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Supplementary Material

Using Quenching Kinetics and Thermodynamics of Amino-Fluorophores As Empirical Tools for Predicting Boronic Acid Sensors Suitable for Use in Physiological Conditions

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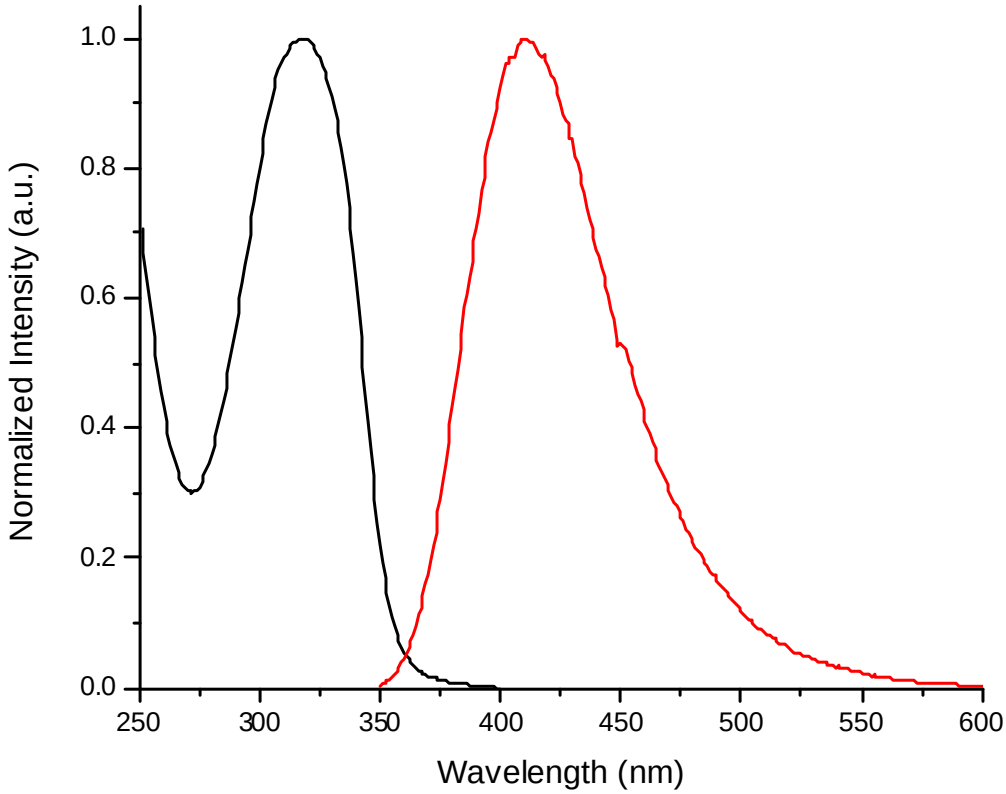


Figure 1: Normalized absorbance (black) and fluorescence (red) spectra of **1**.

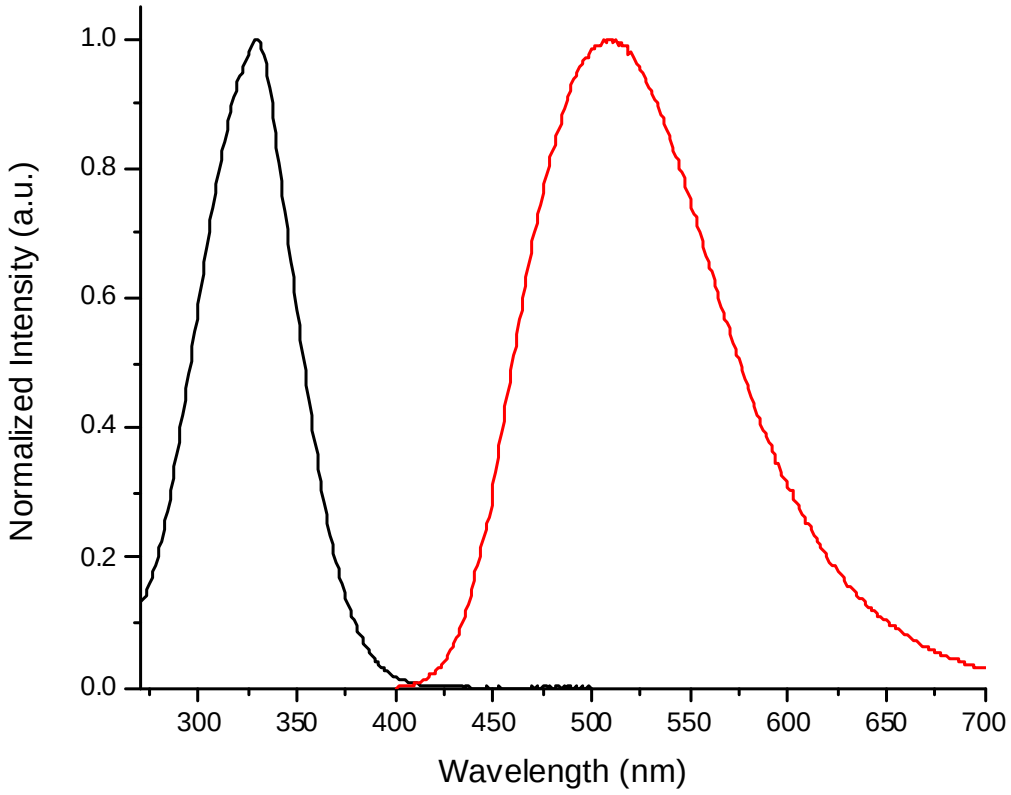


Figure 2: Normalized absorbance (black) and fluorescence (red) spectra of **2**.

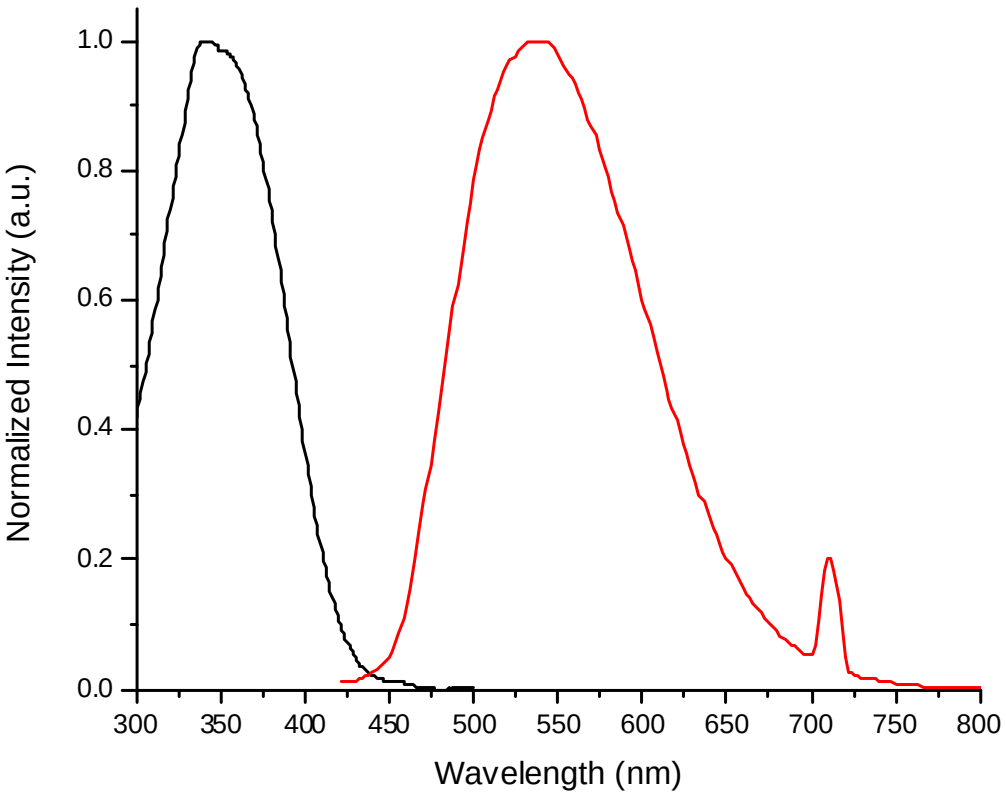


Figure 3: Normalized absorbance (black) and fluorescence (red) spectra of **3**.

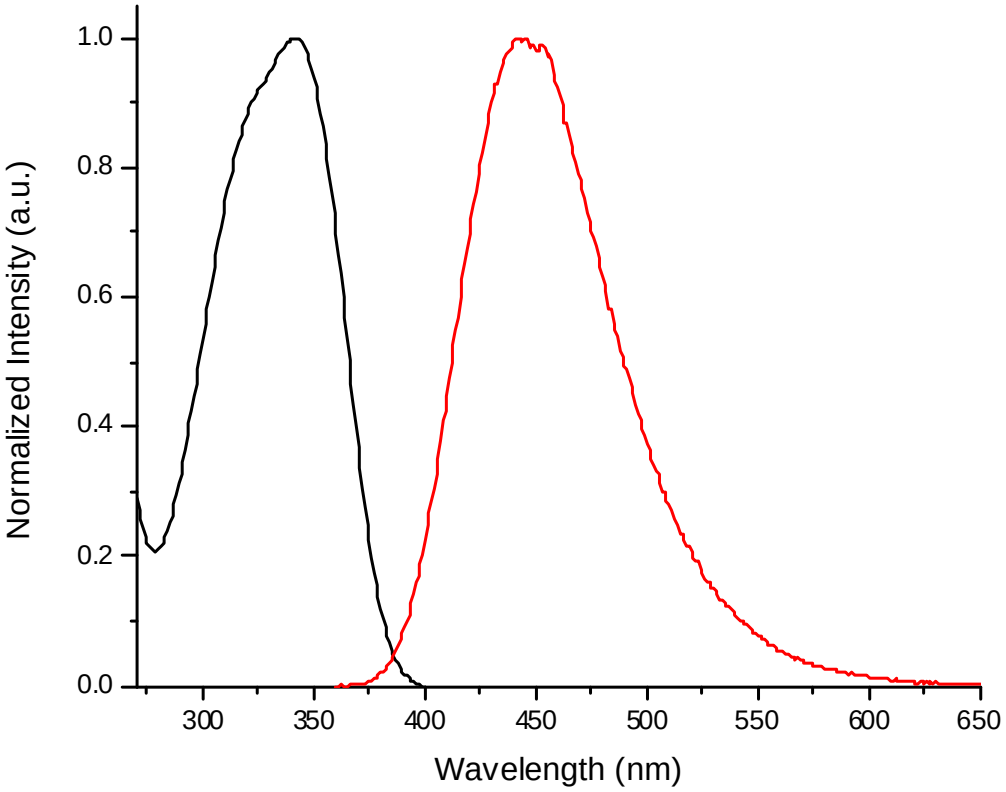


Figure 4: Normalized absorbance (black) and fluorescence (red) spectra of **4**.

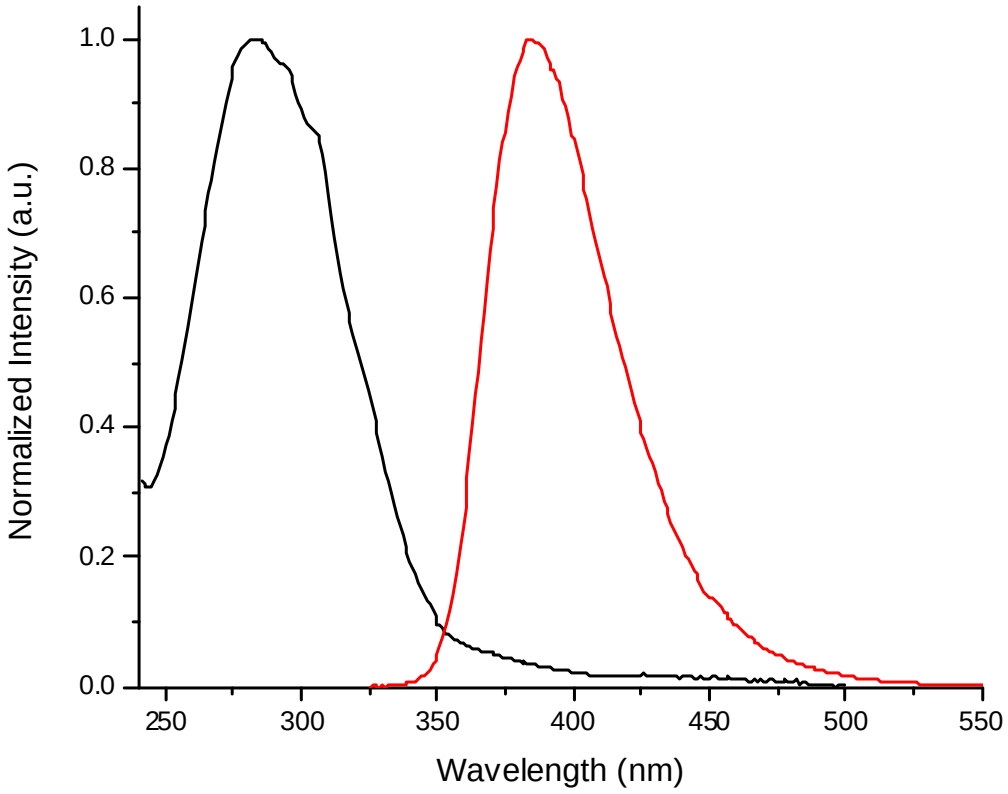


Figure 5: Normalized absorbance (black) and fluorescence (red) spectra of **5**.

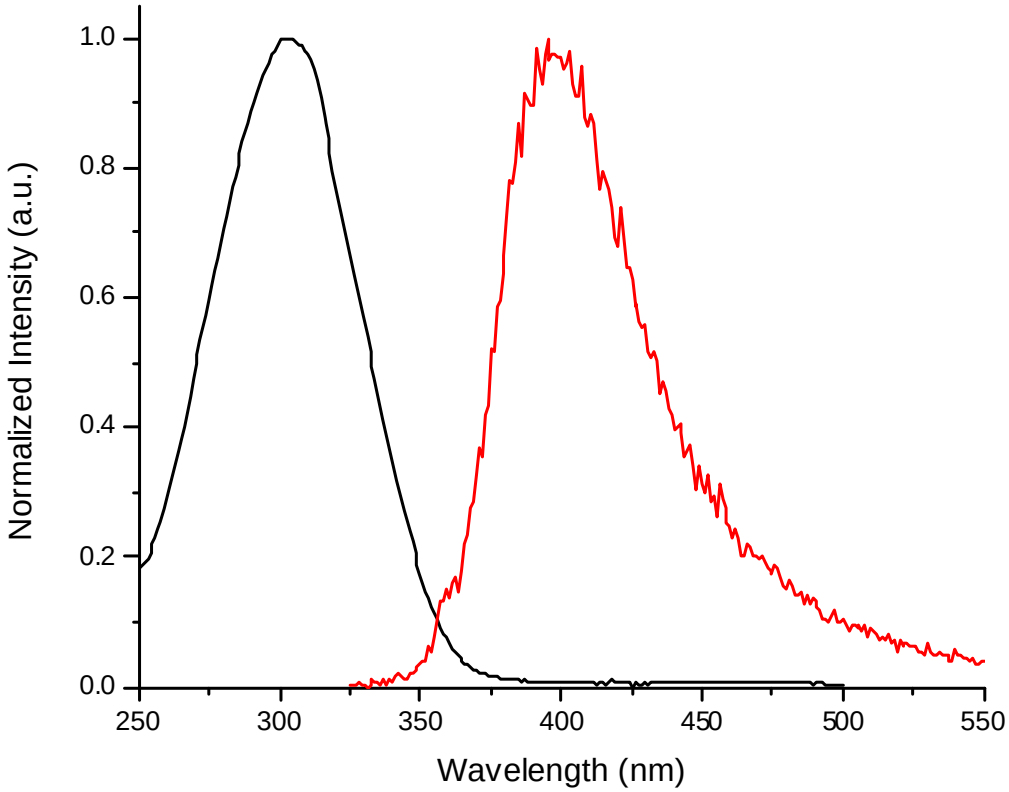


Figure 6: Normalized absorbance (black) and fluorescence (red) spectra of **6**.

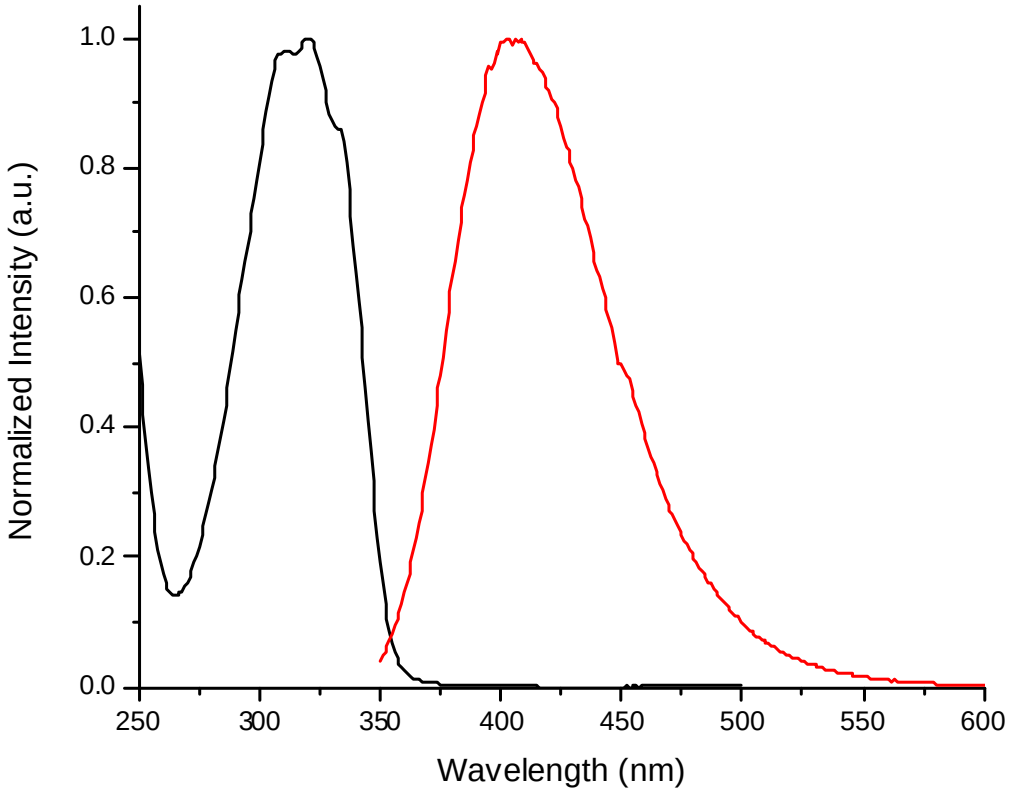


Figure 7: Normalized absorbance (black) and fluorescence (red) spectra of **11**.

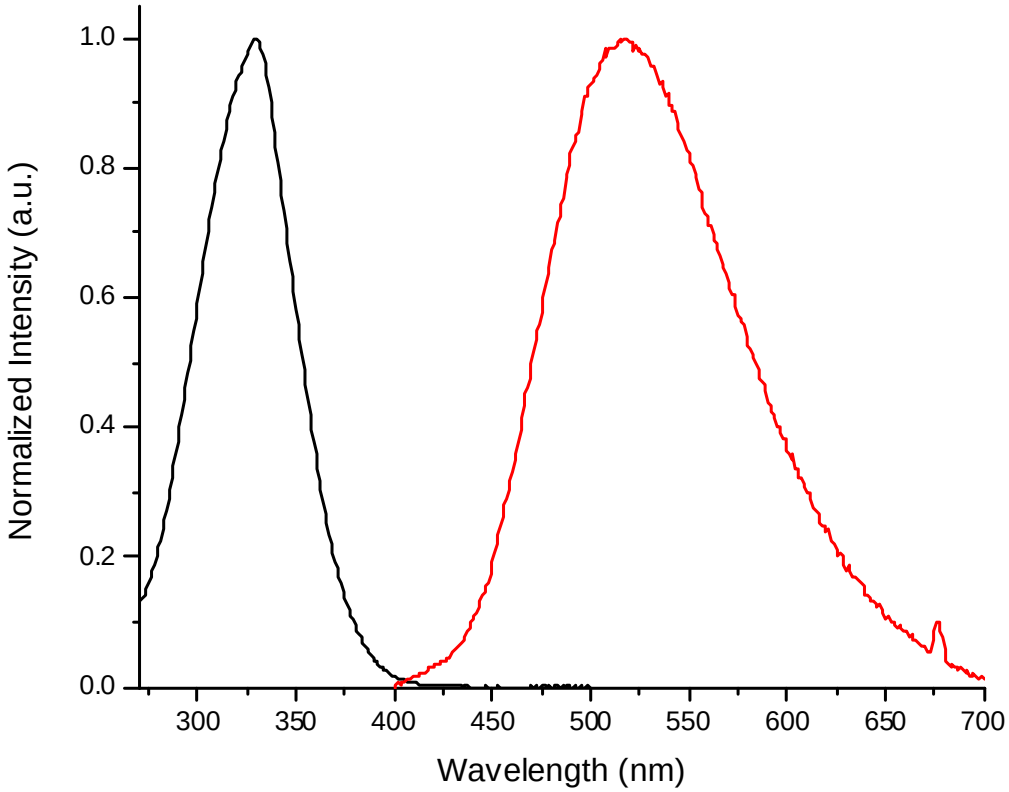


Figure 8: Normalized absorbance (black) and fluorescence (red) spectra of **12**.

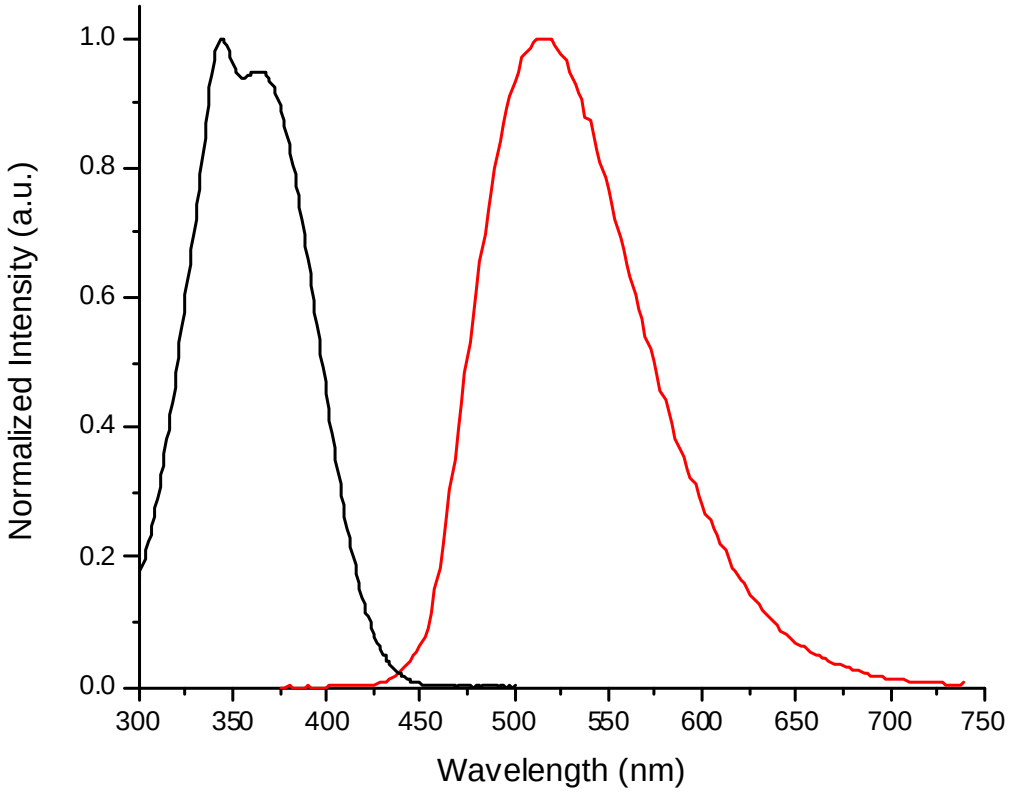


Figure 9: Normalized absorbance (black) and fluorescence (red) spectra of **13**.

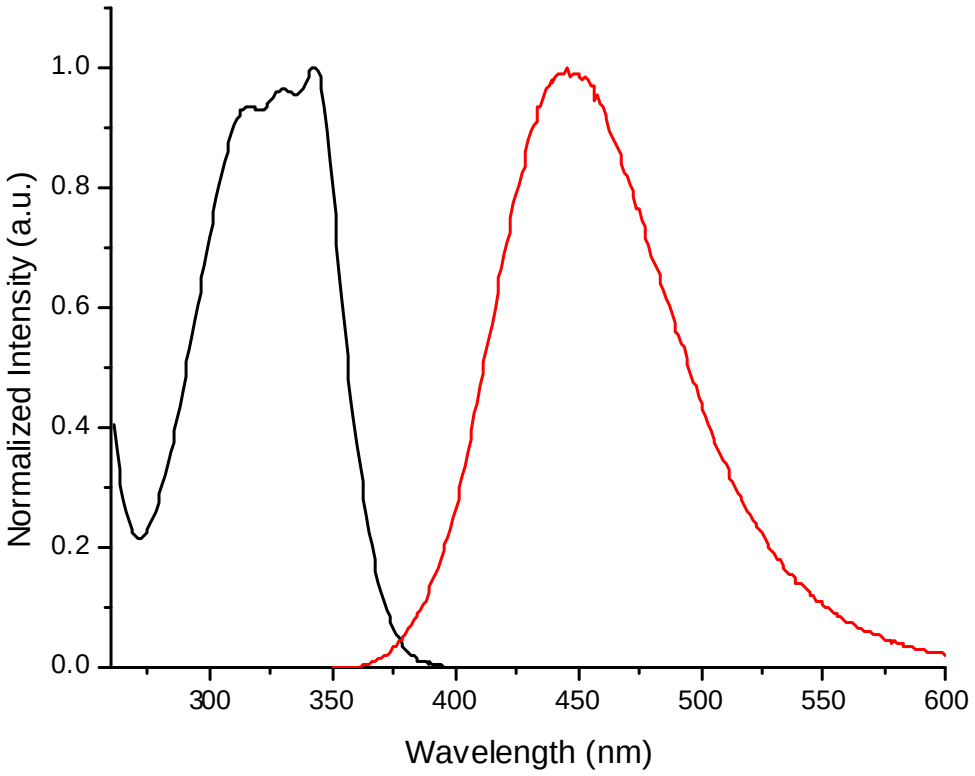


Figure 10: Normalized absorbance (black) and fluorescence (red) spectra of **14**.

