Supporting Information

Title: Para-Selective, Iridium–Catalyzed C–H Borylations of Sulfated Phenols, Benzyl Alcohols, and Anilines Directed by Ion-Pair Electrostatic Interactions

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General Information

All commercially available chemicals were used as received unless otherwise indicated. Bis(pinacolato)diboron (B_2pin_2) was generously supplied by BoroPharm, Inc. Bis(η^4-1,5-cyclooctadiene)-di-μ-methoxy-diiridium(I) [Ir(cod)(OMe)]$_2$ was made by a literature procedure[1] or purchased from Sigma-Aldrich. Dioxane was refluxed over sodium/benzophenone ketyl, distilled and degassed.

Column chromatography was performed on 240 - 400 mesh Silica P-Flash silica gel. Thin layer chromatography was performed on 0.25 mm thick aluminum–backed silica gel plates and visualized with ultraviolet light (λ = 254 nm) and alizarin stain to visualize boronic esters according to a literature procedure.[2]

^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on a Varian 500 MHz DD2 Spectrometer equipped with a 1H-19F/15N-31P 5 mm Pulsed Field Gradient (PFG) Probe, or an Innova 300 MHz spectrometer equipped with a QUAD (^{1}H/^{19}F and ^{11}B) PFG probe. Spectra were taken in $CDCl_3$ referenced to 7.26 ppm in ^{1}H NMR and 77.0 ppm in ^{13}C NMR. Resonances for the boron-bearing carbon atom were not observed due to quadrupolar relaxation. All coupling constants are apparent *J* values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, bs = broad singlet). NMR spectra were processed for display using the MNova software program with only phasing and baseline corrections applied.

High-resolution mass spectra (HRMS) were obtained at the Michigan State University Mass Spectrometry Service Center using electrospray ionization (ESI+ or ESI-) on quadrupole time-of-flight (Q-TOF) instruments. Melting points were measured in a capillary melting point apparatus and are uncorrected.

Determining Product Ratios by NMR Integration: Product ratios were determined by integration of ^{1}H or ^{19}F NMR spectra. To verify the accuracy of the ^{1}H NMR integration, stock solutions of commercial samples of 3-chloro-4-hydroxyphenylBpin (meta borylated **2a**) and

4-chloro-3-hydroxyphenylBpin (para borylated **2a**) were accurately mixed in known amounts with Hamilton gas-tight micro syringes. The ratio determined by integration was compared to the known ratio. All ^{1}H NMR spectra were taken at 500 MHz with 32 scans and a delay of 10 seconds. All spectra were processed in MNova software with application of an auto-phase correction and a Bernstein polynomial fit baseline correction, followed by manual peak integration.

Two 0.196 M stock solutions of 3-chloro-4-hydroxyphenylBpin (meta borylated **2a**) and 4-chloro-3-hydroxyphenylBpin (para borylated **2a**) were prepared as follows: A mass of 50.0 mg of commercial 3-chloro-4-hydroxyphenylBpin (meta-**2a**) was dissolved in $CDCl_3$ in a 1.0 mL volumetric flask and $CDCl_3$ was added up to the mark. A mass of 100.0 mg of commercial 4-chloro-3-hydroxyphenylBpin (para-**2a**) was dissolved in $CDCl_3$ in a 2.0 mL volumetric flask and $CDCl_3$ was added up to the mark.

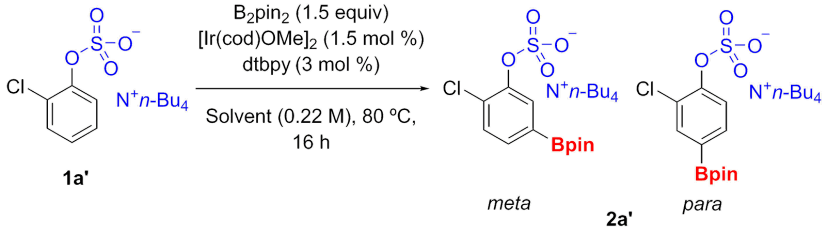
A volume of 6 µL of meta-**2a** stock solution was diluted with $CDCl_3$ to 1.0 mL in a 1.0 mL volumetric flask, resulting in a 1.18 x 10^{-3} M solution. A volume of 600 µL of this solution was transferred into an NMR tube, making 7.0 x 10^{-7} mols of the meta-**2a** compound present in the sample. A ^{1}H NMR spectrum was taken. Meta-**2a** was clearly observed and all peaks integrated properly, with the data as follows: ^{1}H NMR (500 MHz, $CDCl_3$ δ 7.43 (d, J = 1.2 Hz, 1H), 7.34 – 7.27 (m, 2H), 5.47 (s, 1H), 1.33 (s, 12H). The ^{1}H data for the commercial sample of para-**2a** was as follows: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 1.5 Hz, 1H), 7.62 (dd, J = 8.1, 1.5 Hz, 1H), 7.01 (d, J = 8.1 Hz, 1H), 5.75 (s, 1H), 1.33 (s, 12H).

A sequence of additions of 50 microliters of para-**2a** stock solution was added directly into the NMR tube and NMR spectra were taken after each addition. For each 50 microliters of stock solution added, 9.8 x 10^{-6} mols of para compound was introduced into the NMR tube. This was repeated 4 times for a total of 3.92 x 10^{-5} mols para-**2a** compound to 7.0 x 10^{-7} mols of meta-**2a** compound, a 56-fold excess of para-**2a** compound. The integration of the peak at 7.43 ppm of the meta-**2a** compound was compared to the integration of the peak at 7.77 ppm of the para-**2a** compound for all determinations of para:meta ratio. The results are shown in Table S1. All NMR spectra are shown in the NMR data section.

Table S1: Integration of known ratios of para-2a to meta-2a

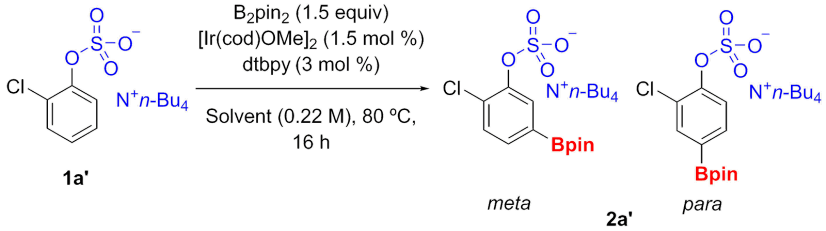
entry	mols para-**2a**	mols meta-**2a**	calculated para:meta ratio	integrated para:meta ratio
1	0	7.0×10^{-7}	--	--
2	9.8×10^{-6}	7.0×10^{-7}	14:1	14.10:1.00
3	1.96×10^{-5}	7.0×10^{-7}	28:1	27.26:1.00
4	2.94×10^{-5}	7.0×10^{-7}	42:1	44.19:1.00
5	3.92×10^{-5}	7.0×10^{-7}	56:1	54.68:1.00

Optimization of Conditions: Solvent Effect



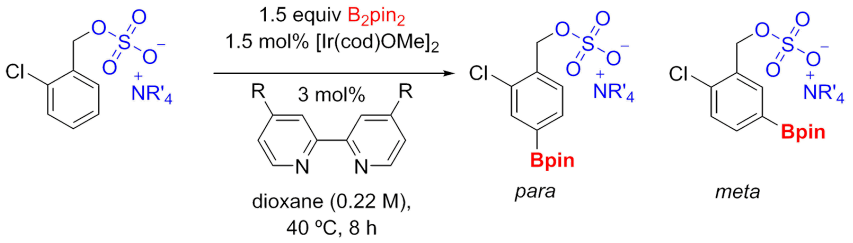
Entry	Solvent	Conversion	para:meta
1	hexane	91	5.5:1
2	cyclohexane	100	4.8:1
3	THF	100	5.6:1
4	dioxane	100	5.9:1

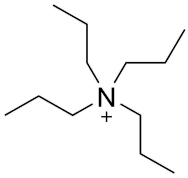
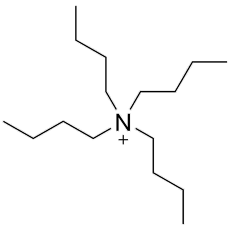
Optimization of Conditions: Ligand-Counterion Effect



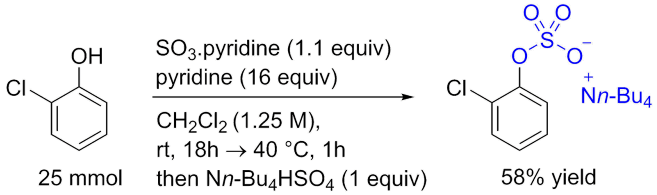
	L1	L4	L5
Et_4N^+	100% para : meta = 5:1 (dioxane, 40 °C)	76% para : meta = 5:1 (dioxane, 40 °C)	100% para : meta = 6:1 (dioxane, 40 °C)
$n\text{-}Pr_4N^+$	100% para: meta = 8:1 (dioxane, 40 °C)	76% para: meta = 10:1 (dioxane, 40 °C)	100% para : meta = 21:1 (dioxane, 40 °C)
$n\text{-}Bu_4N^+$	100% para : meta = 6:1 (THF, 80 °C)	96% para : meta = 10:1 (THF, 80 °C)	100% para : meta = 17:1 (dioxane, 40 °C)

Optimization of Conditions: Benzyl sulfate alcohols



Entry	NR_4	Ligand	Conversion	para:meta ratio
1		R=t-Bu (**L1**)	100	8:1
2		R=Me (**L4**)	87	11:1
3		R=OMe (**L5**)	100	18:1
4		R=NMe_2 (**L8**)	100	13:1
5		R=t-Bu (**L1**)	100	9:1
6		R=Me (**L4**)	100	13:1
7		R=OMe (**L5**)	100	15:1
8		R=NMe_2 (**L8**)	100	14:1

Synthesis of tetrabutylammonium 2-chlorophenyl sulfate (1a′)

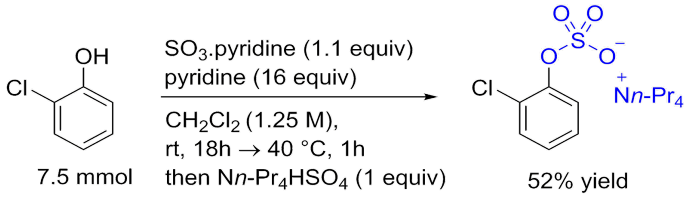


2-Chlorophenol (3.21 g, 25 mmol) and SO_3•pyridine complex (4.39 g, 27.5 mmol) were placed in a 100 mL round bottom flask. Pyridine (33 mL) and dry dichloromethane (20 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (300 mL) was added and the mixture was washed once with dichloromethane (1 x 300 mL). The aqueous phase was treated with tetrabutylammonium hydrogensulfate (8.45 g, 25 mmol) and stirred for 1 h. The solution was extracted with

dichloromethane (3 x 300 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum **1a′** (6.56 g, 58% yield) was isolated as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.15 (td, *J* = 7.9, 1.6 Hz, 1H), 6.95 (td, *J* = 7.9, 1.5 Hz, 1H), 3.23–3.01 (m, 8H), 1.64–1.45 (m, 8H), 1.35 (m, 8H), 0.93 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 129.7, 127.3, 125.2, 123.8, 122.0, 58.3, 23.8, 19.6, 13.6. HRMS (ESI) *m/z* calc for $C_6H_4ClO_4S$ $[M–N\textit{n}\text{-}Bu_4]^-$ 206.9519, found 206.9722

Synthesis of tetrapropylammonium 2-chlorophenyl sulfate (1a)

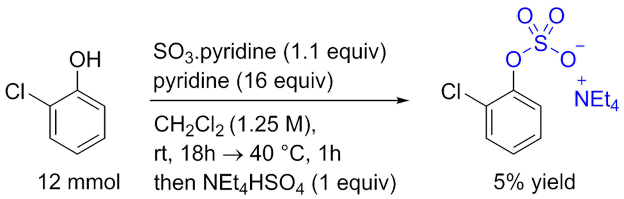


2-Chlorophenol (0.964 g, 7.5 mmol) and SO_3•pyridine complex (1.31 g, 8.2 mmol) were placed in a 100 mL round bottom flask. Pyridine (10 mL) and dry dichloromethane (6 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (90 mL) was added and the mixture was washed once with dichloromethane (1 x 90 mL). The aqueous phase was treated with tetrapropyl ammonium hydrogensulfate (2.12 g, 7.5 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 90 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1a**) was obtained as a white solid (1.53 g, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.15 (td, *J* = 8.0, 1.7 Hz, 1H), 6.95 (td, *J* = 7.8, 1.5 Hz, 1H), 3.15–3.01 (m, 8H), 1.59 (m, *J* = 17.0, 7.3 Hz, 8H), 0.91 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 129.7, 127.3,

125.4, 124.0, 122.2, 60.2, 15.5, 10.7. HRMS (ESI) *m/z* calc for $C_6H_4ClO_4S$ $[M–N\textit{n}\text{-}Bu_4]^-$ 206.9519, found 206.9505

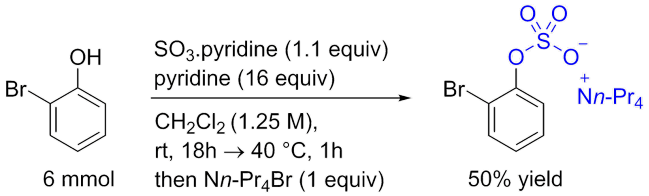
Synthesis of tetraethylammonium 2-chlorophenyl sulfate (1a″)



2-Chlorophenol (1.54 g, 12 mmol) and SO_3•pyridine complex (2.1 g, 12.2 mmol) were placed in a 100 mL round bottom flask. Pyridine (16 mL) and dry dichloromethane (10 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (140 mL) was added and the mixture was washed once with dichloromethane (1 x 140 mL). The aqueous phase was treated with tetraethyl ammonium hydrogensulfate (2.73 g, 12 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The concentrated oil was dissolved in dichloromethane (50 mL) and washed once with 0.1 M NaOH aq. (1 x 50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was concentrated by rotary evaporation. This hexane/ether process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1a"**) was obtained as a white solid (216 mg, 5% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, J = 8.0, 1.5 Hz, 1H), 7.32 (dd, J = 8.0, 1.6 Hz, 1H), 7.18 (td, J = 8.0, 1.6 Hz, 1H), 7.00 (td, J = 8.0, 1.5 Hz, 1H), 3.21 (q, J = 7.3 Hz, 8H), 1.21 (t, J = 7.3, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 129.8, 127.5, 125.6, 124.3, 122.4, 52.3, 7.5. HRMS (ESI) *m/z* calcd for $C_6H_4ClO_4S$ $[M–NEt_4]^-$ 206.9519, found 206.8556.

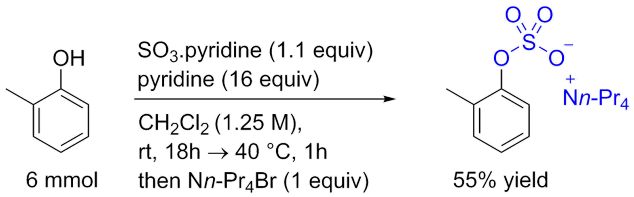
Synthesis of tetrapropylammonium 2-bromophenyl sulfate (1b)



2-Bromophenol (1.038 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes were added and the suspension was concentrated by rotary evaporation. This process was repeated the product was obtained as a white solid. After overnight drying under high vacuum (**1b**) was obtained as a white solid (1.31 g, 50% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.3, 1.5 Hz, 1H), 7.41 (dd, J = 8.0, 1.6 Hz, 1H), 7.14 (ddd, J = 8.3, 8.0, 1.6 Hz, 1H), 6.84 (td, J = 8.0, 1.5 Hz, 1H), 3.11–2.82 (m, 8H), 1.52 (m, 8H), 0.84 (t, J = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 132.8, 128.0, 124.3, 121.8, 114.7, 60.1, 15.4, 10.7. HRMS (ESI) *m/z* calcd for $C_6H_4BrO_4S$ $[M–Nn\text{-}Pr_4]^-$ 250.9014, found 250.9032.

Synthesis of tetrapropylammonium 2-methylphenyl sulfate (1c)

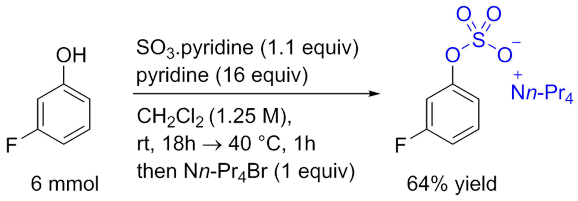


2-Methylphenol (0.645 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were

added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes were added and the suspension was concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1c**) was obtained as a yellowish white solid (1.24 g, 55% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.7, 1.2 Hz, 1H), 7.10 (dd, J = 7.7, 1.7 Hz, 1H), 7.06 (td, J = 7.7, 1.7 Hz, 1H), 6.95 (td, J = 7.7, 1.2 Hz, 1H), 3.17 – 2.88 (m, 8H), 2.32 (s, 3H), 1.69 – 1.43 (m, 8H), 0.92 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 131.1, 130.5, 126.1, 123.8, 122.0, 60.1, 16.9, 15.5, 10.7. HRMS (ESI) *m/z* calcd for $C_7H_7O_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 187.0065, found 187.0069.

Synthesis of tetrapropylammonium 3-fluorophenyl sulfate (1d)

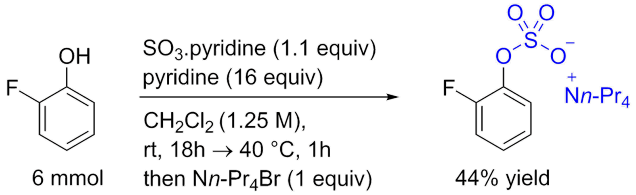


3-Fluorophenol (0.673 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes were added and the suspension was concentrated by rotary evaporation. This

process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1d**) was obtained as a white solid (1.46 g, 64% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (td, J = 8.2, 6.8 Hz, 1H), 7.14 (dt, J = 10.6, 2.4 Hz, 1H), 7.07 (ddd, J = 8.2, 2.4, 0.9 Hz, 1H), 6.74 (tdd, J = 8.2, 2.4, 0.9 Hz, 1H), 3.15–2.90 (m, 8H), 1.68–1.51 (m, 8H), 0.94 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (d, J = 244.6 Hz), 154.8 (d, J = 11.2 Hz), 129.6 (d, J = 9.6 Hz), 116.5 (d, J = 2.9 Hz), 110.1 (d, J = 21.1 Hz), 108.3 (d, J = 24.3 Hz), 60.3, 15.5, 10.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ –115.73 (m) HRMS (ESI) *m/z* calcd. for $C_6H_4FO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 190.9814, found 190.9821.

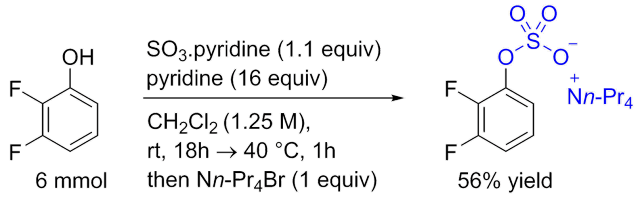
Synthesis of tetrapropylammonium 2-fluorophenyl sulfate (1e)



2-Fluorophenol (0.673 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1e**) was obtained as a white solid (1.00 g, 44% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71–7.60 (m, 1H), 7.07–6.94 (m, 3H), 3.23–3.03 (m, 8H), 1.76 – 1.46 (m, 8H), 0.93 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3 (d, J = 247.1 Hz), 141.2 (d, J = 11.3 Hz), 124.2 (d, J = 7.1 Hz), 124.0 (d, J = 3.8 Hz), 123.7, 116.0 (d, J = 18.8 Hz), 60.2, 15.5, 10.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ –133.9. HRMS (ESI) *m/z* calcd. for $C_6H_4FO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 190.9814, found 190.9830.

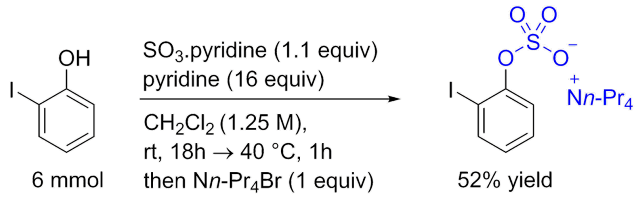
Synthesis of tetrapropylammonium 2,3-difluorophenyl sulfate (1f)



2,3-Difluorophenol (0.78 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1f**) was obtained as a white solid (1.33 g, 56% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (ddt, J = 8.4, 6.9, 1.6 Hz, 1H), 6.92 (tdd, J = 8.4, 6.2, 2.2 Hz, 1H), 6.82 (dddd, J = 9.7, 8.4, 6.8, 1.6 Hz, 1H), 3.23 – 2.95 (m, 8H), 1.60 (m, 8H), 0.91 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0 (dd, J = 246.4, 11.0 Hz), 143.2 (dd, J = 248.2, 14.0 Hz), 142.8 (dd, J = 8.7, 2.6 Hz), 122.7 (dd, J = 8.3, 5.1 Hz), 118.7 (d, J = 3.3 Hz), 111.7 (d, J = 17.1 Hz), 60.3, 15.4, 10.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ –141.1 (ddd, J = 20.3, 9.7, 6.2 Hz), –158.23 (dt, J = 20.3, 6.8 Hz). HRMS (ESI) *m/z* calcd. for $C_6H_3F_2O_4S$ [M–N*n*-Pr_4]$^-$ 208.9720, found 208.8767.

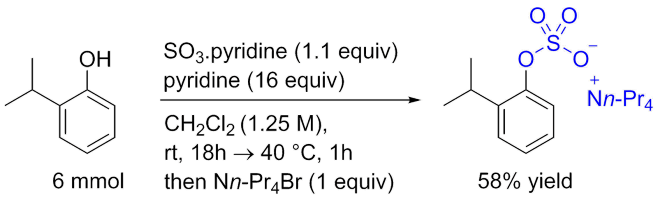
Synthesis of tetrapropylammonium 2-iodophenyl sulfate (1g)



2-Iodophenol (1.32 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1g**) was obtained as a white solid (1.51 g, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) 7.65 (m, 2H), 7.17 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 6.70 (td, J = 7.6, 1.5 Hz, 1H), 3.15–2.81 (m, 8H), 1.68–1.22 (m, 8H), 0.84 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 138.9, 129.1, 124.8, 120.7, 89.5, 60.2, 15.5, 10.8. HRMS (ESI) *m/z* calcd. for $C_6H_4IO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 298.8875, found 298.8890.

Synthesis of tetrapropylammonium 2-isopropylphenyl sulfate (1h)

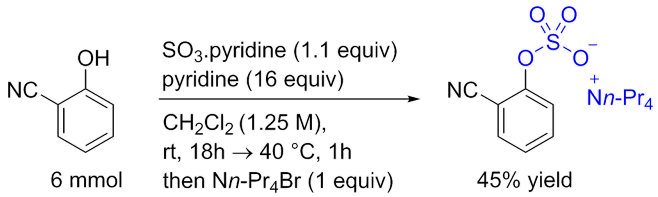


2-Isopropylphenol (0.645 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid.

After overnight drying under high vacuum (**1h**) was obtained as a white solid (1.39 g, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.16 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.01 (td, *J* = 7.3, 2.1 Hz, 1H), 6.98 (td, *J* = 7.3, 1.6 Hz, 1H), 3.53 (p, *J* = 6.9 Hz, 1H), 3.13 – 2.94 (m, 8H), 1.59 – 1.44 (m, 8H), 1.14 (d, *J* = 7.0 Hz, 6H), 0.88 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 140.9, 125.9, 125.7, 123.9, 121.4, 60.1, 26.4, 23.3, 15.4, 10.7. HRMS (ESI) *m/z* calcd. for $C_9H_{11}O_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 215.0378, found 215.0397.

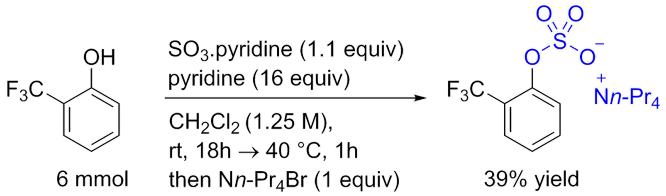
Synthesis of tetrapropylammonium 2-cyanophenyl sulfate (1i)



2-Cyanophenol (0.714 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1i**) was obtained as a white solid (1.03 g, 45% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.6, 1.1 Hz, 1H), 7,46 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.45 (td, *J* = 7.6, 1.8 Hz, 1H), 7.05 (td, *J* = 7.6, 1.1 Hz, 1H), 3.26 – 2.73 (m, 8H), 1.61 (m, 8H), 0.90 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 133.9, 132.9, 123.2, 121.0, 116.9, 104.6, 60.2, 15.5, 10.7. HRMS (ESI) *m/z* calcd. for $C_7H_4NO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 197.9861, found 197.8931.

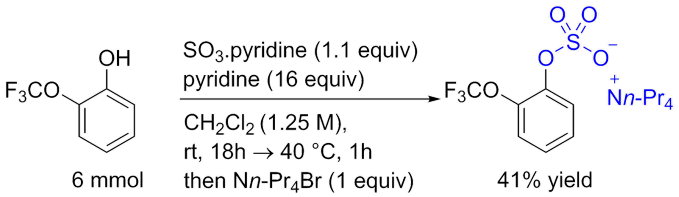
Synthesis of tetrapropylammonium 2-(trifluoromethyl)phenyl sulfate (1j)



2-(Trifluoromethyl)phenol (0.973 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1j**) was obtained as a white solid (0.991 g, 39% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8 Hz, 1H), 7.46 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 (td, J = 8.0, 1.6 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 3.13–2.93 (m, 8H), 1.67–1.45 (m, 8H), 0.85 (t, J = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9 (q, J = 1.8 Hz), 132.8 (s), 126.2 (q, J = 5.0 Hz), 123.5 (q, J = 272.4 Hz), 122.2 (s), 120.7 (s), 120.4 (q, J = 30.6 Hz), 60.1, 15.4, 10.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ –64.1. HRMS (ESI) *m/z* calcd. for $C_7H_4F_3O_4S$ $[M–Nn\text{-}Pr_4]^-$ 240.9782, found 240.9784.

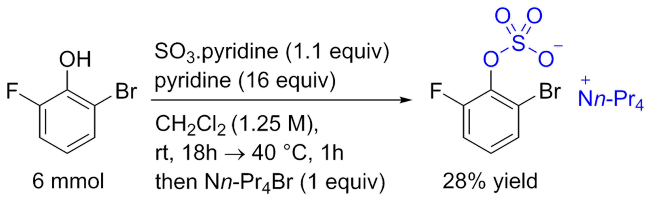
Synthesis of tetrapropylammonium 2-(trifluoromethoxy)phenyl sulfate (1k)



2-(Trifluoromethoxy)phenol (1.07 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1k**) was obtained as a white solid (1.09 g, 41% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, J = 8.2, 1.6 Hz, 1H), 7.23 – 7.10 (m, 2H), 7.01 (t, J = 7.1 Hz, 1H), 3.27 – 2.89 (m, 8H), 1.85 – 1.40 (m, 8H), 0.91 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 139.68, 127.3, 123.3, 122.4, 121.9, 120.6 (q, J = 257 Hz), 60.2, 15.4, 10.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.5. HRMS (ESI) *m/z* calcd. for $C_7H_4F_3O_5S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 256.9732, found 256.9768.

Synthesis of tetrapropylammonium 2-bromo-6-fluorophenyl sulfate (1l)

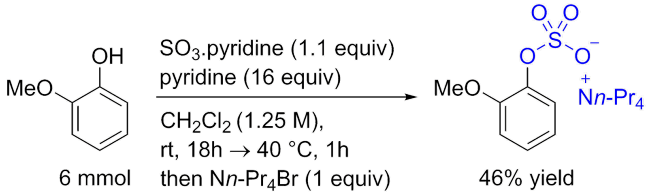


2-Bromo-6-fluorophenol (1.15 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the

concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1l**) was obtained as a white solid (0.78 g, 28% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.2 Hz, 1H), 6.97 (t, J = 8.2 Hz, 1H), 6.89 (td, J = 8.2, 5.1 Hz, 1H), 3.16 – 2.96 (m, 8H), 1.63 – 1.42 (m, 8H), 0.89 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7 (d, J = 253.7 Hz), 139.7 (d, J = 14.6 Hz), 128.3 (d, J = 3.5 Hz), 125.5 (d, J = 8.1 Hz), 119.8 (d, J = 1.9 Hz), 115.7 (d, J = 19.9 Hz), 60.2, 15.5, 10.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ –124.4 (dd, J = 8.2, 5.1 Hz). HRMS (ESI) *m/z* calcd. for $C_6H_3BrFO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 268.8919, found 268.8919.

Synthesis of tetrapropylammonium 2-methoxyphenyl sulfate (1m)

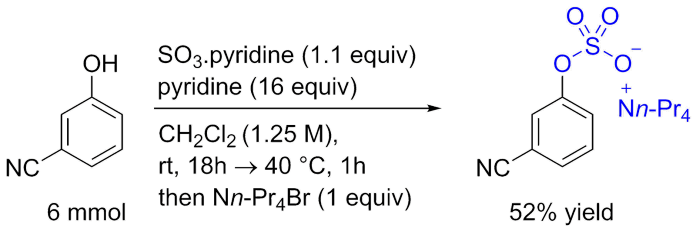


2-Methoxyphenol (0.74 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1m**) was obtained as a white solid (1.08 g, 46% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, J = 8.0, 1.6 Hz, 1H), 6.97 (ddd, J = 8.0, 7.3, 1.6 Hz, 1H), 6.87 – 6.80 (m, 2H), 3.79 (s, 3H), 3.26 – 3.04 (m, 8H), 1.68 – 1.46 (m, 8H), 0.92 (t, J = 7.3

Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.2, 143.0, 123.8, 121.9, 120.6, 113.0, 60.2, 56.3, 15.5, 10.7. HRMS (ESI) *m/z* calcd. for $C_7H_7O_5S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 203.0014, found 203.0053.

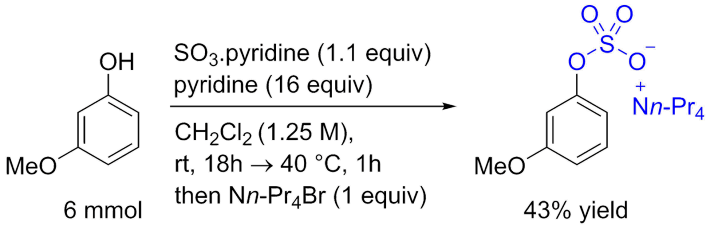
Synthesis of tetrapropylammonium 3-cyanophenyl sulfate (1n)



3-Cyanophenol (0.72 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1n**) was obtained as a white solid (1.19 g, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 2.4, 1.4 Hz, 1H), 7.53 (ddd, J = 8.2, 2.4, 1.3 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.32 (dt, J = 7.6, 1.4 Hz, 1H), 3.24 – 2.94 (m, 8H), 1.60–1.72 (m, 8H), 0.96 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 130.0, 127.0, 125.8, 124.0, 118.8, 112.5, 60.4, 15.5, 10.7. HRMS (ESI) *m/z* calcd. for $C_7H_4NO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 197.9861, found 197.9884.

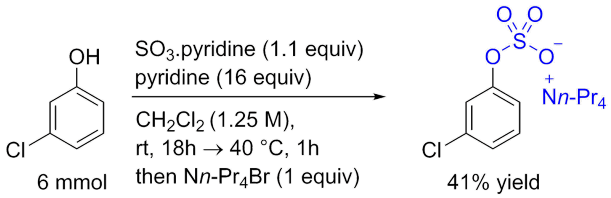
Synthesis of tetrapropylammonium 3-methoxyphenyl sulfate (1o)



3-Methoxyphenol (0.74 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1o**) was obtained as a white solid (1.01 g, 43 yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (t, J = 8.2 Hz, 1H), 6.96-6.85 (m, 2H), 6.57 (dt, J = 8.2, 1.8 Hz, 1H), 3.71 (s, 3H), 3.11 – 3.03 (m, 8H), 1.63 – 1.46 (m, 8H), 0.91 (t, J = 7.3 Hz, 12H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 154.7, 129.1, 113.3, 109.2, 107.0, 60.2, 55.3, 15.5, 10.7. HRMS (ESI) *m/z* calcd. for $C_7H_7O_5S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 203.0014, found 203.0050.

Synthesis of tetrapropylammonium 3-chlorophenyl sulfate (1p)

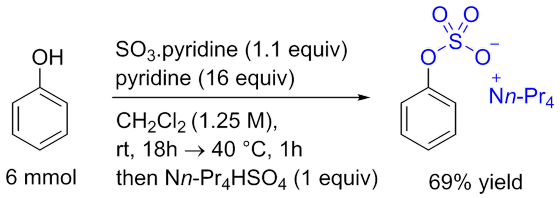


3-Chlorophenol (0.77 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary

evapoation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1p**) was obtained as a white solid (0.96 g, 41% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, J = 2.1 Hz, 1H), 7.18 – 7.12 (m, 2H), 6.99 (dt, J = 6.5, 2.1 Hz, 1H), 3.20 – 2.91 (m, 8H), 1.64 – 1.46 (m, 8H), 0.91 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 133.7, 129.7, 123.4, 121.0, 119.2, 60.1, 15.3, 10.6. HRMS (ESI) *m/z* calcd. for $C_6H_4ClO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 206.9519, found 206.9544.

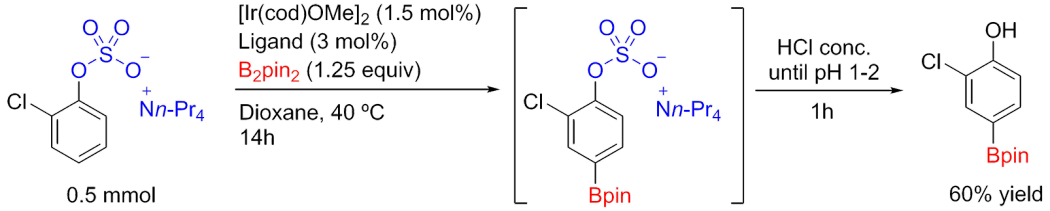
Synthesis of tetrapropylammonium 1-phenyl sulfate (1q)



Phenol (0.56 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at 40 °C for 7 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in a clear oil. To the concentrated oil, hexanes and ether were added and the suspension was again concentrated by rotary evaporation. This process was repeated until the product was obtained as a white solid. After overnight drying under high vacuum (**1q**) was obtained as a white solid (1.50 g, 69% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.17 (m, 2H), 7.01 (td, J = 7.0, 5.4 Hz, 1H), 3.14 – 2.89 (m, 8H), 1.70 – 1.35 (m, 8H), 0.89 (t, J = 7.3 Hz, 12H) . ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 128.8, 123.4, 121.0, 60.1, 15.4, 10.7. HRMS (ESI) *m/z* calcd. for $C_6H_5O_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 172.9909, found 173.0117.

Para borylation of tetrapropyl ammonium 2-chlorophenyl sulfate (2a)



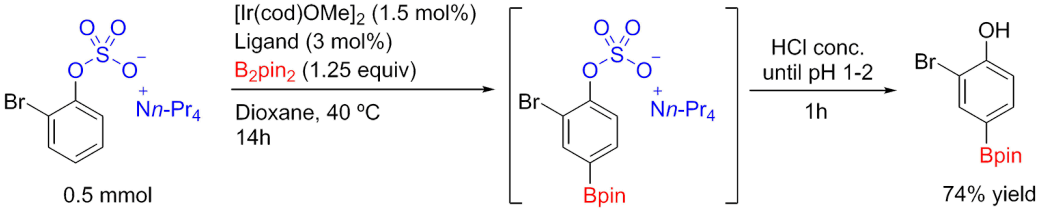
crude reaction mixture isomer ratio (NMR) = 22:1
96% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-chlorophenyl sulfate (197 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 14 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and washed with hexanes (0.5 mL). The hexane layer was decanted, and the remaining solution subjected to chromatographic separation with silica gel ($CHCl_3$ as eluent) to give 76 mg of *para* borylated 2-chlorophenol with traces of the *meta* isomer (< 2%) as a white solid (60% yield, mp 118.6–120.1 °C). The NMR data were consistent with previously reported NMR values.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 1.4 Hz, 1H), 7.62 (dd, J = 8.1, 1.4 Hz, 1H), 7.00 (d, J = 8.1 Hz, 1H), 6.05 (bs, 1H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 135.7, 135.1, 119.8, 115.8, 84.0, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.2. HRMS (ESI) *m/z* calcd. for $C_{12}H_{15}BClO_3$ $[M–H]^-$ 253.0803, found 253.1007.

Performing the same borylation with tetraethylammonium 2-chlorophenyl sulfate gave a para:meta ratio of 6:1, while borylation of tetrabutylammonium 2-chloro sulfate gave a para:meta ratio of 17:1.

Para borylation of tetrapropyl ammonium 2-bromophenyl sulfate (2b)

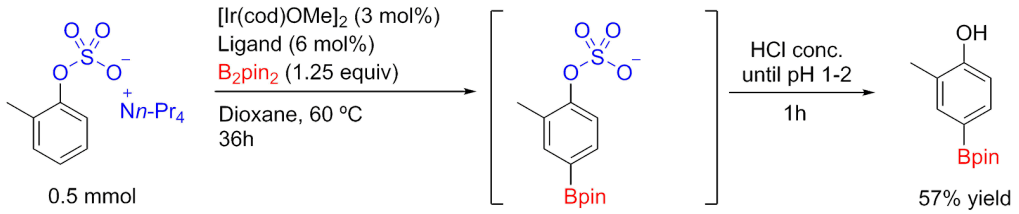


crude reaction mixture isomer ratio (NMR) = 23:1
98% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-bromophenyl sulfate (219 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 14 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and washed with hexanes (0.5 mL). The hexane layer was decanted, and the remaining solution subjected to chromatographic separation with silica gel ($CHCl_3$ as eluent) to give 110 mg of *para* borylated 2-bromophenol with traces of the *meta* isomer (< 2%) as a white solid (74% yield, mp 118.4–119.6 °C). The NMR data were consistent with previously reported values.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 1.5 Hz, 1H), 7.64 (dd, J = 8.1, 1.5 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 5.92 (bs, 1H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 138.7, 135.9, 115.7, 110.3, 84.0, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.1. HRMS (ESI) *m/z* calcd. for $C_{12}H_{15}BBrO_3$ $[M–H]^-$ 297.0298, found 297.0304.

Para borylation of tetrapropyl ammonium 2-methylphenyl sulfate (2c)

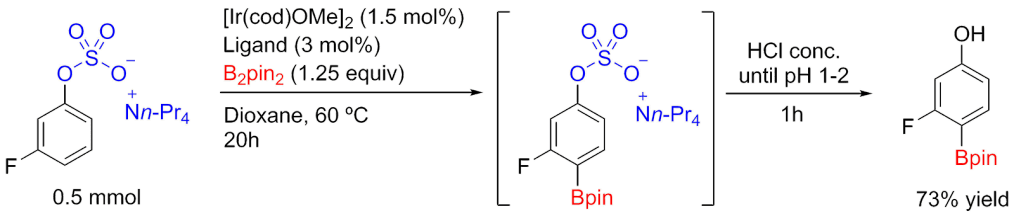


crude reaction mixture isomer ratio (NMR) = 11:1
73% conversion

2-Methylphenyl sulfate (187 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (10 mg, 3 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and washed with hexanes (0.5 mL). The hexane layer was decanted, and the remaining solution subjected to chromatographic separation with silica gel ($CHCl_3$ as eluent) to give 67 mg of *para* borylated 2-methylphenol with traces of the *meta* isomer (*para*:*meta* = 39:1) as a white solid (57% yield, mp 100.0–102.4 °C). The NMR values were consistent with previously reported NMR values.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 1.7 Hz, 1H), 7.54 (dd, J = 7.9, 1.6 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 5.81 (bs, 1H), 2.24 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 137.9, 134.2, 123.4, 114.5, 83.7, 24.8, 15.5. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.6. HRMS (ESI) m/z calcd for $C_{13}H_{18}BO_3$ $[M–H]^-$ 233.1349, found 233.1367.

Para borylation of tetrapropyl ammonium 3-fluorophenyl sulfate (2d)



crude reaction mixture isomer ratio (NMR) = 2.3:1
>99.9% conversion

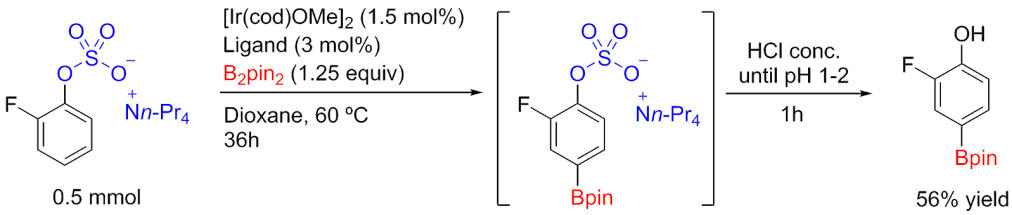
In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 3-fluorophenyl sulfate (189 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 20 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and washed with hexanes (0.5 mL). The hexane layer was decanted, and the remaining solution subjected to

chromatographic separation with silica gel (12% EtOAc in $CHCl_3$ as eluent) to give 87 mg of a mixture *para* borylated 3-fluorophenol with the *meta* isomer (*para*:*meta* = 3:1) as a white solid (73% yield, mp 89.4-91.2 °C) The NMR values were consistent with previously reported values.[6]

Para: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.2, 7.1 Hz, 1H), 6.77 (s, 1H), 6.62 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.52 (dd, *J* = 10.9, 2.2 Hz, 1H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5 (d, *J* = 250.4 Hz), 160.7 (d, *J* = 12.3 Hz), 138.0 (d, *J* = 10.2 Hz), 111.5 (d, *J* = 2.6 Hz), 103.0 (d, *J* = 27.3 Hz), 84.0, 24.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ –103.8 (dd, *J* = 10.9, 7.1 Hz). HRMS (ESI) m/z calcd for $C_{12}H_{15}BFO_3$ $[M–H]^-$ 237.1098, found 237.1320.

Meta: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (m, 2H), 6.68 (dt, *J* = 9.4, 2.4 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3 (d, *J* = 246.6 Hz), 156.7 (d, *J* = 10.5 Hz), 117.1 (d, *J* = 2.5 Hz), 113.0 (d, *J* = 19.8 Hz), 106.2 (d, *J* = 24.4 Hz), 84.4, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ –115.7 (t, *J* = 9.4 Hz). HRMS (ESI) m/z calcd for $C_{12}H_{15}BFO_3$ $[M–H]^-$ 237.1098, found 237.1320.

Para borylation of tetrapropyl ammonium 2-fluorophenyl sulfate (2e)



crude reaction mixture isomer ratio (NMR) = 2.3:1:0.2 di-meta
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-fluorophenyl sulfate (189 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 36 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and washed with hexanes (0.5 mL). The hexane layer was decanted, and the remaining solution subjected to

chromatographic separation with silica gel (10% EtOAc in $CHCl_3$ as eluent) to give 67 mg of a mixture of *para* and *meta* borylated 2-fluorophenol (*para*:*meta* = 11:1) as a white solid (56% yield, mp 85.0-91.0 °C). The NMR data were consistent with previously reported NMR values, designated as compound **22a** in the cited paper.[7]

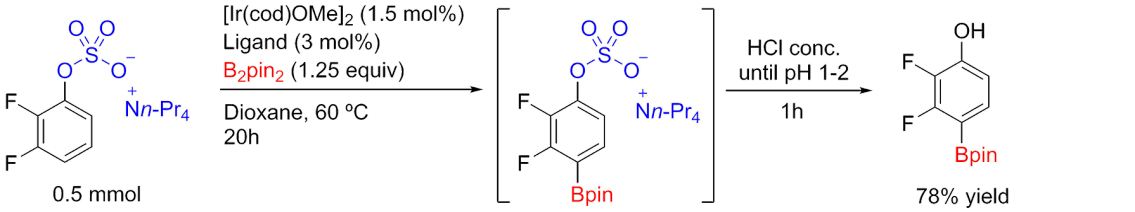
Para:

^{1}H NMR (500 MHz, C_6D_6) δ 7.81 (dd, J = 11.1, 1.4 Hz, 1H), 7.71 (dd, J = 8.1, 1.4 Hz, 1H), 6.84 (t, J = 8.1 Hz, 1H), 1.08 (s, 12H). ^{13}C NMR (126 MHz, C_6D_6) δ 151.1 (d, J = 239.2 Hz), 146.9 (d, J = 13.9 Hz), 132.1 (d, J = 3.4 Hz), 121.7 (d, J = 15.8 Hz), 117.2 (d, J = 1.7 Hz), 83.6, 24.4. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ –142.97 (dd, J = 11.1, 8.1 Hz). HRMS (ESI) m/z calcd for $C_{12}H_{15}BFO_3$ $[M–H]^-$ 237.1098, found 237.1097.

Meta:

^{1}H NMR (500 MHz, C_6D_6) δ 7.49 (ddd, J = 7.4, 5.0, 1.7 Hz, 1H), 6.93 (ddd, J = 8.7, 8.0, 1.7 Hz, 1H), 6.74 (ddd, J = 8.0, 7.4, 0.7 Hz, 1H).^{13}C NMR (126 MHz, C_6D_6) δ 155.6 (d, J = 243.3 Hz), 143.8 (d, J = 16.1 Hz), 124.4 (d, J = 3.9 Hz), 120.6 (d, J = 2.8 Hz), 83.7, 24.4 (owing to the small amount of the isomer in the mixture some peaks were not observed). ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ –132.41 (dd, J = 8.7, 5.0 Hz). HRMS (ESI) m/z calcd for $C_{12}H_{15}BFO_3$ $[M–H]^-$ 237.1098, found 237.1097.

Para borylation of tetrapropyl ammonium 2,3-difluorophenyl sulfate (2f)



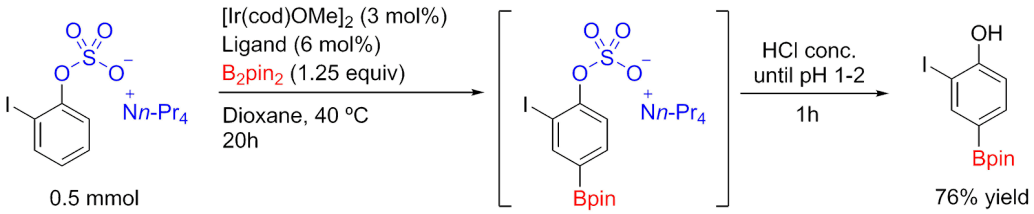
crude reaction mixture isomer ratio (NMR) = 23:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2,3-difluorophenyl sulfate (198 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 20 h, an aliquot of the reaction mixture was taken and analyzed

directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and subjected directly to chromatographic separation with silica gel (10% EtOAc in $CHCl_3$ as eluent) to give 100 mg of a mixture of *para* borylated 2,3-difluorophenol with the *meta* isomer (para:meta = 30:1) as a white solid (78% yield, mp 125.2–125.9 °C)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (ddd, J = 8.3, 6.0, 2.2 Hz, 1H), 6.75 (ddd, J = 8.3, 7.1, 1.6 Hz, 1H), 5.95 (bs, 1H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3 (dd, J = 251.9, 9.6 Hz), 148.2 (dd, J = 11.0, 2.9 Hz), 139.9 (dd, J = 240.9, 16.5 Hz), 130.8 (dd, J = 9.0, 4.8 Hz), 112.7 (d, J = 2.9 Hz), 84.2, 24.6. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ –131.0 (dd, J = 21.3, 6.0 Hz), –167.9 (ddd, J = 21.3, 7.1, 2.2 Hz). HRMS (ESI) m/z calcd for $C_{12}H_{14}BF_2O_3$ $[M–H]^-$ 255.1004, found 254.9811.

Para borylation of tetrapropyl ammonium 2-iodophenyl sulfate (2g)

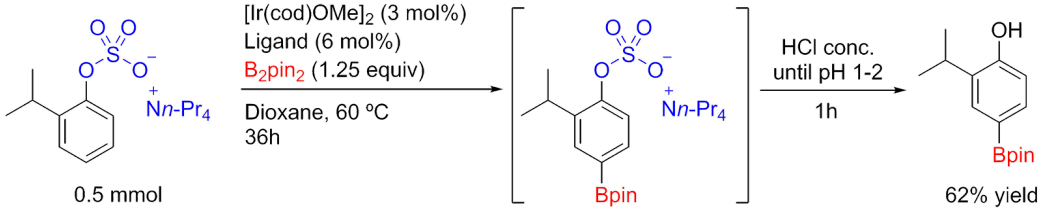


crude reaction mixture isomer ratio (NMR) = 22:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-iodophenyl sulfate (243 mg, 0.5 mmol), $[[Ir(cod)(OMe)]_2$ (10 mg, 3 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 20 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and subjected directly to chromatographic separation with silica gel ($CHCl_3$ as eluent) to give 132 mg of *para* borylated 2-iodophenol with traces of the meta isomer (< 2%) as a white solid (76% yield, mp 119.7–121.2 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.89 (bs, 1H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 145.2, 136.9, 114.8, 85.9, 84.0, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.8. HRMS (ESI) m/z calcd for $C_{12}H_{15}BIO_3$ $[M–H]^-$ 345.0159, found 345.0211.

Para borylation of tetrapropyl ammonium 2-isopropylphenyl sulfate (2h)

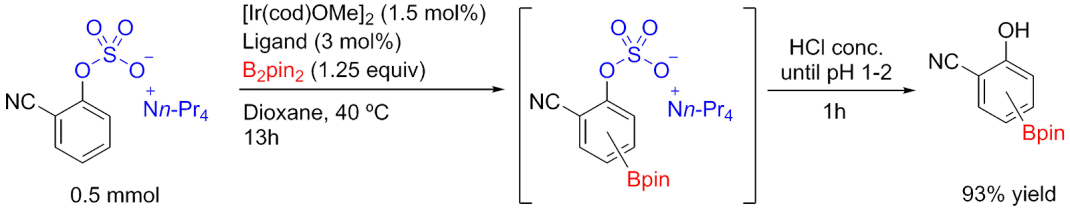


crude reaction mixture isomer ratio (NMR) = 25:1
62% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-isopropylphenyl sulfate (201 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (10 mg, 3 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 36 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and subjected directly to chromatographic separation with silica gel (2% EtOAc in $CHCl_3$ as eluent) to give 81 mg of *para* borylated 2-isopropylphenol with traces of the meta isomer (*para*:*meta* = 23:1) as a white solid (62% yield, mp 138.3–145.9 °C). The NMR values were consistent with previously reported NMR values.[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.6 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.82 (s, 1H), 3.23 (hept, *J* = 6.9 Hz, 1H), 1.36 (s, 12H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 134.0, 133.9, 133.4, 114.8, 83.7, 27.1, 24.8, 22.4. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7. HRMS (ESI) m/z calcd for $C_{15}H_{22}BO_3$ $[M–H]^-$ 261.1662, found 261.1696.

Para borylation of tetrapropylammonium 2-cyanophenyl sulfate (2i)



crude reaction mixture isomer ratio (NMR): para:meta:dimeta = 7.5:1:0.4
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-cyanophenyl sulfate (193 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 13 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel (4% EtOAc in $CHCl_3$ as eluent). The fractions containing product were collected and concentrated to give 117 mg of a mixture of *para* borylated 2-cyanophenol with the *meta* and *dimeta* isomers (*para*:*meta*:*dimeta* = 1:7:0.4) as a white solid (93% yield, mp 156.6–162.8 °C). The NMR data were consistent with previously reported NMR values.[9]

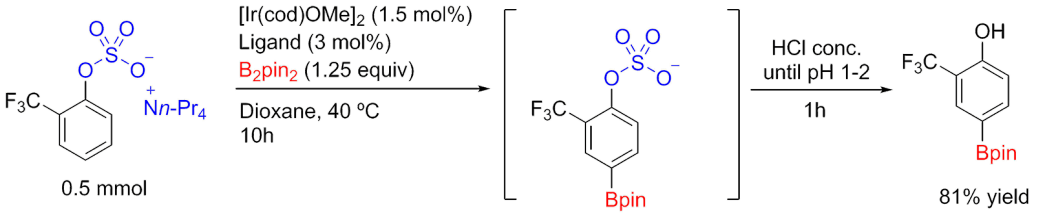
Para:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 1.7 Hz, 1H), 8.15-7.55 (bs, 1H), 7.83 (dd, J = 8.3, 1.7 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 140.9, 140.4, 116.5, 115.8, 99.4, 84.3, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.4. HRMS (ESI) m/z calcd for $C_{13}H_{15}BNO_3$ $[M–H]^-$ 244.1145, found 244.0003.

Meta:

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-7.55 (bs, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.39 (d, J = 0.9 Hz, 1H), 7.34 (dd, J = 7.6, 0.9 Hz, 1H), 1.32 (s, 12H). Carbon peaks were indistinguishable due to the small amount of the meta isomer in the mixture. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.4. HRMS (ESI) m/z calcd for $C_{13}H_{15}BNO_3$ $[M–H]^-$ 244.1145, found 244.0003.

Para borylation of tetrapropyl ammonium 2-trifluoromethylphenyl sulfate (2j)

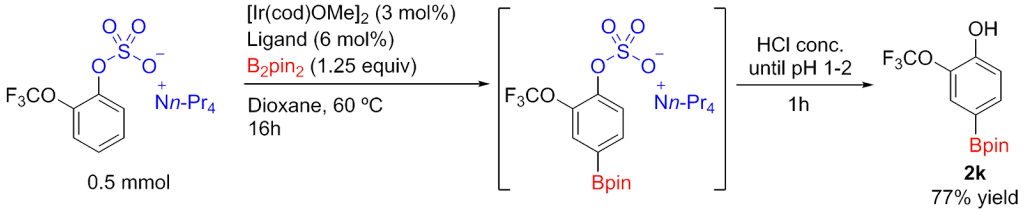


crude reaction mixture isomer ratio (NMR) = 11:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-trifluoromethylphenyl sulfate (214 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 10 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and washed with hexanes (0.5 mL). The hexane layer was decanted, and the remaining solution subjected to chromatographic separation with silica gel (12% EtOAc in $CHCl_3$ as eluent) to give 116 mg of *para* borylated 2-trifluoromethylphenol with traces of the *meta* isomer (*para*:*meta* = 46:1) as a white solid (81% yield, mp 128.1–129.9 °C). The NMR data were consistent with previously reported NMR values.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 1.6 Hz, 1H), 7.80 (dd, J = 8.2, 1.6 Hz, 1H), 6.98 (bs, 1H), 6.87 (d, J = 8.2 Hz, 1H), 1.35 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6 (q, J = 1.9 Hz), 139.9, 133.9 (q, J = 4.7 Hz), 124.0 (q, J = 272.3 Hz), 116.7, 116.5 (q, J = 30.3 Hz), 84.4, 24.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ –63.84. HRMS (ESI) m/z calcd for $C_{13}H_{15}BF_3O_3$ $[M–H]^-$ 287.1066, found 286.9732.

Para borylation of tetrapropyl ammonium 2-trifluoromethoxyphenyl sulfate (2k)

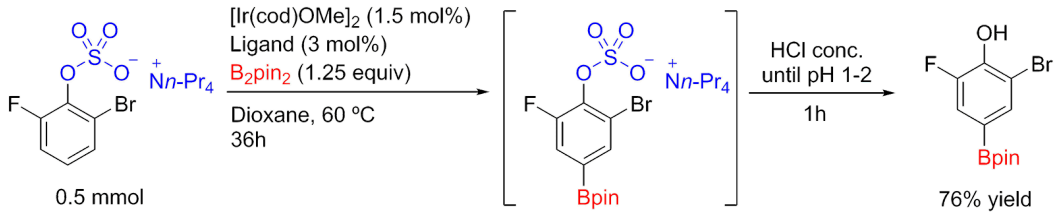


crude reaction mixture isomer ratio (NMR) = 23:1
96% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-trifluoromethoxyphenyl sulfate (198 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 16 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel (4% EtOAc in $CHCl_3$ as eluent). The fractions containing product were collected, concentrated and washed with hexanes (0.5 mL). The hexane layer was decanted and the residue was evaporated to give 117 mg of a mixture of *para* borylated 2-trifluoromethoxyphenol with traces of the *meta* isomer (<2%) as a white solid (77% yield, mp 129.6–131.9 °C)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.63 (d, J = 8.08 Hz, 1H), 7.01 (d, J = 8.08 Hz, 1H), 5.97 (bs, 1H), 1.33 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 136.2, 134.9, 127.7, 120.7 (q, J = 259.0 Hz), 116.8, 84.1, 24.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.97. HRMS (ESI) m/z calcd for $C_{13}H_{15}BF_3O_4$ $[M–H]^-$ 303.1015, found 303.1244.

Para borylation of tetrapropylammonium 2-bromo-6-fluorophenyl sulfate (2l)

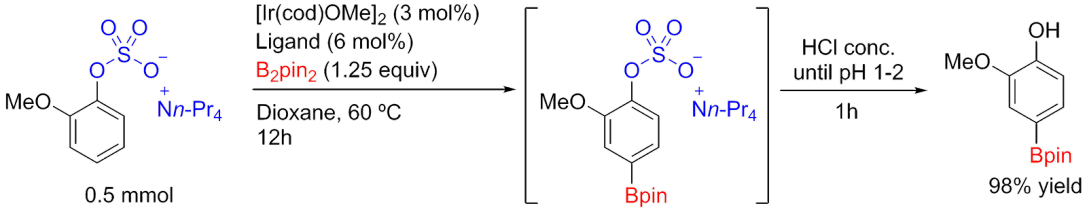


crude reaction mixture isomer ratio (NMR) = 8:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-bromo-6-fluorophenyl sulfate (228 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (128 mg, 0.5 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 ºC. After 12 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel ($CHCl_3$ as eluent). The fractions containing product were collected and concentrated to give 120 mg of a mixture of *para* borylated 2-bromo-6-fluorophenol with traces of the *meta* isomer (para:meta = 35:1) as a white solid (76% yield, mp 127.6–129.0 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 1.3 Hz, 1H), 7.44 (dd, J = 10.3, 1.3 Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6 (d, J = 246.0 Hz), 143.9 (d, J = 14.6 Hz), 134.2 (d, J = 3.0 Hz), 121.0 (d, J = 16.6 Hz), 110.7 (d, J = 1.6 Hz), 84.3, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ –137.97 (d, J = 10.3 Hz). HRMS (ESI) m/z calcd for $C_{12}H_{14}BBrFO_3$ $[M–H]^-$ 315.0203, found 314.8771.

Para borylation of tetrapropylammonium 2-methoxyphenyl sulfate (2m)

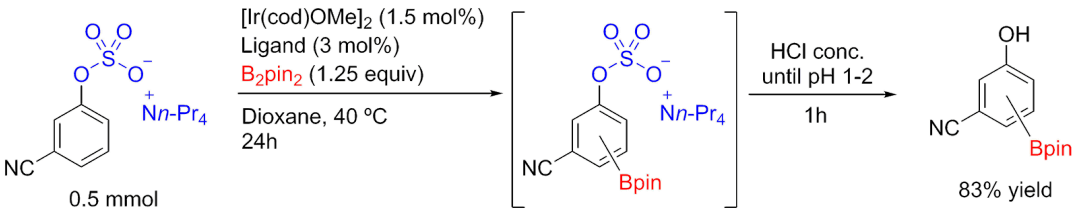


crude reaction mixture isomer ratio (NMR) = 39:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-methoxyphenyl sulfate (195 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (10 mg, 3 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 12 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel ($CHCl_3$ as eluent) to give 122 mg of a mixture of *para* borylated 2-methoxyphenol with the *meta* isomer (*para*:*meta* = 39:1) as a white solid (98% yield, mp 96.7–100.0 °C)

^{1}H NMR (500 MHz, C_6D_6) δ 7.71 (dd, J = 7.8, 1.3 Hz, 1H), 7.46 (d, J = 1.3 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 5.95 (bs, 1H), 3.11 (s, 3H), 1.10 (s, 12H). ^{13}C NMR (126 MHz, C_6D_6) δ 149.2, 146.2, 129.5, 116.7, 114.4, 83.2, 54.7, 24.6. ^{11}B NMR (160 MHz, C_6D_6) δ 31.1. HRMS (ESI) m/z calcd for $C_{13}H_{18}BO_4$ $[M–H]^-$ 249.1298, found 249.0159.

Para borylation of tetrapropylammonium 3-cyanophenyl sulfate (2n)



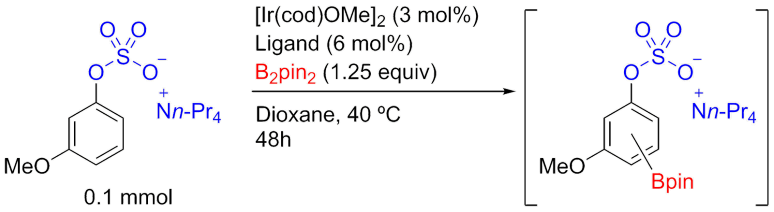
crude reaction mixture isomer ratio (NMR): para:meta = 1:7
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 3-cyanophenyl sulfate (192 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 24 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel (2% EtOAc in $CHCl_3$ as eluent). The fractions containing product

were collected, concentrated and washed with water (0.5 mL). The water layer was decanted and the residue was dried to give 102 mg of a mixture of *para* borylated 3-cyanophenol with the *meta* isomer (*para*:*meta* = 1:9.3) as a white solid (83% yield, mp 131.8–146.0 °C)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 1H), 7.47 (dd, *J* = 2.7, 1.0 Hz, 1H), 7.20 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.44 (s, 0H), 1.33 (s, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.16, 130.23, 126.37, 121.15, 118.69, 112.44, 84.62, 24.80. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.52. HRMS (ESI) m/z calcd for $C_{13}H_{15}BNO_3$ $[M–H]^-$ 244.1145, found 244.1147.

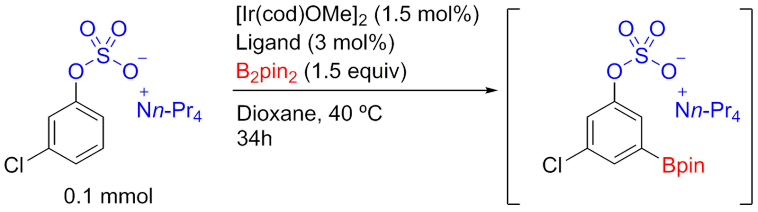
Para borylation of tetrapropylammonium 3-methoxyphenyl sulfate (2o)



crude reaction mixture isomer ratio (NMR): para:meta = 1:12
80% conversion

In a glove box, a 3.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 3-methoxyphenyl sulfate (39 mg, 0.1 mmol), $[Ir(cod)(OMe)]_2$ (0.3 mL of 0.01 M solution, 3 mol %), 4,4′-dimethoxy-2,2′-bipyridine (0.2 mL of 0.03 M solution, 6.0 mol %) and B_2pin_2 (32 mg, 0.125 mmol). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 48 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio.

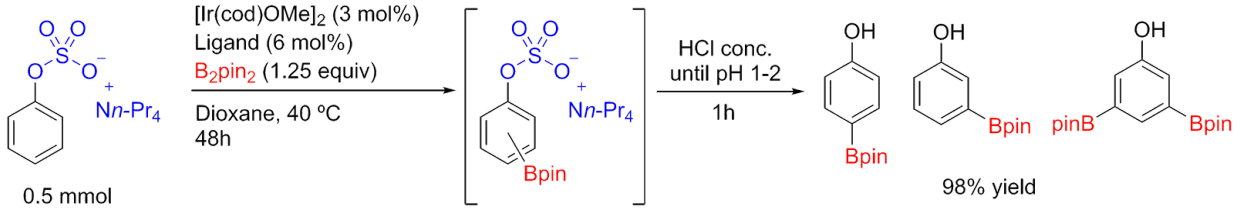
Para borylation of tetrapropyl ammonium 3-chlorophenyl sulfate (2p)



crude reaction mixture isomer ratio (NMR): para:meta < 1:20
87% conversion

In a glove box, a 3.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 3-chlorophenyl sulfate (39 mg, 0.1 mmol), $[Ir(cod)(OMe)]_2$ (0.1 mL of 0.015 M solution, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (0.1 mL of 0.03 M solution 3.0 mol %), B_2pin_2 (38 mg, 0.15 mmol) and dioxane (0.2 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 34 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio.

Para borylation of tetrapropylammonium phenyl sulfate (2q)



crude reaction mixture isomer ratio (NMR): para:meta:dimeta = 4.4:1:1.8
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropylammonium phenyl sulfate (180 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (10 mg, 3 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol, 1.0 equiv) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 48 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel (2% EtOAc in $CHCl_3$ as eluent). The fractions containing product were collected, concentrated and washed with water (0.5 mL). The water layer was decanted and the residue was dried to give 123 mg of a mixture of *para* borylated phenol with the *meta* and *dimeta* isomer (*para*:*meta* = 1:0.22:0.44) as a colorless oil (98% yield). The NMR data of the borylated compounds in the mixture were in accordance with the literature reported data.[10,11]

Para:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.5 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 5.73 (s, 1H), 1.33 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 136.8, 114.8, 83.7, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.9.

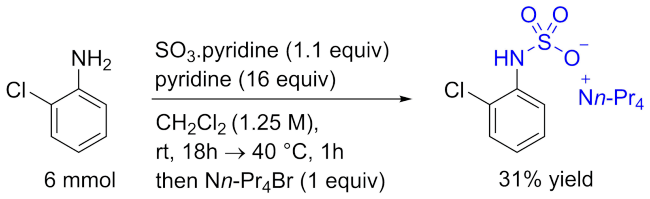
Meta:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (1H), 7.26 (2H), 6.95 (ddd, J = 8.1, 2.7, 1.1 Hz, 1H), 5.29 (s, 1H), 1.34 (s, 12H). The peaks at 7.26 and 6.95 are overlap with the *para* isomer and the solvent peak. ^{3}C NMR (126 MHz, $CDCl_3$) δ 155.1, 129.3, 127.0, 121.1, 118.4, 84.0, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.9.

Dimeta:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (t, J = 1.0 Hz, 1H), 7.36 (d, J = 1.0 Hz, 2H), 5.16 (s, 1H), 1.33 (s, 24H). ^{3}C NMR (126 MHz, $CDCl_3$) δ 154.6, 133.5, 124.1, 83.9, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) 30.9.

Synthesis of tetrapropylammonium 2-chlorophenyl sulfamate (3a)

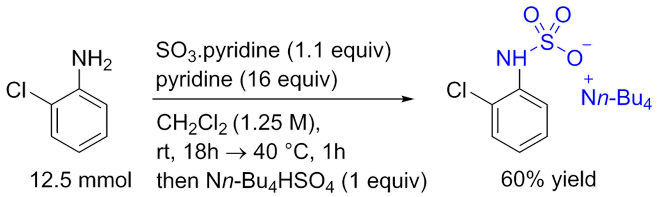


2-Chloroaniline (0.77 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (150 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropylammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes, and ether were added and the suspension was again evaporated. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After

overnight drying under high vacuum (**3a**) was obtained as a light orange solid (0.72 g, 31% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.08 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.99 (ddd, *J* = 8.3, 7.7, 1.5 Hz, 1H), 6.61 (td, *J* = 7.7, 1.6 Hz, 1H), 6.50 (bs, 1H), 3.03 – 2.79 (m, 8H), 1.44 (m, 8H), 0.80 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) 139.0, 128.5, 127.4, 120.1, 119.5, 117.3, 60.0, 15.3, 10.6. HRMS (ESI) m/z calcd for $C_6H_5ClNO_3S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 205.9679, found 205.8718

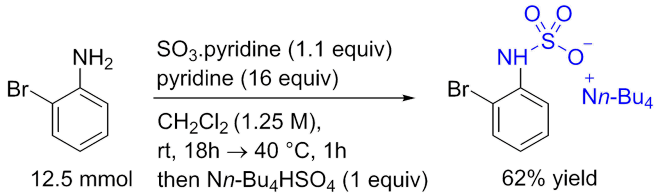
Synthesis of tetrabutylammonium 2-chlorophenyl sulfamate (3a′)



2-Chloroaniline (1.63 g, 12.74 mmol) and SO_3•pyridine complex (2.19 g, 13.75 mmol) were placed in a 100 mL round bottom flask. Pyridine (17 mL) and dry dichloromethane (10 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (150 mL) was added and the mixture was washed once with dichloromethane (1 x 150 mL). The aqueous phase was treated with tetrabutylammonium hydrogen sulfate (4.24 g, 12.5 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 150 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes, and ether were added and the suspension was again evaporated. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**3a′**) was obtained as a tannish white solid (3.821 g, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.8, 1H), 7.11 (t, J – 7.8 Hz, 1H), 6.71 (t, J = 7.8 Hz, 1H), 6.65 (bs, 1H), 3.30 – 2.98 (m, 8H), 1.60 – 1.45 (m, 8H), 1.42 – 1.13 (m, 8H), 0.94 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 128.5, 127.5, 119.9, 119.7, 117.5, 58.5, 23.9, 19.6, 13.7. HRMS (ESI) m/z calcd for $C_6H_5ClNO_3S$ $[M–N\textit{n}\text{-}Bu_4]^-$ 205.9679, found 205.9897.

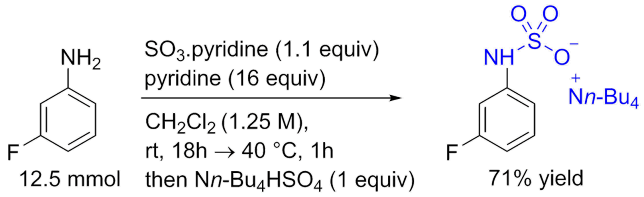
Synthesis of tetrabutylammonium 2-bromophenyl sulfamate (3b´)



2-Bromoaniline (2.14 g, 12.5 mmol) and SO_3•pyridine complex (2.19 g, 13.75 mmol) were placed in a 100 mL round bottom flask. Pyridine (17 mL) and dry dichloromethane (10 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (150 mL) was added and the mixture was washed once with dichloromethane (1 x 150 mL). The aqueous phase was treated with tetrabutylammonium hydrogen sulfate (4.24 g, 12.5 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 150 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in an oil. To the concentrated oil, hexanes, and ether were added and the suspension was again evaporated. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**3b′**) was obtained as a white solid (3.84 g, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, J = 8.3, 1.5 Hz, 1H), 7.37 (dd, J = 8.0, 1.5 Hz, 1H), 7.16 (ddd, J = 8.3, 7.3, 1.5 Hz, 1H), 6.67 (bs, 1H), 6.66 (ddd, J = 8.0, 7.3, 1.5 Hz, 1H), 3.22 – 3.15 (m, 8H), 1.62 – 1.52 (m, 8H), 1.37 (m, 8H), 0.96 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 131.7, 128.2, 120.4, 117.6, 110.4, 58.5, 23.9, 19.7, 13.7. HRMS (ESI) m/z calcd for $C_6H_5BrNO_3S$ $[M–Nn\text{-}Bu_4]^-$ 249.9173, found 249.8044.

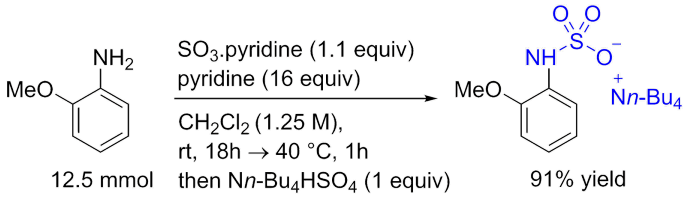
Synthesis of tetrabutylammonium 3-fluorophenyl sulfamate (3c´)



3-Fluoroaniline (1.3872 g, 12.5 mmol) and SO_3•pyridine complex (2.19 g, 13.75 mmol) were placed in a 100 mL round bottom flask. Pyridine (17 mL) and dry dichloromethane (10 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (150 mL) was added and the mixture was washed once with dichloromethane (1 x 150 mL). The aqueous phase was treated with tetrabutylammonium hydrogen sulfate (4.25 g, 12.5 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 150 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in an oil. To the concentrated oil, hexanes, and ether were added and the suspension was again evaporated. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**3c′**) was obtained as a light orange solid (4.12 g, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 6.88 (m, 3H), 6.78 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.44 (td, *J* = 8.5, 2.5 Hz, 1H), 3.19 – 3.08 (m, 8H), 1.51 (m, 8H), 1.33 (m, 8H), 0.91 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3 (d, *J* = 241.3 Hz), 144.7 (d, *J* = 11.2 Hz), 129.4 (d, *J* = 9.8 Hz), 112.2 (d, *J* = 2.3 Hz), 105.6 (dd, *J* = 21.5, 2.0 Hz), 103.5 (d, *J* = 25.5 Hz), 58.1, 23.7, 19.5, 13.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ –116.67 (ddd, *J* = 11.7, 8.4, 6.7 Hz). HRMS (ESI) m/z calcd for $C_6H_5FNO_3S$ $[M–N\textit{n}\text{-}Bu_4]^-$ 189.9974, found 189.9108.

Synthesis of tetrabutylammonium 2-methoxyphenyl sulfamate (3d′)

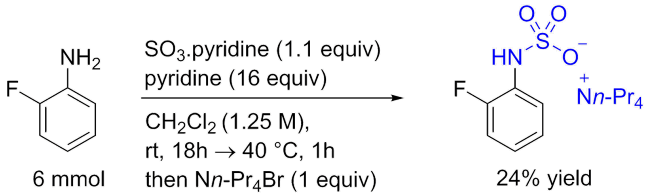


o-Anisidine (1.34 g, 11 mmol) and SO_3•pyridine complex (2.19 g, 13.75 mmol) were placed in a 100 mL round bottom flask. Pyridine (17 mL) and dry dichloromethane (10 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (150 mL) was added and the mixture was washed once with dichloromethane (1 x 150 mL). The aqueous phase was treated with tetrabutylammonium hydrogen sulfate (4.24 g, 12.5 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 150 mL). The

organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in an oil. To the concentrated oil, hexanes, and ether were added and the suspension was again evaporated. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**3d′**) was obtained as a pinkish white solid (4.88 g, 91% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, J = 7.8, 1.4 Hz, 1H), 6.81 (ddd, J = 7.8, 6.4, 2.4 Hz, 1H), 6.74 (ddd, J = 7.1, 6.4, 1.4 Hz, 1H), 6.72 (dd, J = 7.1, 2.4 Hz, 1H), 6.64 (bs, 1H), 3.75 (s, 3H), 3.23 – 3.04 (m, 8H), 1.52 (m, 8H), 1.35 (m, 8H), 0.94 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.0, 132.4, 121.1, 119.4, 116.6, 109.8, 58.5, 55.5, 23.9, 19.6, 13.7. HRMS (ESI) m/z calcd for $C_7H_8NO_4S$ [M–N*n*-Bu_4]$^-$ 202.0174, found 202.0198.

Synthesis of tetrapropylammonium 2-fluorophenyl sulfamate (3e)



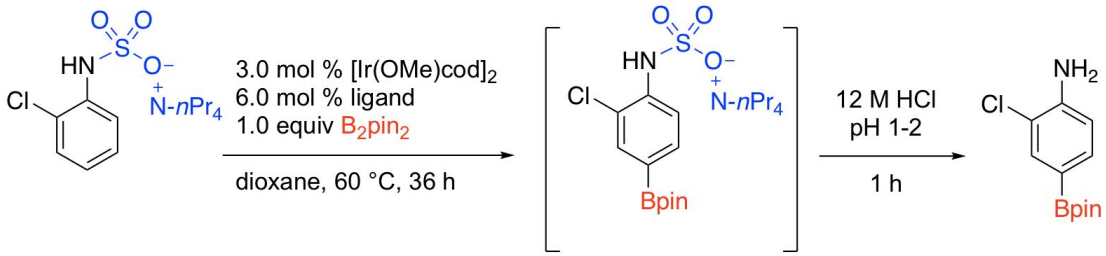
6 mmol 24% yield

2-Fluoroaniline (0.67 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in an oil. To the concentrated oil, hexanes and ether were added and the suspension was again evaporated. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**3e**) was obtained as a white solid (0.55 g, 24% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (td, J = 8.4, 1.7 Hz, 1H), 6.92 (ddd, J = 8.4, 7.7, 1.5 Hz, 1H), 6.87 (ddd, J = 11.2, 8.1, 1.5 Hz, 1H), 6.68 (dddd, J = 8.1, 7.7, 5.0, 1.7 Hz, 1H), 6.24 (s, 1H), 3.09 – 3.01 (m, 8H), 1.61 – 1.49 (m, 8H), 0.89 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$)

δ 151.3 (d, J = 238.6 Hz), 130.8 (d, J = 11.7 Hz), 124.3 (d, J = 3.6 Hz), 119.8 (d, J = 7.1 Hz), 118.5 (d, J = 2.2 Hz), 114.2 (d, J = 19.2 Hz), 60.2, 15.5, 10.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ –137.7 (ddd, J = 10.9, 8.4, 5.0 Hz). HRMS (ESI) m/z calcd for $C_6H_5FNO_3S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 189.9974, found 190.0019.

Para borylation of tetrapropylammonium 2-chlorophenyl sulfamate (4a)



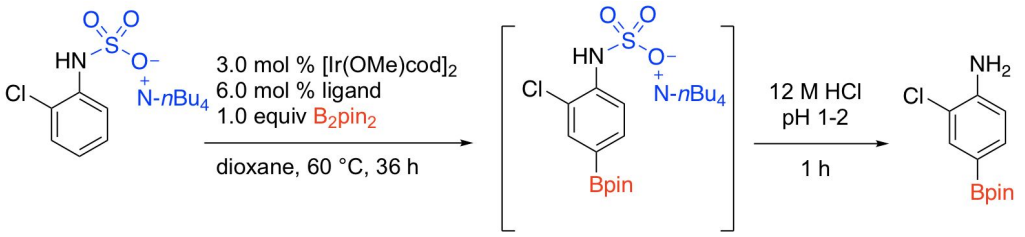
crude reaction mixture *para* to *meta* isomer ratio (NMR) = 40:1
86% conversion, 76% yield

In a glove box, a 5.0 mL Wheaton microreactor equipped with a stir bar was charged with tetrapropylammonium 2-chlorophenyl sulfamate (196 mg, 0.5 mmol, 1 equiv), $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 3.0 mol %), B_2pin_2 (128 mg, 0.5 mmol, 1 equiv) and dioxane (1.5 mL). The microreactor was capped with a Supelco teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction was removed and concentrated under vacuum. The residue was dissolved in $CDCl_3$ and a ^{1}H NMR spectrum showed 86% conversion with a ratio of 40:1 para to meta borylation. Crude para borylated 2-chlorosulfamate: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 1.4 Hz, 1H), 7.52 (dd, J = 8.1, 1.5 Hz, 1H), 6.82 (s, 1H), 3.10 – 3.03 (m, 8H), 1.62 – 1.52 (m, 8H), 1.28 (s, 12H), 0.93 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 134.2, 116.4, 83.6, 82.9, 67.0, 60.1, 24.8, 24.5, 15.5, 10.7.

Concentrated HCl was added (2 drops, pH = 1–2) and the resultant mixture was stirred for 1 h. TLC eluting in CH_2Cl_2 showed the appearance of a new spot at r_f = 0.5, whereas the crude borylated sulfamate did not move off the baseline. The solution was concentrated and pumped down under vacuum. The crude material was dissolved in CH_2Cl_2 and applied to a 5 g silica plug packed in 1:99 hexane/CH_2Cl_2 to yield 96 mg of *para* borylated 2-chloroaniline as a white solid. (76% yield, mp 100–102 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 1.3 Hz, 1H), 7.49 (dd, J = 7.9, 1.4 Hz, 1H), 6.73 (d, J = 7.9 Hz, 1H), 4.24 (s, 2H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) 139.1, 128.5, 127.5, 119.97, 119.8, 117.5, 58.6, 23.9, 19.7, 13.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.3. HRMS (ESI) m/z calcd for $C_{12}H_{18}BClNO_2$ $[M+H]^+$ 254.1119, found 254.1151.

Para borylation of tetrabutylammonium 2-chlorophenyl sulfamate (4a′)

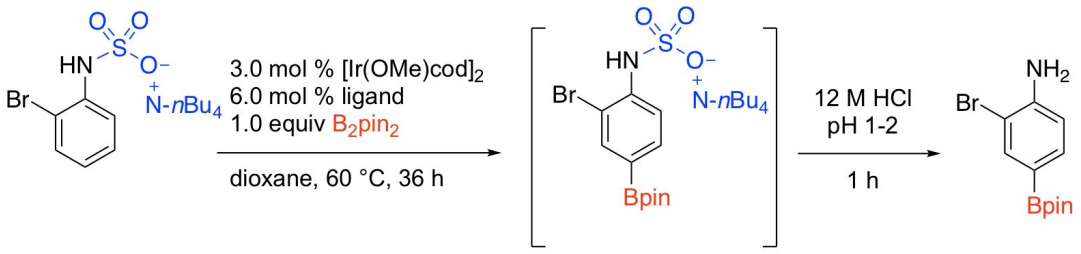


crude reaction mixture isomer ratio (NMR) = 43:1
98% conversion, 95% yield

In a glove box, a 5.0 mL Wheaton microreactor equipped with a stir bar was charged with tetrabutylammonium 2-chlorophenyl sulfamate (225 mg, 0.5 mmol, 1 equiv), $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6.0 mol %), B_2pin_2 (128 mg, 0.5 mmol, 1.0 equiv) and dioxane (1.5 mL). The microreactor was capped with a Supelco teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction was removed and concentrated under vacuum. The residue was dissolved in $CDCl_3$ and a ^{1}H NMR spectrum showed 98% conversion with a ratio of 43:1 para to meta borylation. Concentrated HCl was added (2 drops, pH = 1–2) and the resultant mixture was stirred for 1 h. TLC eluting in CH_2Cl_2 showed the appearance of a new spot at r_f = 0.5, whereas the crude borylated sulfamate did not move off the baseline. The solution was concentrated and pumped down under vacuum. The crude material was dissolved in CH_2Cl_2 and applied to a 5 g silica plug packed in 1:99 hexane/CH_2Cl_2 to yield 120 mg of *para* borylated 2-chloroaniline as a white solid. (95% yield, mp 100–102 °C). The NMR data were consistent with previously reported values.[12]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 1.3 Hz, 1H), 7.49 (dd, J = 7.9, 1.4 Hz, 1H), 6.73 (d, J = 7.9 Hz, 1H), 4.24 (s, 2H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) 139.1, 128.5, 127.5, 120.0, 119.8, 117.5, 58.6, 23.9, 19.7, 13.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.3. HRMS (ESI) m/z calcd for $C_{12}H_{18}BClNO_2$ $[M+H]^+$ 254.1119, found 254.1310.

Para borylation of tetrabutylammonium 2-bromophenyl sulfamate (4b′)



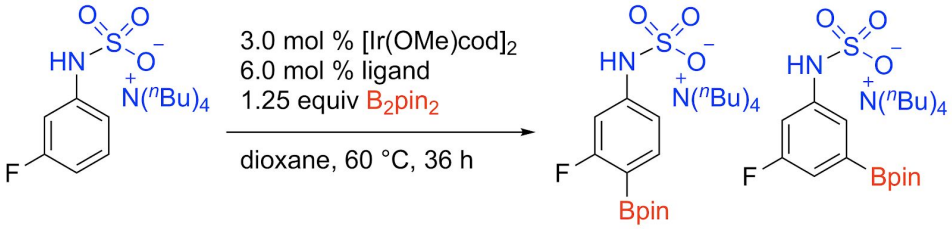
crude reaction mixture isomer ratio (NMR) = 66:1
89% conversion, 72% yield

In a glove box, a 5.0 mL Wheaton microreactor equipped with a stir bar was charged with tetrabutylammonium 2-bromophenyl sulfamate (247 mg, 0.5 mmol, 1 equiv), $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol%), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6.0 mol %), B_2pin_2 (128 mg, 0.5 mmol, 1.0 equiv) and dioxane (1.5 mL). The microreactor was capped with a Supelco teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction was removed and concentrated under vacuum. The residue was dissolved in $CDCl_3$ and a ^1H NMR spectrum showed 89% conversion with a ratio of 66:1 para to meta borylation. Para borylated 2-bromosulfamate determined from the crude reaction mixture: ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 1H), 7.75 (dd, J = 8.2, 0.8 Hz, 1H), 7.57 (dd, J = 8.1, 1.4 Hz, 1H), 6.86 (s, 1H), 3.25 – 3.09 (m, 8H), 1.56 (m, 8H), 1.37 (m, 8H), 1.29 (s, 12H), 0.97 – 0.93 (m, 12H).

Concentrated HCl was added (2 drops, pH = 1–2) and the resultant mixture was stirred for 1 h. TLC eluting in CH_2Cl_2 showed the appearance of a new spot at r_f = 0.5, whereas the crude borylated sulfamate did not move off the baseline. The solution was concentrated and pumped down under vacuum. The crude material was dissolved in CH_2Cl_2 and applied to a 5 g silica plug packed in 1:99 hexane/CH_2Cl_2 to yield 128 mg material. ^1H NMR showed B_2pin_2 contamination in the isolated product. The mass of B_2pin_2 was calculated from mol fraction based on NMR integrations and subtracted from the mass of the isolated material. The mass of *para* borylated 2-bromoaniline present in the material was 88 mg. (72% yield). The material was washed in cold hexane and dried under vacuum to yield 55 mg of the pure *para* borylated 2-bromoaniline. (37% yield, mp 101–102 °C). NMR data was consistent with previously reported NMR values.[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.52 (d, J = 7.9 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 4.29 (s, 2H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 139.3, 135.0, 114.8, 108.9, 83.6, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.2. HRMS (ESI) m/z calcd for $C_{12}H_{18}BBrNO_2$ $[M+H]^+$ 298.0614, found 298.0787.

Para borylation of tetrabutylammonium 3-fluorophenyl sulfamate (4c′)



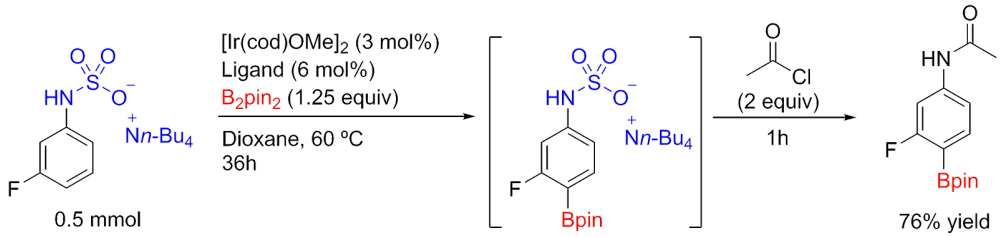
crude reaction mixture para to meta isomer ratio (^{19}F NMR) = 2.8:1
96% conversion to borylated sulfamate

In a glove box, a 5.0 mL Wheaton microreactor equipped with a stir bar was charged with tetrabutylammonium 3-fluorophenyl sulfamate (216 mg, 0.5 mmol, 1 equiv), $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6 mol %), B_2pin_2 (159 mg, 0.625 mmol, 1.25 equiv) and dioxane (1.5 mL). The microreactor was capped with a Supelco teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction was removed and diluted with $CDCl_3$ and a ^{19}F NMR spectrum showed 96% conversion with a ratio of 2.8:1 para to meta borylation.

Characterization data was determined from the crude mixture of borylated material and borate byproducts. Para borylated 3-fluorophenyl sulfamate: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, J = 8.1, 7.1 Hz, 1H), 6.93 (dd, J = 12.1, 1.9 Hz, 1H), 6.73 (dd, J = 8.2, 1.9 Hz, 1H), 5.91 (s, 1H), 3.16 – 3.07 (m, 8H), 1.48 (m, 8H), 1.33 – 1.28 (m, 8H), 1.27 (s, 12H), 0.88 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5 (d, J = 247.9 Hz), 147.7 (d, J = 12.1 Hz), 137.1 (d, J = 10.2 Hz), 111.9 (d, J = 2.1 Hz), 102.9 (d, J = 28.8 Hz), 83.8, 58.6, 50.7, 24.8, 24.0, 19.6, 13.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ –105.54. Meta borylated 3-fluorophenyl sulfamate: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dt, J = 11.6, 2.4 Hz, 1H), 6.96 (d, J = 2.1 Hz, 1H), 6.85 (dd, J = 8.6, 2.5 Hz, 1H), 6.75 (s, 1H), 3.17 – 3.06 (m, 8H), 1.48 (m, 8H), 1.30 (m, 8H), 1.25 (s, 12H), 0.88 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (d, J = 242.9 Hz), 144.0 (d, J = 10.2 Hz),

129.6 (d, J = 9.9 Hz), 112.2 (d, J = 20.0 Hz), 107.2 (d, J = 26.0 Hz), 83.7, 58.6, 24.8, 23.9, 19.6, 13.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ –117.5. HRMS (ESI) m/z calcd for $C_{12}H_{16}BFNO_5S$ $[M–N\textit{n}\text{-}Bu_4]^-$ 316.0826, found 316.1525.

Borylation of tetrabutylammonium 3-fluorophenyl sulfamate - Acylation work-up (4c′)



crude reaction mixture isomer ratio (NMR): para:meta = 2.4:1
96% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrabutyl ammonium 3-fluorophenyl sulfamate (216 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (10 mg, 3 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. Acetyl chloride (0.08 mL, 1 mmol) was added and the resultant mixture was stirred for 4 h. The solution was concentrated and passed through a plug of silica gel (2% EtOAc in $CHCl_3$ as eluent). The fractions containing product were collected, concentrated and washed with water (2 mL). The water layer was decanted and the residue was dried to give 106 mg of a mixture of *para* borylated N-(3-fluorophenyl)acetamide with the *meta* isomer (*para*:*meta* = 2.1:1) as a white solid (76% yield, mp 147.1–146.7 °C) NMR data was consistent with previously reported NMR values.[14]

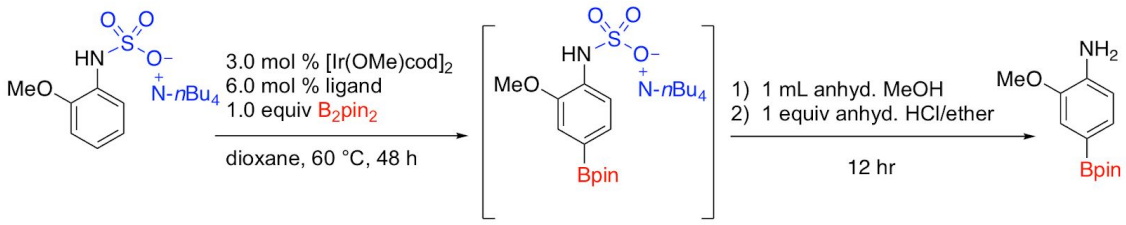
Para:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (bs, 1H), 7.65 (dd, J = 8.1, 6.8 Hz, 1H), 7.47 (dd, J = 11.4, 1.9 Hz, 1H), 7.14 (dd, J = 8.1, 1.9 Hz, 1H), 2.17 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 167.7 (d, J = 250.0 Hz), 142.5 (d, J = 11.7 Hz), 137.3 (d, J = 9.7 Hz), 114.2, 106.4 (d, J = 29.6 Hz), 83.8, 24.8, 24.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.05. ^{19}F NMR (470 MHz, $CDCl_3$) δ –103.81 (dd, J = 11.4, 6.8 Hz).

Meta:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dt, *J* = 11.1, 2.3 Hz, 1H), 7.62 (bs, 1H), 7.35 (dd, *J* = 2.3, 0.8 Hz, 1H), 7.20 (dd, *J* = 8.3, 2.3 Hz, 1H), 2.16 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 162.7 (d, *J* = 246.0 Hz), 139.0 (d, *J* = 10.2 Hz), 120.9 (d, *J* = 2.8 Hz), 116.5 (d, *J* = 19.7 Hz), 110.3 (d, *J* = 26.9 Hz), 84.23, 24.85, 24.53.. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.05. ^{19}F NMR (470 MHz, $CDCl_3$) δ –115.34 (dd, *J* = 11.1, 8.3 Hz). HRMS (ESI) m/z calcd for $C_{14}H_{18}BFNO_3$ $[M–H]^-$ 278.1364, found 278.1364.

Para borylation of tetrabutylammonium 2-methoxyphenyl sulfamate (4d′)



crude reaction mixture isomer *para* to *meta* ratio (NMR) = 20:1
75% conversion, 59% isolated yield

In a glove box, a 5.0 mL Wheaton microreactor equipped with a stir bar was charged with tetrabutylammonium 2-methoxyphenyl sulfamate (222 mg, 0.5 mmol, 1 equiv), $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6 mol %), B_2pin_2 (128 mg, 0.5 mmol, 1.0 equiv) and dioxane (1.5 mL). The microreactor was capped with a Supelco teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 48 h, an aliquot of the reaction was removed and concentrated under vacuum. The residue was dissolved in $CDCl_3$ and a ^{1}H NMR spectrum showed 75% conversion with a ratio of 20:1 para to meta borylation.

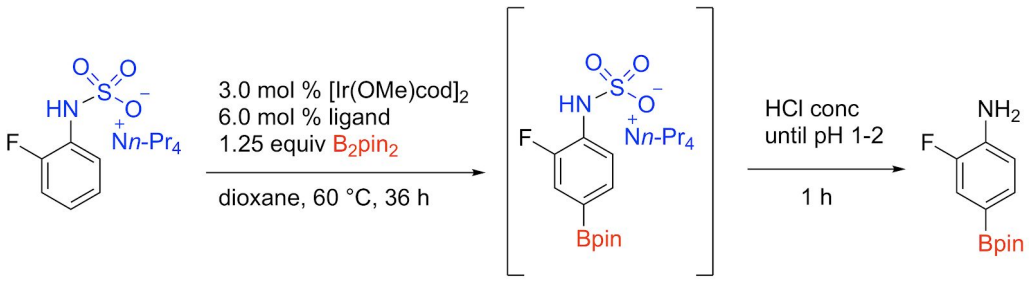
Para borylated 2-methoxyphenyl sulfamate determined from the crude material: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.08 (s, 1H), 6.76 (s, 1H), 3.75 (s, 3H), 3.07 – 3.00 (m, 8H), 1.42 (p, *J* = 7.8 Hz, 8H), 1.31 – 1.23 (m, 8H), 1.26 (s, 12H), 0.87 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 135.3, 128.8, 115.3, 115.2, 83.3, 24.8, 24.5, 23.8, 19.5, 13.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.9.

Anhydrous methanol (1 mL) was added to the reaction with stirring. 1M HCl in ether (0.5 mmol, 0.5 mL, 1 equiv) was added dropwise by syringe, until the pH was 7. The mixture was

stirred 12 hours, then concentrated to a brown oil. The crude material was dissolved in CH_2Cl_2 and applied to a 7 g silica plug eluting in CH_2Cl_2. After 100 mL CH_2Cl_2 was eluted, the elutant was changed to 1:1:98 ethyl acetate:triethylamine:CH_2Cl_2. Fractions were combined and concentrated to 68 mg of a pale pink solid, 59% yield, m.p 116–117 °C.

Para borylated 2-methoxyaniline: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, J = 7.6, 1.3 Hz, 1H), 7.20 (d, J = 1.3 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 4.00 (s, 2H), 3.89 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 139.5, 128.8, 115.8, 114.0, 83.3, 55.5, 24.9. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.9. HRMS (ESI) m/z calcd for $C_{13}H_{21}BNO3$ $[M+H]^+$ 250.1614, found 250.1677.

Para borylation of tetrapropylammonium 2-fluorophenyl sulfamate (4e)



crude reaction mixture isomer *para* to *meta* ratio (NMR) = 2:1
94% conversion, 52% isolated yield (10:1)

In a glove box, a 5.0 mL Wheaton microreactor equipped with a stir bar was charged with tetrapropylammonium 2-fluorophenyl sulfamate (188 mg, 0.5 mmol, 1 equiv), $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6 mol %), B_2pin_2 (159 mg, 0.625 mmol, 1.25 equiv) and dioxane (1.5 mL). The microreactor was capped with a Supelco teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel ($CHCl_3$ as eluent) to give 62 mg of a mixture of *para* borylated 2-fluoroaniline with the *meta* isomer (*para*:*meta* = 10:1) as a white solid (52% yield, mp 90.6–96.2 °C).

Para:

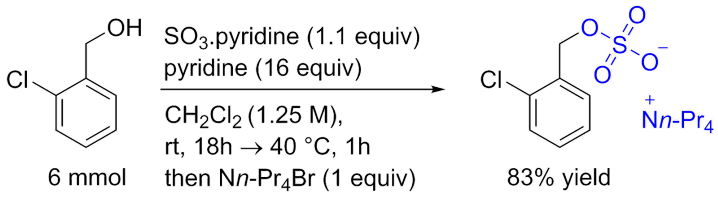
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 2H), 6.77 – 6.69 (m, 1H), 3.94 (br s, 2H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.1 (d, *J* = 239.2 Hz), 137.6 (d, *J* = 12.5 Hz), 131.5 (d, *J* = 3.2 Hz), 121.0 (d, *J* = 16.2 Hz), 115.9 (d, *J* = 3.0 Hz), 83.6, 24.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ –140.50 (dd, *J* = 11.7, 8.7 Hz). ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.3

Meta:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (ddd, *J* = 7.6, 5.1, 1.8 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.87 (ddd, *J* = 9.4, 7.6, 1.8 Hz, 1H), 3.78 (br s, 2H), 1.36 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7 (d, *J* = 243.6 Hz), 134.3 (d, *J* = 14.8 Hz), 125.2 (d, *J* = 7.1 Hz), 124.0 (d, *J* = 3.6 Hz), 120.0 (d, *J* = 4.3 Hz), 83.8, 24.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ –128.76 (dt, *J* = 9.4, 5.1 Hz). ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.3.

HRMS (ESI) m/z calcd for $C_{12}H_{18}BFNO_2$ $[M+H]^+$ 238.1415, found 238.1488.

Synthesis of tetrapropylammonium 2-chlorobenzyl sulfate (5a)

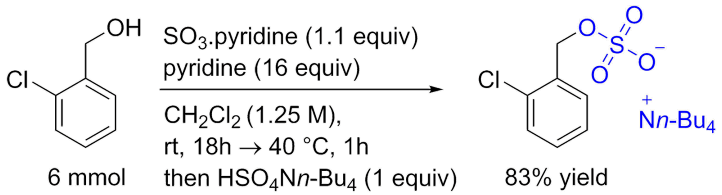


2-Chlorobenzyl alcohol (0.86 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. Diethyl ether and hexanes were added to evaporate the solvent to dryness and the product was obtained as a white solid (2.02 g, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.5, 1.8Hz, 1H), 7.26 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.19 (td, *J* = 7.5, 1.5 Hz, 1H), 7.15 (td, *J* = 7.5, 1.8 Hz, 1H), 5.14 (s, 2H), 3.26 – 2.93 (m, 8H),

1.74 – 1.46 (m, 8H), 0.96 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 132.1, 129.1, 128.8, 128.4, 126.6, 65.6, 60.1, 15.4, 10.7. HRMS (ESI) m/z calcd for $C_7H_6ClO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 220.9675, found 220.9680.

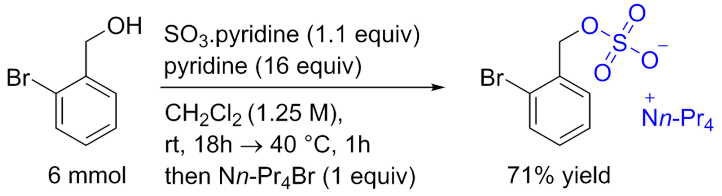
Synthesis of tetrabutylammonium 2-chlorobenzyl sulfate (5a´)



2-Chlorobenzyl alcohol (0.86 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrabutyl ammonium hydrogen sulfate (2.13 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. Diethyl ether and hexanes were added to evaporate the solvent to dryness and the product was obtained as a white solid (2.28 g, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.5, 1.8Hz, 1H), 7.26 (dd, J = 7.5, 1.5 Hz, 1H), 7.19 (td, J = 7.5, 1.5 Hz, 1H), 7.15 (td, J = 7.5, 1.8 Hz, 1H), 5.13 (s, 2H), 3.34 – 3.04 (m, 8H), 1.56 (dq, J = 11.9, 8.0, 7.5 Hz, 8H), 1.35 (h, J = 7.4 Hz, 8H), 0.92 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 132.0, 129.0, 128.7, 128.3, 126.5, 65.6, 58.3, 23.7, 19.5, 13.6. HRMS (ESI) m/z calcd for $C_7H_6ClO_4S$ $[M–N\textit{n}\text{-}Bu_4]^-$ 220.9675, found 220.9689.

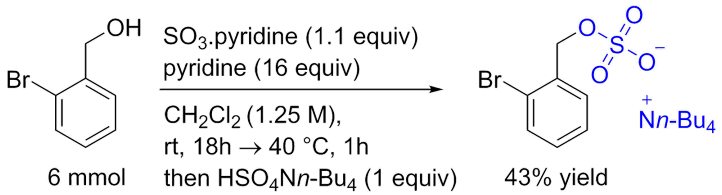
Synthesis of tetrapropylammonium 2-bromobenzyl sulfate (5b)



2-Bromobenzyl alcohol (1.12 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated, resulting in an oil. To the concentrated oil, hexanes and ether were added and the suspension was again evaporate. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**5b**) was obtained as a white solid (1.93 g, 71% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.55 (dd, J = 7.7, 1.7 Hz, 1H), 7.44 (dd, J = 7.7, 1.2 Hz, 1H), 7.23 (td, J = 7.7, 1.2 Hz, 1H), 7.07 (td, J = 7.7, 1.7 Hz, 1H), 5.06 (s, 2H), 3.21 – 3.04 (m, 8H), 1.68 – 1.50 (m, 8H), 0.92 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2, 132.0, 129.2, 128.7, 127.2, 121.9, 67.9, 60.2, 15.5, 10.8. HRMS (ESI) m/z calcd for $C_7H_6BrO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 264.91702, found 264.7968.

Synthesis of tetrabutylammonium 2-bromobenzyl sulfate (5b′)

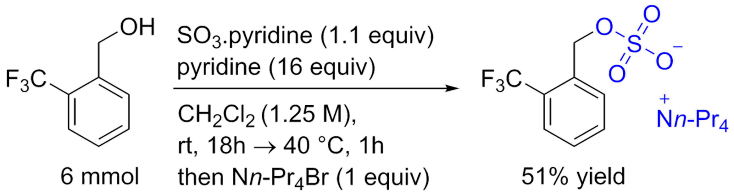


2-Bromobenzyl alcohol (1.12 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrabutyl ammonium hydrogen sulfate (2.13 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes

and ether were added and the suspension was again evaporate. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**5b'**) was obtained as a white solid (1.321 g, 43% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.8, 1.6 Hz, 1H), 7.37 (dd, J = 8.0, 1.1 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.01 (td, J = 8.0, 1.6 Hz, 1H), 4.98 (s, 2H), 3.18 – 2.88 (m, 8H), 1.62 – 1.40 (m, 8H), 0.84 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2, 132.0, 129.04, 128.7, 127.2, 121.8, 67.8, 60.1, 15.4, 10.7. HRMS (ESI) m/z calcd for $C_7H_6BrO_4S$ $[M–N\textit{n}\text{-}Bu_4]^-$ 264.9170, found 264.9280.

Synthesis of tetrapropylammonium 2-trifluoromethylbenzyl sulfate (5c)

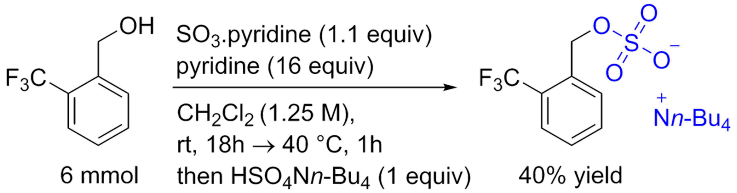


2-Trifluoromethylbenzyl alcohol (1.06 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes and ether were added and the suspension was again evaporate. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**5c**) was obtained as a white solid (1.34 g, 51% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 5.18 (s, 2H), 3.28–2.91 (m, 8H), 1.69–1.42 (m, 8H), 0.90 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 131.8, 129.1, 127.1, 126.8 (q, J = 31

Hz), 125.2 (q, J = 5.67 Hz), 124.3 (q, J = 275 Hz), 64.5 (q, J = 3.3 Hz), 60.2, 15.46, 10.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.16. HRMS (ESI) m/z calcd for $C_8H_6F_3O_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 254.9939, found 254.8768.

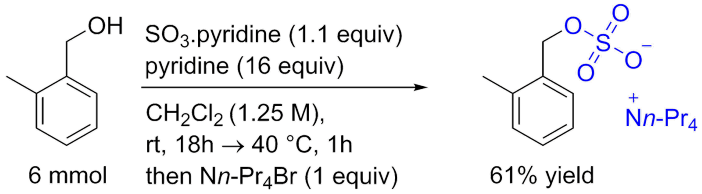
Synthesis of tetrabutylammonium 2-trifluoromethylbenzyl sulfate (5c')



2-Trifluoromethylbenzyl alcohol (1.06 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrabutylammonium hydrogensulfate (2.04 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes and ether were added and the suspension was again evaporate. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**5c'**) was obtained as a white solid (1.20 g, 40% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.7 Hz, 1H), 7.55 (dd, J = 7.7, 1.2 Hz, 1H), 7.47 (td, J = 7.7, 1.2 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 5.22 (s, 2H), 3.36 – 3.09 (m, 8H), 1.61–1.50 (m, 8H), 1.39–1.29 (m, 8H), 0.91 (t, J = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7 (q, J = 1.9 Hz), 131.7, 129.1, 126.9, 126.7 (q, J = 30.6 Hz), 125.1 (q, J = 5.8 Hz), 124.3 (q, J = 273.7 Hz), 64.5 (q, J = 3.1 Hz), 58.5, 23.8, 19.6, 13.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.3. HRMS (ESI) m/z calcd for $C_8H_6F_3O_4S$ $[M–N\textit{n}\text{-}Bu_4]^-$ 254.9939, found 255.0028.

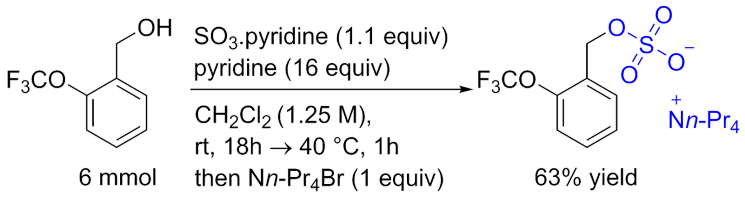
Synthesis of tetrapropylammonium 2-methylbenzyl sulfate (5d)



o-Tolylmethanol (0.73 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes and ether were added and the suspension was again evaporate. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**5d**) was obtained as a white solid (1.41 g, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ δ 7.31 (dd, J = 7.8, 1.5 Hz, 1H), 7.13 – 7.01 (m, 3H), 4.96 (s, 2H), 3.11 – 2.84 (m, 8H), 2.29 (s, 3H), 1.60–1.44 (m, 8H), 0.88 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.9, 135.5, 129.9, 128.8, 127.7, 125.5, 67.0, 60.1, 18.8, 15.4, 10.7. HRMS (ESI) m/z calcd for $C_8H_9O_4S$ $[M–Nn\text{-}Pr_4]^-$ 201.0222, found 201.0271.

Synthesis of tetrapropylammonium 2-(trifluoromethoxy)benzyl sulfate (5e)

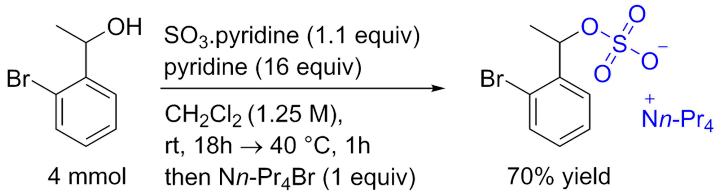


(2-(Trifluoromethoxy)phenyl)methanol (1.15 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at rt for 18 h. After this time,

the reaction was heated to 40 °C for 1 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes and ether were added and the suspension was again evaporate. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**5e**) was obtained as a white solid (1.72 g, 63% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.2, 2.2 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.13 (dp, J = 7.5, 1.7 Hz, 1H), 5.09 (s, 2H), 3.20 – 2.95 (m, 8H), 1.70 – 1.43 (m, 8H), 0.91 (t, J = 7.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2 (q, J = 1.9 Hz), 130.8, 129.7, 128.4, 126.7, 120.5 (q, J = 257.3 Hz), 120.0, 62.7, 60.3, 15.5, 10.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.42. HRMS (ESI) m/z calcd for $C_8H_6F_3O_5S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 270.9888, found 270.9895.

Synthesis of tetrapropylammonium 1-(2-bromophenyl)ethyl sulfate (5f)

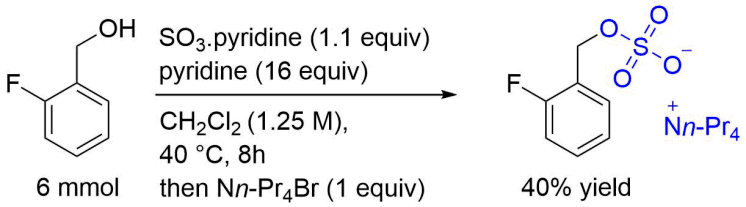


1-(2-Bromophenyl)ethan-1-ol (0.80 g, 4 mmol) and SO_3•pyridine complex (0.70 g, 4.4 mmol) were placed in a 100 mL round bottom flask. Pyridine (5.3 mL) and dry dichloromethane (3.3 mL) were added and the mixture was stirred at rt for 18 h. After this time, the reaction was heated to 40 °C for 1 h. Water (50 mL) was added and the mixture was washed once with dichloromethane (1 x 50 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.06 g, 4 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes and ether were added and the suspension was again evaporate. This hexane/ether process was repeated until following the evaporation of solvent the product was

obtained as a white solid. After overnight drying under high vacuum (**5f**) was obtained as a white solid (1.30 g, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.24 (td, *J* = 7.7, 1.2 Hz, 1H), 7.03 (td, *J* = 7.7, 1.7 Hz, 1H), 5.71 (q, *J* = 6.4 Hz, 1H), 3.17 – 2.88 (m, 8H), 1.66 – 1.54 (m, 8H), 1.51 (d, *J* = 6.4 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 132.1, 128.1, 127.9, 127.4, 120.8, 74.2, 60.2, 23.2, 15.5, 10.8. HRMS (ESI) m/z calcd for $C_8H_8BrO_4S$ $[M–N\textit{n}\text{-}Pr_4]^-$ 278.9327, found 278.9380.

Synthesis of tetrapropylammonium 2-fluorobenzyl sulfate (5g)

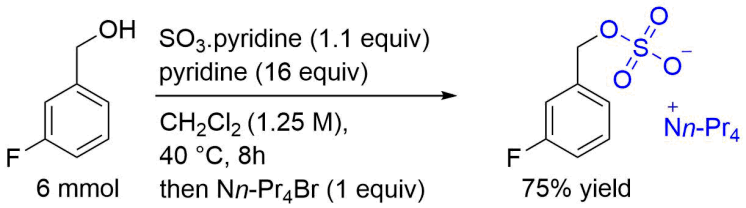


(2-Fluorophenyl)methanol (0.76, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at 40 °C for 8 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes and ether were added and the suspension was again evaporate. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**5g**) was obtained as a white solid (0.94 g, 40% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (td, *J* = 7.5, 1.8 Hz, 0H), 7.18 (tdd, *J* = 7.6, 5.2, 1.8 Hz, 0H), 7.02 (td, *J* = 7.5, 1.2 Hz, 0H), 6.92 (ddd, *J* = 9.7, 8.2, 1.2 Hz, 0H), 5.03 (d, *J* = 1.4 Hz, 0H), 3.58 – 2.62 (m, 1H), 1.89 – 1.24 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.41 (d, *J* = 246.9 Hz), 130.52 (d, *J* = 4.0 Hz), 129.21 (d, *J* = 7.9 Hz), 124.83 (d, *J* = 14.4 Hz), 123.88 (d, *J* = 3.7 Hz), 114.81 (d, *J* = 21.4 Hz), 62.26 (d, *J* = 4.4 Hz), 60.18 (d, *J* = 2.3 Hz),

15.45, 10.67.^{19}F NMR (470 MHz, $CDCl_3$) δ –122.02 (d, *J* = 8.4 Hz), –164.90. HRMS (ESI) m/z calcd for $C_7H_6FO_4S$ [M–N*n*-Pr_4]$^-$ 204.9971, found 205.0033.

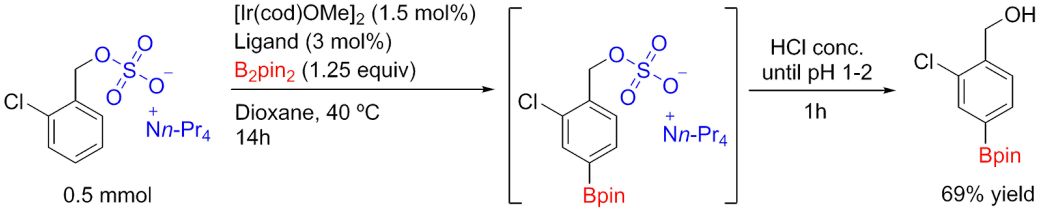
Synthesis of tetrapropylammonium 3-fluorobenzyl sulfate (5h)



(3-Fluorophenyl)methanol (0.76 g, 6 mmol) and SO_3•pyridine complex (1.05 g, 6.6 mmol) were placed in a 100 mL round bottom flask. Pyridine (8 mL) and dry dichloromethane (5 mL) were added and the mixture was stirred at 40 °C for 8 h. Water (70 mL) was added and the mixture was washed once with dichloromethane (1 x 70 mL). The aqueous phase was treated with tetrapropyl ammonium bromide (1.60 g, 6 mmol) and stirred for 1 h. The solution was extracted with dichloromethane (3 x 70 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. To the concentrated oil, hexanes and ether were added and the suspension was again evaporate. This hexane/ether process was repeated until following the evaporation of solvent the product was obtained as a white solid. After overnight drying under high vacuum (**5c**) was obtained as a white solid (1.75 g, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (td, *J* = 8.1, 6.0 Hz, 1H), 7.14 – 6.94 (m, 2H), 6.94 – 6.76 (m, 1H), 4.92 (s, 1H), 3.58 – 2.54 (m, 7H), 1.93 – 1.25 (m, 8H), 0.87 (t, *J* = 7.3 Hz, 11H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.62 (d, *J* = 244.9 Hz), 140.46 (d, *J* = 7.5 Hz), 129.62 (d, *J* = 8.1 Hz), 123.18 (d, *J* = 2.8 Hz), 114.53 (dd, *J* = 21.8, 1.5 Hz), 114.15 (d, *J* = 21.2 Hz), 67.84 (d, *J* = 1.9 Hz), 60.20, 15.43, 10.66. ^{19}F NMR (470 MHz, $CDCl_3$) δ –116.13 – –118.06 (m), –164.90. HRMS (ESI) m/z calcd for $C_7H_6FO_4S$ [M–N*n*-Pr_4]$^-$ 204.9971, found 205.0026.

Para borylation of tetrapropyl ammonium 2-chlorobenzyl sulfate (6a)

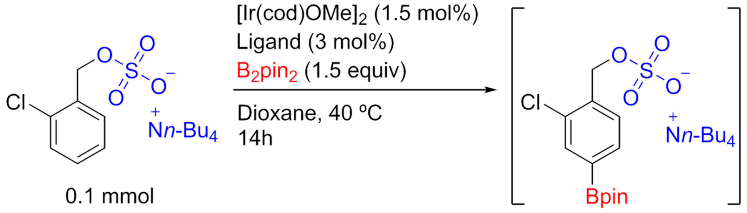


crude reaction mixture isomer ratio (NMR) = 18:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-chlorobenzyl sulfate (204 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 12 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and washed with hexanes (0.5 mL). The hexane layer was decanted, and the remaining solution subjected to chromatographic separation with silica gel (6% EtOAc in $CHCl_3$ as eluent) to give 93 mg of para-borylated 2-chlorobenzyl alcohol as an oil (69% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 4.76 (s, 2H), 2.36 (s, 1H), 1.33 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 135.3, 133.2, 132.2, 127.8, 84.2, 62.7, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) 30.6. HRMS (APCI+) m/z calcd for $C_{13}H_{17}BClO_2$ [M–OH$^-$] 251.1010, found 251.1057.

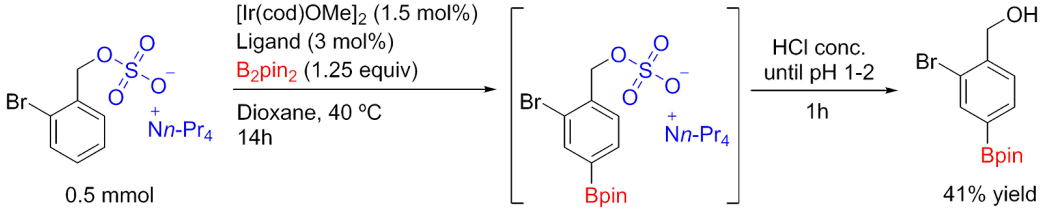
Para borylation of tetrabutyl ammonium 2-chlorobenzyl sulfate (6a′)



crude reaction mixture isomer ratio (NMR): para:meta = 15:1
>99.9% conversion

In a glove box, a 3.0 mL Wheaton microreactor was charged with tetrabutyl ammonium 2-chlorobenzyl sulfate (46 mg, 0.1 mmol), $[Ir(cod)(OMe)]_2$ (0.1 mL of 0.015 M solution, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (0.1 mL of 0.03 M solution 3.0 mol %), B_2pin_2 (38 mg, 0.15 mmol) and dioxane (0.2 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 14 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio.

Para borylation of tetrapropyl ammonium 2-bromobenzyl sulfate (6b)

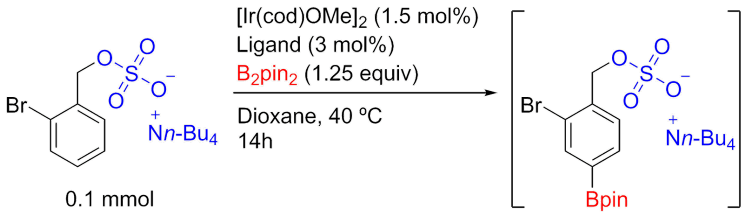


crude reaction mixture isomer ratio (NMR) = 30:1
82% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-bromo benzyl sulfate (226 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 12 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and subjected directly to chromatographic separation with silica gel (10% EtOAc in $CHCl_3$ as eluent) to give 64 mg of *para* borylated 2-bromobenzyl alcohol with traces of the *meta* (para:meta = 35:1) isomer as an oil (41% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 1.1 Hz, 1H), 7.73 (dd, J = 7.5, 1.1 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 4.74 (s, 2H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 138.5, 133.9, 127.9, 122.2, 84.2, 65.0, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) 30.3. HRMS (APCI+) m/z calcd for $C_{13}H_{17}BBrO_2$ [M–OH–] 295.0505, found 295.0595.

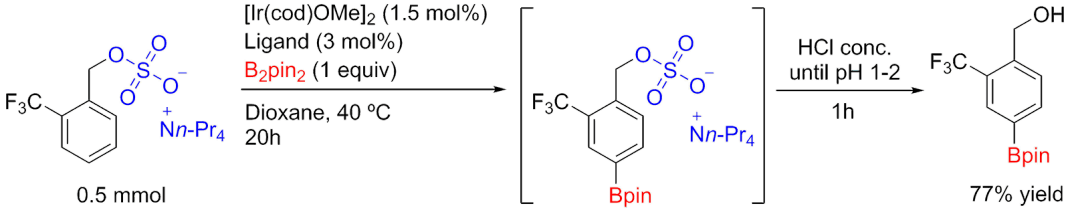
Para borylation of tetrabutyl ammonium 2-bromobenzyl sulfate (6b′)



crude reaction mixture isomer ratio (NMR): para:meta = 23:1
>99.9% conversion

In a glove box, a 3.0 mL Wheaton microreactor was charged with tetrabutyl ammonium 2-bromobenzyl sulfate (51 mg, 0.1 mmol), $[Ir(cod)(OMe)]_2$ (0.1 mL of 0.015 M solution, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (0.1 mL of 0.03 M solution 3.0 mol %), B_2pin_2 (32 mg, 0.125 mmol) and dioxane (0.2 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 14 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio.

Para borylation of tetrapropyl ammonium 2-trifluoromethylbenzyl sulfate (6c)

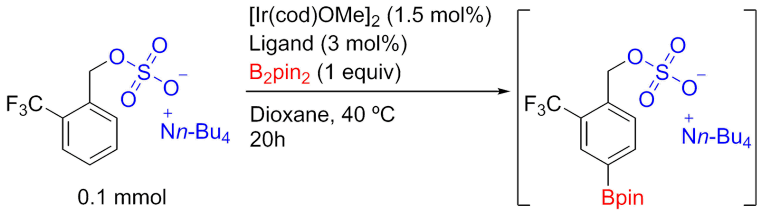


crude reaction mixture isomer ratio (NMR) = 9:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-trifluoromethyl benzyl sulfate (221 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (128 mg, 0.5 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 20 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel (4% EtOAc in $CHCl_3$ as eluent) to give 117 mg of a mixture of *para* borylated 2-trifluorobenzyl alcohol with the *meta* isomer (*para*:*meta* = 9:1) as an oil (77% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 4.84 (s, 2H), 2.80 (bs, 1H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3 (q, *J* = 1.6 Hz), 138.4 (q, *J* = 1.4 Hz), 131.8 (q, *J* = 5.6 Hz), 127.5, 126.3 (q, *J* = 30.7 Hz), 124.5 (q, J = 275.0 Hz), 84.3, 61.1 (q, *J* = 5.5 Hz), 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) 30.8. ^{19}F NMR (470 MHz, $CDCl_3$) -63.2. HRMS (APCI+) m/z calcd for $C_{14}H_{17}BF_3O_2$ [M–OH–] 285.1274, found 285.1302.

Para borylation of tetrabutyl ammonium 2-trifluoromethylbenzyl sulfate (6c′)

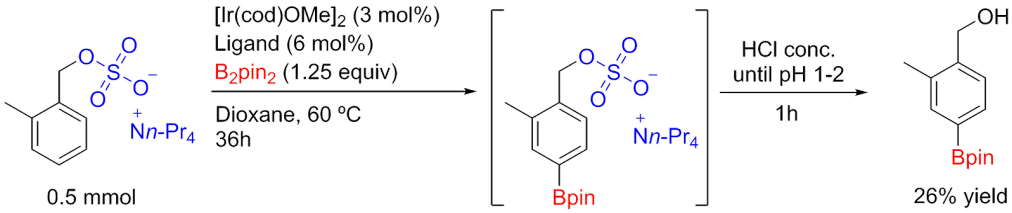


0.1 mmol

crude reaction mixture isomer ratio (NMR): para:meta = 8:1
>99.9% conversion

In a glove box, a 3.0 mL Wheaton microreactor was charged with tetrabutylammonium 2-trifluoromethylbenzyl sulfate (50 mg, 0.1 mmol), $[Ir(cod)(OMe)]_2$ (0.1 mL of 0.015 M solution, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (0.1 mL of 0.03 M solution 3.0 mol %), B_2pin_2 (25 mg, 0.10 mmol) and dioxane (0.2 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 20 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio.

Para borylation of tetrapropyl ammonium 2-methylbenzyl sulfate (6d)



0.5 mmol

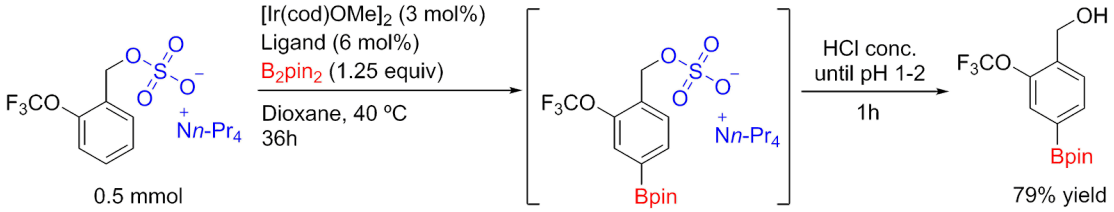
26% yield

crude reaction mixture isomer ratio (NMR) = 5:1
78% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropylammonium 2-methyl benzyl sulfate (194 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (10 mg, 3 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and subjected directly to chromatographic separation with silica gel (1.5% EtOAc in $CHCl_3$ as eluent) to give 33 mg of *para* borylated 2-methylbenzyl alcohol with traces of the *meta* (para:meta = 35:1) isomer as a colorless oil (26% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 1H), 7.40 (d, J = 7.5 Hz, 1H), 4.73 (d, J = 4.6 Hz, 2H), 2.36 (s, 3H), 1.58 (bs, 1H) 1.36 (s, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.84, 136.57, 135.10, 132.64, 126.50, 83.77, 63.48, 24.85, 18.41. ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.01. HRMS (APCI+) m/z calcd for $C_{14}H_{20}BO_2$ [M–OH–] 231.1556, found 231.1573.

Para borylation of tetrapropyl ammonium 2-trifluoromethoxybenzyl sulfate (6e)



0.5 mmol

79% yield

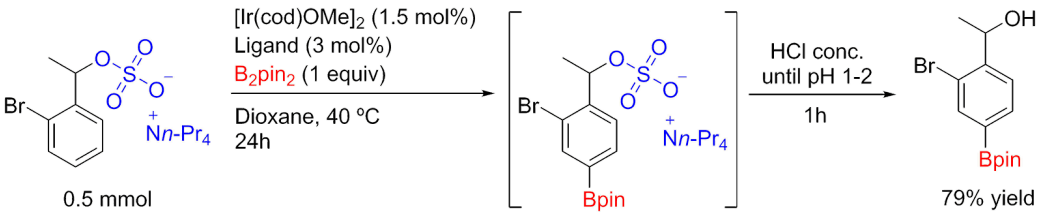
crude reaction mixture isomer ratio (NMR) = 22:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-trifluoromethoxy benzyl sulfate (229 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (10 mg, 3 mol %), 4,4′-dimethoxy-2,2′-bipyridine (6.6 mg, 6.0 mol %), B_2pin_2 (159 mg, 0.625 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 36 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed

through a plug of silica gel (2% EtOAc in $CHCl_3$ as eluent) to give 126 mg of a mixture of *para* borylated 2-trifluoromethoxyphenol with the *meta* isomer (*para*:*meta* = 24:1) as an oil (79% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.61 (d, *J* = 1.0 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 4.75 (s, 2H), 2.69 (bs, 1H), 1.33 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 136.4, 133.3, 128.0, 126.1, 120.4 (q, *J* = 257.5 Hz), 84.1, 59.4, 24.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.20. ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.26. HRMS (APCI+) m/z calcd for $C_{14}H_{17}BF_3O_3$ [M–OH–] 301.1223, found 301.1248.

