Supporting Information

Iron-Catalyzed, Markovnikov Selective Hydroboration of Styrenes

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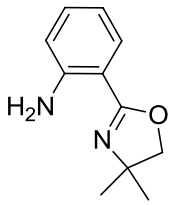
I. General Information

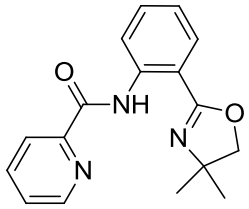
Ether, tetrahydrofuran, 1,4-dioxane and toluene were distilled from sodium benzophenoneketyl prior to use and dichloromethane was distilled from CaH_2. Pinacolborane (HBpin) (97%) was purchased from TCI and used as received. $NaHBEt_3$ (1.0 M in THF) were purchased from Aldrich and used as received. $FeCl_2$ (99%) were purchased from Alfa and used as received. The other commercial available chemicals were used as received. Alkenes were prepared according to Wittig Reaction or the previously reported procedures.[1] NMR spectra were recorded on a Bruker-400 instrument. ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. High-resolution mass spectra (HRMS) were recorded on EI-TOF (electrospray ionization-time of flight).

II. Procedures for Preparation of Ligands.

La-**Lc** were prepared according to the previously reported procedures by our group.[2]

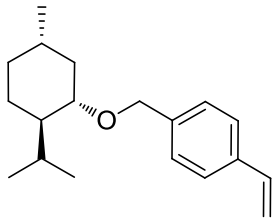


2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline (**Sa**)**.** Prepared according to the literature.[3] 79% yield, white solid. M.p. 105.6-106.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.22-7.14 (m, 1H), 6.72-6.60 (m, 2H), 6.07 (s, 2H), 3.98 (s, 2H), 1.35 (s, 6H). ^{13}C NMR: (101 MHz, $CDCl_3$) δ 161.9, 148.4, 131.8, 129.4, 115.9, 115.5, 109.2, 77.2, 67.7, 28.7. ^{1}H and ^{13}C NMR data agree with the previously reported data.[4]

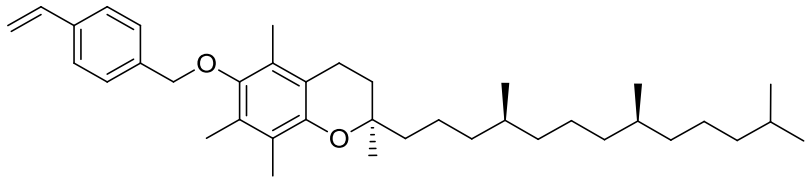


N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)picolinamide (**Ld**) Prepared according to the literature.[5] 96% yield, white solid. M.p. 112.9-113.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.87 (s, 1H), 9.01 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.67 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 8.28 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.9-7.84 (m, 2H), 7.56-7.48 (m, 1H), 7.45 (ddd, *J* = 7.6, 4.4, 1.2 Hz, 1H), 7.13 (td, *J* = 7.6, 0.8 Hz, 1H), 4.11 (s, 2H), 1.49 (s, 6H). ^{13}C NMR: (101 MHz, $CDCl_3$) δ 164.0, 161.2, 151.2, 148.1, 139.4, 137.1, 132.1, 129.0, 126.0, 122.7, 122.6, 120.1, 115.0, 77.9, 68.1, 28.6. ^{1}H and ^{13}C NMR data agree with the previously reported data.[5]

III. Procedures for Preparation of Alkenes (**1y** and **1z**).



1-((((*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-4-vinylbenzene (**1y**). Prepared according to the literature.[6] 48% yield, white solid. M.p. 45.0-46.4 ^{o}C; IR (neat): 2954, 2922, 2867, 1630, 1455, 1368 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 3.16 (td, *J* = 10.8, 4.4 Hz, 1H), 2.35-2.25 (m, 1H), 2.22-2.14 (m, 1H), 1.72-1.56 (m, 2H), 1.43-1.21 (m, 2H), 1.03-0.84 (m, 9H), 0.71 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 136.8, 136.7, 128.0, 126.1, 113.5, 78.7, 70.1, 48.3, 40.3, 34.6, 31.6, 25.5, 23.3, 22.4, 21.0, 16.1; HRMS (EI) calculated for $[C_{19}H_{28}O]^{+}$ requires m/z 272.2140, found m/z 272.2138.

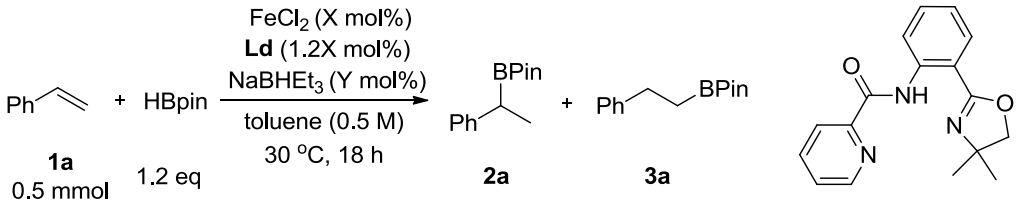


(*R*)-2,5,7,8-tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)-6-((4-vinylbenzyl)oxy)chroman (**1z**). Prepared according to the literature.[6] 63% yield, colorless oil. IR (neat): 2926, 2865, 1460, 1373, 1256 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.35 (m, 4H), 6.74 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.25 (d, *J* = 10.8 Hz, 1H), 4.68 (s, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.21 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), 1.87-1.75 (m, 2H), 1.59-1.01 (m, 24H), 0.89-0.83 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.9, 137.7, 137.1, 136.6, 127.91, 127.86, 126.3, 125.9, 122.9, 117.6, 113.8, 74.8, 74.4, 40.0, 39.4, 37.48, 37.46, 37.4, 37.3, 32.8, 32.7, 31.3, 28.0, 24.8, 24.4, 23.9, 22.7, 22.6, 21.0, 20.7, 19.75, 19.66, 12.9, 12.0, 11.8; HRMS (EI) calculated for $[C_{38}H_{58}O_2]^+$ requires m/z 546.4437, found m/z 546.4432.

IV. Iron-Catalyzed, Markovnikov-Selective Hydroboration of Alkenes

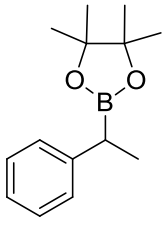
General Procedures for Hydroboration of Alkenes: To a 25 ml flame-dried Schlenk flask cooled under nitrogen, $FeCl_2$ (0.0032 g, 0.025 mmol), **Ld** (0.03 mmol), toluene (1 ml), were added. The mixture was stirred at 30 ^oC for 2 h. Then, HBpin (180 μL, 1.2 mmol), alkenes (1 mmol), $NaBHEt_3$ (50 μL, 1 M in THF) were added in sequence and stirred at 30 ^oC for 18 h. The resulting solution was filtered by a short pad of silica gel and the filtrate was concentrated. TMSPh (20 uL) was added as an internal standard. The resulting mixture was assessed by ^1H NMR and purified by flash column chromatography using PE/EtOAc (100/1) as the eluent to give the corresponding products.

Table S1 Optimization studies on solvent, amount of styrene, HBpin, ligand loading, reaction temperature



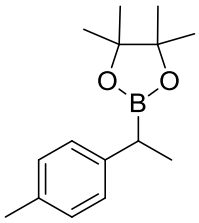
Entry	FeX_2	solvent	Yield (%)[a]	
			2a	**3a**
1	$FeCl_2$	toluene	65	0.8
2	$FeCl_2$	THF	43	0.5
3	$FeCl_2$	MeCN	16	1.0
4	$FeCl_2$	DCM	/	/
5	$FeCl_2$	Et_2O	36	0.6
6	$FeCl_2$	dioxane	50	0.9
7[b]	$FeCl_2$	toluene	64	0.1
8[c]	$FeCl_2$	toluene	43	0.5
9[d]	$FeCl_2$	toluene	50	0.7
10[e]	$FeCl_2$	toluene	52	0.6
11[f]	$FeCl_2$	toluene	56	1.3
12[g]	$FeCl_2$	toluene	52	1.3
13[h]	$FeCl_2$	toluene	9	/

[a] Yields were determined using TMSPh as an internal standard. [b]HBpin (1.0 mmol, 2.0 equiv.). [c] HBpin (0.5 mmol), **1a** (0.75 mol). [d]HBpin (0.5 mmol), **1a** (1.0 mol). [e]**Ld** (10 mol%). [f] Reaction temperature (40 °C). [g]Reaction temperature (50 °C). [h]Using *t*BuONa (10 mol%) instead of $NaBHEt_3$.

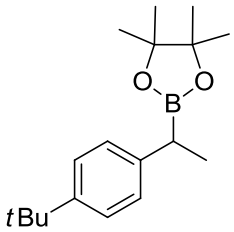


4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (**2a**). Prepared according to the general procedure using **Ld** (0.0090 g, 0.03 mmol), $FeCl_2$ (0.0032 g, 0.025 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and styrene (115 μL, 0.91 g/ml, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by

ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2a** (0.1717 g, 0.74 mmol, 74% yield, b/l > 50/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.18 (m, 4H), 7.16-7.08 (m, 1H), 2.43 (q, *J* = 7.6 Hz, 1H), 1.33 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 128.3, 127.7, 125.0, 83.2, 24.59, 24.55, 17.0. ^{1}H and ^{13}C NMR data agree with the previously reported data.[7]

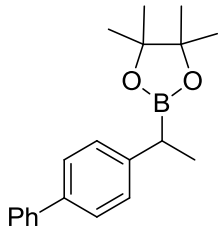


4,4,5,5-tetramethyl-2-(1-(*p*-tolyl)ethyl)-1,3,2-dioxaborolane (**2b**). Prepared according to the general procedure using **Ld** (0.0091 g, 0.03 mmol), $FeCl_2$ (0.0034 g, 0.026 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 4-methylphenylene (0.1189 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2b** (0.1997 g, 0.81 mmol, 81% yield, b/l > 50/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 2.38 (q, *J* = 7.6 Hz, 1H), 2.29 (s, 3H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 134.3, 129.0, 127.6, 83.2, 24.60, 24.57, 20.9, 17.2. ^{1}H and ^{13}C NMR data agree with the previously reported data.[7]

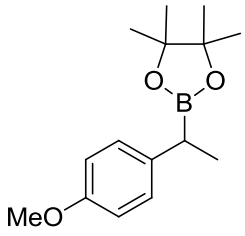


2-(1-(4-(*tert*-butyl)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2c**). Prepared according to the general procedure using **Ld** (0.0093 g, 0.031 mmol), $FeCl_2$ (0.0034 g, 0.026 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 4-*tert*-Butylstyrene (0.1610 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2c** (0.2071 g, 0.72 mmol, 72% yield, b/l > 50/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H),

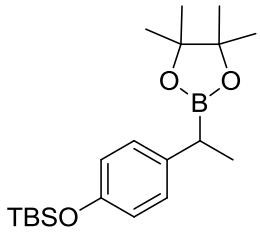
7.17-7.11 (m, 2H), 2.40 (q, *J* = 7.6 Hz, 1H), 1.31 (d, *J* = 7.6 Hz, 3H), 1.30 (s, 9H), 1.22 (s, 6H), 1.21 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 141.7, 127.4, 125.2, 83.2, 34.2, 31.4, 24.63, 24.60, 17.2. ^{1}H and ^{13}C NMR data agree with the previously reported data.[8]



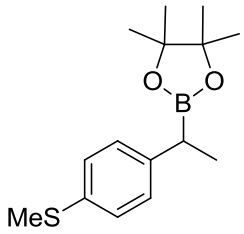
2-(1-([1,1'-biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2d**)**.** Prepared according to the general procedure using **Ld** (0.0092 g, 0.031 mmol), $FeCl_2$ (0.0033 g, 0.026 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-ethenyl-4-phenylbenzene (0.1802 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2d** (0.2094 g, 0.68 mmol, 68% yield, b/l > 50/1) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33-7.26 (m, 3H), 2.48 (q, *J* = 7.6 Hz, 1H), 1.37 (d, *J* = 7.2 Hz, 3H), 1.23 (s, 6H), 1.21 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 141.2, 137.9, 128.6, 128.2, 127.0, 126.9, 126.8, 83.3, 24.63, 24.60, 17.1. ^{1}H and ^{13}C NMR data agree with the previously reported data.[9]



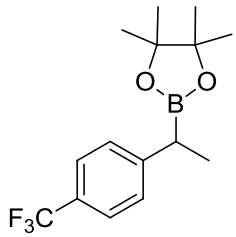
2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**). Prepared according to the general procedure using **Ld** (0.0092 g, 0.031 mmol), $FeCl_2$ (0.0033 g, 0.026 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 4-methoxystyrene (0.1345 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 20/1 as the eluent to afford **2e** (0.0921 g, 0.35 mmol, 35% yield, b/l = 50/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.09 (m, 2H), 6.85-6.77 (m, 2H), 3.77 (s, 3H), 2.37 (q, *J* = 7.6 Hz, 1H), 1.29 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, CDCl3) δ 157.2, 137.0, 128.6, 113.7, 83.2, 55.2, 24.61, 24.57, 17.3. ^{1}H and ^{13}C NMR data agree with the previously reported data.[9]



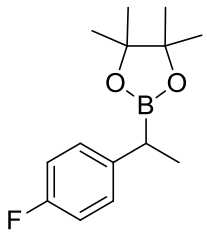
tert-butyldimethyl(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenoxy)silane (**2f**)**.** Prepared according to the general procedure using **Ld** (0.0090 g, 0.03 mmol), $FeCl_2$ (0.0033 g, 0.026 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and *tert*-butyldimethyl (4-vinylphenoxy)silane (0.2359 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2f** (0.2725 g, 0.75 mmol, 75% yield, b/l > 50/1) as a colorless oil. IR (neat): 2958, 2860, 1508, 1354, 1321, 1253, 1144 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-7.01 (m, 2H), 6.76-6.70 (m, 2H), 2.36 (q, *J* = 7.6 Hz, 1H), 1.29 (d, *J* = 7.6 Hz, 3H), 1.20 (s, 6H), 1.18 (s, 6H), 0.97 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 137.4, 128.5, 119.8, 83.1, 25.7, 24.6, 24.5, 18.2, 17.1, -4.4; HRMS (EI) calculated for $[C_{20}H_{35}BO_3Si]^+$ requires m/z 362.2449, found m/z 362.2450.



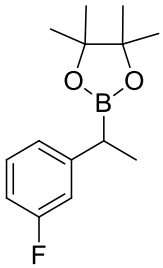
4,4,5,5-tetramethyl-2-(1-(4-(methylthio)phenyl)ethyl)-1,3,2-dioxaborolane (**2g**). Prepared according to the general procedure using **Ld** (0.0092 g, 0.031 mmol), $FeCl_2$ (0.0033 g, 0.026 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-ethenyl-4-methyl-sulfanylbenzene (0.1508 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2g** (0.1976 g, 0.71 mmol, 71% yield, b/l = 40/1) as a colorless oil. IR (neat): 2977, 2926, 1493, 1375, 1352, 1322, 1143 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.12 (m, 4H), 2.45 (s, 3H), 2.39 (q, *J* = 7.6 Hz, 1H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 134.2, 128.3, 127.3, 83.3, 24.59, 24.56, 17.0, 16.4; HRMS (EI) calculated for $[C_{15}H_{23}BO_2S]^+$ requires m/z 278.1512, found m/z 278.1517.



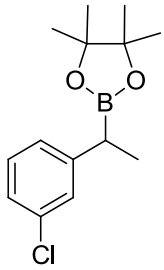
4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)-1,3,2-dioxaborolane (**2h**)**.** Prepared according to the general procedure using **Ld** (0.0090 g, 0.03 mmol), $FeCl_2$ (0.0034 g, 0.027 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-(Trifluoromethyl)-4-vinylbenzene (0.1718 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2h** (0.1710 g, 0.57 mmol, 57% yield, b/l > 50/1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.50 (q, *J* = 7.6 Hz, 1H), 1.34 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 128.0, 127.4 (q, *J* = 32.4 Hz, 1C), 125.2 (q, *J* = 3.6 Hz, 1C), 124.5 (q, *J* = 268.8 Hz, 1C), 83.5, 24.6, 24.5, 16.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.1; ^{1}H and ^{13}C NMR data agree with the previously reported data.[9]



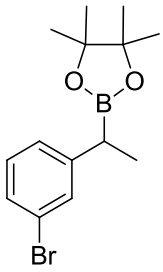
2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2i**). Prepared according to the general procedure using **Ld** (0.0092 g, 0.031 mmol), $FeCl_2$ (0.0033 g, 0.026 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-fluoro-4-vinylbenzene (0.1230 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2i** (0.1626 g, 0.65 mmol, 65% yield, b/l > 50/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.10 (m, 2H), 7.00-6.86 (m, 2H), 2.41 (q, *J* = 7.6 Hz, 1H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (d, *J* = 121.5 Hz, 1C), 140.5 (d, *J* = 2.9 Hz, 1C), 129.0 (d, *J* = 7.4 Hz, 2C), 114.9 (d, *J* = 20.6 Hz, 2C), 83.3, 24.60, 24.55, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.0; ^{1}H and ^{13}C NMR data agree with the previously reported data.[8]



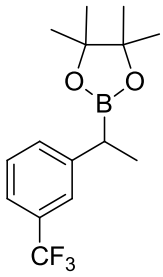
2-(1-(3-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2j**). Prepared according to the general procedure using **Ld** (0.0093 g, 0.031 mmol), $FeCl_2$ (0.0034 g, 0.027 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-fluoro-3-vinylbenzene (0.1228 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2j** (0.1584 g, 0.63 mmol, 63% yield, b/l = 44/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.16 (m, 1H), 7.00-6.90 (m, 2H), 6.85-6.78 (m, 1H), 2.44 (q, *J* = 7.6 Hz, 1H), 1.32 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 246.0 Hz, 1C), 147.6 (d, *J* = 7.4 Hz, 1C), 129.5 (d, *J* = 8.9 Hz, 1C), 123.4 (d, *J* = 2.2 Hz, 1C), 114.5 (d, *J* = 21.4 Hz, 1C), 111.9 (d, *J* = 20.6 Hz, 1C), 83.4, 24.6, 24.5, 16.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.0; ^{1}H and ^{13}C NMR data agree with the previously reported data.[8]



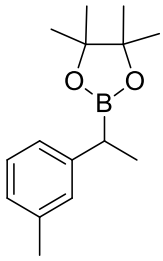
2-(1-(3-chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2k**). Prepared according to the general procedure using **Ld** (0.0093 g, 0.031 mmol), $FeCl_2$ (0.0033 g, 0.026 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-chloro-3-vinylbenzene (0.1390 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2k** (0.1674 g, 0.63 mmol, 63% yield, b/l > 50/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.14 (m, 2H), 7.13-7.06 (m, 2H), 2.41 (q, *J* = 7.6 Hz, 1H), 1.31 (d, *J* = 7.2 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 134.0, 129.4, 127.8, 126.0, 125.2, 83.5, 24.58, 24.55, 16.8. ^{1}H and ^{13}C NMR data agree with the previously reported data.[10]



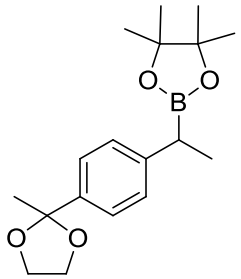
2-(1-(3-bromophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2l**). Prepared according to the general procedure using **Ld** (0.0091 g, 0.031 mmol), $FeCl_2$ (0.0034 g, 0.027 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-bromo-3-vinylbenzene (0.1829 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2l** (0.1247 g, 0.40 mmol, 40% yield, b/l = 37/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.28-7.24 (m, 1H), 7.17-7.09 (m, 2H), 2.40 (q, *J* = 7.6 Hz, 1H), 1.31 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 130.8, 129.8, 128.2, 126.5, 122.4, 83.5, 24.59, 24.56, 16.8. ^{1}H and ^{13}C NMR data agree with the previously reported data.[11]



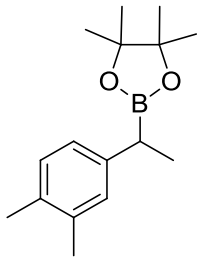
4,4,5,5-tetramethyl-2-(1-(3-(trifluoromethyl)phenyl)ethyl)-1,3,2-dioxaborolane (**2m**). Prepared according to the general procedure using **Ld** (0.0091 g, 0.031 mmol), $FeCl_2$ (0.0035 g, 0.027 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-(trifluoromethyl)-3-vinylbenzene (0.1720 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2m** (0.1779 g, 0.59 mmol, 59% yield, b/l > 50/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.43-7.33 (m, 3H), 2.50 (q, *J* = 7.6 Hz, 1H), 1.34 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 131.2, 130.5 (q, *J* = 31.6 Hz, 1C), 128.6, 124.4 (q, *J* = 273.2 Hz, 1C), 124.5 (q, *J* = 3.7 Hz, 1C), 122.0 (q, *J* = 3.7 Hz, 1C), 83.5, 24.6, 24.5, 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5; ^{1}H and ^{13}C NMR data agree with the previously reported data.[8]



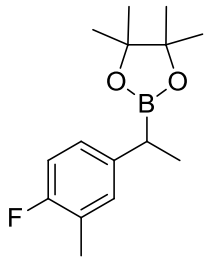
4,4,5,5-tetramethyl-2-(1-(*m*-tolyl)ethyl)-1,3,2-dioxaborolane (**2n**)**.** Prepared according to the general procedure using **Ld** (0.0094 g, 0.032 mmol), $FeCl_2$ (0.0035 g, 0.028 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol), 1-methyl-3-vinylbenzene (0.1192 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2n** (0.1683 g, 0.68 mmol, 68% yield, b/l > 50/1) as a colorless oil. IR (neat): 2978, 2931, 1605, 1461, 1376, 1352, 1322, 1144 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.6 Hz, 1H), 7.05-6.97 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 2.39 (q, *J* = 7.6 Hz, 1H), 2.31 (s, 3H), 1.31 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 137.7, 128.6, 128.1, 125.8, 124.8, 83.2, 24.57, 24.55, 21.4, 17.1; HRMS (EI) calculated for $[C_{15}H_{23}BO_2]^+$ requires m/z 246.1791, found m/z 246.1794.



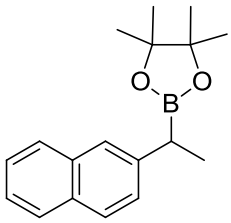
4,4,5,5-tetramethyl-2-(1-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)ethyl)-1,3,2-dioxaborolane (**2o**). Prepared according to the general procedure using **Ld** (0.0091 g, 0.031 mmol), $FeCl_2$ (0.0034 g, 0.027 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 2-methyl-2-(4-vinylphenyl)-1,3-dioxolane (0.1928 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2o** (0.1368 g, 0.42 mmol, 42% yield, b/l > 50/1) as a white solid. M.p. 62.5-63.7 ^oC; IR (neat): 2980, 2884, 1461, 1375, 1352, 1322, 1144 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.29 (m, 2H), 7.23-7.09 (m, 2H), 4.15-3.93 (m, 2H), 3.93-3.71 (m, 2H), 2.43 (q, *J* = 7.6 Hz, 1H), 1.65 (s, 3H), 1.31 (d, *J* = 7.6 Hz, 3H), 1.22 (s, 6H), 1.21 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 139.8, 127.5, 125.2, 108.9, 83.3, 64.4, 27.5, 24.62, 24.58, 17.1; HRMS (EI) calculated for $[C_{18}H_{27}BO_4]^+$ requires m/z 318.2002, found m/z 318.2003.



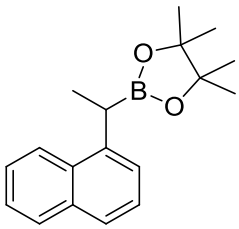
2-(1-(3,4-dimethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2p**). Prepared according to the general procedure using **Ld** (0.0093 g, 0.031 mmol), $FeCl_2$ (0.0035 g, 0.028 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1,2-dimethyl-4-vinylbenzene (0.1331 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2p** (0.1600 g, 0.61 mmol, 61% yield, b/l > 50/1) as a white solid. M.p. 66.8-67.6 ^{o}C; IR (neat): 2976, 2926, 1456, 1351, 1324, 1143 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-6.90 (m, 3H), 2.35 (q, *J* = 7.6 Hz, 1H), 2.22 (s, 3H), 2.20 (s, 3H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 136.2, 133.0, 129.6, 129.2, 125.1, 83.2, 24.6, 19.8, 19.2, 17.4; HRMS (EI) calculated for $[C_{16}H_{25}BO_2]^+$ requires m/z 260.1948, found m/z 260.1949.



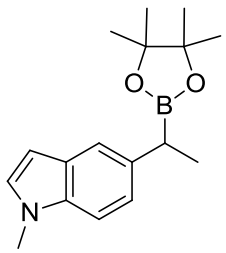
2-(1-(4-fluoro-3-methylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2q**). Prepared according to the general procedure using **Ld** (0.0090 g, 0.030 mmol), $FeCl_2$ (0.0034 g, 0.027 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1,2-dimethyl-4-vinylbenzene (0.1365 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2q** (0.1414 g, 0.53 mmol, 53% yield, b/l > 50/1) as a colorless oil. IR (neat): 2978, 2931, 1503, 1461, 1353, 1323, 1145 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01-6.94 (m, 2H),, 6.87 (dd, *J* = 9.6, 8.4 Hz, 1H), 2.36 (q, *J* = 7.2 Hz, 1H), 2.23 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 (d, *J* = 242.3 Hz, 1C), 140.2 (d, *J* = 3.6 Hz, 1C), 130.6 (d, *J* = 5.2 Hz, 1C), 126.2 (d, *J* = 8.1 Hz, 1C), 124.2 (d, *J* =17.7 Hz, 1C), 114.6 (d, *J* = 22.1 Hz, 1C), 83.3, 24.58, 24.55, 17.3, 14.6 (d, *J* = 3.6 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.4;HRMS (EI) calculated for $[C_{15}H_{22}BFO_2]^+$ requires m/z 264.1697, found m/z 264.1700.



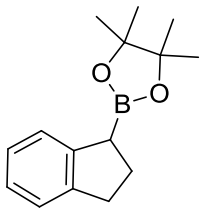
4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (**2r**). Prepared according to the general procedure using **Ld** (0.0093 g, 0.031 mmol), $FeCl_2$ (0.0036 g, 0.028 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 2-vinylnaphthalene (0.1558 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2r** (0.1811 g, 0.64 mmol, 64% yield, b/l > 50/1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.71 (m, 3H), 7.64 (s, 1H), 7.45-7.33 (m, 3H), 2.61 (q, *J* = 7.6 Hz, 1H), 1.42 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 133.9, 131.7, 127.6, 127.50, 127.46, 127.2, 125.6, 125.2, 124.7, 83.4, 24.62, 24.59, 16.8. ^{1}H and ^{13}C NMR data agree with the previously reported data.[9]



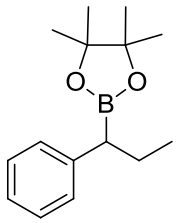
4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (**2s**). Prepared according to the general procedure using **Ld** (0.0093 g, 0.031 mmol), $FeCl_2$ (0.0034 g, 0.027 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-vinylnaphthalene (0.1556 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2s** (0.1703 g, 0.60 mmol, 60% yield, b/l = 13/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.51-7.36 (m, 4H), 3.11 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.6 Hz, 3H), 1.19 (s, 6H), 1.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 133.9, 132.0, 128.7, 125.8, 125.3, 125.2, 124.2, 124.0, 83.4, 24.6, 24.5, 16.4. ^{1}H and ^{13}C NMR data agree with the previously reported data.[9]



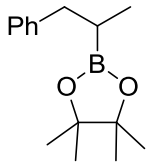
1-methyl-5-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1*H*-indole (**2t**). Prepared according to the general procedure using **Ld** (0.0093 g, 0.031 mmol), $FeCl_2$ (0.0035 g, 0.028 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-methyl-5-vinyl-1*H*-indole (0.1580 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2t** (0.1190 g, 0.42 mmol, 42% yield, b/l > 50/1) as a yellow oil. IR (neat): 2976, 1487, 1446, 1350, 1320, 1142 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.10 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.97 (d, *J* = 2.8 Hz, 1H), 6.39 (d, *J* = 2.8 Hz, 1H), 3.74 (s, 3H), 2.51 (q, *J* = 7.6 Hz, 1H), 1.37 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 135.1, 128.8, 128.5, 122.2, 119.2, 108.9, 100.5, 83.1, 32.7, 24.61, 17.9; HRMS (EI) calculated for $[C_{17}H_{24}BNO_2]^+$ requires m/z 285.1900, found m/z 285.1895.



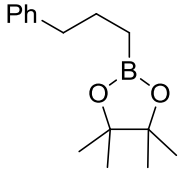
2-(2,3-dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2u**)**.** Prepared according to the general procedure using **Ld** (0.0094 g, 0.032 mmol), $FeCl_2$ (0.0034 g, 0.027 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and indene (0.1186 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2u** (0.1232 g, 0.49 mmol, 49% yield, b/l = 11/1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 6.8 Hz, 1H), 7.23-7.17 (m, 1H), 7.14-7.05 (m, 2H), 3.00-2.85 (m, 2H), 2.72 (t, *J* = 8.4 Hz, 1H), 2.29-2.16 (m, 1H), 2.15-2.03 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 144.2, 125.9, 125.5, 124.3, 124.2, 83.3, 33.3, 27.8, 24.8, 24.7. ^{1}H and ^{13}C NMR data agree with the previously reported data.[12]



4,4,5,5-tetramethyl-2-(1-phenylpropyl)-1,3,2-dioxaborolane (**2v**). Prepared according to the general procedure using **Ld** (0.0090 g, 0.030 mmol), $FeCl_2$ (0.0032 g, 0.025 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and *β*-methylstyrene (0.1180 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2v** (0.0947 g, 0.38 mmol, 38% yield, b/l > 50/1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.27-7.18 (m, 4H), 7.15-7.09 (m, 1H), 2.22 (t, *J* = 7.6 Hz, 1H), 1.93-1.82 (m, 1H), 1.75-1.60 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H), 0.91 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 128.4, 128.2, 125.1, 83.2, 25.8, 24.63, 24.55, 13.9. ^{1}H and ^{13}C NMR data agree with the previously reported data.[12]

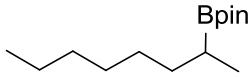


2w

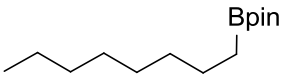


3w

Prepared according to the general procedure using **Ld** (0.0091 g, 0.031 mmol), $FeCl_2$ (0.0034 g, 0.027 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and allylbenzene (0.1198 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis and compared to the literature.[13] The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford two isomers **2v** and **3w** (0.2294 g, 0.90 mmol, 90% yield, n_{2w}/n_{3w} = 3:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.10 (m, 7H), 2.80 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.60 (t, *J* = 7.6 Hz, 0.66H), 2.54 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.79-1.68 (m, 0.70H), 1.40-1.31 (m, 1H), 1.23 (s, 3.96 H), 1.18 (s, 6H), 1.17 (s, 6H), 0.97 (d, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.6 Hz, 0.69H).



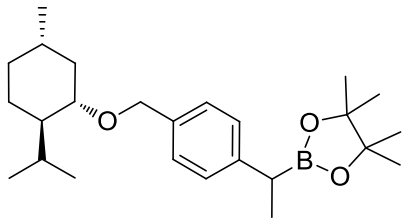
2x



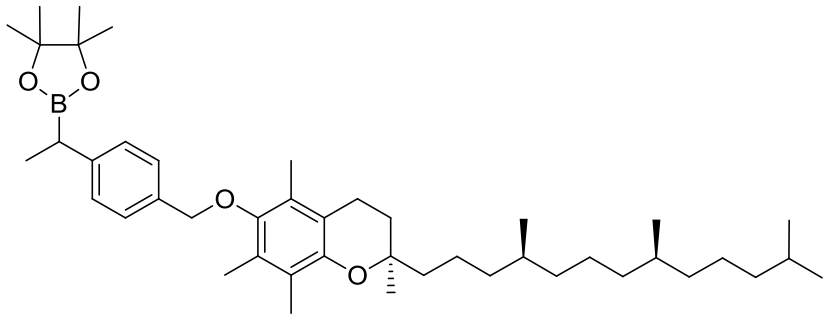
3x

Prepared according to the general procedure using **Ld** (0.0090 g, 0.030 mmol), $FeCl_2$ (0.0031 g, 0.025 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and 1-octene (0.1120 g, 1.0 mmol).

After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis and compared to the literature.[13] The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford two isomers **2x** and **3x** (0.1514 g, 0.63 mmol, 63% yield, $n_{\mathbf{2x}}/n_{\mathbf{3x}}$= 1:1) as a colorless oil.



2-(1-(4-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy) methyl)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2y**) (diastereomer 1:1). Prepared according to the general procedure using **Ld** (0.0090 g, 0.030 mmol), $FeCl_2$ (0.0033 g, 0.025 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (180 μL, 1.2 mmol) and **1y** (0.2728 g, 1.0 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2y** (0.2006 g, 0.5 mmol, 50% yield, b/l > 50/1) as a colorless oil. IR (neat): 2955, 2924, 1453, 1374, 1350, 1323, 1145 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.60 (d, *J* = 11.2 Hz, 1H), 4.35 (d, *J* = 11.2 Hz, 1H), 3.15 (td, *J* = 10.4, 4.0 Hz, 1H), 2.41 (qd, *J* = 7.6, 2.0 Hz, 1H), 2.34–2.24 (m, 1H), 2.24–2.13 (m, 1H), 1.69–1.55 (m, 2H), 1.38–1.24 (m, 5H), 1.20 (s, 6H), 1.19 (s, 6H), 0.94–0.83 (m, 9H), 0.68 (d, *J* = 6.8 Hz, 3H); HRMS (EI) calculated for $[C_{25}H_{41}BO_3]^+$ requires m/z 400.3149, found m/z 400.3149.



