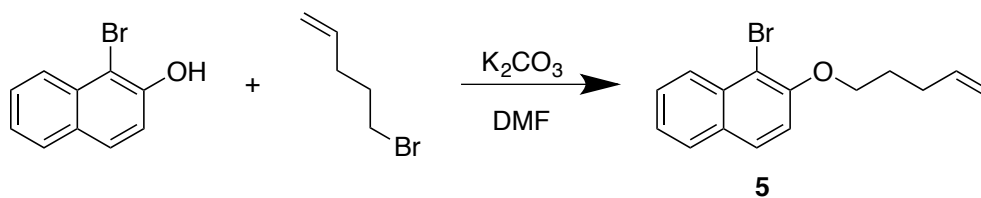
Procedure adapted from Amiratu, R.; Catarzi, F.; Menichetti, S.; Pedulli, G. F.; Viglianisi. *J. Am. Chem. Soc.* **2008**, *130*, 237–244.

1-(allyloxy)-2-bromo-4-(tert-butyl)benzene (4): Under Ar, in an oven-dried round bottom flask charged with a stir bar, 2-bromo-4-(tert-butyl)phenol (20.62 g, 1 equiv, 90 mmol)³ was added to a round bottom flask containing K_2CO_3 (37.3 g, 3 equiv) and allyl bromide (21.78 g, 2 equiv). The reaction was stirred for 24 h at room temperature after which H_2O was added until the salt was dissolved. The desired product was extracted with 3 x 25 mL of DCM. The organic layer was then dried with Na_2SO_4 , filtered, and concentrated. The desired product **4** (19.8 g, 82% yield over two steps) was isolated via automated flash chromatography to as a clear oil. $R_f = 0.39$ in 10% EtOAc/Hexanes.

^1H NMR (400 MHz, CDCl_3 , δ): 7.58 (s, 1H), 7.27 (d, $J = 8.6$ Hz, 1H), 6.86 (d, $J = 8.6$ Hz, 1H), 6.04–6.15 (m, 1H), 5.50 (d, $J = 16.2$ Hz, 1H), 5.33 (d, $J = 10.5$ Hz, 1H), 4.62 (d, $J = 4.6$ Hz, 2H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3 , δ): 152.6, 145.0, 132.8, 130.4, 125.1, 117.4, 114.1, 113.2, 111.9, 69.6, 34.1, 31.4.

HRMS-DART(m/z): Predicted: $[\text{M}+\text{H}]^+$: 269.0536 m/z Found: $[\text{M}+\text{H}]^+$: 269.0534 m/z .



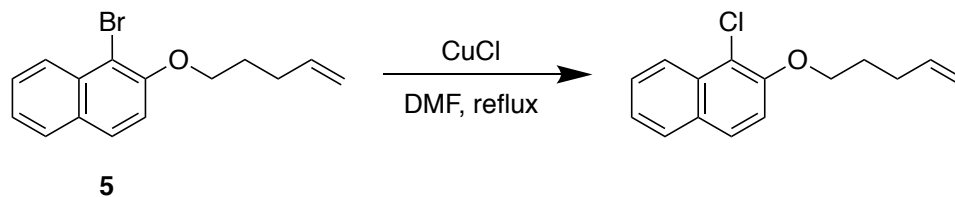
Procedure adapted from Amiratu, R.; Catarzi, F.; Menichetti, S.; Pedulli, G. F.; Viglianisi. *J. Am. Chem. Soc.* **2008**, *130*, 237–244.

1-bromo-2-(pent-4-en-1-yloxy)naphthalene (5): Under Ar, in an oven-dried round bottom flask charged with a stir bar, DMF (25 mL) was added to 1-bromo-2-naphthol (5.58 g, 1 equiv, 25 mmol) and K₂CO₃ (10.37 g, 3 equiv, 75 mmol). 5-bromopent-1-ene (7.45 g, 2 equiv, 50 mmol) was added via syringe and the reaction was stirred for 18 h at 50 °C. Then H₂O was added until the salt was dissolved and the desired product was extracted with 3 x 25 mL Et₂O. The organic layer was then dried over Na₂SO₄, filtered and concentrated. The desired product **5** (5.31 g, 73% yield) was isolated via automated flash chromatography followed by crystallization in hexanes as an oil. R_f = 0.56 in 10% EtOAc/Hexanes, 0.15 in 100% Hexanes.

¹H NMR (400 MHz, CDCl₃, δ): 8.27 (d, *J* = 8.9 Hz, 1H), 7.79, (dd, *J* = 8.9 Hz, 2H), 7.59 (t, *J* = 7.1 Hz, 1H), 7.41 (t, *J* = 7.1 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 1H), 5.86–5.98 (m, 1H), 5.14 (dt, *J* = 1.8 Hz, 1H), 5.06 (dt, *J* = 1.8 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 2.38 (q, *J* = 6.6 Hz, 2H), 2.00 (quintet, *J* = 6.6 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃, δ): 153.4, 137.8, 133.3, 130.0, 128.9, 128.1, 127.7, 126.3, 124.4, 115.5, 115.3, 109.6, 69.4, 30.2, 28.7.

HRMS-DART(*m/z*): Predicted: [M+H]⁺: 291.0379 *m/z* Found: [M+H]⁺: 291.0368 *m/z*.



Procedure adapted from Wu, L.; Drinkel, E.; Gaggia, F.; Capolicchio, S.; Linden, A.; Falivene, L.; Cavallo, L.; Dorta, R. *Chem. Eur. J.* **2011**, *17*, 12886–12890.

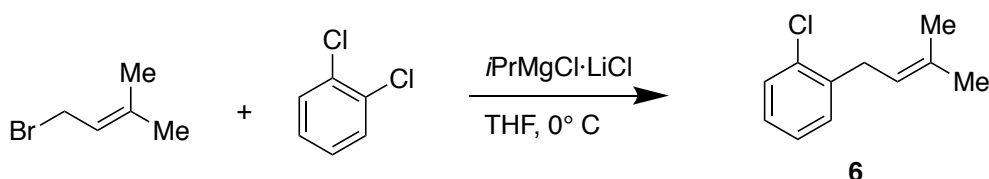
1-chloro-2-(pent-4-en-1-yloxy)naphthalene: Under Ar, 1-bromo-2-(pent-4-en-1-yloxy)naphthalene **5** (2.91 g, 1 equiv, 10 mmol) and CuCl (1.09 g, 1.1 equiv, 11 mmol) were added to an oven dried round bottom flask with a stir bar. The flask was evacuated and refilled with Ar three times. DMF (60 mL) was added and a reflux condenser was fitted to the flask. The flask was evacuated and refilled with Ar three times. The reaction was then heated to reflux and stirred for 18 h. The reaction was then taken off heat and quenched with NH₄OH and extracted with 25 mL Et₂O. The organic solution was washed once each with 30% aq NH₄OH and water. The organic layer was dried over Na₂SO₄,

filtered, and concentrated under vacuum. The product (2.26 g, 92% yield) was purified via automated column chromatography (0 to 15% EtOAc in Hexanes) to give a clear oil. R_f = 0.11 in 100% Hexanes.

^1H NMR (400 MHz, CDCl_3 , δ): 8.25 (d, J = 8.3 Hz, 1H), 7.77 (m, 2H), 7.58 (dd, J = 8.3 Hz, 1H), 7.41 (dd, J = 8.3 Hz, 1H), 7.27 (d, J = 8.3 Hz, 1H), 5.90 (m, 1H), 5.12 (dq, J = 1.6 Hz, 1H), 5.07 (dq, J = 1.6 Hz, 1H), 4.19 (t, J = 6.6 Hz, 2H), 2.35 (q, J = 6.6 Hz, 2H), 1.99 (quintet, J = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3 , δ): 152.1, 137.7, 131.9, 129.5, 128.0, 127.8, 127.3, 124.2, 123.5, 117.5, 115.3, 115.2, 69.2, 30.0, 28.6.

HRMS-DART(m/z): Predicted: $[\text{M}+\text{H}]^+$: 247.0884 m/z Found: $[\text{M}+\text{H}]^+$: 247.0890 m/z .



Procedure adapted from Xu, L.; Liu, Z.; Dong, W.; Song, J.; Miao, M.; Xu, J.; Ren, H. *Org. Biomol. Chem.* **2015**, *13*, 6333–6337.

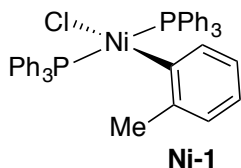
1-chloro-2-(3-methylbut-2-en-1-yl)benzene (6): Under Ar, in an oven-dried round bottom flask charged with a stir bar, 1.2M $i\text{-PrMgBr}$ LiCl (6 mL, 7.8 mmol, 1.3 equiv) is added to 1-chloro-2-iodo benzene (0.72 g, 6 mmol, 1 equiv) in THF (5 mL) at 0°C . This reaction was stirred for 2h and monitored for conversion. Then prenylbromide (2.1 g, 18 mmol, 3 equiv) was added, the reaction is warmed to room temperature and stirred for 3 h. Then the reaction was filtered through silica with 100% hexanes and then the solvent was removed via rotary evaporation. Compound **6** (0.35 g, 32% yield) was purified via automated column chromatography with 100% hexanes to give a light yellow oil. R_f = 0.63 in 100% hexanes

^1H NMR (400 MHz, CDCl_3 , δ): 7.34 (dd, J = 7.9 Hz, 1H), 7.15–7.24 (m, 2H), 7.10–7.15 (m, 1H), 5.26–5.32 (m, 1H), 3.44 (d, J = 7.6 Hz, 2H), 1.76, (d, J = 1.3, 3H), 1.73 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3 , δ): 139.4, 134.1, 133.7, 130.1, 129.5, 127.3, 126.9, 121.4, 32.2, 25.9, 18.1.

HRMS-DART(m/z): Predicted: $[\text{M}-\text{H}]$: 179.0622 m/z Found: $[\text{M}-\text{H}]$: 179.0629 m/z .

III. Characterization of the Carbonyl –Ene Reaction



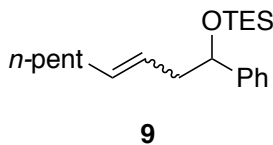
Synthesized via previously reported procedure in a 78% yield.¹

¹H NMR (400 MHz, C₆D₆, δ): 7.88–7.71 (m, 12H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.07–6.91 (m, 18H), 6.45 (t, *J* = 7.2 Hz, 1H), 6.25 (t, *J* = 7.5 Hz, 1H), 6.18 (d, *J* = 7.4 Hz, 1H), 2.45 (s, 3H).

¹³C NMR (101 MHz, C₆D₆, δ): 151.4 (t, *J* = 32.8 Hz), 144.1 (t, *J* = 3.3 Hz), 136.9 (t, *J* = 4.0 Hz), 134.6 (t, *J* = 5.5 Hz), 131.6 (t, *J* = 21.0 Hz), 129.6, 129.0 (t, *J* = 3.1 Hz), 127.6 (t, *J* = 4.7 Hz), 123.6 (t, *J* = 2.3 Hz), 122.0 (t, *J* = 2.3 Hz), 26.8.

³¹P NMR (121 MHz, C₆D₆, δ): 22.0.

Consistent with previously reported characterization data.⁴

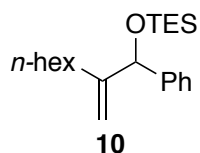


¹H NMR (400 MHz, CDCl₃, δ): 7.22–7.40 (m, 5H), 5.36–5.50 (m, 2H), 4.61 (dd, *J* = 5.8 Hz, 1H), 2.43 (quintet, *J* = 6.2 Hz, 1H), 2.33 (quintet, *J* = 5.8 Hz, 1H); 1.33 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 12H), 0.57 (dq, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃, δ): 145.5, 133.2, 128.1, 127.1, 126.5, 126.1, 75.5, 44.4, 32.8, 31.7, 29.3, 22.7, 14.2, 7.0, 5.1.

HRMS-DART (*m/z*): Predicted: [M+H]⁺: 331.2452 Found: [M+H]⁺: 331.2455.

Consistent with previously reported characterization data.¹

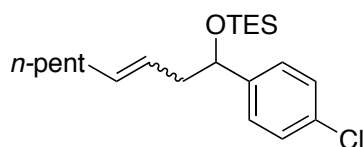


PCy₂Ph was used instead of PPh₃ to synthesize **10**.

¹H NMR (400 MHz, CDCl₃, δ): 7.33–7.38 (m, 2H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.19–7.25 (m, 1H), 5.21 (dq, *J* = 1.4 Hz, 1H), 5.13 (s, 1H), 4.86 (qd, *J* = 1.4 Hz, 1H), 1.88–2.01 (m, 1H), 1.69–1.80 (m, 1H), 1.18–1.37 (m, 8H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.87 (t, *J* = 8.0 Hz, 3H), 0.60 (dq, *J* = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃, δ): 152.2, 143.7, 128.0, 127.0, 126.5, 109.4, 78.2, 31.9, 30.7, 29.3, 27.8, 22.8, 14.2, 7.0, 5.0.

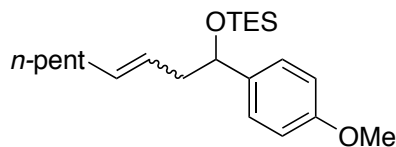
Consistent with previously reported characterization data.¹



¹H NMR (400 MHz, CDCl₃, δ): 7.29–7.24 (m, 4H), 5.28–5.43 (m, 2H), 4.60 (dd, *J* = 6.0 Hz, 1H), 2.24–2.42 (m, 2H), 1.88–1.97 (m, 2H), 1.21–1.59 (m, 6H), 0.94 (t, *J* = 7.8 Hz, 3H), 0.86 (t, *J* = 7.8 Hz, 9H), 0.50 (q, *J* = 7.8 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃, δ): 144.1, 133.8, 132.3, 128.2, 127.5, 126.1, 75.0, 44.4, 32.7, 31.5, 29.2, 22.7, 14.2, 6.9, 5.0.

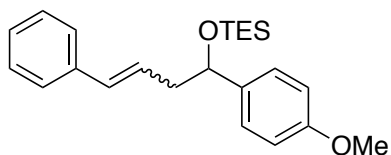
Consistent with previously reported characterization data.¹



¹H NMR (400 MHz, CDCl₃, δ): 7.23 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.33–5.43 (m, 2H), 4.60 (dd, *J* = 6.2 Hz, 1H), 3.81 (s, 3H), 2.27–2.42 (m, 2H), 1.93–1.98 (m, 2H), 1.22–1.60 (m, 6H), 0.95 (t, *J* = 8.1 Hz, 3H), 0.88 (t, *J* = 8.1 Hz, 9H), 0.53 (q, *J* = 8.1 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃, δ): 158.7, 137.8, 133.1, 127.2, 126.7, 113.4, 75.1, 55.3, 44.5, 32.8, 31.5, 29.3, 22.7, 14.2, 7.0, 5.0.

Consistent with previously reported characterization data.¹

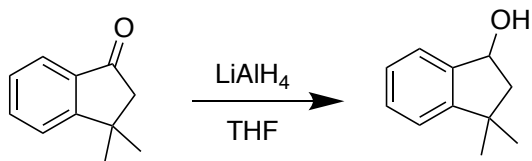


^1H NMR (400 MHz, CDCl_3 , δ): 7.28–7.46 (m, 7H), 6.96 (d, $J = 8.8$ Hz, 2H), 6.50 (d, $J = 15.7$ Hz, 1H), 6.32 (dt, $J = 15.7$ Hz, 1H), 4.83 (dd, $J = 6.5$ Hz, 1H), 3.87 (s, 3H), 2.62–2.81 (m, 2H), 1.03 (t, $J = 7.8$ Hz, 2H), 0.70 (q, $J = 7.8$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3 , δ): 158.9, 137.9, 137.6, 132.2, 128.7, 127.4, 127.2, 127.1, 126.2, 113.6, 75.0, 55.3, 45.0, 7.0, 5.1.

Consistent with previously reported characterization data.¹

IV. Procedure and Characterization for Authentic Heck Product.



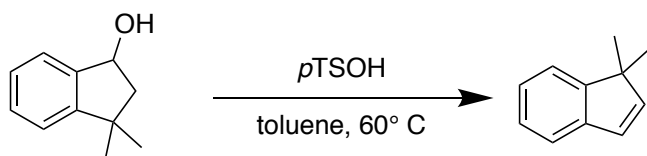
Procedure adapted from Knorr, R.; Stephenson, D. S.; Lattke, E.; Böhrer, P.; Ruhdorfer, J. *Beilstein J. Org. Chem.* **2016**, *12*, 1178–1184.

In an oven dried round bottom flask attached to an Ar line, 1M lithium aluminum hydride (0.60 mL, 0.6 mmol, 2 equiv) was added dropwise to a solution of 3,3-dimethyl-2,3-dihydroinden-1-one (48 mg, 0.3 mmol, 1 equiv) in 4 mL of THF at 0 °C. This reaction was stirred for 3 h. The reaction was then quenched with aq. NaOH at 0 °C. The desired product was extracted with 2 x 5 mL of Et₂O, washed with 1 x 5 mL portion of brine, and dried over NaSO₄ to give the desired product (41 mg, 83% yield).

¹H NMR (400 MHz, CDCl₃, δ): 7.40 (d, *J* = 7.3 Hz, 1H), 7.27–7.33 (m, 2H), 7.21 (d, *J* = 7.3 Hz, 1H), 5.27 (t, *J* = 6.6 Hz, 1H), 2.39 (dd, *J* = 6.6 Hz, 1H), 1.84 (dd, *J* = 6.0 Hz, 1H), 1.70 (brs, 1H, OH), 1.40 (s, 3H), 1.23 (s, 3H).

¹³C NMR (101 MHz, CDCl₃, δ): 152.0, 143.8, 128.7, 127.1, 124.2, 122.5, 74.7, 52.1, 42.4, 30.1, 30.0.

Consistent with previously reported characterization data.⁵



11

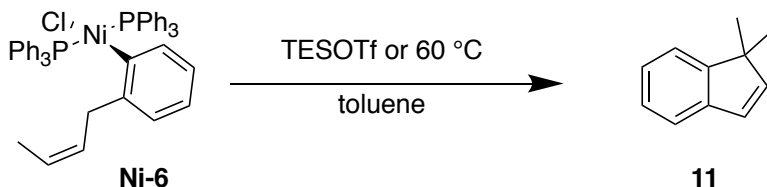
Procedure adapted from Knorr, R.; Stephenson, D. S.; Lattke, E.; Böhrer, P.; Ruhdorfer, J. *Beilstein J. Org. Chem.* **2016**, *12*, 1178–1184.

In a round bottom flask, *p*-toluenesulfonic acid (4 mg, 0.022 mmol, 0.1 equiv) was added via syringe to a stirred solution of 3,3-dimethyl-2,3-dihydroinden-1-ol (36 mg, 1 equiv 0.22 mmol) in 5 mL of toluene. The reaction was then heated to 60 °C for 2 h. The reaction is then cooled to room temperature and quenched with aq. NaOH. The product is extracted with 2 x 5 mL portions of Et₂O and washed with 1 x 5 mL portion of brine. The product is dried over NaSO₄ and purified via automated column chromatography to give desired product **11** as a clear oil (11 mg, 35% yield).

^1H NMR (400 MHz, CDCl_3 , δ): 7.20–7.36 (m, 4H), 6.65 (d, $J = 5.4$ Hz, 1H), 6.39 (d, $J = 5.4$ Hz, 1H), 1.34 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3 , δ): 153.4, 147.5, 142.8, 127.8, 126.5, 125.2, 121.3, 121.0, 49.8, 24.6.

Consistent with previously reported characterization data.⁶



Heat activation: In an oven-dried 2 dram vial, 3 mL of toluene was added to precatalyst **Ni-6** (20 mg, 1 equiv). The reaction was heated to 60 °C for 24 hours. The reaction was then cooled to room temperature and filtered through a plug of silica. The contents were then analyzed by GC/MS and HRMS.

TESOTf activation: In an oven-dried 2 dram vial, TESOTf (2 equiv) was added to precatalyst **Ni-6** (20 mg, 1 equiv) in toluene (3 mL). The reaction was stirred for 24 hours. The reaction was then opened to air and filtered through a plug of silica. The contents were then analyzed by GC/MS.

HRMS-DART (m/z): Predicted: $[\text{M}+\text{H}]^+$: 145.1012 Found: $[\text{M}+\text{H}]^+$: 145.1011

V. X-Ray Diffraction Characterization of the Precatalysts.

General Information: Low temperature diffraction data (ϕ -and ω -scans) was collected on a Bruker X8 Kappa DUO four-cycle diffractometer coupled to a Smart Apex2 CCD detector for complexes **Ni-2**, **Ni-3a**, **Ni-3b**, **Ni-5a**, and **Ni-6** with Mo K α radiation ($\lambda = 0.71073$ Å) from an I μ S micro-source. The crystal structures were then solved using SHELXS⁷ and refined against F^2 on all data by full-matrix least squares with SHELXL-97,⁸ following established refinement strategies.⁹ All hydrogen atoms bound to carbon atoms were included into the model at geometrically calculated positions using AFIX/HFIX commands and refined using a riding model. The isotropic displacement parameter of all hydrogen atoms was fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). All non-H atoms were refined anisotropically.

Figure S1. Thermal ellipsoid depiction of compound **Ni-2**. ORTEP at 50% probability.

