Catalytic Generation of Borenium Ions by Cooperative B–H Bond Activation: The Elusive Direct Electrophilic Borylation of Nitrogen Heterocycles with Pinacolborane

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1 General Information

All reactions were performed in flame-dried glassware using an MBraun glove box (O_2 < 0.5 ppm, H_2O < 0.5 ppm) or conventional Schlenk techniques under a static pressure of argon or nitrogen. Liquids and solutions were transferred with syringes. Solvents (DMF, toluene, *n*-hexane and CH_2Cl_2) were purified and dried following standard procedures. Technical grade solvents for extraction or chromatography (cyclohexane, *tert*-butyl methyl ether, Et_3N) were distilled prior to use. C_6D_6 (purchased from *Eurisotop*) was dried over CaH_2 and stored under nitrogen after distillation. $CDCl_3$ and CD_2Cl_2 (both purchased from *Eurisotop*) were dried over $CaCO_3$ instead. $(9\text{-BBN})_2$ (**2a**), pinBH (**2c**), catBH (**2d**), 1-methylindole (**6a**), and 1,2,5-trimethylpyrrole (**8**) were obtained from commercial sources and distilled prior to use. Dicyclohexyl borane (**2b**),[S1] 1,2-dimethylindole (**6b**), [S2] 1,5-dimethylindole (**6c**),[S2] and 7-ethyl-1-methylindole (**6d**)[S2] were prepared according to reported procedures. All other *N*-protected indoles were synthesized from commercially obtained *N*-free indoles. Ruthenium complexes $[(Et_3P)Ru(SDmp)][BAr^F{}_4]$ (**1a**) and $[\{(p\text{-}FC_6H_4)_3P\}Ru(SDmp)][BAr^F{}_4]$ (**1b**) were prepared according to a previously reported procedure by our group.[S3,S4] ^1H, ^{11}B, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded in C_6D_6, CD_2Cl_2 or $CDCl_3$ on Bruker DRX500 and Bruker AV400 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (C_6HD_5: δ = 7.16 ppm for ^1H NMR and C_6D_6: δ = 128.1 ppm for ^{13}C NMR; $CHCl_3$: δ = 7.26 ppm for ^1H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR; $CDHCl_2$: δ = 5.32 ppm for ^1H NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrophotometer equipped with an ATR unit and are reported as wave numbers (cm^{-1}). Gas liquid chromatography (GLC) was performed on a Shimadzu GC-17A gas chromatograph equipped with a SE-54 capillary column (30 m × 0.32 mm, 0.25 µm film thickness) by CS-Chromatographie Service using the following program: N_2 as carrier gas, column flow 1.7 mL/min, injection temperature 280 °C, detector temperature 300 °C, start temperature 40 °C, heating rate 10 °C/min, final temperature 280 °C for 10 min. Melting points (M.p.) were determined with a Stuart SMP20 apparatus and are not corrected. Mass spectra (MS) were obtained from the Analytical Facility of the Institut für Chemie, Technische Universität Berlin.

2 General Procedures (GPs)

2.1 GP1: General Procedure for *N*-Methylation of Indoles

In a flame-dried Schlenk flask, a solution of the corresponding 1*H*-indole (1.0 equiv.) in dry DMF (0.5 M) is added slowly via syringe to a suspension of sodium hydride (1.2 equiv.) in dry DMF (0.3 M) at ambient temperature. After complete addition, the reaction mixture is stirred for 1 h, followed by dropwise addition of methyl iodide (1.3 equiv.). The reaction mixture is stirred at ambient temperature for 1–3 h until analysis of an aliquot by GLC or TLC indicates complete consumption of the unprotected indole. The reaction is carefully quenched with saturated aqueous NH_4Cl solution. After addition of *tert*-butyl methyl ether, the organic phase is washed with water (4 ×) and dried over anhydrous Na_2SO_4. Subsequent evaporation of the solvents under reduced pressure and purification of the residue by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether mixtures afford the *N*-methylated indoles in analytically pure form.

General Comment on Catalyses Performed in a Sealed Vessel (GP2 and GP3)

Reactions are performed in a sealed vessel to rigorously exclude air/oxygen. The volume of the reaction vessel relative to the scale of the catalyses leaves room for the formation of dihydrogen gas. When changing this proportion, pressure build-up must be considered.

2.2 GP2: General Procedure for Screening of Reaction Conditions

In a glove box, a flame-dried 10-mL reaction vessel equipped with a magnetic stir bar is charged with ruthenium thiolate complex **1** (1.0 mol %). After addition of borane (1.0 equiv.) and the corresponding *N*-protected indole (8.0 equiv.) the vessel is sealed, removed from the glove box, and maintained for 24 h at elevated temperatures (45 °C – 120 °C). For determination of conversion, an aliquot from the reaction mixture is subjected to NMR analysis (^{1}H NMR and ^{11}B NMR). For experiments with pinacolborane and equimolar amounts of indole, GLC analysis of an aliquot is used to determine conversion with *n*-tetracosane as internal standard.

2.3 GP3: General Procedure for Catalytic Borylation

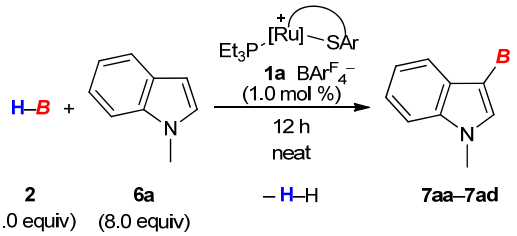
In a glove box, a flame-dried 10-mL reaction vessel equipped with a magnetic stir bar is charged with ruthenium thiolate complex **1b** (1.0 mol %). After addition of pinacolborane (1.5 equiv.) and the corresponding *N*-protected indole (1.0 equiv.), the vessel is sealed, removed from the glove box, and maintained for 24 h at elevated temperatures (80 °C – 110 °C). No remaining pinacolborane is present, i.e., it is fully consumed and/or decomposed. The reaction is

quenched by addition of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (2 mL) and directly subjected to flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether/Et_3N mixtures as eluent. This procedure affords the C–3 borylated indoles (C–3:C–2 > 99:1) as colorless to pale yellow solids.

The regioselectivity was verified by GLC analysis prior to purification. The assignment of the C–3 regioselectivity was confirmed by 2D NMR data sets (COSY, HSQC, and HMBC correlation).

3 Optimization of the Procedure for Catalytic Borylation

Table S1: Screening of Borane and Temperature[a]

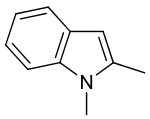


entry	catalyst loading	borane	temp. (° C)	conv. (%)[b]
1	1.0 mol %	$(9\text{-BBN})_2$ (**2a**)	45	0%
2	1.0 mol %	$(9\text{-BBN})_2$ (**2a**)	80	not complete
3	1.0 mol %	$(9\text{-BBN})_2$ (**2a**)	100	>95%
4	1.0 mol %	$(9\text{-BBN})_2$ (**2a**)	120	>95%
5	—	$(9\text{-BBN})_2$ (**2a**)	120	0%
6	1.0 mol %	$HBCy_2$ (**2b**)	100	complex mixture
7	1.0 mol %	$HBCy_2$ (**2b**)	120	complex mixture
8	—	$HBCy_2$ (**2b**)	120	0%
9	1.0 mol %	HBpin (**2c**)	45	not complete
10	1.0 mol %	HBpin (**2c**)	60	not complete
11	1.0 mol %	HBpin (**2c**)	80	>95%
12	1.0 mol %	HBpin (**2c**)	100	>95%
13	—	HBpin (**2c**)	120	0%
14	1.0 mol %	HBcat (**2d**)	45	not complete
15	1.0 mol %	HBcat (**2d**)	60	>95%
16	1.0 mol %	HBcat (**2d**)	80	>95%
17	1.0 mol %	HBcat (**2d**)	100	>95%
18	—	HBcat (**2d**)	120	0%

[a]All reactions were performed according to the **GP2**. [b]Determined by ^{1}H NMR and ^{11}B NMR analysis.

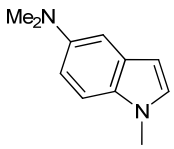
4 Characterization Data

4.1 Characterization Data of *N*-Protected Indoles



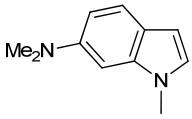
6b
$C_{10}H_{11}N$
M = 145.2 g/mol

1,2-Dimethylindole (6b): Prepared from 2-methylindole (1.0 g, 7.6 mmol, 1.0 equiv.) according to the general procedure **GP1**. Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether = 10:1) afforded the analytically pure product **6b** (0.75 g, 68% yield) as a white solid. **M.p.** = 54 °C (cyclohexane). $\mathbf{R_f}$ = 0.47 (cyclohexane:*tert*-butyl methyl ether = 10:1). **GLC**: t_R= 11.9 min. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 3.67 (s, 3H), 6.26 (s, 1H), 7.08 (dd, *J* = 7.7 Hz, *J* = 7.1 Hz, 1H), 7.23 (dd, *J* = 7.9 Hz, *J* = 7.1 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 12.8, 29.4, 99.6, 108.7, 119.3, 119.6, 120.4, 128.0, 136.8, 137.3 ppm. The analytical and spectroscopic data are in accordance with those reported.[S5]



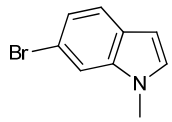
6e
$C_{11}H_{14}N_2$
M = 174.2 g/mol

5-(*N*,*N*-Dimethylamino)-1-methylindole (6e): Prepared from 5-(*N*,*N*-dimethylamino)indole (1.0 g, 7.6 mmol, 1.0 equiv.) according to the general procedure **GP1**. Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether = 5:1) afforded the analytical pure product **6e** (0.91 g, 69% yield) as a brown-yellow solid. **M.p.** = 50 °C (cyclohexane). $\mathbf{R_f}$ = 0.18 (cyclohexane:*tert*-butyl methyl ether = 5:1). **GLC**: t_R= 15.0 min. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.94 (s, 6H), 3.76 (s, 3H), 6.38 (d, *J* = 2.9 Hz, 1H), 6.96 (dd, *J* = 8.9 Hz, *J* = 2.1 Hz, 1H), 6.99 (d, *J* = 2.9 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 7.23 (d, *J* = 8.9 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 32.9, 43.1, 100.1, 105.2, 109.5, 112.8, 129.0, 129.1, 131.5, 145.9 ppm. **IR** (ATR): $\tilde{\nu}$ = 2873 (w), 2795 (w), 1620 (s), 1569 (s), 1495 (s), 1418 (s), 1323 (s), 1289 (s), 1221 (m), 1126 (m), 1095 (s), 961 (s), 820 (s) cm^{-1}. **HRMS** (APCI) calcd for $C_{11}H_{15}N_2$ $[M+H]^+$: 175.1230, Found: 175.1226.



6f
$C_{11}H_{14}N_2$
M = 174.2 g/mol

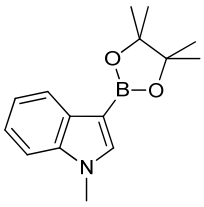
6-(*N*,*N*-Dimethylamino)-1-methylindole (6f): Prepared from 5-(*N*,*N*-dimethylamino)indole (0.8 g, 6.1 mmol, 1.0 equiv.) according to the general procedure **GP1**. Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether:Et_3N = 10:5:1) afforded the analytical pure product **6f** (0.25 g, 24% yield) as a brown solid. $\mathbf{R_f}$ = 0.35 (cyclohexane:*tert*-butyl methyl ether:Et_3N = 10:5:1). **GLC**: t_R= 15.1 min. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.99 (s, 6H), 3.73 (s, 3H), 6.37 (d, *J* = 3.1 Hz, 1H), 6.61 (s, 1H), 6.78 (dd, *J* = 8.6 Hz, *J* = 2.1 Hz, 1H), 6.89 (d, *J* = 3.1 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 32.7, 42.2, 93.3, 100.5, 109.4, 120.9, 121.1, 126.9, 138.0, 147.7 ppm. **IR** (ATR): $\tilde{\nu}$ = 2793 (w), 1620 (s), 1562 (s), 1494 (m), 1439 (m), 1304 (m), 1244 (s), 1163 (s), 1055 (s), 789 (s) cm^{-1}. **HRMS** (APCI) calcd for $C_{11}H_{15}N_2$ $[M+H]^+$: 175.1230, Found: 175.1227.



6g
C_9H_8NBr
M = 210.1 g/mol

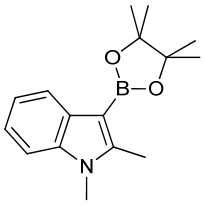
6-Bromo-1-methylindole (6g): Prepared from 6-bromoindole (1.0 g, 5.1 mmol, 1.0 equiv.) according to the general procedure **GP1**. Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether = 4:1) afforded the analytical pure product **6g** (0.91 g, 91% yield) as a pale brown oil. $\mathbf{R_f}$ = 0.43 (cyclohexane:*tert*-butyl methyl ether = 4:1). **GLC**: t_R= 13.9 min. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.76 (s, 3H), 6.46 (d, *J* = 3.4 Hz, 1H), 7.02 (d, *J* = 3.2 Hz, 1H), 7.20 (dd, *J* = 8.4 Hz, *J* = 1.5 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 32.9, 101.2, 112.3, 115.2, 122.1, 122.6, 127.3, 129.5, 137.6 ppm. **IR** (ATR): $\tilde{\nu}$ = 2922 (w), 1604 (s), 1510 (s), 1453 (m), 1417 (s), 1321 (s), 1299 (s), 1233 (s), 1080 (s), 1052 (s) cm^{-1}. **HRMS** (APCI) calcd for C_9H_9NBr $[M+H]^+$: 209.9913, Found: 209.9909.

4.2 Characterization Data of C–3-Borylated Indoles and Pyrroles



7ac
$C_{15}H_{20}NO_2B$
M = 257.1 g/mol

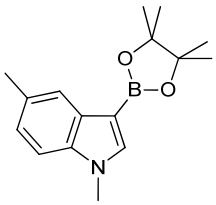
1-Methyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)indole (7ac): Prepared from *N*-methylindole (**6a**, 40 mg, 0.31 mmol, 1.0 equiv.) and pinacolborane (**2c**, 60 mg, 0.47 mmol, 1.5 equiv.) according to the general procedure **GP3**. The reaction mixture was stirred for 24 h at 80 °C and quenched with a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (1 mL). Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether = 20:1) afforded the analytical pure product **7ac** (56 mg, 71%) as a white solid. $\mathbf{R_f}$: 0.15 (cyclohexane:*tert*-butyl methyl ether = 20:1). **M.p.**: 115 °C (cyclohexane). **GLC**: t_R = 18.6 min. ^{1}**H NMR** (500 MHz, C_6D_6): δ = 1.23 (s, 12H), 2.85 (s, 3H), 7.02 (d, *J* = 8.3 Hz, 1H), 7.25 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 7.31 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.37 (s, 1H), 8.60 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}**C NMR** (126 MHz, C_6D_6): δ = 25.1, 32.1, 82.7, 109.5, 120.7, 122.1, 123.5, 133.6, 138.4, 138.9 ppm. The boron-substituted quaternary carbon atom was not detected. ^{11}**B NMR** (161 MHz, C_6D_6): δ = 30.1 ppm. **IR** (ATR): $\tilde{\nu}$ = 2971 (w), 1529 (s), 1467 (m), 1295 (s), 1234 (s), 1139 (m), 1100 (s), 983 (s), 854 (s) cm^{-1}. **HRMS** (EI) calcd for $C_{15}H_{20}NO_2B$ $[M]^+$: 257.1582, Found: 257.1589. The analytical and spectroscopic data are in accordance with those reported.[S6]



7bc
$C_{16}H_{22}NO_2B$
M = 271.2 g/mol

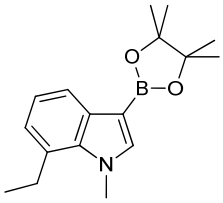
1,2-Dimethyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)indole (7bc): Prepared from 1,2-dimethylindole (**6b**, 44 mg, 0.31 mmol, 1.0 equiv.) and pinacolborane (**2c**, 60 mg, 0.47 mmol, 1.5 equiv.) according to the general procedure **GP3**. The reaction mixture was stirred for

24 h at 80 °C and quenched with a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (1 mL). Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether = 20:1) afforded the analytical pure product **7bc** (49 mg, 59%) as a white solid. **R*f***: 0.15 (cyclohexane:*tert*-butyl methyl ether = 20:1). **M.p.**: 148 °C. **GLC**: t_R = 19.8 min. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.35 (s, 12H), 2.64 (s, 3H), 3.67 (s, 3H), 7.09–7.18 (m, 2H), 7.24 (dd, *J* = 7.4 Hz, *J* = 1.3 Hz, 1H), 8.00 (dd, *J* = 7.4 Hz, *J* = 2.0 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, C_6D_6): δ = 12.7, 25.1, 29.6, 82.4, 108.6, 120.2, 120.9, 121.9, 132.6, 138.1, 147.6 ppm. The boron-substituted quaternary carbon atom was not detected. **^{11}B NMR** (161 MHz, C_6D_6): δ = 30.8 ppm. **IR** (ATR): $\tilde{\nu}$ = 2974 (w), 1534 (s), 1408 (s), 1368 (m), 1270 (m), 1226 (s), 1142 (m), 1095 (m), 1032 (s), 971 (s), 858 (s) cm^{-1}. **HRMS** (APCI) calcd for $C_{16}H_{23}NO_2B$ $[M+H]^+$: 272.1816, Found: 272.1818.



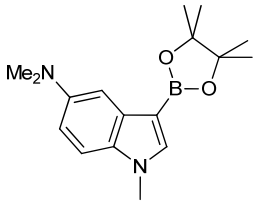
7cc
$C_{16}H_{22}NO_2B$
M = 271.2 g/mol

1,5-Dimethyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)indole (7cc): Prepared from 1,5-dimethylindole (**6c**, 44 mg, 0.31 mmol, 1.0 equiv.) and pinacolborane (**2c**, 60 mg, 0.47 mmol, 1.5 equiv.) according to the general procedure **GP3**. The reaction mixture was stirred for 24 h at 80 °C and quenched with a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (1 mL). Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether = 20:1) afforded the analytical pure product **7cc** (65 mg, 78%) as a white solid. **R*f***: 0.07 (cyclohexane:*tert*-butyl methyl ether = 20:1). **M.p.**: 107 °C (cyclohexane). **GLC**: t_R = 19.4 min. **^{1}H NMR** (500 MHz, C_6D_6): δ = 1.25 (s, 12H), 2.44 (s, 3H), 2.87 (s, 3H), 6.97 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 7.39 (s, 1H), 8.42 (s, 1H) ppm. **^{13}C NMR** (126 MHz, C_6D_6): δ = 21.7, 25.2, 32.2, 82.7, 109.2, 123.4, 123.6, 129.6, 133.9, 137.0, 139.2 ppm. The boron-substituted quaternary carbon atom was not detected. **^{11}B NMR** (161 MHz, C_6D_6): δ = 30.7 ppm. **IR** (ATR): $\tilde{\nu}$ = 2976 (w), 2924 (w), 1528 (s), 1458 (m), 1400 (s), 1366 (s), 1270 (m), 1238 (s), 1140 (m), 1102 (m), 979 (s), 876 (s) cm^{-1}. **HRMS** (APCI) calcd for $C_{16}H_{23}NO_2B$ $[M+H]^+$: 272.1816, Found: 272.1808.



7dc
$C_{17}H_{24}NO_2B$
M = 285.2 g/mol

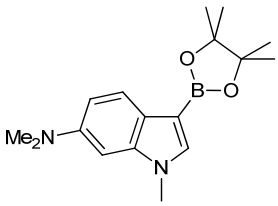
7-Ethyl-1-methyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)indole (7dc): Prepared from 7-ethyl-1-methylindole (**6d**, 49 mg, 0.31 mmol, 1.0 equiv.) and pinacolborane (**2c**, 60 mg, 0.47 mmol, 1.5 equiv.) according to the general procedure **GP3**. The reaction mixture was stirred for 24 h at 80 °C and quenched with a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (1 mL). Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether = 20:1) afforded the analytical pure product **7dc** (66 mg, 76%) as a white solid. **R_f**: 0.07 (cyclohexane:*tert*-butyl methyl ether = 20:1). **M.p.**: 122 °C (cyclohexane). **GLC**: t_R = 20.8 min. **^{1}H NMR** (500 MHz, C_6D_6): δ = 1.34 (t, *J* = 7.5 Hz, 3H), 1.37 (s, 12H), 3.11 (q, *J* = 7.5 Hz, 2H), 4.04 (s, 3H), 6.99 (d, *J* = 7.7 Hz, 1H), 7.10 (dd, *J* = 7.7 Hz, *J* = 7.7 Hz, 1H), 7.43 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, C_6D_6): δ = 17.0, 25.0, 25.5, 37.0, 82.8, 120.7, 120.9, 122.9, 127.9, 134.1, 135.8, 140.5 ppm. The boron-substituted quaternary carbon atom was not detected. **^{11}B NMR** (161 MHz, C_6D_6): δ = 30.3 ppm. **IR** (ATR): $\tilde{\nu}$ = 2971 (w), 2933 (w), 1539 (s), 1453 (m), 1360 (s), 1292 (s), 1266 (s), 1143 (s), 1108 (m), 1066 (s), 969 (s), 882 (s), 855 (s) cm^{-1}. **HRMS** (APCI) calcd for $C_{17}H_{25}NO_2B$ $[M+H]^+$: 286.1973, Found: 286.1968.



7ec
$C_{17}H_{25}N_2O_2B$
M = 300.2 g/mol

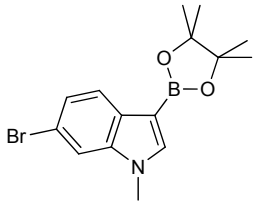
5-(*N*',*N*'-Dimethylamino)-1-methyl-3-(4'',4'',5'',5''-tetramethyl-1'',3'',2''-dioxaborolan-2''-yl)indole (7ec): Prepared from 5-(*N*',*N*'-Dimethylamino)-1-methylindole (**7e**, 53 mg, 0.31 mmol, 1.0 equiv.) and pinacolborane (**2c**, 60 mg, 0.47 mmol, 1.5 equiv.) according to the general procedure **GP3**. The reaction mixture was stirred for 24 h at 80 °C and quenched with a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (1 mL). Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether:Et_3N = 20:1:1)

and subsequent bulb-to-bulb distillation to remove volatiles afforded the analytical pure product **7ec** (48 mg, 53%) as a white solid. **R*f***: 0.22 (cyclohexane:*tert*-butyl methyl ether:Et_3N = 20:5:1). **M.p.**: 113 °C (cyclohexane). **GLC**: t_R = 21.8 min. **^{1}H NMR** (500 MHz, C_6D_6): δ = 1.35 (s, 12H), 2.95 (s, 6H), 3.75 (s, 3H), 6.93 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 7.46 (s, 1H) ppm. **^{13}C NMR** (126 MHz, C_6D_6): δ = 25.1, 33.2, 43.2, 82.7, 107.5, 109.6, 112.8, 132.7, 133.5, 138.7, 146.9 ppm. The boron-substituted quaternary carbon atom was not detected. **^{11}B NMR** (161 MHz, C_6D_6): δ = 30.4 ppm. **IR** (ATR): $\tilde{\nu}$ = 2977 (w), 1621 (m), 1573 (m), 1529 (s), 1492 (m), 1326 (s), 1288 (s), 1212 (m), 1141 (s), 1101 (m), 946 (s), 855 (s) cm^{-1}. **HRMS** (APCI) calcd for $C_{17}H_{26}N_2O_2B$ $[M+H]^+$: 301.2082, Found: 301.2088.



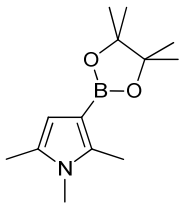
7fc
$C_{17}H_{25}N_2O_2B$
M = 300.2 g/mol

6-(*N*',*N*'-Dimethylamino)-1-methyl-3-(4'',4'',5'',5''-tetramethyl-1'',3'',2''-dioxaborolan-2''-yl)indole (7fc): Prepared from 6-(*N*',*N*'-Dimethylamino)-1-methylindole (**6f**, 53 mg, 0.31 mmol, 1.0 equiv.) and pinacolborane (**2c**, 60 mg, 0.47 mmol, 1.5 equiv.) according to the general procedure **GP3**. The reaction mixture was stirred for 24 h at 80 °C and quenched with a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (1 mL). Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether:Et_3N = 10:1:1) afforded the analytical pure product **7fc** (34 mg, 37%) as a white solid. **R*f***: 0.18 (cyclohexane:*tert*-butyl methyl ether:NEt_3 = 10:1:1). **M.p.**: 174 °C (cyclohexane). **GLC**: t_R = 22.5 min. **^{1}H NMR** (500 MHz, C_6D_6): δ = 1.24 (s, 12H), 2.70 (s, 6H), 2.93 (s, 3H), 6.45 (s, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 7.35 (s, 1H), 8.47 (d, *J* = 8.9 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, C_6D_6): δ = 25.1, 32.0, 41.7, 82.6, 93.5, 110.3, 123.7, 125.7, 137.3, 139.8, 148.2 ppm. The boron-substituted quaternary carbon atom was not detected. **^{11}B NMR** (161 MHz, C_6D_6): δ = 30.6 ppm. **IR** (ATR): $\tilde{\nu}$ = 2978 (w), 2925 (w), 2802 (w), 1624 (s), 1533 (s), 1501 (s), 1473 (m), 1343 (m), 1274 (m), 1240 (m), 1142 (m), 1089 (m), 978 (s), 794 (s) cm^{-1}. **HRMS** (APCI) calcd for $C_{17}H_{26}N_2O_2B$ $[M+H]^+$: 301.2082, Found: 301.2077.



7gc
$C_{15}H_{19}NO_2BBr$
M = 336.0 g/mol

6-Bromo-1-methyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)indole (7gc): Prepared from 6-Bromo-1-methylindole (**6g**, 64 mg, 0.31 mmol, 1.0 equiv.) and pinacolborane (**2c**, 60 mg, 0.47 mmol, 1.5 equiv.) according to the general procedure **GP3**. The reaction mixture was stirred for 24 h at 110 °C and quenched with a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (1 mL). Purification by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether = 20:1) and subsequent bulb-to-bulb distillation to remove volatiles afforded the analytical pure product **7gc** (42 mg, 41%) as a white solid. **R_f**: 0.15 (cyclohexane:*tert*-butyl methyl ether = 10:1). **M.p.**: 132 °C (cyclohexane). **GLC**: t_R = 21.5 min. **^{1}H NMR** (500 MHz, C_6D_6): δ = 1.20 (s, 12H), 2.62 (s, 3H), 7.20 (s, 1H), 7.24 (d, *J* = 1.7 Hz, 1H), 7.44 (dd, *J* = 8.4 Hz, *J* = 1.7 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, C_6D_6): δ = 25.1, 32.0, 82.9, 113.0, 115.9, 123.9, 124.7, 132.3, 139.2, 139.5 ppm. The boron-substituted quaternary carbon atom was not detected. **^{11}B NMR** (161 MHz, C_6D_6): δ = 30.3 ppm. **IR** (ATR): $\tilde{\nu}$ = 2980 (w), 2932 (w), 1607 (m), 1529 (m), 1472 (s), 1353 (m), 1299 (s), 1269 (m), 1224 (s), 1149 (s), 1107 (s), 978 (s), 814 (s) cm^{-1}. **HRMS** (APCI) calcd for $C_{15}H_{19}NO_2BBr$ $[M+H]^+$: 336.0765, Found: 336.0757.

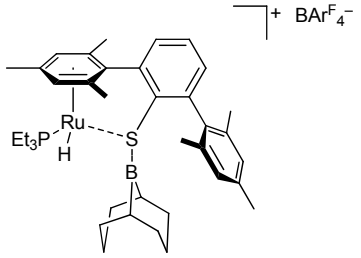


9c
$C_{13}H_{22}NO_2B$
M = 235.1 g/mol

1,2,5-Trimethyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)pyrrole (9c): Prepared from 1,2,5-trimethylpyrrole (**8**, 33 mg, 0.31 mmol, 1.0 equiv.) and pinacolborane (**2c**, 60 mg, 0.47 mmol, 1.5 equiv.) according to the general procedure **GP3**. The reaction mixture was stirred for 24 h at 80 °C and quenched with a solution of cyclohexane and *tert*-butyl methyl ether (90:10) containing 4% Et_3N (1 mL). Purification by flash column chromatography on silica gel

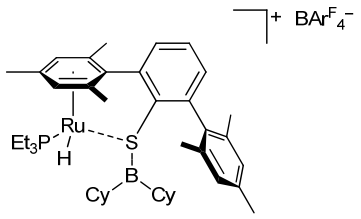
(cyclohexane:*tert*-butyl methyl ether = 5:1) afforded the analytical pure product **9c** (58 mg, 81%) as a white solid. **R_f**: 0.33 (cyclohexane:*tert*-butyl methyl ether = 5:1). **M.p.**: 81 °C (cyclohexane). **GLC**: t_R = 15.2 min. **^{1}H NMR** (500 MHz, C_6D_6): δ = 1.20 (s, 12H), 1.89 (s, 3H), 2.44 (s, 3H), 2.63 (s, 3H), 6.62 (s, 1H) ppm. **^{13}C NMR** (126 MHz, C_6D_6): δ = 12.4, 12.8, 25.1, 29.4, 82.1, 112.4, 137.8, 138.1 ppm. The boron-substituted quaternary carbon atom was not detected. **^{11}B NMR** (161 MHz, C_6D_6): δ = 30.8 ppm. **IR** (ATR): $\tilde{\nu}$ = 2975 (w), 2926 (w), 1573 (s), 1529 (s), 1434 (m), 1415 (m), 1276 (m), 1243 (s), 1141 (s), 1205 (s), 1033 (s), 995 (s), 862 (s) cm^{-1}. **HRMS** (APCI) calcd for $C_{13}H_{23}NO_2B$ $[M+H]^+$: 236.1816, Found: 236.1818 .

4.3 Characterization Data of Sulfur-Stabilized Boreniumion Intermediates



3aa
$C_{70}H_{67}B_2F_{24}PSRu$
M = 1550 g/mol

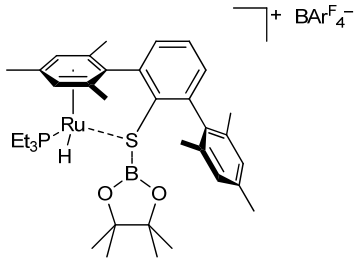
[(Et$_3$P)Ru(SDmp)·(9-BBN)]BAr$^F_4$ (3aa): In a glove box, an NMR tube was charged with [(Et$_3$P)Ru(SDmp)]BAr$^F_4$ (**1a**, 8.0 mg, 5.6 µmol, 1.0 equiv.) and (9-BBN)$_2$ (**2a**, 1.4 mg, 5.6 µmol, 1.0 equiv.). After addition of CD_2Cl_2 (0.6 mL), the sample was shaken vigorously and directly subjected to NMR analysis. Crystals suitable for Xray analysis were grown over 1 week from a solution prepared in C_6H_6 layered with *n*-hexane at room temperature. Selected NMR data: **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = –11.87 (d, *J* = 17.7 Hz, 1H), 0.17 (s, 1H), 0.42 (s, 1H), 0.89–1.00 (m, 2H), 1.07–1.16 (m, 11H), 1.18–1.28 (m, 2H), 1.31 (s, 1H), 1.56–1.62 (m, 6H), 2.09 (s, 3H), 2.11 (s, 3H), 2.17 (s, 3H), 2.27 (s, 3H), 2.35 (s, 3H), 2.43 (s, 3H), 5.76 (s, 1H), 6.02 (s, 1H), 7.02 (s, 1H), 7.04 (s, 1H), 7.42–7.48 (m, 2H), 7.61 (s, 4H), 7.65 (dd, *J* = 7.8 Hz, *J* = 7.2 Hz, 1H), 7.77 (s, 8H) ppm. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ = –62.9 ppm. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2): δ = 27.7 ppm. **Xray**: For complete crystal data, see chapter 6.2.



3ab
$C_{74}H_{75}B_2F_{24}PSRu$
M = 1606 g/mol

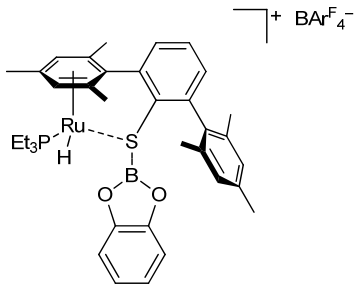
[(Et$_3$P)Ru(SDmp)·HBCy$_2$]BAr$^F_4$ (3ab): In a glove box, an NMR tube was charged with [(Et$_3$P)Ru(SDmp)]BAr$^F_4$ (**1a**, 8.0 mg, 5.6 µmol, 1.0 equiv.) and HBCy$_2$ (**2b**, 2.1 mg, 11 µmol, 2.0 equiv.). After addition of CD_2Cl_2 (0.6 mL), the sample was shaken vigorously and directly subjected to NMR analysis. Selected NMR data: **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = –12.09 (d, *J* = 18.9 Hz, 1H), –0.43 (t, *J* = 11.2 Hz, 1H), –0.03 (s, 1H), 0.49 (d, *J* = 11.2 Hz, 1H), 0.64–0.85 (m, 4H), 1.11 (dt, *J* = 16.9 Hz, *J* = 7.2 Hz, 9H), 1.59–1.67 (m, 6H), 2.00 (s, 3H), 2.11 (d, *J* = 3.0 Hz,

3H), 2.14 (s, 3H), 2.22 (s, 3H), 2.34 (s, 3H), 2.43 (s, 3H), 5.73 (d, *J* = 3.2 Hz, 1H), 6.07 (s, 1H), 7.02 (s, 1H), 7.04 (s, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.61 (s, 4H), 7.66 (dd, *J* = 7.6 Hz, *J* = 7.3 Hz, 1H), 7.78 (s, 8H) ppm. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ = –62.9 ppm. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2): δ = 28.6 ppm.



3ac
$C_{68}H_{65}O_2B_2F_{24}PSRu$
M = 1556 g/mol

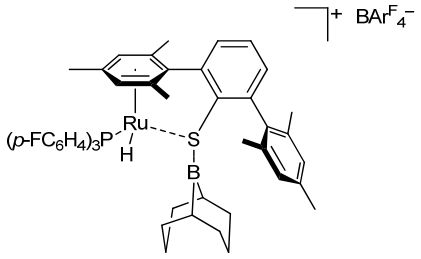
[(Et$_3$P)Ru(SDmp)·HBPin]BAr$^F_4$ (3ac): In a glove box, an NMR tube was charged with [(Et$_3$P)Ru(SDmp)]BAr$^F_4$ (**1a**, 8.0 mg, 5.6 μmol, 1.0 equiv.) and pinacolborane (**2c**, 1.4 mg, 11 μmol, 2.0 equiv.). After addition of CD_2Cl_2 (0.6 mL), the sample was shaken vigorously and directly subjected to NMR analysis. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = –8.93 (d, *J* = 45.5 Hz, 1H), 1.05 (dt, *J* = 16.5 Hz, *J* = 8.3 Hz, 9H), 1.14 (s, 12 H), 1.65 (qd, *J* = 8.3 Hz, *J* = 7.4 Hz, 6H), 1.99 (s, 3H), 2.04 (bs, 6H), 2.10 (bs, 3H), 2.16 (bs, 3H), 2.34 (s, 3H), 5.79 (s, 1H), 5.99 (s, 1H), 7.00 (s, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.61 (s, 4H), 7.67 (dd, *J* = 7.5 Hz, *J* = 7.4 Hz, 1H), 7.77 (s, 8H) ppm. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ = –62.9 ppm. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2): δ = 38.8 ppm.



3ad
$C_{68}H_{57}O_2B_2F_{24}PSRu$
M = 1548 g/mol

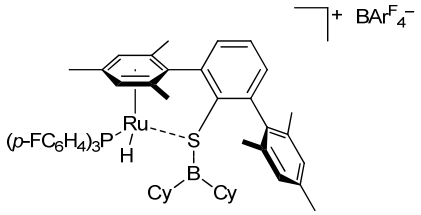
[(Et$_3$P)Ru(SDmp)·HBcat]BAr$^F_4$ (3ad): In a glove box, an NMR tube was charged with [(Et$_3$P)Ru(SDmp)]BAr$^F_4$ (**1a**, 8.0 mg, 5.6 μmol, 1.0 equiv.) and catecholborane (**2d**, 1.3 mg, 11 μmol, 2.0 equiv.). After addition of CD_2Cl_2 (0.6 mL), the sample was shaken vigorously and

directly subjected to NMR analysis. Selected NMR data: **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = –9.74 (bs, 1H), 1.04 (dt, *J* = 16.9 Hz, *J* = 7.0 Hz, 9H), 1.70–1.90 (m, 6H), 2.13 (s, 3H), 2.27 (s, 3H), 5.86 (bs, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.61 (s, 4H), 7.68 (d, *J* = 7.0 Hz, 1H), 7.73–7.80 (m, 9H) ppm. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ = –62.9 ppm. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2): δ = 38.0 ppm.



