Supporting Information for:

Highly regioirregular polypropylene from asymmetric group IV anilide(pyridyl)phenoxide complexes

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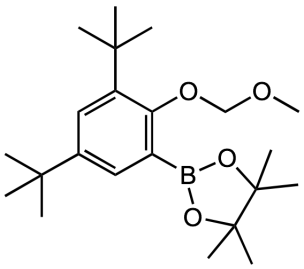
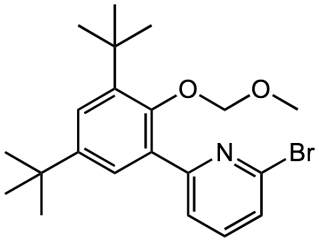
General Considerations and Instrumentation. All air- and moisture-sensitive compounds were manipulated using standard high-vacuum and Schlenk techniques or manipulated in a glovebox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl and stored over titanocene where compatible, or dried by the method of Grubbs.[1] $TiCl_2(NMe)_2$[2], $ZrBn_4$, $HfBn_4$[3] and 2-bromophenyl(1-phenylethyl)aniline[4] were prepared following literature procedures. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was purchased from Sigma Aldrich and distilled prior to use. Butyllithium solution, potassium phosphate tribasic, barium hydroxide octahydrate and palladium(II)acetate were purchased from Sigma Aldrich and used as received. $Pd(PPh_3)_4$ and 2-(dicyclohexylphosphino)biphenyl were purchased from Strem and used as received. Pinacolborane was purchased from Alfa Aesar. 1,4-dioxane and pinacolborane were dried over 3 Å molecular sieves prior to use. Methylaluminoxane (MAO) was purchased as a toluene solution from Albemarle and was dried in vacuo at 150 °C overnight to remove free trimethylaluminum before use. Propylene was dried by passage through a column of activated alumina and molecular sieves. Benzene-d_6, toluene-d_8, C_6D_5Cl, $CDCl_3$ and 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2) were purchased from Cambridge Isotopes. Benzene-d_6 and toluene-d_8 were dried over sodium benzophenone ketyl then over titanocene. C_6D_5Cl was distilled from CaH_2 and passed through a plug of activated alumina prior to use. NMR spectra were recorded on Varian Mercury 300, Varian INOVA 500 or Varian INOVA 600 spectrometers and referenced to the solvent residual peak. High resolution mass spectra (HRMS) were obtained at the California Institute of Technology Mass Spectral Facility using a JEOL JMS-600H magnetic sector mass spectrometer. Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN 46250.

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
[2] Benzing, E.; Kornicker, W. *Chem. Ber.* **1961**, *94*, 2263.
[3] Felten, J. J.; Anderson, W. P. *J. Organomet. Chem.* **1972**, *36*, 87.
[4] Rivas, F. M.; Riaz, U.; Giessert, A.; Smulik, J. A.; Diver, S. T. *Org. Lett.* **2001**, *3*, 2673.



2-(3,5-di-*tert*-butyl-2-(methoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 26.20 g (0.0796 mol) of 1-bromo-3,5-di-*tert*-butyl-2-(methoxymethoxy)benzene was placed in a 250 mL Schlenk flask charged with a stir bar. The vessel was evacuated and refilled with Ar three times, and then 200 mL of dry Et_2O was added via cannula to the flask. The reaction solution was cooled to -78 °C in a dry ice/acetone bath, and 46.5 mL (1.5 eq) of nBuLi (2.5 M in hexanes) was added dropwise using an addition funnel. The solution was stirred at -78 °C for 30 min, then 26.0 mL (1.6 eq) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added via syringe. After 30 min at -78 °C, the flask was removed from the cooling bath and allowed to warm to room temperature while stirring; stirring was continued for an additional 2 hours. The reaction was quenched with saturated aqueous ammonium chloride and extracted with Et_2O (3 x 70 mL). The combined organics were dried over magnesium sulfate and rotovapped to yield a yellow white solid, which was further dried under vacuum. Recrystallization from hot MeOH yielded white microcrystals (21.38 g, 0.0568 mol, 71% yield).

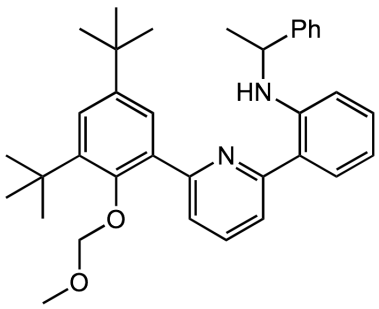
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 9H, C(CH_3)$_3$), 1.36 (s, 12H, BOC(CH_3)$_2$), 1.44 (s, 9H, C(CH_3)$_3$), 3.57 (s, 3H, CH_2OCH_3), 5.16 (s, 2H, CH_2OCH_3), 7.47 (d, J = 2.6 Hz, 1H, aryl-C*H*), 7.53 (d, J = 2.6 Hz, 1H, aryl-C*H*). ^{13}C NMR ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.00 (C(CH_3)$_2$), 30.91 (BOC(CH_3)$_2$), 31.68 (C(CH_3)$_2$), 34.54 (C(CH_3)$_2$), 35.34 (BOC(CH_3)$_2$), 57.58 (CH_2OCH_3), 83.72 (C(CH_3)$_2$), 100.59 (CH_2OCH_3), 120.98, 127.75, 130.97, 140.53, 144.58, 159.34 (aryl-*C*H). HRMS (FAB+) *m*/*z*: calcd for $C_{22}H_{37}O_4B$ $[M]^+$ 376.2785; found 376.2776.



2-bromo-6-(3,5-di-*tert*-butyl-2-(methoxymethoxy)phenyl)pyridine (1). An oven-dried 350 mL Schlenk bomb was charged with a stirbar, evacuated and refilled with Ar. Under positive Ar pressure, 6.88 g (0.0292 mol) of 2,6-dimethylpyridine, 10.02 g (0.0266 mol) of 2-(3,5-di-*tert*-butyl-2-(methoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 1.55 g (0.00134 mol) of $Pd(PPh_3)_4$ and 11.33 g (0.0534 mol) of K_3PO_4[5] were added and the vessel was sealed with a septum. The vessel was evacuated and refilled with Ar three times. 100 mL of dry toluene was added via syringe and the vessel was sealed with a Kontes valve. The reaction mixture was stirred at room temperature for 25 min, during which time the bright yellow color faded to pale yellow (with insoluble white K_3PO_4). The vessel was placed in a 115 °C oil bath for 7 days, then cooled to room temperature, and the suspension filtered through celite with the aid of Et_2O. Solvent was removed in vacuo and the resulting residue was purified by chromatography on SiO_2 using 1:3 Et_2O/hexanes (R_f = 0.625). 9.52 g (82% yield). (This product contains 7% of the bis-arylated pyridine product 2,6-bis(3,5-di-*tert*-butyl-2-(methoxymethoxy)phenyl)pyridine reported previously[6], but we have found that we can carry this product on and remove the impurity completely during a later purification step.)

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (s, 9H, C(CH_3)$_3$), 1.46 (s, 9H, C(CH_3)$_3$), 3.32 (s, 3H, CH_2OCH_3), 4.56 (s, 2H, CH_2OCH_3), 7.39 (d, *J* = 2.5 Hz, 1H, aryl-C*H*), 7.47 – 7.41 (m, 2H, aryl-C*H*), 7.56 (t, *J* = 7.7 Hz, 1H, aryl-C*H*), 7.66 (d, *J* = 7.7 Hz, 1H, aryl-C*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 31.05 (C(CH_3)$_3$), 31.61 (C(CH_3)$_3$), 34.80 ($C(CH_3)_2$), 35.58 ($C(CH_3)_2$), 57.51 (CH_2OCH_3), 99.85 (CH_2OCH_3), 124.11, 125.69, 126.12, 126.48, 132.68, 138.28, 141.90, 142.63, 146.34, 151.40, 159.83 (aryl-*C*H). HRMS (FAB+) *m*/*z*: calcd for $C_{21}H_{29}O_2NBr$ $[M + H]^+$ 406.1382; found 406.1385.

[5] K_3PO_4 was crushed with a mortar and pestle prior to use.
[6] Agapie, T.; Henling, L. M.; DiPasquale, A. G.; Rheingold, A. L.; Bercaw, J. E. *Organometallics* **2008**, *27*, 6245



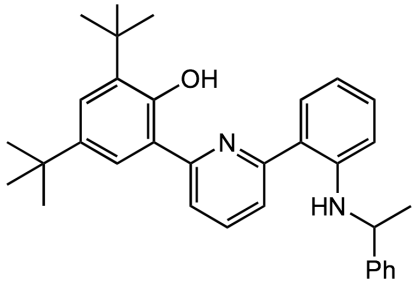
2-(6-(3,5-di-*tert*-butyl-2-(methoxymethoxy)phenyl)pyridin-2-yl)-*N*-(1-phenylethyl)aniline, NNO-MOM.

This synthesis is based on reported procedures.[7] To a 350 mL Schlenk bomb charged with a stirbar was added 1.50 g (0.00544 mol) of 2-bromo-*N*-(1-phenylethyl)aniline, and the bomb was evacuated and refilled with Ar. Under positive Ar pressure, 0.0611 g (0.272 mmol) of $Pd(OAc)_2$ and 0.382 g (1.09 mmol) of 2-(dicyclohexylphosphino)biphenyl were added and the vessel was sealed with a septum. The reaction vessel was then evacuated and refilled with Ar three times and 15 mL of dry dioxane was added via syringe, followed by 3.79 mL triethylamine (0.0272 mol) and 2.37 mL pinacolborane (0.0163 mol). The reaction vessel was sealed with a Kontes valve and placed in an 80 °C oil bath for 1.5 h, during which time the color changed to olive green, then cooled to room temperature and 3.75 mL of H_2O was added via syringe. Under positive Ar pressure, 5.15 g of $Ba(OH)_2$•8 H_2O (0.0163 mol) and 2.38 g (1 eq) **1** were added successively. The reaction vessel was sealed with a Kontes valve and placed in a 90 °C oil bath overnight (~16 h), then cooled to room temperature and the mixture filtered through celite with the aid of Et_2O. Brine was added to the filtrate, which was extracted with additional Et_2O (3 x 50 mL). The combined extracts were dried over magnesium sulfate and rotovapped to yield a brown oil, which was further purified by passage through SiO_2 with dichloromethane to yield a yellow oil. (2.6558 g, 0.00508 mol, crude yield 93%; some impurities were subsequently removed following deprotection).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (s, 9H, $C(CH_3)_3$), 1.43 (d, J = 6.7 Hz, 3H, $CH(CH_3)$), 1.51 (s, 9H, $C(CH_3)_3$), 3.27 (s, 3H, CH_2OCH_3), 4.61 – 4.52 (m, 3H, $CH(CH_3)$, CH_2OCH_3), 6.55 (d, J =

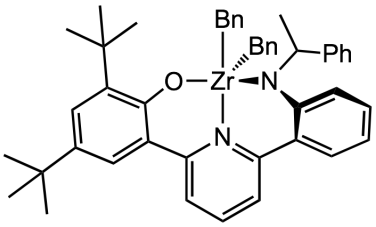
[7] a) Baudoin, O.; Guénard, D.; Guéritte, F. *J. Org. Chem.* **2000**, *65*, 9268. b) Rebstock, A. S.; Mongin, F.; Trécourt, F.; Quéguiner, G. *Org. Biomol. Chem.* **2003**, *1*, 3064.

8.4 Hz, 1H, aryl-C*H*), 6.70 (t, *J* = 7.5 Hz, 1H, aryl-C*H*), 7.14 – 7.09 (m, 1H, aryl-C*H*), 7.16 (d, *J* = 7.1 Hz, 1H, aryl-C*H*), 7.19 (t, *J* = 7.1 Hz, 2H, aryl-C*H*), 7.33 (d, *J* = 6.9 Hz, 2H, aryl-C*H*), 7.49 – 7.46 (m, 2H, aryl-C*H*), 7.53 (dd, *J* = 7.7, 0.9 Hz, 1H, aryl-C*H*), 7.68 (dd, *J* = 7.9, 1.4 Hz, 1H, aryl-C*H*), 7.73 (d, *J* = 8.1 Hz, 1H, aryl-C*H*), 7.83 (t, *J* = 7.9 Hz, 1H, aryl-C*H*), 9.37 (d, *J* = 6.0 Hz, 1H, N*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.37 (CH(*C*H_3)), 31.11 (C(*C*H_3)$_3$), 31.68 (C(*C*H_3)$_3$), 34.78 (*C*(CH$_3$)$_3$), 35.62 (*C*(CH$_3$)$_3$), 53.15 (*C*H(CH$_3$), 57.57 (CH_2OCH_3), 99.69 (*C*H_2OCH$_3$), 112.96, 115.61, 119.96, 120.60, 122.21, 124.95, 125.99, 126.28, 126.62, 128.58, 129.23, 130.36, 134.32, 136.99, 142.36, 145.86, 145.96, 147.33, 151.52, 156.55, 159.70 (aryl-*C*H). HRMS (FAB+) *m*/*z*: calcd for $C_{35}H_{43}O_2N_2$ $[M + H]^+$ 523.3325; found 523.3299.



2,4-di-*tert*-butyl-6-(6-(2-((1-phenylethyl)amino)phenyl)pyridin-2-yl)phenol, NNO (2).
3.150 g of NNO-MOM was placed in a 250 mL round bottom flask charged with a stir bar, and 30-mL of THF added to give a yellow solution. The flask was cooled to 0 °C using a water-ice bath; a 30 mL solution of 2:1 conc. HCl/THF was added dropwise; the reaction mixture was stirred for 30 minutes at 0 °C, then removed from the ice bath and allowed to reach room temperature while stirring was continued overnight. The reaction was recooled again to 0 °C and quenched with a 2 M aq. NaOH solution to give a solution with neutral pH. The organic layer was extracted with Et_2O (3 x 50 mL) and the combined organics were dried over magnesium sulfate and rotovapped to yield a yellow-white solid, which was redissolved and passed through a SiO_2 plug, using 10% Et_2O/hexanes as an eluent, to give an off-white solid. Recrystallization by dissolving in hot hexanes followed by cooling in the freezer yielded a clean off-white powder (868.4 mg, 0.00181 mol, yield: 34%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (s, 9H, C(C*H*$_3$)$_3$), 1.45 (d, *J* = 6.7 Hz, 3H, CH(C*H*$_3$)), 1.50 (s, 9H C(C*H*$_3$)$_3$), 4.57 – 4.47 (m, 1H, C*H*(CH$_3$)), 6.00 (d, *J* = 4.6 Hz, 1H, N*H*), 6.51 (d, *J* = 8.3 Hz, 1H, aryl-C*H*), 6.78 – 6.69 (m, 1H, aryl-C*H*), 7.13 (t, *J* = 7.8 Hz, 1H, aryl-C*H*), 7.22 (t, *J* = 7.3

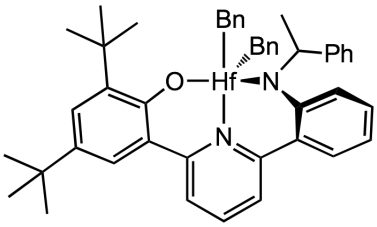
Hz, 1H, aryl-C*H*), 7.31 (t, *J* = 7.6 Hz, 2H, aryl-C*H*), 7.36 (dd, *J* = 7.6, 1.5 Hz, 1H, aryl-C*H*), 7.44 (d, *J* = 2.3 Hz, 1H, aryl-C*H*), 7.51 – 7.46 (m, 3H, aryl-C*H*), 7.73 (d, *J* = 2.3 Hz, 1H, aryl-C*H*), 7.89 (d, *J* = 8.2 Hz, 1H, aryl-C*H*), 7.96 (t, *J* = 8.0 Hz, 1H, aryl-C*H*), 14.03 (s, 1H, O*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.43 (CH(*C*H$_3$)), 29.81 (C(*C*H$_3$)$_3$), 31.80 (C(*C*H$_3$)$_3$), 34.55 (*C*(CH$_3$)$_3$), 35.46 (*C*(CH$_3$)$_3$), 53.89 (*C*H(CH$_3$), 112.58, 116.56, 118.13, 118.41, 121.38, 121.69, 123.05, 126.07, 126.47, 126.89, 128.79, 130.44, 130.61, 137.85, 139.09, 140.16, 145.09, 145.55, 156.31, 156.41, 158.24 (aryl-*C*H). HRMS (FAB+) *m*/*z*: calcd for $C_{33}H_{38}N_2O$ $[M]^+$ 478.2984; found 478.2993.



