Outer-Sphere Direction in Iridium C-H Borylation

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Supporting Information

Contents:

General Information

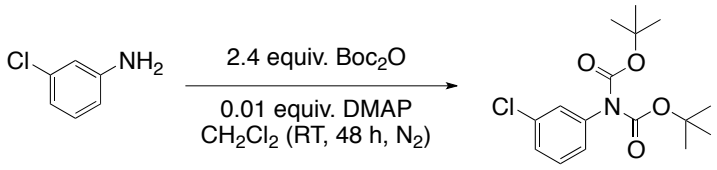
All commercially available chemicals were used as received unless otherwise indicated. Pinacolborane (HBPin) and bis(pinacolato)diboron (B_2Pin_2) were generously supplied by BASF. Bis(η^4-1,5-cyclooctadiene)-di-μ-methoxy-diiridium(I) $[Ir(OMe)COD]_2$ was prepared per literature procedure.[1] Methyl *tert*-butylether (MTBE), tetrahydrofuran (THF) and diethyl ether were refluxed over sodium/benzophenone ketyl, distilled and degassed. Column chromatography was performed on Silia P-Flash silica gel. Thin layer chromatography was performed on 0.25 mm thick aluminum-backed silica gel plates purchased from Silicycle and visualized with ultraviolet light (λ = 254 nm). Sublimations were conducted with a water-cooled cold finger.

^1H and ^{13}C NMR spectra were recorded on an Inova-600 spectrometer (599.81 and 150.84 MHz respectively), Varian VXR-500 spectrometer (499.96 and 125.73 MHz respectively), Varian UnityPlus-500 spectrometer (499.74 and 125.67 MHz respectively) or Varian VXR-300 spectrometer (300.11 and 75.47 MHz respectively) and referenced to residual solvent signals. ^{11}B and ^{19}F spectra were recorded on an Inova-600 spectrometer (192.45 MHz for ^{11}B), Varian UnityPlus-500 spectrometer (160.34 MHz for ^{11}B) or a Varian VXR-300 spectrometer (96.18 MHz and 282.08 MHz respectively) and were referenced to either neat boron trifluoride etherate ($BF_3{\cdot}OEt_2$) or neat trichlorofluoromethane ($CFCl_3$) as the external standard. The boron bearing carbon atom was not observed due to quadrupolar relaxation. All coupling constants are apparent *J* values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, bs = broad singlet). High-resolution mass spectra (HRMS) were obtained at the Michigan State University Mass Spectrometry Service Center using a Waters GCT Premier instrument run on electron ionization (EI) direct probe or a Waters QTOF Ultima instrument run on electrospray ionization (ESI+).[2] Infrared spectroscopy was obtained at Michigan State University using an FT-IR Mattson spectrometer. Melting points were measured on a MEL-TEMP® capillary melting apparatus and stand uncorrected.

General Procedure for preparing *N*-t-Boc protected anilines[3]

A flask was charged with a stir bar, substrate, 1 mL water per 1 mmol substrate and t-Boc_2O. After stirring for the given time, ethyl acetate and 1,4-dioxane were added and the solution was acidified with saturated $KHSO_4$ in water at 0 °C. After extracting three times with ethyl acetate, the organic phase was washed with concentrated brine, dried over $MgSO_4$ and concentrated in vacuo. This solid was loaded onto a filter frit and washed three times with a minimal amount of cold hexanes. The remaining solid was dried under high vacuum.

Preparation of *N,N*-di-(*tert*-butoxycarbonyl)-3-chloroaniline (6)

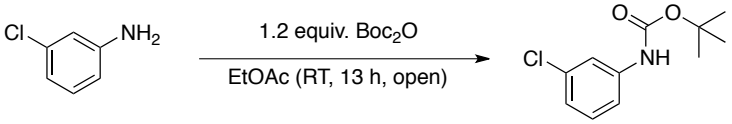


6

A solution containing 2.01 g (15.8 mmol) 3-chloroaniline, 19 mg (0.2 mmol) *N*,*N*-dimethyl-4-aminopyridine and 8.24 g (37.8 mmol) t-Boc_2O in 10 mL dichloromethane was stirred via magnetic stirbar. After 48 hours, the solution was mixed with 1,4-dioxane, acidified with saturated $KHSO_4$ in water at 0 °C, extracted with dichloromethane, washed with saturated brine, dried over $MgSO_4$ and filtered. The volatiles were evaporated in vacuo to afford a colorless oil. Once this oil crystallized, residual t-Boc_2O was sublimed out (0.02 mmHg, 25 °C). Then the solid was further sublimed (0.02 mmHg, 50 °C) to afford 2.80 g **6** as white needles (55% yield, mp = 76 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.27–7.24 (m, 2H), 7.15–7.14 (m, 1H), 7.03–7.01 (m, 1H), 1.41 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 151.43, 140.39, 133.98, 129.53, 128.37, 127.62, 126.30, 83.10, 27.88; FT-IR (thin film): 3000, 2974, 2944, 2880, 1735, 1702, 1586, 1475, 1366, 1273, 1239, 1160, 1125, 1075, 1044, 1023, 876, 842, 806, 773, cm^{-1}; HRMS calcd. for $C_{16}H_{22}ClNO_4$ $[M]^+$ 327.1237, found 327.1239.

Preparation of *N*-(*tert*-butoxycarbonyl)-3-chloroaniline (7)

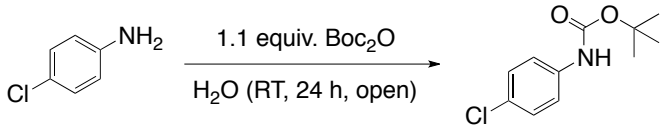


7

A solution of 10.00 g (78.4 mmol) 3-chloroaniline and 20.53 g (94.1 mmol) t-Boc_2O in 15 mL ethyl acetate was stirred by magnetic stirbar open to air. All volatiles were removed after 13 hours to provide a pink solid that was washed three times with hexanes. The solid was collected and the procedure repeated on the filtrate. This provided 16.50 g **7** as a white solid (93% yield, mp = 82-84 °C, lit mp = 83 °C[4]).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.50 (s, 1H), 7.18–7.12 (m, 2H), 6.99–6.96 (m, 1H), 6.54 (bs, 1H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.42, 139.56, 134.69, 129.85, 122.97, 118.51, 116.39, 80.96, 28.25; FT-IR (thin film): 3320, 2978, 1709, 1603, 1537, 1480, 1449, 1426, 1404, 1390, 1287, 1244, 1159, 1078, 1059, 853, 772, 739, 691, 681 cm^{-1}; HRMS calcd. for $C_{11}H_{14}ClNO_2$ $[M]^+$ 227.0713, found 227.0715.

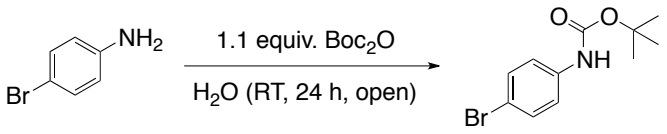
Preparation of *N*-(*tert*-butoxycarbonyl)-4-chloroaniline



The general procedure was applied using 5.00 g (39.2 mmol) 4-chloroaniline, 40 mL water and 9.41 g (43.1 mmol) t-Boc_2O for 24 hours to provide 6.56 g *N*-(*tert*-butoxycarbonyl)-4-chloroaniline as a white solid (74% yield, mp = 98-100 °C, lit mp = 105-106 °C[4]). The hexane washings were concentrated to approximately 5 mL and cooled to –30 °C to yield 1.60 g *N*-(*tert*-butoxycarbonyl)-4-chloroaniline as white needles (18% yield, mp = 98 °C, lit mp = 105-106 °C[4]; combined crops = 8.16 g, 91% yield).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.28 (d, ^3J = 8.8 Hz, 2H), 7.22 (d, ^3J = 9.0 Hz, 2H), 6.47 (bs, 1H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.56, 136.95, 128.92, 127.94, 119.71, 80.84, 28.29; FT-IR (thin film): 3366, 2988, 1696, 1591, 1522, 1495, 1451, 1401, 1364, 1306, 1269, 1240, 1179, 1165, 818, 772, 758, 617 cm^{-1}; HRMS calcd. for $C_{11}H_{14}ClNO_2$ $[M]^+$ 227.0713, found 227.0719.

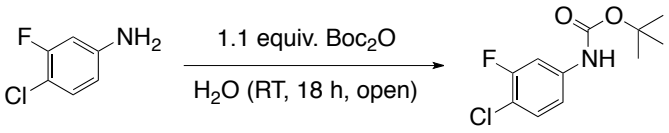
Preparation of *N*-(*tert*-butoxycarbonyl)-4-bromoaniline



The general procedure was applied using 3.46 g (20.1 mmol) 4-bromoaniline, 22 mL water and 4.85 g (22.2 mmol) t-Boc_2O for 24 hours to provide 5.40 g *N*-(*tert*-butoxycarbonyl)-4-bromoaniline as a white solid (98% yield, mp = 104 °C, lit mp = 102 °C[3]).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.35 (d, ^3J = 8.8 Hz, 2H), 7.23 (d, ^3J = 9.0 Hz, 2H), 6.56 (bs, 1H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.52, 137.46, 131.80, 120.06, 115.37, 80.82, 28.26; FT-IR (thin film): 3367, 3000, 2982, 2933, 2899, 1695, 1591, 1520, 1491, 1413, 1394, 1366, 1306, 1267, 1238, 1178, 1160, 1070, 1055, 1008, 815, 763, 631, 613 cm^{-1}; HRMS calcd. for $C_{11}H_{14}BrNO_2$ $[M]^+$ 271.0208, found 271.0211.

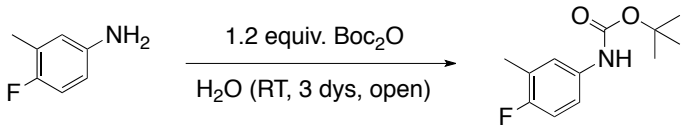
Preparation of *N*-(*tert*-butoxycarbonyl)-4-chloro-3-fluoroaniline



The general procedure was applied using 3.00 g (20.6 mmol) 4-chloro-3-fluoroaniline, 20 mL water and 4.95 g (22.7 mmol) t-Boc_2O for 18 hours to provide 4.87 g *N*-(*tert*-butoxycarbonyl)-4-chloro-3-fluoroaniline as a white solid (97% yield, mp = 98-100 °C, lit mp = 103-104 °C[5]).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.41 (d, $J_{H\text{-}F}$ = 9.5 Hz, 1H), 7.25–7.22 (m, 1H), 6.93–6.91 (m, 1H) 6.51 (bs, 1H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 158.18 (d, $^1J_{C\text{-}F}$ = 246.7), 152.24 (s), 138.54 (s), 138.46 (s), 130.38 (s), 114.39 (s), 107.01 (d, $^2J_{C\text{-}F}$ = 26.2), 81.30 (s), 28.24 (s); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$ = 0 ppm): δ –113.74 (dd, $^3J_{F\text{-}H}$ = 10.7, $^4J_{F\text{-}H}$ = 7.6); FT-IR (thin film): 3431, 3325, 3098, 2981, 2936, 1724, 1598, 1524, 1499, 1426, 1407, 1394, 1368, 1281, 1236, 1151, 1068, 1027, 977, 948, 867, 811, 722, 728, 666, 611, 554, 450, 429, 419 cm^{-1}; HRMS calcd. for $C_{11}H_{13}ClFNO_2$ $[M]^+$ 245.0619, found 245.0625.

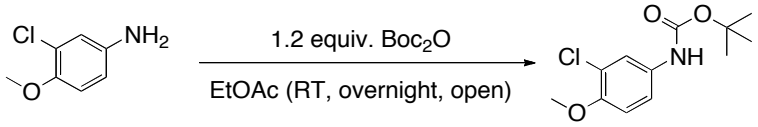
Preparation of *N*-(*tert*-butoxycarbonyl)-4-fluoro-3-methylaniline



The general procedure was applied using 10.00 g (80 mmol) 4-fluoro-3-methylaniline, 85 mL water and 20.93 g (96 mmol) t-Boc_2O for 3 days to provide 16.76 g *N*-(*tert*-butoxycarbonyl)-4-fluoro-3-methylaniline as a fluffy white solid (93% yield, mp = 76-78 °C). TLC analysis with dichloromethane as the eluent (R_f = 0.68) showed complete conversion of 4-fluoro-3-methylaniline after 3 hours.

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.23 (s, 1H), 7.05–7.02 (m, 1H), 6.88 (t, ^3J = 9.0 Hz, 1H), 6.34 (s, 1H), 2.22 (d, $^4J_{H\text{-}F}$ = 2.0 Hz, 3H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 157.35 (d, $^1J_{C\text{-}F}$ = 240.2), 152.94 (s), 133.90 (d, $^3J_{C\text{-}F}$ = 2.6), 125.23 (d, $^2J_{C\text{-}F}$ = 18.6), 121.74 (s), 117.54 (s), 115.06 (d, $^2J_{C\text{-}F}$ = 23.8), 80.48 (s), 28.31 (s), 14.63 (d, $^3J_{C\text{-}F}$ = 3.6); ^{19}F NMR (282 MHz, $CFCl_3$ = 0 ppm): δ –124.59; FT-IR (thin film): 3322, 3079, 2978, 2932, 1698, 1623, 1603, 1531, 1506, 1454, 1412, 1368, 1315, 1283, 1243, 1214, 1153, 1114, 1018, 1031, 1004, 884, 816, 771, 764 cm^{-1}; HRMS calcd. for $C_{12}H_{16}FNO_2$ $[M]^+$ 225.1165, found 225.1169.

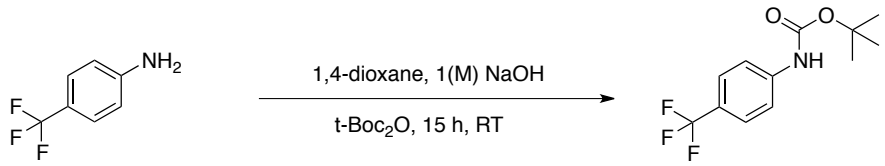
Preparation of *N*-(*tert*-butoxycarbonyl)-2-chloro-4-aminoanisole



A solution of 4.00 g (25.3 mmol) 3-chloro-4-methoxyaniline and 6.62 g (30.3 mmol) t-Boc_2O in ethyl acetate was stirred overnight. All volatiles were removed in vacuo to provide an off-white solid. The collected product was loaded onto a filter frit and washed three times with hexanes to provide 5.64 g *N*-(*tert*-butoxycarbonyl)-2-chloro-4-aminoanisole as a white solid (86% yield, mp = 88-90 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.44 (s, 1H), 7.15 (d, ^3J = 7.3 Hz, 1H), 6.82 (d, ^3J = 9.0 Hz, 1H), 6.36 (bs, 1H), 3.83 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.83, 151.11, 132.03, 122.65, 121.31, 118.23, 112.46, 80.64, 56.45, 28.31; FT-IR (thin film): 3328, 3002, 2978, 2934, 2841, 1698, 1590, 1502, 1454, 1442, 1393, 1367, 1279, 1255, 1239, 1161, 1062, 1023, 937, 836, 809, 735 cm^{-1}; HRMS calcd. for $C_{12}H_{16}ClNO_3$ $[M]^+$ 257.0819, found 257.0816.

Preparation of *N*-(*tert*-butoxycarbonyl)-4-trifluoromethylaniline[6]

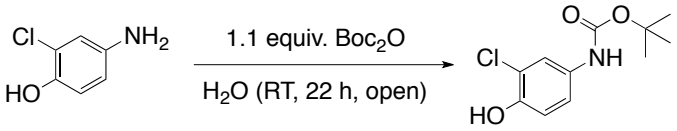


The literature procedure was followed as described.[7] A flask was charged with a stirbar, 0.97 g (6.0 mmol) 4-trifluoromethylaniline and 6 mL 1,4-dioxane. Upon mixing, 6 mL 1M NaOH in water was added to the flask. After the addition of 1.31 g (6.0 mmol) t-Boc_2O the mixture was stirred at room temperature for 15 hours. The contents were poured into water and extracted with ethyl acetate. The organic layer was washed with saturated brine, dried over Na_2SO_4 and

volatiles removed in vacuo. The obtained solid was loaded onto a filter frit and washed with hexanes to provide 0.58 g *N*-(*tert*-butoxycarbonyl)-4-trifluoromethylaniline as a white fluffy solid (37% yield, mp = 118-120 °C, lit mp = 115-117 °C[7]).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.51 (d, ^3J = 8.8 Hz, 2H), 7.45 (d, ^3J = 8.8 Hz, 2H), 6.64 (bs, 1H), 1.51 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.29 (s), 141.53 (d, $^4J_{C\text{-}F}$ = 1.4), 126.25 (q, $^3J_{C\text{-}F}$ = 3.7), 124.81 (q, $^2J_{C\text{-}F}$ = 32.7), 124.23 (q, $^1J_{C\text{-}F}$ = 271.1), 117.88 (s), 81.27 (s), 28.25 (s); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$ = 0 ppm): δ –62.10; FT-IR (thin film): 3364, 3012, 2986, 2940, 1703, 1617, 1596, 1528, 1507, 1445, 1410, 1395, 1372, 1334, 1317, 1274, 1237, 1158, 1108, 1071, 1024, 1016, 905, 838, 767, 632, 614, 505, 464 cm^{-1}; HRMS calcd. for $C_{12}H_{14}F_3NO_2$ $[M]^+$ 261.0977, found 261.0978.

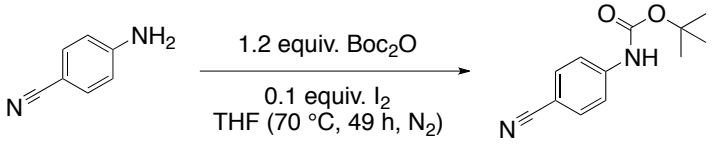
Preparation of *N*-(*tert*-butoxycarbonyl)-2-chloro-4-aminophenol



The general procedure was applied using 5.00 g (34.8 mmol) 2-chloro-4-aminophenol, 40 mL water and 8.40 g (38.5 mmol) t-Boc_2O for 22 hours to provide 7.98 g *N*-(*tert*-butoxycarbonyl)-2-chloro-4-aminophenol as a white solid (99% yield, mp = 90-92 °C, lit mp = 77-79 °C[8]).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.51, (s, 1H), 6.99 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1H), 6.89 (d, ^3J = 8.8 Hz, 1H), 6.35 (bs, 1H), 5.40, (s, 1H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.91, 147.40, 131.82, 119.91, 119.39, 116.16, 80.75, 28.31; FT-IR (thin film): 3341, 3038, 2979, 2934, 1692, 1596, 1515, 1455, 1413, 1394, 1368, 1280, 1241, 1147, 1060, 1015, 938, 871, 816, 774, 746, 689, 588 cm^{-1}; HRMS calcd. for $C_{11}H_{14}ClNO_2$ $[M]^+$ 243.0662, found 243.0669.

Preparation of *N*-(*tert*-butoxycarbonyl)-4-aminobenzonitrile

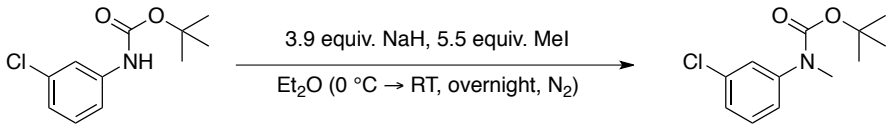


A modified literature procedure was followed.[9] A solution of 4.91 g (42.5 mmol) 4-aminobenzonitrile, 1.05 g (4.2 mmol) I_2 and 10.87 g (49.8 mmol) t-Boc_2O in 6 mL THF was stirred for 49 hours at 70 °C under N_2. After the addition of an additional 9.06 g (42.5mmol) t-Boc_2O and a total of 4 days at 70 °C under N_2 the contents were diluted with diethyl ether. The

organic layer was washed with saturated $Na_2S_2O_3$ in water, washed twice with 2M HCl in water, washed with saturated brine, dried over $MgSO_4$ and all volatiles removed in vacuo to provide a yellow liquid. After the addition of 20 mL 1 : 1 (diethyl ether / pentane) all volatiles were removed to afford a yellow solid. This crude solid was loaded onto a filter frit and washed extensively with pentane to provide a yellow-tinged solid (mp = 106-112 °C, lit mp = 120-120.5 °C[10]). The yellow-tinged solid was sublimed (120 °C, 0.001 mmHg) to afford 4.20 g *N*-(*tert*-butoxycarbonyl)-4-aminobenzonitrile as a white solid (46% yield, mp = 116-118 °C, lit mp = 120-120.5 °C[10]). This solid was then passed through a pad of silica-gel with dichloromethane as the eluent to yield 3.5 g *N*-(*tert*-butoxycarbonyl)-4-aminobenzonitrile a white solid (38% yield, mp = 118-120 °C, lit mp = 120-120.5°C[10], R_f = 0.53).

^{1}H NMR (600 MHz, $CDCl_3$ = 7.24 ppm): δ 7.55 (d, ^3J = 8.8 Hz, 2H), 7.46 (d, ^3J = 8.8 Hz, 2H), 6.67 (bs, 1H), 1.50 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$ = 77 ppm): δ 151.90, 142.53, 133.29, 119.01, 118.06, 105.81, 81.71, 28.21; FT-IR (thin film): 3328, 2979, 2933, 2225, 1732, 1710, 1607, 1590, 1523, 1411, 1370, 1318, 1233, 1156, 1056, 1027, 900, 838, 772, 701 cm^{-1}; HRMS calcd. for $C_{12}H_{14}N_2O_2$ $[M]^+$ 218.1055, found 218.1053.

Preparation of *N*-(*tert*-butoxycarbonyl)-*N*-methyl-3-chloroaniline (12a)



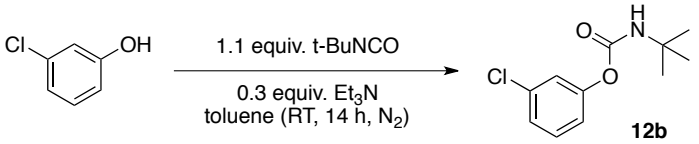
7 **12a**

A flask was charged with a stirbar, 5 mL diethyl ether and 380 mg (1.7 mmol) **7** and cooled to 0 °C under a N_2 atmosphere. The contents were stirred during the slow addition of 160 mg (6.7 mmol) NaH powder. Once no more gas evolution was observed 0.6 mL (9.4 mmol) methyl iodide was added and the contents stirred at room temperature overnight. The reaction was quenched with saturated NH_4Cl in water, extracted with diethyl ether, the organic layer washed with brine, dried over $MgSO_4$ and concentrated in vacuo. After column chromatography with dichloromethane as the eluent (R_f = 0.65) the obtained liquid was taken into the glovebox and passed through a short pad of activated neutral alumina with diethyl ether to afford 400 mg **12a** as a colorless liquid (99% yield).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.25–7.21 (m, 2H), 7.13–7.11 (m, 2H), 3.23 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 154.36, 144.97, 133.94, 129.42, 125.64,

125.37, 123.49, 80.79, 37.12, 28.29; FT-IR (thin film): 3057, 2975, 2927, 2855, 1705, 1615, 1594, 1577, 1482, 1457, 1434, 1391, 1364, 1352, 1305, 1253, 1153, 1120, 1091, 985, 865, 824, 777, 725, 694, 587, 418 cm^{-1}; HRMS calcd. for $C_{12}H_{16}ClNO_2$ $[M]^+$ 241.0870, found 241.0870.

Preparation of 3-chlorophenyl *tert*-butylcarbamate (12b)

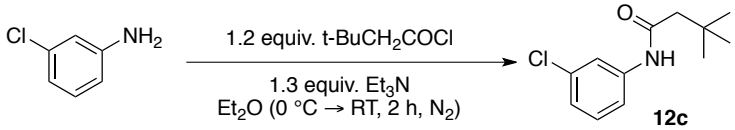


12b

A solution containing 3.00 g (23.3 mmol) 3-chlorophenol, 2.8 mL (25.0 mmol) *tert*-butyl isocyanate and 1 mL (7.2 mmol) triethylamine in 10 mL toluene was stirred via magnetic stirbar at room temperature under a N_2 atmosphere. After 14 hours all volatiles were removed in vacuo and the remaining solid loaded onto a filter frit and washed with hexanes to afford 4.81 g **12b** as a white solid (92% yield, mp = 96 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.27–7.24 (m, 2H), 7.15–7.14 (m, 1H), 7.03–7.01 (m, 1H), 5.01 (bs, 1H), 1.41 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 151.43, 140.39, 133.98, 129.53, 128.37, 127.62, 126.30, 83.10, 27.88; FT-IR (thin film): 3331, 3068, 3035, 3006, 2967, 2934, 2907, 2875, 1718, 1588, 1537, 1475, 1458, 1427, 1393, 1366, 1279, 1258, 1212, 1152, 1087, 1068, 1050, 1022, 1000, 927, 897, 881, 867, 793, 769, 689, 673, 650, 559, 460, 440 cm^{-1}; HRMS calcd. for $C_{11}H_{14}ClNO_4$ $[M]^+$ 227.0713, found 227.0719.

Preparation of *N*-(3-chlorophenyl)-3,3-dimethylbutanamide (12c)



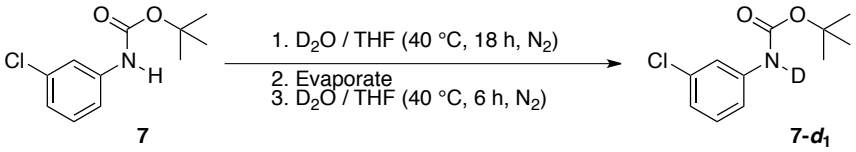
12c

A stirring solution of 1.57 g (12.3 mmol) 3-chloroaniline and 2.2 mL (15.8 mmol) triethylamine in 30 mL diethyl ether at 0 °C was prepared under a N_2 atmosphere. The addition of 2.0 mL (14.4 mmol) 3,3-dimethylbutyryl chloride via syringe was done dropwise. After 2 hours at room temperature, the contents were poured into 10 mL water and the solution extracted three times with diethyl ether, washed with saturated brine, dried over $MgSO_4$ and evaporated in vacuo. The off-white solid was loaded onto a filter frit and washed three times with hexanes to afford 2.66 g **12c** as a white solid (96% yield, mp = 110-112 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.64 (bs, 1H), 7.61 (s, 1H), 7.31 (d, ^3J = 7.3 Hz, 1H), 7.16 (t, ^3J = 8.1 Hz, 1H), 7.02 (d, ^3J = 7.8 Hz, 1H), 2.19 (s, 2H), 1.06 (s, 9H); ^{13}C NMR (126

MHz, $CDCl_3$ = 77 ppm): δ 170.57, 139.01, 134.47, 129.81, 124.20, 120.22, 118.07, 51.31, 31.30, 29.74; FT-IR (thin film): 3280, 3249, 3182, 3118, 3072, 2962, 2925, 2900, 2867, 1656, 1590, 1532, 1442, 1417, 1367, 1333, 1268, 1253, 1235, 1200, 1133, 1092, 1077, 998, 925, 869, 792, 751, 688, 542, 430 cm^{-1}; HRMS calcd. for $C_{12}H_{16}ClNO$ $[M]^+$ 225.0920, found 225.0918.

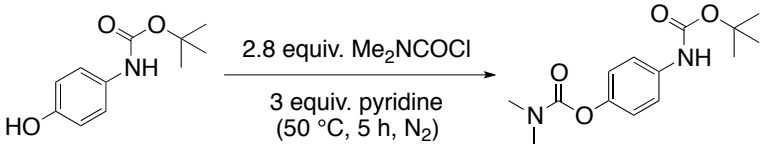
Preparation of *N*-(*tert*-butoxycarbonyl)-*N*-deuterio-3-chloroaniline (7-d_1)



A 100 mL Schlenk flask was washed with D_2O and evaporated under N_2 flow prior to use. The flask was charged with a stir bar, 2.04 g (8.8 mmol) **7**, 5 mL D_2O and 5 mL THF, then heated to 40 °C. After 18 hours of stirring all volatiles were removed under N_2 flow at 90 °C. The white solid was redissolved in 5 mL D_2O and 5 mL THF and stirred at 40 °C for an additional 6 hours. All volatiles were removed under N_2 flow at 90 °C. The remaining solid was sublimed (0.005 mmHg, 70 °C) to the side of the flask. The solid was scraped onto a filter frit in the glovebox, washed with a minimal amount of pentane and dried to afford 1.63 g **7-d_1** as a white solid (80% yield, >98% D-incorporation by NMR, mp = 82-84 °C).

^1H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.50 (s, 1H), 7.18–7.12 (m, 2H), 6.99–6.97 (m, 1H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.56, 139.46, 134.72, 129.88, 122.97, 118.39, 116.26, 80.99, 28.27; FT-IR (neat): 2979, 2931, 2432, 1694, 1600, 1576, 1486, 1453, 1397, 1369, 1299, 1247, 1167, 1101, 1079, 1063, 1037, 998, 905, 852, 773, 708, 681 cm^{-1}; HRMS calcd. for $C_{11}{}^1H_{13}{}^2HClNO_2$ $[M]^+$ 228.0776, found 228.0780.

Preparation of *O*-(*N',N'*-dimethylcarbamoyl)-*N*-(*tert*-butoxycarbonyl)-4-aminophenol[6]

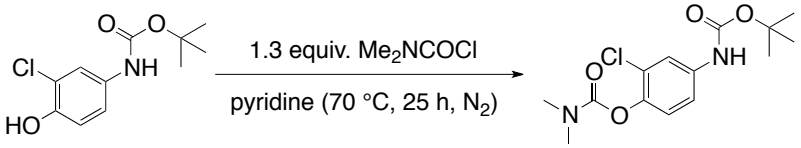


A flask was charged with a stirbar, 1.51 g (7.2 mmol) *N*-(*tert*-butoxycarbonyl)-4-aminophenol and 1.7 mL (21.6 mmol) pyridine under a N_2 atmosphere. After the addition of 1.9 mL (20.2 mmol) *N*,*N*-dimethylcarbamoyl chloride the mixture was heated at 50 °C for 5 hours. The contents were diluted with ethyl acetate, washed with 1M HCl in water and the organic layer dried over $MgSO_4$. Crystallization from 3 : 1 (ethyl acetate / hexanes) afforded 1.33 g *O*-(*N',N'*-

dimethylcarbamoyl)-*N*-(*tert*-butoxycarbonyl)-4-aminophenol as a white solid (66% yield, mp = 178-180 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.29 (d, ^3J = 8.6 Hz, 2H), 6.99 (d, ^3J = 8.8 Hz, 2H), 6.56 (bs, 1H), 3.06 (s, 3H), 2.98 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 155.09, 152.79, 146.87, 135.48, 122.07, 119.37, 80.39, 36.68, 36.39, 28.32; FT-IR (thin film): 3297, 3131, 3053, 2979, 2932, 1706, 1606, 1535, 1513, 1490, 1458, 1407, 1369, 1309, 1239, 1207, 1163, 1108, 1050, 1017, 873, 873, 825, 757, 746, 694, 600, 525 cm^{-1}; HRMS calcd. for $C_{14}H_{20}N_2O_4$ $[M]^+$ 280.1423, found 280.1429.

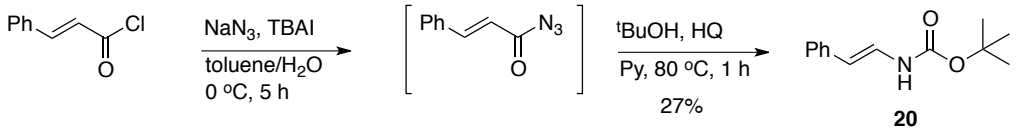
Preparation of *O*-(*N'*,*N'*-dimethylcarbamoyl)-*N*-(*tert*-butoxycarbonyl)-2-chloro-4-aminophenol[6]



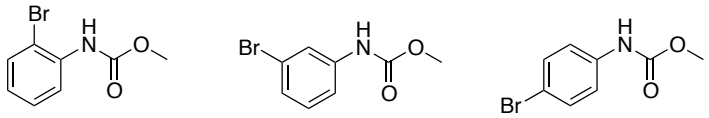
A flask was charged with a stirbar and 2.00 g (8.2 mmol) *N*-(*tert*-butoxycarbonyl)-2-chloro-4-aminophenol in pyridine under a N_2 atmosphere. After the addition of 1.0 mL (10.7 mmol) *N*,*N*-dimethylcarbamoyl chloride the mixture was heated at 70 °C for 25 hours. The contents were diluted with ethyl acetate, washed with 1M HCl in water and the organic layer dried over $MgSO_4$. Impurities were removed by washing the product with hexanes to afford 1.94 g *O*-(*N'*,*N'*-dimethylcarbamoyl)-*N*-(*tert*-butoxycarbonyl)-2-chloro-4-aminophenol as a white solid (75% yield, mp = 162 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.50 (s, 1H), 7.02–6.96 (m, 3H), 3.10 (s, 3H), 3.00 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 154.26, 152.63, 142.49, 136.75, 126.98, 123.75, 119.82, 117.56, 80.44, 36.81, 36.46, 28.23; FT-IR (thin film): 3429, 3321, 3055, 2986, 1718, 1606, 1518, 1456, 1392, 1265, 1209, 1155, 1059, 910, 875, 823, 740, 706 cm^{-1}; HRMS(ESI+) calcd. for $C_{14}H_{19}ClN_2O_4$ $[M+H]^+$ 315.1115, found 315.1118.

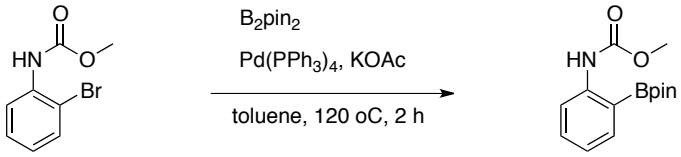
Preparation of Enamine 20: This compound was prepared according to the previously reported procedure.[11]



Preparation of *o*-bromo-, *m*-bromo- and *p*-bromo-phenyl carbamic acid methyl esters These compounds were prepared according to the previously reported procedure.[12,13,14]



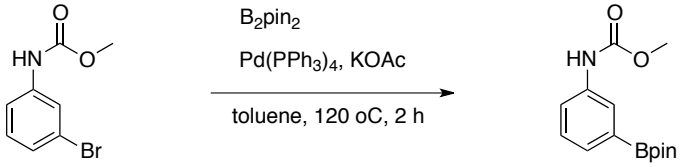
Preparation of methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl) phenylcarbamate:



To a degassed solution of 2-bromophenyl carbamic acid methyl ester (0.5 g, 2.17 mmol), bis(pinacolate)diborane (1.104 g, 4.34 mmol), and potassium acetate (0.646 g, 6.52 mmol) in toluene (22 mL) was added tetrakistriphenylphosphine palladium (0.0678 g, 2.7 mol%). The reaction mixture was immediately heated to 120^{o} C for 2 hours, and subsequently cooled to room temperature. After cooling, the reaction mixture was washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated. The remaining residue (1.11 g) was purified by flash chromatography (95% hexane, 5% EtOAc) to give methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl)phenylcarbamate as a white powder. Two main fractions of product were obtained, one pure (268 mg, 44.5% yield) and one impure (283 mg) containing 59 mg (9.8% yield). Overall yield: 342 mg, 54.3% [mp = 113^{o}C];

^{1}HNMR (500 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.72 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.43 (td, *J* = 8.3, 1.6 Hz, 1H), 6.99 (td, *J* = 7.4, 1.0 Hz, 1H), 3.75 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (126 MHz, $CHCl_3$): δ 154.2, 144.8, 136.2, 132.9, 121.8, 117.5, 84.3, 52.0, 24.8; ^{11}B NMR ($CDCl_3$, 96 MHz): δ 30.4; HRMS (ES^+) calcd. for $C_{14}H_{20}BNO_4$: 278.1564 (M+H). Found: 278.1568.

Preparation of methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl) phenylcarbamate:

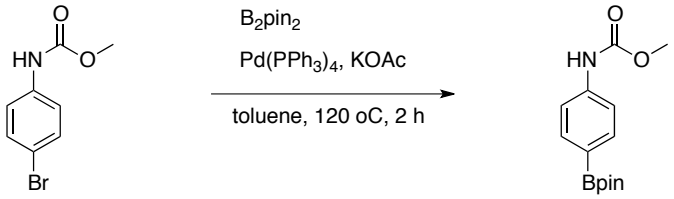


To a degassed solution of 3-bromophenyl carbamic acid methyl ester (0.5 g, 2.17 mmol), bis(pinacolate)diborane (1.104 g, 4.34 mmol), and potassium acetate (0.646 g, 6.52 mmol) in toluene (22 mL) was added tetrakistriphenylphosphine palladium (0.0678 g, 2.7 mol%). The

reaction mixture was immediately heated to 120^{o} C for 2 hours, and subsequently cooled to room temperature. After cooling, the reaction mixture was washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated. The remaining residue (1.25 g) was purified by flash chromatography (80% hexane, 20% EtOAc) and subsequent washing with hexane to give (methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl)phenylcarbamate. A series of two columns were used to purify the product. The first column failed to separate off much of the B_2Pin_2 but effectively removed the heavier contaminants (mass after first column: 1.12 g). The second column afforded 227 mg (37.7% yield) of pure product (white powder), and an 83 mg impure fraction that contained 66 mg (11% yield) of product. Overall yield: 293 mg, 48.7% [mp = 136^{o}C];

^{1}HNMR (500 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.57 (s, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.60 (s, 1H), 3.75 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (126 MHz, $CHCl_3$): δ 154.3, 139.7, 137.6, 130.1, 128.8, 119.4, 84.2, 52.5, 25.1; ^{11}B NMR ($CDCl_3$, 96 MHz): δ 30.3; HRMS (ES^+) calcd. for $C_{14}H_{20}BNO_4$: 278.1564 (M+H). Found: 278.1570.

Preparation of methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl) phenylcarbamate:



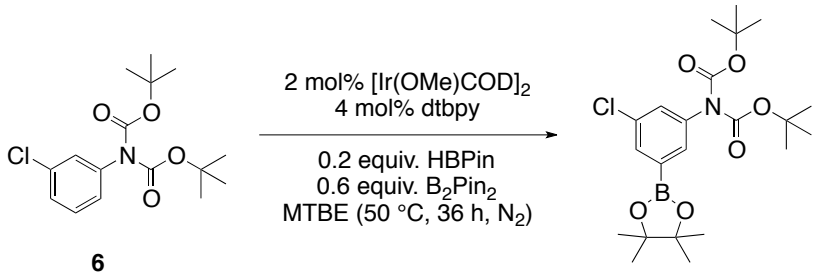
To a degassed solution of 4-bromophenyl carbamic acid methyl ester (0.5 g, 2.17 mmol), bis(pinacolate)diborane (1.104 g, 4.34 mmol), and potassium acetate (0.646 g, 6.52 mmol) in toluene (22 mL) was added tetrakistriphenylphosphine palladium (0.0678 g, 2.7 mol%). The reaction mixture was immediately heated to 120^{o} C for 2 hours, and subsequently cooled to room temperature. After cooling, the reaction mixture was washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated. The remaining residue (1.85 g) was purified by flash chromatography (90% hexane, 10% EtOAc to 80% hexane, 20% EtOAc) to give (methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl)phenylcarbamate. A series of two columns were used to purify the product. The first column failed to separate off much of the B_2Pin_2 but effectively removed the heavier contaminants (mass after first column: 0.892 g). The second afforded a 483mg impure fraction, 252 mg of which was the desired product (42% yield). [mixed mp = 147 ^{o}C].

^{1}H NMR (500 MHz, $CHCl_3$): δ 7.73 (d, *J* = 8.6 Hz, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 6.69 (br. s., 1 H), 3.75 (s, 3 H), 1.31 (s, 12 H); ^{13}C NMR (126 MHz, $CHCl_3$): δ 153.9, 147.2, 140.8, 136.1, 83.9, 52.6, 25.1; ^{11}B NMR ($CDCl_3$, 96 MHz): δ 30.2; Satisfactory HRMS results for $C_{14}H_{20}BNO_4$ were not obtained.

General Procedure for iridium C–H borylations

In a glovebox, a solution of 30 μL (0.2 mmol) HBPin and 13.1 mg (0.02 mmol) $[Ir(OMe)COD]_2$ in minimal MTBE was added to 10.7 mg (0.04 mmol) dtbpy. The solution was subsequently transferred to an air free flask equipped with a stir bar, B_2Pin_2, 1.0 mmol substrate and MTBE. The entire procedure was conducted using 2.0 mL MTBE. The reaction was allowed to proceed at 50 °C under a N_2 atmosphere connected to a mercury bubbler for the time noted.

Borylation of Compound 6

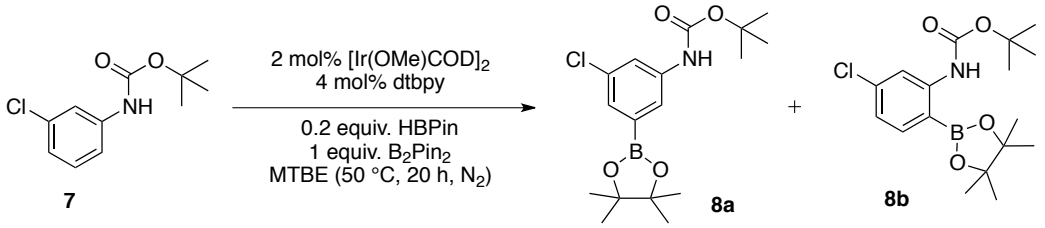


6

The general procedure was applied using 152 mg (0.6 mmol) B_2Pin_2, 327 mg (1.0 mmol) **6** for 36 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude solid was passed through a short pad of silica gel with dichloromethane as the eluent (R_f = 0.57) to afford a colorless oil which crystallized upon standing for several days. The colorless crystals were loaded onto a filter frit and washed with a minimal amount of –78 °C pentane to afford 410 mg borylated product as colorless crystals (91% yield, mp = 122-124 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.68 (dd, ^{4}J = 0.7 Hz, ^{4}J = 2.0 Hz, 1H), 7.44 (dd, ^{4}J = 0.7 Hz, ^{4}J = 2.0 Hz, 1H), 7.22 (t, ^{4}J = 2.0 Hz, 1H), 1.41 (s, 18H), 1.31 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 151.57, 139.88, 133.72, 133.60, 132.40, 131.01, 84.27, 83.06, 27.91, 24.842; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.2; FT-IR (thin film): 2980, 2934, 1794, 1752, 1729, 1716, 1572, 1470, 1455, 1419, 1391, 1369, 1355, 1328, 1272, 1242, 1149, 1118, 964, 887, 868, 851, 782, 715, 702, 490, 438, 424 cm^{-1}; HRMS calcd. for $C_{22}H_{33}BClNO_6$ $[M]^+$ 453.2089, found 453.2091.

Borylation of Compound 7



The general procedure was applied using 254 mg (1.0 mmol) B_2Pin_2 and 227 mg (1.0 mmol) **6** for 20 hours. The reaction was transferred to a 20 mL scintillation vial with dichloromethane. A small amount of methanol was added and all volatiles were removed in vacuo. A silica gel column was run using 1 : 1 (dichloromethane / hexanes) as the eluent to afford 176 mg **8b** as a white solid (50% yield, mp 108-110 °C, $R_f = 0.46$) and 90 mg **8a** as a white solid (25% yield, mp = 130-132 °C, $R_f = 0.12$).

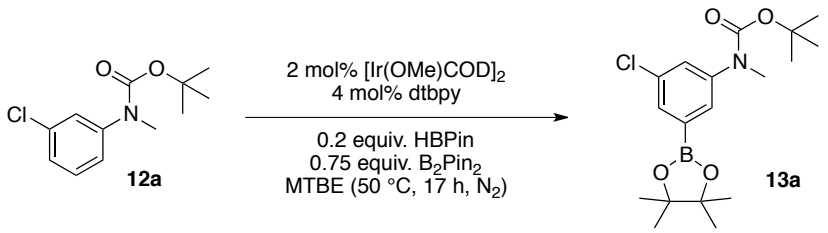
***N*-(*tert*-butoxycarbonyl)-5-chloro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (8a)**

^{1}H NMR (600 MHz, $CDCl_3$ = 7.24 ppm): δ 7.73 (s, 1H), 7.41 (d, ^4J = 1.2 Hz, 1H), 7.40 (d, ^4J = 2.0 Hz, 1H), 6.50 (bs, 1H), 1.49 (s, 9H), 1.30 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$ = 77 ppm): δ 152.43, 139.09, 134.59, 128.90, 122.40, 121.21, 84.18, 80.87, 28.27, 24.83; ^{11}B NMR (192 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.2; FT-IR (thin film): 3333, 2978, 2932, 1733, 1708, 1602, 1579, 1540, 1455, 1432, 1355, 1325, 1269, 1244, 1159, 1144, 1117, 1064, 994, 966, 870, 857, 773, 716, 703, 667 cm^{-1}; HRMS calcd. for $C_{17}H_{25}BClNO_4$ $[M]^+$ 353.1565, found 353.1566.

***N*-(*tert*-butoxycarbonyl)-5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (8b)**

^{1}H NMR (600 MHz, $CDCl_3$ = 7.24 ppm): δ 8.69 (s, 1H), 8.27 (s, 1H), 7.60 (d, ^3J = 8.1 Hz, 1H), 6.93 (dd, ^3J = 8.1 Hz, ^4J = 2.0 Hz, 1H), 1.51 (s, 9H), 1.34 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$ = 77 ppm): δ 152.79, 146.32, 139.03, 137.13, 121.71, 117.62, 84.39, 80.22, 28.30, 24.84; ^{11}B NMR (192 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.3; FT-IR (thin film): 3365, 2979, 2933, 1733, 1605, 1574, 1524, 1419, 1381, 1351, 1315, 1276, 1233, 1161, 1125, 1098, 1069, 1046, 1026, 962, 934, 854, 815, 768, 744, 668 cm^{-1}; HRMS calcd. for $C_{17}H_{25}BClNO_4$ $[M]^+$ 353.1565, found 353.1563.

Borylation of 12a



The general procedure was applied using 191 mg (0.75 mmol) B_2Pin_2, 181 mg (0.75 mmol) **12a** for 17 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane, quenching with a small amount of methanol and removing all volatiles in vacuo. The crude solid was passed through a short pad of silica gel with dichloromethane as the eluent to afford a colorless oil that crystallized upon standing for several days to afford 262 mg of *N*-(*tert*-butoxycarbonyl)-*N*-methyl-3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline **13a** as colorless crystals (95% yield, mp = 64-66 °C, R_f = 0.72). ^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.55 (d, ^4J = 1.2 Hz, 1H), 7.50 (d, ^4J = 1.2 Hz, 1H), 7.33 (s, 1H), 3.23 (s, 3H), 1.43 (s, 9H), 1.32 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 154.37, 144.49, 133.64, 131.38, 129.18, 128.74, 84.23, 80.67, 37.12, 28.27, 24.83; ^{11}B NMR (192 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.2; FT-IR (thin film): 2978, 2931, 1706, 1569, 1560, 1506, 1472, 1458, 1425, 1353, 1293, 1269, 1250, 1145, 994, 964, 882, 849, 769, 704, 604 cm^{-1}; HRMS calcd. for $C_{18}H_{27}BClNO_4$ $[M]^+$ 367.1722, found 367.1723.

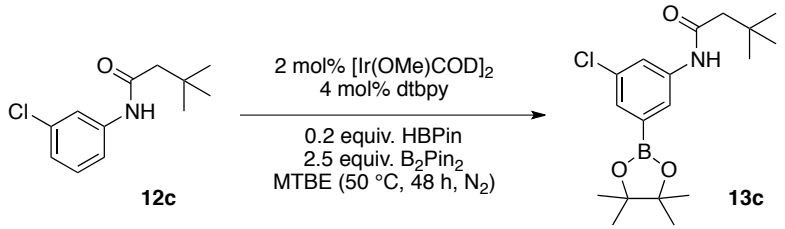
Borylation of 12b

The general procedure was applied using 254 mg (1.0 mmol) B_2Pin_2, 227 mg (1.0 mmol) **12b** for 24 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude solid was passed through a short pad of silica gel with dichloromethane as the eluent to afford a colorless oil containing 3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl *tert*-butylcarbamate (**13b**) and 3-chlorophenol (5:1). This mixture was diluted with ethyl acetate and washed with 2M NaOH in water until the aqueous layer was colorless. The organic layer was subsequently

washed with saturated brine, dried over $MgSO_4$ and concentrated in vacuo to afford 178 mg **13b** as a white solid (50% yield, mp = 106-108 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.58 (d, ^4J = 1.22 Hz, 1H), 7.40 (d, ^4J = 1.5 Hz, 1H), 7.21 (t, ^4J = 2.2 Hz, ^4J = 2.0 Hz, 1H), 4.98 (s, 1H), 1.36 (s, 9H), 1.31 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.25, 151.03, 134.11, 131.35, 125.98, 125.15, 84.25, 50.293, 28.76, 24.823; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.5; FT-IR (thin film): 3339, 2981, 2932, 1736, 1571, 1522, 1446, 1412, 1370, 1350, 1327, 1266, 1199, 1144, 1097, 1052, 1025, 965, 935, 914, 864, 844 cm^{-1}; HRMS calcd. for $C_{17}H_{25}BClNO_4$ $[M]^+$ 353.1565, found 353.1565.

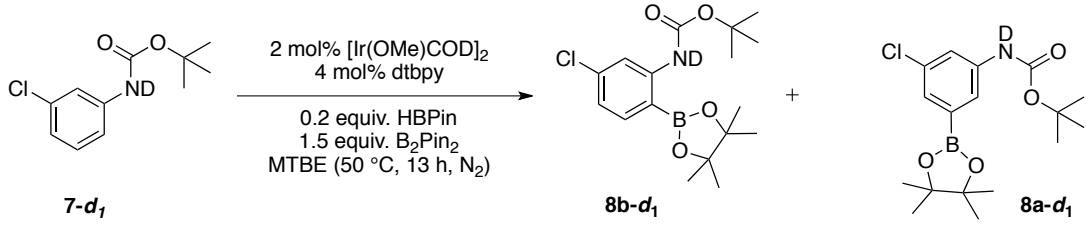
Borylation of 12c



The general procedure was applied using 635 mg (2.5 mmol) B_2Pin_2, 225 mg (1.0 mmol) **12c** for 48 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude mixture was purified via column chromatography using dichloromethane as the eluent to afford 183 mg of *N*-(3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-3,3-dimethylbutanamide **13c** as a white solid (52% yield, mp = 160-162 °C, R_f = 0.27).

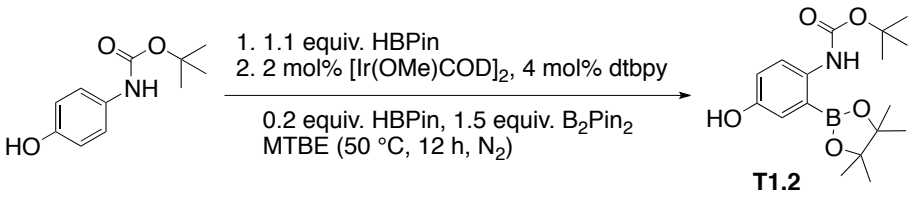
^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 7.99 (s, 1H), 7.47 (d, ^4J = 1.7 Hz, 1H), 7.45 (d, ^4J = 2.2 Hz, 1H), 7.17 (bs, 1H), 2.18 (s, 2H), 1.30 (s, 12H), 1.06 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 170.09, 138.54, 134.58, 130.10, 123.43, 122.75, 84.24, 51.62, 31.29, 29.79, 24.83; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.6; FT-IR (thin film): 3306, 3124, 2977, 2869, 1672, 1629, 1578, 1543, 1468, 1353, 1266, 1232, 1143, 1116, 868, 715, 707 cm^{-1}; HRMS calcd. for $C_{18}H_{27}BClNO_3$ $[M]^+$ 351.1773, found 351.1775.

Borylation of 7-*d*$_1$



The general procedure was applied using 192 mg (0.75 mmol) B_2Pin_2, 227 mg (1.0 mmol) *N*-deuterio-*N*-(tert-butoxycarbonyl)-3-chloroaniline and 3.0 mL MTBE for 13 hours. The reaction at 92% conversion was 66.3 : 33.7 (**8b-*d*$_1$** / **8a-*d*$_1$**).

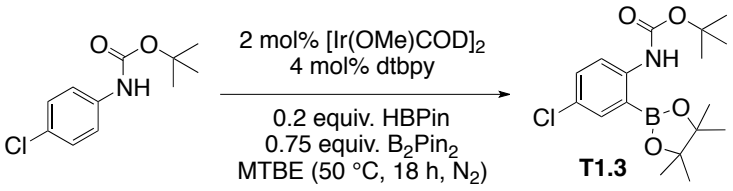
Preparation of *N*-(*tert*-butoxycarbonyl)-4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (Table 1, entry 2)



An air free flask was charged with a stir bar and 209 mg (1.0 mmol) N-(*tert*-butoxycarbonyl)-4-aminophenol. The addition of 160 μL (1.1 mmol) HBPin produced vigorous bubbling. A mixture of 13.2 mg (0.02 mmol) $[Ir(COD)OMe]_2$ and 30 μL (0.2 mmol) HBPin was added to 10.8 mg (0.04 mmol) dtbpy. This was added to the air free flask with 2 mL MTBE, 381 mg (1.5 mmol) B_2Pin_2 and allowed to react under N_2 at 50 °C for 12 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and methanol, then removing all volatiles in vacuo. A column was run with 40 : 60 (ethyl acetate / hexanes) to provide 262 mg **T1.2** as a white solid (78% yield, mp = 109-111 °C, R_f = 0.57).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.40 (s, 1H), 7.99 (d, ^3J = 8.6 Hz, 1H), 7.14 (d, ^4J = 2.9 Hz, 1H), 6.90 (dd, ^3J = 8.8 Hz, ^4J = 2.9 Hz, 1H), 4.70 (s, 1H), 1.49 (s, 9H), 1.33 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 153.54, 150.36, 138.23, 121.81, 119.69 (2 C's), 84.21, 79.74, 28.38, 24.81; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.3; FT-IR (thin film): 3383, 2980, 2932, 1731, 1630, 1593, 1493, 1449, 1370, 1306, 1244, 1163, 1123, 1076, 1034, 966, 891, 855 cm^{-1}; HRMS (ESI+) calcd. for $C_{17}H_{27}BNO_5$ $[M+H]^+$ 336.1982, found 336.1985.

Preparation of *N*-(*tert*-butoxycarbonyl)-4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, entry 3)

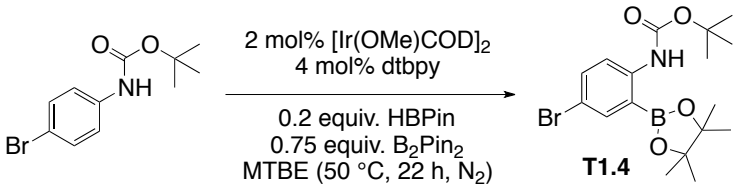


The general procedure was applied using 191 mg (0.75 mmol) B_2Pin_2 and 227 mg (1.0 mmol) *N*-(*tert*-butoxycarbonyl)-4-chloroaniline for 18 hours. Isolation involved transferring the solution to

a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude solid was passed through a short pad of silica gel with minimal dichloromethane as the eluent (R_f = 0.67). After removing all volatiles in vacuo, the residual starting material was sublimed (0.02 mmHg, 50 °C) leaving behind 278 mg **T1.3** as a white solid (79% yield, mp = 106-108 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.60 (bs, 1H), 8.13 (d, ^3J = 9.0 Hz, 1H), 7.64 (d, ^4J = 2.7 Hz, 1H), 7.33 (dd, ^3J = 9.0 Hz, ^4J = 2.9 Hz, 1H), 1.50 (s, 9H), 1.34 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.93, 143.74, 135.41, 132.42, 126.66, 119.09, 84.57, 80.06, 28.31, 24.82; ^{11}B (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.2; FT-IR (thin film): 3405, 2979, 2932, 1733, 1605, 1579, 1524, 1470, 1408, 1393, 1374, 1345, 1313, 1257, 1235, 1162, 1134, 1110, 1077, 1046, 1029, 963, 869, 848, 829, 744, 690, 667, 530, 440 cm^{-1}; HRMS calcd. for $C_{17}H_{25}BClNO_4$ $[M]^+$ 353.1565, found 353.1566.

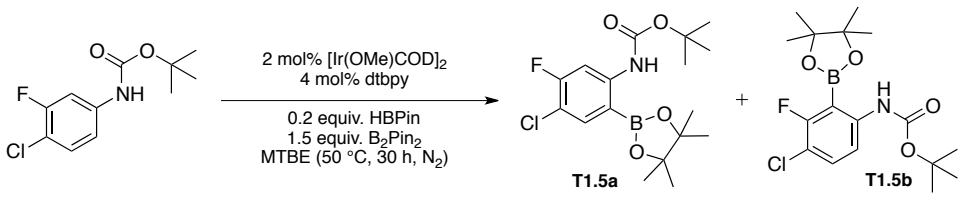
Preparation of *N*-(*tert*-butoxycarbonyl)-4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, entry 4)



The general procedure was applied using 192 mg (0.75 mmol) B_2Pin_2 and 273 mg (1.0 mmol) *N*-(*tert*-butoxycarbonyl)-4-bromoaniline for 22 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude solid was passed through a short pad of silica gel with dichloromethane as the eluent to afford 354 mg **T1.4** as a white solid (89% yield, mp = 120-122 °C, R_f = 0.68). Diffraction quality crystals were grown from pentane solution at –20 °C.

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.60 (bs, 1H), 8.08 (d, ^3J = 8.8 Hz, 1H), 7.78 (d, ^4J = 2.4 Hz, 1H), 7.47 (dd, ^3J = 8.8 Hz, ^4J = 2.7 Hz, 1H), 1.50 (s, 9H), 1.34 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.88, 144.23, 138.35, 135.33, 119.46, 114.27, 84.58, 80.10, 28.31, 24.82; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.6; FT-IR (thin film): 3371, 2978, 2932, 1733, 1603, 1574, 1522, 1469, 1405, 1370, 1313, 1229, 1136, 1080, 1047, 1025, 962, 902, 863, 828, 770, 743, 680, 638, 527, 442 cm^{-1}; HRMS calcd. for $C_{17}H_{25}BBrNO_4$ $[M]^+$ 397.1060, found 397.1061. X-Ray quality crystals were grown from pentane at –20 °C.

Preparation of *N*-(*tert*-butoxycarbonyl)-4-chloro-5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, entry 5) and *N*-(*tert*-butoxycarbonyl)-4-chloro-3-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (B)



The general procedure was applied using 381 mg (1.5 mmol) B_2Pin_2 and 245 mg (1.0 mmol) *N*-(*tert*-butoxycarbonyl)-4-chloro-3-fluoroaniline for 30 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude product consisted of 76 : 24 (**T1.5a**/**b**) and was fractioned through neutral Al_2O_3 (III) with 1 : 3 (dichloromethane / hexanes) as the eluent to provide 251 mg **T1.5a** as a white solid (68% yield, mp = 120-122 °C).

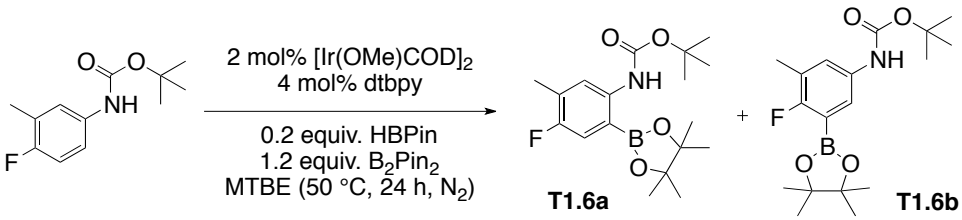
T1.5a

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.69 (bs, 1H), 8.10 (d, $^3J_{F-H}$ = 12.5 Hz, 1H), 7.68 (d, $^4J_{F-H}$ = 8.8 Hz, 1H), 1.50 (s, 9H), 1.34 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 160.70 (d, $^1J_{C-F}$ = 250.4 Hz), 152.64 (s), 145.65 (d $^3J_{C-F}$ = 11.1 Hz), 137.61 (s), 113.33 (d, $^3J_{C-F}$ = 17.5), 106.34 (d, $^2J_{C-F}$ = 27.2 Hz), 84.64 (s), 80.50 (s), 28.27 (s), 24.82 (s); ^{11}B (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.0; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$ = 0 ppm): δ –108.01 (t, $^3J_{F-H}$ = 12.1); FT-IR(thin film): 3366, 3126, 2980, 2933, 1734, 1591, 1530, 1473, 1452, 1419, 1382, 1353, 1319, 1283, 1242, 1160, 1139, 1092, 1063, 1004, 961, 906, 890, 860, 828, 771, 734, 689, 672, 622, 597, 439 cm^{-1}; HRMS calcd. for $C_{17}H_{24}BFClNO_4$ $[M]^+$ 371.1471, found 371.1480.

T1.5b

^{1}H (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.79 (bs, 1H), 7.92 (d, ^3J = 9.0 Hz, 1H), 7.35 (t, ^3J = 8.8 Hz, $^4J_{F-H}$ = 8.6 Hz, 1H), 1.49 (s, 9H), 1.36 (s, 12H); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$ = 0 ppm): δ –102.7 (d, $^4J_{F-H}$ = 9.2 Hz).

Preparation of *N*-(*tert*-butoxycarbonyl)-4-fluoro-5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, entry 6a) and *N*-(*tert*-butoxycarbonyl)-4-fluoro-5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, entry 6b)



The general procedure was applied using 305 mg (1.2 mmol) B_2Pin_2, 225 mg (1 mmol) *N*-(*tert*-butoxycarbonyl)-4-fluoro-3-methylaniline for 24 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane, quenching with a small amount of methanol and removing all volatiles in vacuo to provide a 91 : 9 (**T1.6a** / **T1.6b**) mixture. The crude solid was passed through a pad of silica gel with dichloromethane as the eluent. This solid was further purified by crystallization from minimal chloroform and 1 mL pentane at –80 °C to afford 244 mg 92 : 8 (**T1.6a** / **T1.6b**) as a white solid (70% yield, mp = 108-116 °C). Column chromatography on 99 mg using 10 : 1 (ethyl acetate / hexanes) as the eluent afforded 75 mg **T1.6a** as a white solid (76% yield based on 99 mg mixture, mp = 124-126 °C, R_f = 0.41) while **T1.6b** was fractioned with impurities.

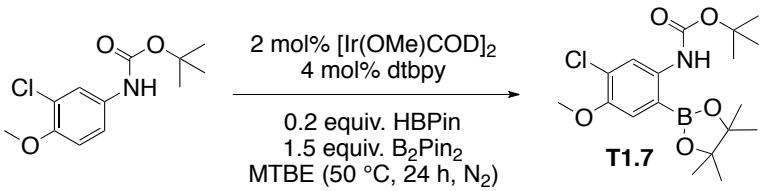
T1.6a

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.50 (s, 1H), 8.01 (d, $^4J_{H\text{-}F}$ = 6.6 Hz, 1H), 7.27 (d, $^3J_{H\text{-}F}$ = 9.8 Hz, 1H), 2.26 (d, $^4J_{H\text{-}F}$ = 1.7 Hz, 3H), 1.50 (s, 9H), 1.33 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$ = 77 ppm): δ 156.36 (d, $^1J_{C\text{-}F}$ = 239.9 Hz), 153.23 (s), 140.99 (s), 129.67 (d, $^2J_{C\text{-}F}$ = 17.8 Hz), 121.17 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 120.70 (s), 84.32 (s), 79.75 (s), 28.35 (s), 24.82 (s), 15.16 (d, $^3J_{C\text{-}F}$ = 3.5 Hz); ^{11}B NMR (192 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 29.9; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$ = 0 ppm): δ –127.06 (t, $^3J_{H\text{-}F}$ = 8.61 Hz, $^4J_{H\text{-}F}$ = 6.89 Hz); FT-IR (thin film): 3357, 3042, 2979, 2926, 1723, 1652, 1582, 1540, 1420, 1370, 1350, 1311, 1292, 1254, 1170, 1139, 1067, 1009, 961, 893, 854, 836, 763, 738, 687 cm^{-1}; HRMS calcd. for $C_{18}H_{27}BFNO_4$ $[M]^+$ 351.2017, found 351.2011.

T1.6b

^{1}H NMR (600 MHz, $CDCl_3$ = 7.24 ppm): δ 7.50 (s, 1H), 7.27-7.25 (m, 1H), 6.39-6.38 (m, 1H), 2.22 (d, *J* = 2.0 Hz, 3H), 1.48 (s, 9H), 1.32 (s, 12H), ^{19}F NMR (282 MHz, CDCl3 = 0 ppm): δ -114.0.

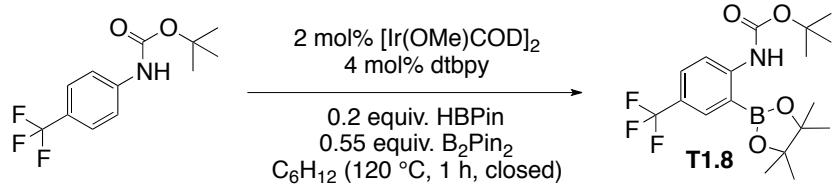
Prepparation of *N*-(*tert*-butoxycarbonyl)-5-chloro-4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, entry 7)



The general procedure was applied using 382 mg (1.5 mmol) B_2Pin_2, 385 mg (1.0 mmol) *N*-(*tert*-butoxycarbonyl)-2-chloro-4-aminoanisole for 24 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude solid was passed through a short pad of silica gel with dichloromethane as the eluent to afford 365 mg **T1.7** as an off-white solid (95% yield, mp = 130 °C, R_f = 0.39).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.49 (s, 1H), 8.27 (s, 1H), 7.20 (s, 1H), 3.87 (s, 3H), 1.50 (s, 9H), 1.34 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.99, 149.62, 139.37, 127.20, 120.07, 118.49, 84.44, 79.91, 56.46, 28.33, 24.82; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.5; FT-IR (thin film): 3370, 3112, 2977, 2938, 2835, 1727, 1604, 1586, 1520, 1467, 1401, 1351, 1305, 1265, 1232, 1200, 1162, 1090, 1057, 956, 855, 743, 428, 408 cm^{-1}; HRMS calcd. for $C_{28}H_{27}BClNO_5$ $[M]^+$ 383.1671, found 383.1674. X-Ray quality crystals were grown from pentane at –20 °C.

Preparation of *N*-(*tert*-butoxycarbonyl)-4-trifluoromethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (Table 1, entry 8)

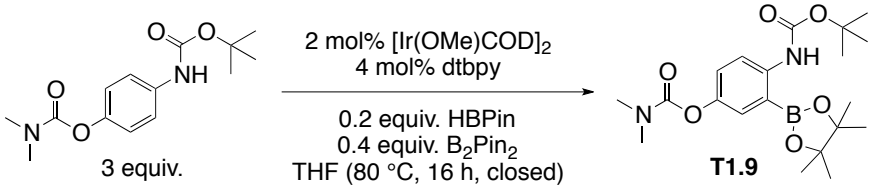


In a glovebox, a solution of 29 µL (0.2 mmol) HBPin and 13.1 mg (0.02 mmol) $[Ir(OMe)COD]_2$ in minimal cyclohexane was added to 10.7 mg (0.04 mmol) dtbpy. The solution was subsequently transferred to an air free equipped with a stir bar, 139 mg (0.55 mmol) B_2Pin_2 and 263 mg (1.0 mmol) *N*-(*tert*-butoxycarbonyl)-4-trifluoromethylaniline with cyclohexane. The entire procedure was conducted using 2.0 mL cyclohexane. The reaction was allowed to proceed at 120 °C in a closed system for 1 hour. Isolation involved cooling to room temperature, transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude solid was passed through a short

pad of silica gel with dichloromethane as the eluent (R_f = 0.73). The residual starting material was sublimed (0.02 mmHg, 80 °C) leaving behind 317 mg **T1.8** as a white solid (82% yield, mp = 108-110 °C). Diffraction quality crystals were grown from pentane solution at –20 °C.

