Electronic Supplementary Material (ESI) for ChemComm.

One-pot oxidative hydrolysis-oxidative cleavage of 7-borylindoles enables access to *o*-amidophenols and 4-acylbenzoxazoles

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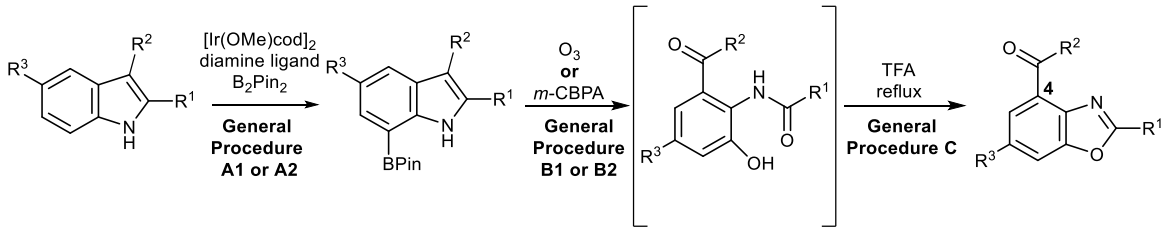
SUPPORTING INFORMATION

General Experimental Details

Commercially available reagents were used throughout without purification unless otherwise stated. Anhydrous solvents were used as supplied. Dichloromethane, methanol and tetrahydrofuran were dried using an LC Technology Solutions Inc. SP-1 solvent purification system under an atmosphere of dry nitrogen. All reactions were routinely carried out in oven-dried glassware under a nitrogen atmosphere unless otherwise stated. Analytical thin layer chromatography was performed using silica plates and compounds were visualized at 254 and/or 360 nm ultraviolet irradiation followed by staining ethanolic vanillin solution. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Infrared spectra were obtained using a Perkin Elmer spectrum One Fourier Transform Infrared spectrometer as thin films between sodium chloride plates. Absorption maxima are expressed in wavenumbers (cm^{-1}). NMR spectra were recorded on either a Bruker AV300, AVIII400 or AVIIIHD500 spectrometer operating at 300, 400, 500 MHz for ^{1}H nuclei respectively and 75, 100, 125 MHz for ^{13}C nuclei respectively. Chemical shifts are reported in parts per million (ppm) relative to the tetramethylsilane peak recorded as δ 0.00 ppm in $CDCl_3$/TMS solvent, or the residual chloroform (δ 7.26 ppm), or DMSO (δ 2.50 ppm). The ^{13}C NMR values were referenced to the residual chloroform (δ 77.1 ppm), DMSO (δ 39.5 ppm). ^{13}C NMR values are reported as chemical shift δ and assignment. ^{1}H NMR shift values are reported as chemical shift δ, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (*J* in Hz) and assignment. Assignments are made with the aid of COSY, NOESY, HMBC and edited HSQC experiments. All experiments were conducted at 298 K. Conventional NMR tubes (5 mm diameter, Norell) using a sample volume of 400 – 500 μL were used. High resolution mass spectra were obtained by electrospray ionization in positive ion mode at a nominal accelerating voltage of 70 eV on a Bruker micrOTOF-QII mass spectrometer.

General Procedures for Synthesis of 4-Acylbenzoxazoles 8-20



General procedure A1

A catalyst solution was prepared by adding bis(pinacolato)-diboron (B_2Pin_2) (1.0 – 1.1 equiv.) to a solution of (1,5-cyclooctadiene)(methoxy)iridium(I) dimer {$[Ir(OMe)COD]_2$} (3 mol %) and 4,4′-di-*tert*-butyl-2,2′-bypyridine (d^tbpy, 6 mol %) or 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen, 6 mol %) in tetrahydrofuran (THF, 1 – 2 mL) and stirred for 1 min. The resulting solution was transferred to a sealed tube, followed by the addition of the indole (1.04 – 1.37 mmol) in THF (1 – 2 mL). The reaction was sealed and stirred at 60 °C for 18 h (unless otherwise stated) under a blanket of nitrogen. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel eluting with light petroleum-ethyl acetate to give the 7-borylindole.

General procedure A2

To a sealed tube containing the indole (0.48 – 1.52 mmol), $[Ir(OMe)COD]_2$ (3 – 5 mol %), ligand (d^tbpy or Me_4Phen, 6 – 10 mol %) and B_2Pin_2 (0.7 – 1.1 equiv.) was added the solvent (*n*-hexane, THF or methyl *tert*-butyl ether, 0.5 – 3 mL) under a heavy stream of nitrogen. The reaction mixture was heated to 60 °C (unless otherwise stated) for 4 h (unless otherwise stated) under a blanket of nitrogen. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel eluting with light petroleum-ethyl acetate to give the 7-borylindole.

General procedure B1

A solution of 7-borylindole (0.11 – 0.18 mmol) in ethanol-saturated aqueous sodium bicarbonate (2:1, 9 – 15 mL total volume) was cooled to -20 °C. A solution of *m*-chloroperoxybenzoic acid (*m*CPBA, 77% w/w purity, 4 equiv.) in ethanol (2.5 – 3 mL) was added and the resulting mixture warmed to room temperature gradually over 1 h. The reaction was quenched with saturated aqueous sodium sulfite solution (2.5 – 3 mL) and concentrated *in vacuo*. The resulting aqueous solution was extracted with ethyl acetate (3 x 10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude *o*-amidophenol, in some instances had to be purified through a short plug of silica gel. The ring opening was confirmed by ^1H NMR and the product subsequently used immediately in the next step.

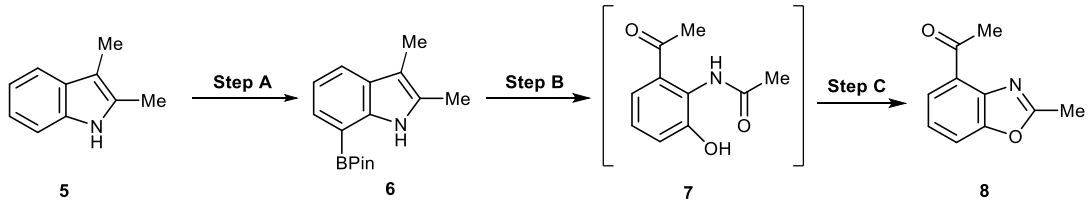
General procedure B2

A solution of the 7-borylindole (0.13 – 0.2 mmol) in ethanol-water (9:1, 0.03 M) was purged with ozone for 15 min (unless otherwise specified) followed by oxygen for 5 min. The resulting solution was concentrated *in vacuo* (unless otherwise specified). Purification by flash chromatography on silica gel eluting with methanol-dichloromethane (1:19) gave the *o*-amidophenol. The ring opening was confirmed by ^1H NMR and the product subsequently used immediately in the next step.

General procedure C

A solution of the *o*-amidophenol (0.05 – 0.1 mmol) in trifluoroacetic acid (TFA, 2 – 4 mL) was heated to reflux for 1 – 16 h. The reaction mixture was cooled to room temperature and neutralised to pH 7 with saturated aqueous sodium bicarbonate solution. The resulting solution was extracted with ethyl acetate (x 3), and the combined organic layers dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography on silica gel eluting with ethyl acetate-light petroleum (1:4, unless otherwise specified) gave the benzoxazole.

4-Acetyl-2-methylbenzoxazole (8)



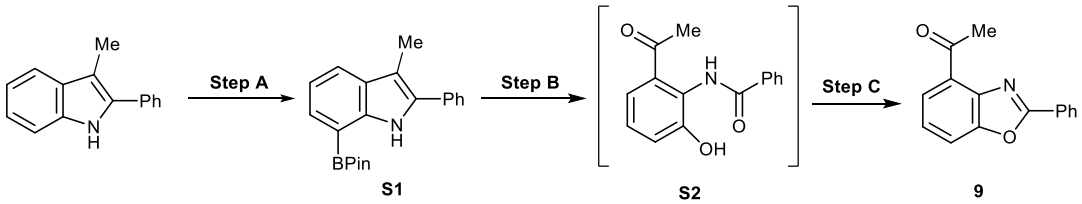
General procedure A1 was performed using a 2,3-dimethylindole (**5**, 200 mg, 1.37 mmol), $[Ir(OMe)COD]_2$ (27 mg, 0.04 mmol, 3 mol %), d^tbpy (22 mg, 0.08 mmol, 6 mol %), and B_2Pin_2 (350 mg, 1.37 mmol, 1.1 equiv.) in THF (2 mL total). Purification eluting with ethyl acetate-light petroleum (1:19) gave the 7-borylindole **6** (213 mg, 0.78 mmol, 57%) as a colourless solid, m.p. 88 – 91 °C (lit.[1] 89 – 93°C); δ_H (400 MHz, $CDCl_3$) 8.66 (1 H, bs, NH), 7.57 (1 H, d, *J* 7.7 Hz, ArH), 7.54 (1 H, dd, *J* 6.9, 0.9, ArH), 7.07 (1 H, t, *J* 14.9, 7.7, ArH), 2.40 (3 H, s, Me), 2.22 (3 H, s, Me), 1.39 (12 H, s, 4 x Me); Spectroscopic data in agreement with literature values.[1]

General procedure B1 was performed using **6** (50 mg, 0.18 mmol) in ethanol (10 mL) and saturated aqueous sodium bicarbonate (5 mL) and *m*-chloroperbenzoic acid (77% w/w purity, 165 mg, 0.74 mmol) in ethanol (2.5 mL) gave the *o*-amidophenol **7** (11 mg, 0.06 mmol, 31%) as a pale brown solid which was used in the subsequent step without purification, m.p. 90 – 93 °C; ν_{max} (neat)/cm^{-1} 3096, 2924, 2852, 2585, 1643, 1604, 1523, 1447; δ_H (400 MHz, $CDCl_3$) 11.78 (1 H, bs, NH), 9.95 (1 H, s, OH), 7.48 (1 H, dd, *J* 7.6, 1.6, ArH), 7.28 – 7.23 (1 H, m, ArH), 7.19 (1 H, t, *J* 7.9, ArH), 2.67 (3 H, s, Me), 2.33 (3 H, s, Me); δ_C (100 MHz, $CDCl_3$) 203.6 (C), 171.8 (C), 150.1 (C), 127.9 (C), 126.2 (CH), 126.1 (C), 125.8 (CH), 123.5 (CH), 29.1 (Me), 24.3 (Me); HRMS (ESI) found: 216.0637 $[C_{10}H_{11}NO_3+Na]^+$ requires: 216.0631.

General procedure C was performed using **7** (11 mg, 0.06 mmol) and TFA (2.5 mL). Purification as described in the general procedure gave the *title compound* (5 mg, 0.06 mmol, 50%) as a colourless solid, m.p. 72 – 75 °C (lit.[2] 72 – 75 °C); δ_H (400 MHz, $CDCl_3$) 7.90 (1 H, dd, *J* 7.9, 0.9, ArH), 7.66 (1 H, dd, *J* 7.9, 1.0, ArH), 7.34 (1 H, t, *J* 7.9, ArH), 2.93 (3 H, s, Me), 2.70 (3 H, s, Me); δ_C (100 MHz, $CDCl_3$) 197.7

(C), 164.8 (C), 151.7 (C), 141.0 (C), 128.9 (C), 124.5 (CH), 123.9 (CH), 114.5 (CH), 30.8 (Me), 14.7 (Me); HRMS (ESI) found 198.0525 $[C_{10}H_9NO_2+Na]^+$ requires: 198.0525.

1-(2-Phenylbenzo[*d*]oxazol-4-yl)ethan-1-one (9)



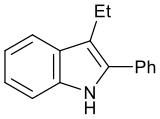
General procedure A2 was performed using 3-methyl-2-phenylindole[3] (100 mg, 0.48 mmol), $[Ir(OMe)COD]_2$ (9.6 mg, 0.014 mmol, 3 mol %), Me_4Phen (6.8 mg, 0.028 mmol, 6 mol %), B_2Pin_2 (123 mg, 0.48 mmol, 1 equiv.) and MTBE (2 mL). Purification by flash chromatography on silica gel eluting with ethyl acetate-light petroleum (1:40) gave the 7-borylindole **S1** (64 mg, 0.19 mmol, 40%) as a colourless solid, m.p. 110 – 112 °C; ν_{max} (neat)/cm^{-1} 3446, 3046, 2987, 2963, 2920, 2862, 1564, 1605, 1442, 1286, 1321, 1090; δ_H (400 MHz, $CDCl_3$) 9.01 (1 H, bs, NH), 7.73 (1 H, m, ArH), 7.66 (1 H, dd, *J* 6.8, 0.9, ArH), 7.62 (2 H, m, ArH), 7.51 (2 H, t, *J* 7.5, ArH), 7.38 (1 H, m, ArH), 7.16 (1 H, dd, *J* 7.9, 6.7, ArH), 2.48 (3 H, s, Me), 1.40 (12 H, s, 4 x Me); δ_C (100 MHz, $CDCl_3$) 141.1 (C), 133.9 (C), 133.8 (C), 129.6 (CH), 128.9 (2 x CH), 127.9 (2 x CH), 127.3 (CH), 122.6 (CH), 119.1 (CH), 108.2 (C), 83.9 (2 x C), 25.1 (4 x Me), 9.7 (Me), 2 x C not observed; HRMS (ESI) found 356.1791 $[C_{21}H_{24}BNO_2+Na]^+$ requires: 356.1796.

General procedure B1 was performed using **S1** (51 mg, 0.15 mmol) in ethanol (8 mL) and saturated aqueous sodium bicarbonate (4 mL) and *m*-chloroperbenzoic acid (77% w/w purity, 137 mg, 0.61 mmol, 4 equiv.) in ethanol (3 mL) gave the *o*-amidophenol **S2** (25 mg, 0.1 mmol, 64%) which was used in the subsequent step without purification; δ_H (300 MHz, $CDCl_3$) 12.65 (1 H, bs, NH), 10.24 (1 H, s, OH), 8.12

(2 H, m, ArH), 7.64 – 7.54 (4 H, m, ArH), 7.35 – 7.32 (1 H, m, ArH), 7.27 – 7.22 (1 H, m, ArH), 2.72 (3 H, s, Me).

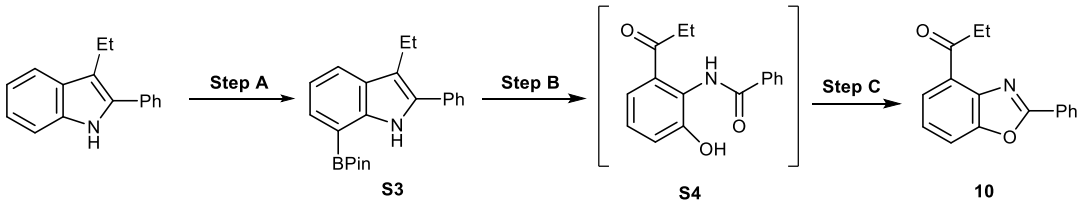
General procedure C was performed using **S2** (26 mg, 0.1 mmol) and TFA (2.5 mL). Purification as described in the general procedure gave the *title compound* (12 mg, 0.05 mmol, 50%) as a colourless solid, m.p. 110 – 112 °C; ν_{max} (neat)/cm^{-1} 2917, 2849, 1674, 1549, 1284, 1223, 751, 703; δ_H (400 MHz, $CDCl_3$) 8.34 – 8.32 (2 H, m, ArH), 7.97 (1 H, dd, *J* 7.8, 0.9, ArH), 7.77 (1 H, dd, *J* 7.9, 0.9, ArH), 7.61 – 7.52 (3 H, m, ArH), 7.42 (1 H, t, *J* 7.9, ArH), 3.07 (3 H, s, Me); δ_C (100 MHz in $CDCl_3$) 197.9 (C), 163.8 (C), 151.7 (C), 141.9 (C), 132.2 (CH), 129.3 (C), 129.1 (2 x CH), 128.2 (2 x CH), 126.9 (C), 125.0 (CH), 124.7 (CH), 114.9 (CH), 31.4 (Me); HRMS (ESI) found: 260.0692 $[C_{15}H_{11}NO_2+Na]^+$ requires: 260.0682.

3-Ethyl-2-phenylindole



2-Phenylindole (200 mg, 1.03 mmol), $[Cp^*IrCl_2]_2$ (8.2 mg, 0.01 mmol, 1 mol %), potassium *tert*-butoxide (115 mg, 1.03 mmol) and ethanol (3.5 mL) was added to a sealed tube. The tube was sealed with a screw-cap and stirred at 120 °C for 24 h. After cooling, the reaction mixture was concentrated *in vacuo*. Purification by flash chromatography eluting with light petroleum-ethyl acetate (40:1) gave the *title compound* (166 mg, 0.75 mmol, 80%) as a yellow oil; δ_H (400 MHz, $CDCl_3$) 7.98 (1 H, bs, NH), 7.65 (1 H, d, *J* 7.6, ArH), 7.56 (2 H, m, ArH), 7.47 (2 H, t, *J* 7.9, ArH), 7.40-7.34 (2 H, m, ArH), 7.20 (1 H, m, ArH), 7.14 (1 H, m, ArH), 2.92 (2 H, q, *J* 7.4, CH_2), 1.35 (3 H, t, *J* 7.7, Me). Spectroscopic data in agreement with literature values.[4]

1-(2-Phenylbenzo[*d*]oxazol-4-yl)propan-1-one (10)



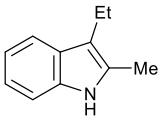
General procedure A2 was performed 3-ethyl-2-phenylindole (42 mg, 0.18 mmol), $[Ir(OMe)COD]_2$ (9.6 mg, 0.014 mmol, 5 mol %), d^{t}bpy (5 mg, 0.018 mmol, 10 mol %), B_2Pin_2 (48 mg, 0.18 mmol, 1 equiv.) and MTBE (0.5 mL) Purification eluting with ethyl acetate-light petroleum (1:40) gave the 7-borylindole **S3** (27 mg, 0.08 mmol, 44%) as a beige solid, m.p. 106 – 108 °C; ν_{max} (neat)/cm^{-1} 3441, 2981, 2958, 2926, 2861, 1592, 1444, 1371, 1330, 1289, 1134, 852, 706; δ_H (400 MHz, $CDCl_3$) 9.12 (1 H, bs, NH), 7.82 (1 H, d, *J* 7.7, ArH), 7.72 (1 H, d, *J* 6.6, ArH), 7.72 – 7.41 (5 H, m, ArH), 7.20 (1 H, t, *J* 7.4, ArH), 2.98 (2 H, q, *J* 7.3, CH_2), 1.43 (12 H, s, 4 x Me), 1.39 (3 H, t, *J* 7.3, Me); δ_C (100 MHz, $CDCl_3$) 141.2 (C), 133.8 (C), 133.5 (C), 129.5 (CH), 128.9 (2 x CH), 128.0 (2 x CH), 127.9 (CH), 127.4 (CH), 122.7 (CH), 119.0 (CH), 115.0 (C), 83.8 (2 x C), 25.0 (4 x Me), 17.8 (CH_2), 15.9 (Me), 1 x C not observed; HRMS (ESI) found: 370.1939 $[C_{22}H_{26}BNO_2+Na]^+$ requires: 370.1953.

General procedure B1 was performed using **S3** (43 mg, 0.12 mmol) in ethanol (6 mL) and saturated aqueous sodium bicarbonate (3 mL) and m-chloroperbenzoic acid (77% w/w purity, 86 mg, 0.50 mmol, 4 equiv.) in ethanol (2.6 mL) gave the *o*-amidophenol **S4** (23 mg, 0.08 mmol, 69%) which was used in the next step without further purification, δ_H (300 MHz, CDCl3) 12.67 (1 H, bs, NH), 10.11 (1 H, s, OH), 8.13 – 8.10 (2 H, m, ArH), 7.62 – 7.54 (4 H, m, ArH), 7.34 – 7.30 (1 H, m, ArH), 7.25 – 7.21 (1 H, m, ArH), 3.11 (2 H, q, J 7.2, CH2), 1.28 – 1.24 (3 H, m, Me).

General procedure C was performed using S4 (23 mg, 0.08 mmol) and TFA (2 mL). Purification as described in the general procedure gave the title compound (11 mg, 0.04 mmol, 51%) as a pale yellow oil, ν_{max} (neat)/cm^{-1} 2962, 2915, 2849, 2324, 1691, 1471, 1259, 1016, 796; δ_H (400 MHz, $CDCl_3$) 8.34-8.31 (2 H, m, ArH), 7.98 (1 H, dd, J

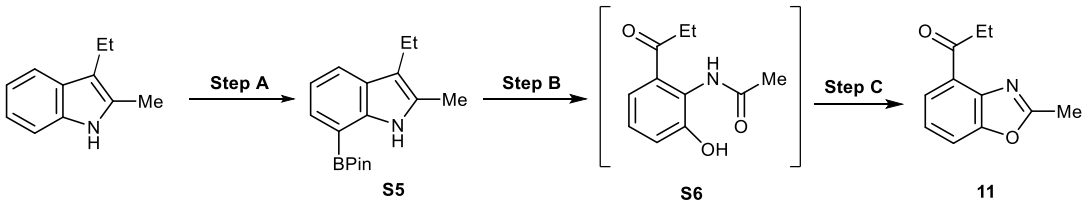
7.6, 1.0, ArH), 7.75 (1 H, dd, J 8.0, 1.6, ArH), 7.58 – 7.54 (3 H, m, ArH), 7.42 (1 H, t, J 7.9, ArH), 3.57 (2 H, q, J 7.2, CH_2), 1.31 (3 H, J 7.2, Me); δ_C (100 MHz, $CDCl_3$) 200.7 (C), 163.6 (C), 151.5 (C), 141.3 (C), 132.0 (CH), 129.1 (C), 128.9 (2 x CH), 128.0 (2 x CH), 126.8 (C), 124.9 (CH), 124.6 (CH), 114.5 (CH), 36.6 (CH2), 8.2 (Me); HRMS (ESI) found 274.0845 $[C_{16}H_{13}NO_3+Na]^+$ requires: 274.0838.

3-Ethyl-2-methylindole



2-Methylindole (200 mg, 1.52 mmol), $[Cp^*IrCl_2]_2$ (36 mg, 0.046 mmol, 3 mol %), potassium *tert*-butoxide (171 mg, 1.52 mmol) and ethanol (2 mL) was added to a sealed tube. The tube was sealed with a screw-cap and stirred at 140 °C for 24 h. After cooling, the reaction mixture was concentrated *in vacuo*. Purification by flash chromatography eluting with ethyl acetate-light petroleum (1:40) gave the *title compound* (155 mg, 0.97 mmol, 64%) as a yellow oil; δ_H (400 MHz, $CDCl_3$) 7.67 (1 H, bs, NH), 7.54-7.48 (1 H, m, ArH), 7.28-7.24 (1 H, m, ArH), 7.13-7.03 (2 H, m, ArH), 2.71 (2 H, q, *J* 7.6, CH_2), 2.37 (3 H, s, Me), 1.22 (3 H, t, *J* 7.6, Me). Spectroscopic data in agreement with literature values.[5]

1-(2-Methylbenzo[*d*]oxazol-4-yl)propan-1-one (11)



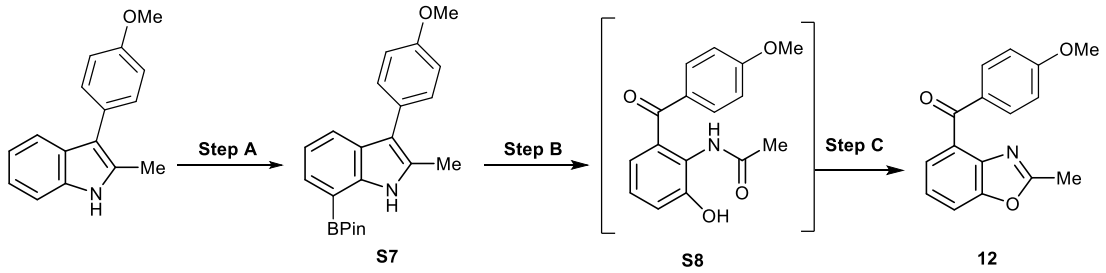
General procedure A1 was performed using 3-ethyl-2-methylindole (166 mg, 1.04 mmol), $[Ir(OMe)COD]_2$ (21 mg, 0.031 mmol, 3 mol %), Me_4Phen (15 mg, 0.062 mmol, 6 mol %), B_2Pin_2 (265 mg, 0.62 mmol, 1 equiv.) in THF (4 mL total). Purification eluting with ethyl acetate-light petroleum (1:9)

gave the 7-borylindole **S5** (123 mg, 0.43 mmol, 41%) as beige solid, m.p. 105 – 108 °C; ν_{max} (neat)/cm^{-1} 3455, 3055, 2897, 2974, 2926, 2858, 1615, 1591, 1409, 1369, 1329, 1130, 1099; δ_H (400 MHz, $CDCl_3$) 8.67 (1 H, s, NH), 7.63 (1 H, d, *J* 8.0, ArH), 7.54 (1 H, d, *J* 6.5, ArH), 7.07 (1 H, t, *J* 7.6, ArH), 2.71 (2 H, q, *J* 7.5, CH_2), 2.41 (3 H, s Me), 1.38 (12 H, s, 4 x Me), 1.21 (3 H, t, *J* 7.6, Me); δ_C (100 MHz, $CDCl_3$) 140.5 (C), 130.0 (C), 128.0 (CH), 127.4 (C), 121.5 (C), 118.4 (CH), 113.4 (C), 83.6 (2 x C), 24.9 (4 x Me), 17.3 (CH_2), 15.6 (Me), 11.6 (CH_2), 1 x C not observed; HRMS (ESI) found 308.1790 $[C_{17}H_{24}BNO_2+Na]^+$ requires: 308.179.

General procedure B1 was performed using **S5** (32 mg, 0.11 mmol) in ethanol (6 mL) and saturated aqueous sodium bicarbonate (3 mL) and *m*-chloroperbenzoic acid (77% w/w purity, 77 mg, 0.34 mmol, 3.1 equiv.) in ethanol (3 mL) gave the *o*-amidophenol **S6** (14 mg, 0.07 mmol, 60%) which was used in the subsequent step without further purification, m.p. 56 – 59 °C; ν_{max} (neat)/cm^{-1} 2919, 2568, 1644, 1563, 1513, 1459, 1314, 1295, 1266, 1229, 1168, 1124, 1054, 831, 773; δ_H (400 MHz, $CDCl_3$) 11.82 (1 H, bs, NH), 9.88 (1 H, bs, OH), 7.50 (1 H, dd, *J* 7.6, 1.5, ArH), 7.25 – 7.23 (1 H, m, ArH), 7.20 – 7.16 (1 H, m, ArH), 3.07 (2 H, q, *J* 7.18, CH_2), 2.34 (3 H, s, Me), 1.22 (3 H, t, *J* 7.2, Me); δ_C (100 MHz, $CDCl_3$) 206.2 (C), 171.9 (C), 150.2 (C), 127.8 (C), 126.0 (C), 125.91 (CH), 125.86 (CH), 122.6 (CH), 33.8 (CH_2), 24.3 (Me), 8.5 (Me); HRMS (ESI) found: 230.0791 $[C_{11}H_{13}NO_3+Na]^+$ requires: 230.0788.

General procedure C was performed using **S6** (11 mg, 0.05 mmol) and TFA (2.5 mL). Purification as described in the general procedure gave the *title compound* (3 mg, 0.015 mmol, 30%) as a yellow oil, ν_{max} (neat)/cm^{-1} 2961, 2918, 2850, 1678, 1609, 1570, 1419, 1260, 1229, 1095, 1026, 799; δ_H (400 MHz, $CDCl_3$) 7.90 (1 H, dd, *J* 7.5, 0.9, ArH), 7.64 (1 H, d, *J* 8.1, ArH), 7.36 (1 H, t, *J* 7.9, ArH), 3.41 (2 H, q, *J* 7.2, CH_2), 2.69 (3 H, s, Me), 1.27 – 1.25 (3 H, m, Me); δ_C (100 MHz, $CDCl_3$) 200.8 (C), 164.8 (C), 151.8 (C), 140.8 (C), 128.9 (C), 124.6 (CH), 124.2 (CH), 114.4 (CH), 36.4 (CH_2), 14.8 (Me), 8.2 (Me); HRMS (ESI) found 212.0683 $[C_{11}H_{11}NO_2+Na]^+$ requires: 212.0682.

(4-Methoxyphenyl)(2-methylbenzo[*d*]oxazol-4-yl)methanone (12)



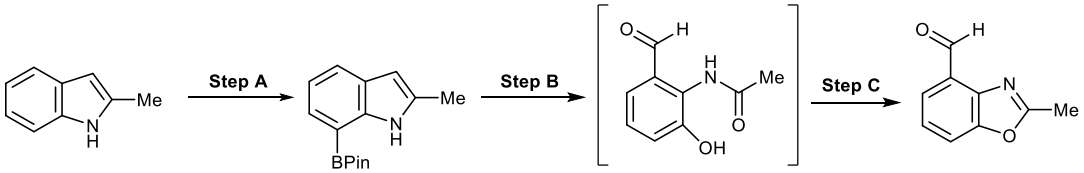
General procedure A2 was performed using 3-(4-methoxyphenyl)-2-methylindole[6] (104 mg, 0.44 mmol), $[Ir(OMe)COD]_2$ (8.7 mg, 0.013 mmol, 3 mol %), d^{t}bpy (7.1 mg, 0.026 mmol, 6 mol %), B_2Pin_2 (100 mg, 0.396 mmol, 0.9 equiv.) and THF (1 mL). Purification eluting with ethyl acetate-light petroleum (1:4) to afford the 7-borylindole **S7** (74 mg, 0.62 mmol, 52%) as a pale brown oil, ν_{max} (neat)/cm^{-1} 3446, 2977, 1590, 1575, 1562, 1509, 1440, 1415, 1366, 1324, 1271, 1236, 1127, 1037, 971, 856, 838, 794, 754, 729, 703; δ_H (400 MHz, $CDCl_3$) 8.94 (1 H, bs, NH), 7.73 (1 H, d, *J* 7.8, ArH), 7.60 (1 H, dd, *J* 7.0, 1.0), 7.46 – 7.38 (2 H, m, ArH), 7.11 (1 H, dd, *J* 7.9, 7.0, ArH), 7.04 – 6.97 (2 H, m, ArH), 3.87 (3 H, s, OMe), 2.53 (3 H, s, Me), 1.41 (12 H, s, 4 x Me); δ_C (100 MHz in $CDCl_3$) 157.9 (C), 140.5 (C), 131.2 (C), 130.7 (2 x CH), 128.8 (CH), 128.2 (C), 127.2 (C), 122.4 (CH), 119.5 (CH), 114.1 (2 x CH), 113.8 (C), 83.9 (2 x C), 55.5 (OMe), 25.1 (4 x Me), 12.7 (Me), 1 x C not observed; HRMS (ESI) found 386.1895 $[C_{22}H_{26}BNO_3+Na]^+$ requires 386.1902.

A solution of **S7** (54 mg, 0.15 mmol) in dichloromethane (6 mL) at -78 °C was purged with ozone for 35 min followed by oxygen for 5 min. Methanol (1 mL) and concentrated hydrochloric acid (1 mL) were added to the reaction mixture and stirred for 30 min, gradually warming to room temperature. The methanol was removed *in vacuo* and the crude material quenched with saturated aqueous sodium bicarbonate solution (15 mL). The resulting aqueous solution was extracted with dichloromethane (3 x 10 mL), dried over Na_2SO_4 and concentrated *in vacuo* gave the *o*-amidophenol **S8** (32 mg, 0.11 mmol, 75%)

as a brown oil which was used in the subsequent step without further purification, δ_H (300 MHz, $CDCl_3$) 10.72 (1 H, bs, NH), 9.43 (1 H, s, OH), 8.04 (1 H, d, *J* 9.0, ArH), 7.78 (2 H, d, *J* 8.9, ArH), 7.17 (1 H, t, *J* 7.8, ArH), 7.09 (1 H, d, *J* 1.8, ArH), 6.97 (2 H, d, *J* 8.9, ArH), 3.90 (3 H, s, OMe), 2.29 (3 H, s, Me).

General procedure C was performed using **S8** (32 mg, 0.11 mmol) and TFA (2 mL) for 3.5 h. Purification eluting with ethyl acetate-light petroleum (1:2.5) to afford the *title compound* (14 mg, 0.05 mmol, 47%) as a colourless solid, ν_{max} (neat)/cm^{-1} 2922, 2850, 1647, 1597, 1570, 1508, 1458, 1423, 1319, 1294, 1262, 1244, 1167, 1152, 1019, 928, 891, 841, 804, 759, 702; δ_H (400 MHz, $CDCl_3$) 7.91 – 7.86 (2 H, m, ArH), 7.63 (1 H, d, *J* 8.2, ArH), 7.50 (1 H, dd, *J* 7.5, 0.9, ArH), 7.37 (1 H, t, *J* 7.8, ArH), 6.96 – 6.90 (2 H, m, ArH), 3.88 (3 H, s, OMe), 2.64 (3 H, s, Me); δ_C (100 MHz in $CDCl_3$) 193.1 (CH), 165.2 (C), 163.9 (C), 151.4 (C), 140.3 (C), 133.0 (2 x CH), 130.7 (C), 130.4 (C), 125.1 (CH), 124.0 (CH), 113.7 (2 x CH), 112.8 (CH), 55.6 (OMe), 14.8 (Me); HRMS (ESI) found: 290.079 $[C_{16}H_{13}NO_3+Na]^+$ requires 290.0788.

2-Methylbenzo[*d*]oxazole-4-carbaldehyde (13)

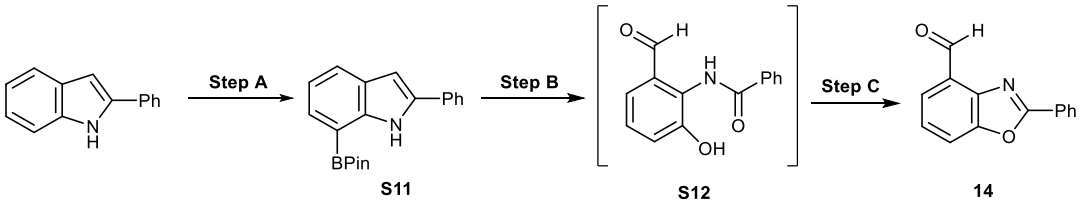


General procedure A2 was performed using 2-methylindole (200 mg, 1.52 mmol), $[Ir(OMe)COD]_2$ (26.3 mg, 0.04 mmol 3 mol %), d^tbpy (21 mg, 0.08 mmol, 6 mol %), B_2Pin_2 (387 mg, 1.52 mmol, 1 equiv.) and THF (4 mL). Purification eluting with ethyl acetate-light petroleum (1:9) gave the 7-borylindole **S9** (262 mg, 1.02 mmol, 67%) as a colourless solid, m.p. 73 – 75 °C; δ_H (400 MHz, $CDCl_3$) 8.85 (1 H, bs, NH), 7.62 (1 H, d, *J* 7.8, ArH), 7.55 (1 H, dd, *J* 7.2, 0.7, ArH), 7.07 (1 H, t, *J* 7.5, ArH), 6.20 (1 H, q, *J* 1.2, ArH), 2.49 (3 H, s, Me), 1.40 (12 H, s, 4 x Me). Spectroscopic data in agreement with literature values.[7]

General procedure B2 was performed using **S9** (51 mg, 0.2 mmol) in ethanol-water (9:1, 1 mL) was purged with ozone for 10 min. Purification as described in the general procedure gave the *o*-amidophenol **S10** (14 mg, 0.08 mmol, 39%) as a colourless oil, ν_{max} (neat)/cm^{-1} 3451, 2977, 2917, 1603, 1553, 1423, 1403, 1386, 1369, 1331, 1288, 1214, 1195, 1139, 1010, 963, 851, 752; δ_H (300 MHz, $CDCl_3$) 11.30 (1 H, bs, NH), 10.51 (1 H, s, OH), 9.89 (1 H, s, CHO), 7.31 – 7.24 (3 H, m, ArH), 2.35 (3 H, s, Me); δ_C (100 MHz in $CDCl_3$) 195.9 (CH), 172.1 (C), 149.6 (C), 128.7 (CH), 127.5 (C), 127.4 (CH), 126.4 (CH), 125.2 (C), 24.3 (Me).

General procedure C was performed using **S10** (19 mg, 0.1 mmol) and TFA (4 mL) for 3 h. Purification eluting with ethyl acetate-light petroleum (1:4) gave the *title compound* (10 mg, 0.06 mmol, 60%) as a colourless solid, m.p. 52 – 56 °C; ν_{max} (neat)/cm^{-1} 3119, 3068, 3032, 2919, 2859, 2753, 1692, 1674, 1608, 1567, 1515, 1439, 1424, 1386, 1366, 1350, 1272, 1239, 1195, 1076, 1056, 995, 922, 868, 786, 754, 700, 656; δ_H (300 MHz, $CDCl_3$) 10.62 (1 H, s, CHO), 7.86 (1 H, dd, *J* 7.7, 1.0, ArH), 7.73 (1 H, dd, *J* 8.1, 1.1, ArH), 7.44 (1 H, t, *J* 7.9, ArH), 2.73 (3 H, s, Me); δ_C (100 MHz in $CDCl_3$) 189.5 (CH), 166.6 (C), 151.9 (C), 142.6 (C), 126.9 (C), 124.4 (CH), 124.3 (CH), 115.9 (CH), 14.8 (Me); HRMS (ESI) found 184.0371 $[C_9H_7NO_2+Na]^+$ requires: 184.0369.

2-Phenylbenzo[*d*]oxazole-4-carbaldehyde (14)



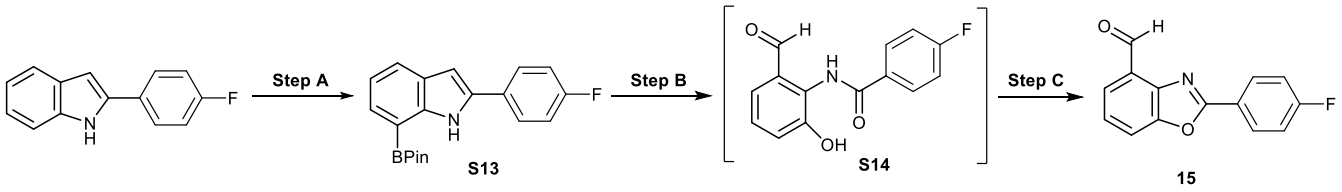
General procedure A2 was performed using 2-phenylindole (193 mg, 1 mmol), $[Ir(OMe)COD]_2$ (19.9 mg, 0.03 mmol, 3 mol %), d^{t}bpy (16.1 mg, 0.06 mmol, 6 mol %), B_2Pin_2 (177 mg, 0.7 mmol, 0.7 equiv.) and *n*-hexane (2 mL). Purification eluting with ethyl acetate-light petroleum (1:4) to afford the 7-

borylindole **S11** (218 mg, 0.68 mmol, 68%) as a beige solid, m.p. 101 – 105 °C; δ_H (300 MHz, $CDCl_3$) 9.45 (1 H, br s, NH), 7.74 (1 H, d, *J* 7.8, ArH), 7.69 (2 H, d, *J* 8.4, ArH), 7.47 (2 H, t, *J* 7.4, ArH), 7.33 (1 H, t, *J* 7.5, ArH), 7.13 (1 H, dd, *J* 7.7, 7.1, ArH), 6.82 (1 H, d, *J* 2.3, ArH), 1.43 (12 H, s, 4 x Me). Spectroscopic data in agreement with literature values.[7]

General procedure B2 was performed using **S11** (64 mg, 0.2 mmol) in ethanol-water (9:1, 6 mL). Purification as described in the general procedure gave the *o*-amidophenol **S12** (14 mg, 0.06 mmol, 29%) as a yellow solid, δ_H (400 MHz, $CDCl_3$) 12.14 (1 H, bs, NH), 10.84 (1 H, bs, OH), 9.96 (1 H, s, CHO), 8.13 (2 H, d, *J* 8.5, ArH), 7.63 – 7.53 (3 H, m, ArH), 7.39 – 7.33 (3 H, m, ArH); HRMS (ESI) found 264.0635 $[C_{14}H_{11}NO_3+Na]^+$ requires: 264.0631.

General procedure C was performed using **S12** (13 mg, 0.05 mmol) and TFA (3 mL) for 4.5 h. Purification eluting with ethyl acetate-light petroleum (1:9) gave the *title compound* (5 mg, 0.02 mmol, 42%) as a colourless solid, m.p. 115 – 117 °C; ν_{max} (neat)/cm^{-1} 3074, 2918, 2848, 1688, 1607, 1548, 1485, 1426, 1384, 1280, 1235, 1155, 1007, 865, 799, 761, 779; δ_H (500 MHz, $CDCl_3$) 10.79 (1 H, s, CHO), 8.35 – 8.33 (2 H, m, ArH), 7.92 (1 H, m, ArH), 7.84 (1 H, m, ArH), 7.60 – 7.55 (3 H, m, ArH), 7.48 (1 H, t, *J* 7.8, ArH); δ_C (125 MHz in $CDCl_3$) 189.6 (CH), 165.4 (C), 151.8 (C), 143.8 (C), 132.6 (CH), 129.3 (2 x CH), 128.4 (2 x CH), 127.3 (C), 126.7 (C), 125.0 (CH), 123.9 (CH), 116.2 (CH); HRMS (ESI) found 246.0533 $[C_{14}H_9NO_2+Na]^+$ requires 246.0525.

2-(4-Fluorophenyl)benzo[*d*]oxazole-4-carbaldehyde (**15**)



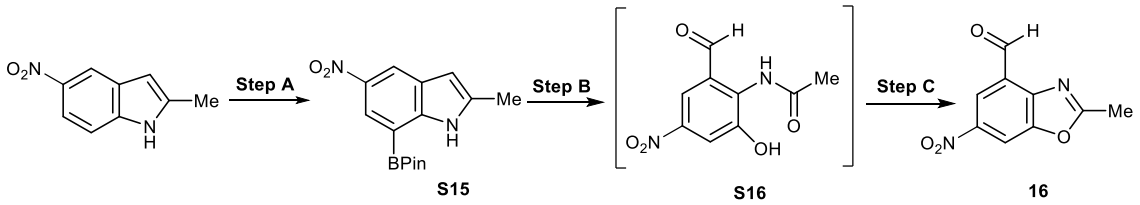
General procedure A2 was performed using 2-(4-fluorophenyl)indole (211 mg, 1 mmol), $[Ir(OMe)COD]_2$ (19.9 mg, 0.03 mmol, 3 mol %), d^{t}bpy (16.1 mg, 0.06 mmol, 6 mol %), B_2Pin_2 (254 mg, 1 mmol, 1 equiv.) and *n*-hexane (2 mL) for 7 h. Purification eluting with ethyl acetate-light petroleum (1:9) gave the 7-borylindole **S13** (127 mg, 0.81 mmol, 38%) as a pale yellow solid, m.p. 124 – 126 °C; ν_{max} (neat)/cm^{-1} 3436, 3062, 2979, 1594, 1551, 1503, 1488, 1427, 1374, 1284, 1325, 1270, 1128, 977, 847, 835, 806, 754; δ_H (400 MHz, $CDCl_3$) 9.37 (1 H, bs, NH), 7.74 (1 H, d, *J* 7.9, ArH), 7.67 – 7.62 (3 H, m, ArH), 7.20 – 7.11 (3 H, m, ArH), 6.75 (1 H, d, *J* 2.3, ArH), 1.43 (12 H, s, 4 x Me); δ_C (100 MHz in $CDCl_3$) 162.5 (d, *J* 246, C=O), 142.2 (C), 136.9 (C), 129.7 (CH), 129.1 (d, *J* 3.8, C), 128.3 (C), 127.0 (d, *J* 8, 2xCH), 124.2 (CH), 119.9 (CH), 116.1 (d, *J* 21, 2 x CH), 99.4 (CH), 84.1 (2 x C), 25.2 (4 x Me), 1 x C not observed; δ_F (376 MHz, $CDCl_3$) -114.2 (s); HRMS (ESI) found: 338.1714 $[C_{20}H_{21}BFNO_2+H]^+$ requires: 338.1726.

General procedure B2 was performed **S13** (67 mg, 0.2 mmol) in ethanol-water (9:1, 6 mL). Purification as described in the general procedure gave the *o*-amidophenol **S14** (18 mg, 0.07 mmol, 35%) as a yellow solid, δ_H (400 MHz, $CDCl_3$) 12.12 (1 H, bs, NH), 10.77 (1 H, s, OH), 9.96 (1 H, s, CHO), 8.18 – 8.14 (2 H, m, ArH), 7.36 – 7.29 (3 H, m, ArH), 7.26 – 7.19 (2 H, m, ArH).

General procedure C was performed using **S14** (18 mg, 0.07 mmol) and TFA (1.5 mL) for 4 h. Purification eluting with ethyl acetate-light petroleum (1:4) to obtain the *title compound* (9 mg, 0.03 mmol,

54%) as a colourless solid, m.p. 135 – 138 °C; ν_{max} (neat)/cm^{-1} 2924, 2845, 1700, 1610, 1559, 1499, 1418, 1259, 1239, 1162, 1002, 924, 841, 788, 756, 734; δ_H (500 MHz, $CDCl_3$) 10.77 (1 H, s, CHO), 8.36 – 8.34 (2 H, m, ArH), 7.92 (1 H, d, *J* 7.9, ArH), 7.83 (1 H, d, *J* 7.9, ArH), 7.48 (1 H, t, *J* 7.8, ArH), 7.27 – 7.24 (2 H, m, ArH); δ_C (125 MHz, $CDCl_3$) 189.4 (CH), 165.4 (C, d, *J* 254), 164.4 (C), 151.7 (C), 143.6 (C), 130.6 (2 x CH, d, *J* 9), 127.3 (C), 124.9 (CH), 124.0 (CH), 122.9 (C, d, *J* 4), 116.5 (2 x CH, d, *J* 22), 116.1 (CH); δ_F (376 MHz, $CDCl_3$) -105.9 (s); HRMS (ESI) found: 264.0435 $[C_{14}H_8FNO_2+Na]^+$ requires: 264.0431.

2-Methyl-6-nitrobenzo[*d*]oxazole-4-carbaldehyde (16)

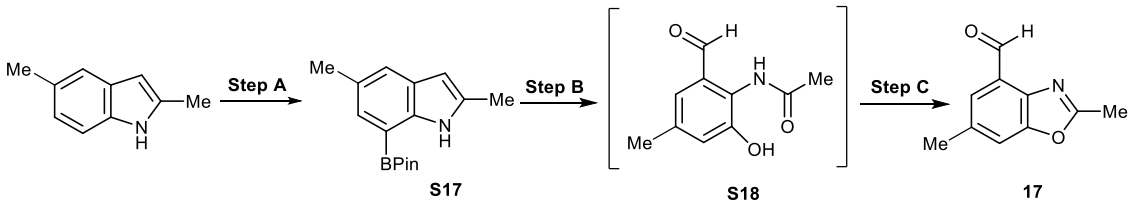


A modified **general procedure A2** was performed using 2-methyl-5-nitroindole (88 mg, 0.5 mmol), $[Ir(OMe)COD]_2$ (10 mg, 0.015 mmol, 3 mol %), d^{t}bpy (8 mg, 0.03 mmol, 6 mol %), B_2Pin_2 (190 mg, 0.75 mmol, 1 equiv.) in a microwave vial was added THF (2.5 mL) and capped under nitrogen. The reaction was heated to 80°C in a microwave for 2 h. Purification eluting with ethyl acetate-light petroleum (2:3) gave the 7-borylindole **S15** (40 mg, 0.13 mmol, 27%) as a pale red oil, δ_H (400 MHz, $CDCl_3$) 9.10 (1 H, bs, NH), 8.53 (1 H, d, *J* 2.2, ArH), 8.47 (1 H, d, *J* 2.2, ArH), 6.38 – 6.37 (1 H, m, ArH), 2.52 (3 H, d, *J* 0.9, Me), 1.42 (12 H, s, 4 x Me). Spectroscopic data in accordance with literature values.[1]

General procedure B2 was performed using **S15** (40 mg, 0.13 mmol) in ethanol-water (9:1, 4.3 mL). Purification as described in the general procedure gave *o*-amidophenol **S16** (17 mg, 0.07 mmol, 57%) as a yellow oil, δ_H (300 MHz, $CDCl_3$) 11.57 (1 H, bs, NH), 11.12 (1 H, bs, OH), 9.97 (1 H, s, CHO), 8.15 (1 H, d, *J* 2.6), 8.1 (1 H, d, *J* 2.6), 2.41 (3 H, s, Me).

General procedure C was performed using **S16** (17 mg, 0.07 mmol) and TFA (2.5 mL) for 3.5 h. Purification eluting with ethyl acetate-light petroleum (1:1) gave the *title compound* (8 mg, 0.04 mmol, 51%) as a colourless solid, m.p. 144 – 148 °C; ν_{max} (neat)/cm^{-1} 3086, 2923, 2853, 1682, 1626, 1562, 1533, 1462, 1345, 1280, 1251, 1198, 1027, 919, 910, 808, 747; δ_H (400 MHz, $CDCl_3$) 10.65 (1 H, s, CHO), 8.79 (1 H, d, *J* 2.0, ArH), 8.61 (1 H, d, *J* 2.3, ArH), 2.83 (3 H, s, Me); δ_C (100 MHz, $CDCl_3$) 187.3 (CH), 171.3 (C), 151.4 (C), 147.2 (C), 145.1 (C), 126.2 (C), 119.8 (CH), 111.1 (CH), 15.2 (Me); HRMS (ESI) found 207.0395 $[C_9H_6N_2O_4+H]^+$ requires: 207.0400.

2,6-Dimethylbenzo[*d*]oxazole-4-carbaldehyde (17)

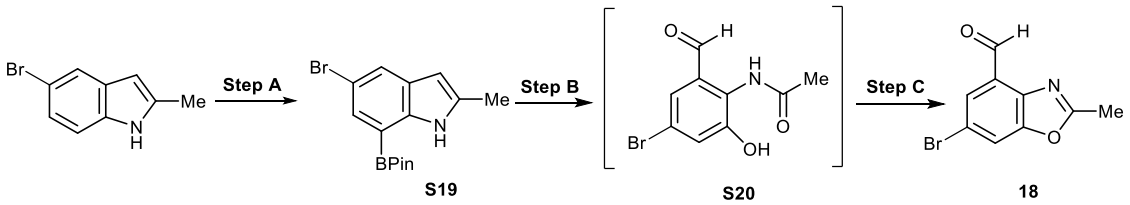


General procedure A2 was performed using 2,5-dimethylindole (200 mg, 1.38 mmol), $[Ir(OMe)COD]_2$ (27.4 mg, 0.04 mmol, 3 mol %), d^{t}bpy (22.2 mg, 0.083 mmol, 6 mol %), B_2Pin_2 (385 mg, 1.52 mmol, 1.1 equiv.) and THF (3 mL) for 4.5 h. Purification eluting with ethyl acetate-light petroleum (1:4) gave the 7-borylindole **S17** (295 mg, 1.08 mmol, 79%) as a colourless solid, m.p. 107 – 110 °C; δ_H (300 MHz, $CDCl_3$) 8.72 (1 H, bs, NH), 7.41 (1 H, s, ArH), 7.39 (1 H, s, ArH), 6.12 (1 H, q, *J* 1.0, ArH), 2.47 (3 H, d, *J* 0.8, Me), 2.42 (3 H, s, Me), 1.40 (12 H, s, 4 x Me). Spectroscopic data in agreement with literature values.[1]

General procedure B2 was performed using **S17** (54 mg, 0.2 mmol) in ethanol-water (9:1, 6 mL). Purification as described in the general procedure gave the *o*-amidophenol **S18** (11 mg, 0.06 mmol, 29%) as a yellow solid, δ_H (300 MHz, $CDCl_3$) 11.18 (1 H, bs, NH), 10.50 (1 H, s, OH), 9.84 (1 H, s, CHO), 7.11 (1 H, d, *J* 1.7, ArH), 7.04 (1 H, d, *J* 1.7, ArH), 2.36 (3 H, bs, Me), 2.33 (3 H, s, Me).

General procedure C was performed using **S18** (6 mg, 0.031 mmol) and TFA (1 mL) for 4 h. Purification eluting with ethyl acetate-light petroleum (1:9) to obtain the *title compound* (4 mg, 0.02 mmol, 74%) as a colourless solid, m.p. 83 – 86 °C; ν_{max} (neat)/cm^{-1} 2918, 2850, 1678, 1615, 1573, 1428, 1294, 1253, 1235, 1210, 1039, 996, 975, 916, 861, 855, 751, 691, 635; δ_H (400 MHz, $CDCl_3$) 10.56 (1 H, s, CHO), 7.66 (1 H, d, *J* 1.03, ArH), 7.52 (1 H, d, *J* 1.03, ArH), 2.69 (3 H, s, Me), 2.53 (3 H, s, Me); δ_C (100 MHz in $CDCl_3$) 189.6 (CH), 165.9 (C), 152.2 (C), 140.5 (C), 135.0 (C), 126.3 (C), 125.2 (CH), 116.3 (CH), 21.6 (Me), 14.8 (Me); HRMS (ESI) found 198.0531 $[C_{10}H_9NO_2+Na]^+$ requires: 198.0525.

6-Bromo-2-methylbenzo[*d*]oxazole-4-carbaldehyde (18)



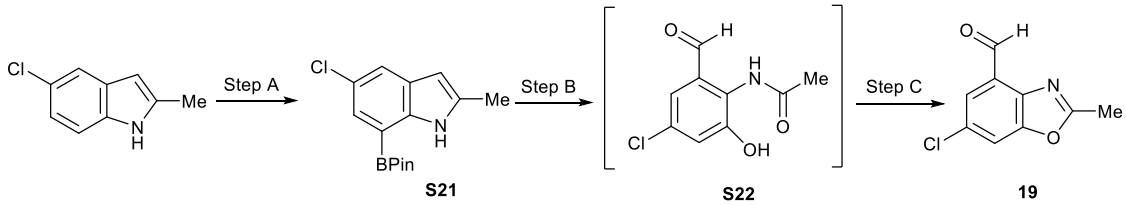
General procedure A2 was performed using 5-bromo-2-methylindole (210 mg, 1 mmol), $[Ir(OMe)COD]_2$ (19.9 mg, 0.03 mmol, 3 mol %), d^{t}bpy (16.1 mg, 0.06 mmol, 6 mol %), B_2Pin_2 (254 mg, 1 mmol, 1 equiv.) and *n*-hexane (3 mL). Purification as described in the general procedure gave the 7-borylindole **S19** (286 mg, 0.85 mmol, 85%) as a colourless solid, m.p. 147 – 150 °C; ν_{max} (neat)/cm^{-1} 3417, 2976, 1605, 1583, 1558, 1456, 1406, 1419, 1387, 1365, 1318, 1278, 1189, 1136, 976, 870, 847, 758, 702; δ_H (400 MHz, $CDCl_3$) 8.82 (1 H, bs, NH), 7.72 (1 H, d, *J* 1.9, ArH), 7.63 (1 H, d, *J* 1.9, ArH), 6.16 – 6.13 (1 H, m, ArH), 2.48 (3 H, d, *J* 0.9, Me), 1.39 (12 H, s, 4 x Me); δ_C (100 MHz in $CDCl_3$) 140.1 (C), 136.6 (C), 130.3 (CH), 130.2 (C), 125.4 (CH), 112.8 (C), 99.6 (CH), 84.3 (2 x C), 25.1 (4 x Me), 12.0 (Me), 1 x C not observed.

General procedure B2 was performed using **S19** (67 mg, 0.2 mmol) in ethanol-water (9:1, 6 mL). Purification as described in the general procedure gave the *o*-amidophenol **S20** (27 mg, 0.10 mmol, 52%)

as an orange solid, δ_H (300 MHz, $CDCl_3$) 11.90 (1 H, bs, NH), 10.84 (1 H, s, OH), 9.80 (1 H, s, CHO), 7.41 (1 H, d, *J* 2.2, ArH), 7.34 (1 H, d, *J* 2.2, ArH), 2.34 (3 H, s, Me).

General procedure C was performed using **S20** (27 mg, 0.1 mmol) and TFA (4 mL) for 3 h. Purification as described in the general procedure gave the *title compound* (11 mg, 0.04 mmol, 44%) as a colourless solid, m.p. 142 – 144 °C; ν_{max} (neat)/cm^{-1} 3078, 2920, 1685, 1597, 1570, 1452, 1418, 1382, 1327, 1269, 1244, 1219, 1071, 1031, 921, 876, 836, 765, 721; δ_H (400 MHz, $CDCl_3$) 10.55 (1 H, s, CHO), 7.97 (1 H, d, *J* 1.6, ArH), 7.87 (1 H, d, *J* 1.6, ArH), 2.72 (3 H, s, Me); δ_C (100 MHz in $CDCl_3$) 188.0 (CH), 167.0 (C), 152.4 (C), 141.9 (C), 127.3 (C), 126.9 (CH), 118.9 (CH), 117.8 (C), 14.8 (Me); HRMS (ESI) found 261.9479 $[C_9H_6BrNO_2+Na]^+$ requires: 261.9474.