Para borylation of tetrapropyl ammonium 1-(2-bromophenyl)ethyl sulfate (6f)



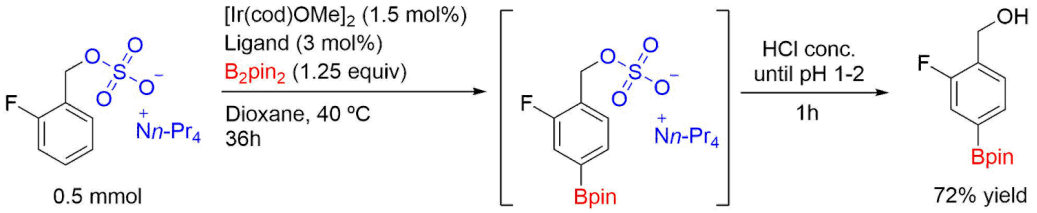
crude reaction mixture isomer ratio (NMR) = 11:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 1-(2-bromophenyl)ethyl sulfate (233 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (128 mg, 0.5 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 °C. After 24 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel ($CHCl_3$ as eluent) to give 129 mg of a mixture of *para* borylated 1-(2-bromophenyl)ethan-1-ol with the *meta* isomer (*para*:*meta* = 13:1) as an oil (79% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.1 Hz, 1H), 7.75 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 5.23 (q, *J* = 6.4 Hz, 1H), 2.24 (bs, 1H), 1.47 (d, *J* = 6.4 Hz, 3H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 138.8, 134.1, 126.1, 121.6, 84.1, 69.3, 24.8, 23.5.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.4. HRMS (APCI+) m/z calcd for $C_{14}H_{19}BBrO_2$ [M–OH–] 309.0661, found 309.0687.

Para borylation of tetrapropyl ammonium 2-fluorobenzyl sulfate (6g)

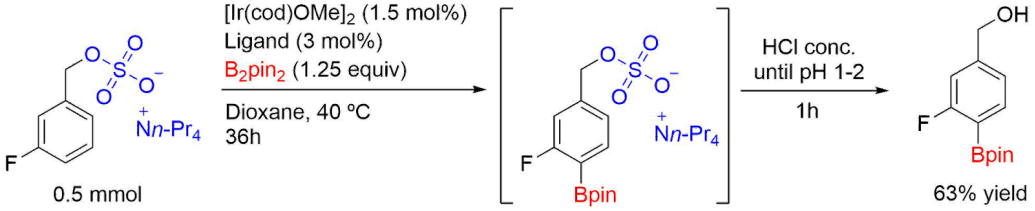


crude reaction mixture isomer ratio (NMR): para:meta:dimeta = 7:1:4
97% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 2-fluorobenzyl sulfate (196 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.626 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel (5% EtOAc in $CHCl_3$ as eluent) to give 91.2 mg of a mixture of *para* borylated (2-fluorophenyl)methanol with the *meta* isomer and diborylated product (*para*:*meta*:*di* = 10.6:1:1.2) as an oil (69% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 1H), 7.48 – 7.37 (m, 2H), 4.75 (d, J = 12.7 Hz, 3H), 2.17 (bs, 1H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1 (d, J = 246.6 Hz), 130.9 (d, J = 14.7 Hz), 130.6 (d, J = 3.4 Hz), 128.5 (d, J = 3.9 Hz), 120.8 (d, J = 19.5 Hz), 84.1, 59.2 (d, J = 4.6 Hz), 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.47.^{19}F NMR (470 MHz, $CDCl_3$) δ –108.48, –112.94 (d, J = 6.6 Hz), –124.36, –164.90 (t, J = 0.9 Hz). HRMS (APCI+) m/z calcd for $C_{13}H_{17}BFO_2$ [M–OH–] 235.1306, found 235.1337.

Para borylation of tetrapropyl ammonium 3-fluorobenzyl sulfate (6h)



crude reaction mixture isomer ratio (NMR) = 2:1
>99.9% conversion

In a glove box, a 5.0 mL Wheaton microreactor was charged with tetrapropyl ammonium 3-fluorobenzyl sulfate (196 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (5 mg, 1.5 mol %), 4,4′-dimethoxy-2,2′-bipyridine (3.3 mg, 3.0 mol %), B_2pin_2 (159 mg, 0.626 mmol) and dioxane (1.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 °C. After 36 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* ratio. HCl 12 M was added until pH = 1–2 and the resultant mixture was stirred for 1 h. The solution was concentrated and passed through a plug of silica gel (4% EtOAc in $CHCl_3$ as eluent) to give 79.1 mg of a mixture of *para* borylated (3-fluorophenyl)methanol with the *meta* isomer (*para*:*meta* = 1:1.9) as an oil (63% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, J = 7.6, 6.2 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 7.01 (dd, J = 10.1, 1.4 Hz, 1H), 4.65 (s, 2H), 2.71 (bs, 1H), 2.62 (bs, 1H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4 (d, J = 250.9 Hz), 162.7 (d, J = 246.8 Hz), 147.3 (d, J = 8.0 Hz), 143.1 (d, J = 6.3 Hz), 136.9 (d, J = 8.2 Hz), 128.4 (d, J = 2.8 Hz), 121.5 (d, J = 3.0 Hz), 119.9 (d, J = 19.5 Hz), 116.5 (d, J = 21.9 Hz), 113.2 (d, J = 24.6 Hz), 84.2, 83.9, 75.1, 64.3 (d, J = 1.7 Hz), 64.2 (d, J = 1.8 Hz), 24.8, 24.8. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ –103.79 – –107.40 (m), –117.31, –164.90. HRMS (APCI+) m/z calcd for $C_{13}H_{17}BFO_2$ [M–OH–] 235.1306, found 235.1387.

References

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Cyclooctadiene, and Barrelene Complexes of Rhodium(I) and Iridium(I): Kirschner/Inorganic. In *Inorganic Syntheses*; Kirschner, S., Ed.; Inorganic Syntheses; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1985; Vol. 231, pp 126–130.

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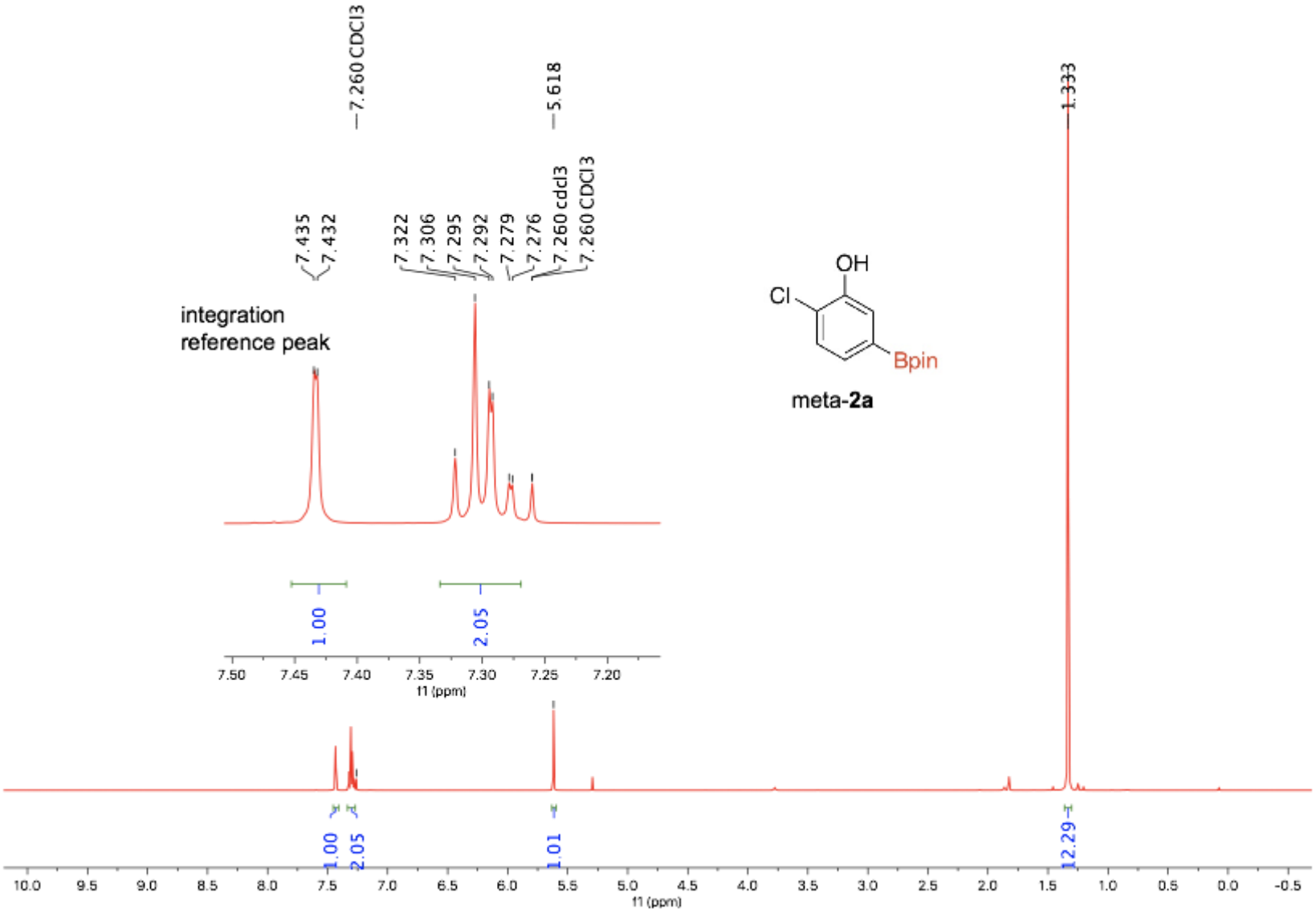
^{1}H NMR of commercial 4-chloro-3-hydroxyphenylBpin (meta borylated 2-chlorophenol, 2a)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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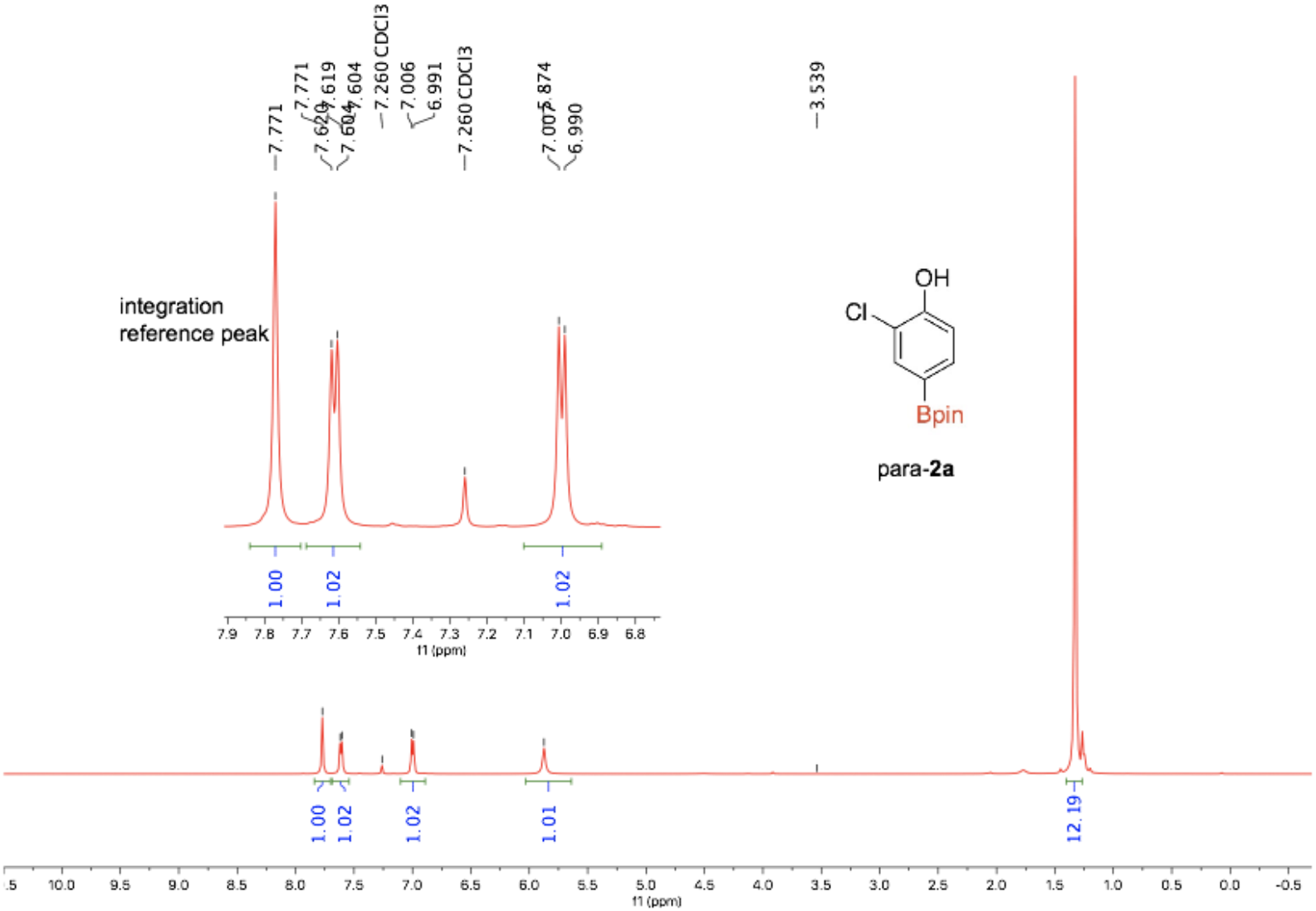
^{1}H NMR of commercial 3-chloro-4-hydroxyphenylBpin (para borylated 2-chlorophenol, 2a)



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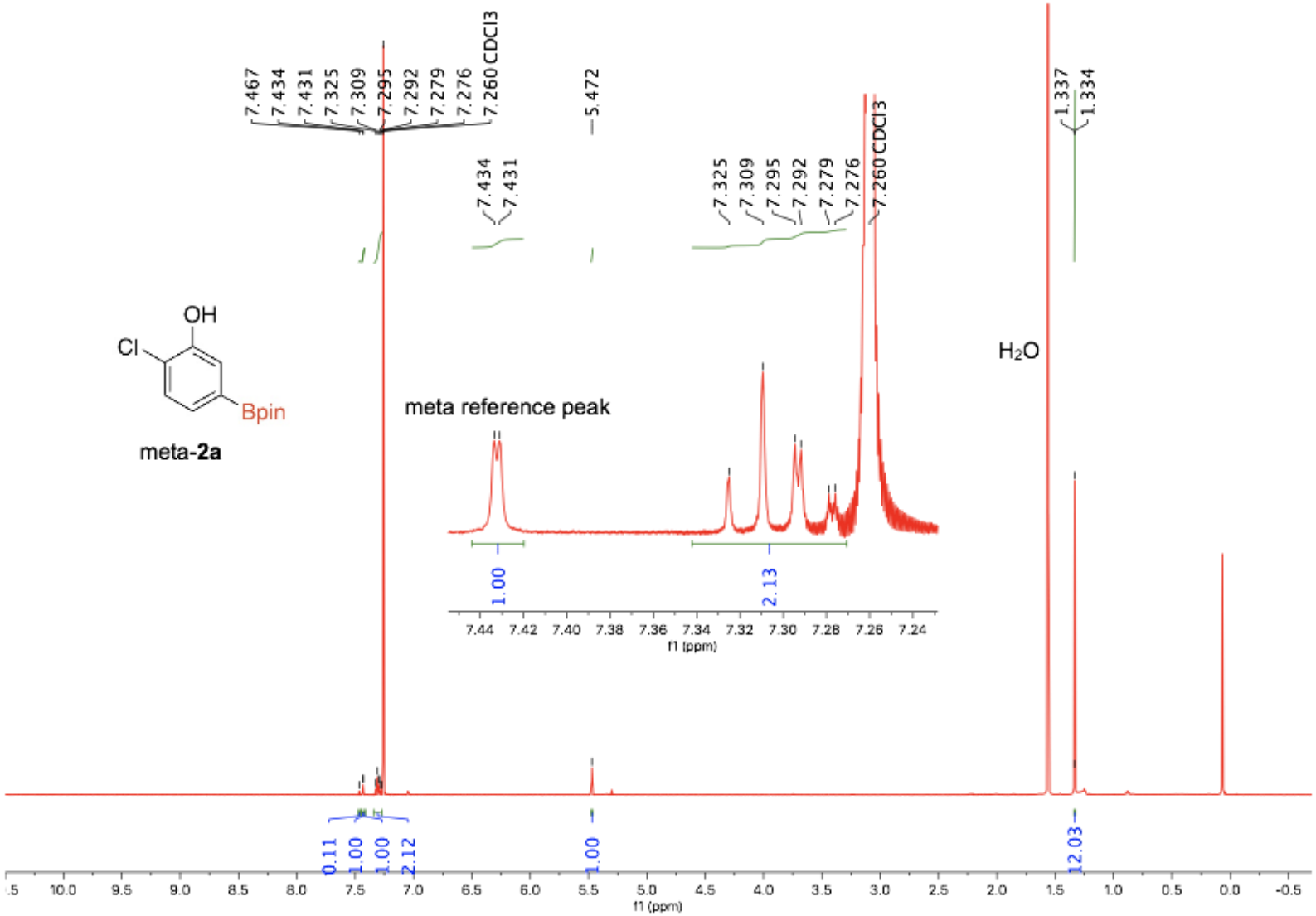
^{1}H NMR control spectrum of 7.0 x 10^{-7} mols meta-2a



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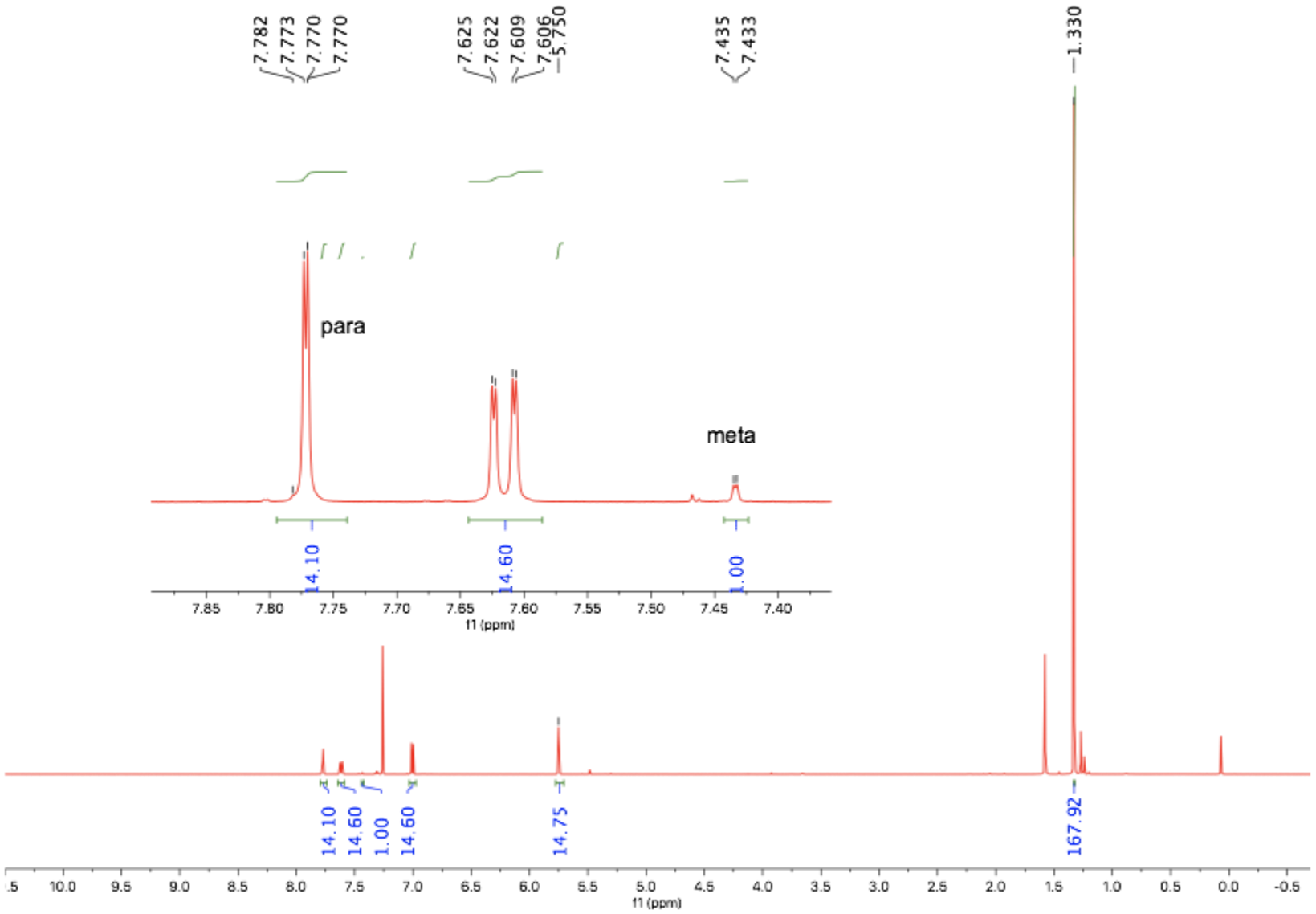
^{1}H NMR spectrum of 14:1 mixture of para-2a to meta-2a



Conditions: 25 °C, 500 MHz, $CDCl_3$

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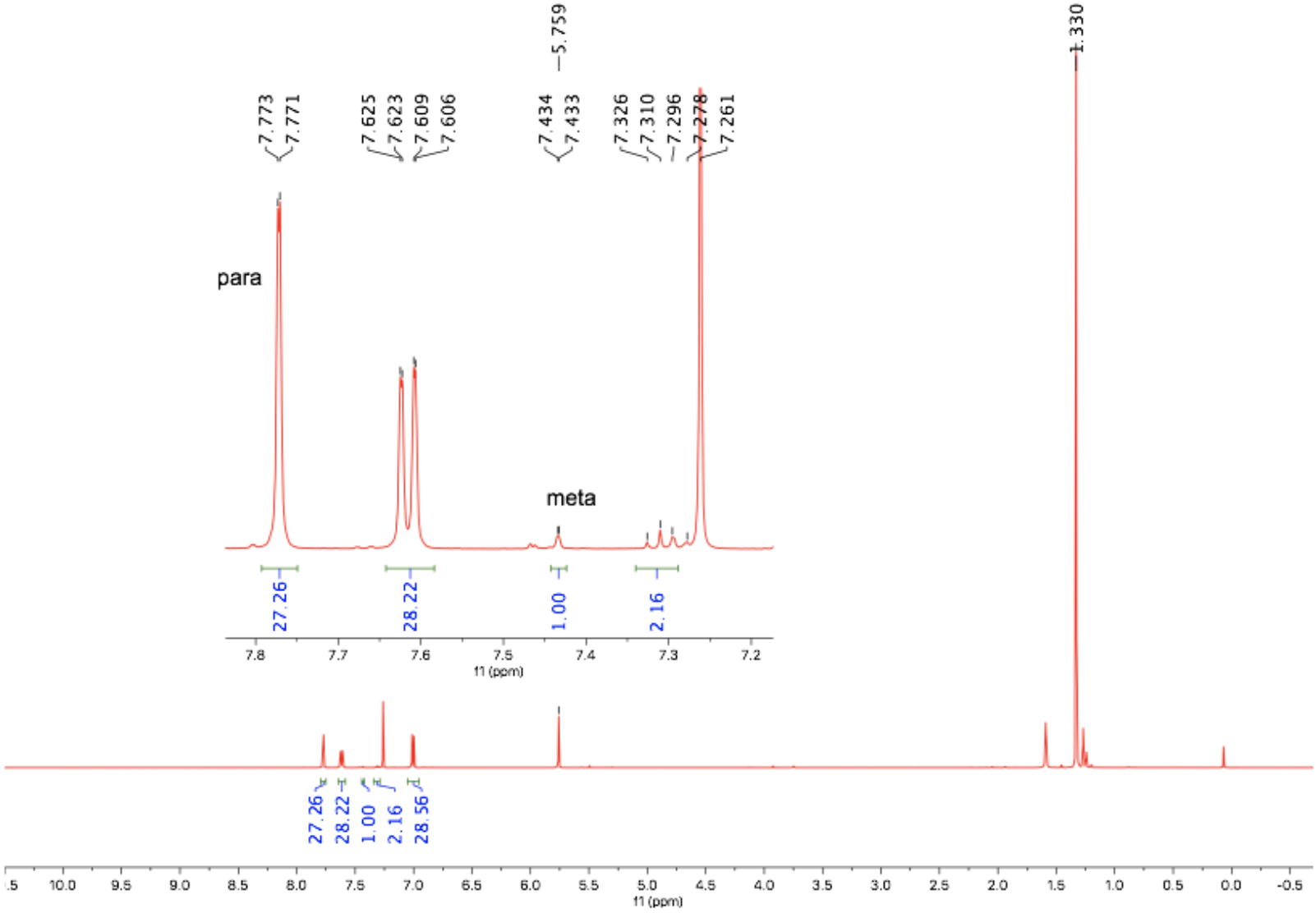
^{1}H NMR spectrum of 28:1 mixture of para-2a to meta-2a



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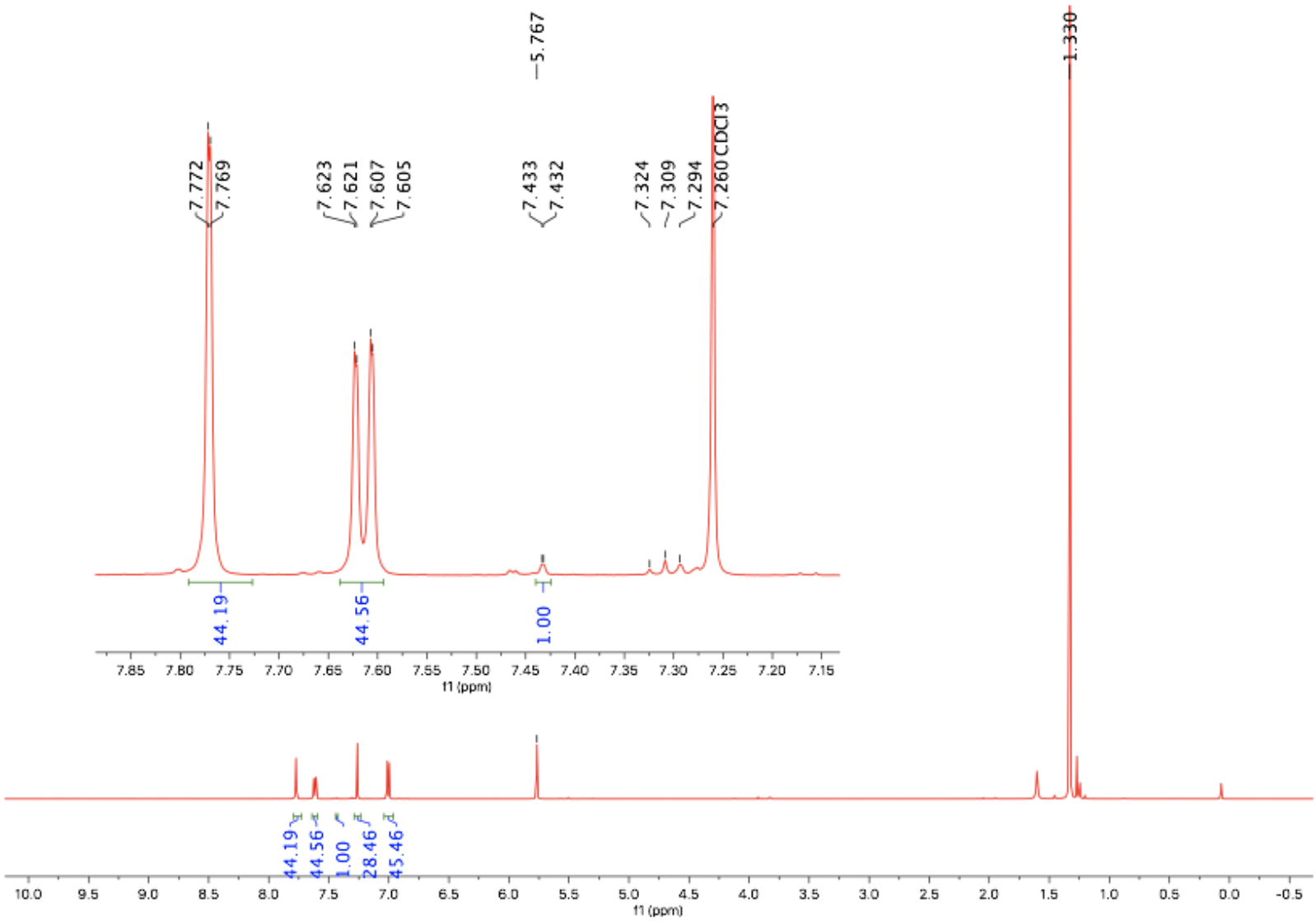
^{1}H NMR spectrum of 42:1 mixture of para-2a to meta-2a



Conditions: 25 °C, 500 MHz, $CDCl_3$

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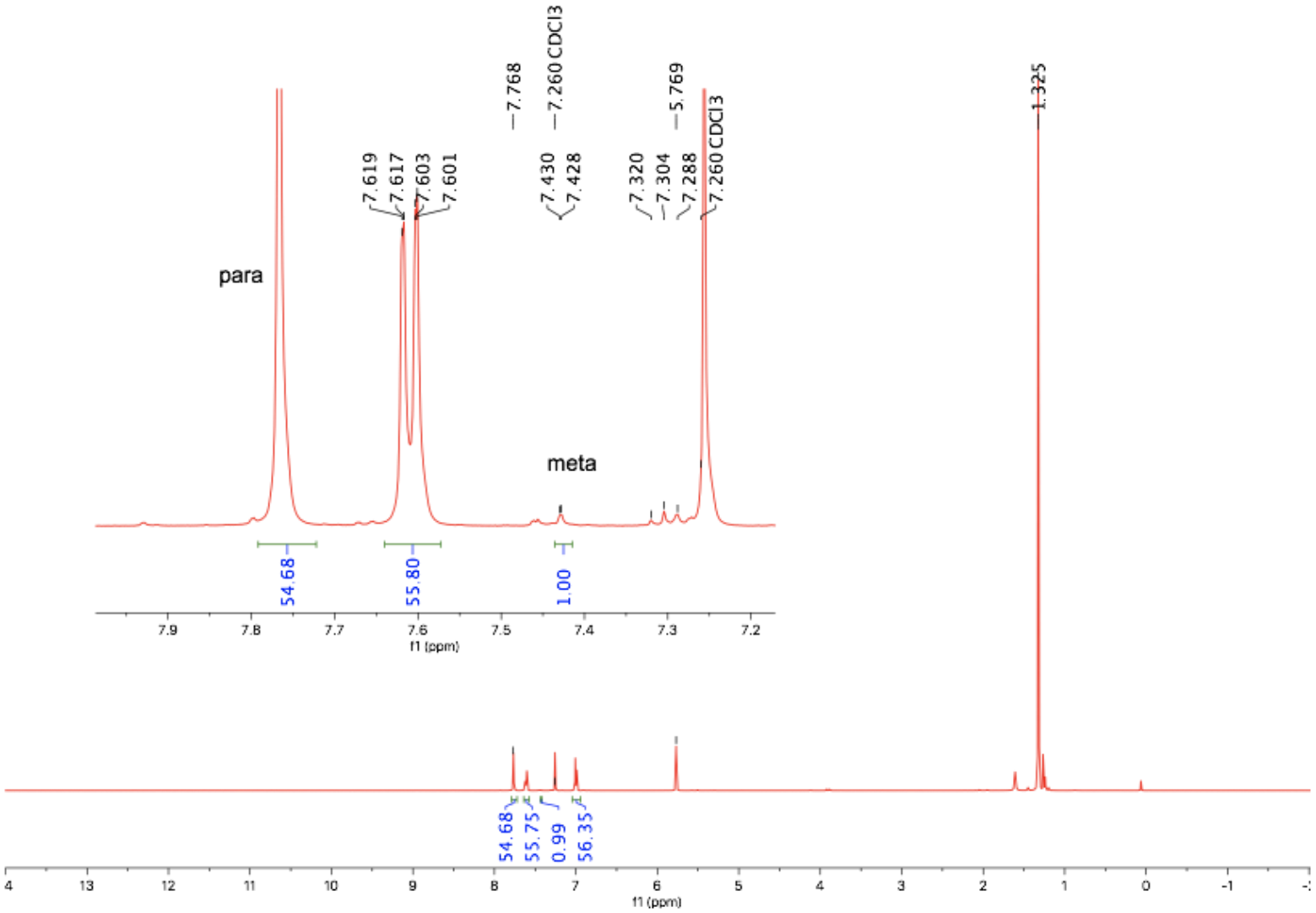
^{1}H NMR spectrum of 56:1 mixture of para-2a to meta-2a



Conditions: 25 °C, 500 MHz, $CDCl_3$

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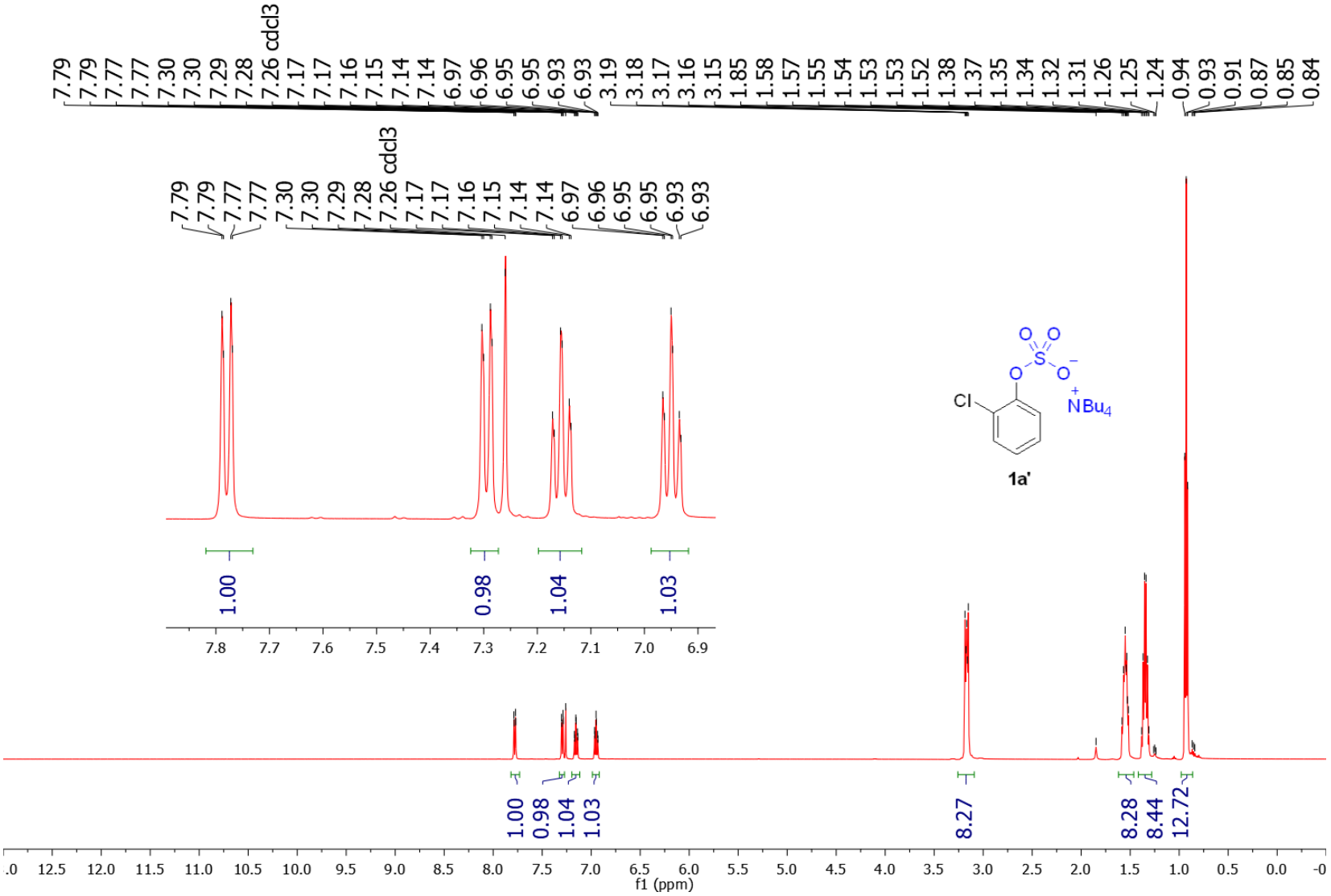
^{1}H NMR spectrum of tetrabutylammonium 2-chlorophenylsulfate (1a′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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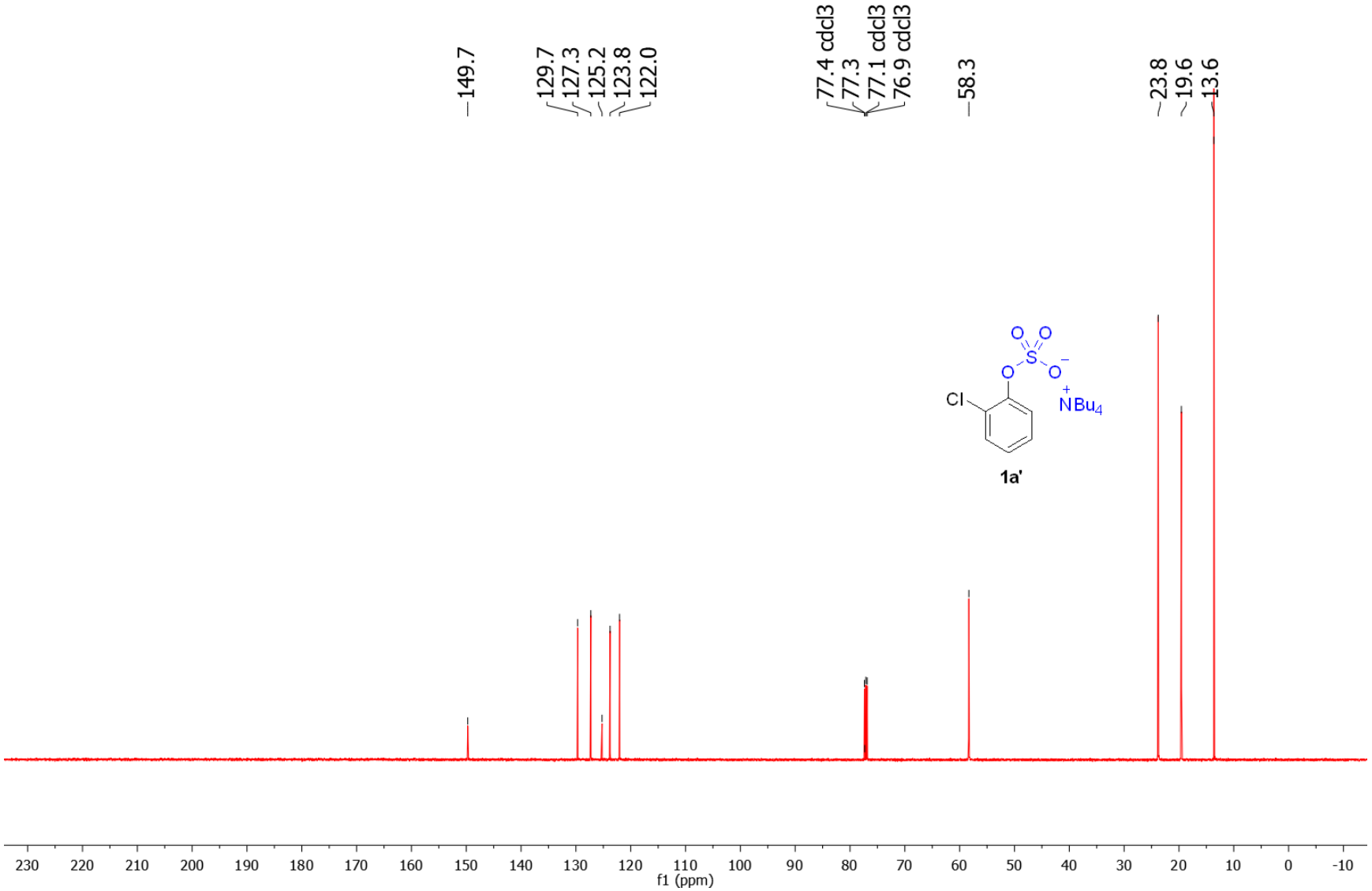
^{13}C NMR spectrum of tetrabutylammonium 2-chlorophenylsulfate (1a′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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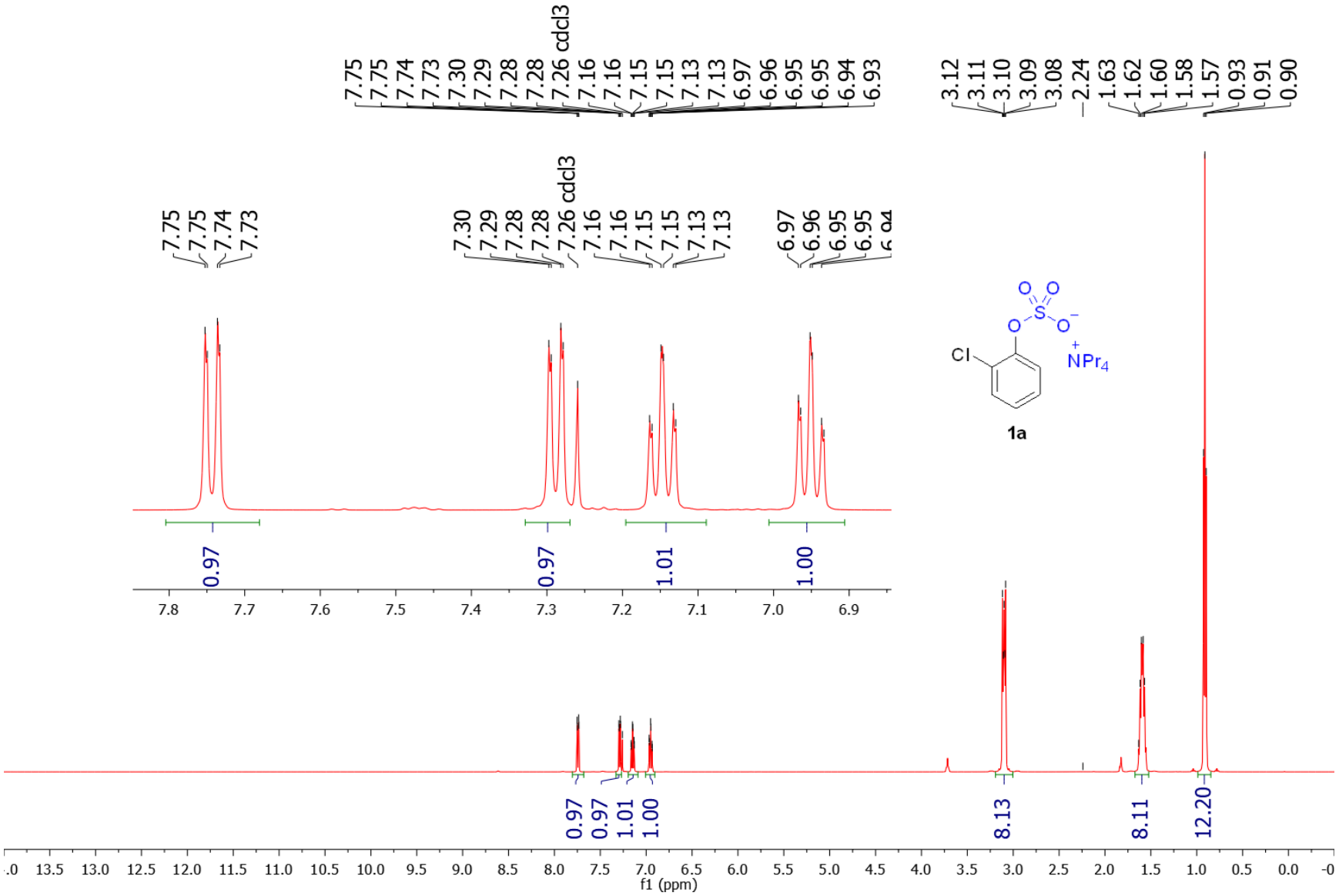
^{1}H NMR spectrum of tetrapropylammonium 2-chlorophenylsulfate (1a)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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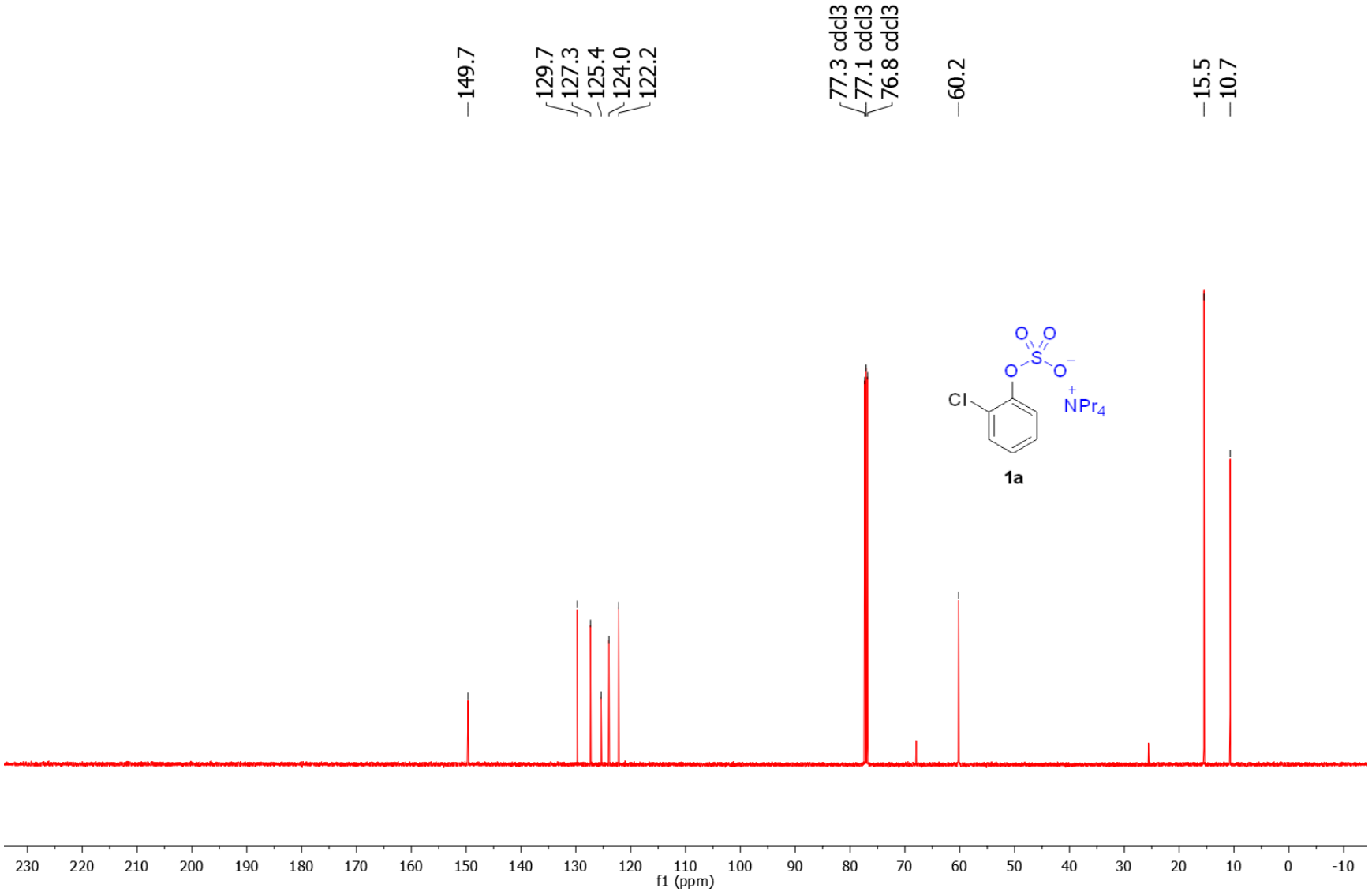
^{13}C NMR spectrum of tetrapropylammonium 2-chlorophenylsulfate (1a)



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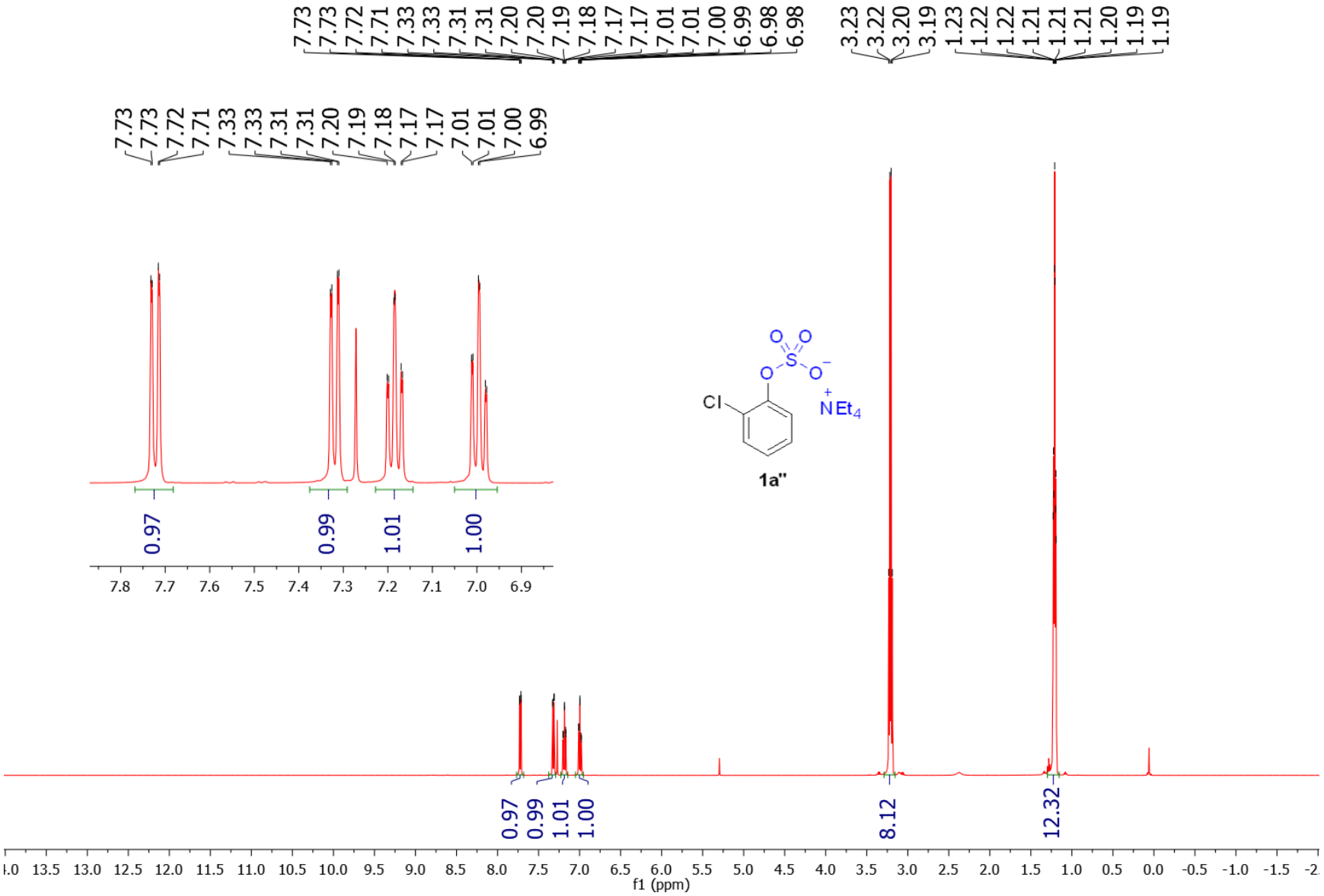
^{1}H NMR spectrum of tetraethylammonium 2-chlorophenylsulfate (1a″)



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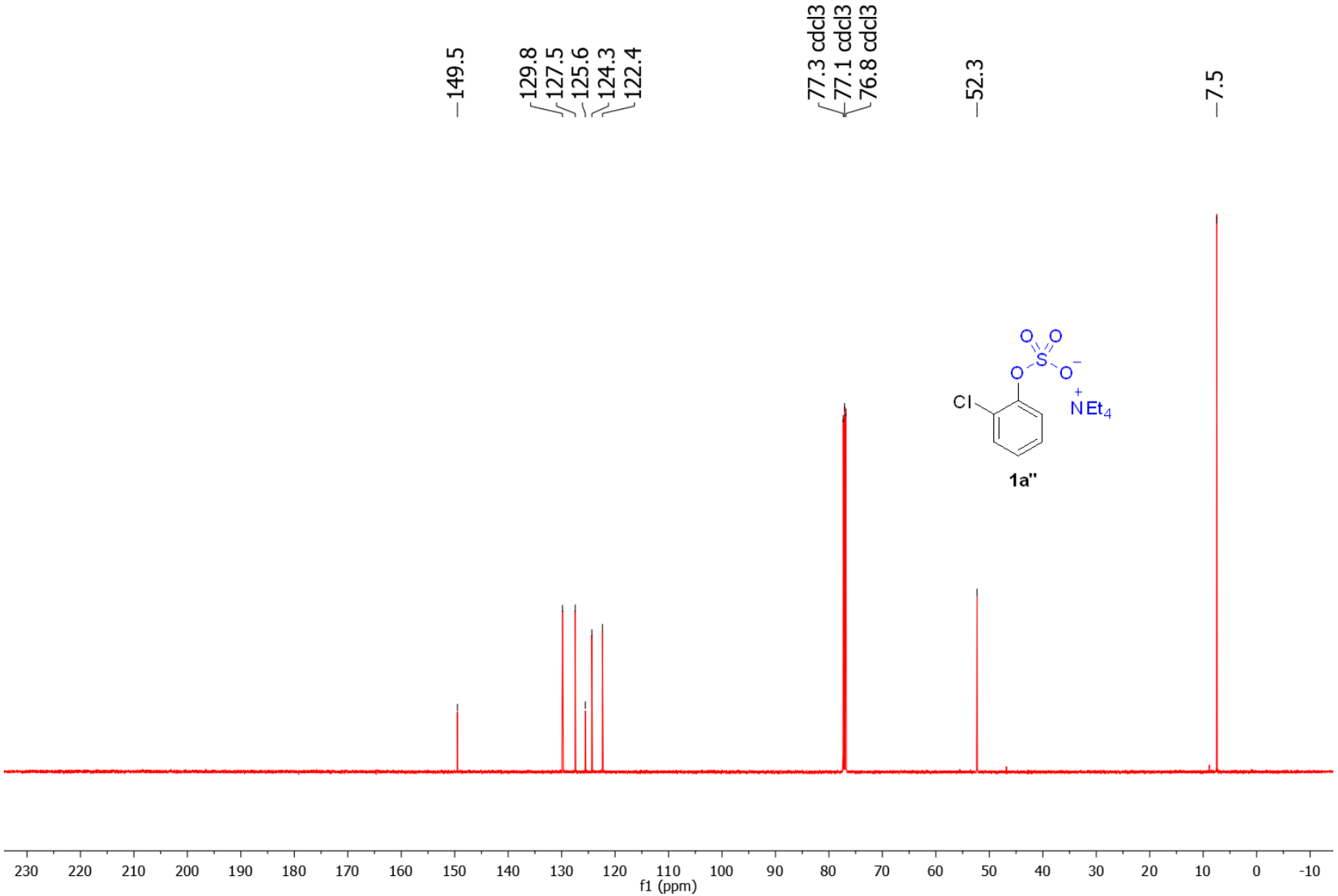
^{13}C NMR spectrum of tetraethylammonium 2-chlorophenylsulfate (1a′′)



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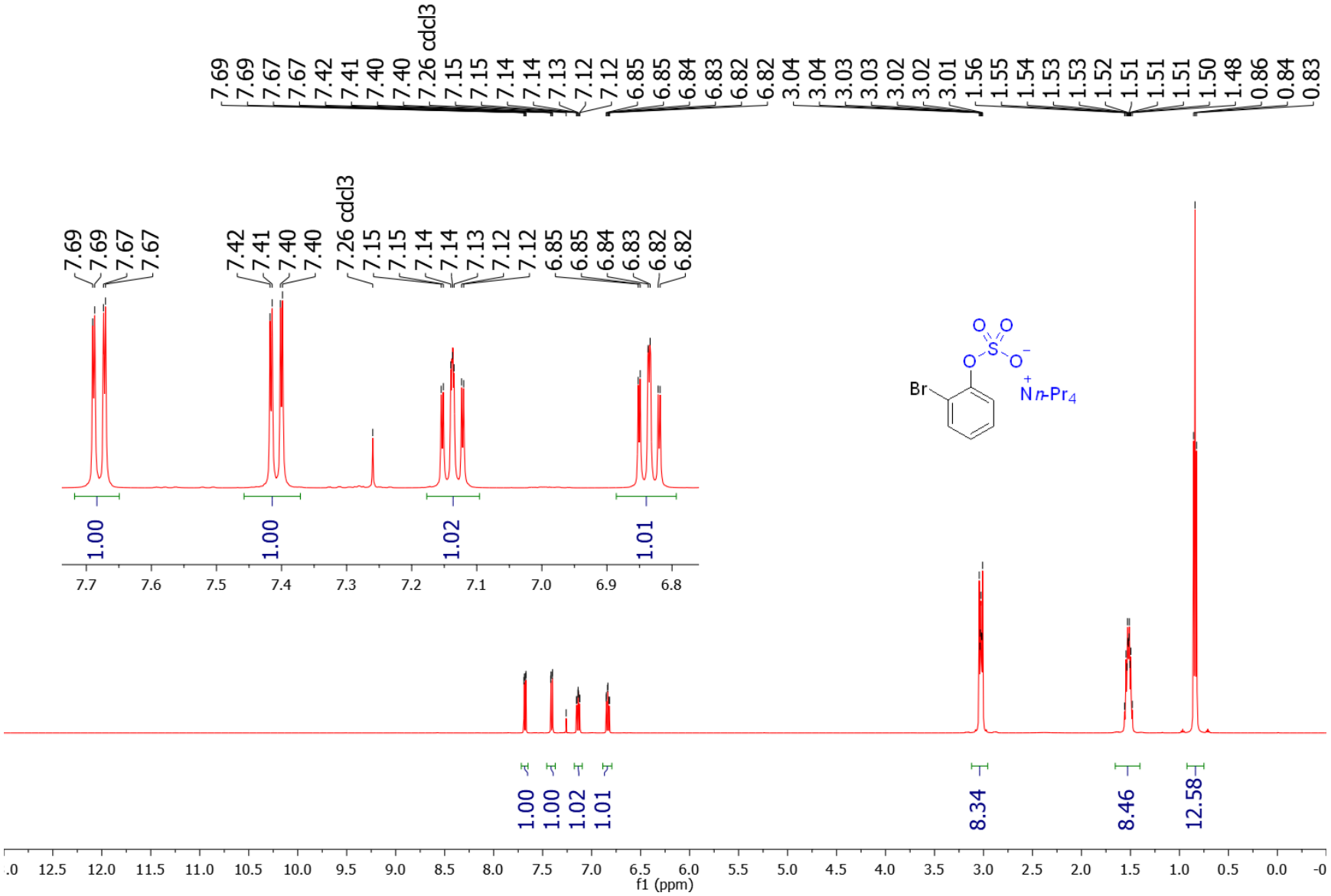
^{1}H NMR spectrum of tetrapropylammonium 2-bromophenylsulfate (1b)



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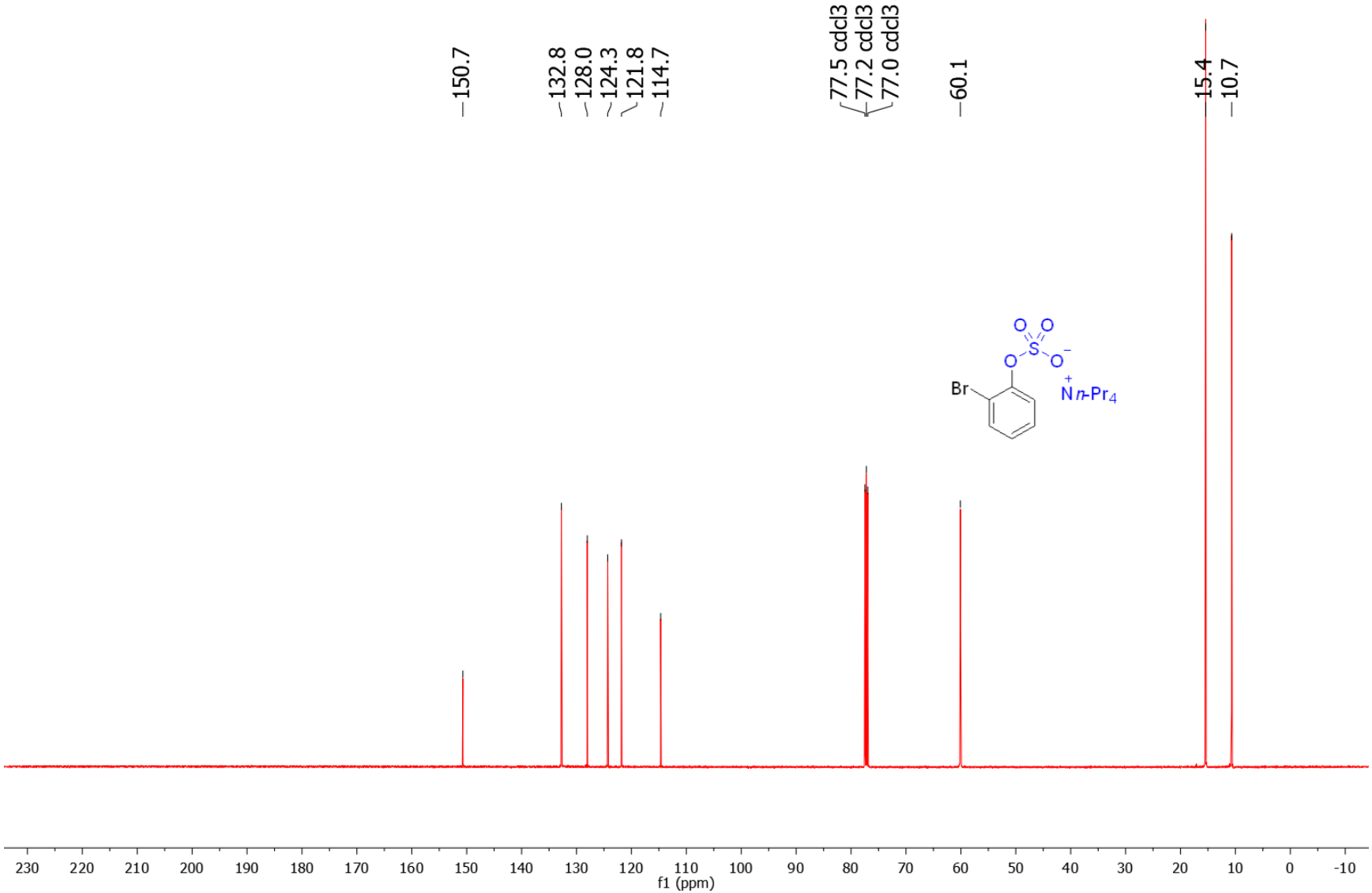
^{13}C NMR spectrum of tetrapropylammonium 2-bromophenylsulfate (1b)



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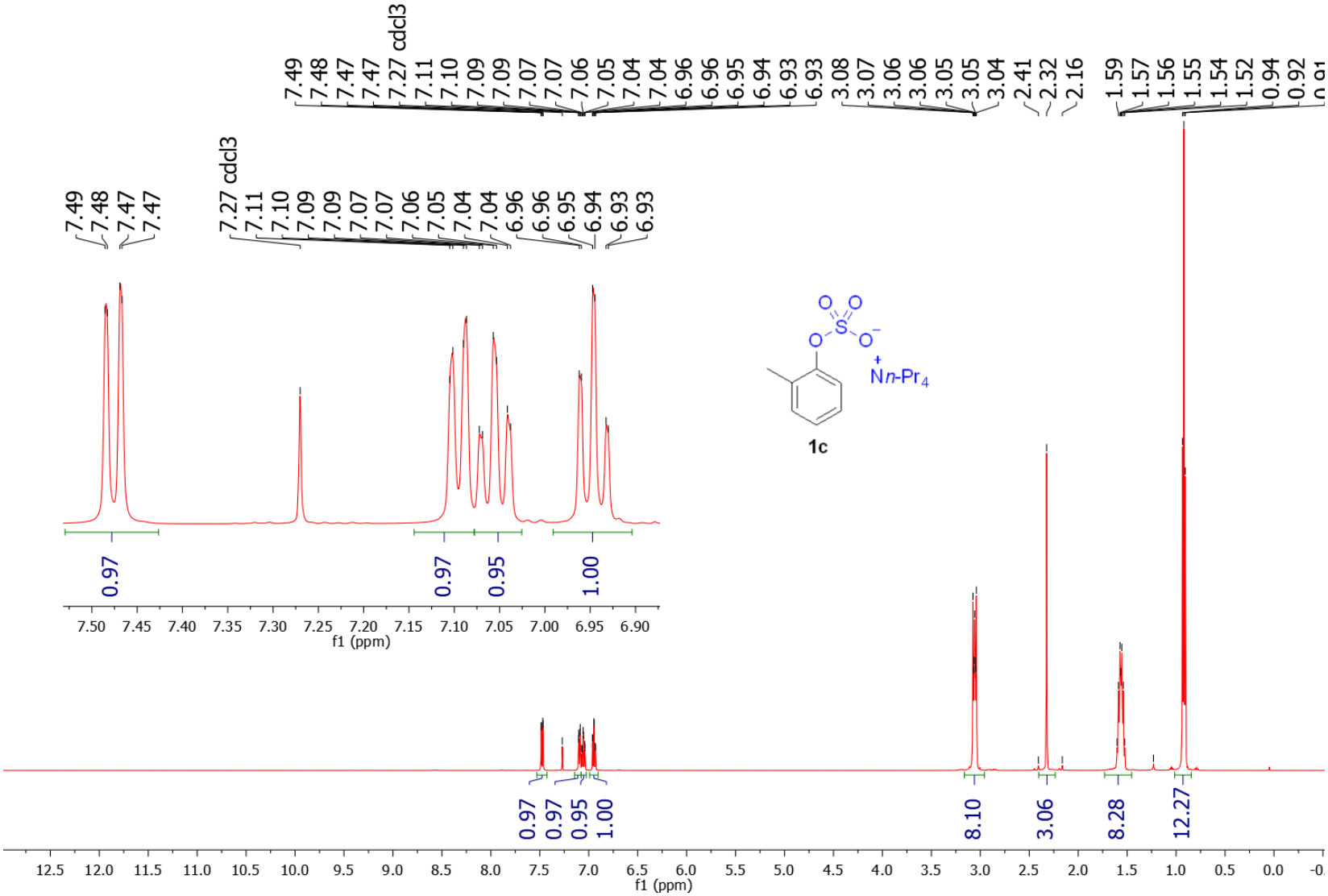
^{1}H NMR spectrum of tetrapropylammonium 2-methylphenylsulfate (1c)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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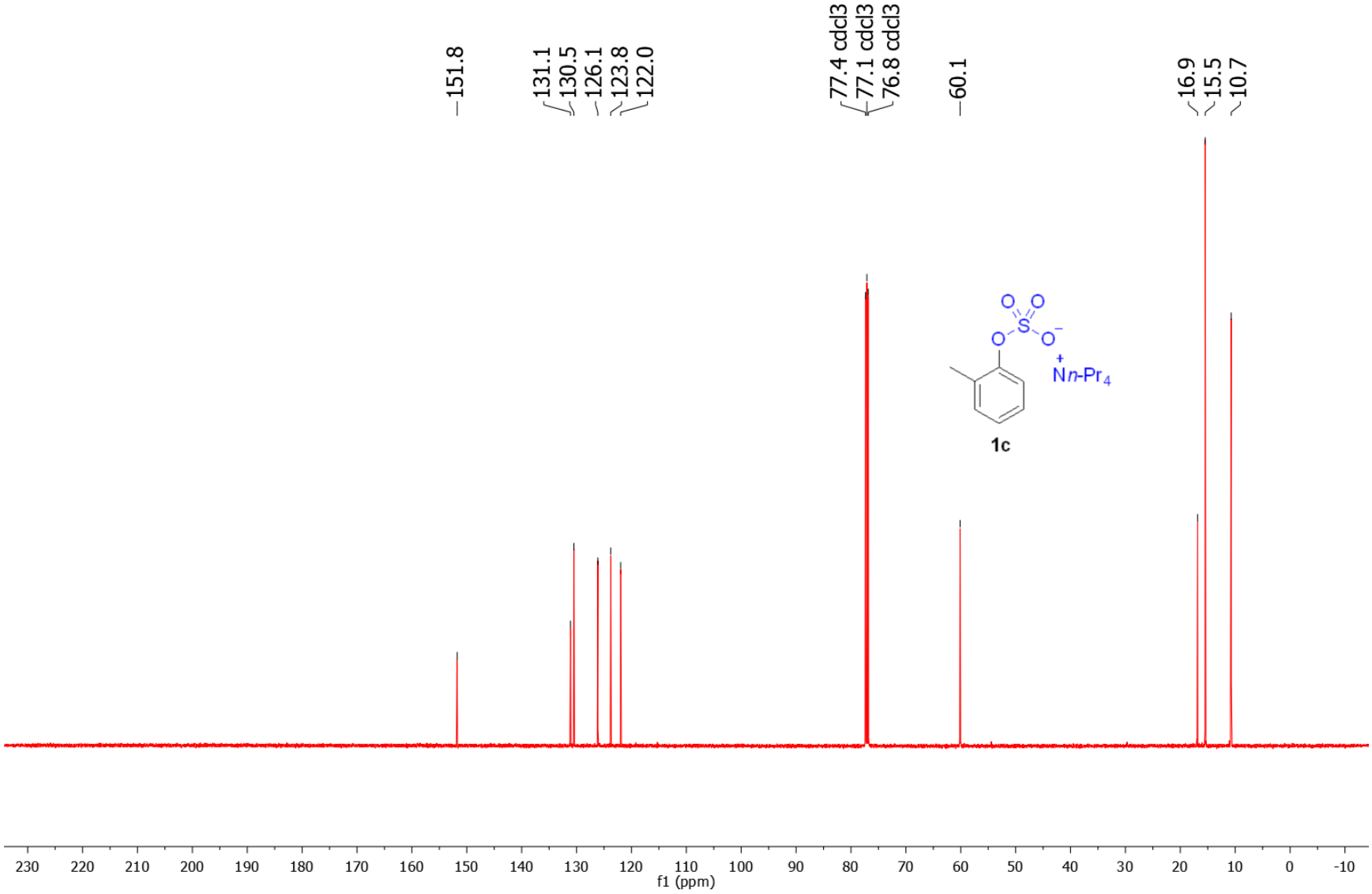
^{13}C NMR spectrum of tetrapropylammonium 2-methylphenylsulfate (1c)



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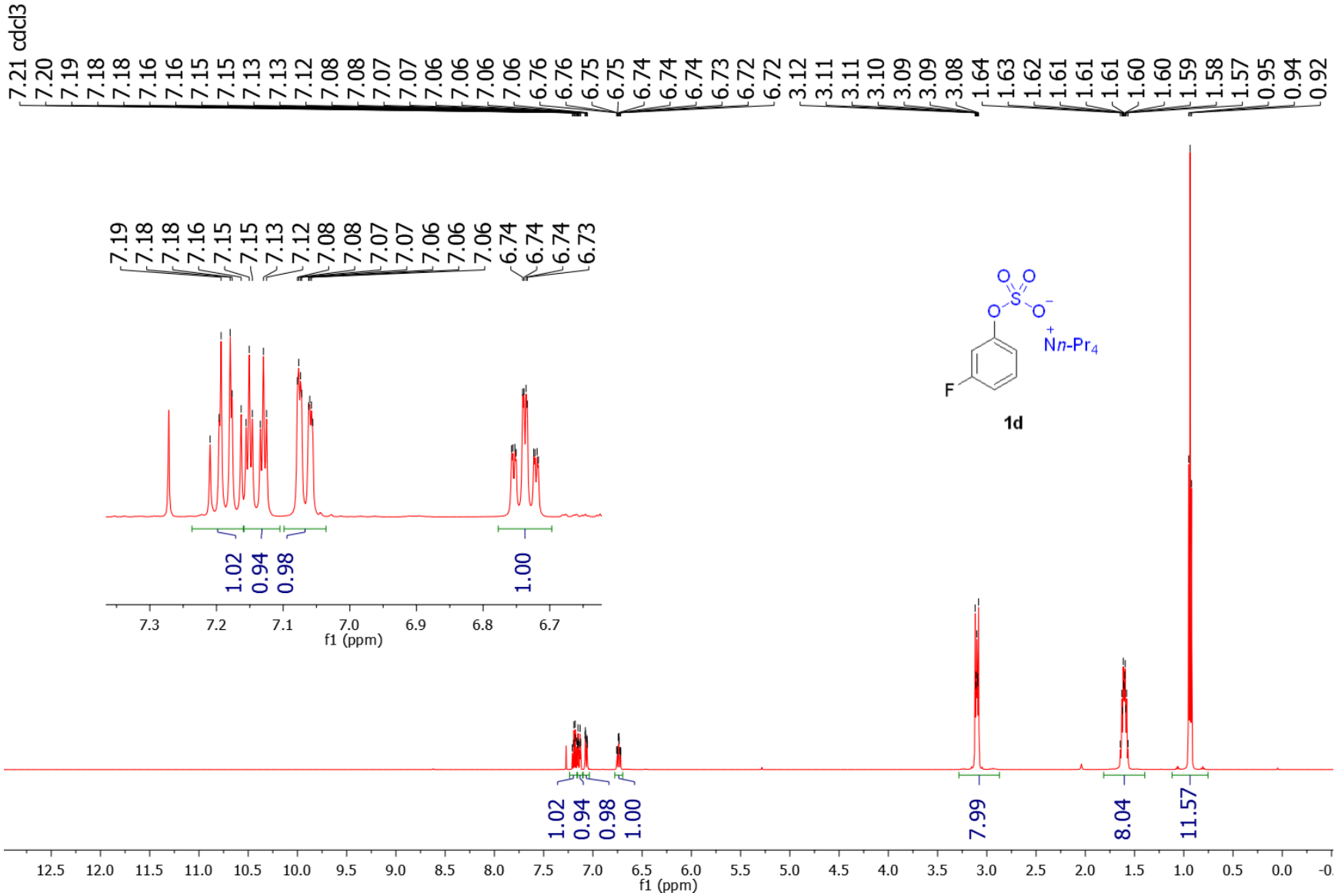
^{1}H NMR spectrum of tetrapropylammonium 3-fluorophenylsulfate (1d)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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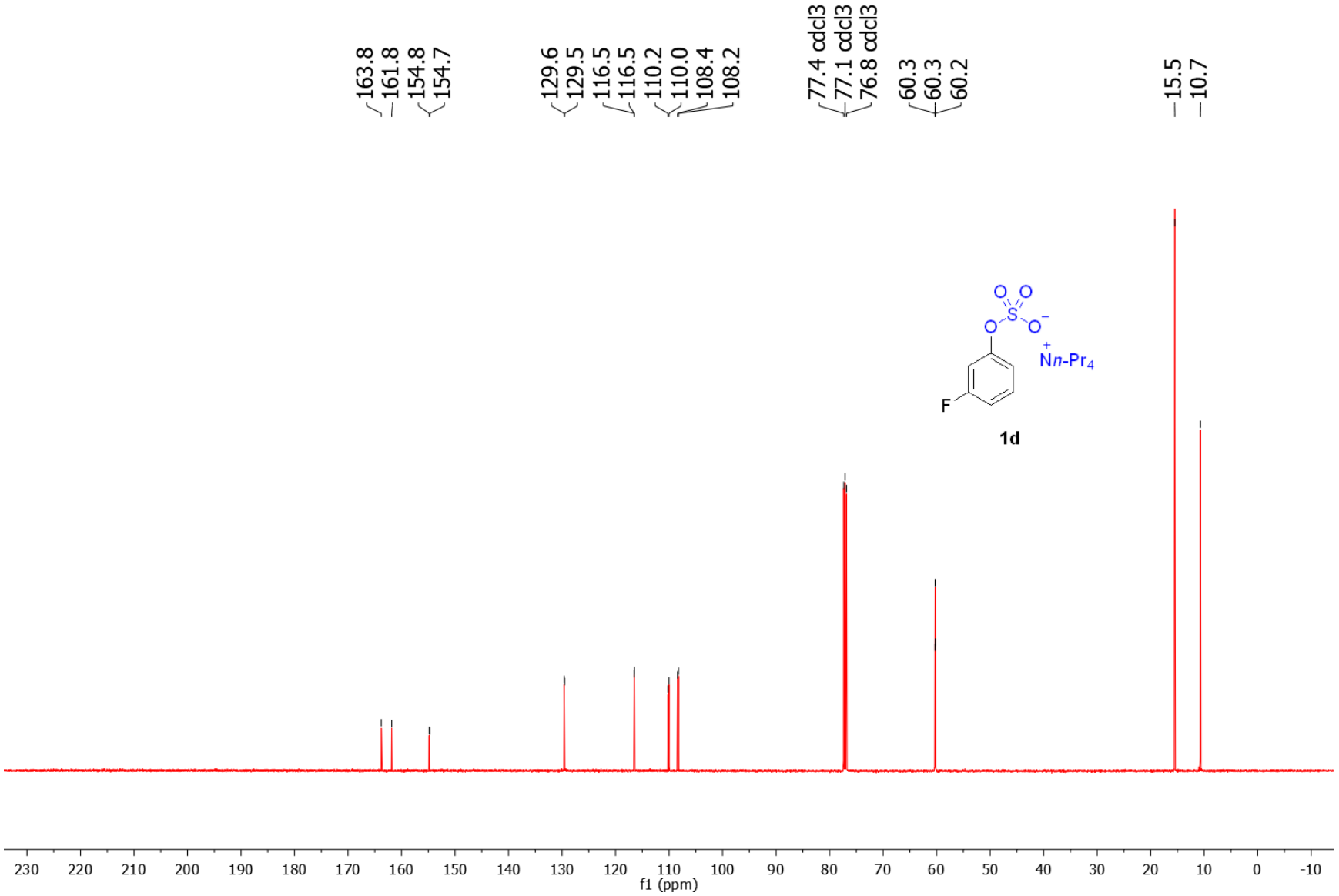
^{13}C NMR spectrum of tetrapropylammonium 3-fluorophenylsulfate (1d)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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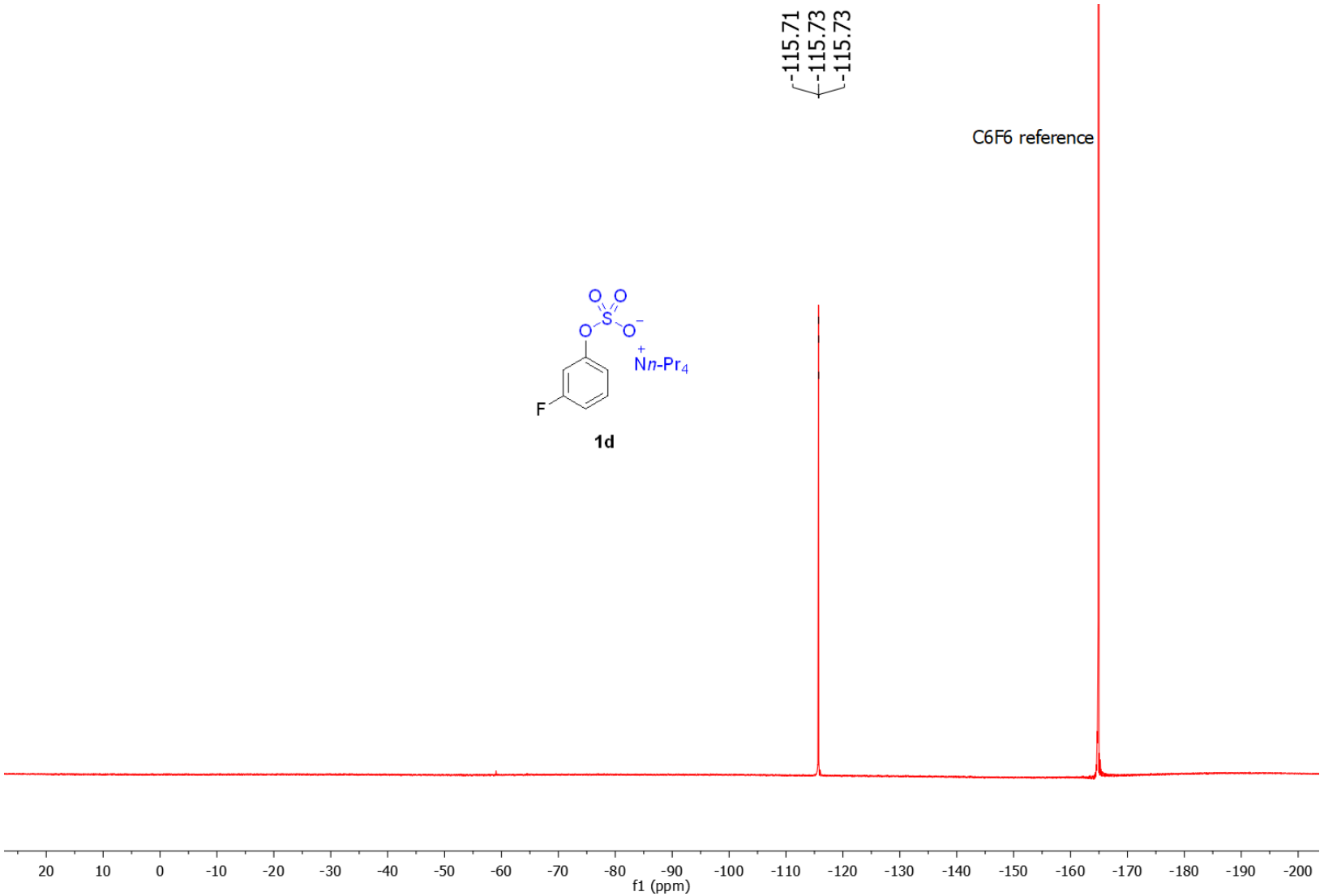
^{19}F NMR spectrum of tetrapropylammonium 3-fluorophenylsulfate (1d)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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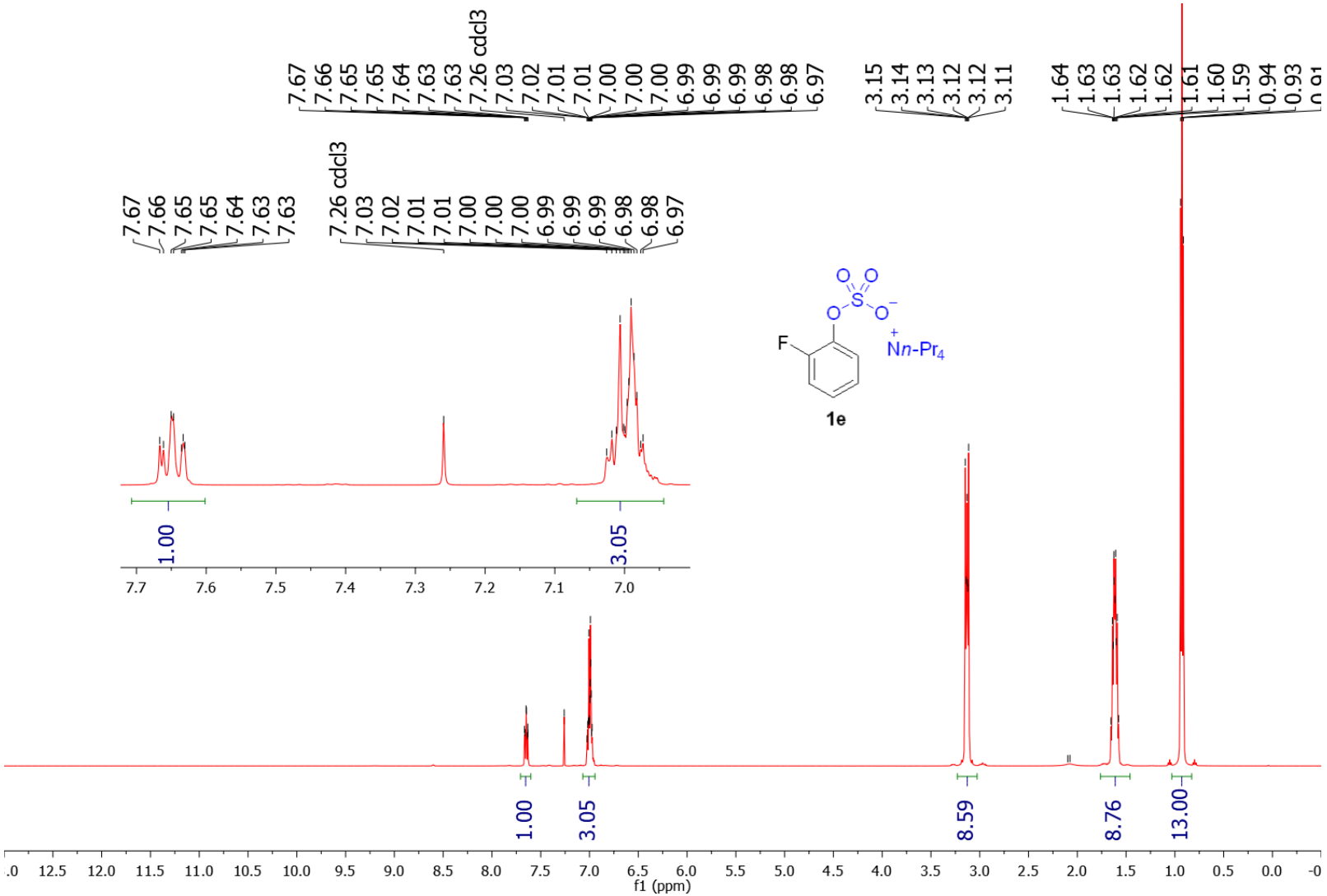
^{1}H NMR spectrum of tetrapropylammonium 2-fluorophenylsulfate (1e)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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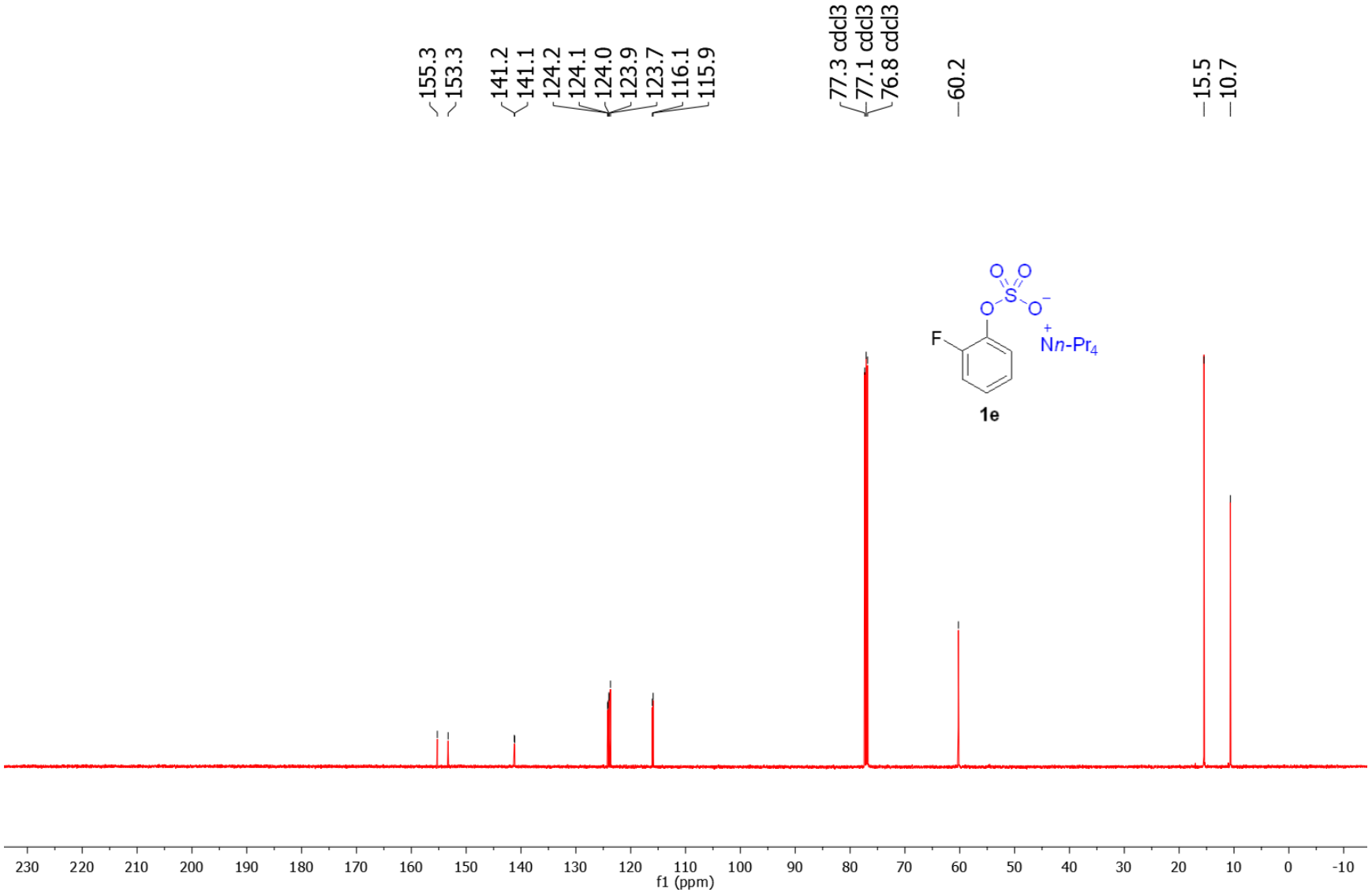
^{13}C NMR spectrum of tetrapropylammonium 2-fluorophenylsulfate (1e)



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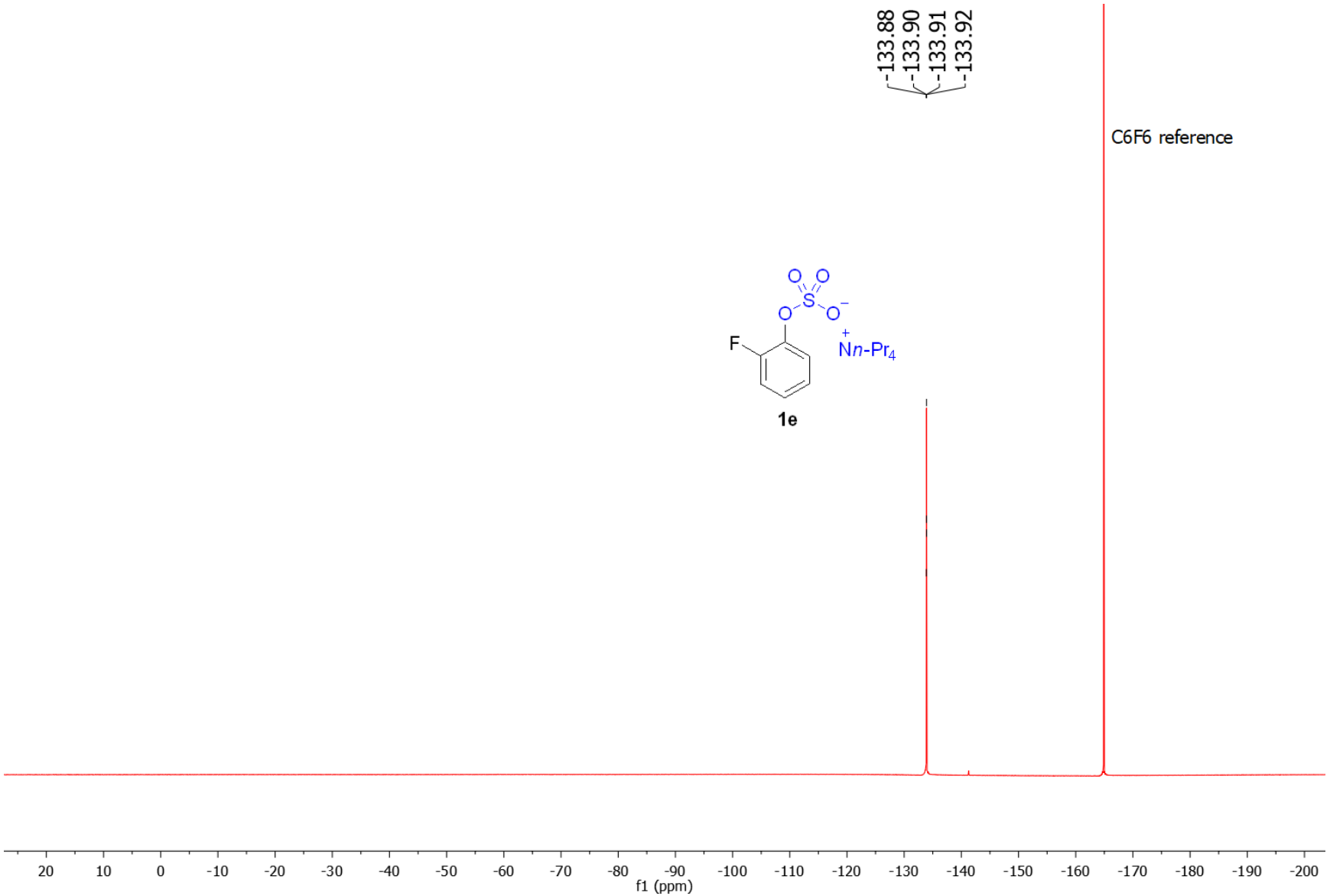
^{19}F NMR spectrum of tetrapropylammonium 2-fluorophenylsulfate (1e)



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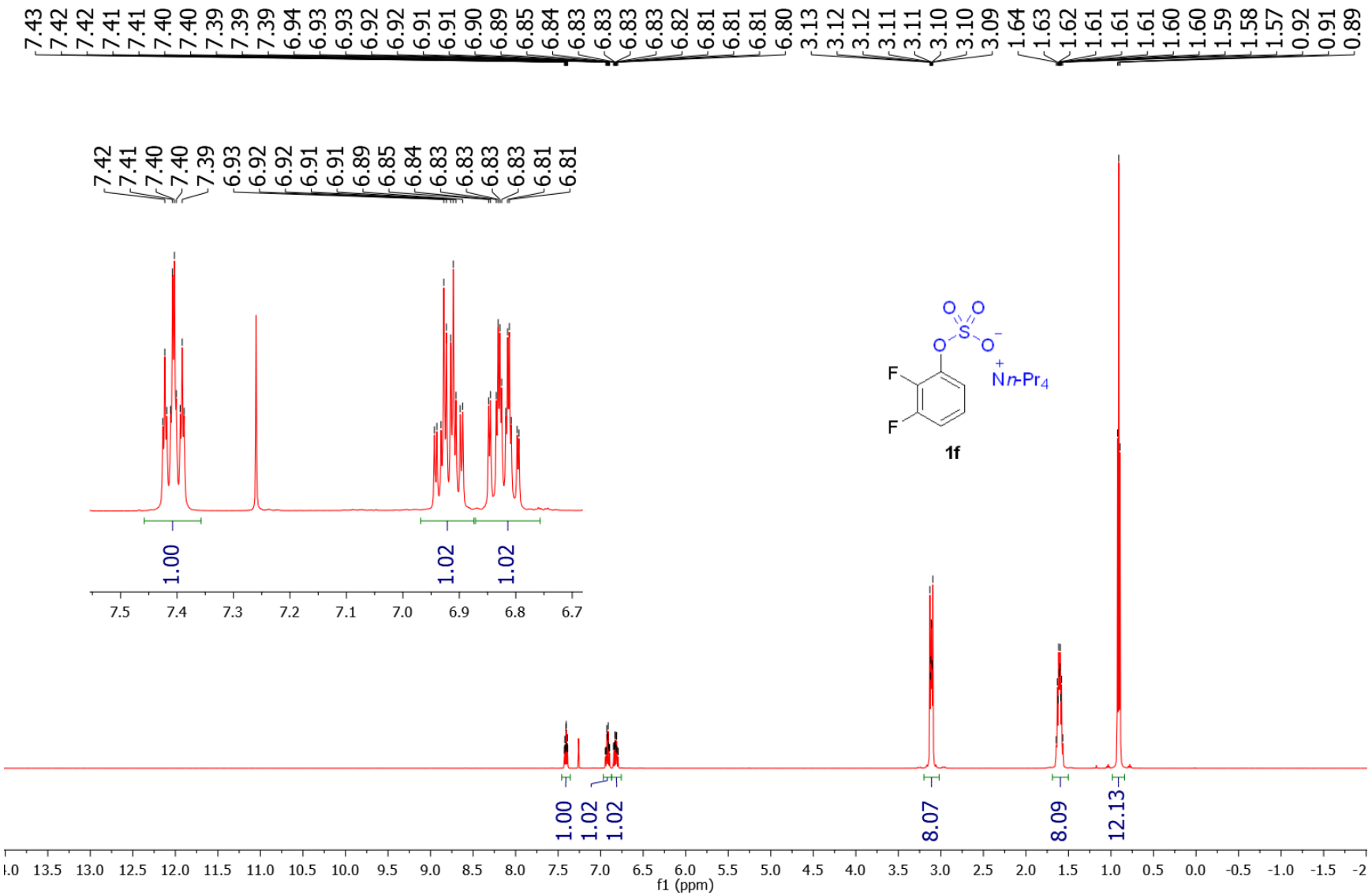
^{1}H NMR spectrum of tetrapropylammonium 2,3-difluorophenylsulfate (1f)



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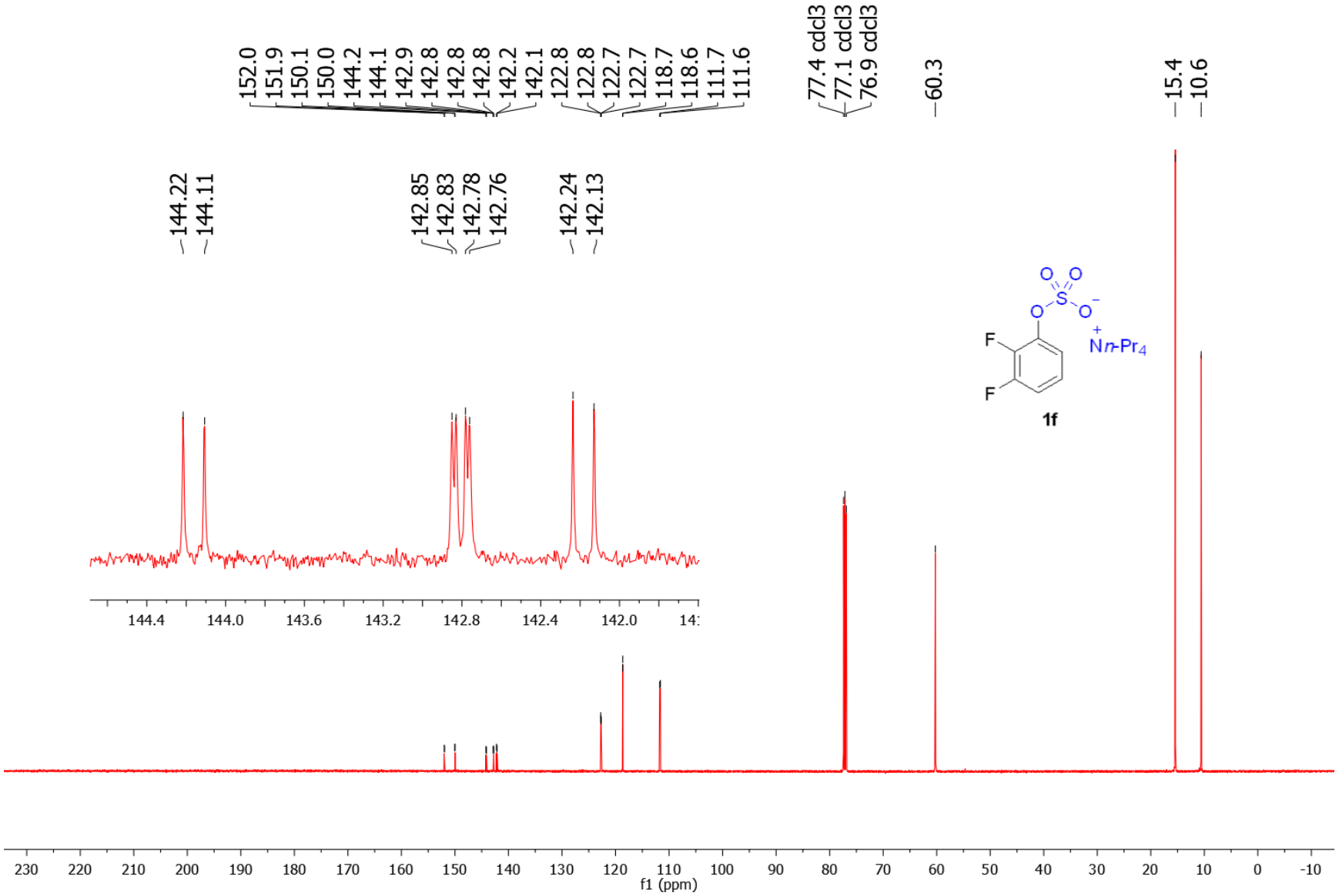
^{13}C NMR spectrum of tetrapropylammonium 2,3-difluorophenylsulfate (1f)



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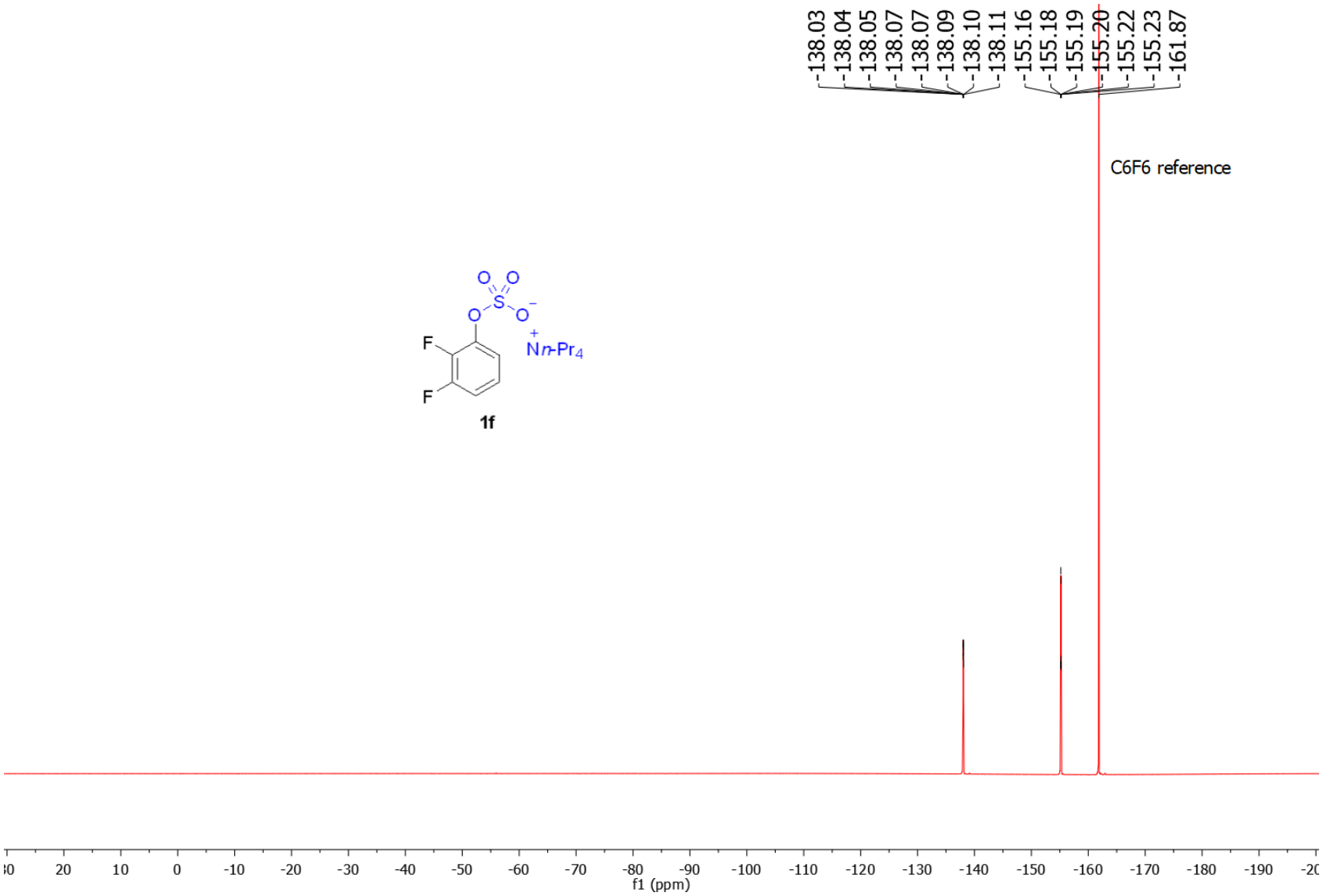
^{19}F NMR spectrum of tetrapropylammonium 2,3-difluorophenylsulfate (1f)



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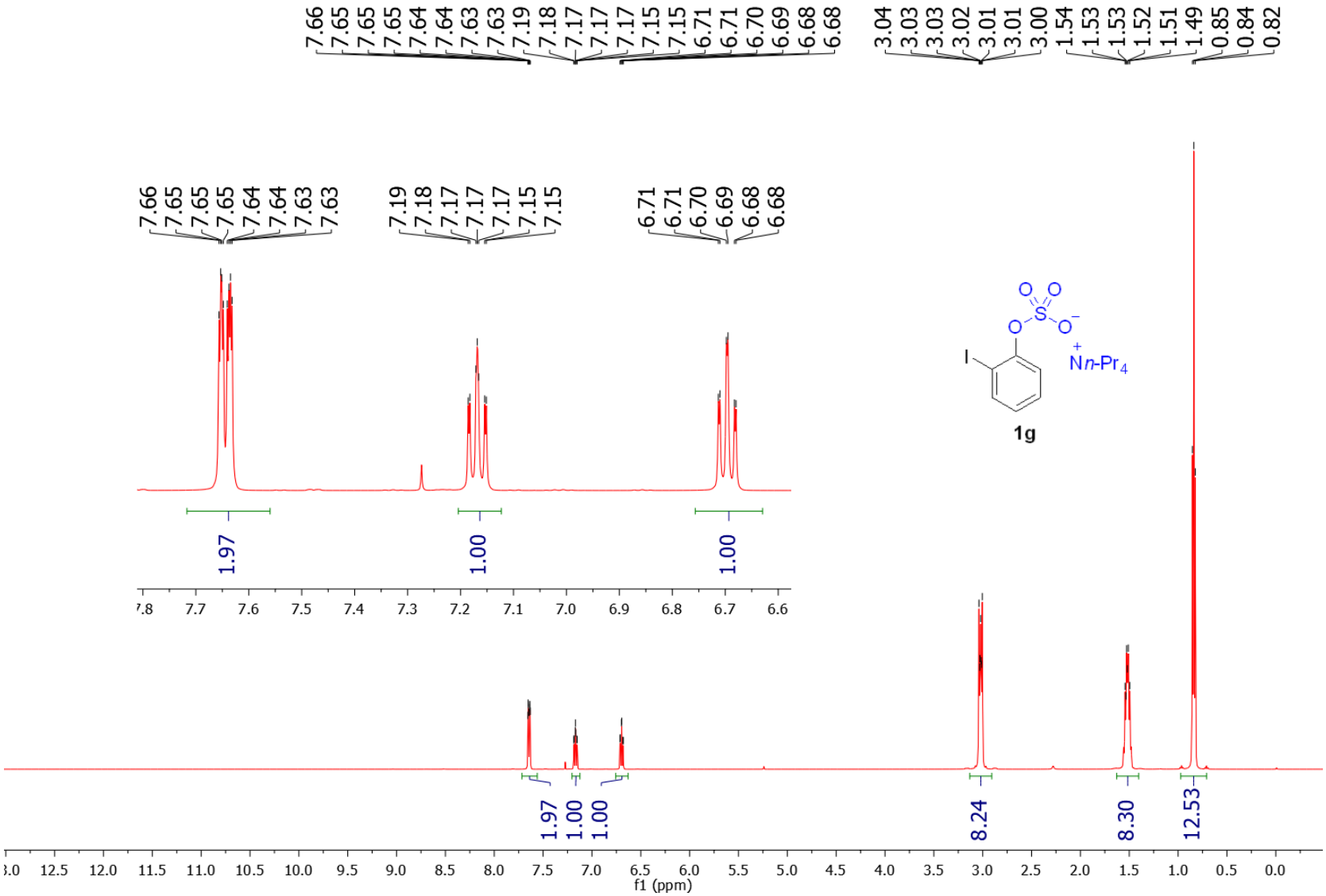
^{1}H NMR spectrum of tetrapropylammonium 2-iodophenylsulfate (1g)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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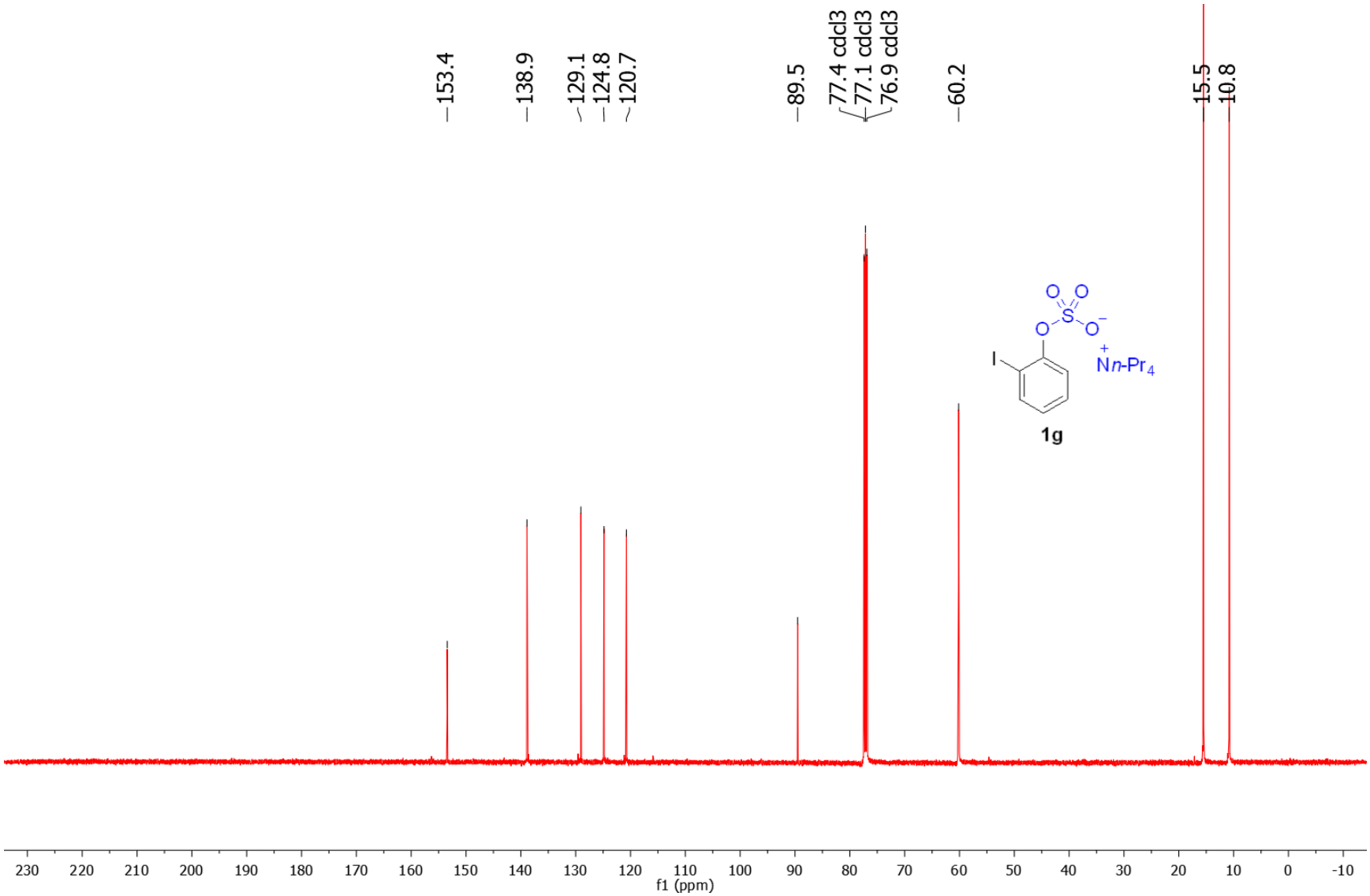
^{13}C NMR spectrum of tetrapropylammonium 2-iodophenylsulfate (1g)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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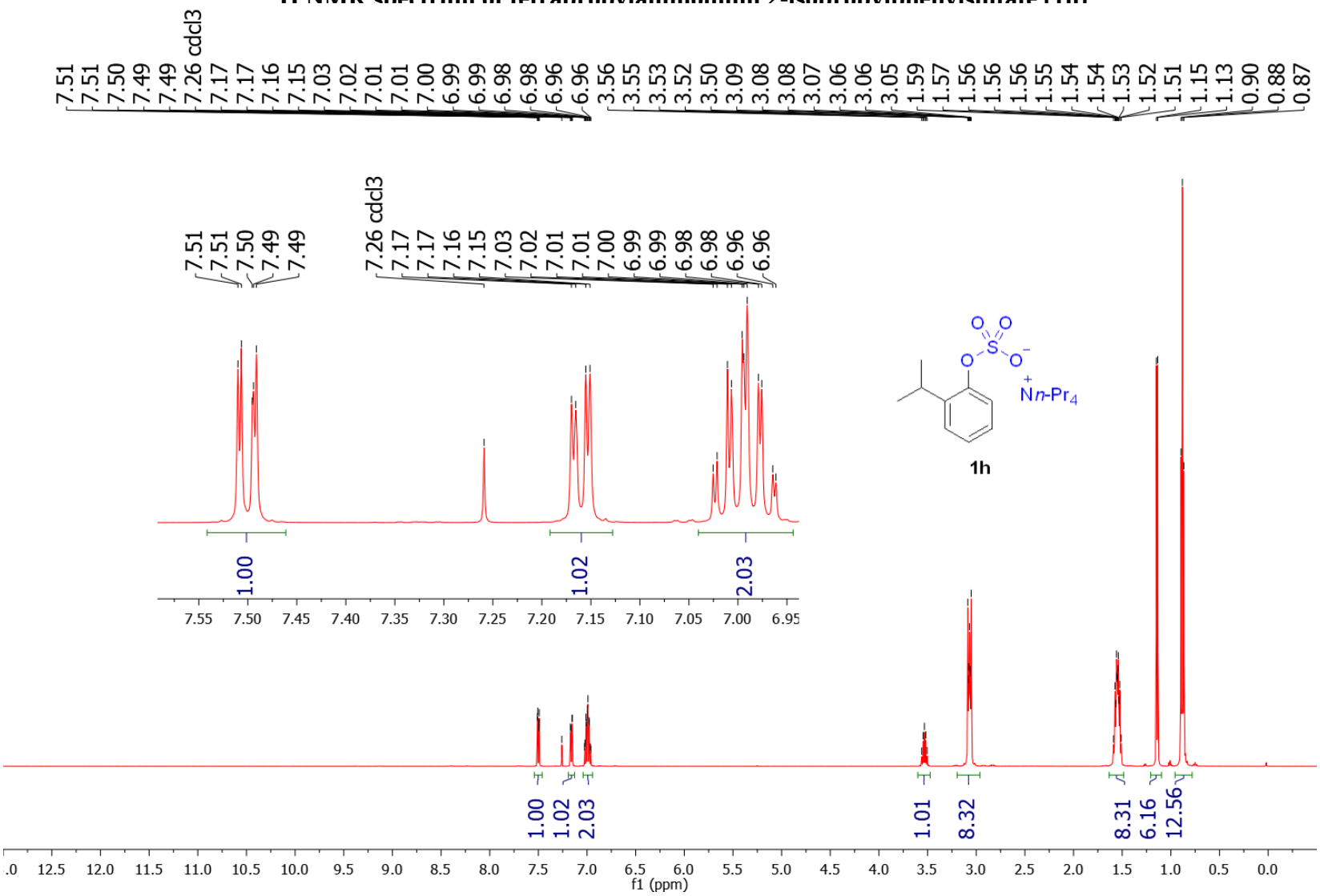
^{1}H NMR spectrum of tetrapropylammonium 2-isopropylphenylsulfate (1h)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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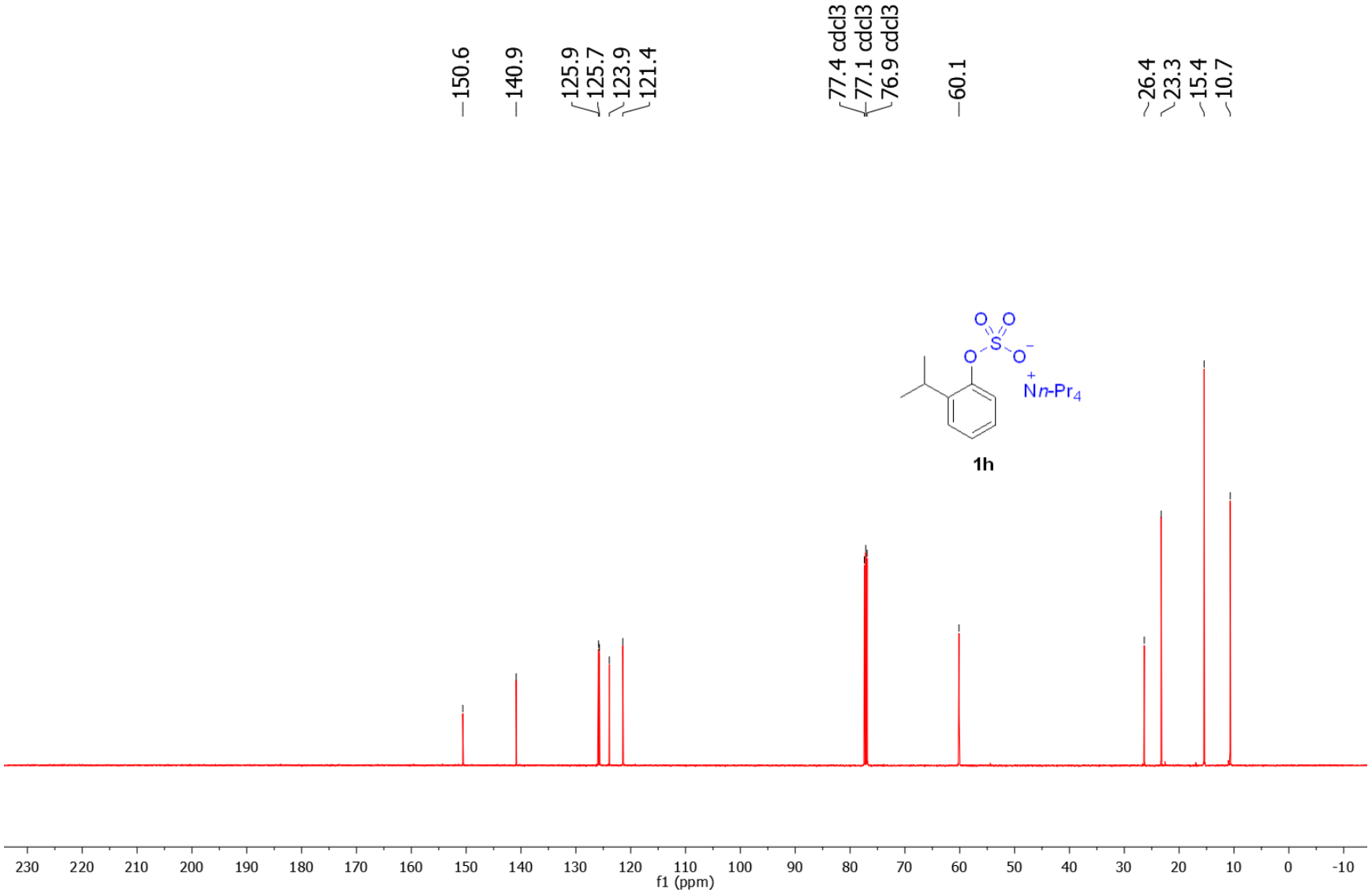
^{13}C NMR spectrum of tetrapropylammonium 2-isopropylphenylsulfate (1h)



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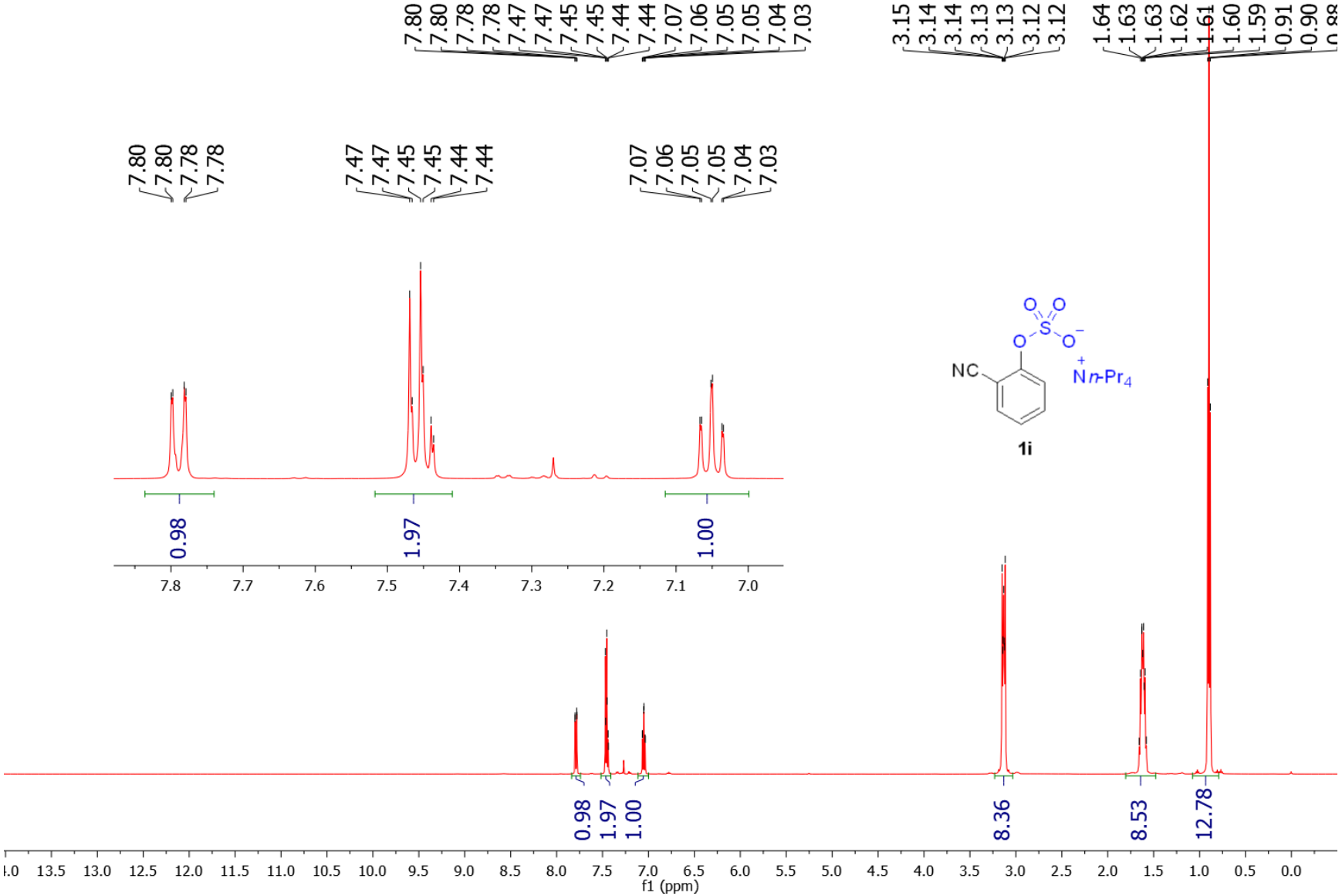
^{1}H NMR spectrum of tetrapropylammonium 2-cyanophenylsulfate (1i)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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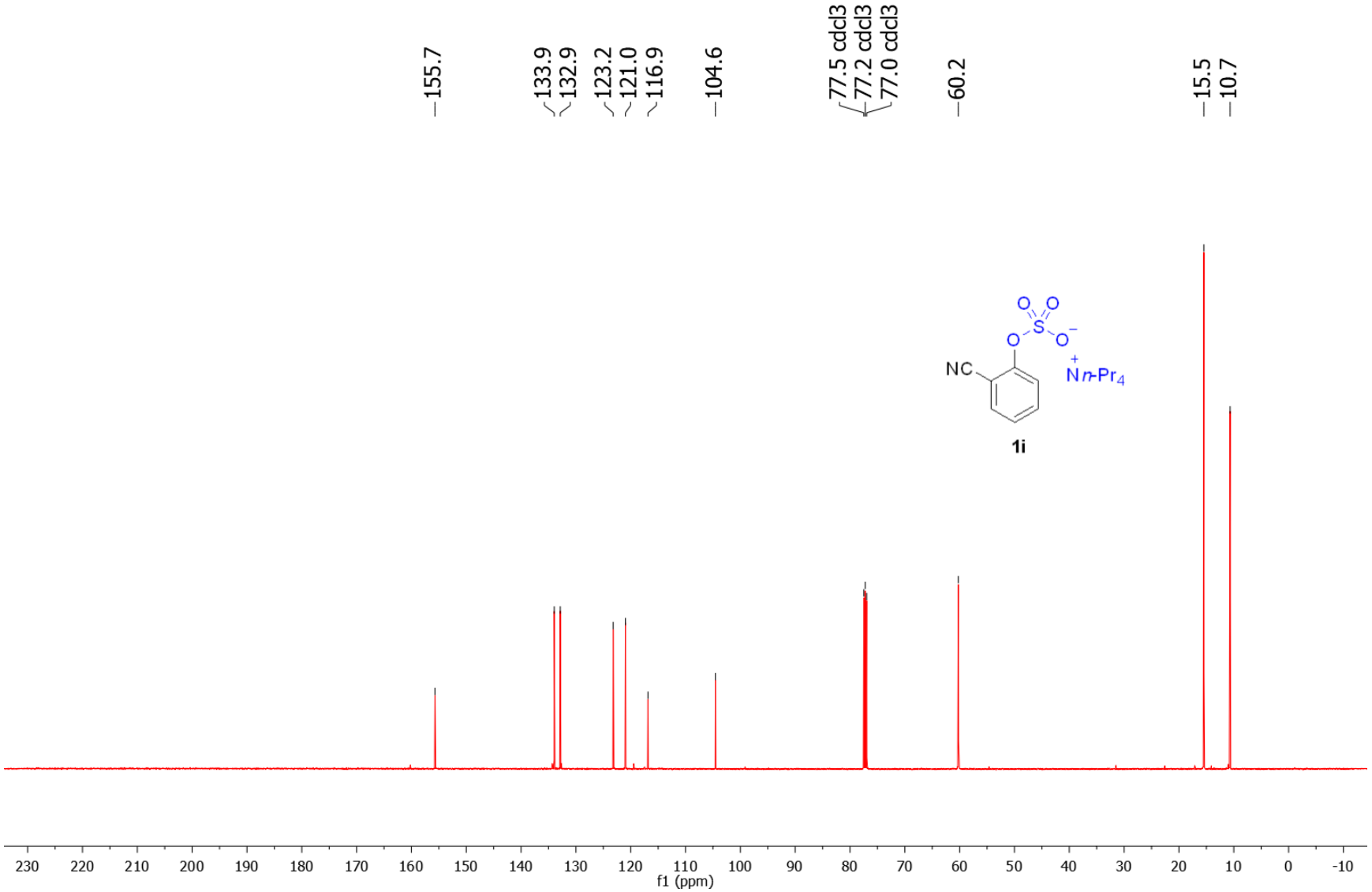
^{13}C NMR spectrum of tetrapropylammonium 2-cyanophenylsulfate (1i)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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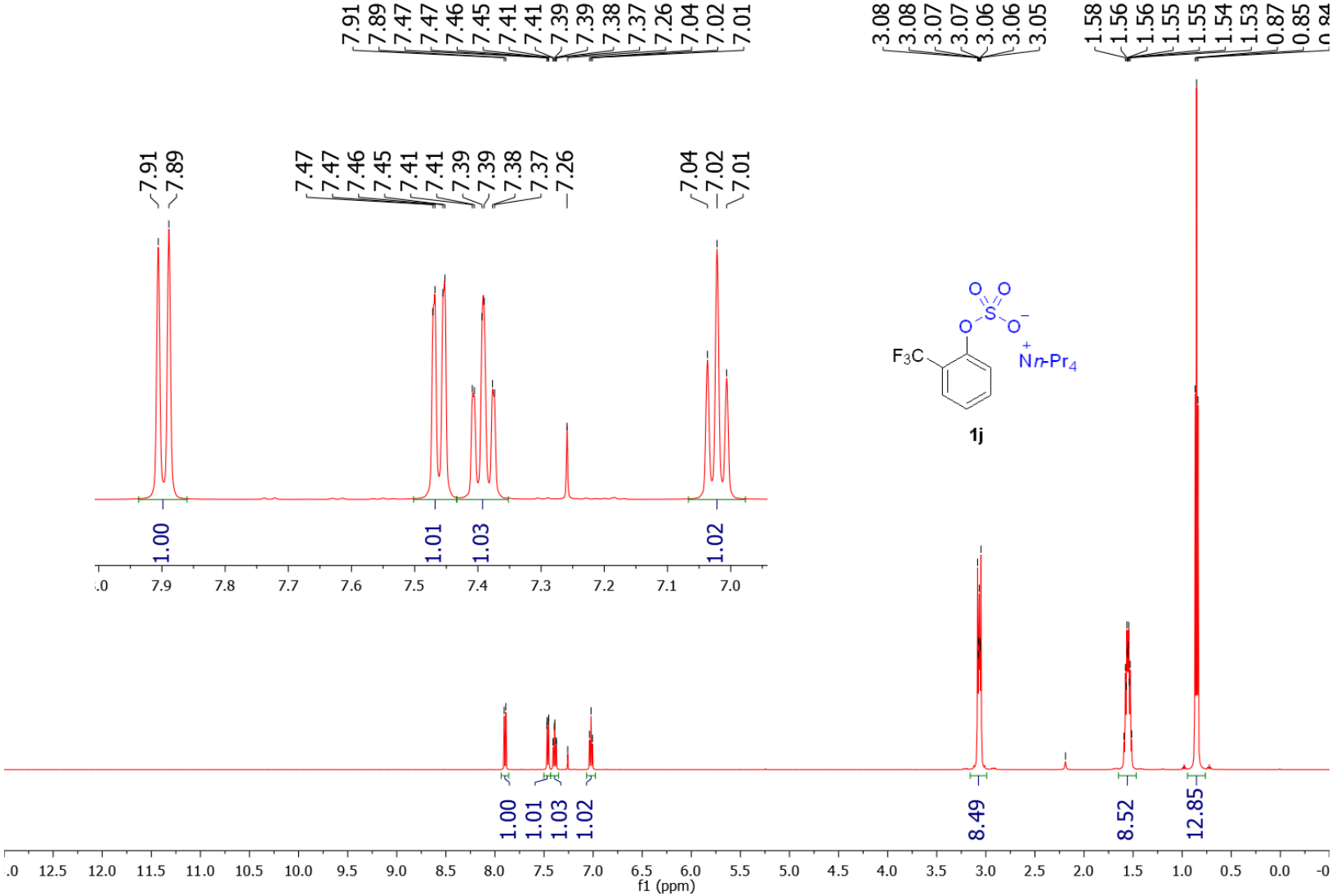
^{1}H NMR spectrum of tetrapropylammonium 2-(trifluoromethyl)phenylsulfate (1j)