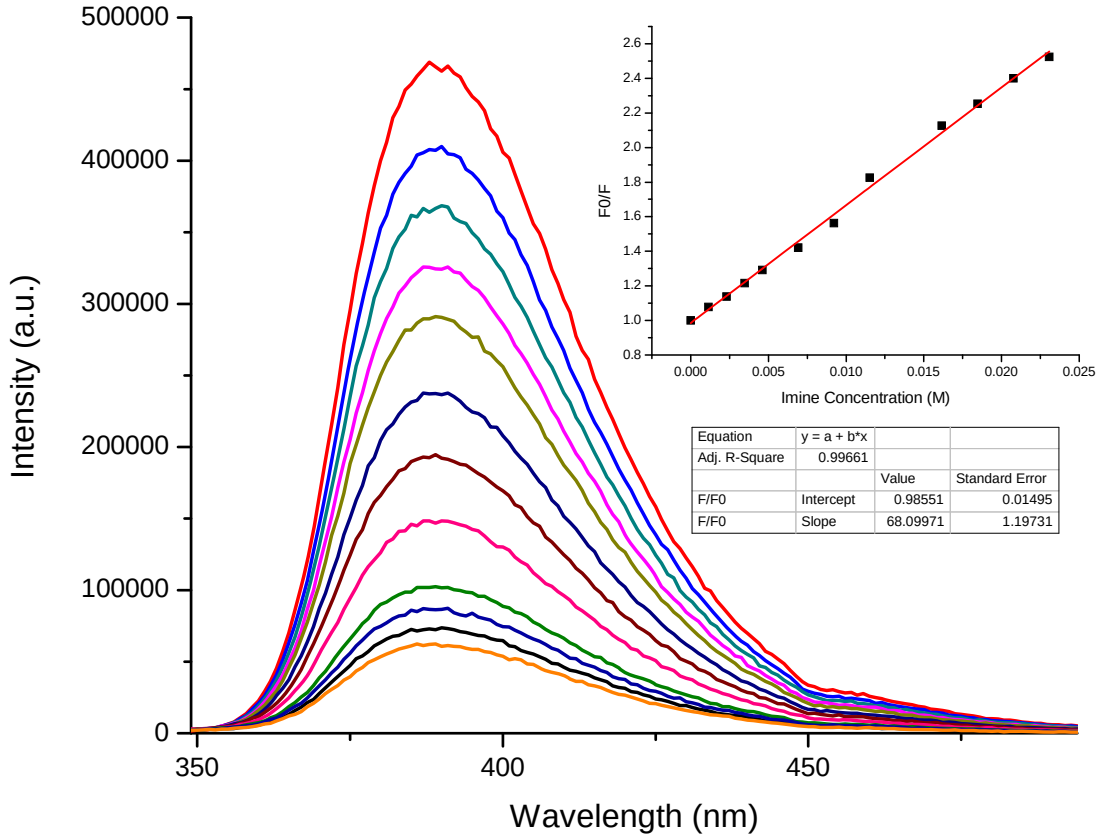


Figure 11: Fluorescence spectra of **21** with increasing concentrations of **10** in anhydrous acetonitrile. Inset: Stern-Volmer plot of Φ_0/Φ vs. [**10**] including linear fit and basic statistics showing diffusion limited fluorescence quenching of **21** with **10**.

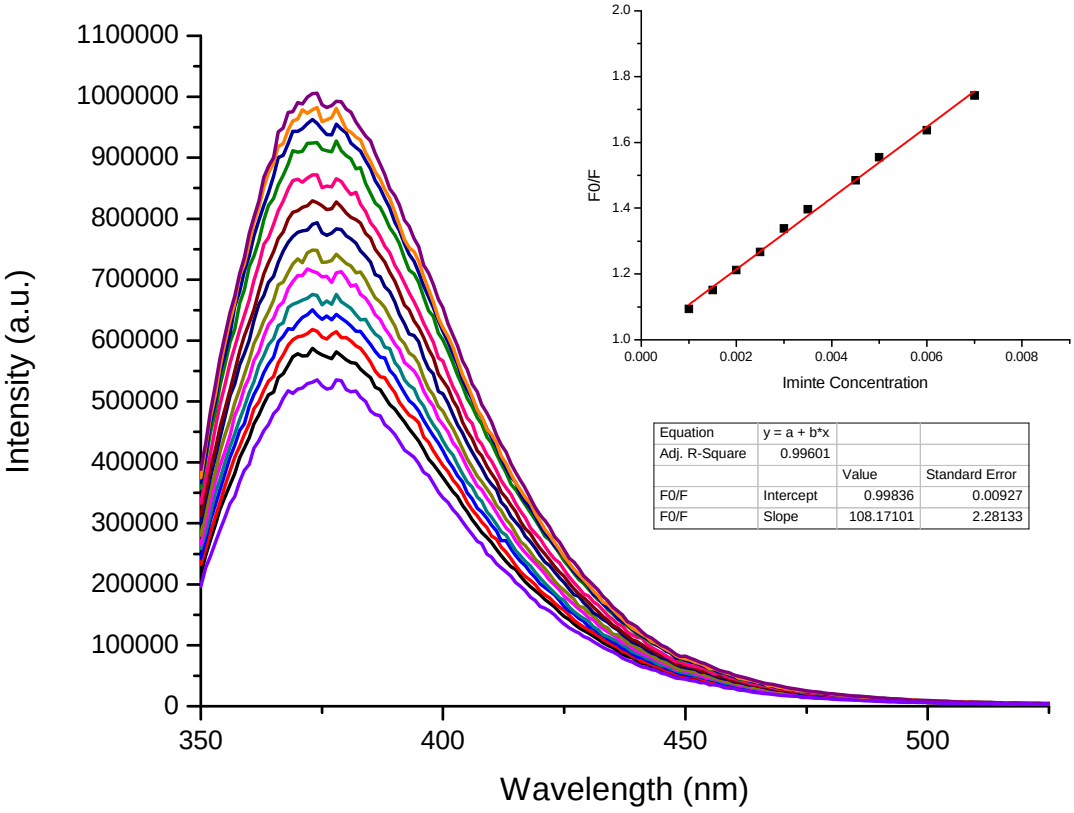


Figure 12: Fluorescence spectra of **11** with increasing concentrations of **10** in anhydrous acetonitrile. Inset: Stern-Volmer plot of Φ_0/Φ vs. [**10**] including linear fit and basic statistics showing the diffusion limited relationship between imine concentration and fluorescence quenching.

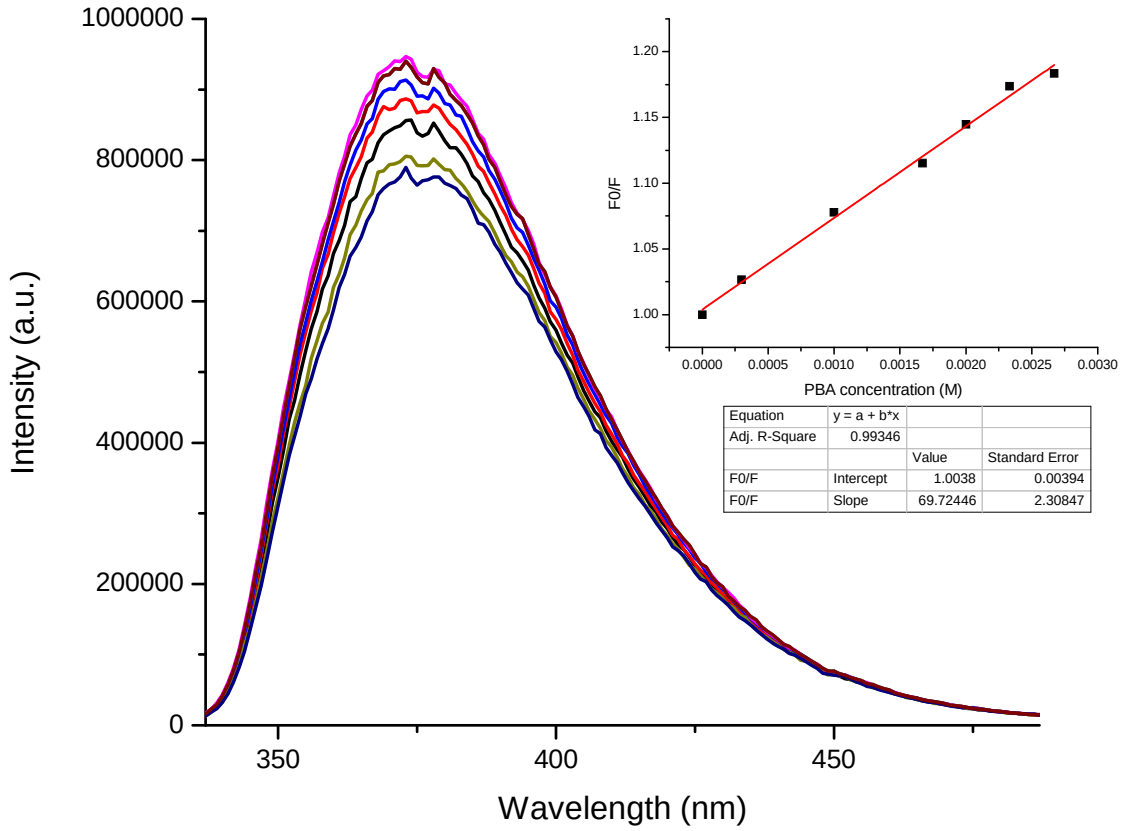


Figure 13: Fluorescence spectra of **11** with increasing concentrations of phenylboronic acid in anhydrous acetonitrile. Inset: Stern-Volmer plot of Φ_0/Φ vs. [phenylboronic acid] including linear fit and basic statistics showing the diffusion limited relationship between phenylboronic acid concentration and fluorescence quenching.

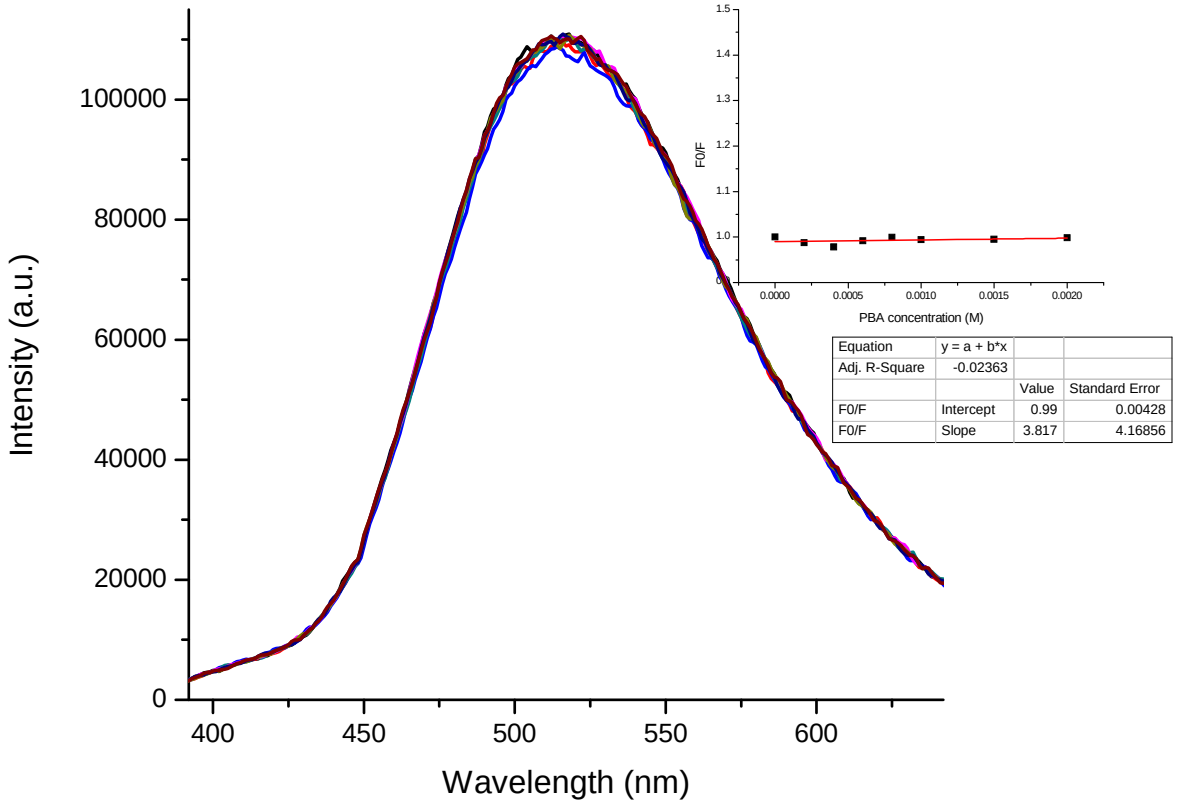


Figure 14: Fluorescence spectra of **12** with increasing concentrations of phenylboronic acid in pH 7.4 PBS. Inset: Stern-Volmer plot of Φ_0/Φ vs. [phenylboronic acid] including linear fit and basic statistics showing the lack of fluorescence quenching of **12** with phenylboronic acid.

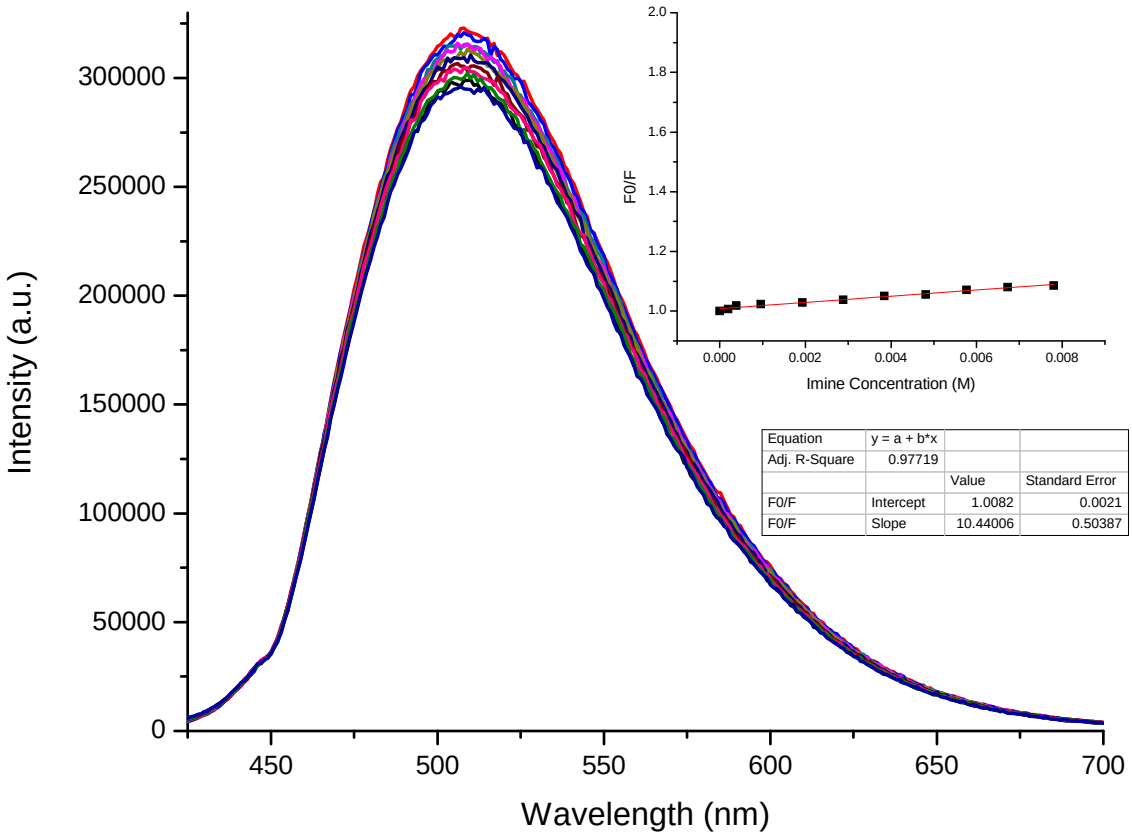


Figure 15: Fluorescence spectra of **13** with increasing concentrations of **10** in anhydrous acetonitrile. Inset: Stern-Volmer plot of Φ_0/Φ vs. [10] including linear fit and basic statistics showing the lack of fluorescence quenching of **13** with **10**.

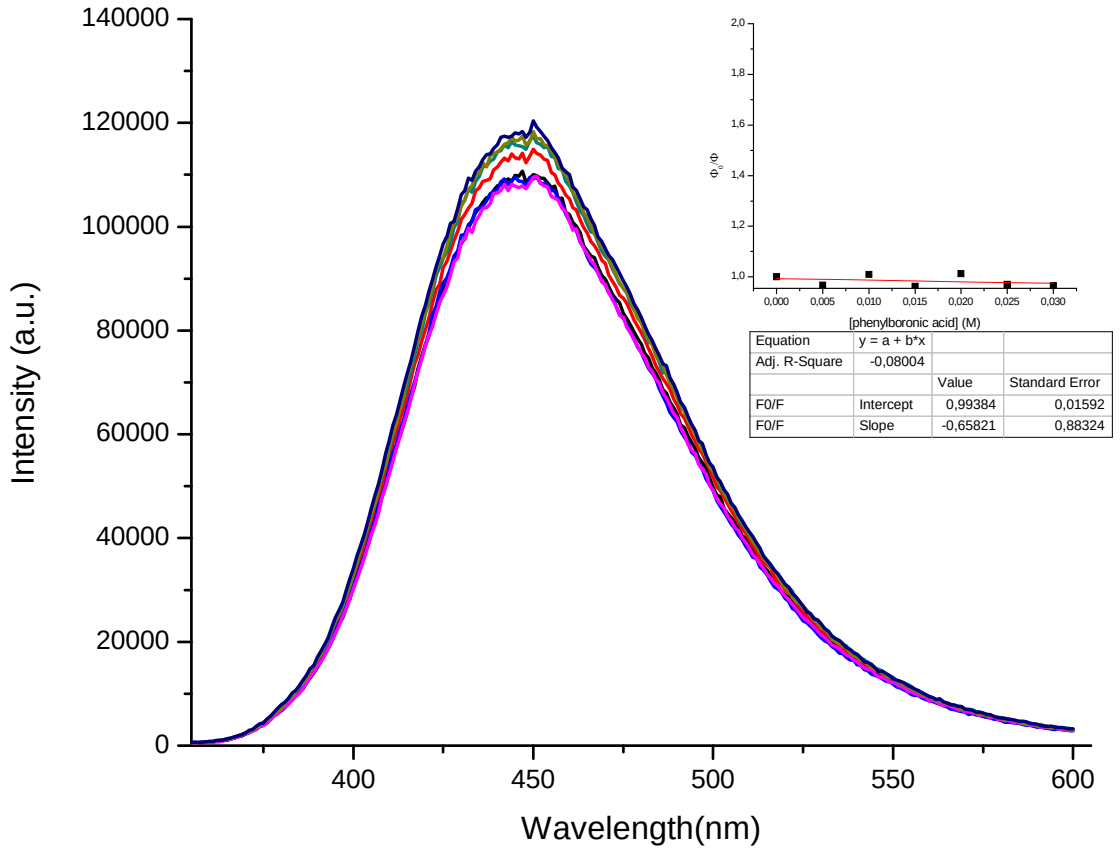


Figure 16: Fluorescence spectra of **14** with increasing concentrations of phenylboronic acid in pH 7.4 PBS. Inset: Stern-Volmer plot of Φ_0/Φ vs. [phenylboronic acid] including linear fit and basic statistics showing the lack of fluorescence quenching of **14** with phenylboronic acid.

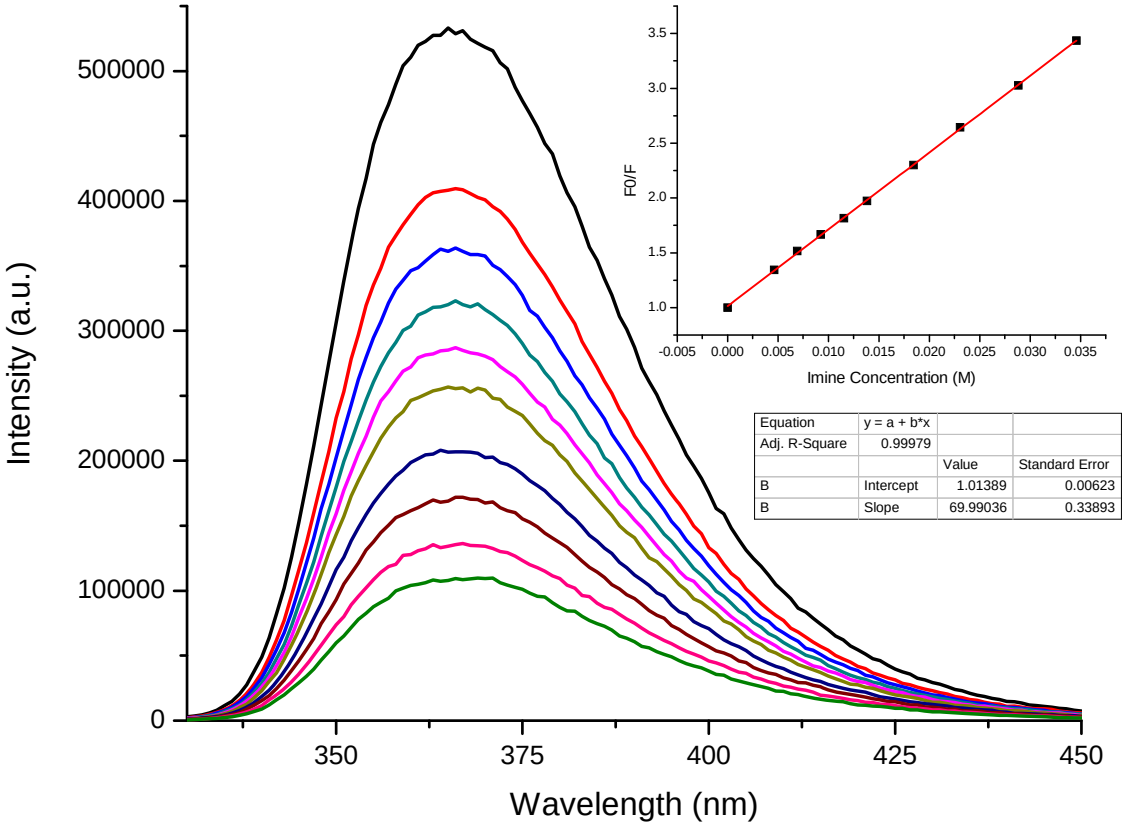


Figure 17: Fluorescence spectra of **20** with increasing concentrations of **10** in anhydrous acetonitrile. Inset: Stern-Volmer plot of Φ_0/Φ vs. [**10**] including linear fit and basic statistics showing diffusion limited fluorescence quenching of **20** with **10**.

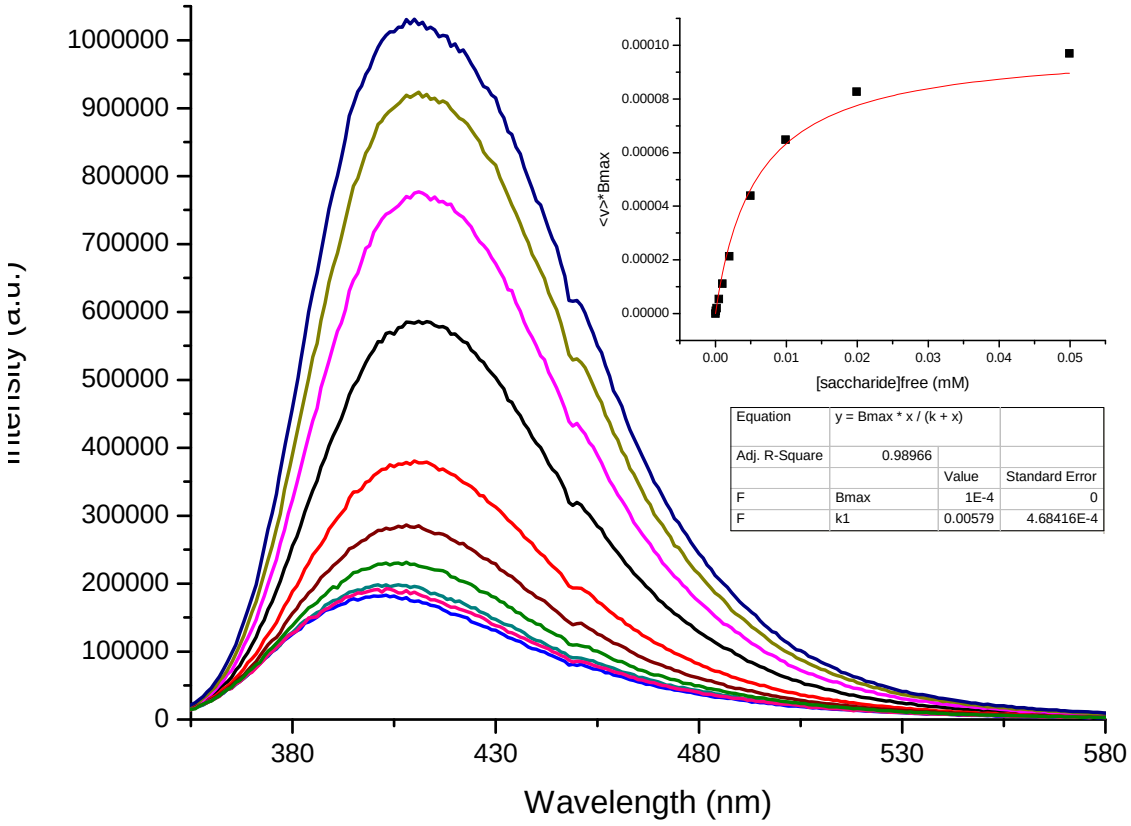


Figure 18: Fluorescence spectra of **1** in pH 7.4 PBS with added fructose demonstrating the fluorescence revival of **1** upon saccharide addition. Inset: Plot of [**1**:fructose] vs. [fructose] with a one-site binding fit overlayed and basic statistics used to determine the binding constant of **1** with fructose.

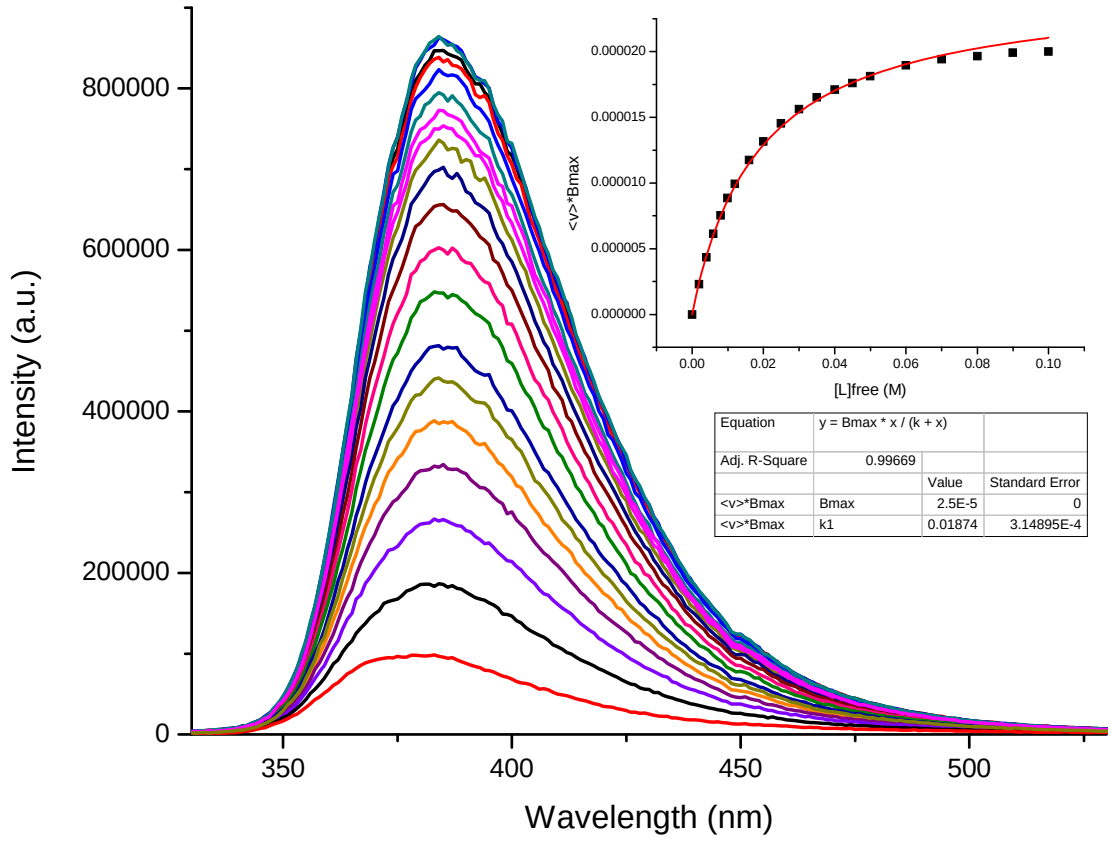


Figure 19: Fluorescence spectra of **5** in pH 7.4 PBS with added fructose demonstrating the fluorescence revival of **5** upon saccharide addition. Inset: Plot of [**5**:fructose] vs. [fructose] with a one-site binding fit overlayed and basic statistics used to determine the binding constant of **5** with fructose.