3ba
$C_{82}H_{64}B_2F_{27}PSRu$
M = 1748 g/mol

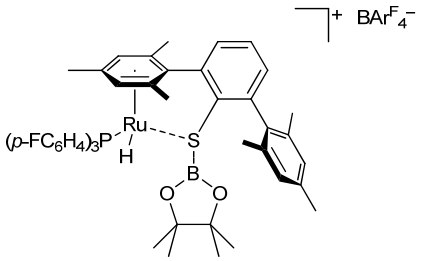
[{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)·(9-BBN)]BAr$^F_4$ (3ba): In a glove box, an NMR tube was charged with [{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)]BAr$^F_4$ (**1b**, 9.1 mg, 5.6 μmol, 1.0 equiv.) and (9-BBN)$_2$ (**2a**, 1.4 mg, 5.6 μmol, 1.0 equiv.). After addition of CD_2Cl_2 (0.6 mL), the sample was shaken vigorously and directly subjected to NMR analysis. Selected NMR data: **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = –11.77 (d, *J* = 19.5 Hz, 1H), –1.24 (s, 1H), –0.20 (s, 1H), 0.40 (s, 1H), 0.93 (s, 2H), 1.11 (s, 3H), 1.80 (s, 4H), 2.08 (s, 3H), 2.17 (s, 3H), 2.18 (d, *J* = 3.0 Hz, 3H), 2.38 (s, 3H), 2.56 (s, 3H) 4.39 (d, *J* = 3.8 Hz, 1H), 6.15 (s, 1H), 7.02 (s, 1H), 7.16 (s, 1H), 7.28 (t, *J* = 8.4 Hz, 6H), 7.45 (dd, *J* = 7.6 Hz, *J* = 1.1 Hz, 1H), 7.54 (dd, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H), 7.59 (s, 4H), 7.63–7.71 (m, 7H), 7.76 (s, 8H) ppm. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ = –106.8, –62.9 ppm. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2): δ = 34.5 ppm.



3bb
$C_{86}H_{72}B_2F_{27}PSRu$
M = 1804 g/mol

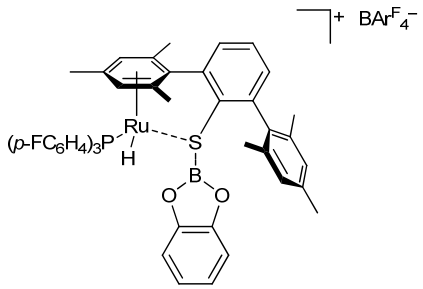
[{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)·HBCy$_2$]BAr$^F_4$ (3bb): In a glove box, an NMR tube was charged with [{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)]BAr$^F_4$ (**1b**, 9.1 mg, 5.6 μmol, 1.0 equiv.) and HBCy$_2$ (**2c**, 2.1 mg, 11 μmol, 2.0 equiv.). After addition of CD_2Cl_2 (0.6 mL), the sample was shaken vigorously and

directly subjected to NMR analysis. Selected NMR data: **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = –11.43 (d, *J* = 18.1 Hz, 1H), –0.94 (bs, 1H), –0.41–0.12 (m, 4H), 1.78 (s, 3H), 2.00 (s, 3H), 2.14 (d, *J* = 3.1 Hz, 3H), 2.28 (s, 6H), 2.40 (s, 3H), 4.52 (d, *J* = 5.0 Hz, 1H), 6.23 (s, 1H), 6.99 (s, 1H), 7.00 (s, 1H), 7.29 (t, *J* = 8.1 Hz, 6H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 4H), 7.62–7.69 (m, 6H), 7.71 (dd, *J* = 8.1 Hz, *J* = 8.0 Hz, 1H), 7.76 (s, 8H) ppm. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ = –107.1, –62.9 ppm. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2): δ = 36.6 ppm.



3bc
$C_{80}H_{62}O_2B_2F_{27}PSRu$
M = 1754 g/mol

[{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)·HBPin]BAr$^F_4$ (3bc): In a glove box, an NMR tube was charged with [{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)]BAr$^F_4$ (**1b**, 9.1 mg, 5.6 μmol, 1.0 equiv.) and pinacolborane (**2c**, 1.4 mg, 11 μmol, 2.0 equiv.). After addition of CD_2Cl_2 (0.6 mL), the sample was shaken vigorously and directly subjected to NMR analysis. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = –8.12 (d, *J* = 45.0 Hz, 1H), 1.31 (s, 12H), 1.60 (s, 3H), 1.77 (s, 3H), 1.86 (s, 3H), 2.09 (s, 3H) 2.20 (s, 3H), 2.32 (s, 3H), 4.76 (s, 1H), 6.33 (s, 1H), 6.83 (s, 1H), 6.93 (s, 1H), 7.16 (t, *J* = 8.2 Hz, 6H), 7.41 (dd, *J* = 7.6 Hz, 1H), 7.43–7.52 (m, 6H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.60 (s, 4H), 7.67 (dd, *J* = 7.8 Hz, *J* = 7.4 Hz, 1H), 7.76 (s, 8H) ppm. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ = –108.9, –62.9 ppm. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2): δ = 48.9 ppm.



3bd
$C_{80}H_{54}O_2B_2F_{27}PSRu$
M = 1746 g/mol

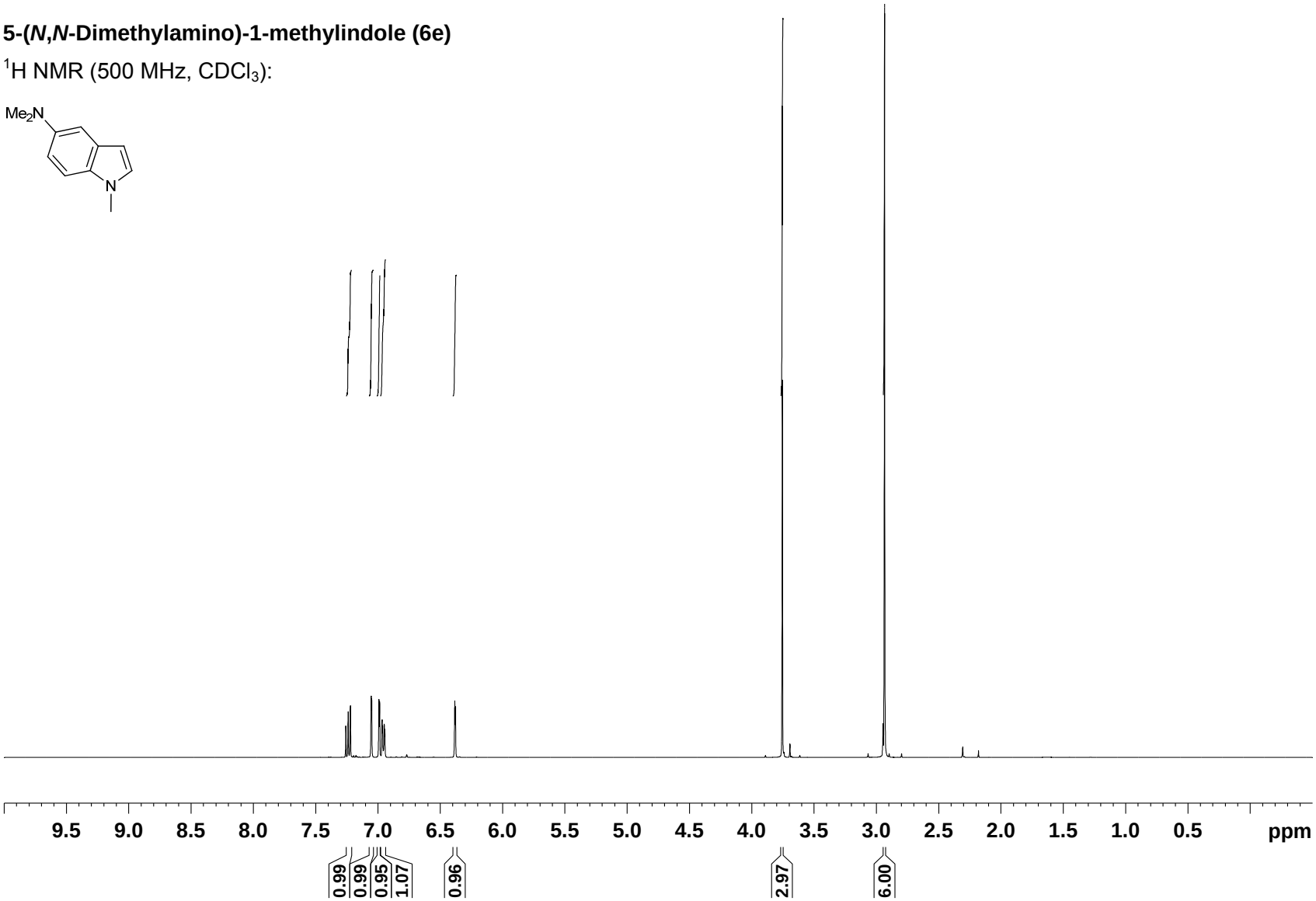
[{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)·HBcat]BAr$^F_4$ (3bd): In a glove box, an NMR tube was charged with [{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)]BAr$^F_4$ (**1b**, 9.1 mg, 5.6 µmol, 1.0 equiv.) and catecholborane (**2d**, 1.3 mg, 11 µmol, 2.0 equiv.). After addition of CD_2Cl_2 (0.6 mL), the sample was shaken vigorously and directly subjected to NMR analysis. Selected NMR data: **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = –8.62 (d, *J* = 42.1 Hz, 1H), 1.53 (s, 3H), 1.75 (s, 3H), 1.86 (s, 3H), 2.03 (s, 3H), 2.20 (s, 3H), 2.32 (s, 3H), 5.02 (s, 1H), 6.14 (s, 1H), 6.53 (s, 1H), 6.74 (s, 1H), 7.17 (t, *J* = 8.6 Hz, 6H), 7.39–7.48 (m, 6H), 7.60 (s, 4H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.73–7.81 (m, 9H) ppm. **^{19}F{^{1}H} NMR** (471 MHz, CD_2Cl_2): δ = –108.3, –62.9 ppm. **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2): δ = 48.5 ppm.

5 NMR Spectra

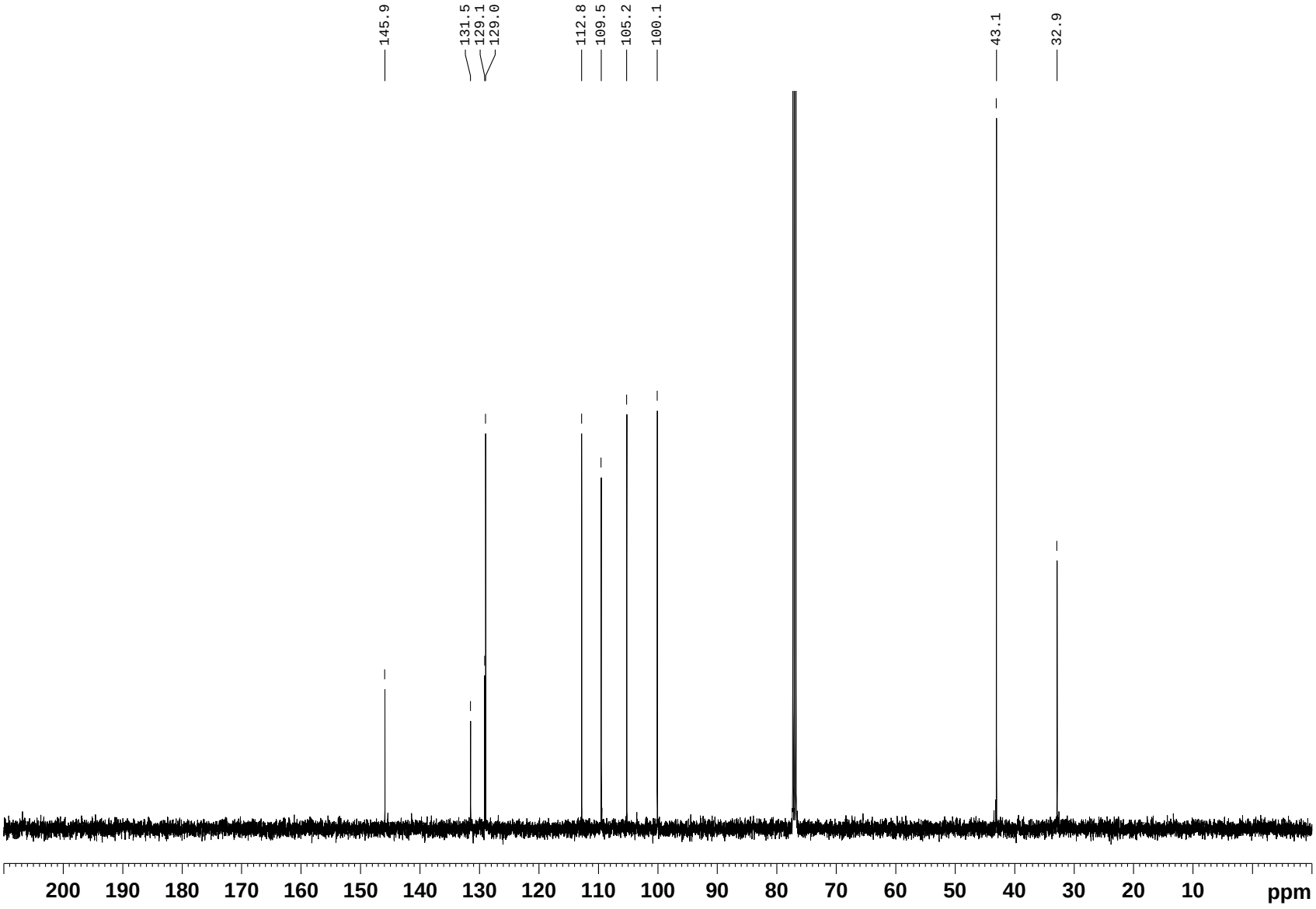
5.1 NMR Spectra of *N*-Protected Indoles

5-(*N*,*N*-Dimethylamino)-1-methylindole (6e)

^{1}H NMR (500 MHz, $CDCl_3$):

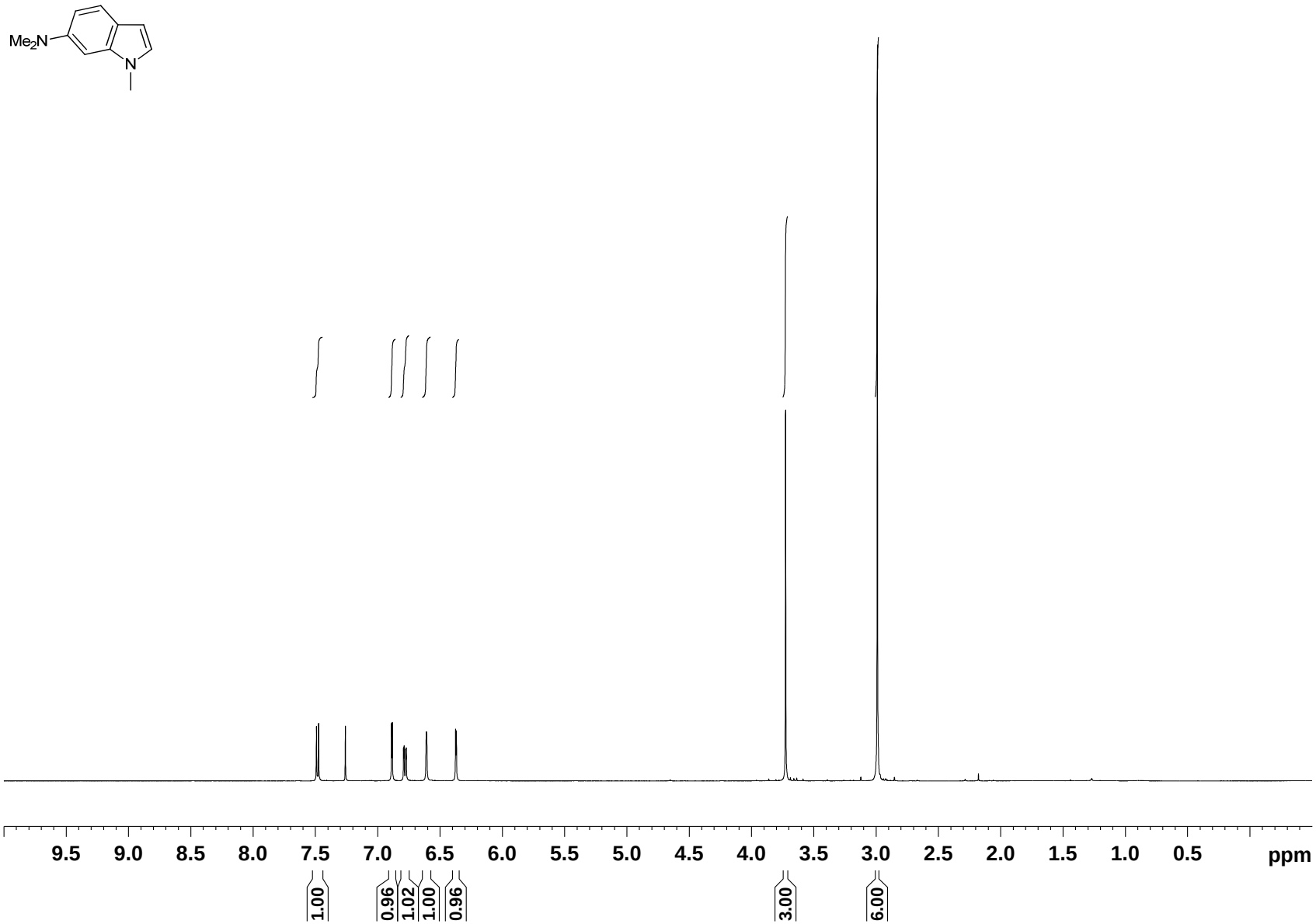


^{13}C NMR (126 MHz, $CDCl_3$):

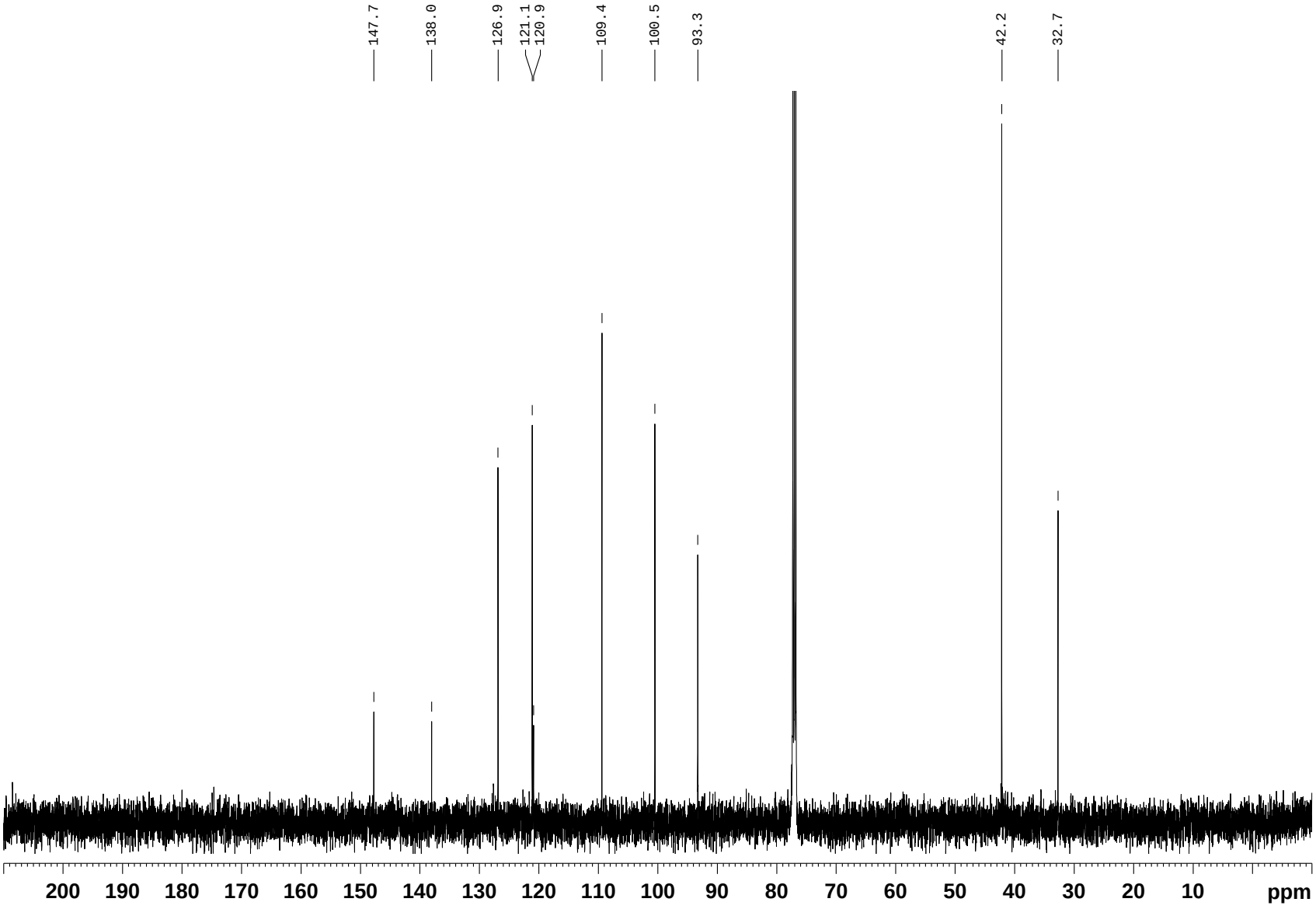


5-(*N*,*N*-Dimethylamino)-1-methylindole (6f)

^{1}H NMR (500 MHz, $CDCl_3$):

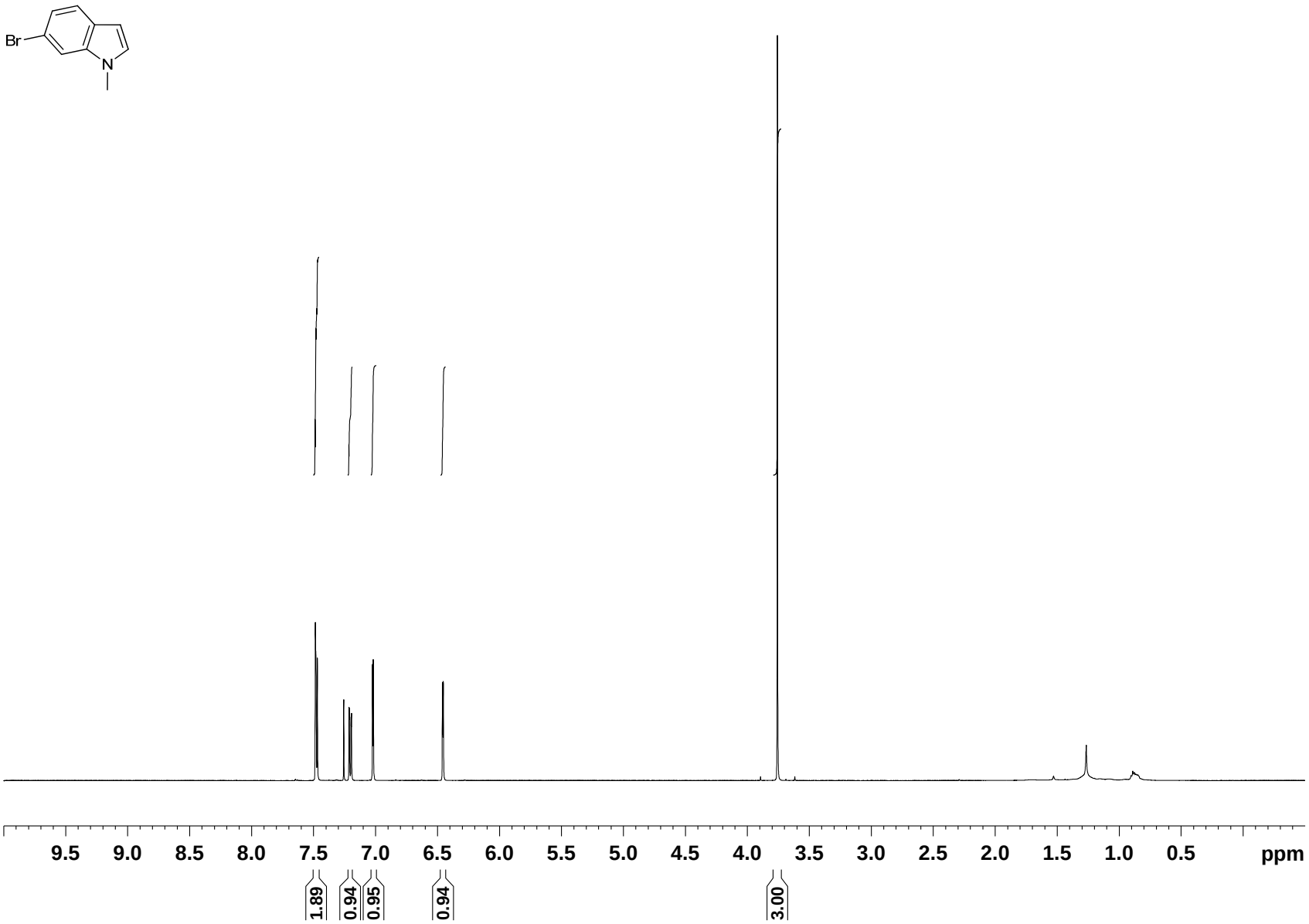


^{13}C NMR (126 MHz, $CDCl_3$):

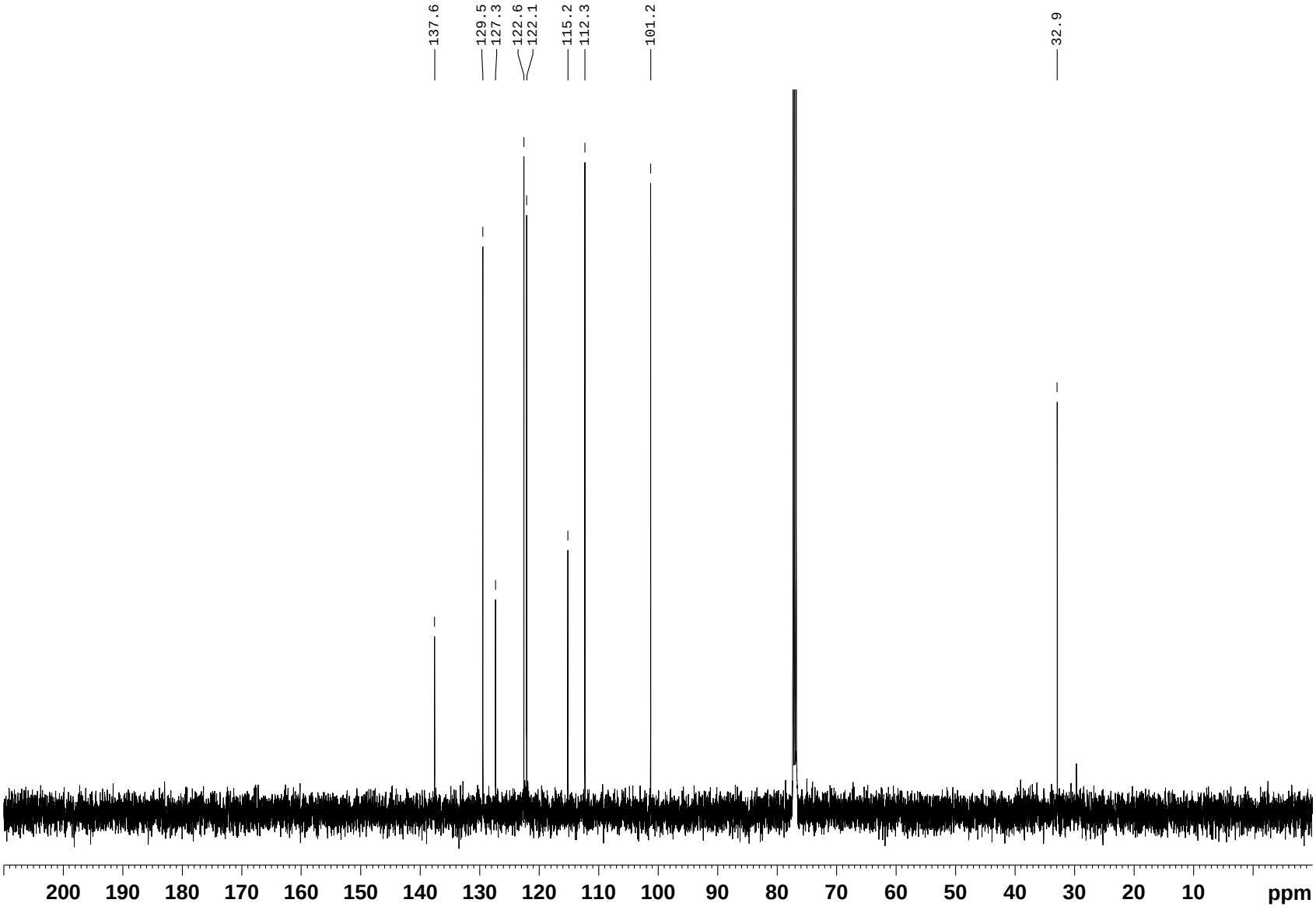


6-(*N*,*N*-Dimethylamino)-1-methylindole (6g)

^{1}H NMR (500 MHz, $CDCl_3$):



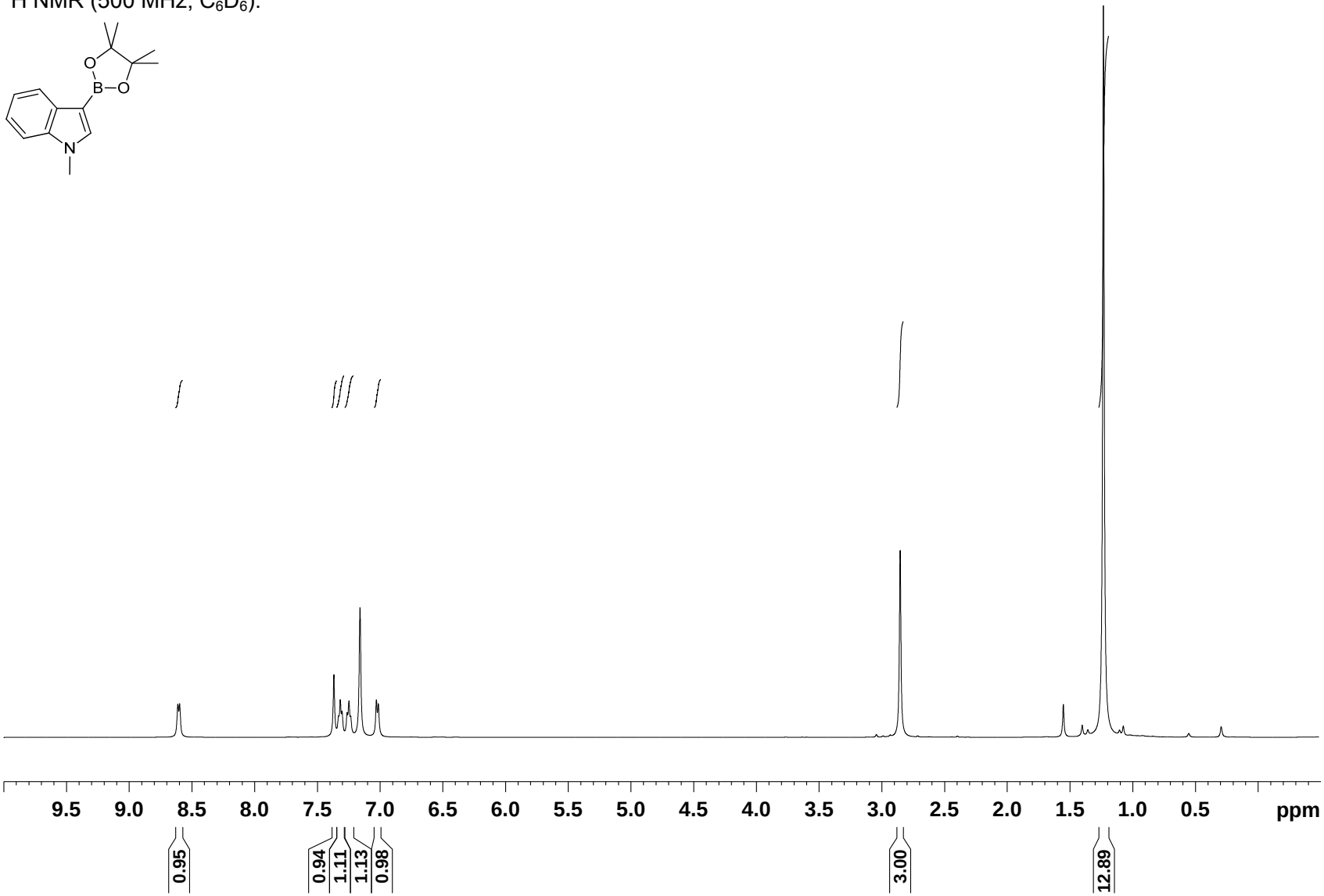
^{13}C NMR (126 MHz, $CDCl_3$):



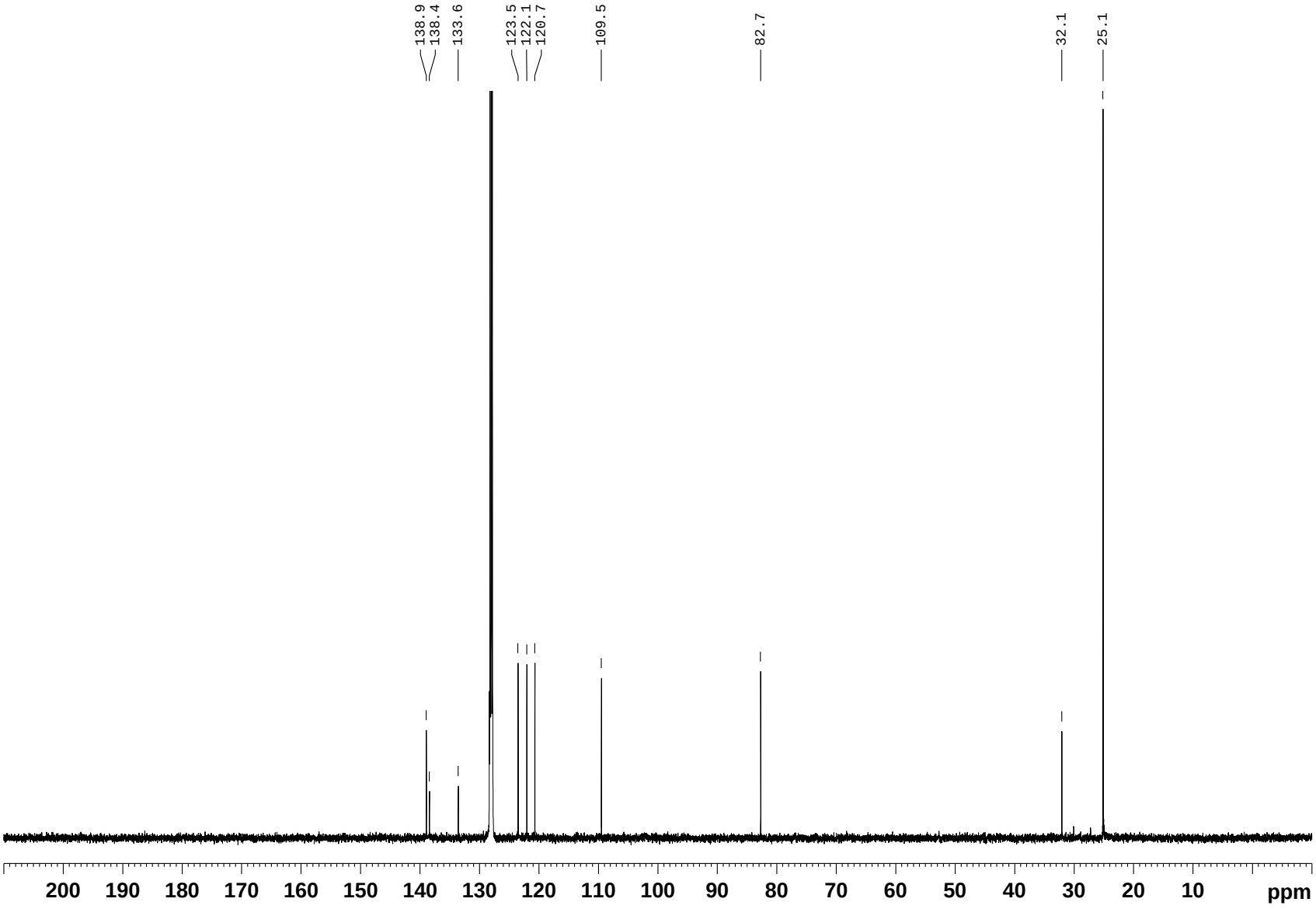
5.2 NMR Spectra of C–3-Borylated Indoles and Pyrroles