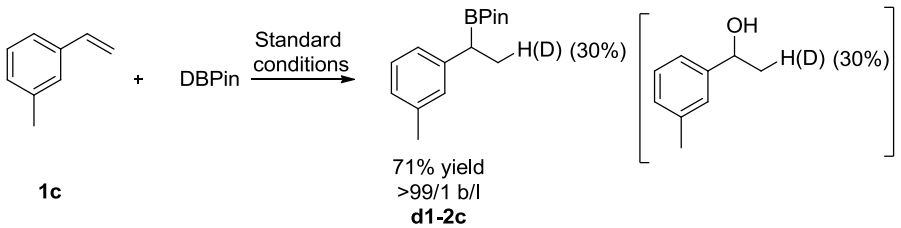
4,4,5,5-tetramethyl-2-(1-(4-((((*R*)-2,5,7,8-tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)phenyl)ethyl)-1,3,2-dioxaborolane (**2z**) (diastereomer 1:1). Prepared according

to the general procedure using **Ld** (0.0092 g, 0.031 mmol), $FeCl_2$ (0.0033 g, 0.025 mmol), toluene (1 ml), $NaBHEt_3$ (50 μL, 0.05 mmol), HBpin (90 μL, 0.6 mmol) and **1z** (0.2658 g, 0.5 mmol). After 18 h, the resulting solution was added 20 ml of ether and filtered through a pad of silica gel, washed by ether (10 ml x 1). The combined filtrates were concentrated and regioselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2z** (0.1316 g, 0.2 mmol, 40% yield, b/l = 40/1) as a colorless oil. IR (neat): 2926, 2867, 1459, 1374, 1322, 1256, 1144, 1087 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.64 (s, 2H), 2.58 (t, *J* = 6.8 Hz, 2H), 2.45 (q, *J* = 7.6 Hz, 1H), 2.21 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), 1.87-1.72 (m, 2H), 1.59-1.00 (m, 39H), 0.92-0.80 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 147.8, 144.7, 134.6, 128.02, 128.00, 127.9, 126.0, 122.8, 117.5, 83.3, 74.79, 74.76, 40.1, 39.4, 37.47, 37.45, 37.4, 37.3, 32.8, 32.7, 31.3, 28.0, 24.8, 24.6, 24.4, 23.9, 22.7, 22.6, 21.0, 20.7, 19.74, 19.66, 17.2, 12.9, 12.0, 11.8; HRMS (EI) calculated for $[C_{44}H_{71}BO_4]^+$ requires m/z 674.5445, found m/z 674.5462.

Gram-scale Reaction:

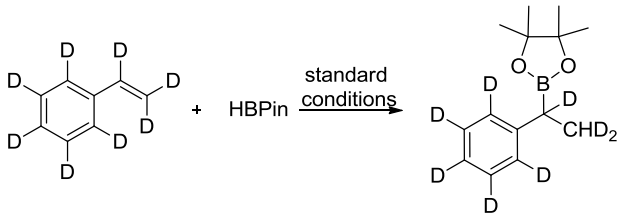
Prepared according to the general procedure, the reaction using **Ld** (0.0712 g, 0.24 mmol), $FeCl_2$ (0.0253 g, 0.20 mmol), toluene (8 ml), $NaBHEt_3$ (400 μL, 0.4 mmol), HBpin (1.44 ml, 9.6 mmol) and styrene (0.92 ml, 0.91 g/ml, 8.0 mmol). After 18 h, the resulting solution was concentrated and purified by flash column chromatography using PE/EtOAc = 100/1 as the eluent to afford **2a** (1.7230 g, 7.44 mmol, 93% yield, b/l > 50/1) as a colorless oil.

Deuterium Experiments



The reaction was performed according to the general procedure by using DBpin instead of HBpin. The deuteration of products was determined by ^{1}H NMR spectra of the alcohols from oxidation of corresponding boronates. The deuterated atom was only observed at the methyl position (30%

deuteration) and the hydrogen atom might come from reductant $NaBHEt_3$ or the β–hydride elimination from alkene.



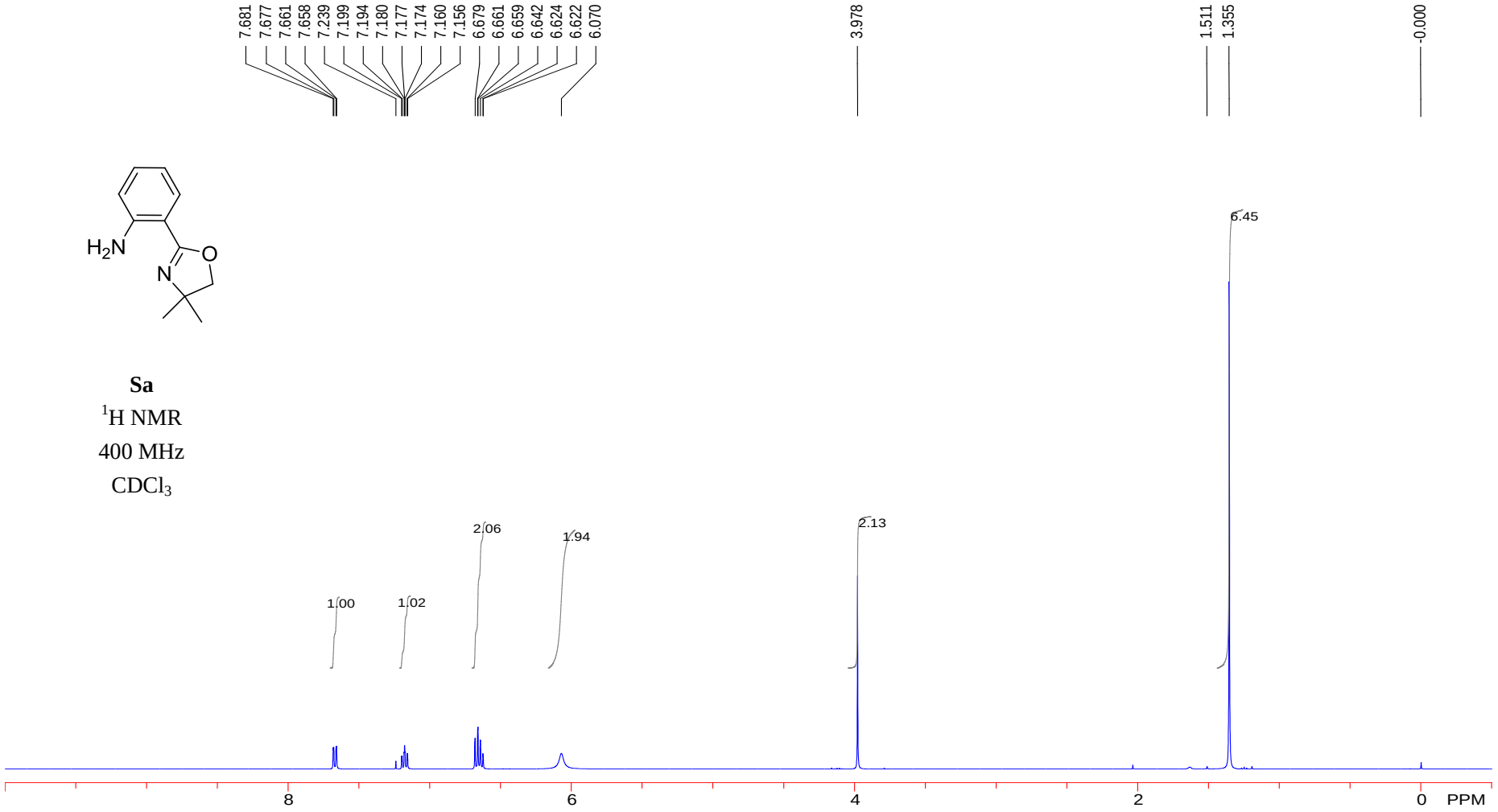
65% yield
>99/1 b/l
d8-**2a**

The reaction was performed according to the general procedure by using d8-styrene instead of styrene, which gave the monoprotio-boronic ester d8-**2a** in 65% yield with H incorporation at the terminal methyl group. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (brs, 1H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ144.7, 127.7 (t, *J* = 24.2 Hz), 127.3 (t, *J* = 24.2 Hz), 124.5 (t, *J* = 24.3 Hz), 83.2, 24.6, 24.5, 16.3 (quint., *J* = 19.2 Hz).

V. References

1. Garcia-Barrantes, P. M.; Lindsley, C. W. *Org. Lett.* **2016**, *18*, 3810-3813.
2. (a) Chen, J. H.; Cheng, B.; Cao, M. Y.; Lu, Z. *Angew. Chem. Int. Ed.* **2015**, *54*, 4661-4664; (b) Zhang, H. Y.; Lu, Z. *ACS Catal.* **2016**, *6*, 6596-6600; (c) Chen, X.; Lu, Z. *Org. Lett.* **2016**, *18*, 4658-4661.
3. Wolinska, E. *Tetrahedron* **2013**, *69*, 7269-7278.
4. Giri, R.; Maugel, N.; Foxman, B. M.; Yu, J.-Q. *Organometallics* **2008**, *27*, 1667-1670.
5. Decken, A.; Gossage, R. A.; Yadav, P. N. *Can. J. Chem.* **2005**, *83*, 1185-1189.
6. Urgoitia, G.; SanMartin, R.; Herrero, M. T.; Domínguez, E. *Adv. Synth. Catal.* **2016**, *358*, 3307-3312.
7. Zhang, G. Q.; Zeng, H. S.; Wu, J.; Yin, Z. W.; Zheng, S. P.; Fettinger, J. C. *Angew. Chem. Int. Ed.* **2016**, *55*, 14367-14370.
8. MacNair, A. J.; Millet, C. R. P.; Nichol, G. S.; Ironmonger, A.; Thomas, S. P. *ACS Catal.* **2016**, *6*, 7217-7221.
9. Touney, E. E.; Van Hoveln, R.; Buttke, C. T.; Freidberg, M. D.; Guzei, I. A.; Schomaker, J. M. *Organometallics* **2016**, *35*, 3436-3439.
10. Noh, D.; Chea, H.; Ju, J.; Yun, J. *Angew. Chem. Int. Ed.* **2009**, *48*, 6938-6938.
11. Endo, K.; Hirokami, M.; Shibata, T. *Organometallics* **2008**, *27*, 5390-5393.
12. Scheuermann, M. L.; Johnson, E. J.; Chirik, P. J. *Org. Lett.* **2015**, *17*, 2716-2719.
13. (a) Kerchner, H. A.; Montgomery, J. *Org. Lett.* **2016**, *18*, 5760-5763; (b) Yin, Q.; Kemper, S.; Klare, H. F. T.; Oestreich, M. *Chem-Eur. J.* **2016**, *22*, 13840-13844.

VI. NMR Spectra

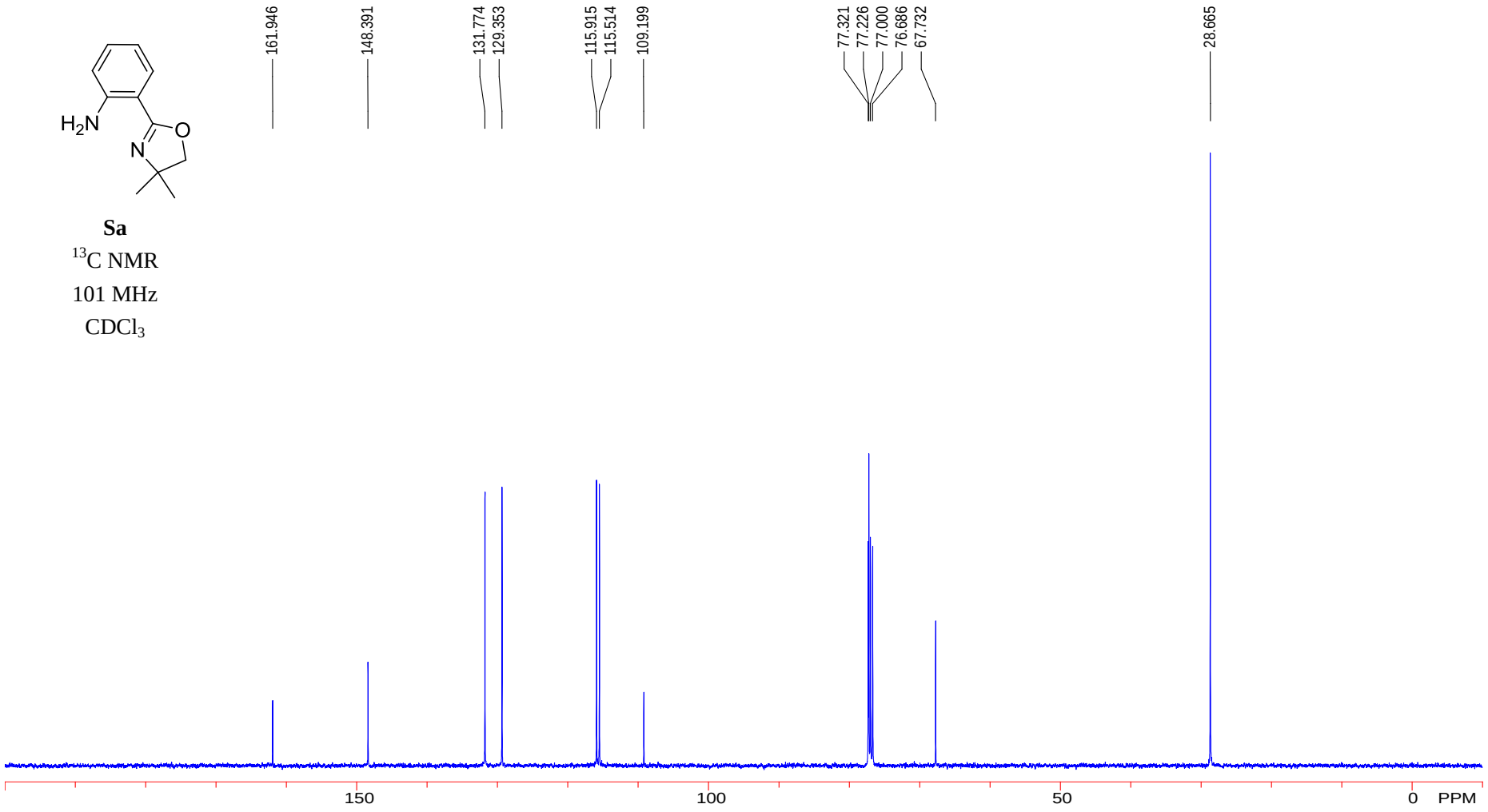


Sa

^{1}H NMR

400 MHz

$CDCl_3$

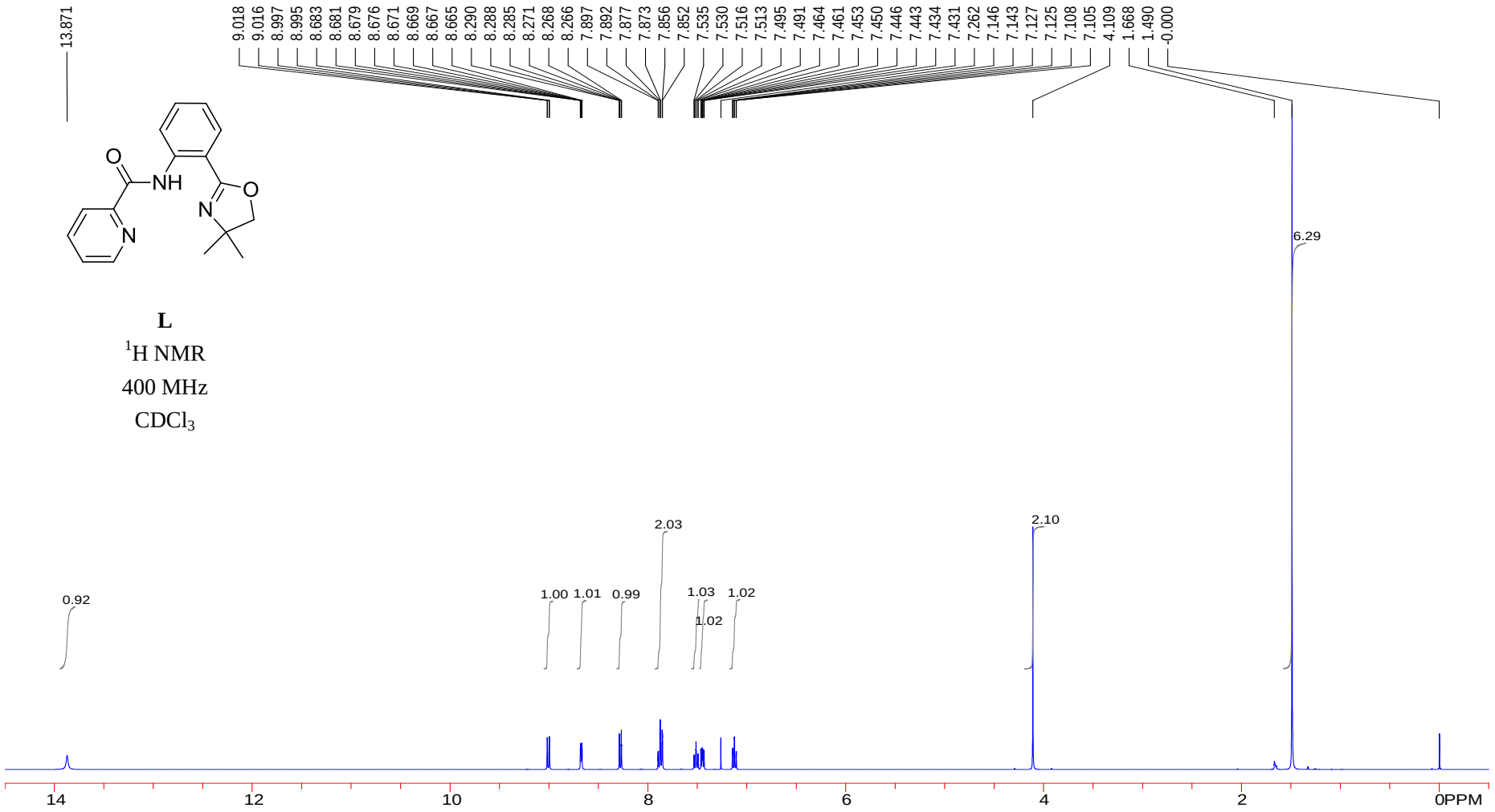


Sa

^{13}C NMR

101 MHz

$CDCl_3$

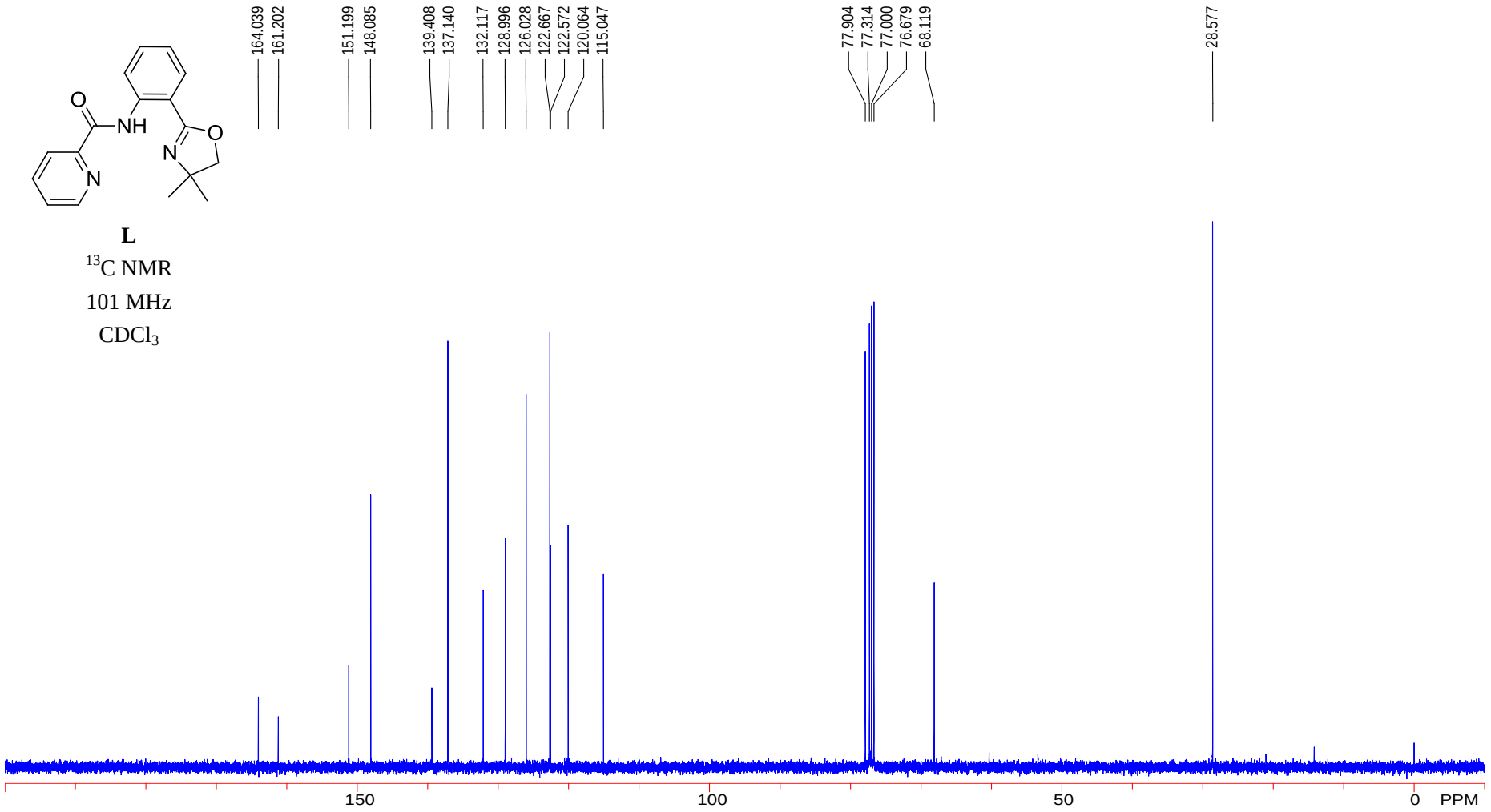


L

^{1}H NMR

400 MHz

$CDCl_3$

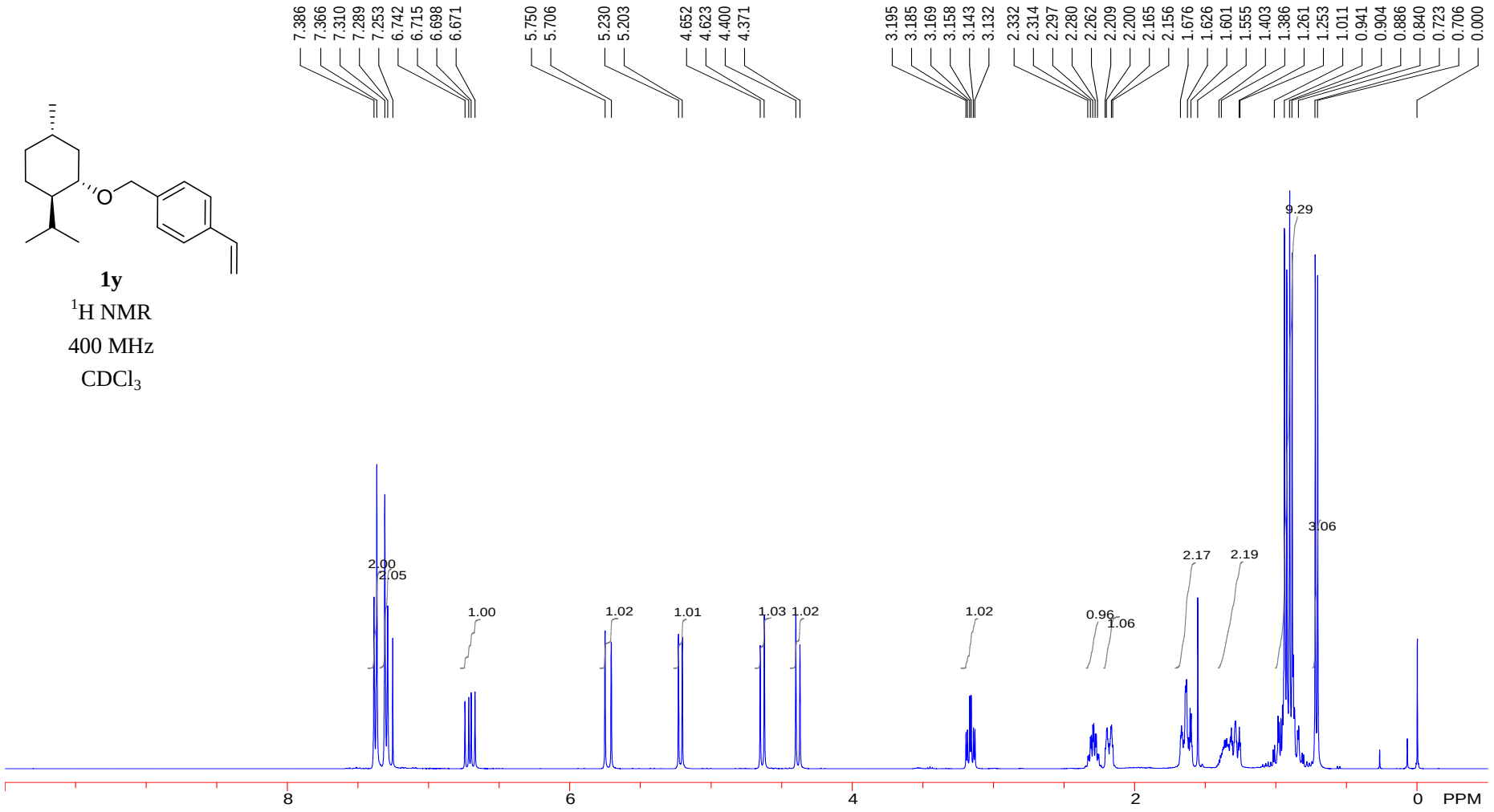


L

^{13}C NMR

101 MHz

$CDCl_3$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5.706
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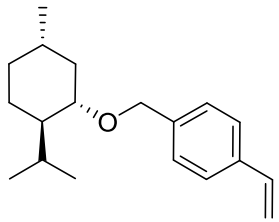
5.203
4.652
4.623
4.400
4.371
3.195
3.185
3.169
3.158
3.143
3.132
2.332
2.314
2.297
2.280
2.262
2.209
2.200
2.165
2.156
1.676
1.626
1.601
1.555
1.403
1.386
1.261
1.253
1.011
0.941
0.904
0.886
0.840
0.723
0.706
0.000
O
1y
1H NMR
400 MHz
CDCl3
9.29
3.06
2.17
2.19
2.00
2.05
1.00
1.02
1.01
1.03
1.02
1.02
0.96
1.06
8
6
4
2
0
PPM

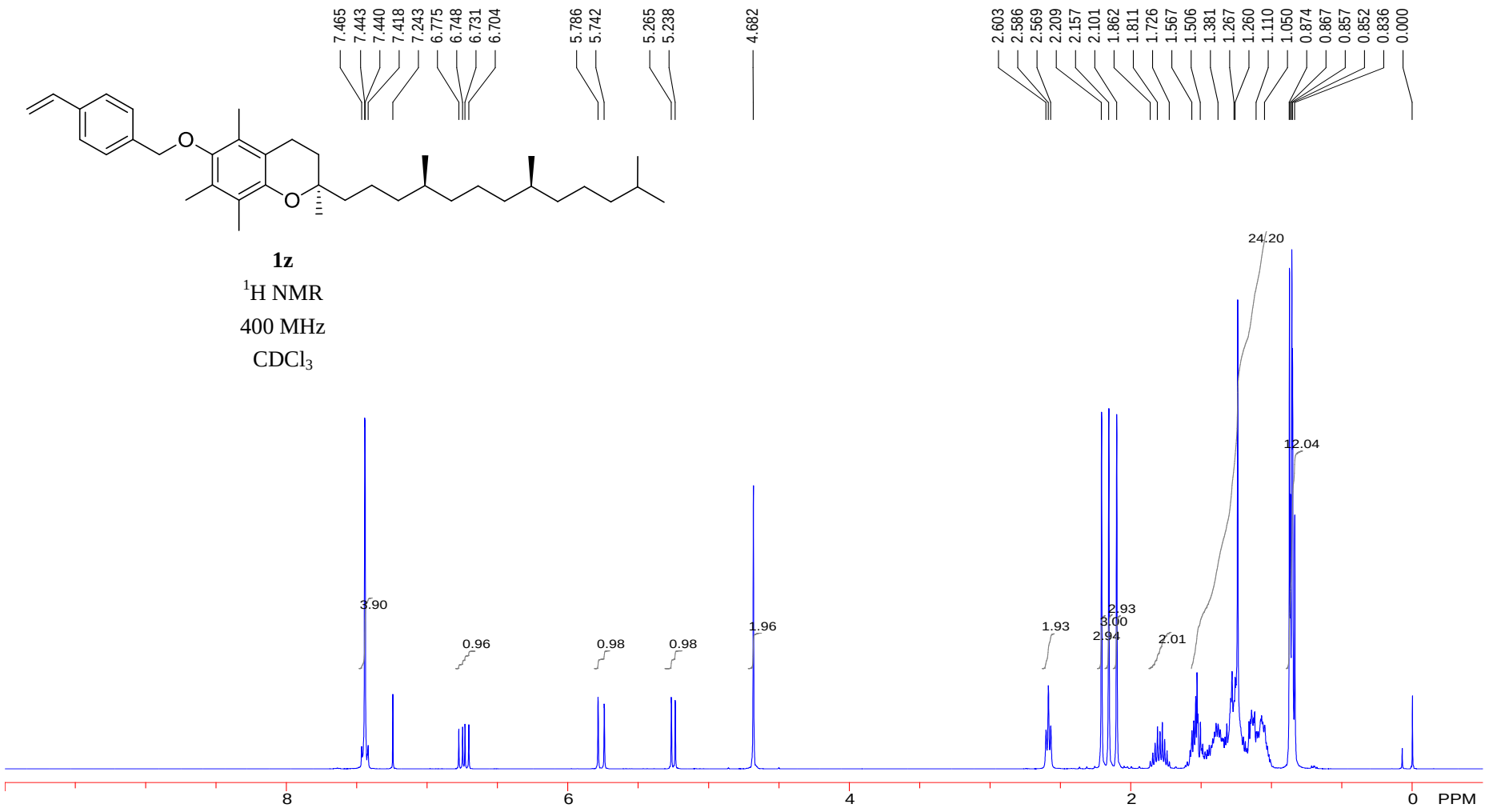


1y

^{13}C NMR

101 MHz

$CDCl_3$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7.440
7.418
7.243
6.775
6.748
6.731
6.704
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5.742
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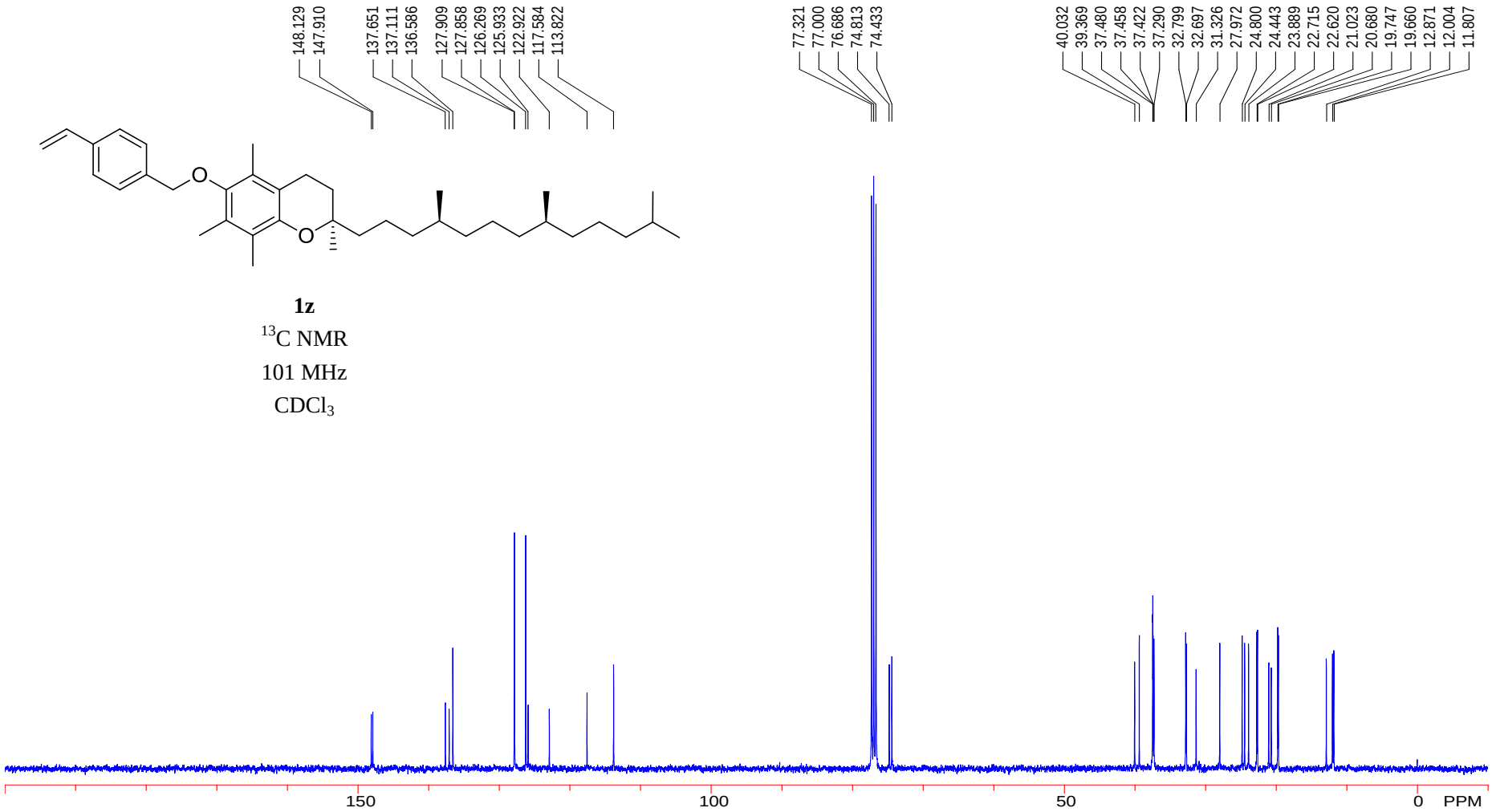
5.238
4.682
2.603
2.586
2.569
2.209
2.157
2.101
1.862
1.811
1.726
1.567
1.506
1.381
1.267
1.260
1.110
1.050
0.874
0.867
0.857
0.852
0.836
0.000
O
O
1z
1H NMR
400 MHz
CDCl3
24.20
12.04
3.90
0.96
0.98
0.98
1.96
1.93
2.93
3.00
2.94
2.01
8
6
4
2
0
PPM