6-Chloro-2-methylbenzo[*d*]oxazole-4-carbaldehyde (19)



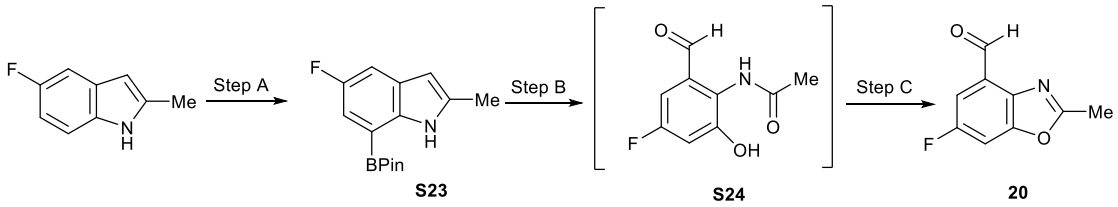
General procedure A2 was performed using 5-chloro-2-methylindole (165 mg, 1 mmol), $[Ir(OMe)COD]_2$ (19.9 mg, 0.03 mmol, 3 mol %), d^tbpy (16.1 mg, 0.06 mmol, 6 mol %), B_2Pin_2 (254 mg, 1 mmol, 1 equiv.) and *n*-hexane (3 mL). Purification eluting with ethyl acetate-light petroleum (1:4) gave the 7-borylindole **S21** (236 mg, 0.81 mmol, 81%) as a beige solid, m.p. 131 – 135 °C; δ_H (400 MHz, $CDCl_3$) 8.81 (1 H, bs, NH), 7.56 (1 H, d, *J* 1.8, ArH), 7.49 (1 H, *J* 2.0, ArH), 6.15 (1 H, m, ArH), 2.48 (3 H, d, *J* 0.7, Me), 1.39 (12 H, 4 x Me); Spectroscopic data in agreement with literature values.[7]

General procedure B2 was performed using **S21** (44 mg, 0.2 mmol) in ethanol-water (9:1, 6 mL). Purification as described in the general procedure gave the *o*-amidophenol **S22** (11 mg, 0.05 mmol, 34%)

as a yellow solid, δ_H (300 MHz, $CDCl_3$) 8.97 (1 H, s, CHO), 8.95 (1 H, bs, NH), 7.14 (1 H, d, *J* 2.8, ArH), 7.02 (1 H, d, *J* 2.5, ArH), 2.28 (3 H, s, Me).

General procedure C was performed using **S22** (11 mg, 0.05 mmol) and TFA (2 mL) for 1.5 h. Purification as described in the general procedure gave the *title compound* (7 mg, 0.04 mmol, 69%) as a colourless solid, m.p. 142 – 146 °C; ν_{max} (neat)/cm^{-1} 3084, 2923, 2853, 1607, 1684, 1569, 1458, 1422, 1384, 1330, 1273, 1246, 1013, 1075, 1031, 926, 847, 731; δ_H (400 MHz, $CDCl_3$) 10.57 (1 H, s, CH), 7.83 (1 H, d, *J* 1.9, ArH), 7.72 (1 H, d, *J* 1.9, ArH), 2.72 (3 H, s, Me); δ_C (100 MHz in $CDCl_3$) 188.1 (CH), 167.2 (C), 152.2 (C), 141.5 (C), 130.8 (C). 126.9 (C). 124.2 (CH), 116.2 (CH), 14.9 (Me); HRMS (ESI) found: 217.9974 $[C_9H_6ClNO_2+Na]^+$ requires: 217.9979.

6-Fluoro-2-methylbenzo[*d*]oxazole-4-carbaldehyde (20)



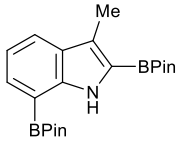
General procedure A2 was performed using 5-fluoro-2-methylindole (149 mg, 1 mmol), $[Ir(OMe)COD]_2$ (19.9 mg, 0.03 mmol, 3 mol %), d^tbpy (16.1 mg, 0.06 mmol, 6 mol %), B_2Pin_2 (254 mg, 1 mmol, 1 equiv.) and *n*-hexane (3 mL) for 4.5 h. Purification eluting with ethyl acetate-light petroleum (1:4) gave the 7-borylindole **S23** (216 mg, 0.78 mmol, 79%) as a beige solid, m.p. 87 – 90 °C; ν_{max} (neat)/cm^{-1} 3450, 3427, 2978, 1597, 1555, 1487, 1426, 1399, 1372, 1335, 1263, 1208, 1133, 1105, 964, 848, 756; δ_H (400 MHz, $CDCl_3$) 8.80 (1 H, bs, NH), 7.27 – 7.25 (2 H, m, ArH), 6.17 – 6.16 (1 H, m, ArH), 2.48 (3 H, d, Me), 1.40 (12 H, s, 4 x Me); δ_C (100 MHz in $CDCl_3$) 157.8 (C, d, *J* 234), 138.1 (C), 137.1 (C), 128.9 (C, d, *J* 9), 114.9 (CH, d, *J* 24), 108.3 (CH, d, *J* 24), 100.1 (CH, d, *J* 4), 84.2 (2 x C), 25.1 (4 x Me), 14.1 (Me), 1 x C not observed.

General procedure B2 was performed using **S23** (55 mg, 0.2 mmol) in ethanol-water (9:1, 6 mL). Purification as described in the general procedure gave the *o*-amidophenol **S24** (20 mg, 0.1 mmol, 51%) as a yellow solid, δ_H (300 MHz, $CDCl_3$) 11.12 (1 H, bs, NH), 10.90 (1 H, s, OH), 9.82 (1 H, s, CHO), 7.03-6.95 (2 H, m, 2 x ArH), 2.35 (3 H, s, Me).

General procedure C was performed using **S24** (20 mg, 0.1 mmol) and TFA (2 mL) for 1.5 h. Purification as described in the general procedure gave the *title compound* (9 mg, 0.05 mmol, 50%) as a colourless solid, m.p. 139 – 141 °C; ν_{max} (neat)/cm^{-1} 3088, 2923, 2853, 1736, 1683, 1617, 1578, 1475, 1433, 1389, 1298, 1195, 1118, 985, 913, 867, 858, 762; δ_H (400 MHz, $CDCl_3$) 10.60 (1 H, d, *J* 2.5, CHO), 7.58 (1 H, dd, *J* 9.5, 2.4, ArH), 7.46 (1 H, dd, *J* 7.3, 2.4, ArH), 2.72 (3 H, s, Me); δ_C (100 MHz in $CDCl_3$) 188.1 (CH), 166.9 (C, d, *J* 3), 160.1 (C, d, *J* 246), 152.0 (C, d, *J* 13), 139.3 (C), 126.7 (C, d, *J* 8), 110.6 (CH, d, *J* 25), 104.1 (CH, d, *J* 29), 14.83 (Me); δ_F (376 MHz in $CDCl_3$) -114.7 (s); HRMS (ESI) found 202.0279 $[C_9H_6FNO_2+Na]^+$ requires: 202.0275.

4-Acylbenzoxazoles from 3-Substituted Indoles

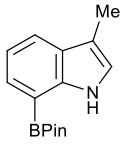
3-Methyl-2,7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indole (22)



To a sealed tube containing 3-methylindole **21** (100 mg, 0.48 mmol), $[Ir(OMe)COD]_2$ (9.6 mg, 0.014 mmol, 3 mol %), Me_4Phen (6.8 mg, 0.028 mmol, 6 mol %) and B_2Pin_2 (123 mg, 0.48 mmol) under nitrogen was added MTBE (2 mL). The reaction was sealed and stirred at 90°C for 4 h. The reaction was diluted with ethyl acetate (5 mL) and concentrated *in vacuo*. Purification by flash chromatography on silica gel eluting with ethyl acetate-light petroleum (1:20) gave the *title compound* (227 mg, 0.59 mmol 39%) as a colourless solid, m.p. 118 – 121 °C; δ_H (400 MHz, $CDCl_3$) 9.09 (1 H, s, NH), 7.74 – 7.69 (2 H, m, ArH),

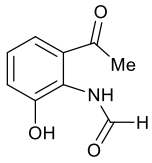
7.09 (1 H, dd, *J* 7.9, 6.9, ArH), 2.54 (3 H, s, Me), 1.38 (12 H, s, 4 x Me), 1.35 (12 H, s, 4 x Me). Spectroscopic data in agreement with literature values.[8]

3-Methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indole (23)



To a solution of **22** (50 mg, 0.13 mmol) in dichloromethane (7.5 mL) at 0 °C was added TFA (0.1 mL, 1.3 mmol, 10 equiv.). The reaction mixture was stirred for 0.25 h and then neutralized with saturated sodium bicarbonate solution (20 mL) was added. The resulting aqueous solution was extracted with ethyl acetate (4 x 15 mL), washed with brine (20 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give the *title compound* (33 mg, 0.13 mmol, 98%) as a colourless oil which was used in the subsequent step without further purification; δ_H (300 MHz, $CDCl_3$) 8.94 (1 H, bs, NH), 7.70 (1 H, d, *J* 7.9, ArH), 7.64 (1 H, dd, *J* 7.0, 1.1, ArH), 7.12 (1 H, dd, *J* 7.7, 6.9, ArH), 7.01 (1 H, q, *J* 1.0, ArH), 2.34 (3 H, *J* 1.1, Me), 1.39 (12 H, s, 4 x Me). Spectroscopic data in accordance with literature values.[8]

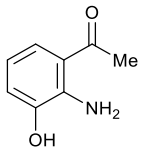
***N*-(2-Acetyl-6-hydroxyphenyl)formamide (24)**



A solution of **23** (50 mg, 0.19 mmol) in dichloromethane (6 mL) was cooled to -78 °C. The reaction mixture was purged with ozone for 15 min followed by oxygen for 10 min. Pyridine (0.15 mL, 1.9 mmol, 10 equiv.) was added to the reaction mixture at room temperature and stirred for 10 min. The reaction mixture was diluted with saturated aqueous sodium bicarbonate solution (20 mL). The resulting aqueous solution was extracted with dichloromethane (3 x 10 mL), dried over Na_2SO_4, filtered and concentrated

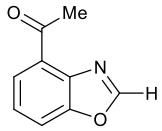
in vacuo. Purification by flash chromatography on silica gel eluting with methanol-dichloromethane (1:19) gave the *title compound* (10 mg, 0.06 mmol, 29%) as a yellow solid, m.p. 121 – 124 °C; ν_{max} (neat)/cm^{-1} 3076, 2925, 1615, 1580, 1516, 1477, 1368, 1287, 1240, 1199, 1132, 1027, 017, 918, 782, 723; δ_H (400 MHz, $CDCl_3$) 11.81 (1 H, bs, NH), 9.61 (1 H, s, OH), 8.18 (1 H, d, *J* 2.4, ArH), 7.44 (1 H, dd, *J* 7.6, 1.7, ArH), 7.23 – 7.14 (2 H, m, ArH), 2.61 (3 H, Me); δ_C (100 MHz, $CDCl_3$) 203.6 (C), 160.9 (CH), 150.0 (C), 127.0 (C), 126.5 (CH), 126.4 (CH), 126.2 (C), 123.8 (CH), 29.2 (Me); HRMS (ESI) found: 202.0476 $[C_9H_9NO_3+Na]^+$ requires: 202.0475.

1-(2-Amino-3-hydroxyphenyl)ethan-1-one (25)



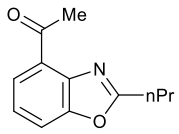
A solution of **23** (100 mg, 0.39 mmol) in dichloromethane (13 mL) at -78 °C was purged with ozone for 15 min followed by oxygen for 10 min. Methanol (5 mL) and concentrated hydrochloric acid (2 mL) were added to the reaction mixture and warmed to room temperature over 0.5 h. The reaction mixture was concentrated *in vacuo* and neutralised with saturated aqueous sodium bicarbonate solution (30 mL). The resulting aqueous solution was extracted with dichloromethane (6 x 20 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography on silica gel eluting with methanol-dichloromethane (1:19) gave the *title compound* (21 mg, 0.14 mmol, 36%) as a yellow solid, m.p. 148 – 149 °C; δ_H (300 MHz, DMSO-d_6) 9.63 (1 H, bs, OH), 7.24 (1 H, dd, *J* 8.3, 1.2, ArH), 6.82 (1 H, dd, *J* 7.5, 1.1, ArH), 6.67 (2 H, bs, NH_2), 6.41 (1 H, t, *J* 7.9, ArH), 2.48 (3 H, s, Me). Spectroscopic data in agreement with literature values.[9]

1-(Benzo[*d*]oxazol-4-yl)ethan-1-one (26)



Trimethyl orthoformate (0.6 mL) was added to **25** (26 mg, 0.17 mmol) and heated to reflux for 0.5 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. Purification by flash chromatography on silica gel eluting with ethyl acetate-light petroleum (1:4) gave the *title compound* (21 mg, 0.13 mmol, 76%) as a pale yellow solid, m.p. 122 – 125 °C; ν_{max} (neat)/cm^{-1} 3120, 3102, 3072, 3017, 1809, 1668, 1610, 1591, 1515, 1424, 1365, 1350, 1276, 1239, 1205, 1078, 1055, 976, 949, 906, 839, 760, 802, 657; δ_H (300 MHz, $CDCl_3$) 8.21 (1 H, s, ArH), 8.00 (1 H, dd, *J* 7.7, 1.1, ArH), 7.79 (1 H, dd, *J* 8.1, 1.1, ArH), 7.49 (1 H, t, *J* 7.9, ArH), 2.98 (3 H, s, Me); δ_C (125 MHz in $CDCl_3$) 197.4 (C), 153.1 (CH), 150.8 (C), 139.4 (C), 129.9 (C), 125.4 (CH), 125.3 (CH), 115.5 (CH), 31.1 (Me); HRMS (ESI) found 184.0375 $[C_9H_7NO_2+Na]^+$ requires: 184.0369.

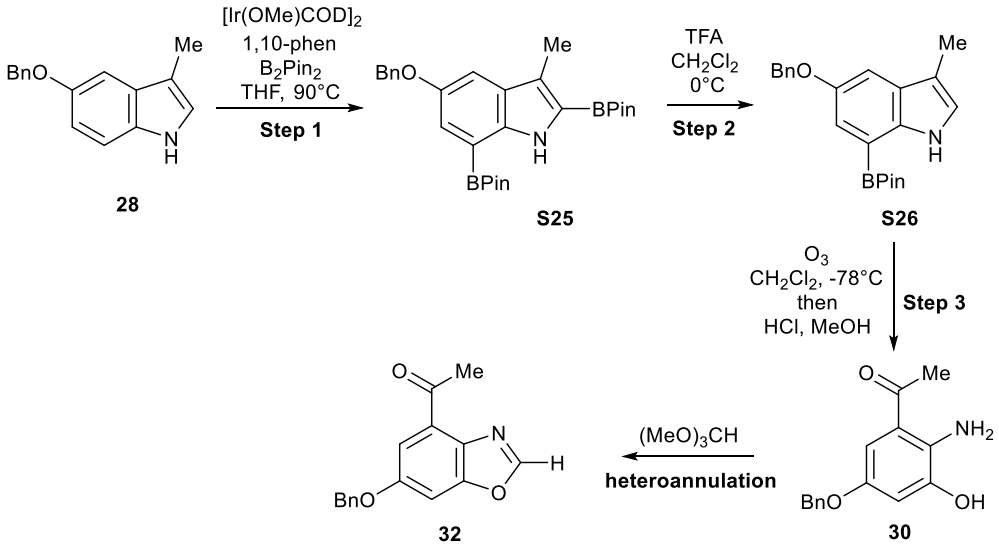
1-(2-Propylbenzo[*d*]oxazol-4-yl)ethan-1-one (27)



Trimethyl orthobutyrate (0.16 mL) was added to **25** (7 mg, 0.05 mmol, 1 equiv) and heated to reflux for 0.5 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. Purification by flash chromatography on silica gel, eluting with ethyl acetate-light petroleum (1:4) gave the *title compound* (9 mg, 0.05 mmol, 96%) as a pale yellow solid, m.p. 40 – 43 °C; ν_{max} (neat)/cm^{-1} 3063, 2971, 2817, 1668, 1600, 1567, 1420, 1362, 1279, 1219, 1120, 1056, 956, 949, 941, 806, 763, 753, 746; δ_H (400 MHz, $CDCl_3$) 7.89 (1 H, dd, *J* 7.9, 1.0, ArH), 7.66 (1 H, dd, *J* 8.3, 1.3, ArH), 7.36 (1 H, t, *J* 7.9, ArH), 2.98 – 2.94 (5 H, m, Me+CH_2) 1.95 (2H, sext, *J* 7.4, CH_2), 1.08 (3 H, t, *J* 7.4, Me); δ_C (100 MHz in $CDCl_3$)

197.9 (C), 168.2 (C), 151.7 (C), 141.1 (C), 129.1 (C), 124.5 (CH), 124.0 (CH), 114.7 (CH), 31.1 (CH_2), 30.7 (Me), 20.4 (CH_2), 13.9 (Me); HRMS (ESI) found 226.0847 $[C_{12}H_{13}NO_2+Na]^+$ requires: 226.0838.

1-(6-(Benzyloxy)benzo[*d*]oxazol-4-yl)ethan-1-one (32)



Step 1: To a sealed tube containing 5-(benzyloxy)-3-methylindole (145 mg, 0.61 mmol), $[Ir(OMe)COD]_2$ (20.3 mg, 0.03 mmol, 5 mol %), 1,10-phenanthroline (1 mg, 0.06 mmol, 10 mol %), B_2Pin_2 (232.8 mg, 0.92 mmol, 1.5 equiv.) was added THF (1.6 mL) under a heavy stream of nitrogen and heated to 90°C for 2 h. The reaction mixture was then diluted with ethyl acetate (3 mL) and concentrated *in vacuo*. Purification by flash chromatography on silica gel eluting with ethyl acetate-light petroleum (1:9) gave the 2,7-diborylindole **S25** (96 mg, 0.19 mmol, 31%) as a colourless solid, m.p. 152 – 155 °C; ν_{max} (neat)/cm^{-1} 3461, 2978, 1599, 1549, 1446, 1419, 1379, 1371, 1304, 1256, 1137, 961, 850, 706; δ_H (400 MHz, $CDCl_3$) 8.95 (1 H, bs, NH), 7.49 – 7.47 (3 H, m, ArH), 7.39 – 7.36 (2 H, m, ArH), 7.32 (1 H, d, *J* 7.3, ArH), 7.25 (1 H, m , ArH), 5.13 (2 H, s, CH_2), 2.50 (3 H, s, Me), 1.40 (12 H, s, 4 x Me), 1.37 (12 H, s, 4 x Me); δ_C (100 MHz, $CDCl_3$) 152.6 (C), 138.8 (C), 138.0 (C), 128.7 (C), 128.5 (2 x CH), 127.7 (CH), 127.7 (2 x CH), 123.7 (C), 121.7 (CH), 107.4 (CH), 84.0 (2 x C), 83.6 (2 x C), 71.3 (CH_2), 25.1 (4 x Me),

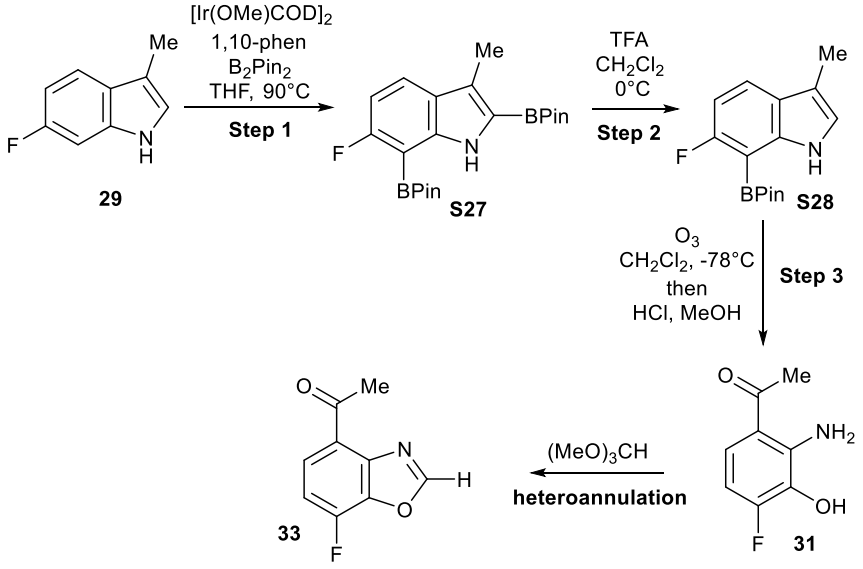
25.0 (4 x Me), 10.3 (Me), 2 x C not observed; HRMS (ESI) found 512.2760 $[C_{28}H_{37}B_2NO_5+Na]^+$ requires: 512.2760.

Step 2: To a solution of **S25** (83 mg, 0.17 mmol) in dichloromethane (9.9 mL) at 0 °C was added TFA (0.13 mL, 1.7 mmol). The reaction was stirred for 15 min before diluting with saturated aqueous sodium bicarbonate solution (20 mL). The resulting aqueous solution was extracted with dichloromethane (3 x 10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* gave the 7-diborylindole **S26** (61 mg, 0.17 mmol, quant) as a dark green oil which was used in the subsequent step without further purification, ν_{max} (neat)/cm^{-1} 3463, 2977, 2927, 2858, 1601, 1430, 1408, 1363, 1307, 1266, 1140, 1075, 966, 850, 732; δ_H (400 MHz, $CDCl_3$) 8.81 (1 H, bs, NH), 7.50 (2 H, d, *J* 3.4, ArH), 7.42 (1 H, d, *J* 2.5, ArH), 7.41 – 7.37 (2 H, m, ArH), 7.32 (1 H, d, *J* 7.3, ArH), 7.28 (1 H, d, *J* 2.5, ArH), 7.01 (1 H, bs, ArH), 5.14 (2 H, s, CH_2), 2.31 (3 H, d, *J* 0.9, Me), 1.39 (12 H, s, 4 x Me); δ_C (100 MHz, $CDCl_3$) 152.7 (C), 138.1 (C), 137.3 (C), 128.5 (2 x CH), 128.1 (C), 127.7 (CH), 127.6 (2 x CH), 122.6 (CH), 118.6 (CH), 110.8 (C), 107.6 (CH), 84.0 (2 x C), 71.5 (CH_2), 25.1 (4 x Me), 9.8 (Me), 1 x C not observed; HRMS (ESI) found 386.1892, $[C_{22}H_{26}BNO_3+Na]^+$ requires: 386.1902.

Step 3: A solution of **S26** (60 mg, 0.17 mmol) in dichloromethane (5.5 mL) was cooled to -78°C and purged with ozone for 10 min, followed by oxygen for 5 min. Methanol (2 mL) and concentrated hydrochloric acid (1 mL) were added and the reaction mixture stirred at room temperature for 15 min, then concentrated *in vacuo*. The residue was neutralised using saturated aqueous sodium bicarbonate (20 mL) and the resulting aqueous solution was extracted with dichloromethane (15 mL x 3), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting *o*-aminophenol **30** (9 mg, 0.03 mmol, 21%) was used in the subsequent step without further purification.

Heteroannulation: Trimethyl orthoformate (0.3 mL) was added to the crude **30** (5.5 mg, 0.021 mmol) and the solution heated at reflux for 0.5 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. Purification by flash chromatography on silica gel, eluting with ethyl acetate-light petroleum (1:4) gave the *title compound* (2 mg, 0.007 mmol, 35%) as a colourless oil, ν_{max} (neat)/cm^{-1} 3108, 3046, 3037, 2925, 2855, 1679, 1615, 1522, 1412, 1364, 1276, 1169, 1107, 1059, 1023, 852, 739; δ_H (500 MHz, $CDCl_3$) 8.10 (1 H, s, ArH), 7.68 (1 H, d, *J* 2.5, ArH), 7.45 (2 H, d, *J* 7.2 , ArH), 7.40 (2 H, t, *J* 7.2, ArH), 7.36 (1 H, d, *J* 2.5, ArH), 7.35 – 7.33 (1 H, m, ArH), 5.17 (2 H, s, CH_2), 2.96 (3 H, s, Me); δ_C (100 MHz, $CDCl_3$) 197.0 (C), 157.2 (C), 152.3 (CH), 151.8 (C), 136.3 (C), 133.6 (C), 129.6 (C), 128.9 (2 x CH), 128.4 (CH), 127.7 (2 x CH), 112.9 (CH), 102.2 (CH), 71.2 (CH_2), 31.1 (Me); HRMS (ESI) found 290.0781 $[C_{16}H_{13}NO_3+Na]^+$ requires: 290.0788.

1-(7-Fluorobenzo[*d*]oxazol-4-yl)ethan-1-one (33)



Step 1: To a sealed tube containing 6-fluoro-3-methylindole (100 mg, 0.67 mmol), $[Ir(OMe)COD]_2$ (22 mg, 0.033 mmol, 5 mol %), 1,10-phenanthroline (12 mg, 0.067 mmol, 10 mol %), B_2Pin_2 (255 mg, 1 mmol, 1.5 equiv.) was added THF (1.8 mL) under a heavy stream of nitrogen. The tube was sealed under a blanket of nitrogen and the reaction mixture heated to 90 °C for 2.5 h. The reaction mixture was then

diluted with ethyl acetate (3 mL) and concentrated *in vacuo*. Purification by flash chromatography on silica gel eluting with ethyl acetate-light petroleum (1:19) gave the 2,7-diborylindole **S27** (136 mg, 0.34 mmol, 51%) as a colourless solid, m.p. 118 – 120 °C; ν_{max} (neat)/cm^{-1} 3457, 2978, 2938, 1596, 1556, 14933, 1421, 1386, 1284, 1261, 1140, 1128, 1098, 962, 854, 814, 707; δ_H (400 MHz, DMSO-*d*$_6$) 9.20 (1 H, s, NH), 7.72 (1 H, dd, *J* 8.6, 5.4, ArH), 6.85 (1 H, dd, *J* 9.9, 8.7, ArH), 2.42 (3 H, s, Me), 1.36 (12 H, s, 4 x Me), 1.32 (12 H, s, 4 x Me); δ_C (100 MHz, DMSO-*d*$_6$) 165.3 (C, d, *J* 245), 142.1 (C, d, *J* 13), 124.9 (CH, d, *J* 11), 124.5 (C), 123.5 (C), 107.7 (C, *J* 27), 83.7 (2 x C), 83.6 (2 x C), 24.7 (4 x Me), 24.6 (4 x Me), 9.9 (Me), 2 x C not observed; δ_F (376 MHz, DMSO-*d*$_6$) -106.5 (s); HRMS (ESI) found: 424.2246 $[C_{21}H_{30}B_2FNO_4+Na]^+$ requires: 424.2245.

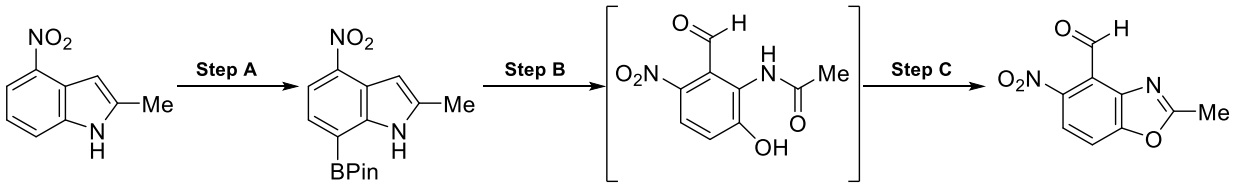
Step 2: To a solution **S27** (141 mg, 0.35 mmol) in dichloromethane (20.5 mL) at 0 °C was added TFA (0.26 mL, 3.5 mmol). The reaction mixture was stirred for 15 min before neutralising with saturated aqueous sodium bicarbonate solution (20 mL). The resulting aqueous solution was extracted with dichloromethane (3 x 10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* gave the 7-diborylindole **S28** (97 mg, 0.35 mmol, quant) as a pale pink solid which was used in the subsequent step without further purification, m.p. 123 – 126 °C; ν_{max} (neat)/cm^{-1} 3438, 2980, 2929, 1603, 1553, 1444, 1365, 1300, 1282, 1196, 1141, 1123, 1081, 997, 964, 853, 814, 717; δ_H (400 MHz, $CDCl_3$) 9.96 (1 H, bs, NH), 7.60 (1 H, dd, *J* 8.5, 5.5, ArH), 7.10 (1 H, bs, ArH), 6.78 (1 H, dd, *J* 9.9, 8.9, ArH), 2.24 (3 H, s, Me), 1.35 (12 H, s, 4 x Me); δ_C (100 MHz, $CDCl_3$) 163.8 (C, d, *J* 242), 140.0 (C, d, *J* 13), 124.2 (C), 123.7 (CH, *J* 4), 123.2 (CH, *J* 11), 109.4 (C), 106.4 (CH, *J* 27), 83.4 (2 x C), 24.6 (4 x Me), 9.4 (Me), 1 x C not observed; δ_F (376 MHz, DMSO-*d*$_6$) -110.4 (s); HRMS (ESI) found 298.139, $[C_{15}H_{19}BFNO_2+Na]^+$ requires: 298.1388.

Step 3: A solution of **S28** (55 mg, 0.2 mmol) in dichloromethane (6.7 mL) was cooled to -78°C and purged with ozone for 15 min, followed by oxygen for 5 min. Methanol (3 mL) and concentrated hydrochloric

acid (1 mL) were added and the reaction mixture stirred for 10 min, then concentrated *in vacuo*. The residue was neutralised using saturated aqueous sodium bicarbonate (20 mL) and the resulting aqueous solution was extracted with dichloromethane (3 x 15 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography on silica gel eluting with methanol-dichloromethane (1:19) gave the *o*-aminophenol **31** (11 mg, 0.07 mmol, 33%) as a yellow solid, m.p. 158 – 160 °C; ν_{max} (neat)/cm^{-1} 3473, 3351, 3097, 2921, 2851, 1637, 1618, 1558, 1496, 1427, 1364, 1243, 1216, 1044, 1025, 876, 770, 756, 682; δ_H (400 MHz, DMSO-d_6) 9.59 (1 H, bs, OH), 7.33 (1 H, dd, *J* 9.2, 5.6, ArH), 6.97 (2 H, bs, NH_2), 6.41 (1 H, dd, *J* 9.9, 9.2, ArH), 2.47 (3 H, s, Me); δ_C (100 MHz, DMSO-d_6) 199.4 (C), 153.2 (C, d, *J* 242), 144.0 (C, d, *J* 7), 130.4 (C, d, *J* 16), 123.9 (CH, d, *J* 10), 114.2 (C), 102.5 (CH, d, *J* 20.6), 27.9 (Me); δ_F (376 MHz, DMSO-d_6) -128.6 (s); HRMS (ESI) found 170.0617 $[C_8H_8NO_2F+H]^+$requires: 170.0612.

Heteroannulation: Trimethyl orthoformate (0.13 mL) was added to **31** (7 mg, 0.037 mmol) and the solution heated at reflux for 0.25 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. Purification by flash chromatography on silica gel eluting with ethyl acetate-light petroleum (1:4) gave the *title compound* (6 mg, 0.03 mmol, 81%) as a beige solid, m.p. 85 – 89 °C; ν_{max} (neat)/cm^{-1} 3131, 3048, 1682, 1642, 1620, 1598, 1504, 1361, 1258, 1191, 1080, 912, 831, 772, 723; δ_H (400 MHz, $CDCl_3$) 8.23 (1 H, s, ArH), 8.02 (1 H, dd, *J* 8.7, 4.7, ArH), 7.23 (1 H, t, *J* 9.0, ArH), 2.94 (3 H, s, Me); δ_C (100 MHz, $CDCl_3$) 195.9 (C), 153.3 (CH), 150.3 (C, d, *J* 261), 142.9 (C, d, *J* 3), 137.7 (C, d, *J* 11), 127.1 (CH, d, *J* 7), 126.2 (C, d, *J* 4), 112.6 (CH, d, *J* 17), 30.9 (Me); δ_F (376 MHz, $CDCl_3$) -125.9 (s); HRMS (ESI) found 202.0279 $[C_9H_6FNO_2+Na]^+$ requires: 202.0275.

2-Methyl-5-nitrobenzo[*d*]oxazole-4-carbaldehyde (35)

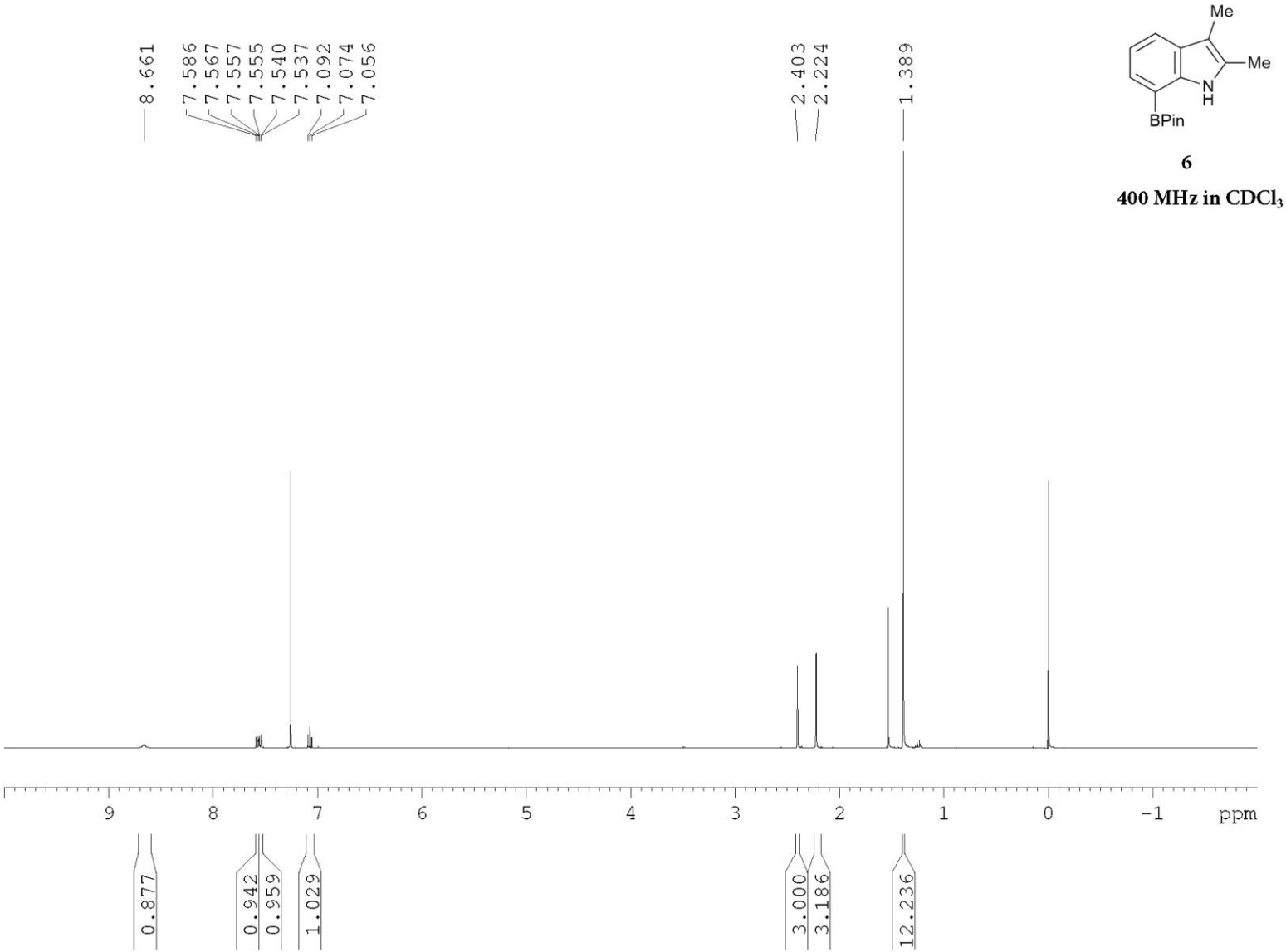


34 **S29** **S30** **35**

General procedure A was performed using 2-methyl-4-nitroindole[10] **34** (88 mg, 0.5 mmol), $[Ir(OMe)COD]_2$ (16.6 mg, 0.025 mmol, 5 mol %), dtbpy (13.4 mg, 0.05 mmol, 10 mol %), B_2Pin_2 (190 mg, 0.75 mmol, 1.5 equiv.) in a microwave vial was added THF (2 mL) and capped under nitrogen. The reaction was heated to 80°C in a microwave for 2 h. Purification eluting with acetone-toluene (1:40) gave the 7-borylindole **S30** (24 mg, 0.08 mmol, 16%) as a yellow oil, ν_{max} (neat)/cm^{-1} 3376, 2980, 2930, 1592, 1547, 1502, 1373, 1349, 1318, 1256, 1211, 1138, 1109, 992,849, 820, 793, 139, 703; δ_H (500 MHz in DMSO-*d*$_6$) 10.69 (1 H, bs, NH), 7.96 (1 H, d, *J* 7.9, ArH), 7.48 (1 H, d, *J* 7.9, ArH), 6.85-6.84 (1 H, m, ArH), 2.56 (3 H, s, Me), 1.38 (12 H, s, 4 x Me) ; δ_C (125 MHz in DMSO-*d*$_6$) 143.32 (C), 142.9 (C), 139.9 (C), 126.0 (CH), 121.8 (C), 115.5 (CH), 99.9 (CH), 84.4 (2 x C), 24.6 (4 x Me), 13.9 (Me), 1 x C not observed; HRMS (ESI) found 325.133 $[C_{15}H_{19}BFNO_2+Na]^+$ requires: 325.1331.

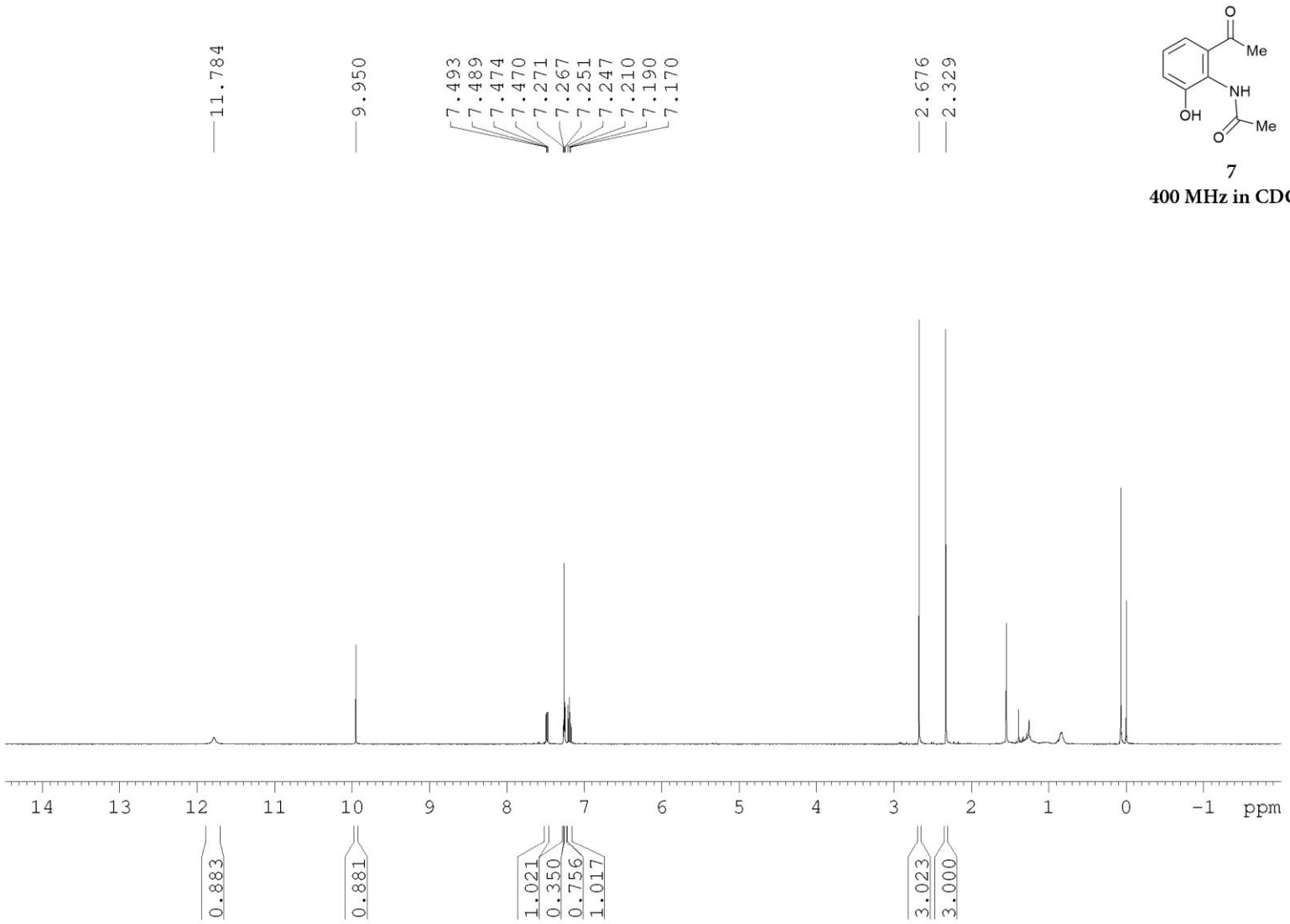
General procedure B was performed using **S29** (37 mg, 0.12 mmol) in ethanol-water (9:1, 4.1 mL). Purification as described in the general procedure gave the *o*-amidophenol **S30** (14 mg, 0.06 mmol, 51%) as a yellow solid, δ_H (400 MHz in DMSO-*d*$_6$) 10.99 (1 H, s, NH), 9.93 (1 H, s, CHO), 9.76 (1 H, bs, OH), 7.96 (1 H, d, *J* 9.1, ArH), 6.99 – 6.97 (1 H, m, ArH), 1.99 (3 H, s, Me).

General procedure C was performed using **S30** (14 mg, 0.06 mmol) and TFA (1 mL) for 1 h. Purification eluting with methanol-dichloromethane (1:9) to obtain the *title compound* (8 mg, 0.04 mmol, 62%) as a brown solid, m.p 119 – 121 °C; ν_{max} (neat)/cm^{-1} 3107, 3085, 3020, 2922, 2851, 1697, 1615, 1515, 1421, 1402, 1338, 1249, 1273, 1135, 1022, 906, 830, 792, 736, 710; δ_H (400 MHz, $CDCl_3$) 10.55 (1 H, s, CHO), 8.16 (1 H, d, *J* 8.9, ArH), 7.73 (1 H, d, *J* 8.8, ArH), 2.75 (3 H, s, Me); δ_C (100 MHz, $CDCl_3$) 186.7 (CH), 169.3 (C), 154.4 (C), 144.9 (C), 141.2 (C), 124.7 (C), 121.3 (CH), 113.3 (CH), 14.9 (Me); HRMS (ESI) found 229.022 $[C_9H_6N_2O_4+Na]^+$ requires: 229.022.



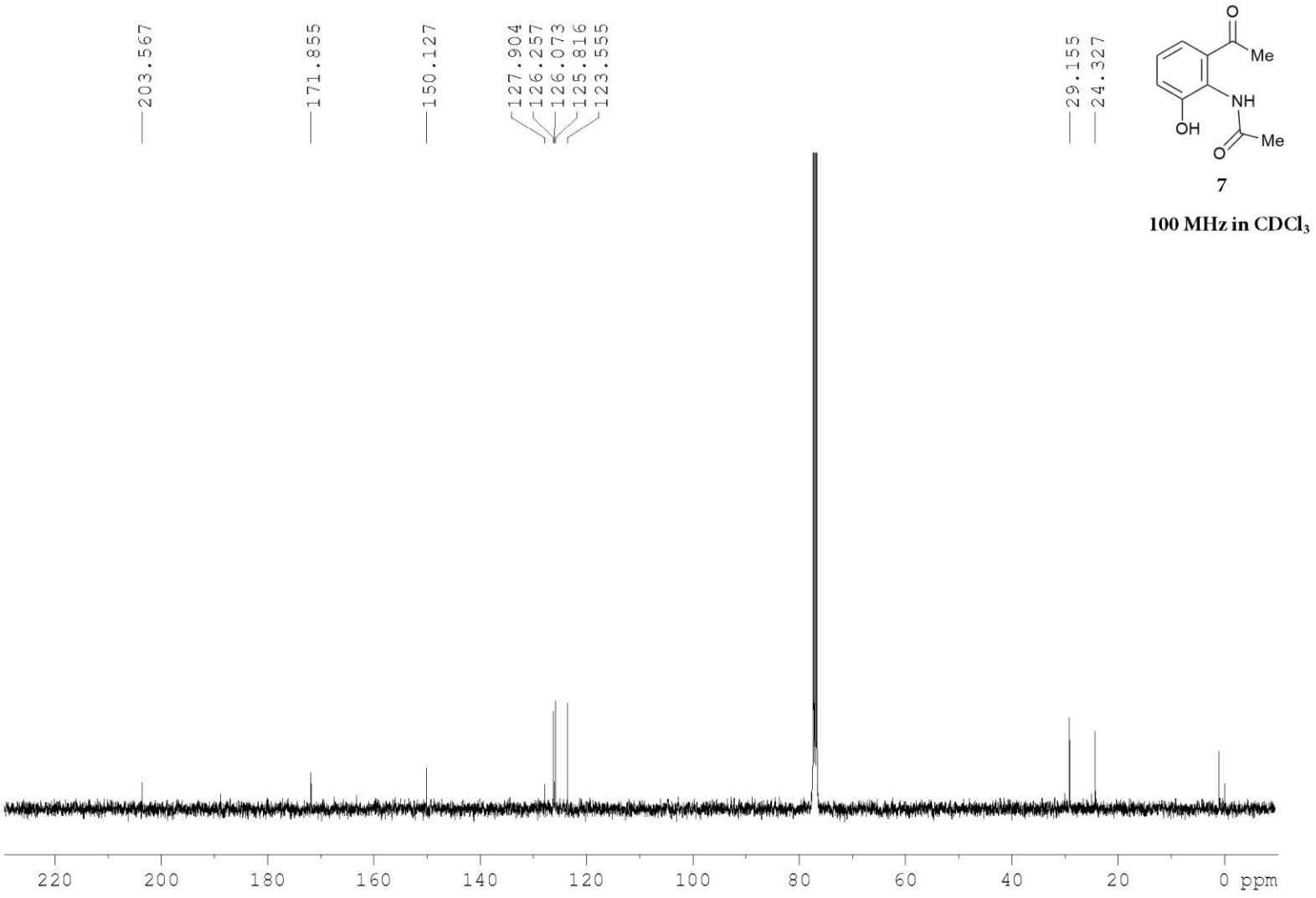
6

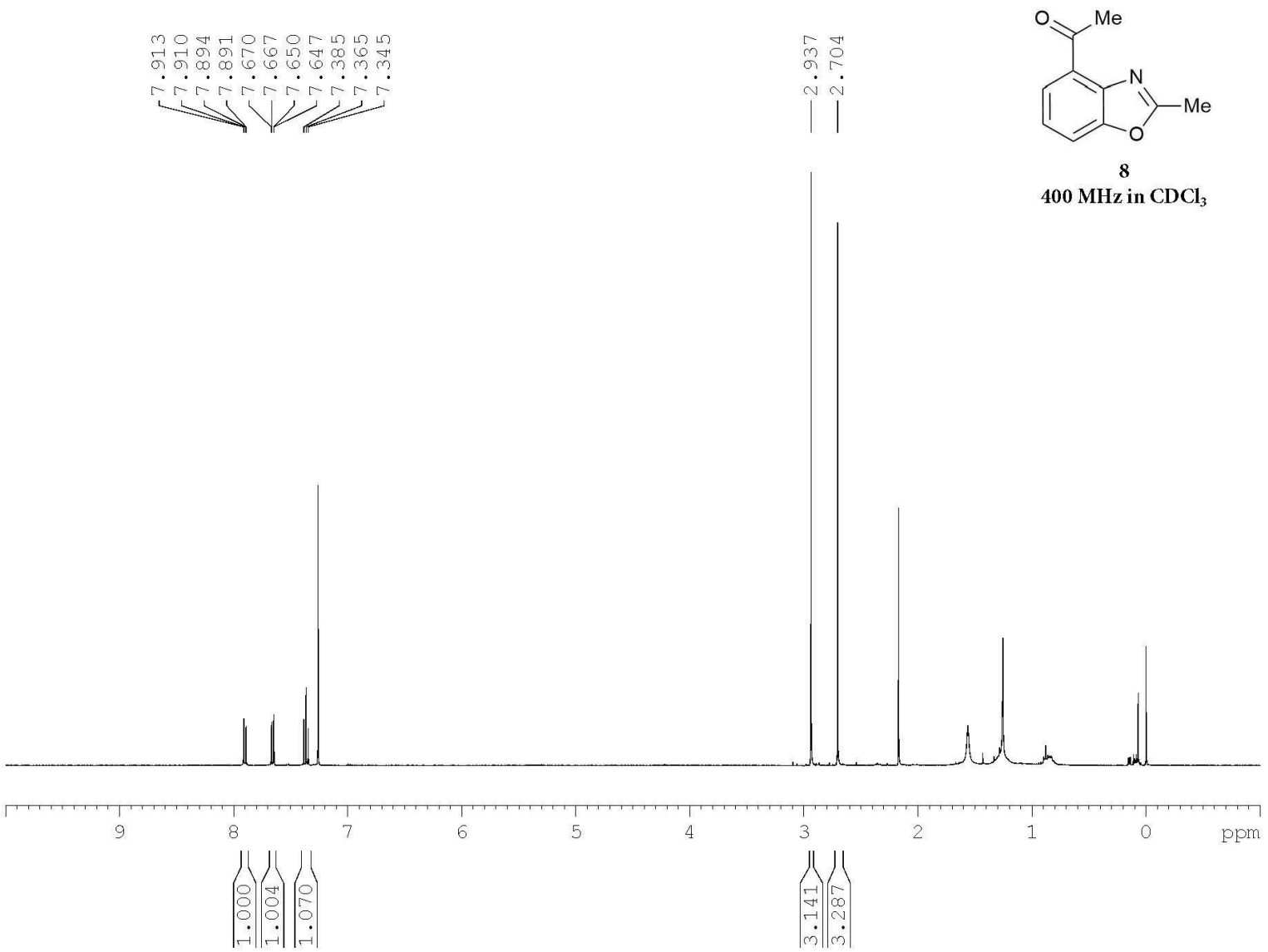
400 MHz in $CDCl_3$

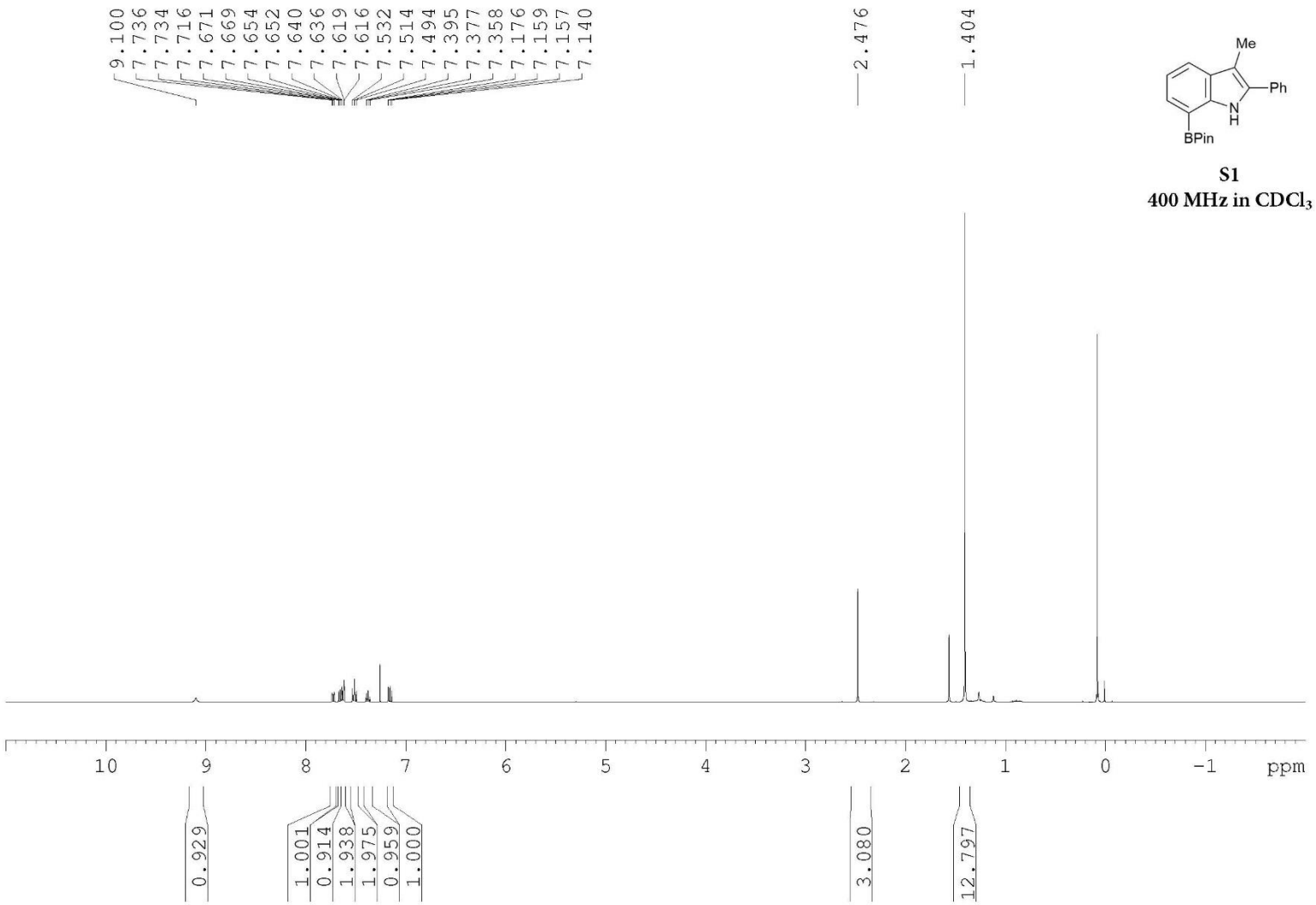


7

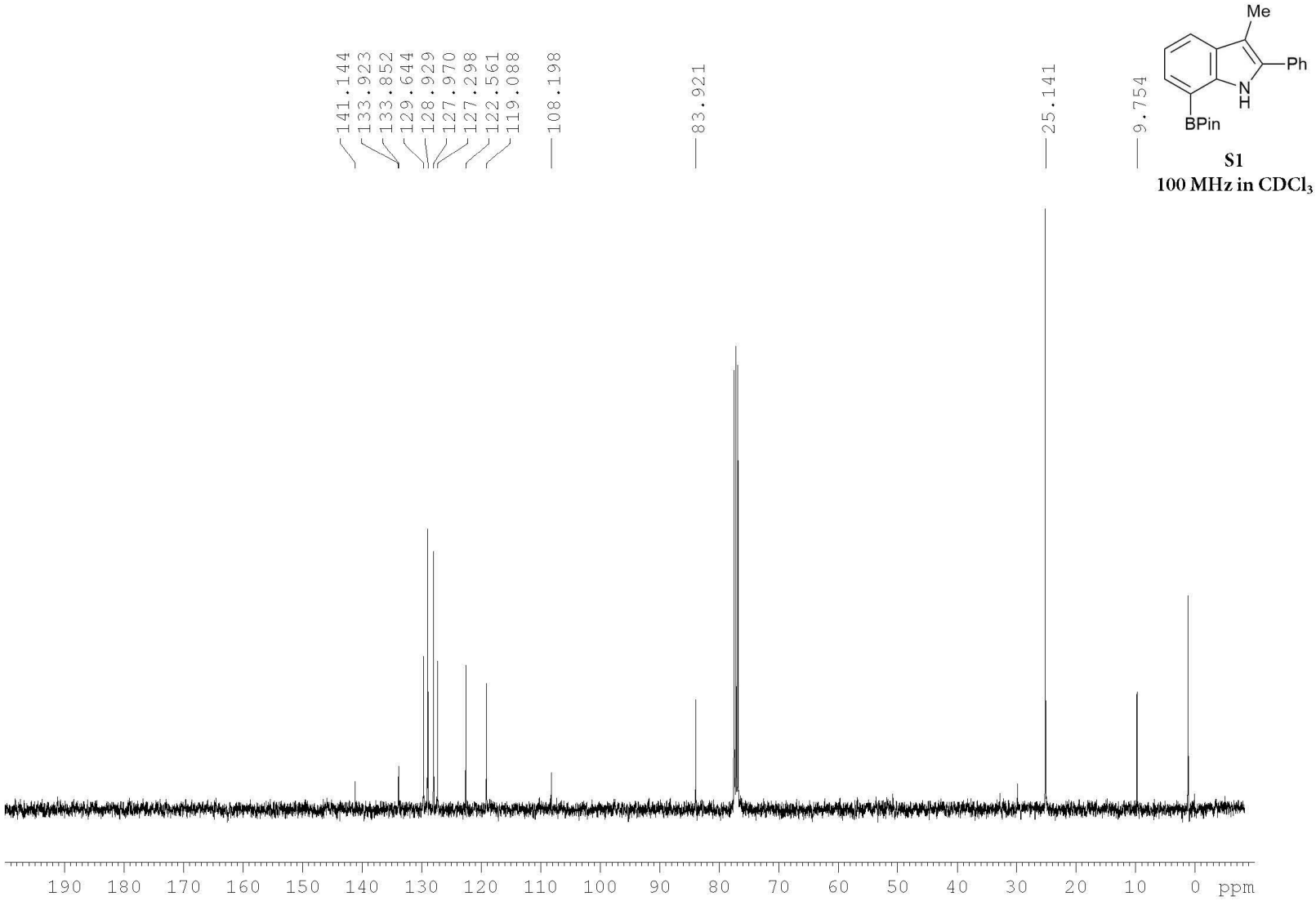
400 MHz in CDCl3


203.567
171.855
150.127
127.904
126.257
126.073
125.816
123.555
29.155
24.327
O
Me
NH
OH
O
Me
7
100 MHz in CDCl3
220
200
180
160
140
120
100
80
60
40
20
0 ppm


7.913
7.910
7.894
7.891
7.670
7.667
7.650
7.647
7.385
7.365
7.345
2.937
2.704
O
Me
N
Me
O
8
400 MHz in CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.004
1.070
3.141
3.287