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.82 (bs, 1H), 8.30 (d, ^3J = 8.8 Hz, 1H), 7.94 (d, ^4J = 2.0 Hz, 1H), 7.61 (dd, ^3J = 8.8 Hz, ^4J = 2.2 Hz, 1H), 1.51, (s, 9H), 1.36 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.75 (s), 148.18 (s), 133.21 (d, $^3J_{C\text{-}F}$ = 3.7), 129.54 (d, $^3J_{C\text{-}F}$ = 3.2 Hz), 124.38 (q, $^1J_{C\text{-}F}$ = 271.6 Hz), 123.37 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 117.28 (s), 84.72 (s), 80.44 (s), 28.25 (s), 24.81 (s); ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.6; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$ = 0 ppm): δ –62.01; FT-IR (thin film): 3367, 2980, 2934, 1738, 1620, 1594, 1539, 1430, 1362, 1270, 1238, 1162, 1144, 1120, 1079, 1047, 1025, 964, 867, 848, 758, 682, 638, 606 cm^{-1}; HRMS calcd. for $C_{18}H_{25}BF_3NO_4$ $[M]^+$ 387.1829, found 387.1827. X-Ray quality crystals were grown from pentane at –20 °C.

Preparation of *N*-(*tert*-butoxycarbonyl)-*O*-(*N'*,*N'*-dimethylcarbamoyl)-4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (Table 1, entry 9)

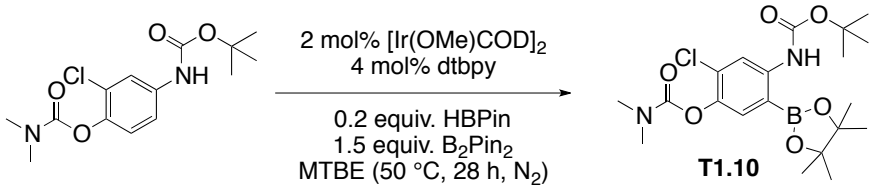


In a glovebox, a solution of 15 μL (0.1 mmol) HBPin and 6.6 mg (0.01 mmol) $[Ir(OMe)COD]_2$ in minimal THF was added to 5.3 mg (0.02 mmol) dtbpy. The solution was subsequently transferred to an air free flask equipped with a stir bar, 51 mg (0.2 mmol) B_2Pin_2 and 610 mg (1.5 mmol) *O*-(*N'*,*N'*-dimethylcarbamoyl)-*N*-(*tert*-butoxycarbonyl)-4-aminophenol in THF. The entire procedure was conducted using 2.0 mL THF. The reaction was allowed to proceed at 80 °C in a closed system for 16 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude solid was passed through a short pad of silica gel with dichloromethane as the eluent (R_f = 0.07). The recovered solid was washed with copious amounts of cyclohexane, concentrated to approximately 4 mL and cooled. The precipitated starting material was filtered and washed sparingly with cold cyclohexane. The filtrate was pumped down and the remaining solid crystallized from pentane at –80 °C overnight to afford 89 mg **T1.9** as white needles (44%

yield, mp = 126-128 °C). Diffraction quality crystals were grown from pentane solution at –20 °C.

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.59 (bs, 1H), 8.15 (d, ^{3}J = 9.0 Hz, 1H), 7.41 (d, ^{4}J = 2.9 Hz, 1H), 7.13 (dd, ^{3}J = 9.0 Hz, ^{4}J = 2.9 Hz, 1H), 3.04 (s, 3H), 2.96 (s, 3H), 1.50 (s, 9H), 1.32 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 155.21, 153.08, 145.61, 142.44, 128.61, 126.04, 118.60, 84.33, 79.73, 36.64, 36.35, 28.34, 24.83; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 30.5; FT-IR (thin film): 3382, 2979, 2933, 1728, 1615, 1592, 1533, 1476, 1455, 1425, 1387, 1347, 1329, 1198, 1158, 1072, 1048, 1023, 965, 915, 854, 822, 791, 770, 743, 678, 547 cm^{-1}; HRMS calcd. for $C_{20}H_{31}BN_2O_6$ $[M]^+$ 406.2275, found 406.2275. X-Ray quality crystals were grown from pentane at –20 °C.

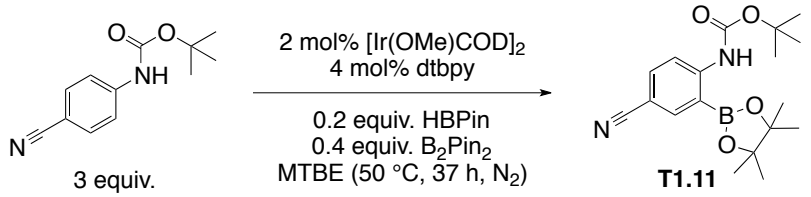
Preparation of *O*-(*N',N'*-dimethylcarbamoyl)-*N*-(*tert*-butoxycarbonyl)-2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-aminophenol (Table 1, entry 10)



The general procedure was applied using 381 mg (1.5 mmol) B_2Pin_2, 314 mg (1.0 mmol) *O*-(*N',N'*-dimethylcarbamoyl)-*N*-(*tert*-butoxycarbonyl)-2-chloro-4-aminophenol for 28 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude solid was passed through a short pad of silica gel with dichloromethane as the eluent twice to afford 272 mg **T1.10** as a white solid (62% yield, mp = 140-142 °C, R_f = 0.26).

^{1}H NMR (300 MHz, $CDCl_3$ = 7.24 ppm): δ 8.62 (s, 1H), 8.34 (s, 1H), 7.48 (s, 1H), 3.09 (s, 3H), 2.99 (s, 3H), 1.50 (s, 9H), 1.32 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$ = 77 ppm): δ 154.20, 152.77, 143.13, 141.69, 131.59, 130.60, 119.05, 84.51, 80.18, 36.80, 36.45, 28.28, 24.82; ^{11}B NMR (96 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 29.9; FT-IR (thin film): 3365, 2977, 2933, 1731, 1609, 1579, 1522, 1470, 1411, 1382, 1345, 1309, 1249, 1155, 1089, 1057, 973, 955, 908, 853, 839, 791, 752, 684, 669, 600, 503, 436 cm^{-1}; HRMS calcd. for $C_{20}H_{30}BClN_2O_6$ $[M]^+$ 340.1885, found 340.1895.

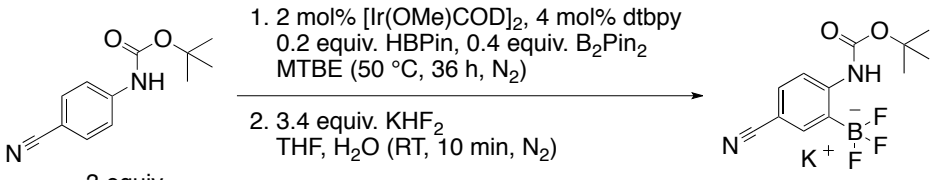
Preparation of *N*-(*tert*-butoxycarbonyl)-4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (Table 1, entry 11)



In a glovebox, a solution of 30 μL (0.2 mmol) HBPin and 13.1 mg (0.02 mmol) $[Ir(OMe)COD]_2$ in minimal MTBE was added to 10.8 mg (0.02 mmol) dtbpy. The solution was subsequently transferred to an air free equipped with a stir bar, 103 mg (0.4 mmol) B_2Pin_2 and 654 mg (2.0 mmol) *N*-(*tert*-butoxycarbonyl)-4-aminobenzonitrile in MTBE. The entire procedure was conducted using 2.0 mL MTBE. The reaction proceeded at 50 °C under N_2 for 37 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. The crude solid was passed through a short pad of silica gel with dichloromethane as the eluent and all volatiles removed in vacuo. This recovered solid was washed with copious amounts of cyclohexane and concentrated. Cyclohexane was found to best solubalize **T1.11** in the presence of *N*-(*tert*-butoxycarbonyl)-4-aminobenzonitrile when compared to room temperature and –78 °C hexanes, pentane and cyclopentane. Column chromatography of the residual white solid, containing a mixture of starting material and borylated product with Florisil® using 1 : 9 (ethyl acetate / hexanes) afforded 136 mg **T1.11** (40% yield, mp = 118 °C).

^{1}H NMR (500 MHz, $CDCl_3$ = 7.24 ppm): δ 8.86 (bs, 1H), 8.32 (d, ^3J = 8.8 Hz, 1H), 7.98 (d, ^4J = 2.2 Hz, 1H), 7.63 (dd, ^3J = 8.8 Hz, ^4J = 2.2 Hz, 1H), 1.51 (s, 9H), 1.35 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$ = 77 ppm): δ 152.43, 148.85, 140.51, 136.17, 119.13, 117.57, 104.68, 84.9, 80.88, 28.22, 24.83; ^{11}B NMR (96 MHz, $CDCl_3$, BF_3OEt_2 = 0 ppm): δ 30.5; FT-IR (thin film): 3354, 2980, 2932, 2221, 1735, 1609, 1585, 1529, 1480, 1414, 1397, 1362, 1321, 1250, 1165, 1139, 1078, 1050, 1030, 979, 966, 914, 891, 850, 832, 768, 748, 693, 563 cm^{-1}; HRMS calcd. for $C_{18}H_{25}BN_2O_4$ $[M]^+$ 344.1907, found 344.1910.

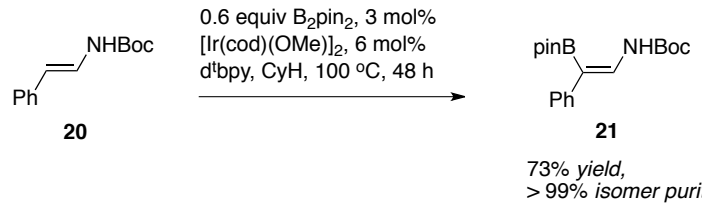
Preparation of Potassium (*N*-(*tert*-butoxycarbonyl)-2-amino-5-cyanophenyl) trifluoroborate (Table 1, entry 12)



In a glovebox, a solution of 15 μL (0.1 mmol) HBPin and 6.6 mg (0.01 mmol) $[Ir(OMe)COD]_2$ in minimal MTBE was added to 5.3 mg (0.02 mmol) dtbpy. The solution was subsequently transferred to an air free equipped with a stir bar, 52 mg (0.2 mmol) B_2Pin_2 and 327 mg (1.5 mmol) *N*-(*tert*-butoxycarbonyl)-4-aminobenzonitrile in MTBE. The entire procedure was conducted using 2.0 mL MTBE. The reaction proceeded at 50 °C under N_2 for 36 hours. Isolation involved transferring the solution to a 20 mL scintillation vial, rinsing the air free flask with dichloromethane and removing all volatiles in vacuo. This recovered solid was washed with copious amounts of cyclohexane and concentrated. Cyclohexane was found to best solubalize **T1.11** in the presence of *N*-(*tert*-butoxycarbonyl)-4-aminobenzonitrile when compared to room temperature and –78 °C hexanes, pentane and cyclopentane. The residual white solid, containing a mixture of starting material and borylated product, was treated with 136 mg (1.7 mmol) KHF_2 in 350 μL THF and 210 μL water for 10 min. After all volatiles were removed in vacuo, the remaining solid was extracted with acetone. Concentrating the solution provided a solid that was washed with hexanes and chloroform to afford 90 mg **T1.12** as a white solid (51% yield, mp > 230 °C).

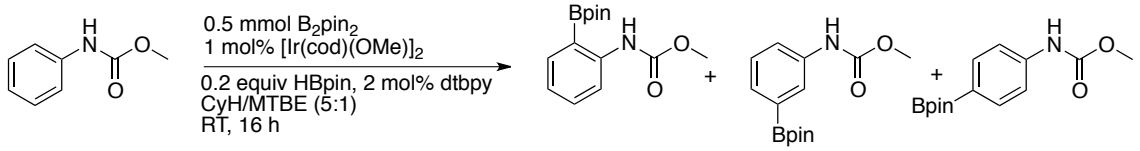
^{1}H NMR (500 MHz, acetone-d_6 = 2.05 ppm): δ 8.44 (bs, 1H), 8.19 (d, ^3J = 8.5 Hz, 1H), 7.66 (d, ^4J = 2.0 Hz, 1H), 7.40 (dd, ^3J = 8.6 Hz, ^4J = 2.2 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, acetone-d_6 = 206 ppm): δ 153.20, 146.76, 136.87, 130.93, 120.90, 116.79, 104.13, 79.76, 28.19; ^{11}B NMR (96 MHz, acetone-d_6, $BF_3{\cdot}OEt_2$ = 0 ppm): δ 3.4; ^{19}F NMR (282 MHz, acetone-d_6, $CFCl_3$ = 0 ppm): δ –139.15; FT-IR (thin film): 3393, 3020, 2985, 2935, 2229, 1724, 1581, 1517, 1392, 1366, 1312, 1245, 1212, 1156, 1119, 1052, 1024, 943, 937, 899, 847, 819, 598 cm^{-1}; HRMS calcd. for $C_{12}H_{13}BF_3N_2O_2$ $[M\text{-}K]^-$ 285.1022, found 285.1025.

Borylation of Enamine 20



In a glovebox, a 5 mL Weaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (~ 10.0 mg, 3.0 mol%), d^{t}bpy (8.0 mg, 6.0 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 0.6 equiv) and substrate **20** (~ 109.56 mg, 0.5 mmol). Dry cyclohexane (3 mL, 0.16 M) was added under an inert atmosphere. The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block at 100 ^{o}C. The reaction mixture was stirred for 48 h. After completion (judged by TLC), cyclohexane was removed under reduced pressure and chromatographic separation with silica gel (dichloromethane as eluent) gave 126 mg of **21** (73%) as white solid (mp = 120–121 °C); ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.58 (d, *J* = 10.0 Hz, 1 H), 7.54 (d, *J* = 10.0 Hz, 1 H), 7.39 (d, *J* = 7.1 Hz, 2 H), 7.25 - 7.33 (m, 2 H), 7.18 (d, *J* = 6.8 Hz, 1 H), 1.53 (s, 9 H), 1.35 (s, 12 H); ^{13}C NMR (126 MHz, $CHCl_3$): δ 153.1, 141.8, 128.8, 128.3, 127.8, 125.7, 125.4, 83.8, 81.1, 28.5, 25.1; ^{11}B NMR ($CDCl_3$, 96 MHz): δ 29.9; HRMS (ES^+) calcd. for $C_{19}H_{28}BNO_4$: 346.2190 (M+H). Found: 346.2194.

Borylation of $PhNHCO_2Me$ at room temperature



In a glovebox, a 5 mL Weaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (~ 6.6 mg, 1.0 mol%), HBpin (29.0 µl, 0.2 equiv), d^{t}bpy (5.4 mg, 2.0 mol%), B_2pin_2 (127 mg, 0.5 mmol) and $PhNHCO_2Me$ (151.2 mg, 1.0 mmol). Dry cyclohexane (2.5 mL) and MTBE (0.5 mL) was added under an inert atmosphere. The microreactor was capped with a Teflon pressure cap and placed into an aluminum block at RT for 16 h. The crude reaction mixture was analyzed by GC-FID which suggested that the ratios of *ortho*-, *meta*-, and *para*- isomers were following: *ortho*:*meta*:*para* = 90:5:5.

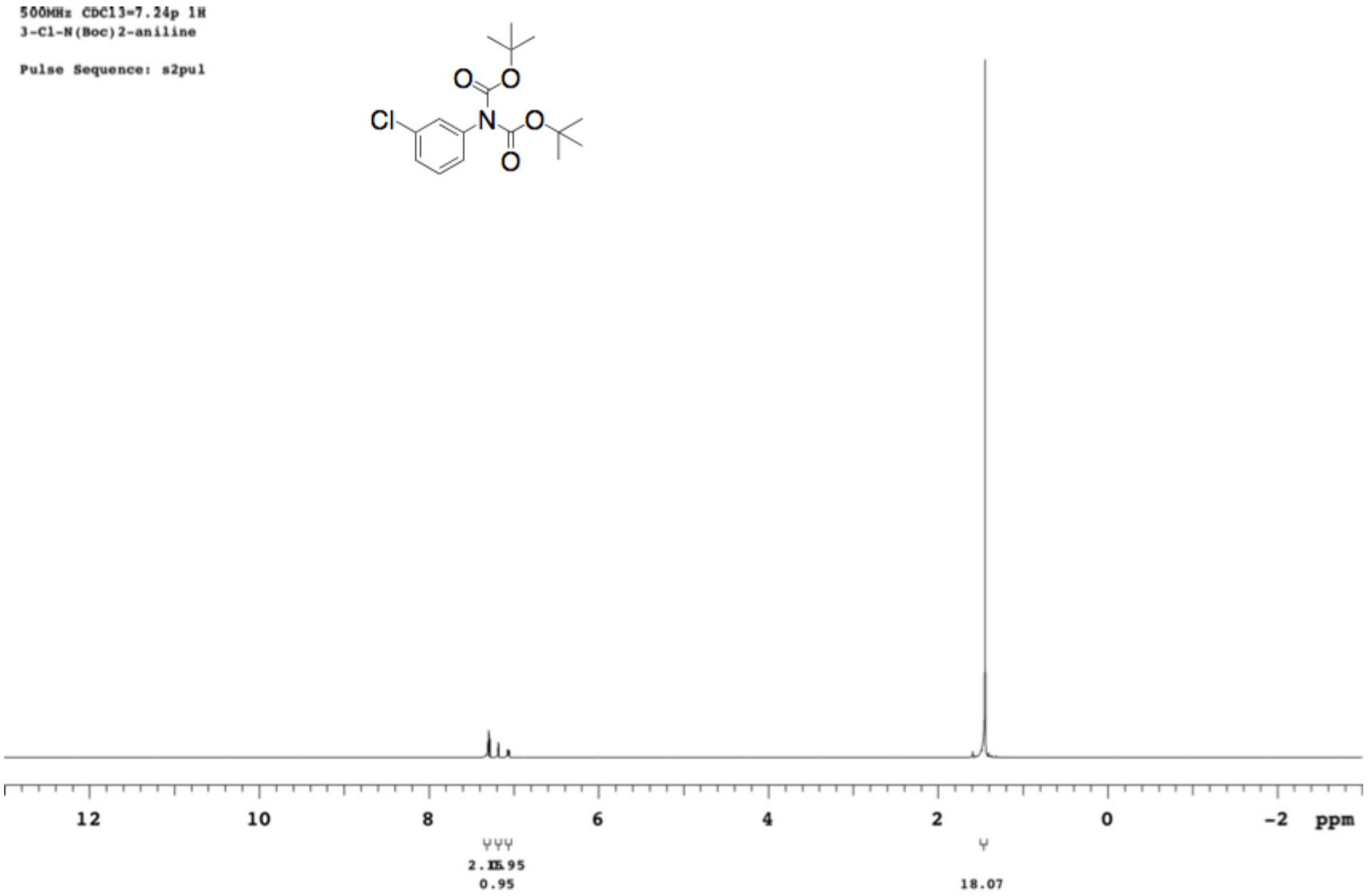


Figure. 500 MHz ^{1}H NMR spectrum of **6**

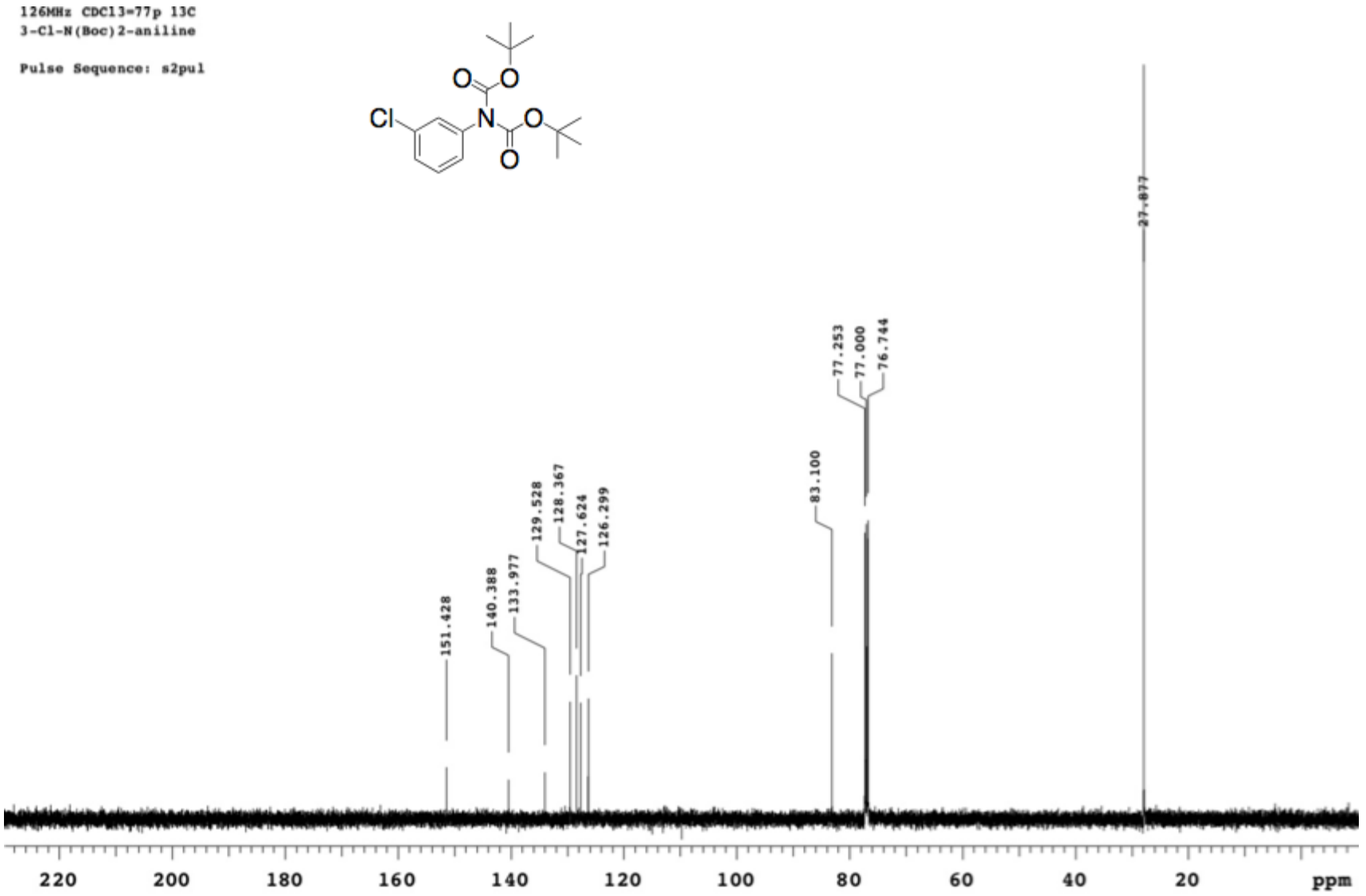


Figure. 126 MHz ^{13}C NMR spectrum of **6**

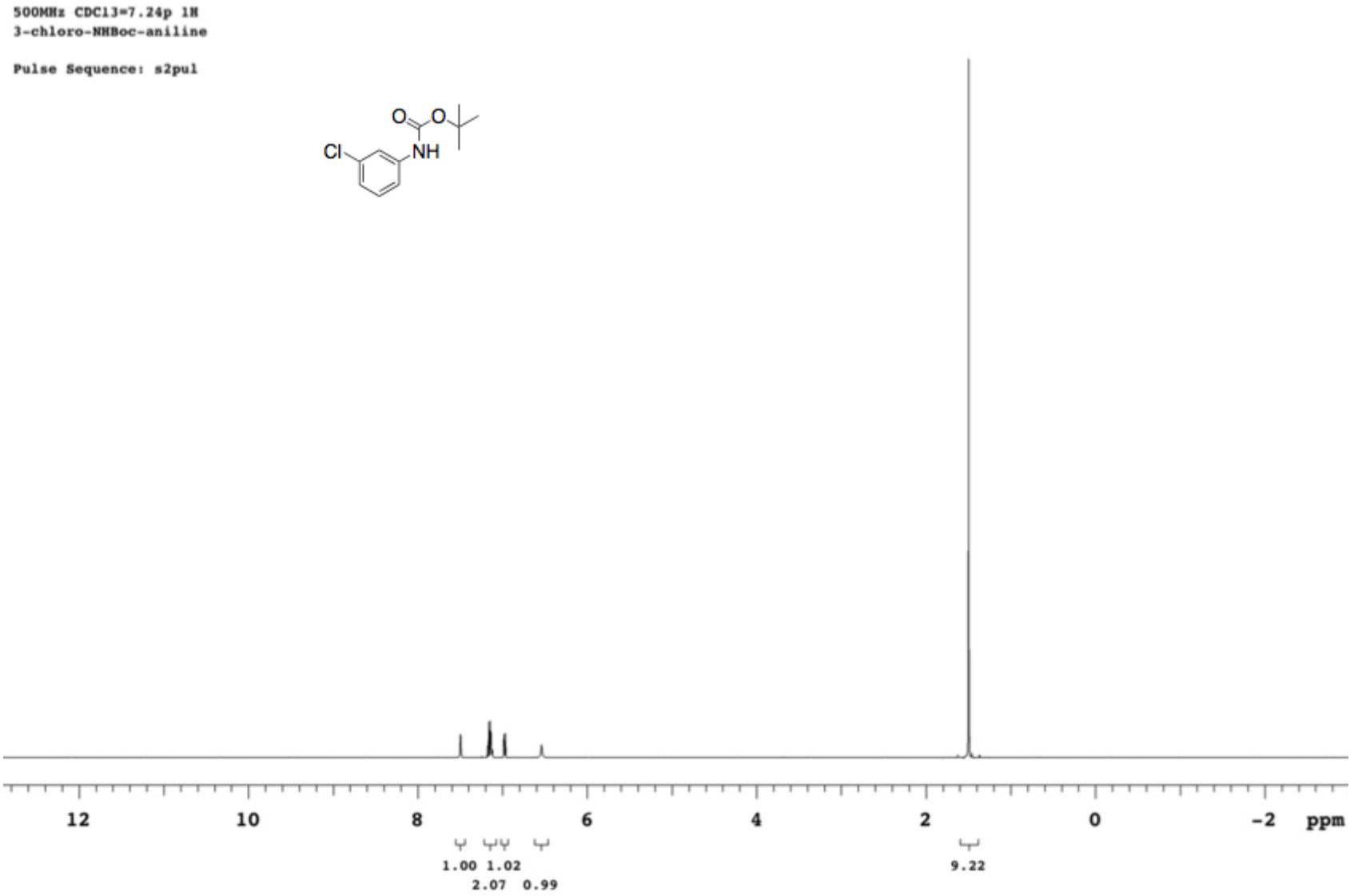


Figure. 500 MHz ^{1}H NMR spectrum of **7**

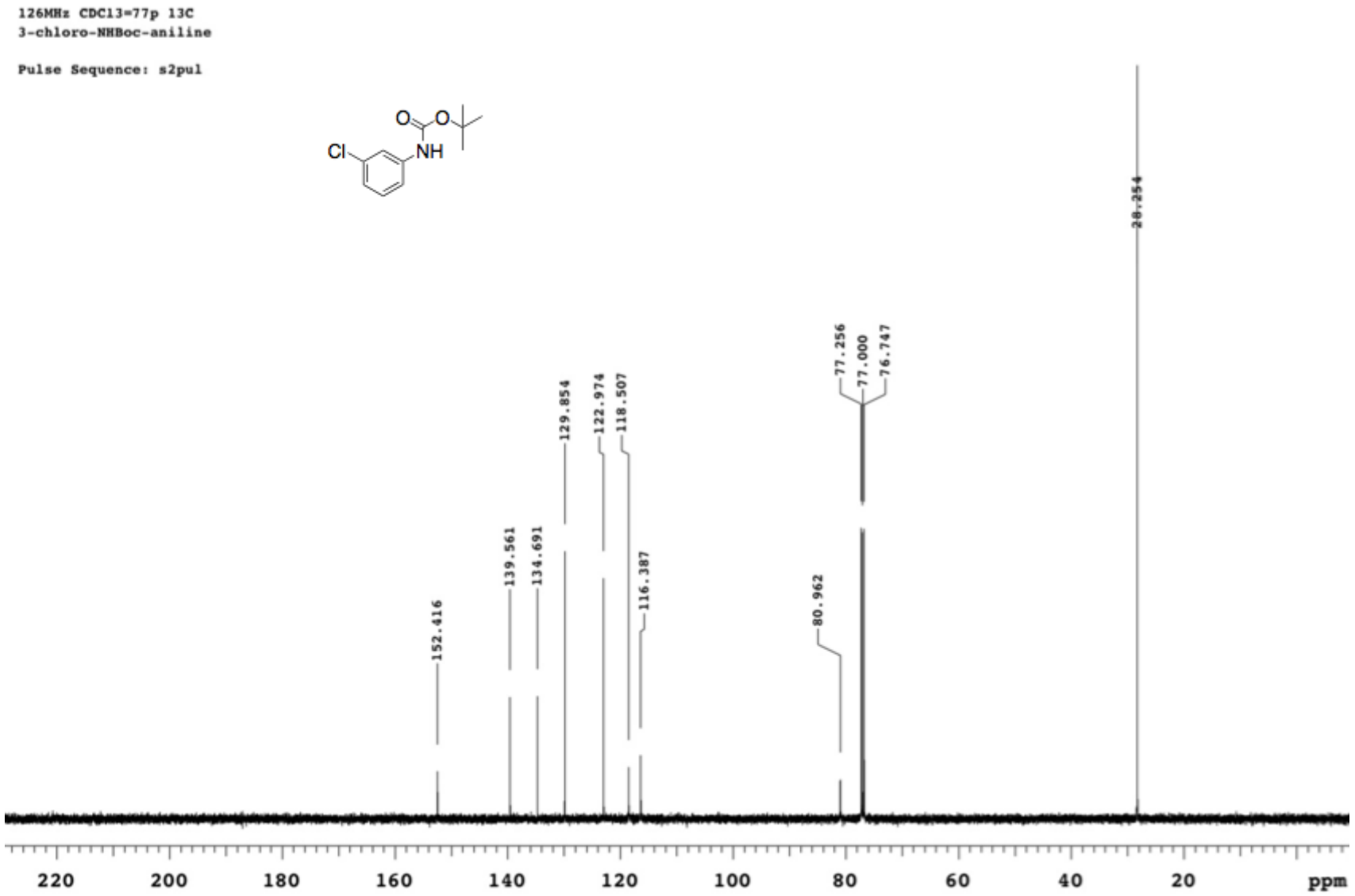
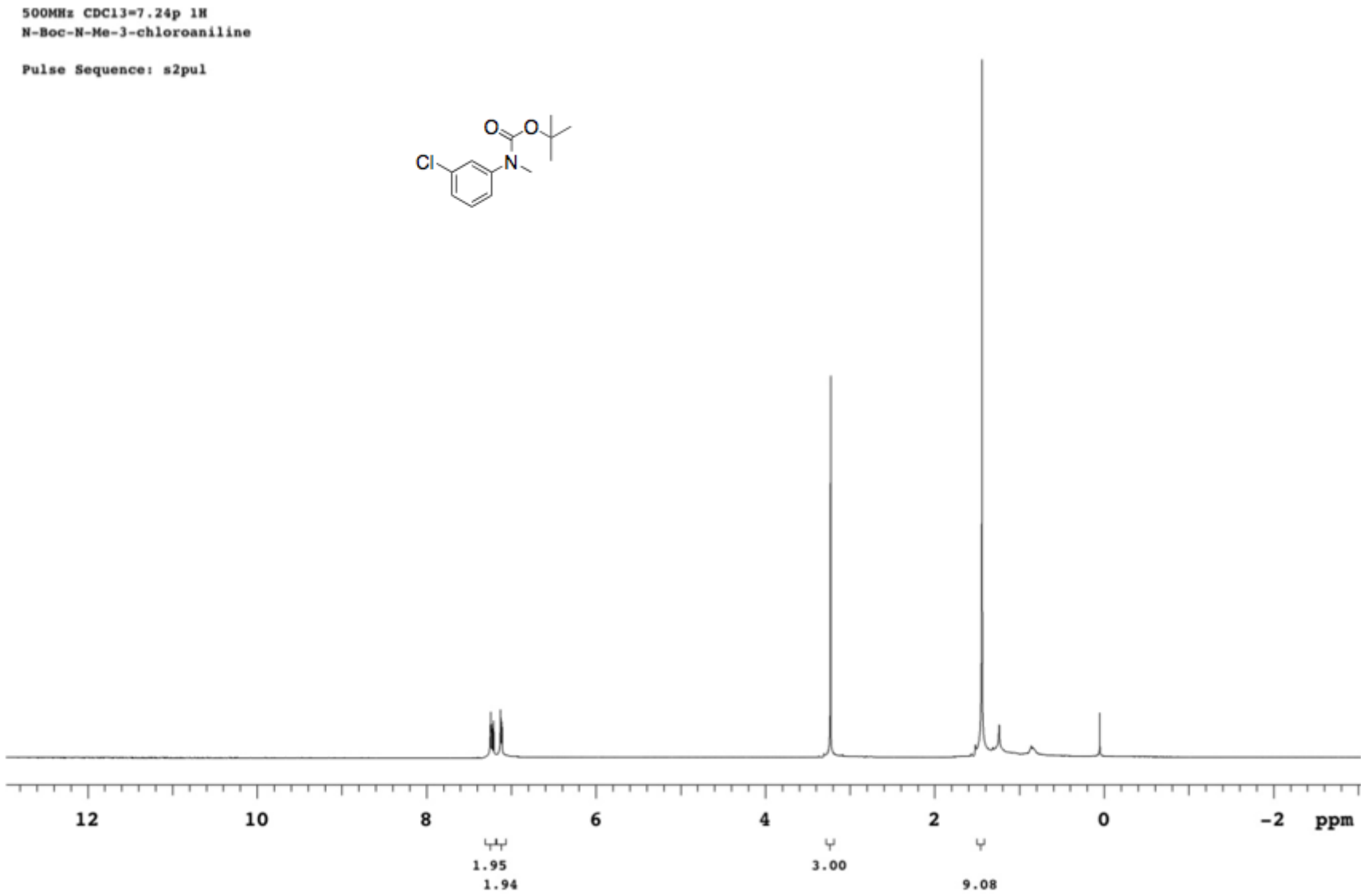


Figure. 126 MHz ^{13}C NMR spectrum of **7**


500MHz CDCl3=7.24p 1H
N-Boc-N-Me-3-chloroaniline
Pulse Sequence: s2pul
O
O
Cl
N
12
10
8
6
4
2
0
-2
ppm
1.95
1.94
3.00
9.08