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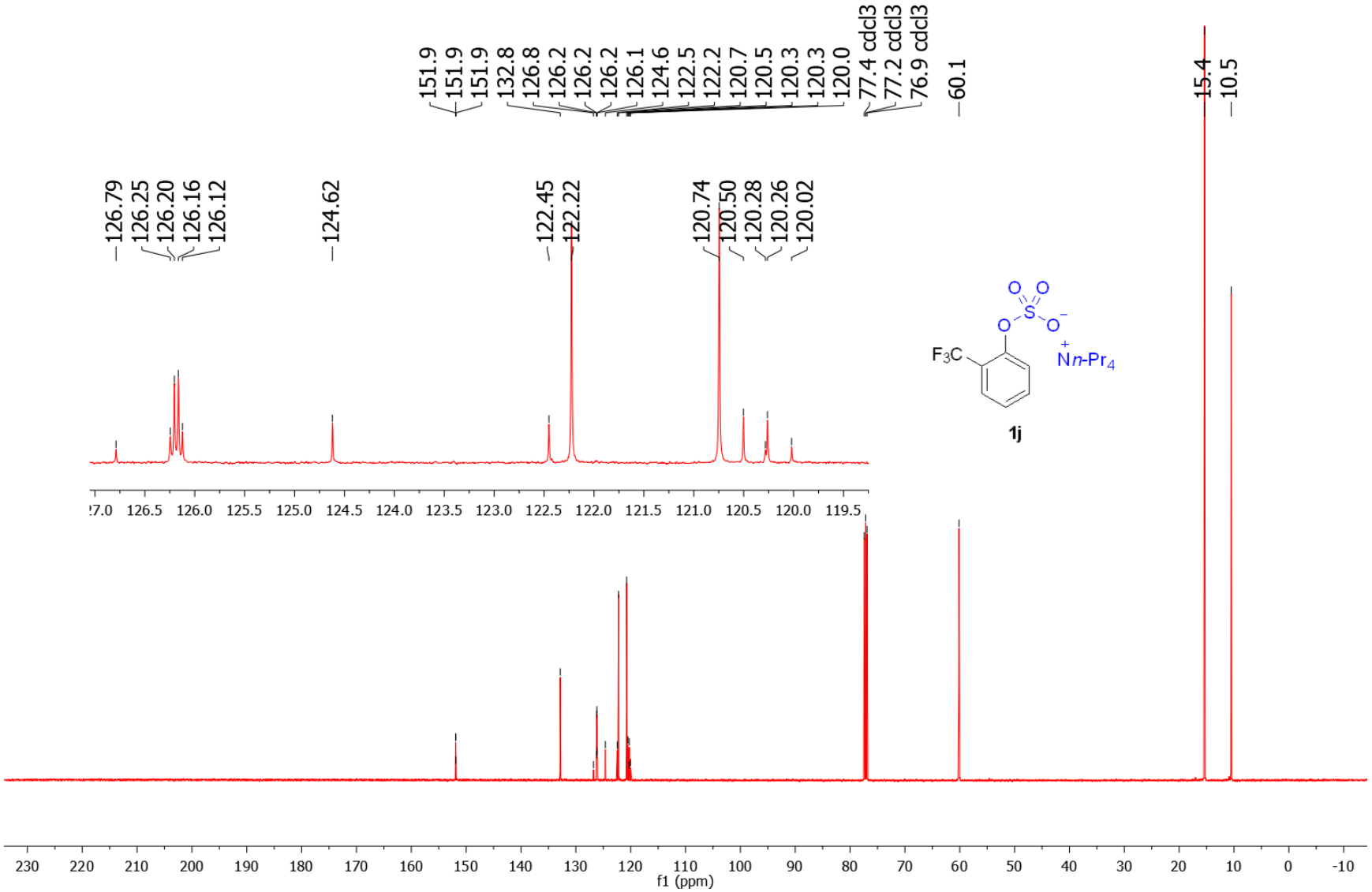
^{13}C NMR spectrum of tetrapropylammonium 2-(trifluoromethyl)phenylsulfate (1j)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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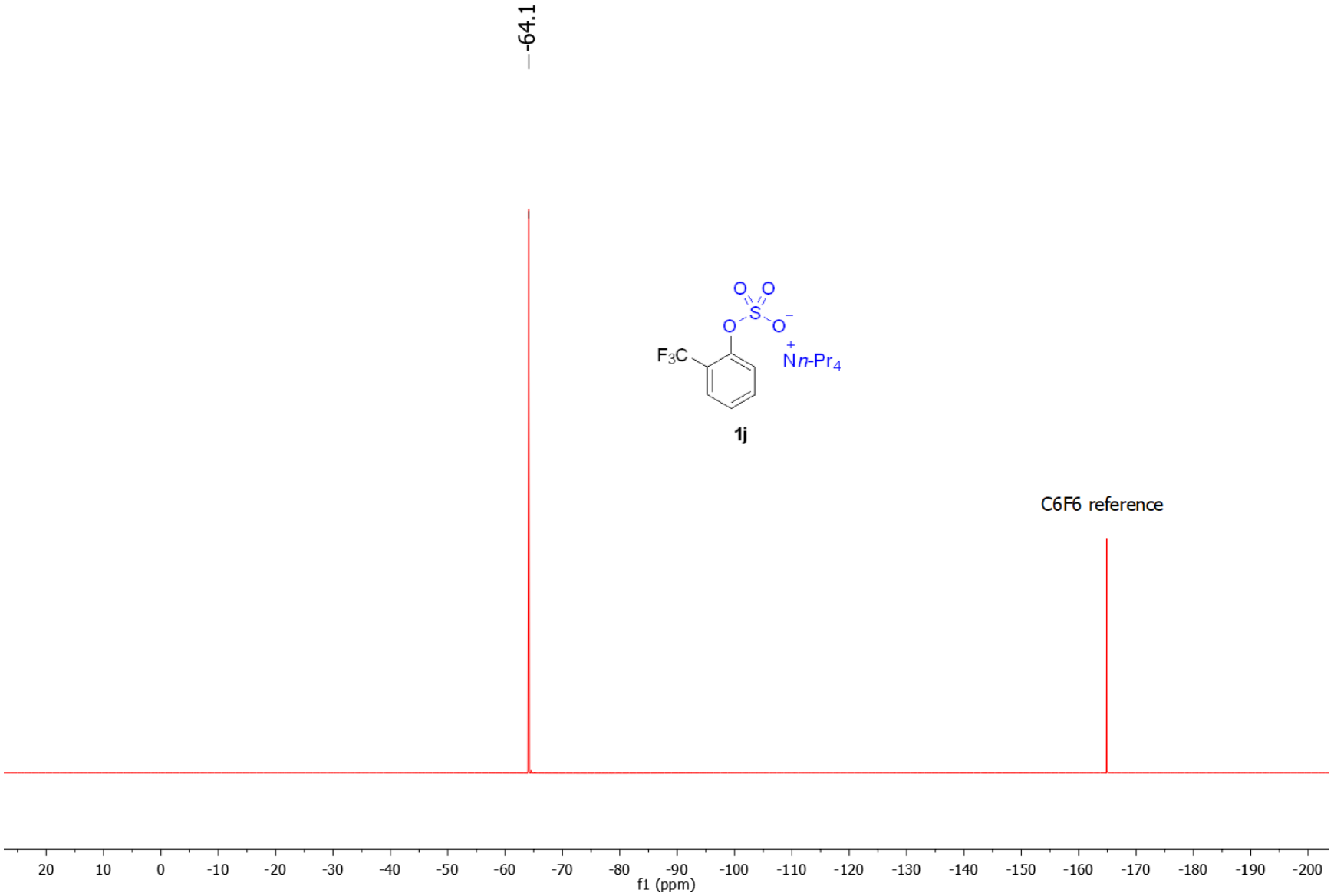
^{19}F NMR spectrum of tetrapropylammonium 2-(trifluoromethyl)phenylsulfate (1j)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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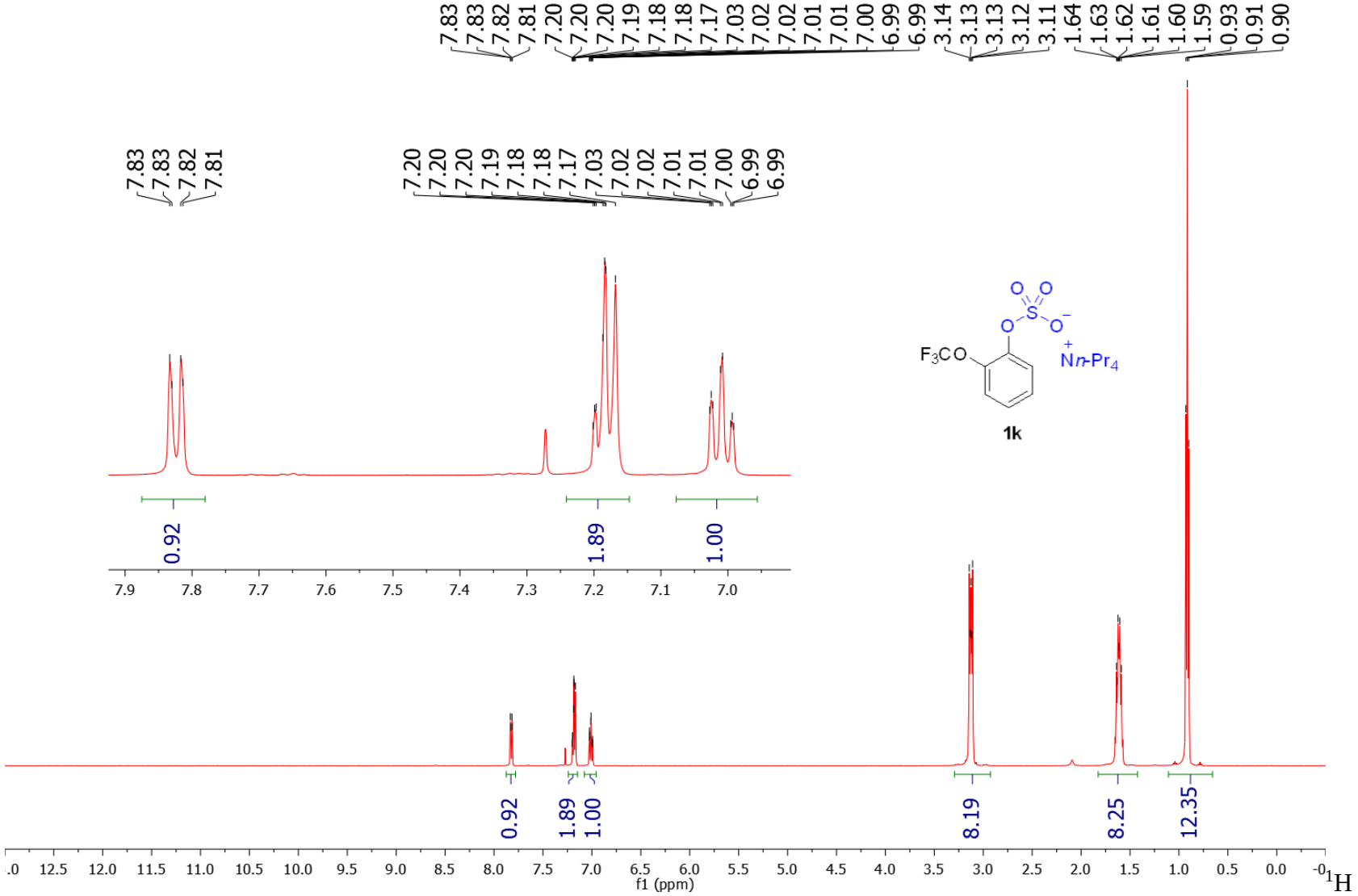
^{1}H NMR spectrum of tetrapropylammonium 2-(trifluoromethoxy)phenylsulfate (1k)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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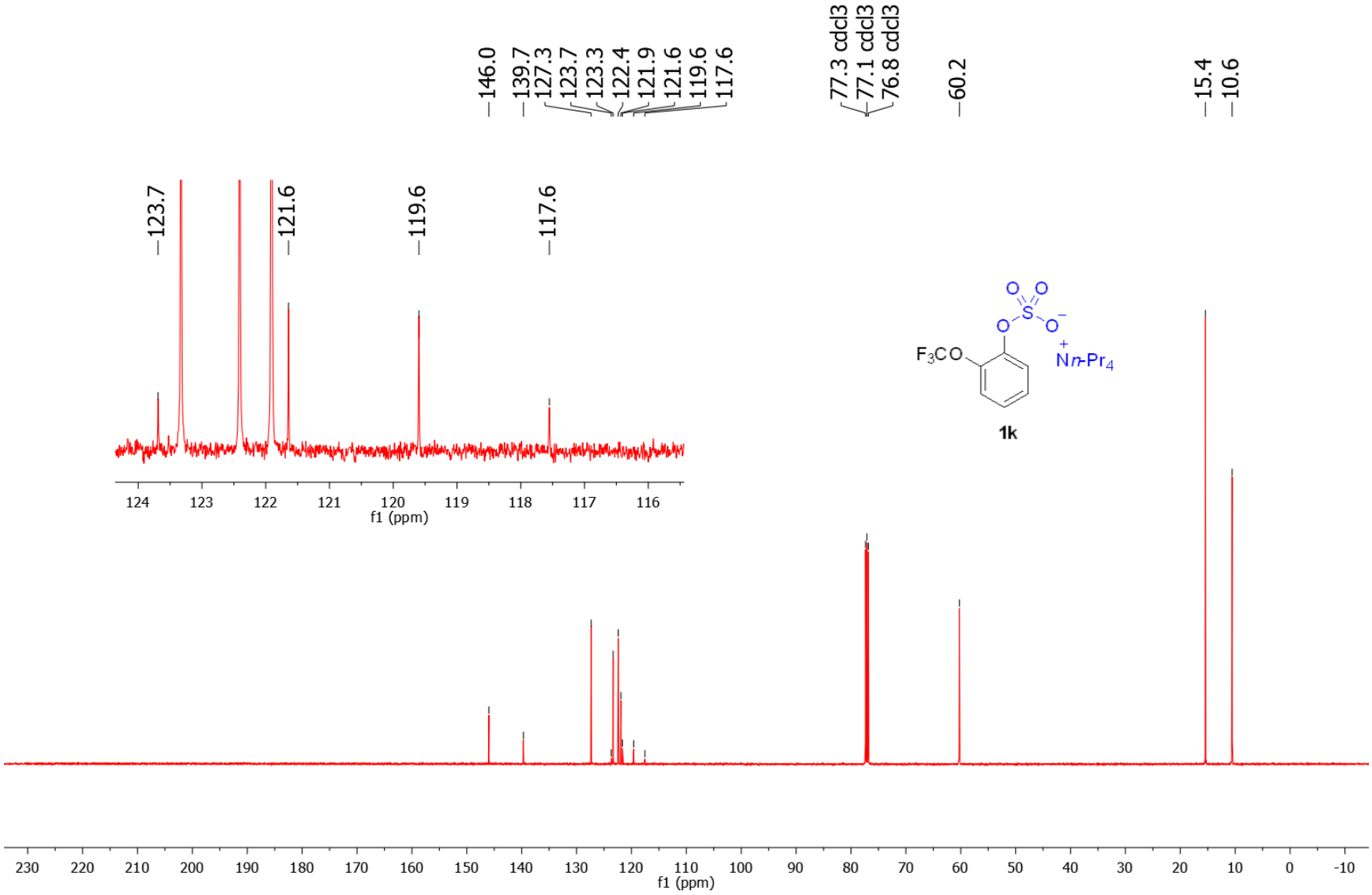
^{13}C NMR spectrum of tetrapropylammonium 2-(trifluoromethoxy)phenylsulfate (1k)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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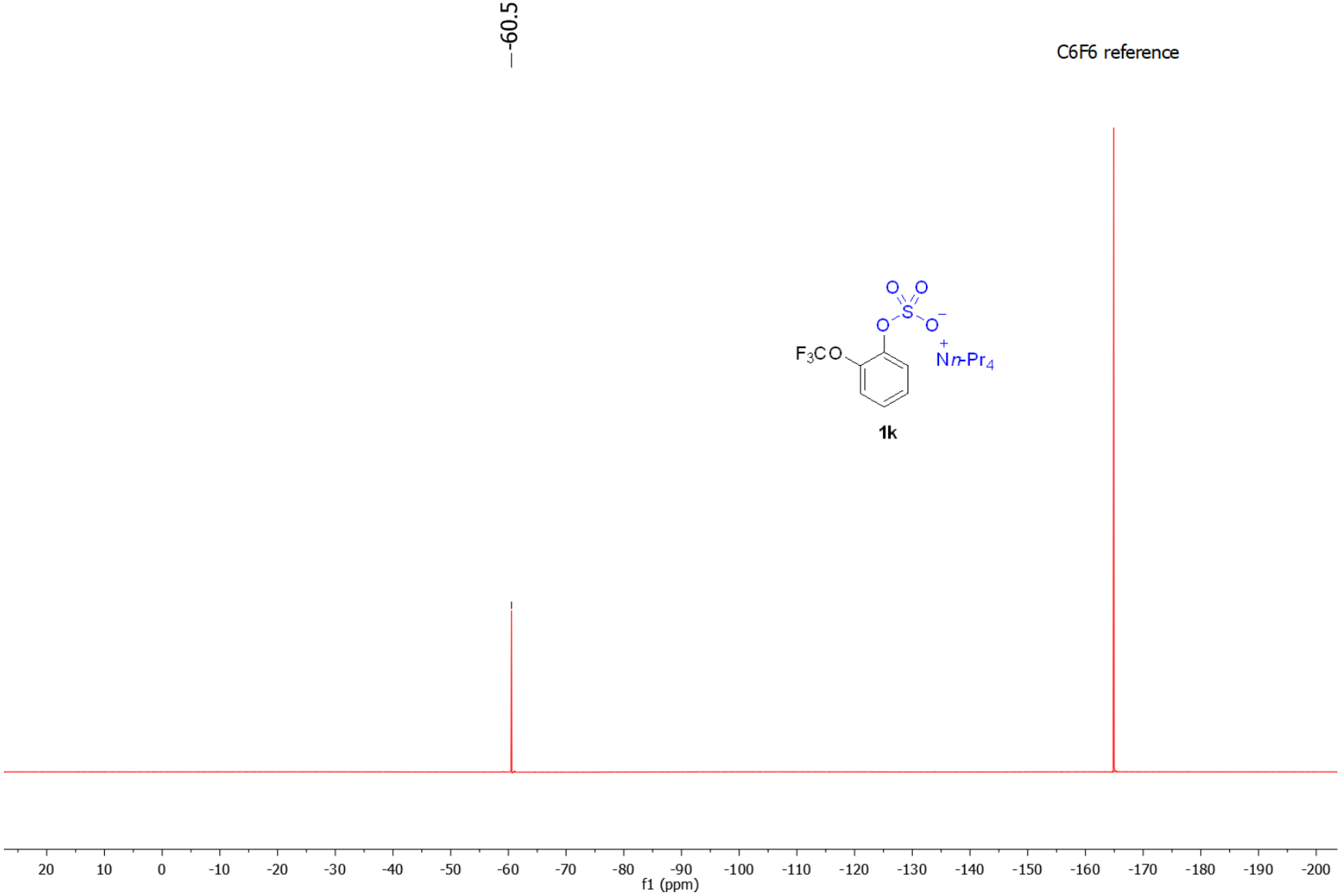
^{19}F NMR spectrum of tetrapropylammonium 2-(trifluoromethoxy)phenylsulfate (1k)



Conditions: 25 ºC, 470 MHz, $CDCl_3$

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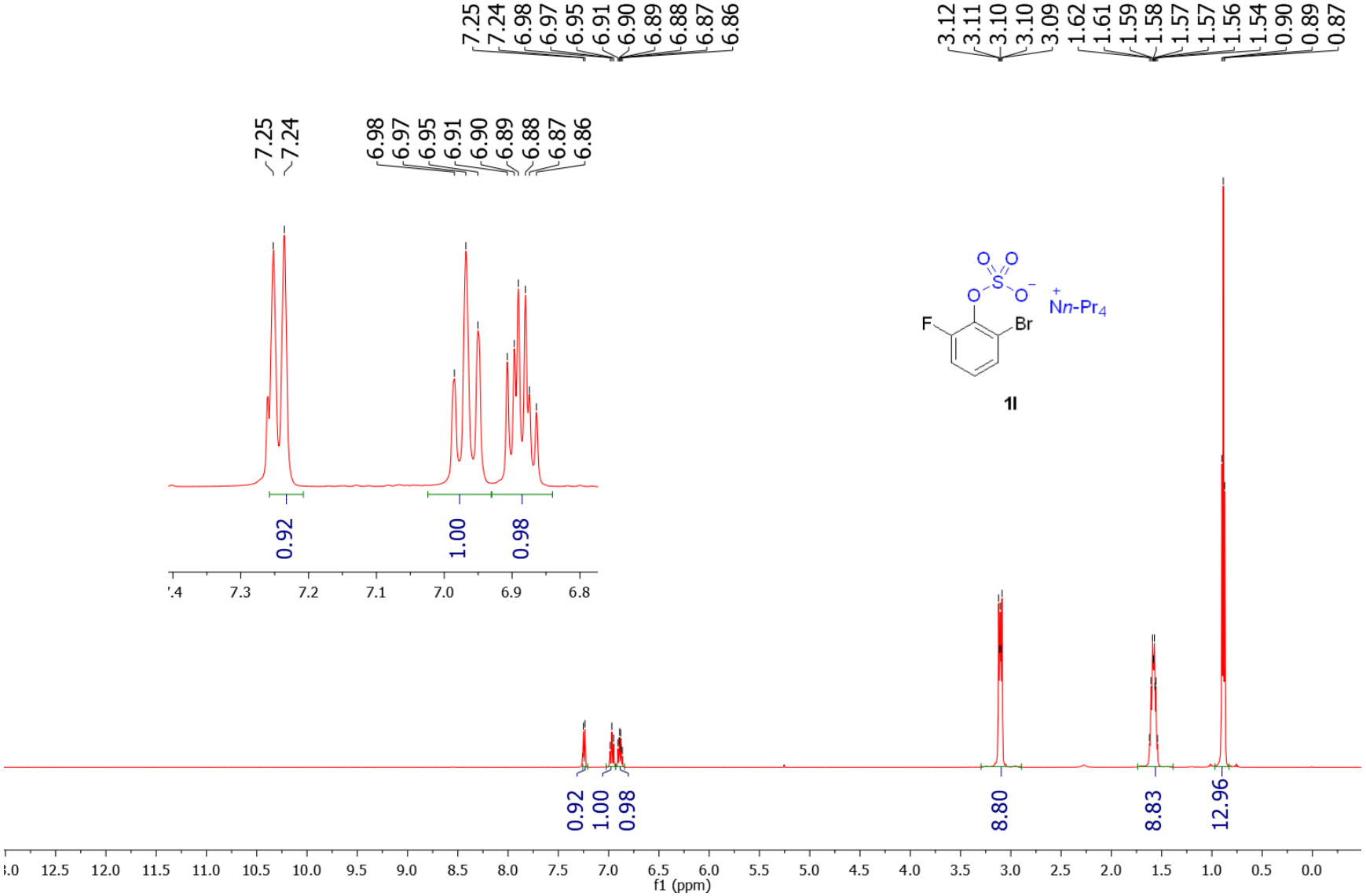
^{1}H NMR spectrum of tetrapropylammonium 2-bromo-6-fluorophenylsulfate (1l)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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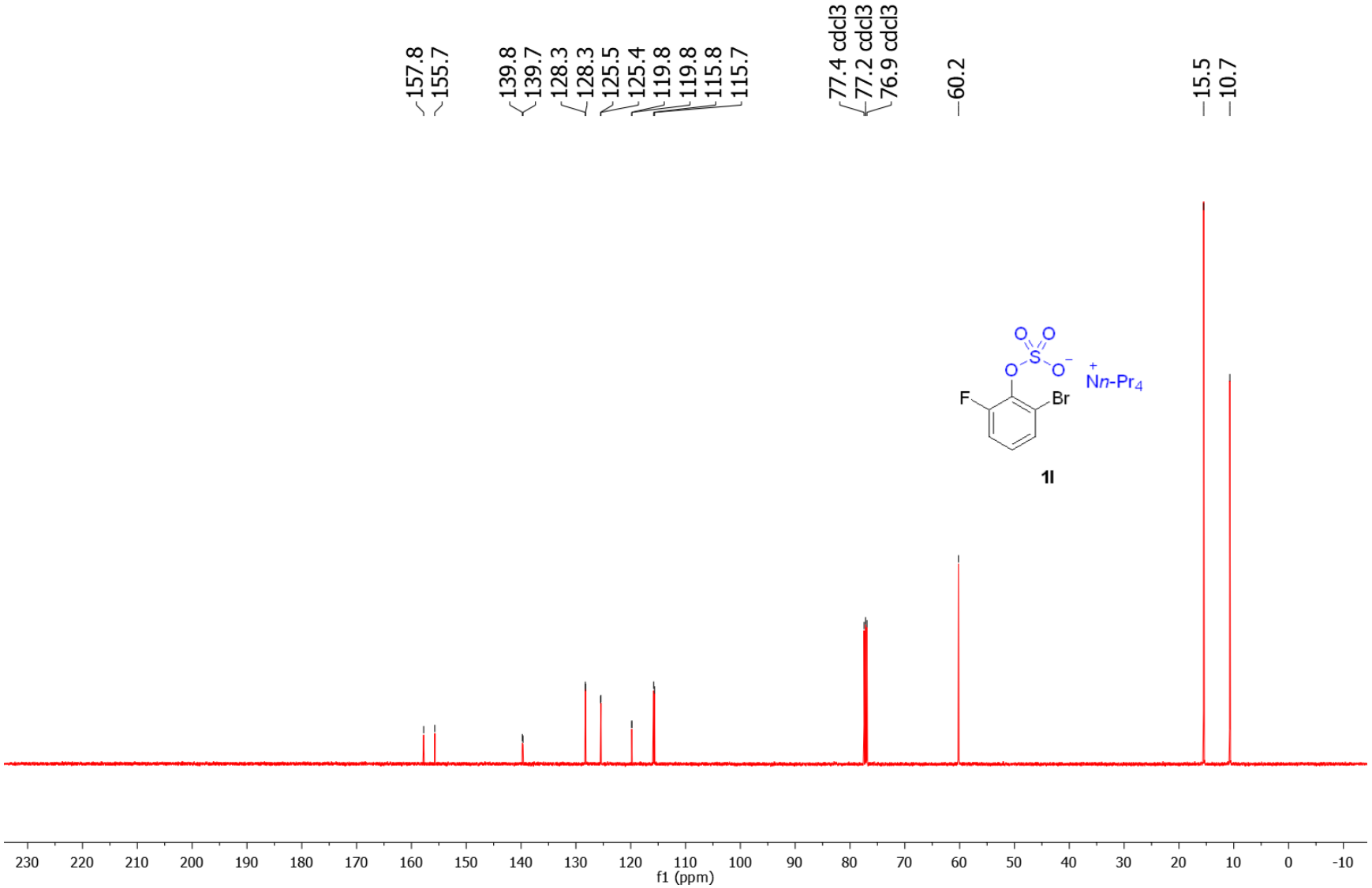
^{13}C NMR spectrum of tetrapropylammonium 2-bromo-6-fluorophenylsulfate (1l)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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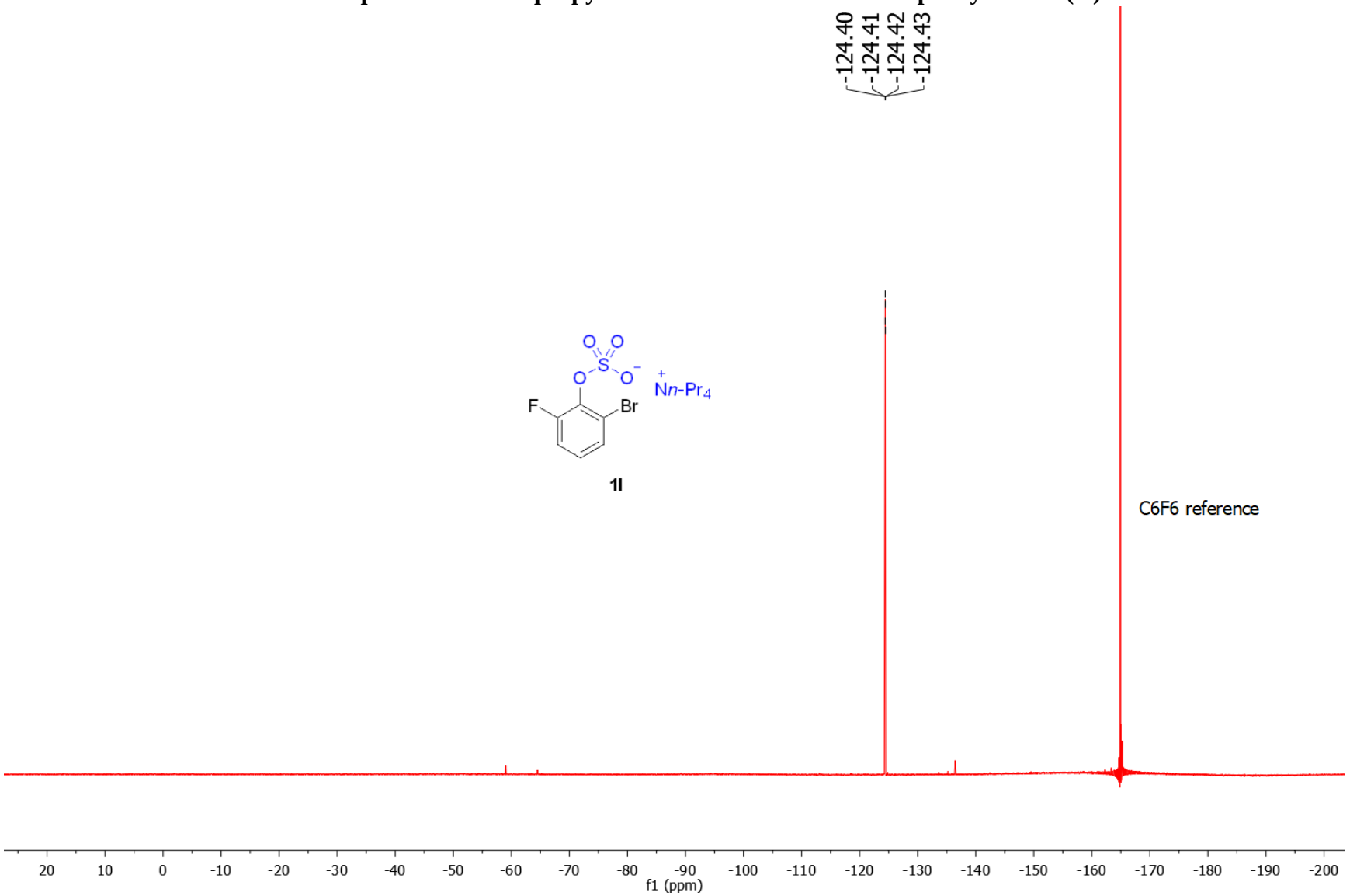
^{19}F NMR spectrum of tetrapropylammonium 2-bromo-6-fluorophenylsulfate (1l)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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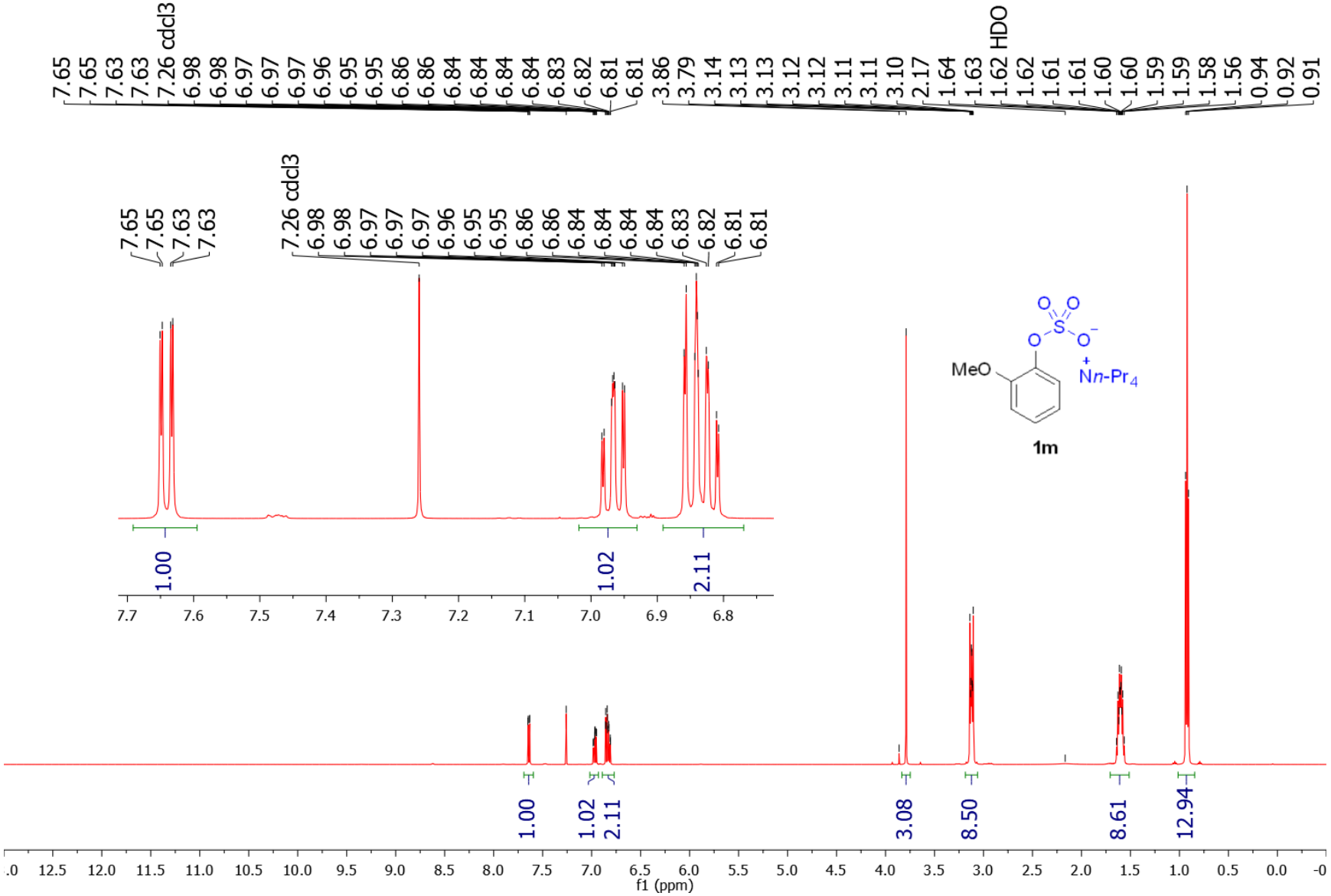
^{1}H NMR spectrum of tetrapropylammonium 2-methoxyphenylsulfate (1m)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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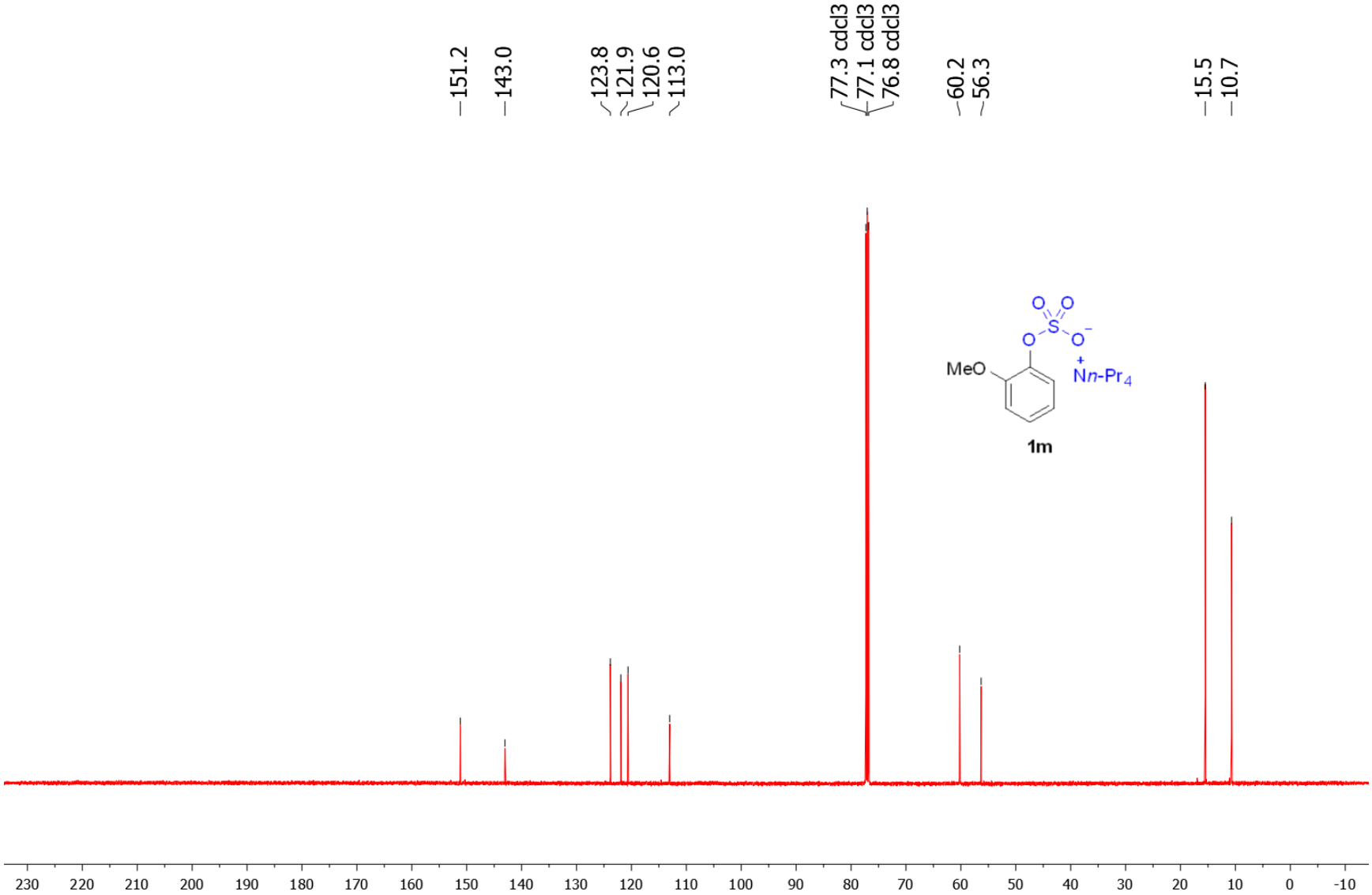
^{13}C NMR spectrum of tetrapropylammonium 2-methoxyphenylsulfate (1m)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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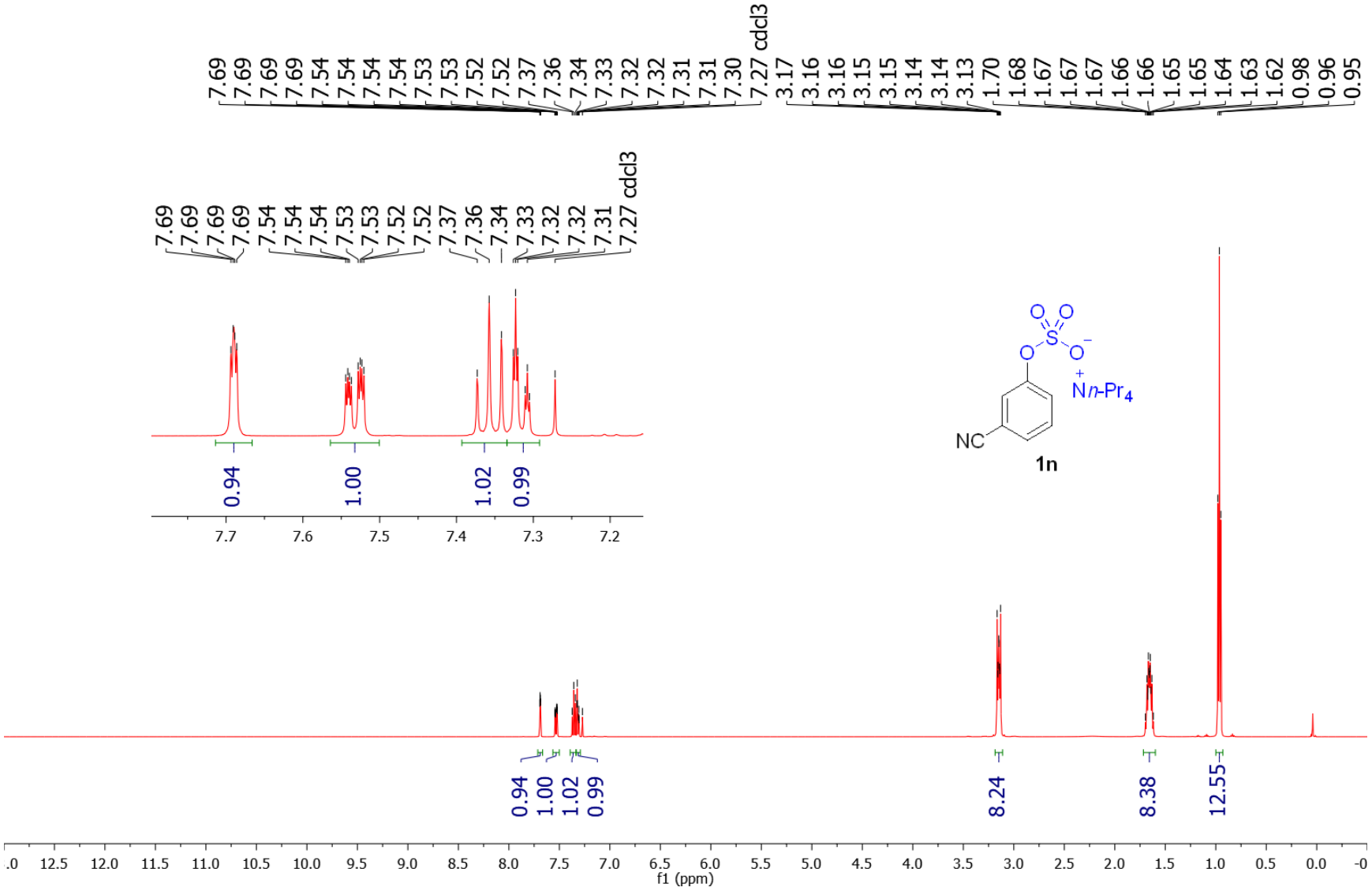
^{1}H NMR spectrum of tetrapropylammonium 3-cyanophenylsulfate (1n)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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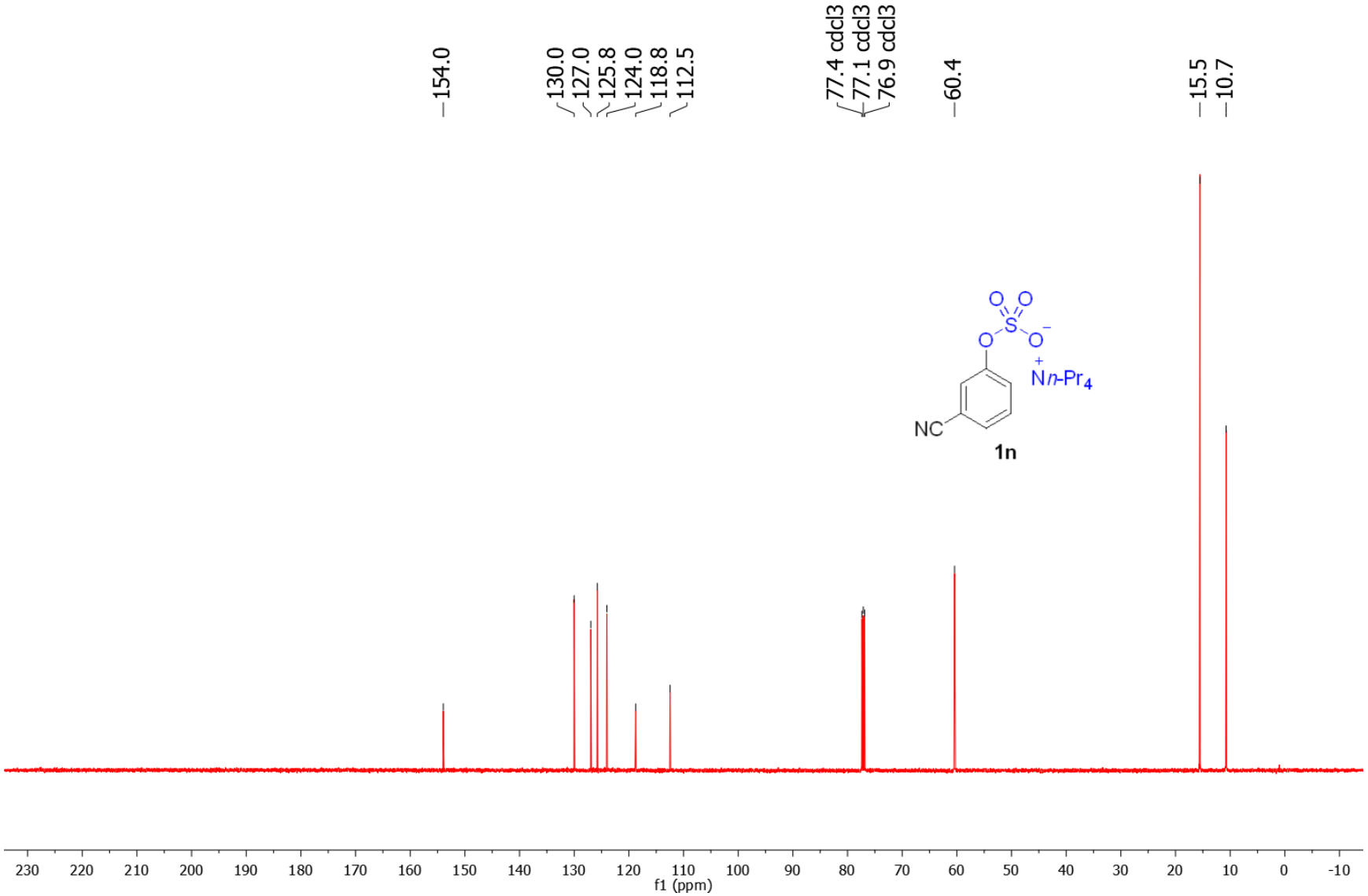
^{13}C NMR spectrum of tetrapropylammonium 3-cyanophenylsulfate (1n)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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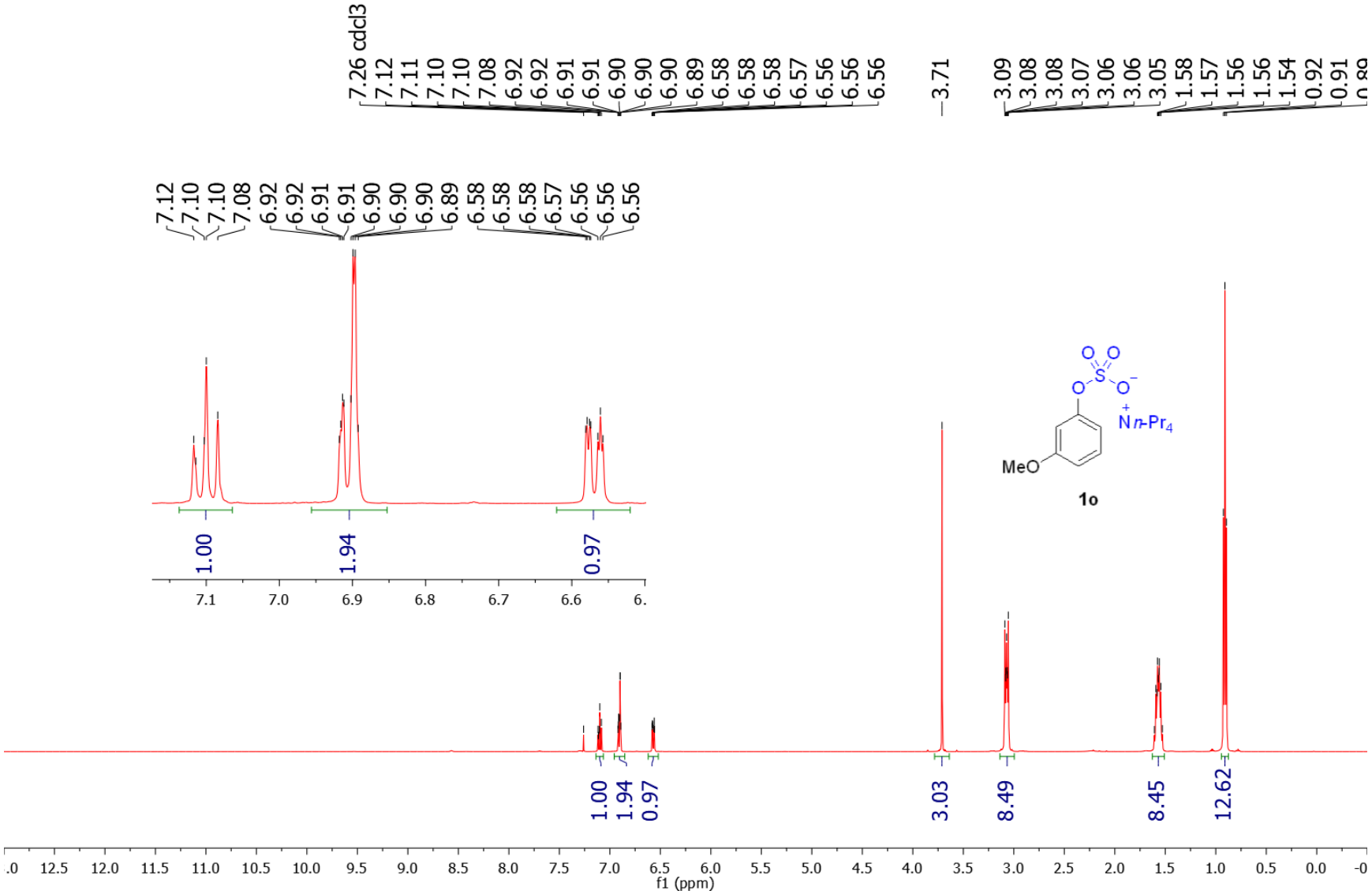
^{1}H NMR spectrum of tetrapropylammonium 3-methoxyphenylsulfate (1o)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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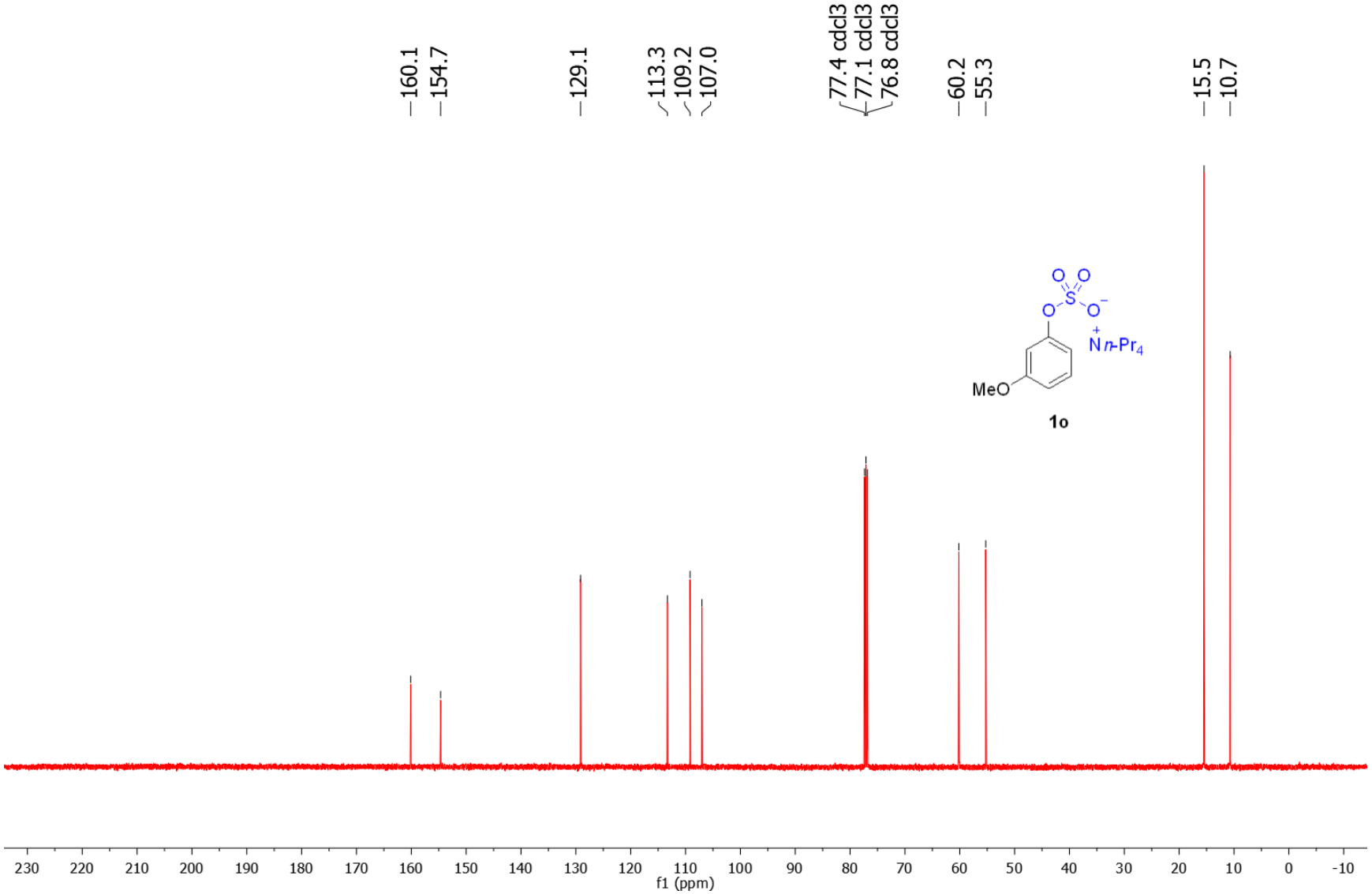
^{13}C NMR spectrum of tetrapropylammonium 3-methoxyphenylsulfate (1o)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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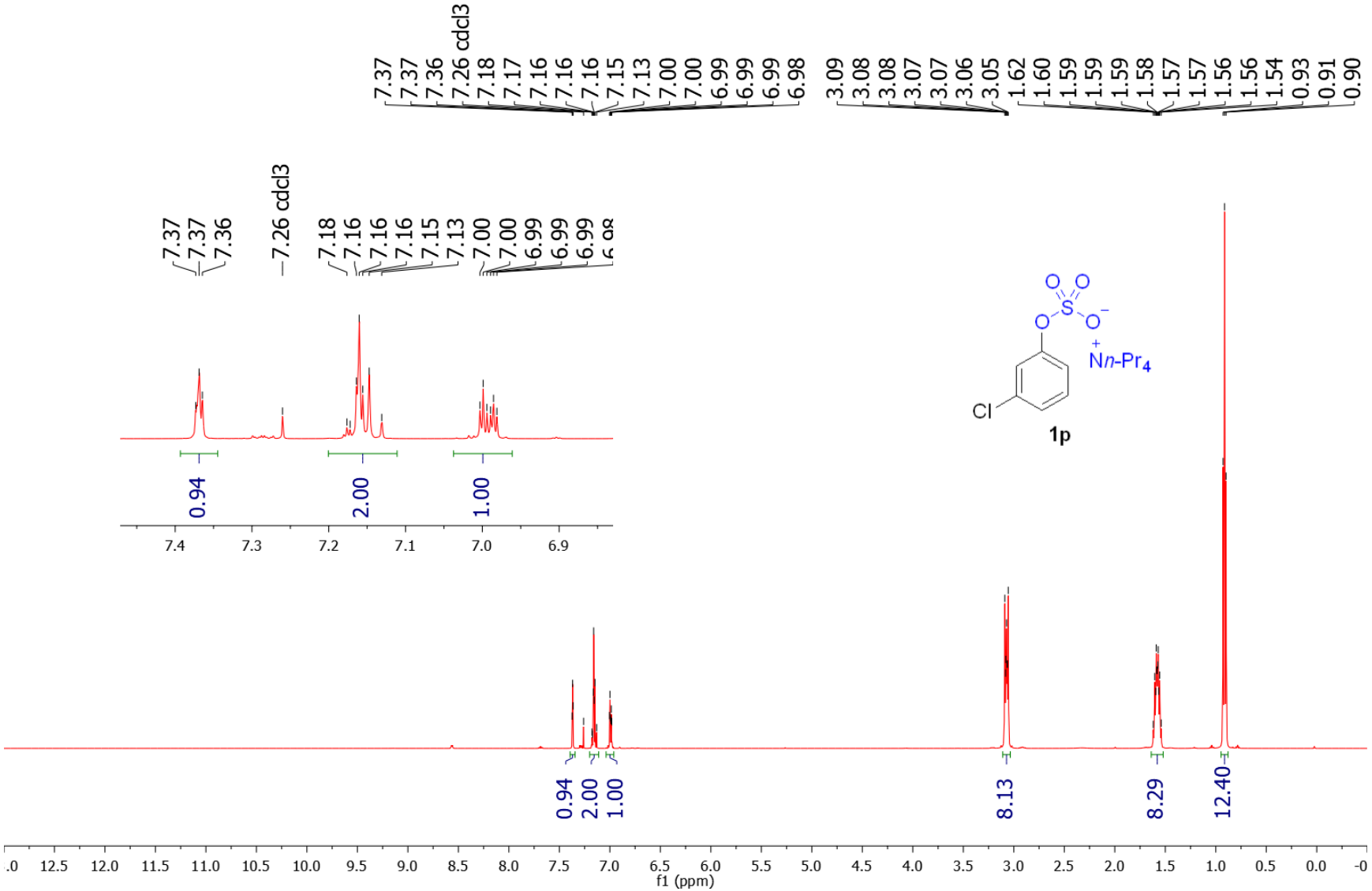
^{1}H NMR spectrum of tetrapropylammonium 3-chlorophenylsulfate (1p)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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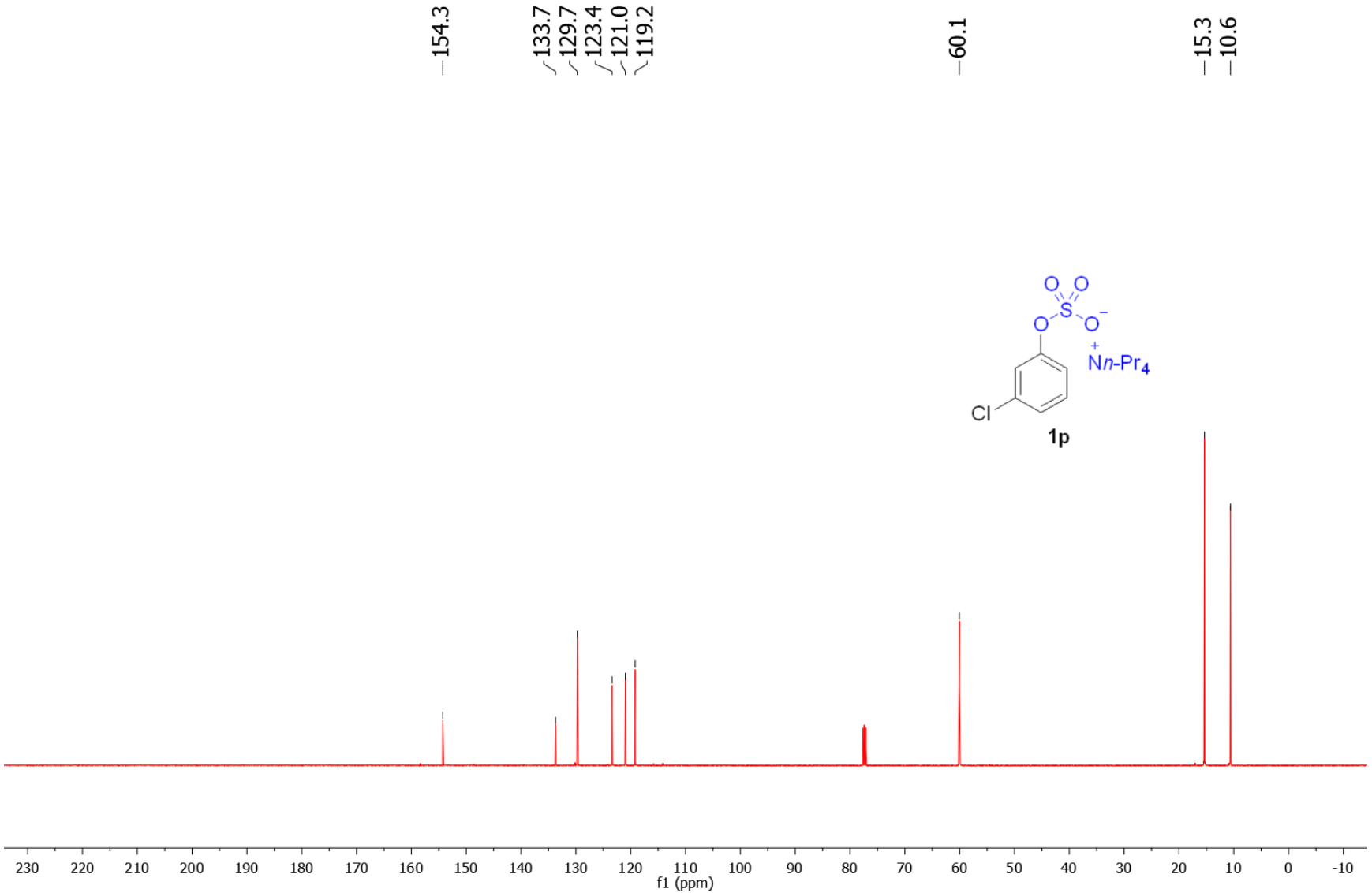
^{13}C NMR spectrum of tetrapropylammonium 3-chlorophenylsulfate (1p)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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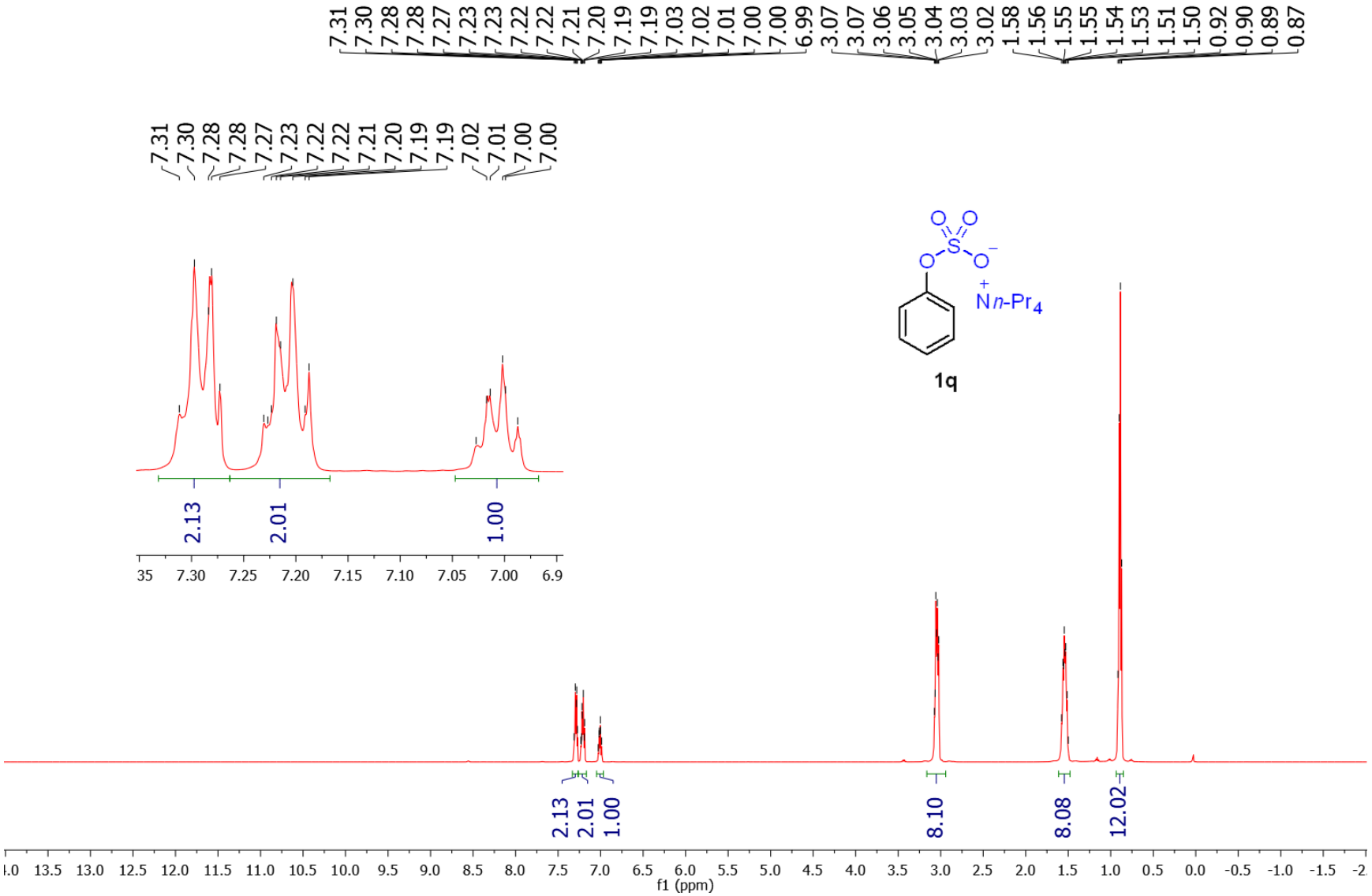
^{1}H NMR spectrum of tetrapropylammonium 2-phenylsulfate (1q)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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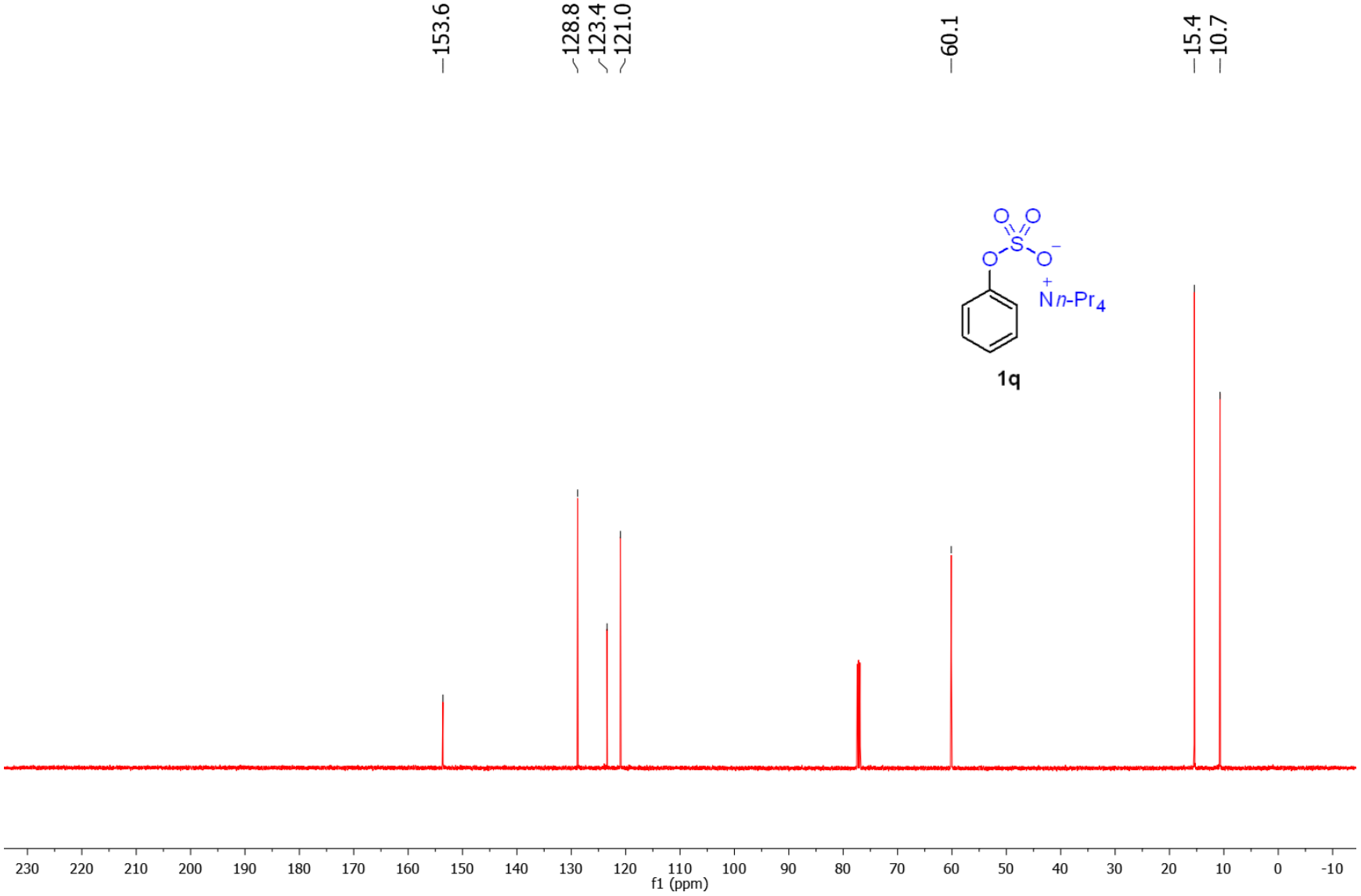
^{13}C NMR spectrum of tetrapropylammonium 2-phenylsulfate (1q)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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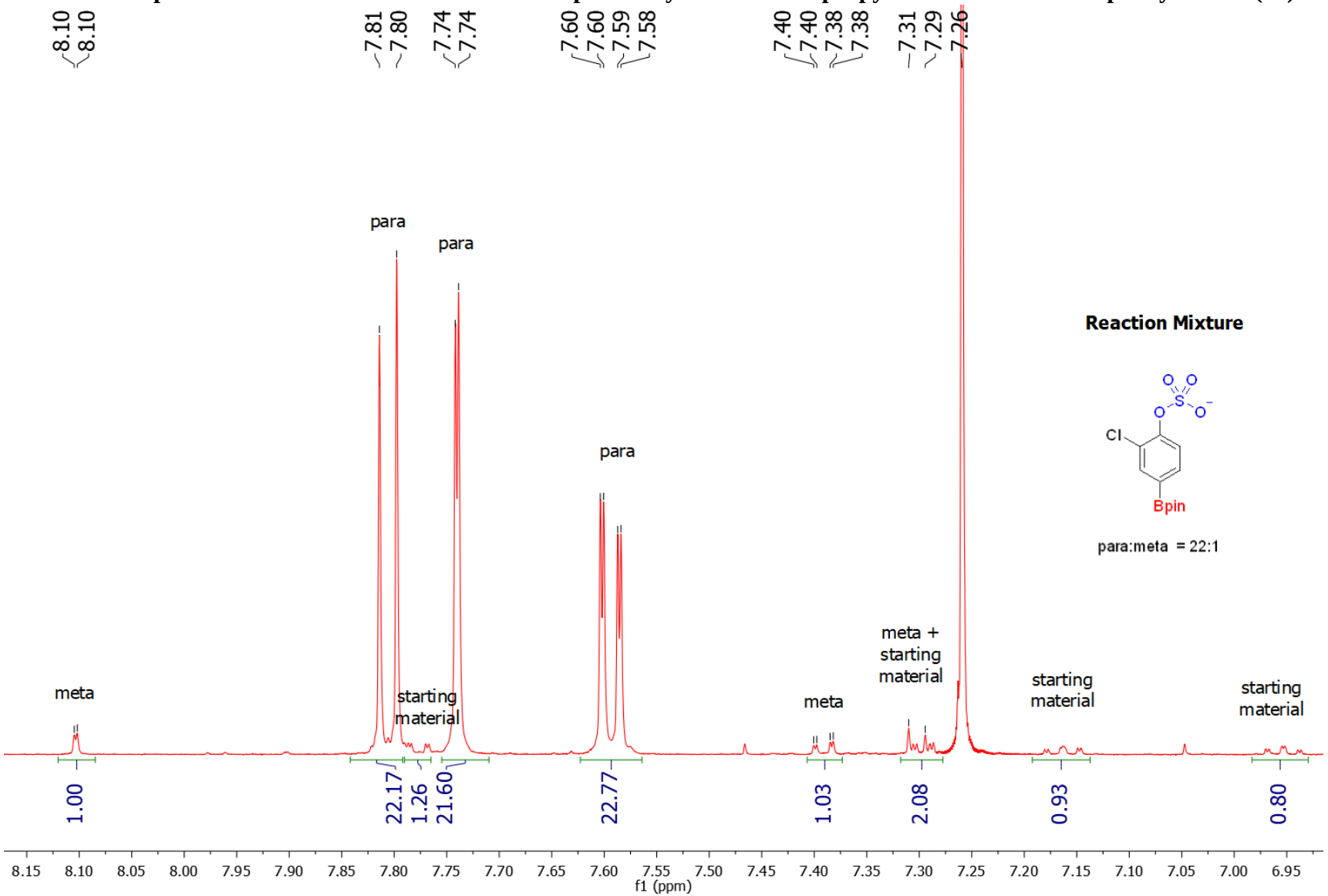
^{1}H NMR spectrum of the reaction mixture for the para borylation of tetrapropylammonium 2-chlorophenylsulfate (2a)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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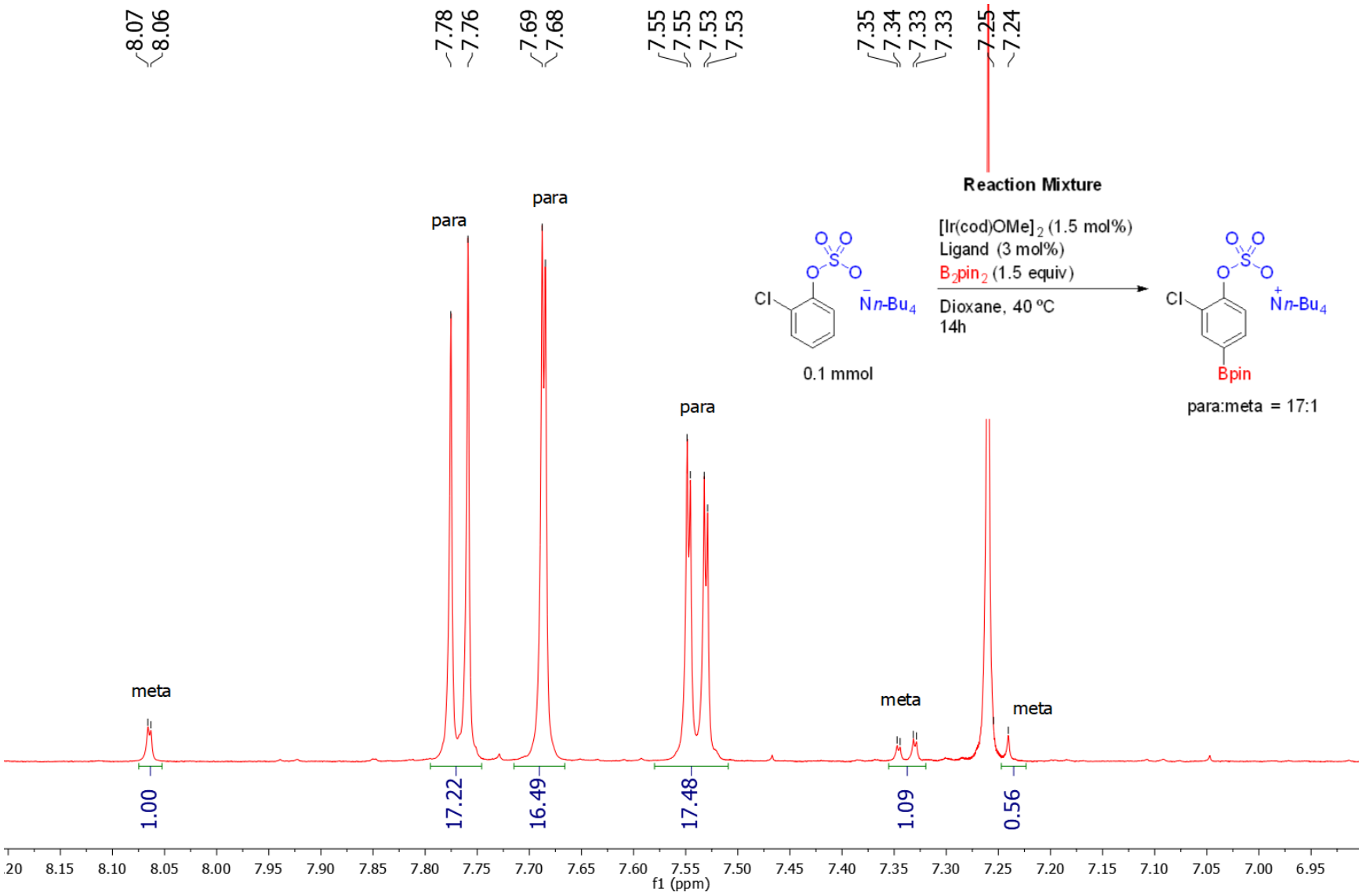
^{1}H NMR spectrum of the reaction mixture for the para borylation of tetrabutylammonium 2-chlorophenylsulfate (2a')



Conditions: 25 °C, 500 MHz, $CDCl_3$

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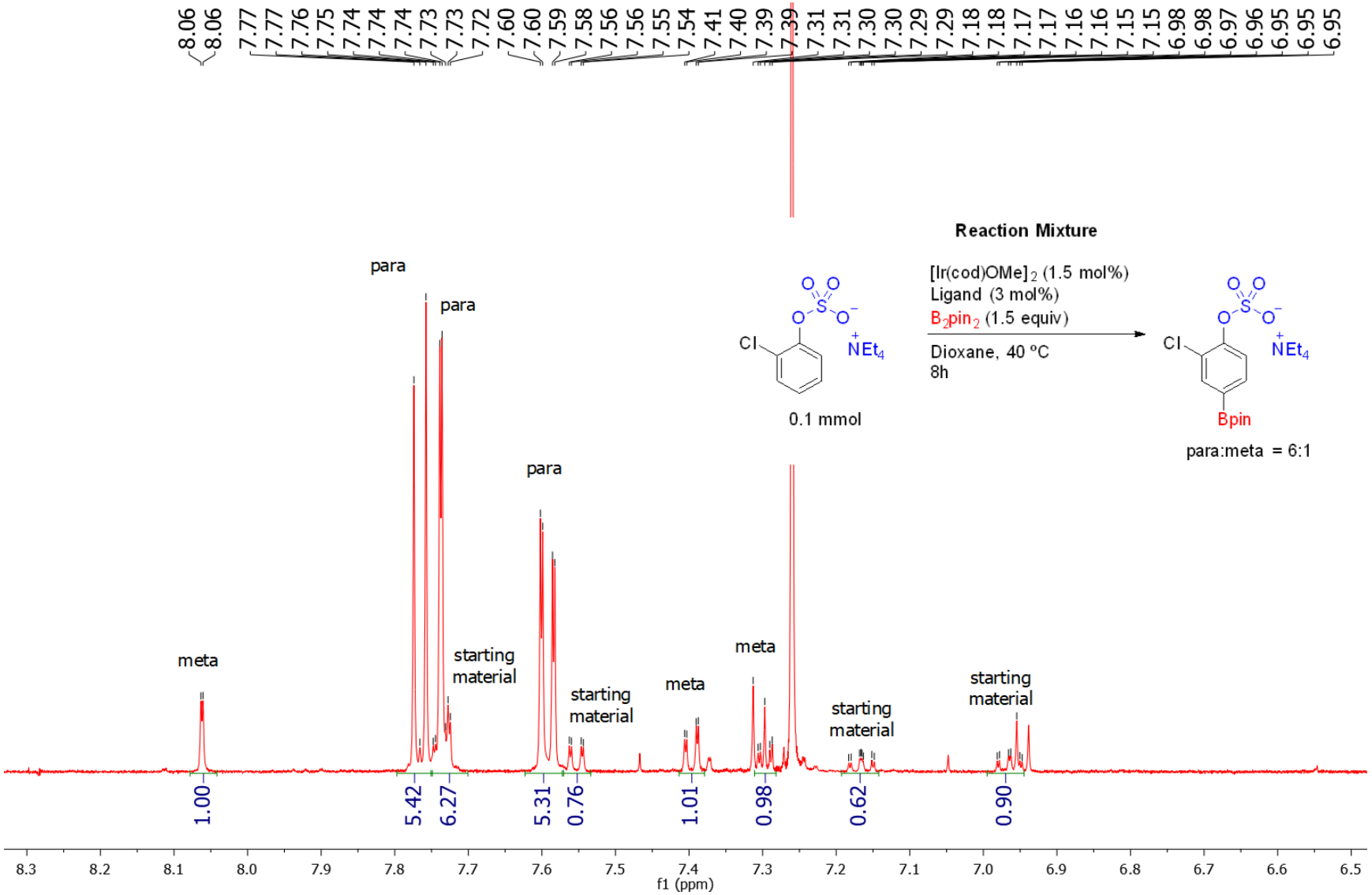
^{1}H NMR spectrum of the reaction mixture for the para borylation of tetraethylammonium 2-chlorophenylsulfate (2a'')



Conditions: 25 °C, 500 MHz, $CDCl_3$

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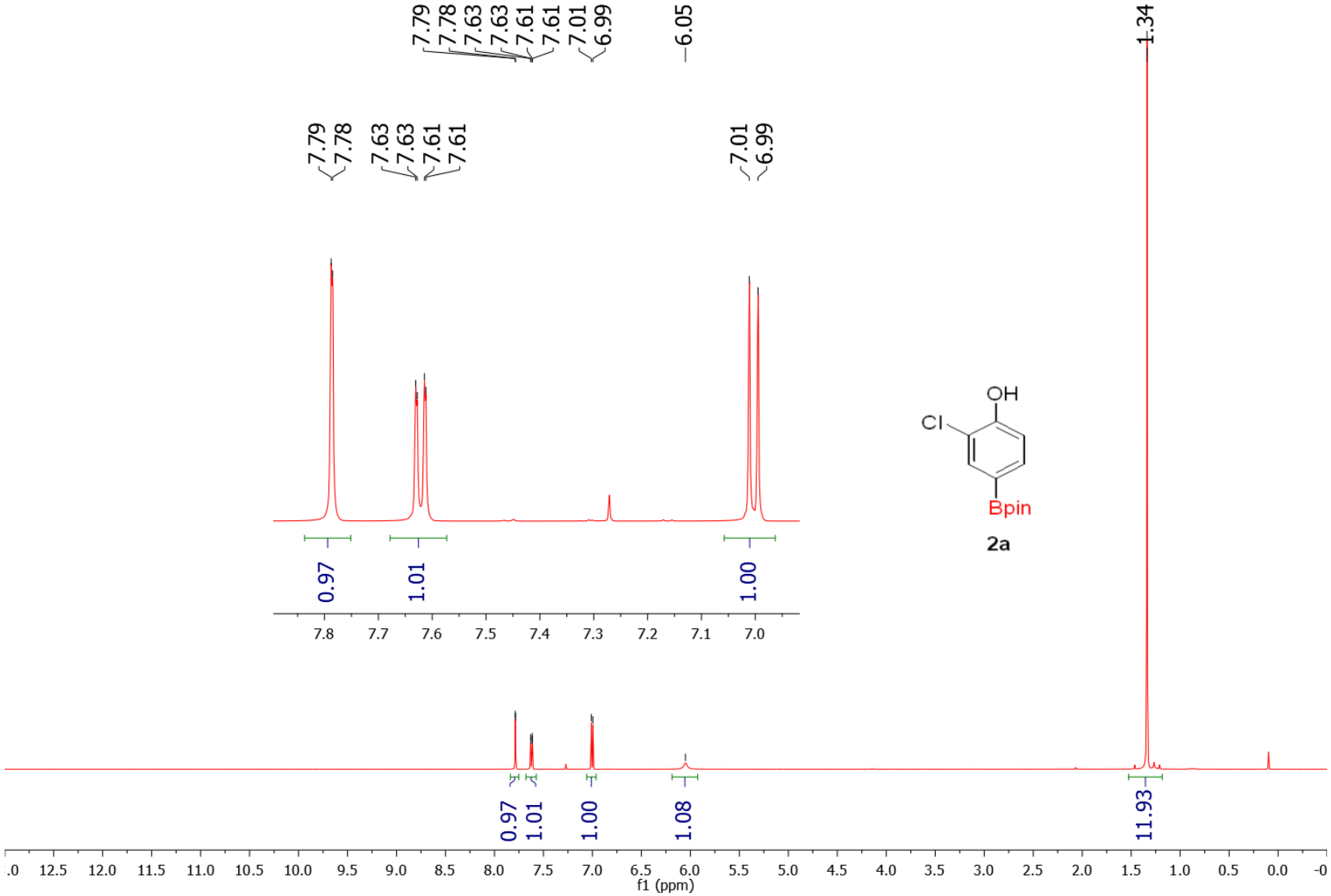
^{1}H NMR spectrum of para borylated 2-chlorophenol (2a)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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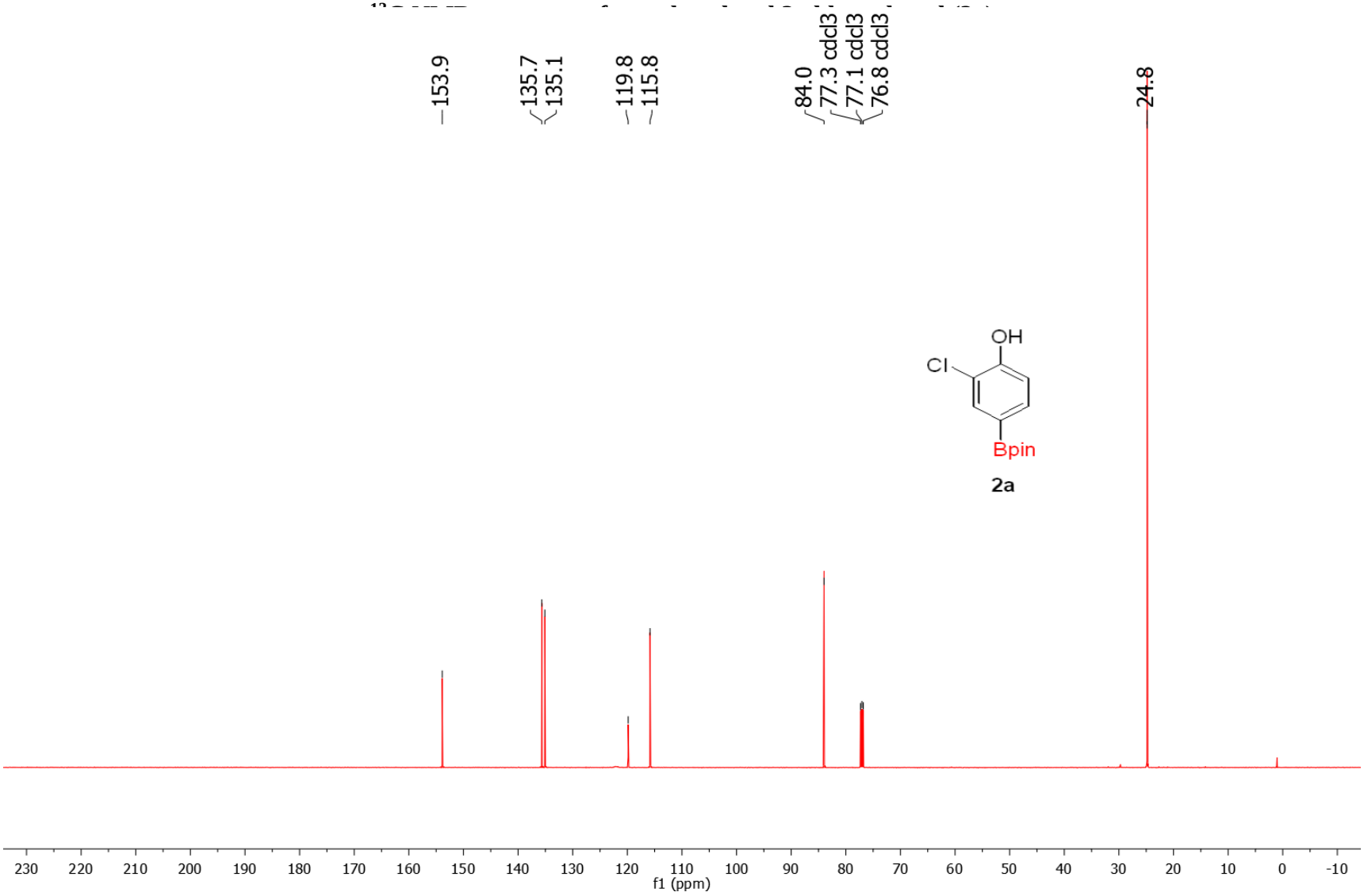

Conditions: 25 ºC, 126 MHz, $CDCl_3$

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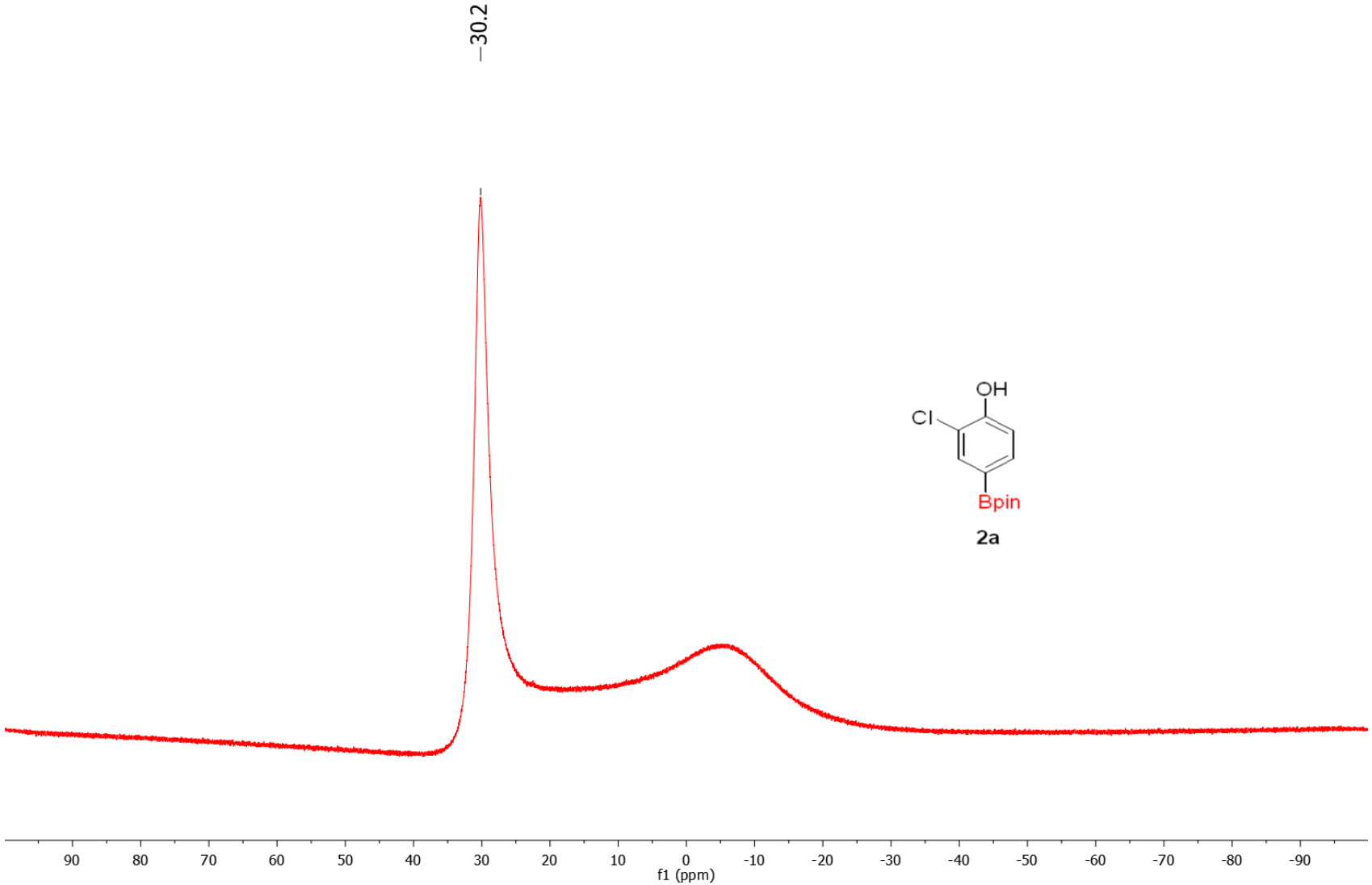
^{11}B NMR spectrum of para borylated 2-chlorophenol (2a)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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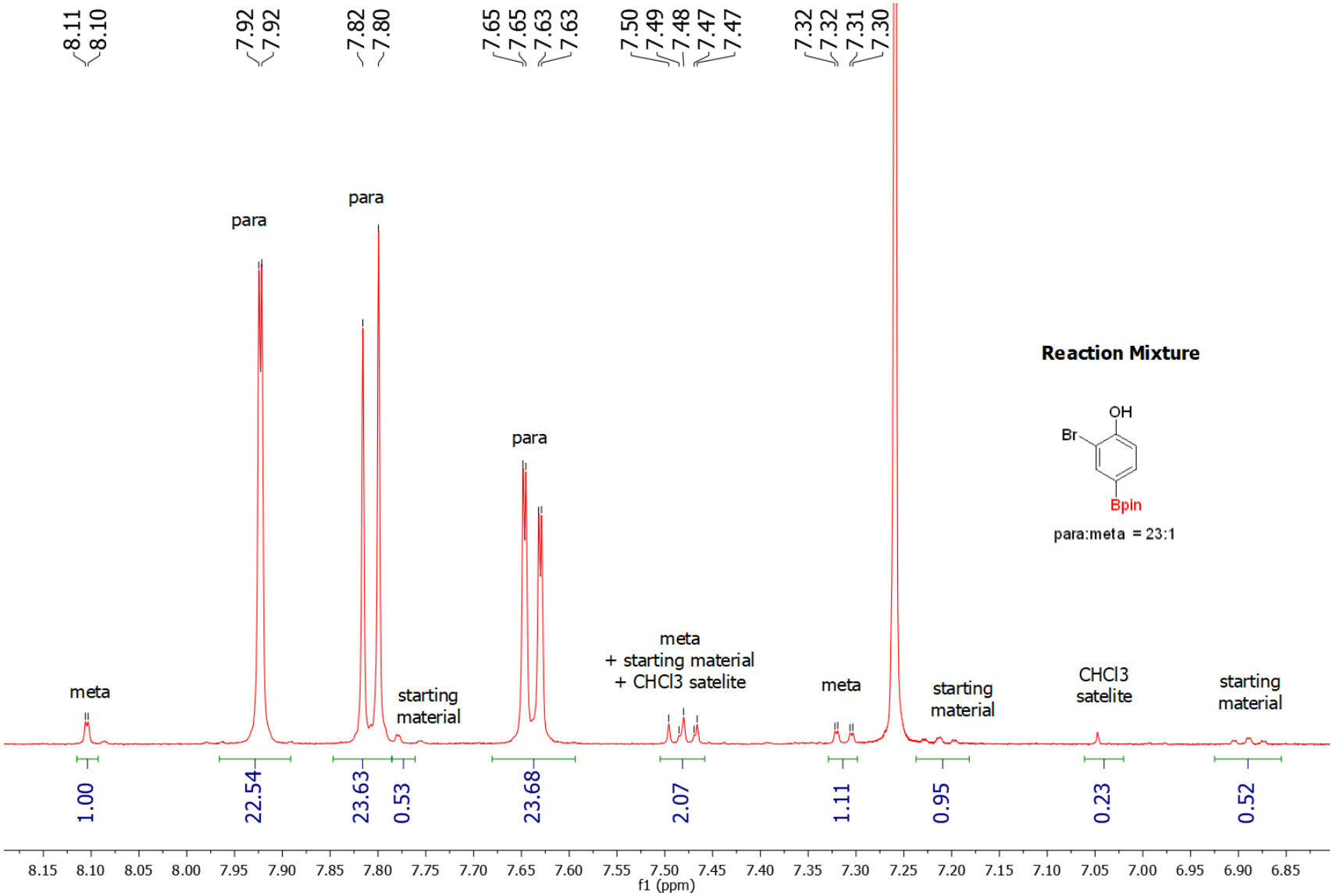
^{1}H NMR spectrum of the reaction mixture for the para borylation of tetrapropyl ammonium 2-bromophenylsulfate (2b)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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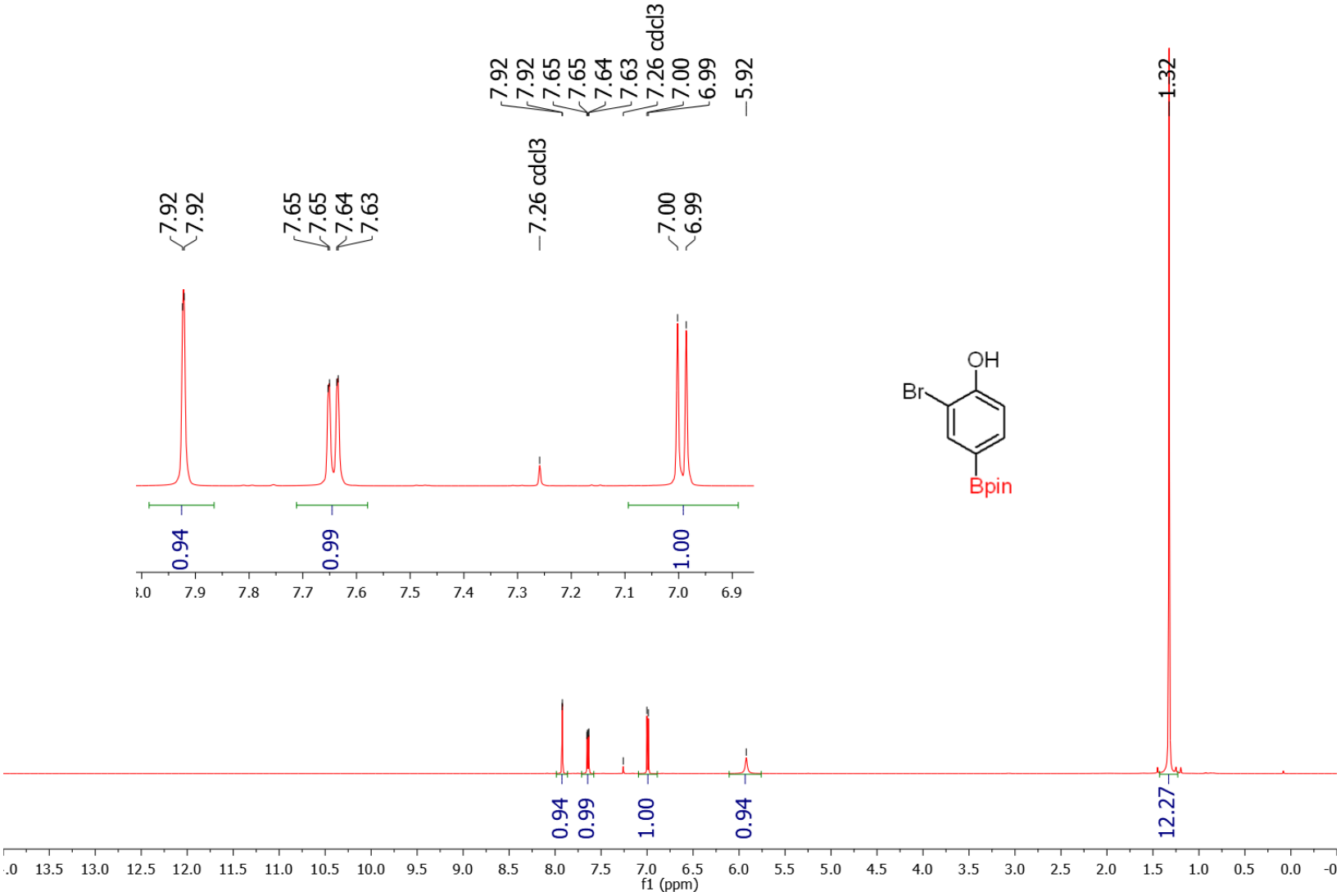
^{1}H NMR spectrum of para borylated 2-bromophenol (2b)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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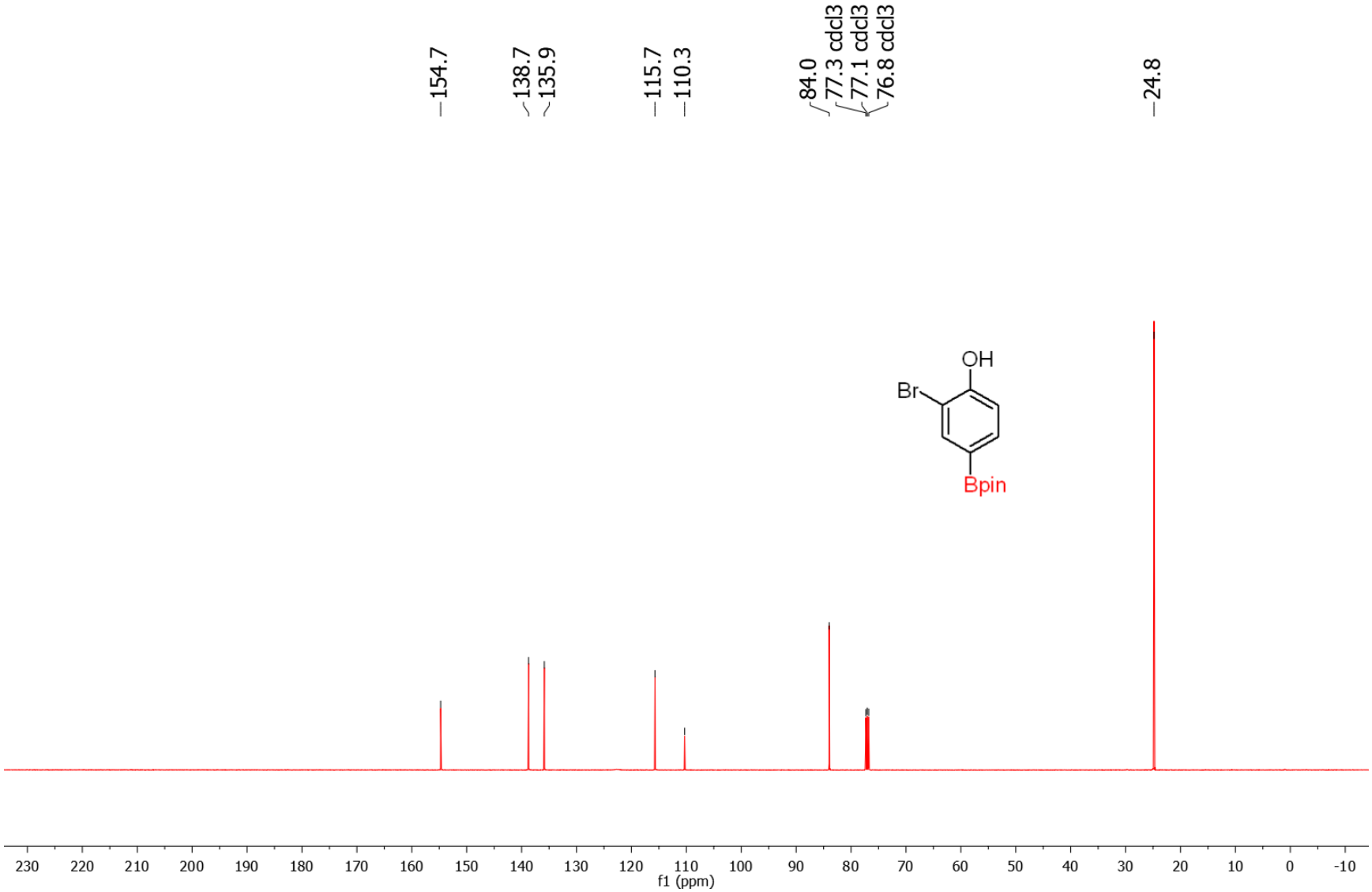
^{13}C NMR spectrum of para borylated 2-bromophenol (2b)



Conditions: 25 ^{o}C, 126 MHz, $CDCl_3$

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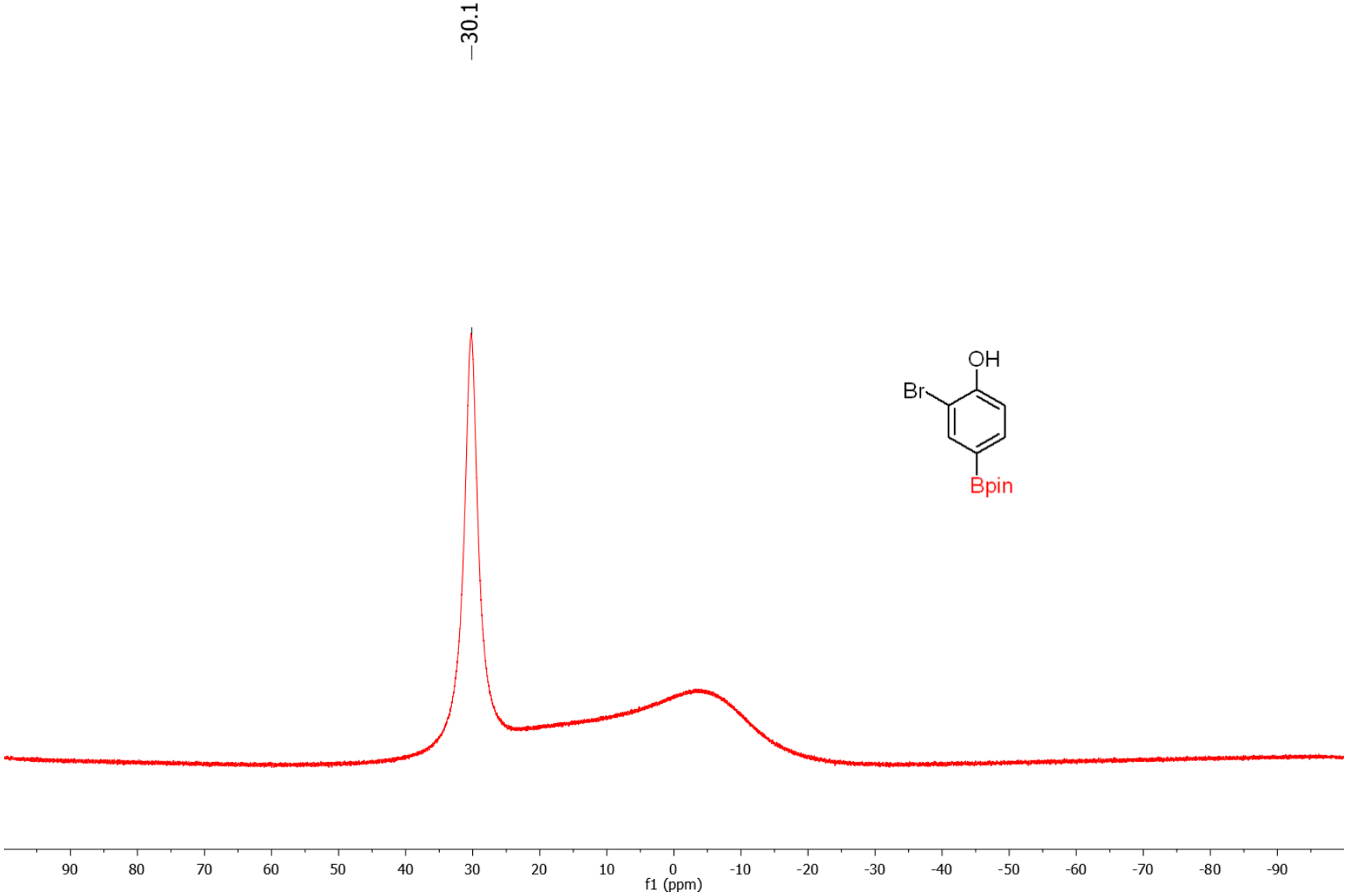
^{11}B NMR spectrum of para borylated 2-bromophenol (2b)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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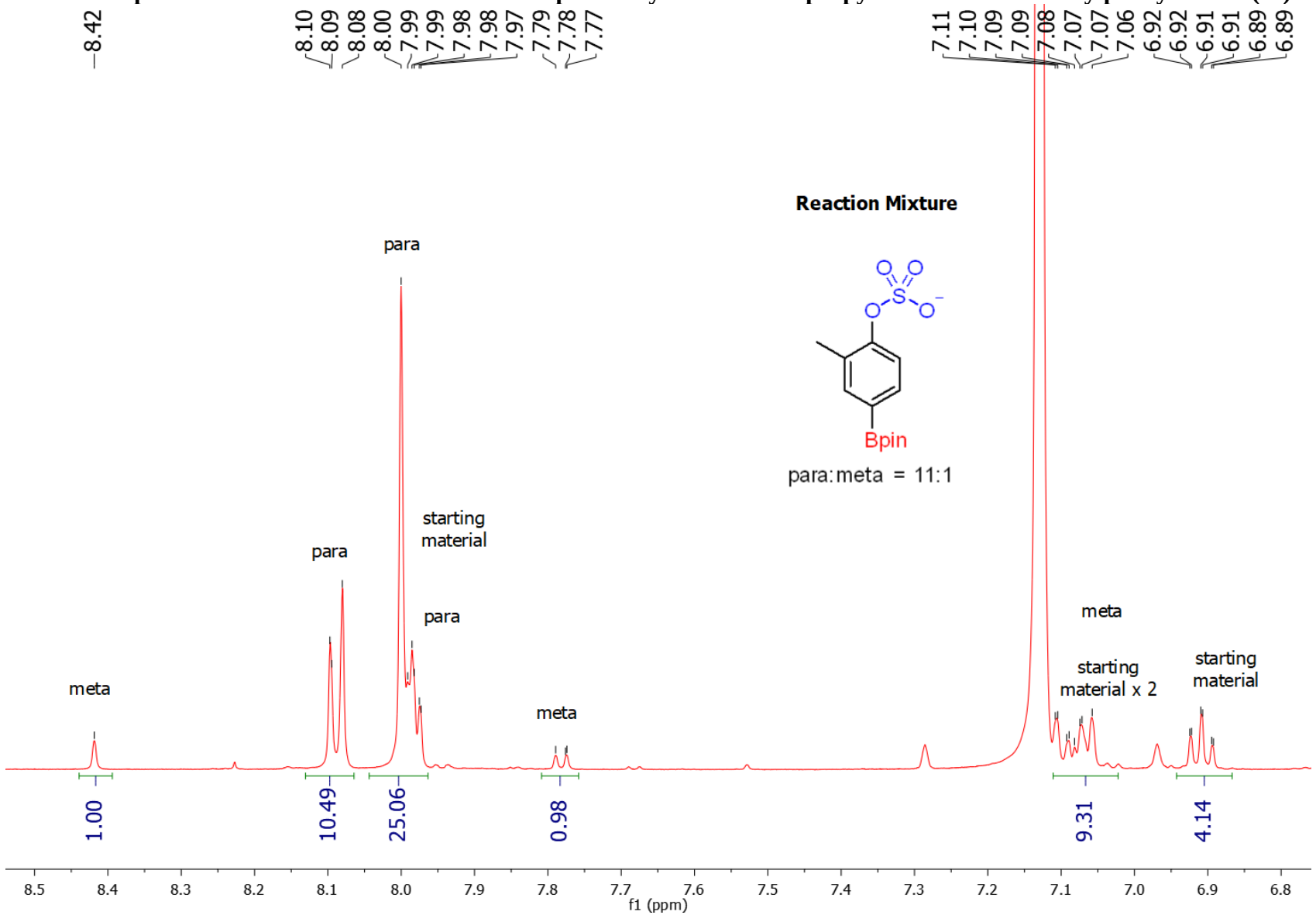
^{1}H NMR spectrum of the reaction mixture for the para borylation of tetrapropyl ammonium 2-methylphenylsulfate (2c)



