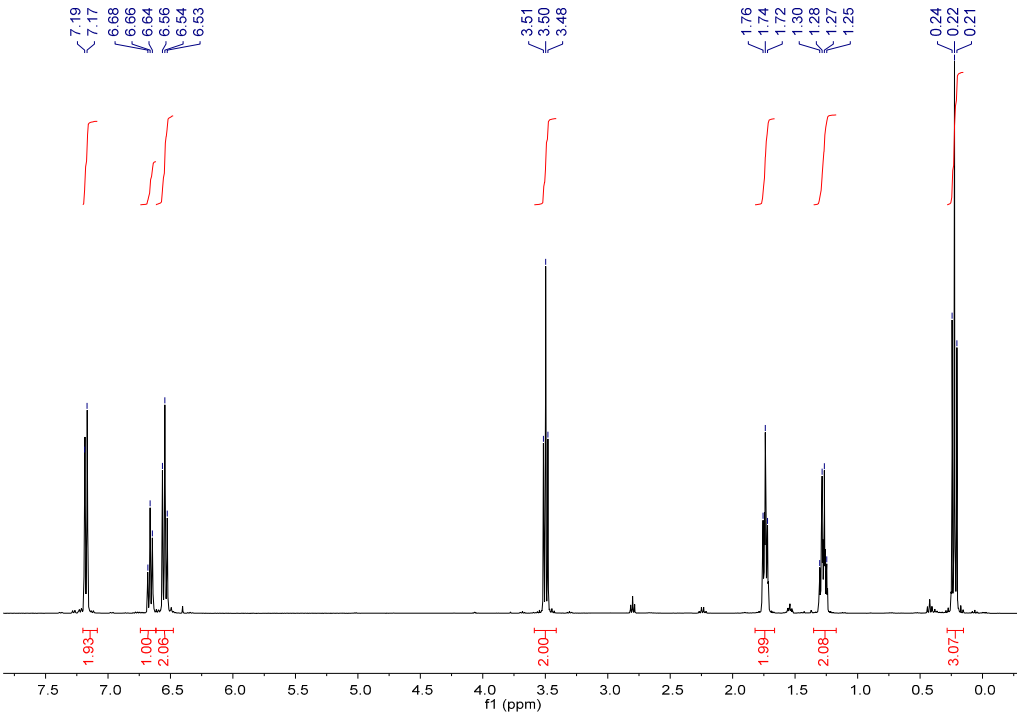
Supplementary Information

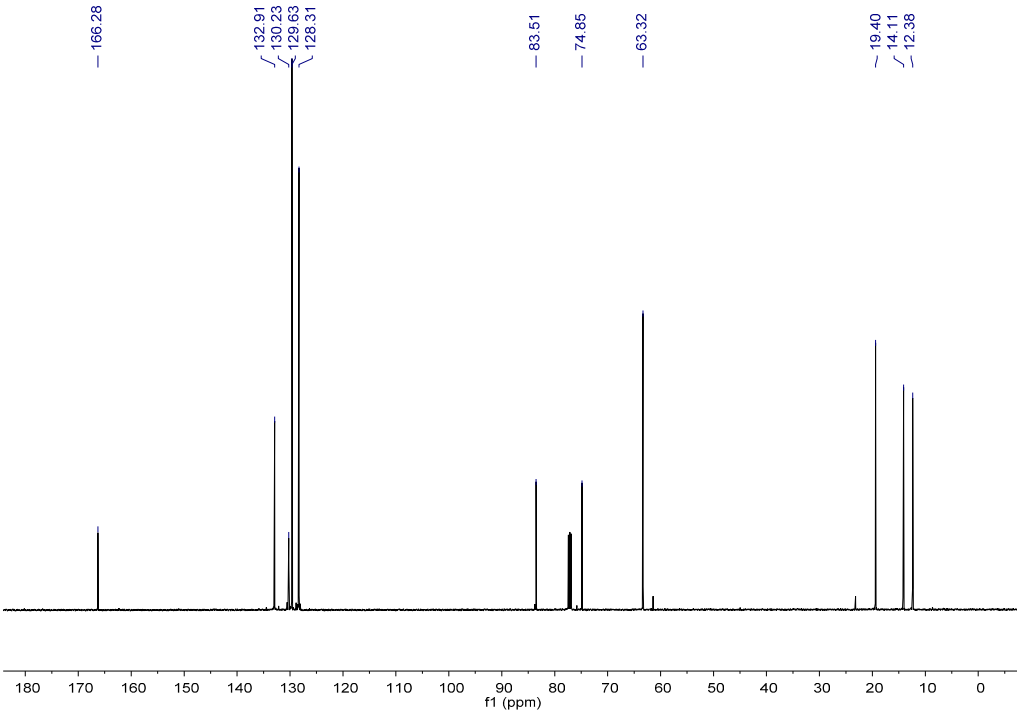
1. Experimental Selected NMR Spectra

1.1. NMR Spectra of Starting Materials

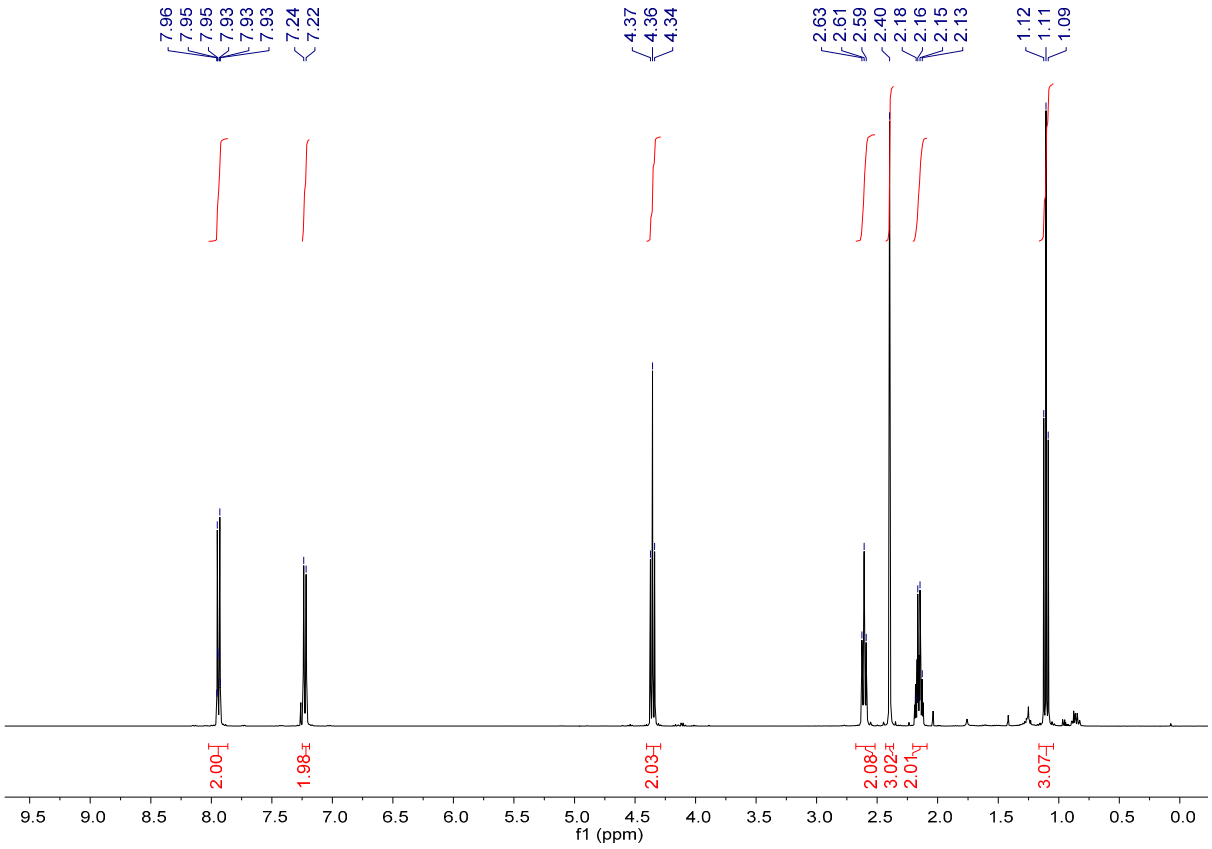
^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectrum of hex-3-yn-1-yl benzoate (**1a**)



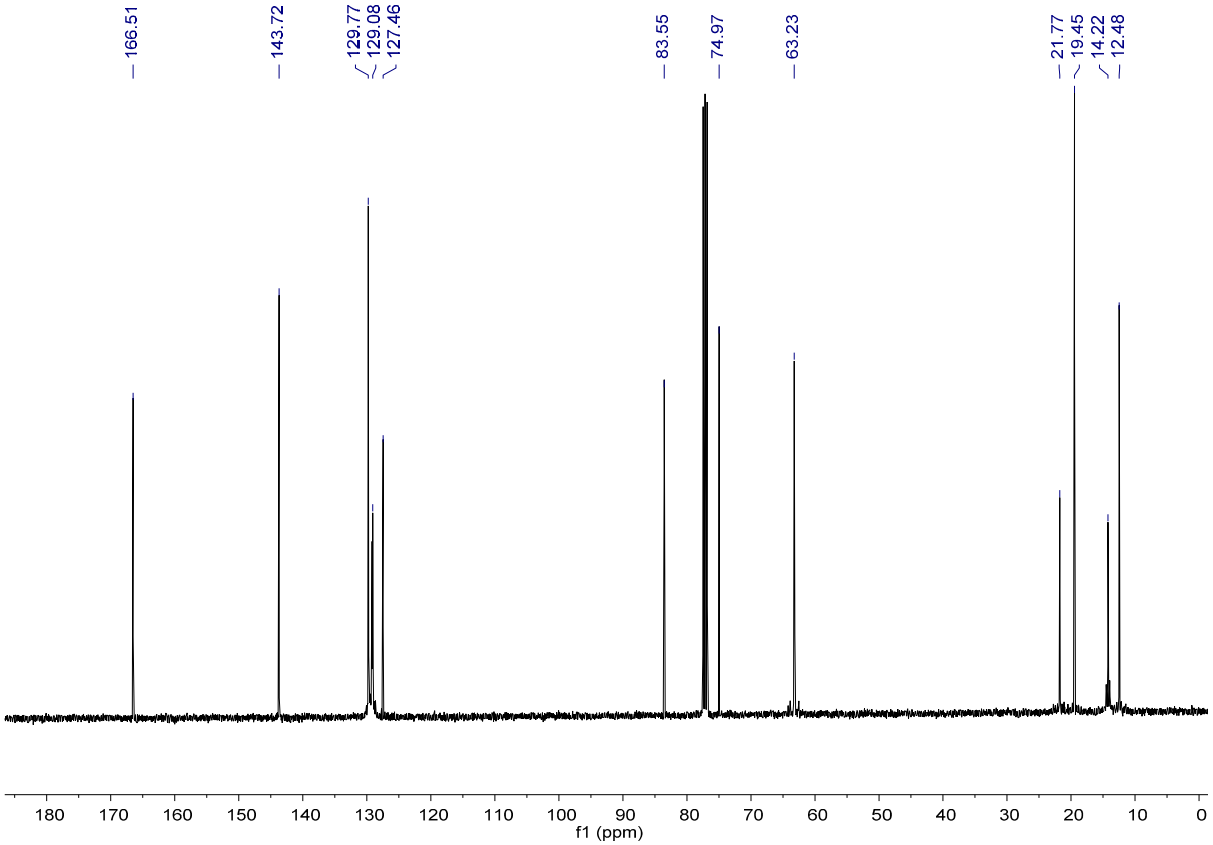
^{13}C-NMR (125 MHz, $CDCl_3$, 298K) spectrum of hex-3-yn-1-yl benzoate (**1a**)



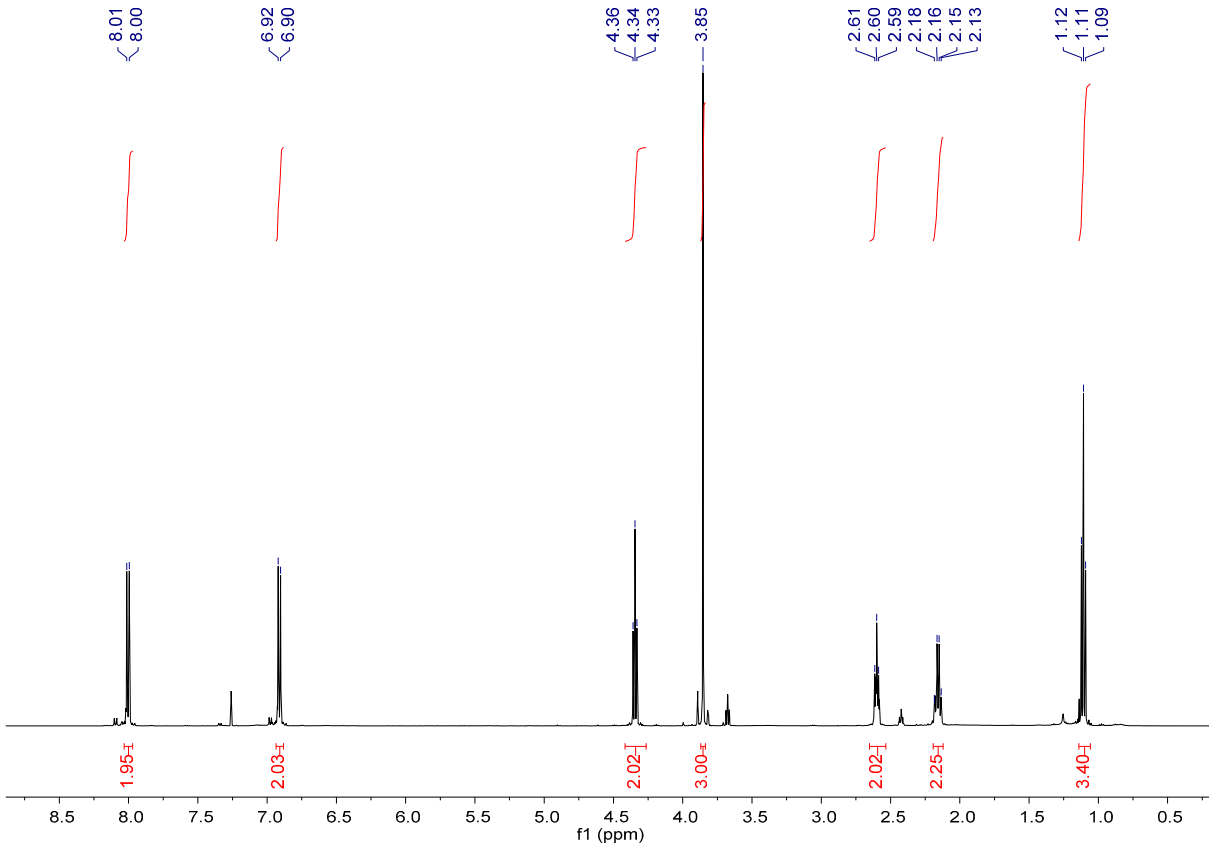
^{1}H-NMR (400 MHz, $CDCl_3$, 298K) spectrum of hex-3-yn-1-yl 4-methylbenzoate (**1b**)