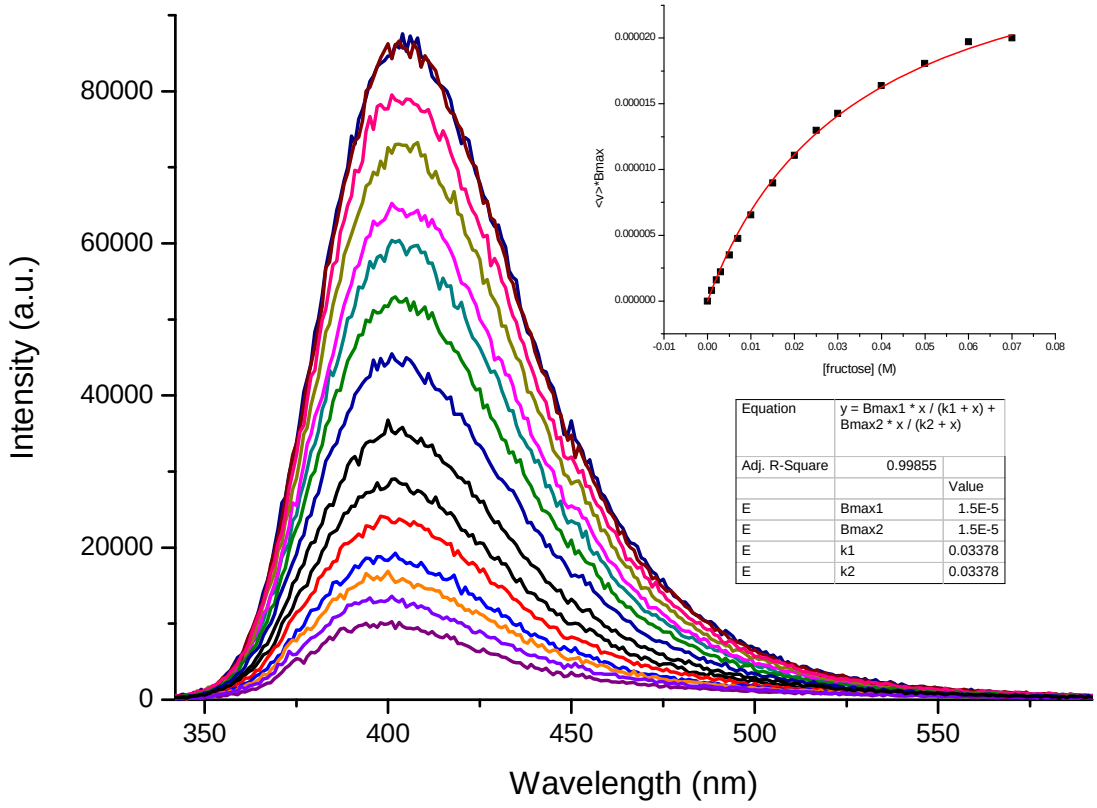


Figure 20: Fluorescence spectra of **6** in pH 7.4 PBS with added fructose demonstrating the fluorescence revival of **6** upon saccharide addition. Inset: Plot of [**6:**fructose] vs. [fructose] with a two-site binding fit overlayed and basic statistics used to determine the binding constant of **6** with fructose.

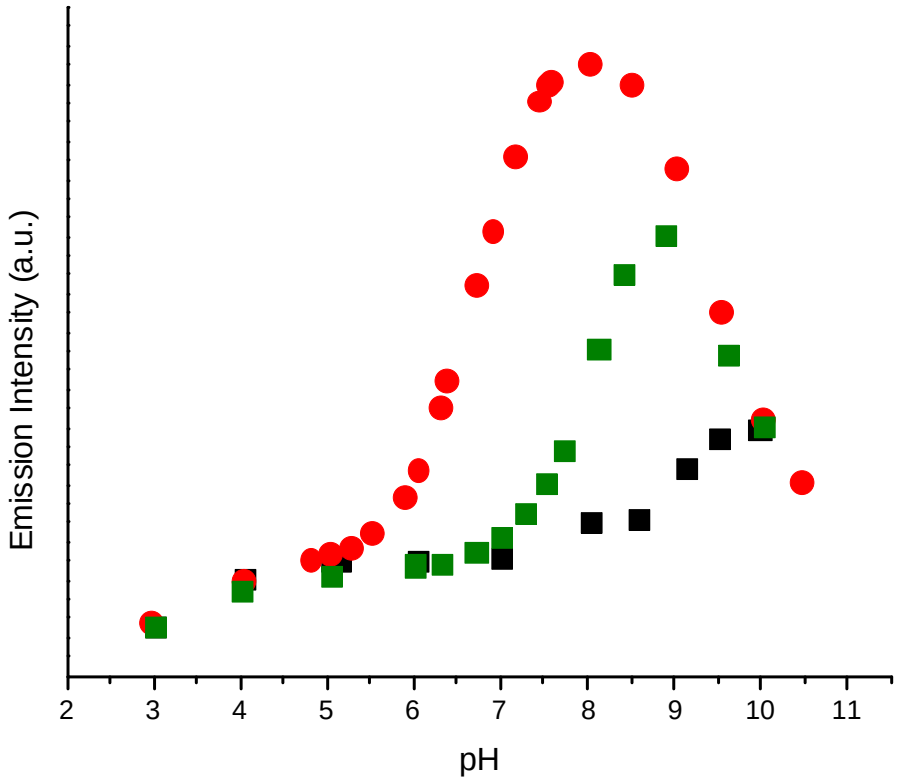


Figure 21: Fluorescence pH titrations of **1** without saccharide (■), with 100 mM glucose (■) and with 50 mM fructose (■) (~saturation) demonstrating the reduction of pKa of the boronic acid by formation of the boronic ester.

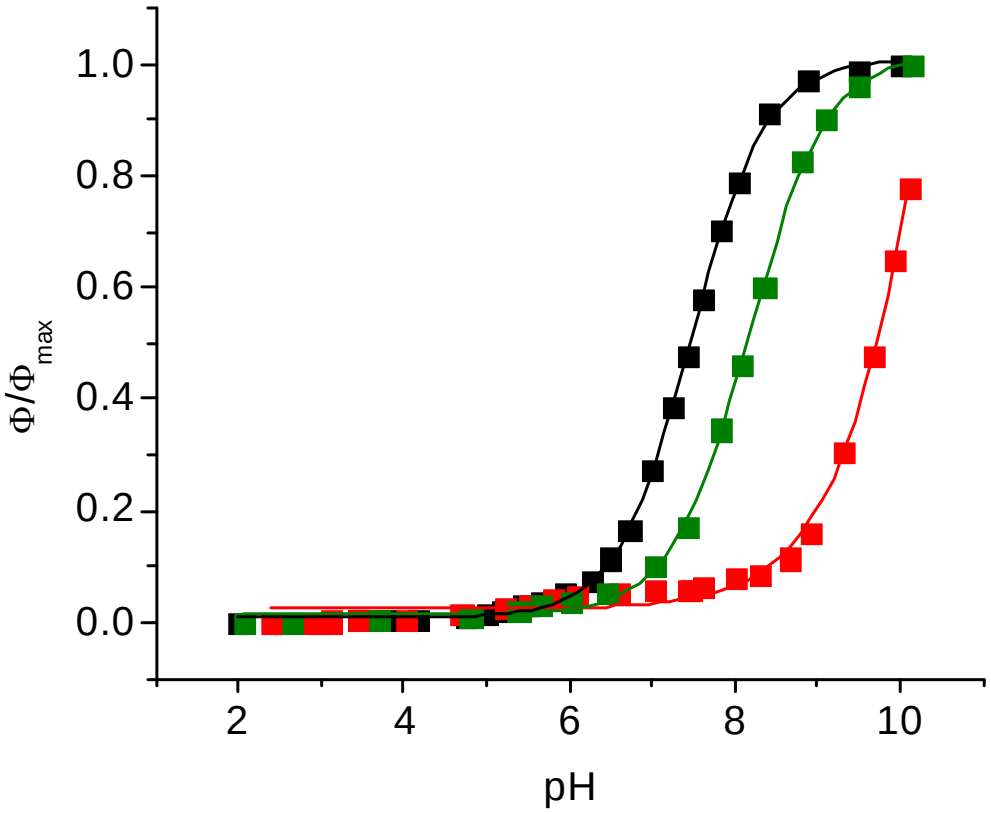


Figure 22: Fluorescence pH titrations of **1** without saccharide (■), with 10 mM fructose (■) and with 100 mM fructose (■) (~saturation) demonstrating the reduction of pKa of the boronic acid by formation of the boronic ester.

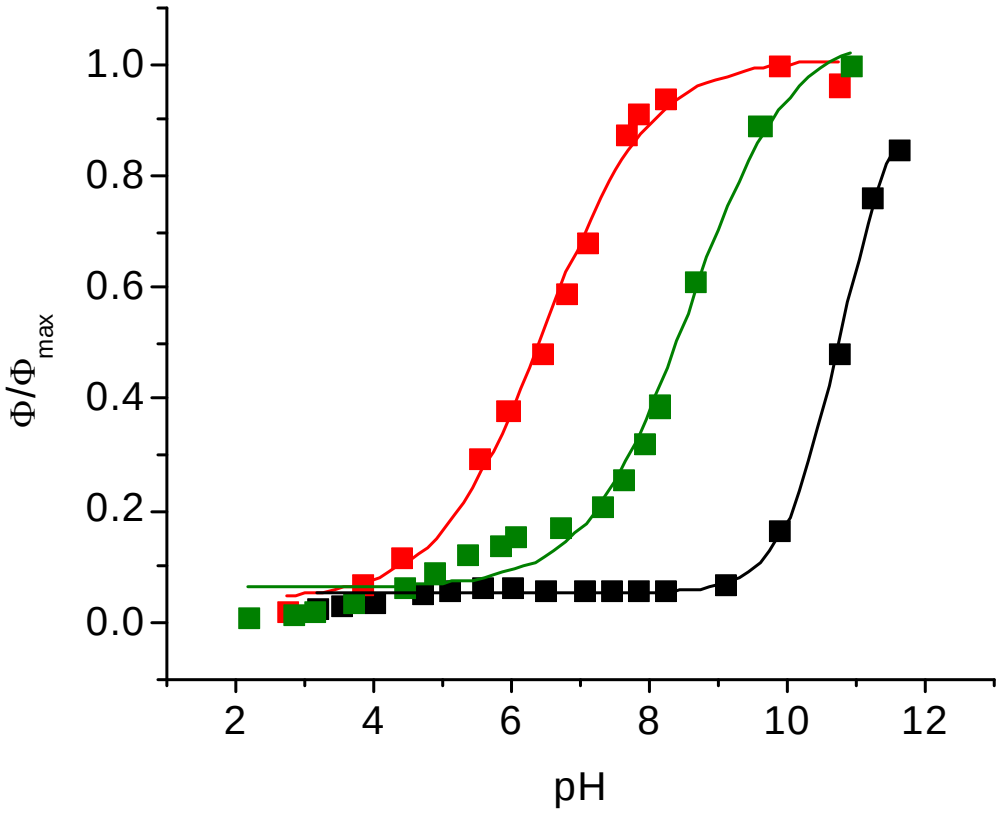


Figure 23: Fluorescence pH titrations of **1** without saccharide (■), with 10 mM fructose (■) and with 100 mM fructose (■) (~saturation) demonstrating the reduction of pKa of the boronic acid by formation of the boronic ester.

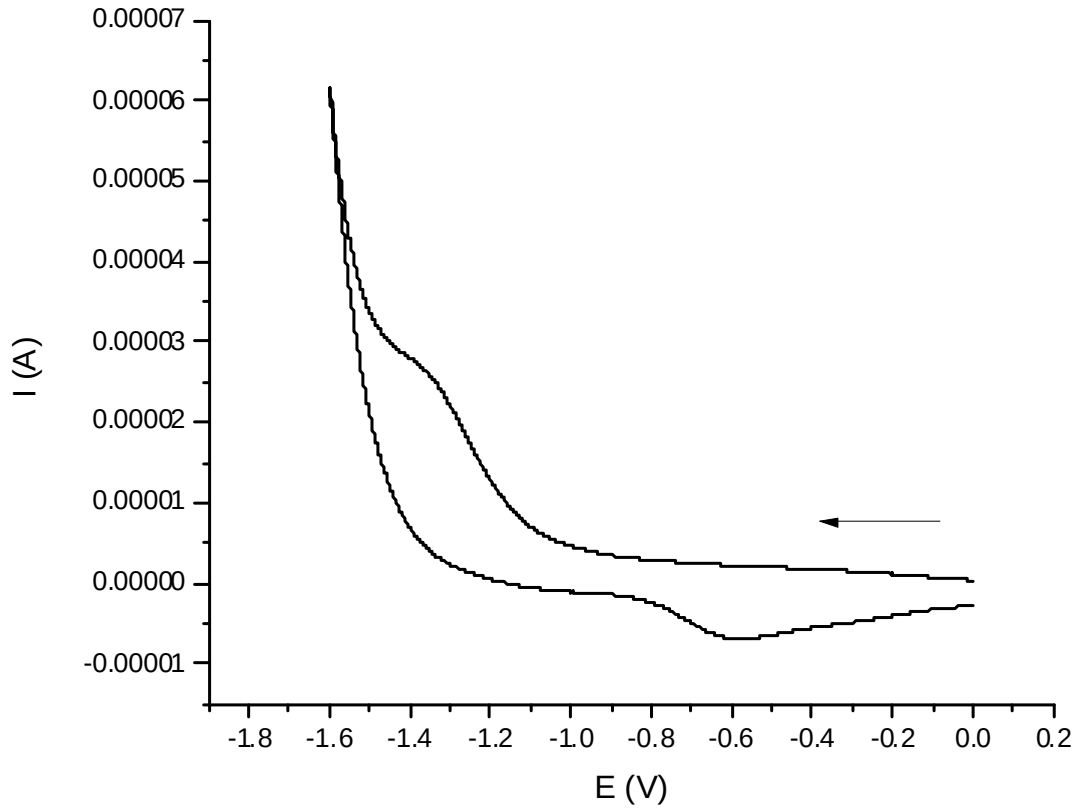


Figure 24: Cyclic voltammogram of the cathodic process of phenylboronic acid in anhydrous dimethylformamide.

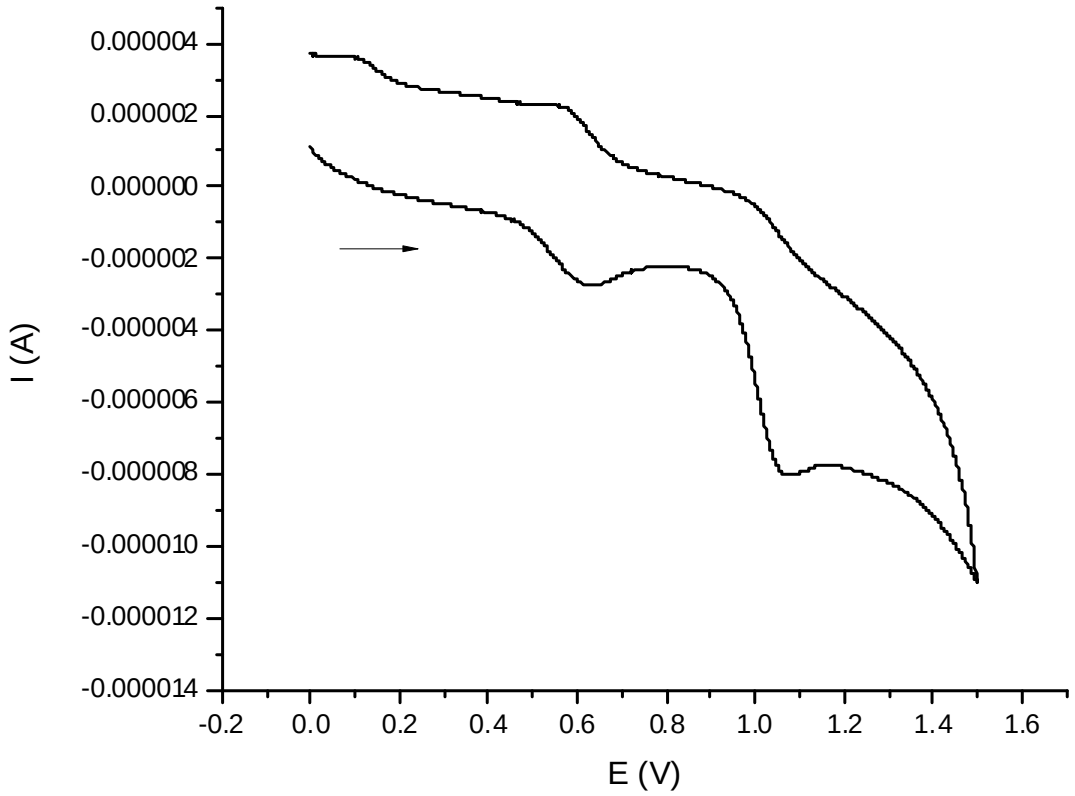


Figure 25: Cyclic voltammogram of the anodic process of **9** in anhydrous dimethylformamide.

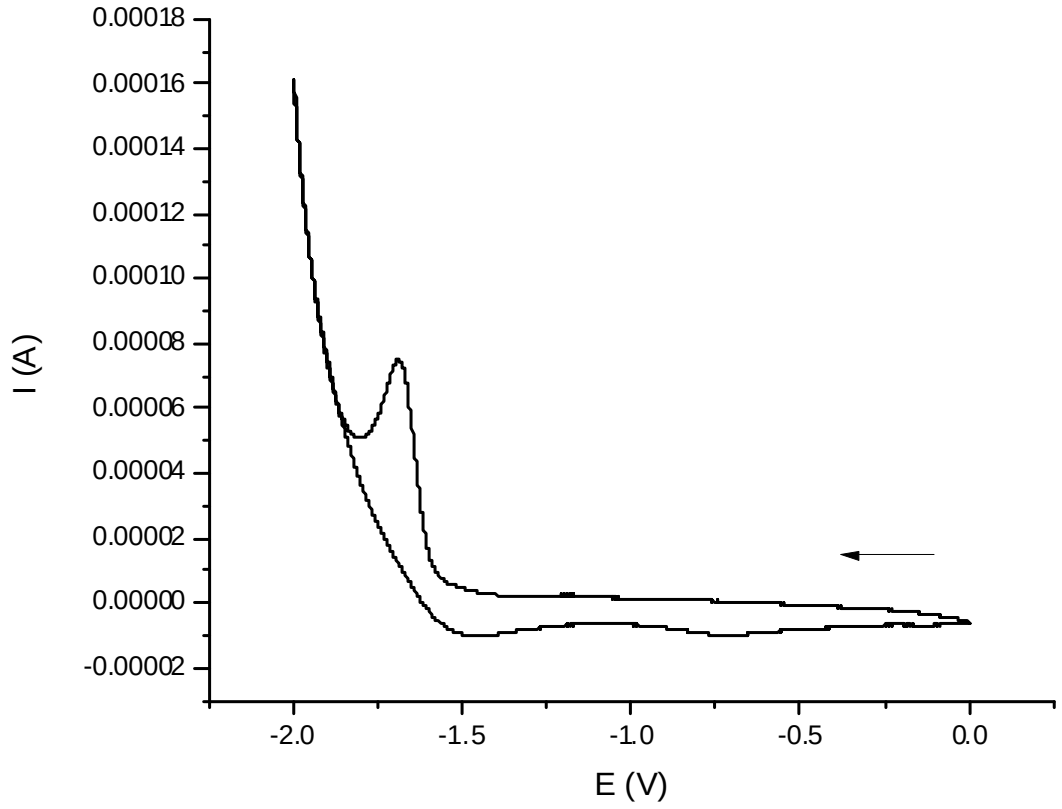


Figure 26: Cyclic voltammogram of the cathodic process of **10** in anhydrous dimethylformamide.

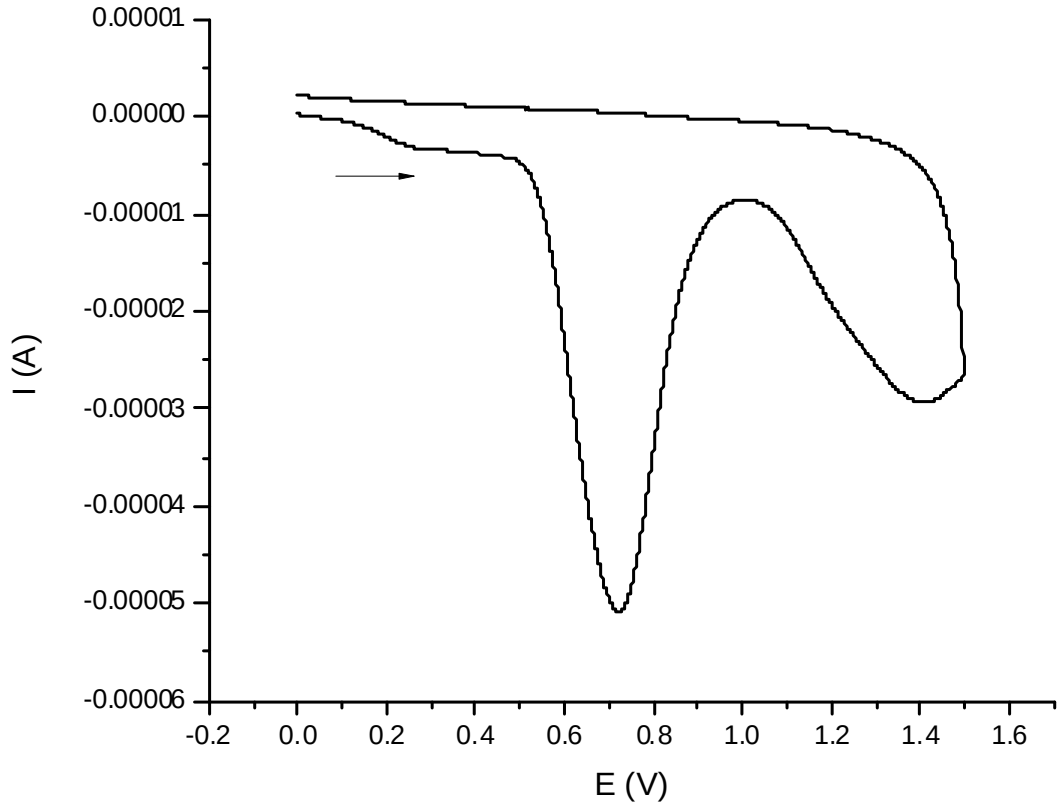


Figure 27: Cyclic voltammogram of the anodic process of **11** in anhydrous dimethylformamide.

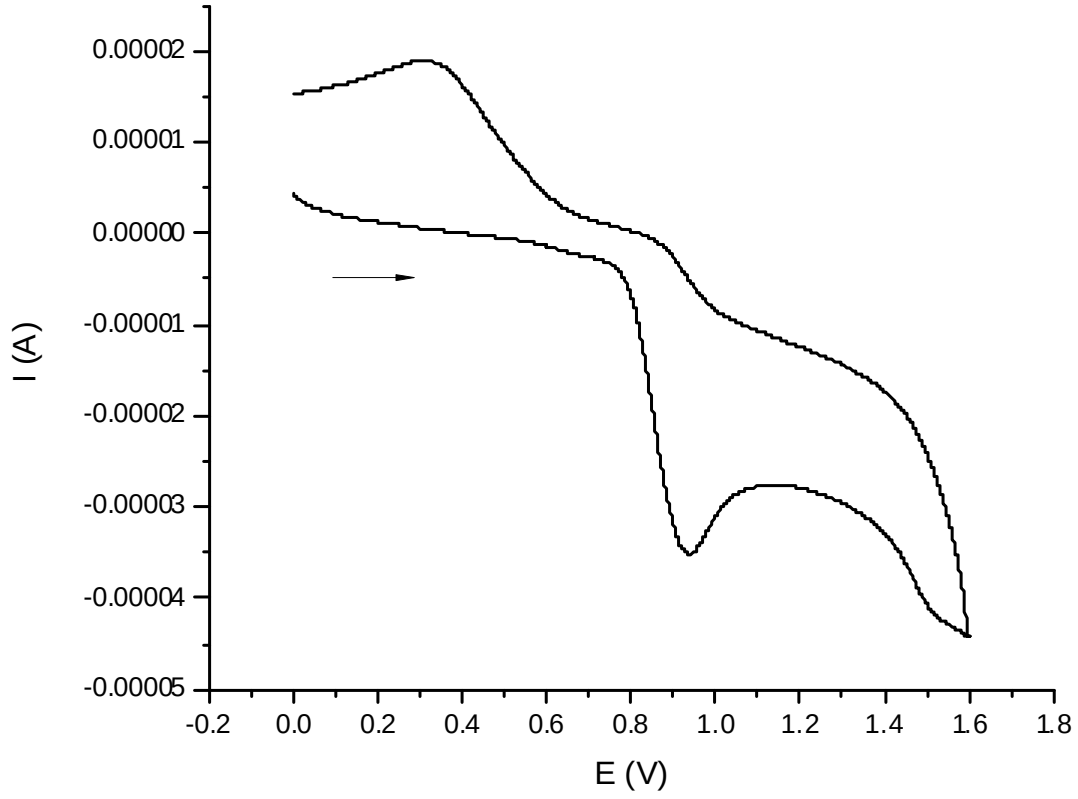


Figure 28: Cyclic voltammogram of the anodic process of **12** in anhydrous dimethylformamide.

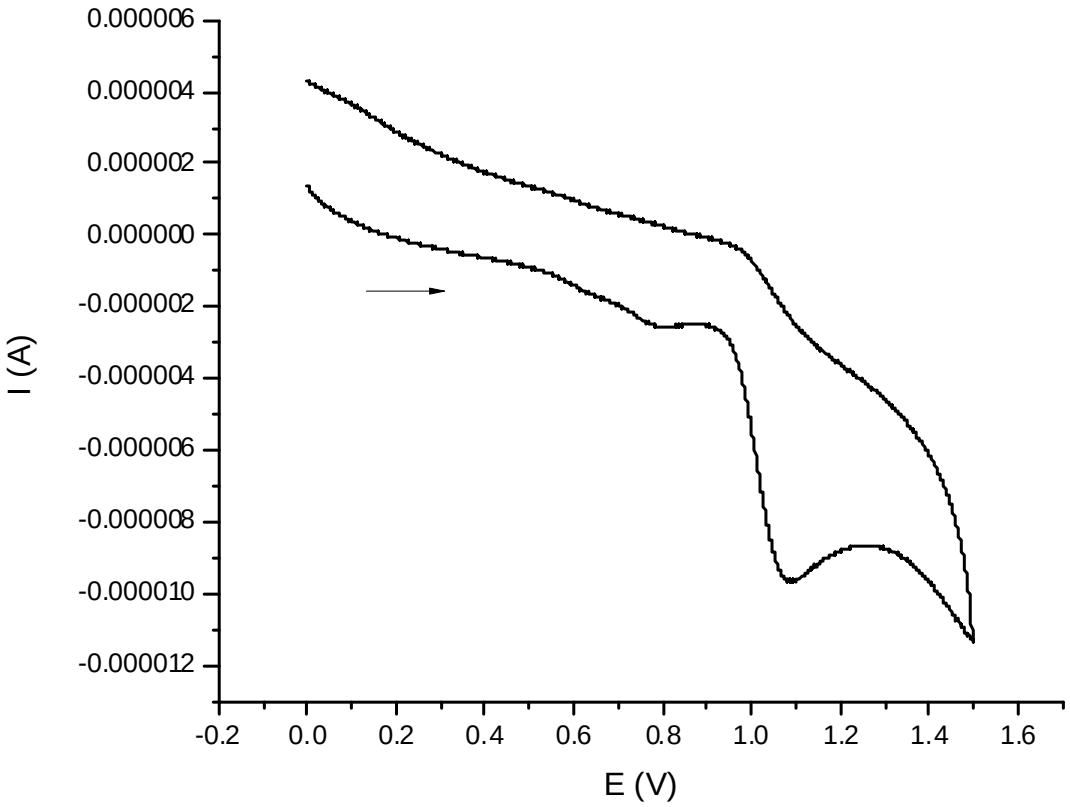


Figure 29: Cyclic voltammogram of the anodic process of **13** in anhydrous dimethylformamide.