Conditions: 25 ºC, 500 MHz, C_6D_6

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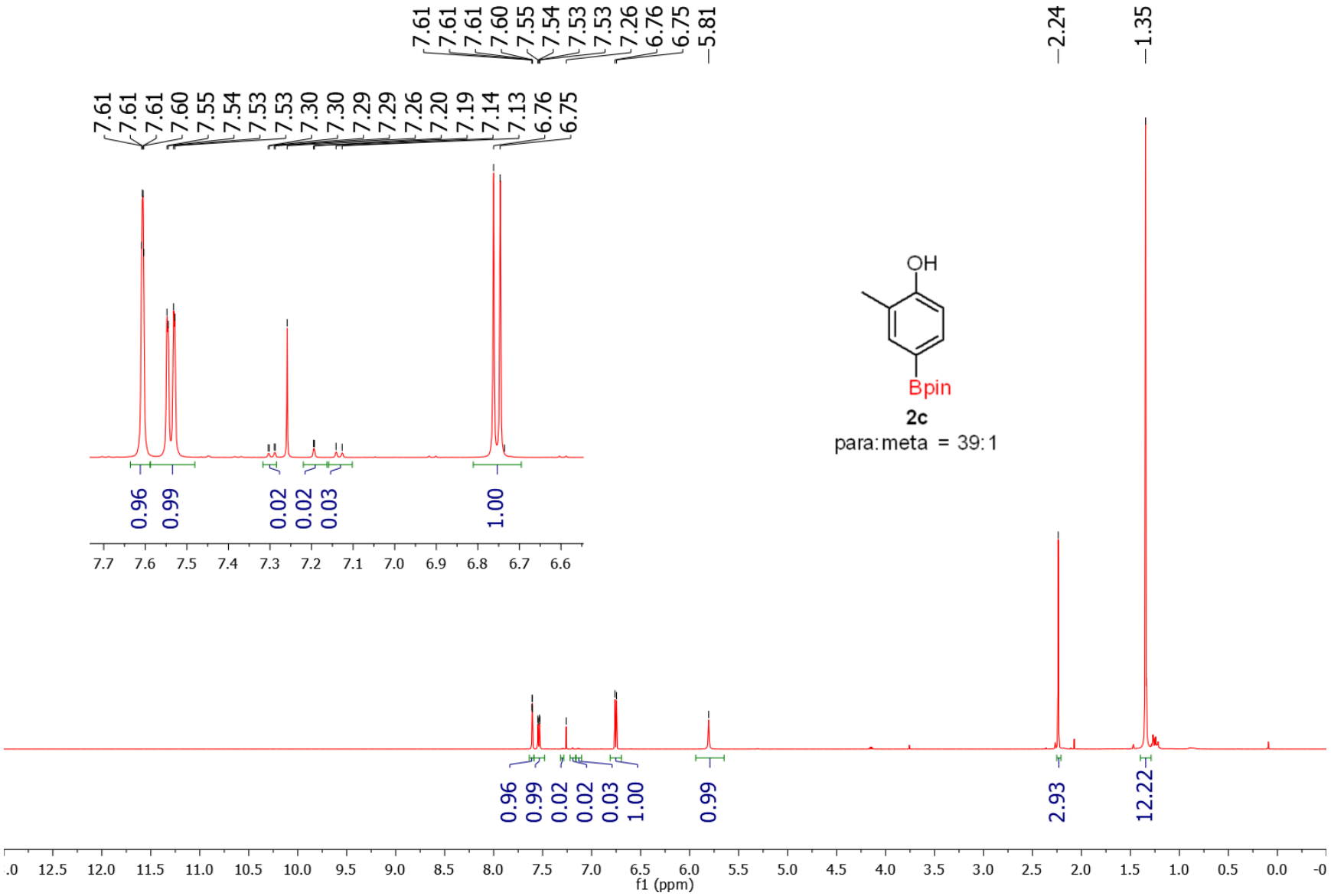
^{1}H NMR spectrum of para borylated 2-methylphenol (2c)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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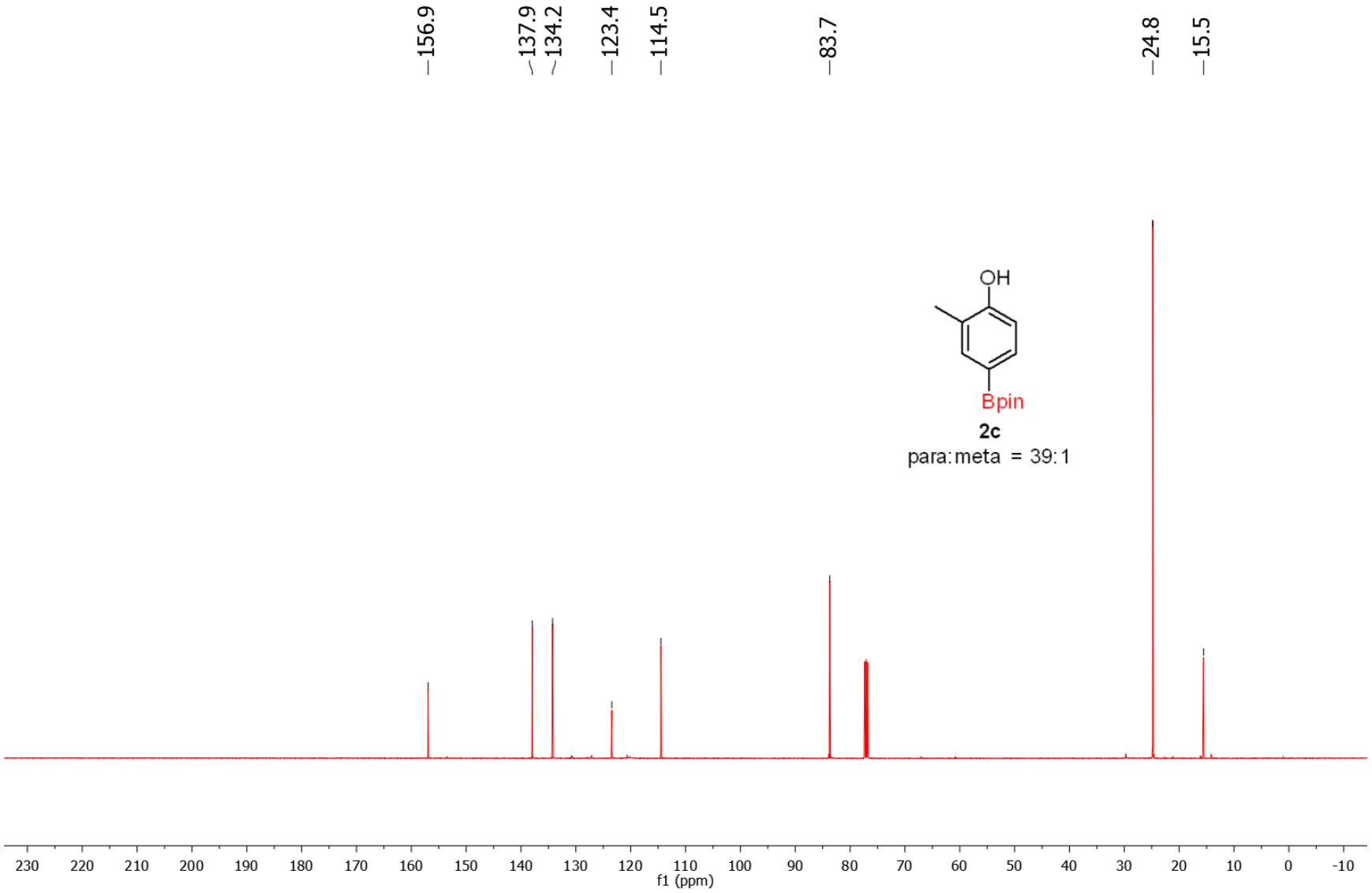
^{13}C NMR spectrum of para borylated 2-methylphenol (2c)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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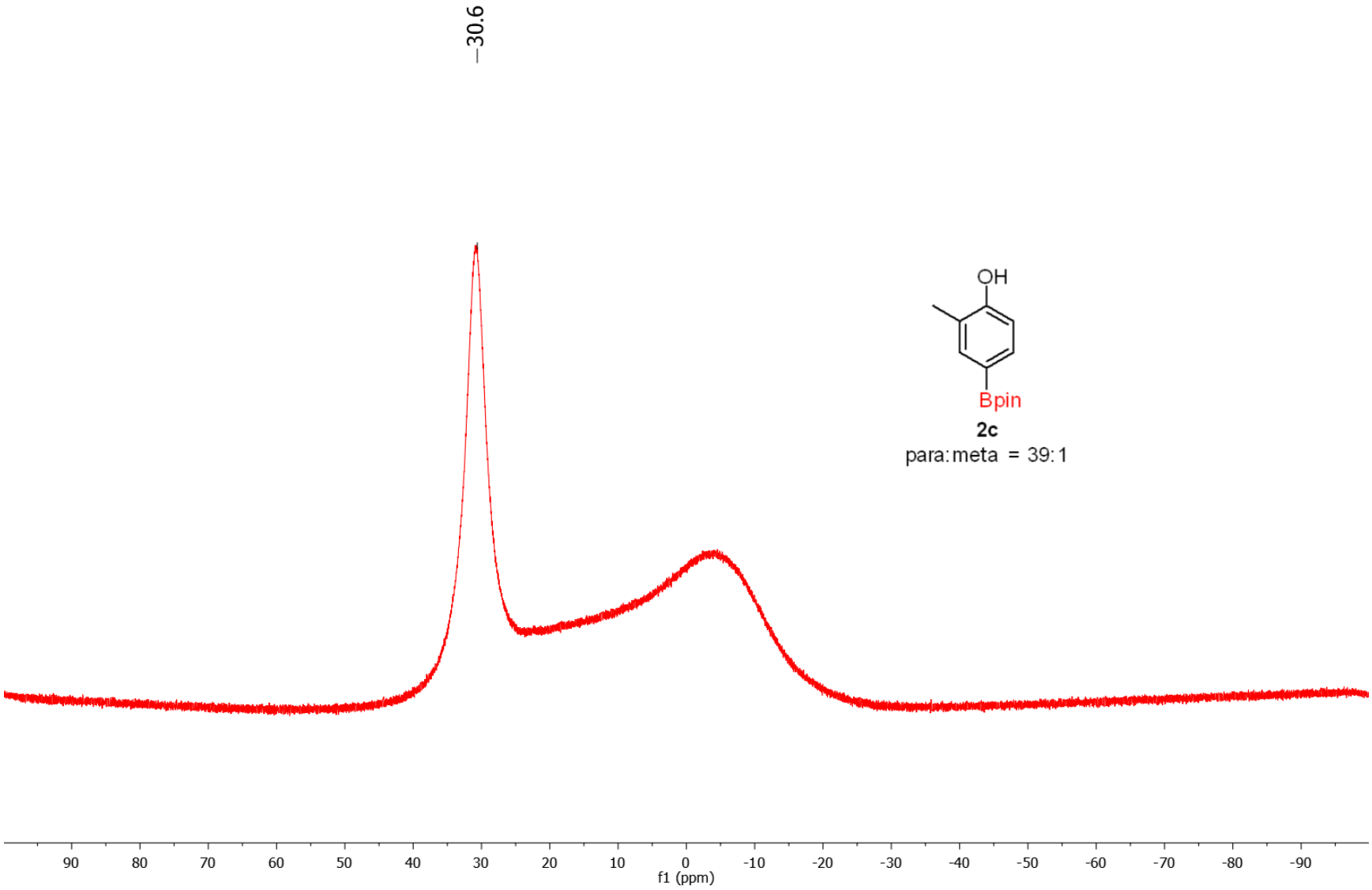
^{11}B NMR spectrum of para borylated 2-methylphenol (2c)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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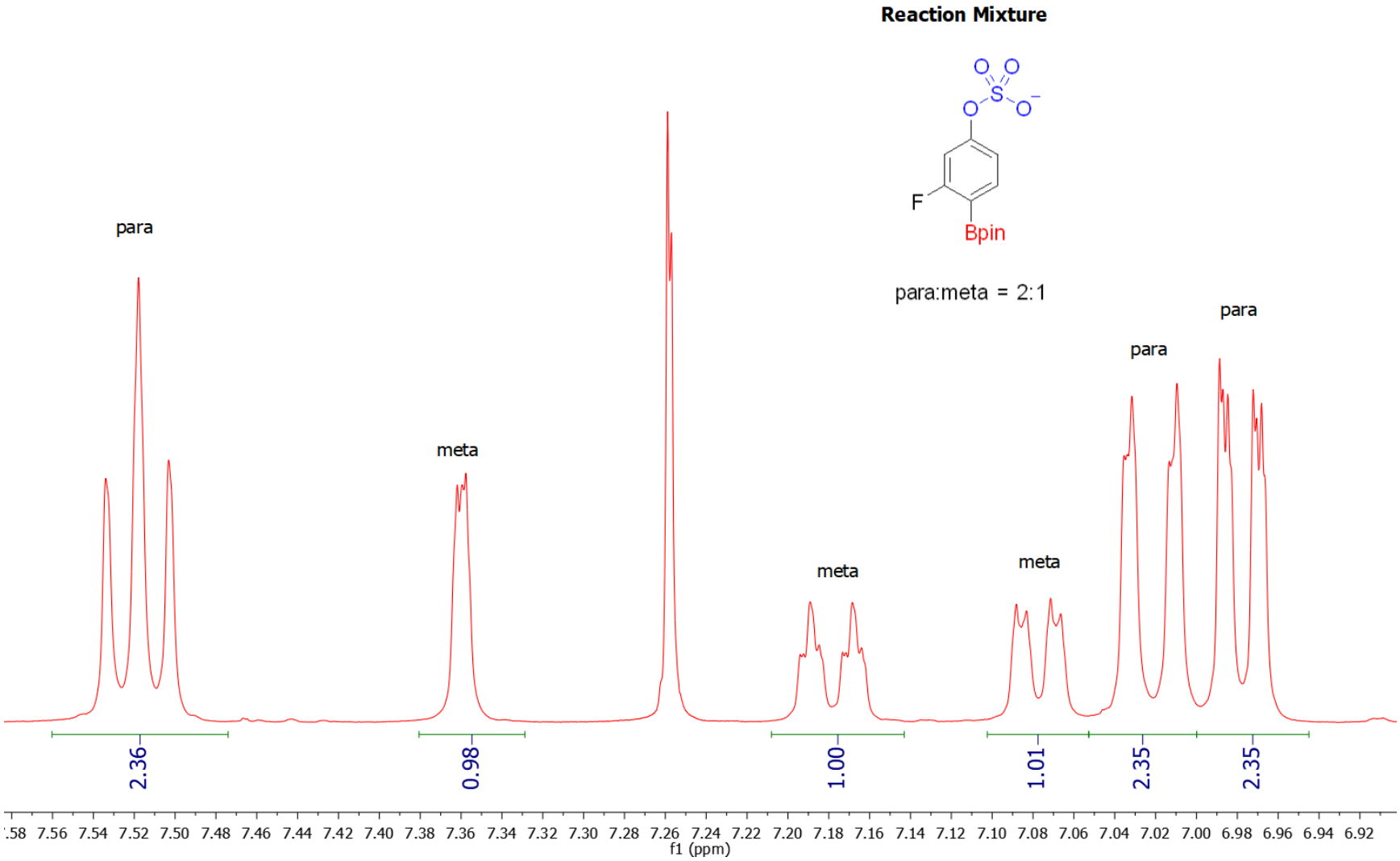
^{1}H NMR spectrum of the reaction mixture for the para borylation of tetrapropylammonium 3-fluorophenylsulfate (2d)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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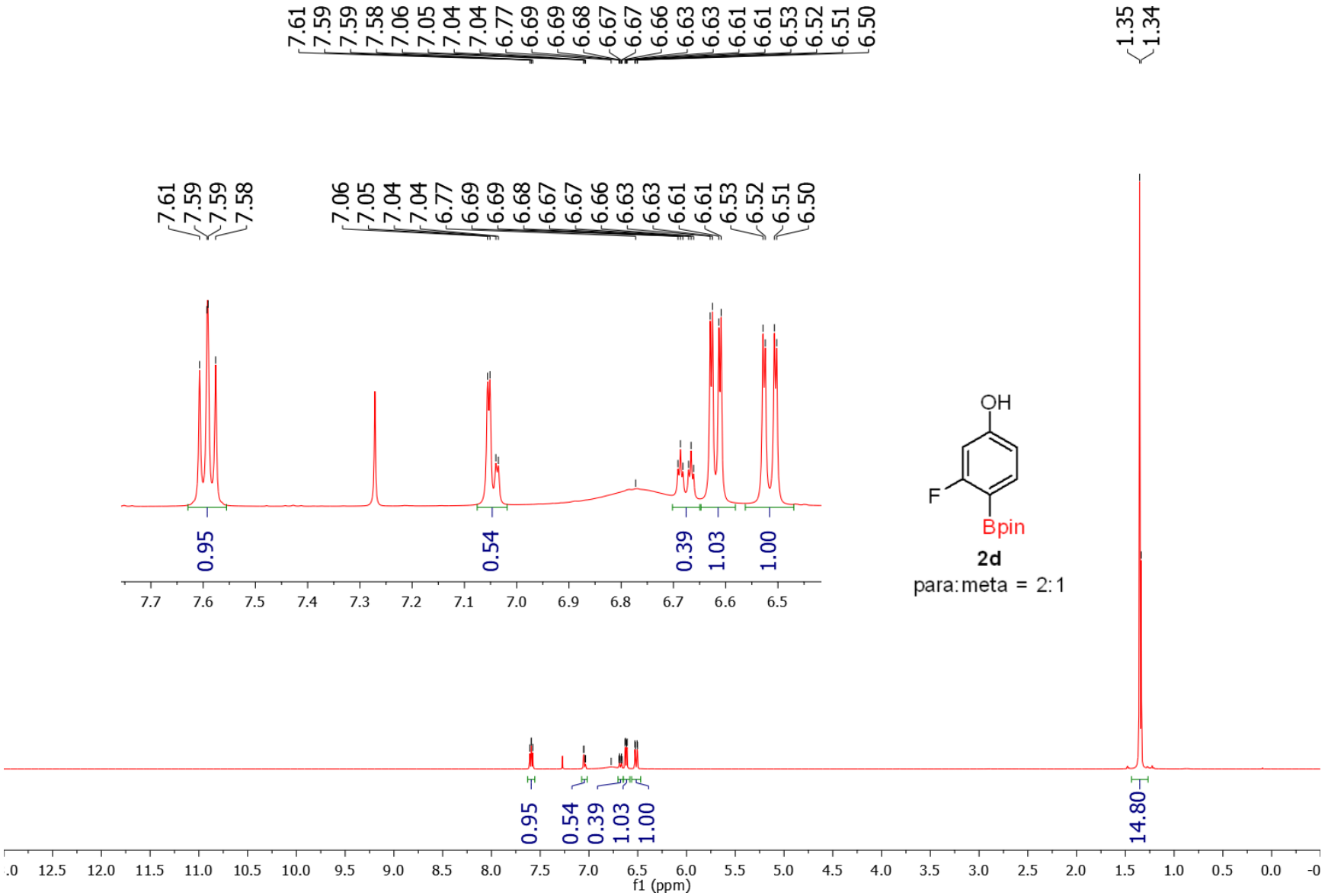
^{1}H NMR spectrum of para borylated 3-fluorophenol (2d)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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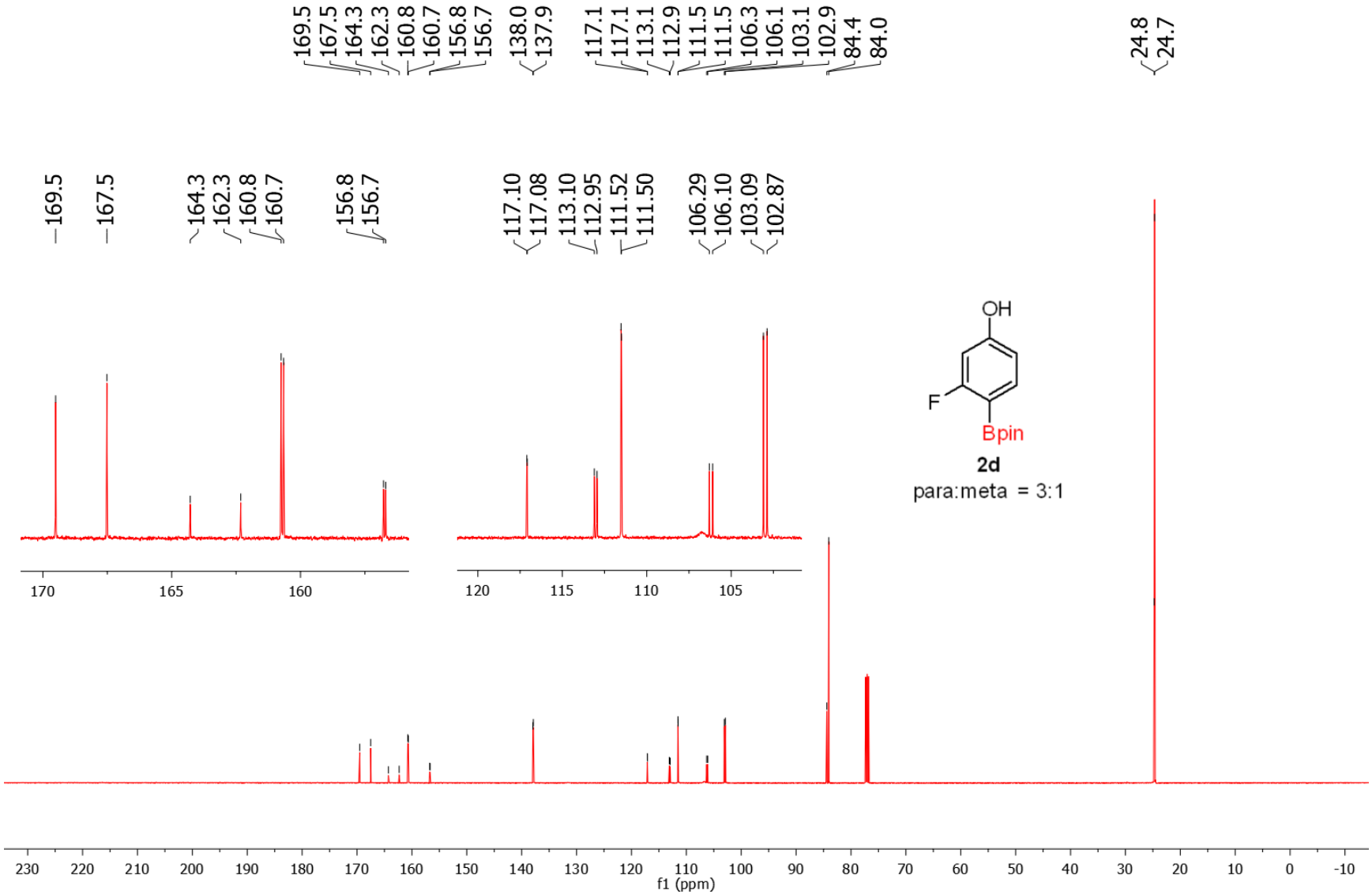
^{13}C NMR spectrum of para borylated 3-fluorophenol (2d)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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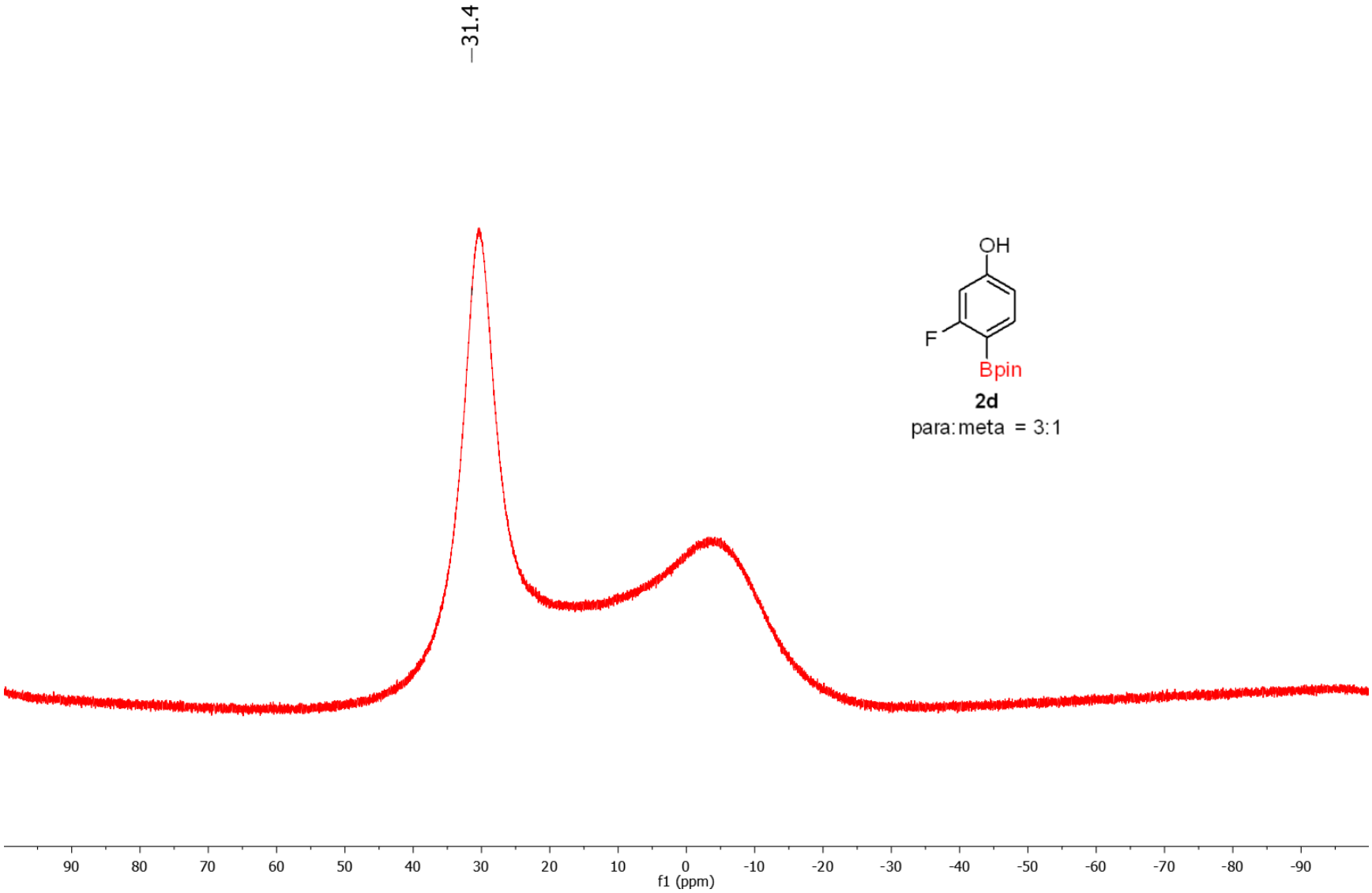
^{11}B NMR spectrum of para borylated 3-fluorophenol (2d)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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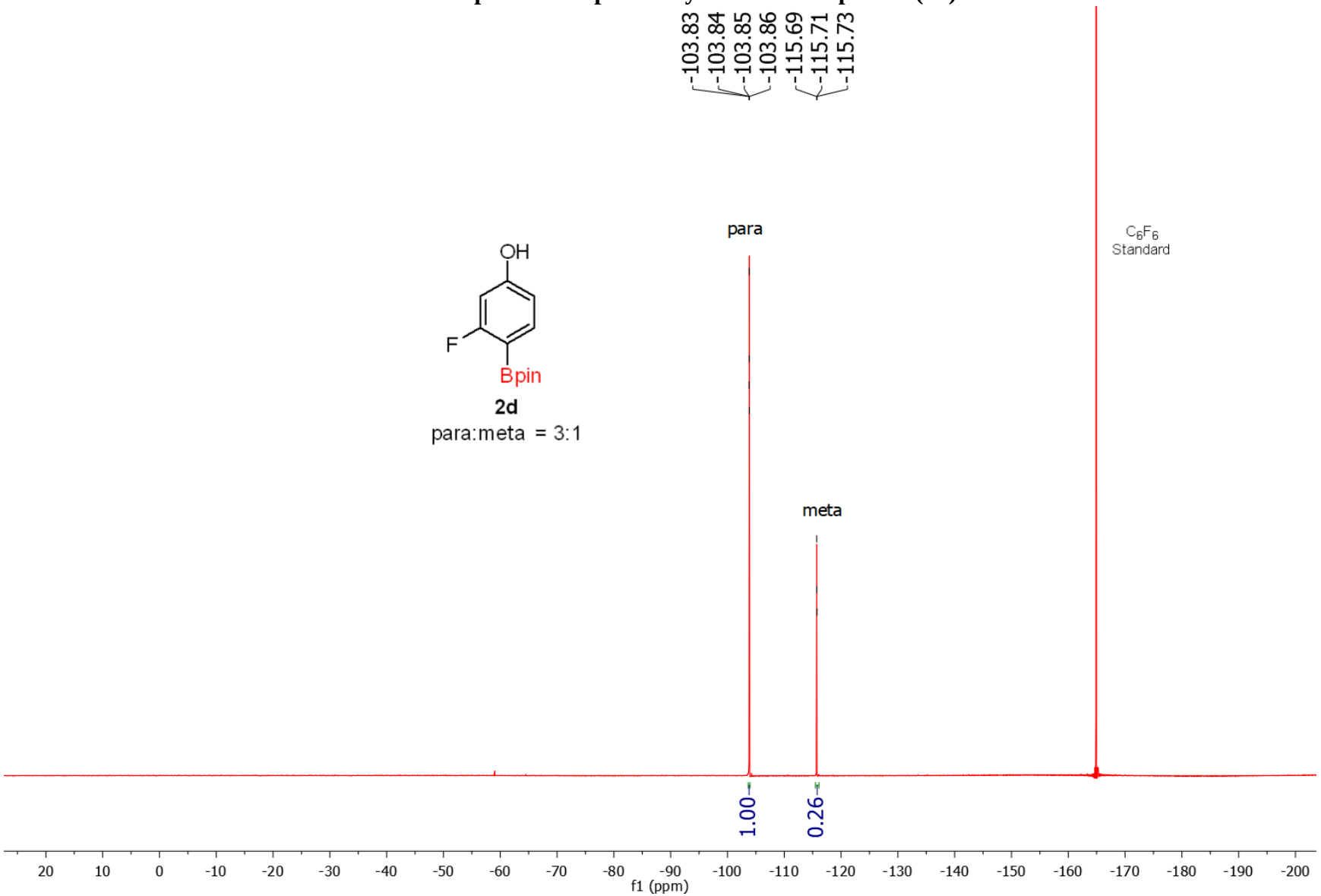
^{19}F NMR spectrum of para borylated 3-fluorophenol (2d)



Conditions: 25 ºC, 470 MHz, $CDCl_3$

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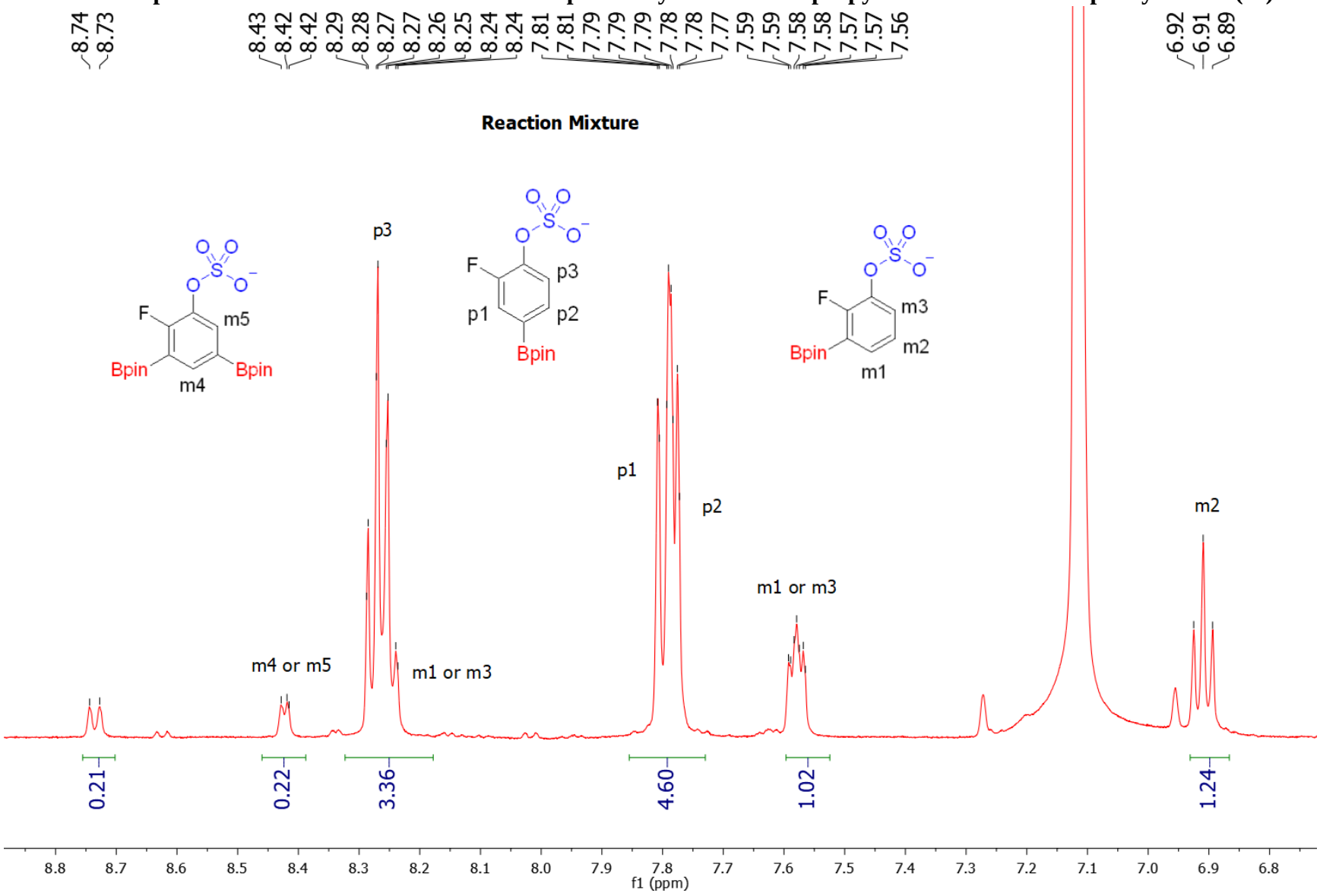
^{1}H NMR spectrum of the reaction mixture for the para borylation of tetrapropylammonium 2-fluorophenylsulfate (2e)



Conditions: 25 ºC, 500 MHz, C_6D_6

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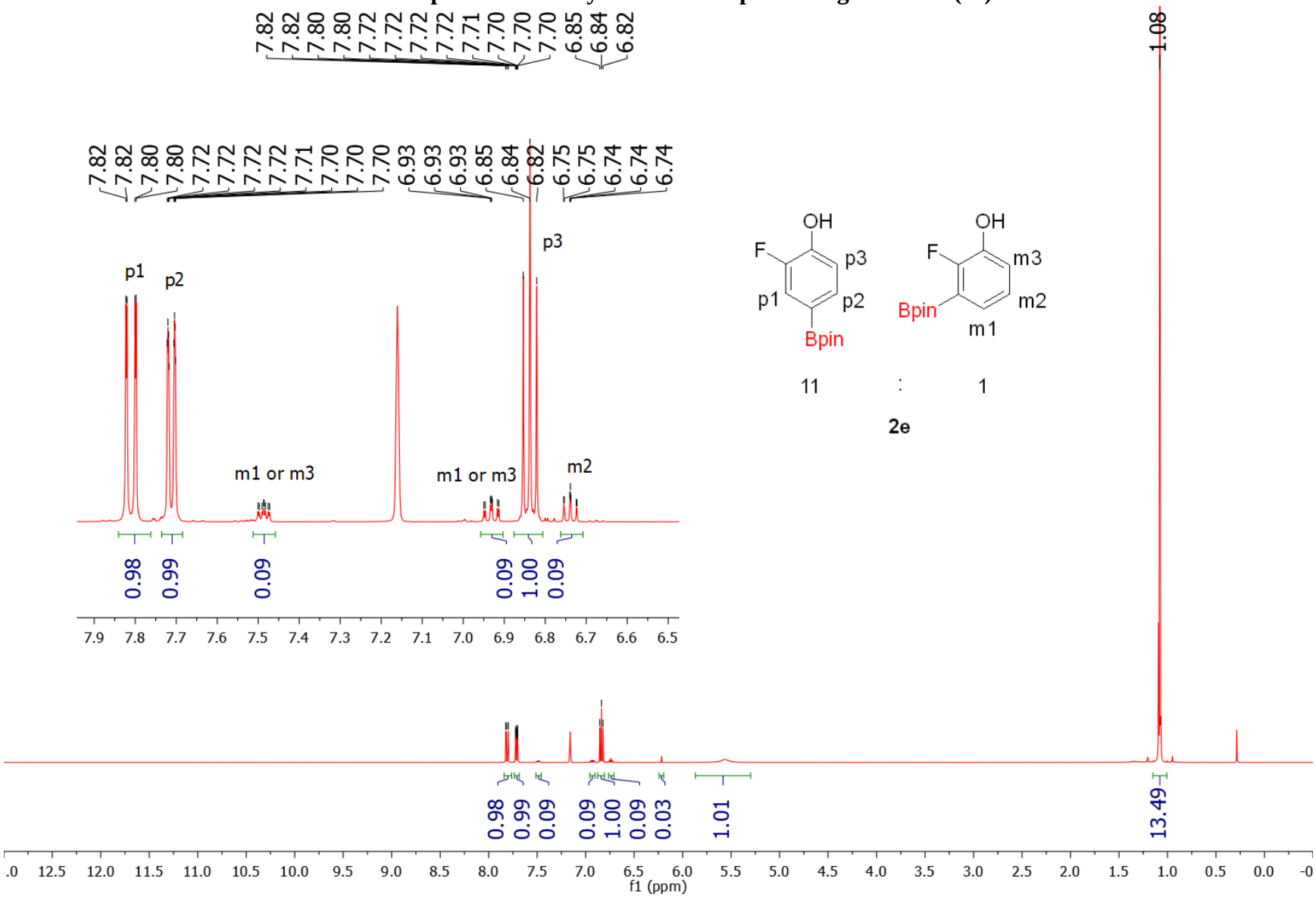
^{1}H NMR spectrum of borylated 2-fluorophenol regioisomers (2e)



Conditions: 25 ºC, 500 MHz, C_6D_6

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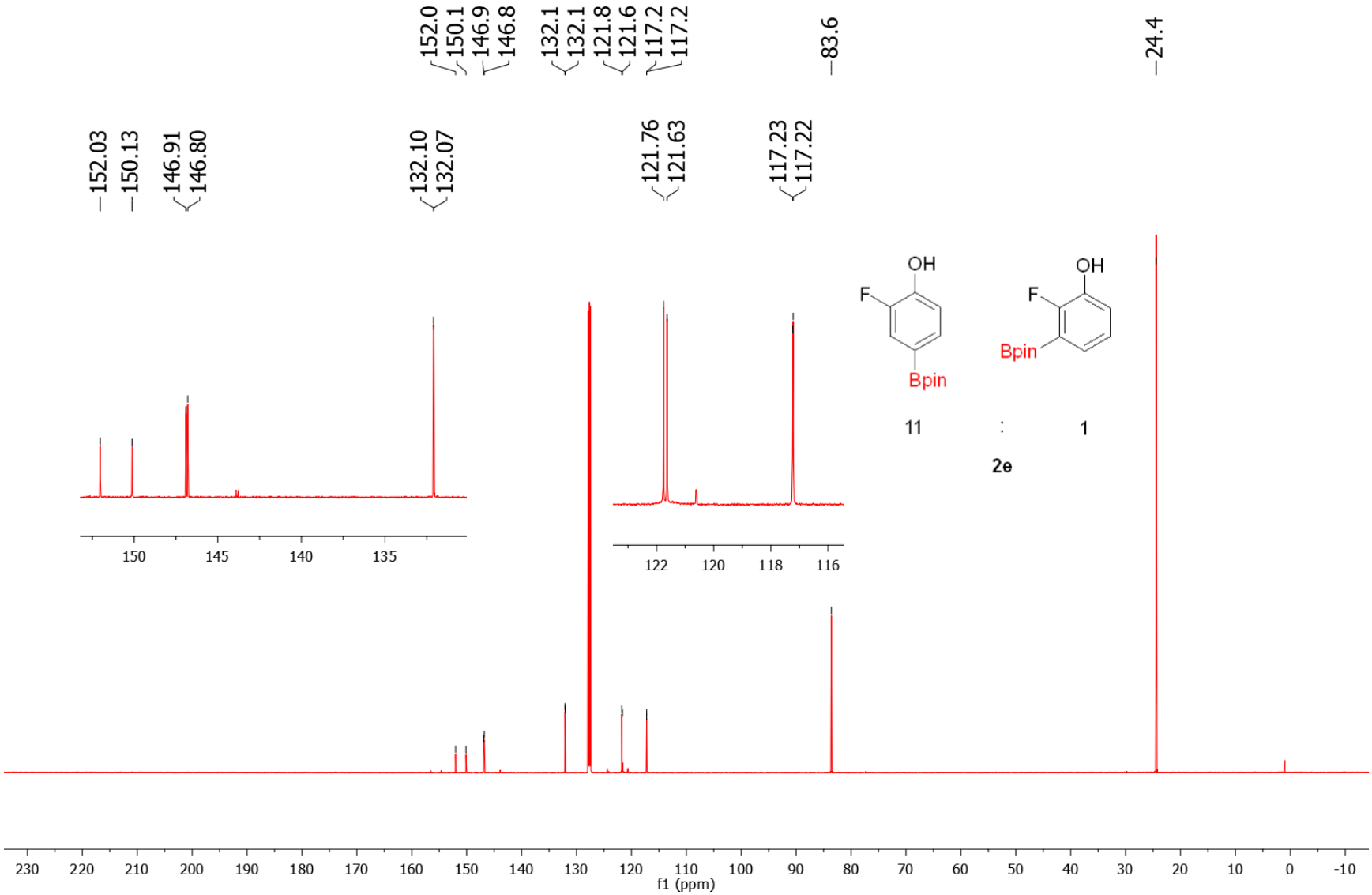
^{13}C NMR spectrum of borylated 2-fluorophenol regioisomers (2e)



Conditions: 25 ºC, 126 MHz, C_6D_6

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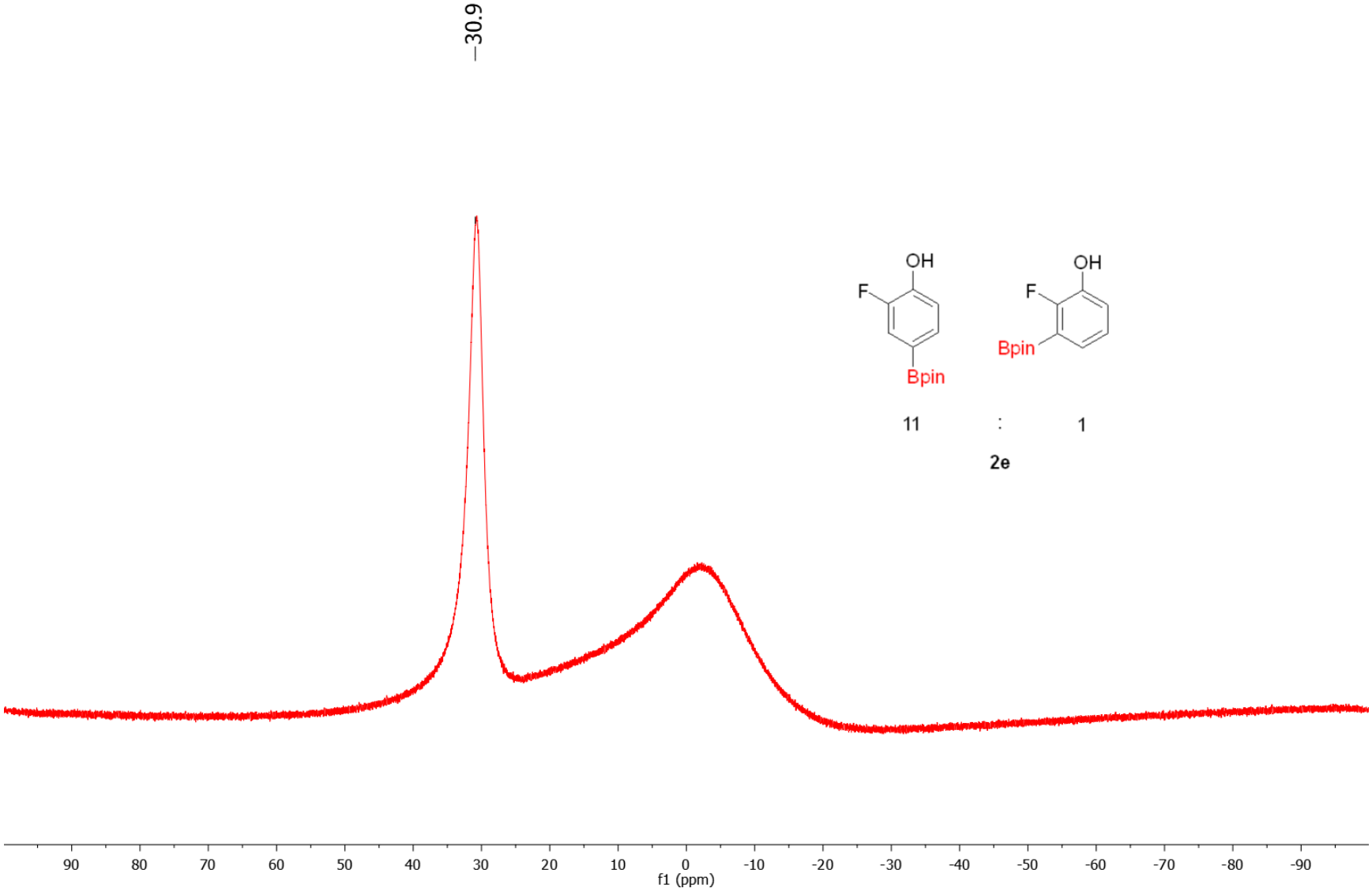
^{11}B NMR spectrum of borylated 2-fluorophenol regioisomers (2e)



Conditions: 25 ºC, 160 MHz, C_6D_6

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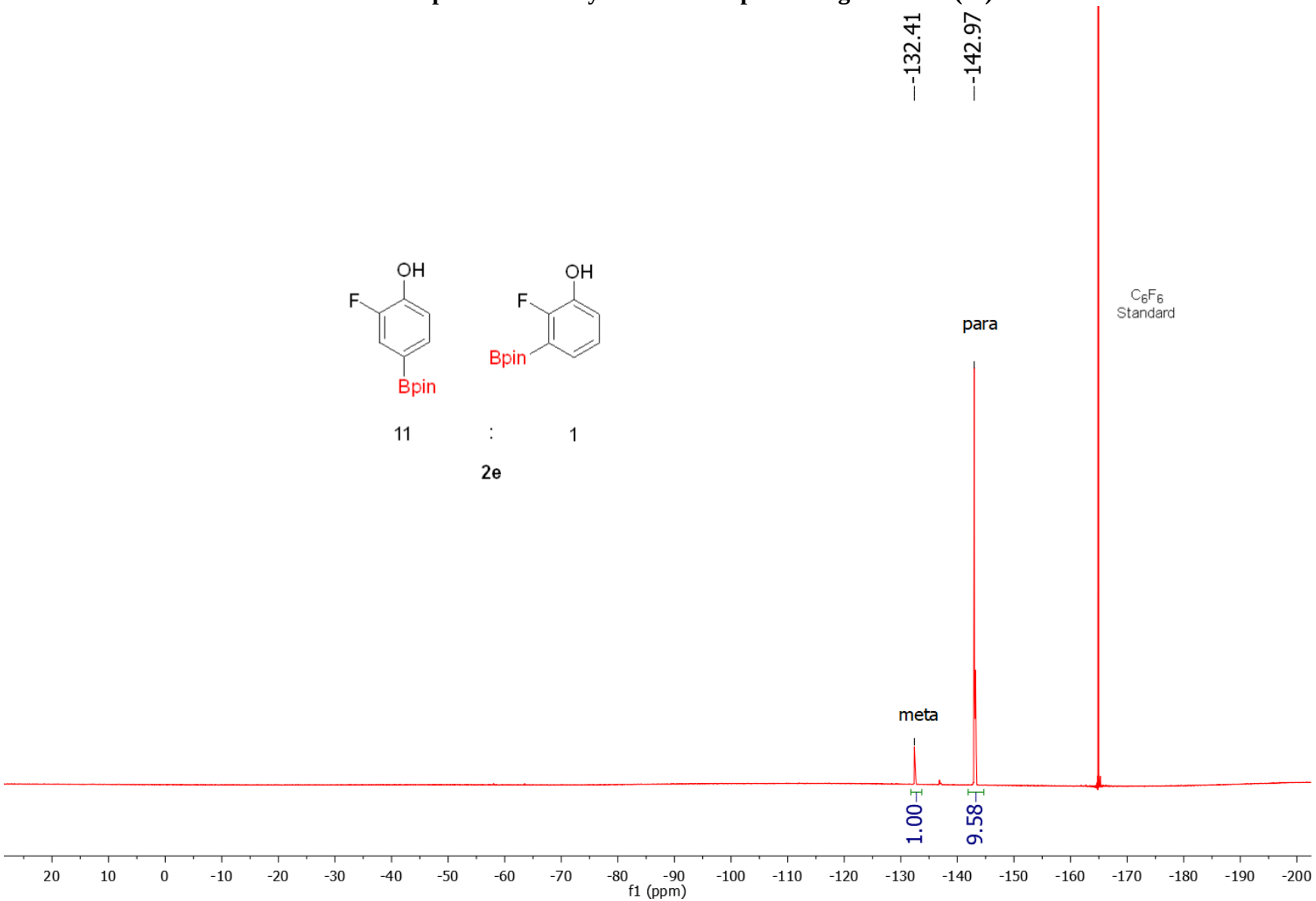
^{19}F NMR spectrum of borylated 2-fluorophenol regioisomers (2e)



Conditions: 25 ºC, 470 MHz, C_6D_6

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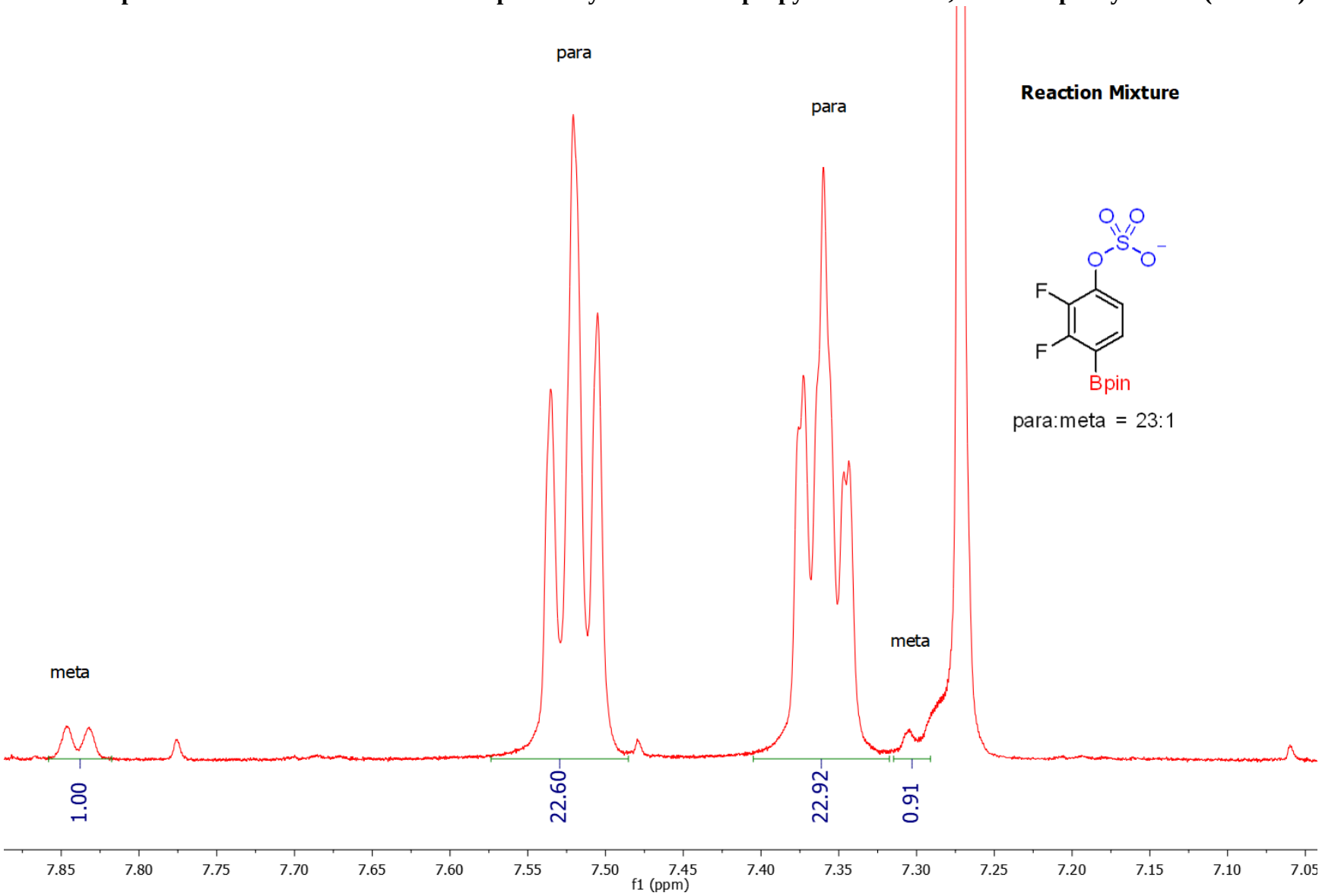
^{1}H NMR spectrum of reaction mixture for the para borylation of tetrapropylammonium 2,3-difluorophenylsulfate (crude 2f)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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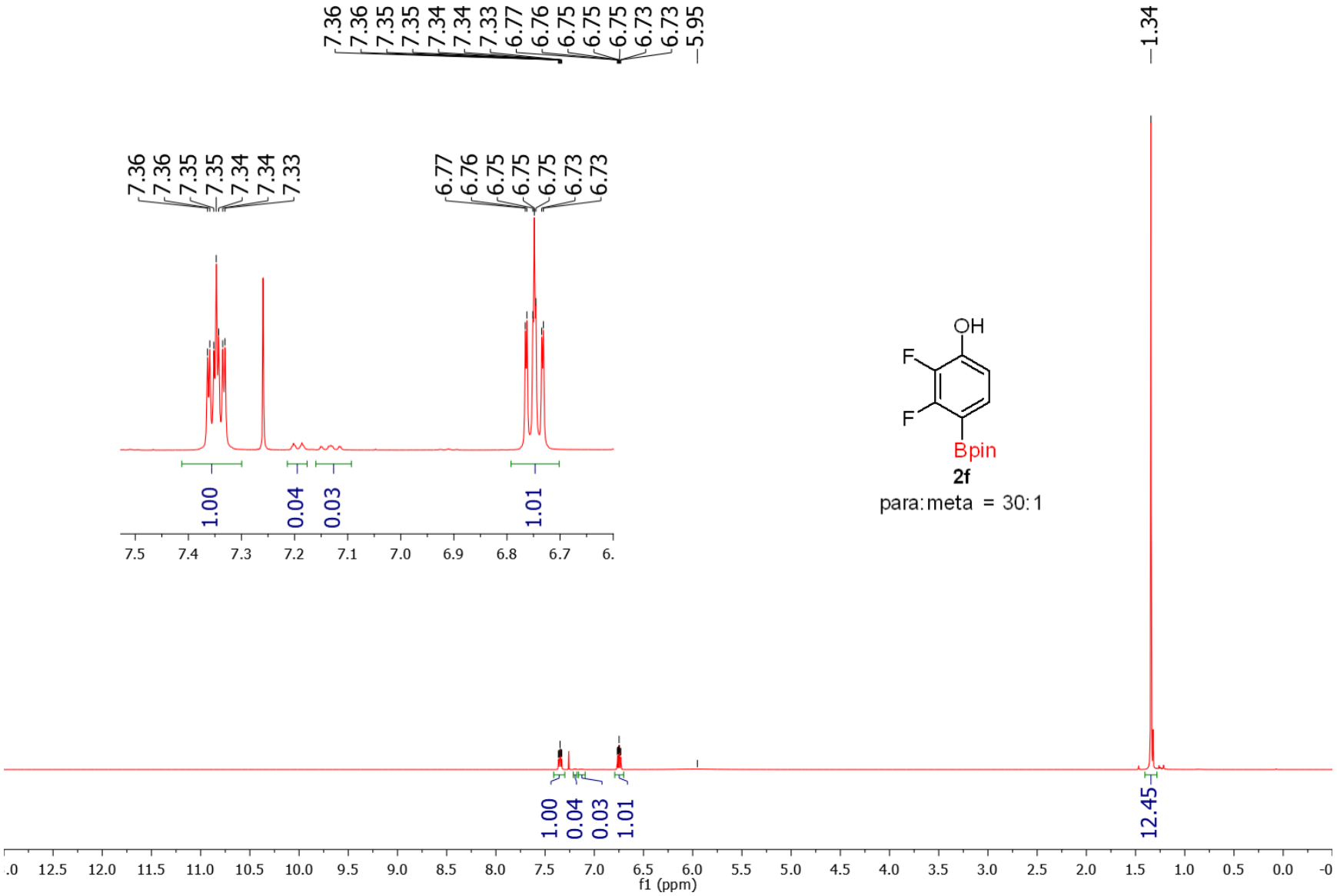
^{1}H NMR spectrum of para borylated 2,3-difluorophenol (2f)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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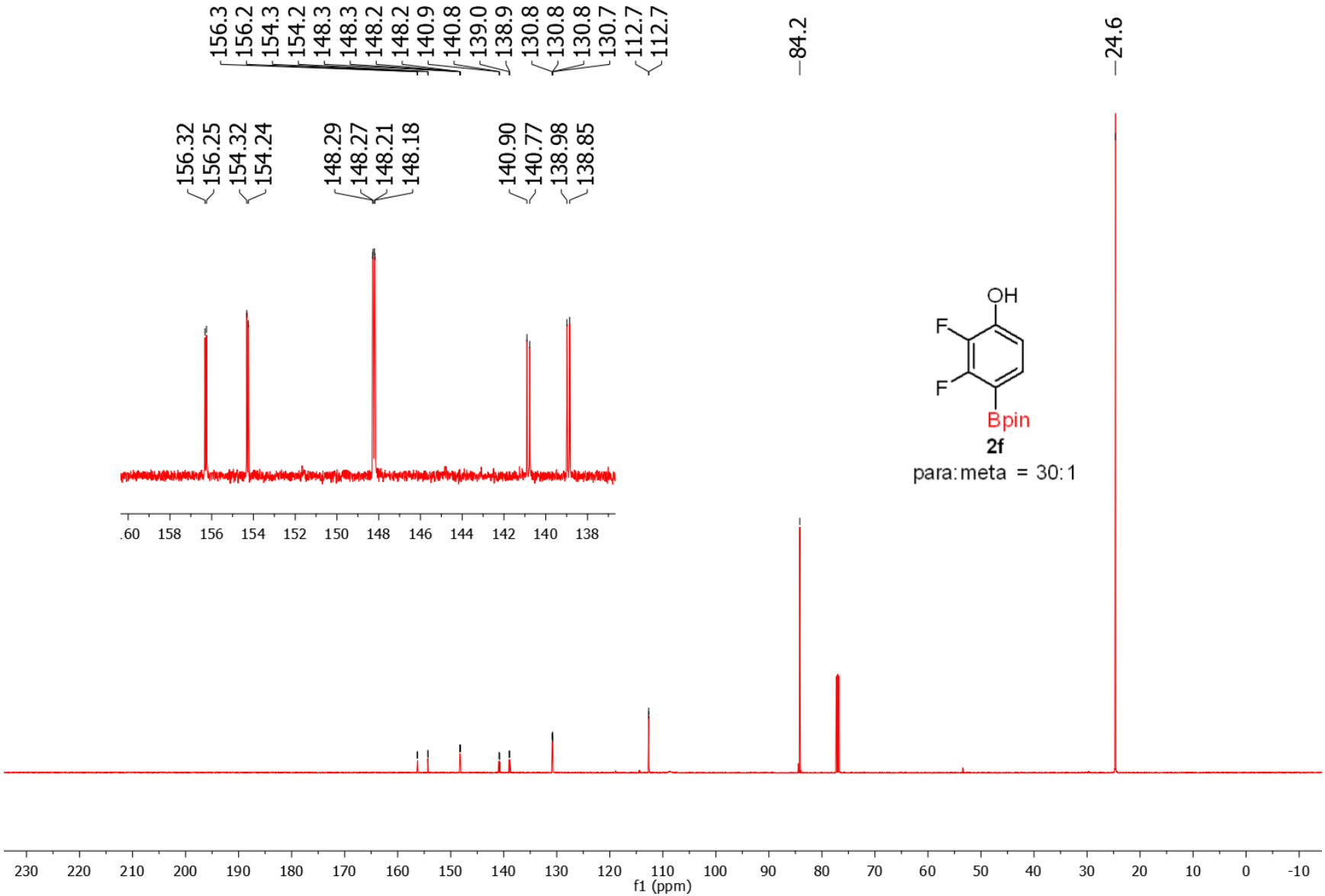
^{13}C NMR spectrum of para borylated 2,3-difluorophenol (2f)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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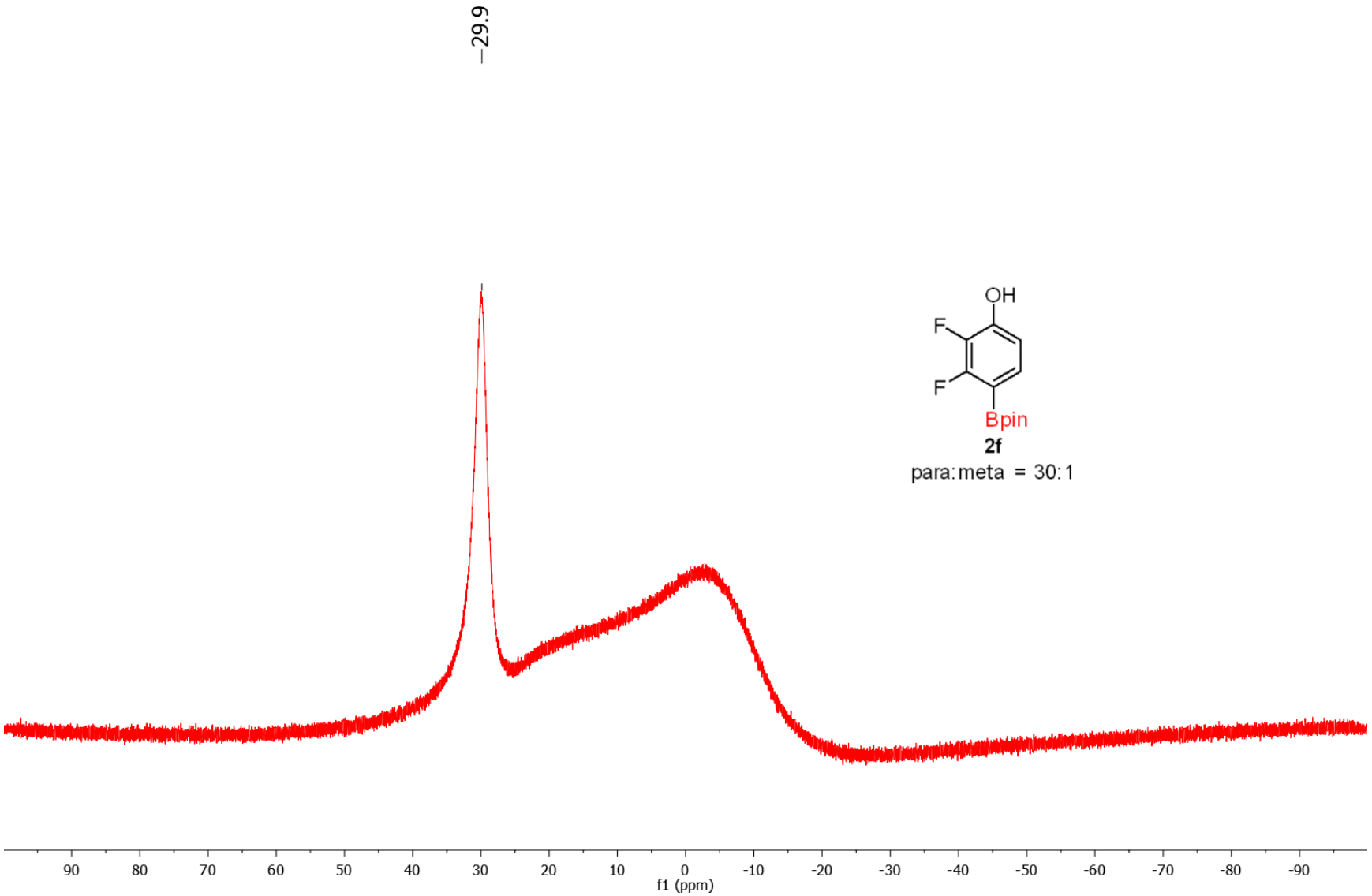
^{11}B NMR spectrum of para borylated 2,3-difluorophenol (2f)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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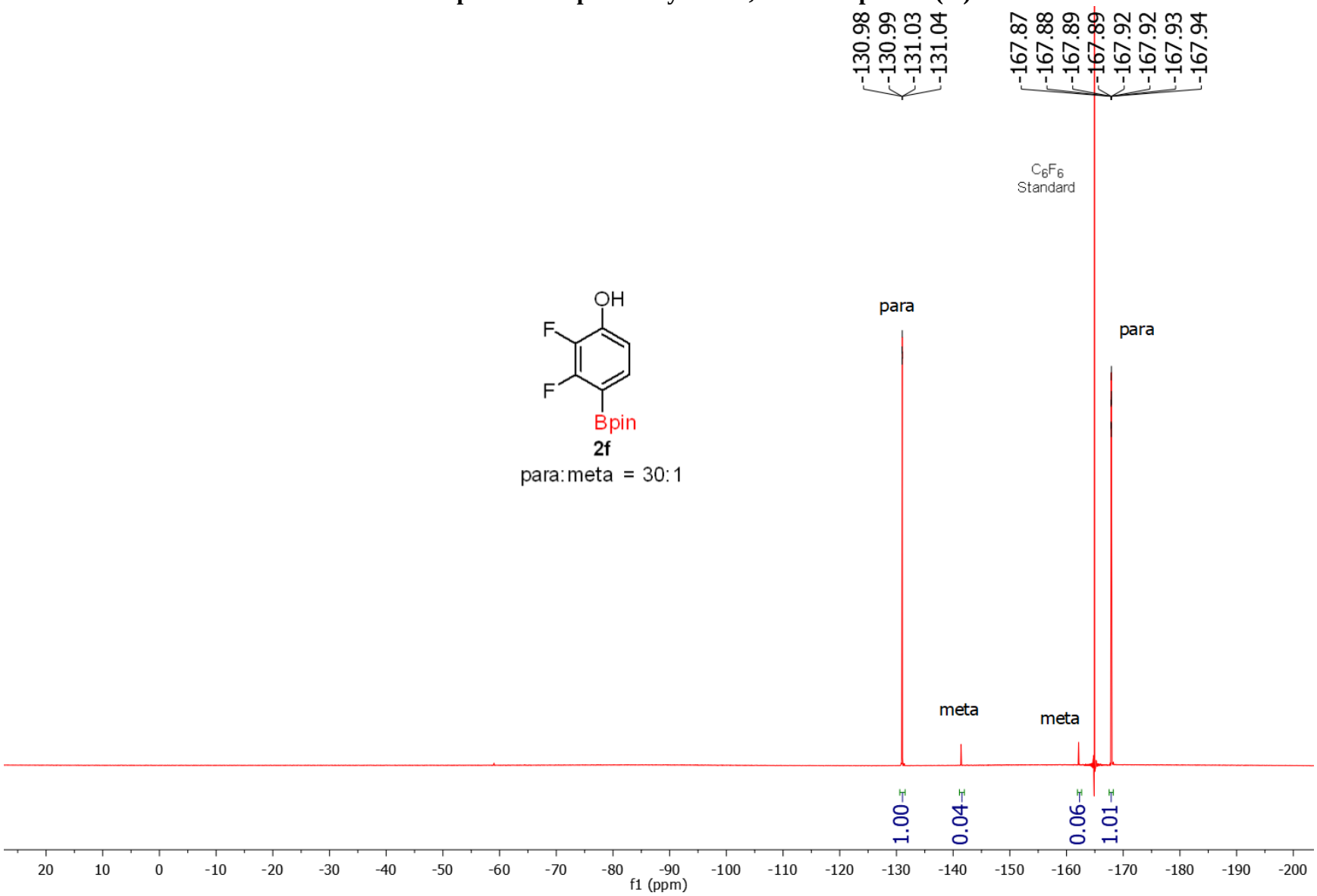
^{19}F NMR spectrum of para borylated 2,3-difluorophenol (2f)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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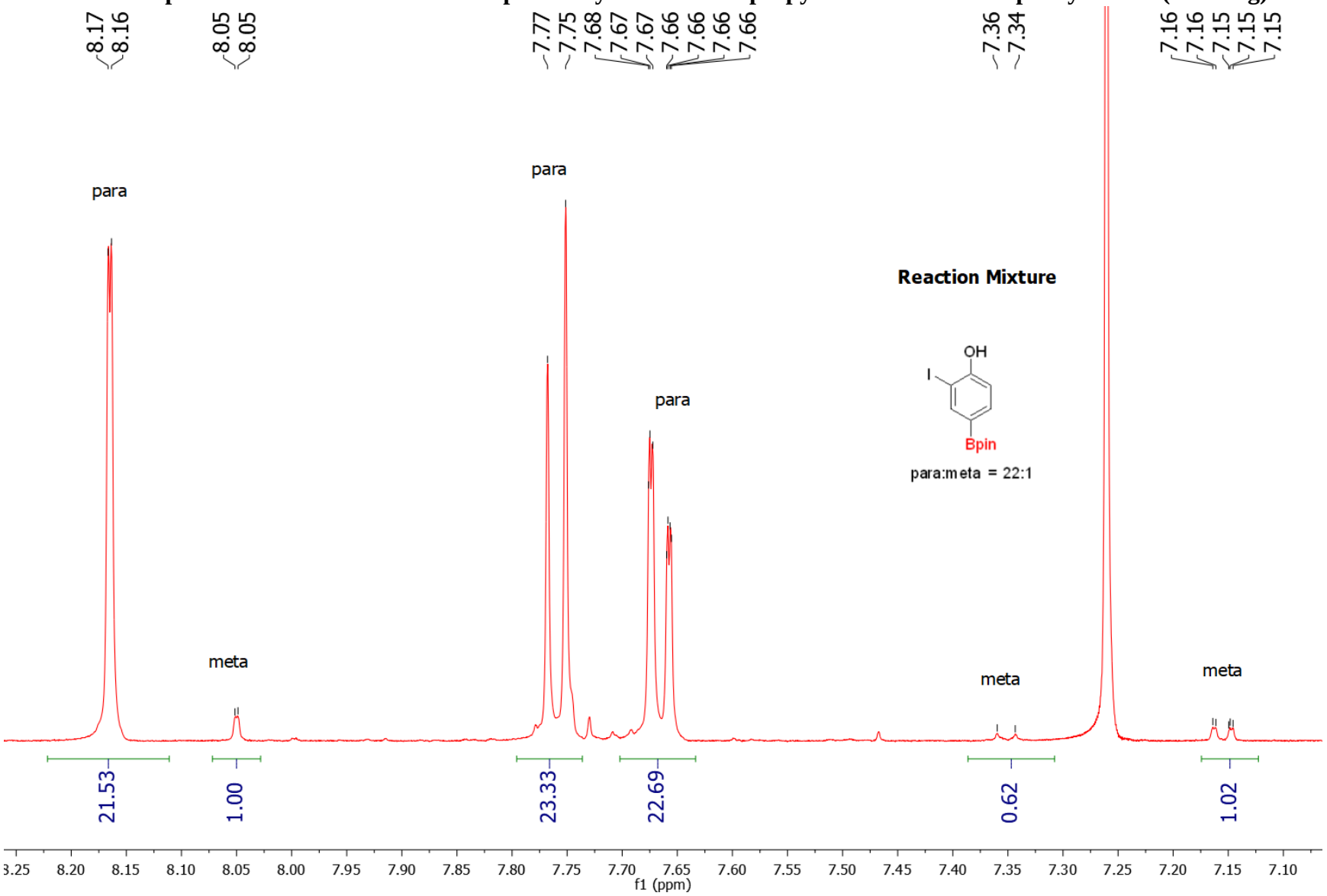
^{1}H NMR spectrum of reaction mixture for para borylation of tetrapropyl ammonium 2-iodophenylsulfate (crude 2g)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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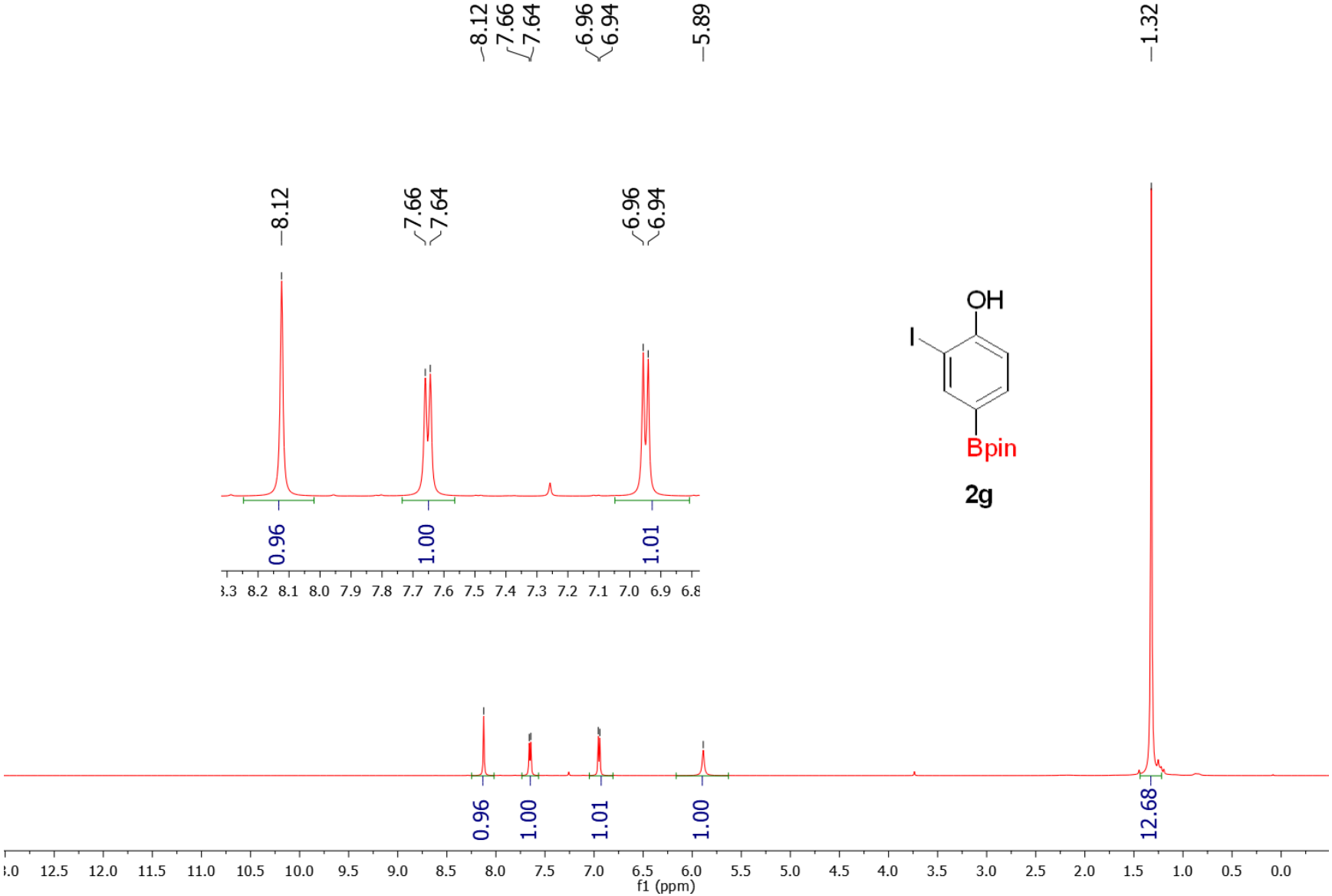
^{1}H NMR spectrum of para borylated 2-iodophenol (2g)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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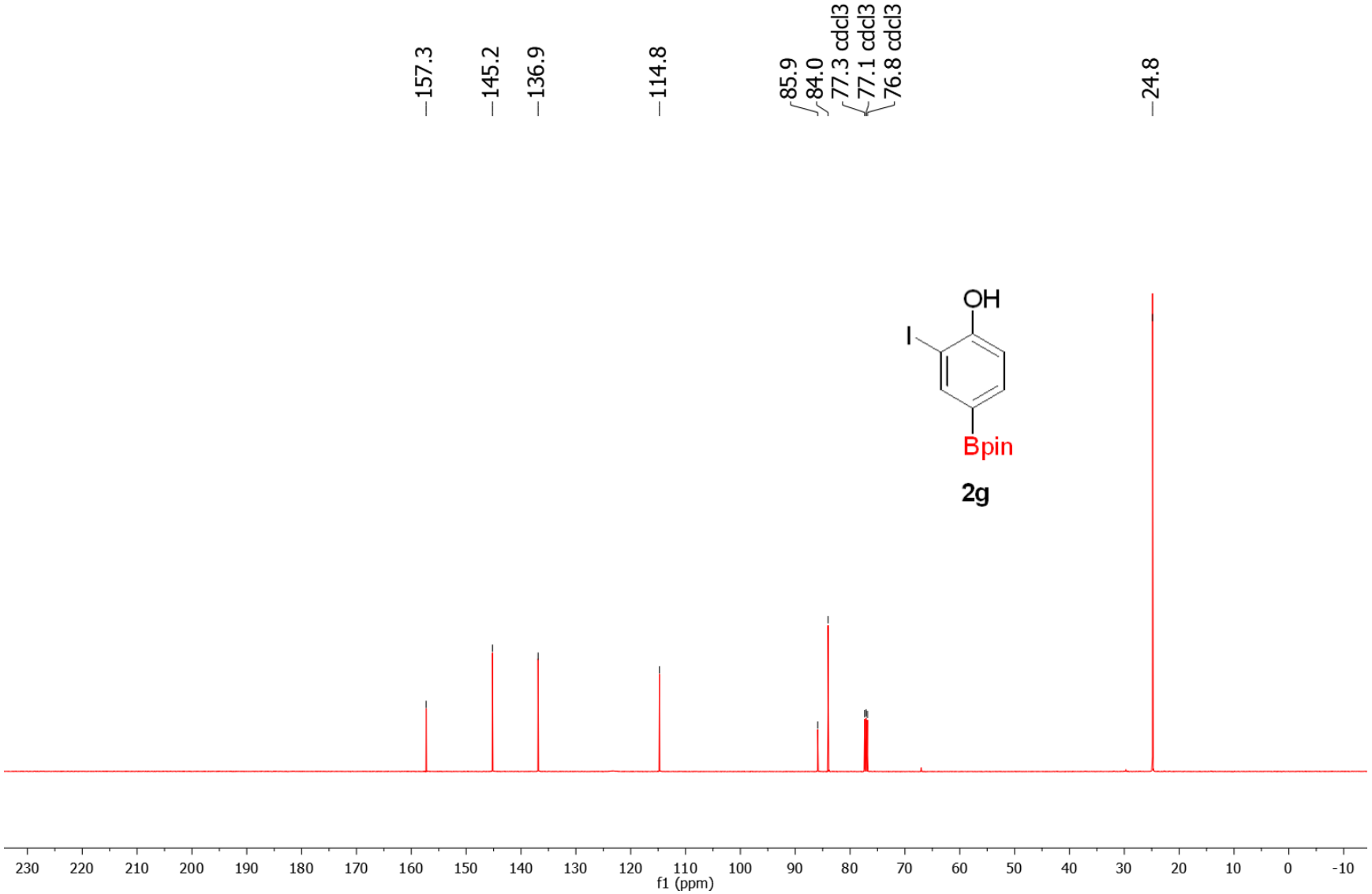
^{13}C NMR spectrum of para borylated 2-iodophenol (2g)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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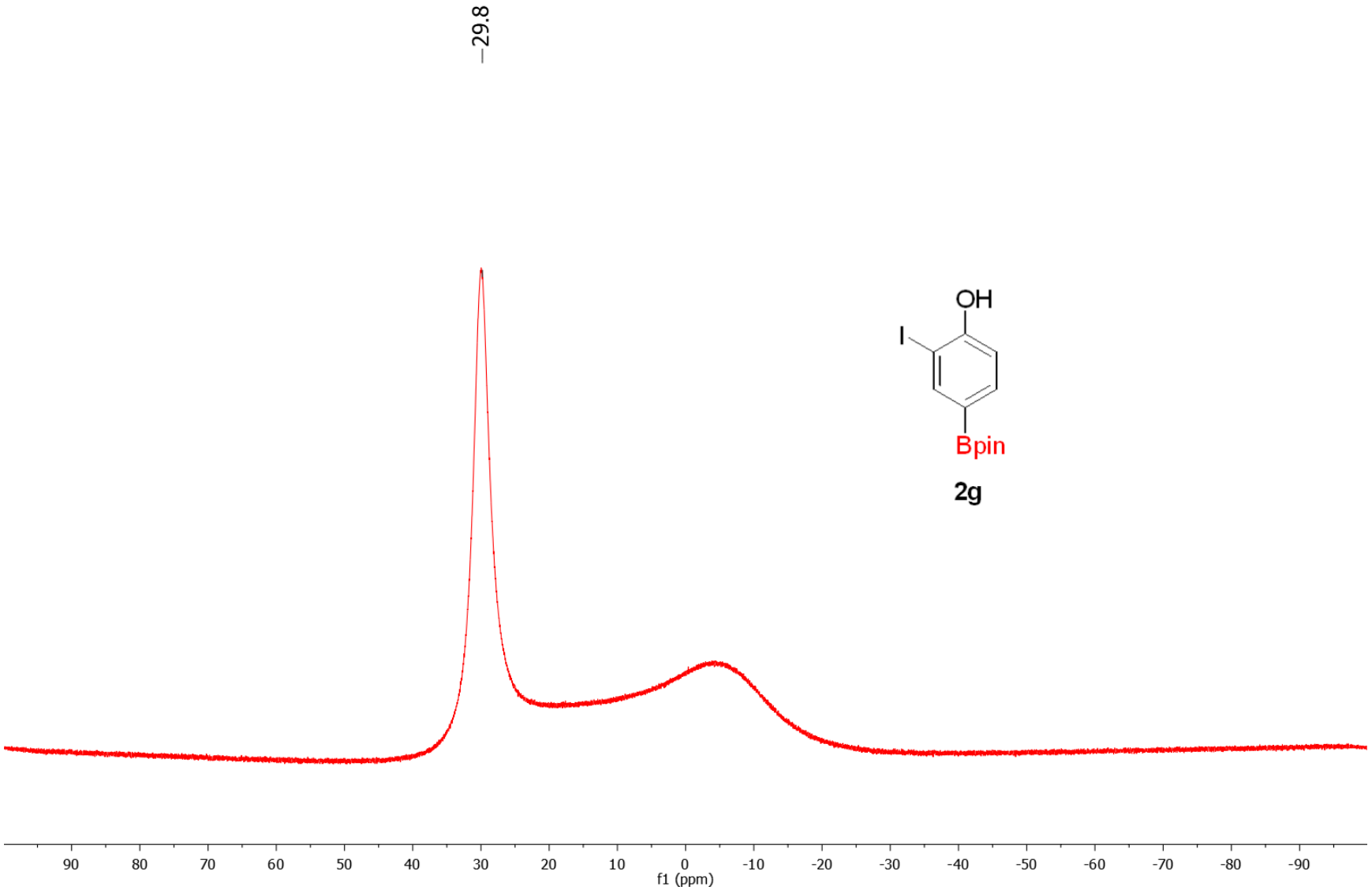
^{11}B NMR spectrum of para borylated 2-iodophenol (2g)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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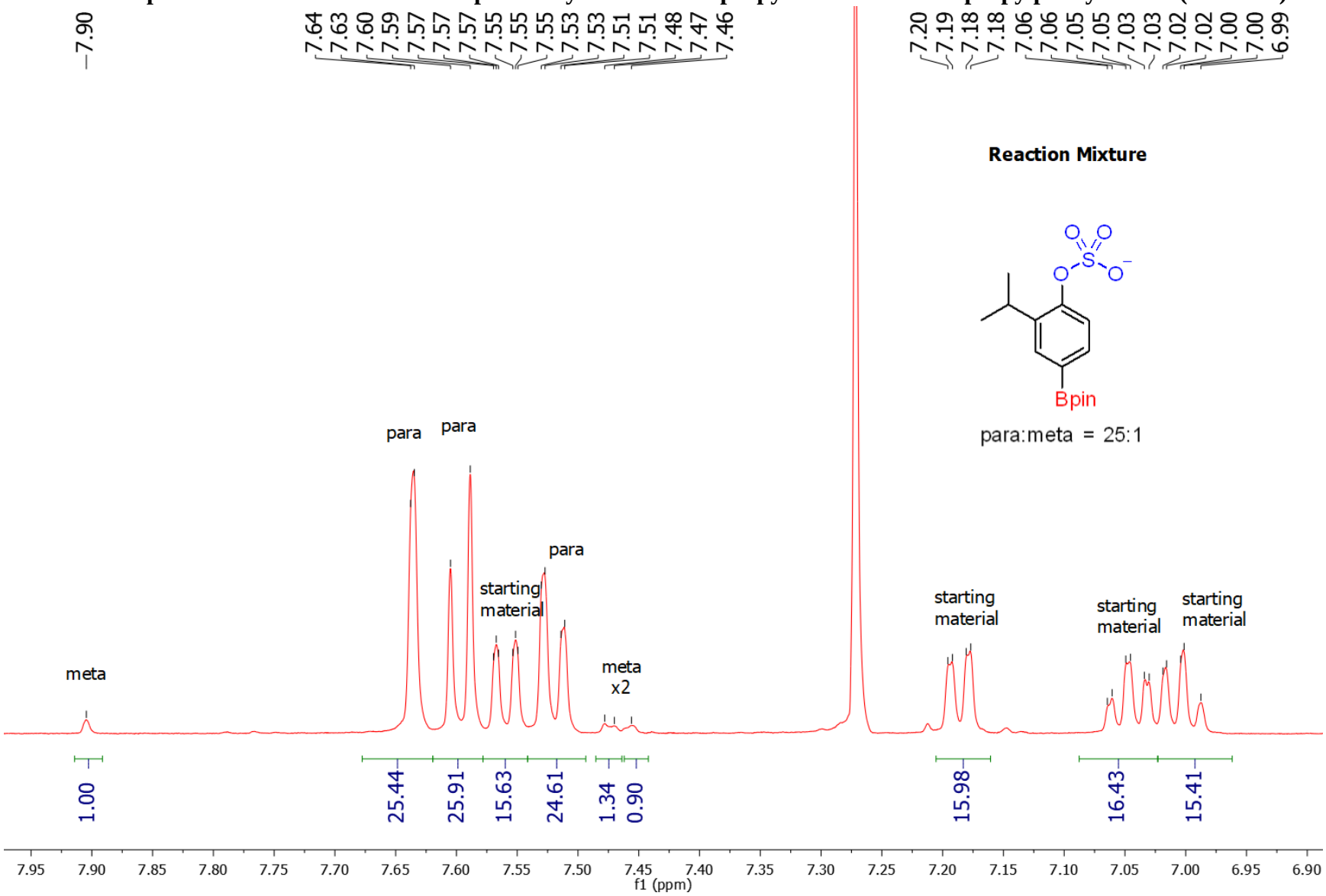
^{1}H NMR spectrum of reaction mixture of para borylation of tetrapropylammonium 2-isopropylphenylsulfate (crude 2h)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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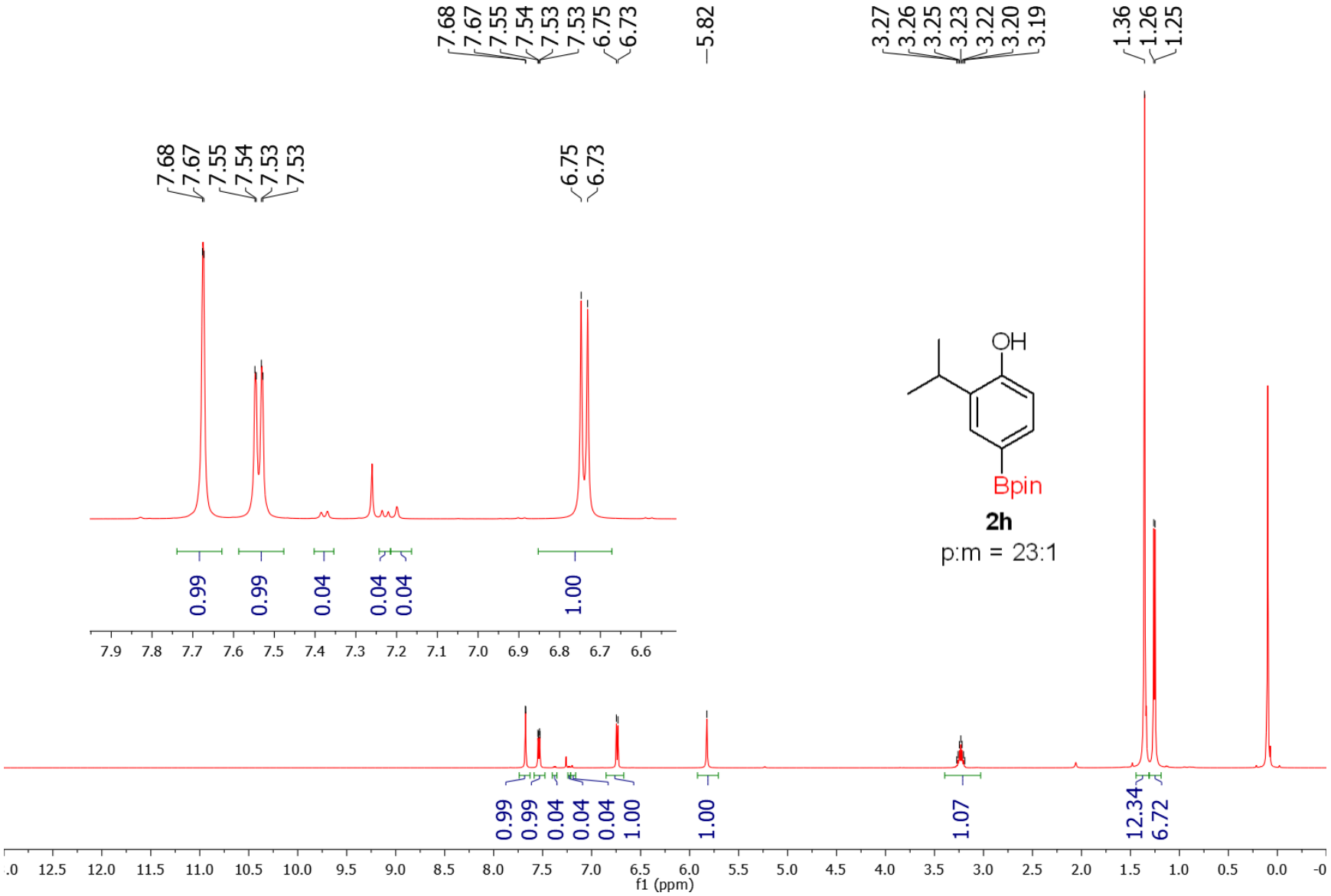
^{1}H NMR spectrum of para borylated 2-isopropylphenol (2h)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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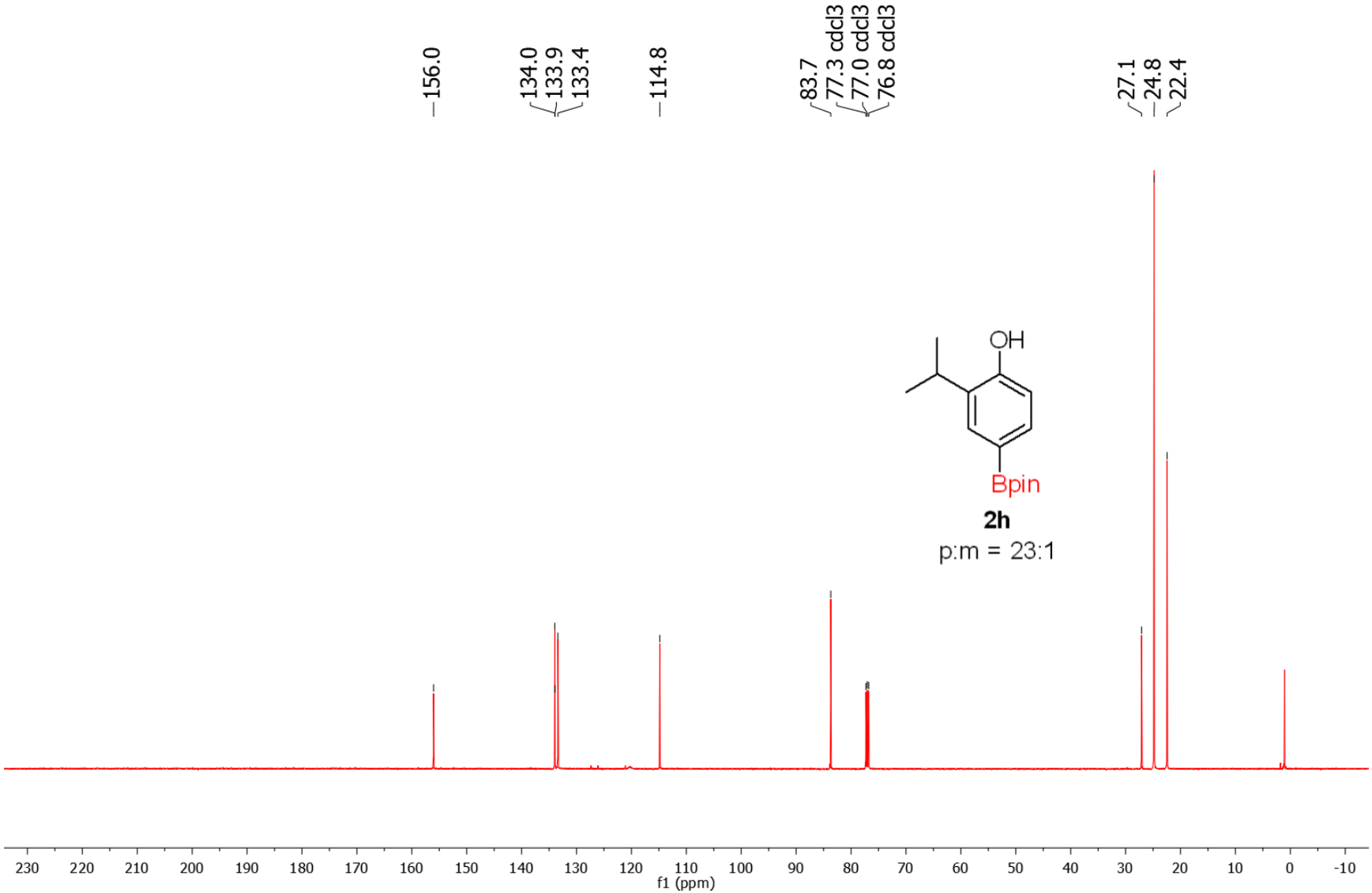
^{13}C NMR spectrum of para borylated 2-isopropylphenol (2h)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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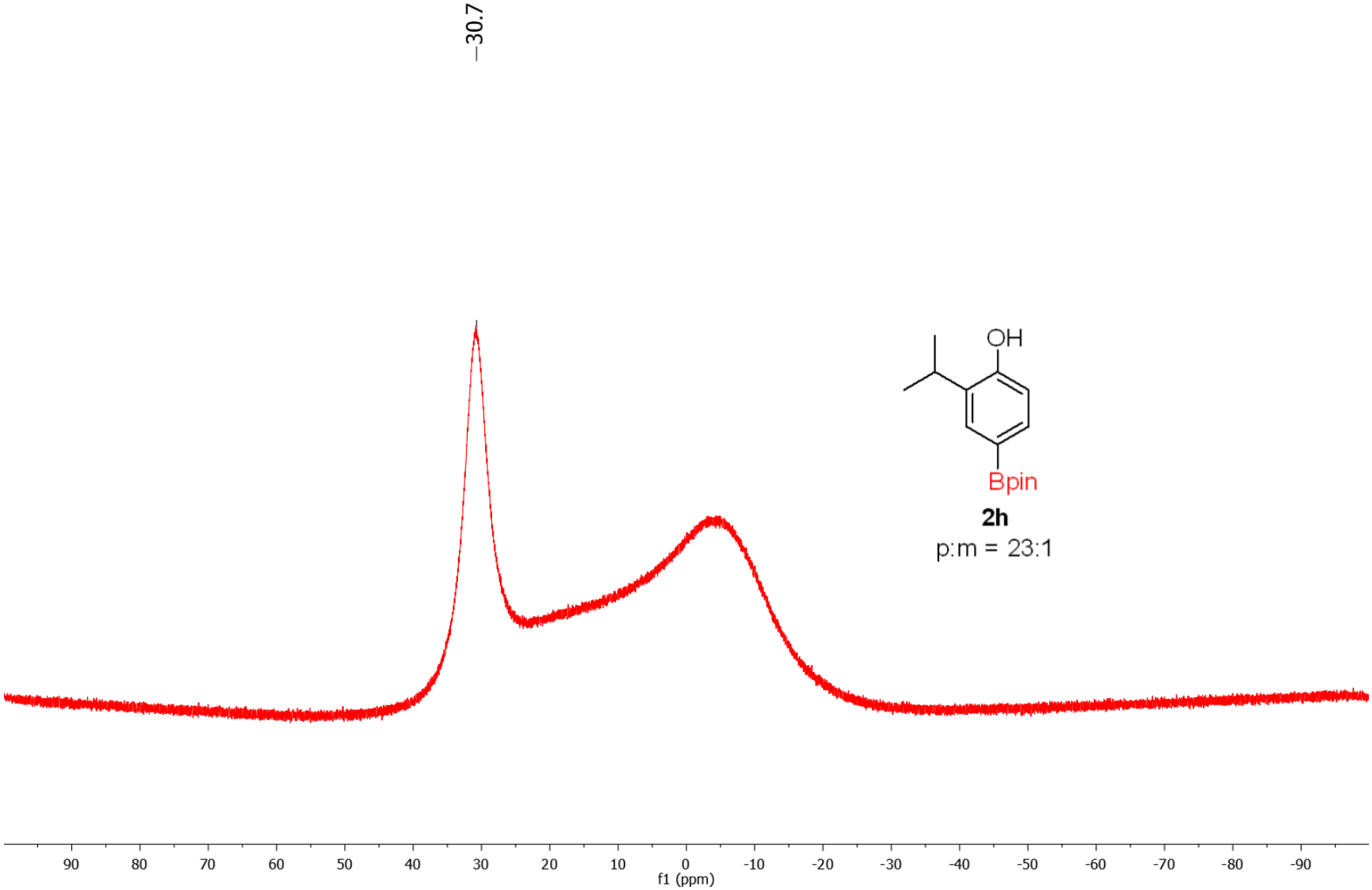
^{11}B NMR spectrum of para borylated 2-isopropylphenol (2h)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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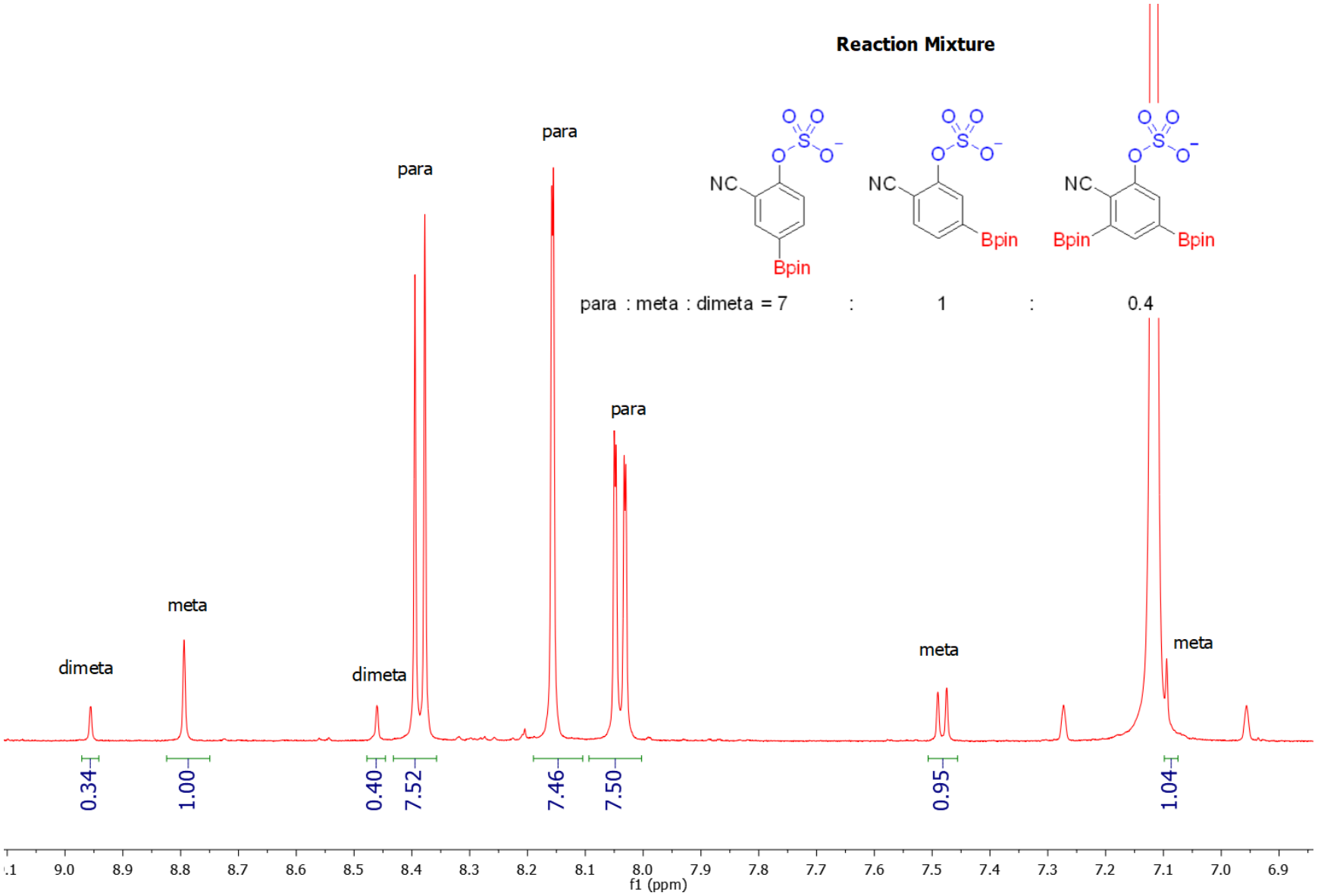
^{1}H NMR spectrum of reaction mixture of para borylation of tetrapropylammonium 2-cyanophenylsulfate (crude 2i)



Conditions: 25 ºC, 500 MHz, C_6D_6

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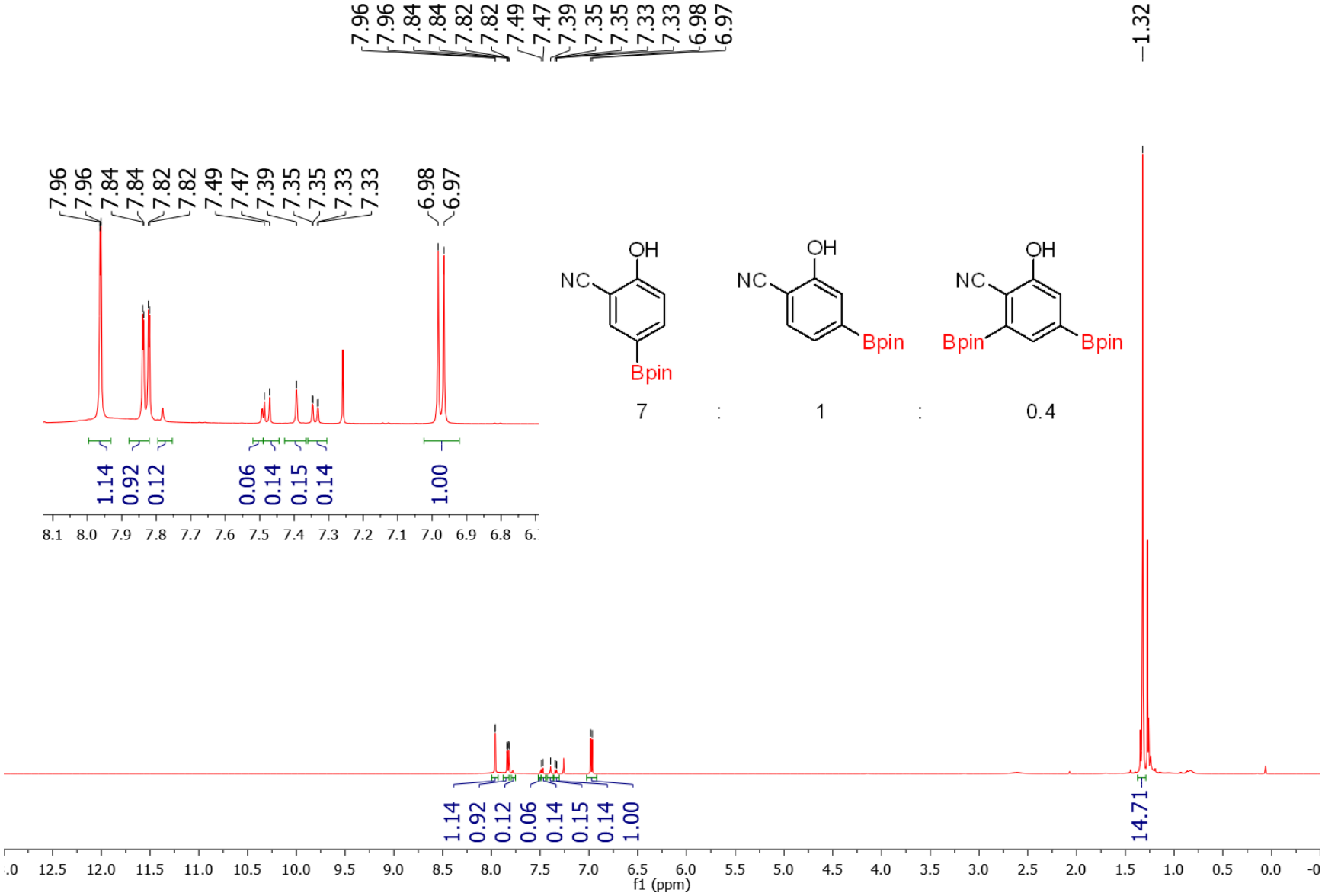
^{1}H NMR spectrum of mixture of borylated 2-cyanolphenol regioisomers (2i)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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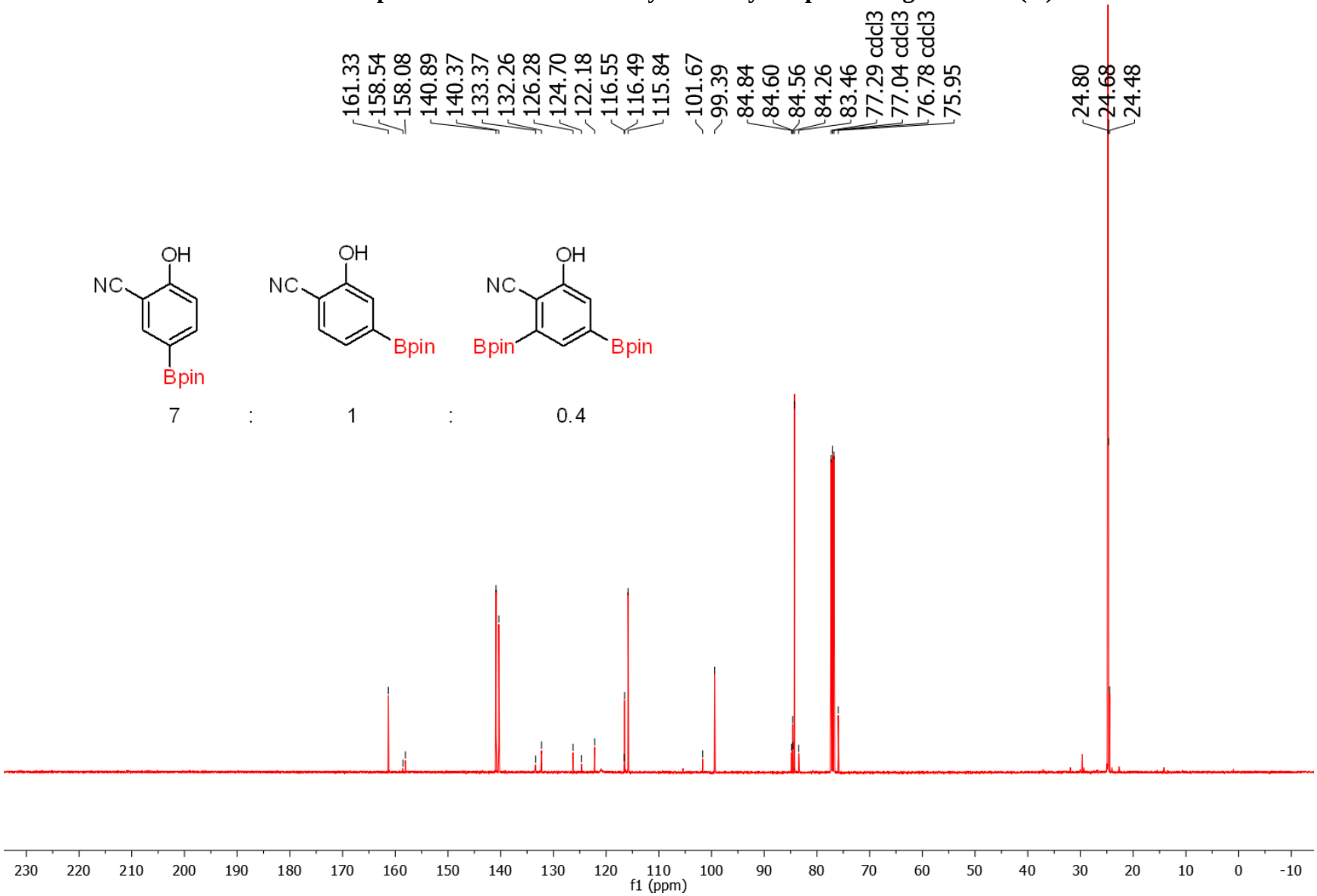
^{13}C NMR spectrum of mixture of borylated 2-cyanolphenol regioisomers (2i)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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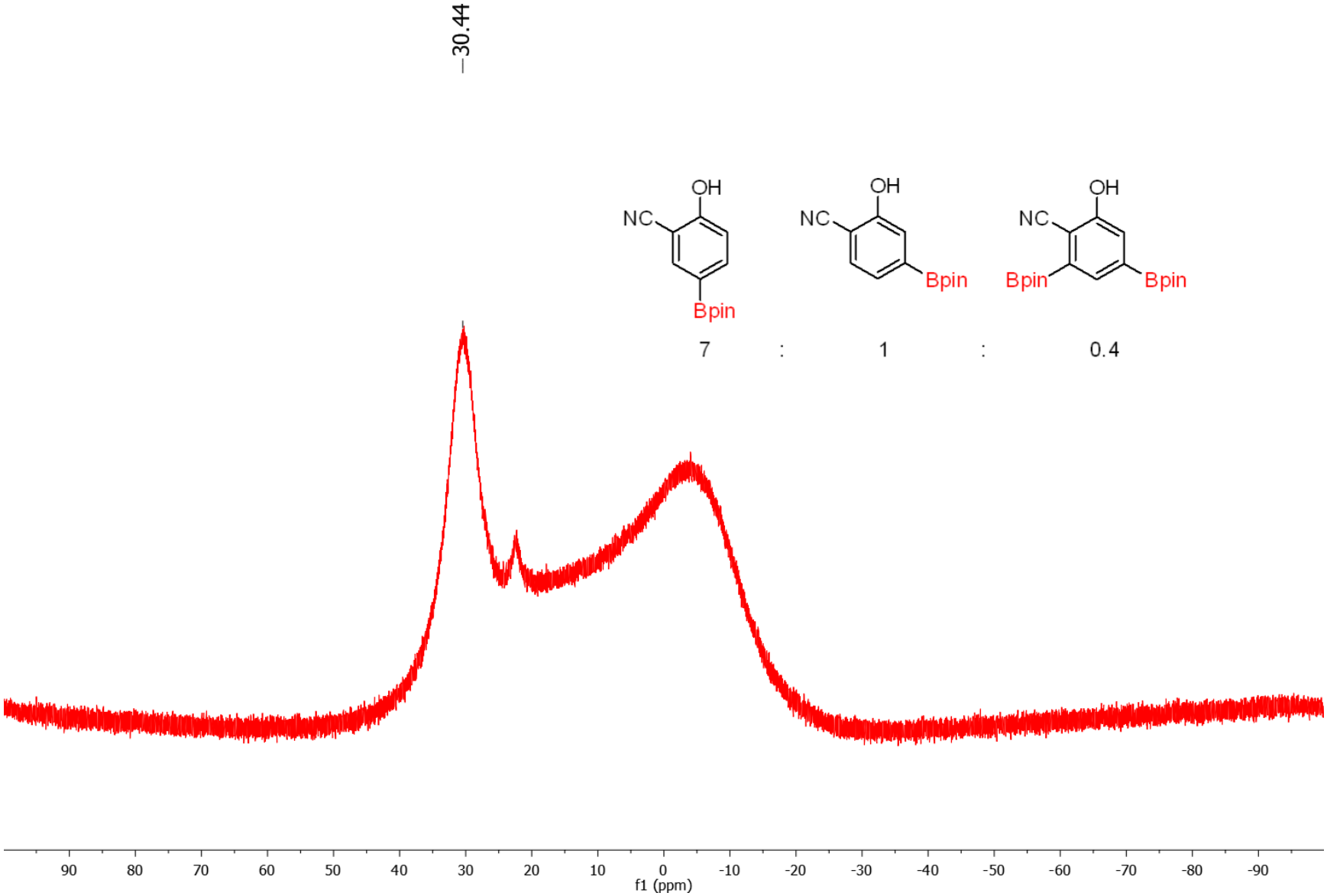
^{11}B NMR spectrum of borylated mixture 2-cyanophenol regioisomers (2i)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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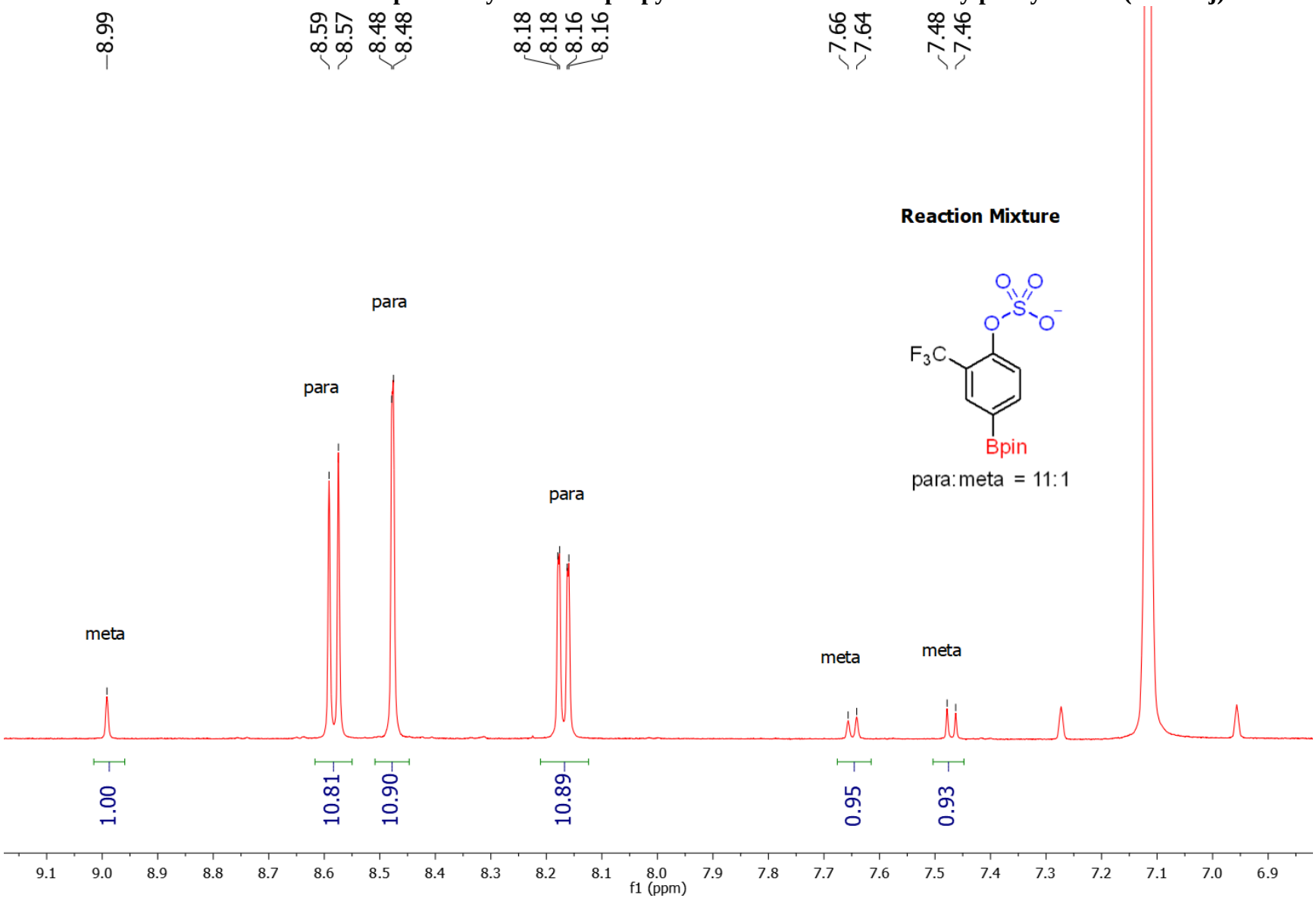
^{1}H NMR reaction mixture of para-borylated tetrapropylammonium 2-trifluoromethylphenylsulfate (crude 2j)



Conditions: 25 ºC, 500 MHz, C_6D_6

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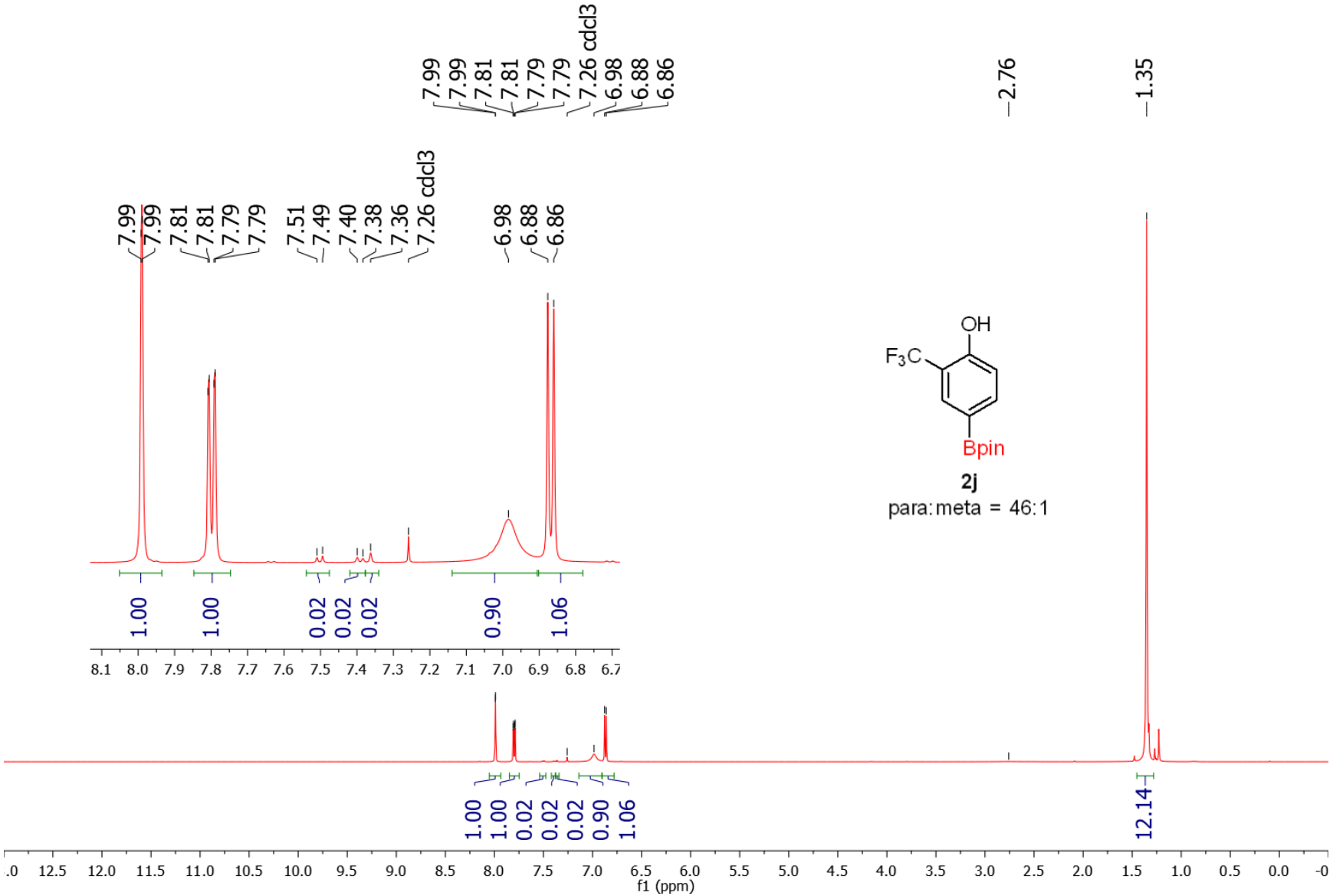
^{1}H NMR spectrum of para borylated 2-trifluoromethylphenol (2j)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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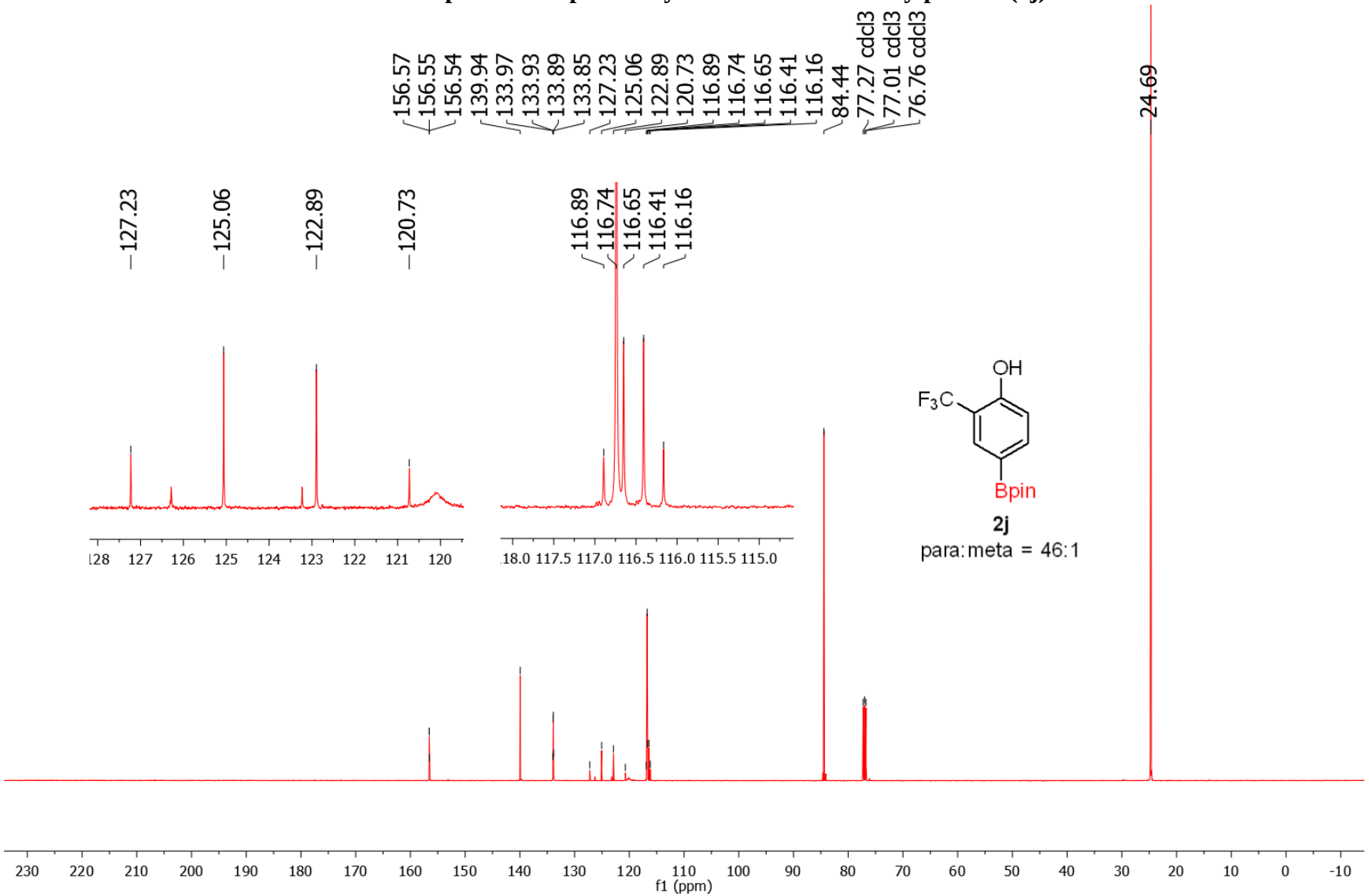
^{13}C NMR spectrum of para borylated 2-trifluoromethylphenol (2j)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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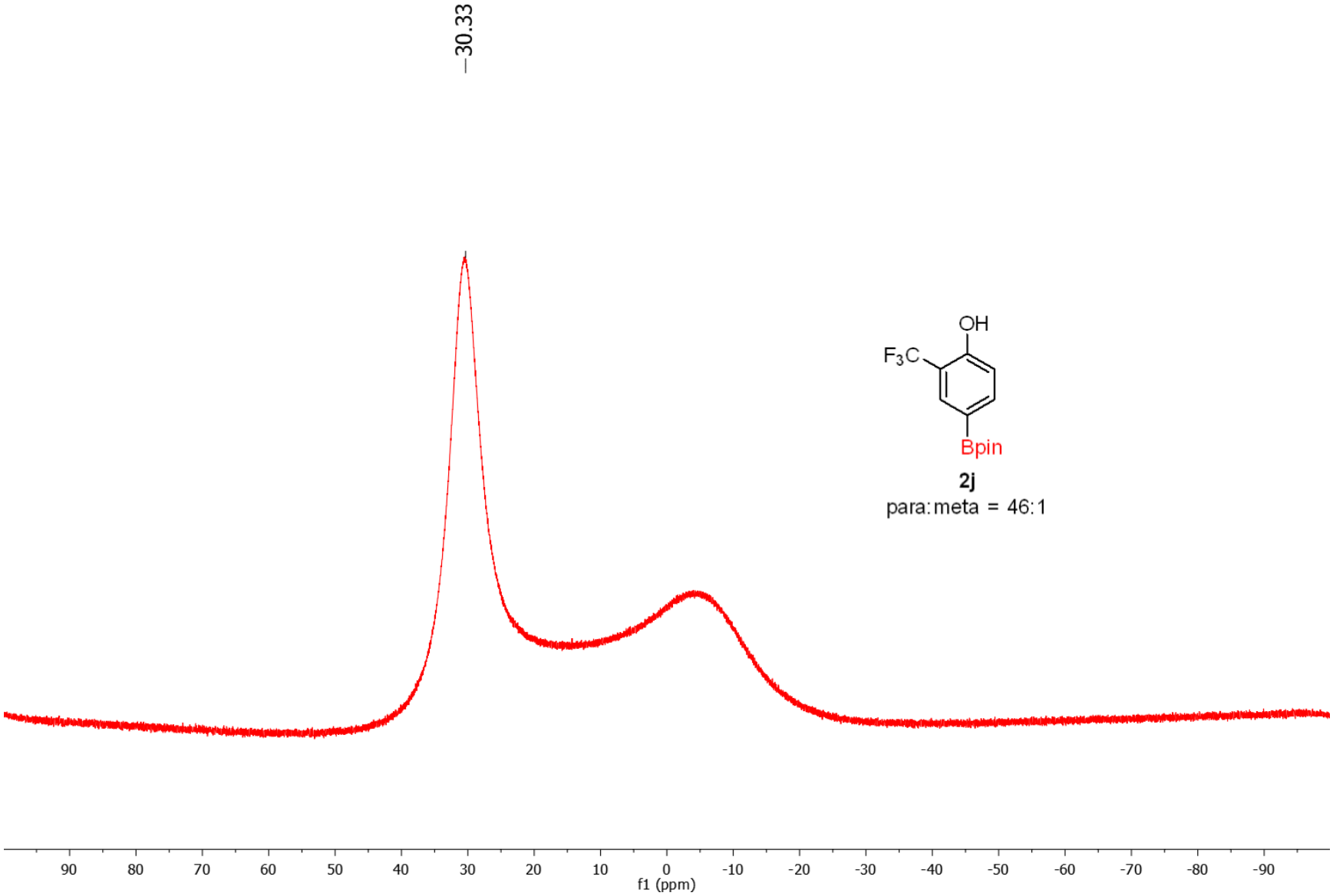
^{11}B NMR of para borylated 2-trifluoromethylphenol (2j)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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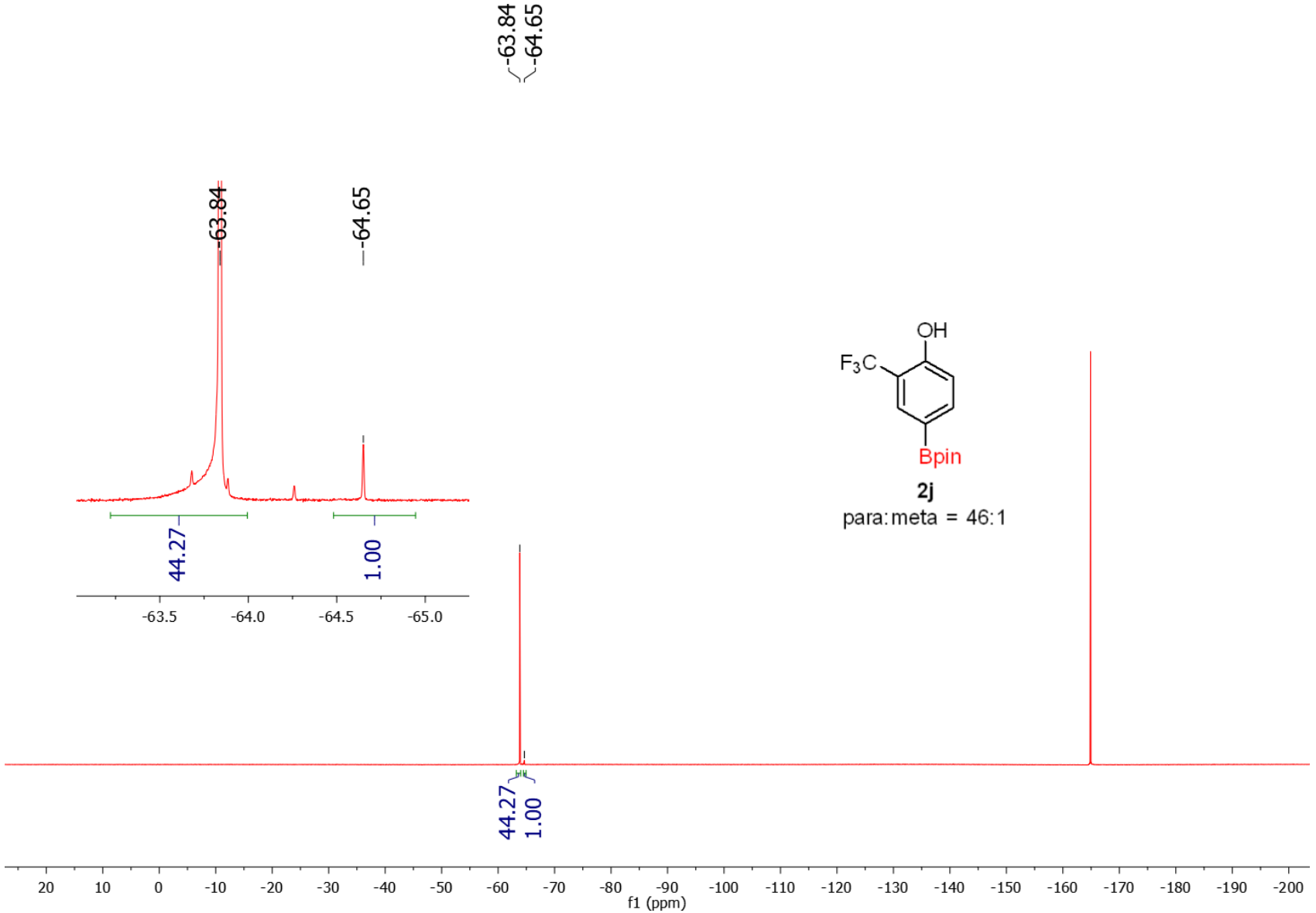
^{19}F NMR spectrum of 2-trifluoromethylphenol (2j)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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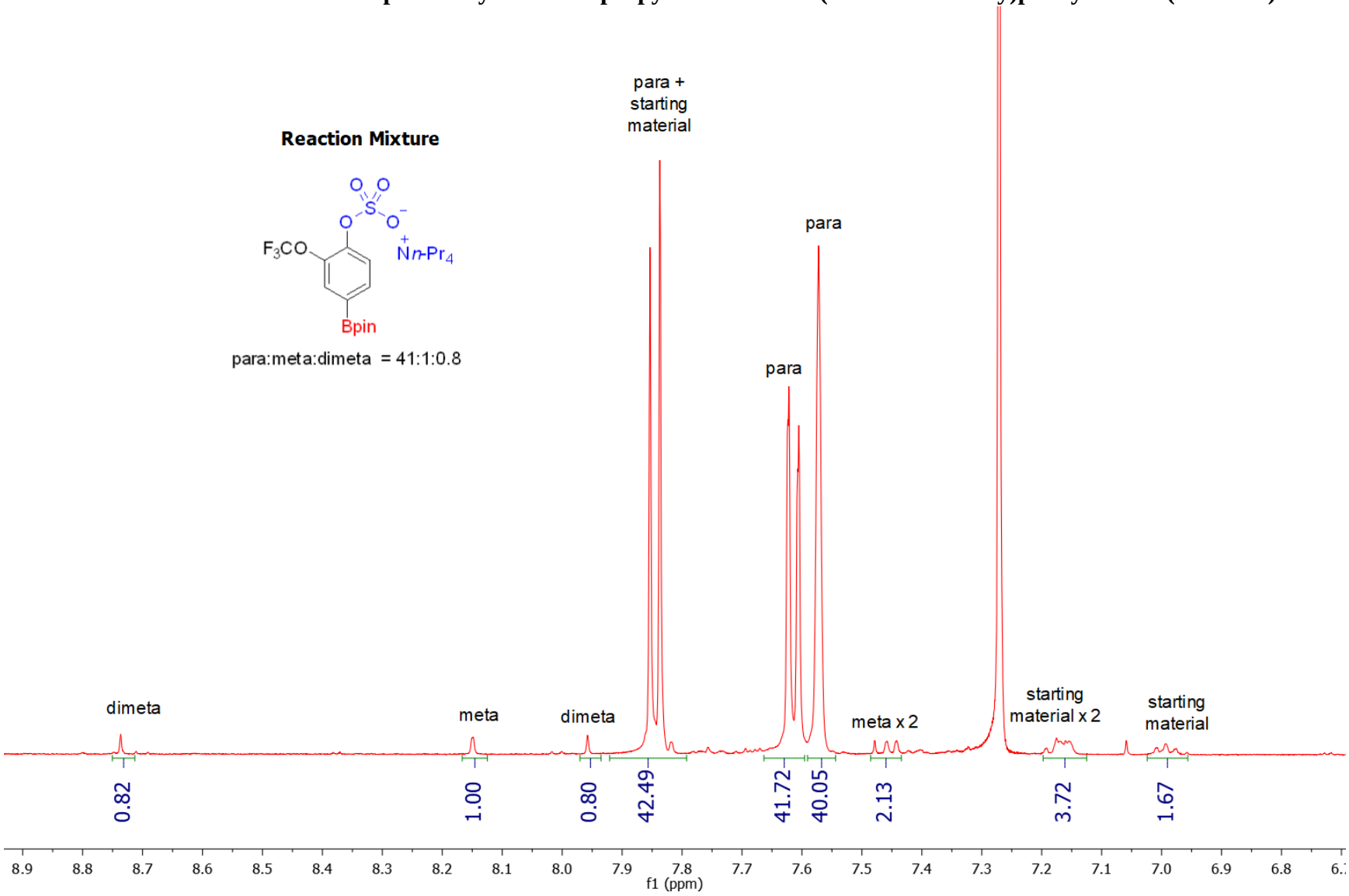
^{1}H NMR reaction mixture of para-borylated tetrapropylammonium 2-(trifluoromethoxy)phenylsulfate (crude 2k)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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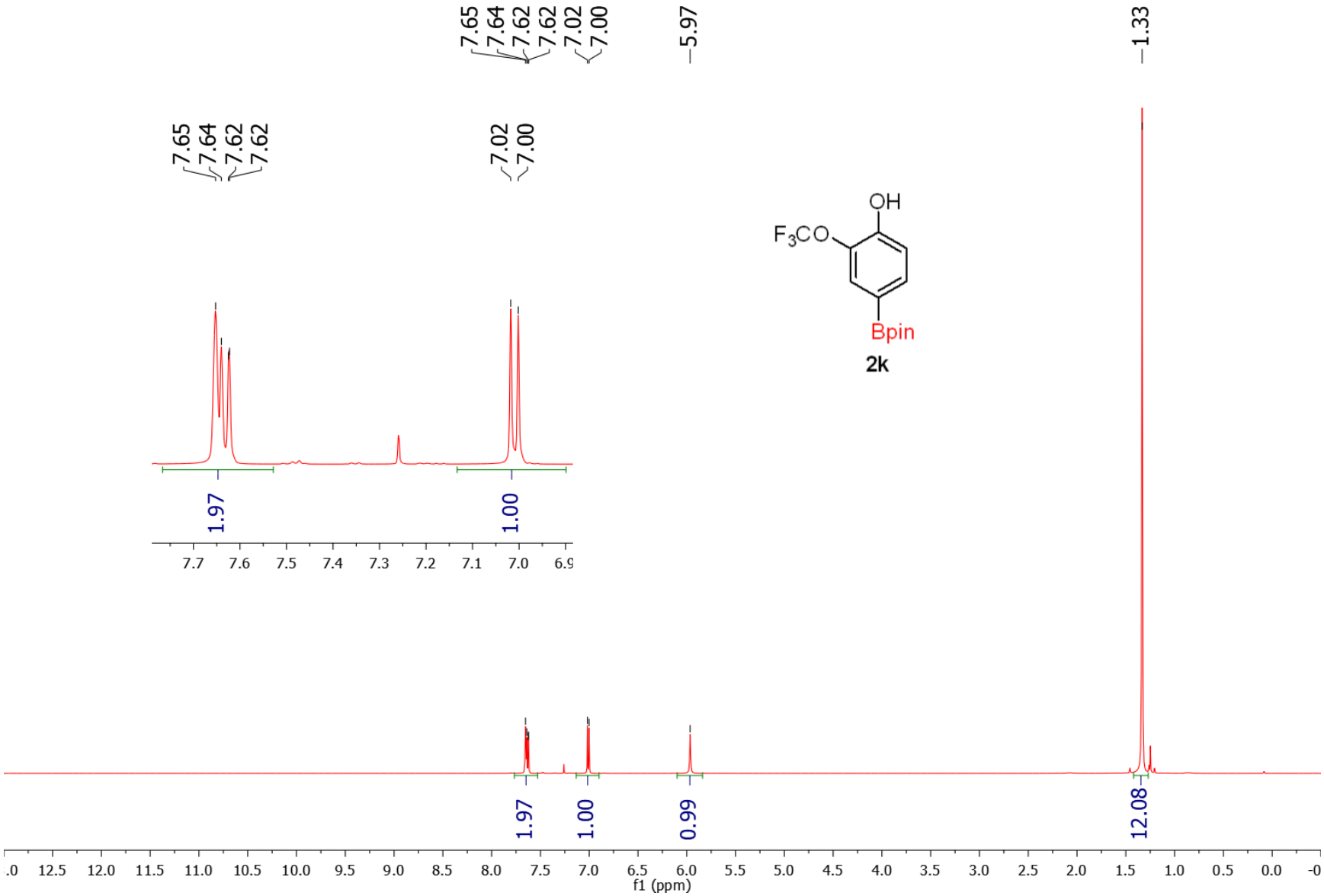
^{1}H NMR spectrum of para borylated 2(trifluoromethoxy)phenol (2k)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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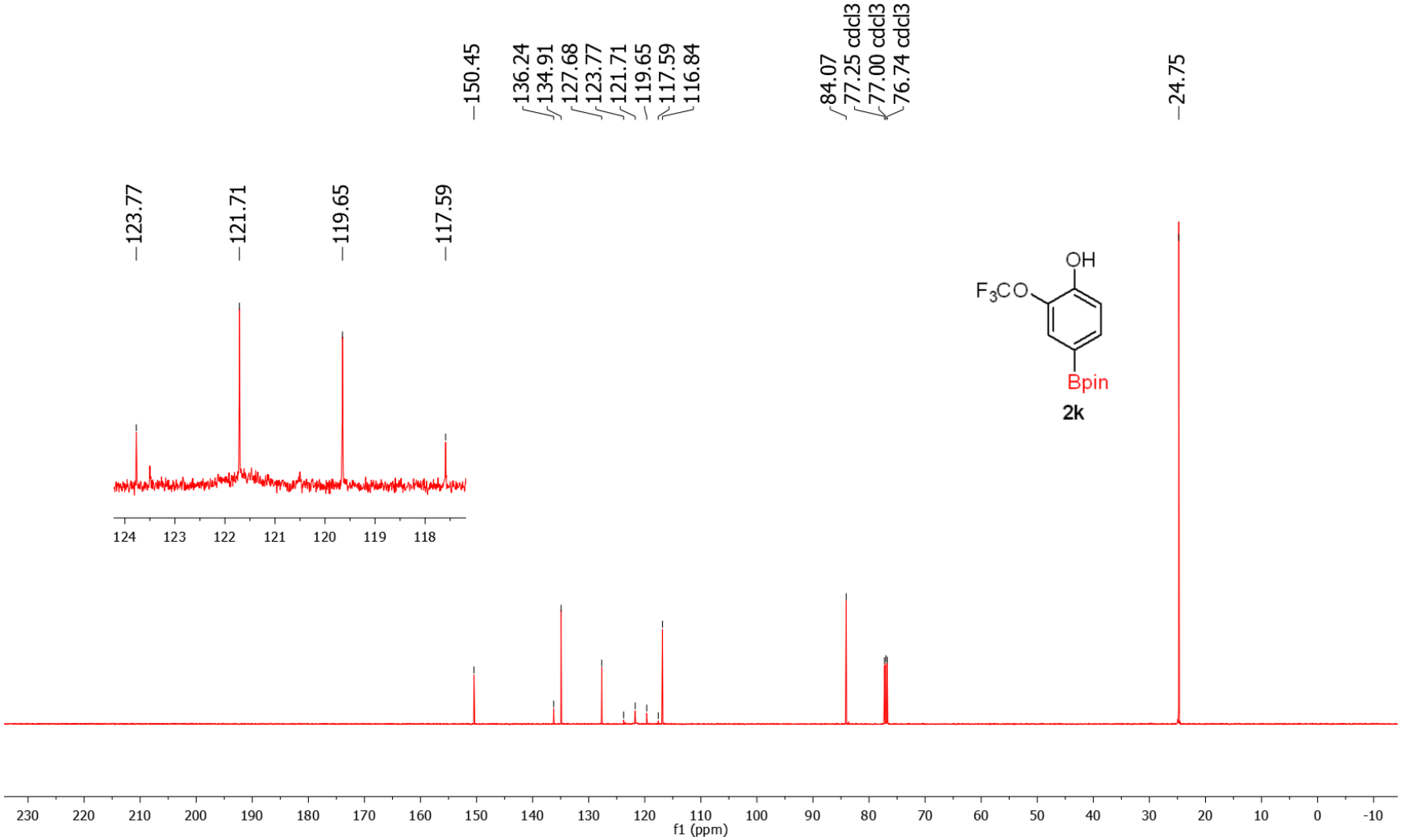
^{13}C NMR spectrum of para borylated 2-(trifluoromethoxy)phenol (2k)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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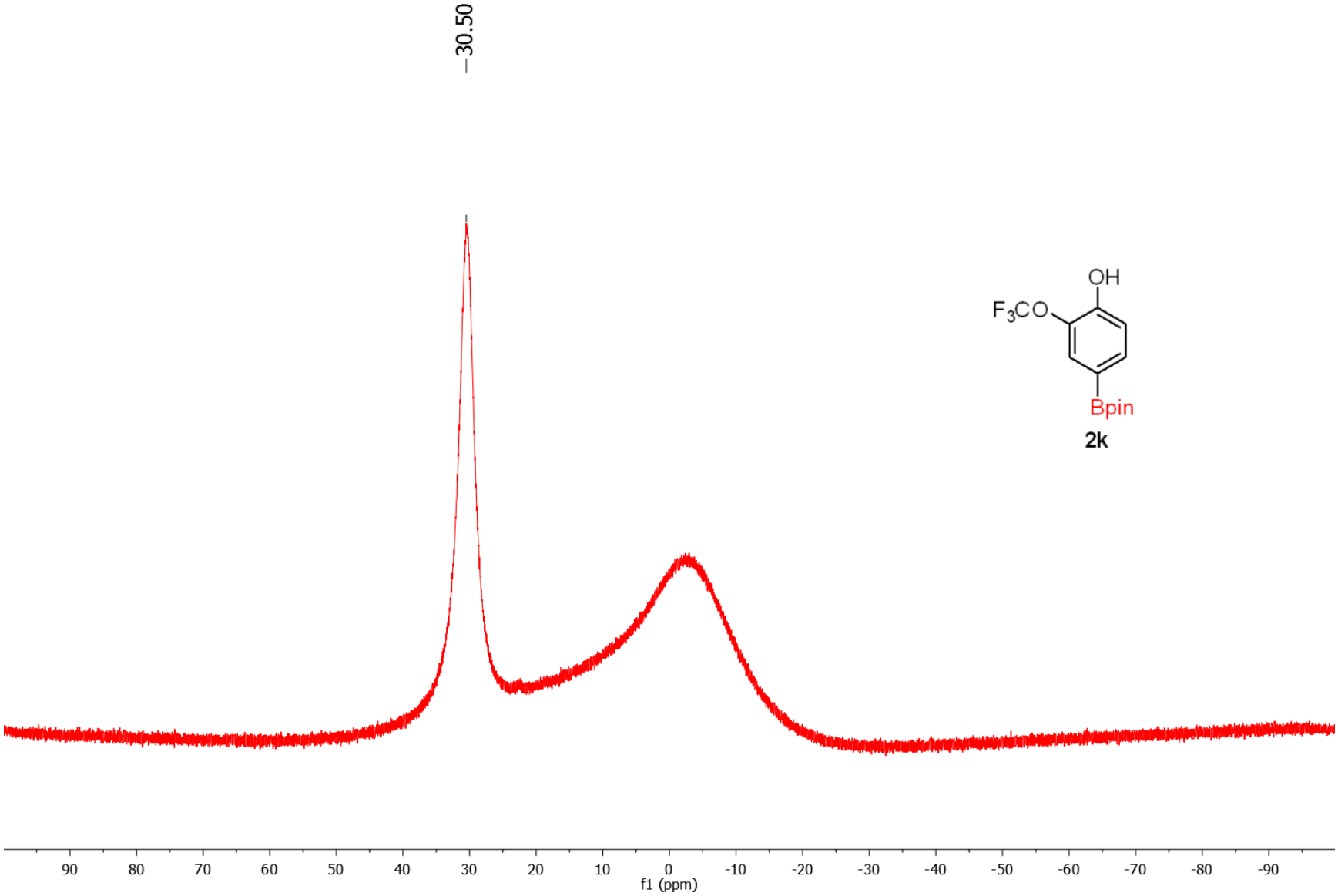
^{11}B NMR spectrum of para borylated 2-(trifluoromethoxy)phenol (2k)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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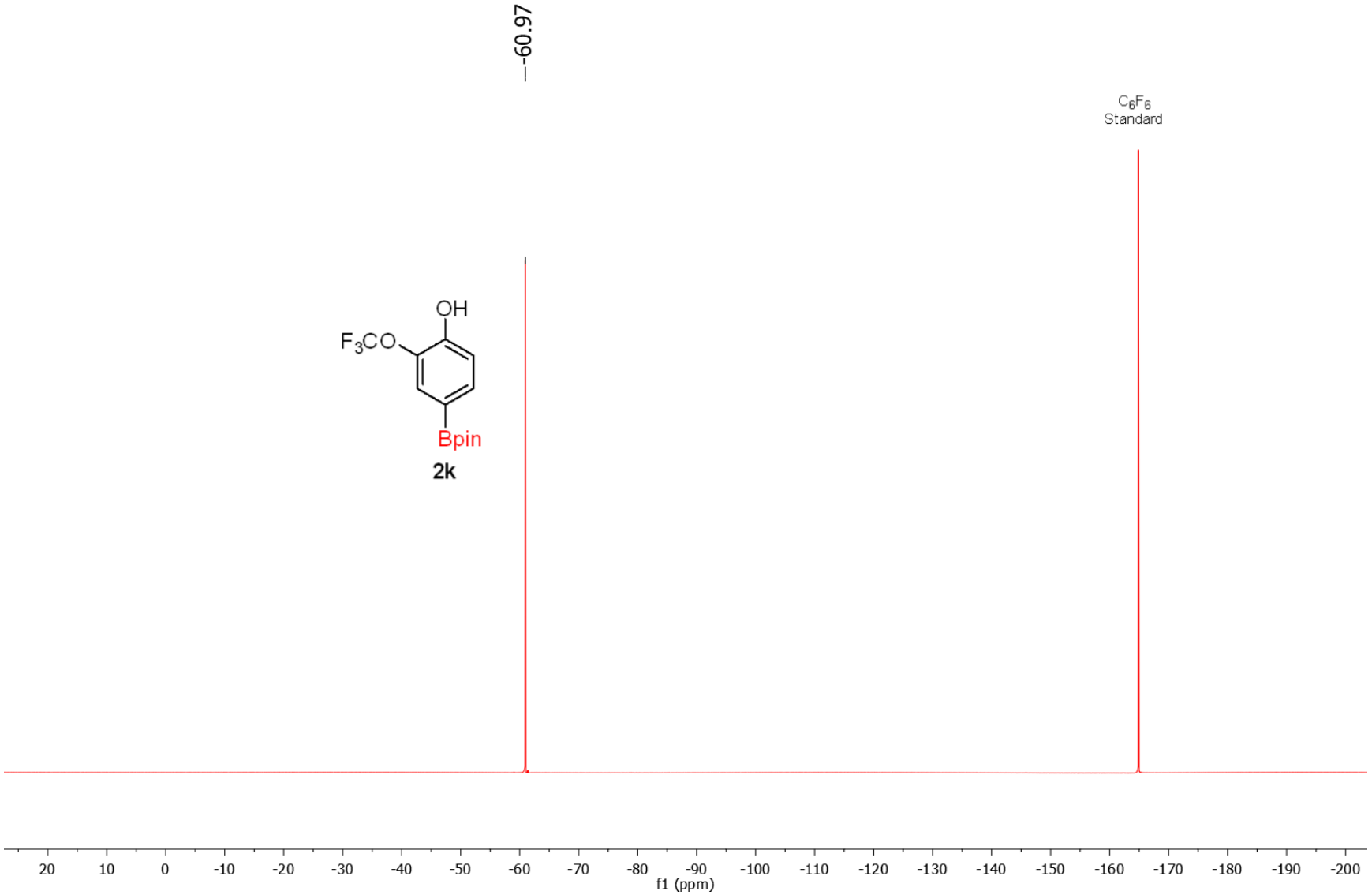
^{19}F NMR spectrum of para borylated 2-(trifluoromethoxy)phenol (2k)