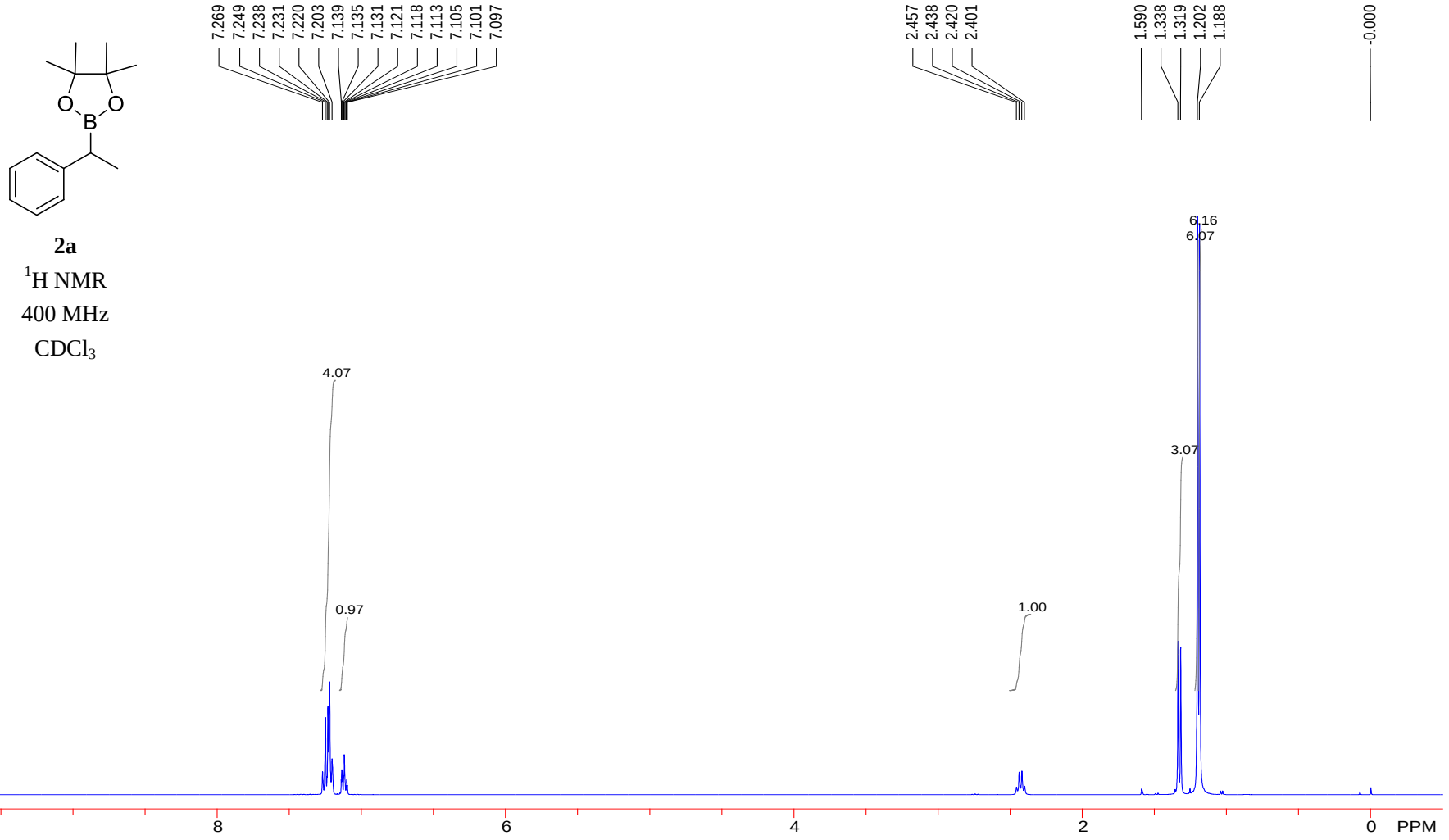


1z

^{13}C NMR

101 MHz

$CDCl_3$

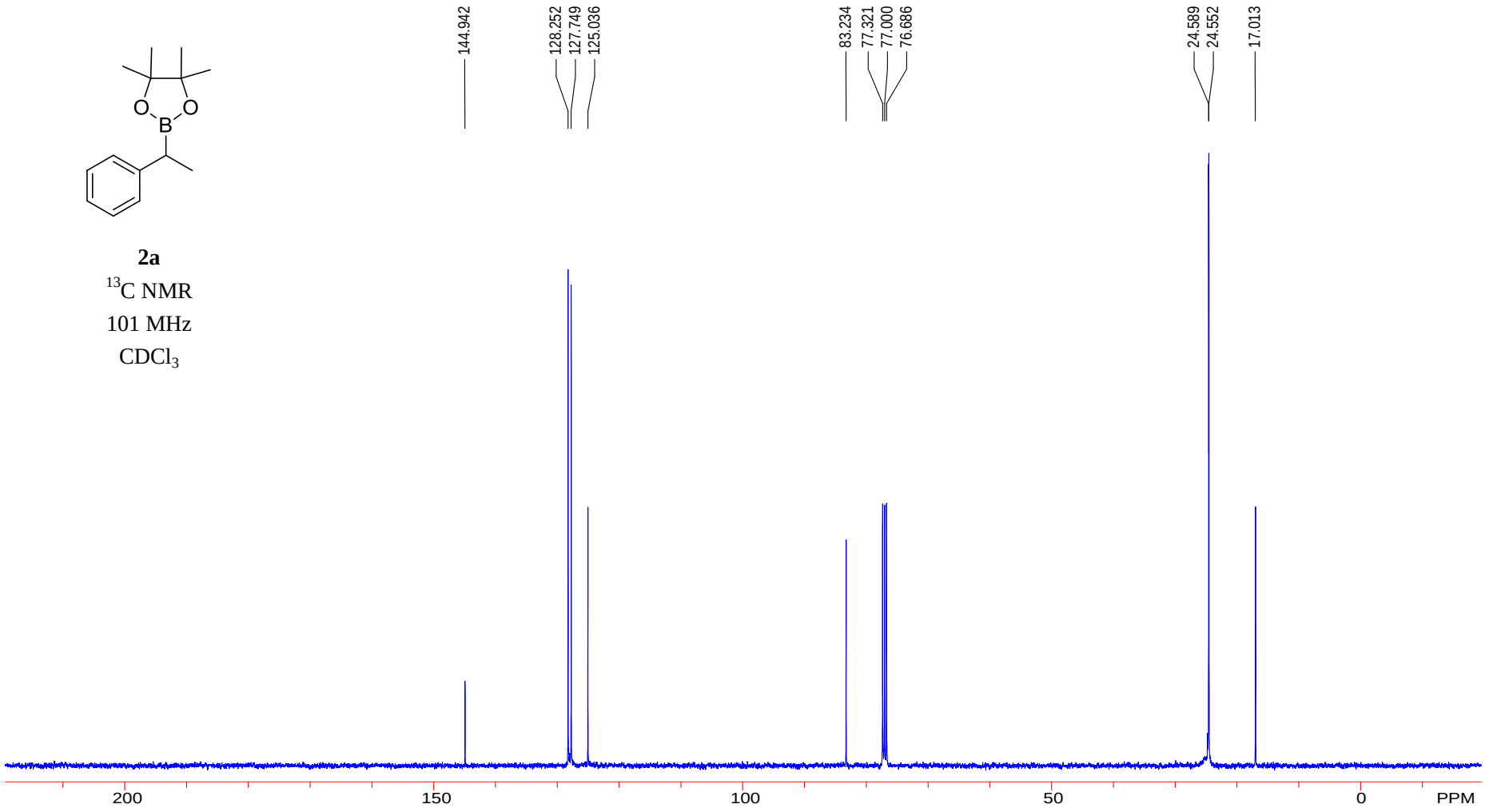


2a

^{1}H NMR

400 MHz

$CDCl_3$

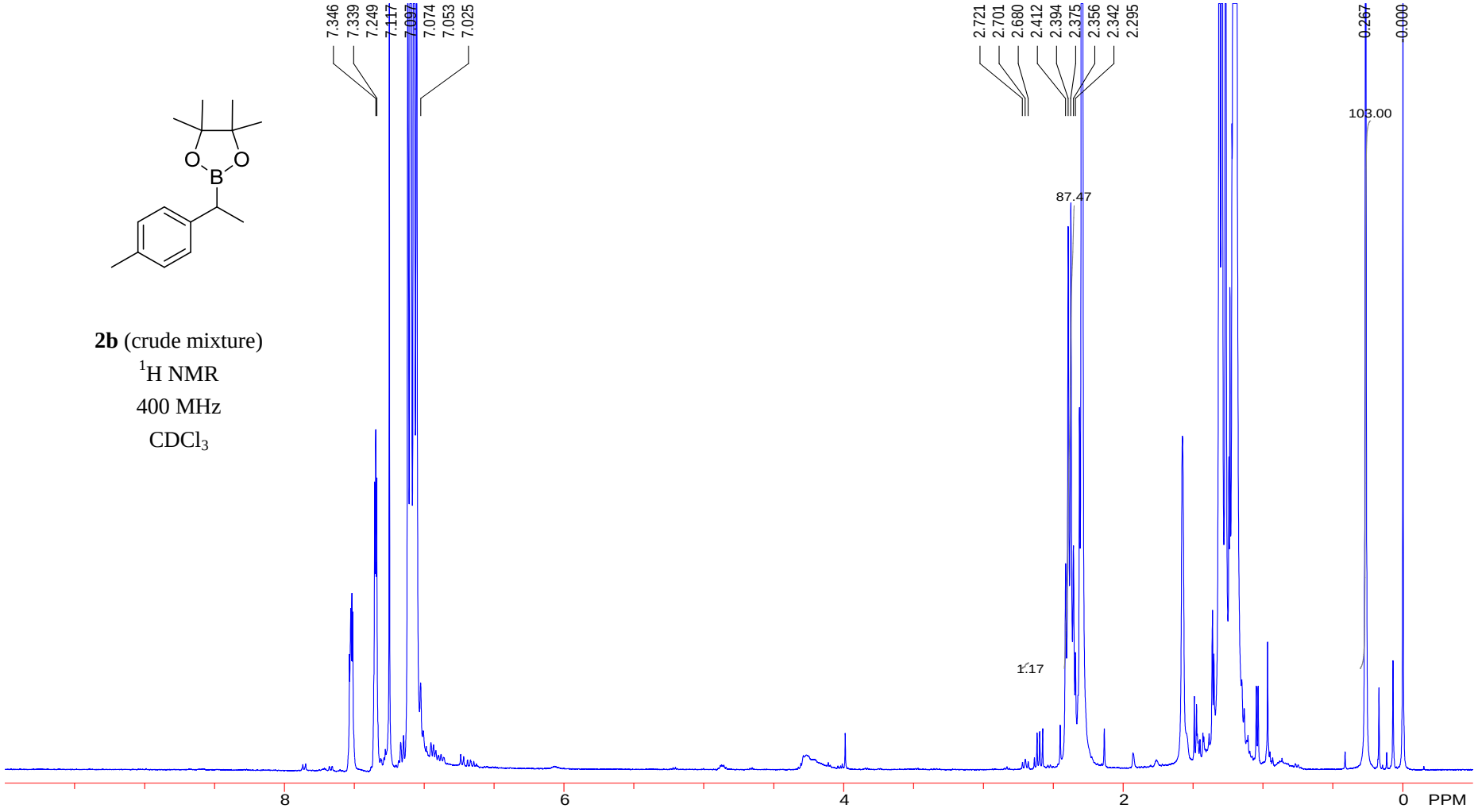


2a

^{13}C NMR

101 MHz

$CDCl_3$



2b (crude mixture)

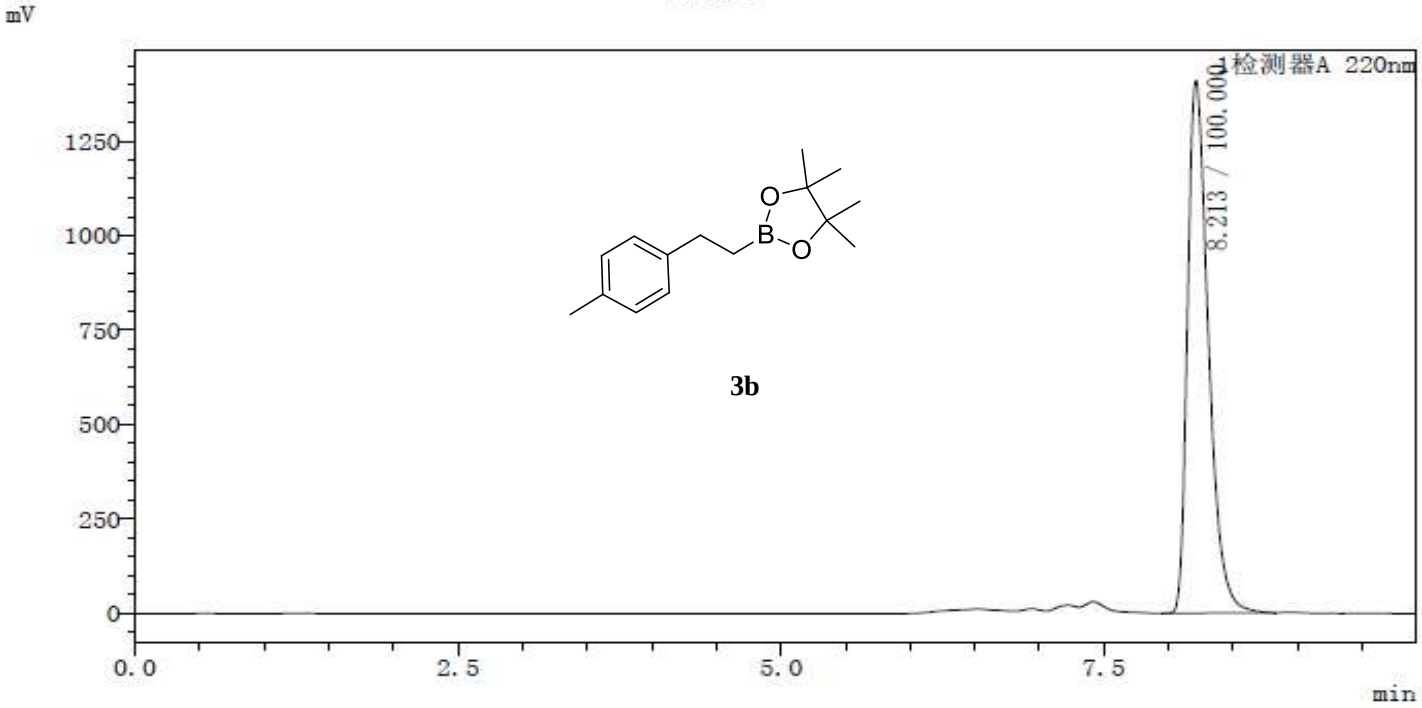
^{1}H NMR

400 MHz

$CDCl_3$

描述 : AD-H, n-Hex:iPrOH =99/1, 0.5 mL/min, 220 nm

色谱图



3b

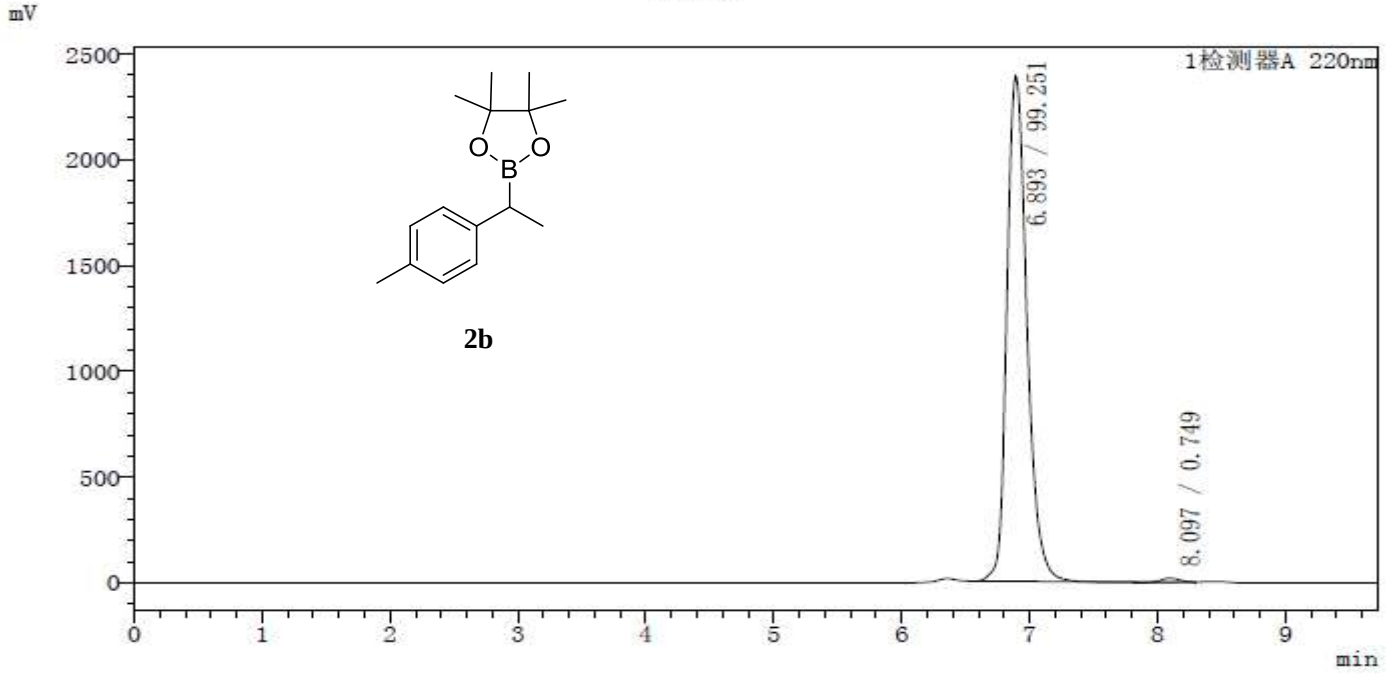
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.213	15812591	1408355		100.000
总计		15812591	1408355		100.000

处理日期/时间 : 2017/2/9 14:25:16
描述 : AD-H, n-Hex:iPrOH =99/1, 0.5 mL/min, 220 nm

色谱图

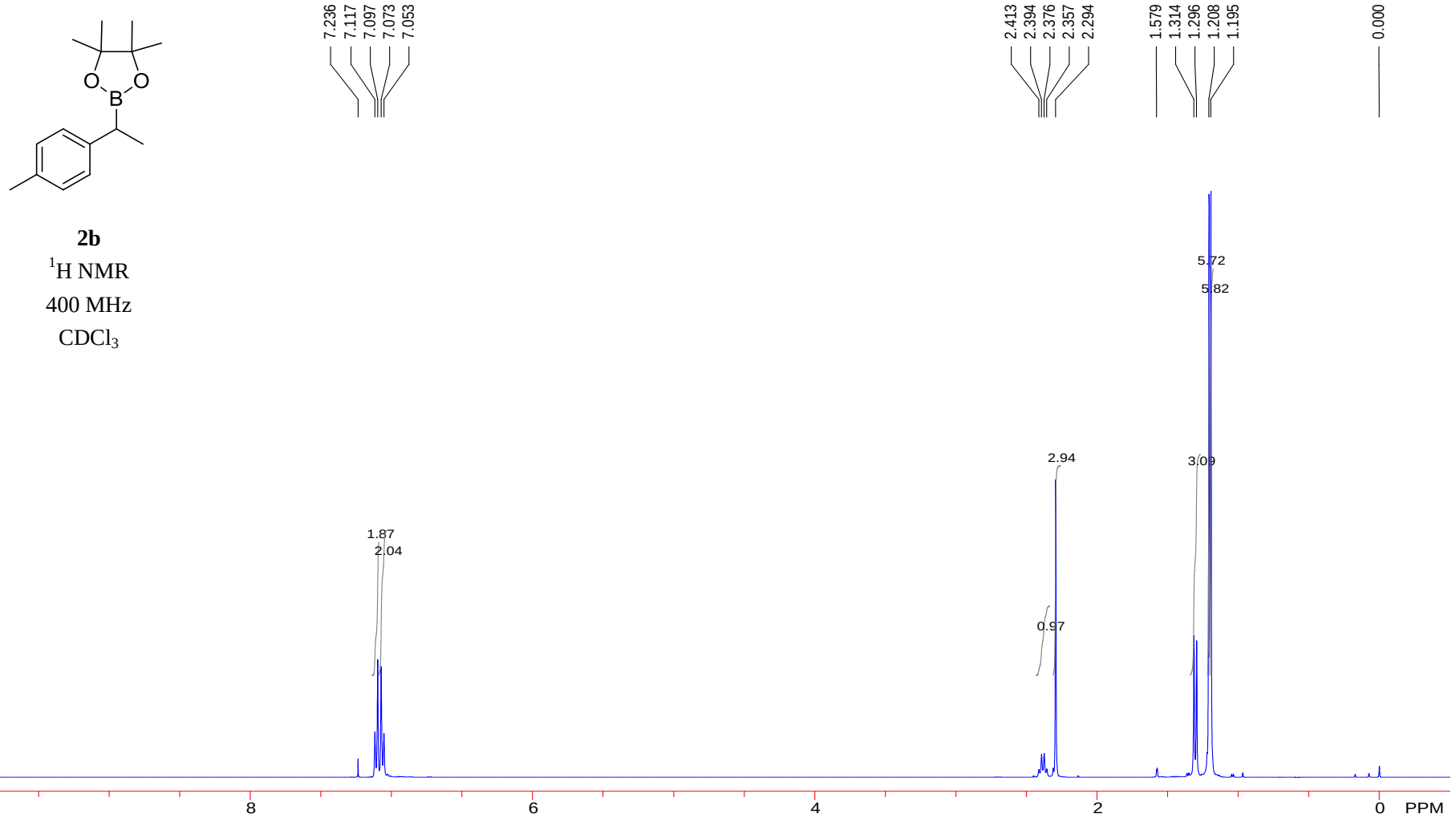


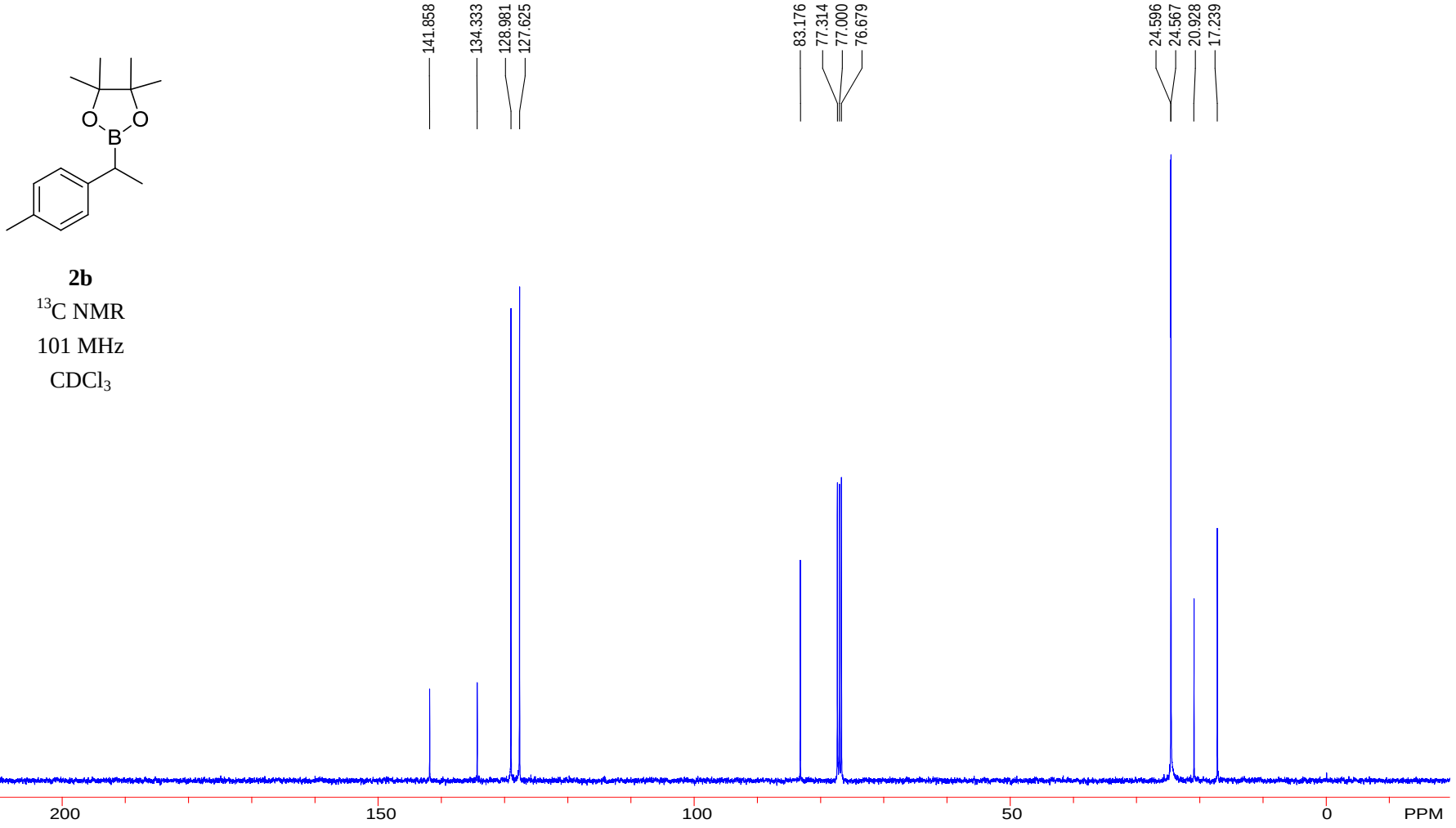
2b

峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.893	25823973	2388508	S	99.251
2	8.097	194869	19586	T	0.749
总计		26018841	2408094		100.000


7.236
7.117
7.097
7.073
7.053
2.413
2.394
2.376
2.357
2.294
1.579
1.314
1.296
1.208
1.195
0.000
O
B
O
2b
1H NMR
400 MHz
CDCl3
5.72
5.82
2.94
3.09
1.87
2.04
0.97
8
6
4
2
0
PPM