(NNO)ZrBn$_2$ (3).

A 2 mL benzene solution of **2** (95.0 mg, 0.198 mmol) was added to a 2 mL benzene solution of $ZrBn_4$ (91.0 mg, 0.200 mmol) and stirred for ten minutes under inert atmosphere in the glovebox. Benzene was removed in vacuo from the resulting yellow-brown solution to yield a yellow-brown oil, which was redissolved in pentane and pumped dry several times to remove residual toluene, before being filtered through celite with pentane. The resulting solution was cooled to -30 °C resulting in precipitation of bright yellow solid. (131.2 mg, 0.174 mmol, yield: 88%. ^{1}H NMR (500 MHz, toluene-d_8, -20 C°) δ 1.48 (s, 9H, C(C*H*$_3$)$_3$), 1.63 (s, 9H, C(C*H*$_3$)$_3$), 1.74 (d, *J* = 6.5 Hz, 3H, CH(C*H*$_3$)), 1.90 (d, *J* = 10.3 Hz, 1H, ZrC*H*$_2$), 2.02 (d, *J* = 10.3 Hz, 1H, ZrC*H*$_2$), 2.61 (d, *J* = 10.7 Hz, 1H, ZrC*H*$_2$), 2.73 (d, *J* = 10.7 Hz, 1H, ZrC*H*$_2$), 4.63 (q, *J* = 6.4 Hz, 1H, C*H*(CH$_3$)), 6.23 (d, *J* = 7.4 Hz, 2H, aryl-C*H*), 6.37 (d, *J* = 7.7 Hz, 1H, aryl-C*H*), 6.52 (t, *J* = 6.5 Hz, 3H, aryl-C*H*), 6.63 (t, *J* = 7.6 Hz, 2H, aryl-C*H*), 6.68 (t, *J* = 7.6 Hz, 2H, aryl-C*H*), 6.75 (t, *J* = 7.3 Hz, 1H, aryl-C*H*), 6.80 (t, *J* = 7.5 Hz, 1H, aryl-C*H*), 7.22 – 7.11 (m, 3H, aryl-C*H*), 7.29 (d, *J* = 7.3 Hz, 2H, aryl-C*H*), 7.33 (d, *J* = 8.2 Hz, 1H, aryl-C*H*), 7.37 (t, *J* = 7.6 Hz, 2H, aryl-C*H*), 7.46 (d, *J* = 2.1 Hz, 1H, aryl-C*H*), 7.57 (d, *J* = 2.2 Hz, 1H, aryl-C*H*). ^{13}C NMR (126 MHz, toluene-d_8, -20 C°) δ 24.87 (CH(*C*H$_3$)), 30.46 (C(*C*H$_3$)$_3$), 32.26 (C(*C*H$_3$)$_3$), 34.97 (*C*(CH$_3$)$_3$), 36.15 (*C*(CH$_3$)$_3$), 64.06 (Zr*C*H$_2$), 65.45 (*C*H(CH$_3$)), 66.19 (Zr*C*H$_2$), 120.07, 121.83, 122.40,

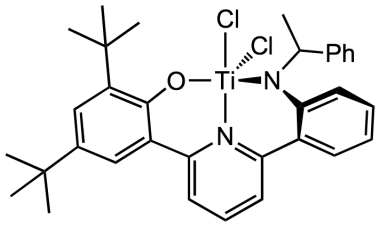
124.02, 124.52, 124.82, 126.35, 126.65, 126.77, 126.86, 127.14, 128.40, 128.61, 128.90, 129.55, 129.75, 130.42, 132.52, 132.75, 134.95, 138.65, 138.87, 142.00, 144.56, 145.89, 149.79, 155.00, 155.11, 158.71 (aryl-*C*H). Anal. Calcd for $C_{47}H_{50}N_2OZr$ (%): C, 75.25; H, 6.72; N, 3.73. Found (1): C, 73.39; H, 6.72; N, 3.68. (2): C, 73.62; H, 6.50; N, 3.68. (This compound is air- and moisture-sensitive and despite repeated attempts satisfactory %C analysis could not be obtained.)



(NNO)HfBn$_2$ (4).

A 2 mL benzene solution of **2** (54.6 mg, 0.114 mmol) was added to a 2 mL benzene solution of $HfBn_4$ (62.5 mg, 0.115 mmol) and stirred for ten minutes under inert atmosphere in the glovebox. Benzene was removed in vacuo from the resulting yellow solution to yield a yellow solid, which was redissolved in pentane and pumped dry several times to remove residual toluene to give a fine pale yellow powder (62.7 mg, 0.075 mmol, yield: 66%).
^{1}H NMR (500 MHz, toluene-d_8, -20 C°) δ 1.48 (s, 9H, C(CH_3)$_3$), 1.64 (s, 9H, C(CH_3)$_3$), 1.67 (d, J = 11.3 Hz, 1H, HfCH_2), 1.80 – 1.74 (m, 4H, HfCH_2, CH(CH_3)), 2.40 (d, J = 11.5 Hz, 1H, HfCH_2), 2.55 (d, J = 11.5 Hz, 1H, HfCH_2), 4.79 (q, J = 6.4 Hz, 1H, CH(CH$_3$)), 6.27 (d, J = 7.4 Hz, 2H, aryl-CH), 6.42 (d, J = 7.7 Hz, 1H, aryl-CH), 6.53 – 6.45 (m, 3H, aryl-CH), 6.67 (dd, J = 17.0, 7.7 Hz, 4H, aryl-CH), 6.76 (dd, J = 13.9, 7.1 Hz, 2H, aryl-CH), 6.88 (d, J = 8.2 Hz, 1H, aryl-CH), 6.93 (d, J = 7.7 Hz, 1H, aryl-CH), 7.16 – 7.11 (m, 3H, aryl-CH), 7.30 (d, J = 7.5 Hz, 2H, aryl-CH), 7.35 (d, J = 8.2 Hz, 1H, aryl-CH), 7.39 (d, J = 7.5 Hz, 2H, aryl-CH), 7.43 (d, J = 2.2 Hz, 1H, aryl-CH), 7.60 (d, J = 2.2 Hz, 1H, aryl-CH). ^{13}C NMR (126 MHz, toluene-d_8, -20 C°) δ 25.13 (CH(*C*H$_3$)), 30.43 (C(*C*H$_3$)$_3$), 32.25 (C(*C*H$_3$)$_3$), 34.95 (*C*(CH$_3$)$_3$), 36.07 (*C*(CH$_3$)$_3$), 64.57 (*C*H(CH$_3$), 71.19 (Hf*C*H$_2$), 72.13 (Hf*C*H$_2$), 120.55, 121.76, 122.37, 124.41, 124.62, 124.86, 125.57, 125.78, 126.73, 126.85, 126.92, 127.16, 128.41, 128.63, 128.94, 129.56, 129.60, 129.66, 131.56, 132.55, 135.73, 138.97, 139.02, 142.12, 145.14, 146.61, 149.61, 154.94, 155.12, 158.14 (aryl-*C*H). Anal. Calcd for $C_{47}H_{50}HfN_2O$ (%): C, 67.41; H, 6.02; N, 3.35. Found (1): C,

61.82; H, 5.65; N, 3.55. (2): C, 59.22; H, 5.68; N, 3.55. (This compound is air- and moisture-sensitive and despite repeated attempts satisfactory %C analysis could not be obtained.)



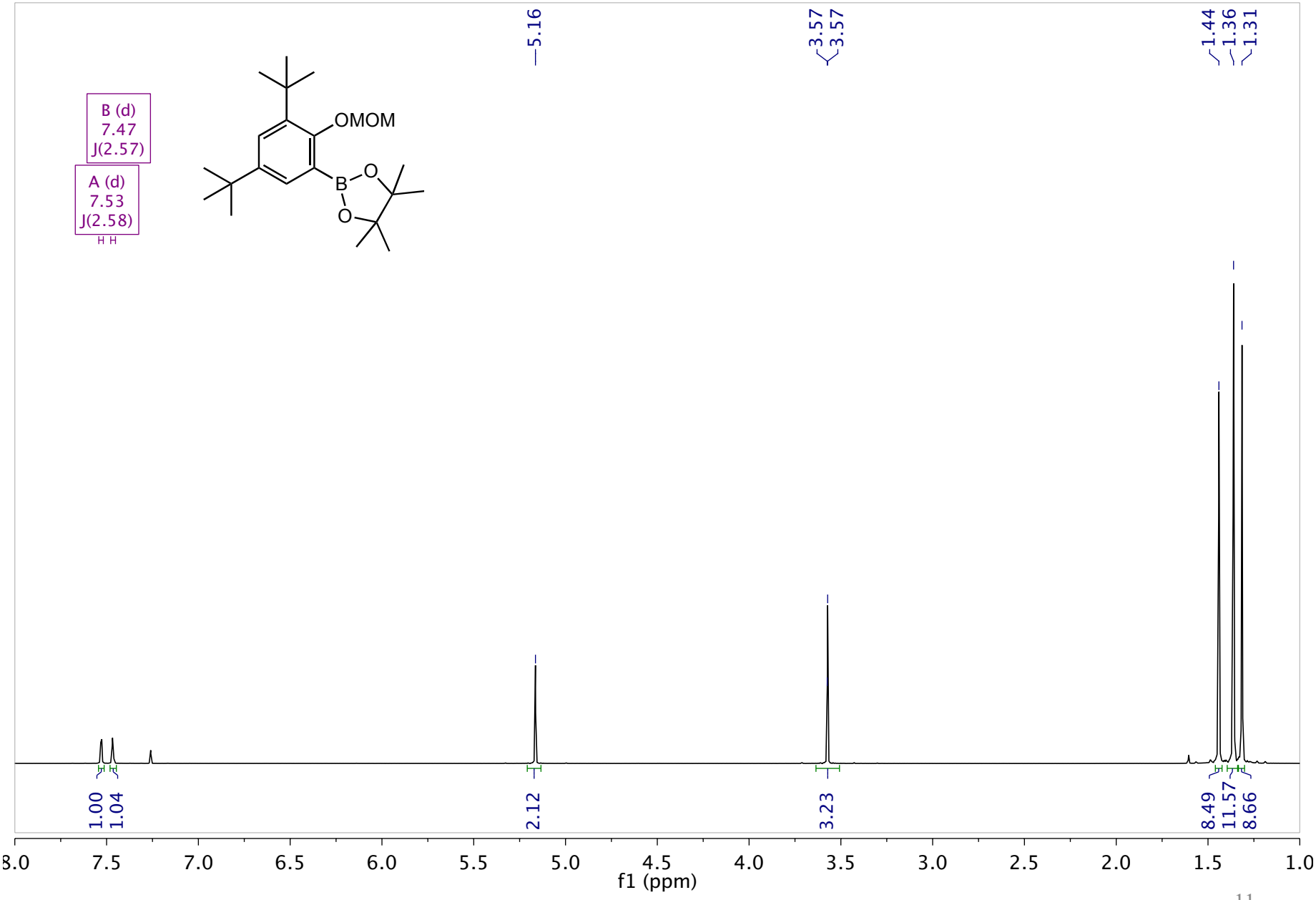
(NNO)TiCl$_2$ (5).

A 4 mL benzene solution of **2** (301.1 mg, 0.629 mmol) was added to a 4 mL benzene solution of $TiCl_2(NMe_2)_2$ (130.8 mg, 0.632 mmol) and stirred for ten minutes under inert atmosphere in the glovebox. Benzene was removed in vacuo from the resulting dark red solution to yield a dark orange solid, which was triturated several times with pentane to remove free dimethylamine (373.6 mg, 0.627 mmol, quantitative yield).

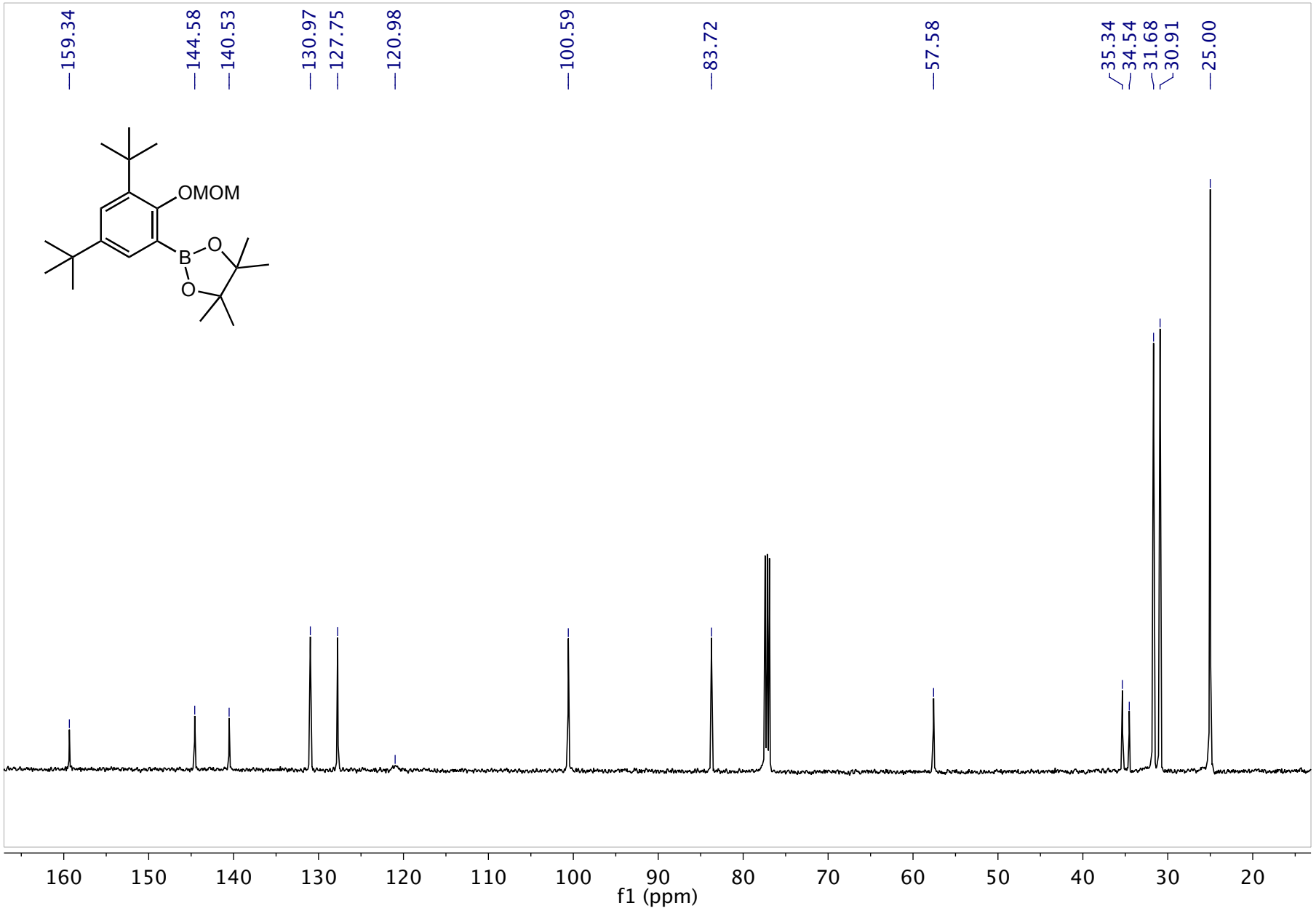
^{1}H NMR (500 MHz, C_5D_5Cl) δ 1.34 (s, 9H, C(C*H*$_3$)$_3$), 1.78 (s, 9H, C(C*H*$_3$)$_3$), 2.31 (d, *J* = 6.7 Hz, 3H, CH(C*H*$_3$))), 5.12 – 5.06 (m, 1H, C*H*(CH$_3$)), 6.36 (dd, *J* = 7.7, 1.7 Hz, 2H, aryl-C*H*), 6.77 – 6.72 (m, 2H, aryl-C*H*), 7.04 – 7.00 (m, 1H, aryl-C*H*), 7.06 (d, *J* = 7.7 Hz, 1H, aryl-C*H*), 7.23 – 7.19 (m, 4H, aryl-C*H*), 7.39 (d, *J* = 7.5 Hz, 1H, aryl-C*H*), 7.51 (t, *J* = 8.0 Hz, 1H, aryl-C*H*), 7.79 – 7.72 (m, 3H, aryl-C*H*). ^{13}C NMR (126 MHz, C_5D_5Cl) δ 25.20 (CH(*C*H$_3$)), 30.50 (C(*C*H$_3$)$_3$), 31.44 (C(*C*H$_3$)$_3$), 34.78 (*C*(CH$_3$)$_3$), 35.80 (*C*(CH$_3$)$_3$), 72.23 (*C*H(CH$_3$), 121.70, 123.57, 123.77, 124.01, 126.20, 127.03, 128.11, 128.33, 128.53, 128.62, 129.53, 132.94, 133.91, 135.26, 137.92, 139.03, 144.16, 145.45, 151.46, 152.70, 158.24 (aryl-*C*H). Anal. Calcd for $C_{33}H_{36}Cl_2N_2OTi$ (%): C, 66.57; H, 6.09; N, 4.70. Found: C, 66.43; H, 5.93; N, 4.78.