Conditions: 25 ºC, 470 MHz, $CDCl_3$

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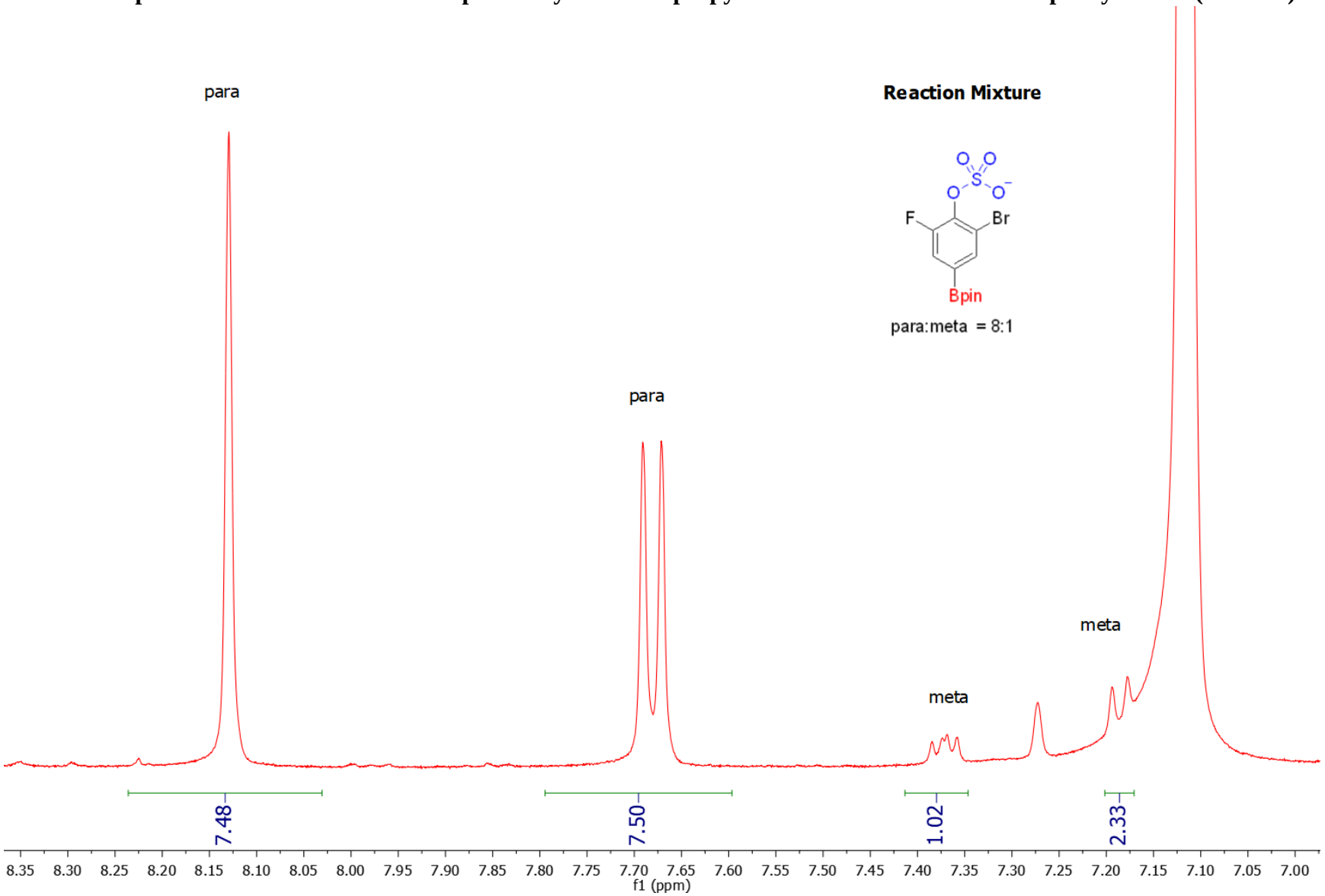
^{1}H NMR spectrum of reaction mixture of para borylated tetrapropylammonium 2-bromo-6-fluorophenylsulfate (crude 2l)



Conditions: 25 ºC, 500 MHz, C_6D_6

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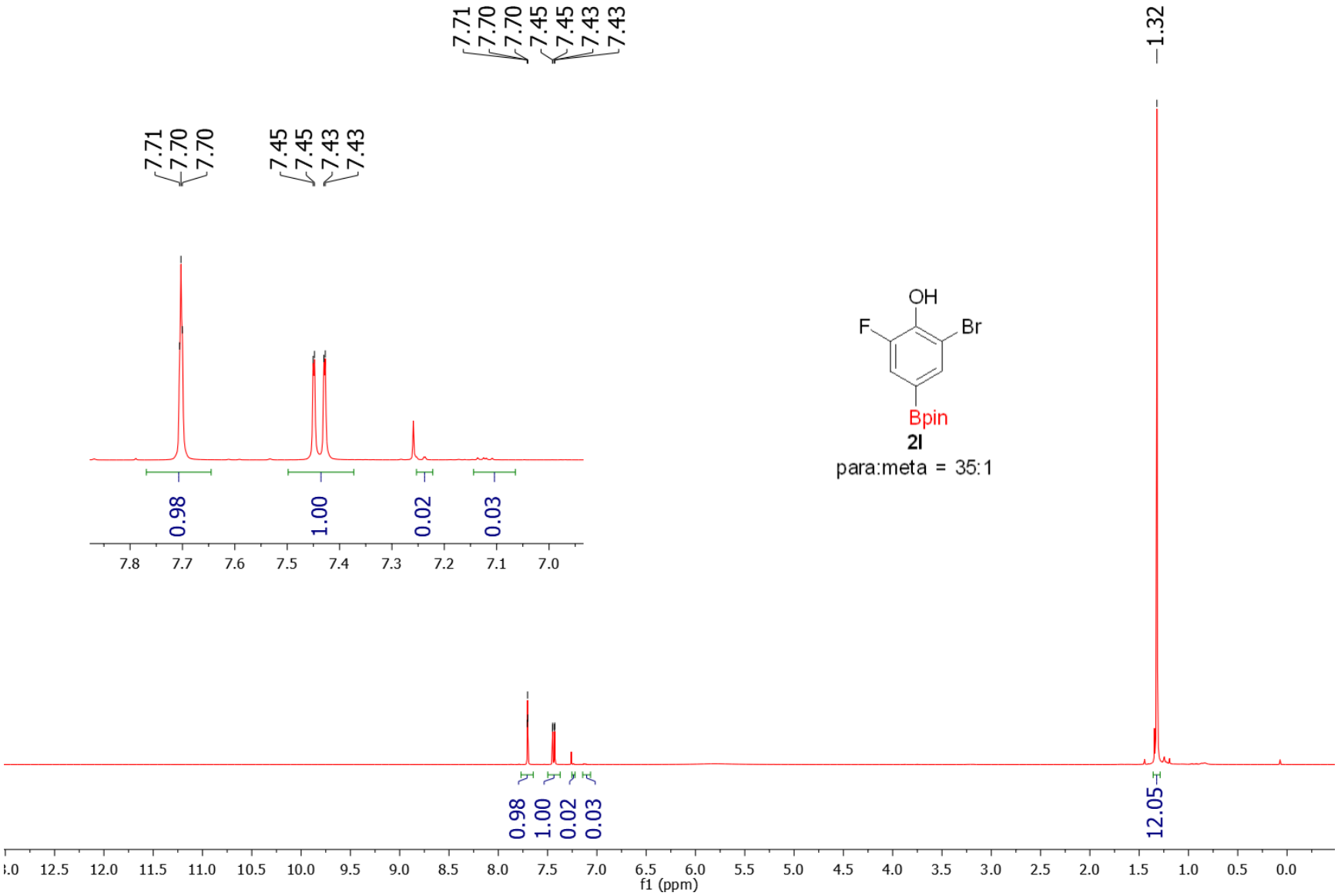
^{1}H NMR spectrum of para borylated 2-bromo-6-fluorophenol (2l)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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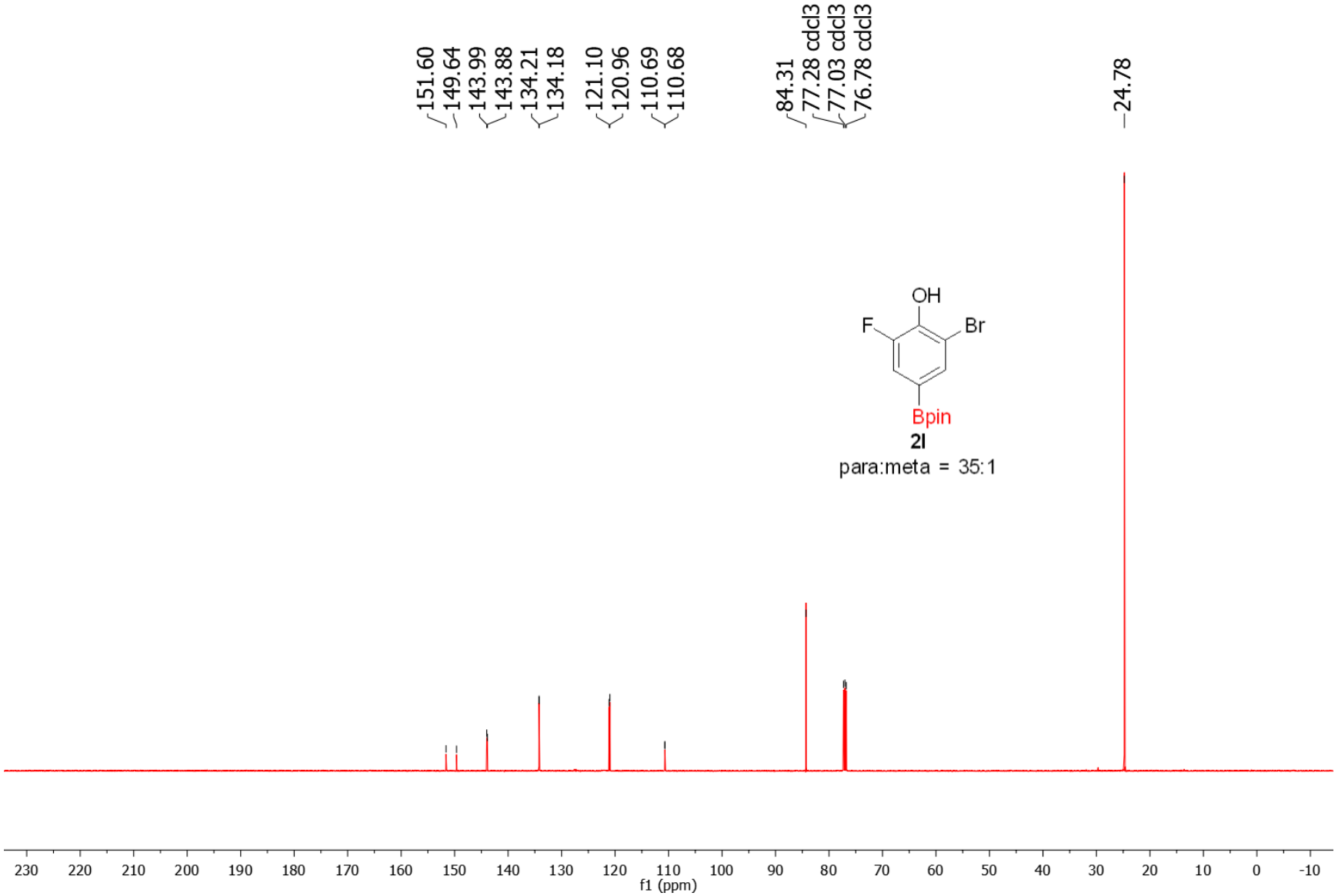
^{13}C NMR spectrum of para borylated 2-bromo-6-fluorophenol (2l)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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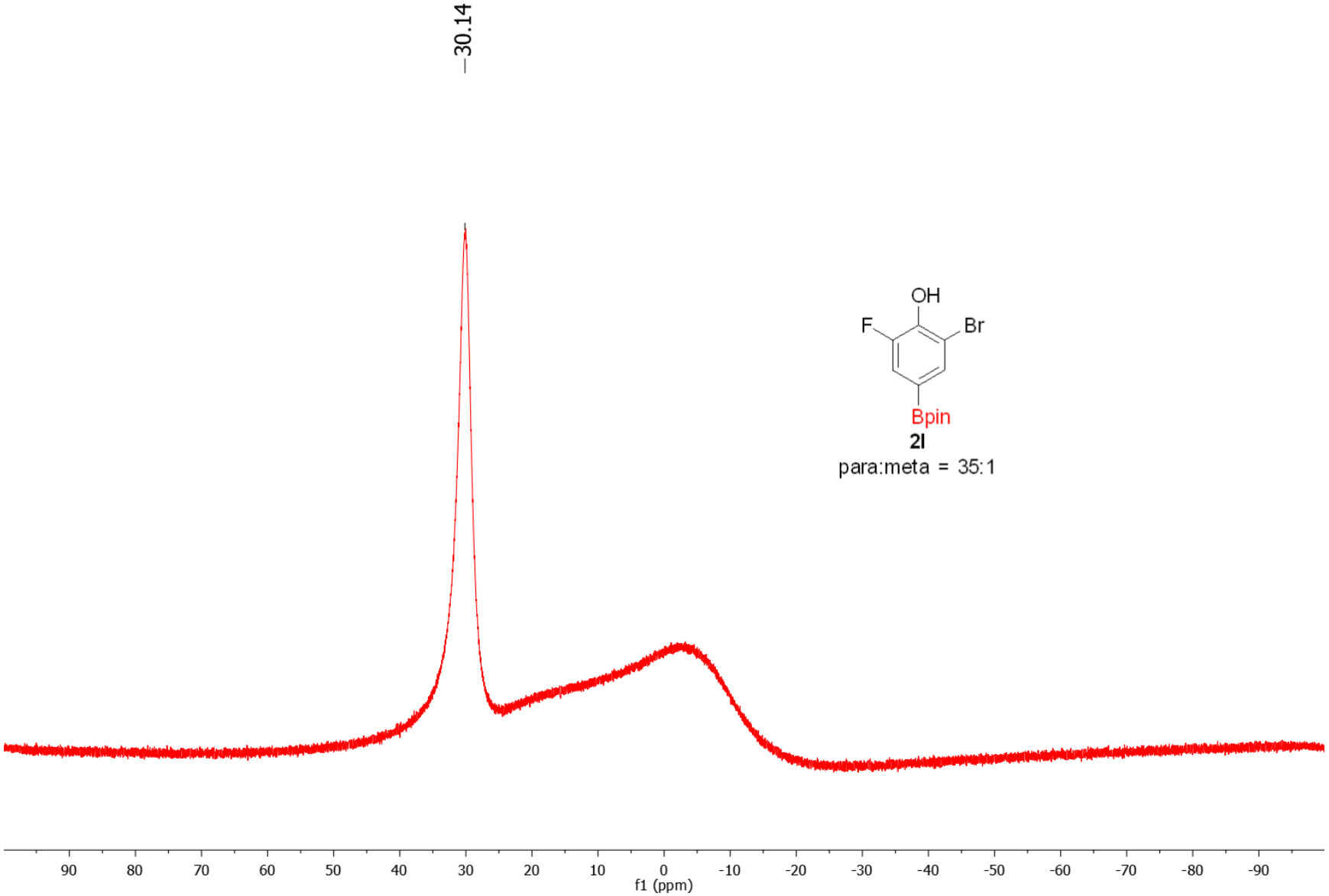
^{11}B NMR spectrum of para borylated 2-bromo-6-fluorophenol (2l)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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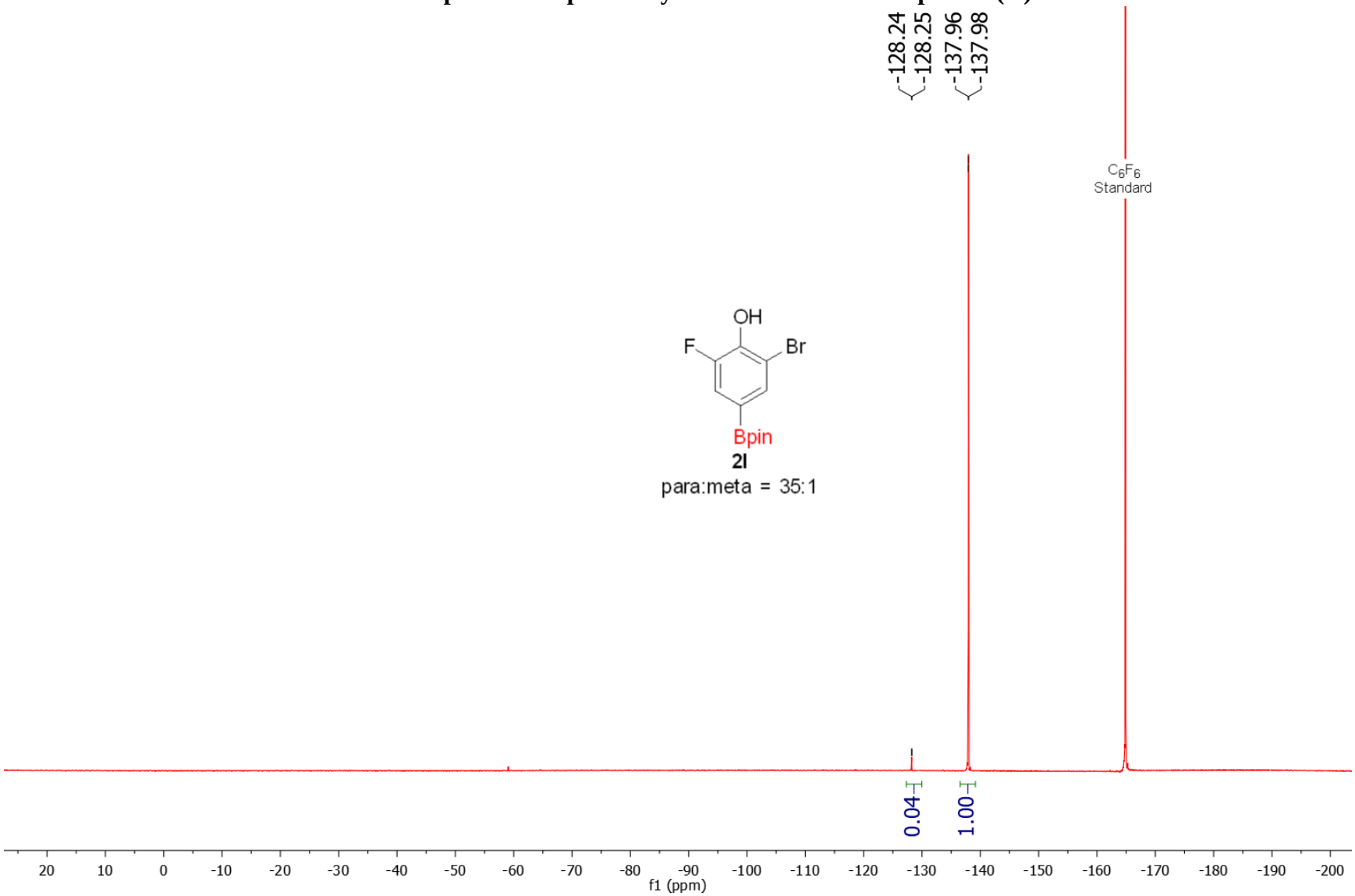
^{19}F NMR spectrum of para borylated 2-bromo-6-fluorophenol (2l)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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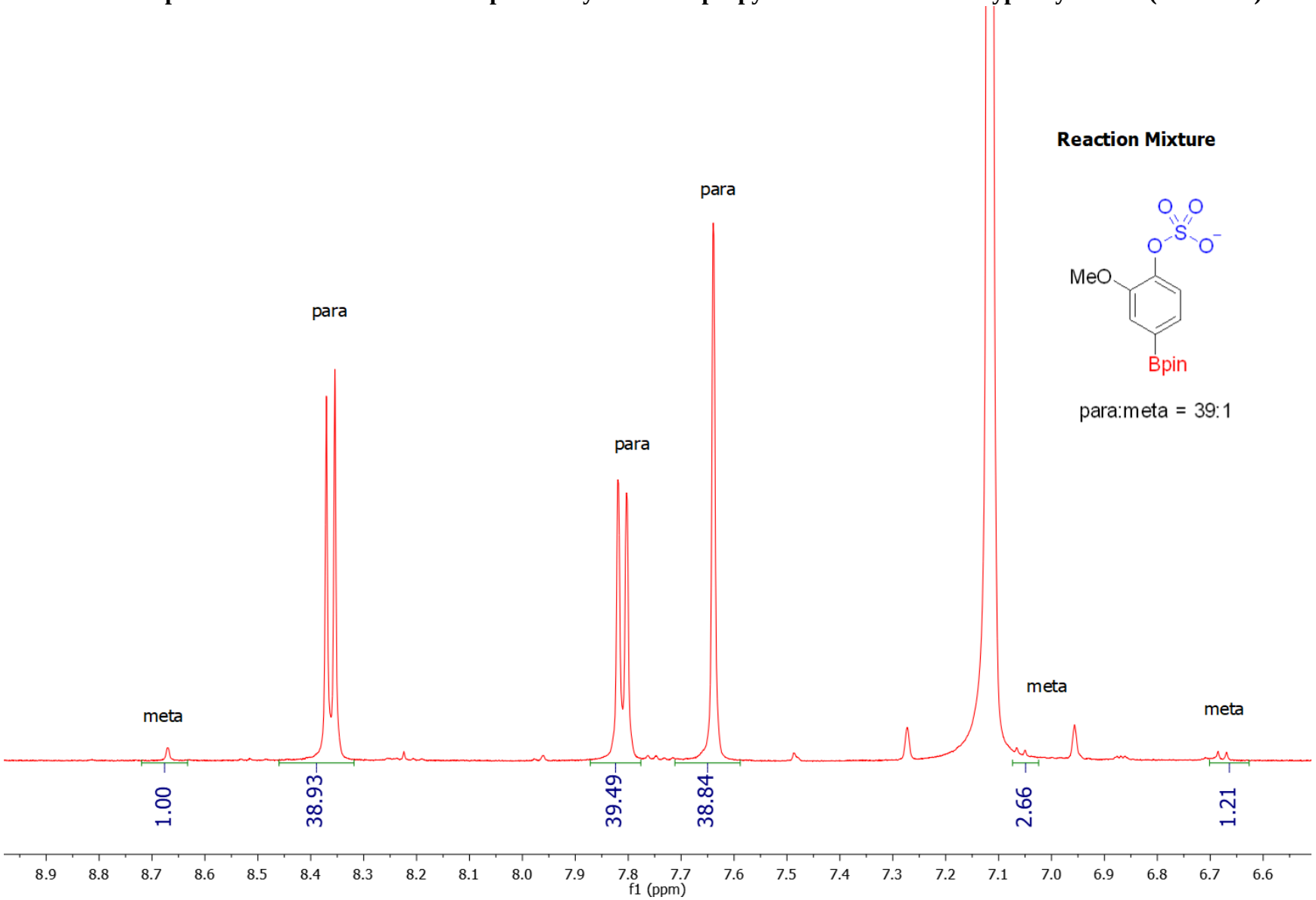
^{1}H NMR spectrum of reaction mixture of para-borylated tetrapropylammonium 2-methoxyphenylsulfate (crude 2m)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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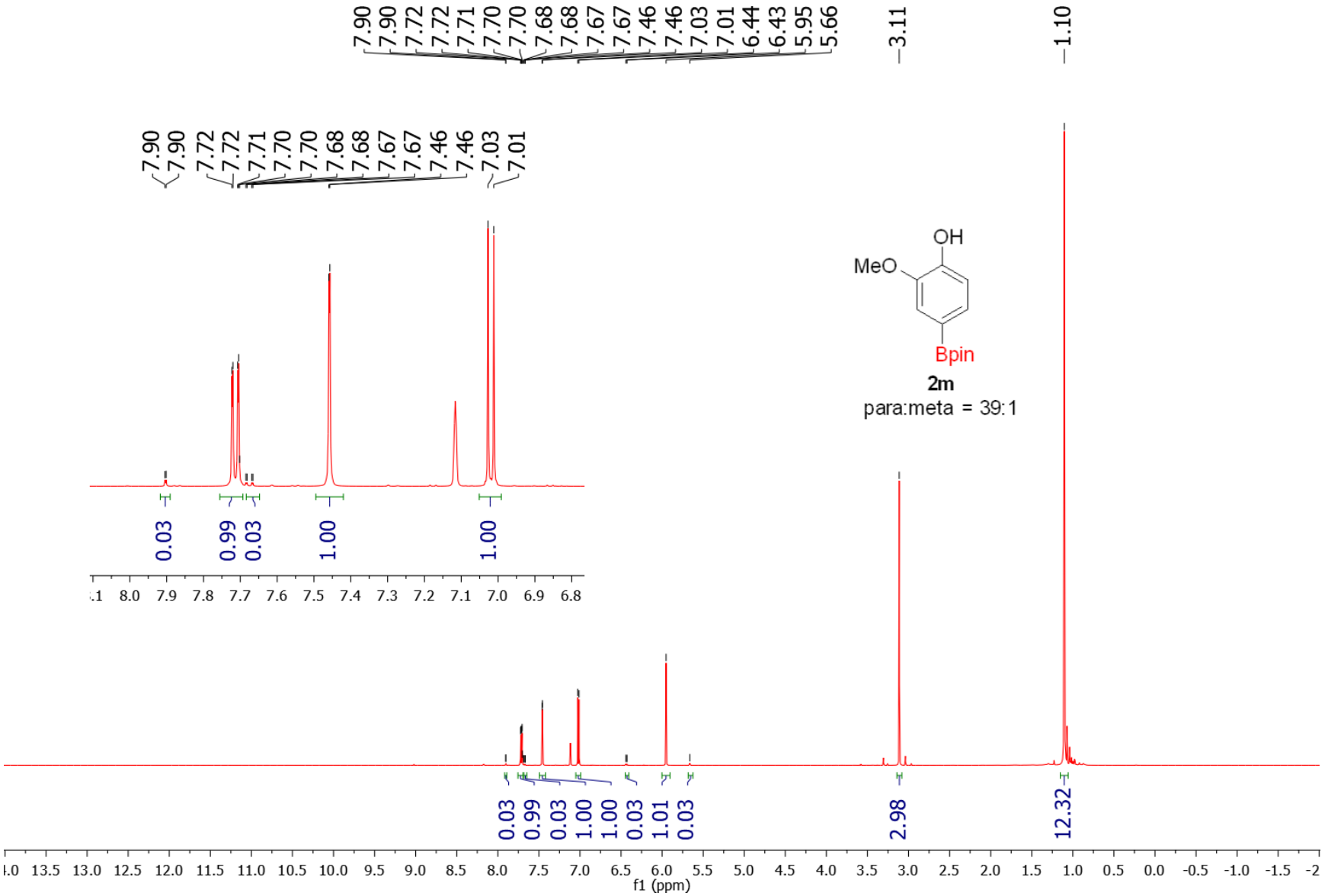
^{1}H NMR spectrum of para borylated 2-methoxyphenol (2m)



Conditions: 25 ºC, 500 MHz, C_6D_6

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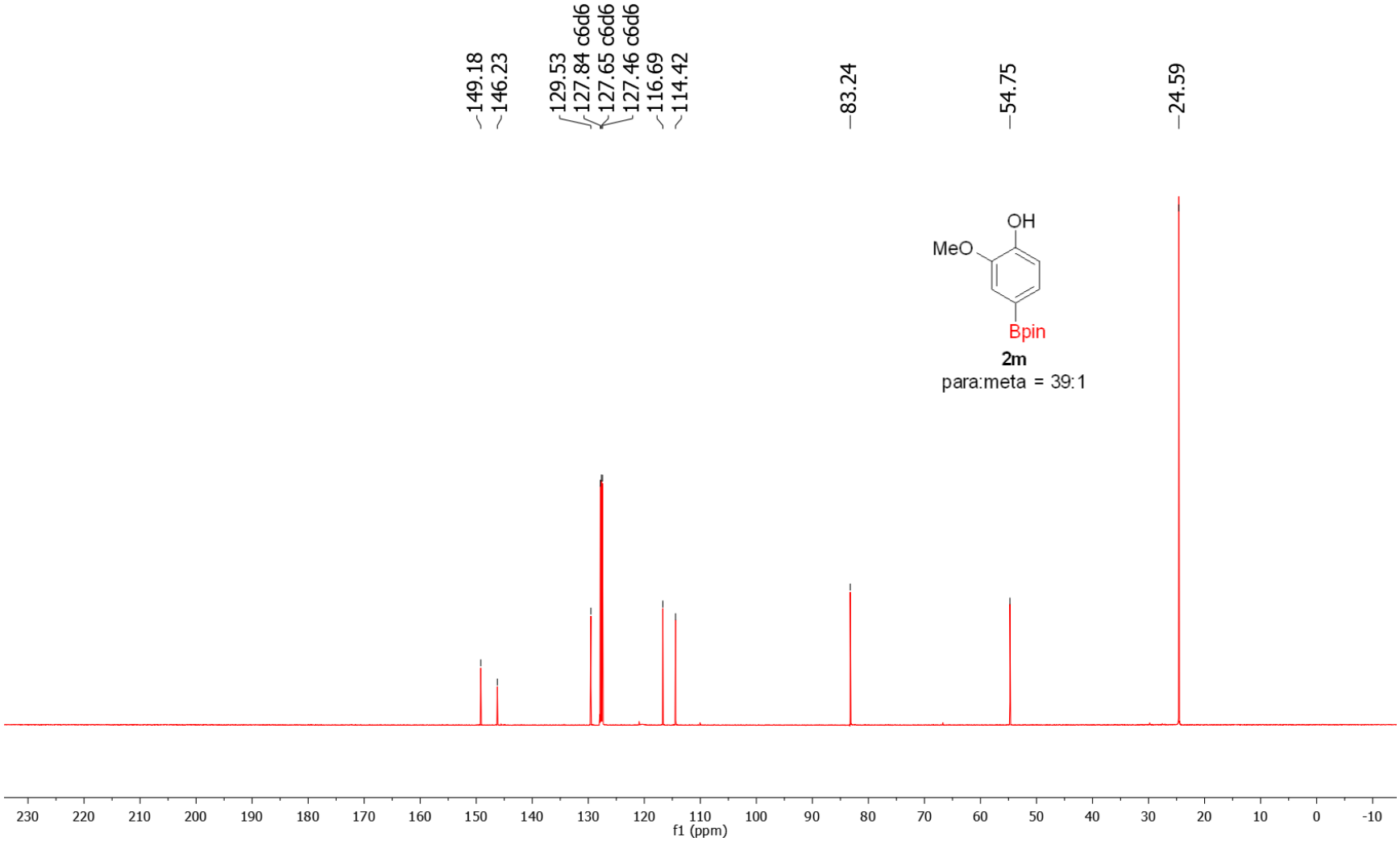
^{13}C NMR spectrum of para borylated 2-methoxyphenol (2m)



Conditions: 25 ºC, 126 MHz, C_6D_6

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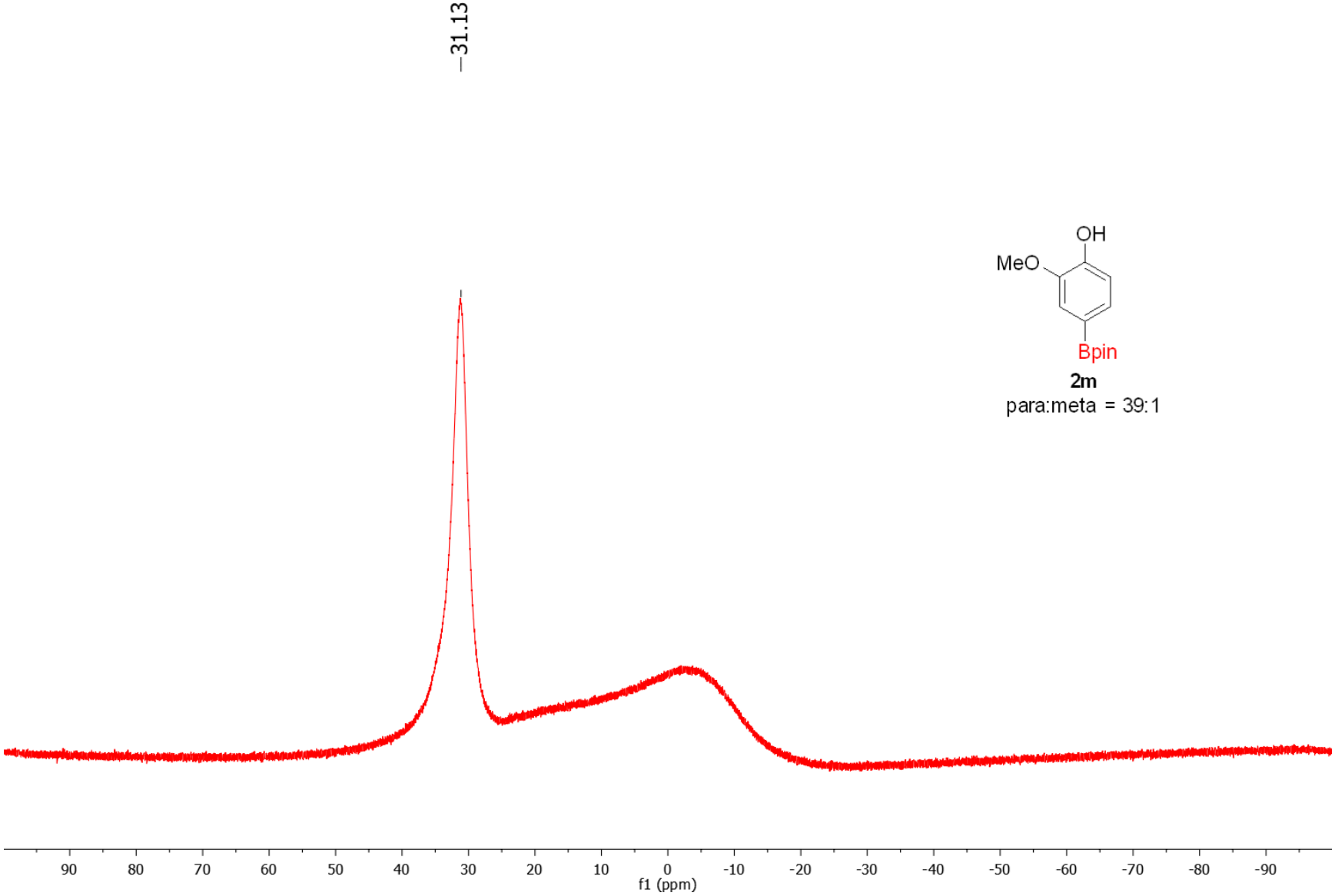
^{11}B NMR spectrum of para borylated 2-methoxyphenol (2m)



Conditions: 25 °C, 160 MHz, C_6D_6

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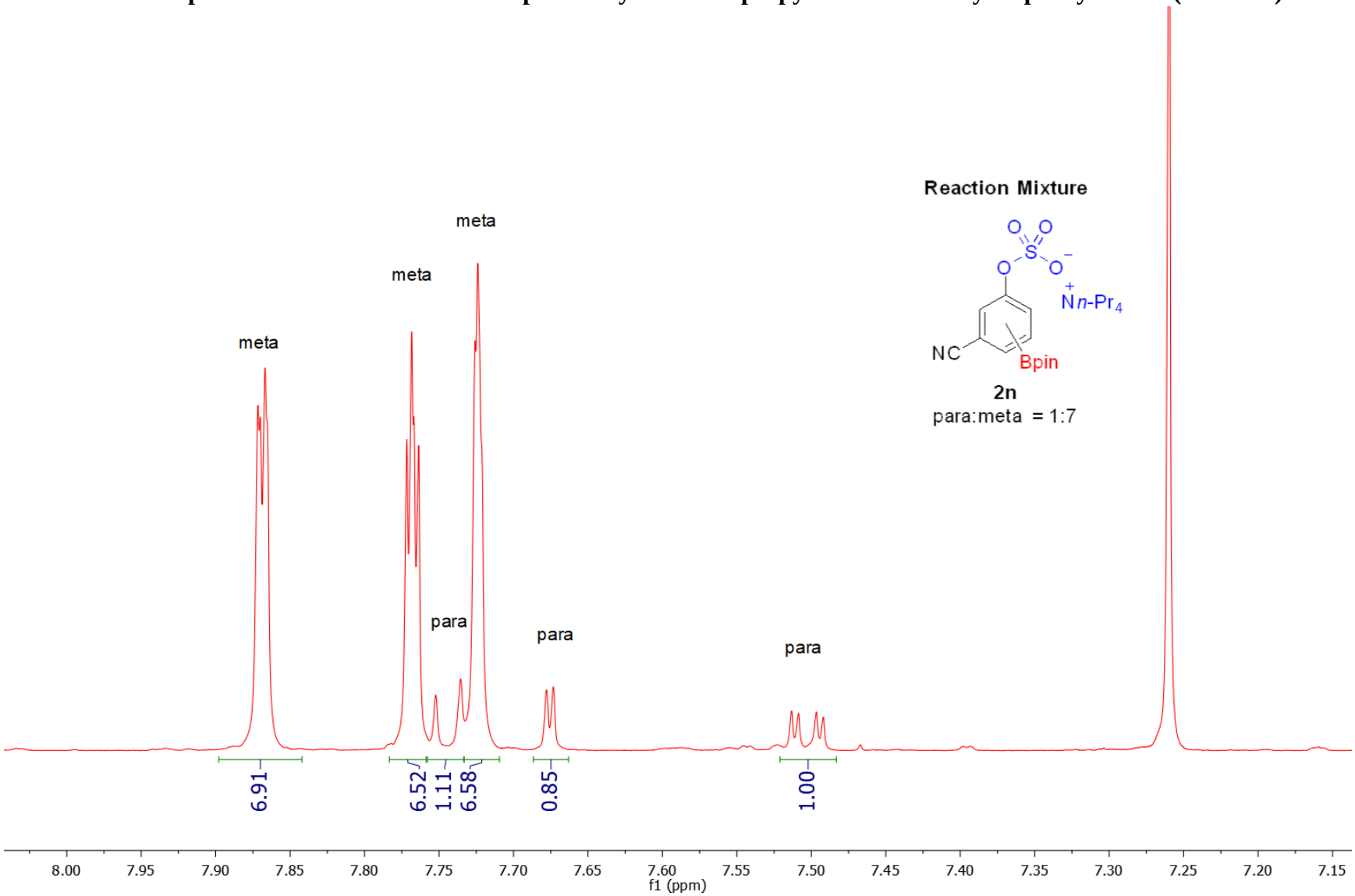
^{1}H NMR spectrum of reaction mixture of para-borylated tetrapropylammonium 3-cyanophenylsulfate (crude 2n)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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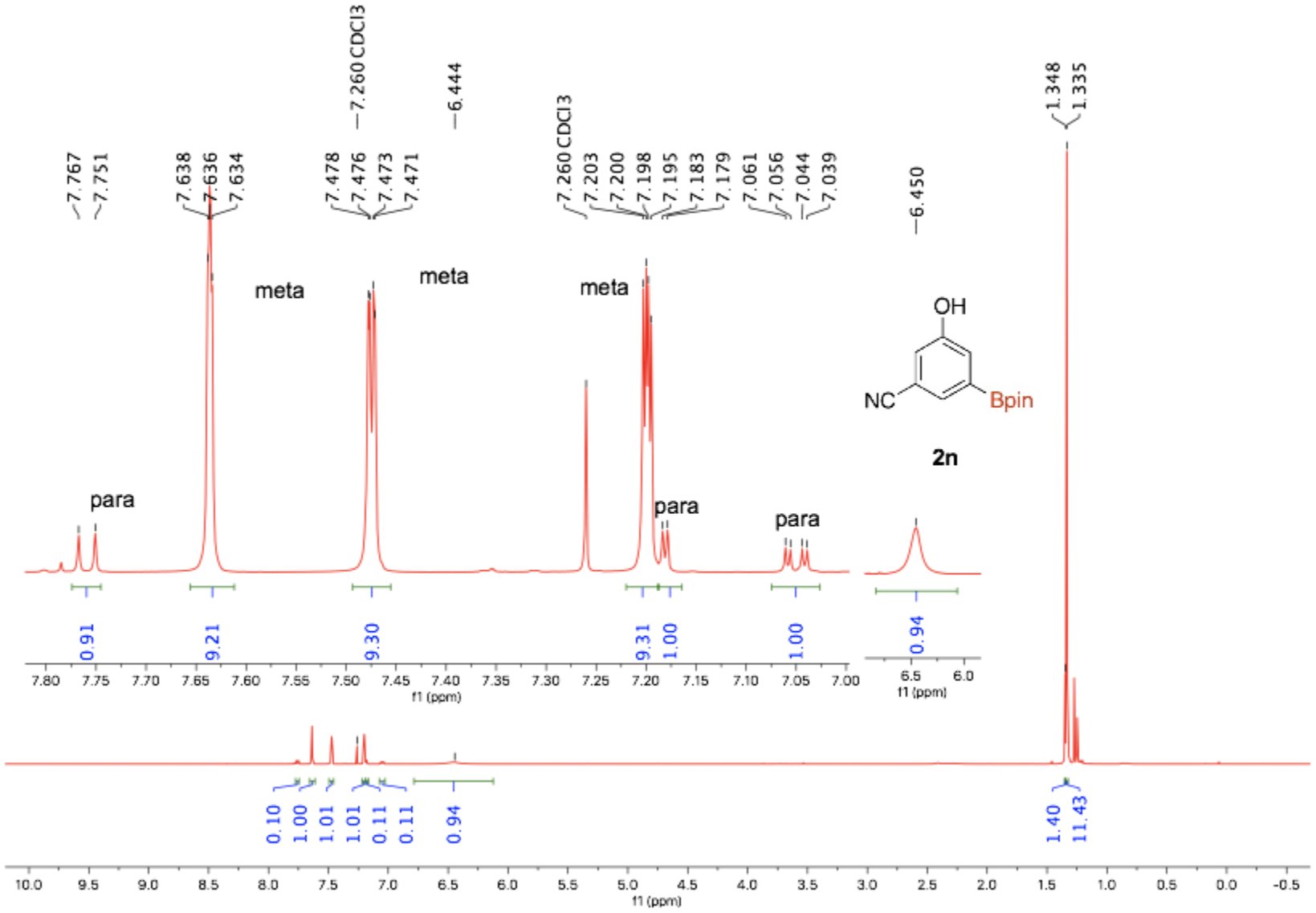
^{1}H NMR spectrum of para-borylated 3-cyanophenylsulfate (2n)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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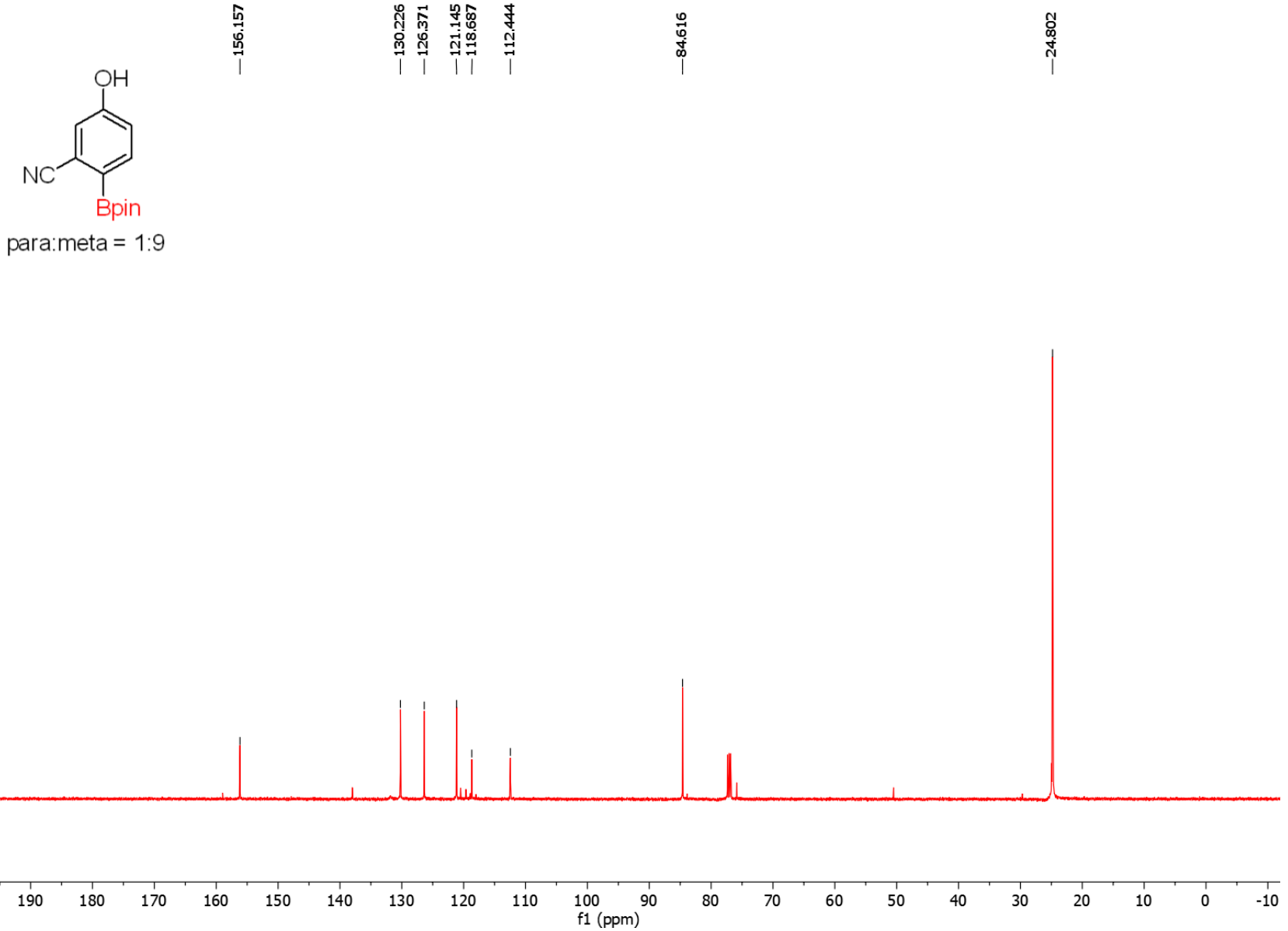
^{13}C NMR spectrum of para borylated 3-hydroxybenzonitrile (2n)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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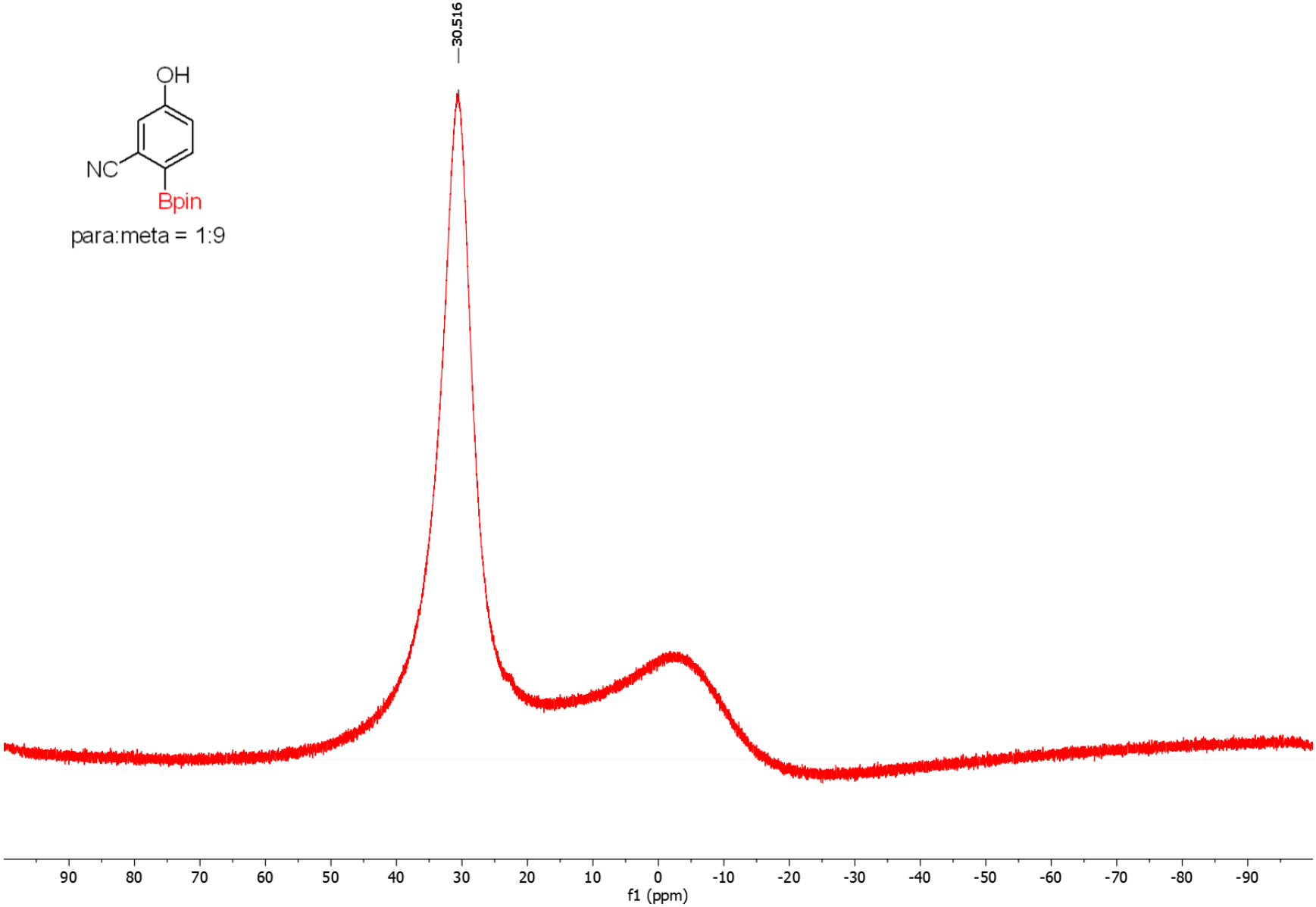
^{11}B NMR spectrum of para borylated 3-hydroxybenzonitrile (2n)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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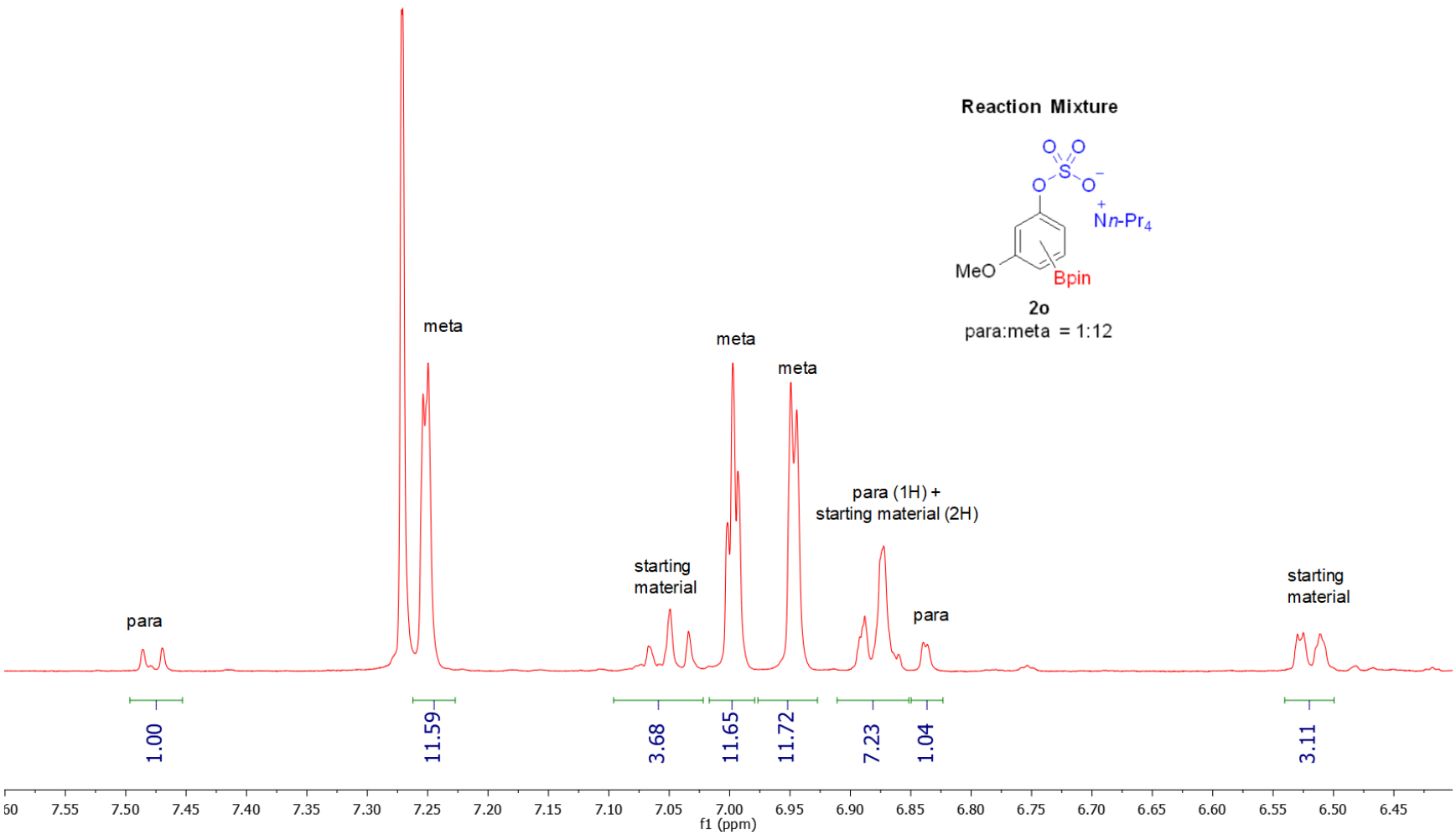
^{1}H NMR spectrum of reaction mixture of para borylated tetrapropylammonium 3-methoxyphenylsulfate (crude 2o)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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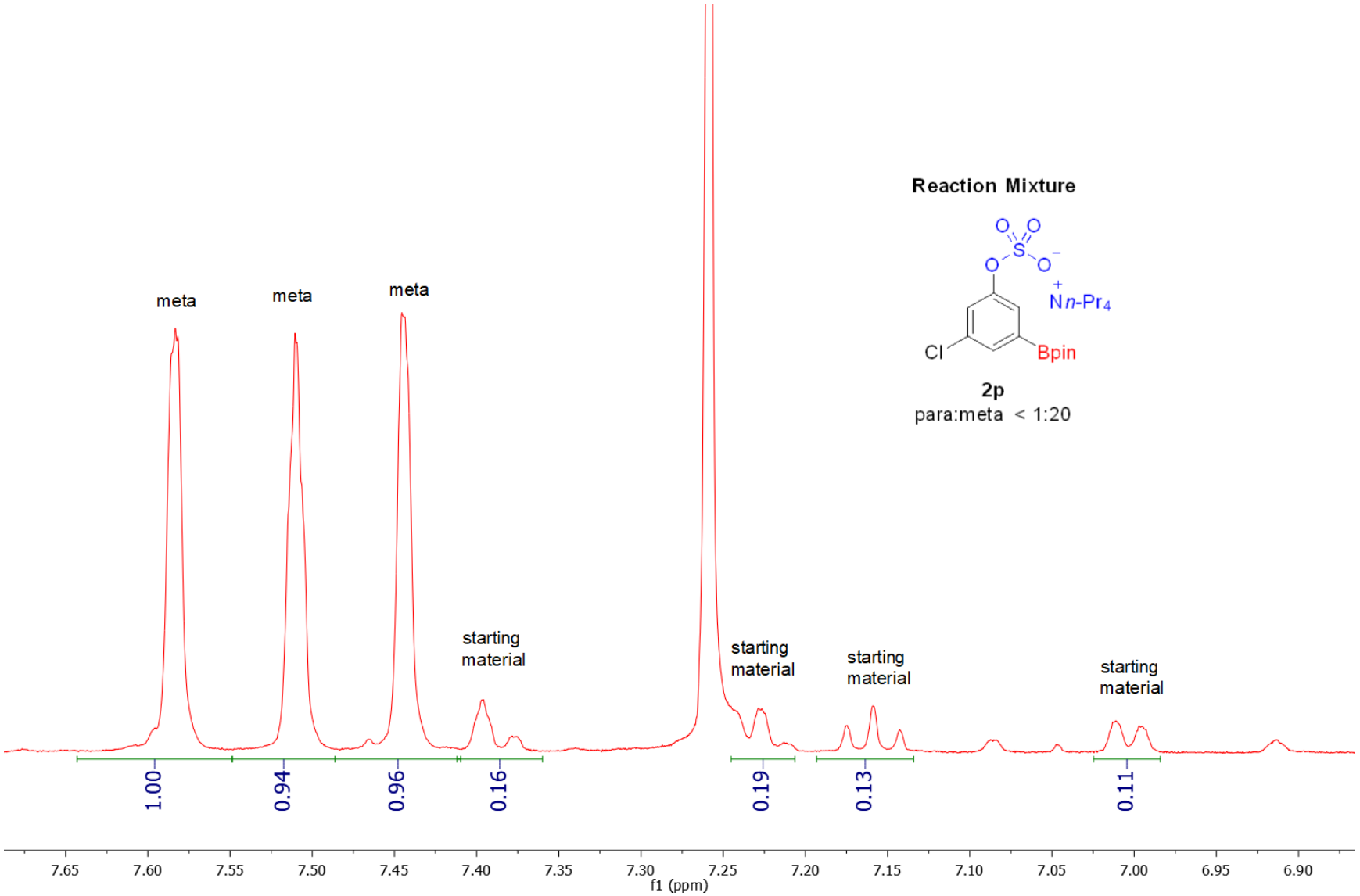
^{1}H NMR spectrum of reaction mixture of para borylated tetrapropylammonium 3-chlorophenylsulfate (crude 2p)



Conditions: 25 ºC, 500 MHz, C_6D_6

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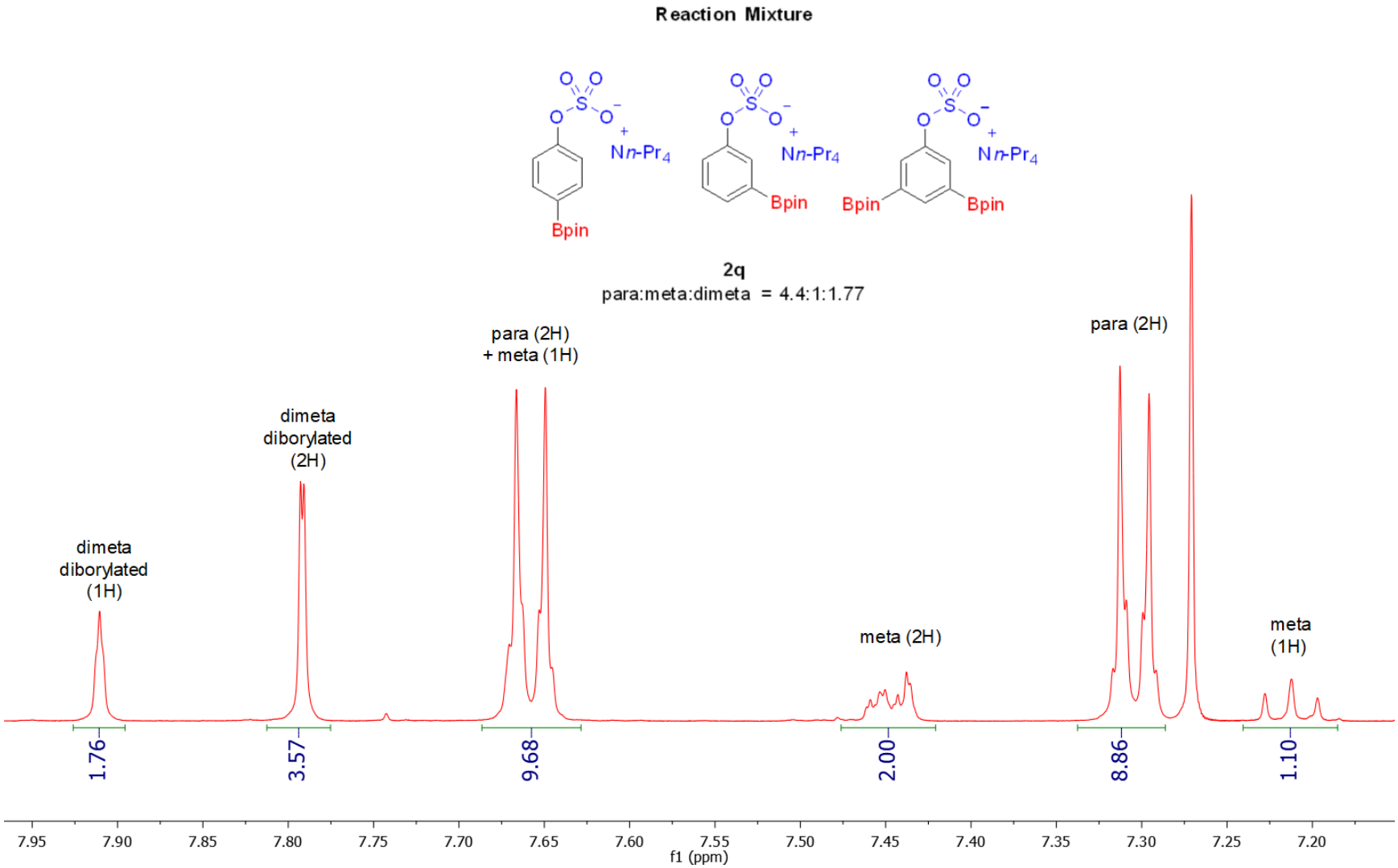
^{1}H NMR expanded spectrum of reaction mixture of borylation of tetrapropylammonium phenylsulfate (crude 2q)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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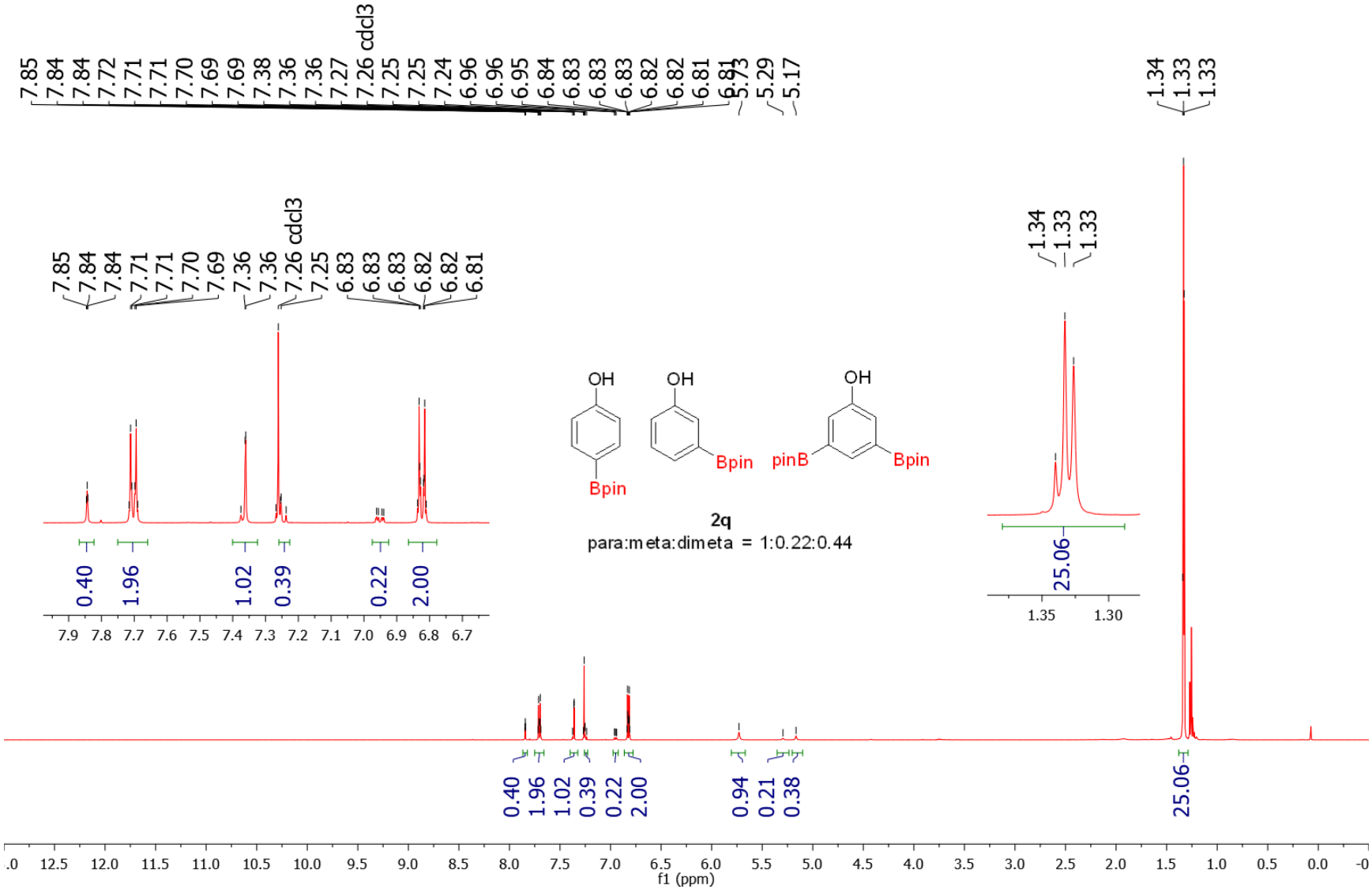
^{1}H NMR spectrum of borylated phenol regioisomers (2q)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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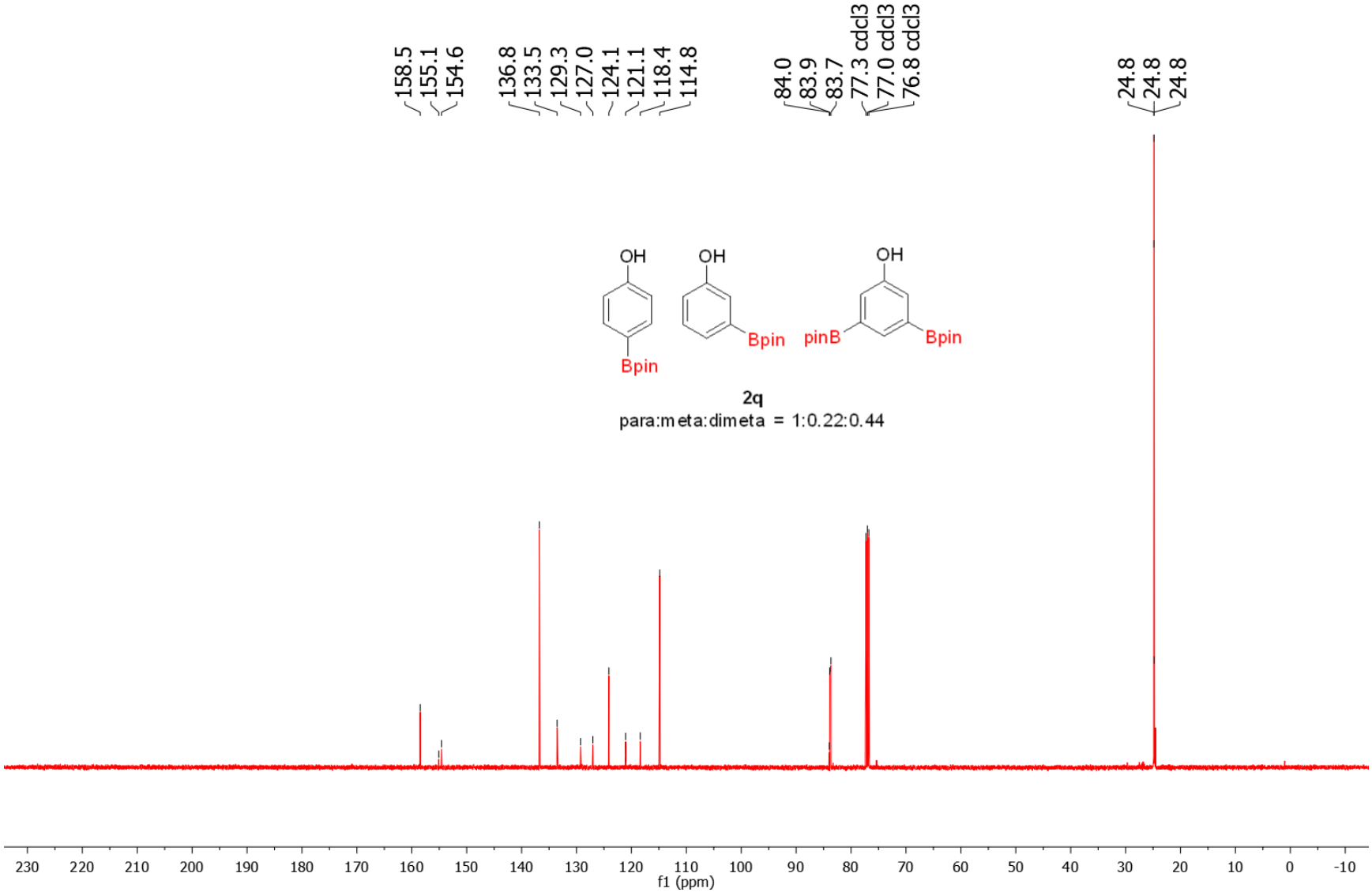
^{13}C NMR spectrum of borylated phenol regioisomers (2q)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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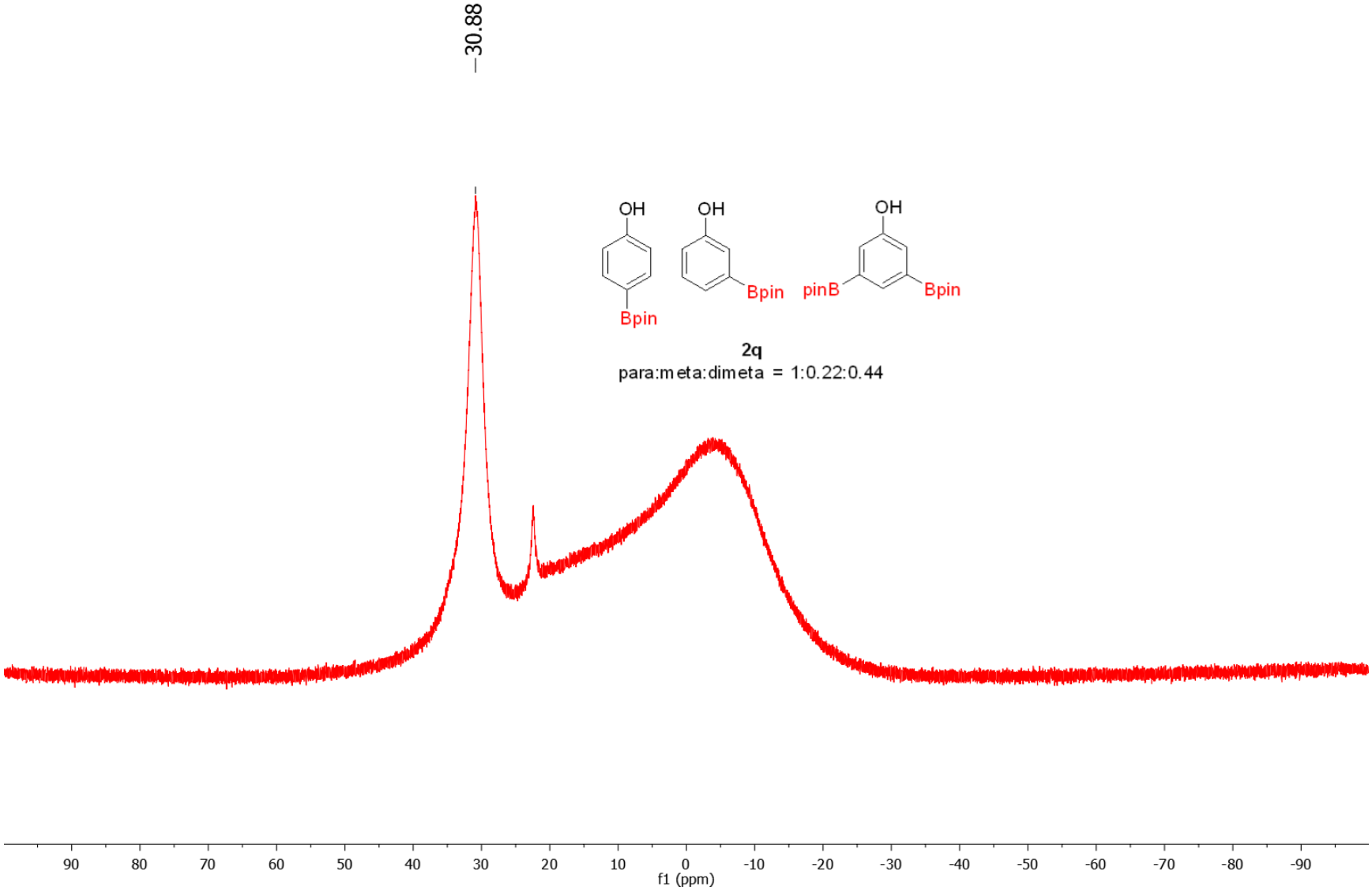
^{11}B NMR spectrum of borylated phenol regioisomers (2q)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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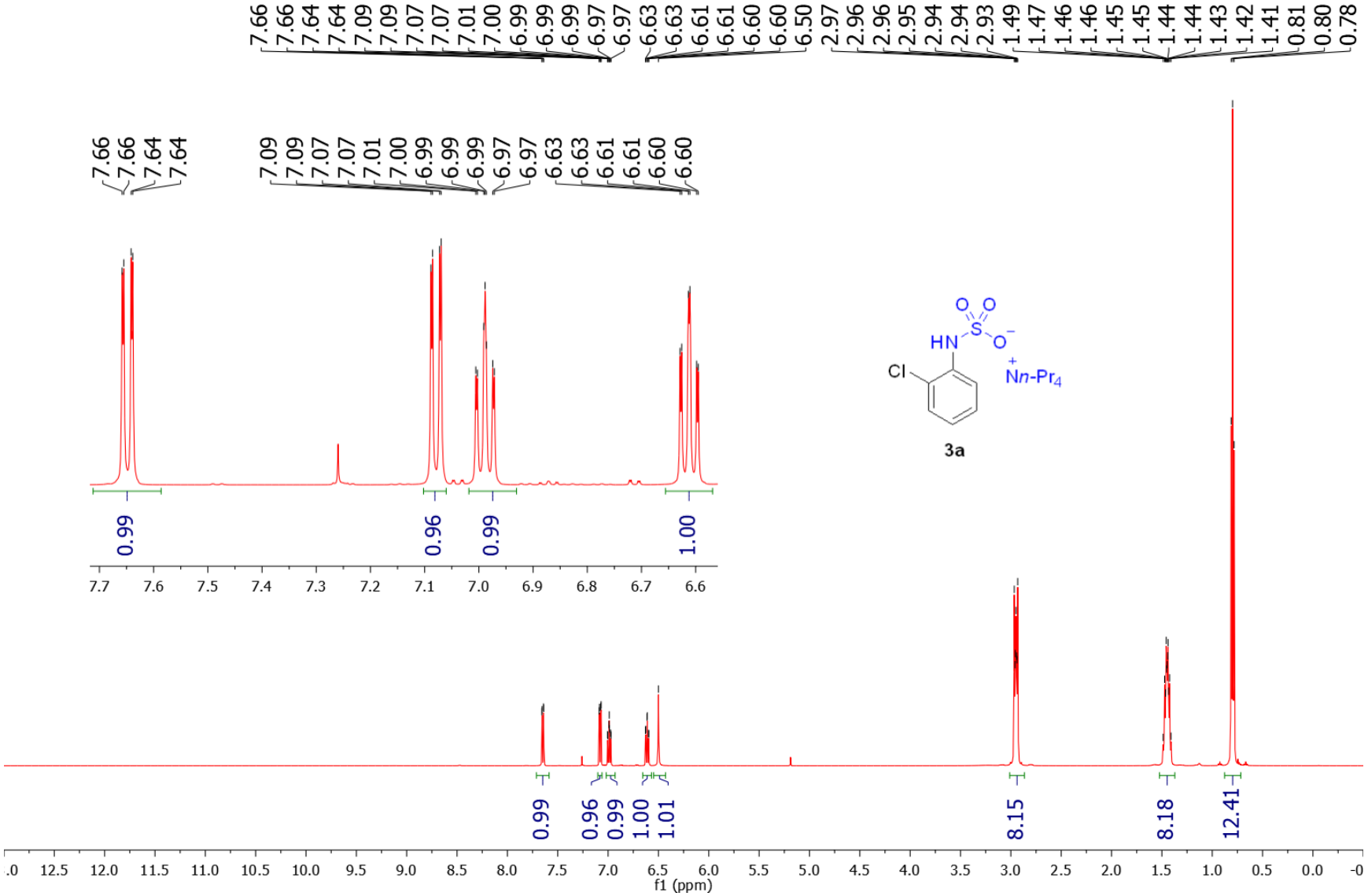
^{1}H NMR spectrum of tetrapropylammonium 2-chlorophenylsulfamate (3a)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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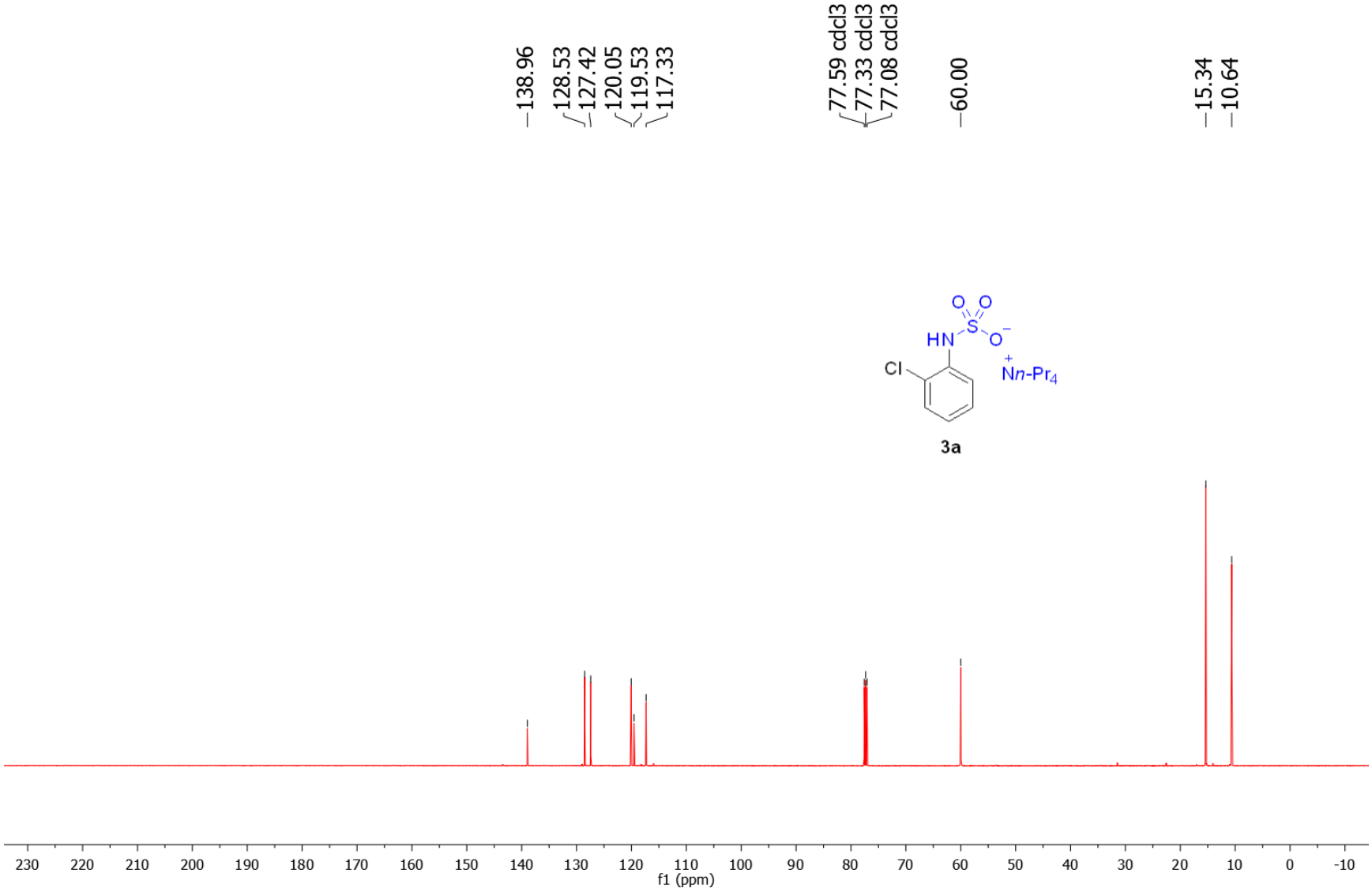
^{13}C NMR spectrum of tetrapropylammonium 2-chlorophenylsulfamate (3a)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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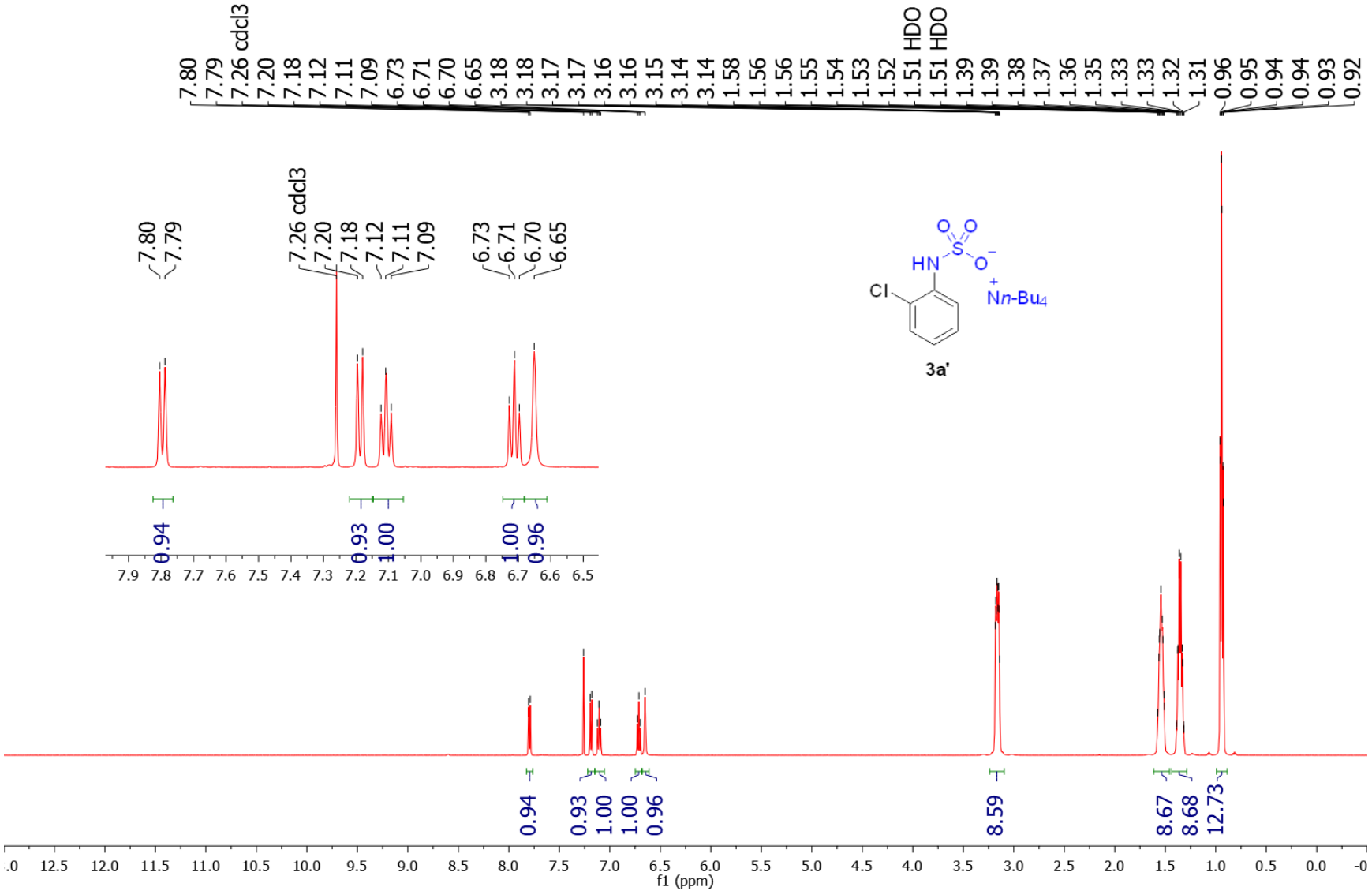
^{1}H NMR spectrum of tetrabutylammonium 2-chlorophenylsulfamate (3a′)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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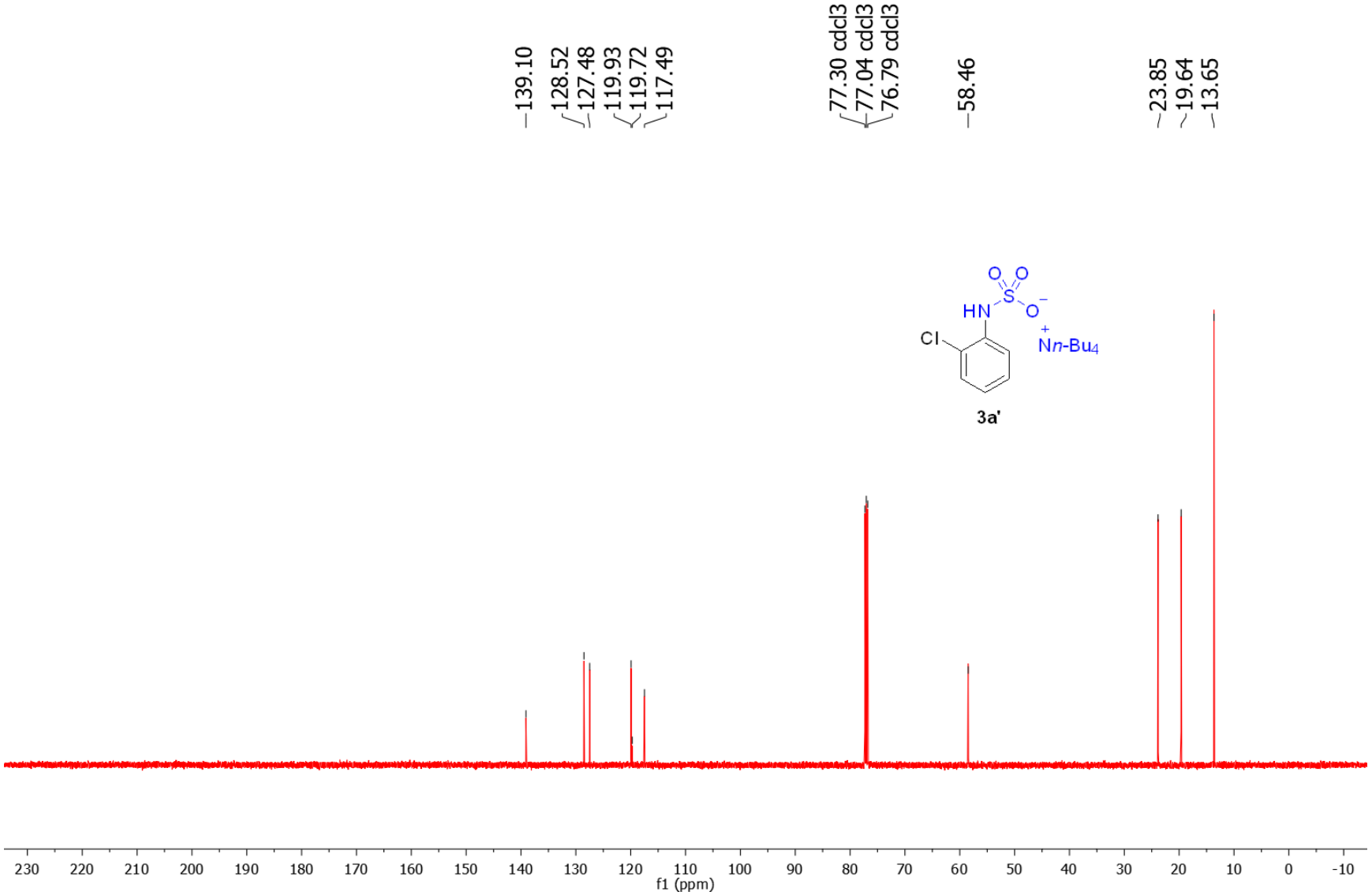
^{13}C NMR spectrum of tetrabutylammonium 2-chlorophenylsulfamate (3a′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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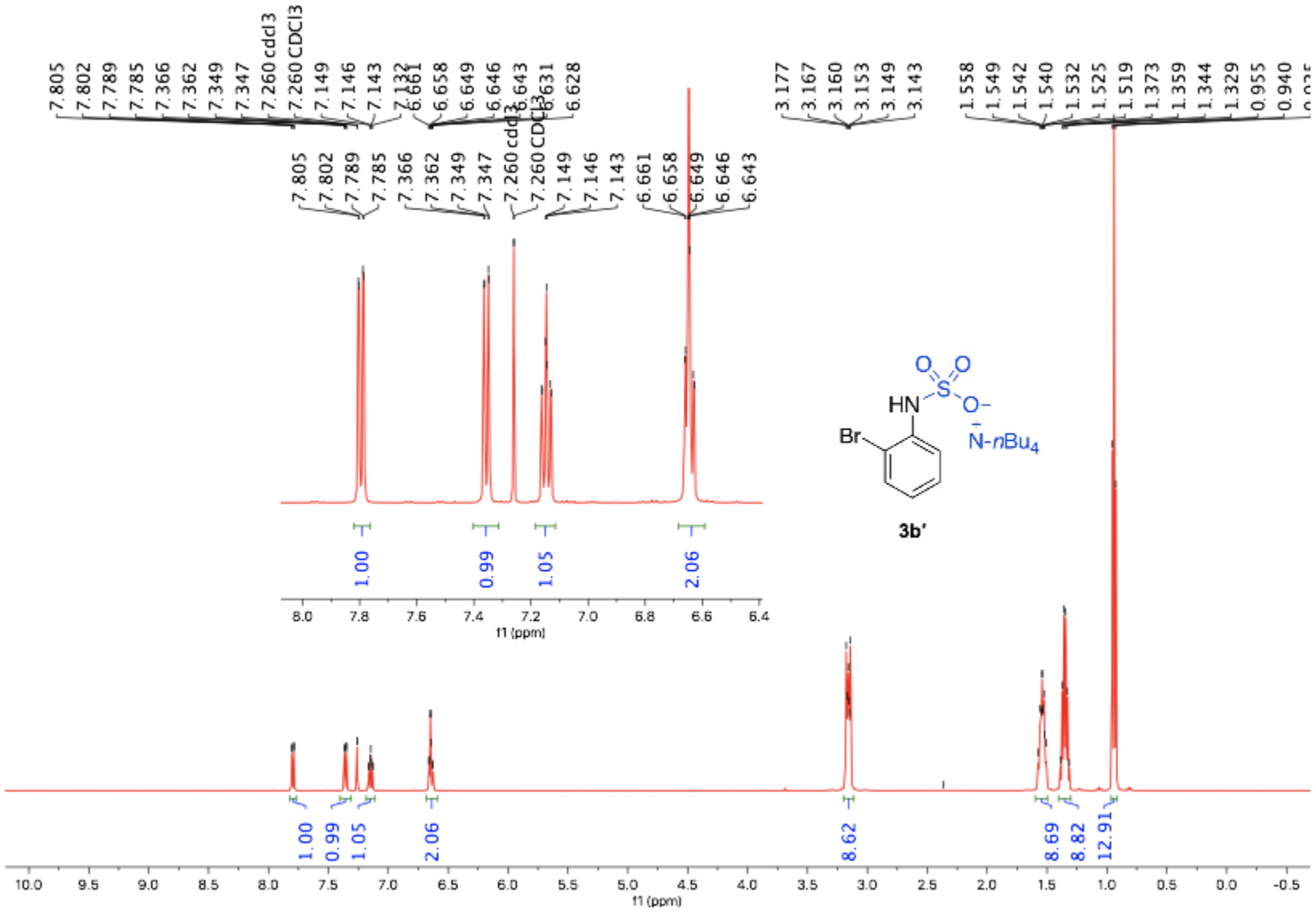
^{1}H NMR spectrum of tetrabutylammonium 2-bromophenylsulfamate (3b′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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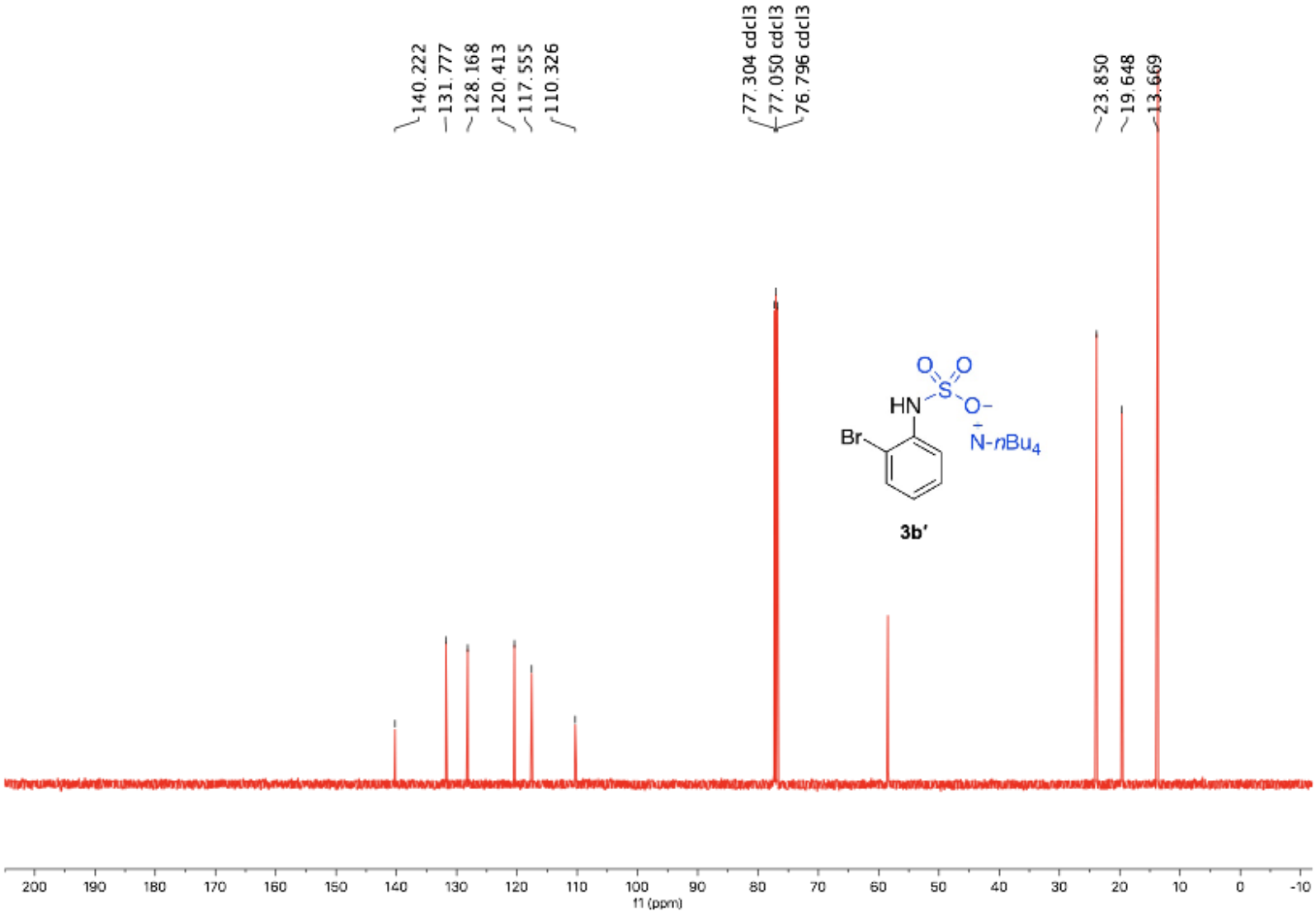
^{13}C NMR spectrum of tetrabutylammonium 2-bromophenylsulfamate (3b′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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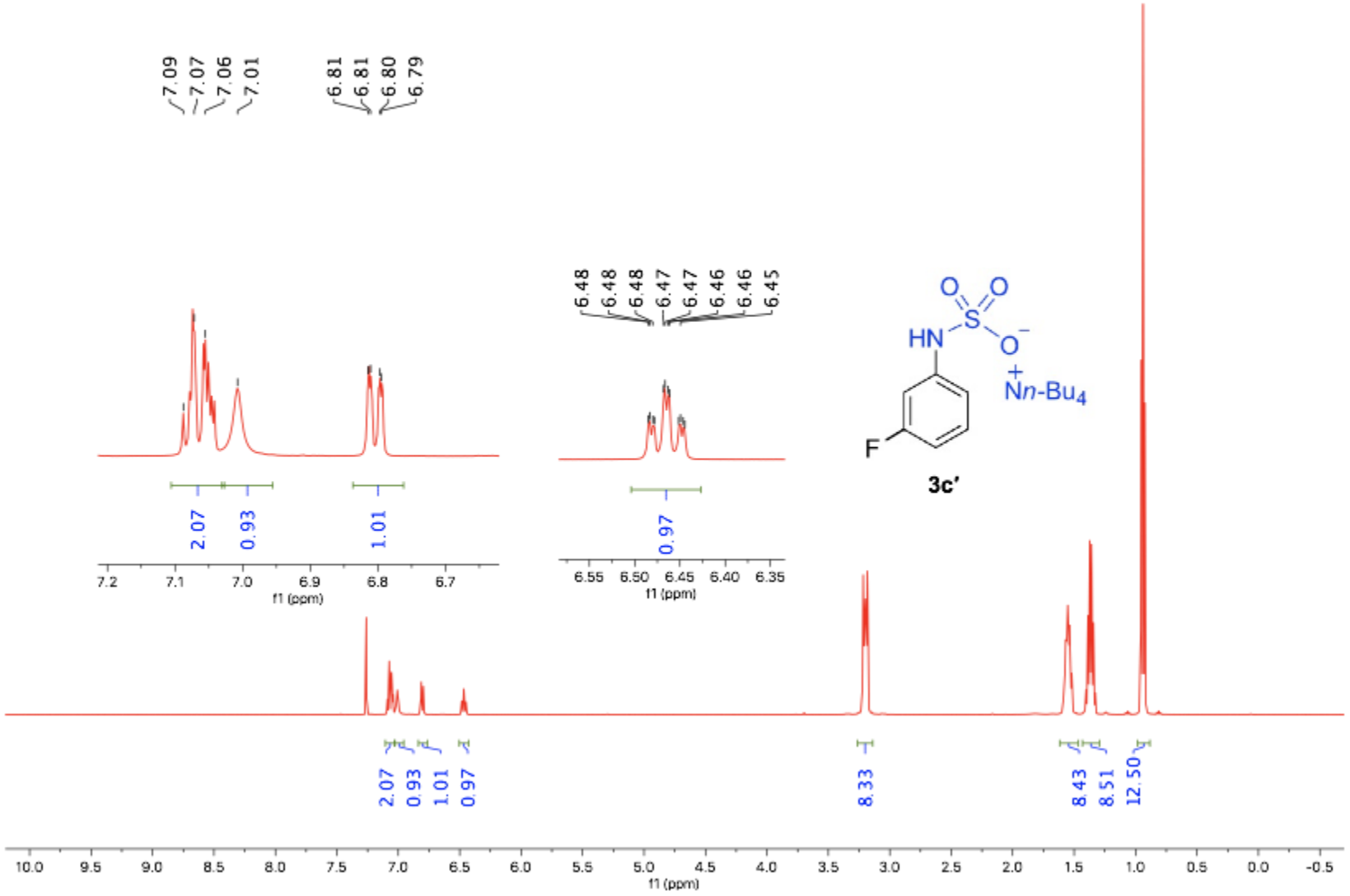
^{1}H NMR spectrum of tetrabutylammonium 3-fluorophenylsulfamate (3c′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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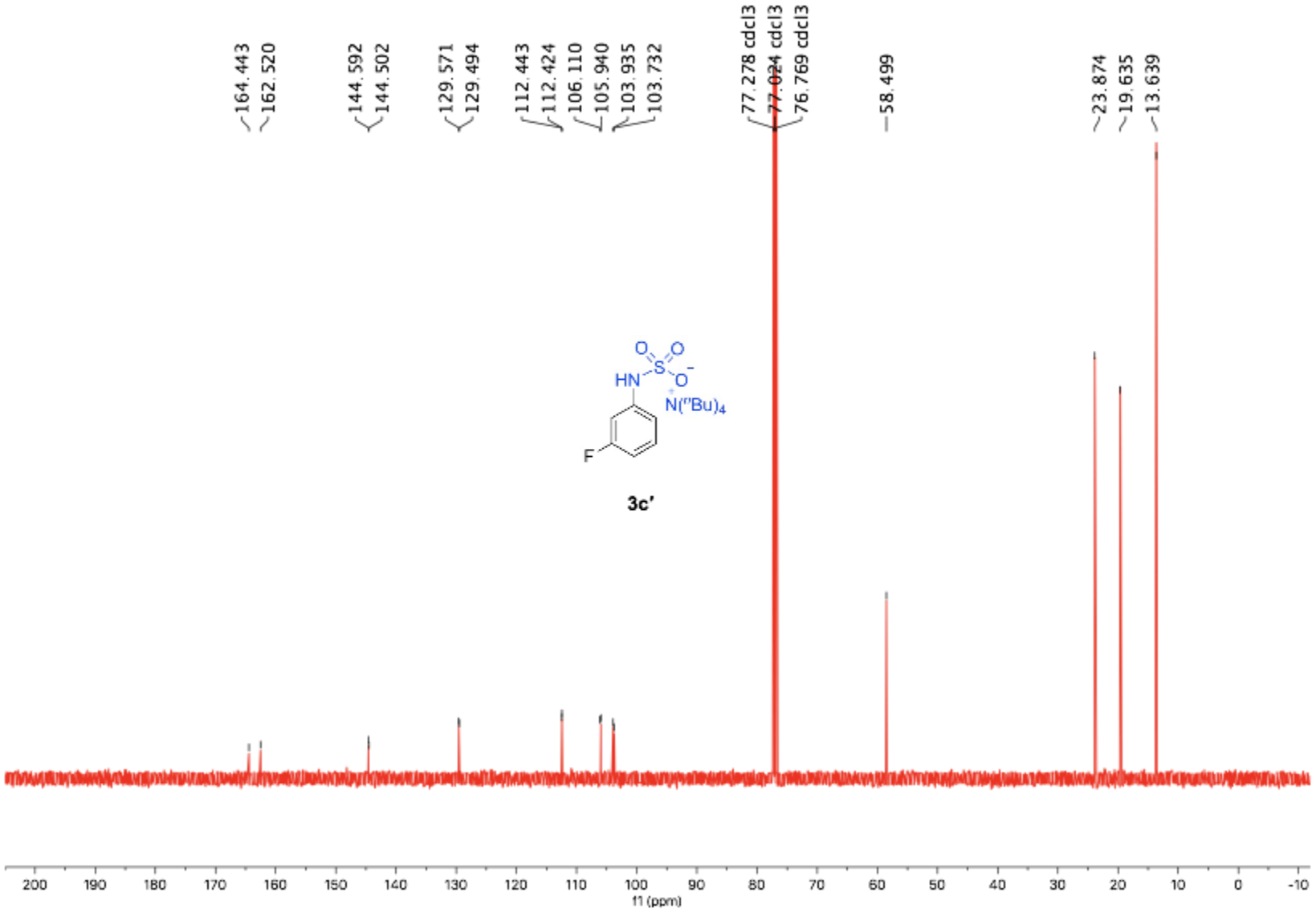
^{13}C NMR spectrum of tetrabutylammonium 3-fluorophenylsulfamate (3c′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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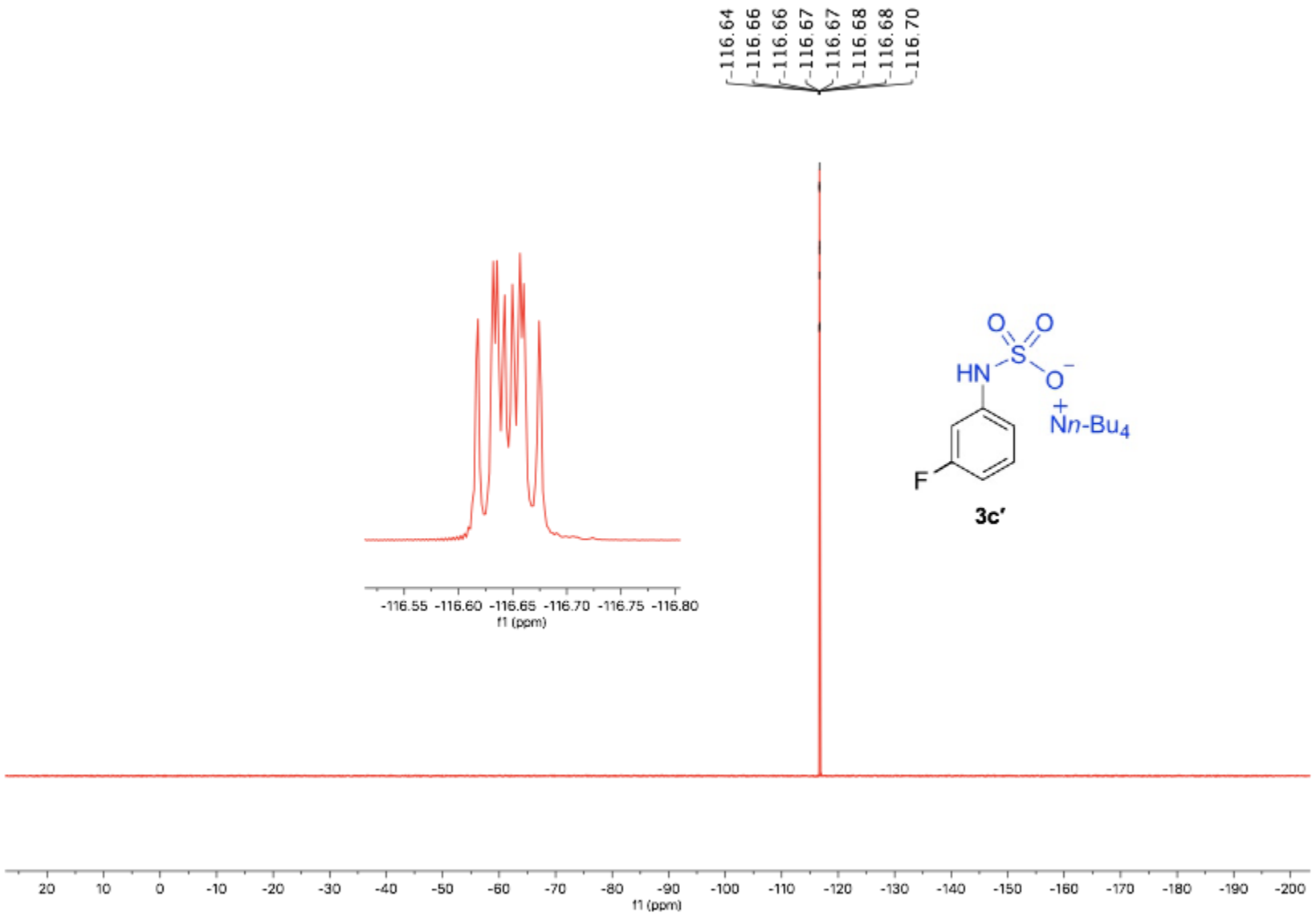
^{19}F NMR spectrum of tetrabutylammonium 3-fluorophenylsulfamate (3c′)