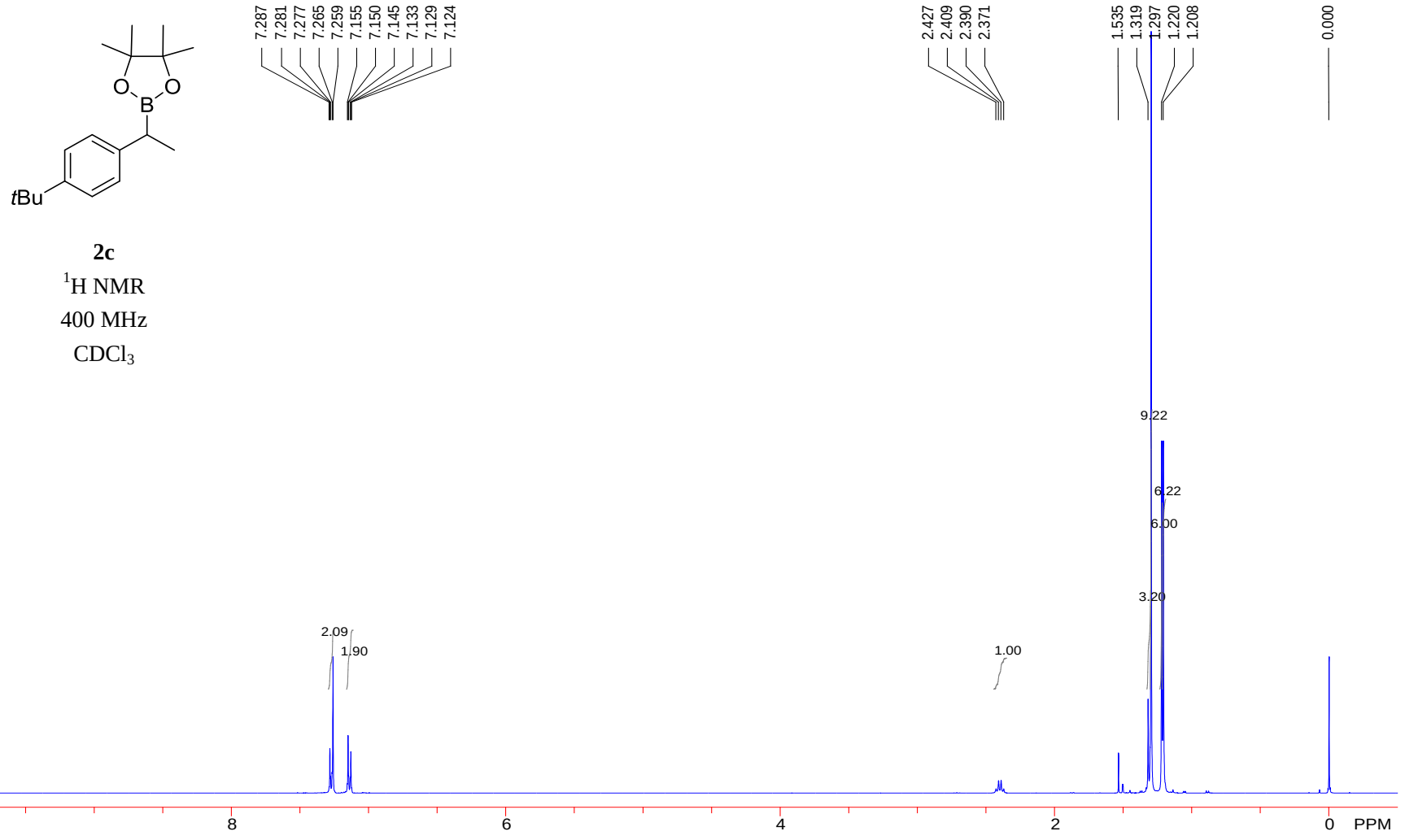


2b

^{13}C NMR

101 MHz

$CDCl_3$

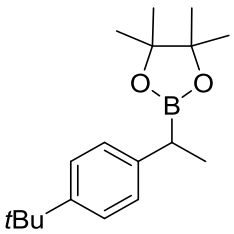


2c

^{1}H NMR

400 MHz

$CDCl_3$

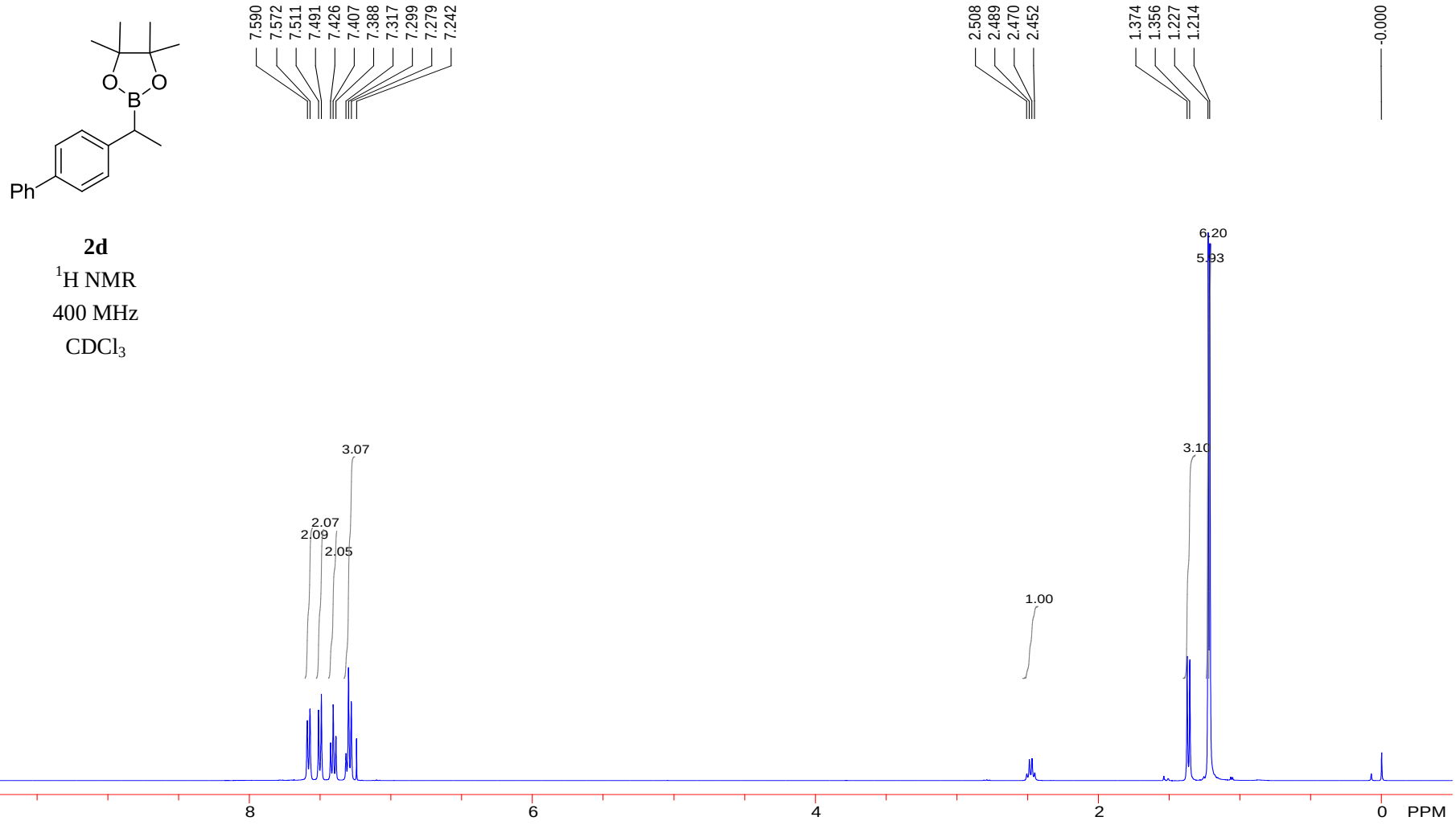


2c

^{13}C NMR

101 MHz

$CDCl_3$

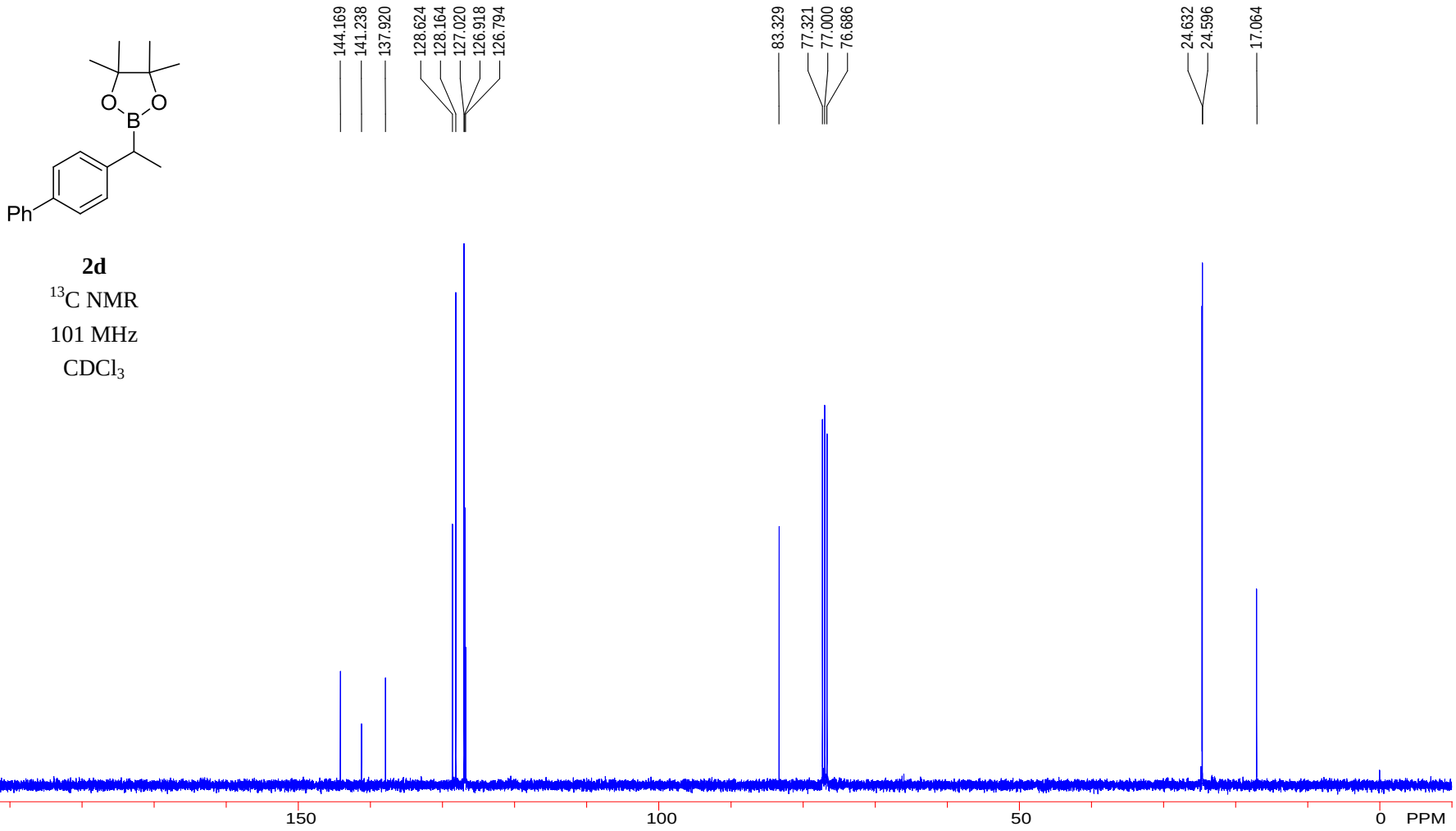


2d

^{1}H NMR

400 MHz

$CDCl_3$

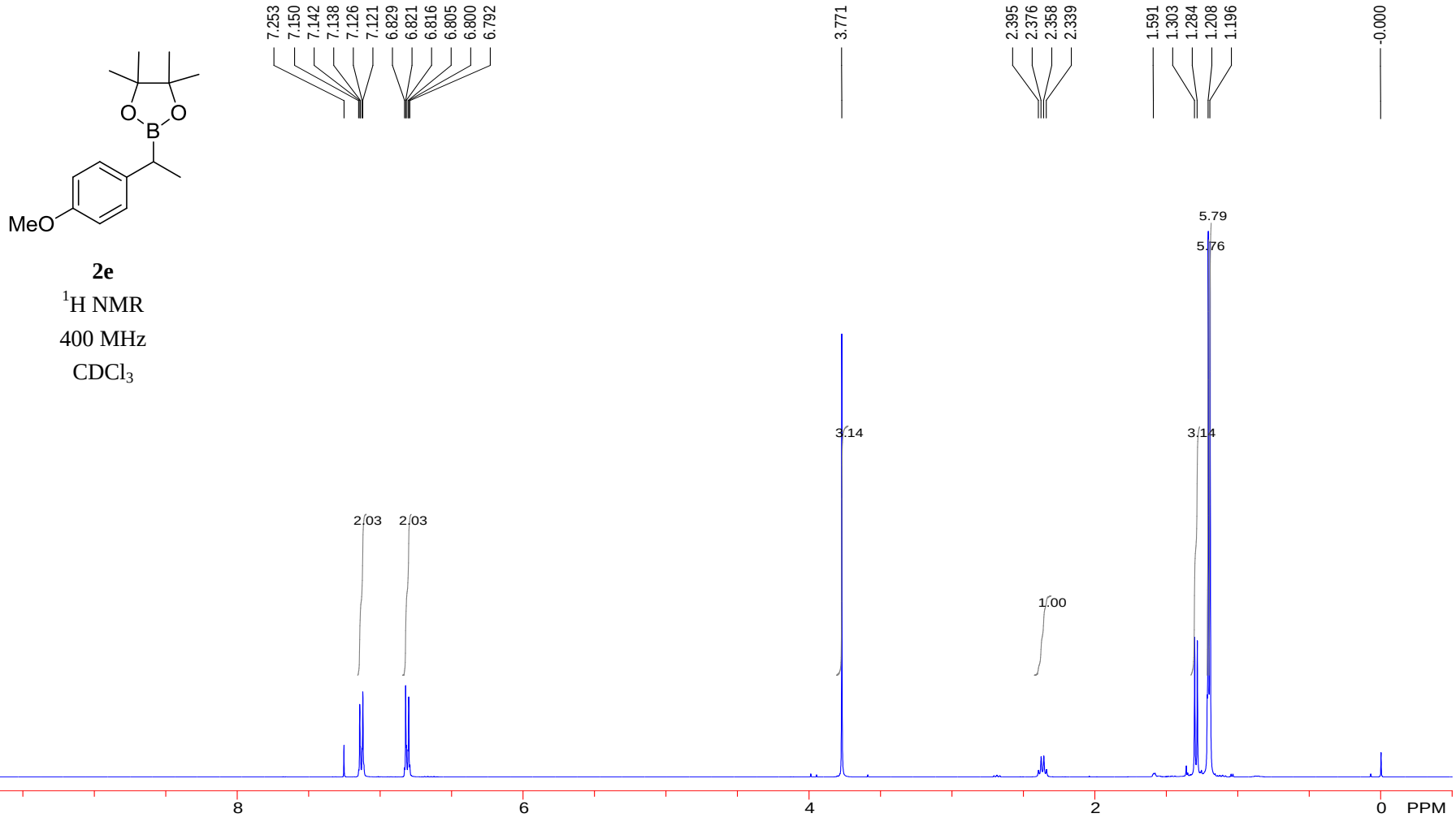


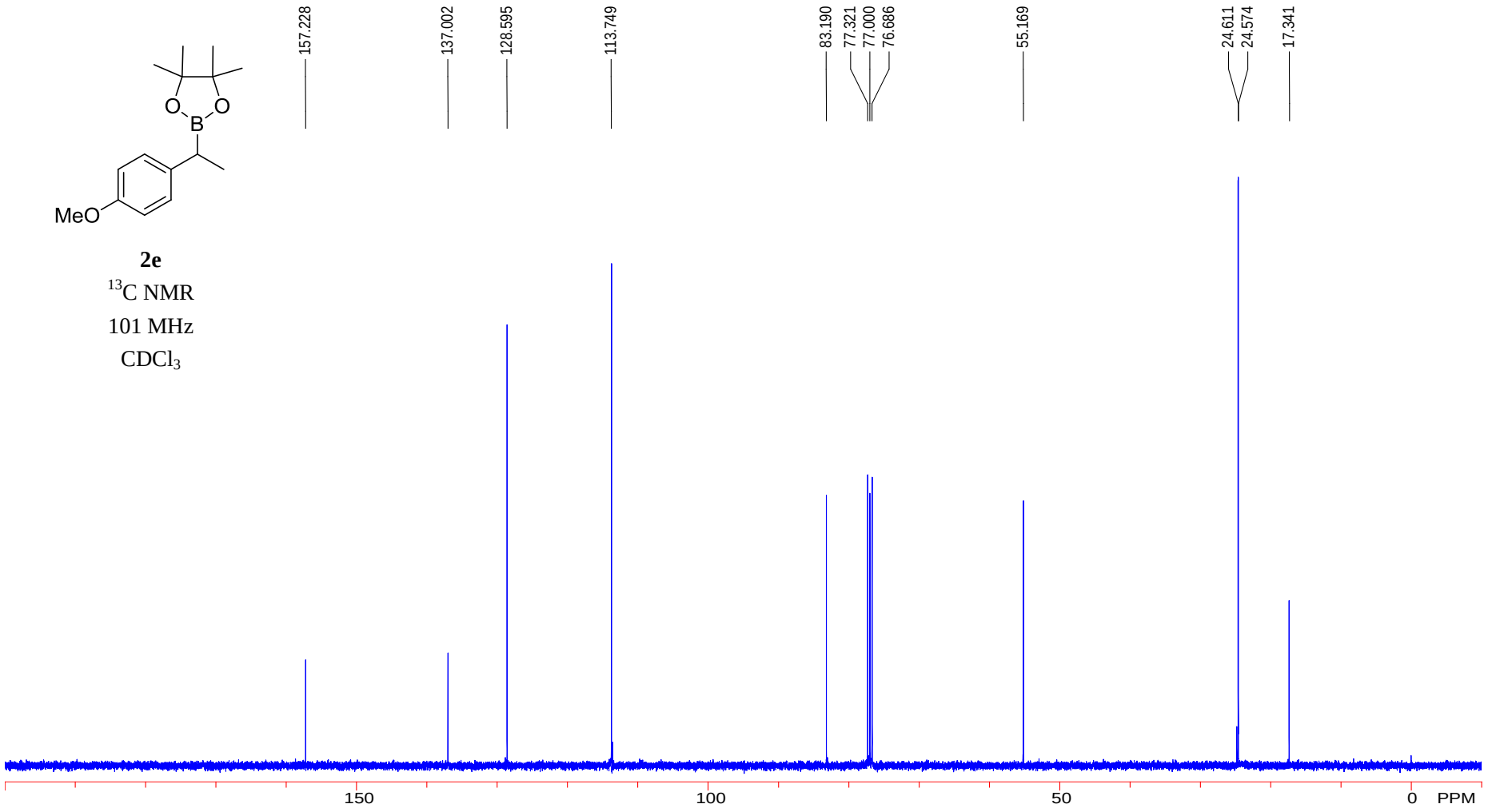
2d

^{13}C NMR

101 MHz

$CDCl_3$


7.253
7.150
7.142
7.138
7.126
7.121
6.829
6.821
6.816
6.805
6.800
6.792
3.771
2.395
2.376
2.358
2.339
1.591
1.303
1.284
1.208
1.196
-0.000
MeO
O
B
O
2e
1H NMR
400 MHz
CDCl3
5.79
5.76
3.14
3.14
2.03
2.03
1.00
8
6
4
2
0
PPM

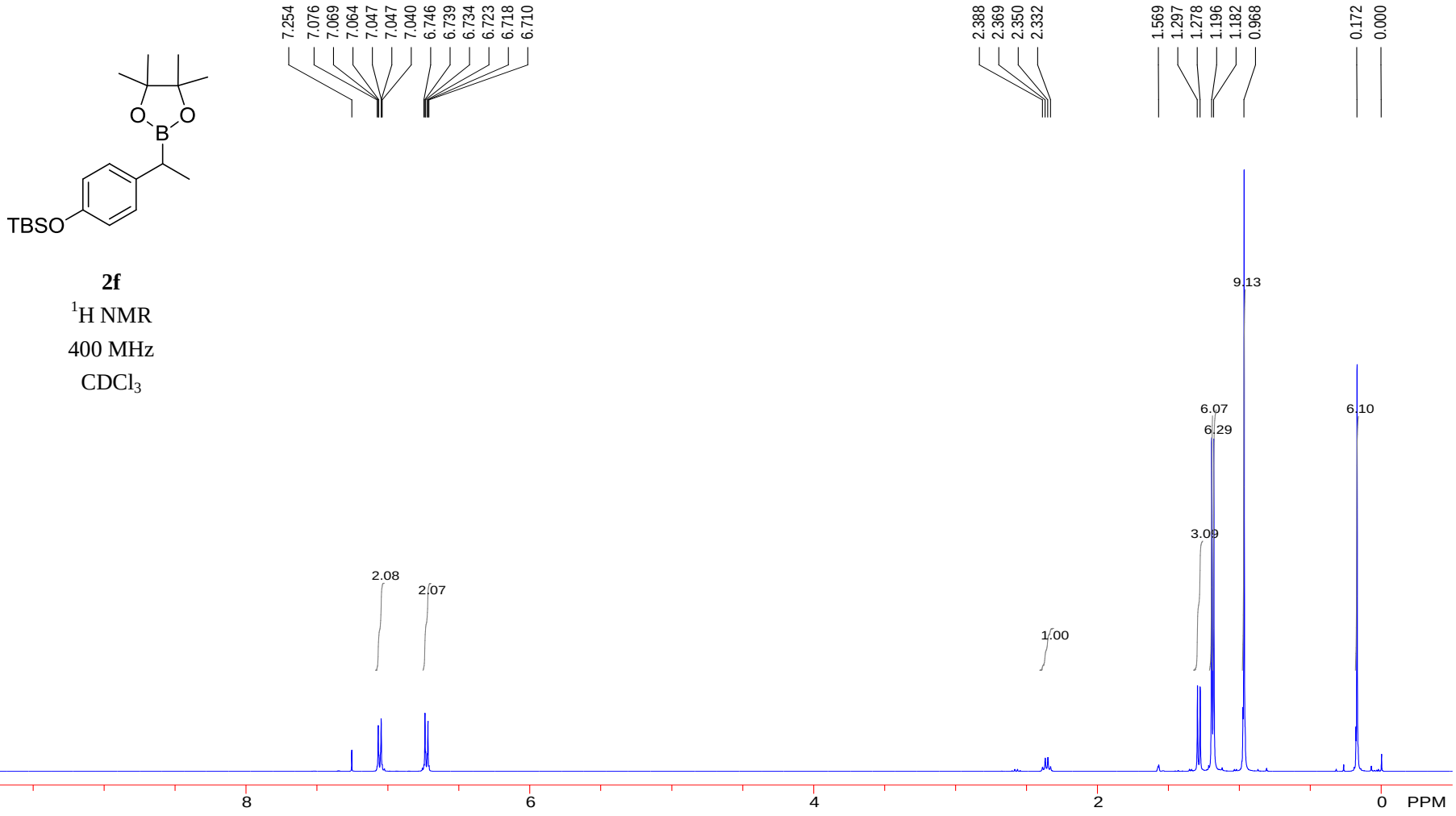


2e

^{13}C NMR

101 MHz

$CDCl_3$

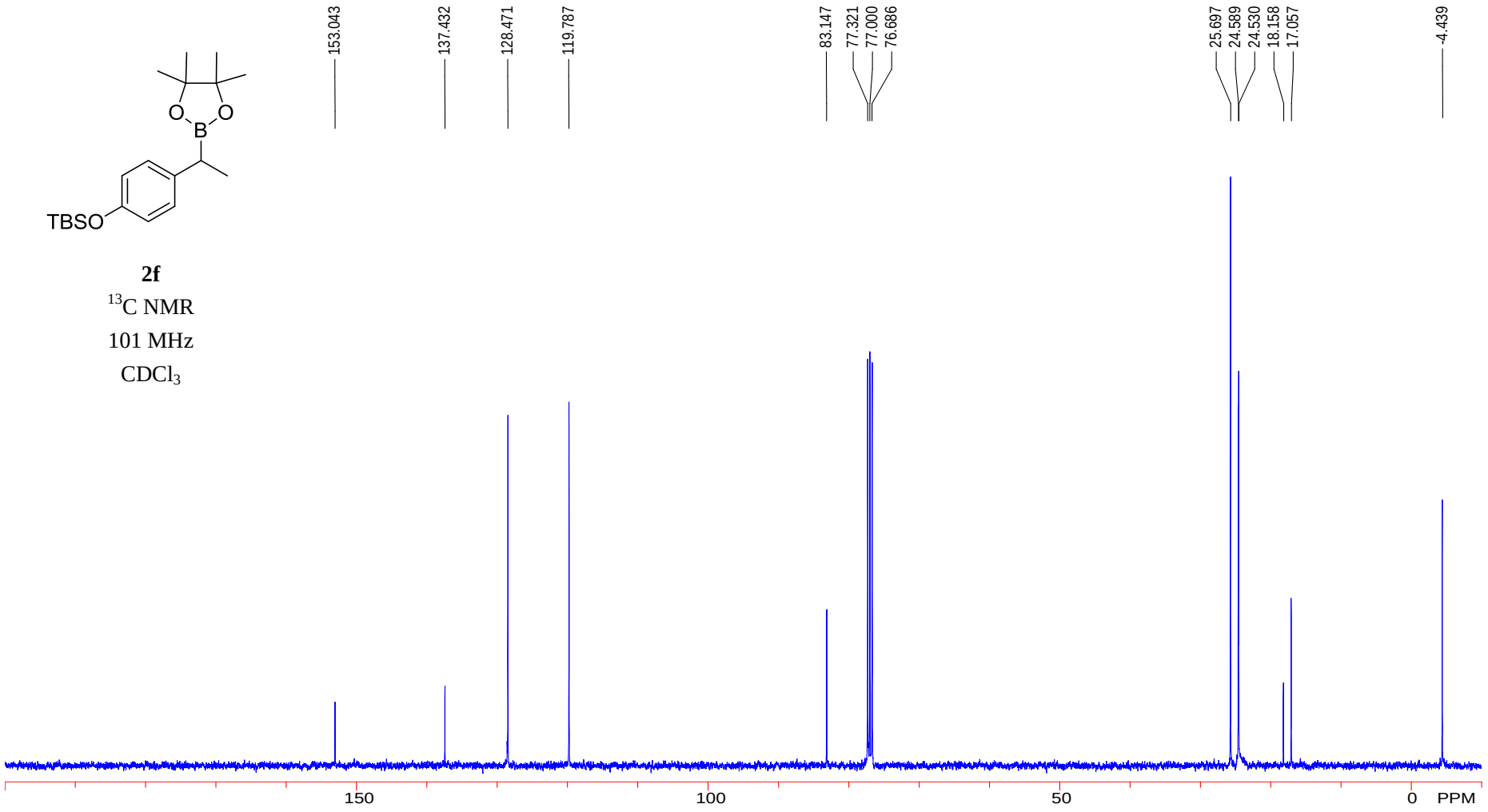


2f

^{1}H NMR

400 MHz

$CDCl_3$

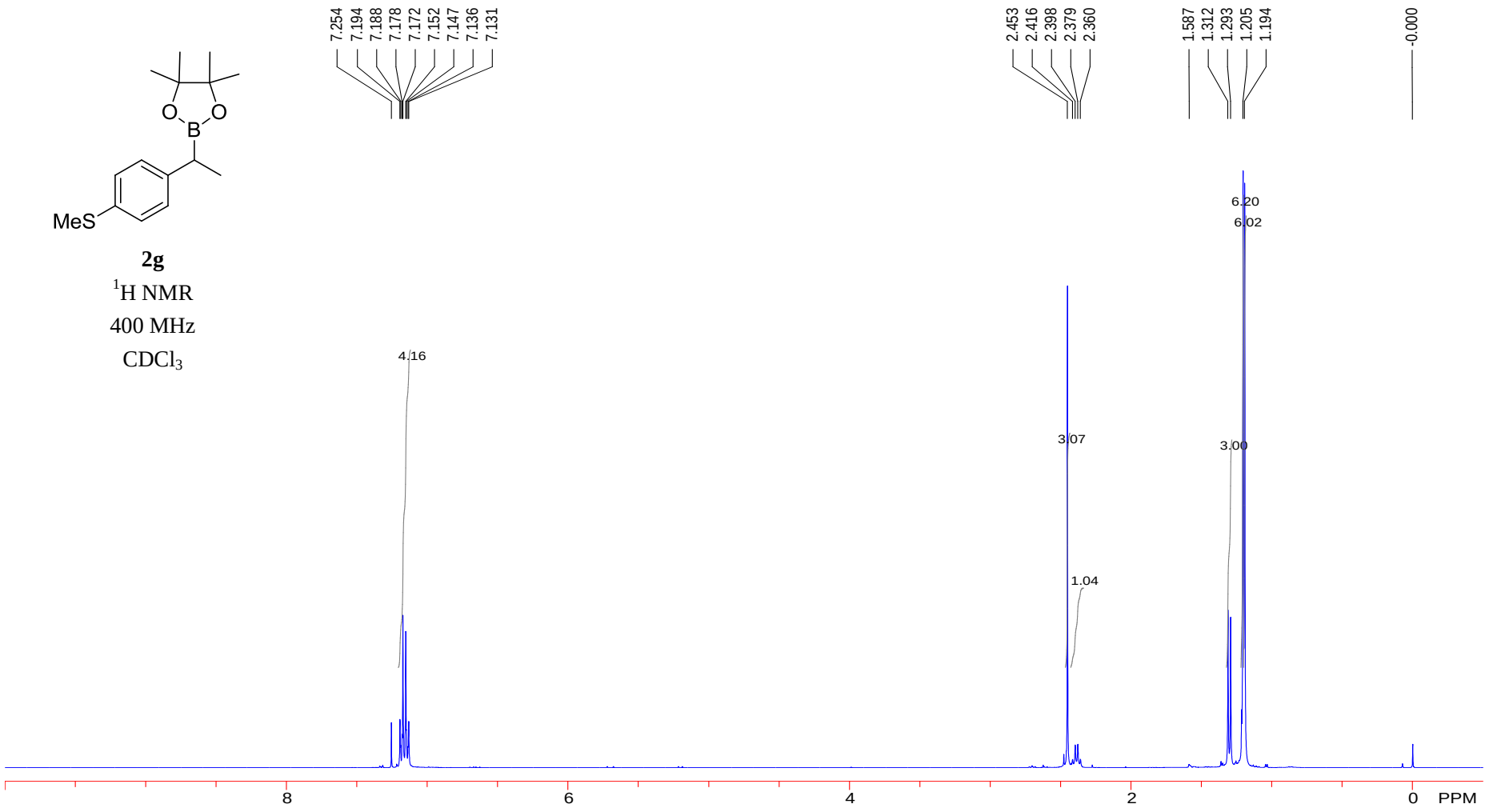


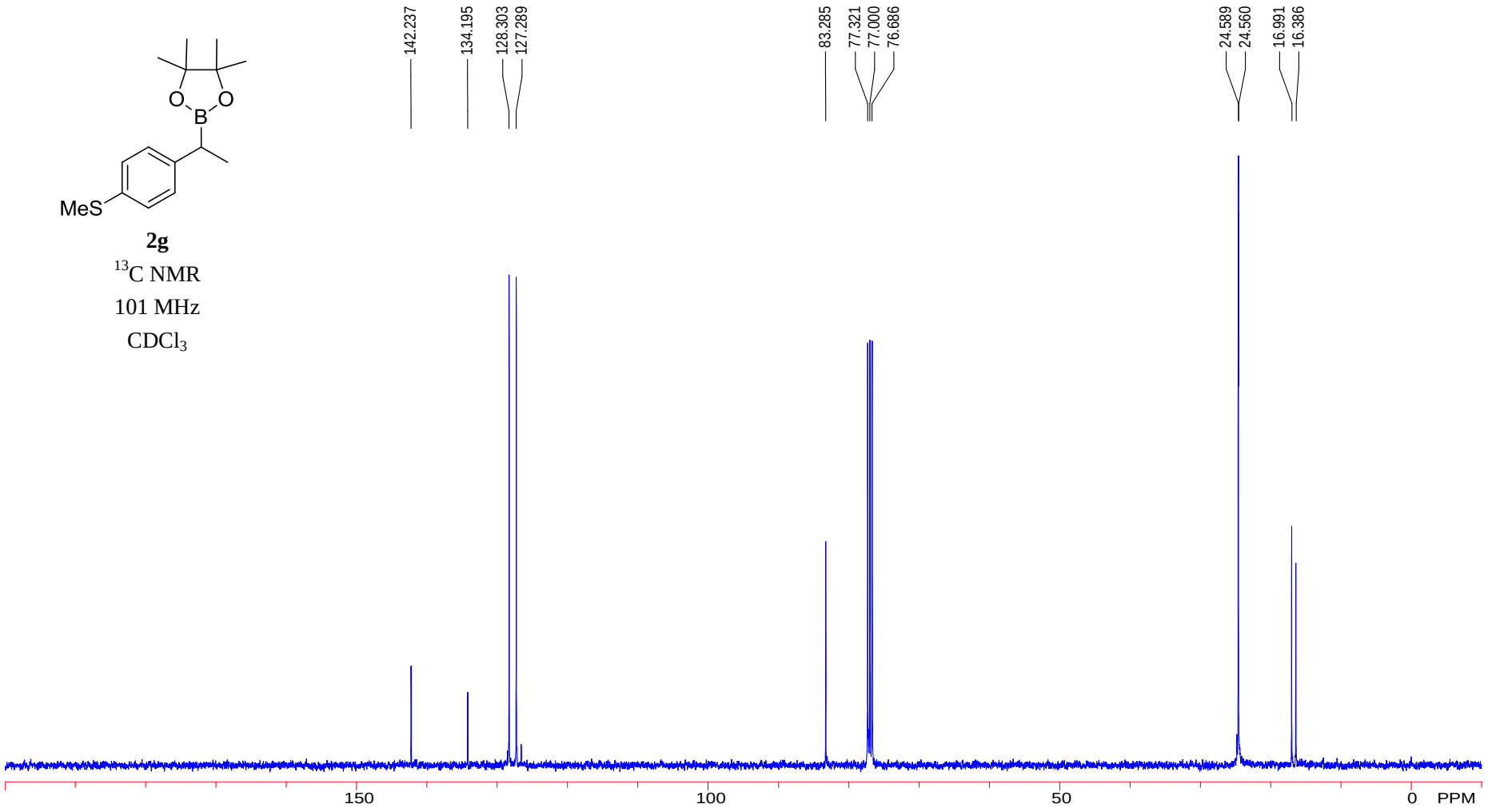
2f

^{13}C NMR

101 MHz

$CDCl_3$


7.254
7.194
7.188
7.178
7.172
7.152
7.147
7.136
7.131
2.453
2.416
2.398
2.379
2.360
1.587
1.312
1.293
1.205
1.194
-0.000
O
B
O
MeS
2g
1H NMR
400 MHz
CDCl3
4.16
3.07
1.04
6.20
6.02
3.00
8
6
4
2
0
PPM