General Polymerization Protocol. A high-pressure glass reactor was charged with solid MAO (1000 equiv), and 2.3 mL toluene (distilled from "Cp_2TiH_2") was added. The vessel was attached to a propylene tank and evacuated, and propylene (~30 mL) was condensed in upon cooling to 0 °C. The appropriate precatalysts was added as a solution (toluene or chlorobenzene, 0.7 mL) via syringe. The reaction mixture was stirred vigorously at 0 °C for the desired amount of time, excess propylene was (carefully) vented, and a 10% solution of HCl/MeOH (50 mL) was added slowly to quench the reaction. The resulting mixture was transferred to an Erlenmeyer flask and stirred at room temperature overnight. The precipitated polymer was collected and washed with methanol (3 x 10 mL), evacuated to remove solvent, further dried under high vacuum for 12 hr, and examined by NMR spectroscopy and GPC. ^{13}C NMR spectra were acquired at 120 °C in tetrachloroethane, using a 2 s relaxation delay with a 2.3 s acquisition time.

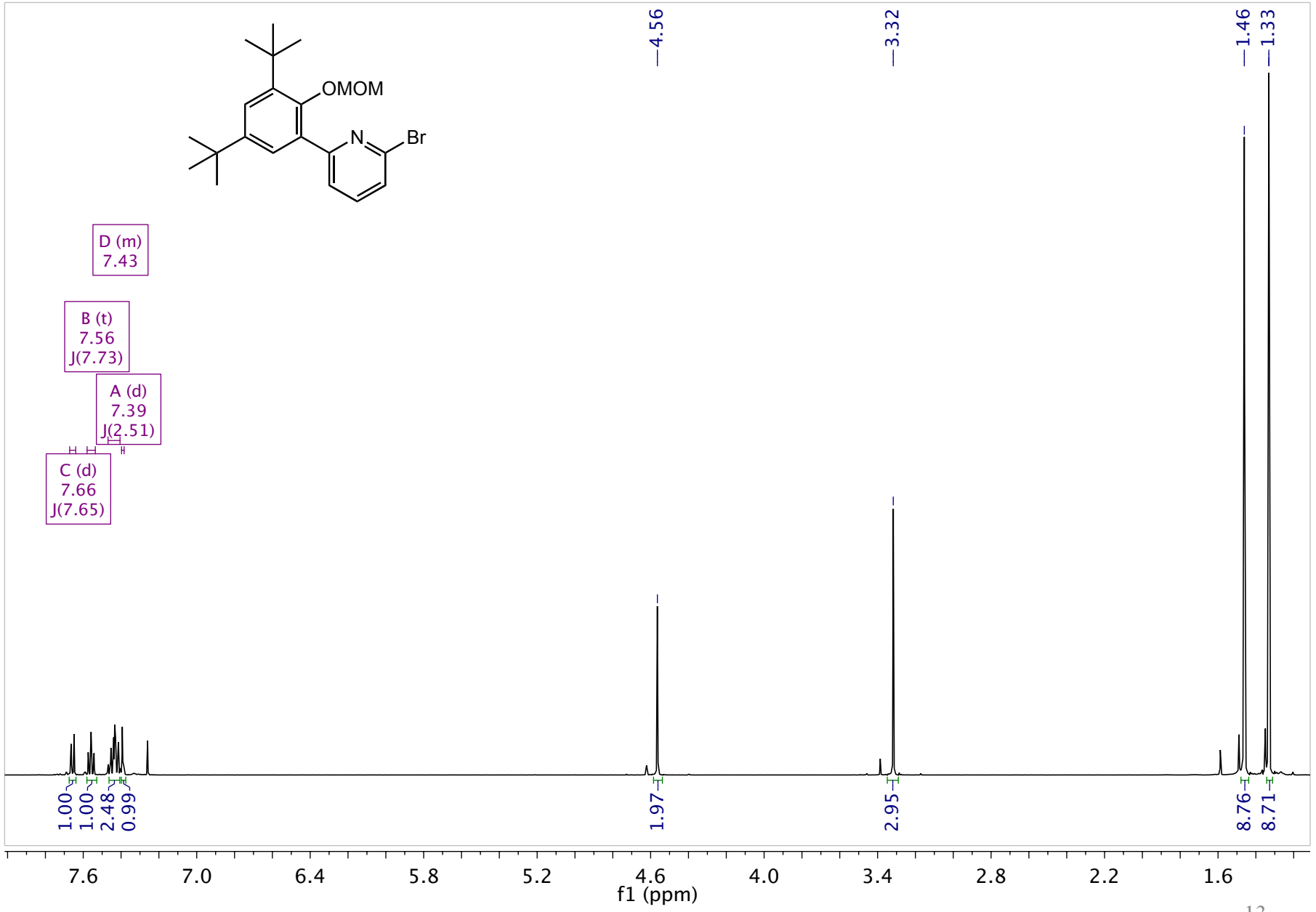
^{1}H Spectrum ($CDCl_3$)



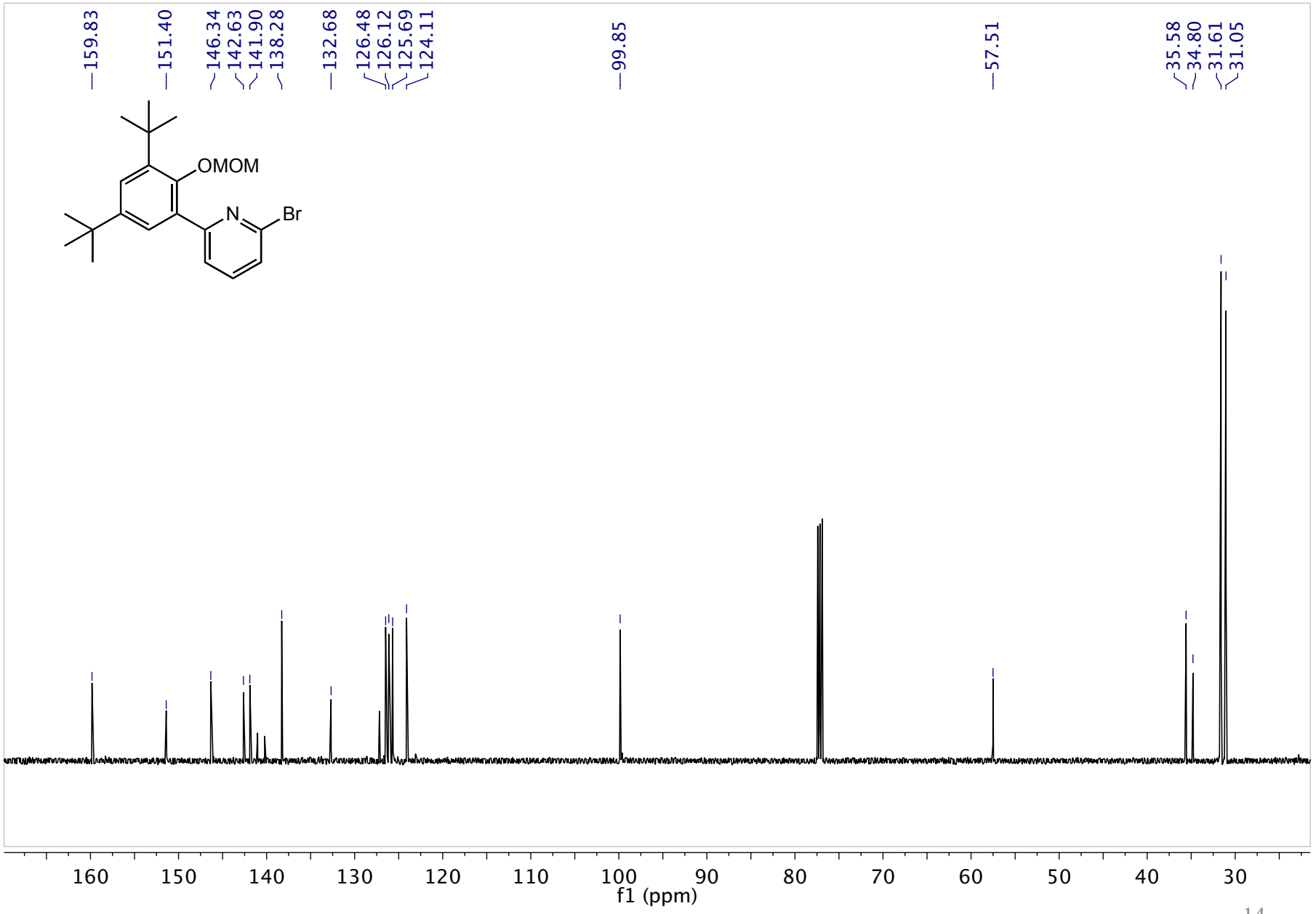
^{13}C Spectrum ($CDCl_3$)



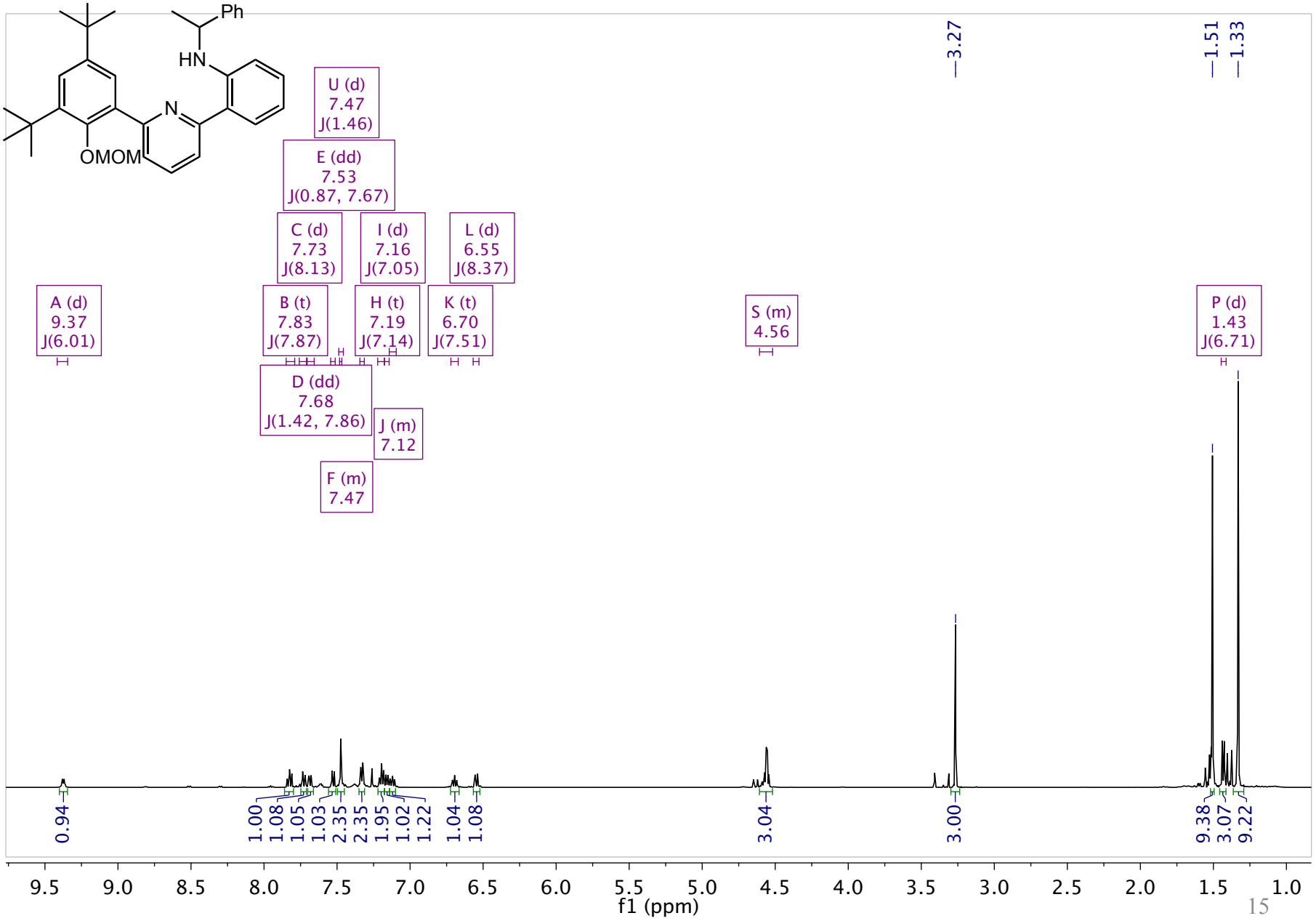
^{1}H Spectrum ($CDCl_3$)



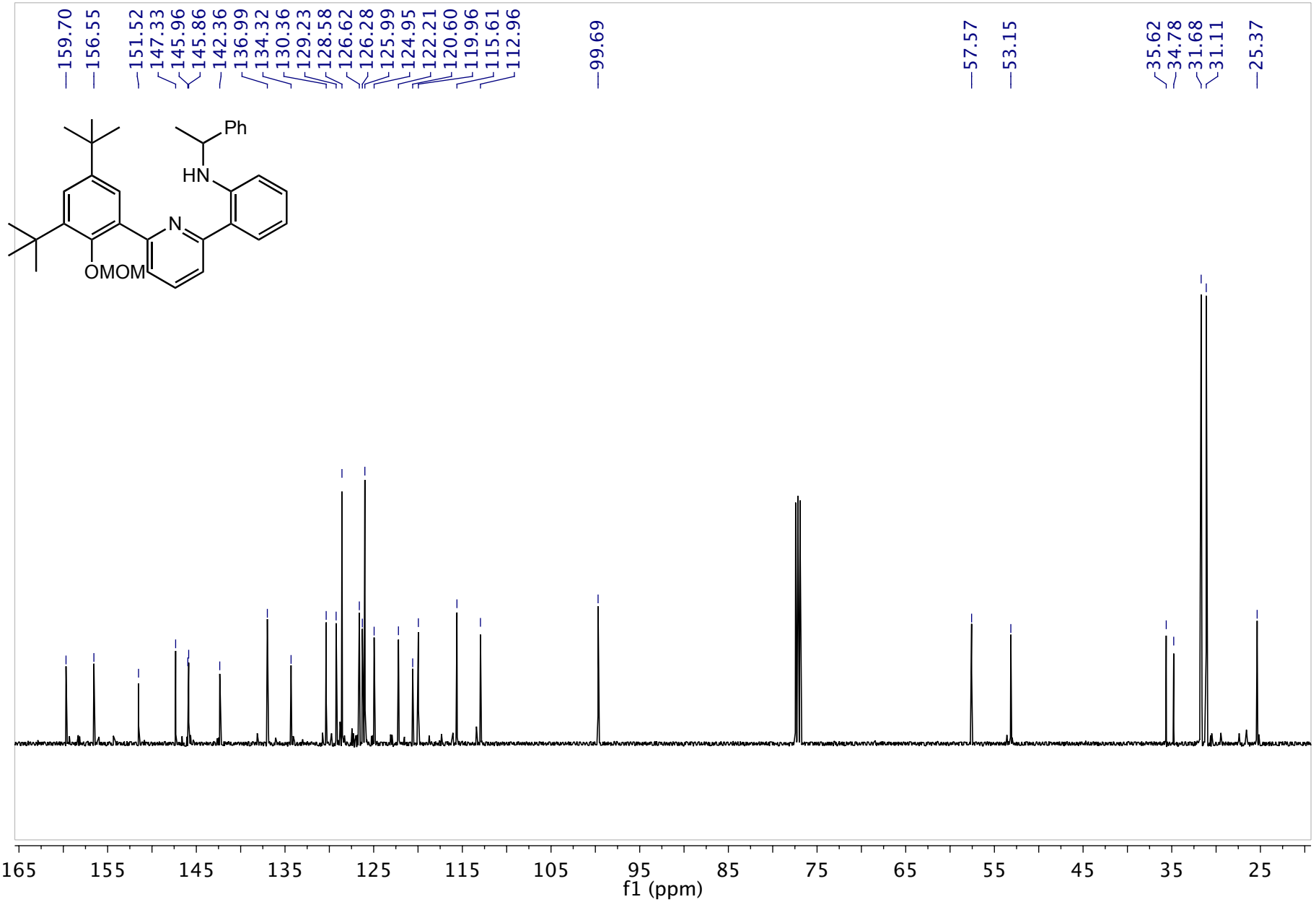
^{13}C Spectrum ($CDCl_3$)