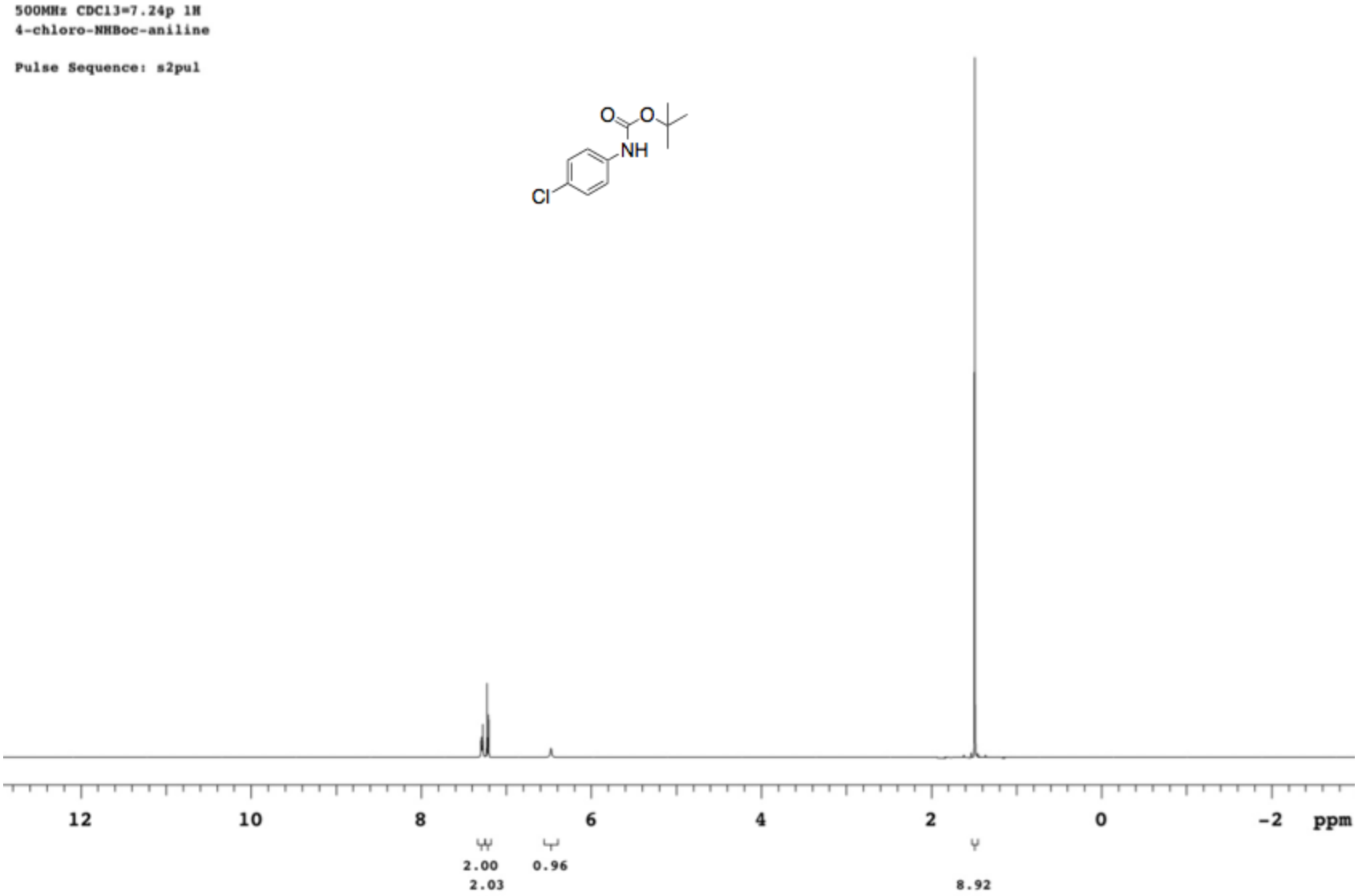


Figure. 500 MHz ^{1}H NMR spectrum

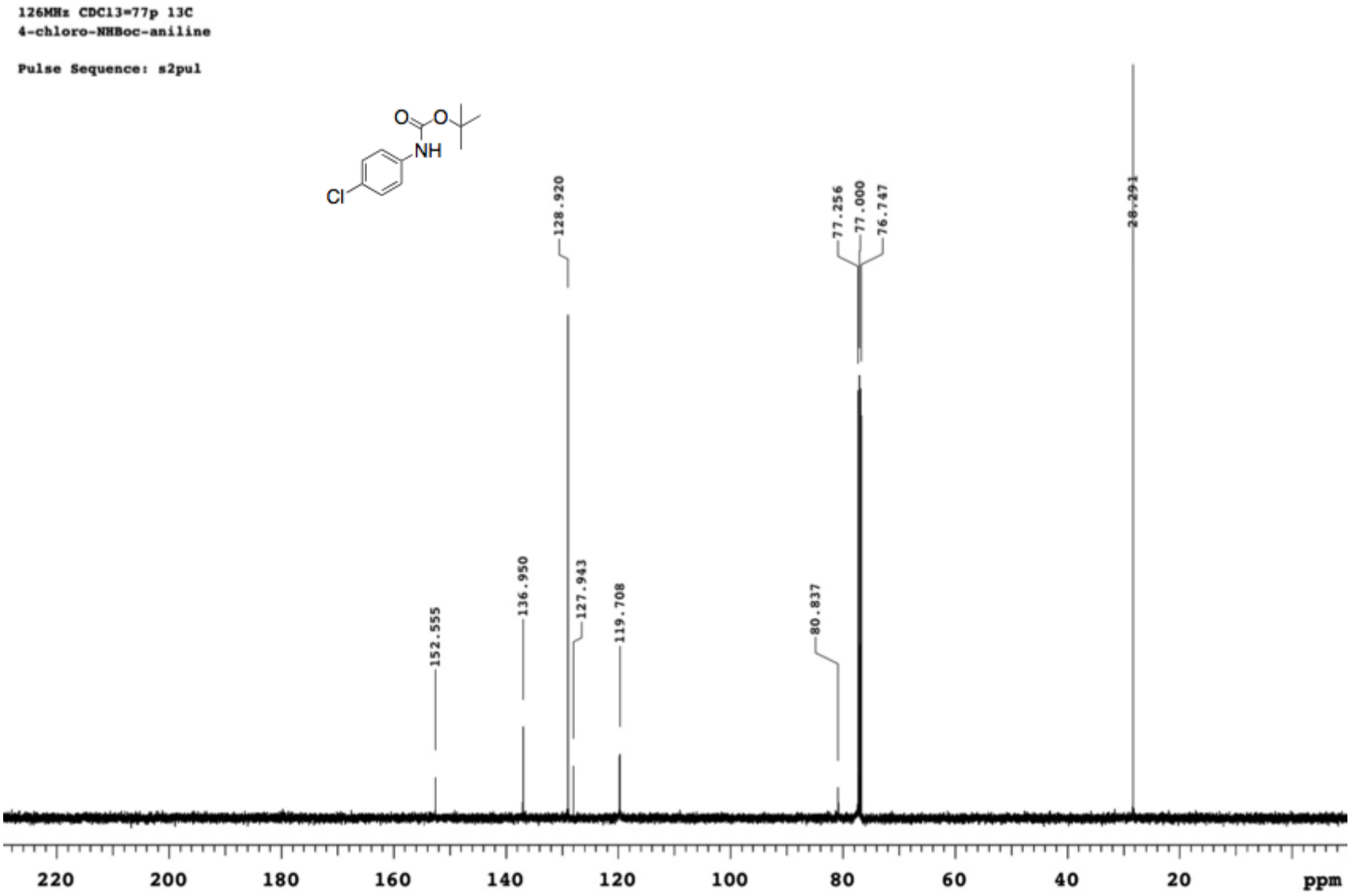


Figure. 126 MHz ^{13}C NMR spectrum

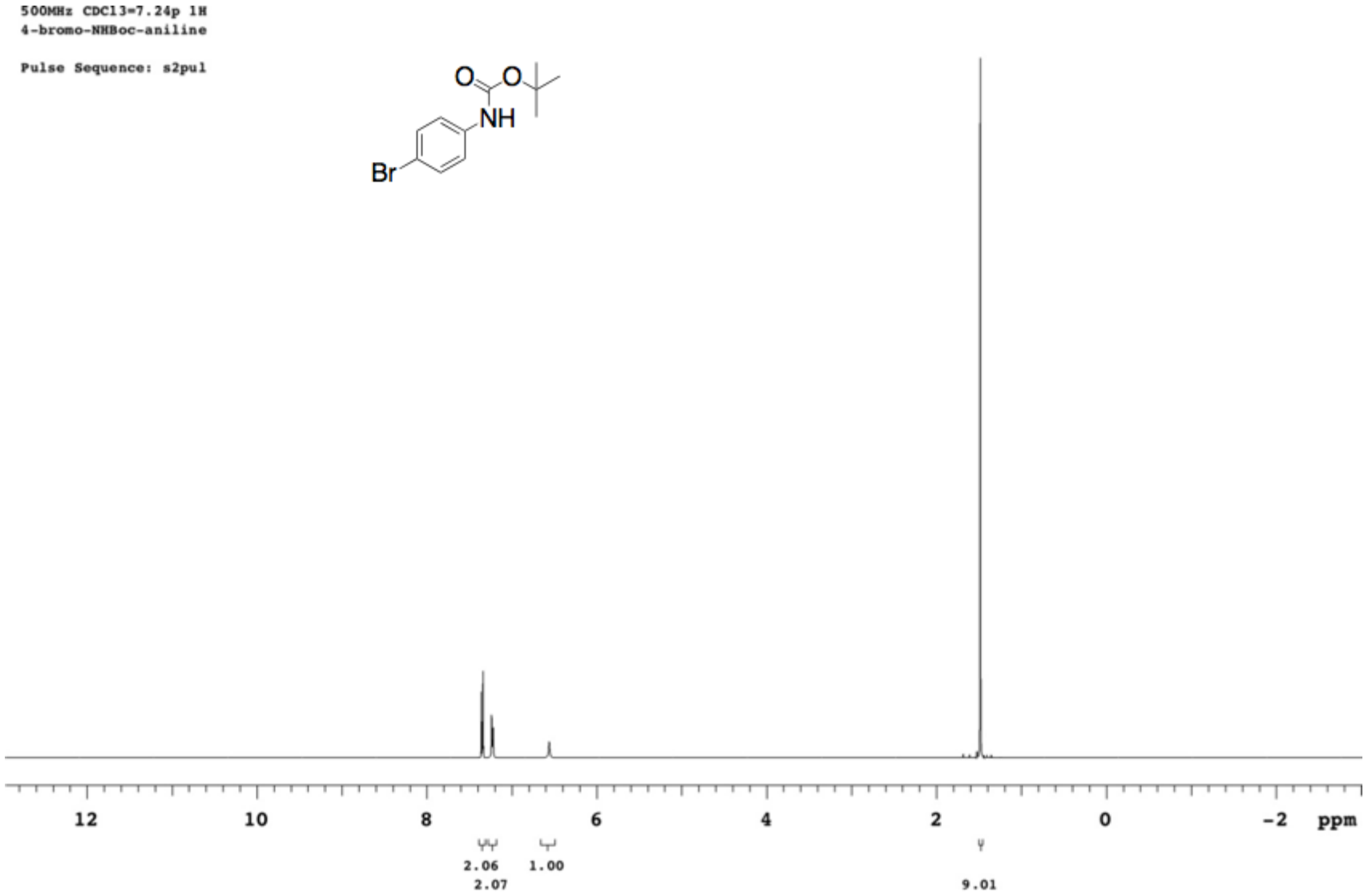


Figure. 500 MHz ^{1}H NMR spectrum

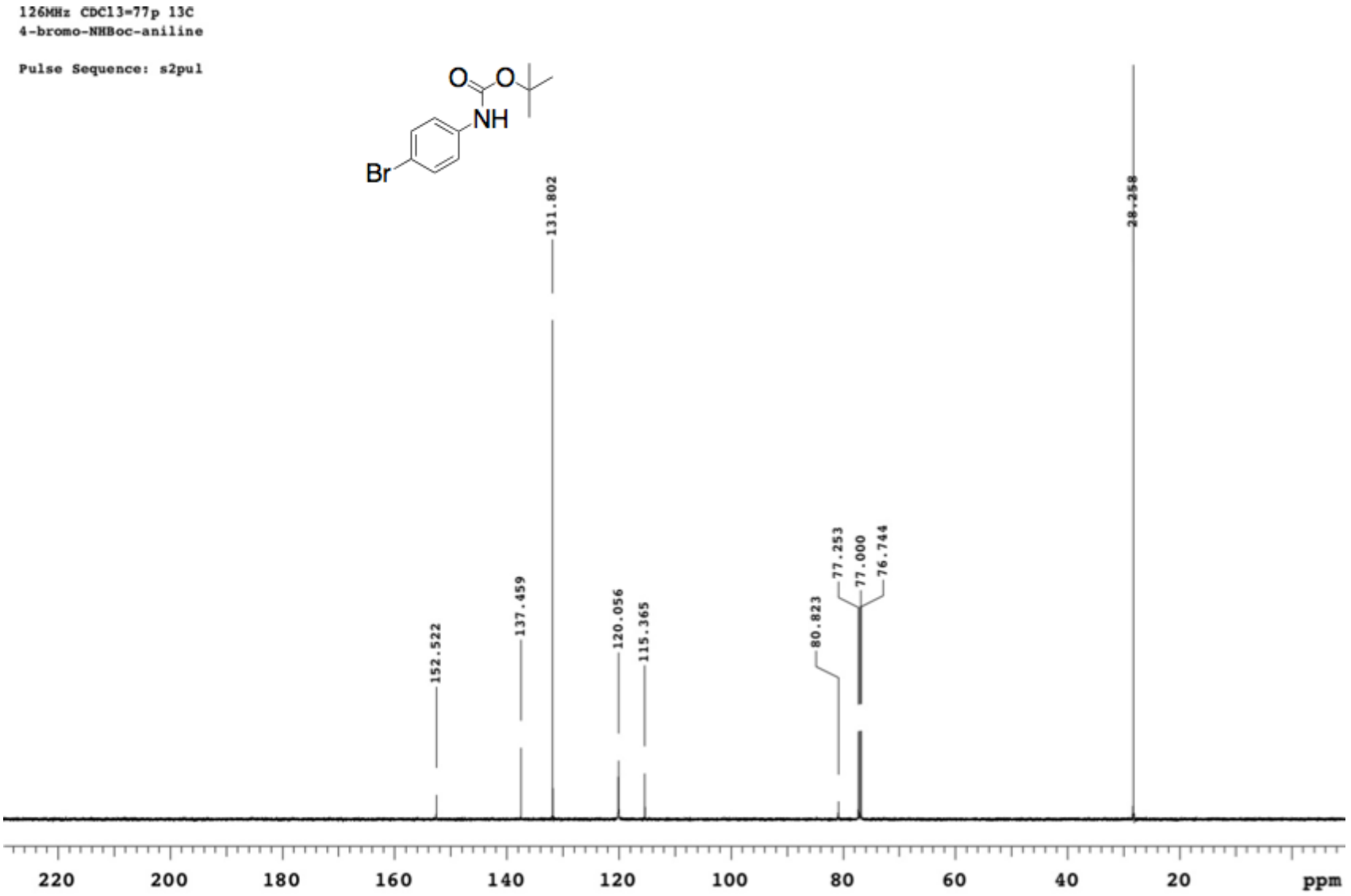


Figure. 126 MHz ^{13}C NMR spectrum

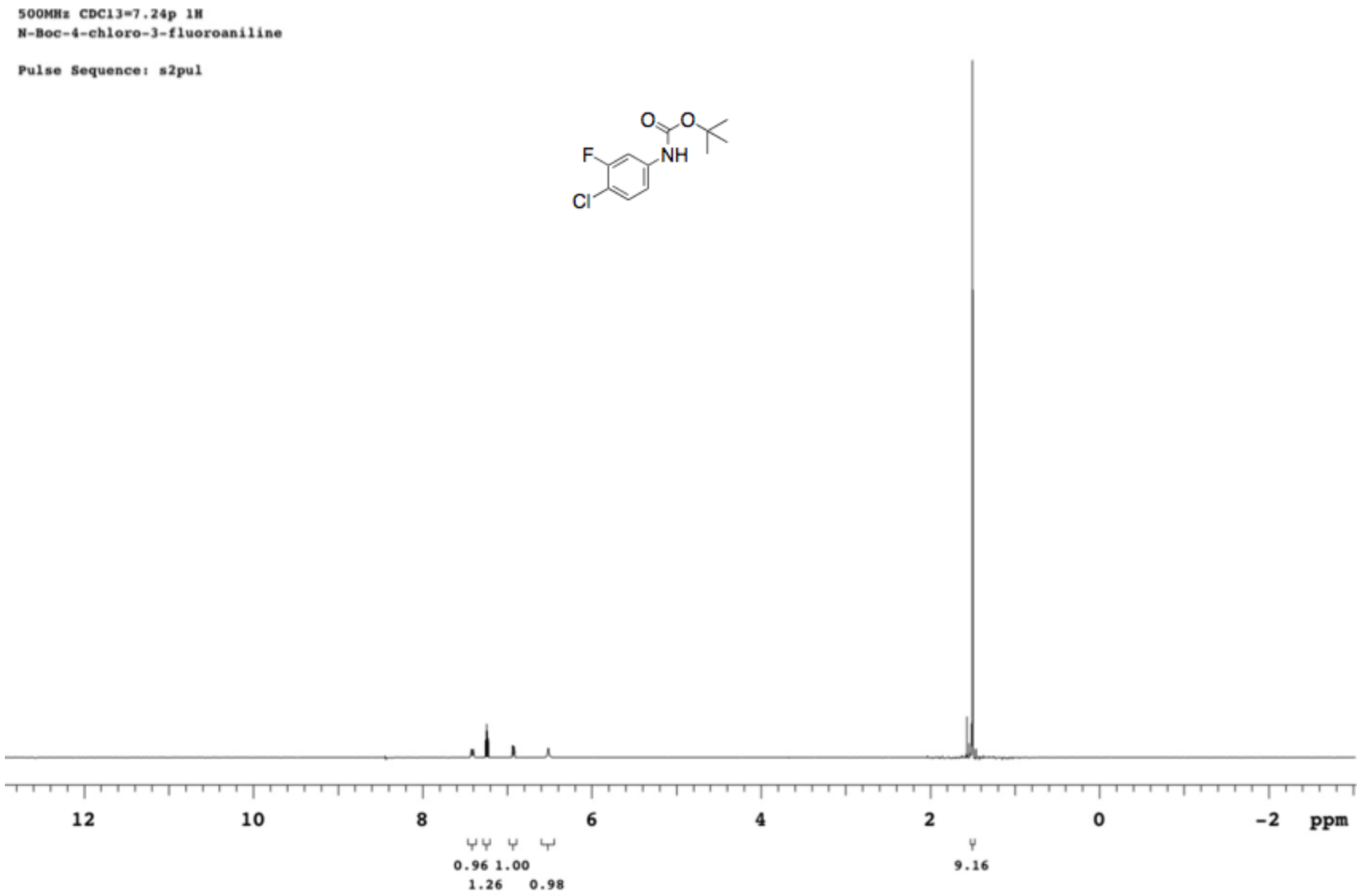


Figure. 500 MHz ^{1}H NMR spectrum

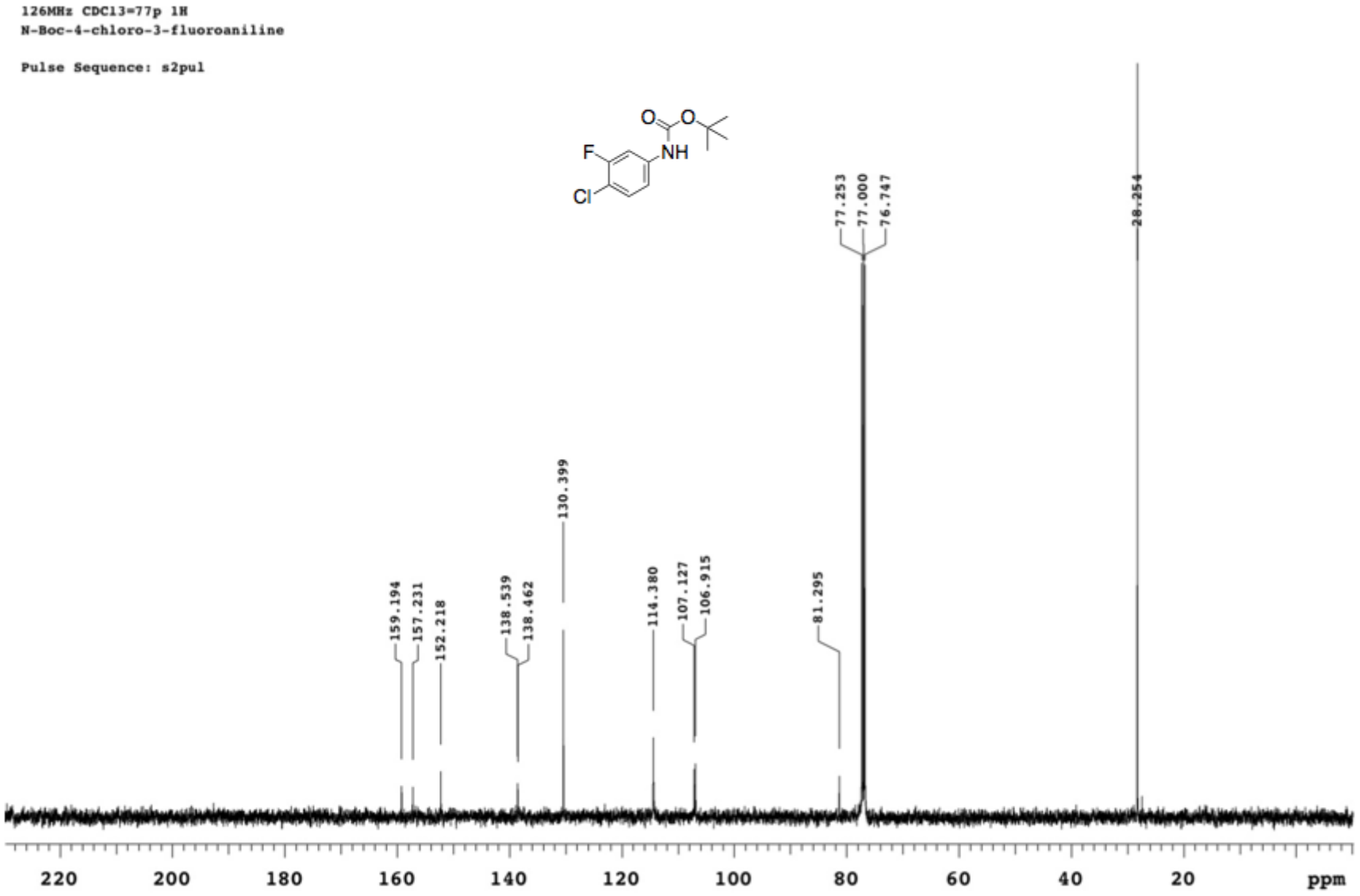


Figure. 126 MHz ^{13}C NMR spectrum

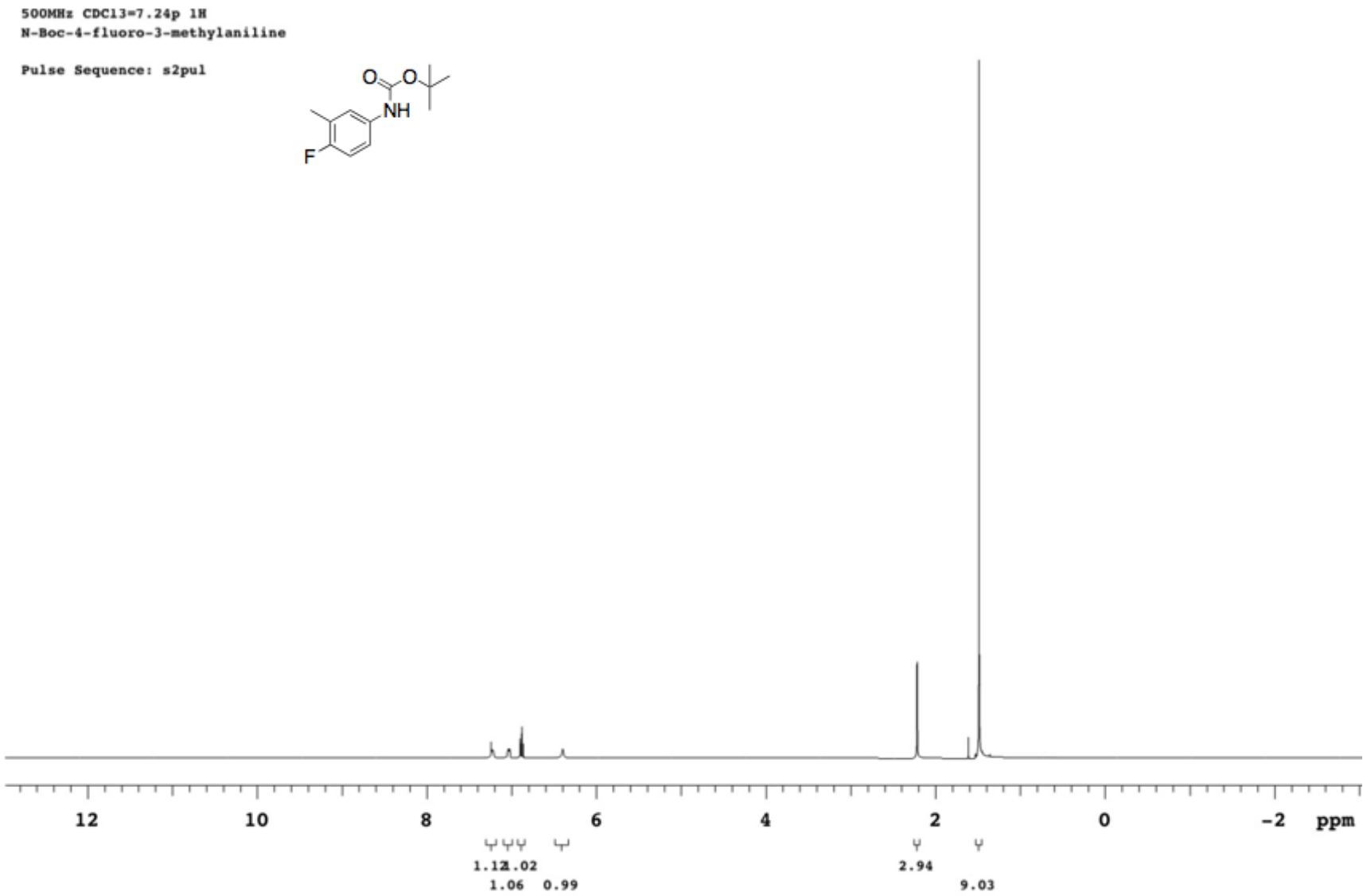


Figure. 500 MHz ^{1}H NMR spectrum

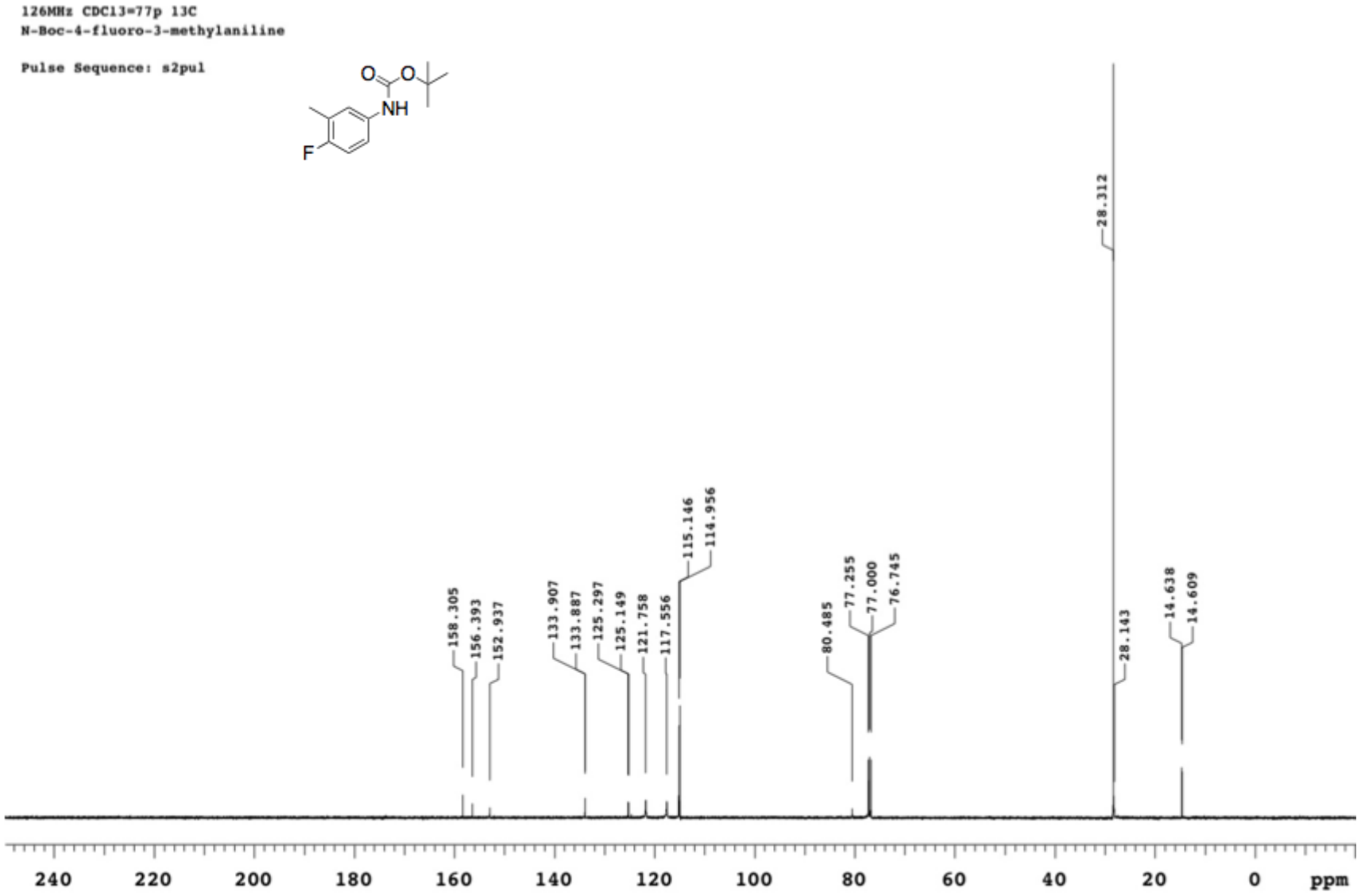


Figure. 126 MHz ^{13}C NMR spectrum

Figure. 500 MHz ^{1}H NMR spectrum of **12a**

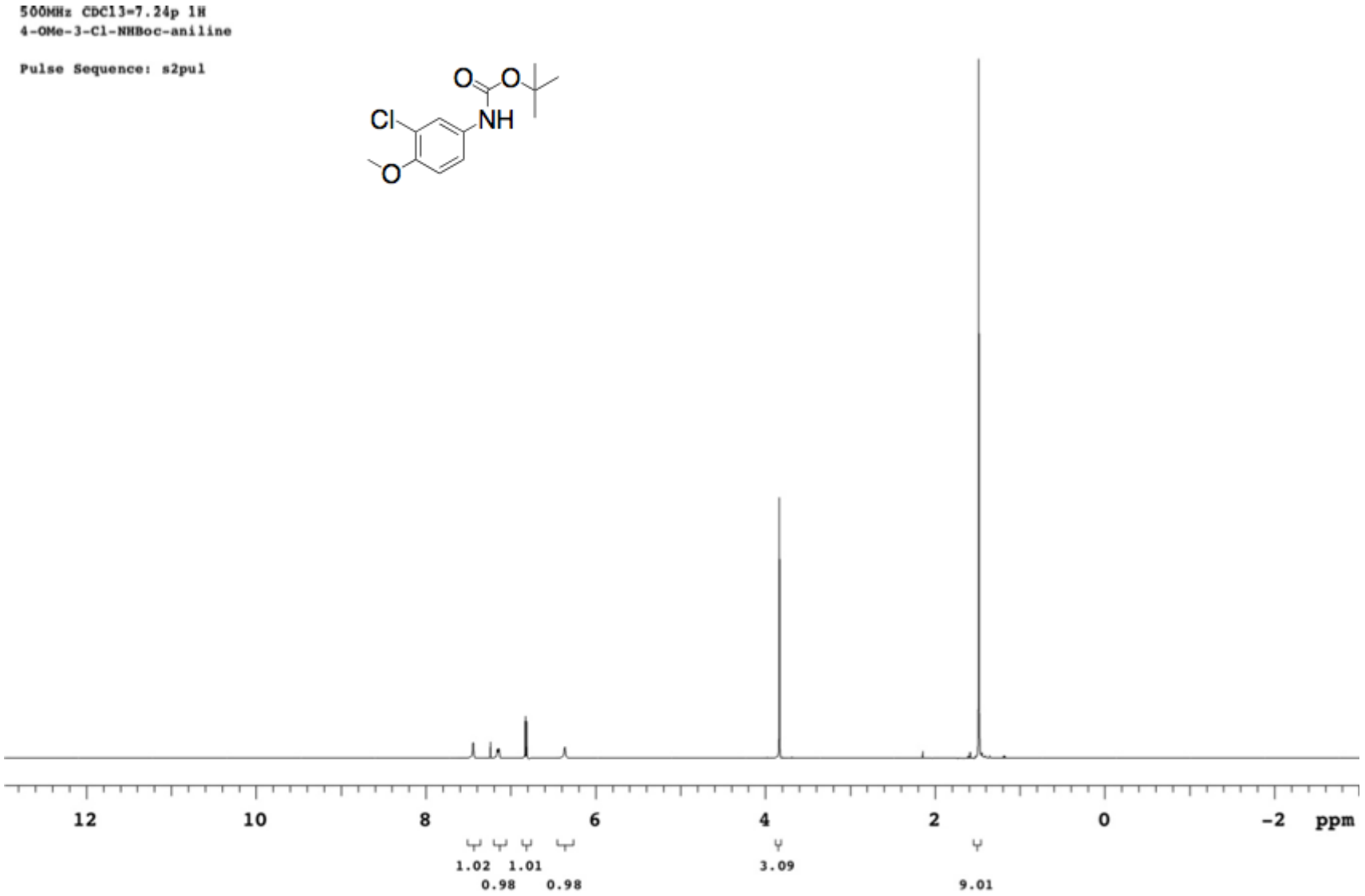


Figure. 500 MHz ^{1}H NMR spectrum

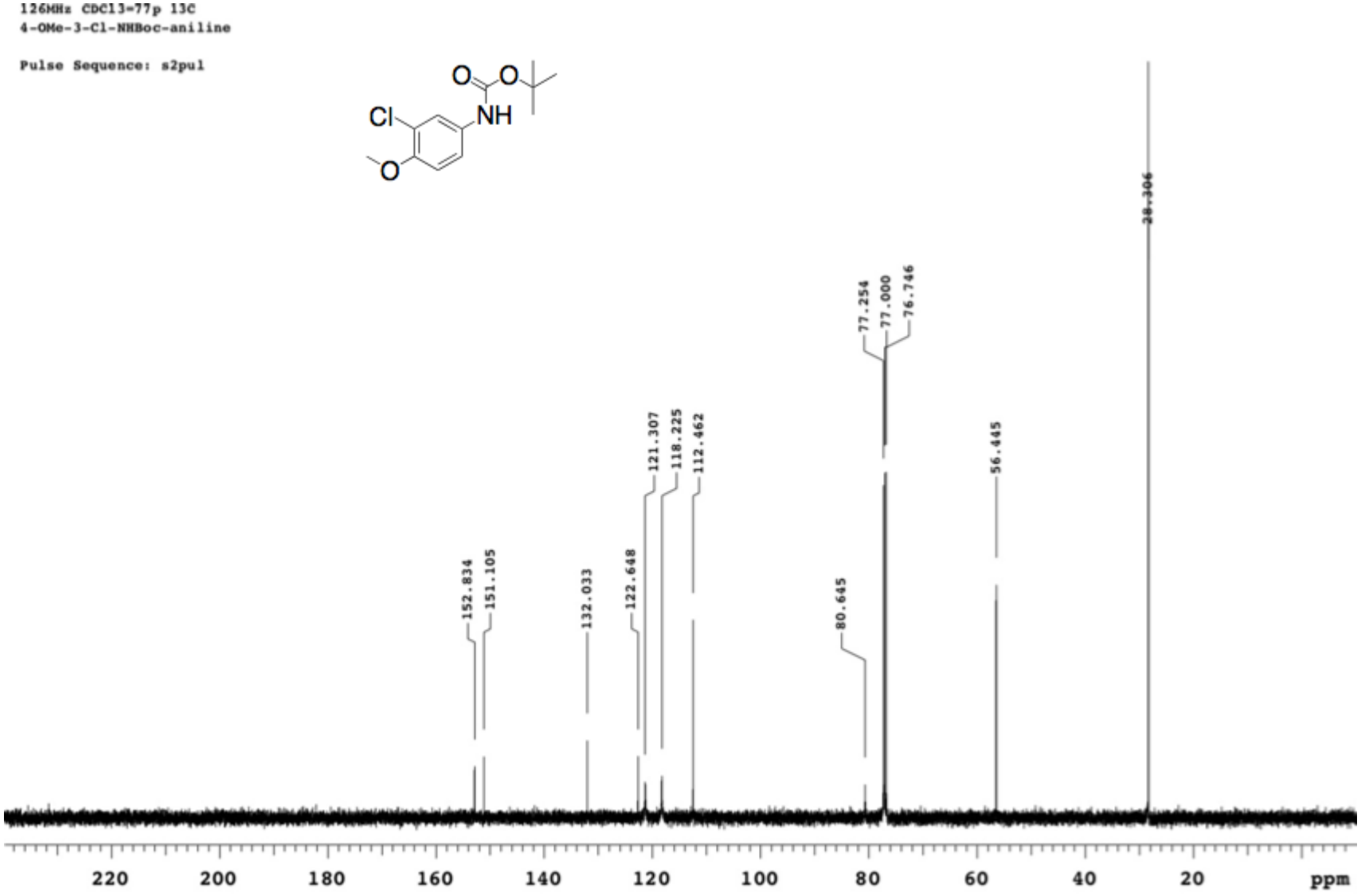


Figure. 126 MHz ^{13}C NMR spectrum

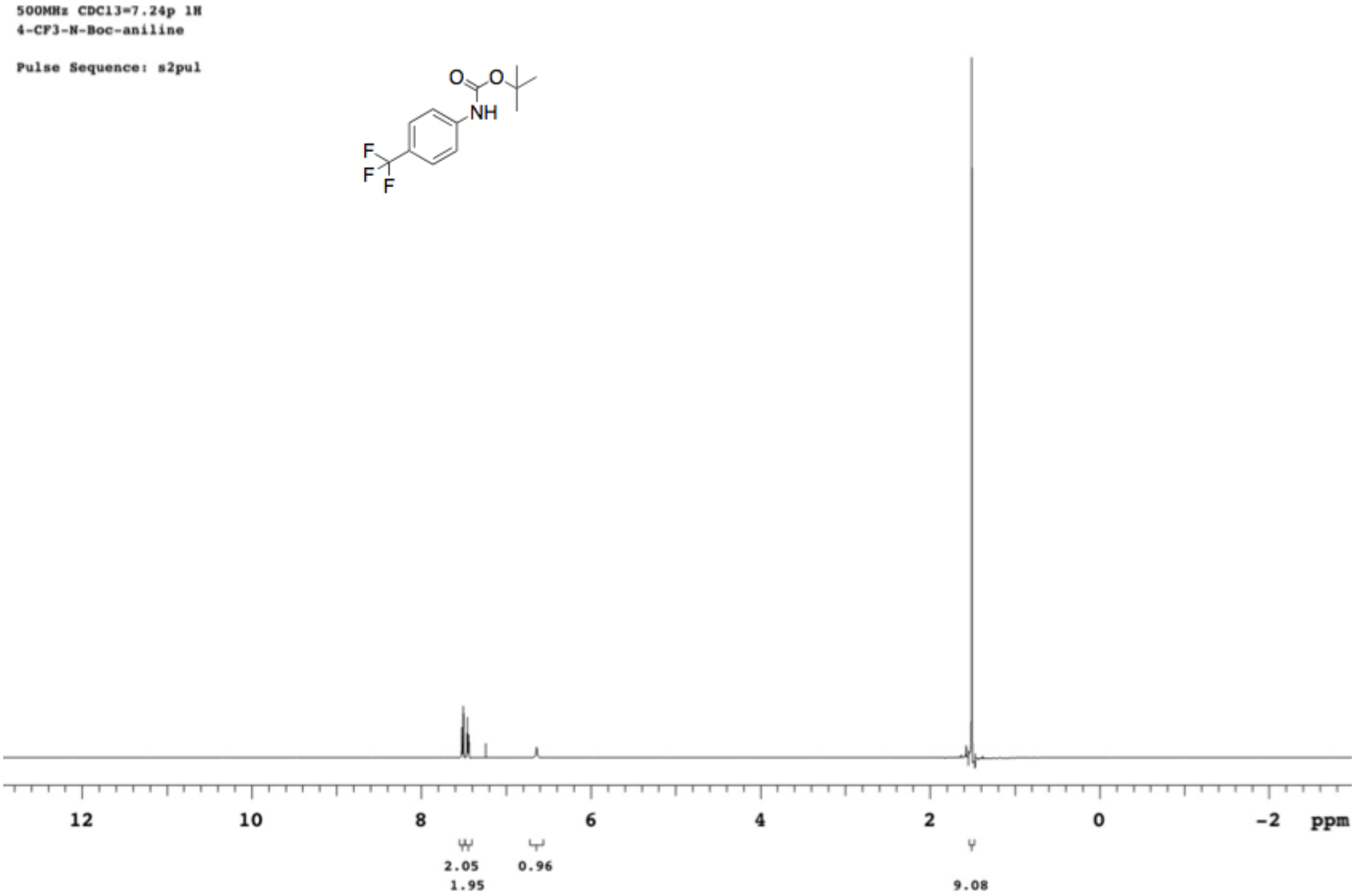


Figure. 500 MHz ^{1}H NMR spectrum

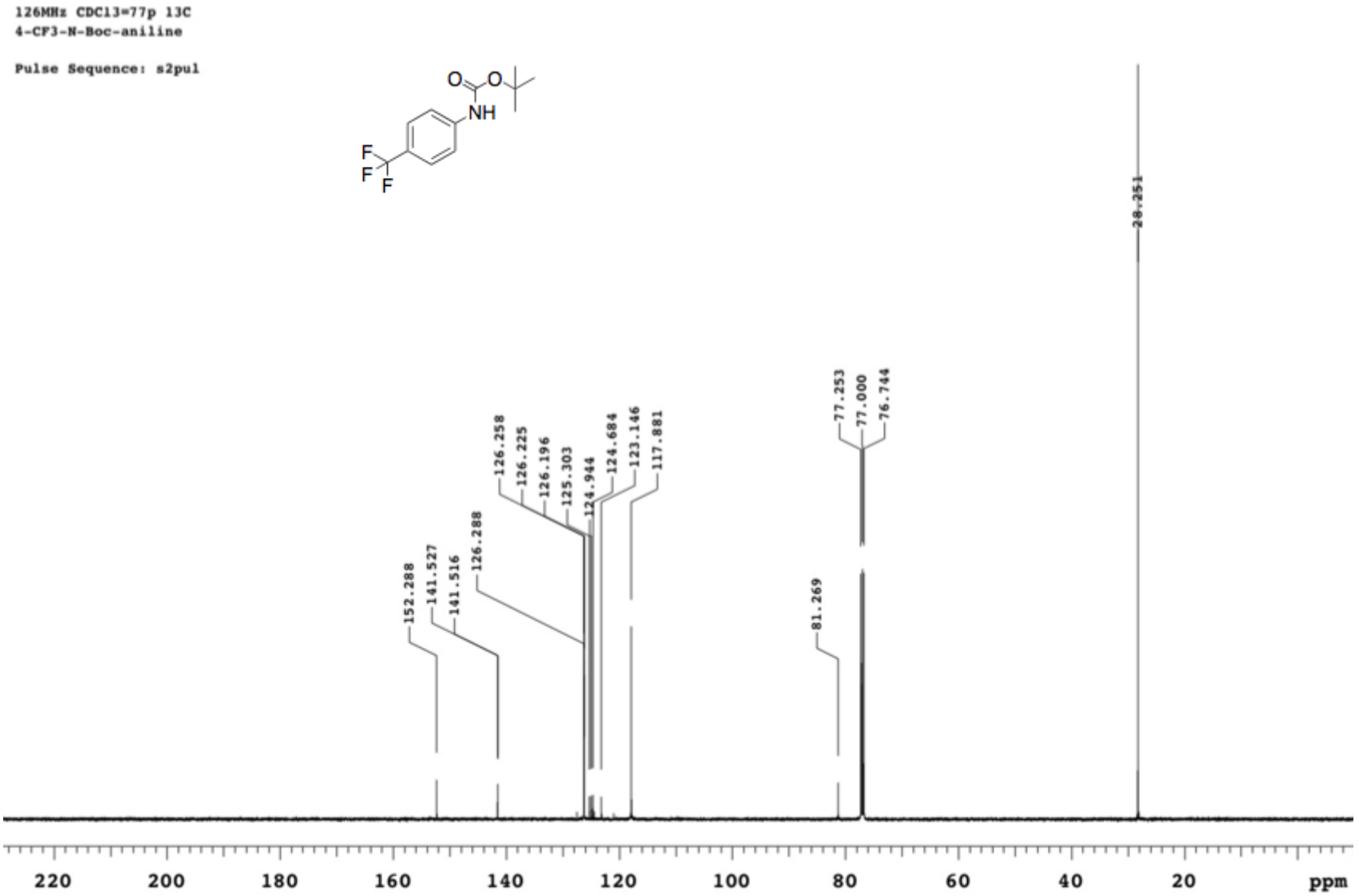


Figure. 126 MHz ^{13}C NMR spectrum

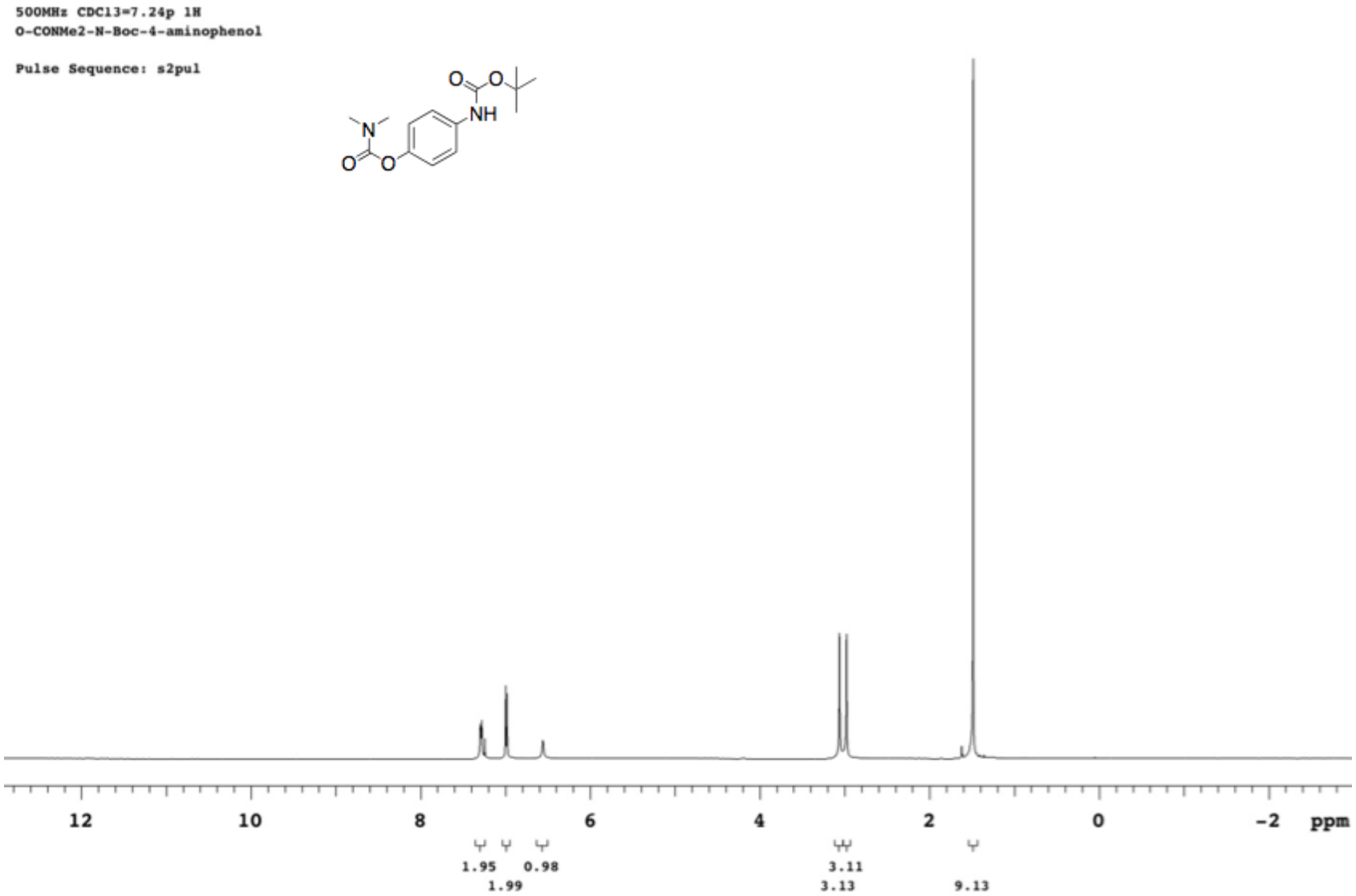


Figure. 500 MHz ^{1}H NMR spectrum

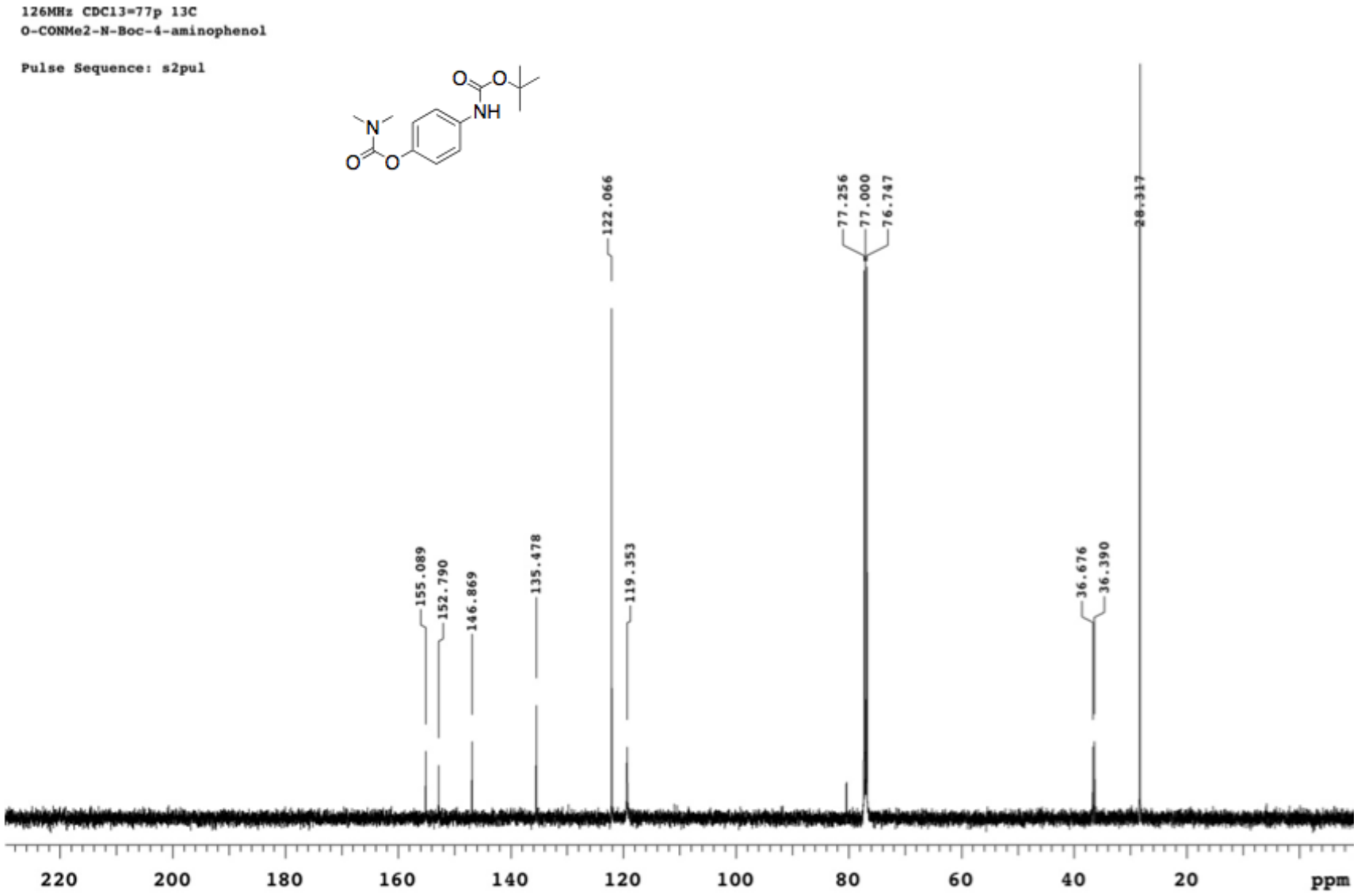


Figure. 126 MHz ^{13}C NMR spectrum

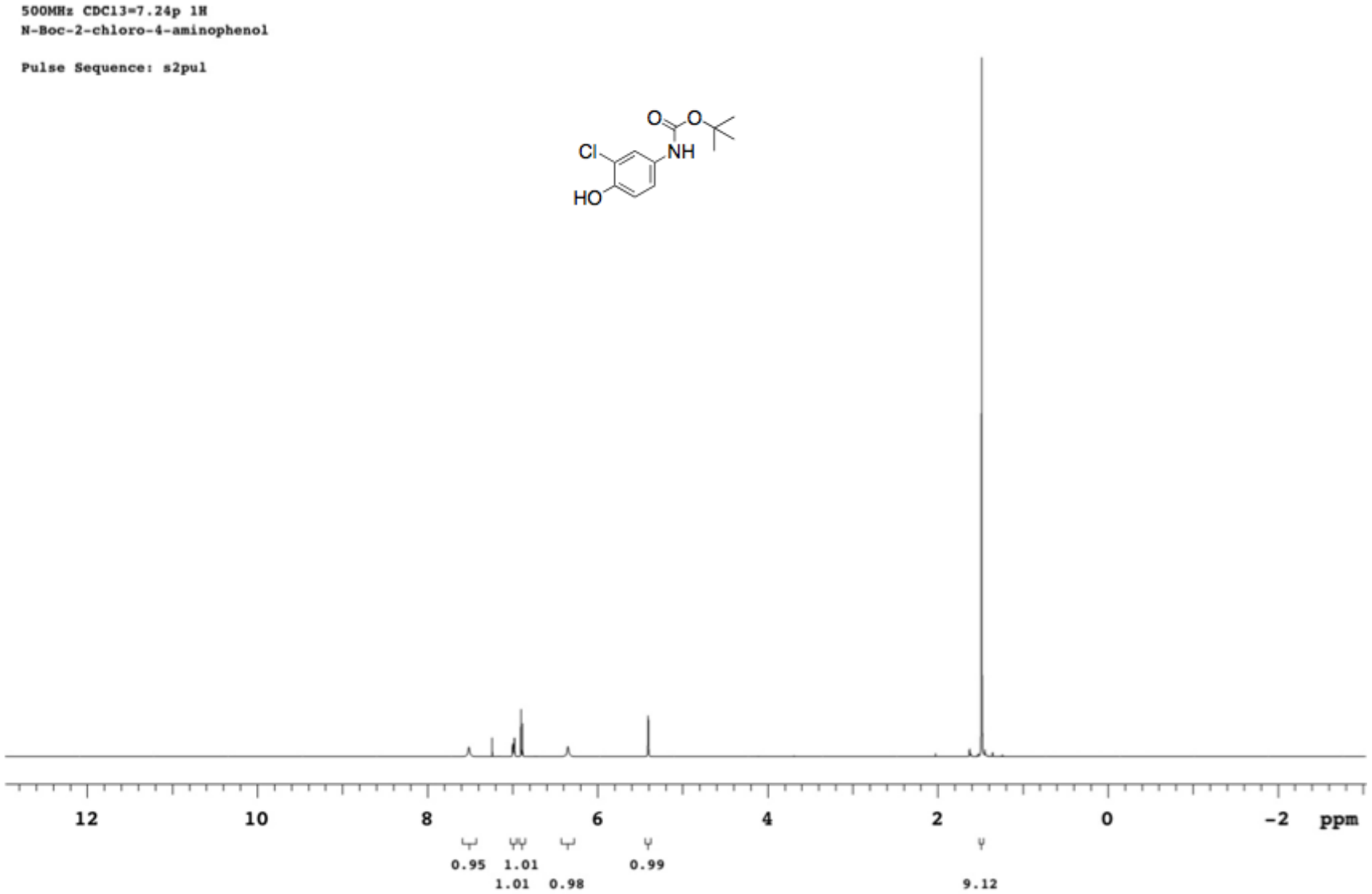


Figure. 500 MHz ^{1}H NMR spectrum

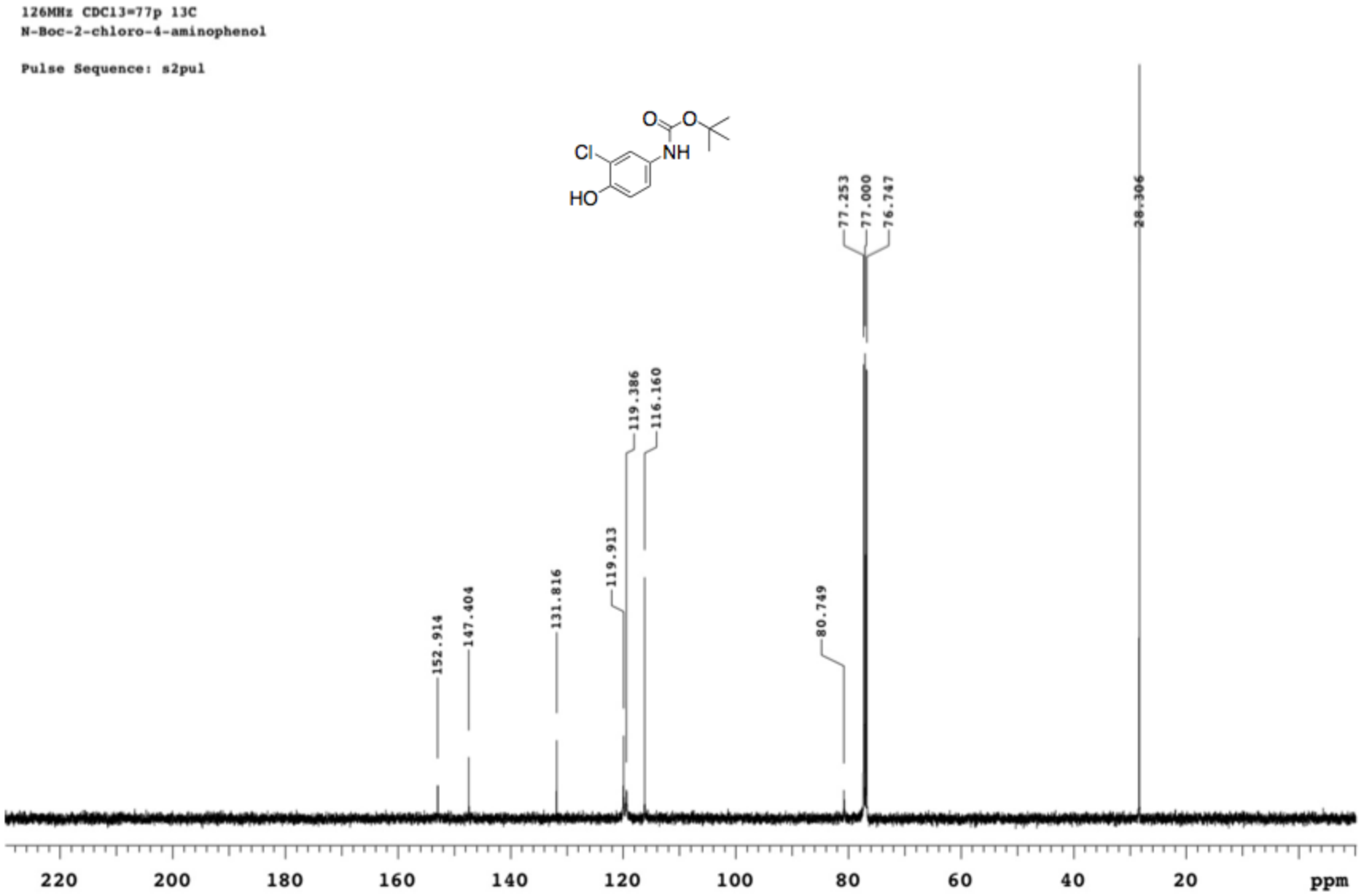


Figure. 126 MHz ^{13}C NMR spectrum

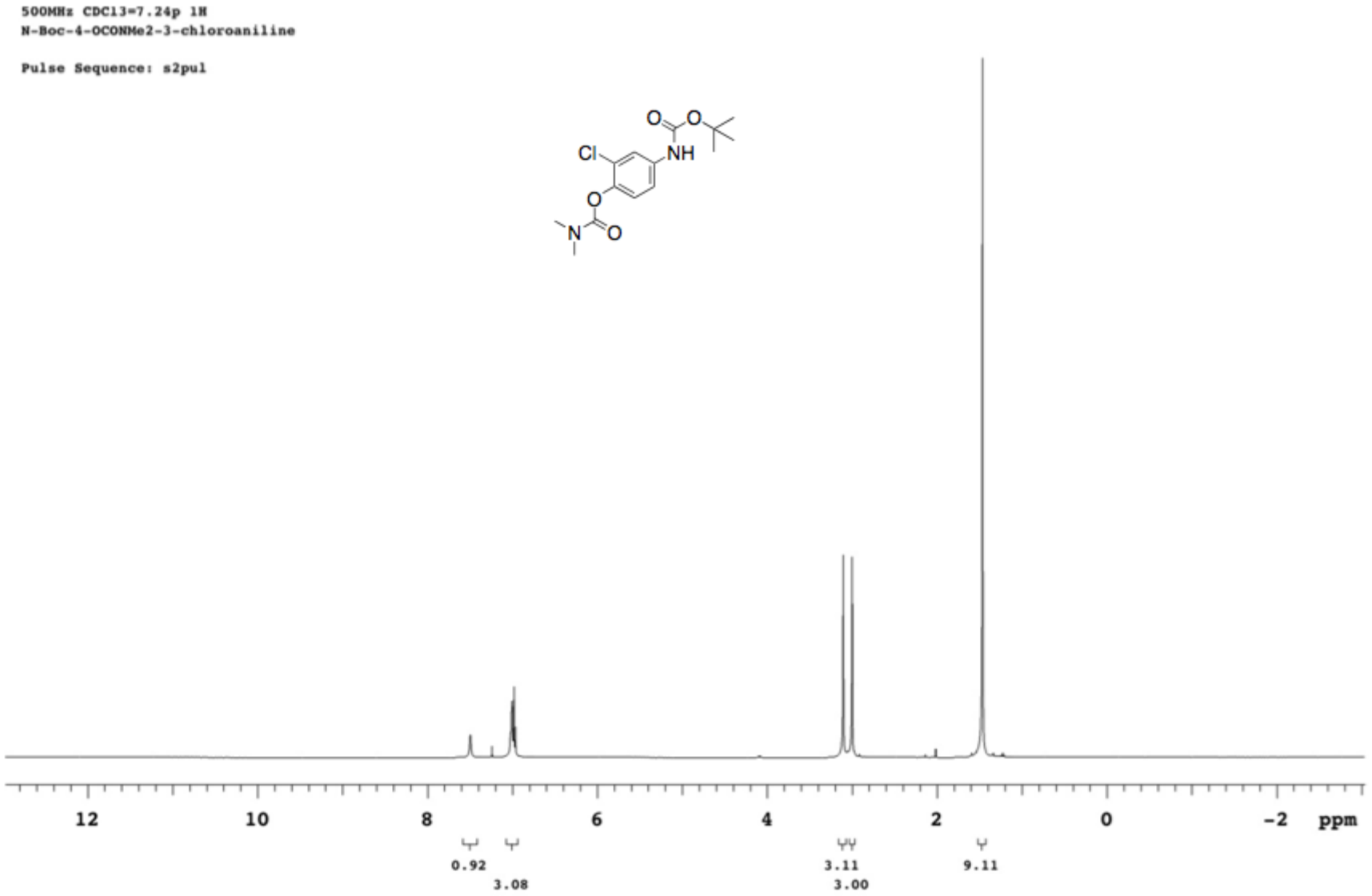


Figure. 500 MHz ^{1}H NMR spectrum

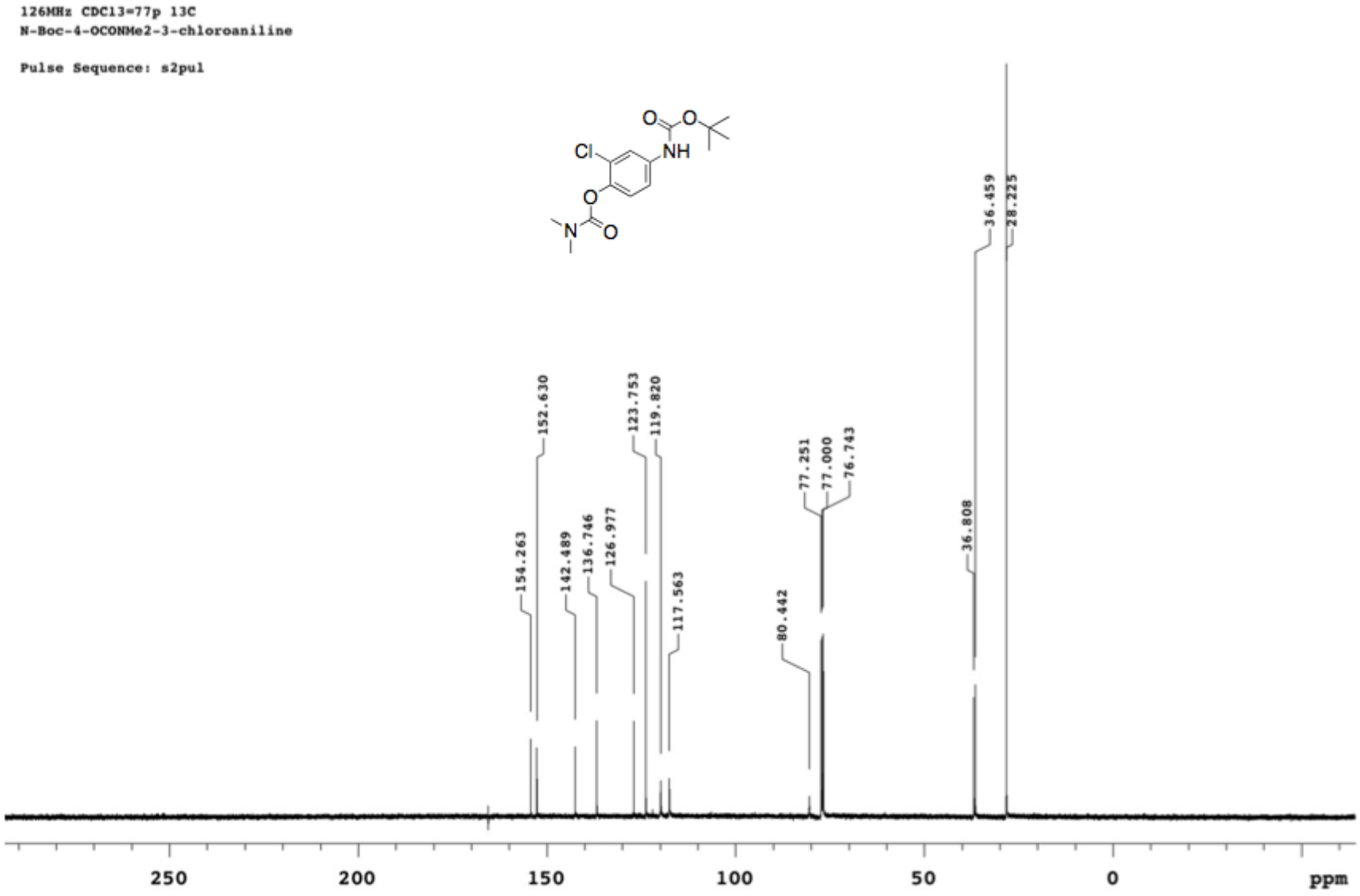


Figure. 126 MHz ^{13}C NMR spectrum

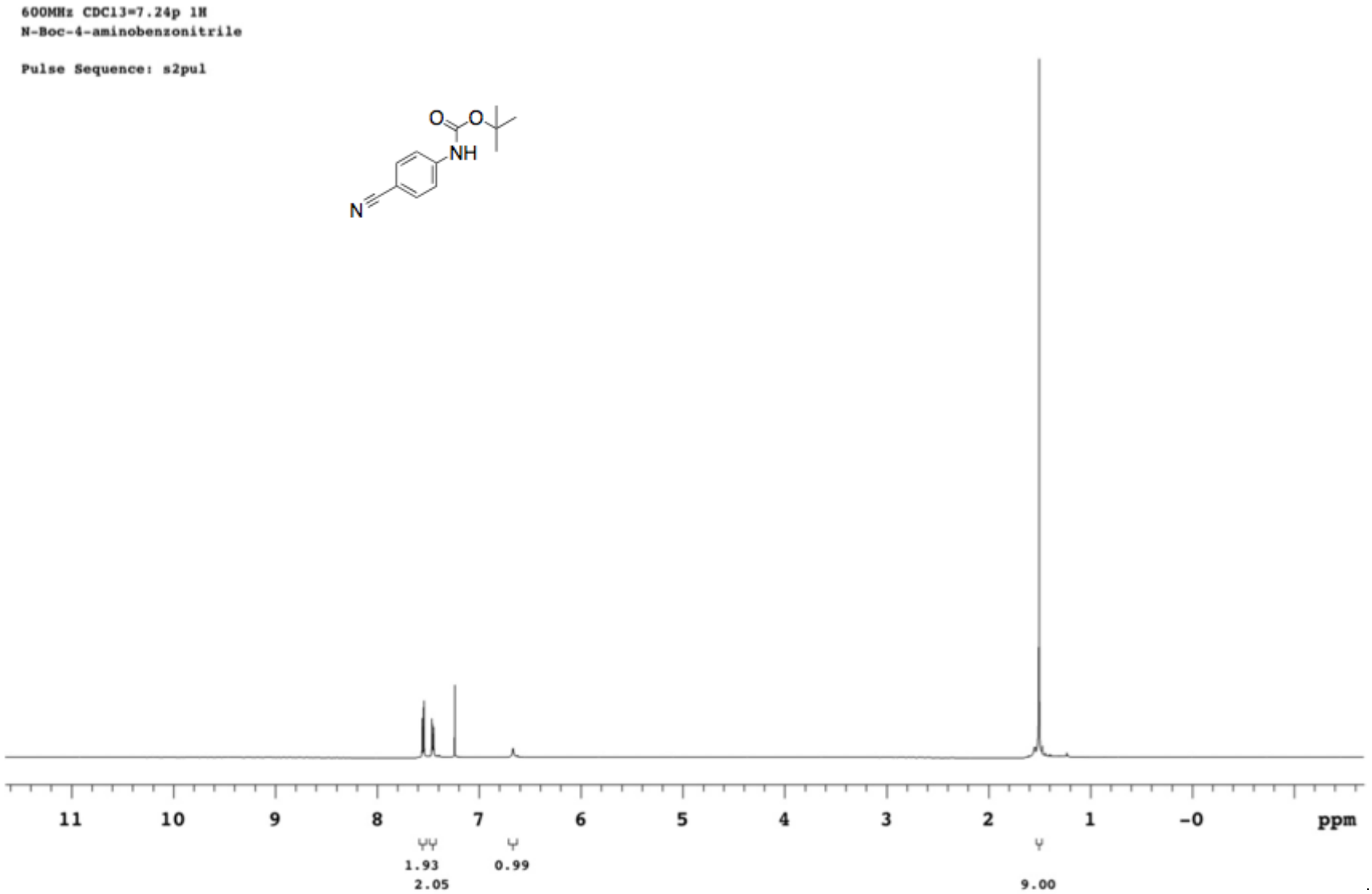


Figure. 600 MHz ^{1}H NMR spectrum

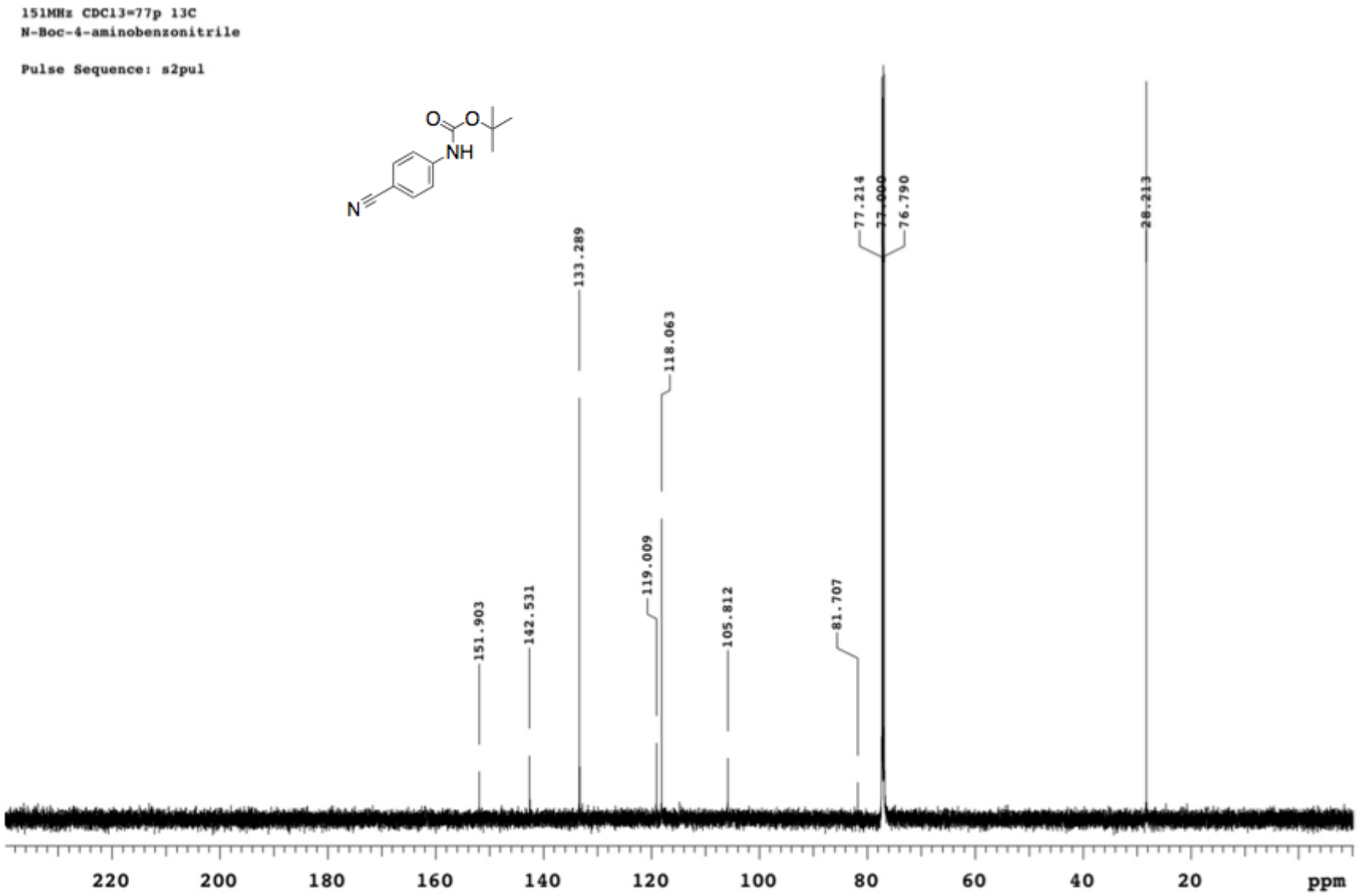


Figure. 151 MHz ^{13}C NMR spectrum

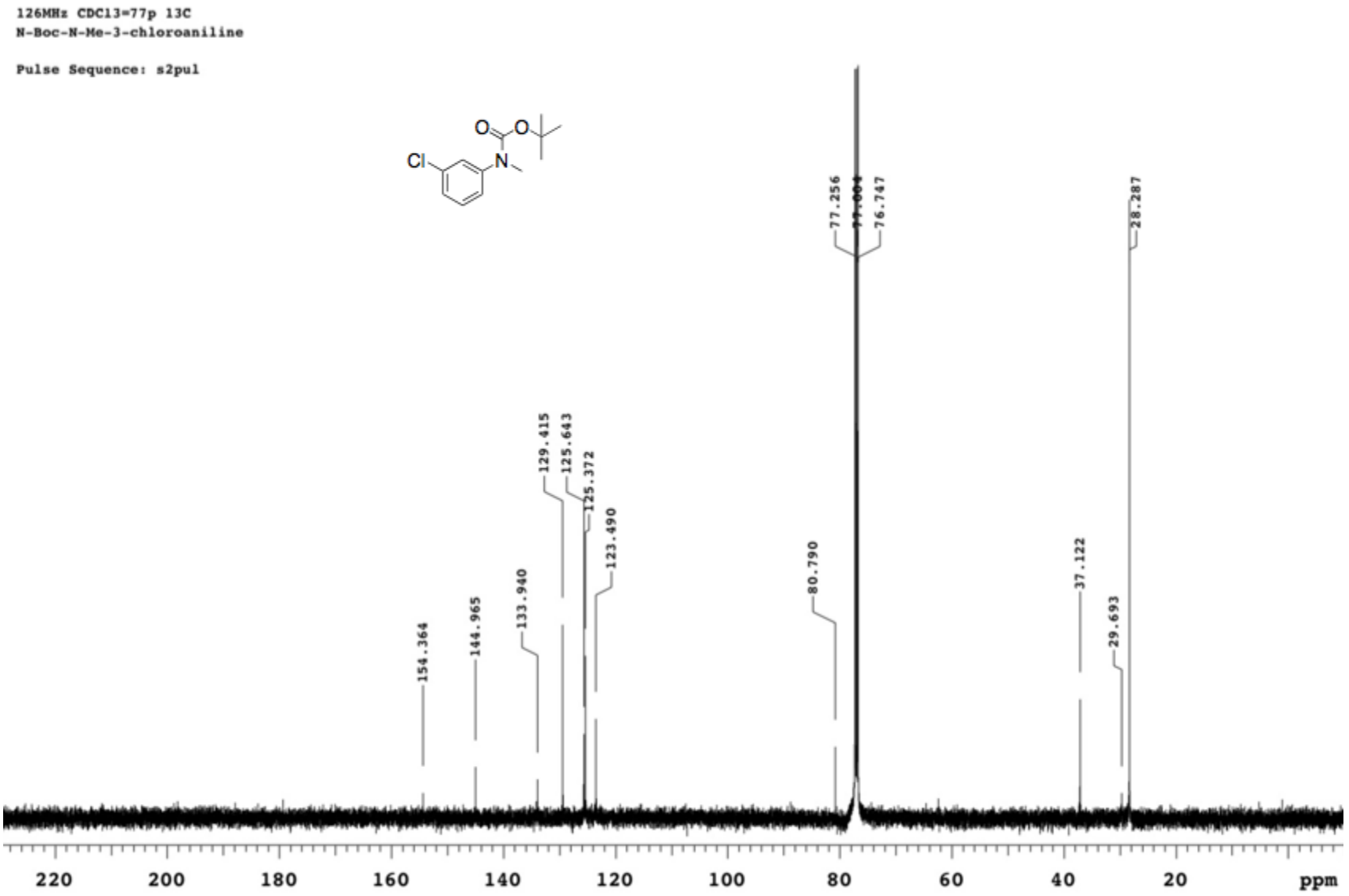


Figure. 126 MHz ^{13}C NMR spectrum of **12a**

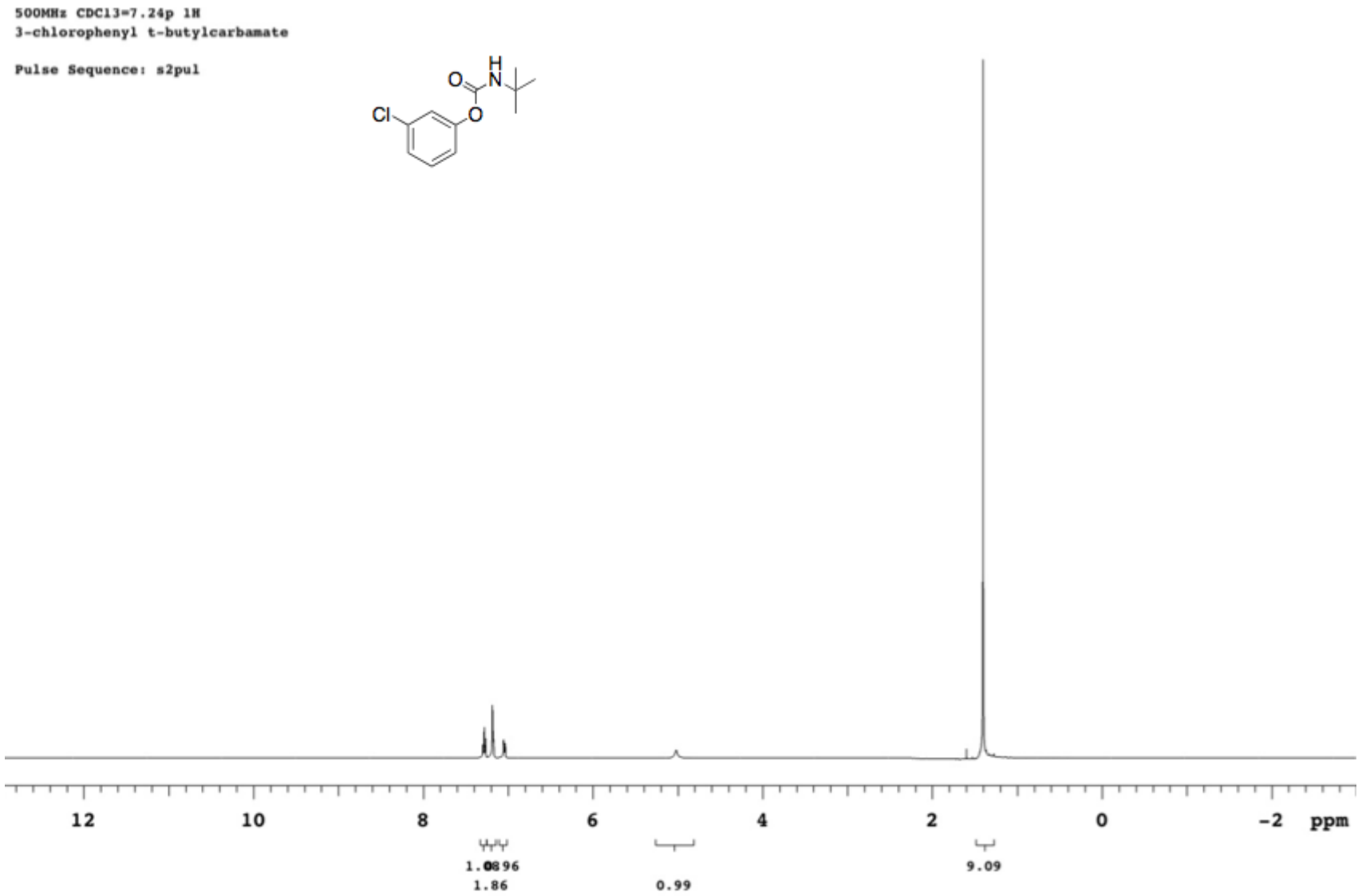


Figure. 500 MHz ^{1}H NMR spectrum of **12b**

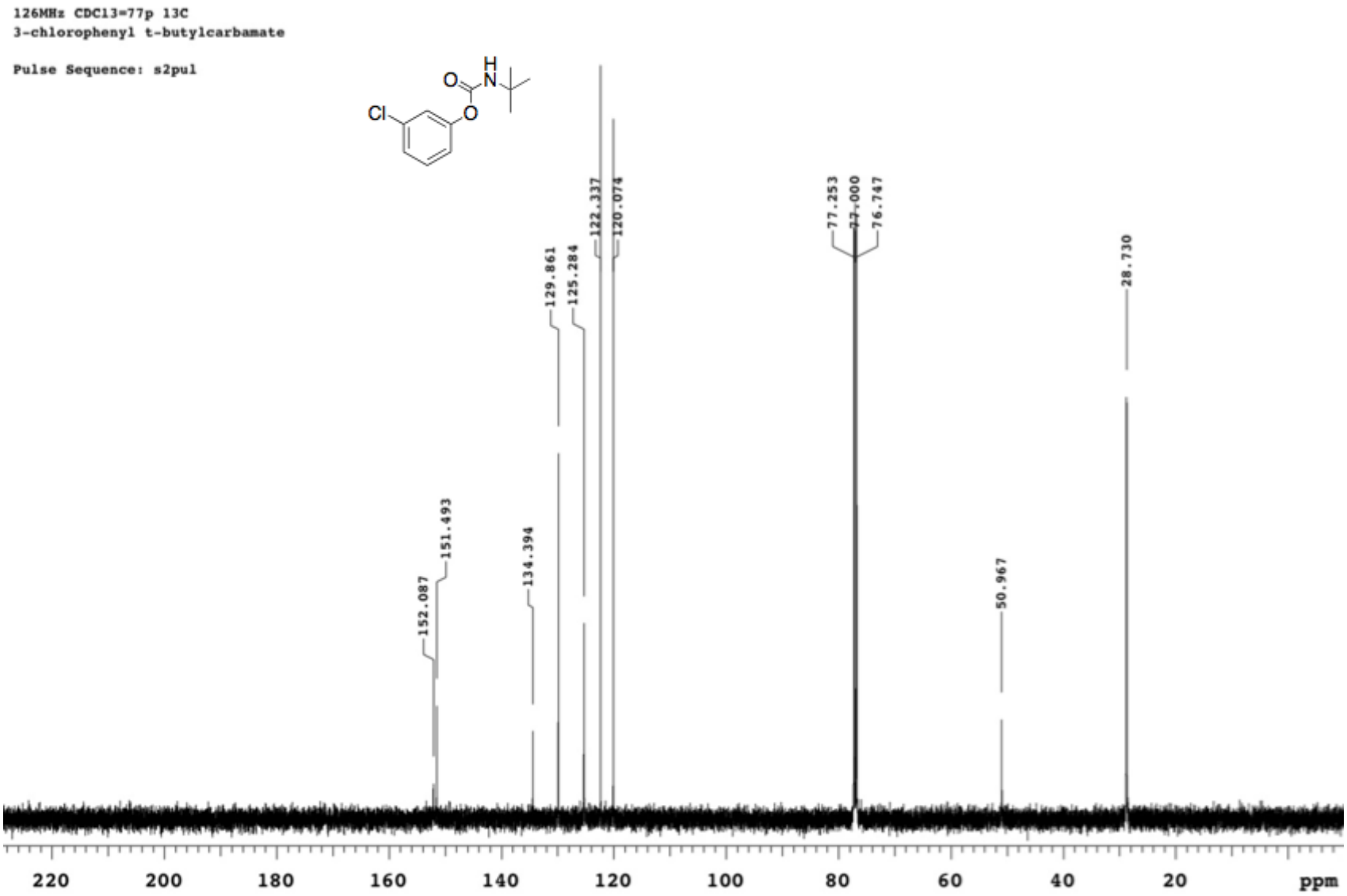


Figure. 126 MHz ^{13}C NMR spectrum of **12b**

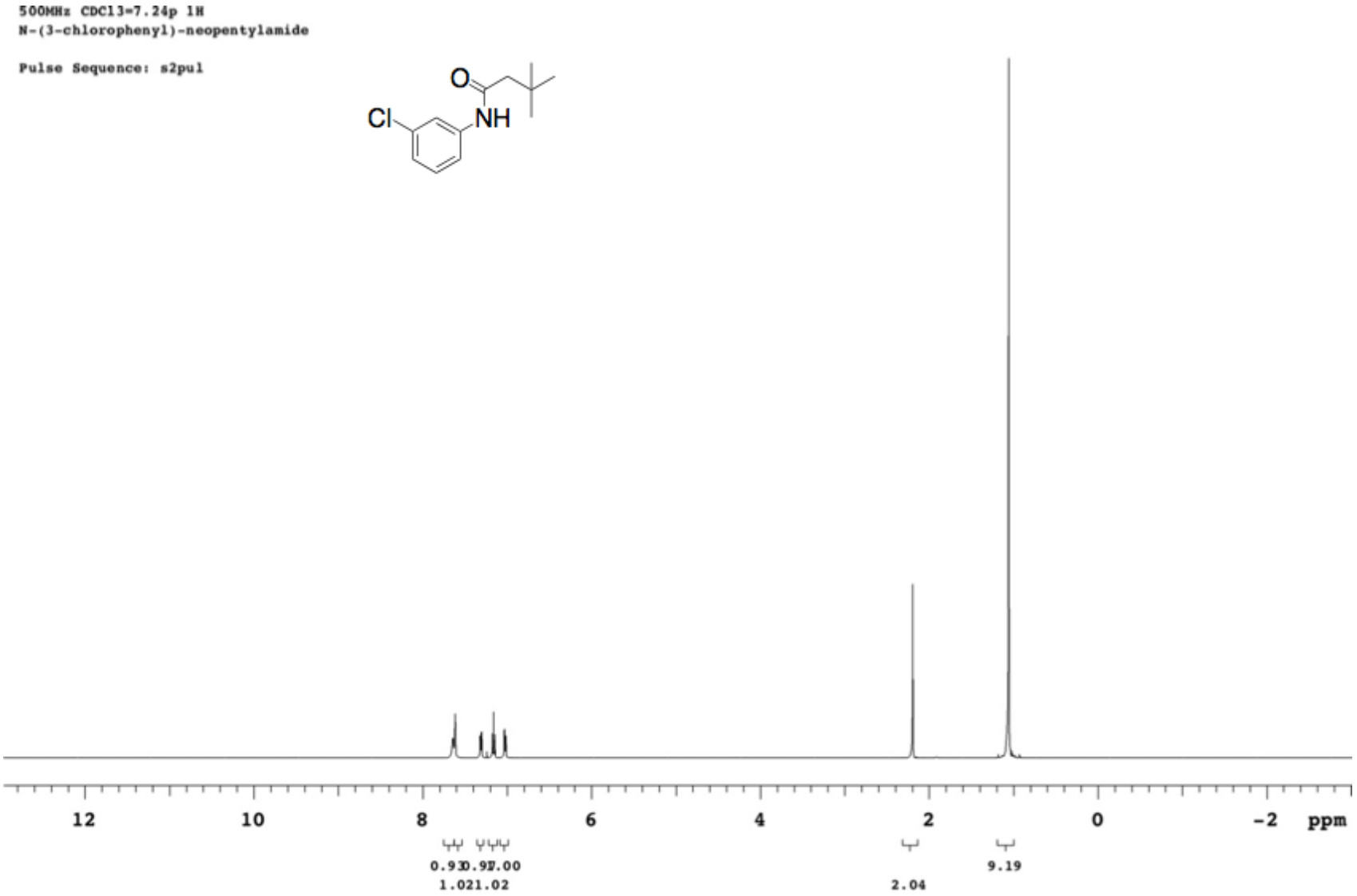