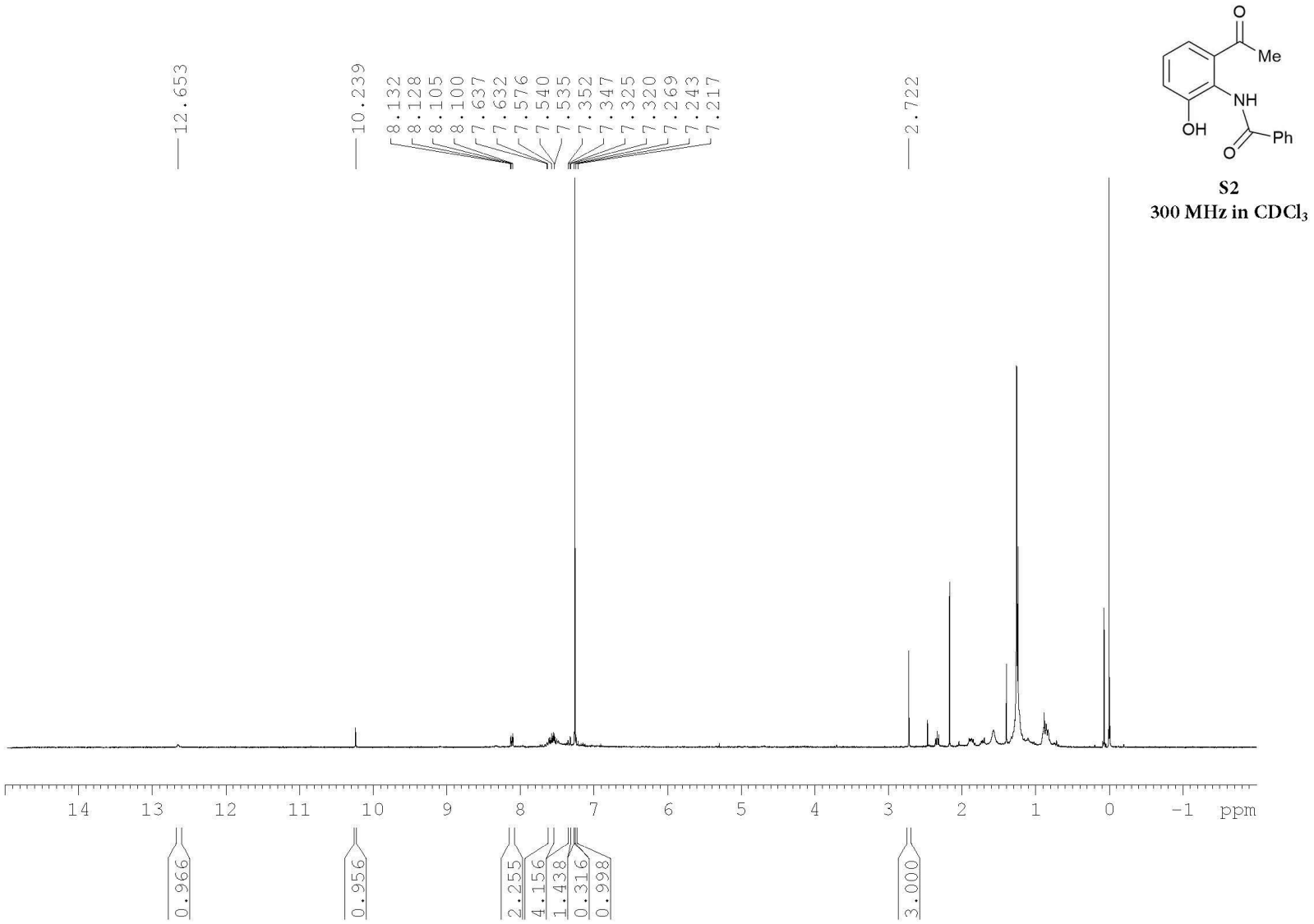


S1
400 MHz in $CDCl_3$



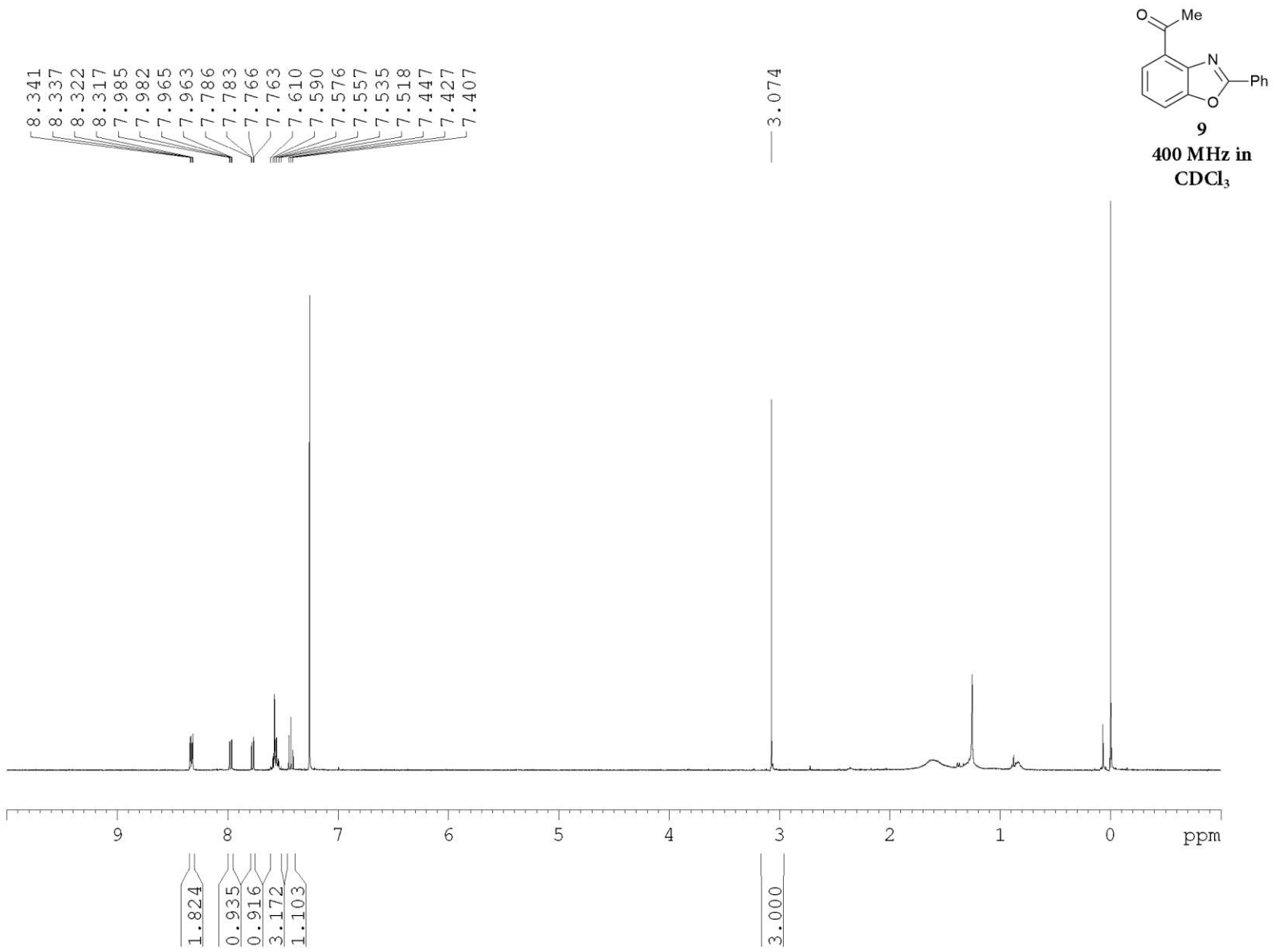
S1

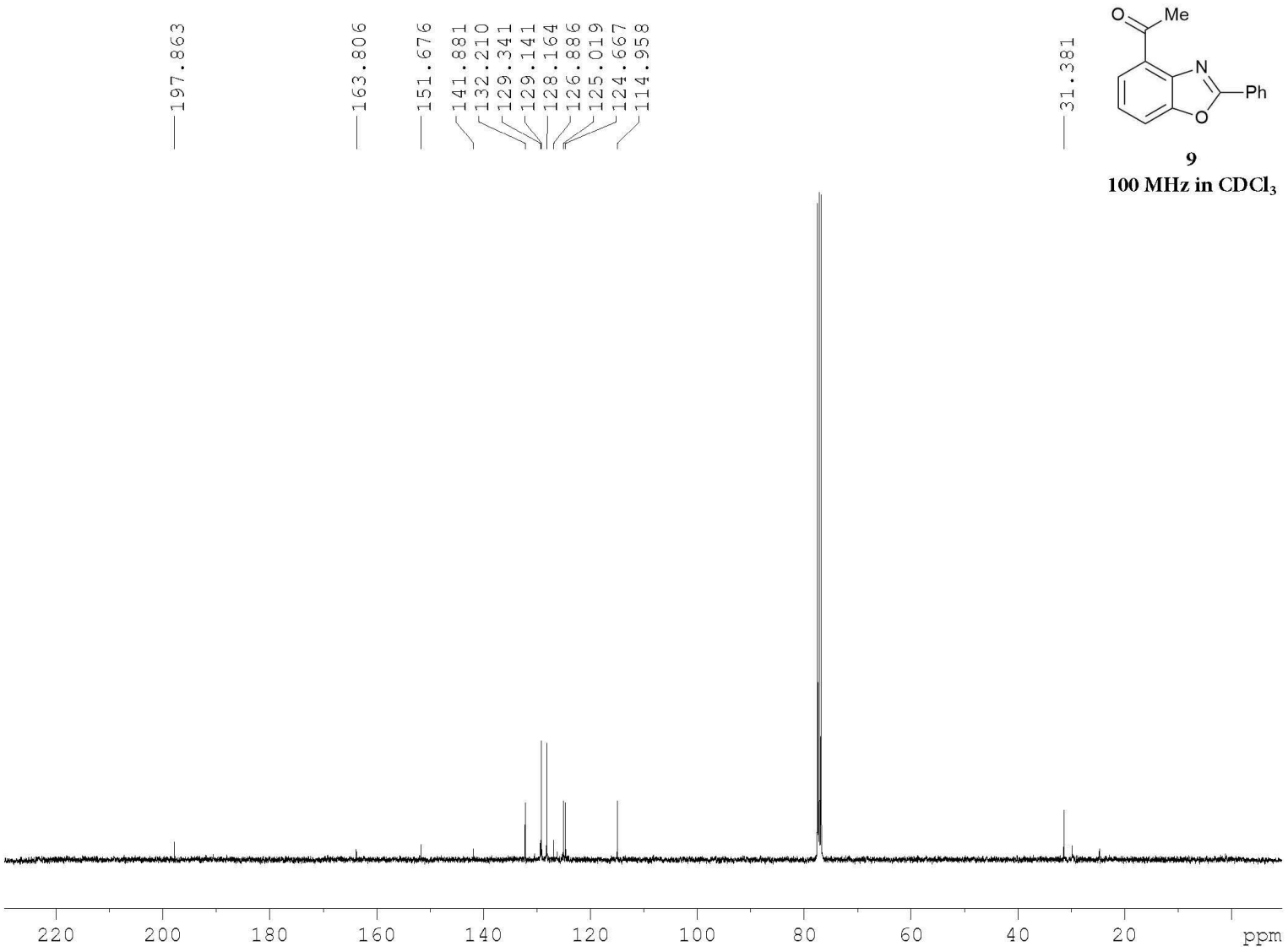
100 MHz in $CDCl_3$



S2

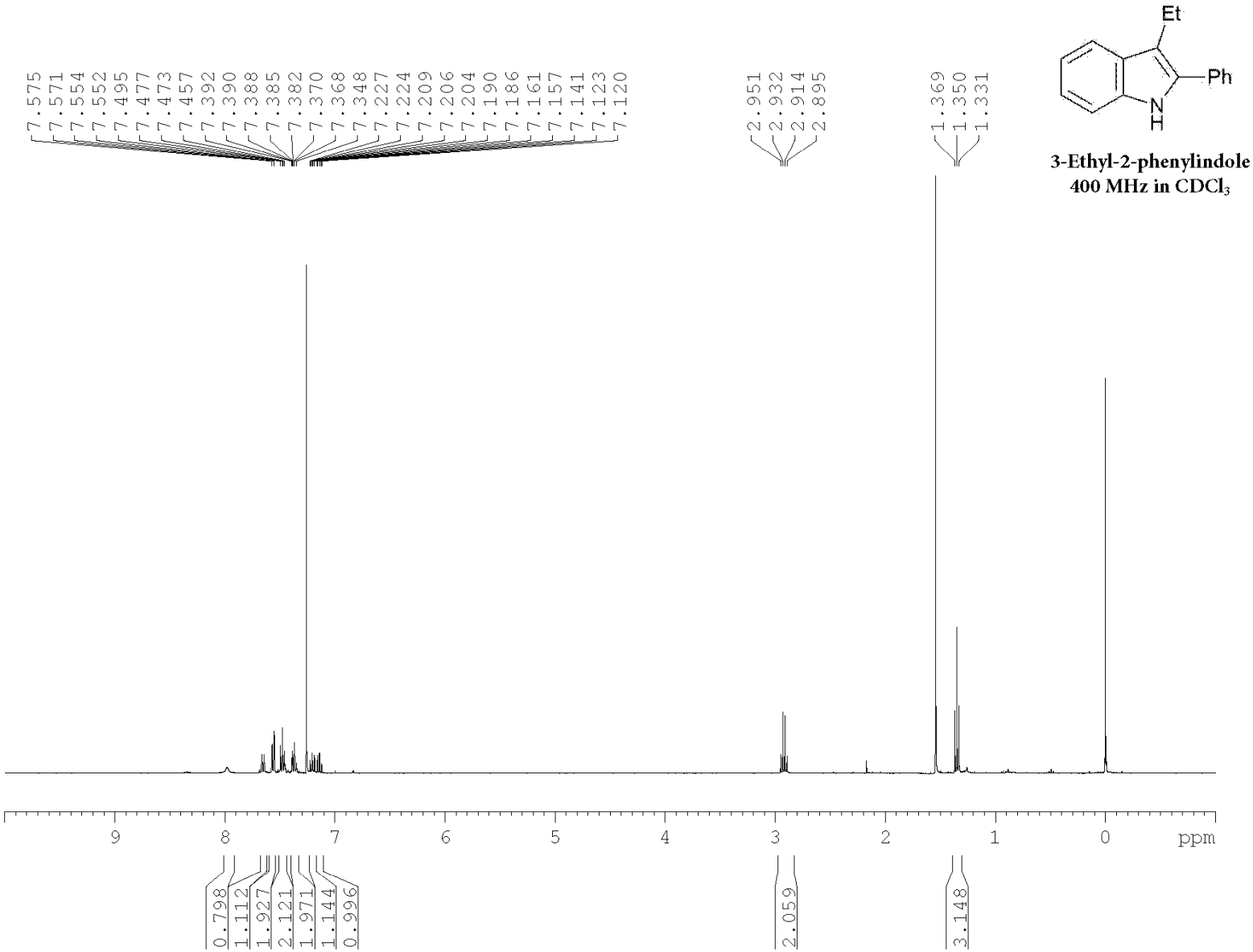
300 MHz in $CDCl_3$

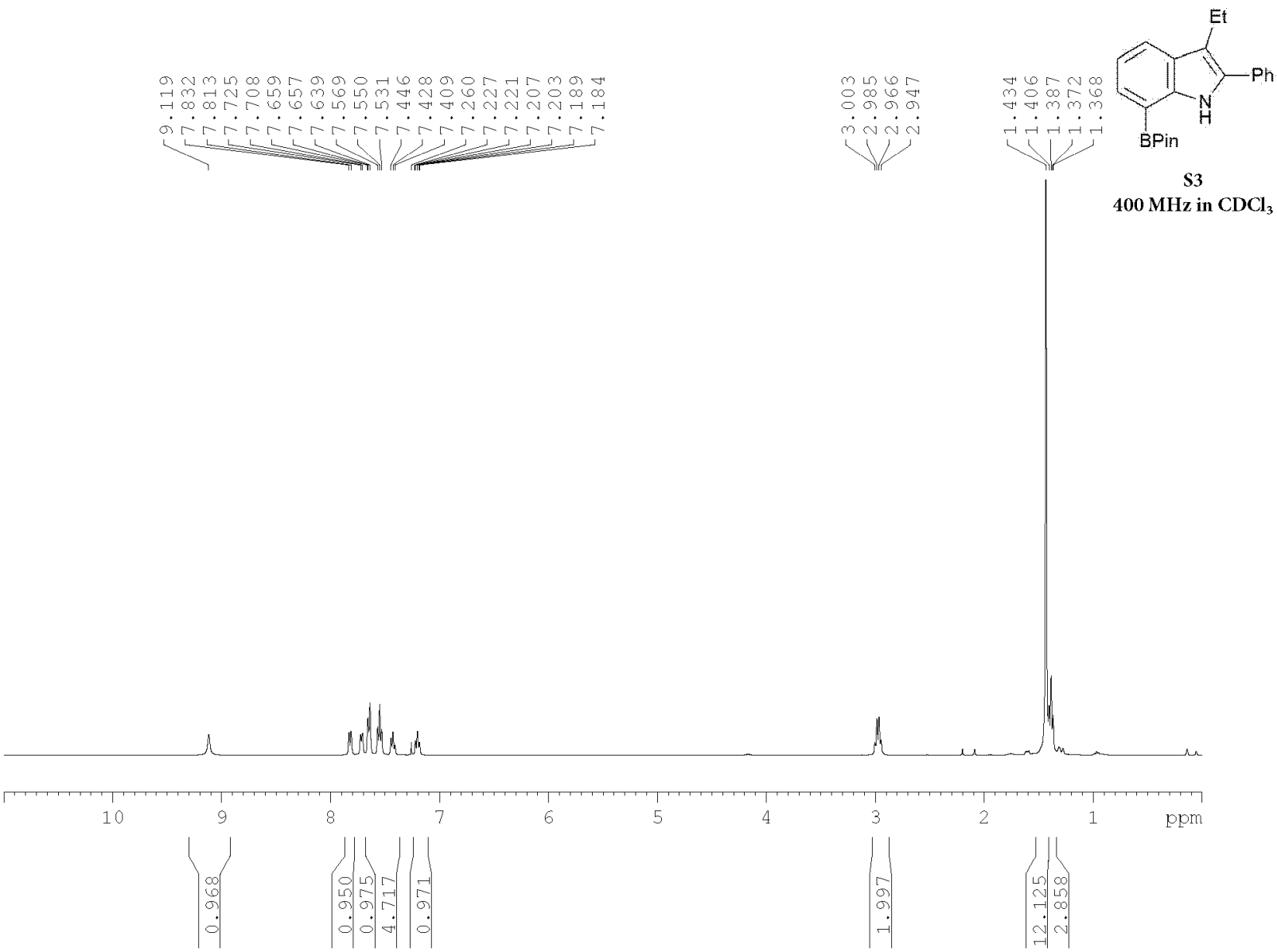

8.341
8.337
8.322
8.317
7.985
7.982
7.965
7.963
7.786
7.783
7.766
7.763
7.610
7.590
7.576
7.557
7.535
7.518
7.447
7.427
7.407
3.074
O
Me
N
Ph
O
9
400 MHz in
CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
1.824
0.935
0.916
3.172
1.103
3.000



9

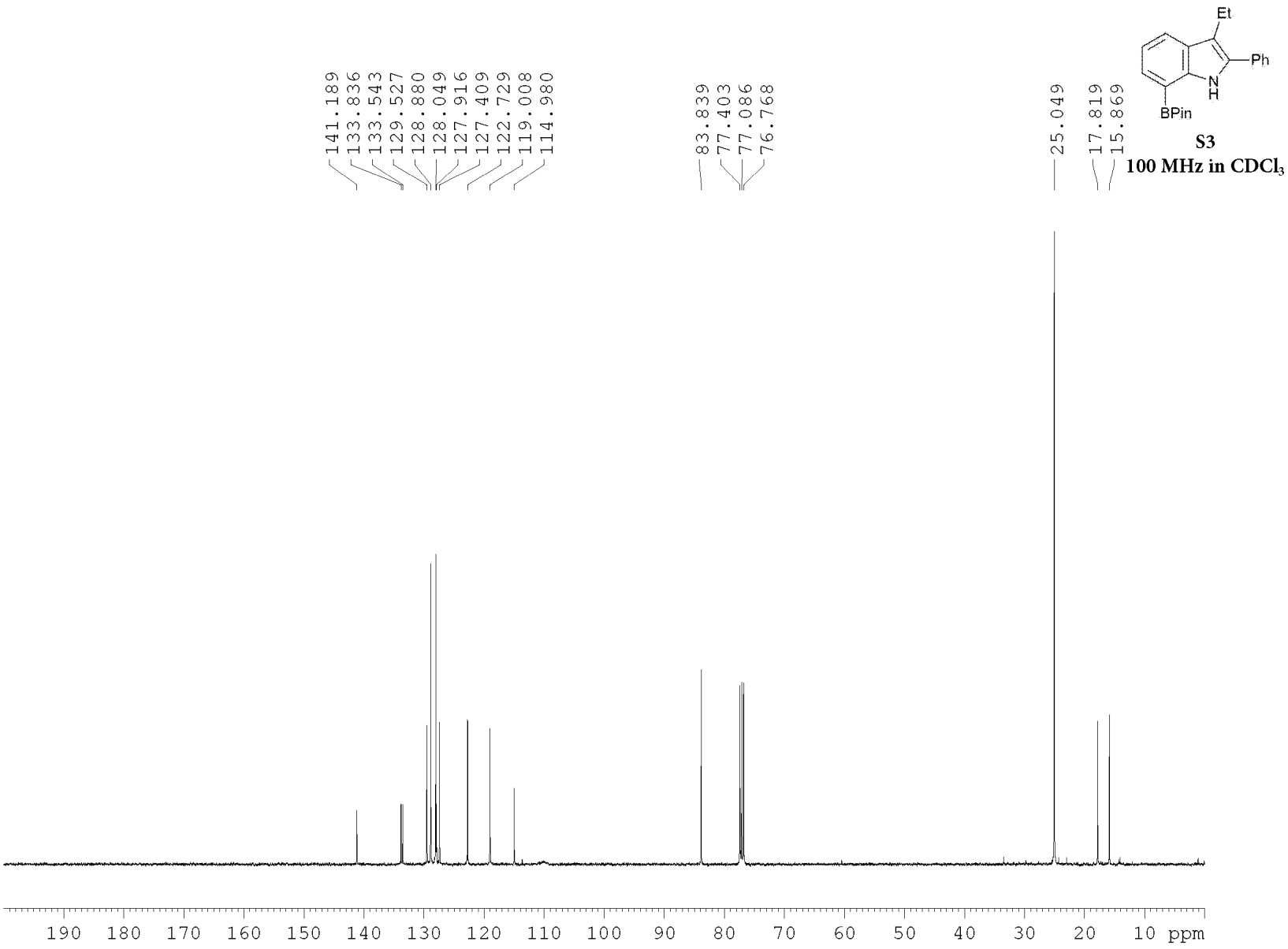
100 MHz in $CDCl_3$


7.575
7.571
7.554
7.552
7.495
7.477
7.473
7.457
7.392
7.390
7.388
7.385
7.382
7.370
7.368
7.348
7.227
7.224
7.209
7.206
7.204
7.190
7.186
7.161
7.157
7.141
7.123
7.120
2.951
2.932
2.914
2.895
1.369
1.350
1.331
Et
Ph
N
H
3-Ethyl-2-phenylindole
400 MHz in CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
0.798
1.112
1.927
2.121
1.971
1.144
0.996
2.059
3.148



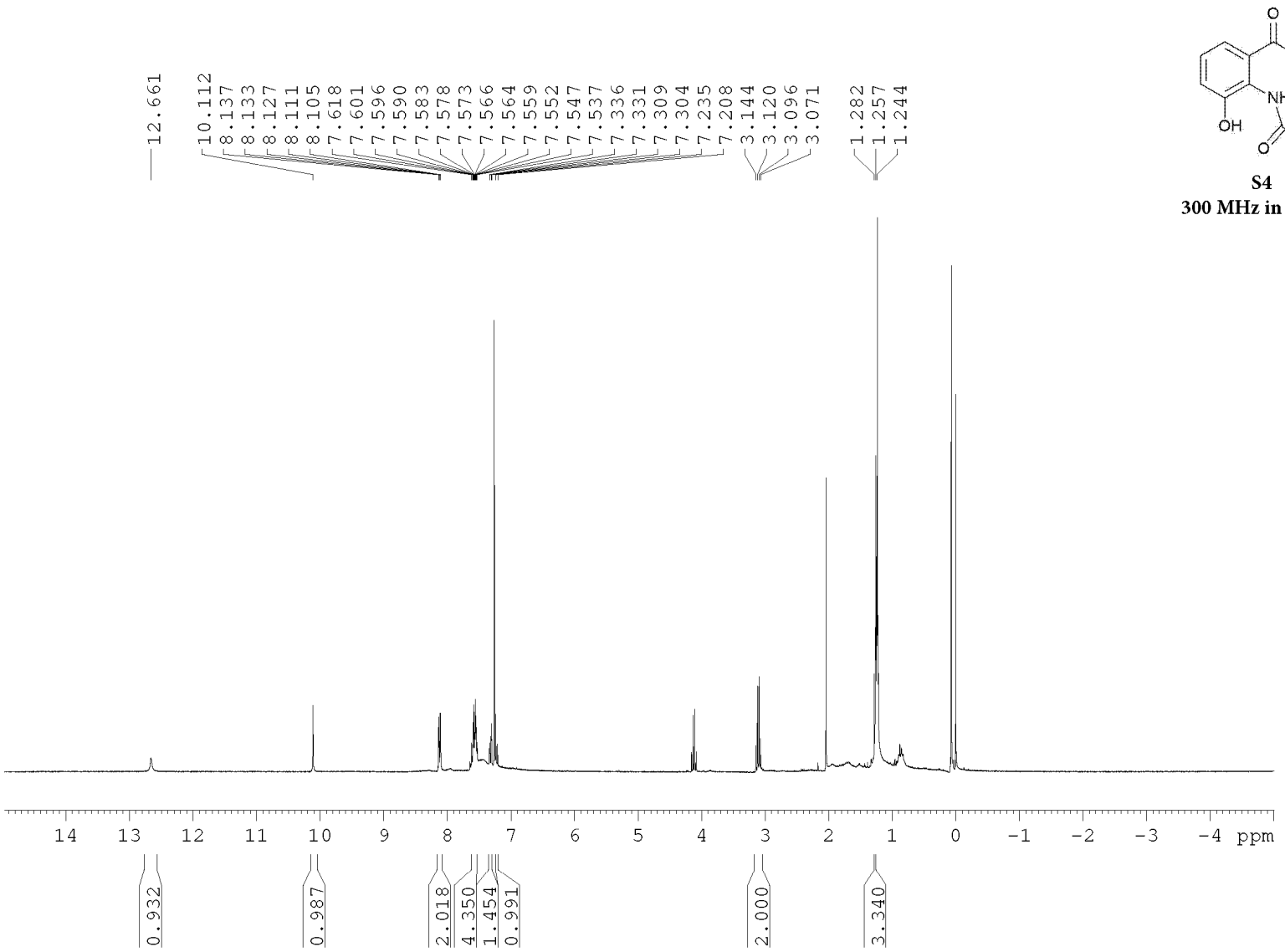
S3

400 MHz in $CDCl_3$



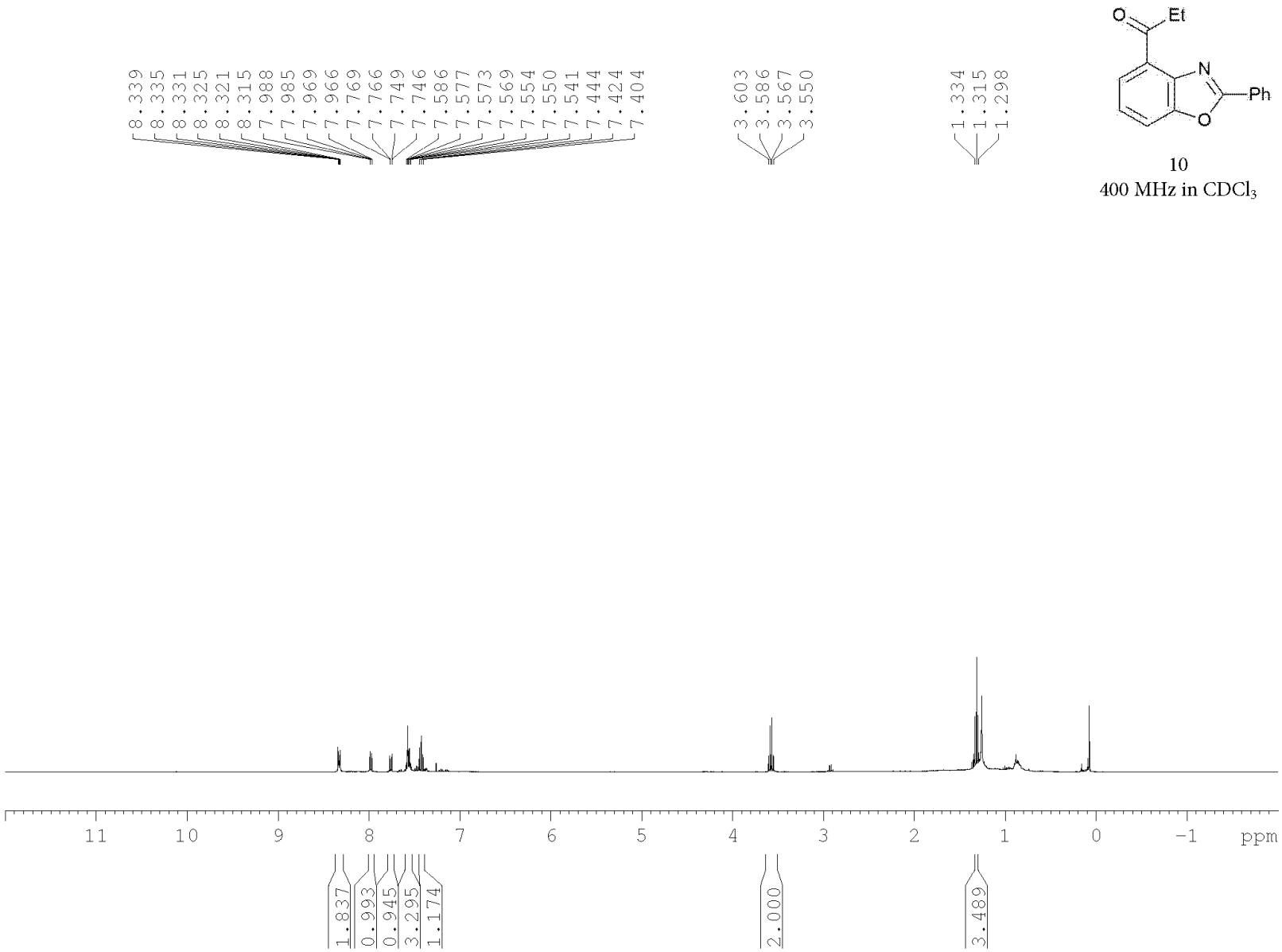
S3

100 MHz in $CDCl_3$

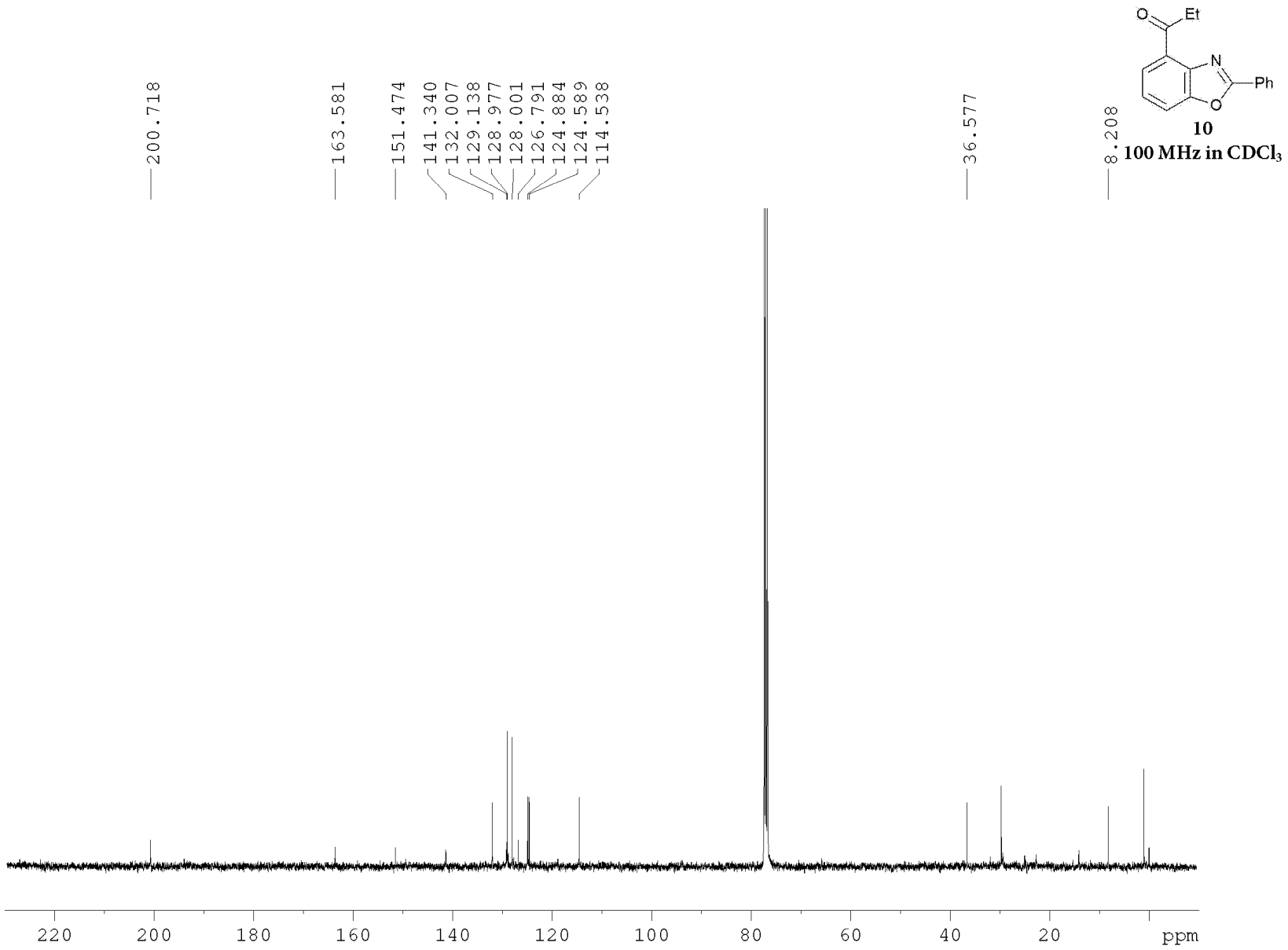


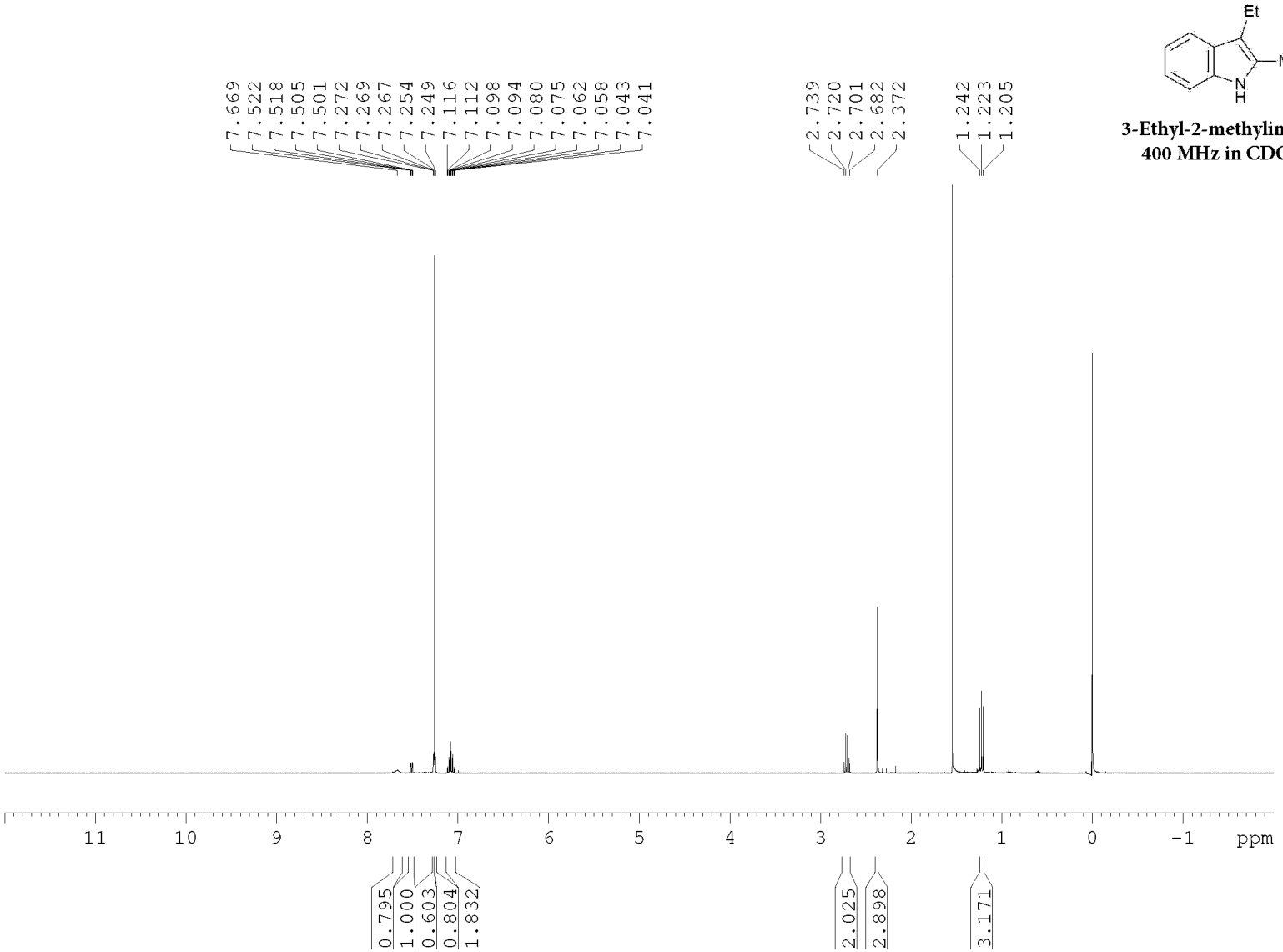
S4

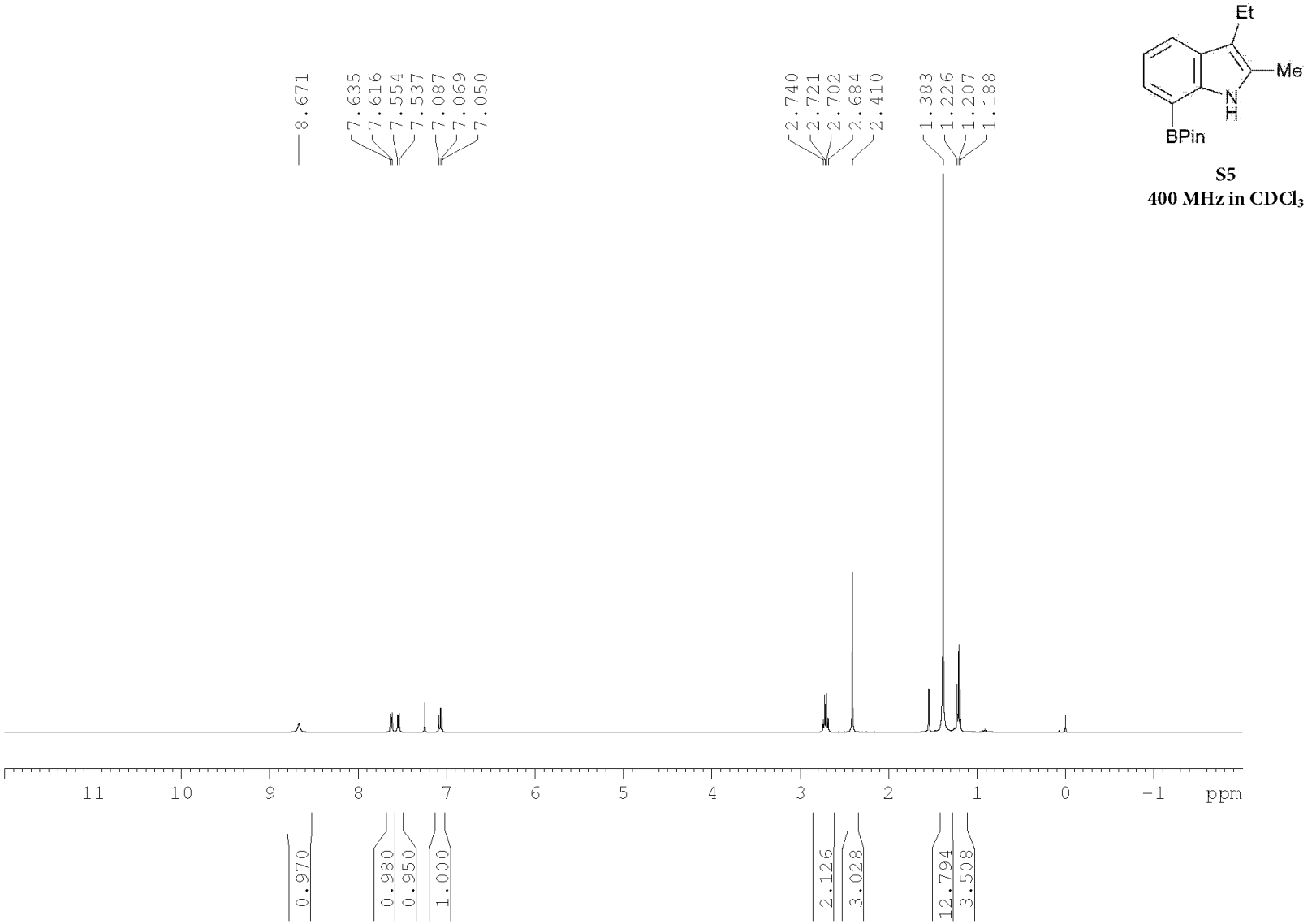
300 MHz in $CDCl_3$



10
400 MHz in $CDCl_3$

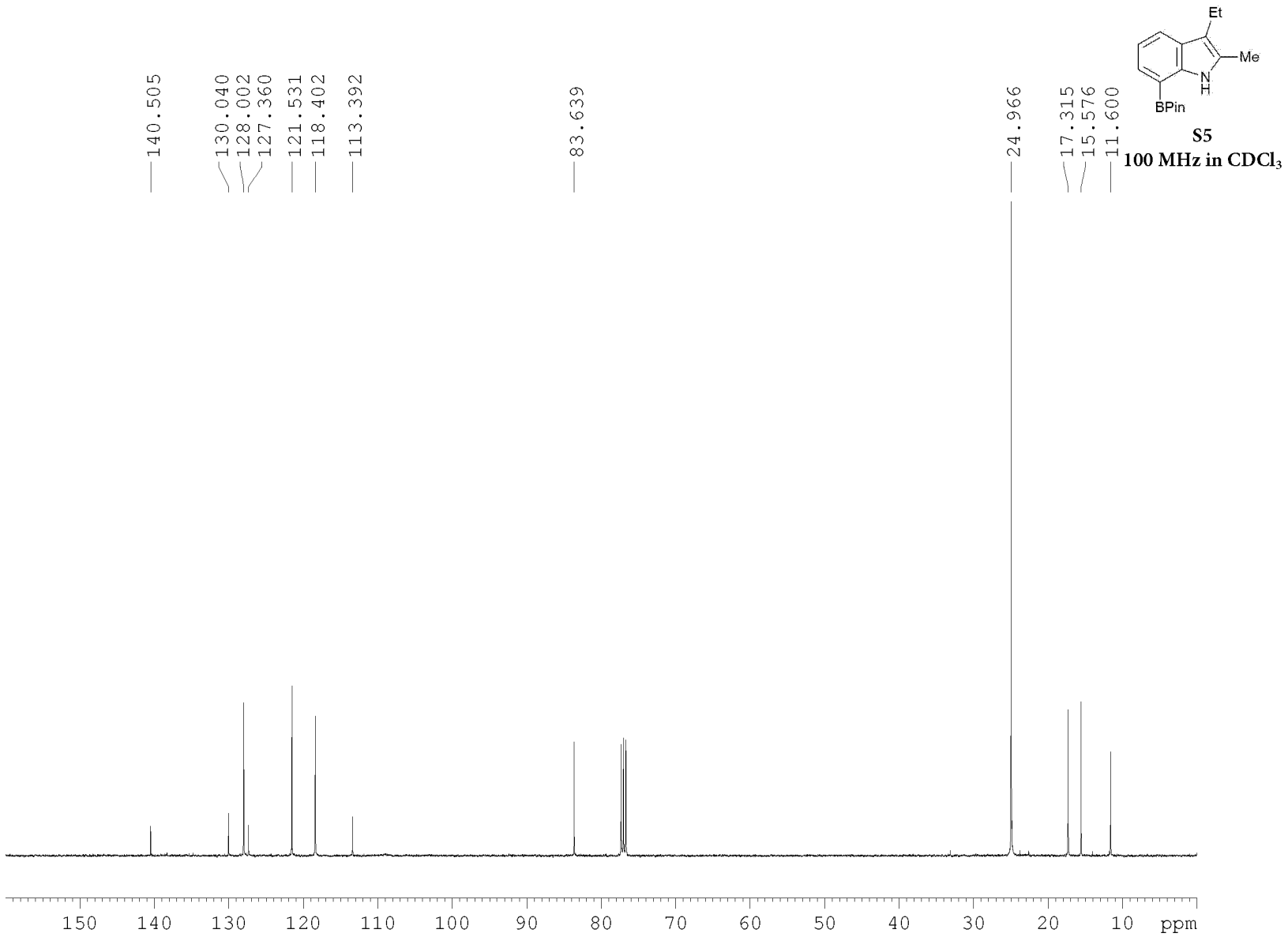

200.718
163.581
151.474
141.340
132.007
129.138
128.977
128.001
126.791
124.884
124.589
114.538
36.577
8.208
O
Et
N
Ph
O
10
100 MHz in CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm


Et
Me
N
H
3-Ethyl-2-methylindole
400 MHz in CDCl3
7.669
7.522
7.518
7.505
7.501
7.272
7.269
7.267
7.254
7.249
7.116
7.112
7.098
7.094
7.080
7.075
7.062
7.058
7.043
7.041
2.739
2.720
2.701
2.682
2.372
1.242
1.223
1.205
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.795
1.000
0.603
0.804
1.832
2.025
2.898
3.171