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

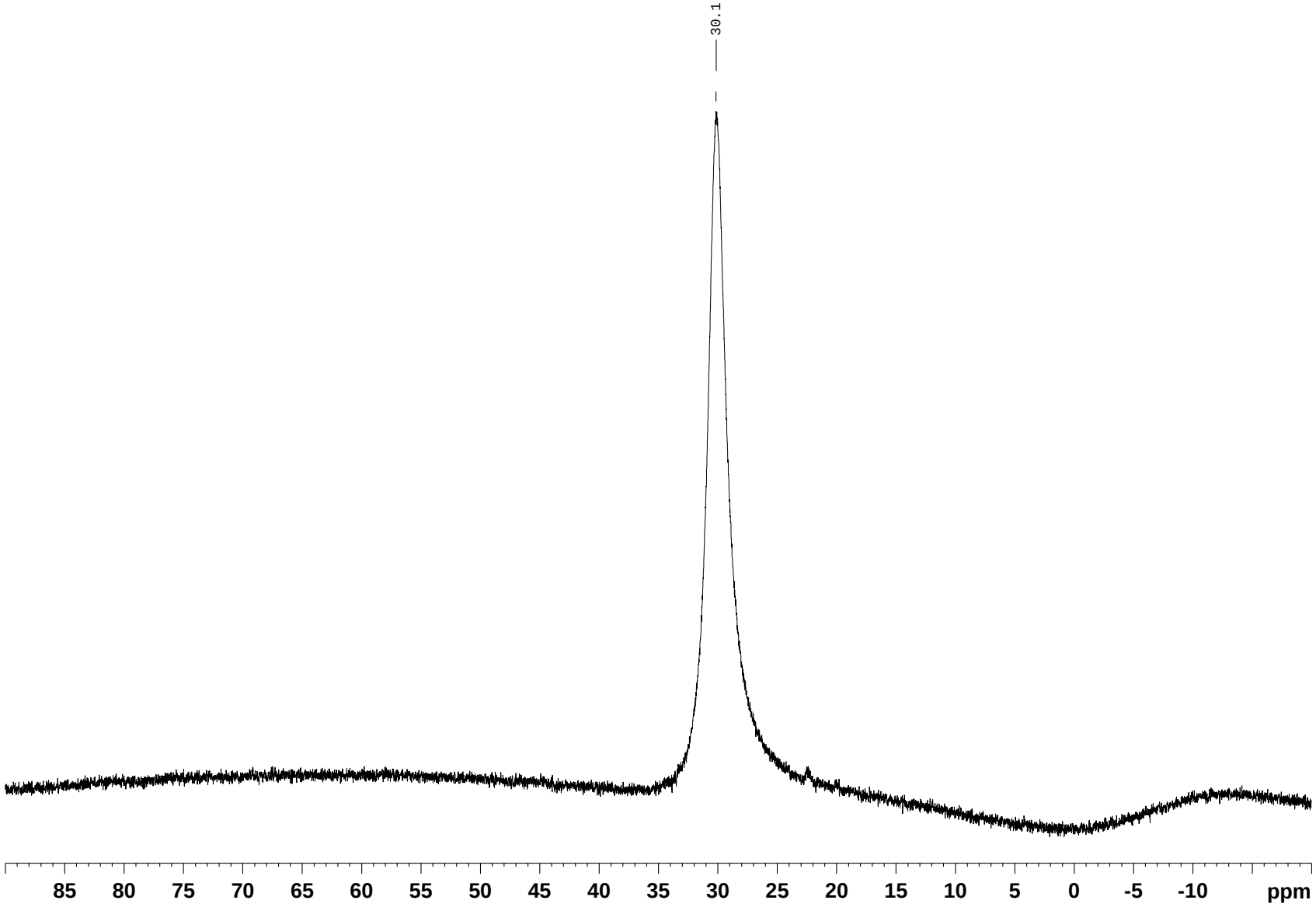
^{1}H NMR (500 MHz, C_6D_6):



^{13}C NMR (126 MHz, C_6D_6):

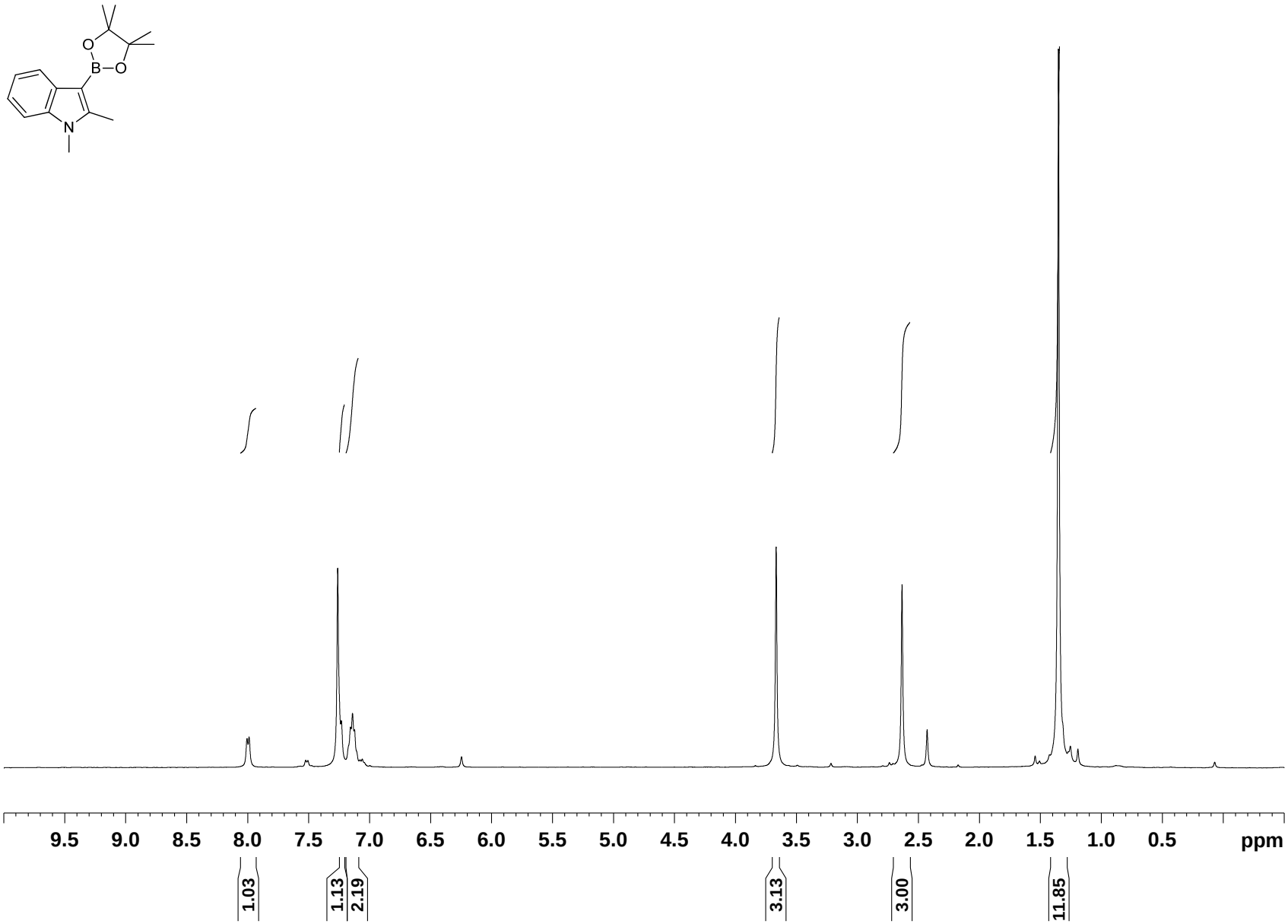


^{11}B NMR (161 MHz, C_6D_6):

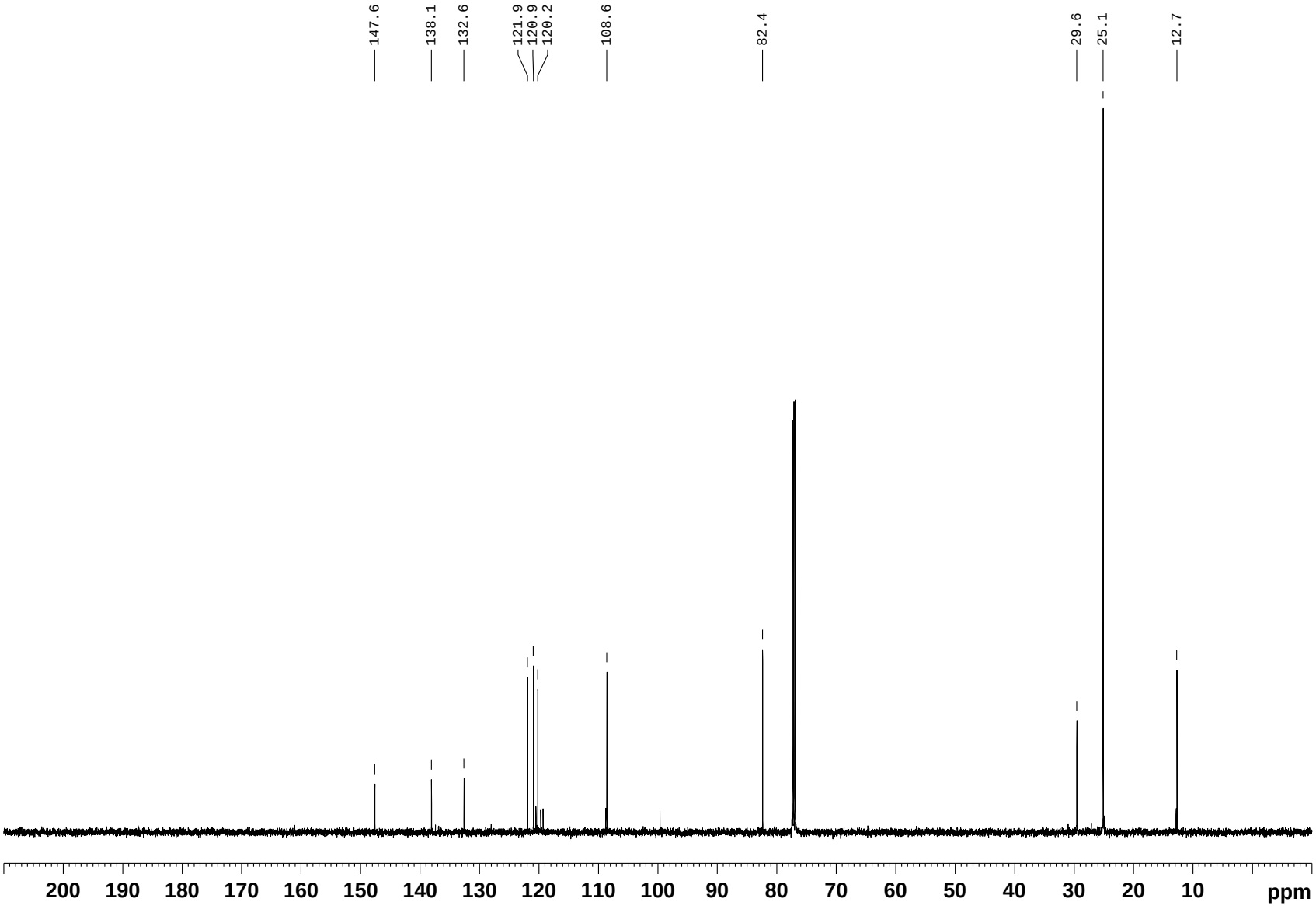


1,2-Dimethyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)indole (7bc)

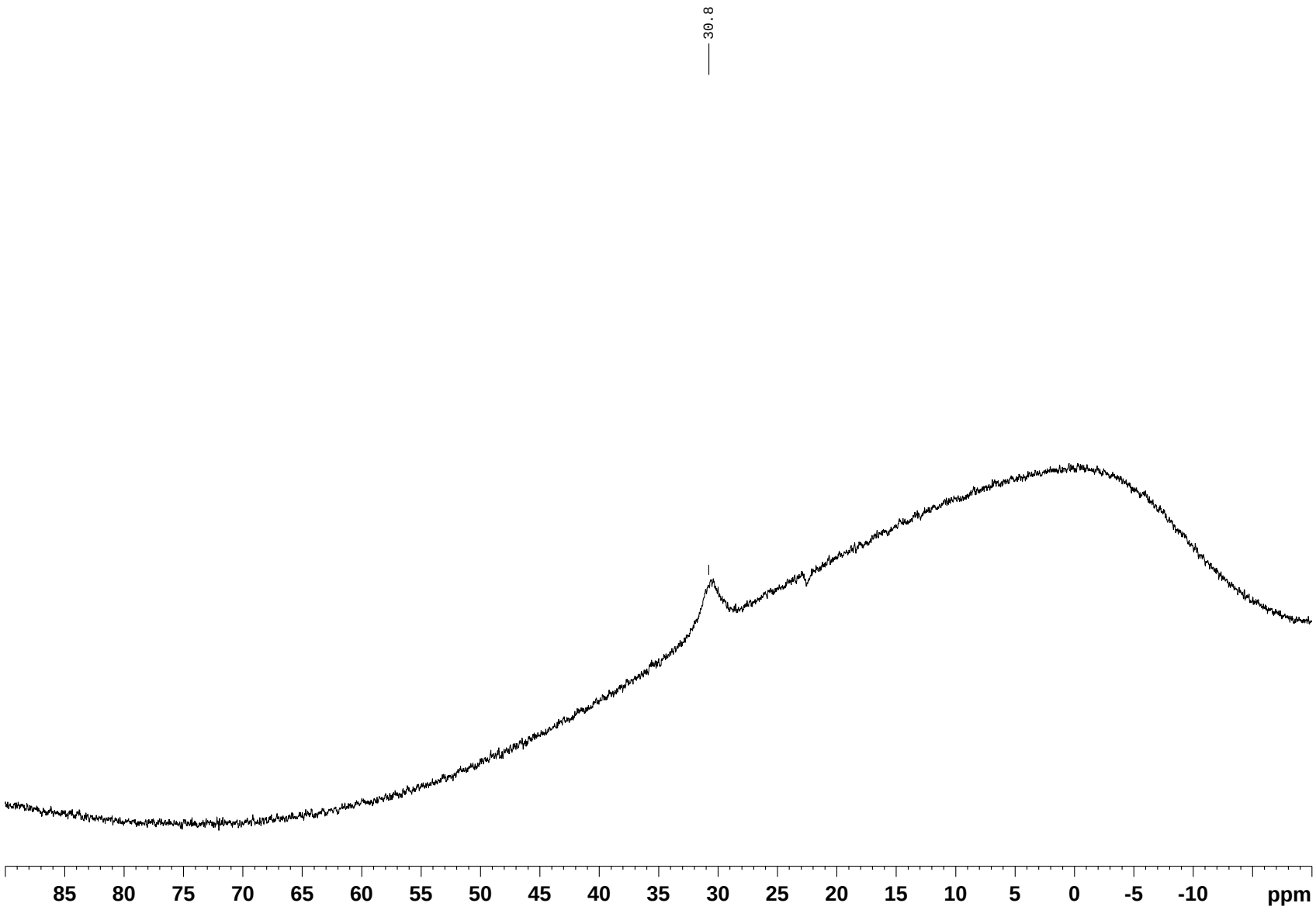
^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (126 MHz, $CDCl_3$):

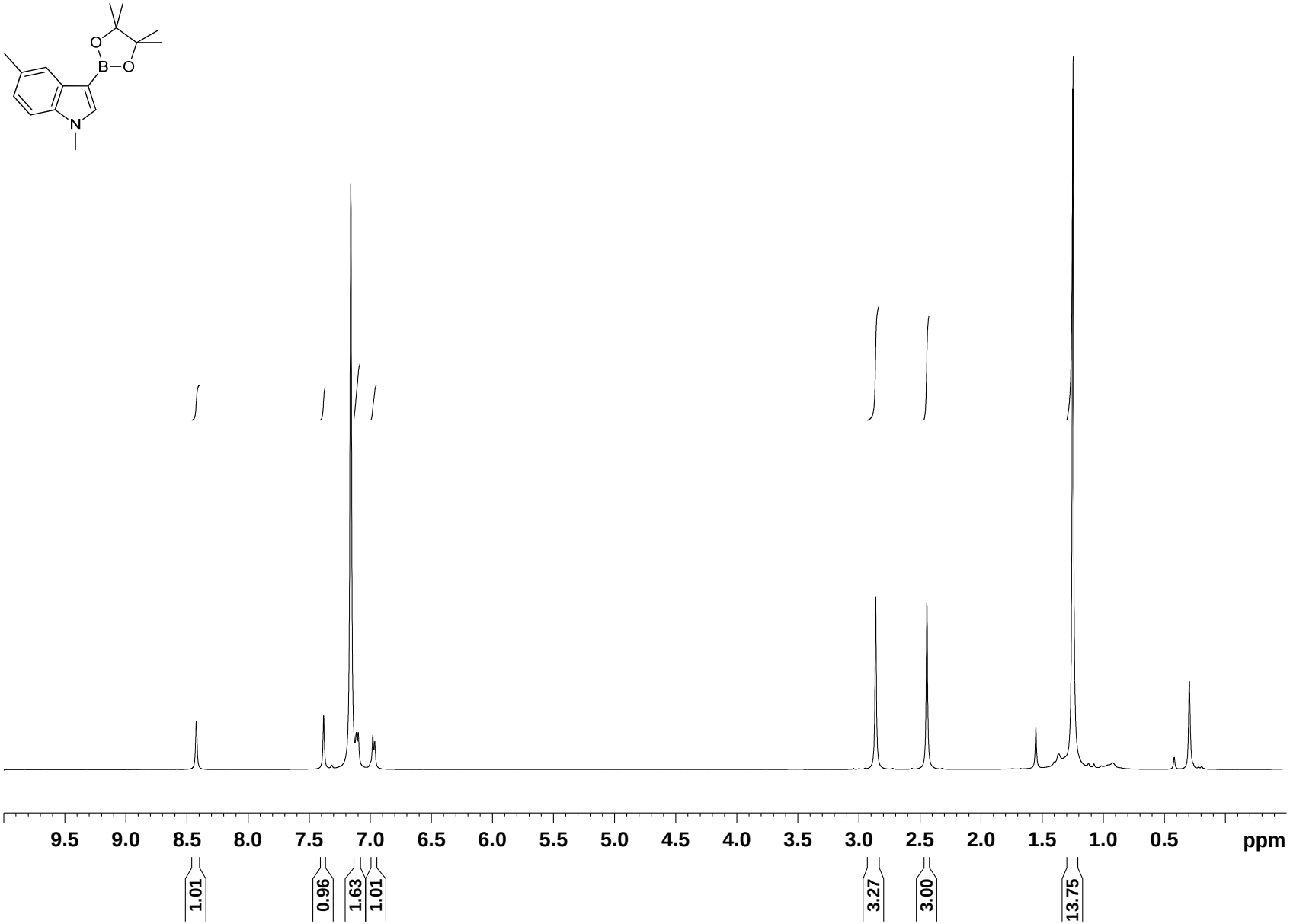


^{11}B NMR (161 MHz, $CDCl_3$):

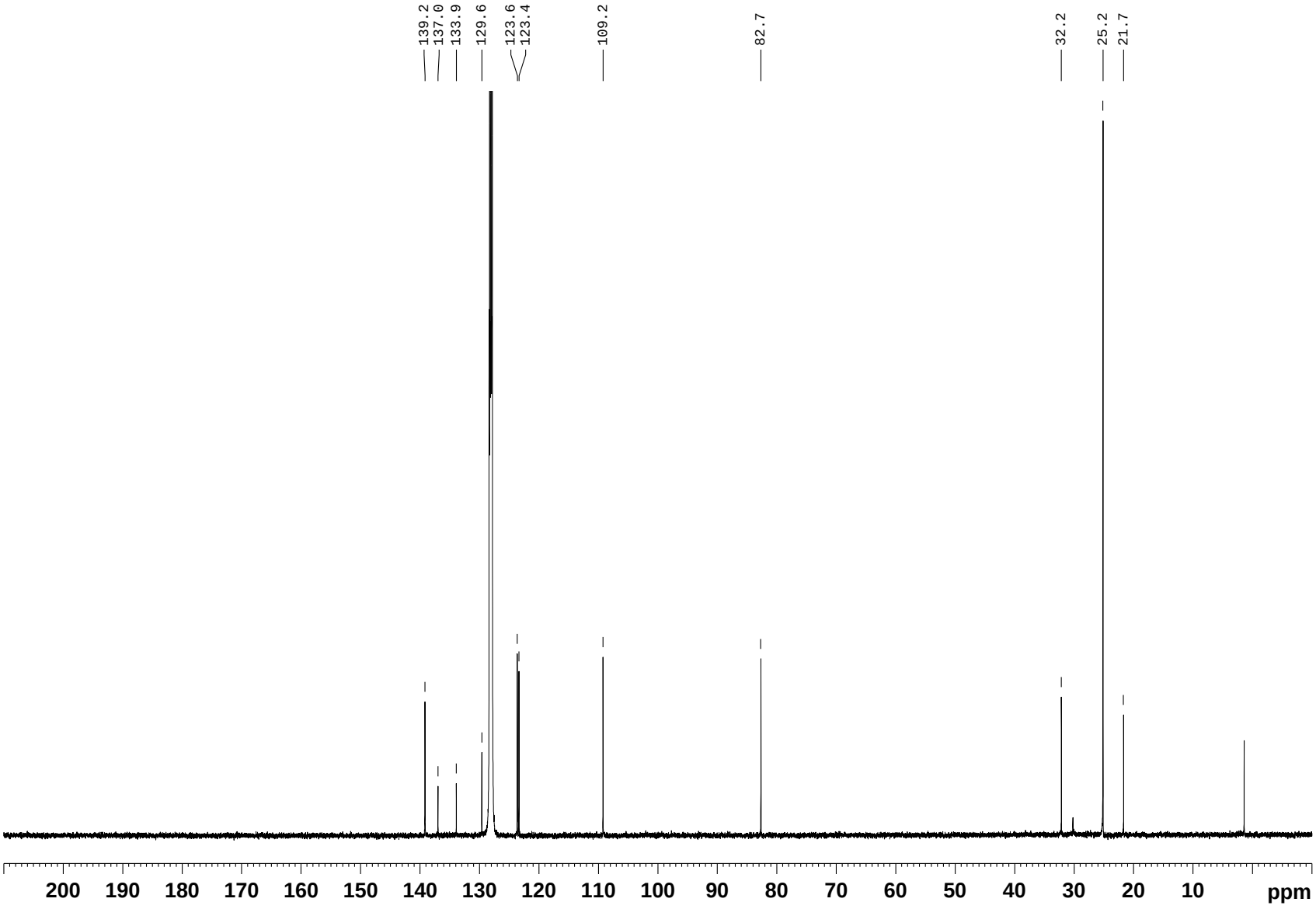


1,5-Dimethyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)indole (7cc)

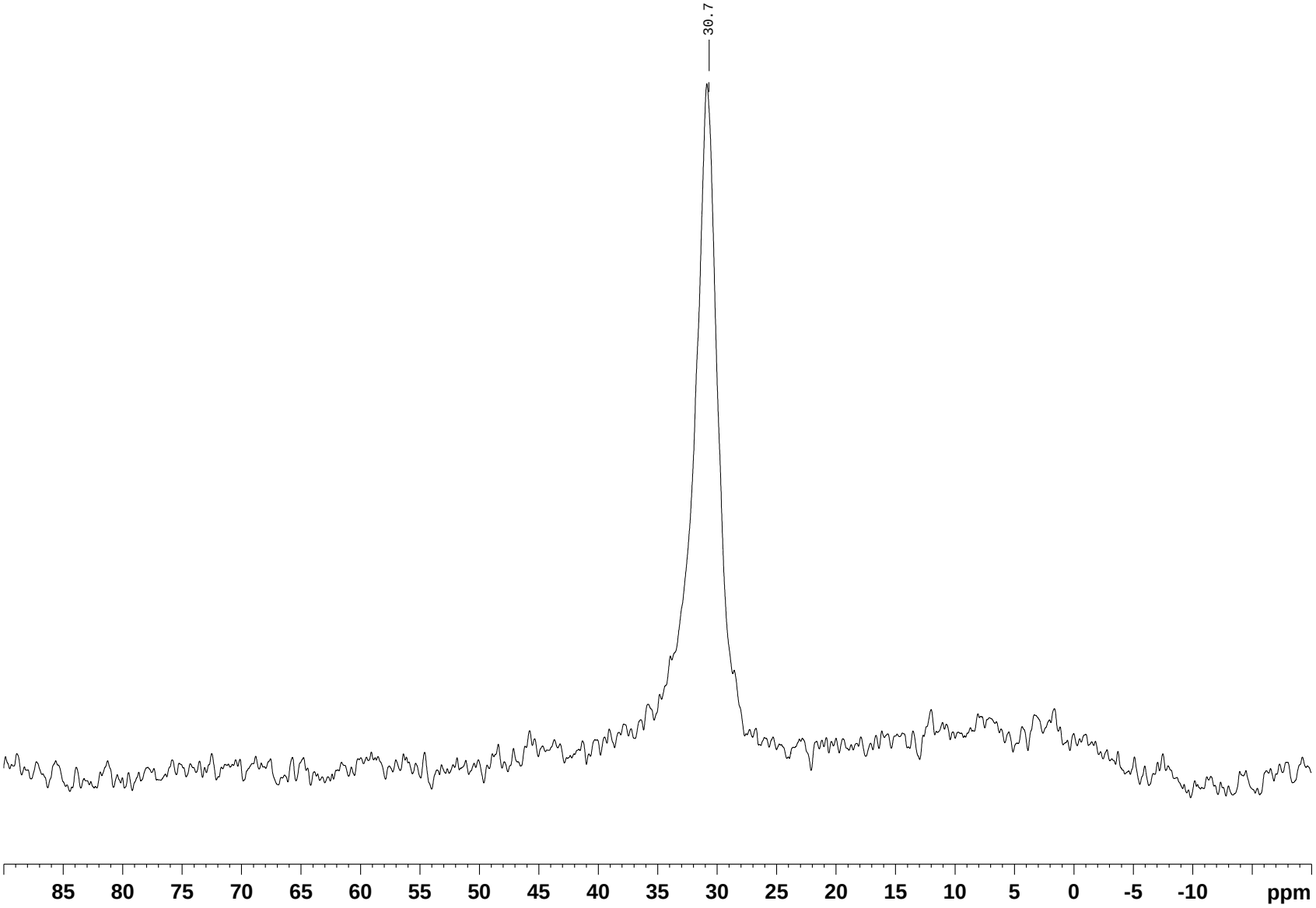
^{1}H NMR (500 MHz, C_6D_6):



^{13}C NMR (126 MHz, C_6D_6):

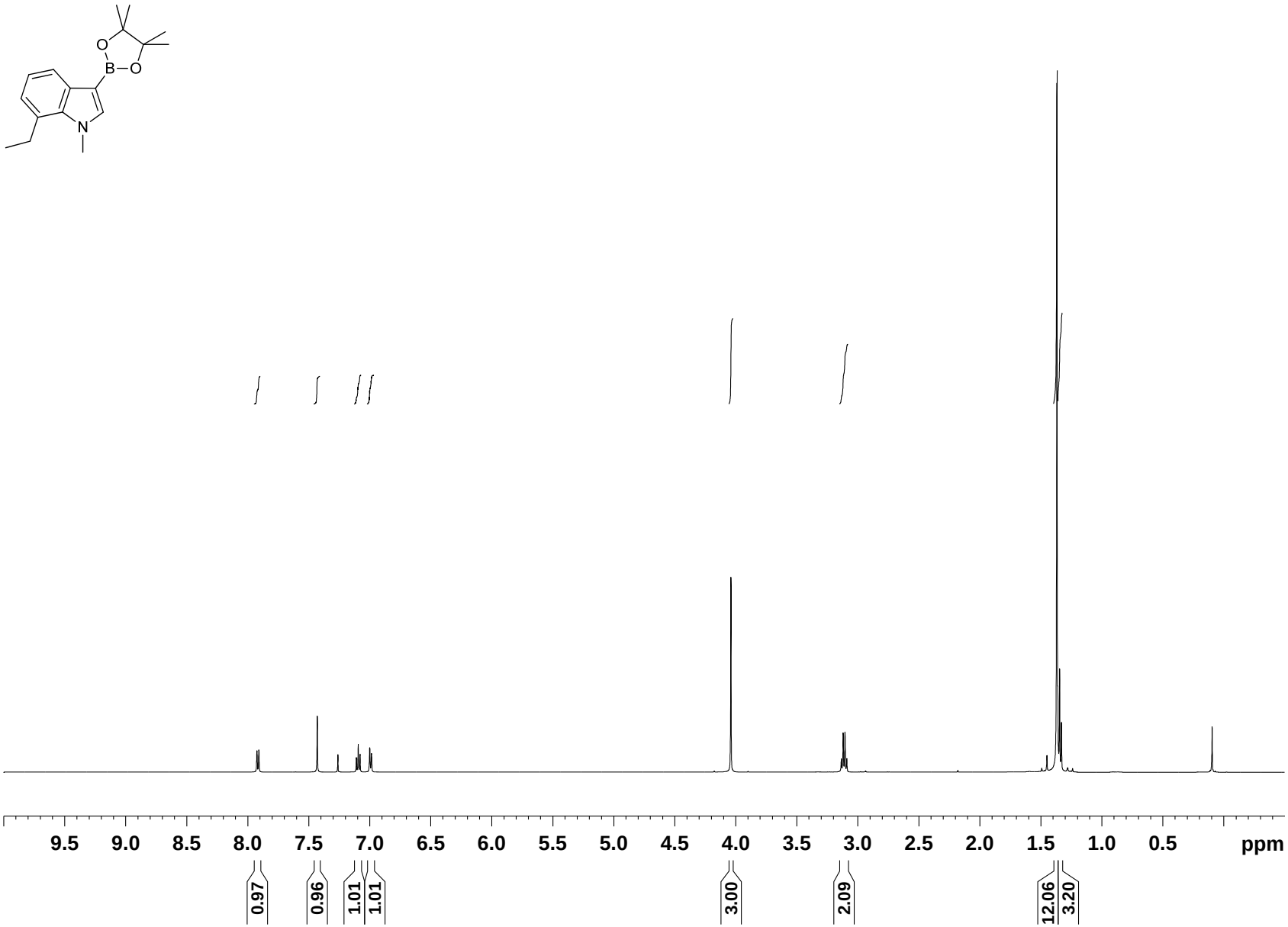


^{11}B NMR (161 MHz, C_6D_6):

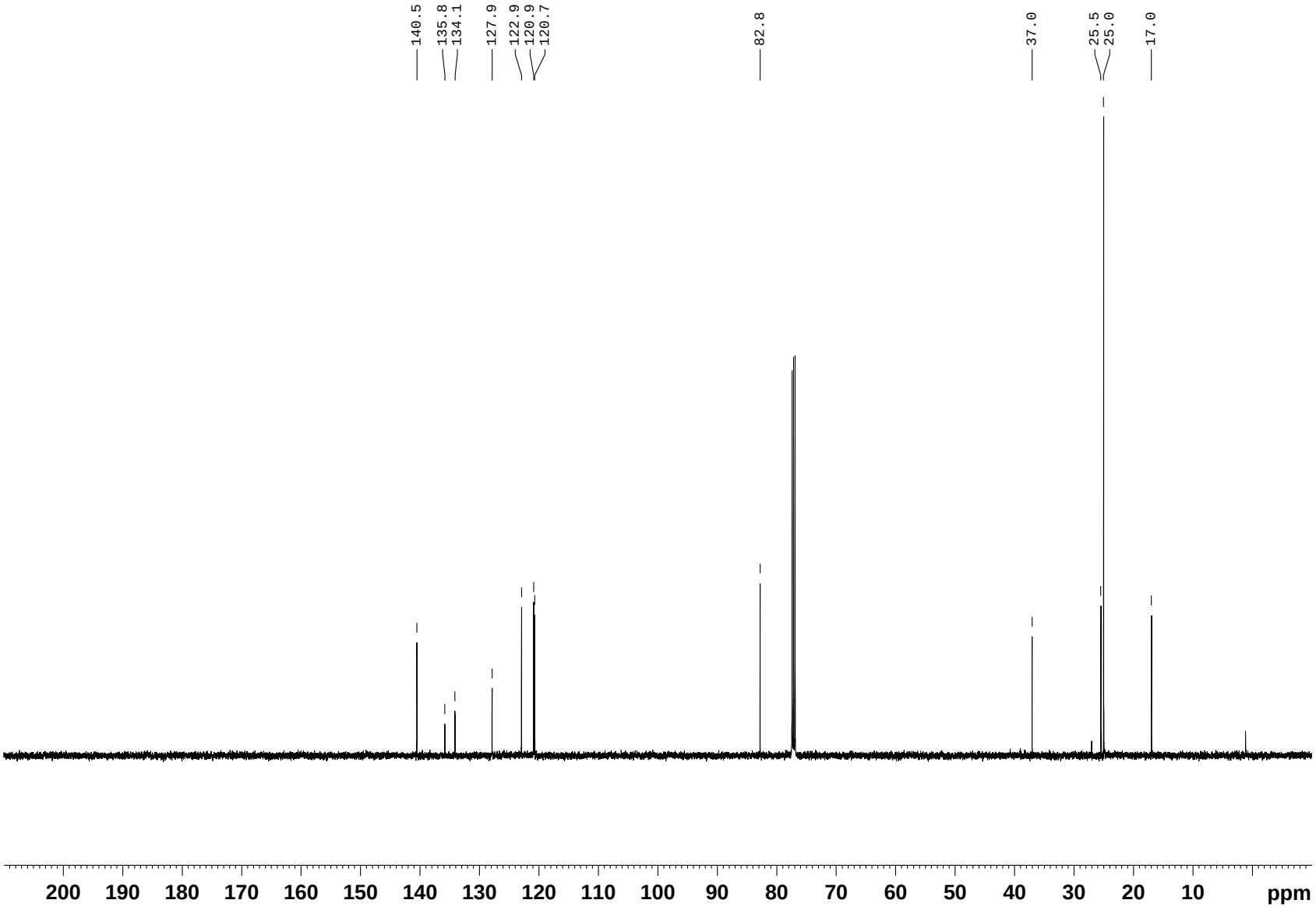


7-Ethyl-1-methyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)indole (7dc)