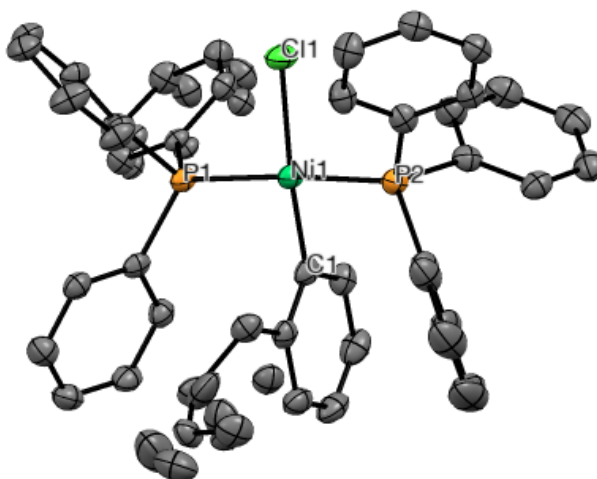
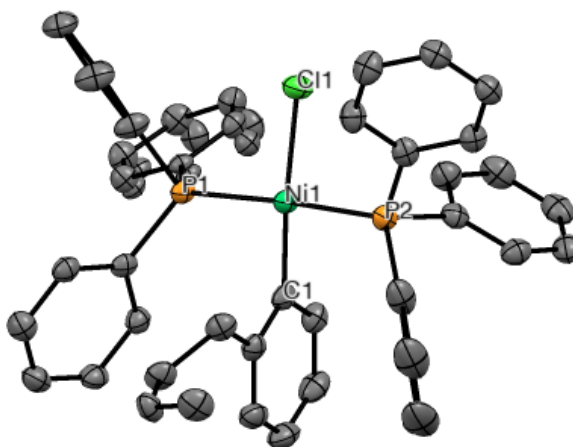


Figure S2. Thermal ellipsoid depiction of compound **Ni-2**. ORTEP at 50% probability with disorder omitted.

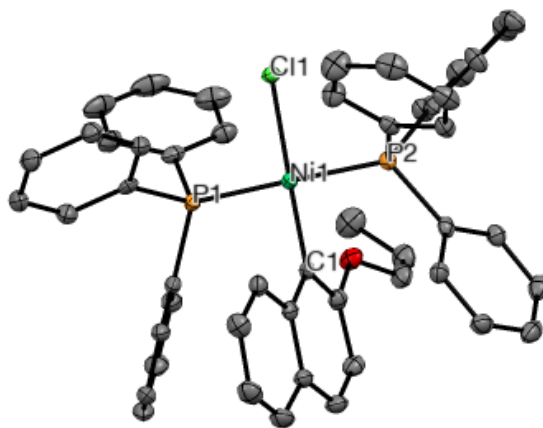


The crystal structure of **Ni-2** was disordered over the aliphatic side chain.

Table S1. Crystal data and structure refinement for compound **Ni-2**.

Identification code	X17053
Empirical formula	C ₄₇ H ₄₃ Cl ₃ NiP ₂
Formula weight	834.81
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 11.824(3) Å b = 24.861(7) Å c = 13.999(4) Å
Volume	4073.7(19) Å ³
Z	4
Density (calculated)	1.361 Mg/m ³
Absorption coefficient	0.785 mm ⁻¹
F(000)	1736
Crystal size	0.603 x 0.061 x 0.045 mm ³
Theta range for data collection	1.923 to 27.479°
Index ranges	-15 ≤ h ≤ 15, -32 ≤ k ≤ 32, -18 ≤ l ≤ 18
Reflections collected	62825
Independent reflections	9348 [<i>R</i> _{int} = 0.0634]
Completeness to theta = 25.242°	100%
Absorption correction	Semi-empirical from equivalents
min and max transmission	0.6641 and 0.7462
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	9348/683/644
Goodness-of-fit on <i>F</i>²	1.074
Largest diff. peak and hole	0.763 and -0.804 e.Å ⁻³
<i>R</i> indices on all data	<i>R</i> 1 = 0.0733, <i>wR</i> 2 = 0.1247
Final <i>R</i> indices [<i>I</i> > 2 σ(<i>I</i>)]	<i>R</i> 1 = 0.0507, <i>wR</i> 2 = 0.1143

Figure S3. Thermal ellipsoid depiction of compound **Ni-3a**. ORTEP at 50% probability.



The residual density in the structure is likely caused by minor non-merohedral twinning.

Table S2. Crystal data and structure refinement for compound **Ni-3a**.

Identification code	X17027
Empirical formula	C _{49.50} H ₄₂ Cl ₂ NiOP ₂
Formula weight	844.38
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 20.485(3) Å b = 10.3610(15) Å c = 21.371(3) Å
Volume	4082.4(11) Å ³
Z	4
Density (calculated)	1.374 Mg/m ³
Absorption coefficient	0.723 mm ⁻¹
F(000)	1756
Crystal size	0.071 x 0.057 x 0.054 mm ³
Theta range for data collection	2.26 to 27.26°
Index ranges	-26 ≤ h ≤ 26, -11 ≤ k ≤ 13, -24 ≤ l ≤ 27
Reflections collected	68545
Independent reflections	9016 [<i>R</i> _{int} = 0.0713]
Completeness to theta = 25.242°	100%
Absorption correction	Semi-empirical from equivalents
Min and max transmission	0.6783 and 0.7458
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	9016/22/515
Goodness-of-fit on <i>F</i>²	1.049
Largest diff. peak and hole	2.607 and -0.533 e.Å ⁻³
<i>R</i> indices on all data	<i>R</i> 1 = 0.0775, <i>wR</i> 2 = 0.1598
Final <i>R</i> indices [<i>I</i> > 2 σ(<i>I</i>)]	<i>R</i> 1 = 0.0587, <i>wR</i> 2 = 0.1487

Figure S4. Thermal ellipsoid depiction of compound **Ni-3b**. ORTEP at 50% probability.

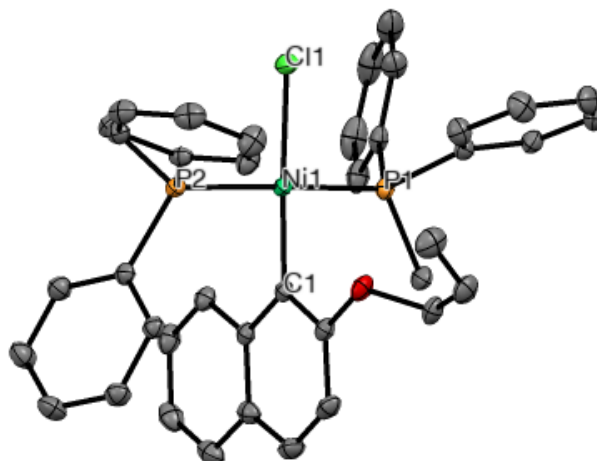


Table S3. Crystal data and structure refinement for compound **Ni-3b**.

Identification code	X17050
Empirical formula	C ₃₉ H ₃₇ ClNiOP ₂
Formula weight	677.78
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 15.3185(14) Å b = 14.2565(13) Å c = 16.5433(15) Å
Volume	3348.9(5) Å ³
Z	4
Density (calculated)	1.344 Mg/m ³
Absorption coefficient	0.785 mm ⁻¹
F(000)	1416
Crystal size	0.453 x 0.151 x 0.132 mm ³
Theta range for data collection	2.50 to 29.86°
Index ranges	-21 ≤ h ≤ 21, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23
Reflections collected	98757
Independent reflections	9795 [<i>R</i> _{int} = 0.0560]
Completeness to theta = 25.242°	100%
Absorption correction	Semi-empirical from equivalents
Min and max transmission	0.6745 and 0.7461
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	9795/0/400
Goodness-of-fit on <i>F</i>²	1.033
Largest diff. peak and hole	0.47 and -0.503 e.Å ⁻³
<i>R</i> indices on all data	<i>R</i> 1 = 0.0420 <i>wR</i> 2 = 0.0778
Final <i>R</i> indices [<i>I</i> > 2 σ(<i>I</i>)]	<i>R</i> 1 = 0.0312, <i>wR</i> 2 = 0.0731

Figure S5. Thermal ellipsoid depiction of compound **Ni-5a**. ORTEP at 50% probability. The disorder was omitted for clarity.

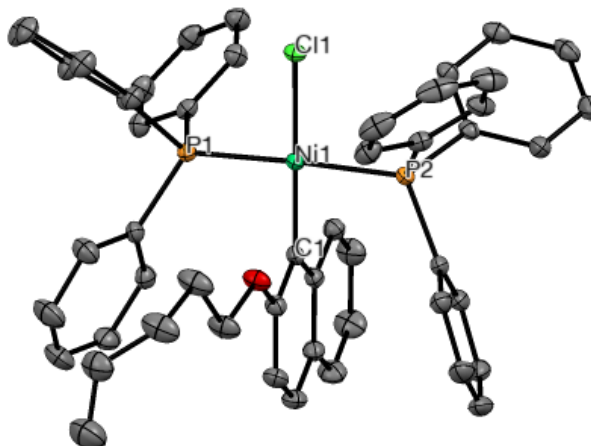
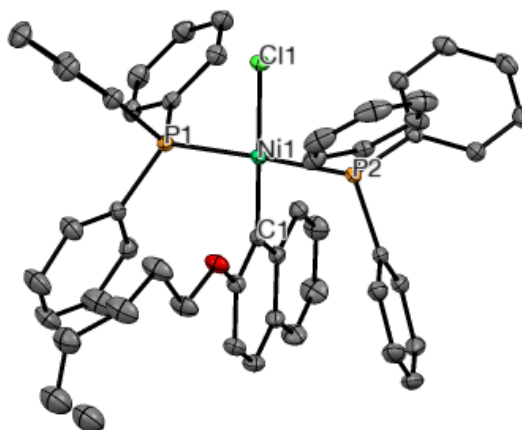


Figure S6. Thermal ellipsoid depiction of compound **Ni-5a**. ORTEP at 50% probability with disorder around the aliphatic chain.



The crystal structure of **Ni-5a** was disordered over the aliphatic side chain.

Table S4. Crystal data and structure refinement for compound **Ni-5a**.

Identification code	X17049
Empirical formula	C _{51.50} H ₄₆ Cl ₂ NiOP ₂
Formula weight	872.43
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 21.060(6) Å b = 10.421(3) Å c = 39.473(11) Å
Volume	8662(4) Å ³
Z	8
Density (calculated)	1.338 Mg/m ³
Absorption coefficient	0.683 mm ⁻¹
F(000)	3640
Crystal size	0.420 x 0.380 x 0.271 mm ³
Theta range for data collection	1.934 to 29.575°
Index ranges	-29 ≤ h ≤ 29, -13 ≤ k ≤ 14, -54 ≤ l ≤ 54
Reflections collected	106601
Independent reflections	12149 [<i>R</i> _{int} = 0.0654]
Completeness to theta = 25.242°	100%
Absorption correction	Semi-empirical from equivalents
Min and max transmission	0.6593 and 0.7461
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	12149/139/548
Goodness-of-fit on <i>F</i>²	1.023
Largest diff. peak and hole	0.963 and -0.881 e.Å ⁻³
<i>R</i> indices on all data	<i>R</i> 1 = 0.0532, <i>wR</i> 2 = 0.0909
Final <i>R</i> indices [<i>I</i> > 2 σ(<i>I</i>)]	<i>R</i> 1 = 0.0402, <i>wR</i> 2 = 0.0856

Figure S7. Thermal ellipsoid depiction of compound **Ni-6**. ORTEP at 50% probability. The crystal structure of **Ni-6** was disordered over the aliphatic side chain. The disorder was omitted for clarity.

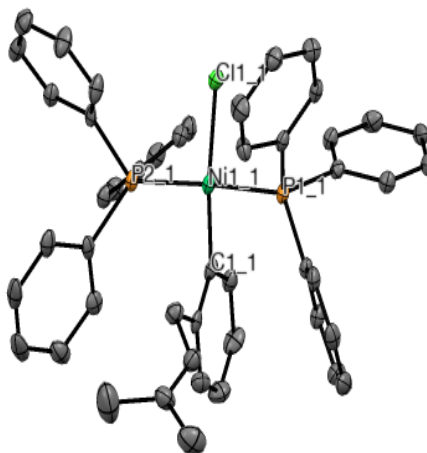
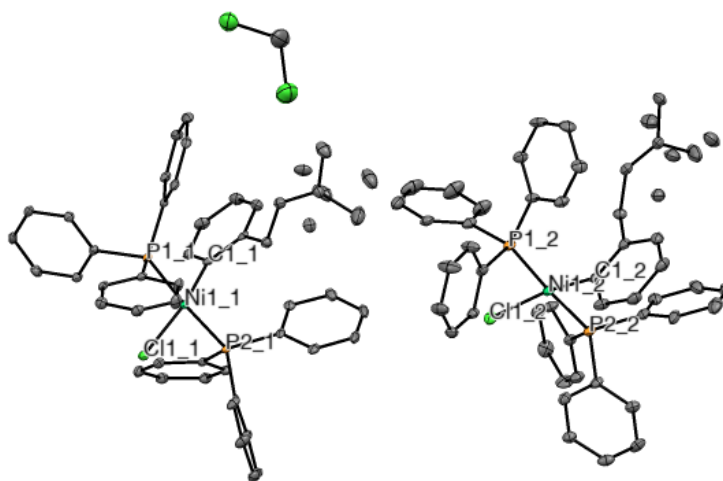


Figure S8. Thermal ellipsoid depiction of compound **Ni-6** with disorder. ORTEP at 50% probability.



The structure was refined as a two-component non-merohedral twin against the HKLF4 reflections file. Refinement against the HKLF5 file was also attempted but resulted in a poorer fit. The structure contained two molecules in the asymmetric unit, each of which exhibited an alkyl group disordered over two positions; this disorder was modeled with the help of similarity restraints on 1,2- and 1,3- distances and displacement parameters as well as enhanced rigid-bond restraints.

Table S5. Crystal data and structure refinement for compound **Ni-6**.

Empirical formula	$\text{C}_{95}\text{H}_{88}\text{Cl}_4\text{Ni}_2\text{P}_4$	
Formula weight	1612.75	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 11.8529(14)$ Å	$a = 100.919(2)^\circ$.
	$b = 14.1583(17)$ Å	$b = 92.094(2)^\circ$.
	$c = 24.919(3)$ Å	$\gamma = 96.431(2)^\circ$.
Volume	$4073.1(8)$ Å ³	
Z	2	
Density (calculated)	1.315 Mg/m ³	
Absorption coefficient	0.719 mm ⁻¹	
F(000)	1684	
Crystal size	0.130 x 0.030 x 0.020 mm ³	
Theta range for data collection	1.467 to 26.372°	
Reflections collected	16584	
Independent reflections	16584 [$R_{int} = 0.1199$]	
Completeness to theta = 25.242°	99.7%	
Absorption correction	Semi-empirical from equivalents	
min and max transmission	0.681983 and 0.746070	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	16454/562/1020	
Goodness-of-fit on F^2	1.080	
Largest diff. peak and hole	0.694 and -1.074 e.Å ⁻³	
R indices on all data	$R1 = 0.1170$, $wR2 = 0.1655$	
Final R indices [$I > 2 \sigma(I)$]	$R1 = 0.0635$, $wR2 = 0.1478$	

VI. GC/MS Spectra of Heck Activation Product

Figure S9. GC/MS trace of Heck activation product **11**.

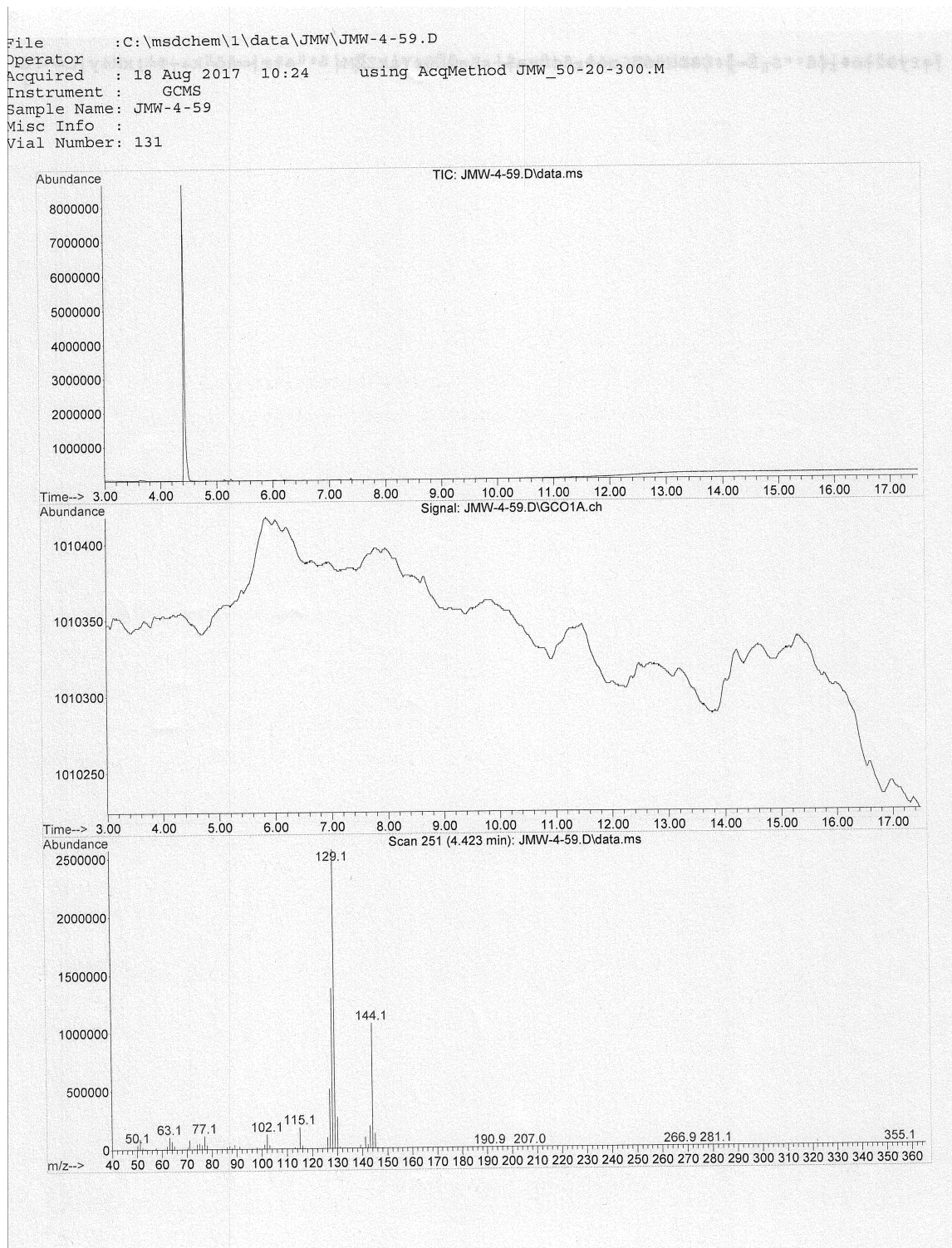


Figure S10. GC/MS of heat activation of Ni-6.

File :C:\msdchem\1\data\JMW\JMW-3-229.D
Operator :
Acquired : 18 May 2017 14:04 using AcqMethod JMW_50-20-300.M
Instrument : GCMS
Sample Name: JMW-3-229
Misc Info :
Vial Number: 141

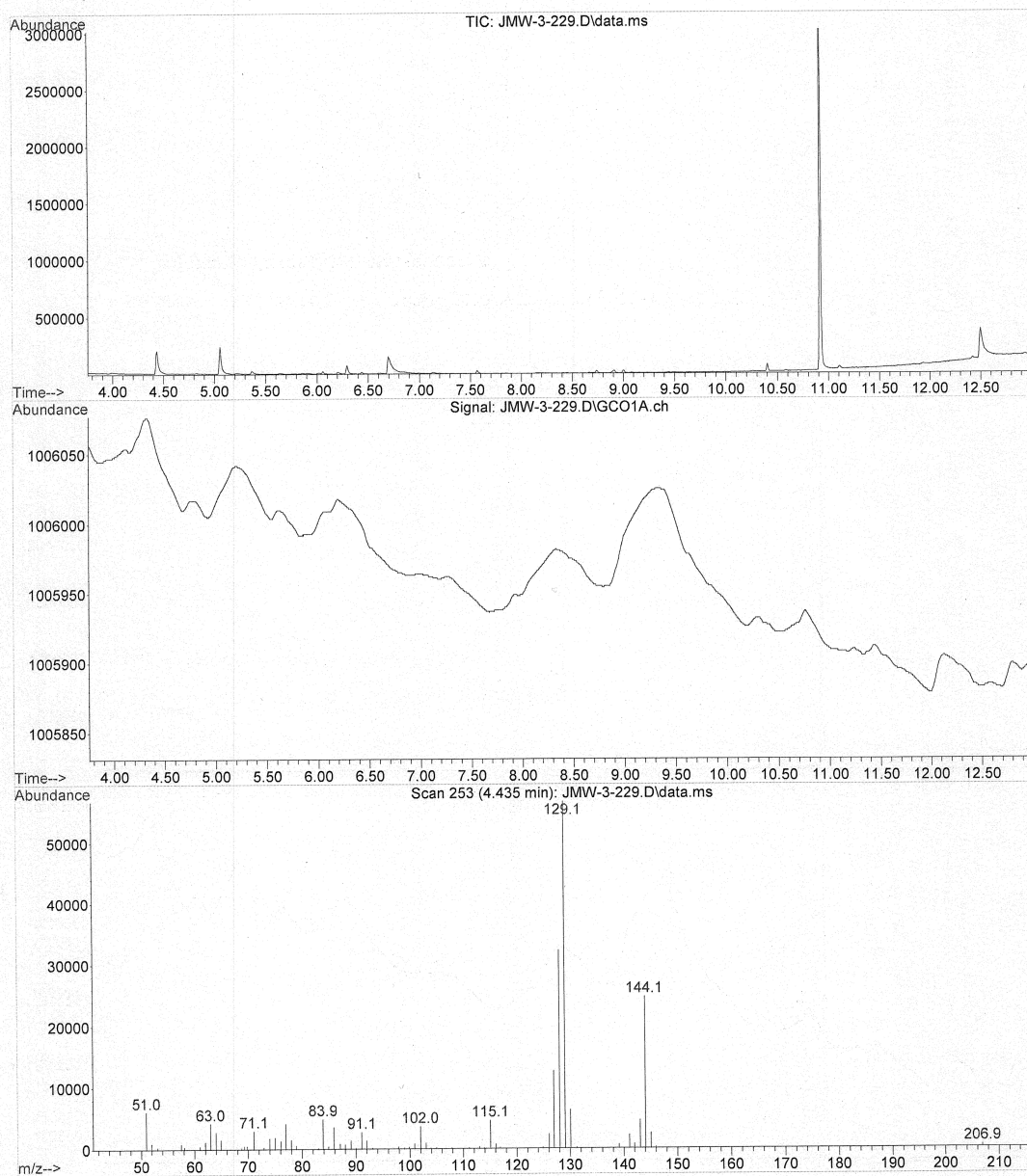
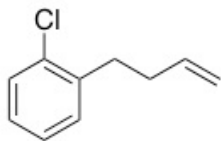


Figure S11. Proton NMR of 2.