Conditions: 25 ºC, 470 MHz, $CDCl_3$

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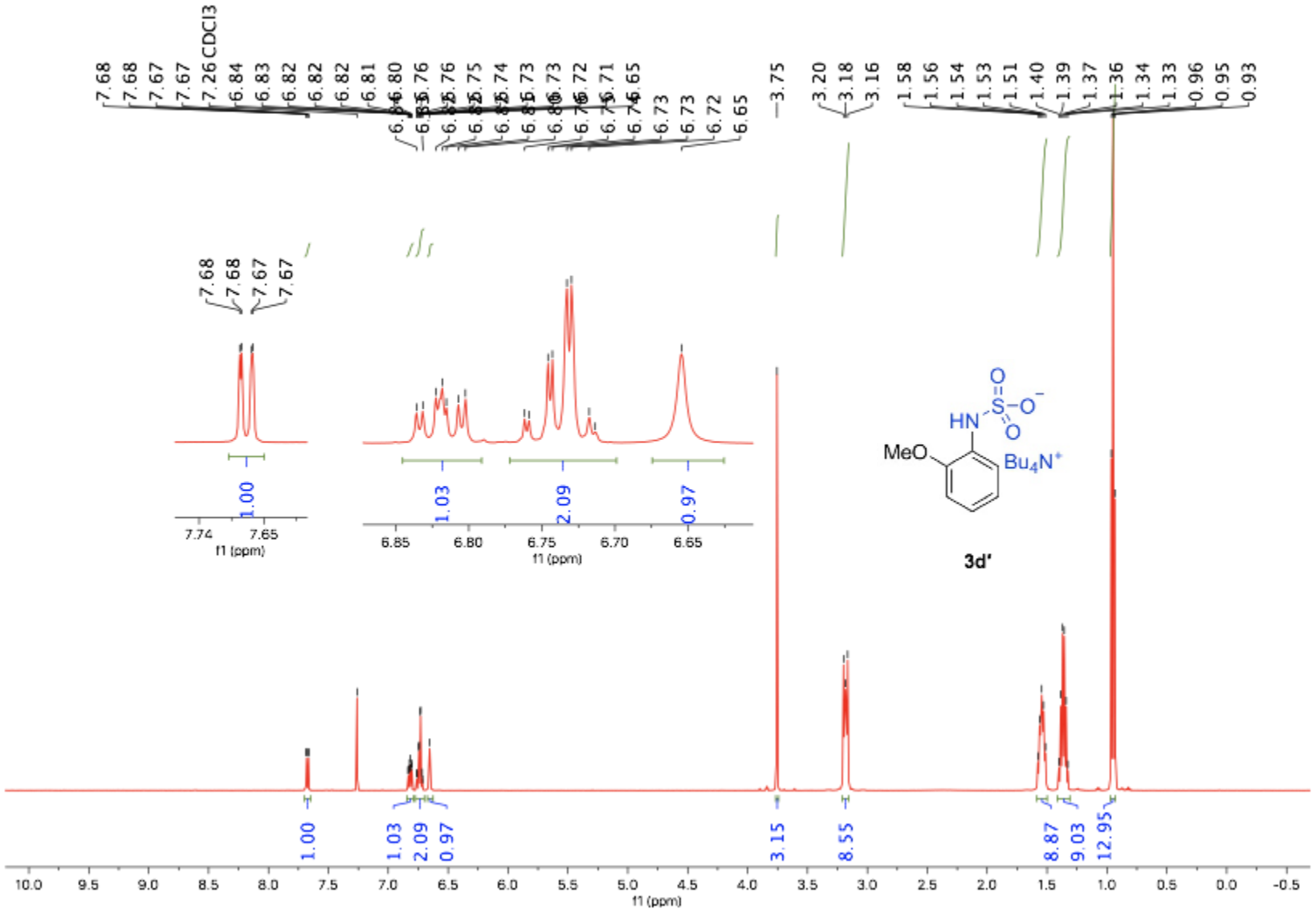
^{1}H NMR spectrum of tetrabutylammonium 2-(methoxy)phenylsulfamate (3d′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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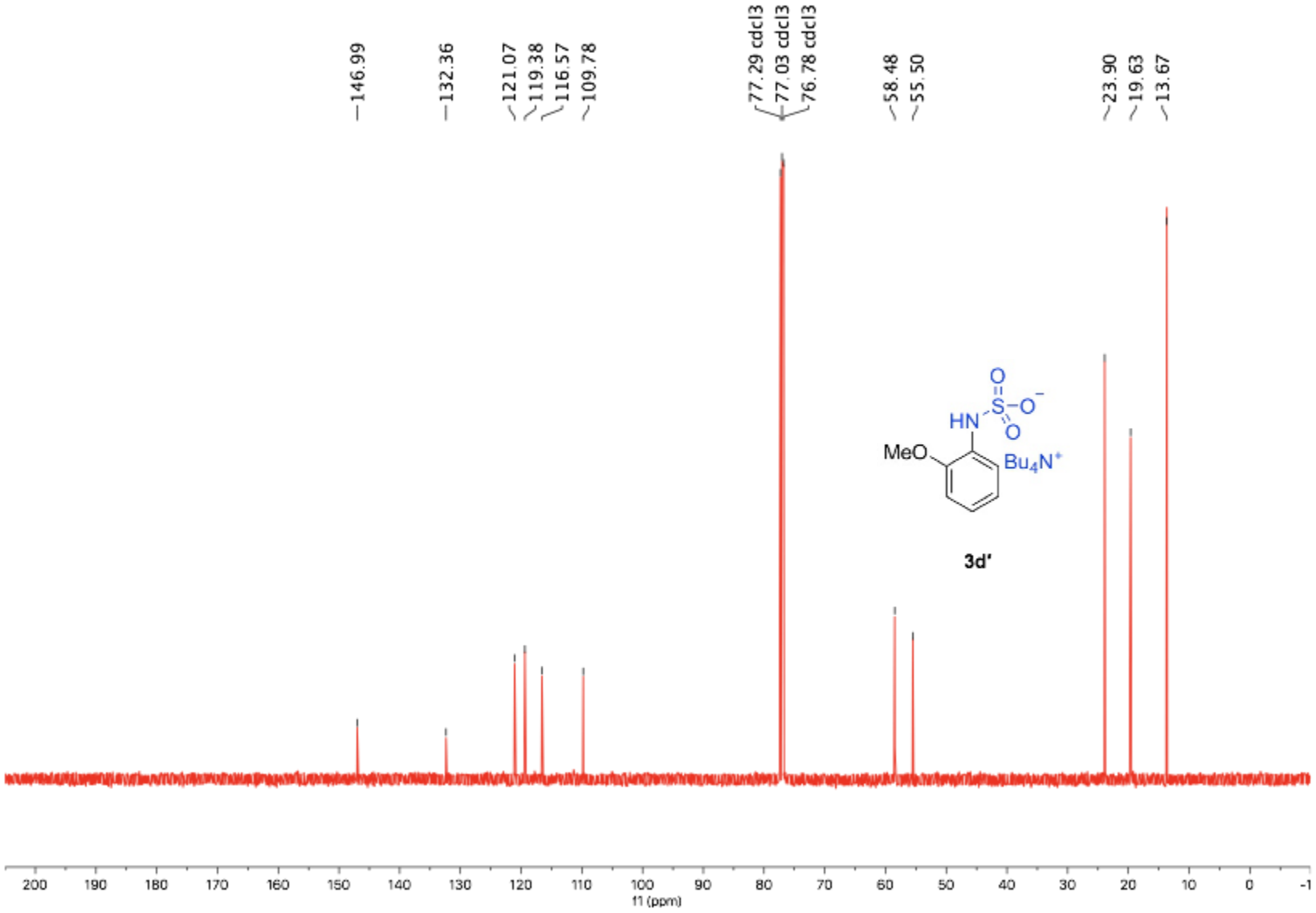
^{13}C NMR spectrum of tetrabutylammonium 2-(methoxy)phenylsulfamate (3d′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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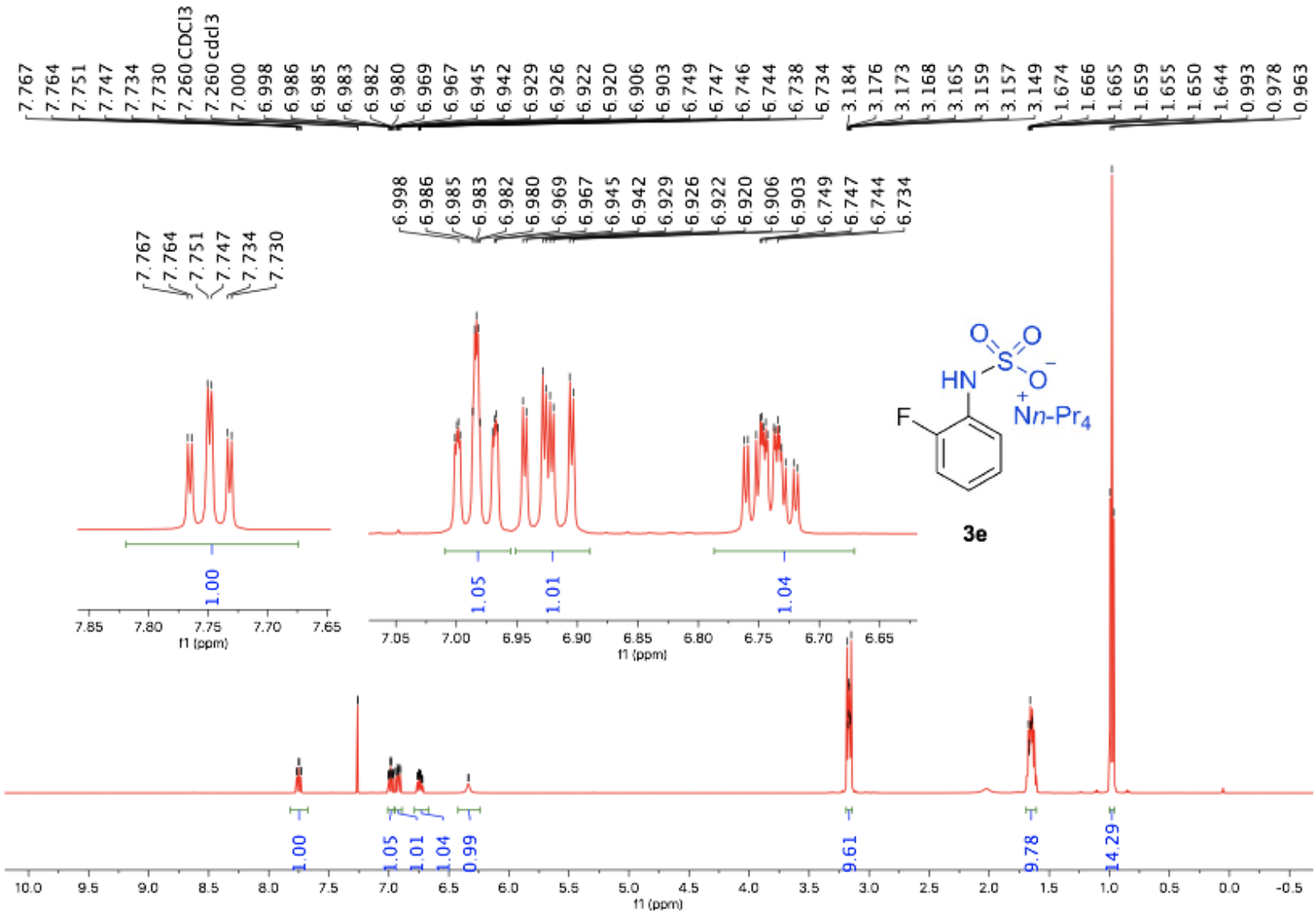
^{1}H NMR spectrum of tetrapropylammonium 2-fluorophenylsulfamate (3e)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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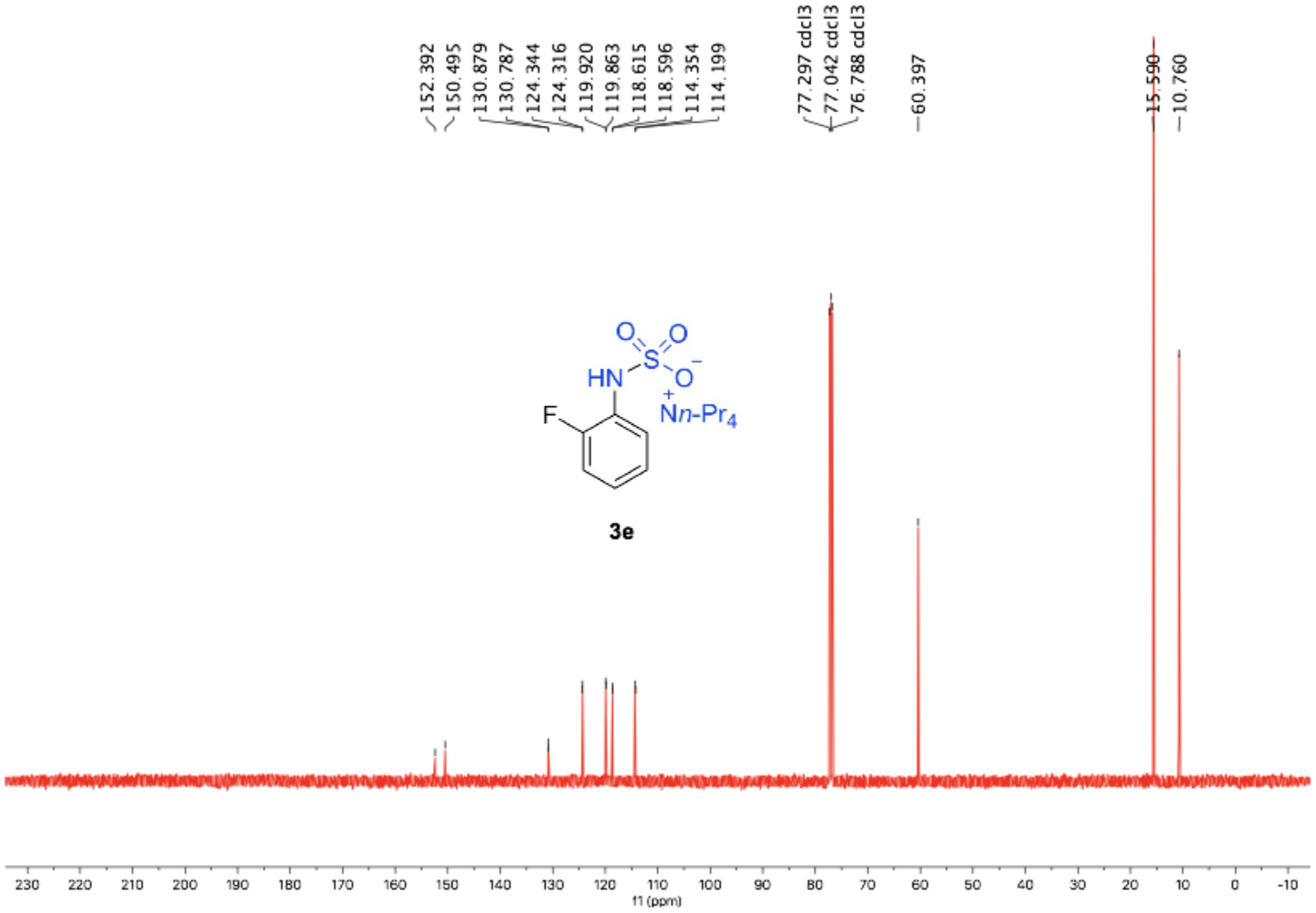
^{13}C NMR spectrum of tetrapropylammonium 2-fluorophenylsulfamate (3e)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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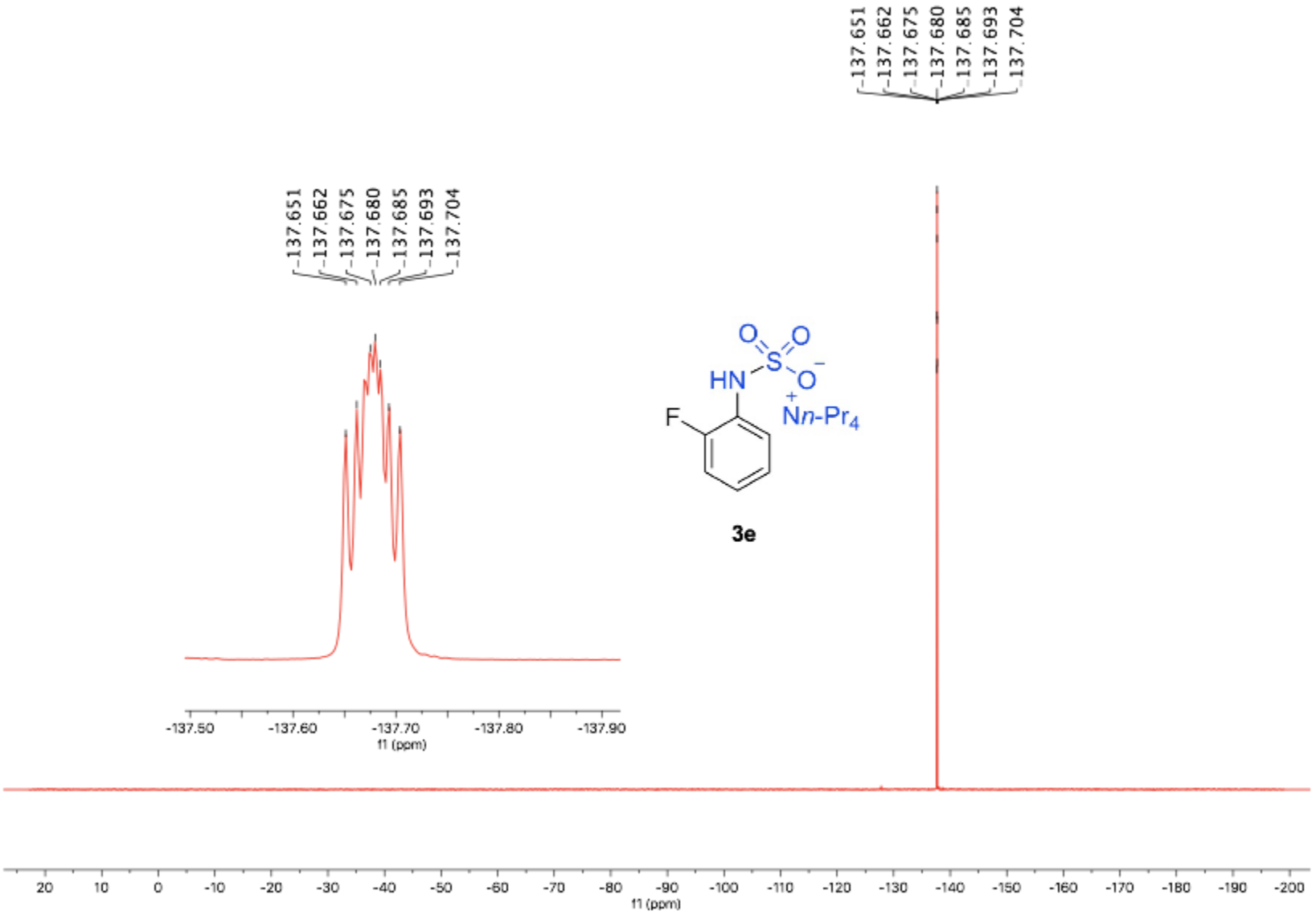
^{19}F NMR spectrum of tetrapropylammonium 2-fluorophenylsulfamate (3e)



Conditions: 25 ºC, 470 MHz, $CDCl_3$

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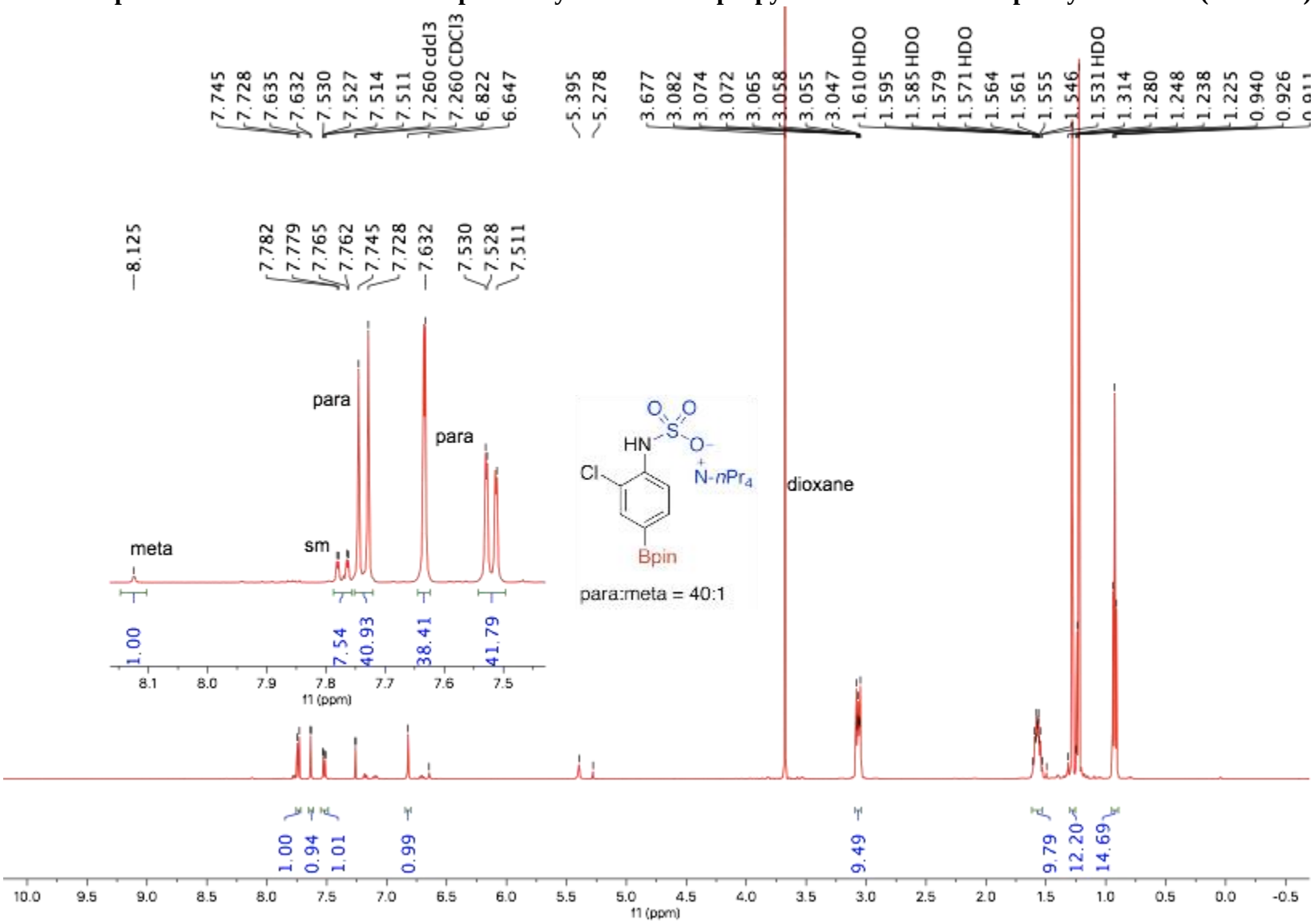
^{1}H NMR spectrum of reaction mixture of para borylation of tetrapropylammonium 2-chlorophenylsulfamate (crude 4a)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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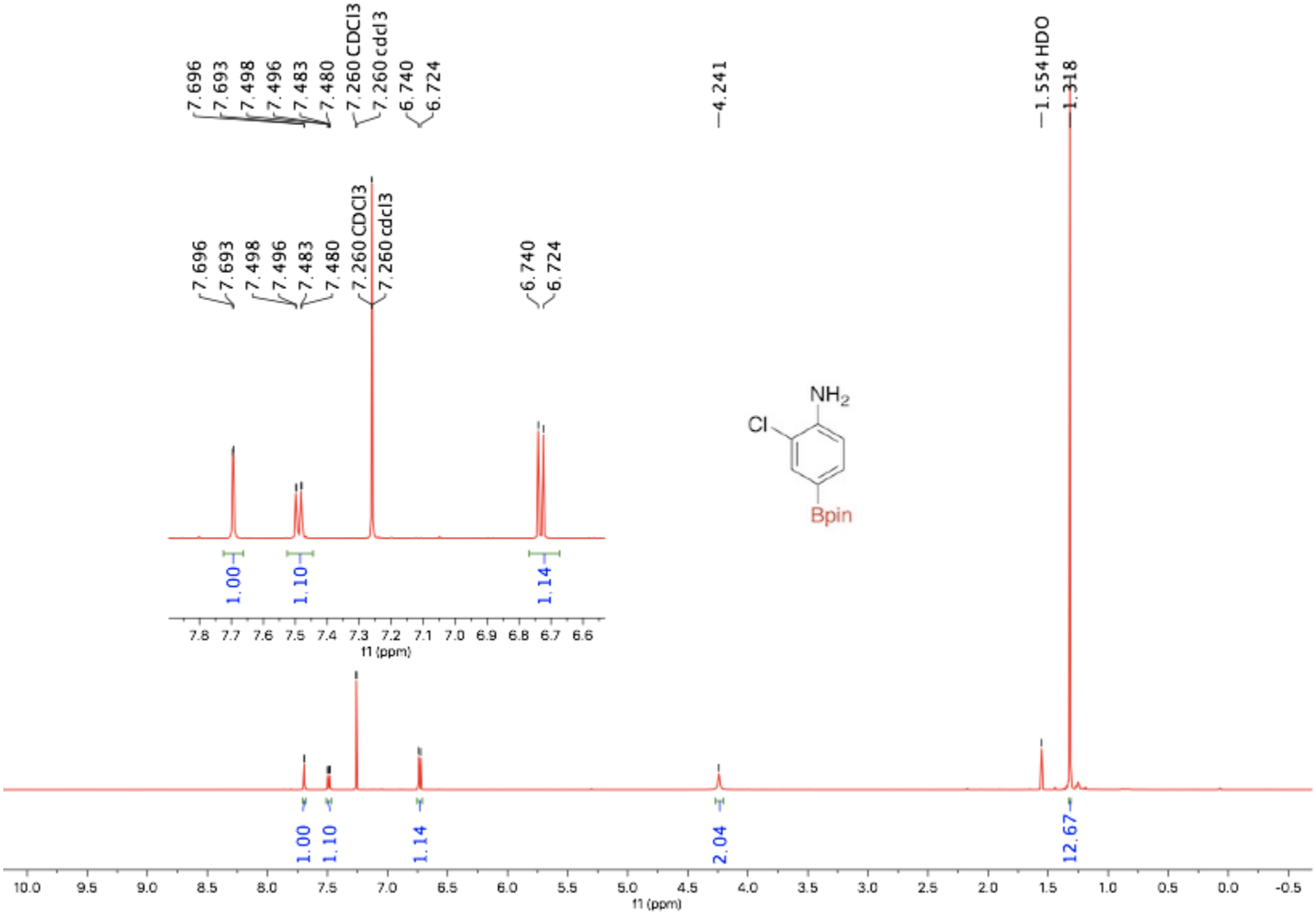
^{1}H NMR spectrum of para borylated 2-chloroaniline (4a)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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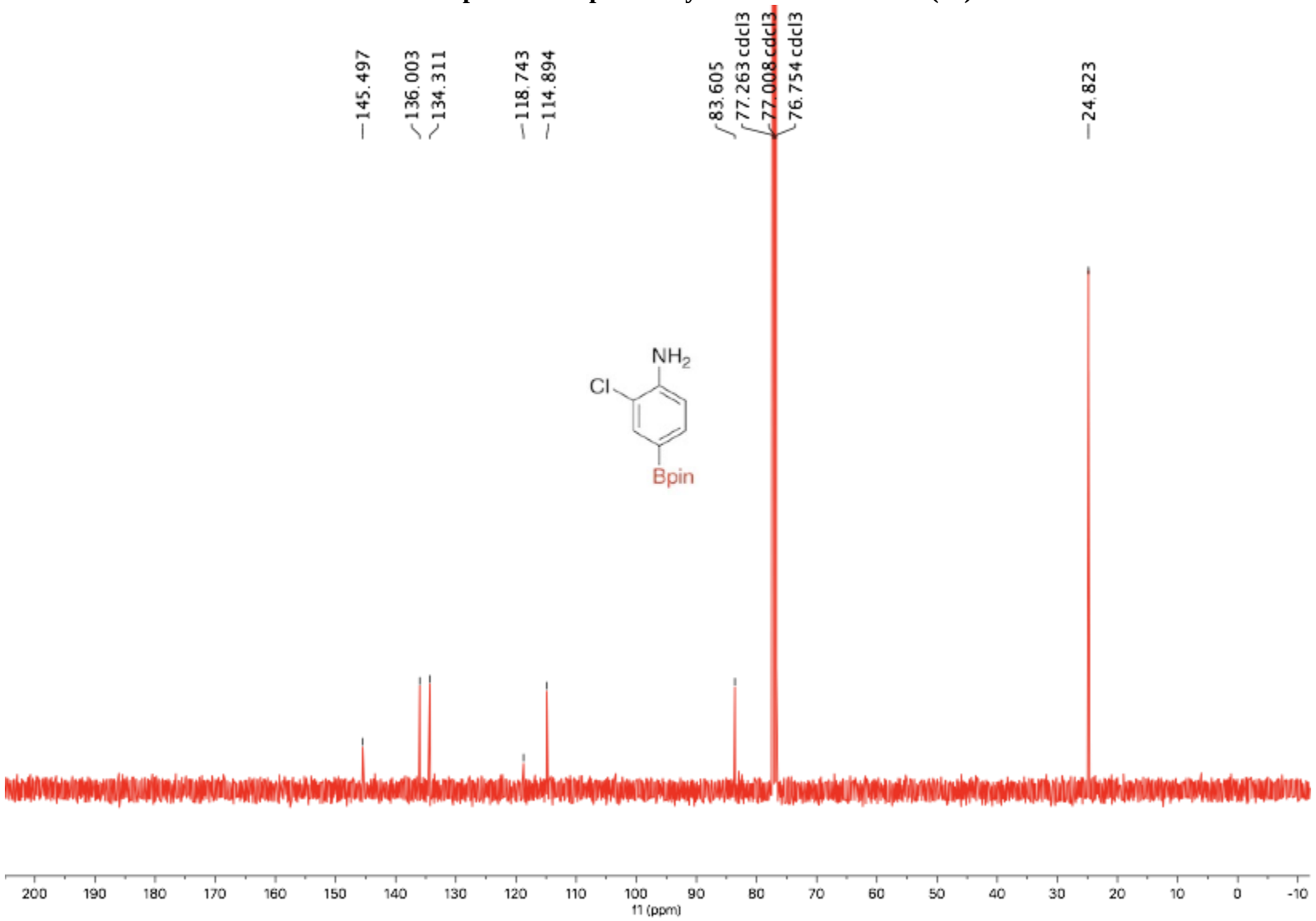
^{13}C NMR spectrum of para borylated 2-chloroaniline (4a)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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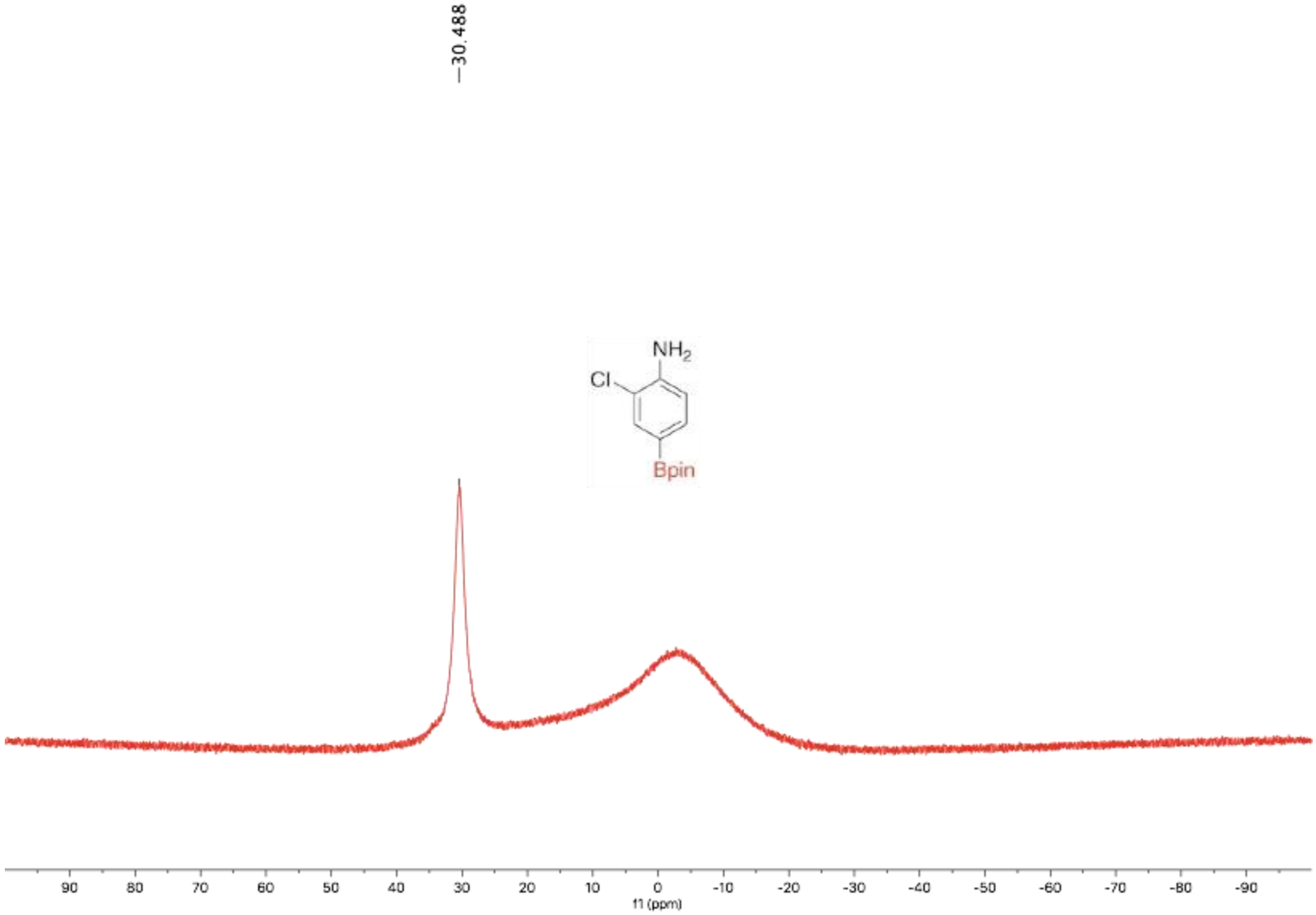
^{11}B NMR spectrum of para borylated 2-chloroaniline (4a)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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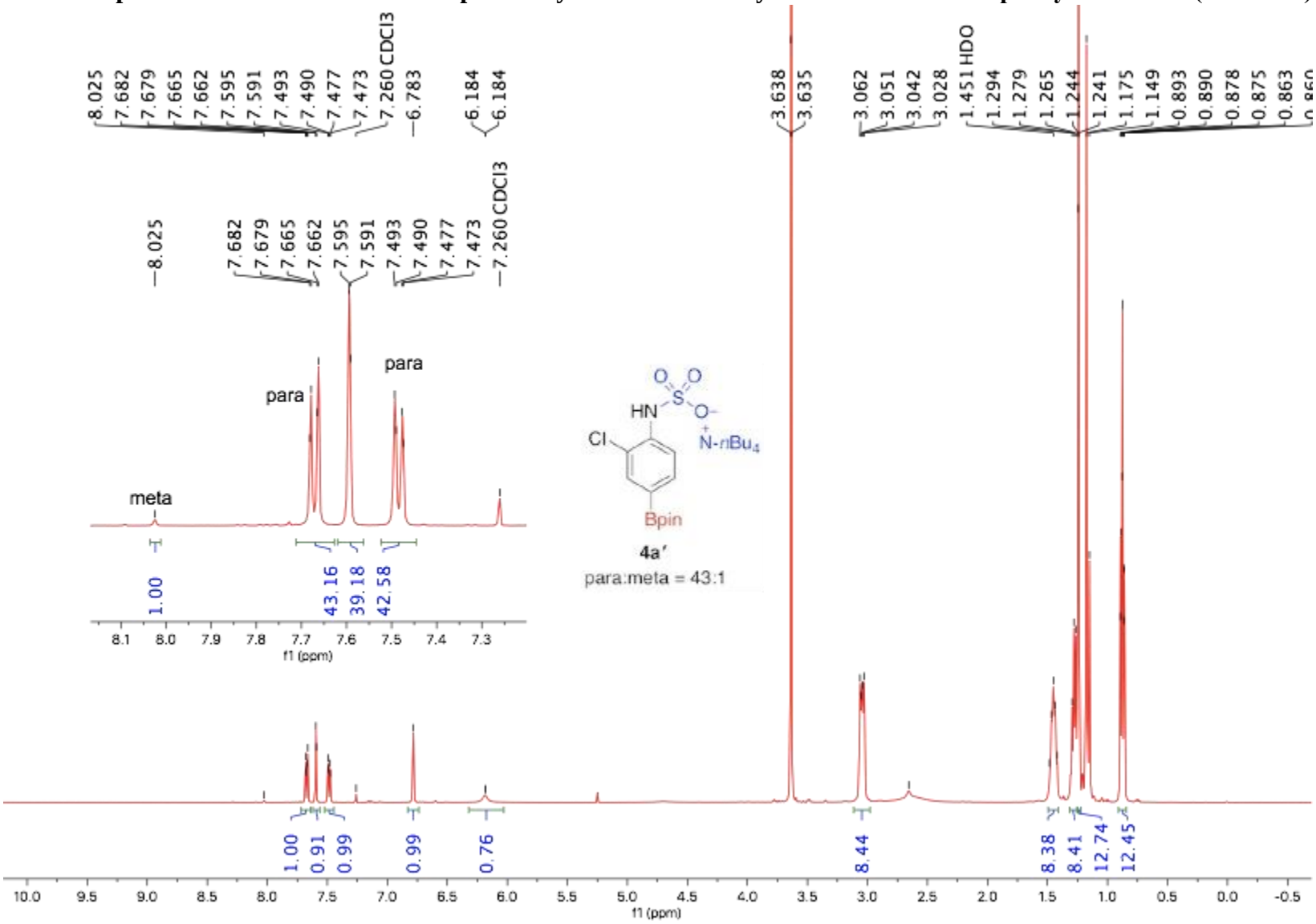
^{1}H NMR spectrum of reaction mixture of para borylation of tetrabutylammonium 2-chlorophenylsulfamate (crude 4a′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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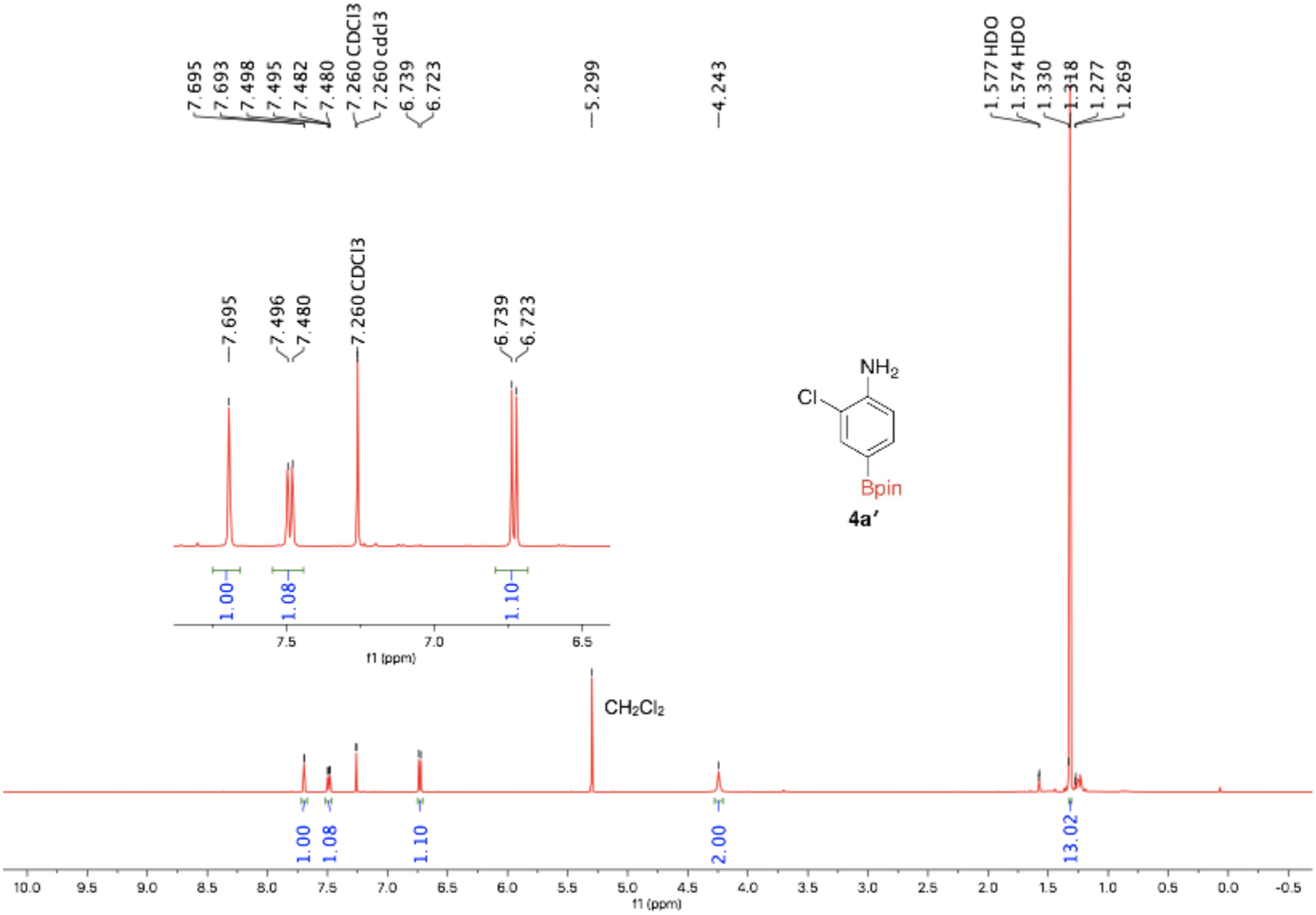
^{1}H NMR spectrum of para borylated 2-chloroaniline (4a′)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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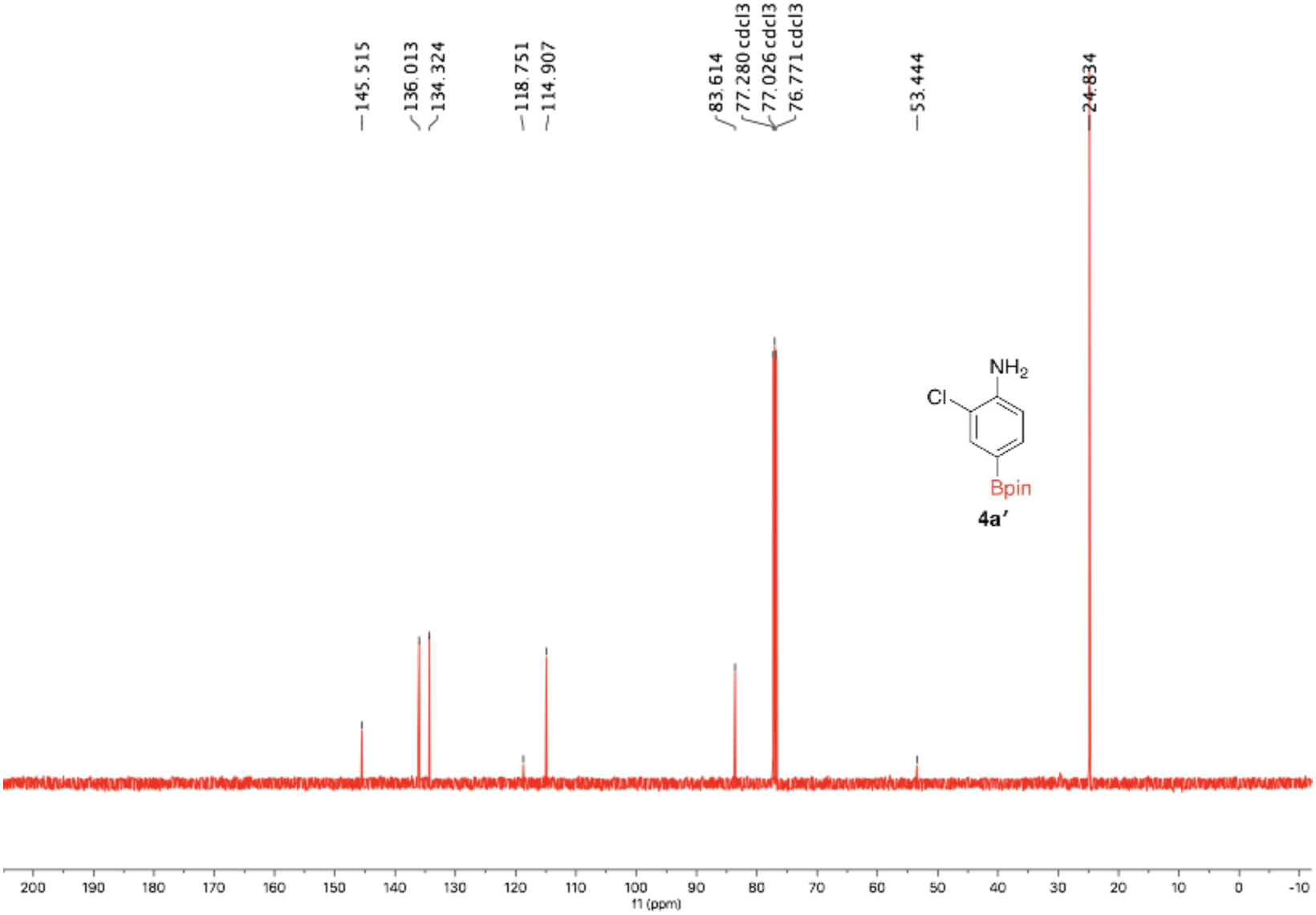
^{13}C NMR spectrum of para borylated 2-chloroaniline (4a′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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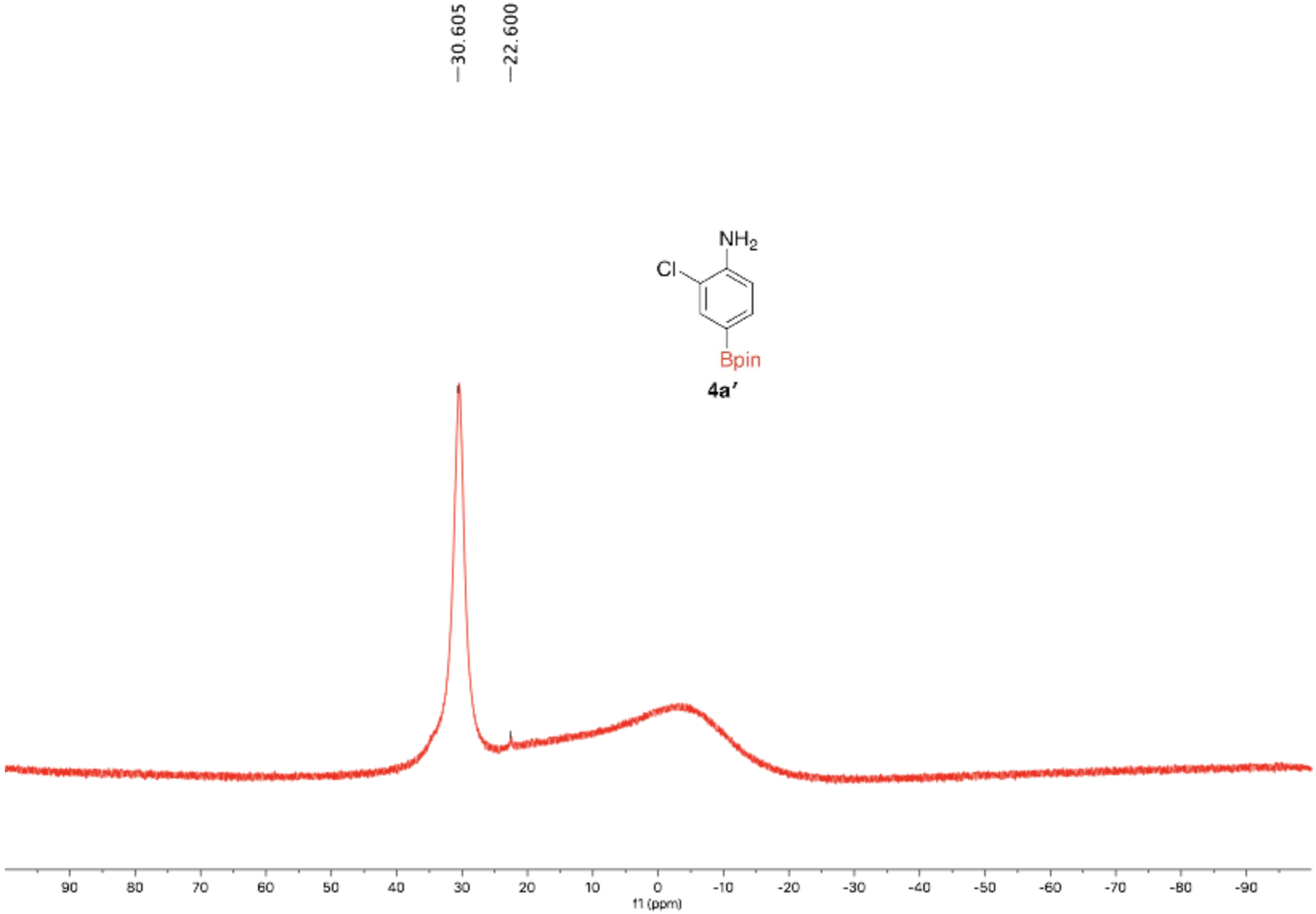
^{11}B NMR spectrum of para borylated 2-chloroaniline (4a′)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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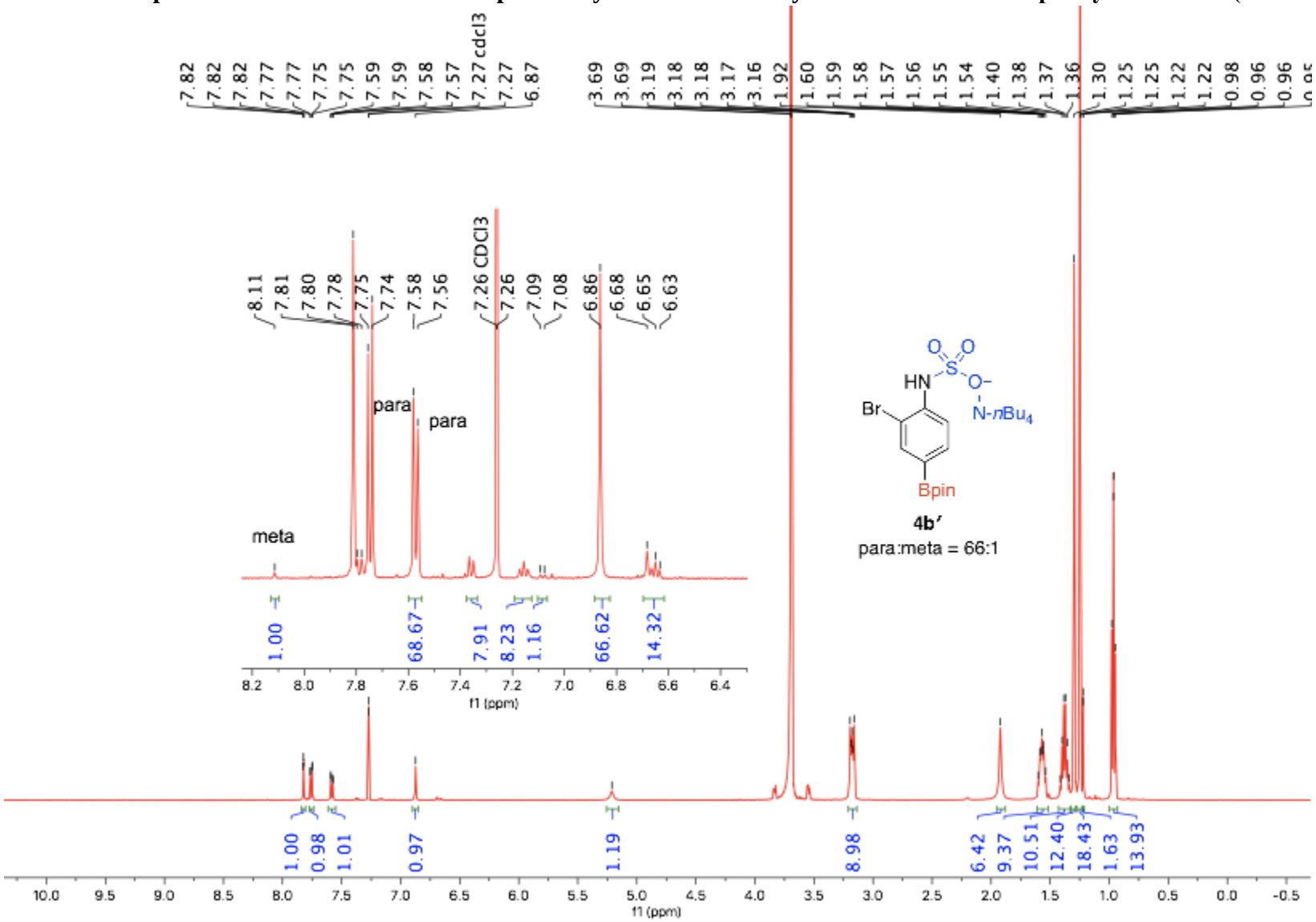
^{1}H NMR spectrum of reaction mixture of para borylation of tetrabutylammonium 2-bromophenylsulfamate (crude 4b′)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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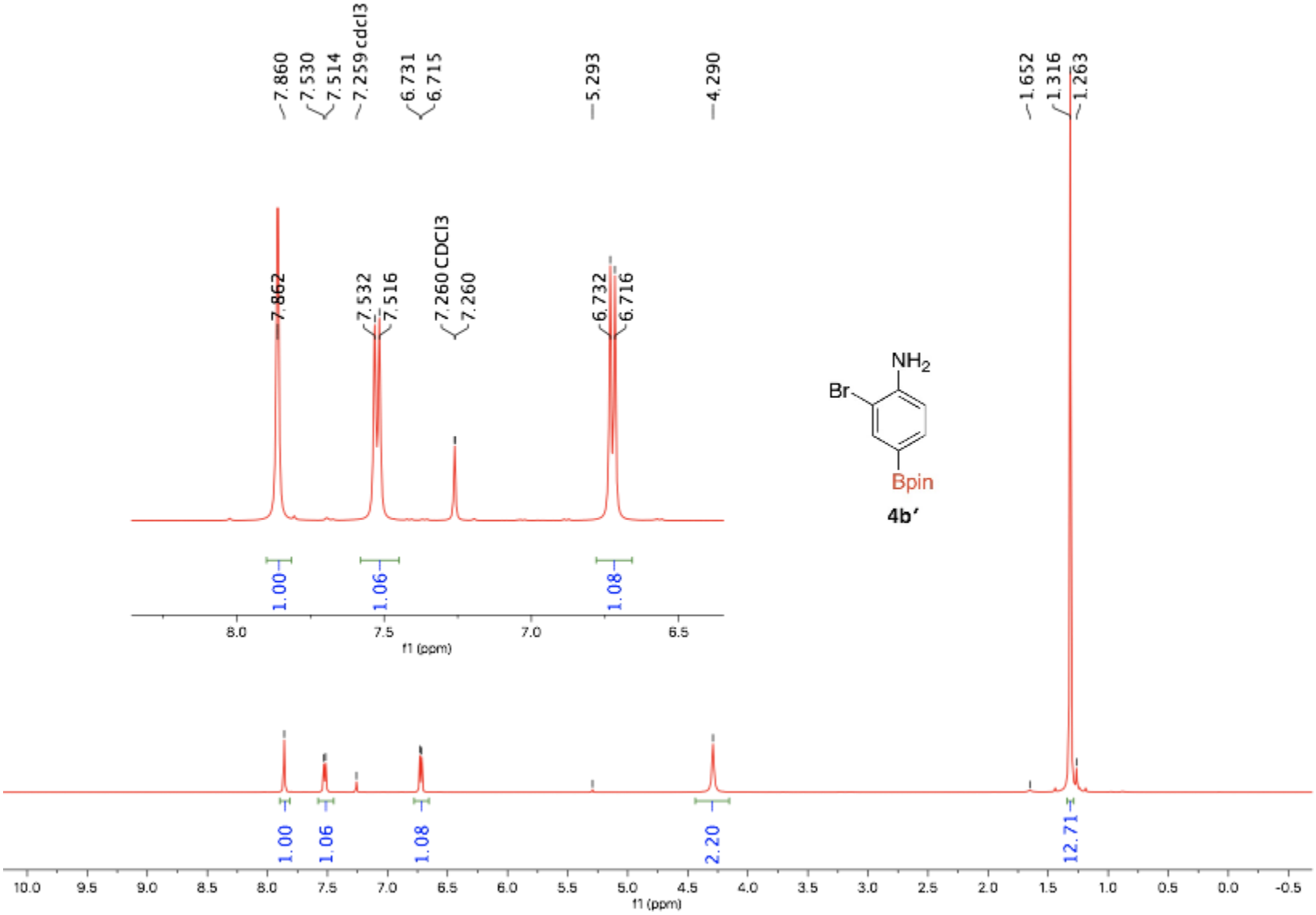
^{1}H NMR spectrum of para-borylated 2-bromoaniline (4b′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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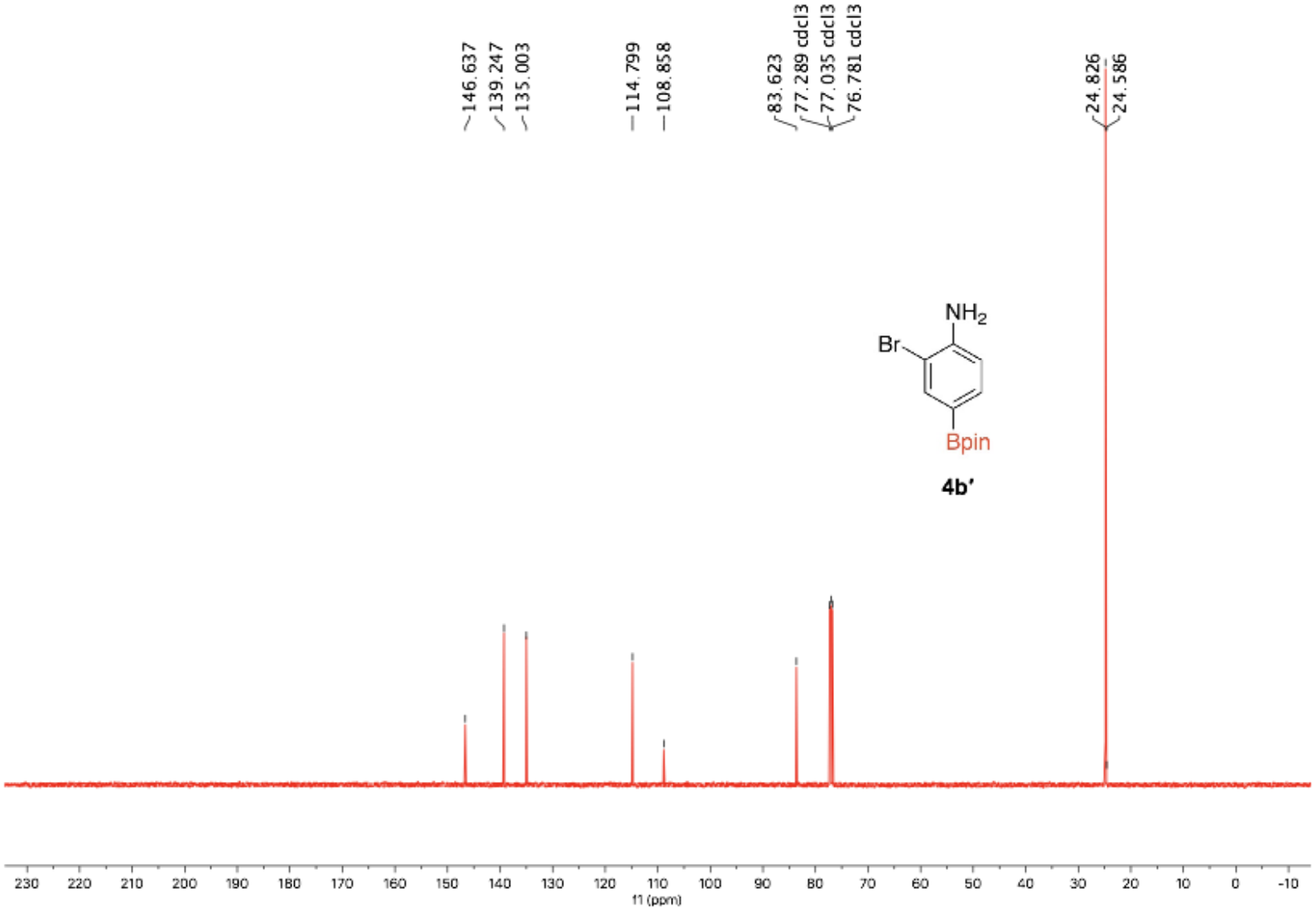
^{13}C NMR spectrum of para-borylated 2-bromoaniline (4b′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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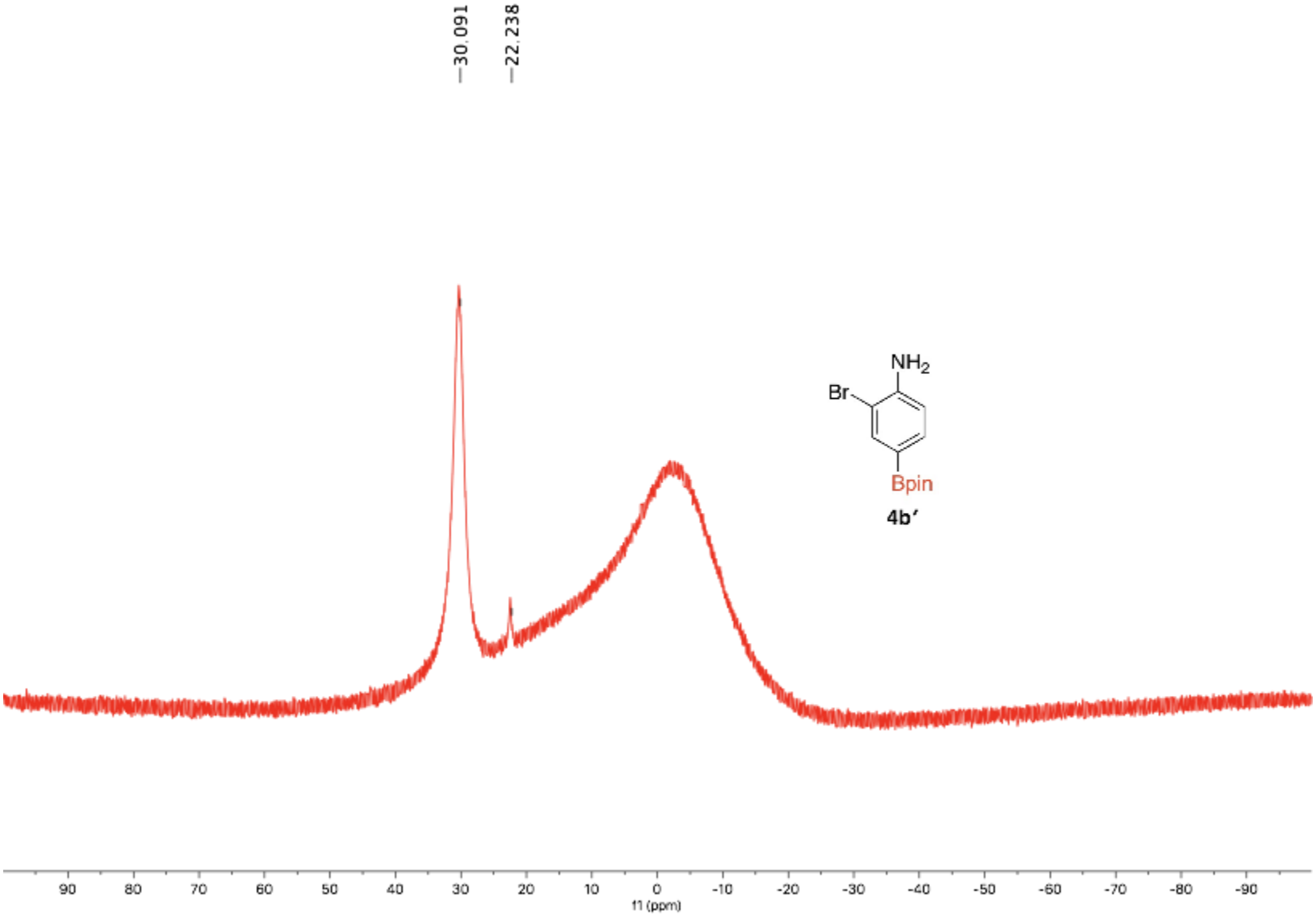
^{11}B NMR spectrum of para borylated 2-bromoaniline (4b′)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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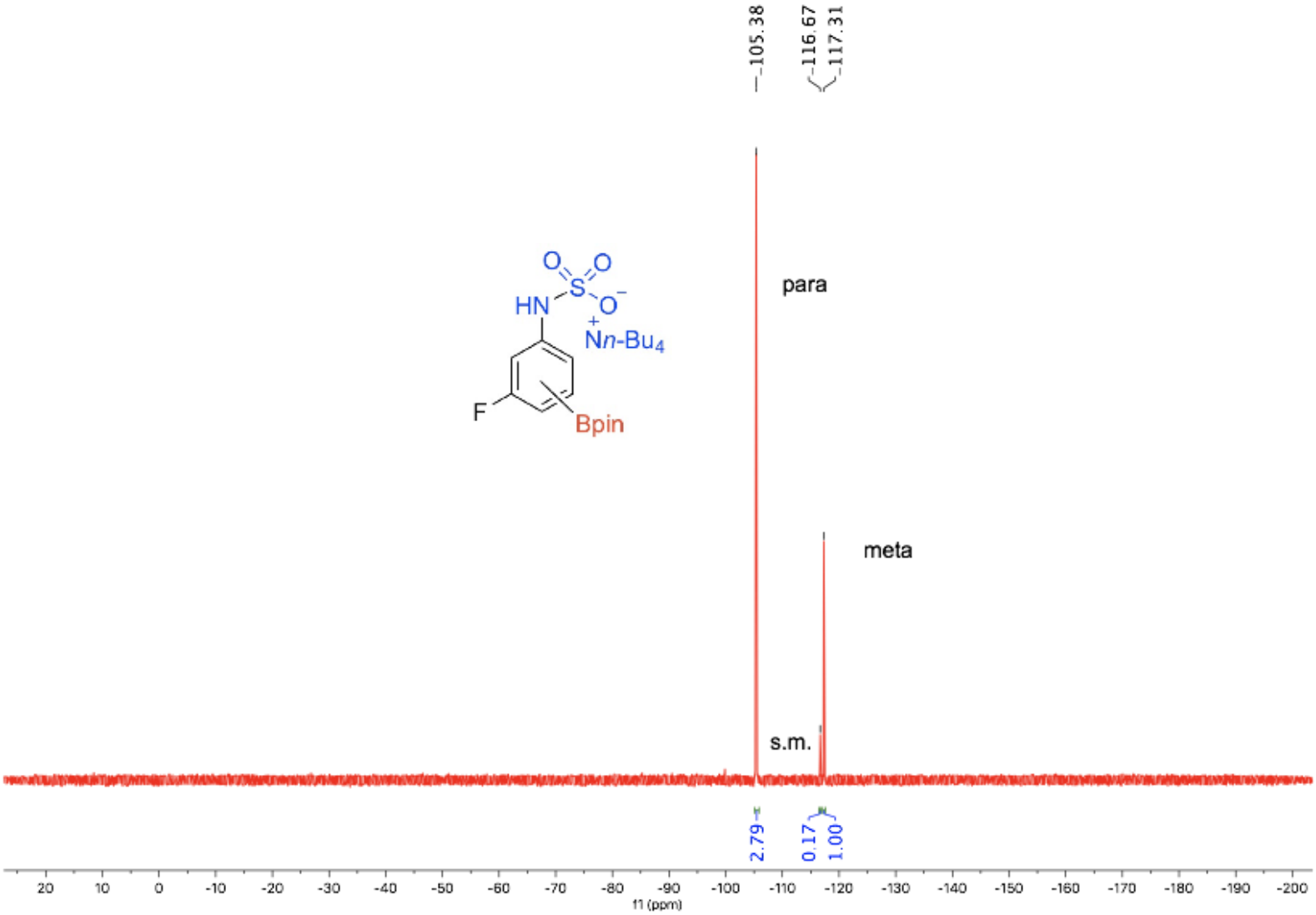
^{19}F NMR spectrum of reaction mixture of para borylation of tetrabutylammonium 3-fluorophenylsulfamate (crude 4c′)



Conditions: 25 ºC, 470 MHz, $CDCl_3$

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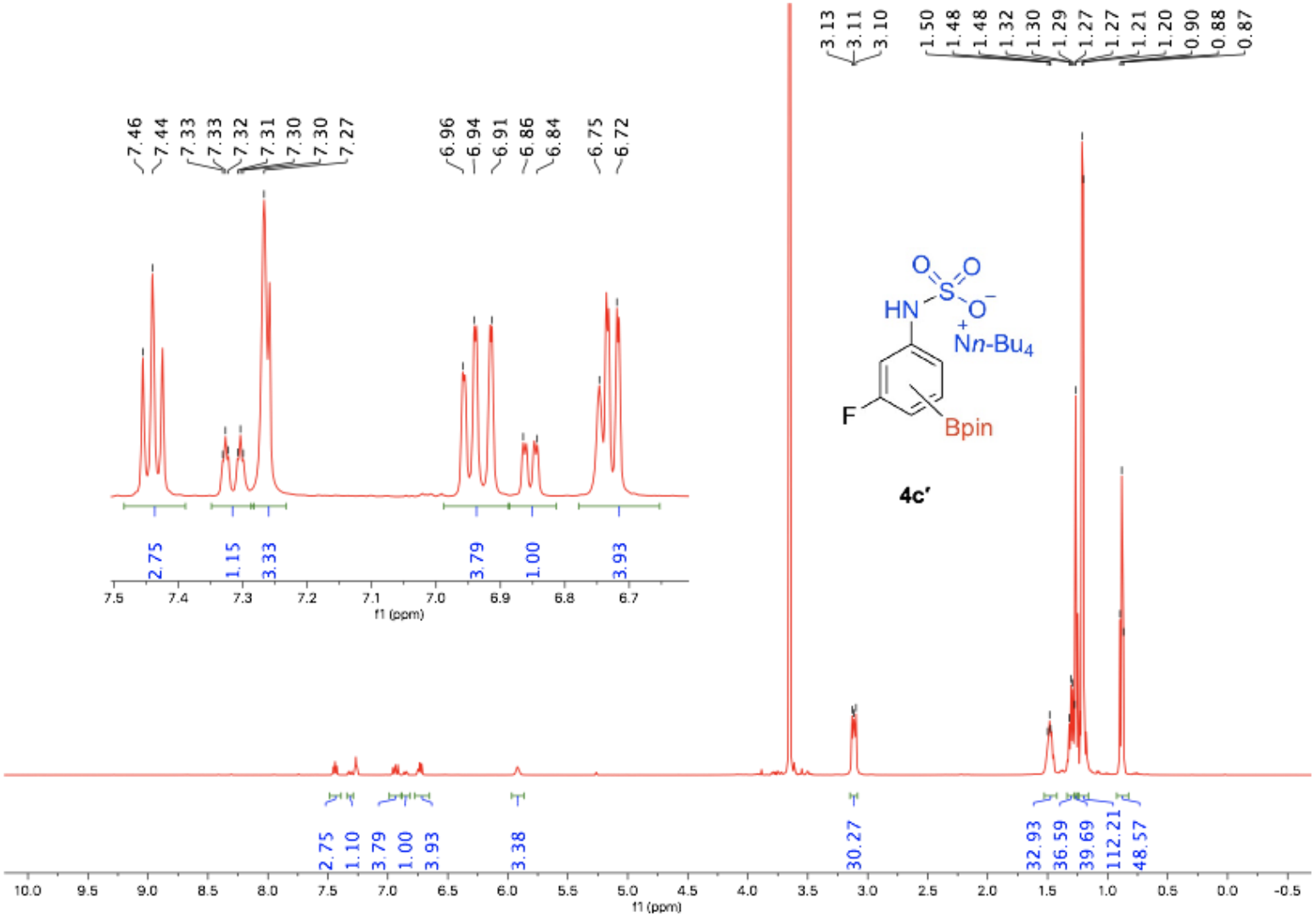
^{1}H NMR spectrum of reaction mixture of para borylation of tetrabutylammonium 3-fluorophenylsulfamate (crude 4c′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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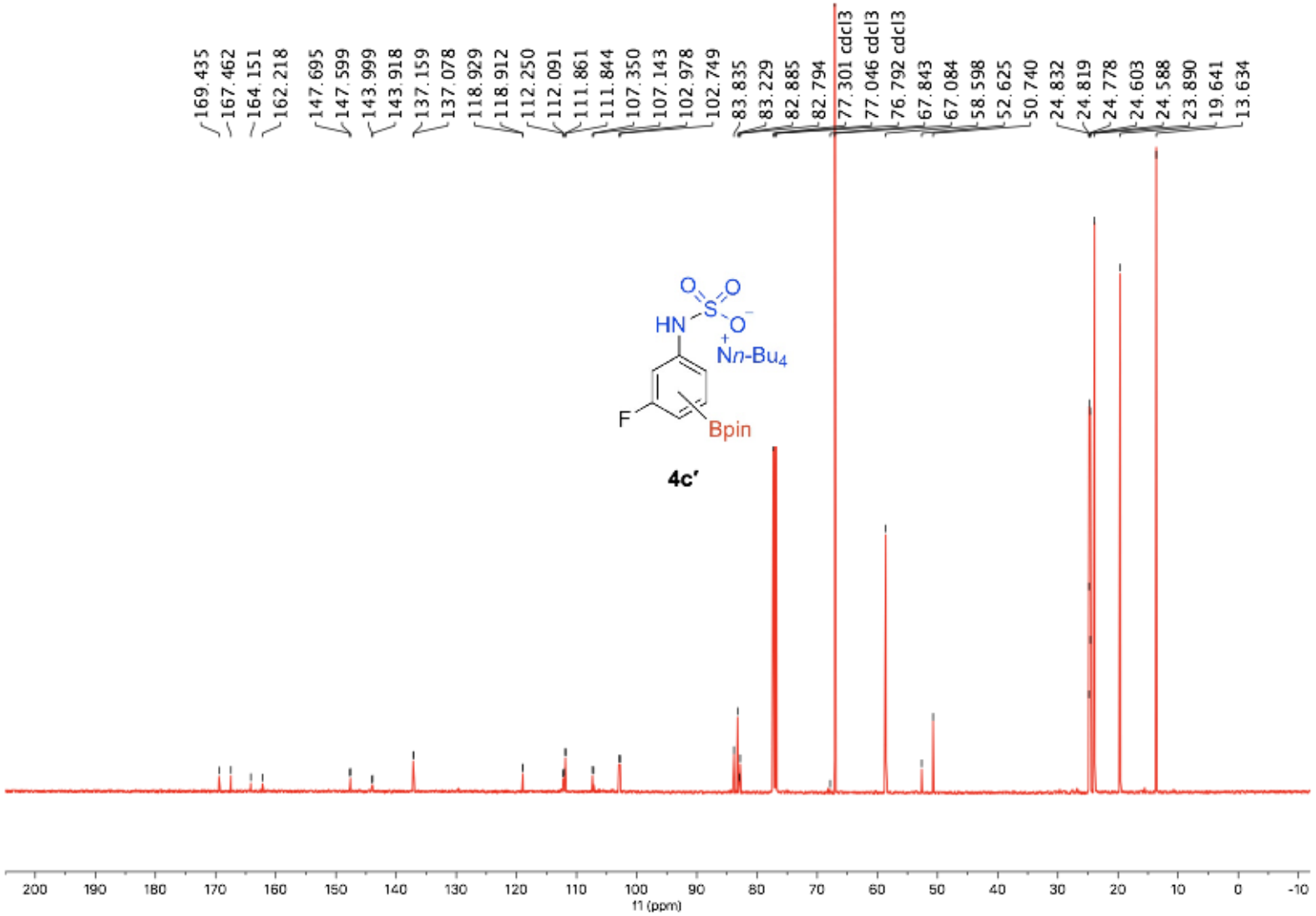
^{13}C NMR spectrum of reaction mixture of para borylation of tetrabutylammonium 3-fluorophenylsulfamate (crude 4c′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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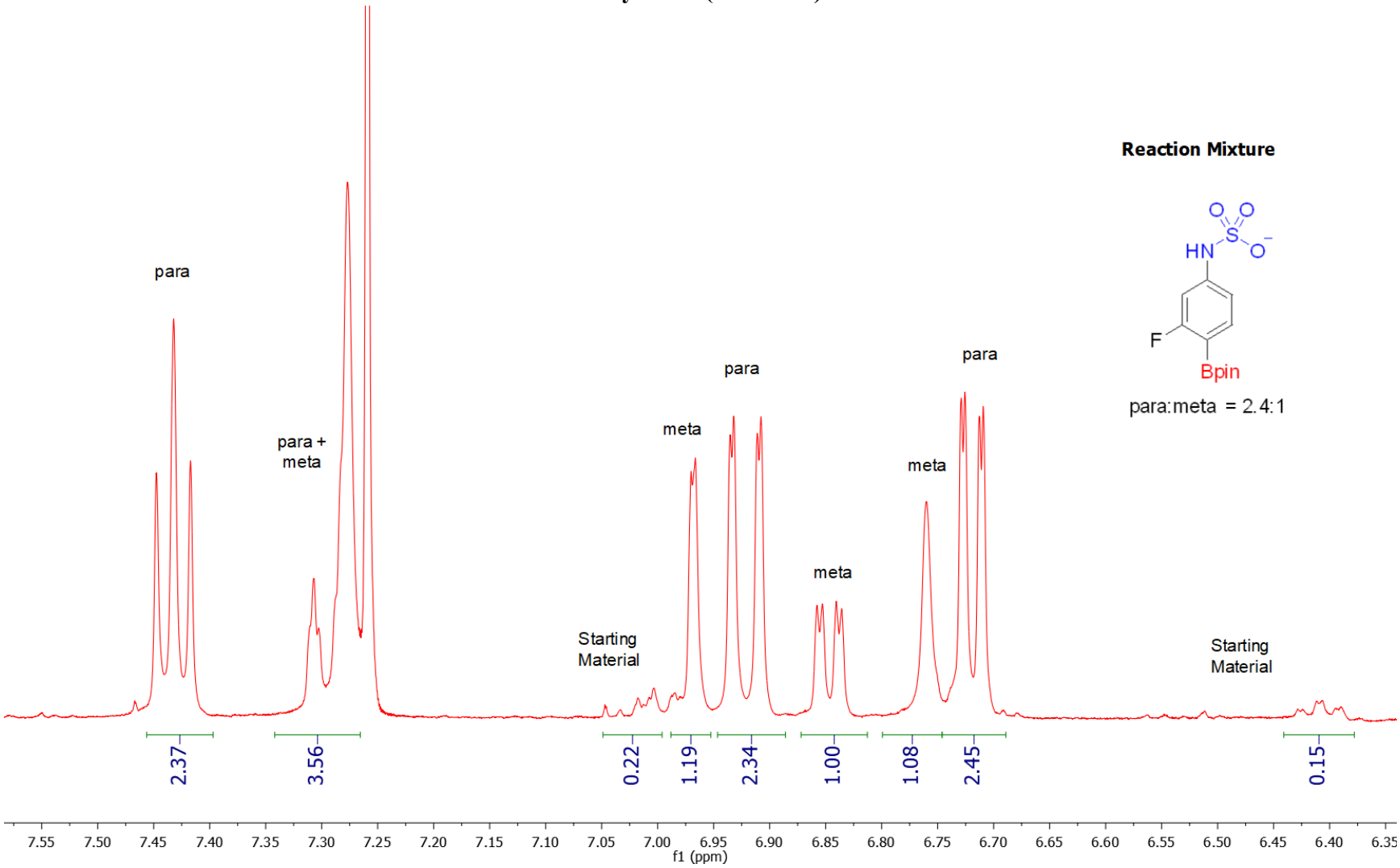
^{1}H NMR spectrum of reaction mixture of para borylation of tetrabutylammonium 3-fluorophenylsulfamate previous acetylation (crude 4c′)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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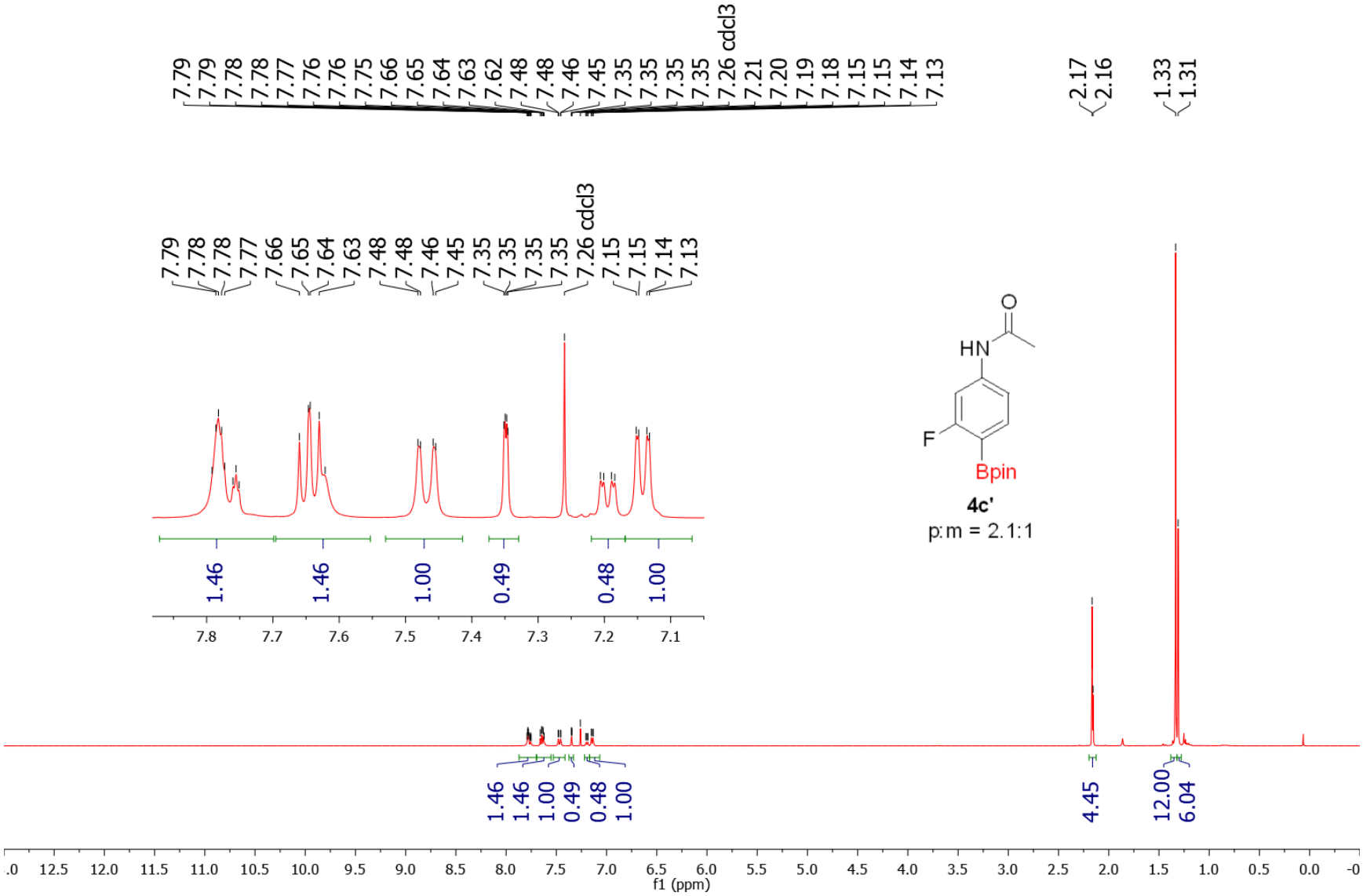
^{1}H NMR spectrum of para borylated N-(3-fluorophenyl)acetamide (4c′)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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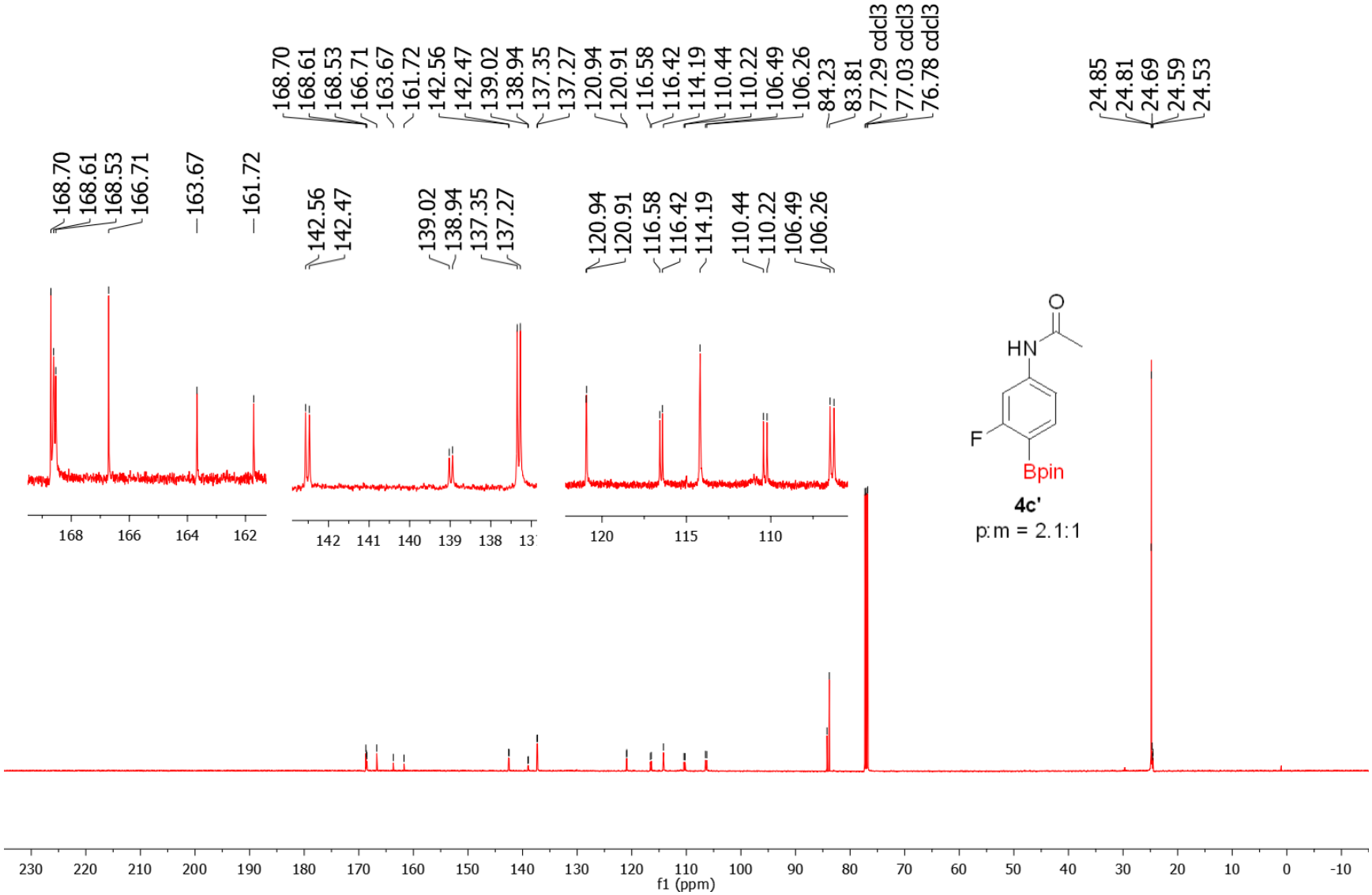
^{13}C NMR spectrum of para borylated N-(3-fluorophenyl)acetamide (4c′)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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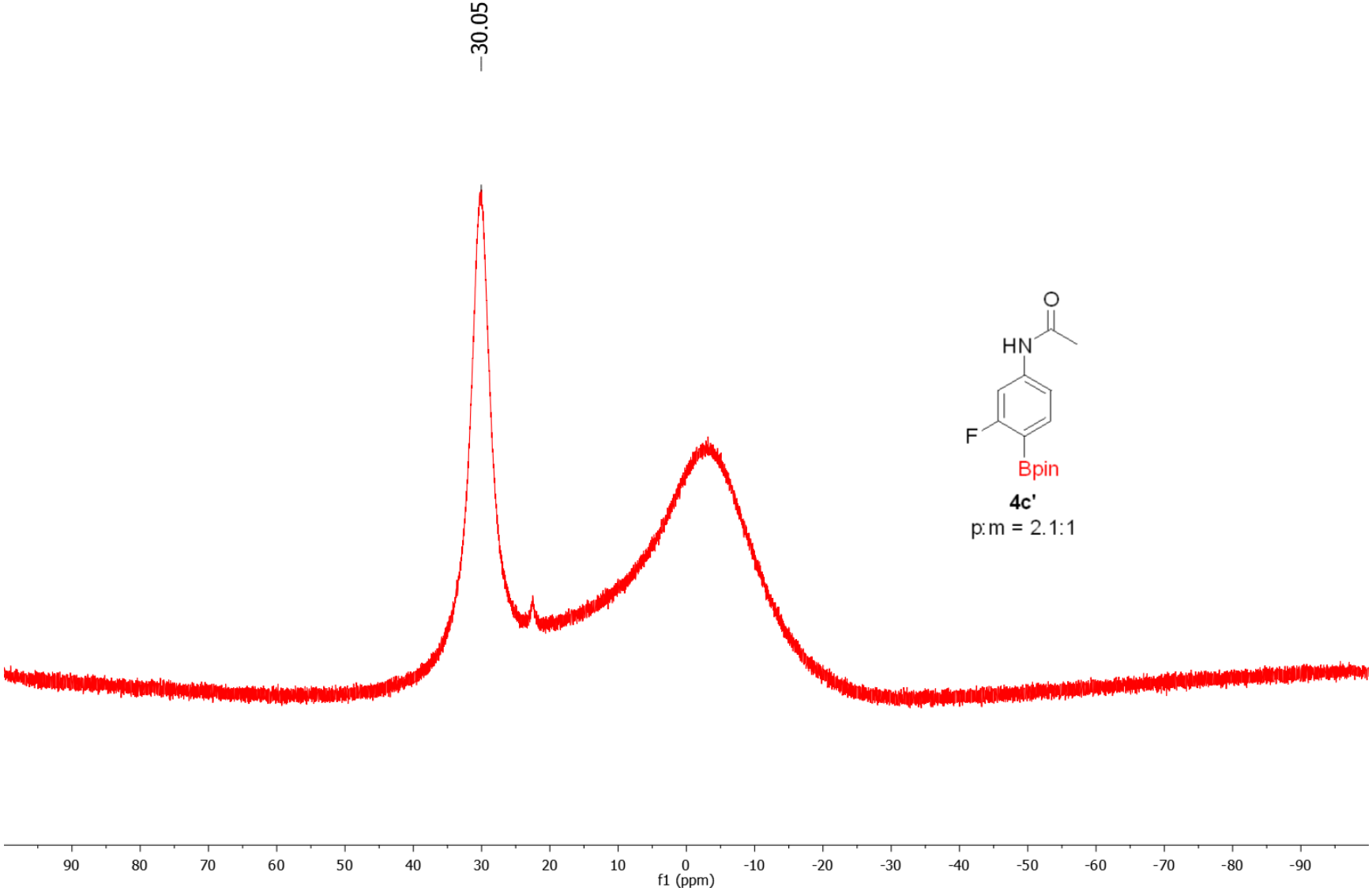
^{11}B NMR spectrum of para borylated N-(3-fluorophenyl)acetamide (4c′)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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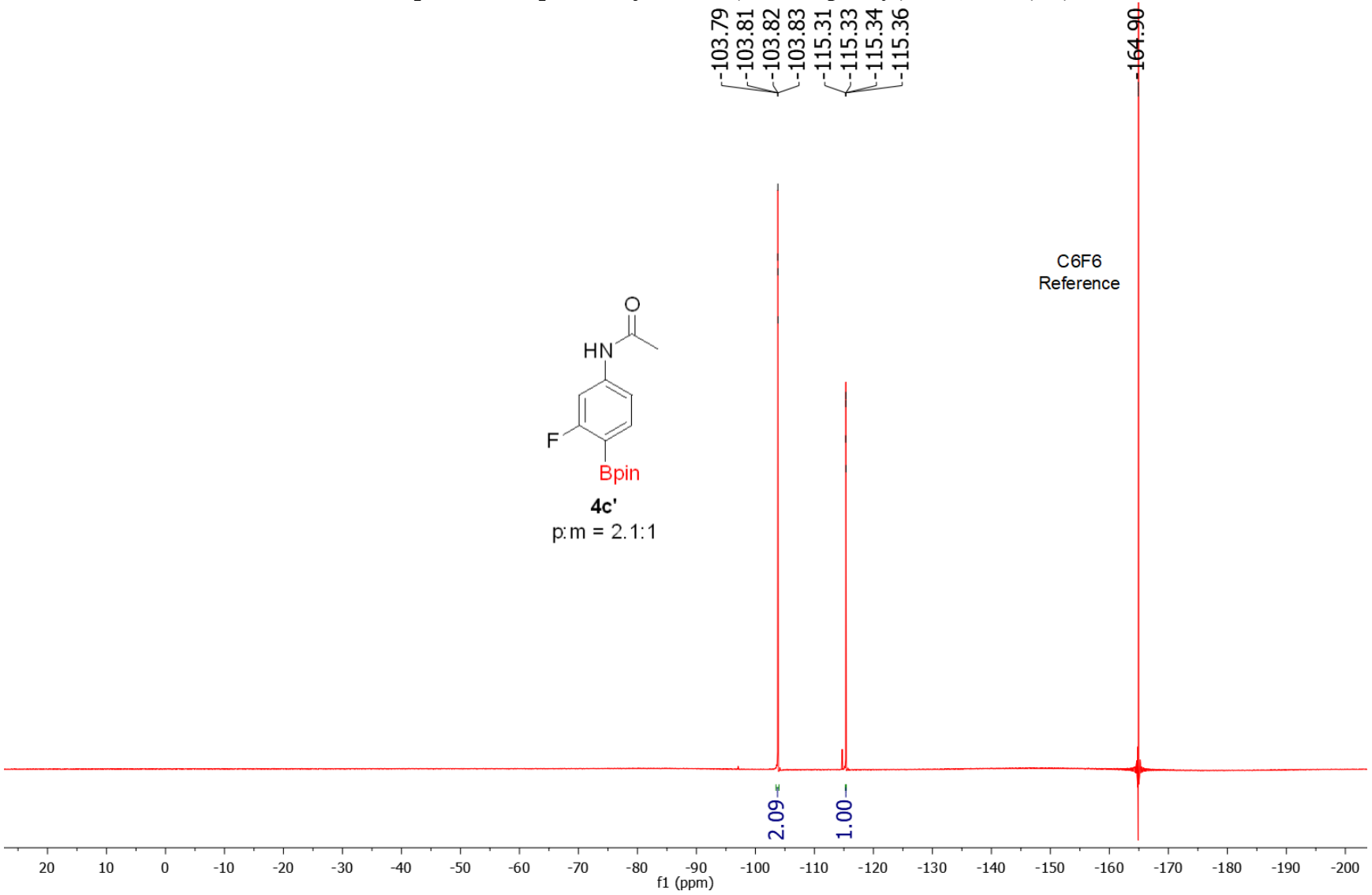
^{19}F NMR spectrum of para borylated N-(3-fluorophenyl)acetamide (4c′)



Conditions: 25 ºC, 470 MHz, $CDCl_3$

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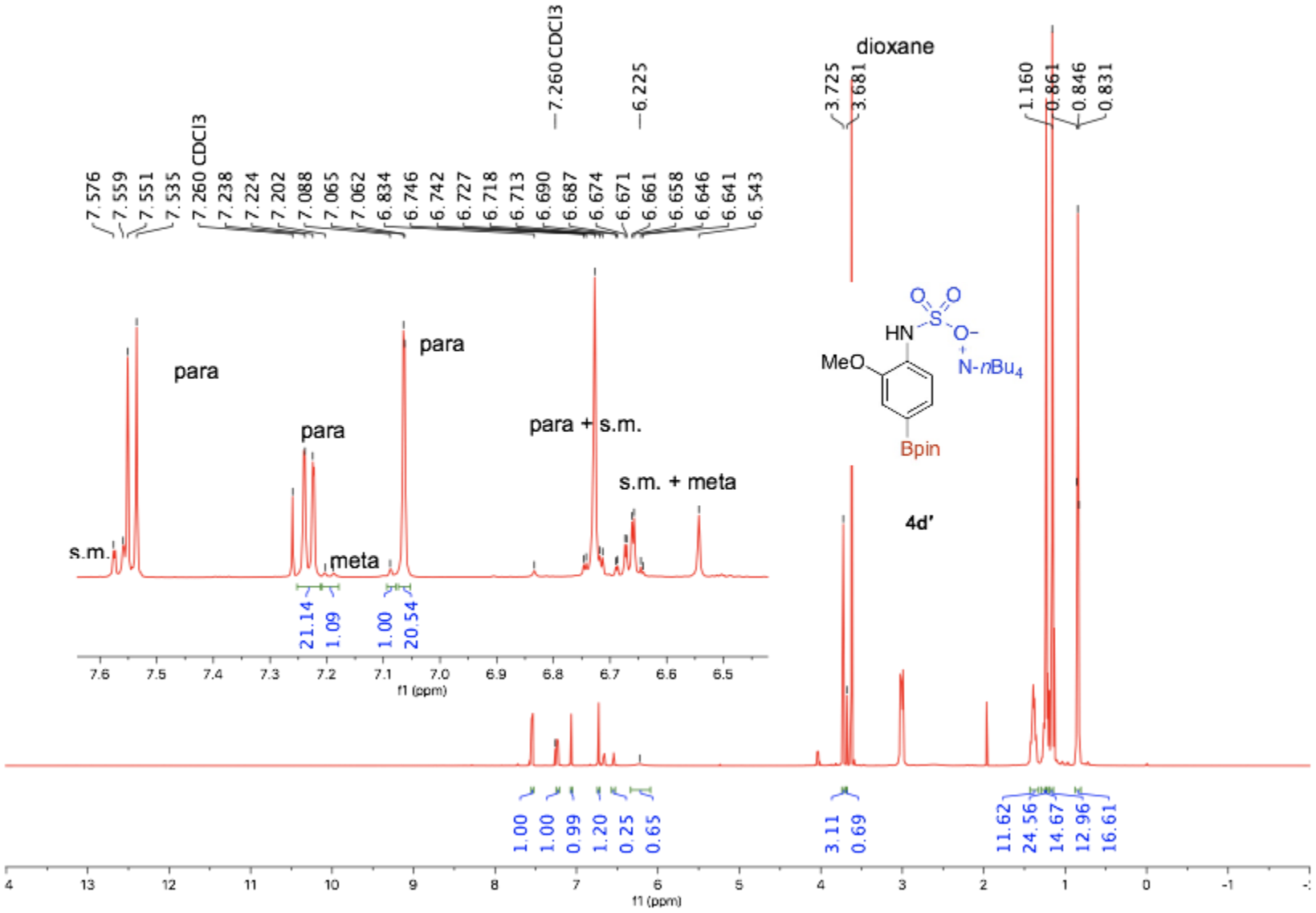
^{1}H NMR spectrum of reaction mixture of para borylation of tetrabutylammonium 2-methoxyphenylsulfamate (crude 4d′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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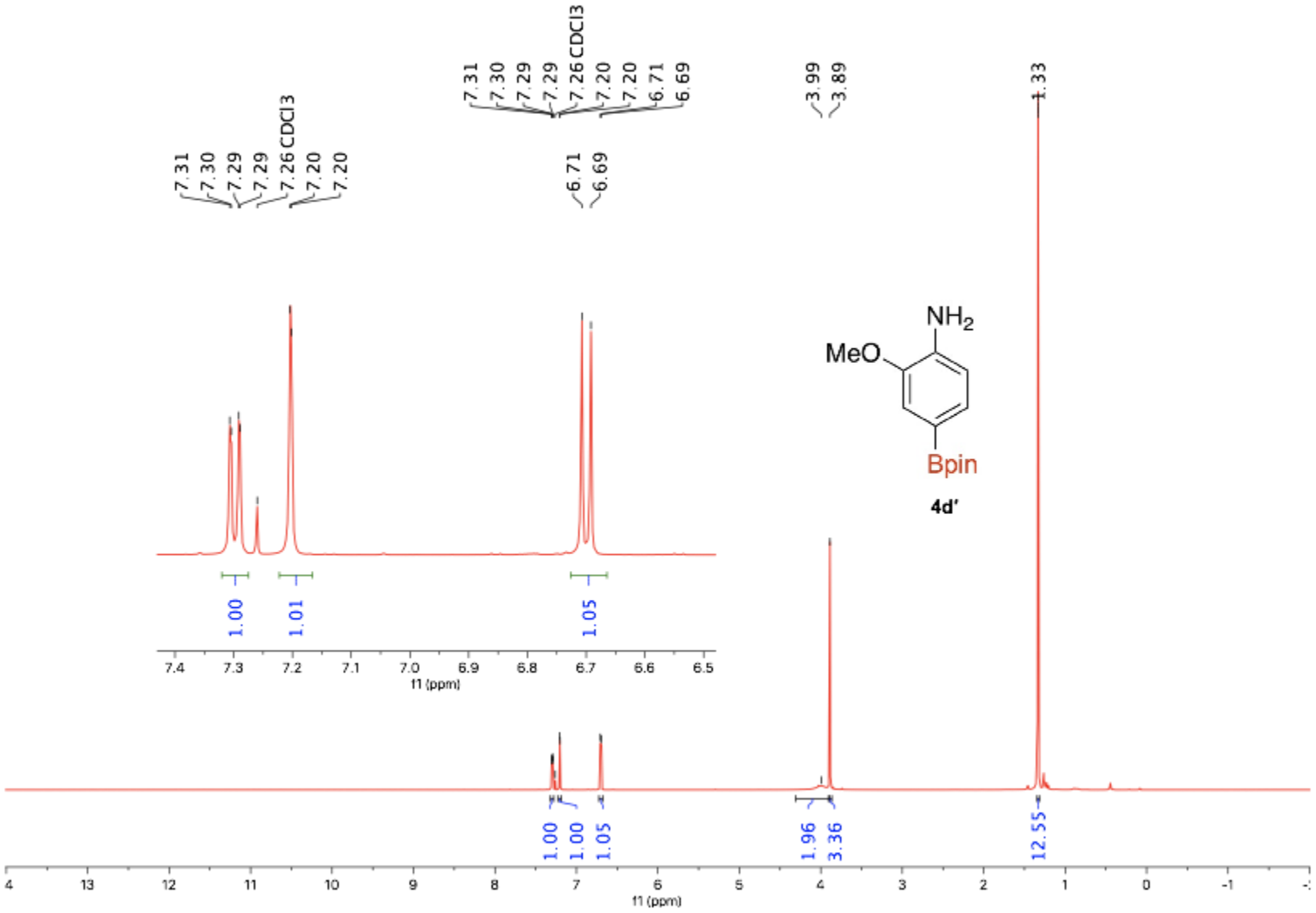
^{1}H NMR spectrum para borylated 2-methoxyaniline (4d′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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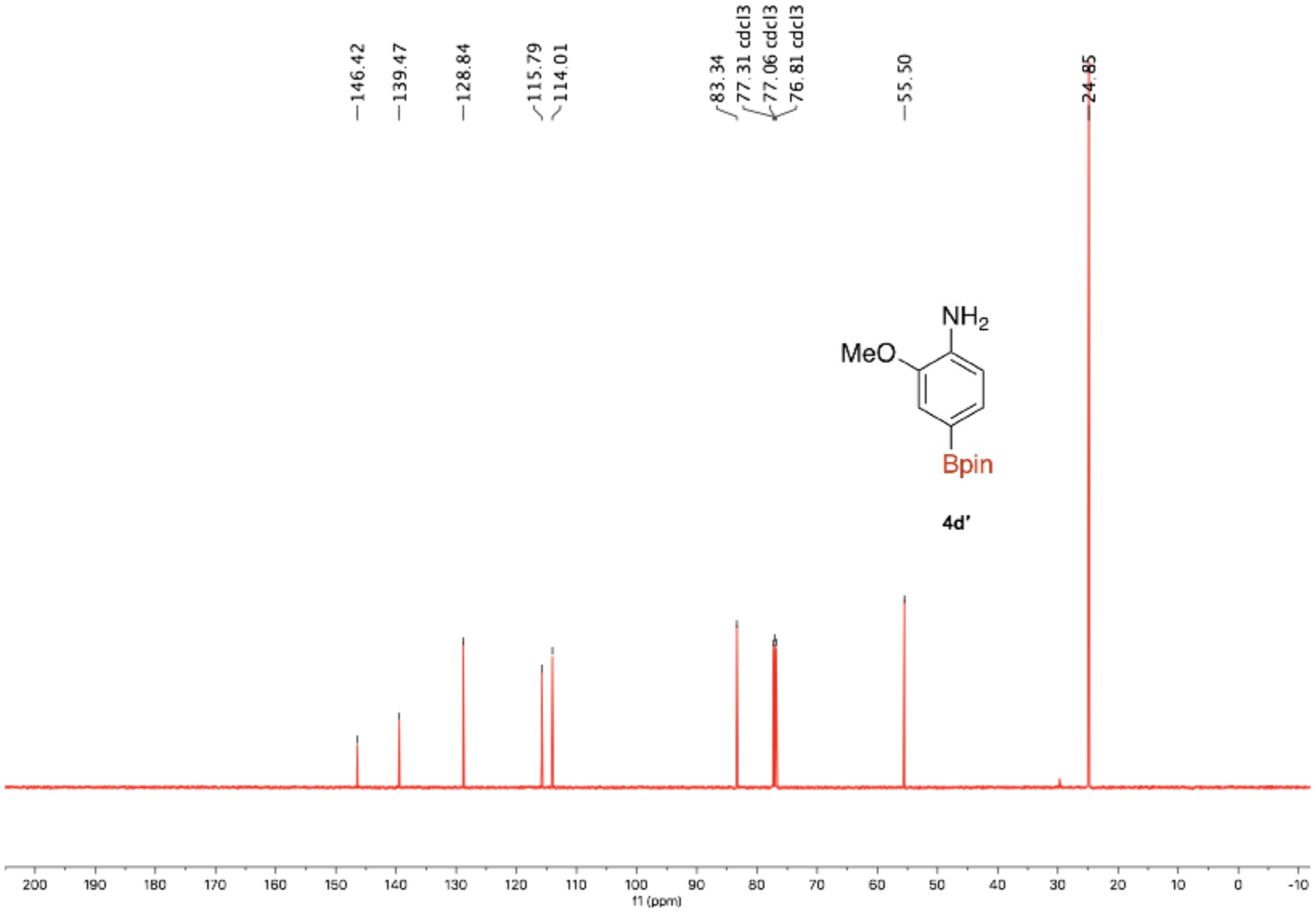
^{13}C NMR spectrum para borylated 2-methoxyaniline (4d′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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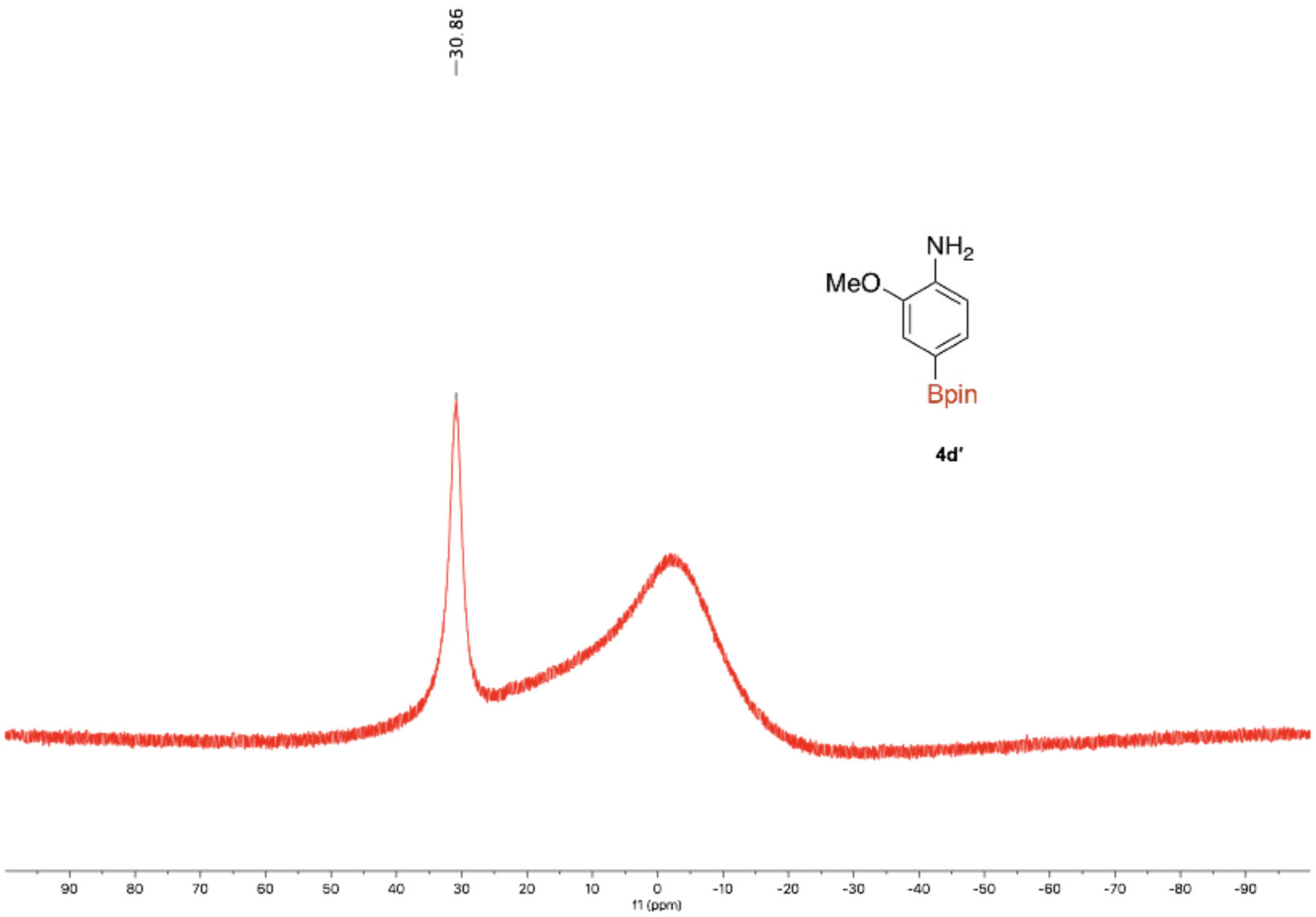
^{11}B NMR spectrum para borylated 2-methoxyaniline (4d′)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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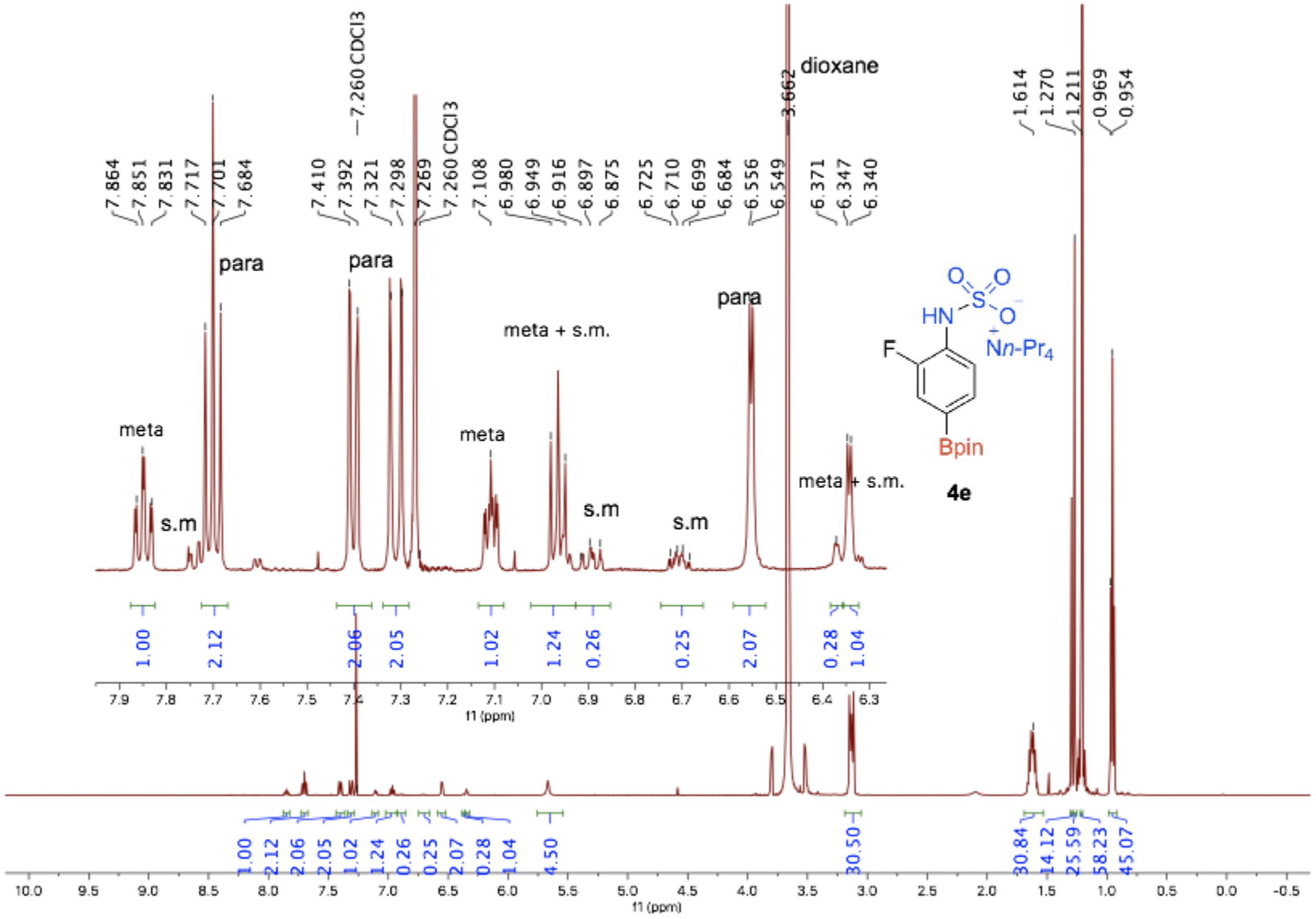
^{1}H NMR spectrum of reaction mixture of para borylation of tetrapropylammonium 2-fluorophenylsulfamate (crude 4e)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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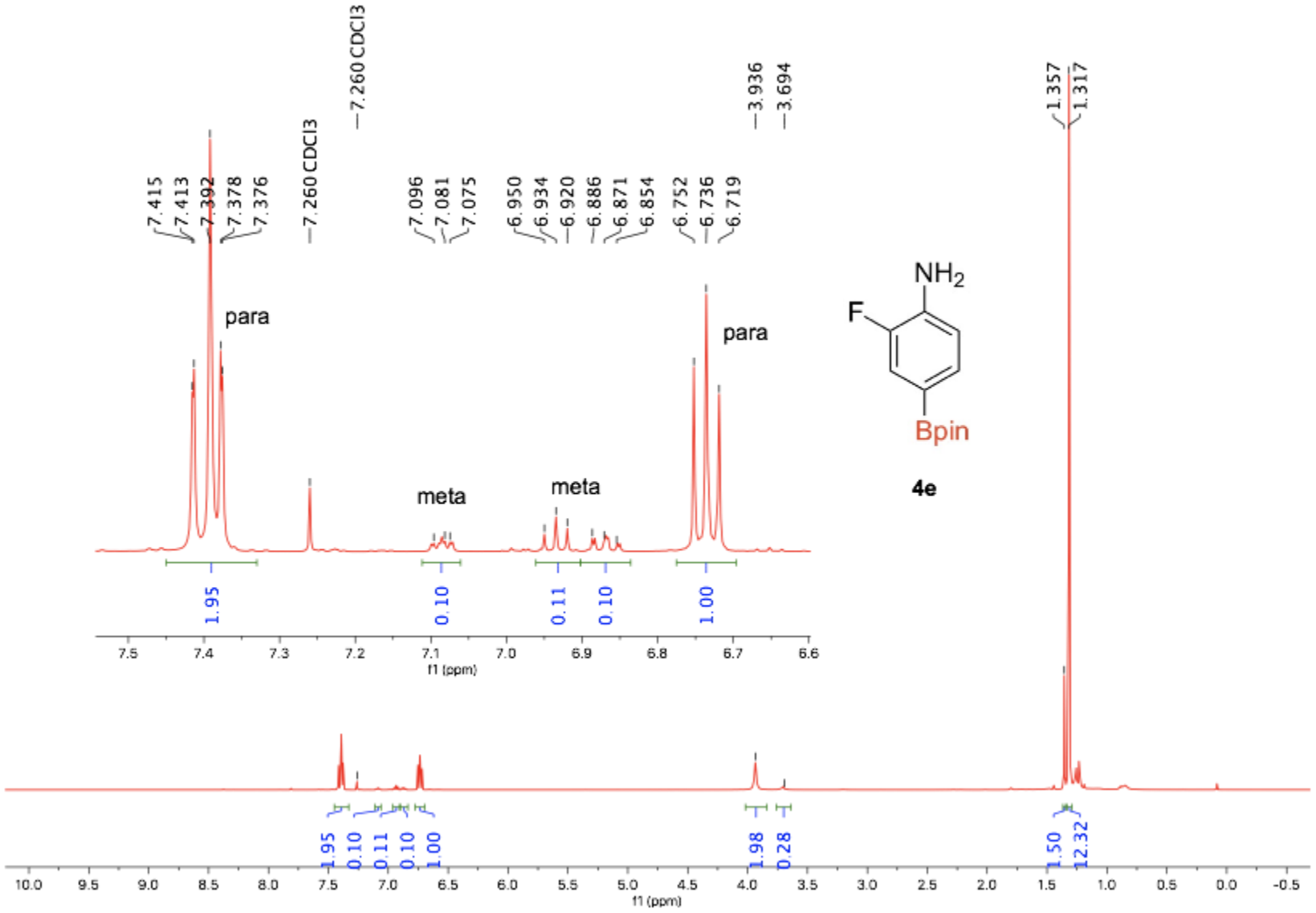
^{1}H NMR spectrum para borylated 2-fluoroaniline (4e)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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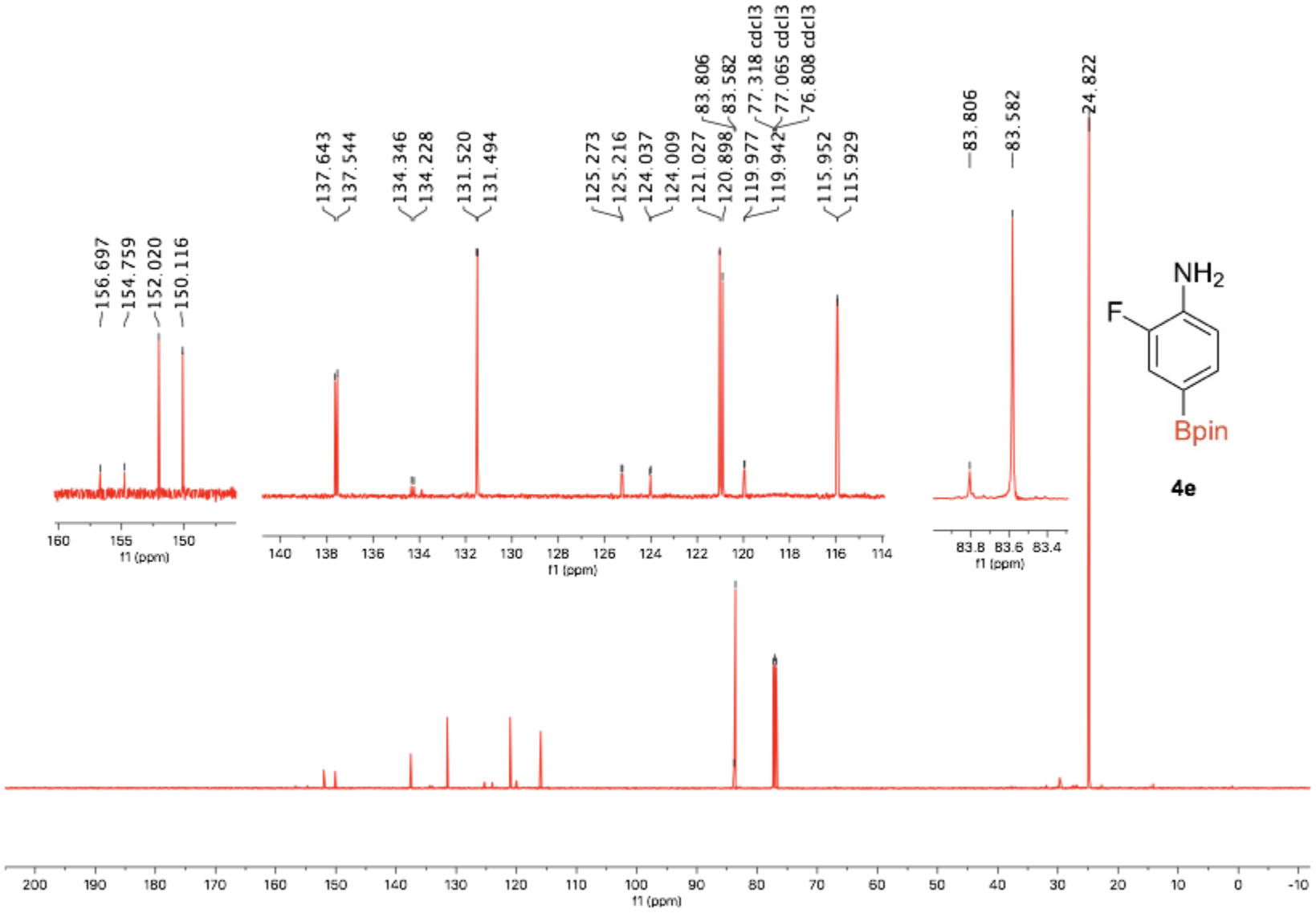
^{13}C NMR spectrum para borylated 2-fluoroaniline (4e)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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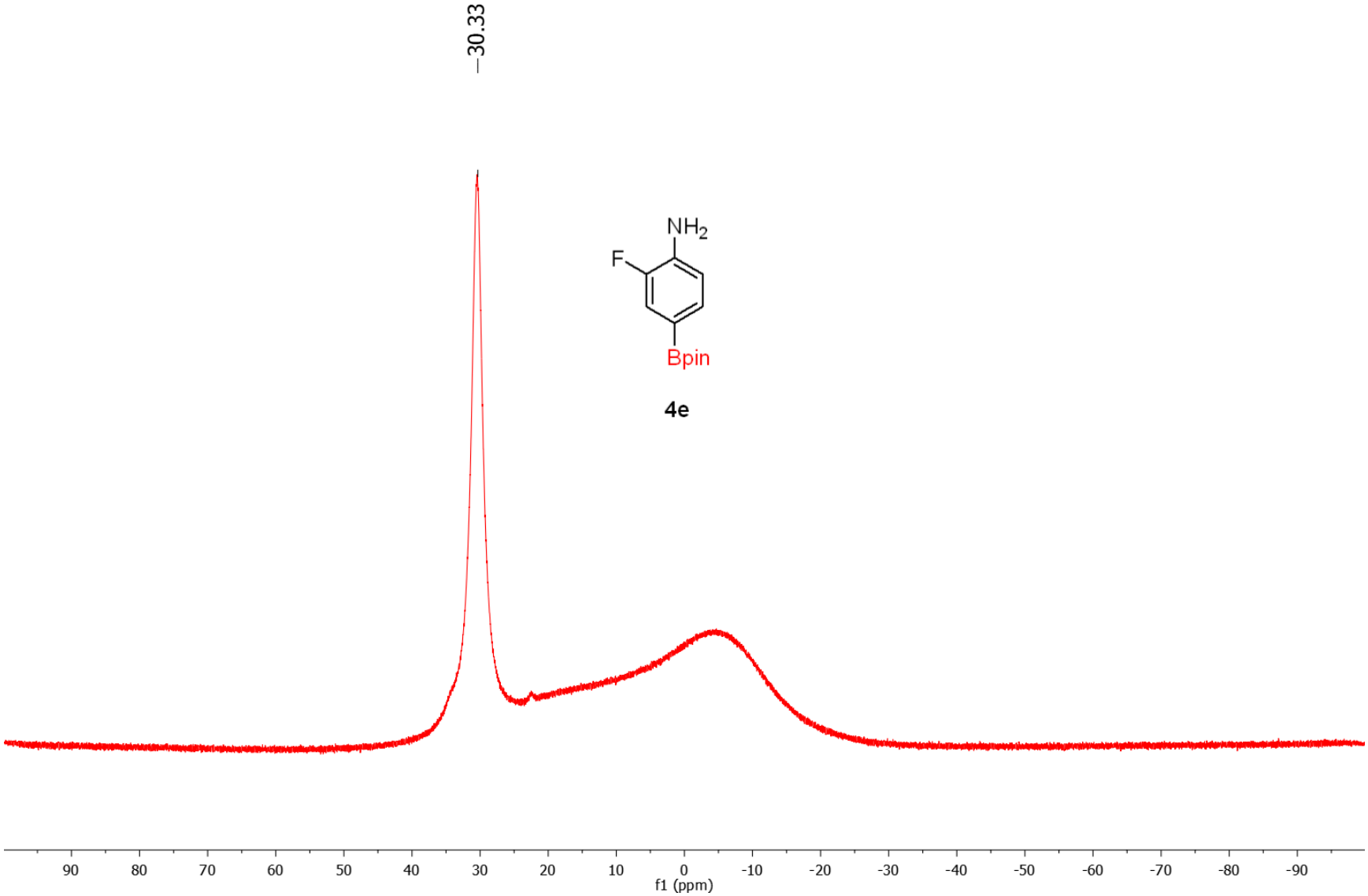
^{11}B NMR spectrum para borylated 2-fluoroaniline (4e)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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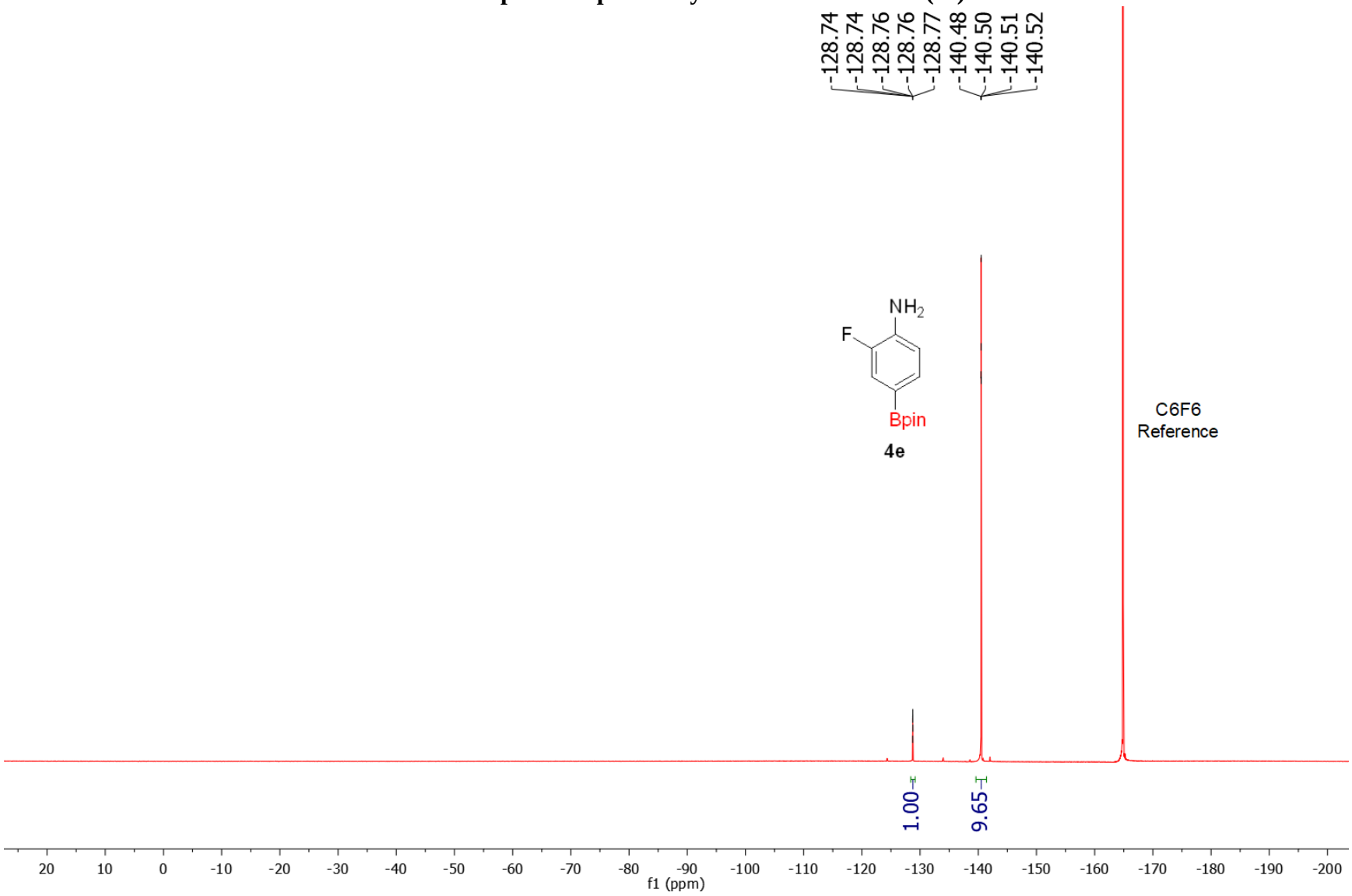
^{19}F NMR spectrum para borylated 2-fluoroaniline (4e)