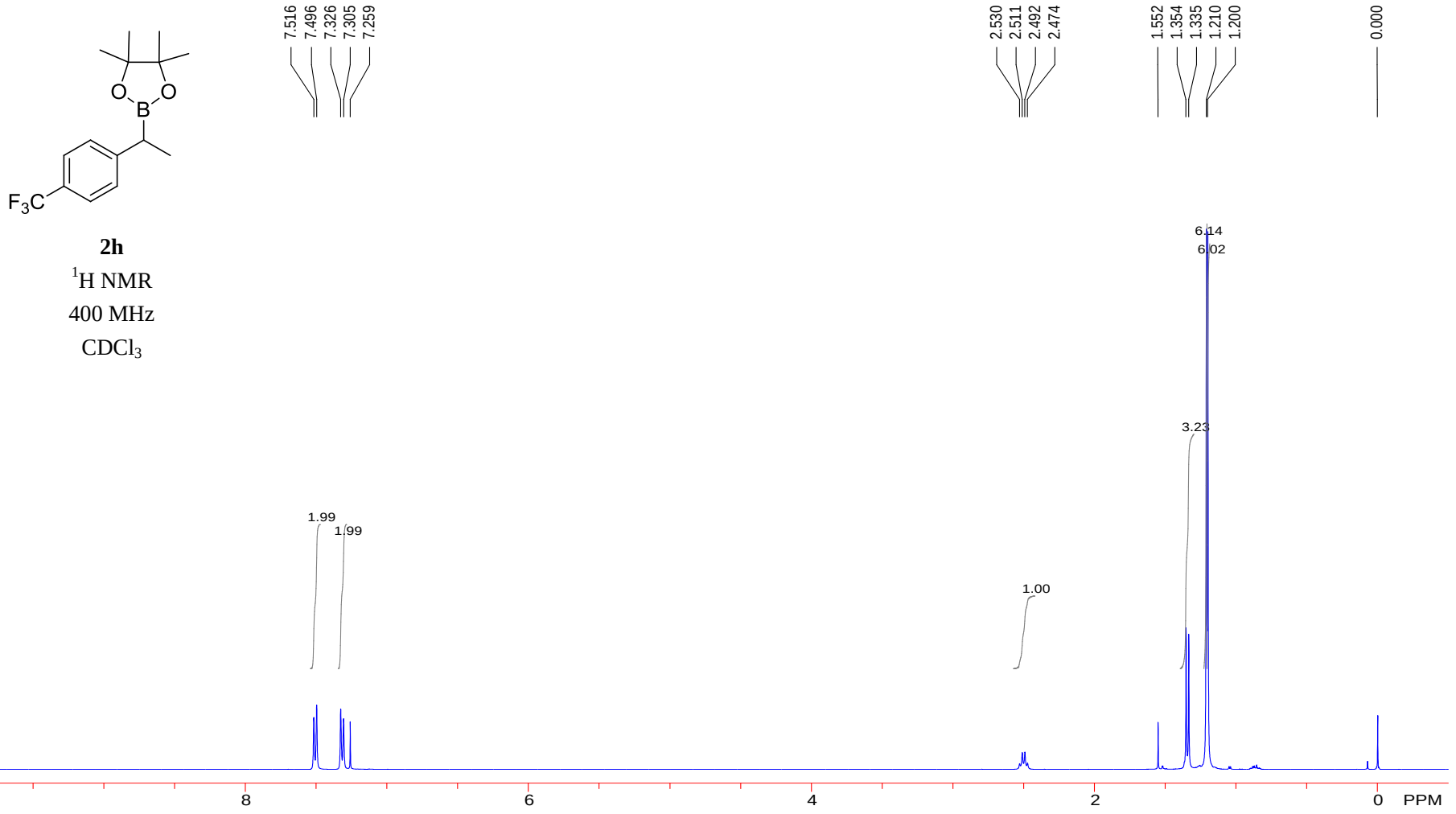


2g

^{13}C NMR

101 MHz

$CDCl_3$

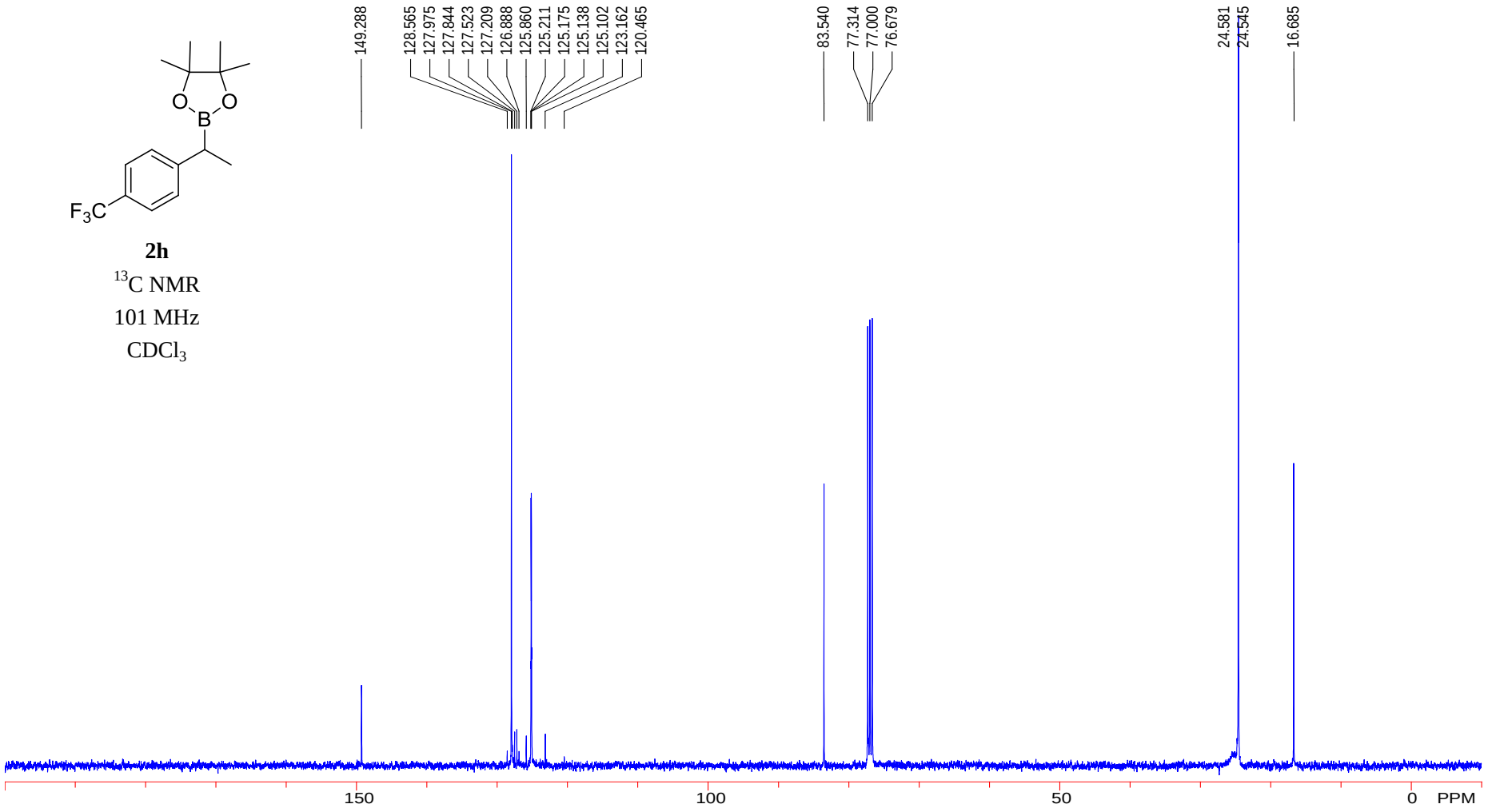


2h

^{1}H NMR

400 MHz

$CDCl_3$

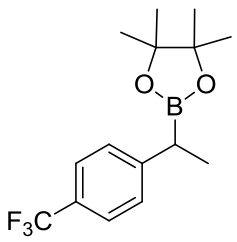


2h

^{13}C NMR

101 MHz

$CDCl_3$

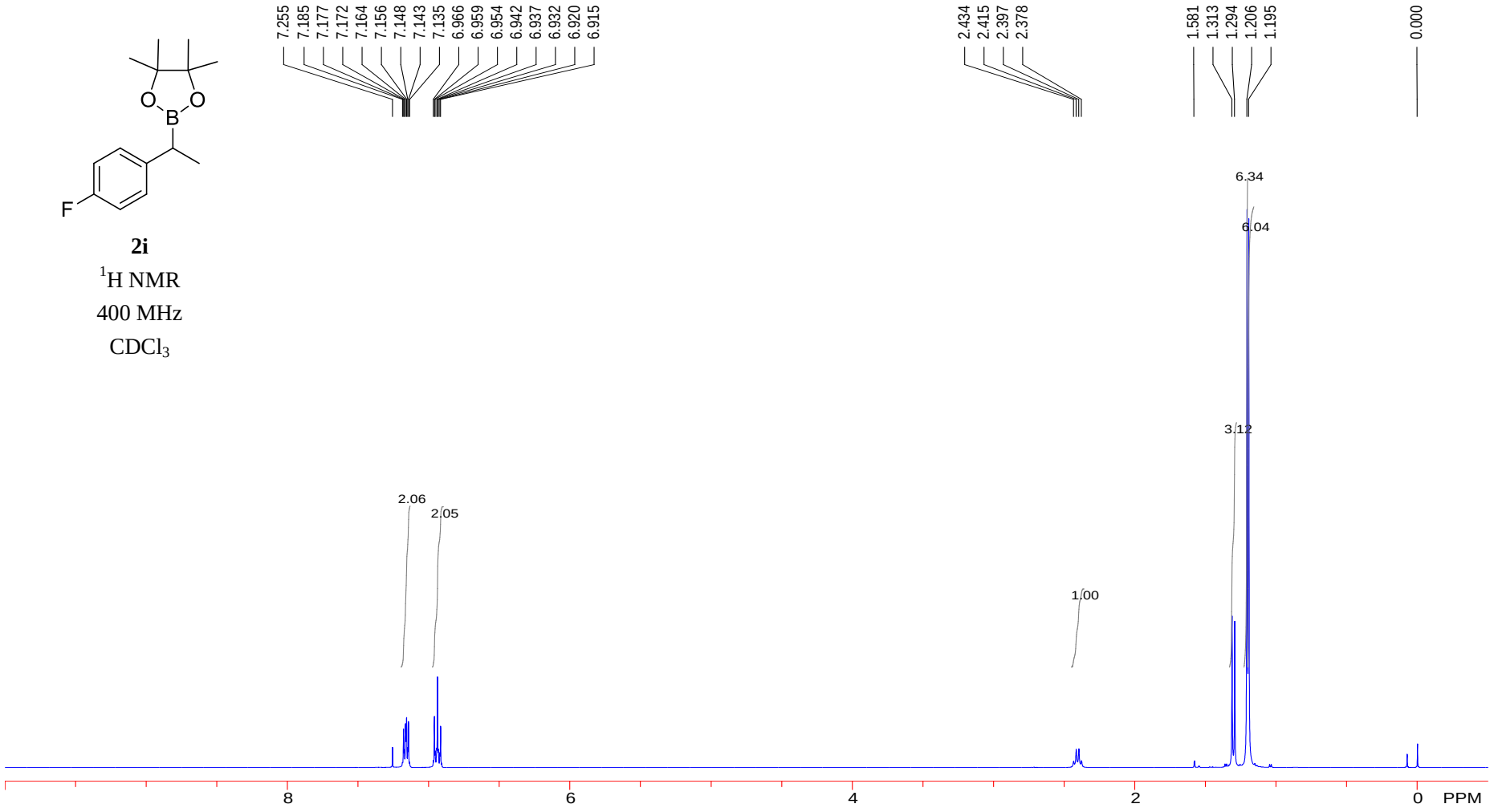


2h

^{19}F NMR

376 MHz

$CDCl_3$

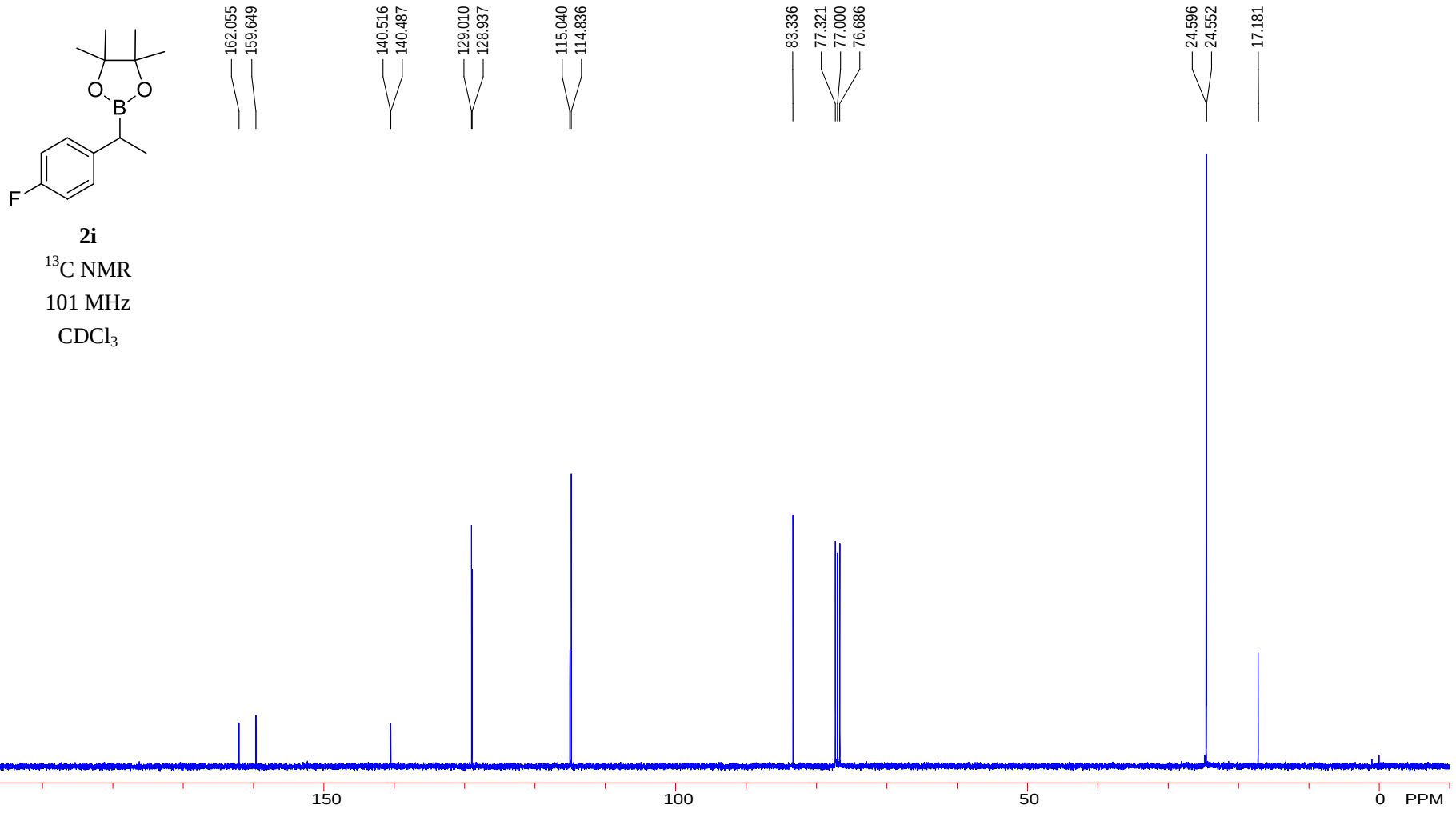


2i

^{1}H NMR

400 MHz

$CDCl_3$

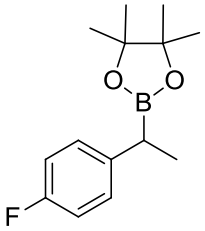


2i

^{13}C NMR

101 MHz

$CDCl_3$

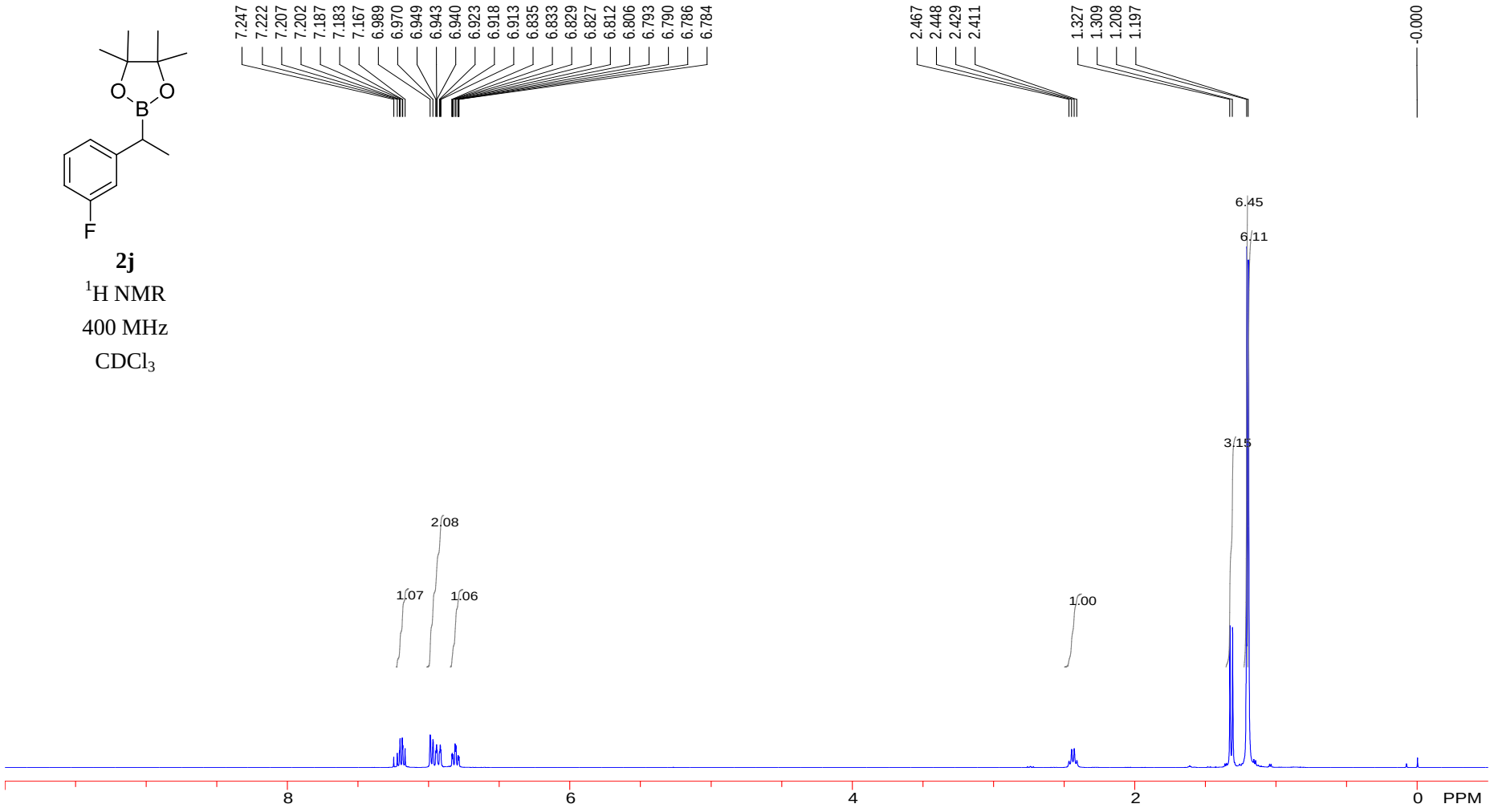


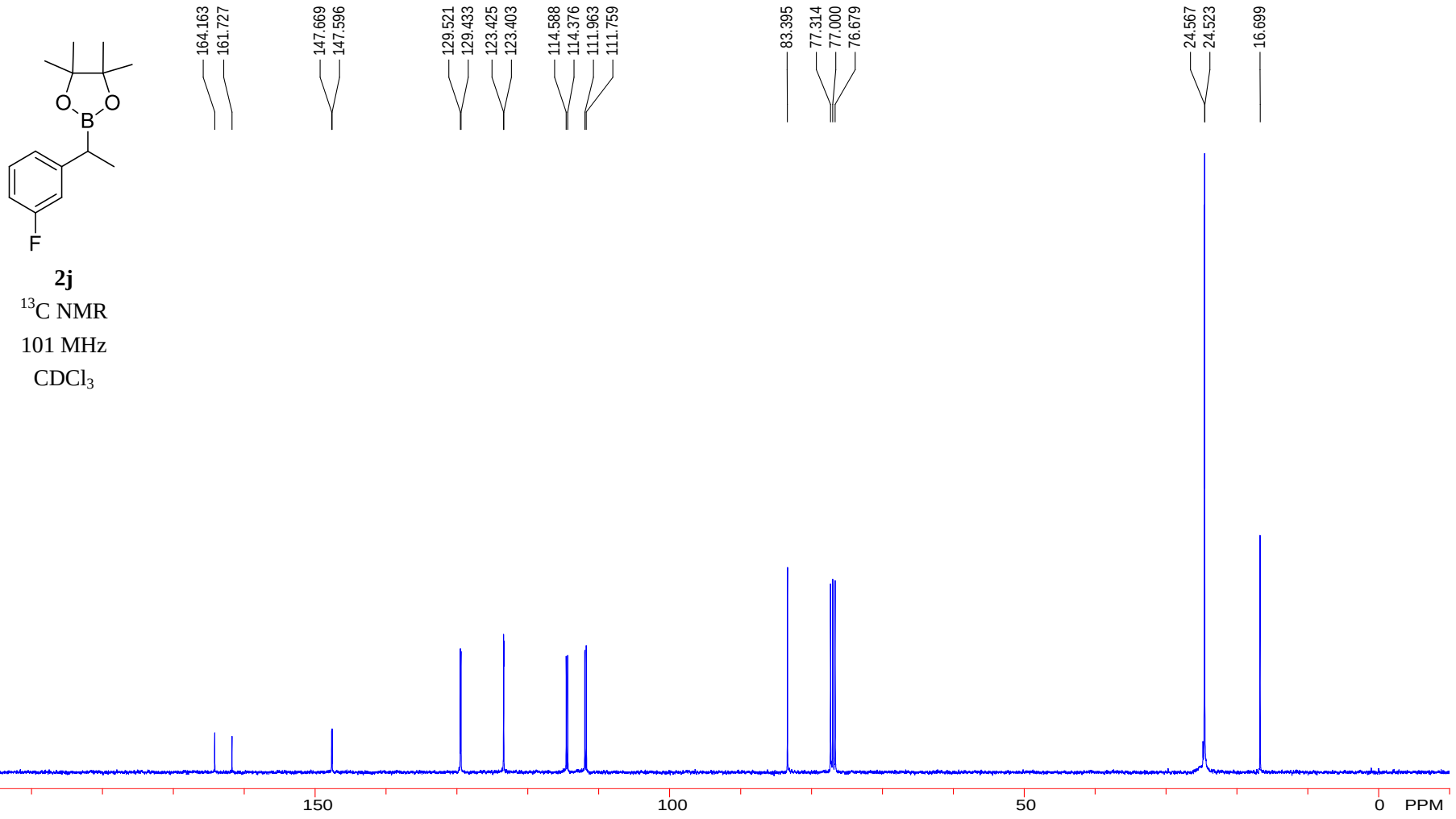
2i

^{19}F NMR

376 MHz

$CDCl_3$


7.247
7.222
7.207
7.202
7.187
7.183
7.167
6.989
6.970
6.949
6.943
6.940
6.923
6.918
6.913
6.835
6.833
6.829
6.827
6.812
6.806
6.793
6.790
6.786
6.784
2.467
2.448
2.429
2.411
1.327
1.309
1.208
1.197
-0.000
O
B
O
F
2j
1H NMR
400 MHz
CDCl3
6.45
6.11
3.15
2.08
1.07
1.06
1.00
8
6
4
2
0
PPM