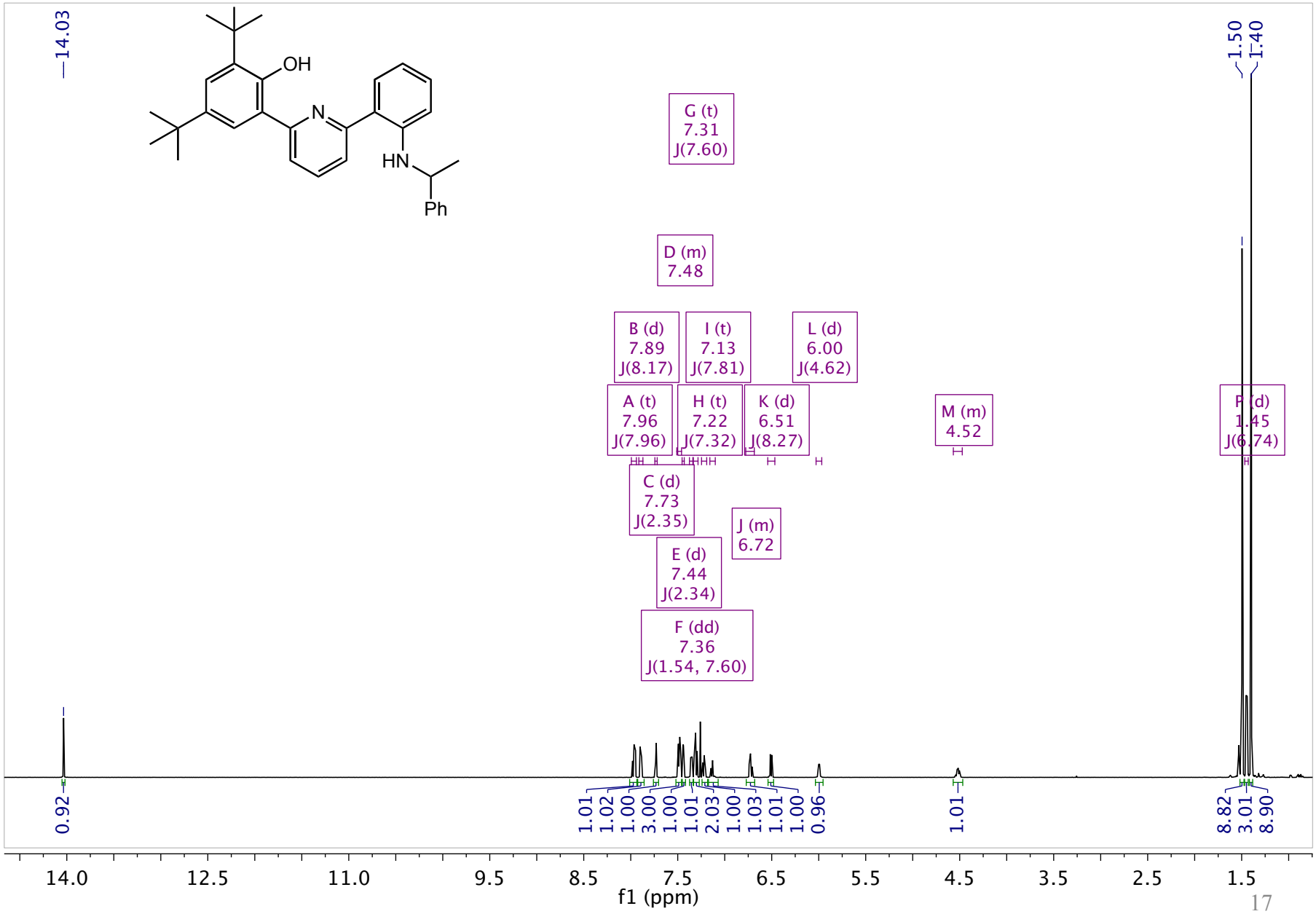
^{1}H Spectrum ($CDCl_3$)



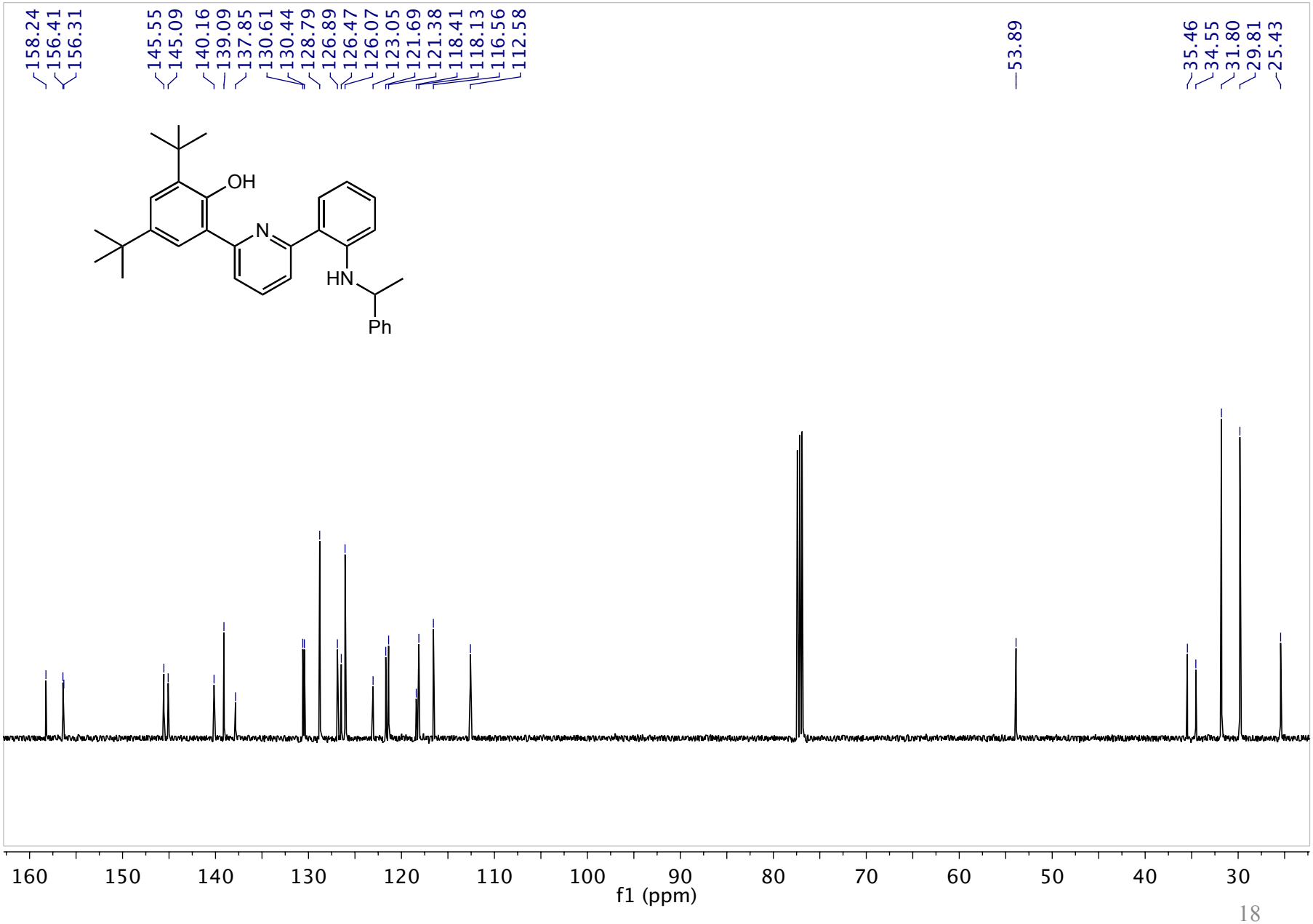
^{13}C Spectrum ($CDCl_3$)



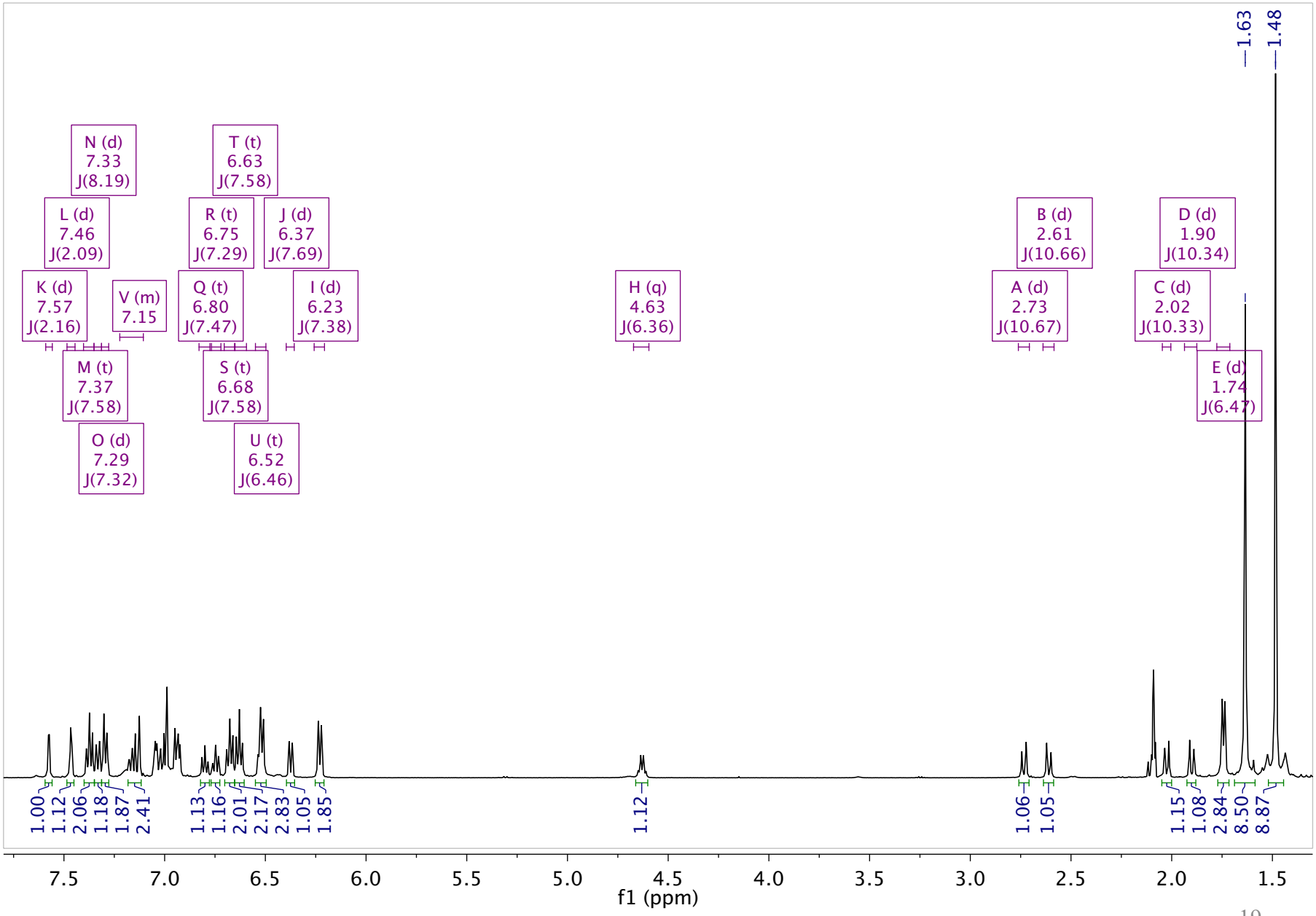
^{1}H Spectrum ($CDCl_3$)



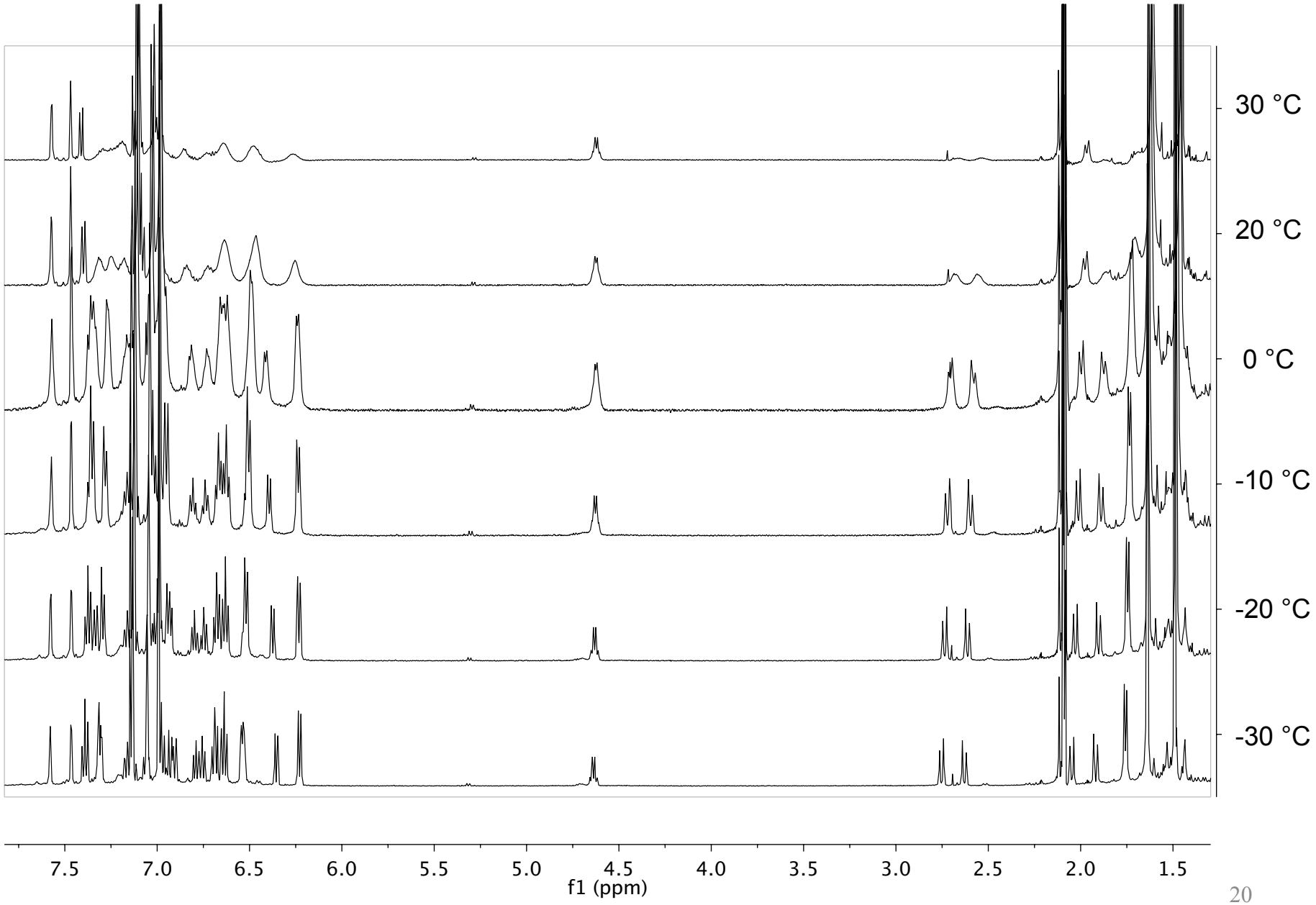
^{13}C Spectrum ($CDCl_3$)



