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Supplementary Information for

Steric Effects on Acetate-Assisted Cyclometallation of N-phenyl and N-benzyl imidazolium salts at $[MCl_2Cp^*]_2$

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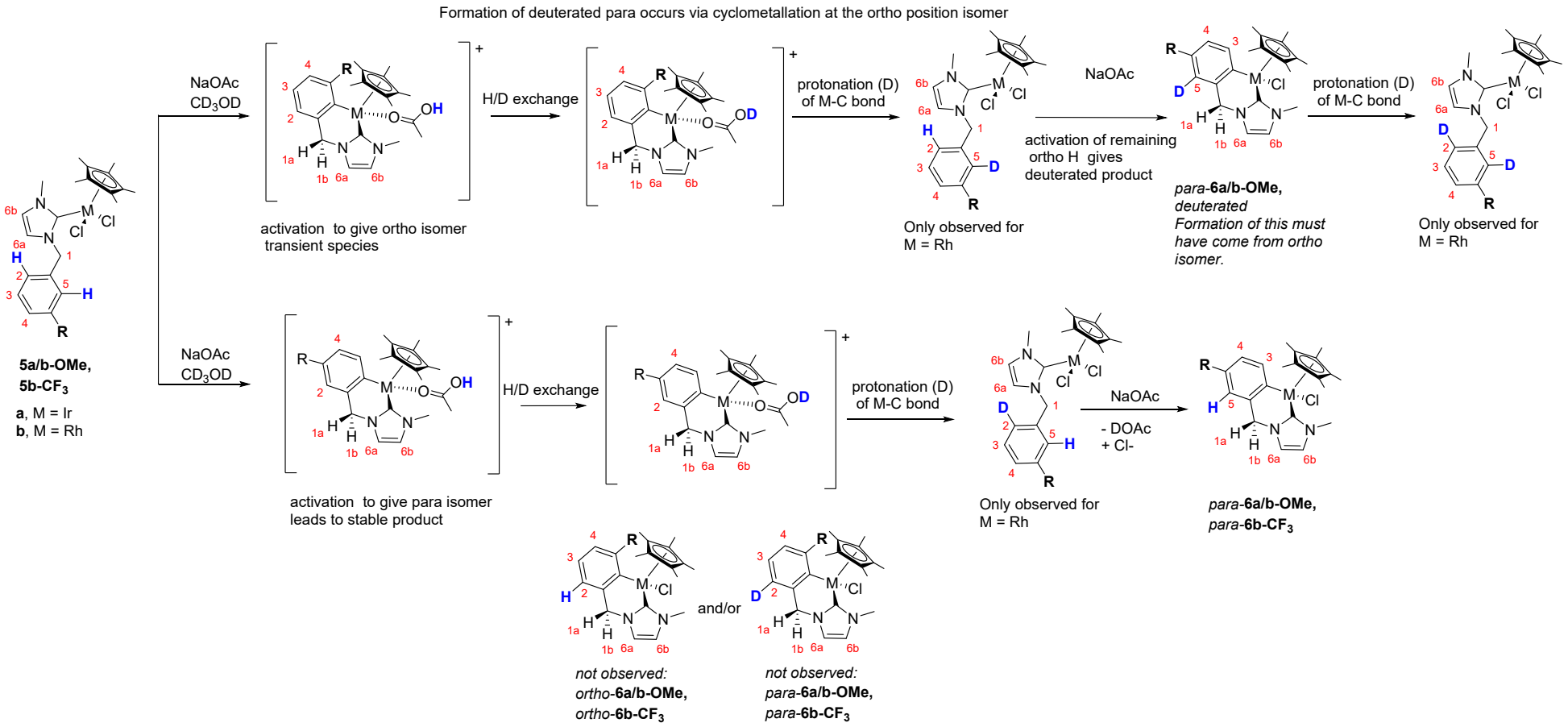
Expanded version of Scheme 5 showing detailed mechanism for deuterium incorporation. Page 2

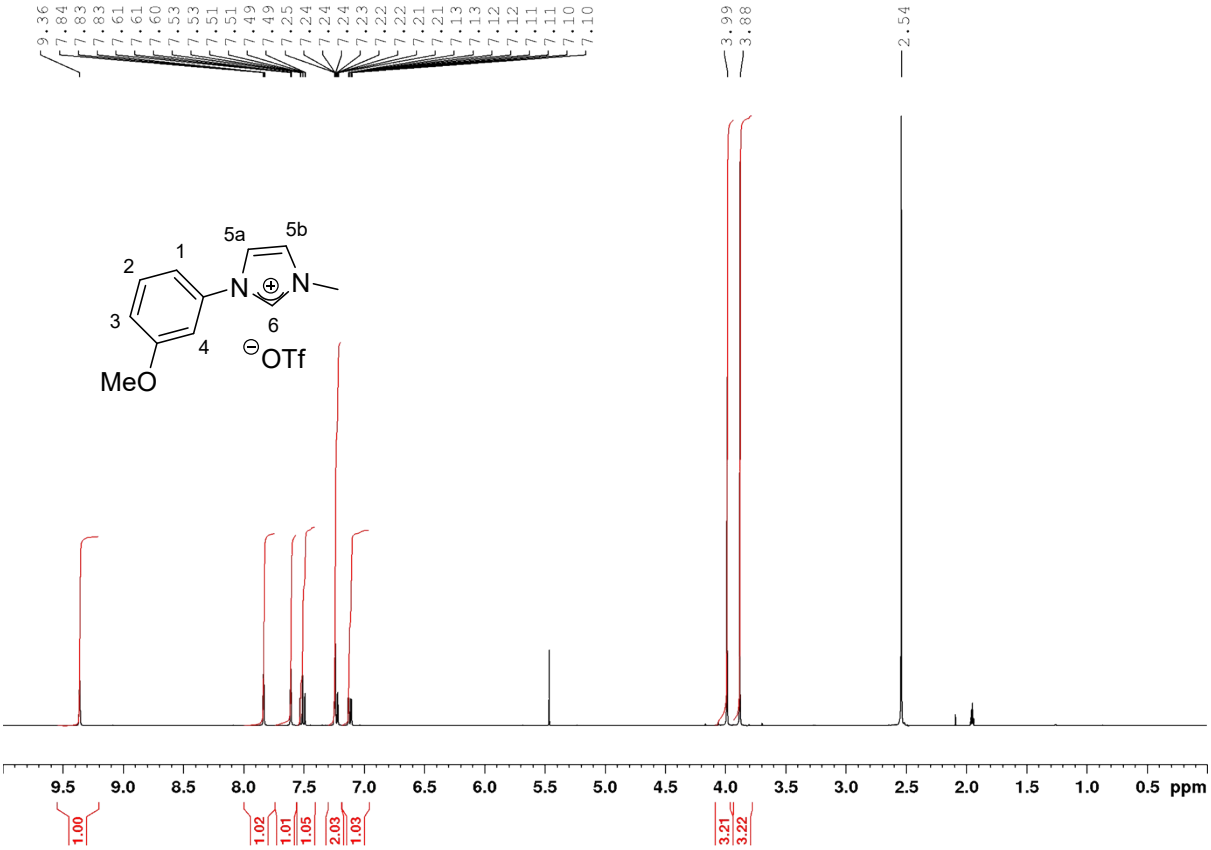
NMR spectra for all new compounds Page 3-82

Deuteration experiments Page 83-84

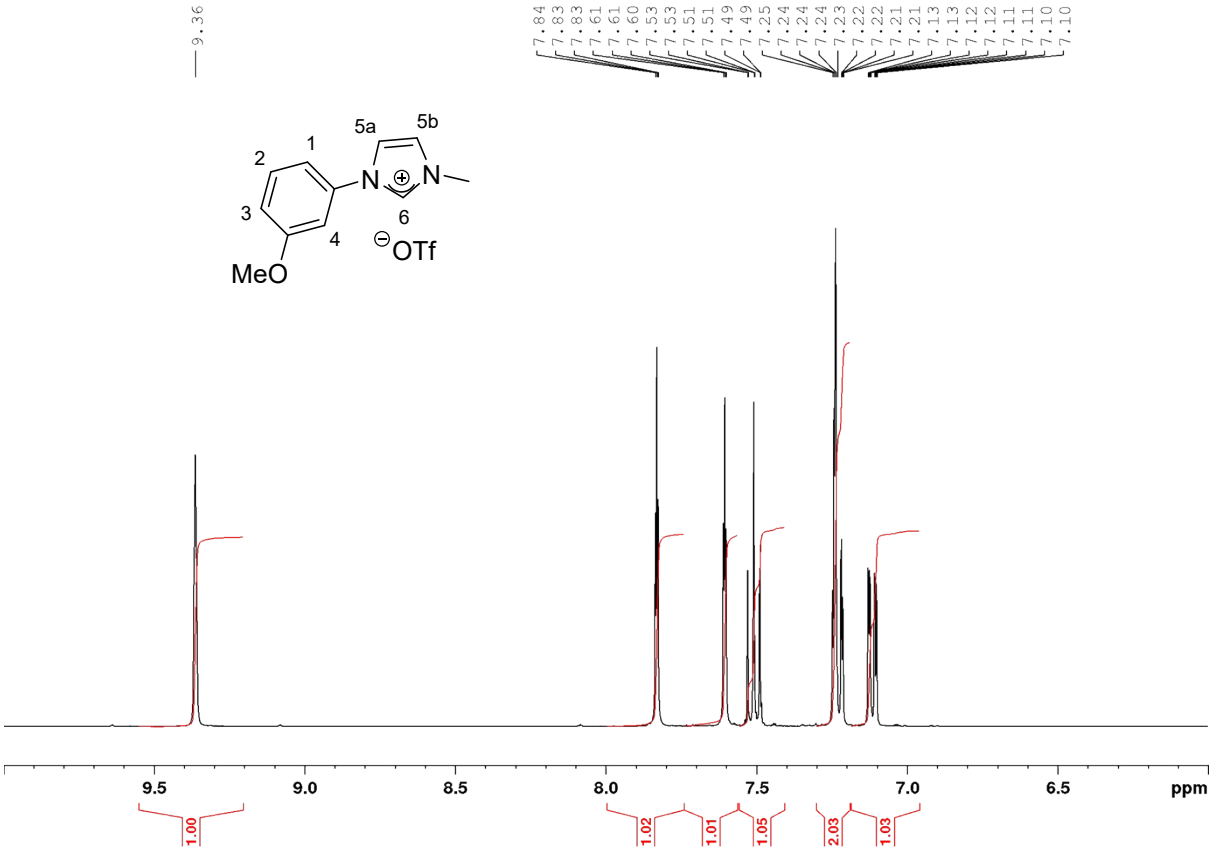
Expanded version of Scheme 5 showing detailed mechanism for deuterium incorporation



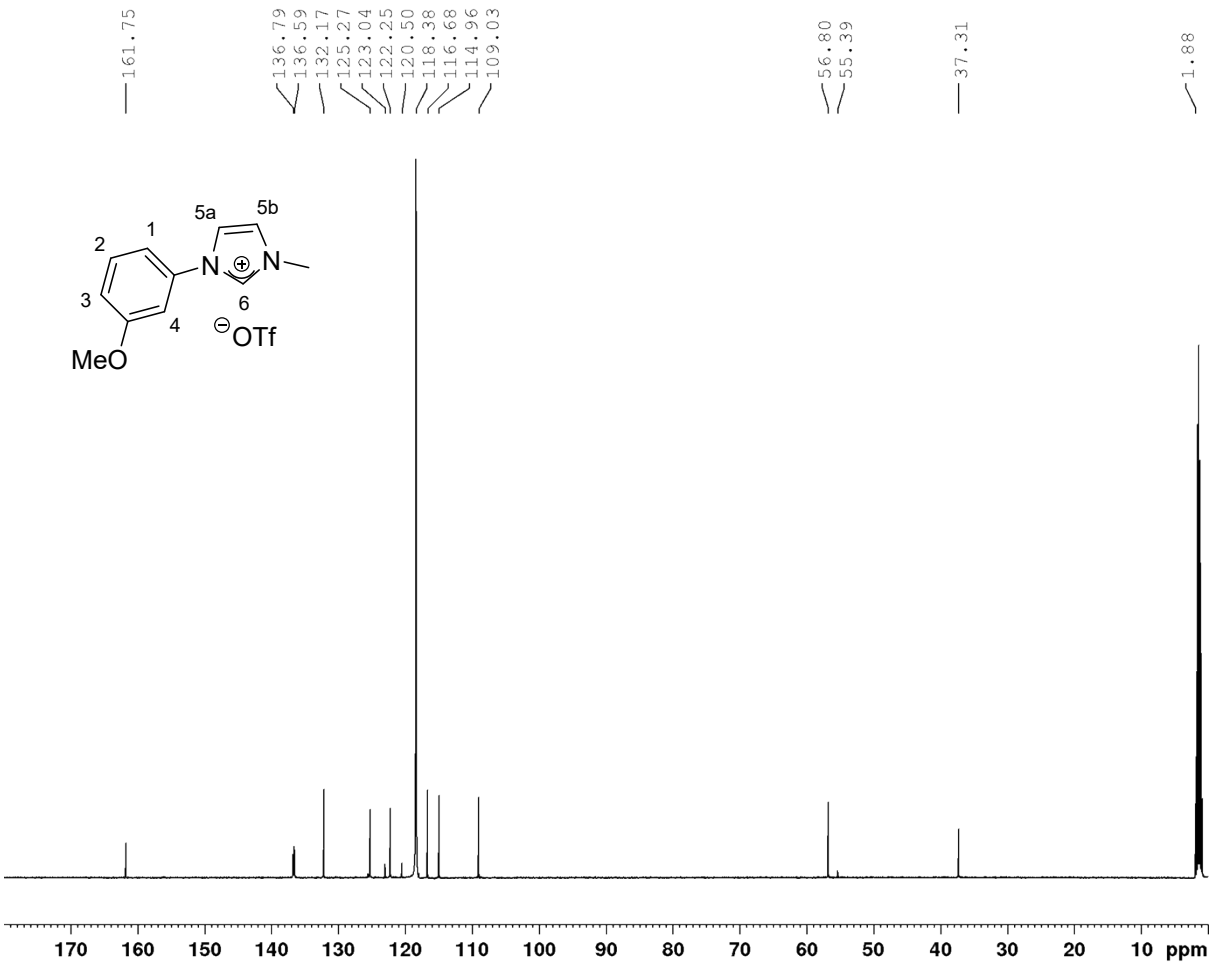
^{1}H NMR of **L4-OMe** in CD_3CN



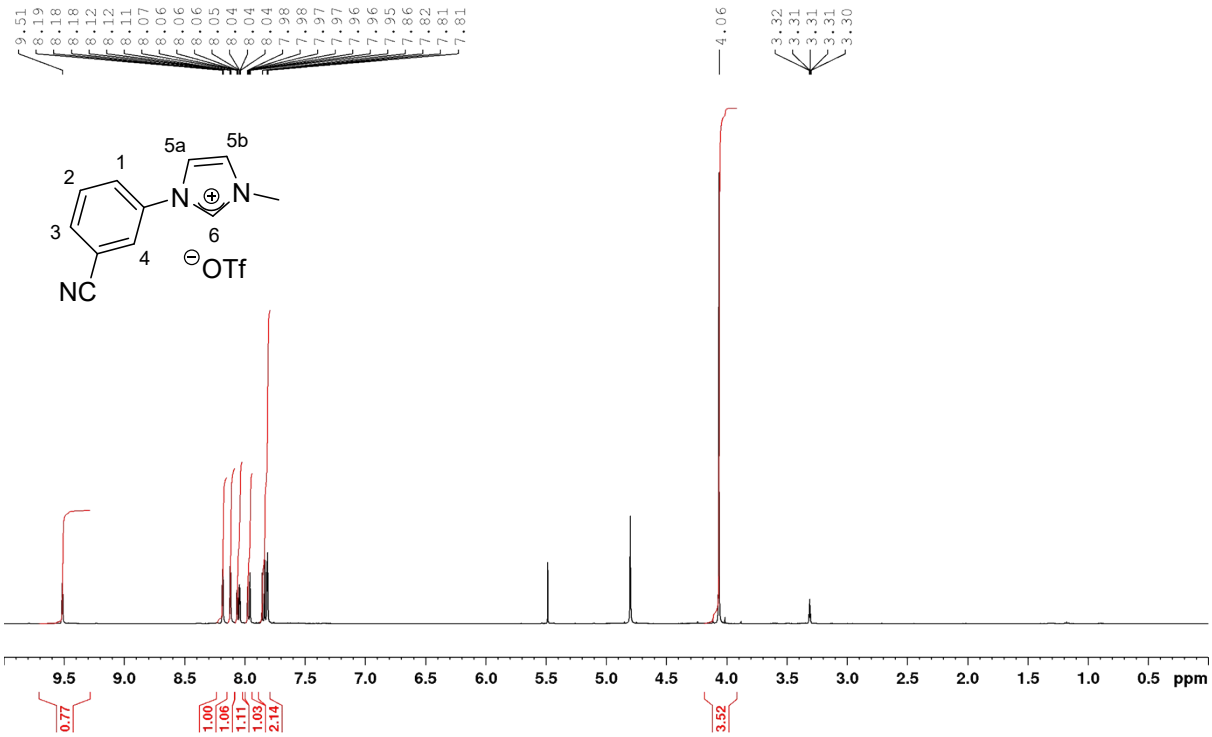
Expansion of ^{1}H NMR of **L4-OMe** in CD_3CN



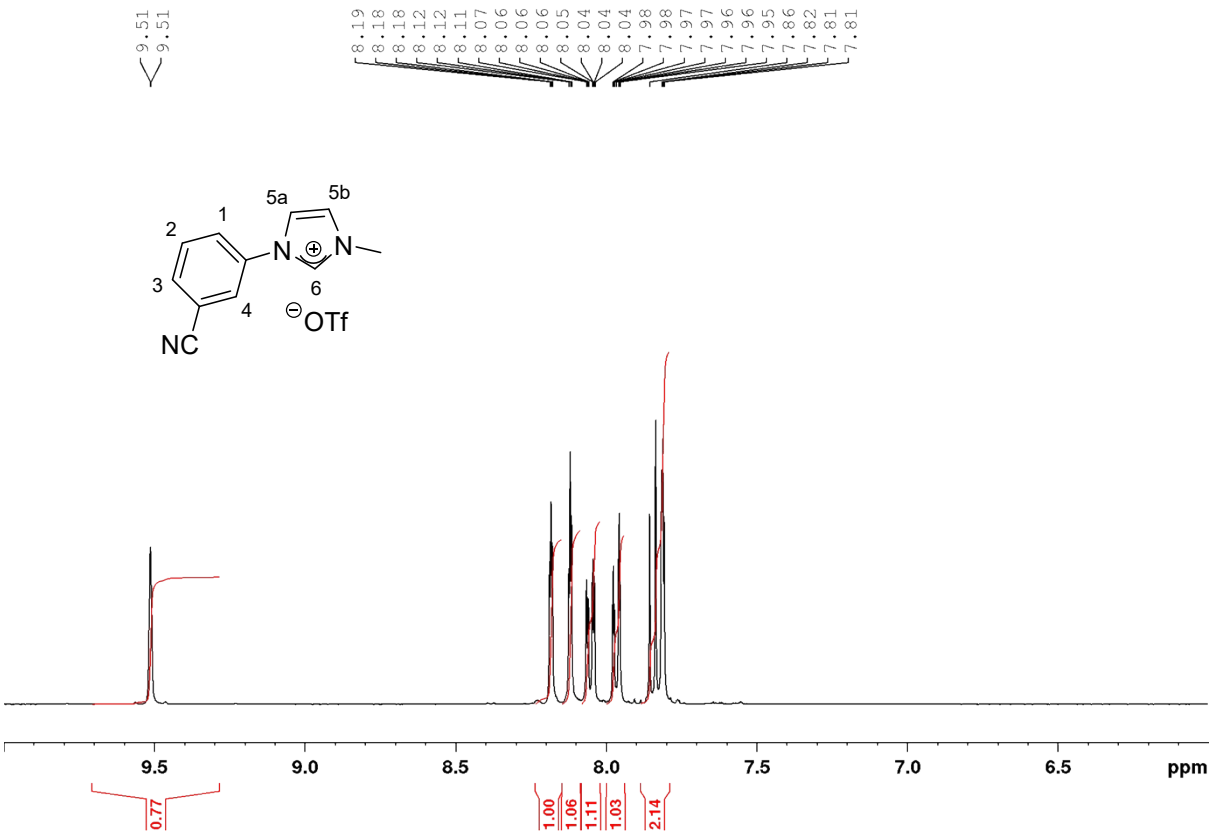
^{13}C NMR of **L4-OMe** in CD_3CN



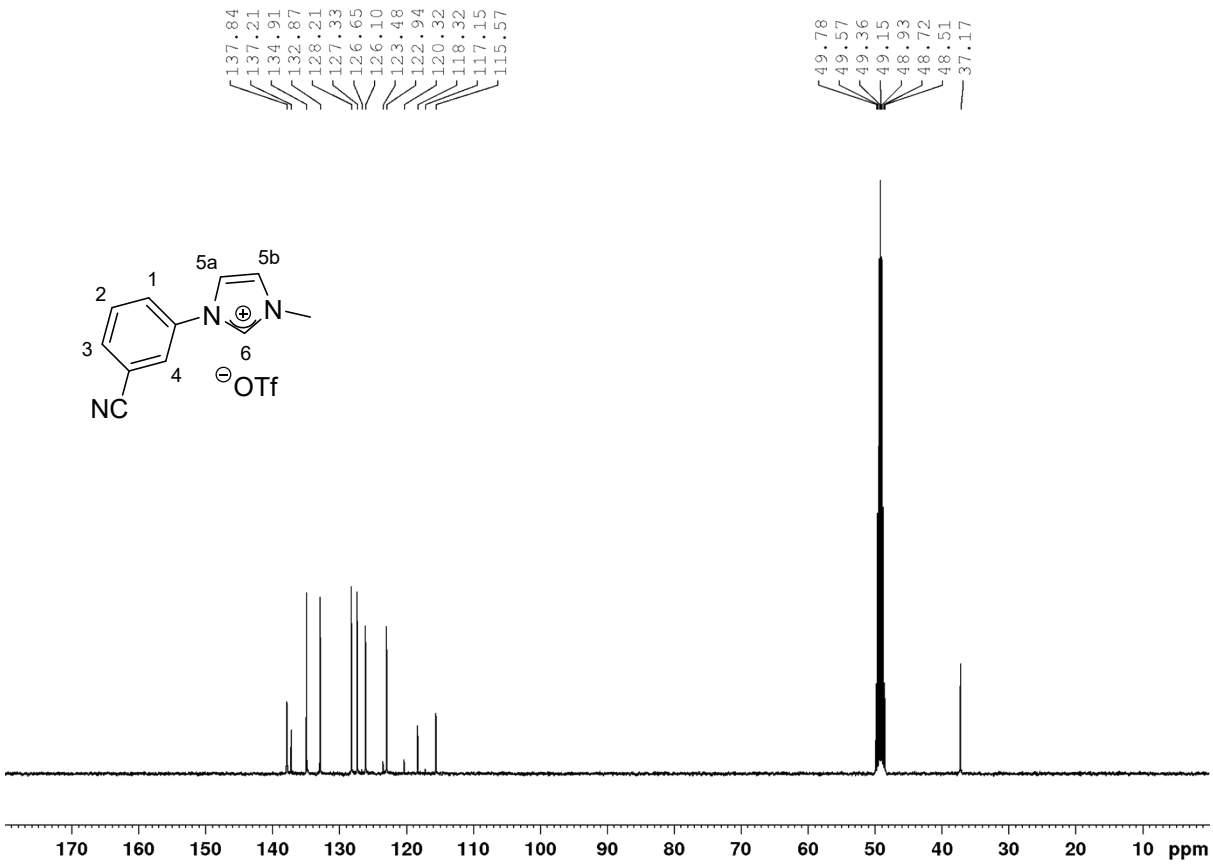
^{1}H NMR of **L4-CN** in CD_3OD – Integration of H6 is low due to H/D exchange with CD_3OD



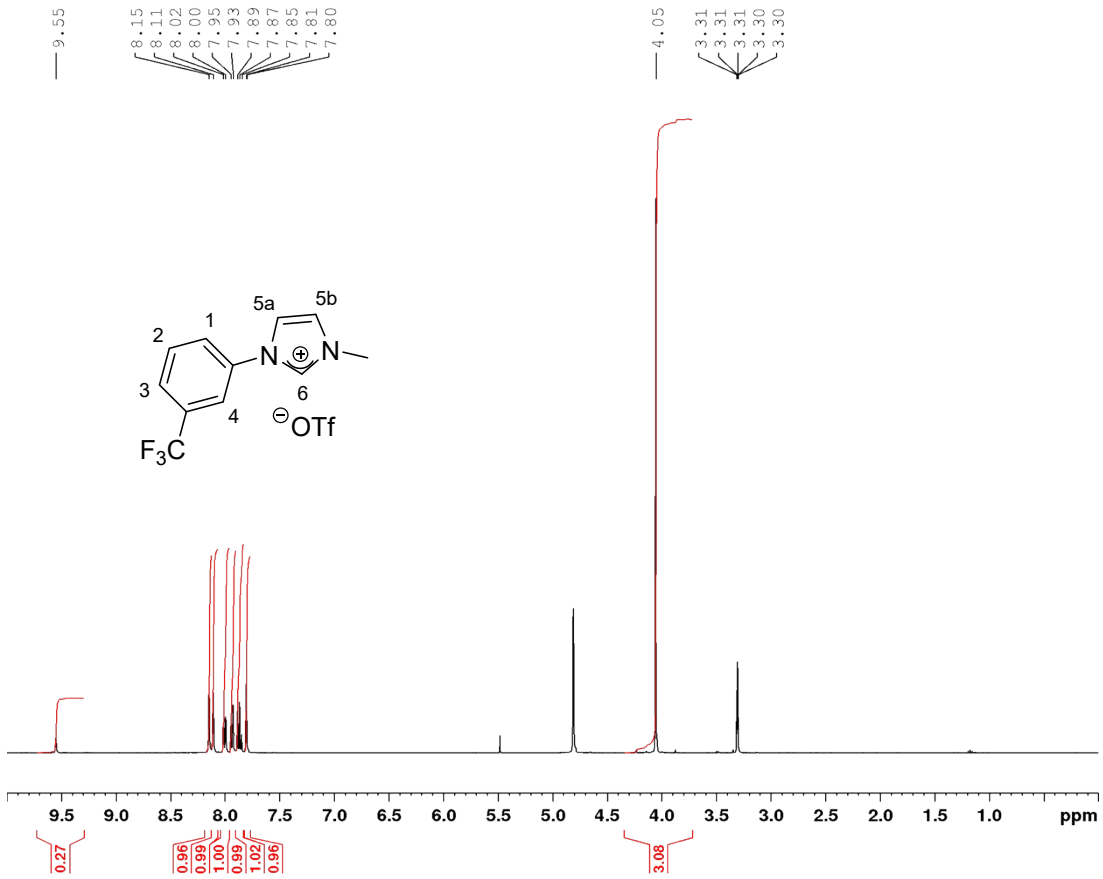
Expansion of ^{1}H NMR of **L4-CN** in CD_3OD



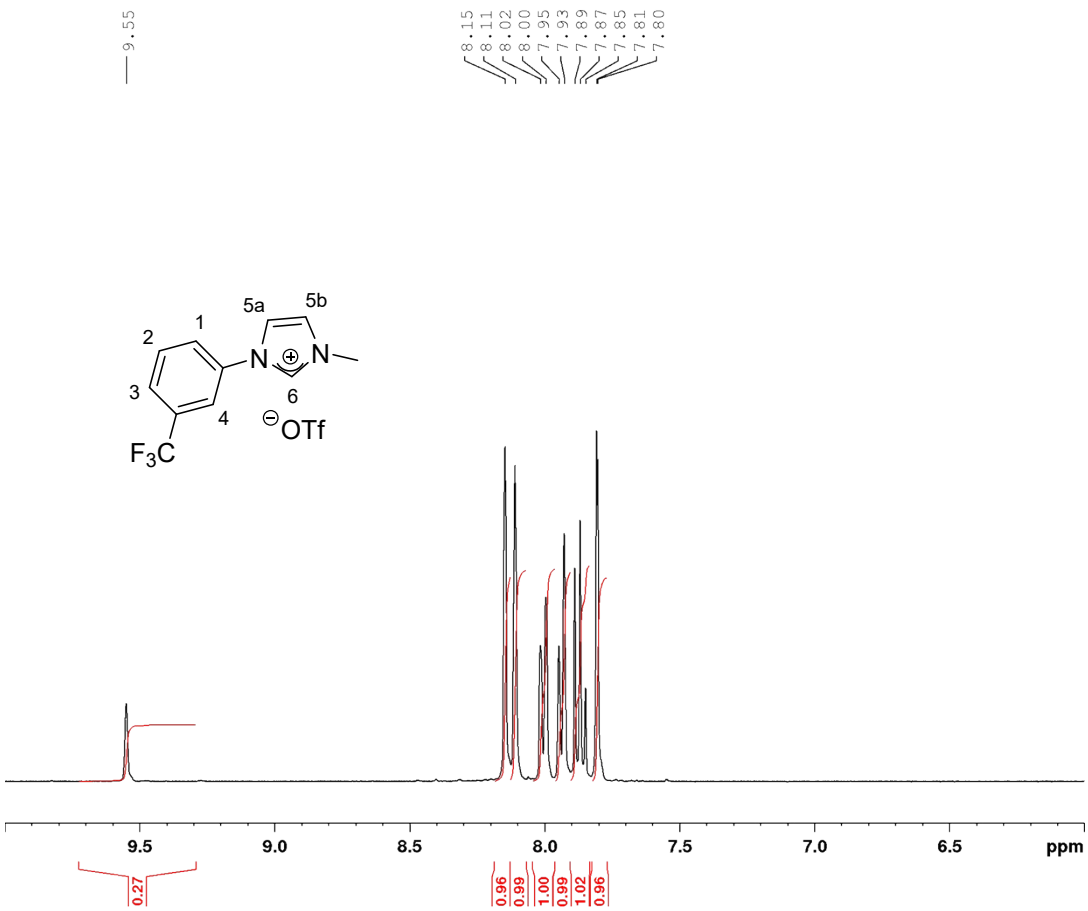
^{13}C NMR of **L4-CN** in CD_3OD



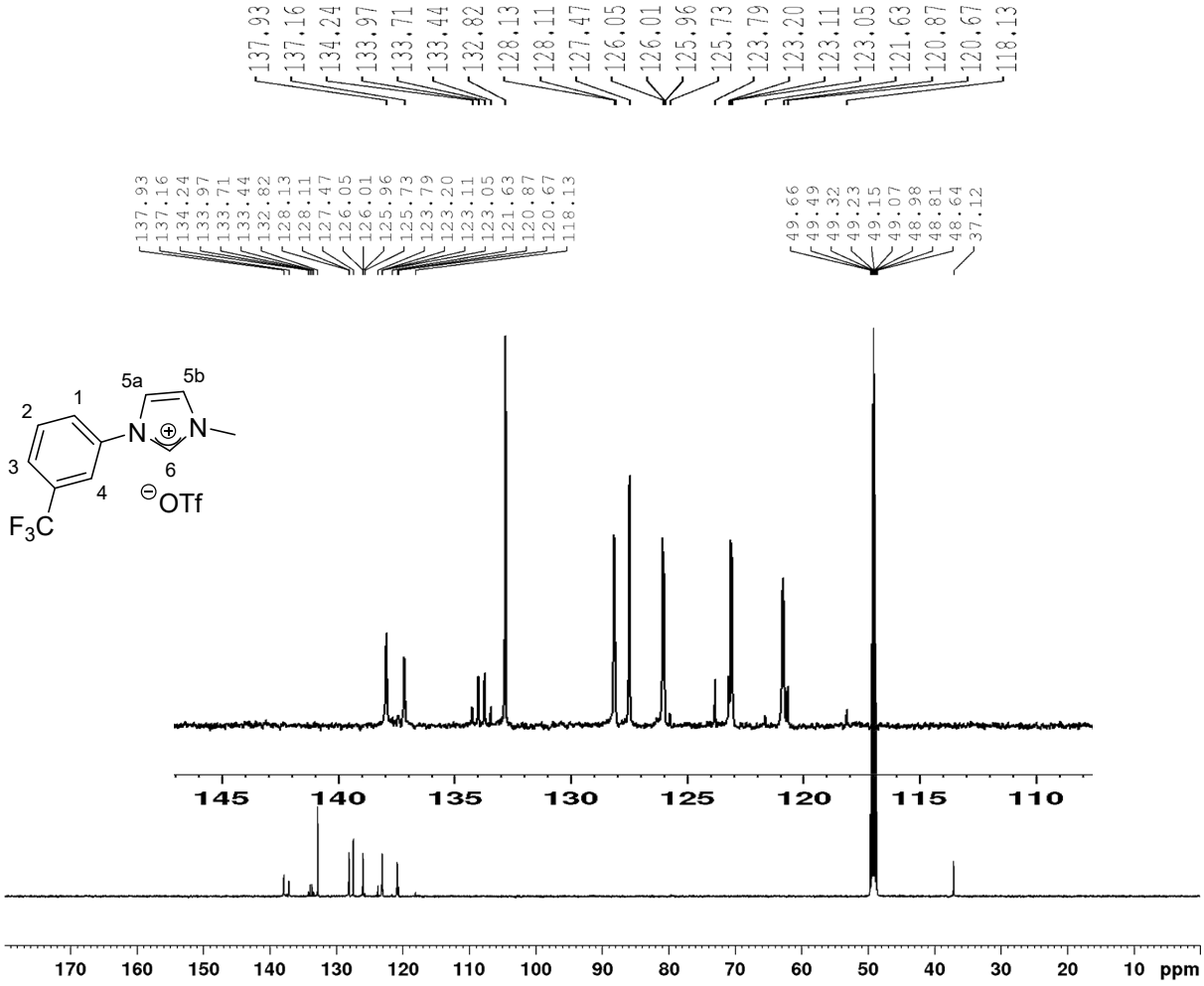
^{1}H NMR of **L4-CF$_3$** in CD_3OD



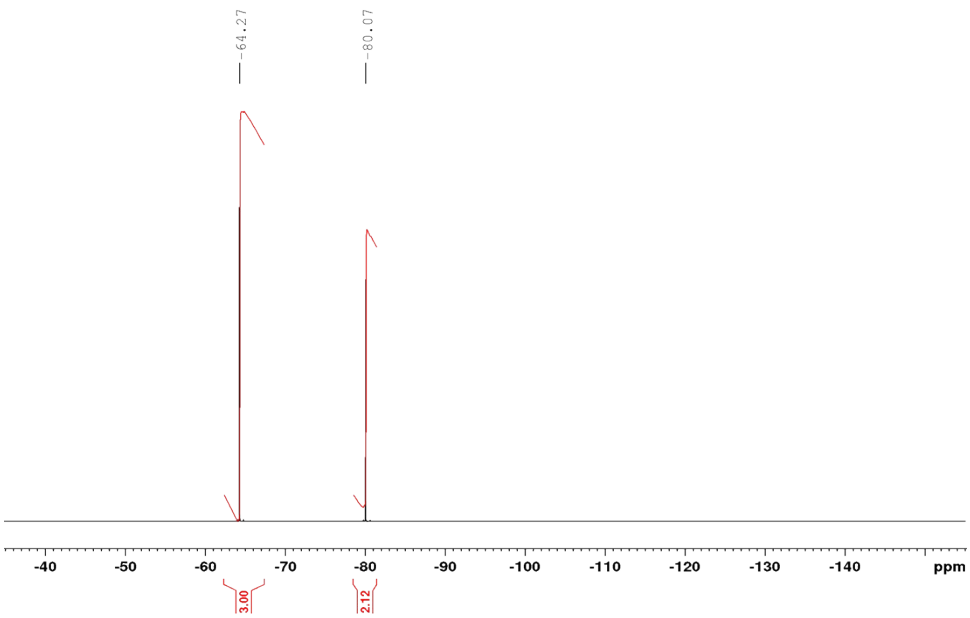
Expansion of ^{1}H NMR of **L4-CF$_3$** in CD_3OD



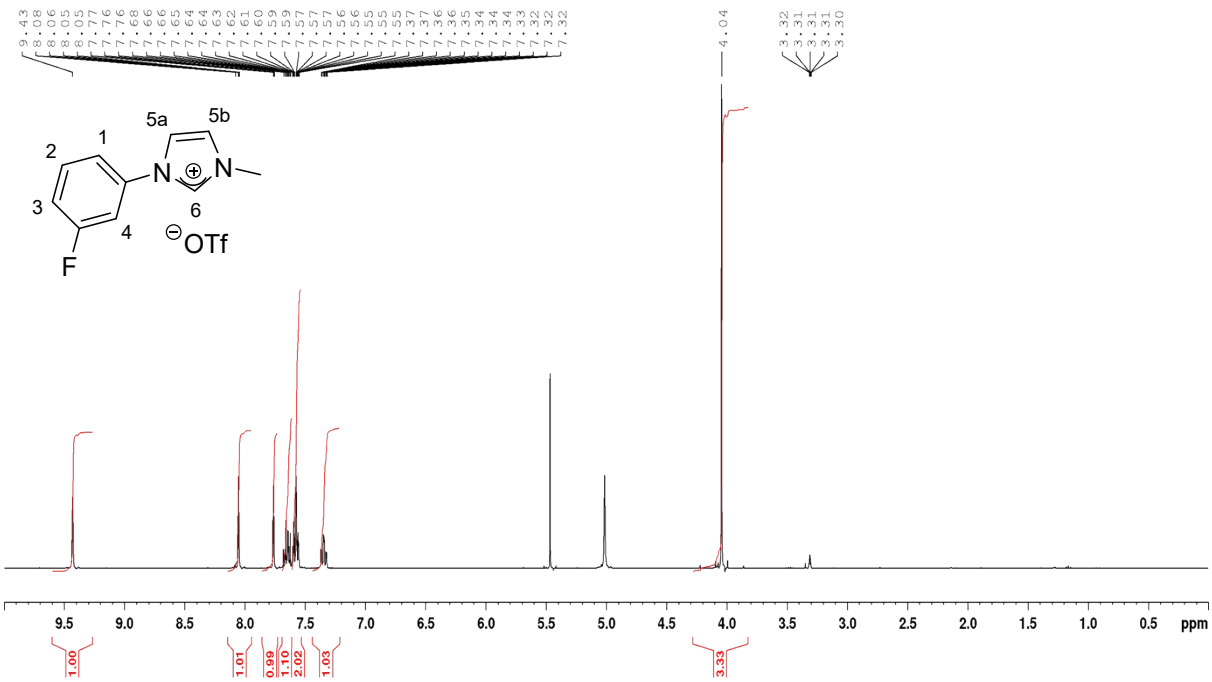
^{13}C NMR of **L4-CF$_3$** in CD$_3$OD with expansion