2

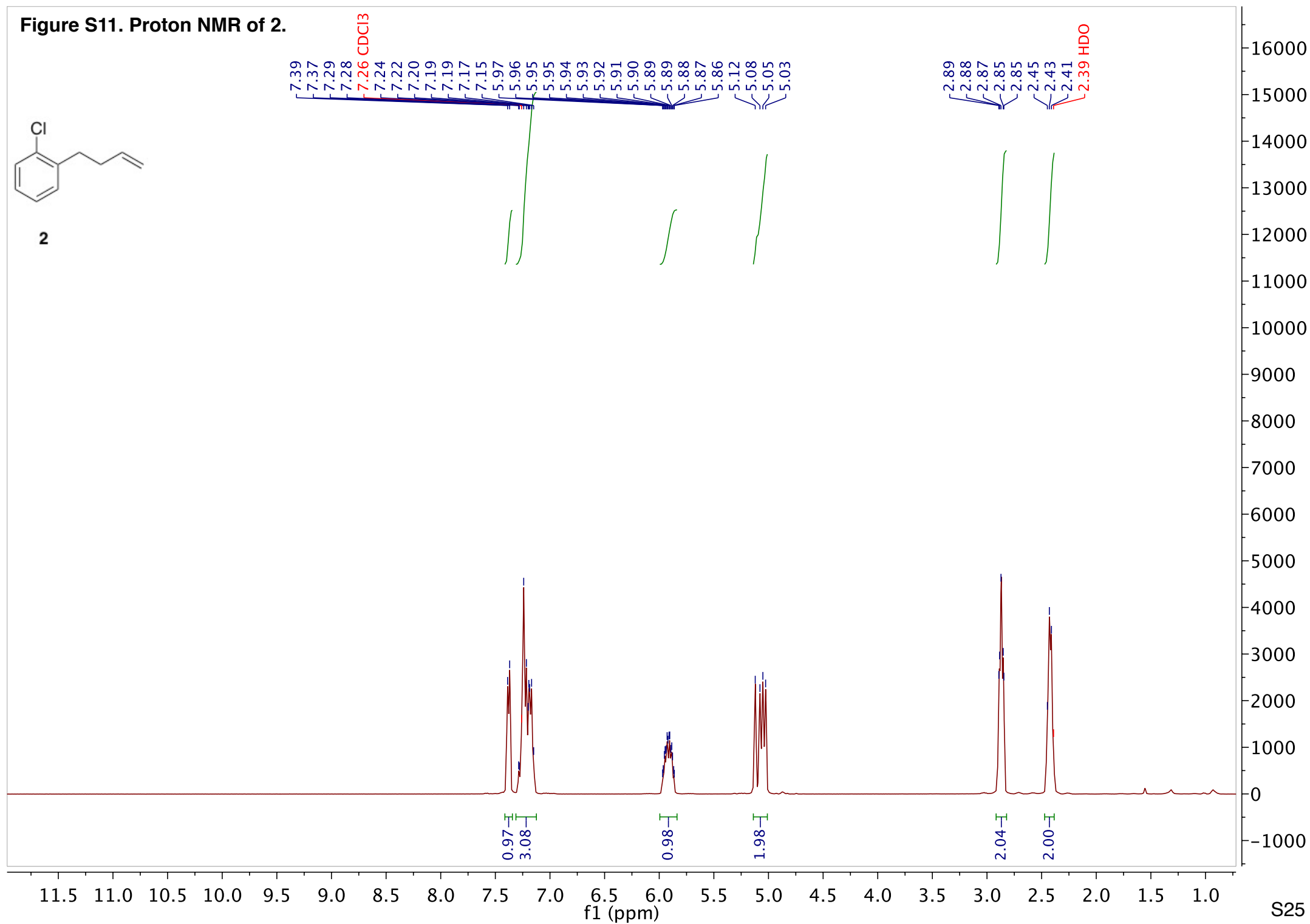
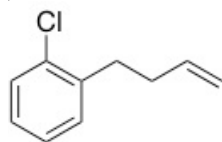


Figure S12. Carbon NMR of 2.



2

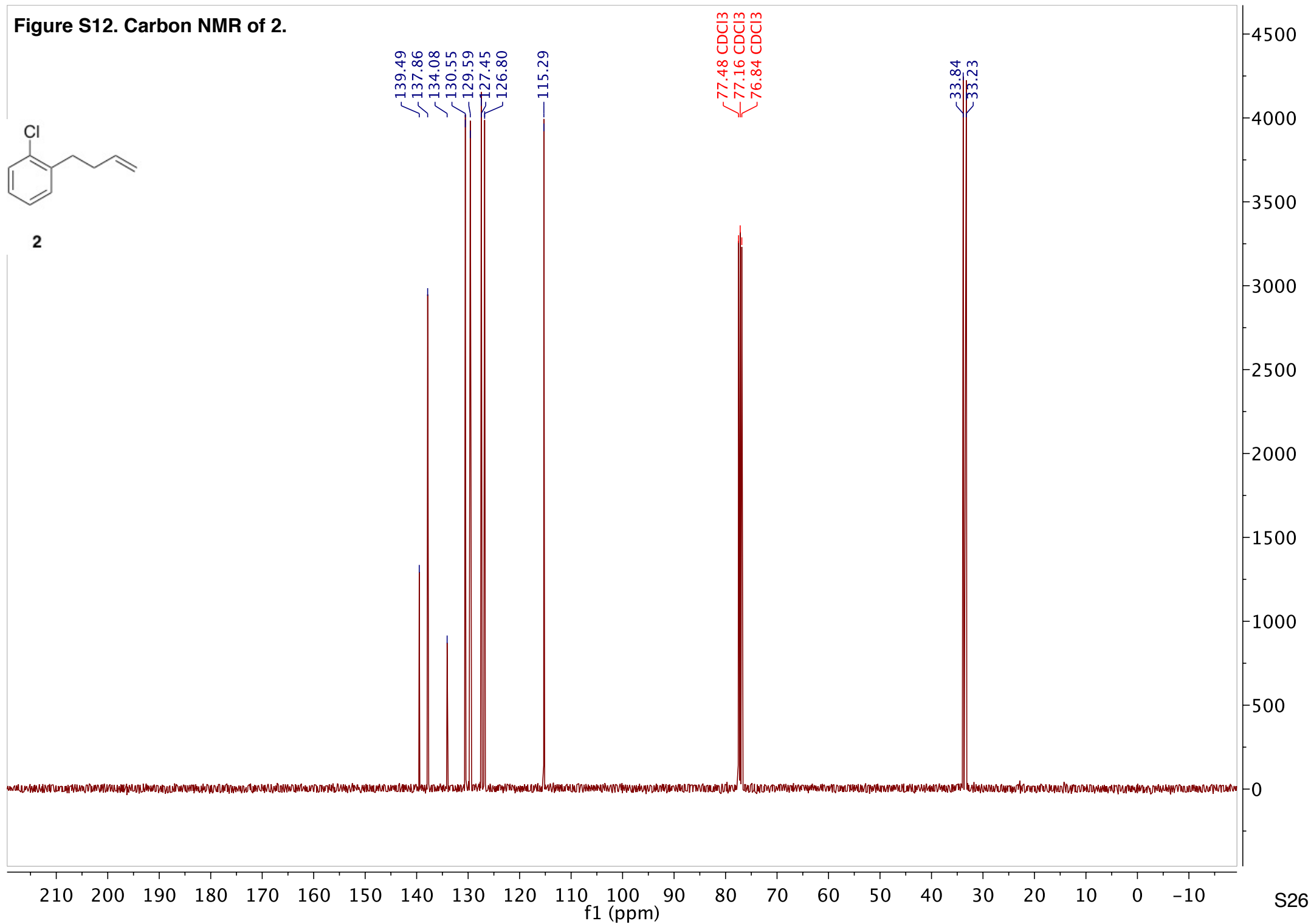
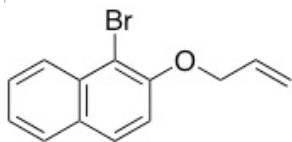


Figure S13. Proton NMR of 3.



3

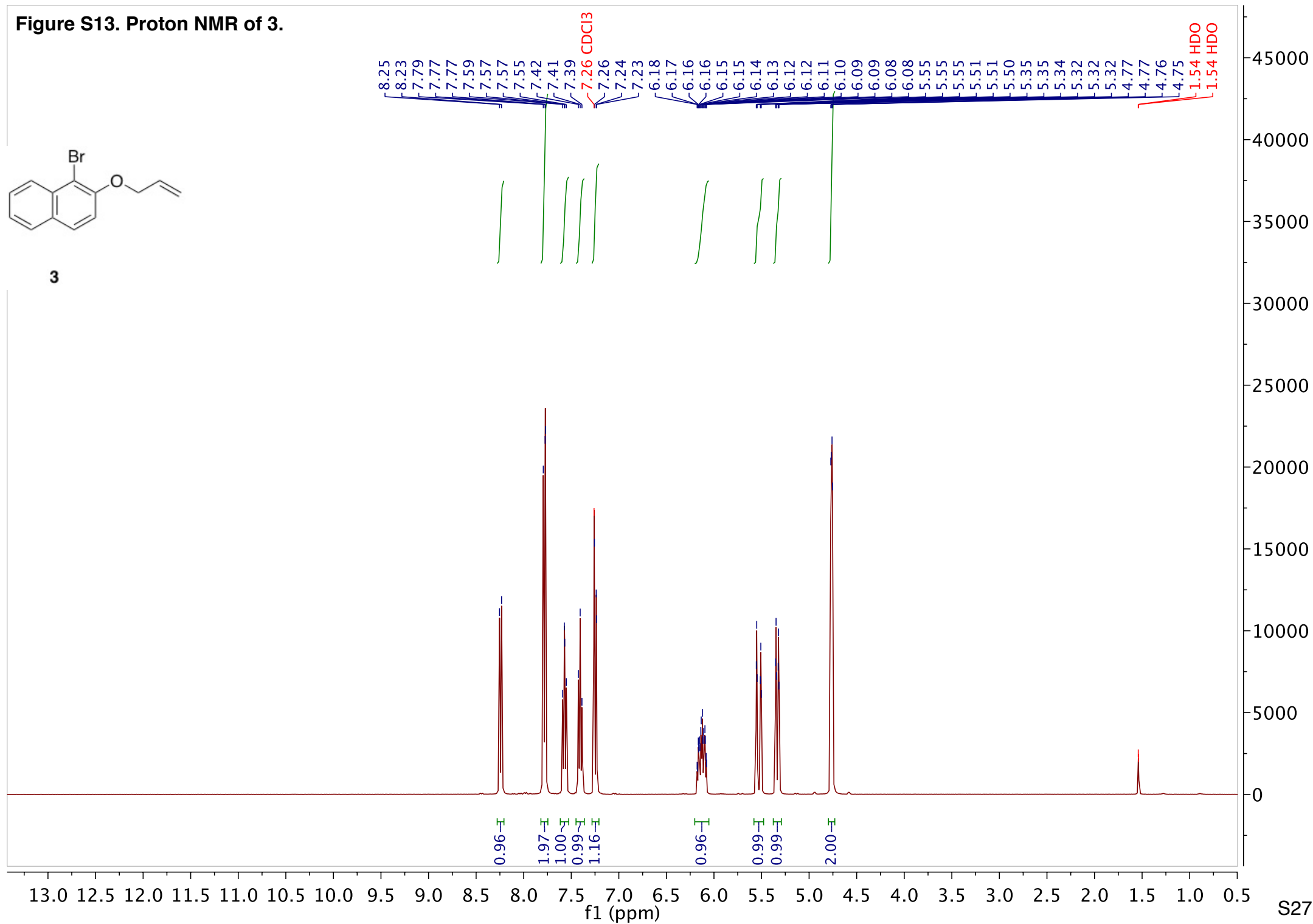
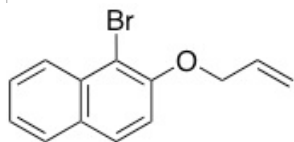


Figure S14. Carbon NMR of 3.



3

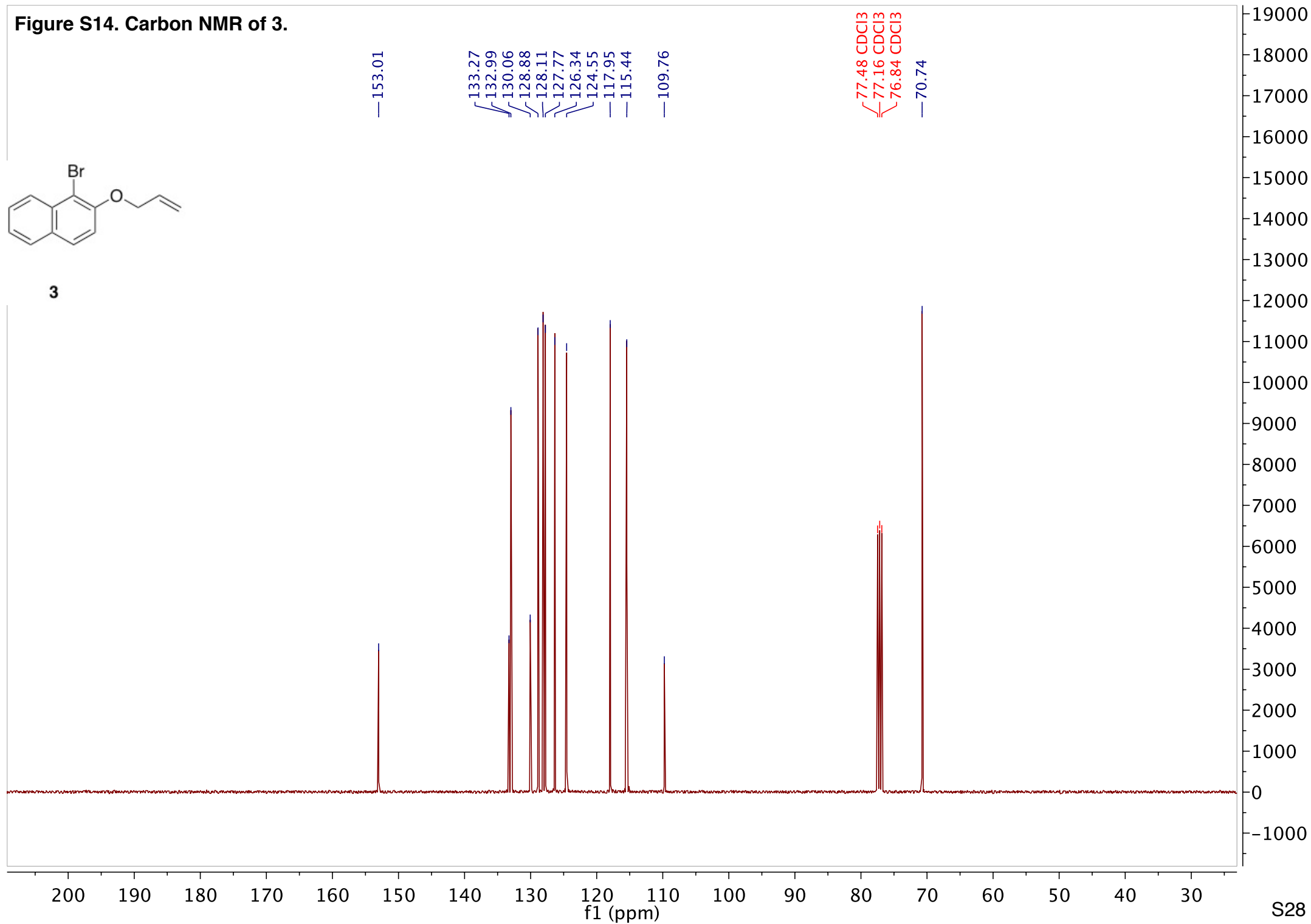
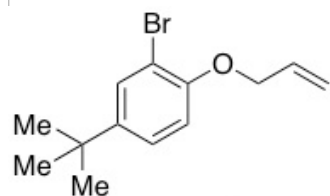


Figure S15. Proton
NMR of 4.



4

7.58
7.28
7.26
7.26 CDCl₃
6.87
6.85
6.14
6.14
6.13
6.12
6.11
6.11
6.10
6.10
6.09
6.08
6.07
6.07
6.06
6.05
6.05
6.04
5.52
5.48
5.34
5.31
4.63
4.61

1.56 HDO
1.33
1.32
1.31

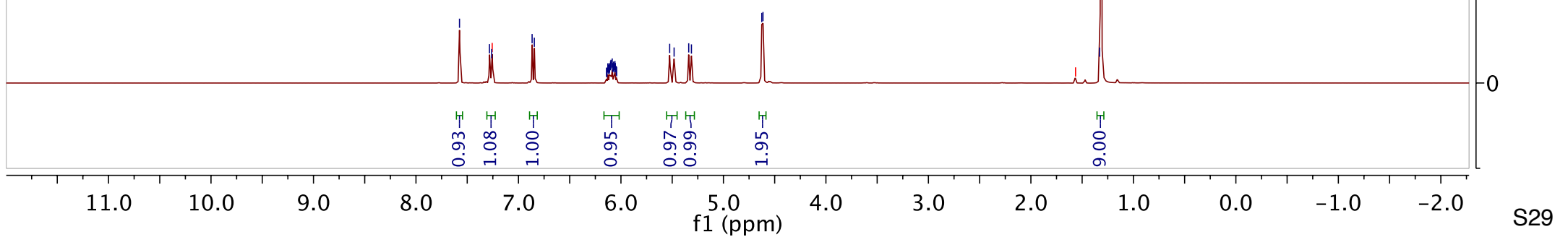
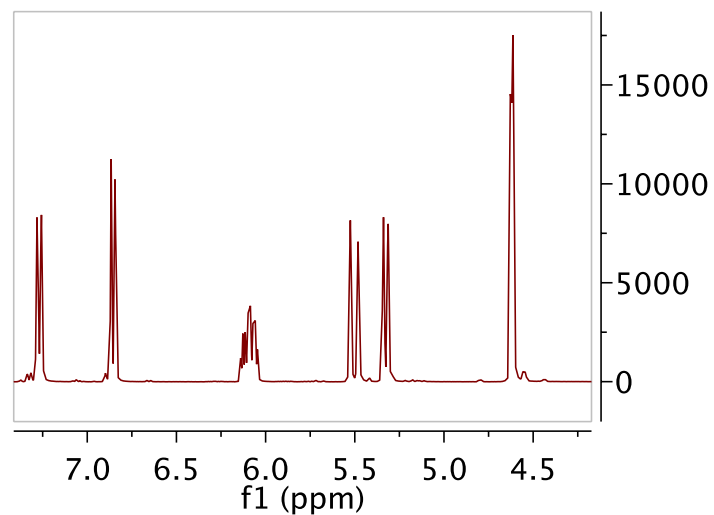
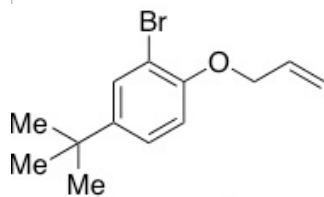
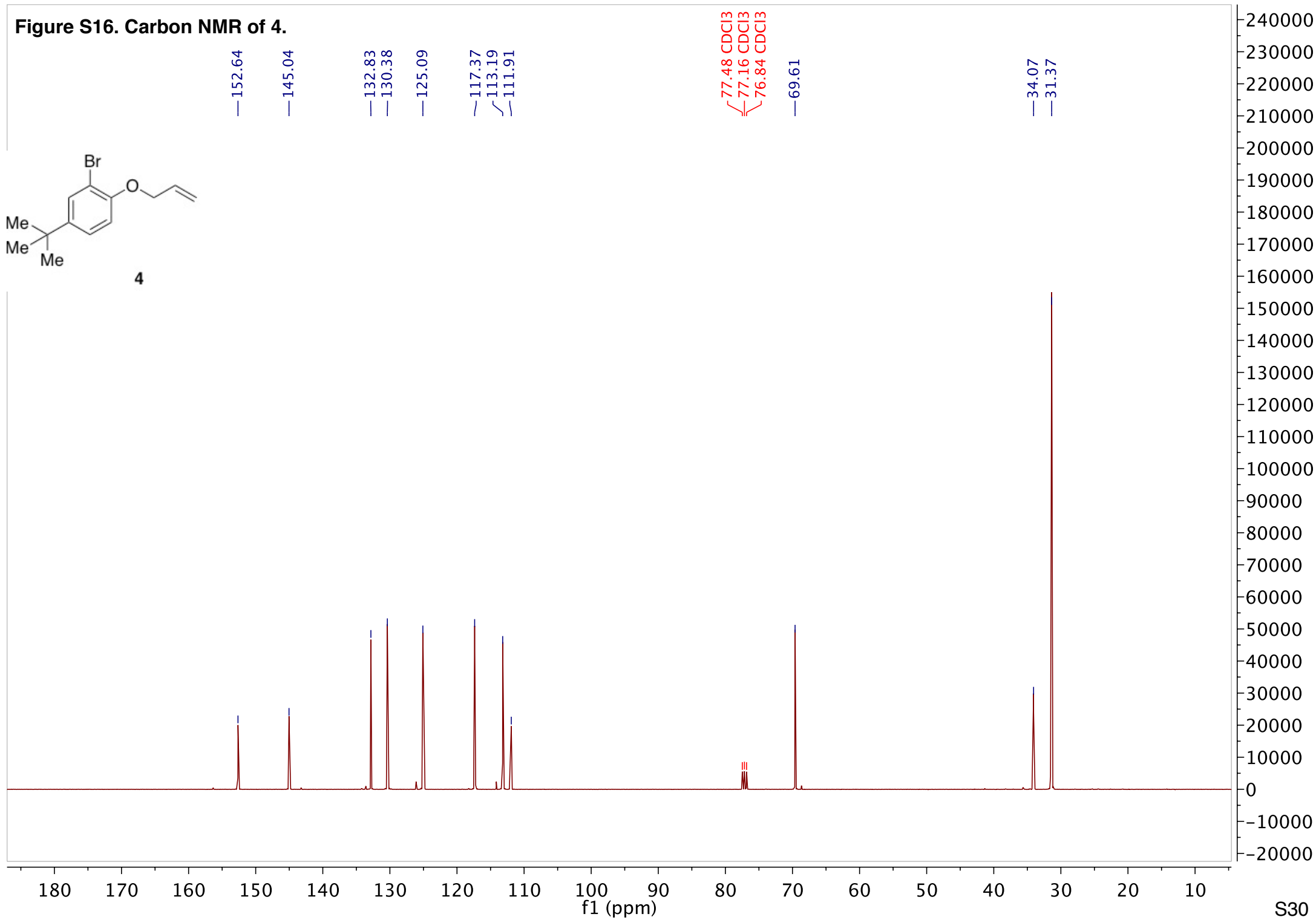


Figure S16. Carbon NMR of 4.