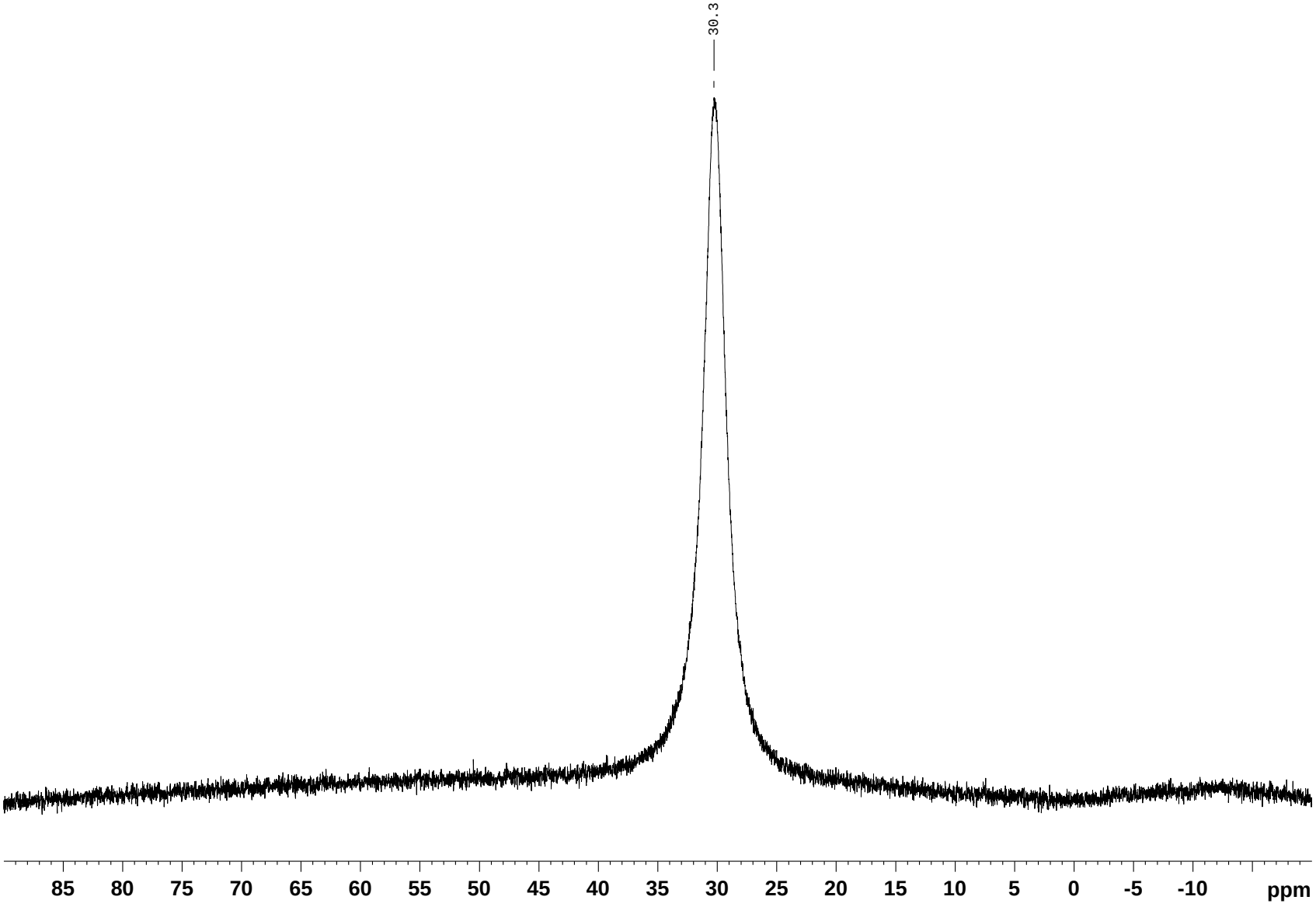
^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (126 MHz, $CDCl_3$):



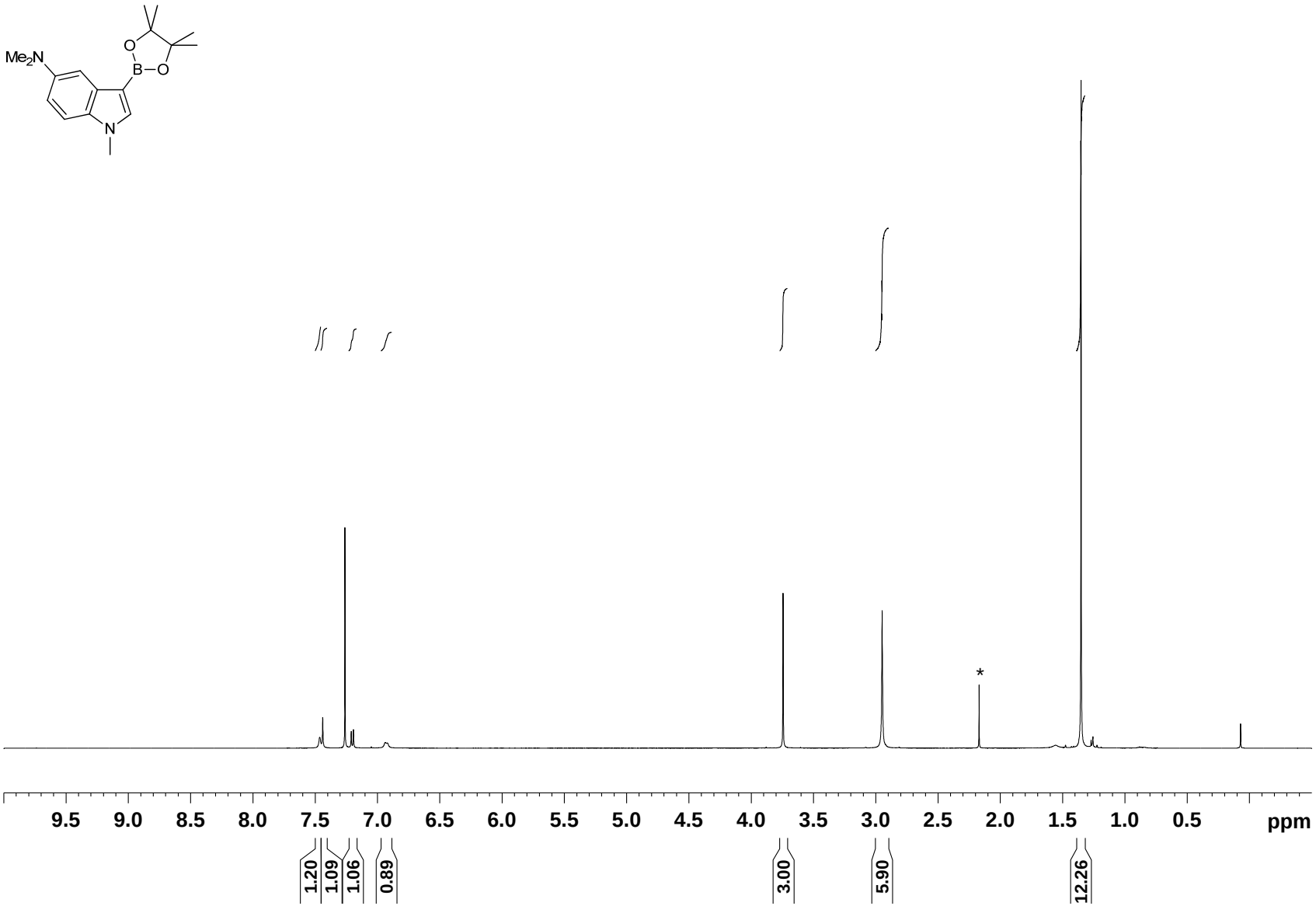
^{11}B NMR (161 MHz, $CDCl_3$):



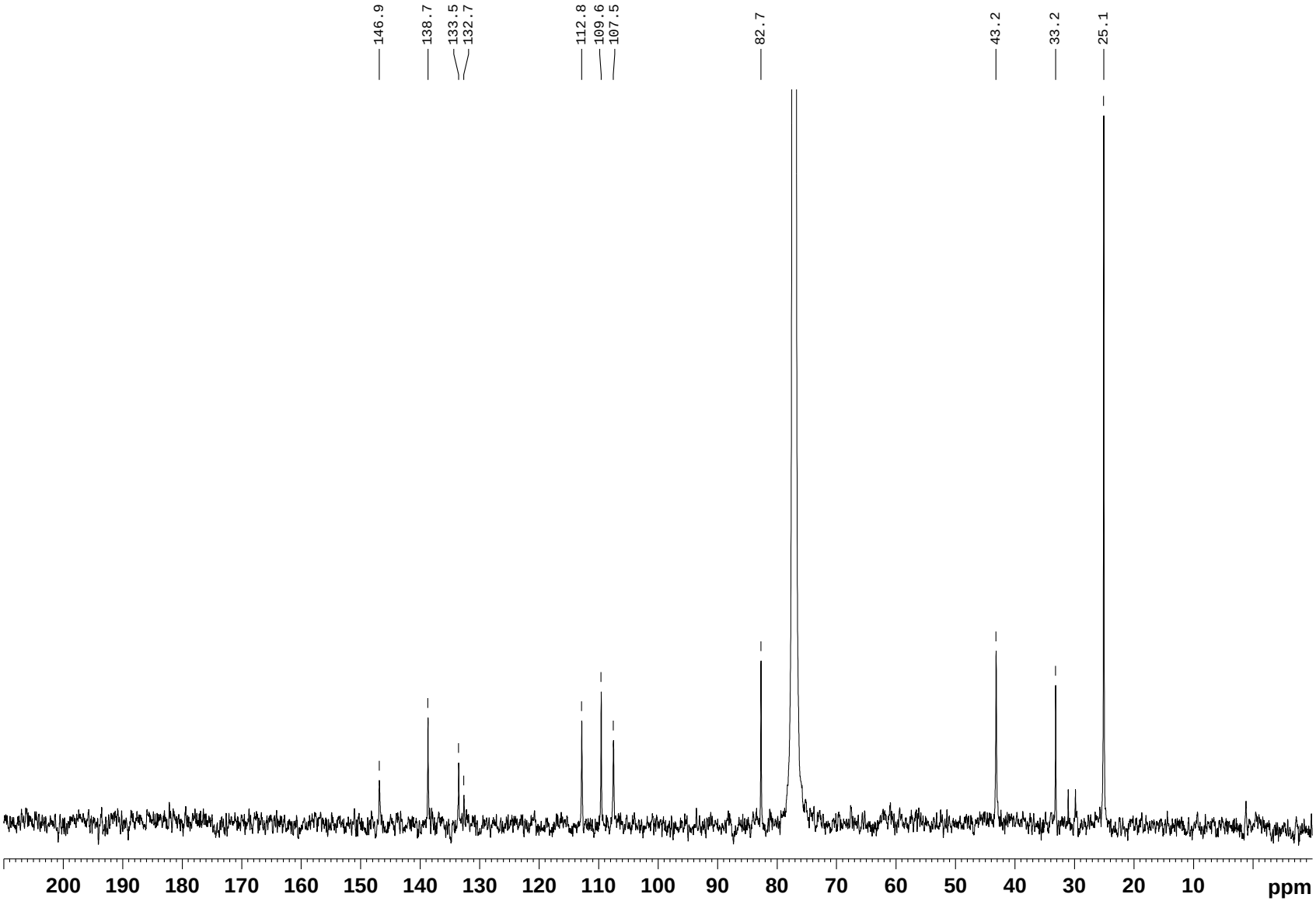
5-(*N*',*N*'-Dimethylamino)-1-methyl-3-(4'',4'',5'',5''-tetramethyl-1'',3'',2''-dioxaborolan-2''-yl)indole (7ec)

^{1}H NMR (500 MHz, $CDCl_3$):

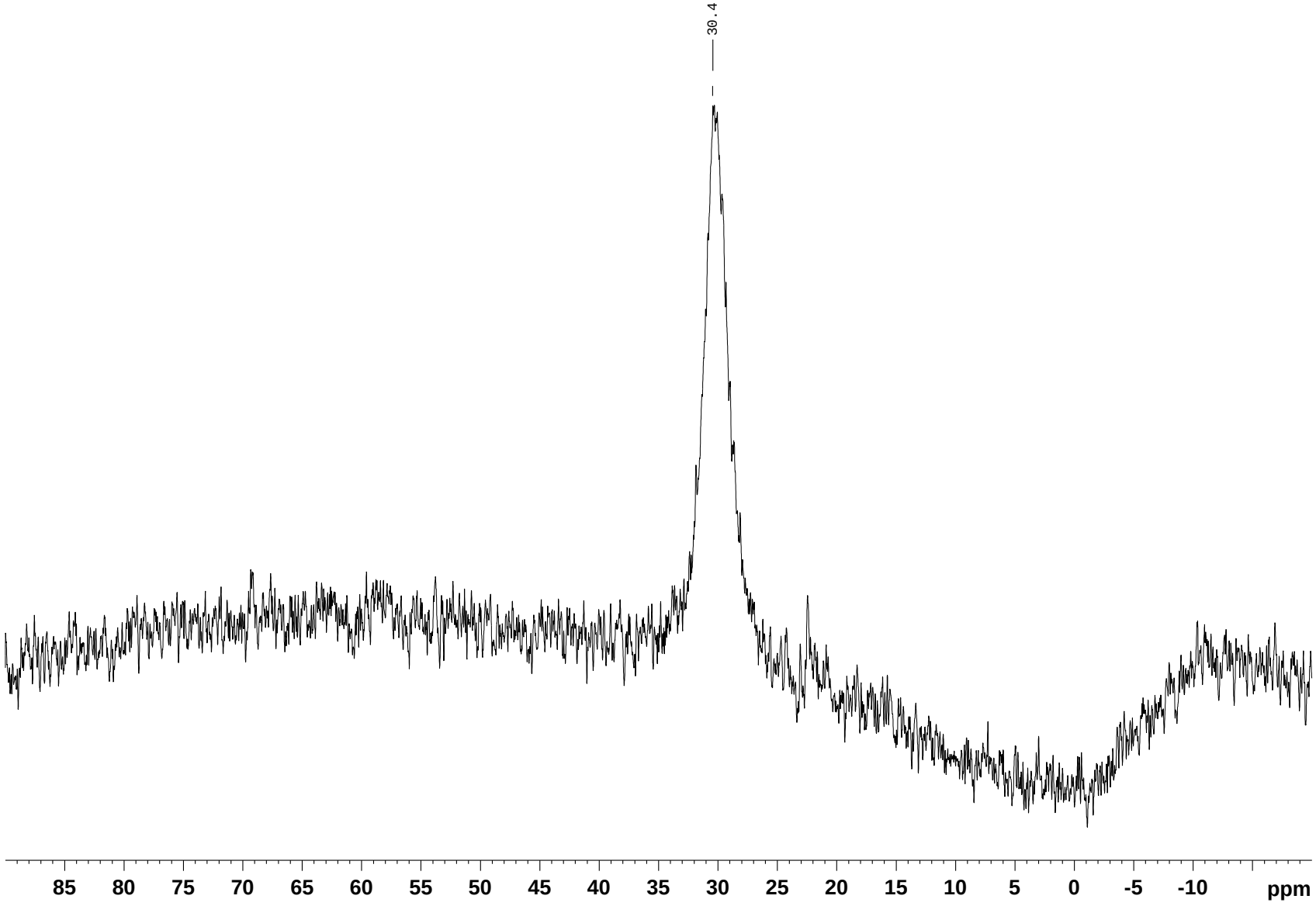
* = Acetone



^{13}C NMR (126 MHz, $CDCl_3$):

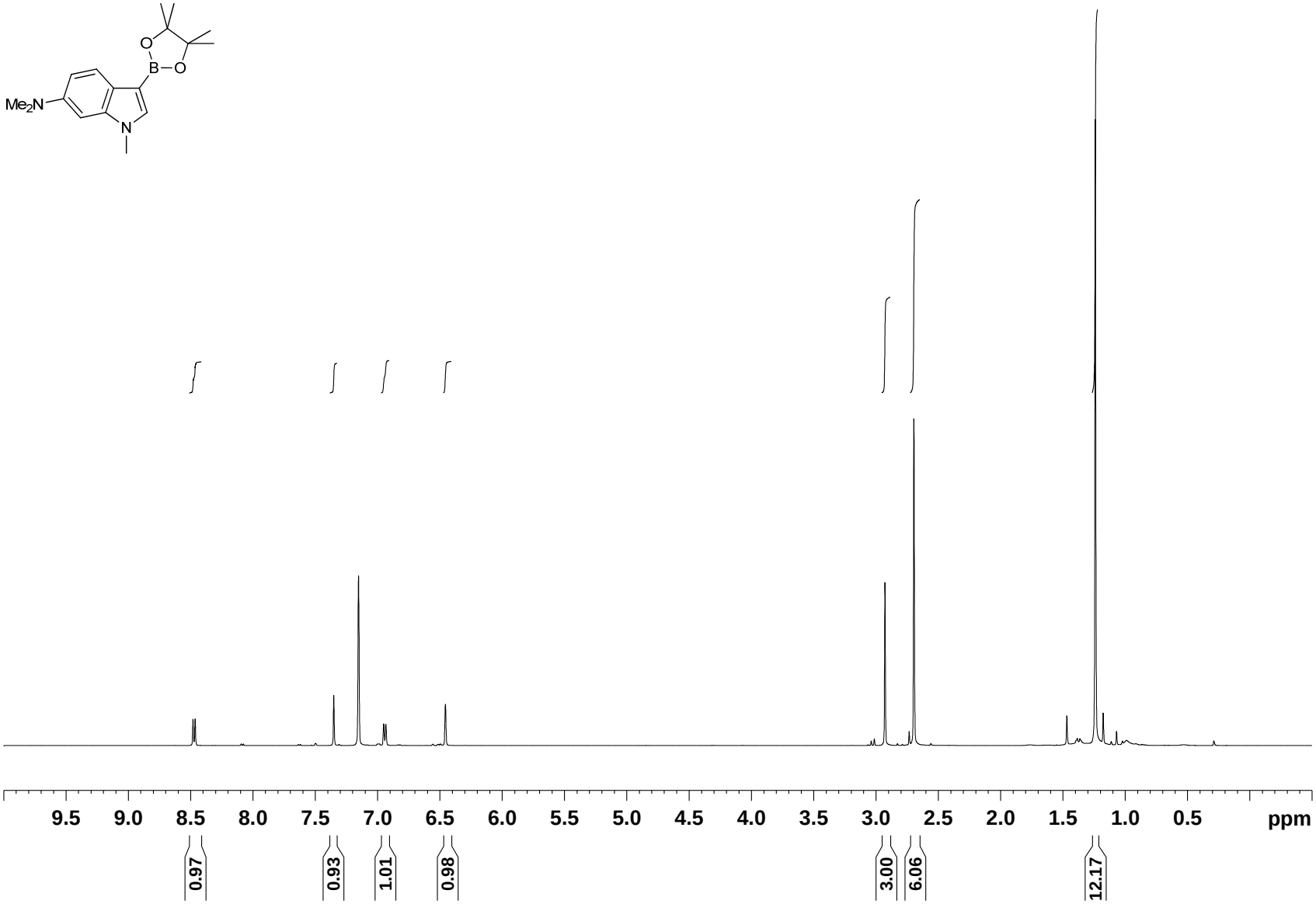


^{11}B NMR (161 MHz, $CDCl_3$):

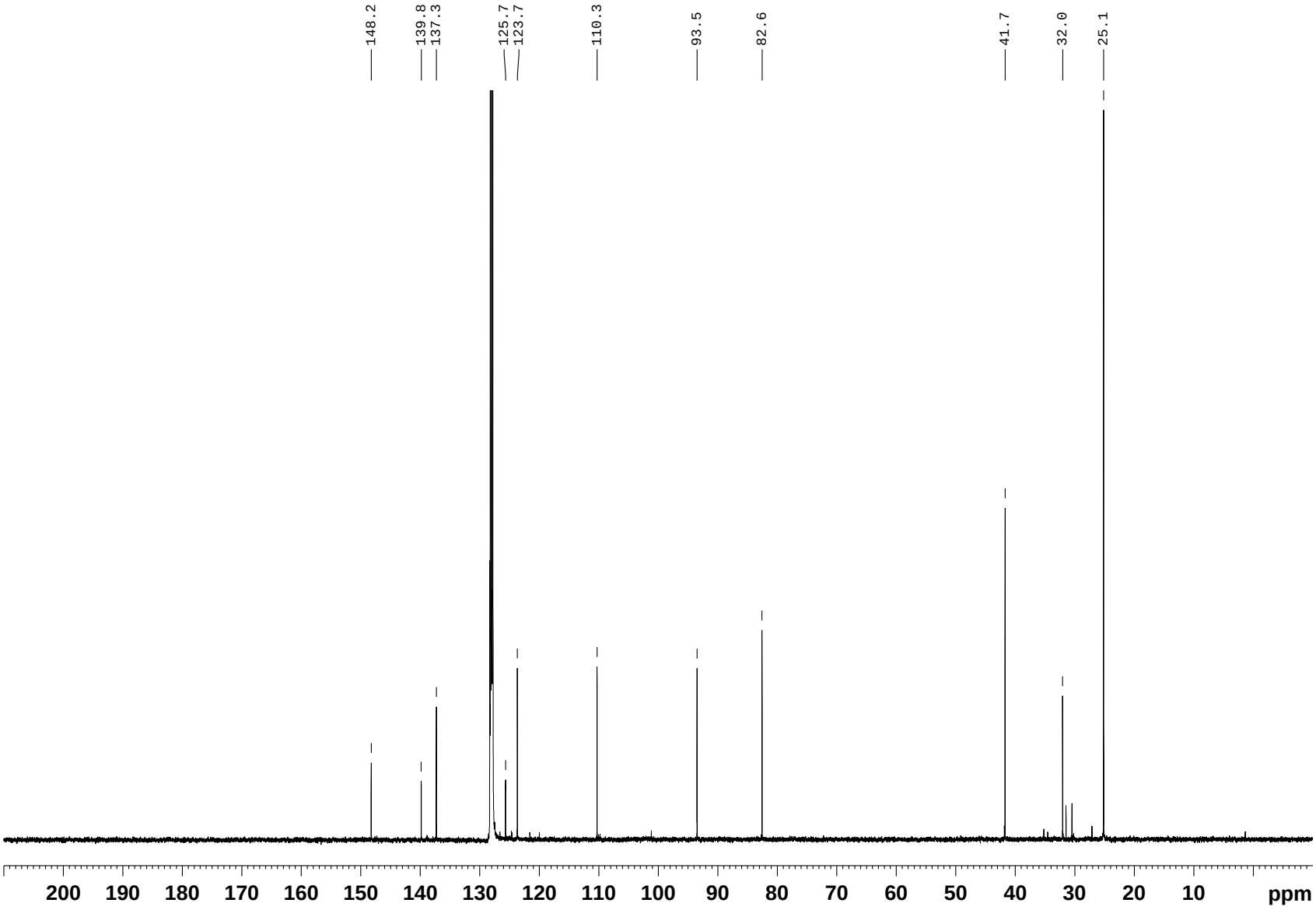


6-(*N*',*N*'-Dimethylamino)-1-methyl-3-(4'',4'',5'',5''-tetramethyl-1'',3'',2''-dioxaborolan-2''-yl)indole (7fc)

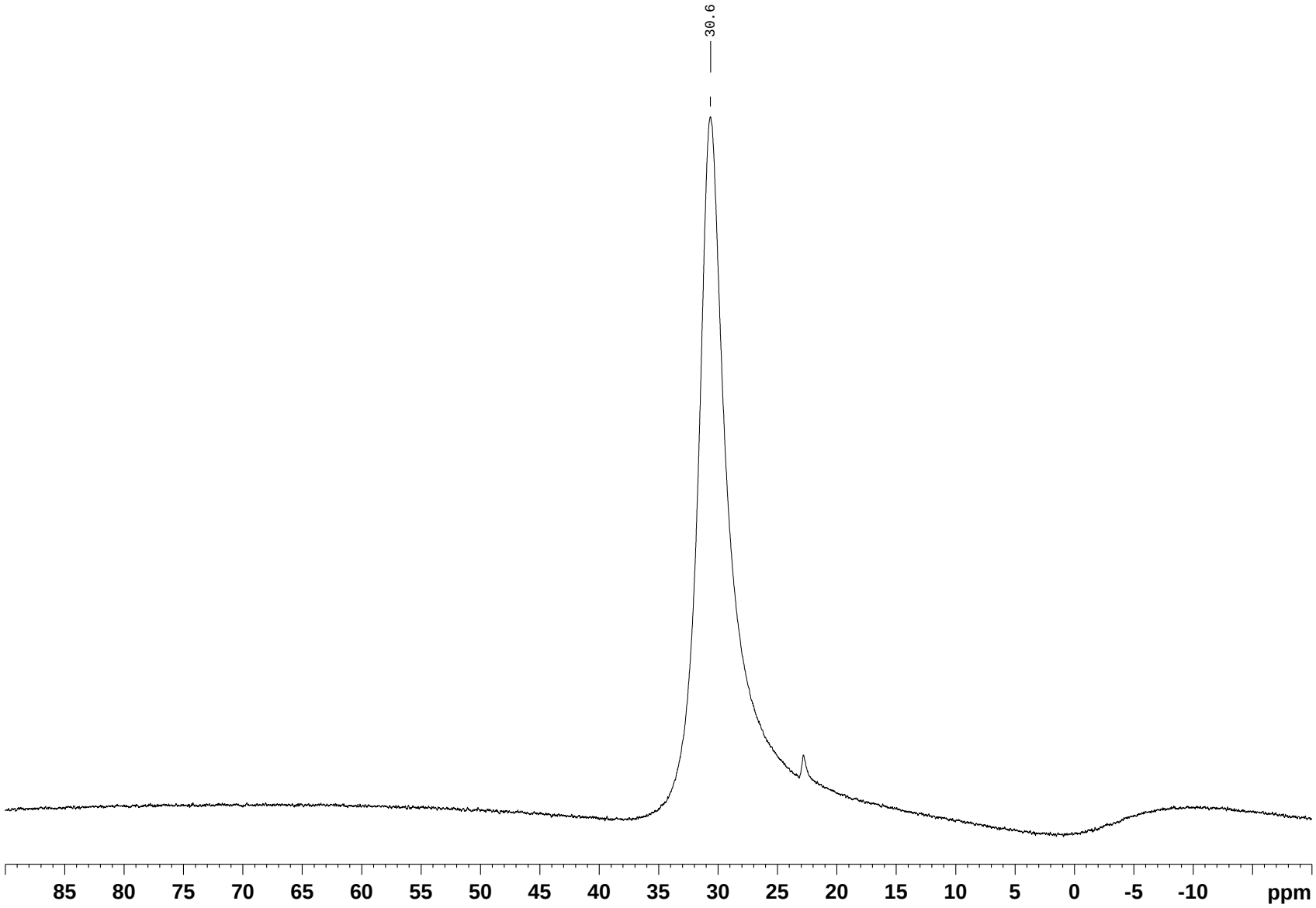
^{1}H NMR (500 MHz, C_6D_6):



^{13}C NMR (126 MHz, C_6D_6):

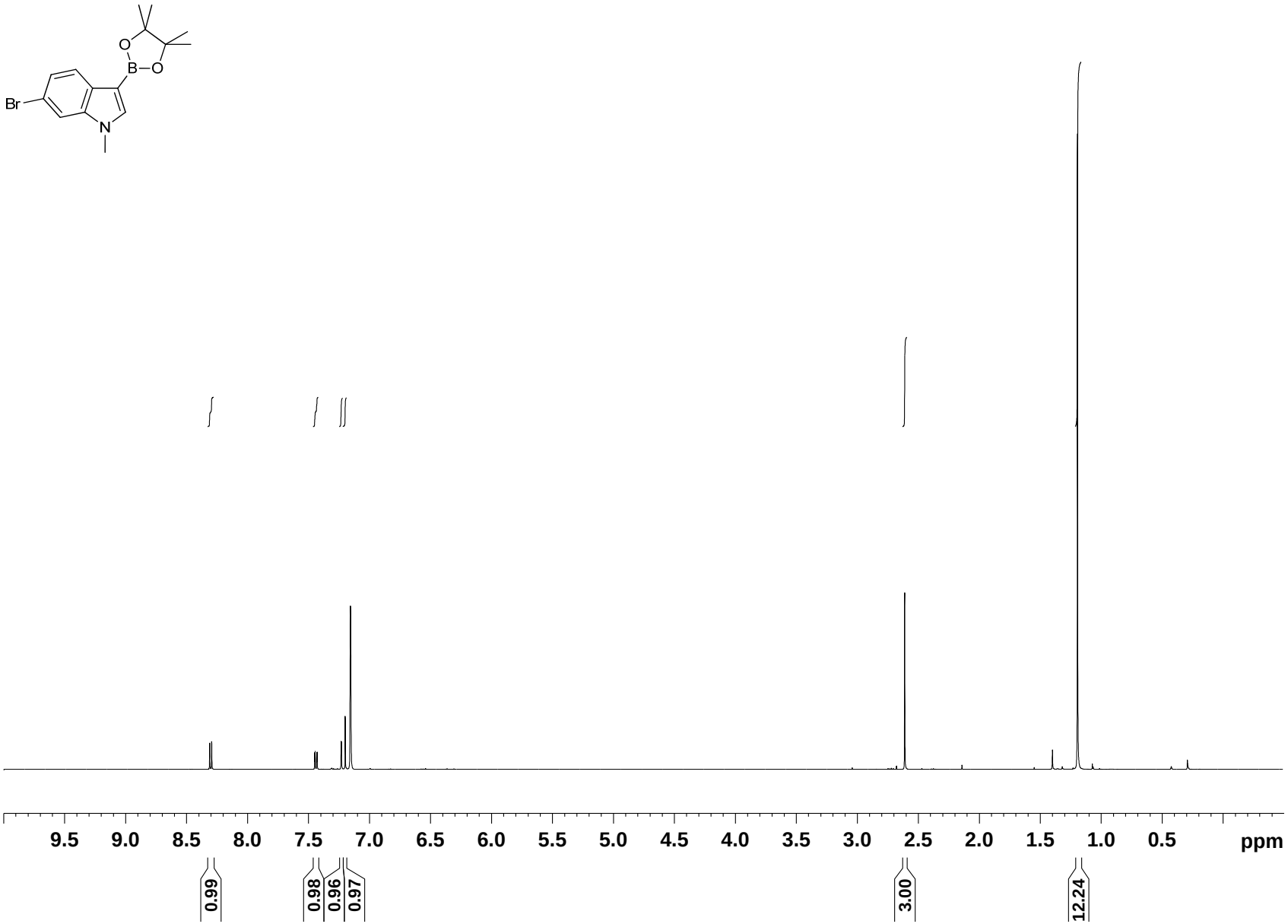


^{11}B NMR (161 MHz, C_6D_6):

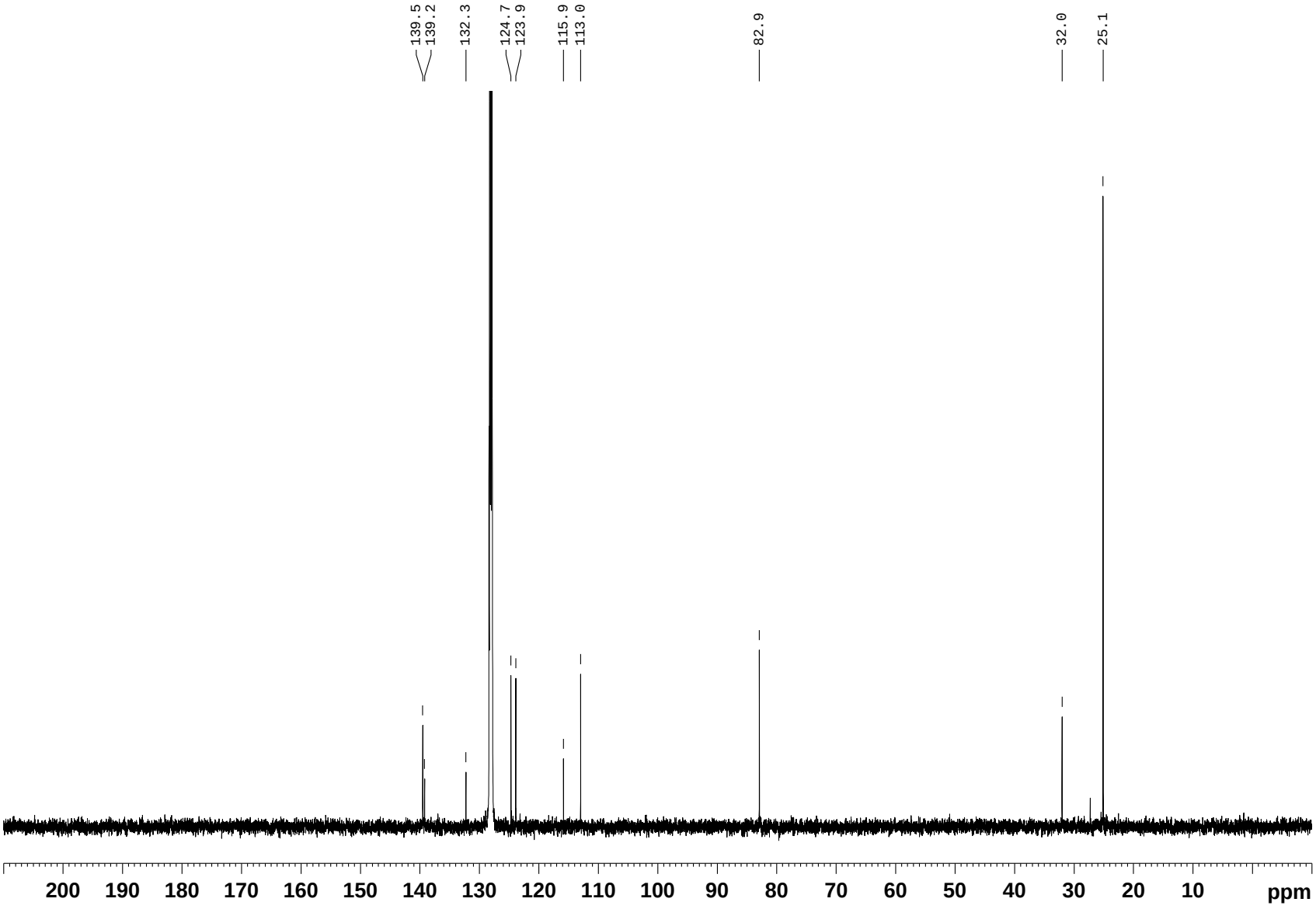


6-Bromo-1-methyl-3-(4'',4'',5'',5''-tetramethyl-1'',3'',2''-dioxaborolan-2''-yl)indole (7gc)

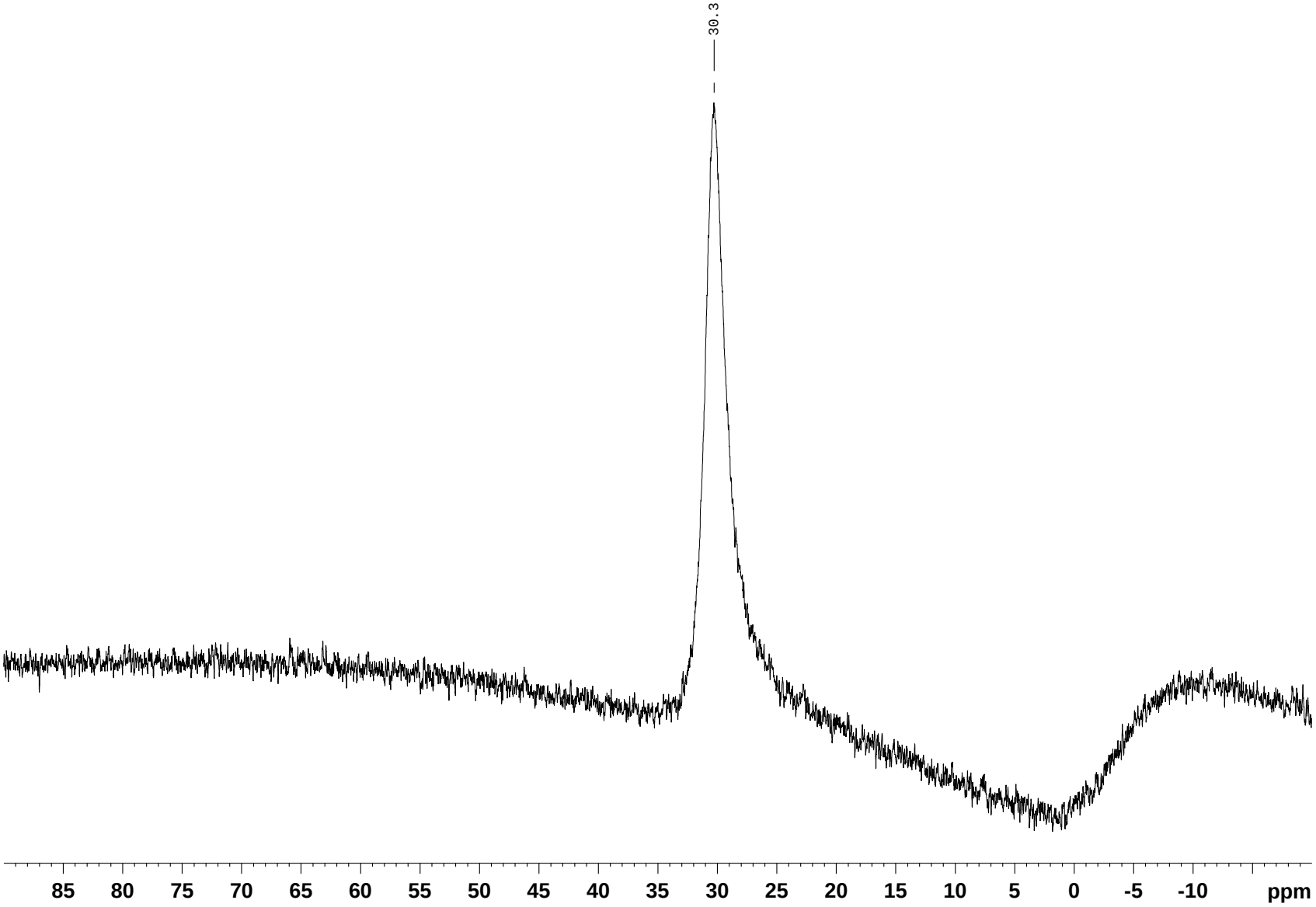
^{1}H NMR (500 MHz, C_6D_6):