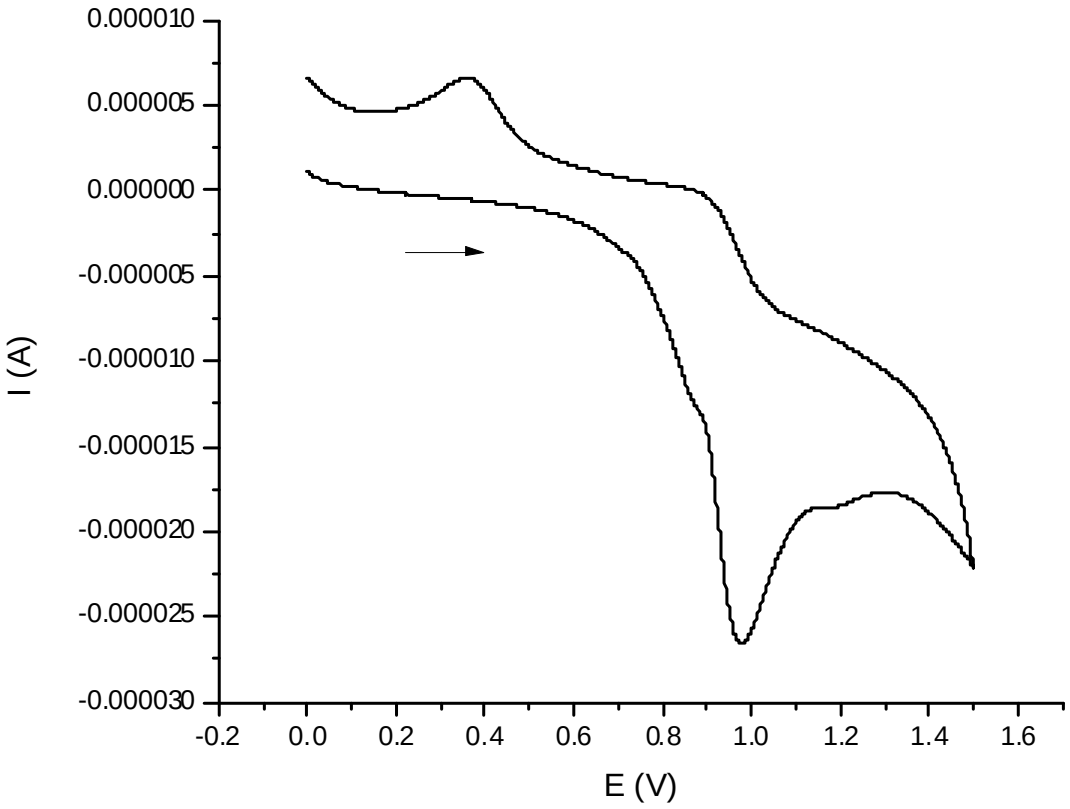


Figure 30: Cyclic voltammogram of the anodic process of **20** in anhydrous dimethylformamide.

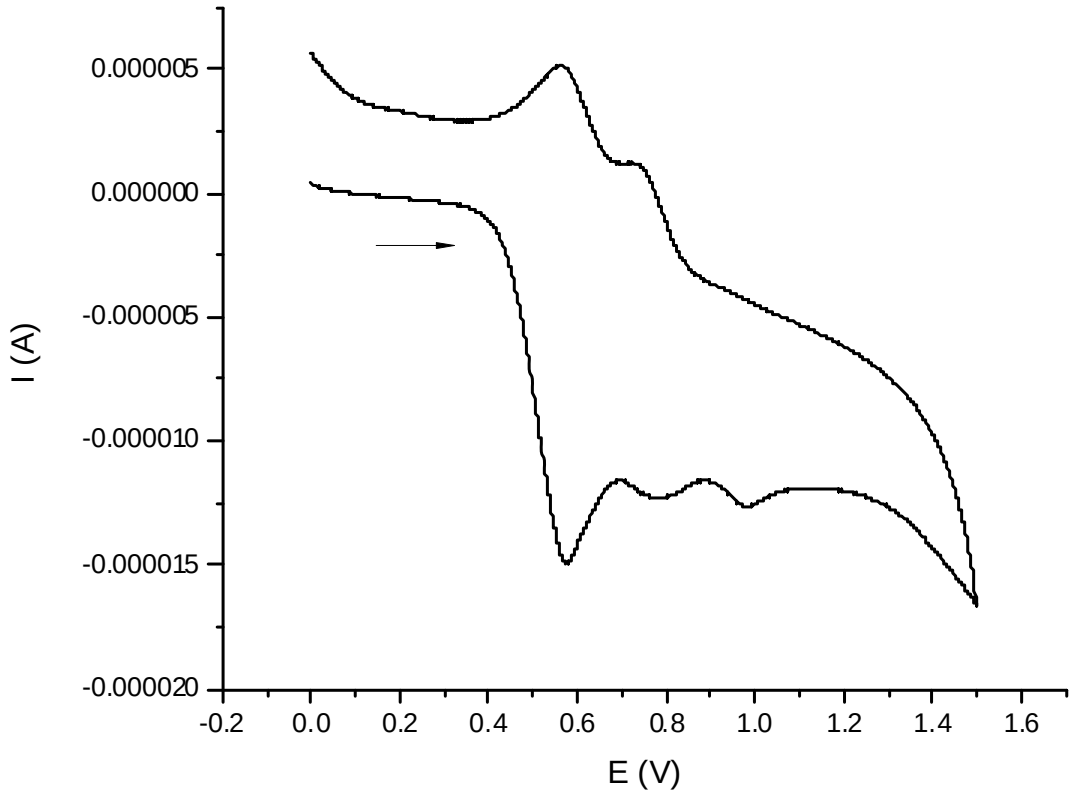


Figure 31: Cyclic voltammogram of the anodic process of **21** in anhydrous dimethylformamide.

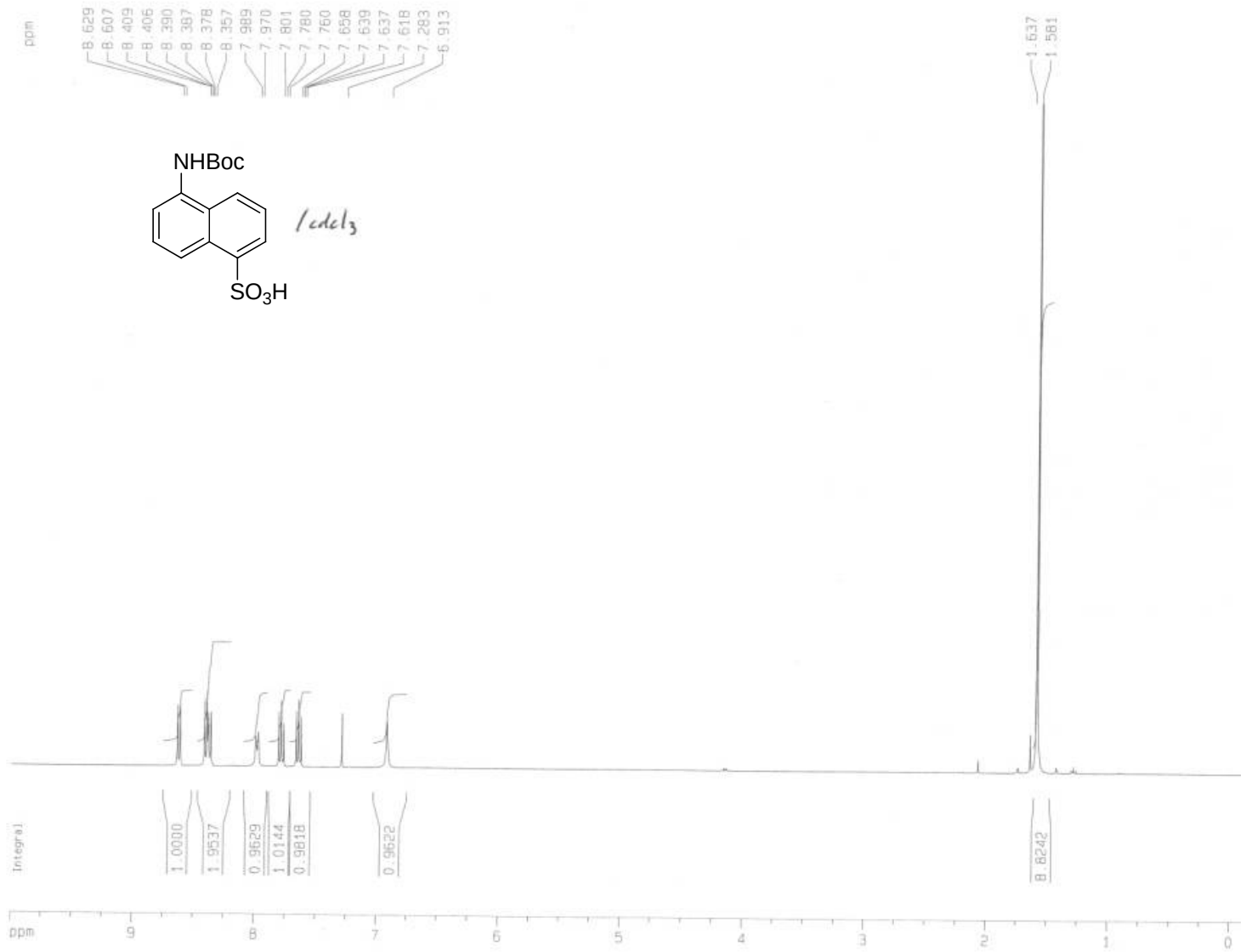


Figure 32: ^{1}H NMR of N-Boc-5-aminonaphthalene-1-sulfonic acid in $CDCl_3$.

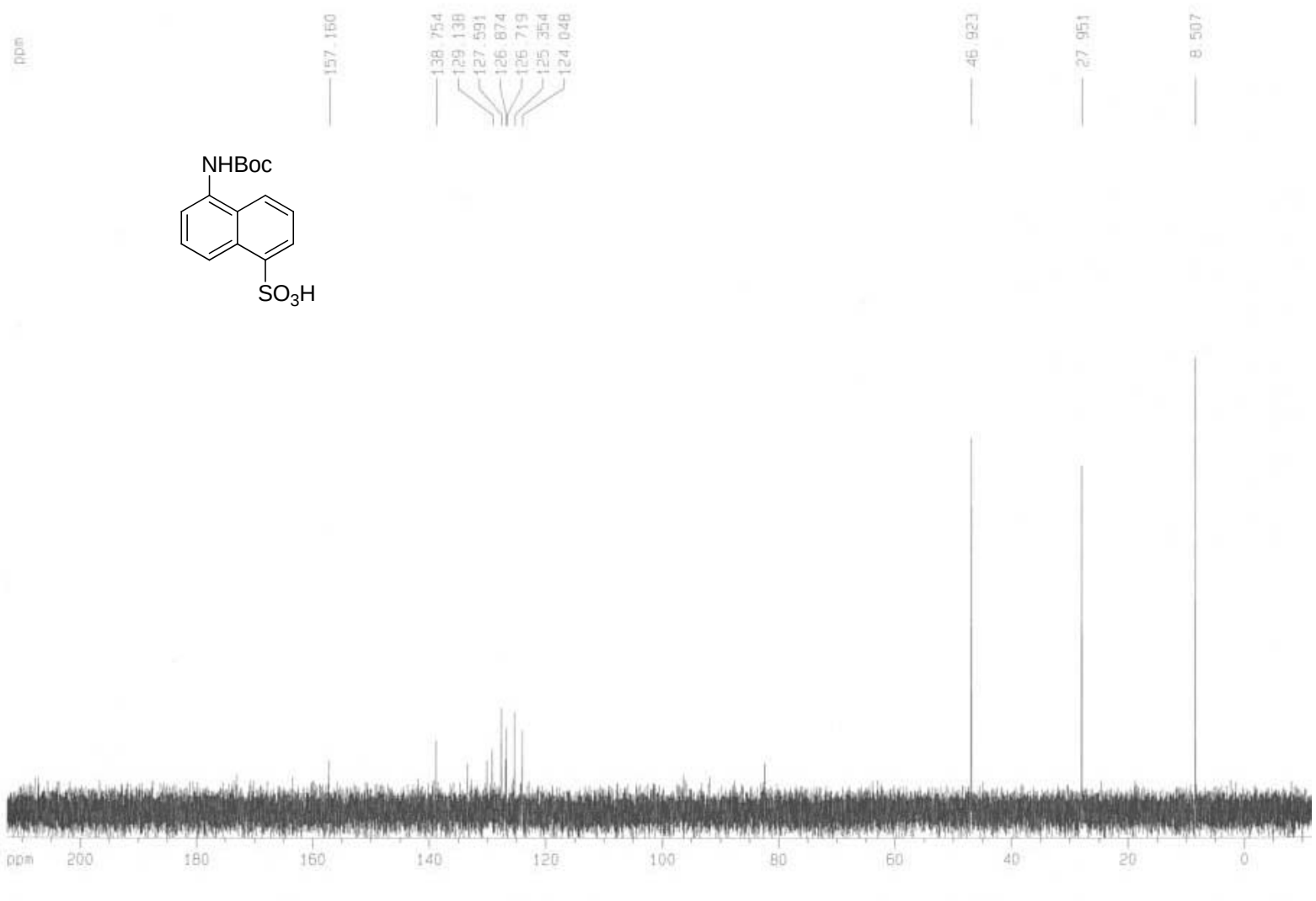


Figure 33: ^{13}C NMR of N-Boc-5-aminonaphthalene-1-sulfonic acid in $CDCl_3$.

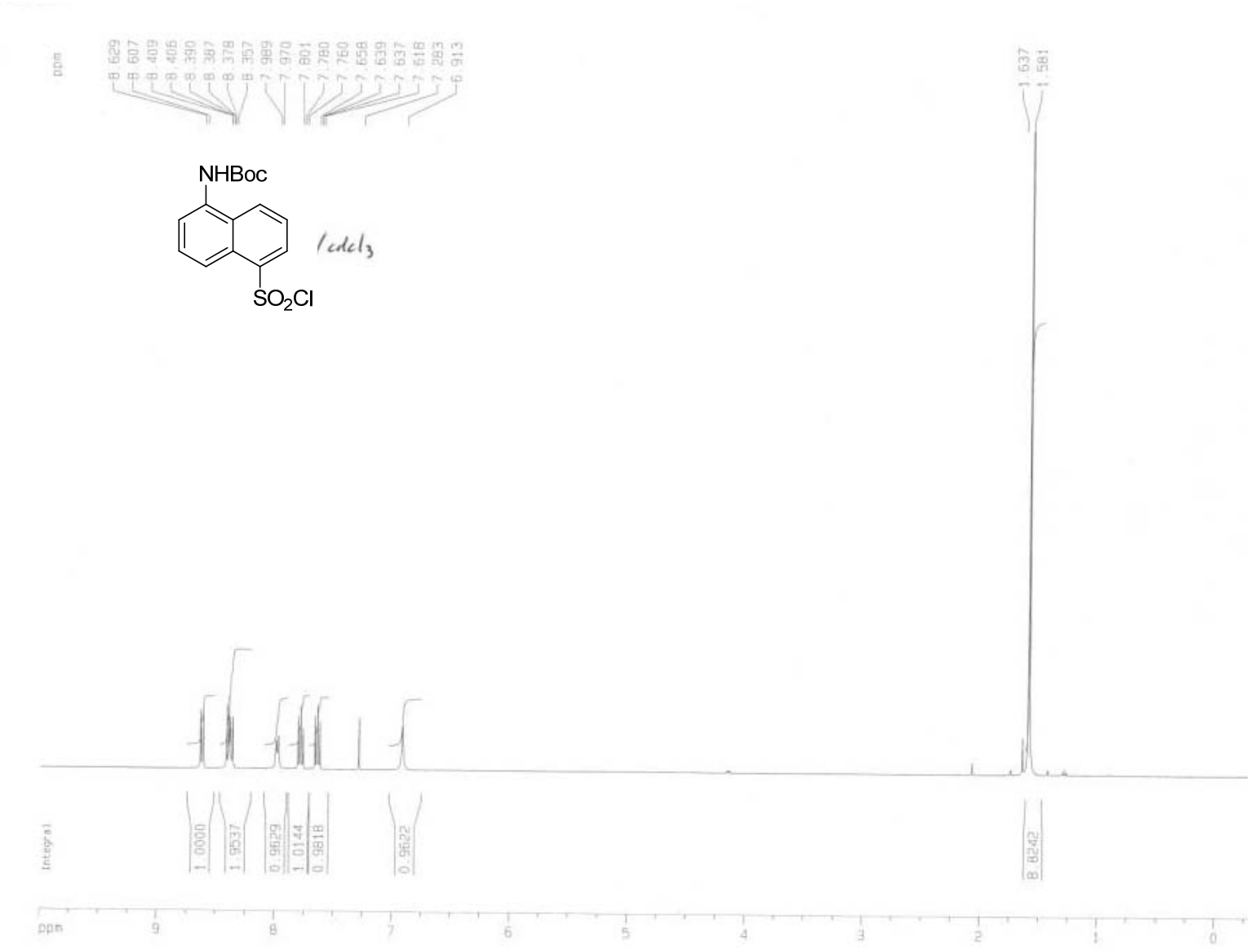


Figure 34: ^{1}H NMR of N-Boc-5-aminonaphthalene-1-sulfonyl chloride in $CDCl_3$.

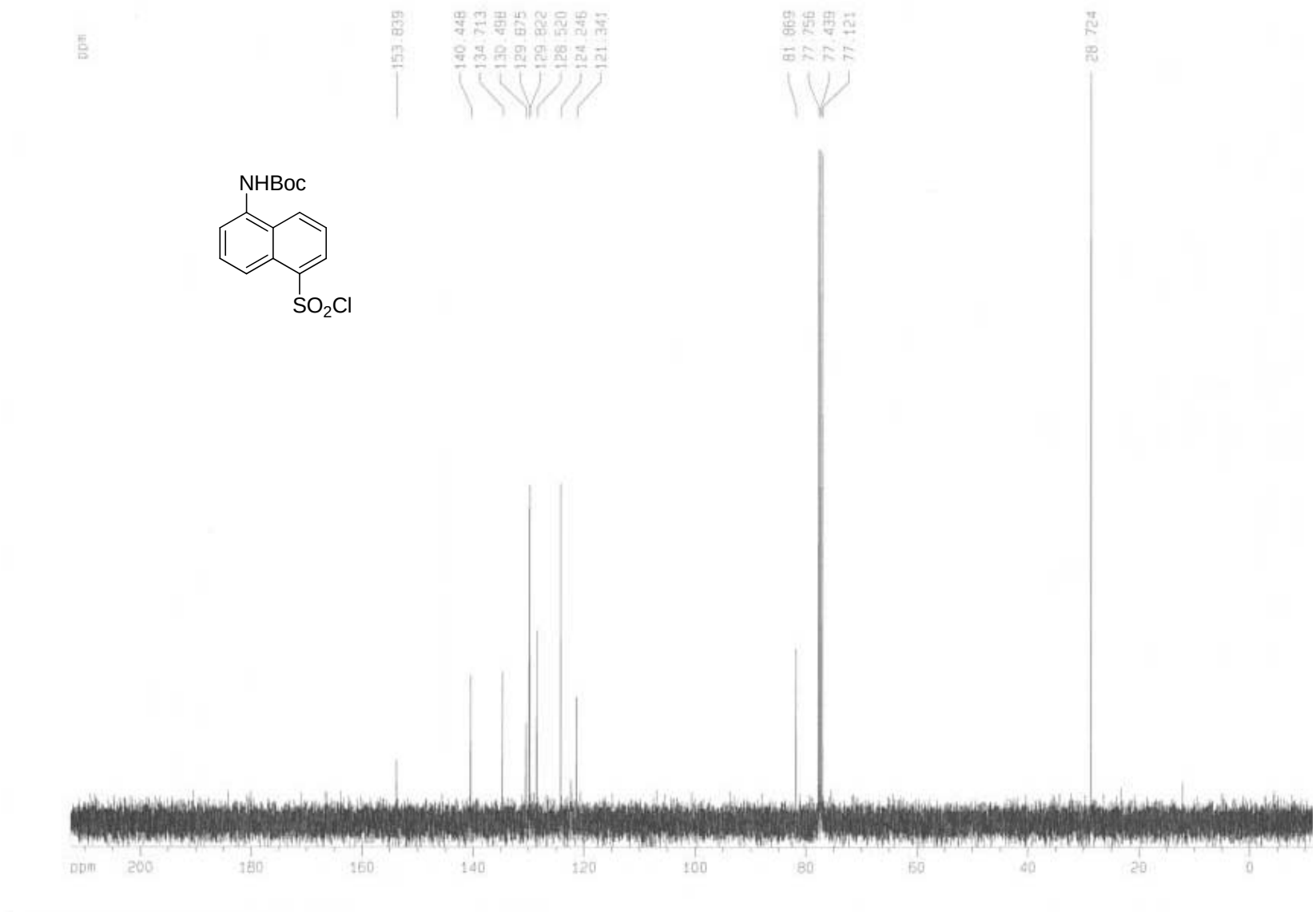


Figure 35: ^{13}C NMR of N-Boc-5-aminonaphthalene-1-sulfonyl chloride in $CDCl_3$.

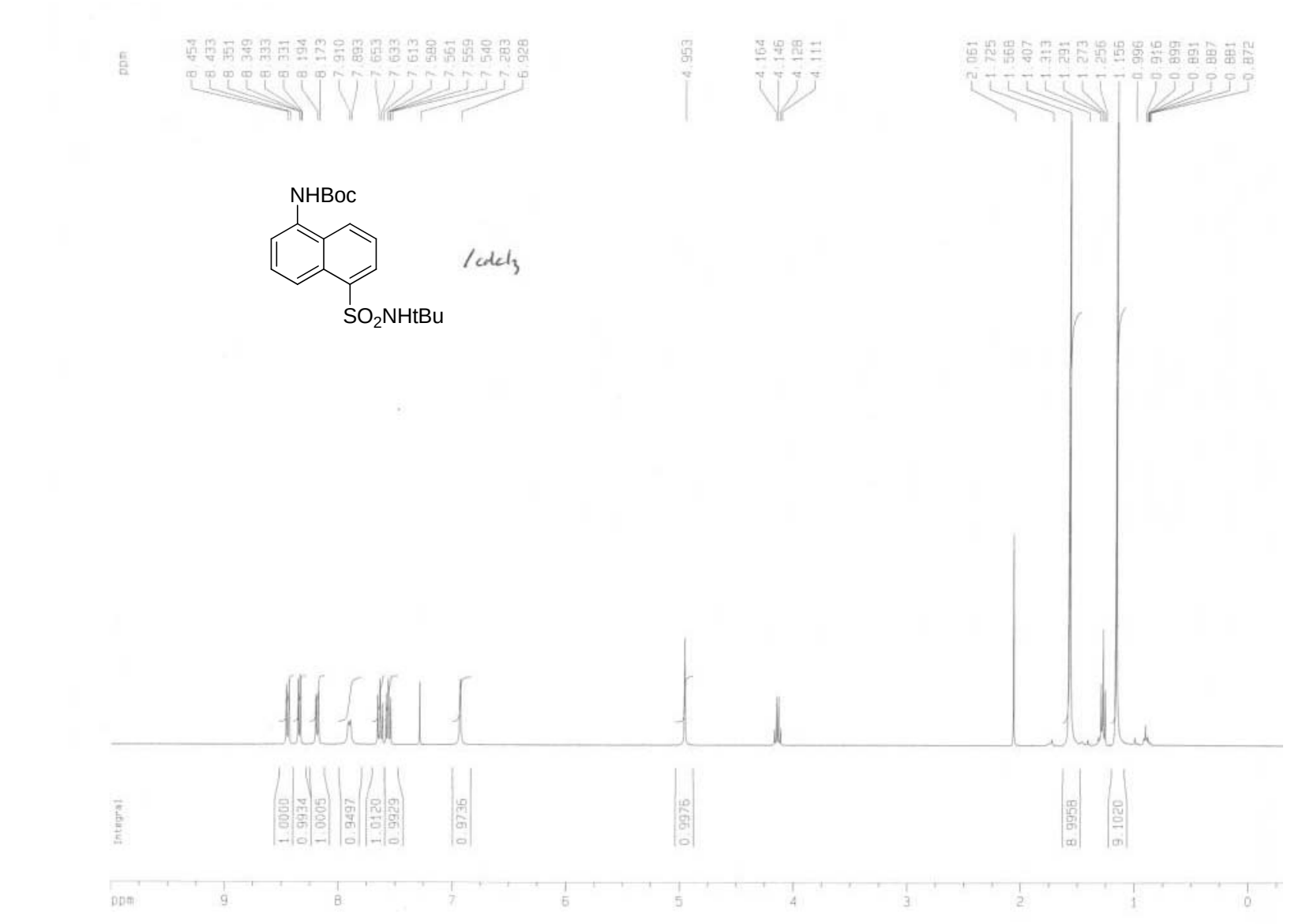


Figure 36: ^{1}H NMR of N-Boc-5-aminonaphthalene-1-*tert*-butylsulfonamide in $CDCl_3$.

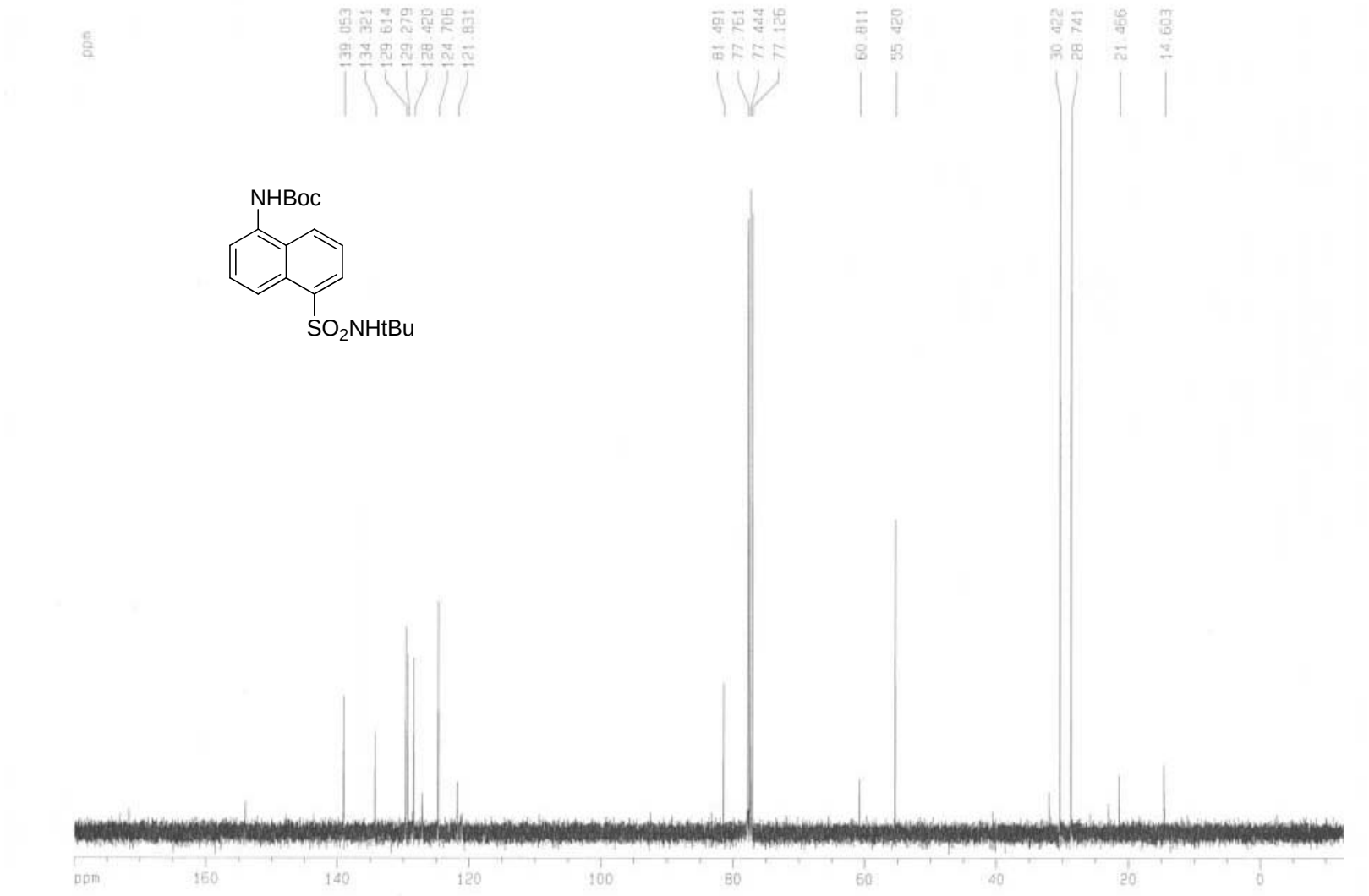


Figure 37: ^{13}C NMR of N-Boc-5-aminonaphthalene-1-*tert*-butylsulfonamide in $CDCl_3$.