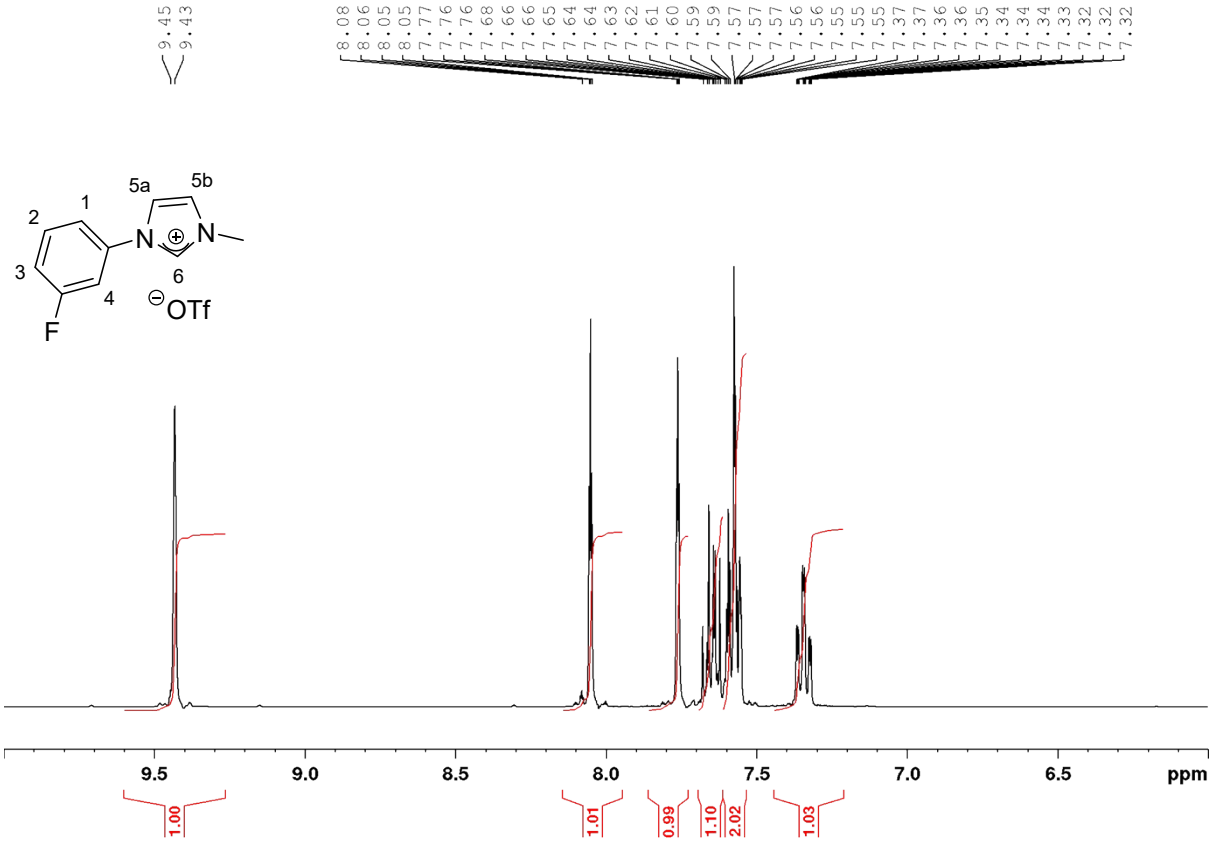
^{19}F NMR of **L4-CF$_3$** in CD$_3$OD



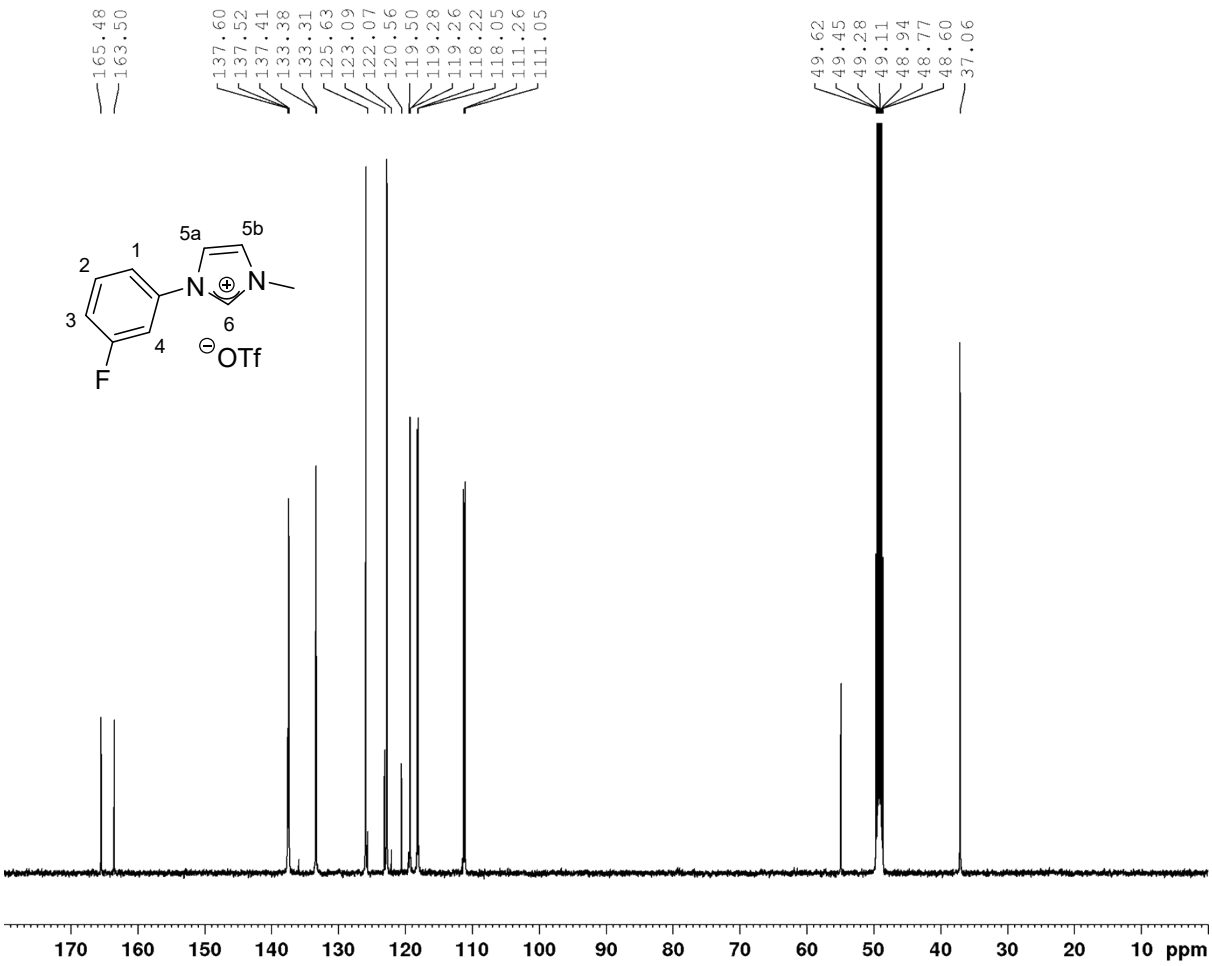
^{1}H NMR of **L4-F** in CD_3OD



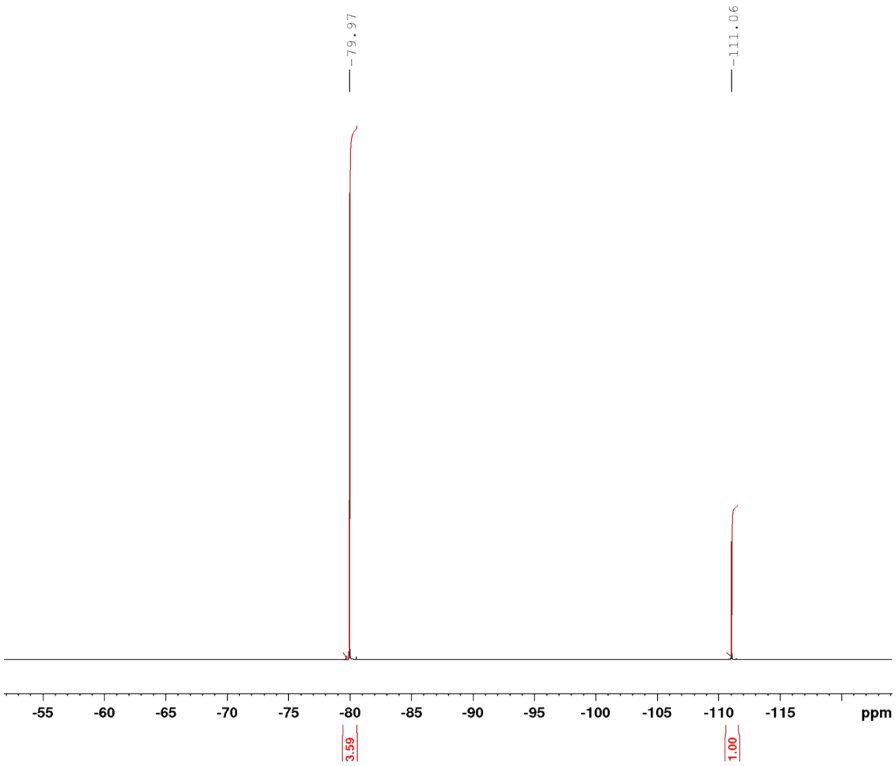
Expansion of ^{1}H NMR of **L4-F** in CD_3OD



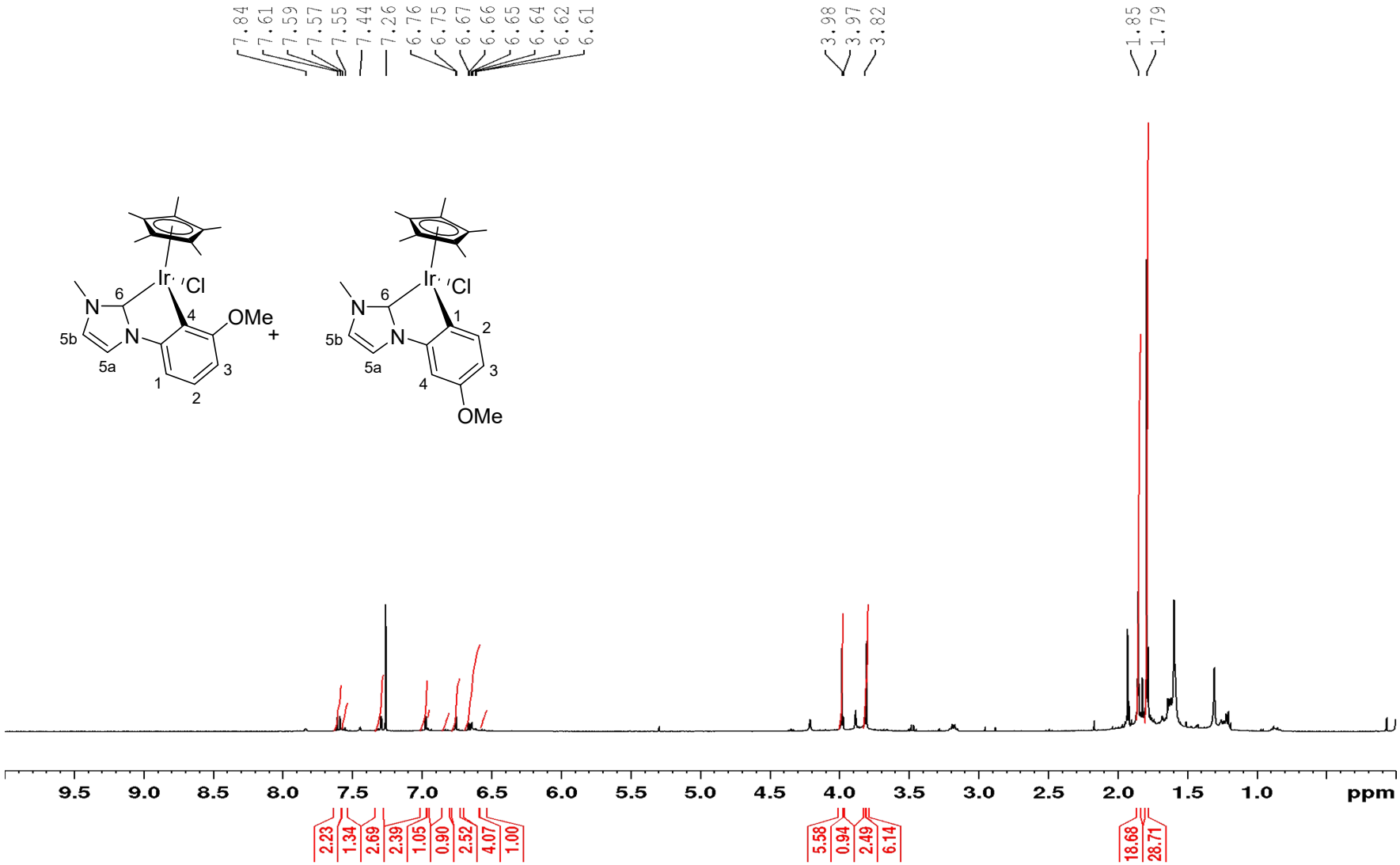
^{13}C NMR of **L4-F** in CD_3OD



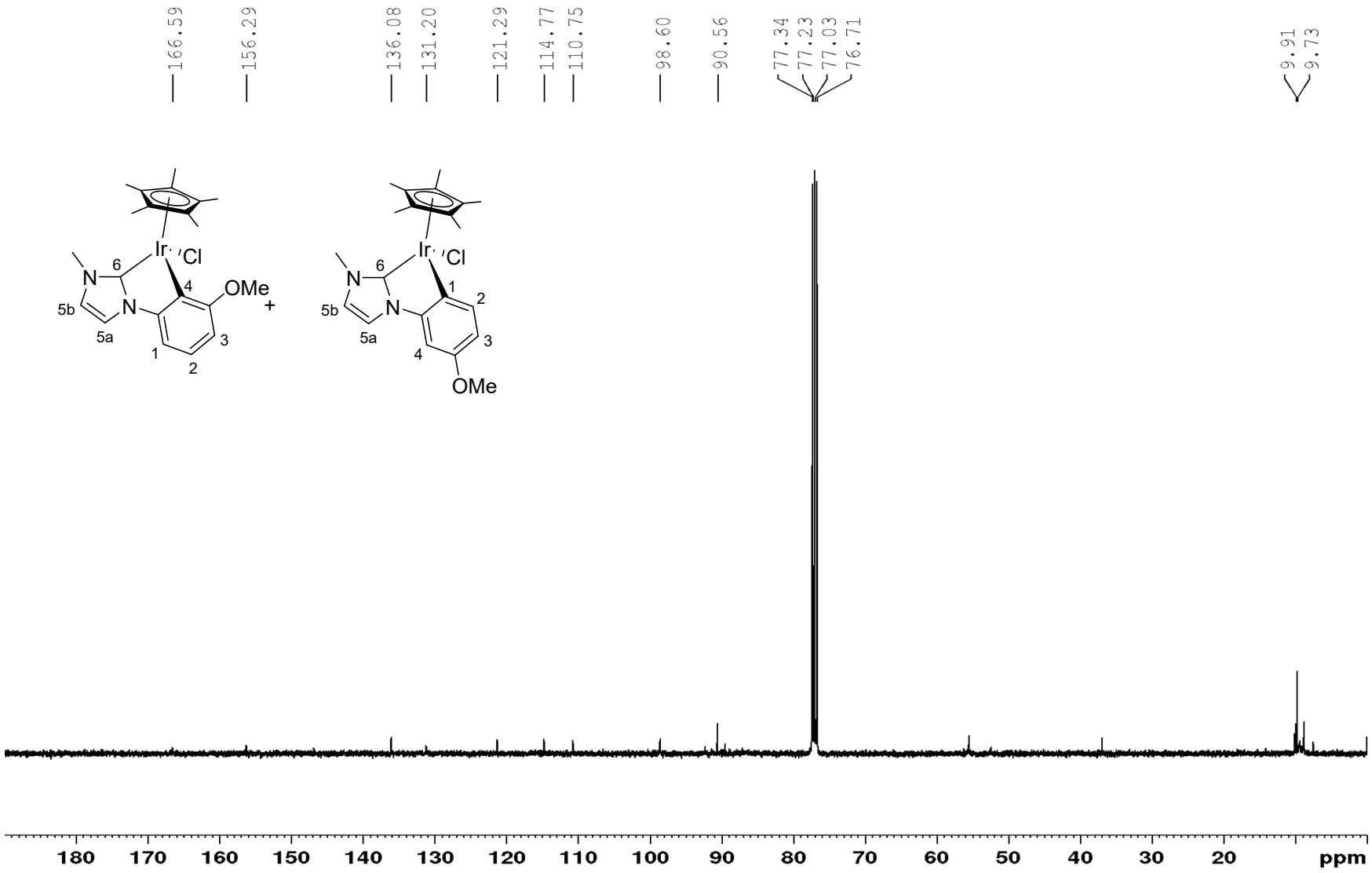
^{19}F NMR of **L4-F** in CD_3OD



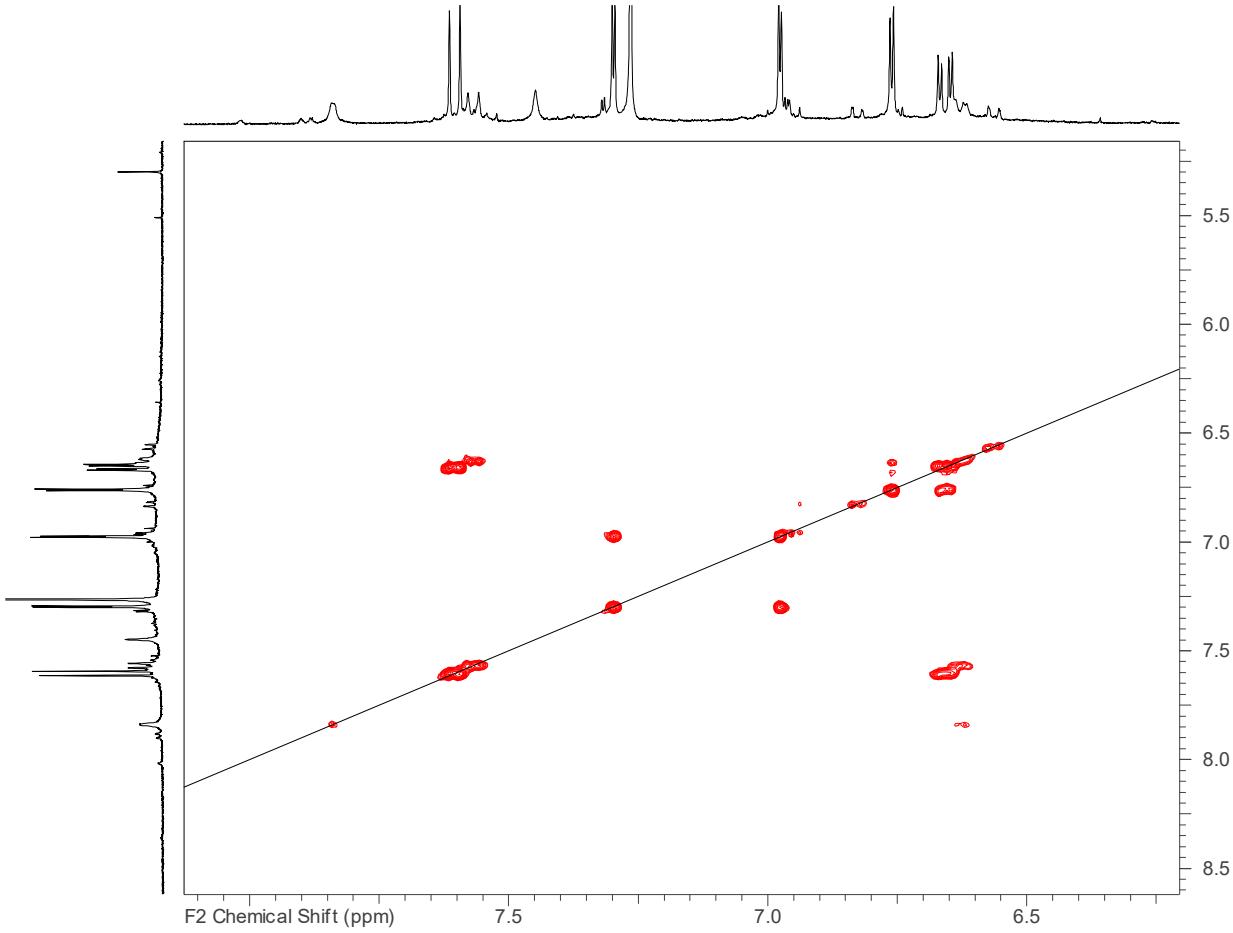
^{1}H NMR of a mixture of ortho and para **4a-OMe** in $CDCl_3$

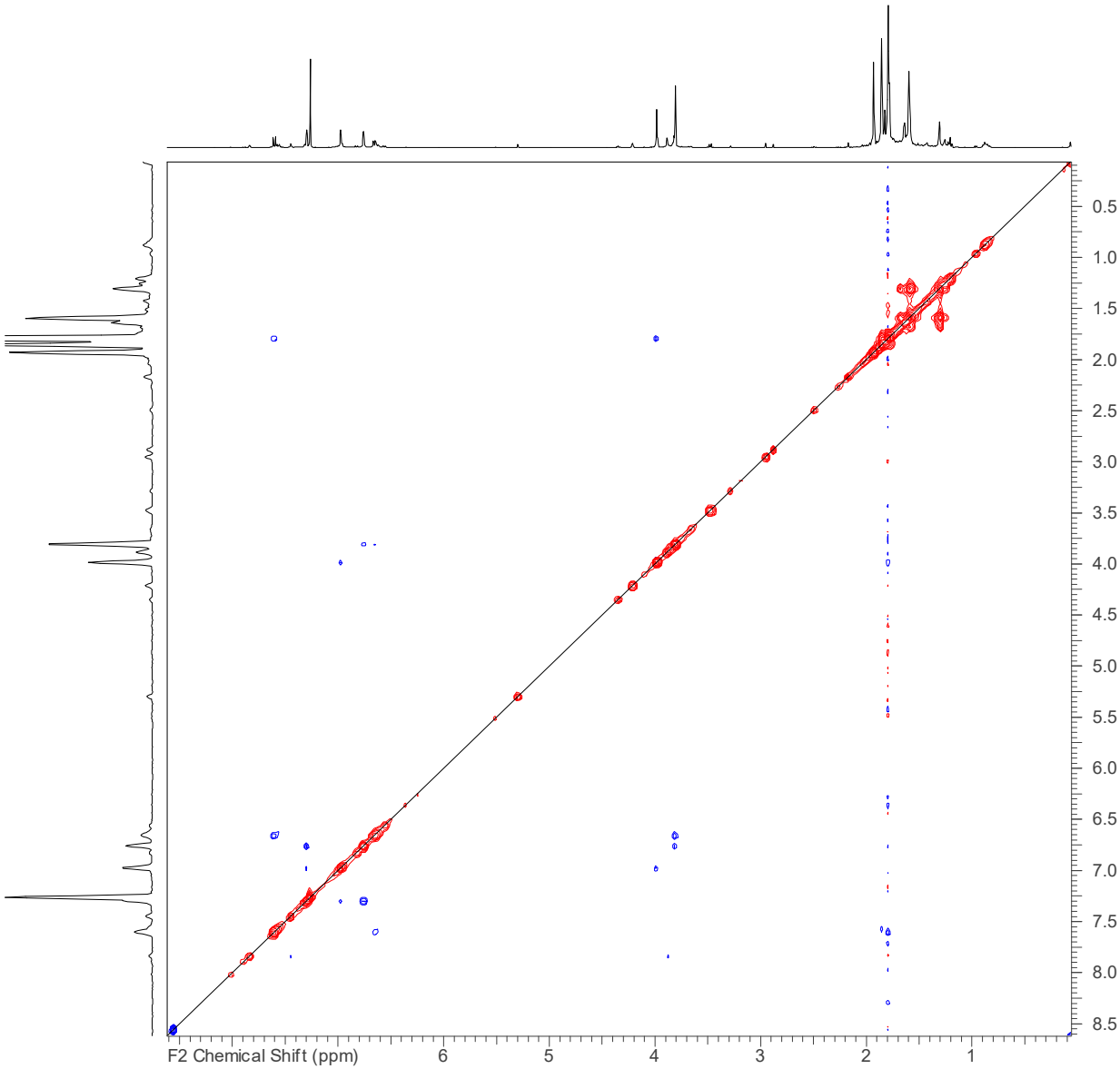


^{13}C NMR of a mixture of ortho and para **4a-OMe** in $CDCl_3$



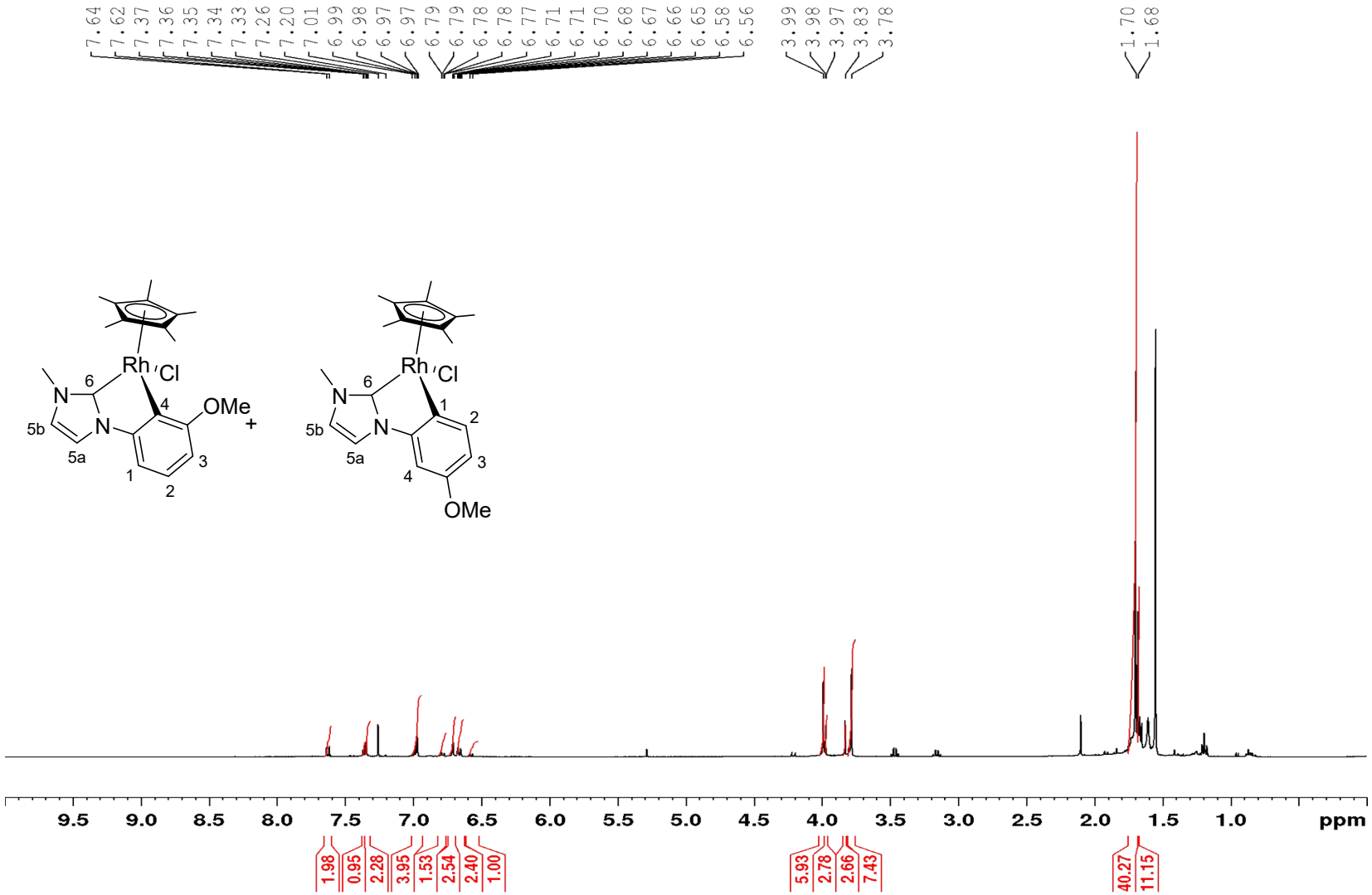
Section of Cosy spectrum for a mixture of ortho and para **4a-OMe** in $CDCl_3$



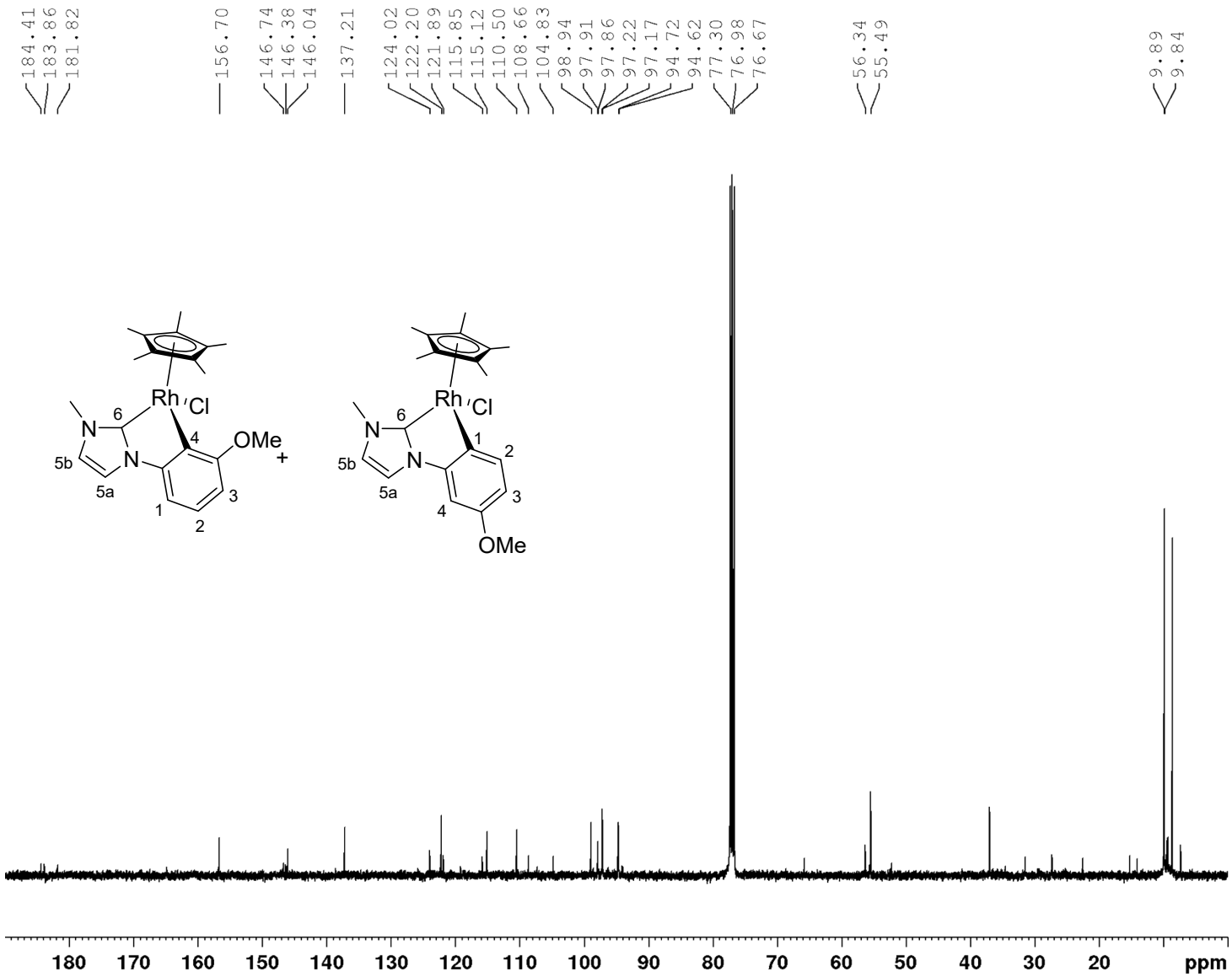


Section of NOESY spectrum for a mixture of ortho and para **4a-OMe** in $CDCl_3$

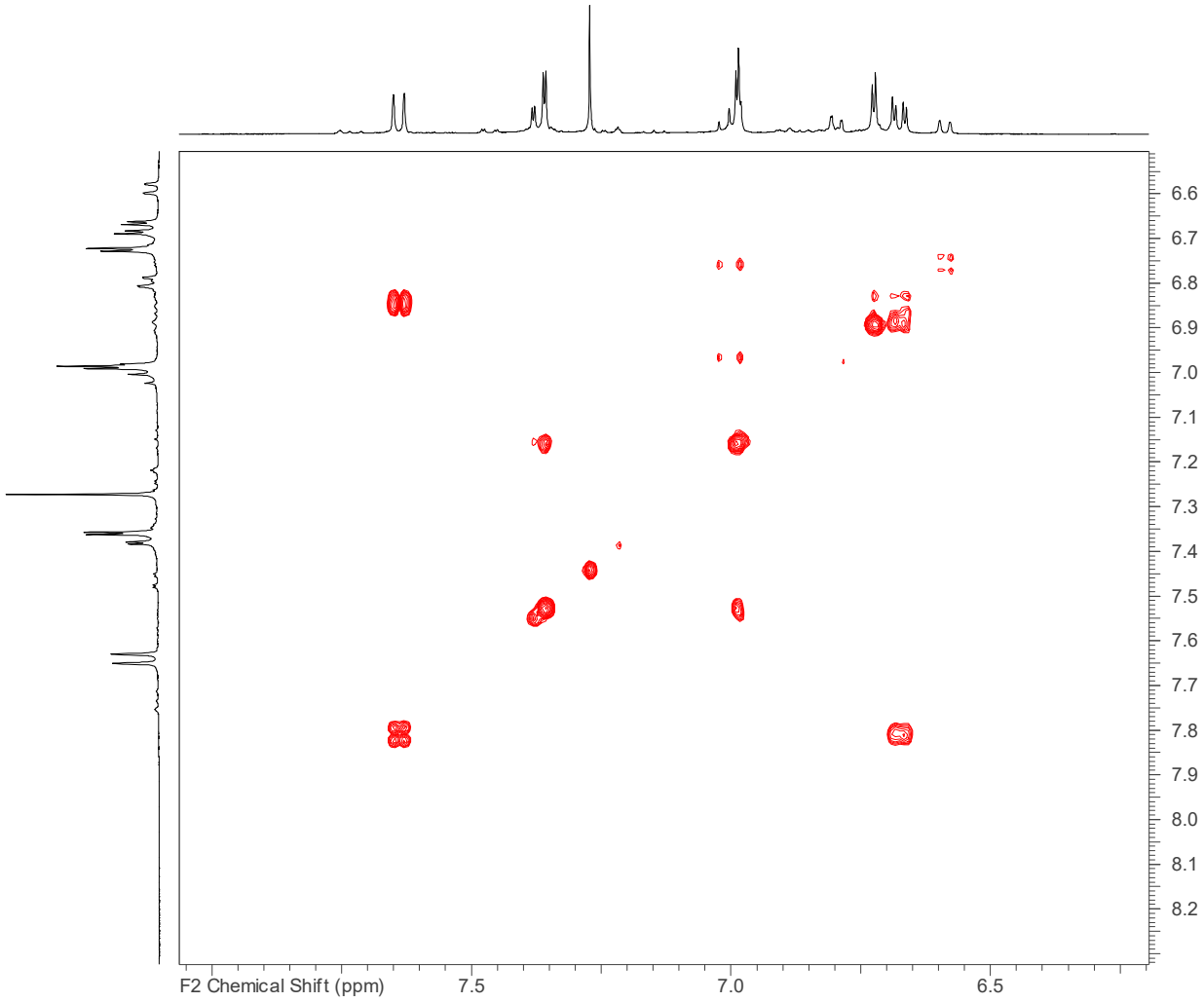
^{1}H NMR of a mixture of ortho and para **4b-OMe** in $CDCl_3$



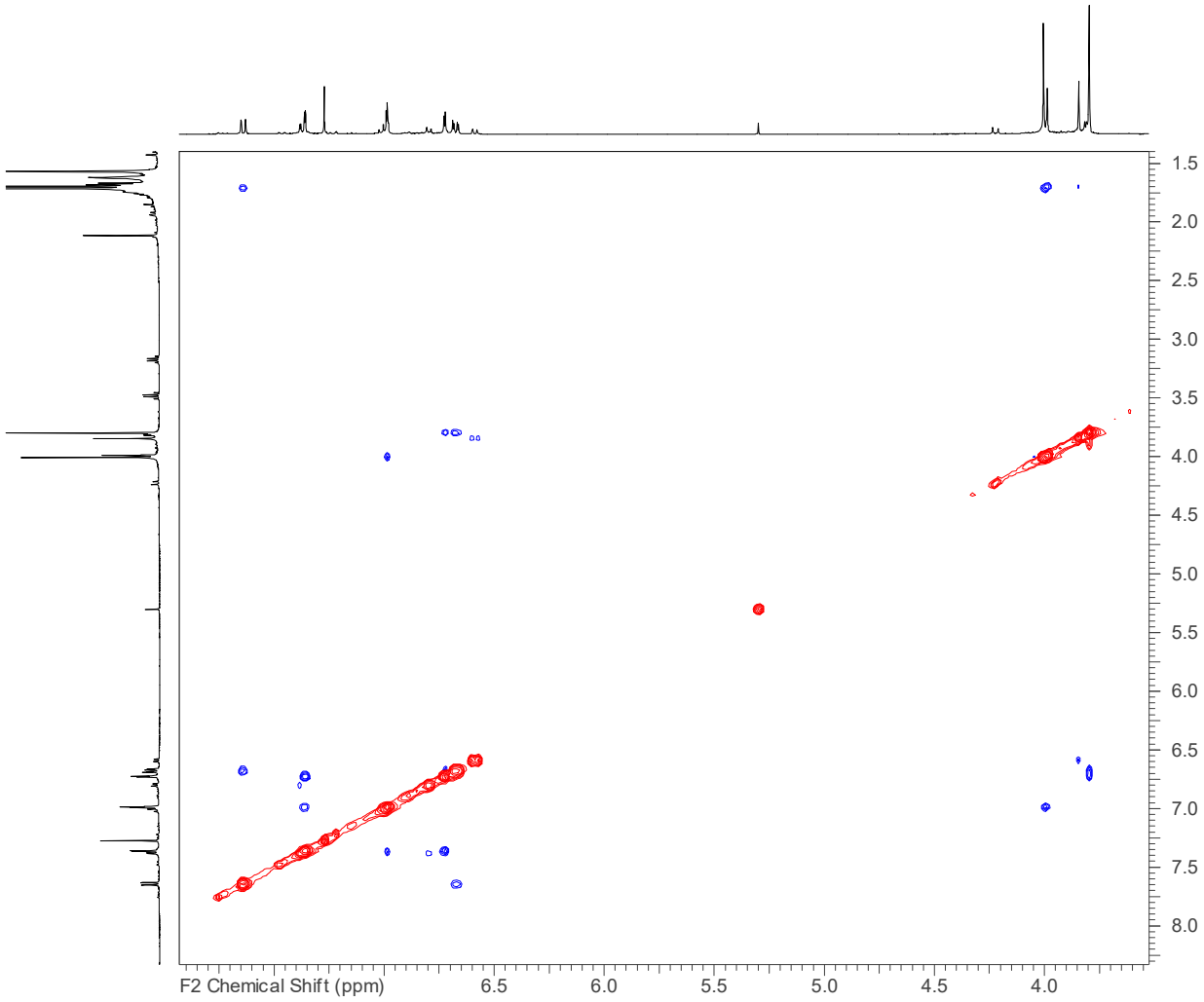
^{13}C NMR of a mixture of ortho and para **4b-OMe** in $CDCl_3$



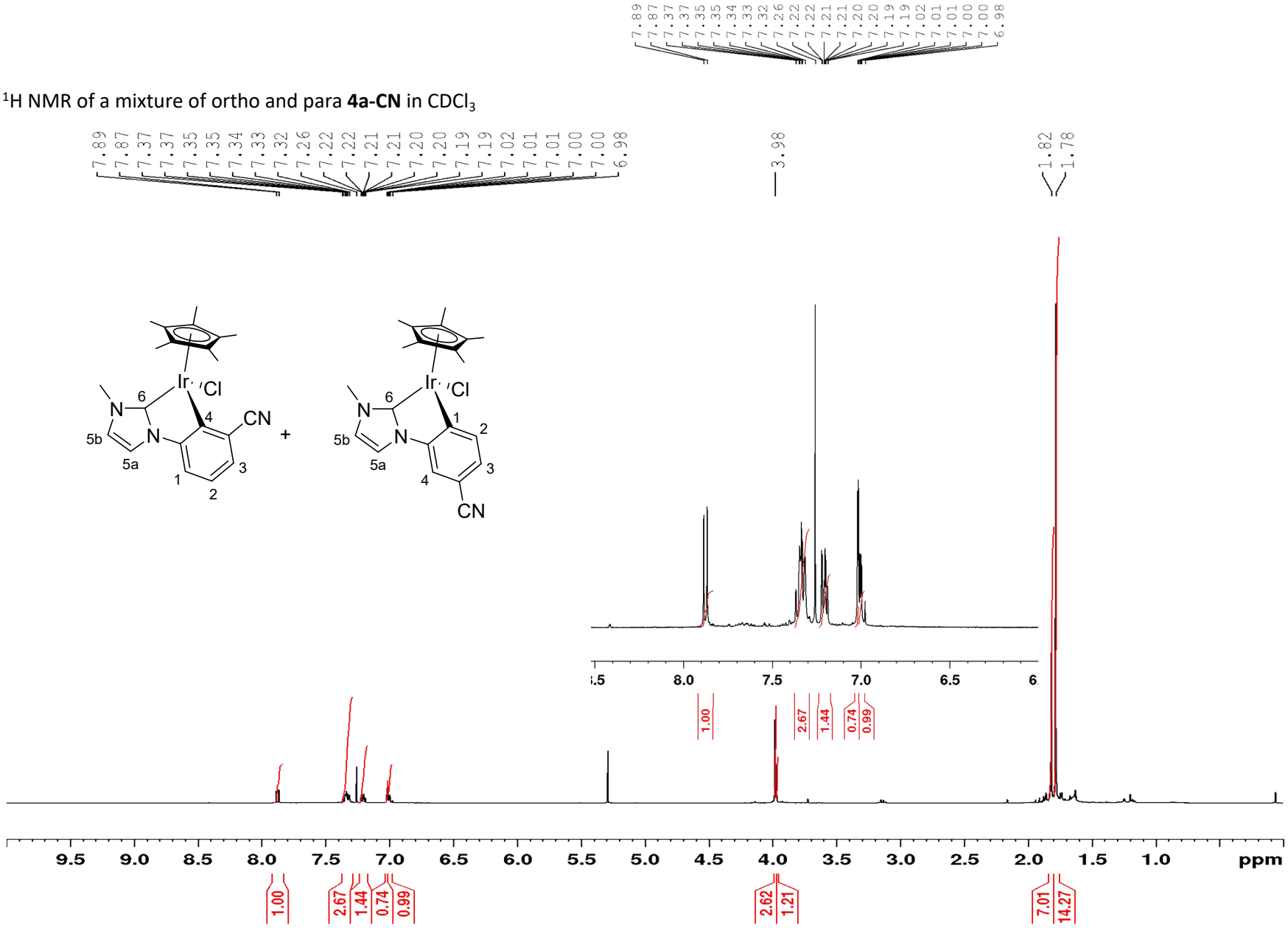
Section of COSY NMR of a mixture of ortho and para **4b-OMe** in $CDCl_3$