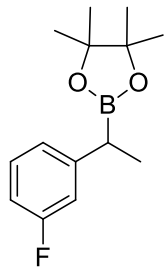


2j

^{13}C NMR

101 MHz

$CDCl_3$

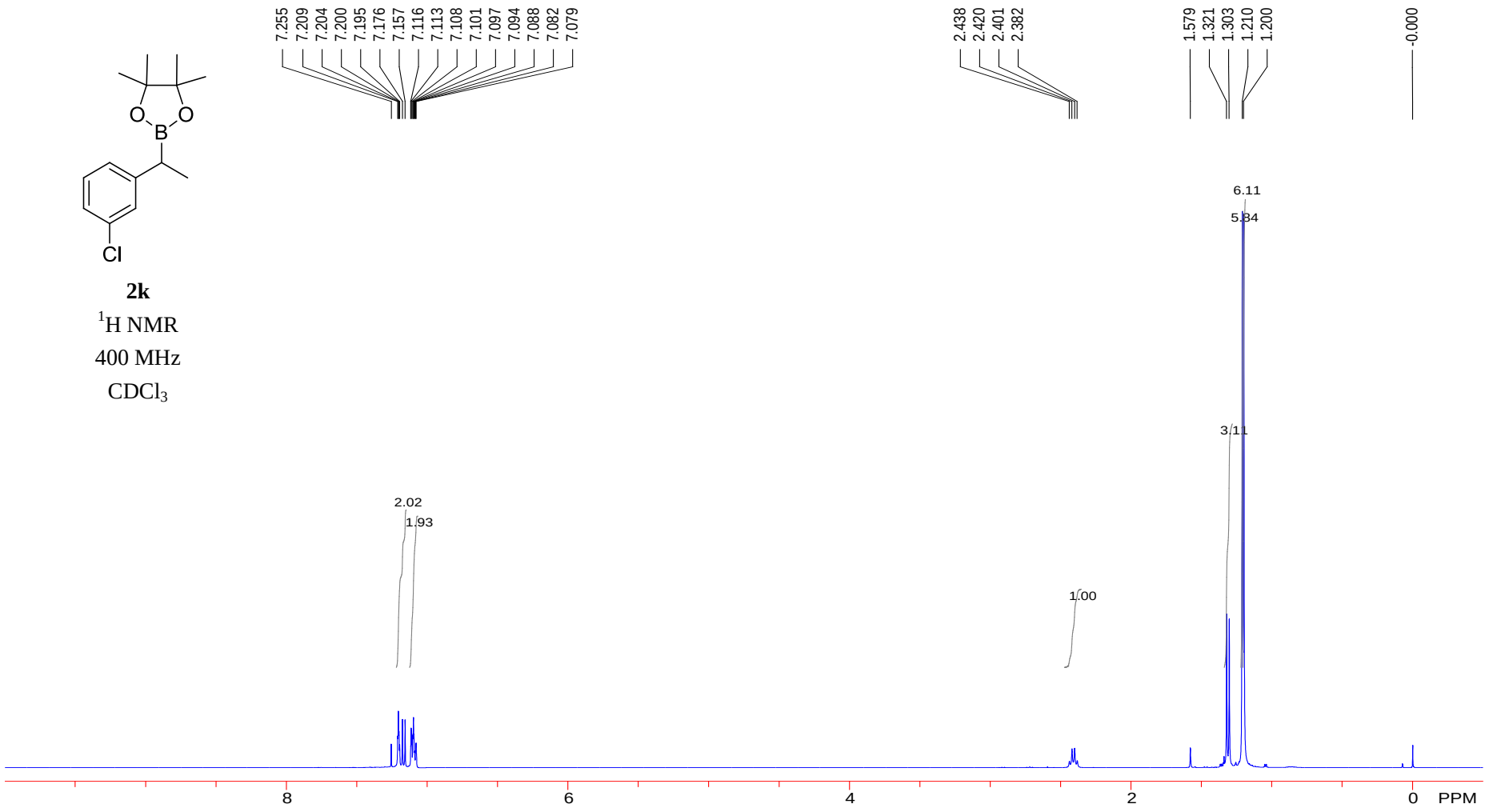


2j

^{19}F NMR

376 MHz

$CDCl_3$

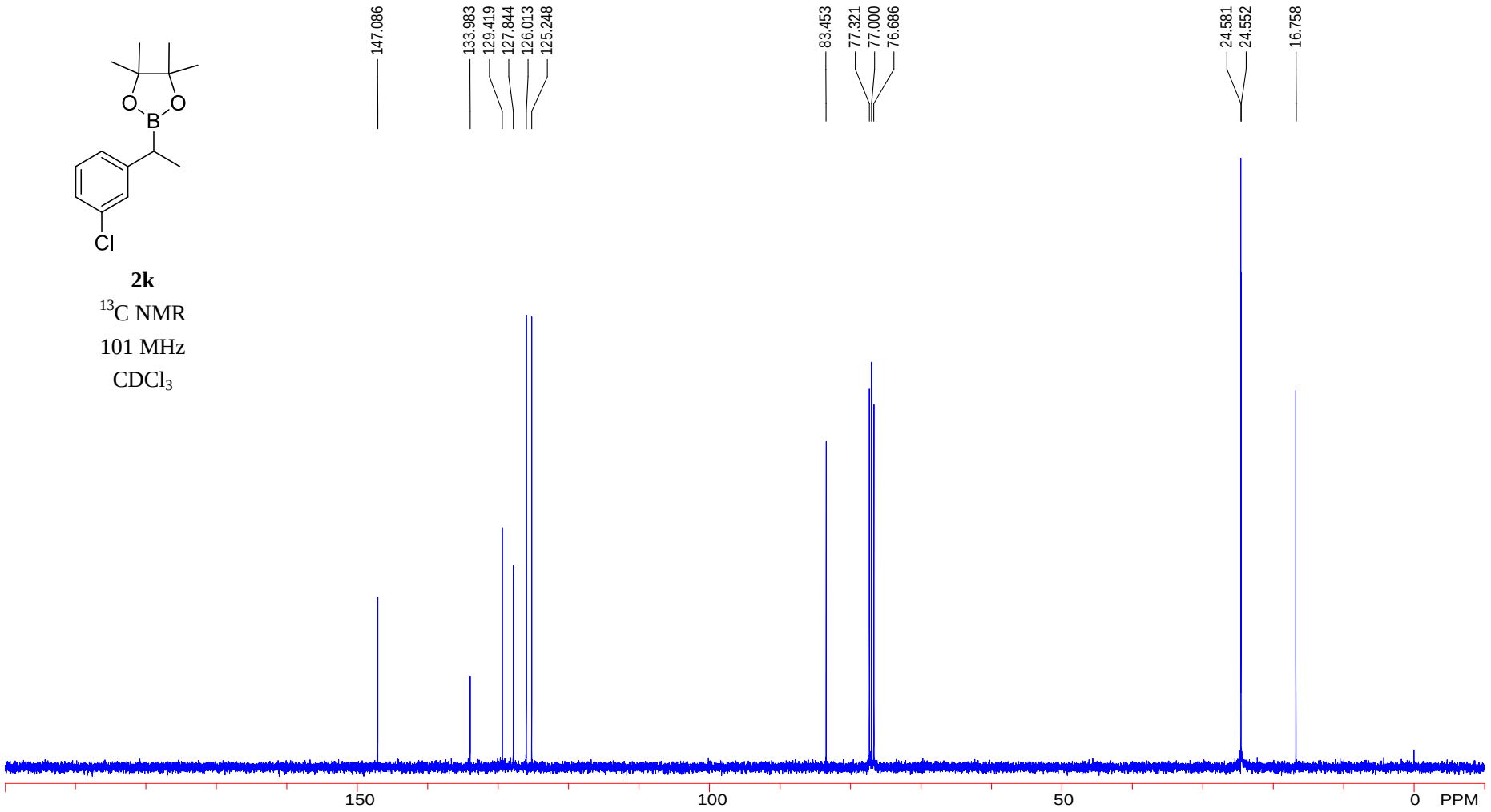


2k

^{1}H NMR

400 MHz

$CDCl_3$

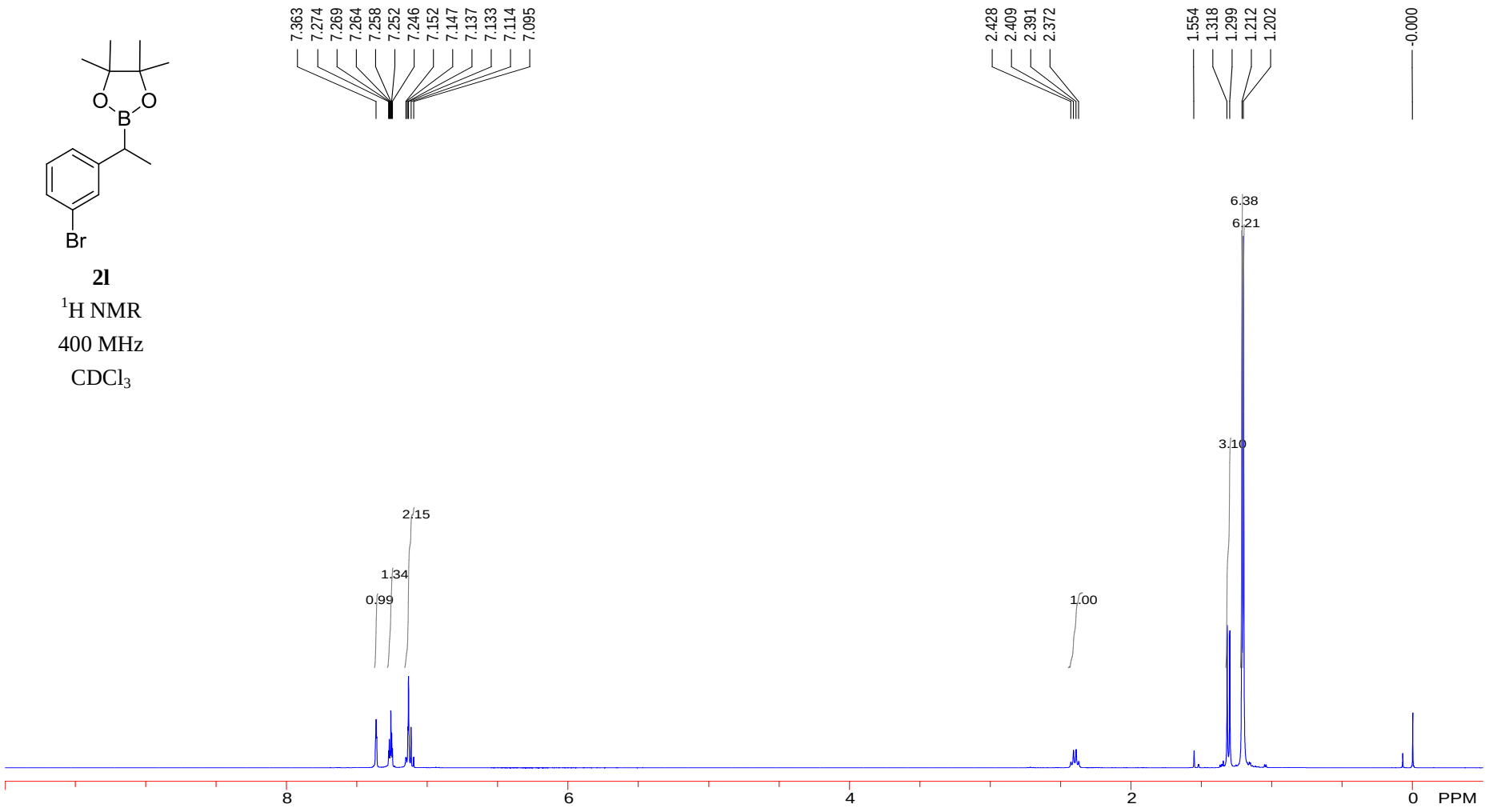


2k

^{13}C NMR

101 MHz

$CDCl_3$

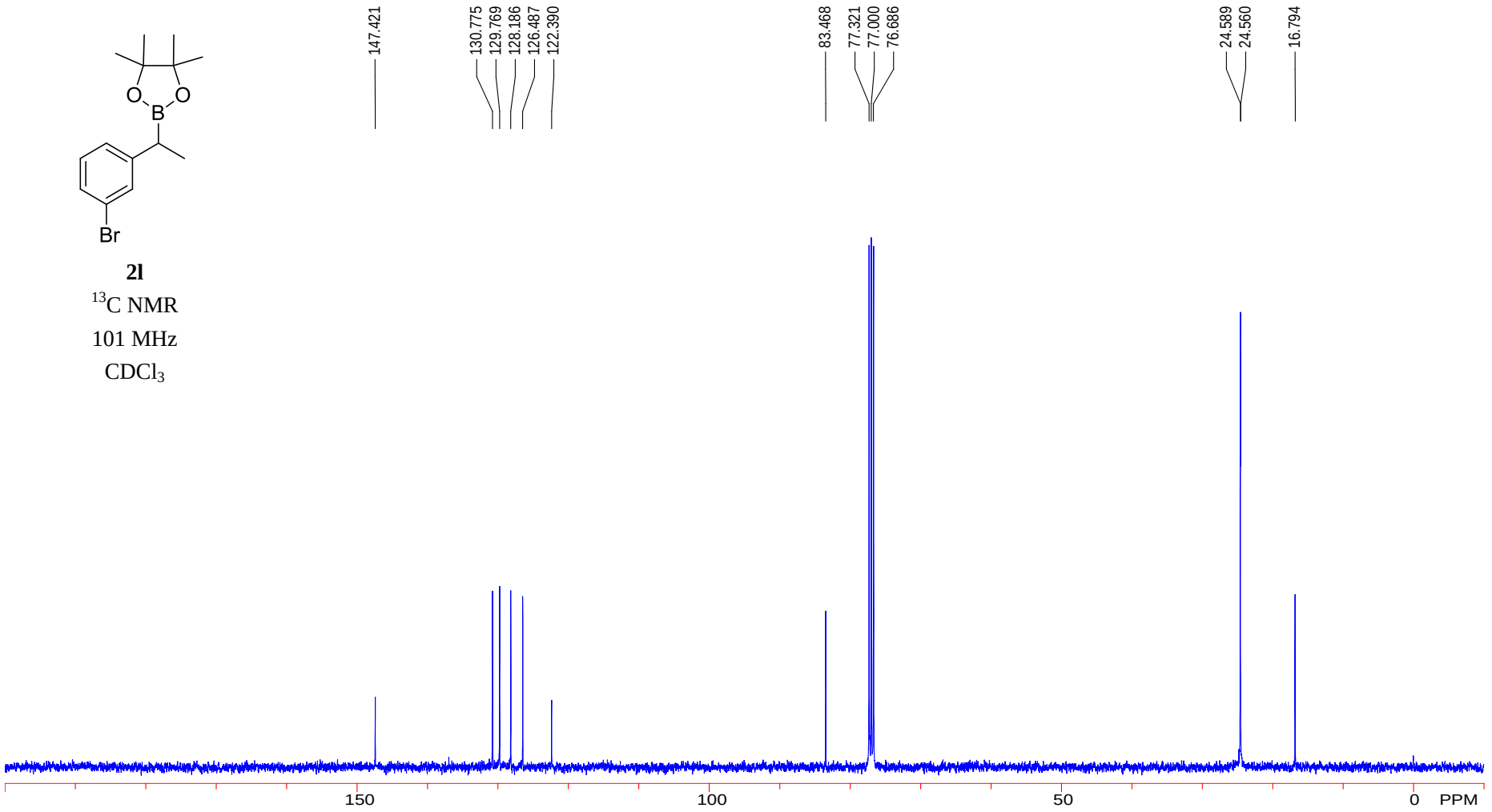


2l

^{1}H NMR

400 MHz

$CDCl_3$

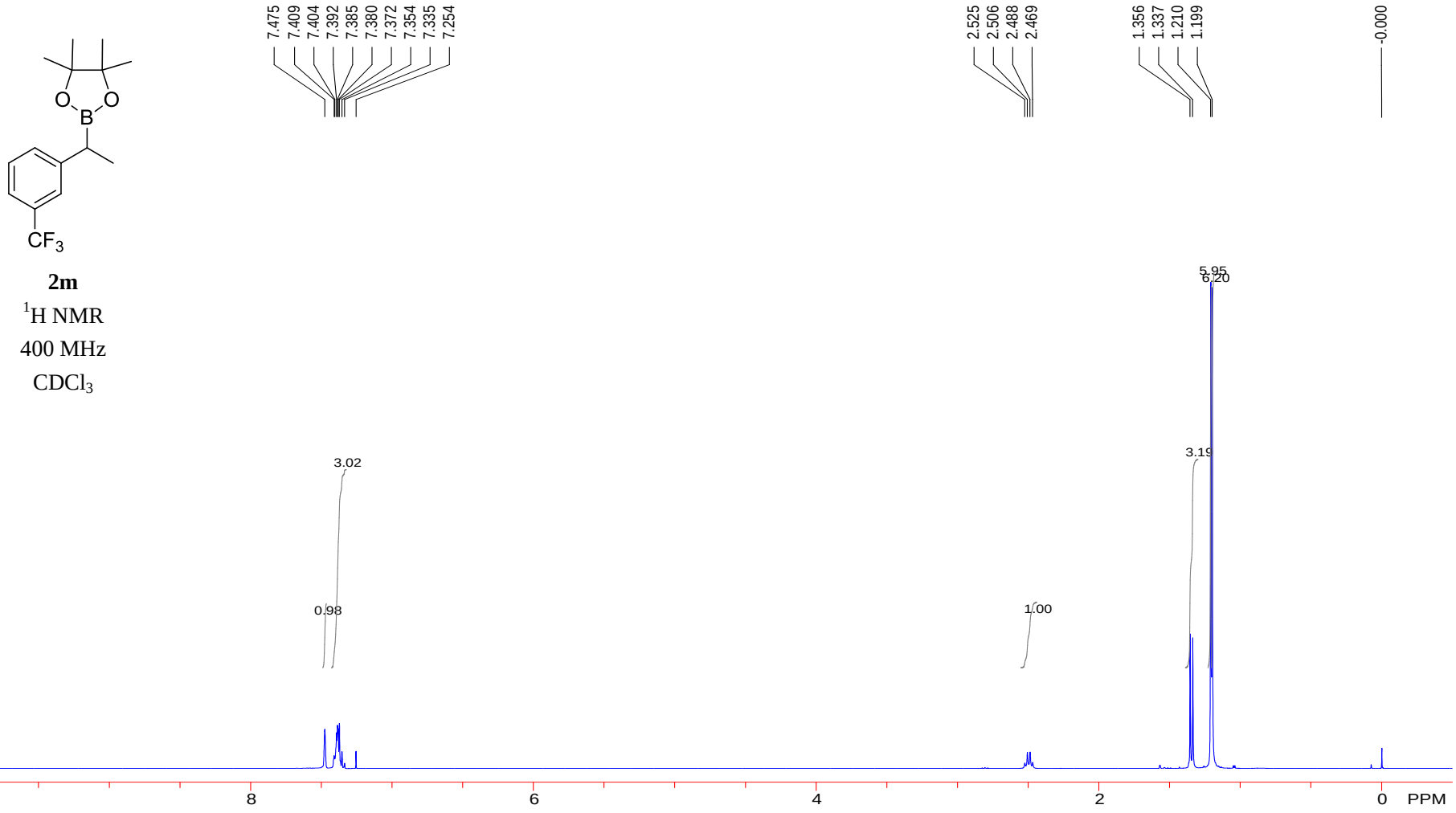


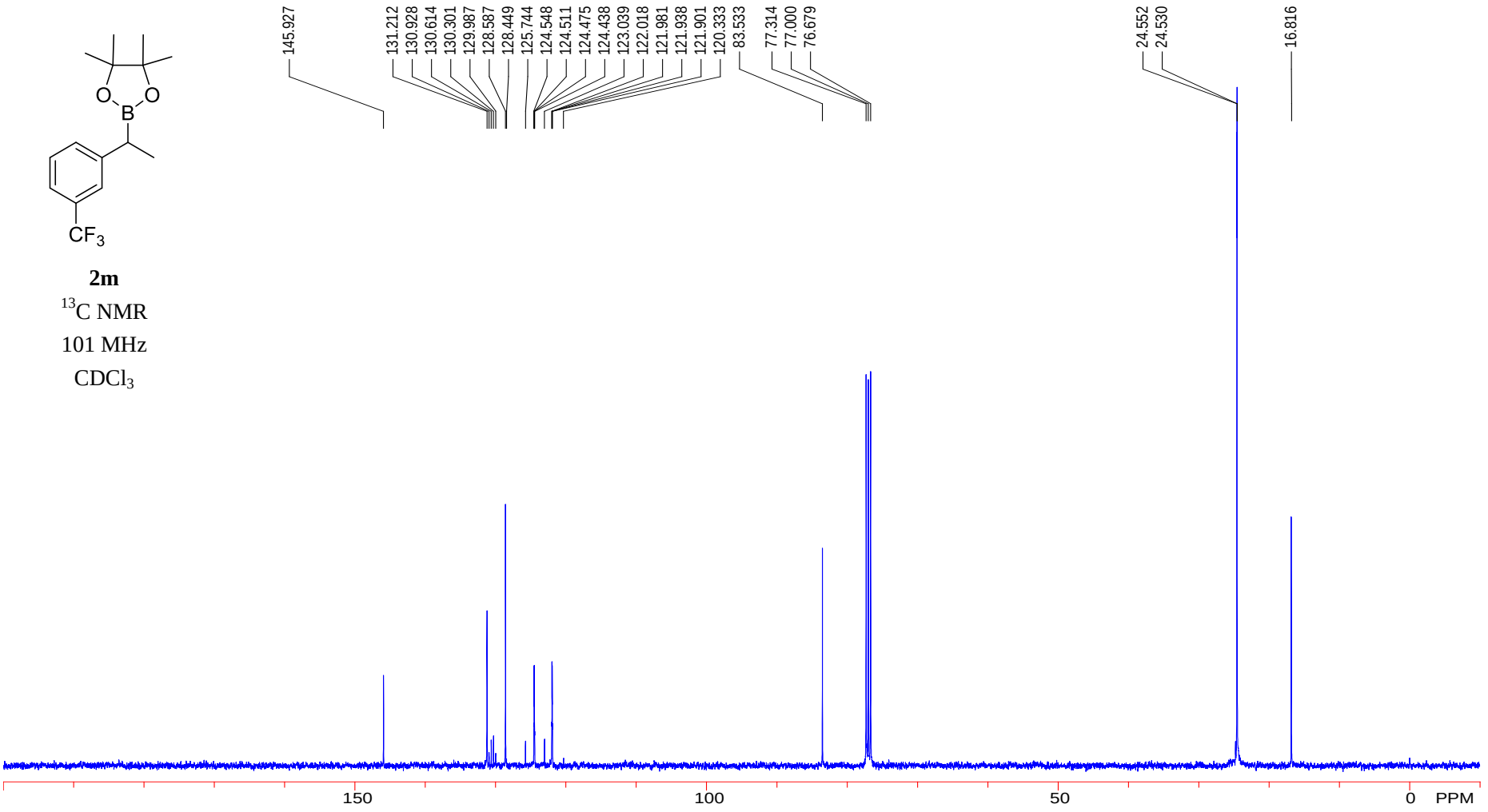
2l

^{13}C NMR

101 MHz

$CDCl_3$


7.475
7.409
7.404
7.392
7.385
7.380
7.372
7.354
7.335
7.254
2.525
2.506
2.488
2.469
1.356
1.337
1.210
1.199
-0.000
O
B
O
CF3
2m
1H NMR
400 MHz
CDCl3
5.95
6.20
3.02
3.19
0.98
1.00
8
6
4
2
0
PPM

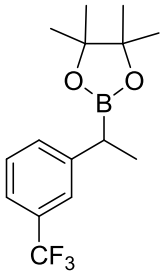


2m

^{13}C NMR

101 MHz

$CDCl_3$

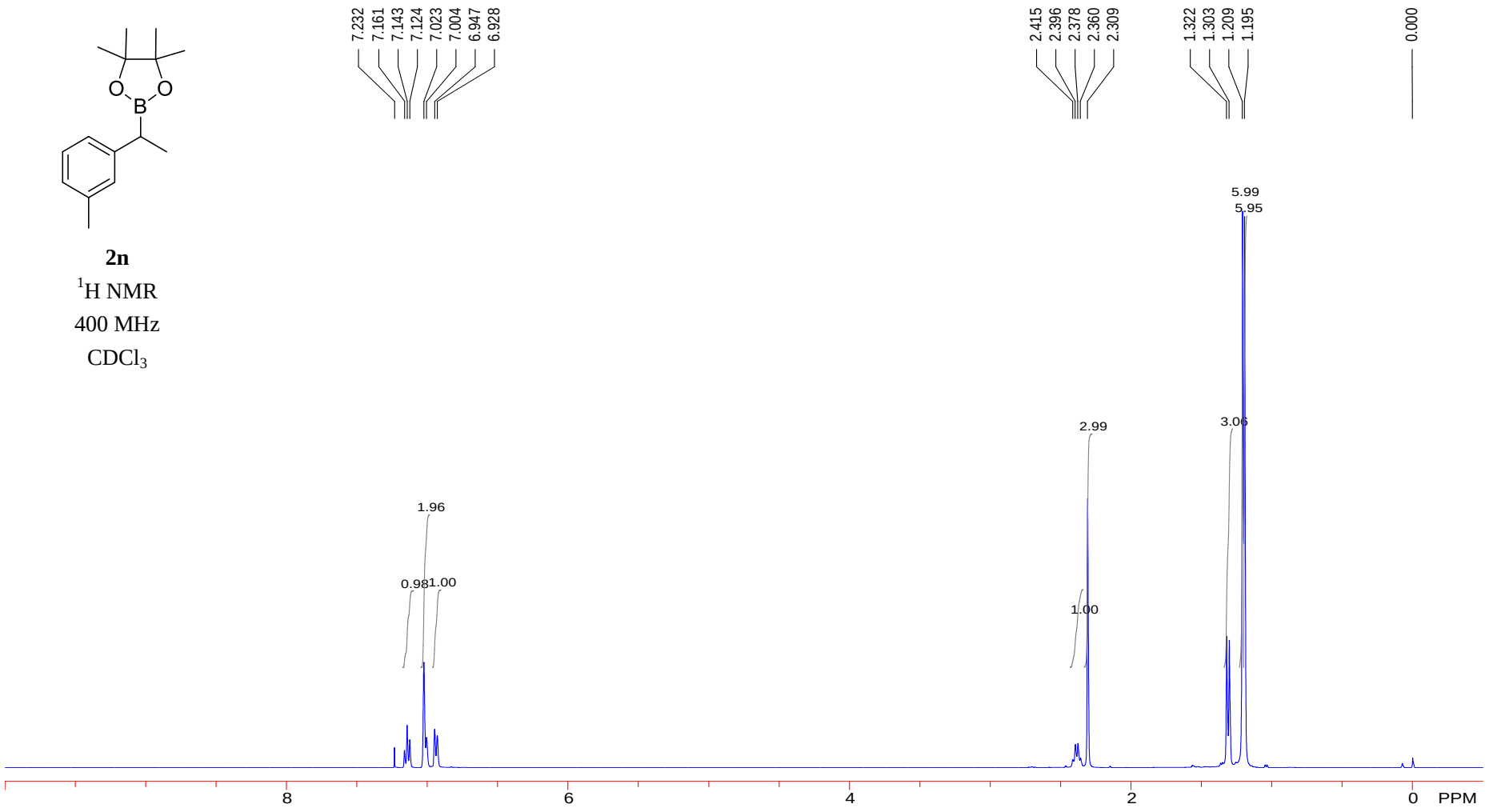


2m

^{19}F NMR

376 MHz

$CDCl_3$

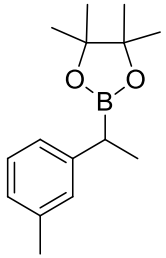


2n

^{1}H NMR

400 MHz

$CDCl_3$

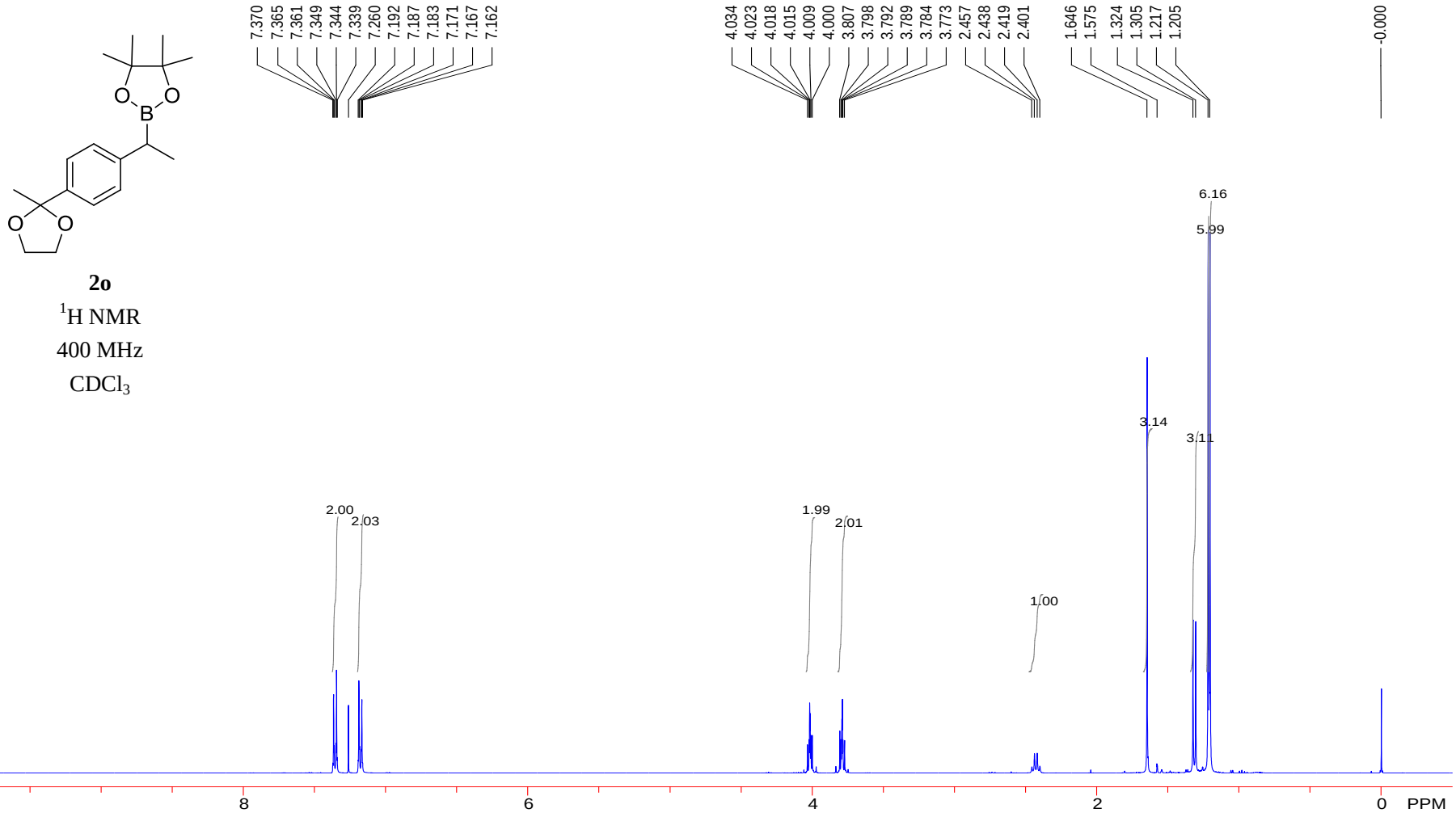


2n

^{13}C NMR

101 MHz

$CDCl_3$

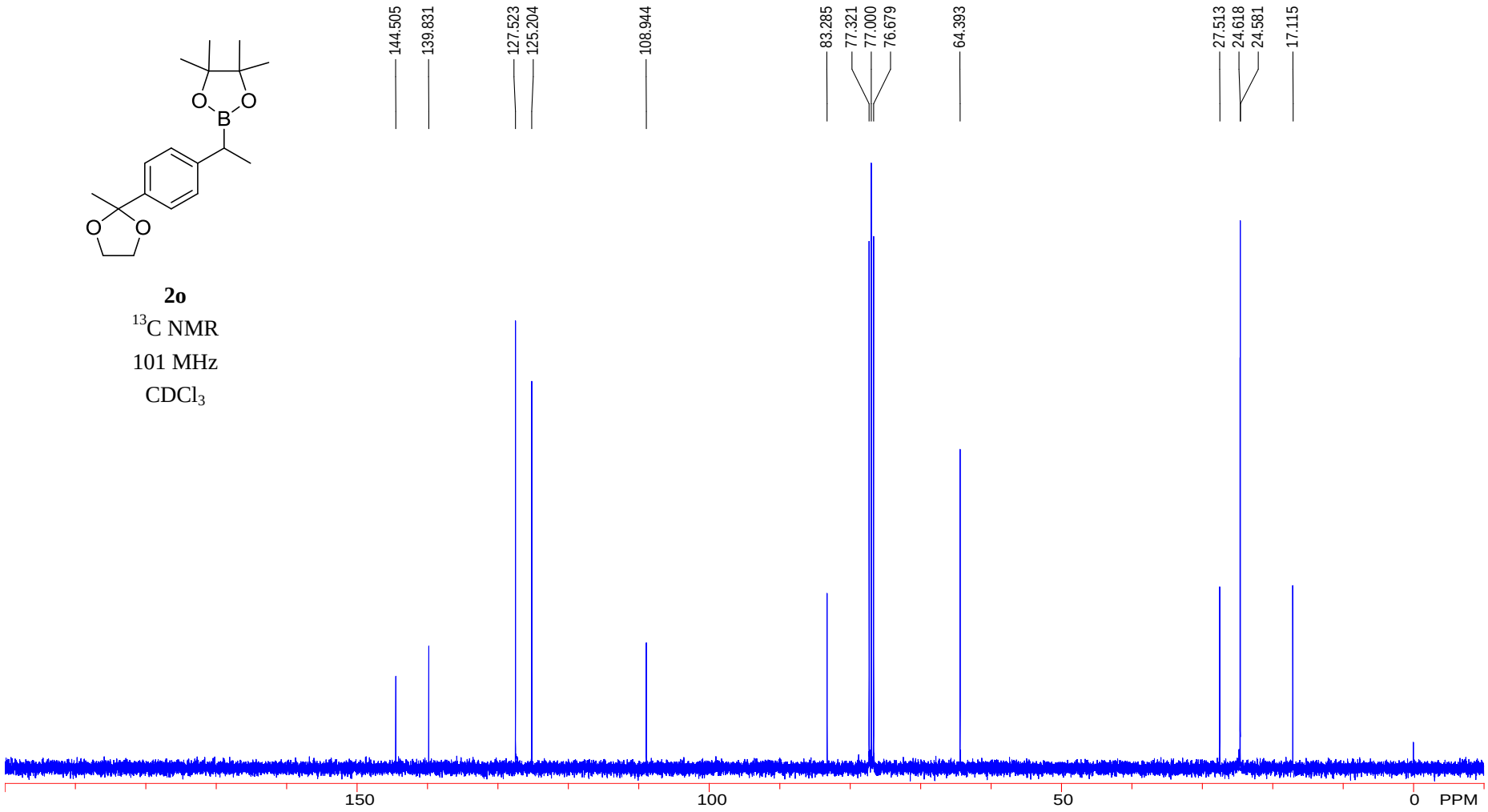


2o

^{1}H NMR

400 MHz

$CDCl_3$

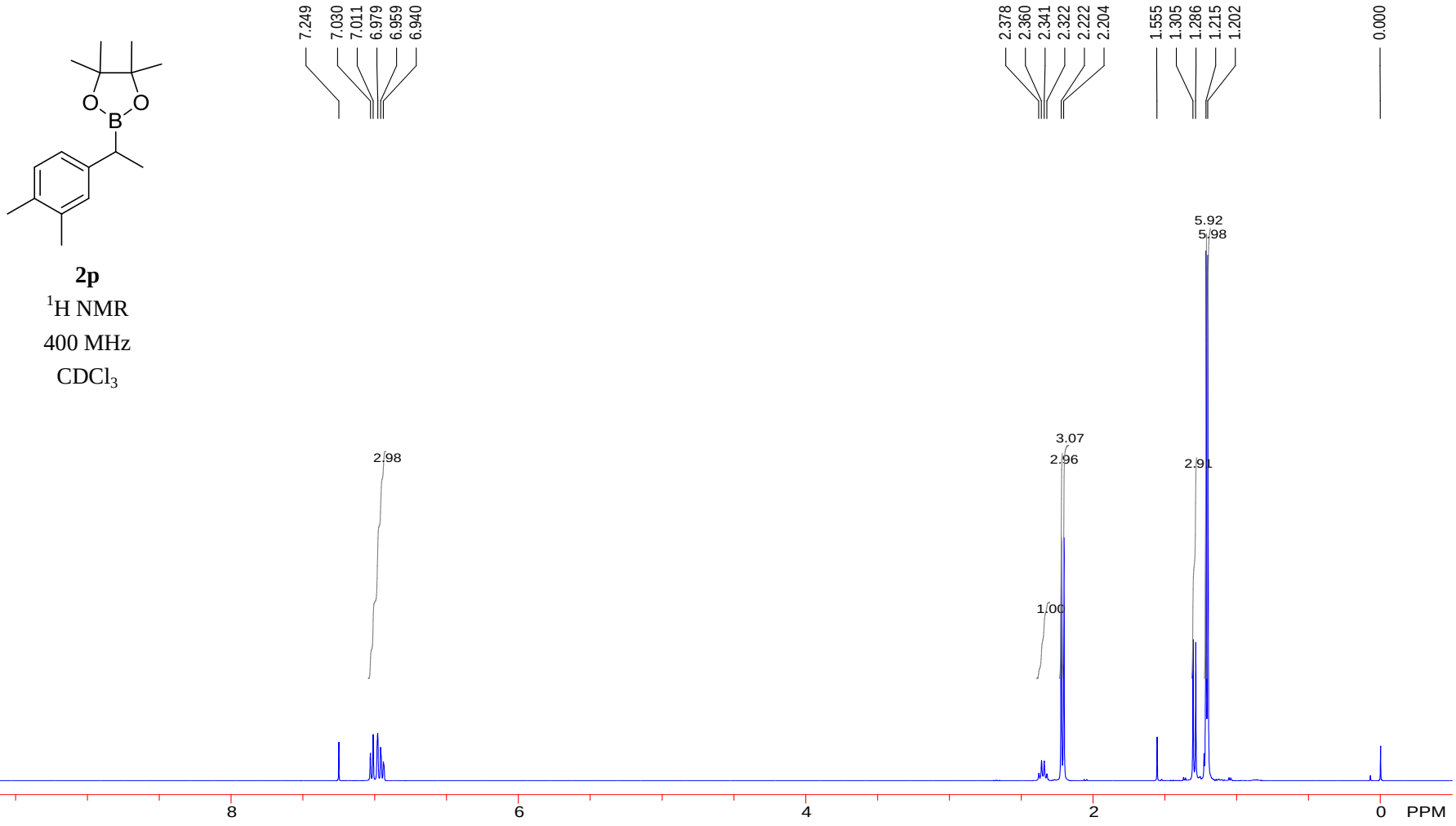


2o

^{13}C NMR

101 MHz

$CDCl_3$

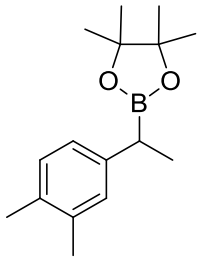


2p

^{1}H NMR

400 MHz

$CDCl_3$

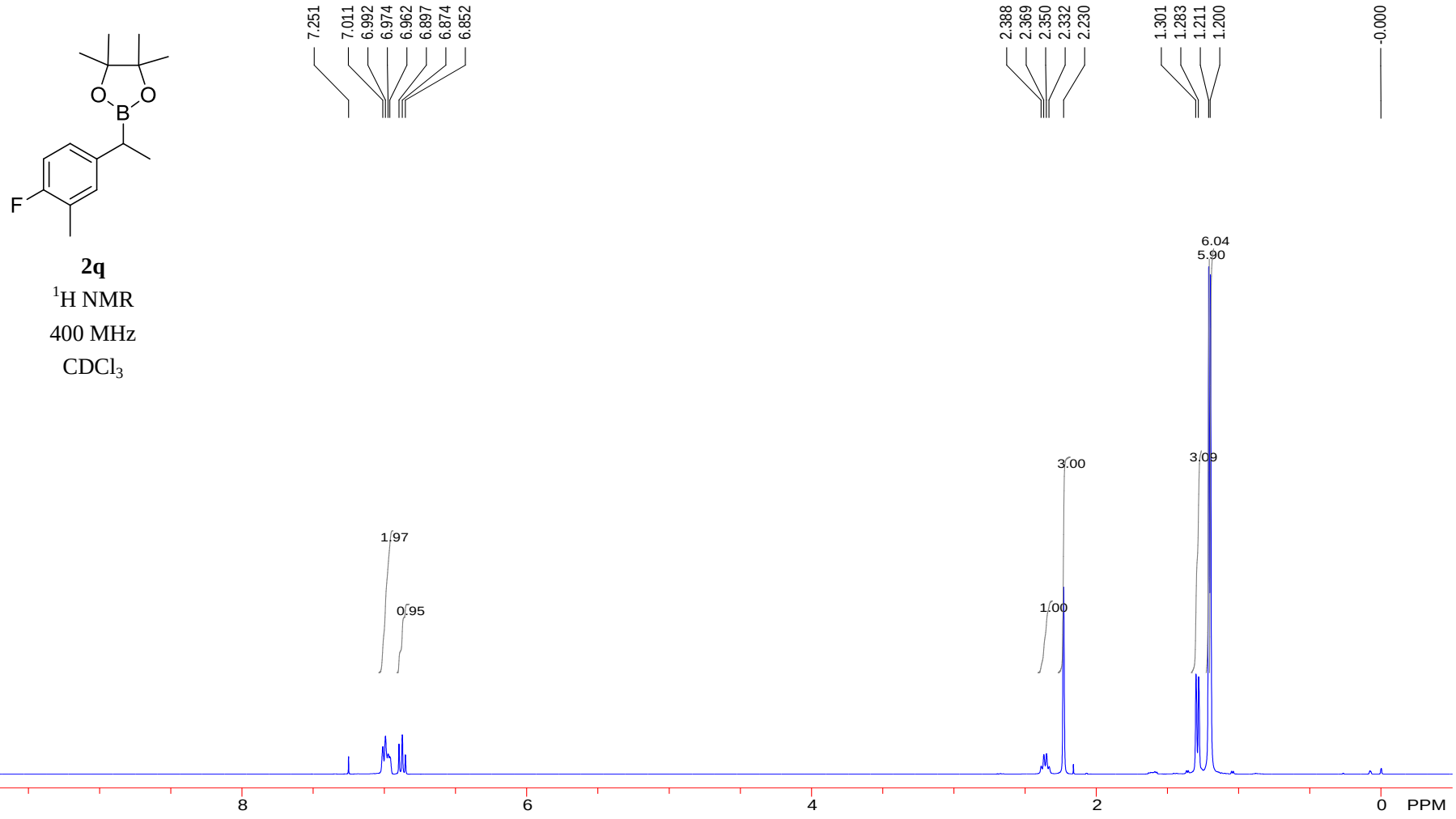


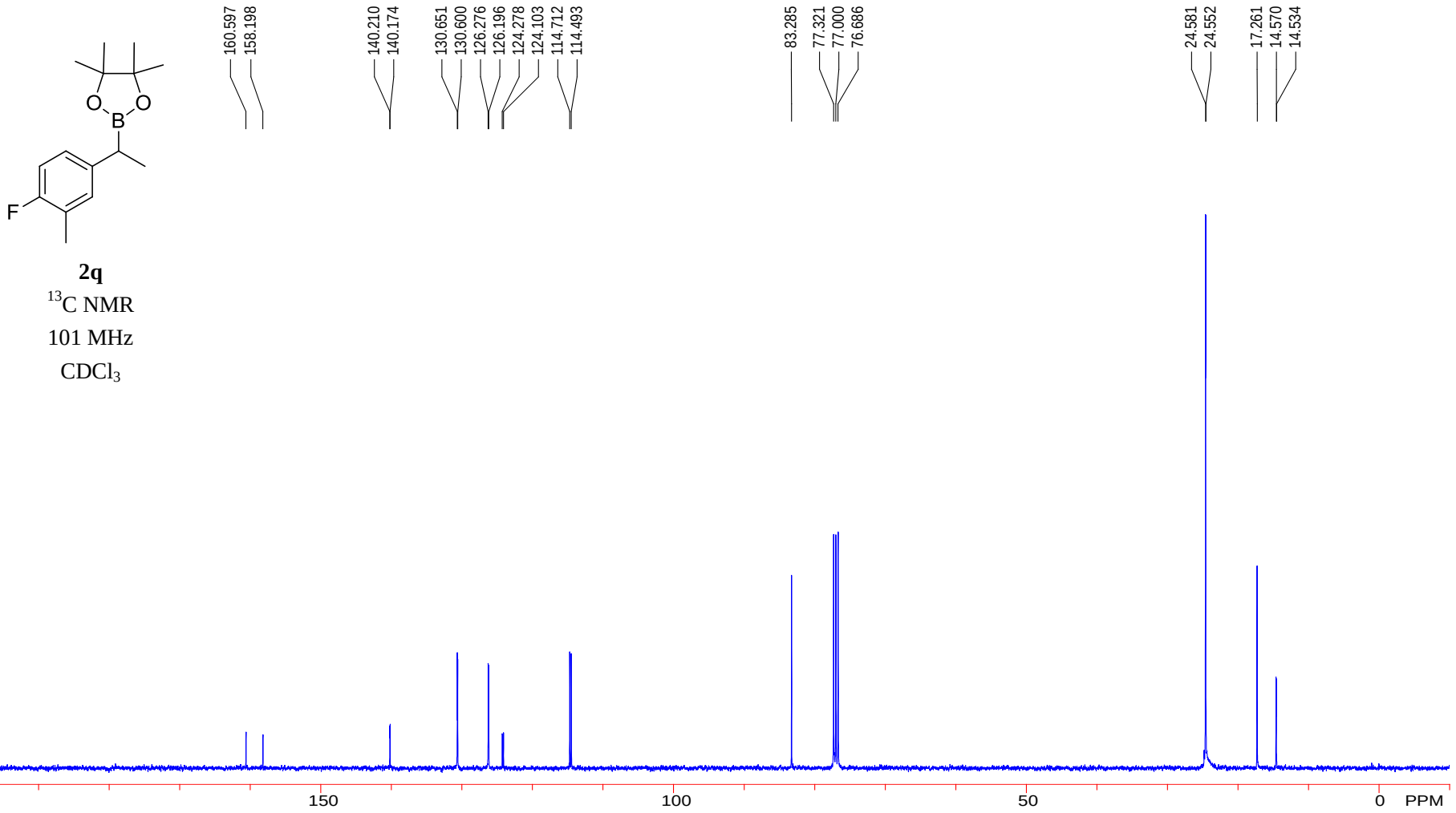
2p

^{13}C NMR

101 MHz

$CDCl_3$


7.251
7.011
6.992
6.974
6.962
6.897
6.874
6.852
2.388
2.369
2.350
2.332
2.230
1.301
1.283
1.211
1.200
-0.000
O
B
O
F
2q
1H NMR
400 MHz
CDCl3
6.04
5.90
3.00
3.09
1.97
0.95
1.00
8
6
4
2
0
PPM

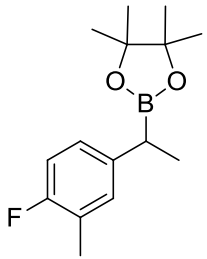


2q

^{13}C NMR

101 MHz

$CDCl_3$

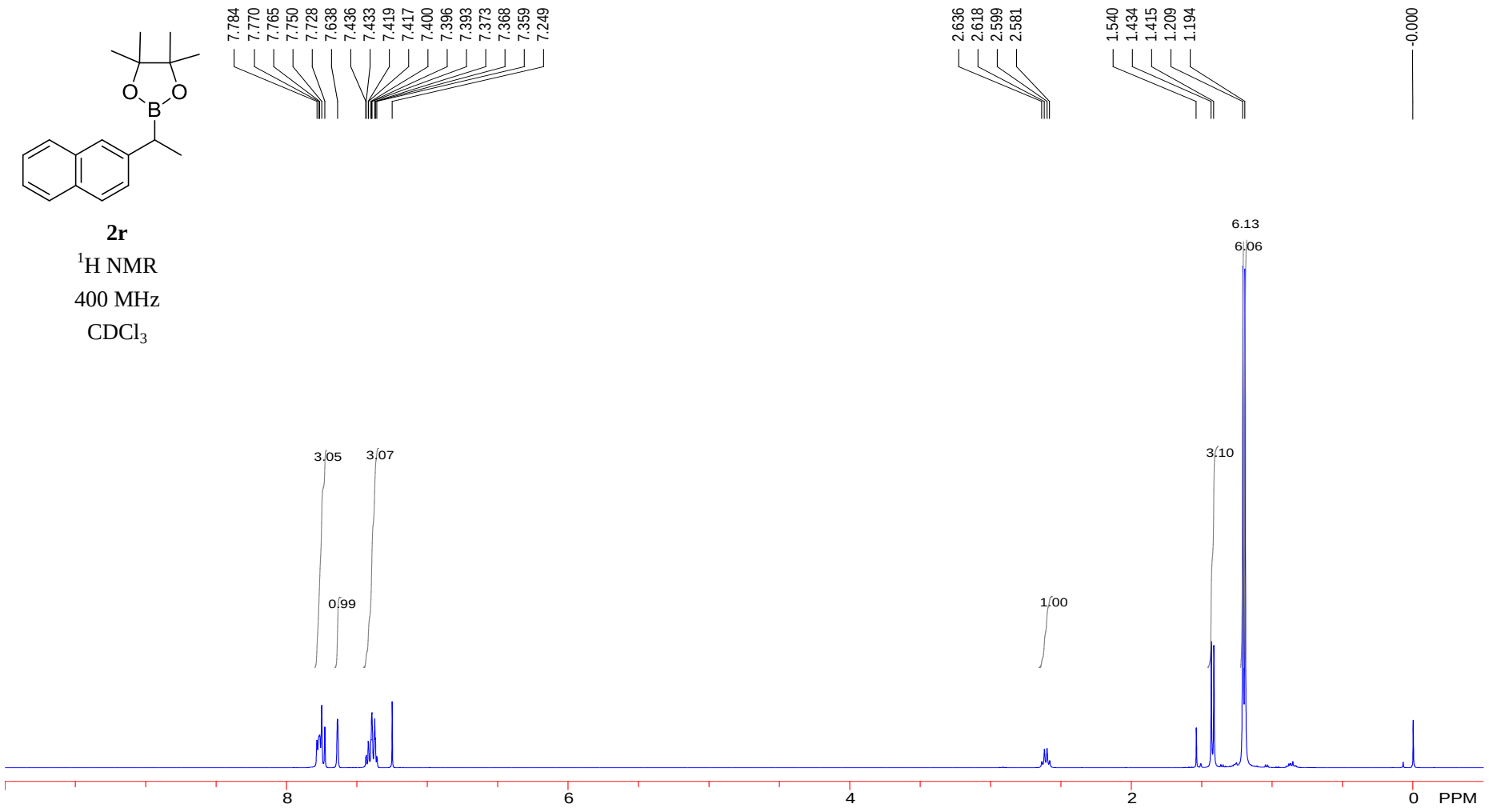


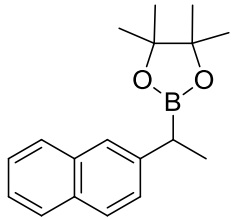
2q

^{19}F NMR

376 MHz

$CDCl_3$


7.784
7.770
7.765
7.750
7.728
7.638
7.436
7.433
7.419
7.417
7.400
7.396
7.393
7.373
7.368
7.359
7.249
2.636
2.618
2.599
2.581
1.540
1.434
1.415
1.209
1.194
-0.000
O
B
O
2r
1H NMR
400 MHz
CDCl3
6.13
6.06
3.05
3.07
3.10
0.99
1.00
8
6
4
2
0
PPM