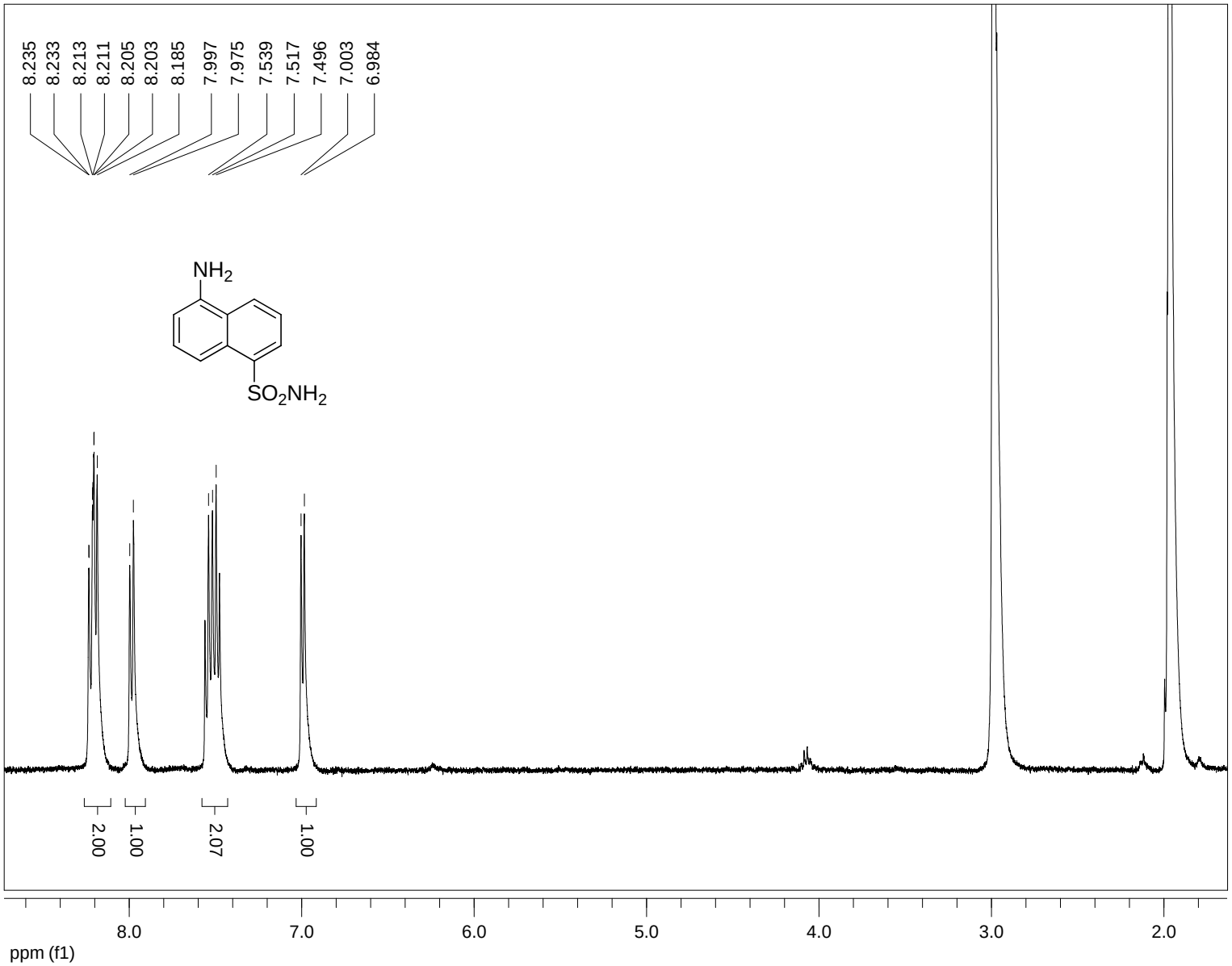


Figure 38: ^{1}H NMR of 5-aminonaphthalene-1-sulfonamide in 5% D_2O in CD_3CN.

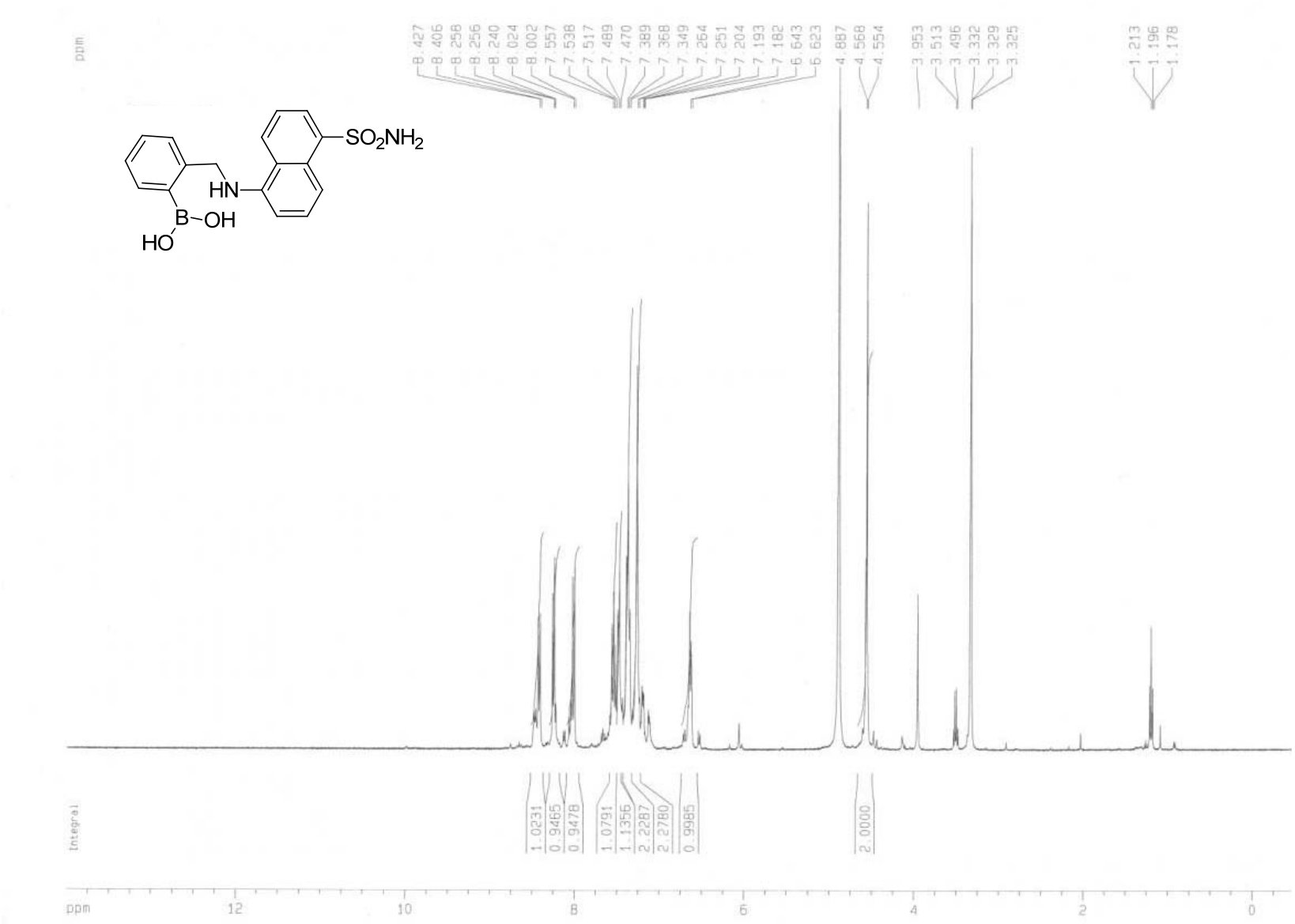


Figure 39: ^{1}H NMR of N-phenylborono-5-aminonaphthalene-1-sulfonamide in CD_3OD.

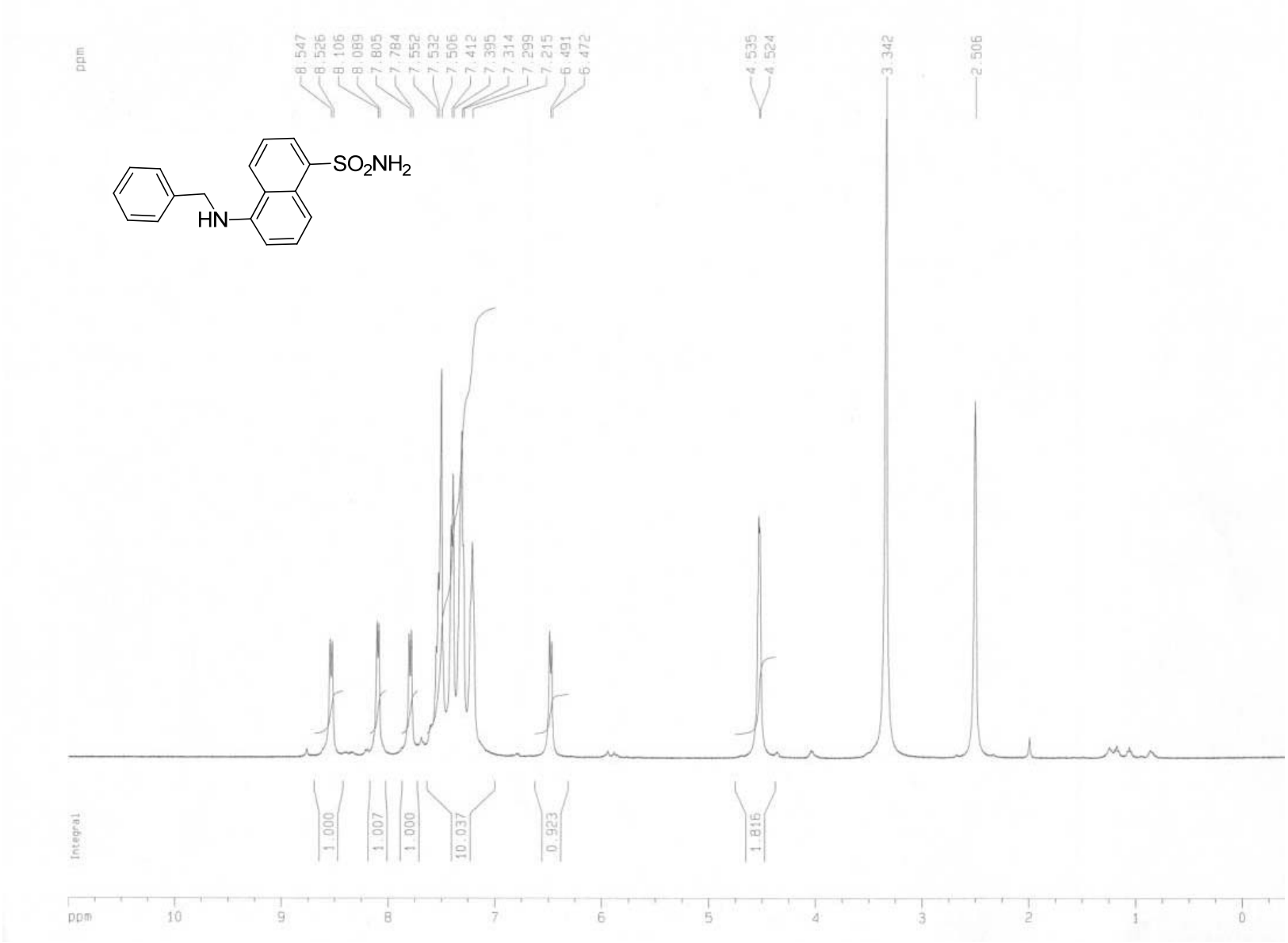


Figure 40: ^{1}H NMR of N-benzyl-5-aminonaphthalene-1-sulfonamide in D_6-DMSO.

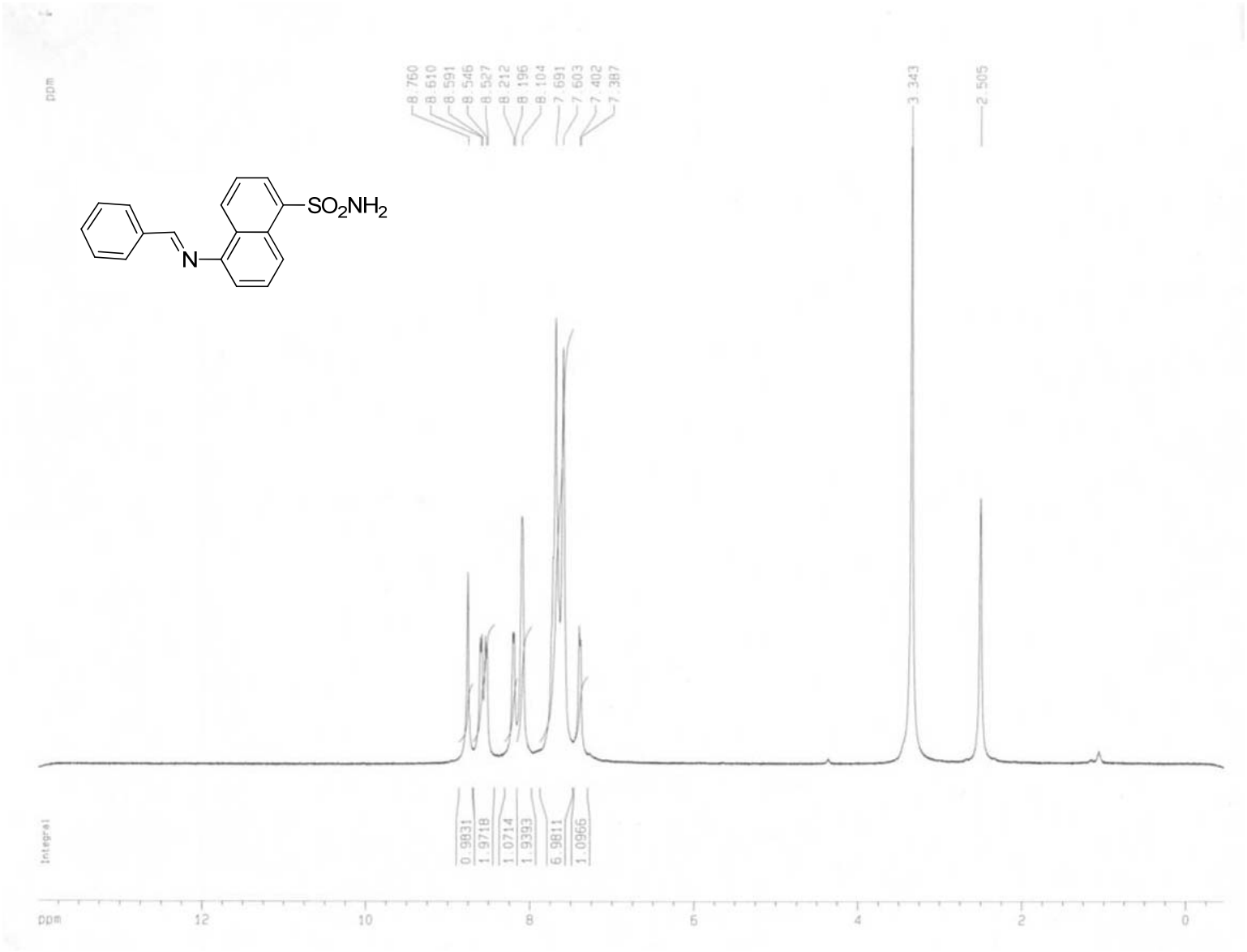


Figure 41: ^{1}H-NMR of N-benzylidine-5-aminonaphthalene-1-sulfonamide in D_6-DMSO.

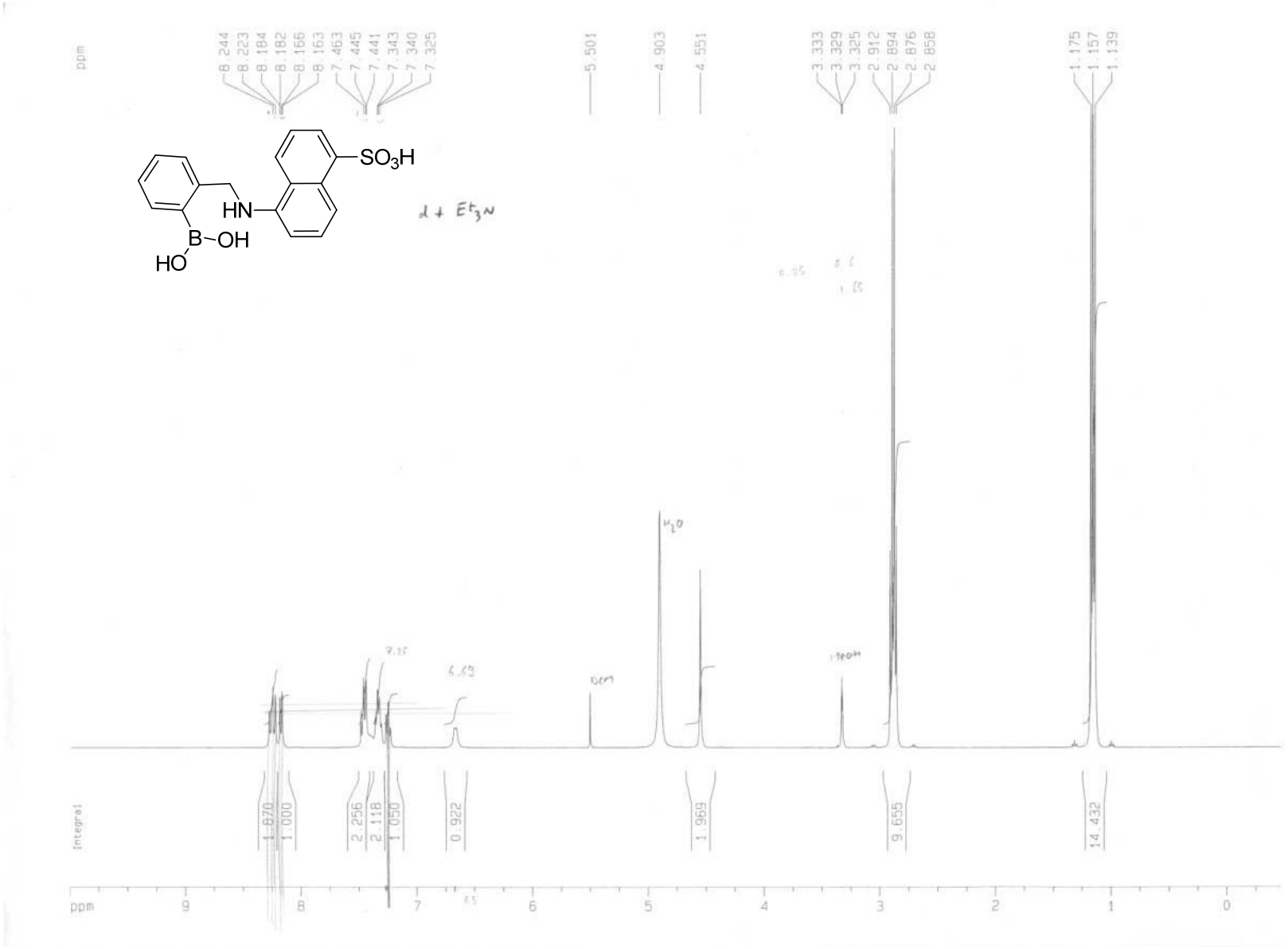


Figure 42: ^{1}H NMR of N-phenylborono-5-aminonaphthalene-1-sulfonic acid in CD_3OD+Et_3N.

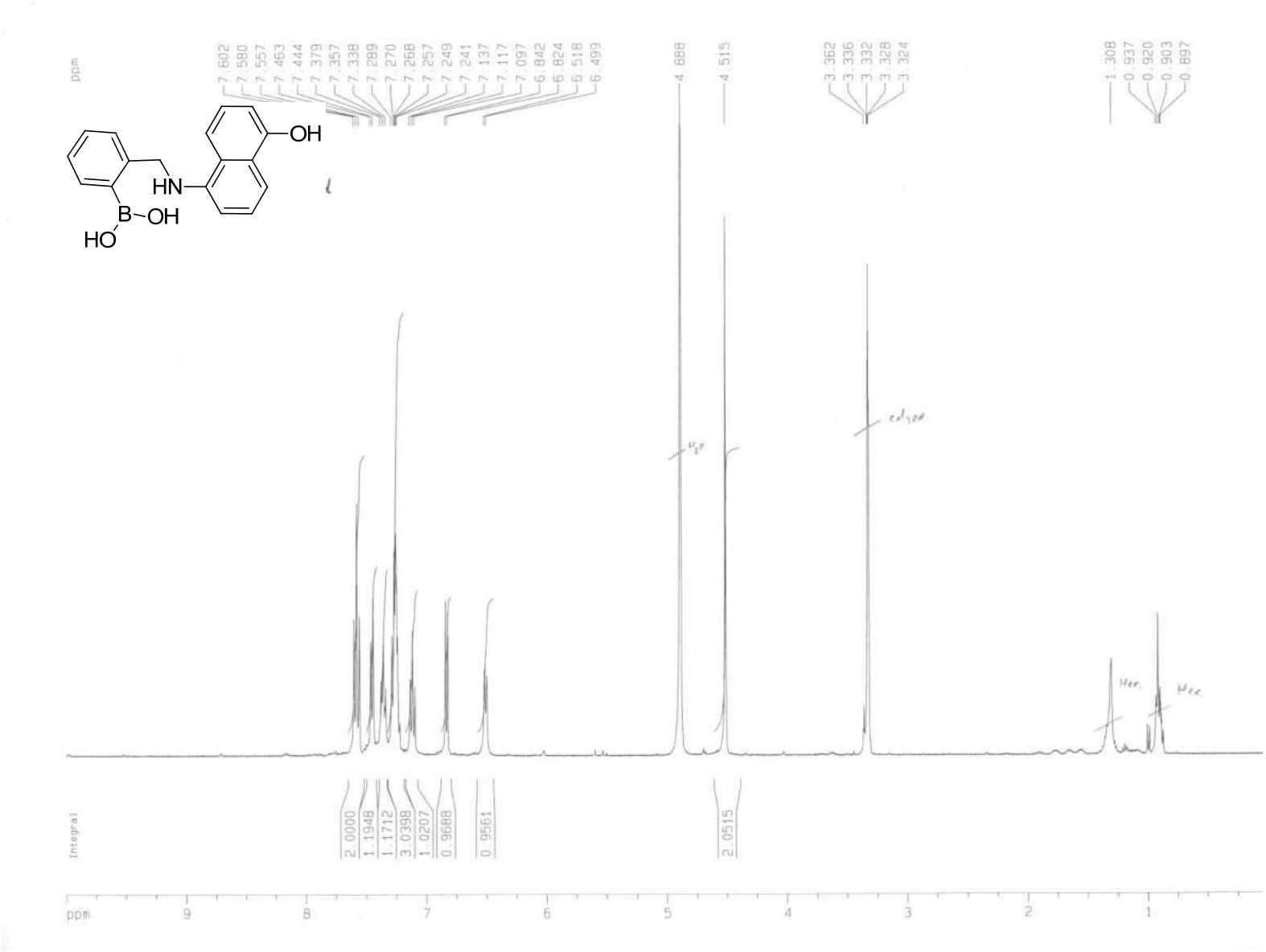


Figure 43: ^{1}H NMR of N-phenylborono-5-amino-1-naphthol in CD_3OD.

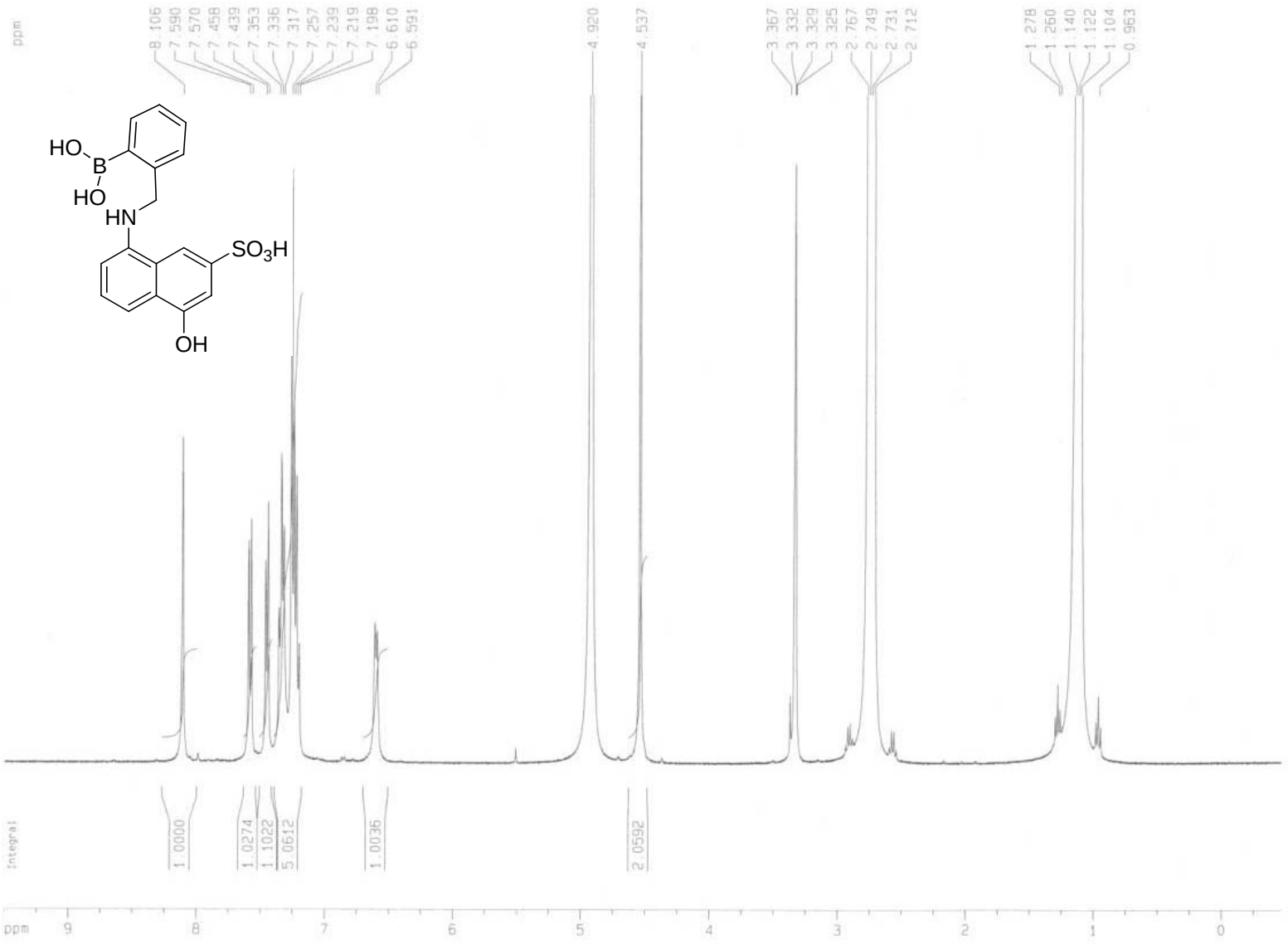


Figure 44: ^{1}H NMR of N-phenylborono-5-amino-1-naphthol-3-sulfonic acid in CD_3OD+Et_3N.