4



S30

Figure S17. Proton NMR of 5.

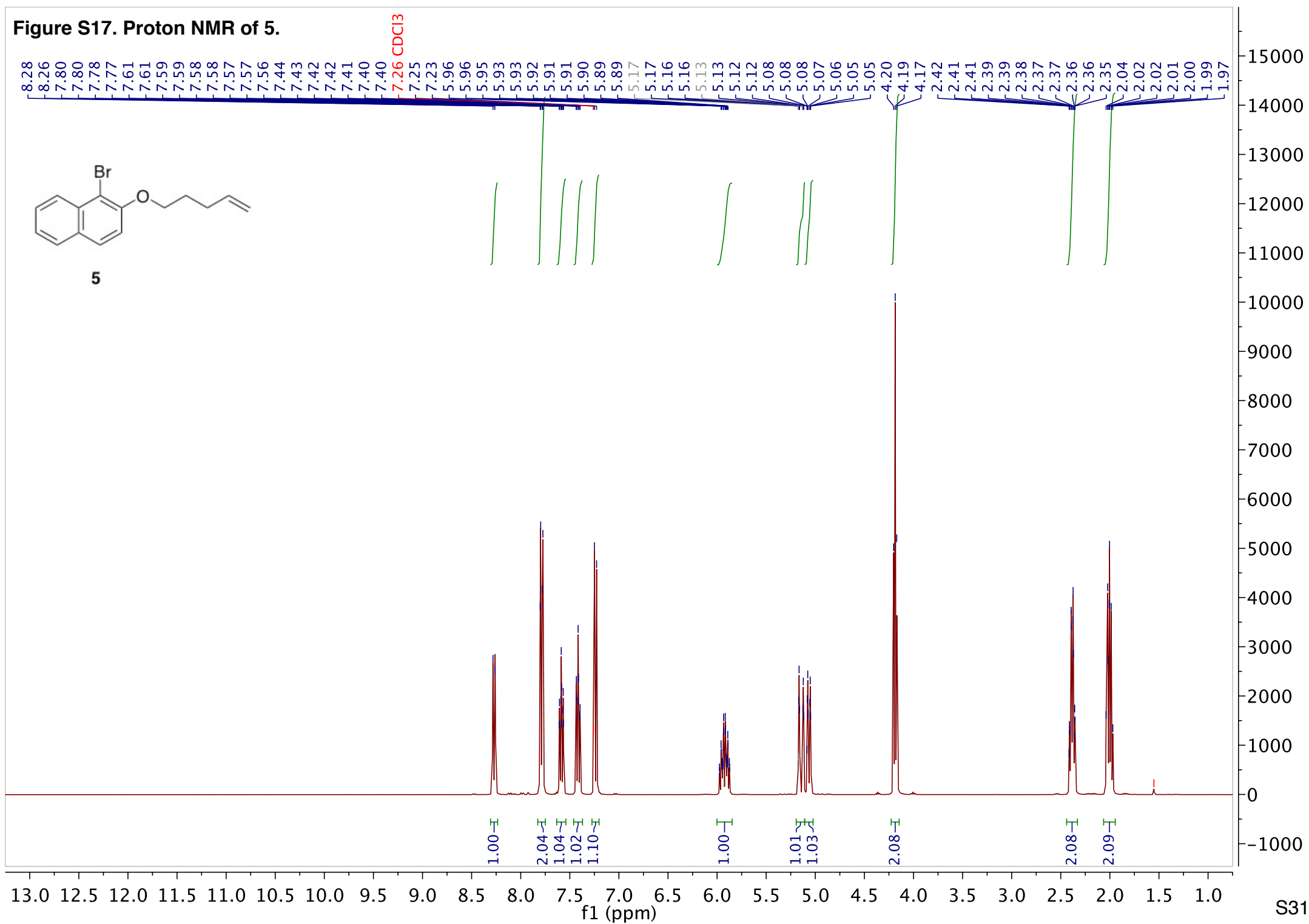


Figure S18. Carbon NMR of 5.

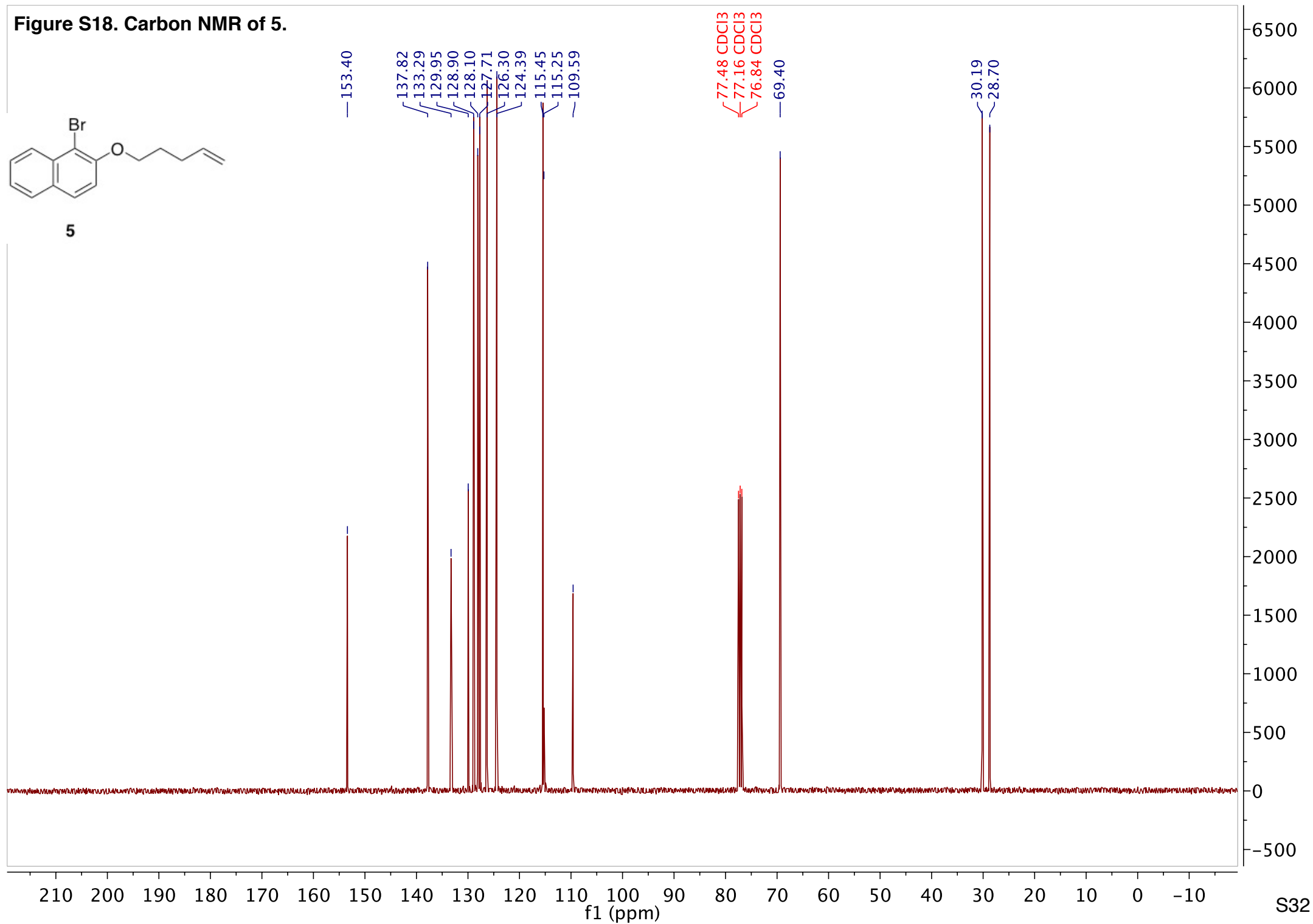
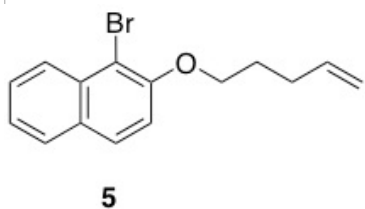
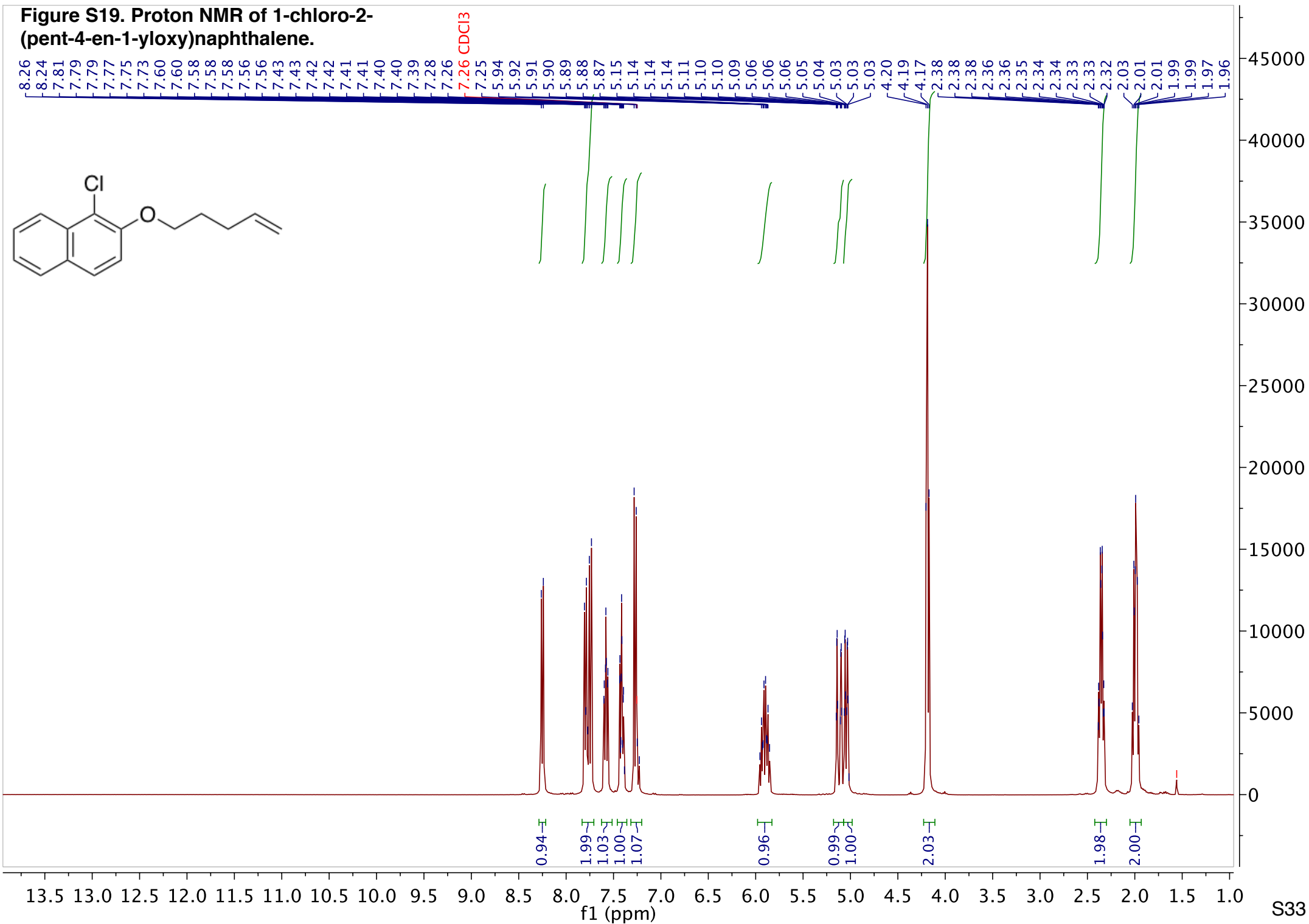


Figure S19. Proton NMR of 1-chloro-2-(pent-4-en-1-yloxy)naphthalene.



**Figure S20. Carbon
NMR of 1-chloro-2-
(pent-4-en-1-
yloxy)naphthalene.**

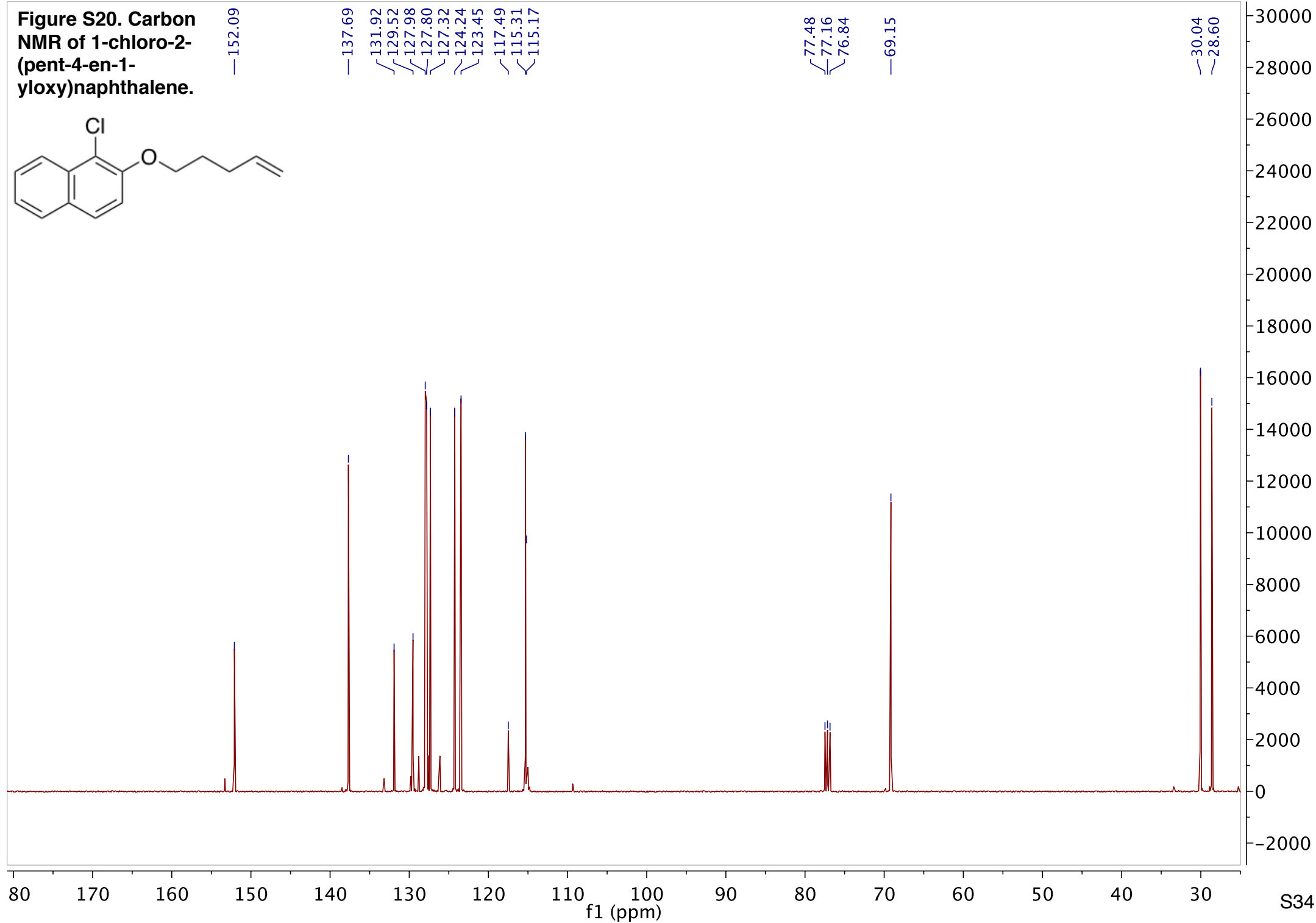
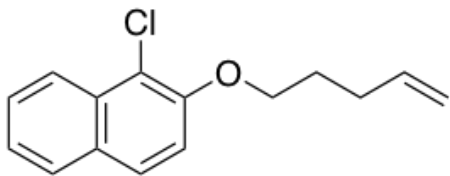
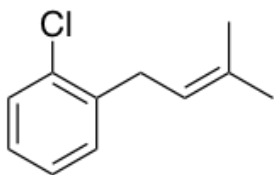
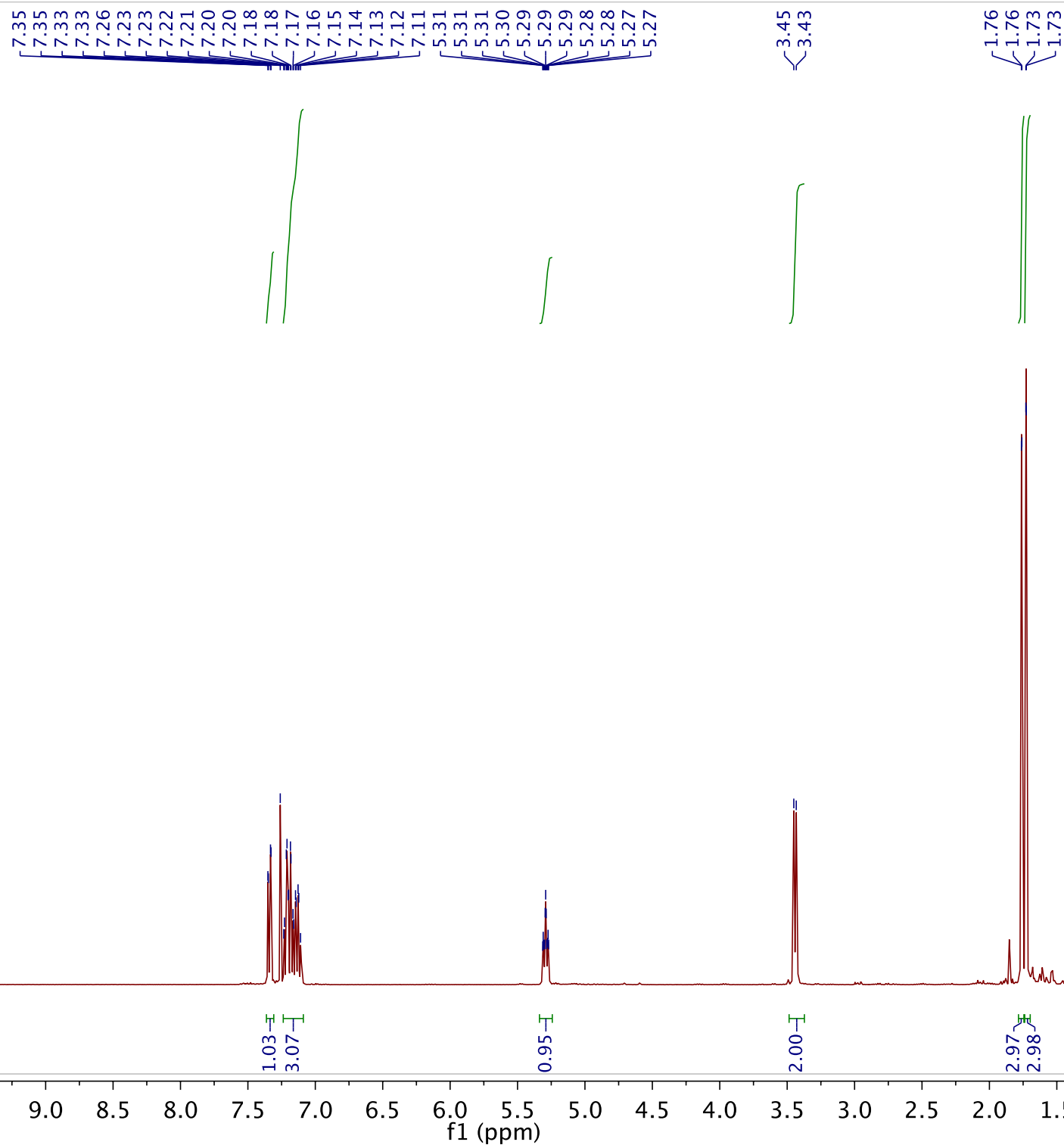


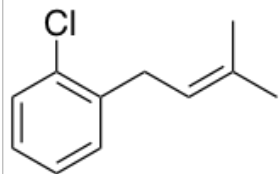
Figure S21. Proton
NMR of 6.