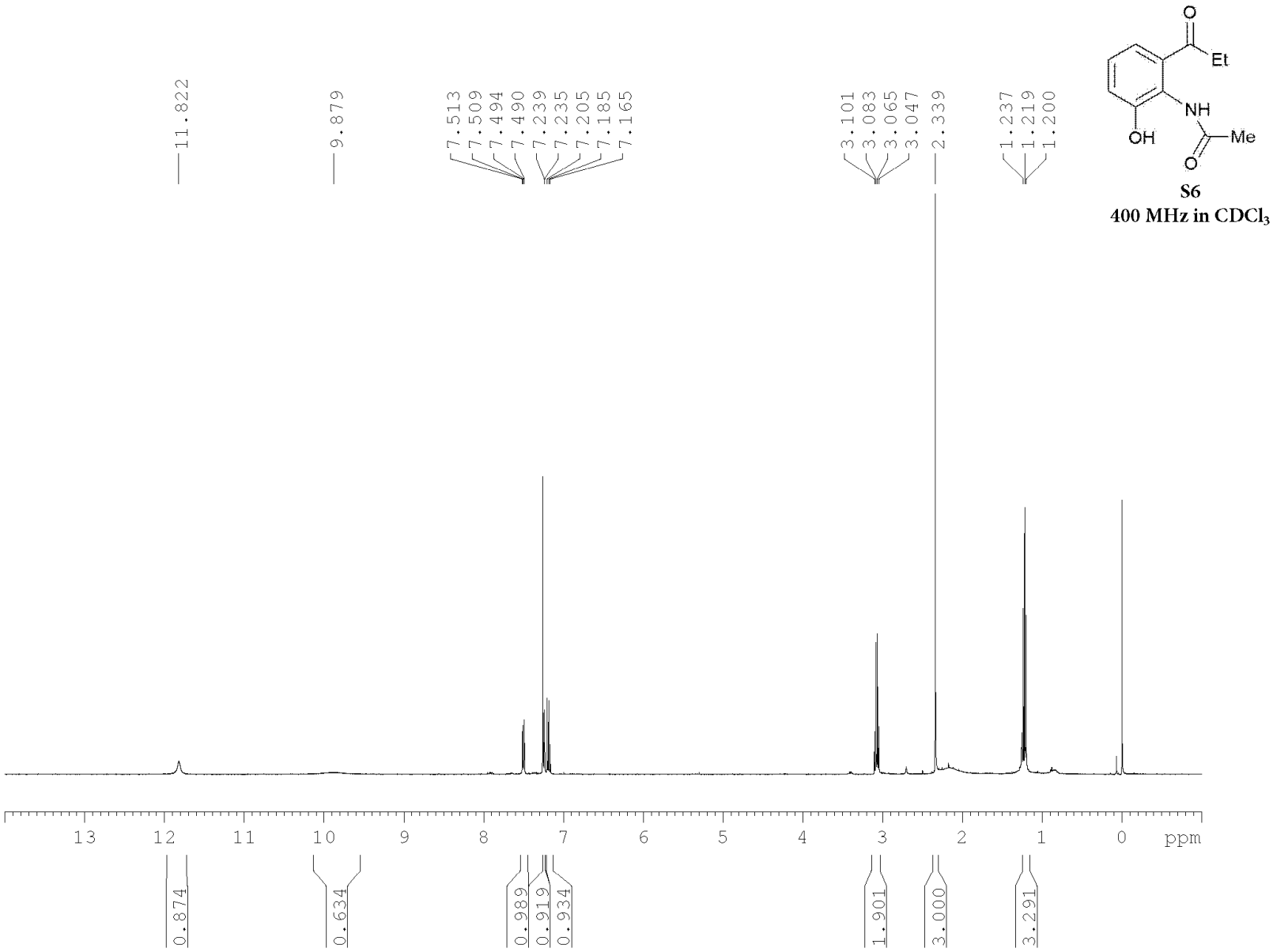
S5

400 MHz in $CDCl_3$



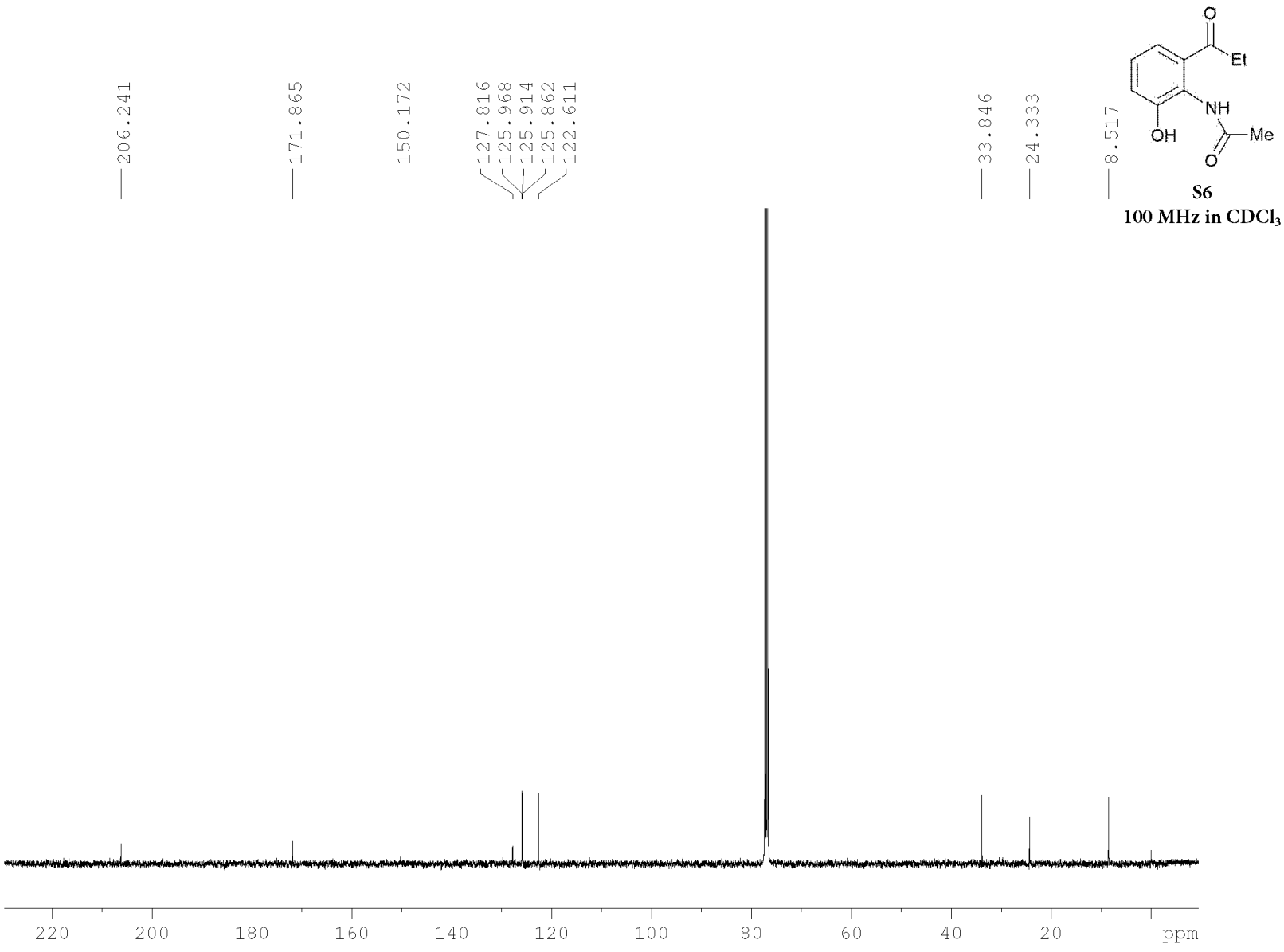
S5

100 MHz in $CDCl_3$



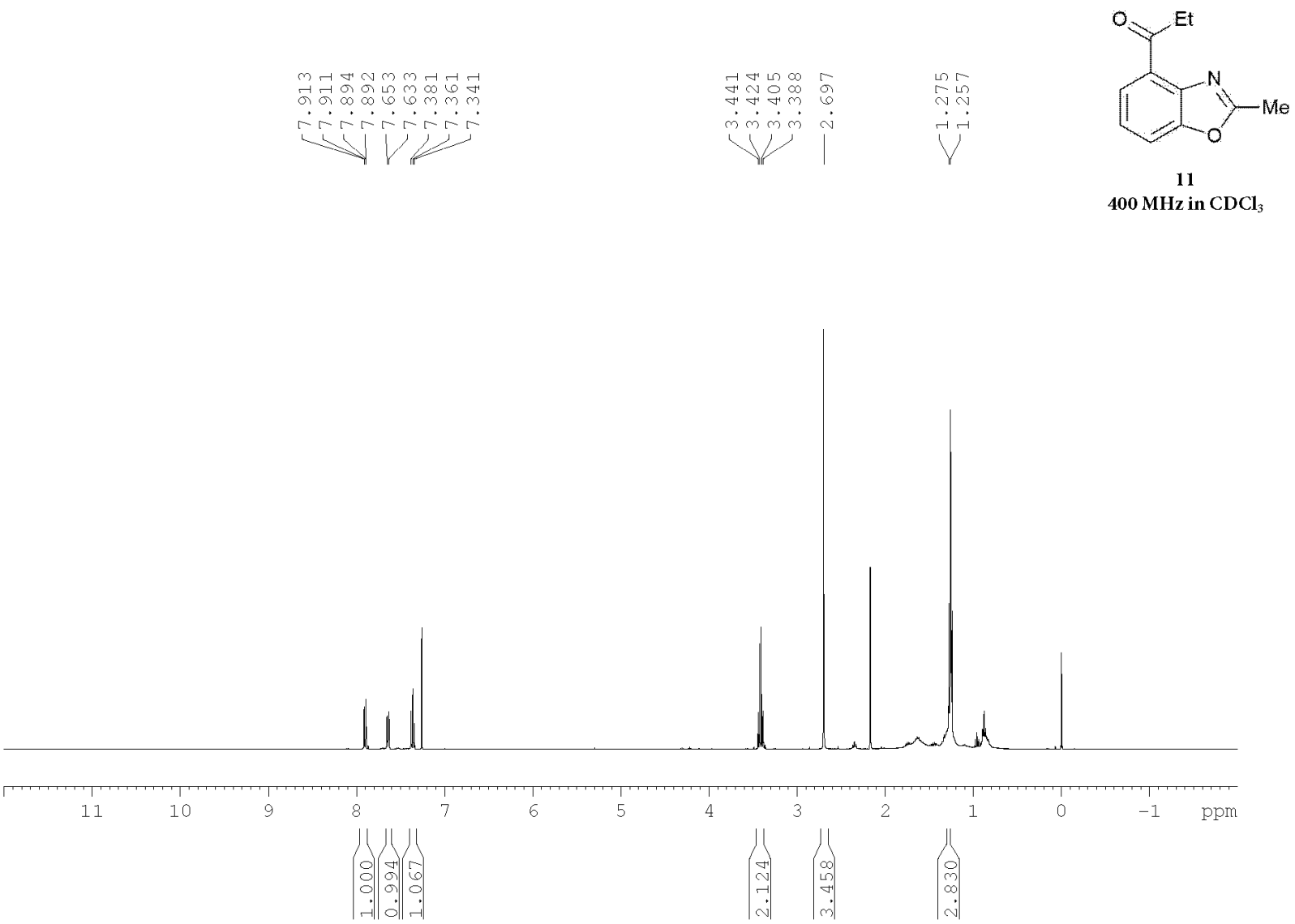
S6

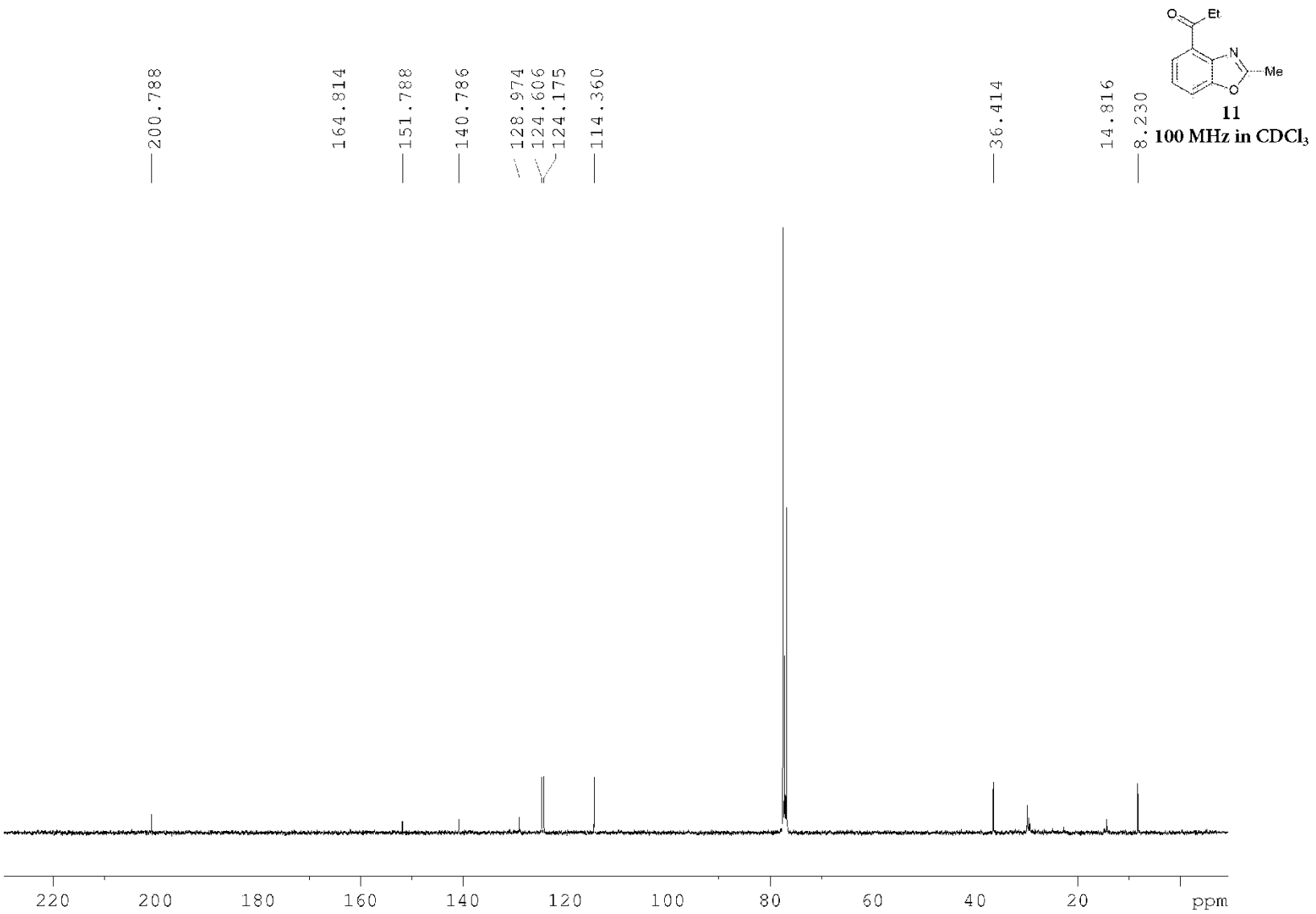
400 MHz in $CDCl_3$

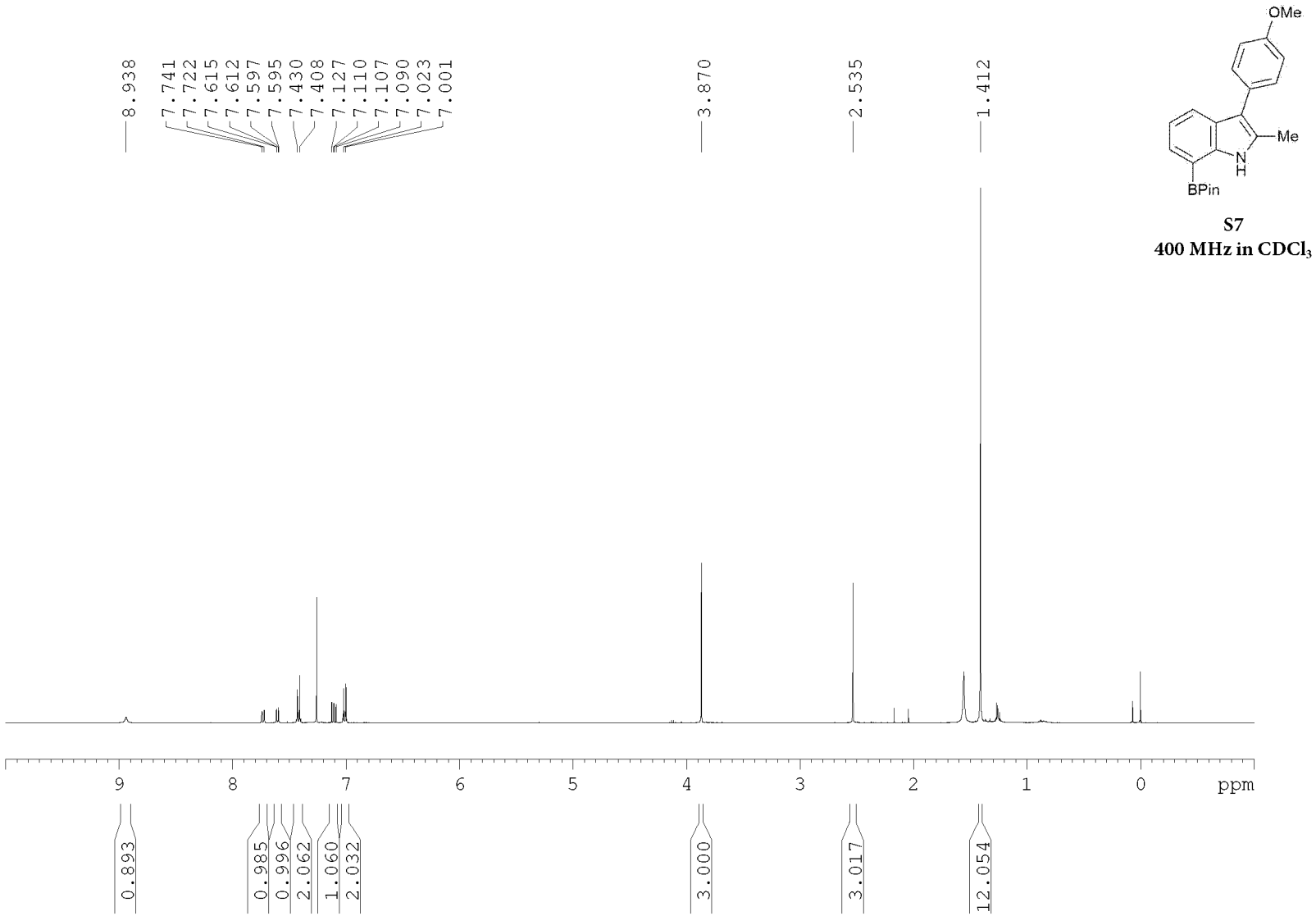


S6

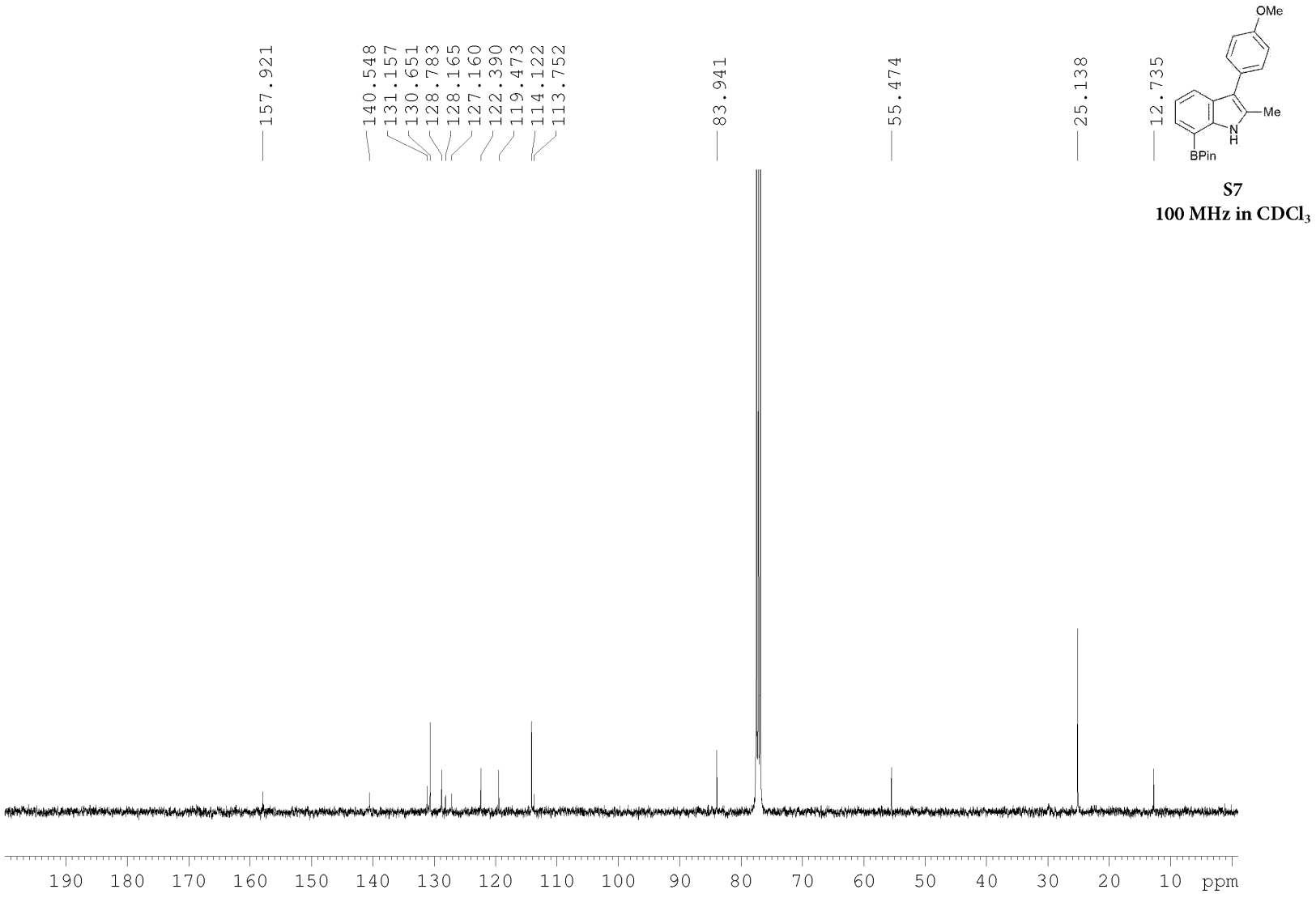
100 MHz in $CDCl_3$


7.913
7.911
7.894
7.892
7.653
7.633
7.381
7.361
7.341
3.441
3.424
3.405
3.388
2.697
1.275
1.257
O
Et
N
Me
O
11
400 MHz in CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.000
0.994
1.067
2.124
3.458
2.830

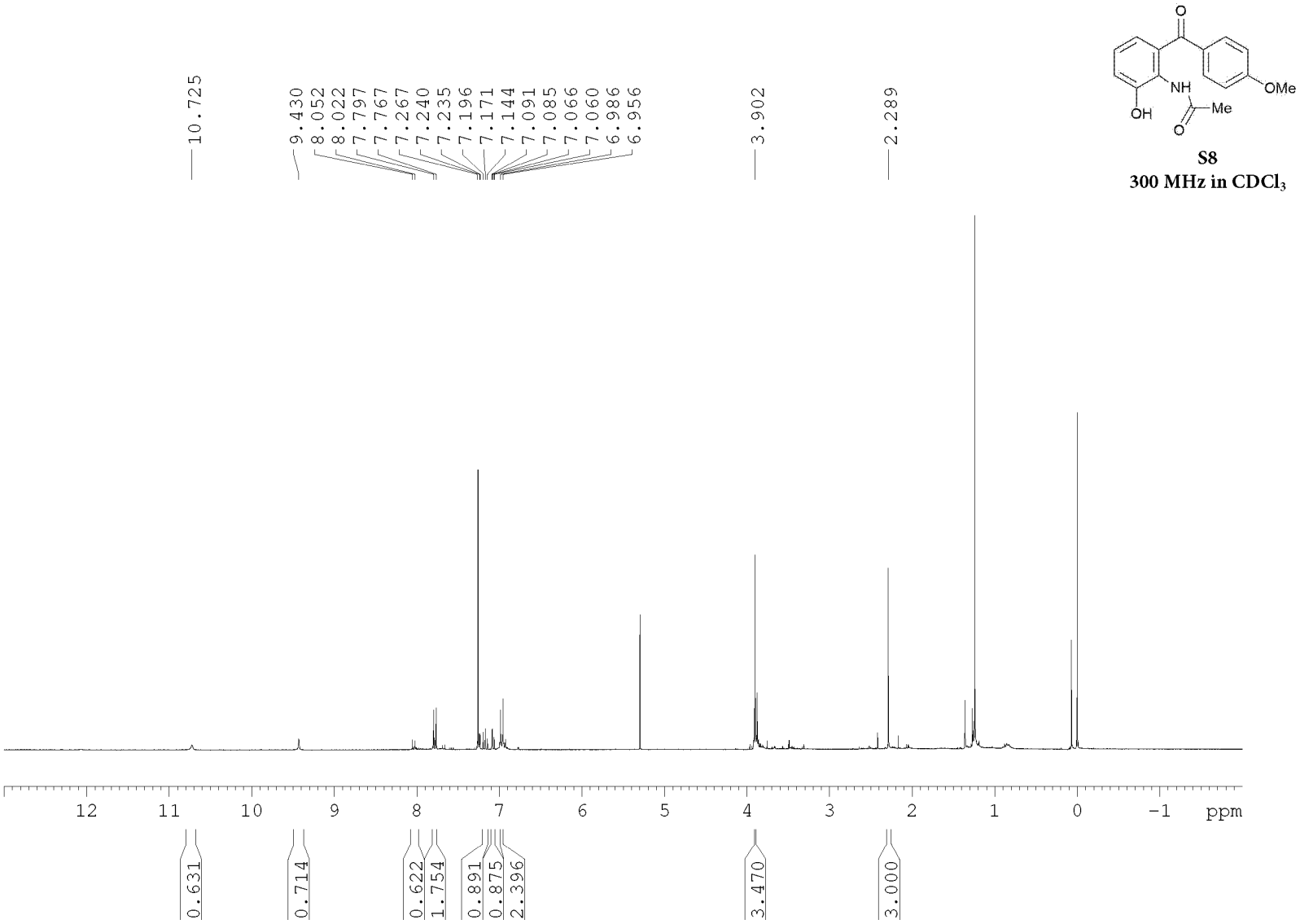

200.788
164.814
151.788
140.786
128.974
124.606
124.175
114.360
36.414
14.816
8.230
Et
N
Me
O
11
100 MHz in CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm



S7
400 MHz in $CDCl_3$

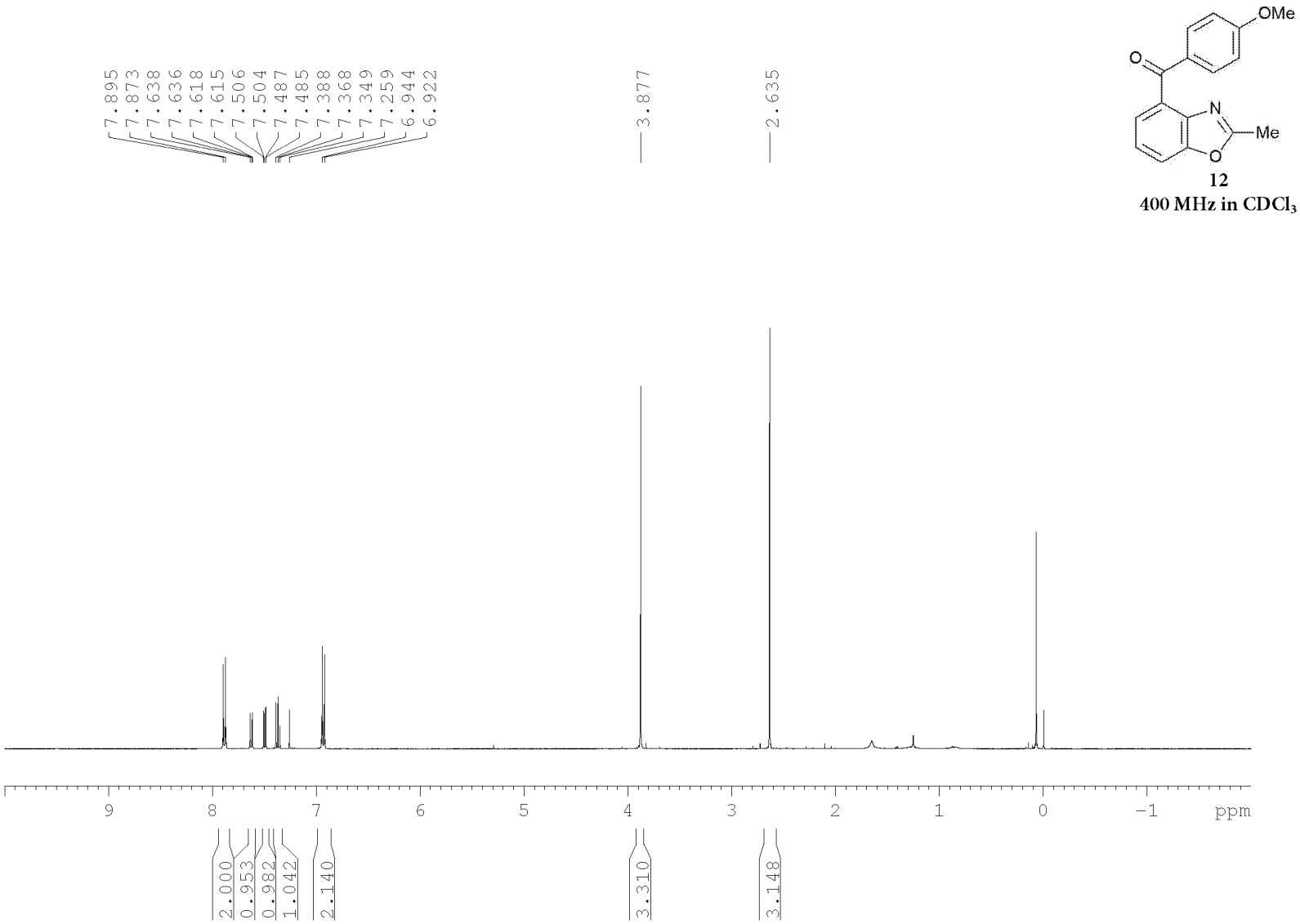


S7
100 MHz in $CDCl_3$



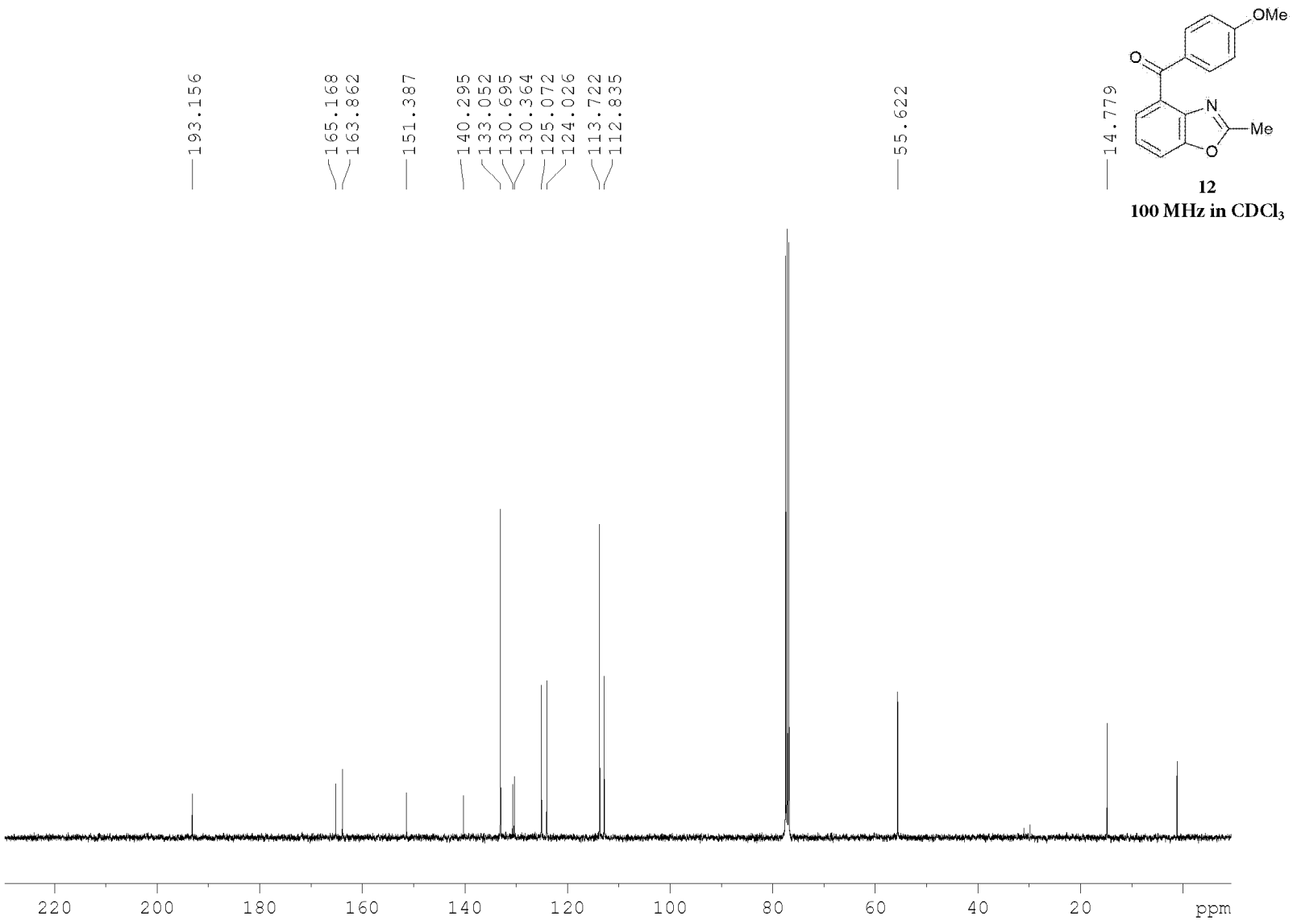
S8

300 MHz in $CDCl_3$



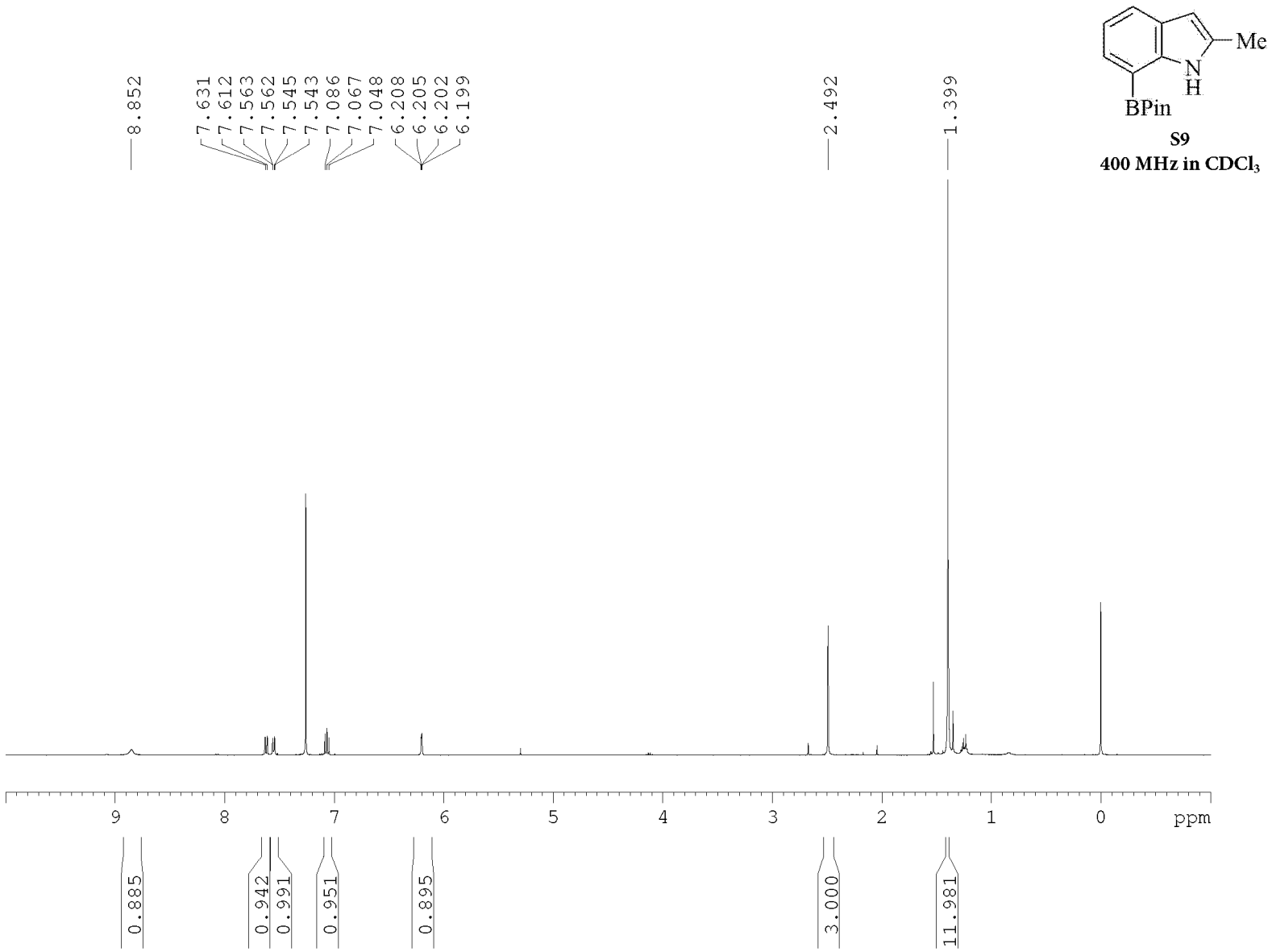
12

400 MHz in $CDCl_3$



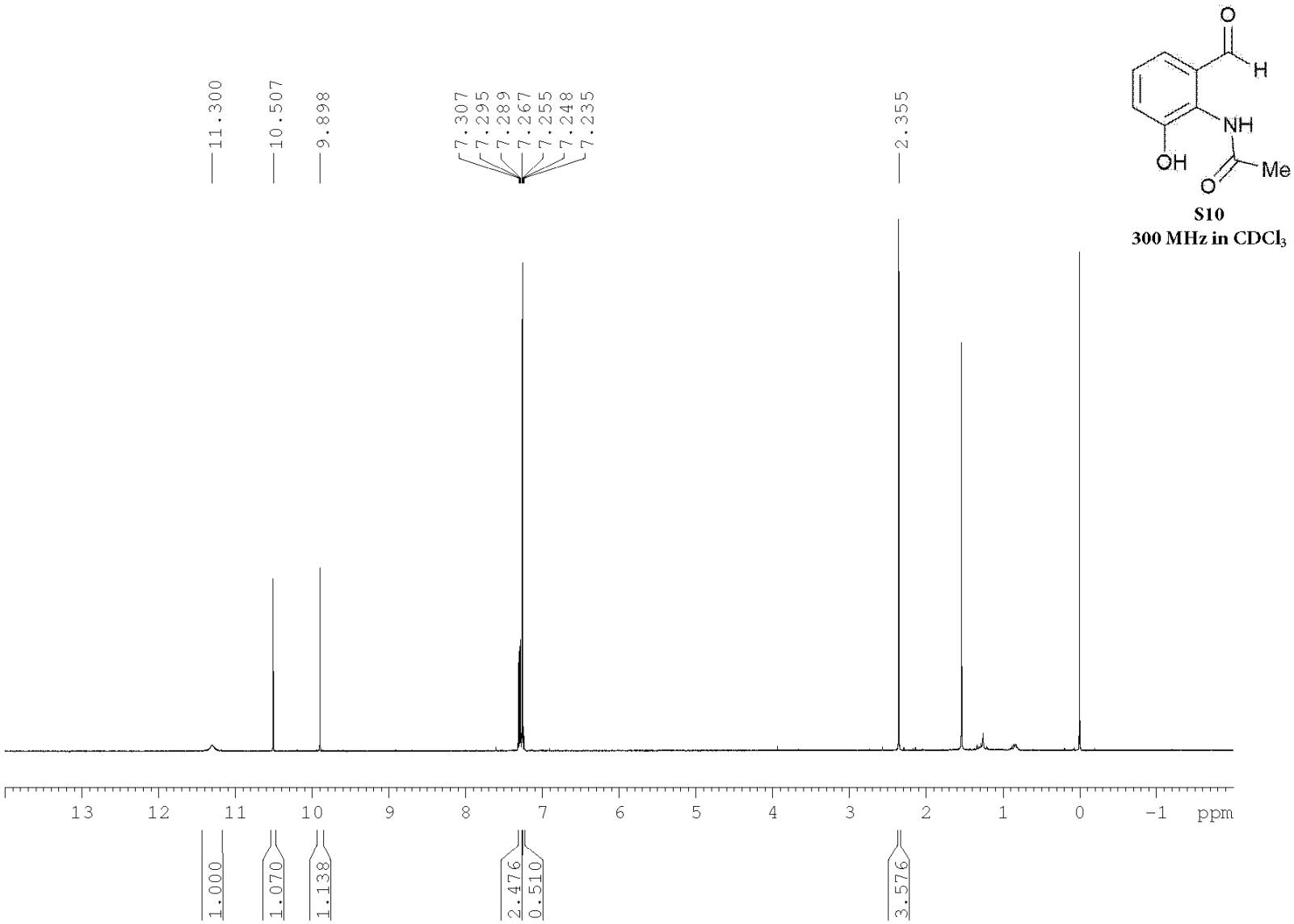
12

100 MHz in $CDCl_3$



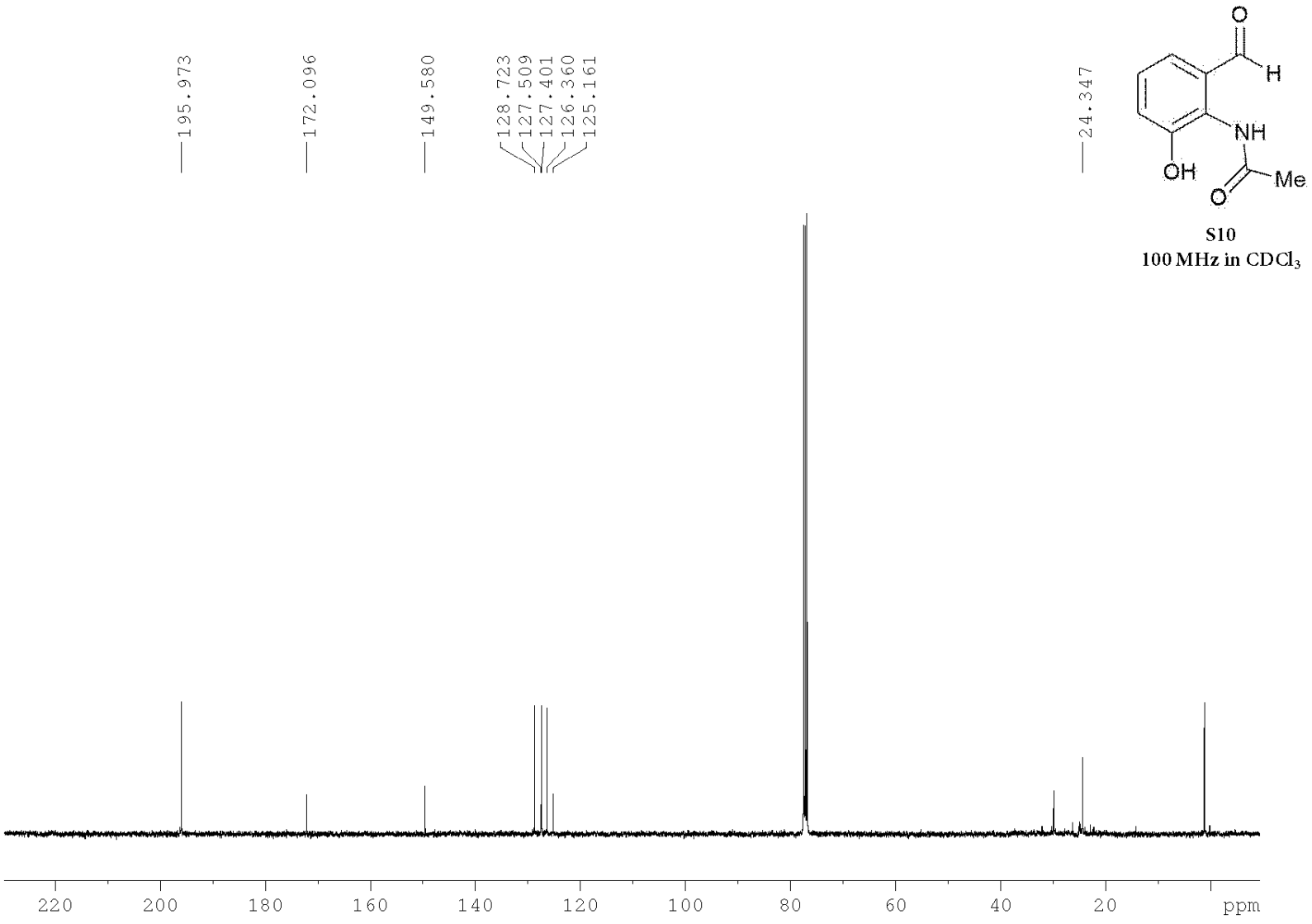
S9

400 MHz in $CDCl_3$

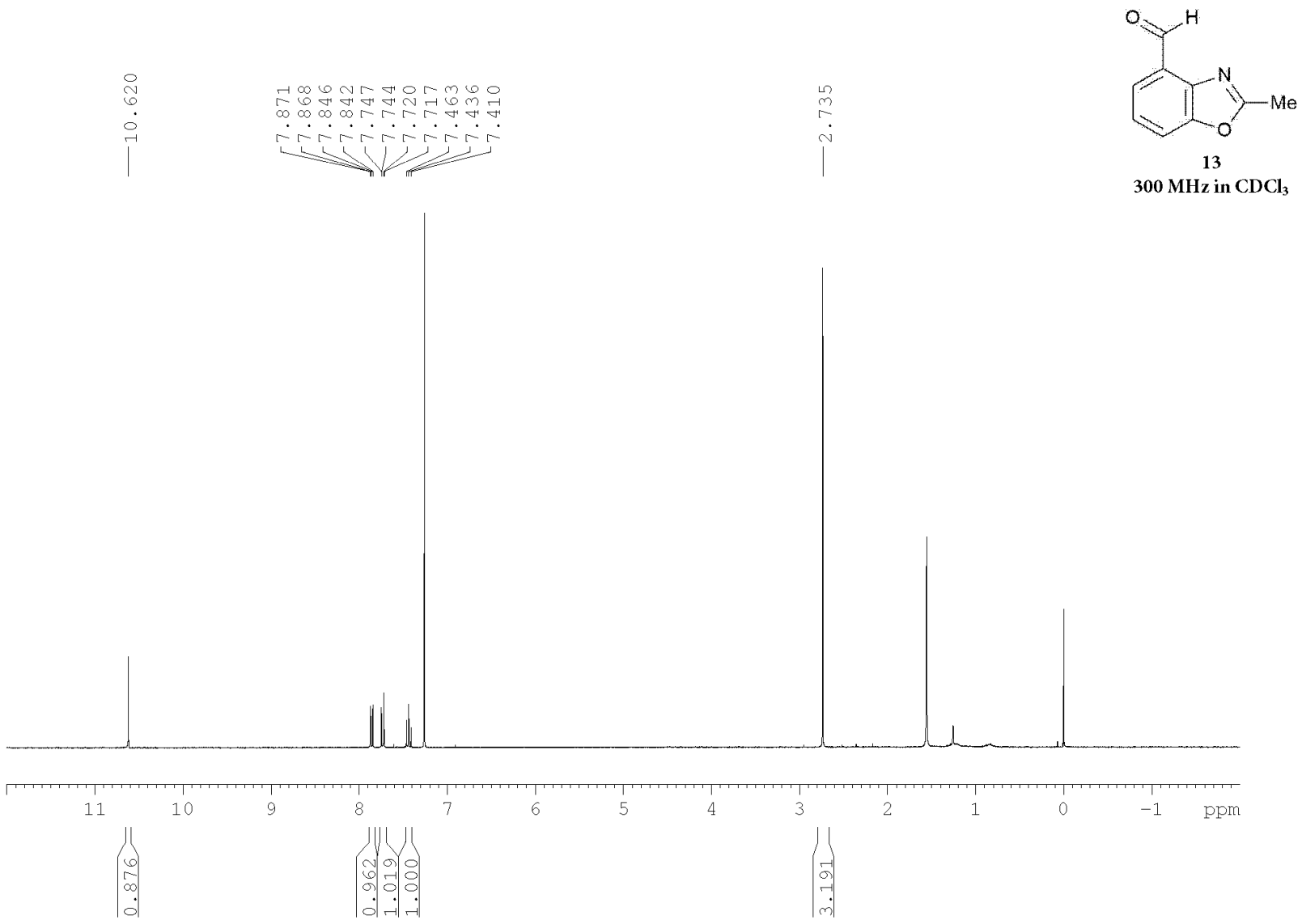


S10

300 MHz in $CDCl_3$

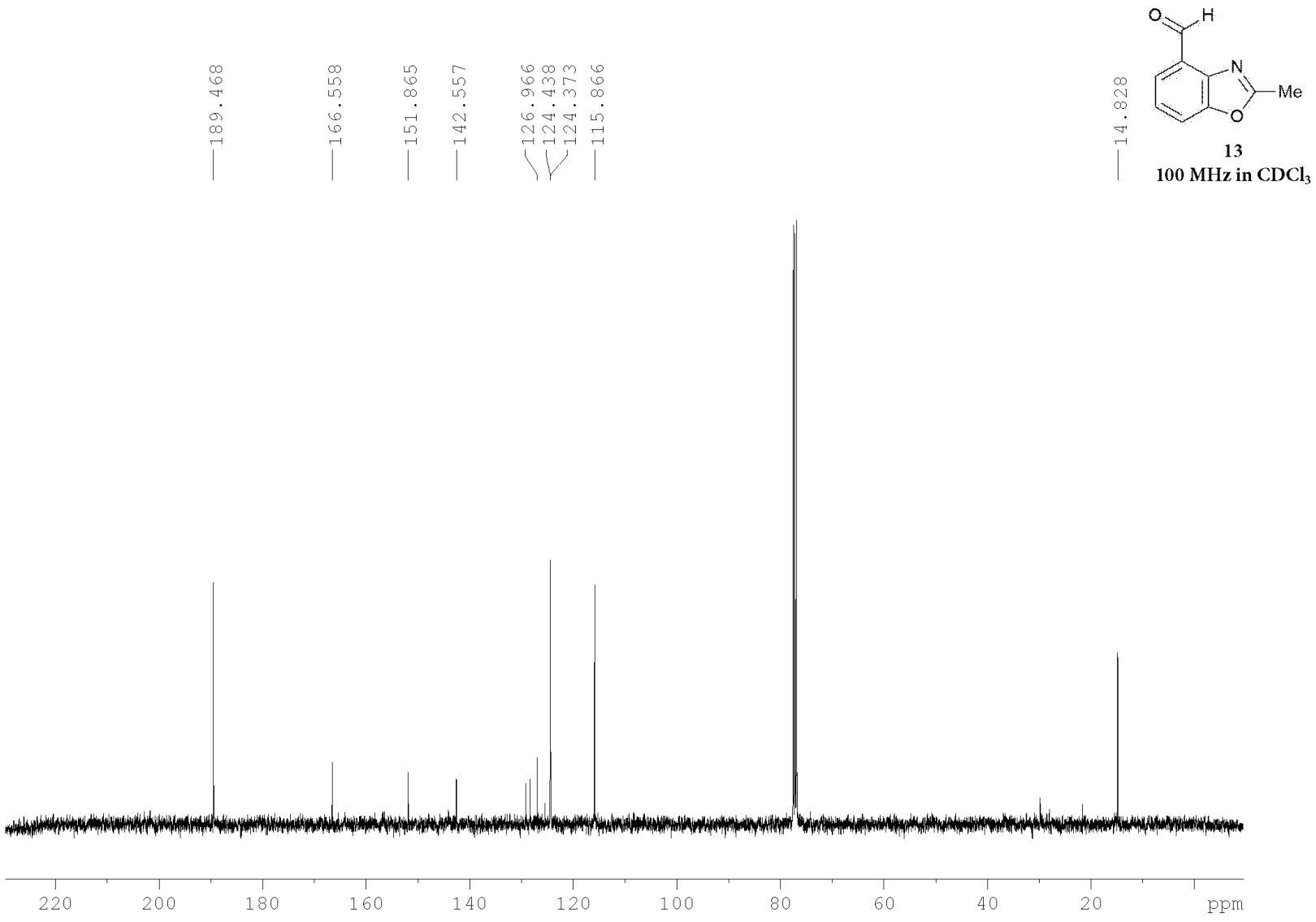


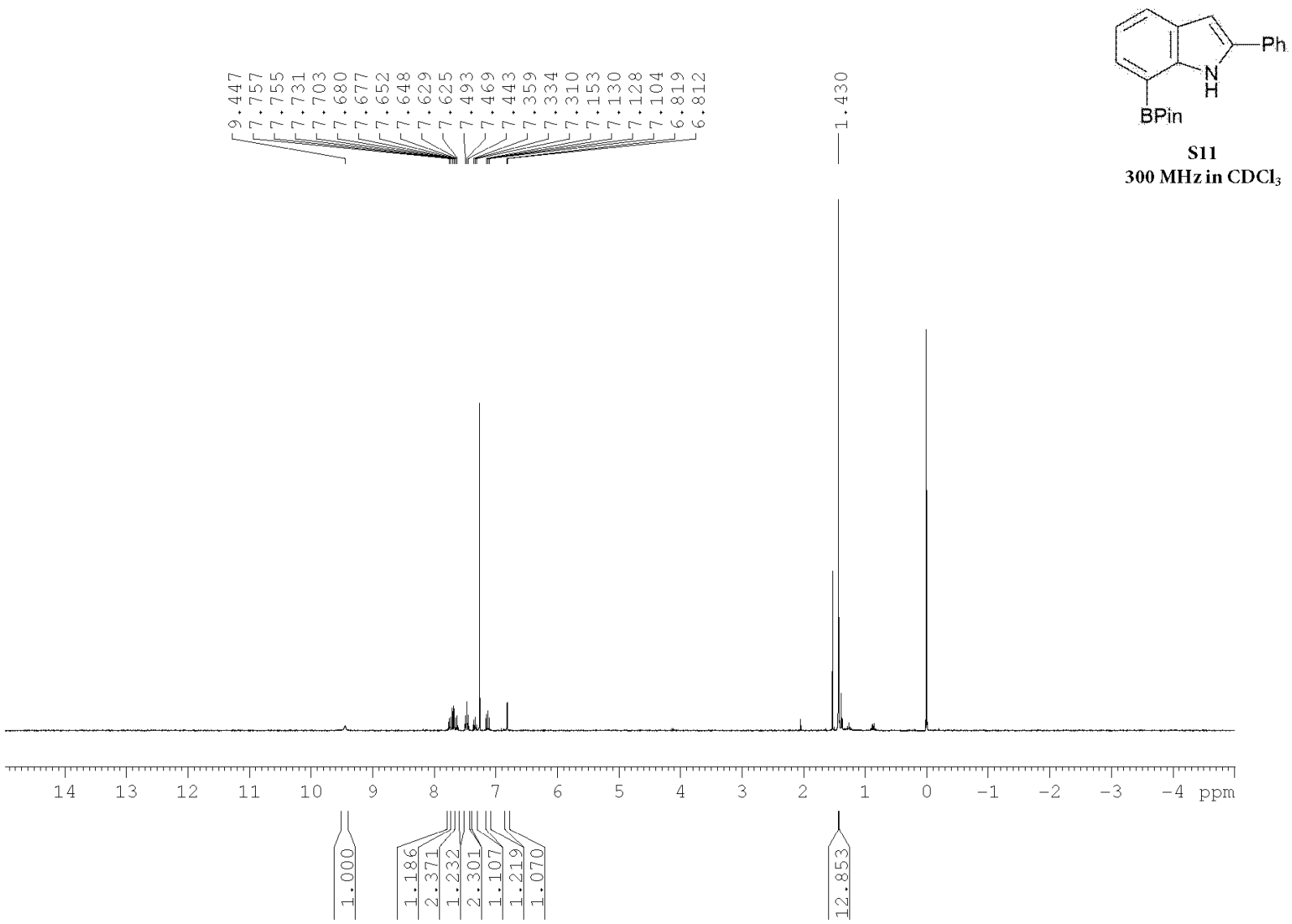
S10
100 MHz in $CDCl_3$



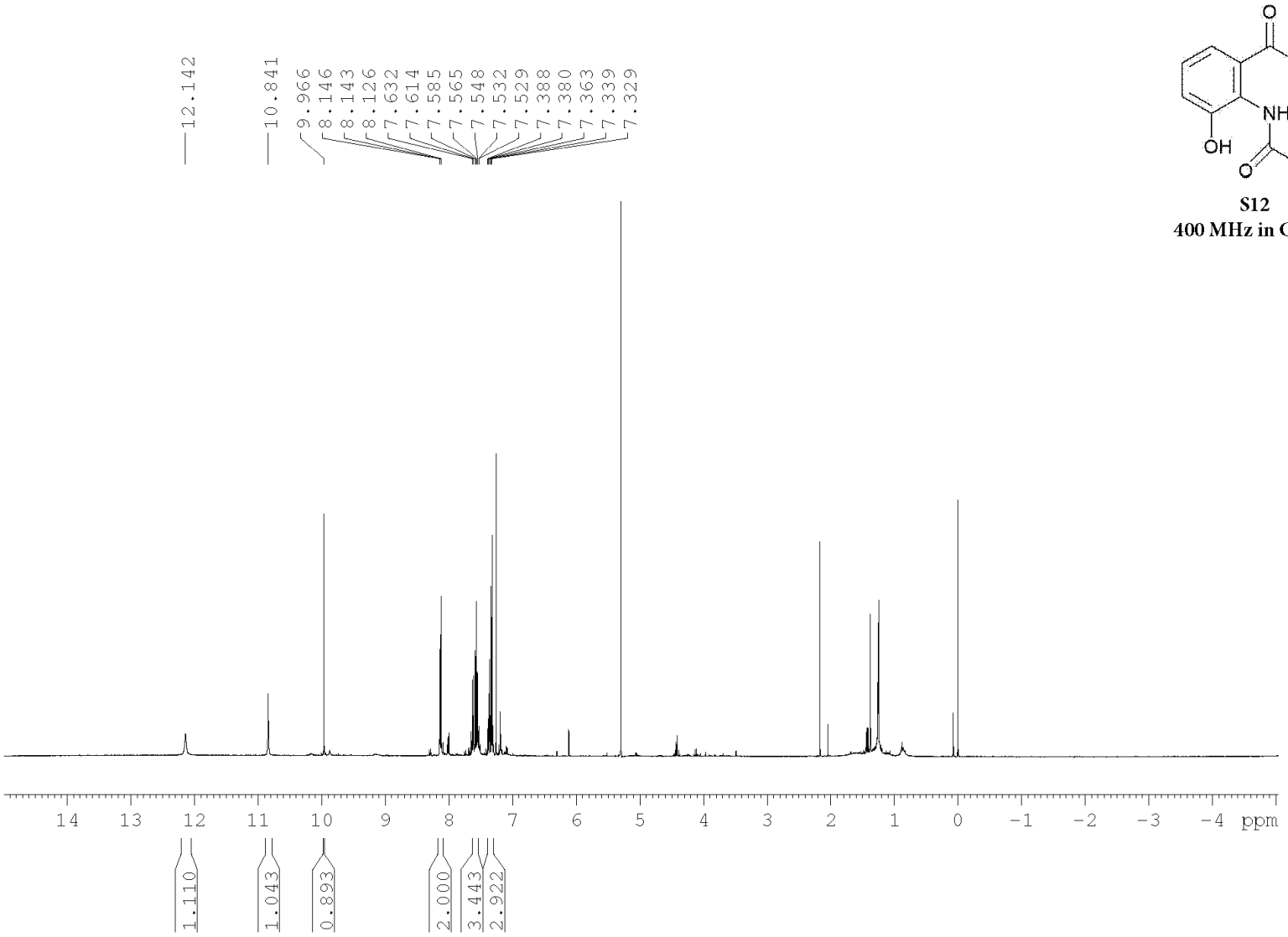
13

300 MHz in $CDCl_3$

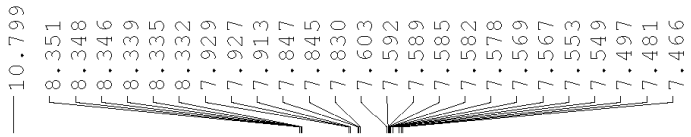

189.468
166.558
151.865
142.557
126.966
124.438
124.373
115.866
14.828
O
H
N
Me
O
13
100 MHz in CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm