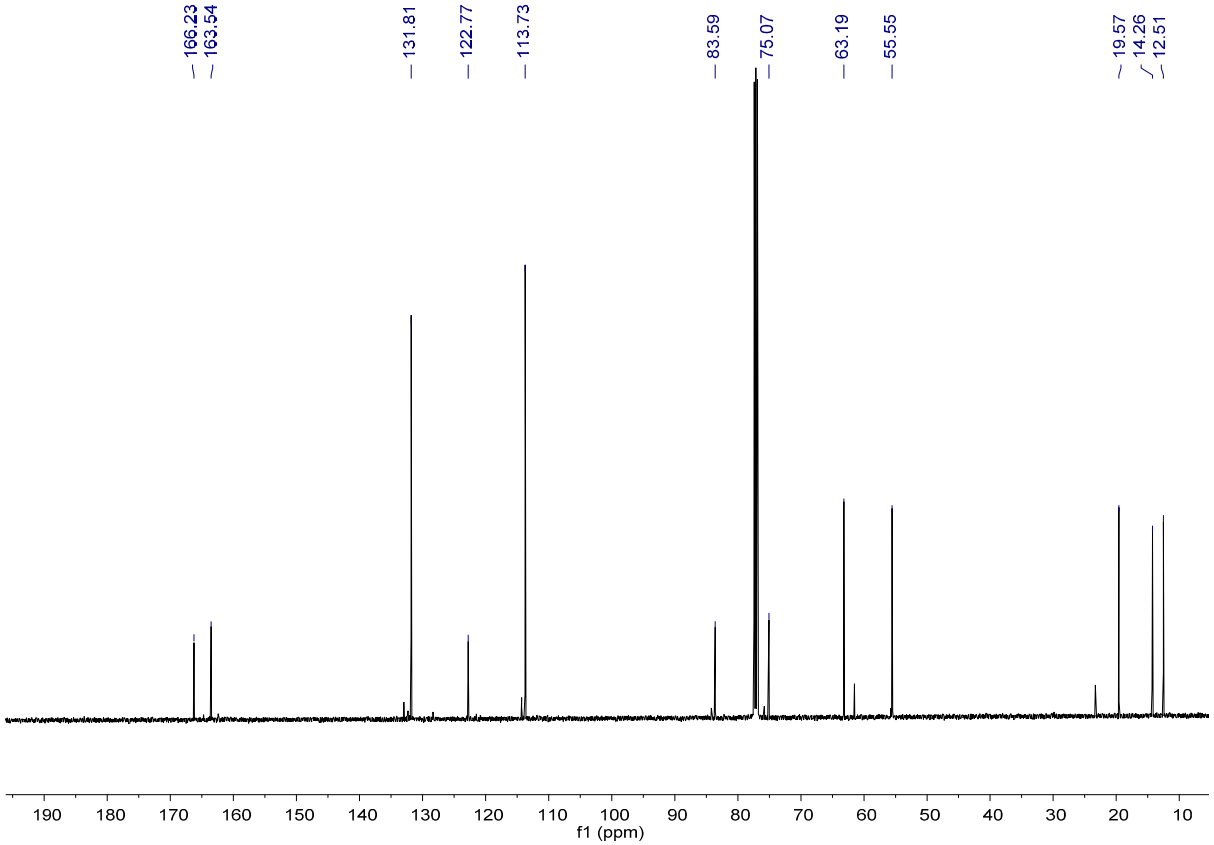
^{13}C-NMR (100.6 MHz, $CDCl_3$, 298K) spectrum of hex-3-yn-1-yl 4-methylbenzoate (**1b**)



^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectrum of hex-3-yn-1-yl 4-methoxybenzoate (**1c**)

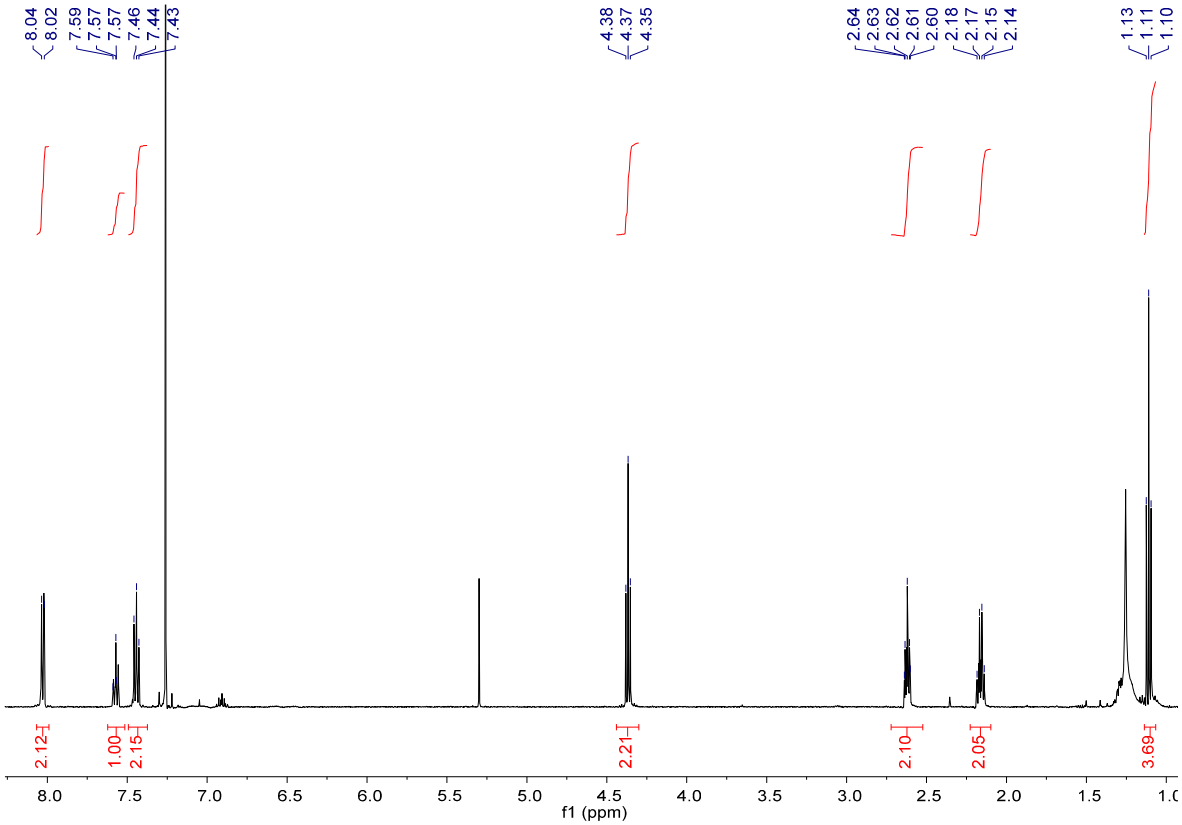


^{13}C-NMR (125 MHz, $CDCl_3$, 298K) spectrum of hex-3-yn-1-yl 4-methoxybenzoate (**1c**)

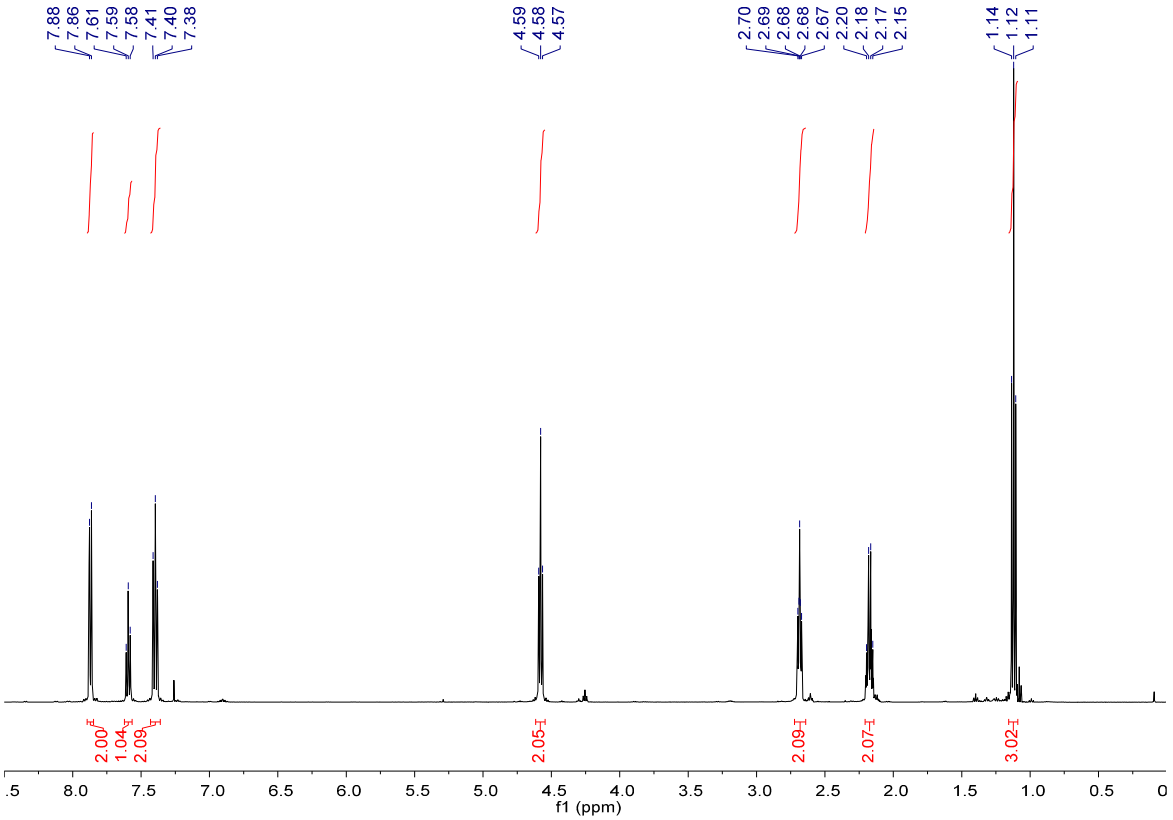


1.2. NMR Spectra of Products

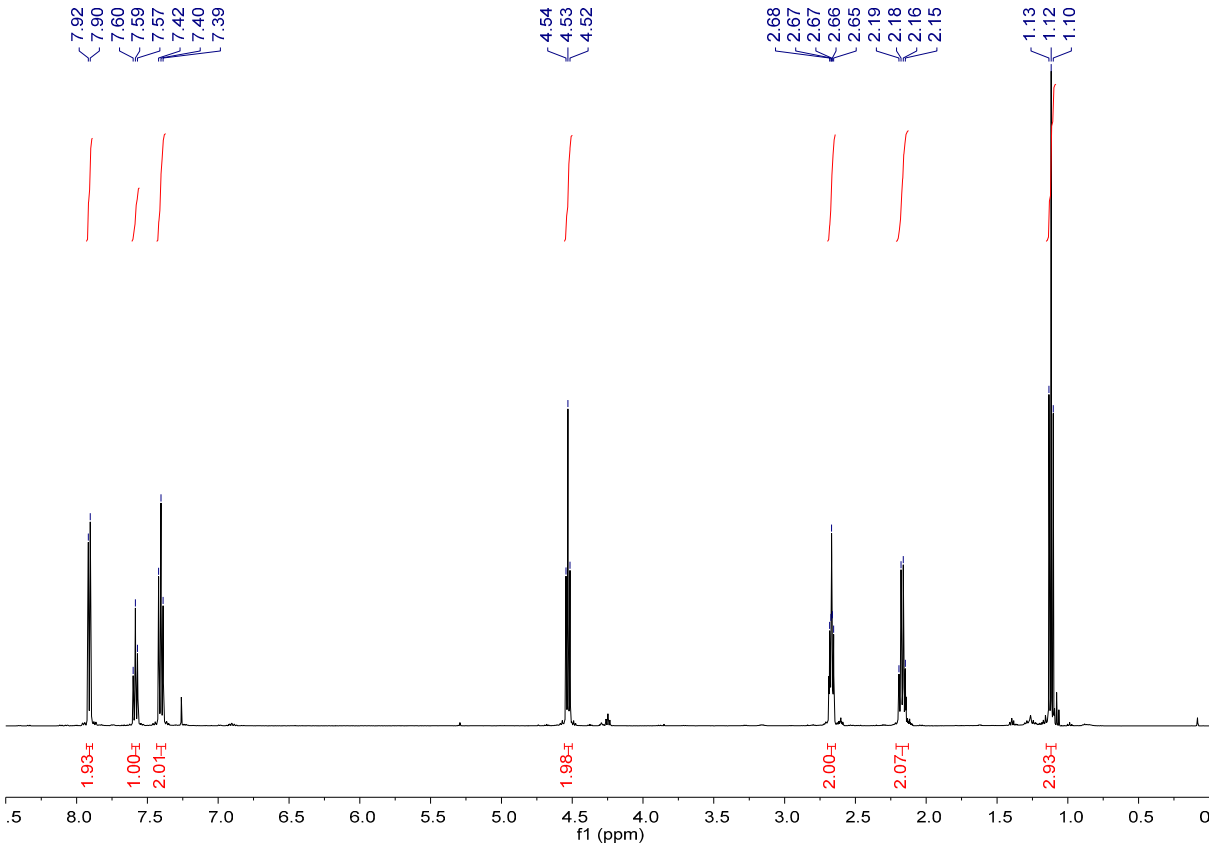
^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectrum of **2a** crystals.



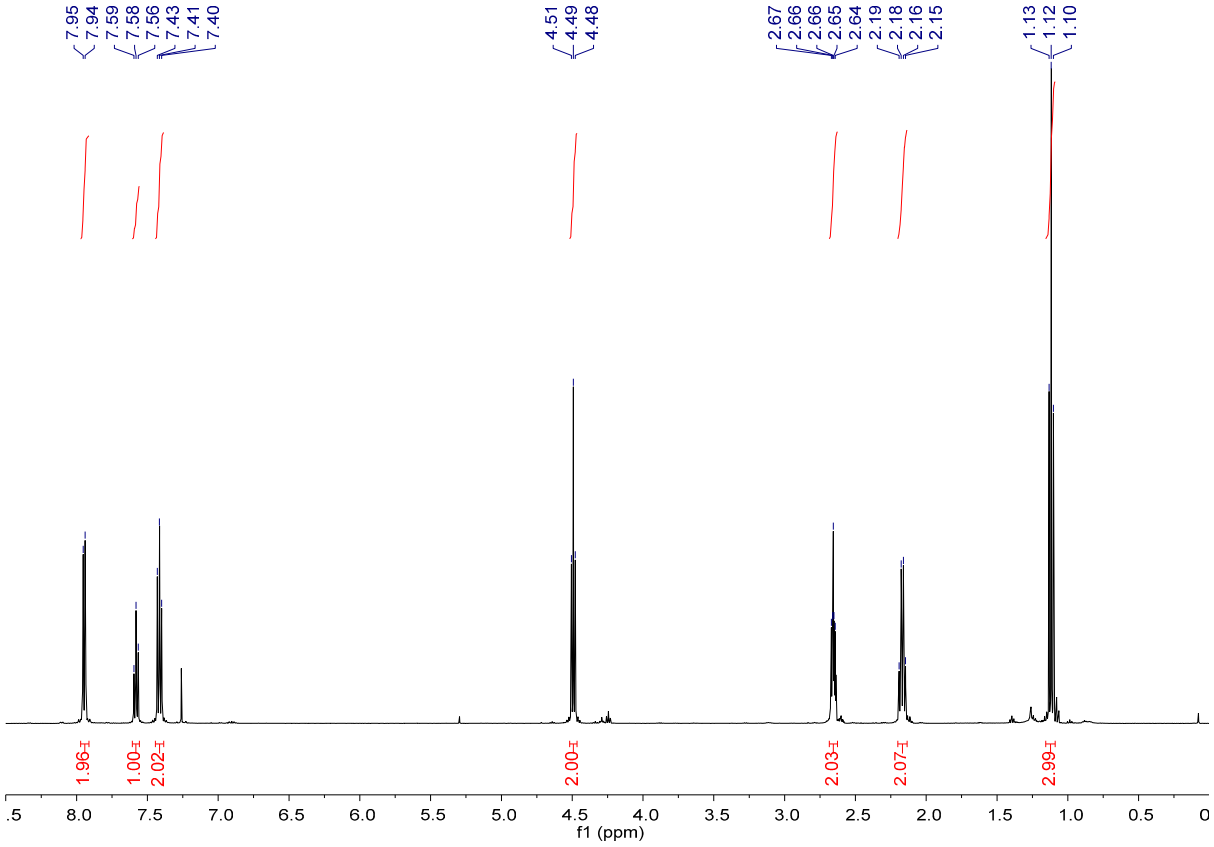
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.4 M) spectrum of **2a**.