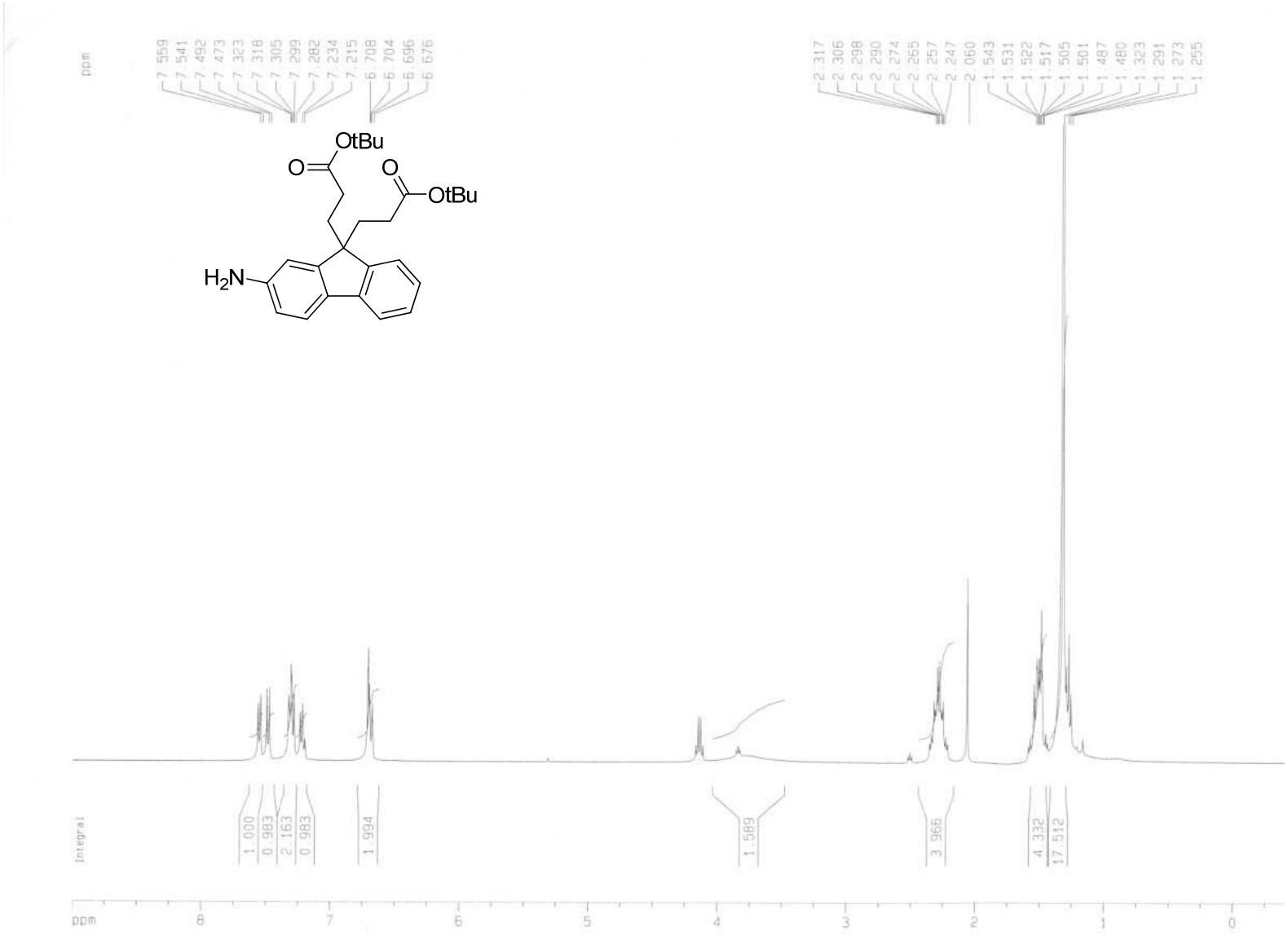


Figure 45: ^{1}H NMR of ^{t}BuFluoHa in $CDCl_3$.

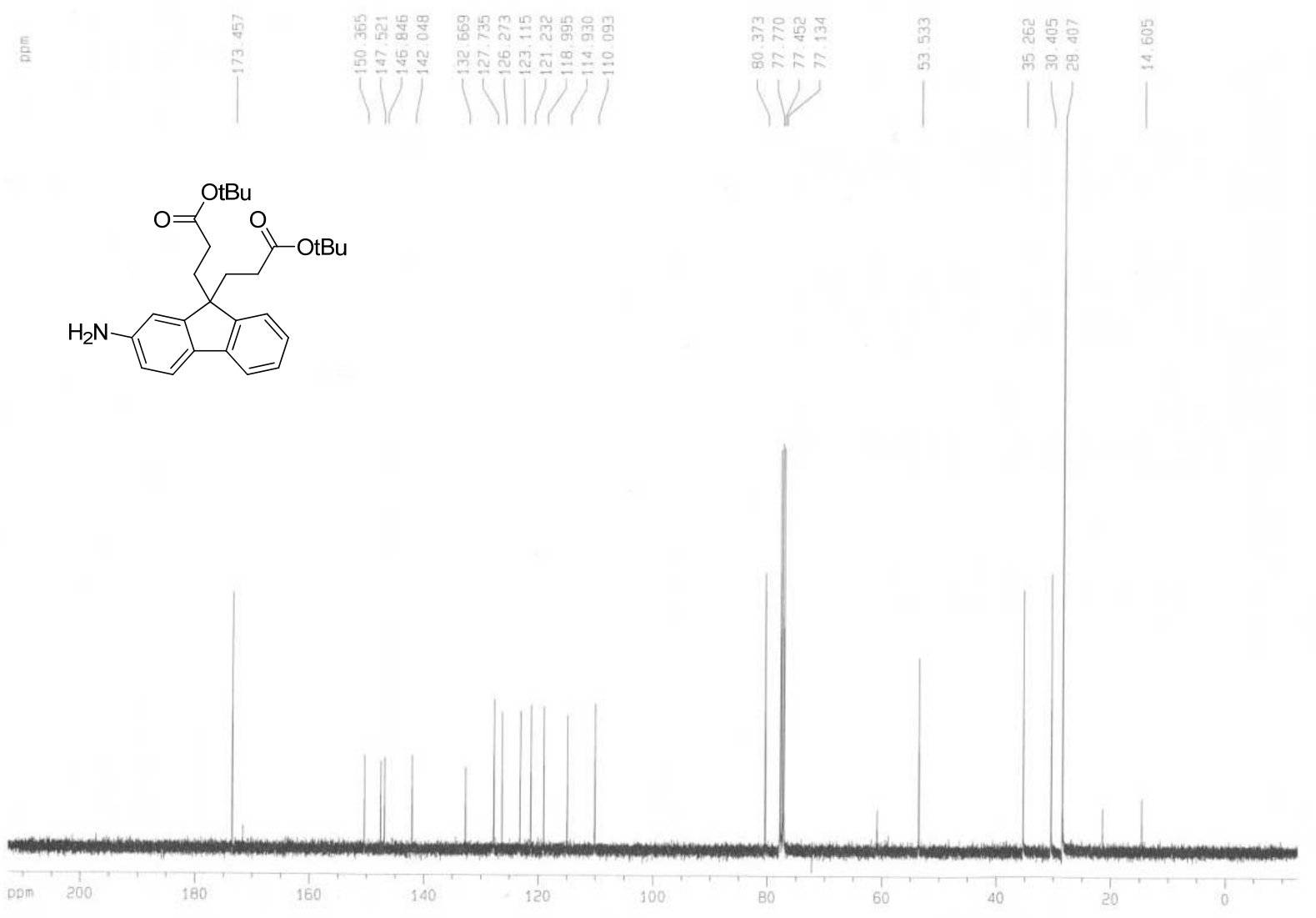


Figure 46: ^{13}C NMR of ^{t}BuFluoHa in $CDCl_3$.

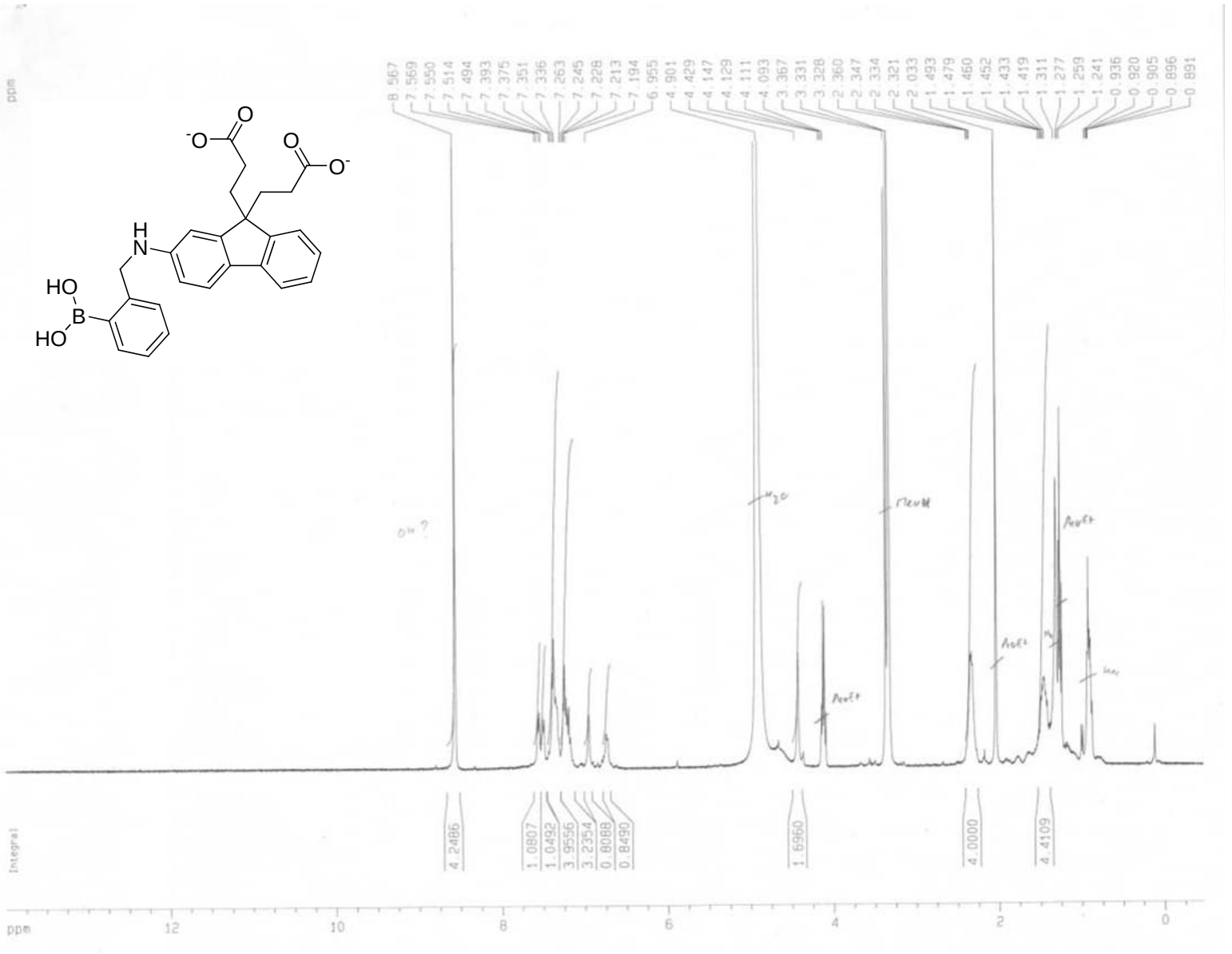


Figure 47: ^{1}H NMR of FluoHc in CD_3OD.

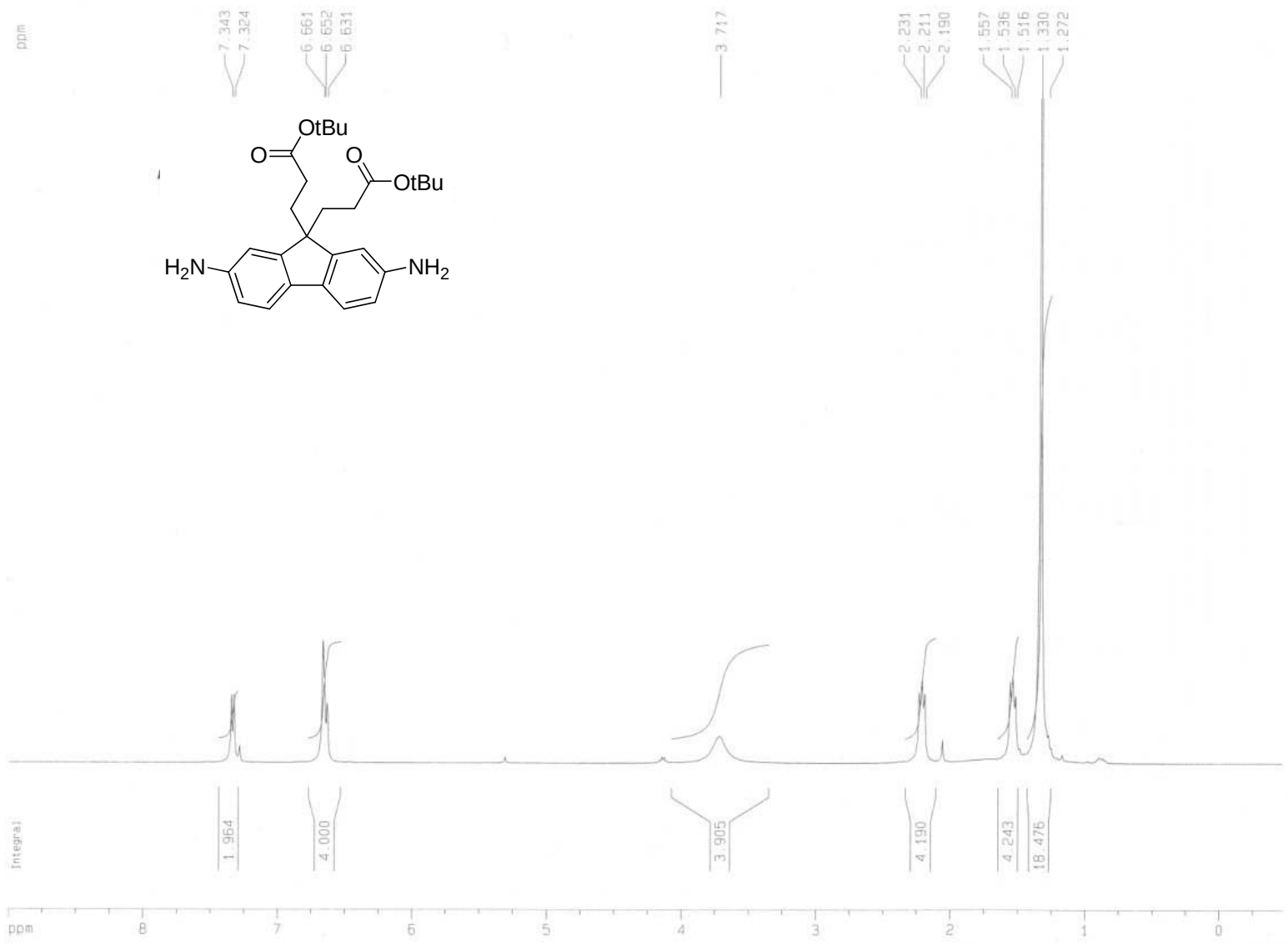


Figure 48: ^{1}H NMR of ^{t}BuFluoNH$_2$a in CDCl$_3$.

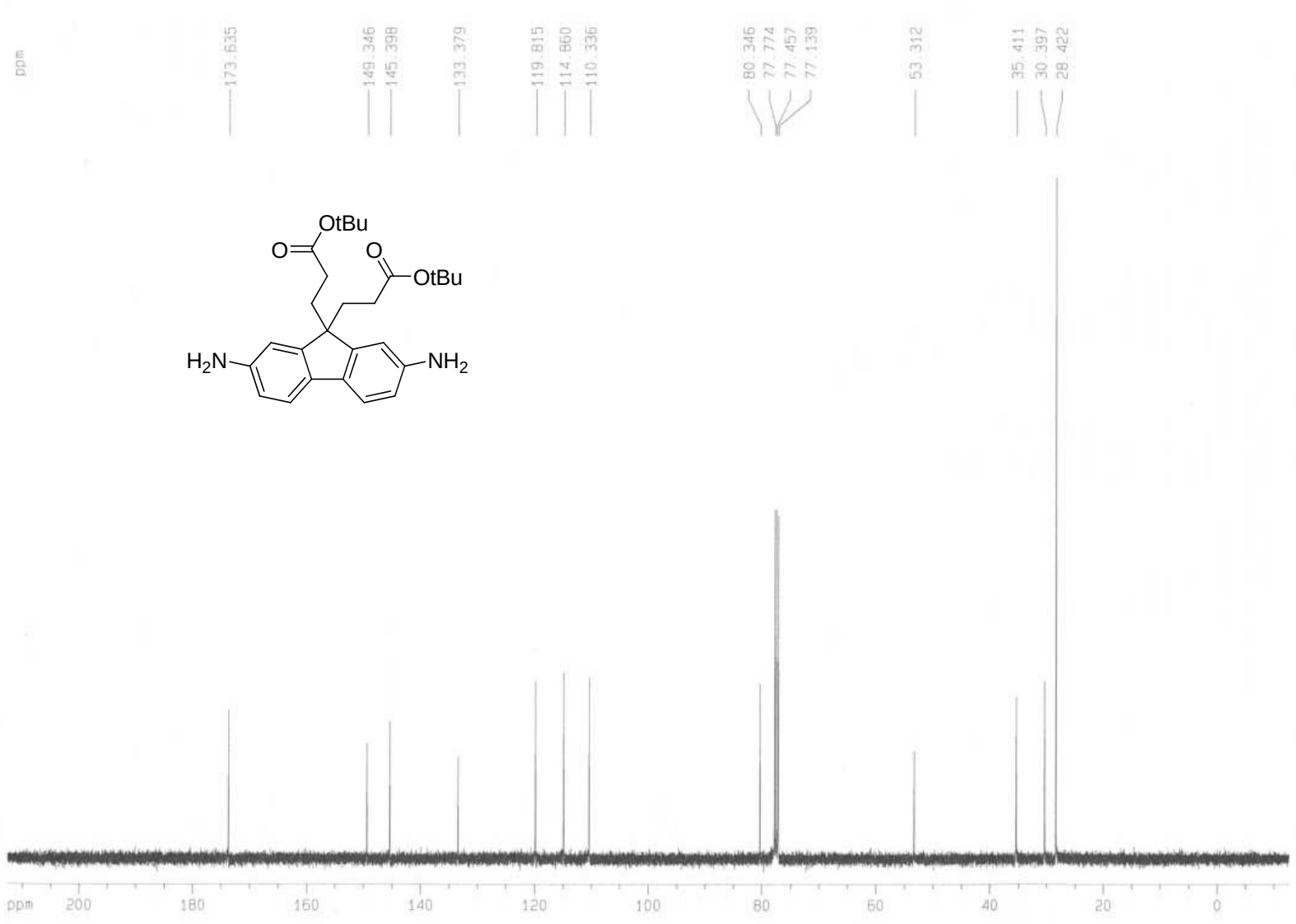


Figure 49: ^{13}C NMR of ^{t}BuFluoNH$_2$a in $CDCl_3$.

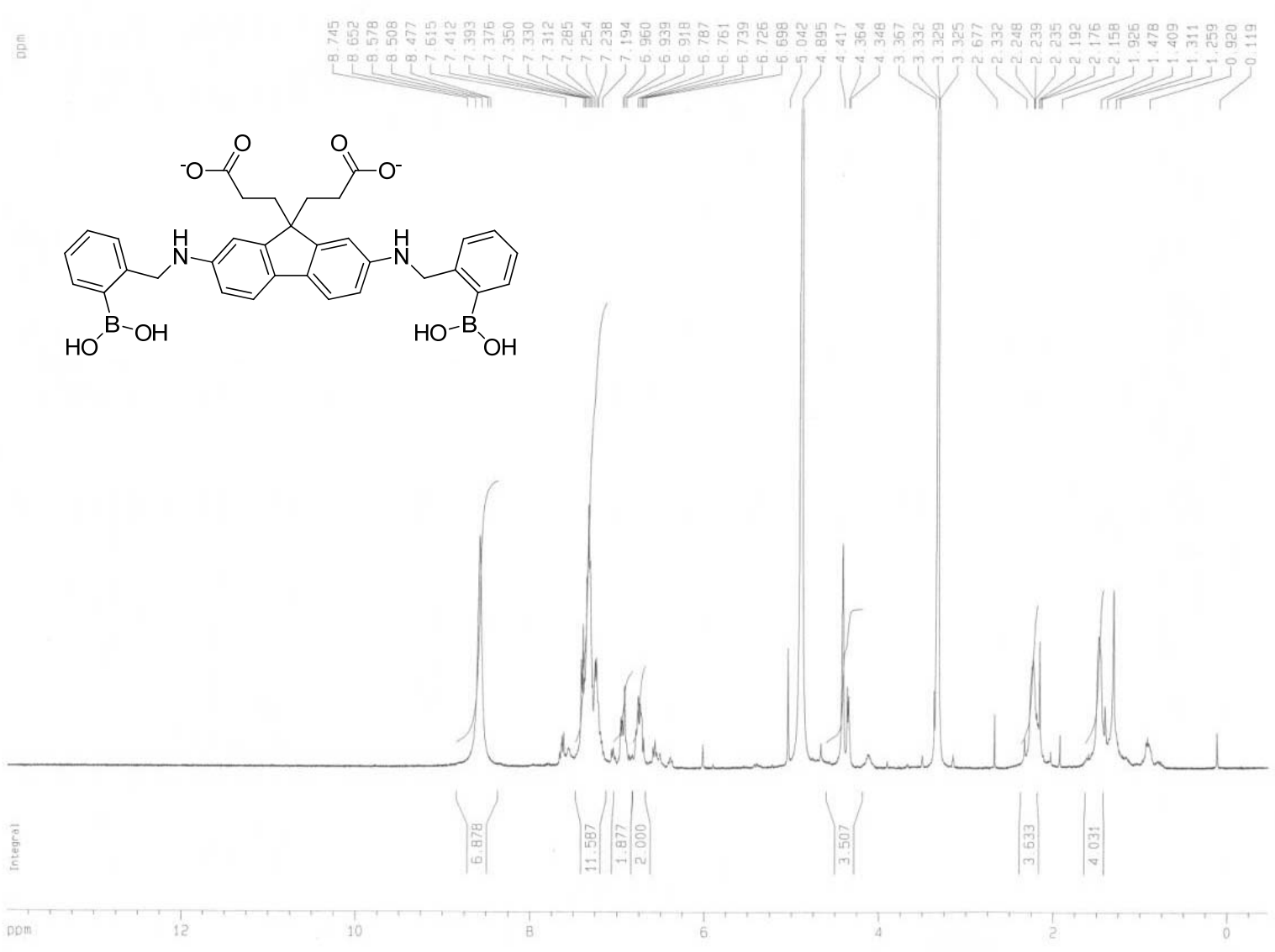
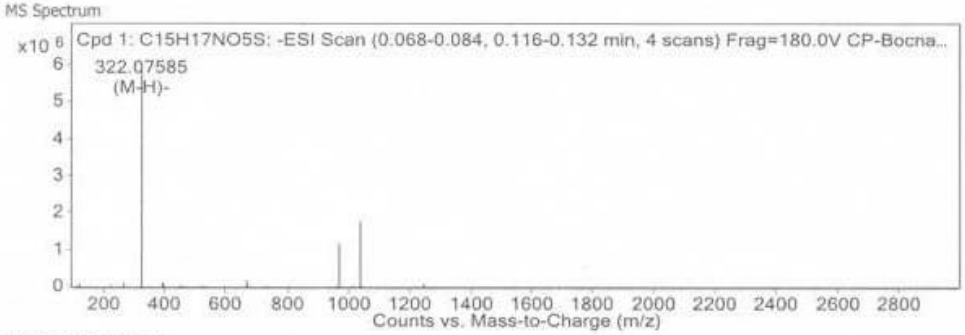


Figure 50: ^{1}H NMR of FluoNH_2c in CD_3OD.

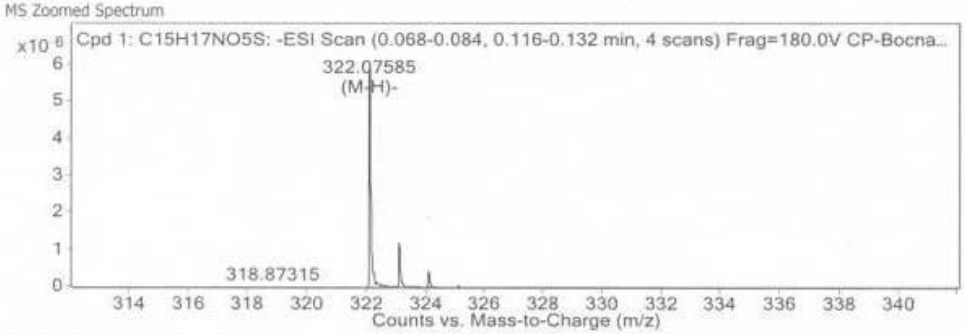
Rapport d'analyse

Data File	CP-Bocnaphsulf_b.d	**Sample Name**	CP-Bocnaphsulf
Sample Type	Sample	**Position**	P1-C6
Analysis Date	5/27/2010 1:56:05 PM	**User Name**	Marie-Christine
Acq Method	ESI_NEG_DI.m	**DA Method**	ESI_NEG_DI.m
Comment			

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M-H)-	C15 H16 N O5 S	6071560	322.07585	322.07547	1.19

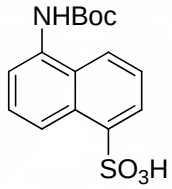


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Figure 51: (-)ESI-HRMS analysis of N-Boc-5-aminonaphthalene-1-sulfonic acid.