Conditions: 25 ºC, 470 MHz, $CDCl_3$

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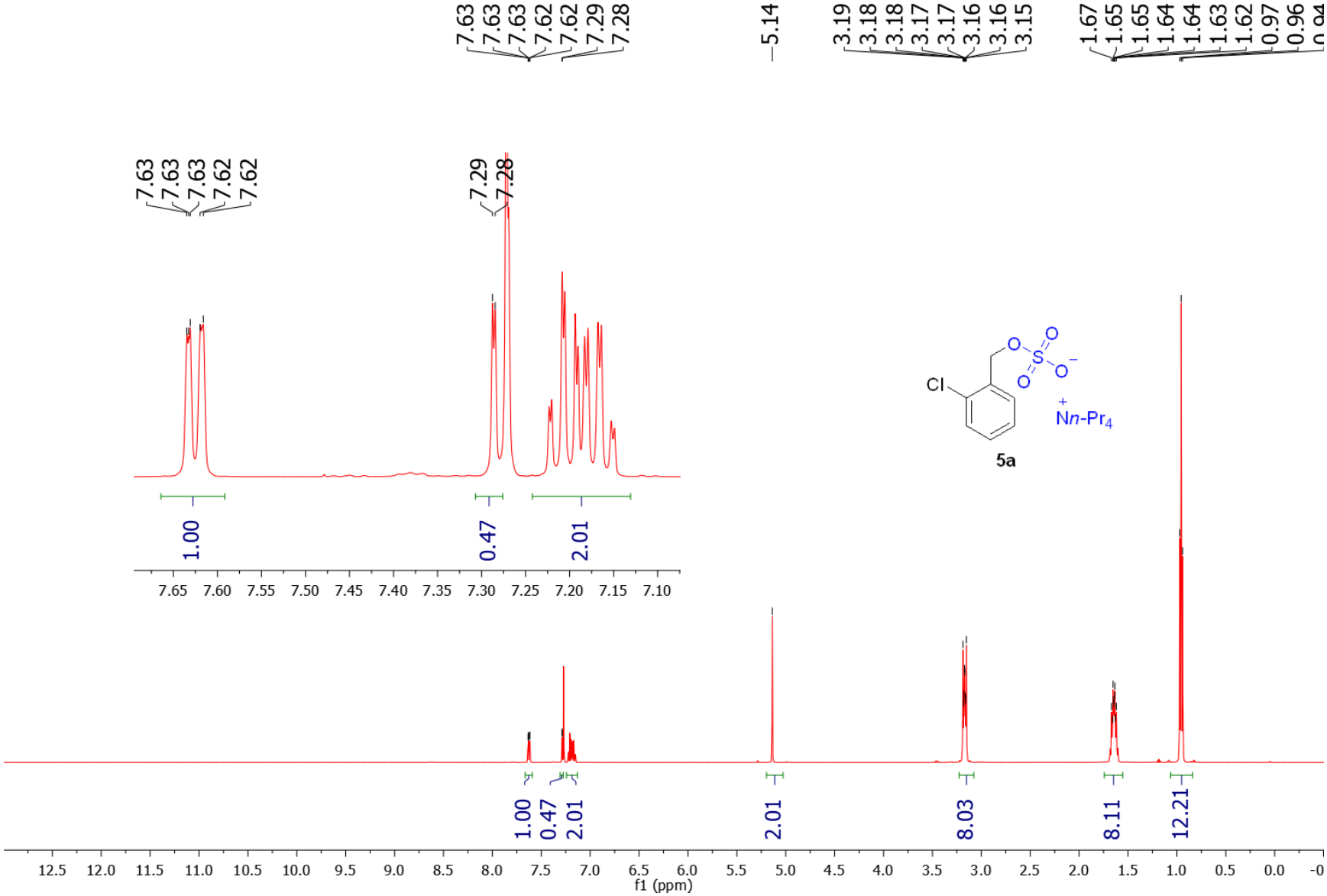
^{1}H NMR spectrum of tetrapropylammonium 2-chlorobenzylsulfate (5a)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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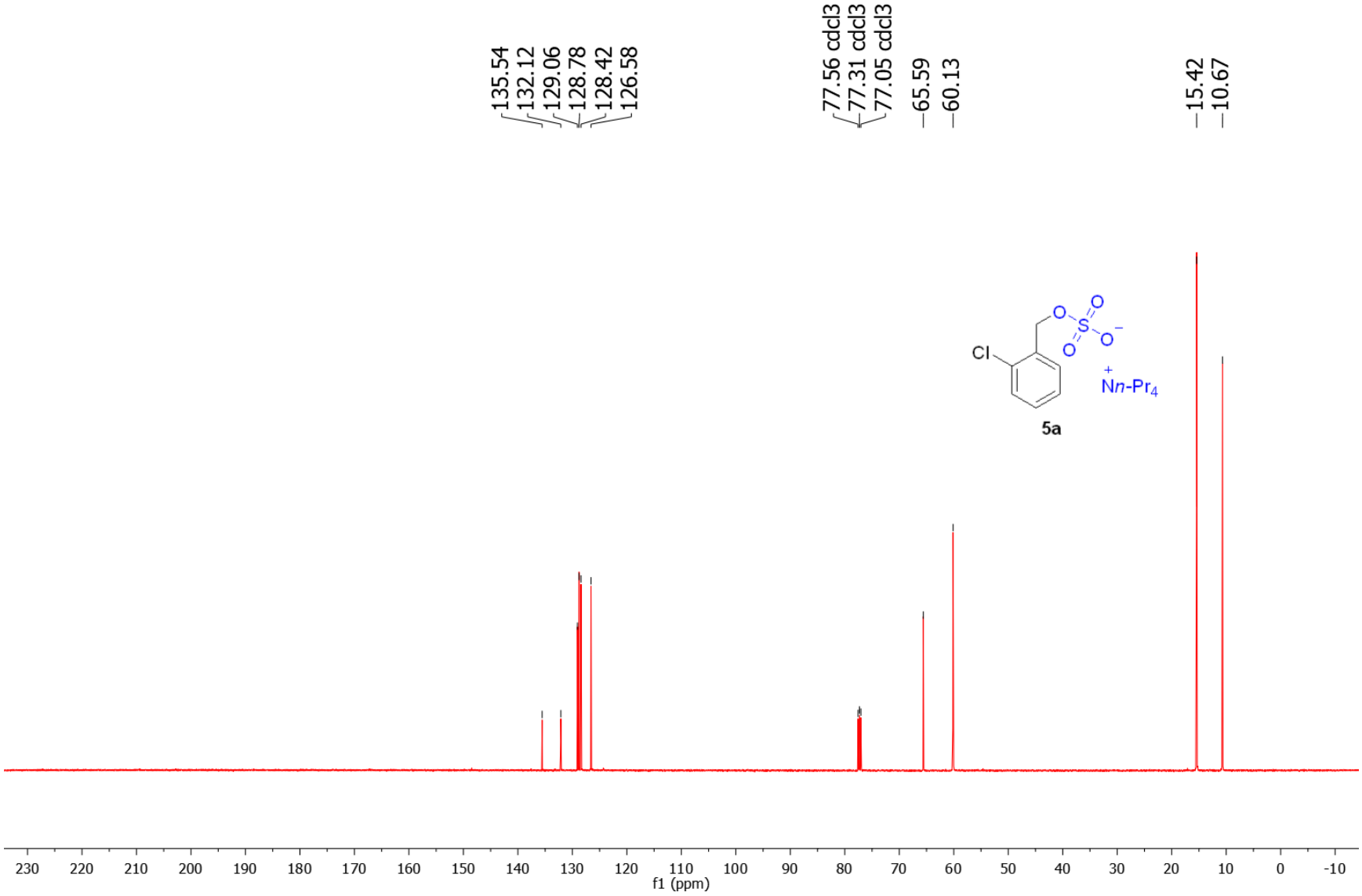
^{13}C NMR spectrum of tetrapropylammonium 2-chlorobenzylsulfate (5a)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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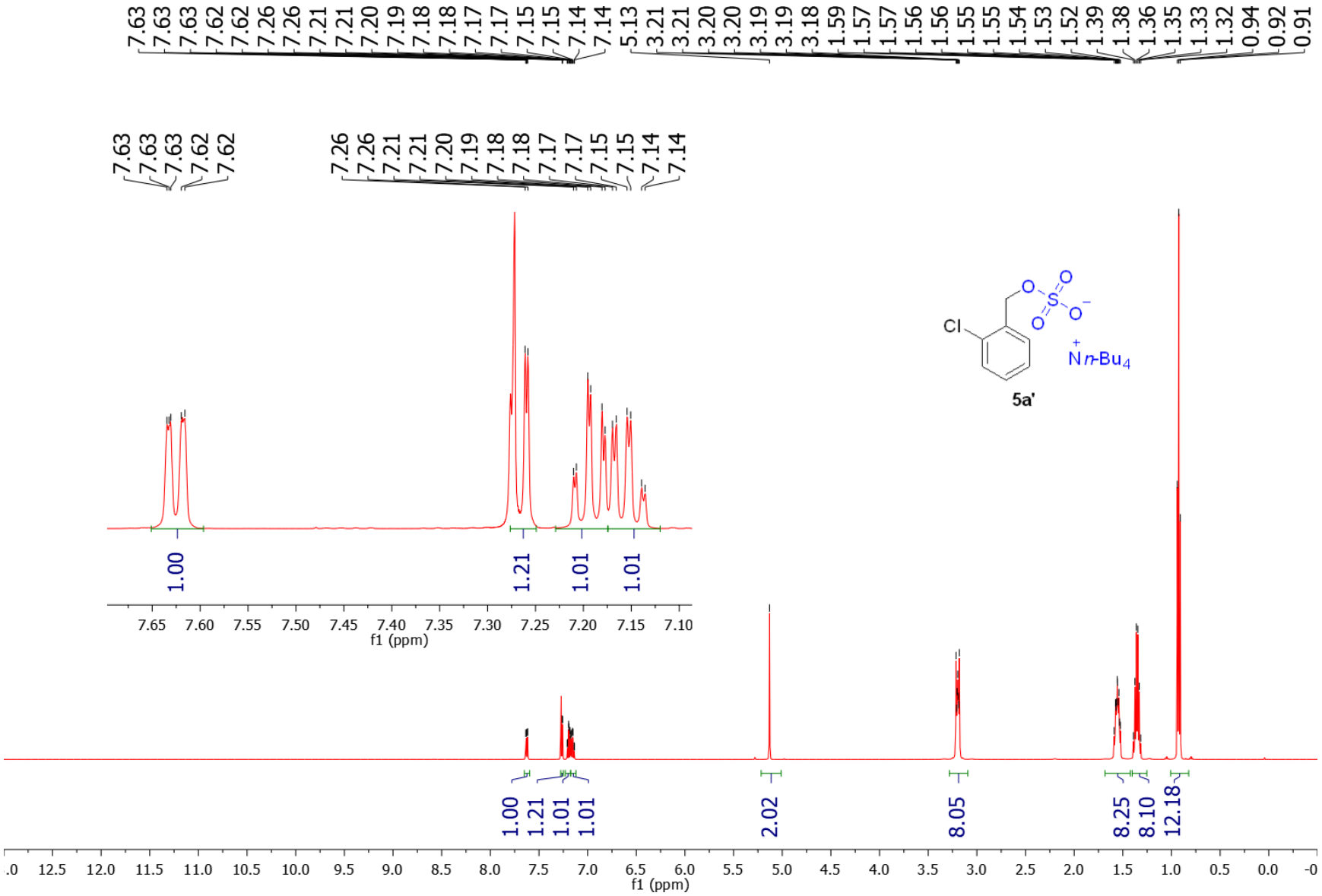
^{1}H NMR spectrum of tetrabutylammonium 2-chlorobenzylsulfate (5a′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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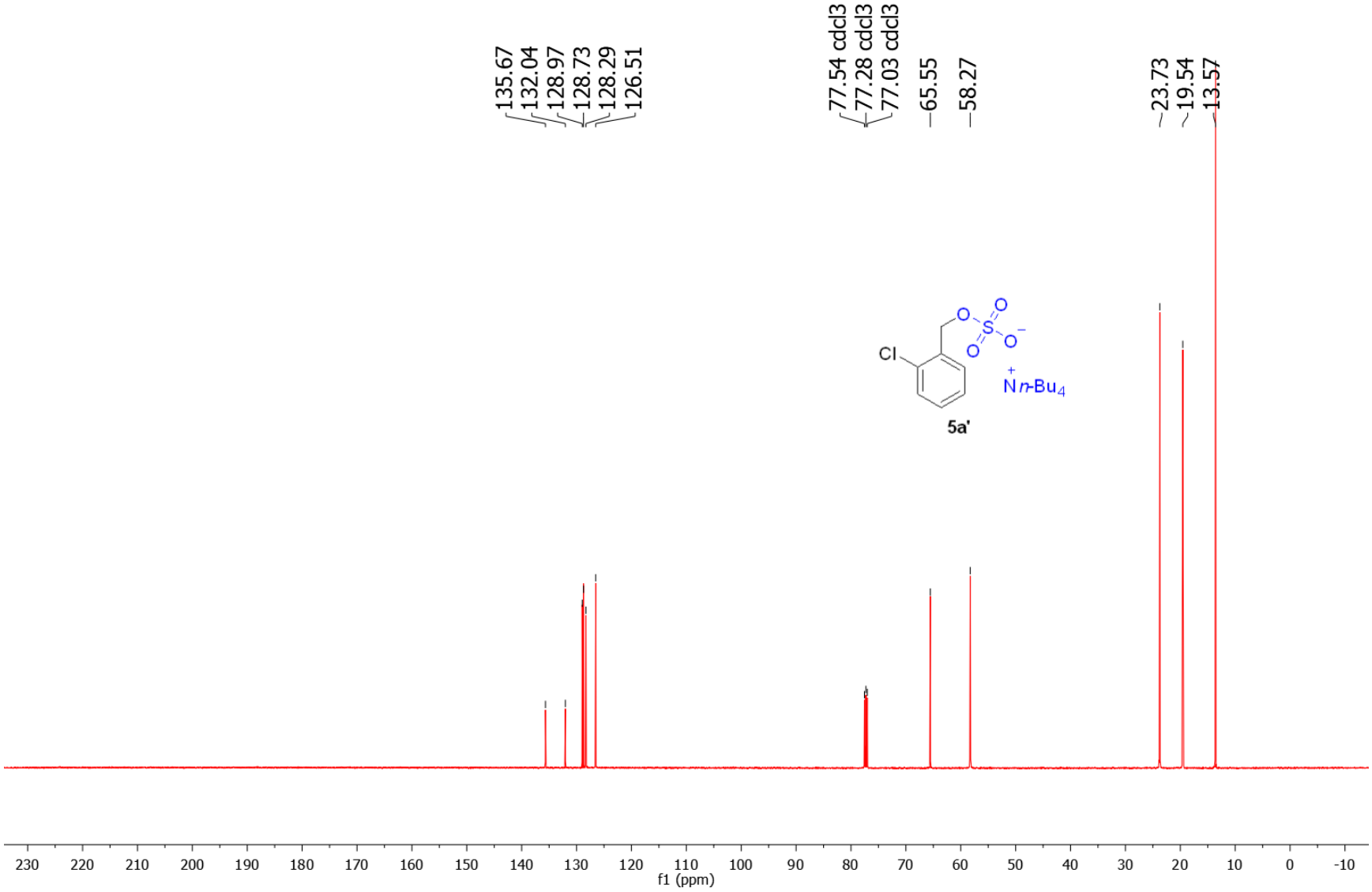
^{13}C NMR spectrum of tetrabutylammonium 2-chlorobenzylsulfate (5a′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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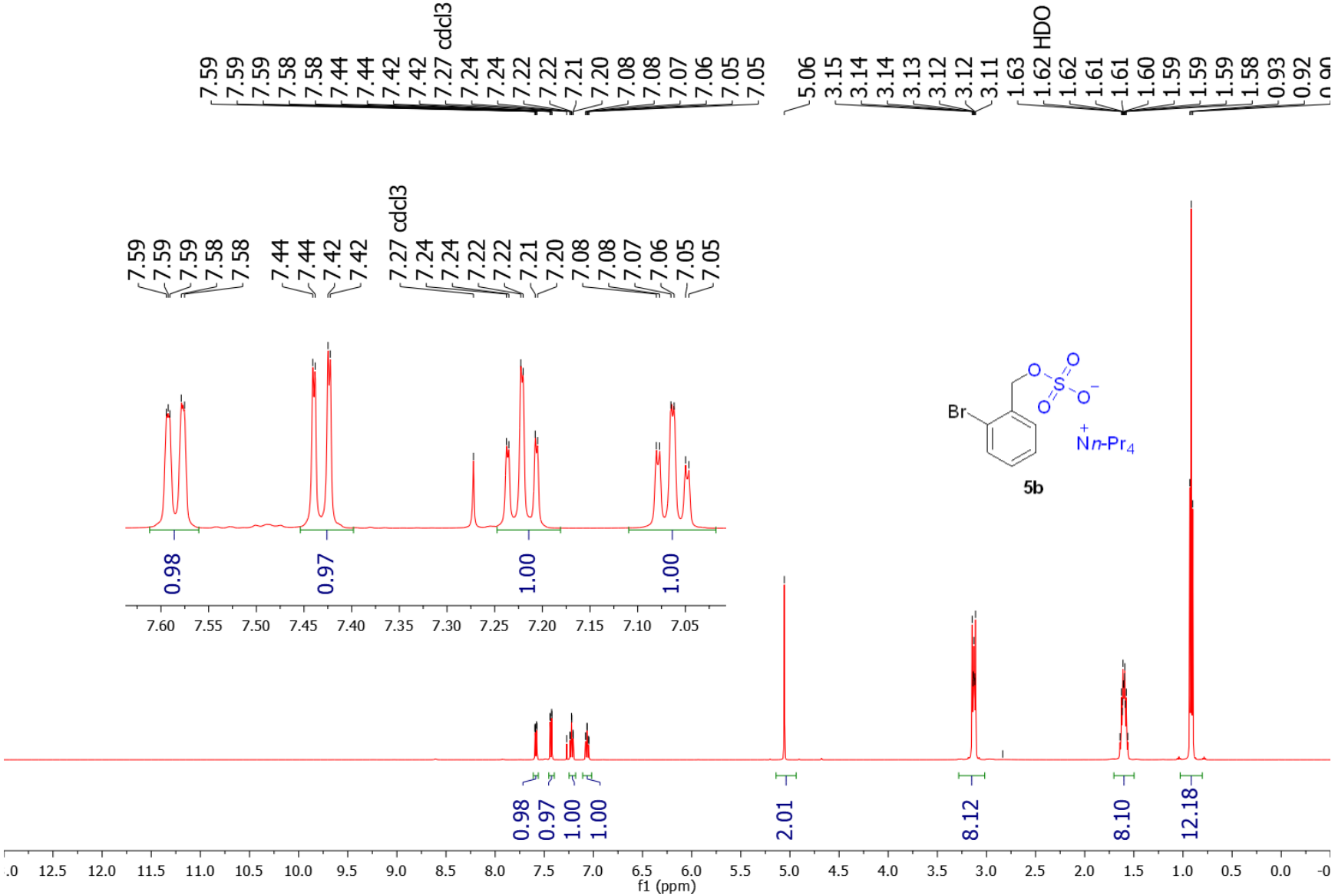
^{1}H NMR spectrum of tetrapropylammonium 2-bromobenzylsulfate (5b)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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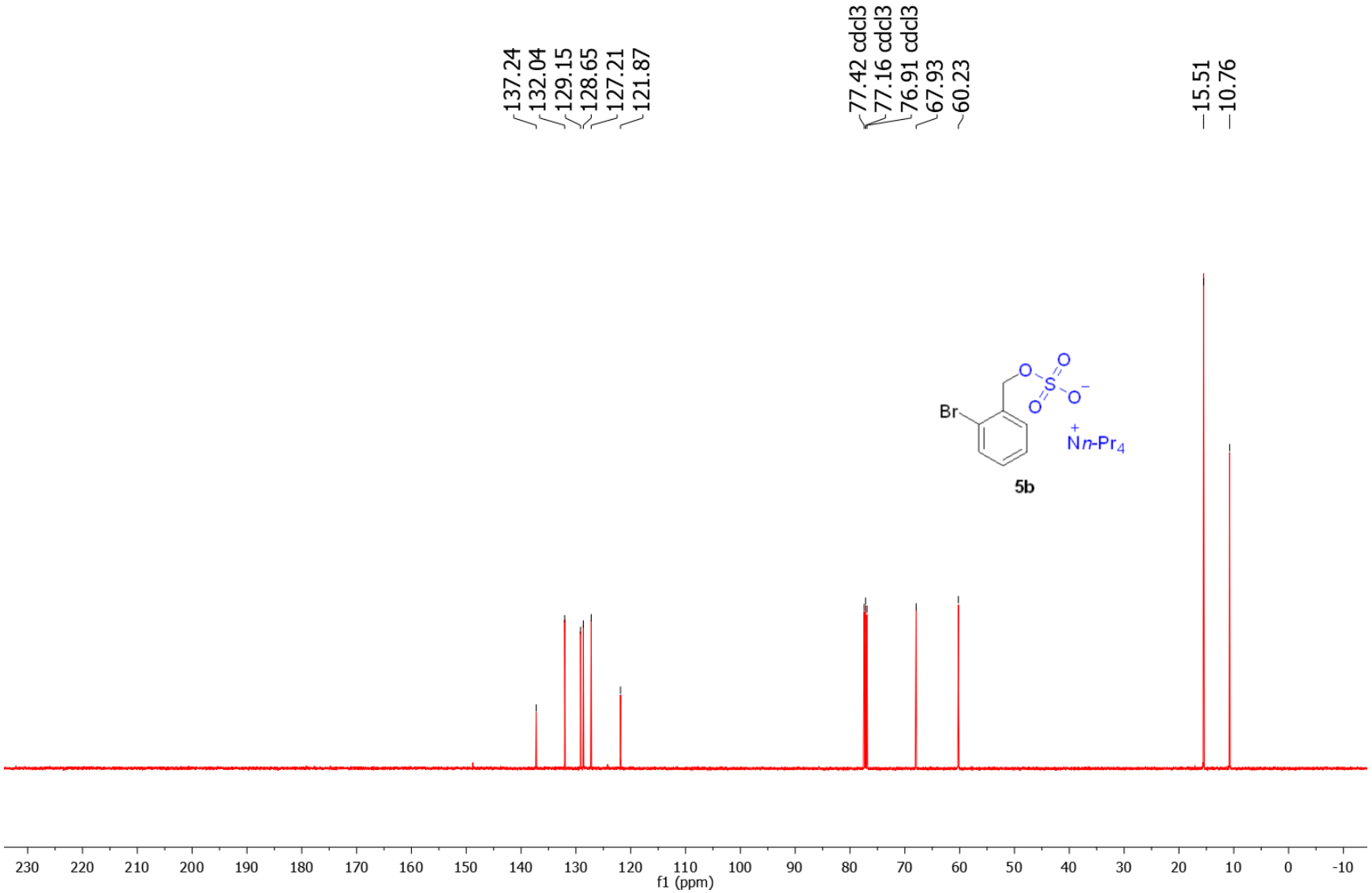
^{13}C NMR spectrum of tetrapropylammonium 2-bromobenzylsulfate (5b)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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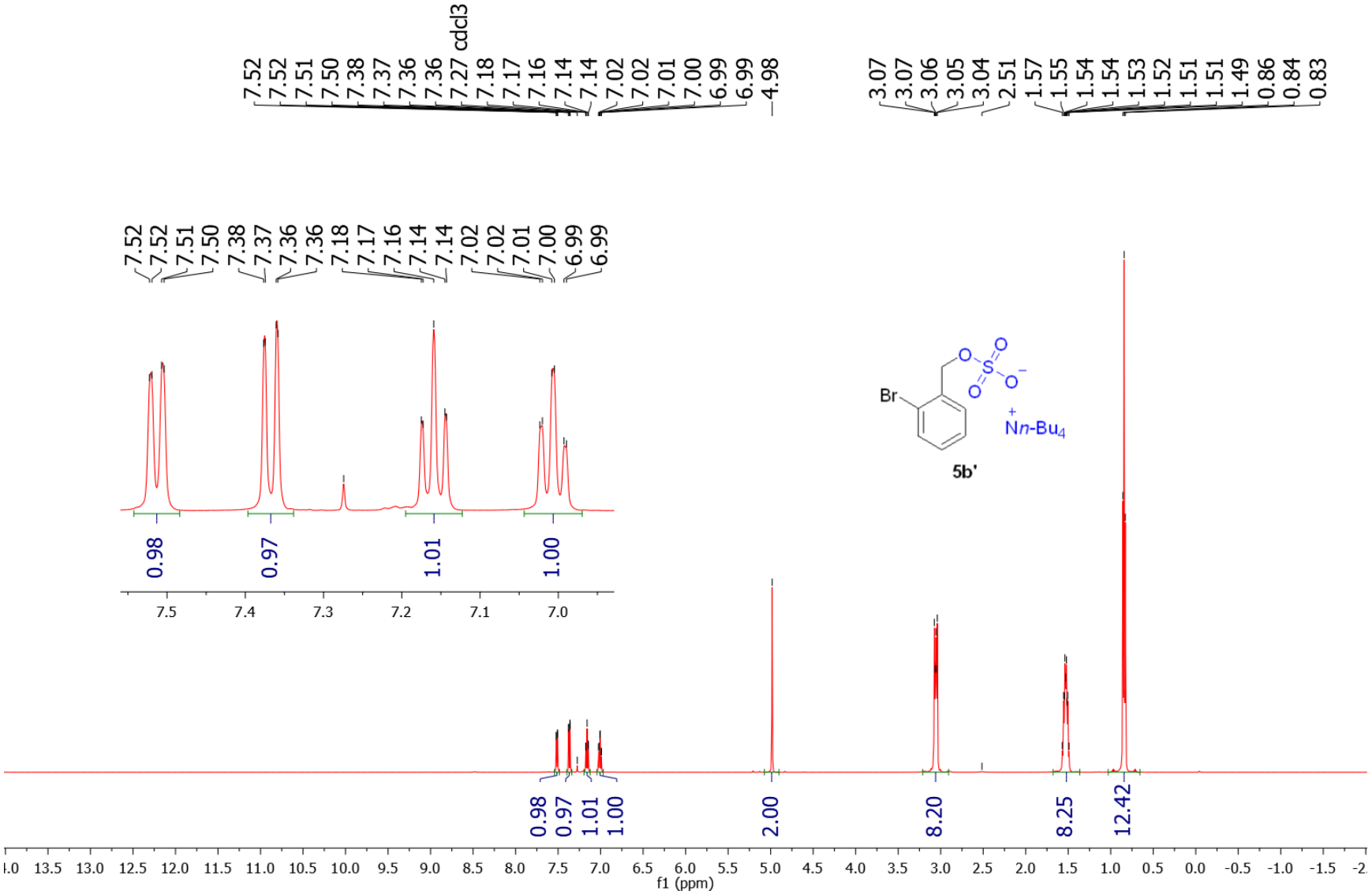
^{1}H NMR spectrum of tetrabutylammonium 2-bromobenzylsulfate (5b′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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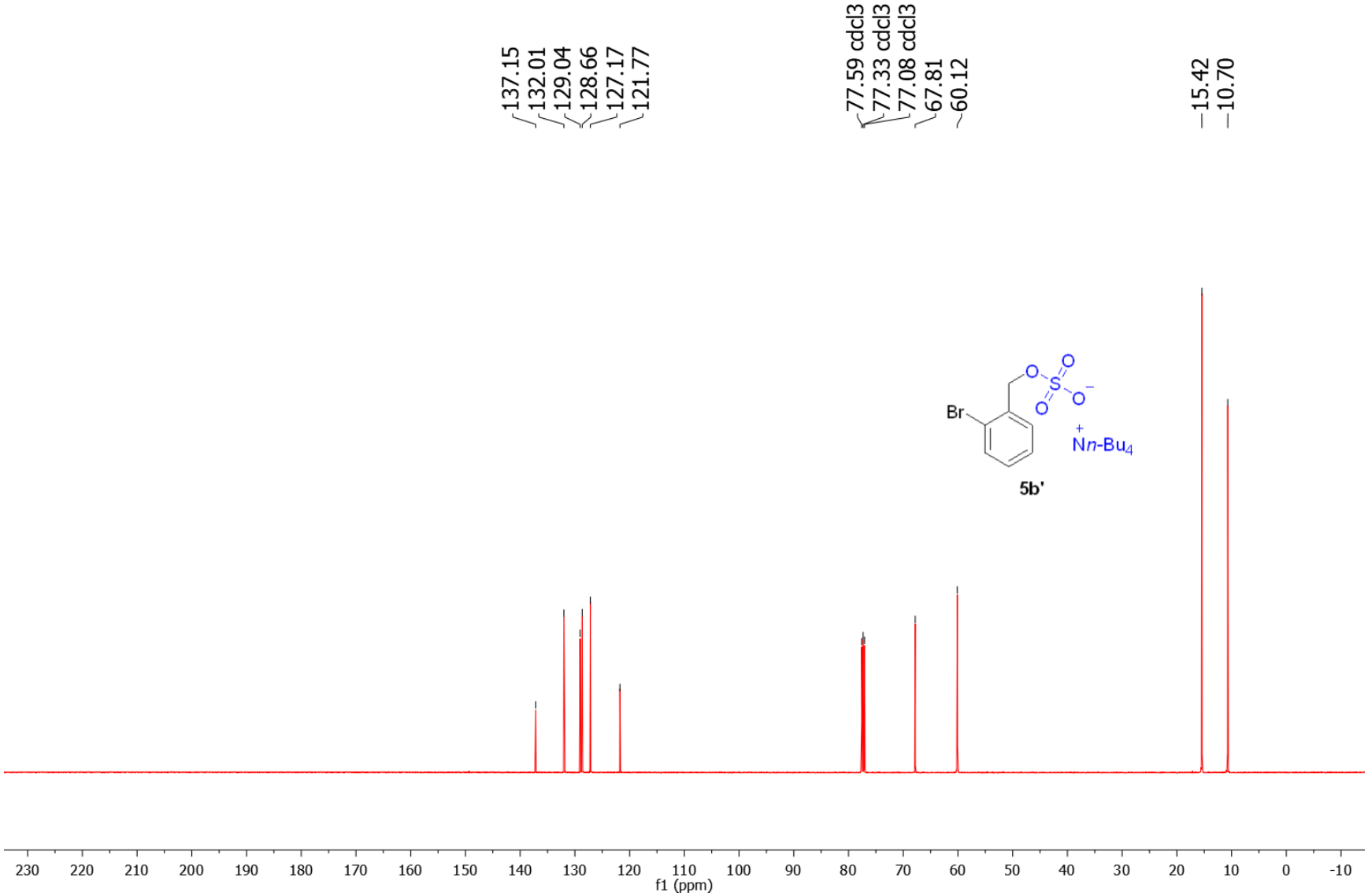
^{13}C NMR spectrum of tetrabutylammonium 2-bromobenzylsulfate (5b′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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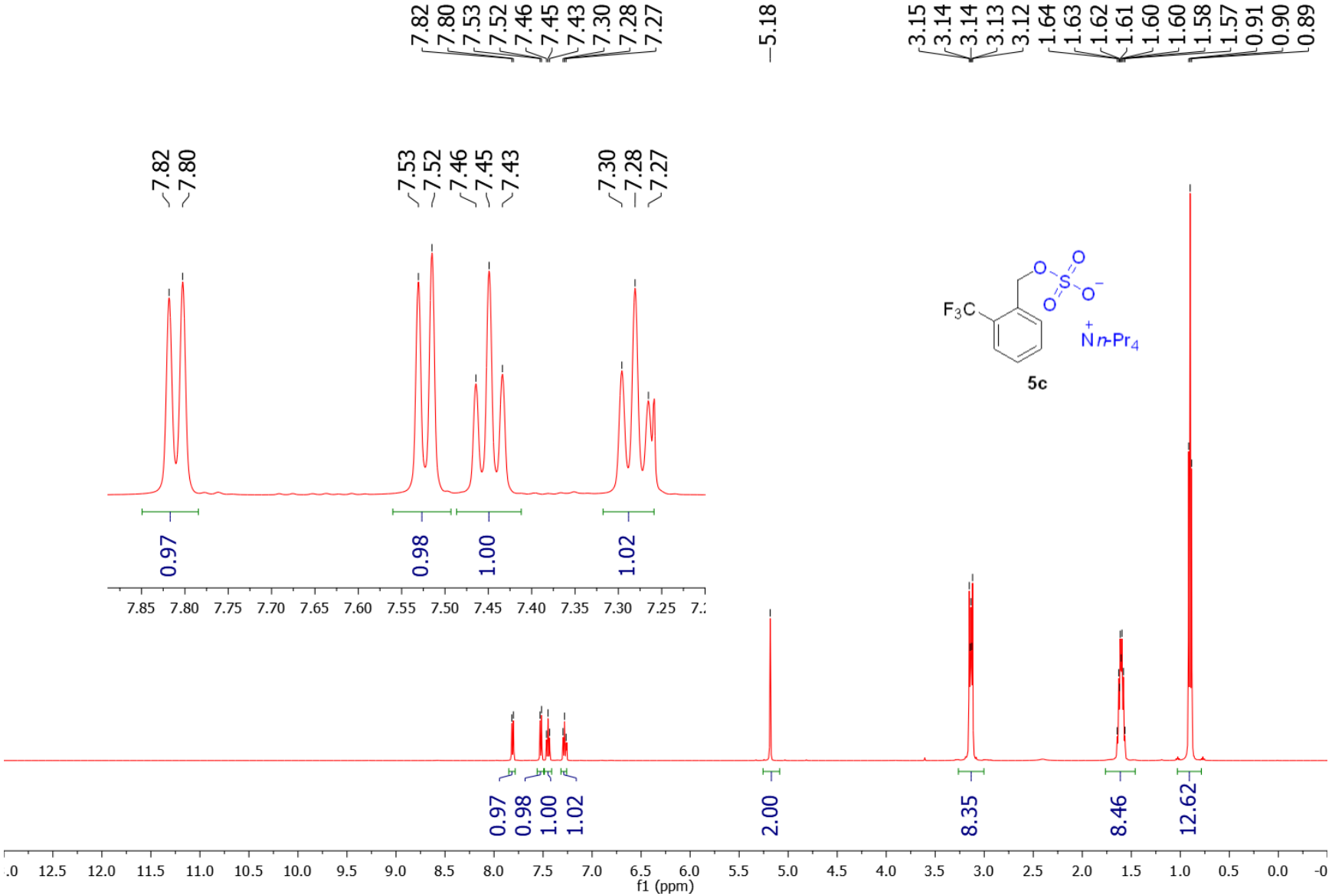
^{1}H NMR spectrum of tetrapropylammonium 2-trifluoromethylbenzylsulfate (5c)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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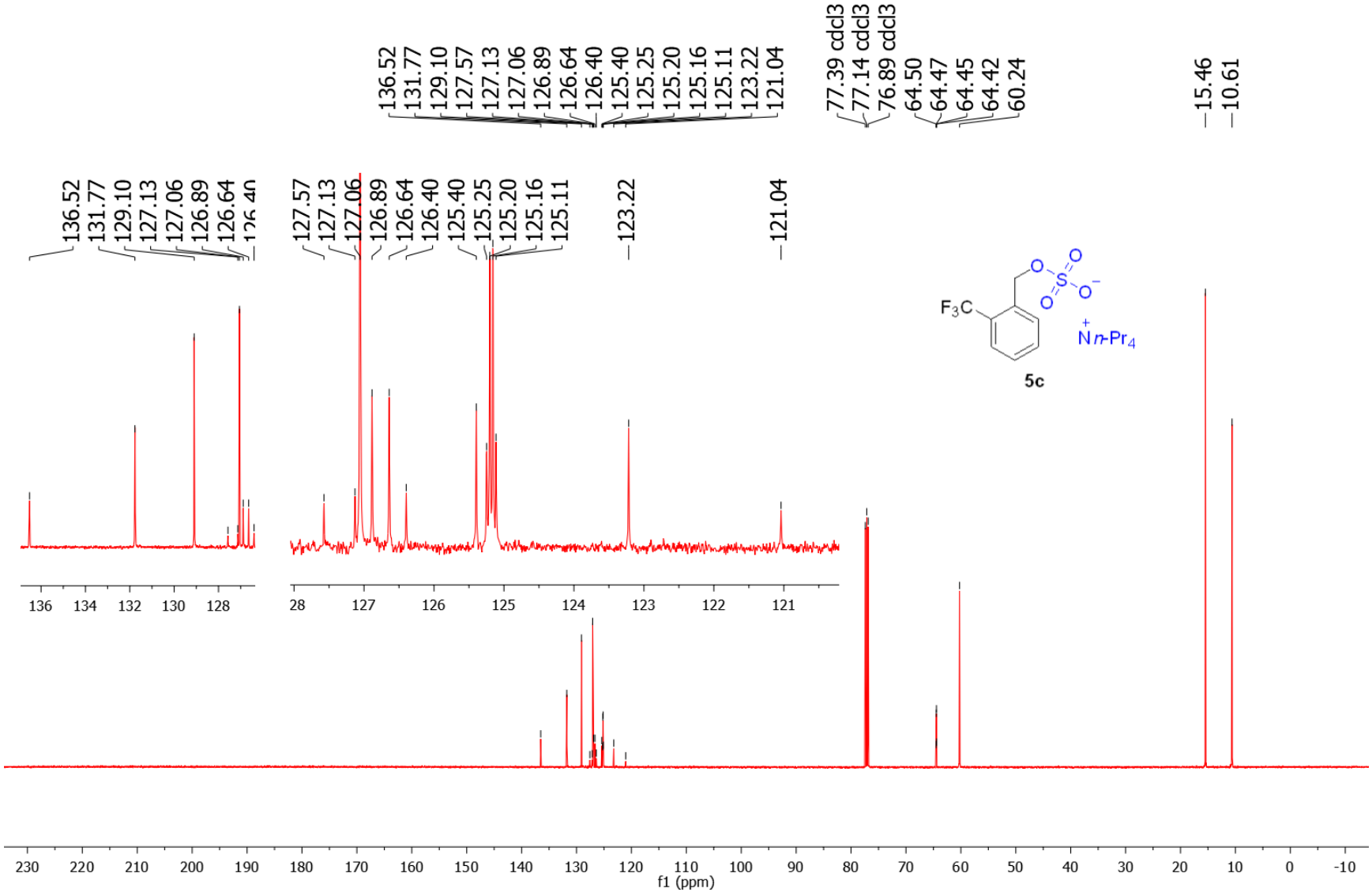
^{13}C NMR spectrum of tetrapropylammonium 2-trifluoromethylbenzylsulfate (5c)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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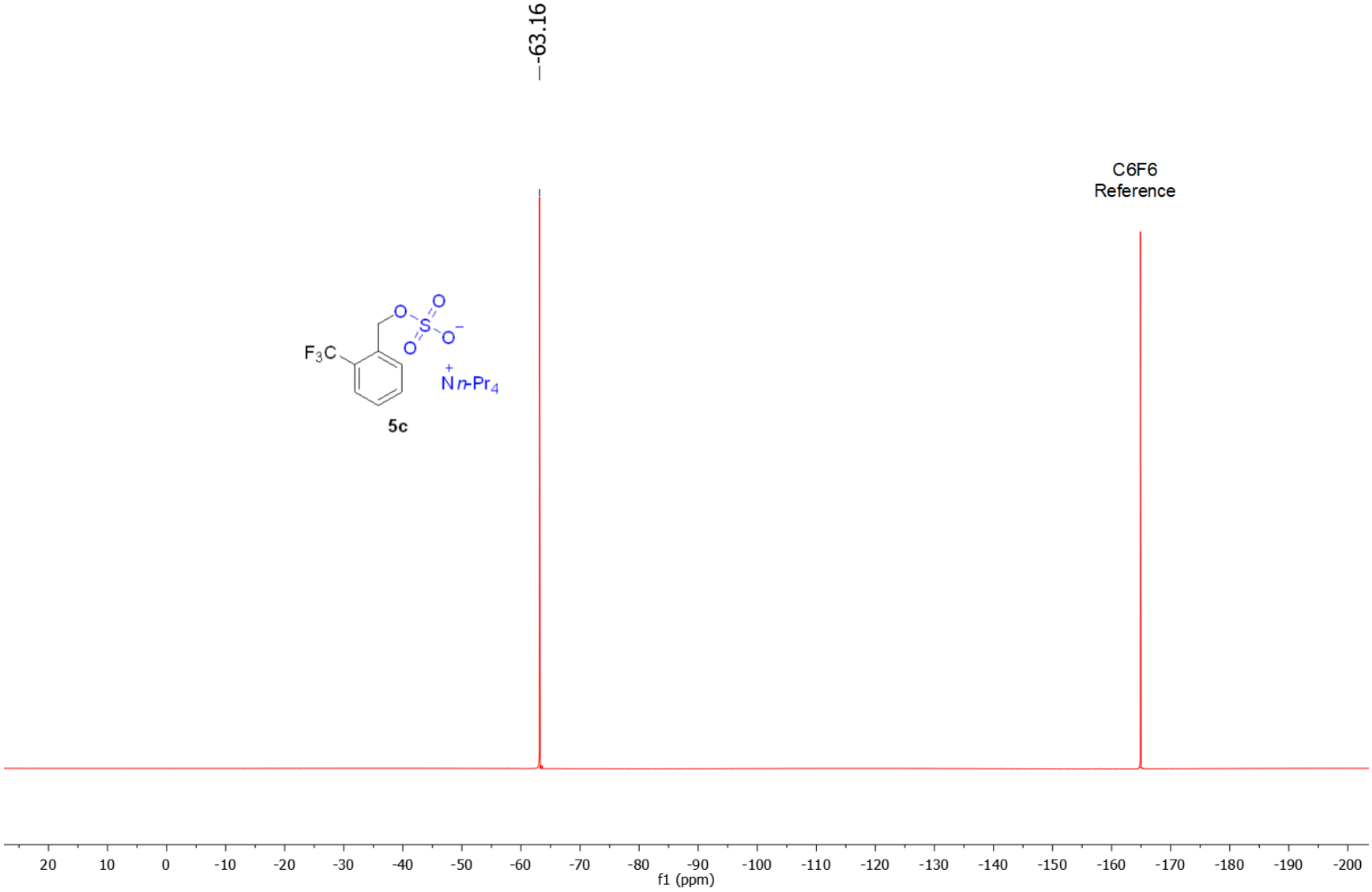
^{19}F NMR spectrum of tetrapropylammonium 2-trifluoromethylbenzylsulfate (5c)



Conditions: 25 ºC, 470 MHz, $CDCl_3$

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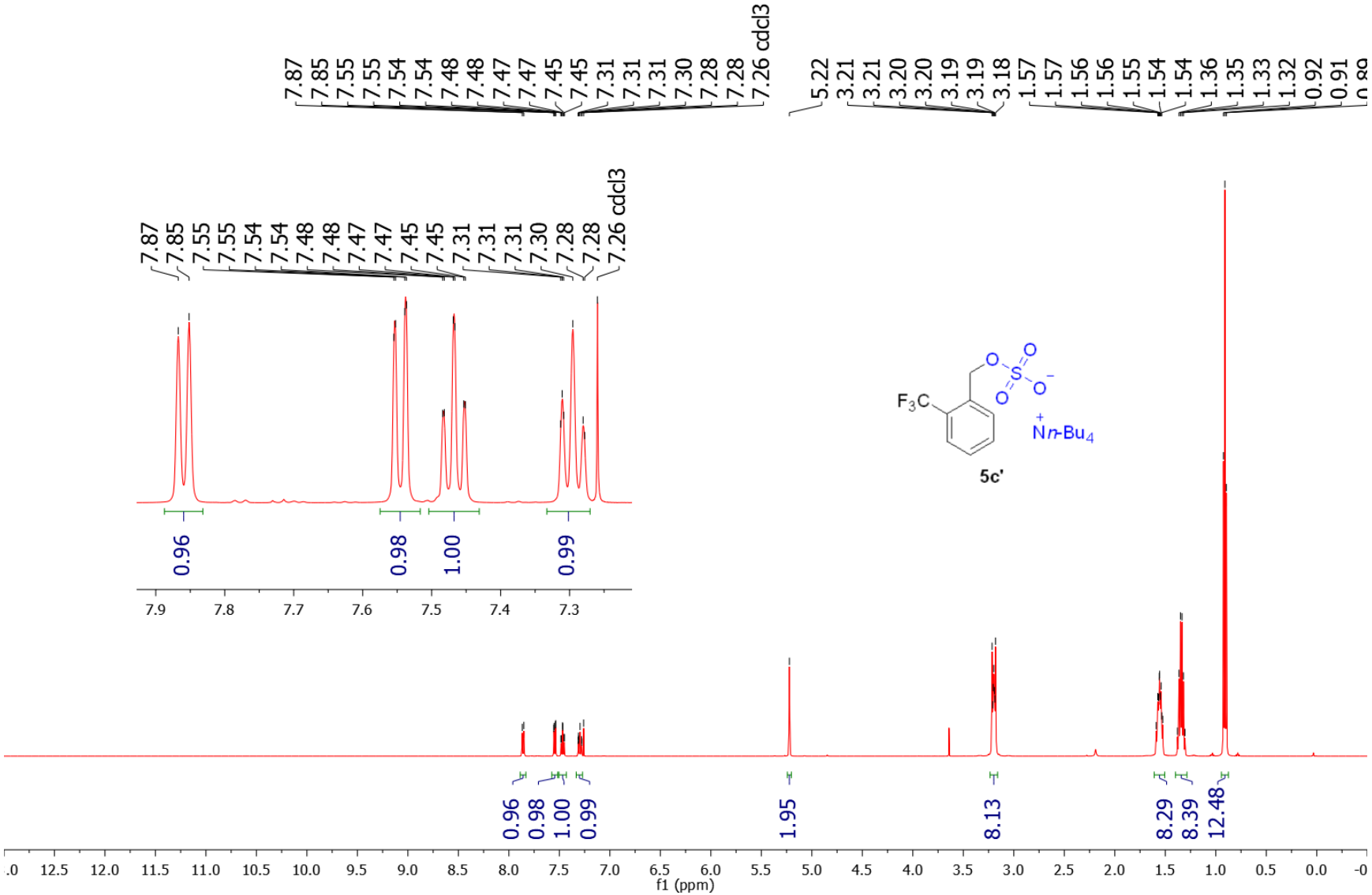
^{1}H NMR spectrum of tetbutylammonium 2-trifluoromethylbenzylsulfate (5c′)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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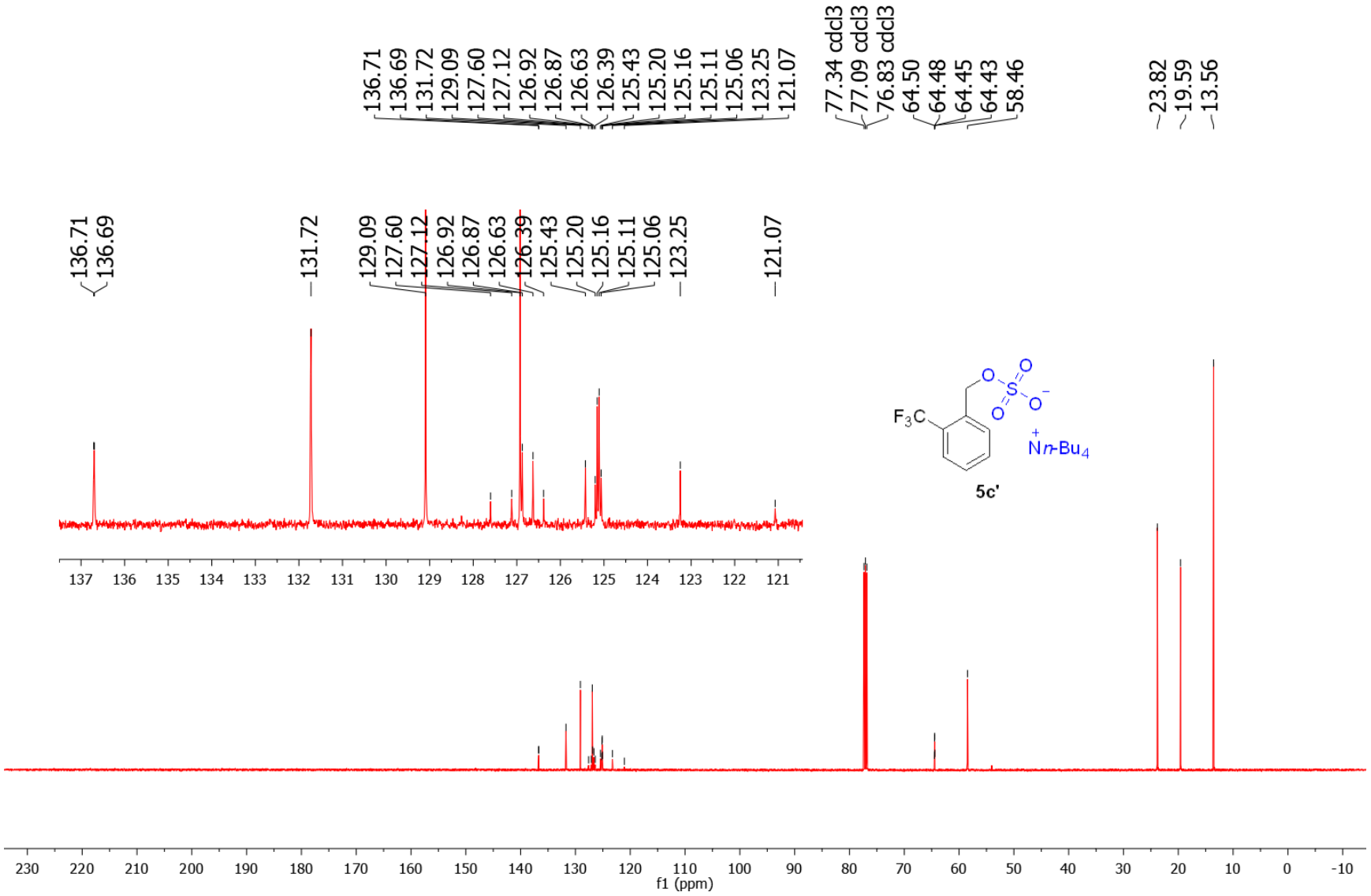
^{13}C NMR spectrum of tetrabutylammonium 2-trifluoromethylbenzylsulfate (5c′)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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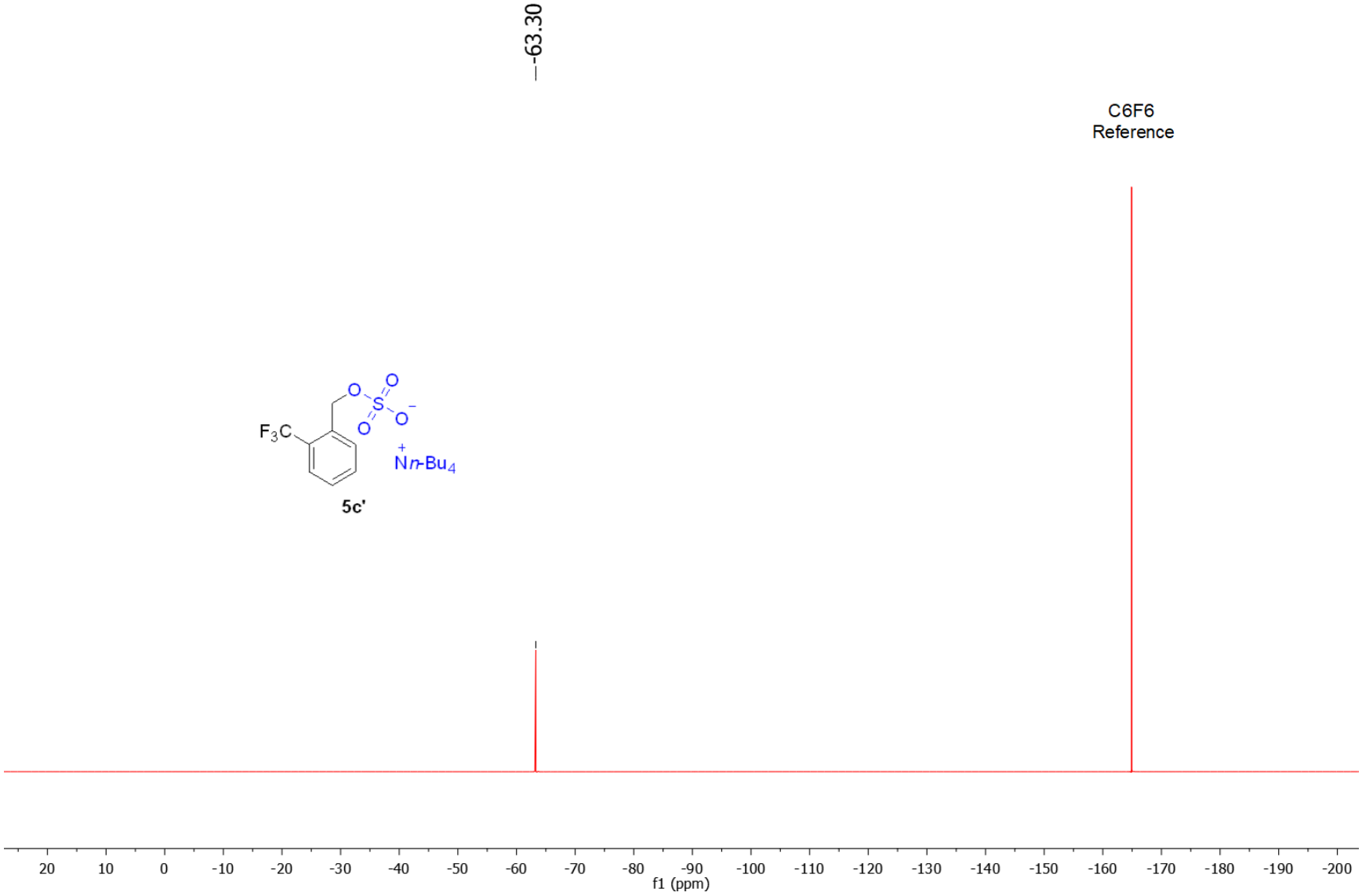
^{19}F NMR spectrum of tetrabutylammonium 2-trifluoromethylbenzylsulfate (5c′)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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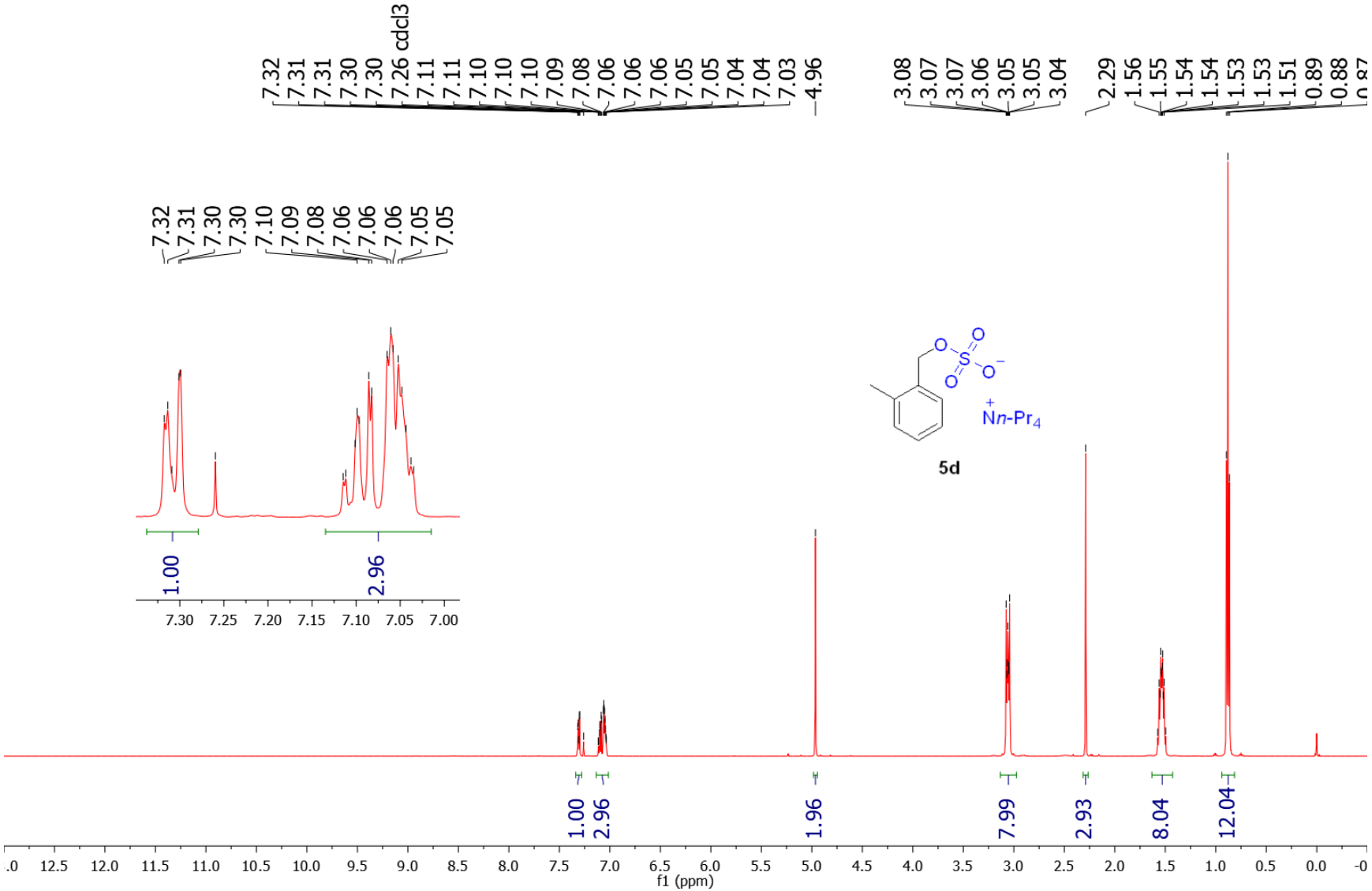
^{1}H NMR spectrum of tetrapropylammonium 2-methylbenzylsulfate (5d)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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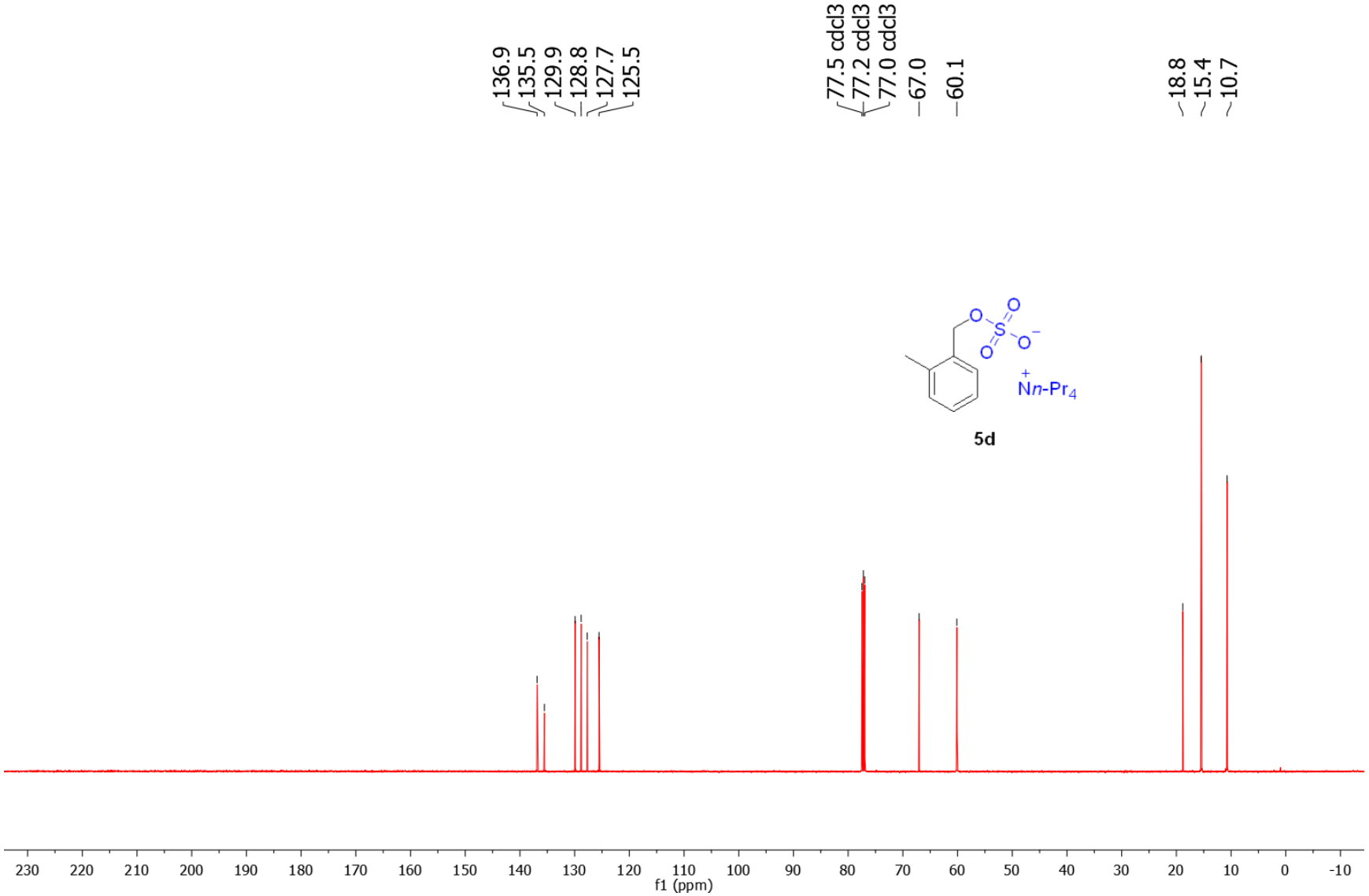
^{13}C NMR spectrum of tetrapropylammonium 2-methylbenzylsulfate (5d)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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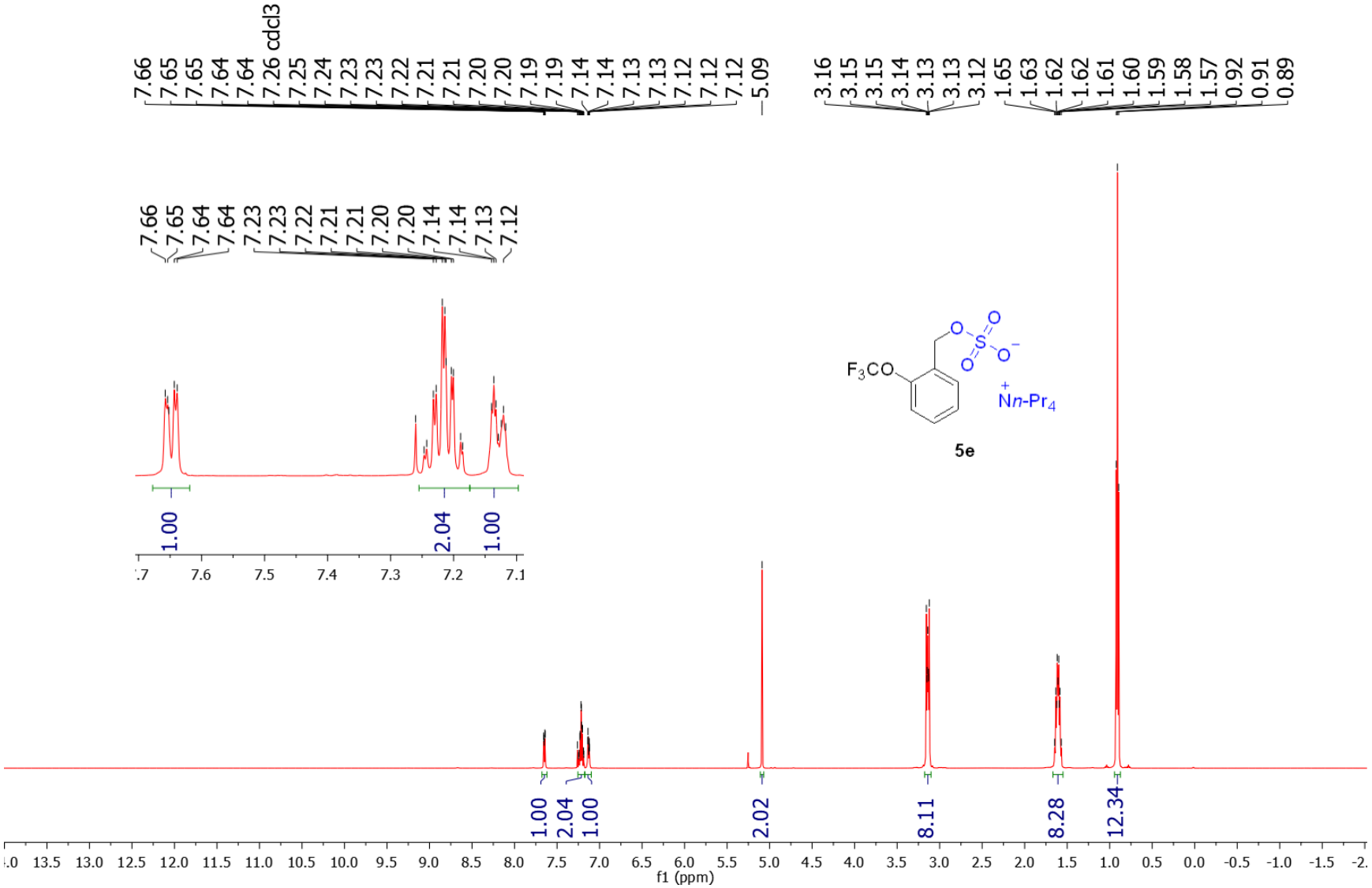
^{1}H NMR spectrum of tetrapropylammonium 2-(trifluoromethoxy)benzylsulfate (5e)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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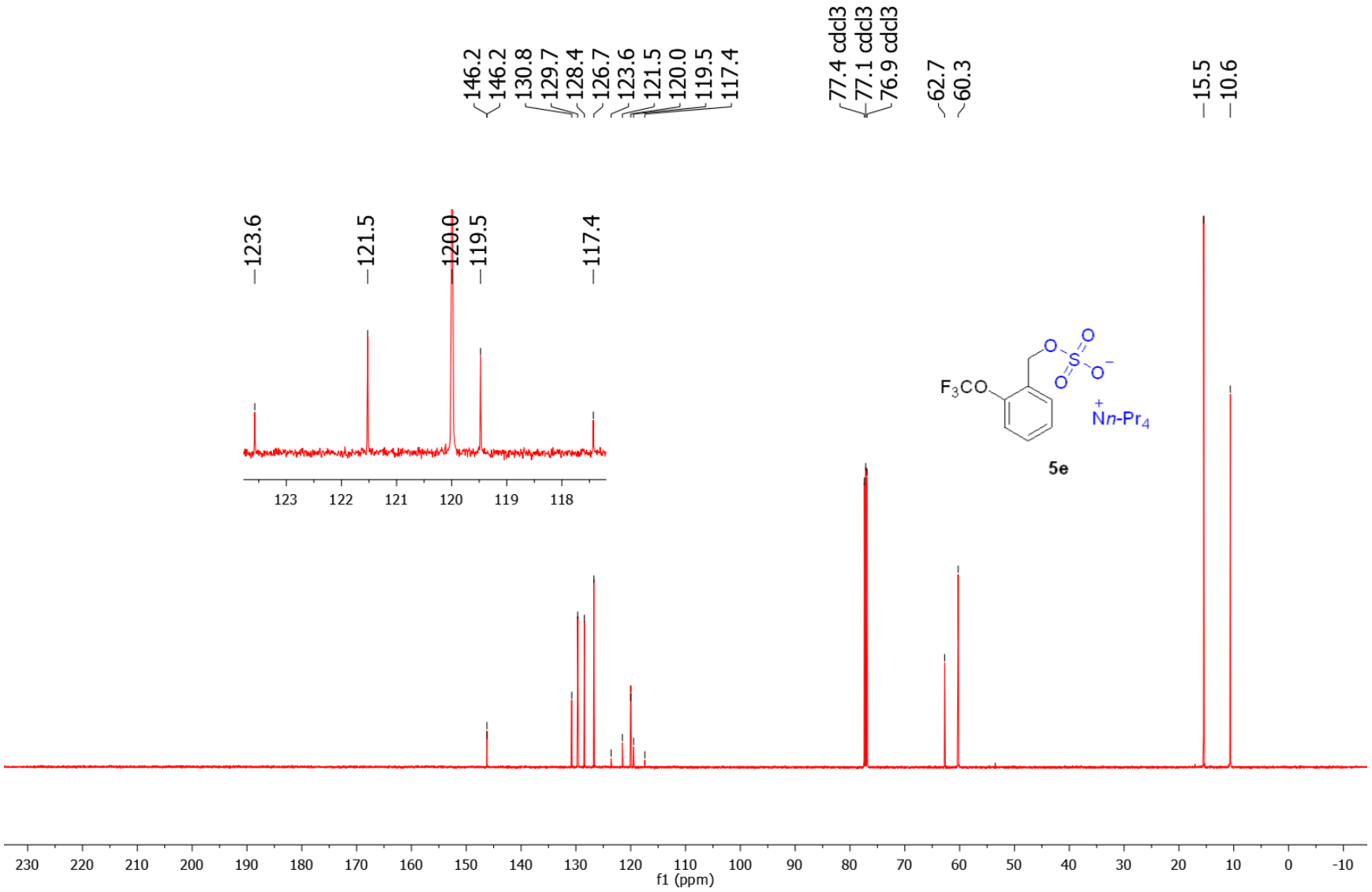
^{13}C NMR spectrum of tetrapropylammonium 2-(trifluoromethoxy)benzylsulfate (5e)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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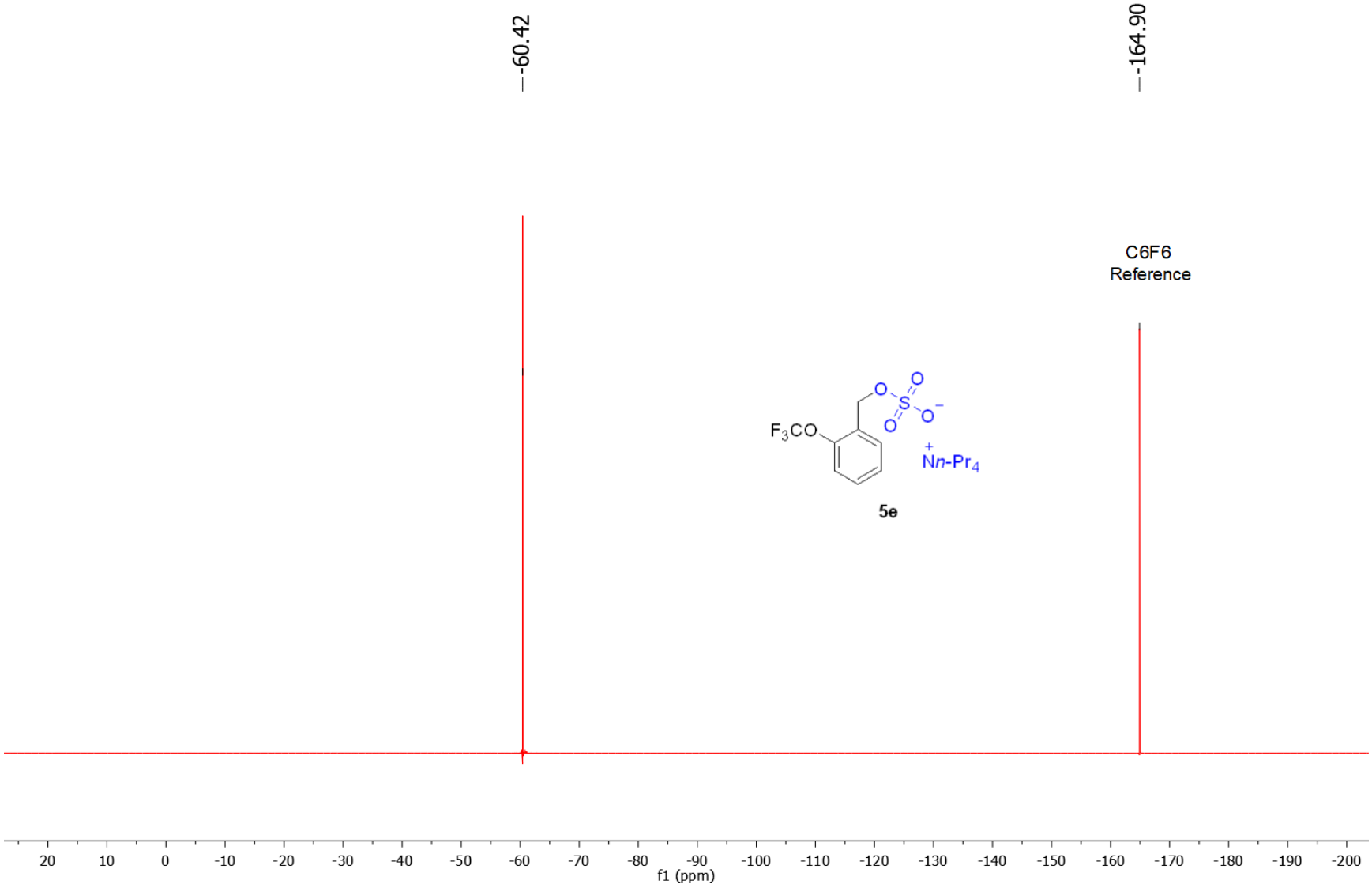
^{19}F NMR spectrum of tetrapropylammonium 2-(trifluoromethoxy)benzylsulfate (5e)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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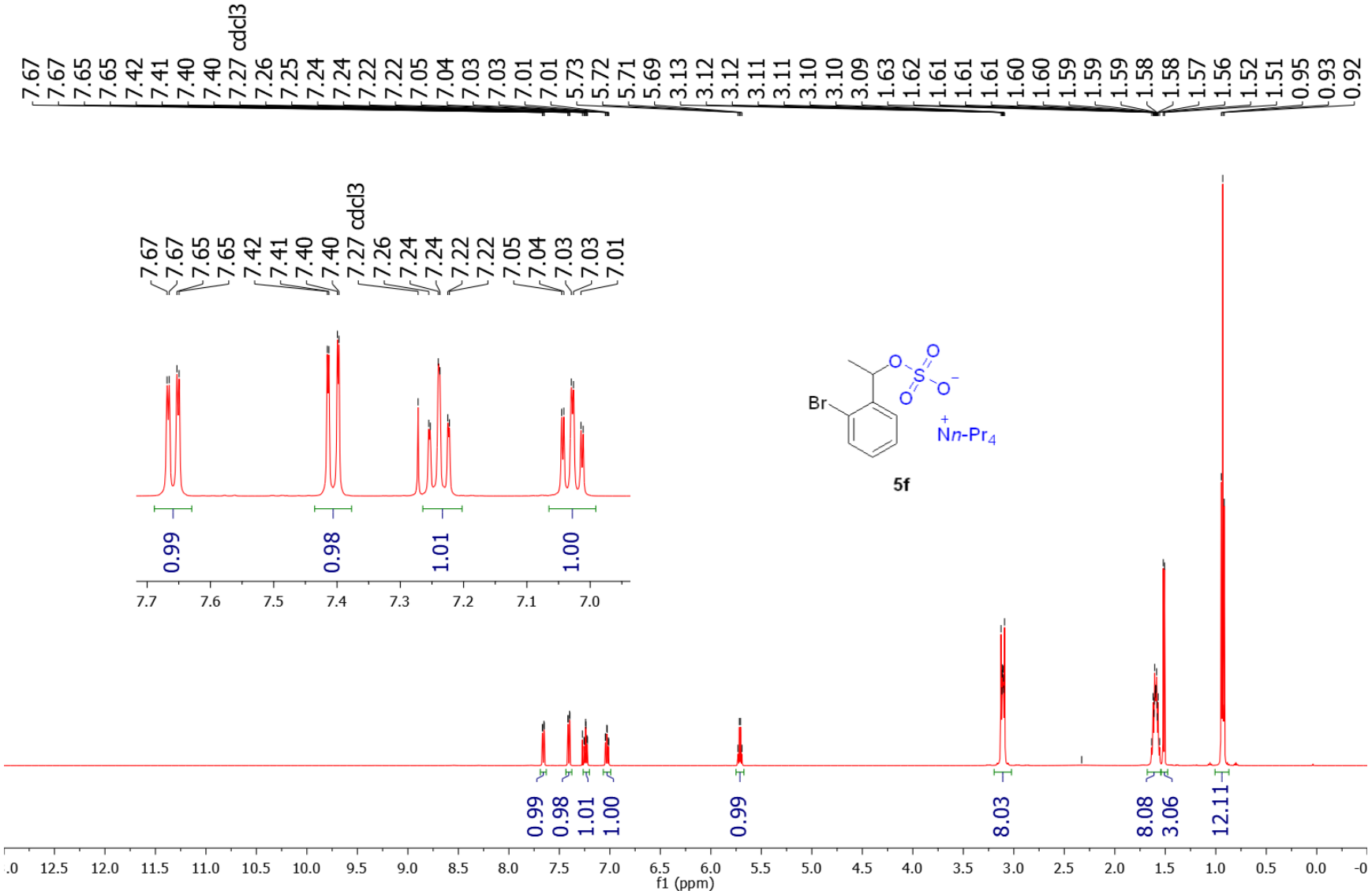
^{1}H NMR spectrum of tetrapropylammonium 1-(2-bromophenyl)ethylsulfate (5f)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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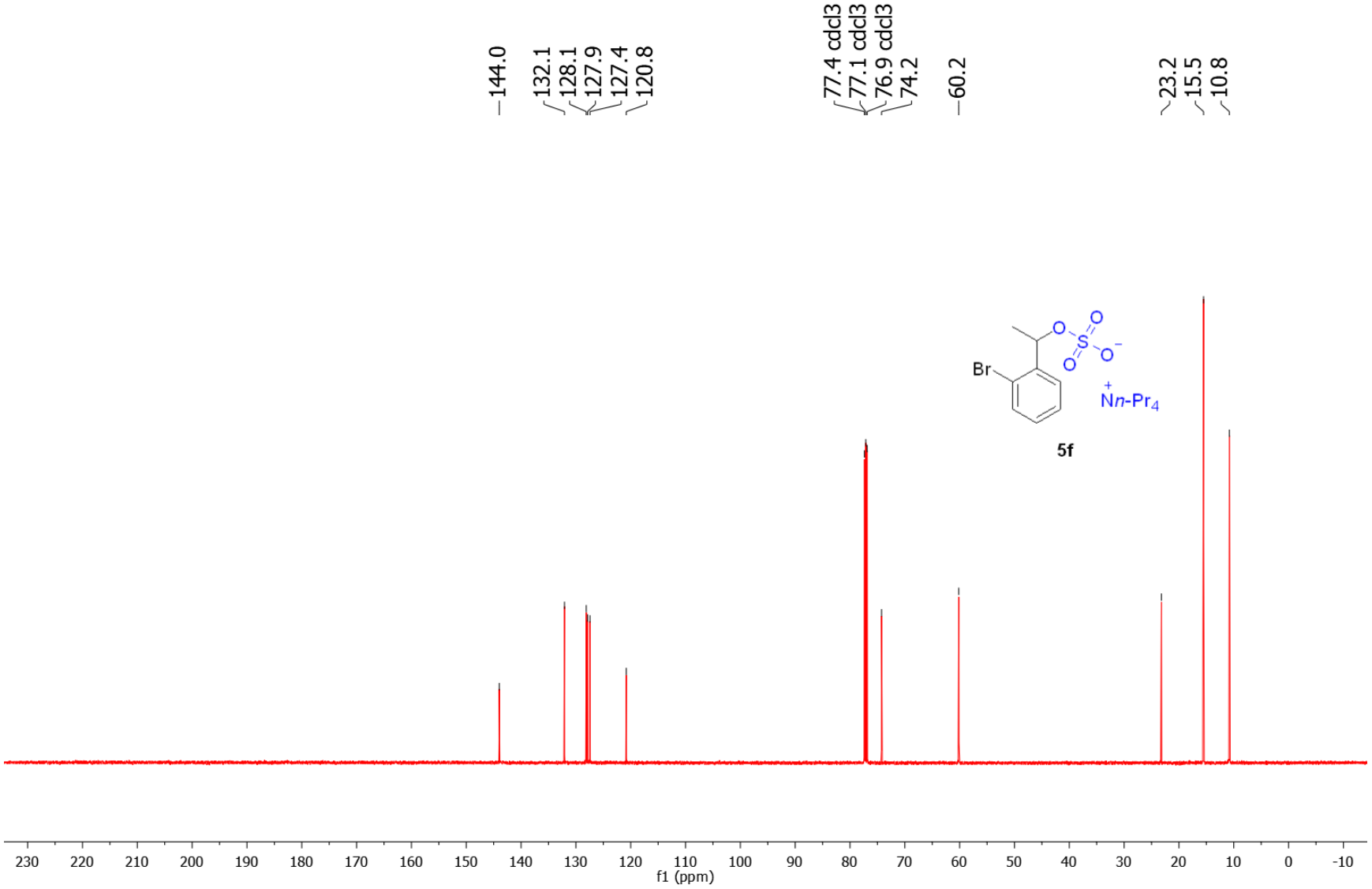
^{13}C NMR spectrum of tetrapropylammonium 1-(2-bromophenyl)ethylsulfate (5f)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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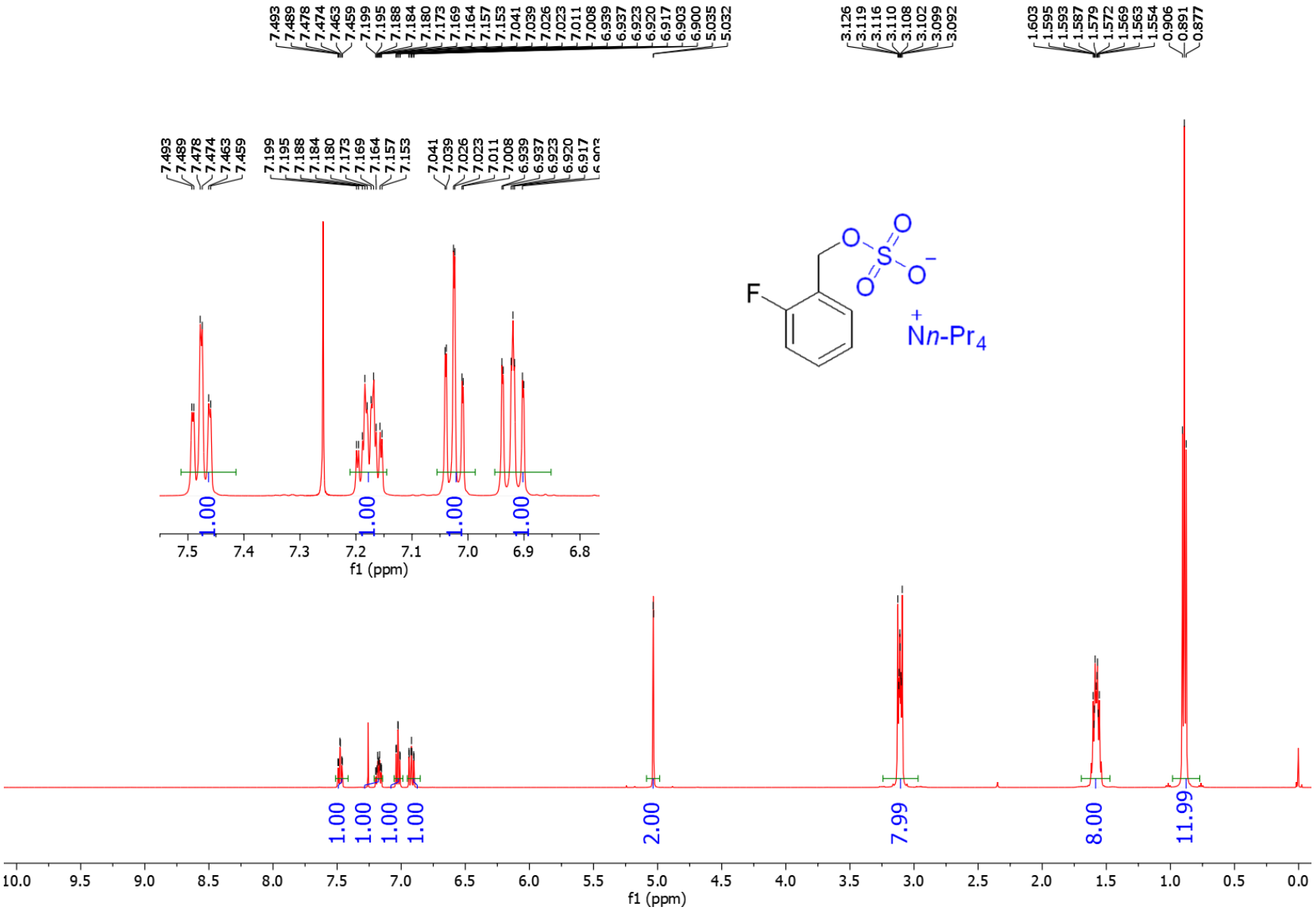
^{1}H NMR spectrum of tetrapropylammonium 2-fluorobenzylsulfate (5g)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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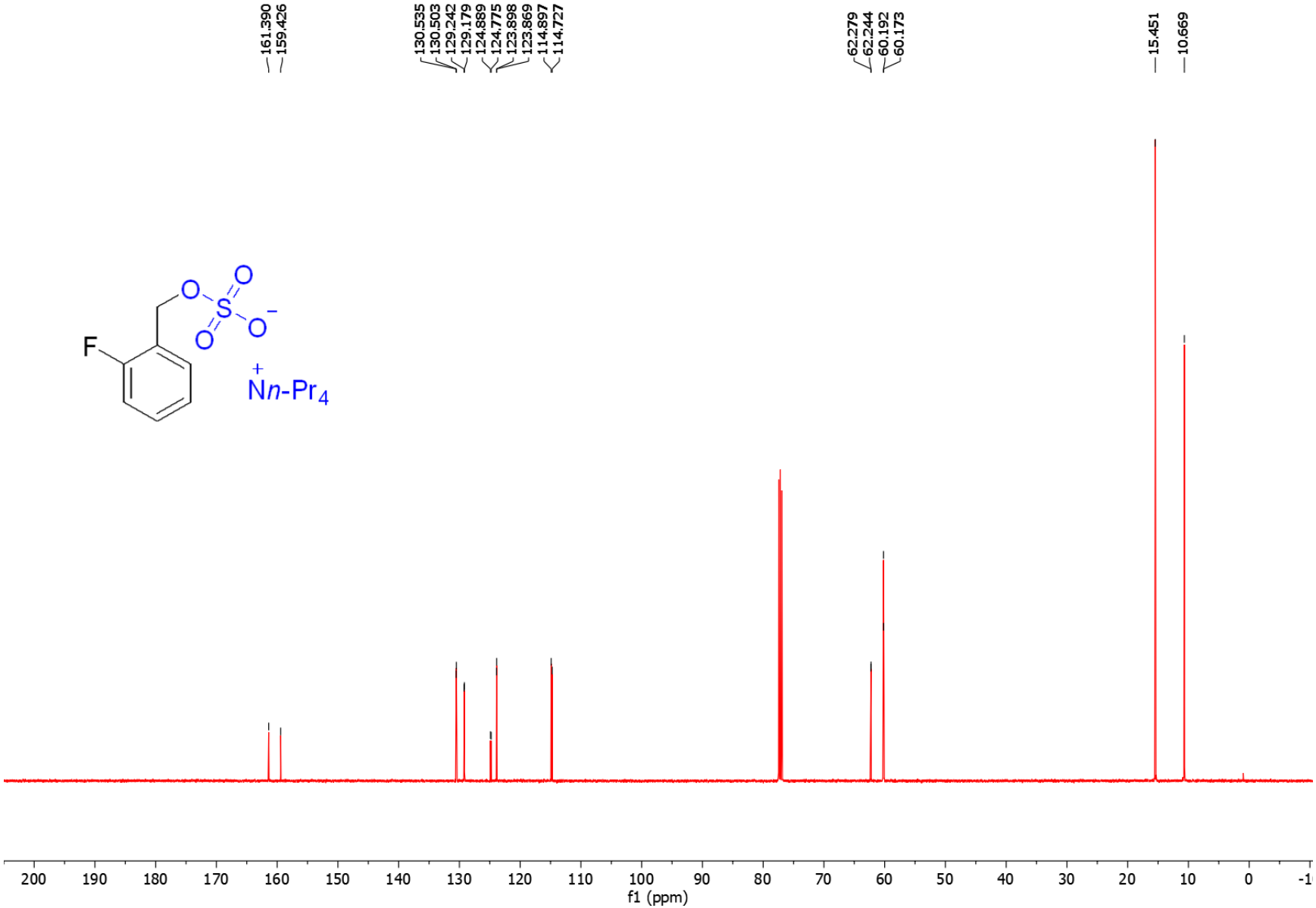
^{13}C NMR spectrum of tetrapropylammonium 2-fluorobenzylsulfate (5g)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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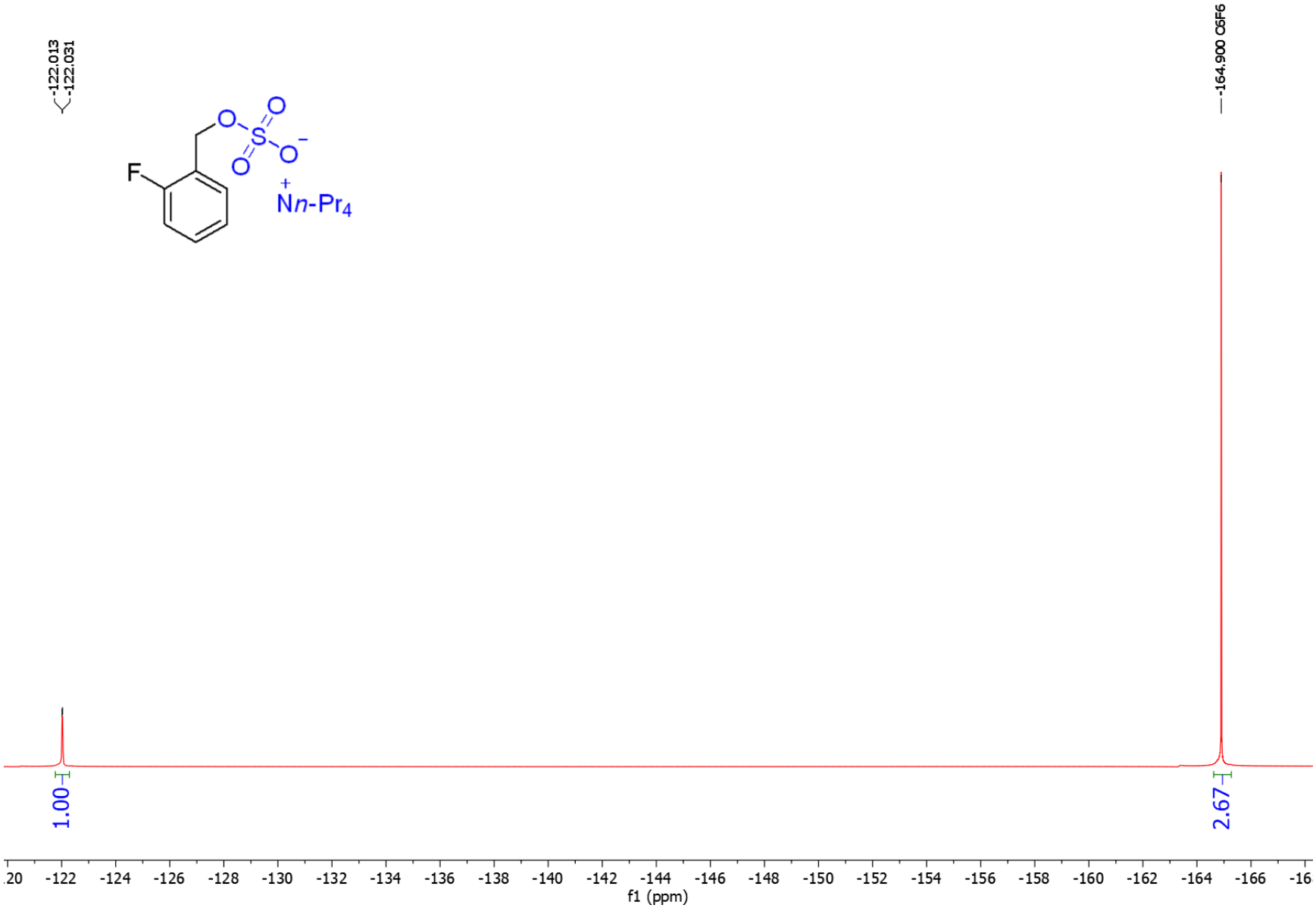
^{19}F NMR spectrum of tetrapropylammonium 2-fluorobenzylsulfate (5g)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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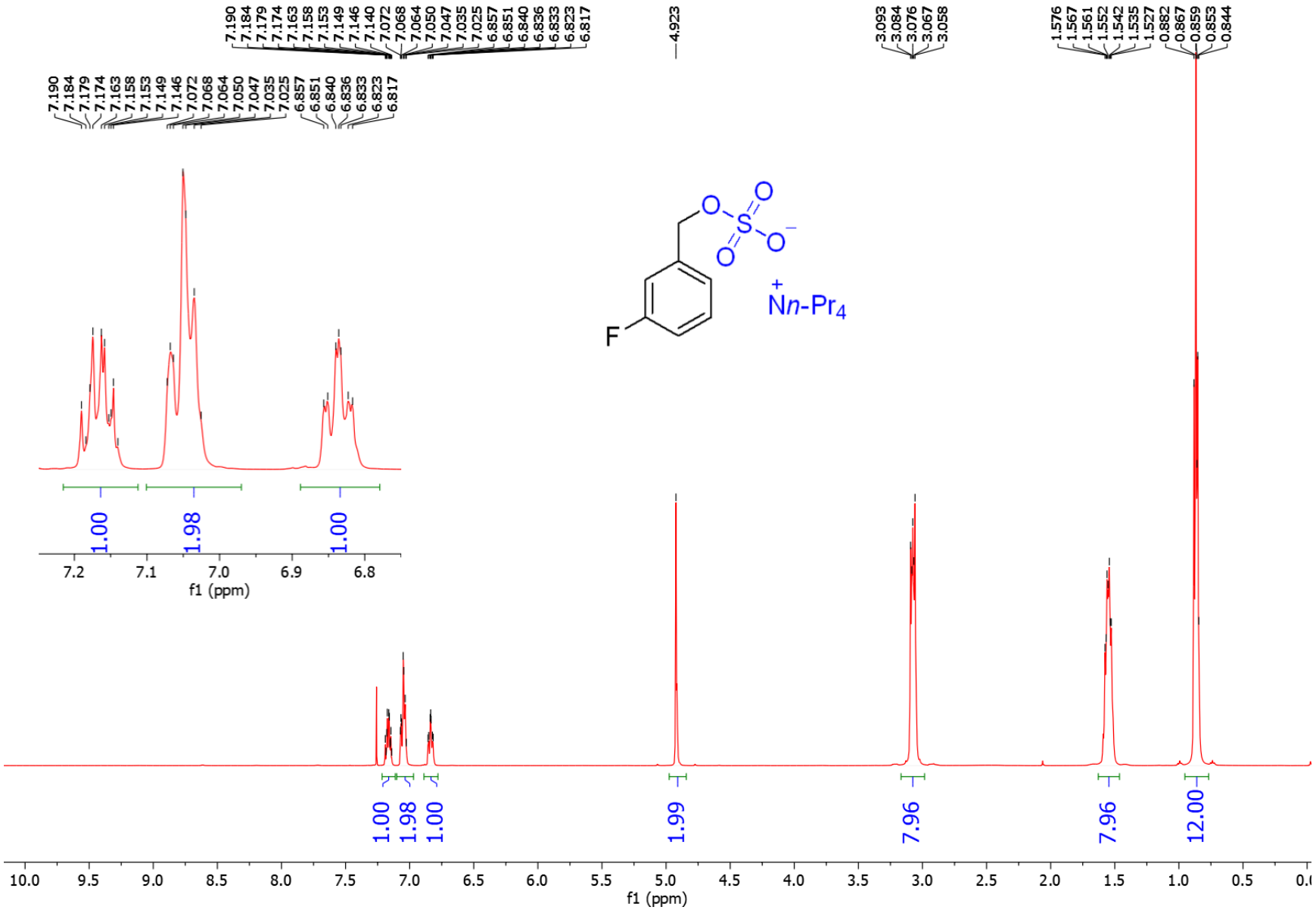
^{1}H NMR spectrum of tetrapropylammonium 3-fluorobenzylsulfate (5h)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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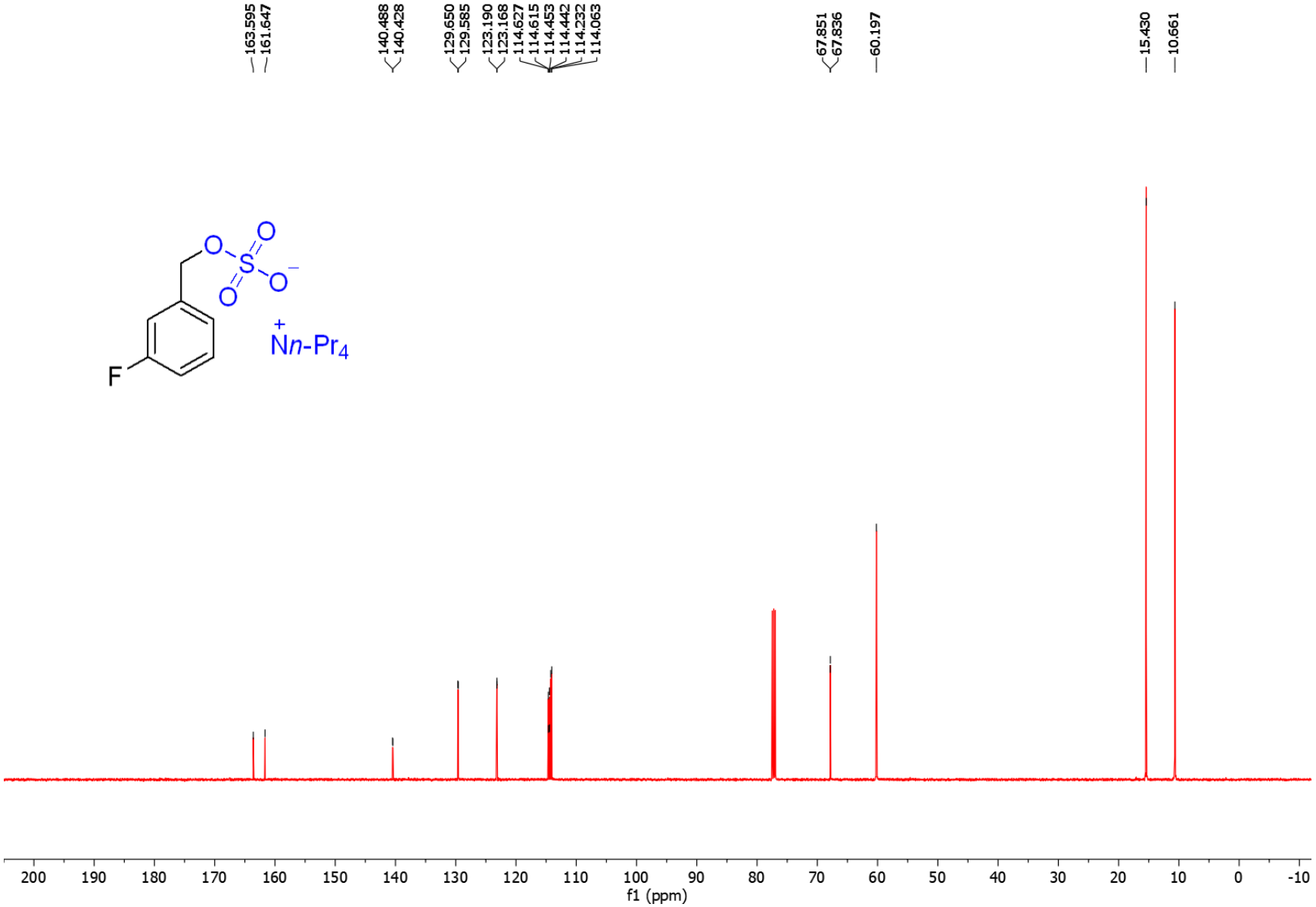
^{13}C NMR spectrum of tetrapropylammonium 3-fluorobenzylsulfate (5h)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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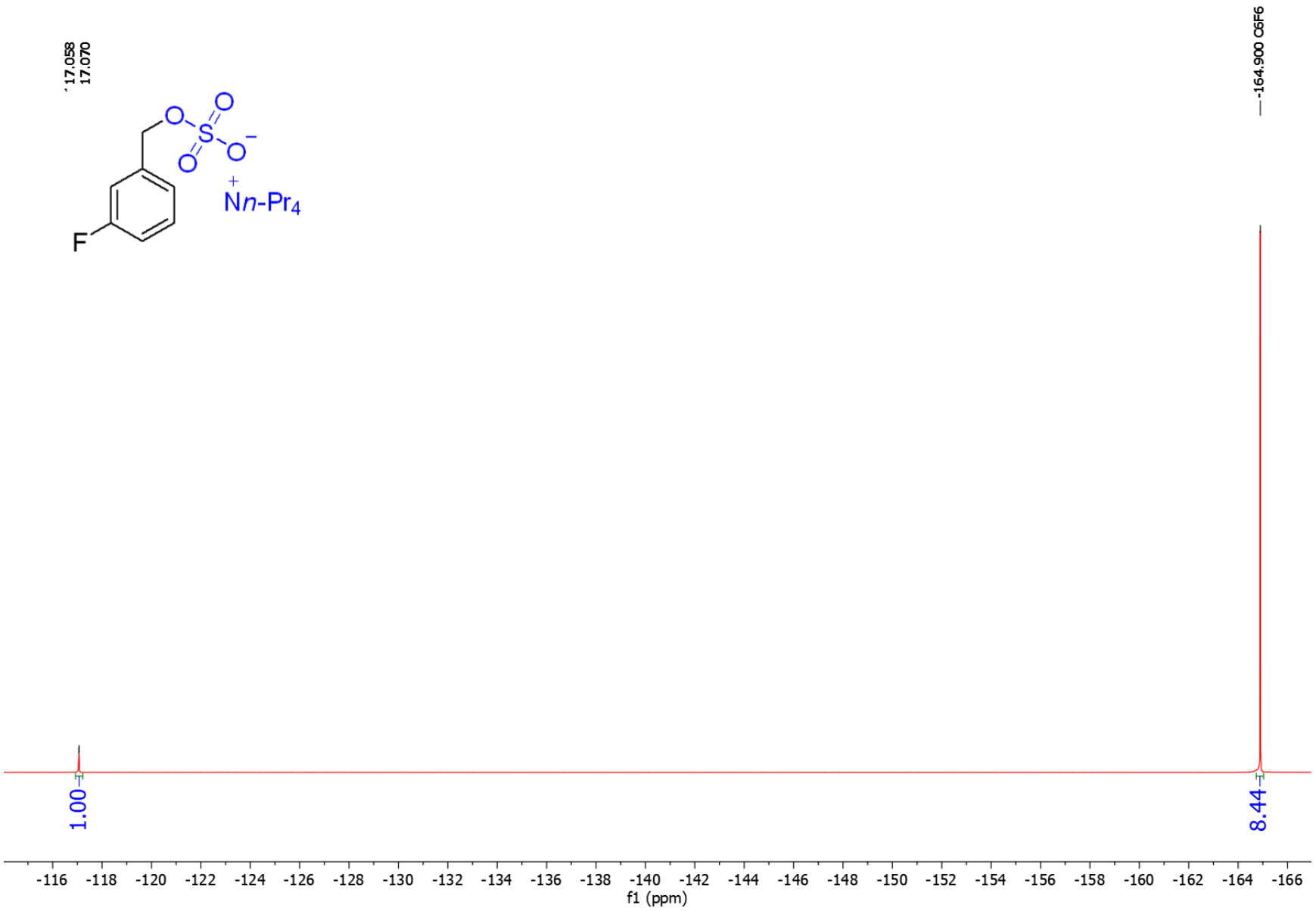
^{19}F NMR spectrum of tetrapropylammonium 3-fluorobenzylsulfate (5h)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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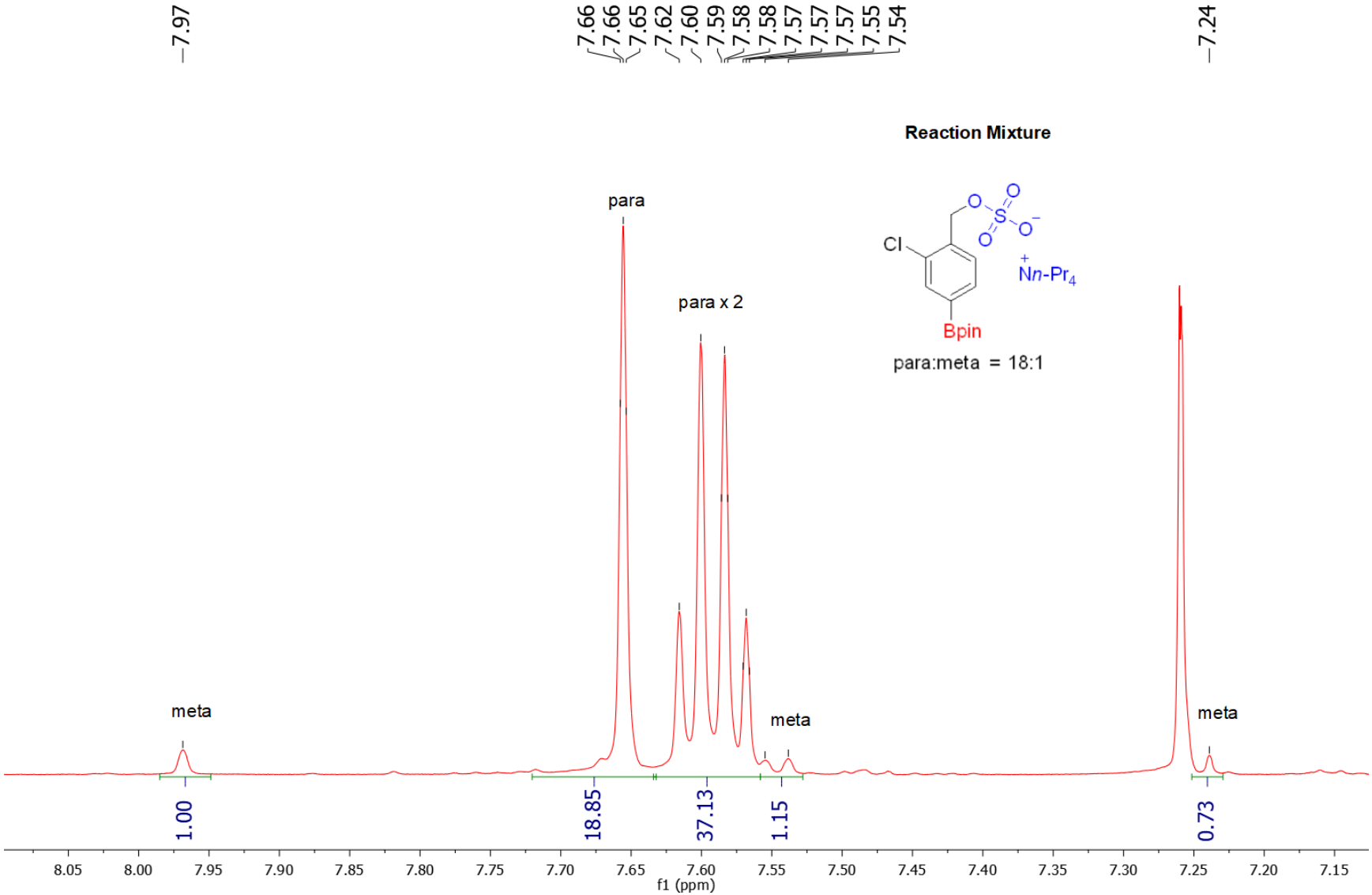
^{1}H NMR spectrum of reaction mixture of para borylation of tetrapropylammonium 2-chlorobenzylsulfate (crude 6a)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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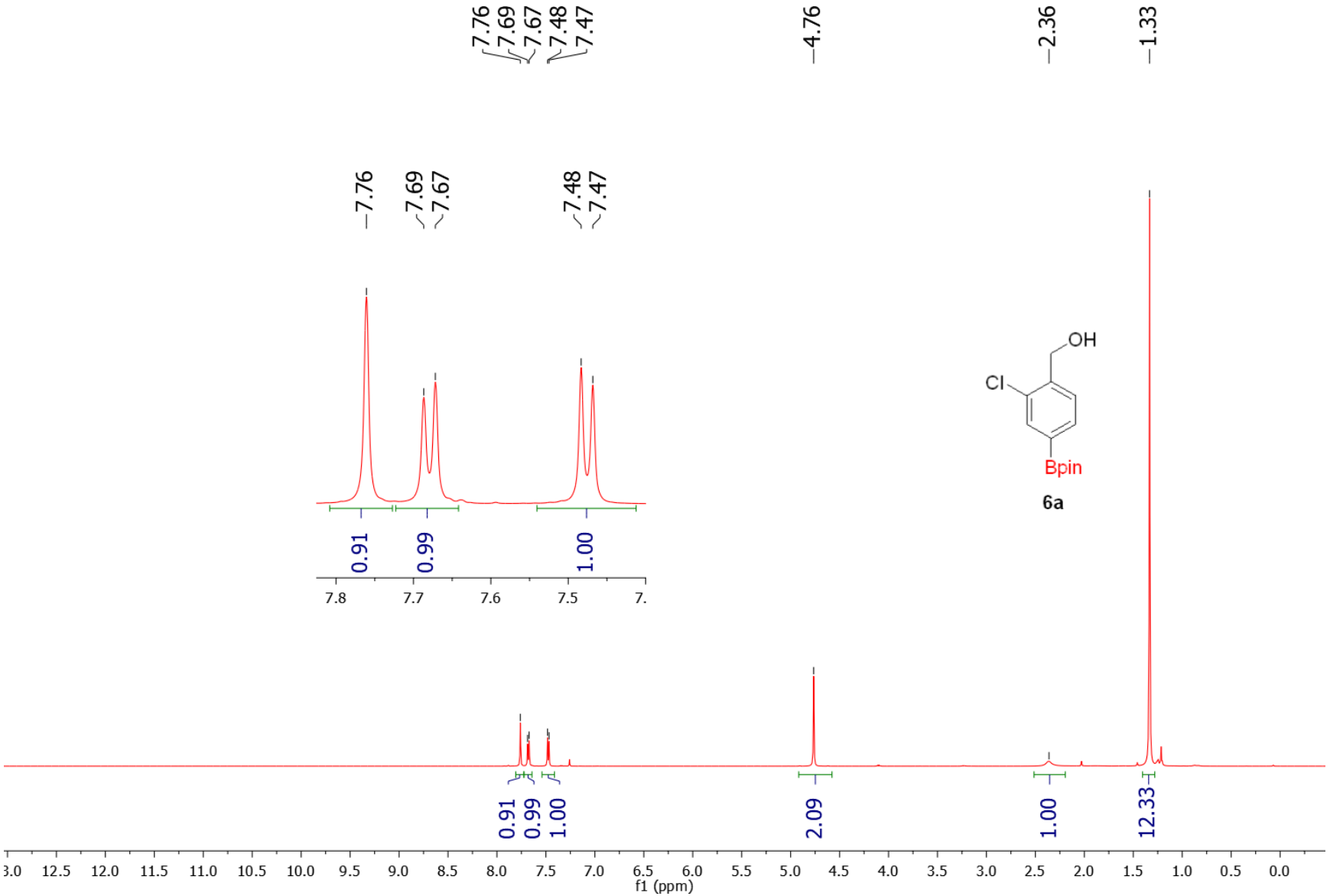
^{1}H NMR spectrum of para borylated 2-chlorobenzylalcohol (6a)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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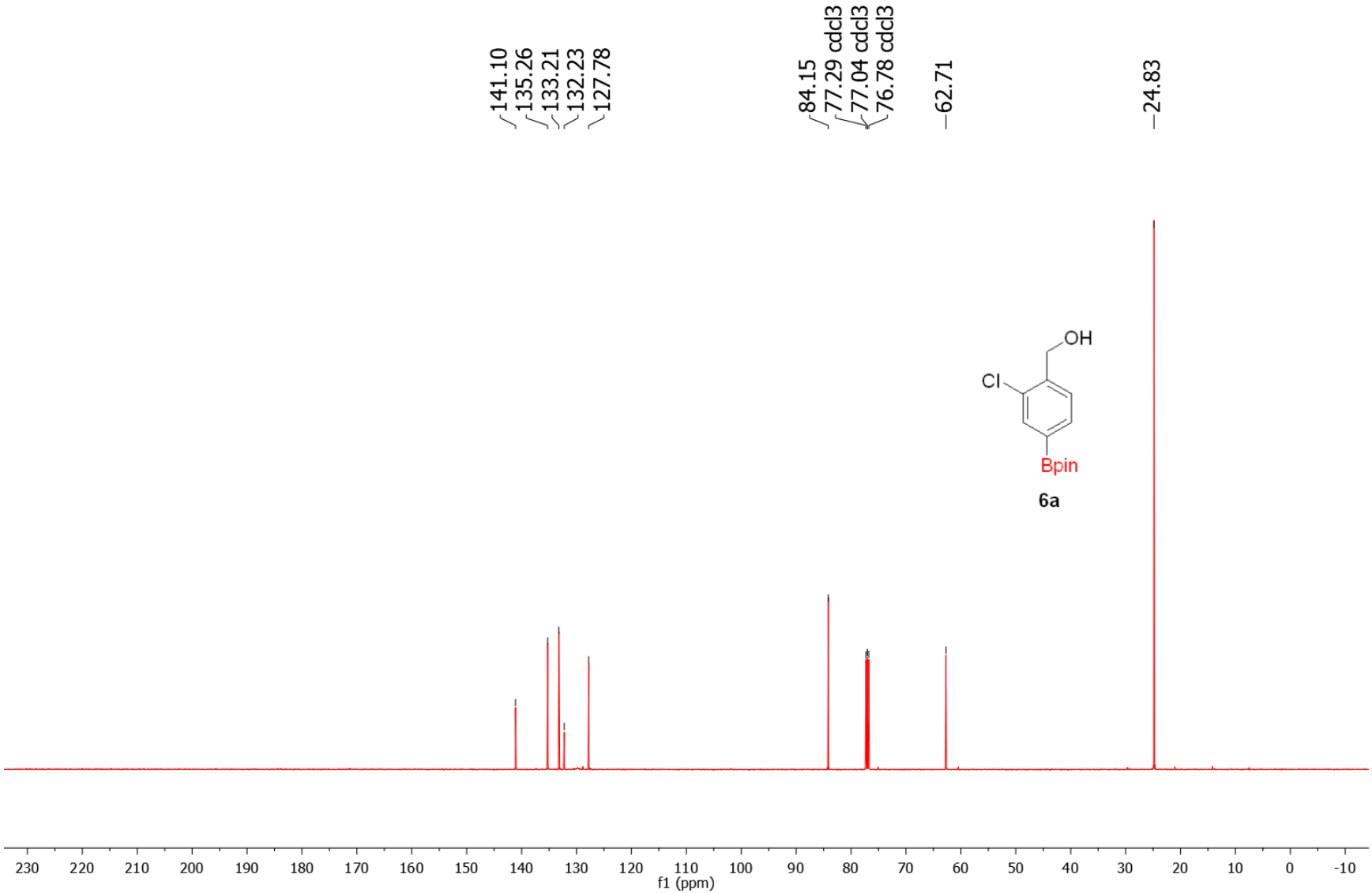
^{13}C NMR spectrum of para borylated 2-chlorobenzylalcohol (6a)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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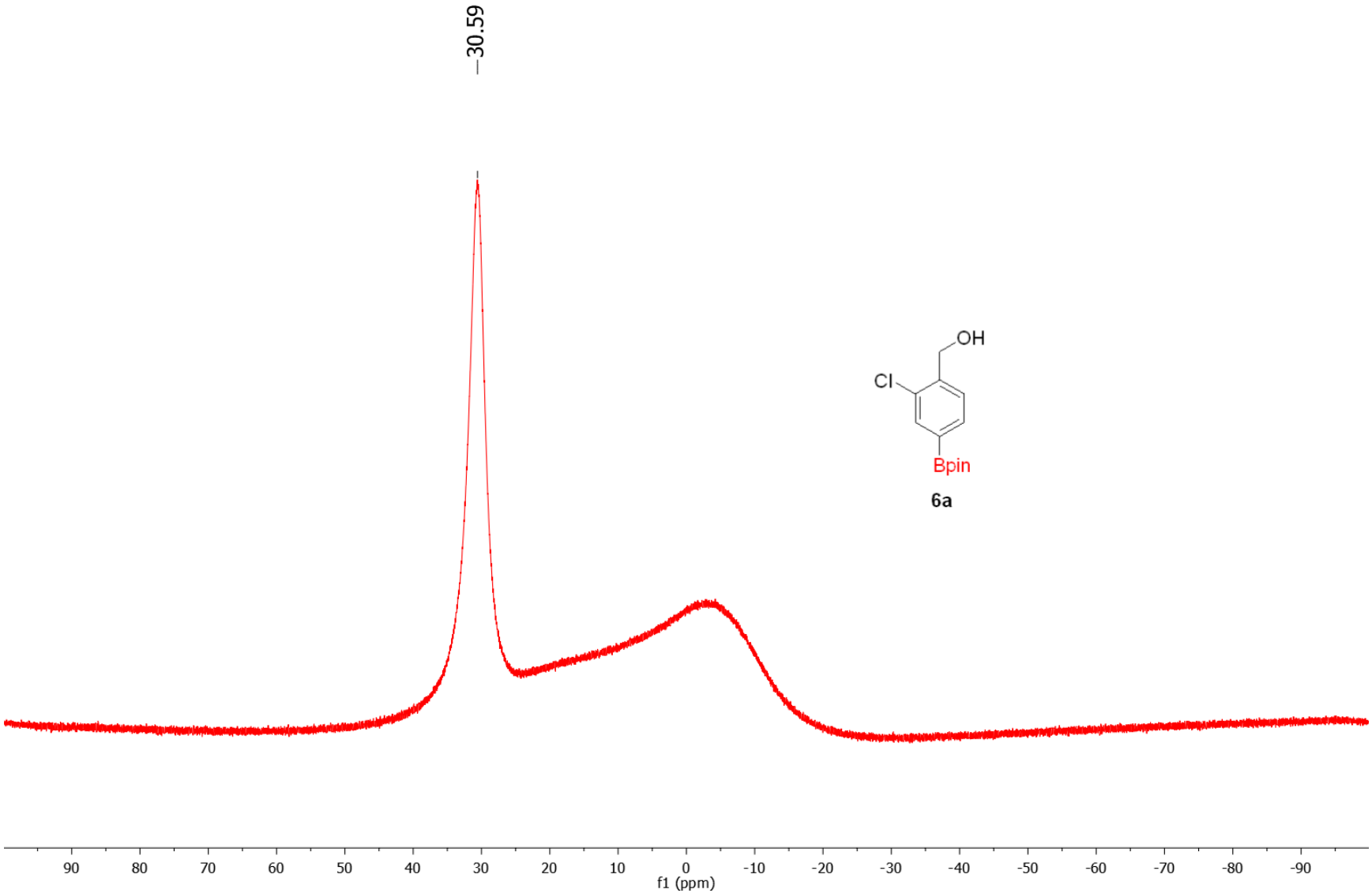
^{11}B NMR spectrum of para borylated 2-chlorobenzylalcohol (6a)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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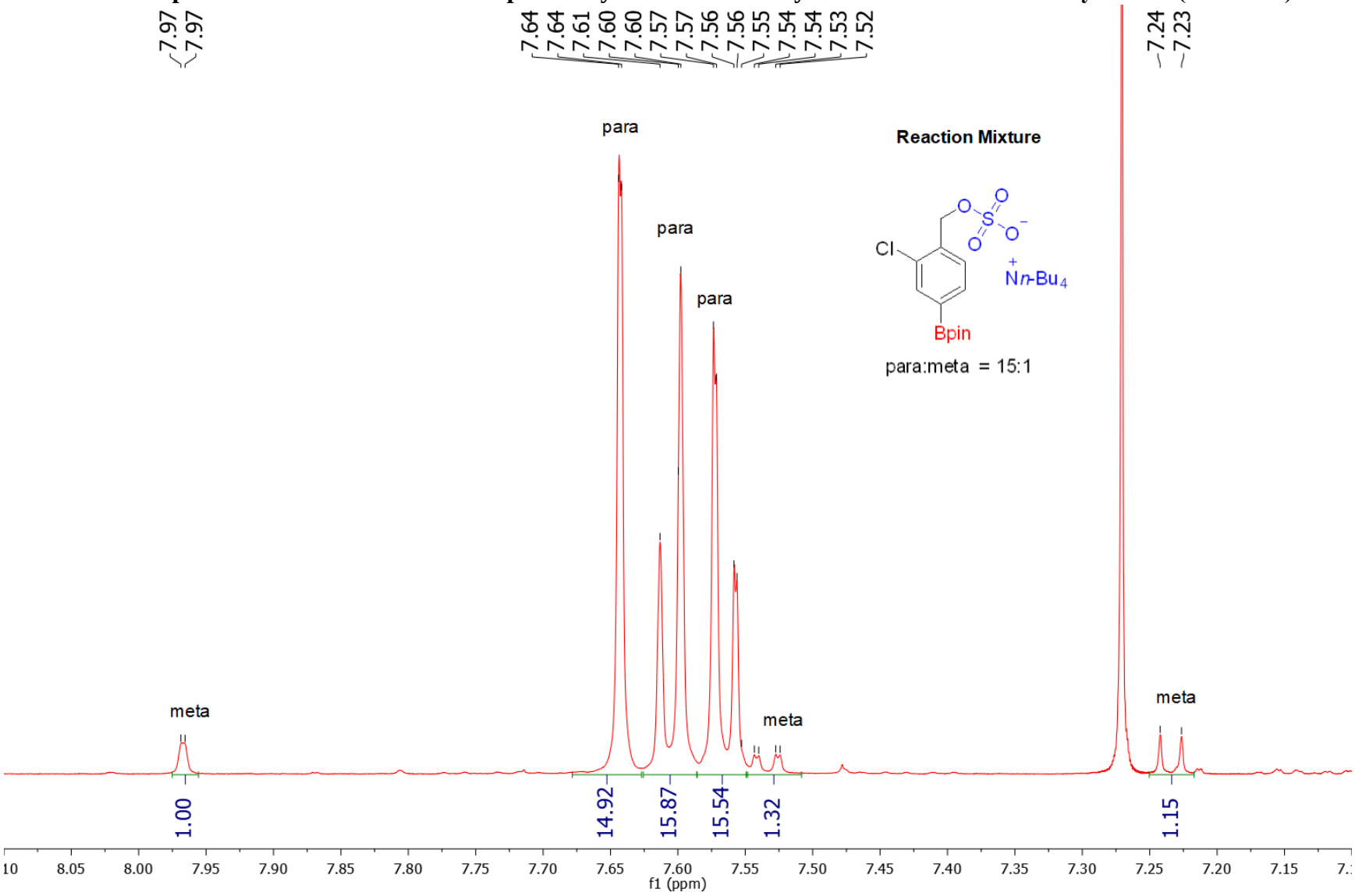
^{1}H NMR spectrum of reaction mixture of para borylation of tetrabutylammonium 2-chlorobenzylsulfate (crude 6a′)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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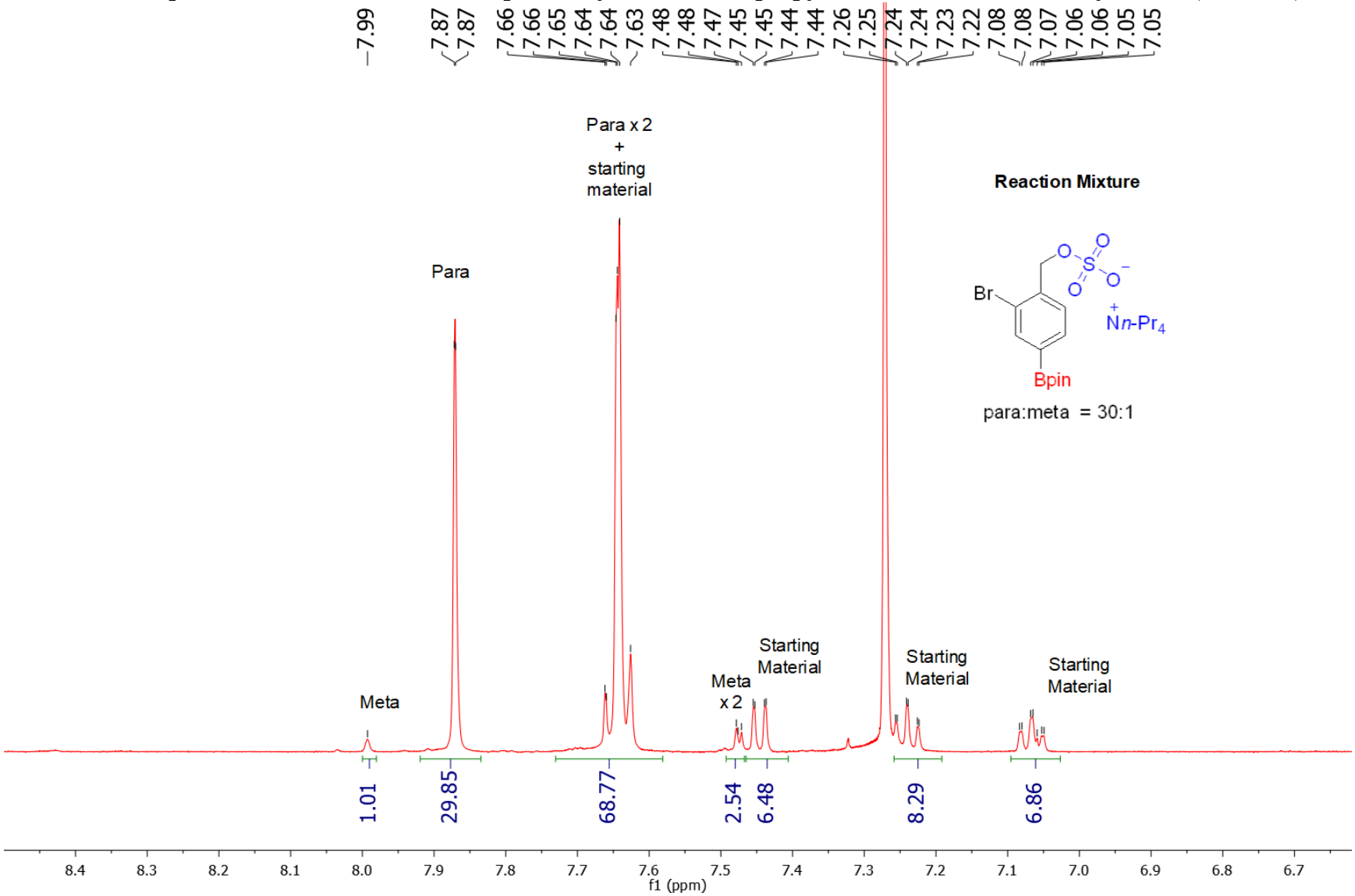
^{1}H NMR spectrum of reaction mixture of para borylation of tetrapropylammonium 2-bromobenzylsulfate (crude 6b)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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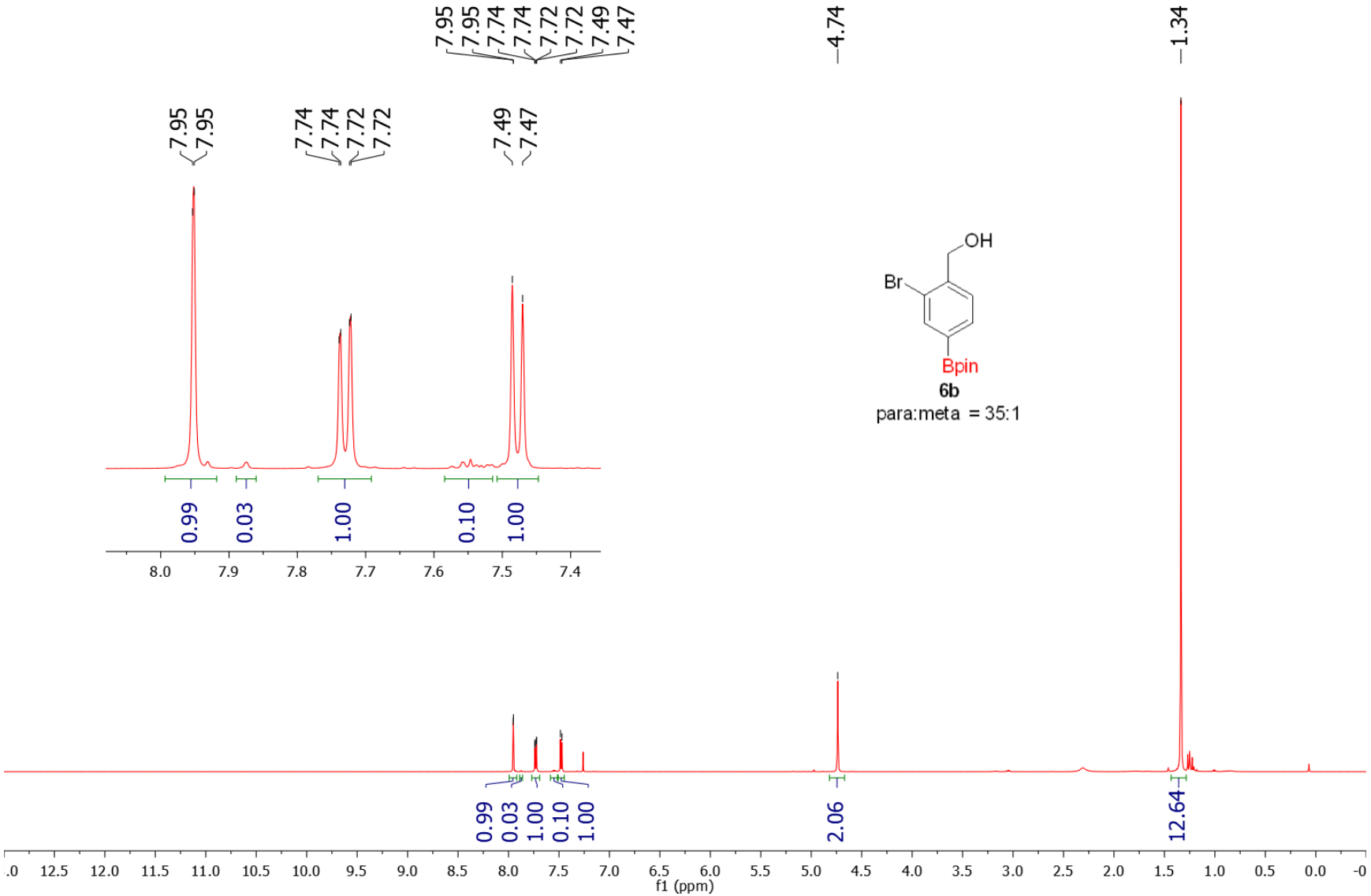
^{1}H NMR spectrum of para borylated of 2-bromobenzylalcohol (6b)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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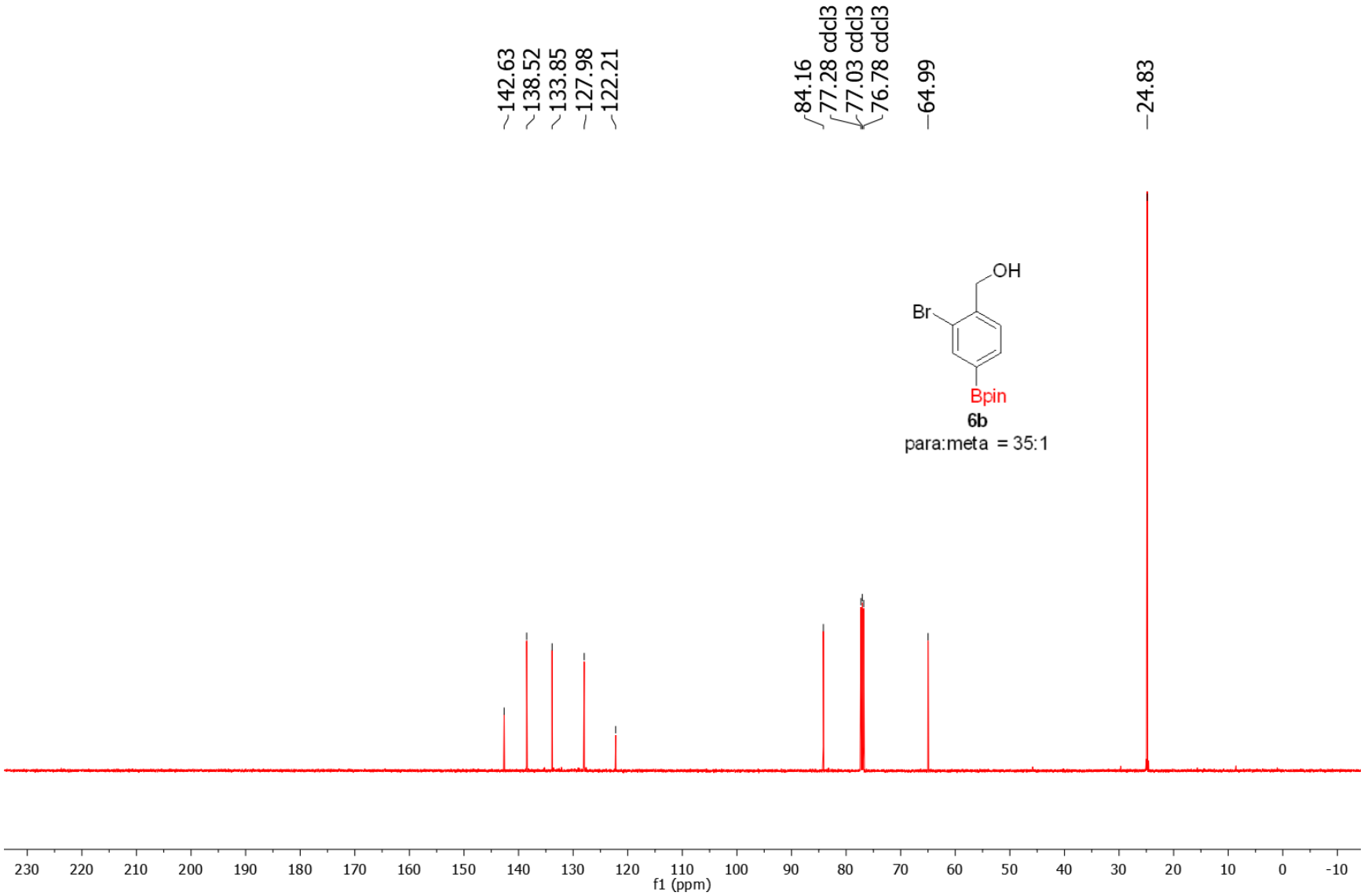
^{13}C NMR spectrum of para borylated 2-bromobenzylalcohol (6b)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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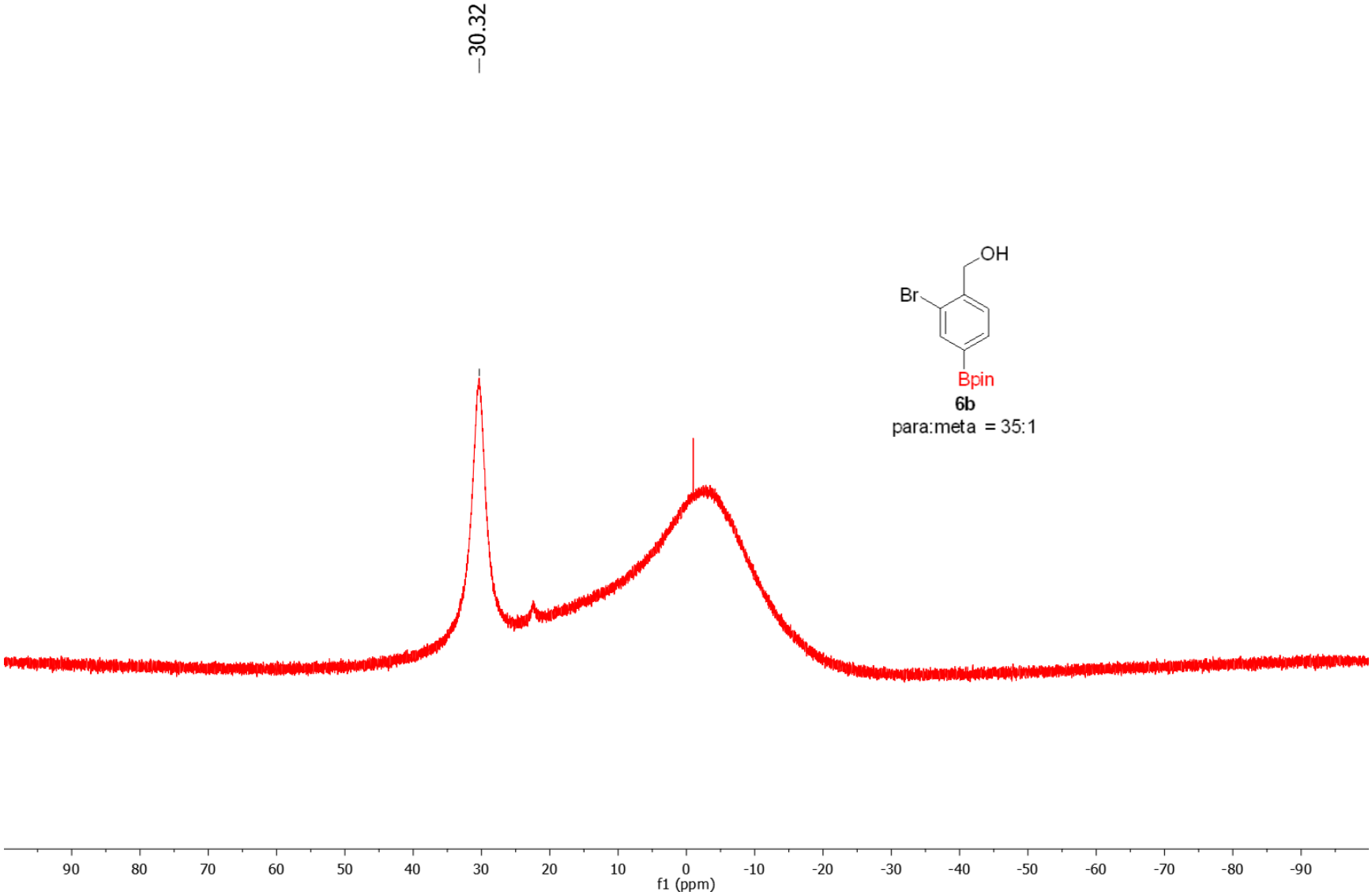
^{11}B NMR spectrum of para borylated 2-bromobenzylalcohol (6b)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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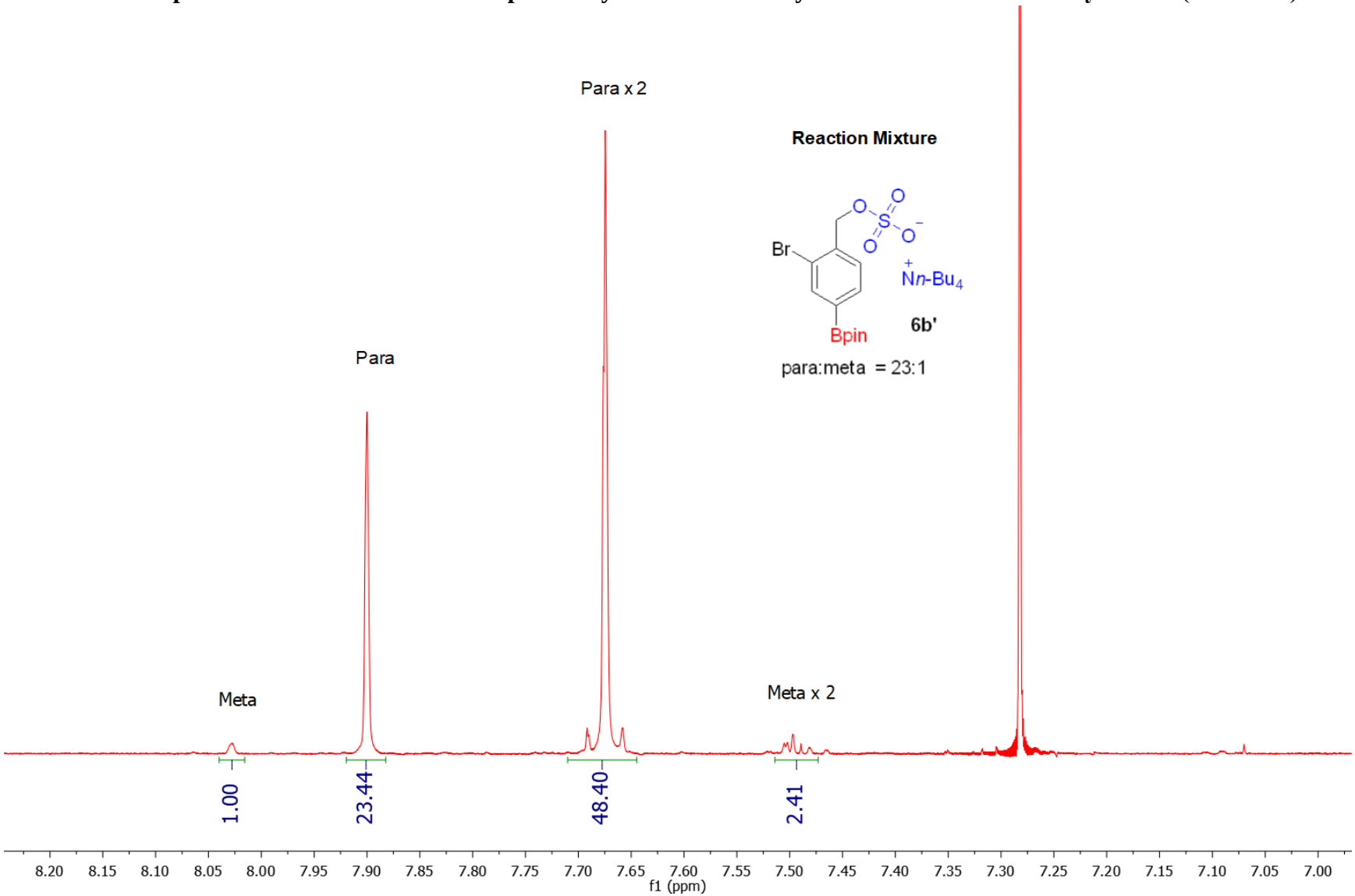
^{1}H NMR spectrum of reaction mixture of para borylation of tetrabutylammonium 2-bromobenzylsulfate (crude 6b′)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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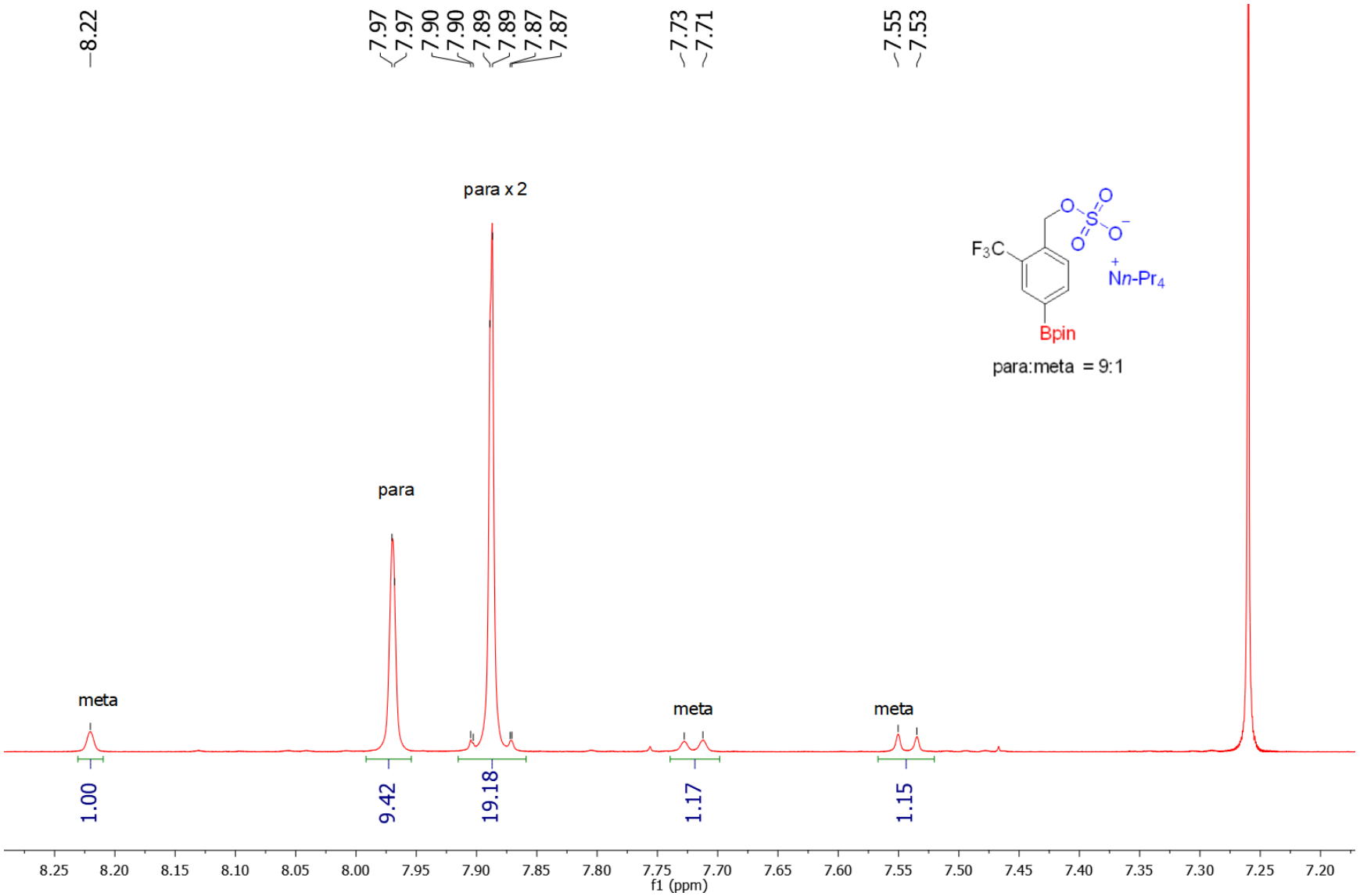
^{1}H NMR spectrum of the reaction mixture of para borylation of 2-(trifluoromethyl)benzylsulfate (crude 6c)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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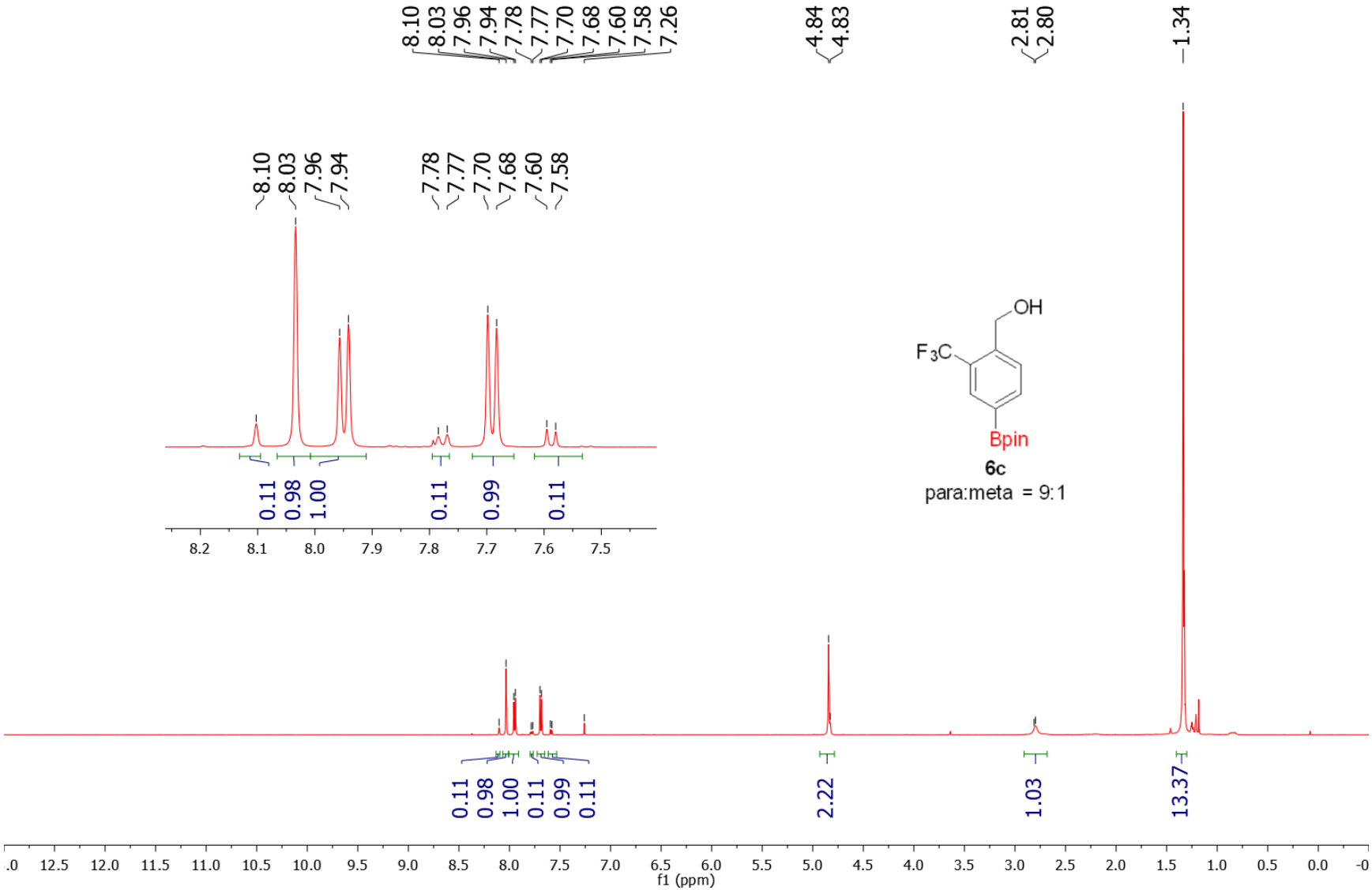
^{1}H NMR spectrum of para borylated 2-(trifluoromethyl)benzylalcohol (6c)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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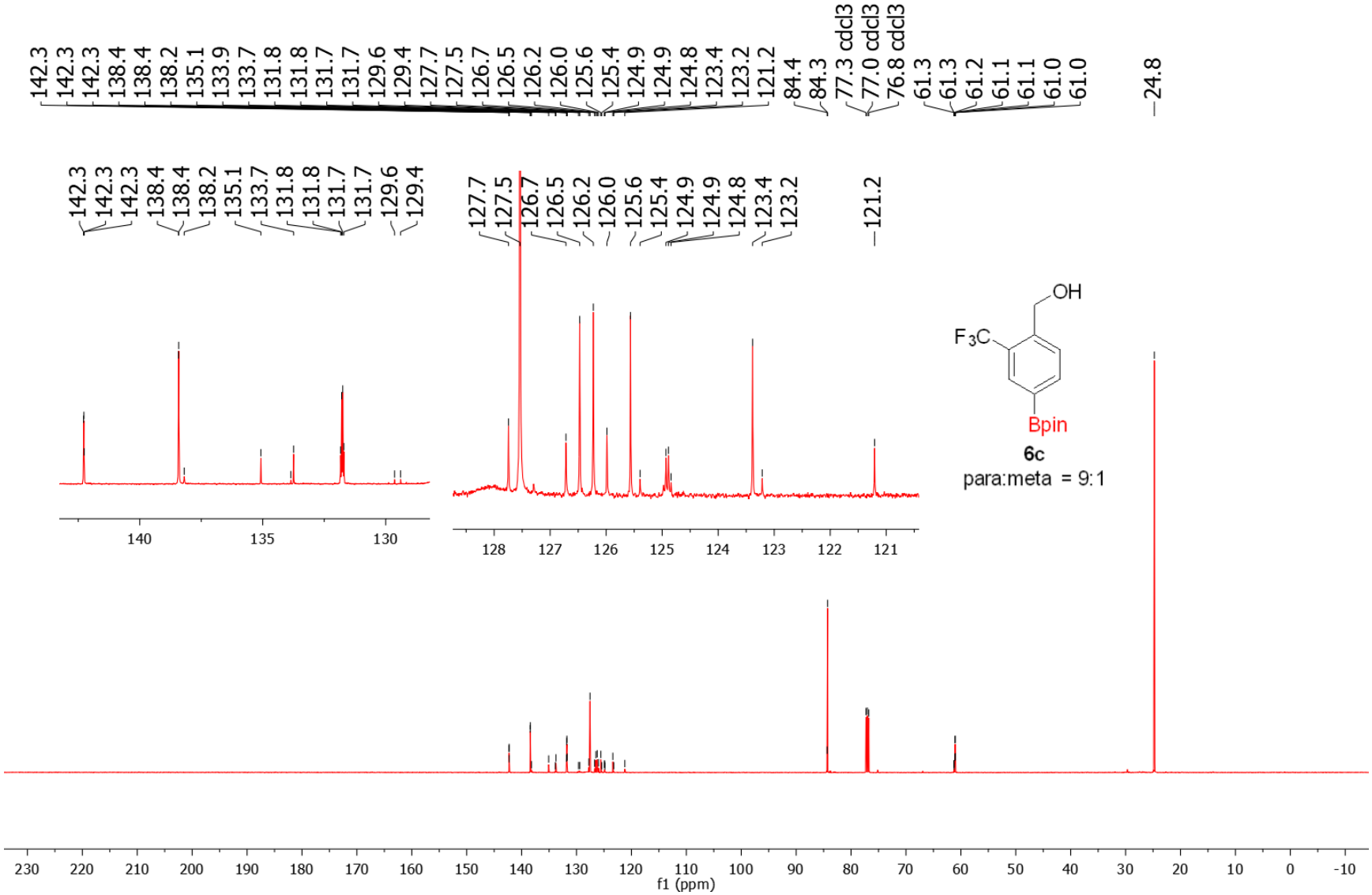
^{13}C NMR spectrum of para borylated 2-(trifluoromethyl)benzylalcohol (6c)