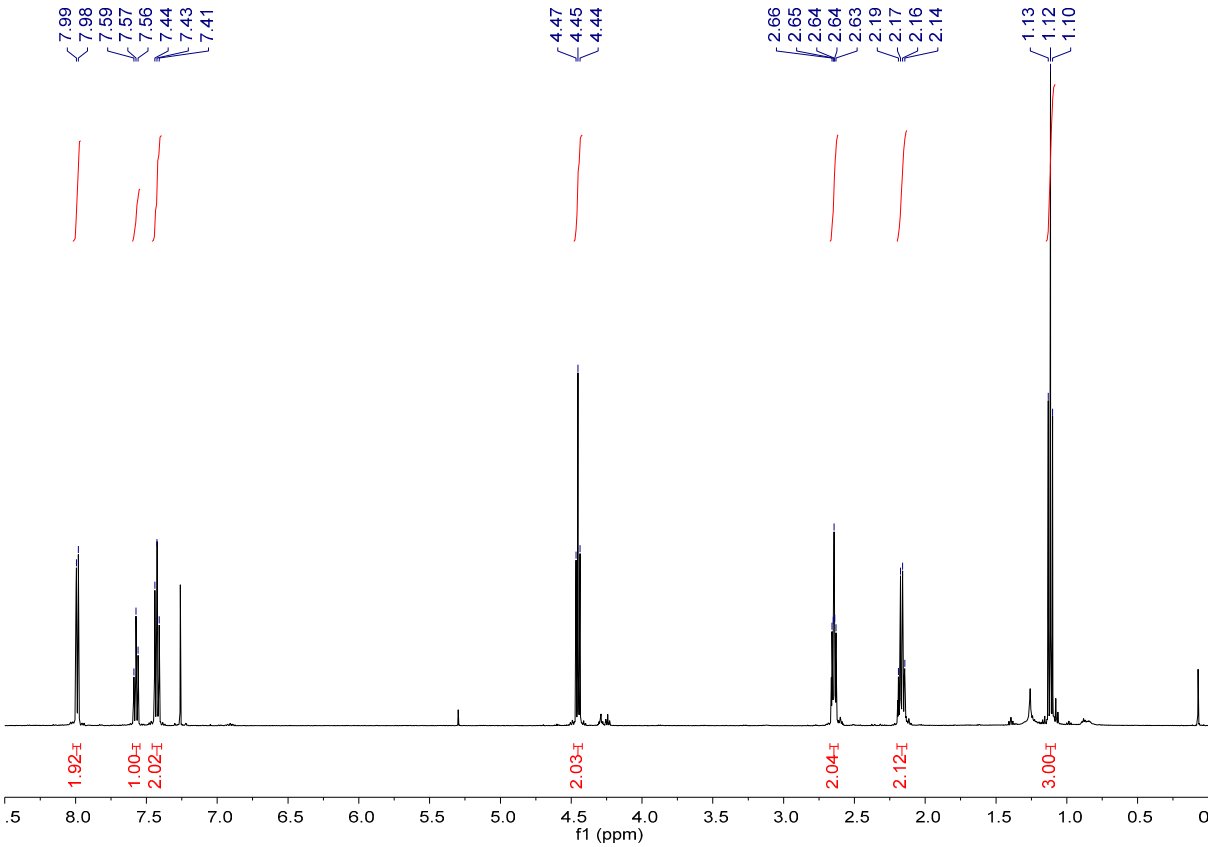
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.2 M) spectrum of **2a**.



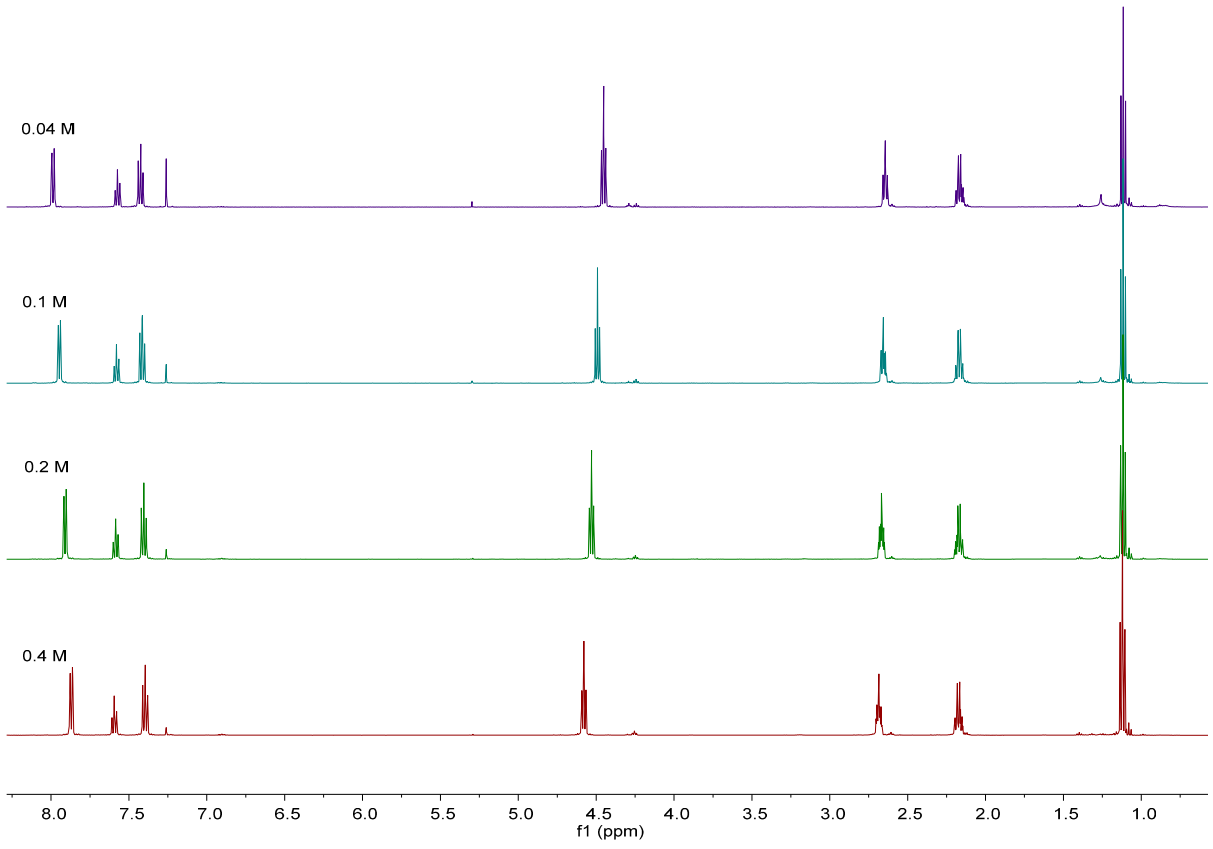
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.1 M) spectrum of **2a**.



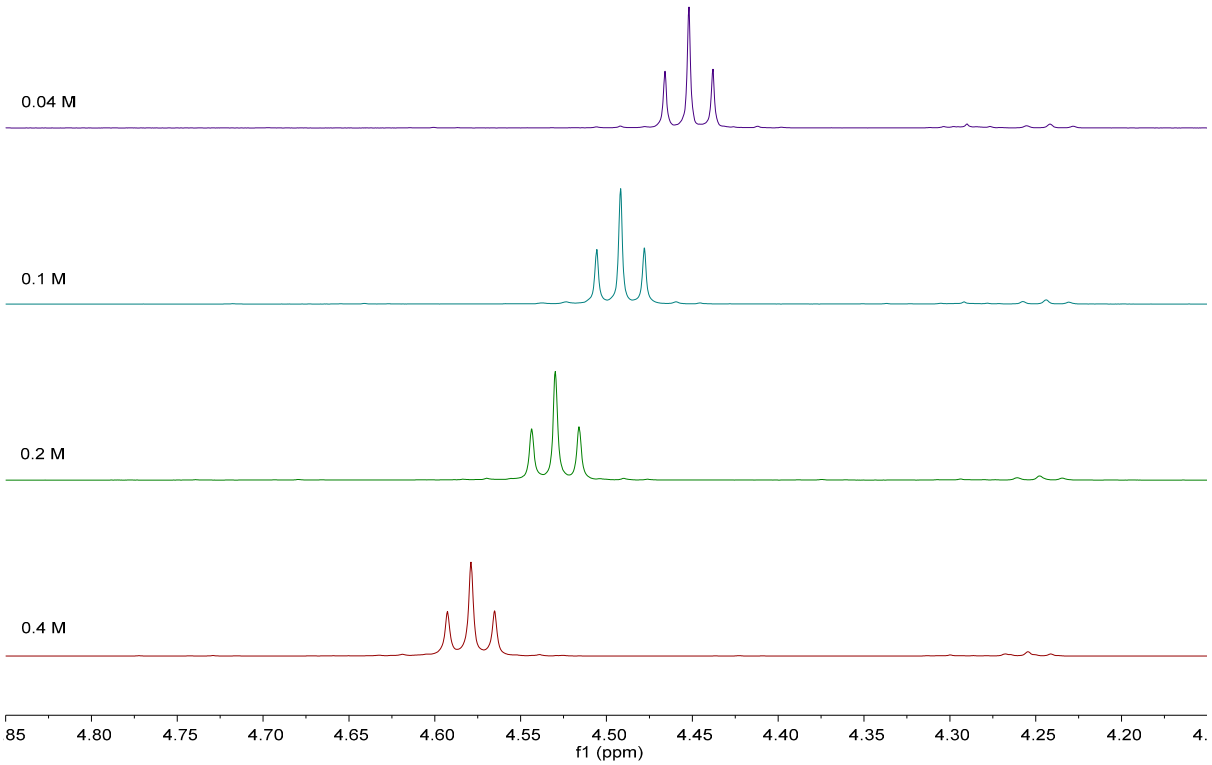
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.04 M) spectrum of **2a**.



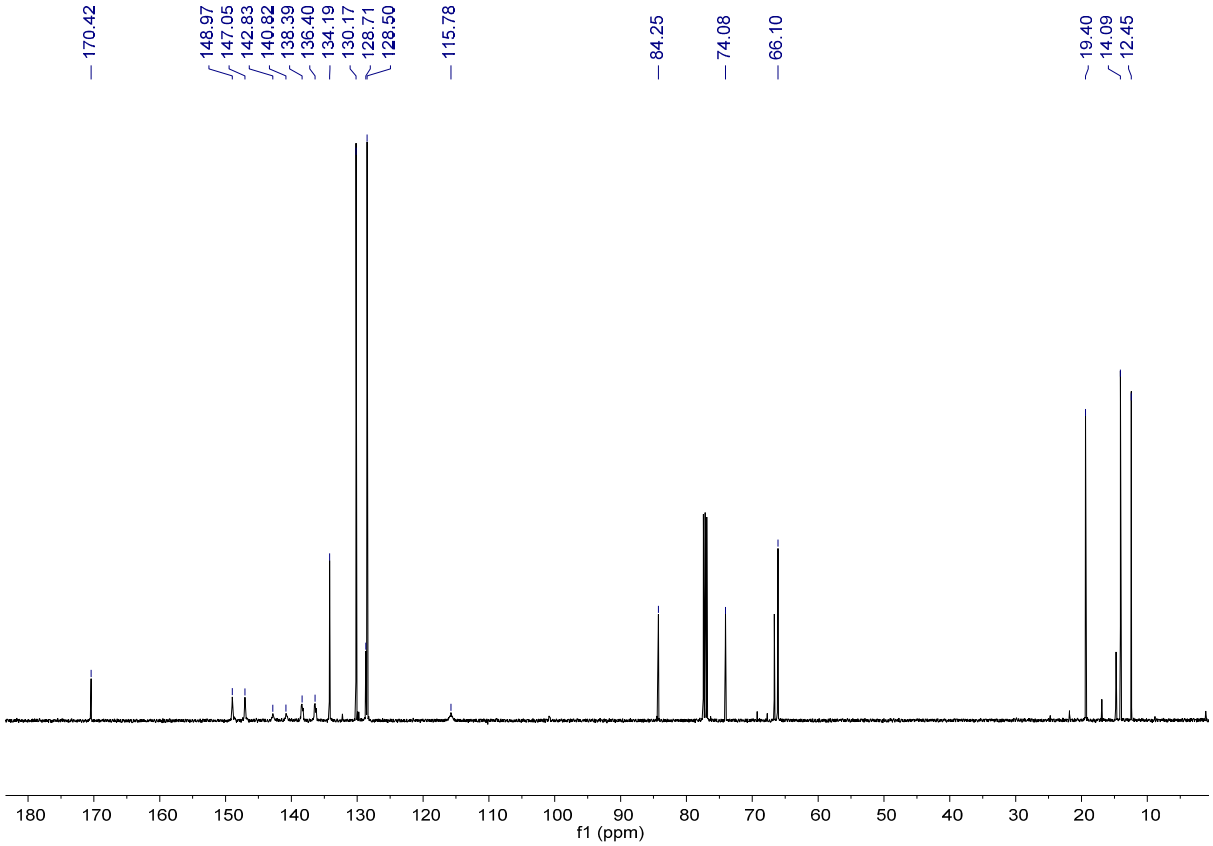
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectra of **2a** across concentrations 0.04–0.4 M.