^{13}C NMR (126 MHz, C_6D_6):

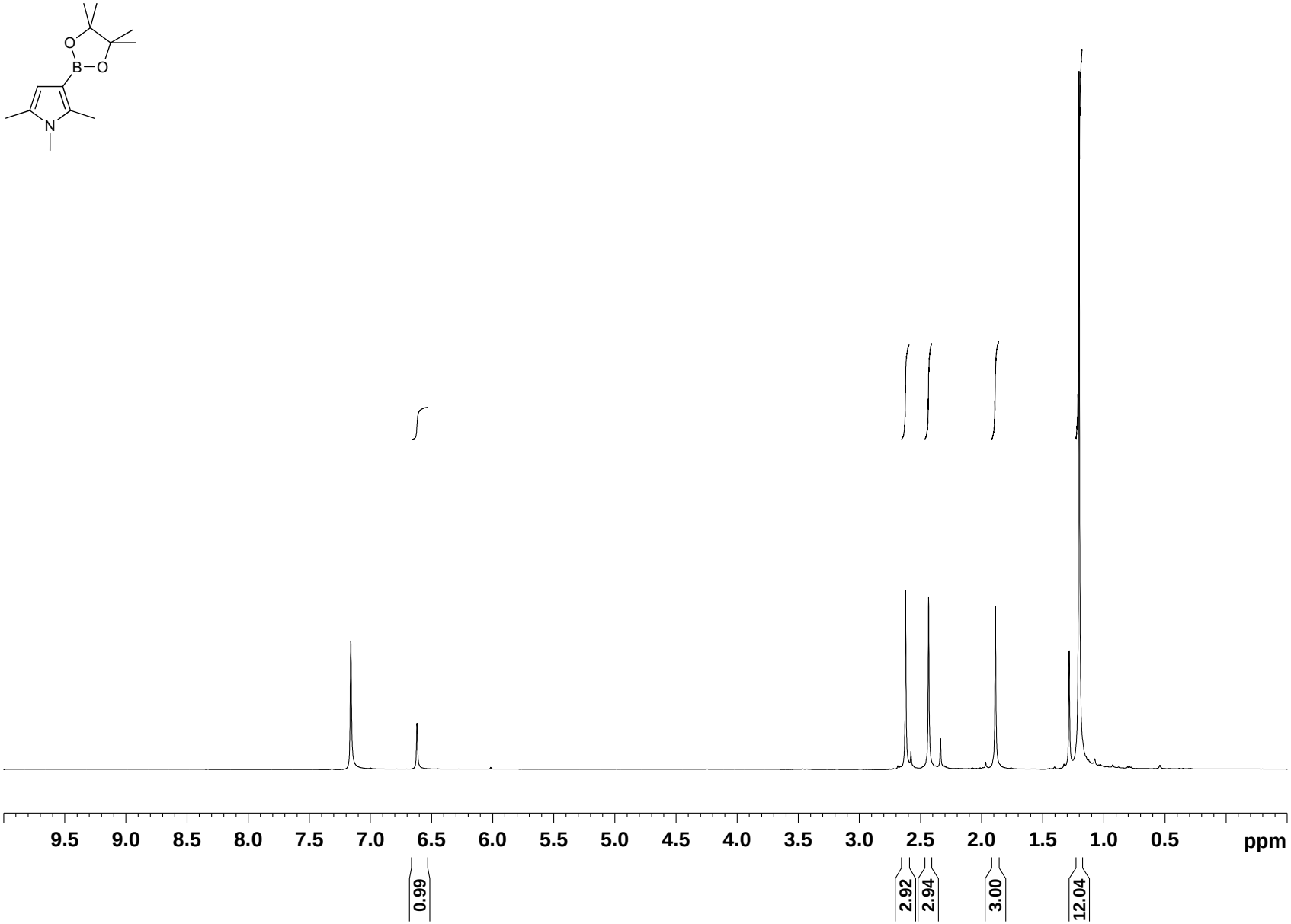


^{11}B NMR (161 MHz, C_6D_6):

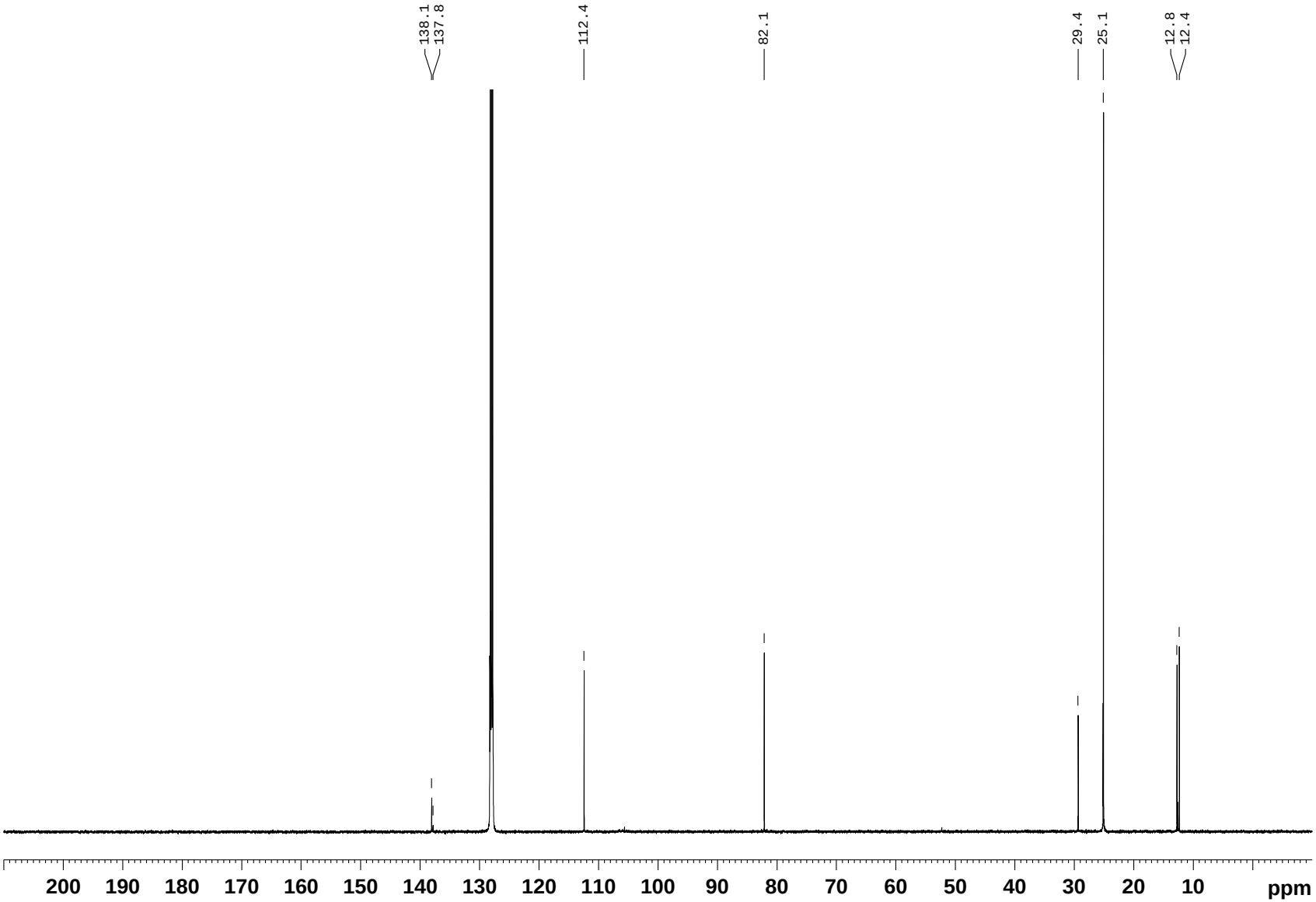


1,2,5-Trimethyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)pyrrole (9c)

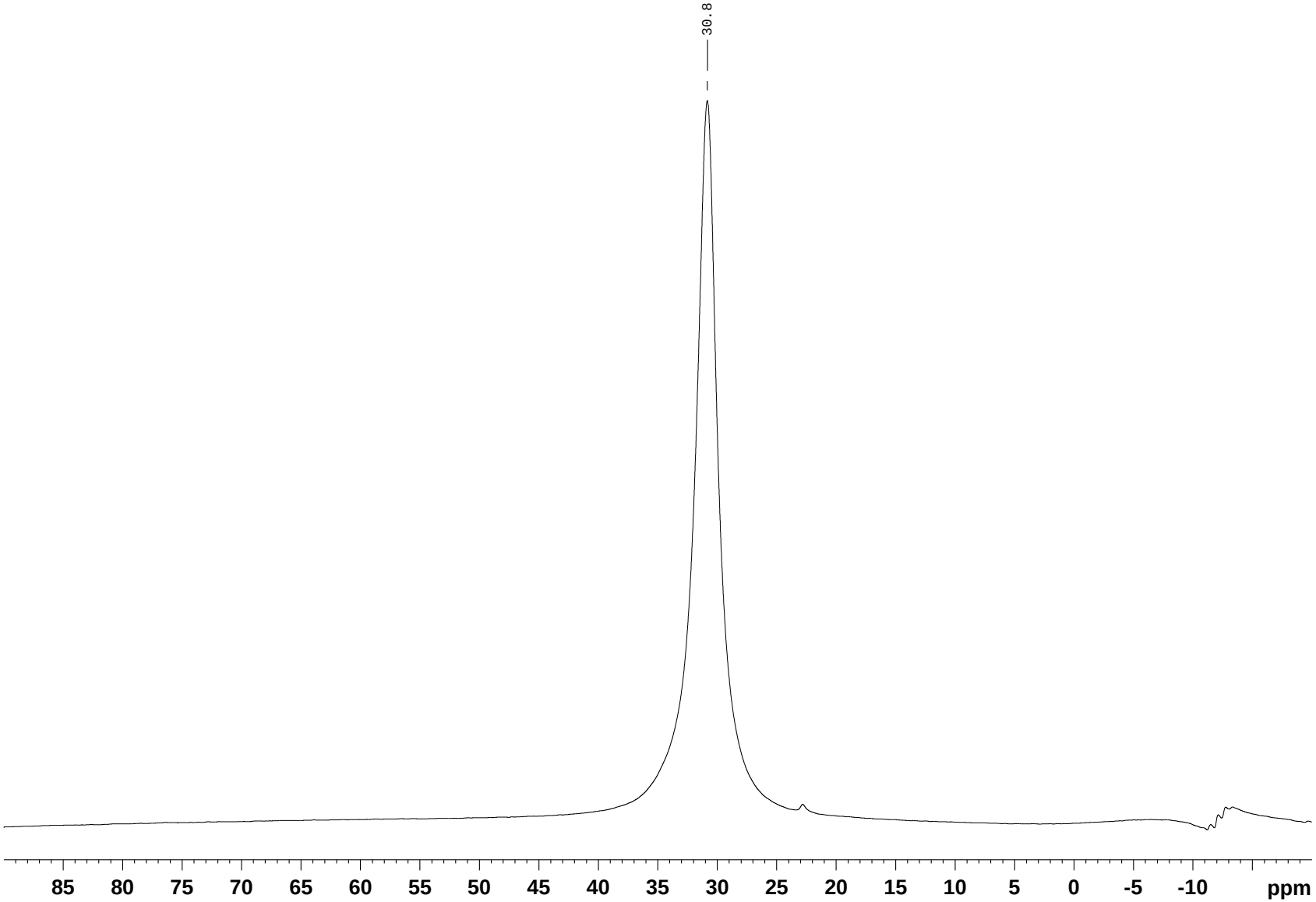
^{1}H NMR (500 MHz, C_6D_6):



^{13}C NMR (126 MHz, C_6D_6):

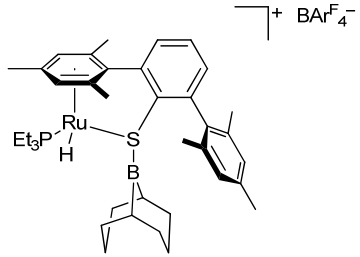


^{11}B NMR (161 MHz, C_6D_6):

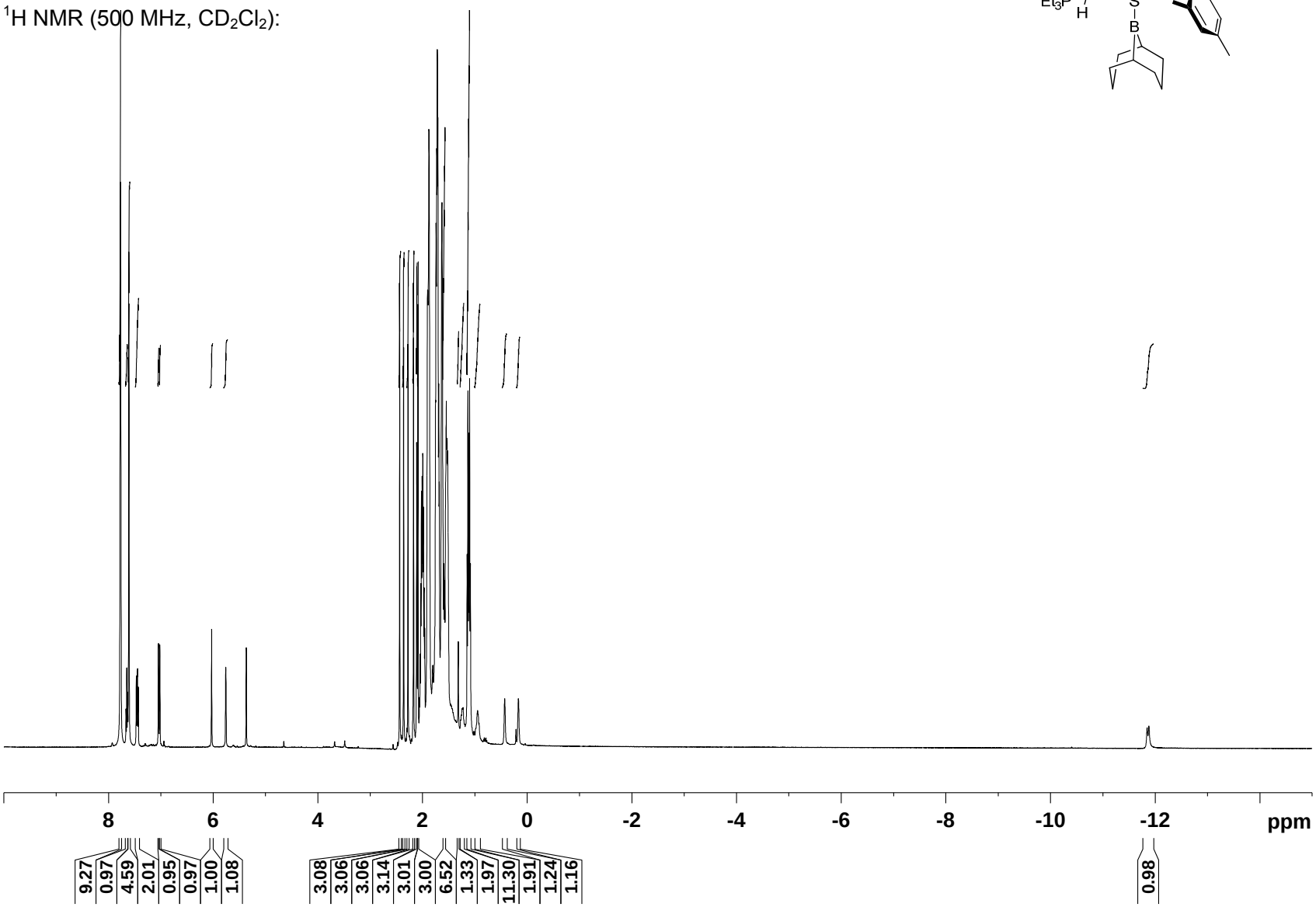


5.3 NMR Spectra of Sulfur-Stabilized Boreniumion Intermediates

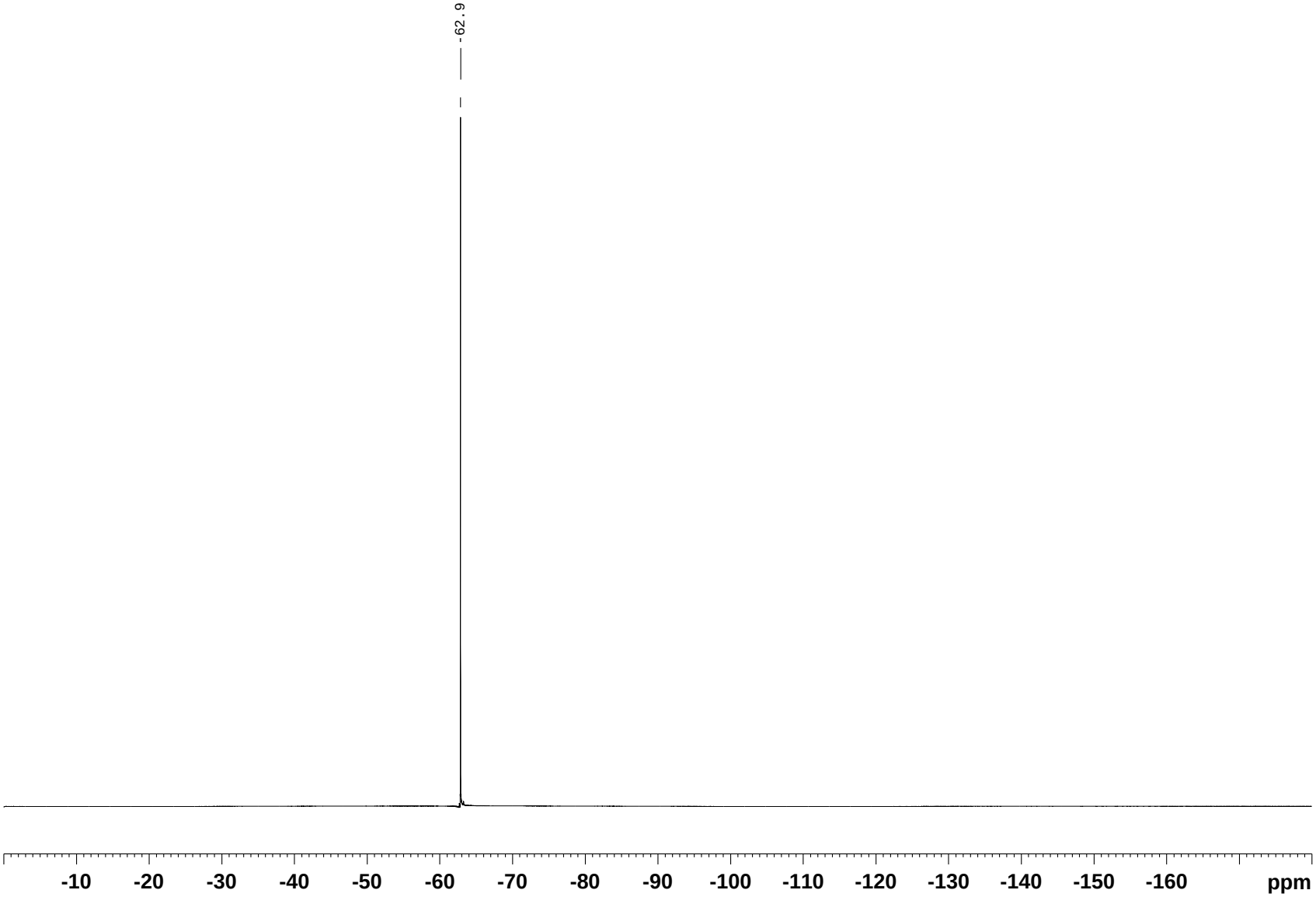
[(Et_3P)Ru(SDmp)·(9-BBN)]BAr^F_4 (3aa)



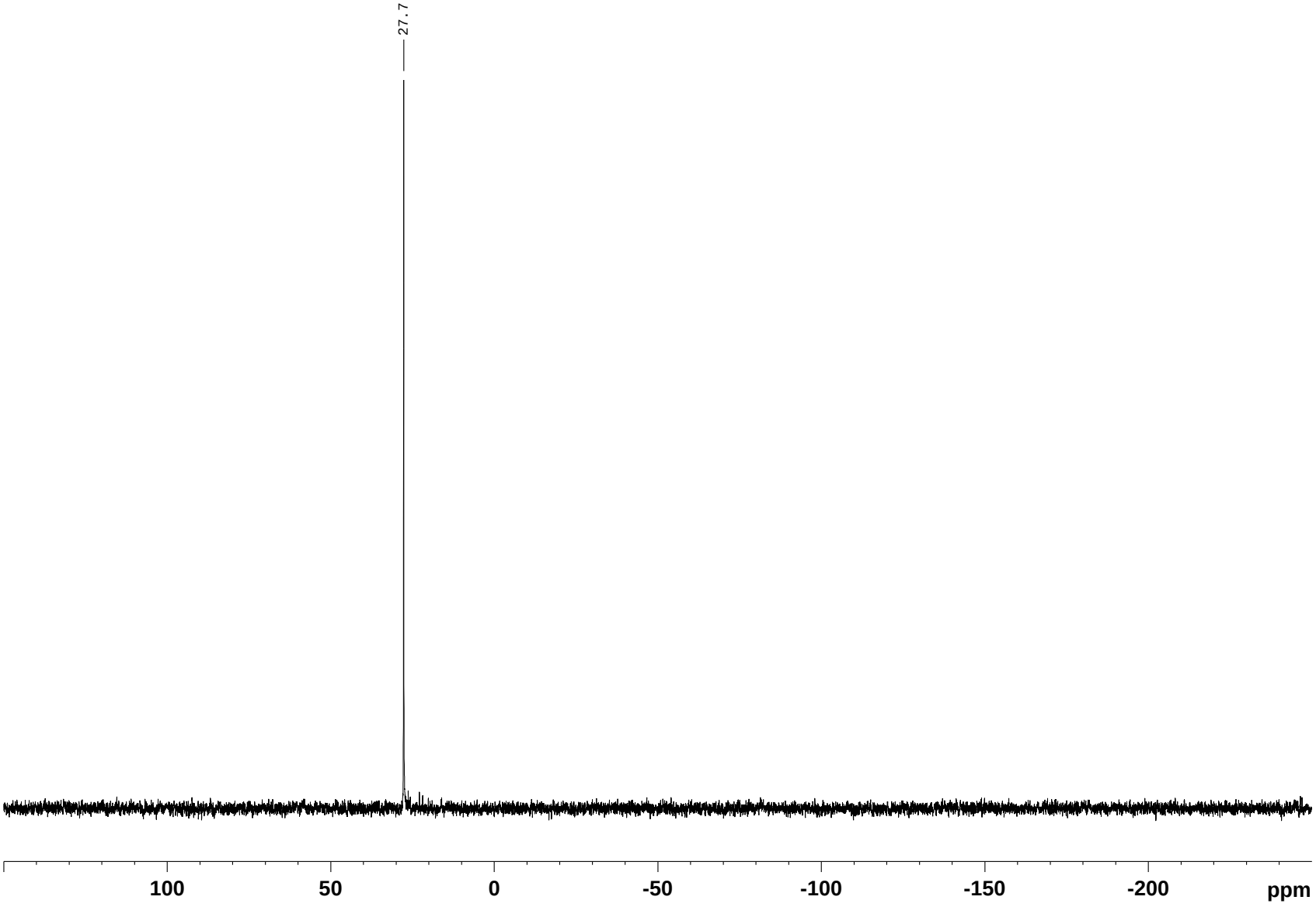
^{1}H NMR (500 MHz, CD_2Cl_2):



$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2):

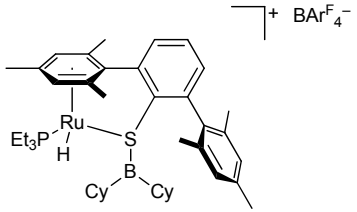


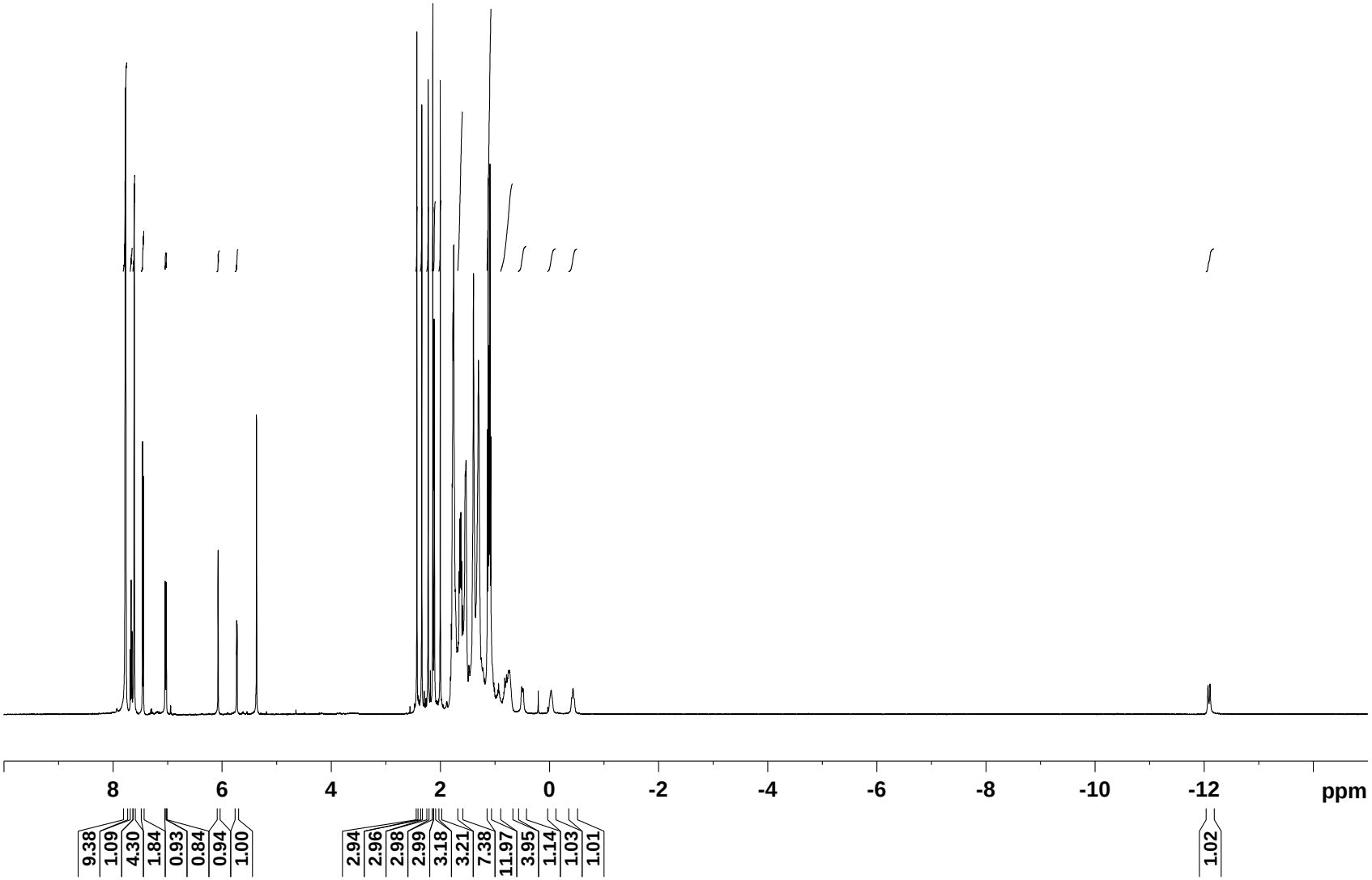
$^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2):



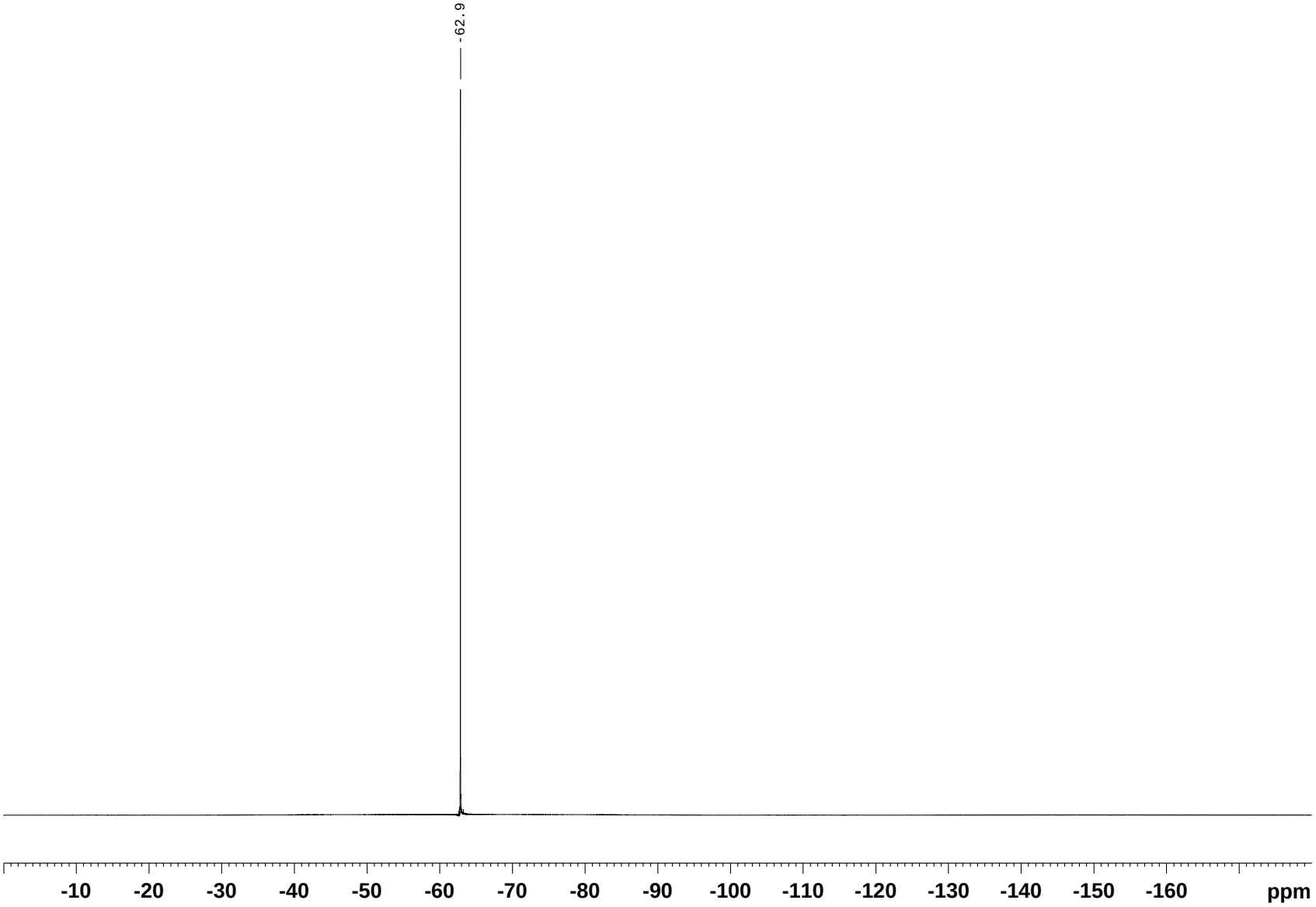
[(Et$_3$P)Ru(SDmp)·HBCy$_2$]BAr$^F_4$ (3ab)

^{1}H NMR (500 MHz, CD_2Cl_2):

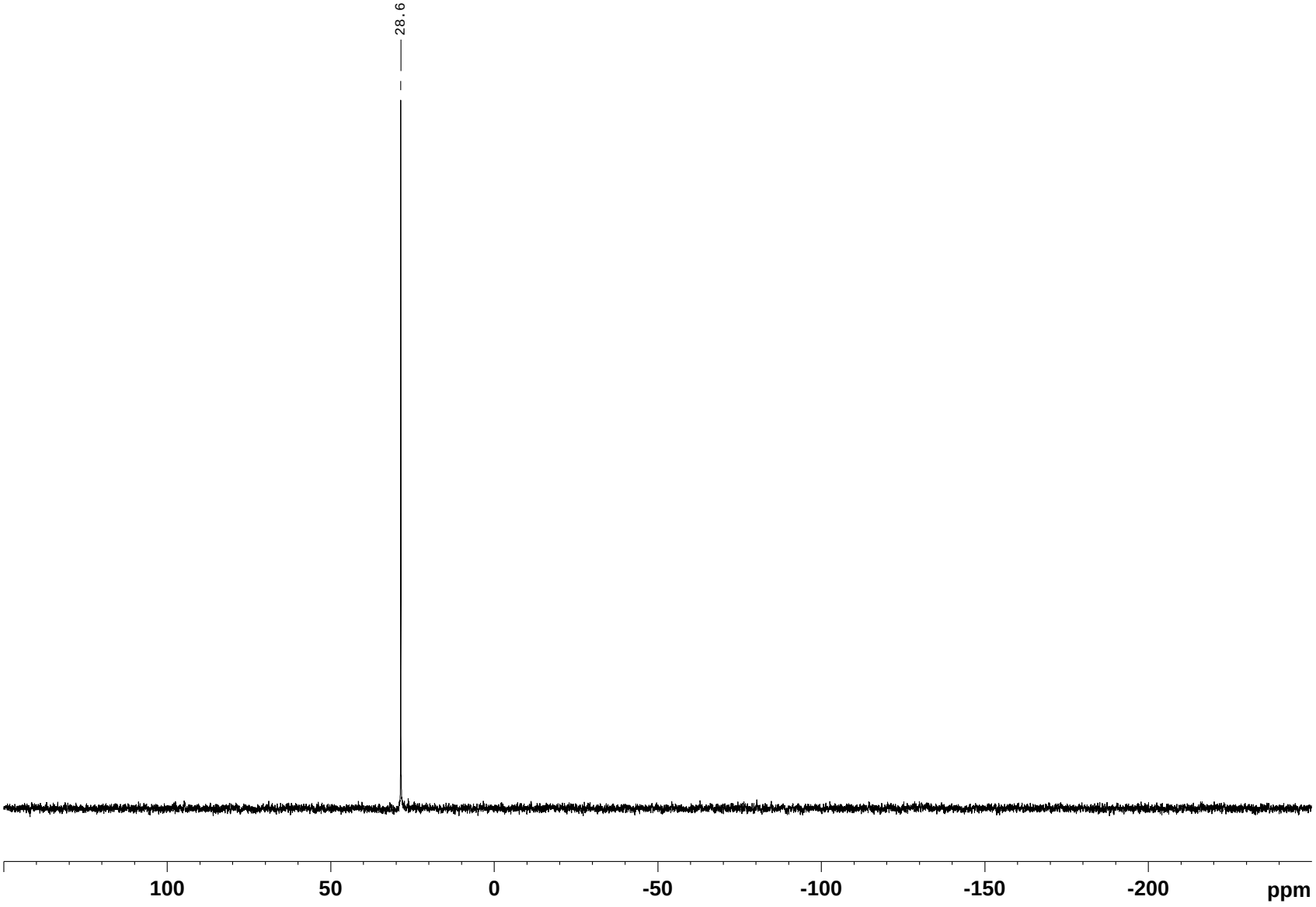




$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2):