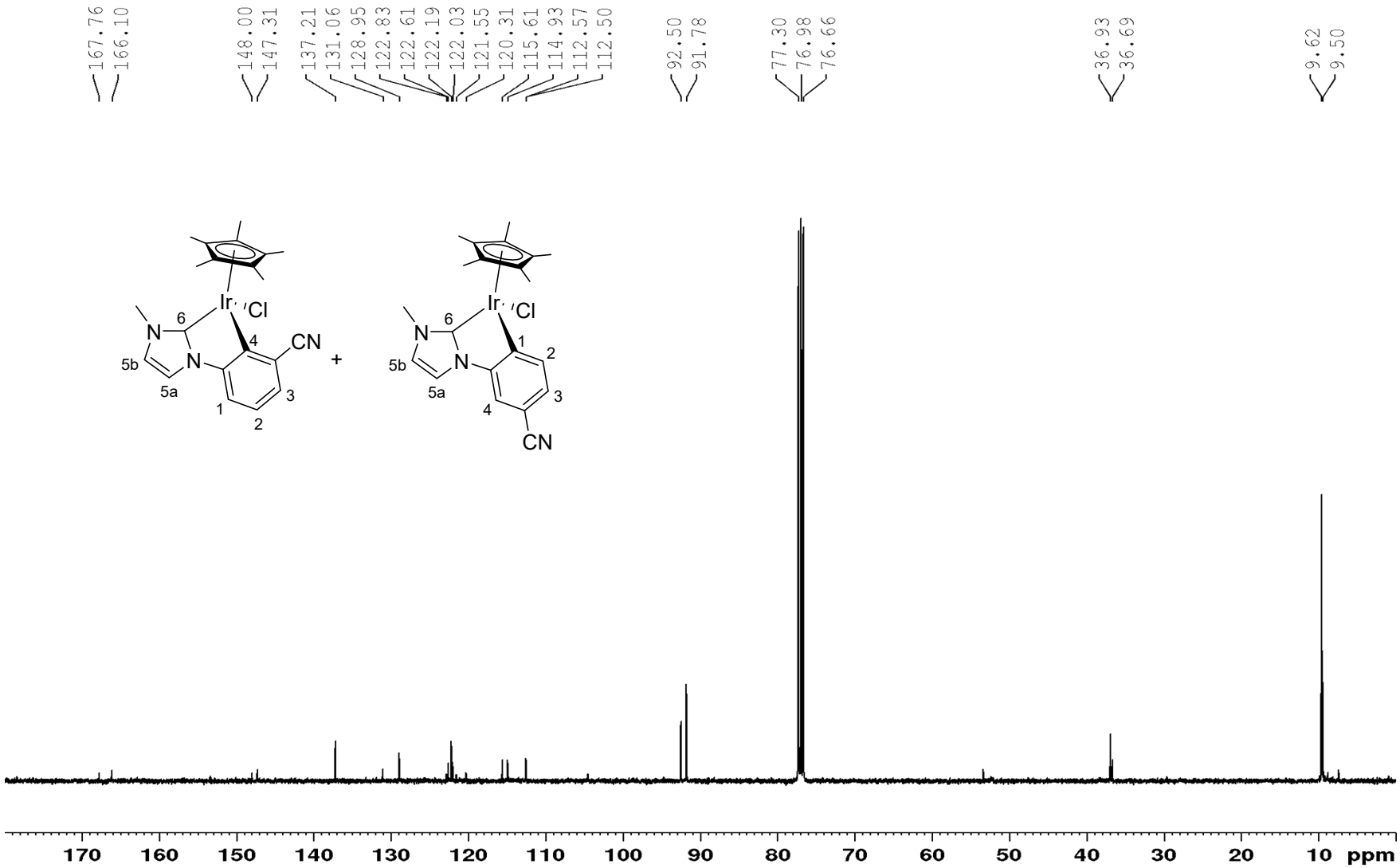
Section of NOESY NMR of a mixture of ortho and para **4b-OMe** in $CDCl_3$



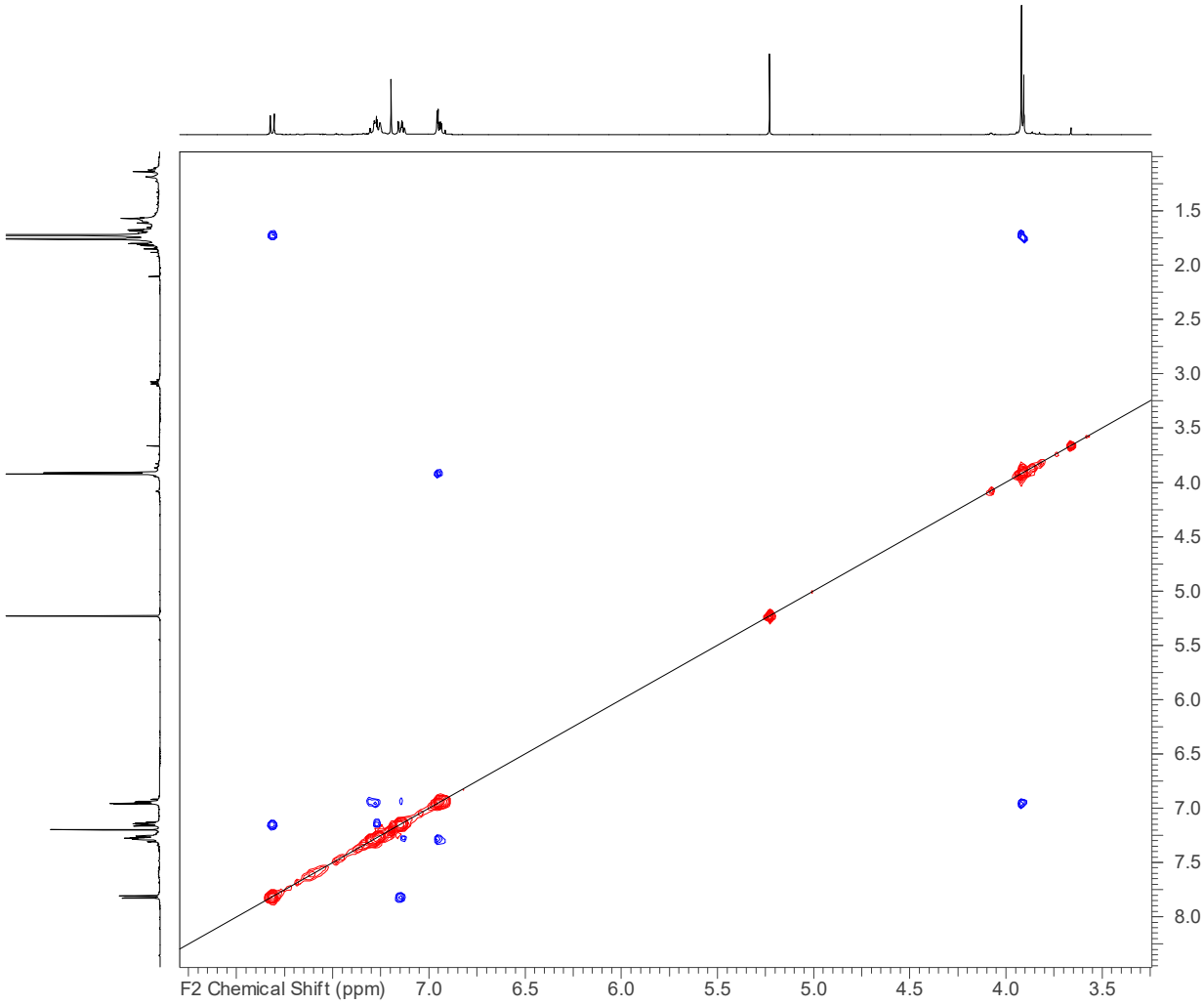
^{1}H NMR of a mixture of ortho and para **4a-CN** in $CDCl_3$



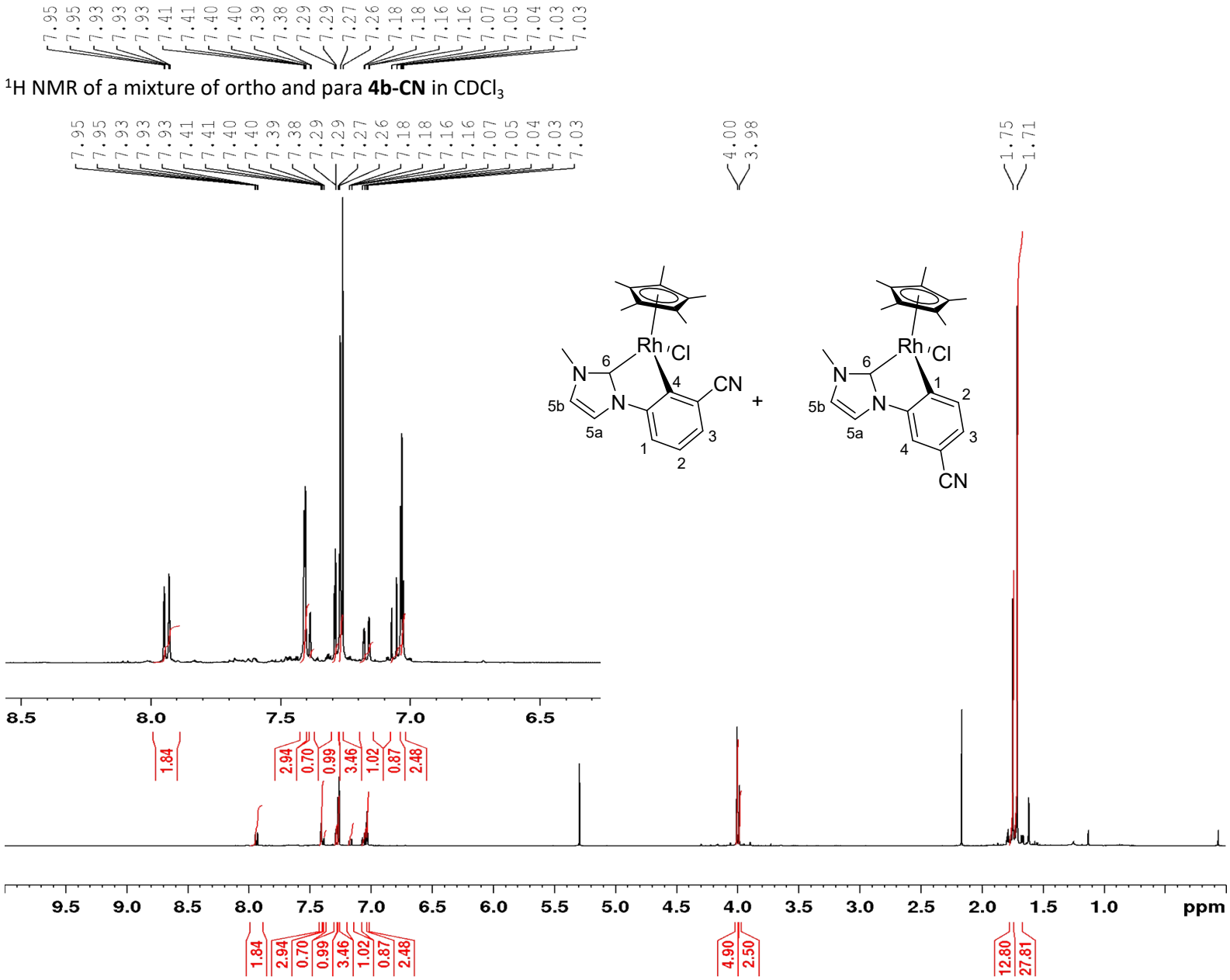
^{13}C NMR of a mixture of ortho and para **4a-CN** in $CDCl_3$



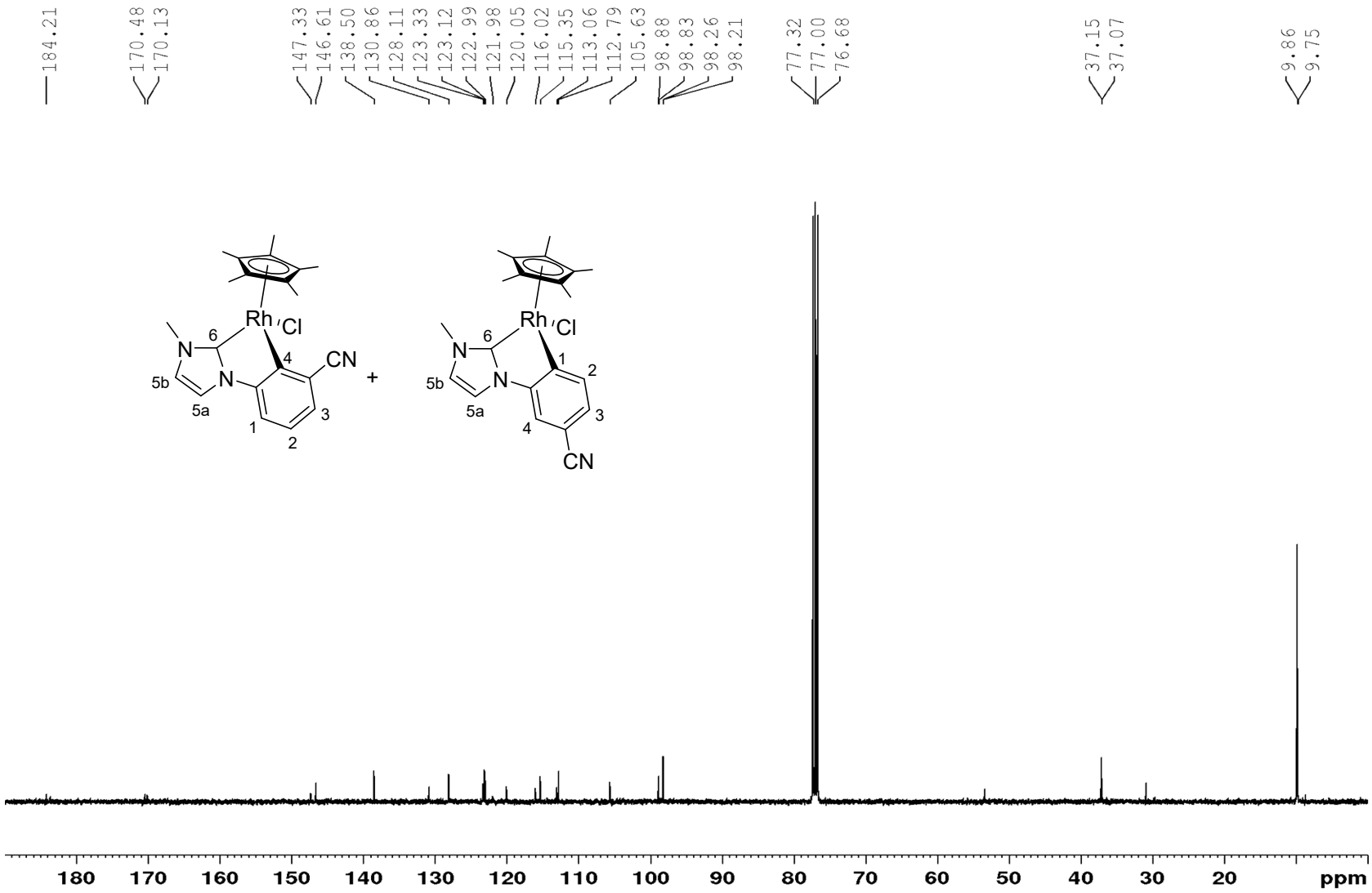
Section of NOESY spectrum of **4a-CN**



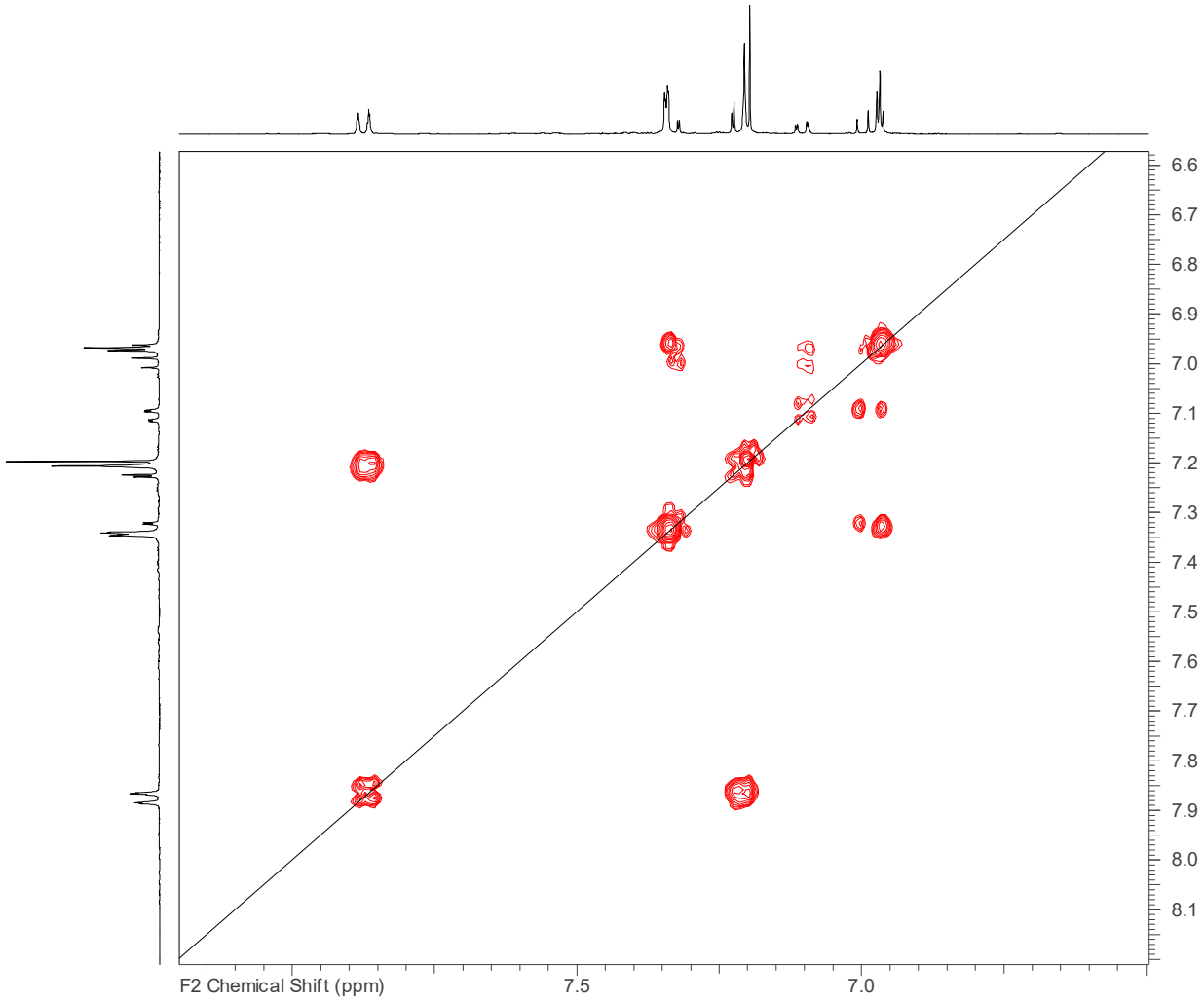
^{1}H NMR of a mixture of ortho and para **4b-CN** in $CDCl_3$

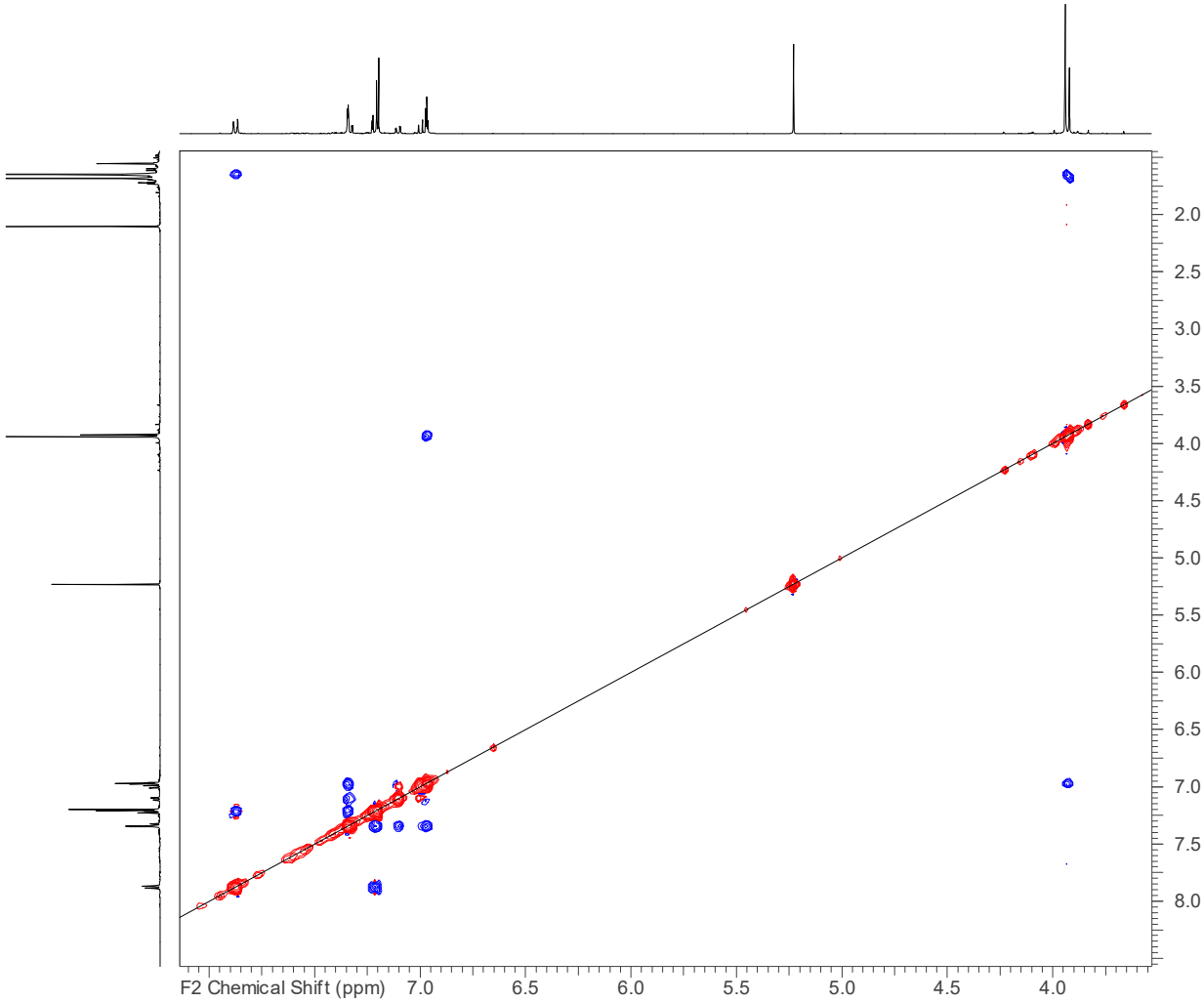


^{13}C NMR of a mixture of ortho and para **4b-CN** in $CDCl_3$

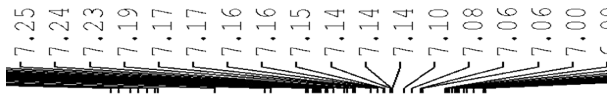


Section of COSY spectrum of a mixture of ortho and para **4b-CN** in $CDCl_3$

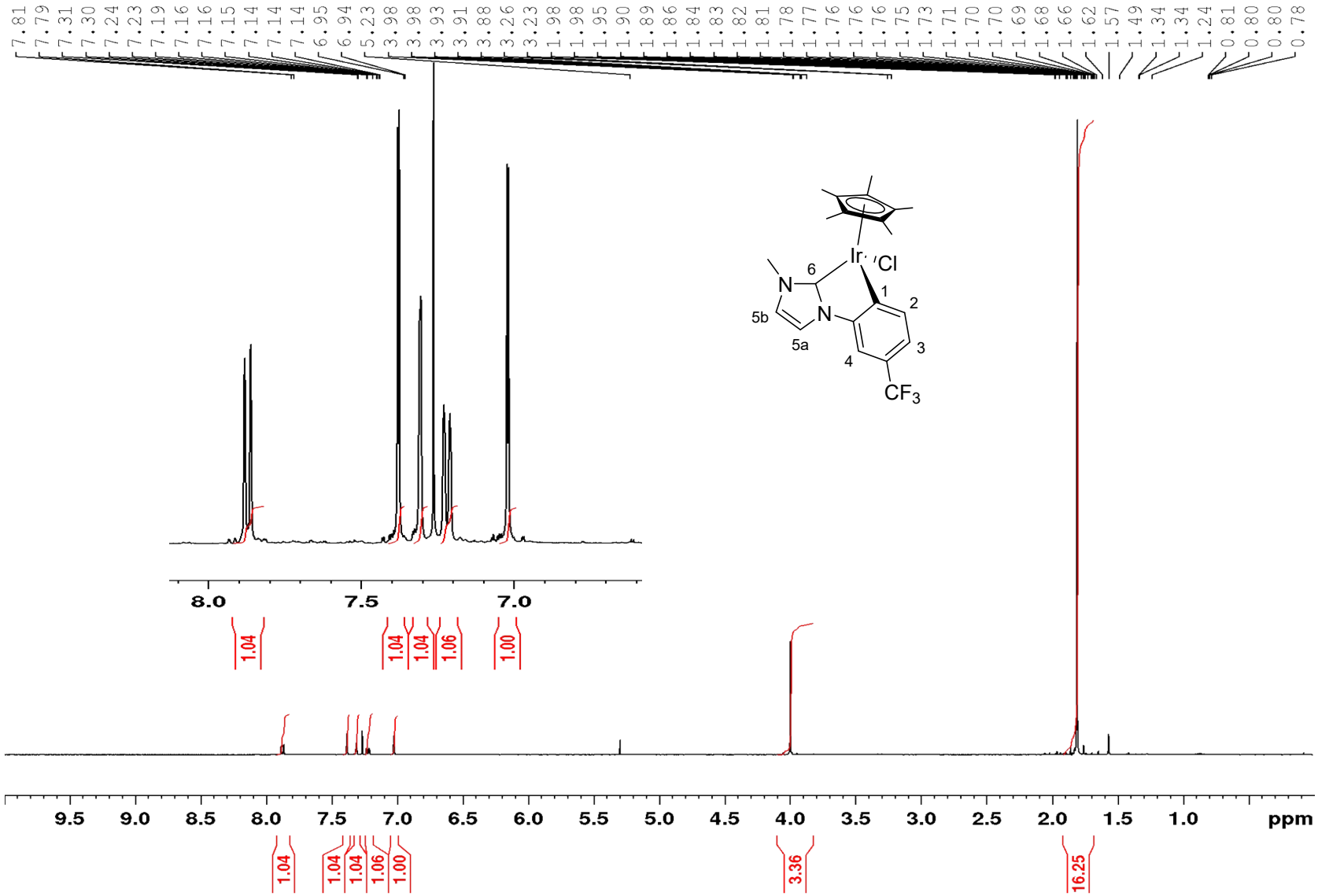




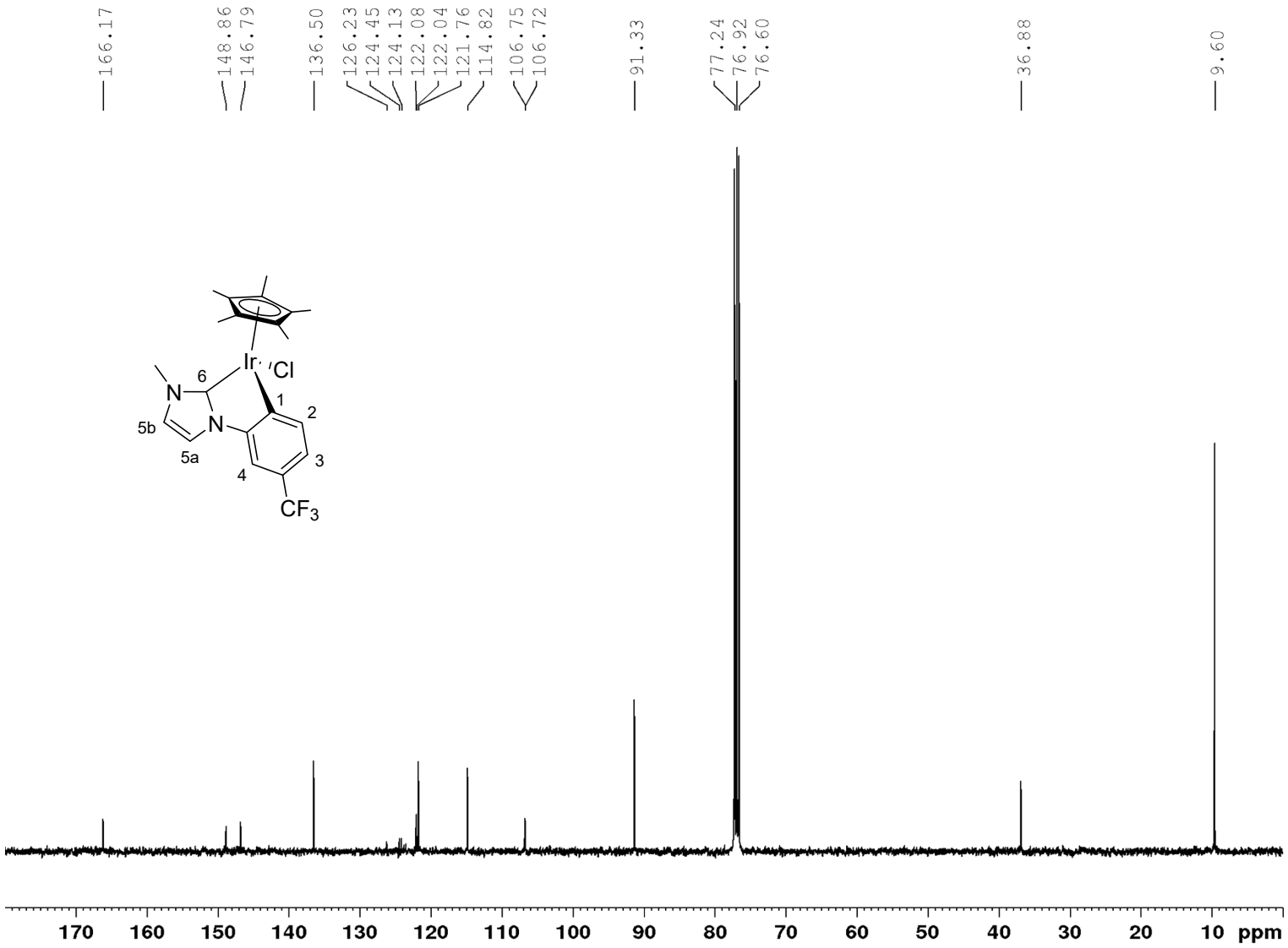
Section of NOESY spectrum of a mixture of ortho and para **4b-CN** in $CDCl_3$



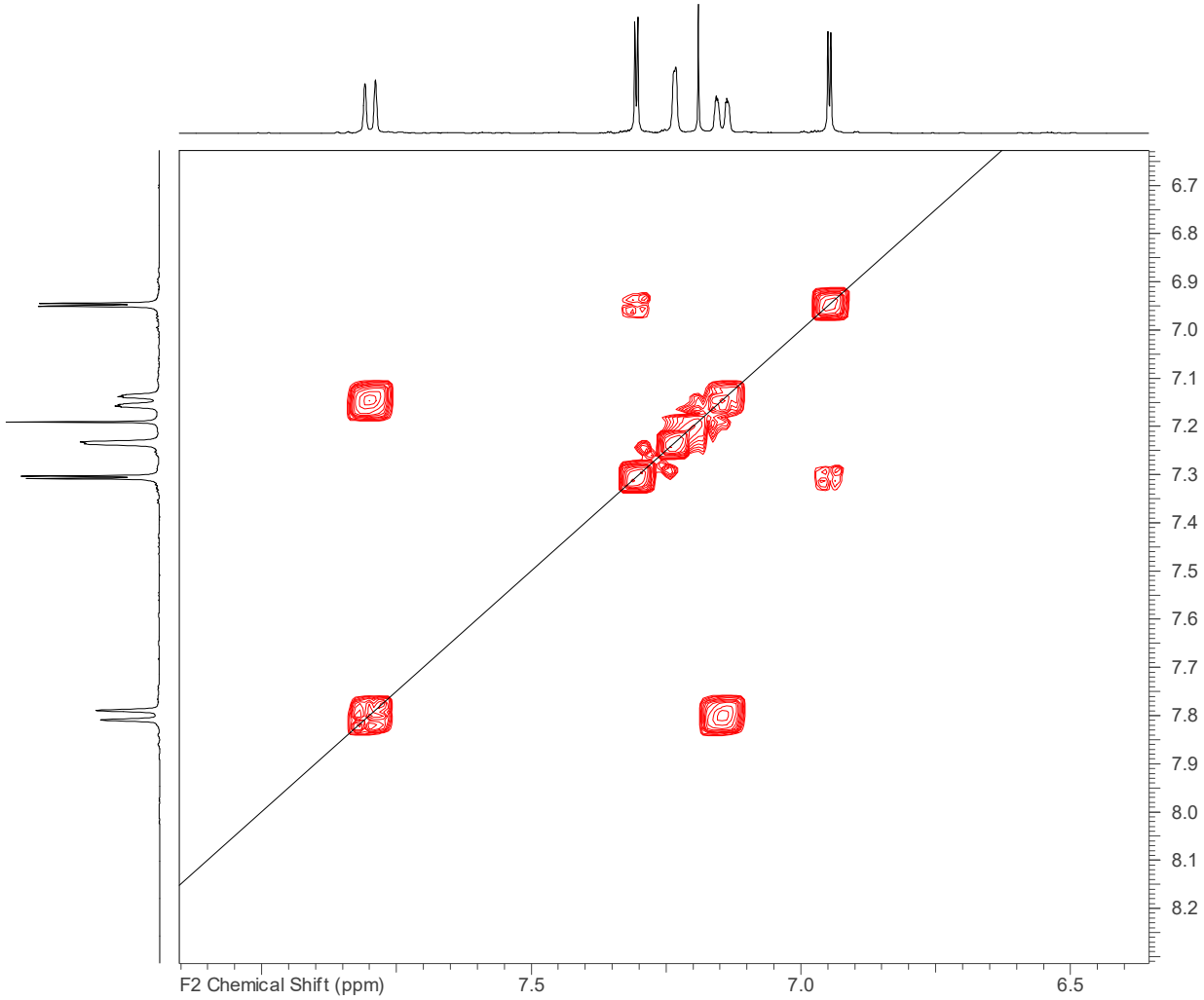
^{1}H NMR of para **4a-CF$_3$** in $CDCl_3$



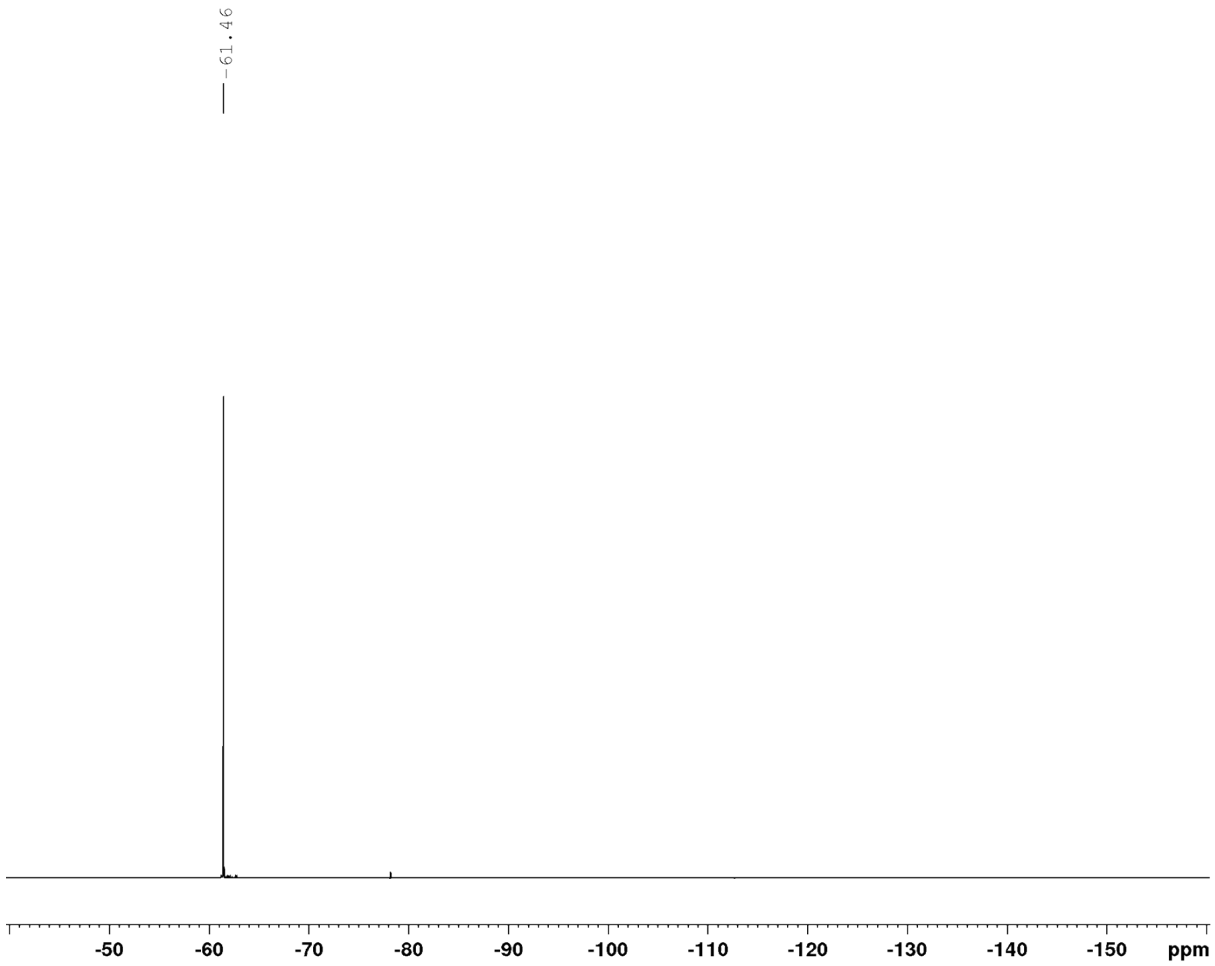
^{13}C NMR of para **4a-CF$_3$** in $CDCl_3$



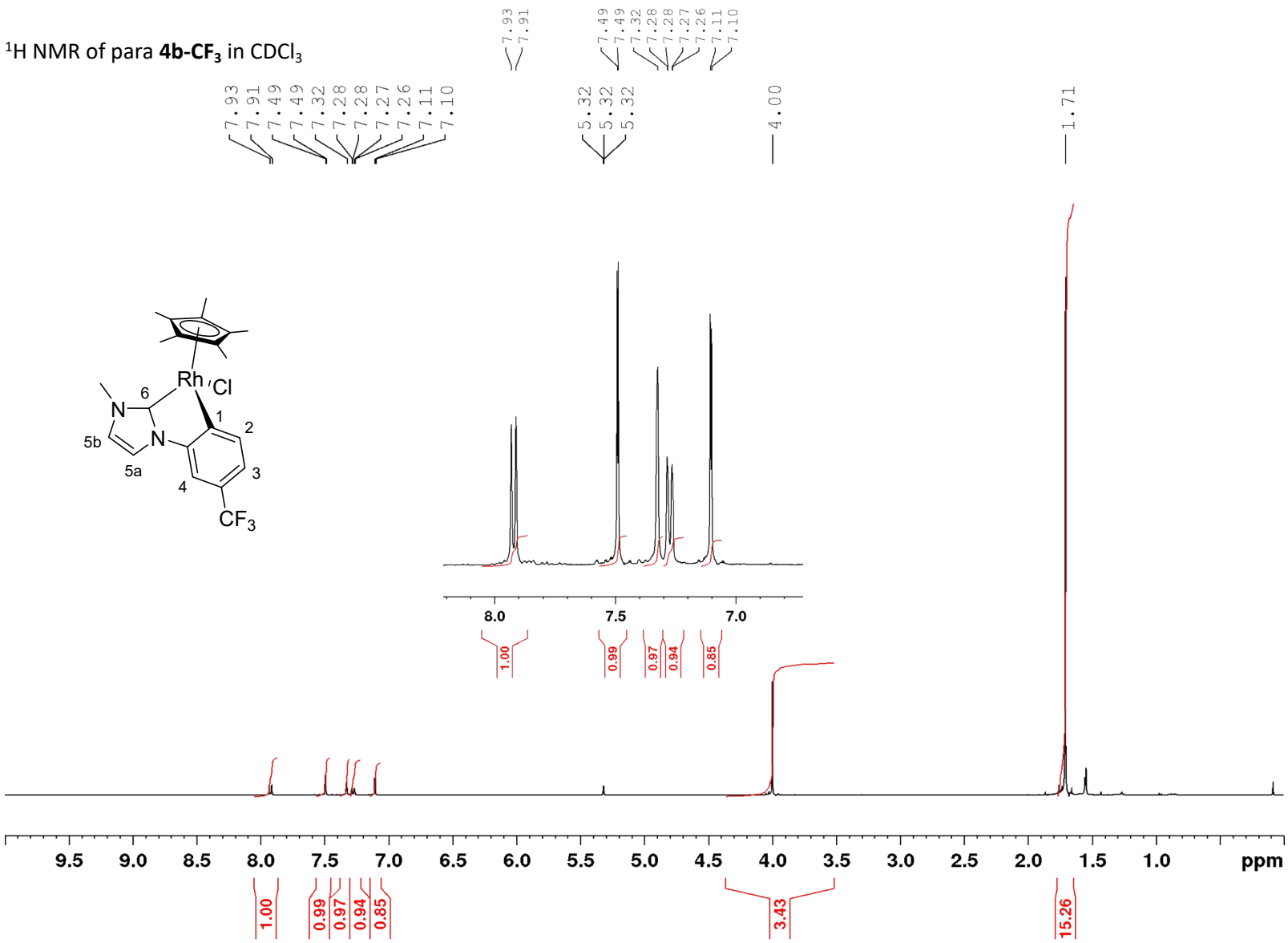
Section of COSY spectrum of para **4a-CF3** in $CDCl_3$