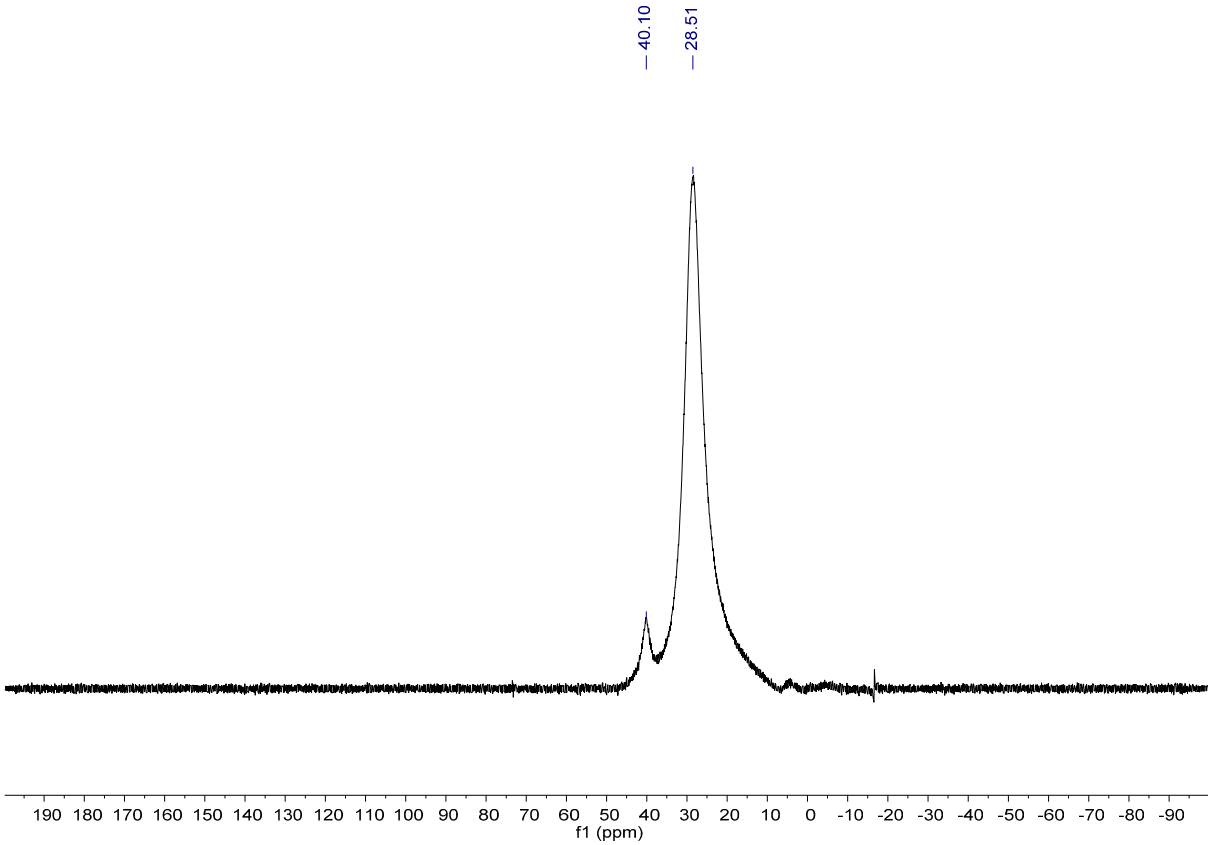
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K) specta of **2a,** expansion of C<u>H</u>$_2$O(CO)-) across concentrations 0.04–0.4 M.



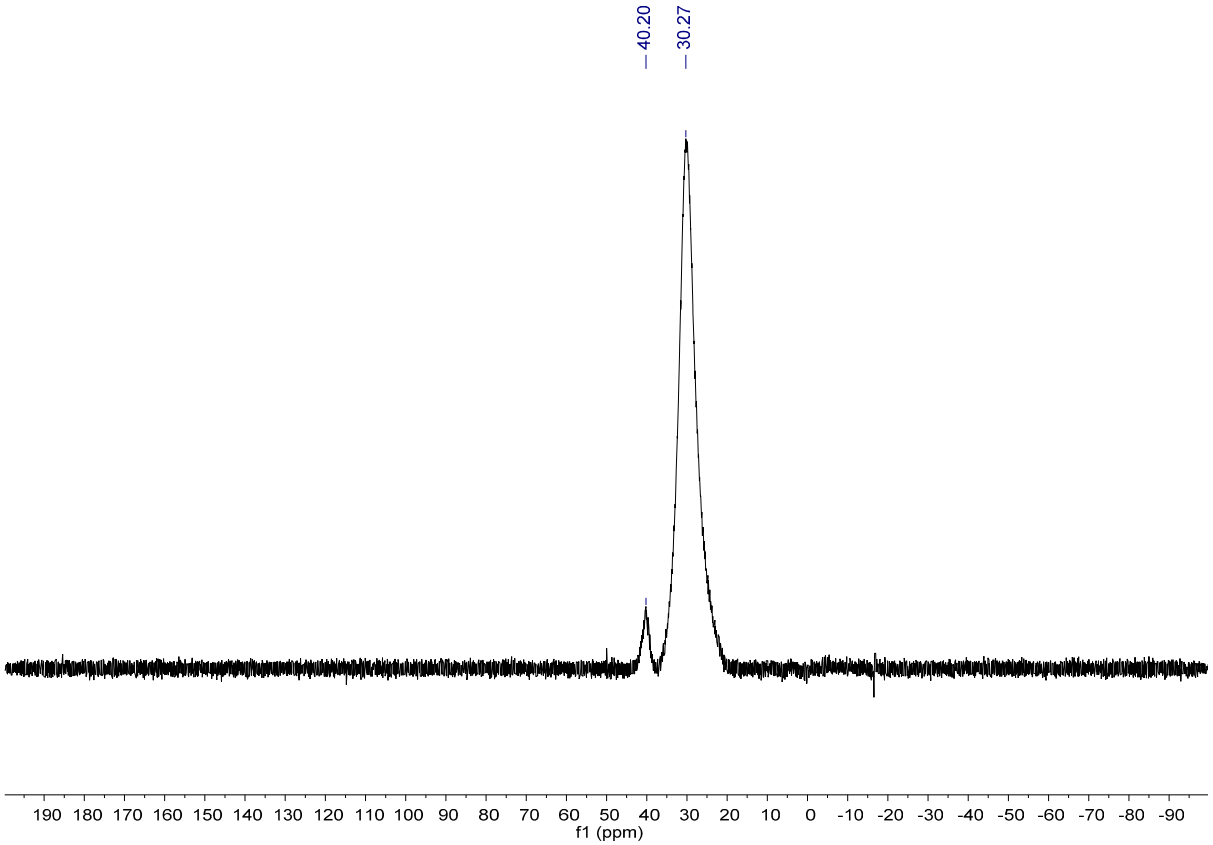
In situ ^{13}C-NMR (125 MHz, $CDCl_3$, 298K, 0.2 M) spectrum of **2a**.



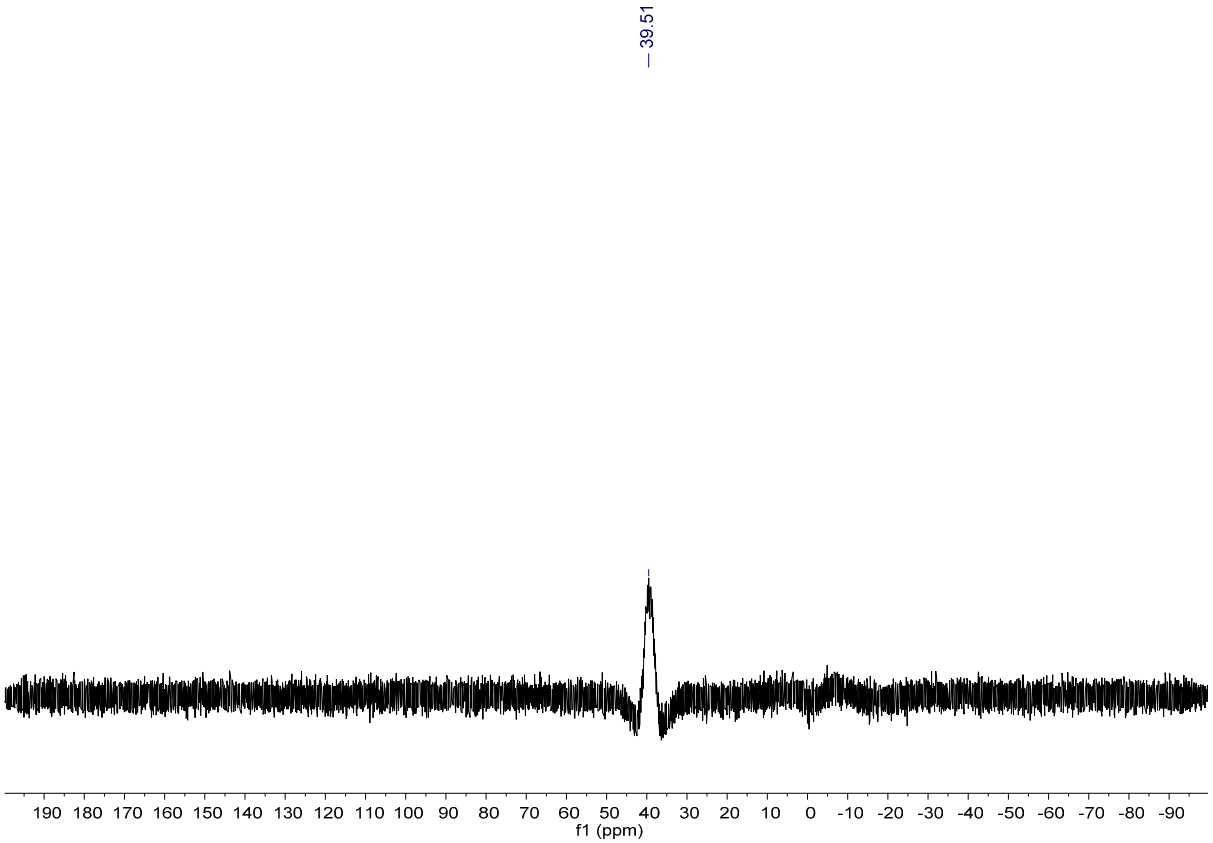
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.4 M) spectrum of **2a**.



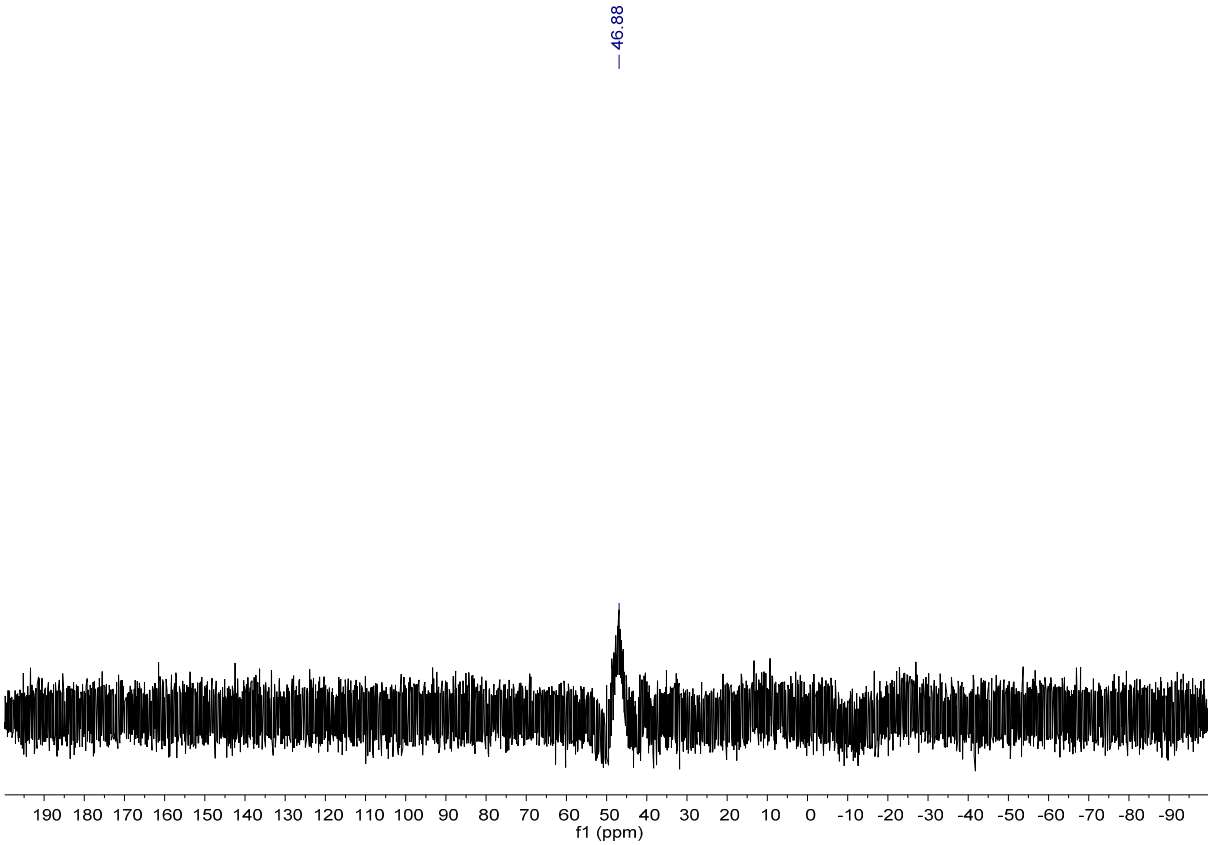
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.2 M) spectrum of **2a**.



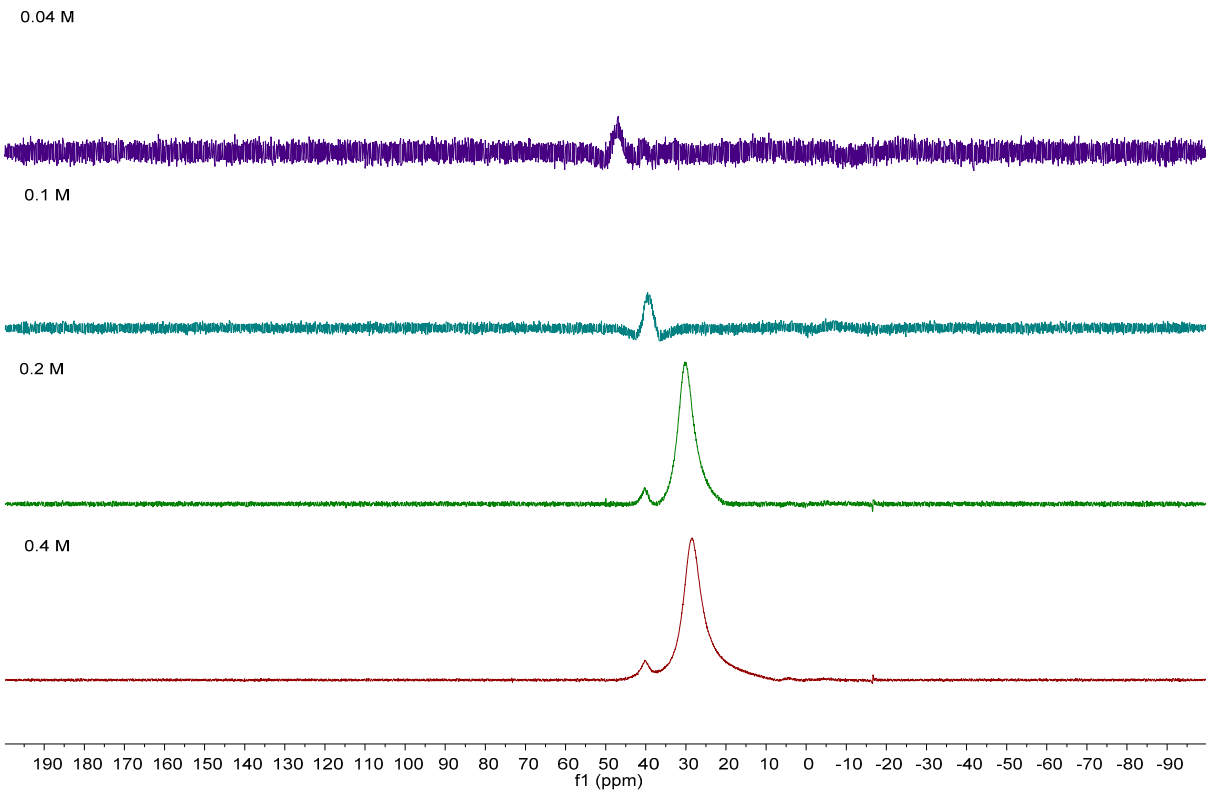
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.1 M) spectrum of **2a**.