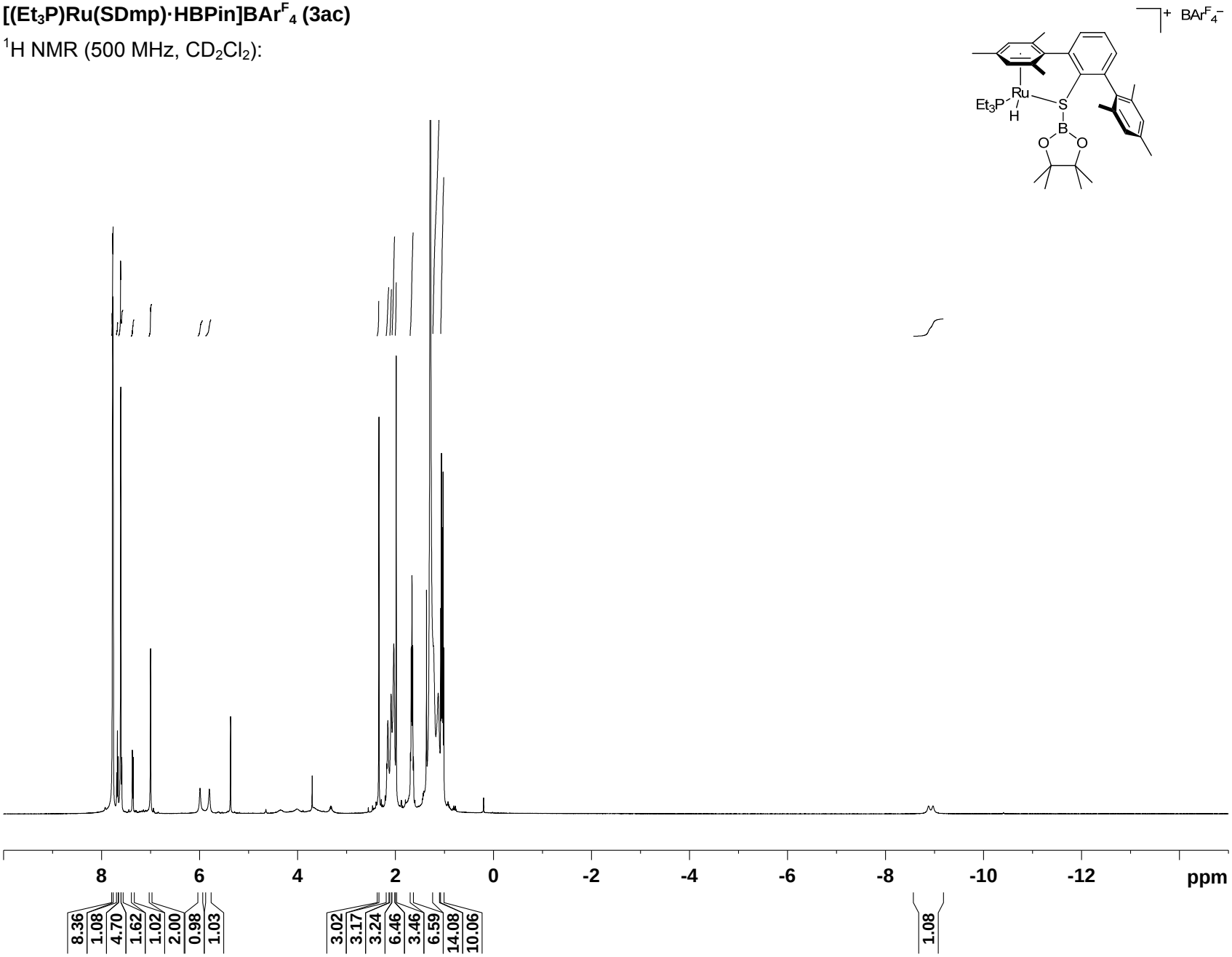


$^{31}P\{^{1}H\}$ NMR (403 MHz, CD_2Cl_2):

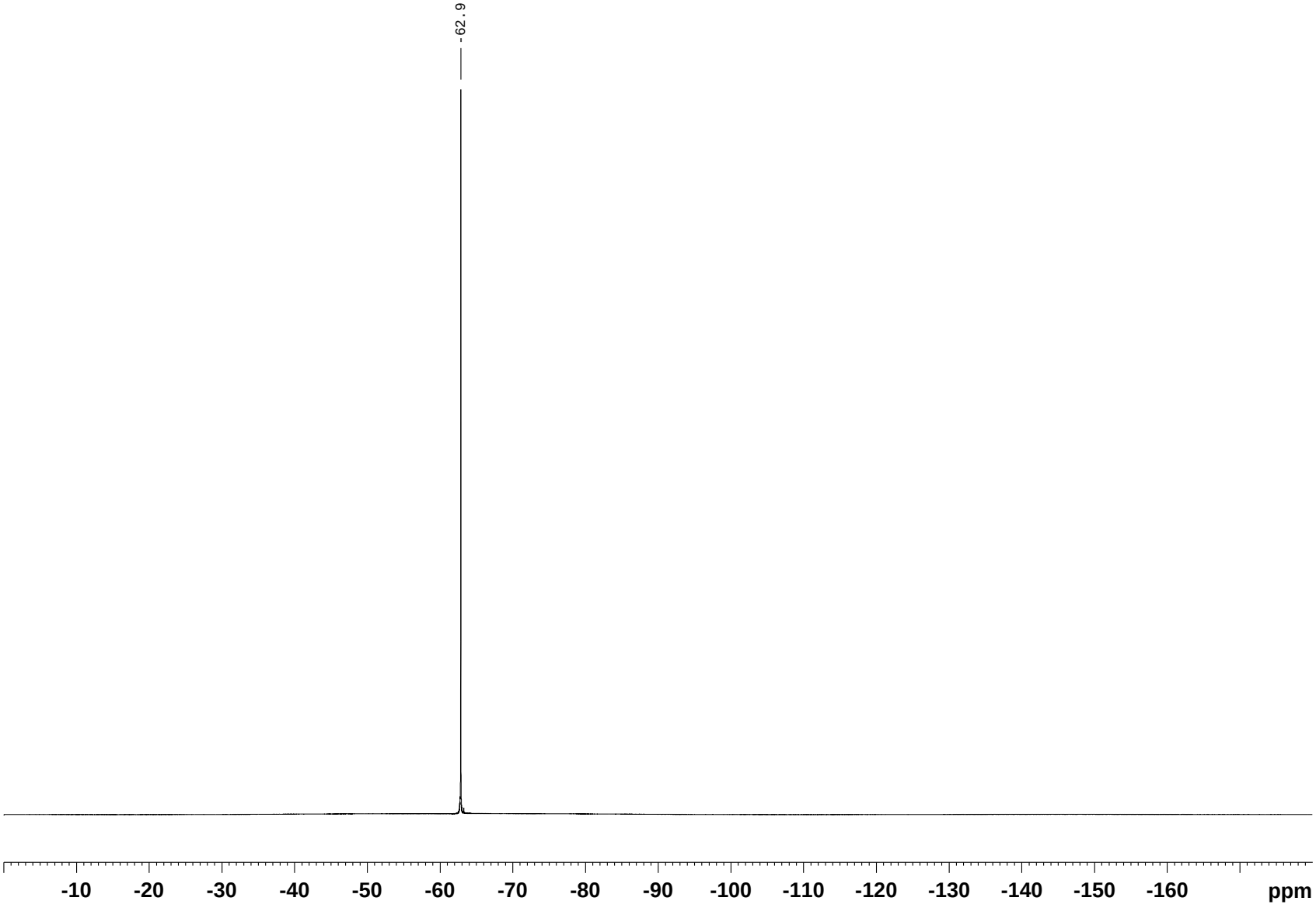


[(Et$_3$P)Ru(SDmp)·HBPin]BAr$^F_4$ (3ac)

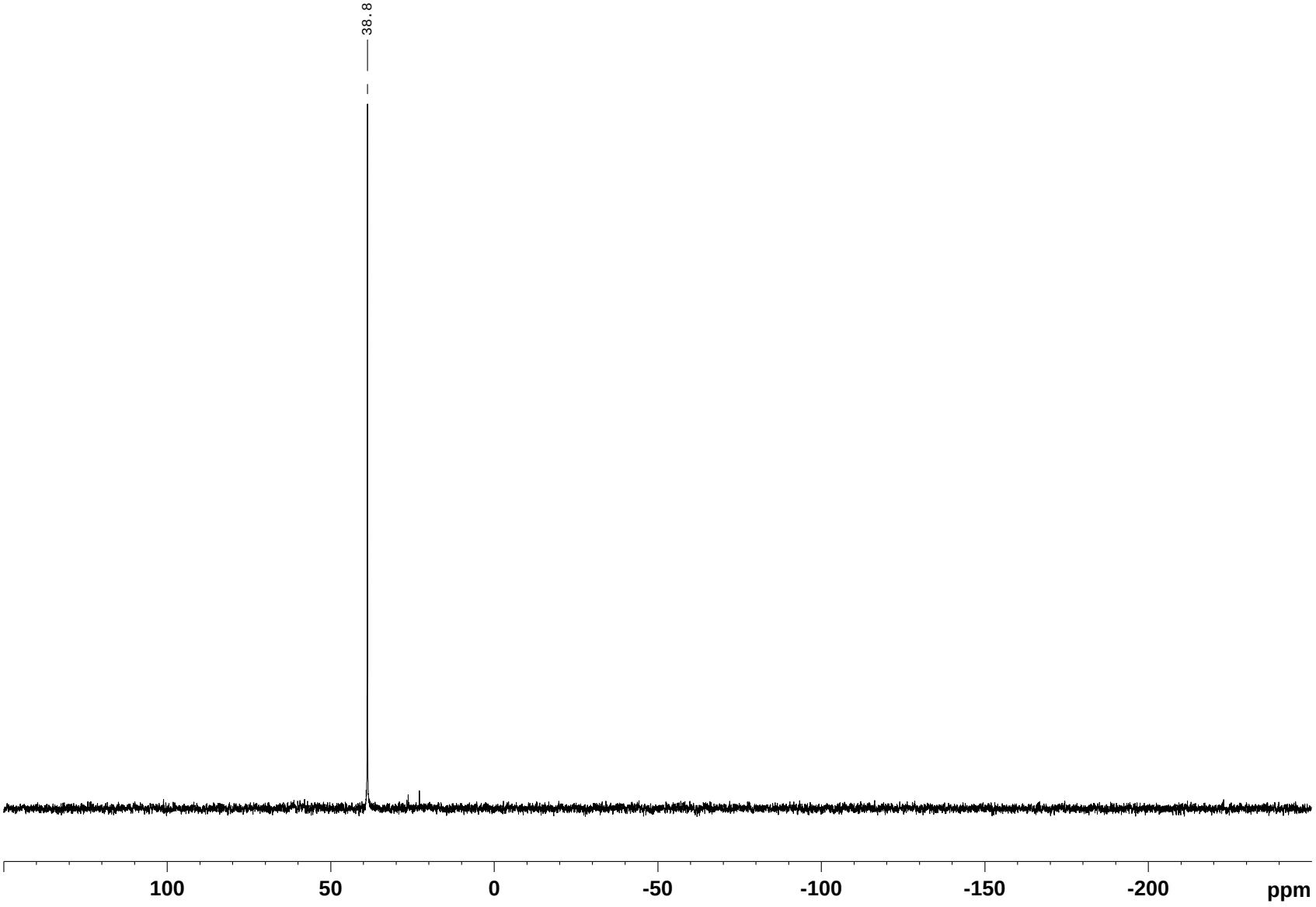
^{1}H NMR (500 MHz, CD_2Cl_2):



$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2):

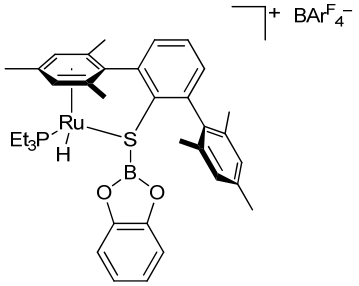


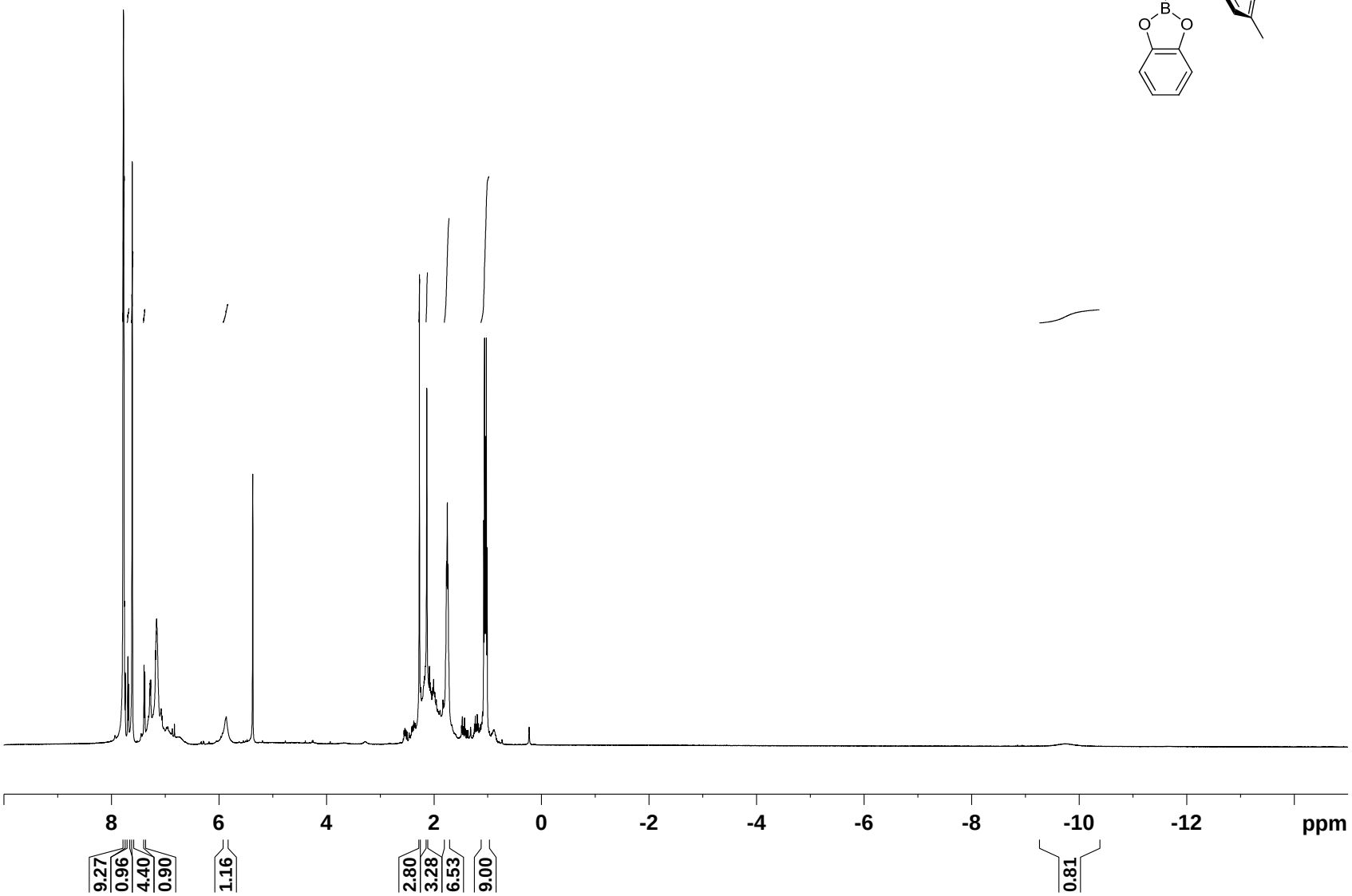
$^{31}P\{^{1}H\}$ NMR (403 MHz, CD_2Cl_2):



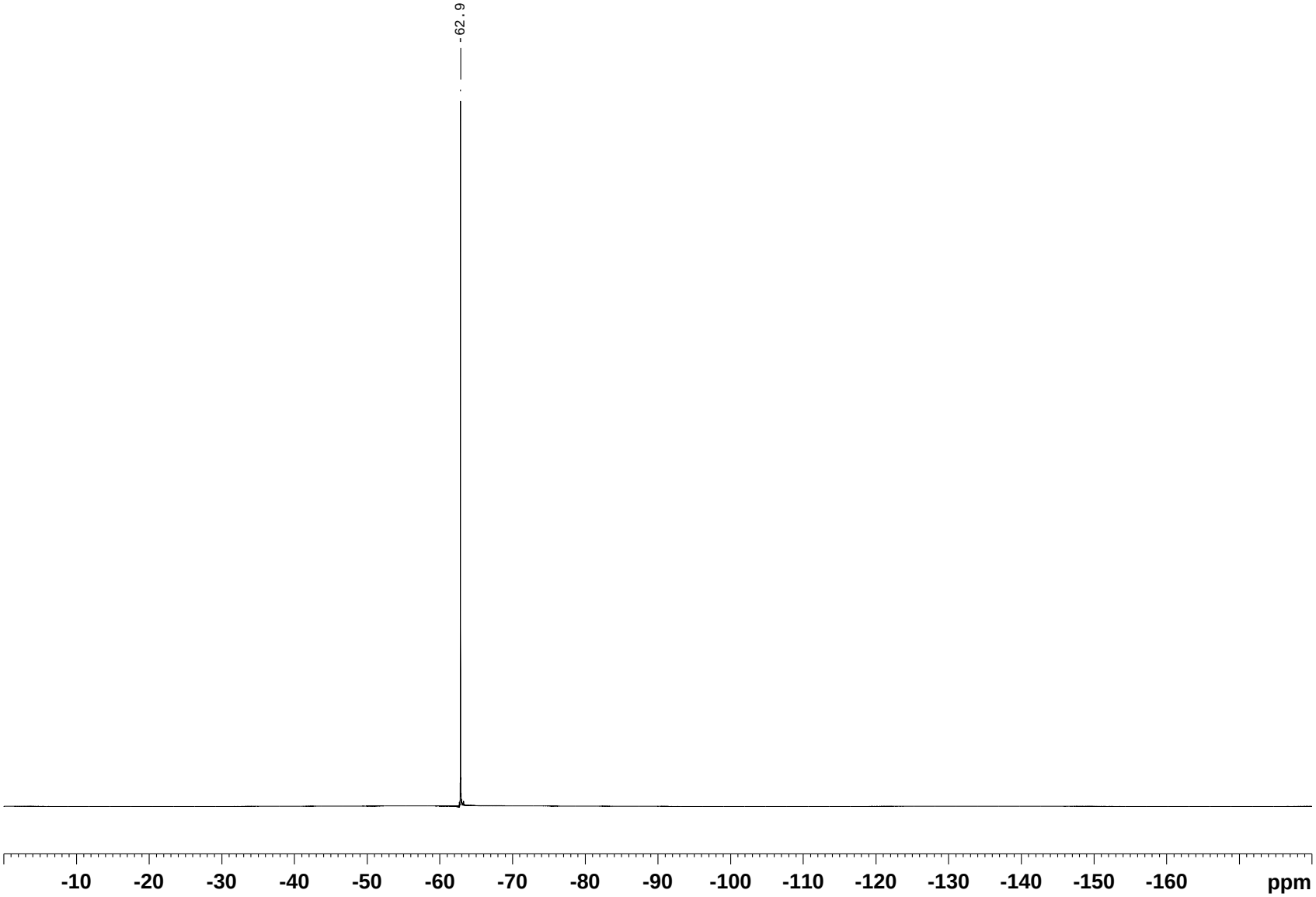
[(Et$_3$P)Ru(SDmp)·HBcat]BAr$^F_4$ (3ad)

^{1}H NMR (500 MHz, CD_2Cl_2):

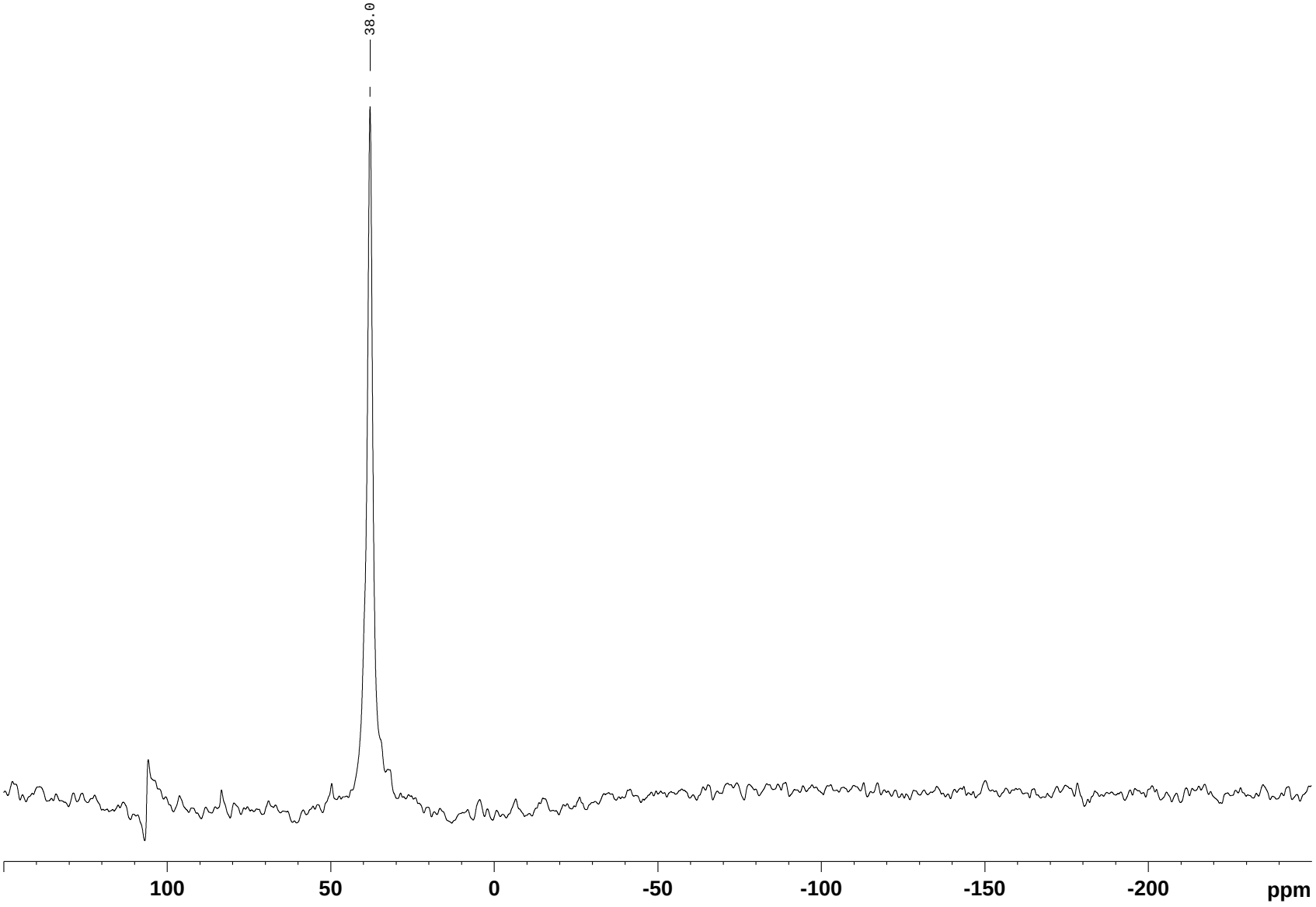




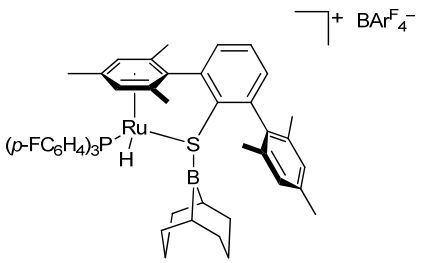
$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2):



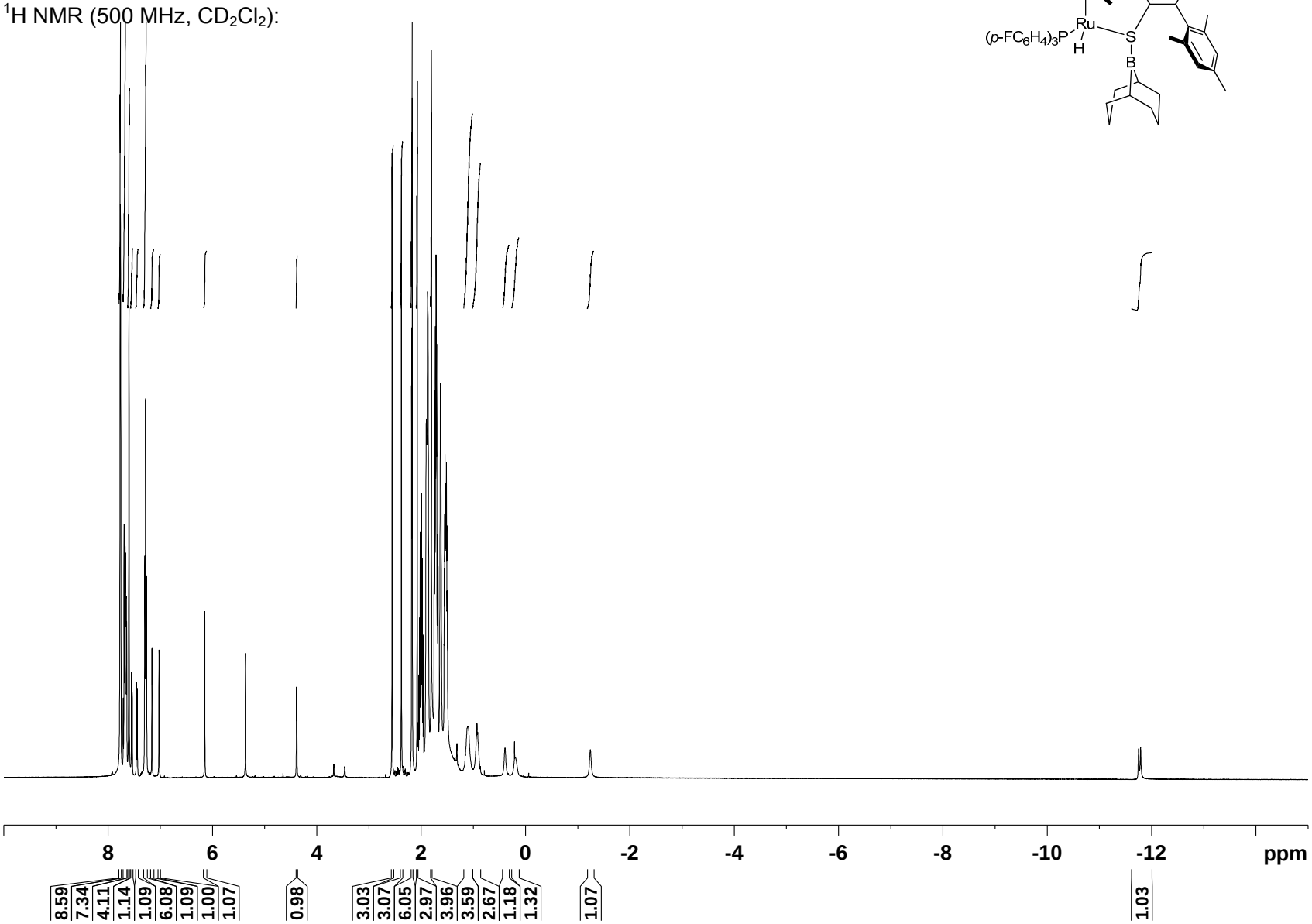
$^{31}P\{^{1}H\}$ NMR (403 MHz, CD_2Cl_2):



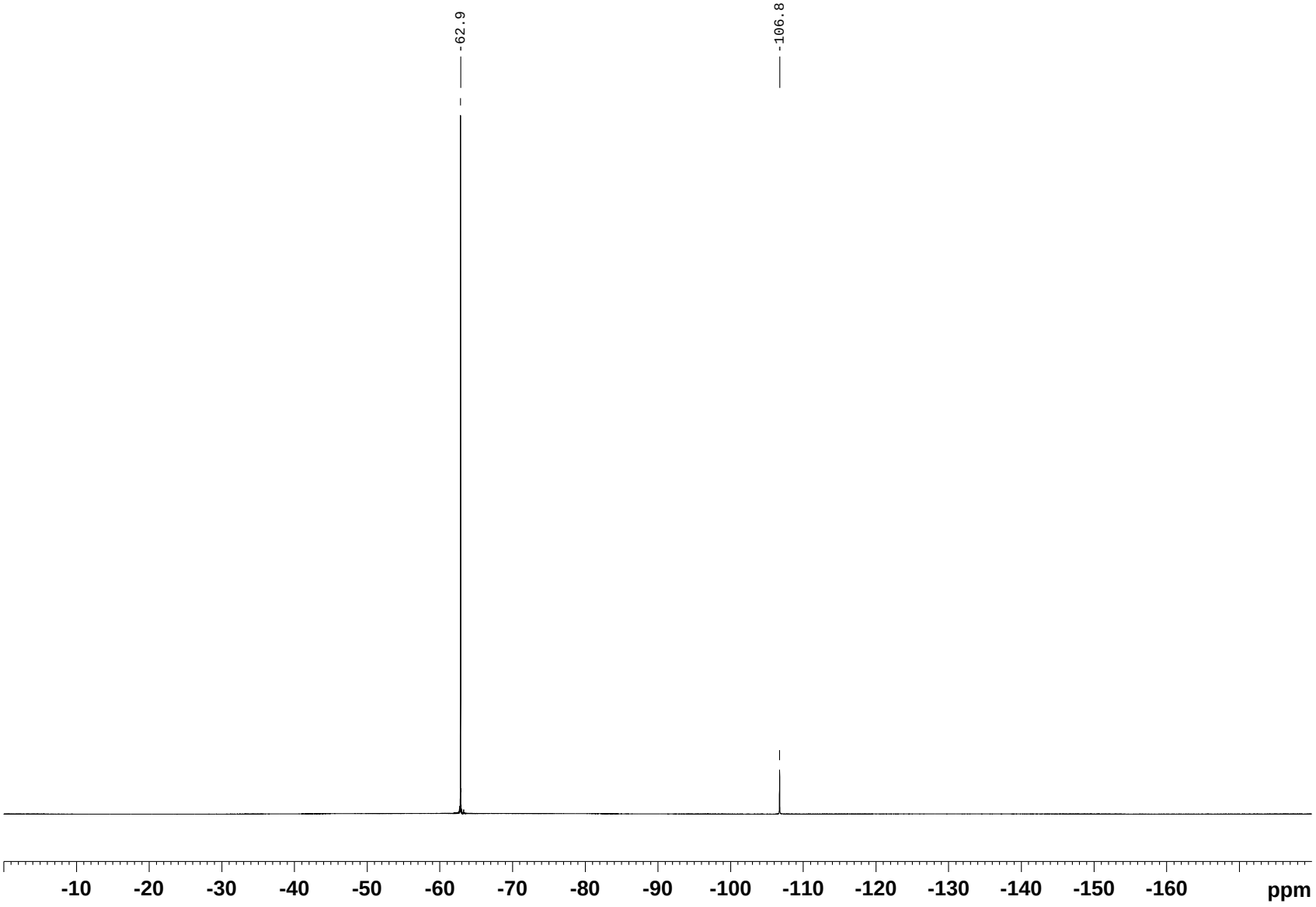
[{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)·(9-BBN)]BAr$^F_4$ (3ba)



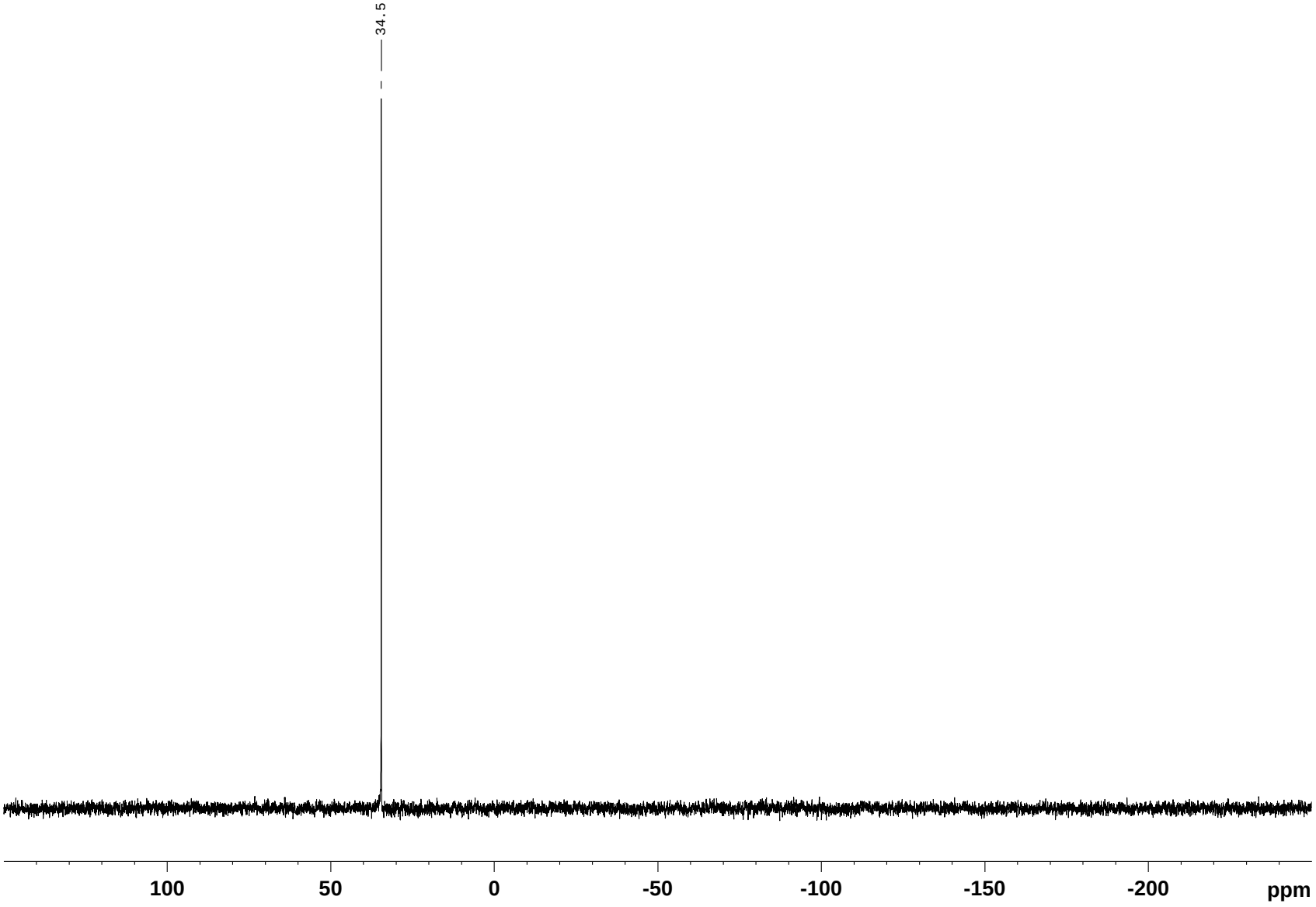
^{1}H NMR (500 MHz, CD_2Cl_2):



$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2):

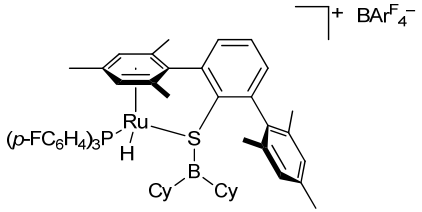


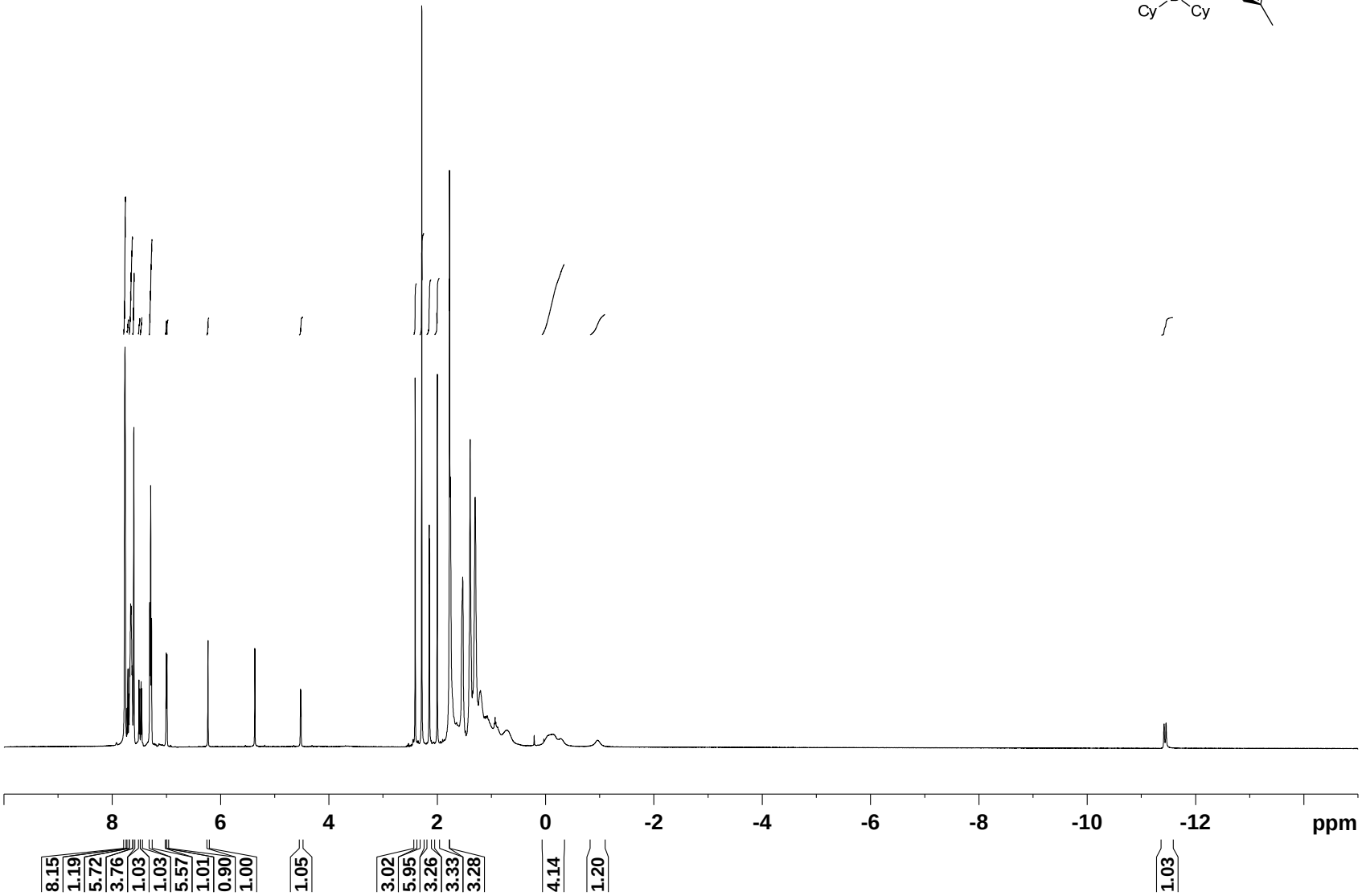
$^{31}P\{^{1}H\}$ NMR (403 MHz, CD_2Cl_2):