Figure. 500 MHz ^{1}H NMR spectrum of **12c**

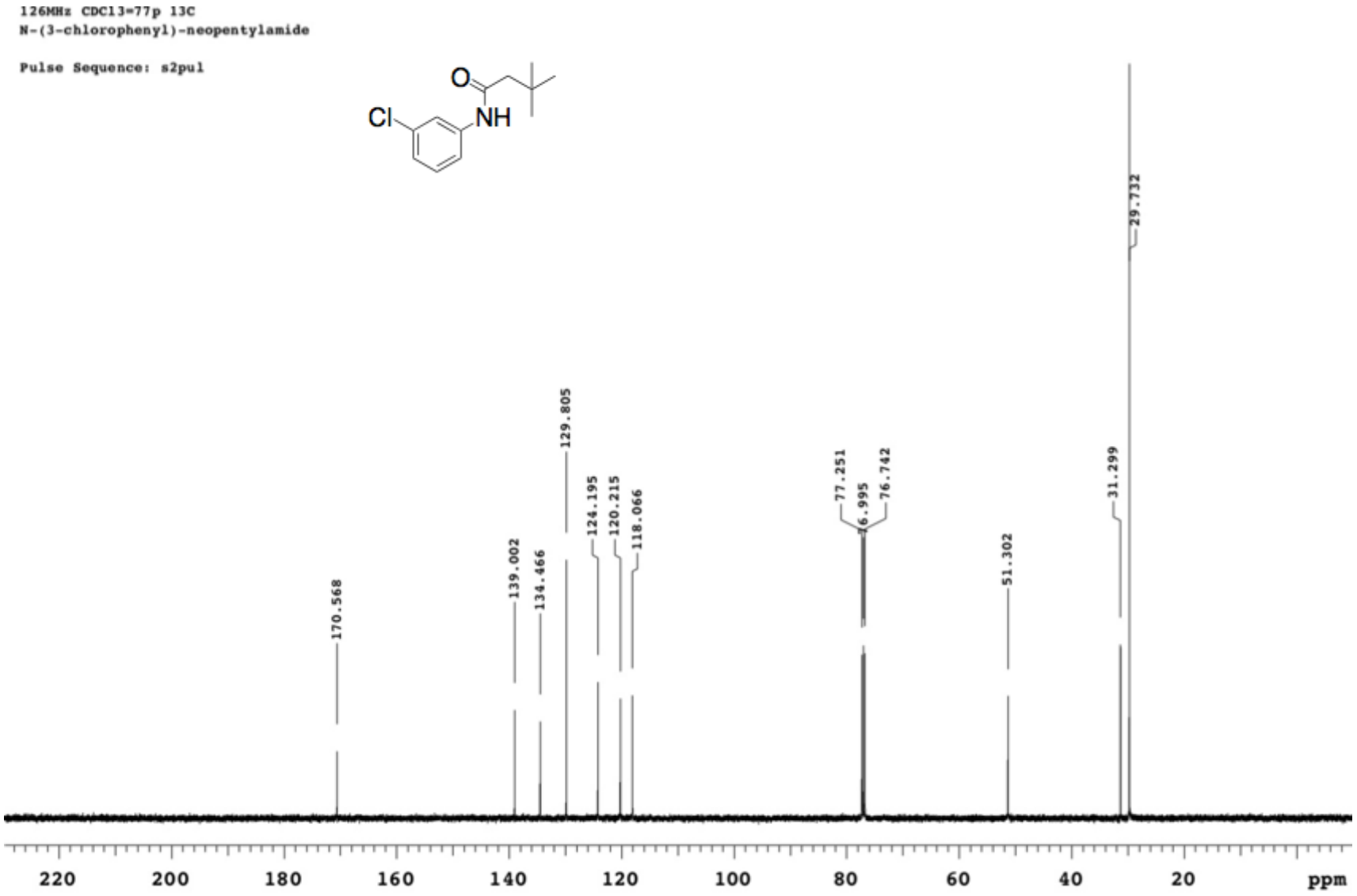


Figure. 126 MHz ^{13}C NMR spectrum of **12c**

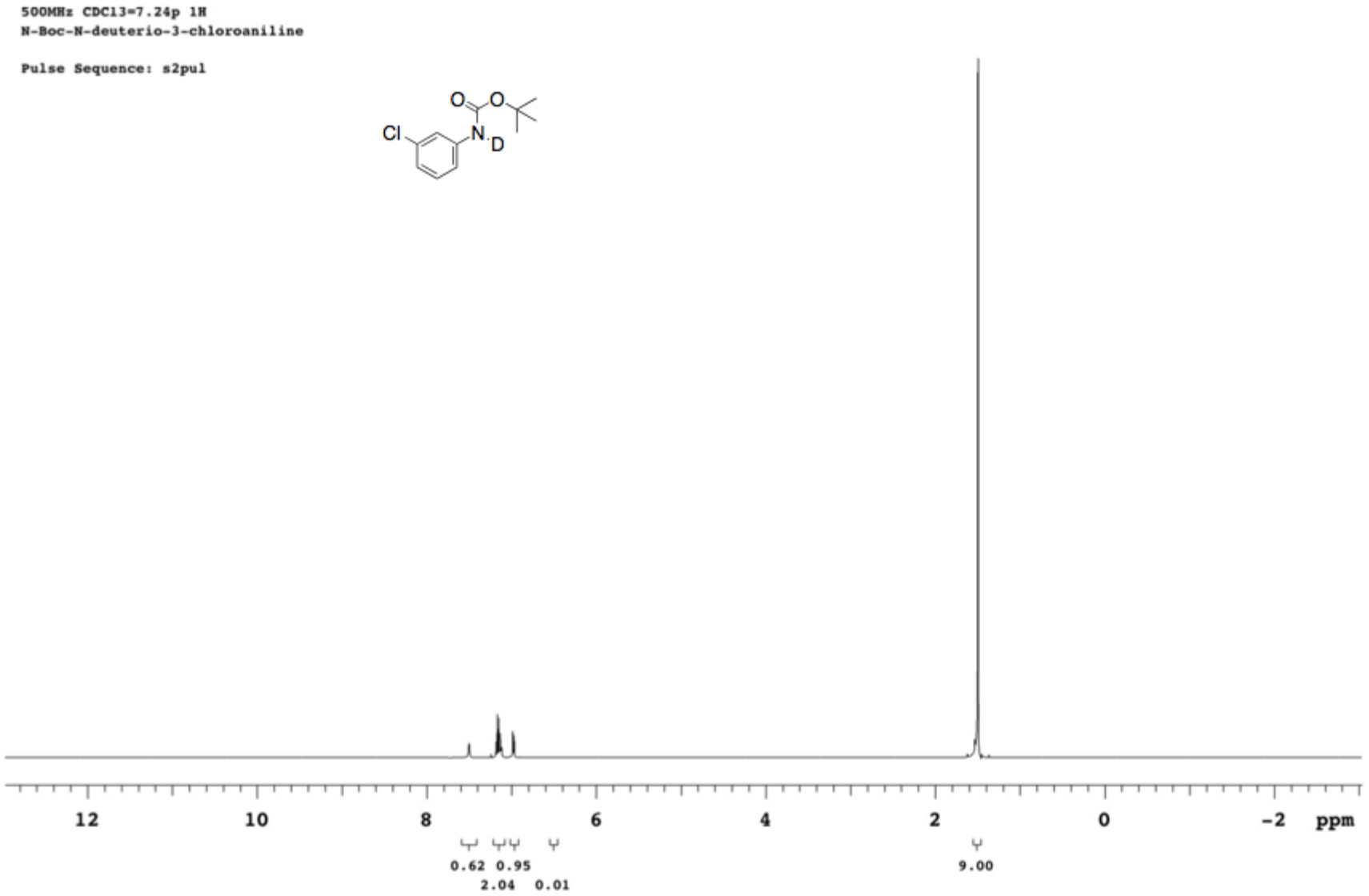


Figure. 500 MHz ^{1}H NMR spectrum **7-*d*$_1$**

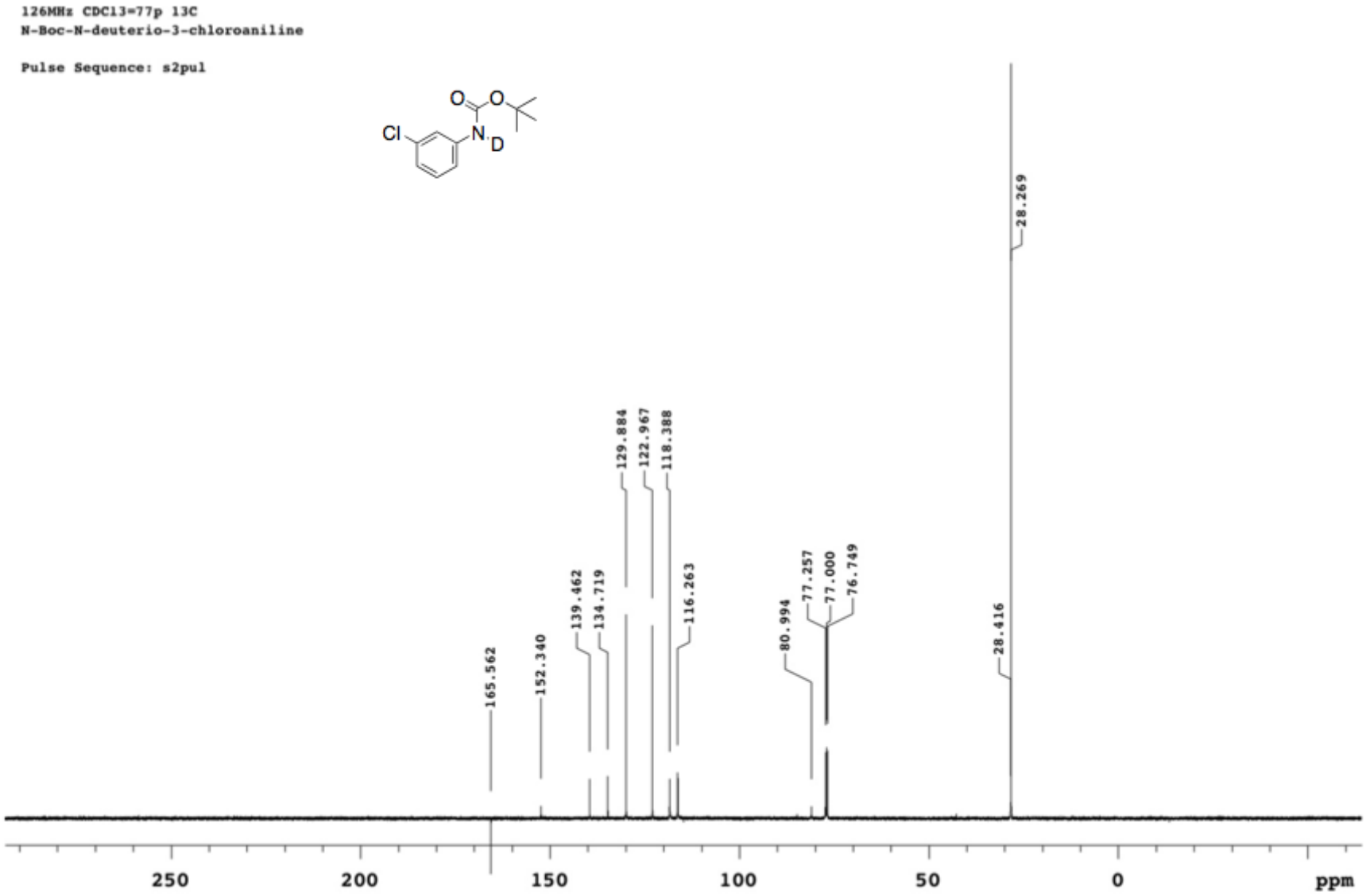


Figure. 126 MHz ^{13}C NMR spectrum **7-*d*$_1$**

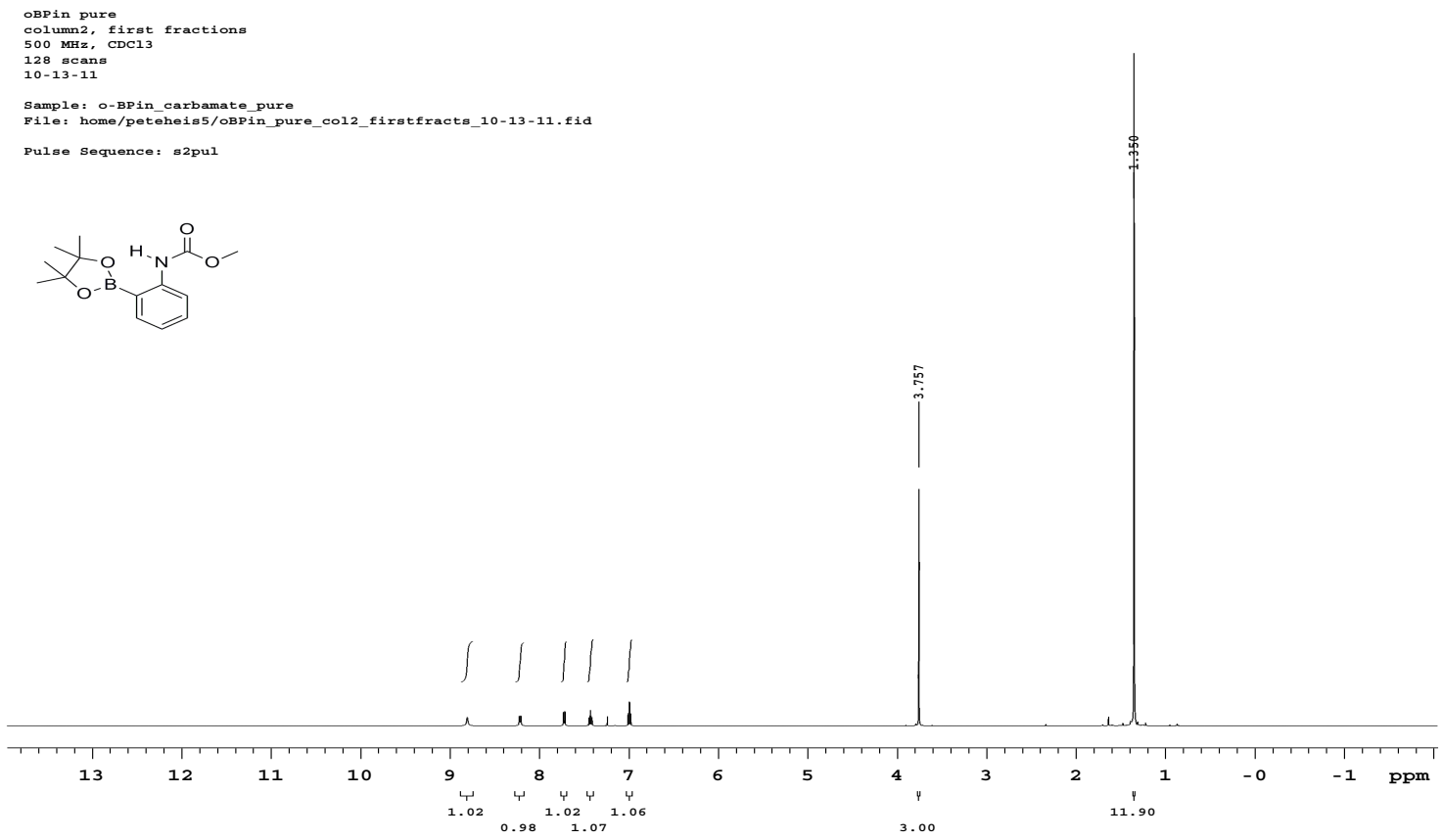


Figure. 500 MHz ^{1}H NMR spectrum

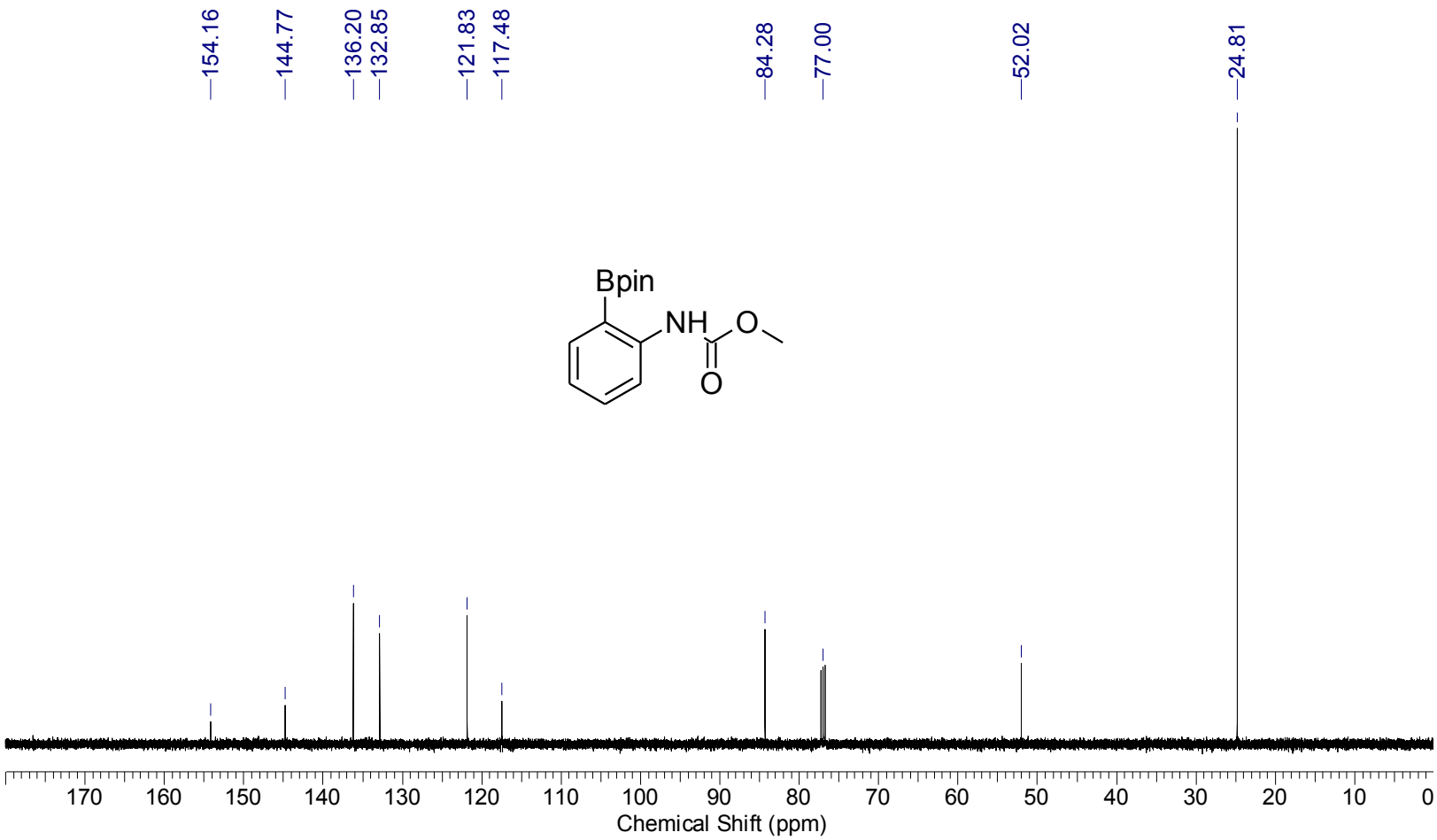


Figure. 126 MHz ^{13}C NMR spectrum

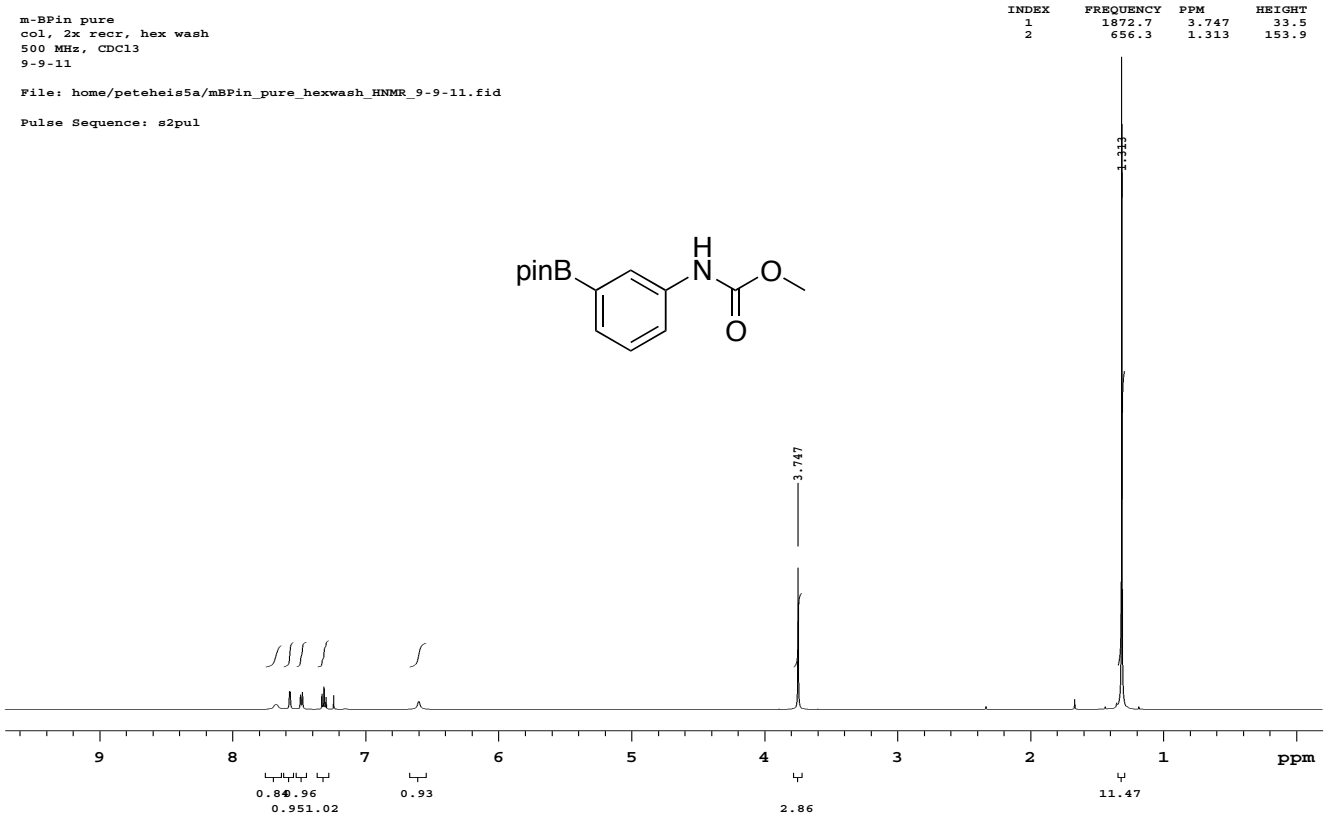


Figure. 500 MHz ^{1}H NMR spectrum

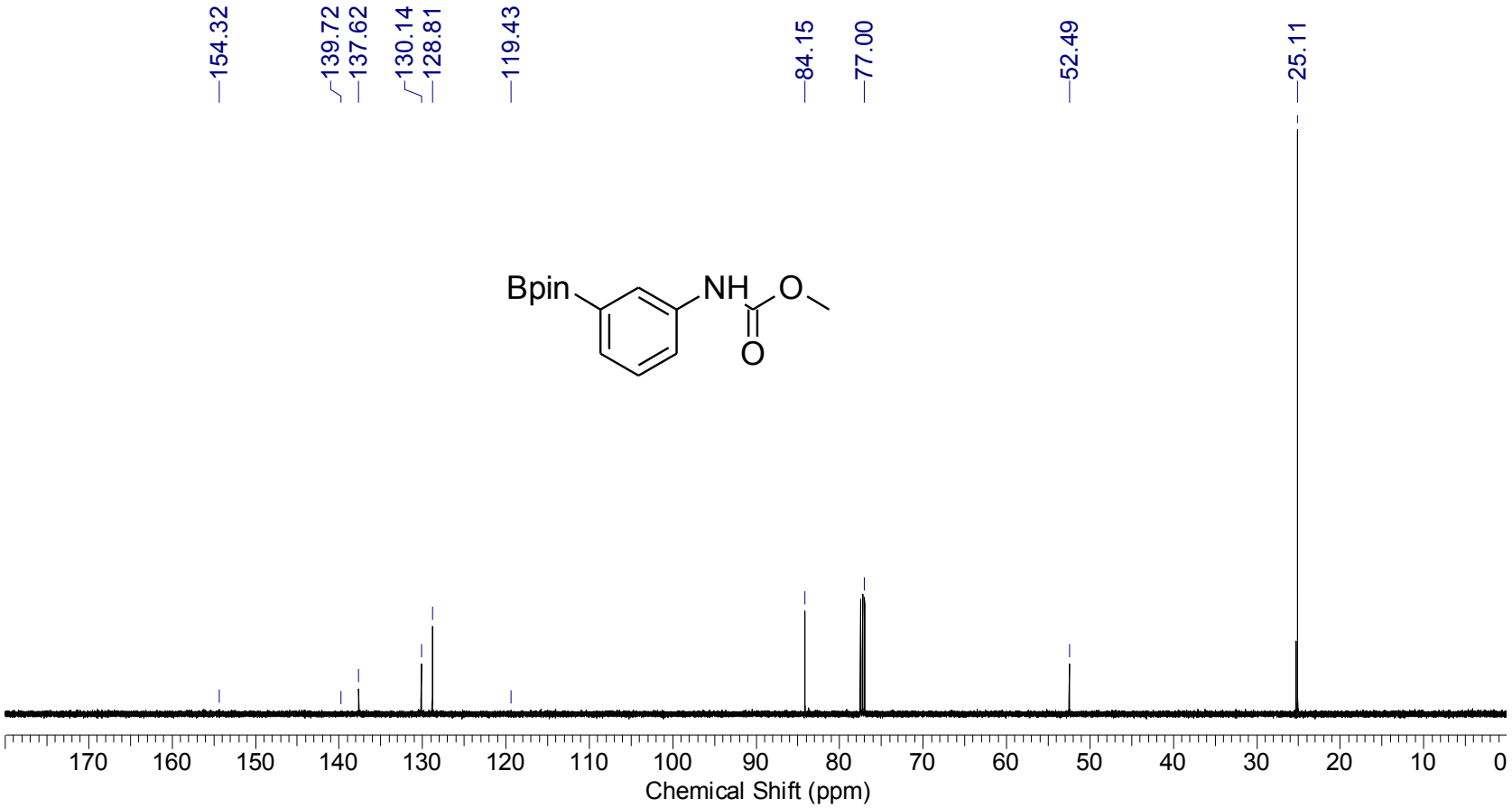


Figure. 126 MHz ^{13}C NMR spectrum

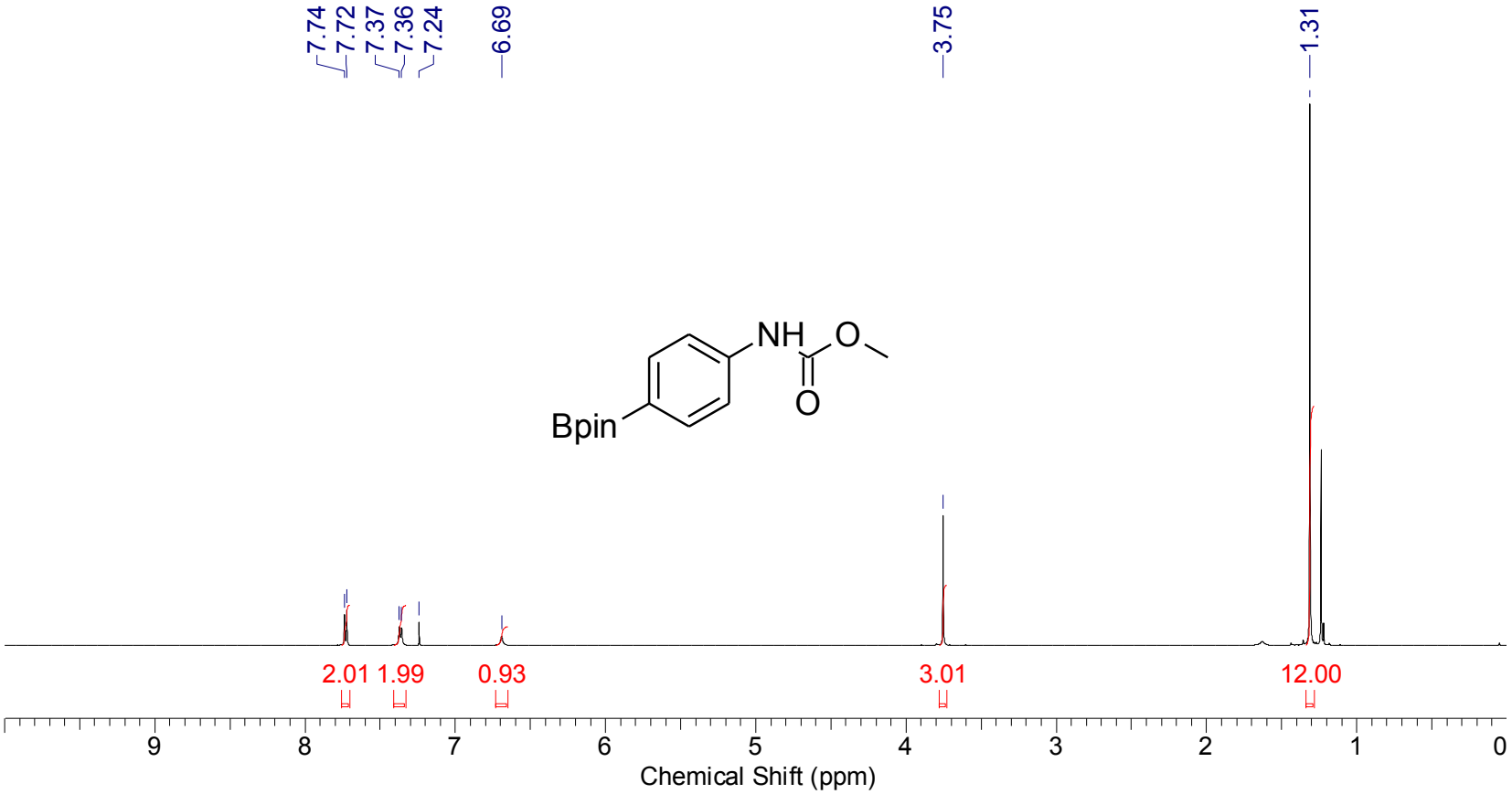


Figure. 500 MHz ^{1}H NMR spectrum

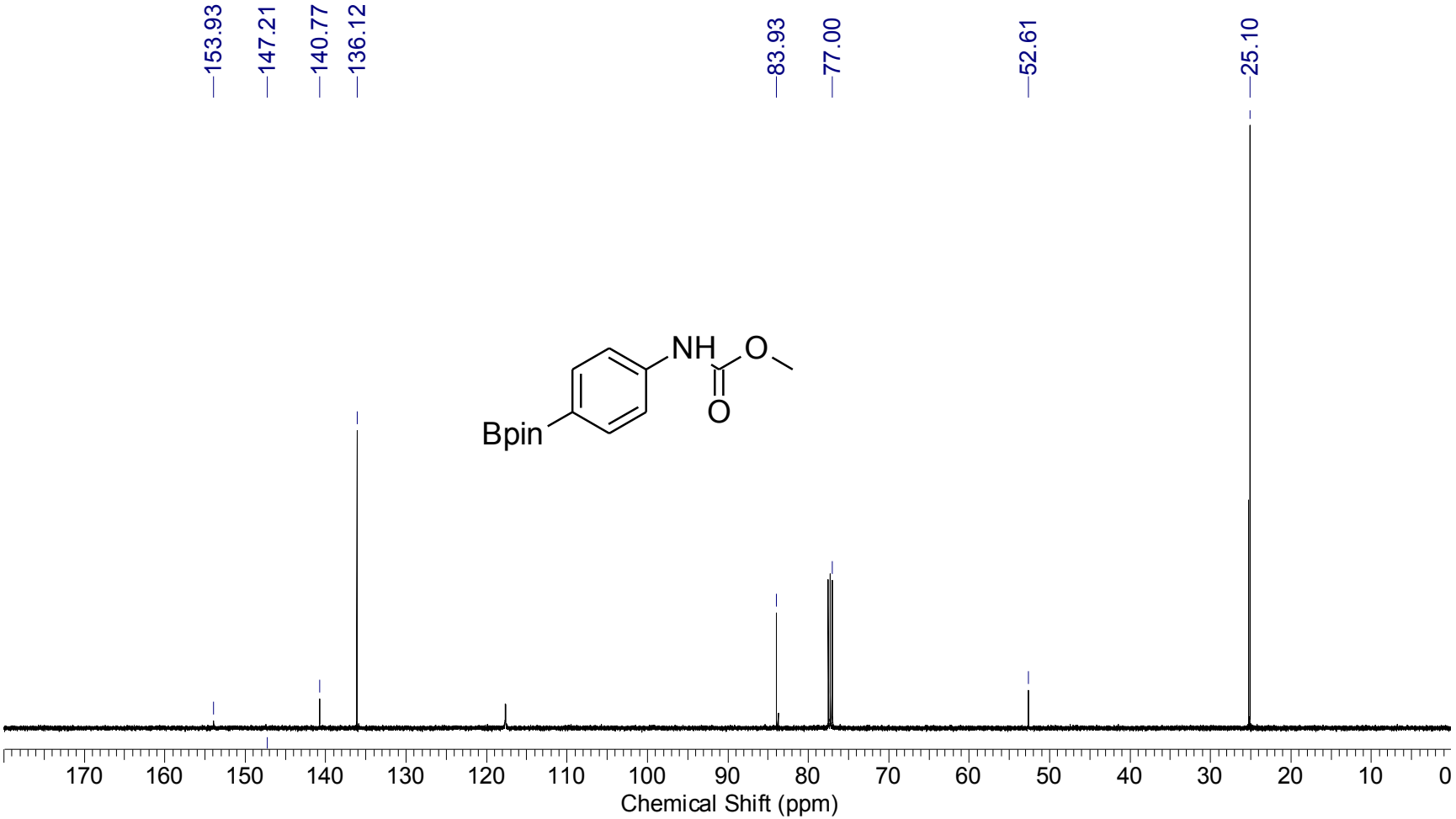


Figure. 126 MHz ^{13}C NMR spectrum

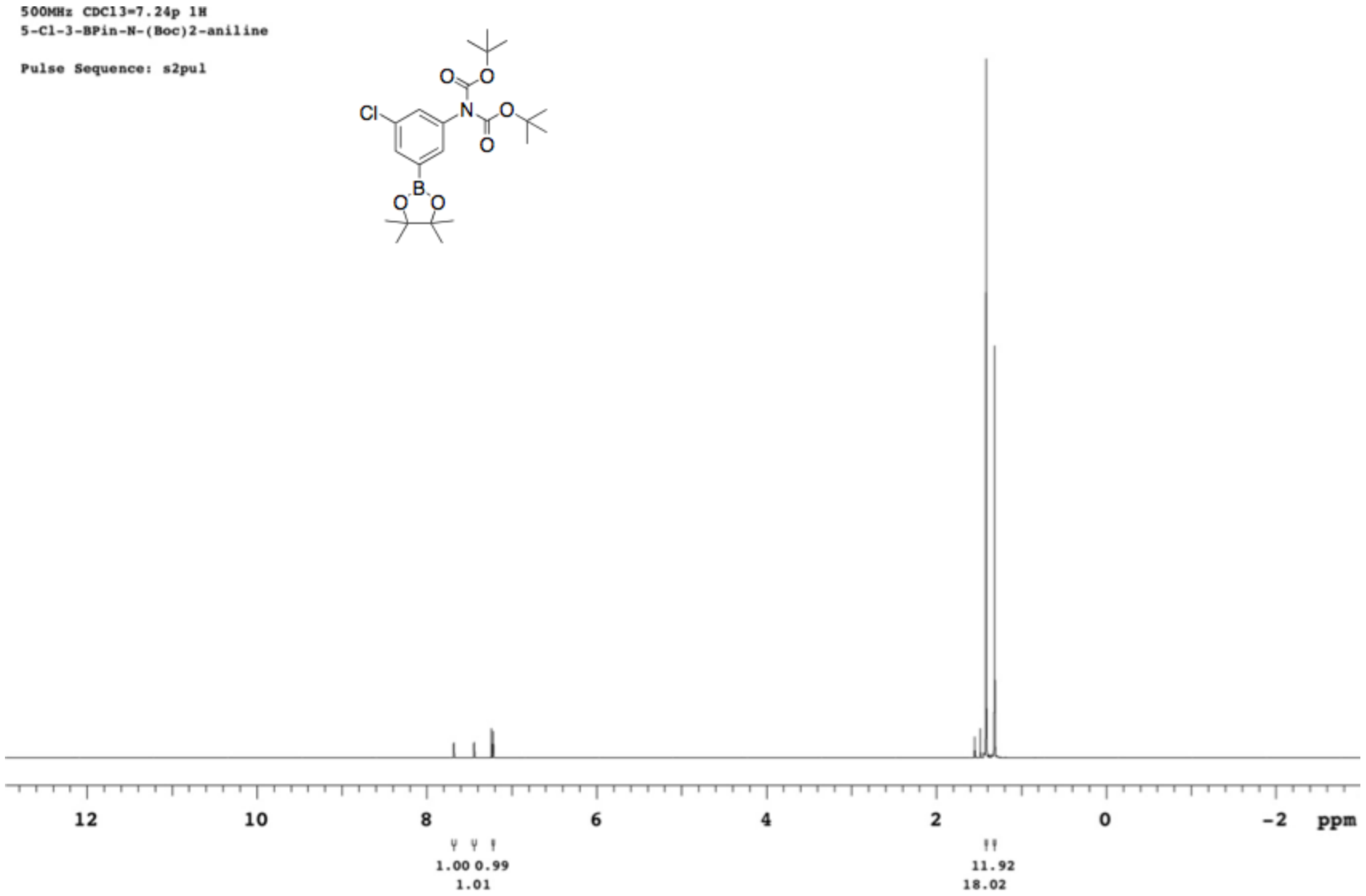


Figure. 500 MHz ^{1}H NMR spectrum

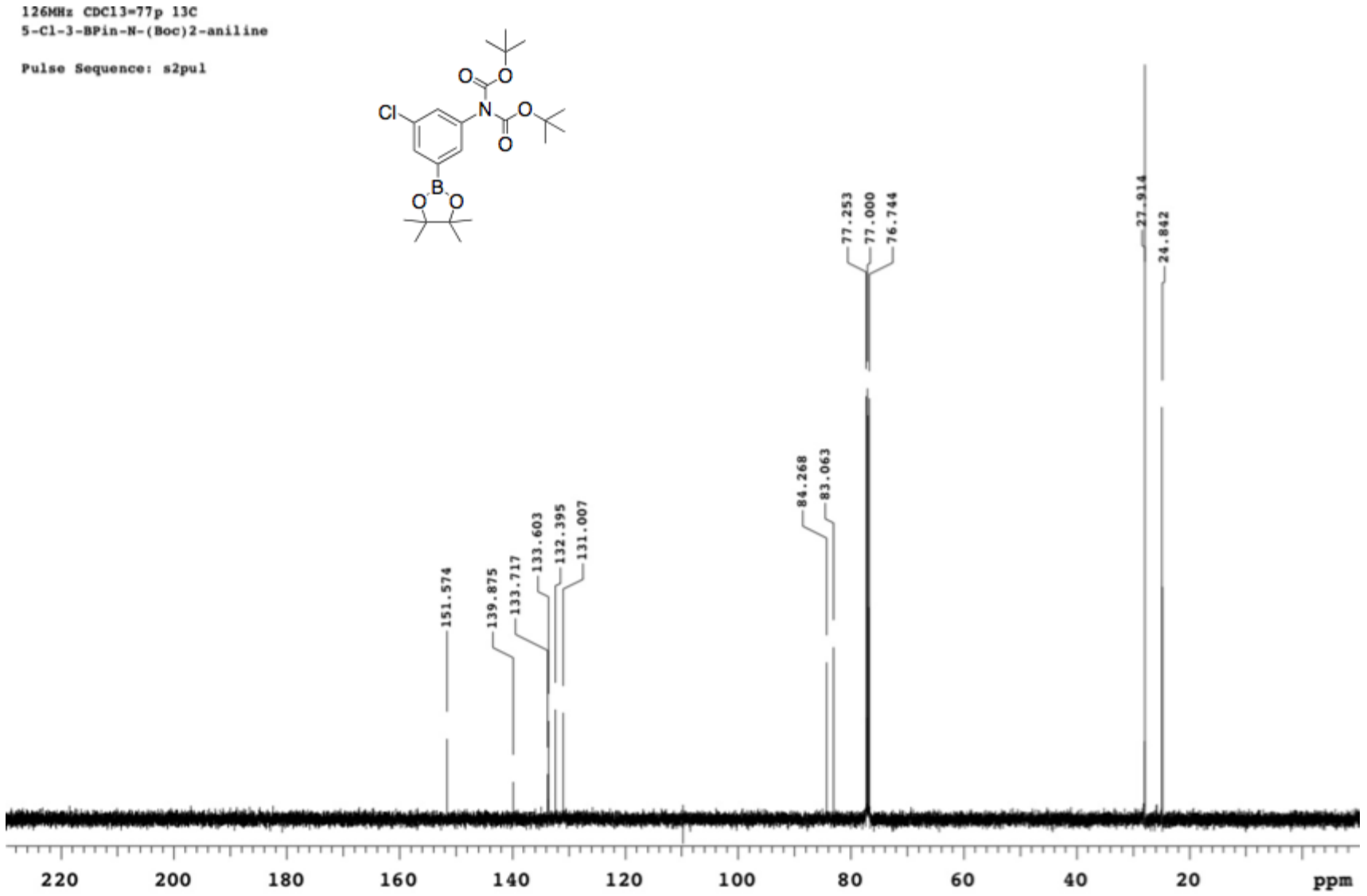


Figure. 126 MHz ^{13}C NMR spectrum

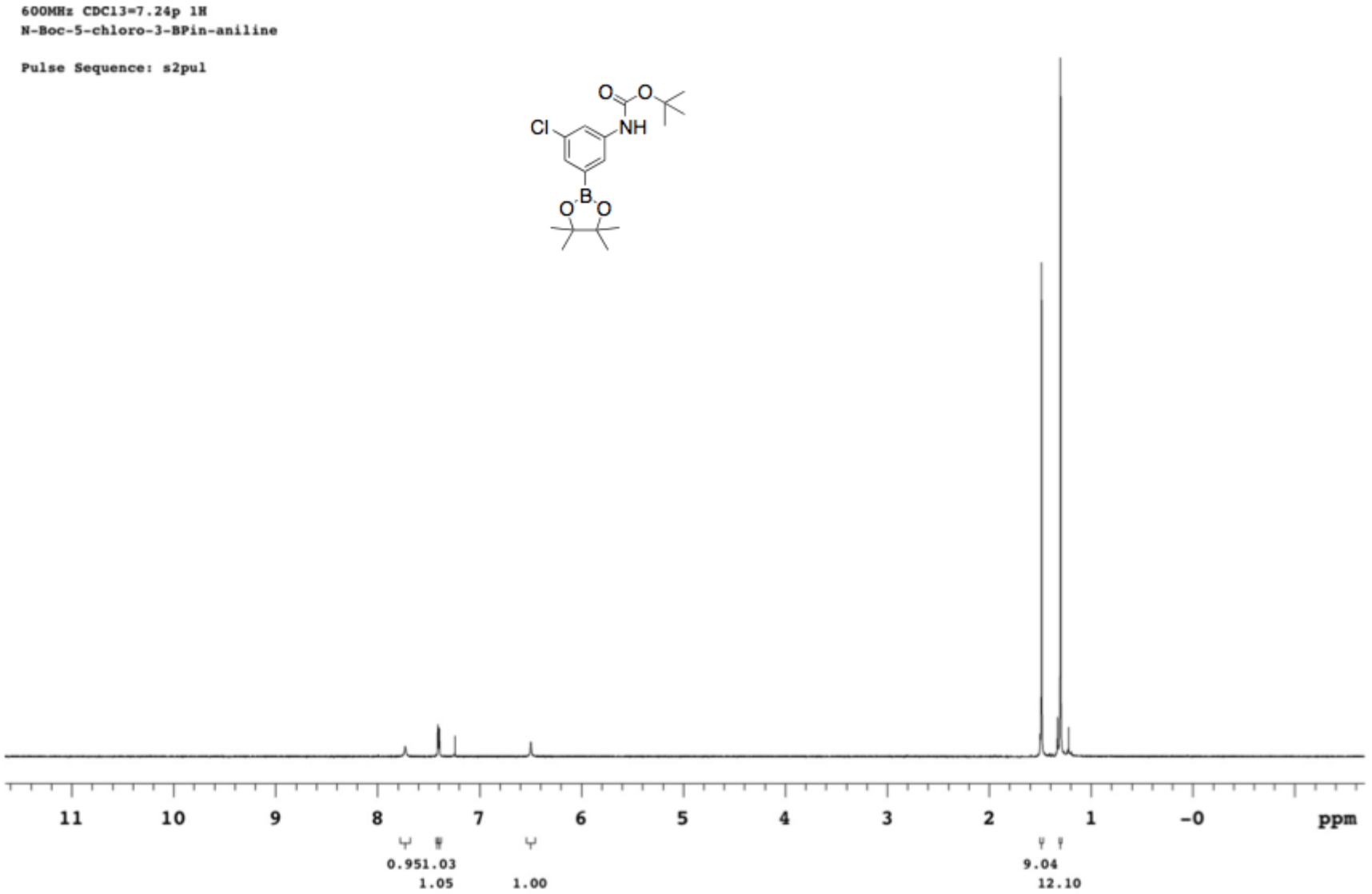


Figure. 600 MHz ^{1}H NMR spectrum of **8a**

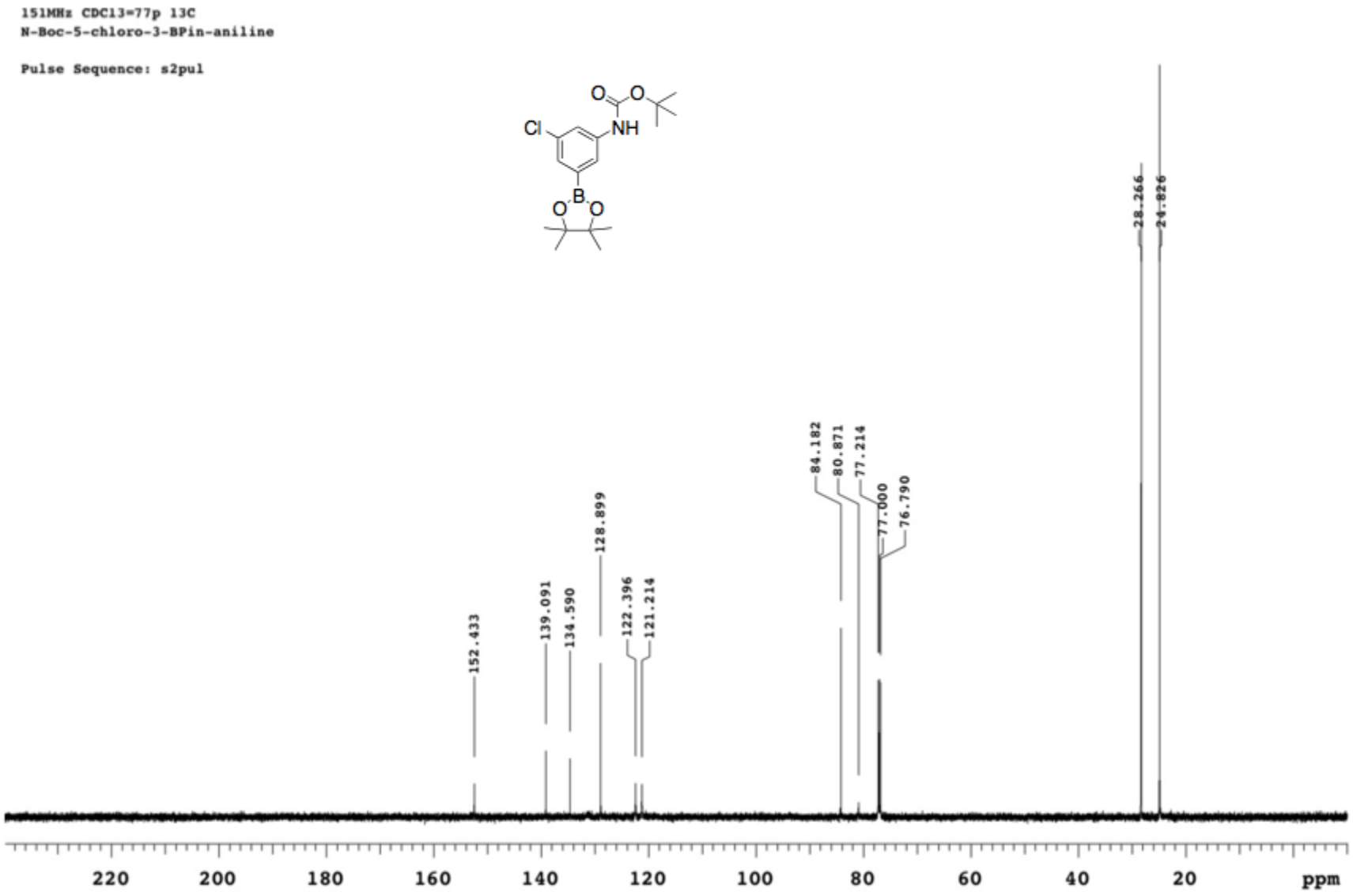


Figure. 151 MHz ^{13}C NMR spectrum of **8a**

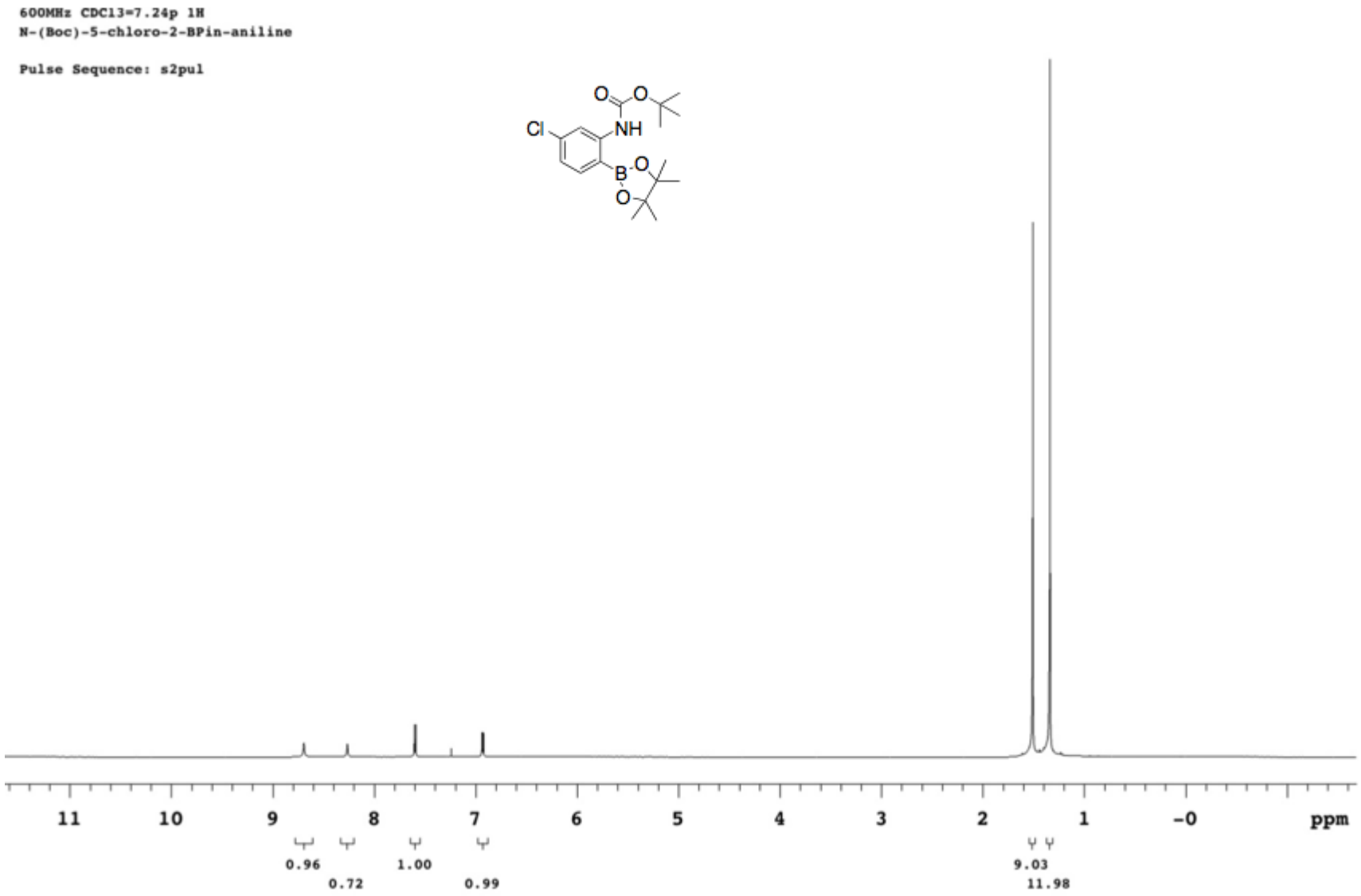


Figure. 600 MHz ^{1}H NMR spectrum of **8b**

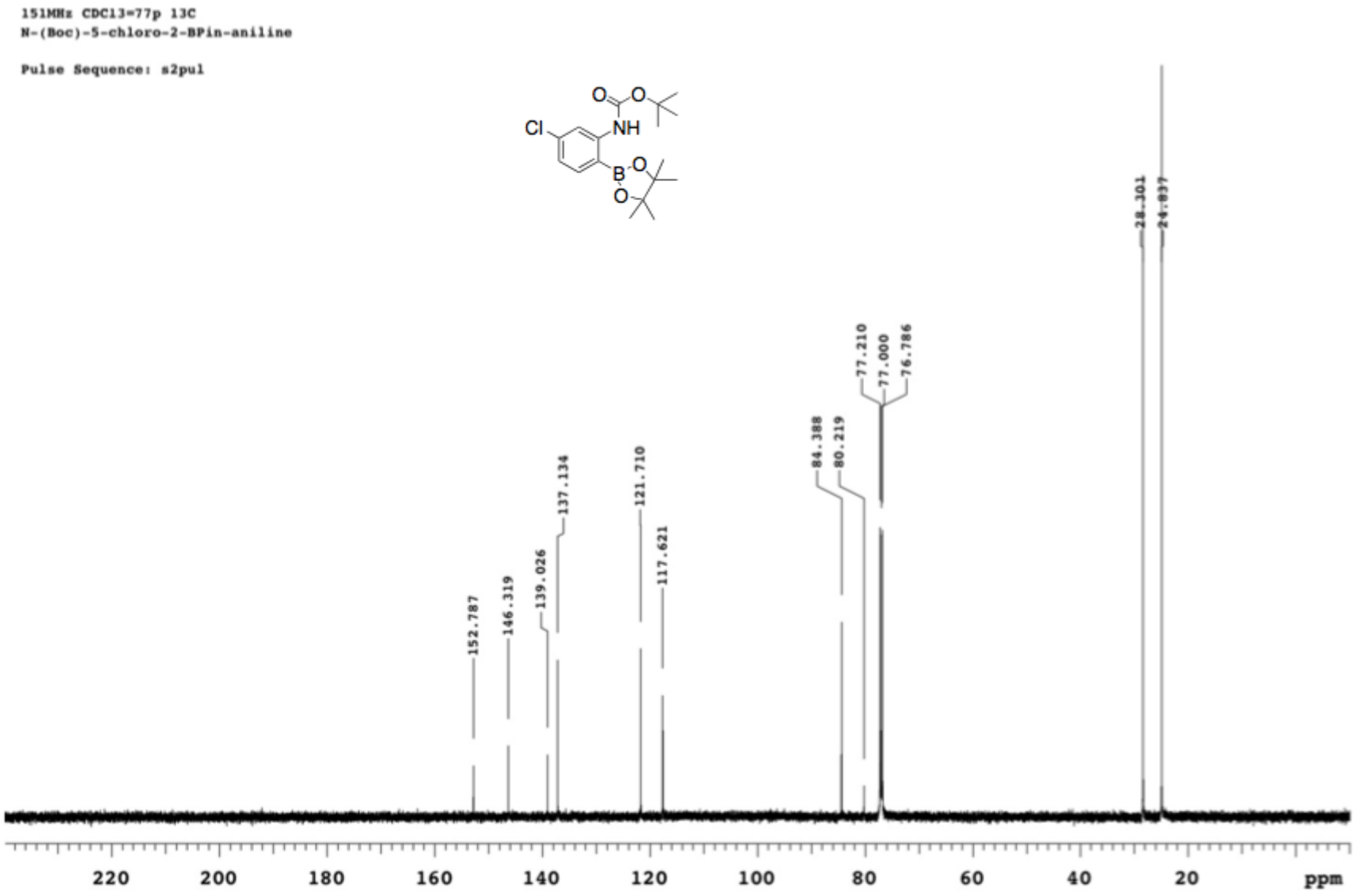


Figure. 151 MHz ^{13}C NMR spectrum of **8b**

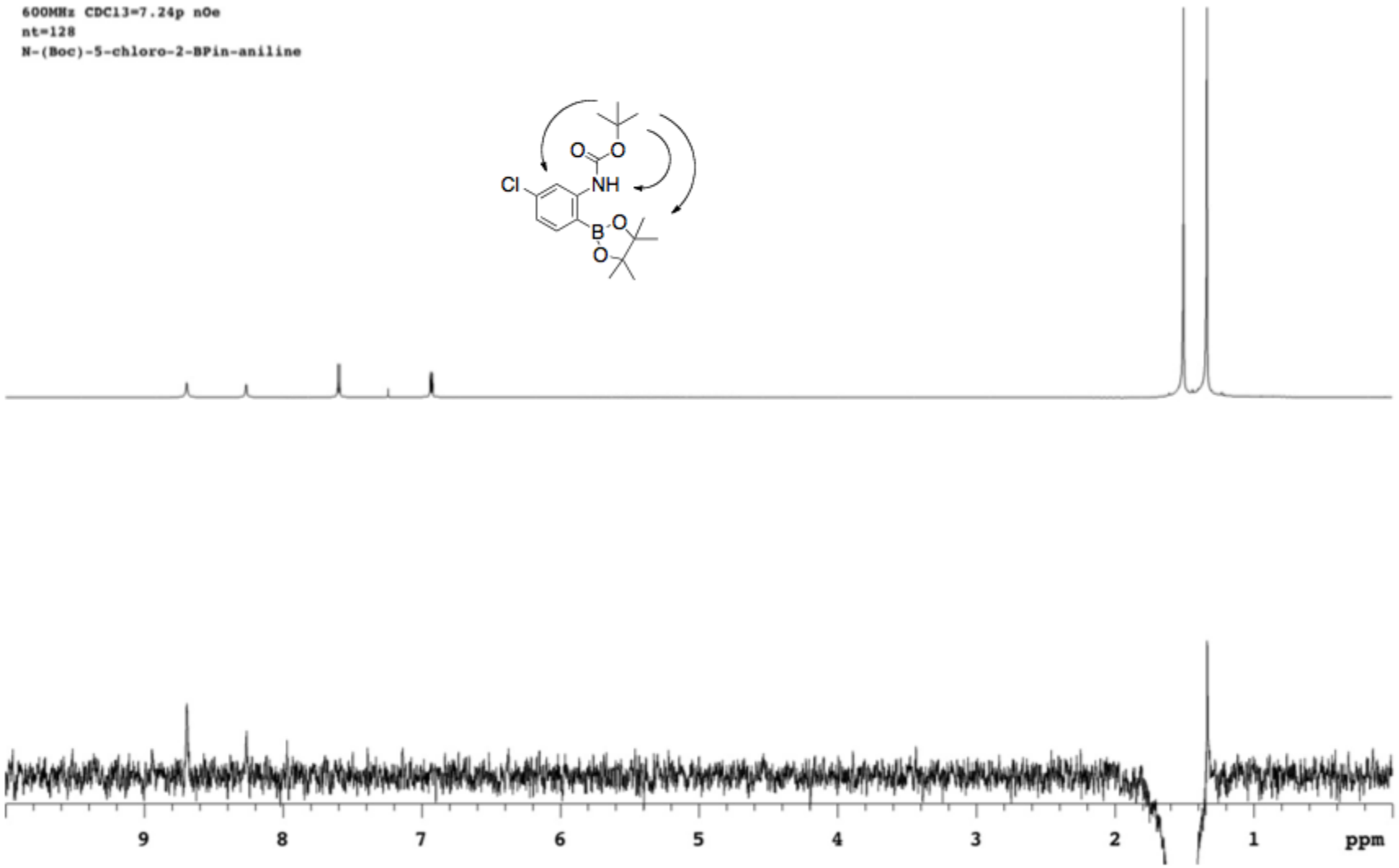


Figure. 600 MHz nOe NMR spectrum of **8b**

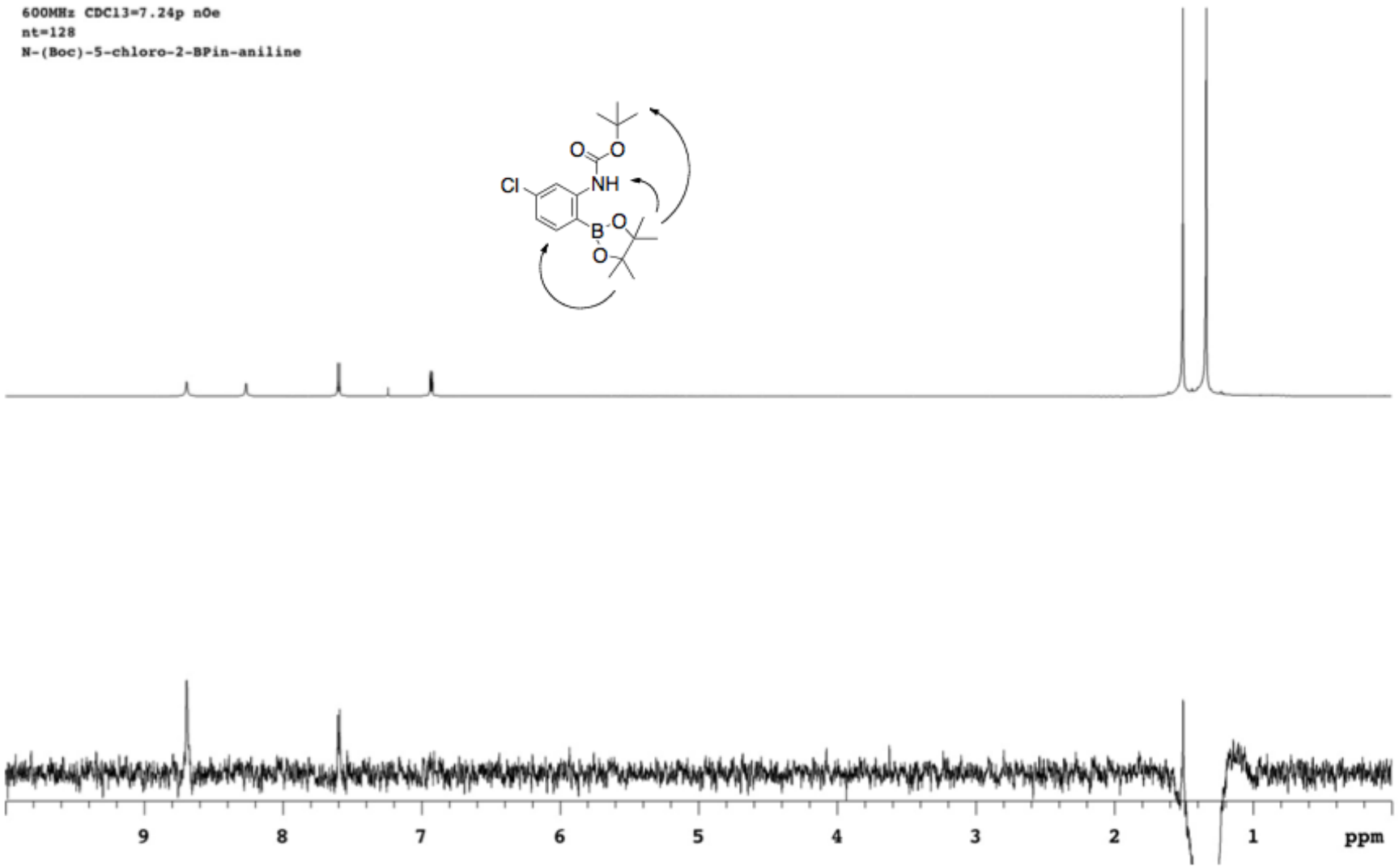


Figure. 600 MHz nOe NMR spectrum of **8b**

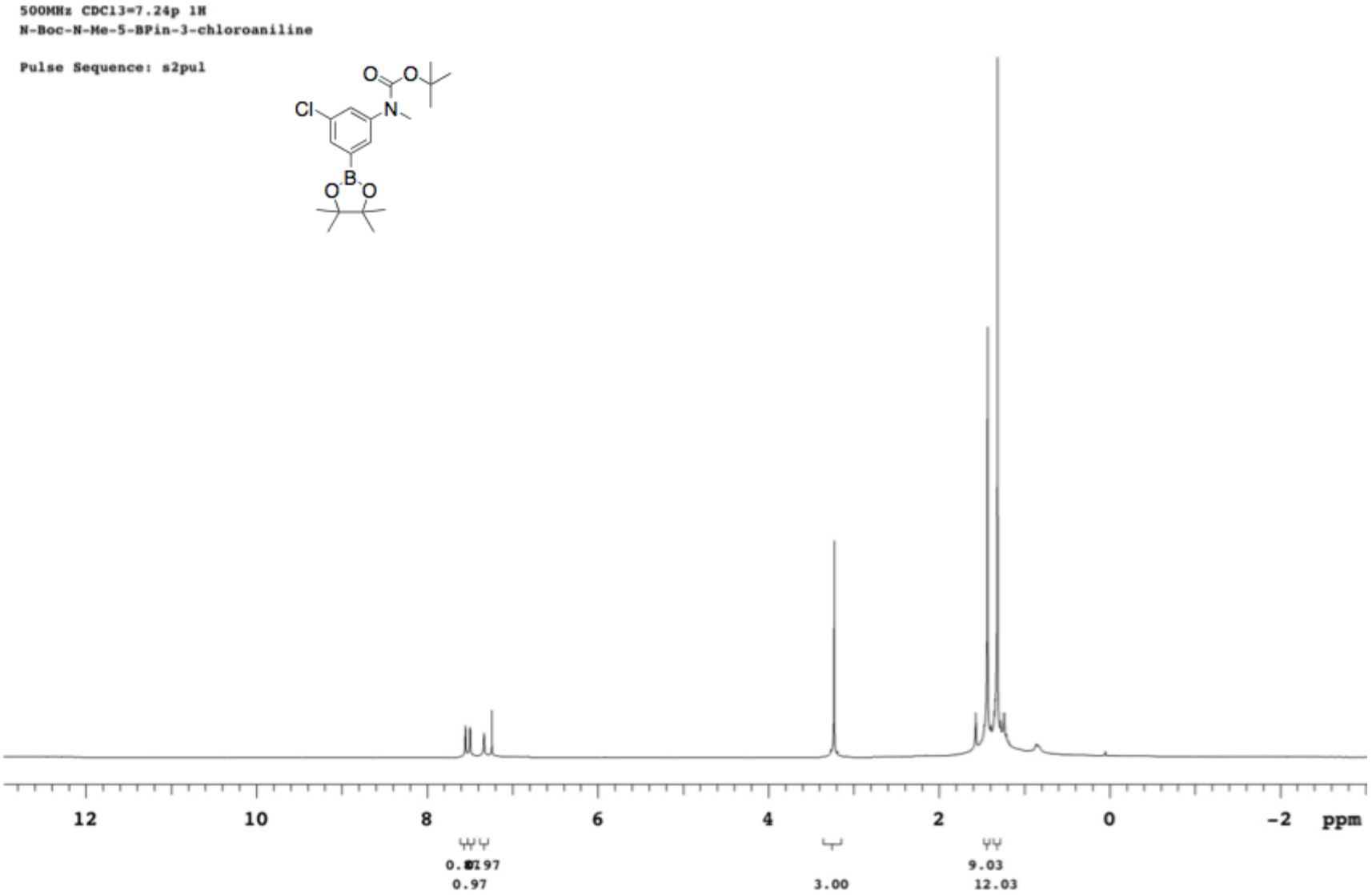


Figure. 500 MHz ^{1}H NMR spectrum of **13a**

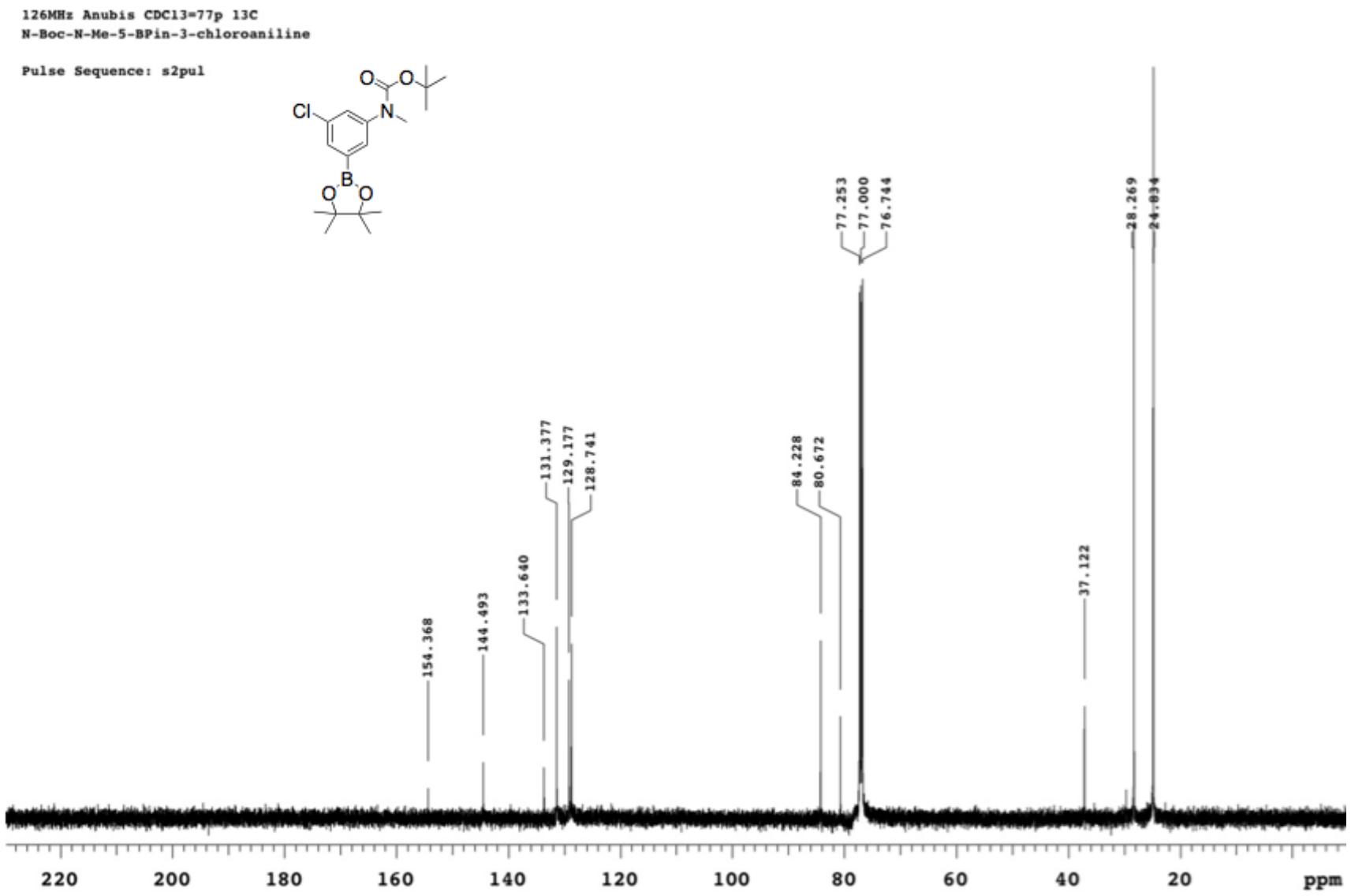


Figure. 126 MHz ^{13}C NMR spectrum of **13a**

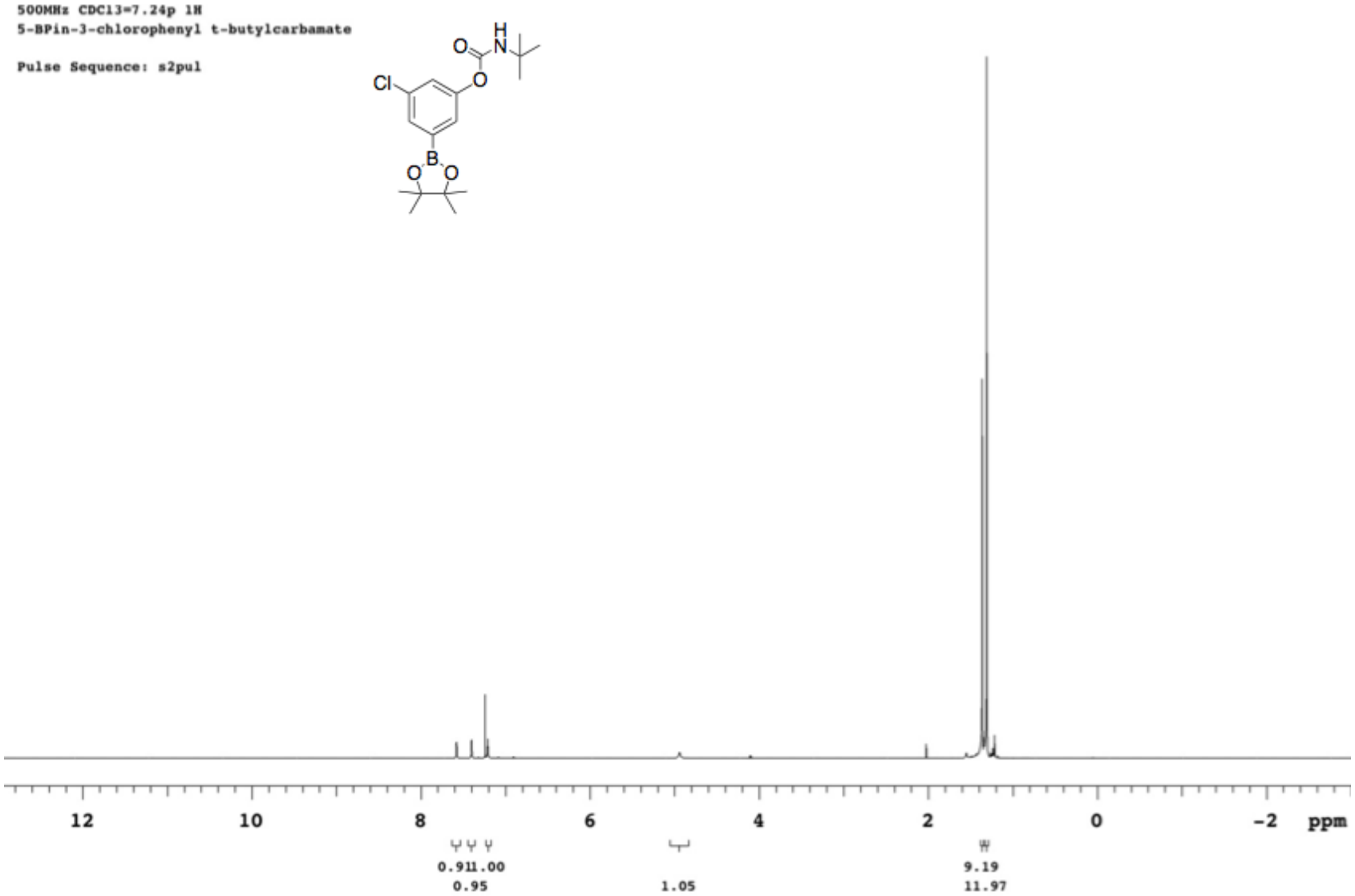


Figure. 500 MHz ^{1}H NMR spectrum of **13b**

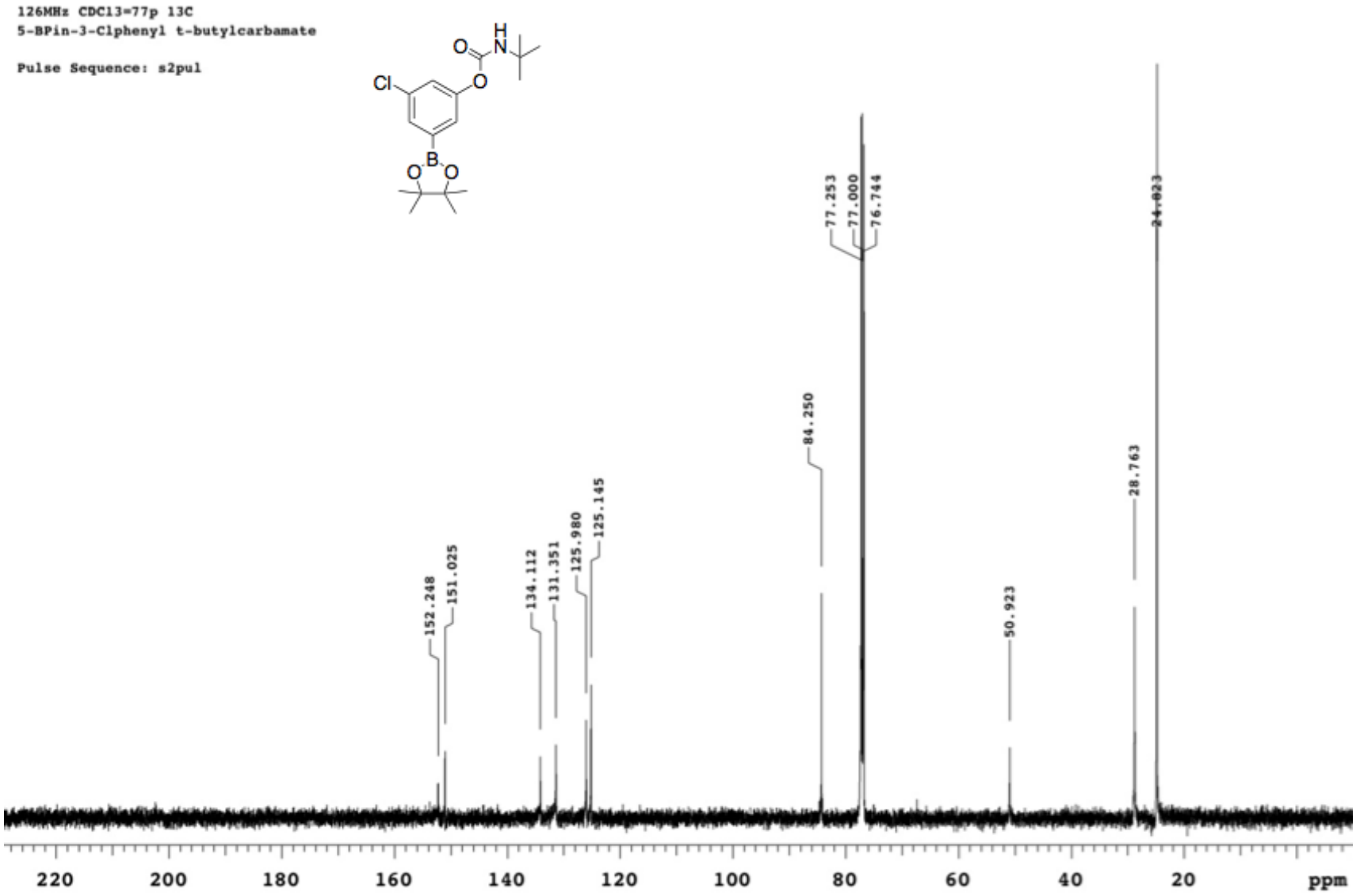


Figure. 126 MHz ^{13}C NMR spectrum of **13b**

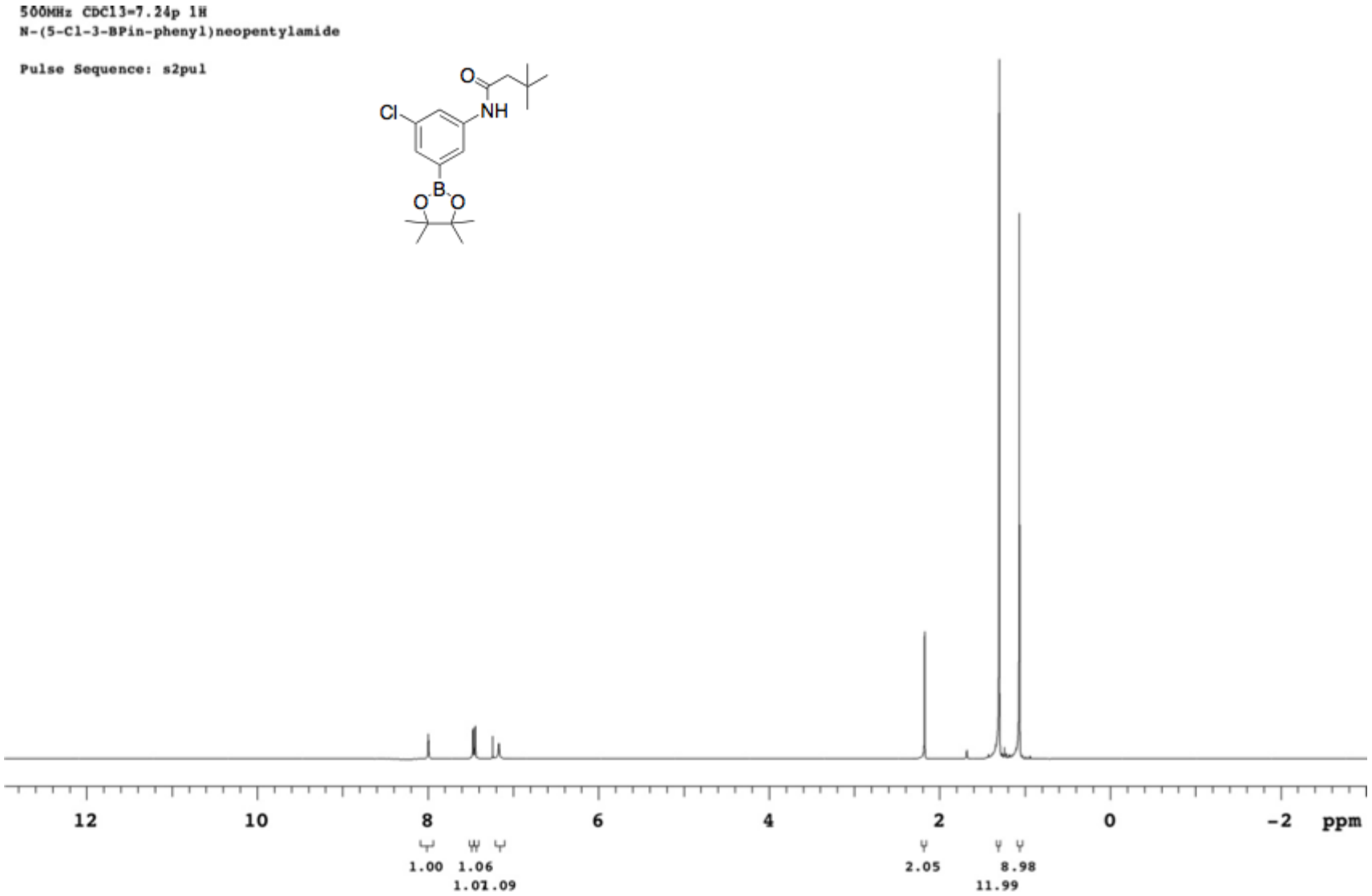


Figure. 500 MHz ^{1}H NMR spectrum of **13c**

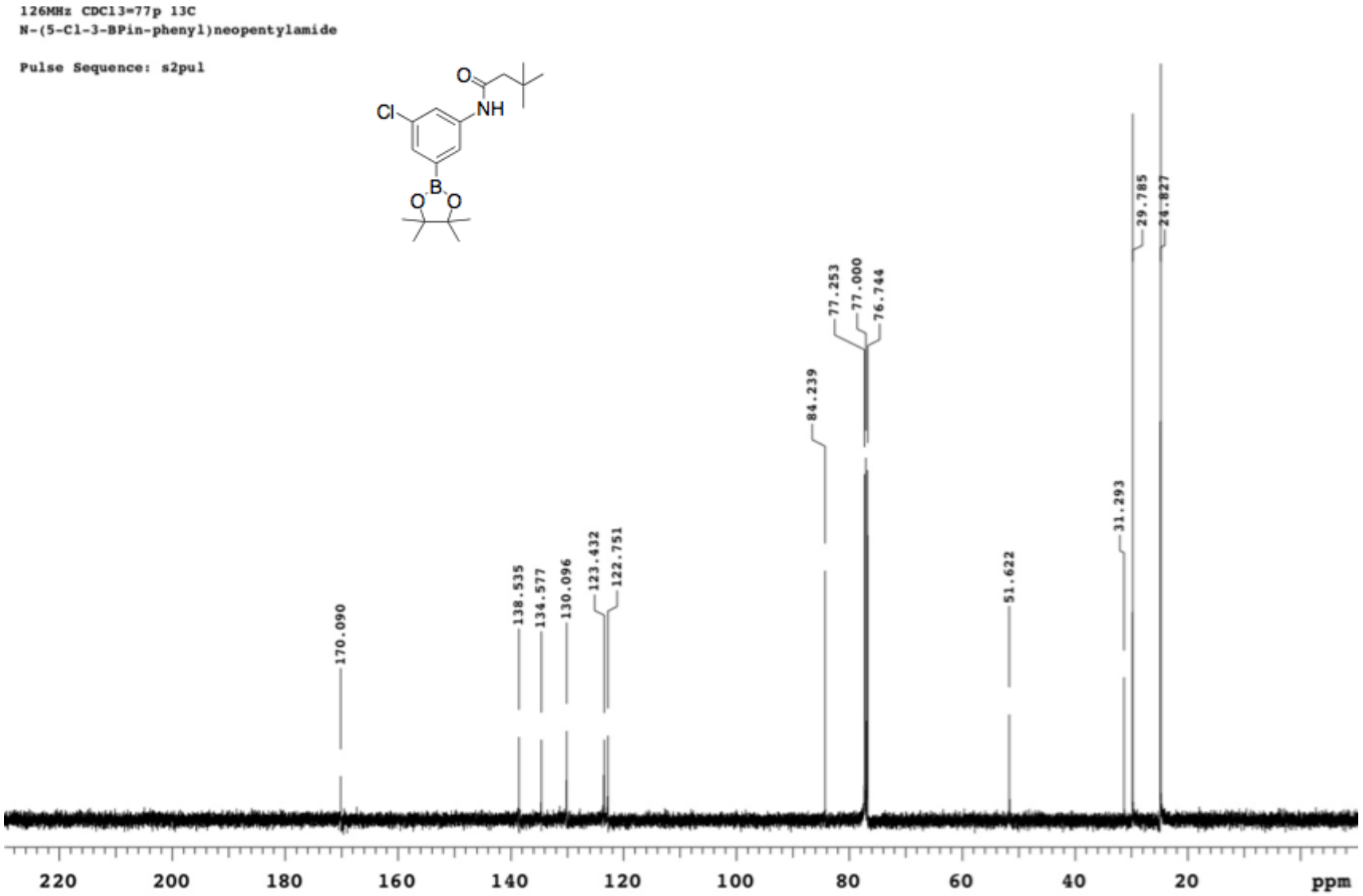