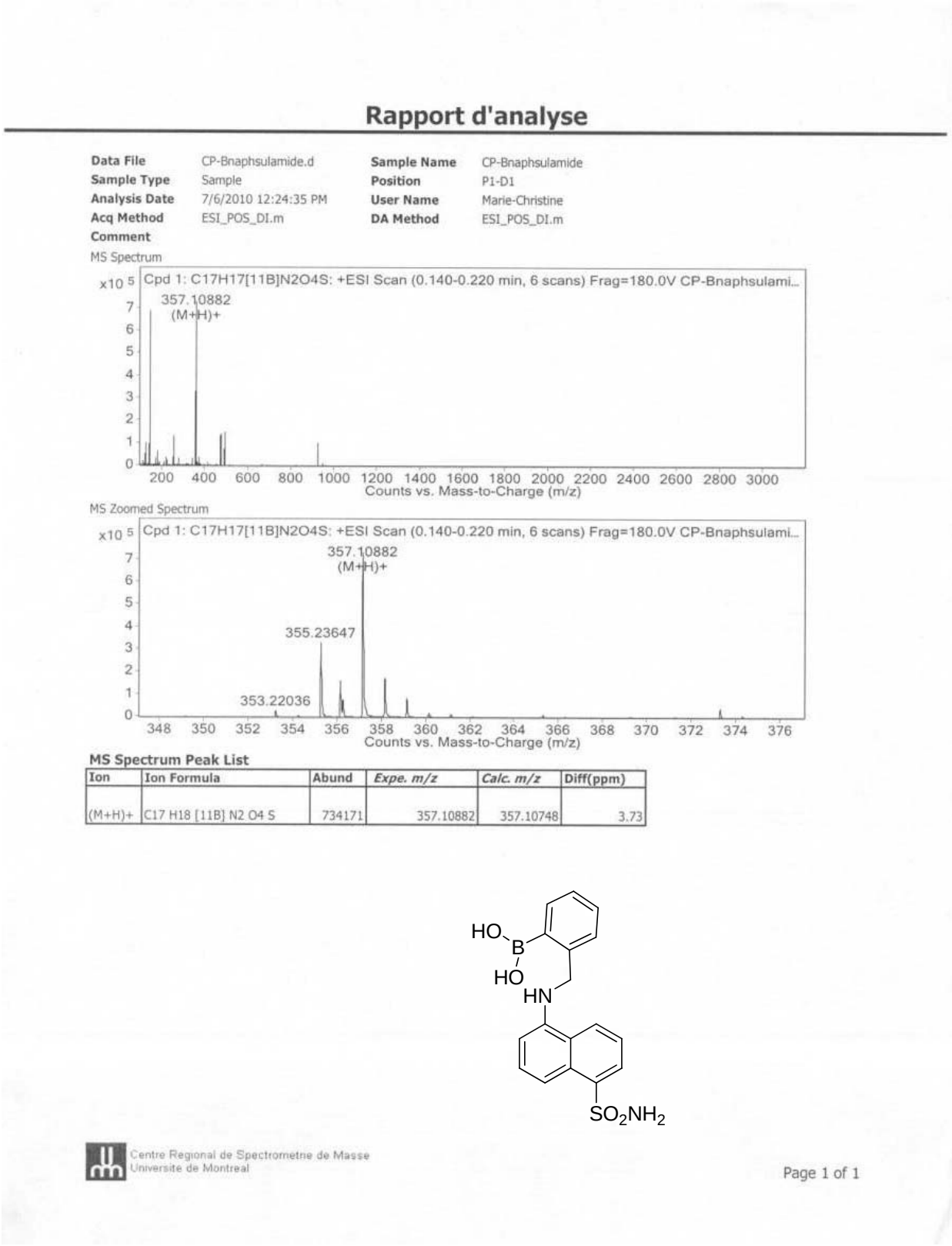


Figure 52: (+)ESI-HRMS of N-phenylborono-5-aminonaphthalene-1-sulfonamide.

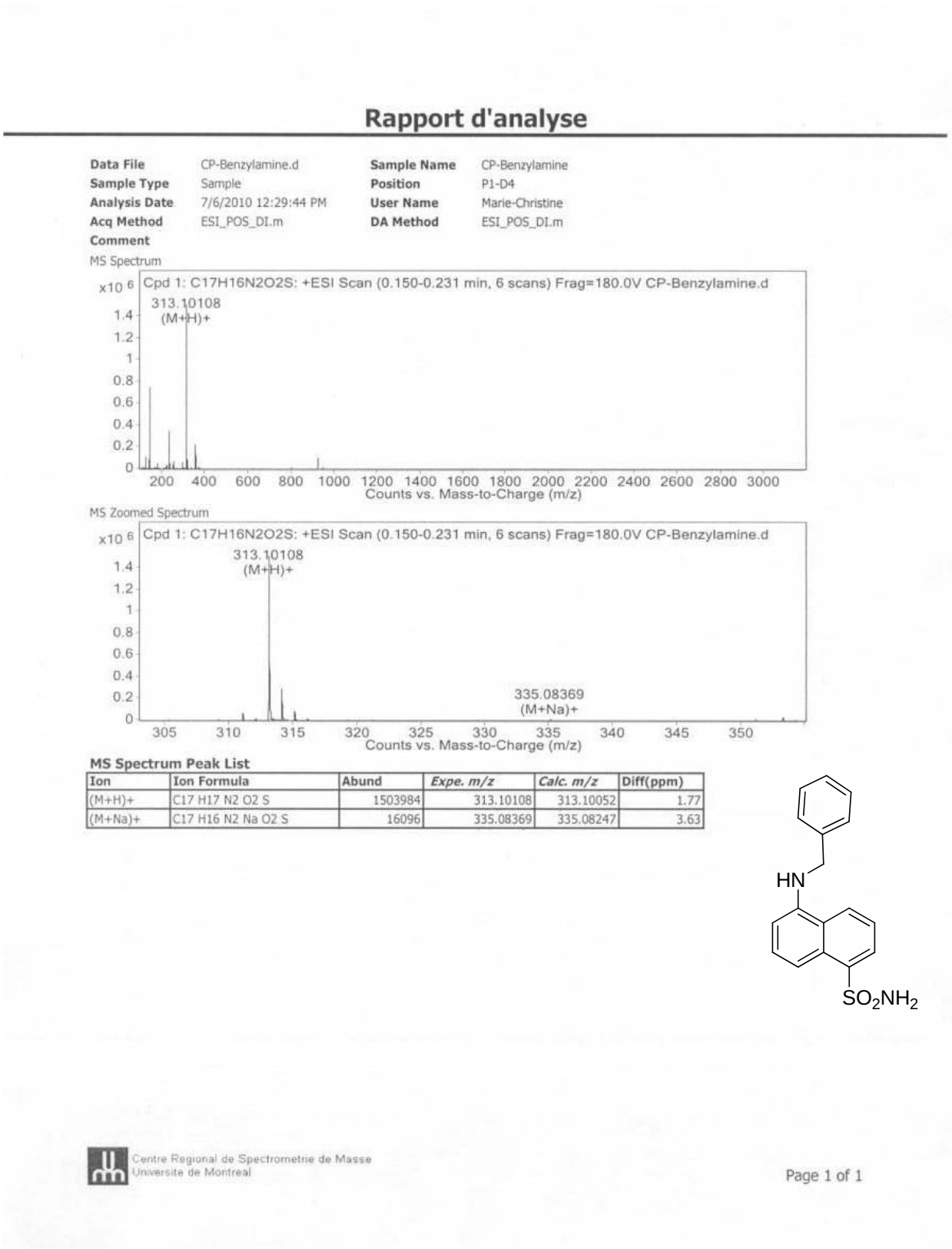


Figure 53: (+)ESI-HRMS of N-benzyl-5-aminonaphthalene-1-sulfonamide.

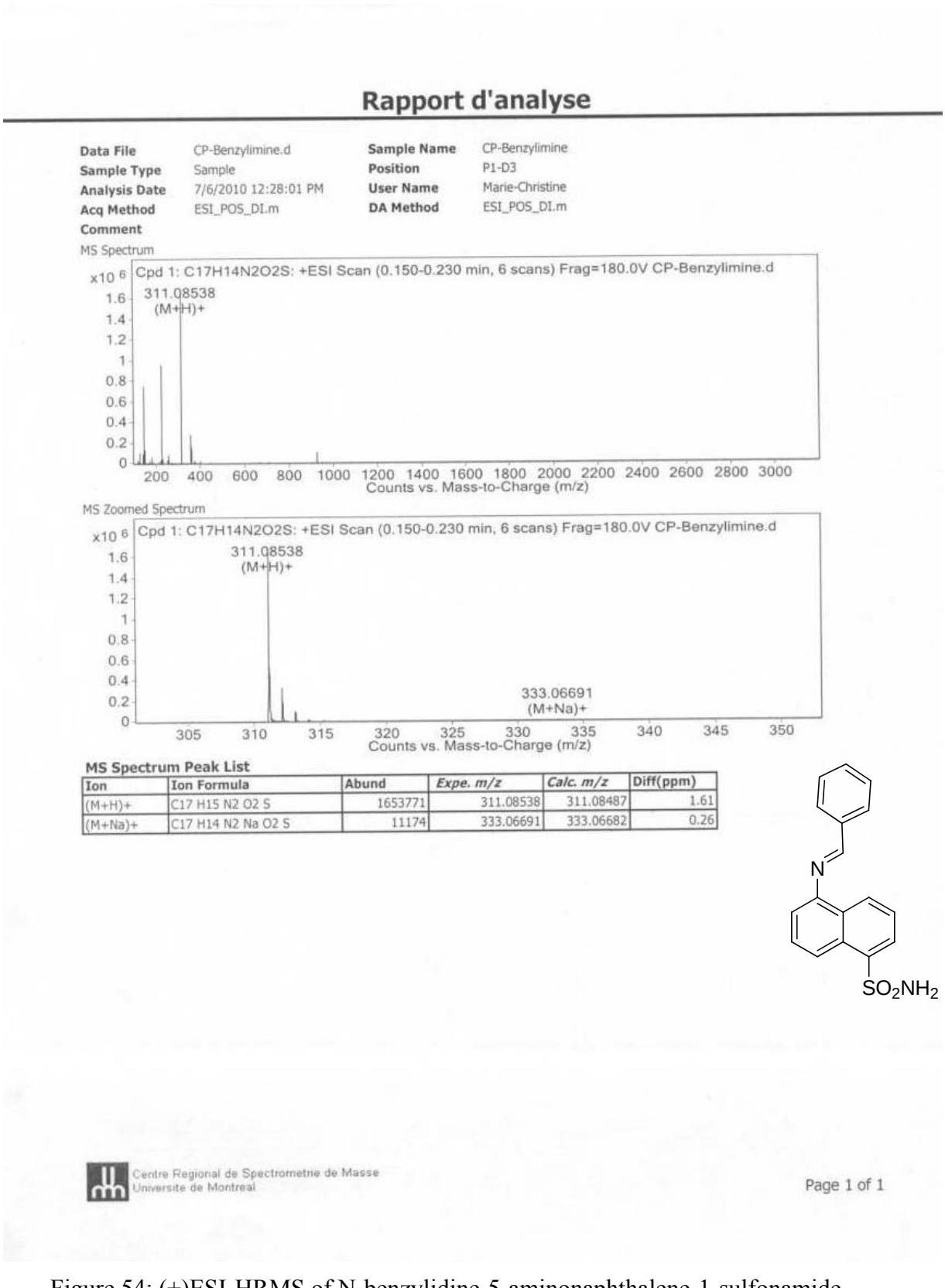
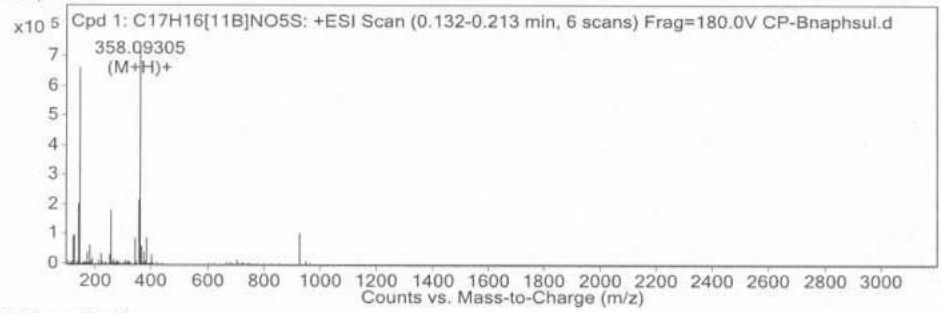


Figure 54: (+)ESI-HRMS of N-benzylidine-5-aminonaphthalene-1-sulfonamide.

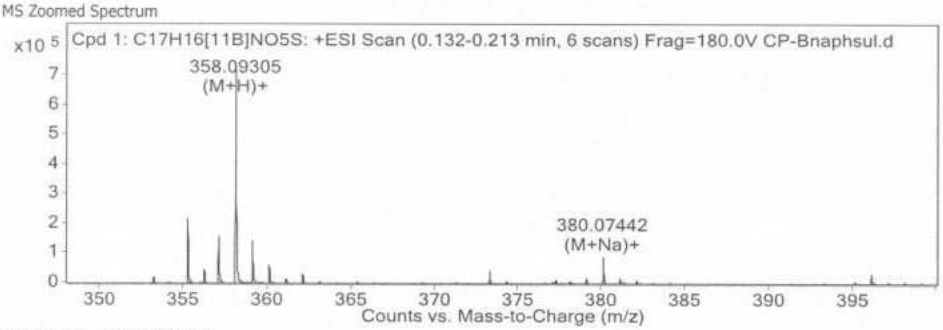
Rapport d'analyse

Data File	CP-Bnaphsul.d	**Sample Name**	CP-Bnaphsul
Sample Type	Sample	**Position**	P1-C9
Analysis Date	7/6/2010 12:22:53 PM	**User Name**	Marie-Christine
Acq Method	ESI_POS_DI.m	**DA Method**	ESI_POS_DI.m
Comment			

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C17 H17 [11B] N O5 S	725398	358.09305	358.0915	4.34
(M+Na)+	C17 H16 [11B] N Na O5 S	88567	380.07442	380.07344	2.57

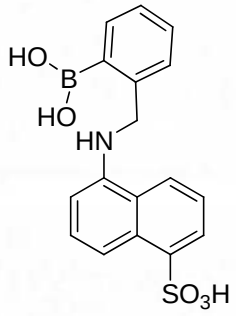


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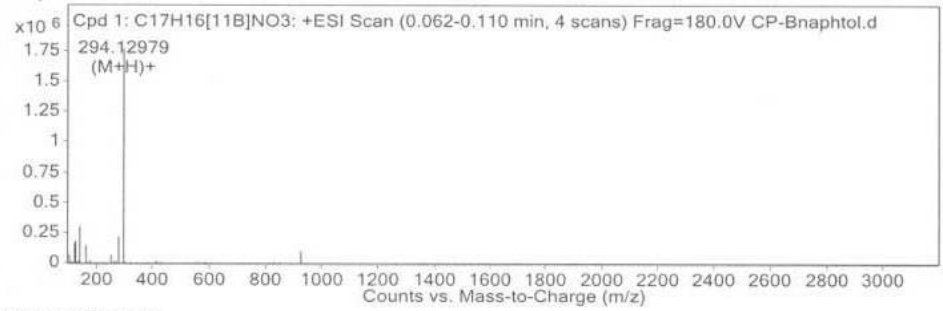
Figure 55: (+)ESI-HRMS of N-phenylborono-5-aminonaphthalene-1-sulfonic acid.

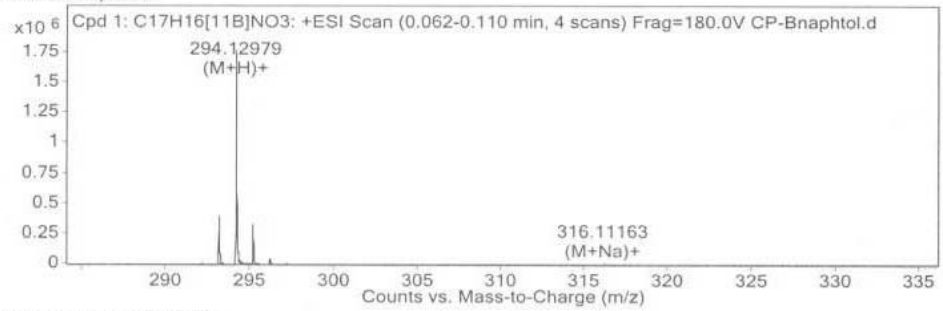
Rapport d'analyse

Data File	CP-Bnaphtol.d	**Sample Name**	CP-Bnaphtol
Sample Type	Sample	**Position**	P1-C5
Analysis Date	5/27/2010 1:44:39 PM	**User Name**	Marie-Christine
Acq Method	ESI_POS_DI.m	**DA Method**	ESI_POS_DI.m
Comment			

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C17 H17 [11B] N O3	1768149	294.12979	294.1296	0.63
(M+Na)+	C17 H16 [11B] N Na O3	13160	316.11163	316.11154	0.27

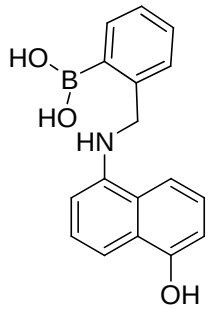


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Figure 56: (+)ESI-HRMS of N-phenylborono-5-amino-1-naphthol.

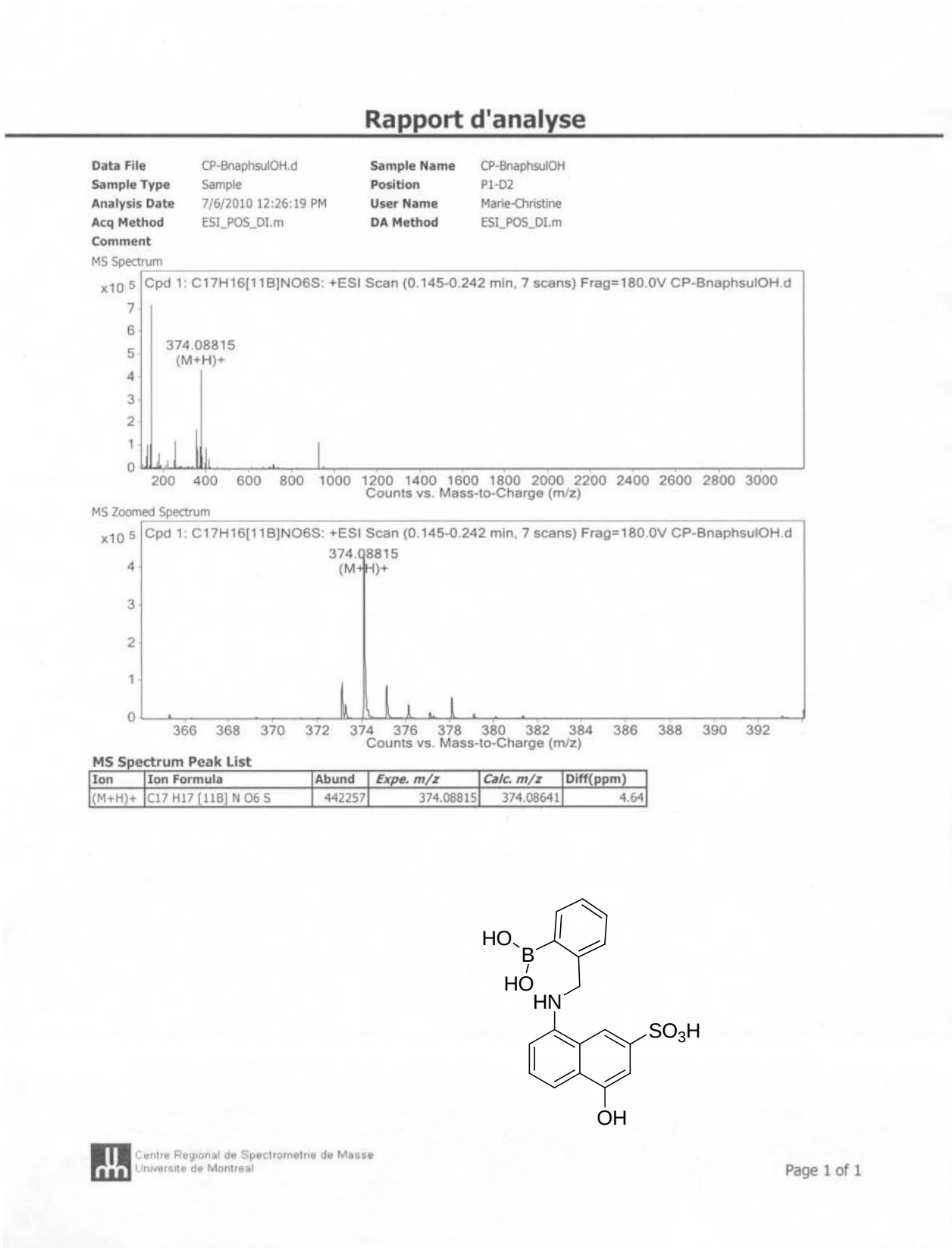
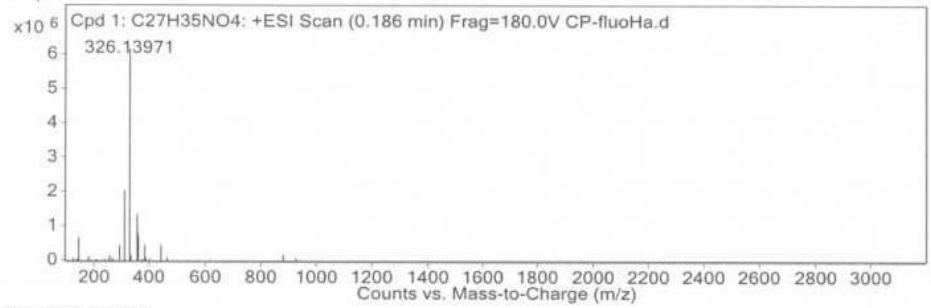


Figure 57: (+)ESI-HRMS of N-phenylborono-5-amino-1-naphthol-3-sulfonic acid.

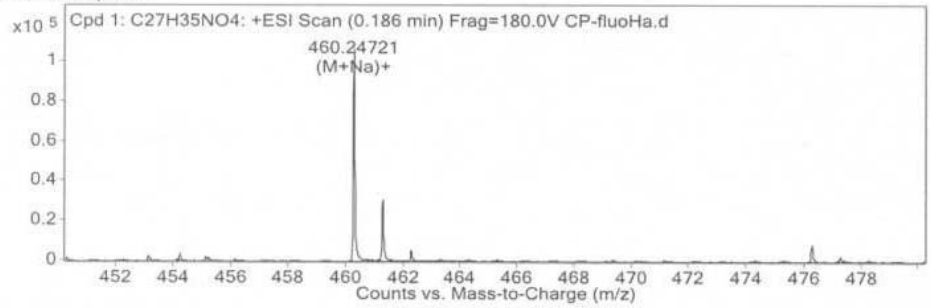
Rapport d'analyse

Data File	CP-fluoHa.d	**Sample Name**	CP-fluoHa
Sample Type	Sample	**Position**	P1-C5
Analysis Date	7/6/2010 12:15:57 PM	**User Name**	Marie-Christine
Acq Method	ESI_POS_DI.m	**DA Method**	ESI_POS_DI.m
Comment			

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+Na)+	C27 H35 N Na O4	107045	460.24721	460.24583	3

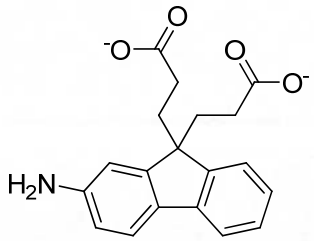


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Figure 58: (+)ESI-HRMS of FluoHa.

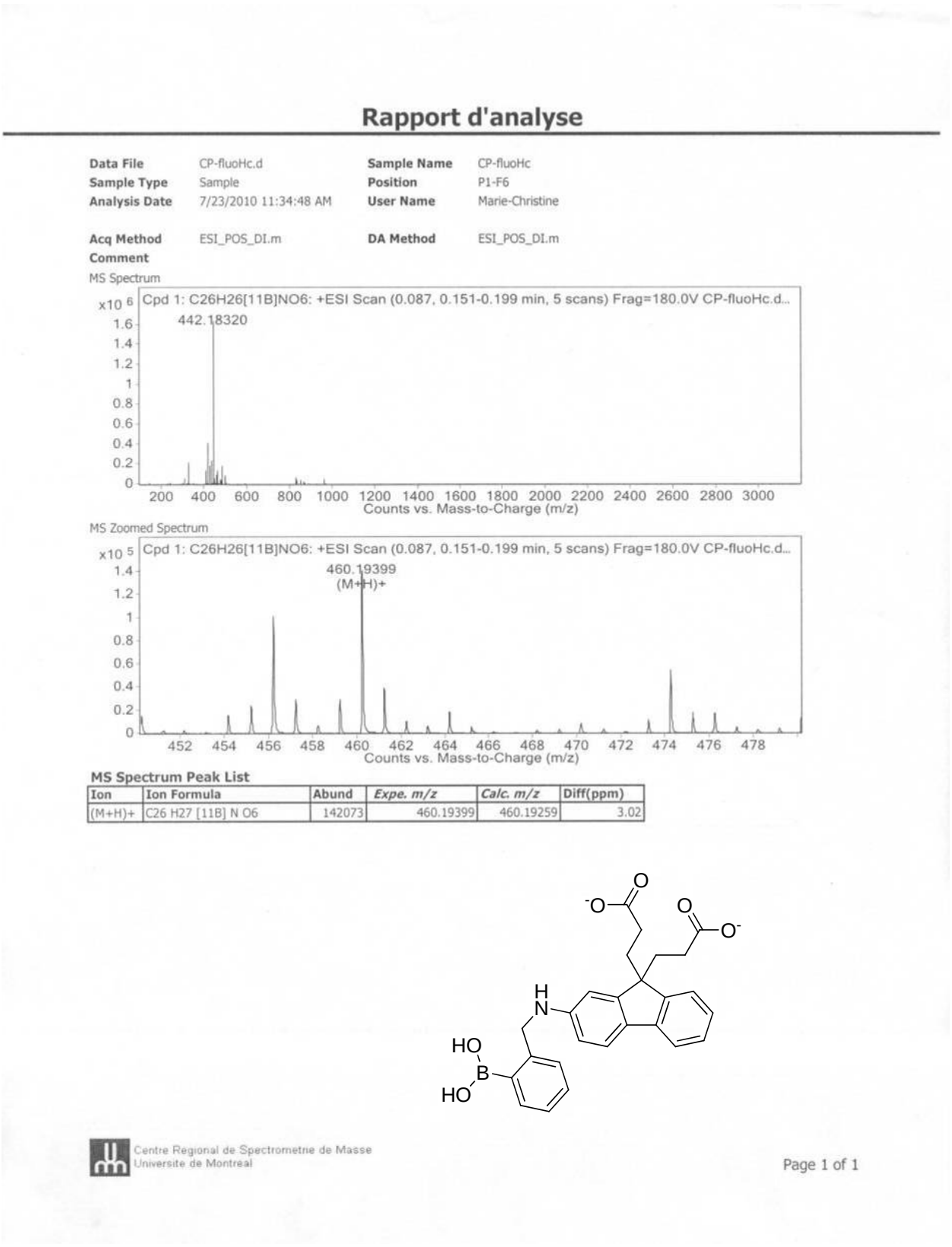
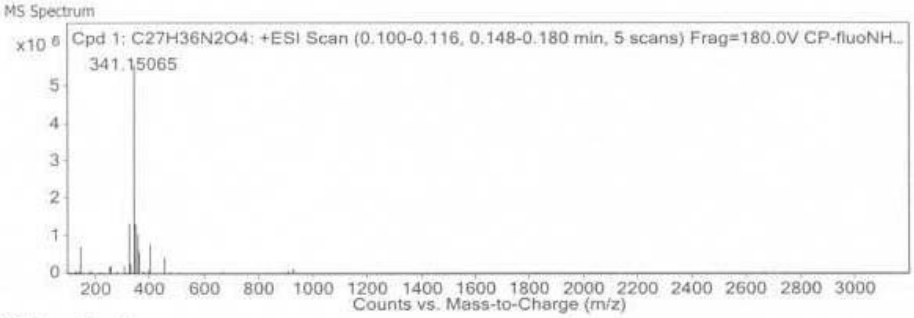


Figure 59: (+)ESI-HRMS of FluoHc.