6



**Figure S22. Carbon NMR
of 6.**



6

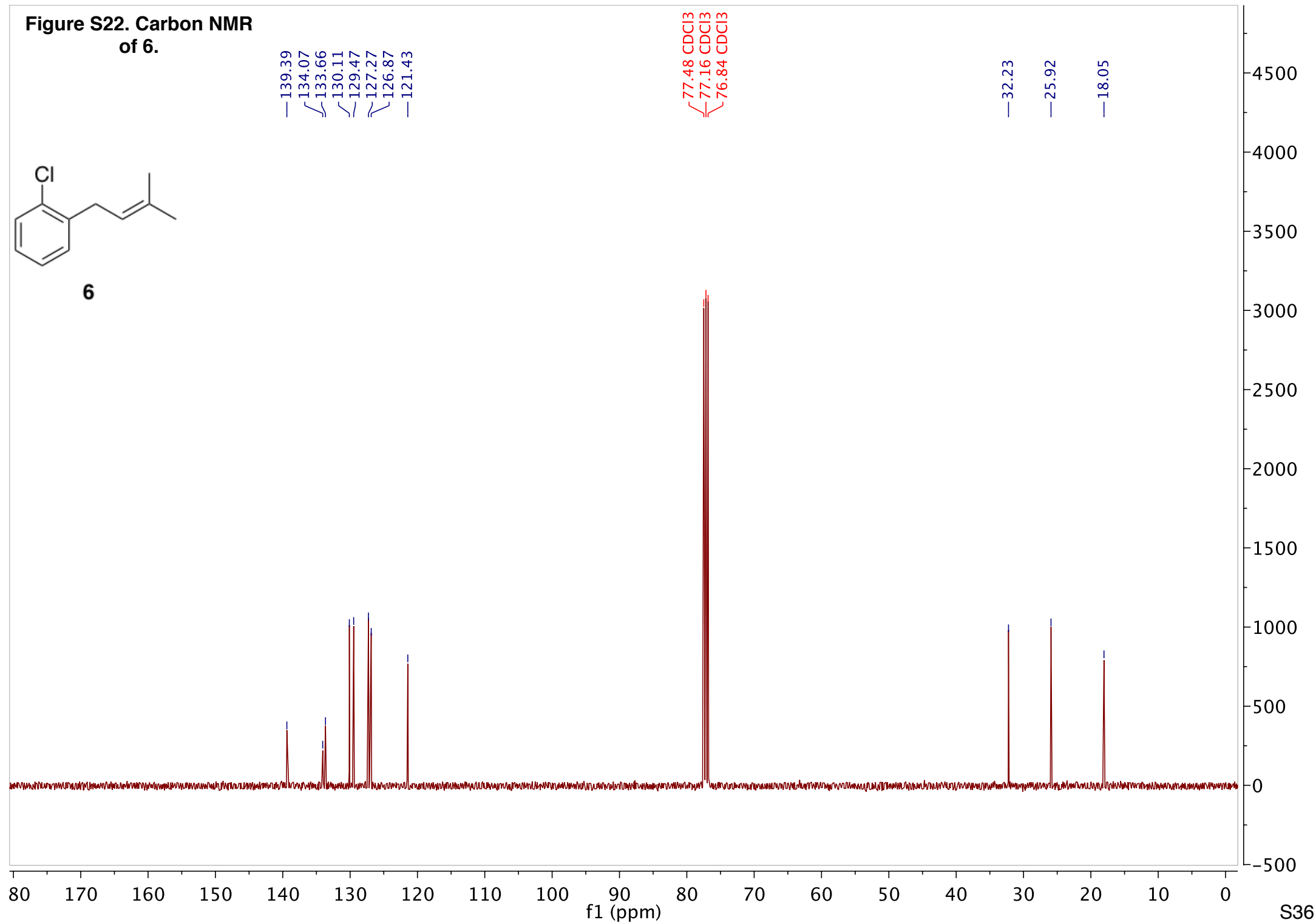


Figure S23. Proton NMR of Ni-2.

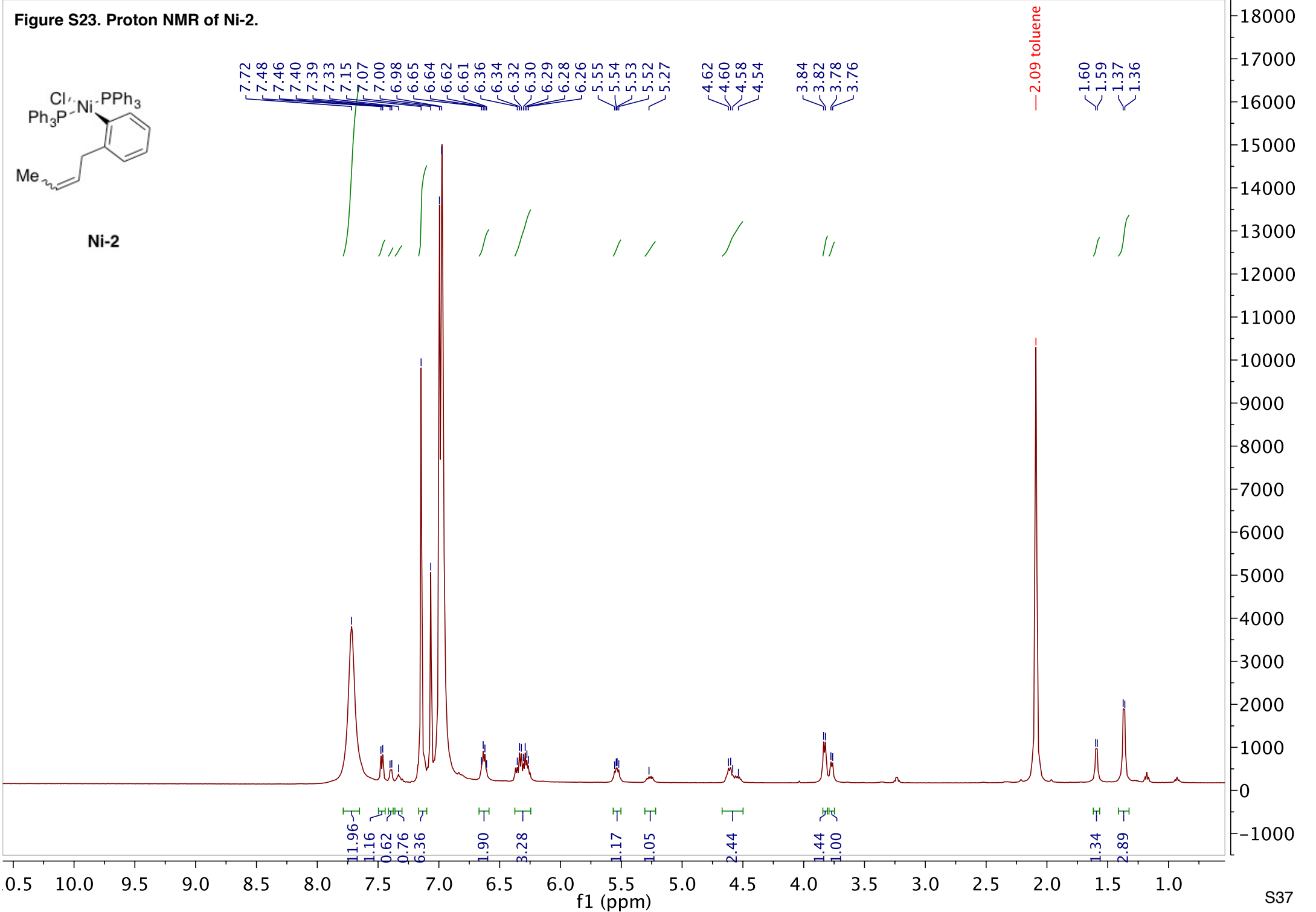
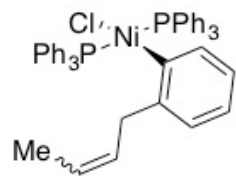


Figure S24. Carbon NMR of Ni-2.



Ni-2

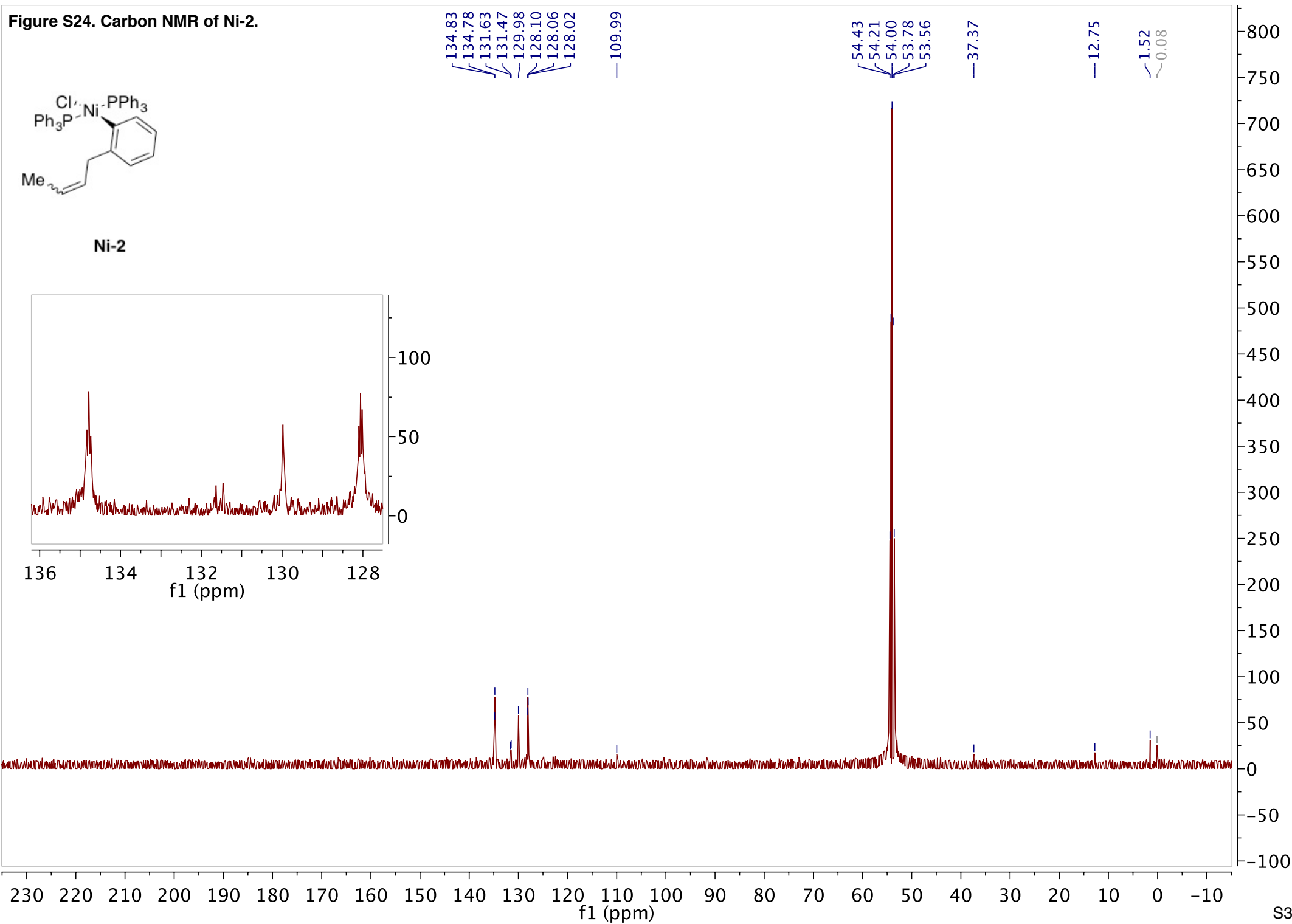
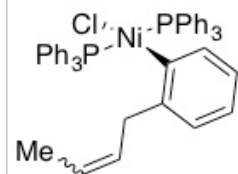


Figure S25. Phosphorus NMR of Ni-2.



Ni-2

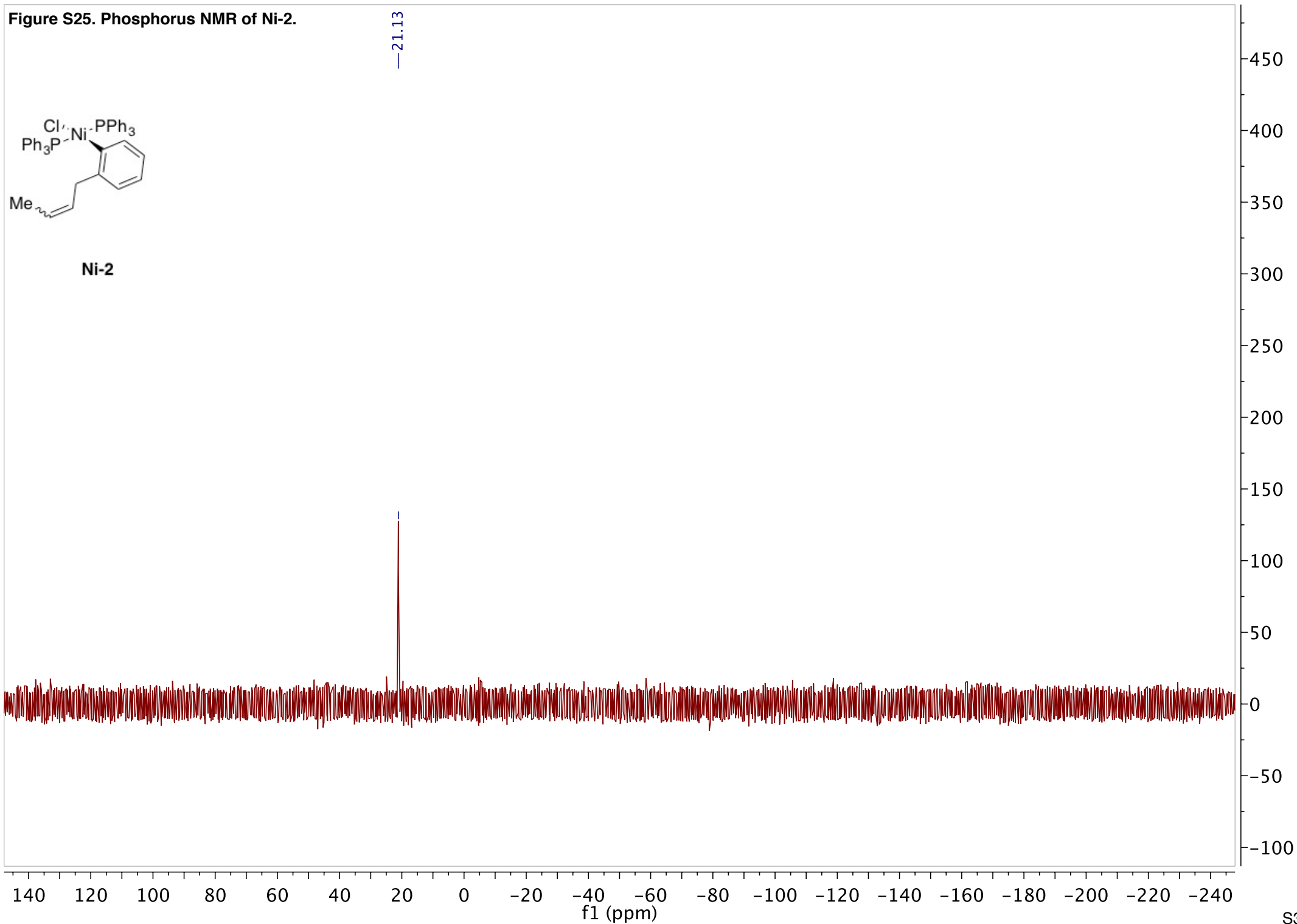
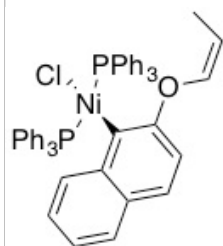


Figure S26. Proton NMR of Ni-3a.



Ni-3a

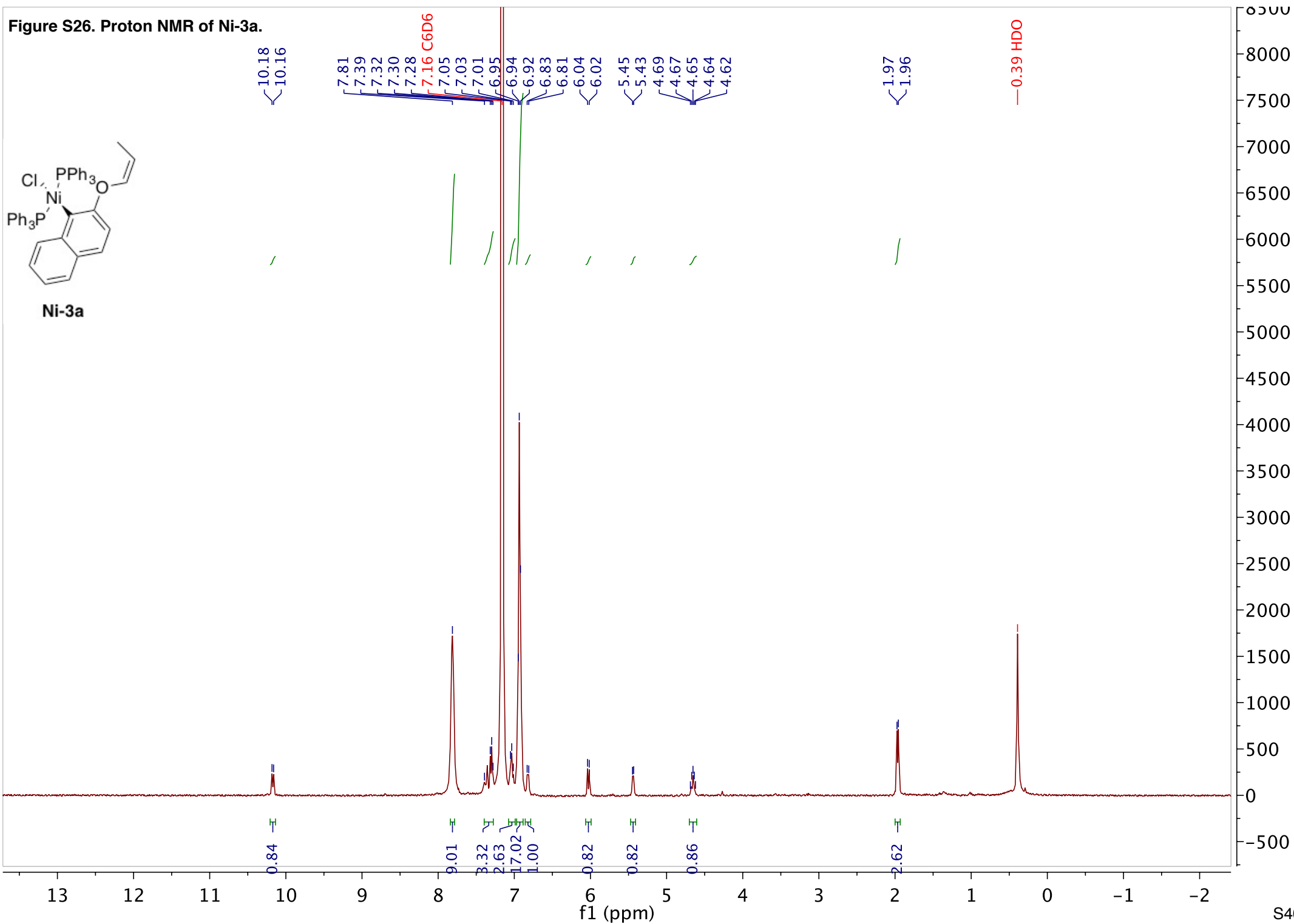
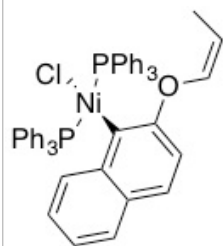


Figure S27. Carbon NMR of Ni-3a.



Ni-3a

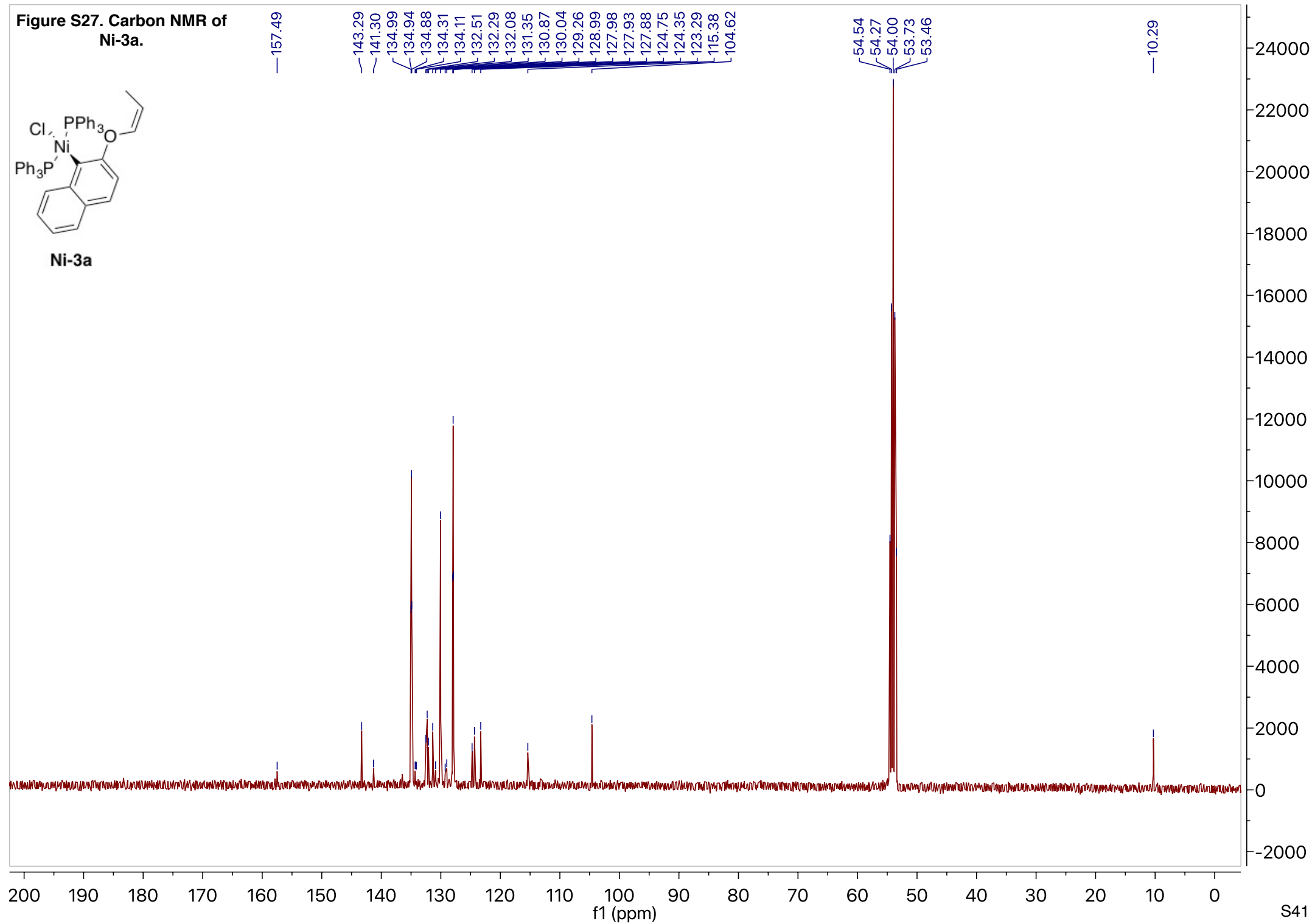
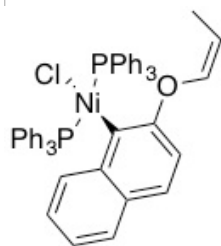


Figure S28. Phosphorus NMR of Ni-3a.