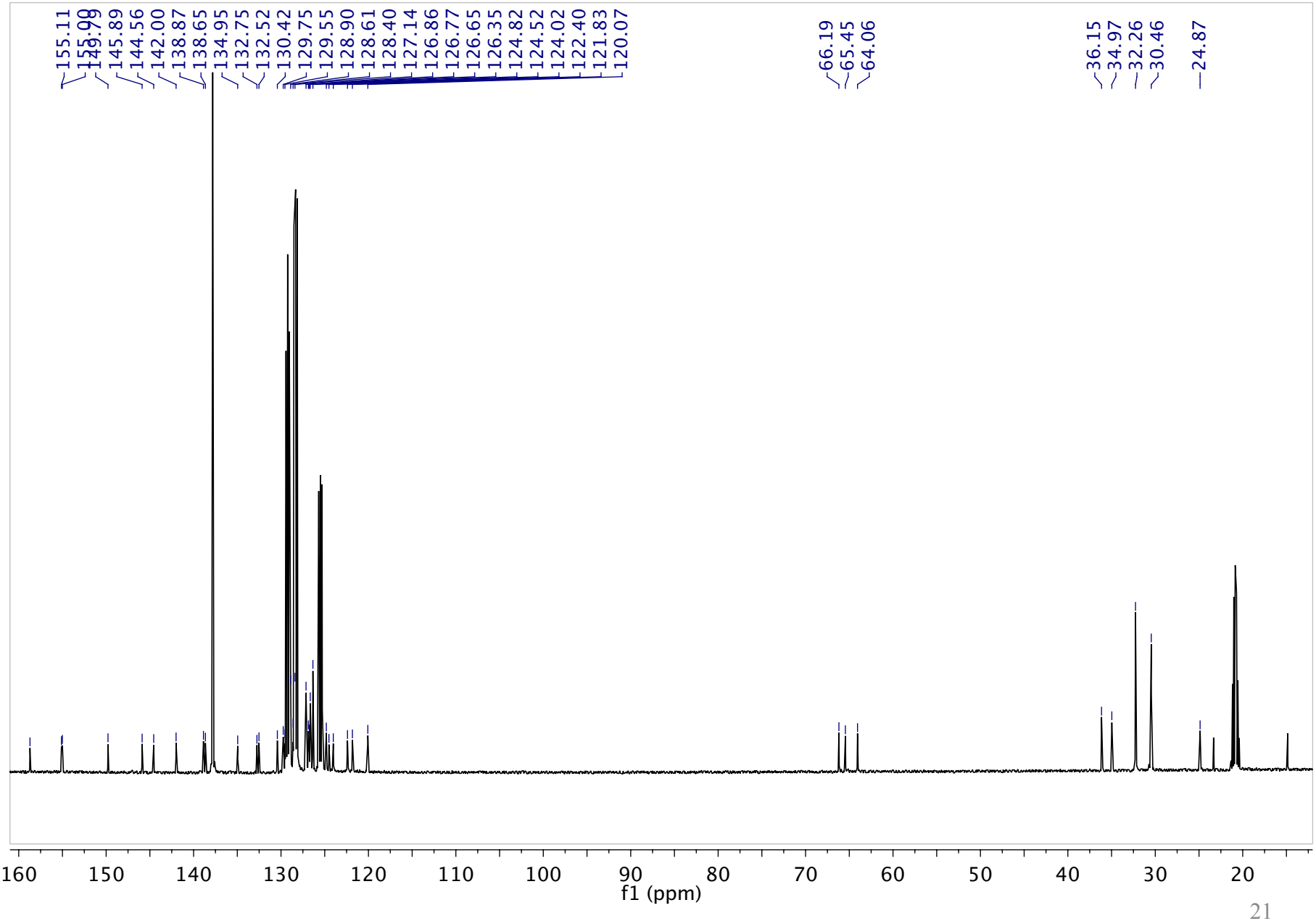
^{1}H Spectrum (NNO)ZrBn$_2$, -20 °C (toluene-d_8)



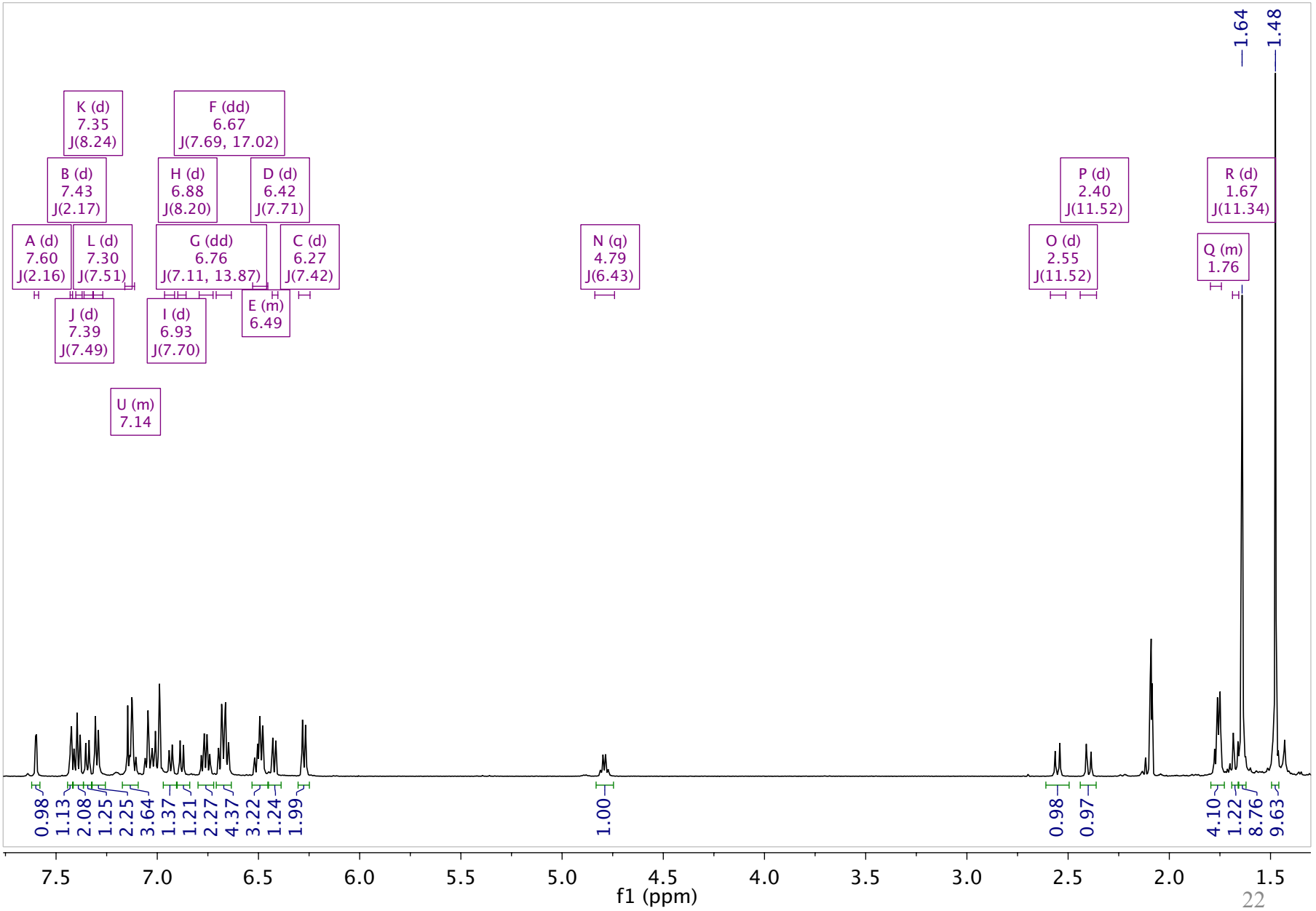
VT ^{1}H Spectrum (NNO)ZrBn$_2$, 30 to -30 °C (toluene-d_8)



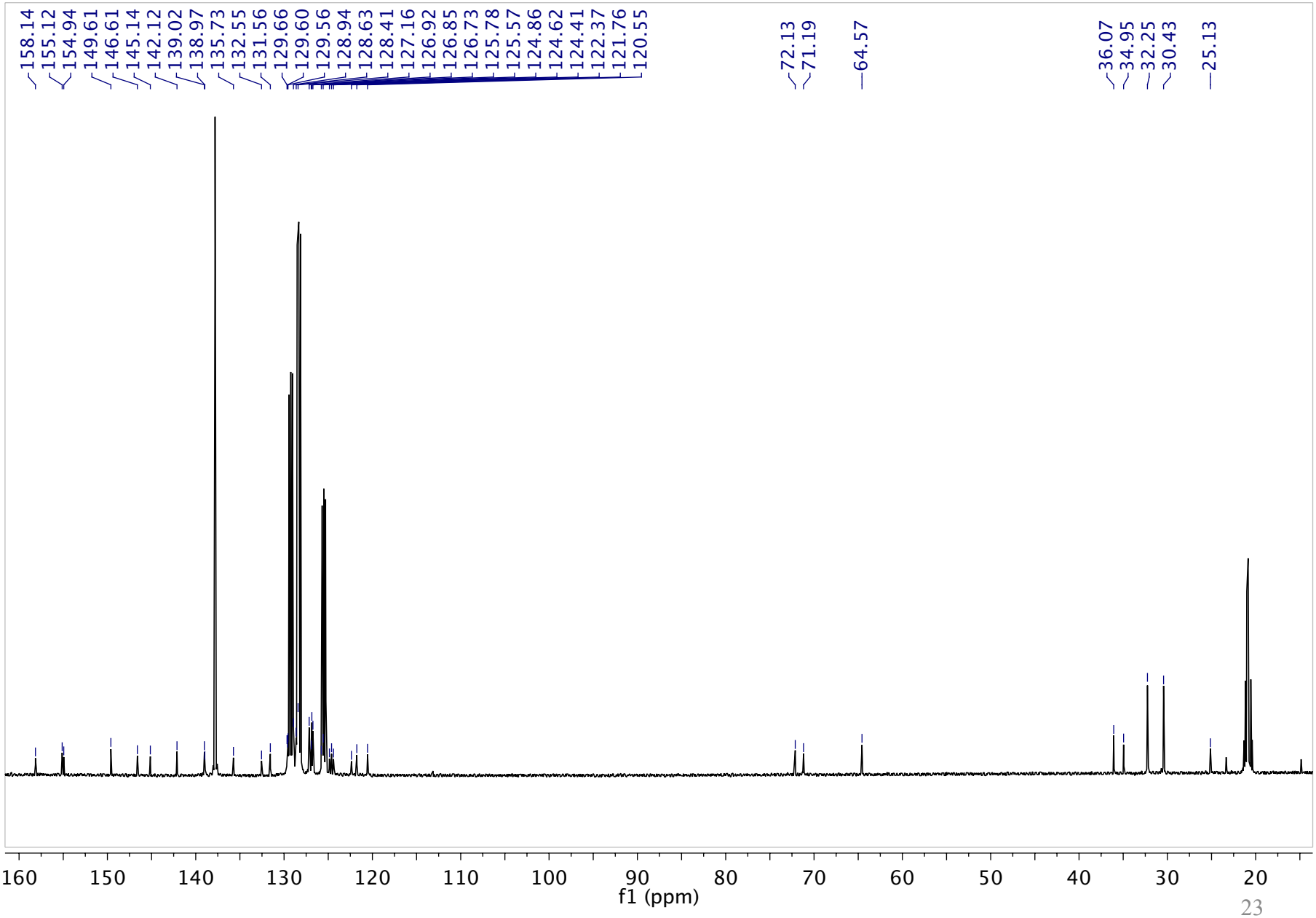
^{13}C Spectrum (NNO)ZrBn$_2$, -20 °C (toluene-d_8)



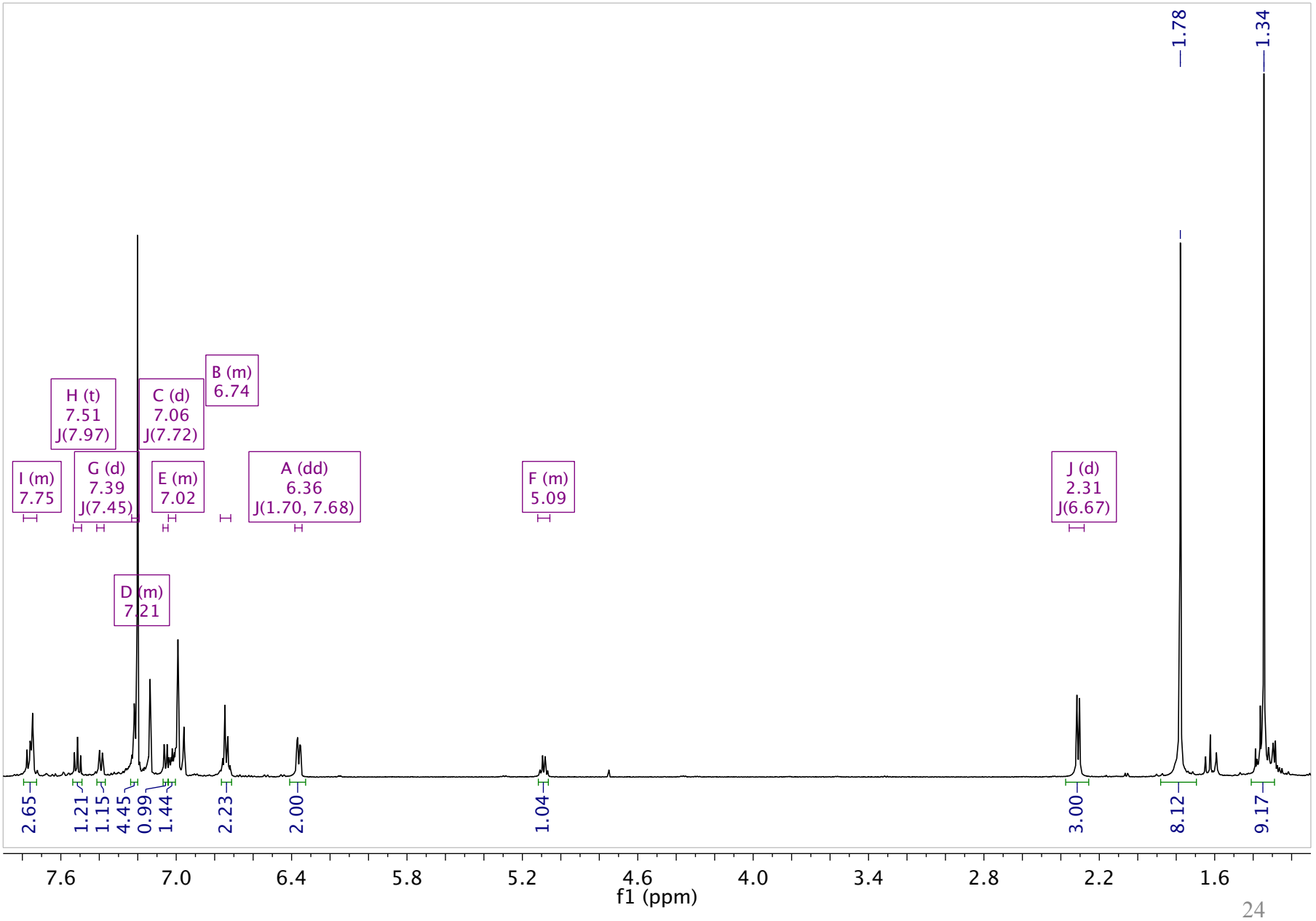
^{1}H Spectrum (NNO)HfBn$_2$, -20 °C (toluene-d_8)