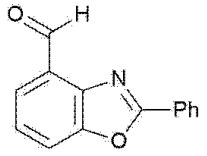


S11
300 MHz in $CDCl_3$

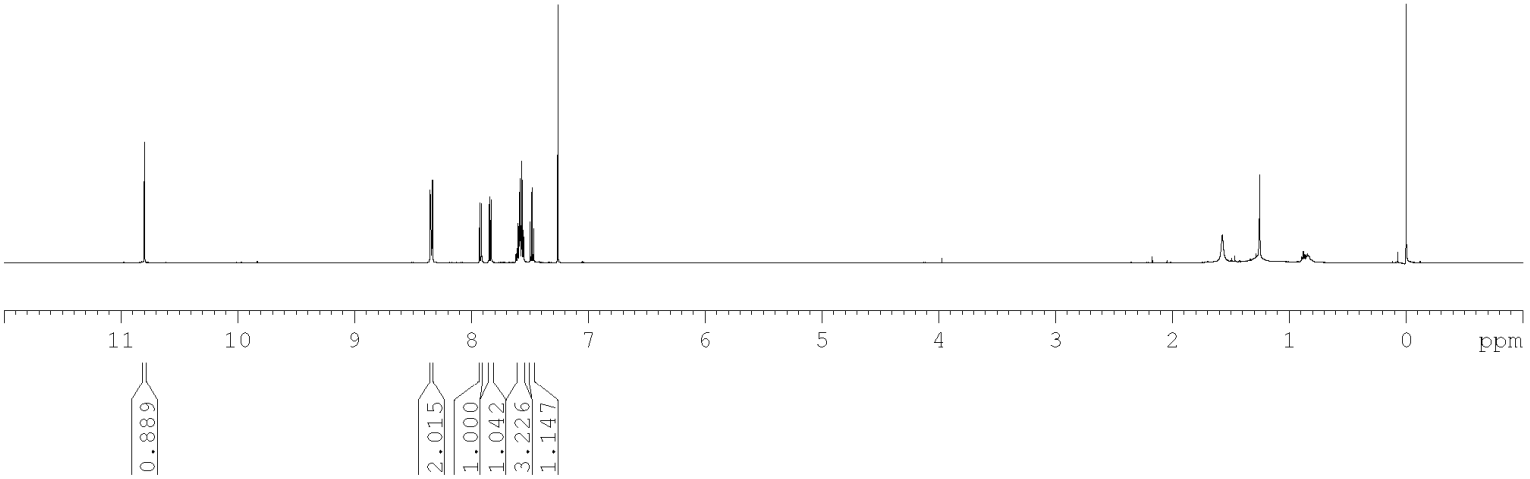


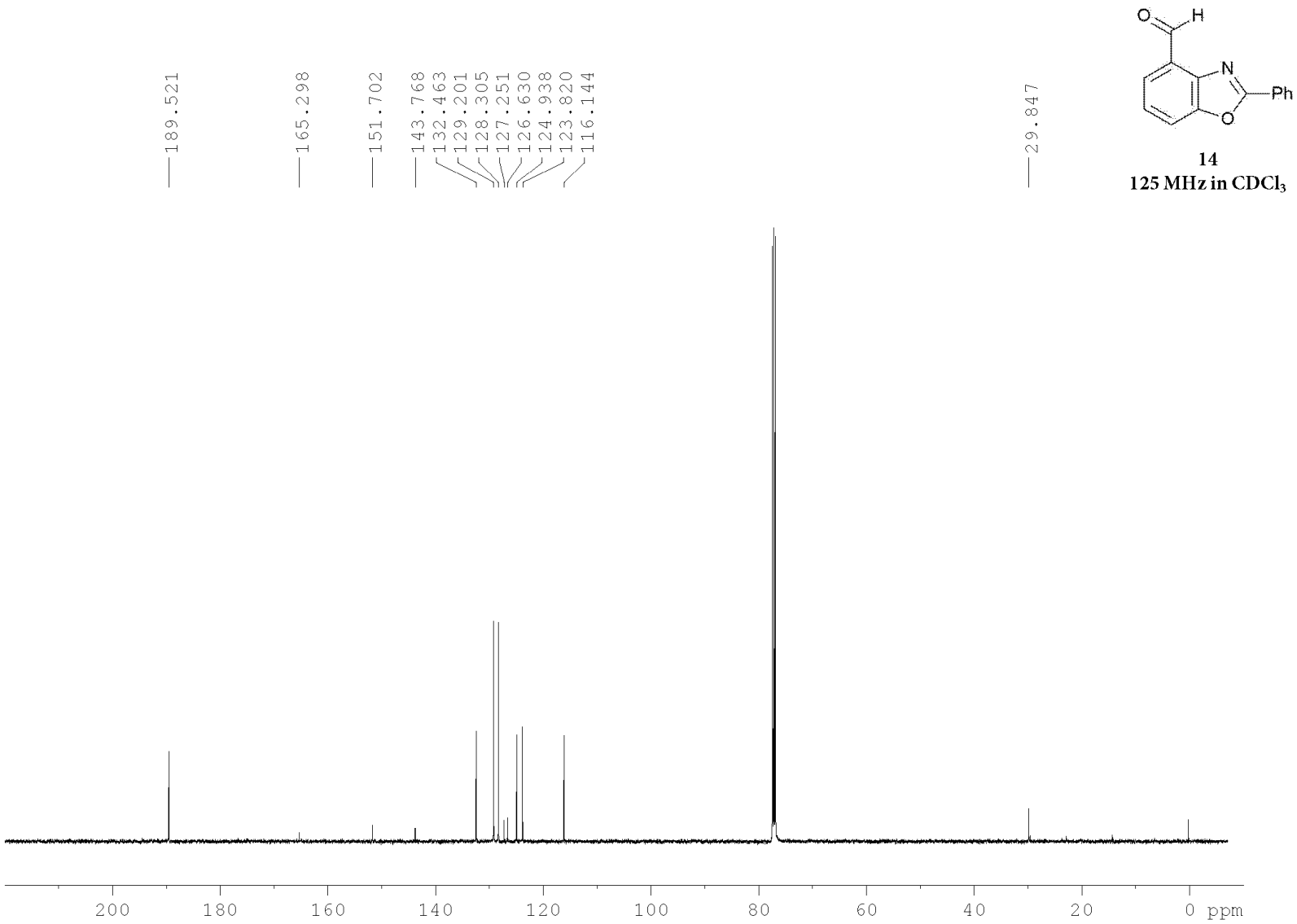
S12
400 MHz in $CDCl_3$



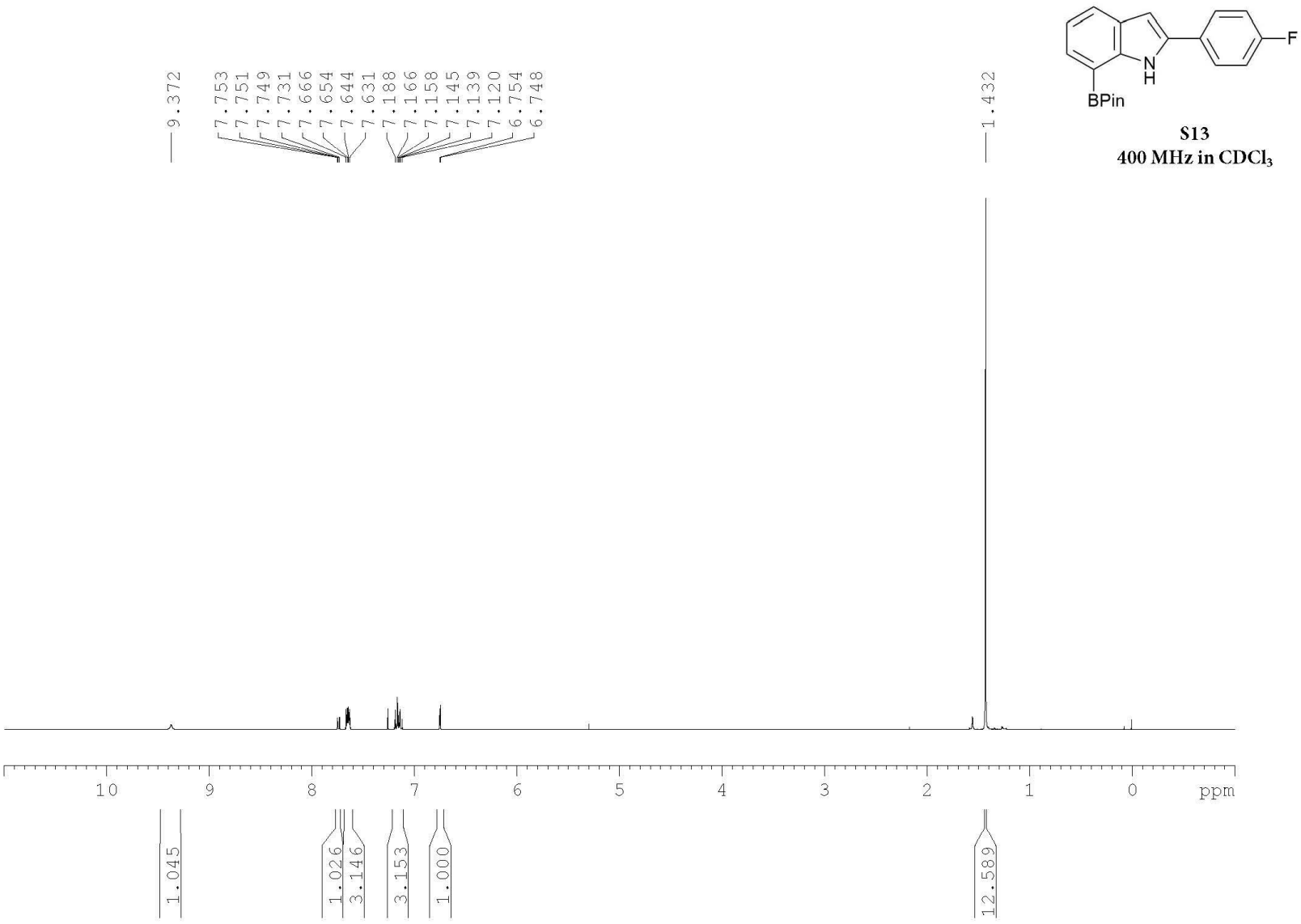


14
500 MHz in $CDCl_3$

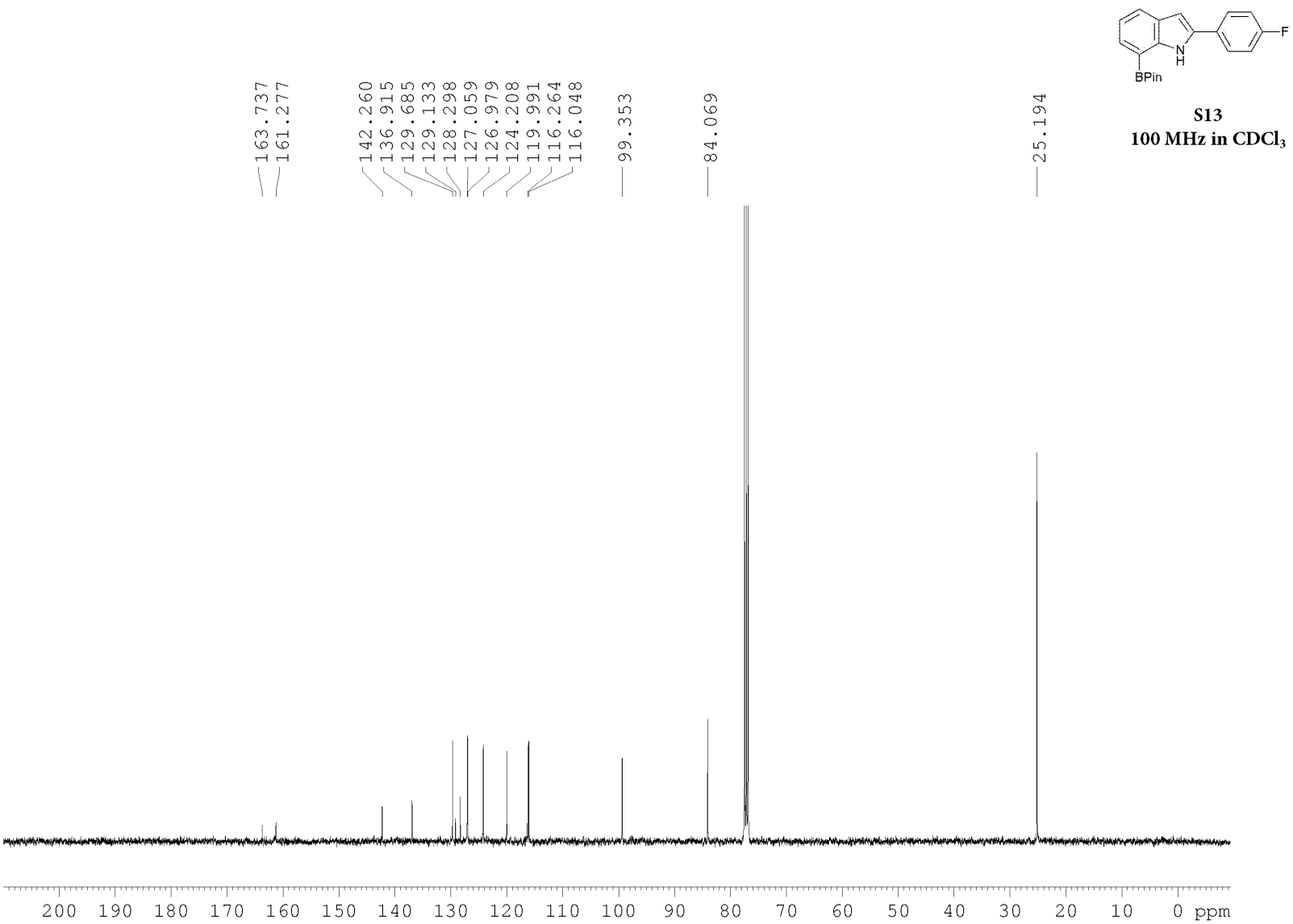




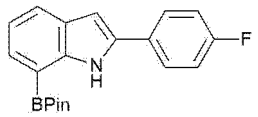
14
125 MHz in $CDCl_3$



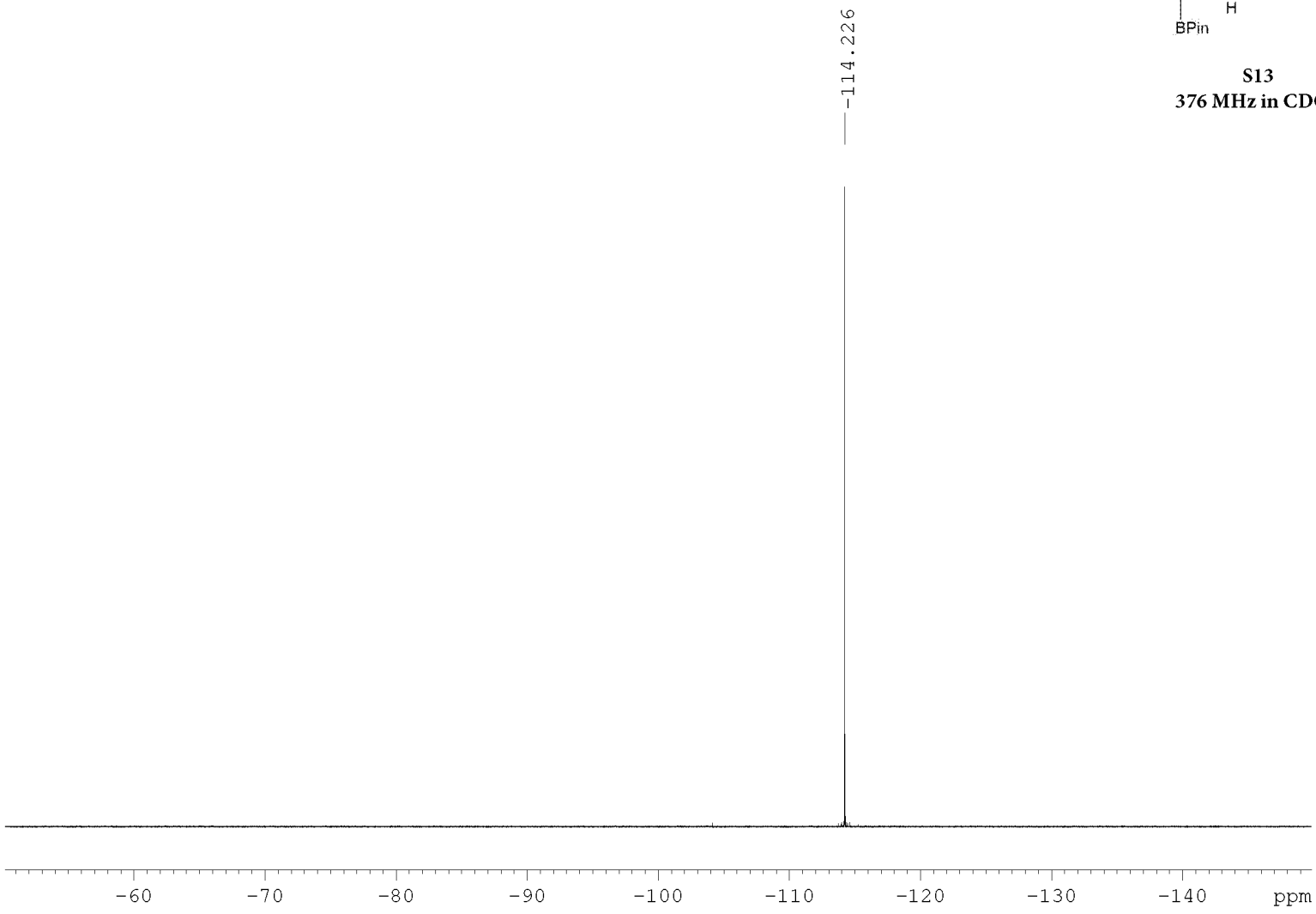
S13
400 MHz in $CDCl_3$

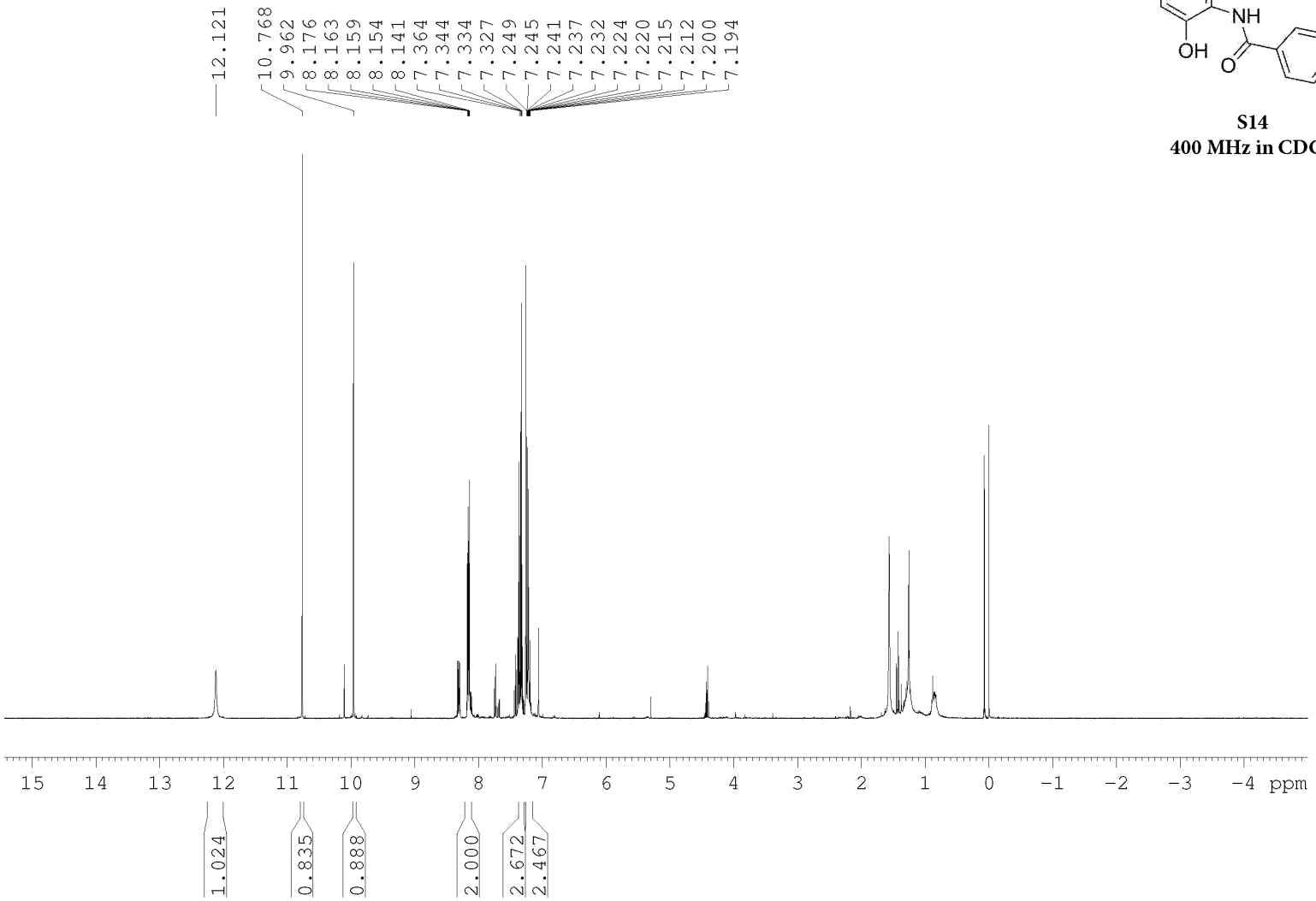


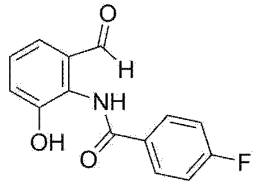
S13
100 MHz in $CDCl_3$



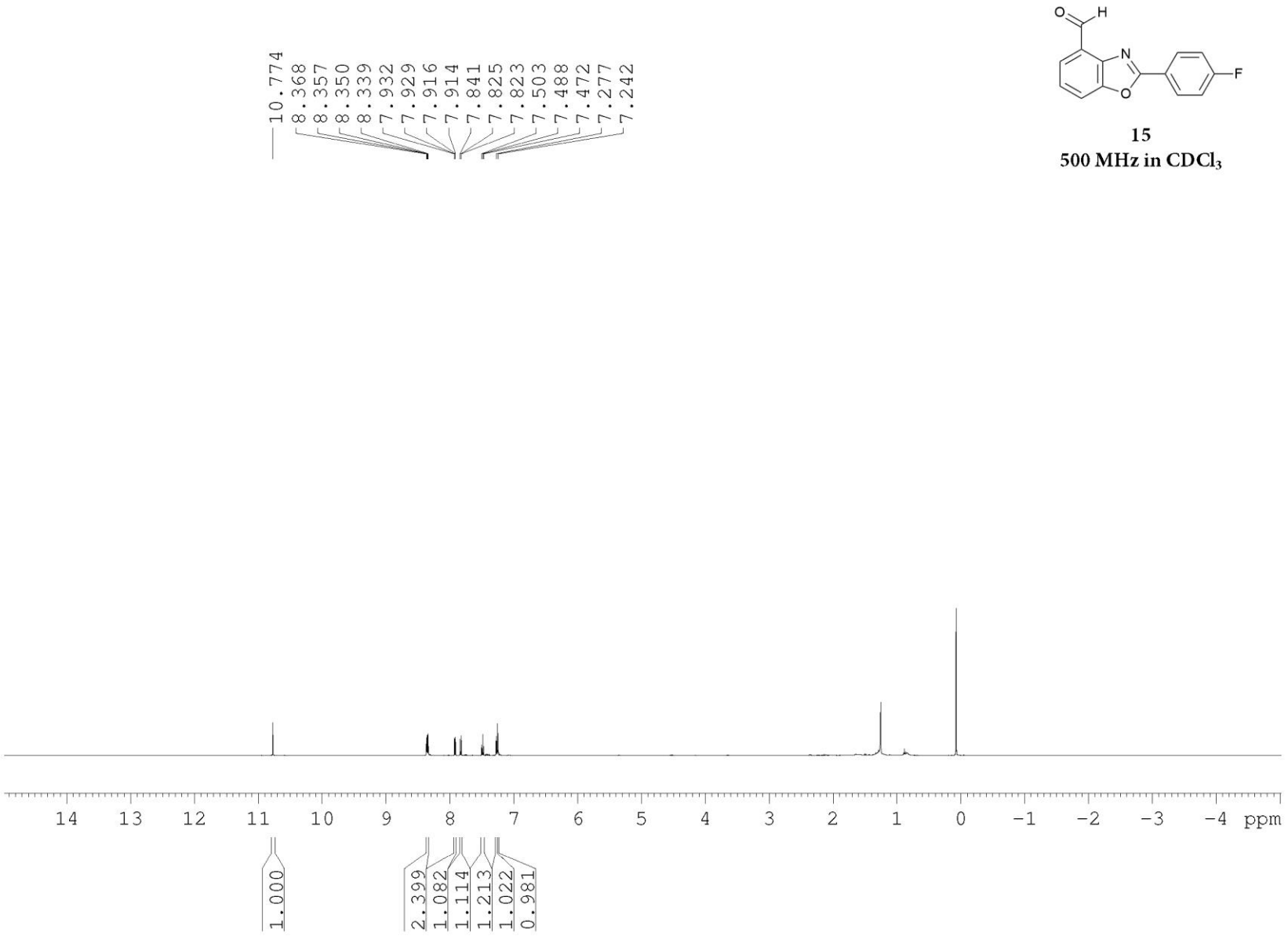
S13
376 MHz in $CDCl_3$



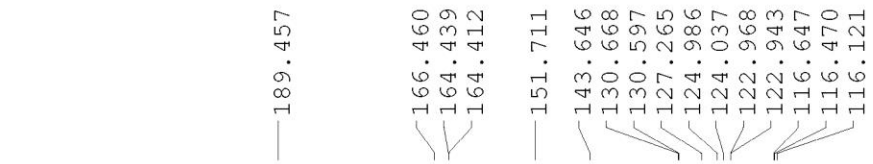


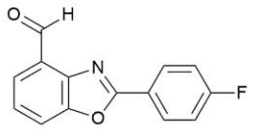


S14
400 MHz in $CDCl_3$

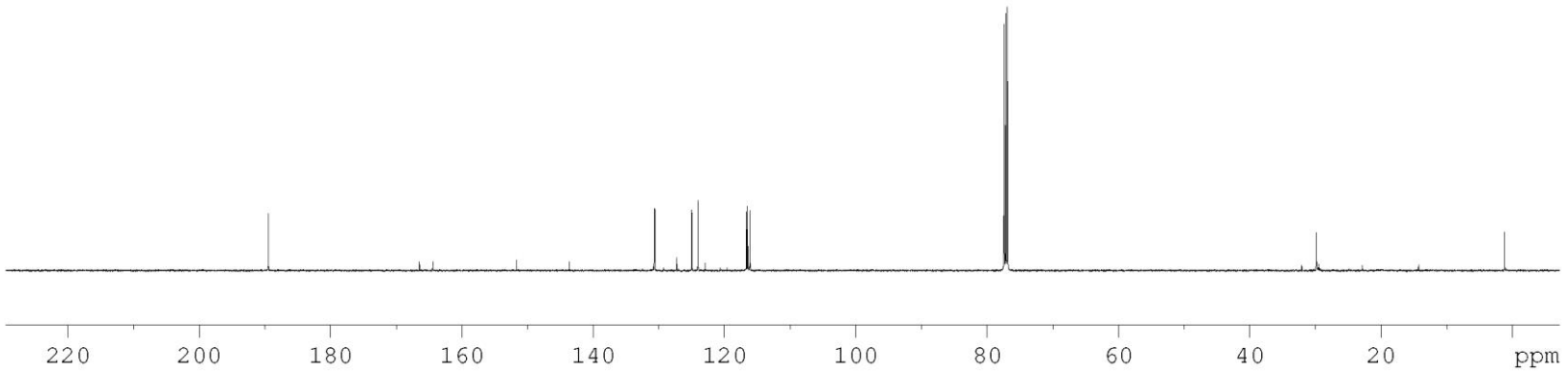


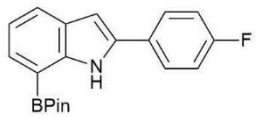
15
500 MHz in $CDCl_3$



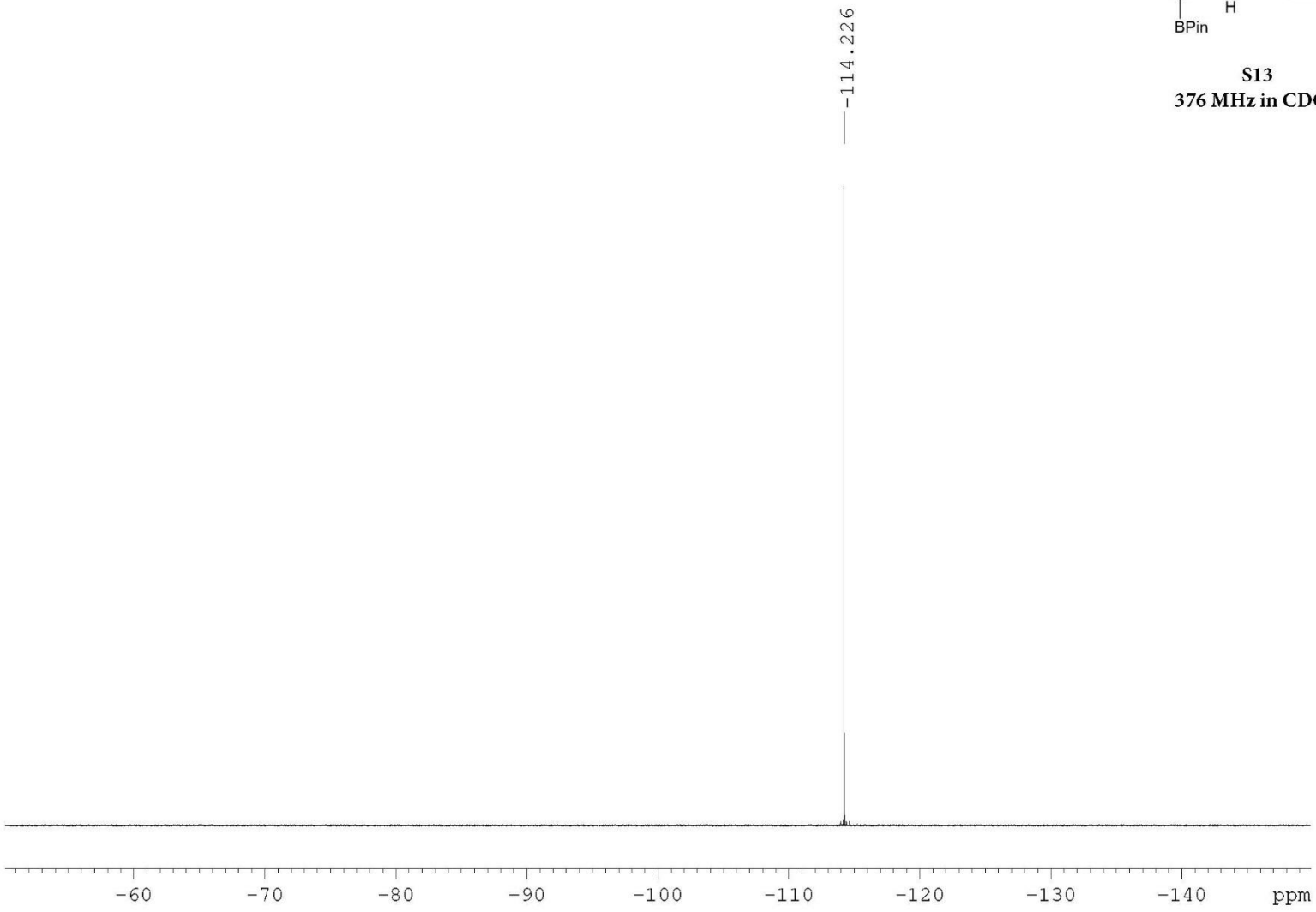


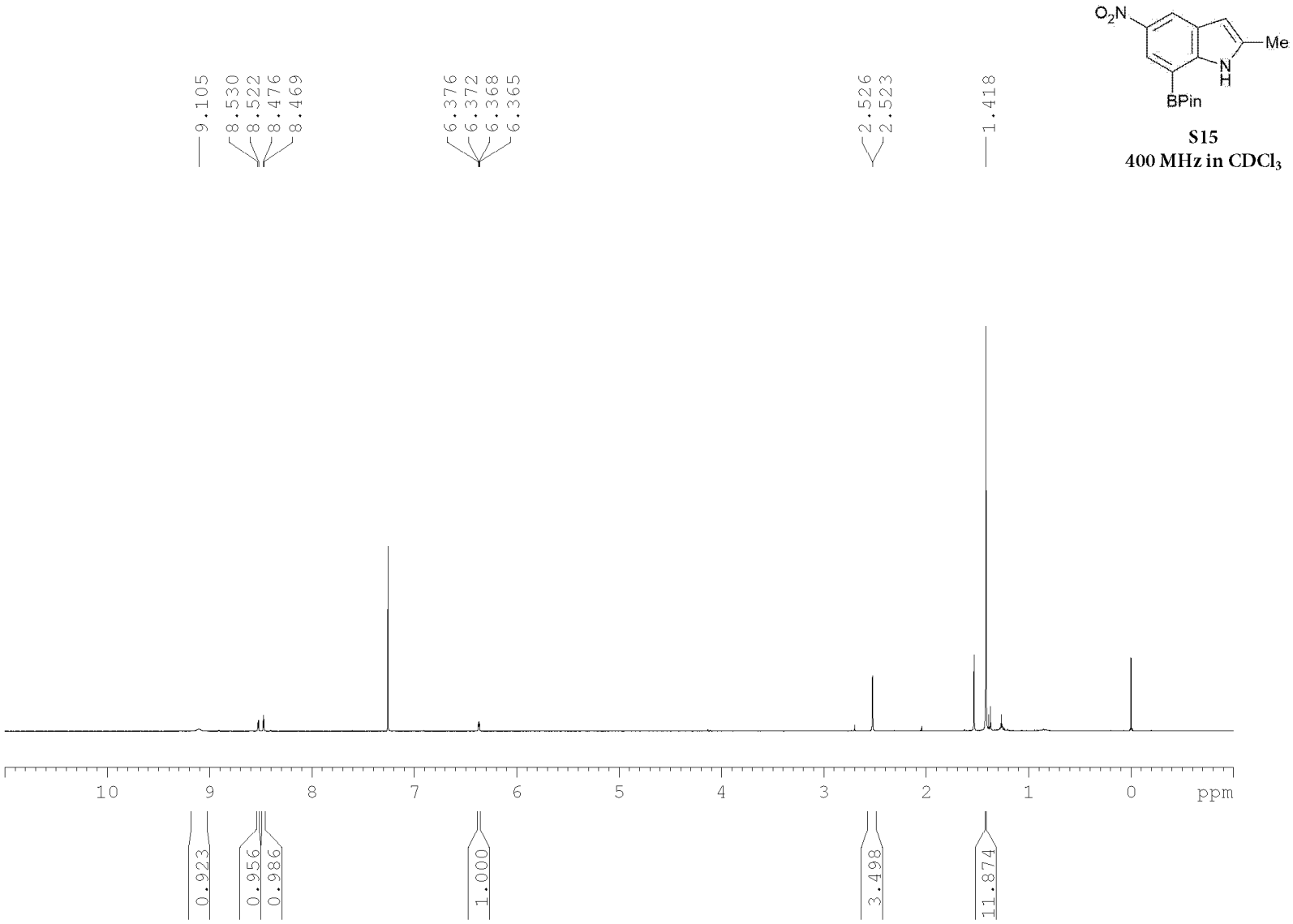
15
125 MHz in $CDCl_3$



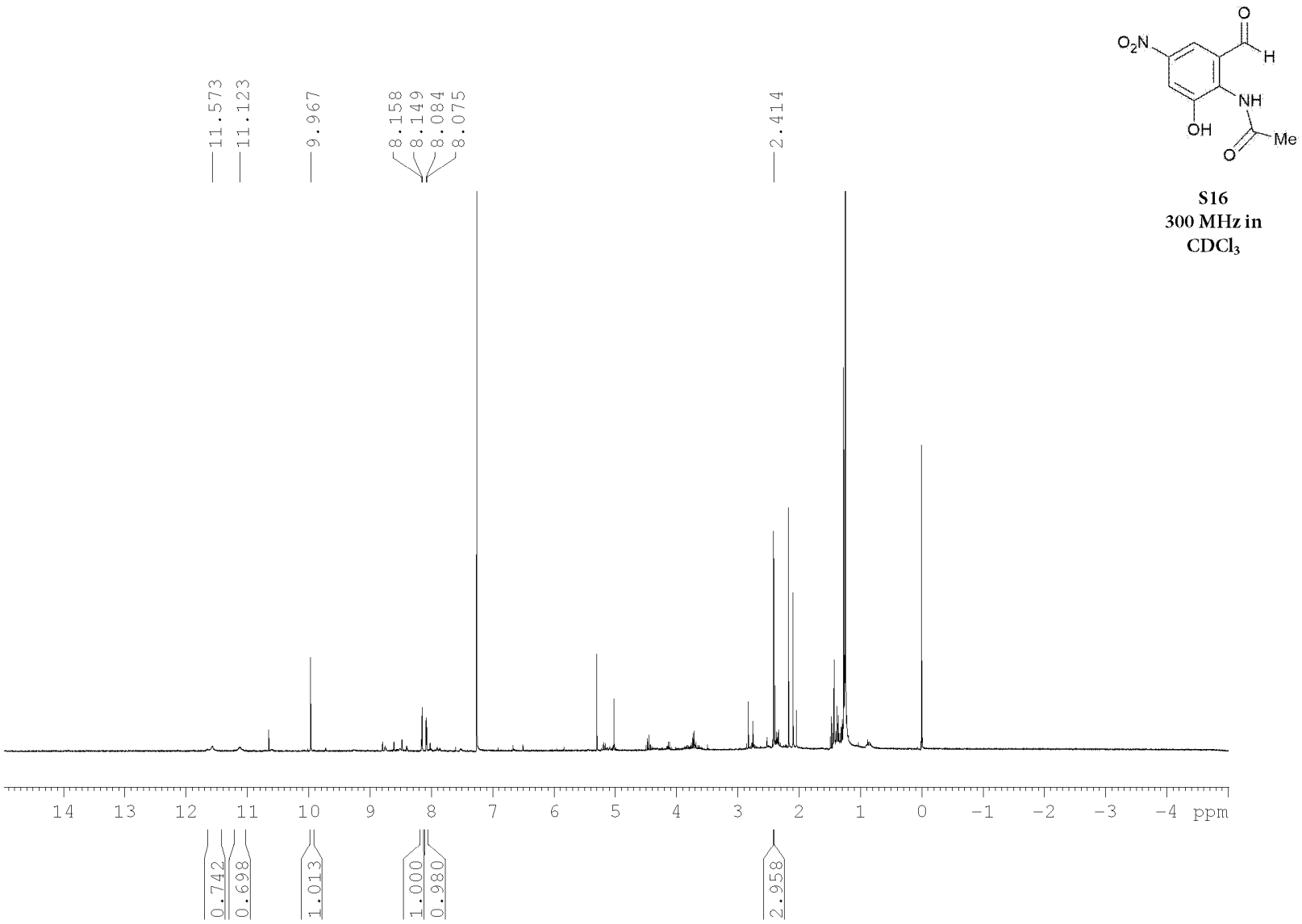


S13
376 MHz in $CDCl_3$

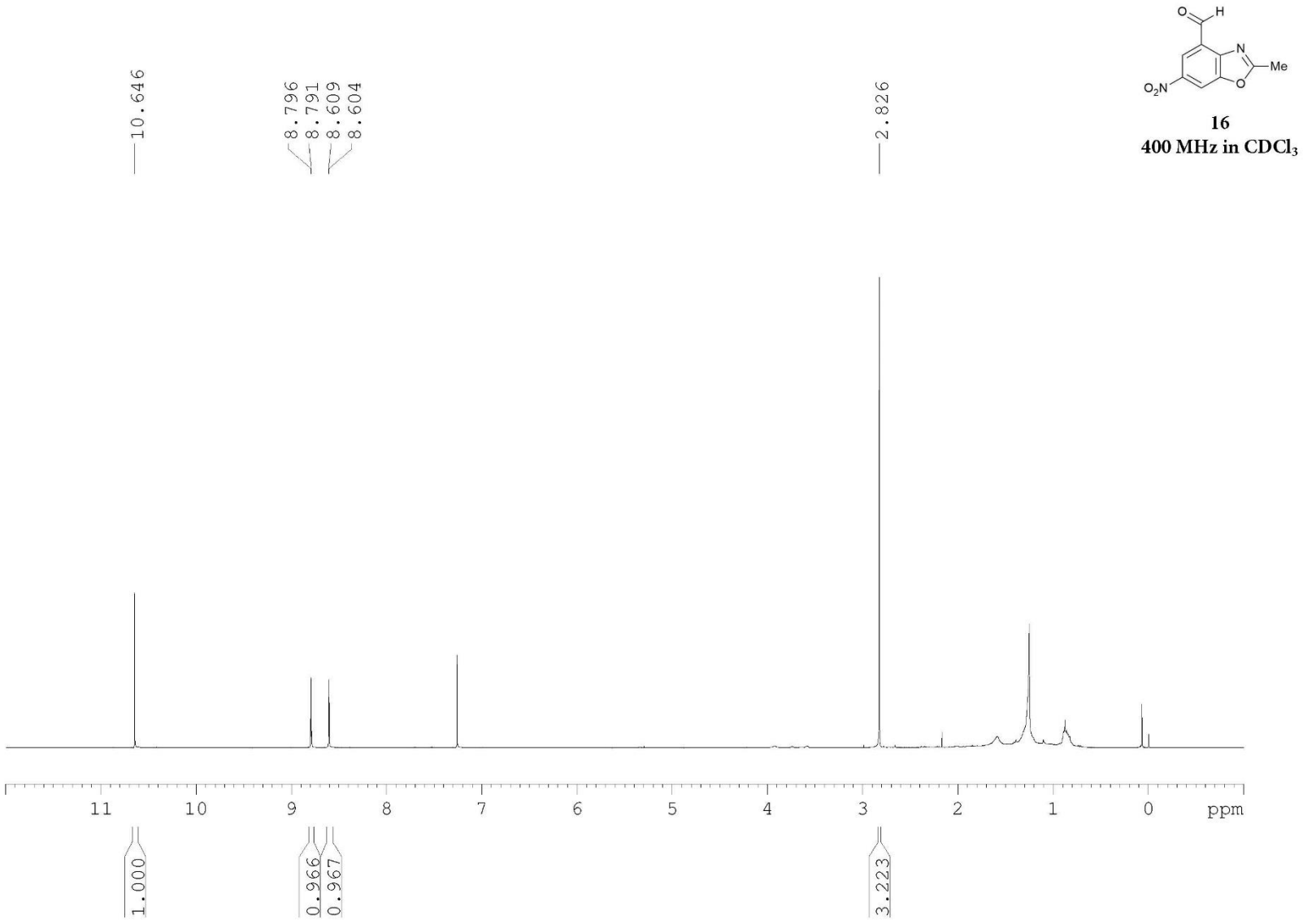




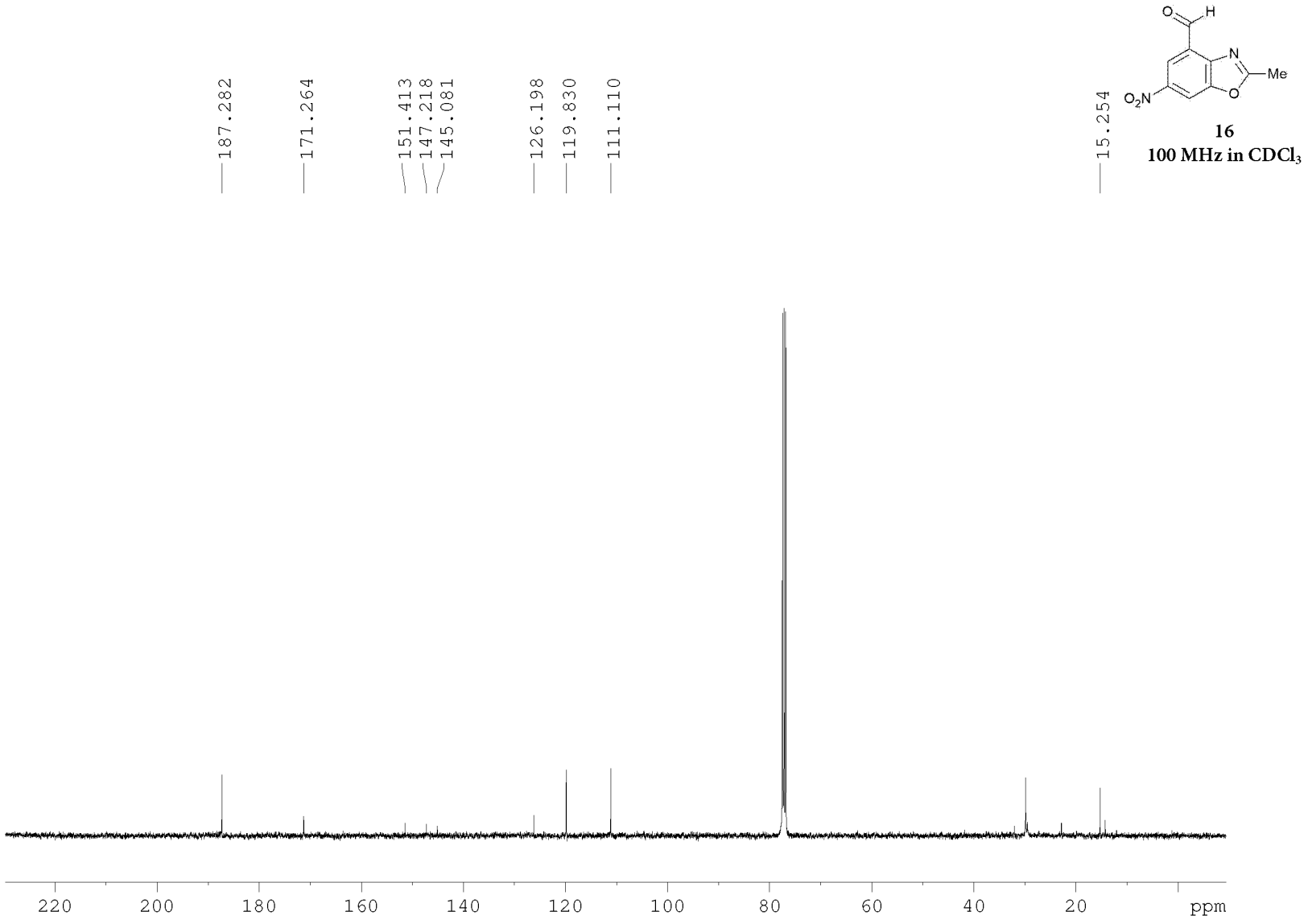
S15
400 MHz in $CDCl_3$

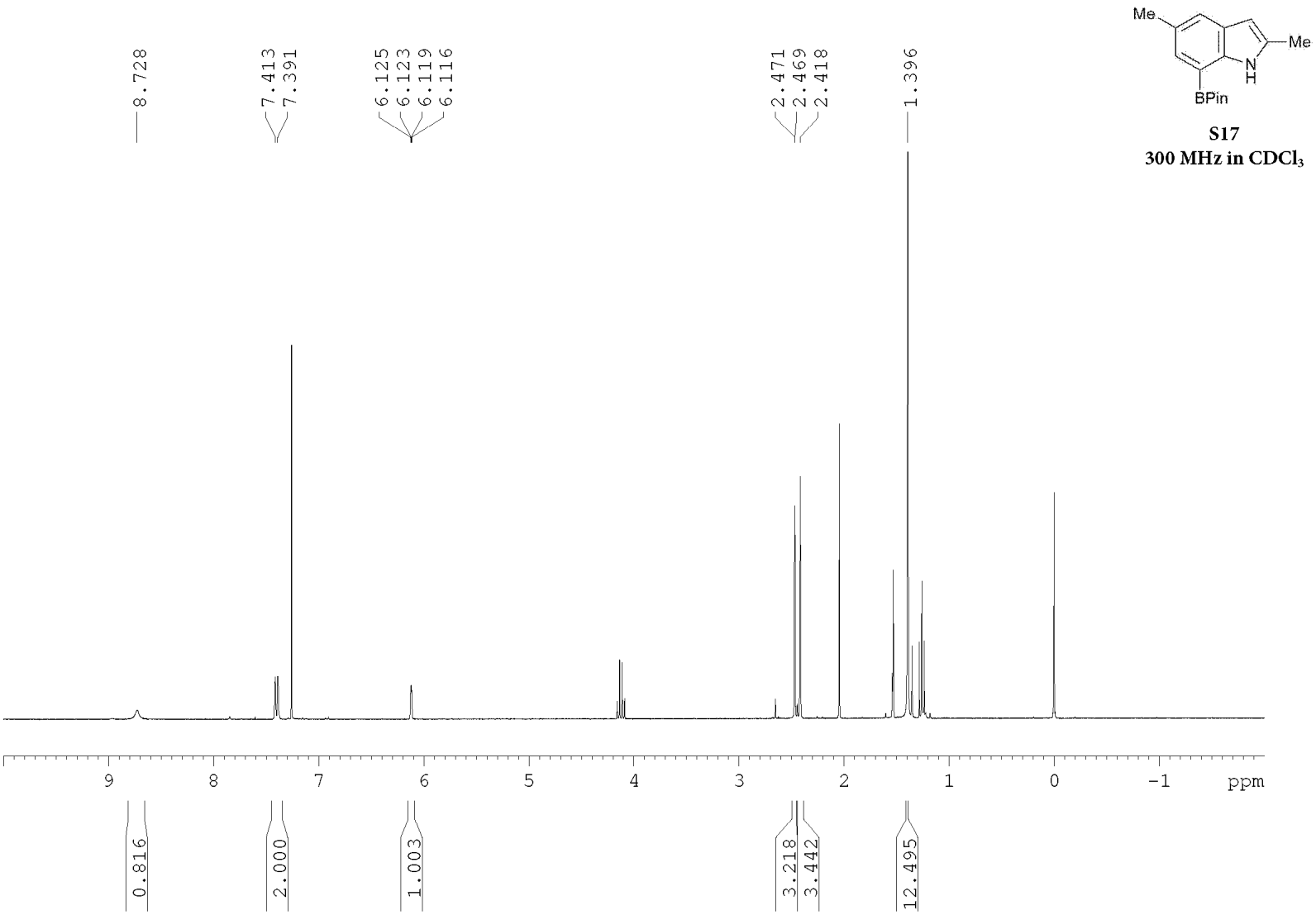


S16
300 MHz in
$CDCl_3$

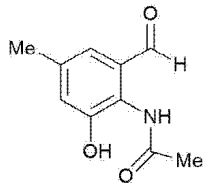


16
400 MHz in $CDCl_3$

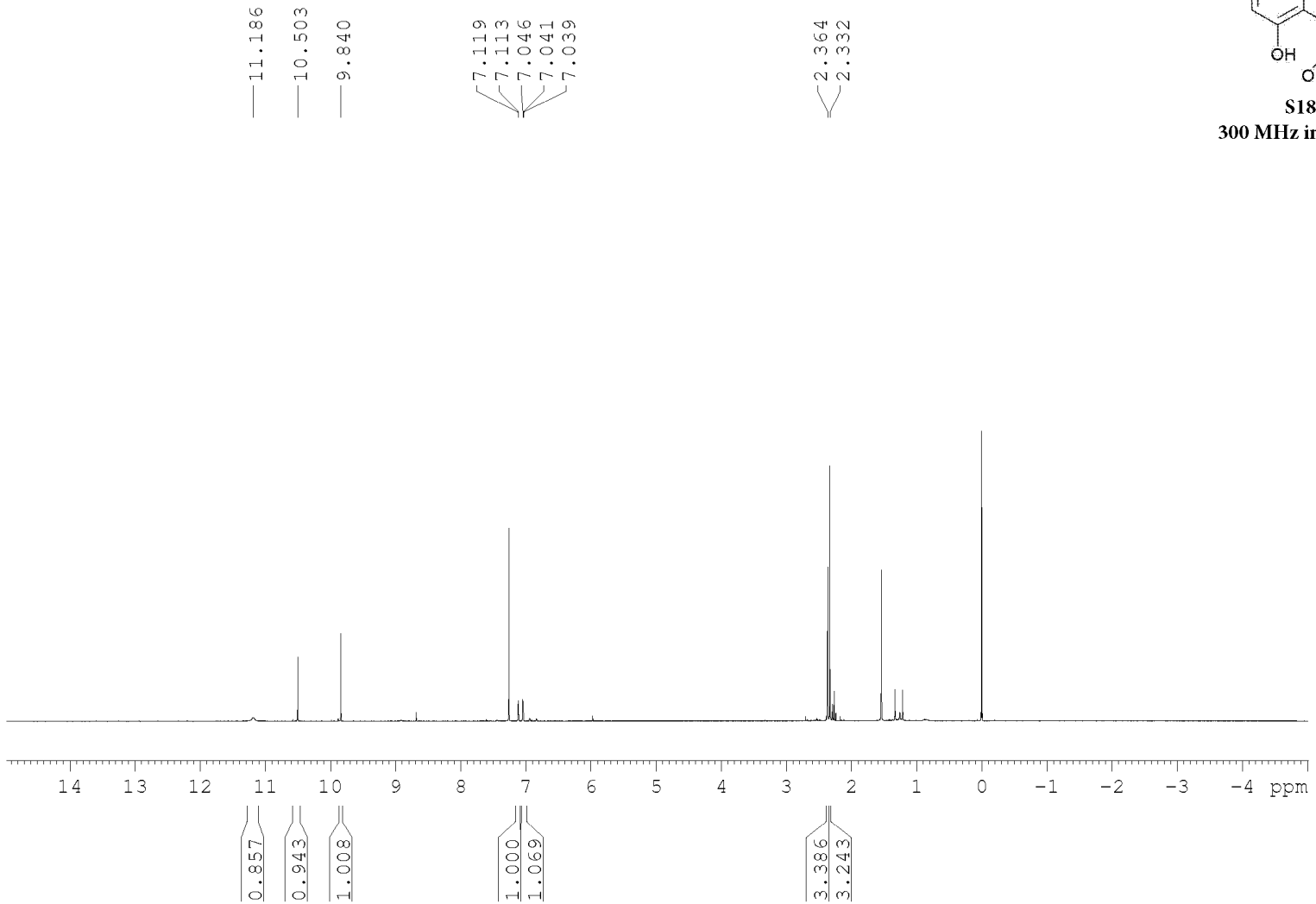

187.282
171.264
151.413
147.218
145.081
126.198
119.830
111.110
15.254
O
H
N
Me
O
O2N
16
100 MHz in CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm

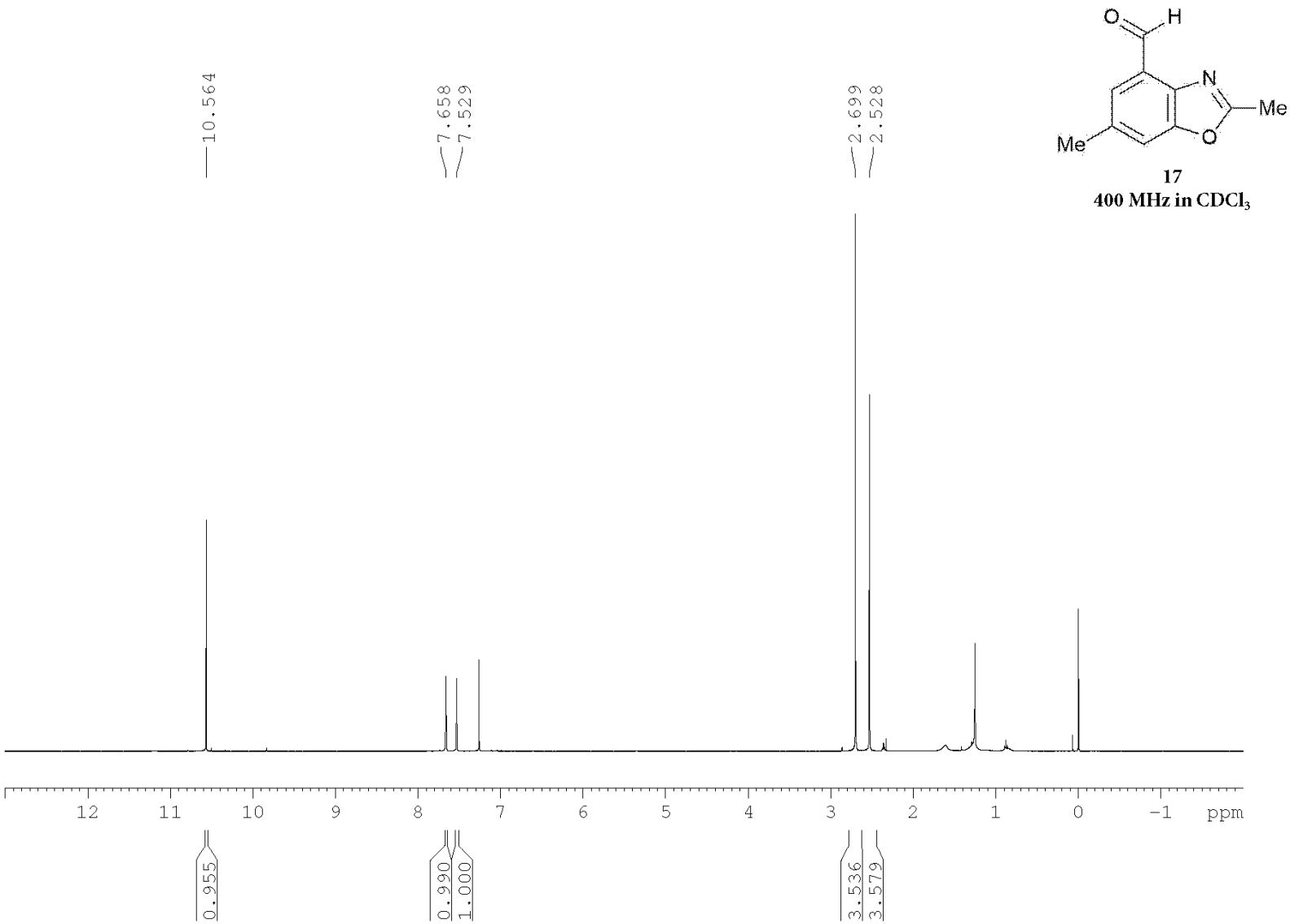


S17
300 MHz in $CDCl_3$

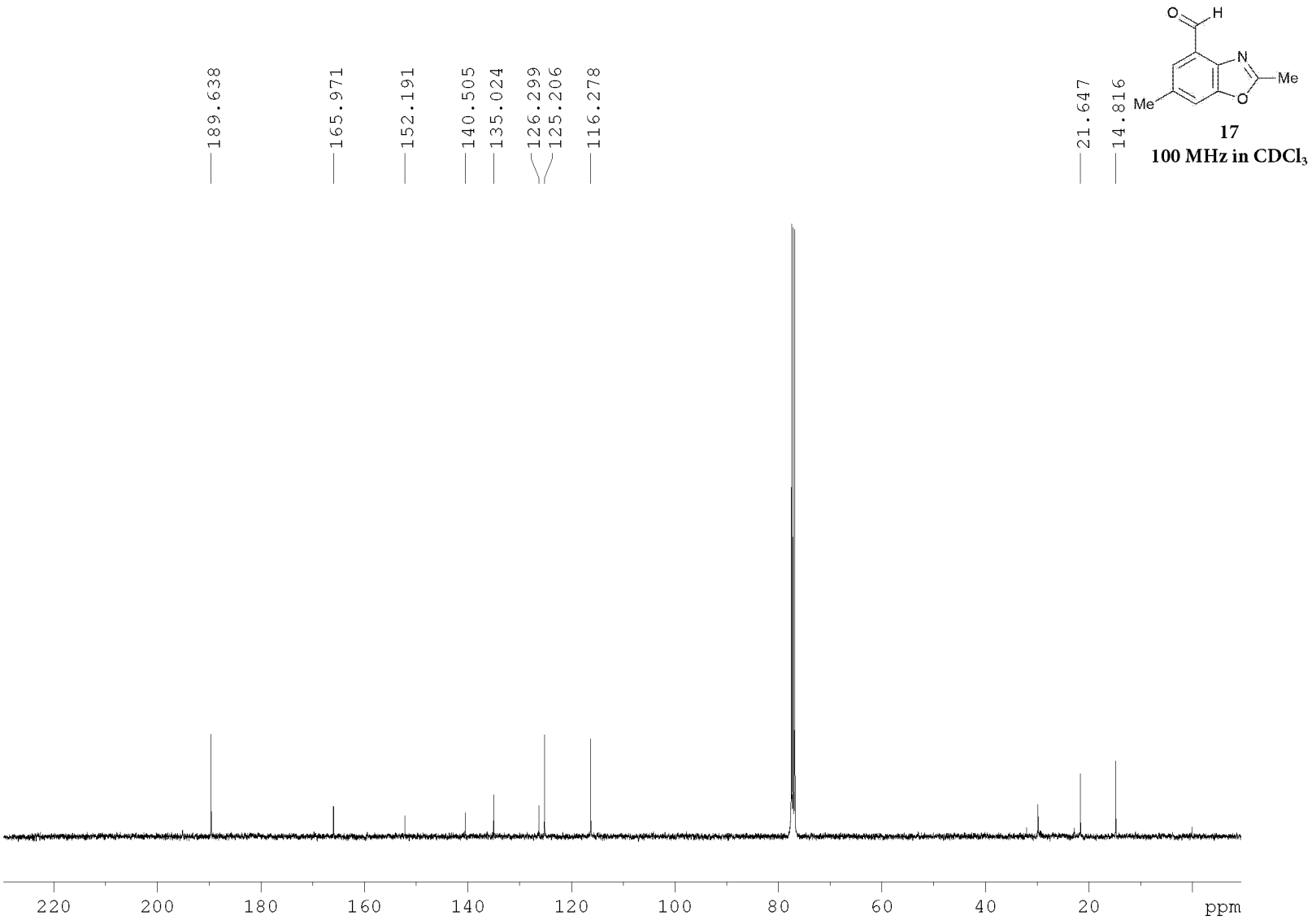


S18
300 MHz in $CDCl_3$



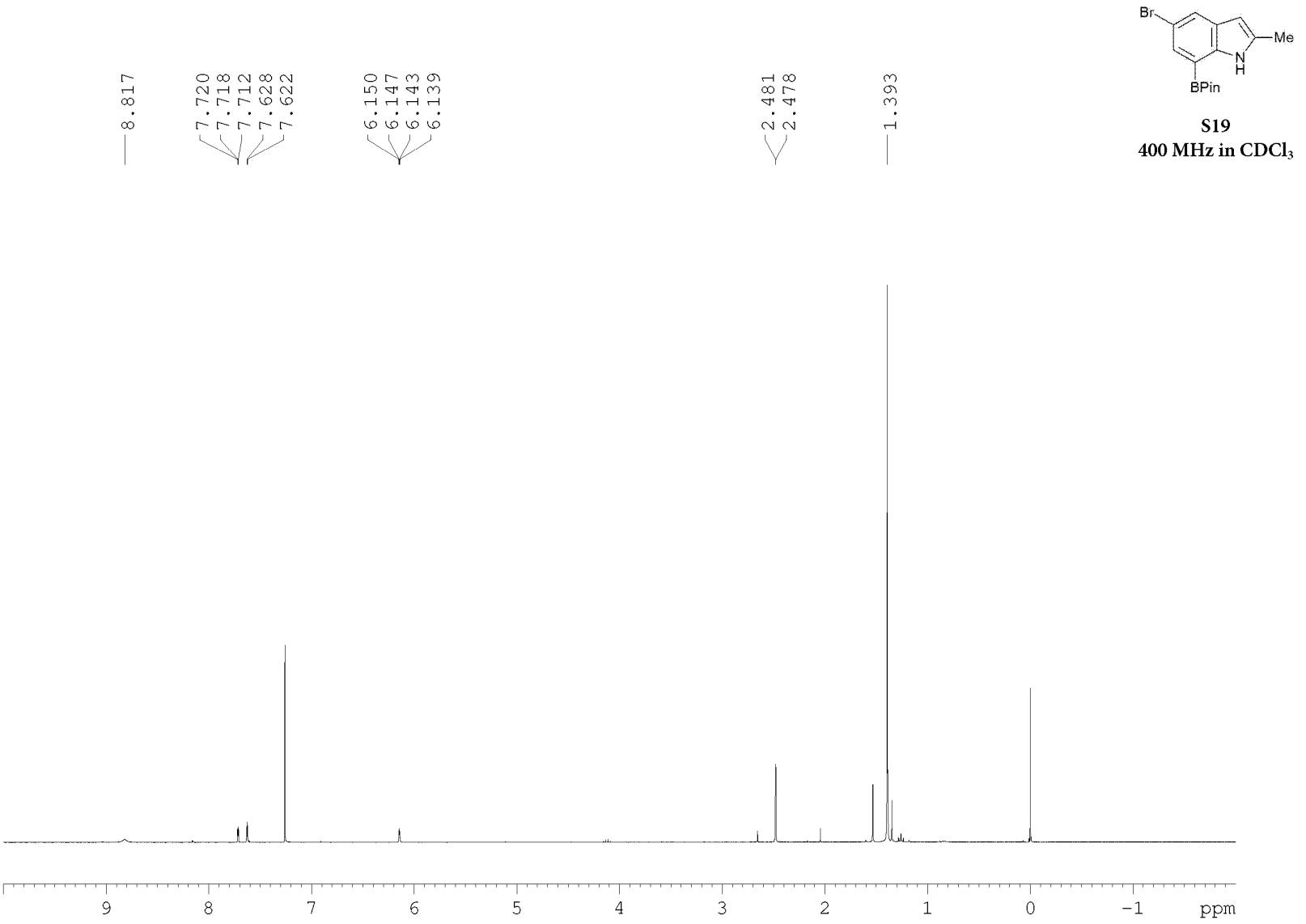


17
400 MHz in $CDCl_3$

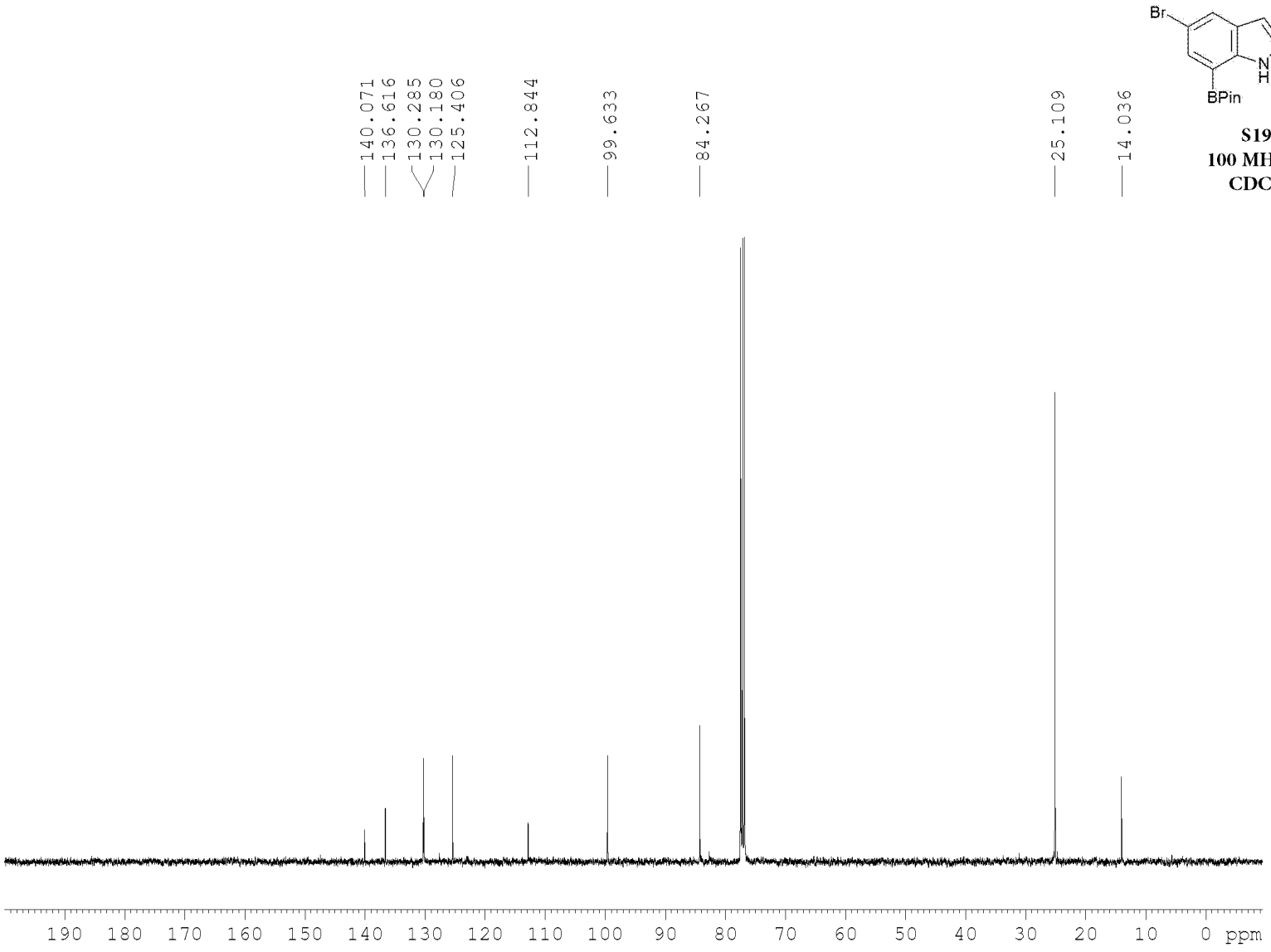


17

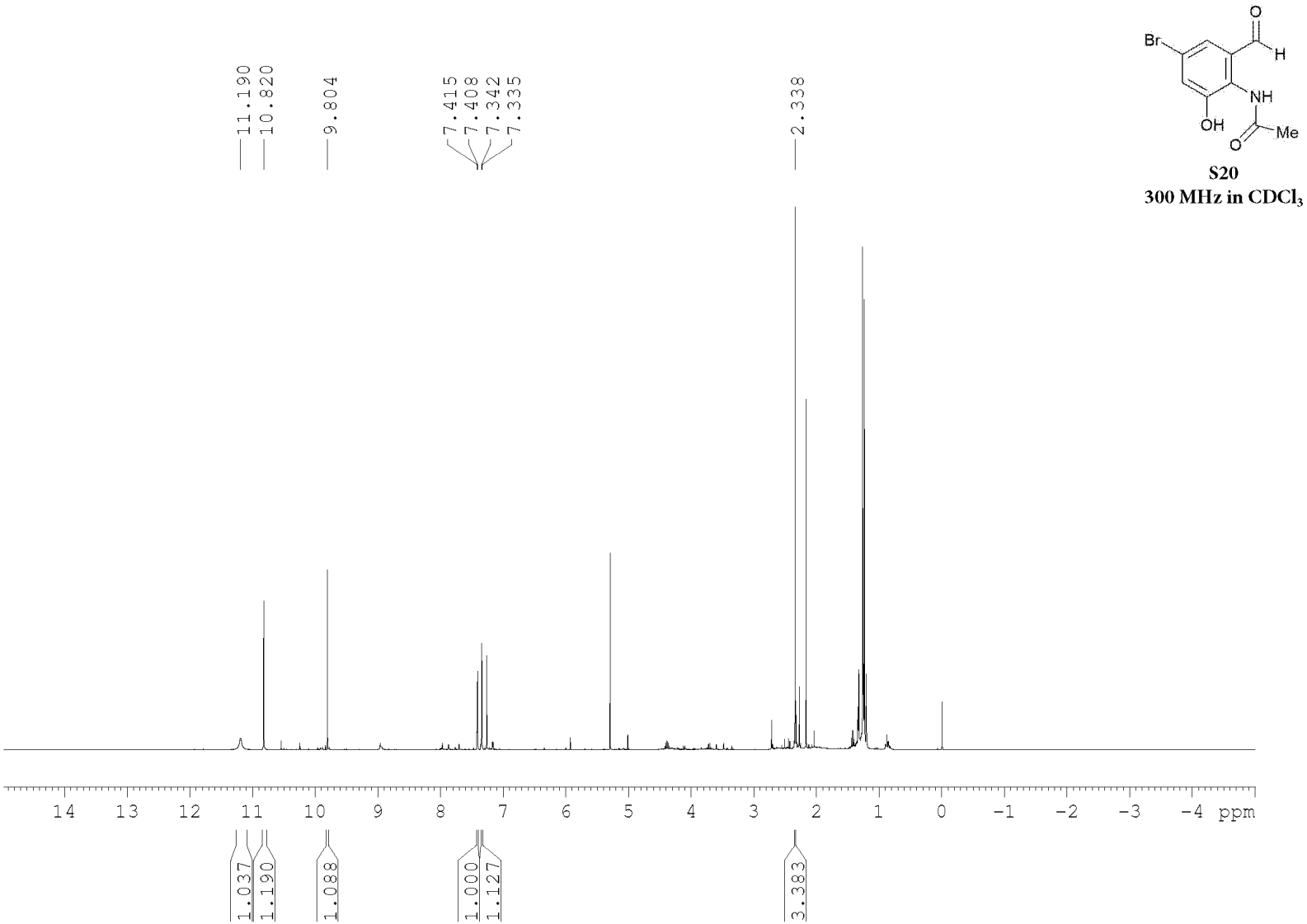
100 MHz in $CDCl_3$



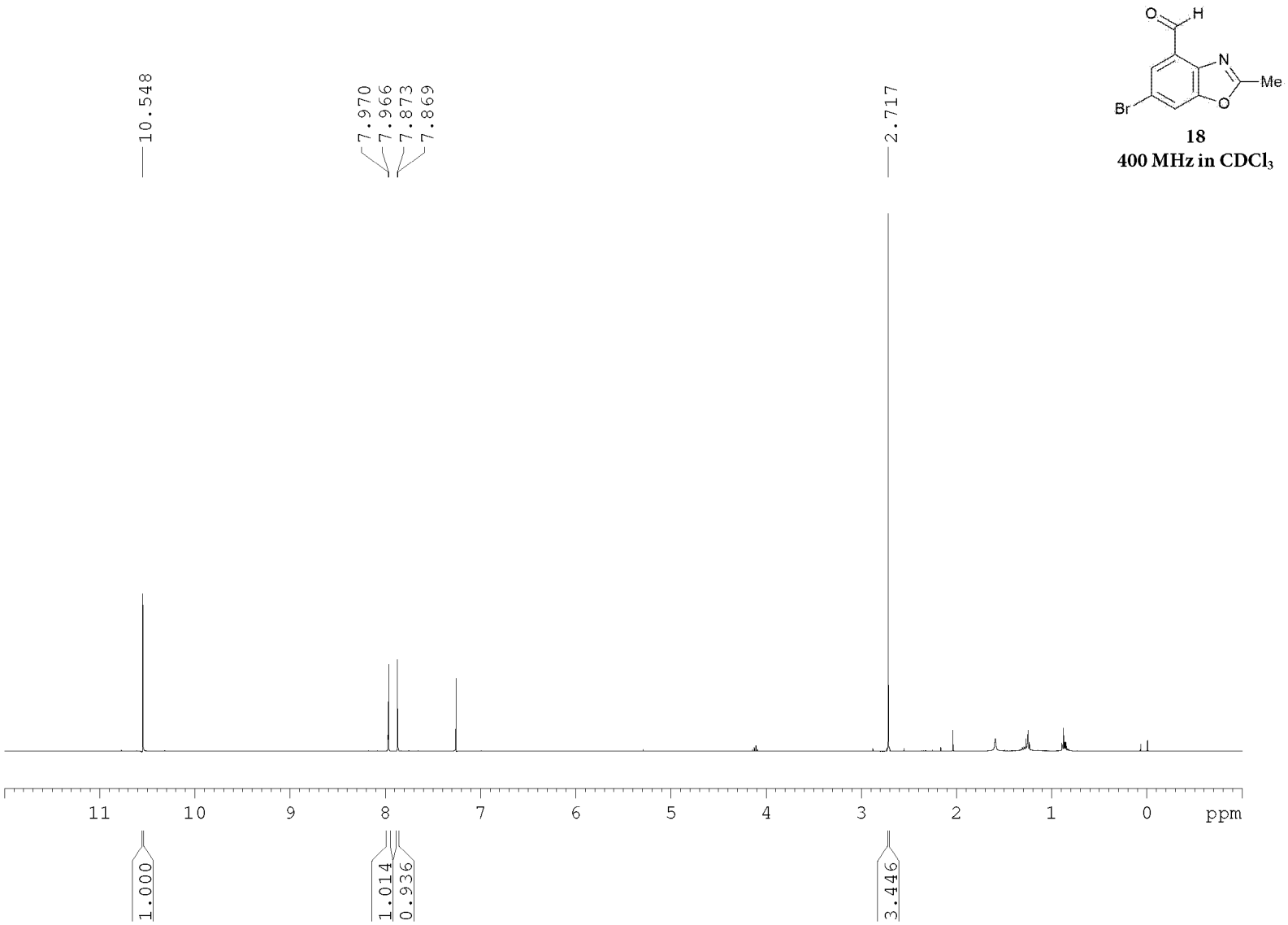
S19
400 MHz in $CDCl_3$



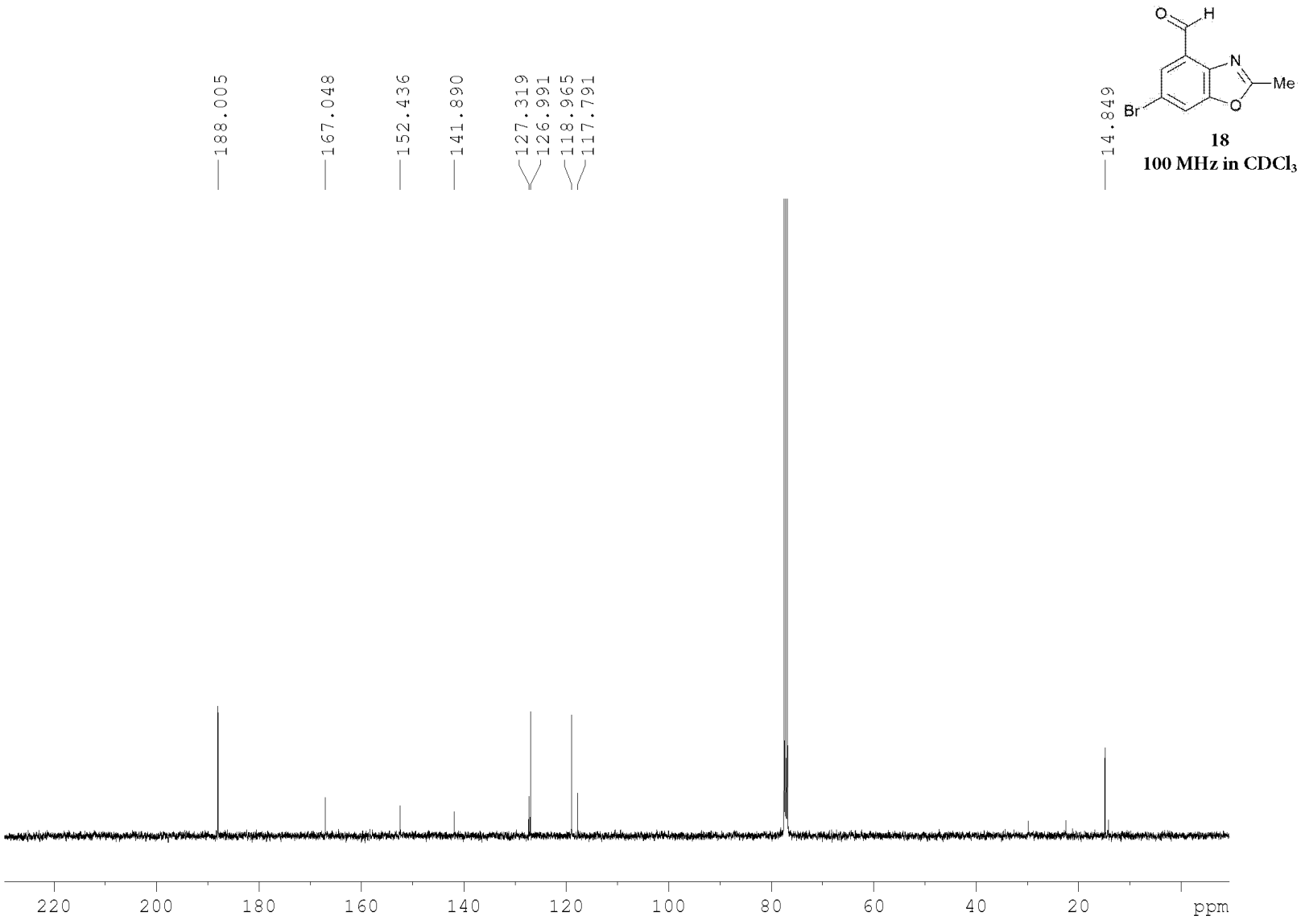
S19
100 MHz in $CDCl_3$

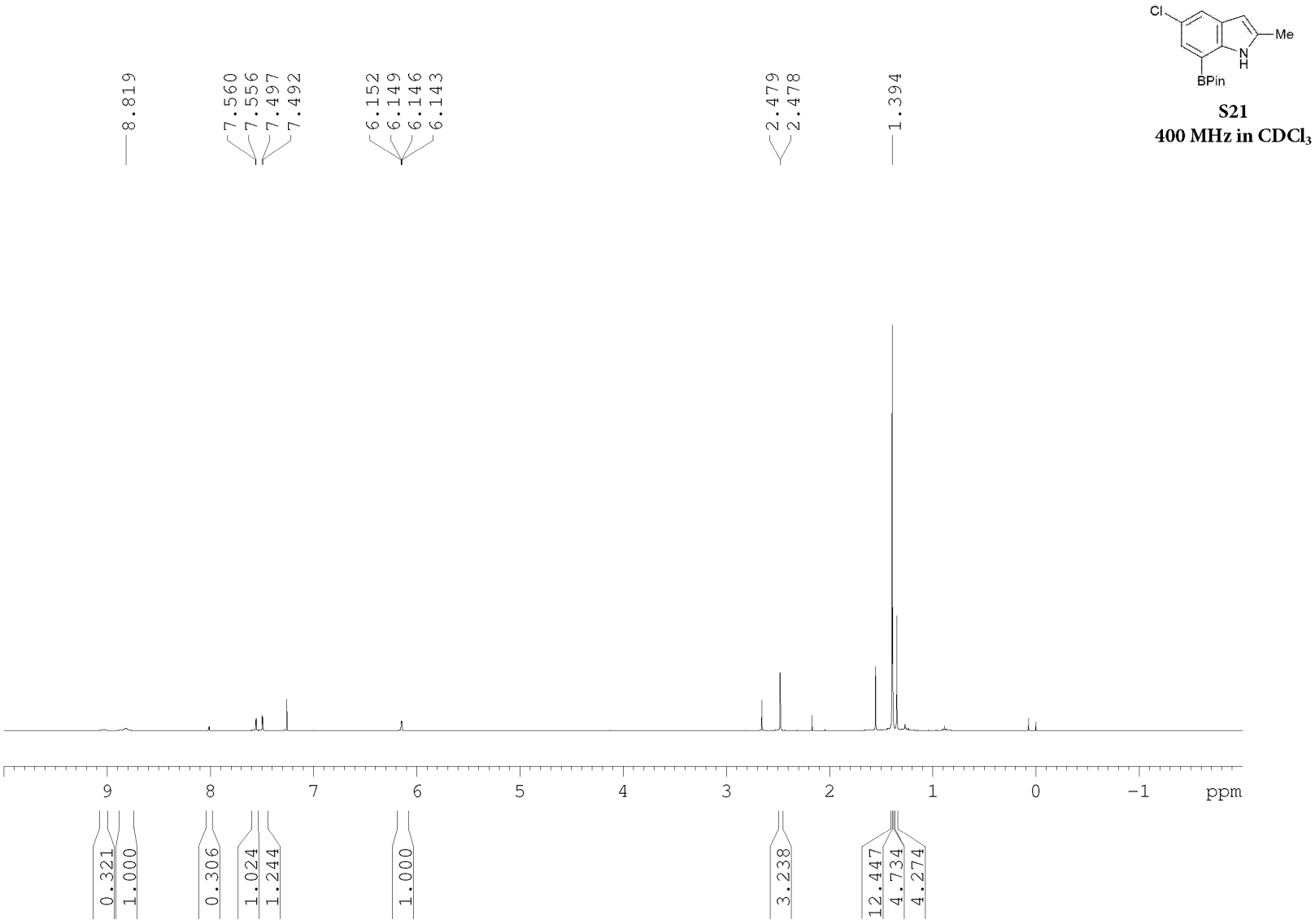


S20
300 MHz in $CDCl_3$

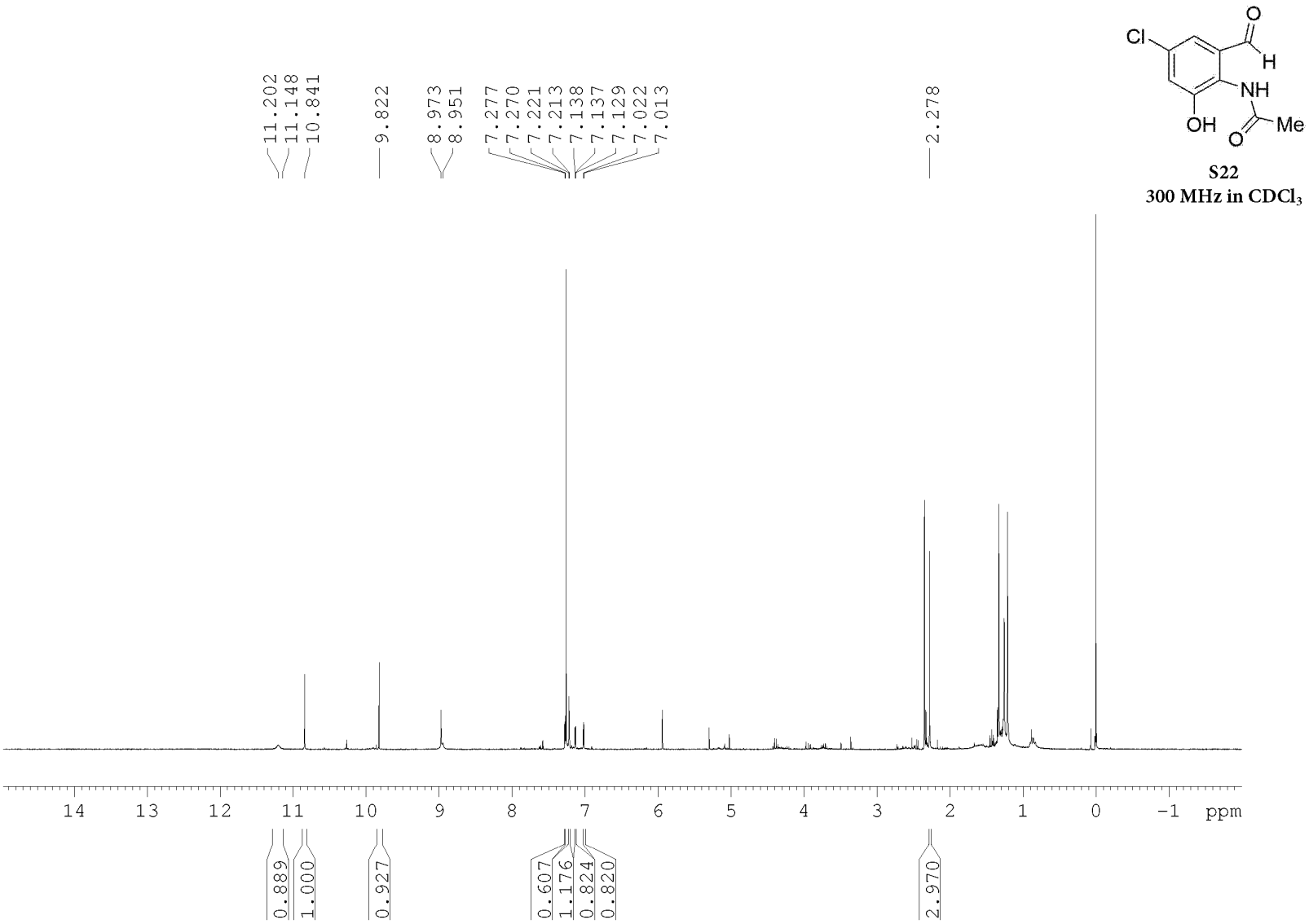


18
400 MHz in $CDCl_3$


188.005
167.048
152.436
141.890
127.319
126.991
118.965
117.791
14.849
O
H
N
Me
Br
O
18
100 MHz in CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm

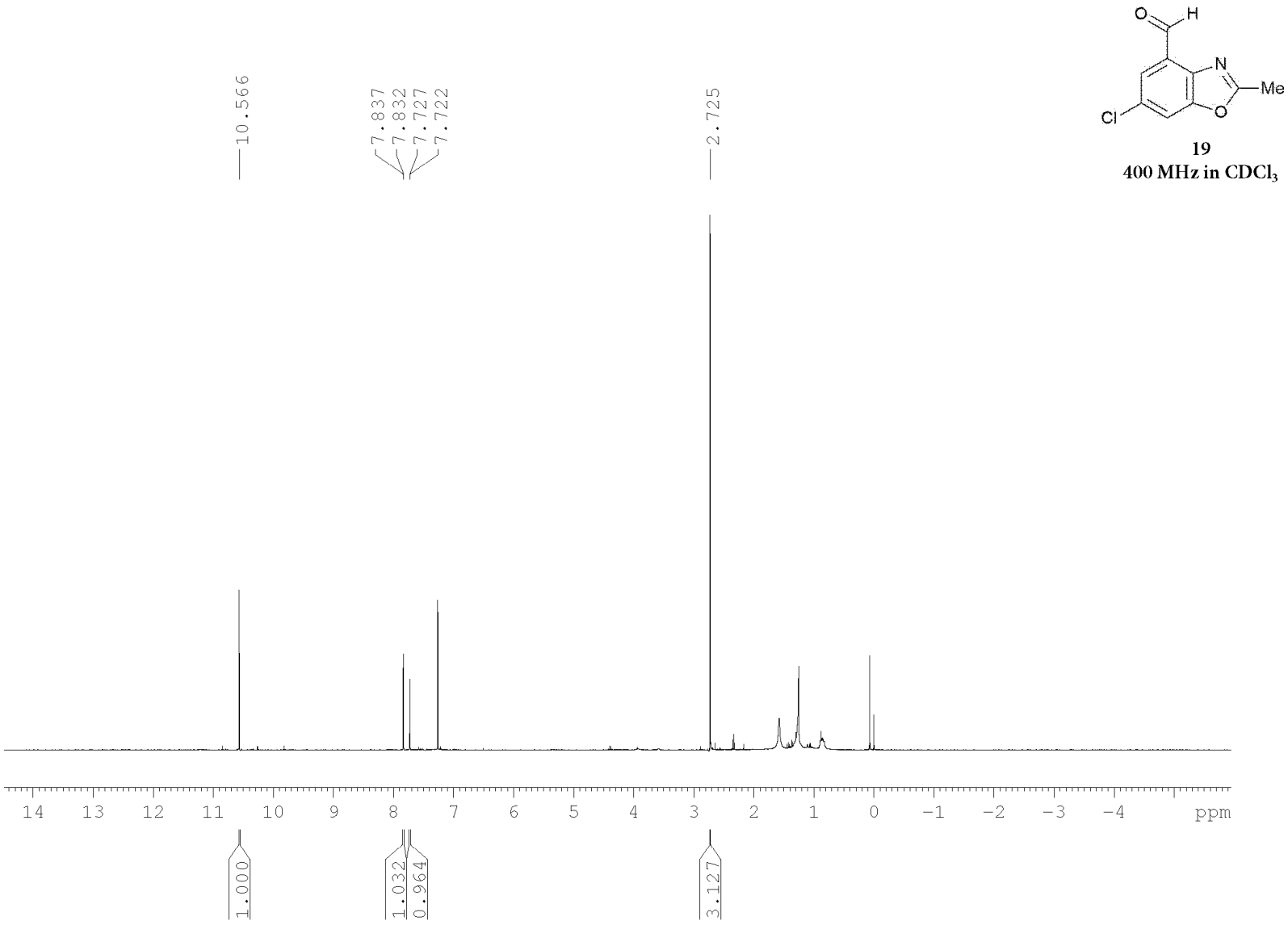


S21
400 MHz in $CDCl_3$

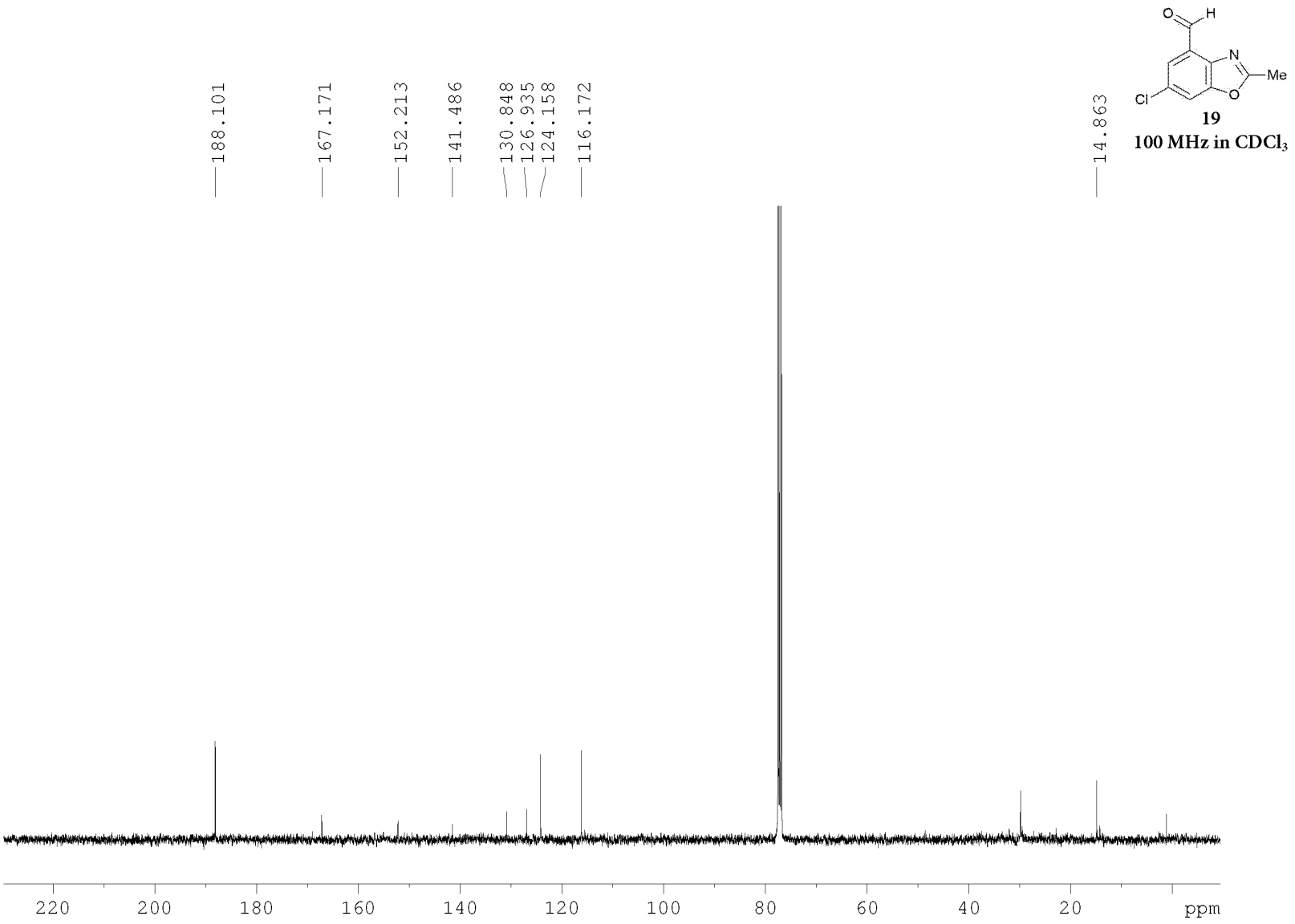


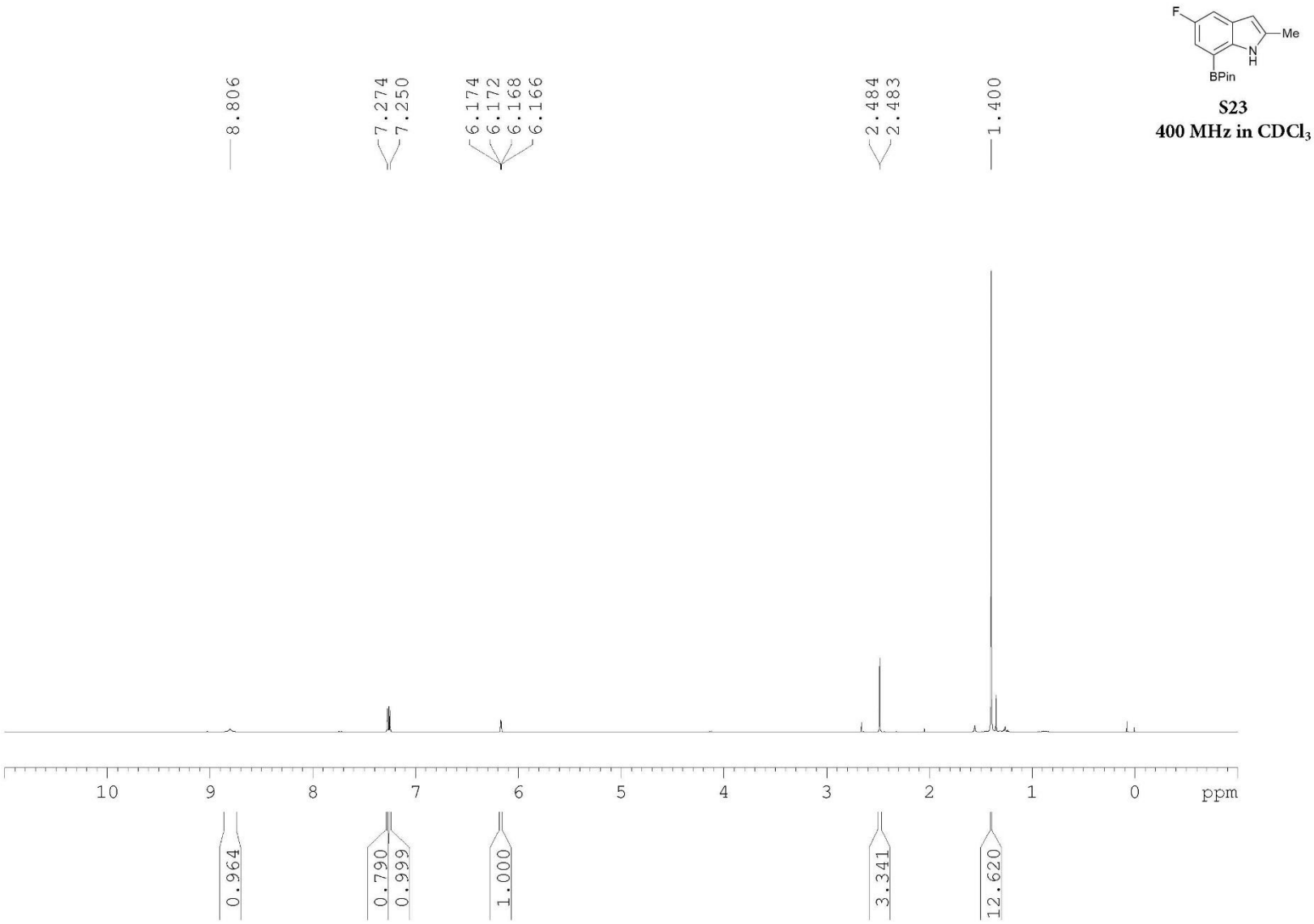
S22

300 MHz in $CDCl_3$

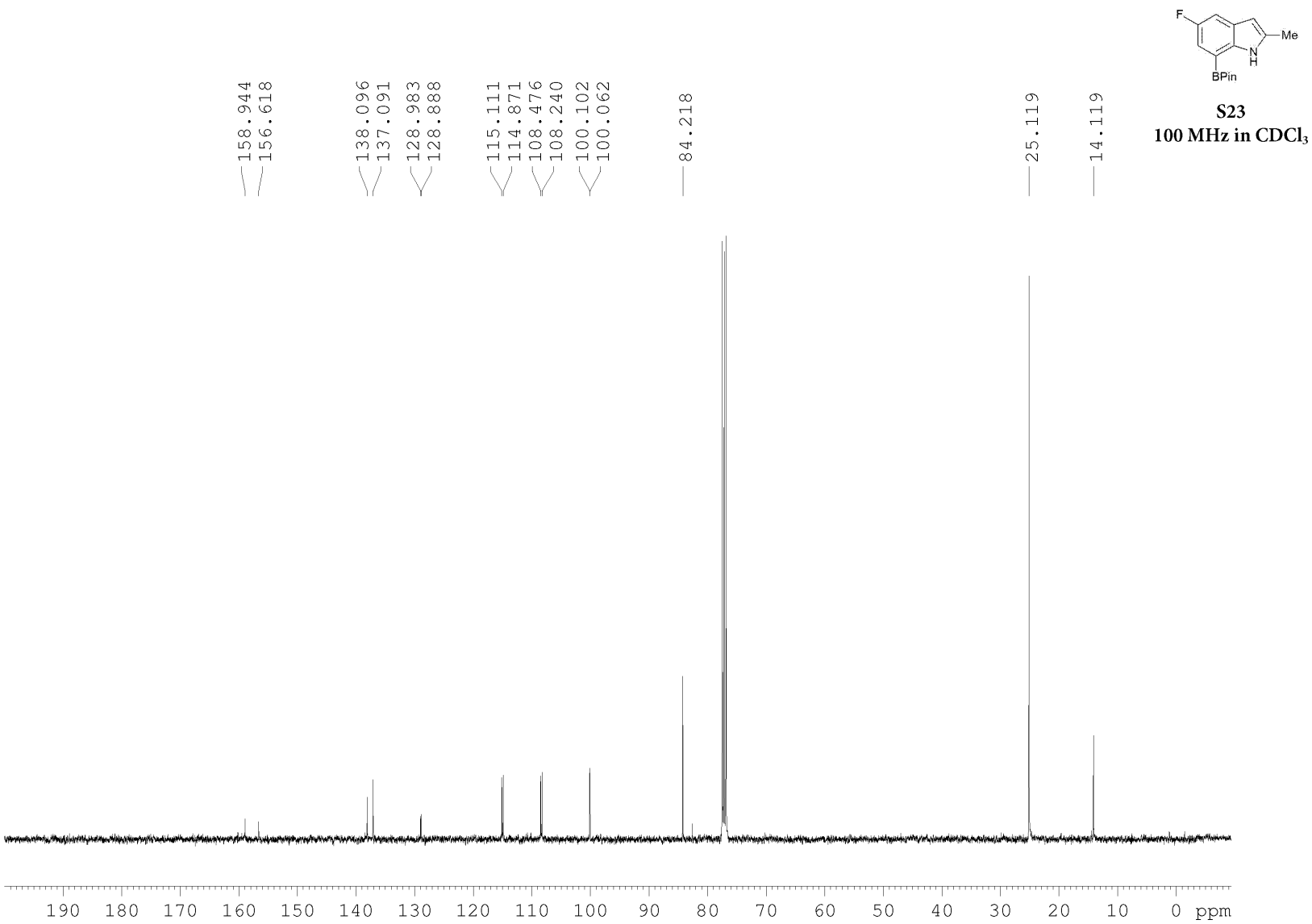


19
400 MHz in $CDCl_3$

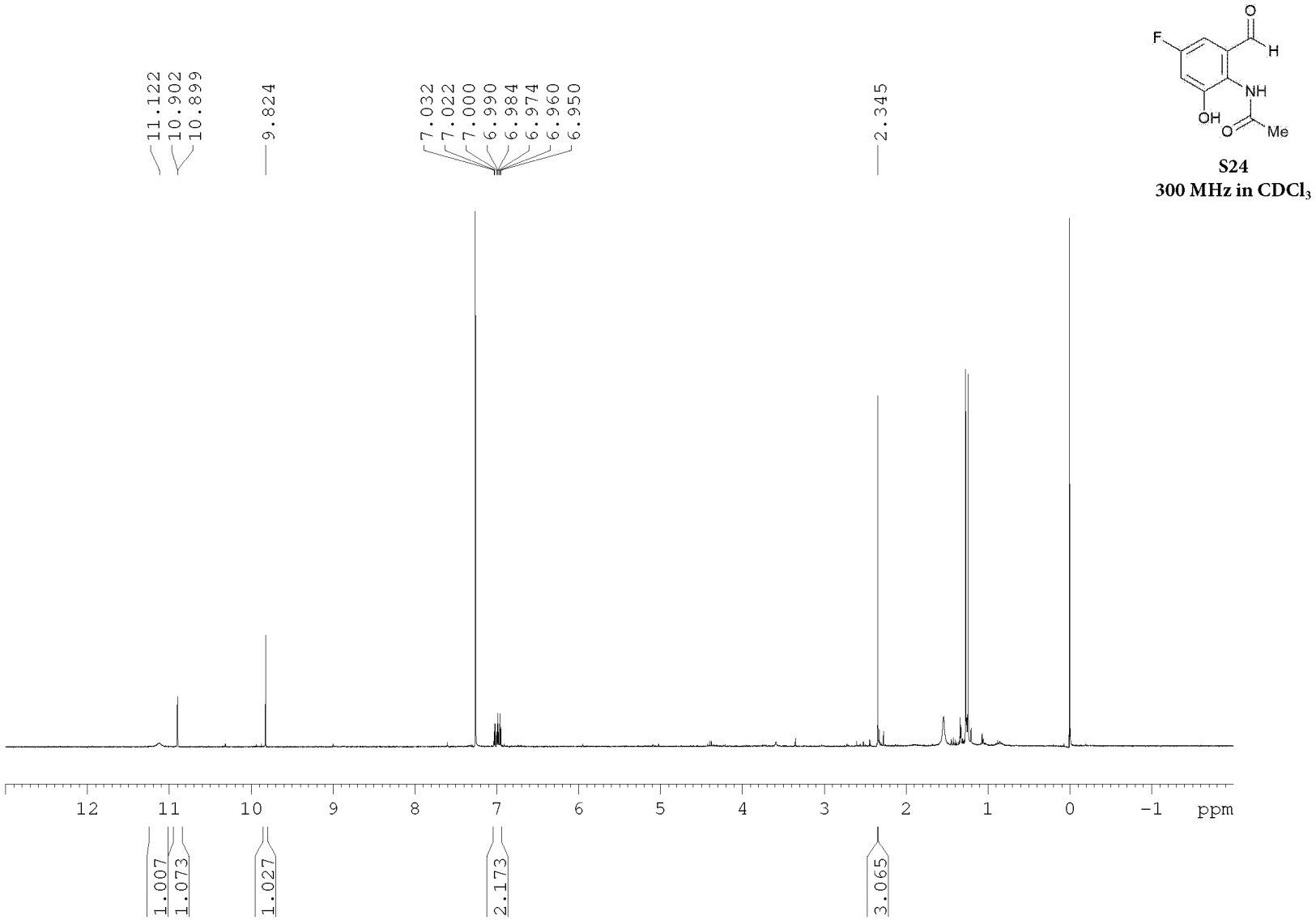

188.101
167.171
152.213
141.486
130.848
126.935
124.158
116.172
14.863
O
H
N
Me
Cl
O
19
100 MHz in CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm



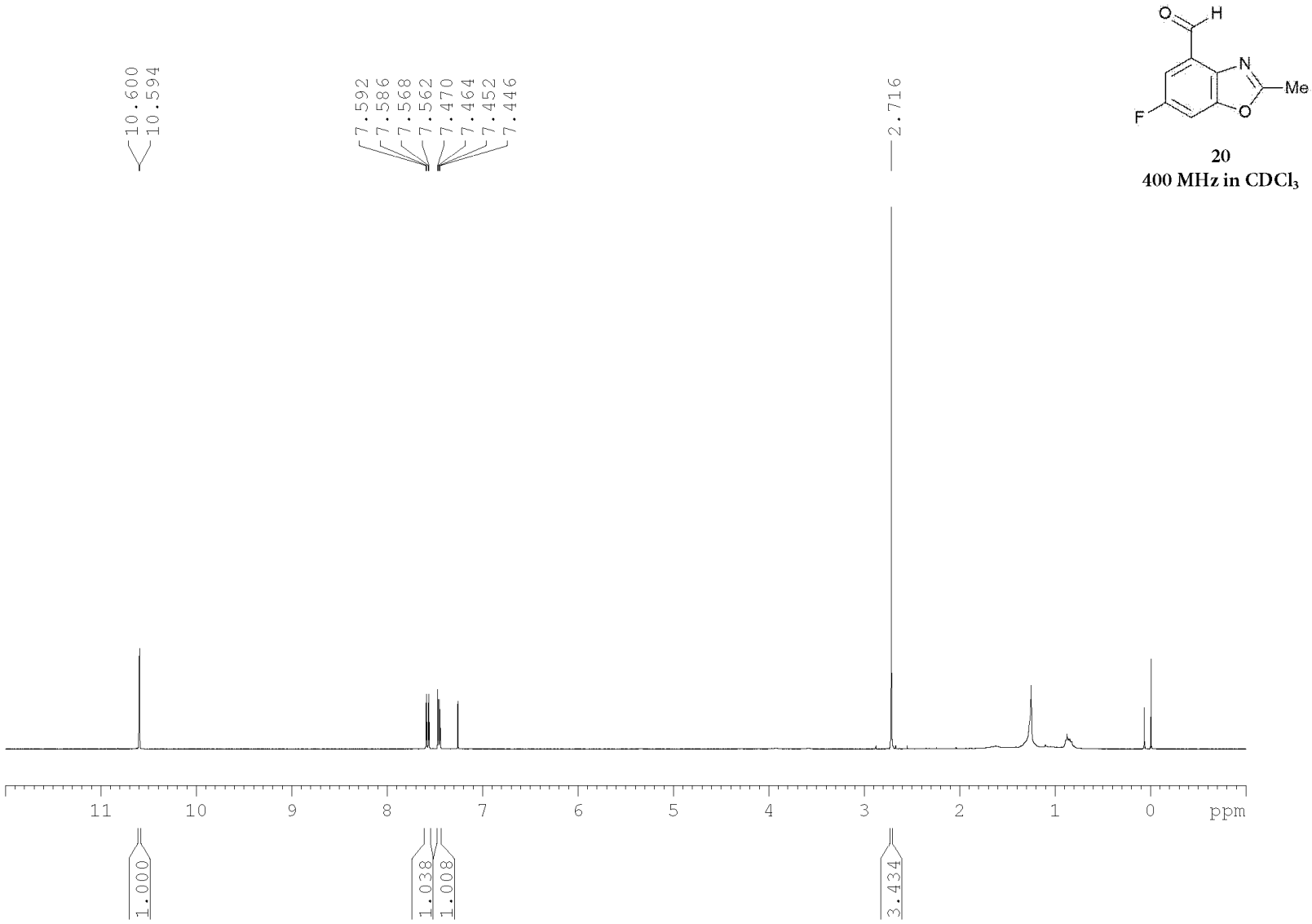
S23
400 MHz in $CDCl_3$



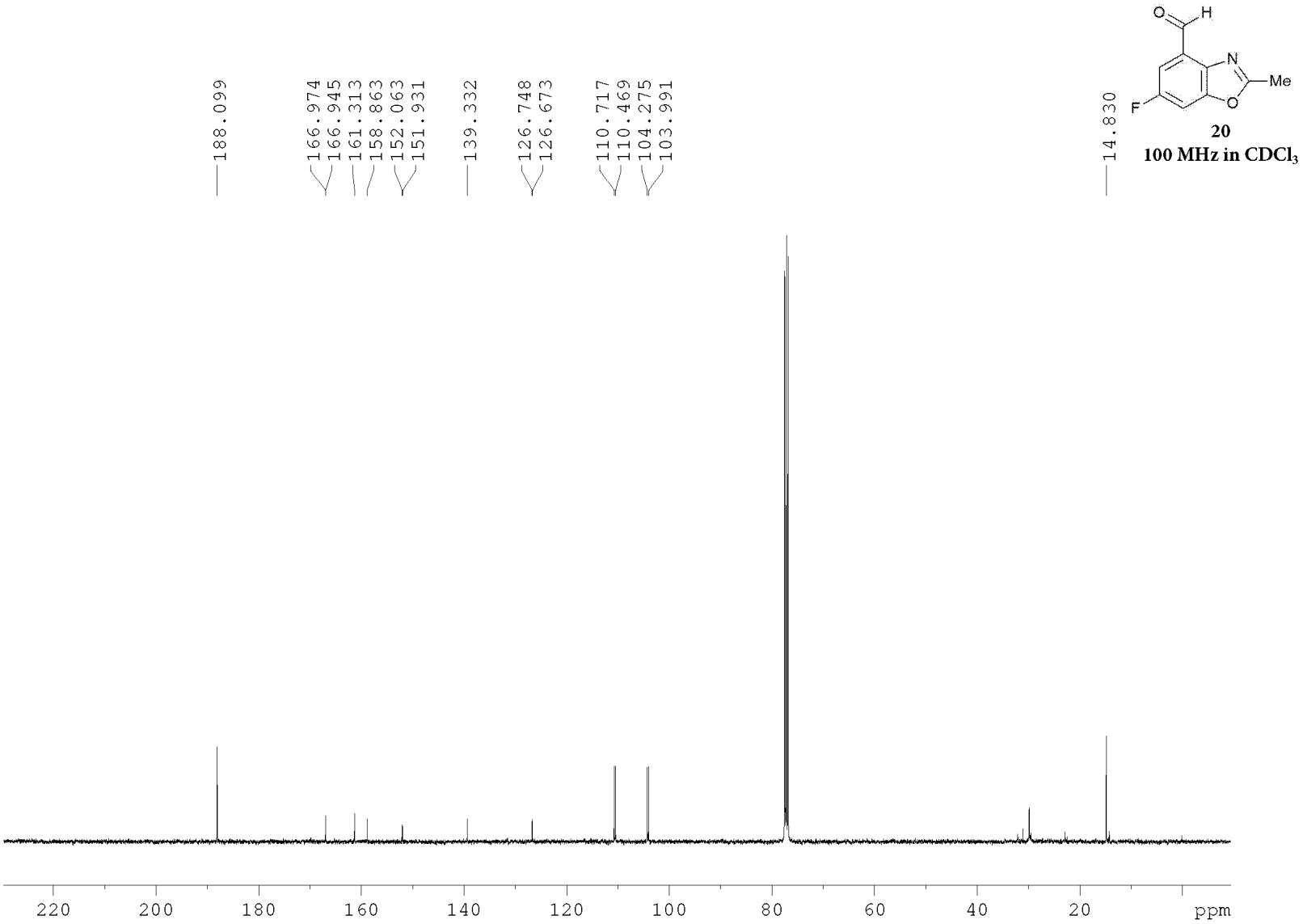
S23
100 MHz in $CDCl_3$



S24
300 MHz in $CDCl_3$

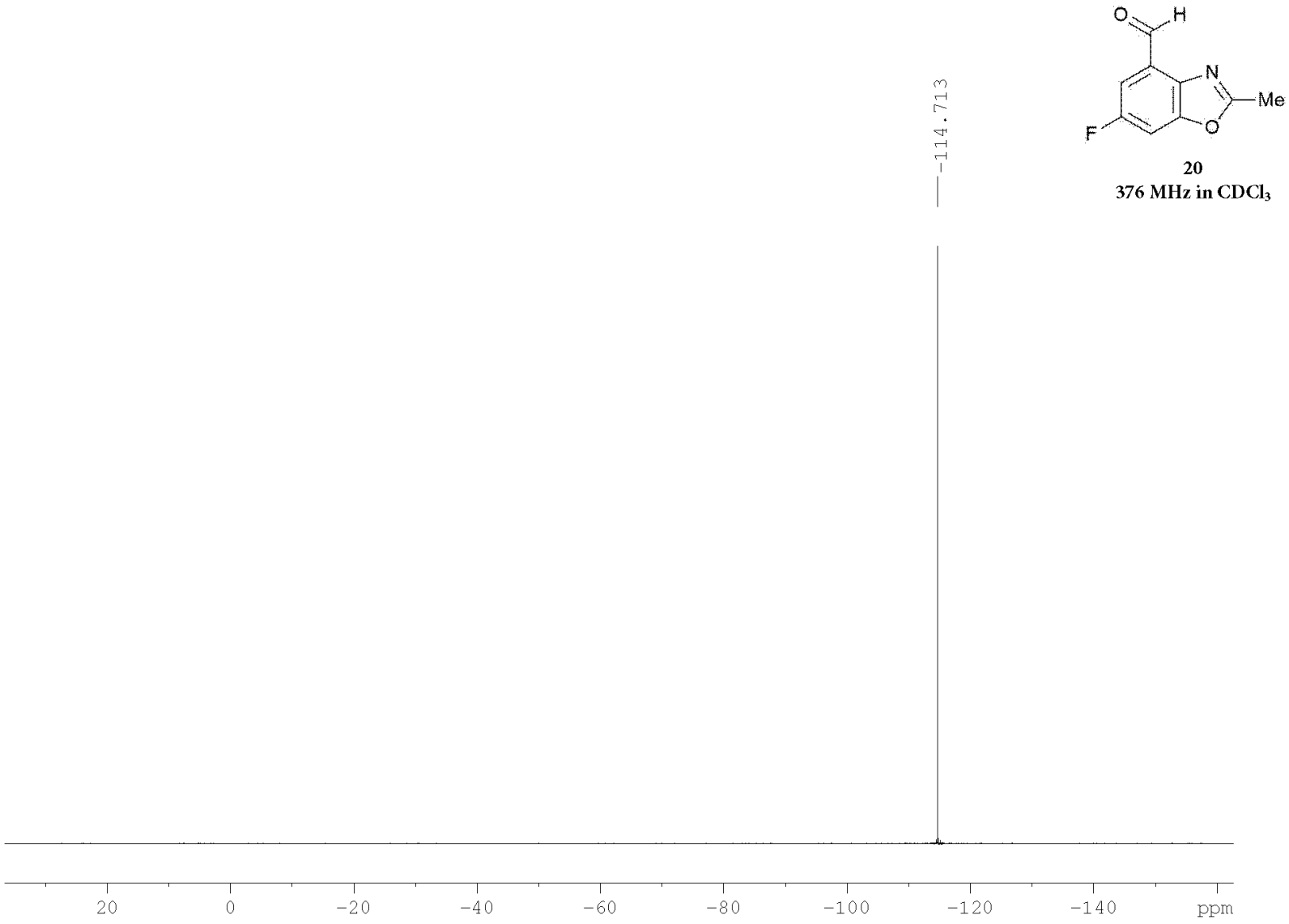


20
400 MHz in $CDCl_3$

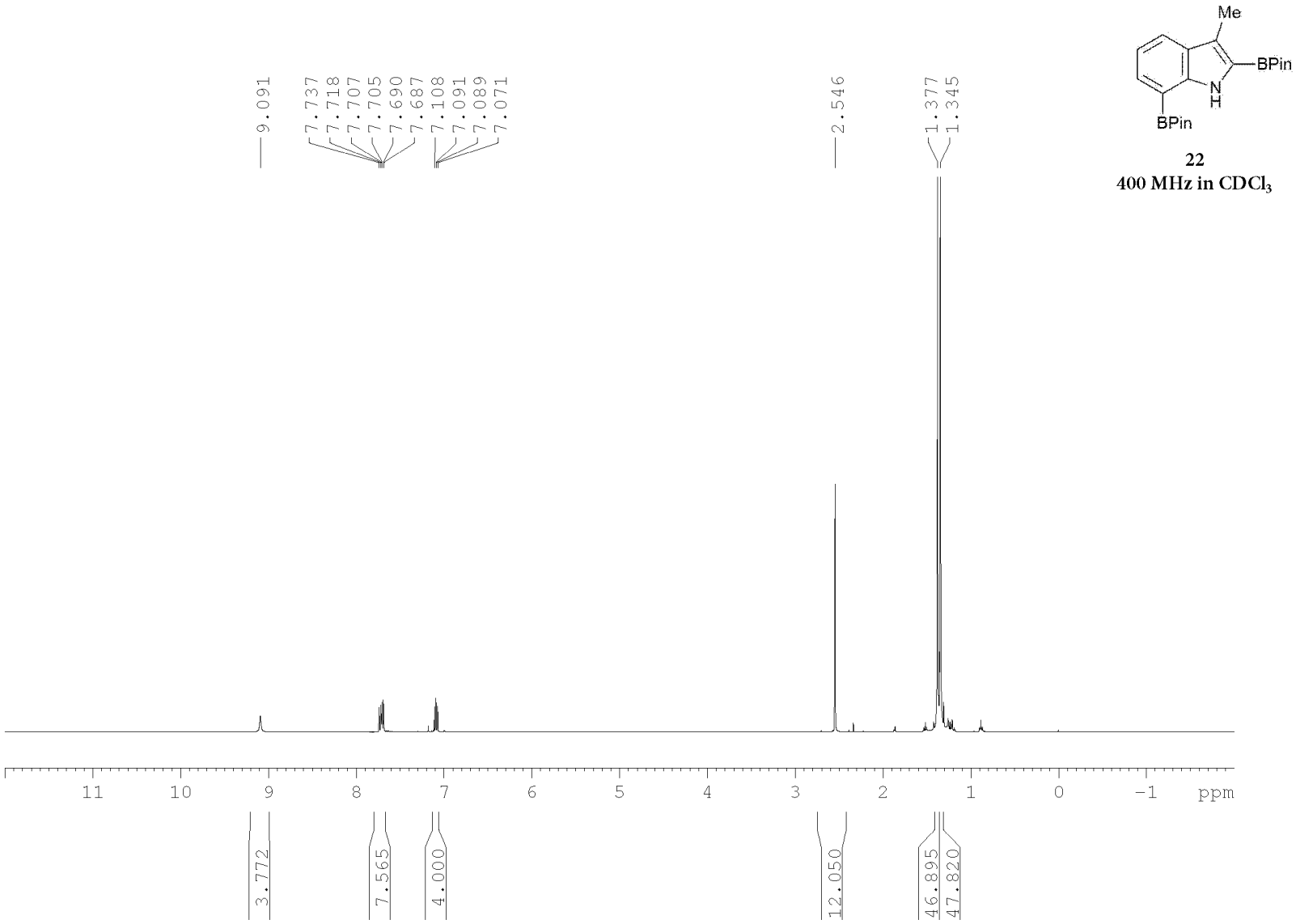


20

100 MHz in $CDCl_3$

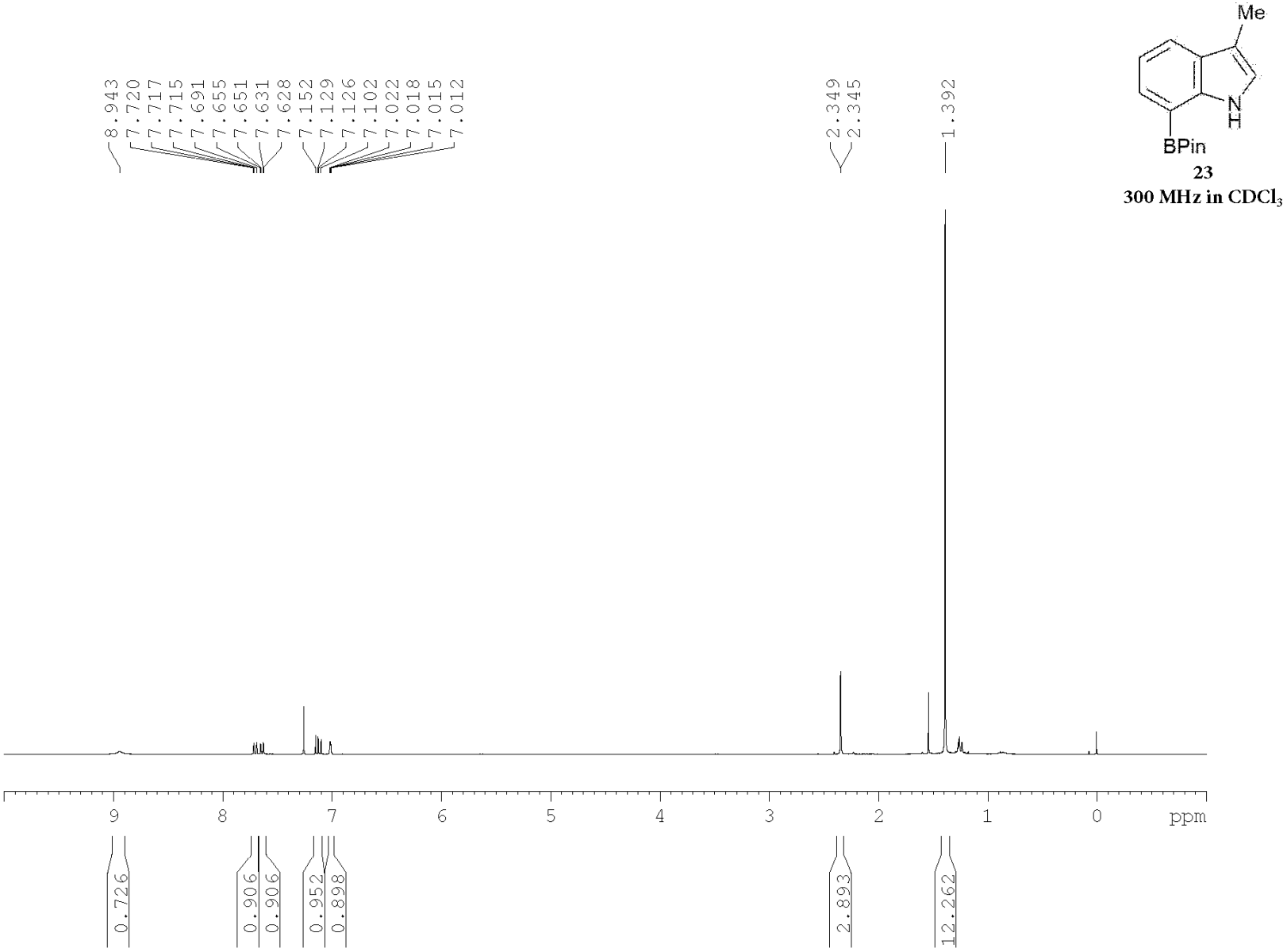


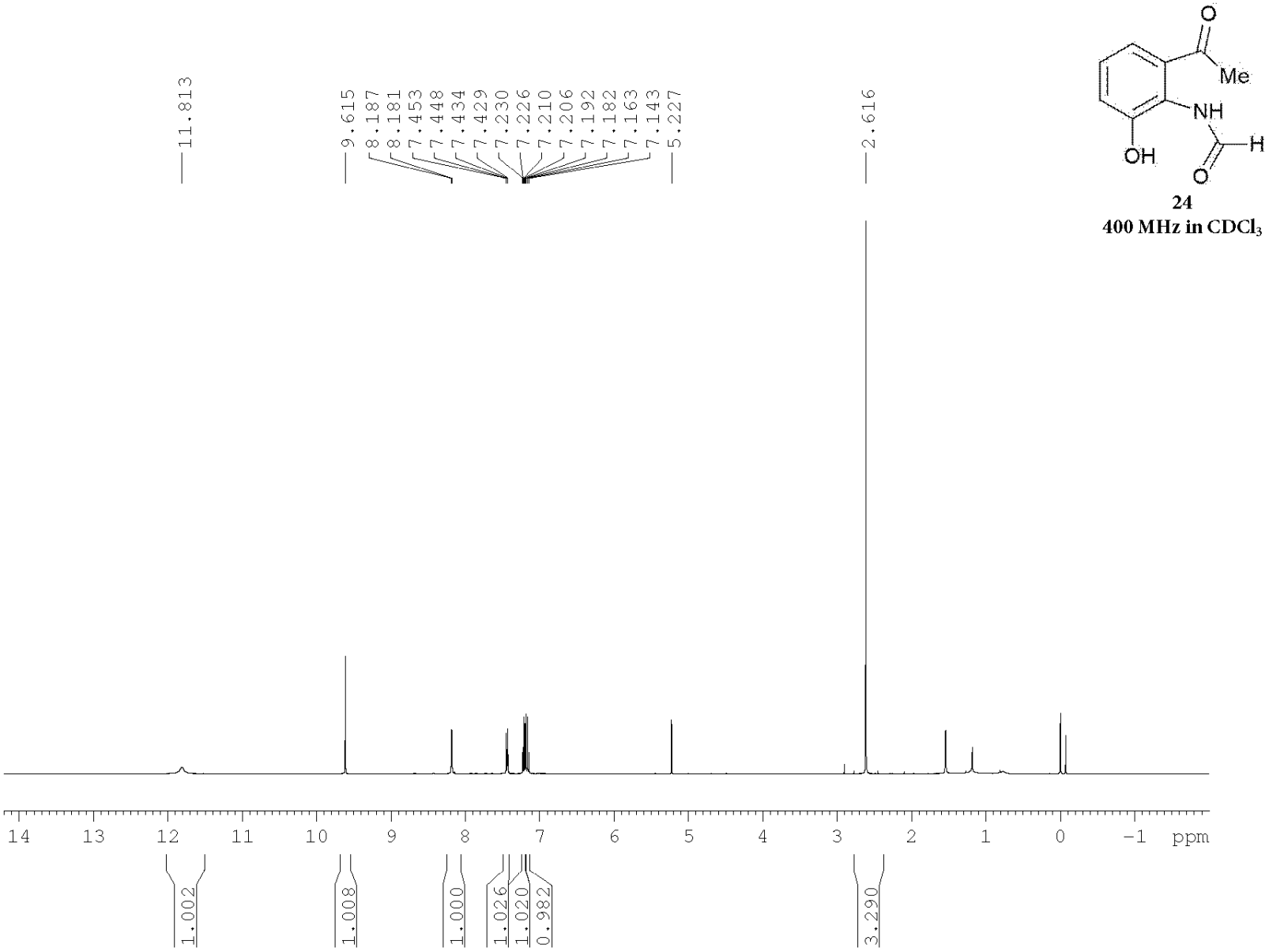
20
376 MHz in $CDCl_3$



22

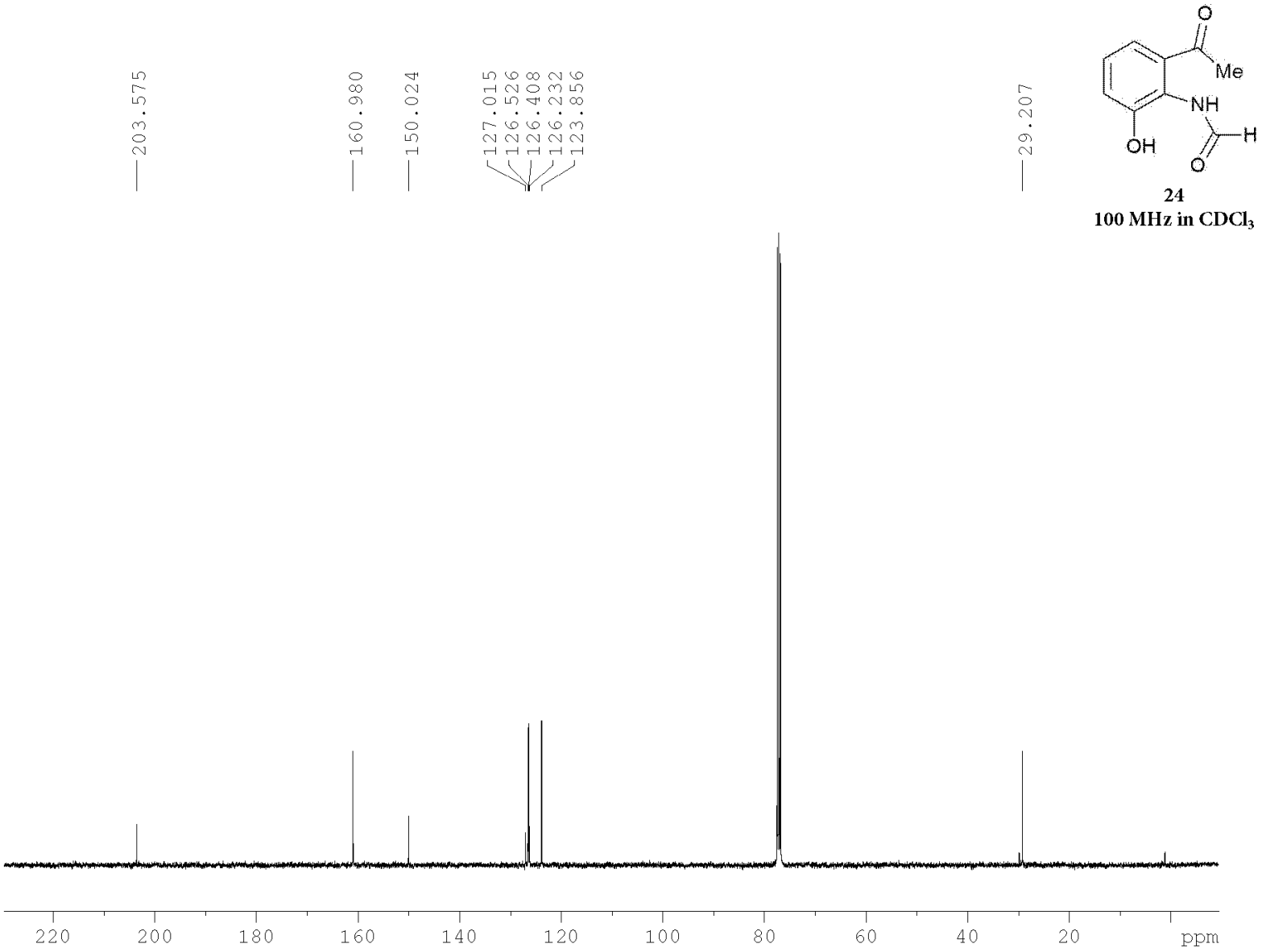
400 MHz in $CDCl_3$


8.943
7.720
7.717
7.715
7.691
7.655
7.651
7.631
7.628
7.152
7.129
7.126
7.102
7.022
7.018
7.015
7.012
2.349
2.345
1.392
Me
N
H
BPin
23
300 MHz in CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
0.726
0.906
0.906
0.952
0.898
2.893
12.262

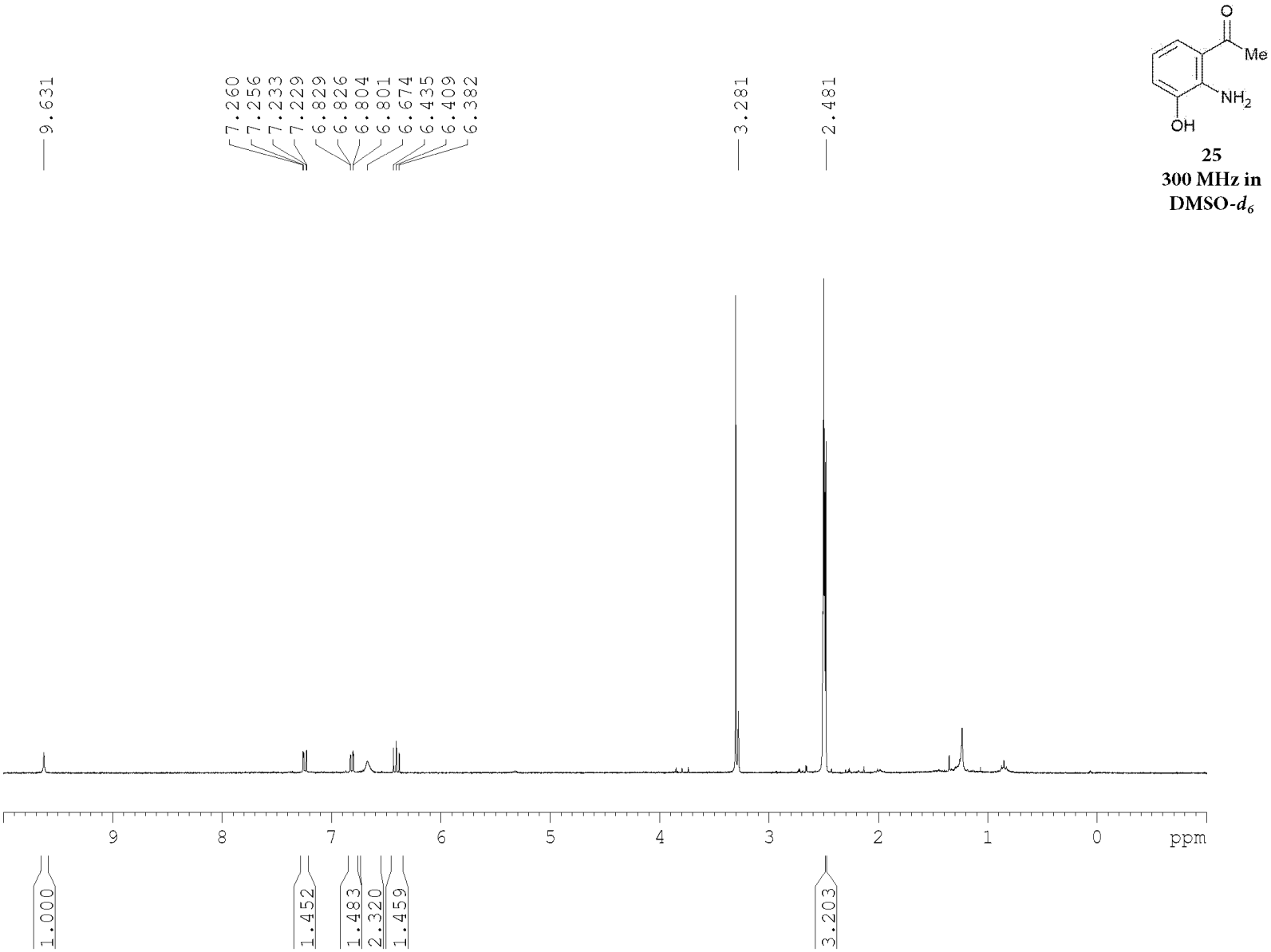


24

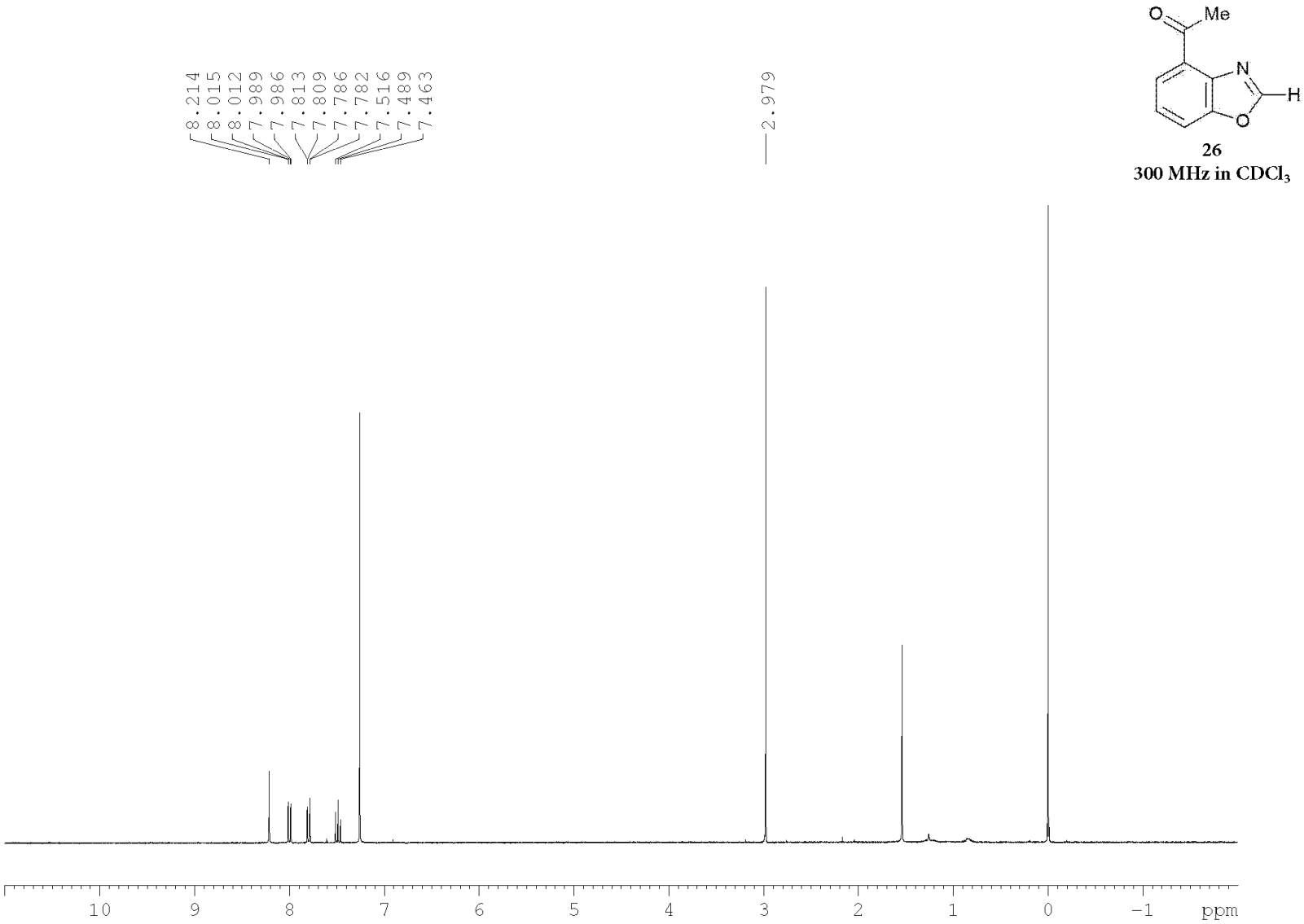
400 MHz in $CDCl_3$



24
100 MHz in $CDCl_3$

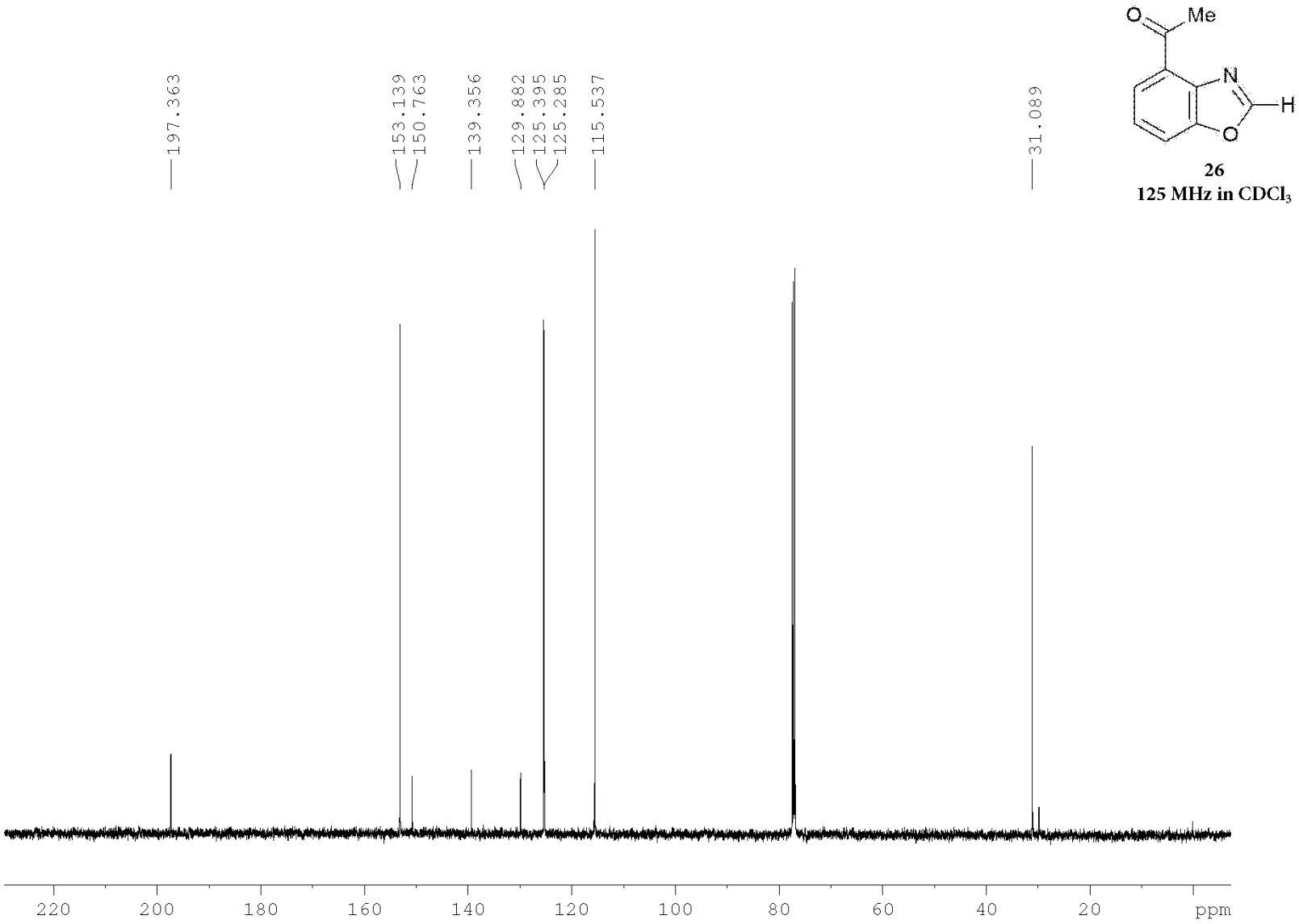


25
300 MHz in
DMSO-d_6



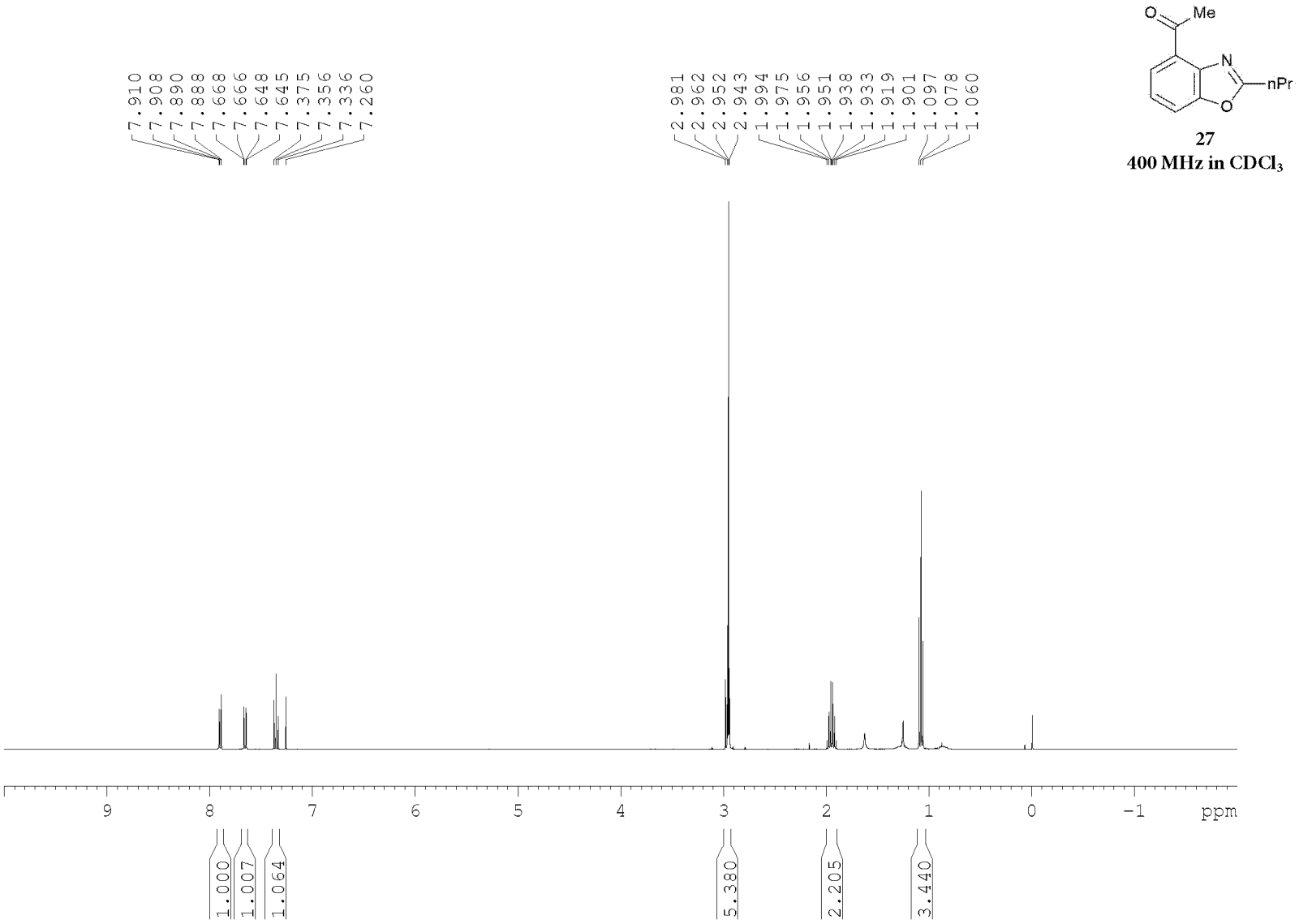
26

300 MHz in $CDCl_3$



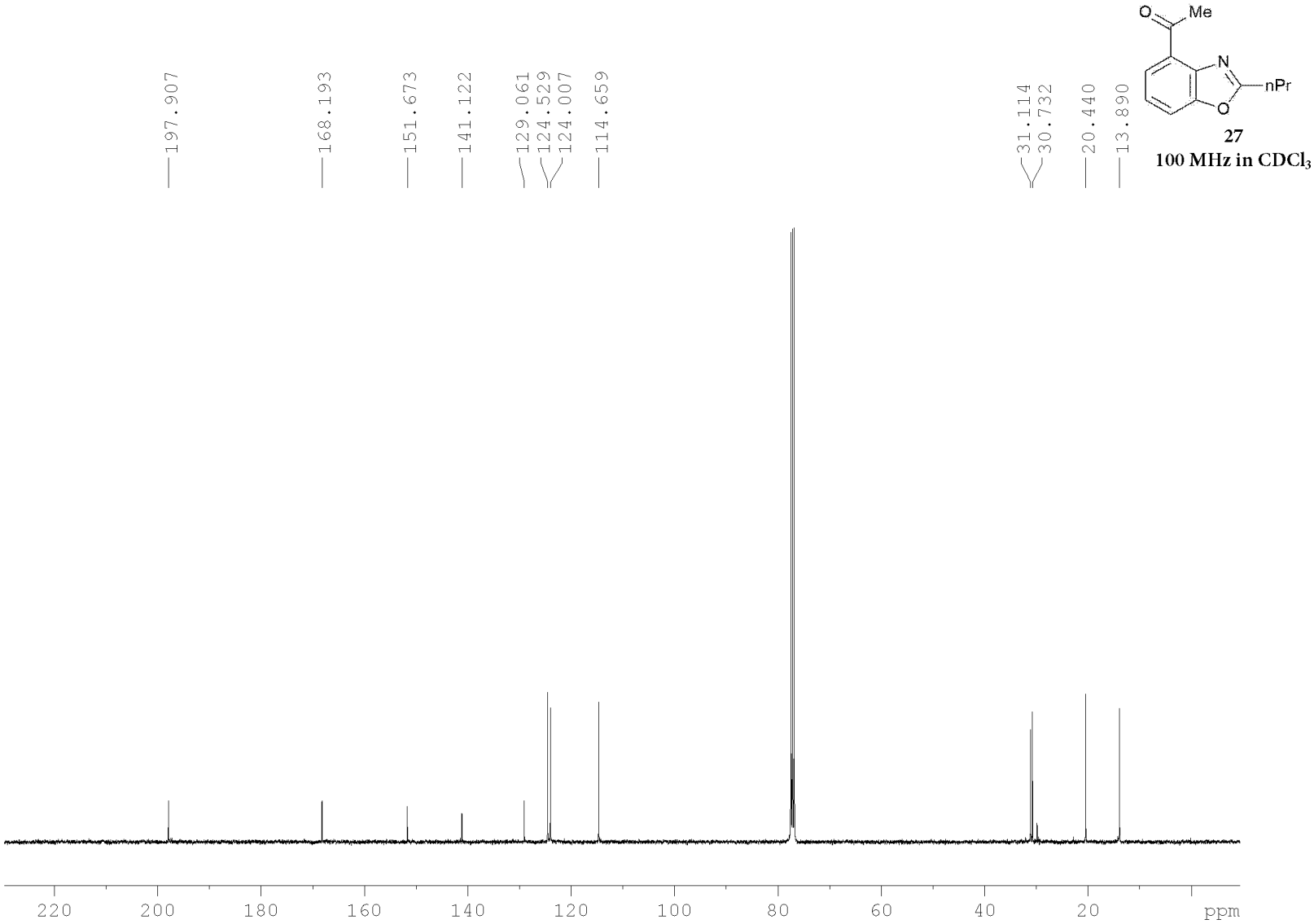
26

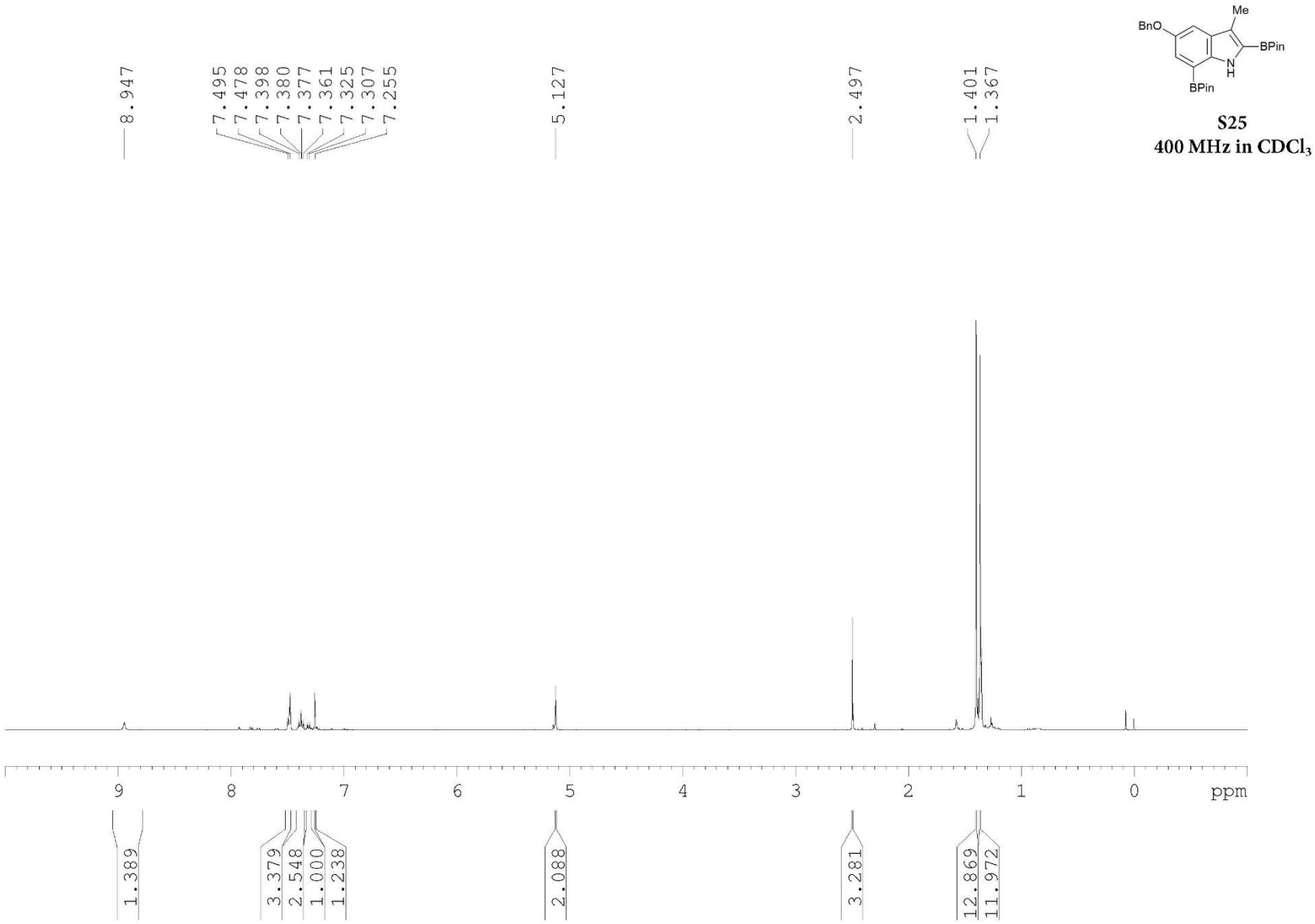
125 MHz in $CDCl_3$



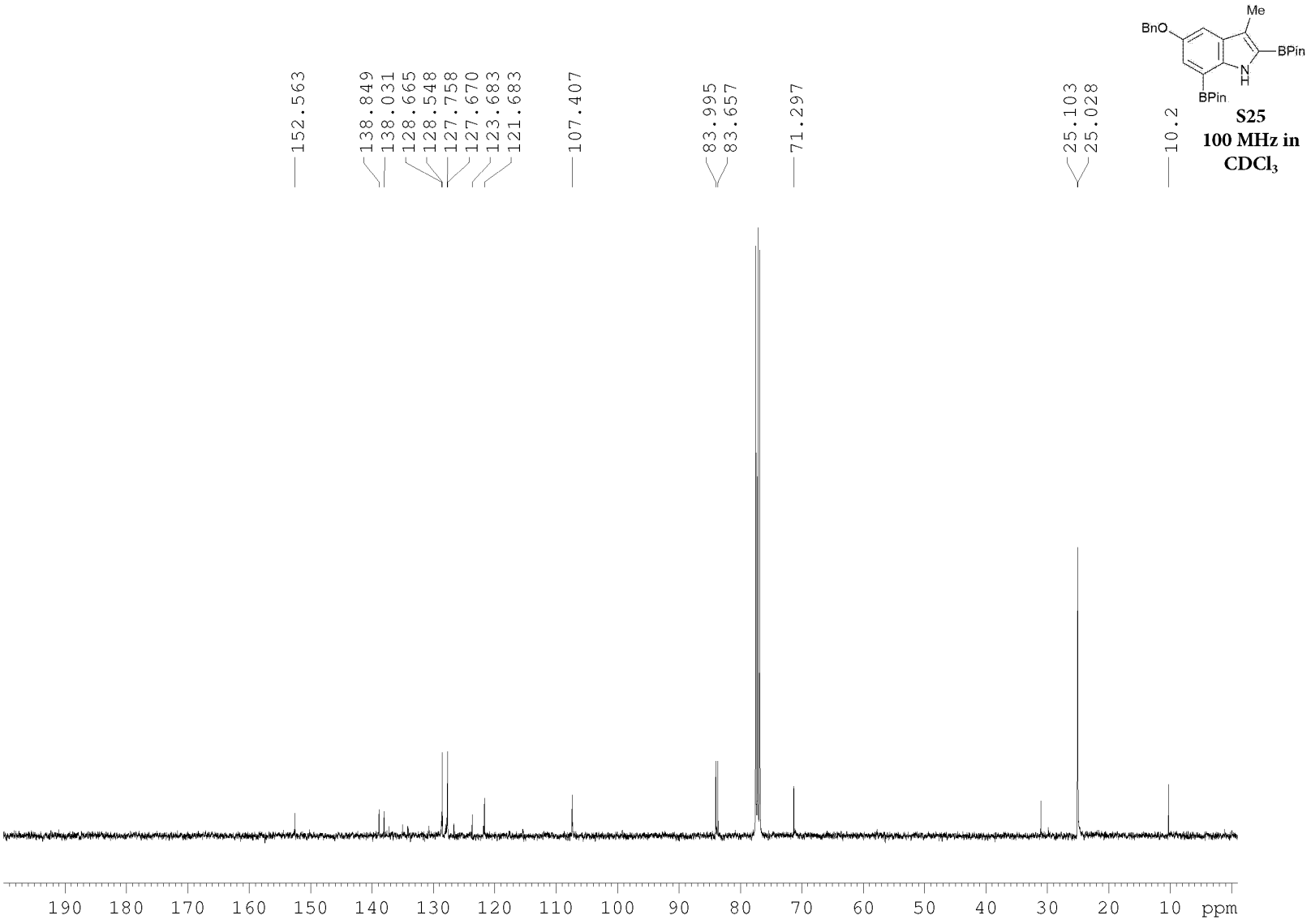
27

400 MHz in $CDCl_3$

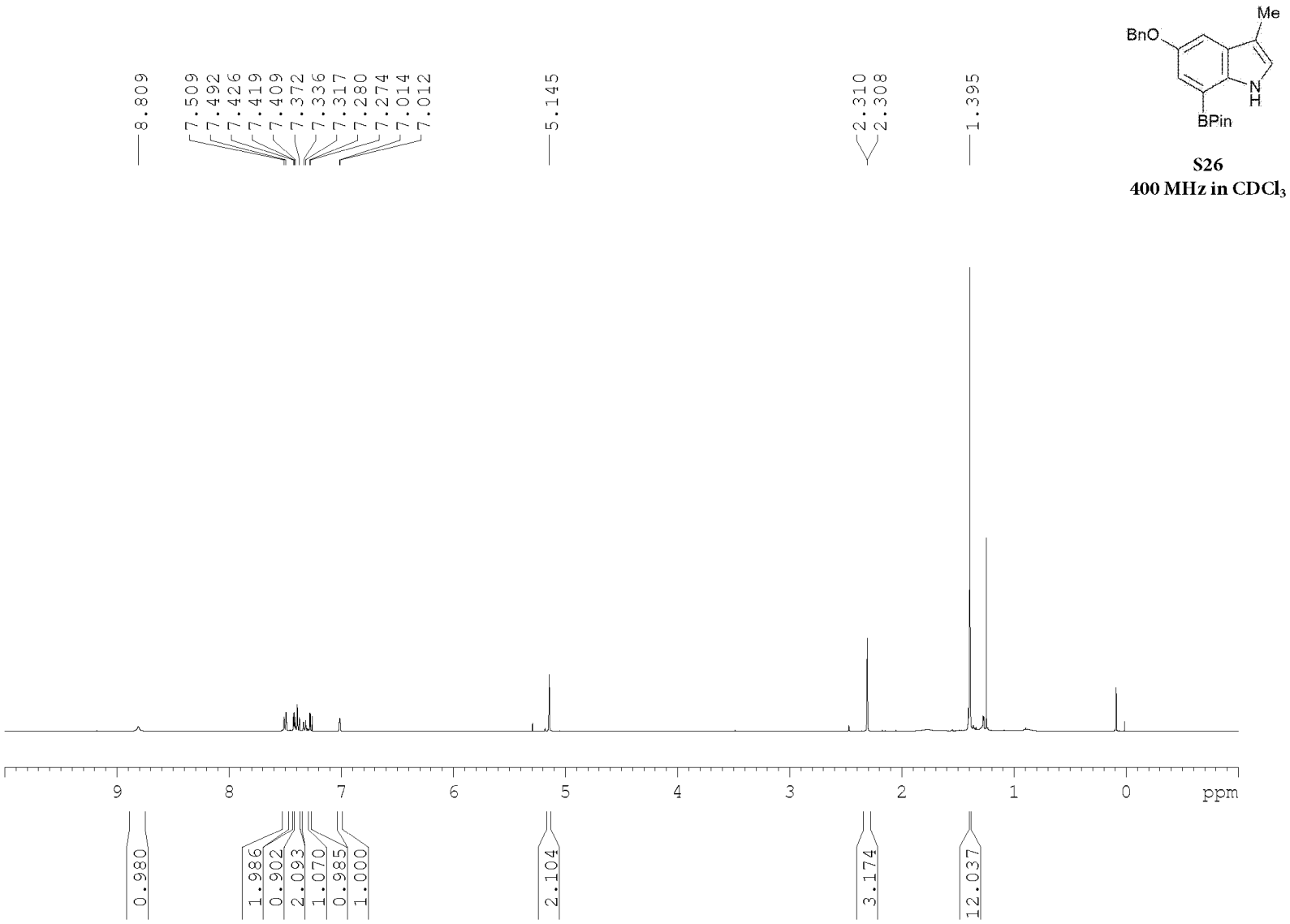

197.907
168.193
151.673
141.122
129.061
124.529
124.007
114.659
31.114
30.732
20.440
13.890
O
Me
N
O
nPr
27
100 MHz in CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm



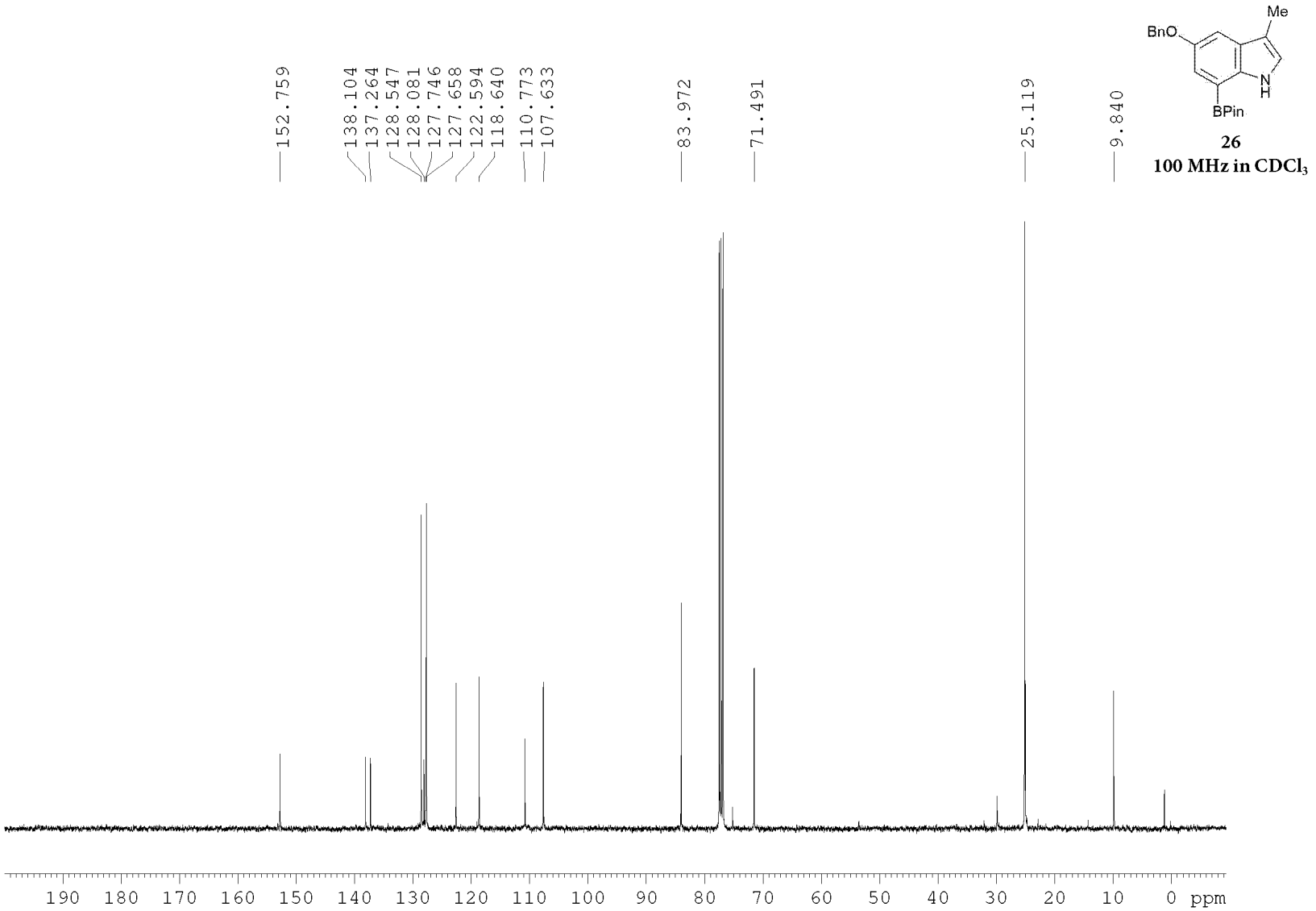
S25
400 MHz in $CDCl_3$

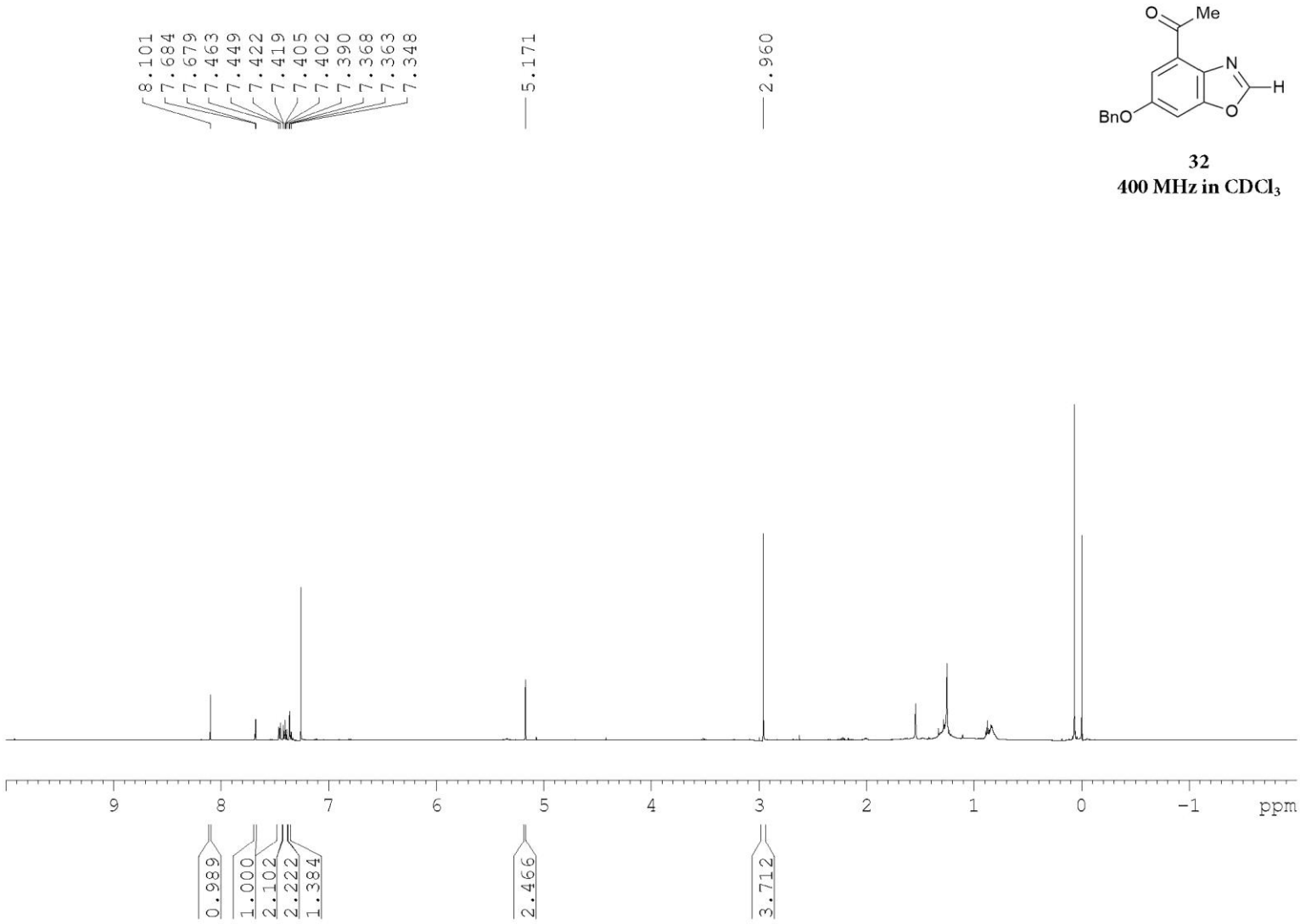


S25
100 MHz in $CDCl_3$

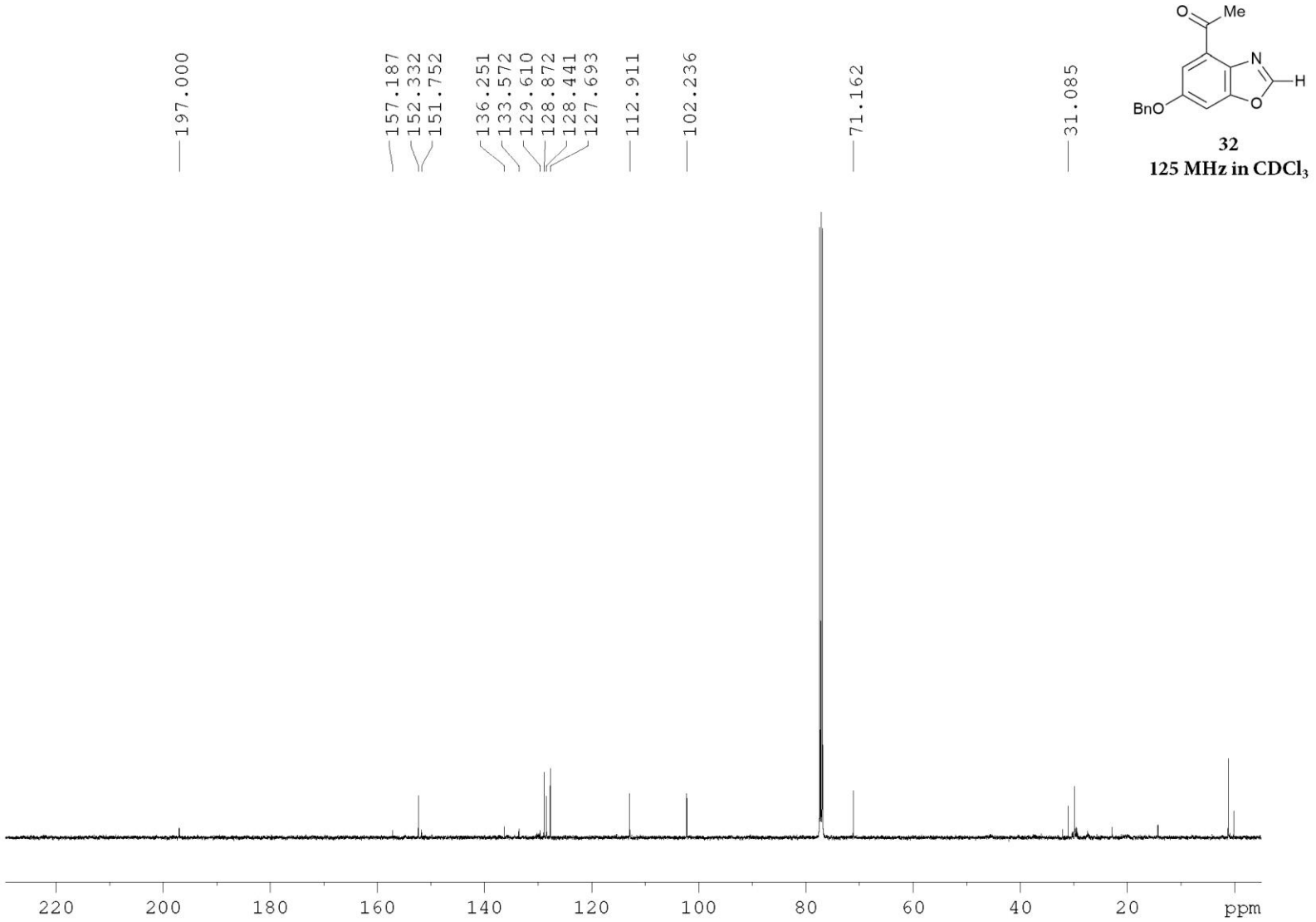


S26
400 MHz in $CDCl_3$


152.759
138.104
137.264
128.547
128.081
127.746
127.658
122.594
118.640
110.773
107.633
83.972
71.491
25.119
9.840
Me
BnO
N
H
BPin
26
100 MHz in CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