Ni-3a

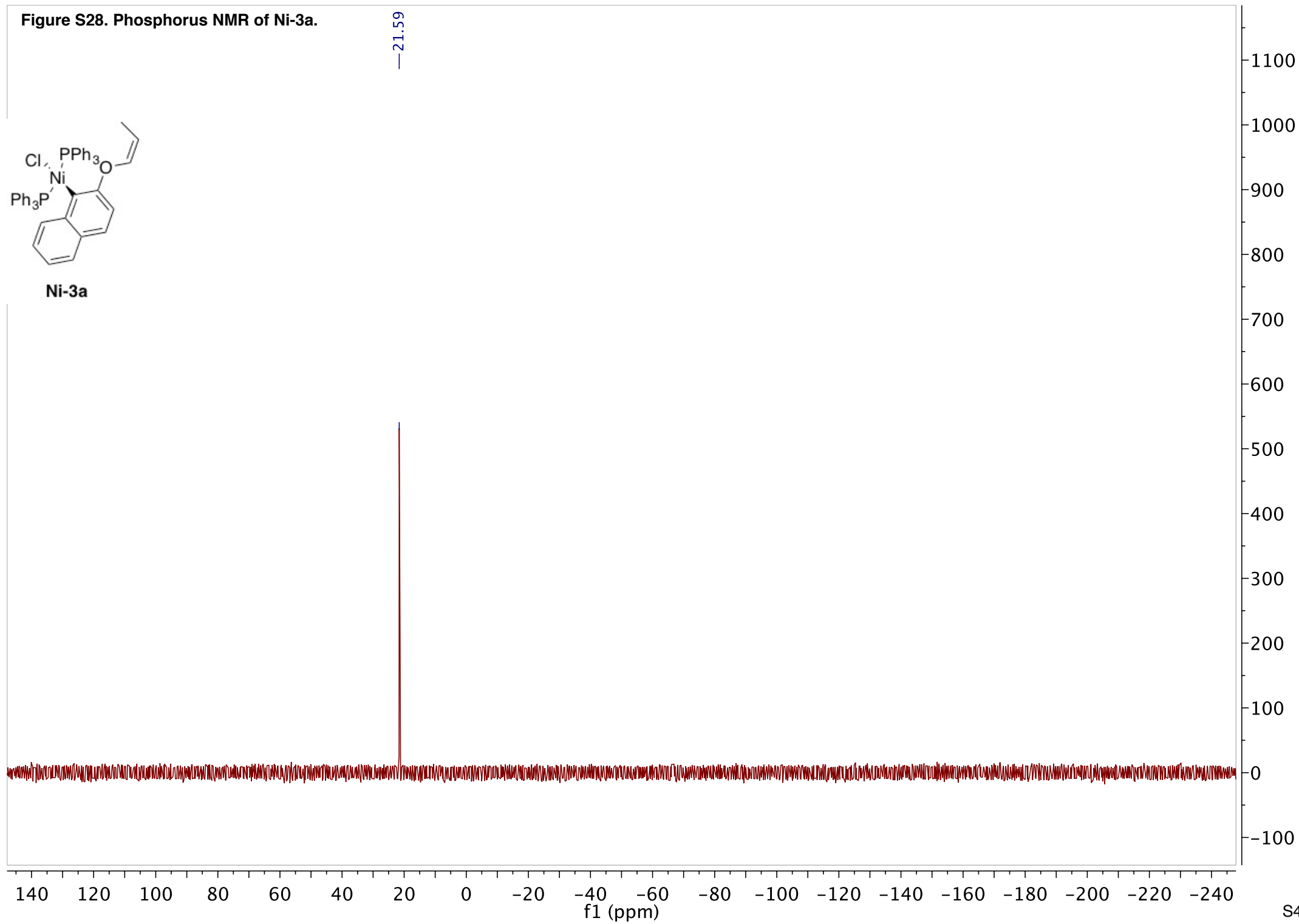


Figure S29. Proton NMR of Ni-3b.

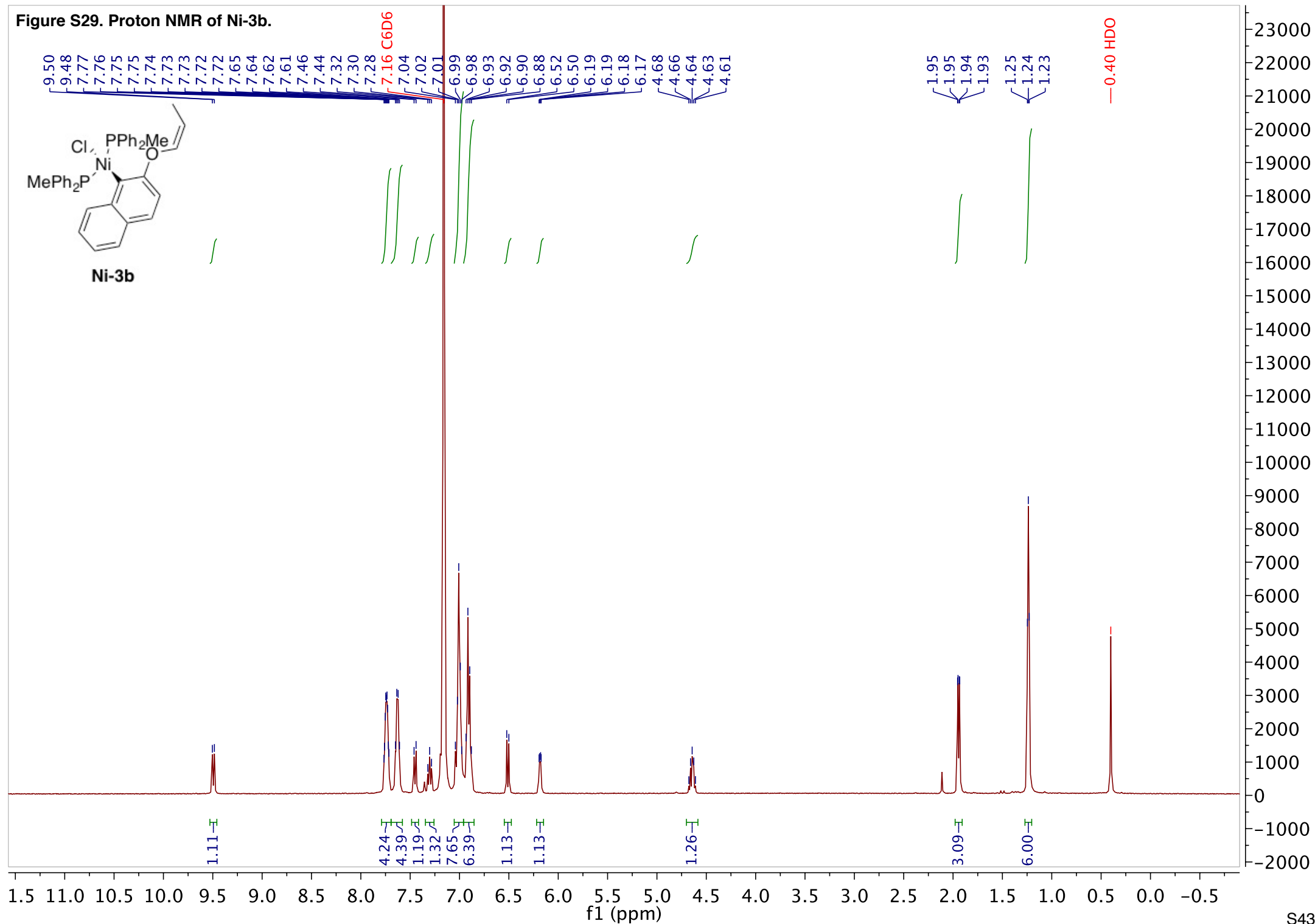


Figure S30. Carbon of Ni-3b.

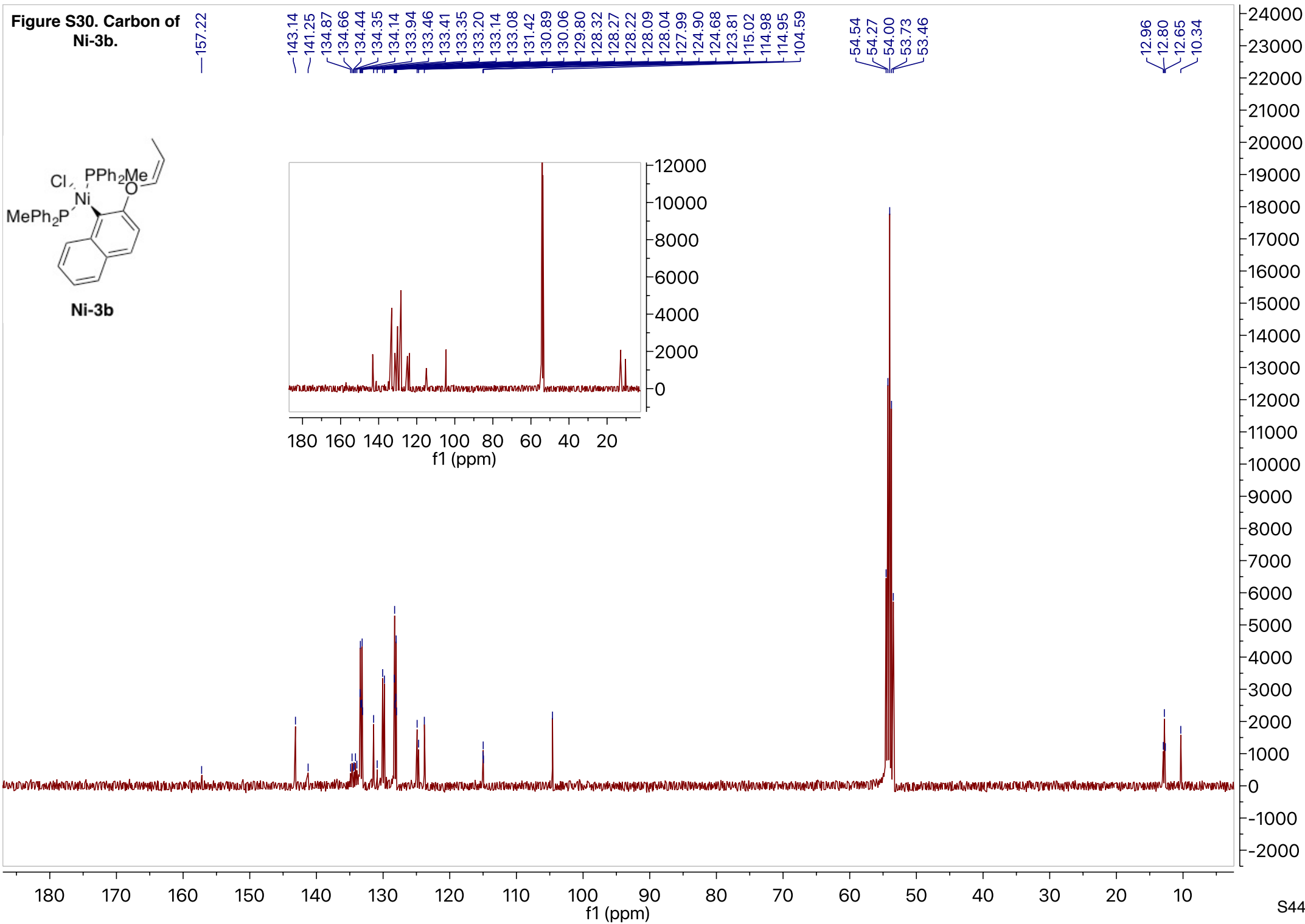
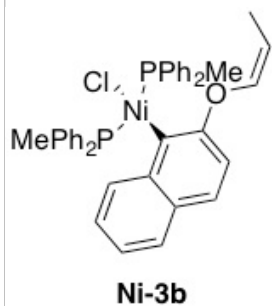


Figure S31. Phosphorus NMR of Ni-3b.

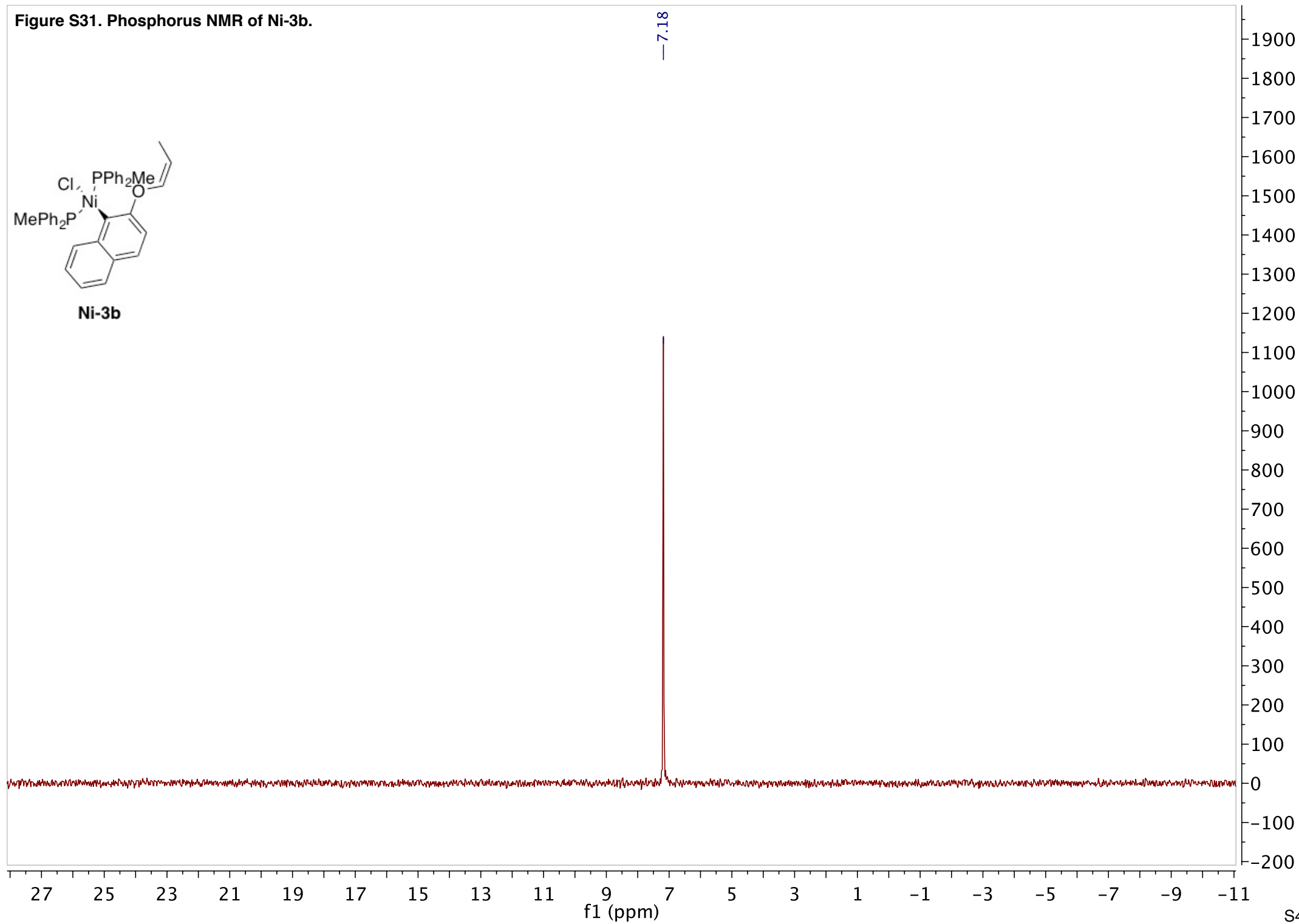
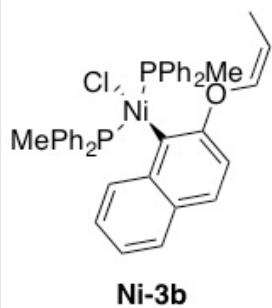
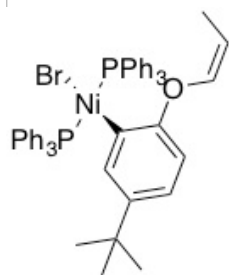


Figure S32. Proton NMR of Ni-4.



Ni-4

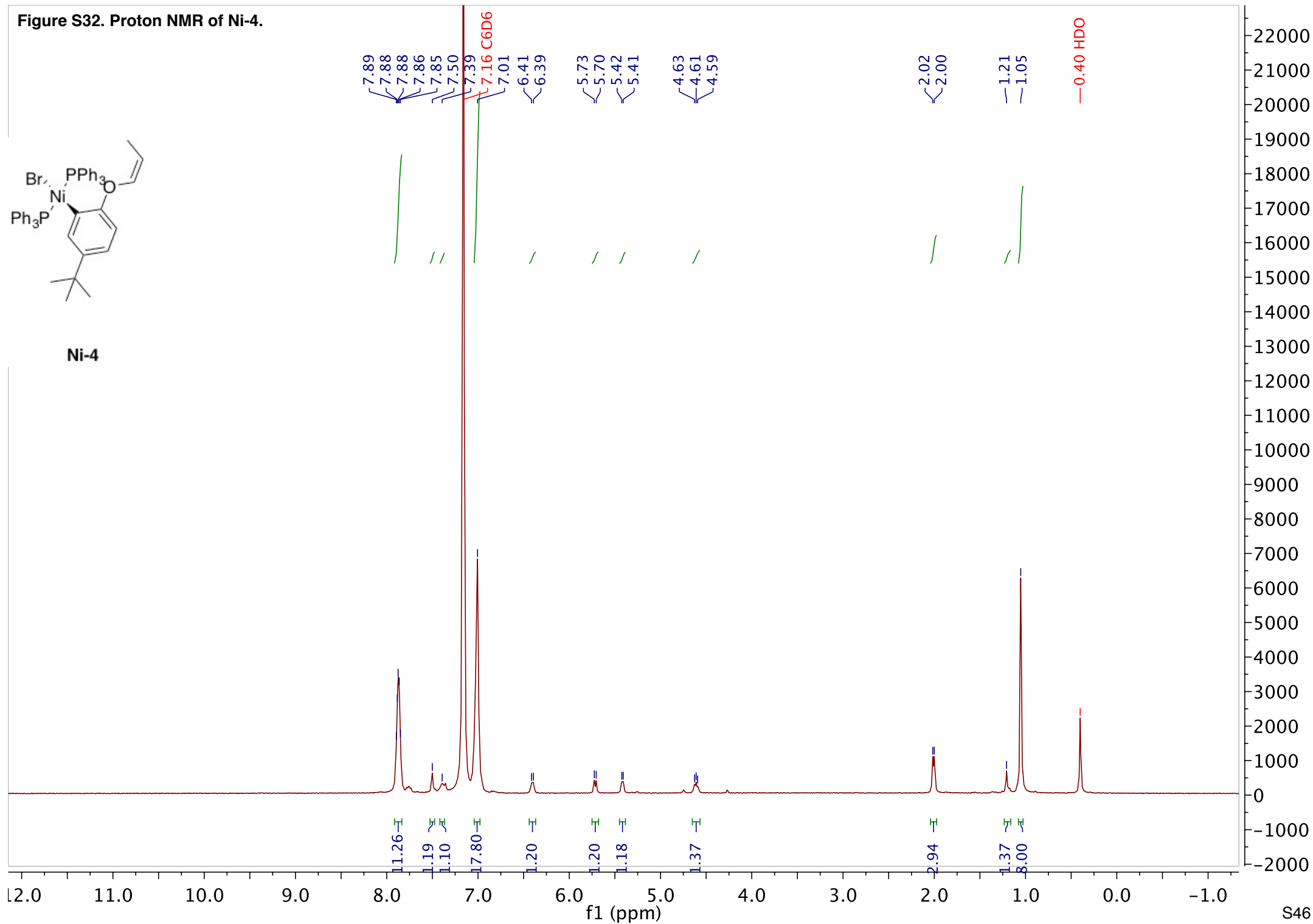
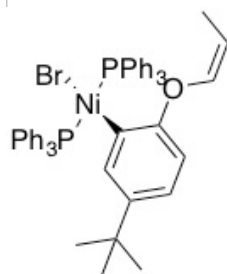


Figure S33. Carbon NMR of Ni-4.