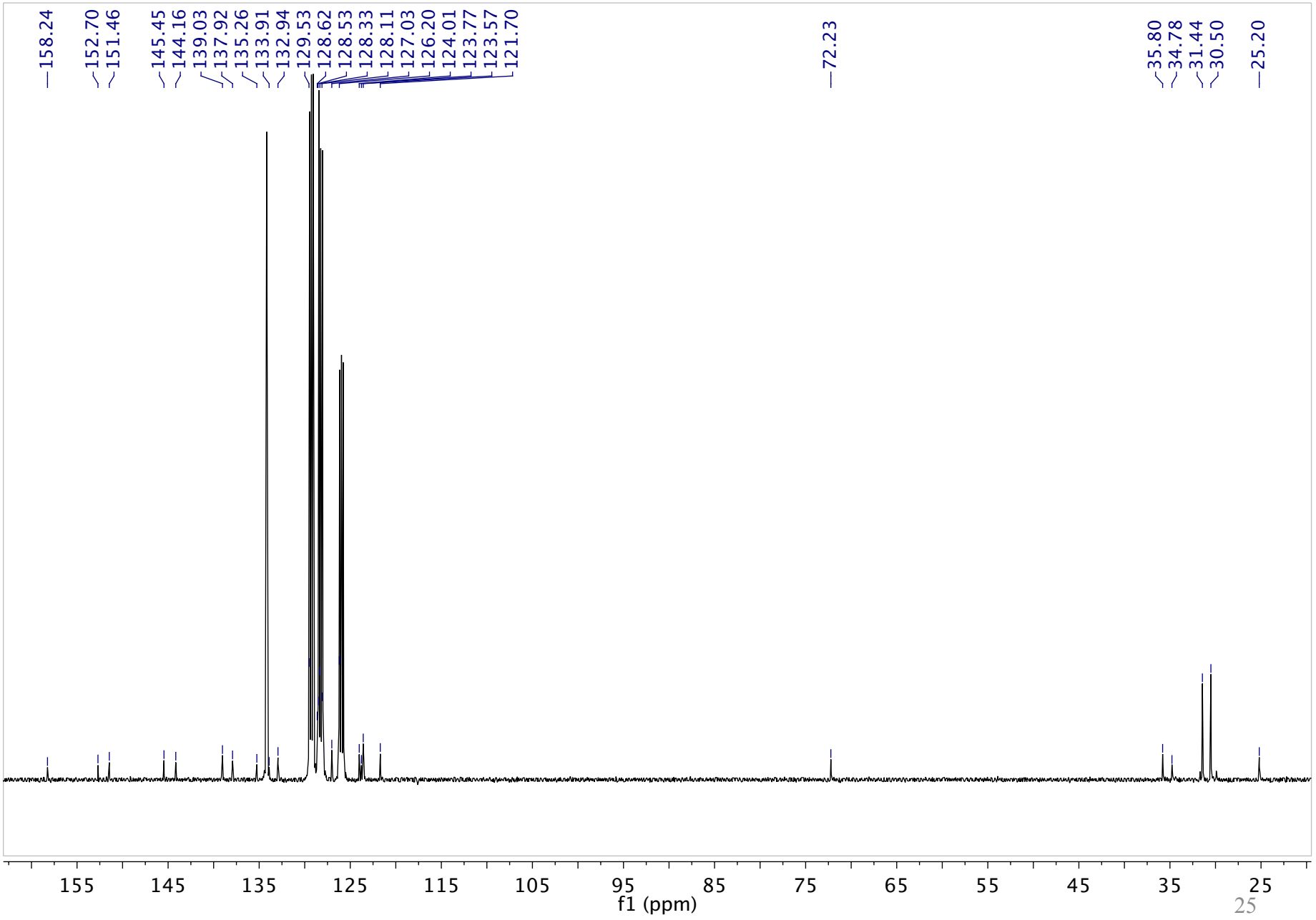
^{13}C Spectrum (NNO)HfBn$_2$, -20 °C (toluene-d_8)



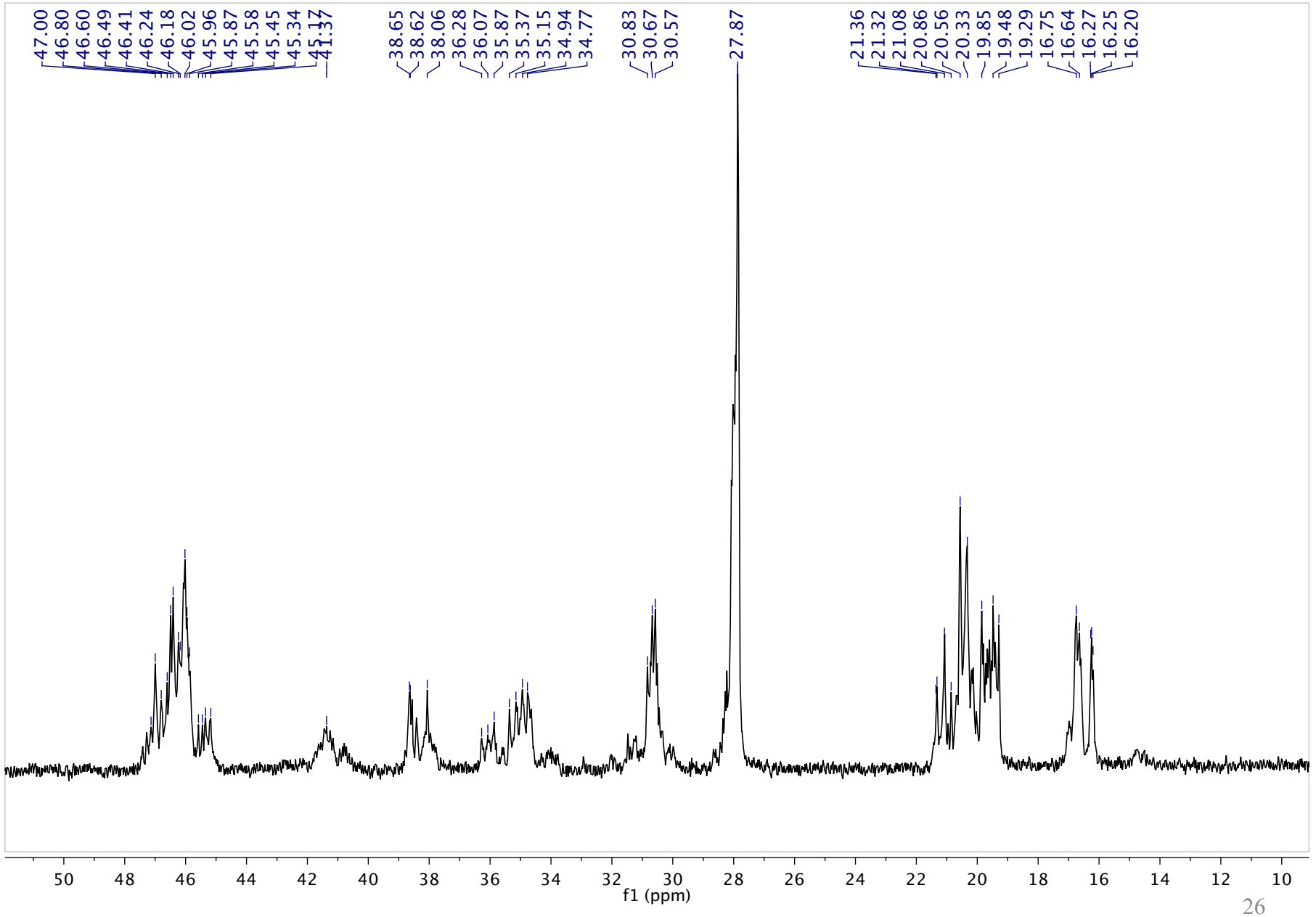
^{1}H Spectrum (NNO)TiCl$_2$ (C_6D_5Cl)



^{13}C Spectrum $(NNO)TiCl_2$ (C_6D_5Cl)



^{13}C Spectrum of PP from (NNO)ZrBn$_2$/1000 eq MAO, 120 °C (TCE-d_2)



^{13}C Spectrum of PP from (NNO)$TiCl_2$/1000 eq MAO, 120 °C (TCE-d_2)

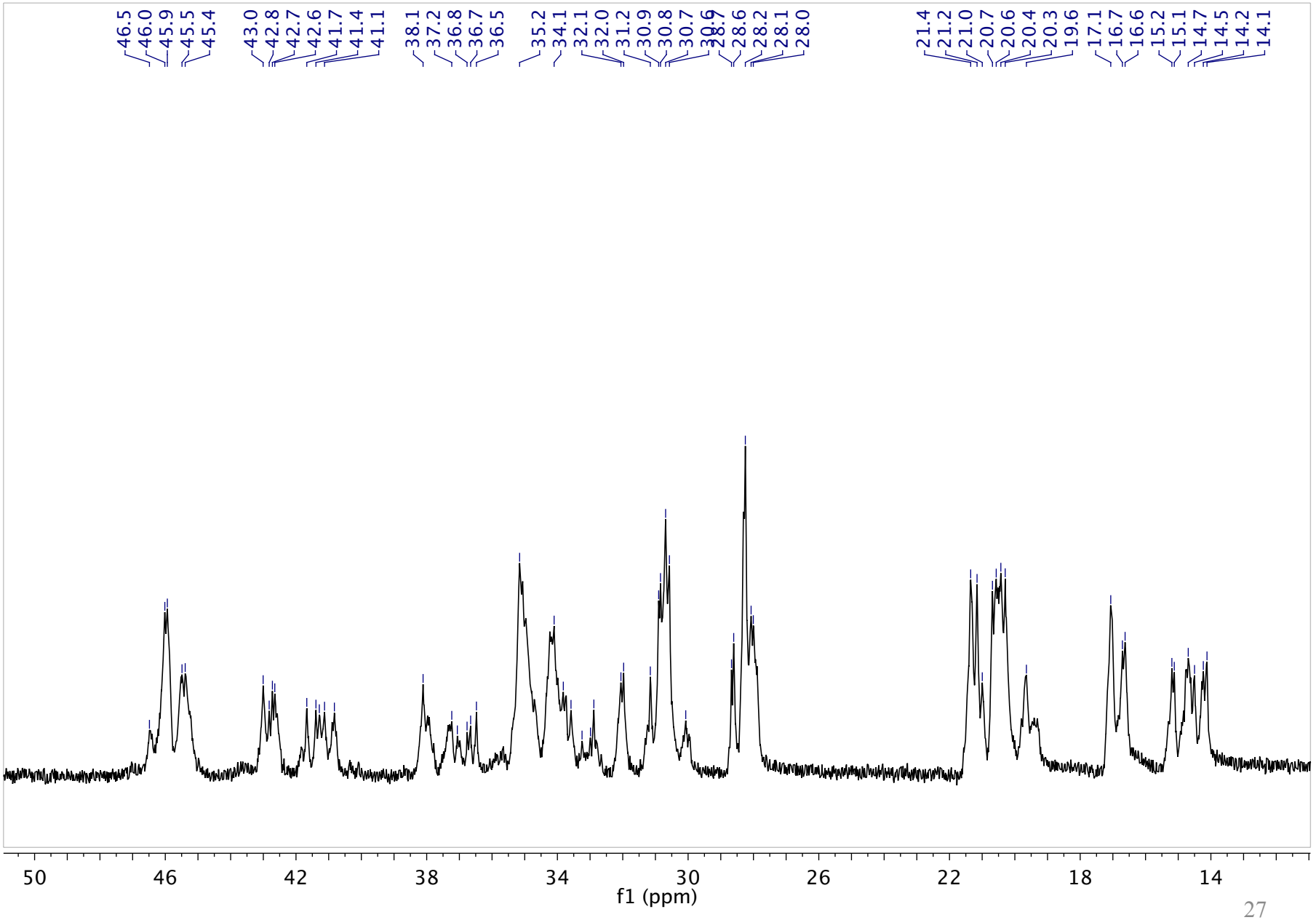


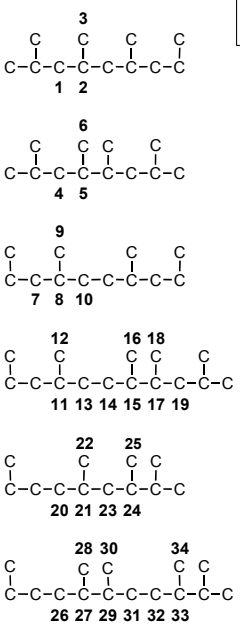
Table of ^{13}C NMR data of PP and Literature Data for Regioirregular PP

The following table compares peaks observed in the ^{13}C spectra of PP from (NNO)$TiCl_2$ with known literature values. The ^{13}C chemical shifts of PP from (NNO)$TiCl_2$ are listed in the column "Expt'l Data". The column to the right of the experimental data shows ranges of chemical shifts reported in the literature and the corresponding type of insertion; the numbers in bold (1-44) correspond to the carbon atoms indicated in the structures to the right of the table, which depict all of the possible sequences obtained from 1,2-, 2,1- and 3,1-insertion modes. S, T and P (in parentheses next to the bold carbon numbers) indicate secondary (methylene), tertiary (methine) and primary (methyl) carbons, respectively, and the chemical shift range reported in the corresponding reference (identified at the top of the column) is shown in the following parentheses. Finally, the colored blocks represent the chemical shift ranges for secondary (orange), tertiary (pink) and primary (blue) carbons in polypropylene as reported in the literature. The range of chemical shifts of the ^{13}C NMR signals for secondary and tertiary carbons overlap in the region of ~32-40 ppm.

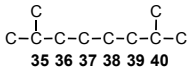
Three points should be noted: 1) The methyl region of the ^{13}C spectra is well separated from the methine and methylene regions. 2) Since our PP spectra exhibit peaks in the overlapping region for secondary and tertiary carbons, we cannot assign methylene and methine carbons from ^{13}C NMR data alone. 3) We observe peaks very close to the reported regions for 3,1-insertions (which overlap regions for 2,1-insertions), so we cannot rule out 3,1-insertions from ^{13}C NMR data alone either.