Figure. 126 MHz ^{13}C NMR spectrum of **13c**

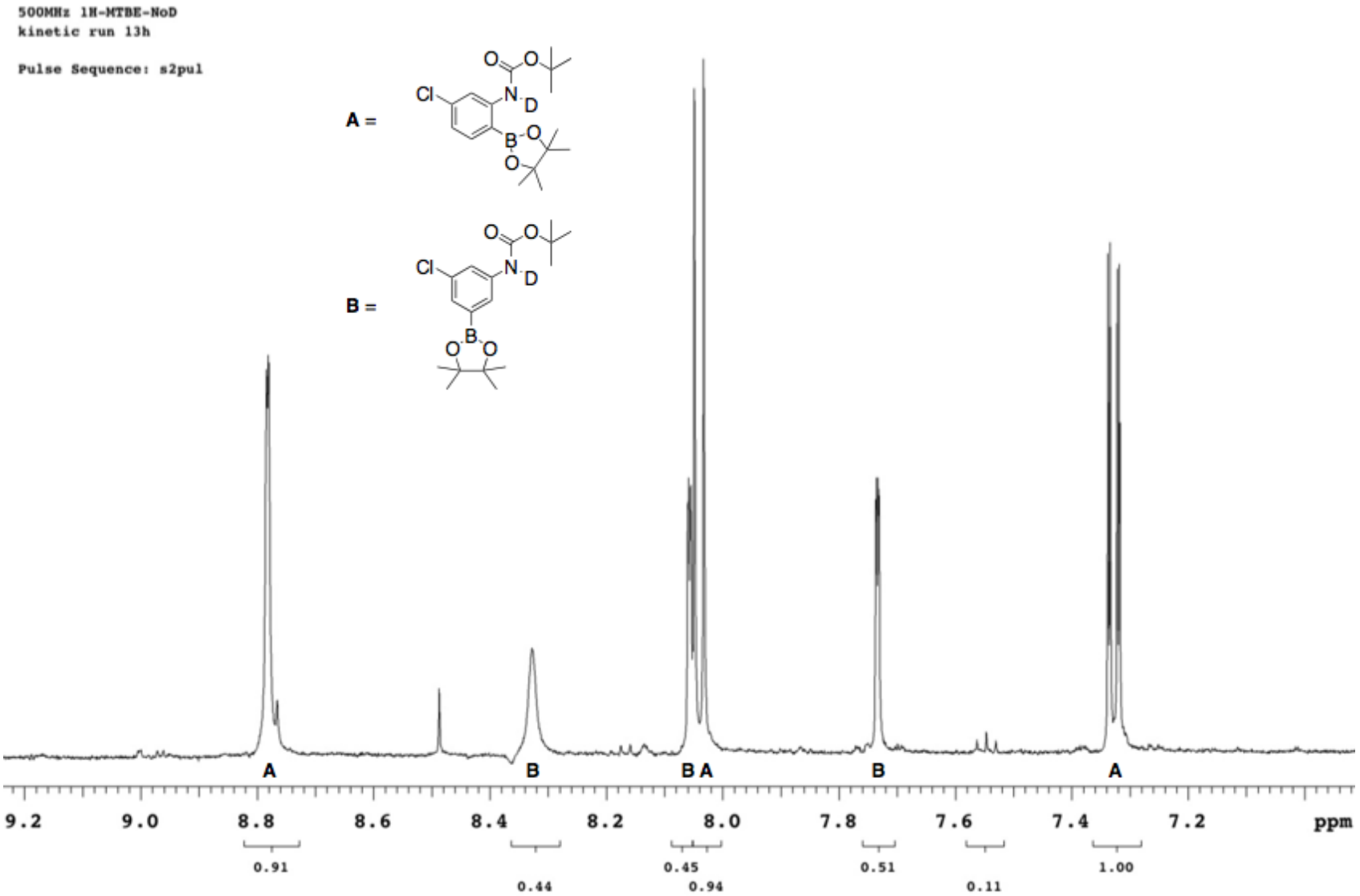


Figure. 500 MHz ^{1}H NMR spectrum of **8a-d_1** / **8b-d_1**

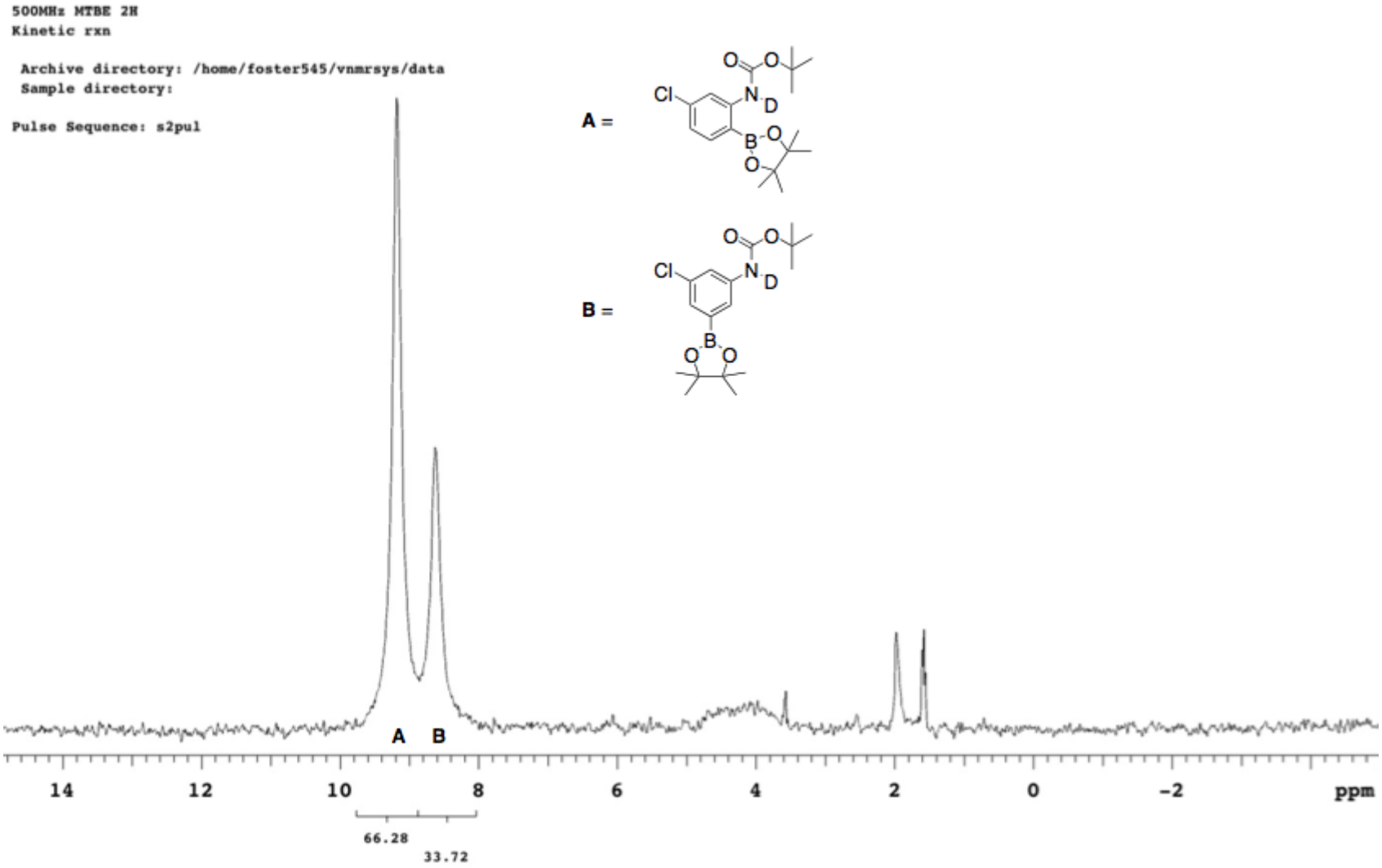


Figure. 77 MHz ^{2}H NMR spectrum of **8a-d_1** / **8b-d_1**

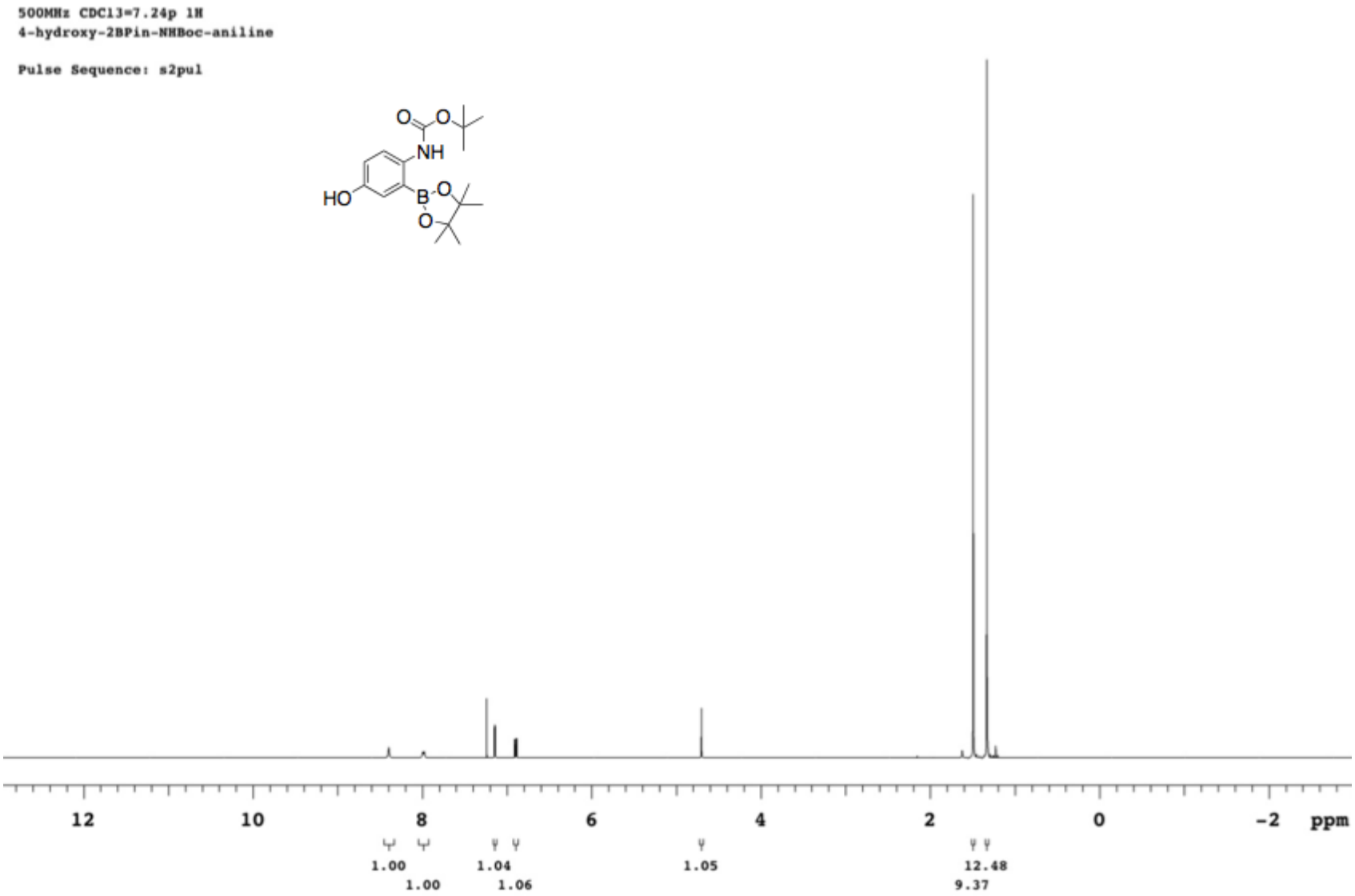


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entry 2**

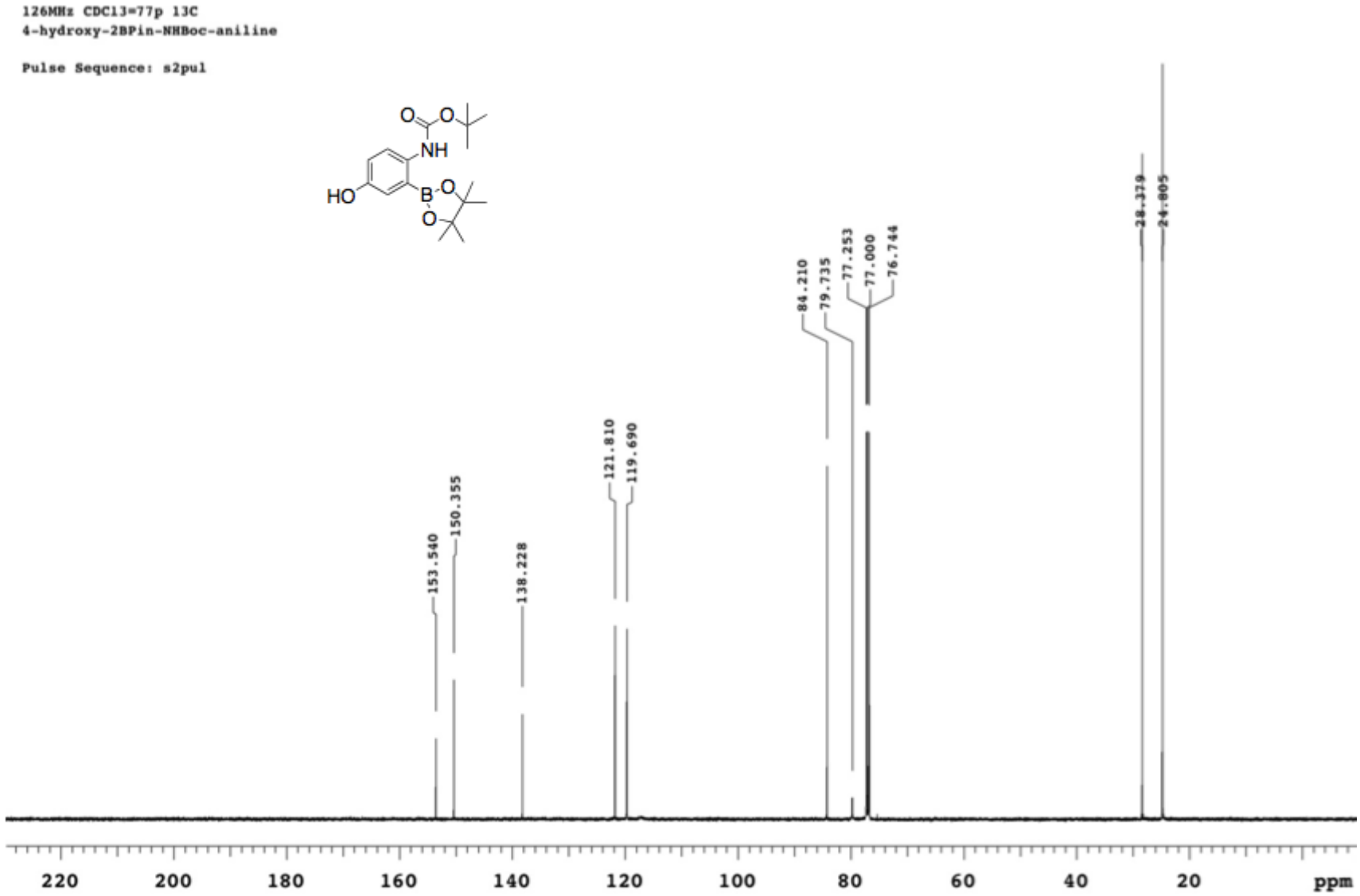


Figure. 126 MHz ^{13}C NMR spectrum of **Table 1, entry 2**

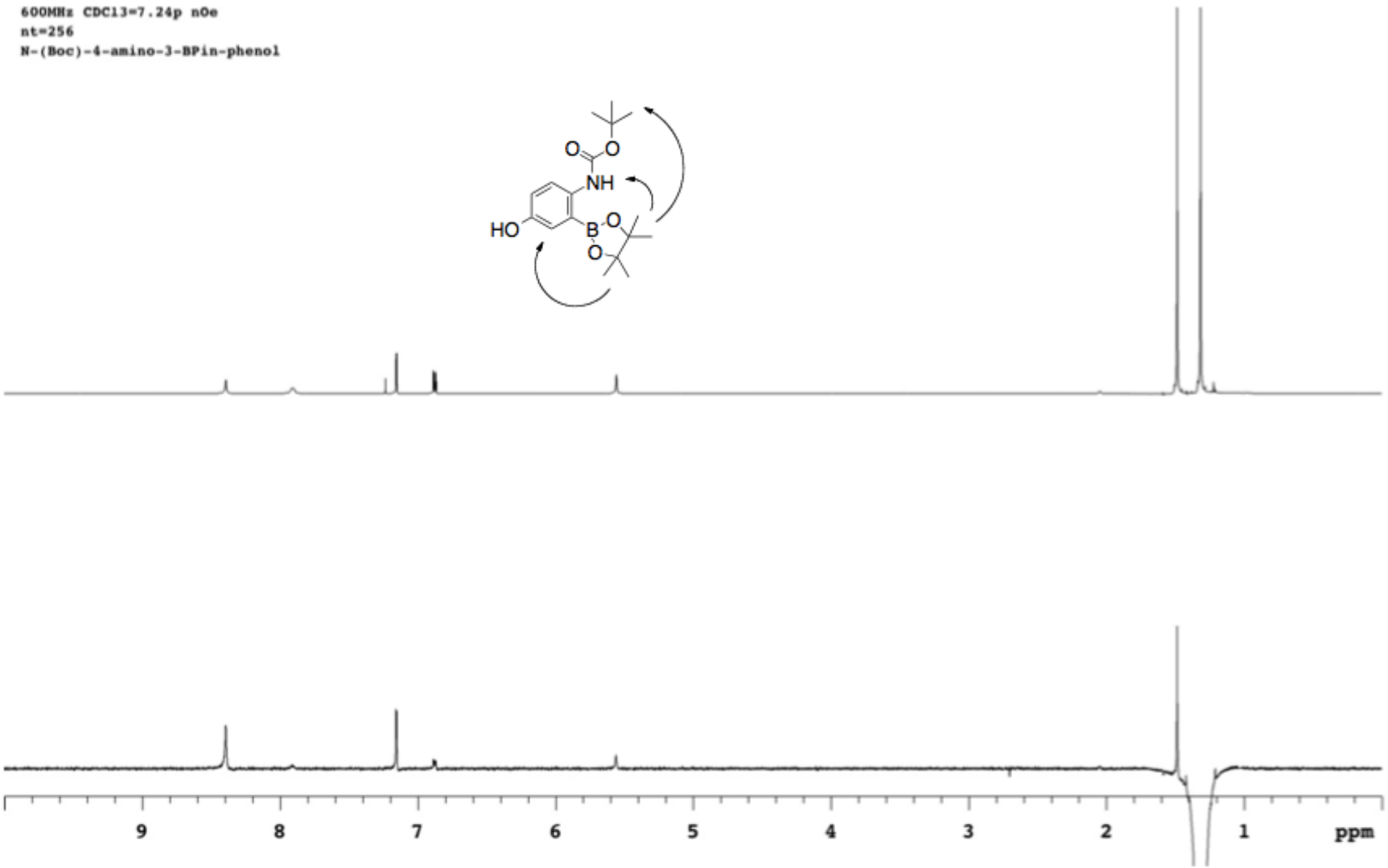


Figure. 600 MHz nOe NMR spectrum of **Table 1, entry 2**

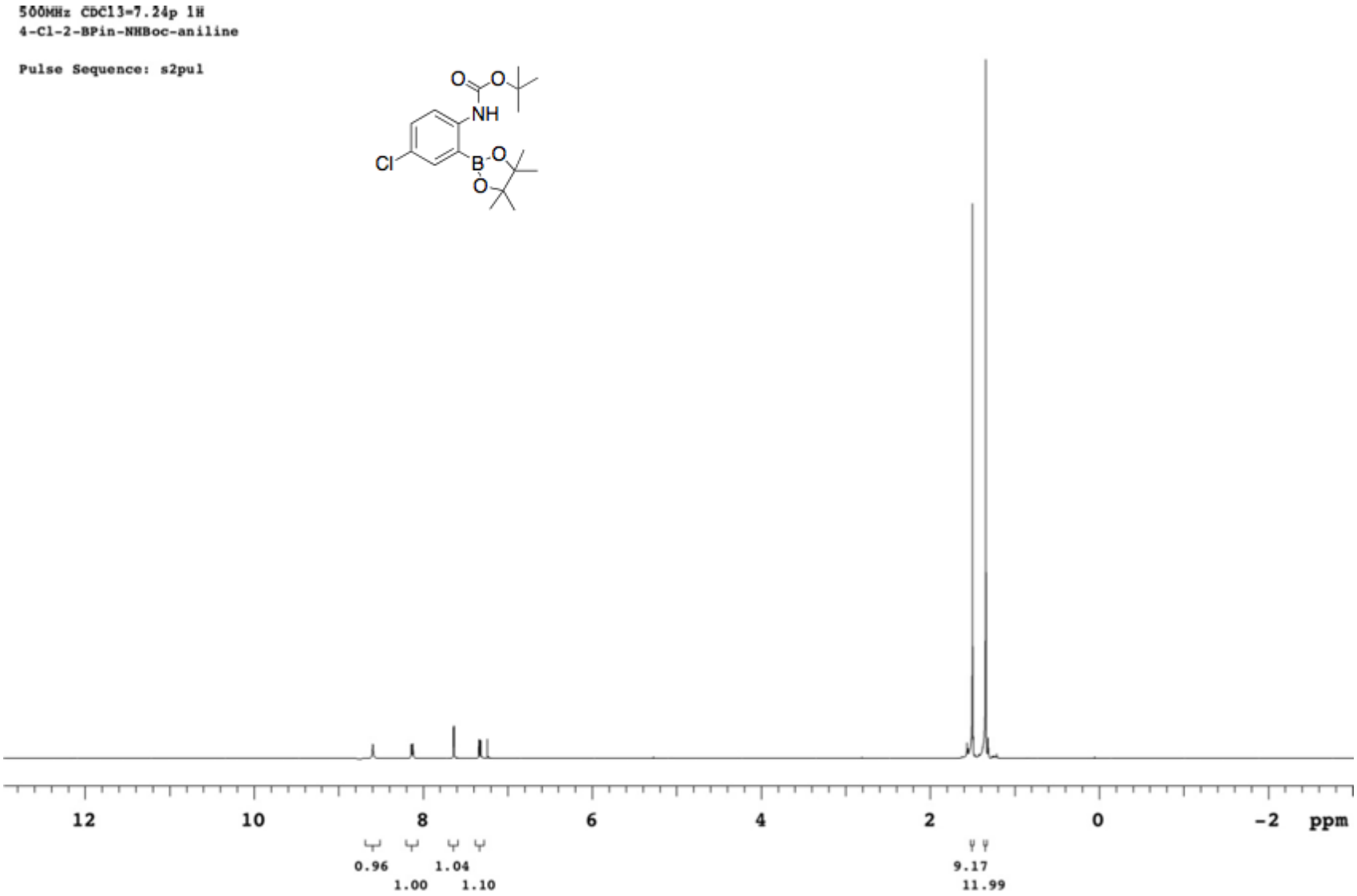


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entry 3**

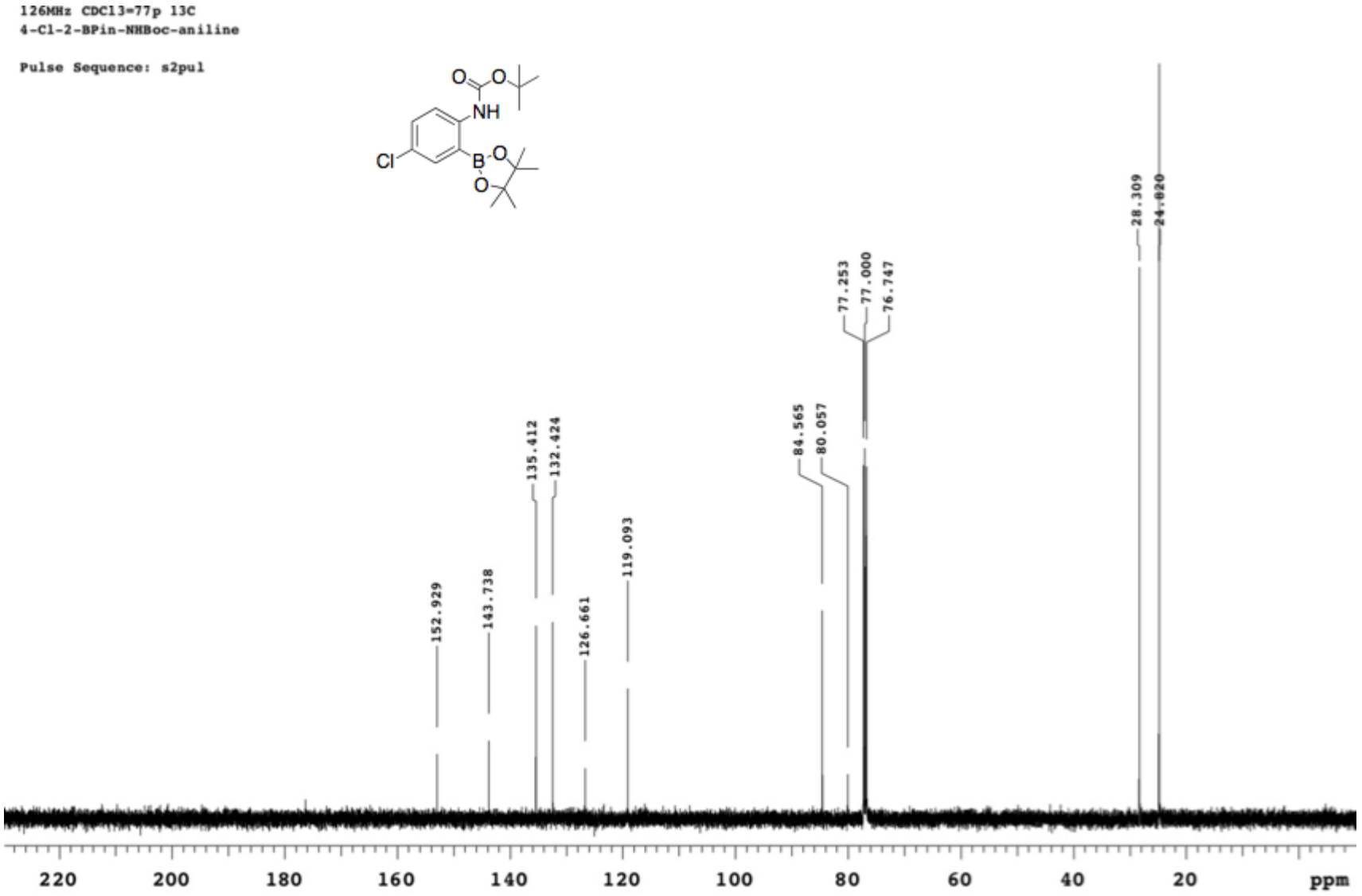


Figure. 126 MHz ^{13}C NMR spectrum of **Table 1, entry 3**

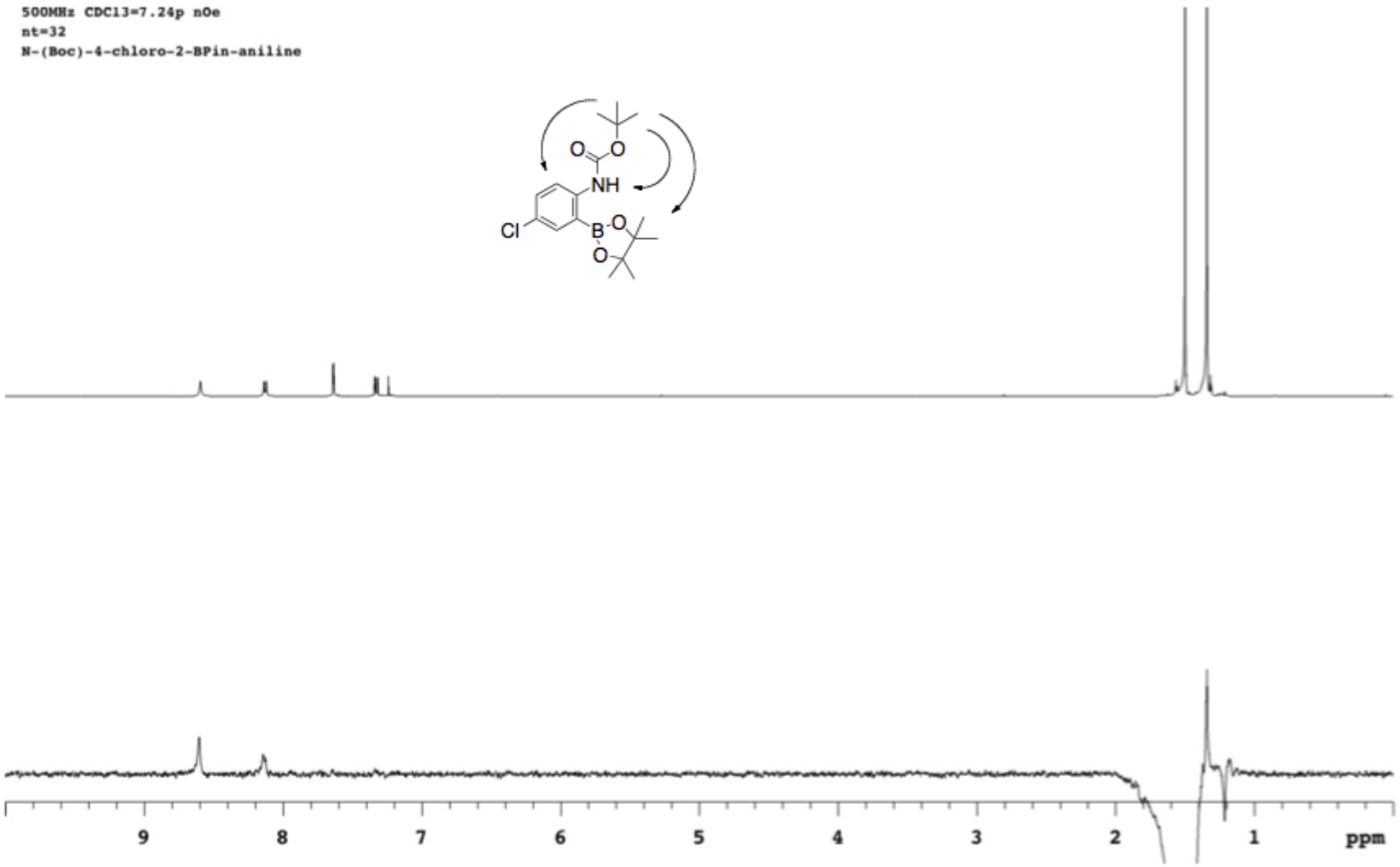


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 3**

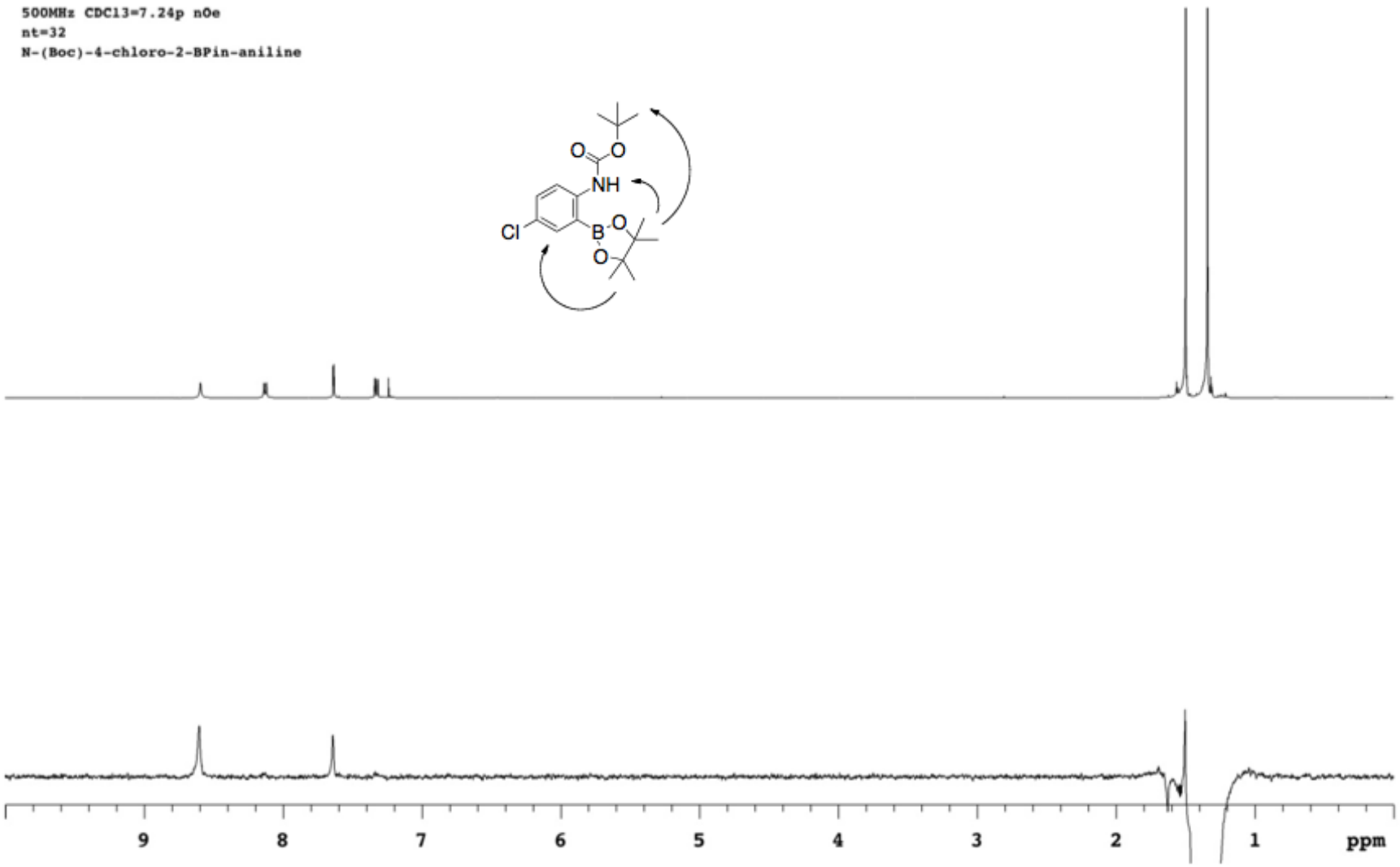


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 3**

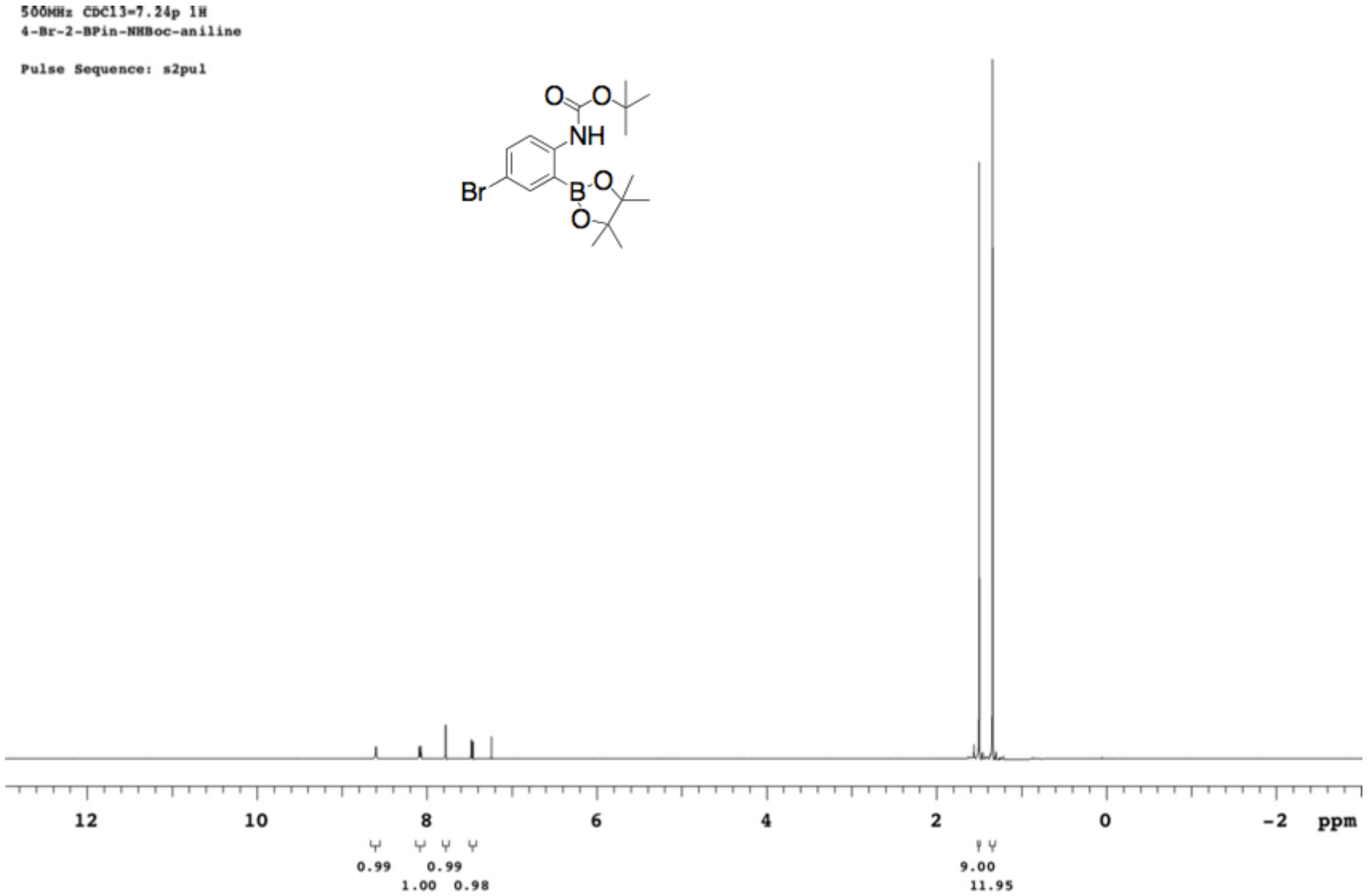


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entry 4**

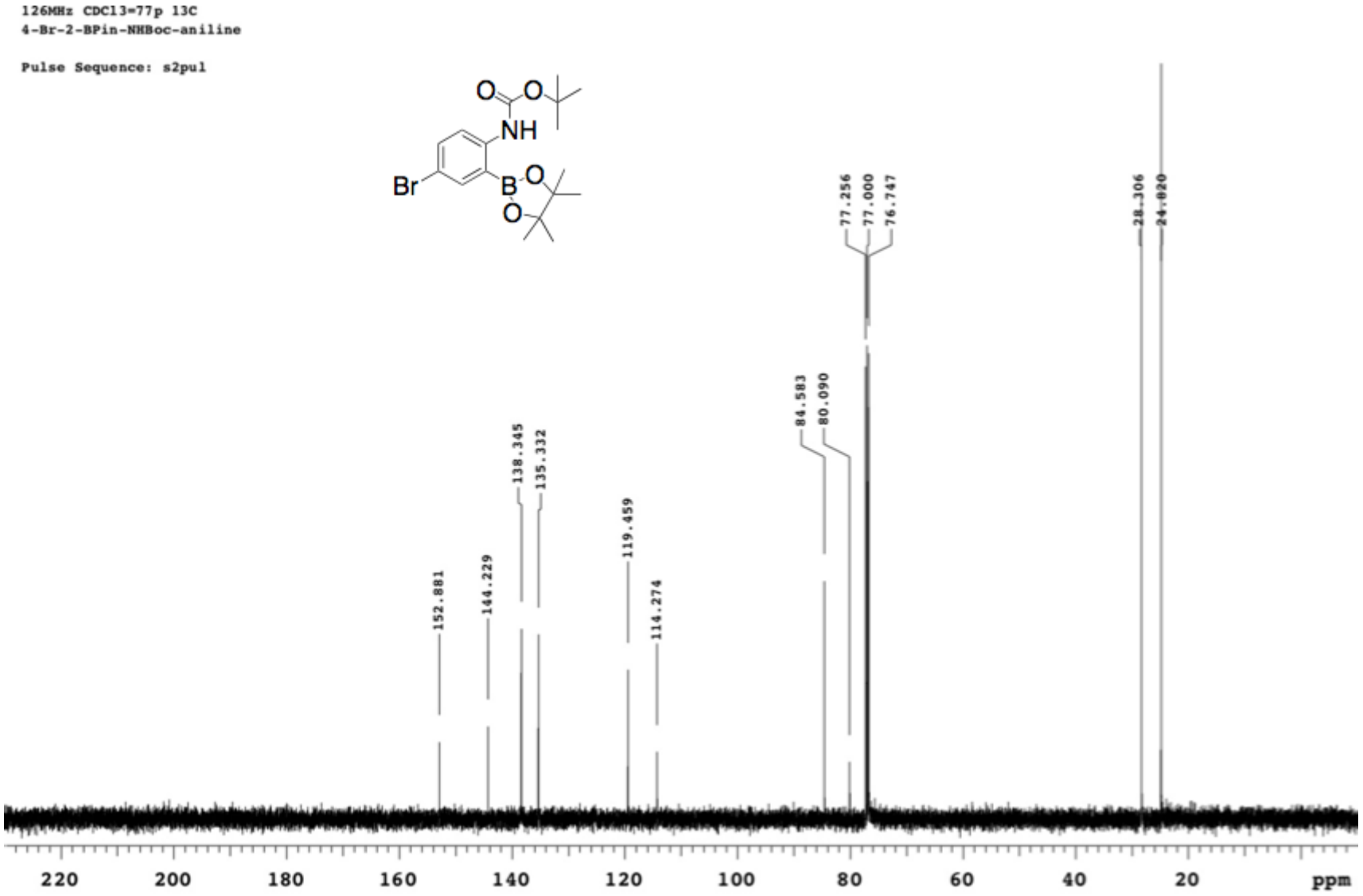


Figure. 126 MHz ^{13}C NMR spectrum of **Table 1, entry 4**

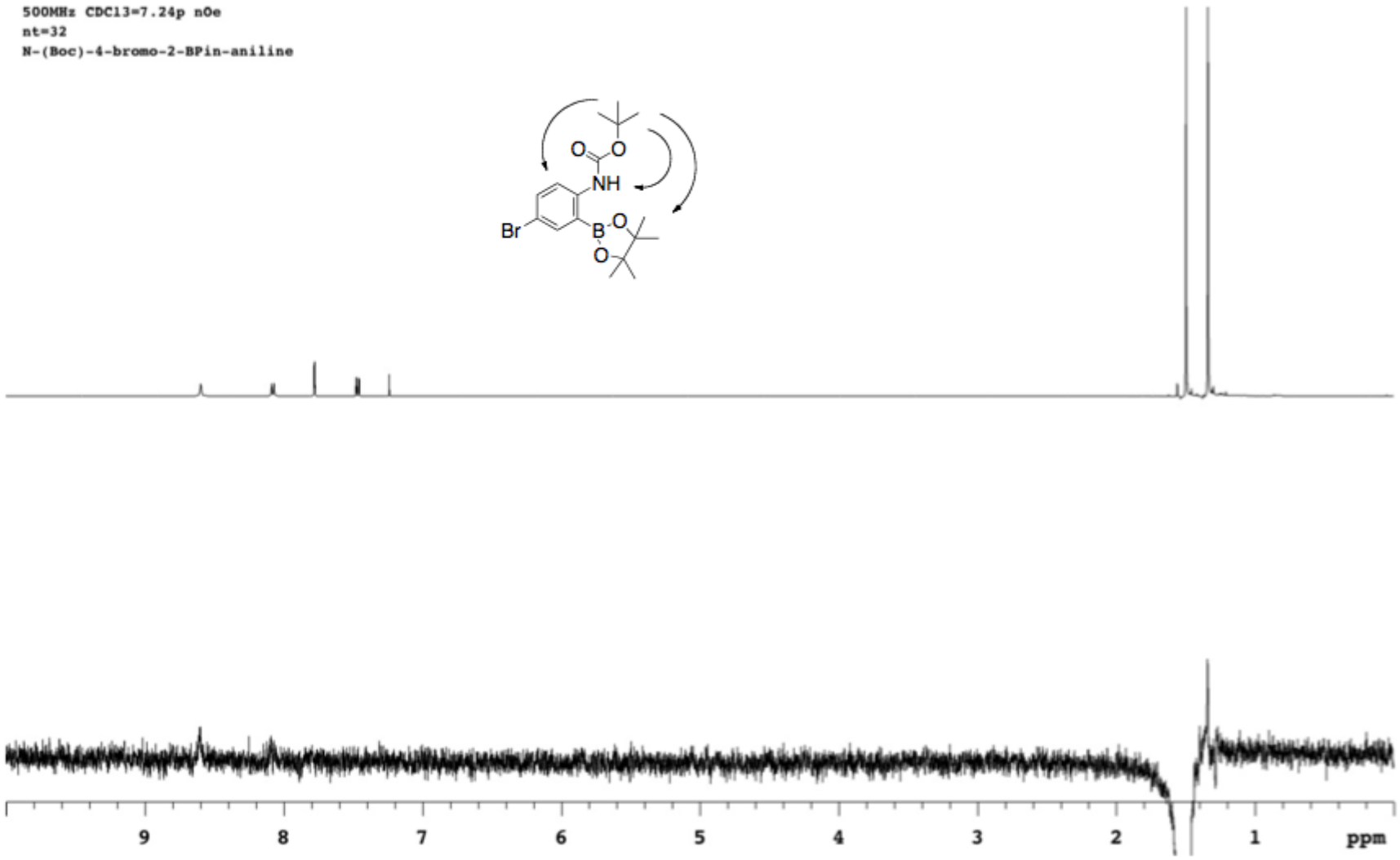


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 4**

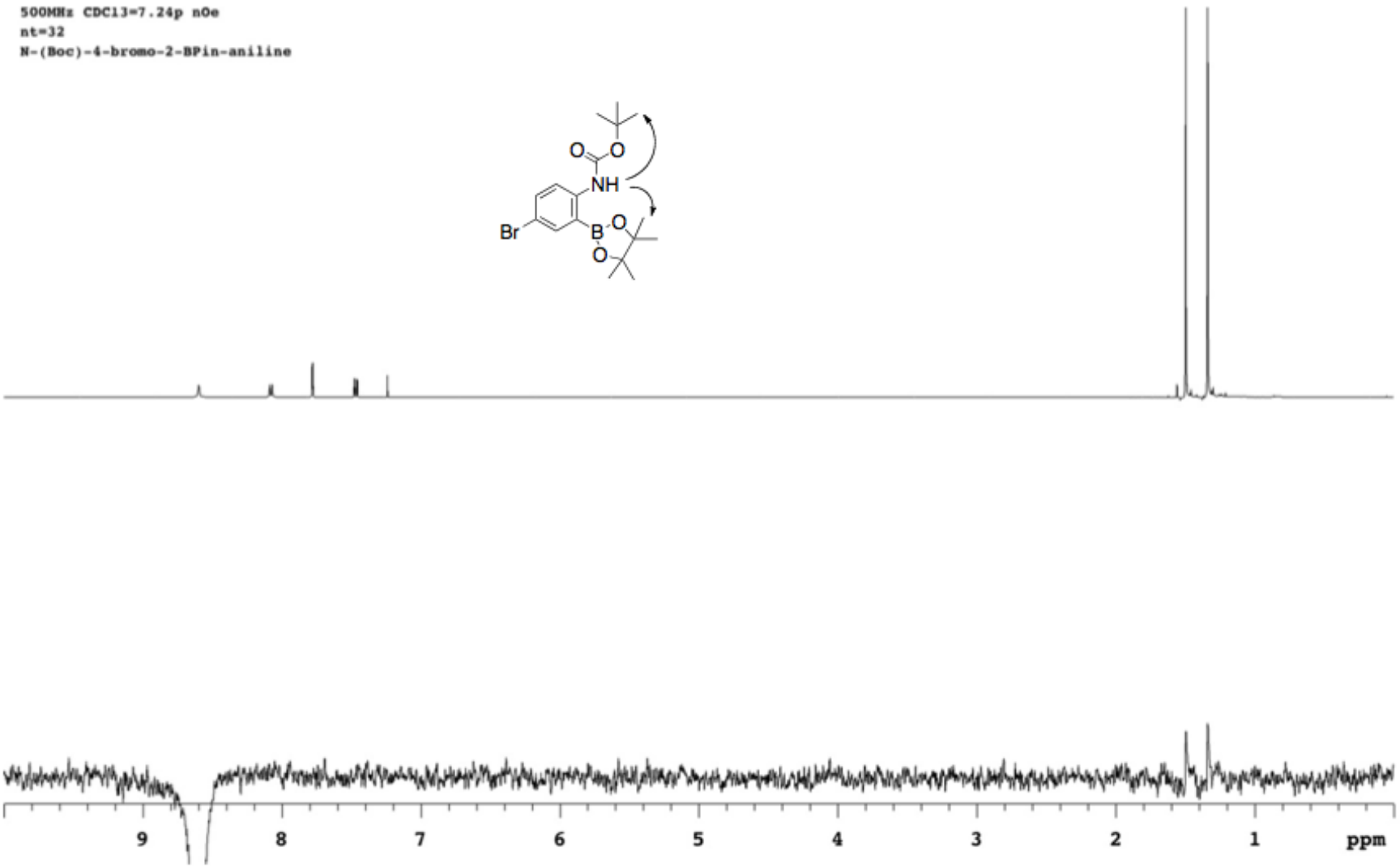


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 4**

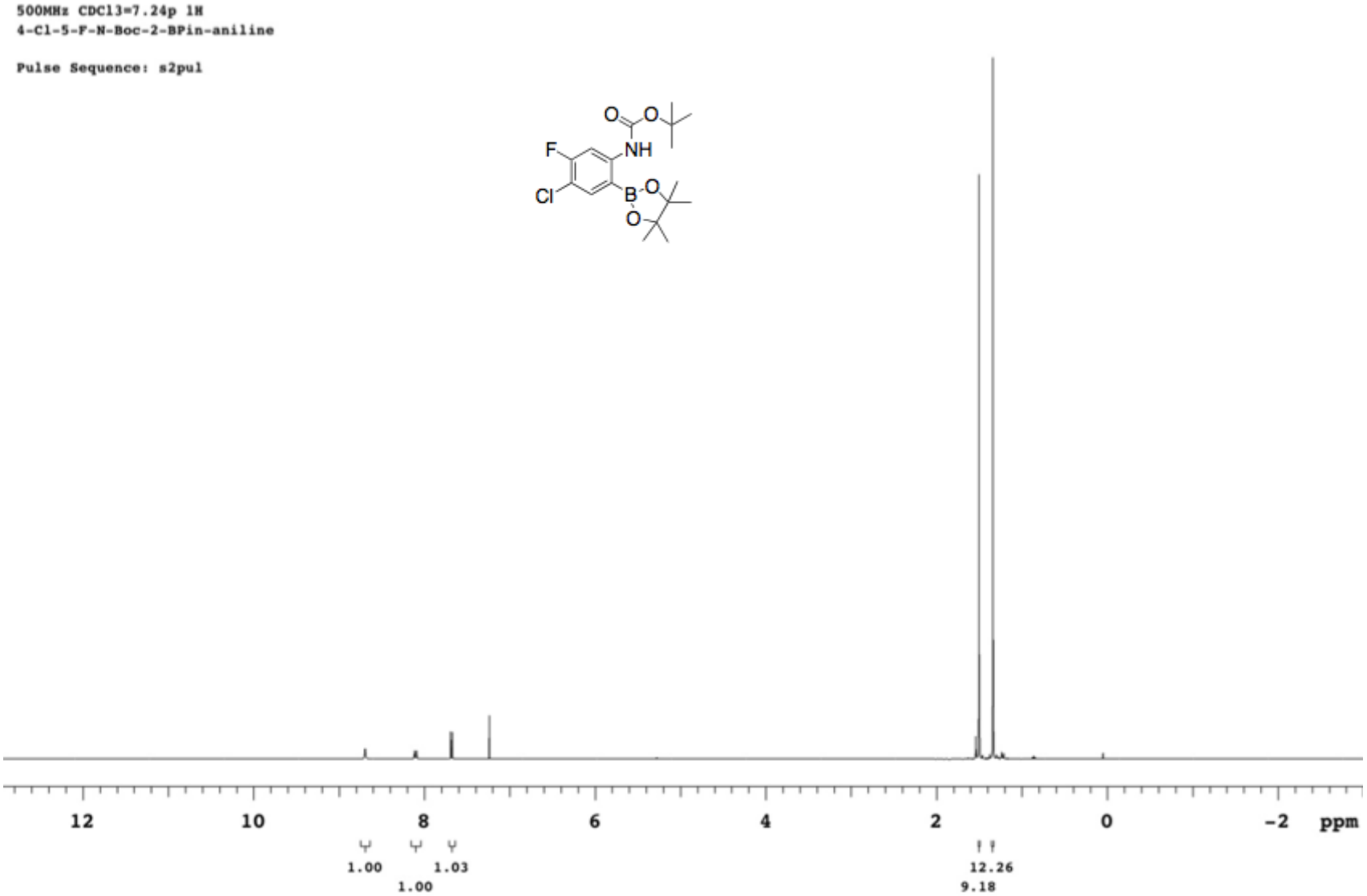


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entry 5**

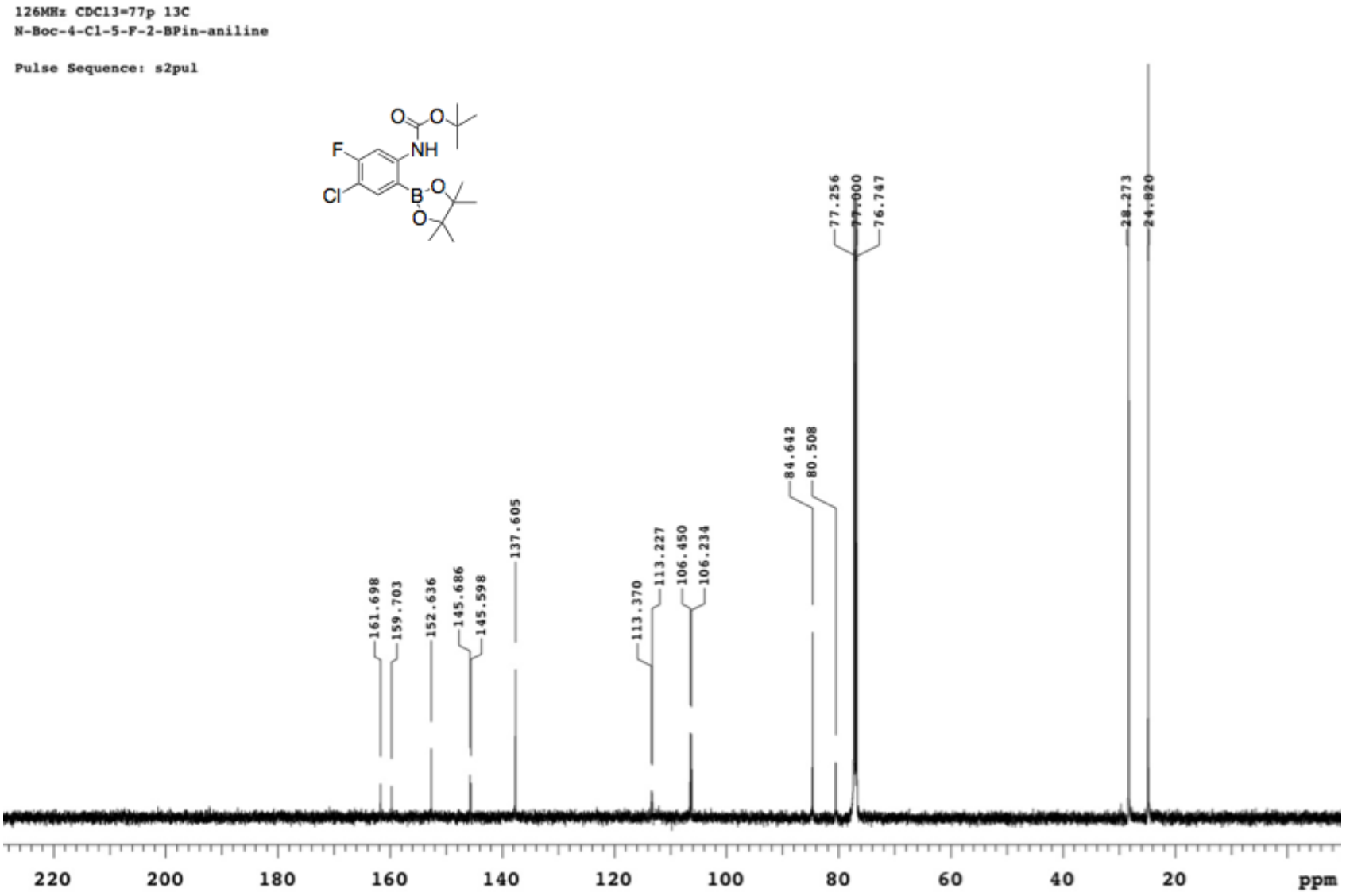


Figure. 126 MHz ^{13}C NMR spectrum of **Table 1, entry 5**

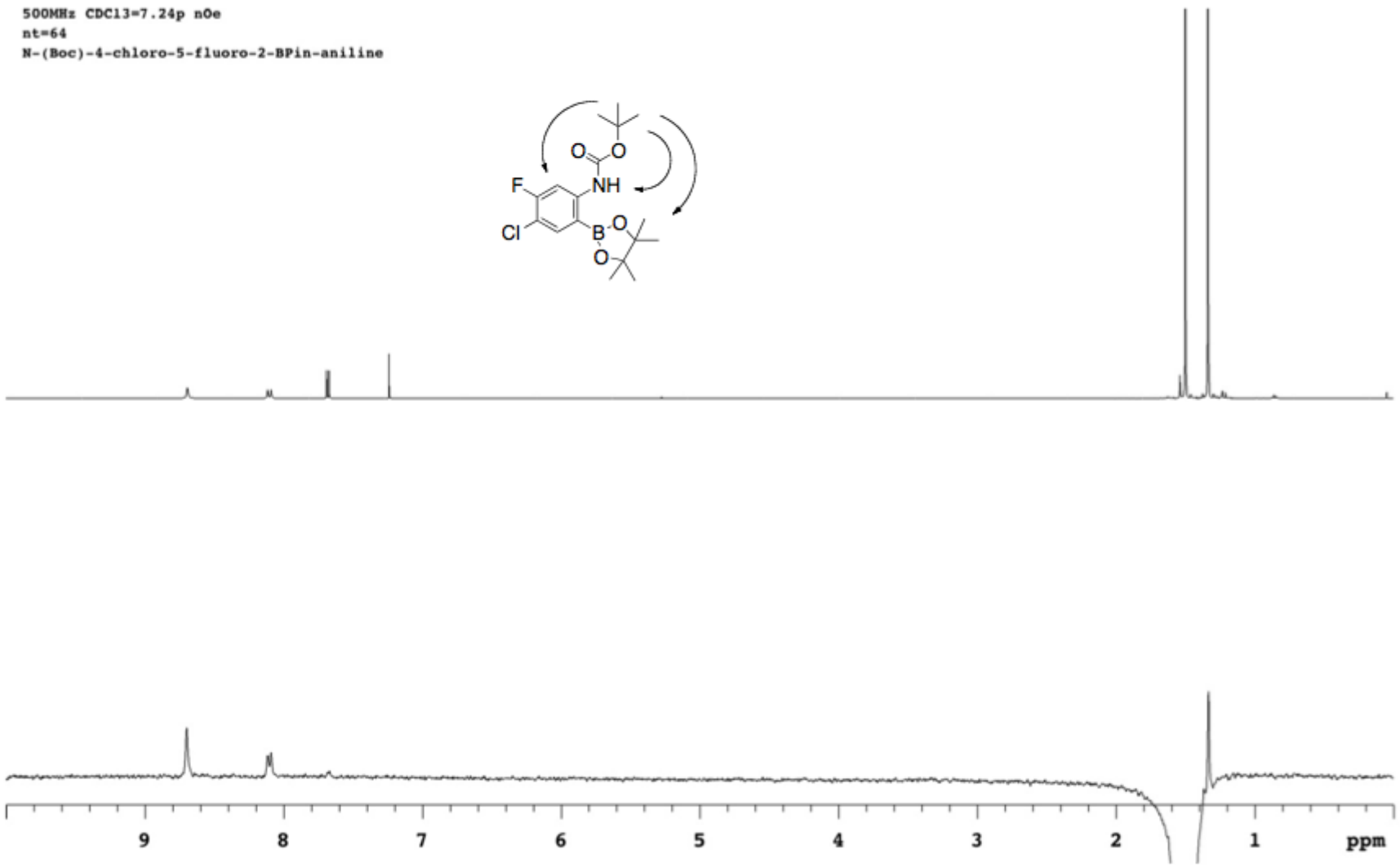


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 5**

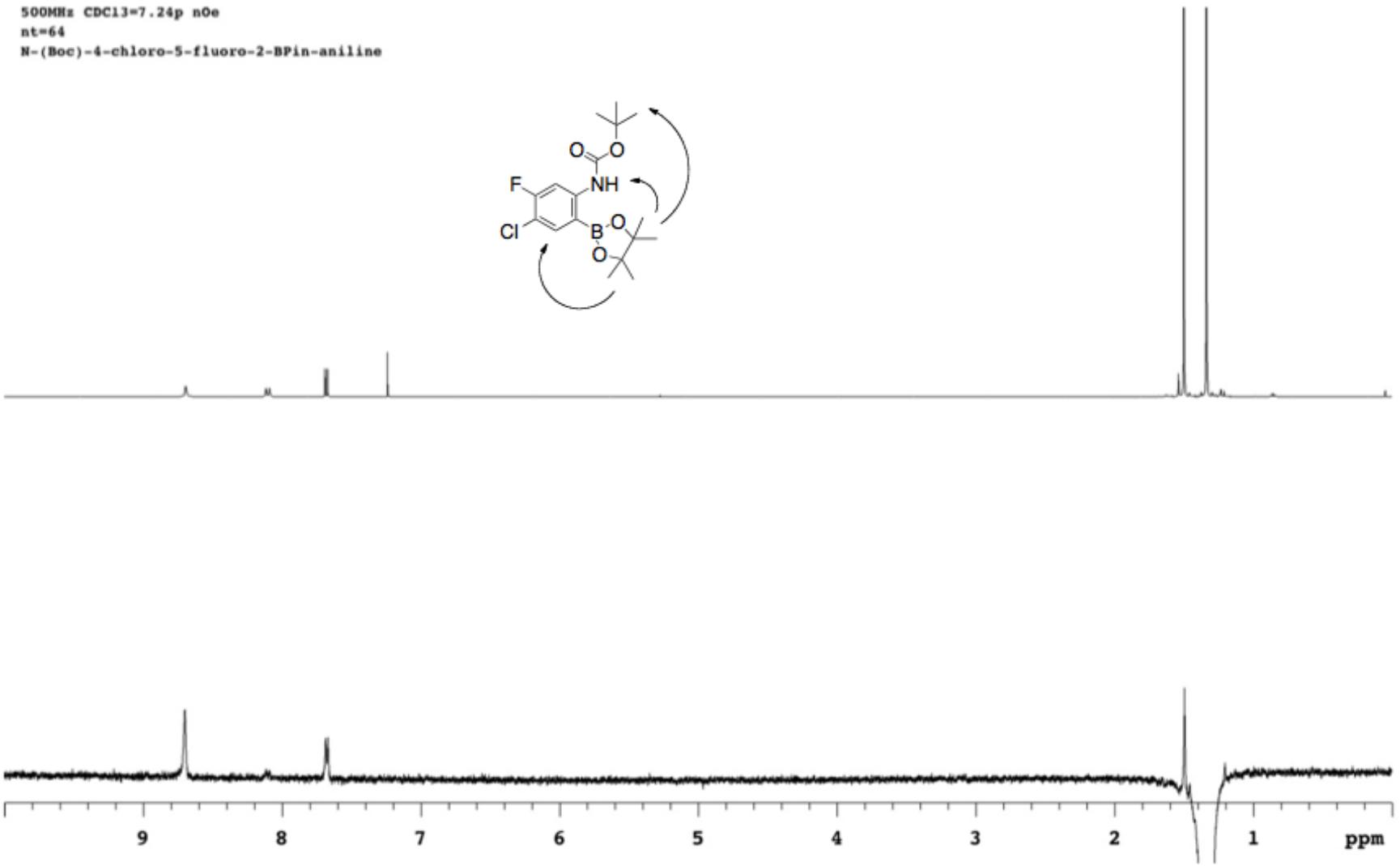


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 5**

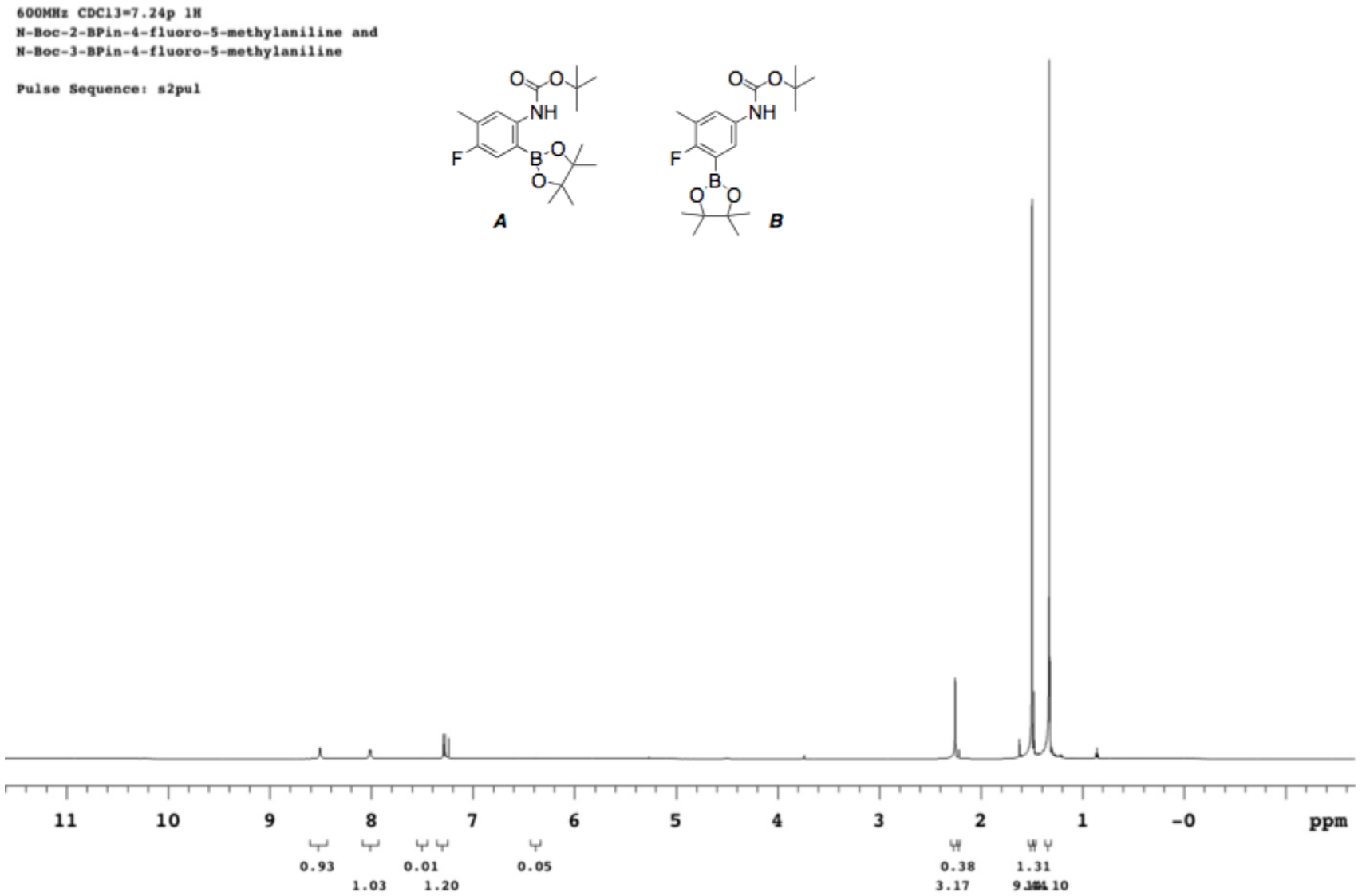


Figure. 600 MHz ^{1}H NMR spectrum of **Table 1, entry 6A** / **Table 1, entry 6B**