Ni-4

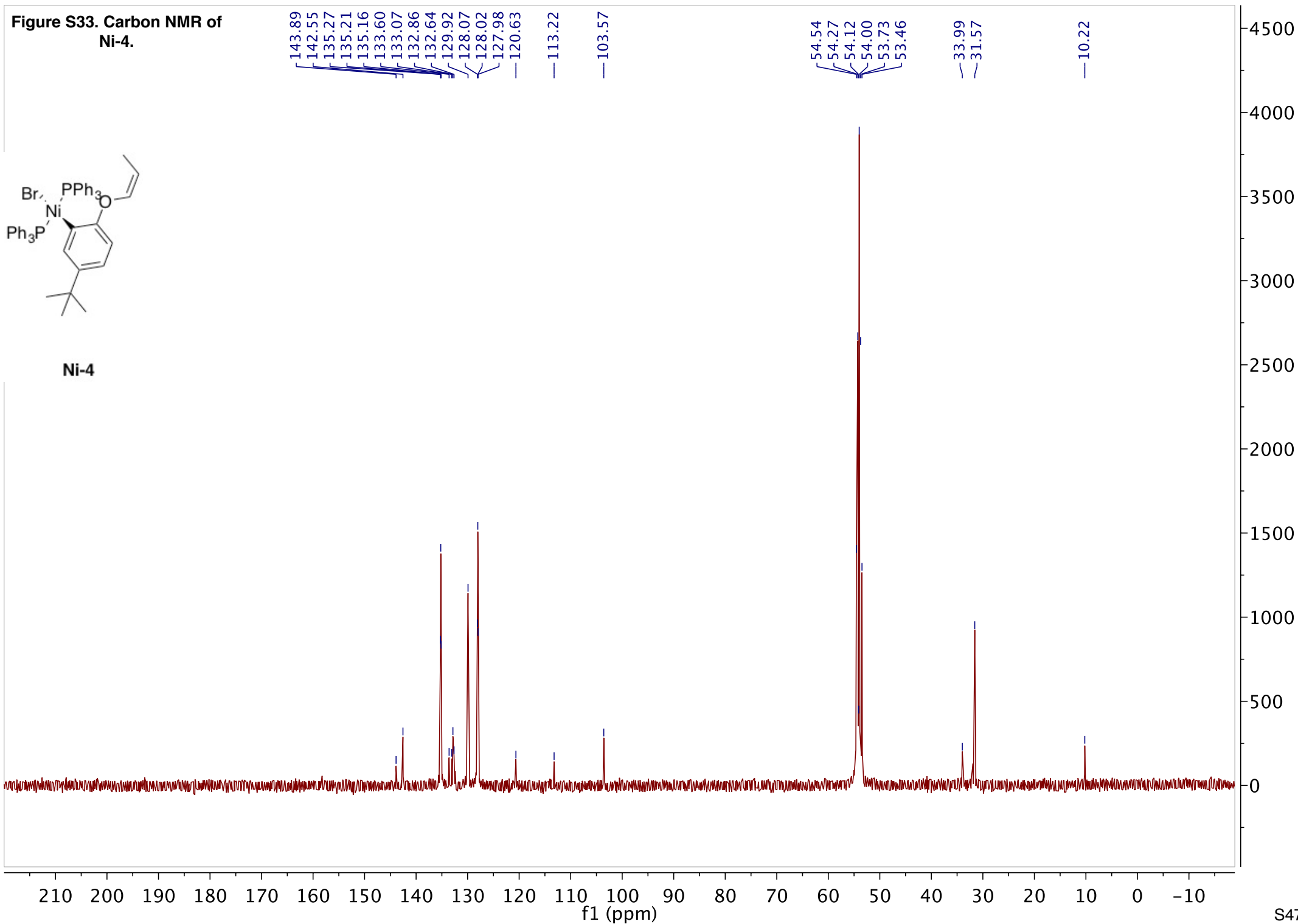
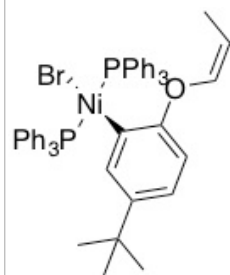


Figure S34. Phosphorus NMR of Ni-4.



Ni-4

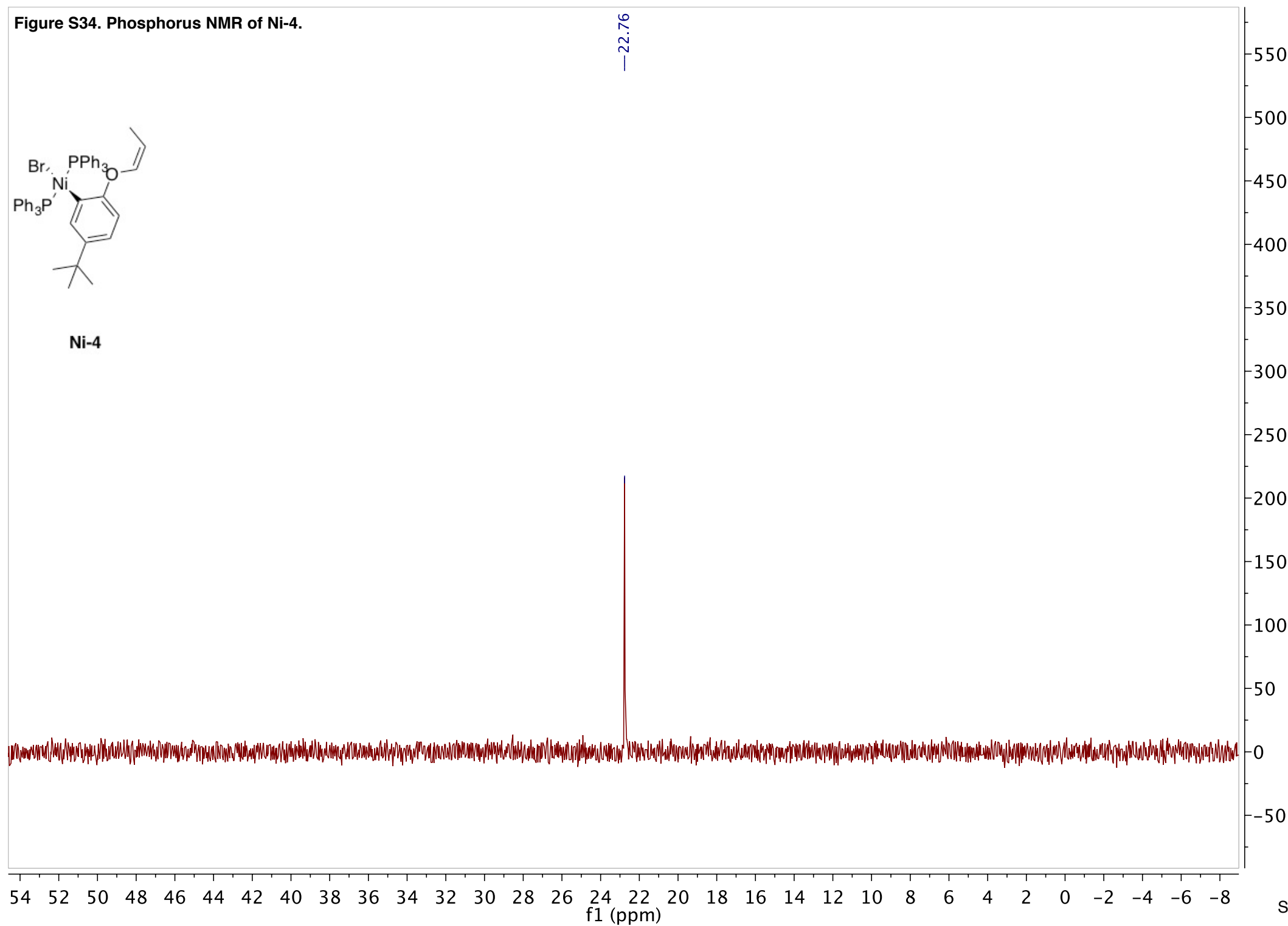
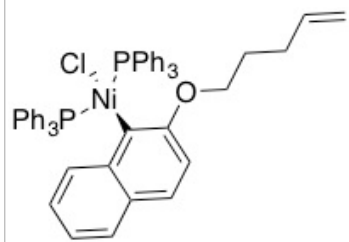


Figure S35. Proton NMR of Ni-5a.



Ni-5a

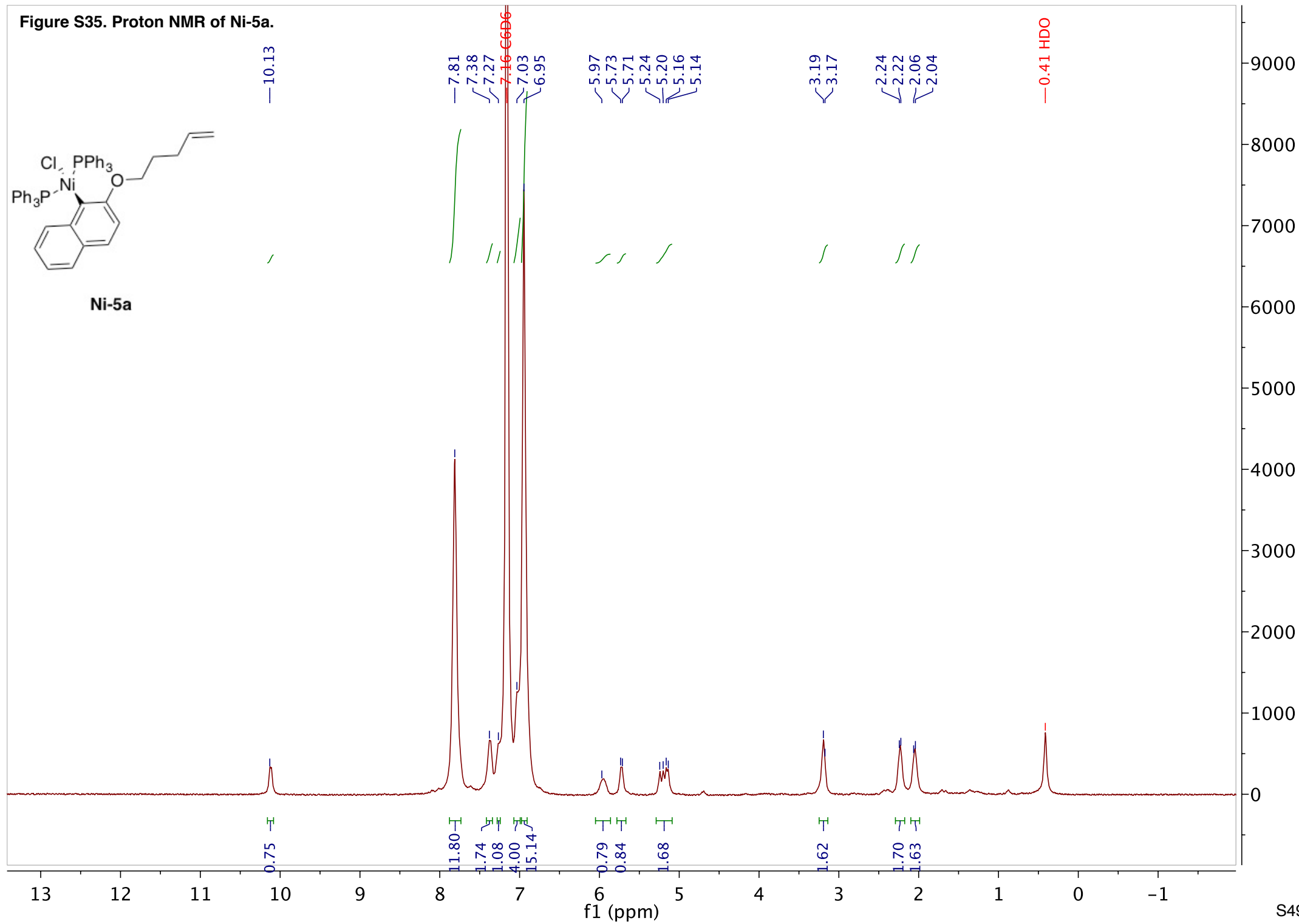
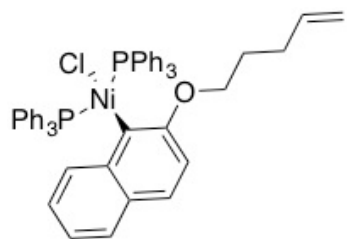


Figure S36. Carbon NMR
of Ni-5a.



Ni-5a

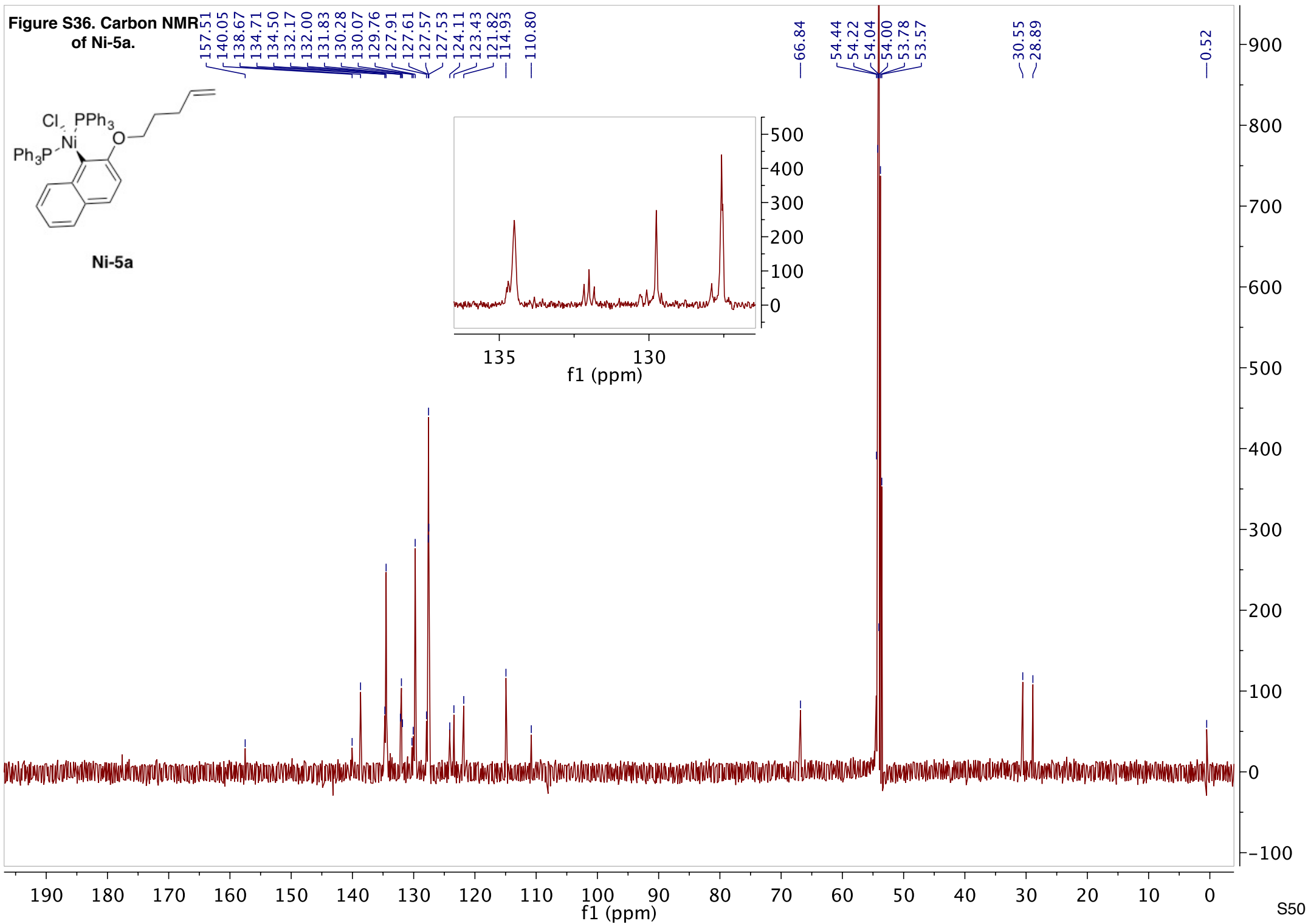
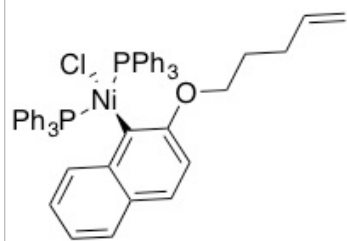


Figure S37. Phosphorus NMR of Ni-5a.



Ni-5a

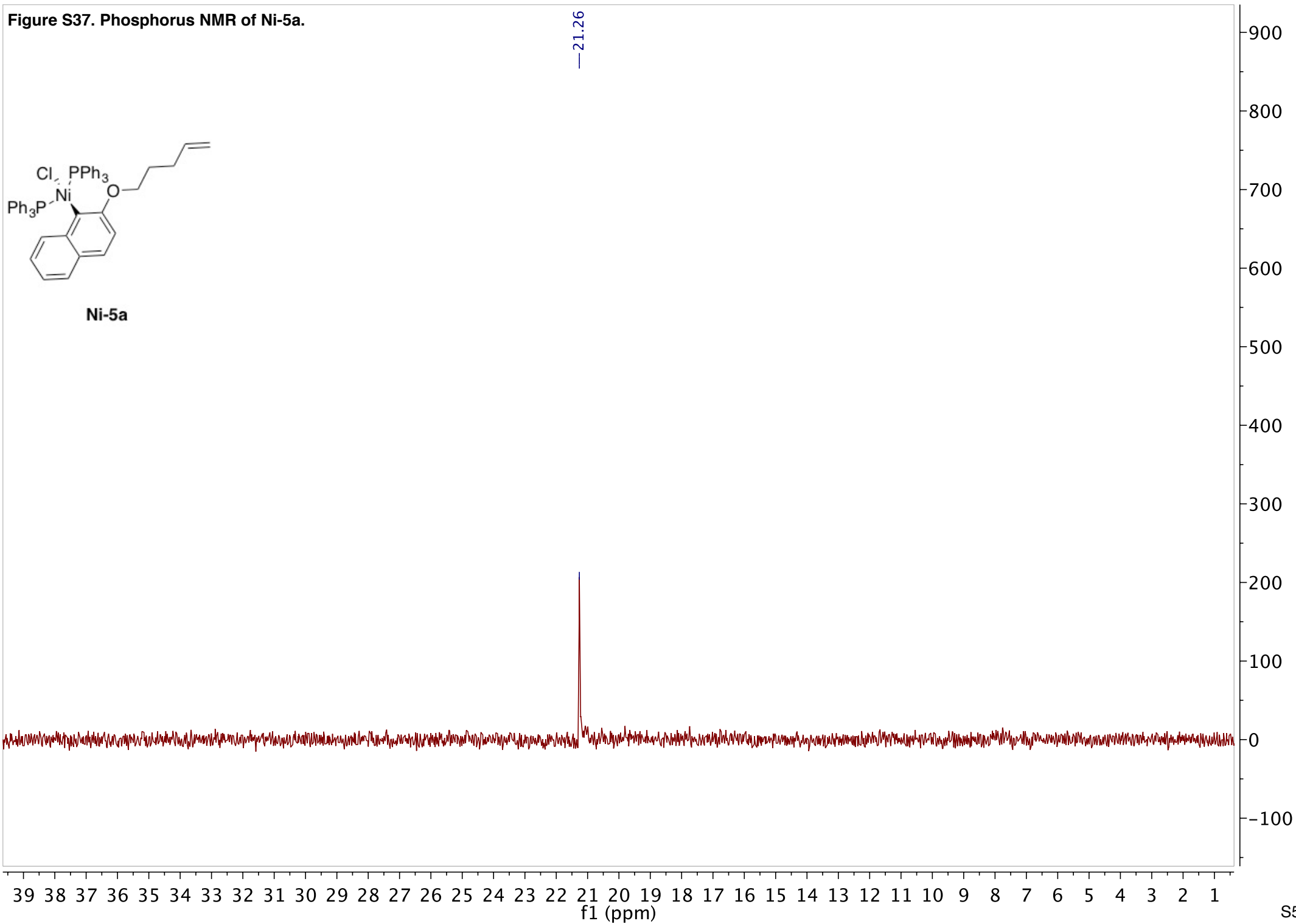


Figure S38. Proton NMR of Ni-5b.

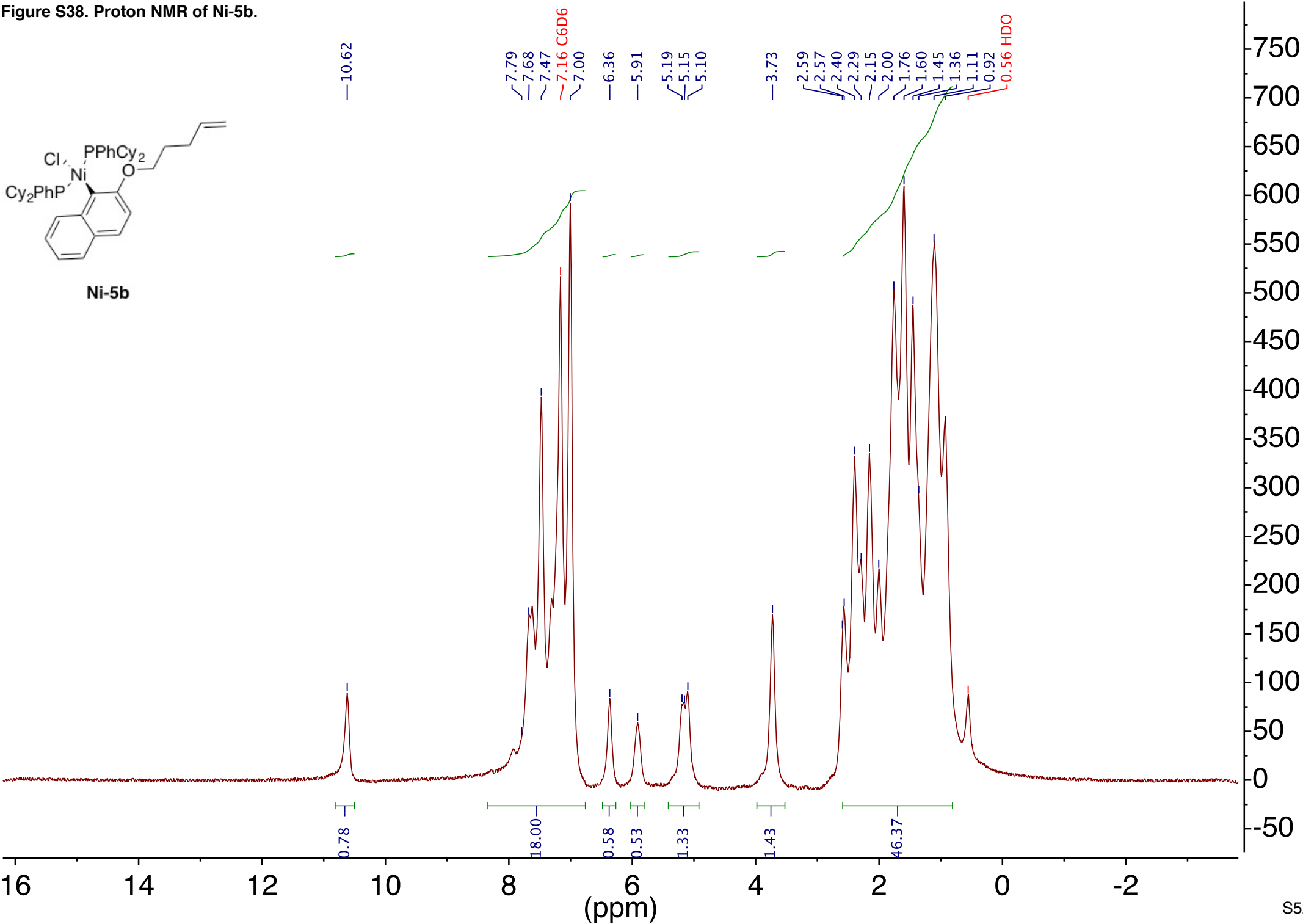


Figure S39. Phosphorus NMR of Ni-5b.