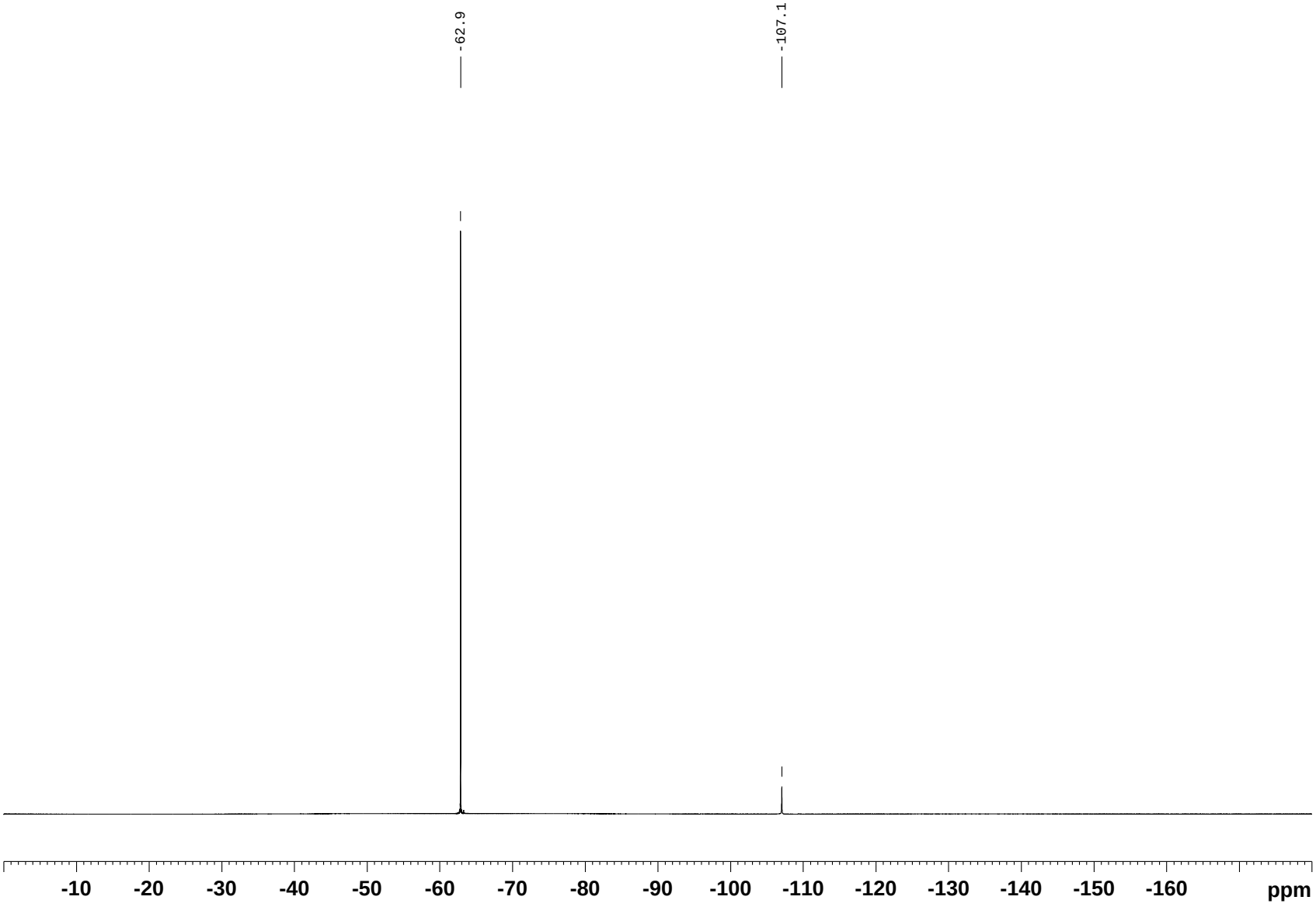
[{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)·HBCy$_2$]BAr$^F_4$ (3bb)

^{1}H NMR (500 MHz, CD_2Cl_2):

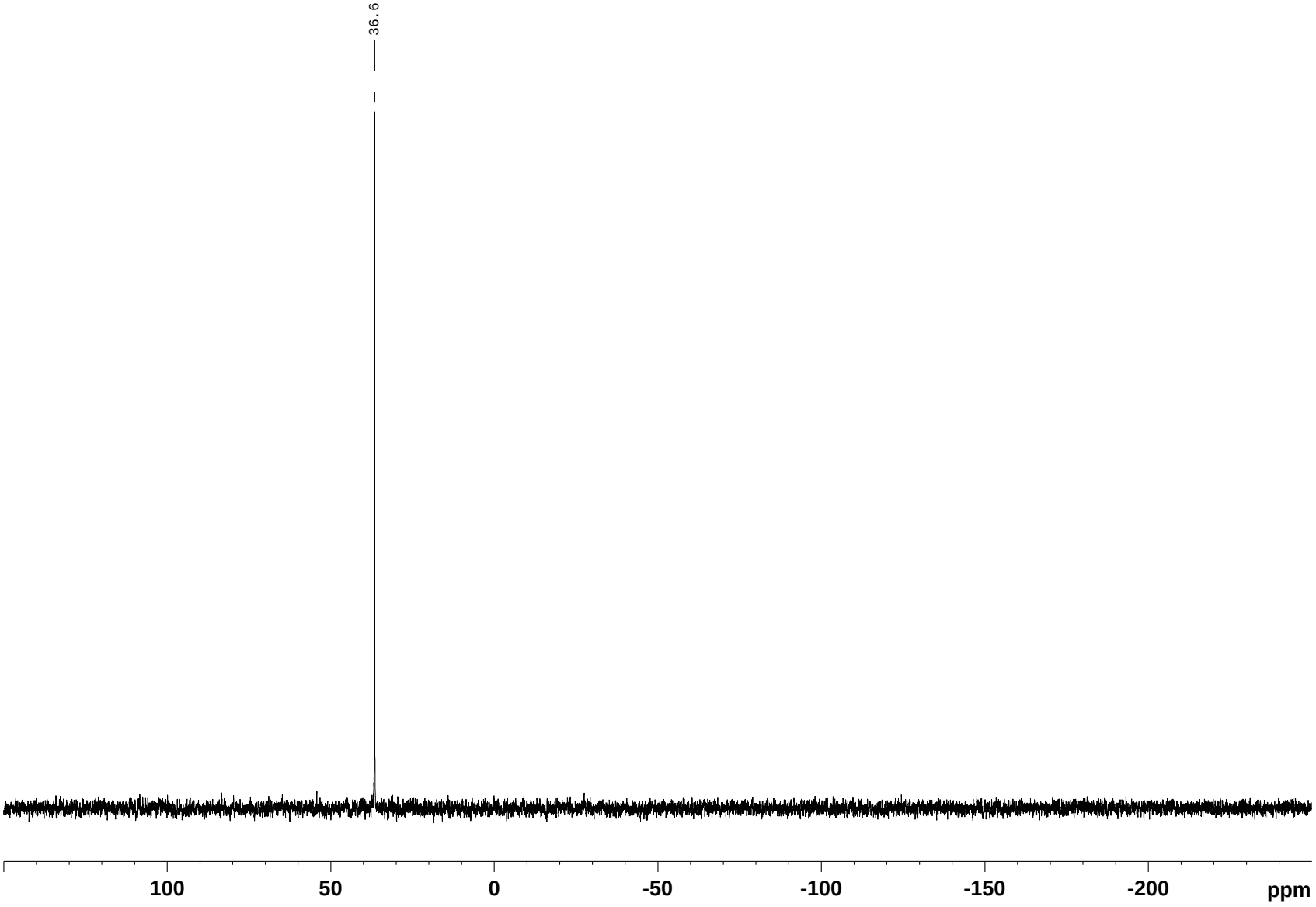




$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2):

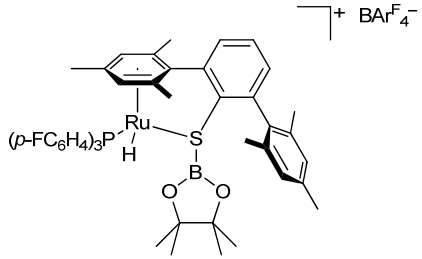


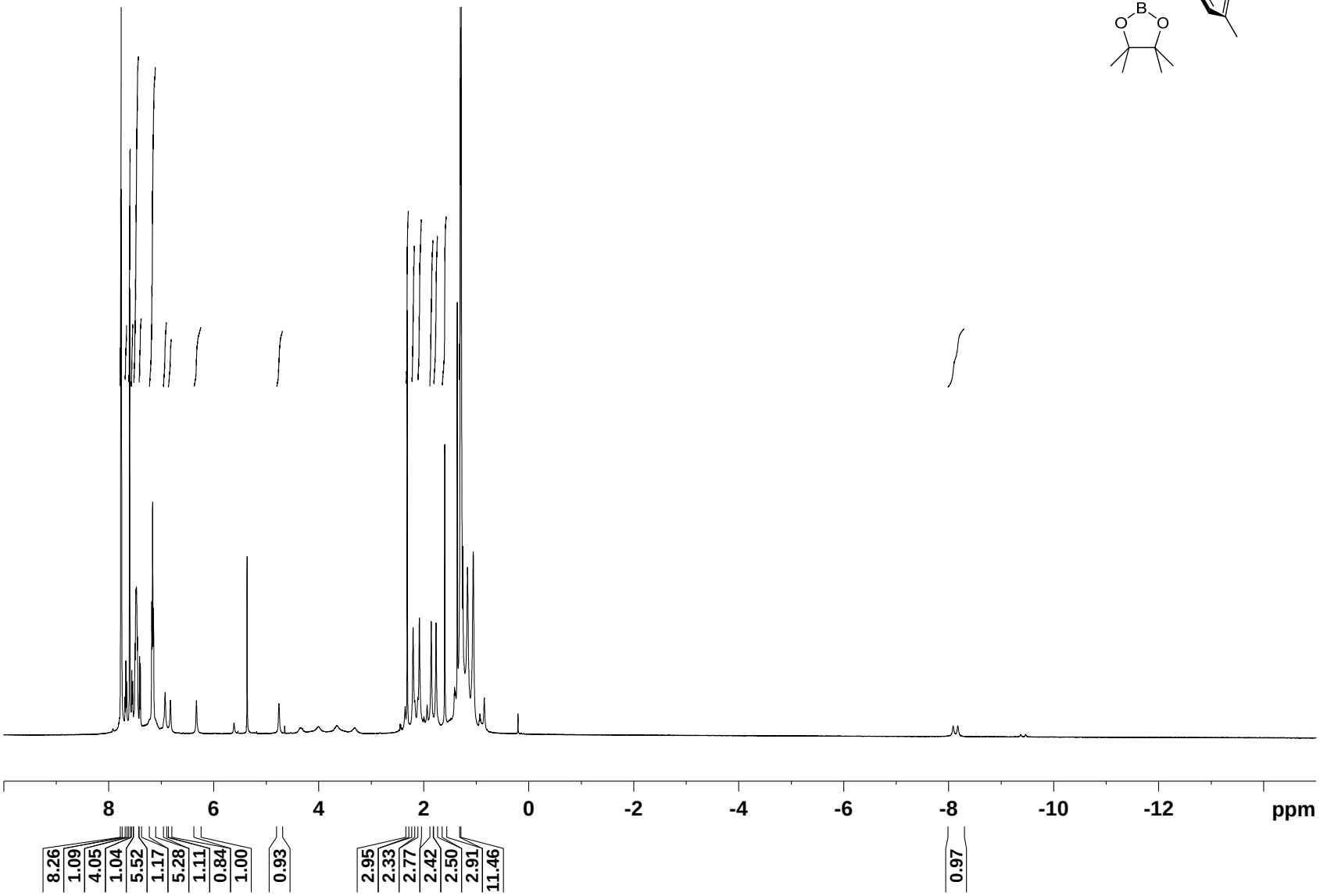
$^{31}P\{^{1}H\}$ NMR (403 MHz, CD_2Cl_2):



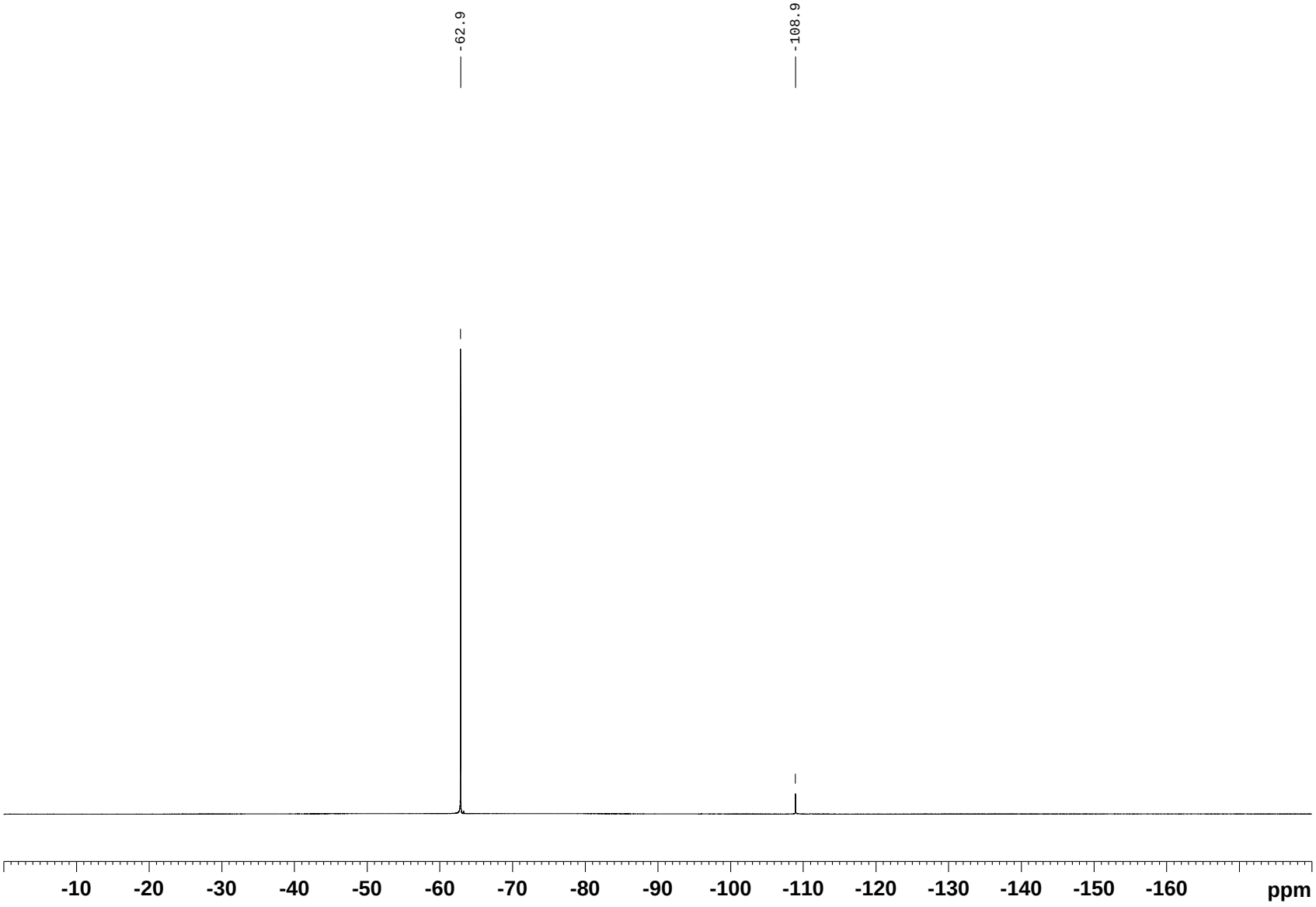
[{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)·HBPin]BAr$^F_4$ (3bc)

^{1}H NMR (500 MHz, CD_2Cl_2):

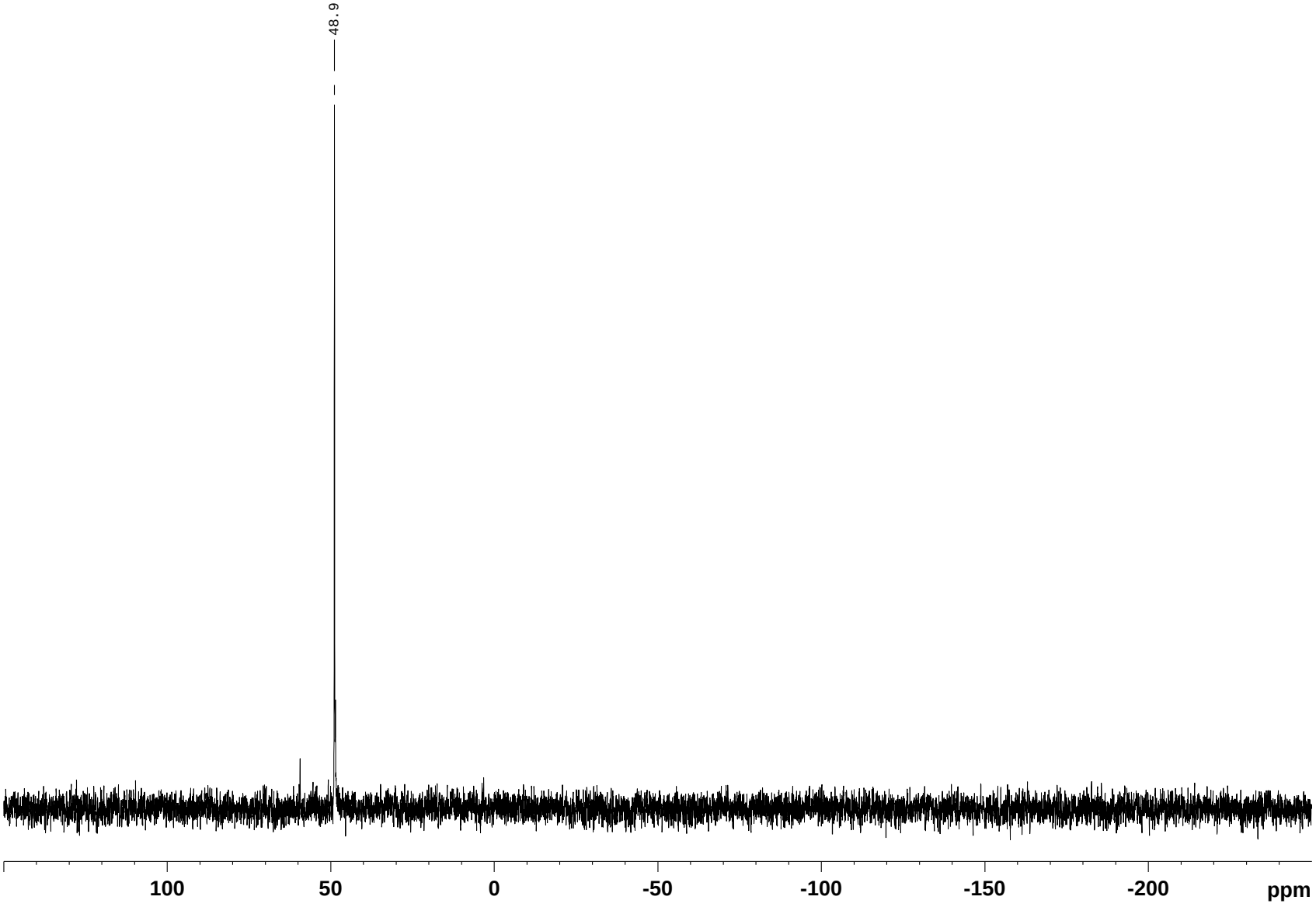




$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2):

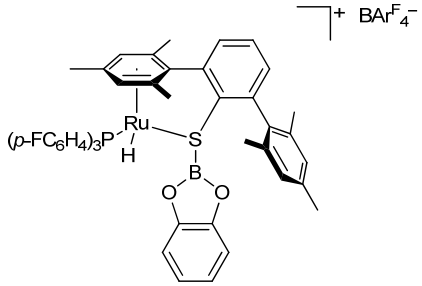


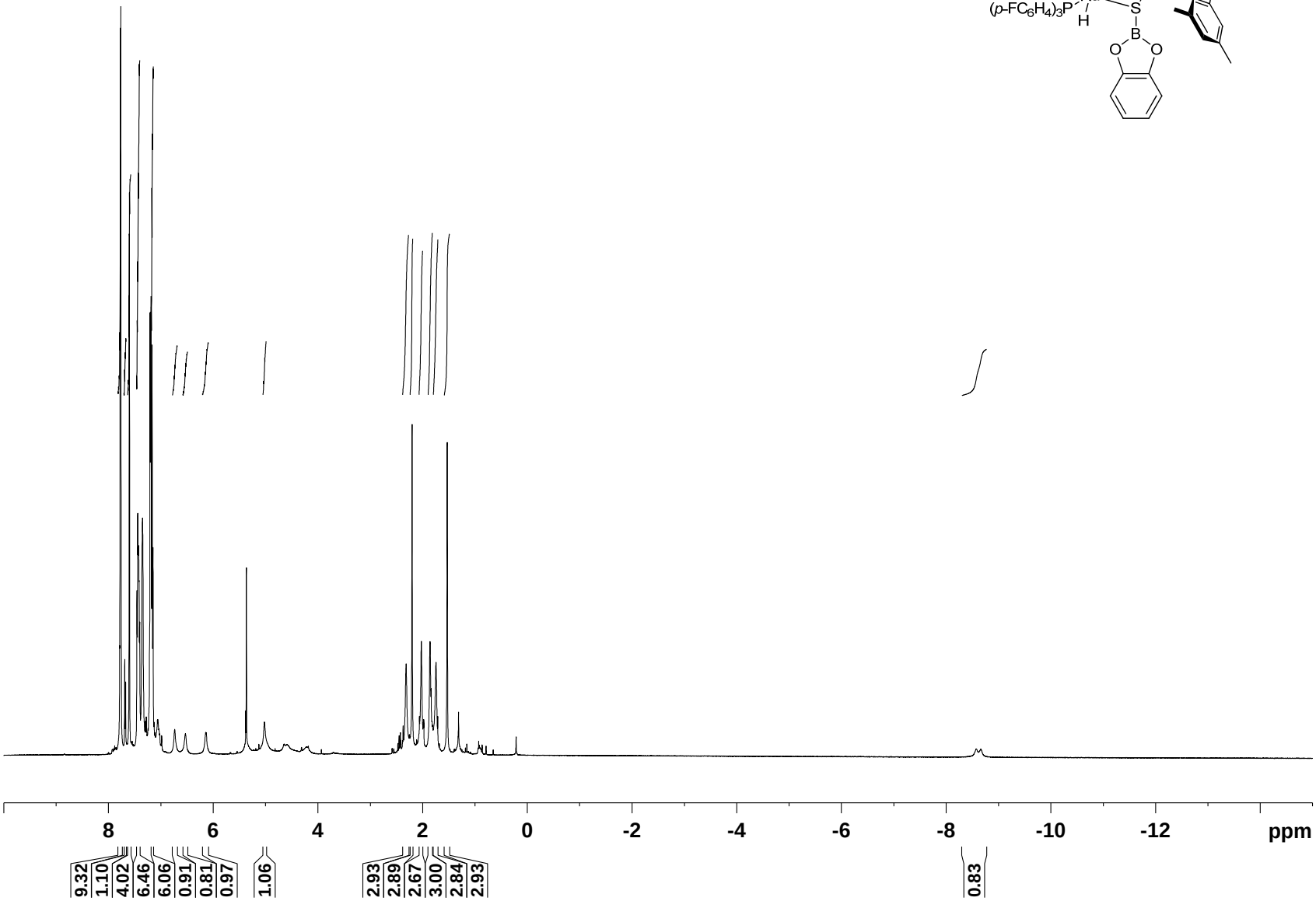
$^{31}P\{^{1}H\}$ NMR (403 MHz, CD_2Cl_2):



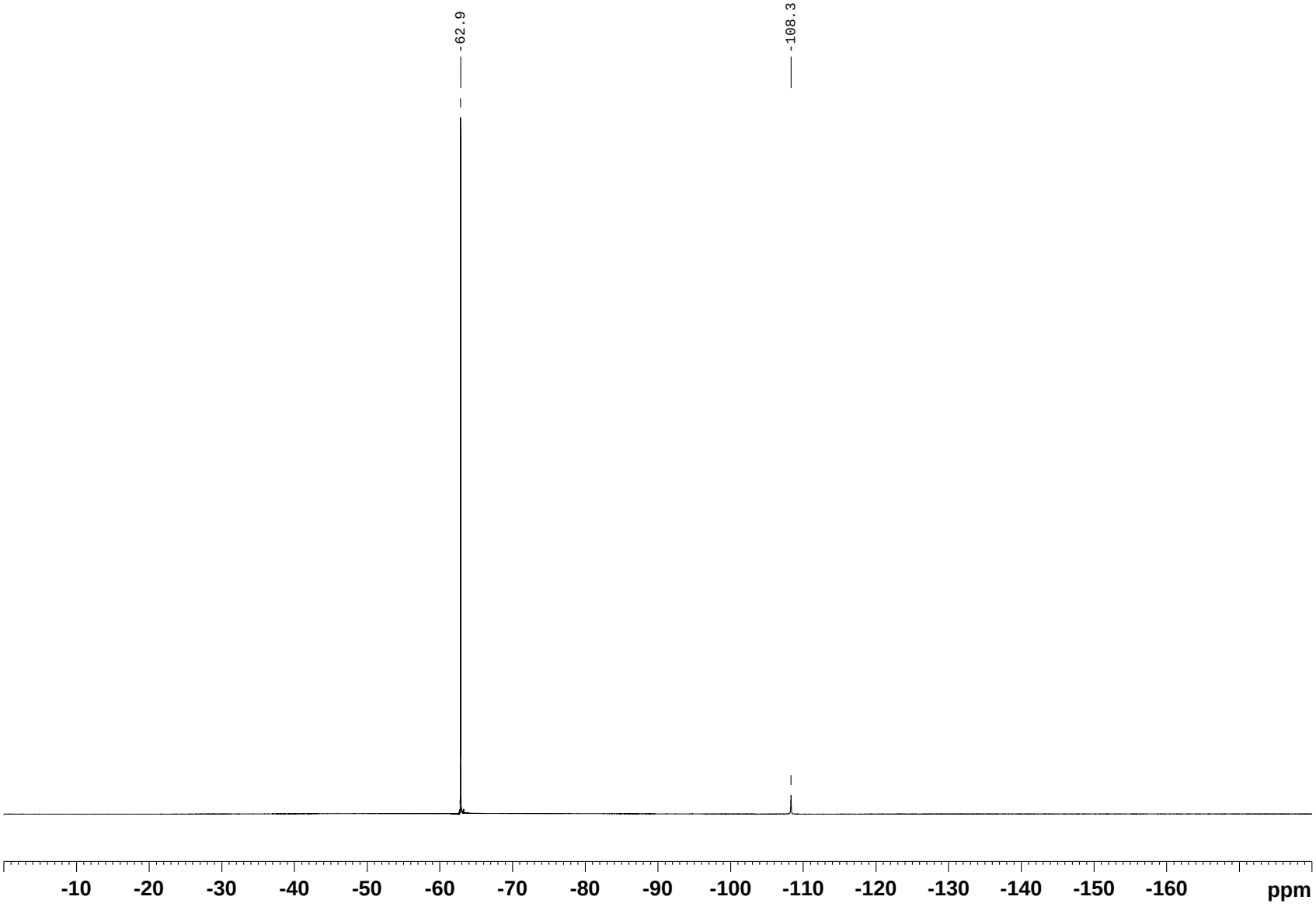
[{(*p*-FC$_6$H$_4$)$_3$P}Ru(SDmp)·HBcat]BAr$^F_4$ (3bd)

^{1}H NMR (500 MHz, CD_2Cl_2):

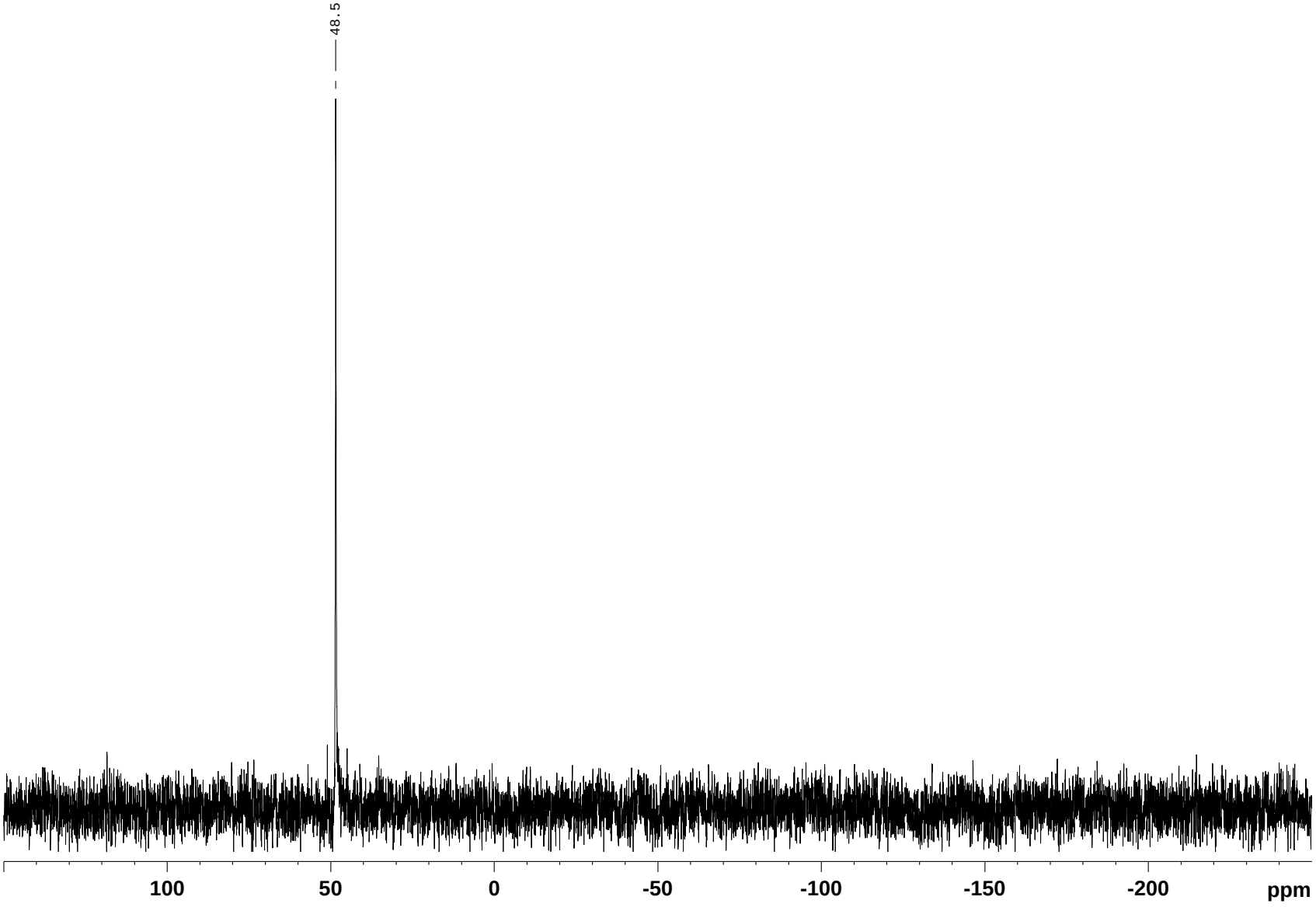




$^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2):

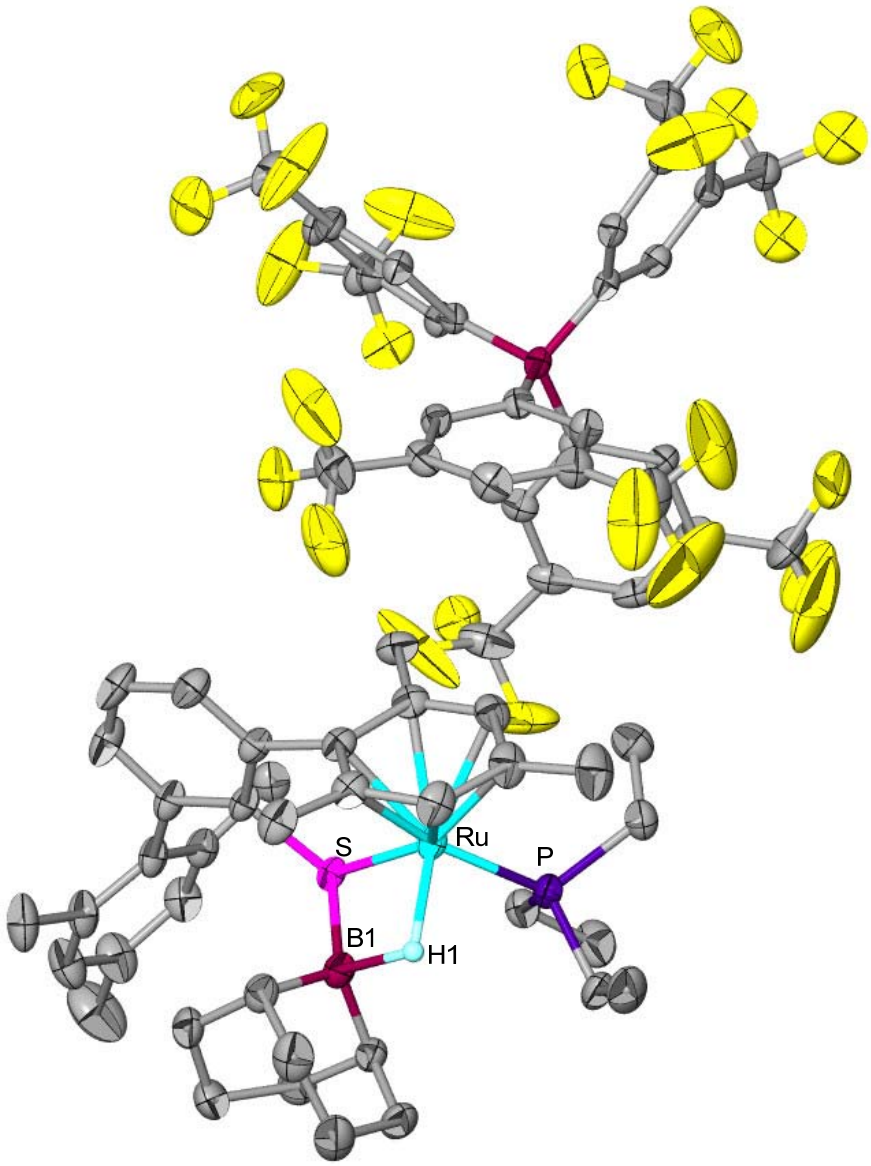


$^{31}P\{^{1}H\}$ NMR (403 MHz, CD_2Cl_2):