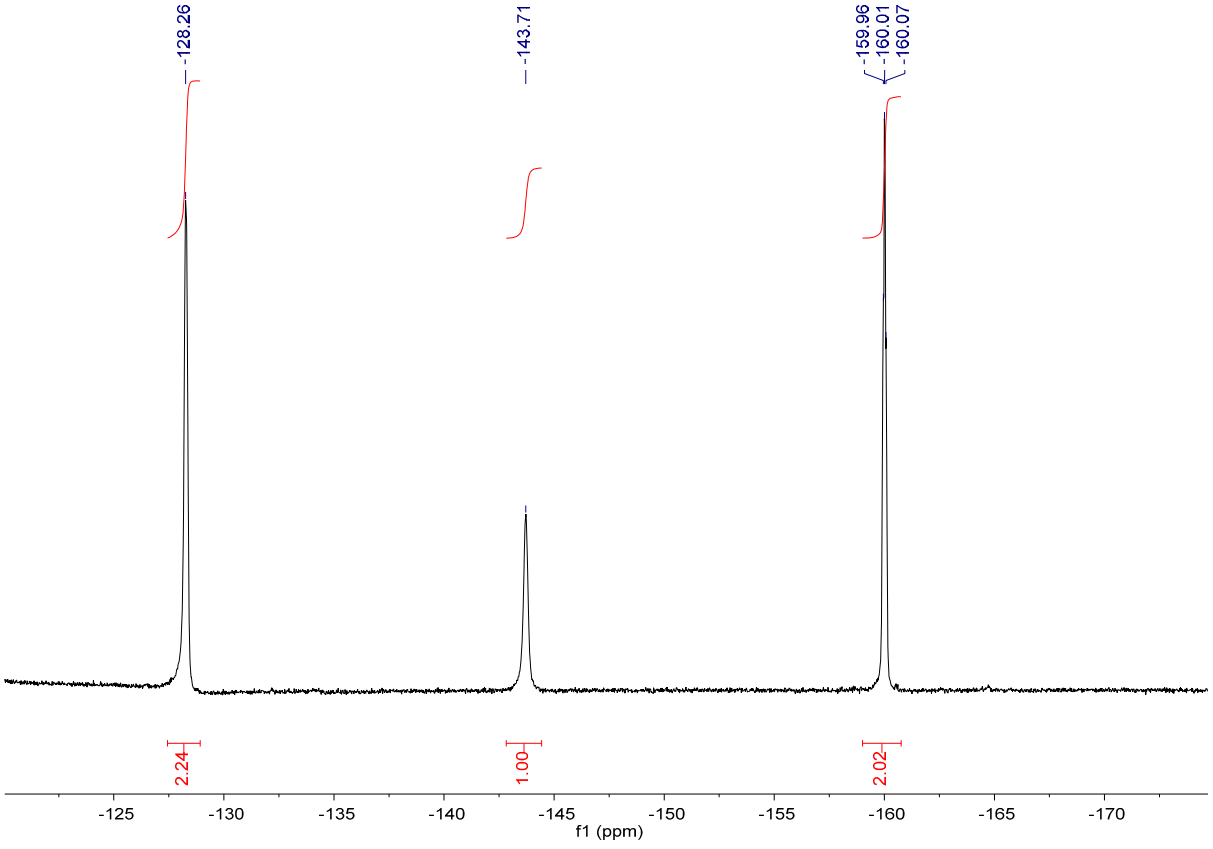
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.04 M) spectrum of **2a**.



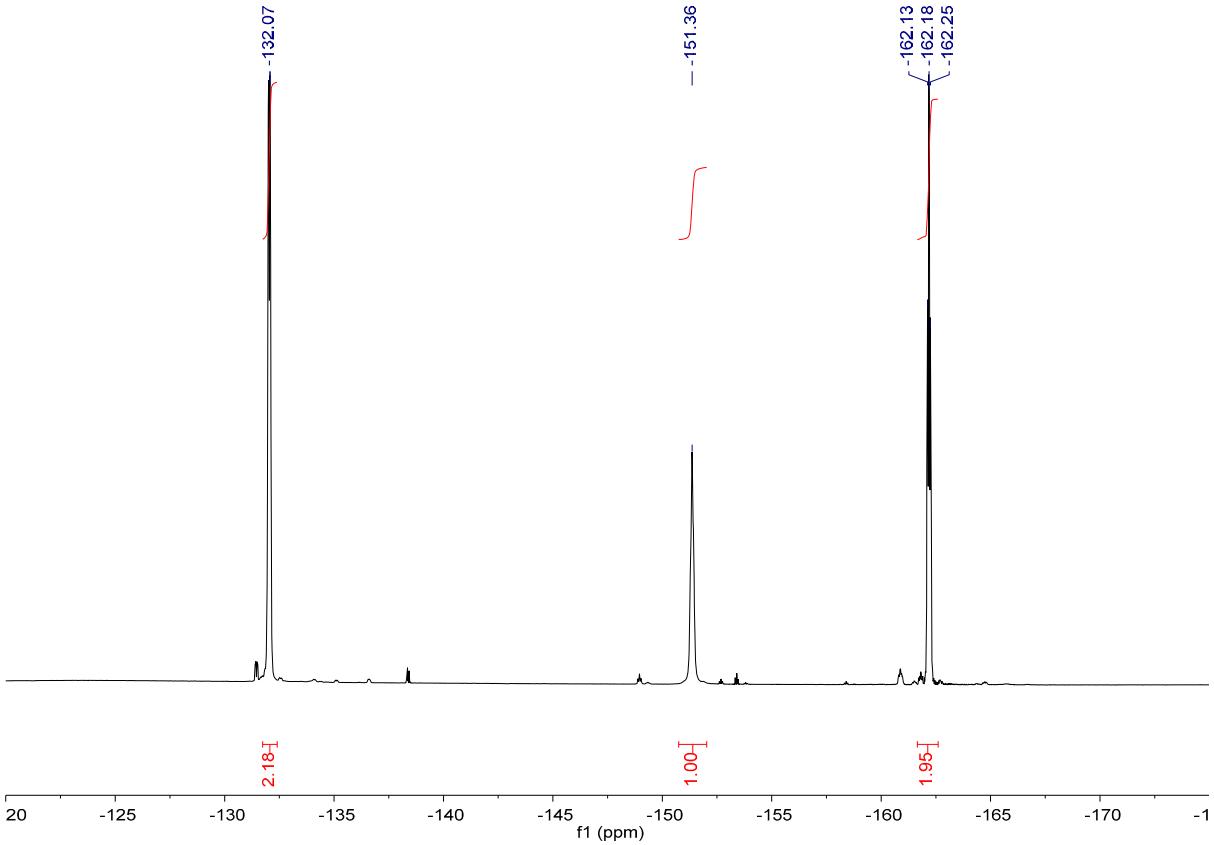
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K) spectra of **2a** across concentrations 0.04–0.4 M.



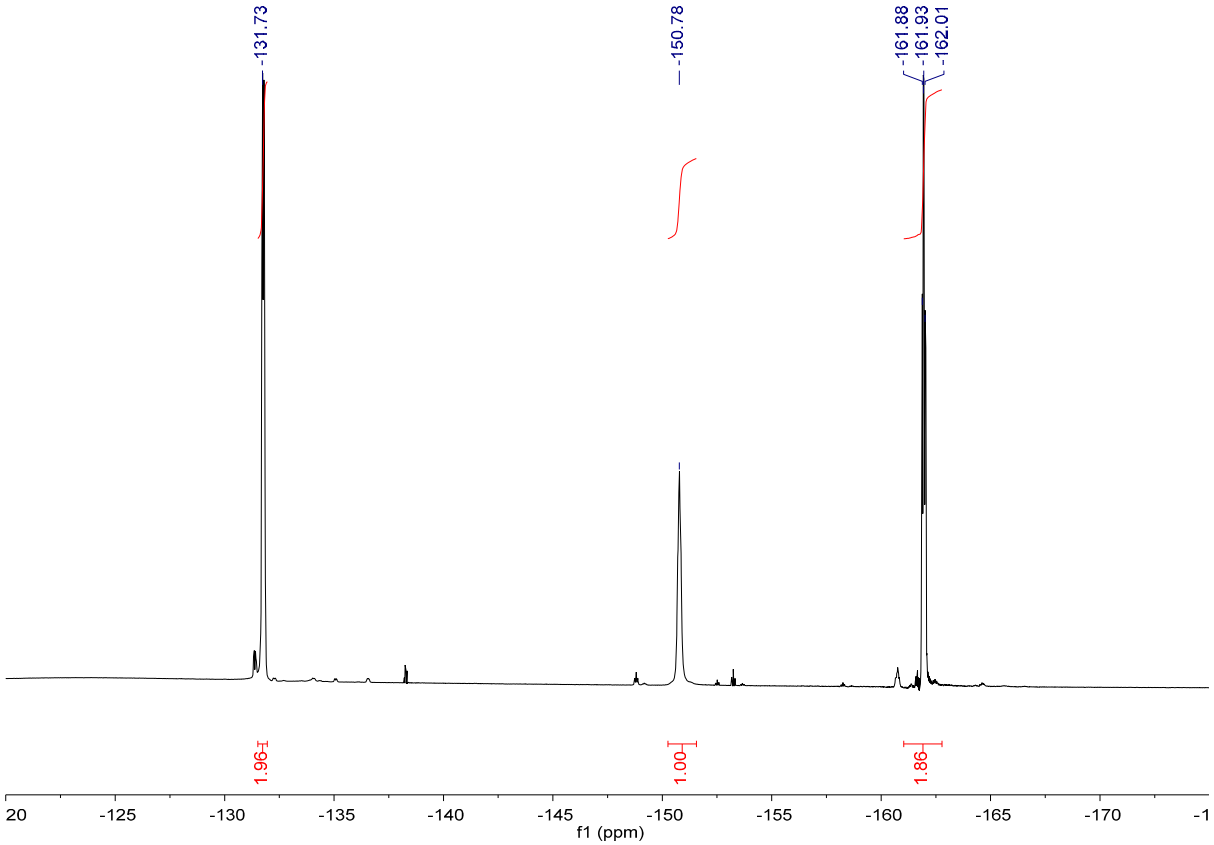
^{19}F-NMR (283 MHz, $CDCl_3$, 298 K) spectrum of **2a** crystals.



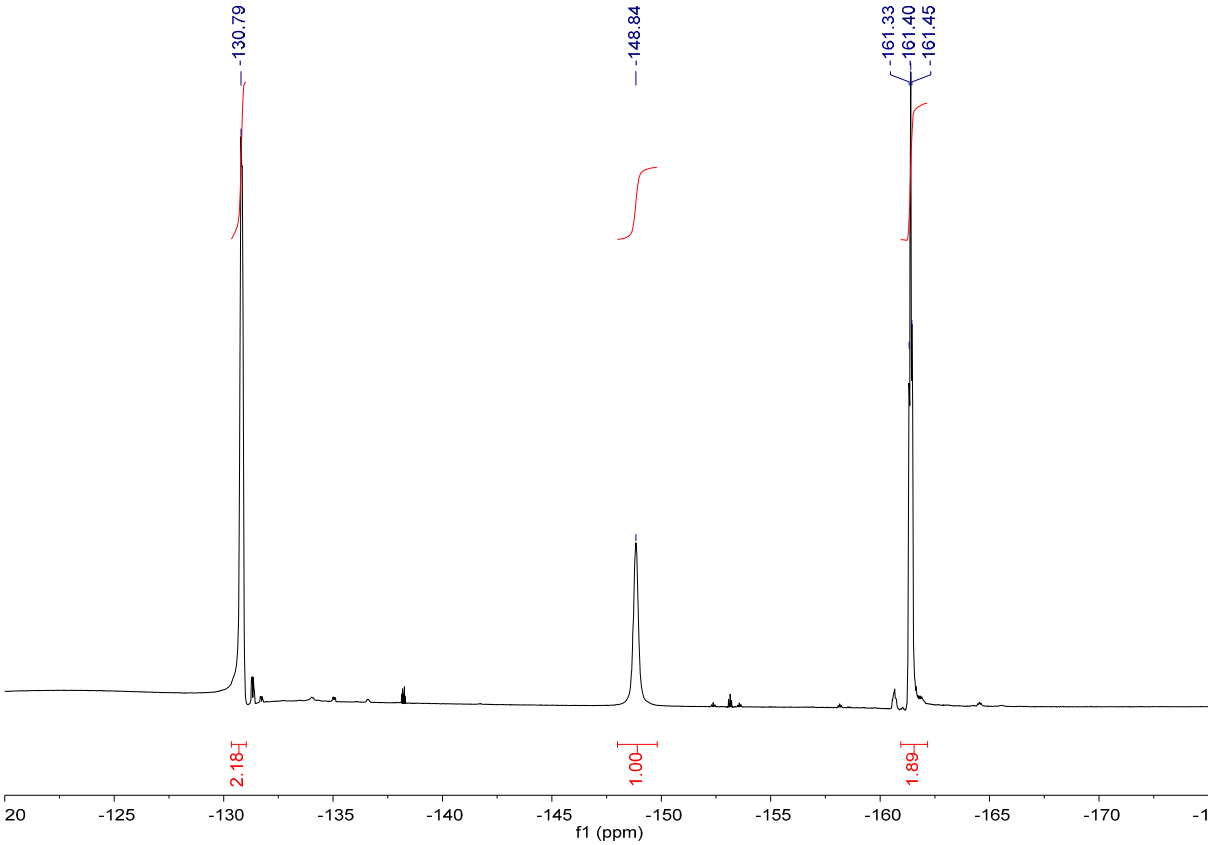
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.4 M) spectrum of **2a**.