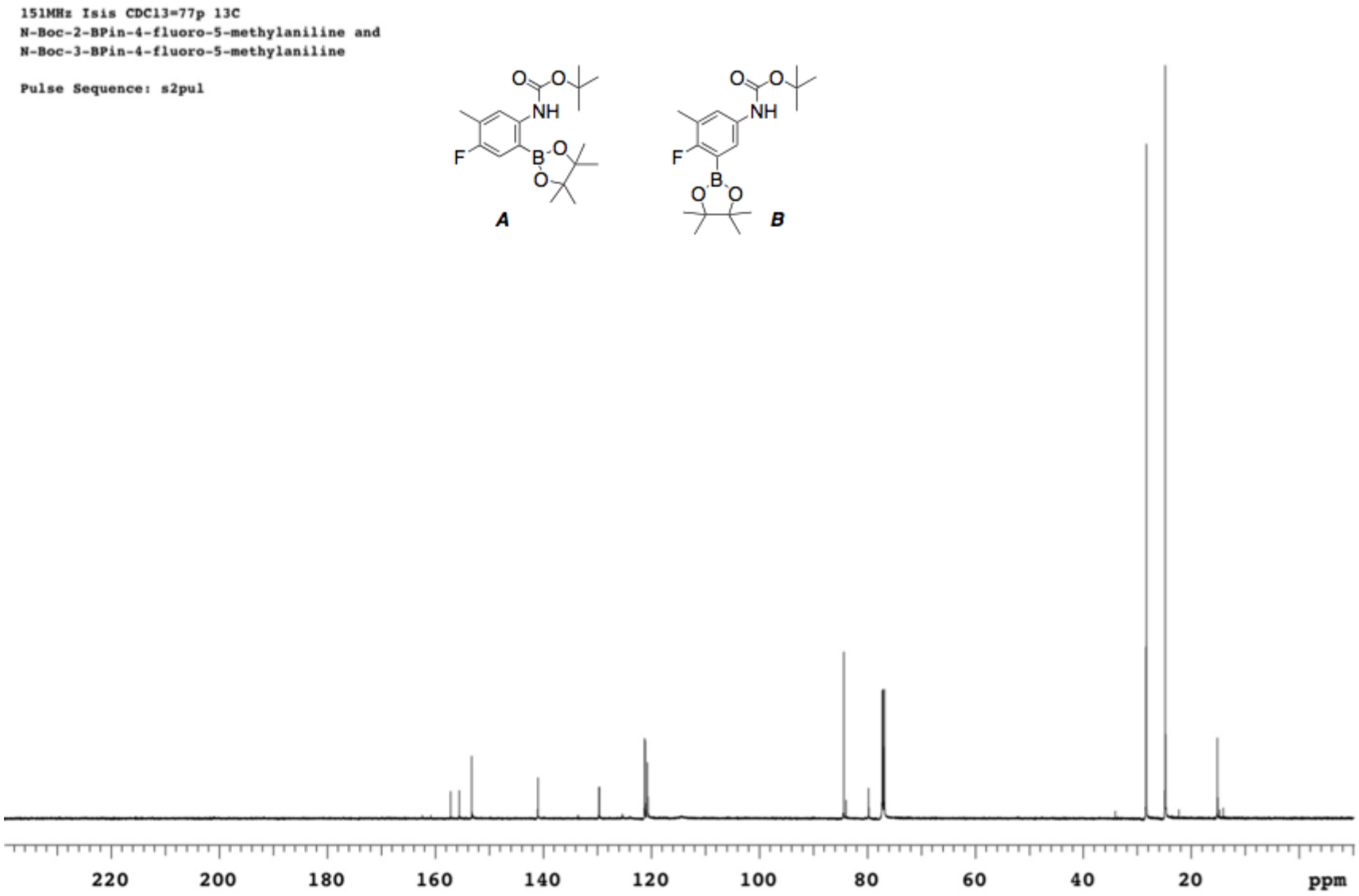


Figure. 151 MHz ^{13}C NMR spectrum of **Table 1, entry 6A / Table 1, entry 6B**

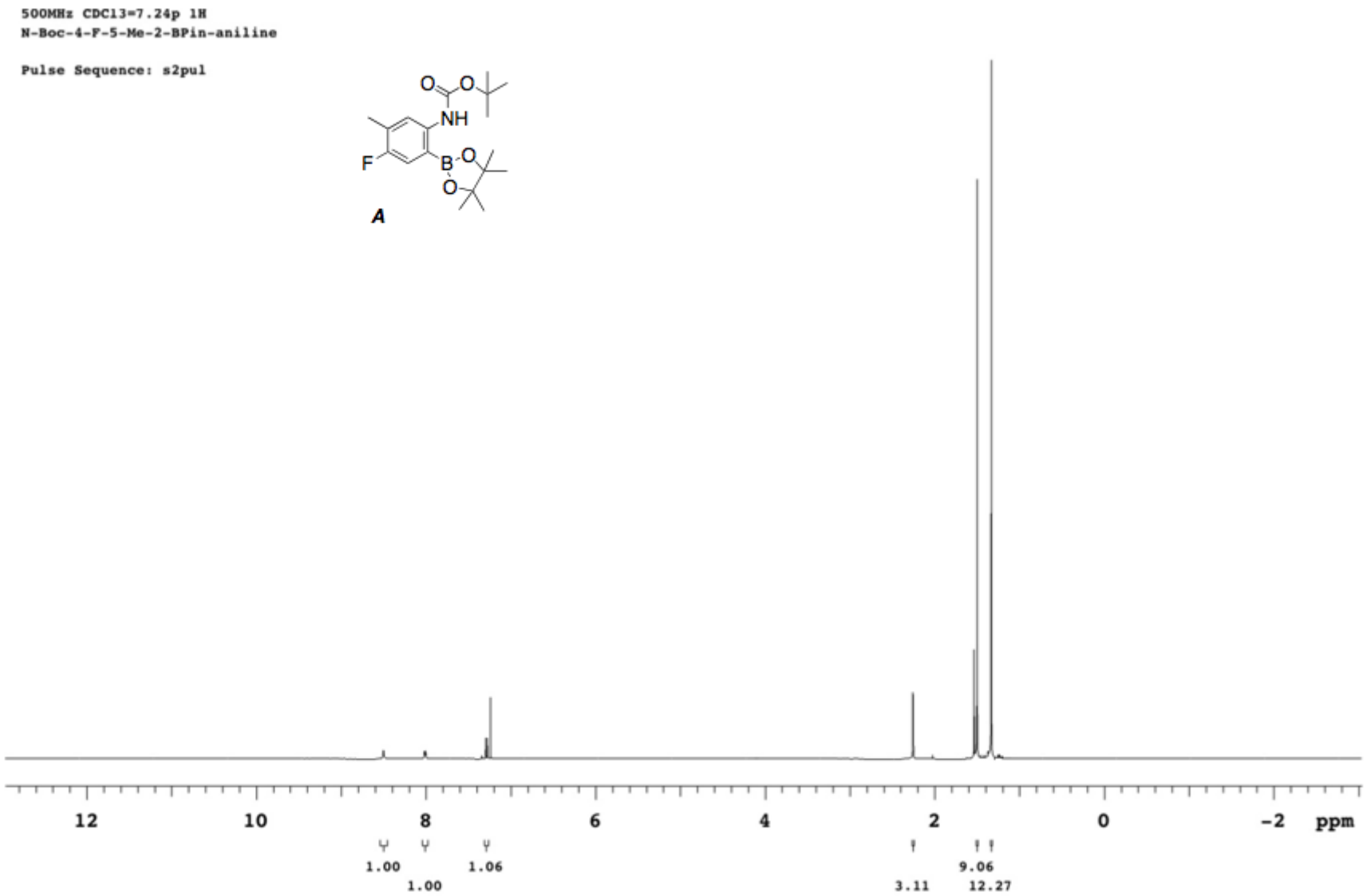


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entry 6A**

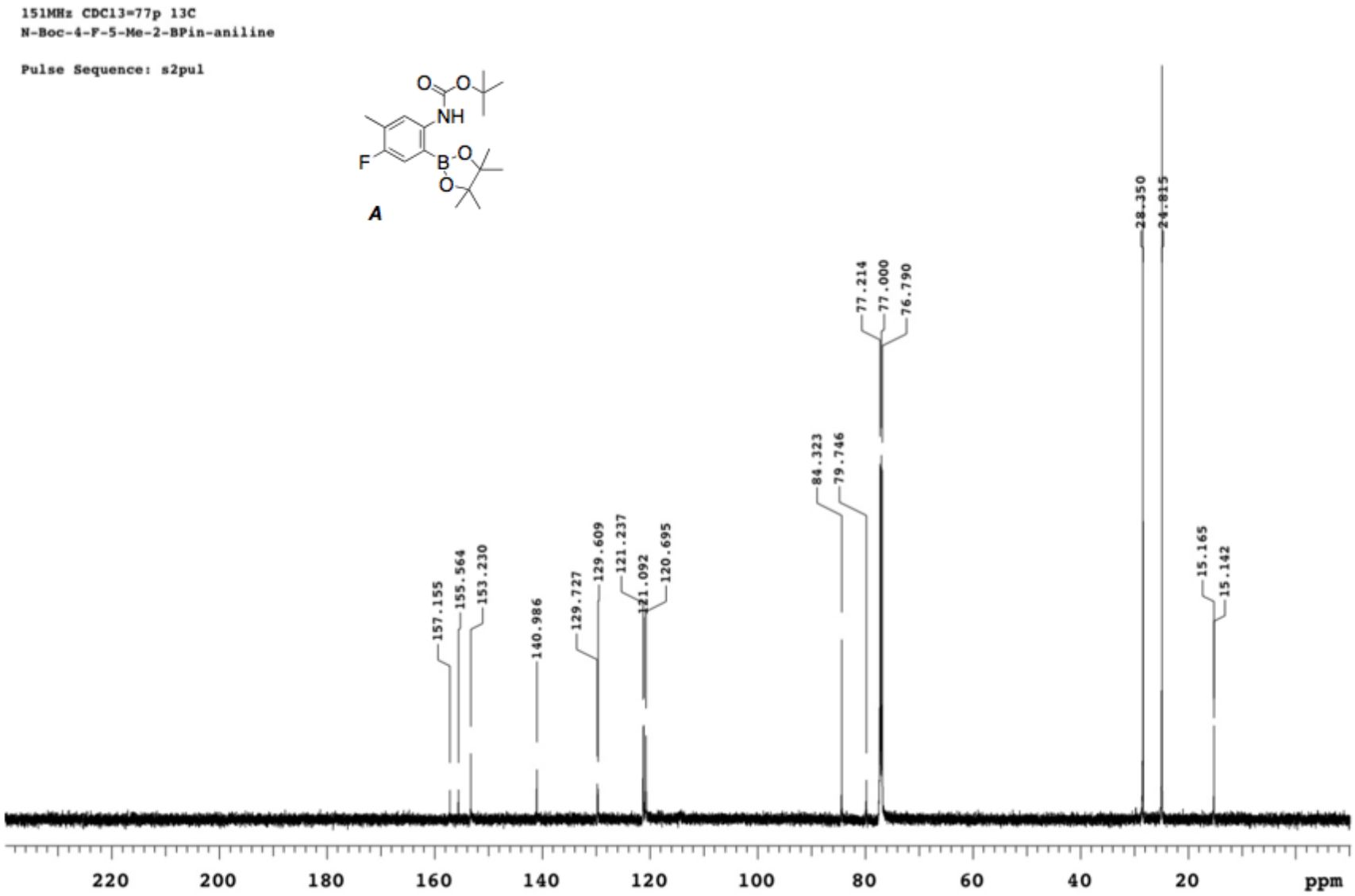


Figure. 151 MHz ^{13}C NMR spectrum of **Table 1, entry 6A**

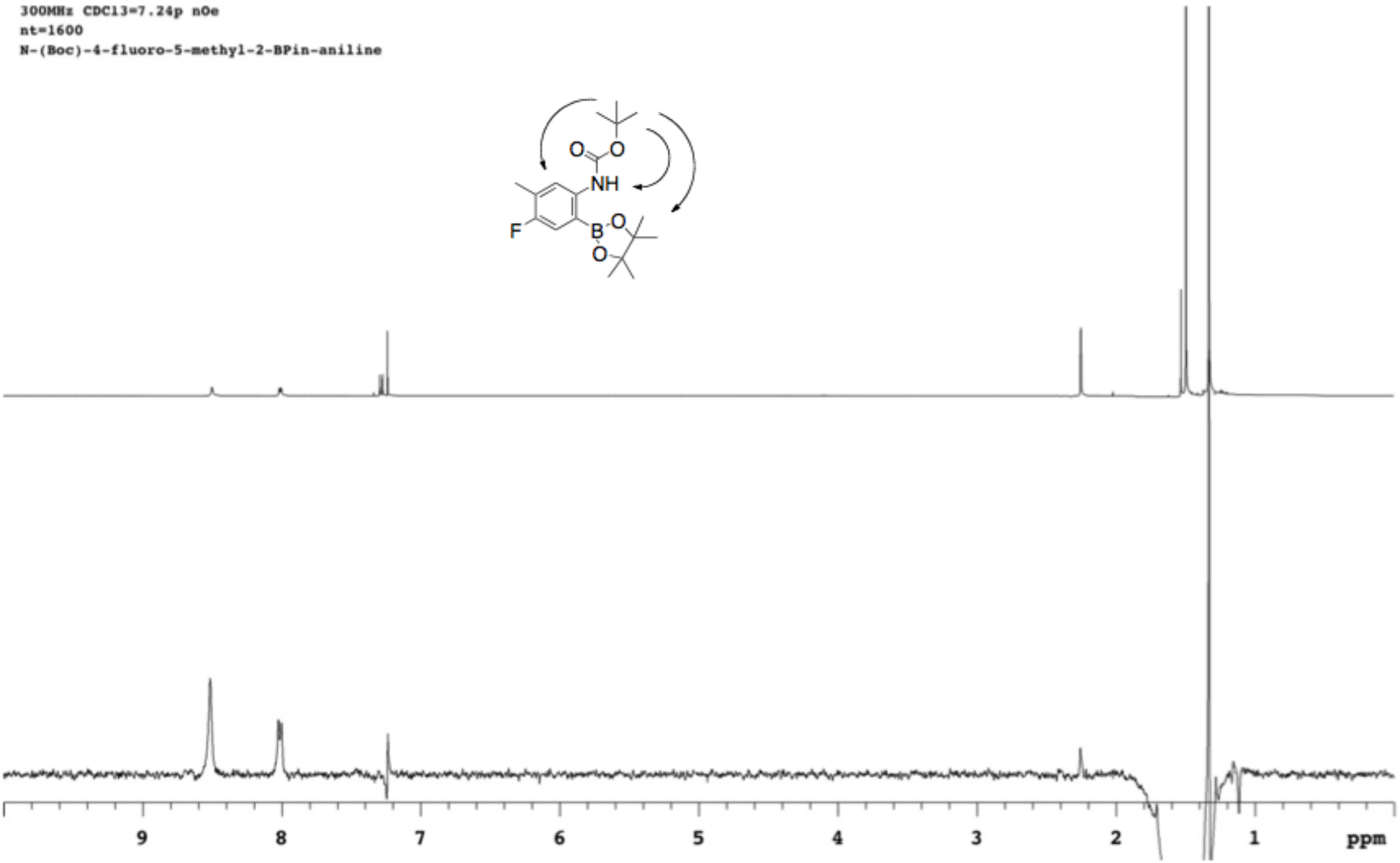


Figure. 300 MHz nOe NMR spectrum of **Table 1, entry 6A**

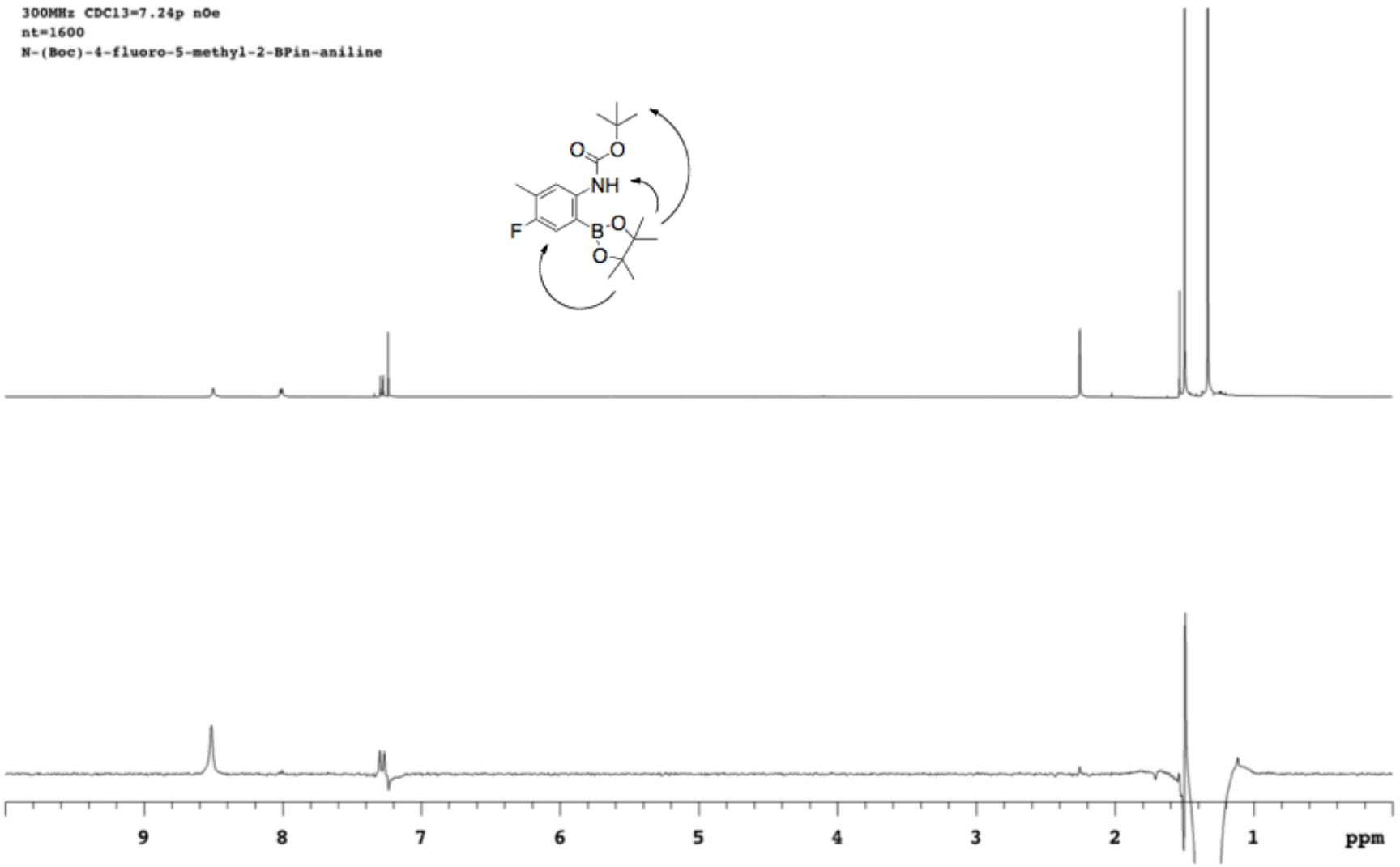


Figure. 300 MHz nOe NMR spectrum of **Table 1, entry 6A**

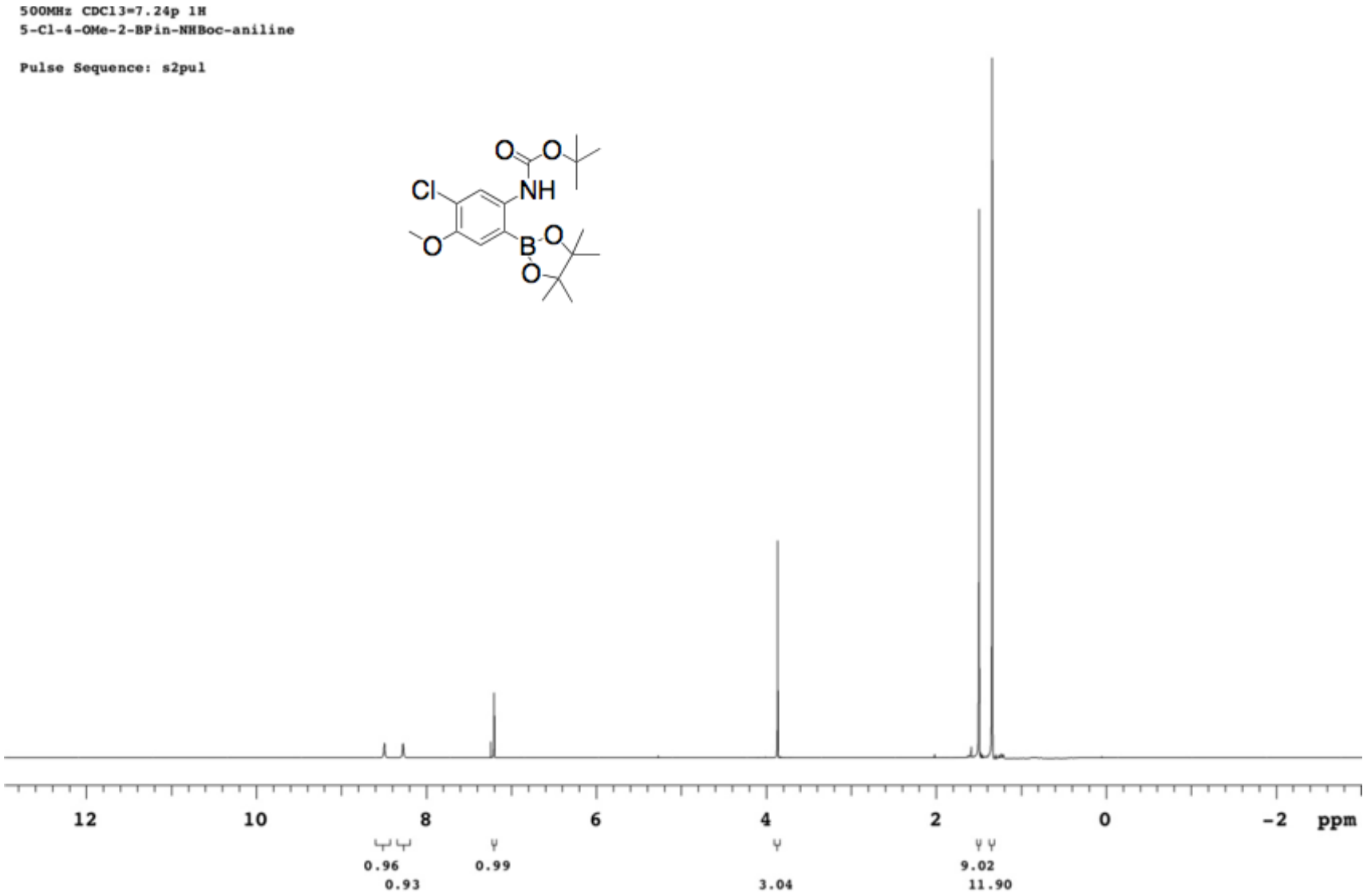


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entrty 7**

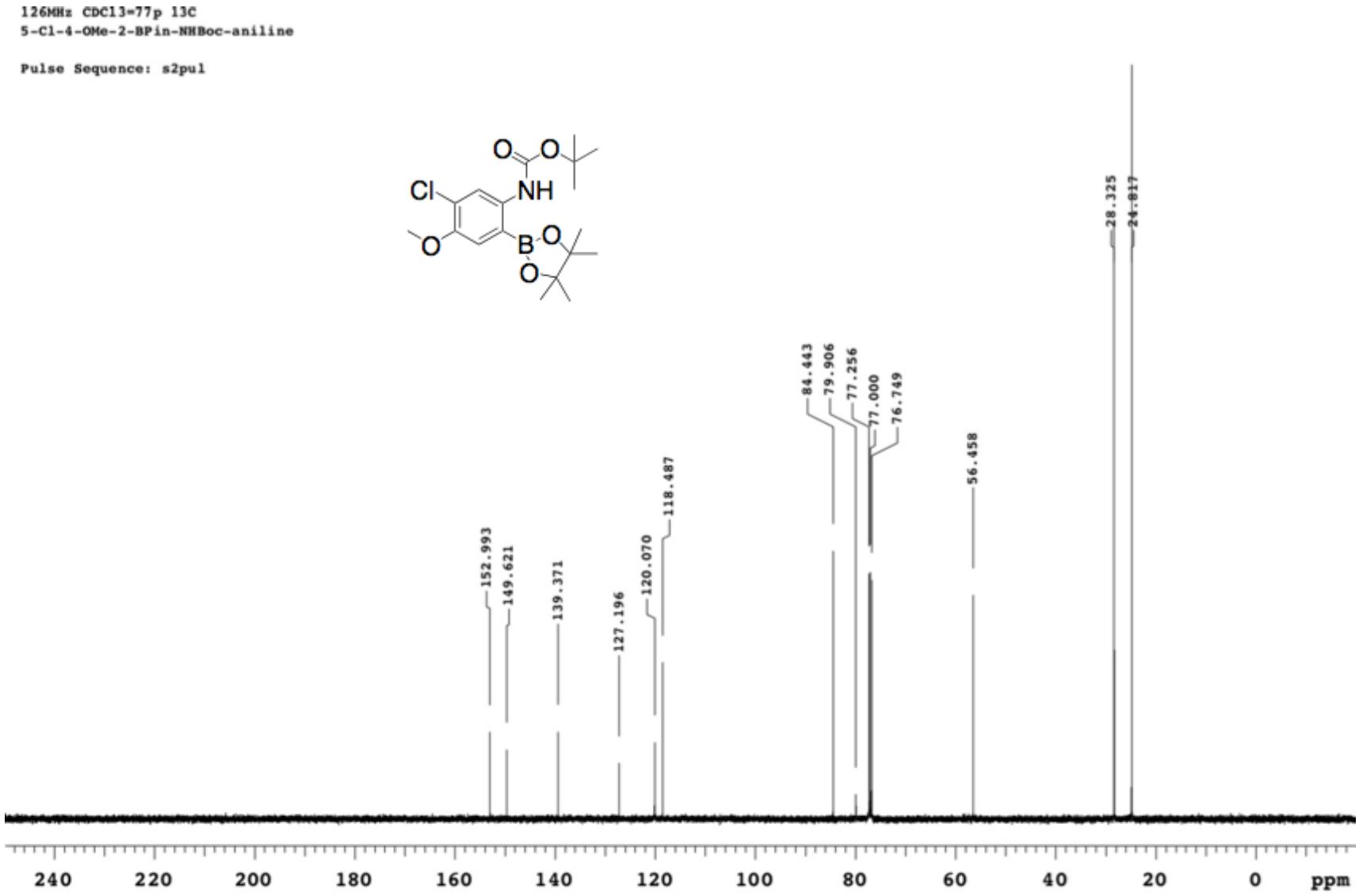


Figure. 126 MHz ^{13}C NMR spectrum of **Table 1, entry 7**

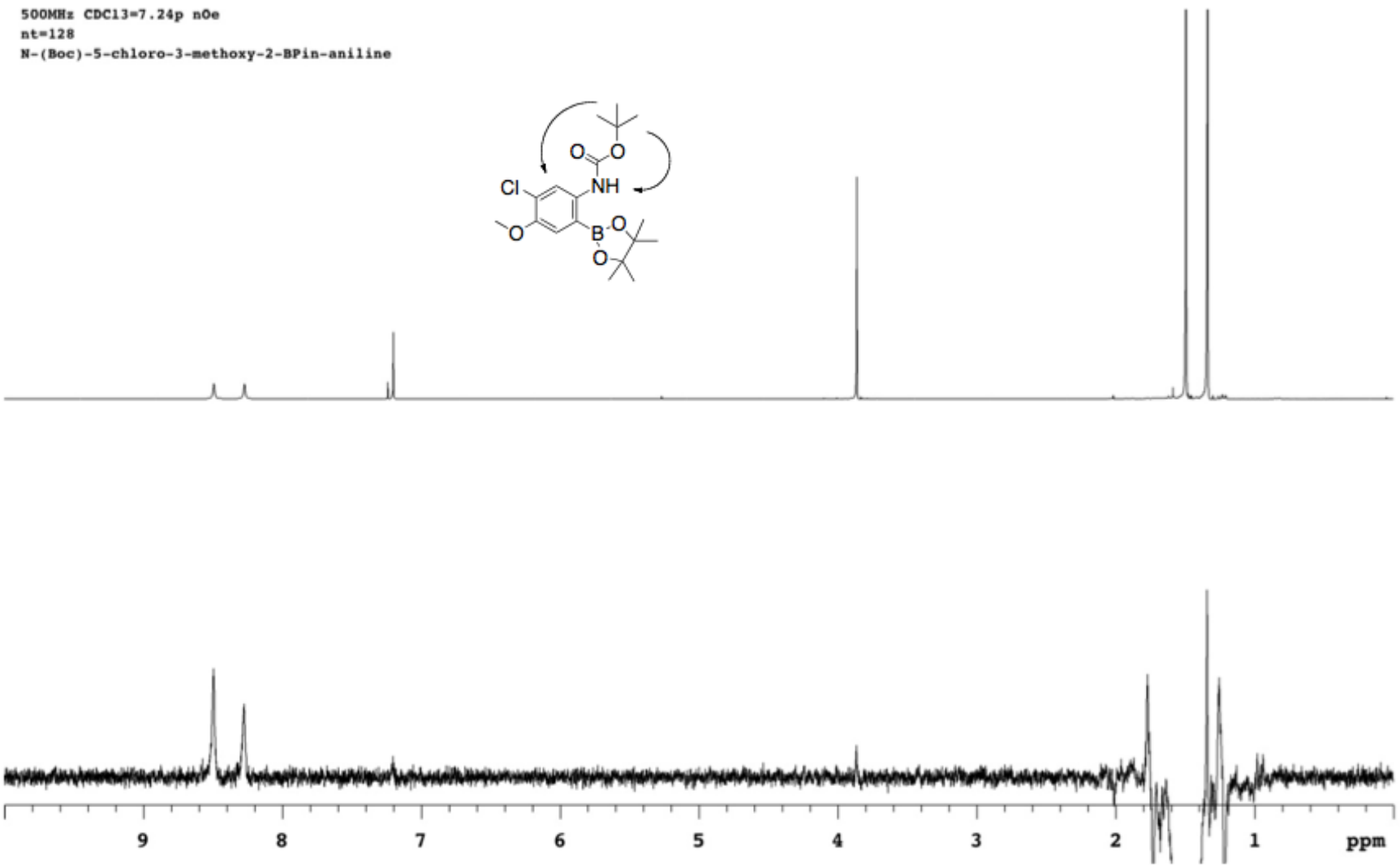


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 7**

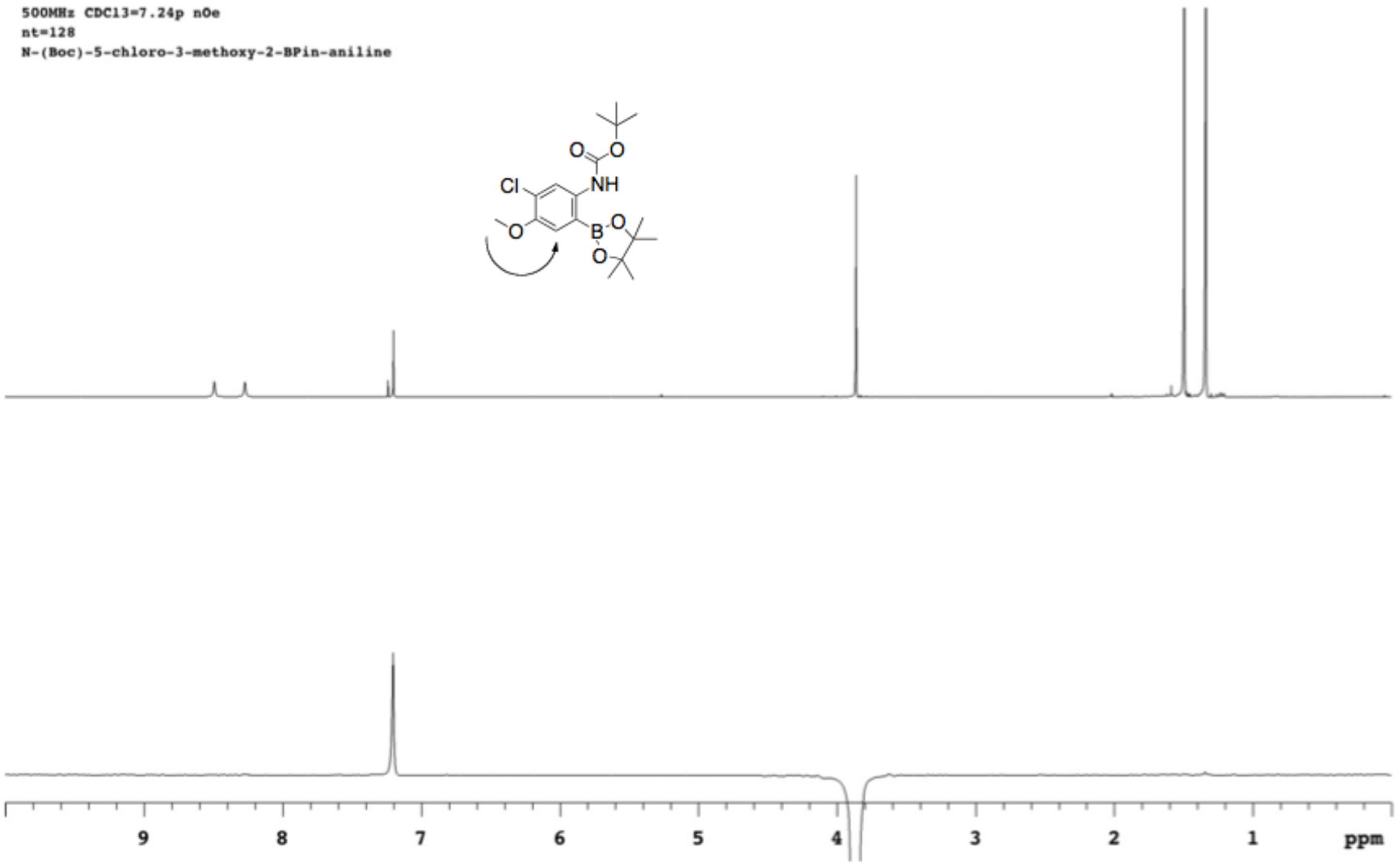


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 7**

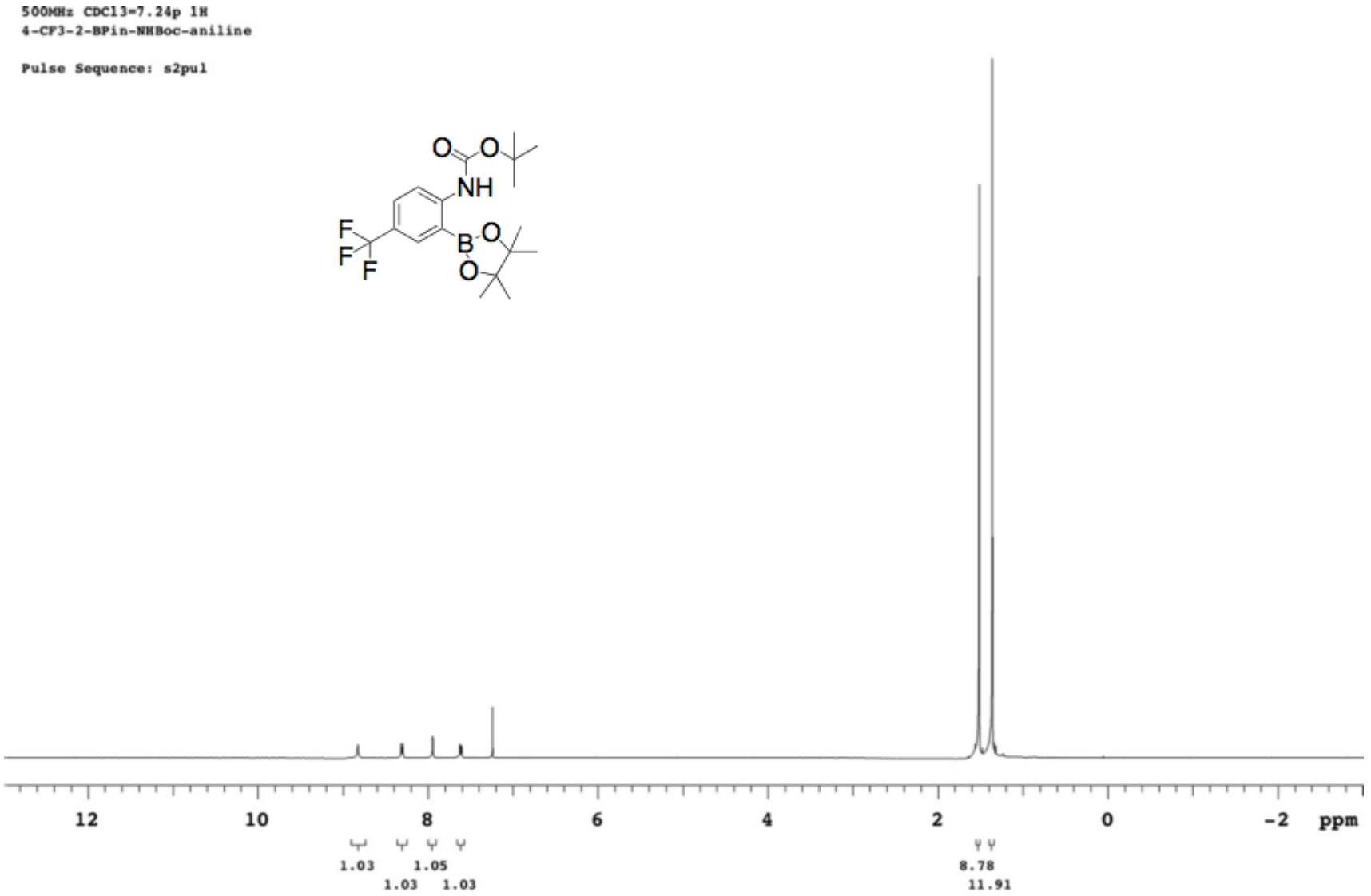


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entry 8**

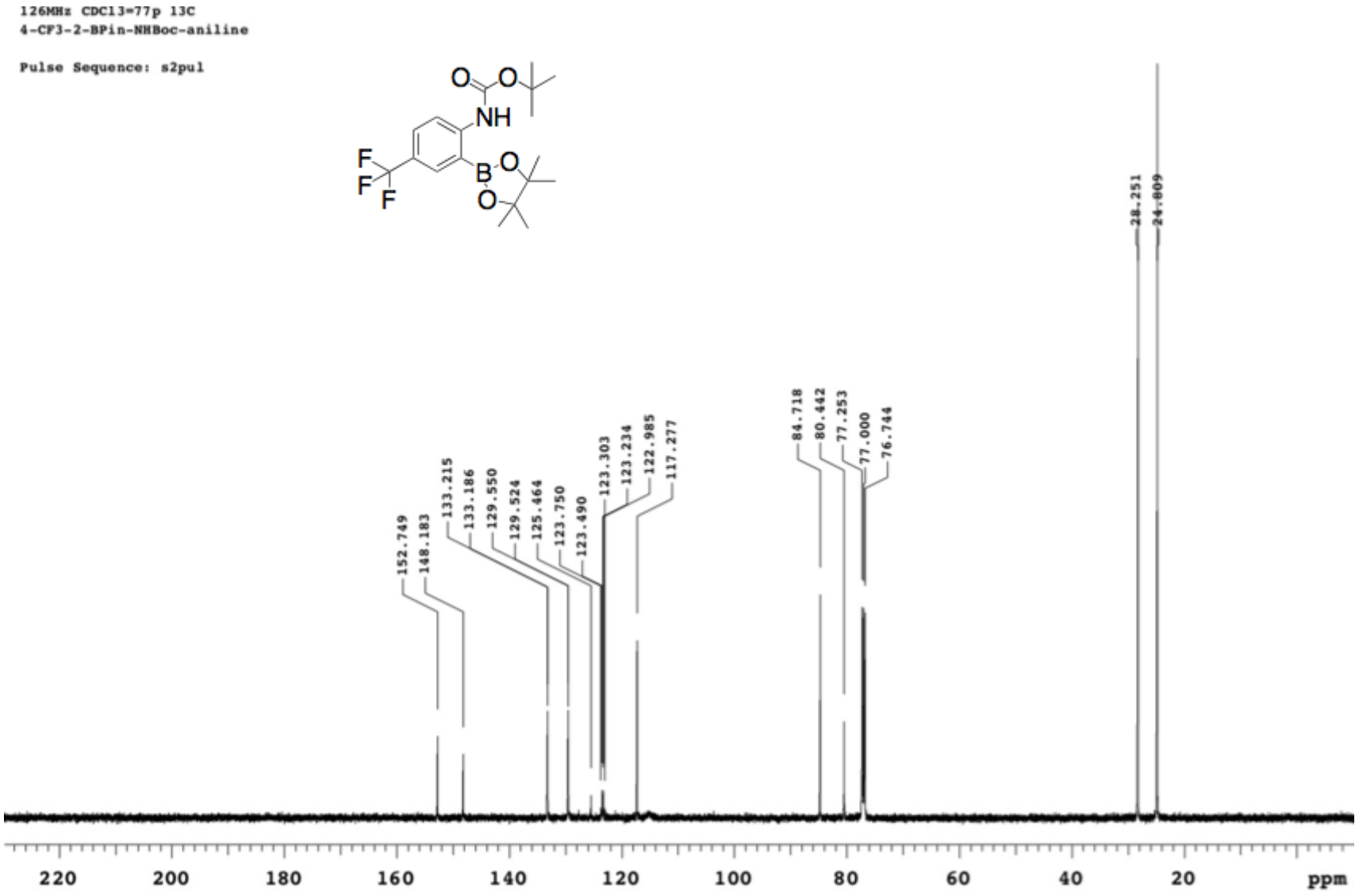


Figure. 126 MHz ^{13}C NMR spectrum of **Table 1, entry 8**

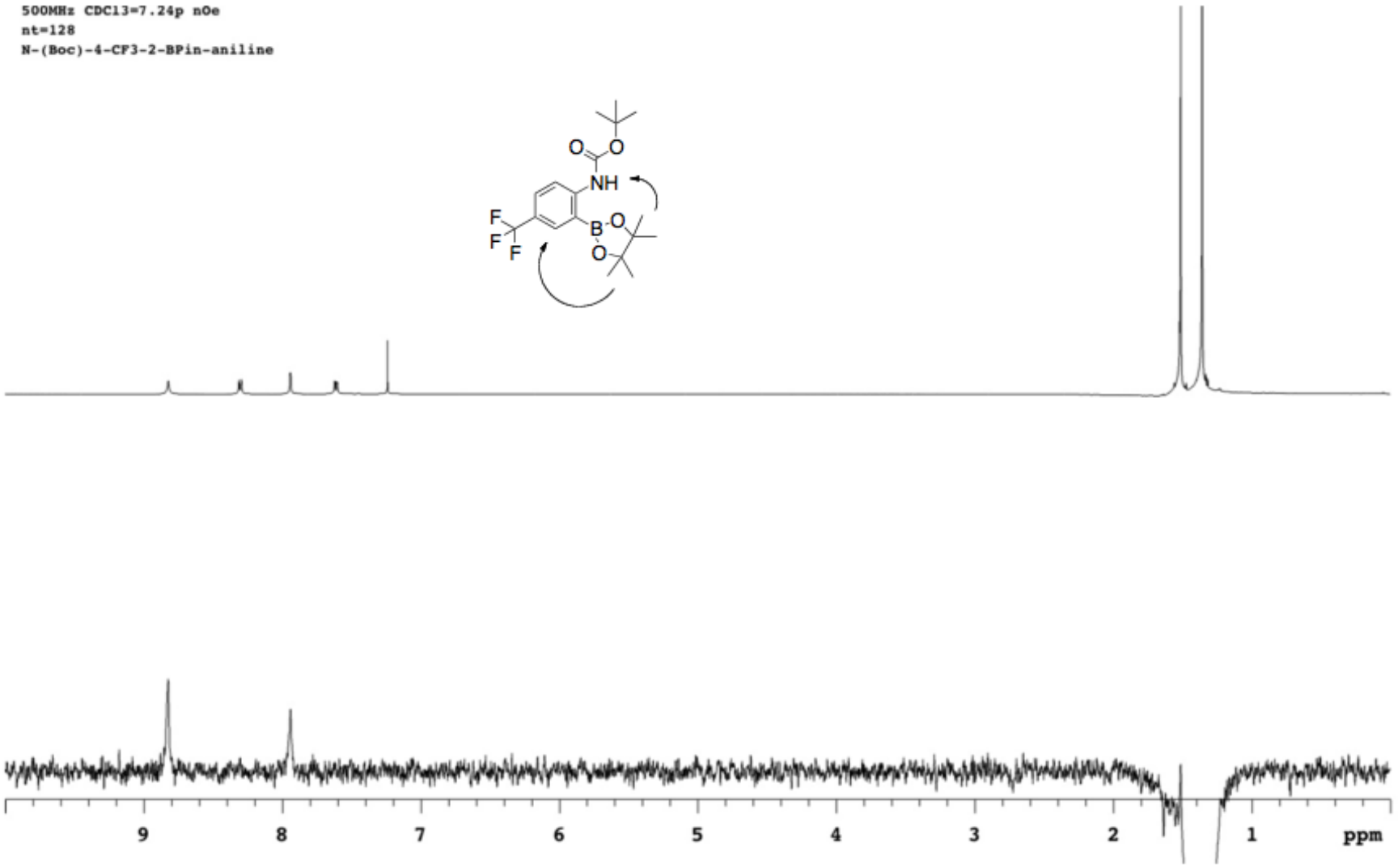


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 8**

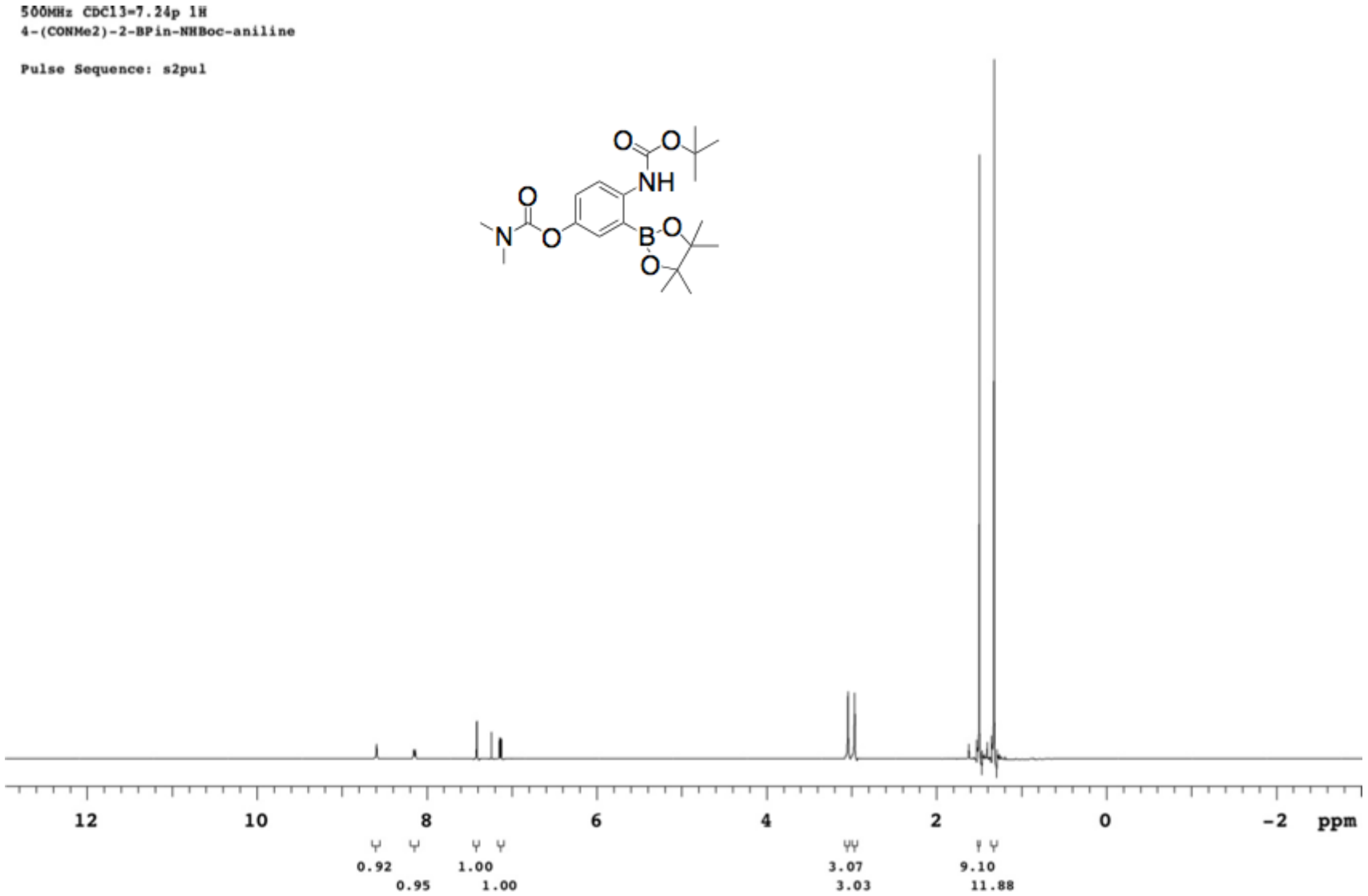


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entry 9**

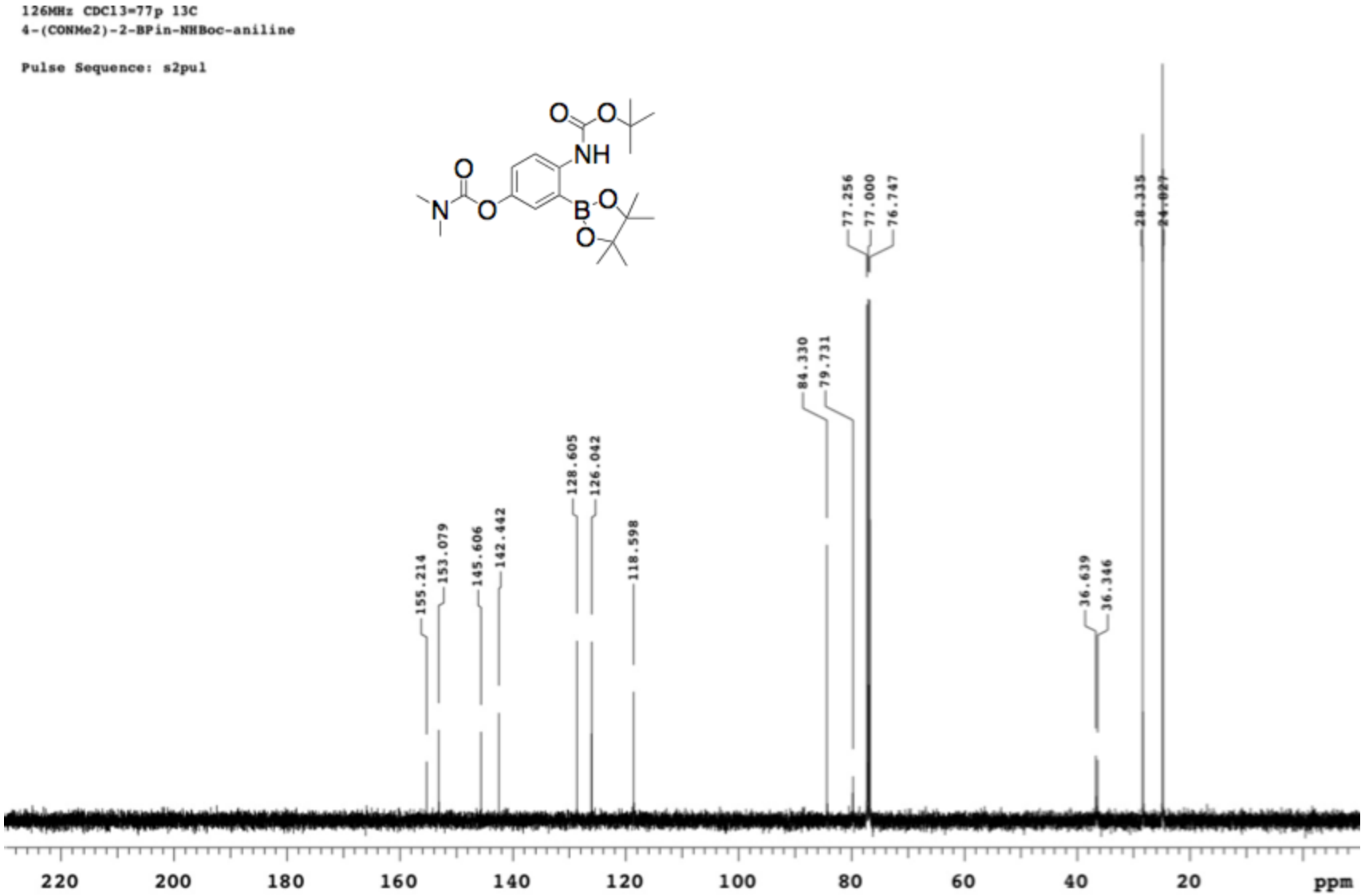


Figure. 126 MHz ^{13}C NMR spectrum of **Table 1, entry 9**

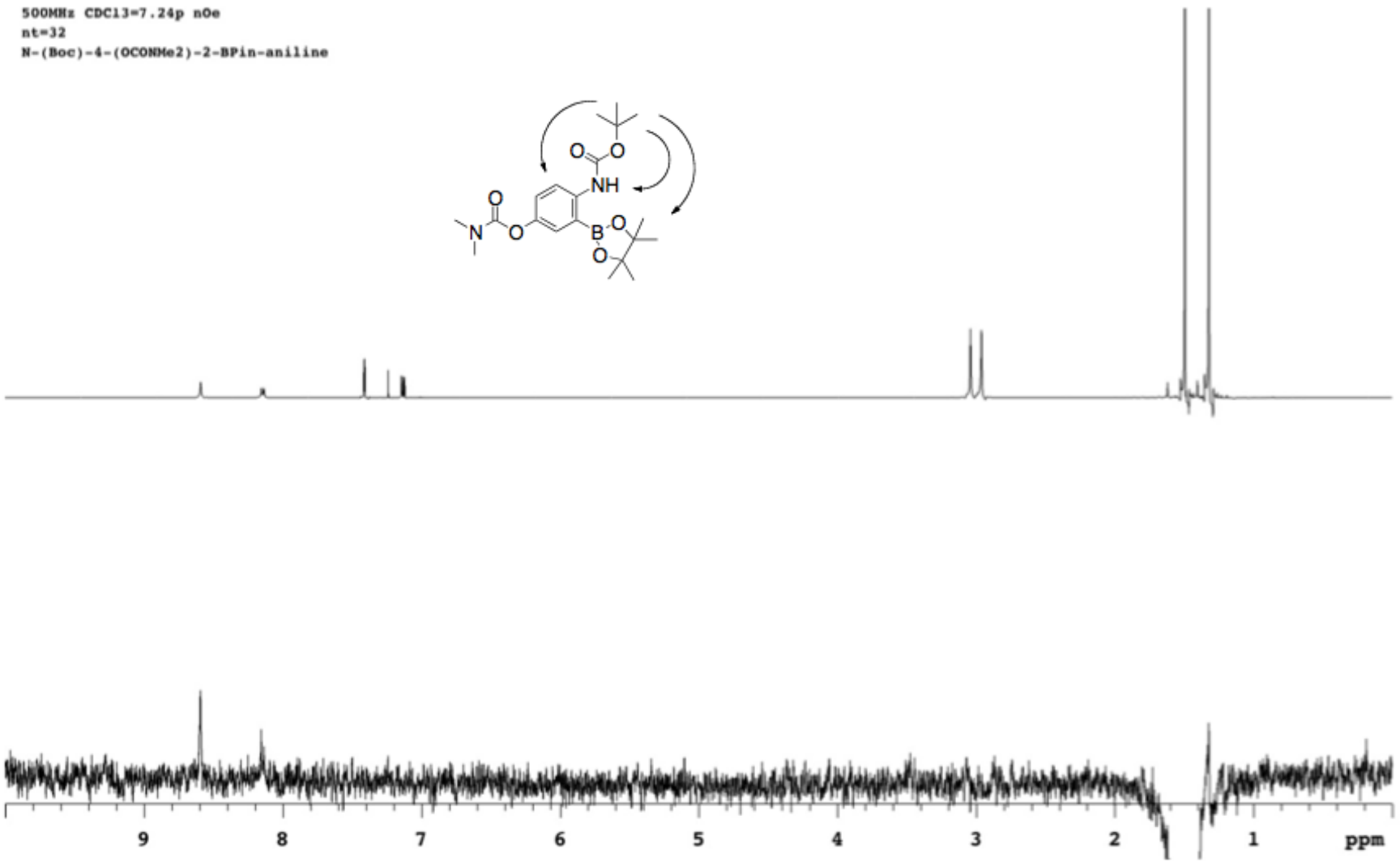


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 9**

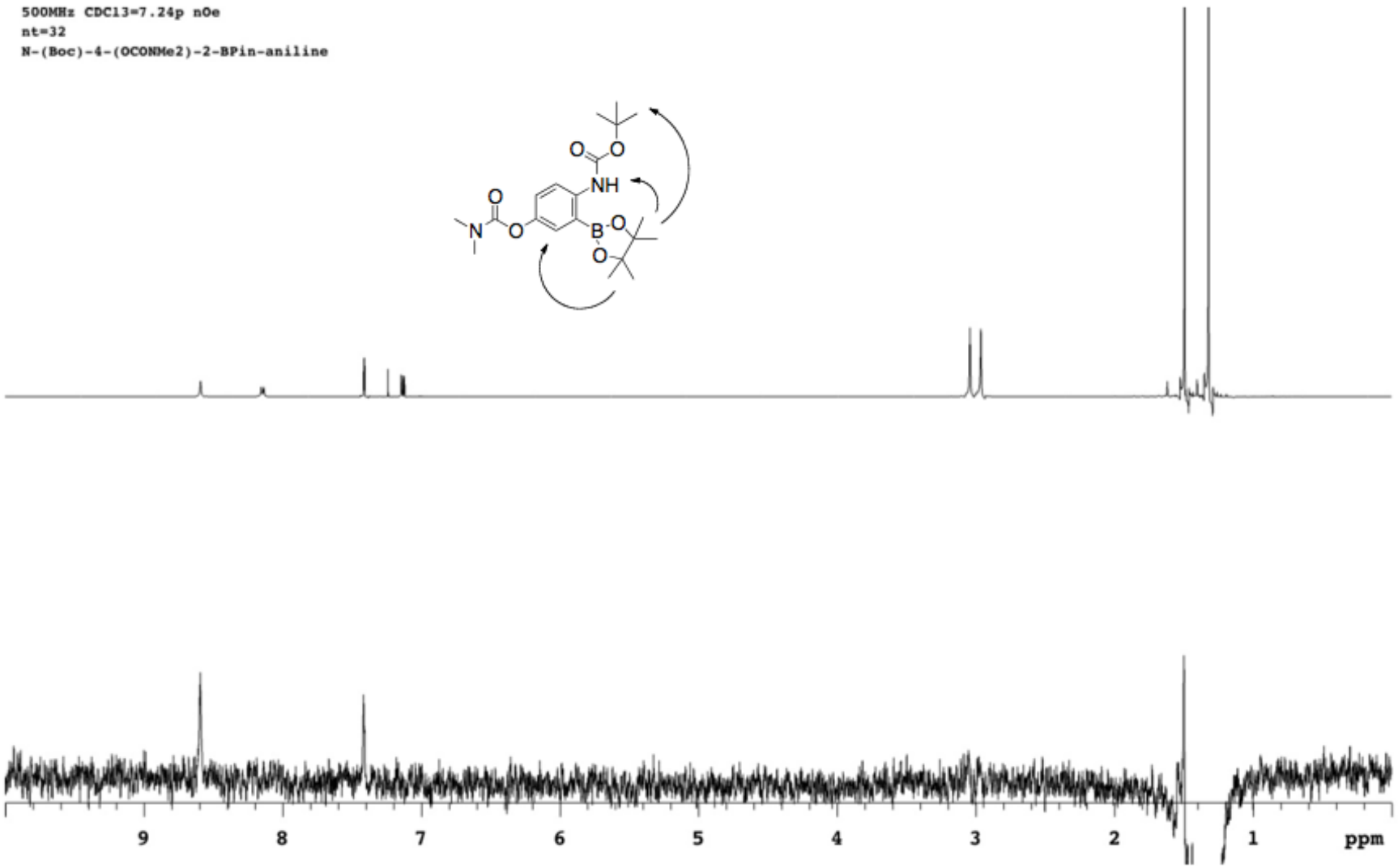


Figure. 500 MHz nOe NMR spectrum of **Table 1, entry 9**

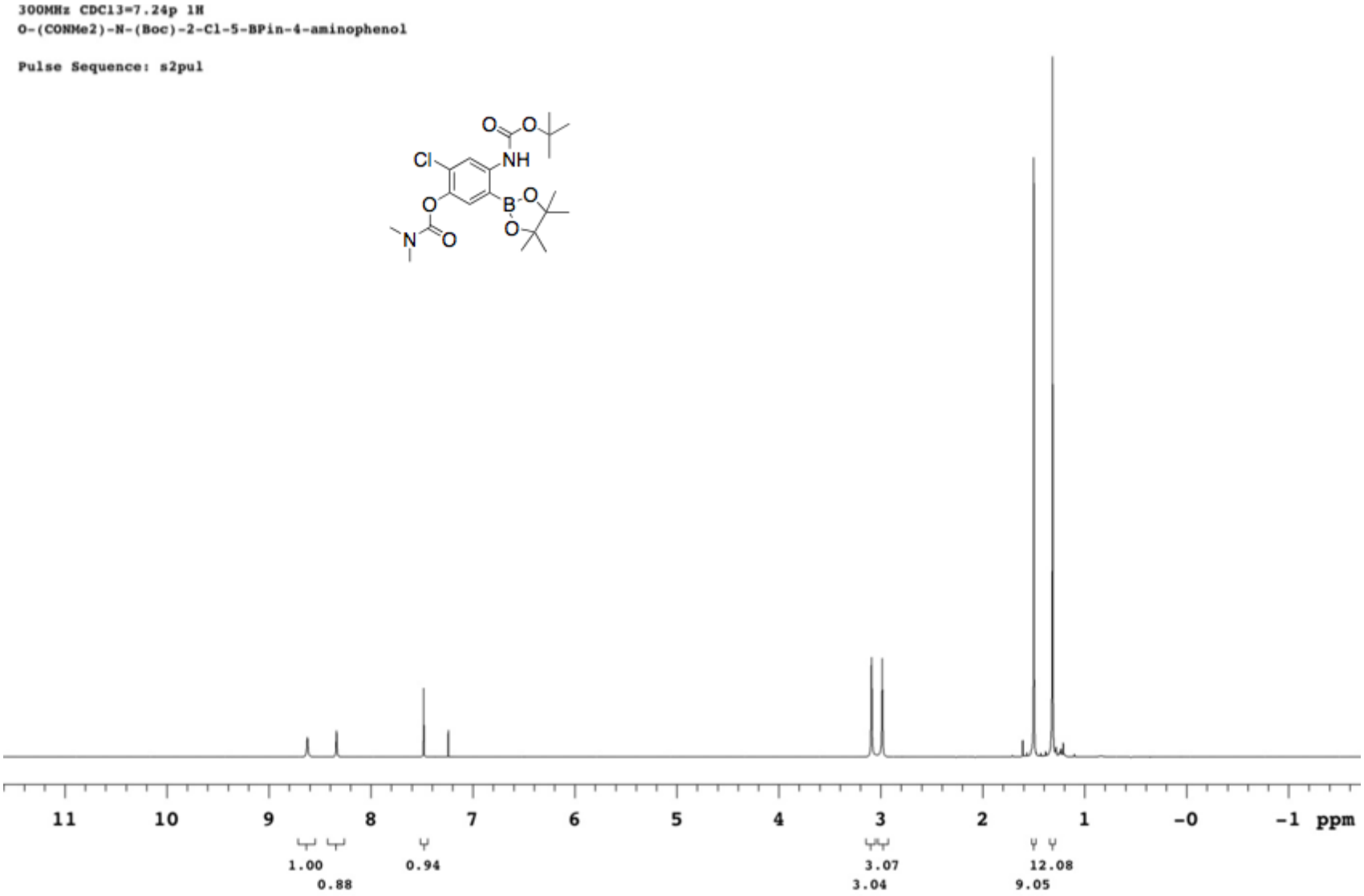


Figure. 300 MHz ^{1}H NMR spectrum of **Table 1, entry 10**

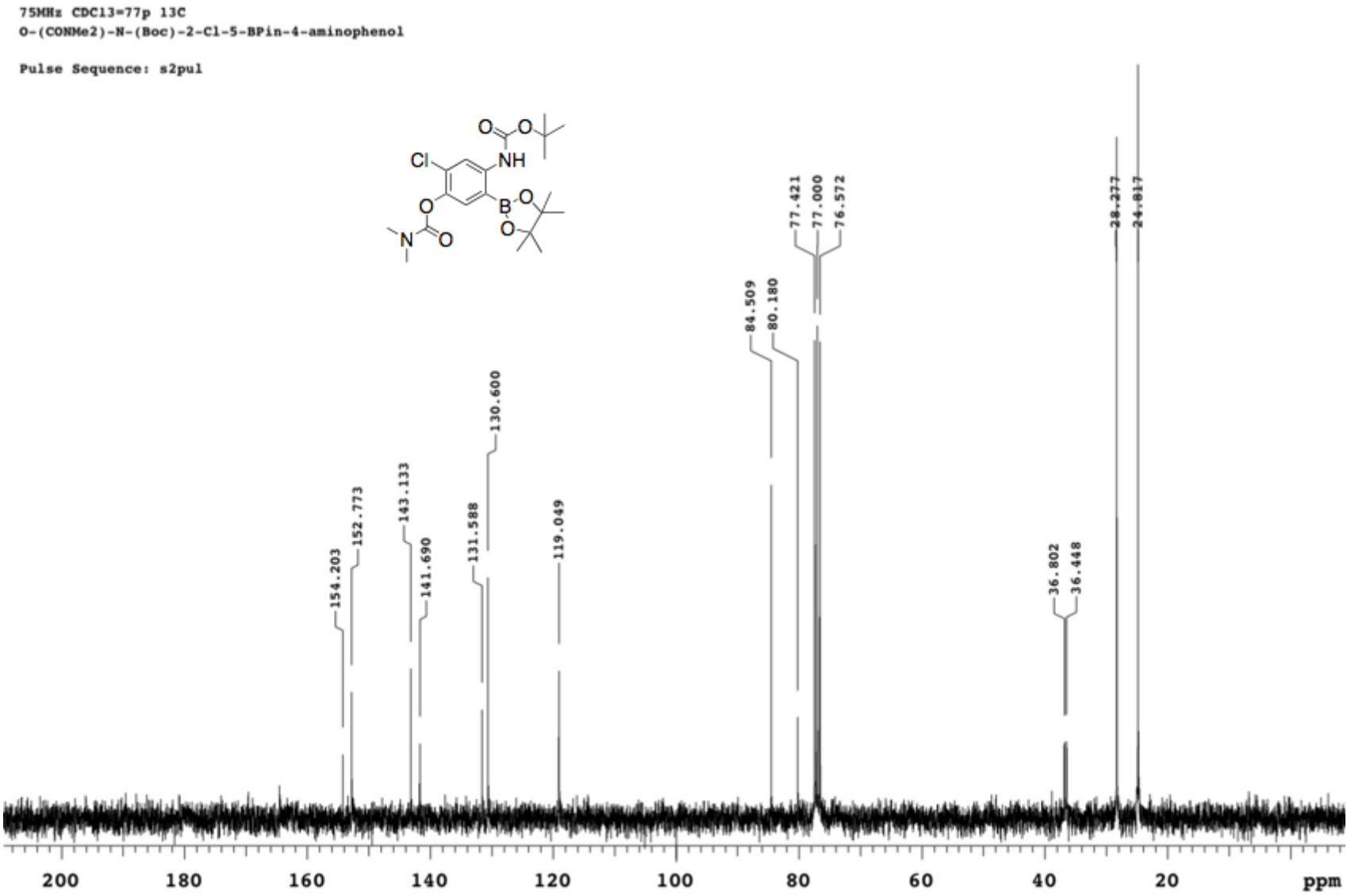


Figure. 75 MHz ^{13}C NMR spectrum of **Table 1, entry 10**

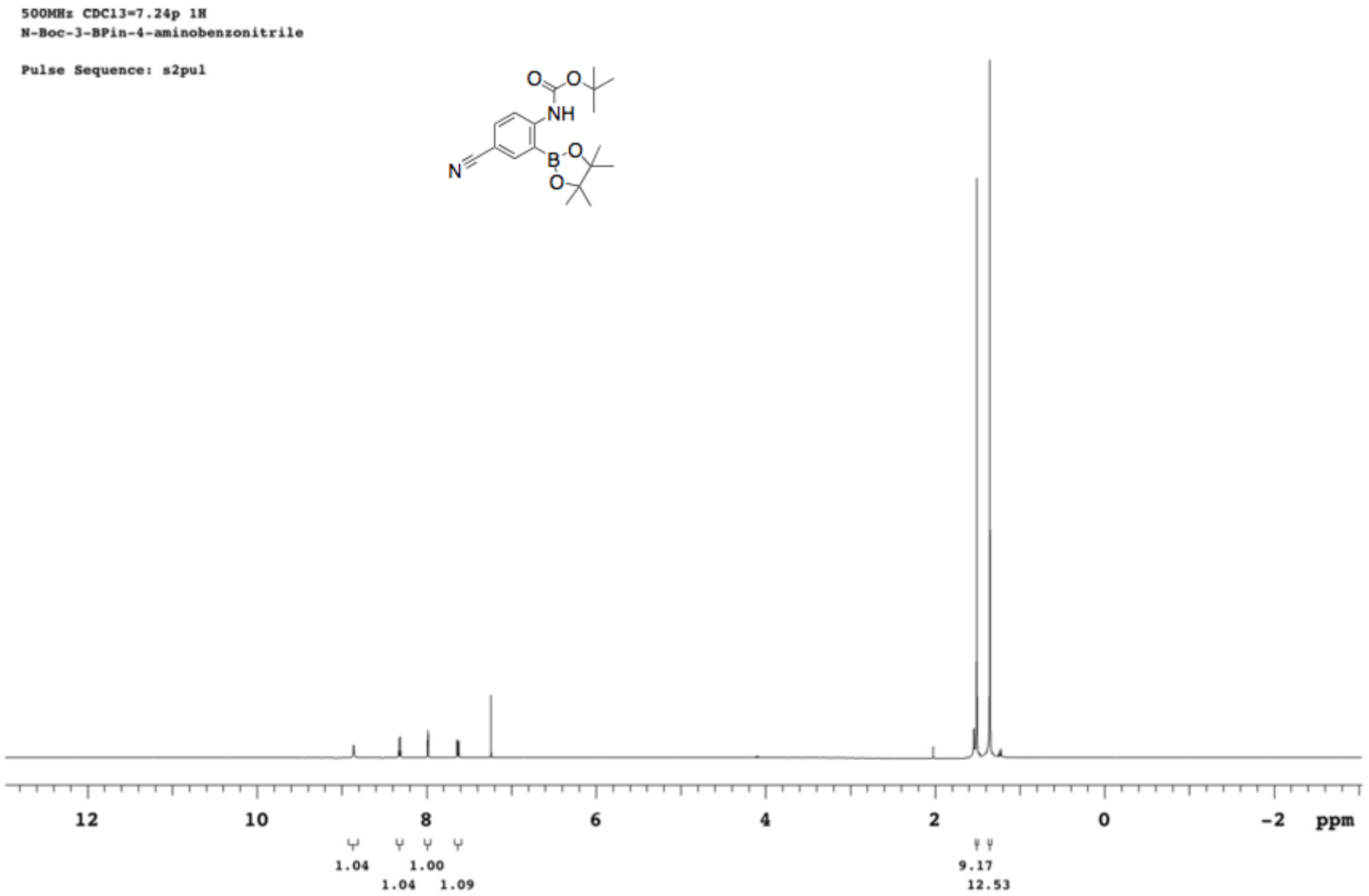