6 Data for Xray Structure Analysis

6.1 Supplementary Figure S1: Crystal Structure of [(Et$_3$P)Ru(SDmp)·(9-BBN)]BAr$^F_4$ (3aa)



6.2 Supplementary Tables S1–S4: Complete Crystal Data

Table S1. Crystal data and structure refinement

Empirical Formula	$C_{70}H_{67}B_2F_{24}PSRu$
Formula Weight	1549.98
Temperature	173 K
Radiation	MoKa (l = 0.71070 Å)
	multi-layer mirror monochromated
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.100 X 0.050 X 0.050 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 12.829(11) Å
	b = 12.878(11) Å
	c = 21.754(15) Å
	a = 82.843(17) o
	b = 81.29(3) o
	g = 89.02(2) o
	V = 3525(5) $Å^3$
Space Group	P-1 (#2)
Z value	2
Dcalc	1.460 g/cm3
Detector Aperture	70 x 70 mm
Data Images	1080 exposures
w oscillation Range	-110.0 - 70.0o
Exposure Rate	64.0 sec./o
Detector Swing Angle	-19.98o
w oscillation Range	-110.0 - 70.0o
Exposure Rate	64.0 sec./o
Detector Swing Angle	-19.98o
w oscillation Range	-110.0 - 70.0o
Exposure Rate	64.0 sec./o
Detector Swing Angle	-19.98o
Detector Position	45.05 mm

Pixel Size	0.137 mm
2qmax	55.1o
Detector Aperture	70 x 70 mm
Data Images	1080 exposures
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	15916
No. Variables	884
Reflection/Parameter Ratio	18
Residuals: R1 (I>2.00s(I))	0.0772
Residuals: R (All reflections)	0.0878
Residuals: wR2 (All reflections)	0.2227
Goodness of Fit Indicator	1.076
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	2.26 e-/Å3
Minimum peak in Final Diff. Map	-1.13 e-/Å3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement

atom	x	y	z	Beq	occ
Ru1	0.32762(2)	0.05501(2)	0.718134(13)	2.411(9)	1
S1	0.26126(7)	-0.03463(7)	0.81747(4)	2.282(15)	1
P1	0.23587(8)	-0.05649(8)	0.66605(4)	2.558(17)	1
F1	-0.1348(4)	-0.0227(3)	0.7656(2)	8.79(15)	1
F2	-0.0843(4)	0.0955(4)	0.8176(3)	12.6(3)	1
F3	-0.2413(3)	0.0513(3)	0.82920(15)	5.15(6)	1
F4	-0.1687(7)	0.1612(7)	0.5321(4)	9.03(19)	0.700
F5	-0.3137(5)	0.0881(6)	0.5850(3)	6.62(14)	0.700
F6	-0.3128(5)	0.2439(5)	0.5468(3)	6.43(12)	0.700
F7	-0.5110(5)	0.4647(6)	0.6046(4)	6.38(13)	0.600
F8	-0.5129(6)	0.6106(6)	0.5444(3)	6.62(14)	0.600
F9	-0.5696(6)	0.6013(6)	0.6394(3)	6.50(14)	0.600
F10	-0.2548(4)	0.8849(3)	0.5470(2)	7.93(13)	1
F11	-0.1698(4)	0.8710(3)	0.62380(18)	6.55(9)	1
F12	-0.1063(5)	0.8173(3)	0.5398(3)	10.47(18)	1
F13	-0.1369(4)	0.6703(3)	0.9317(2)	7.74(11)	1
F14	-0.1068(5)	0.7508(4)	0.8403(2)	11.3(2)	1
F15	-0.2508(4)	0.7677(3)	0.8982(2)	7.46(11)	1
F16	-0.4557(4)	0.4195(4)	0.96474(18)	9.21(16)	1

F17	-0.4488(2)	0.3159(2)	0.89740(15)	4.82(6)	1
F18	-0.5315(3)	0.4564(4)	0.8849(3)	9.51(16)	1
F19	0.1275(5)	0.5384(6)	0.5061(3)	7.03(13)	0.700
F20	0.1452(9)	0.3814(9)	0.5258(5)	11.0(3)	0.700
F21	0.2720(5)	0.4723(6)	0.5353(3)	7.23(14)	0.700
F22	0.2990(4)	0.4414(5)	0.7574(2)	4.23(9)	0.600
F23	0.2464(5)	0.5956(5)	0.7587(3)	5.39(11)	0.600
F24	0.1590(6)	0.4764(6)	0.8246(3)	5.30(16)	0.600
F25	-0.5485(8)	0.5209(8)	0.6531(5)	6.4(2)	0.400
F26	-0.4839(7)	0.4893(7)	0.5658(5)	5.38(16)	0.400
F27	-0.5477(9)	0.6452(9)	0.5846(5)	6.7(2)	0.400
F28	0.1932(7)	0.6062(7)	0.7853(4)	5.07(15)	0.400
F29	0.2979(8)	0.4956(9)	0.7602(5)	6.3(2)	0.400
F30	0.1706(6)	0.4446(7)	0.8251(4)	3.40(14)	0.400
F31	-0.3284(12)	0.1281(13)	0.5689(7)	6.3(3)	0.300
F32	-0.2510(10)	0.2554(9)	0.5268(6)	5.3(2)	0.300
F33	-0.1674(7)	0.1078(7)	0.5472(4)	3.16(13)	0.300
F34	0.2639(7)	0.5297(8)	0.5298(4)	3.76(16)	0.300
F35	0.1149(8)	0.4815(9)	0.5046(5)	4.17(17)	0.300
F36	0.1884(11)	0.3565(10)	0.5413(6)	5.6(2)	0.300
C1	0.2737(3)	0.0645(3)	0.86794(17)	2.47(6)	1
C2	0.3069(3)	0.1654(3)	0.84096(18)	2.67(6)	1
C3	0.3135(4)	0.2441(3)	0.8779(2)	3.43(7)	1
C4	0.2837(4)	0.2240(4)	0.9420(2)	4.17(9)	1
C5	0.2473(4)	0.1255(4)	0.9686(2)	3.94(9)	1
C6	0.2413(3)	0.0437(3)	0.93317(18)	2.98(7)	1
C7	0.2006(3)	-0.0598(3)	0.96622(17)	2.89(6)	1
C8	0.1031(3)	-0.0982(3)	0.95619(18)	3.01(7)	1
C9	0.0653(4)	-0.1934(4)	0.9901(2)	3.58(8)	1
C10	0.1215(4)	-0.2505(4)	1.0327(3)	4.55(10)	1
C11	0.2153(4)	-0.2084(5)	1.0433(2)	4.44(10)	1
C12	0.2563(4)	-0.1148(4)	1.01128(19)	3.63(8)	1
C13	0.3567(4)	-0.0747(5)	1.0283(2)	4.71(11)	1
C14	0.0335(3)	-0.0385(4)	0.9143(2)	3.31(7)	1
C15	0.0773(6)	-0.3517(6)	1.0685(4)	7.10(19)	1
C16	0.3300(3)	0.1872(3)	0.77111(18)	2.66(6)	1
C17	0.4344(3)	0.1824(3)	0.7398(2)	3.05(7)	1
C18	0.4486(4)	0.1765(4)	0.6739(2)	3.57(8)	1
C19	0.3650(4)	0.1898(4)	0.6387(2)	3.86(8)	1
C20	0.2619(4)	0.2040(3)	0.6715(2)	3.20(7)	1
C21	0.2420(3)	0.2023(3)	0.7367(2)	2.96(6)	1
C22	0.1318(3)	0.2155(3)	0.7701(2)	3.46(7)	1
C23	0.5308(4)	0.1857(4)	0.7713(2)	3.71(8)	1

C24	0.3871(5)	0.2009(5)	0.5687(2)	4.93(11)	1
C25	0.3893(3)	-0.2142(3)	0.77946(19)	2.96(6)	1
C26	0.3689(4)	-0.2754(4)	0.8456(2)	3.64(8)	1
C27	0.4504(4)	-0.2557(4)	0.8883(2)	3.97(8)	1
C28	0.4784(4)	-0.1407(4)	0.8861(2)	3.71(8)	1
C29	0.4964(3)	-0.0757(4)	0.8206(2)	3.27(7)	1
C30	0.5959(4)	-0.1070(5)	0.7780(3)	4.53(10)	1
C31	0.5943(4)	-0.2187(5)	0.7603(3)	4.73(11)	1
C32	0.4915(4)	-0.2469(4)	0.7394(2)	3.92(9)	1
C33	0.3181(4)	-0.1463(4)	0.6209(2)	3.65(8)	1
C34	0.4055(4)	-0.0936(5)	0.5736(2)	4.91(11)	1
C35	0.1615(3)	0.0101(4)	0.6061(2)	3.28(7)	1
C36	0.0574(4)	0.0589(4)	0.6309(2)	3.96(8)	1
C37	0.1350(3)	-0.1397(3)	0.7167(2)	3.12(7)	1
C38	0.0776(5)	-0.2163(4)	0.6845(3)	4.60(10)	1
C39	-0.1860(3)	0.3386(3)	0.69674(17)	2.37(5)	1
C40	-0.2098(3)	0.3087(3)	0.64068(18)	2.77(6)	1
C41	-0.2183(3)	0.2037(3)	0.6326(2)	3.46(7)	1
C42	-0.2022(3)	0.1247(3)	0.6785(2)	3.56(8)	1
C43	-0.1764(3)	0.1522(3)	0.7338(2)	3.18(7)	1
C44	-0.1688(3)	0.2570(3)	0.74307(19)	2.69(6)	1
C45	-0.1583(4)	0.0692(4)	0.7864(3)	4.37(10)	1
C46	-0.2455(5)	0.1772(5)	0.5717(3)	5.02(11)	1
C47	-0.2254(3)	0.5433(3)	0.65956(16)	2.23(5)	1
C48	-0.3280(3)	0.5227(3)	0.64826(16)	2.41(6)	1
C49	-0.3842(3)	0.5949(3)	0.61357(17)	2.76(6)	1
C50	-0.3427(3)	0.6936(3)	0.59053(18)	2.88(6)	1
C51	-0.2426(3)	0.7166(3)	0.60152(17)	2.80(6)	1
C52	-0.1846(3)	0.6422(3)	0.63477(17)	2.47(6)	1
C53	-0.1950(5)	0.8217(4)	0.5782(2)	4.17(9)	1
C54	-0.4910(3)	0.5668(4)	0.6006(2)	3.43(7)	1
C55	-0.2140(3)	0.4898(3)	0.77571(16)	2.33(5)	1
C56	-0.1776(3)	0.5772(3)	0.79919(17)	2.69(6)	1
C57	-0.2223(3)	0.6080(3)	0.85565(19)	3.02(7)	1
C58	-0.3085(3)	0.5554(3)	0.89164(18)	3.02(7)	1
C59	-0.3484(3)	0.4706(3)	0.86880(18)	2.94(6)	1
C60	-0.3016(3)	0.4382(3)	0.81242(18)	2.66(6)	1
C61	-0.4464(4)	0.4167(4)	0.9035(2)	4.03(9)	1
C62	-0.1781(4)	0.6990(4)	0.8803(2)	4.25(9)	1
C63	-0.0367(3)	0.4747(3)	0.68968(17)	2.46(6)	1
C64	0.0134(3)	0.4731(3)	0.62831(19)	2.98(6)	1
C65	0.1223(3)	0.4773(4)	0.6121(2)	3.57(8)	1
C66	0.1869(3)	0.4857(4)	0.6572(2)	3.58(8)	1

C67	0.1394(3)	0.4879(3)	0.7185(2)	3.16(7)	1
C68	0.0301(3)	0.4810(3)	0.73456(18)	2.63(6)	1
C69	0.1707(4)	0.4690(6)	0.5464(3)	5.44(13)	1
C70	0.2058(4)	0.5025(4)	0.7675(3)	4.58(10)	1
B1	0.3972(3)	-0.0930(4)	0.7875(2)	2.70(7)	1
B2	-0.1654(3)	0.4611(3)	0.70580(18)	2.19(6)	1

Table S3. Bond lengths [Å]

atom	atom	distance	atom	atom	distance
Ru1	S1	2.3626(16)	Ru1	P1	2.3660(16)
Ru1	C16	2.174(4)	Ru1	C17	2.292(5)
Ru1	C18	2.245(5)	Ru1	C19	2.293(5)
Ru1	C20	2.267(4)	Ru1	C21	2.226(4)
Ru1	B1	2.518(5)	S1	C1	1.808(4)
S1	B1	1.940(5)	P1	C33	1.828(5)
P1	C35	1.848(5)	P1	C37	1.833(4)
F1	C45	1.334(7)	F2	C45	1.320(9)
F3	C45	1.308(6)	F4	F32	1.599(15)
F4	F33	0.727(12)	F4	C46	1.240(10)
F5	F31	0.629(17)	F5	C46	1.429(9)
F6	F31	1.515(17)	F6	F32	0.850(14)
F6	C46	1.334(9)	F7	F25	1.377(13)
F7	F26	0.883(11)	F7	C54	1.334(9)
F8	F26	1.627(11)	F8	F27	1.065(14)
F8	C54	1.349(9)	F9	F25	1.083(13)
F9	F27	1.249(13)	F9	C54	1.322(8)
F10	C53	1.307(7)	F11	C53	1.324(7)
F12	C53	1.311(8)	F13	C62	1.316(7)
F14	C62	1.294(7)	F15	C62	1.323(7)
F16	C61	1.324(7)	F17	C61	1.322(6)
F18	C61	1.297(7)	F19	F35	0.759(14)
F19	C69	1.346(10)	F20	F35	1.384(15)
F20	F36	0.739(18)	F20	C69	1.329(14)
F21	F34	0.742(13)	F21	C69	1.285(9)
F22	F29	0.708(13)	F22	C70	1.424(7)
F23	F28	0.848(10)	F23	F29	1.435(13)
F23	C70	1.296(8)	F24	F30	0.433(12)
F24	C70	1.301(9)	F25	C54	1.338(10)
F26	C54	1.321(11)	F27	C54	1.278(12)
F28	C70	1.436(11)	F29	C70	1.171(12)
F30	C70	1.392(9)	F31	C46	1.259(17)
F32	C46	1.322(13)	F33	C46	1.419(11)

F34	C69	1.415(11)	F35	C69	1.234(12)
F36	C69	1.479(16)	C1	C2	1.403(5)
C1	C6	1.410(5)	C2	C3	1.381(6)
C2	C16	1.495(5)	C3	C4	1.383(6)
C4	C5	1.385(7)	C5	C6	1.390(7)
C6	C7	1.495(6)	C7	C8	1.410(6)
C7	C12	1.413(6)	C8	C9	1.403(6)
C8	C14	1.505(6)	C9	C10	1.391(7)
C10	C11	1.390(8)	C10	C15	1.505(9)
C11	C12	1.385(7)	C12	C13	1.509(8)
C16	C17	1.412(6)	C16	C21	1.444(6)
C17	C18	1.428(6)	C17	C23	1.506(7)
C18	C19	1.405(7)	C19	C20	1.425(7)
C19	C24	1.496(7)	C20	C21	1.401(6)
C21	C22	1.505(6)	C25	C26	1.540(6)
C25	C32	1.543(6)	C25	B1	1.599(6)
C26	C27	1.543(8)	C27	C28	1.523(7)
C28	C29	1.548(6)	C29	C30	1.539(6)
C29	B1	1.586(7)	C30	C31	1.536(9)
C31	C32	1.523(8)	C33	C34	1.510(7)
C35	C36	1.519(6)	C37	C38	1.536(8)
C39	C40	1.401(6)	C39	C44	1.402(5)
C39	B2	1.644(6)	C40	C41	1.392(6)
C41	C42	1.371(6)	C41	C46	1.500(9)
C42	C43	1.384(7)	C43	C44	1.396(6)
C43	C45	1.506(7)	C47	C48	1.411(5)
C47	C52	1.397(5)	C47	B2	1.634(5)
C48	C49	1.385(5)	C49	C50	1.391(6)
C49	C54	1.499(6)	C50	C51	1.384(6)
C51	C52	1.401(5)	C51	C53	1.493(6)
C55	C56	1.406(6)	C55	C60	1.402(5)
C55	B2	1.638(5)	C56	C57	1.377(6)
C57	C58	1.388(6)	C57	C62	1.501(7)
C58	C59	1.390(6)	C59	C60	1.391(6)
C59	C61	1.498(6)	C63	C64	1.394(5)
C63	C68	1.404(6)	C63	B2	1.642(6)
C64	C65	1.389(6)	C65	C66	1.391(7)
C65	C69	1.484(7)	C66	C67	1.385(6)
C67	C68	1.394(6)	C67	C70	1.492(8)
Ru1	H1	1.80(4)	C3	H3	0.93
C4	H4	0.93	C5	H5	0.93
C9	H9	0.93	C11	H11	0.93
C13	H13A	0.96	C13	H13B	0.96

C13	H13C	0.96	C14	H14A	0.96
C14	H14B	0.96	C14	H14C	0.96
C15	H15A	0.96	C15	H15B	0.96
C15	H15C	0.96	C18	H18	0.98
C20	H20	0.98	C22	H22A	0.96
C22	H22B	0.96	C22	H22C	0.96
C23	H23A	0.96	C23	H23B	0.96
C23	H23C	0.96	C24	H24A	0.96
C24	H24B	0.96	C24	H24C	0.96
C25	H25	0.98	C26	H26A	0.97
C26	H26B	0.97	C27	H27A	0.97
C27	H27B	0.97	C28	H28A	0.97
C28	H28B	0.97	C29	H29	0.98
C30	H30A	0.97	C30	H30B	0.97
C31	H31A	0.97	C31	H31B	0.97
C32	H32A	0.97	C32	H32B	0.97
C33	H33A	0.97	C33	H33B	0.97
C34	H34A	0.96	C34	H34B	0.96
C34	H34C	0.96	C35	H35A	0.97
C35	H35B	0.97	C36	H36A	0.96
C36	H36B	0.96	C36	H36C	0.96
C37	H37A	0.97	C37	H37B	0.97
C38	H38A	0.96	C38	H38B	0.96
C38	H38C	0.96	C40	H40	0.93
C42	H42	0.93	C44	H44	0.93
C48	H48	0.93	C50	H50	0.93
C52	H52	0.93	C56	H56	0.93
C58	H58	0.93	C60	H60	0.93
C64	H64	0.93	C66	H66	0.93
C68	H68	0.93	B1	H1	1.55(4)

Table S4. Angles [°]

atom	atom	atom	angle	atom	atom	atom	angle
S1	Ru1	P1	92.13(6)	S1	Ru1	C16	82.98(11)
S1	Ru1	C17	104.24(11)	S1	Ru1	C18	140.09(12)
S1	Ru1	C19	159.80(12)	S1	Ru1	C20	126.47(11)
S1	Ru1	C21	93.76(11)	S1	Ru1	B1	46.69(10)
P1	Ru1	C16	150.50(11)	P1	Ru1	C17	163.61(11)
P1	1	C18	127.02(13)	P1	Ru1	C19	99.11(15)
P1	Ru1	C20	94.21(14)	P1	Ru1	C21	113.78(13)
P1	Ru1	B1	94.15(13)	C16	Ru1	C17	36.73(14)

C16	Ru1	C18	66.63(16)	C16	Ru1	C19	78.97(17)
C16	Ru1	C20	66.63(16)	C16	Ru1	C21	38.28(16)
C16	Ru1	B1	103.12(16)	C17	Ru1	C18	36.67(16)
C17	Ru1	C19	65.59(18)	C17	Ru1	C20	76.98(17)
C17	Ru1	C21	66.79(16)	C17	Ru1	B1	96.37(16)
C18	Ru1	C19	36.05(18)	C18	Ru1	C20	64.96(17)
C18	Ru1	C21	78.45(17)	C18	Ru1	B1	114.33(16)
C19	Ru1	C20	36.41(17)	C19	Ru1	C21	66.37(16)
C19	Ru1	B1	147.40(16)	C20	Ru1	C21	36.33(16)
C20	Ru1	B1	169.43(16)	C21	Ru1	B1	133.46(16)
Ru1	S1	C1	101.31(13)	Ru1	S1	B1	70.88(13)
C1	S1	B1	111.63(19)	Ru1	P1	C33	115.51(17)
Ru1	P1	C35	115.51(17)	Ru1	P1	C37	115.22(16)
C33	P1	C35	101.4(2)	C33	P1	C37	104.9(2)
C35	P1	C37	102.5(2)	F32	F4	F33	138.5(11)
F32	F4	C46	53.7(6)	F33	F4	C46	88.3(10)
F31	F5	C46	61.8(16)	F31	F6	F32	110.4(11)
F31	F6	C46	52.0(7)	F32	F6	C46	70.6(10)
F25	F7	F26	127.8(10)	F25	F7	C54	59.1(6)
F26	F7	C54	69.7(8)	F26	F8	F27	109.1(8)
F26	F8	C54	51.7(5)	F27	F8	C54	62.6(7)
F25	F9	F27	122.6(10)	F25	F9	C54	66.8(7)
F27	F9	C54	59.6(6)	F35	F19	C69	65.0(10)
F35	F20	F36	137.5(17)	F35	F20	C69	54.1(7)
F36	F20	C69	86.3(15)	F34	F21	C69	84.0(10)
F29	F22	C70	54.9(9)	F28	F23	F29	121.1(9)
F28	F23	C70	81.2(8)	F29	F23	C70	50.4(5)
F30	F24	C70	93.0(14)	F7	F25	F9	115.5(9)
F7	F25	C54	58.8(5)	F9	F25	C54	65.2(7)
F7	F26	F8	114.9(10)	F7	F26	C54	71.4(8)
F8	F26	C54	53.2(5)	F8	F27	F9	127.3(11)
F8	F27	C54	69.6(8)	F9	F27	C54	63.1(6)
F23	F28	C70	63.1(7)	F22	F29	F23	152.1(14)
F22	F29	C70	95.4(12)	F23	F29	C70	58.6(6)
F24	F30	C70	68.9(13)	F5	F31	F6	148(2)
F5	F31	C46	92.2(18)	F6	F31	C46	56.6(7)
F4	F32	F6	116.5(11)	F4	F32	C46	49.1(6)
F6	F32	C46	72.1(9)	F4	F33	C46	60.9(9)
F21	F34	C69	64.6(9)	F19	F35	F20	141.0(14)
F19	F35	C69	81.2(11)	F20	F35	C69	60.7(8)
F20	F36	C69	63.8(13)	S1	C1	C2	119.2(3)
S1	C1	C6	120.5(3)	C2	C1	C6	120.1(4)
C1	C2	C3	120.8(4)	C1	C2	C16	118.5(4)

C3	C2	C16	120.6(3)	C2	C3	C4	119.5(4)
C3	C4	C5	119.8(5)	C4	C5	C6	122.4(4)
C1	C6	C5	117.3(4)	C1	C6	C7	124.3(4)
C5	C6	C7	118.3(4)	C6	C7	C8	120.2(4)
C6	C7	C12	119.5(4)	C8	C7	C12	120.1(4)
C7	C8	C9	118.6(4)	C7	C8	C14	123.3(4)
C9	C8	C14	118.0(4)	C8	C9	C10	121.8(4)
C9	C10	C11	118.1(5)	C9	C10	C15	120.0(5)
C11	C10	C15	121.8(5)	C10	C11	C12	122.5(5)
C7	C12	C11	118.8(4)	C7	C12	C13	123.3(4)
C11	C12	C13	117.9(4)	Ru1	C16	C2	117.3(3)
Ru1	C16	C17	76.2(2)	Ru1	C16	C21	72.8(2)
C2	C16	C17	120.5(4)	C2	C16	C21	118.0(3)
C17	C16	C21	121.2(4)	Ru1	C17	C16	67.1(2)
Ru1	C17	C18	69.9(3)	Ru1	C17	C23	136.3(3)
C16	C17	C18	117.5(4)	C16	C17	C23	124.0(4)
C18	C17	C23	118.4(4)	Ru1	C18	C17	73.5(2)
Ru1	C18	C19	73.8(3)	C17	C18	C19	122.5(4)
Ru1	C19	C18	70.1(3)	Ru1	C19	C20	70.8(2)
Ru1	C19	C24	136.3(4)	C18	C19	C20	117.8(4)
C18	C19	C24	120.1(4)	C20	C19	C24	121.8(5)
Ru1	C20	C19	72.8(3)	Ru1	C20	C21	70.2(2)
C19	C20	C21	122.2(4)	Ru1	C21	C16	68.9(2)
Ru1	C21	C20	73.4(2)	Ru1	C21	C22	128.7(3)
C16	C21	C20	118.1(4)	C16	C21	C22	120.9(4)
C20	C21	C22	120.9(4)	C26	C25	C32	113.6(4)
C26	C25	B1	107.3(3)	C32	C25	B1	109.0(3)
C25	C26	C27	114.7(4)	C26	C27	C28	113.8(4)
C27	C28	C29	116.6(4)	C28	C29	C30	113.8(4)
C28	C29	B1	107.5(3)	C30	C29	B1	108.2(4)
C29	C30	C31	114.8(4)	C30	C31	C32	113.6(4)
C25	C32	C31	116.0(4)	P1	C33	C34	114.2(4)
P1	C35	C36	115.8(3)	P1	C37	C38	116.3(3)
C40	C39	C44	116.1(4)	C40	C39	B2	122.8(3)
C44	C39	B2	120.8(3)	C39	C40	C41	121.5(4)
C40	C41	C42	121.8(5)	C40	C41	C46	118.7(4)
C42	C41	C46	119.4(4)	C41	C42	C43	117.8(4)
C42	C43	C44	121.1(4)	C42	C43	C45	120.5(4)
C44	C43	C45	118.3(4)	C39	C44	C43	121.6(4)
F1	C45	F2	109.7(5)	F1	C45	F3	105.2(4)
F1	C45	C43	111.5(5)	F2	C45	F3	104.1(5)
F2	C45	C43	112.7(4)	F3	C45	C43	113.1(4)
F4	C46	F5	110.5(7)	F4	C46	F6	110.8(6)

F4	C46	F31	115.6(10)	F4	C46	F32	77.2(7)
F4	C46	F33	30.8(5)	F4	C46	C41	114.9(7)
F5	C46	F6	97.2(6)	F5	C46	F31	26.1(8)
F5	C46	F32	125.1(8)	F5	C46	F33	85.9(6)
F5	C46	C41	108.1(5)	F6	C46	F31	71.4(8)
F6	C46	F32	37.3(6)	F6	C46	F33	134.5(7)
F6	C46	C41	113.8(5)	F31	C46	F32	100.1(10)
F31	C46	F33	100.9(9)	F31	C46	C41	122.0(8)
F32	C46	F33	106.5(7)	F32	C46	C41	117.3(7)
F33	C46	C41	108.1(6)	C48	C47	C52	115.9(3)
C48	C47	B2	121.1(3)	C52	C47	B2	122.7(3)
C47	C48	C49	122.2(3)	C48	C49	C50	120.8(4)
C48	C49	C54	119.9(4)	C50	C49	C54	119.3(4)
C49	C50	C51	118.2(4)	C50	C51	C52	120.9(4)
C50	C51	C53	120.3(4)	C52	C51	C53	118.9(4)
C47	C52	C51	122.0(4)	F10	C53	F11	107.1(4)
F10	C53	F12	104.7(5)	F10	C53	C51	114.1(5)
F11	C53	F12	104.3(5)	F11	C53	C51	112.7(4)
F12	C53	C51	113.1(4)	F7	C54	F8	106.8(6)
F7	C54	F9	103.5(5)	F7	C54	F25	62.0(6)
F7	C54	F26	38.9(5)	F7	C54	F27	129.6(7)
F7	C54	C49	115.8(5)	F8	C54	F9	101.9(5)
F8	C54	F25	134.7(7)	F8	C54	F26	75.1(6)
F8	C54	F27	47.7(6)	F8	C54	C49	113.8(4)
F9	C54	F25	48.1(6)	F9	C54	F26	132.4(6)
F9	C54	F27	57.4(6)	F9	C54	C49	113.6(5)
F25	C54	F26	100.3(7)	F25	C54	F27	103.0(7)
F25	C54	C49	110.0(6)	F26	C54	F27	117.1(8)
F26	C54	C49	110.5(5)	F27	C54	C49	114.5(6)
C56	C55	C60	115.6(3)	C56	C55	B2	121.1(3)
C60	C55	B2	122.8(3)	C55	C56	C57	122.5(3)
C56	C57	C58	121.1(4)	C56	C57	C62	120.8(4)
C58	C57	C62	118.1(4)	C57	C58	C59	117.9(4)
C58	C59	C60	120.9(4)	C58	C59	C61	119.7(4)
C60	C59	C61	119.3(4)	C55	C60	C59	122.0(4)
F16	C61	F17	104.5(4)	F16	C61	F18	107.7(5)
F16	C61	C59	112.3(5)	F17	C61	F18	106.0(5)
F17	C61	C59	113.2(4)	F18	C61	C59	112.6(4)
F13	C62	F14	107.7(5)	F13	C62	F15	103.1(5)
F13	C62	C57	112.3(4)	F14	C62	F15	106.5(5)
F14	C62	C57	113.5(5)	F15	C62	C57	113.1(5)
C64	C63	C68	115.7(3)	C64	C63	B2	119.6(3)
C68	C63	B2	124.6(3)	C63	C64	C65	122.6(4)

C64	C65	C66	120.7(4)	C64	C65	C69	119.8(4)
C66	C65	C69	119.5(4)	C65	C66	C67	118.0(4)
C66	C67	C68	120.8(4)	C66	C67	C70	119.4(4)
C68	C67	C70	119.7(4)	C63	C68	C67	122.2(4)
F19	C69	F20	98.8(7)	F19	C69	F21	111.5(6)
F19	C69	F34	86.7(6)	F19	C69	F35	33.8(6)
F19	C69	F36	126.3(8)	F19	C69	C65	111.0(5)
F20	C69	F21	104.7(7)	F20	C69	F34	129.4(7)
F20	C69	F35	65.2(8)	F20	C69	F36	29.9(8)
F20	C69	C65	113.3(6)	F21	C69	F34	31.4(5)
F21	C69	F35	122.9(7)	F21	C69	F36	82.7(7)
F21	C69	C65	116.1(6)	F34	C69	F35	111.1(7)
F34	C69	F36	113.2(8)	F34	C69	C65	111.1(6)
F35	C69	F36	94.1(9)	F35	C69	C65	119.2(6)
F36	C69	C65	106.9(7)	F22	C70	F23	100.2(5)
F22	C70	F24	108.6(5)	F22	C70	F28	129.4(6)
F22	C70	F29	29.7(7)	F22	C70	F30	92.8(5)
F22	C70	C67	108.8(5)	F23	C70	F24	113.1(6)
F23	C70	F28	35.7(5)	F23	C70	F29	71.0(7)
F23	C70	F30	126.4(7)	F23	C70	C67	111.2(5)
F24	C70	F28	82.6(6)	F24	C70	F29	115.4(8)
F24	C70	F30	18.1(5)	F24	C70	C67	113.9(5)
F28	C70	F29	100.3(8)	F28	C70	F30	99.5(6)
F28	C70	C67	110.7(5)	F29	C70	F30	105.8(7)
F29	C70	C67	124.1(7)	F30	C70	C67	113.1(5)
Ru1	B1	S1	62.43(13)	Ru1	B1	C25	124.8(3)
Ru1	B1	C29	120.4(3)	S1	B1	C25	112.2(3)
S1	B1	C29	120.3(3)	C25	B1	C29	109.0(3)
C39	B2	C47	112.3(3)	C39	B2	C55	113.0(3)
C39	B2	C63	104.2(3)	C47	B2	C55	103.0(3)
C47	B2	C63	111.5(3)	C55	B2	C63	113.2(3)
S1	Ru1	H1	84.2(13)	P1	Ru1	H1	89.2(16)
C16	Ru1	H1	119.0(16)	C17	Ru1	H1	91.5(15)
C18	Ru1	H1	88.5(14)	C19	Ru1	H1	112.5(13)
C20	Ru1	H1	148.9(13)	C21	Ru1	H1	157.0(16)
B1	Ru1	H1	37.7(13)	C2	C3	H3	120.2
C4	C3	H3	120.2	C3	C4	H4	120.1
C5	C4	H4	120.1	C4	C5	H5	118.8
C6	C5	H5	118.8	C8	C9	H9	119.1
C10	C9	H9	119.1	C10	C11	H11	118.8
C12	C11	H11	118.8	C12	C13	H13A	109.5
C12	C13	H13B	109.5	C12	C13	H13C	109.5
H13A	C13	H13B	109.5	H13A	C13	H13C	109.5

H13B	C13	H13C	109.5	C8	C14	H14A	109.5
C8	C14	H14B	109.5	C8	C14	H14C	109.5
H14A	C14	H14B	109.5	H14A	C14	H14C	109.5
H14B	C14	H14C	109.5	C10	C15	H15A	109.5
C10	C15	H15B	109.5	C10	C15	H15C	109.5
H15A	C15	H15B	109.5	H15A	C15	H15C	109.5
H15B	C15	H15C	109.5	Ru1	C18	H18	118.5
C17	C18	H18	118.5	C19	C18	H18	118.5
Ru1	C20	H20	118.1	C19	C20	H20	118.1
C21	C20	H20	118.1	C21	C22	H22A	109.5
C21	C22	H22B	109.5	C21	C22	H22C	109.5
H22A	C22	H22B	109.5	H22A	C22	H22C	109.5
H22B	C22	H22C	109.5	C17	C23	H23A	109.5
C17	C23	H23B	109.5	C17	C23	H23C	109.5
H23A	C23	H23B	109.5	H23A	C23	H23C	109.5
H23B	C23	H23C	109.5	C19	C24	H24A	109.5
C19	C24	H24B	109.5	C19	C24	H24C	109.5
H24A	C24	H24B	109.5	H24A	C24	H24C	109.5
H24B	C24	H24C	109.5	C26	C25	H25	109
C32	C25	H25	108.9	B1	C25	H25	108.9
C25	C26	H26A	108.6	C25	C26	H26B	108.6
C27	C26	H26A	108.6	C27	C26	H26B	108.6
H26A	C26	H26B	107.6	C26	C27	H27A	108.8
C26	C27	H27B	108.8	C28	C27	H27A	108.8
C28	C27	H27B	108.8	H27A	C27	H27B	107.7
C27	C28	H28A	108.1	C27	C28	H28B	108.1
C29	C28	H28A	108.1	C29	C28	H28B	108.1
H28A	C28	H28B	107.3	C28	C29	H29	109.1
C30	C29	H29	109.1	B1	C29	H29	109.1
C29	C30	H30A	108.6	C29	C30	H30B	108.6
C31	C30	H30A	108.6	C31	C30	H30B	108.6
H30A	C30	H30B	107.5	C30	C31	H31A	108.9
C30	C31	H31B	108.8	C32	C31	H31A	108.8
C32	C31	H31B	108.9	H31A	C31	H31B	107.7
C25	C32	H32A	108.3	C25	C32	H32B	108.3
C31	C32	H32A	108.3	C31	C32	H32B	108.3
H32A	C32	H32B	107.4	P1	C33	H33A	108.7
P1	C33	H33B	108.7	C34	C33	H33A	108.7
C34	C33	H33B	108.7	H33A	C33	H33B	107.6
C33	C34	H34A	109.5	C33	C34	H34B	109.5
C33	C34	H34C	109.5	H34A	C34	H34B	109.5
H34A	C34	H34C	109.5	H34B	C34	H34C	109.5
P1	C35	H35A	108.3	P1	C35	H35B	108.3

C36	C35	H35A	108.3	C36	C35	H35B	108.3
H35A	C35	H35B	107.4	C35	C36	H36A	109.5
C35	C36	H36B	109.5	C35	C36	H36C	109.5
H36A	C36	H36B	109.5	H36A	C36	H36C	109.5
H36B	C36	H36C	109.5	P1	C37	H37A	108.2
P1	C37	H37B	108.2	C38	C37	H37A	108.2
C38	C37	H37B	108.2	H37A	C37	H37B	107.4
C37	C38	H38A	109.5	C37	C38	H38B	109.5
C37	C38	H38C	109.5	H38A	C38	H38B	109.5
H38A	C38	H38C	109.5	H38B	C38	H38C	109.5
C39	C40	H40	119.3	C41	C40	H40	119.3
C41	C42	H42	121.1	C43	C42	H42	121.1
C39	C44	H44	119.2	C43	C44	H44	119.2
C47	C48	H48	118.9	C49	C48	H48	118.9
C49	C50	H50	120.9	C51	C50	H50	120.9
C47	C52	H52	119	C51	C52	H52	119
C55	C56	H56	118.7	C57	C56	H56	118.8
C57	C58	H58	121.1	C59	C58	H58	121.1
C55	C60	H60	119	C59	C60	H60	119
C63	C64	H64	118.7	C65	C64	H64	118.7
C65	C66	H66	121	C67	C66	H66	121
C63	C68	H68	118.9	C67	C68	H68	118.9
Ru1	B1	H1	45.0(16)	S1	B1	H1	107.1(16)
C25	B1	H1	103.7(18)	C29	B1	H1	102.7(18)
Ru1	H1	B1	97(2)				

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