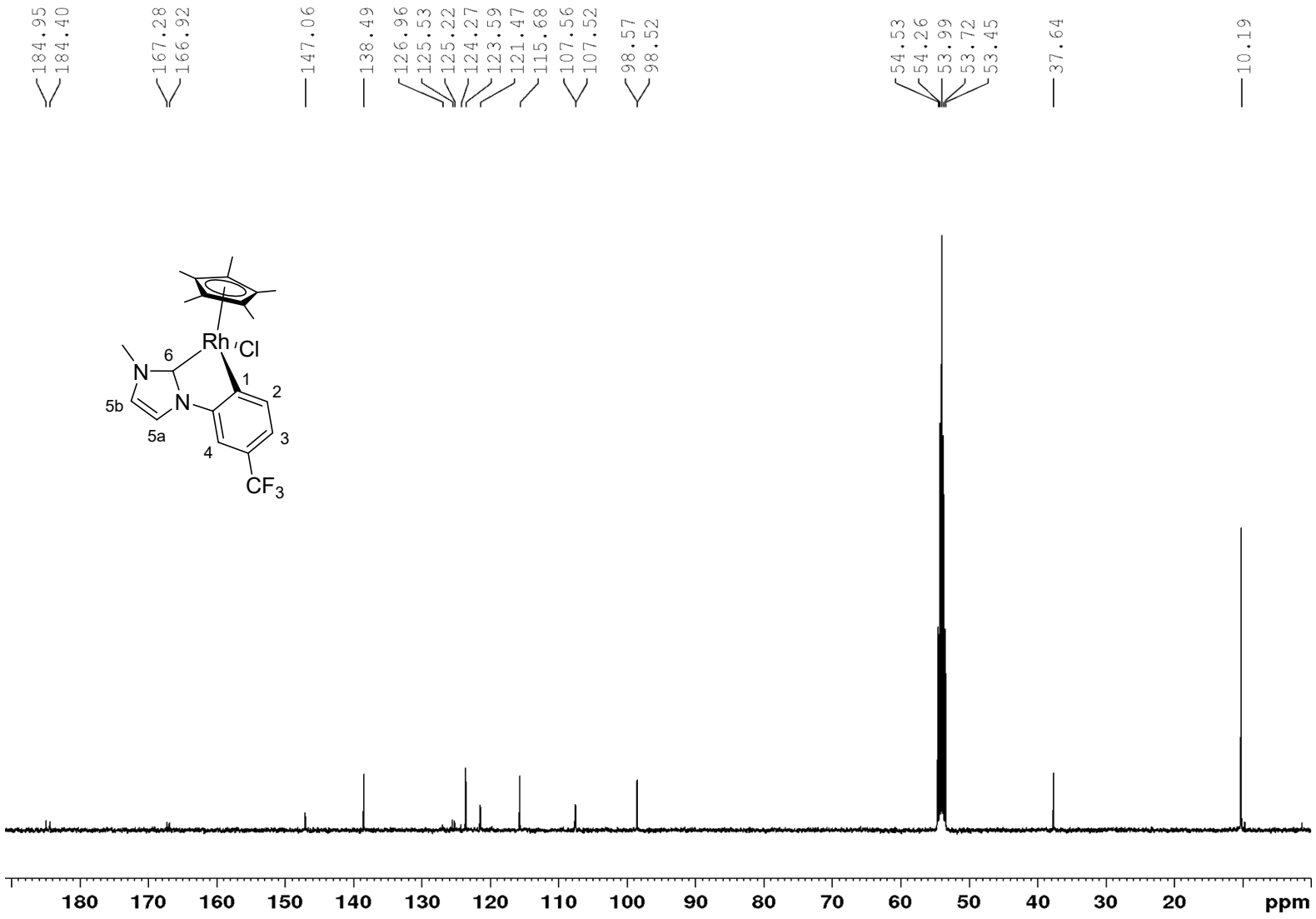
^{19}F NMR of para **4a-CF$_3$** in $CDCl_3$



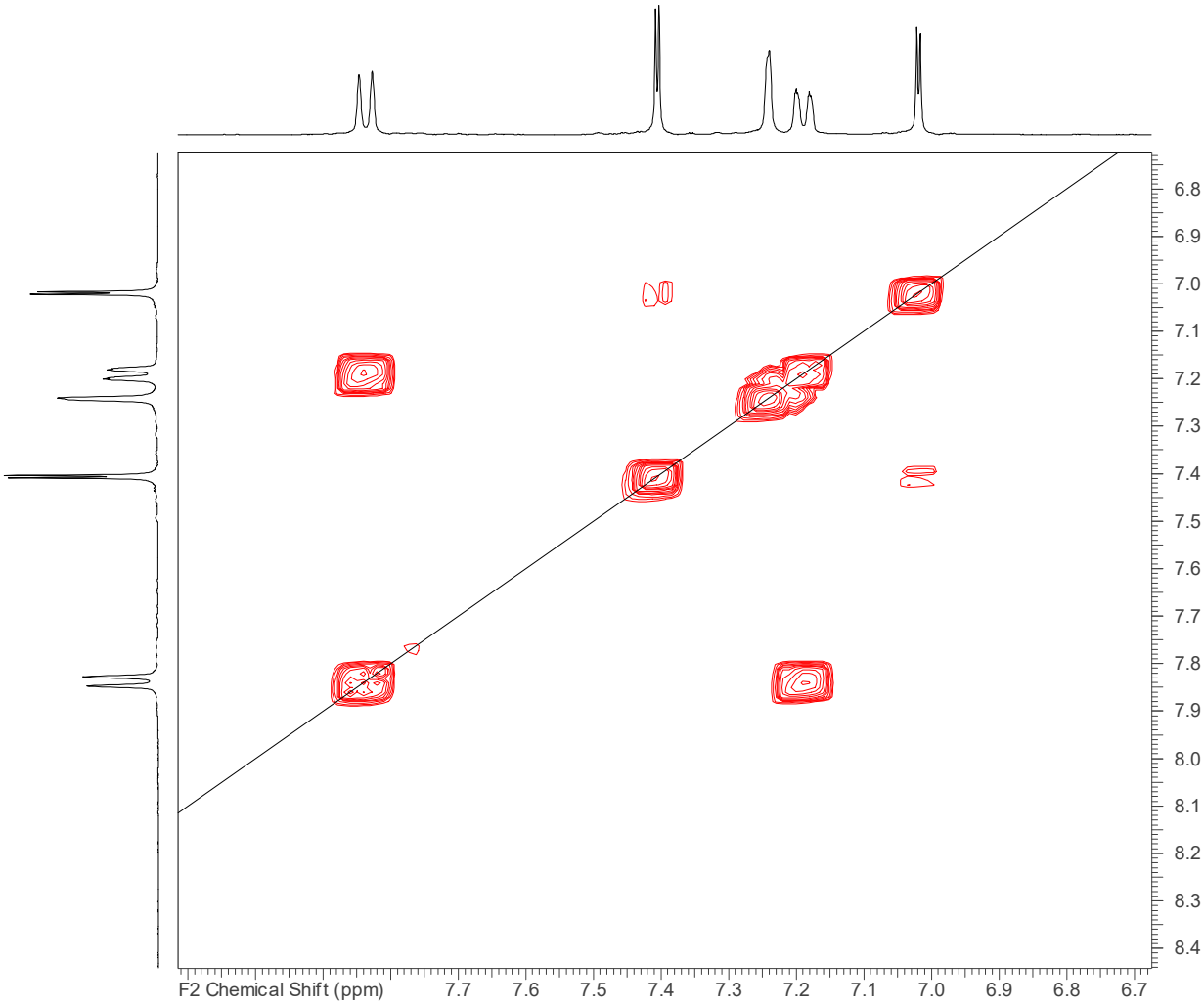
^{1}H NMR of para **4b-CF$_3$** in CDCl$_3$



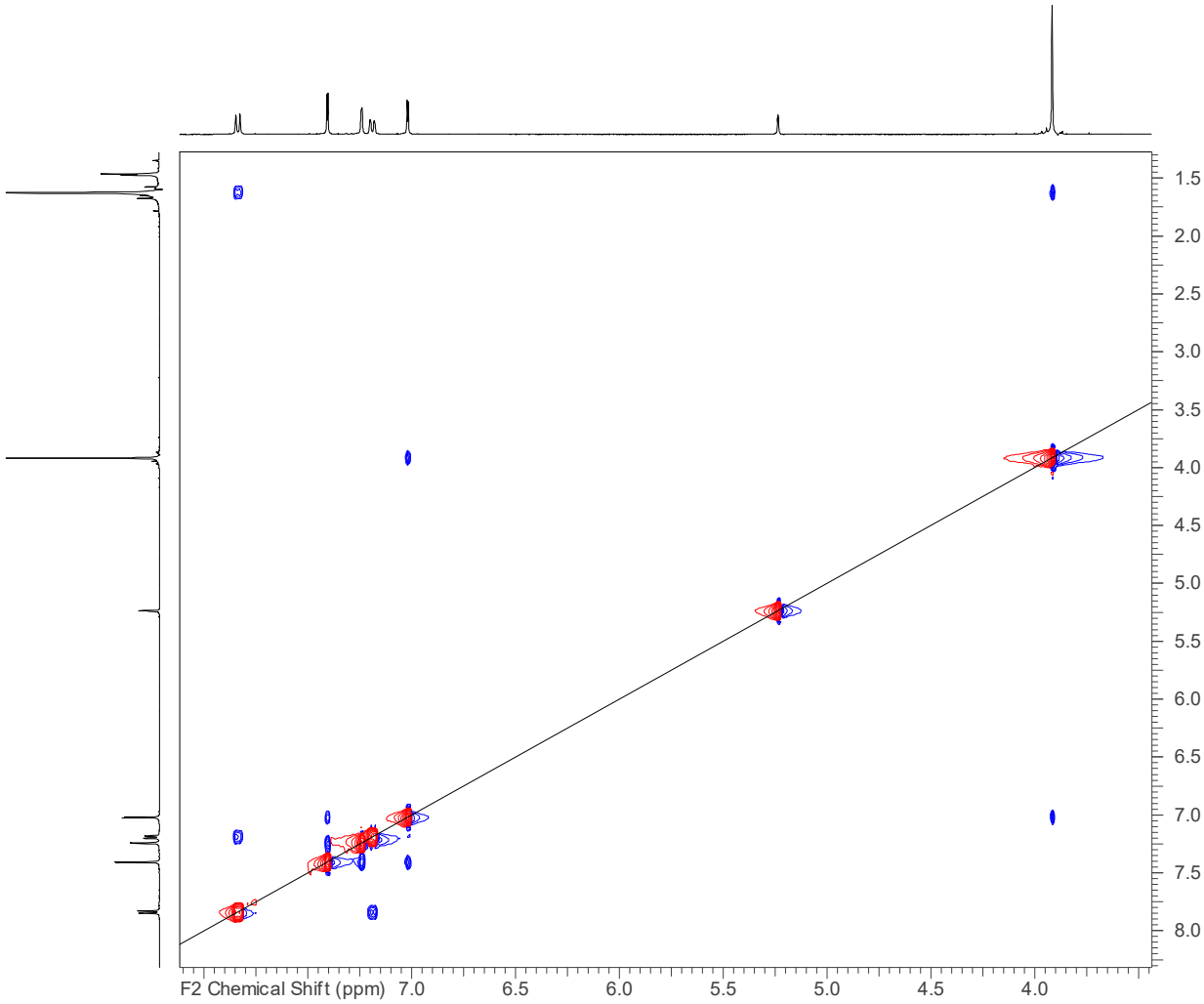
^{13}C NMR of para **4b-CF$_3$** in $CDCl_3$



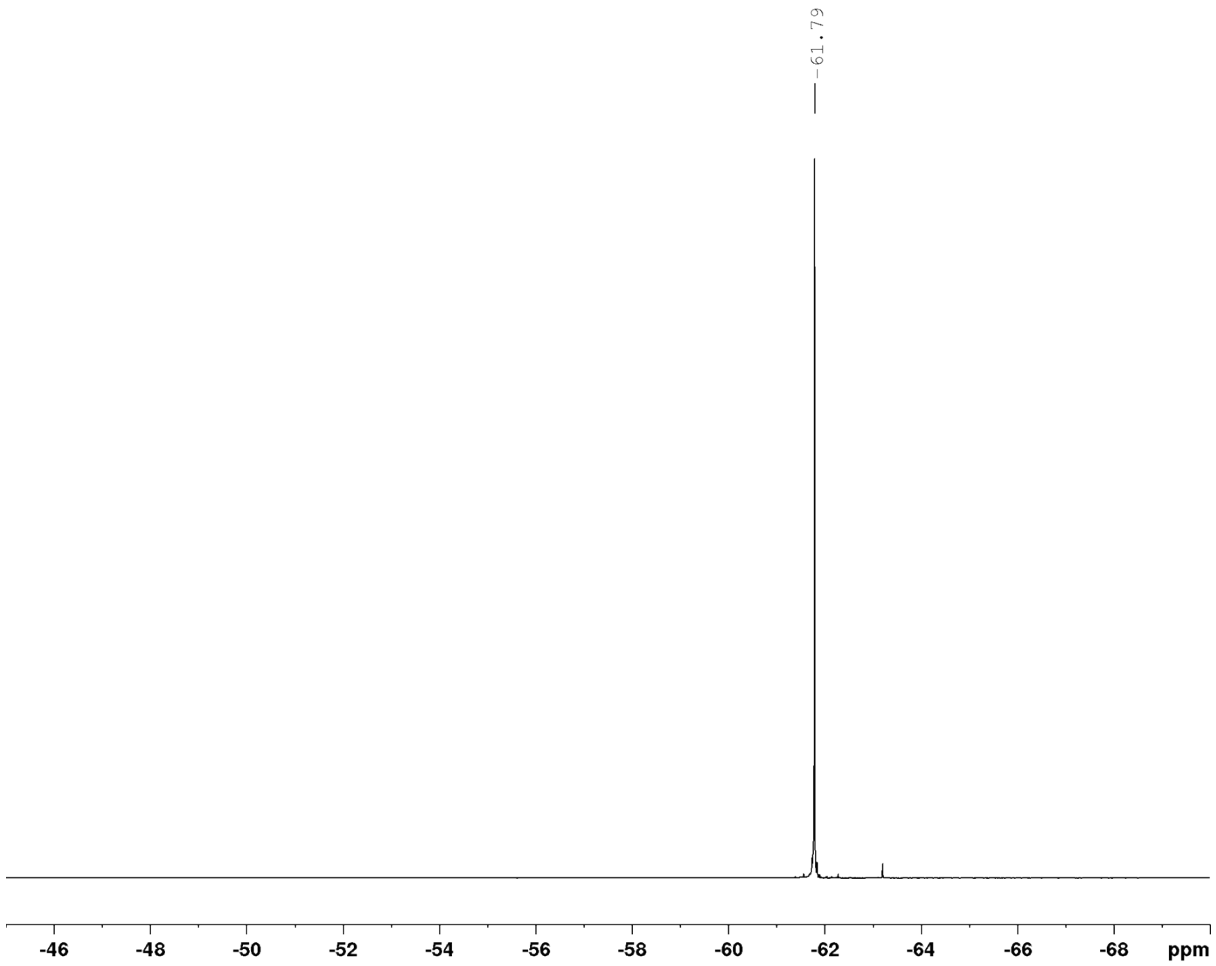
Section of COSY NMR of para **4b-CF3**



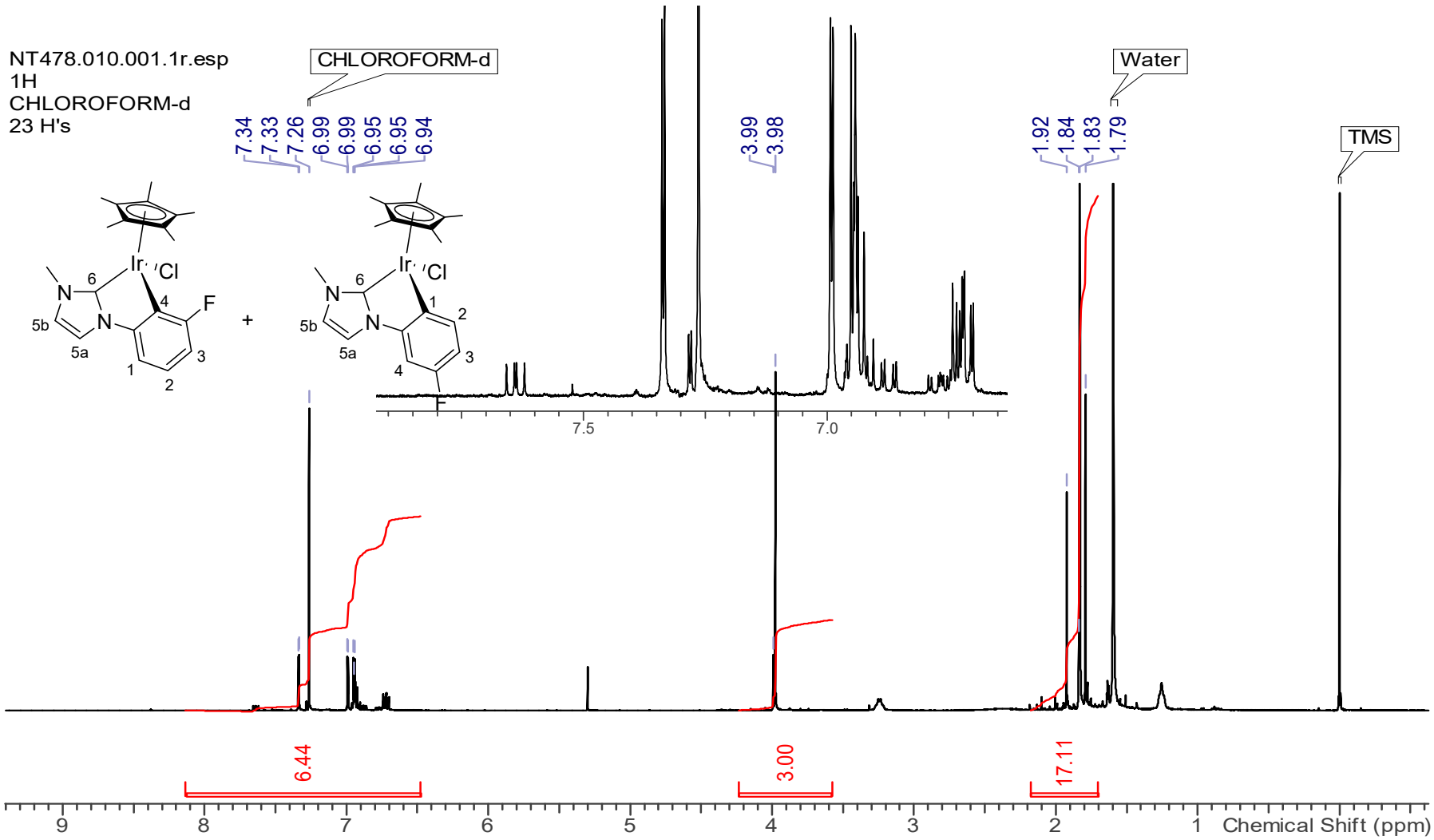
Section of the NOESY NMR of para-**4b-CF3**



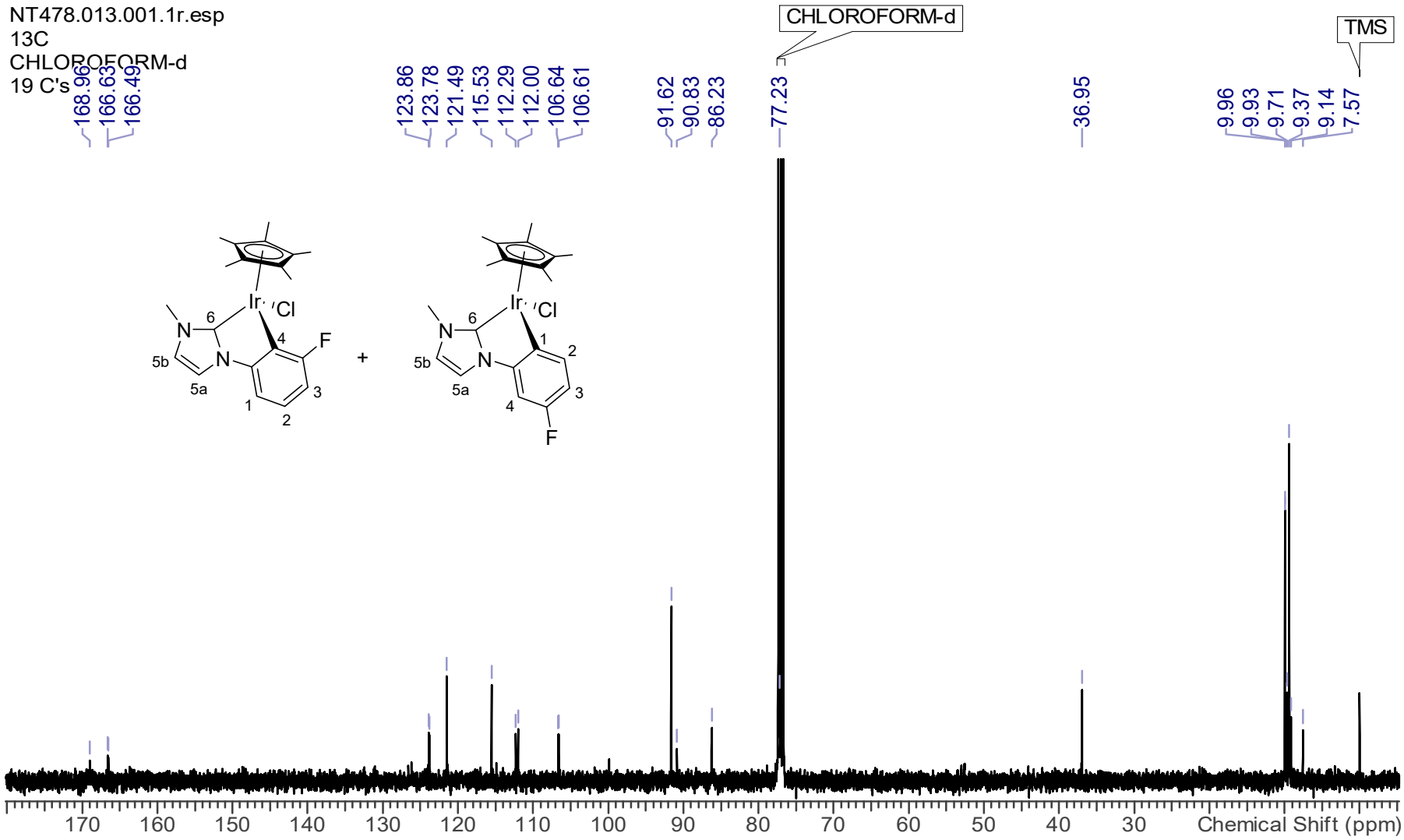
^{19}F NMR of para **4b-CF$_3$** in $CDCl_3$



^{1}H NMR of a mixture of ortho and para **4a-F** in $CDCl_3$



^{13}C NMR of a mixture of ortho and para **4a-F** in $CDCl_3$



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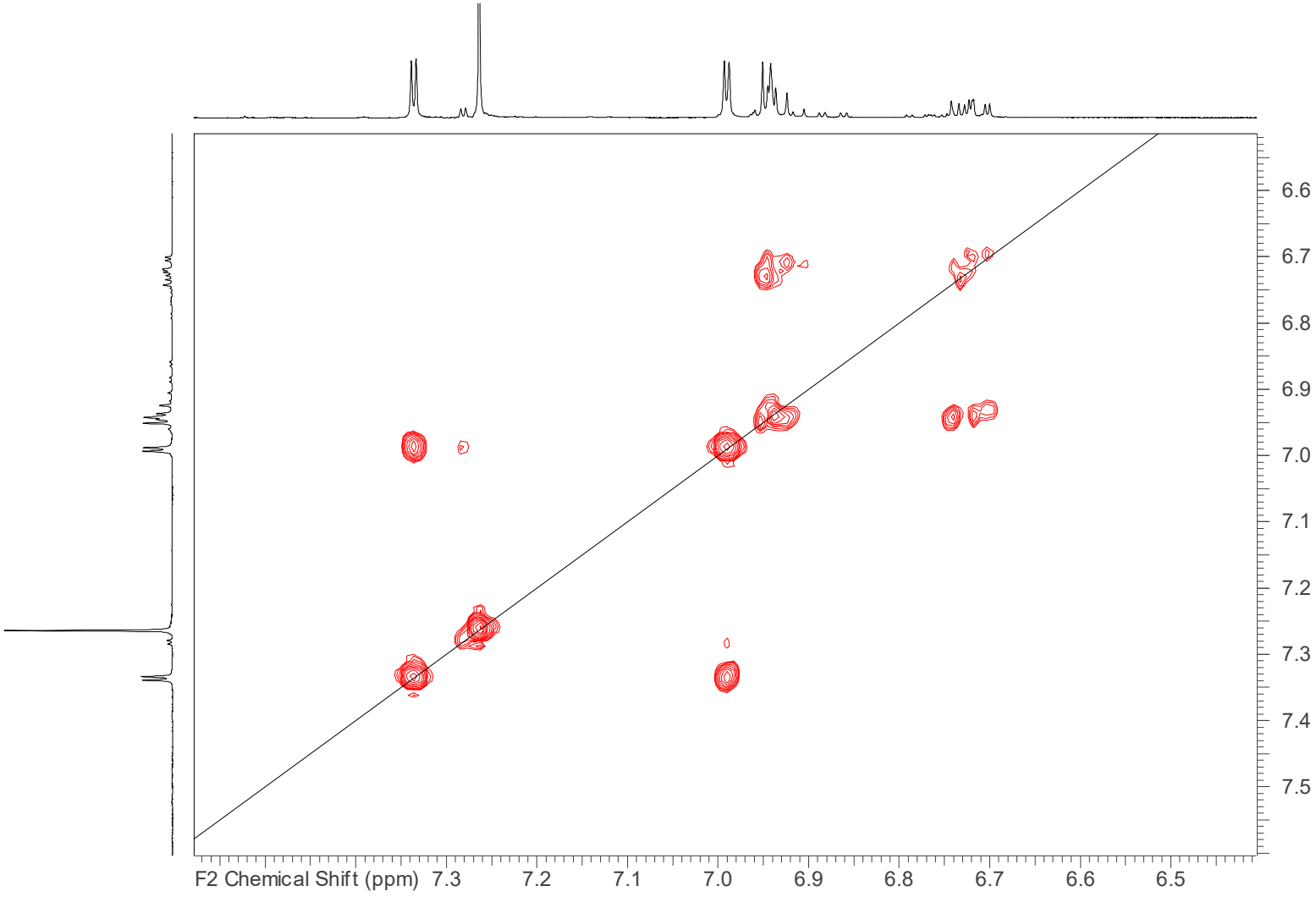
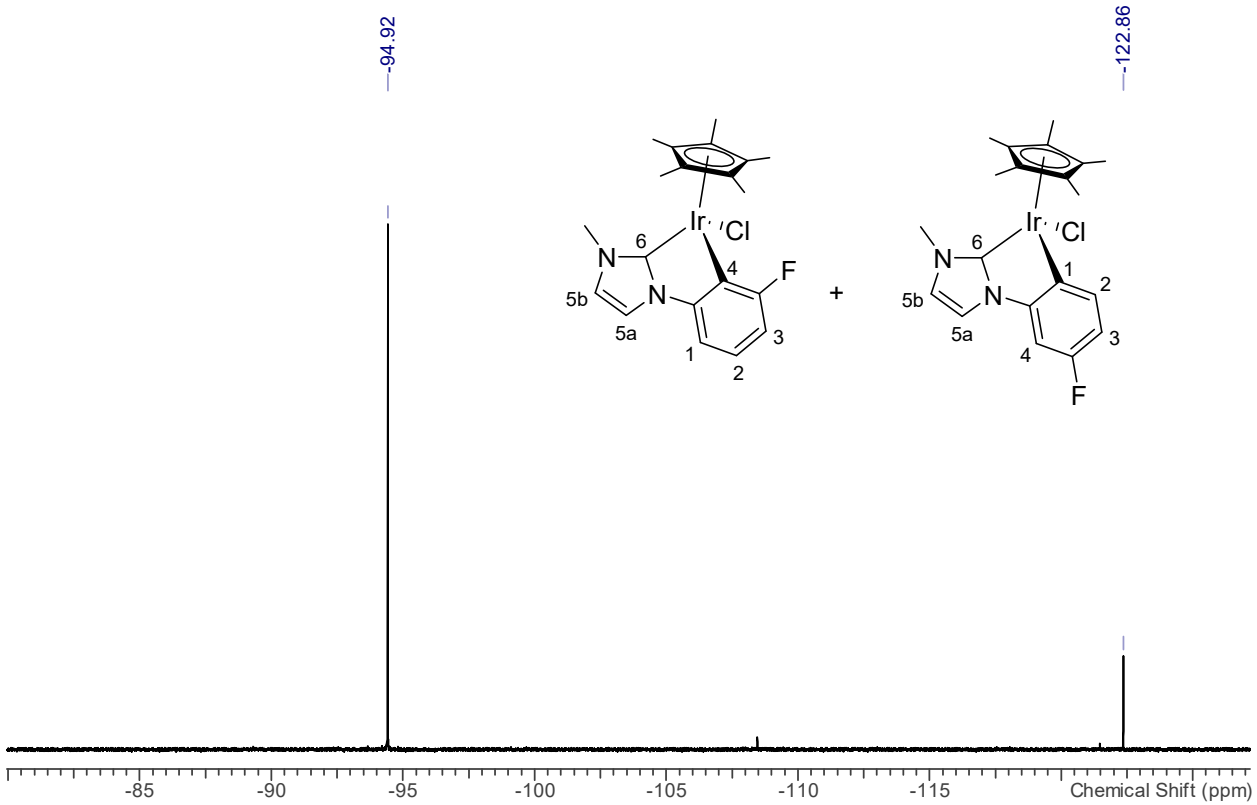
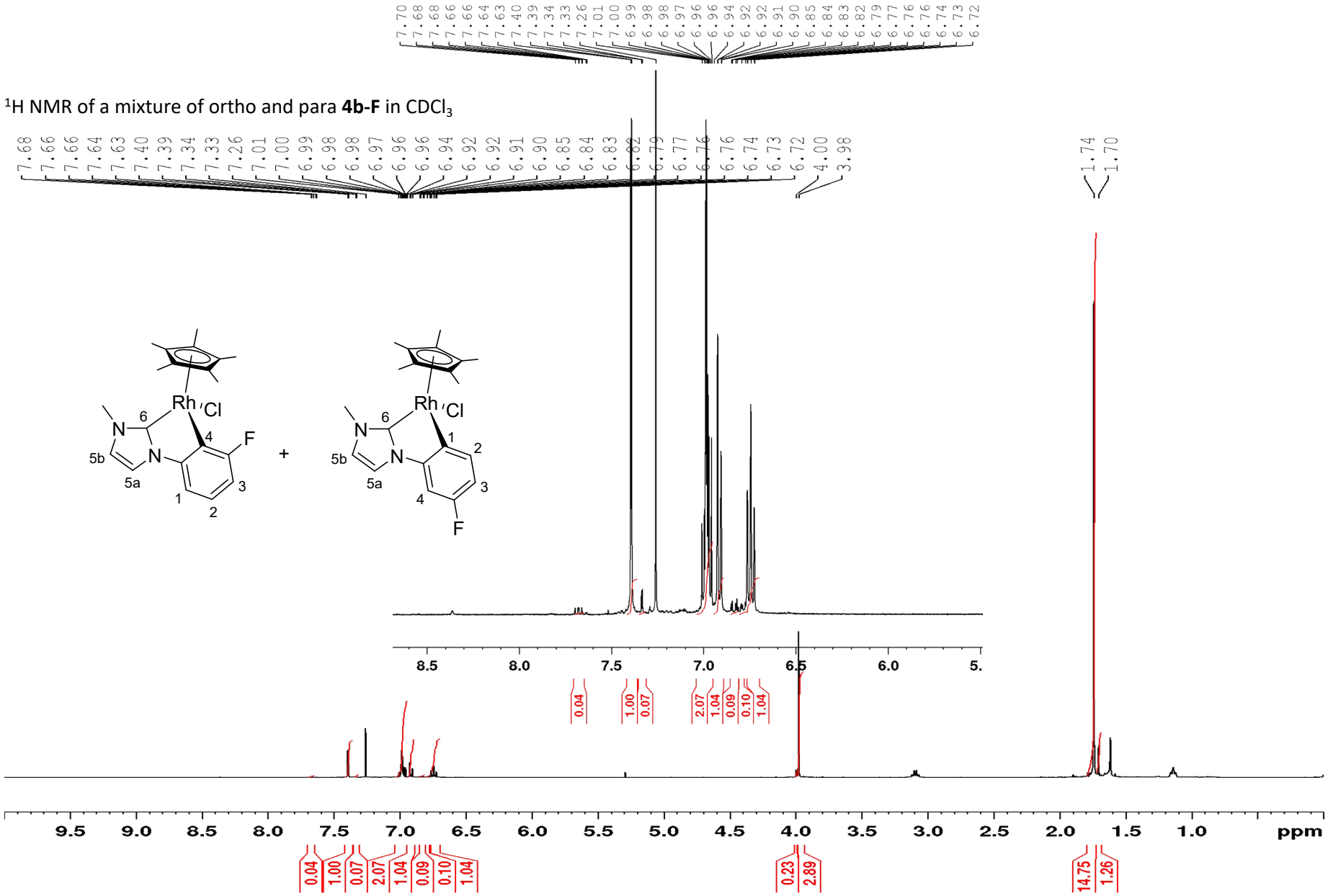


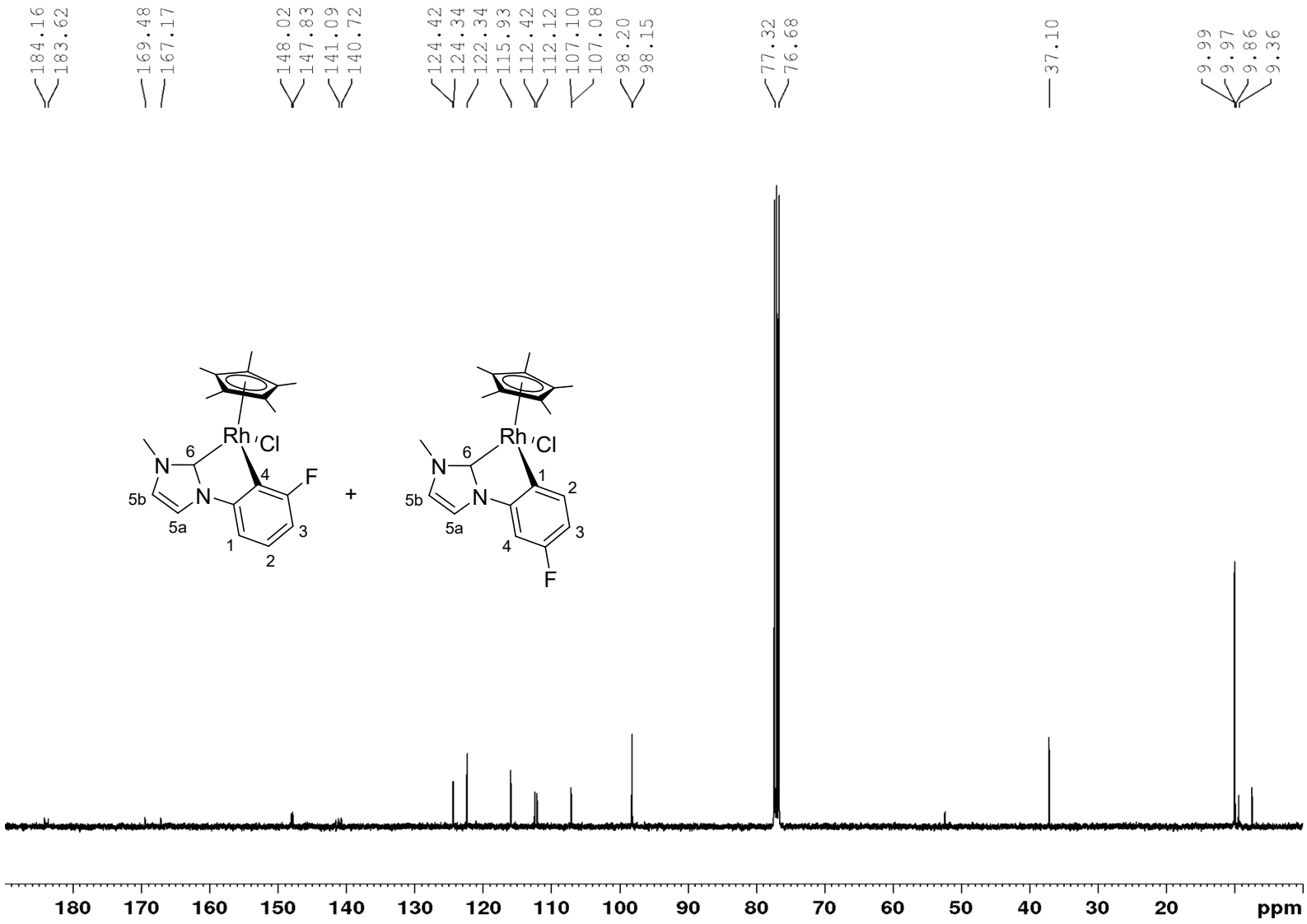
^{19}F NMR of a mixture of ortho and para **4a-F** in $CDCl_3$



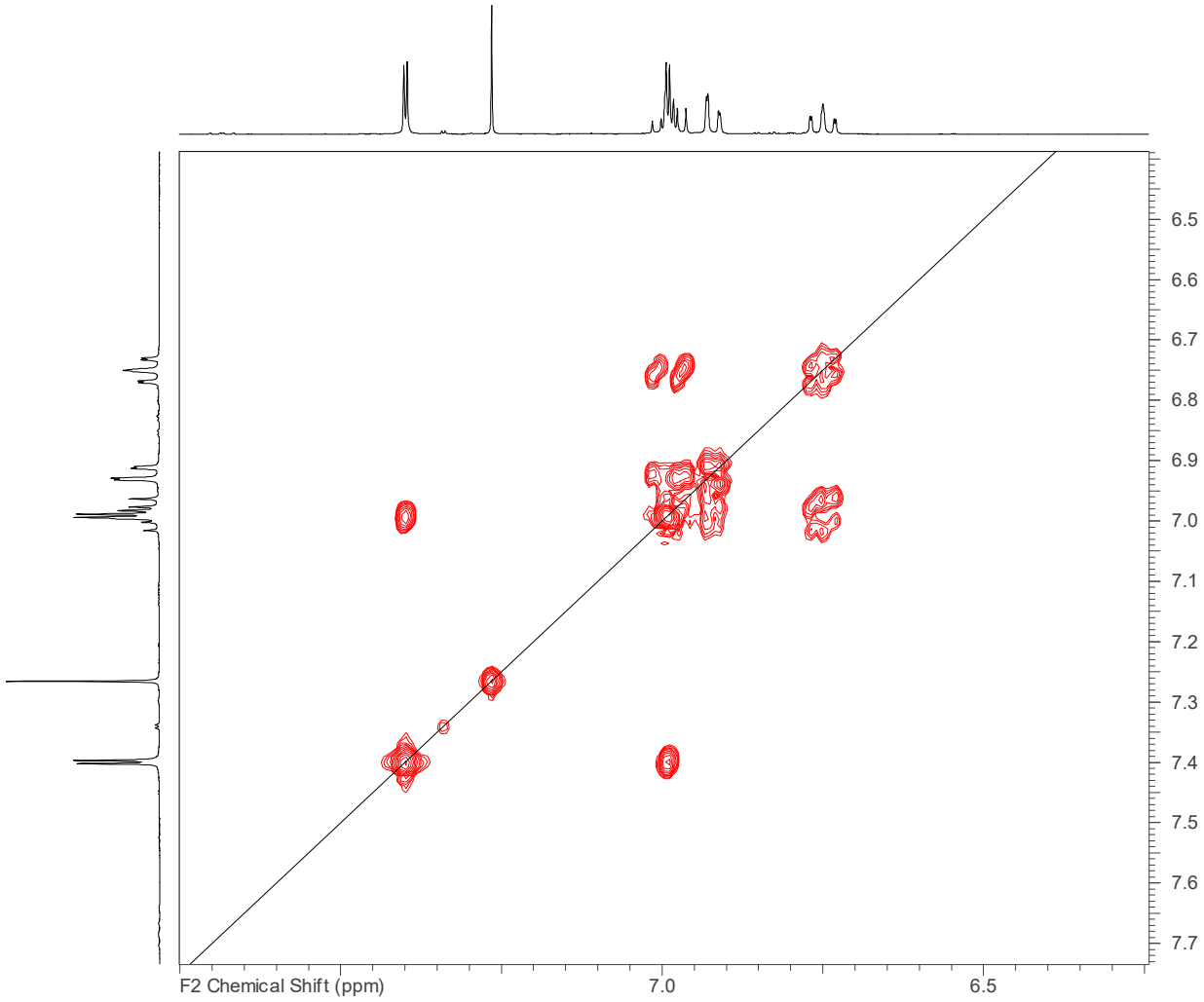
^{1}H NMR of a mixture of ortho and para **4b-F** in $CDCl_3$