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entry 11**

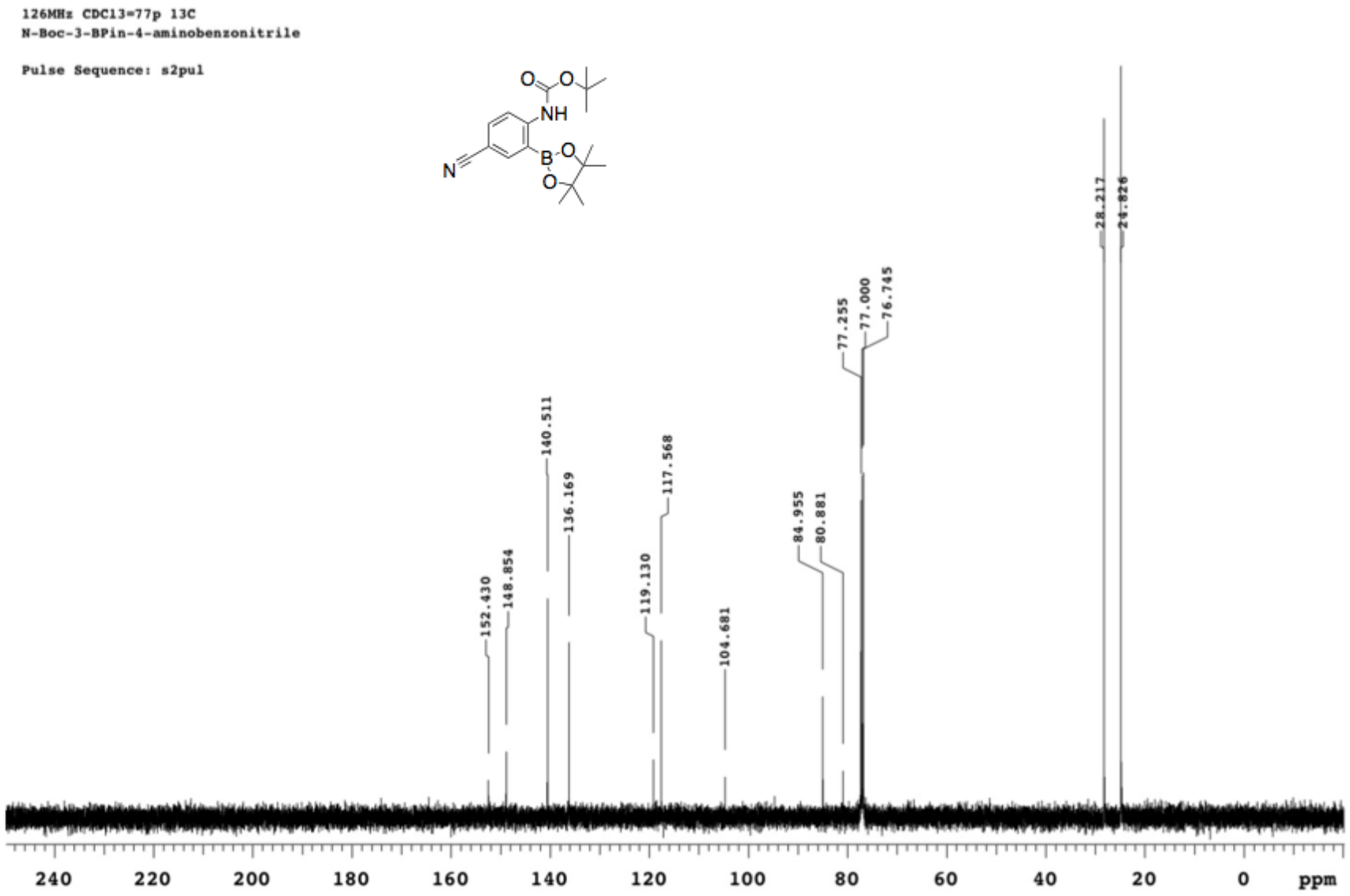


Figure. 126 MHz ^{13}C NMR spectrum of **Table 1, entry 11**

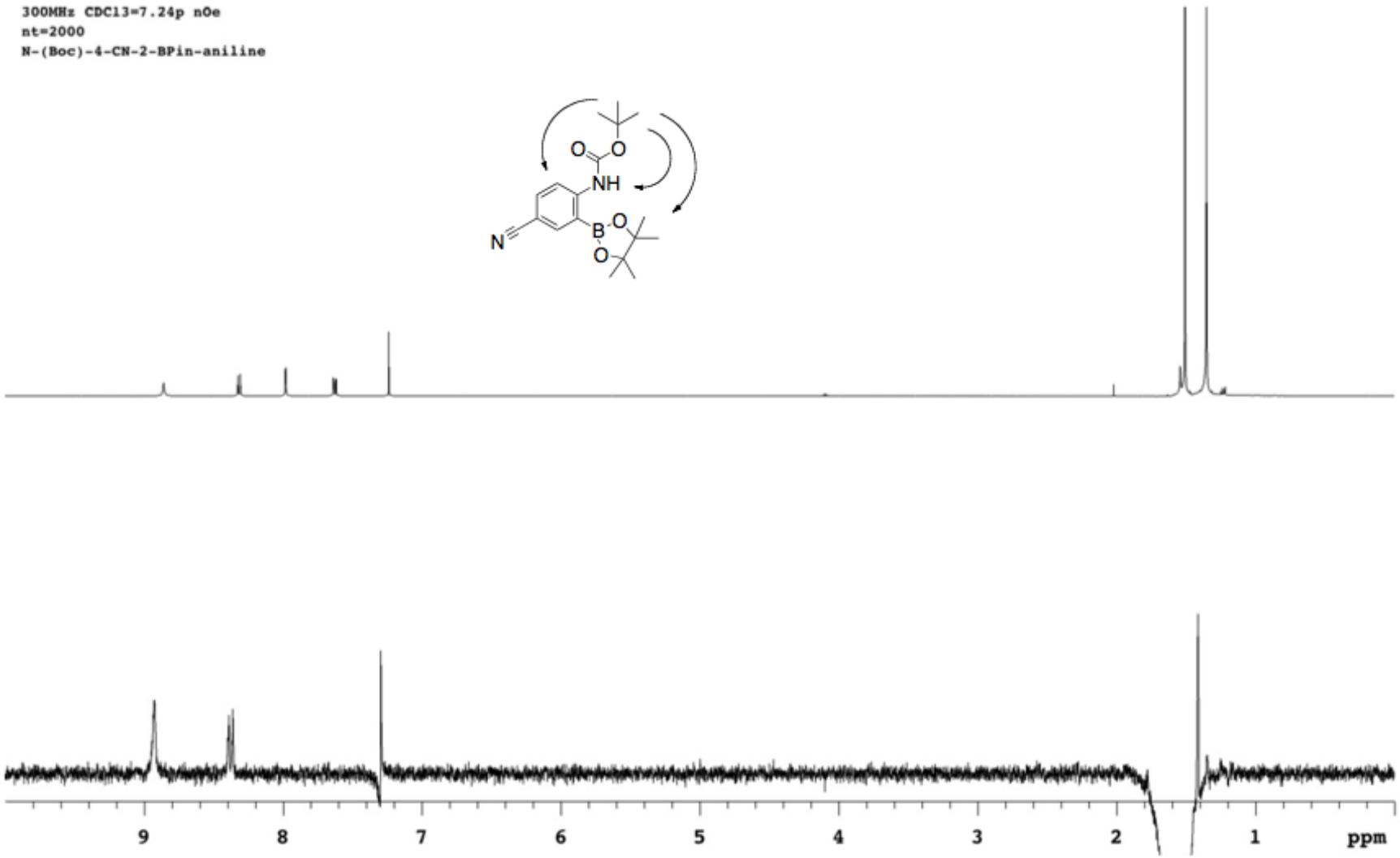


Figure. 300 MHz nOe NMR spectrum of **Table 1, entry 11**

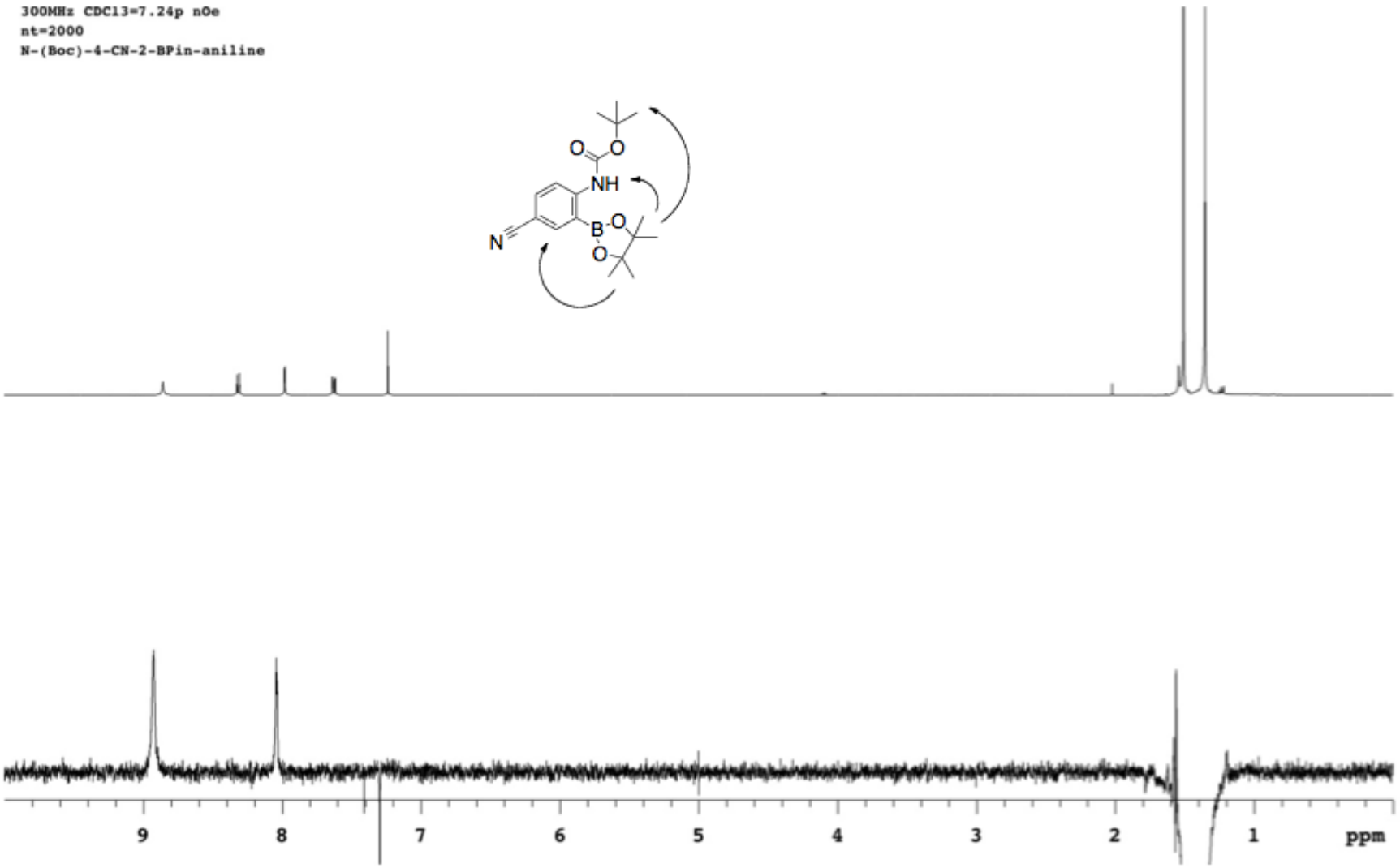


Figure. 300 MHz nOe NMR spectrum of **Table 1, entry 11**

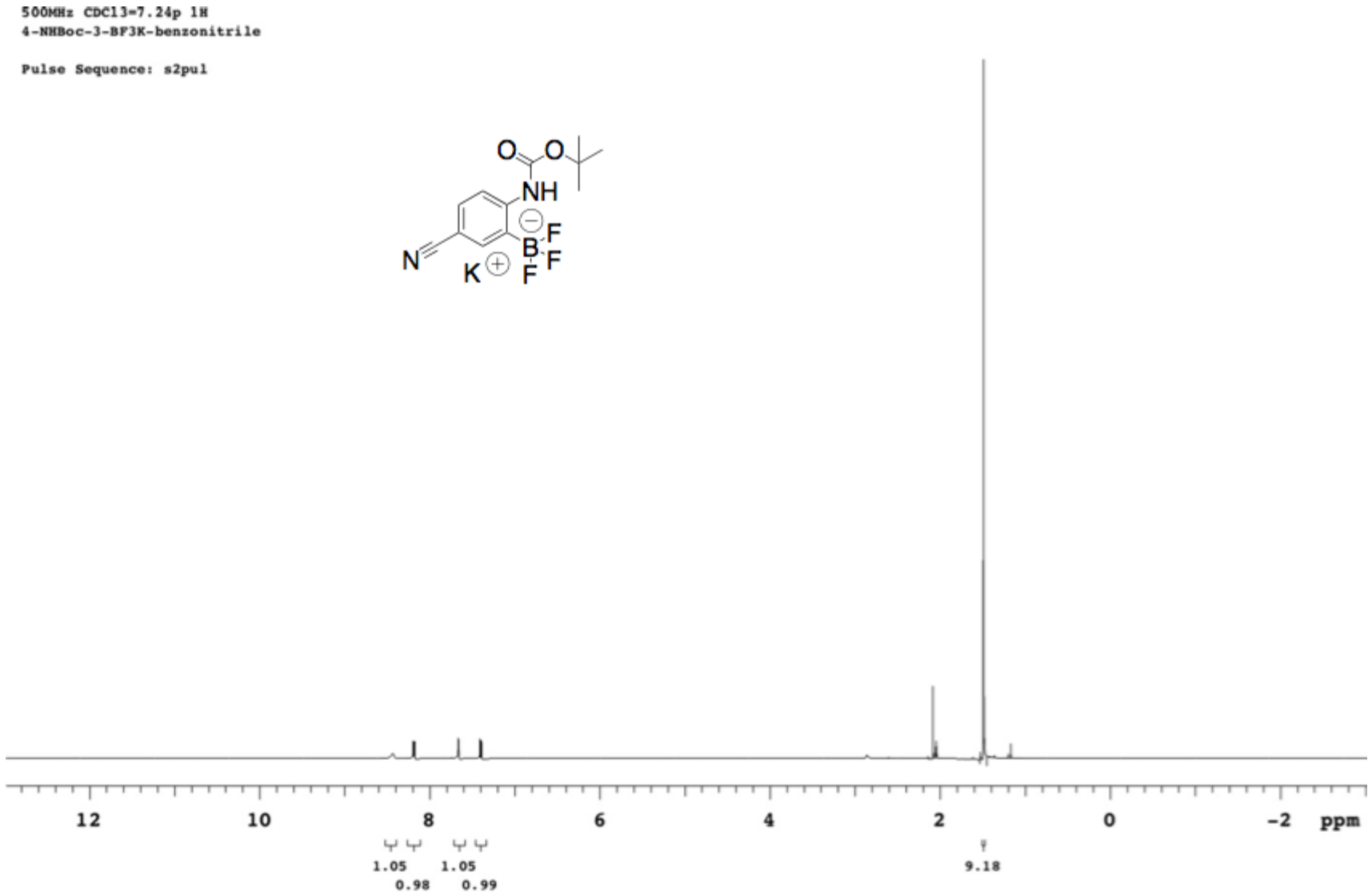


Figure. 500 MHz ^{1}H NMR spectrum of **Table 1, entry 12**

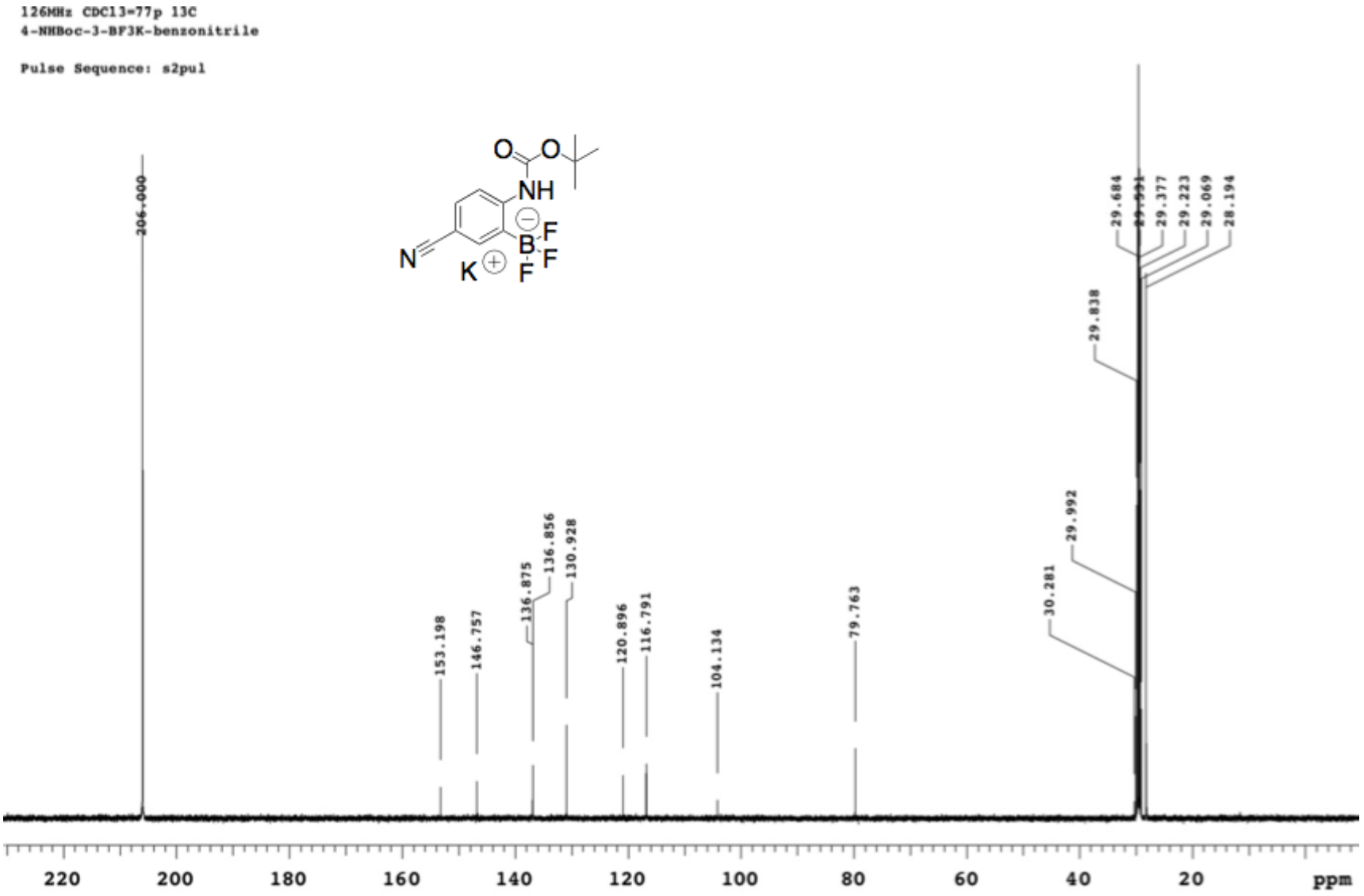


Figure. 126 MHz ^{13}C NMR spectrum of **Table 1, entry 12**

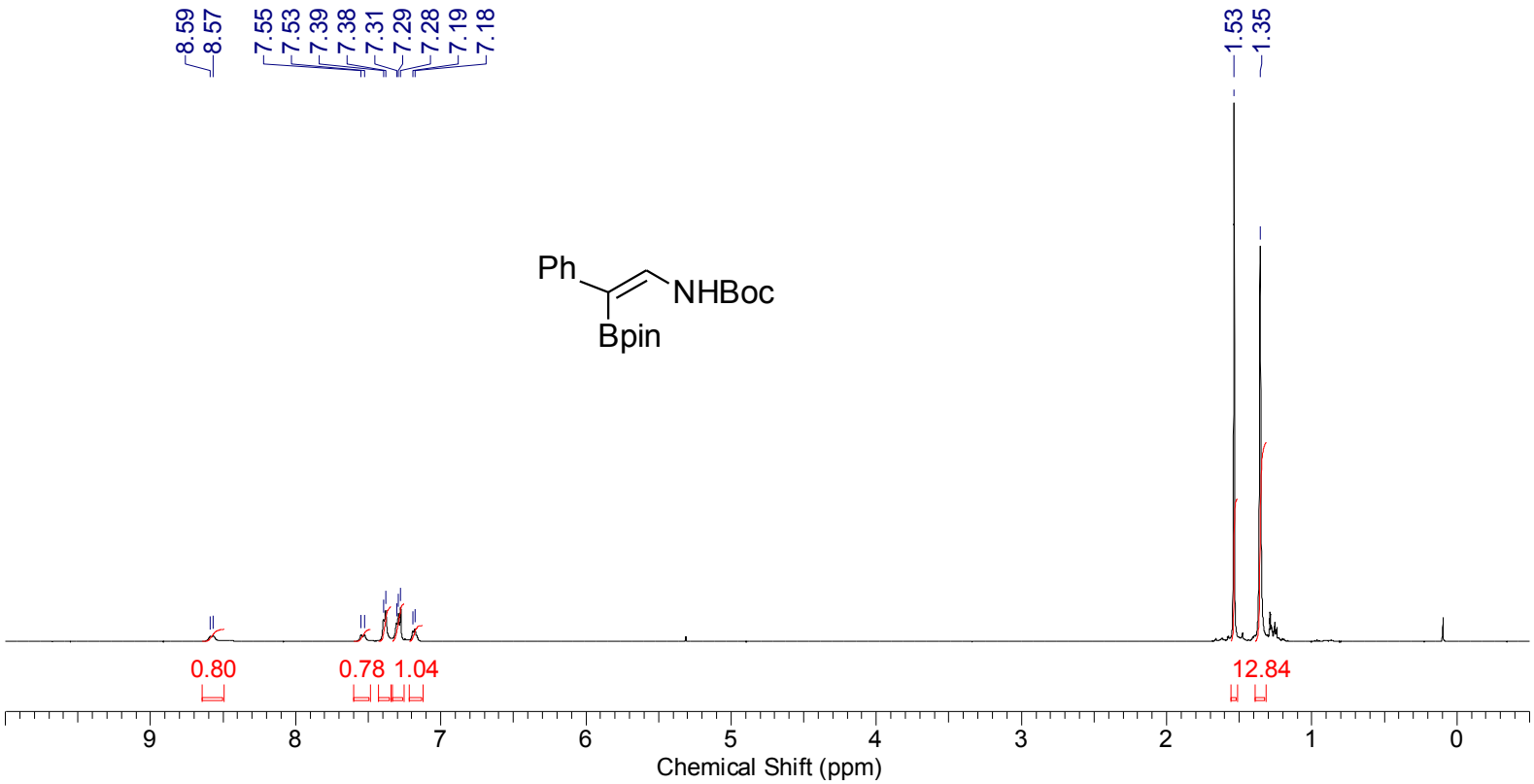


Figure. 500 MHz ^{1}H NMR spectrum of **21**

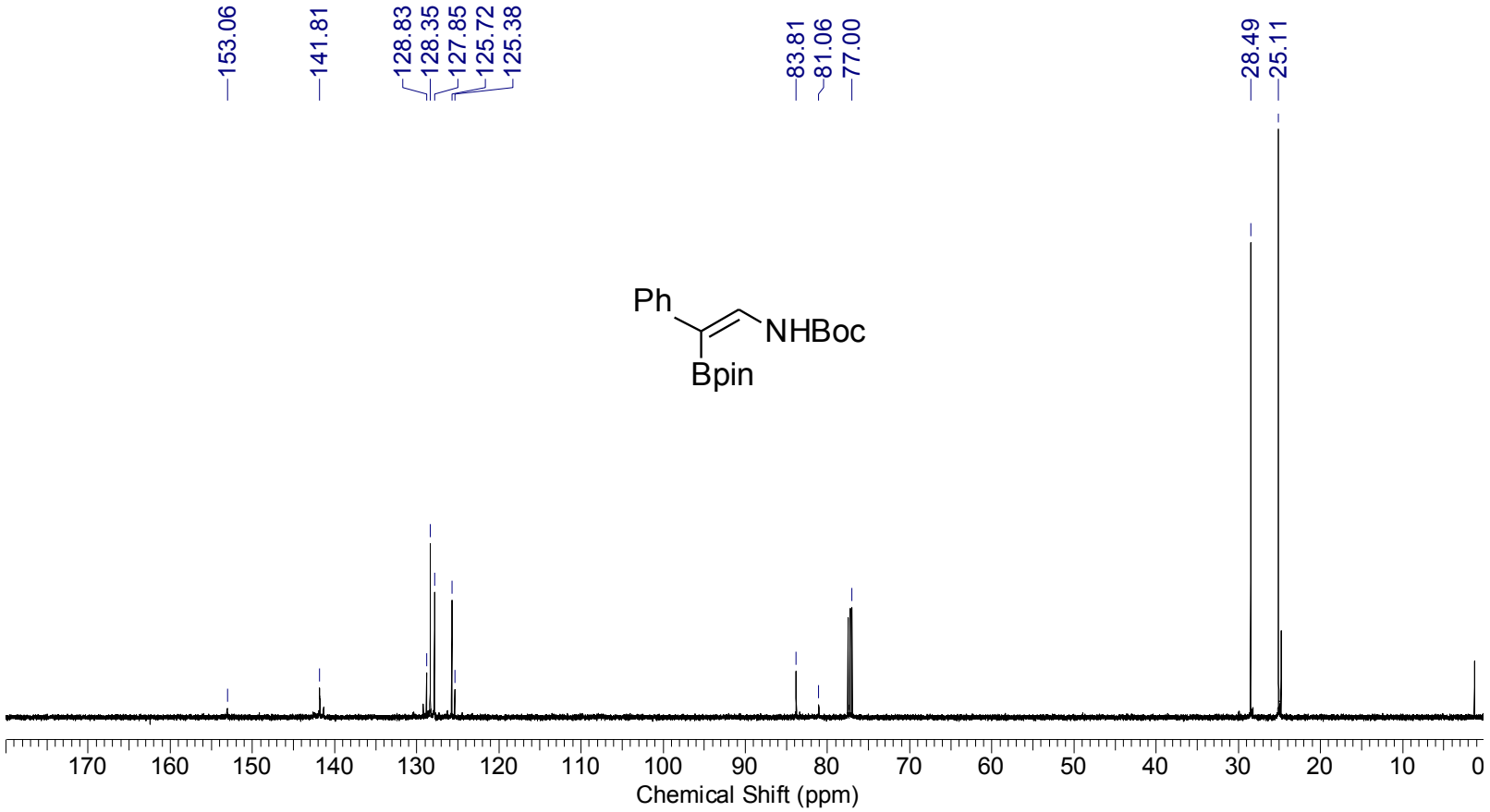


Figure. 126 MHz ^{13}C NMR spectrum of **21**

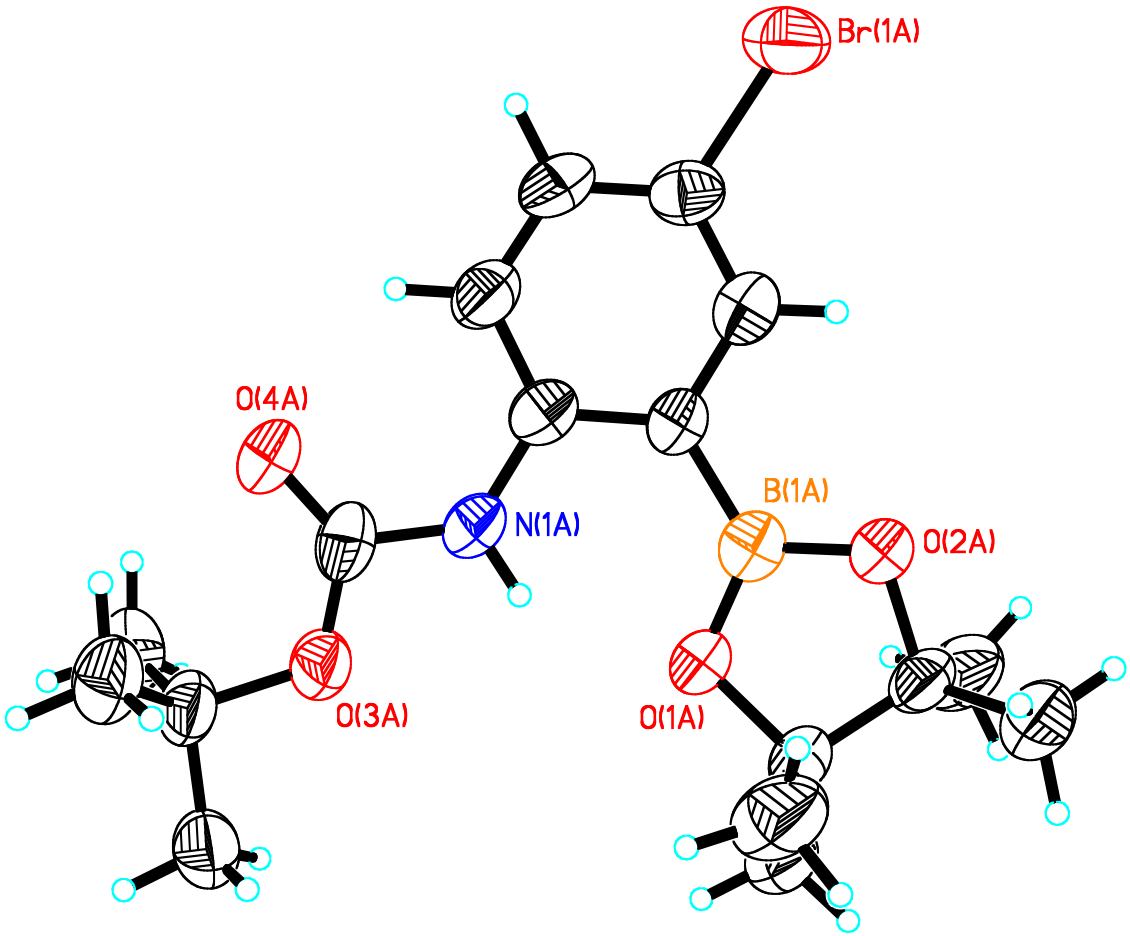


Figure. X-Ray structure of **Table 1, entry 4**

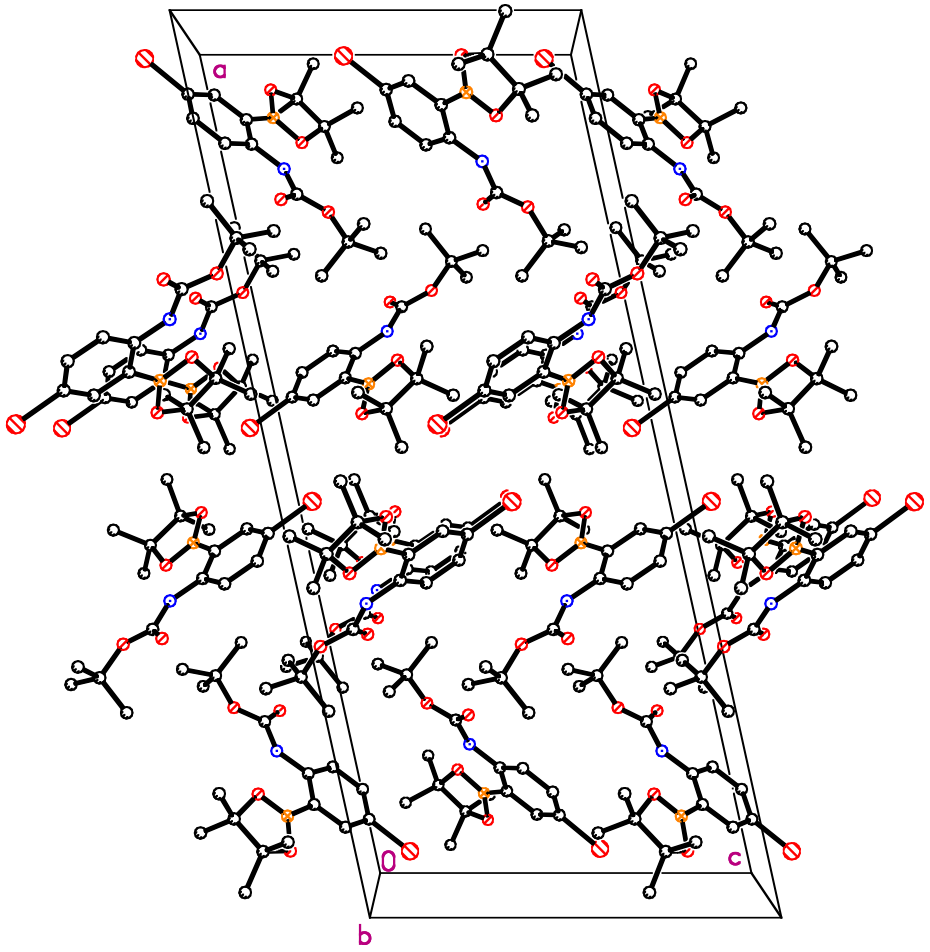


Figure. X-Ray packing structure of **Table 1, entry 4**

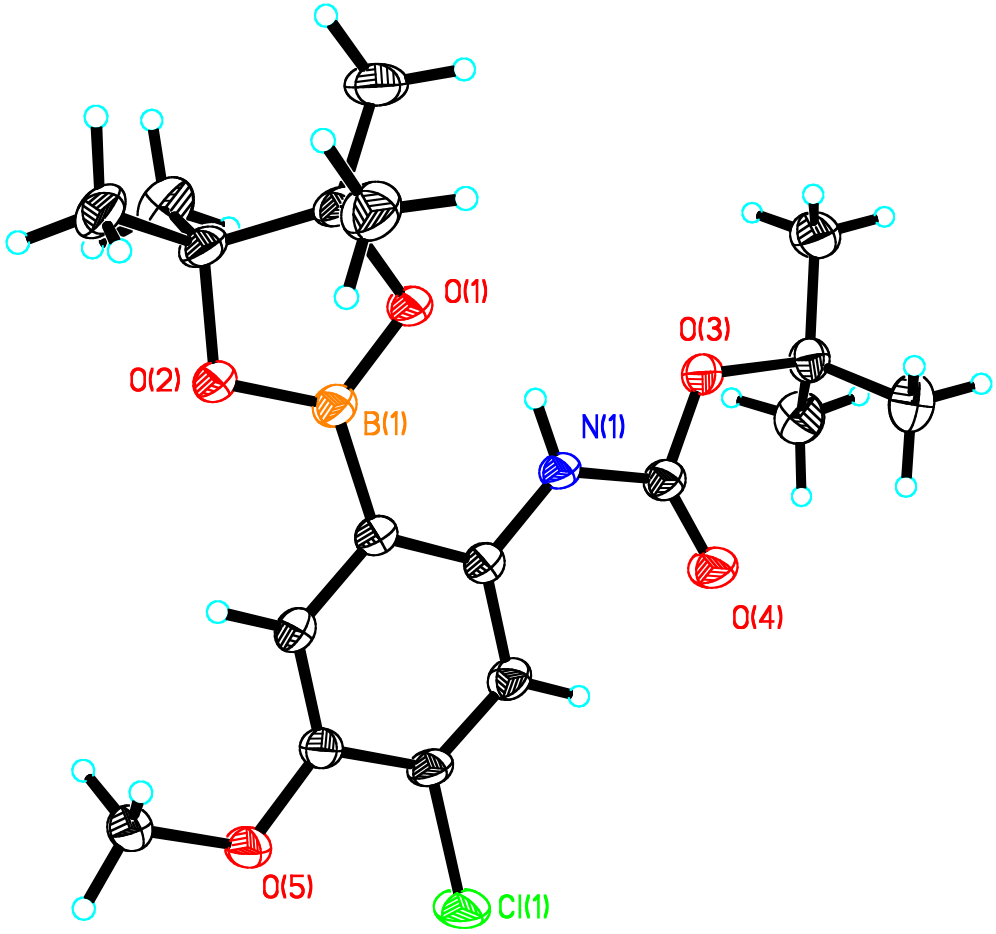


Figure. X-Ray structure of **Table 1, entry 7**

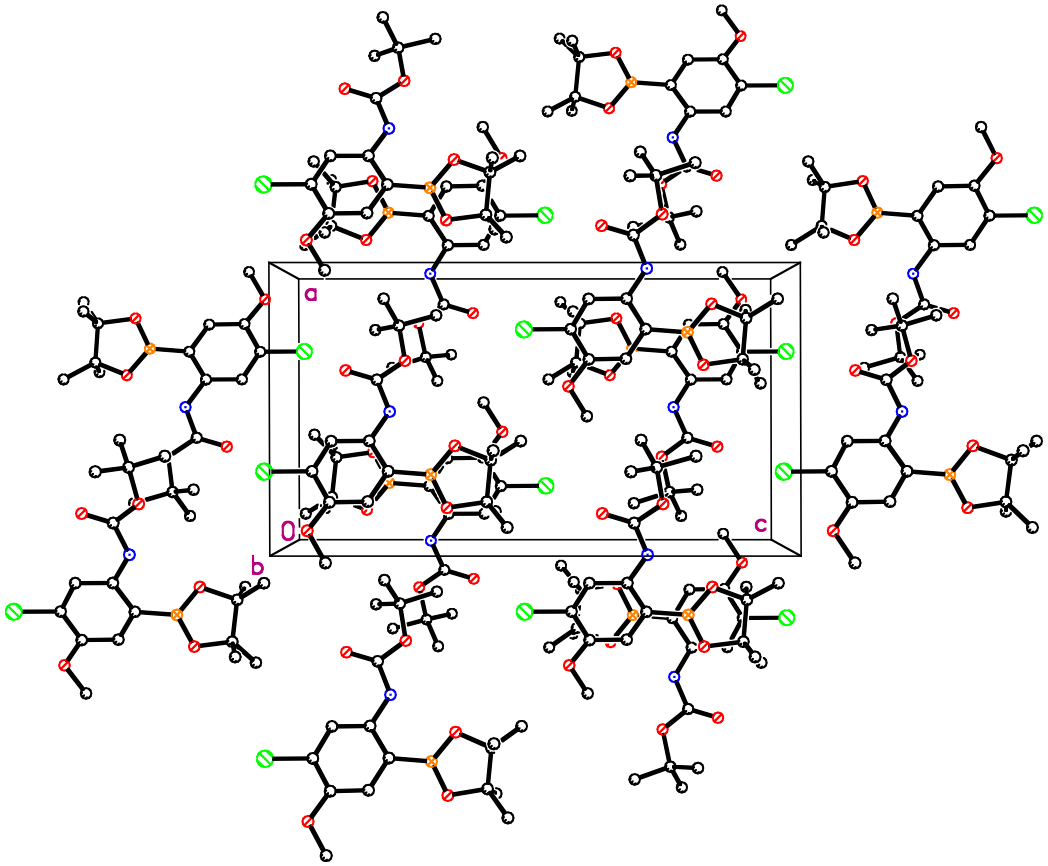


Figure. X-Ray packing structure of **Table 1, entry 7**

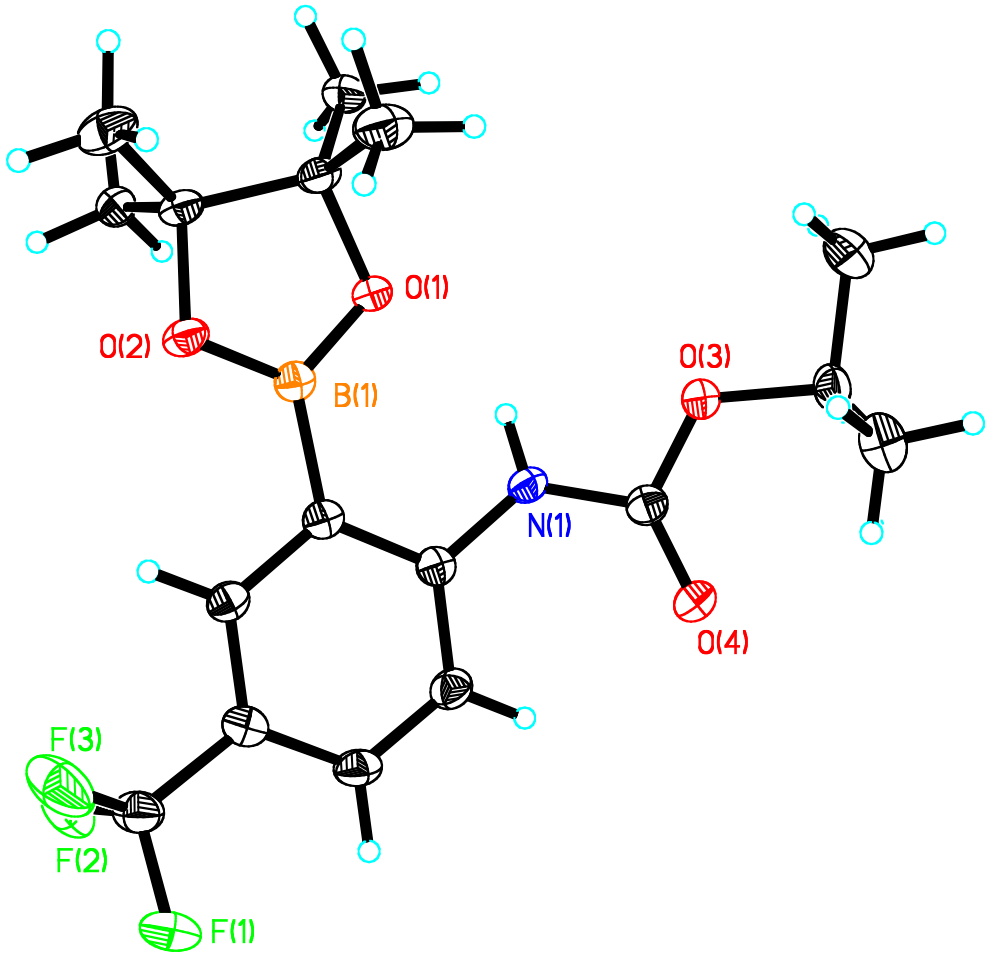


Figure. X-Ray structure of **Table 1, entry 8**

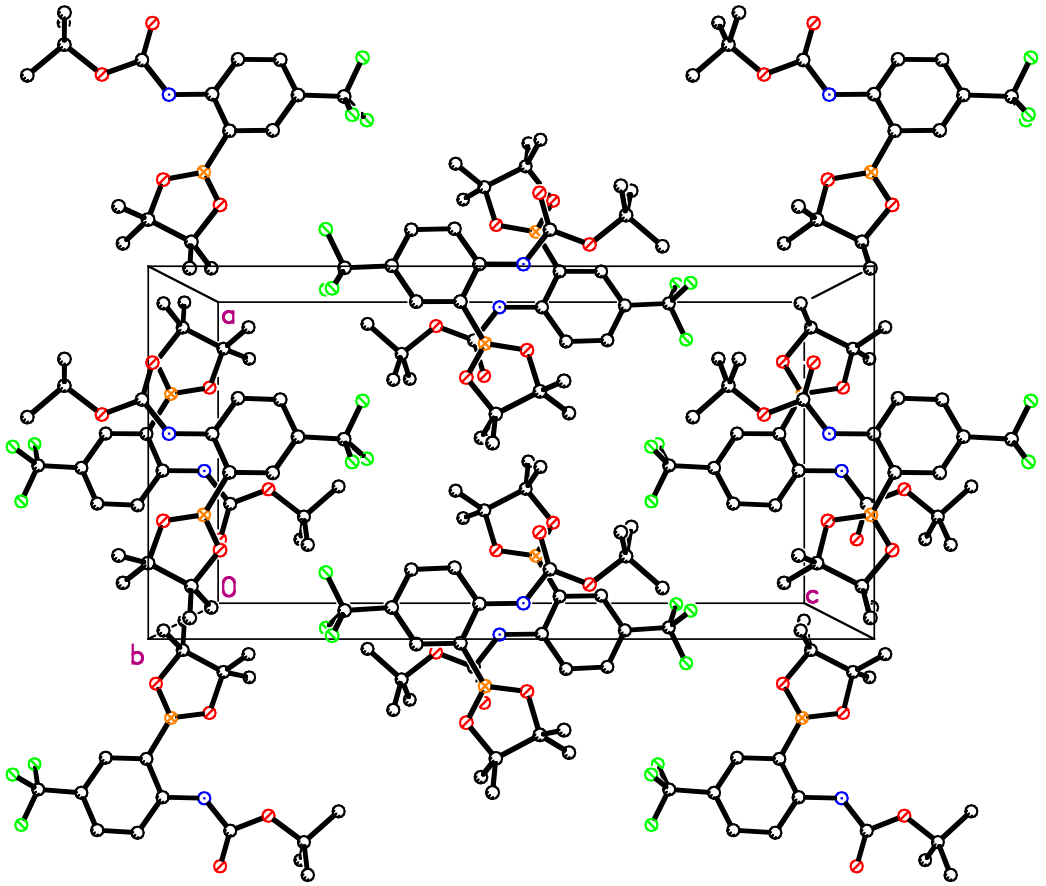


Figure. X-Ray packing structure of **Table 1, entry 8**

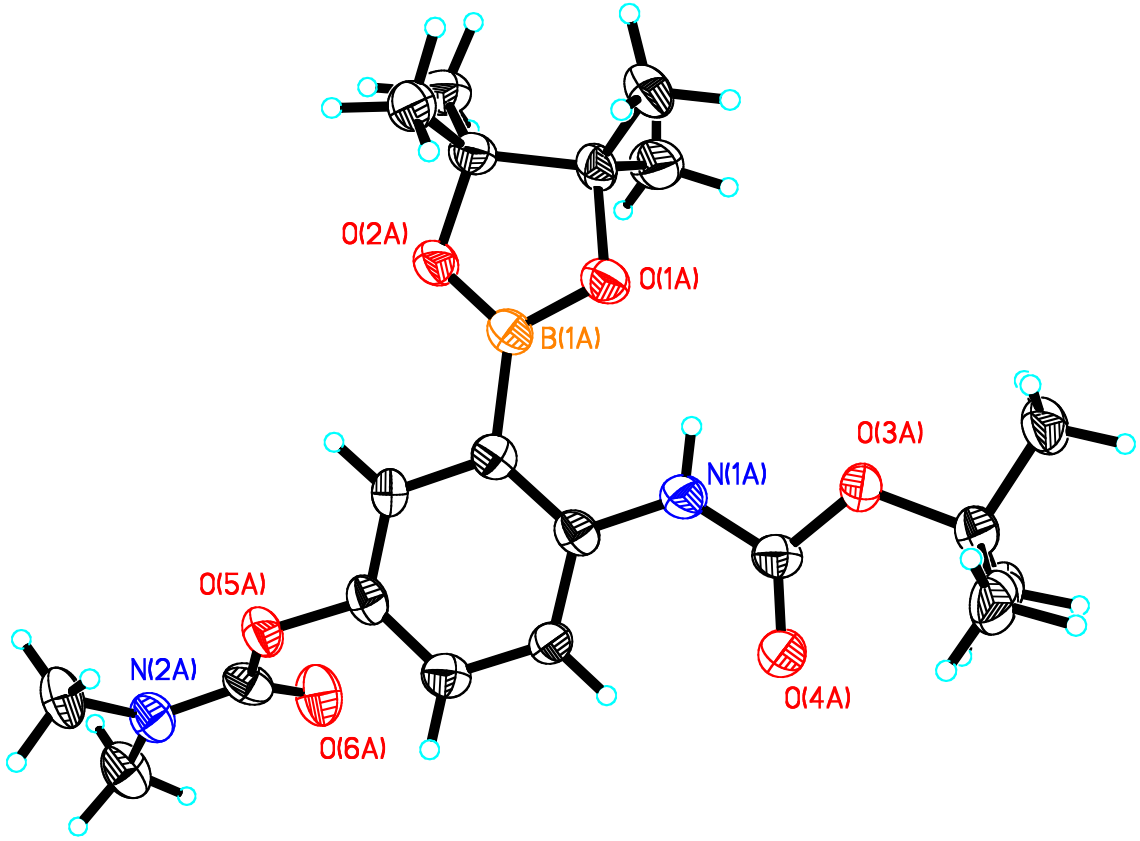


Figure. X-Ray structure of **Table 1, entry 9**

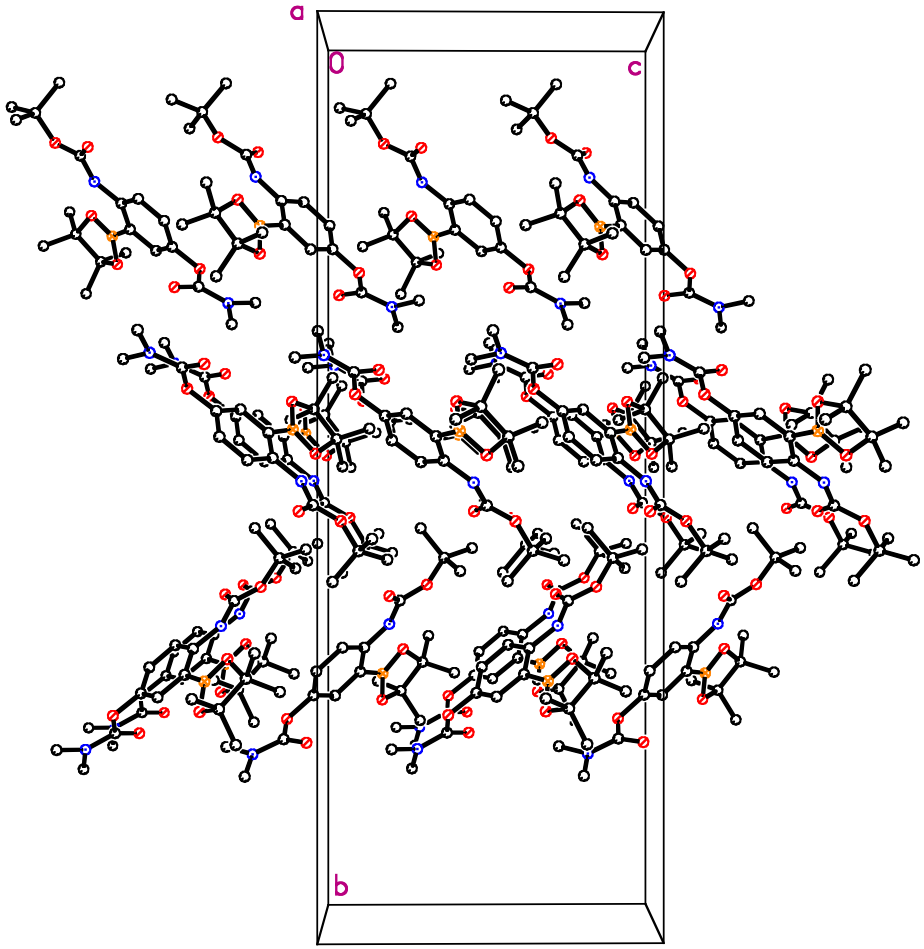


Figure. X-Ray packing structure of **Table 1, entry 9**

Theoretical Methods

General

The structures and energies for all stationary points were obtained using Gaussian 09.[15] Vibrational frequency analyses were carried out on all stationary points. Default methods were employed unless otherwise stated. As a departure from the default methods, frequency calculations were carried out with the Gaussian 09 parameter int=Acc2E=11.