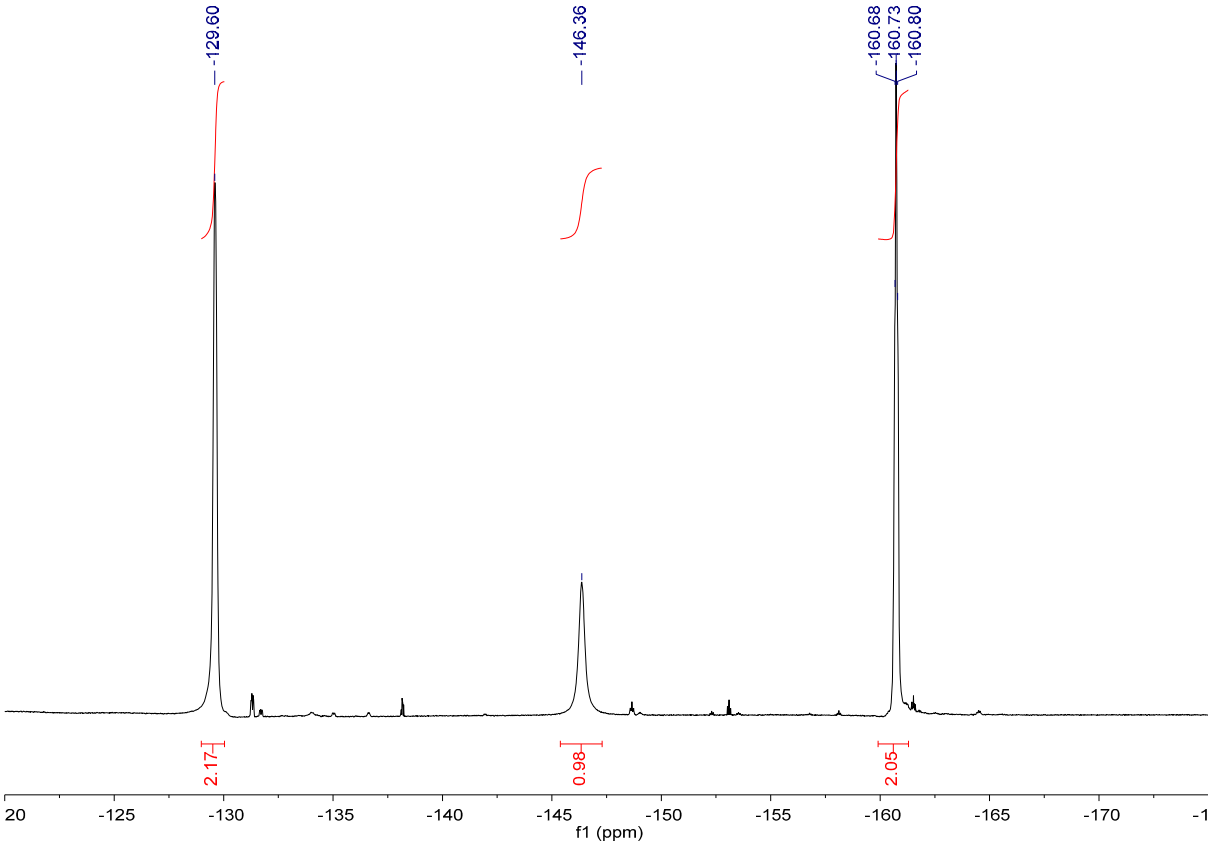
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.2 M) spectrum of **2a**.



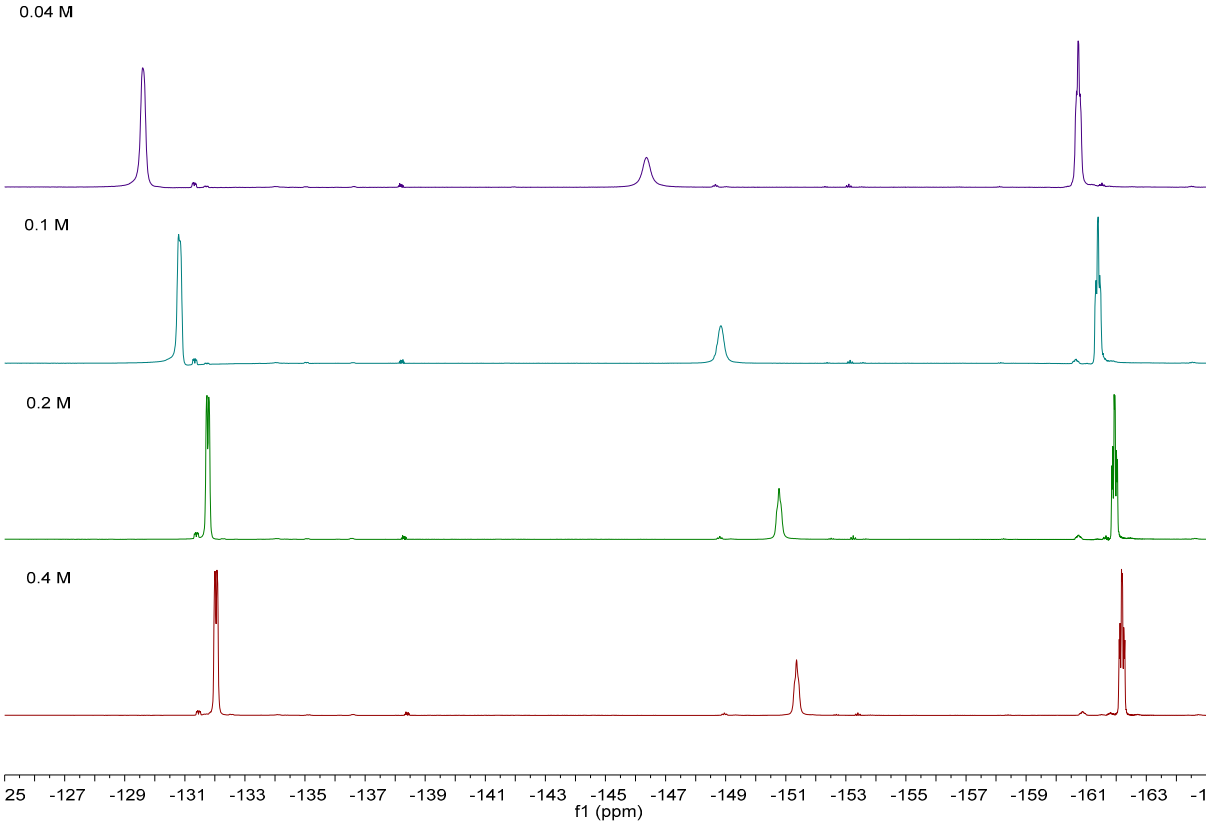
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.1 M) spectrum of **2a**.



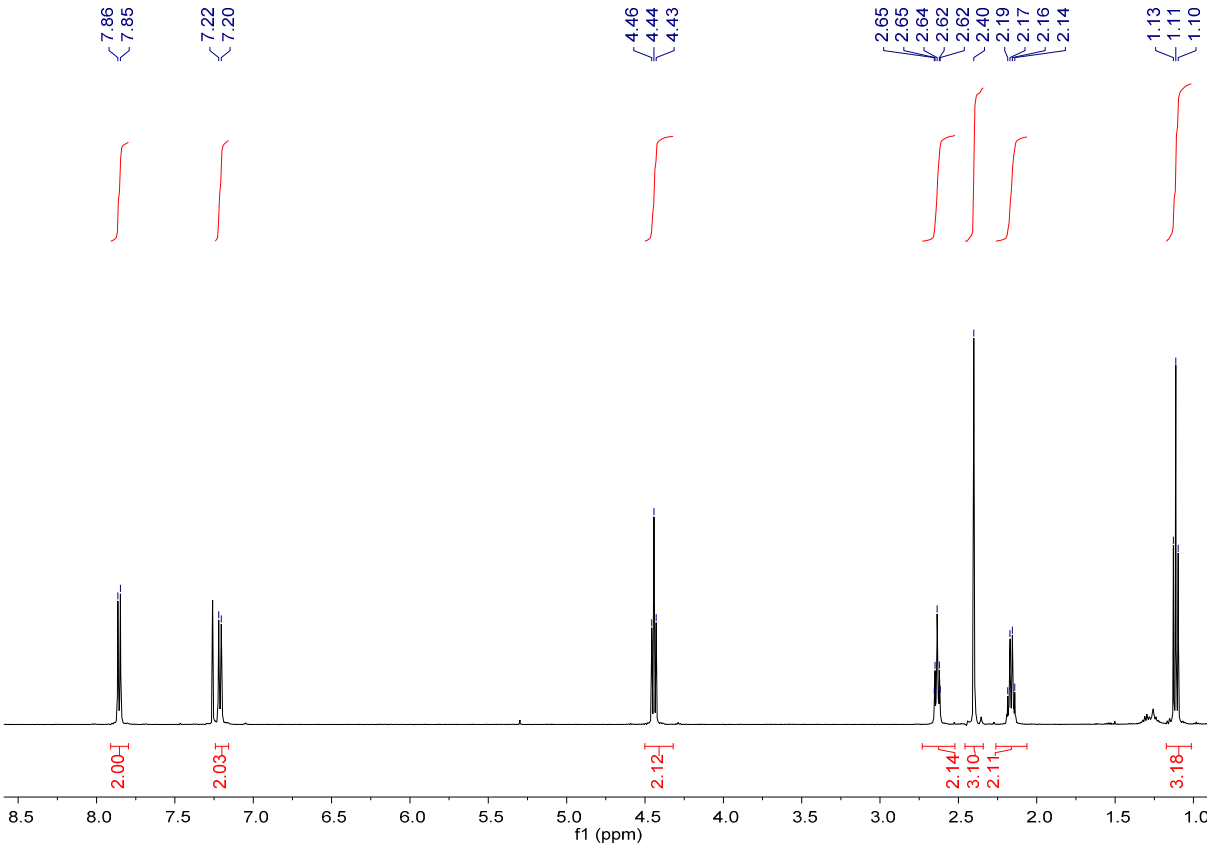
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.04 M) spectrum of **2a**.



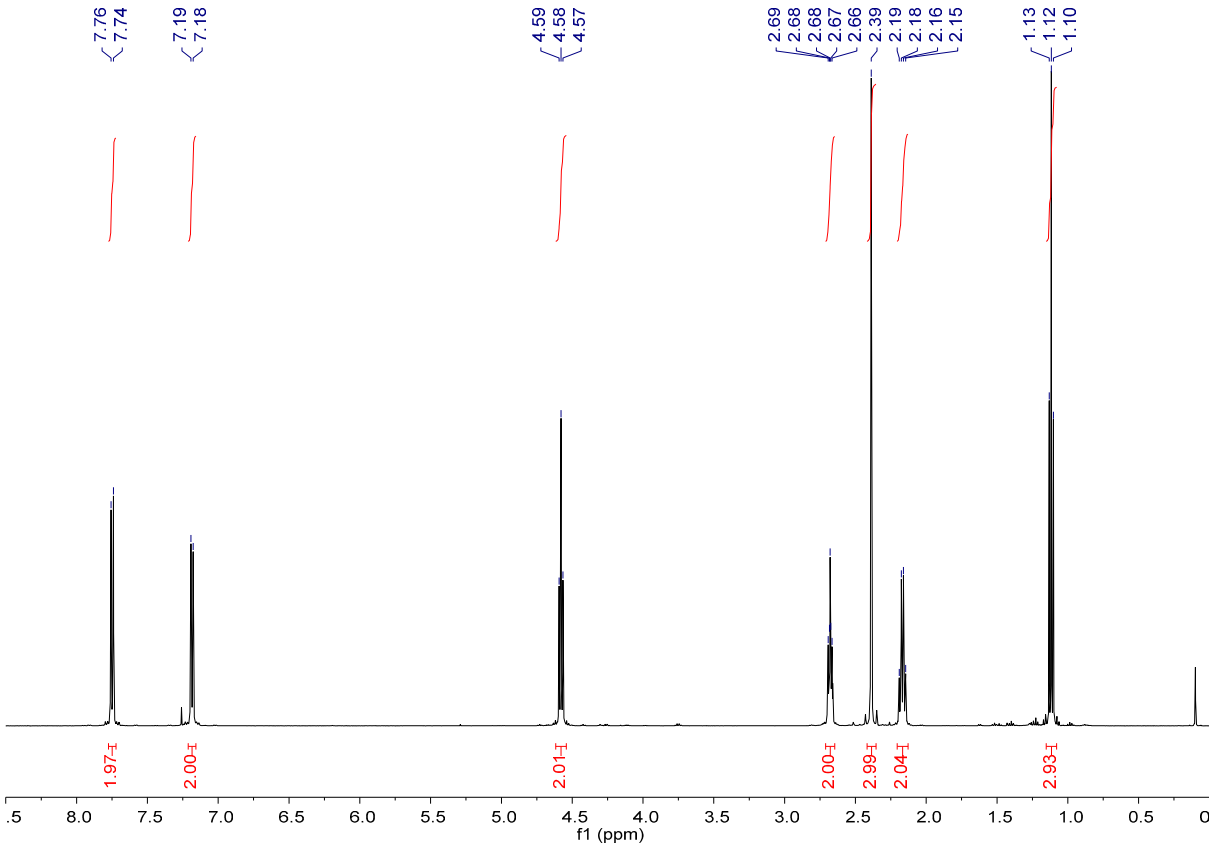
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K) spectra of **2a** across concentrations 0.04–0.4 M



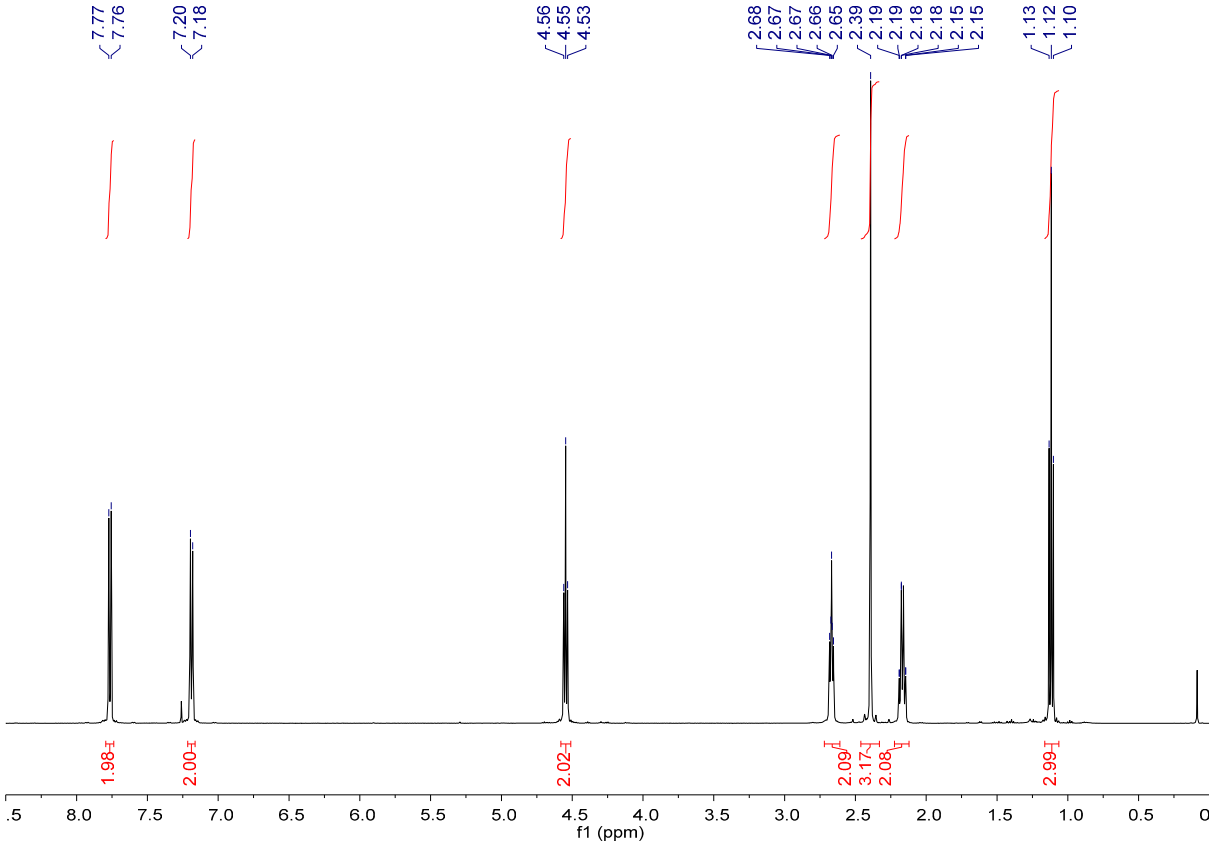
^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectrum of **2b** crystals.