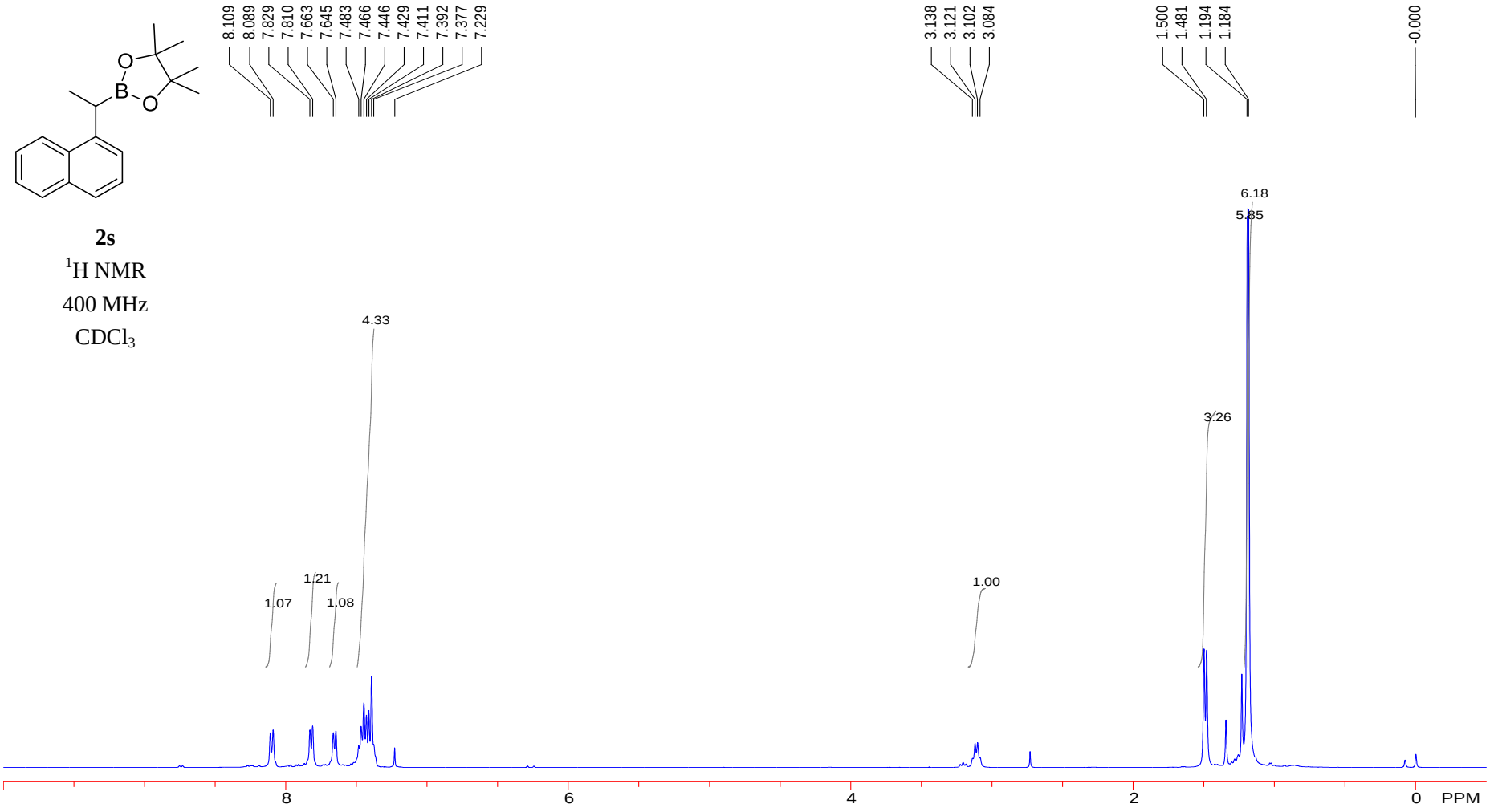


2r

^{13}C NMR

101 MHz

$CDCl_3$

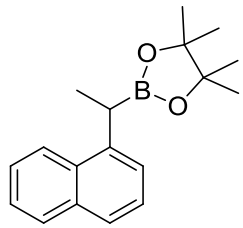


2s

^{1}H NMR

400 MHz

$CDCl_3$

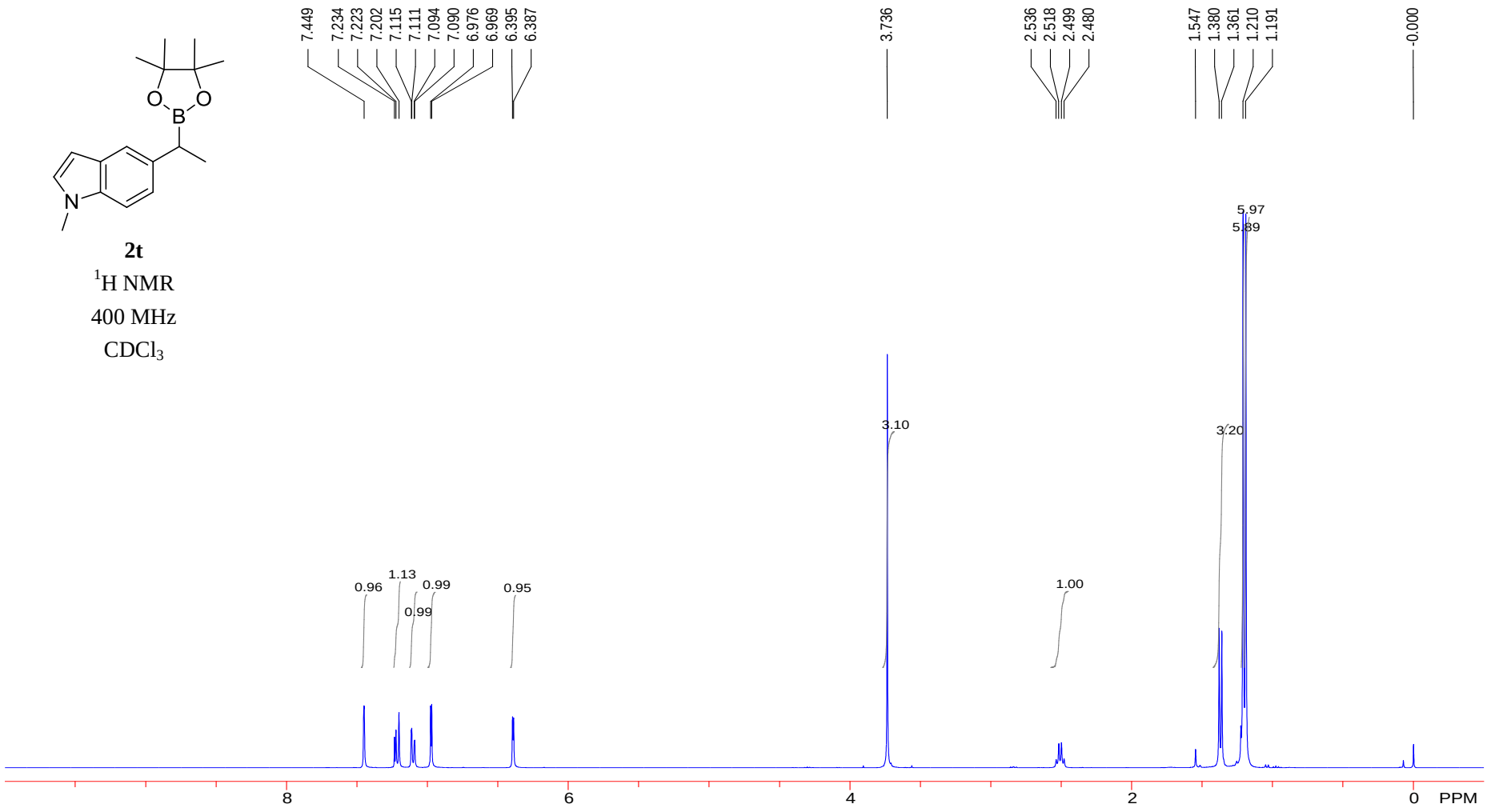


2s

^{13}C NMR

101 MHz

$CDCl_3$

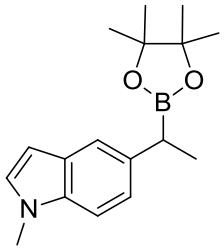


2t

^{1}H NMR

400 MHz

$CDCl_3$

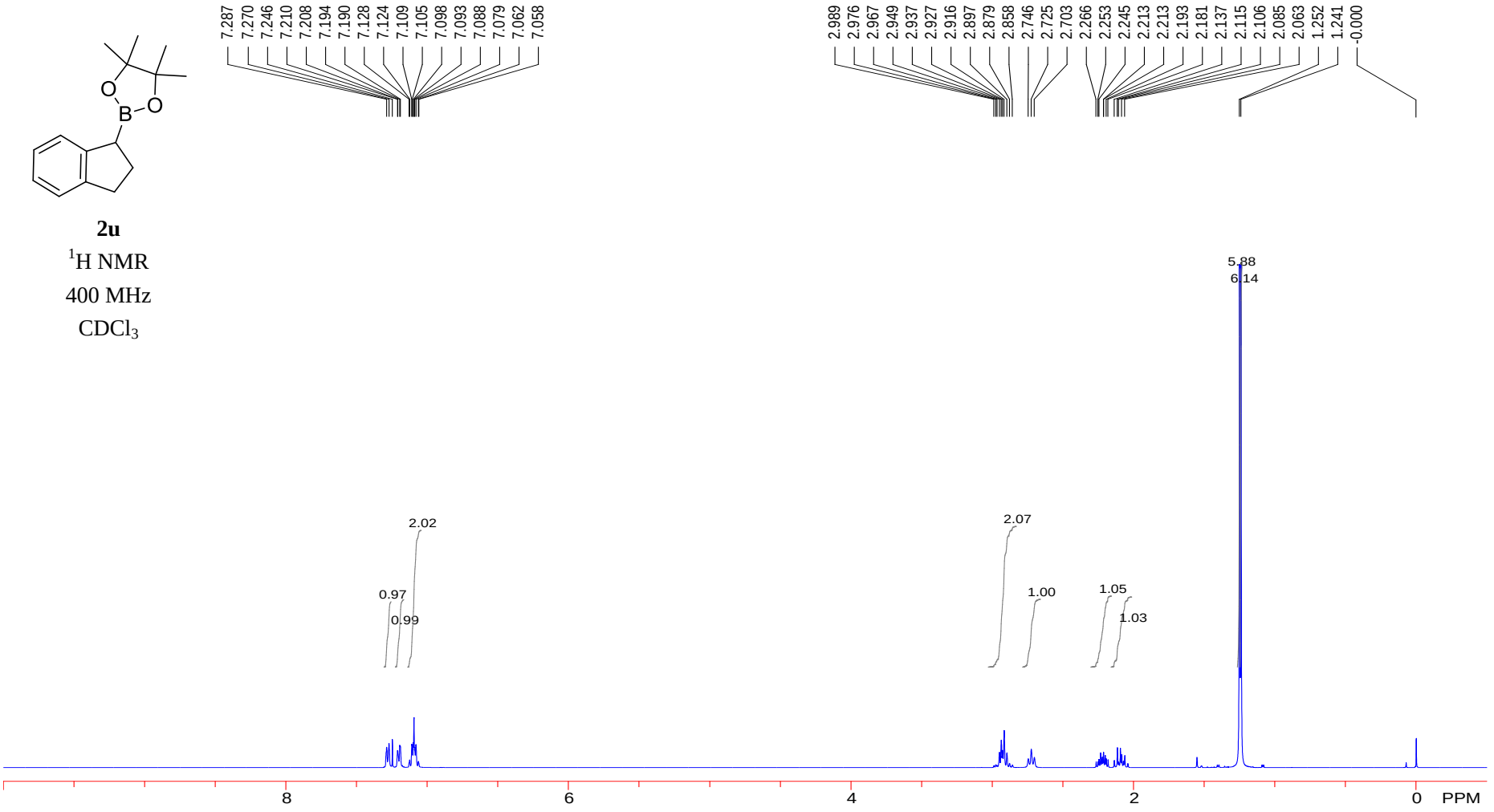


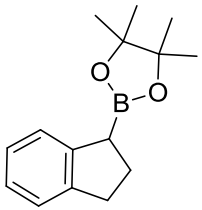
2t

^{13}C NMR

101 MHz

$CDCl_3$


7.287
7.270
7.246
7.210
7.208
7.194
7.190
7.128
7.124
7.109
7.105
7.098
7.093
7.088
7.079
7.062
7.058
2.989
2.976
2.967
2.949
2.937
2.927
2.916
2.897
2.879
2.858
2.746
2.725
2.703
2.266
2.253
2.245
2.213
2.213
2.193
2.181
2.137
2.115
2.106
2.085
2.063
1.252
1.241
-0.000
O
B
O
2u
1H NMR
400 MHz
CDCl3
5.88
6.14
2.02
0.97
0.99
2.07
1.00
1.05
1.03
8
6
4
2
0
PPM

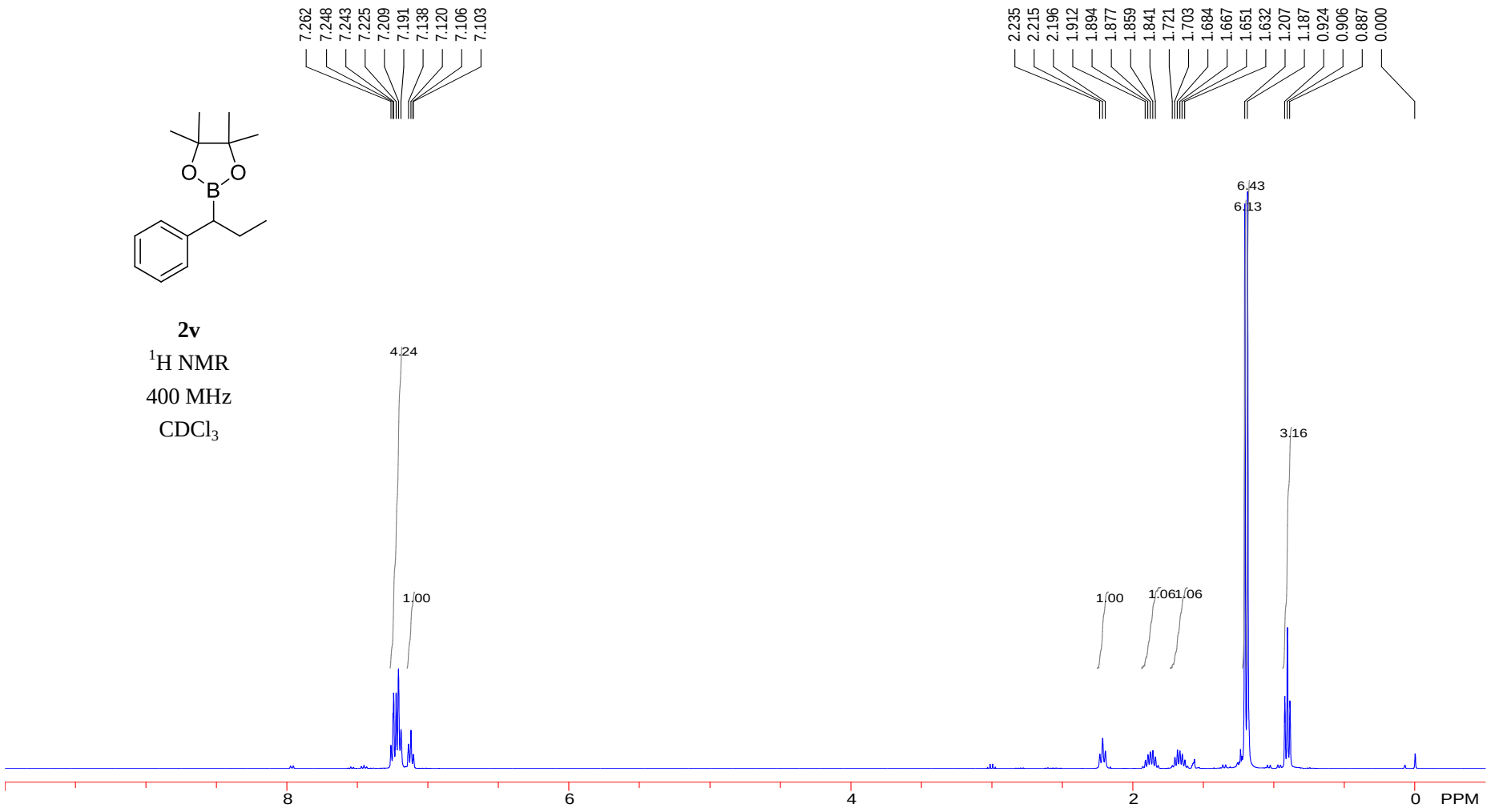


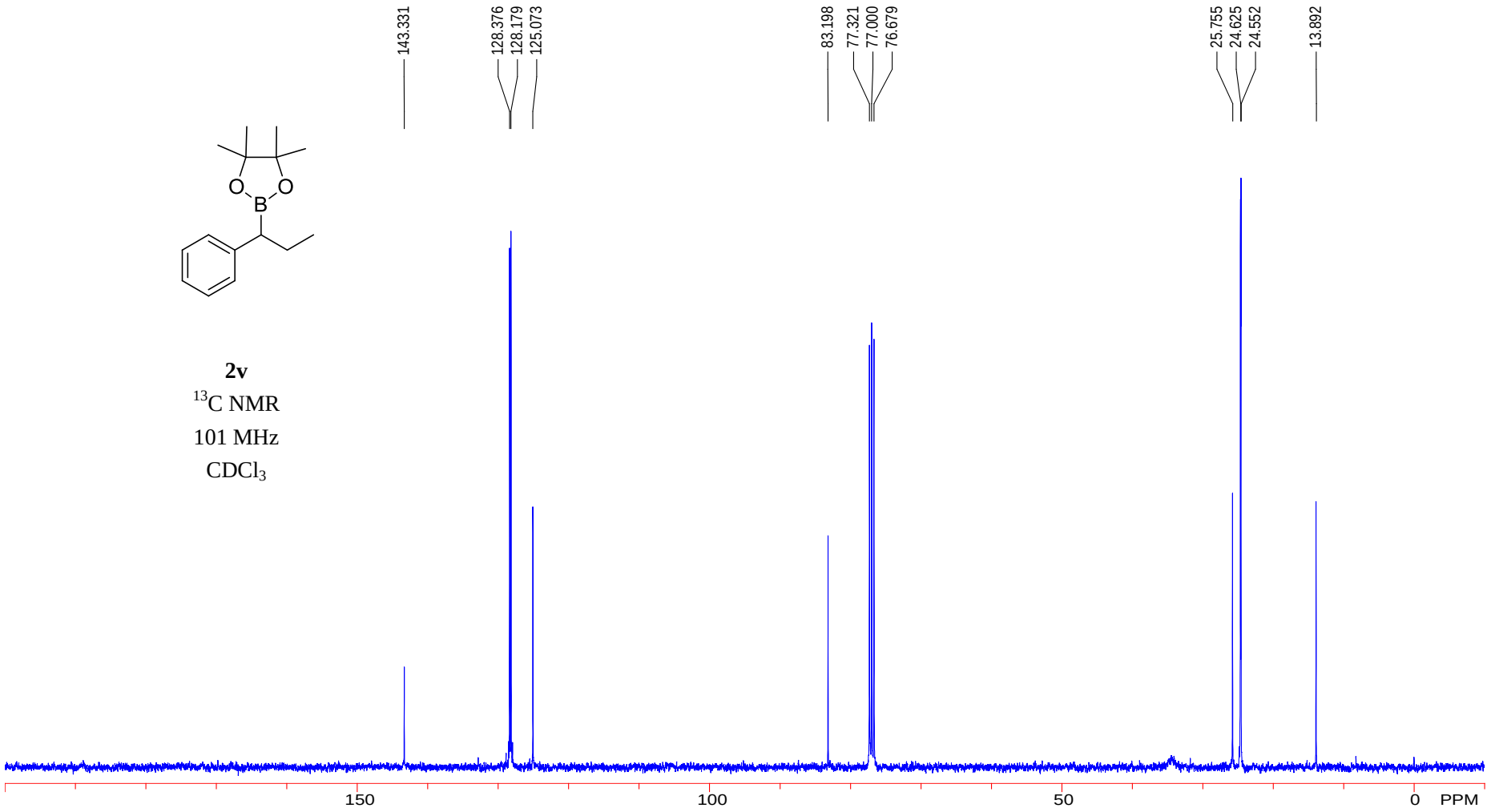
2u

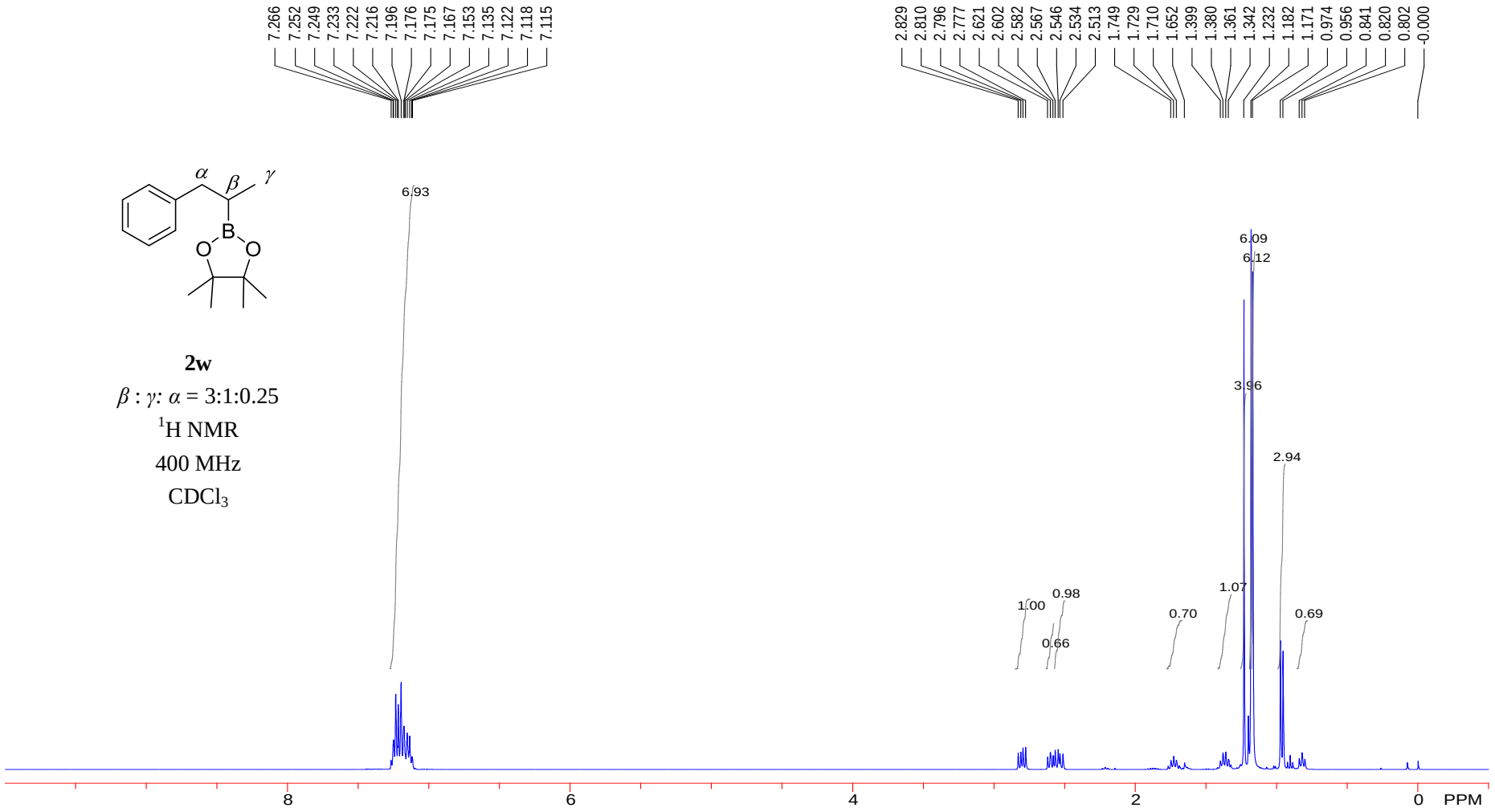
^{13}C NMR

101 MHz

$CDCl_3$


7.262
7.248
7.243
7.225
7.209
7.191
7.138
7.120
7.106
7.103
2.235
2.215
2.196
1.912
1.894
1.877
1.859
1.841
1.721
1.703
1.684
1.667
1.651
1.632
1.207
1.187
0.924
0.906
0.887
0.000
O
O
B
2v
1H NMR
400 MHz
CDCl3
4.24
1.00
6.43
6.13
3.16
1.00
1.06
1.06
8
6
4
2
0
PPM


143.331
128.376
128.179
125.073
83.198
77.321
77.000
76.679
25.755
24.625
24.552
13.892
O
O
B
2v
13C NMR
101 MHz
CDCl3
150
100
50
0
PPM