Choice of Methods and Method Details

We have previously described our exploration of diverse combinations of functionals and basis sets for iridium-mediated C-H activations (reference 6b in the main text), including the use of very large basis sets in single-point calculations. We subsequently found that M06 calculations employing an SDD basis set and core potential on Ir and a 6-31+G** basis set of the remaining atoms led to barriers that were closely consistent with the observed rates of reactions (this is not true of B3LYP calculations) and predicted selectivities that were closely consistent observed regioselectivities for the reactions is reference 6b. Because of this and because of the broader success of M06 calculations in transition metal catalyzed reactions, we have adopted these calculations for the reactions studied here.

The calculations assume the general mechanism calculated by Sakaki and coworkers (H. Tamura, H. Yamazaki, H. Sato and S. Sakaki, *J. Am. Chem. Soc.*, **2003**, *125*, 16114–16126) and the transition structures located here are closely analogous to those found by Sakaki for the reaction of benzene. In our previous work in reference 6b, a broad series of transition structures analogous to those of Sakaki exhibited energetics that fit well with experimental observations. Similar transition structures have been found by other workers (Liskey, C. W., Wei C. S., Pahls, D .R., Hartwig J .F. "Pronounced Effects of Substituents on the Iridium-Catalyzed Borylation of Aryl C–H Bonds" *Chem. Commun.* **2009**, 5603-5605.)

Some Complications in the Calculations

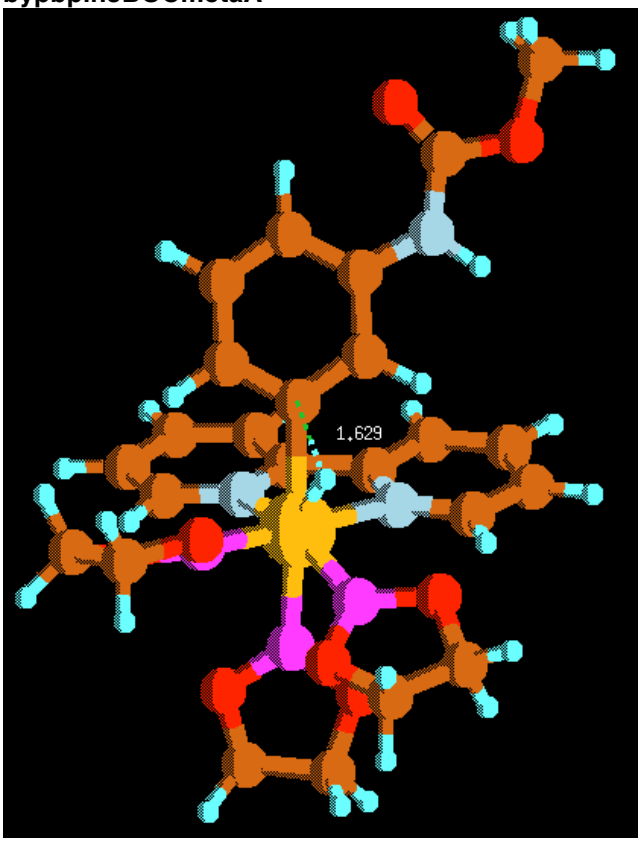
A significant issue that arose in the calculation of the transition structures was the difficulty of fully and tightly optimizing the transition structures and the effect of this difficulty on the frequency calculations and the entropy of the complexes. In particular, with the structure "bypbpin3BOCmetaA," it was possible to obtain structures where the maximum forces and RMS forces on the atoms were barely within normal Gaussian 09 convergence criteria, but with extensive effort it was not possible to obtain any structure where the maximum and RMS displacement of the atoms per step during the optimization was within the convergence criteria. When frequency calculations were carried out on a series of four very similar bypbpin3BOCmeta structures with acceptable maximum and RMS forces, either more than one imaginary frequency was found (three cases) or the structure had multiple very low frequencies (one case). The latter structure is given below, but due to its low frequencies, its entropy is high and its calculated free energy is lower than any other structure in the series. It should be noted that this structure has a relatively high potential energy and energy including zero-point energy. We have accordingly discounted the free energy of this structure as an anomaly.

We view the assignment of this free energy as anomalous as correct, but it should be admitted that this assignment came *after* the recognition that the "predicted" product ratio including this structure was not a good fit with the experimental observations. This may be worth considering when evaluating the significance of the very good agreement of the main text's calculated product ratio with experiment.

Calculated Structures

The structure titles in the following section have retained the original file names for the computational output files. This lets us use a single code name for structures, energies and our records, but a problem is that the titles are relatively cryptic. “BOC” in the title refers to structures containing a methyl carbamate. Structures with “ortho”, “meta”, and “para” in the title are referring to the position of the C-H activation relative to the carbamate group. The various conformational possibilities are labeled A, B, C, etc. “BOC” refers to structures containing a methyl carbamate. Structures with “bpin3” in the title are calculations on structures with three Beg (eg = ethyleneglycolate) groups. The “bpy” has its usual meaning.

bypbpin3BOCmetaA



bypbpin3BOCmeta
M06/gen
E(RM06) = -1876.24505763

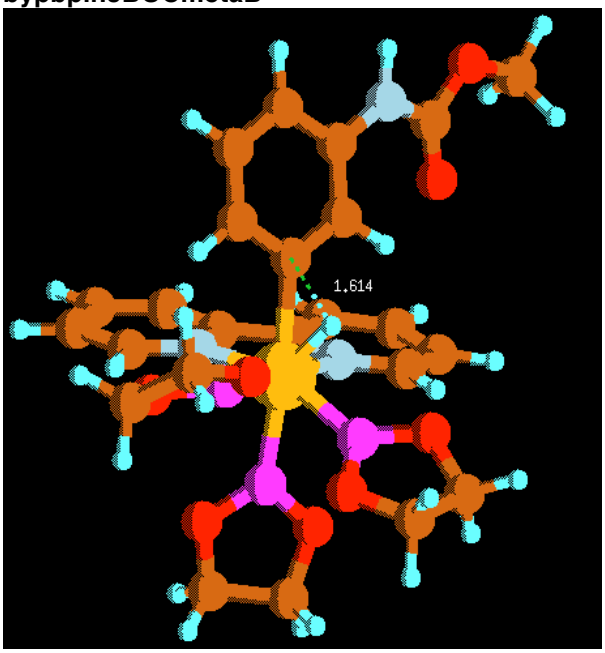
Zero-point correction= 0.527173 (Hartree/Particle)
Thermal correction to Energy= 0.564687
Thermal correction to Enthalpy= 0.565631
Thermal correction to Gibbs Free Energy= 0.451290
Sum of electronic and ZPE= -1875.717884
Sum of electronic and thermal Energies= -1875.680370
Sum of electronic and thermal Enthalpies= -1875.679426
Sum of electronic and thermal Free Energies= -1875.793768

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.347	138.498	240.652

6 -3.639063 2.229078 -0.452533
6 -2.490643 2.998594 -0.276167
6 -1.217503 2.442494 -0.358212
6 -1.051500 1.069008 -0.593349
6 -2.205567 0.312164 -0.808795
6 -3.486880 0.869980 -0.730410
77 0.897830 0.107564 -0.170847
7 -0.289821 -1.724120 0.587453
6 -0.879662 -1.583490 1.788192
6 -1.799204 -2.526469 2.253878
6 -2.092908 -3.632828 1.468735
6 -1.451887 -3.782715 0.243866
6 -0.554374 -2.800670 -0.158914
6 -0.481117 -0.395818 2.575780
7 0.395244 0.448786 1.993029
6 0.846706 1.509861 2.672441
6 0.425617 1.796287 3.964896
6 -0.494018 0.948418 4.569181
6 -0.946305 -0.162138 3.870600
5 2.707381 -0.797071 0.482415
8 2.998720 -2.153177 0.310504
6 4.364525 -2.344114 0.655850
6 4.683858 -1.154538 1.555654
8 3.727790 -0.171514 1.177257
5 1.869749 -0.745184 -1.777795
8 3.124725 -0.436969 -2.283918
6 3.385209 -1.280470 -3.394723
6 2.368030 -2.410598 -3.249975
8 1.332690 -1.841020 -2.458850
5 1.910740 1.805379 -0.635294
8 2.484628 2.666509 0.305356
6 2.825479 3.881570 -0.348585
6 2.830336 3.514690 -1.830805
8 1.997736 2.370250 -1.902318
1 0.128967 0.491057 -1.555528
1 -0.026632 -2.845100 -1.111822
1 -2.289276 -2.401434 3.214622
1 -1.643381 -4.639337 -0.395880
1 -2.811525 -4.371587 1.815250
1 -1.654035 -0.840671 4.336258
1 -0.853095 1.142487 5.576834
1 0.815543 2.670624 4.477470
1 1.567048 2.132167 2.142330
1 2.793314 -3.273783 -2.714701
1 1.959065 -2.755253 -4.206666
1 4.423734 -1.630455 -3.358127
1 3.243621 -0.710787 -4.324846
1 -0.347871 3.085672 -0.220938
1 -2.599999 4.062633 -0.071613
1 -4.628413 2.667968 -0.389085
1 -2.118472 -0.751570 -1.044965
7 -4.569944 -0.006214 -0.947866
1 4.496056 -3.315543 1.146019

1 4.969640 -2.329463 -0.265424
1 4.551480 -1.396256 2.620951
1 5.696225 -0.760319 1.412968
1 2.060695 4.640874 -0.119702
1 3.793617 4.242999 0.016868
1 2.432289 4.307700 -2.474598
1 3.838651 3.252122 -2.184458
1 -4.335094 -0.966099 -1.164509
6 -5.902952 0.273059 -0.918837
8 -6.428220 1.341210 -0.685851
8 -6.594256 -0.861165 -1.195216
6 -8.008622 -0.706301 -1.208797
1 -8.413380 -1.689448 -1.453963
1 -8.374080 -0.378071 -0.230573
1 -8.311152 0.028367 -1.961409

bypbpin3BOCmetaB



bypbpin3BOCmeta low basis temp
M06/gen
Zero-point correction= 0.527593 (Hartree/Particle)
Thermal correction to Energy= 0.564709
Thermal correction to Enthalpy= 0.565653
Thermal correction to Gibbs Free Energy= 0.455112
Sum of electronic and ZPE= -1875.719121
Sum of electronic and thermal Energies= -1875.682005
Sum of electronic and thermal Enthalpies= -1875.681061
Sum of electronic and thermal Free Energies= -1875.791602

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.360	138.300	232.653

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C,0,-1.0527191088,1.008861127,-0.7245186749
C,0,-2.205126283,0.2215987502,-0.8578388395
C,0,-3.4758668195,0.8000117117,-0.8386156973
Ir,0,0.9078717754,0.0876196703,-0.2663352004
N,0,-0.2242150629,-1.7350552228,0.5784405006
C,0,-0.7315333501,-1.5974884396,1.817577286
C,0,-1.5340278049,-2.5903582953,2.3817504461
C,0,-1.8034108904,-3.7405863398,1.6542990575
C,0,-1.2579094601,-3.8799978852,0.3856382438
C,0,-0.4750631446,-2.8482790721,-0.1163860551
C,0,-0.3560207378,-0.3644194104,2.5437777166
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B,0,2.7399723978,-0.7506998077,0.4050040457
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O,0,3.7741947334,-0.0617238476,1.0151800568
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O,0,3.1599211687,-0.5298072009,-2.3317086557
C,0,3.4182495281,-1.3873065871,-3.4321121582
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H,0,3.2688178685,-0.8296895262,-4.3685754185
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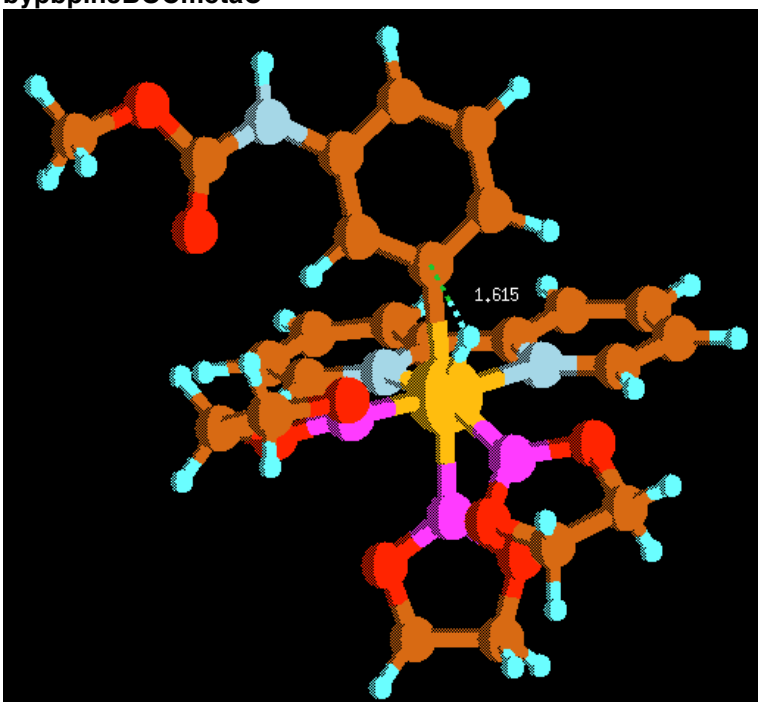
H,0,5.7573078104,-0.6116368904,1.2170575307
H,0,2.8947975516,4.7100068402,-0.2172304018
H,0,4.1546019933,3.5354437132,-0.6741886041
H,0,1.6310879042,4.2974463576,-2.2263834937
H,0,3.1983044852,3.7554576914,-2.8769661631
H,0,-5.5042790624,0.552533598,-1.2080788719
C,0,-4.8383894577,-1.2860157171,-0.7394861993
O,0,-4.0018940211,-2.0931061718,-0.3902532464
O,0,-6.1408309656,-1.5996390344,-0.954249689
C,0,-6.4672758239,-2.9680867827,-0.749414267
H,0,-7.5295093607,-3.0589556314,-0.9812884993
H,0,-5.877512692,-3.611478061,-1.4099159882
H,0,-6.2795987515,-3.2615209326,0.2885253026

bypbpin3BOCmetaC



bypbpin3BOCmetaC
M06/gen
E(RM06) = -1876.24577650

Zero-point correction= 0.527752 (Hartree/Particle)
Thermal correction to Energy= 0.564828
Thermal correction to Enthalpy= 0.565772
Thermal correction to Gibbs Free Energy= 0.456204
Sum of electronic and ZPE= -1875.718025
Sum of electronic and thermal Energies= -1875.680948
Sum of electronic and thermal Enthalpies= -1875.680004
Sum of electronic and thermal Free Energies= -1875.789572

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.435	138.359	230.606

C,0,-3.0559333171,3.126453042,-1.0750556758
C,0,-1.7484876393,3.6193905113,-1.0220209366
C,0,-0.6730081566,2.7382280837,-0.8952820903
C,0,-0.8814354618,1.3538712749,-0.8046276535
C,0,-2.1969580329,0.875895069,-0.8920496175
C,0,-3.2705122959,1.7555683451,-1.0143166215
Ir,0,0.7958228535,0.0562921687,-0.1460263479
N,0,-0.7436266763,-1.4062461017,0.7570833382
C,0,-1.2788527002,-1.0478049572,1.9380284967
C,0,-2.3480083587,-1.7585184476,2.4885889135
C,0,-2.8484267423,-2.8623710867,1.8124427403
C,0,-2.2641108663,-3.2417553875,0.6091424718
C,0,-1.2106819496,-2.4813874745,0.1155827654
C,0,-0.6572706127,0.1144649672,2.6097075414
N,0,0.3358454873,0.7389523626,1.9422569965
C,0,0.9795052649,1.7638446481,2.5144711162
C,0,0.6493872862,2.2312699454,3.7803525814
C,0,-0.3805627685,1.6082502771,4.4737116003
C,0,-1.0365701858,0.5361972525,3.8852040679
B,0,2.3665900936,-1.1037770597,0.6892008755
O,0,2.3855642845,-2.5019874363,0.6825103938
C,0,3.6775788944,-2.9143756072,1.1063412456
C,0,4.2134370224,-1.7103364619,1.8764987805
O,0,3.4734850034,-0.6122322419,1.3583165469
B,0,1.6251115358,-1.1552285562,-1.5950431033
O,0,2.934634446,-1.1709668965,-2.0575228789
C,0,3.0423101087,-2.1553913893,-3.0737151005
C,0,1.8130819576,-3.0364626589,-2.8668717974
O,0,0.8946415442,-2.1877643717,-2.1908392877
B,0,2.1255929477,1.4754457251,-0.7486625432
O,0,2.8297027933,2.3054932031,0.1212190387
C,0,3.386014414,3.3893382146,-0.6159787879
C,0,3.1861891325,3.0035149907,-2.0875462845
O,0,2.2963176816,1.8997356051,-2.0575762003
H,0,0.1367329311,0.3869311207,-1.6015826444
H,0,-0.7114837411,-2.7116415294,-0.8259788075
H,0,-2.7953742057,-1.4546033184,3.4299375673
H,0,-2.6179511692,-4.1051395973,0.0533036035
H,0,-3.6844909009,-3.4214356094,2.2257206982
H,0,-1.8327695499,0.0290766108,4.4216047717
H,0,-0.6681421613,1.9448473066,5.4667817917
H,0,1.1974681661,3.0666616436,4.2057154582
H,0,1.7830596713,2.1993198974,1.9207670557
H,0,2.0374099285,-3.9038038344,-2.2264332257
H,0,1.3701771712,-3.3944166252,-3.8033840535
H,0,3.9873821378,-2.7005903373,-2.9641559959
H,0,3.0377059699,-1.6627106753,-4.0571009644
H,0,0.3304156253,3.1499924457,-0.8744670055
H,0,-4.2867865025,1.3693874002,-1.0741023596
H,0,-3.8950852851,3.8142747409,-1.1804100075
H,0,-2.3917584102,-0.1963830052,-0.8722542131
N,0,-1.5938700354,5.0199418257,-1.1068816601

H,0,3.6022114883,-3.8258468123,1.7105166581
H,0,4.2904718449,-3.1309266294,0.2160980879
H,0,4.0267395968,-1.7948621158,2.9577551837
H,0,5.2848699856,-1.5395932029,1.7225096393
H,0,2.8437136537,4.3104558219,-0.363158413
H,0,4.4419694847,3.5093634023,-0.3438893426
H,0,2.7365152867,3.8181764208,-2.6691127696
H,0,4.123460721,2.6985606059,-2.5740991291
H,0,-2.4440591177,5.5640123617,-1.1712390278
C,0,-0.4451772312,5.7495890364,-1.1645541563
O,0,0.6971281831,5.3402713426,-1.1299809943
O,0,-0.7681153688,7.0625541997,-1.2689588361
C,0,0.3429476198,7.9477191916,-1.3438450876
H,0,-0.080504401,8.9508076192,-1.4126979302
H,0,0.970100948,7.8608084408,-0.4510767882
H,0,0.9531426786,7.7321533068,-2.2266396871

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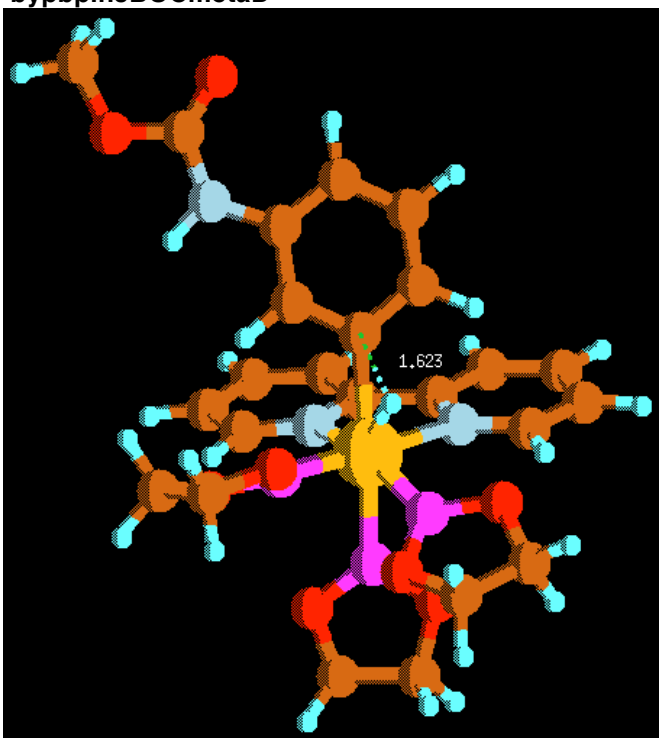

bypbpin3BOCmetaD
M06/gen
E(RM06) = -1876.24521864

Zero-point correction= 0.527729 (Hartree/Particle)
Thermal correction to Energy= 0.564933
Thermal correction to Enthalpy= 0.565877
Thermal correction to Gibbs Free Energy= 0.454139
Sum of electronic and ZPE= -1875.717489
Sum of electronic and thermal Energies= -1875.680286
Sum of electronic and thermal Enthalpies= -1875.679342
Sum of electronic and thermal Free Energies= -1875.791080

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.501	138.270	235.173

C,0,3.071916534,2.453771396,-2.2861275216
C,0,3.352887857,1.4168493203,-1.3941096603
C,0,2.3210894401,0.5945399261,-0.9256886648
C,0,0.9903692707,0.7894350758,-1.303932368
C,0,0.7281403899,1.8173700546,-2.2227470615
C,0,1.7526828425,2.6326846321,-2.6942757412
Ir,0,-0.6253706631,-0.2263090986,-0.1743808215
N,0,-1.9113406107,1.6578519726,-0.4887056807
C,0,-1.617934735,2.7108052176,0.2957780504
C,0,-2.2066151799,3.958091022,0.0765573622
C,0,-3.1194519826,4.1046440187,-0.9583543125
C,0,-3.4354635417,3.001946221,-1.7433673645
C,0,-2.8052140159,1.7931327817,-1.4728541041
C,0,-0.6683169867,2.4576741665,1.4010188679
N,0,-0.1678671788,1.2078230778,1.491756217
C,0,0.6484161925,0.8907628872,2.5041548584
C,0,1.0287007578,1.8162067292,3.4673778735
C,0,0.5403166614,3.11345451,3.3738390353
C,0,-0.3216459845,3.4355308983,2.335315459
B,0,-2.1566637384,-1.0420770085,1.0564544035
O,0,-3.5174069181,-0.9569581399,0.7496556659
C,0,-4.2156670698,-1.8025145513,1.6539974837
C,0,-3.2554979427,-1.9563613395,2.8305847336
O,0,-1.9774453144,-1.6787312805,2.2721055751
B,0,-1.7295624584,-1.5963254725,-1.2510099511
O,0,-1.8907479505,-2.9521123146,-0.997416453
C,0,-2.6976037455,-3.5073785638,-2.024284188
C,0,-3.384755554,-2.2962328178,-2.6487417803
O,0,-2.5133668311,-1.2147108226,-2.3419031979
B,0,0.5781422927,-1.7950118896,0.2883136238
O,0,1.1563144014,-2.0086964421,1.5453564486
C,0,2.1348740665,-3.0313394273,1.4272703125
C,0,1.8109993943,-3.704654135,0.0946283943
O,0,1.0780566226,-2.7239899188,-0.6174999529
H,0,0.0222121859,-0.46724124,-1.6484368515
H,0,-2.9961739888,0.8915620758,-2.0551079145
H,0,-1.9565356438,4.8105480235,0.7004325547
H,0,-4.1518919395,3.0703742432,-2.5567909121
H,0,-3.5810123482,5.0712105448,-1.1451327352
H,0,-0.7204893709,4.4420357464,2.2578490846
H,0,0.8199672443,3.8684463882,4.1043947094
H,0,1.6960265988,1.5161295014,4.2698657304
H,0,0.9907513478,-0.1433323611,2.5215965052
H,0,-4.3675640829,-2.1050876846,-2.1902409607
H,0,-3.5110464003,-2.3766222474,-3.7342667416
H,0,-3.402058944,-4.2291223136,-1.5940880765
H,0,-2.054529151,-4.034510255,-2.744353973
H,0,2.5809925991,-0.2142959113,-0.2376348858
H,0,1.5259259758,3.4260229357,-3.4049980796

H,0,3.8696078791,3.0885156416,-2.6552112751
H,0,-0.2870400967,1.9789498953,-2.5858005354
N,0,4.6510537201,1.1280262864,-0.9272486863
H,0,-5.1757390325,-1.349183037,1.9261447585
H,0,-4.4099795242,-2.7678291269,1.1590274719
H,0,-3.4660424073,-1.2326561255,3.6321349813
H,0,-3.2589826999,-2.9629765007,3.263831125
H,0,3.1378415196,-2.5742922324,1.4232596739
H,0,2.0706756938,-3.709815995,2.2858415942
H,0,2.7038509778,-3.9903987789,-0.4740421128
H,0,1.1834423291,-4.598317295,0.2288554989
H,0,4.7433263672,0.3206219058,-0.3249726635
C,0,5.8117231686,1.7911212431,-1.1906360506
O,0,5.9565906639,2.7790642192,-1.8794549121
O,0,6.8285797016,1.1675740249,-0.5452372238
C,0,8.1081890141,1.7585589488,-0.7388264487
H,0,8.8074884629,1.1470273495,-0.1666686165
H,0,8.3807199571,1.7570277246,-1.7987793589
H,0,8.119532902,2.7904817214,-0.3740132147

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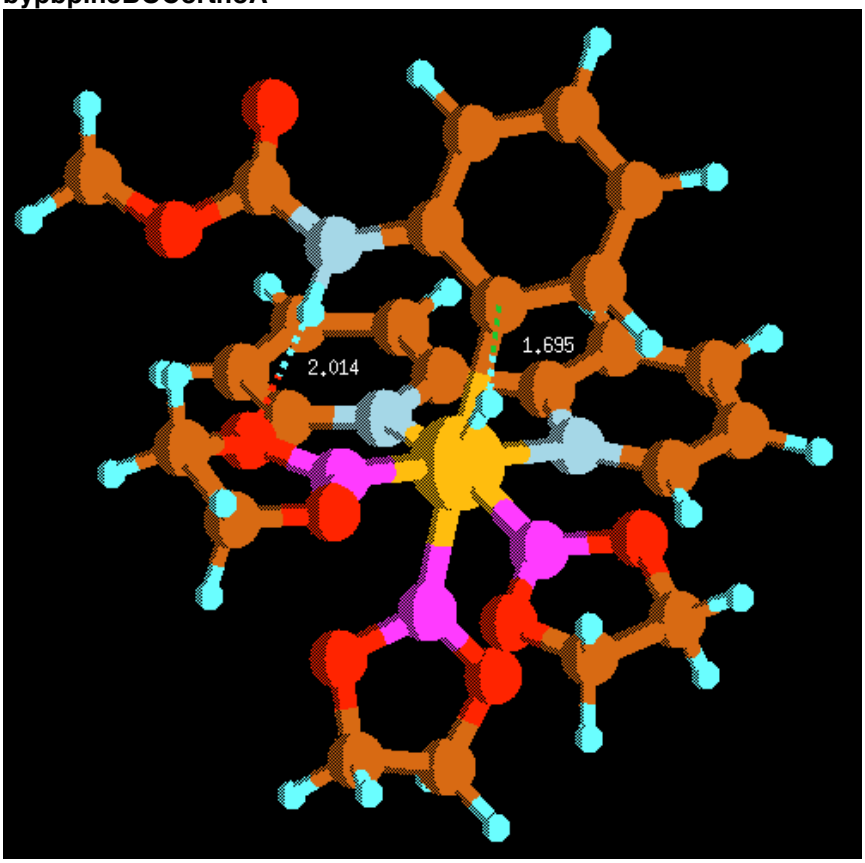

bypbpin3BOCortho
M06/gen
E(RM06) = -1876.24986607

Zero-point correction= 0.528726 (Hartree/Particle)
Thermal correction to Energy= 0.565510

Thermal correction to Enthalpy= 0.566454
Thermal correction to Gibbs Free Energy= 0.458582
Sum of electronic and ZPE= -1875.721140
Sum of electronic and thermal Energies= -1875.684356
Sum of electronic and thermal Enthalpies= -1875.683412
Sum of electronic and thermal Free Energies= -1875.791284

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.863	137.781	227.036

C,0,2.4355062131,2.6782635118,-2.920431008
C,0,3.0013649355,1.6533537227,-2.1705357532
C,0,2.1839390055,0.7085368168,-1.534768968
C,0,0.7783260848,0.8100849174,-1.6090206651
C,0,0.2520493567,1.8222184557,-2.4215484609
C,0,1.0543829453,2.759897062,-3.0659509435
Ir,0,-0.6145318077,-0.1969103739,-0.1766506648
N,0,-1.0255139364,2.0540969611,0.366240423
C,0,0.0040400795,2.669005568,0.97698018
C,0,0.1007769344,4.0605912127,1.0122010645
C,0,-0.903910399,4.8245598386,0.4339125725
C,0,-1.9888674553,4.1815398573,-0.1466538027
C,0,-2.0032614231,2.7912238521,-0.1636896447
C,0,0.9849449174,1.7857992528,1.6416271072
N,0,0.7887521316,0.4581030155,1.5033373198
C,0,1.5529183261,-0.3917511337,2.1996047453
C,0,2.5906156775,0.0330139749,3.0187631789
C,0,2.8500196813,1.394360114,3.10769429
C,0,2.0287796529,2.2800441858,2.4248482232
B,0,-1.9735350879,-0.9861256595,1.2473694343
O,0,-3.0969944906,-0.306239004,1.7085273962
C,0,-3.7350065291,-1.1121159407,2.6932829714
C,0,-3.1207086995,-2.4968677069,2.4976619643
O,0,-1.8845706937,-2.2377241978,1.8426898714
B,0,-2.4091785504,-0.5899372735,-1.1098790334
O,0,-3.1664879496,-1.7482976923,-1.1200502425
C,0,-4.2954229187,-1.54563597,-1.9542774504
C,0,-4.3998469769,-0.027880317,-2.0745593056
O,0,-3.0803489329,0.4271148561,-1.795531058
B,0,-0.0995035134,-2.1534183517,-0.3485120984
O,0,1.0657777012,-2.6294845492,0.2787639812
C,0,1.2936071302,-3.9681342279,-0.1516265087
C,0,-0.0537682394,-4.3882803428,-0.731927631
O,0,-0.6766650916,-3.1656028491,-1.0877156245
H,0,-0.4077629443,-0.3904089499,-1.7667449556
H,0,-2.801251666,2.2310642572,-0.6466387368
H,0,0.9509448857,4.5496457283,1.4773113878
H,0,-2.8056333356,4.7380852692,-0.5969218027
H,0,-0.8387230695,5.9097975467,0.4440235207
H,0,2.1994688688,3.3483279208,2.5091965337
H,0,3.6734211714,1.768058459,3.7110281667
H,0,3.1902885702,-0.6996280082,3.5510541304

H,0,1.3368582028,-1.4475258938,2.0544311648
H,0,-5.089004956,0.3946762914,-1.3273462784
H,0,-4.7067446068,0.3136378057,-3.0694277836
H,0,-5.1808588966,-2.0055068251,-1.5005121443
H,0,-4.1150734702,-2.0261346066,-2.9269606346
N,0,2.7510995966,-0.3632734175,-0.8094995055
H,0,4.0782978859,1.5789268777,-2.0658657114
H,0,3.0865268354,3.4017620198,-3.4072614664
H,0,-0.8312976513,1.8847384615,-2.5358452311
H,0,0.6037766164,3.5398679066,-3.6771499515
H,0,-3.5218478585,-0.6997680546,3.6905123028
H,0,-4.8200122881,-1.0963580156,2.5382609418
H,0,-2.9420433124,-3.0323600524,3.4368783875
H,0,-3.7383418534,-3.1283078103,1.8414653776
H,0,2.0949890216,-3.9691764016,-0.9053370865
H,0,1.6135084591,-4.5804588965,0.698842074
H,0,0.0337395036,-5.0330314176,-1.6136348744
H,0,-0.6760211222,-4.8980708314,0.0187336085
H,0,2.1306762214,-1.1230059046,-0.5300517875
C,0,4.0321545264,-0.4778537401,-0.3680766718
O,0,4.9385885261,0.3259209642,-0.4755044482
O,0,4.1840540566,-1.6782818389,0.2535967689
C,0,5.4852203628,-1.9161731641,0.768874118
H,0,5.4397533677,-2.8925289186,1.2553197318
H,0,6.2291335379,-1.9291932495,-0.0345265785
H,0,5.7702047919,-1.1437528973,1.4916513448

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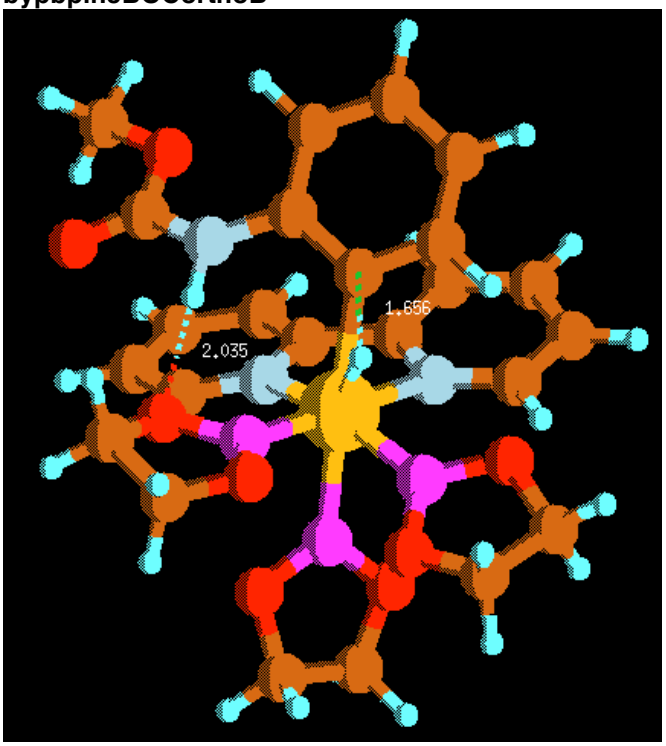


bypbpin3BOCortho low basis temp
M06/gen
E(RM06) = -1876.24734654

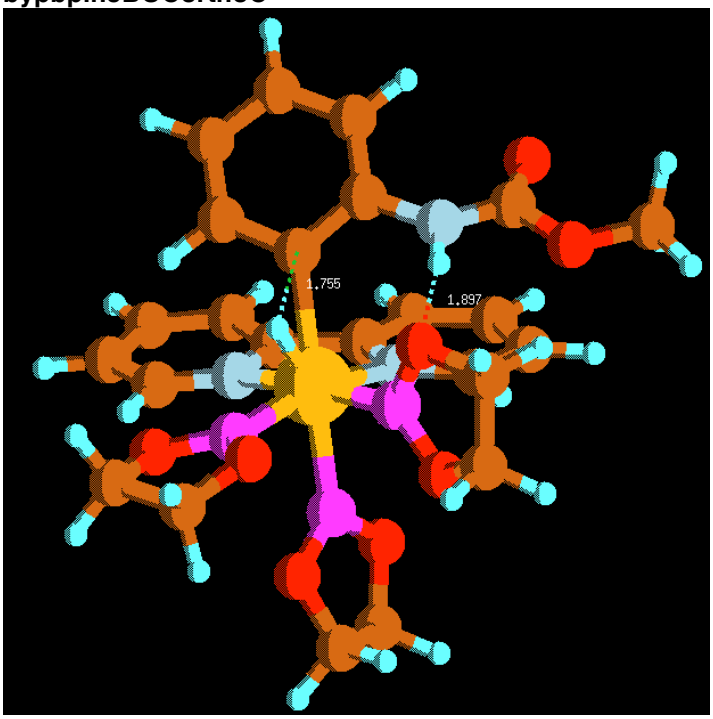
Zero-point correction= 0.528453 (Hartree/Particle)
Thermal correction to Energy= 0.565065
Thermal correction to Enthalpy= 0.566009
Thermal correction to Gibbs Free Energy= 0.459333
Sum of electronic and ZPE= -1875.718894
Sum of electronic and thermal Energies= -1875.682282
Sum of electronic and thermal Enthalpies= -1875.681338
Sum of electronic and thermal Free Energies= -1875.788013

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.583	137.877	224.517

C,0,2.262484521,2.5507804287,-3.3764881947
C,0,2.8855356229,1.6024954201,-2.5753986627
C,0,2.1296899808,0.7048766162,-1.811274135
C,0,0.721088806,0.7437859968,-1.8455158898
C,0,0.1281830818,1.6781680964,-2.7065785347
C,0,0.8727244589,2.5875232065,-3.4514168139
Ir,0,-0.5487619721,-0.2687963819,-0.3078457672
N,0,-0.9845503532,1.9842200604,0.2288799947
C,0,0.0516068887,2.6137829756,0.8118050951
C,0,0.1758732159,4.002761498,0.7703061507
C,0,-0.826243209,4.7538372578,0.1707068777
C,0,-1.9295825313,4.1000268076,-0.3620056119
C,0,-1.9590848599,2.7099931113,-0.3232902954
C,0,1.0174263371,1.7506050758,1.5217480336
N,0,0.9170569436,0.4222287802,1.3076938591
C,0,1.6922537852,-0.4128519151,2.0106305149
C,0,2.6257813693,0.0333185557,2.9378306547
C,0,2.753529059,1.3997071022,3.1473847769
C,0,1.9373497997,2.2671232123,2.4346423154
B,0,-1.7760484415,-1.0566115626,1.2284228031
O,0,-2.8759242397,-0.389343916,1.7589390564
C,0,-3.3962747021,-1.168268629,2.8305960378
C,0,-2.7613382549,-2.5435925879,2.6355515202
O,0,-1.5991327726,-2.2809067349,1.8582970781
B,0,-2.3931842525,-0.7147048074,-1.1037801467
O,0,-3.1348738845,-1.8807666398,-1.0173539541
C,0,-4.3322602486,-1.7164801552,-1.7588354273
C,0,-4.4641492843,-0.2046045178,-1.9202697907
O,0,-3.1316982628,0.2713314012,-1.7679375524
B,0,0.0000413944,-2.2167320946,-0.5007128197
O,0,1.2229671904,-2.6587629322,0.0282338038
C,0,1.4281258318,-4.0125357237,-0.3668710062
C,0,0.0490307821,-4.4584248915,-0.8500230275
O,0,-0.6200938837,-3.2505197765,-1.1717043318
H,0,-0.3909515263,-0.482210443,-1.9032812775
H,0,-2.7666713243,2.1382761791,-0.7765364529
H,0,1.0519235766,4.4927660017,1.1848388525
H,0,-2.7459347852,4.6470239893,-0.8247239632
H,0,-0.7434817271,5.836918515,0.1222550663

H,0,1.9955434851,3.3371616444,2.6092353451
H,0,3.4725185094,1.7896153653,3.8642864534
H,0,3.2468539937,-0.6888164333,3.4590277644
H,0,1.5789733648,-1.4705407048,1.7837490102
H,0,-5.0933330037,0.2364350554,-1.1319648689
H,0,-4.8575340443,0.0992610648,-2.8968157452
H,0,-5.1705287468,-2.1679426235,-1.2158323898
H,0,-4.2296819661,-2.2282401392,-2.7269905883
N,0,2.7822453715,-0.2769608055,-1.0243140434
H,0,3.9697652622,1.5511874782,-2.5372008262
H,0,2.8675026913,3.2405347704,-3.961420318
H,0,-0.9600194609,1.6951779087,-2.786015279
H,0,0.3718654479,3.3073095741,-4.0963350473
H,0,-3.1029398413,-0.7076123561,3.7855432244
H,0,-4.4911180308,-1.1865608639,2.7792988654
H,0,-2.4796865463,-3.0309755064,3.5757998305
H,0,-3.4173824765,-3.2201484725,2.0681752951
H,0,2.1845642151,-4.0406019532,-1.1641625823
H,0,1.8013098862,-4.5918795364,0.4844695208
H,0,0.0880992034,-5.1087585599,-1.7312025528
H,0,-0.5127441965,-4.9743764877,-0.0570889024
H,0,2.2709148707,-1.1363886426,-0.823301289
C,0,3.8999020664,-0.1741482095,-0.2525658621
O,0,4.3596204401,-1.096860113,0.3979089626
O,0,4.4367899155,1.0655249635,-0.2529512285
C,0,5.6054327262,1.2079611004,0.5424741983
H,0,5.9228122961,2.2452893022,0.420450092
H,0,5.3900084002,0.9989613164,1.5966574654
H,0,6.3941360377,0.5266052851,0.2080866595

bypbpin3BOCorthoC



bypbpin3BOCortho low basis temp with boc on wrong side
M06/gen
E(RM06) = -1876.25433741

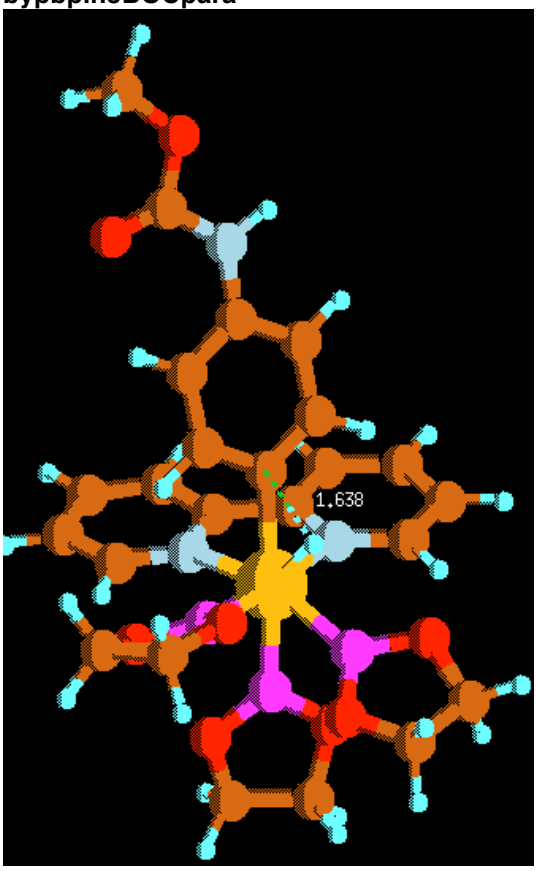
Zero-point correction= 0.529284 (Hartree/Particle)
Thermal correction to Energy= 0.565638
Thermal correction to Enthalpy= 0.566582
Thermal correction to Gibbs Free Energy= 0.460429
Sum of electronic and ZPE= -1875.725053
Sum of electronic and thermal Energies= -1875.688699
Sum of electronic and thermal Enthalpies= -1875.687755
Sum of electronic and thermal Free Energies= -1875.793909

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.943	137.392	223.419

C,0,2.5062978766,2.7924953065,-2.8111150489
C,0,3.008637585,1.7369604868,-2.0542551947
C,0,2.1273484661,0.8022994019,-1.5153957543
C,0,0.7394653632,0.8934801114,-1.6826041946
C,0,0.2731532966,1.9128143638,-2.5336091985
C,0,1.1425551128,2.8693256818,-3.0689375786
Ir,0,-0.5905656438,-0.1795723974,-0.2308513915
N,0,-1.2755736654,1.8513627115,0.3834732865
C,0,-0.3869886374,2.6495501622,1.0068287995
C,0,-0.6687202171,3.9988281108,1.228475412
C,0,-1.8873057058,4.5181224928,0.8201411019
C,0,-2.8130471621,3.6731898131,0.2207729681
C,0,-2.464196497,2.346083689,0.0216609446
C,0,0.8597766251,2.0074942115,1.4763498852
N,0,0.9536519144,0.6788547873,1.2830113365
C,0,2.0189658273,0.0169712459,1.7414680572
C,0,3.0691751922,0.654845224,2.3914489736
C,0,3.0036251805,2.0327796672,2.5585210267
C,0,1.8847413799,2.7170121353,2.1039675381
B,0,-1.8136243181,-0.954289557,1.3210845599
O,0,-2.5827156527,-0.11479373,2.1207085941
C,0,-3.2341289411,-0.9031828755,3.1089165918
C,0,-3.1044662714,-2.3324011329,2.5895571378
O,0,-1.991864119,-2.2779878277,1.7075212732
B,0,-2.1734977423,-0.7735289624,-1.3565701667
O,0,-3.4267587415,-1.1555394383,-0.8863593066
C,0,-4.1856549955,-1.6450561511,-1.984206839
C,0,-3.514194772,-1.0220368719,-3.2036423063
O,0,-2.1864201783,-0.7580613145,-2.758300215
B,0,-0.119007224,-2.1811759698,-0.2030209813
O,0,0.9446215065,-2.6838593922,0.5430589213
C,0,1.040301617,-4.0814591995,0.2859062274
C,0,-0.2973996896,-4.4311624828,-0.3647459017
O,0,-0.7557546075,-3.1971245441,-0.8960970216
H,0,0.1956743195,-0.7670166653,-1.5130827152
H,0,-3.1513035358,1.6488356042,-0.4542445498

H,0,0.0552676781,4.6420902047,1.718089557
H,0,-3.7862466424,4.0312257496,-0.1021926938
H,0,-2.1119644022,5.5701901523,0.9738446271
H,0,1.8204751399,3.792869641,2.2327251962
H,0,3.8137393599,2.5733809388,3.0418713885
H,0,3.9205752325,0.0794223128,2.7431419795
H,0,2.0164473413,-1.057097073,1.5559024222
H,0,-3.9833969548,-0.0699762627,-3.4961001108
H,0,-3.4863234914,-1.6857820049,-4.0744229676
H,0,-5.236694397,-1.356489974,-1.8700083002
H,0,-4.1201071909,-2.7429070073,-1.9984496778
N,0,-1.0988891368,1.9326681854,-2.8735951705
H,0,4.0797729904,1.6389177463,-1.885283196
H,0,3.1761770325,3.5408204599,-3.2295584094
H,0,2.5350439041,-0.0171808194,-0.9207447514
H,0,0.7386774728,3.6680672602,-3.6848602517
H,0,-2.7242452577,-0.7648259182,4.0739953341
H,0,-4.2746408484,-0.5757049151,3.2165626454
H,0,-2.9201694599,-3.0692684369,3.3798606107
H,0,-3.9932938631,-2.6405576379,2.0188079438
H,0,1.8898583073,-4.264927153,-0.3880652584
H,0,1.216421695,-4.6188668263,1.2246520924
H,0,-0.2091136877,-5.1728145315,-1.166560203
H,0,-1.0255904002,-4.7902034489,0.3767665392
H,0,-1.5579388639,1.0228246343,-2.9385645437
C,0,-1.8729163043,3.0265247265,-3.0521133591
O,0,-1.5444412484,4.1964985794,-2.9922497029
O,0,-3.1560020365,2.6284368591,-3.3015493943
C,0,-4.0590852134,3.6889872686,-3.5756845388
H,0,-5.0372618492,3.22448492,-3.715026399
H,0,-4.0909090558,4.4034285806,-2.7457050869
H,0,-3.7662507955,4.228591095,-4.4826425922

bypbpin3BOCpara



bypbpin3BOCpara
M06/gen
E(RM06) = -1876.24401359

Zero-point correction= 0.527814 (Hartree/Particle)
Thermal correction to Energy= 0.564970
Thermal correction to Enthalpy= 0.565915
Thermal correction to Gibbs Free Energy= 0.455277
Sum of electronic and ZPE= -1875.716200
Sum of electronic and thermal Energies= -1875.679043
Sum of electronic and thermal Enthalpies= -1875.678099
Sum of electronic and thermal Free Energies= -1875.788736

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.524	138.297	232.855

C,0,-3.7508781351,2.9205611615,-0.9839072807
C,0,-2.6720288427,3.4502265606,-0.2736824862
C,0,-1.4926321897,2.7150085045,-0.1729671972
C,0,-1.3416302199,1.4385263495,-0.7316122455
C,0,-2.4334315951,0.9481136203,-1.4626412055
C,0,-3.6178656287,1.6662935529,-1.5853229267
Ir,0,0.3530670497,0.1508799273,-0.1232111852
N,0,-1.0526248798,-1.6596689902,-0.3312418255
C,0,-1.9427674839,-1.8312096611,0.6632554613

C,0,-2.9667345832,-2.7751316689,0.5565019143
C,0,-3.0527276689,-3.556348521,-0.5873749758
C,0,-2.1076345682,-3.3907252843,-1.5934958423
C,0,-1.12035649,-2.4275574242,-1.4232962134
C,0,-1.7557477039,-0.9843829943,1.8615727751
N,0,-0.7377148558,-0.0995146709,1.8223140662
C,0,-0.4736787087,0.658179718,2.8935753486
C,0,-1.2331575921,0.5885677205,4.0546238566
C,0,-2.298904824,-0.3010652353,4.1019479272
C,0,-2.5585426518,-1.1005318002,2.997492868
B,0,1.8535179881,-1.127923897,0.672836669
O,0,2.1694721941,-2.3822792969,0.1429952662
C,0,3.3566936979,-2.8303409203,0.7837156065
C,0,3.3960151961,-2.0324873515,2.0838426337
O,0,2.6086692656,-0.881115675,1.8057575206
B,0,1.744391852,-0.2918386522,-1.578954183
O,0,3.0975036943,0.0226910075,-1.5892412835
C,0,3.6590499293,-0.4522504133,-2.8028111858
C,0,2.6415587339,-1.4722414896,-3.3058423585
O,0,1.4224448607,-1.0663358188,-2.6968006545
B,0,1.5085620598,1.776239873,0.2615007064
O,0,1.8274835739,2.2325627662,1.5445811859
C,0,2.3845434088,3.5351685475,1.4358891841
C,0,2.77042929,3.6529443593,-0.0380655696
O,0,1.9603183011,2.6874776391,-0.6855307225
H,0,0.0399410158,0.9856148327,-1.4852578027
H,0,-0.3538136034,-2.2348829466,-2.1745327209
H,0,-3.6954966862,-2.9009253483,1.3513267851
H,0,-2.1314859649,-3.9896237945,-2.4992990187
H,0,-3.8489256799,-4.2900635782,-0.6877629753
H,0,-3.3802705739,-1.8095321881,3.0244773661
H,0,-2.9212181711,-0.3783800494,4.9900676134
H,0,-0.9874360981,1.2259849397,4.8987268098
H,0,0.3773964152,1.3315313983,2.7914794131
H,0,2.8864486191,-2.4911705787,-2.968288028
H,0,2.5305153366,-1.4770740506,-4.3961777482
H,0,4.6469223097,-0.8874579671,-2.6095496728
H,0,3.7795790304,0.3901239669,-3.4999142495
H,0,-0.6672047002,3.1668289582,0.3782781288
H,0,-2.7581140739,4.4263383224,0.1913422127
H,0,-4.4474900943,1.2523530894,-2.1606679882
H,0,-2.3649456402,-0.0212992005,-1.9586919519
N,0,-4.9789695649,3.5918497441,-1.1535628464
H,0,3.3166948534,-3.9154003348,0.9333748442
H,0,4.2185897953,-2.5953831555,0.1379626983
H,0,2.9456613583,-2.5858405574,2.9215524414
H,0,4.4073934269,-1.7272591896,2.3748037717
H,0,1.6234021024,4.2784810823,1.7214140826
H,0,3.236579425,3.6331542179,2.1185653701
H,0,2.5740253721,4.6465433939,-0.4577079143
H,0,3.829714837,3.4065787572,-0.2052425365
H,0,-5.6643298807,3.1423731653,-1.7458368402
C,0,-5.3708455798,4.7808890066,-0.6157836117

O,0,-4.7351331453,5.5005774365,0.1252608981
O,0,-6.6280456737,5.0607649072,-1.0412037832
C,0,-7.1617886386,6.2860083125,-0.5527228315
H,0,-8.1619403069,6.3659186177,-0.9813393666
H,0,-7.2152826206,6.2778318974,0.5404162009
H,0,-6.5434606744,7.1319503506,-0.868572398

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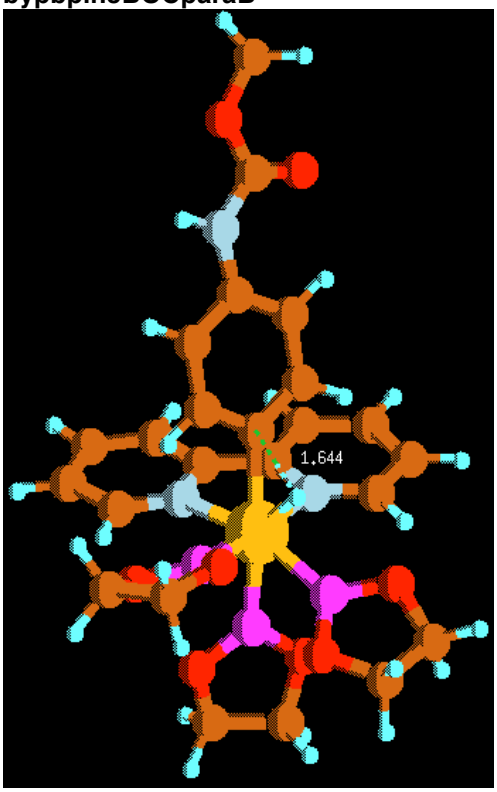

bypbpin3BOCparaB low basis
M06/gen
E(RM06) = -1876.24428321

Zero-point correction= 0.527068 (Hartree/Particle)
Thermal correction to Energy= 0.564490
Thermal correction to Enthalpy= 0.565435
Thermal correction to Gibbs Free Energy= 0.453334
Sum of electronic and ZPE= -1875.717216
Sum of electronic and thermal Energies= -1875.679793
Sum of electronic and thermal Enthalpies= -1875.678849
Sum of electronic and thermal Free Energies= -1875.790949

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.223	138.657	235.936

Zero-point correction= 0.527067 (Hartree/Particle)
Thermal correction to Energy= 0.564490
Thermal correction to Enthalpy= 0.565435
Thermal correction to Gibbs Free Energy= 0.453334
Sum of electronic and ZPE= -1875.717216

Sum of electronic and thermal Energies= -1875.679793
Sum of electronic and thermal Enthalpies= -1875.678849
Sum of electronic and thermal Free Energies= -1875.790949

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	354.223	138.657	235.935

C,0,4.0125151551,0.0033547704,-1.06656327
C,0,3.4732460674,-1.0016399373,-0.2587322856
C,0,2.0967032445,-1.1396746075,-0.1244932444
C,0,1.2004340026,-0.2684021304,-0.7618820957
C,0,1.7714644735,0.7050858072,-1.5928156603
C,0,3.1479889664,0.859415207,-1.7500634455
Ir,0,-0.9222466097,-0.2021637065,-0.1442841021
N,0,-0.9014079955,2.0477541839,-0.6411396715
C,0,-0.2872665202,2.8421748097,0.254128795
C,0,-0.0279222558,4.1840555304,-0.0329948316
C,0,-0.4269435894,4.7044199098,-1.2563071008
C,0,-1.0879268922,3.8805580719,-2.1597942476
C,0,-1.3050403036,2.5530012449,-1.8104835007
C,0,0.0703996552,2.2146420657,1.5453170865
N,0,-0.2004412603,0.8988367214,1.6743944061
C,0,0.0407697863,0.2808055069,2.8370619909
C,0,0.5875385129,0.9433660397,3.9284077425
C,0,0.8897683957,2.2939764953,3.8046833998
C,0,0.6237528331,2.9367706898,2.6040925172
B,0,-2.8879477319,0.0059215264,0.646557004
O,0,-3.8750376617,0.7987651025,0.054351345
C,0,-5.1002035759,0.5332773359,0.7239661329
C,0,-4.6662126081,-0.0408809688,2.0696081008
O,0,-3.3585452257,-0.5434915907,1.8259303163
B,0,-2.3160272792,-0.8536831879,-1.517375158
O,0,-3.2317184016,-1.8904183465,-1.382706887
C,0,-3.9684501441,-1.9984726986,-2.590960414
C,0,-3.7398324391,-0.658065423,-3.2837176762
O,0,-2.5130604536,-0.1953202355,-2.7335645907
B,0,-0.8555223034,-2.1304322723,0.4866958872
O,0,-0.8336209665,-2.5206406937,1.8302013676
C,0,-0.5047126834,-3.9009176597,1.8967755692
C,0,-0.7448879368,-4.4091763825,0.4760249282
O,0,-0.6639983965,-3.2435952671,-0.3251206679
H,0,-0.1812737952,-0.8385791617,-1.446910405
H,0,-1.8035421312,1.8476838501,-2.4758972127
H,0,0.48755616,4.8195361883,0.6804653812
H,0,-1.4245229045,4.2503149333,-3.123985769
H,0,-0.223538618,5.7447762387,-1.4981475762
H,0,0.8401132763,3.9951404995,2.4974985768
H,0,1.3220315618,2.8461578279,4.6356107311
H,0,0.7692757519,0.4023947134,4.8523090361
H,0,-0.2247775479,-0.7757209522,2.8679365967
H,0,-4.5346766784,0.064944638,-3.0433513375
H,0,-3.6528839741,-0.7385064301,-4.3732124541

H,0,-5.0236364207,-2.1937774974,-2.366002136
H,0,-3.5765625176,-2.8404399607,-3.1805902382
H,0,1.7230203746,-1.9483499508,0.5044934852
H,0,4.1403585264,-1.6861384875,0.2676447693
H,0,3.5493752277,1.6313812137,-2.3979684728
H,0,1.1254330982,1.3784247795,-2.1572215845
N,0,5.4174716941,0.0718029653,-1.1606328705
H,0,-5.6897276076,1.4534726812,0.8081638364
H,0,-5.675685444,-0.1997397138,0.1356228591
H,0,-4.6168000141,0.7324393902,2.8508467244
H,0,-5.3132111622,-0.8507187589,2.4251147537
H,0,0.5499807397,-4.0078010375,2.1974070478
H,0,-1.1299124561,-4.3963205089,2.6486930784
H,0,0.0010274686,-5.1423469585,0.1467087762
H,0,-1.7439031949,-4.8570079062,0.3654162251
H,0,5.9399545103,-0.654195876,-0.6887058124
C,0,6.173738129,1.0099526808,-1.7960456866
O,0,5.7812917963,1.9789590444,-2.4117257011
O,0,7.4839047819,0.6979302308,-1.6374551481
C,0,8.3907860714,1.6015370369,-2.2580072038
H,0,9.3878371025,1.2048352081,-2.0606924929
H,0,8.2098160669,1.6548258029,-3.3359797203
H,0,8.2912512704,2.605581367,-1.8336017948

Irbpy_Bpin3

Irbpy_Bpin3 Ir(bpy)(Bpin)3 is the active form of the catalyst. This structure is similar to that calculated by Sakaki with B3LYP and a smaller basis set.
M06/gen
E(RM06) = -1361.09057697

Zero-point correction= 0.371139 (Hartree/Particle)
Thermal correction to Energy= 0.396940
Thermal correction to Enthalpy= 0.397885
Thermal correction to Gibbs Free Energy= 0.313304
Sum of electronic and ZPE= -1360.719438
Sum of electronic and thermal Energies= -1360.693637
Sum of electronic and thermal Enthalpies= -1360.692692
Sum of electronic and thermal Free Energies= -1360.777273

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	249.084	96.118	178.015

Ir,0,0.0176902836,0.0460349192,-0.2888757923
N,0,-1.8538041595,-1.2247832997,-0.0062686815
C,0,-1.7921189396,-2.512223938,0.3476118331
C,0,-2.925488719,-3.2783338526,0.5867282899
C,0,-4.1706197341,-2.6737068195,0.4601133701
C,0,-4.2381755445,-1.3331352882,0.1037065775
C,0,-3.0555300875,-0.6282189365,-0.1270900407
C,0,-3.0348477074,0.8081020573,-0.4900280422
C,0,-4.1944425945,1.5308836279,-0.7723234331
C,0,-4.0959018365,2.8816554699,-1.0808931181

C,0,-2.8434754537,3.4832312595,-1.0955314534
C,0,-1.7281851531,2.7021082344,-0.8139527485
N,0,-1.8215722945,1.3979017099,-0.5257689143
H,0,-0.7907711523,-2.9247908106,0.4510700725
H,0,-2.8263787338,-4.3214269582,0.8716440192
H,0,-5.0828283722,-3.2360202344,0.6432327898
H,0,-5.2041501044,-0.8438912464,0.0216648658
H,0,-5.1667721606,1.0473630666,-0.7631142028
H,0,-4.9910744689,3.456094558,-1.306543683
H,0,-2.7225432075,4.5380019603,-1.3236866231
H,0,-0.7154643933,3.1073838758,-0.8003080974
B,0,1.5158199291,-1.276965962,-0.5563978065
O,0,1.8307402677,-1.7077274494,-1.8475507842
C,0,2.855349522,-2.6844141842,-1.7623855406
C,0,3.4035214562,-2.5298908655,-0.3442258914
O,0,2.3421944955,-1.9178392257,0.371471911
H,0,3.6720079122,-3.4839239519,0.1257077941
H,0,4.28071191,-1.8656733579,-0.3194054792
H,0,3.6109625972,-2.5017527414,-2.5359234675
H,0,2.4238946201,-3.6839514174,-1.9305969819
H,0,2.928543775,-0.782029499,3.1446677002
H,0,2.382349859,0.6113504083,4.125844079
C,0,0.8206051441,-0.8904467008,3.707995069
H,0,1.0305789495,-1.8705017071,4.1527912232
H,0,0.1682852968,-0.3285323849,4.3944129536
O,0,0.1591065156,-1.0577304512,2.4626380706
B,0,0.7088404245,-0.14285599,1.5607710138
O,0,1.7396042896,0.5742092909,2.1597961621
B,0,1.5581203438,1.3566249969,-0.4920498101
O,0,2.9107287967,1.0831538241,-0.6937416922
C,0,3.648407764,2.271146575,-0.4716973054
C,0,2.6228668899,3.3878056911,-0.6551863817
O,0,1.3745088606,2.7502370448,-0.4231518353
H,0,4.0527627755,2.2566569271,0.5521998455
H,0,4.4855469906,2.3331025443,-1.1774553246
H,0,2.7555801873,4.215636433,0.05150383
H,0,2.6385826573,3.796712268,-1.6772687657
C,0,2.0840314197,-0.1080797828,3.3542157095

Irbpy_Bpin3 Isomer B
This is an alternative isomer that is slightly lower in energy.
M06/gen
E(RM06) = -1361.09051610

Zero-point correction= 0.370807 (Hartree/Particle)
Thermal correction to Energy= 0.396820
Thermal correction to Enthalpy= 0.397764
Thermal correction to Gibbs Free Energy= 0.312274
Sum of electronic and ZPE= -1360.719709
Sum of electronic and thermal Energies= -1360.693696
Sum of electronic and thermal Enthalpies= -1360.692752
Sum of electronic and thermal Free Energies= -1360.778242

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	249.008	96.269	179.929

B,0,1.692786538,12.8875448334,5.6407656346
B,0,1.9813407921,11.0298443329,3.7297630086
B,0,2.5173353617,10.5405820385,6.2661351842
C,0,-0.313858819,11.4863345859,8.3591765148
H,0,0.7578461528,11.4258263238,8.536344993
C,0,-1.2139960623,11.7020569535,9.3945373931
H,0,-0.8554876842,11.8022225559,10.4145743272
C,0,-2.5663027972,11.7930745875,9.086367329
C,0,-2.9677323752,11.6680411218,7.7627857913
C,0,-2.0055334431,11.4458336439,6.7760237953
C,0,-2.3443384128,11.3246805757,5.3389888575
C,0,-3.6597886399,11.2669859103,4.877493239
H,0,-4.4937107382,11.2768093166,5.5730802863
C,0,-3.8982838978,11.1824670144,3.5117633314
C,0,-2.8193721186,11.1636806168,2.6362122535
H,0,-2.9611748436,11.1070408649,1.5610692923
C,0,-1.5341434789,11.2137389003,3.1644467089
H,0,-0.641687234,11.210616385,2.5372942534
C,0,2.8456097582,14.8196181405,5.3001008243
C,0,2.4661738637,14.6921788455,6.776041294
C,0,3.721511406,10.674745681,2.2824305398
C,0,2.6229038522,11.4663456143,1.5761223675
C,0,4.6495345825,10.4053582545,7.0468070627
C,0,3.9951349957,9.0272958918,7.1353288773
Ir,0,0.8049060841,11.1320867066,5.382676982
N,0,-0.6976375434,11.3548694517,7.0856429012
N,0,-1.303435399,11.28464317,4.4814613811
O,0,2.5223113011,13.5545856727,4.7468952648
O,0,1.5077292852,13.6453799433,6.7996429221
O,0,3.325246147,10.6691859361,3.6422147631
O,0,1.5055506585,11.3549988938,2.4456980143
O,0,3.564516933,11.2883921813,6.8107521722
O,0,2.7735711824,9.1765045249,6.4302732749
H,0,-4.0190809885,11.7588583445,7.5064017687
H,0,-4.9181772896,11.1331424297,3.1381252705
H,0,-3.3037344439,11.9669904327,9.8659669906
H,0,3.9106673422,15.0304681471,5.1475994242
H,0,2.0303885932,15.6086920765,7.1919229211
H,0,2.260272192,15.6002563754,4.7902101051
H,0,3.3297327658,14.4000872858,7.3923367112
H,0,5.1779455984,10.6965289354,7.9628417092
H,0,3.7842218503,8.7369388026,8.176870744
H,0,3.7832275041,9.6382493623,1.9159221903
H,0,2.3702681998,11.0699632013,0.5850799403
H,0,4.7122539856,11.1346044837,2.1837074623
H,0,2.8891374413,12.5289093149,1.4724844531
H,0,5.3505372492,10.4673992771,6.2006598375
H,0,4.5984865931,8.2362790618,6.6737666376

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