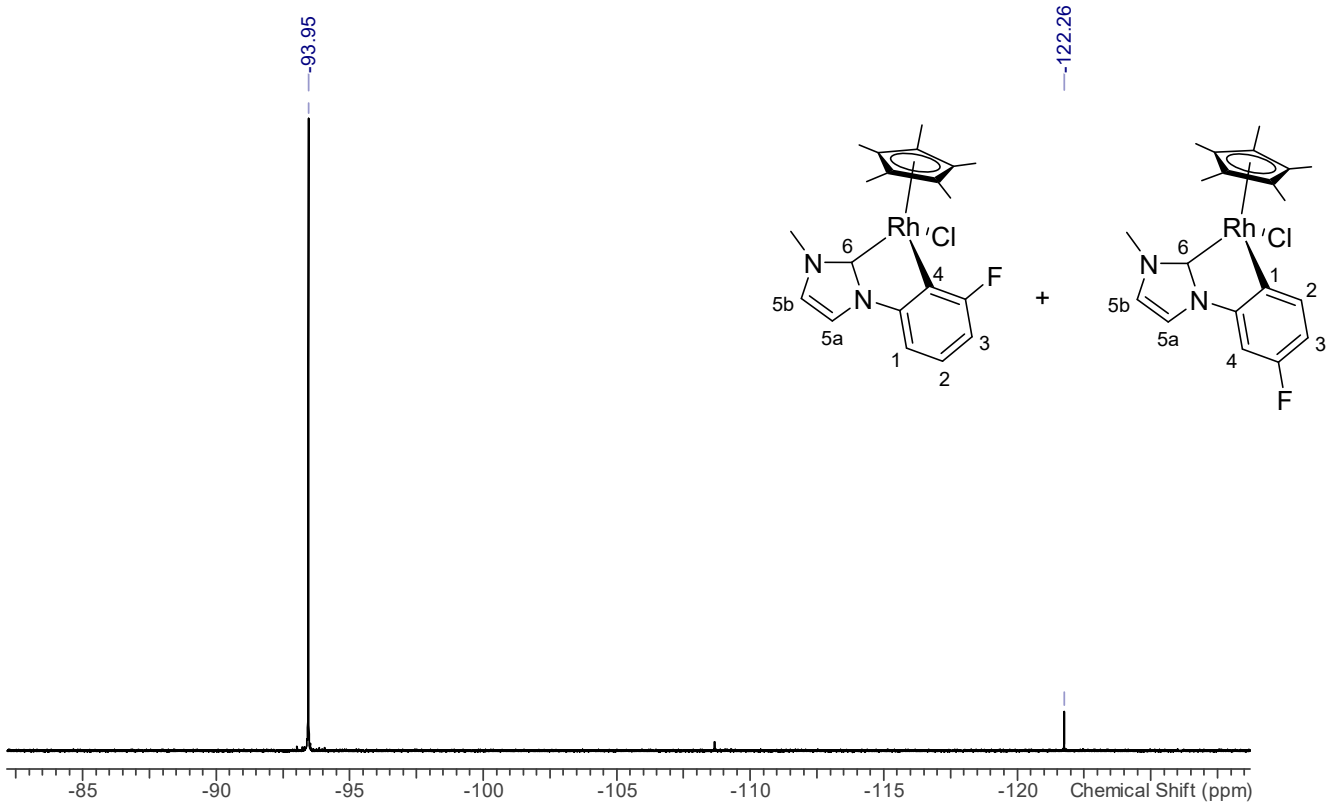
^{13}C NMR of a mixture of ortho and para **4b-F** in $CDCl_3$



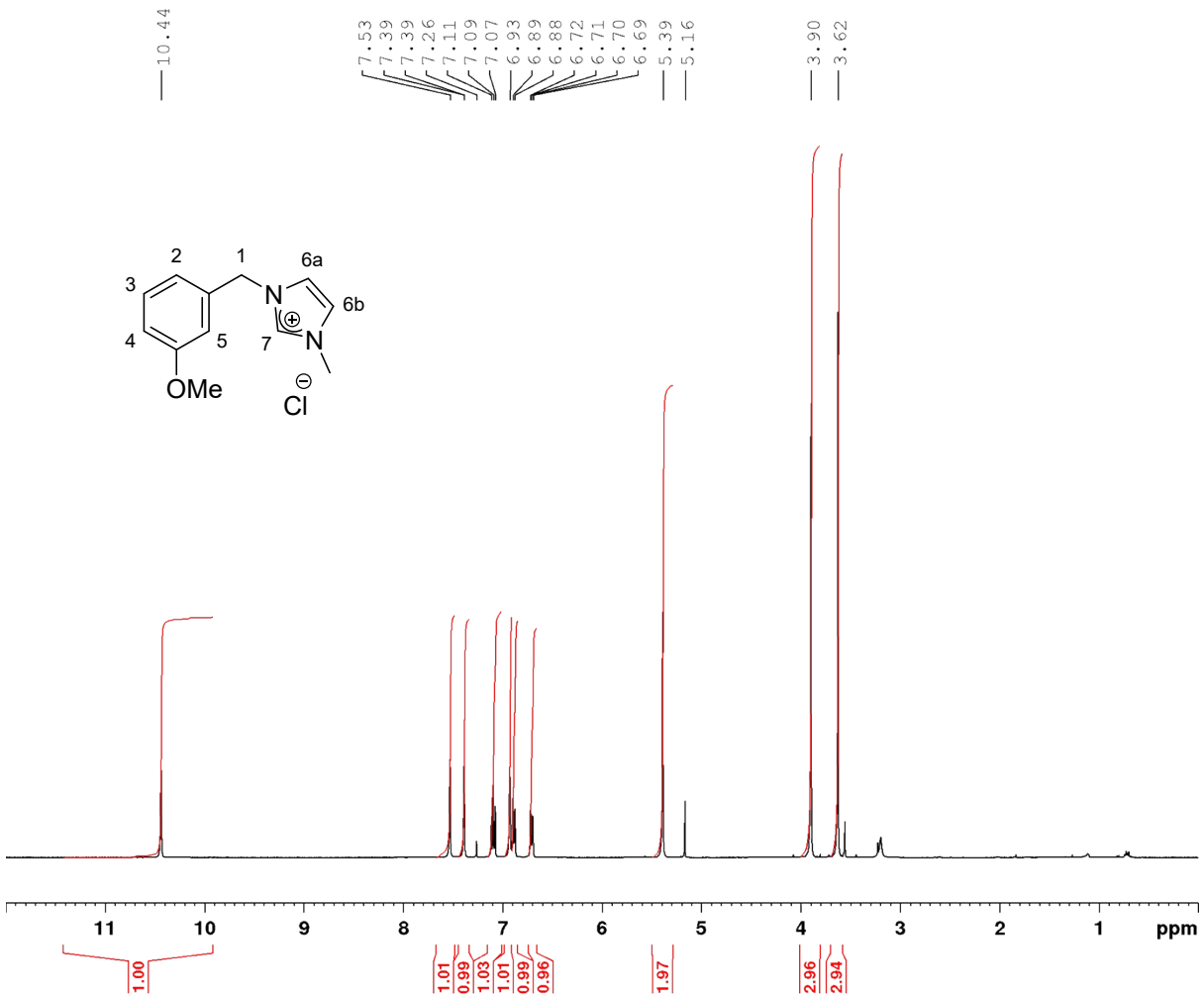
Section of COSY NMR of a mixture of ortho and para **4b-F** in $CDCl_3$



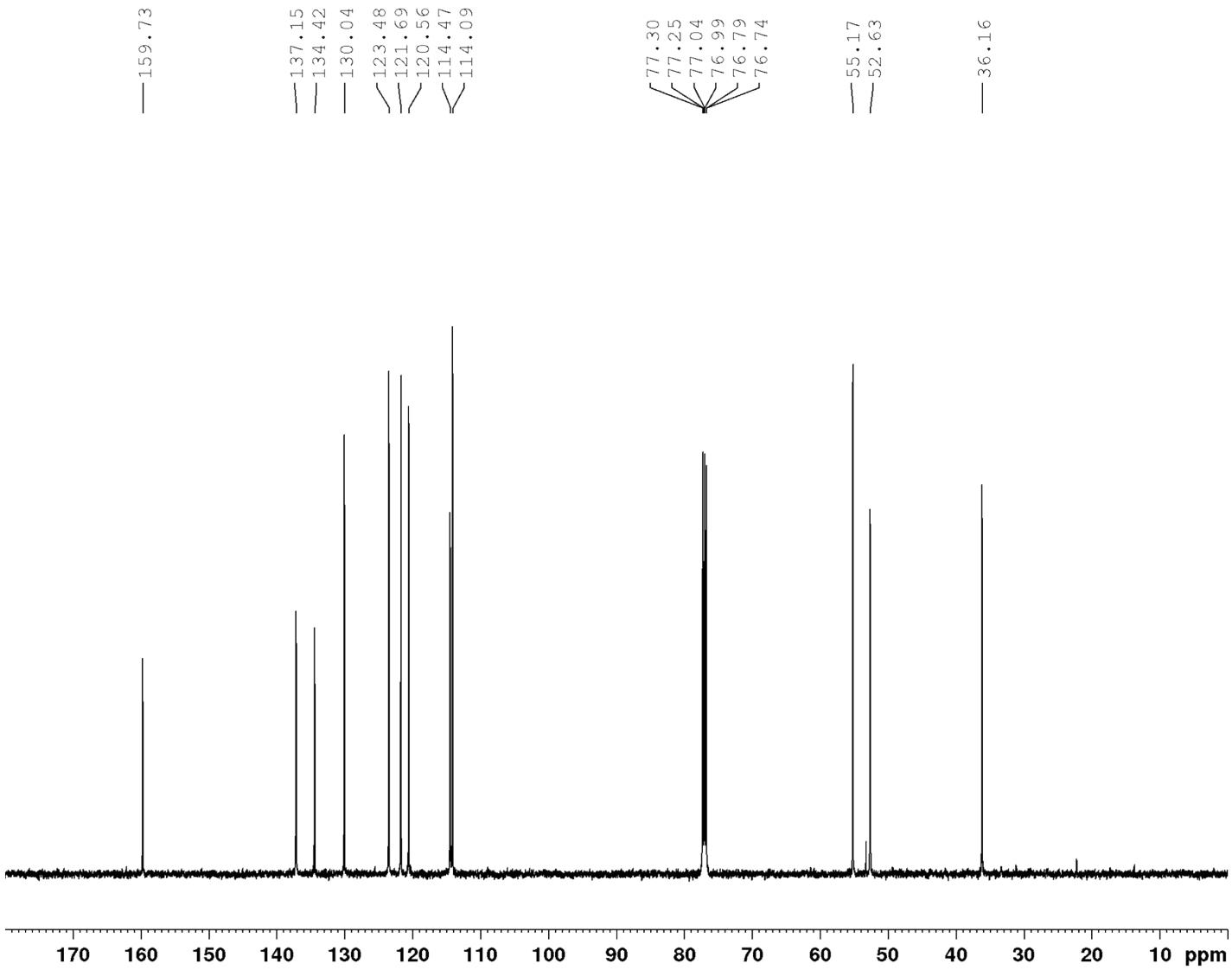
^{19}F NMR of a mixture of ortho and para **4b-F** in $CDCl_3$