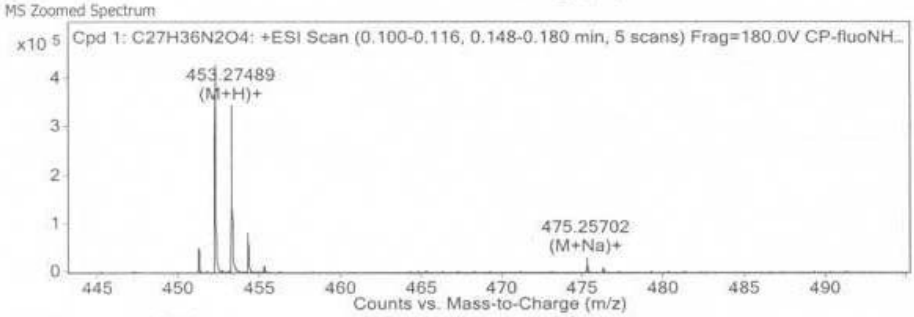
Rapport d'analyse

Data File	CP-fluoNH2a.d	**Sample Name**	CP-fluoNH2a
Sample Type	Sample	**Position**	P1-C6
Analysis Date	7/6/2010 12:17:41 PM	**User Name**	Marie-Christine
Acq Method	ESI_POS_DI.m	**DA Method**	ESI_POS_DI.m
Comment			

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
(M+H)+	C27 H37 N2 O4	350549	453.27489	453.27478	0.24
(M+Na)+	C27 H36 N2 Na O4	29882	475.25702	475.25673	0.62

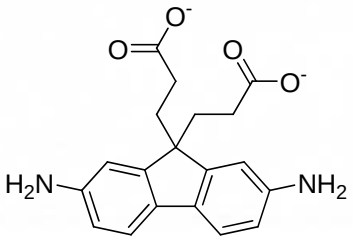


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Figure 60: (+)ESI-HRMS of FluoNH2a.

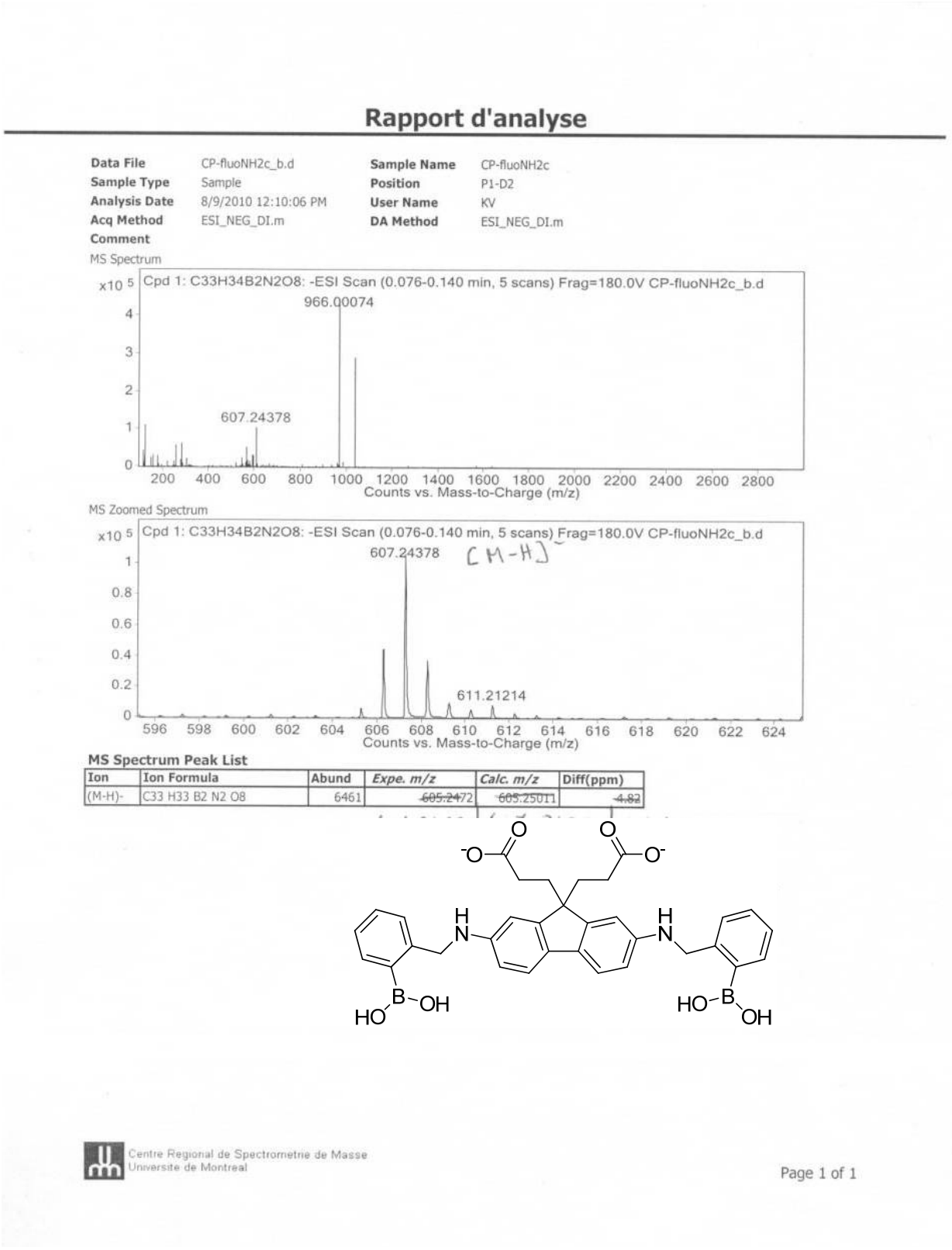

Figure 61: (-)ESI-HRMS of FluoHc.

.

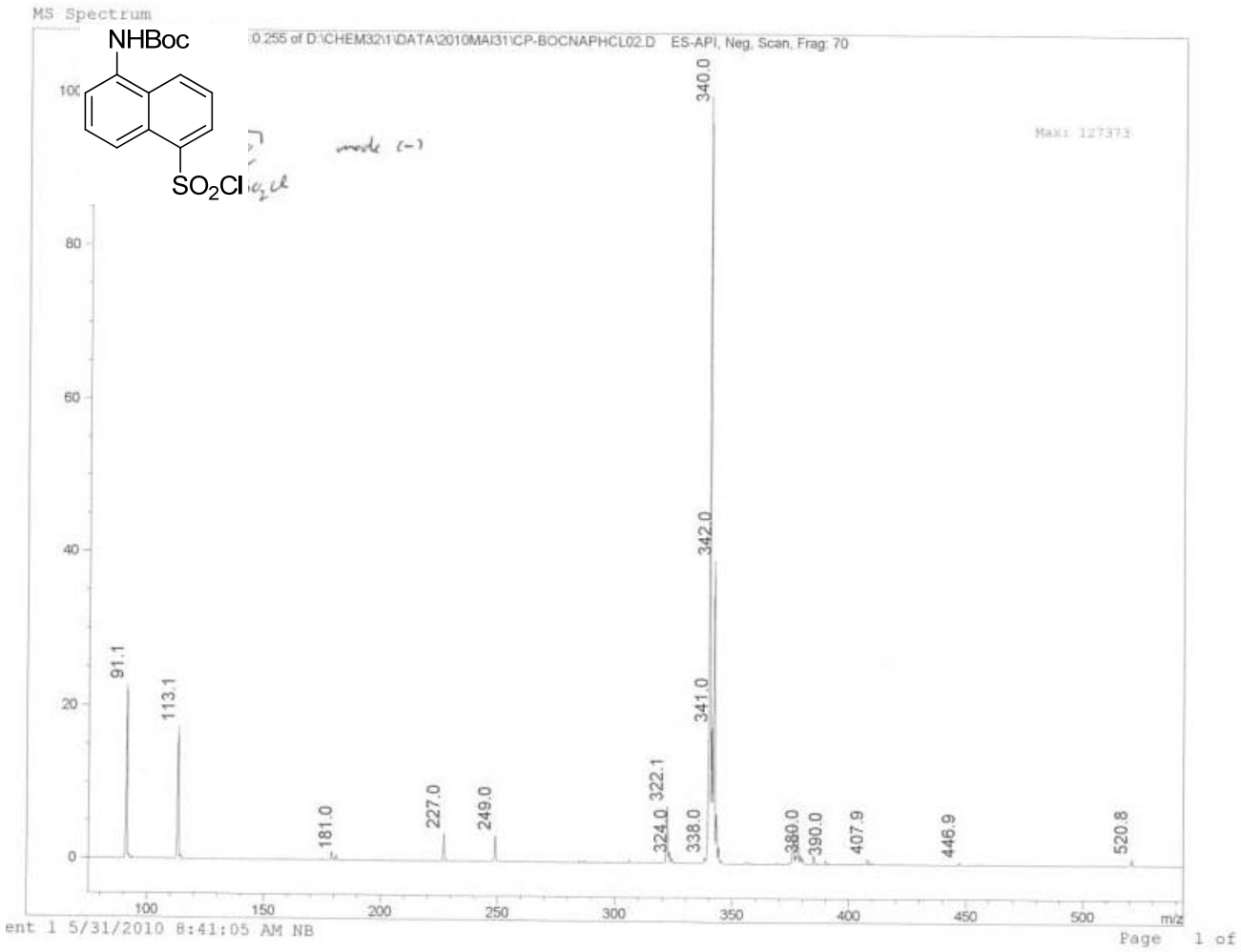

Figure 62: (-)ESI-MS N-Boc-5-aminonaphthalene-1-sulfonyl chloride.

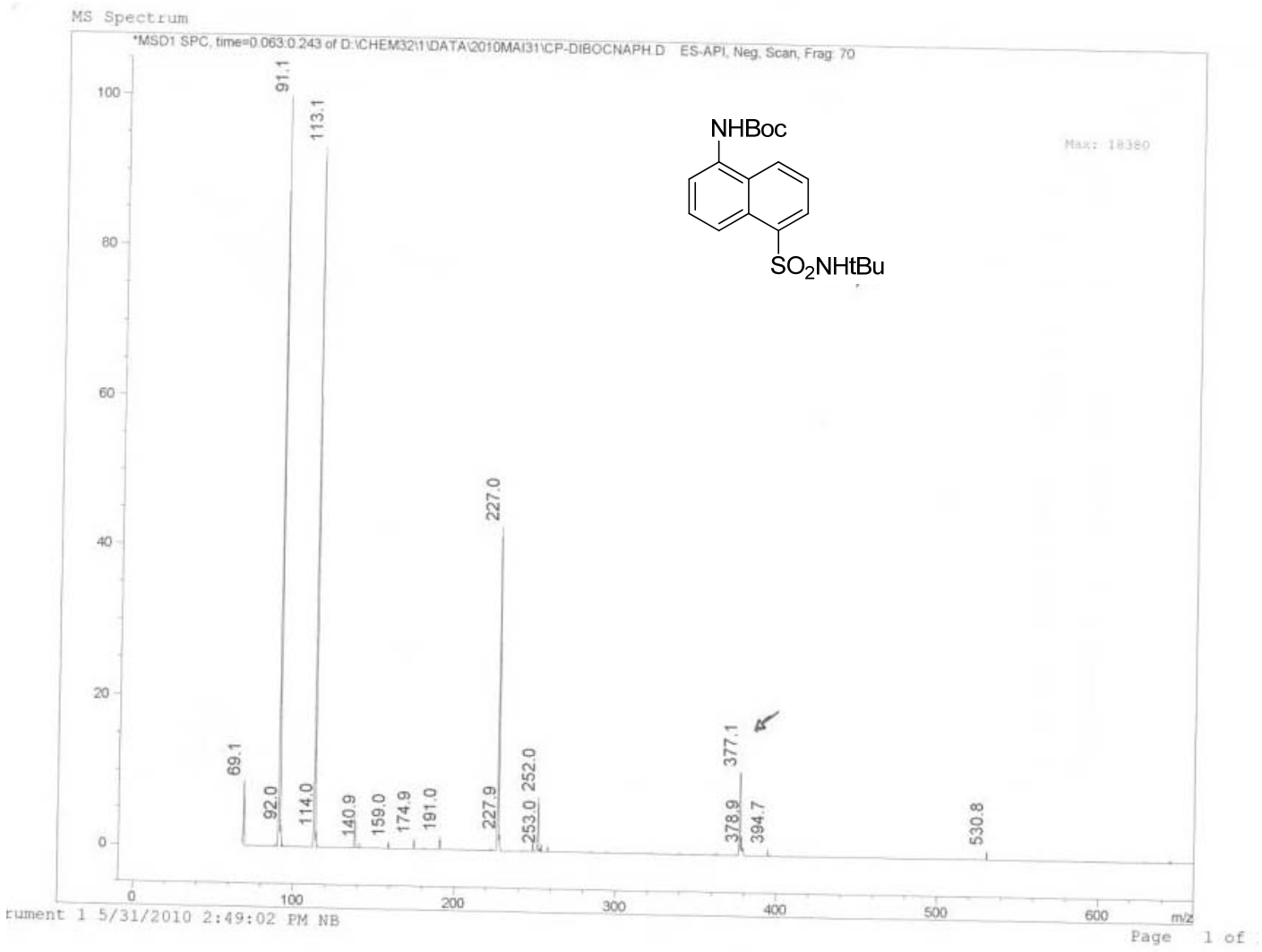

Figure 63: (-)ESI-MS of N-Boc-5-aminonaphthalene-1-*tert*-butylsulfonamide.

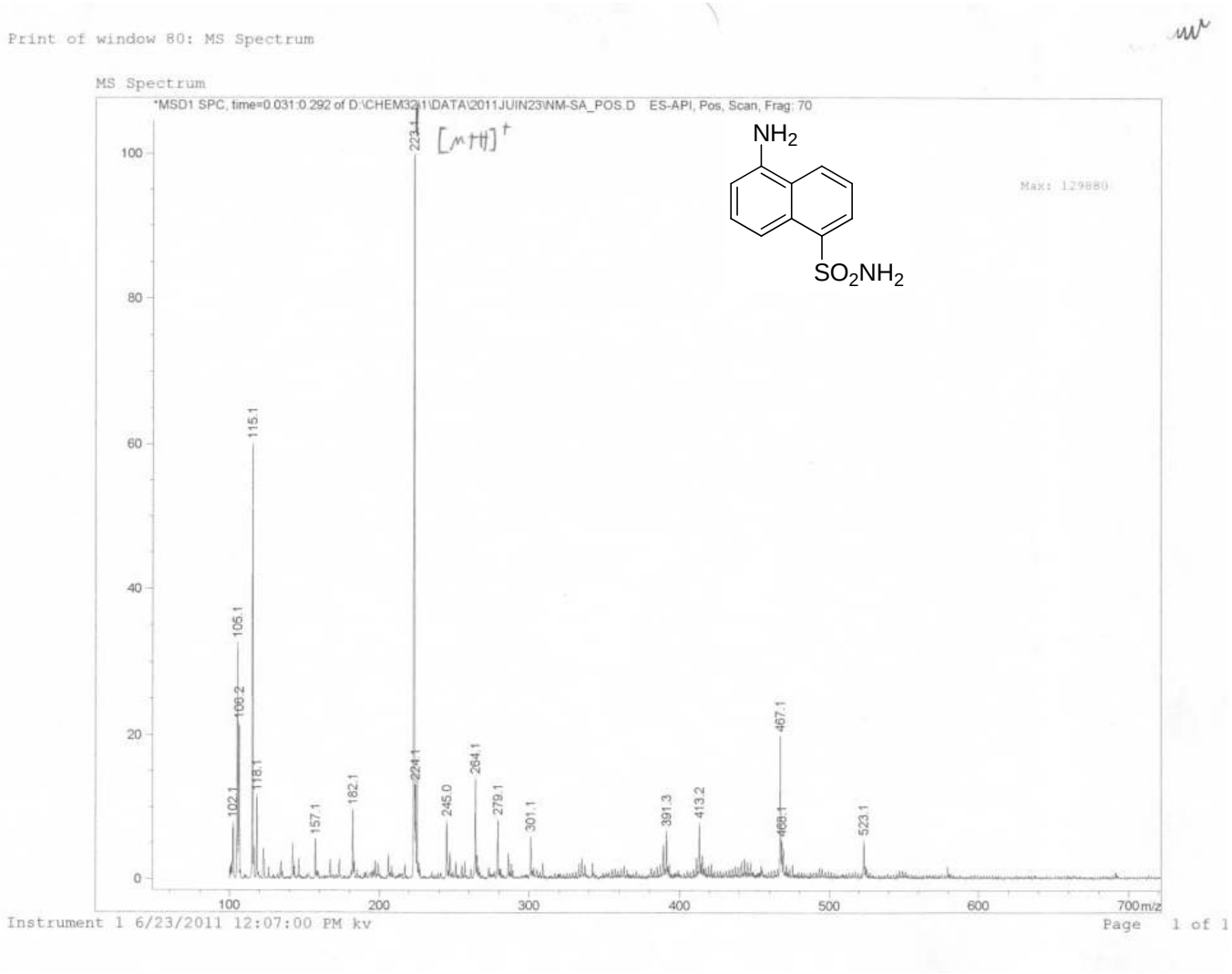

Figure 64: (-)ESI-MS of 5-aminonaphthalene-1-sulfonamide.

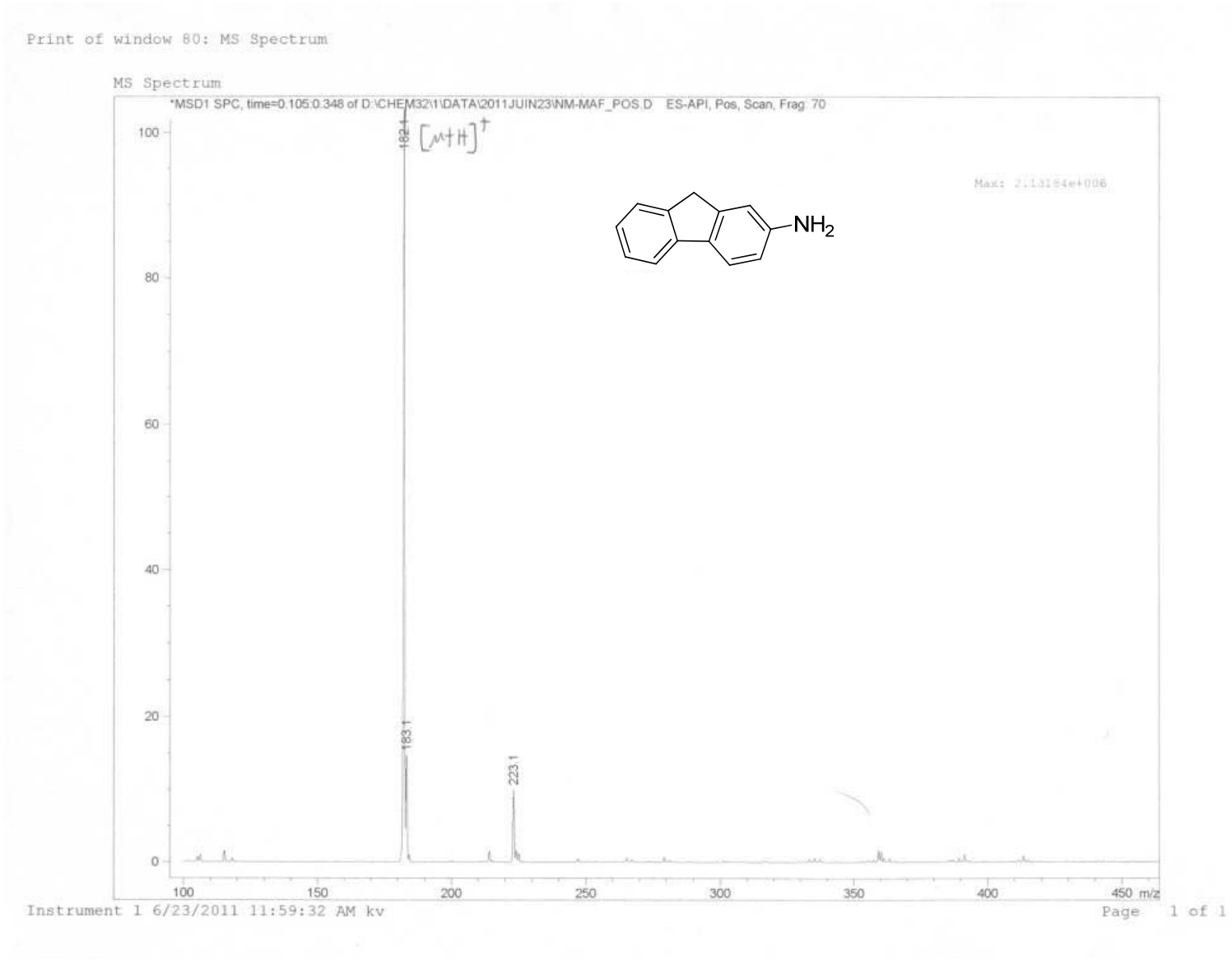

Figure 65: (+)ESI-MS of monoaminofluorene.

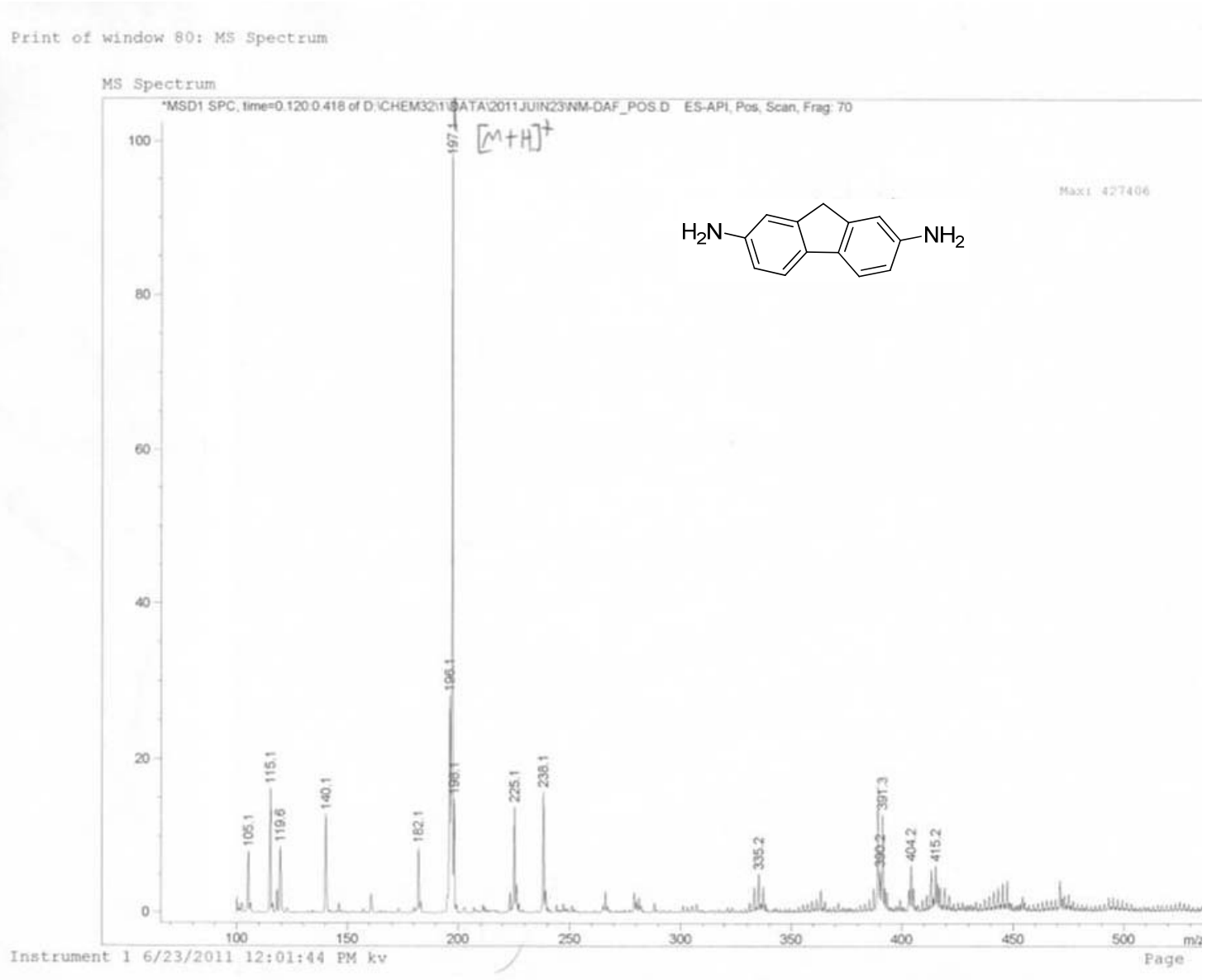

Figure 66: (+)ESI-MS of diaminofluorene.

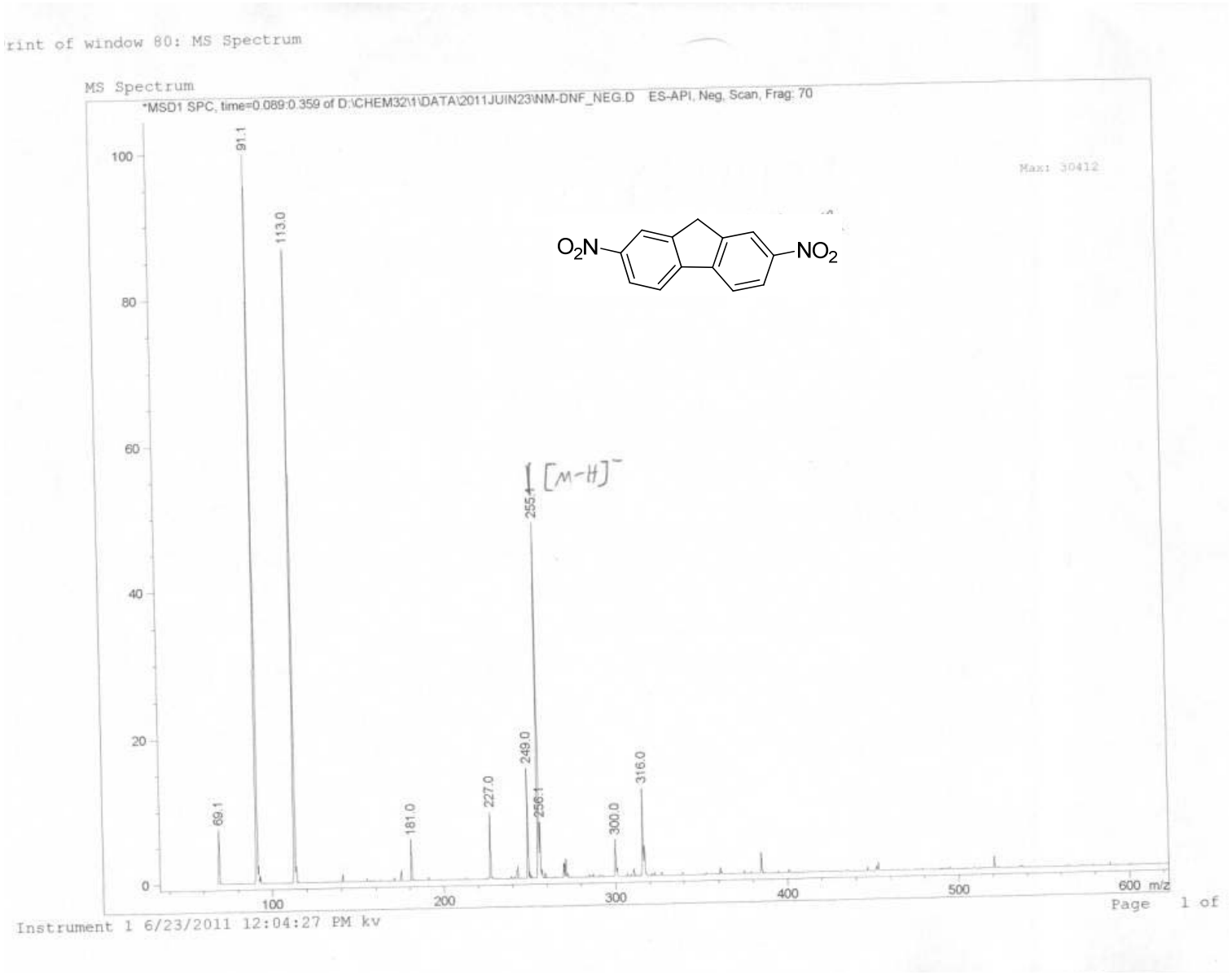

Figure 67: (-)ESI-MS of dinitrofluorene.