Expt'l Data	*Macromolecules* **1992**, *25,* 4876				*Makromol. Chem.* **1989,** *190,* 1931	
	2,1-insertions				**3,1-insertion**	**n-propyl end group**
46.49 46.01 45.94	**1** (S) (45.7-47.7)	**7** (S) (45.7-46.5)	Secondary (methylene)			
45.49 45.39						
43.01	**4, 19, 23** (S) (43.3 - 44.1)					
42.82 42.72 42.65						
41.67 41.39 41.29 41.13	**4** (S) (40.9 - 42.3)					
40.83						**42** (S) (39.59-40.8)
38.11	**15, 27, 29, 33** (T) (36.8-39.1)			Tertiary (methine)	**36, 39** (S) (37.62-38.51)	
37.23 37.06 36.76						
36.65						
36.48	**13** (T) (36.5)					
35.16	**5, 24** (T), **10, 13, 20** (S) (35.4-35.6)					
34.10	**5, 17, 24** (T), **10, 20** (S) (34.2-34.8)					
33.82						
33.58 33.25	**31** (S) (33.4)					
32.99						
32.88	**14, 16** (S) (32.6)					
32.06 31.97						
31.16	**8, 11, 21** (T), **32** (S) (31.1-31.3)					
30.90					**35, 40** (T) (30.8-30.92)	
30.84						**41** (T) (30.3-30.8)
30.69 30.57						
30.07						
28.67 28.60 28.25	**2** (T) (28.3-28.4)					
28.07						
28.00					***37, 38*** *(S) (27.57-27.83)*	
21.35 21.16		**3** (P) (20.1-20.7)		Primary (methyl)		
21.00 20.69 20.57 20.43 20.29	**9, 12, 22** (P) (20.1-20.9)					
19.65						**43** (S) (19.73-20.3)
17.06 16.71 16.63	**6, 25, 34** (P) (16.6-17.2)					
15.19						
15.12 14.69	**6, 16, 18, 25, 28, 30** (P) (14.7-15.1)					
14.50						
14.23 14.12						**44** (P) (14.3-14.51)

2,1-insertion modes



3,1-insertion



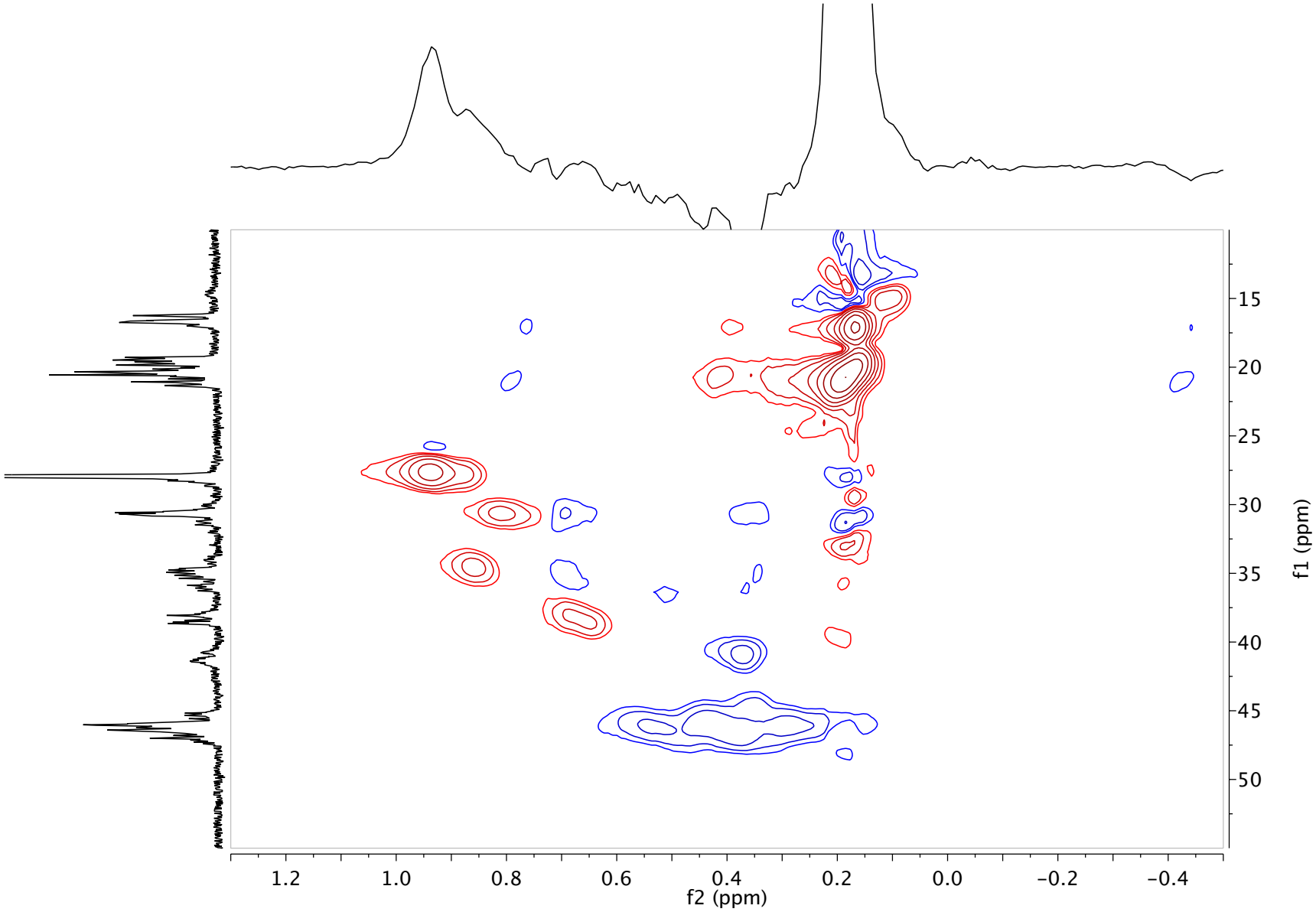
n-propyl end group

Secondary Carbon (methylene) = S
Tertiary Carbon (methine) = T
Primary Carbon (methyl) = P

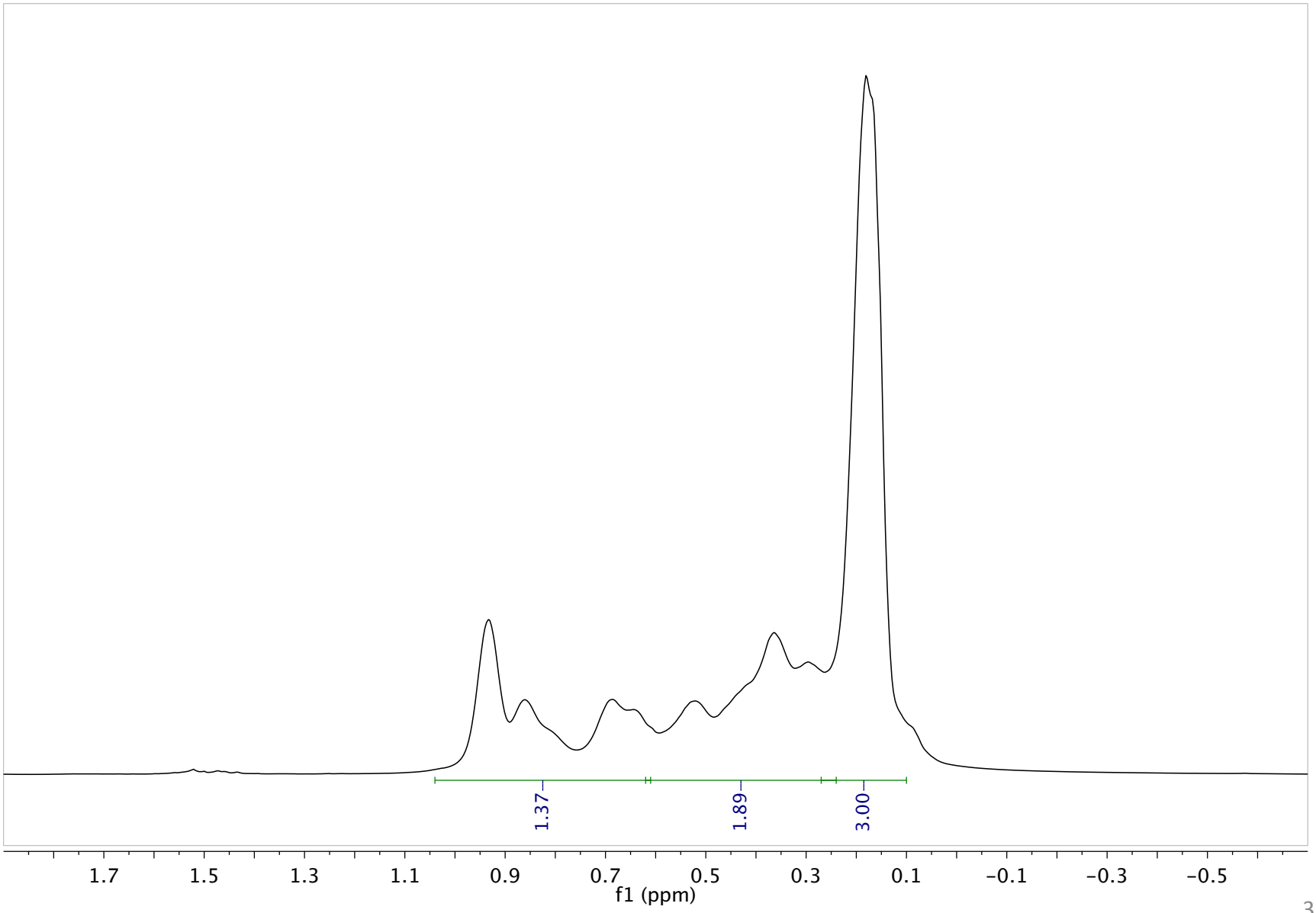
2D ^{1}H-^{13}C HSQC NMR spectroscopy

The 2D ^{1}H-^{13}C HSQC experiment identifies signals corresponding to even and odd proton connectivity to carbons. In the following figure, groups with an odd number of protons (methyls, methines) are shown as red contours in the 2D region and as normal peaks (up) in the horizontal proton spectrum, while those with an even number of protons (methylenes) are inverted in the proton spectrum and shown as blue contours. By examining the correlation of signals it can be seen that despite the substantial overlapping in the ^{13}C spectra, the methylene region of the ^{1}H spectrum is separated from both the methine region on the downfield side and the methyl region on the upfield side. This separation allows for the determination of the ratio of CH:CH_2:CH_3 by integration of the appropriate regions of the ^{1}H NMR spectrum as 1:1:1, within ca. 10% experimental uncertainty, thereby allowing us to conclude that there are only 1,2- and 2,1-insertions of propylene during polymerizations, and no 3,1-insertions.

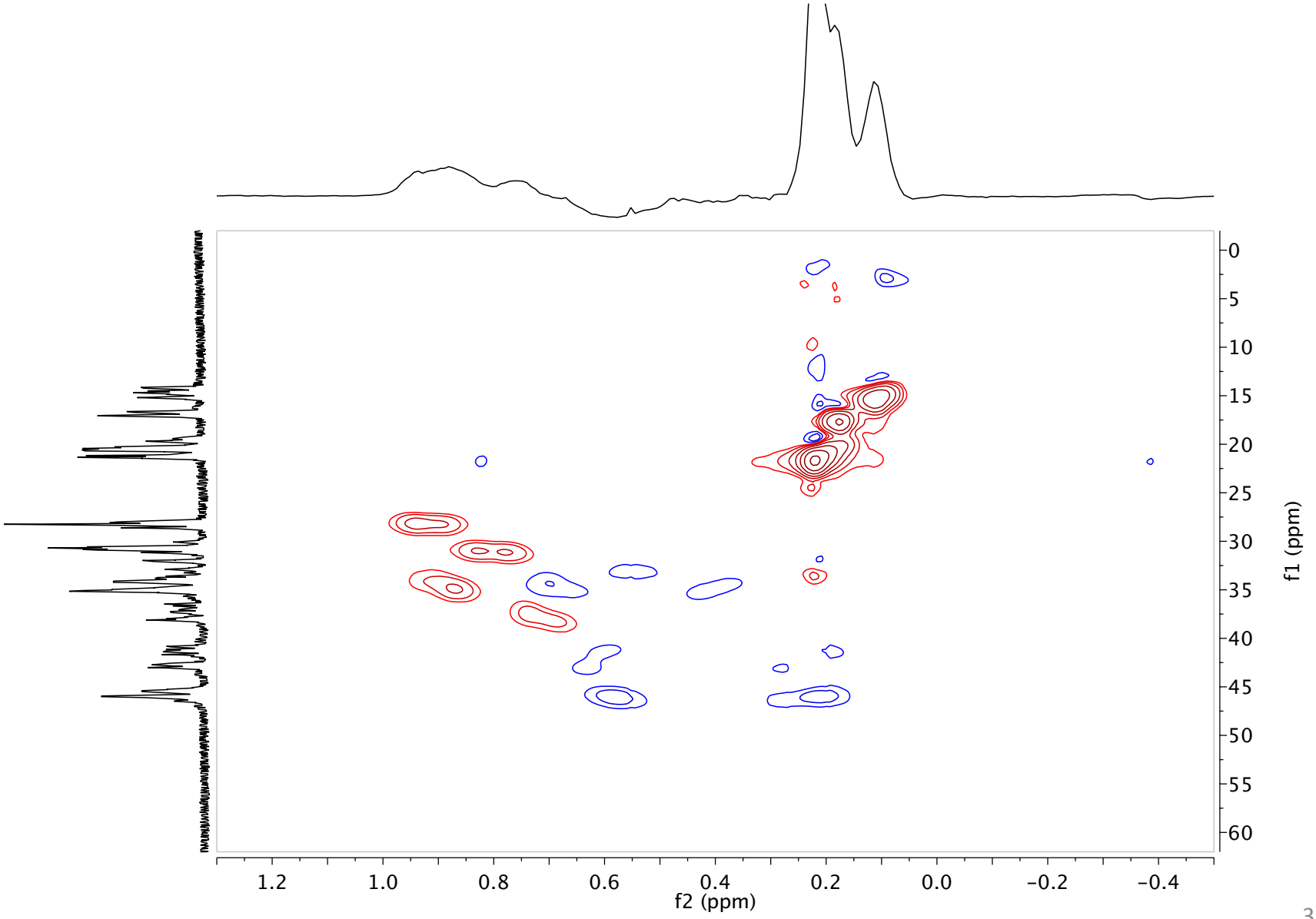
HSQC from PP from (*NNO)ZrBn$_2$ (increased intensity)