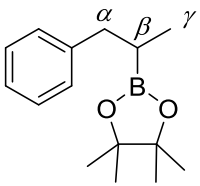
2w

β : γ: α = 3:1:0.25

^{1}H NMR

400 MHz

$CDCl_3$



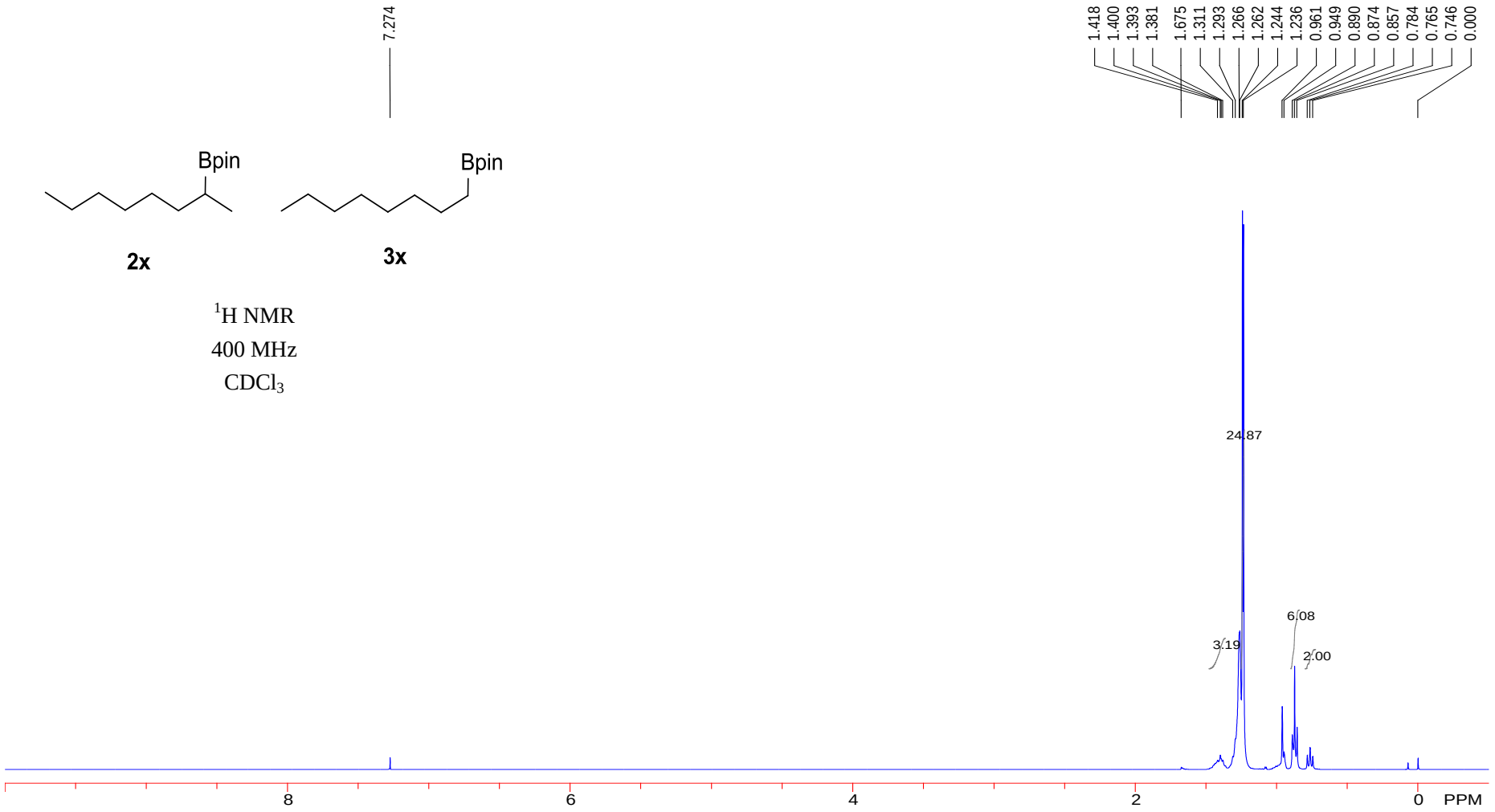
2w

β : γ: α = 3:1:0.25

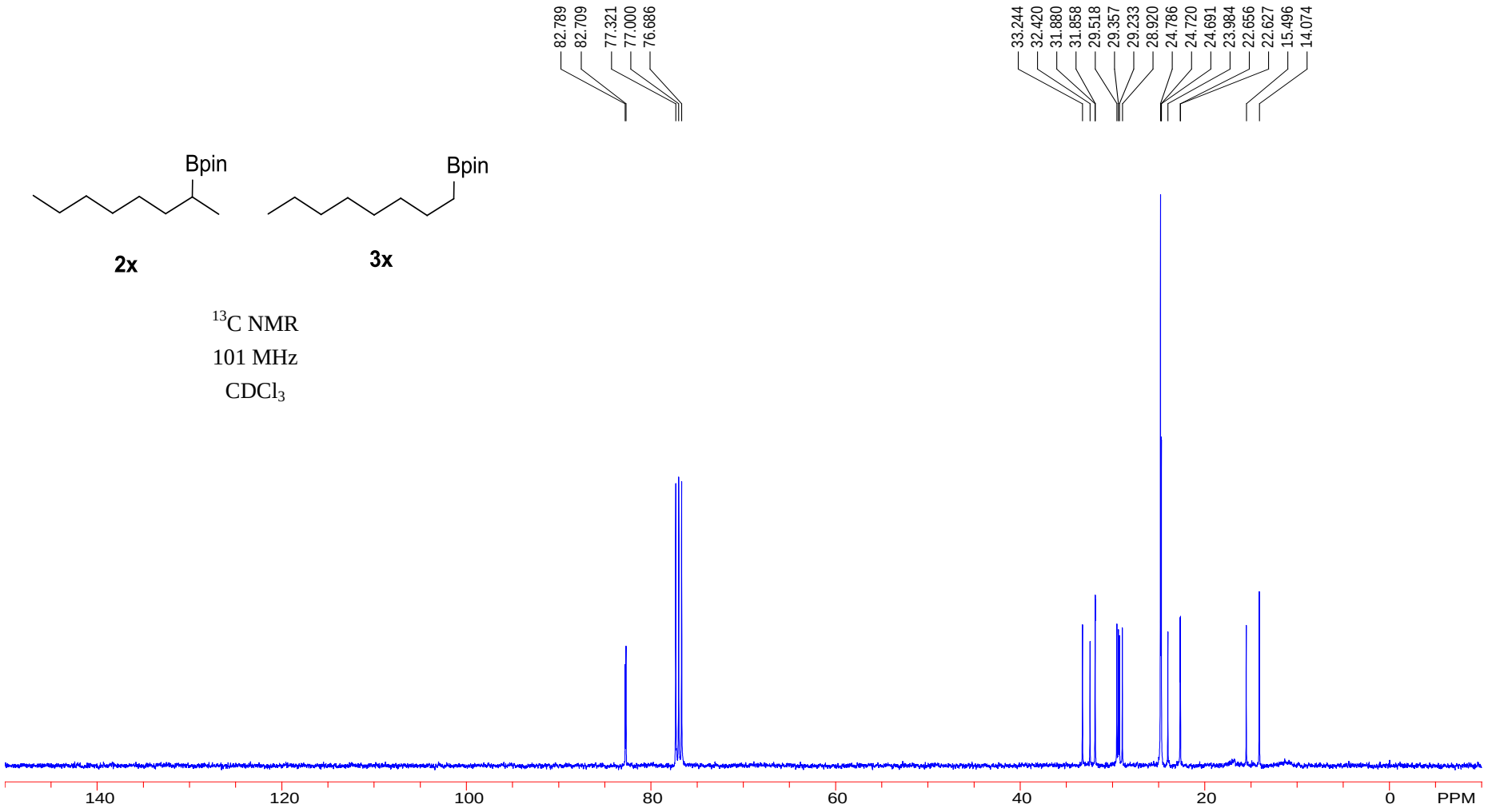
^{13}C NMR

101 MHz

$CDCl_3$



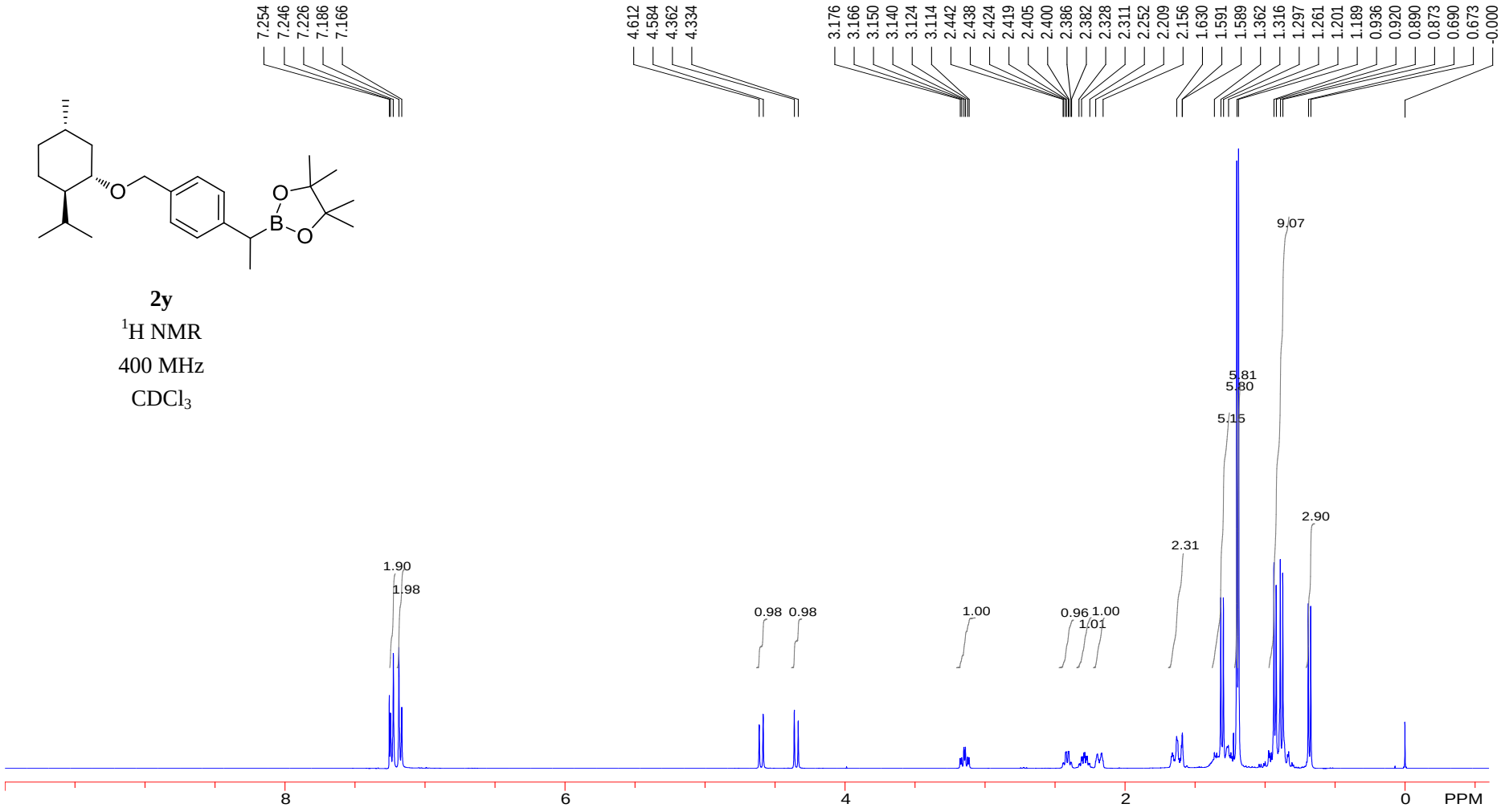
^{1}H NMR
400 MHz
$CDCl_3$

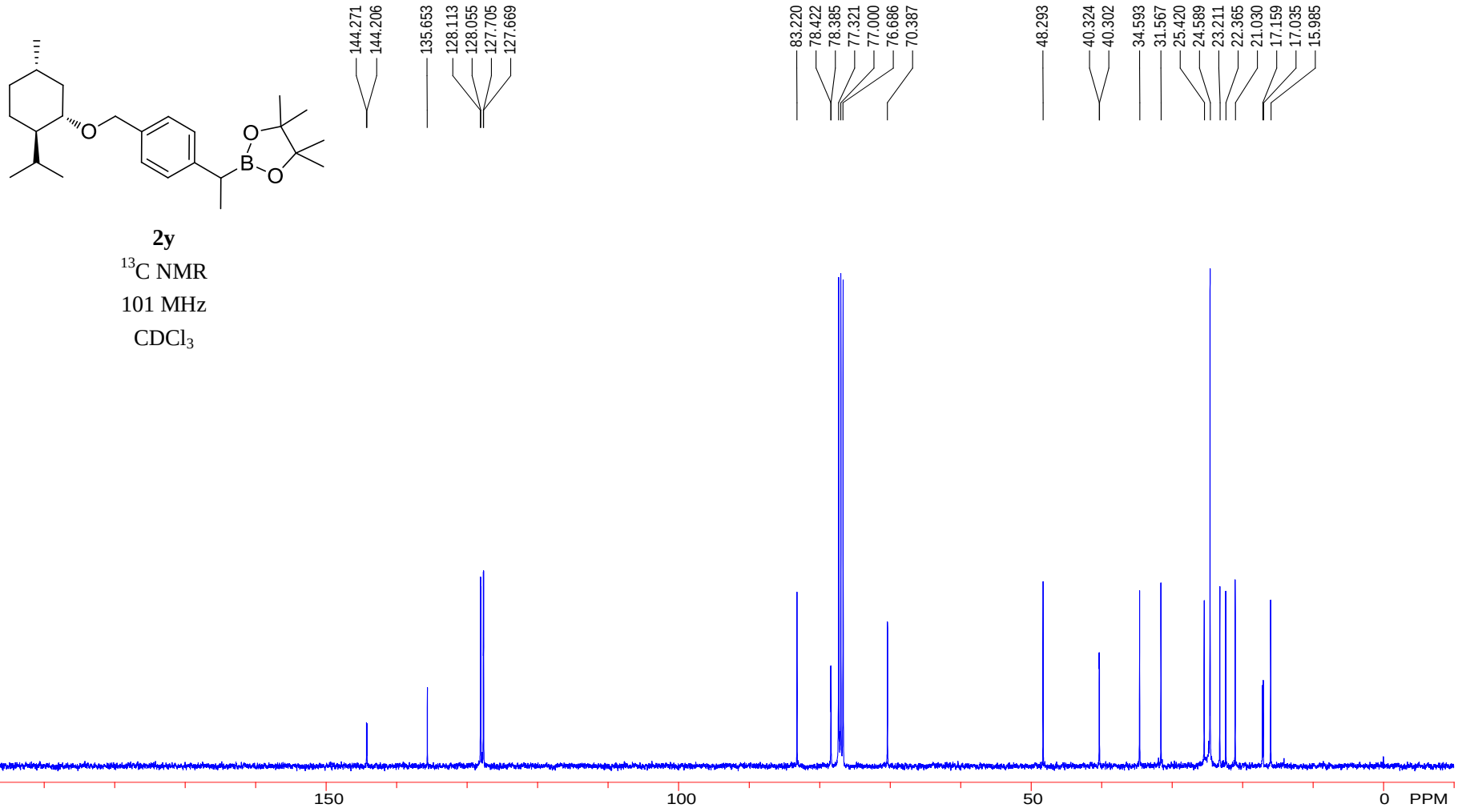


^{13}C NMR

101 MHz

$CDCl_3$


7.254
7.246
7.226
7.186
7.166
4.612
4.584
4.362
4.334
3.176
3.166
3.150
3.140
3.124
3.114
2.442
2.438
2.424
2.419
2.405
2.400
2.386
2.382
2.328
2.311
2.252
2.209
2.156
1.630
1.591
1.589
1.362
1.316
1.297
1.261
1.201
1.189
0.936
0.920
0.890
0.873
0.690
0.673
-0.000
O
O
B
O
2y
1H NMR
400 MHz
CDCl3
9.07
5.81
5.80
5.15
2.90
2.31
1.90
1.98
0.98
0.98
1.00
0.96
1.01
1.00
8
6
4
2
0
PPM

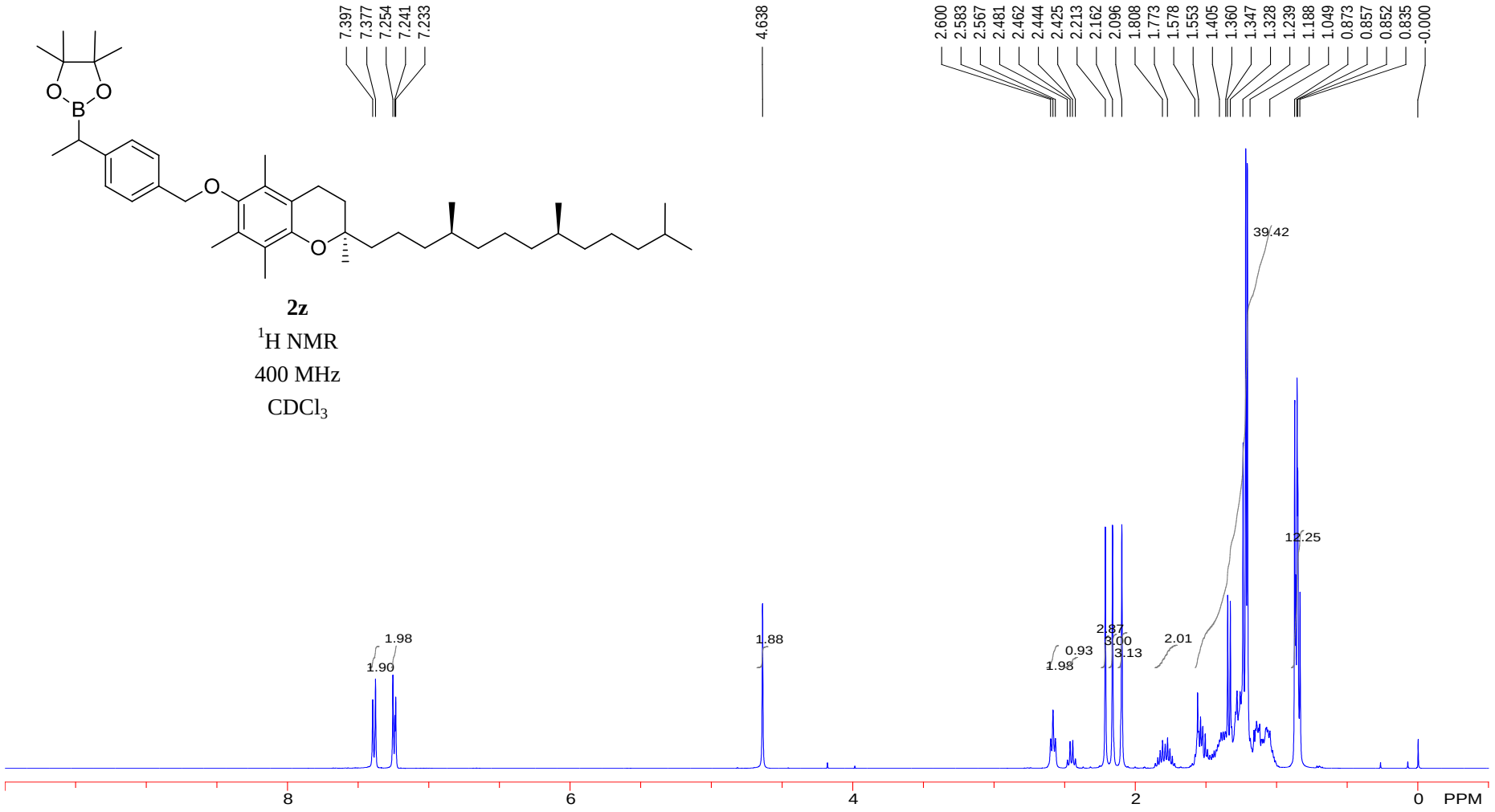


2y

^{13}C NMR

101 MHz

$CDCl_3$

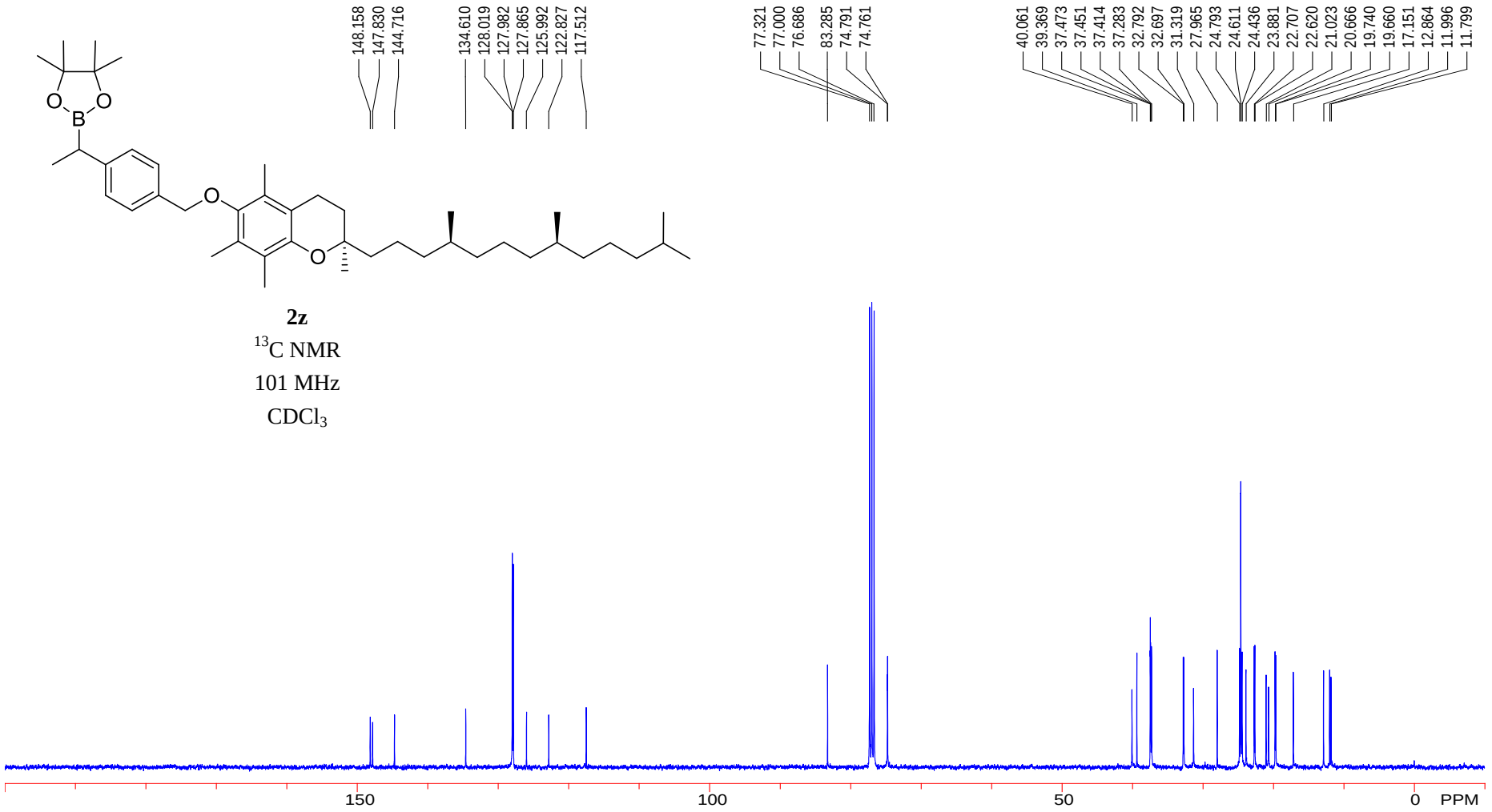


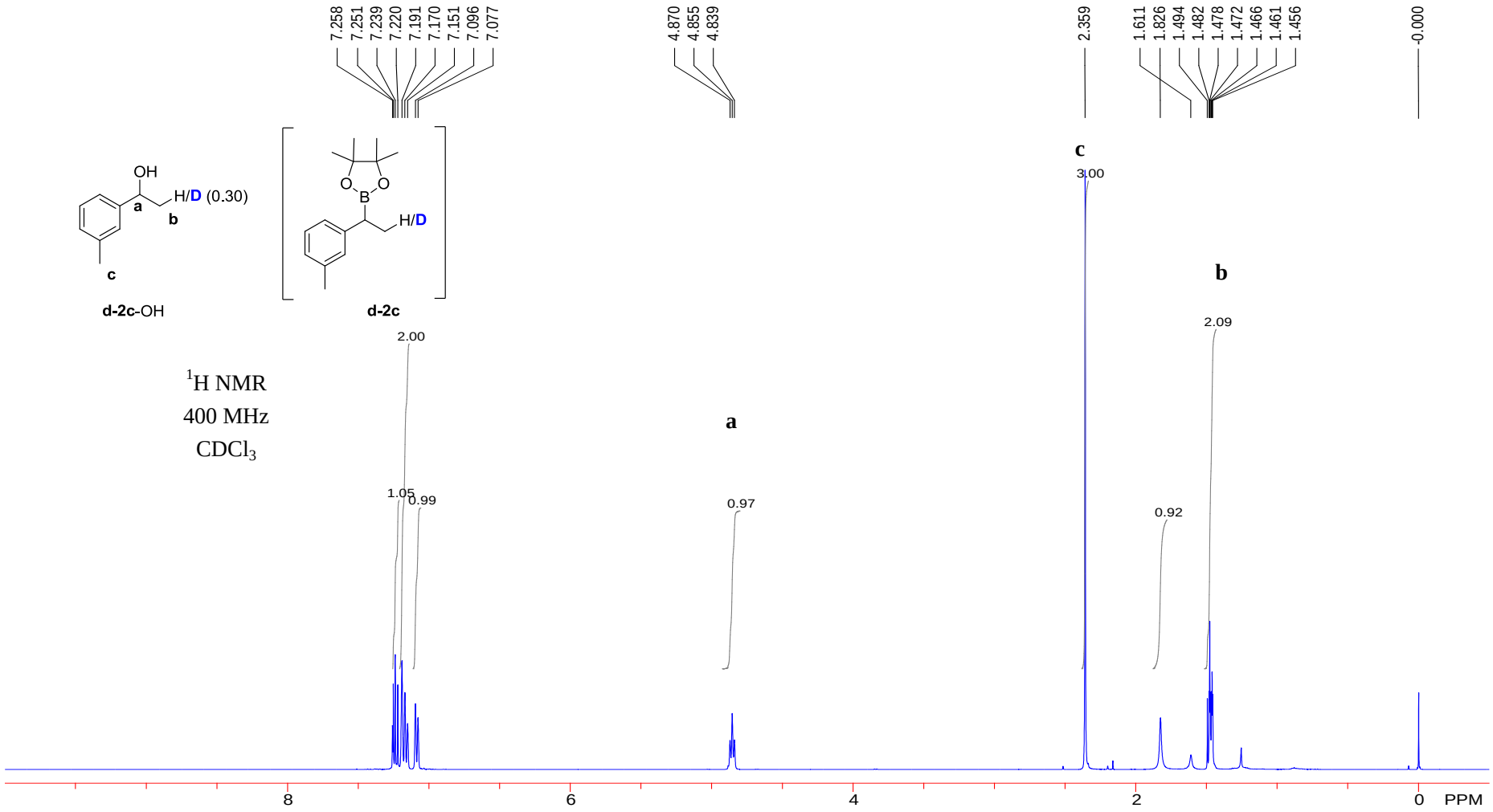
2z

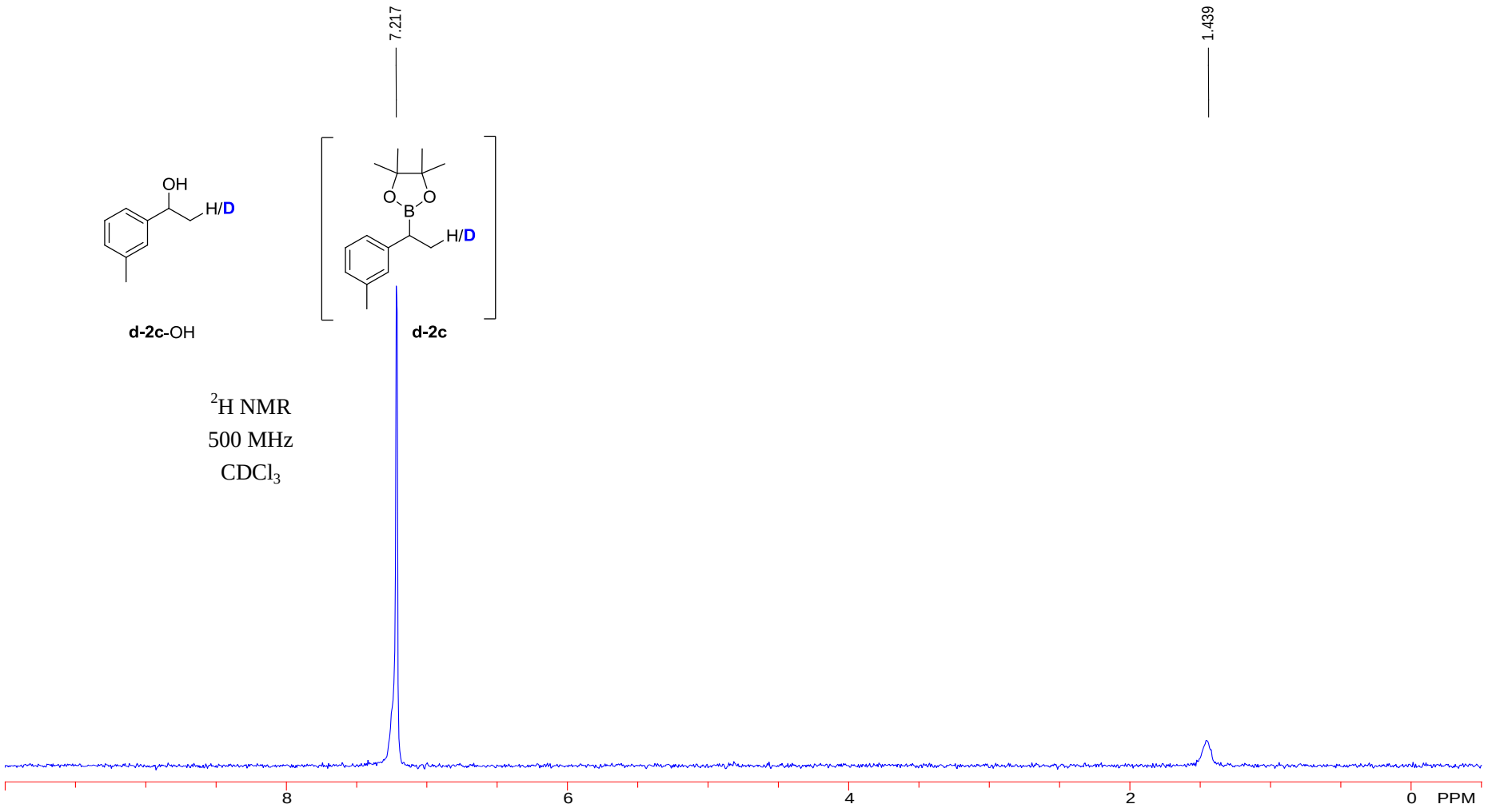
^{1}H NMR

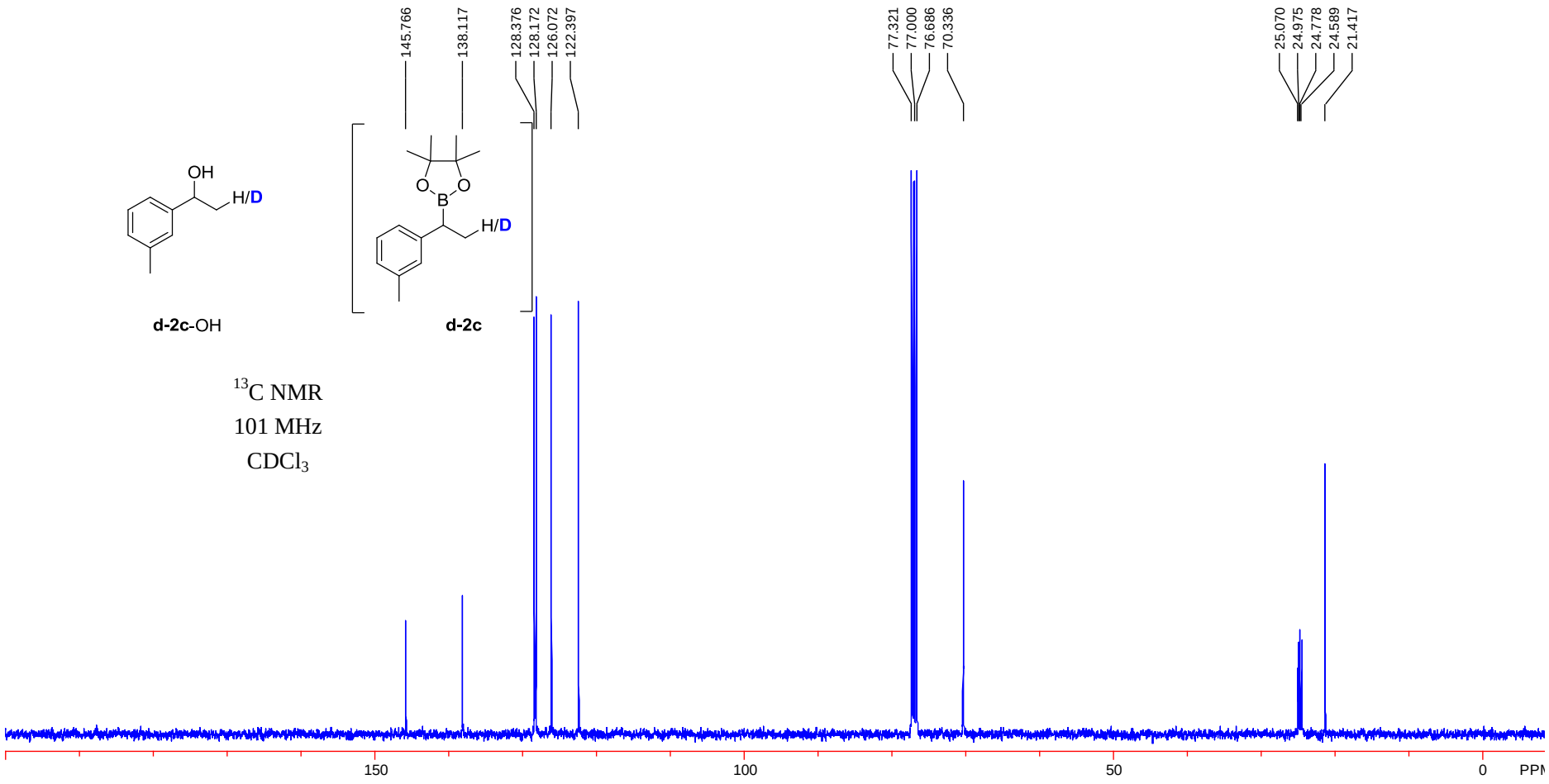
400 MHz

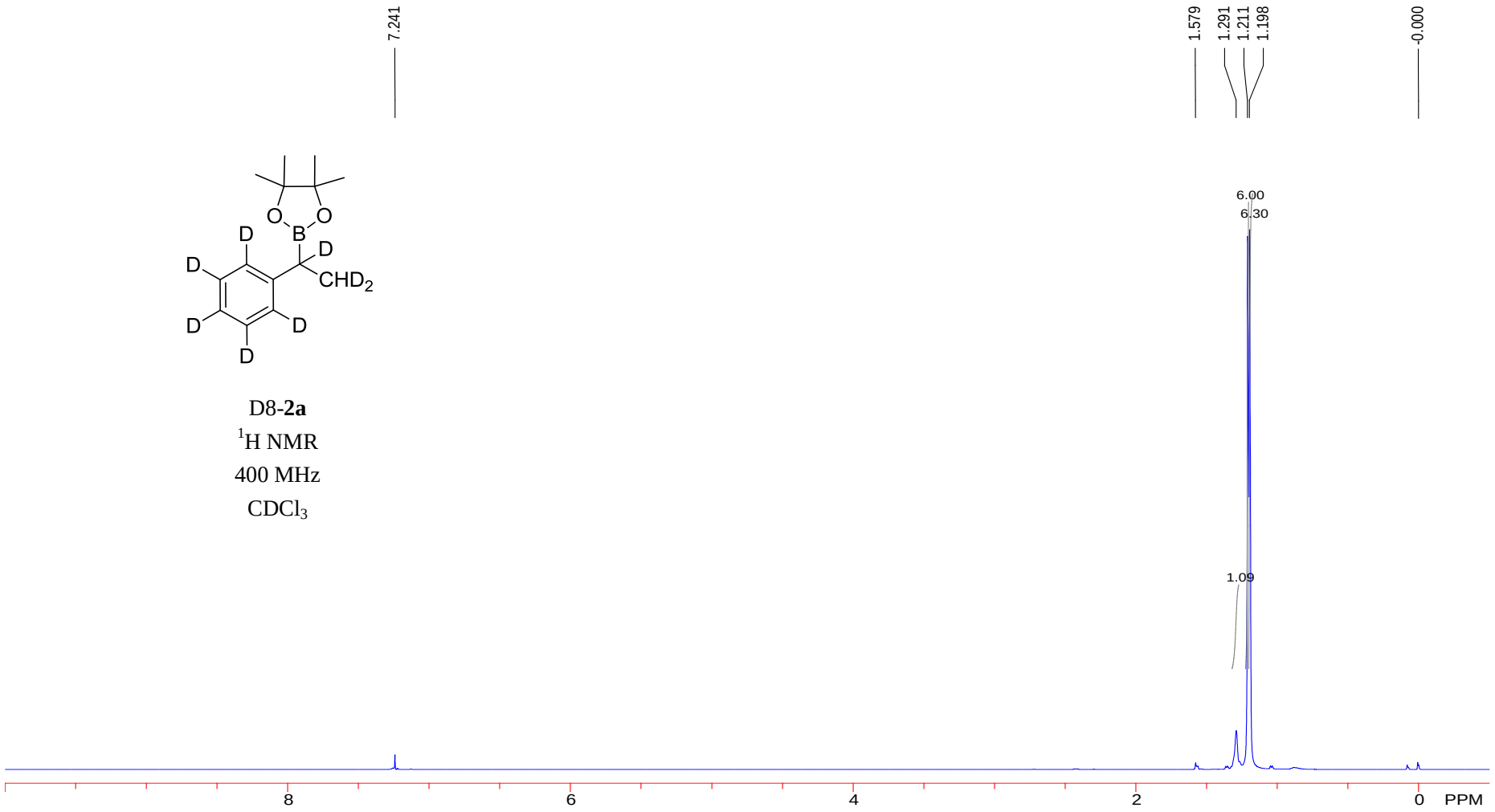
$CDCl_3$

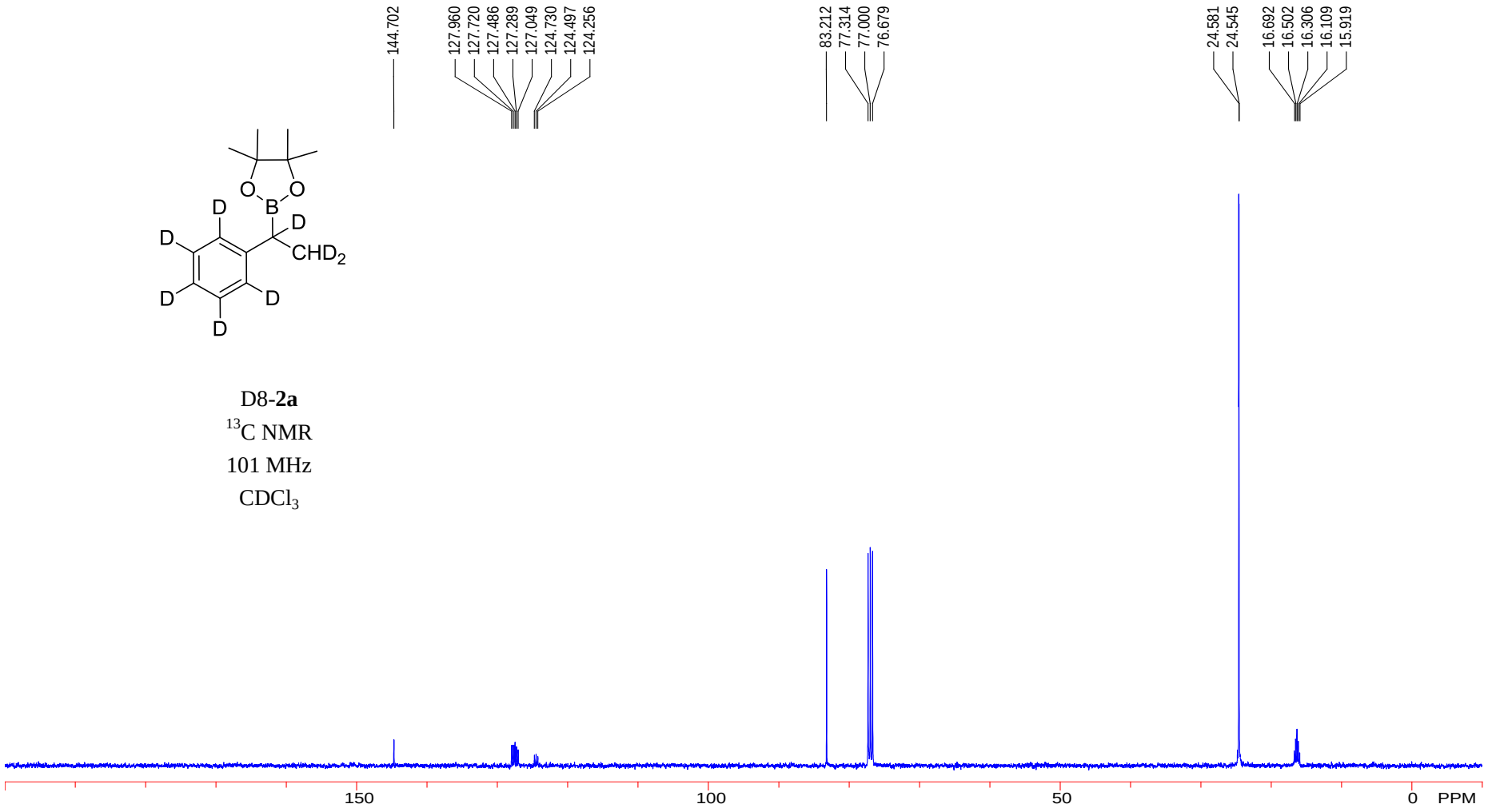

148.158
147.830
144.716
134.610
128.019
127.982
127.865
125.992
122.827
117.512
77.321
77.000
76.686
83.285
74.791
74.761
40.061
39.369
37.473
37.451
37.414
37.283
32.792
32.697
31.319
27.965
24.793
24.611
24.436
23.881
22.707
22.620
21.023
20.666
19.740
19.660
17.151
12.864
11.996
11.799
O
B
O
O
O
O
2z
13C NMR
101 MHz
CDCl3
150
100
50
0
PPM


7.258
7.251
7.239
7.220
7.191
7.170
7.151
7.096
7.077
4.870
4.855
4.839
2.359
1.611
1.826
1.494
1.482
1.478
1.472
1.466
1.461
1.456
-0.000
OH
a
H/D (0.30)
b
c
d-2c-OH
O
O
B
H/D
d-2c
1H NMR
400 MHz
CDCl3
2.00
1.05
0.99
a
0.97
c
3.00
b
2.09
0.92
8
6
4
2
0
PPM


7.217
1.439
OH
H/D
d-2c-OH
O
B
O
H/D
d-2c
^{2}H NMR
500 MHz
$CDCl_3$
8
6
4
2
0
PPM


145.766
138.117
128.376
128.172
126.072
122.397
77.321
77.000
76.686
70.336
25.070
24.975
24.778
24.589
21.417
OH
H/D
d-2c-OH
O
B
O
H/D
d-2c
^{13}C NMR
101 MHz
$CDCl_3$
150
100
50
0
PPM


7.241
1.579
1.291
1.211
1.198
-0.000
D
D
D
D
O
B
O
D
CHD2
D
D
D8-2a
1H NMR
400 MHz
CDCl3
6.00
6.30
1.09
8
6
4
2
0
PPM



D8-**2a**

^{13}C NMR

101 MHz

$CDCl_3$