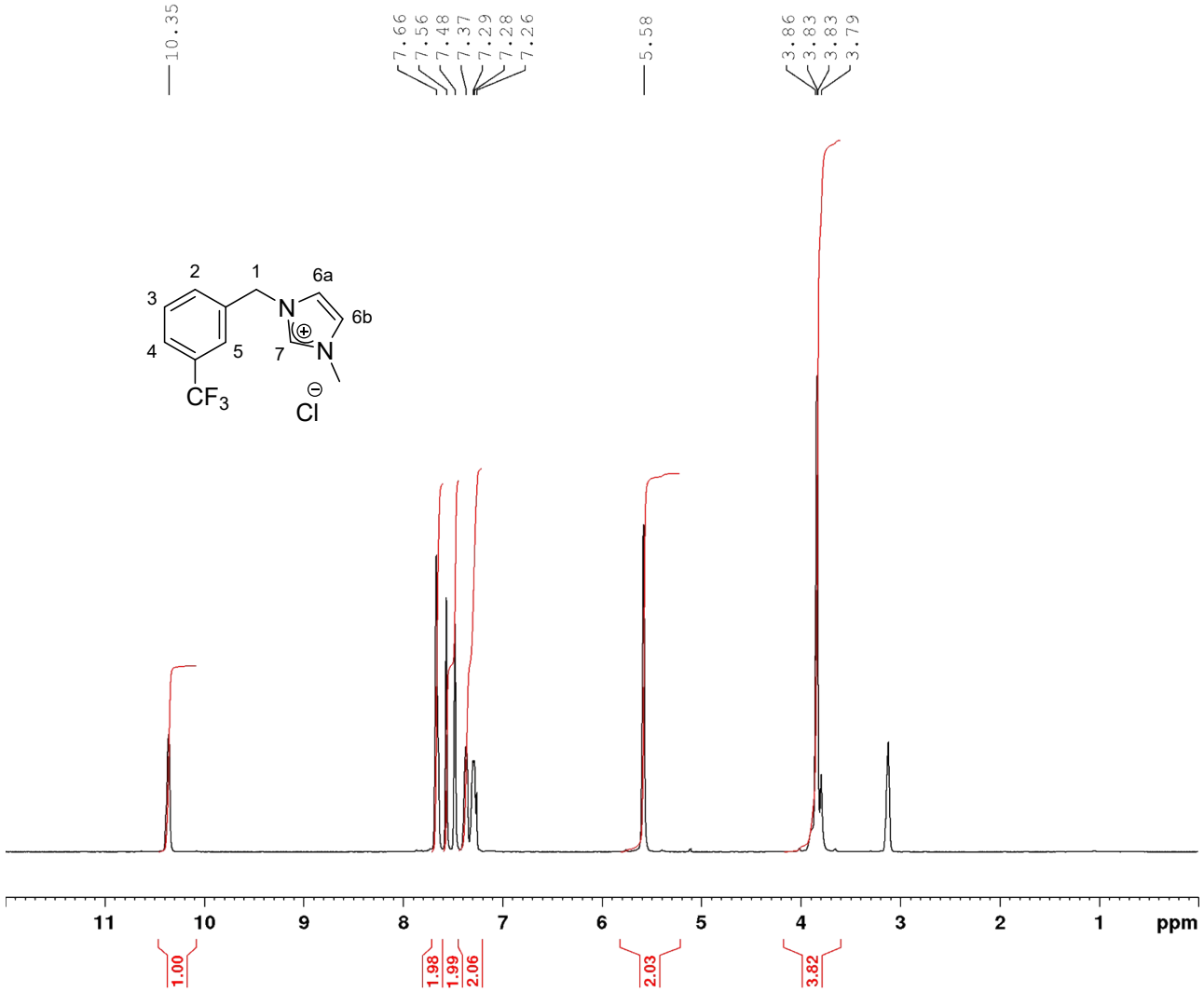
^{1}H NMR of **L5-OMe** in $CDCl_3$



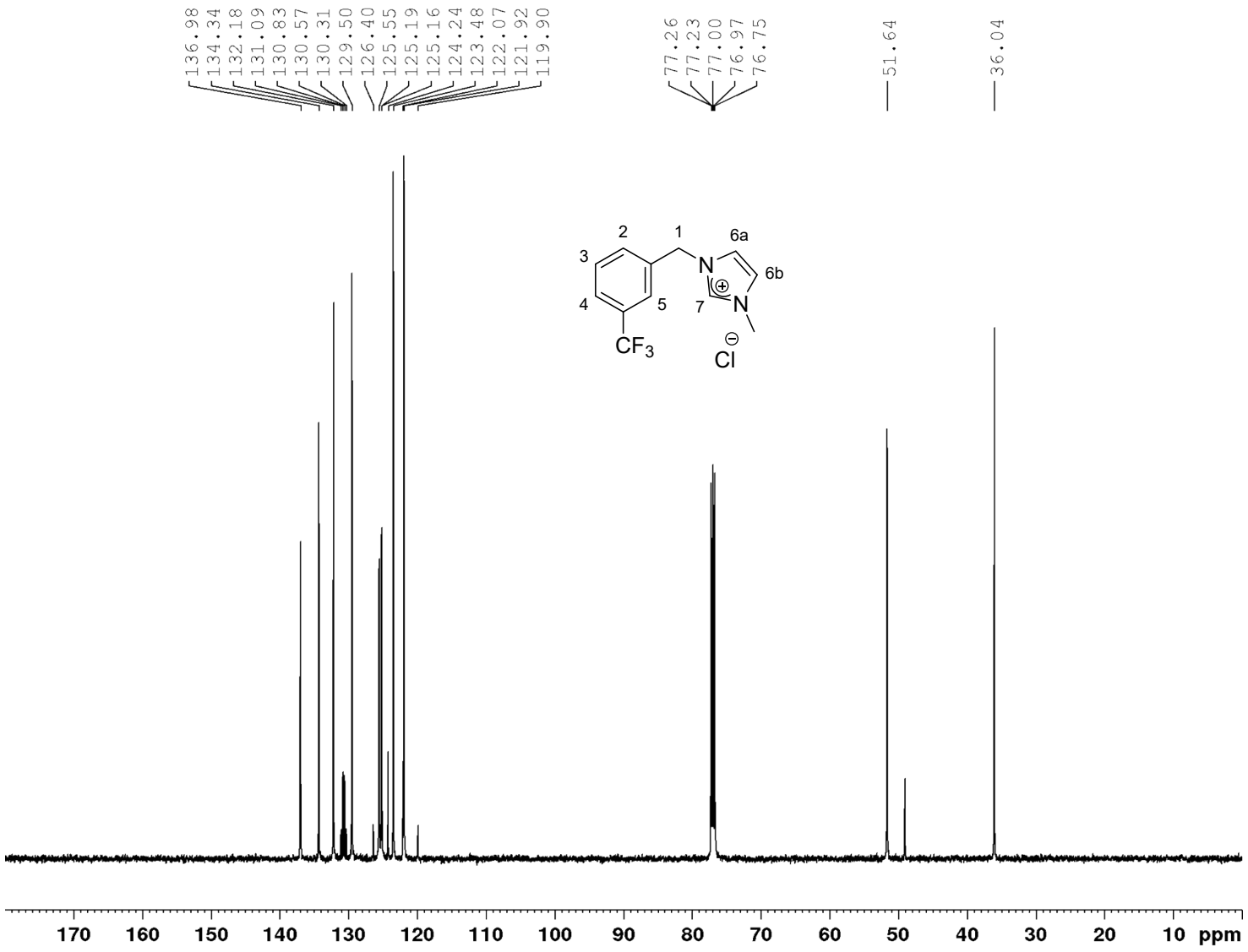
^{13}C NMR of **L5-OMe** in $CDCl_3$



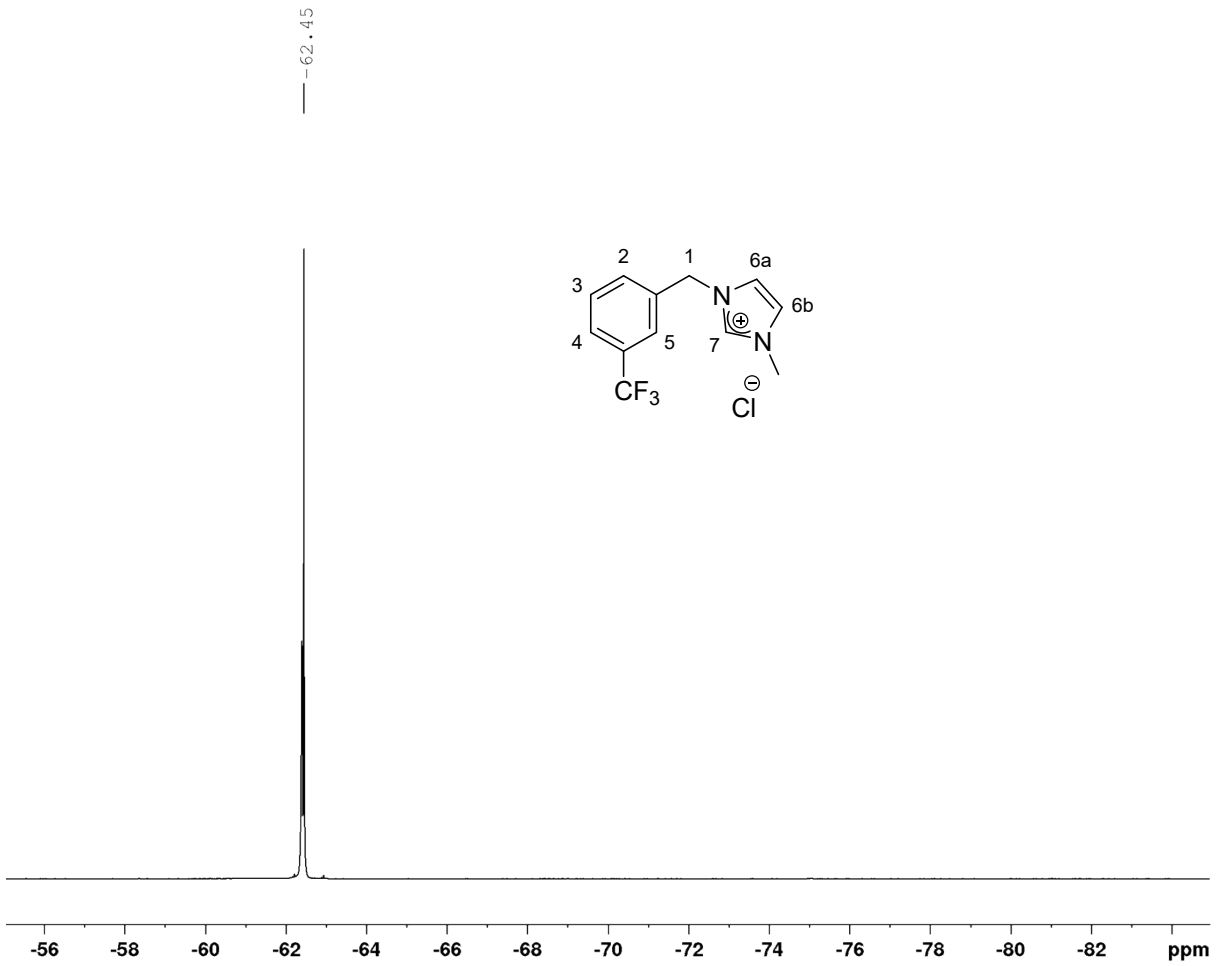
^{1}H NMR of **L5-CF$_3$** in CDCl$_3$



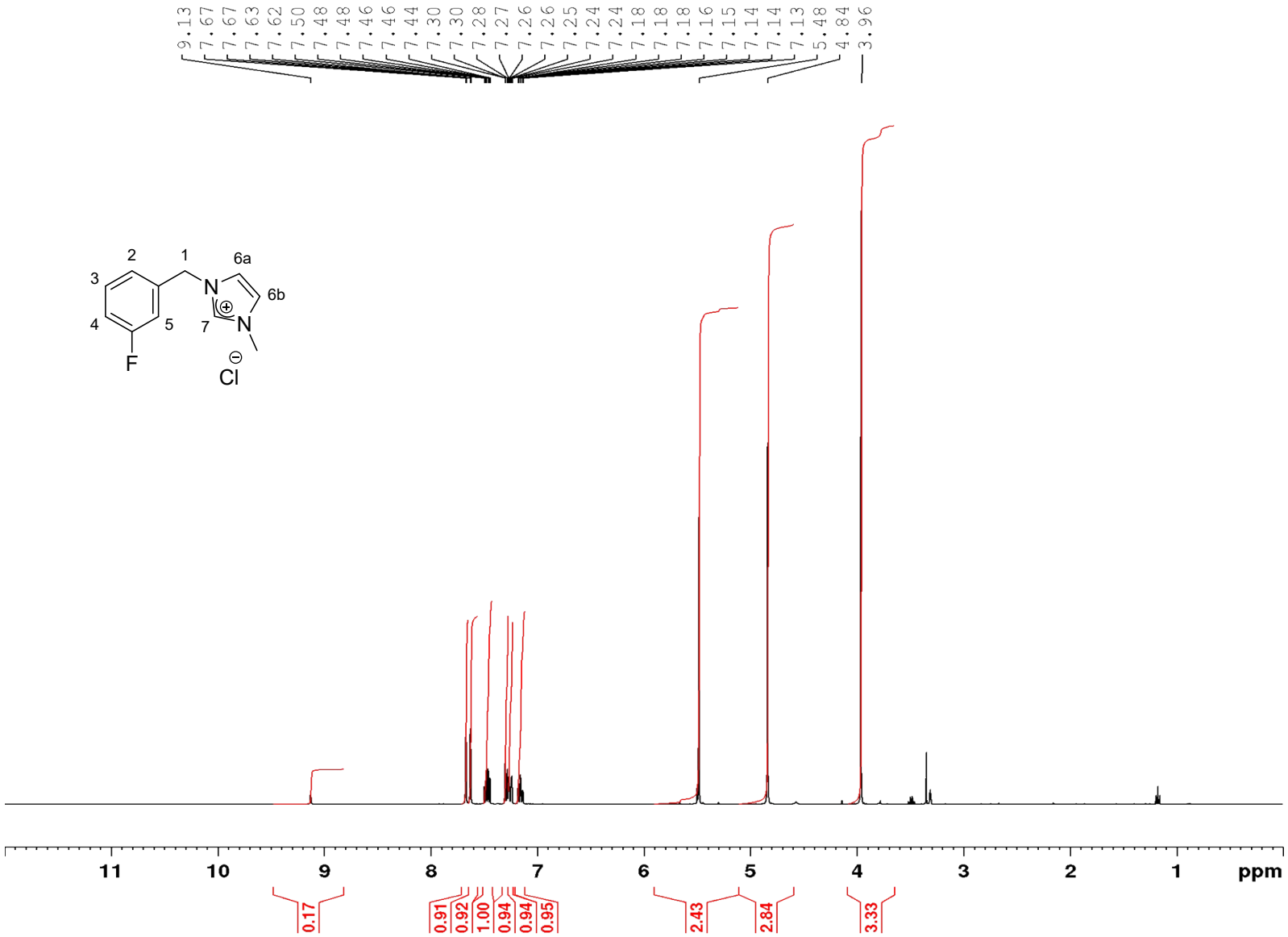
^{13}C NMR of **L5-CF$_3$** in $CDCl_3$



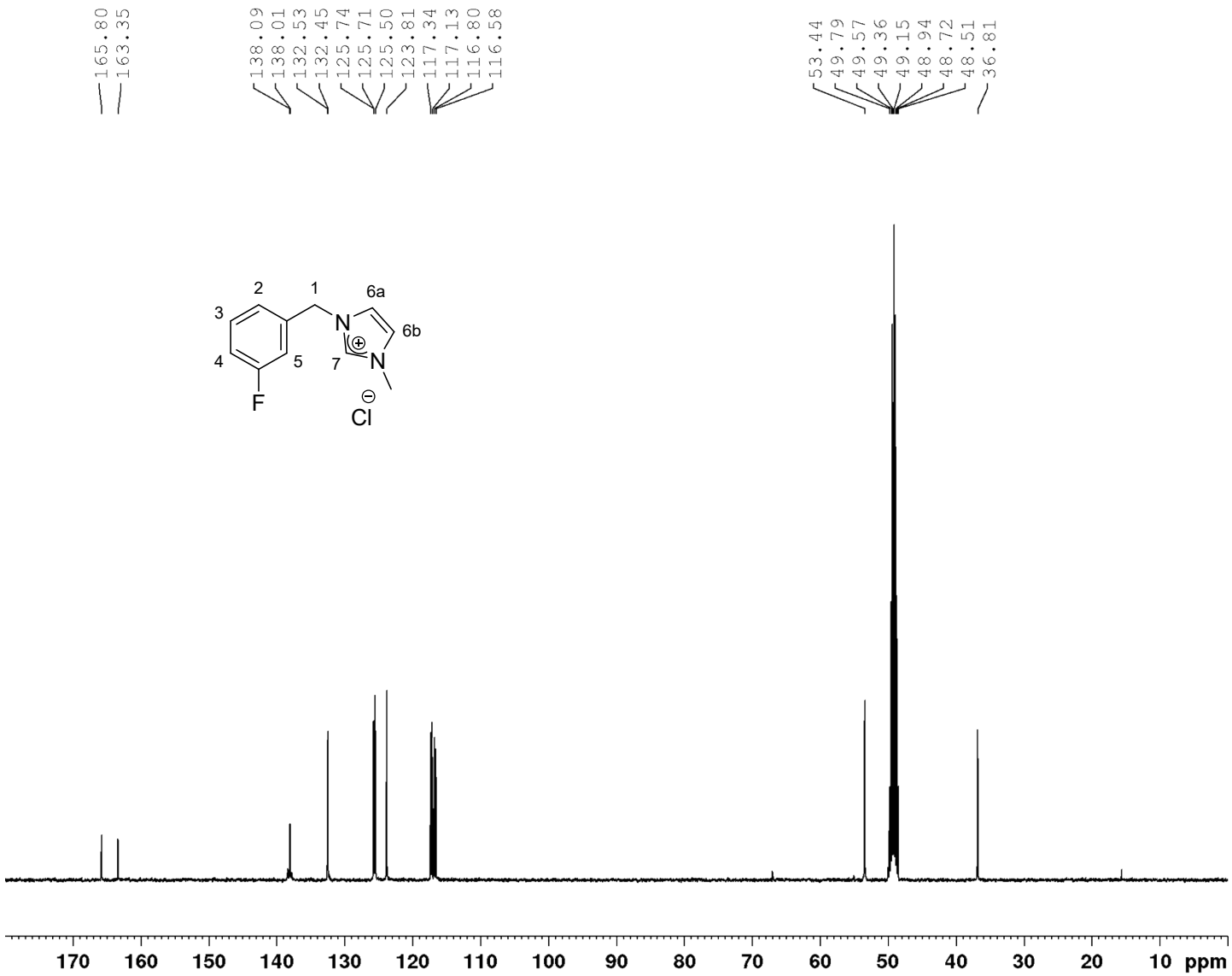
^{19}F NMR of **L5-CF$_3$** in $CDCl_3$



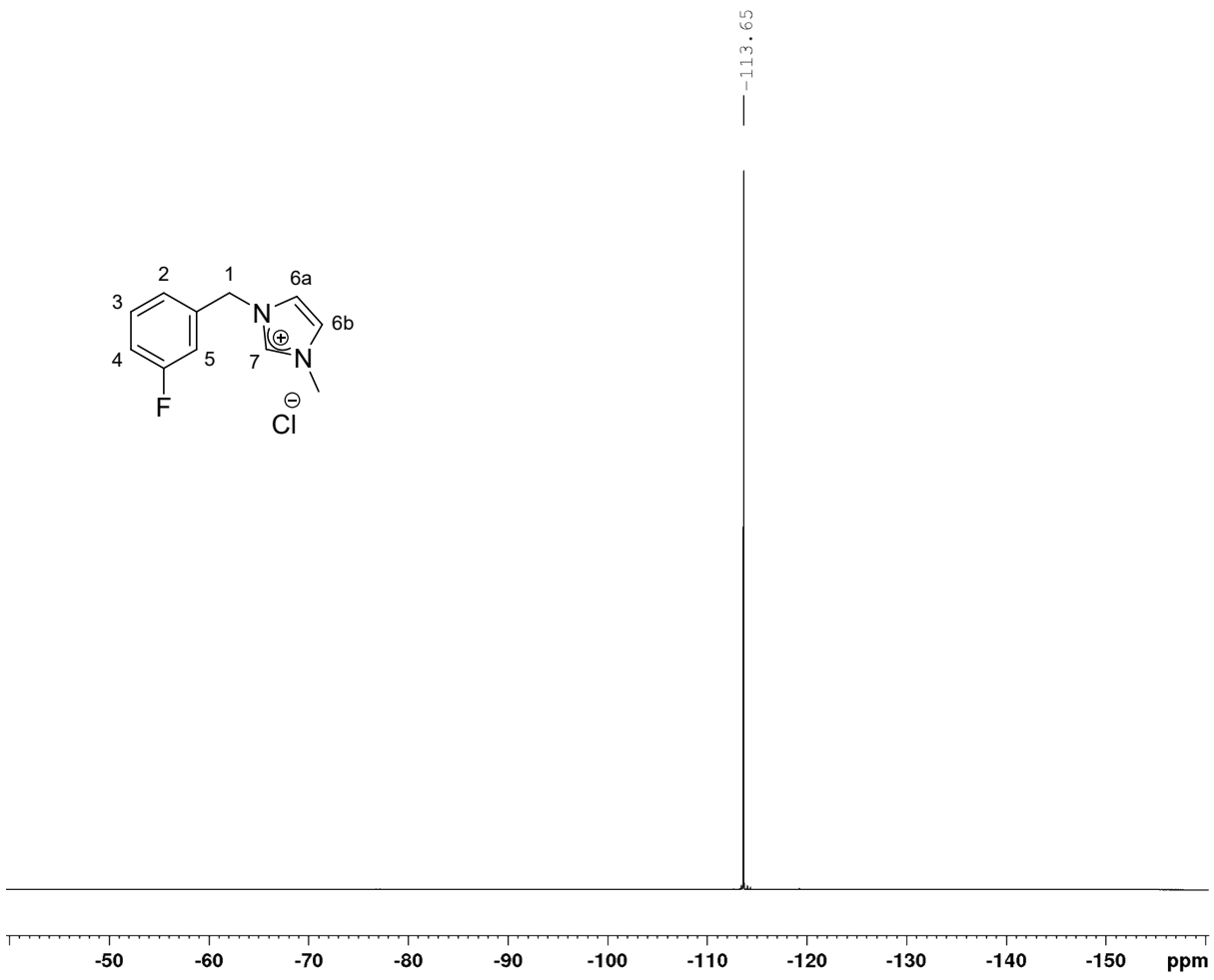
^{1}H NMR of **L5-F** in CD_3OD



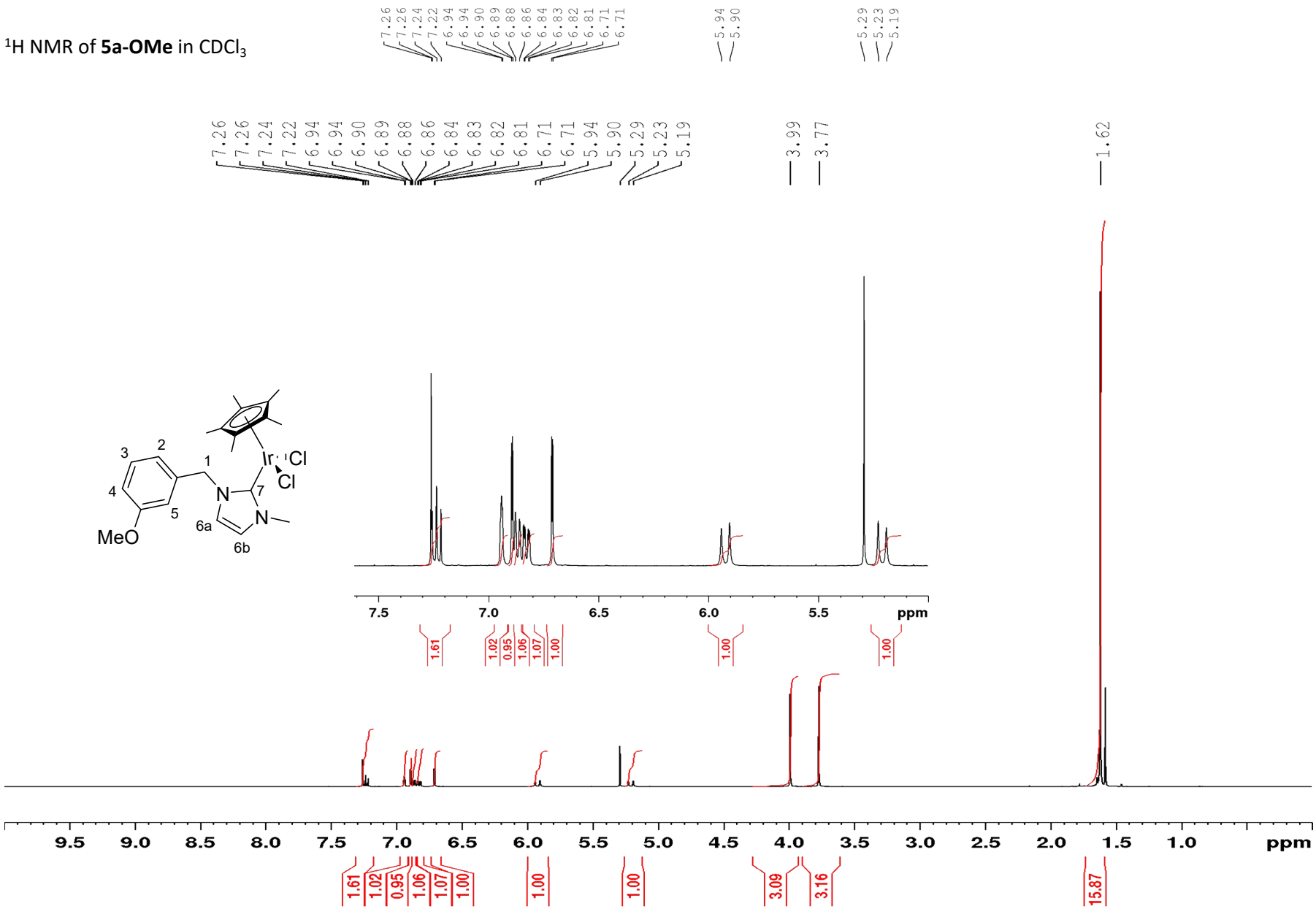
^{13}C NMR of **L5-F** in CD_3OD



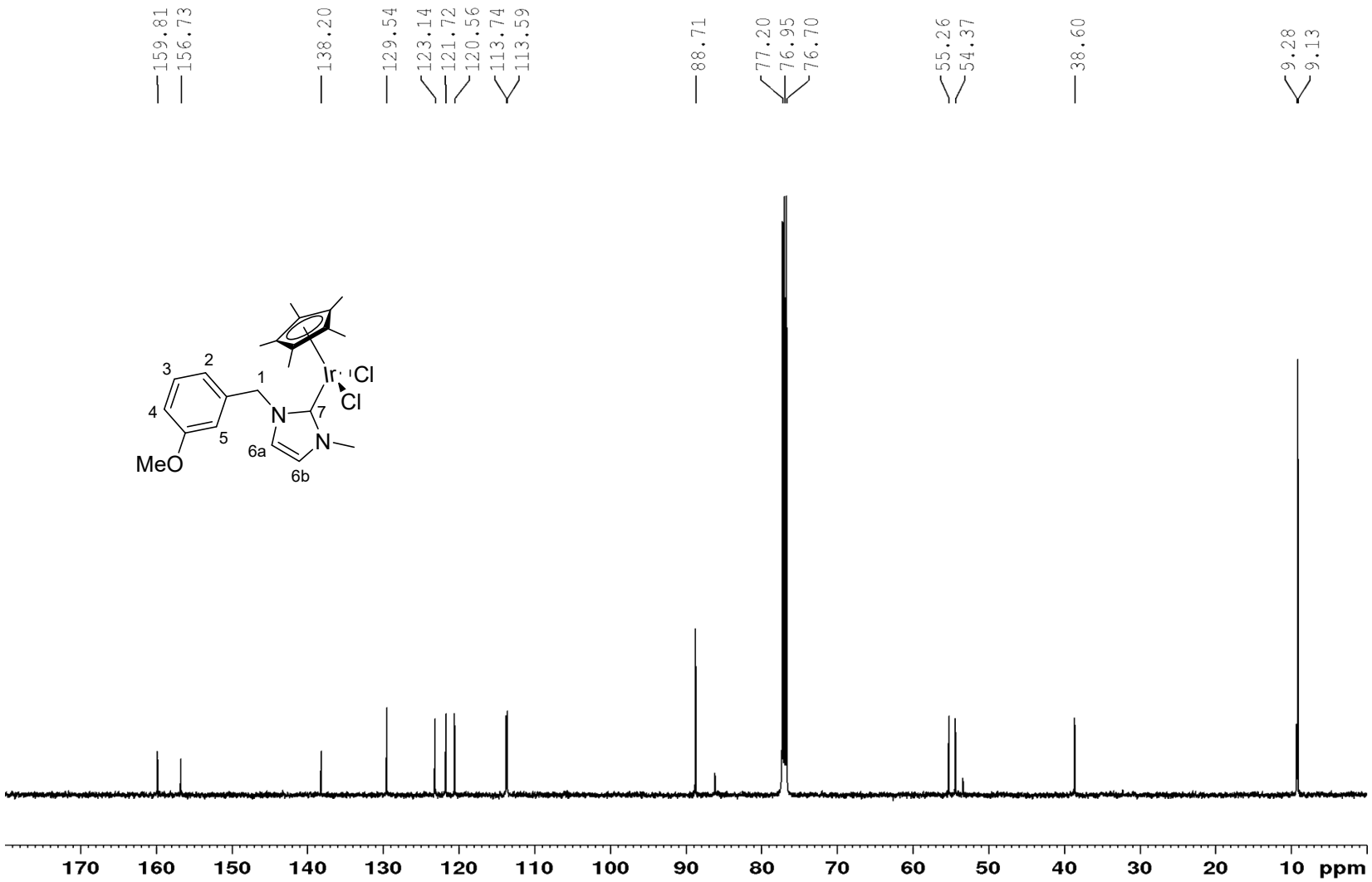
^{19}F NMR of **L5-F** in CD_3OD



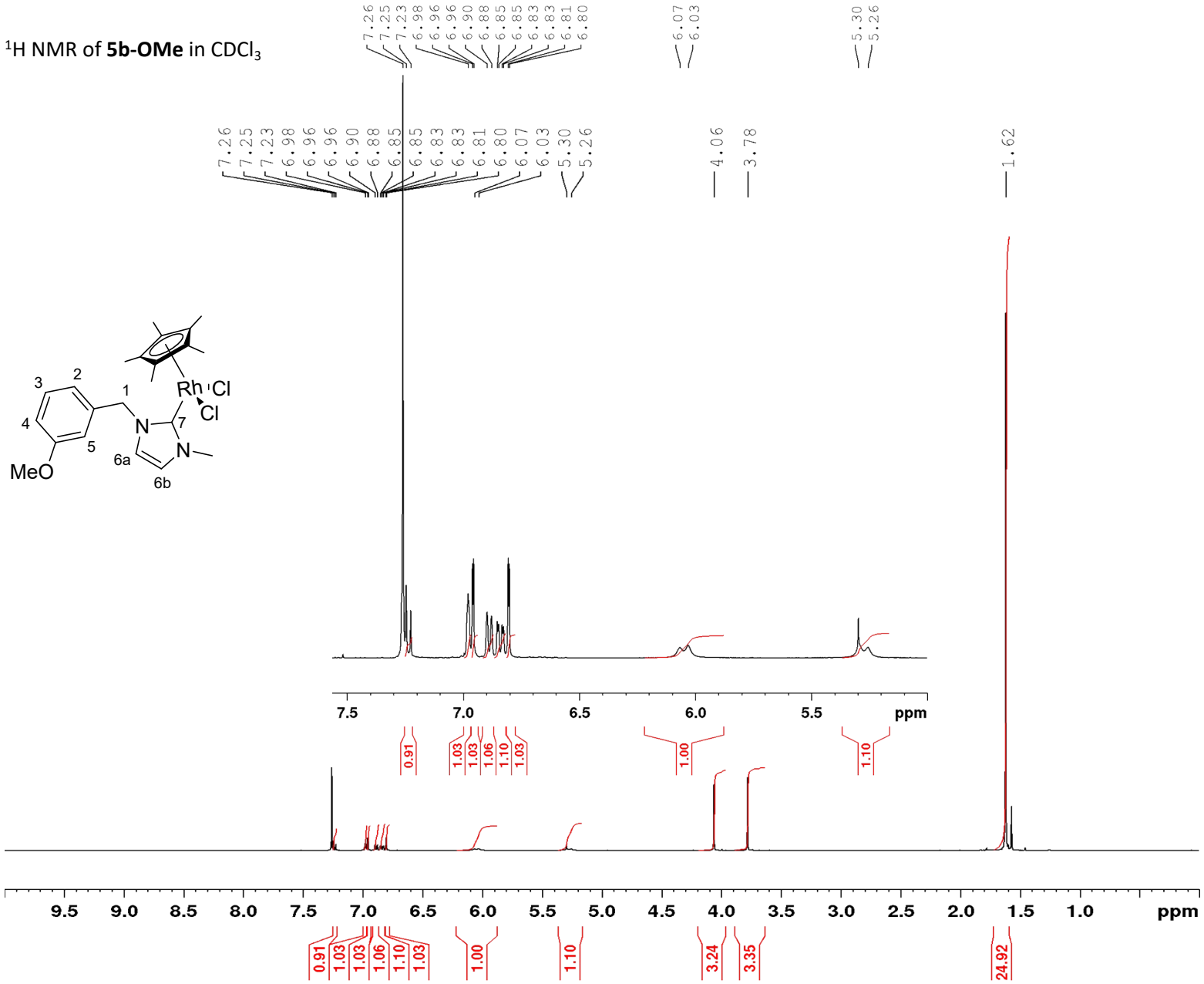
^{1}H NMR of **5a-OMe** in $CDCl_3$



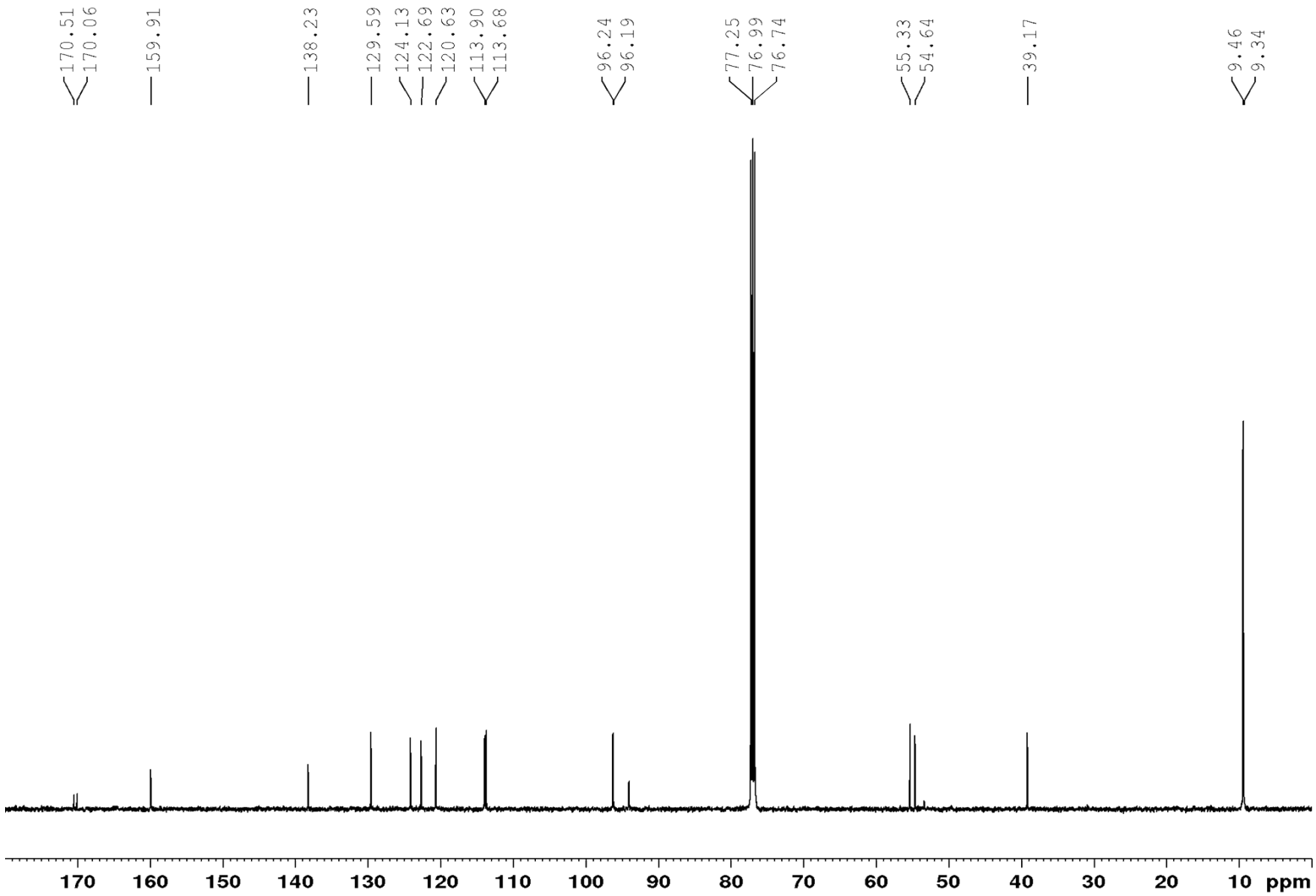
^{13}C NMR of **5a-OMe** in $CDCl_3$



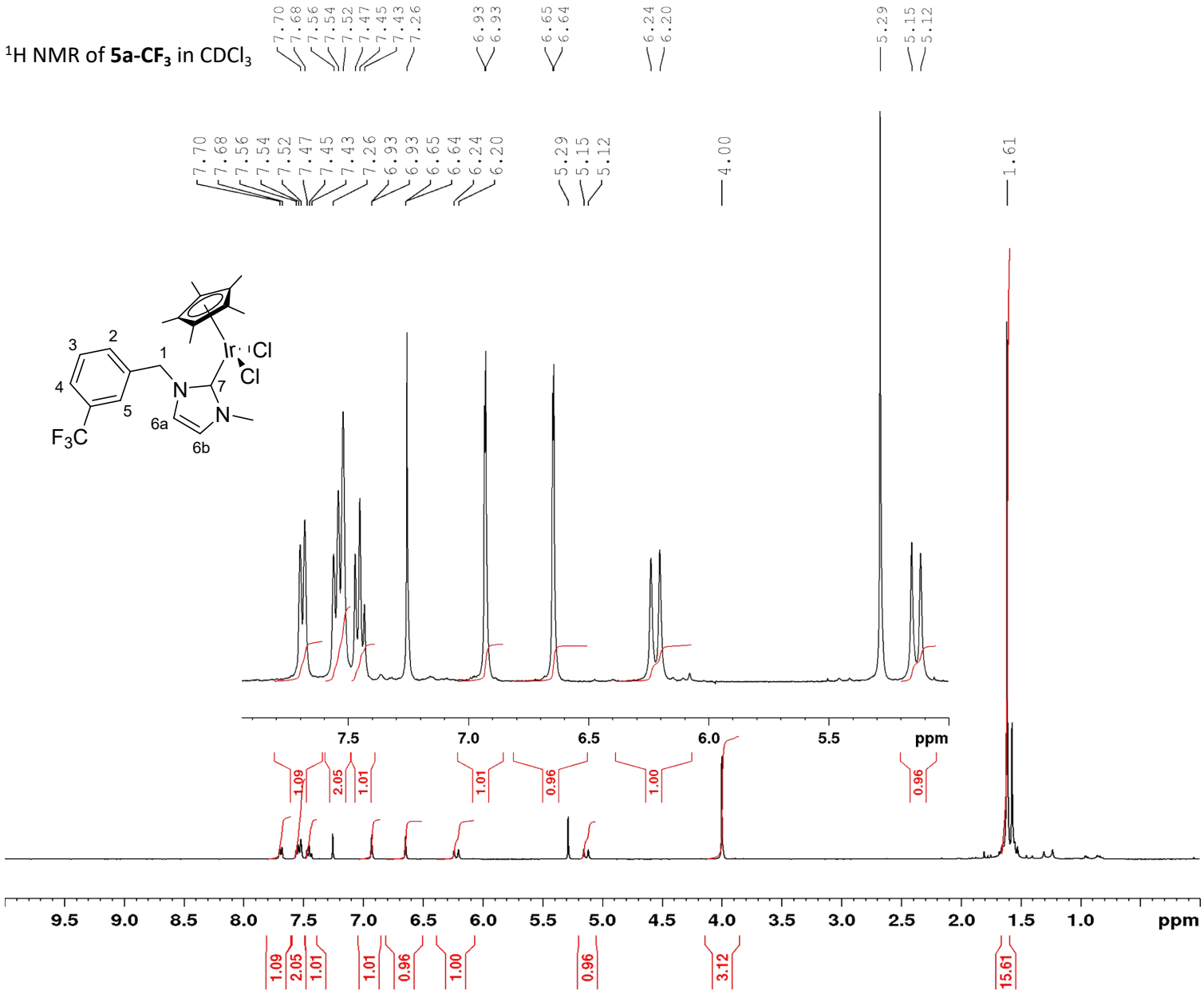
^{1}H NMR of **5b-OMe** in $CDCl_3$



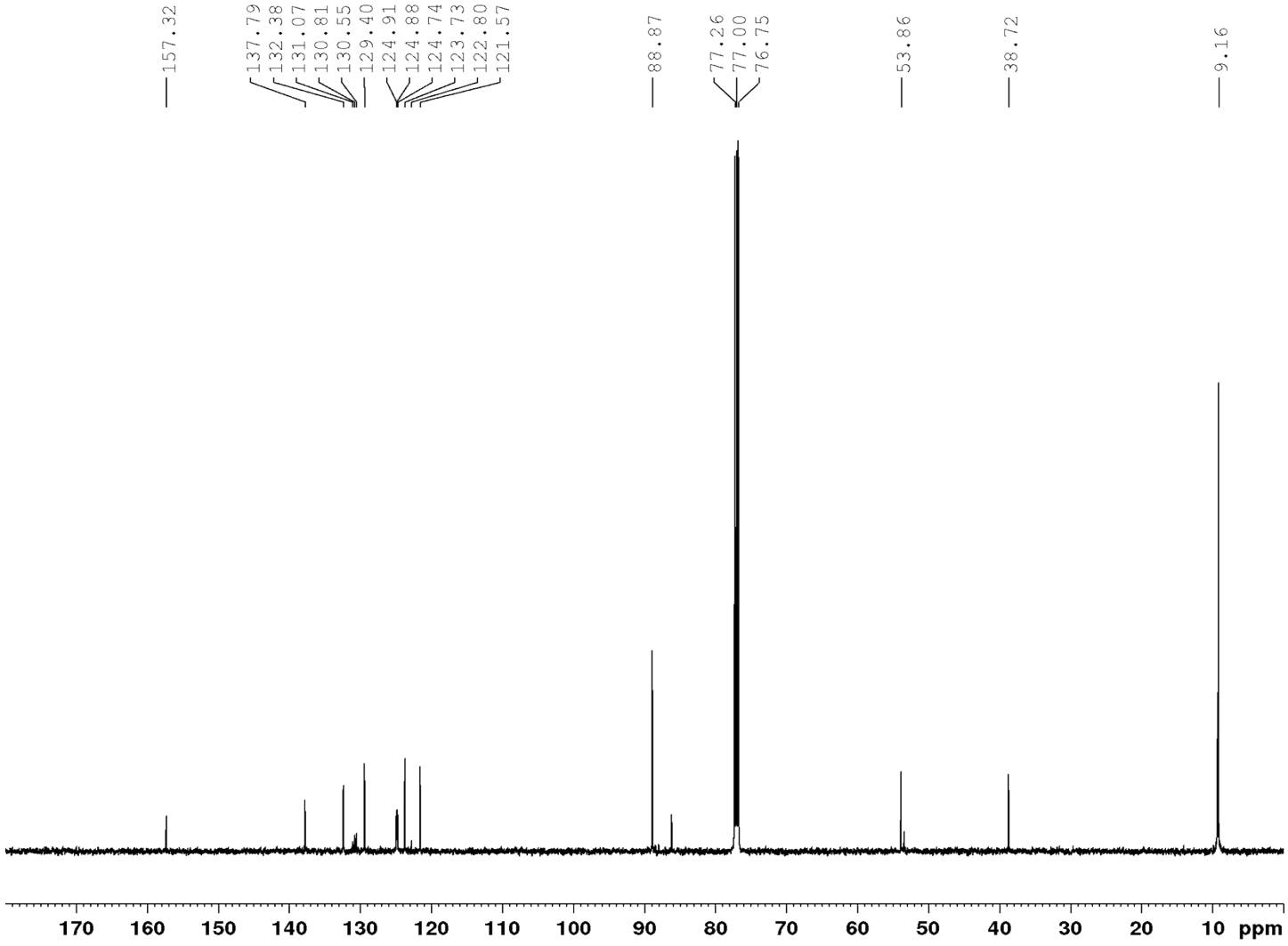
^{13}C NMR of **5b-OMe** in $CDCl_3$



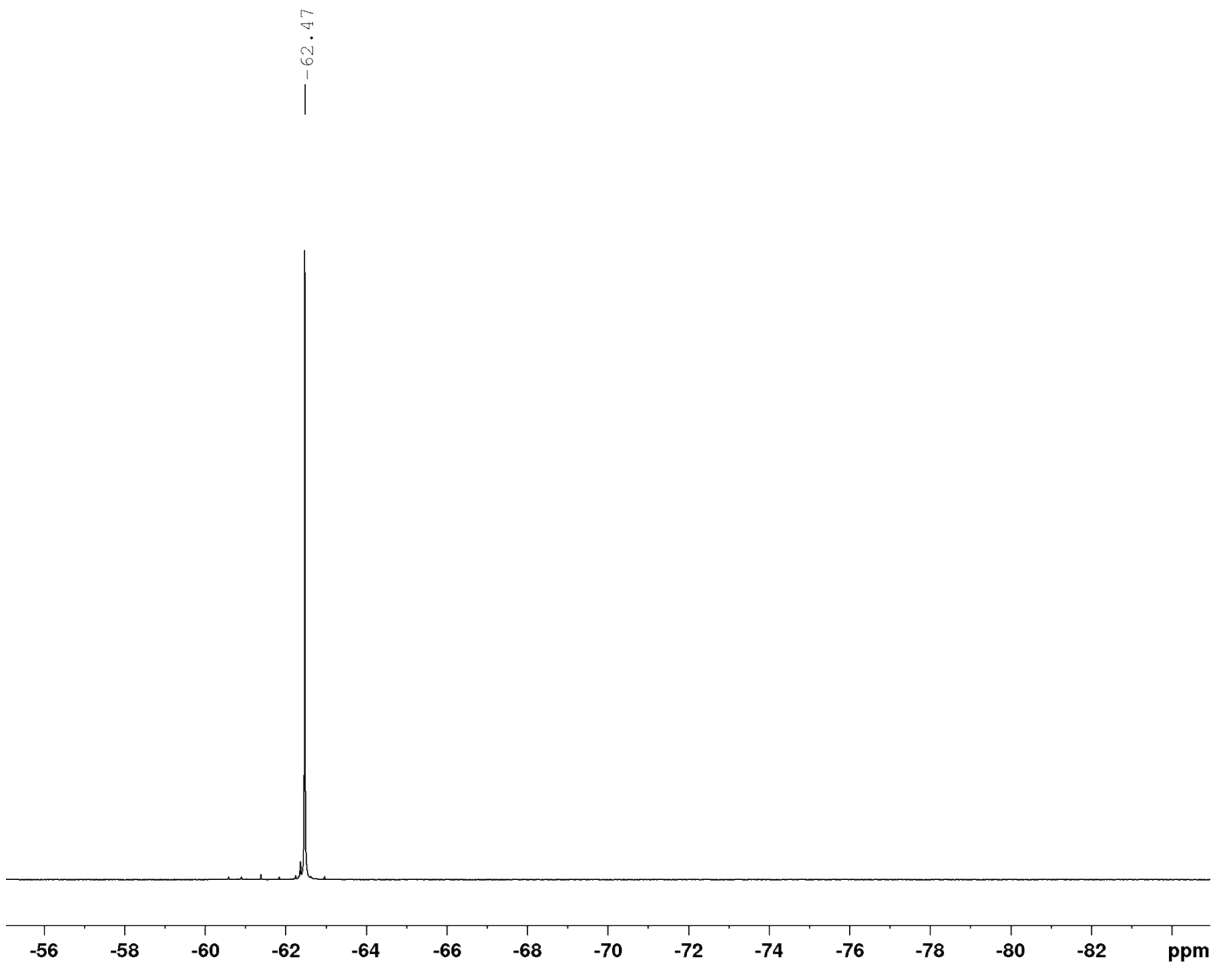
^{1}H NMR of **5a-CF$_3$** in $CDCl_3$



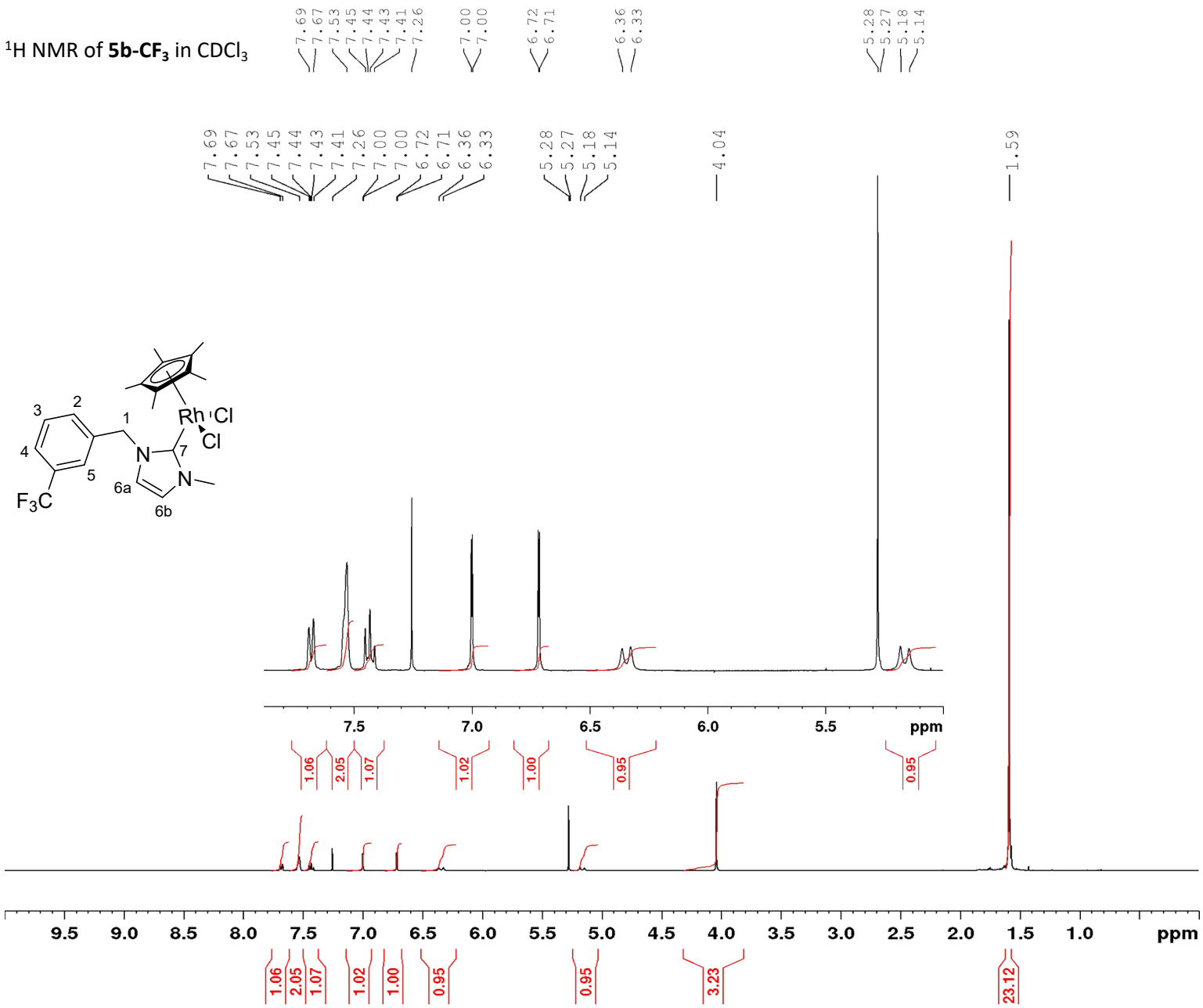
^{13}C NMR of **5a-CF$_3$** in $CDCl_3$



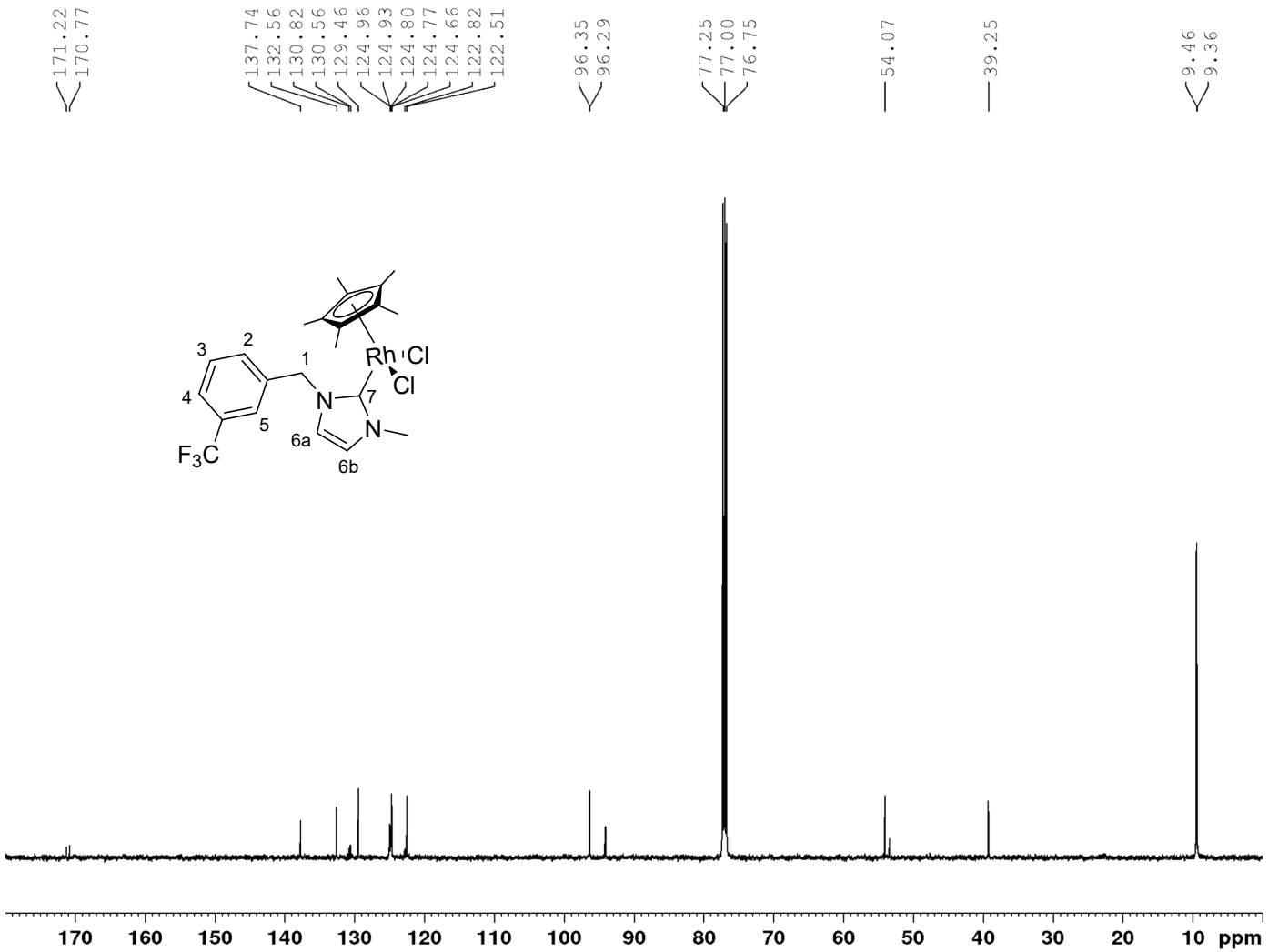
^{19}F NMR of **5a-CF_3** in $CDCl_3$



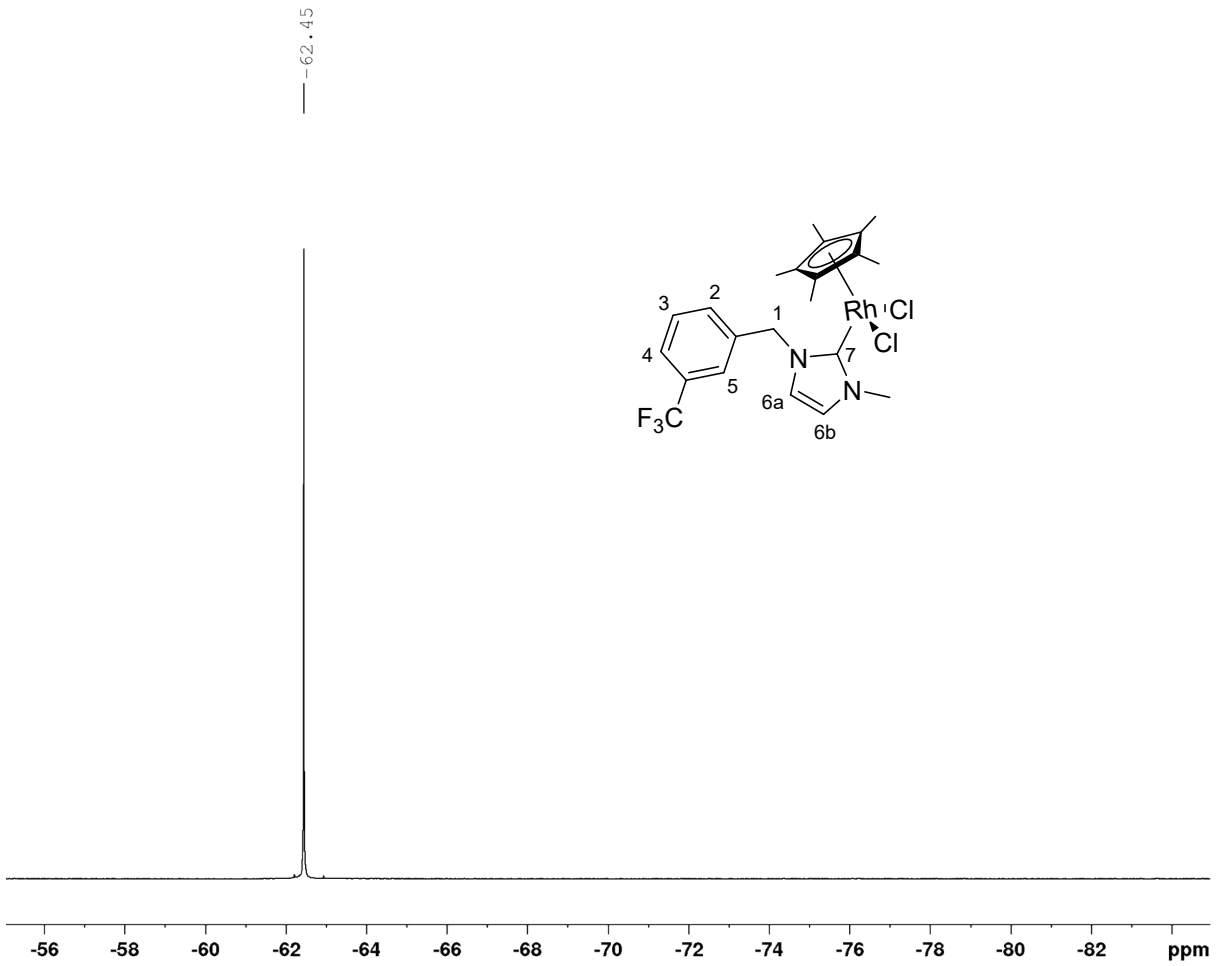
^{1}H NMR of **5b-CF$_3$** in $CDCl_3$



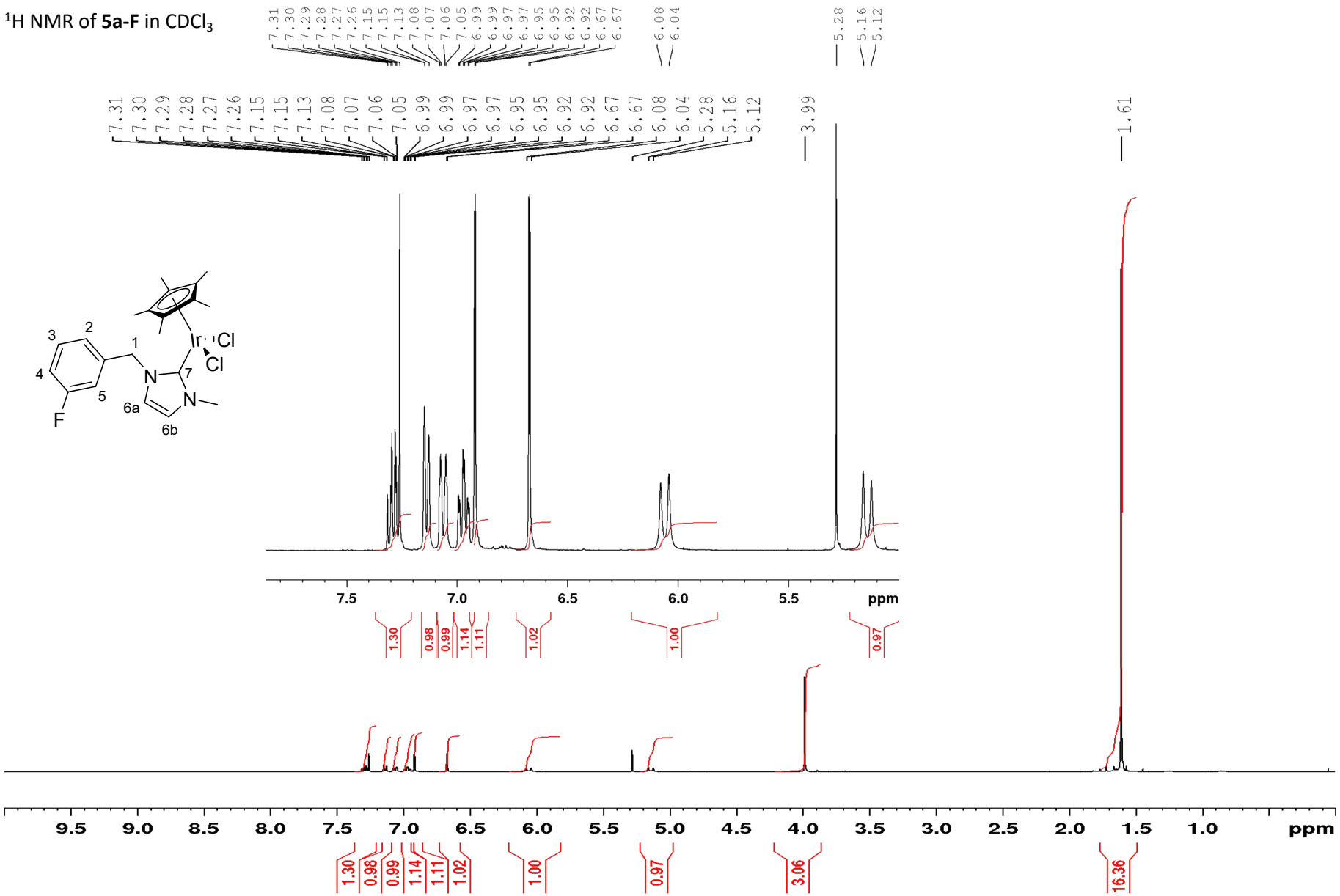
^{13}C NMR of **5b-CF$_3$** in $CDCl_3$



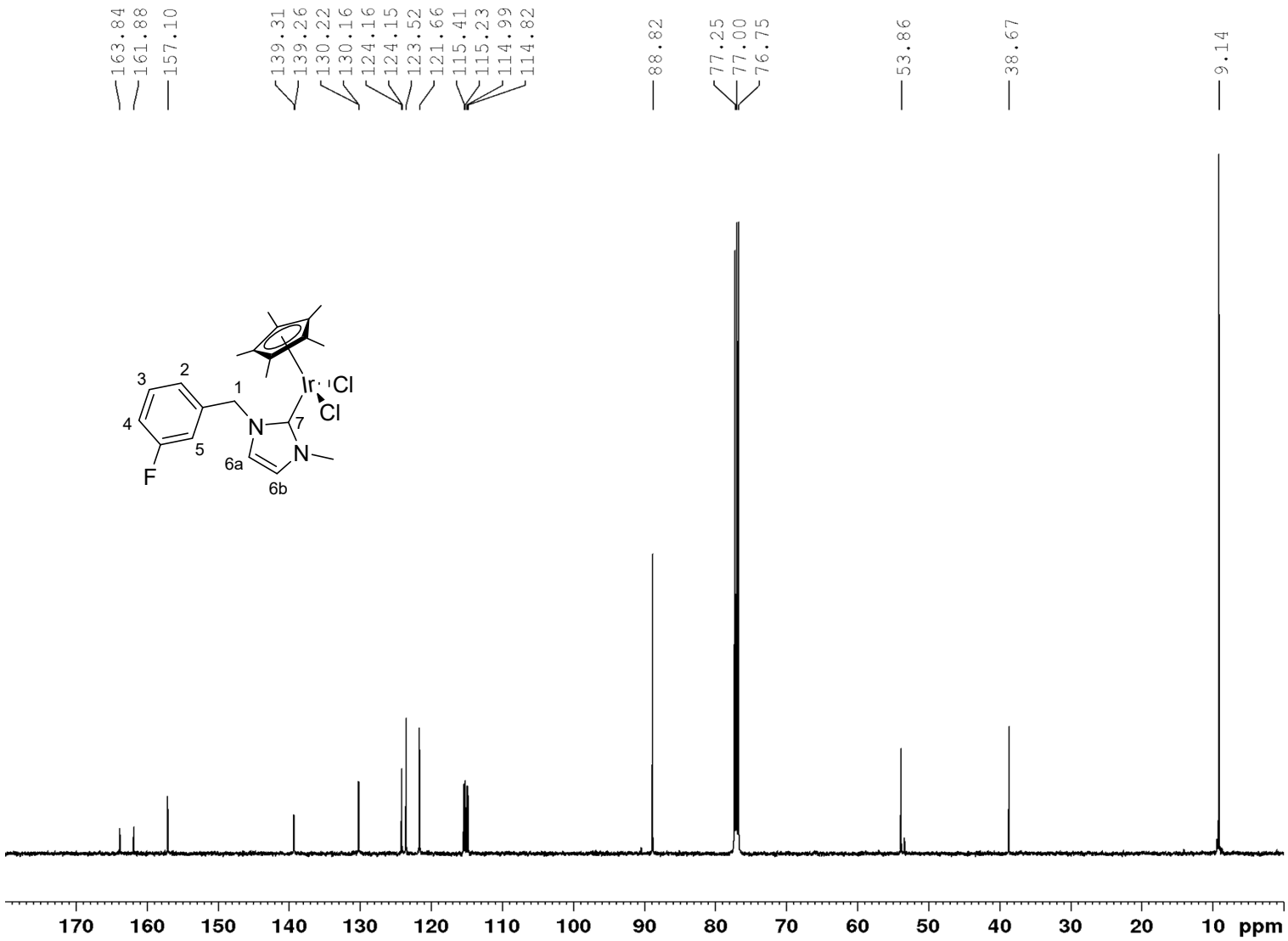