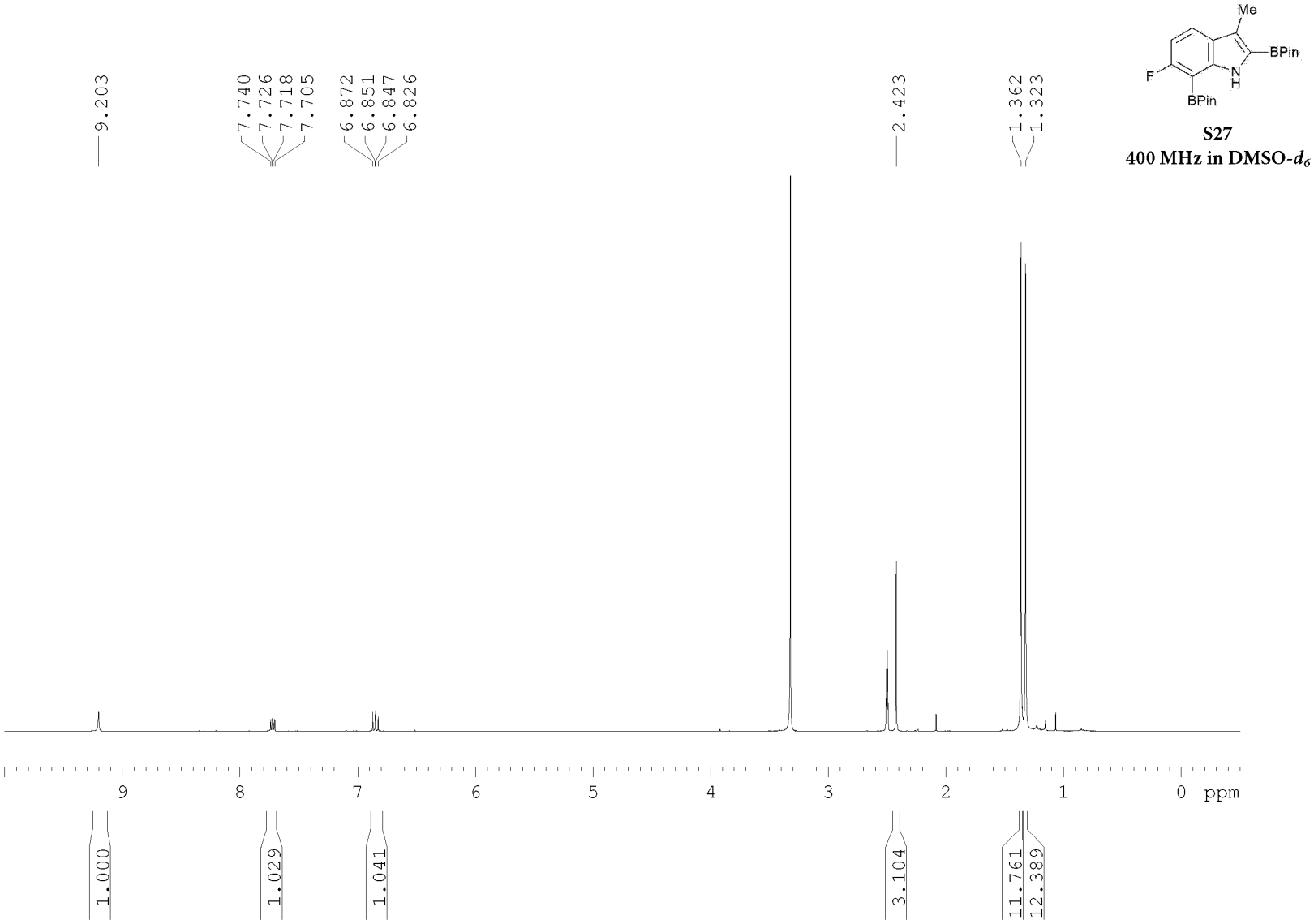


32
400 MHz in $CDCl_3$

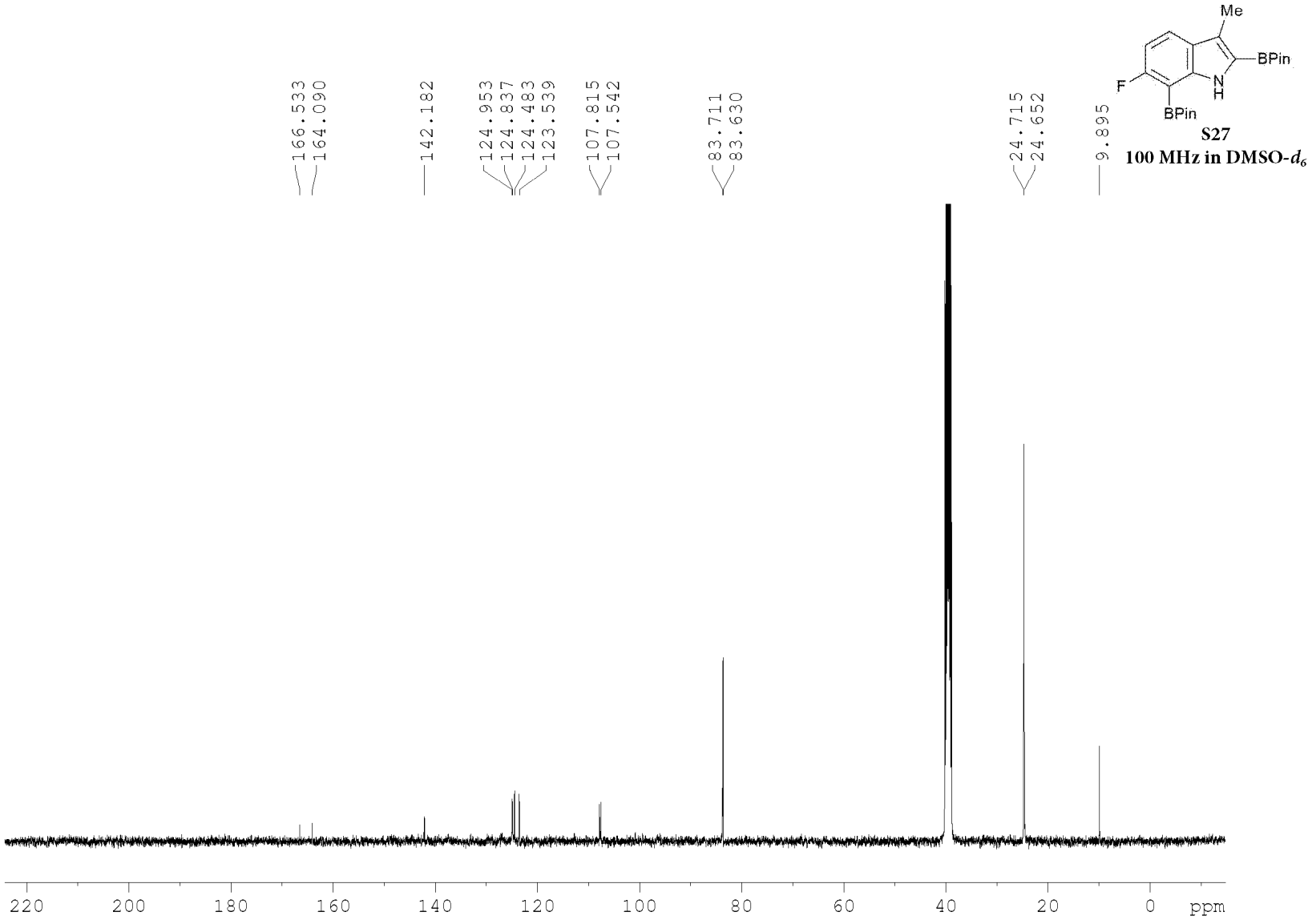


32

125 MHz in $CDCl_3$

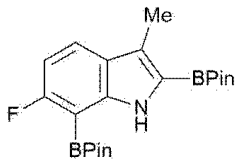


S27
400 MHz in DMSO-d_6

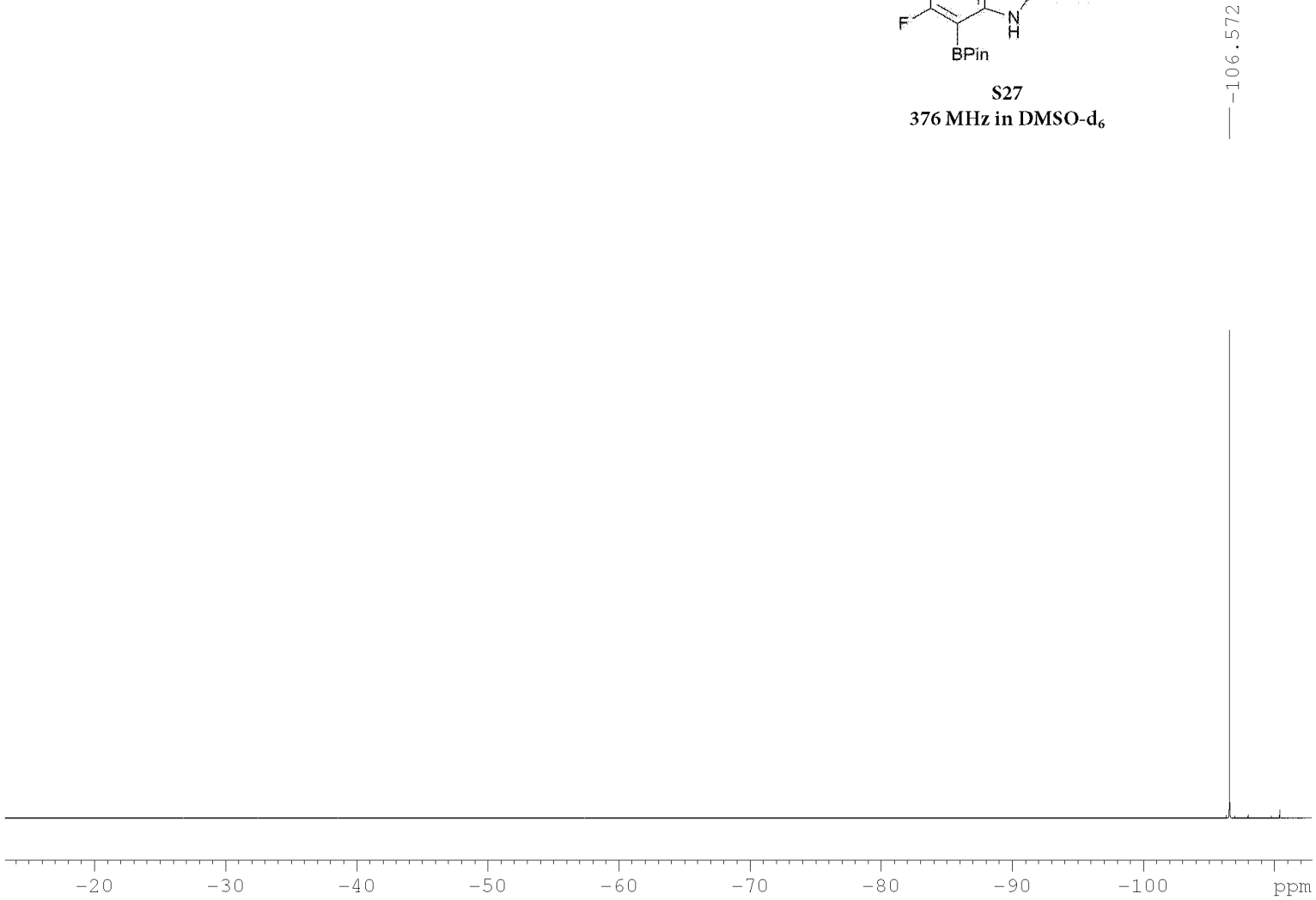


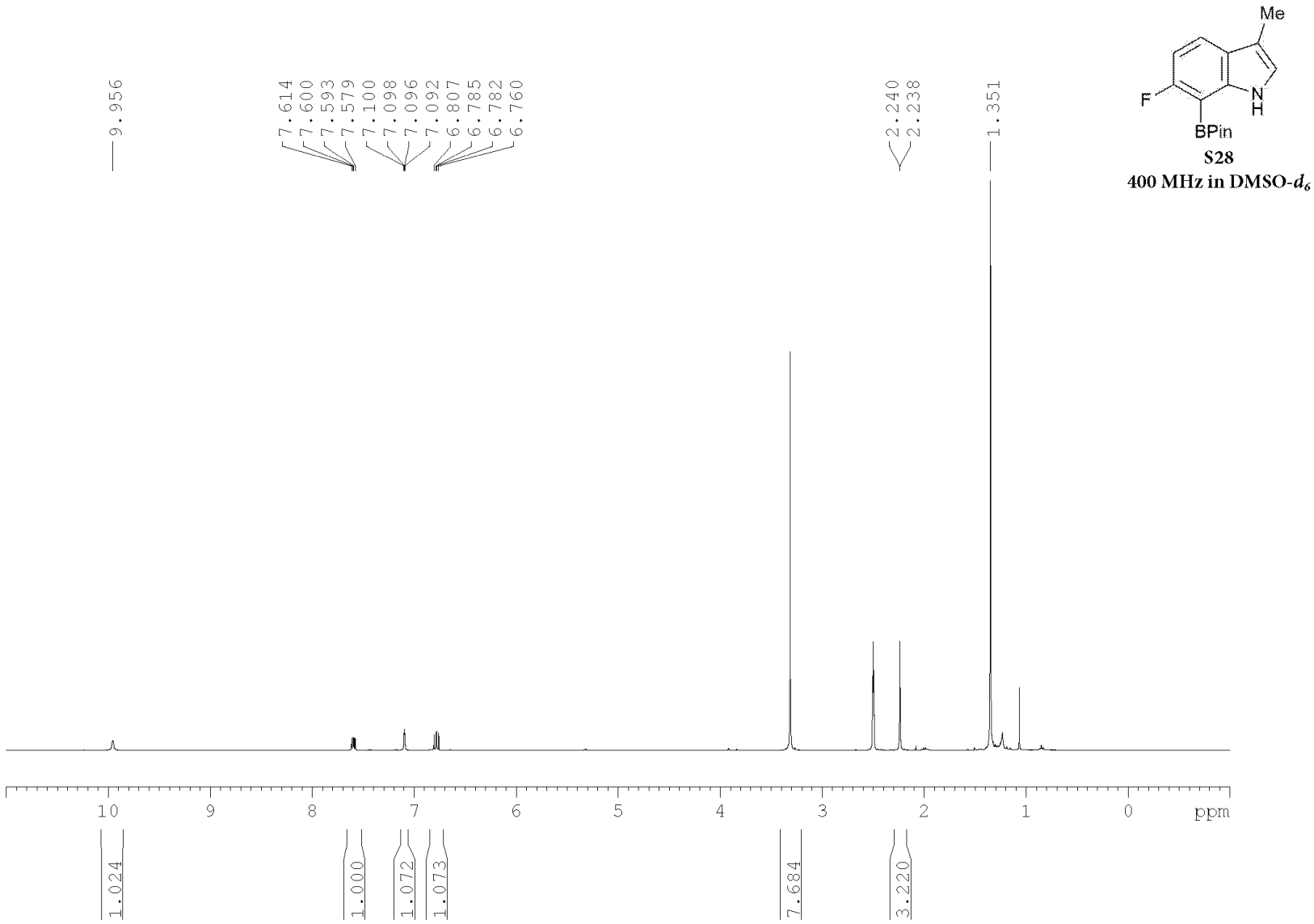
S27

100 MHz in DMSO-d_6



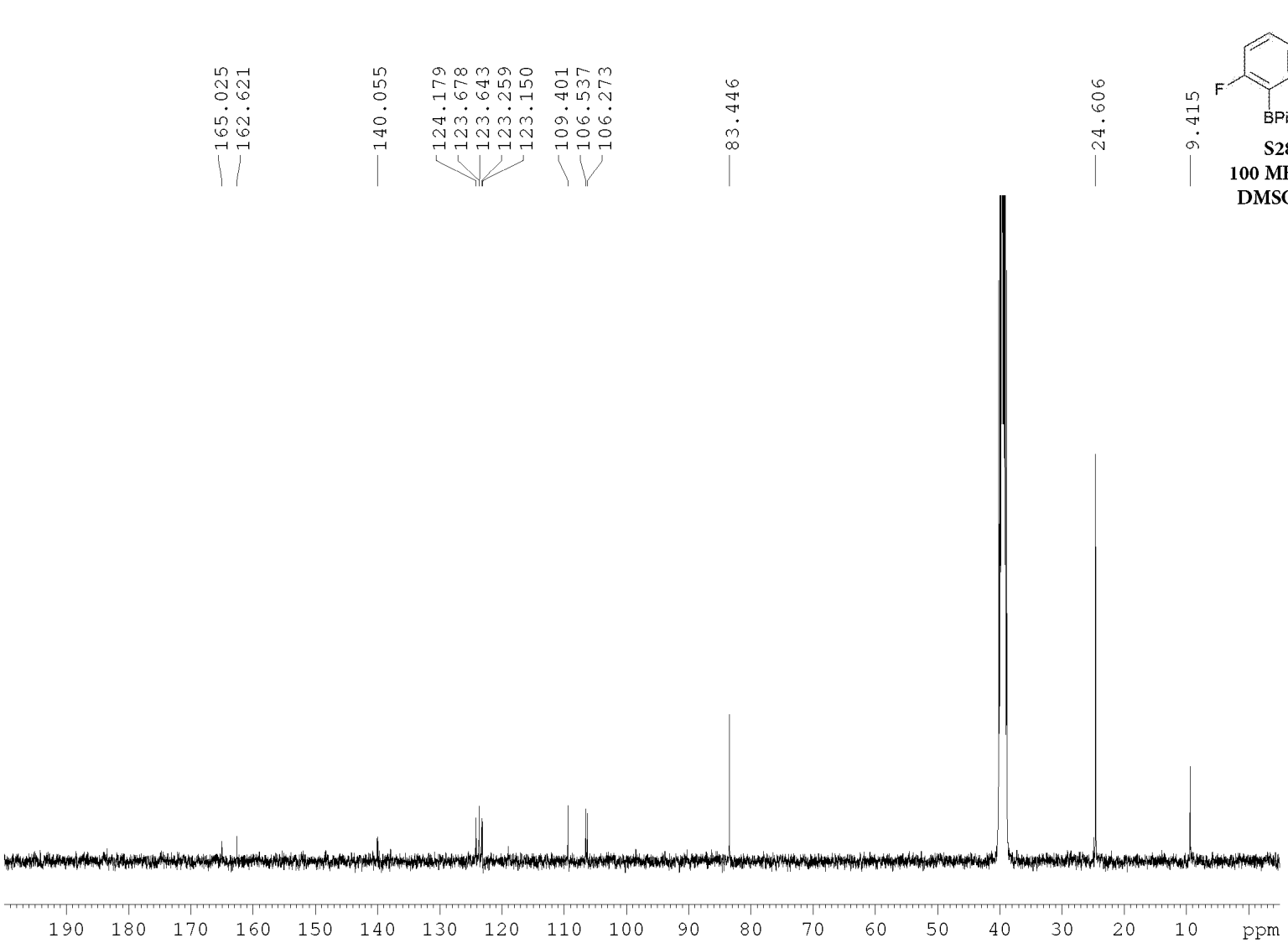
S27
376 MHz in DMSO-d_6



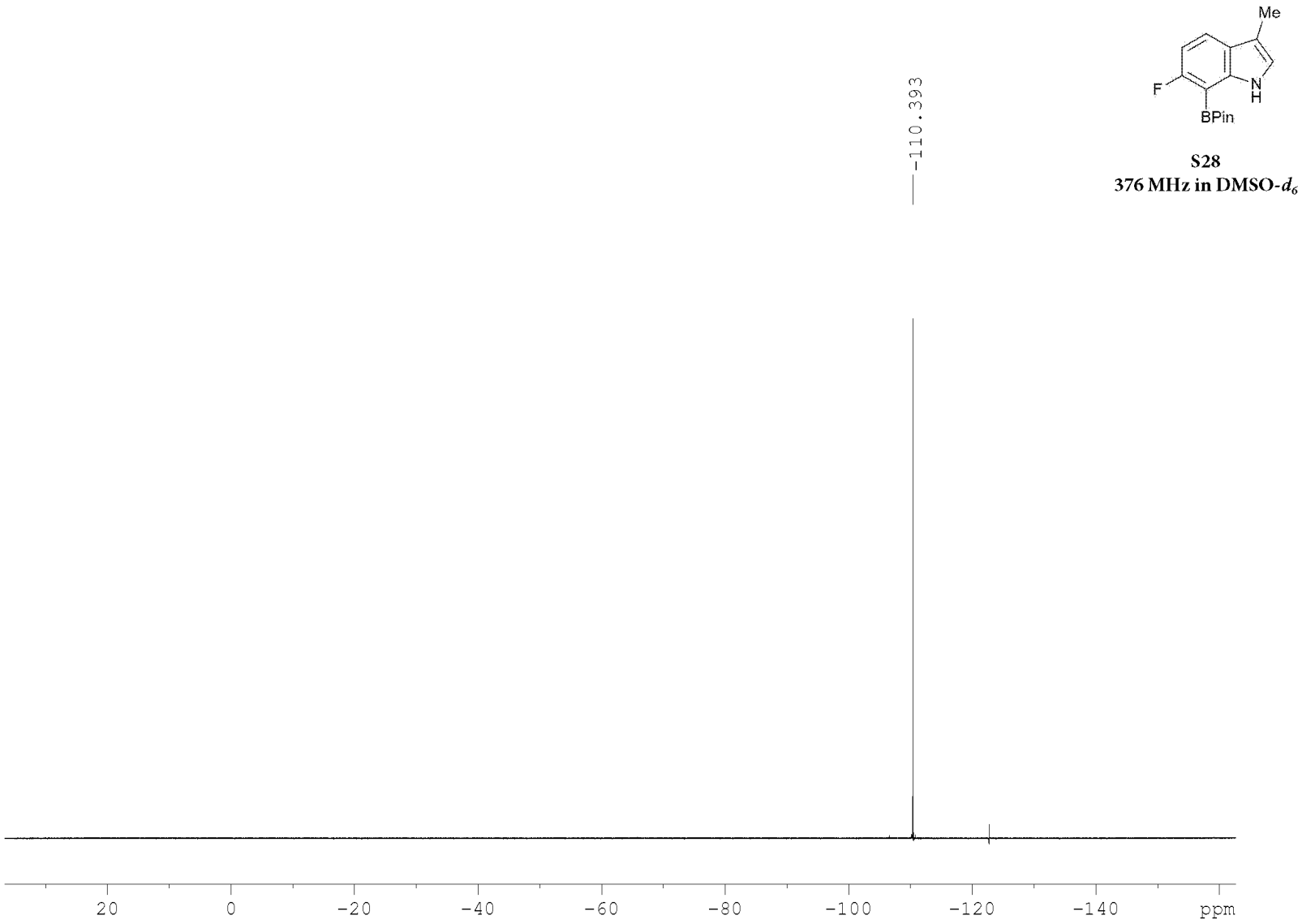


S28

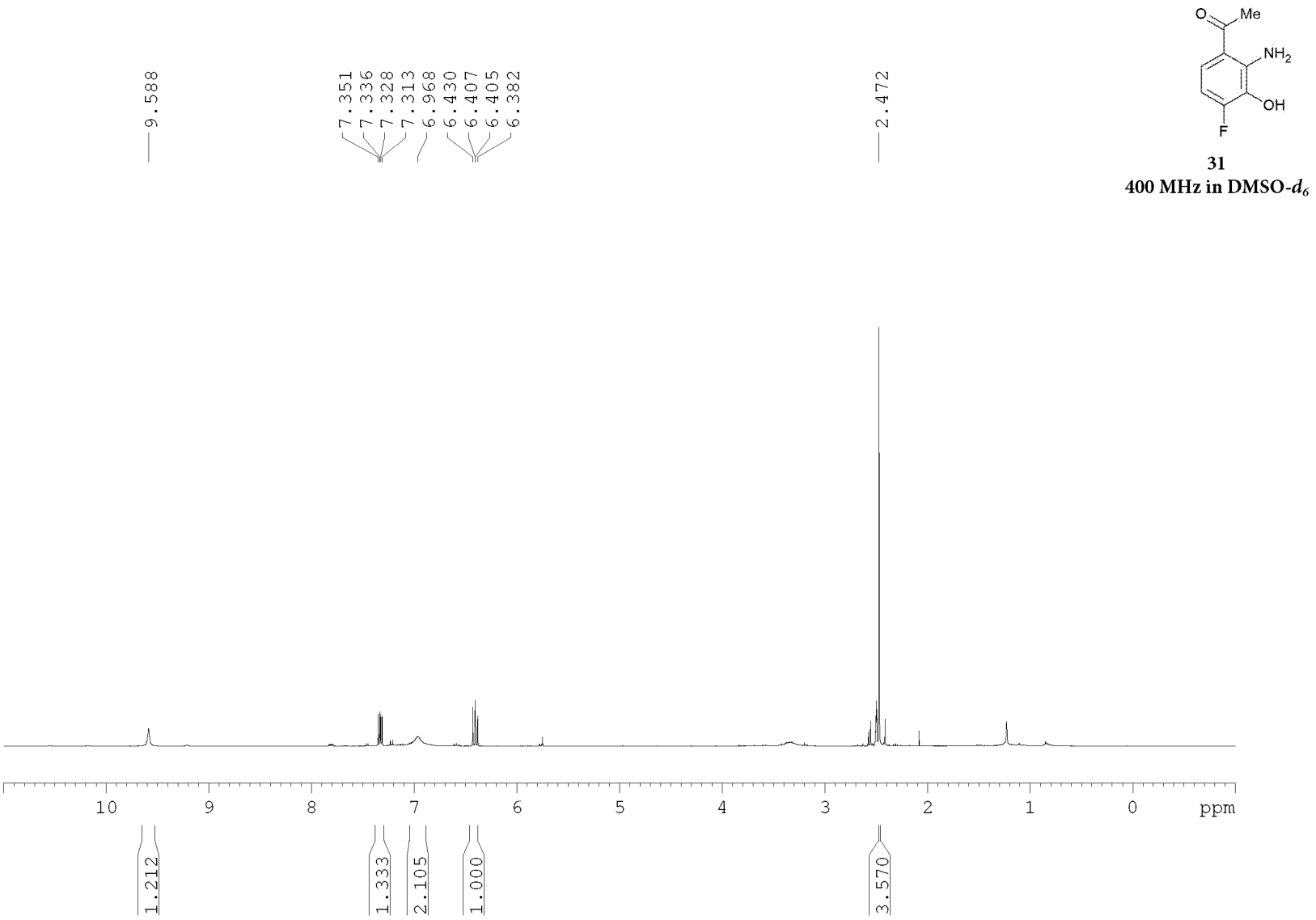
400 MHz in DMSO-d_6



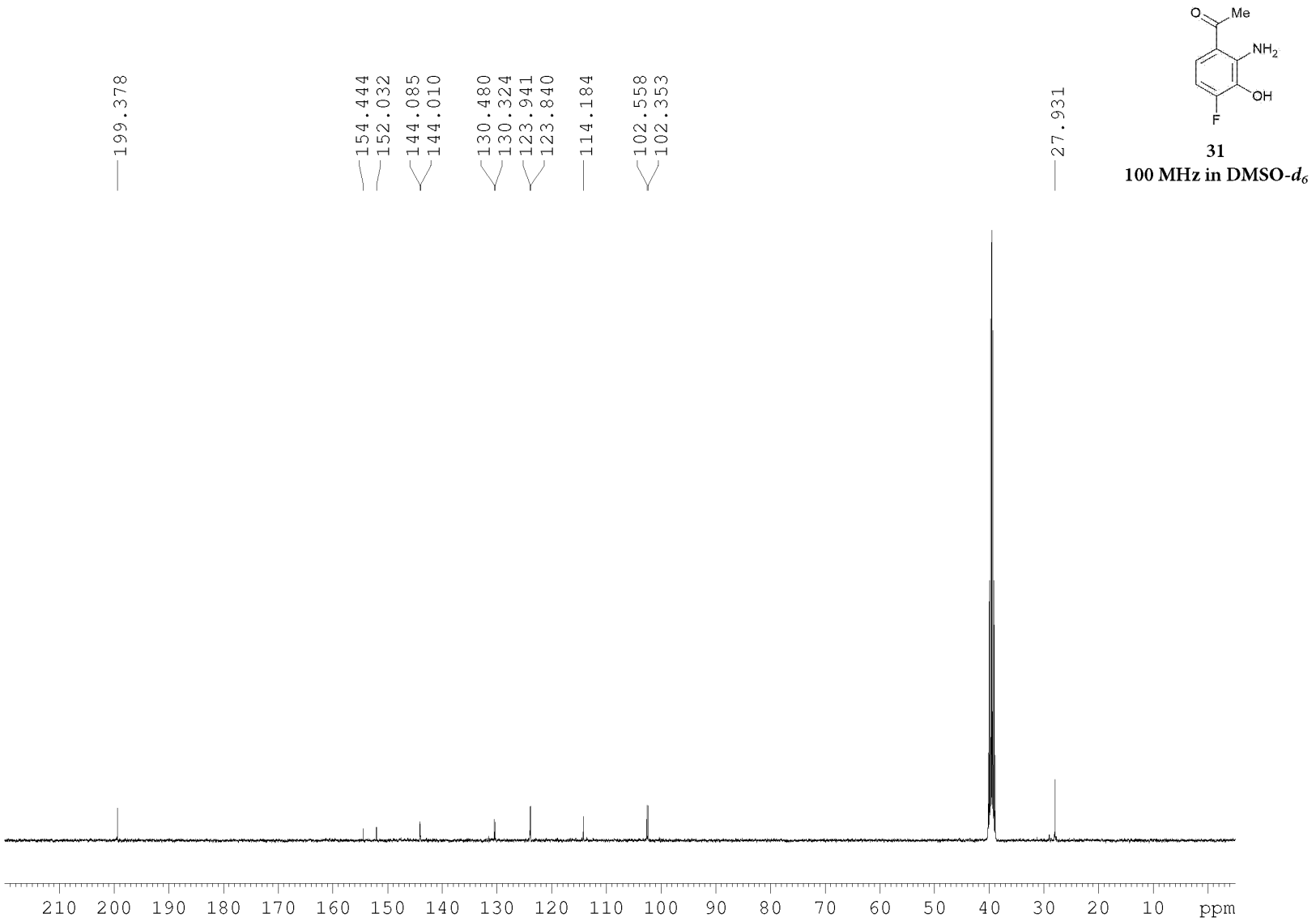
S28
100 MHz in
DMSO-d_6



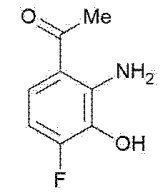
S28
376 MHz in DMSO-d_6



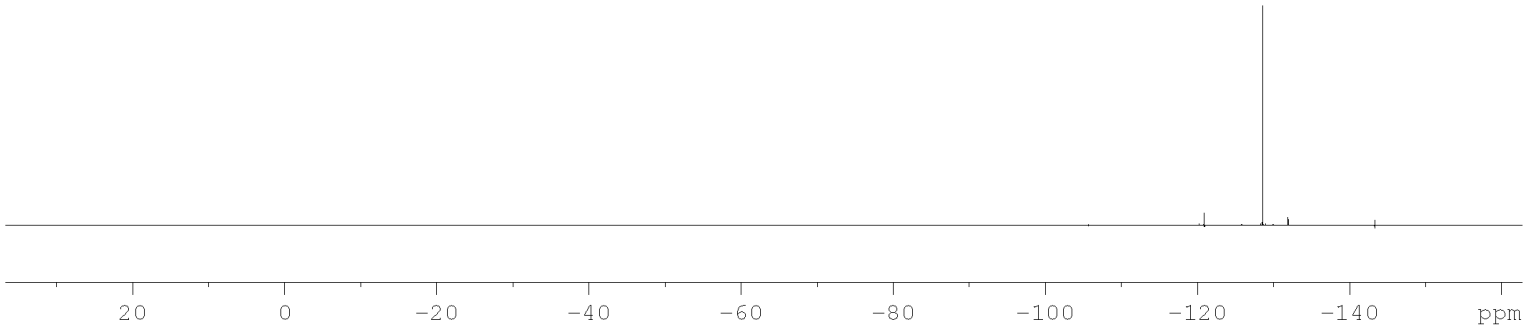
31
400 MHz in DMSO-d_6

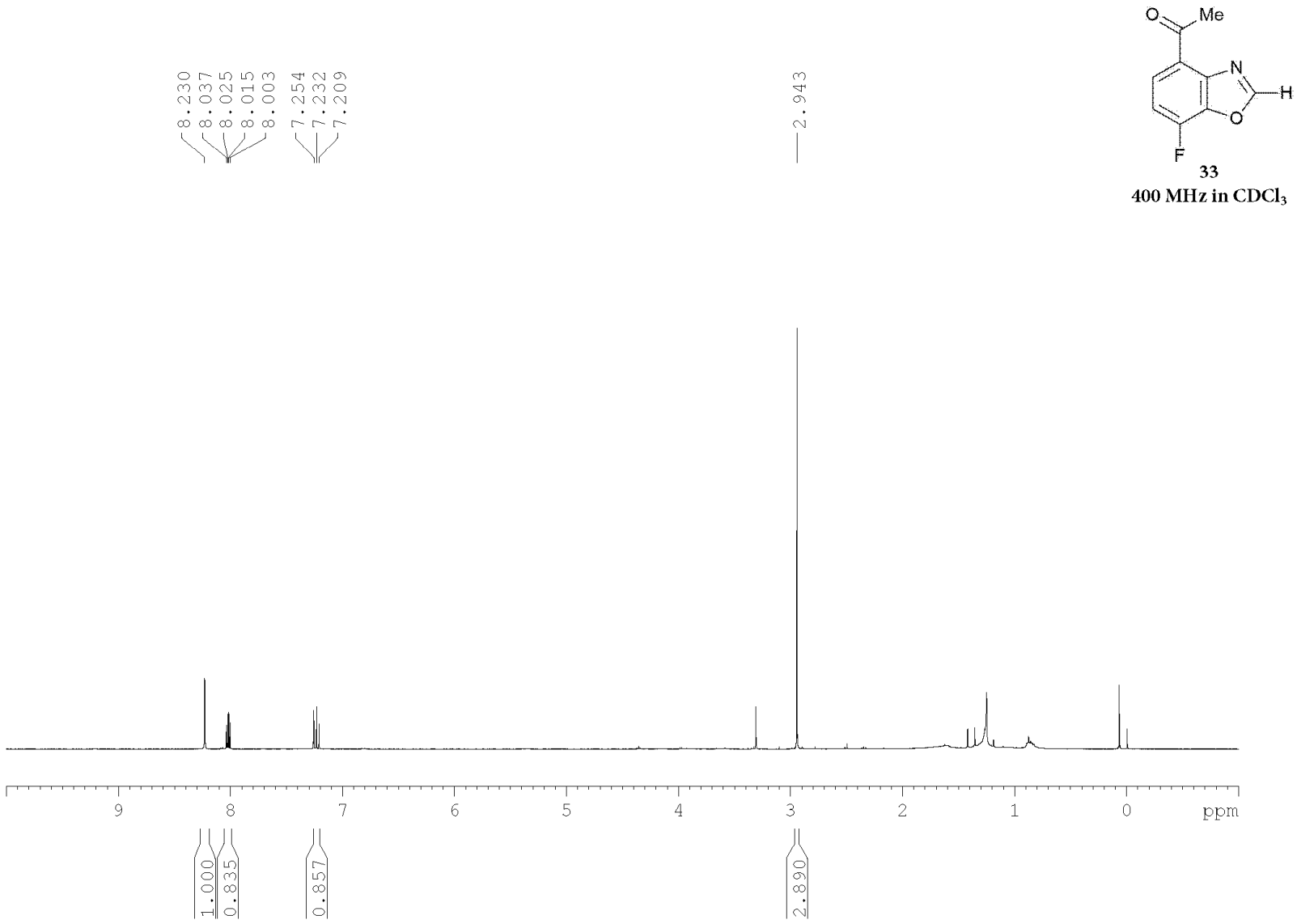


31
100 MHz in DMSO-d_6



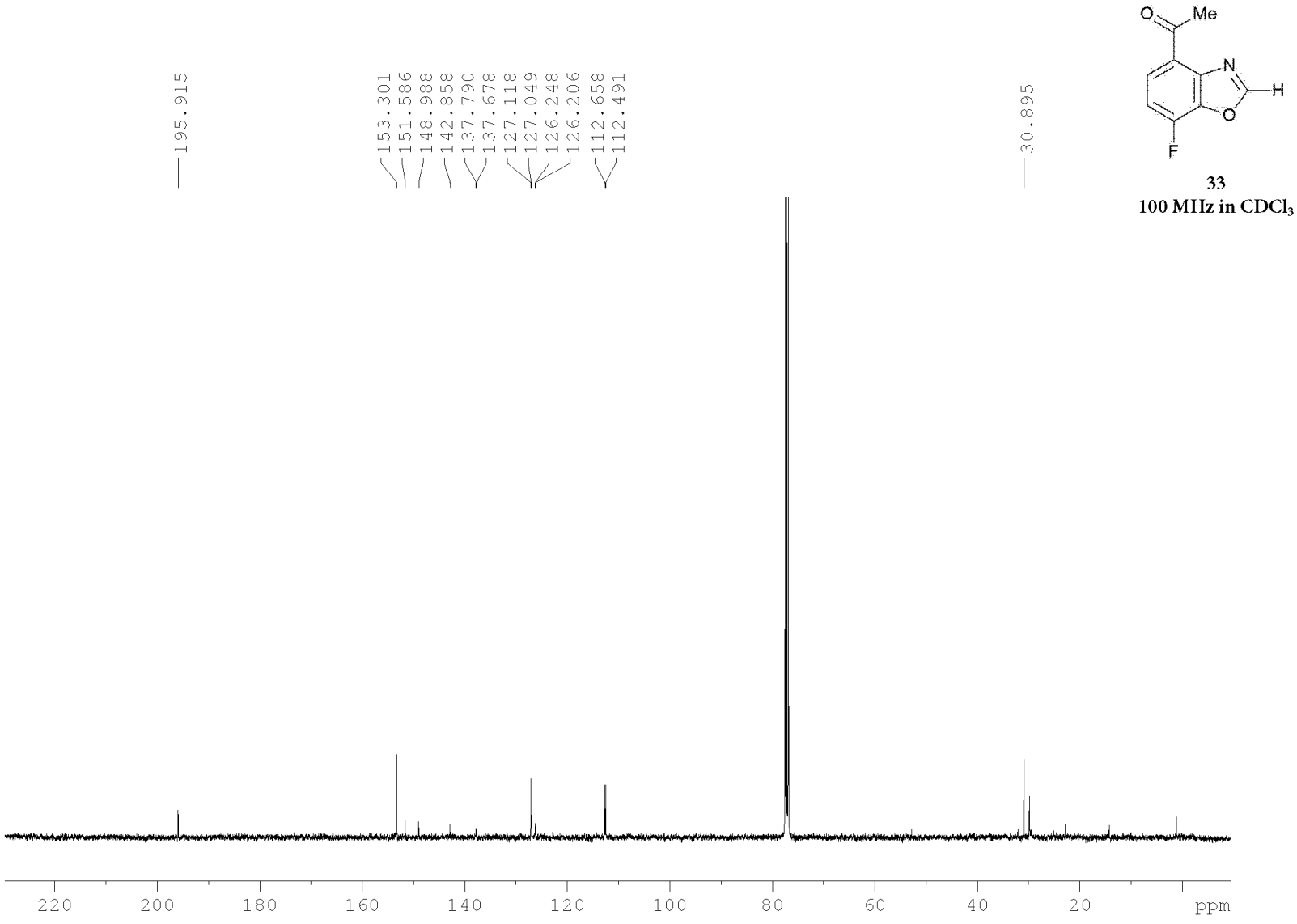
31
376 MHz in DMSO-d_6





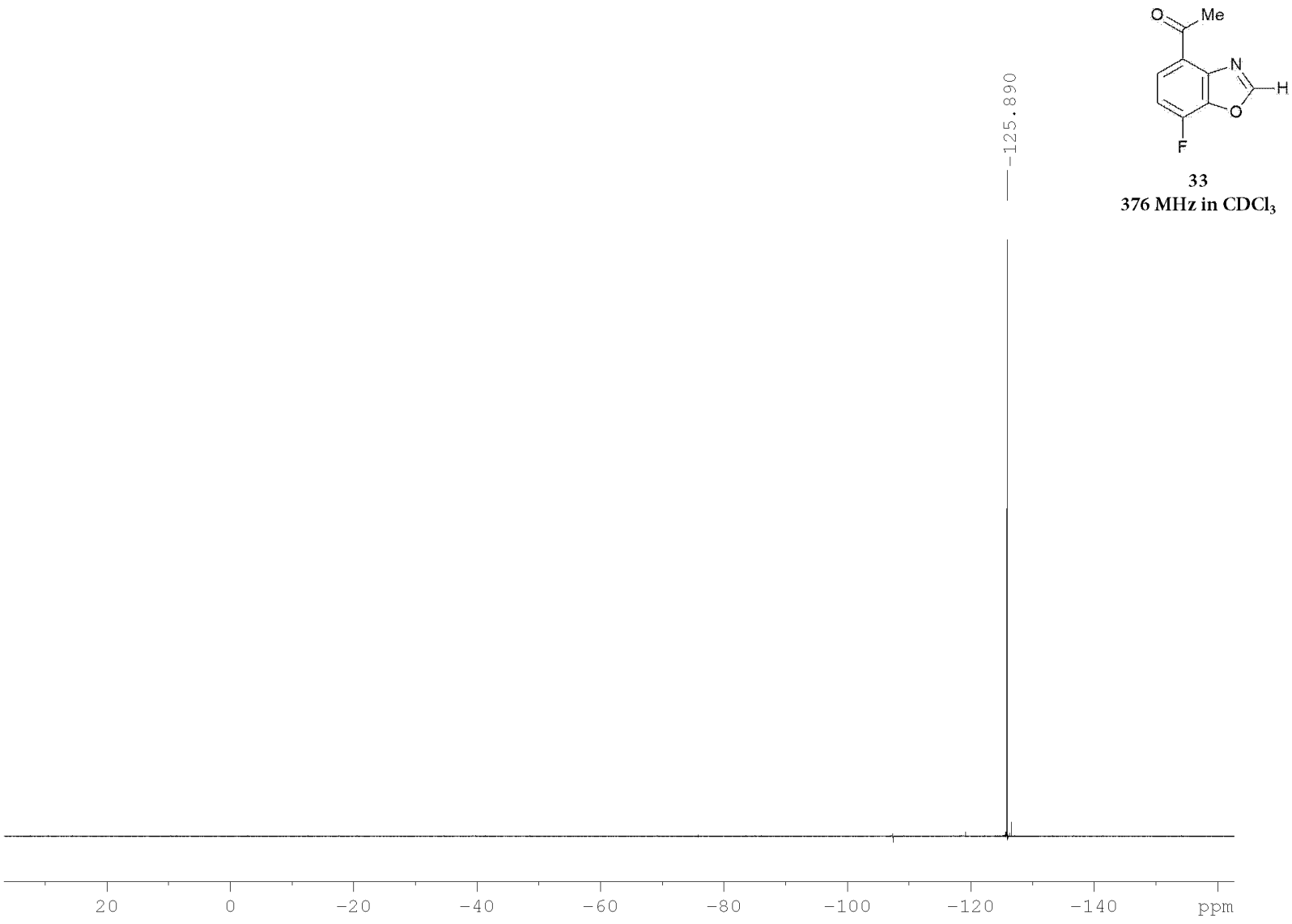
33

400 MHz in $CDCl_3$

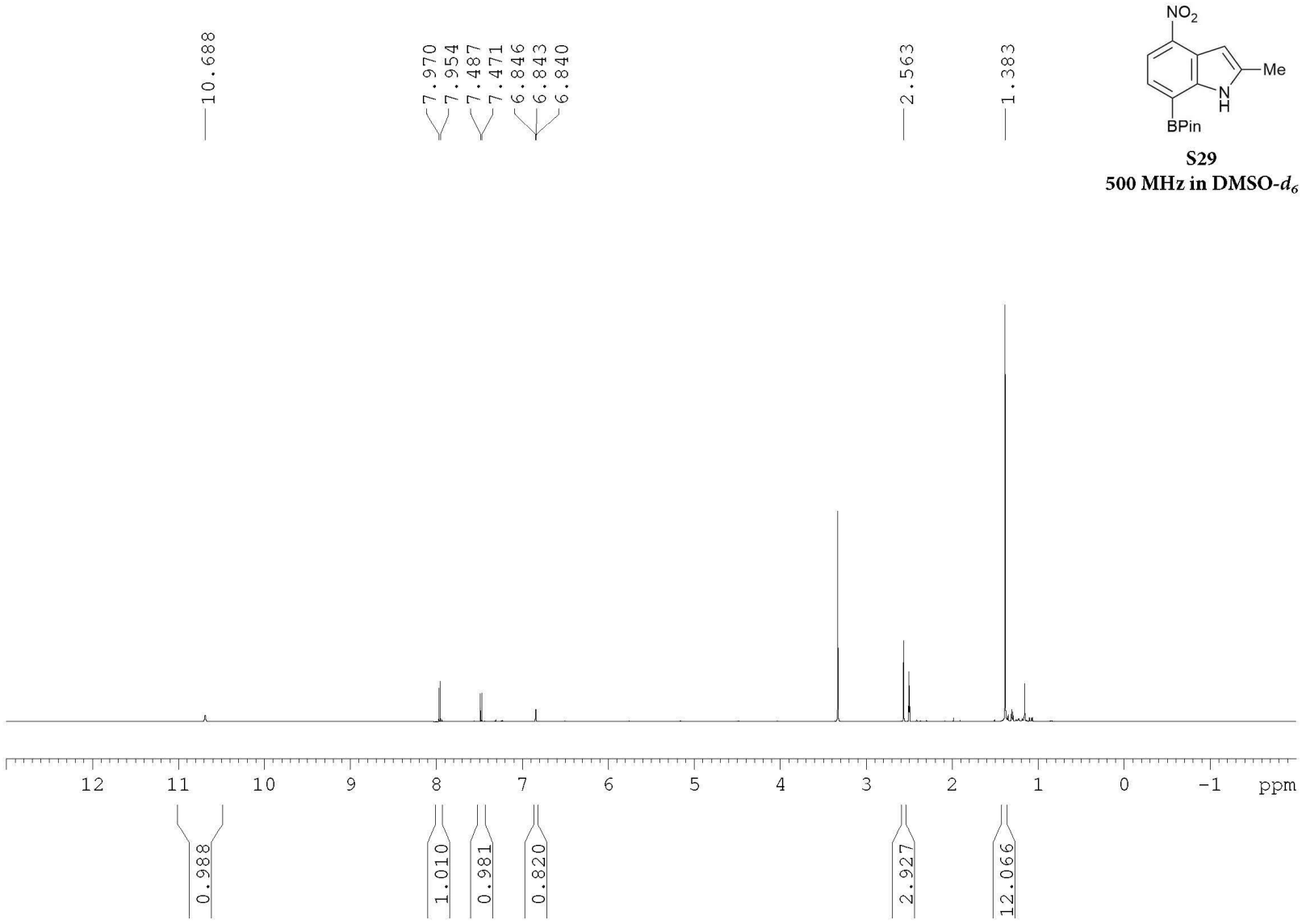


33

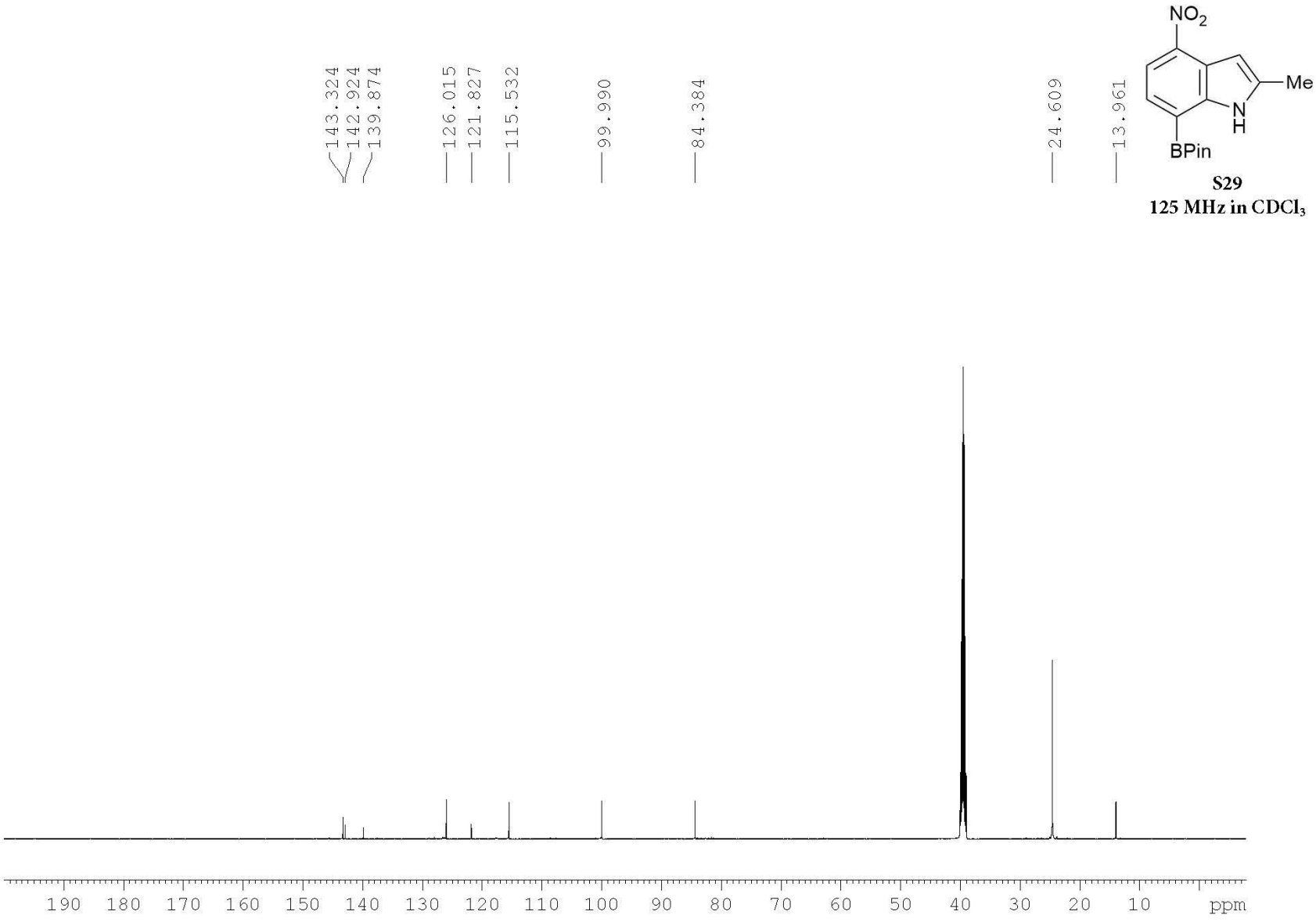
100 MHz in $CDCl_3$



33
376 MHz in $CDCl_3$

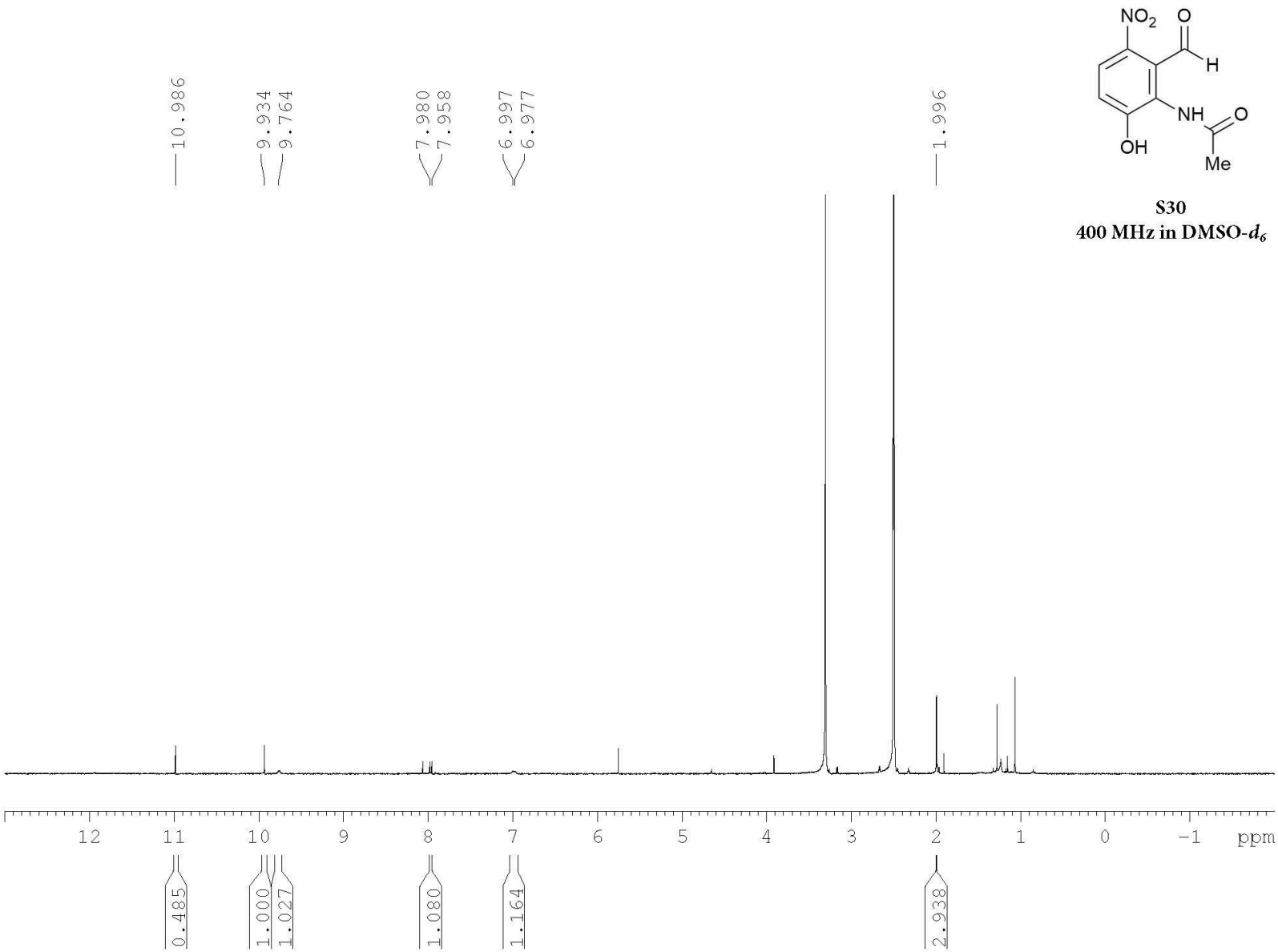


S29
500 MHz in DMSO-d_6

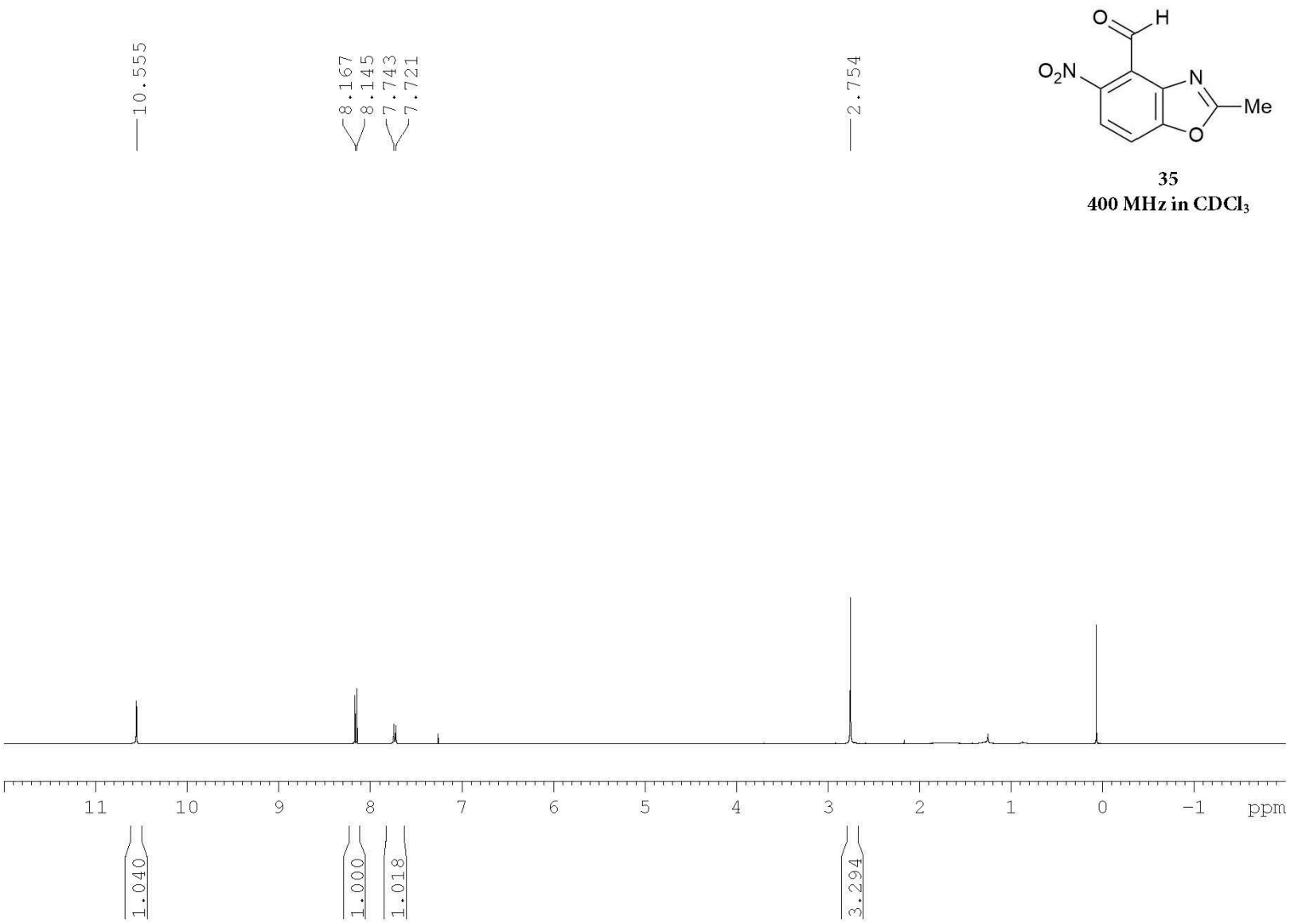


S29

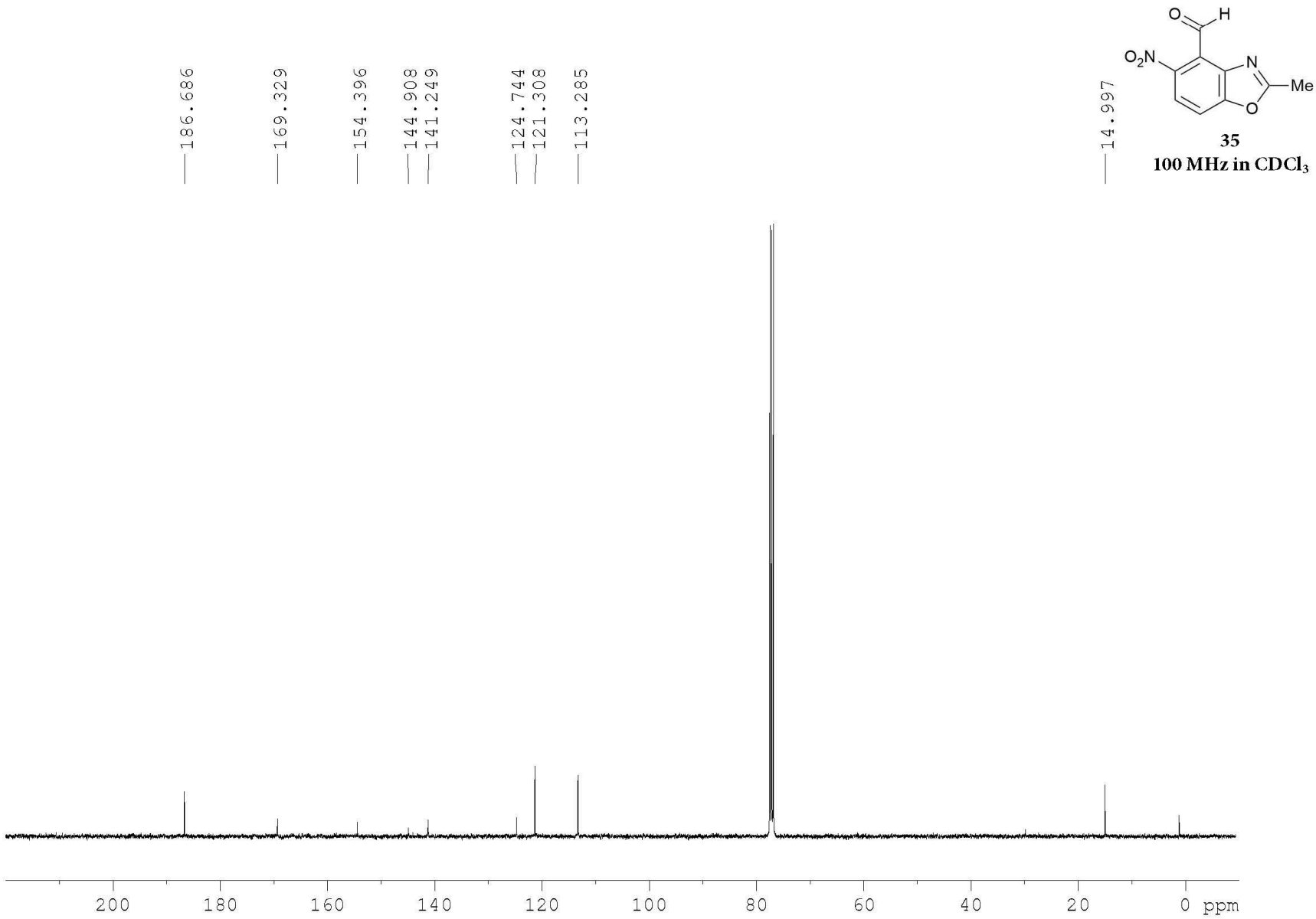
125 MHz in $CDCl_3$



S30
400 MHz in DMSO-d_6



35
400 MHz in $CDCl_3$


186.686
169.329
154.396
144.908
141.249
124.744
121.308
113.285
14.997
O
H
O2N
N
Me
O
35
100 MHz in CDCl3
200
180
160
140
120
100
80
60
40
20
0 ppm

References

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