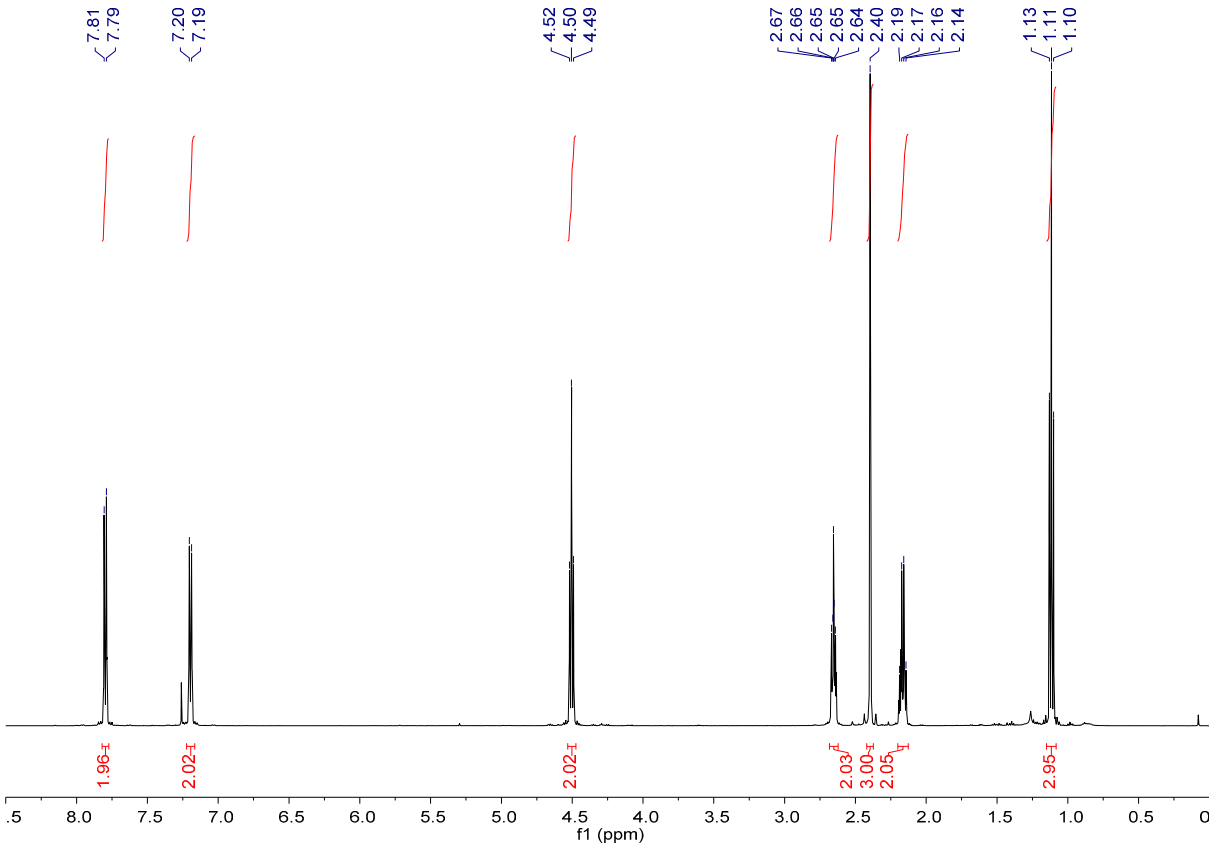
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.4 M) spectrum of **2b**.



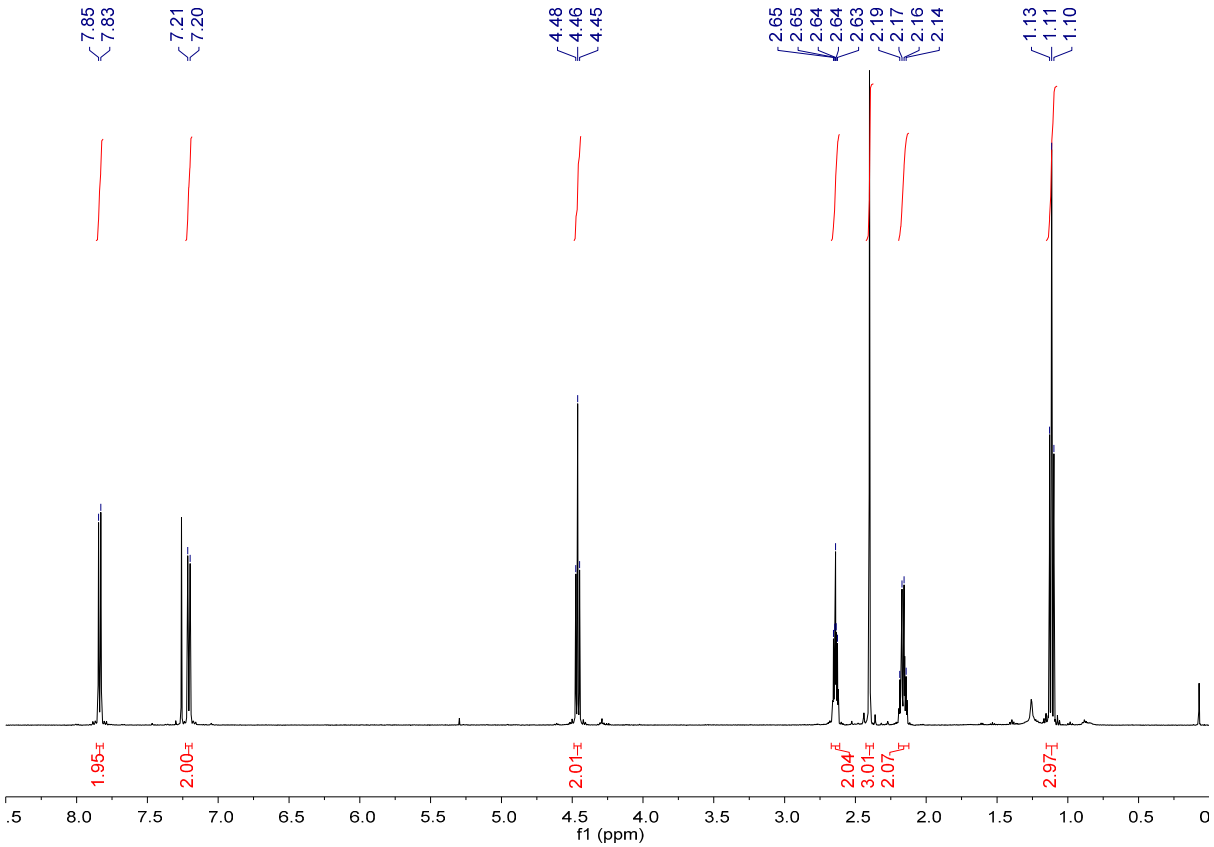
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.2 M) spectrum of **2b**.



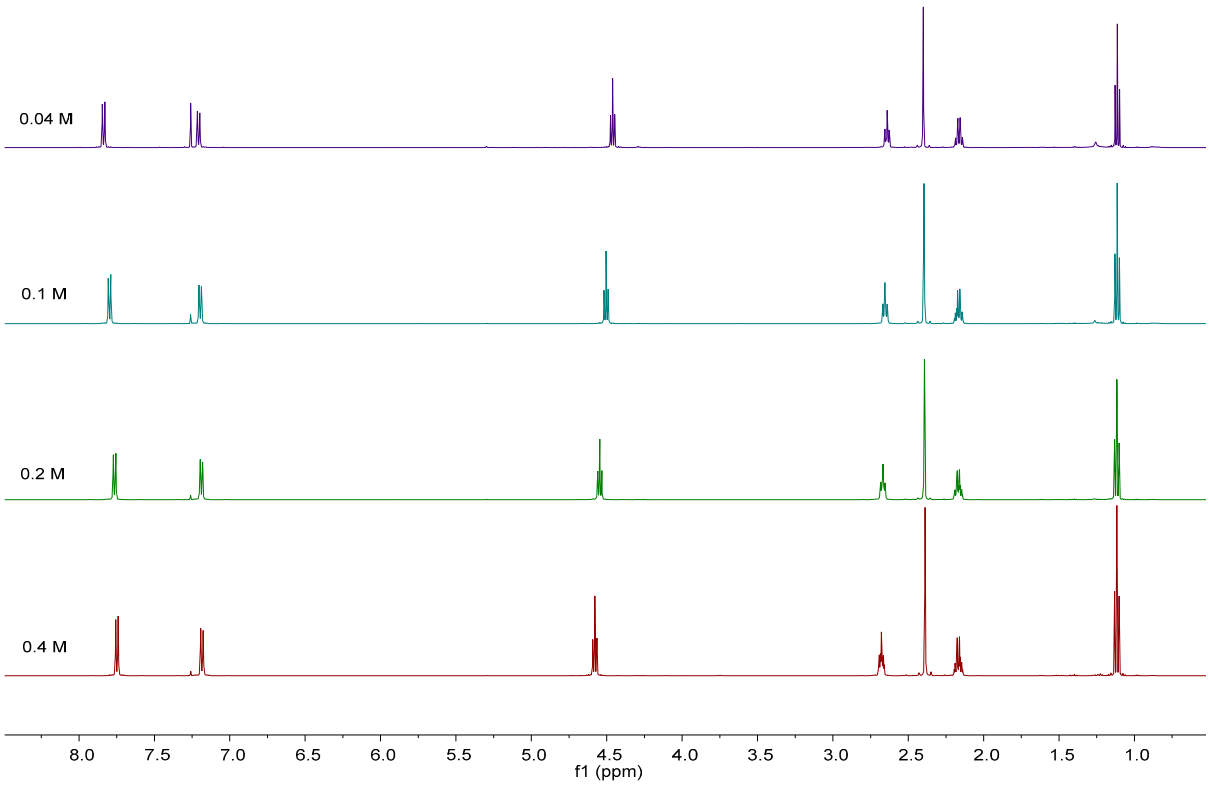
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.1 M) spectrum of **2b**.



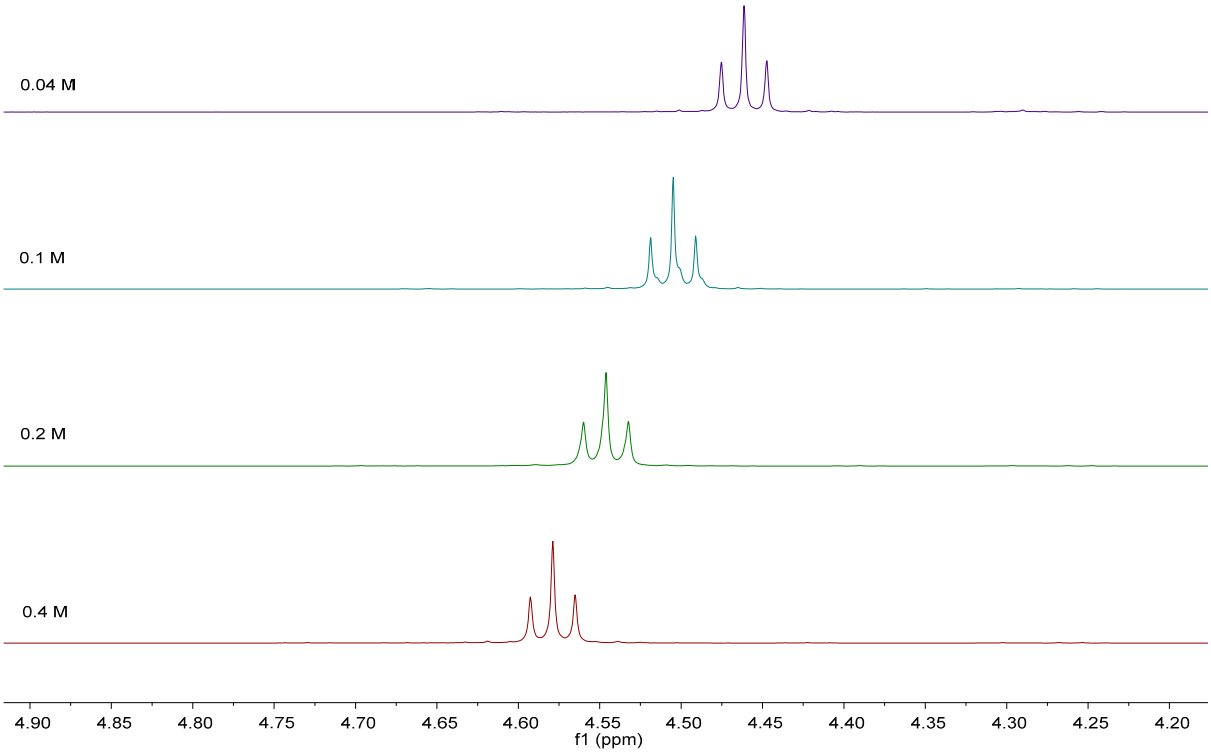
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.04 M) spectrum of **2b**.



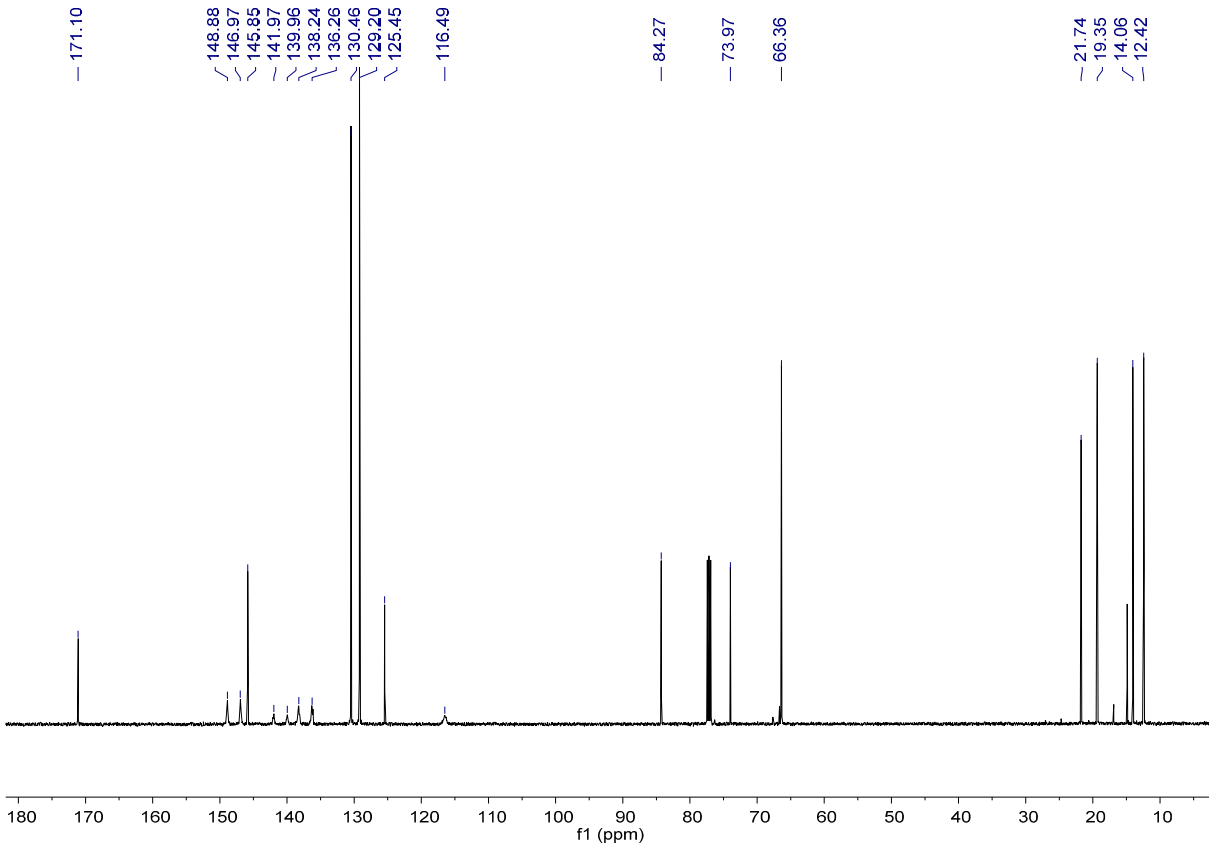
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectra of **2b** across concentrations 0.04–0.4 M.