^{19}F NMR of **5b-CF$_3$** in $CDCl_3$



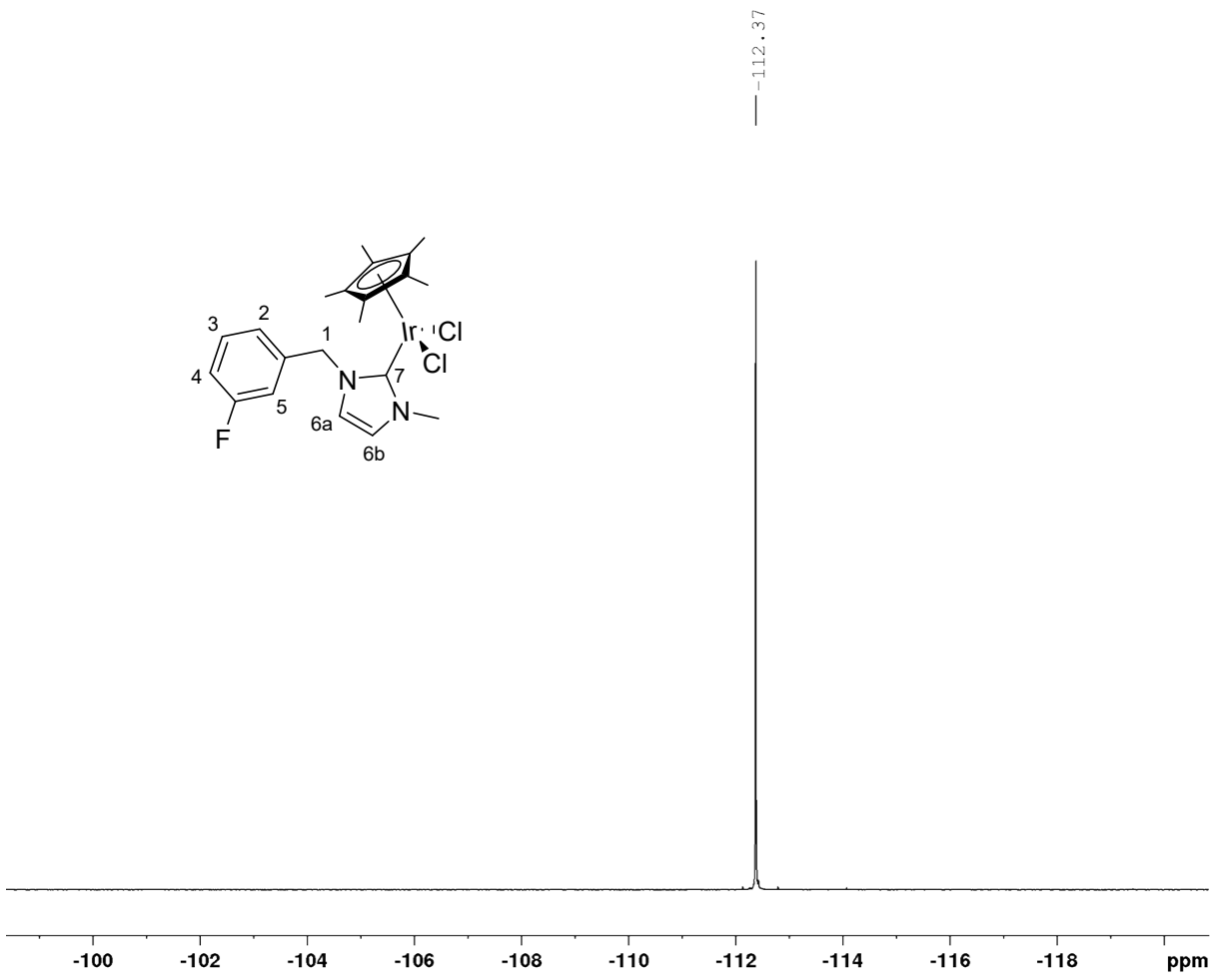
^{1}H NMR of **5a-F** in $CDCl_3$



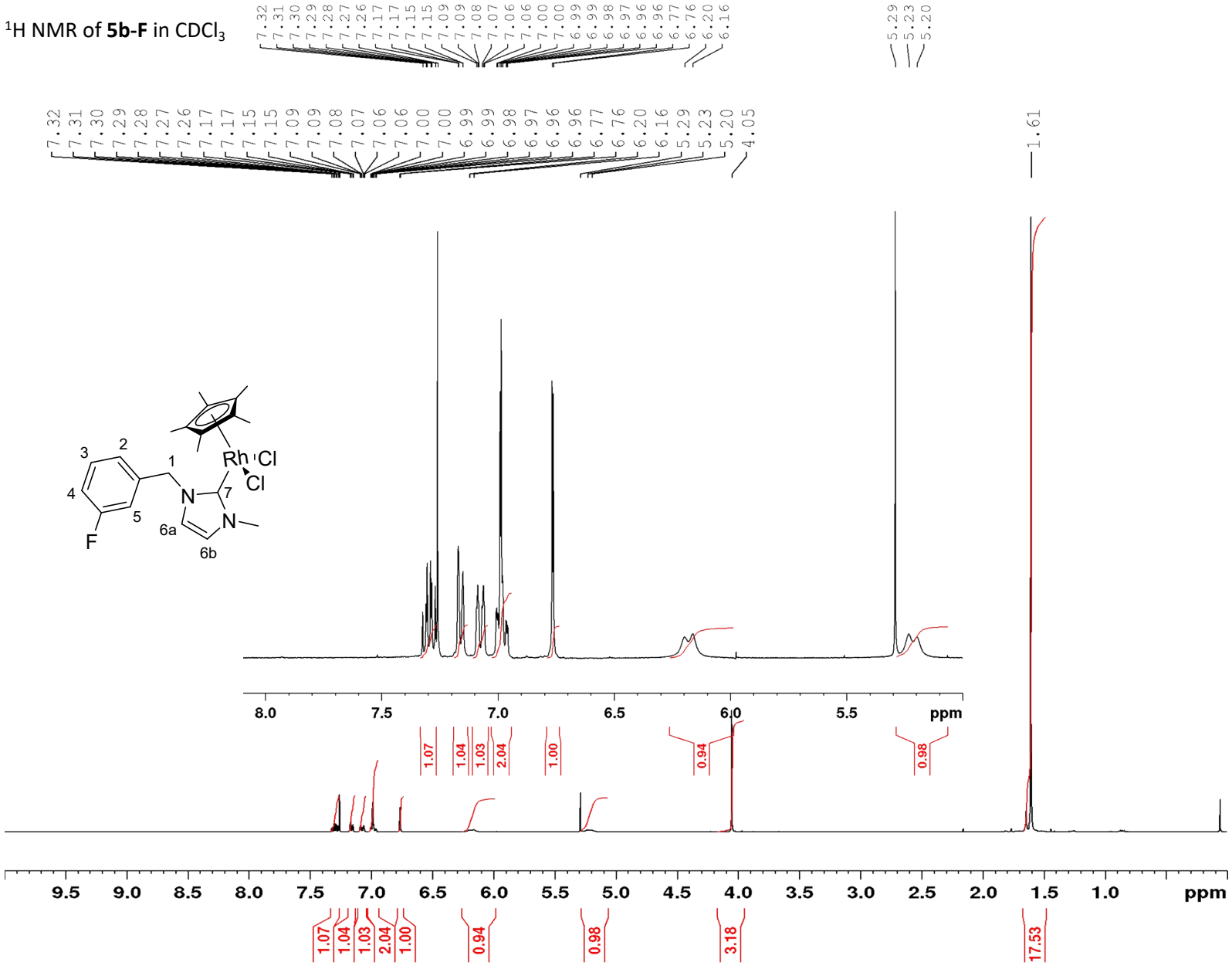
^{13}C NMR of **5a-F** in $CDCl_3$



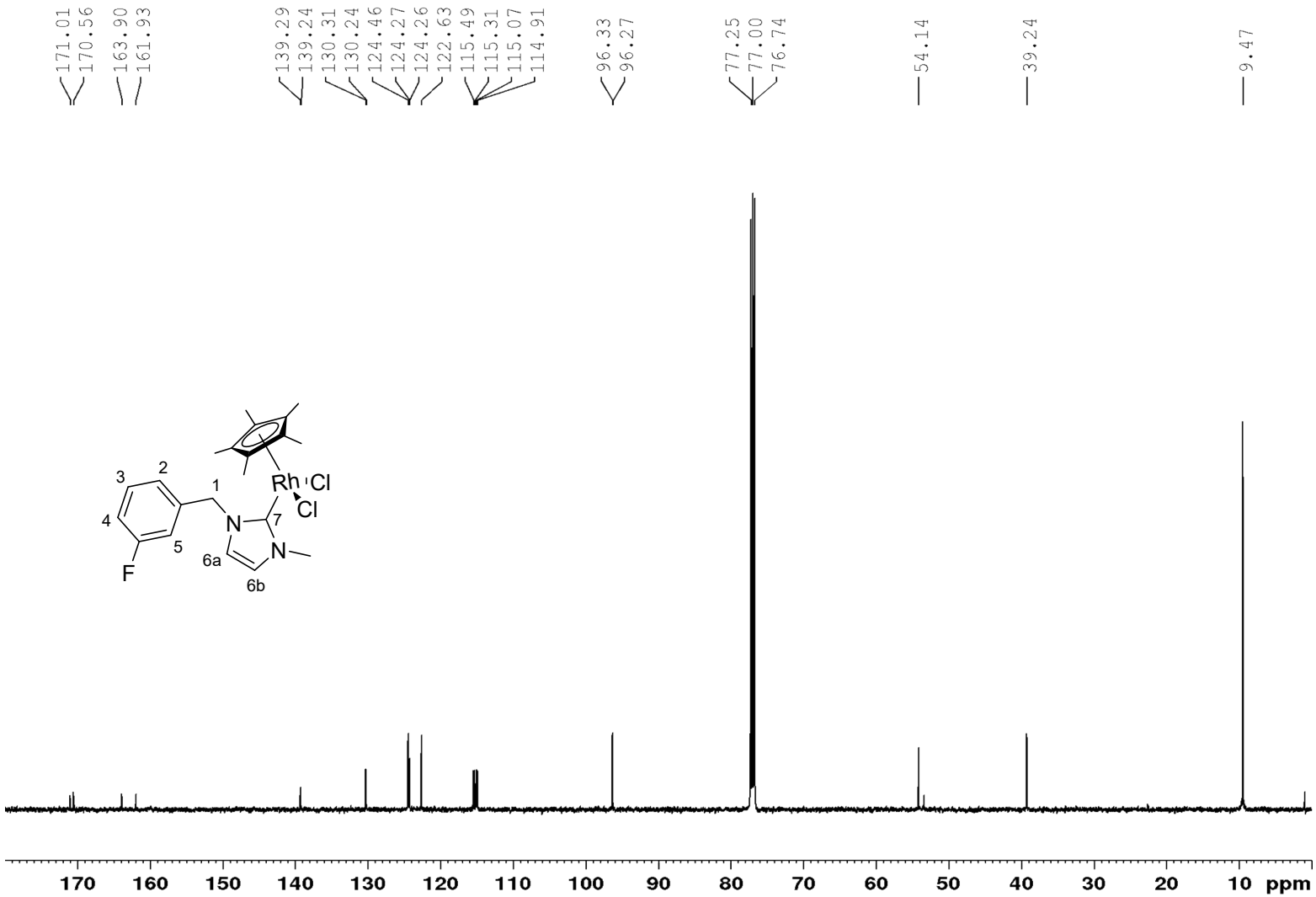
^{19}F NMR of **5a-F** in $CDCl_3$



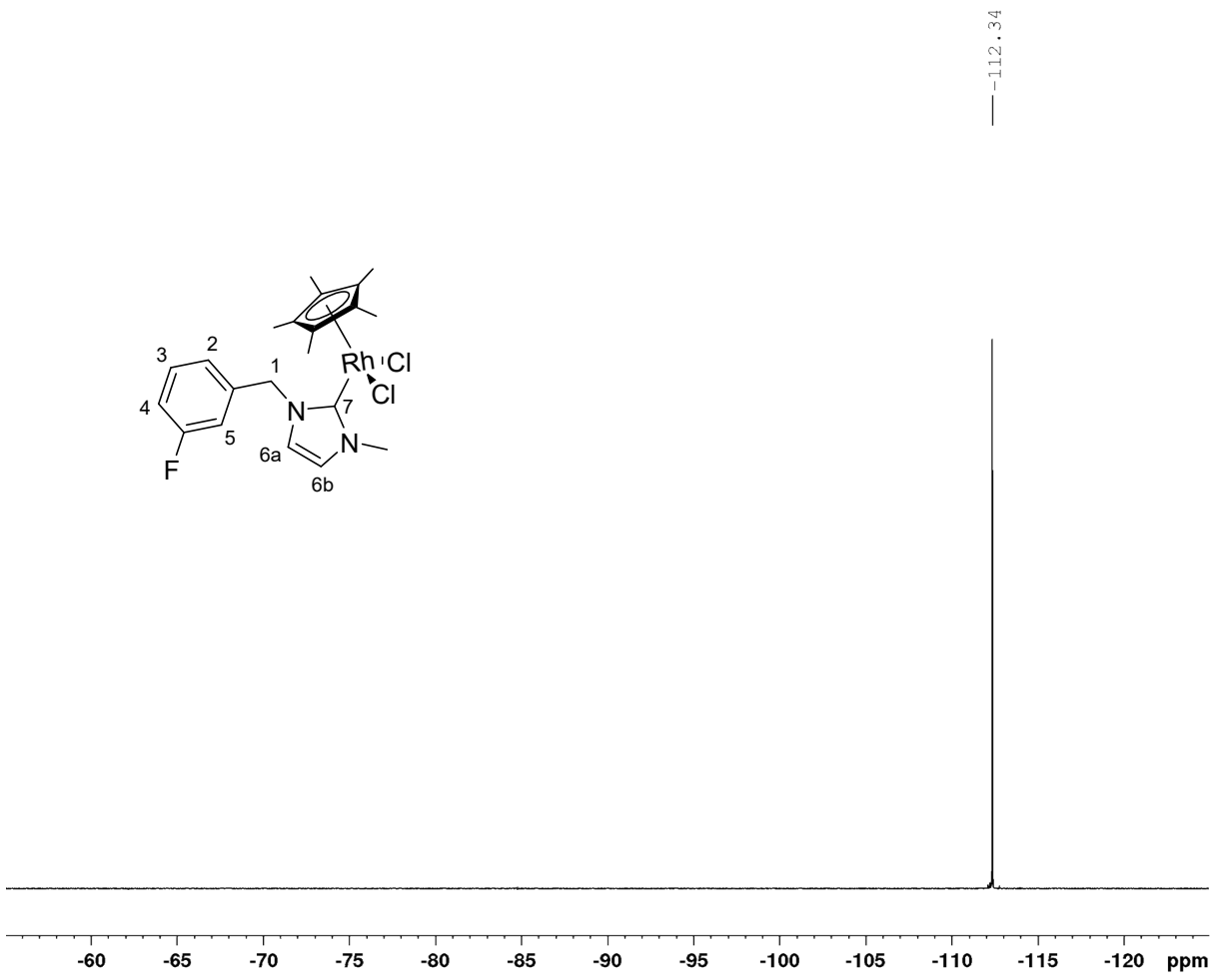
^{1}H NMR of **5b-F** in $CDCl_3$



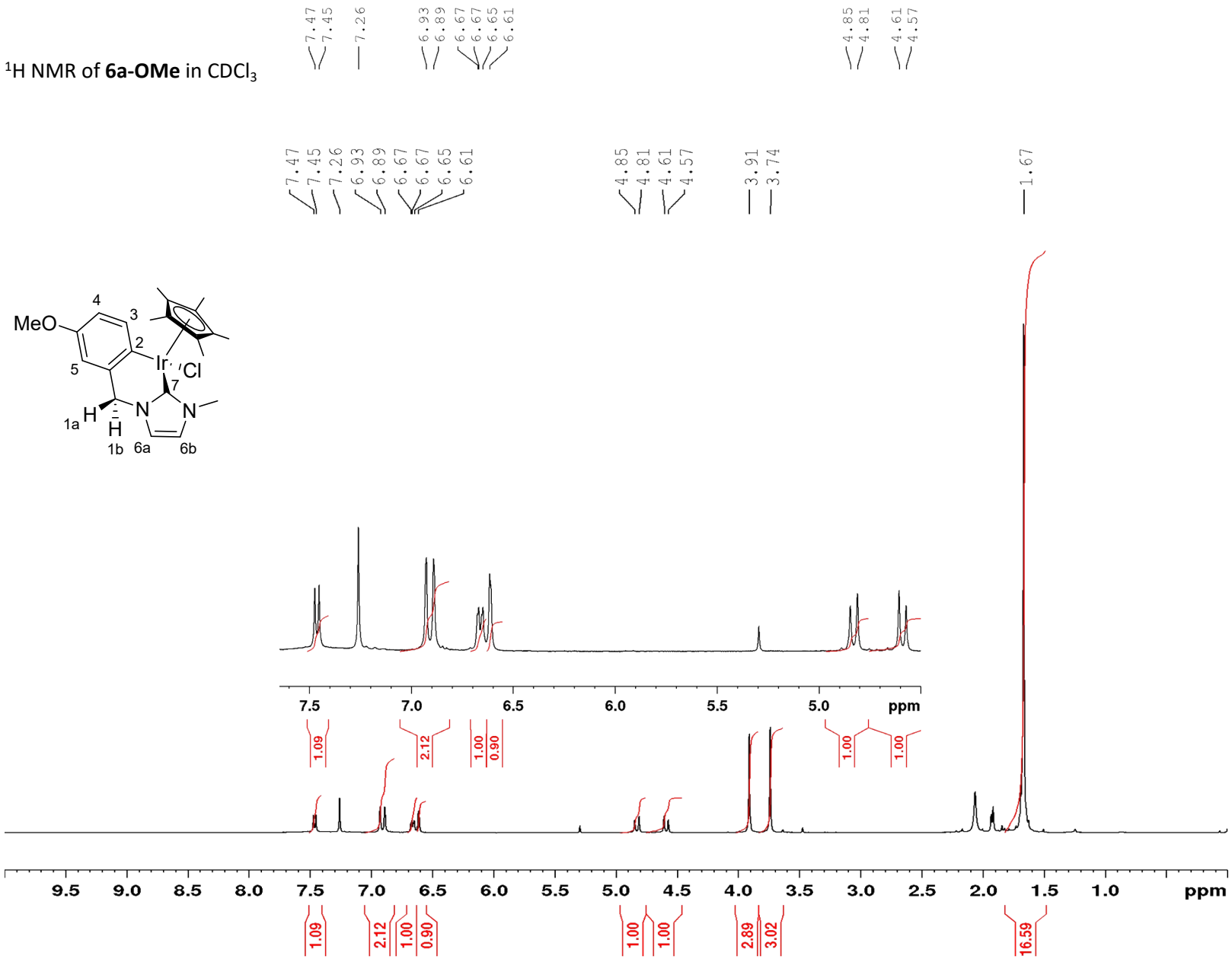
^{13}C NMR of **5b-F** in $CDCl_3$



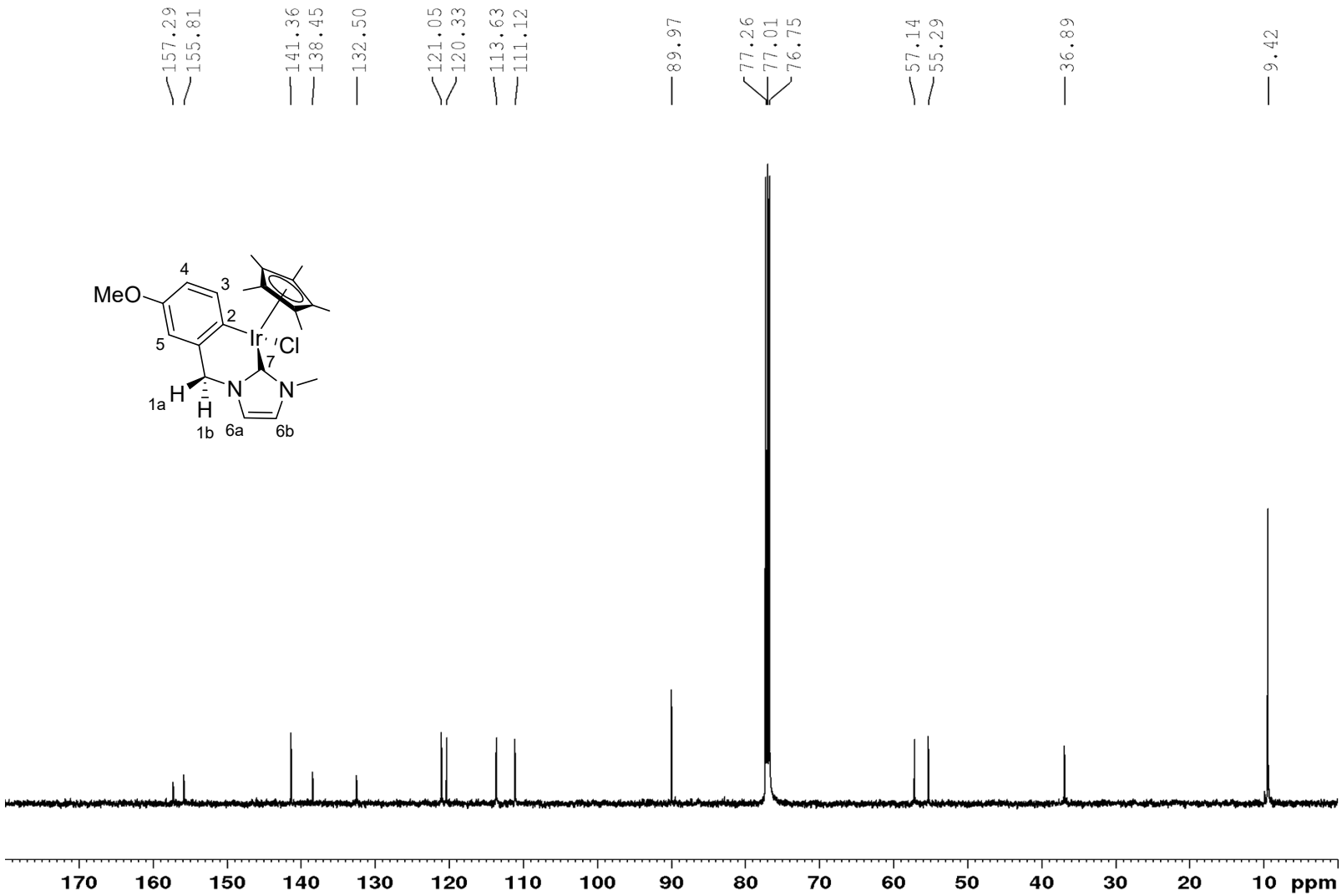
^{19}F NMR of **5b-F** in $CDCl_3$



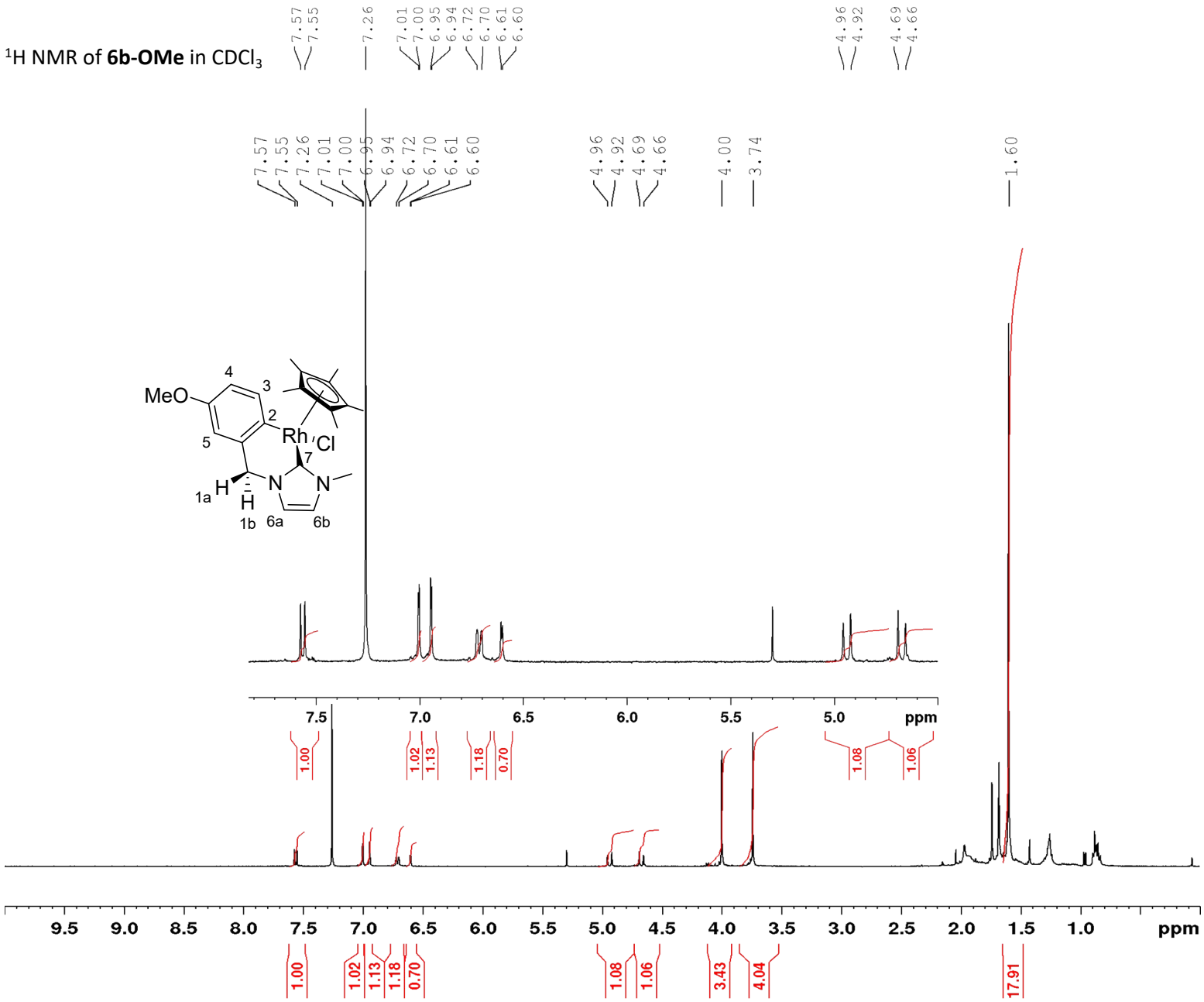
^{1}H NMR of **6a-OMe** in $CDCl_3$



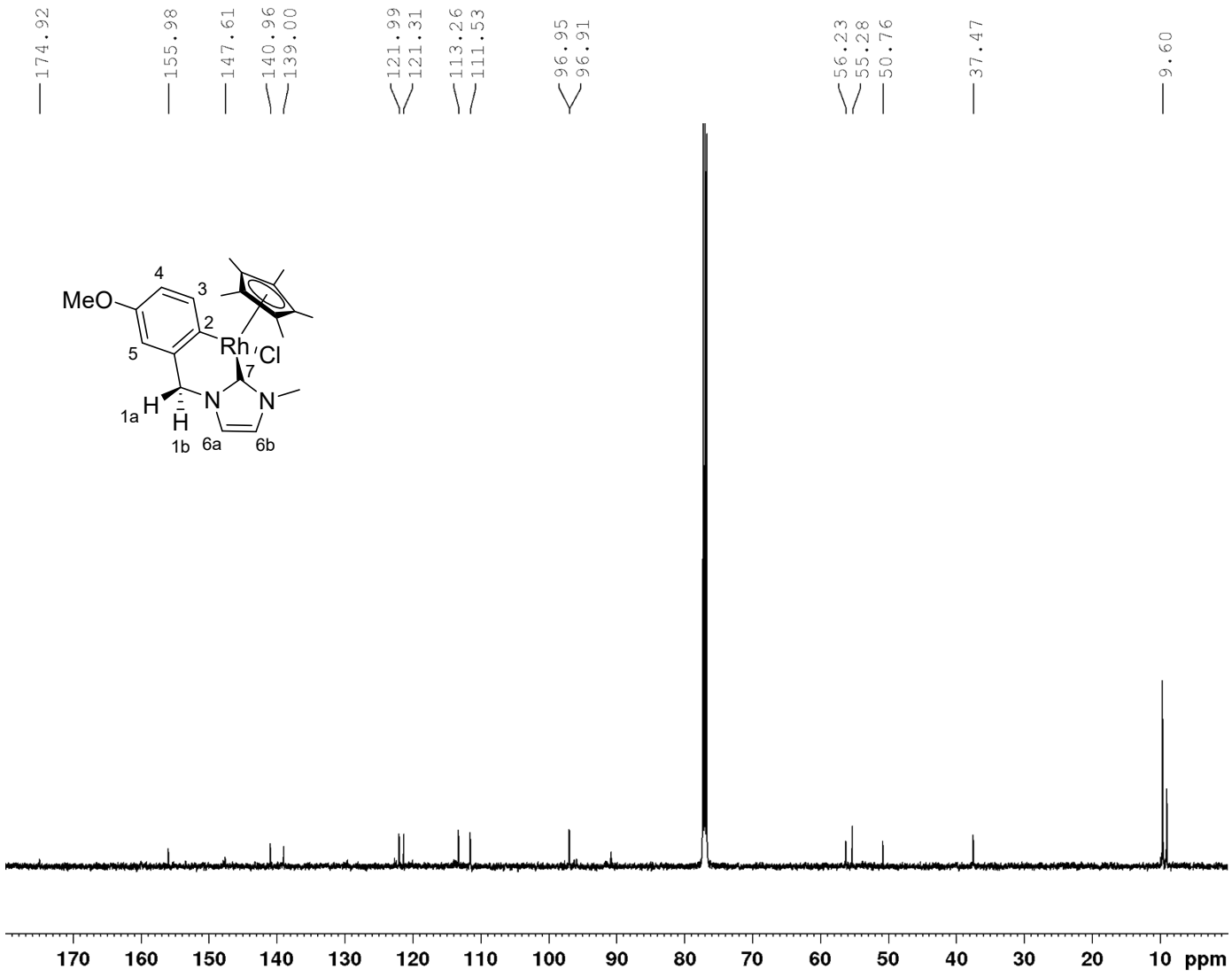
^{13}C NMR of **6a-OMe** in CDCl



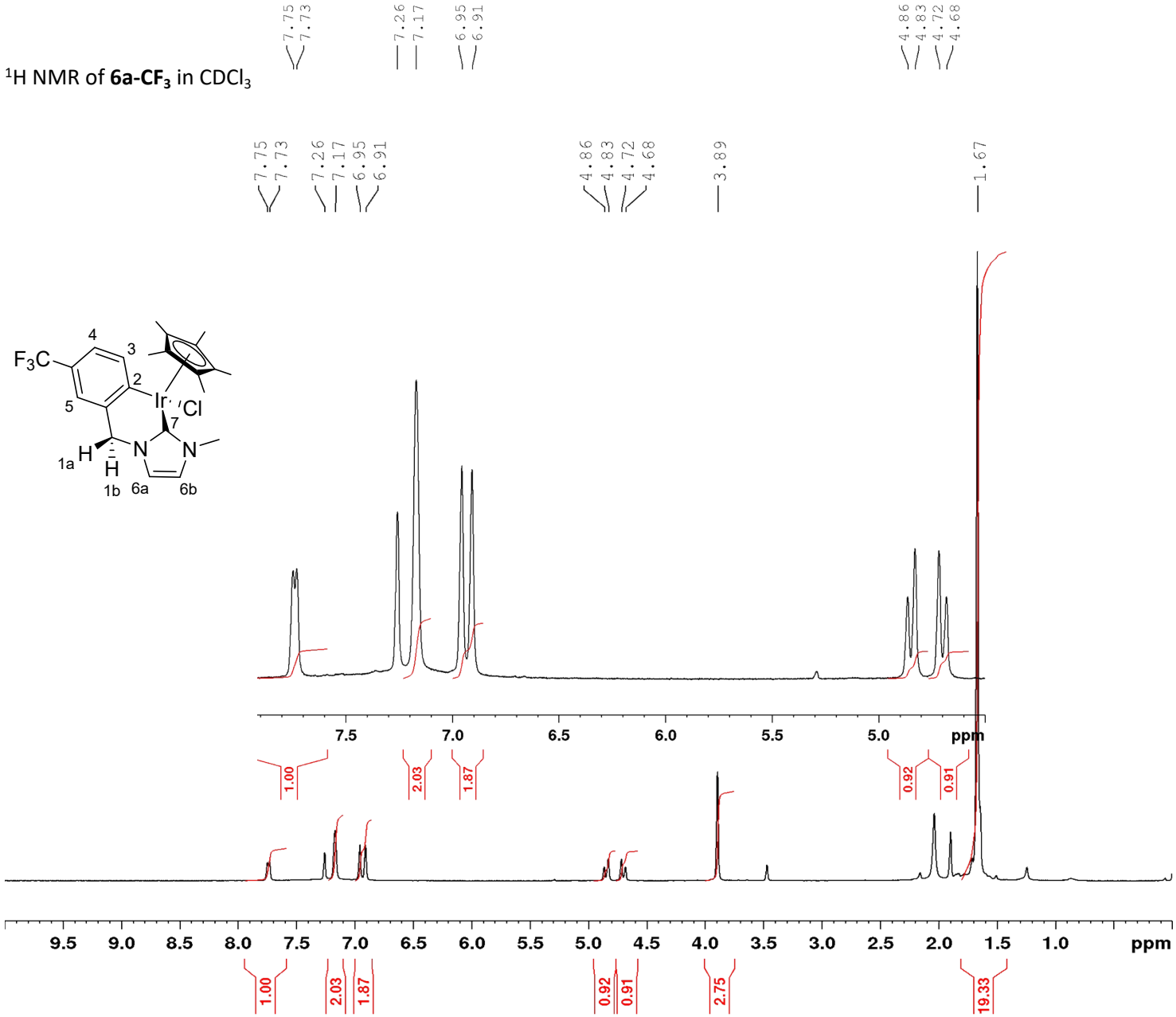
^{1}H NMR of **6b-OMe** in $CDCl_3$



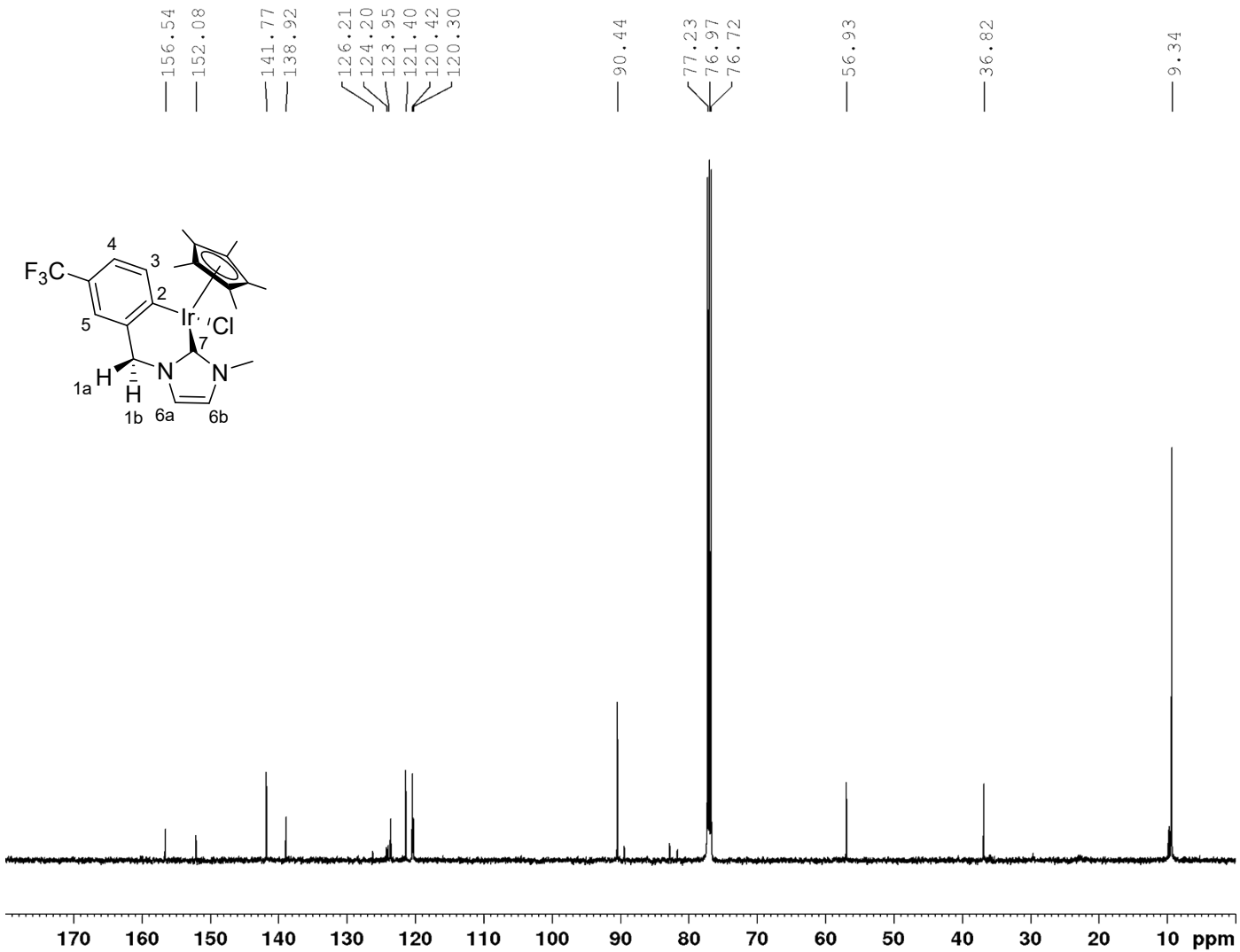
^{13}C NMR of **6b-OMe** in $CDCl_3$



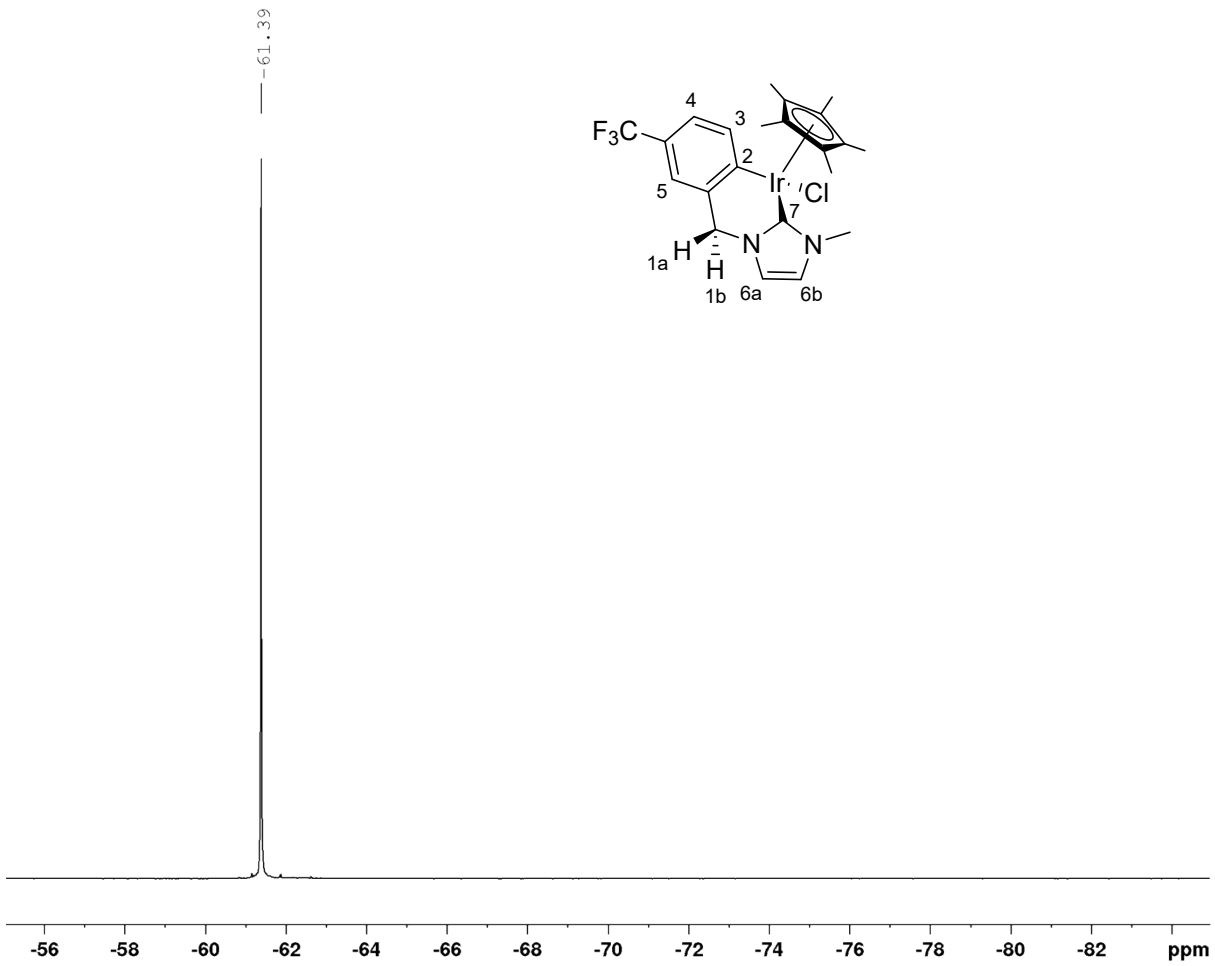
^{1}H NMR of **6a-CF$_3$** in $CDCl_3$



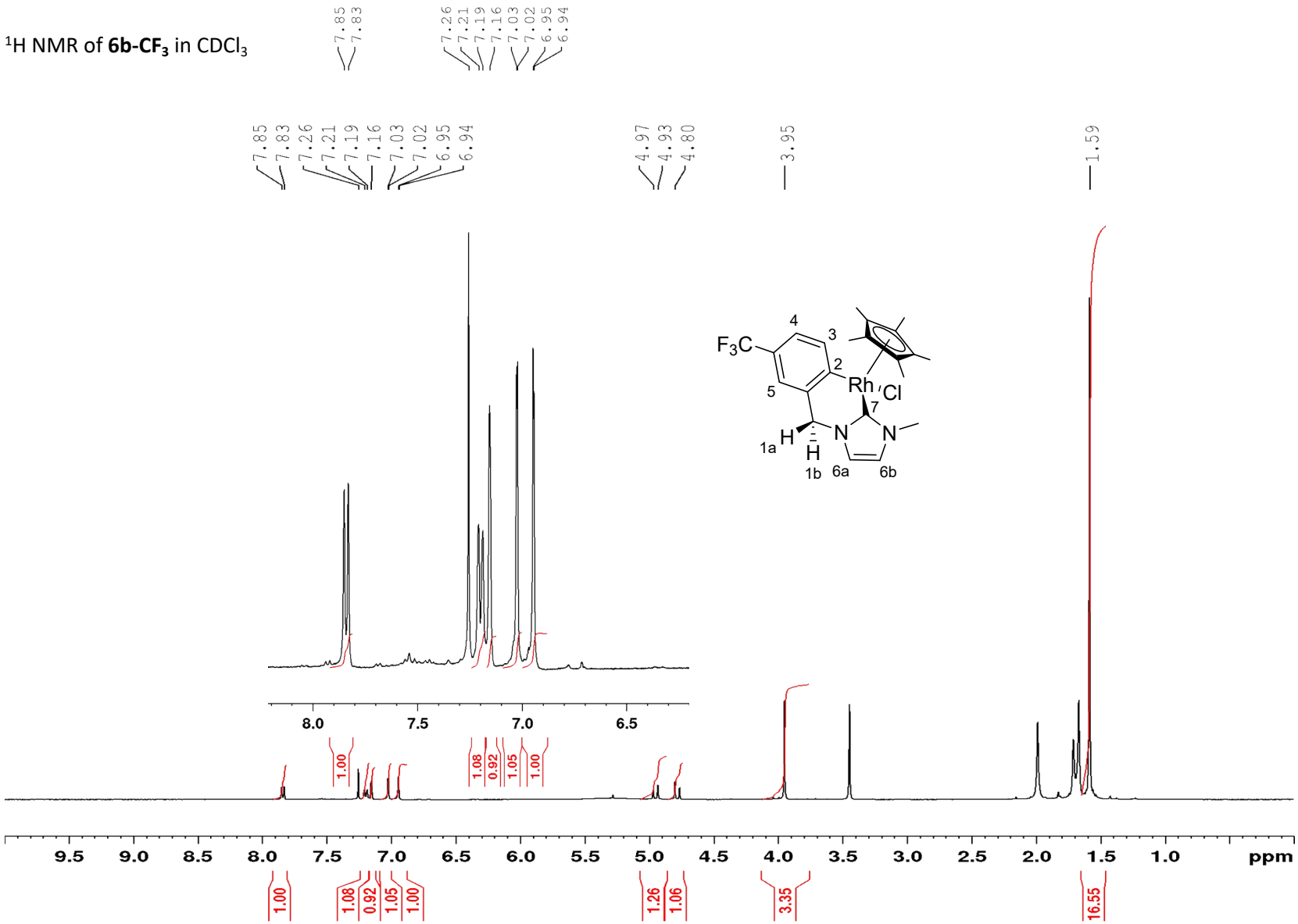
^{13}C NMR of **6a-CF$_3$** in $CDCl_3$



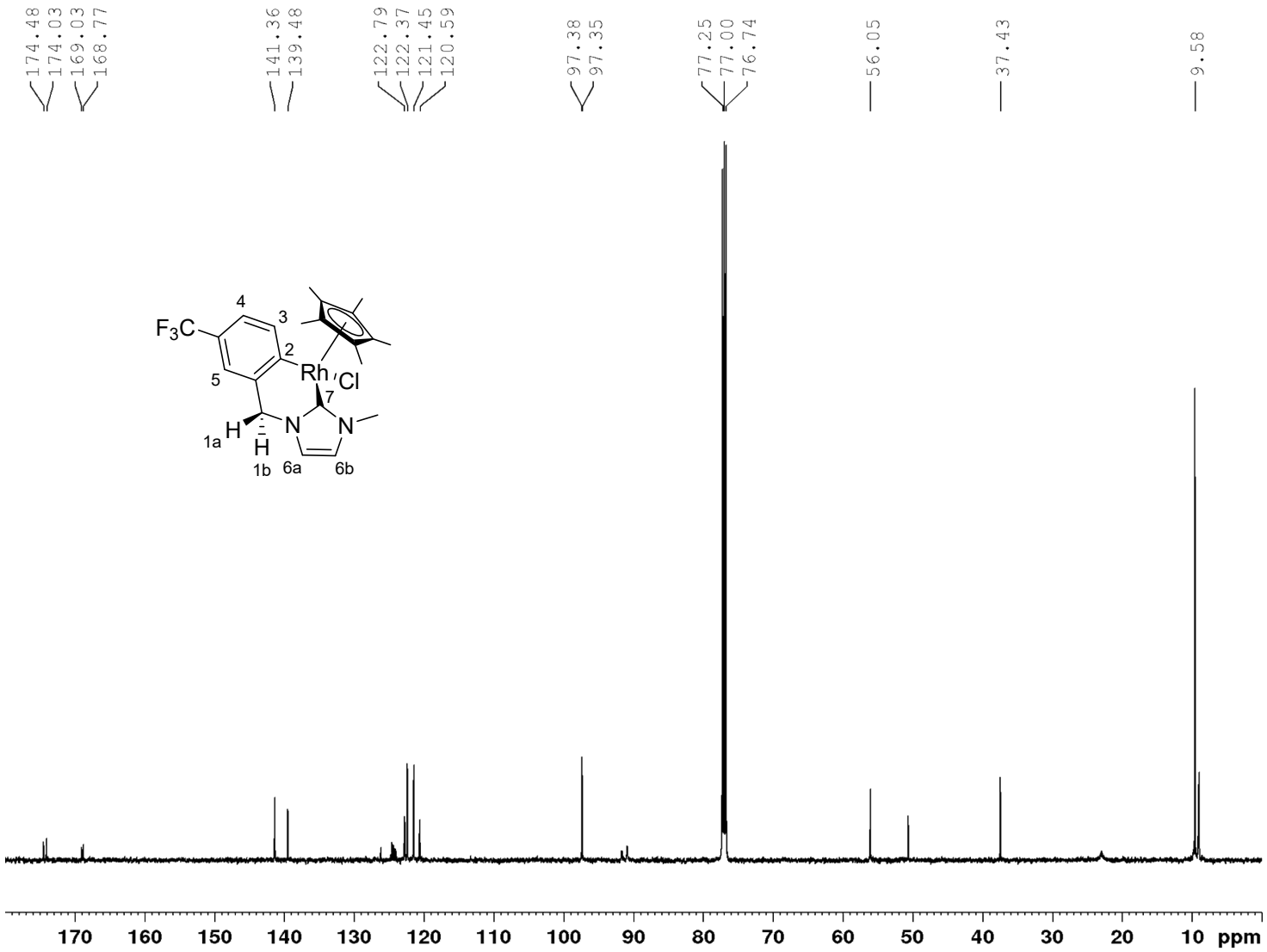
^{19}F NMR of **6a-CF$_3$** in $CDCl_3$



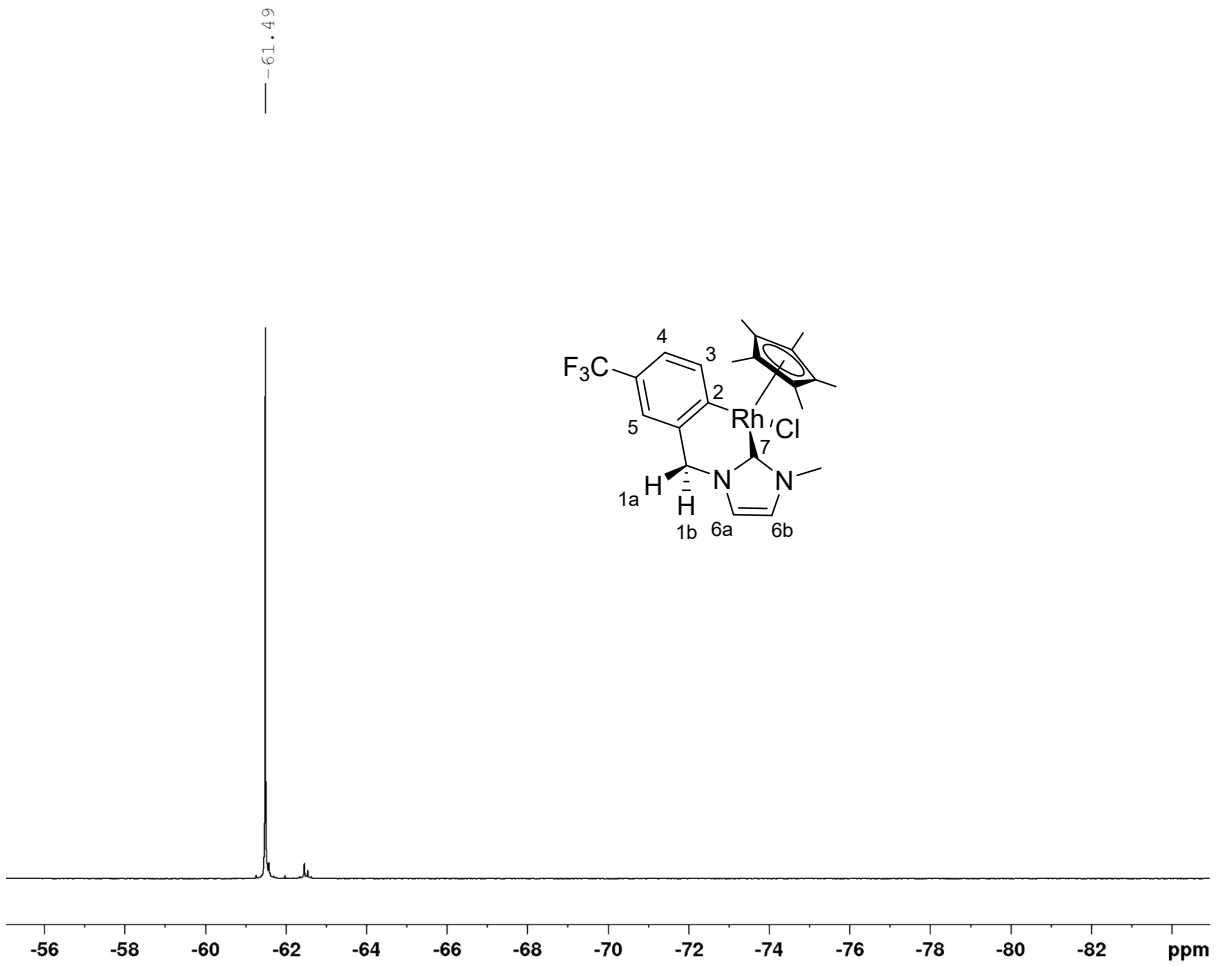
^{1}H NMR of **6b-CF$_3$** in $CDCl_3$



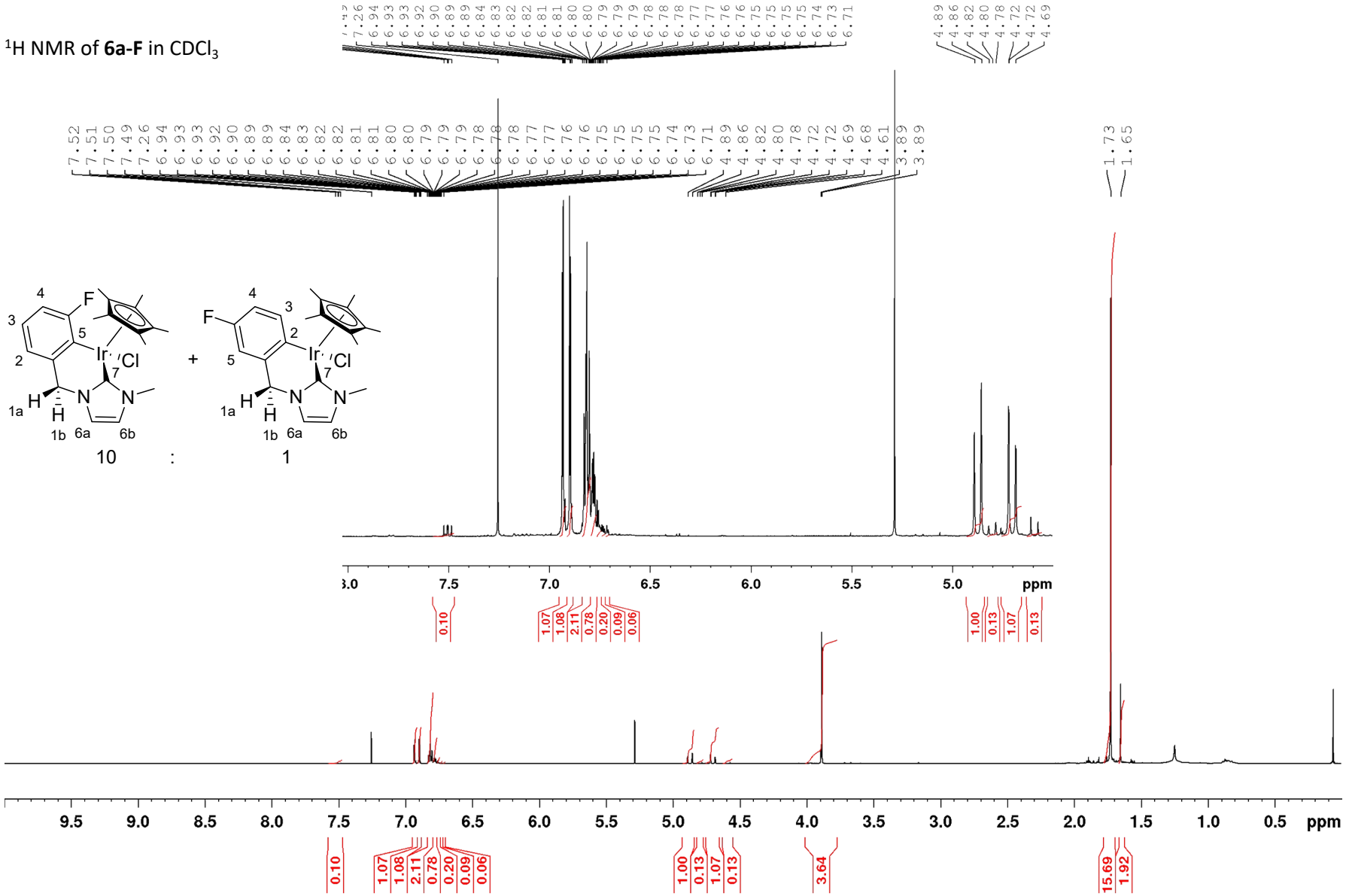
^{13}C NMR of **6b-CF$_3$** in $CDCl_3$



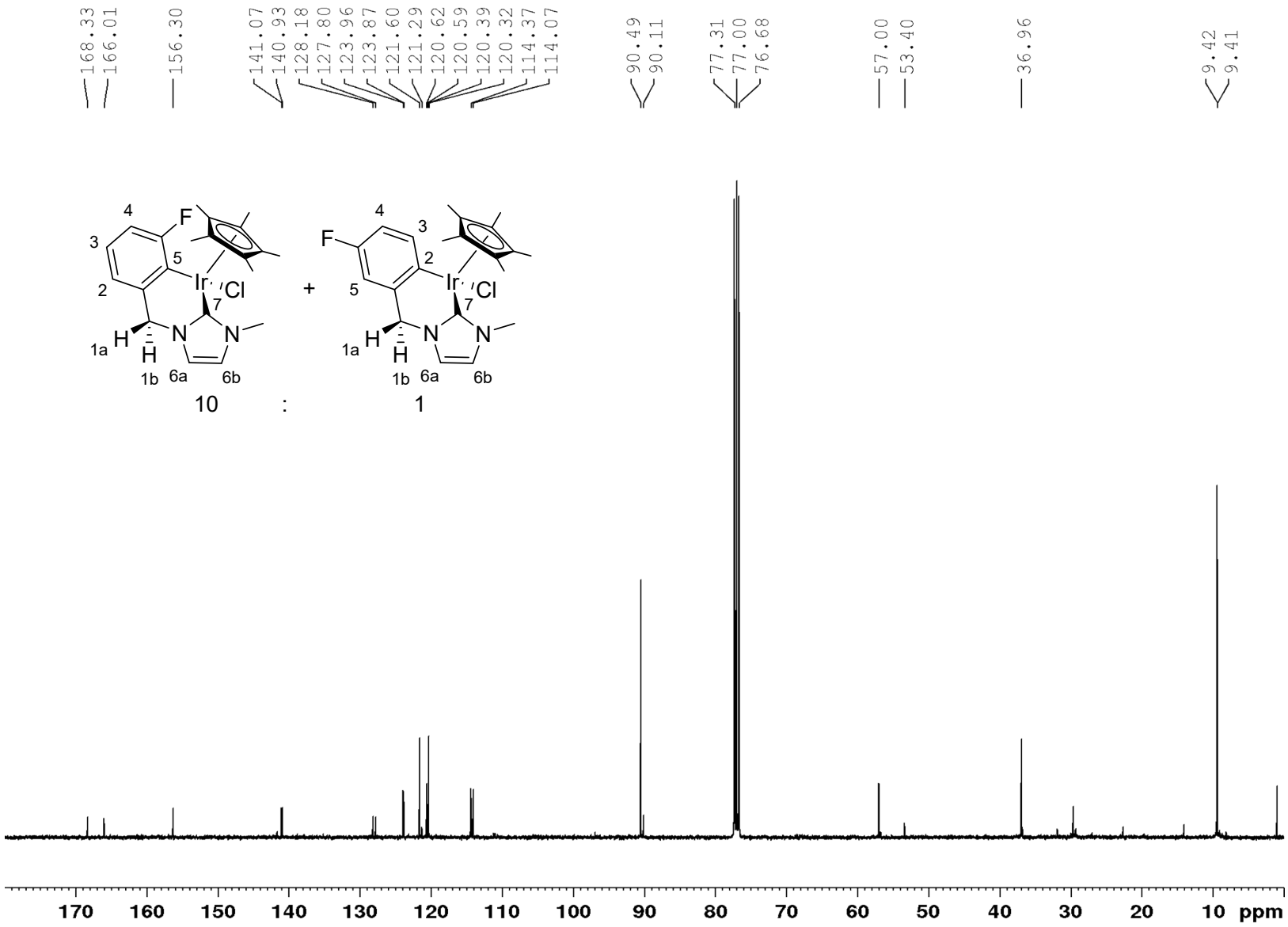
^{19}F NMR of **6bCF$_3$** in $CDCl_3$



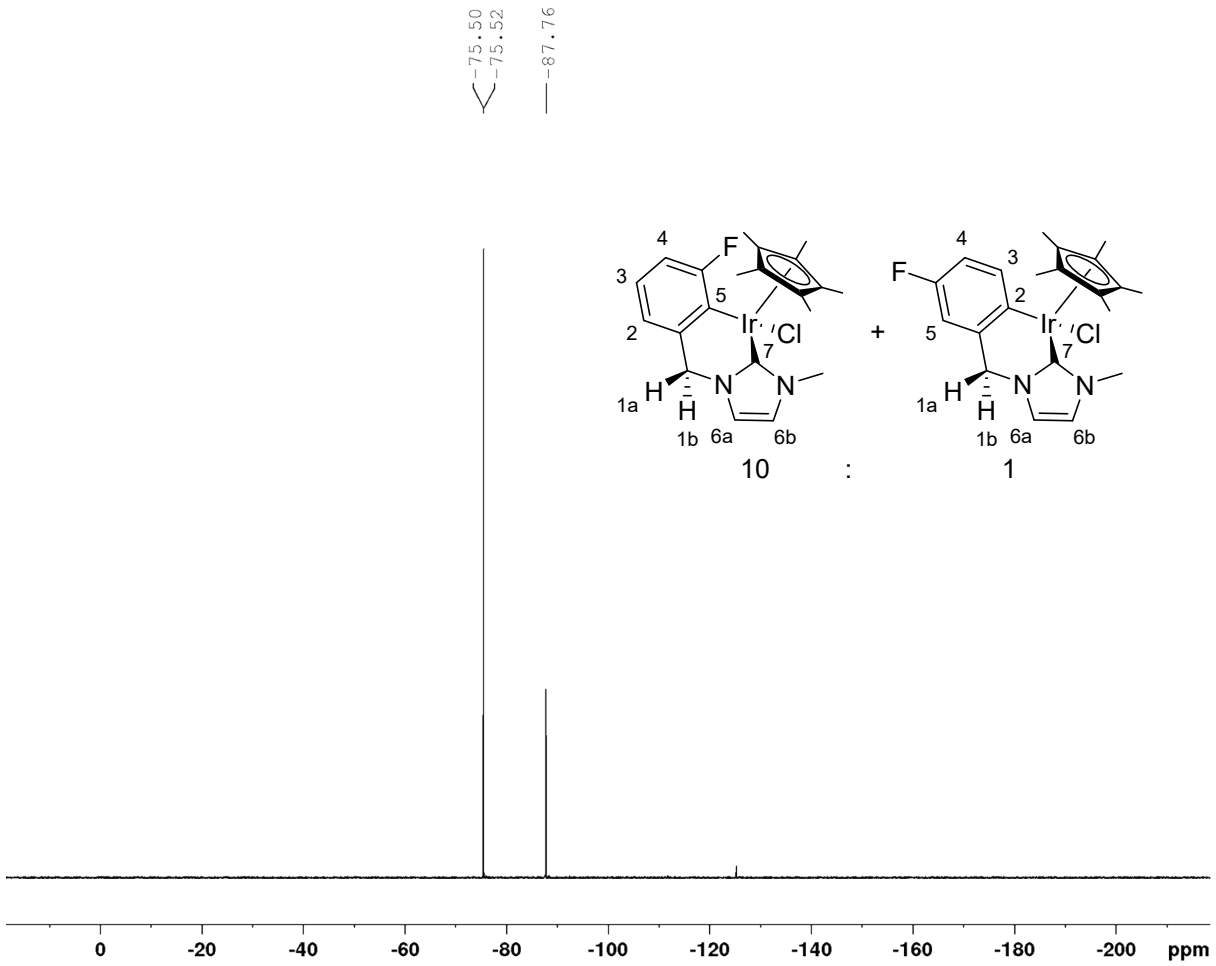