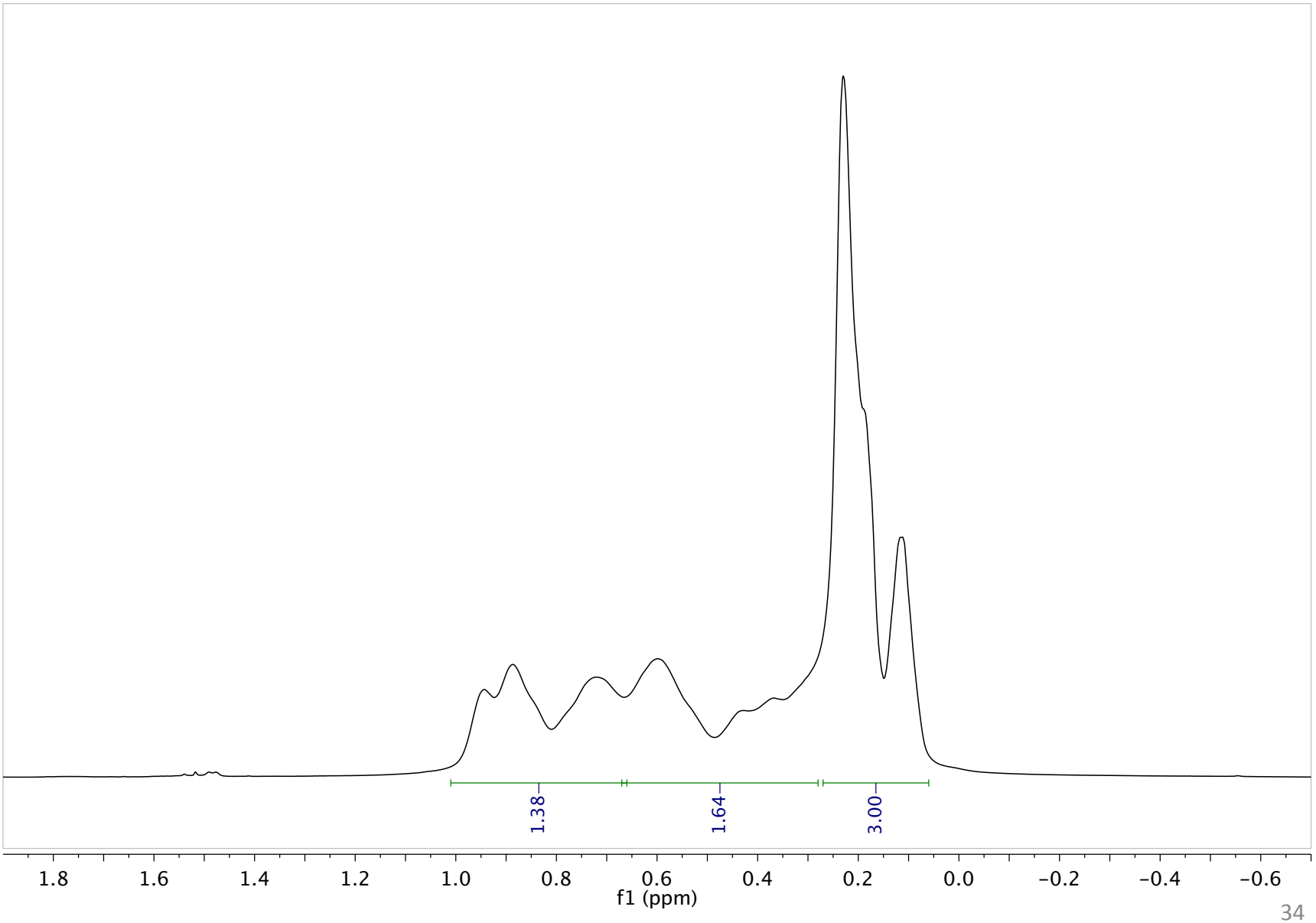
^{1}H from PP from (*NNO)ZrBn$_2$



HSQC PP from (*NNO)$TiCl_2$



^{1}H of PP from (*NNO)$TiCl_2$

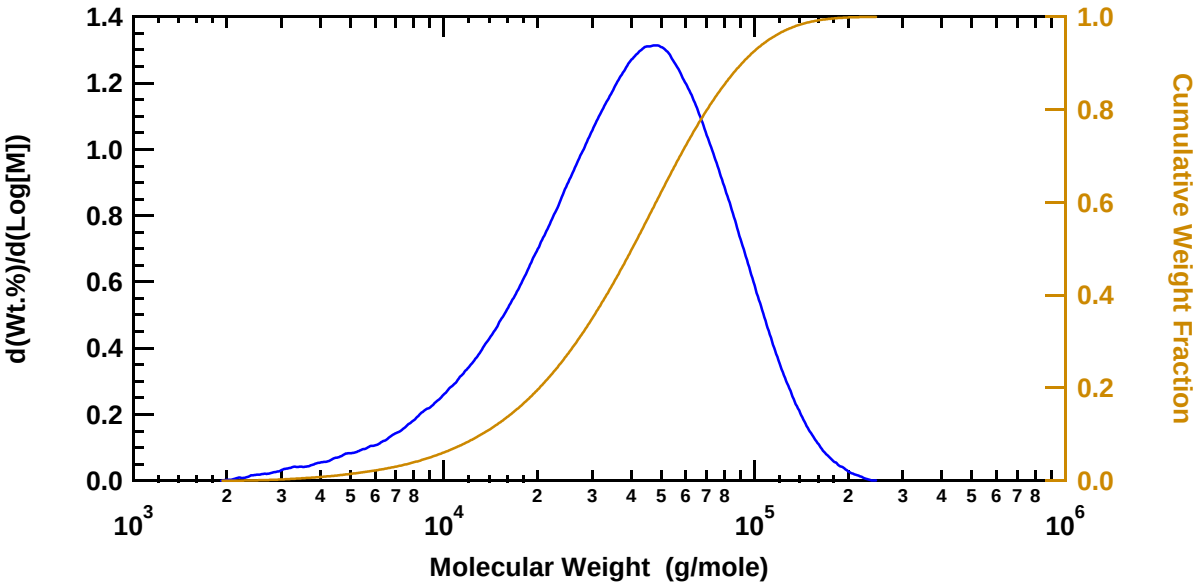


PP from (NNO)ZrBn2/1000 eq MAO

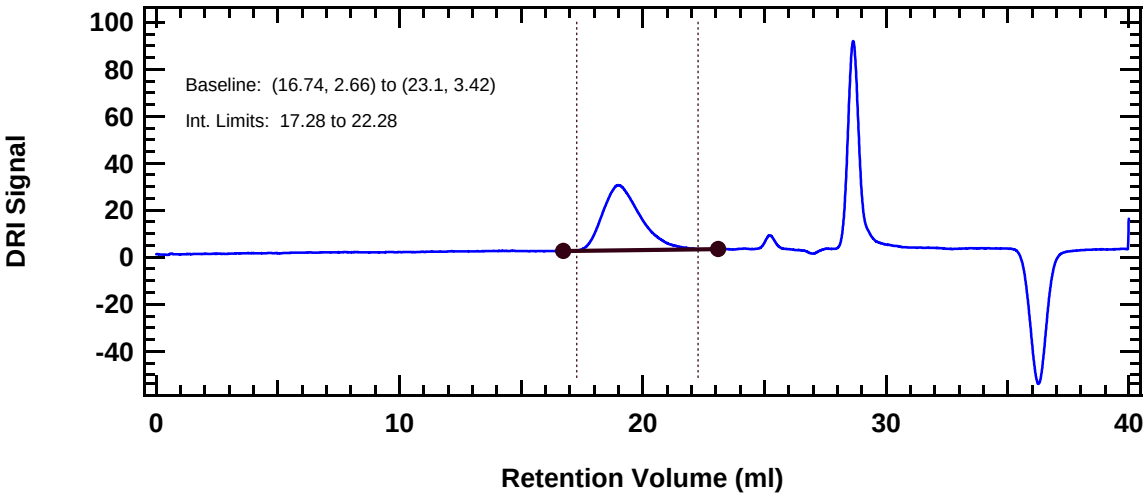
Analyzed as Polypropylene.

Mn = 26,229	Inject Mass (mg) = 0.225
Mw = 47,176	Calc. Mass (mg) = 0.194 (86.3%)
Mz = 69,141	Adjusted Flow Rate (ml/m) = 0.017
Mw/Mn = 1.8	Column Cal. C0 = 12.678
Mz/Mw = 1.47	Column Cal. C1 = -0.39548
K (sample) = 0.0002288	Column Cal. C2 = -0.00091362
alpha (sample) = 0.705	Column Cal. C3 = 0
(dn/dc) = 0.109	Inject Mark (ml) = 28.632
DRI Const. = 4.232e-07	

MWD from DRI Analysis



DRI Chromatogram

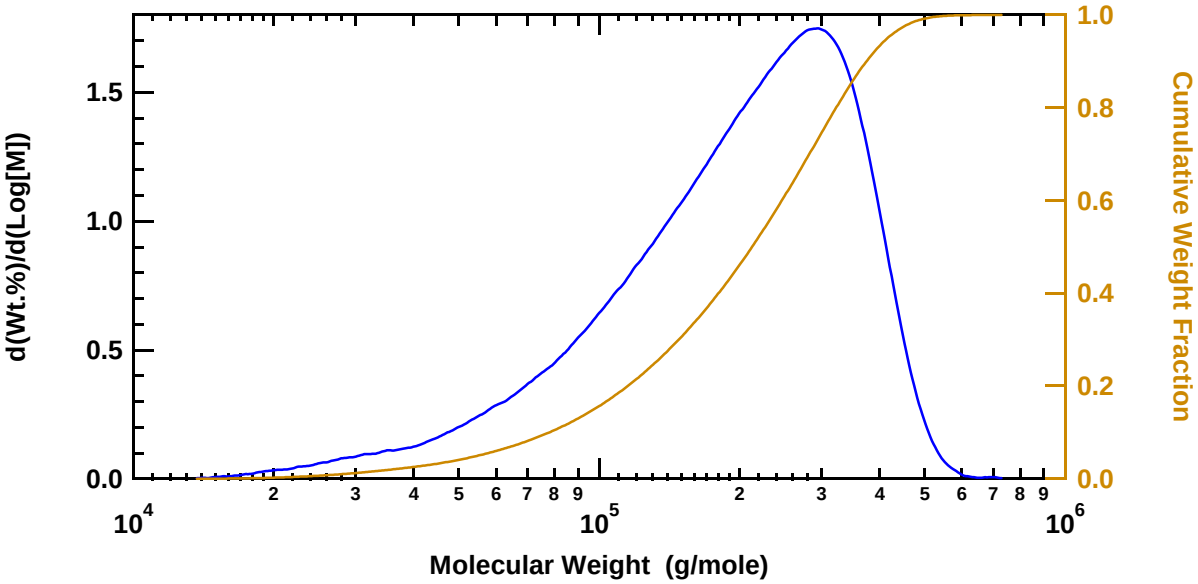


PP from (NNO)TiCl2/1000 eq MAO

Analyzed as Polypropylene.

Mn = 147,032	Inject Mass (mg) = 0.225
Mw = 220,377	Calc. Mass (mg) = 0.161 (71.4%)
Mz = 277,012	Adjusted Flow Rate (ml/m) = 0.017
Mw/Mn = 1.5	Column Cal. C0 = 12.678
Mz/Mw = 1.26	Column Cal. C1 = -0.39548
K (sample) = 0.0002288	Column Cal. C2 = -0.00091362
alpha (sample) = 0.705	Column Cal. C3 = 0
(dn/dc) = 0.109	Inject Mark (ml) = 28.632
DRI Const. = 4.232e-07	

MWD from DRI Analysis



DRI Chromatogram

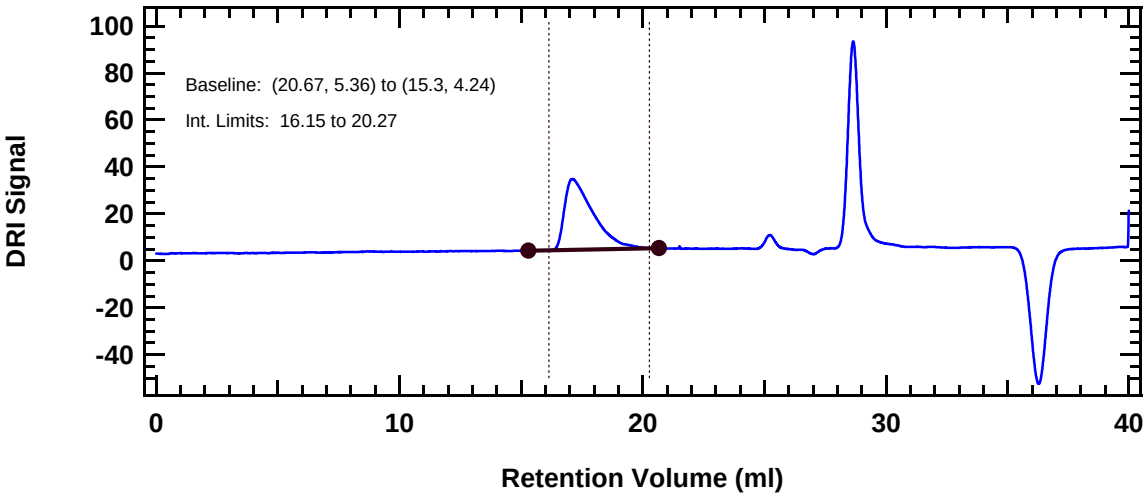


Table 1. Crystal data and structure refinement for **5**.

Empirical formula	$C_{33}H_{36}Cl_2N_2OTi$
Formula weight	595.44
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 9.955(2) Å b = 11.603(3) Å c = 25.865(5) Å α = 90° β = 96.160(9)° γ = 90°
Volume ($Å^3$)	2970.6(11)
Z	4
Calculated density (mg/m^3)	1.331
Absorption coefficient (mm^{-1})	0.497
F(000)	1248
Crystal size (mm^3)	0.37 x 0.17 x 0.07
Θ range for data collection	1.58 to 24.71°
Limiting indices	$-11 \le h \le 11$ $-13 \le k \le 13$ $-30 \le l \le 30$
Reflections collected	39186
Unique reflections	5064 [R(int) = 0.0495]
Completeness to Θ	24.71 (100.0 %)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5064/0 /359
Goodness-of-fit on F^2	1.057
Final R indices [I>2σ(I)]	R1 = 0.0384 wR2 = 0.1052
R indices (all data)	R1 = 0.0509 wR2 = 0.1146
Largest diff. peak and hole (eA^{-3})	0.890 and -0.333

Table 2. Selected Bond Lengths (Å) and Angles (°) of **5**

Ti(1)-O(1)	1.8040(17)	O(1)-Ti(1)-N(1)	110.87(8)
Ti(1)-N(1)	1.879(2)	O(1)-Ti(1)-N(2)	84.04(7)
Ti(1)-N(2)	2.153(2)	N(1)-Ti(1)-N(2)	84.58(8)
Ti(1)-Cl(2)	2.3161(8)	O(1)-Ti(1)-Cl(2)	118.49(6)
Ti(1)-Cl(3)	2.3285(8)	N(1)-Ti(1)-Cl(2)	127.68(7)
Ti(1)-C(1)	2.609(2)	N(2)-Ti(1)-Cl(2)	84.26(6)
		O(1)-Ti(1)-Cl(3)	97.22(6)
		N(1)-Ti(1)-Cl(3)	98.62(7)
		N(2)-Ti(1)-Cl(3)	175.84(6)
		Cl(2)-Ti(1)-Cl(3)	91.66(3)
		O(1)-Ti(1)-C(1)	138.44(8)
		N(1)-Ti(1)-C(1)	31.62(8)
		N(2)-Ti(1)-C(1)	76.91(8)
		Cl(2)-Ti(1)-C(1)	96.14(6)
		Cl(3)-Ti(1)-C(1)	104.44(6)

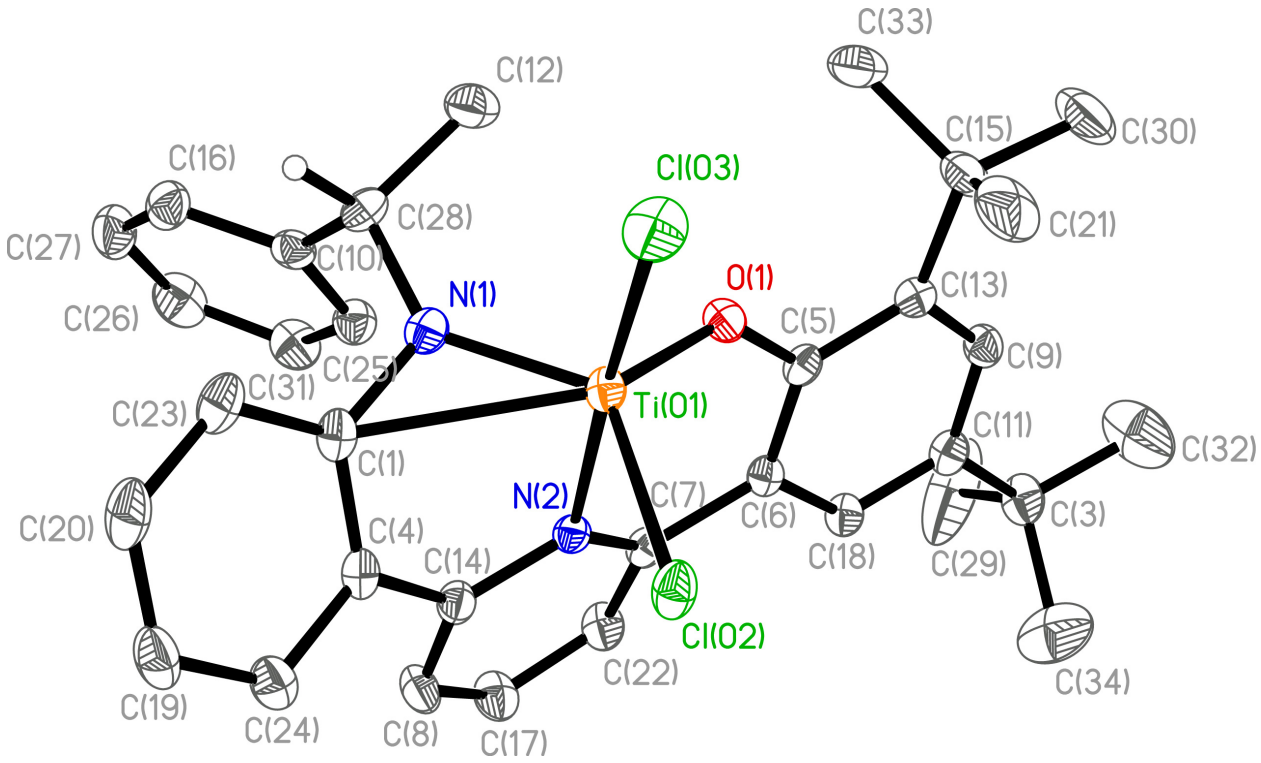


Figure 1. A fully labeled thermal ellipsoid (50%) diagram of the X-ray structure of (NNO)$TiCl_2$ **5**. Hydrogens omitted for clarity.