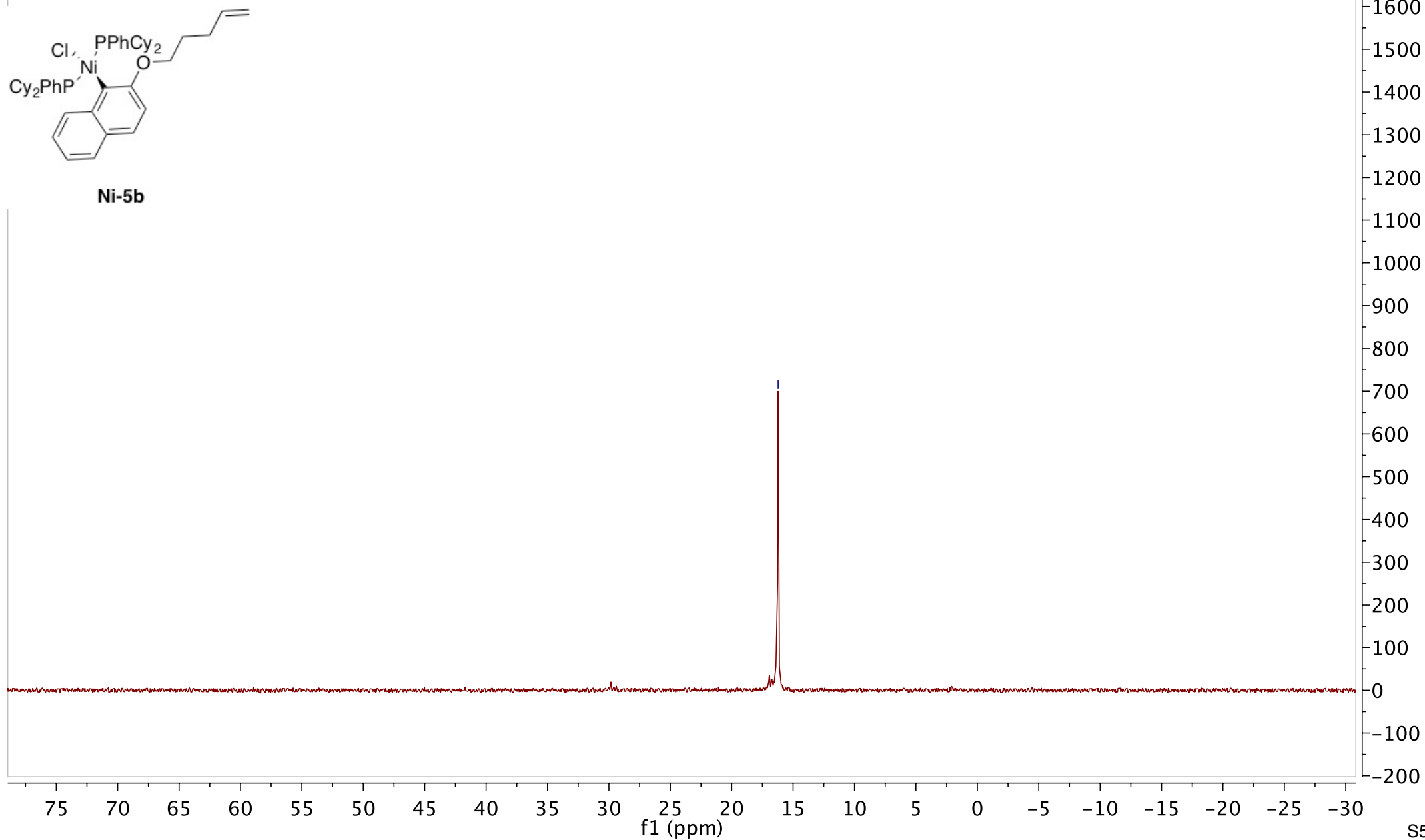
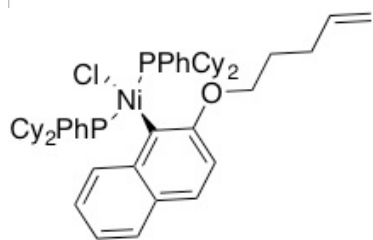


Figure S40. Carbon NMR of Ni-5b.



Ni-5b

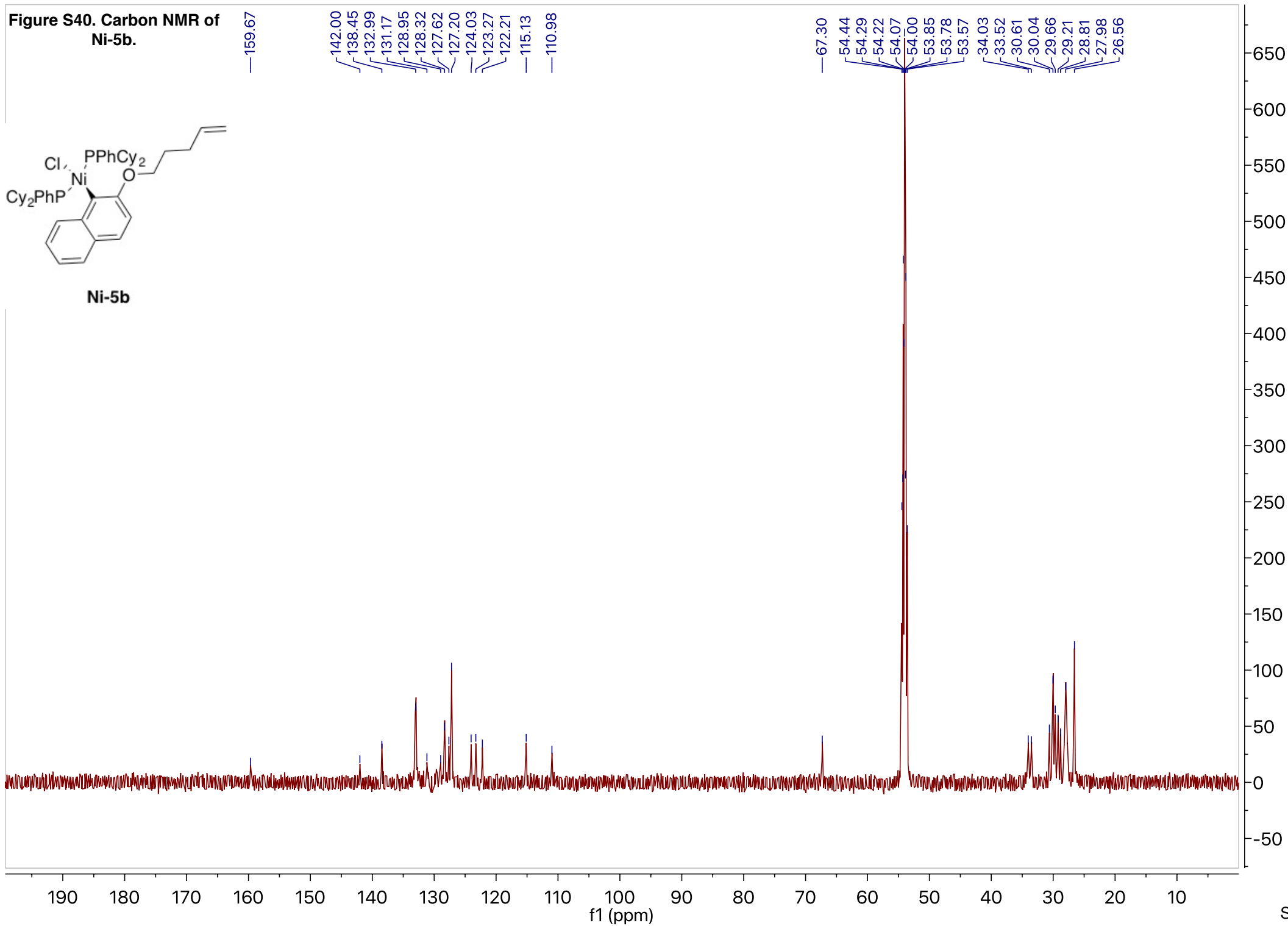
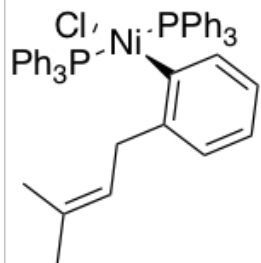


Figure S41. Proton NMR of Ni-6.



Ni-6

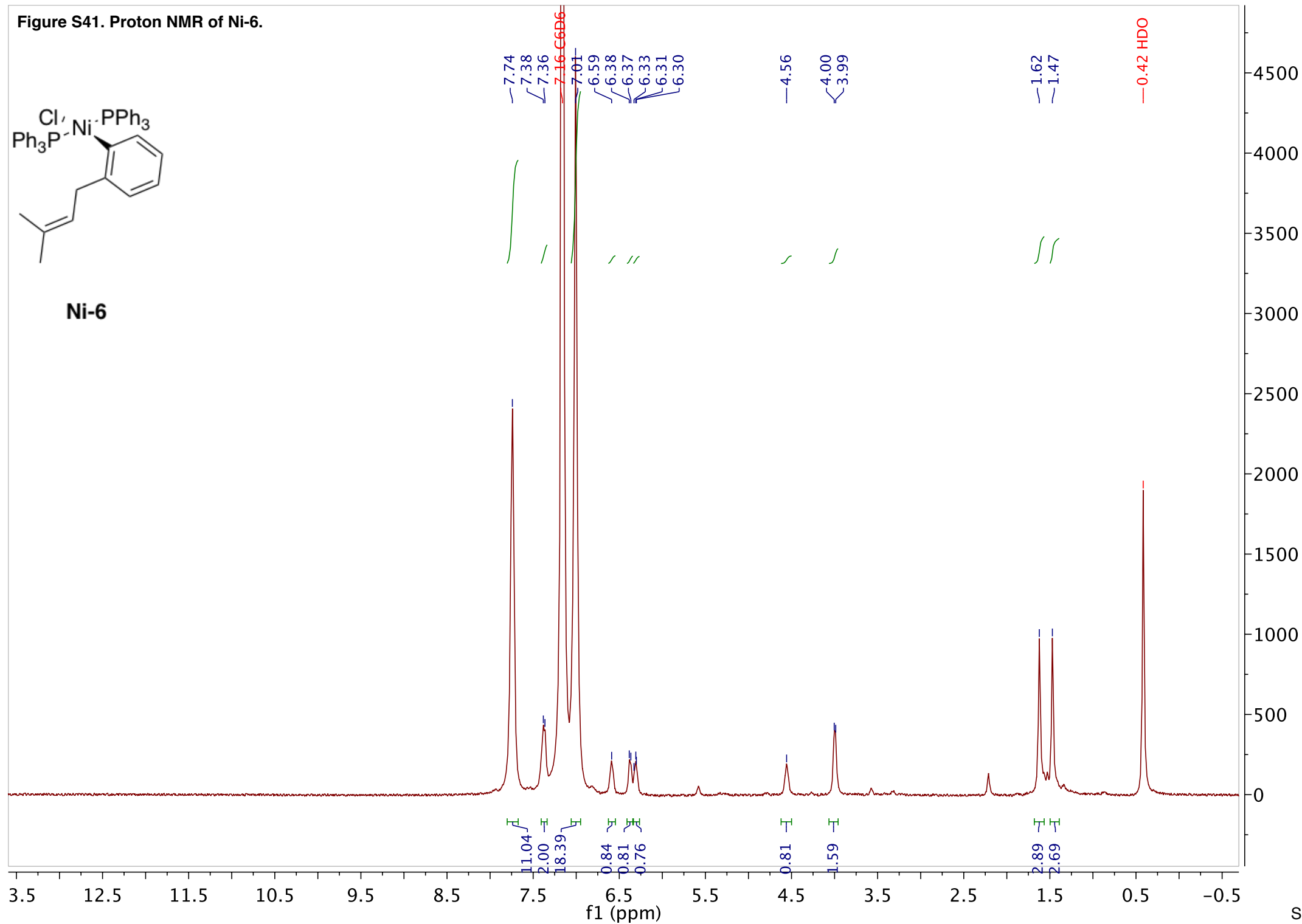
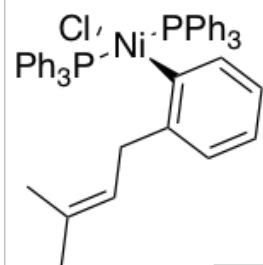


Figure S42. Carbon NMR of Ni-6.



Ni-6

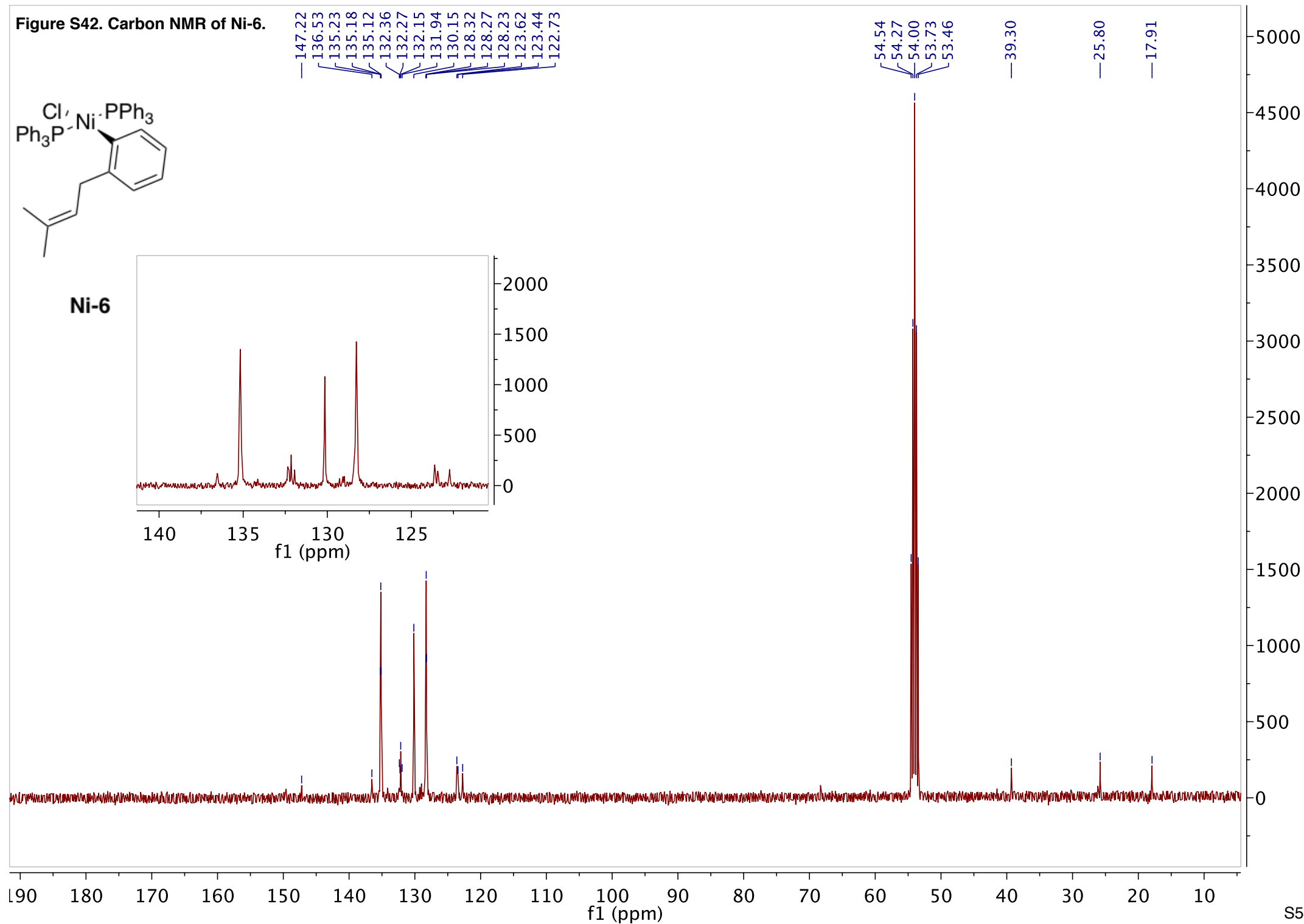
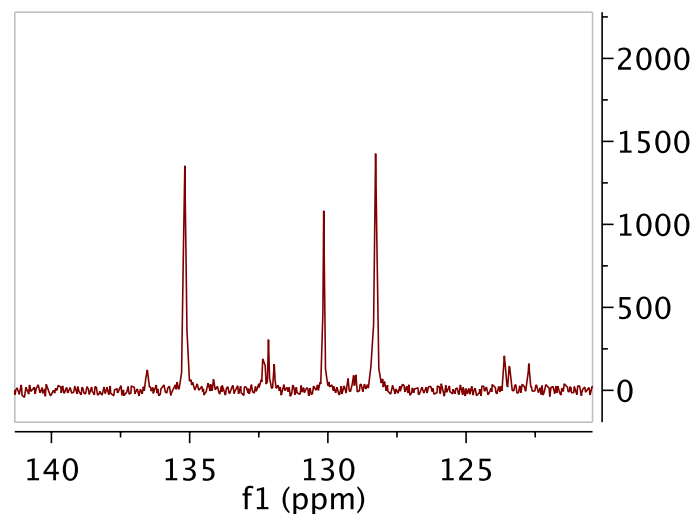
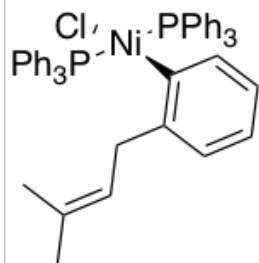
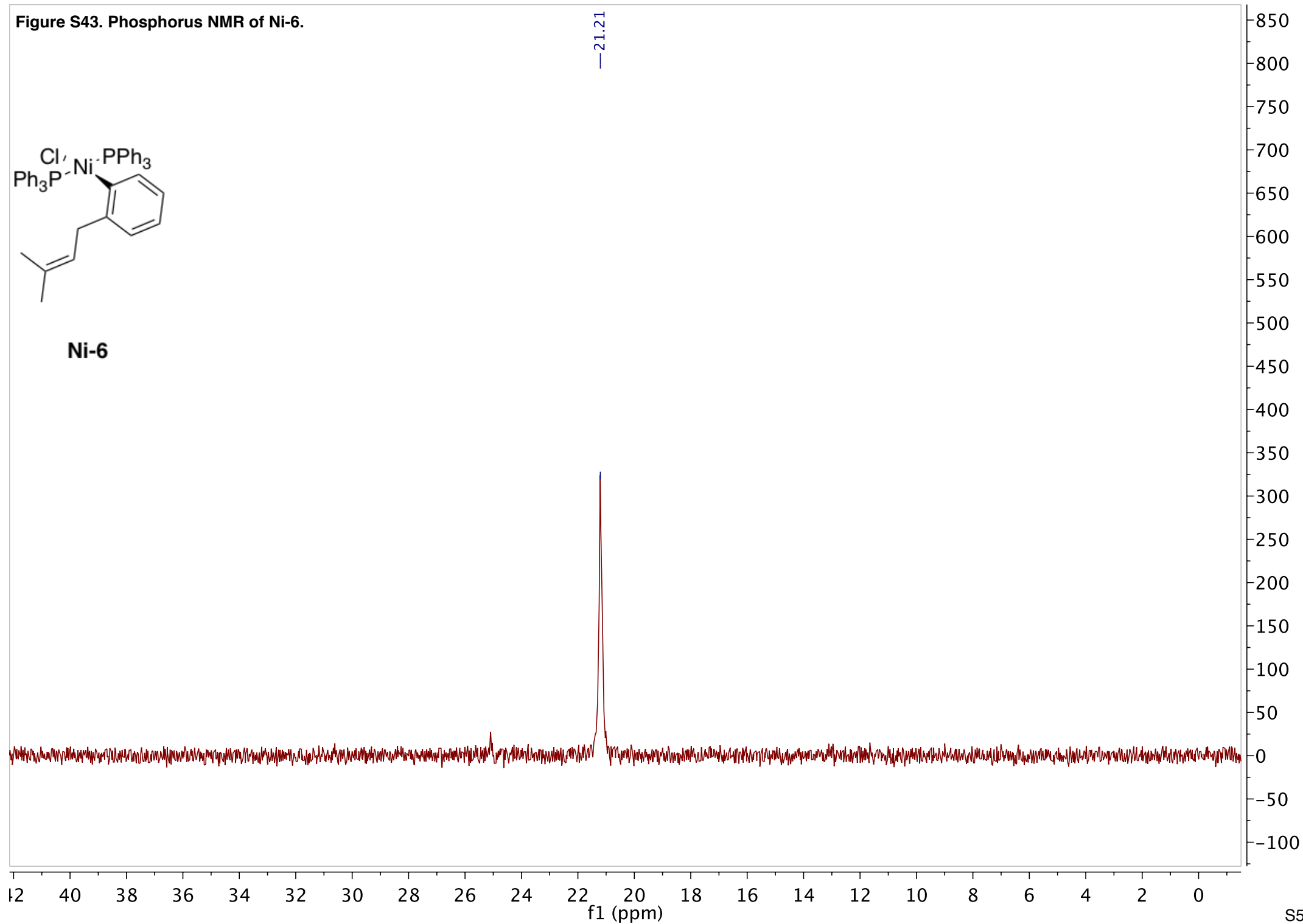


Figure S43. Phosphorus NMR of Ni-6.



Ni-6



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