Conditions: 25 ºC, 126 MHz, $CDCl_3$

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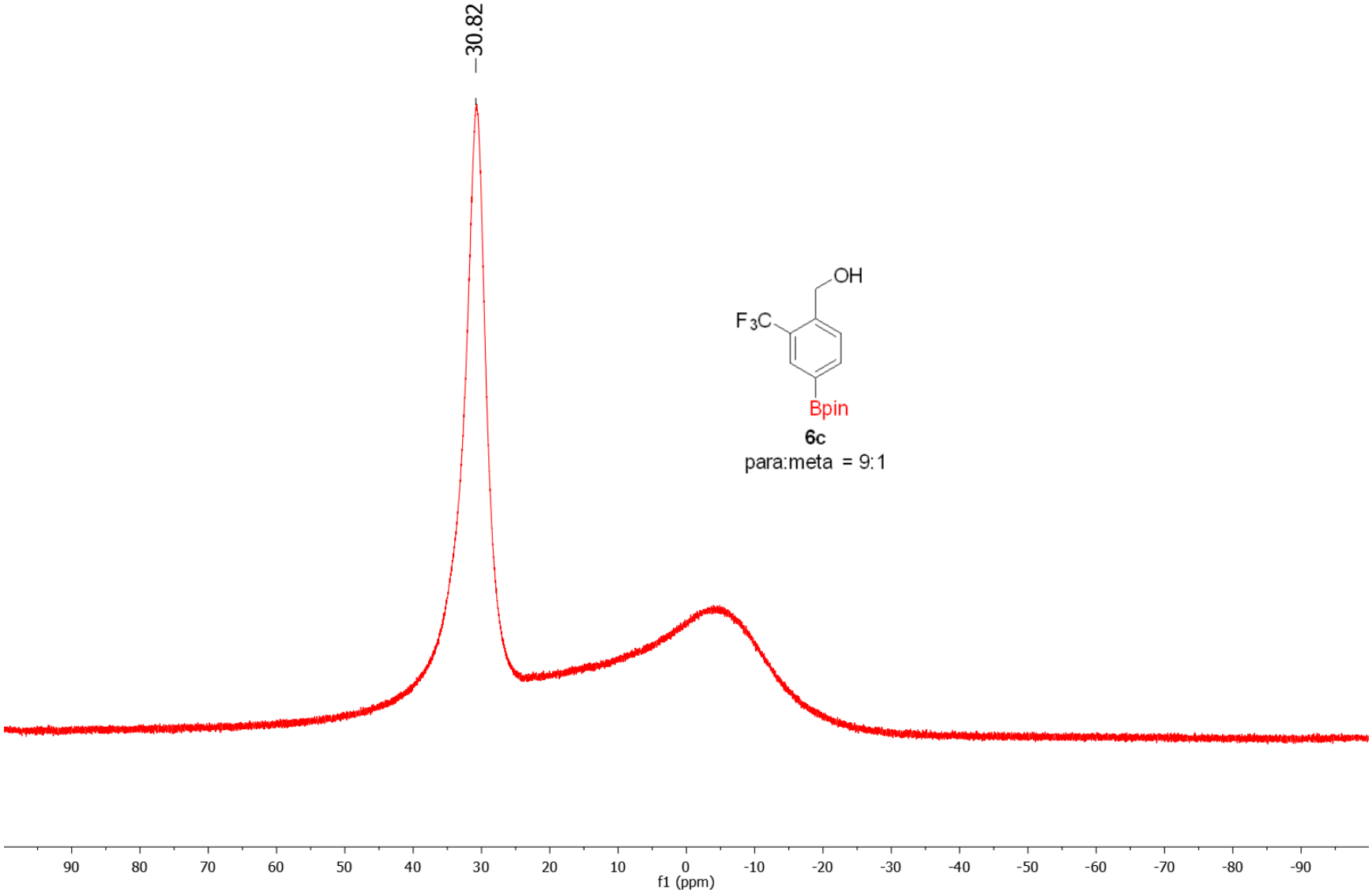
^{11}B NMR spectrum of para borylated 2-(trifluoromethyl)benzylalcohol (6c)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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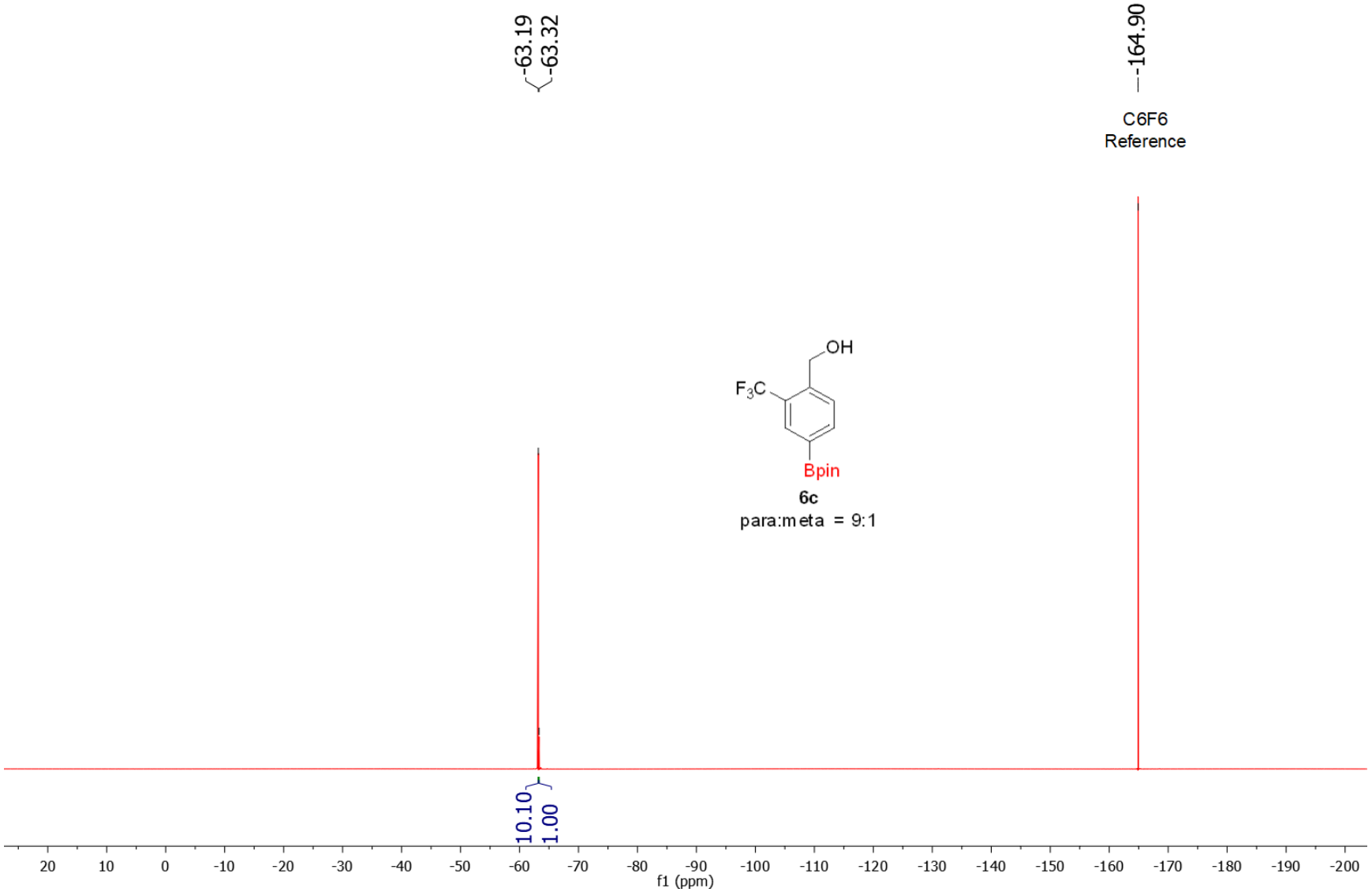
^{19}F NMR spectrum of para borylated 2-(trifluoromethyl)benzylalcohol (6c)



Conditions: 25ºC, 470 MHz, $CDCl_3$

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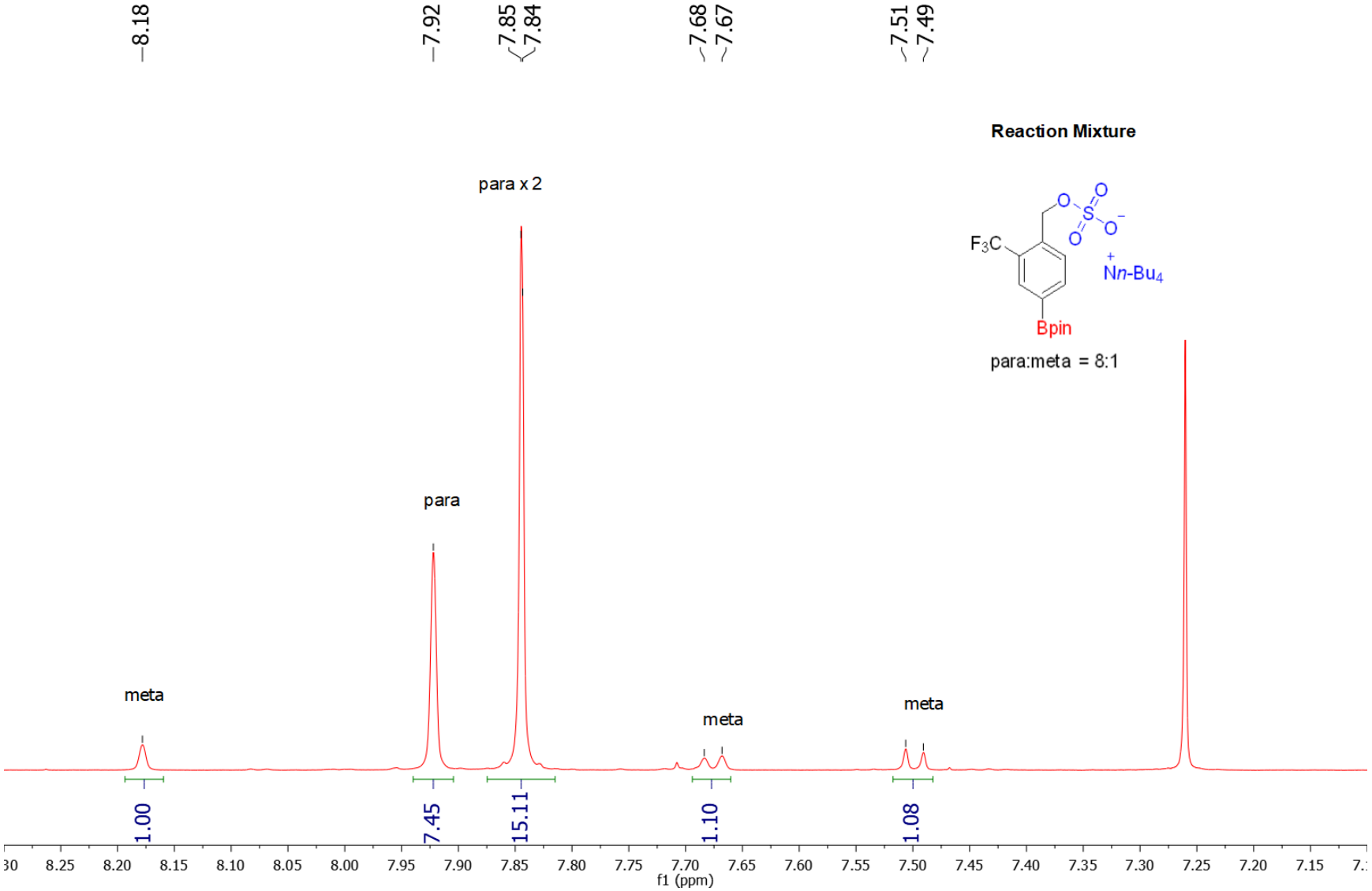
^{1}H NMR spectrum of the reaction mixture of para borylation of 2-(trifluoromethyl)benzylsulfate (crude 6c′)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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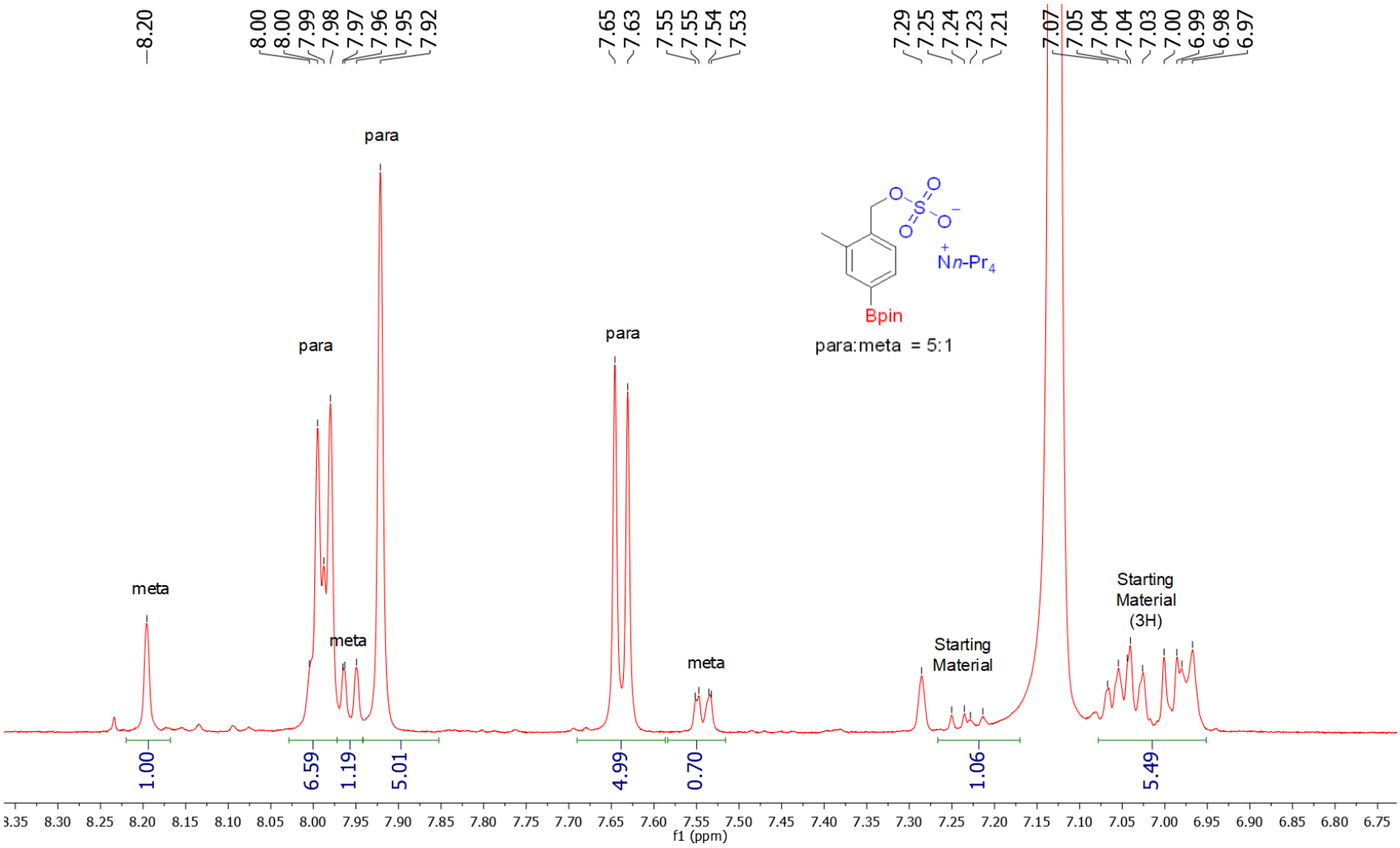
^{1}H NMR spectrum of the reaction mixture of para borylation of 2-methylbenzylsulfate (crude 6d)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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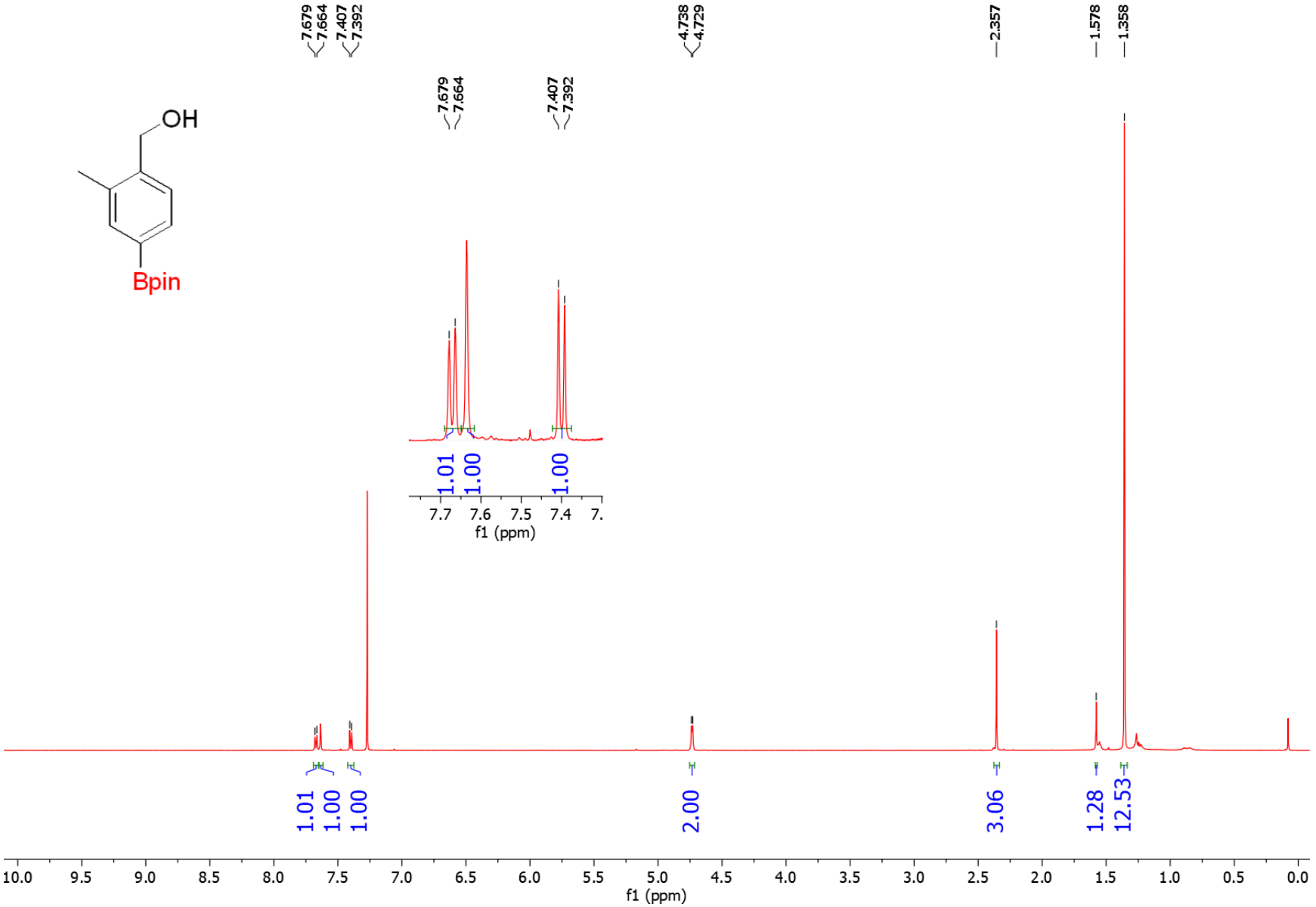
^{1}H NMR spectrum of para borylated 2-(methyl)benzylalcohol (6d)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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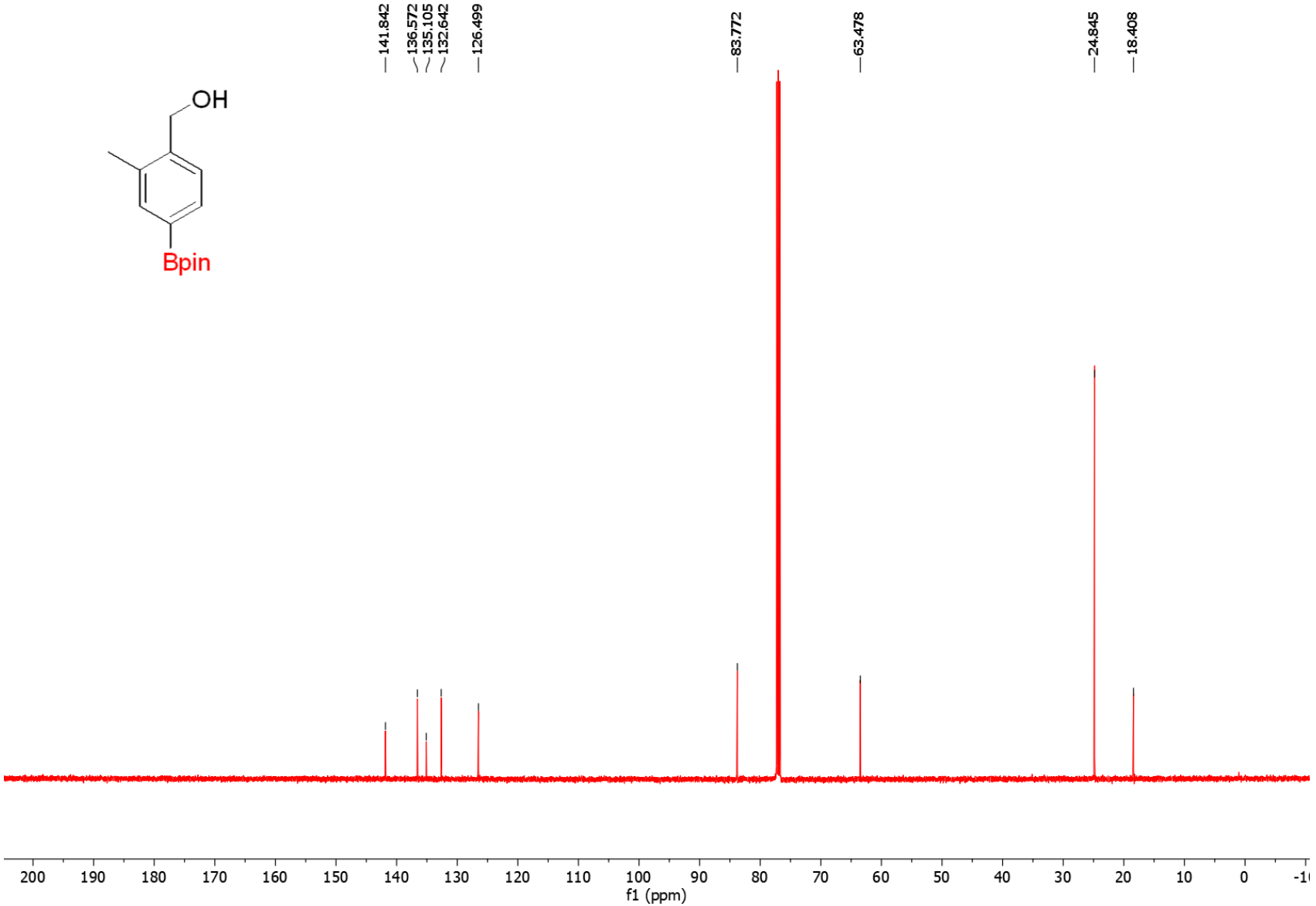
^{13}C NMR spectrum of para borylated 2-(methyl)benzylalcohol (6d)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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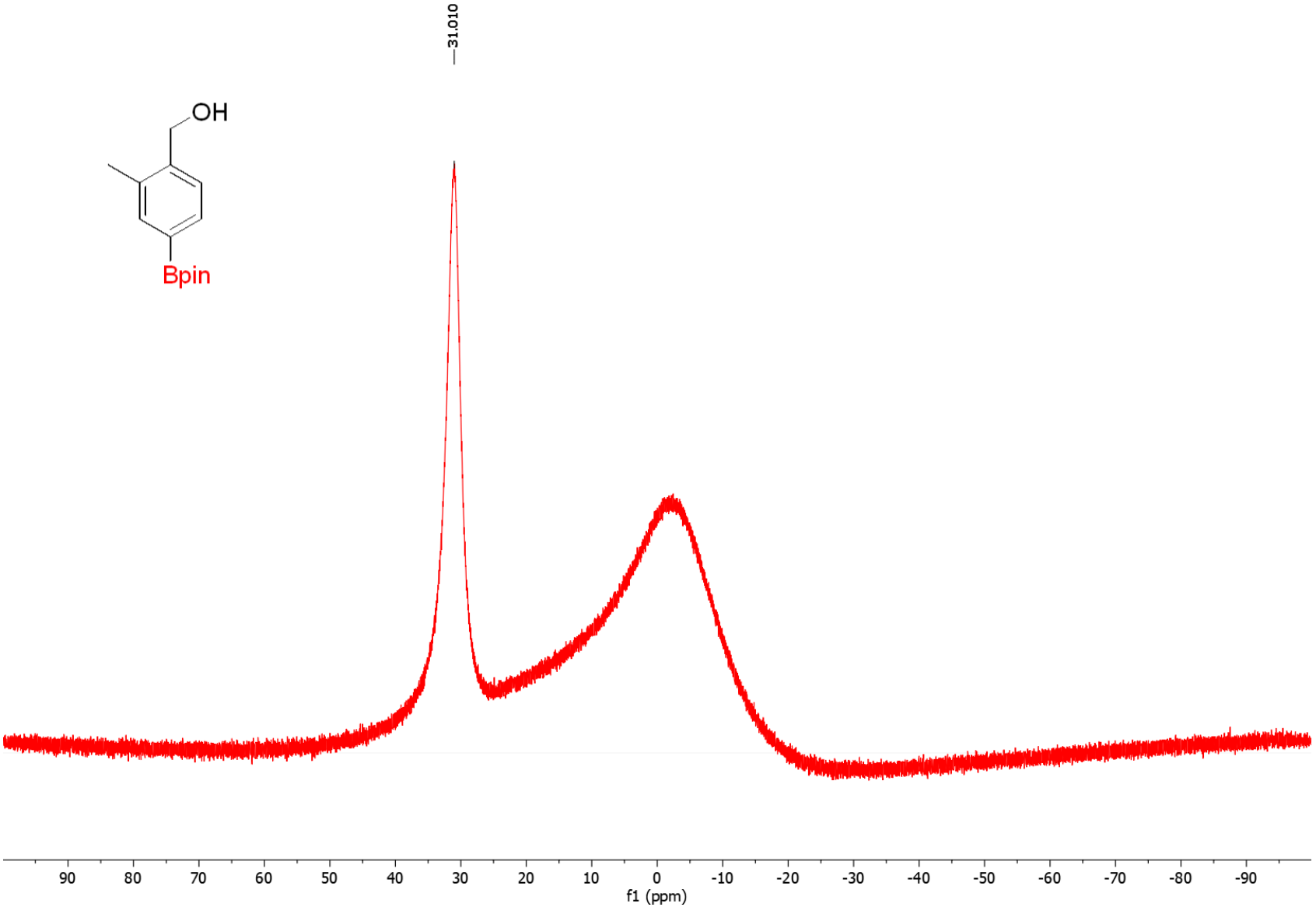
^{11}B NMR spectrum of para borylated 2-(methyl)benzylalcohol (6d)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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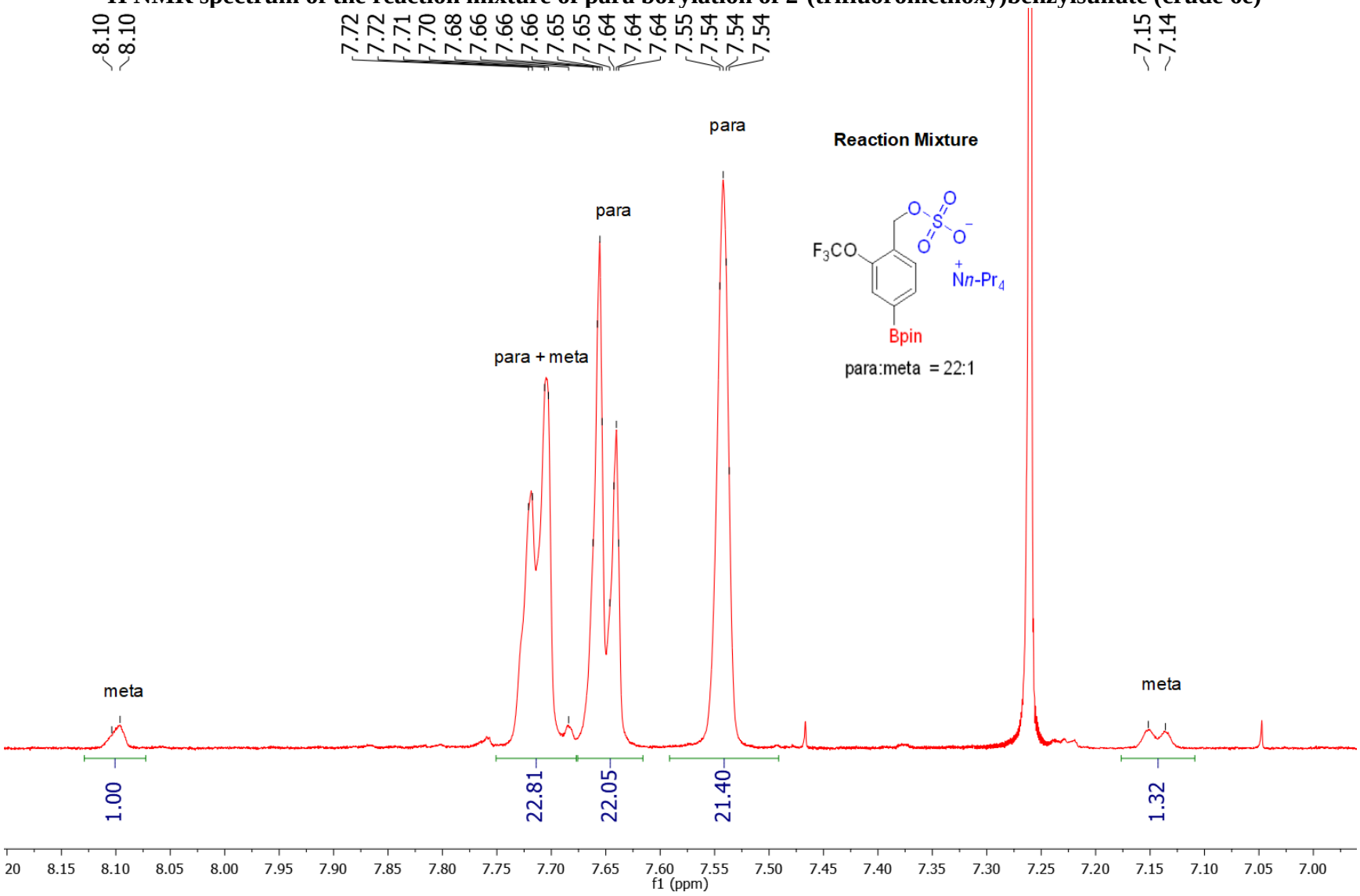
^{1}H NMR spectrum of the reaction mixture of para borylation of 2-(trifluoromethoxy)benzylsulfate (crude 6e)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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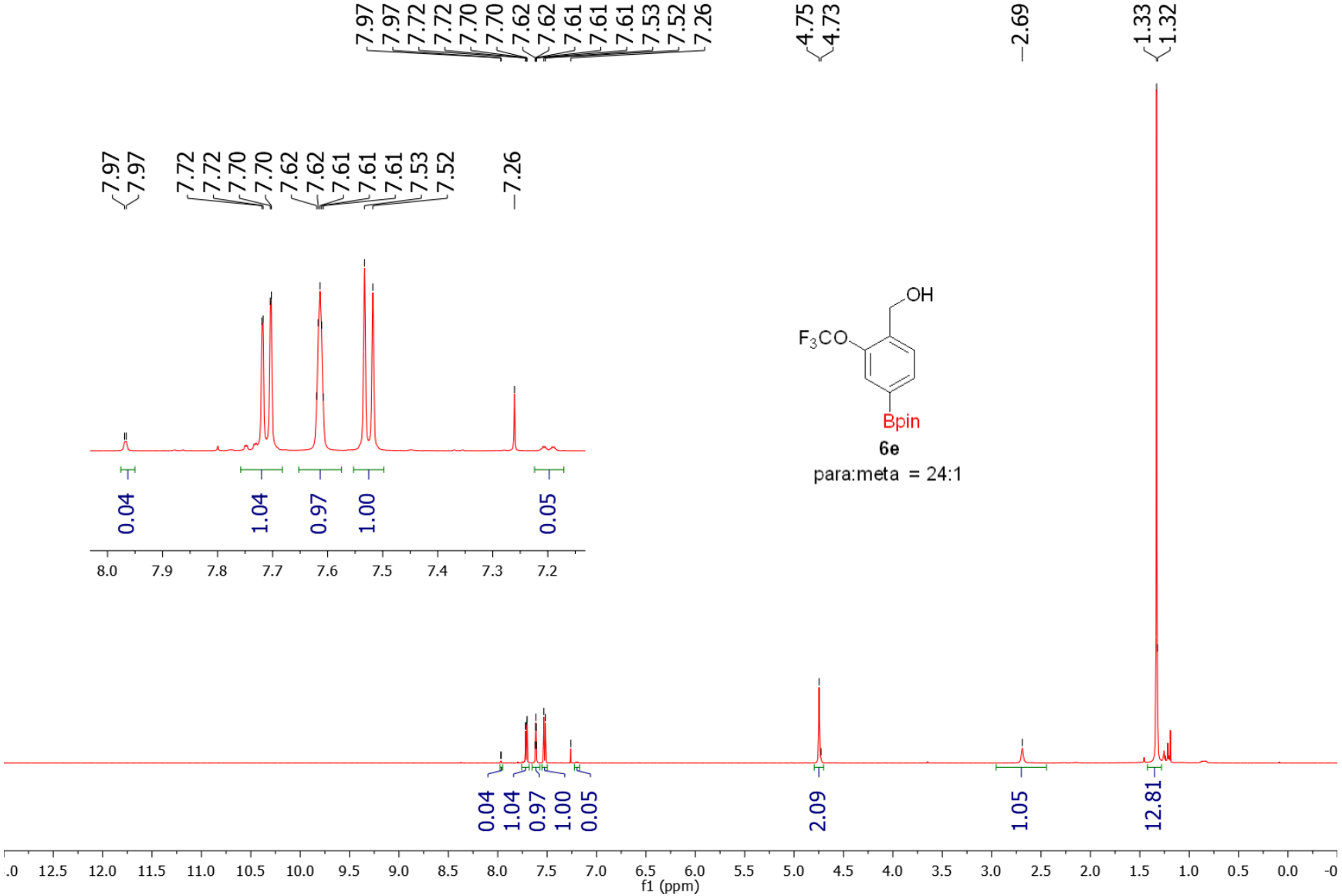
^{1}H NMR spectrum of para borylated 2-(trifluoromethoxy)benzyl alcohol (6e)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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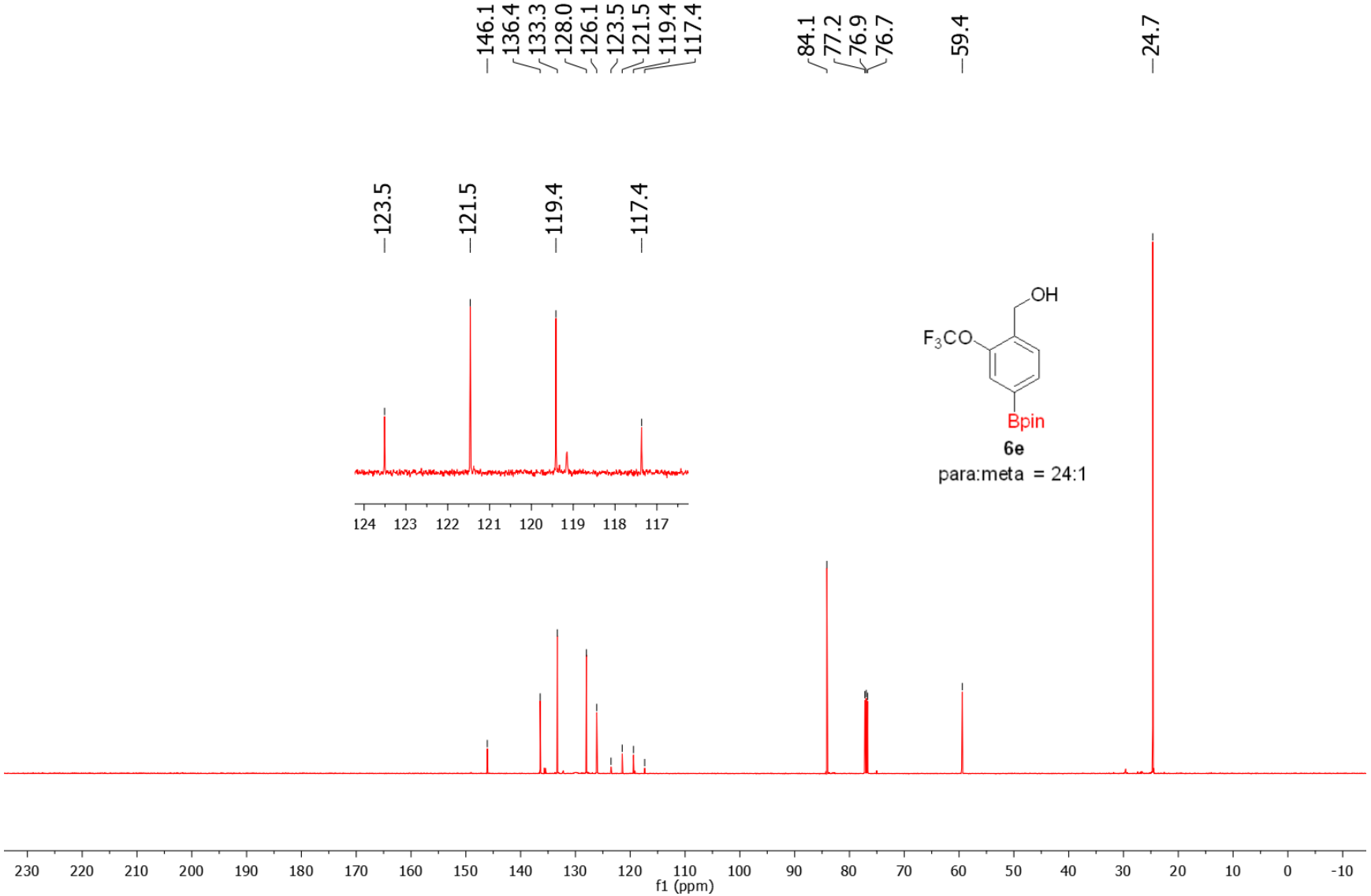
^{13}C NMR spectrum of para borylated 2-(trifluoromethoxy)benzyl alcohol (6e)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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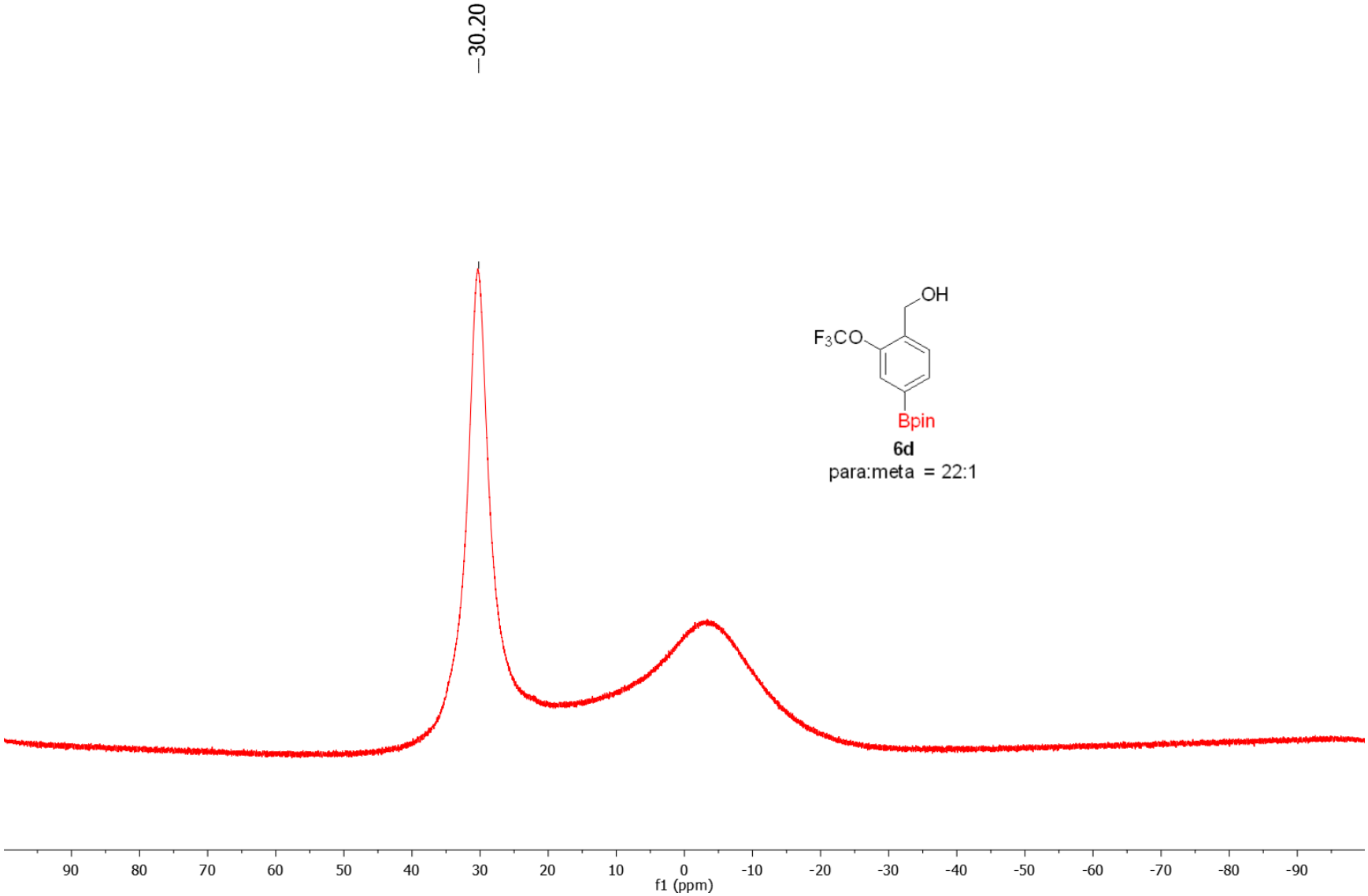
^{11}B NMR spectrum of para borylated 2-(trifluoromethoxy)benzyl alcohol (6e)



Conditions: 25 ºC, 160 MHz, $CDCl_3$

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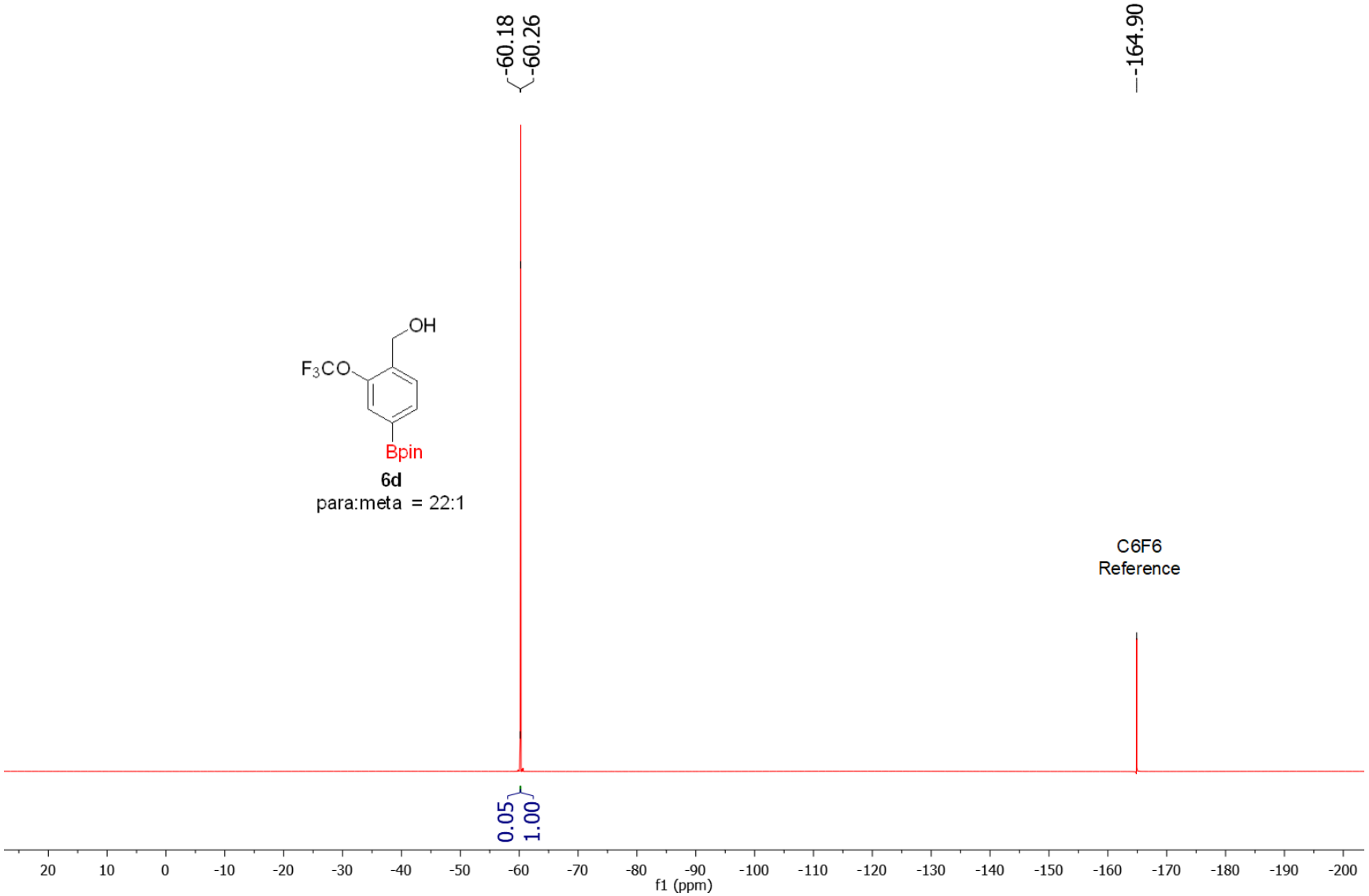
^{19}F NMR spectrum of para borylated 2-(trifluoromethoxy)benzyl alcohol (6e)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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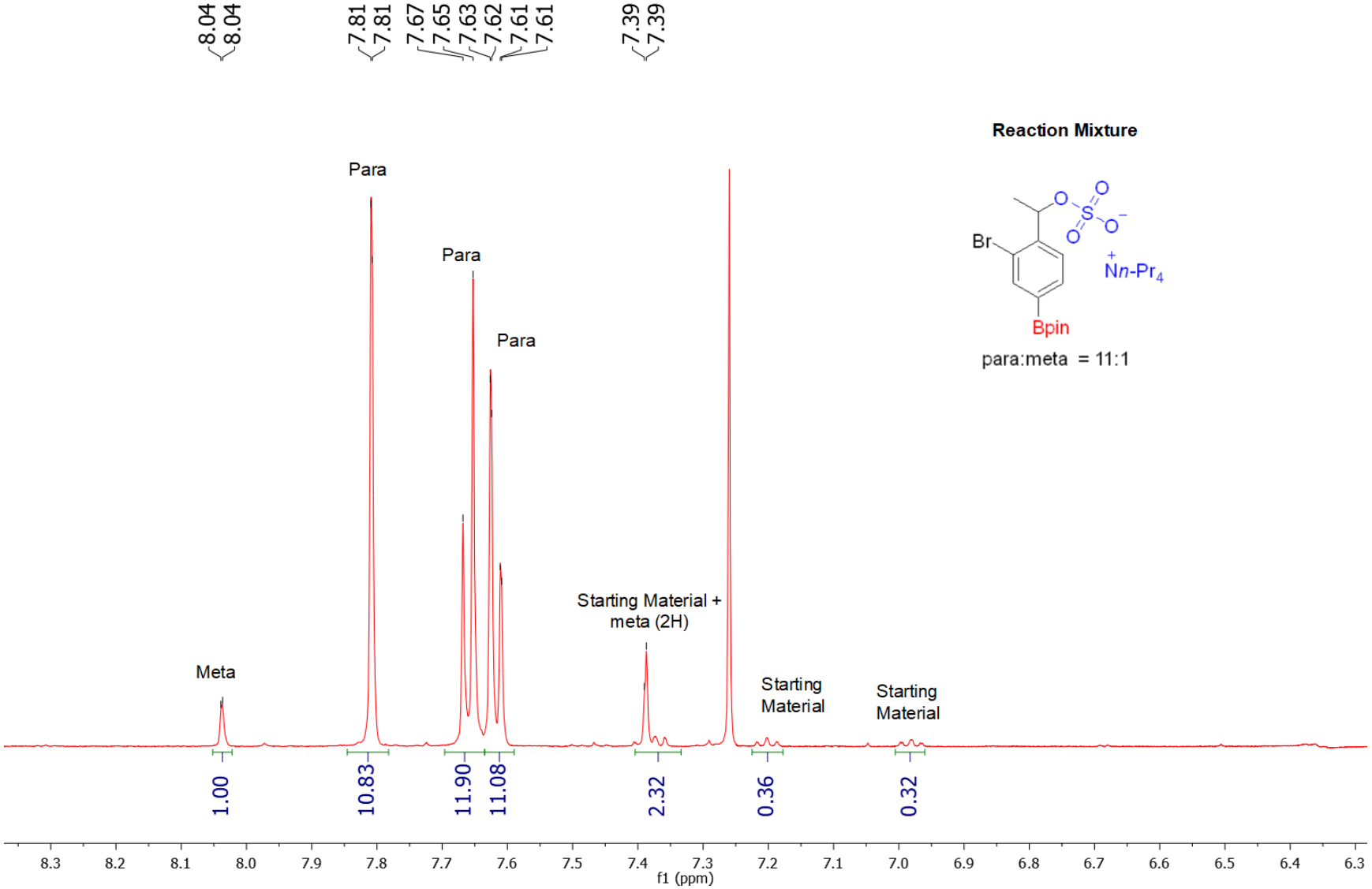
^{1}H NMR spectrum of the reaction mixture of para borylation of 1-(2-bromophenyl)ethyl sulfate (6f)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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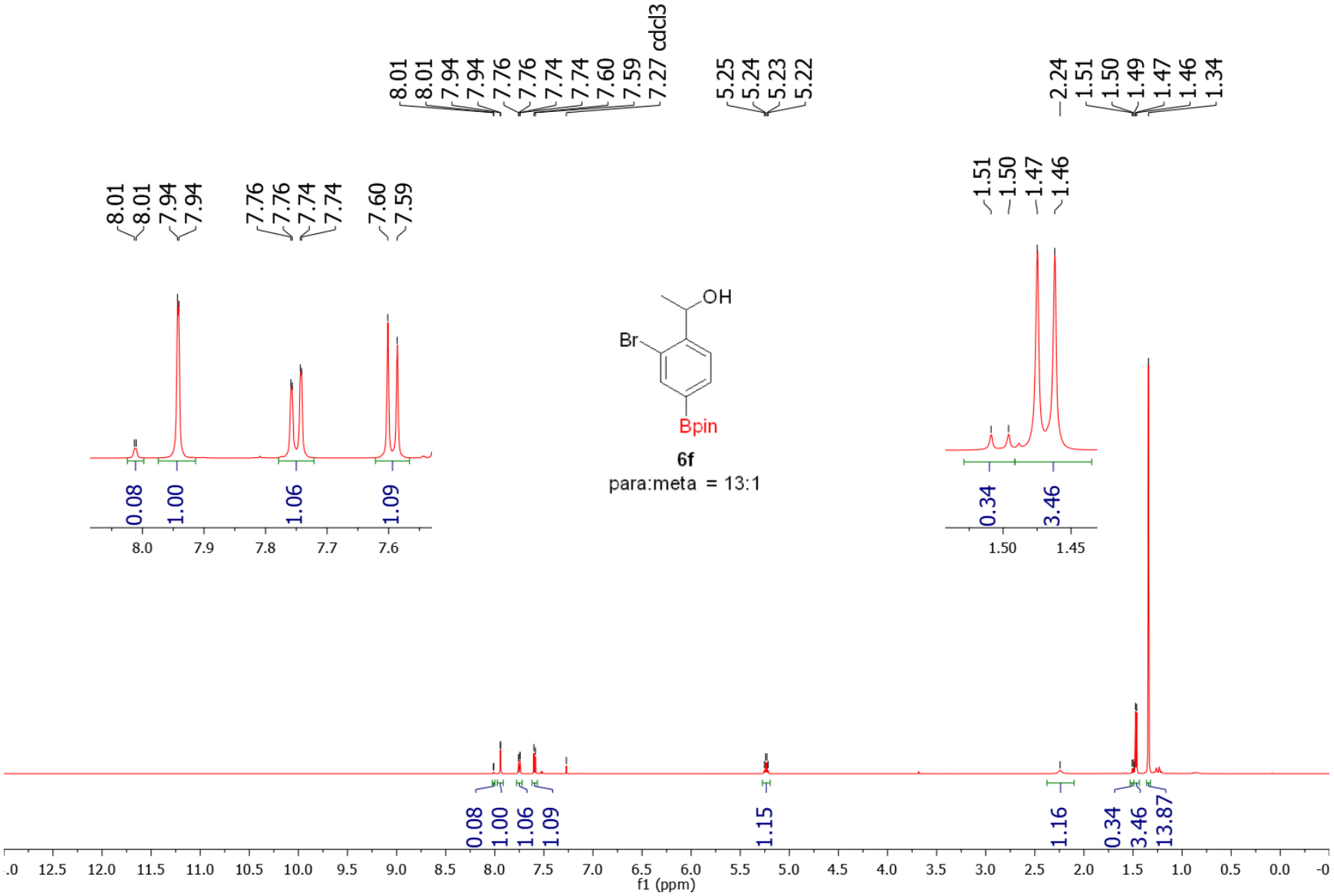
^{1}H NMR spectrum of para borylated 1-(2-bromophenyl)ethanol (6f)



Conditions: 25 ºC, 500 MHz, $CDCl_3$

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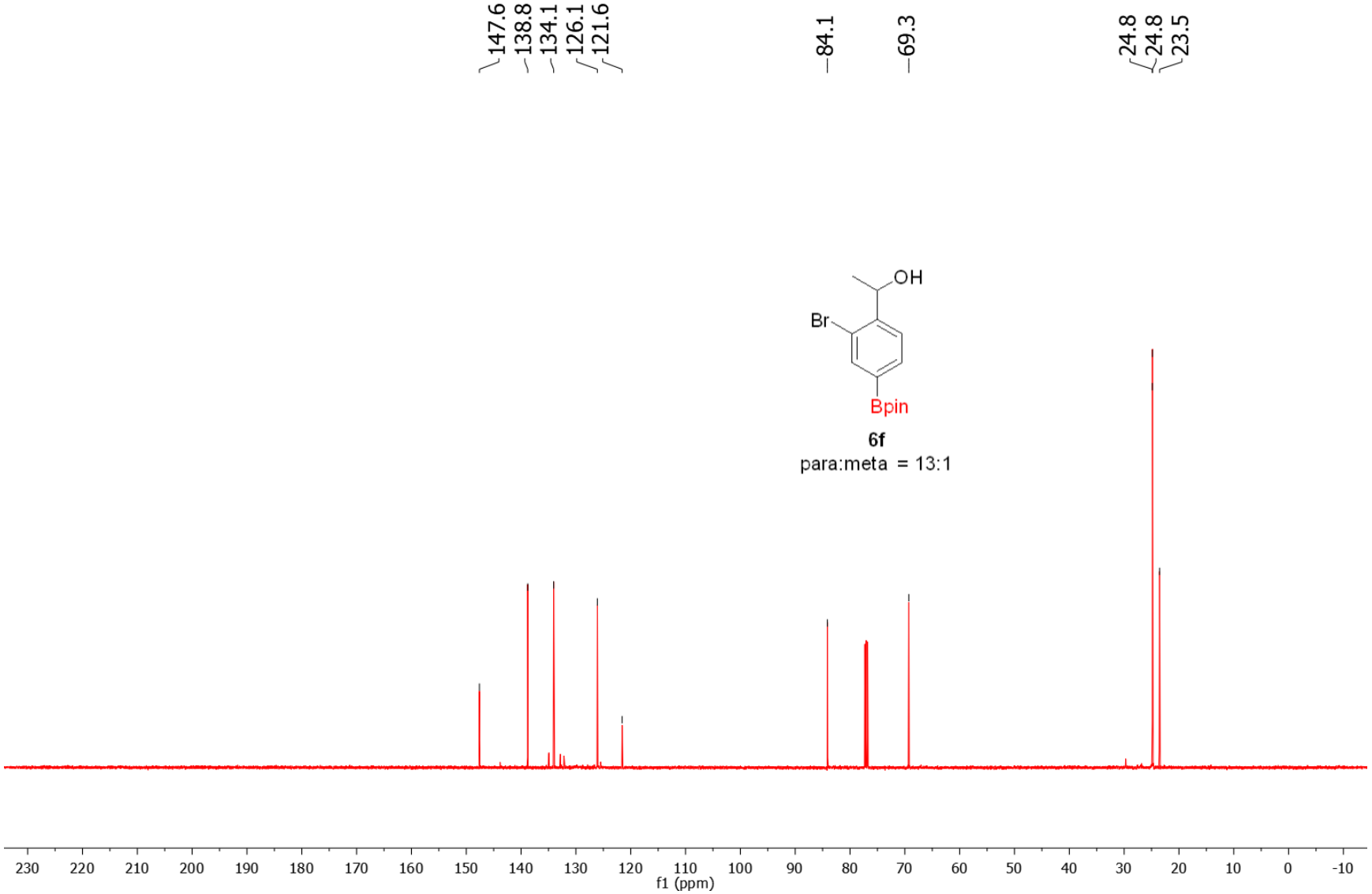
^{13}C NMR spectrum of para borylated 1-(2-bromophenyl)ethanol (6f)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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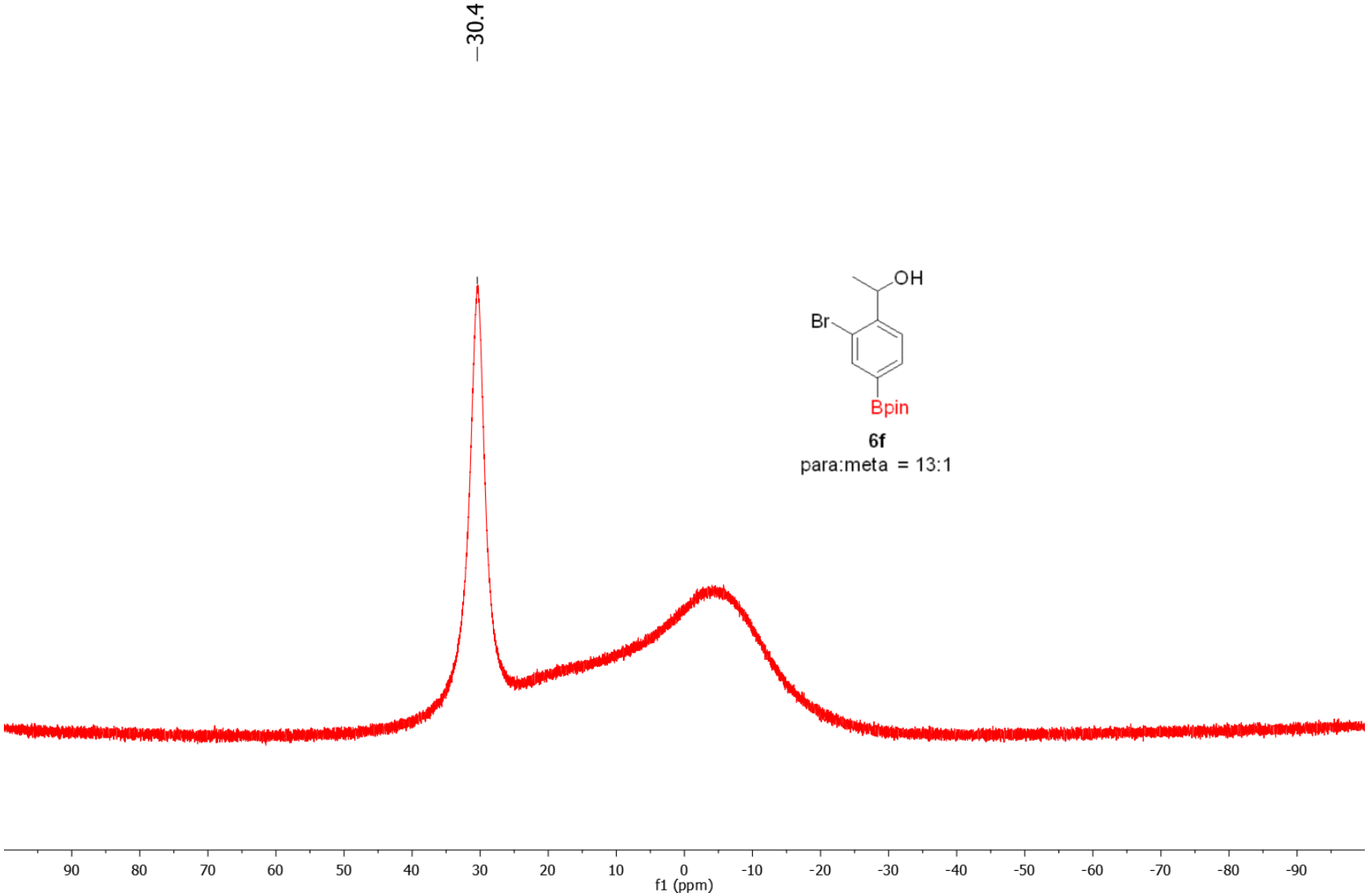
^{11}B NMR spectrum of para borylated 1-(2-bromophenyl)ethanol (6f)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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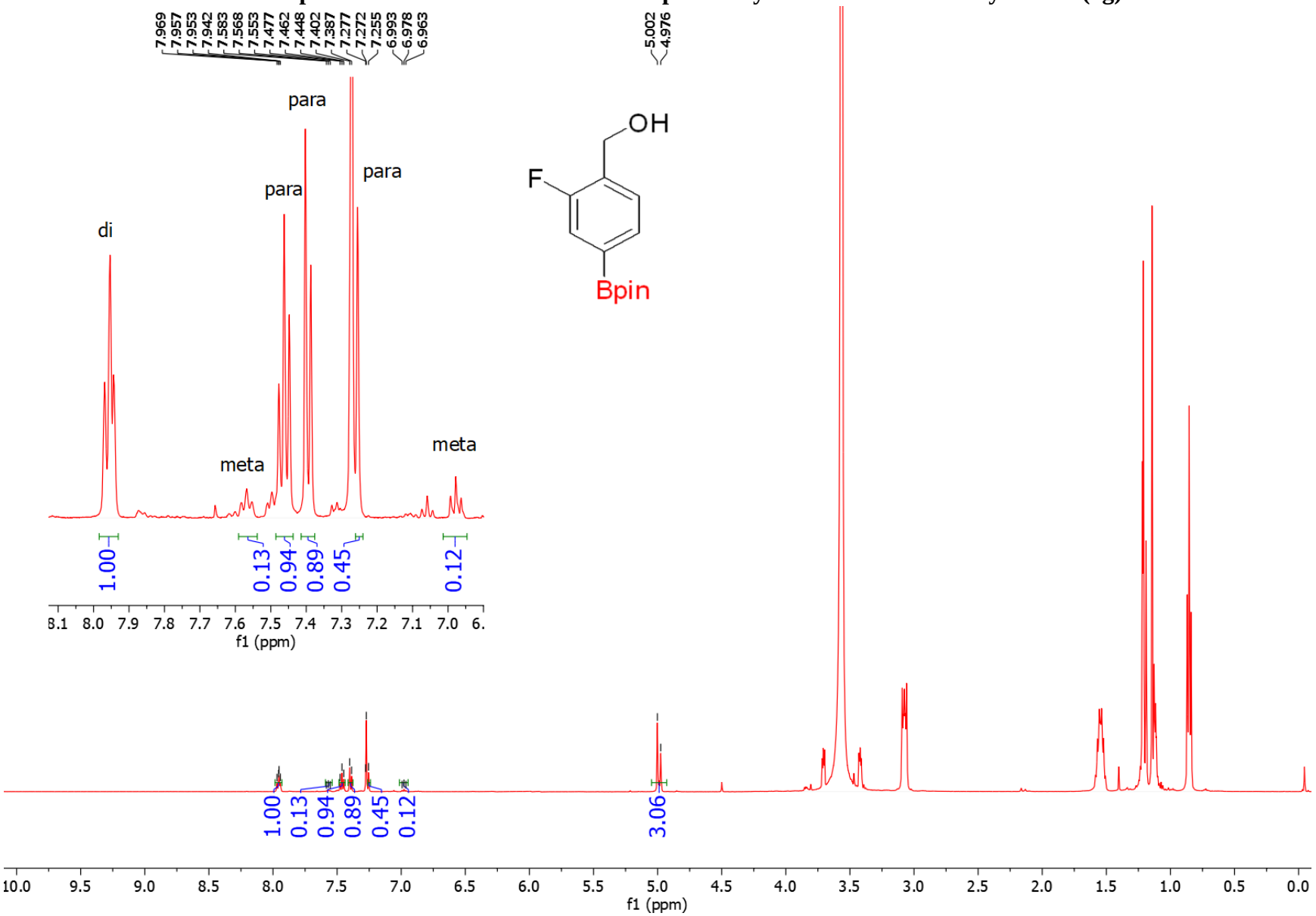
^{1}H NMR spectrum of the reaction mixture of para borylation of 2-fluorobenzylsulfate (6g)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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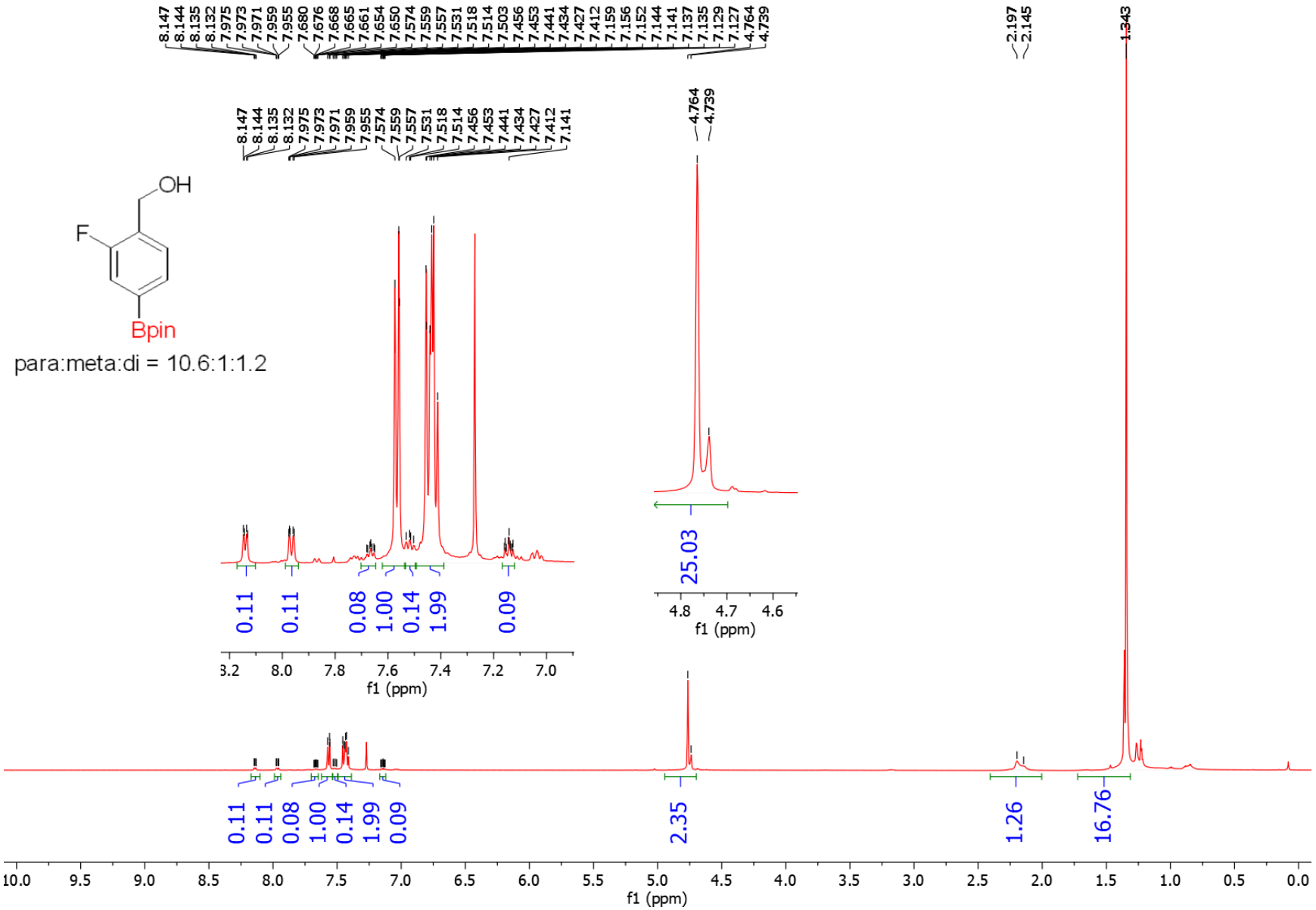
^{1}H NMR spectrum of para borylated (2-fluorophenyl)methanol (6g)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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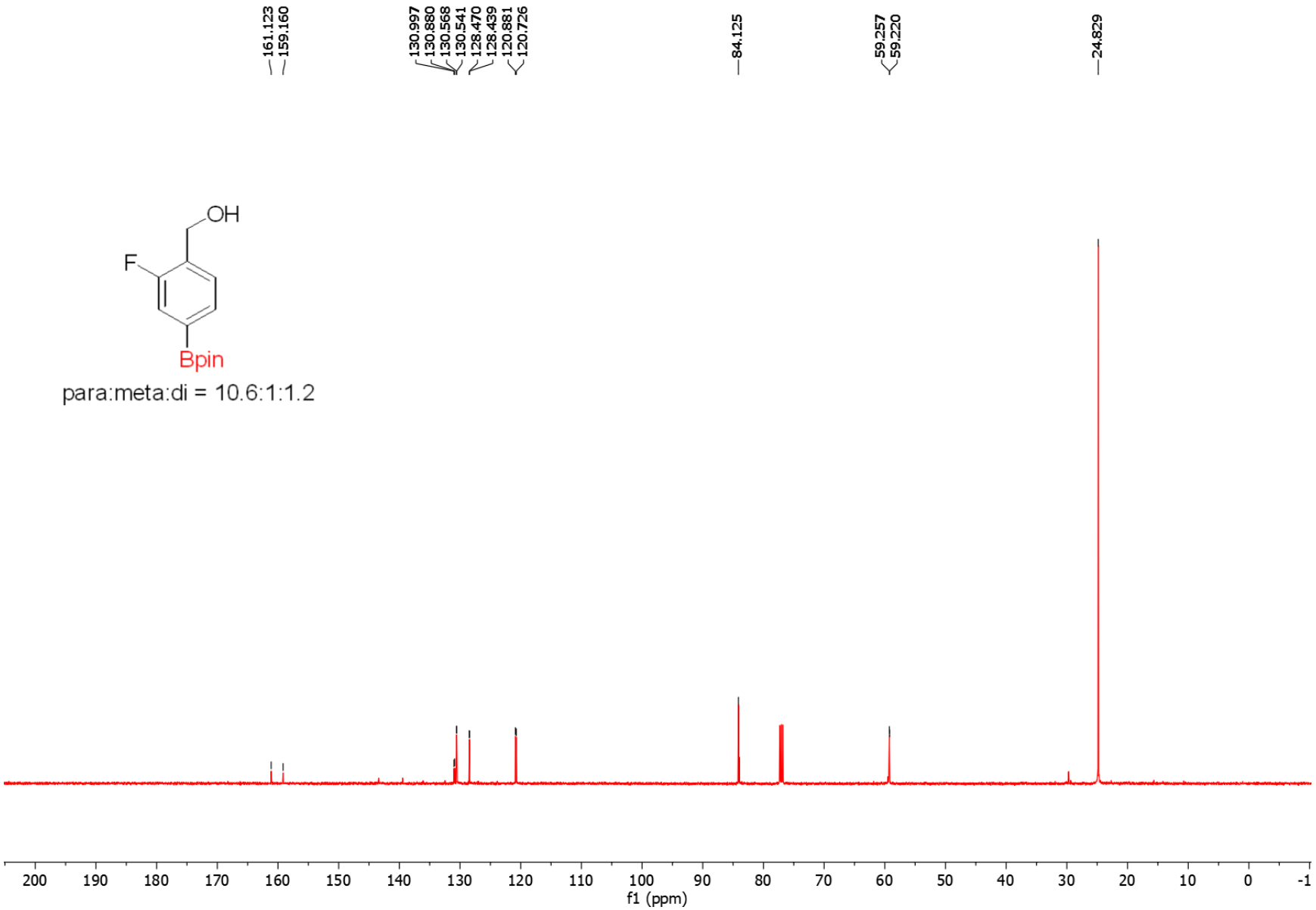
^{13}C NMR spectrum of para borylated (2-fluorophenyl)methanol (6g)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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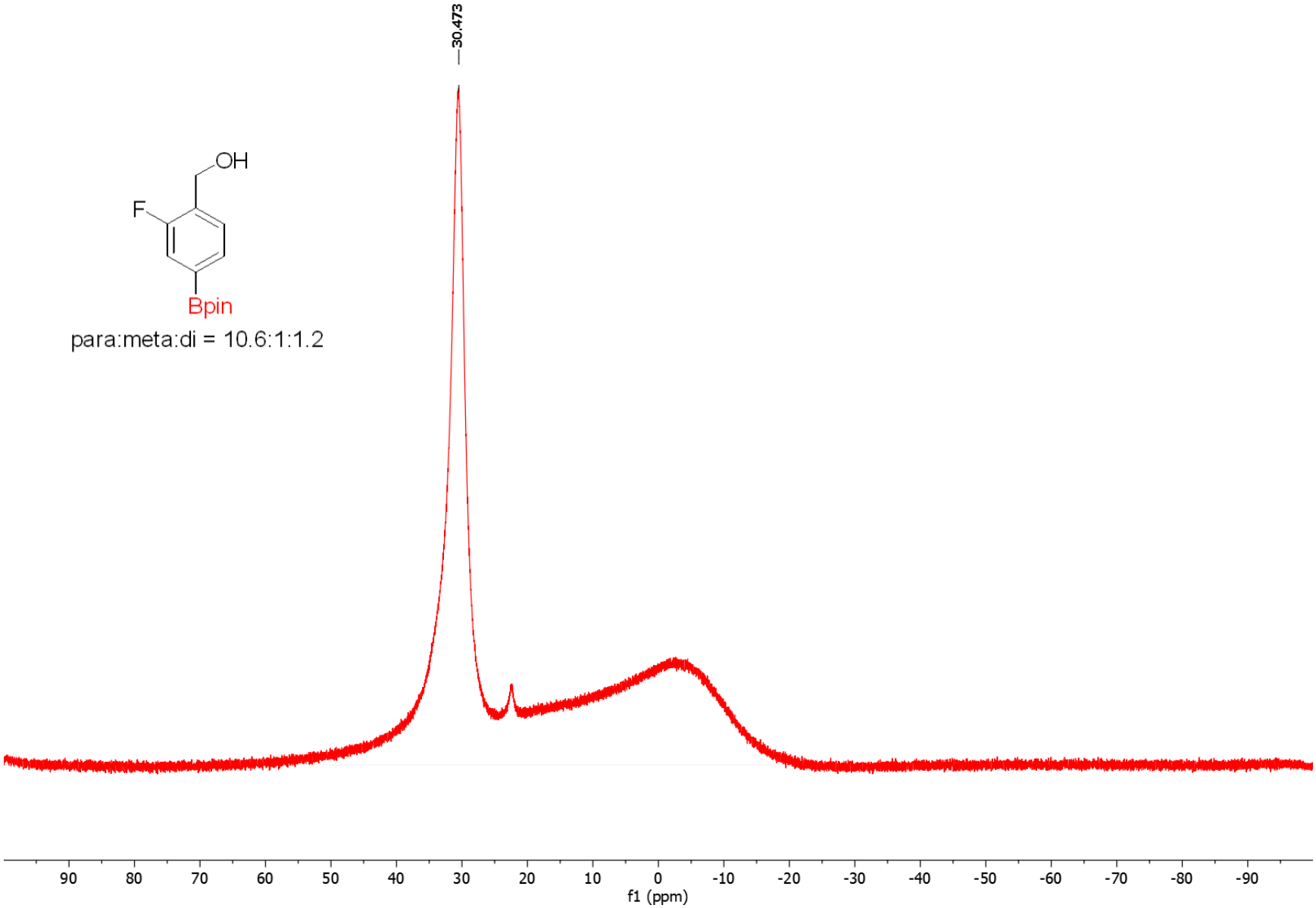
^{11}B NMR spectrum of para borylated (2-fluorophenyl)methanol (6g)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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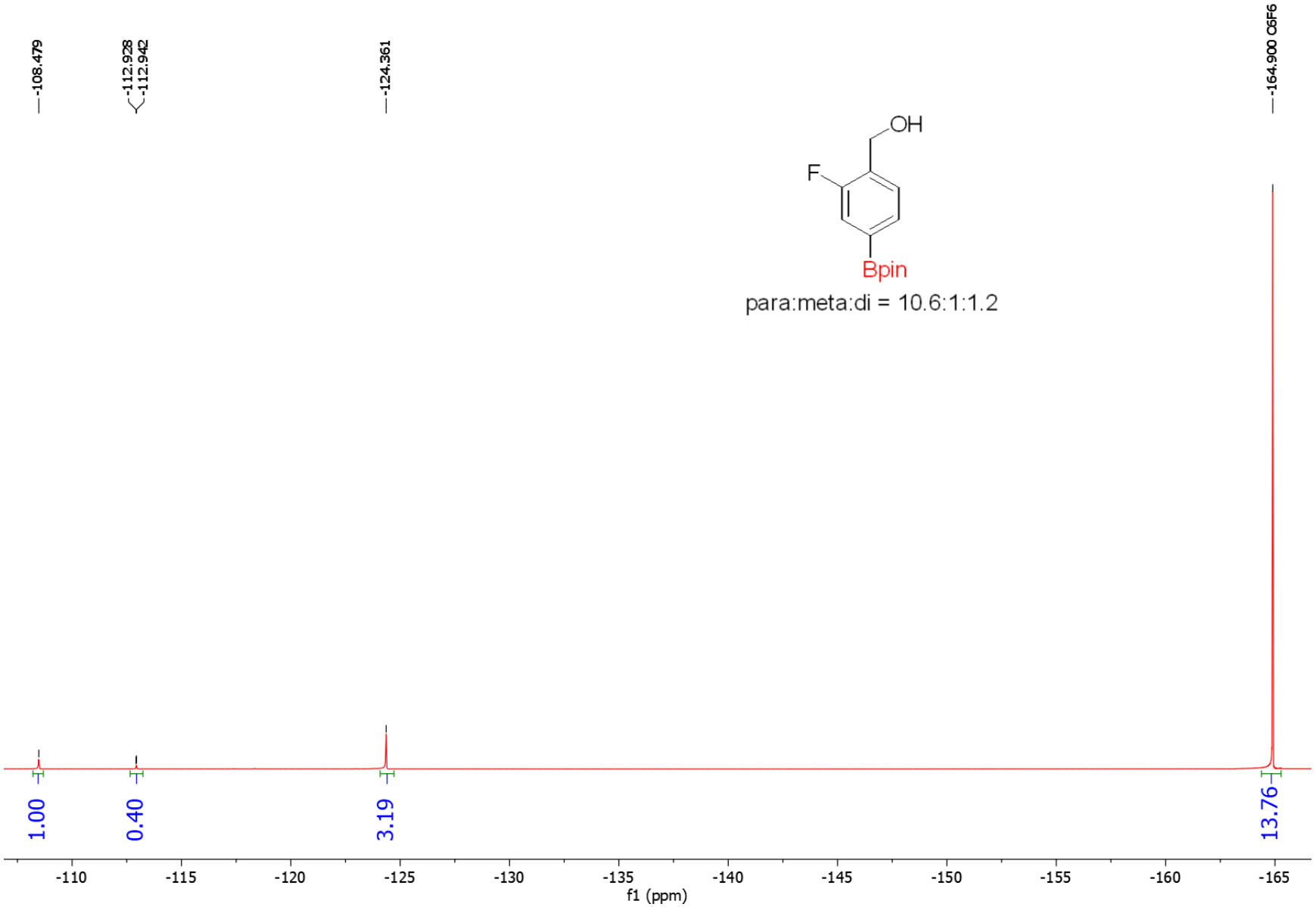
^{19}F NMR spectrum of para borylated (2-fluorophenyl)methanol (6g)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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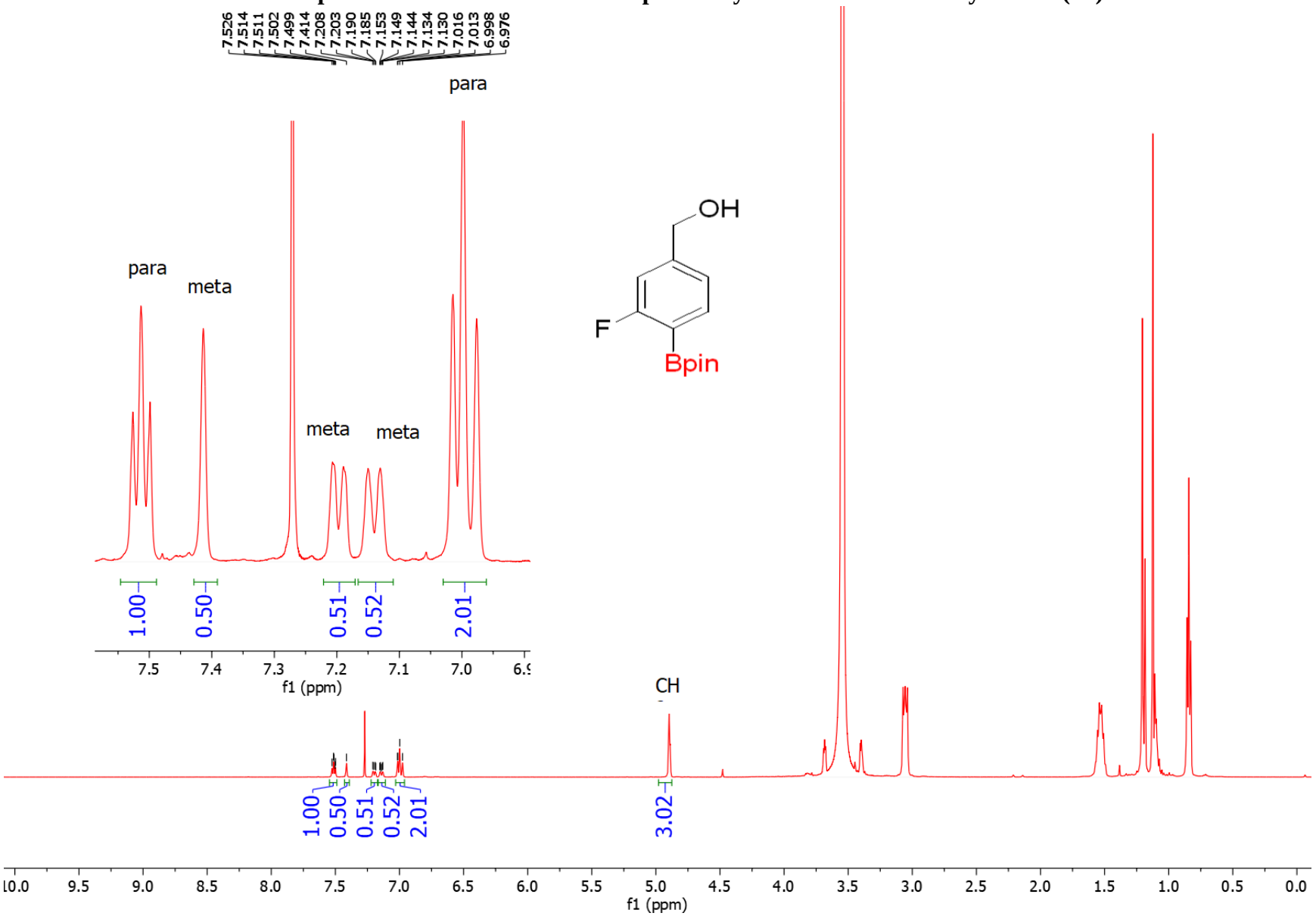
^{1}H NMR spectrum of reaction mixture of para borylation of 3-fluorobenzylsulfate (6h)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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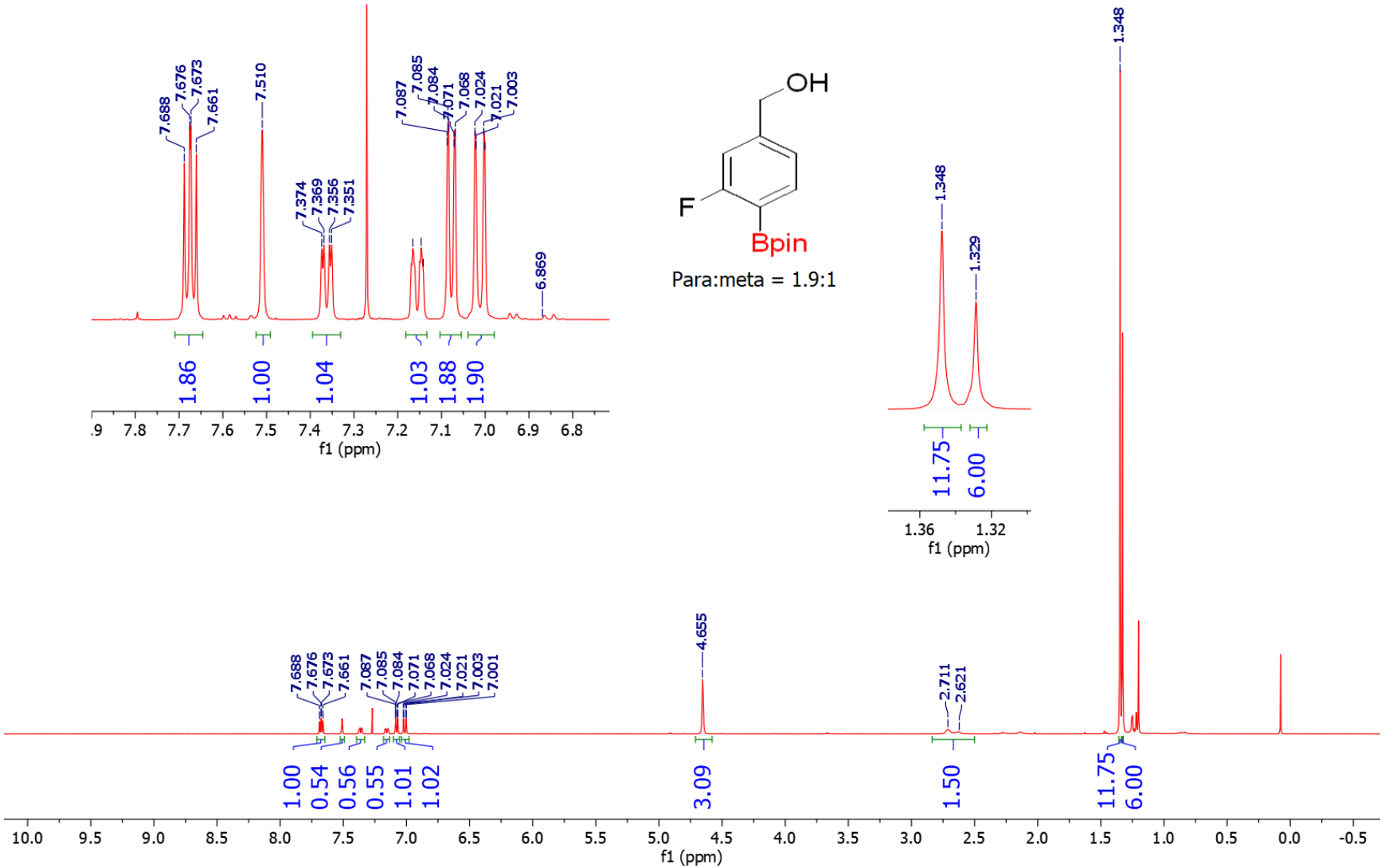
^{1}H NMR spectrum of para borylated (3-fluorophenyl)methanol (6h)



Conditions: 25 °C, 500 MHz, $CDCl_3$

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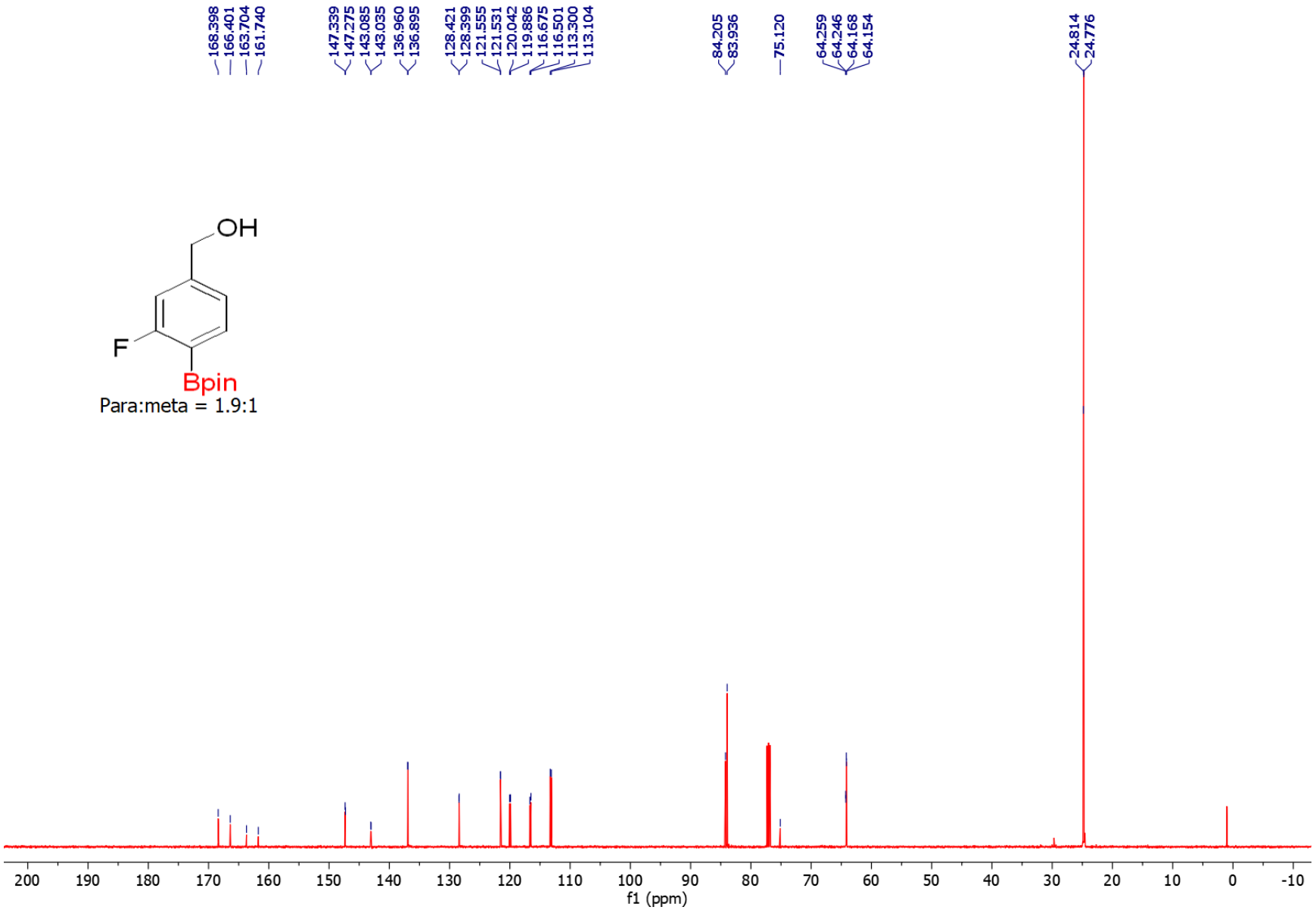
^{13}C NMR spectrum of para borylated (3-fluorophenyl)methanol (6h)



Conditions: 25 °C, 126 MHz, $CDCl_3$

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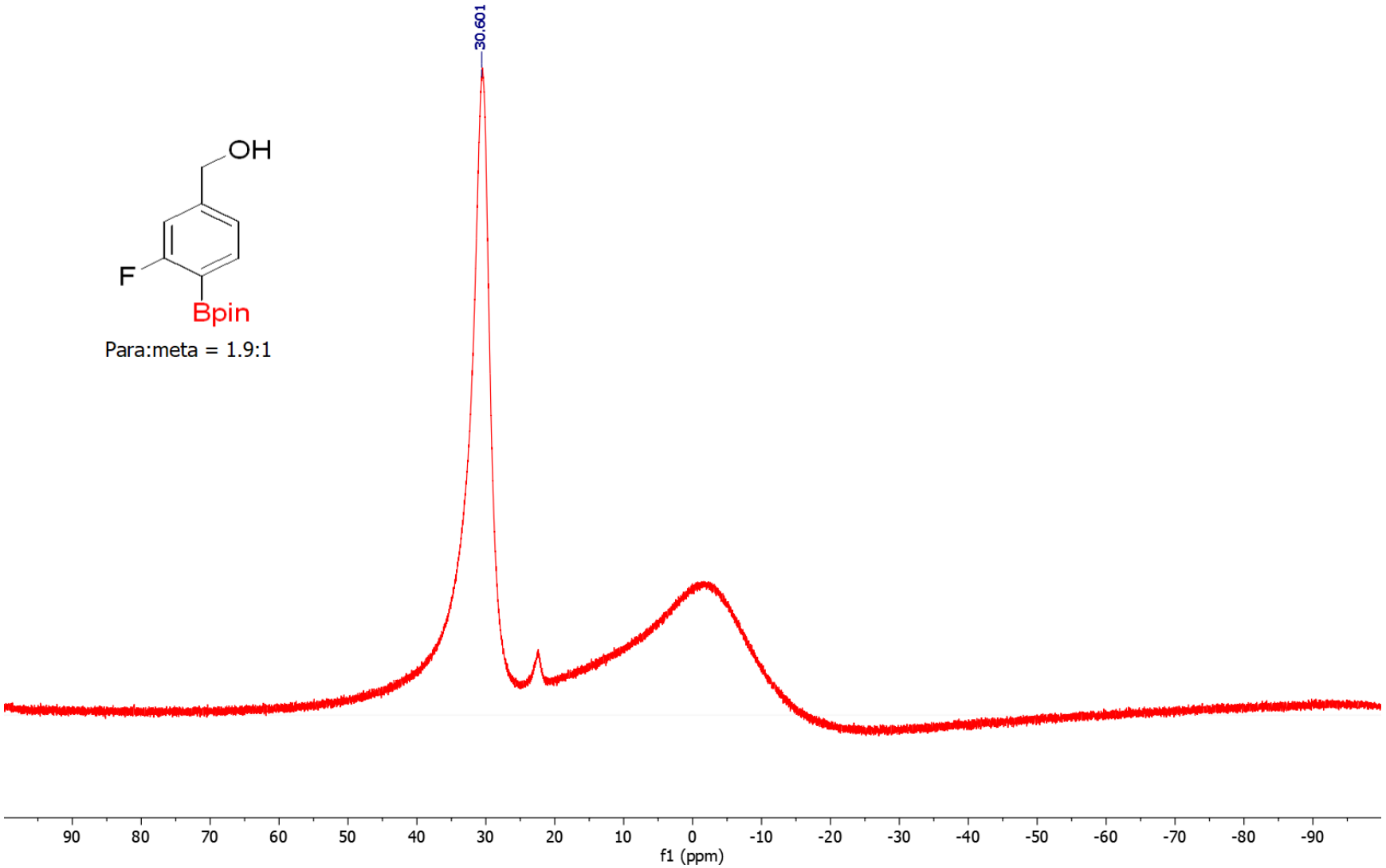
^{11}B NMR spectrum of para borylated (3-fluorophenyl)methanol (6h)



Conditions: 25 °C, 160 MHz, $CDCl_3$

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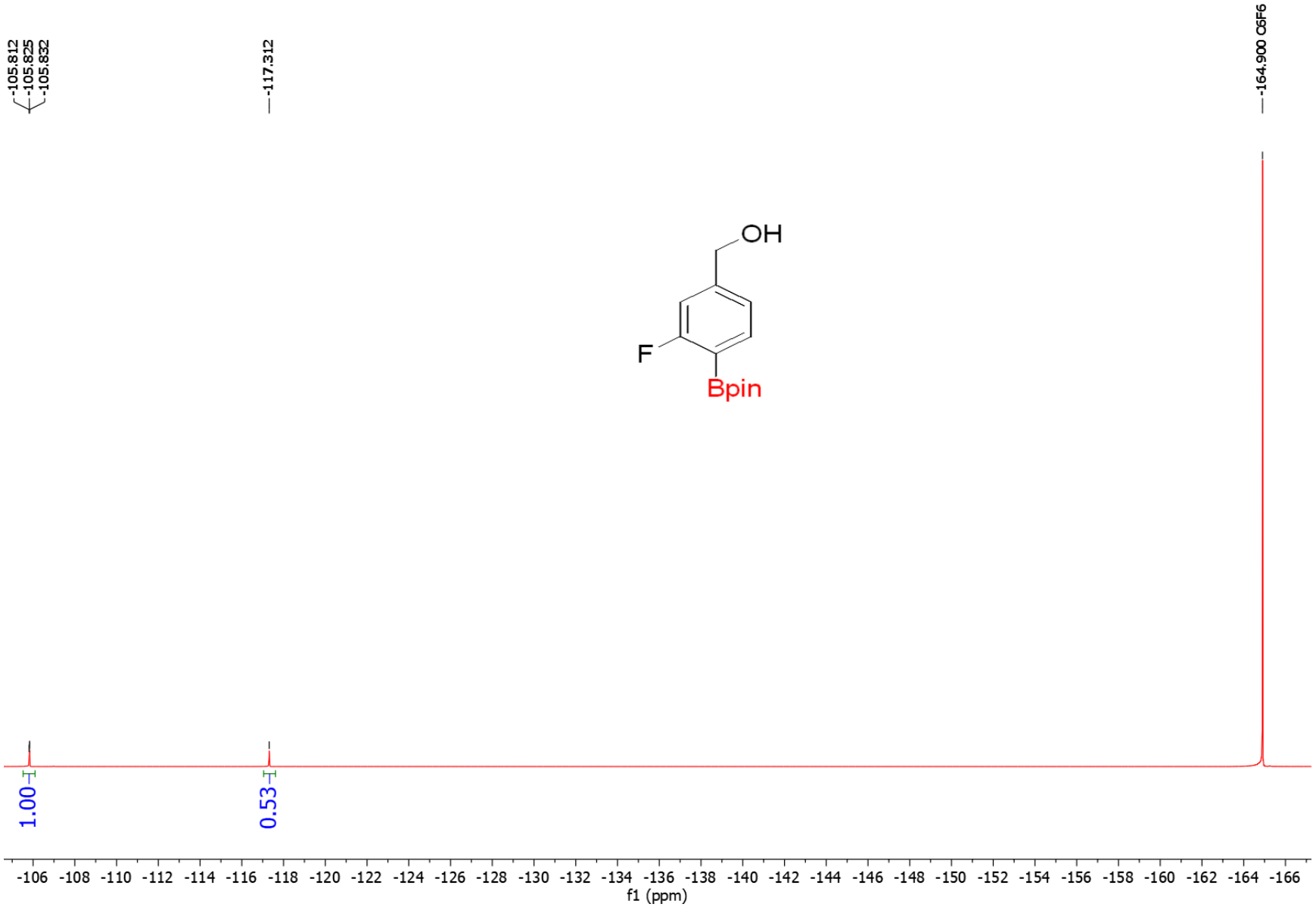
^{19}F NMR spectrum of para borylated (3-fluorophenyl)methanol (6h)



Conditions: 25 °C, 470 MHz, $CDCl_3$

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