^{1}H NMR of **6a-F** in $CDCl_3$



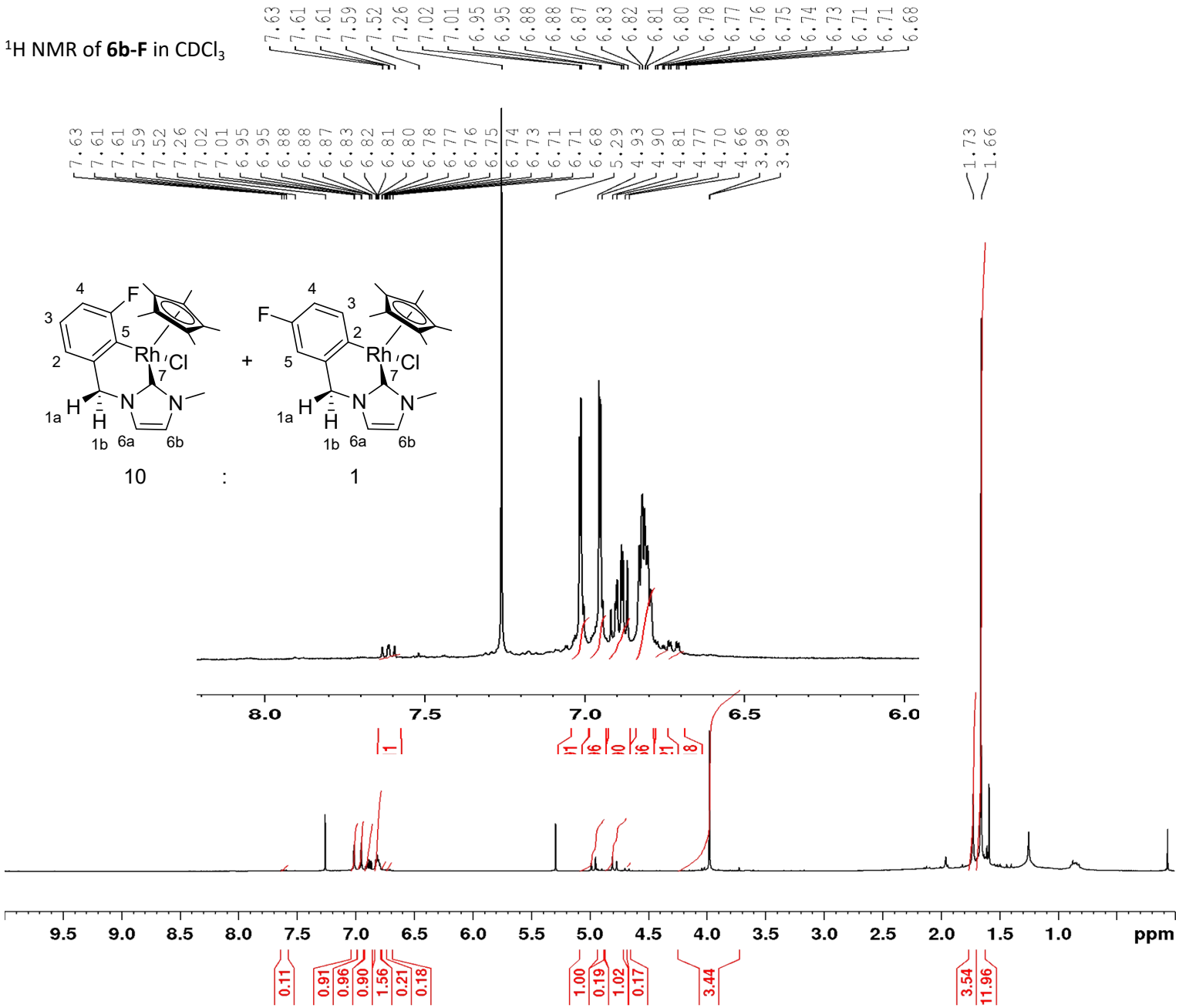
^{13}C NMR of **6a-F** in $CDCl_3$



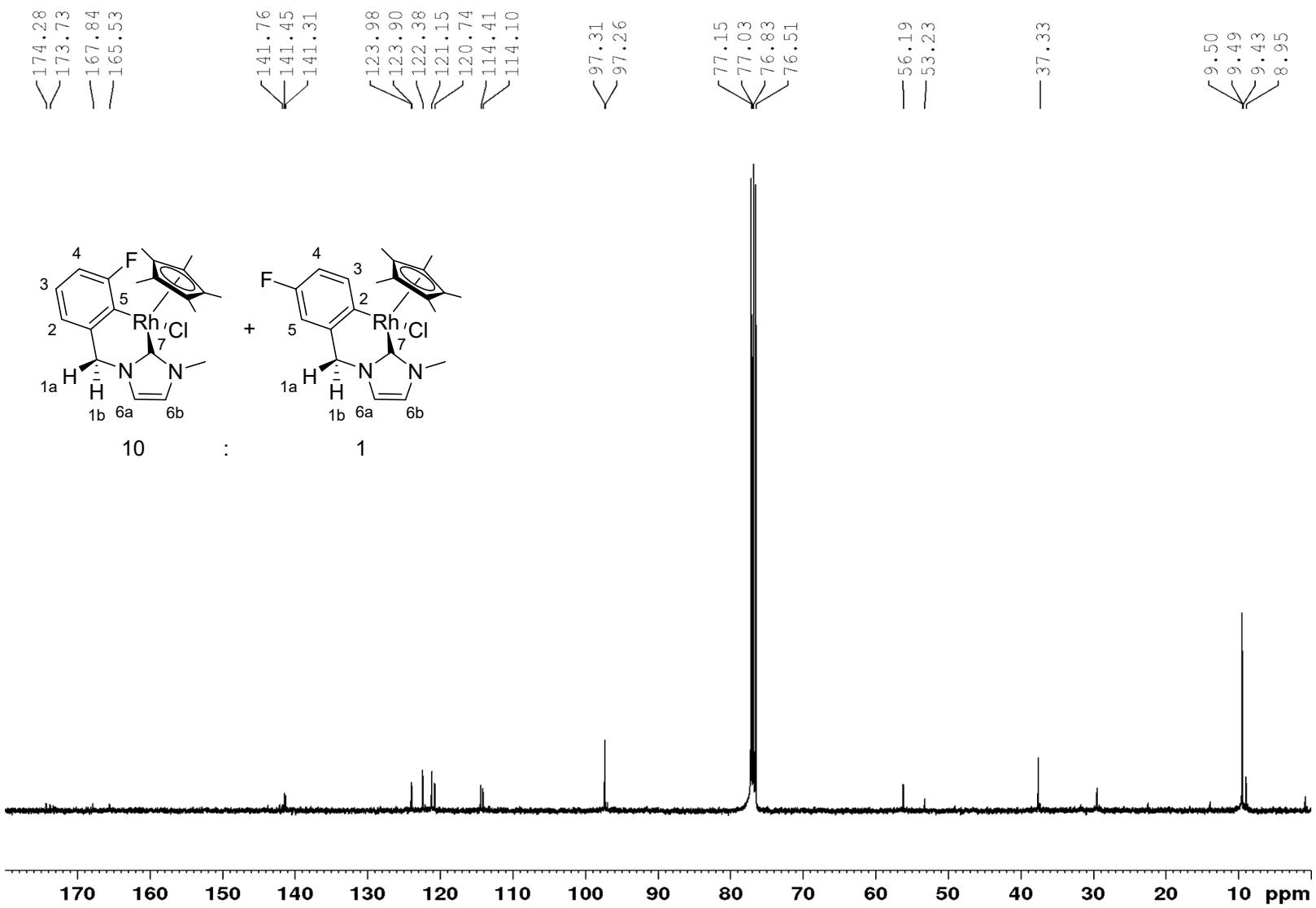
^{19}F NMR of **6a-F** in $CDCl_3$



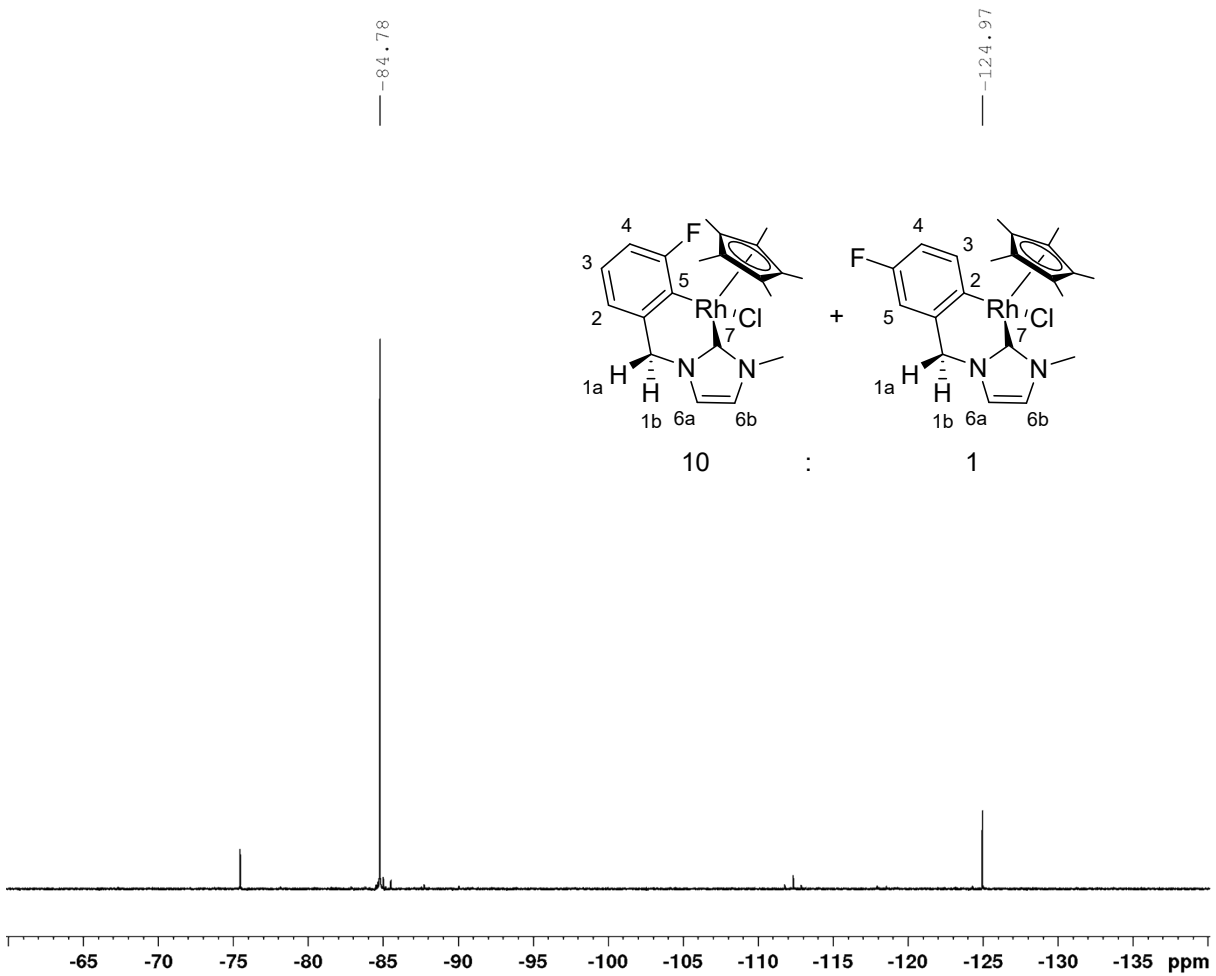
^{1}H NMR of **6b-F** in $CDCl_3$



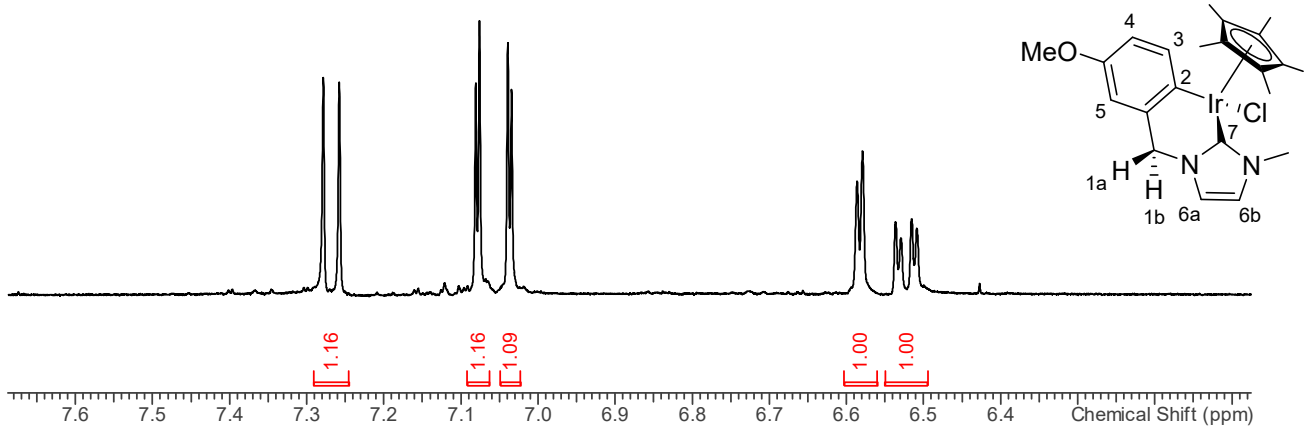
^{13}C NMR of **6b-F** in $CDCl_3$



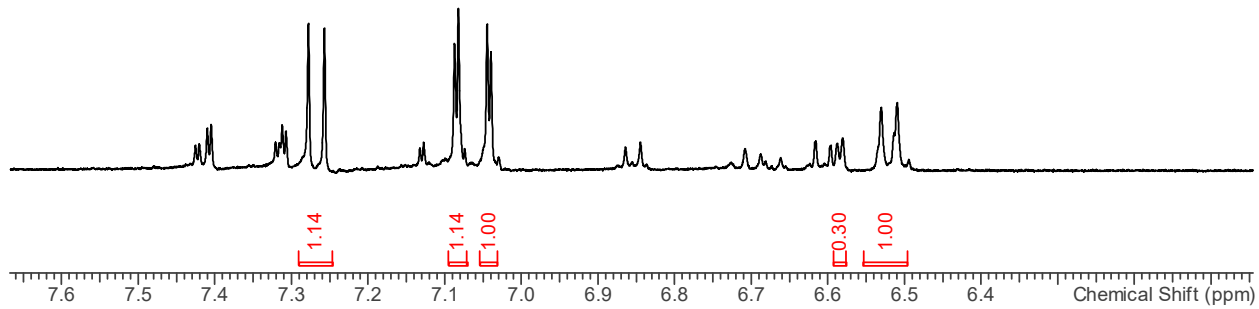
^{19}F NMR of **6b-F** in $CDCl_3$



^{1}H NMR spectra of deuteration reactions.



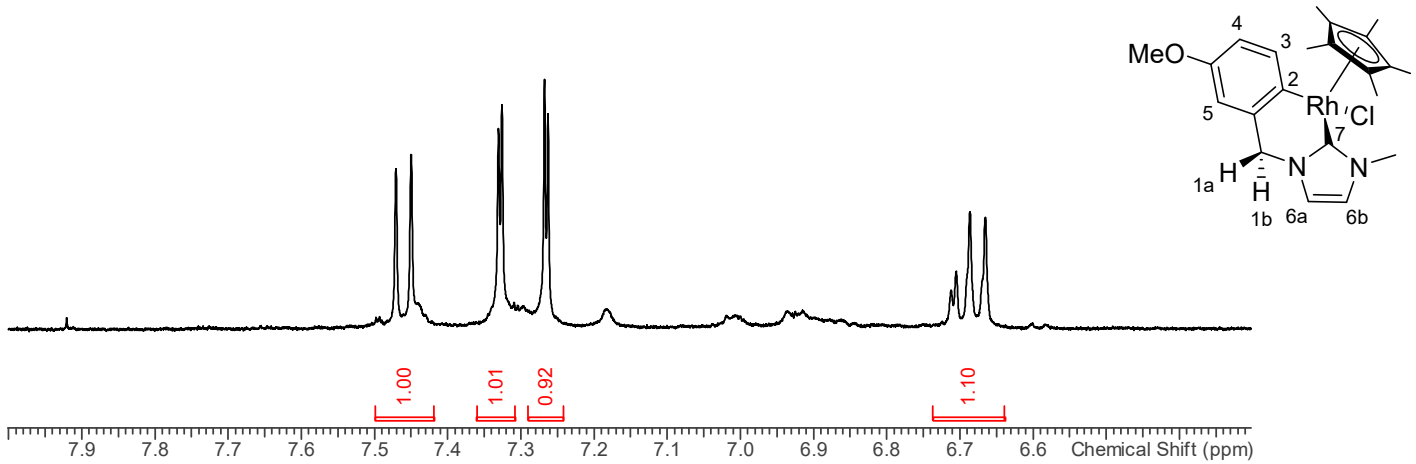
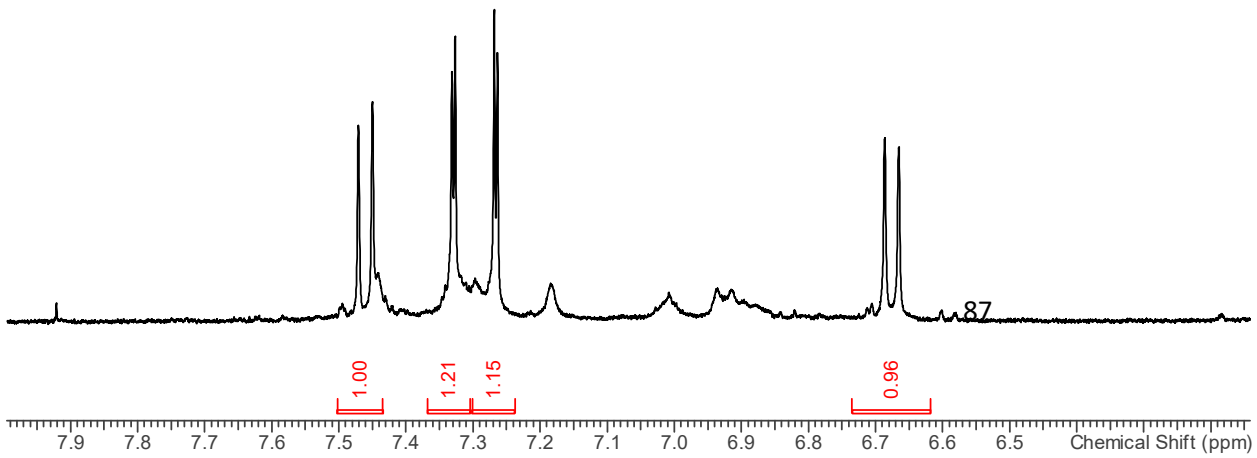
Aromatic region of ^{1}H NMR of **5a-OMe** in d4-methanol afetr 1 hour reaction with NaOAc. Complete conversion to para- **6a-OMe**



Same reaction after 3 days with NaOAc

Signal at about 6.58 due to H^5 has decreased substantially and signal at 6.52 (H^4) becomes just a doublet, loses small cross ring coupling due to deuteration . The other signals of **6a-OMe** integrate to roughly the same amounts. Some other complexes also formed (may be acetate coordinated and or some of the ortho isomer)

Aromatic region of ^{1}H NMR spectrum of **5b-OMe** in d4-methanol after 1 hour reaction with NaOAc. The major species is para- **6b-OMe** there is still a minor amount of **5b-OMe** remaining .Peak at 6.7 (H^5) has already almost gone



Complex after overnight in d4-methanol peak at 6.7 (H^5) has gone and that at 6.67 (H^4) is now a doublet.