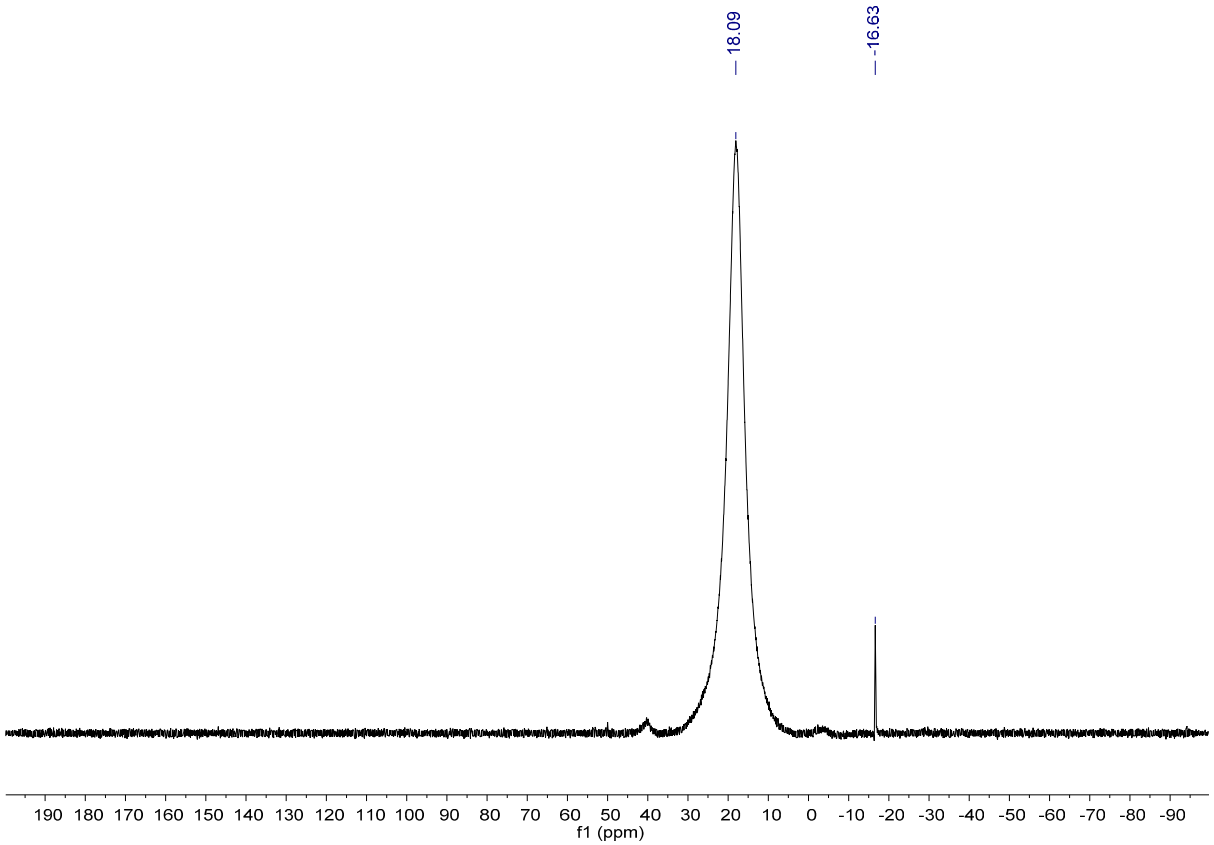
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectra of **2b**, (expansion of C<u>H</u>$_2$O(CO)-) across concentrations 0.04–0.4 M.



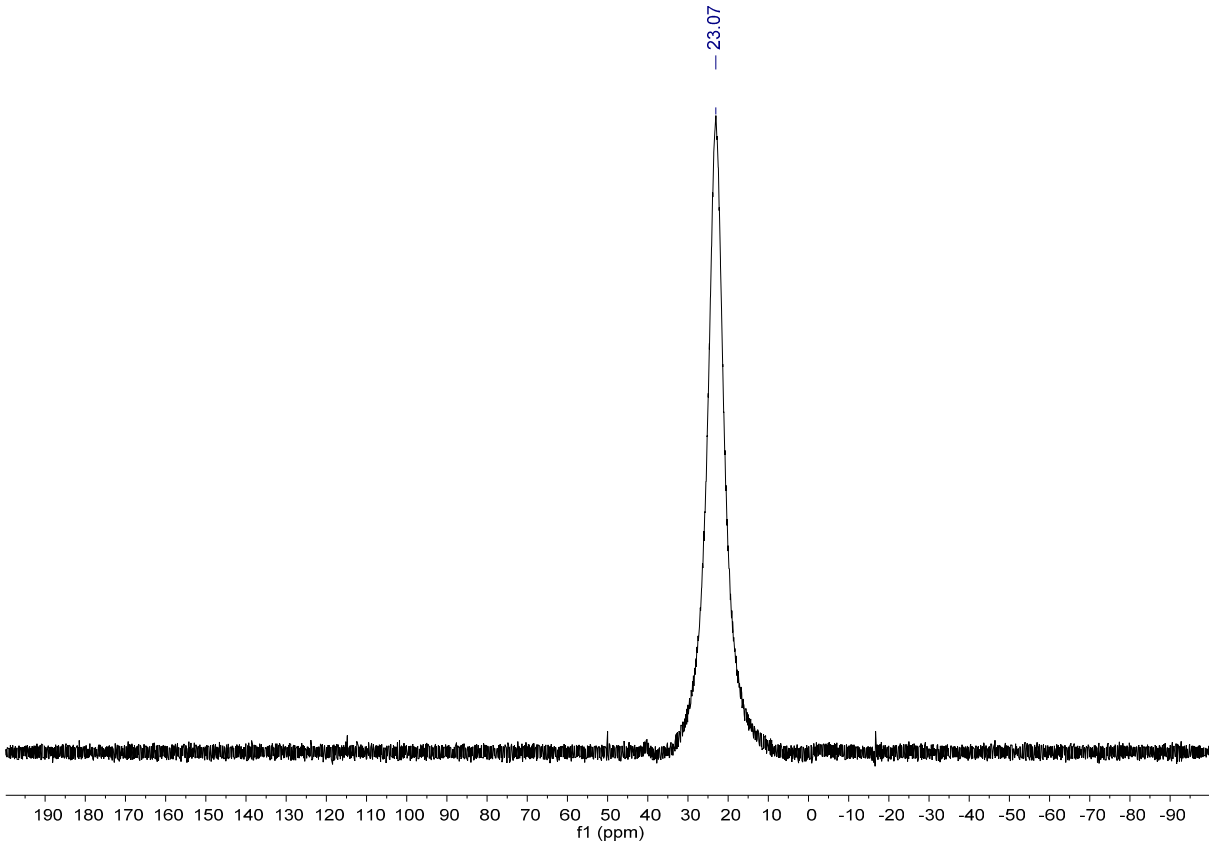
In situ ^{13}C-NMR (125 MHz, $CDCl_3$, 298K, 0.2 M) spectrum of **2b**.



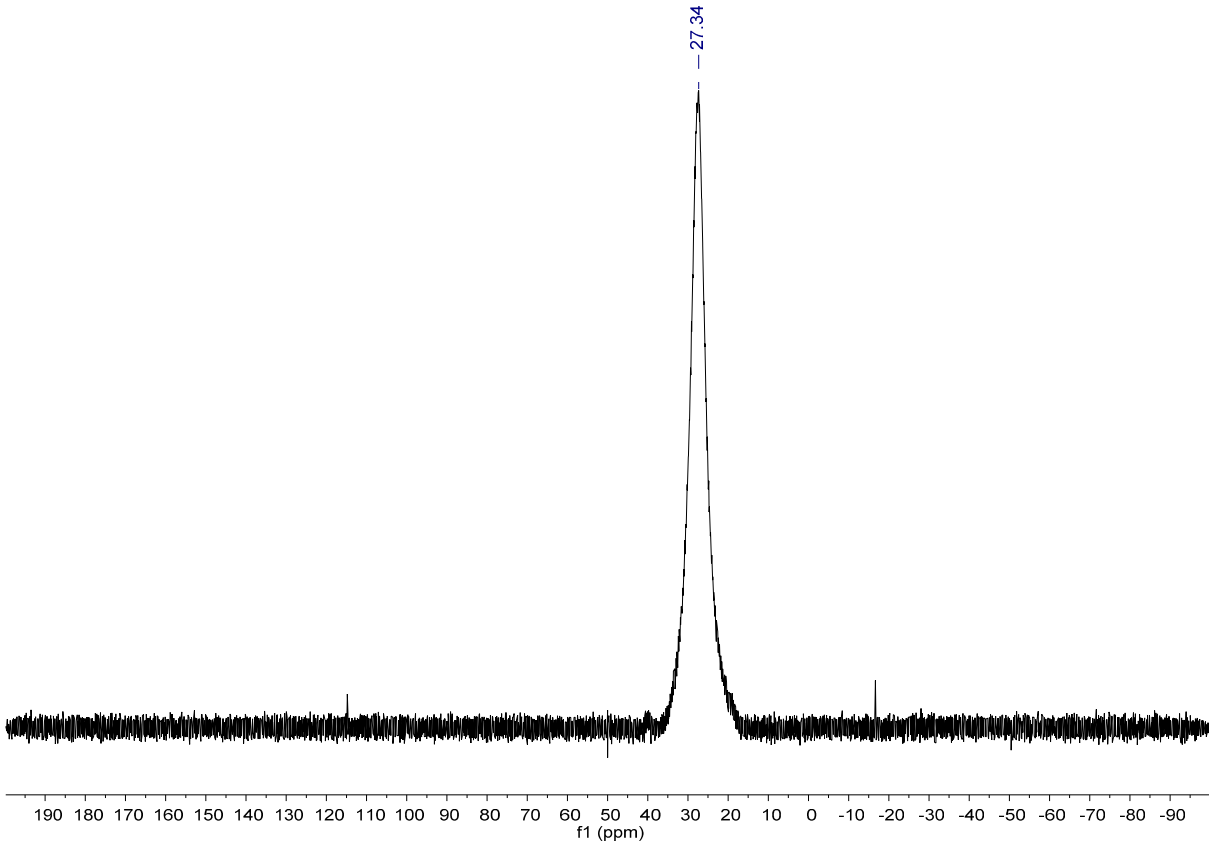
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.4 M) spectrum of **2b**.



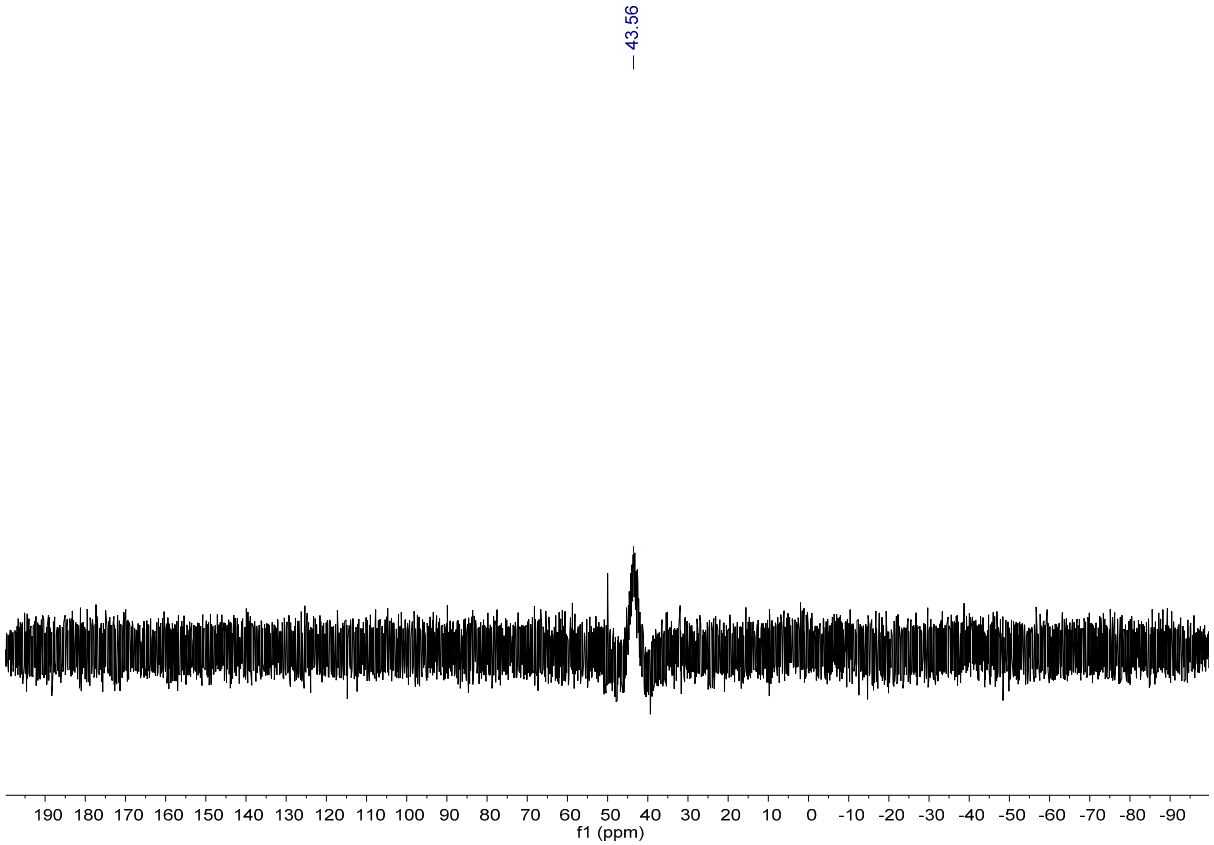
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.2 M) spectrum of **2b**.



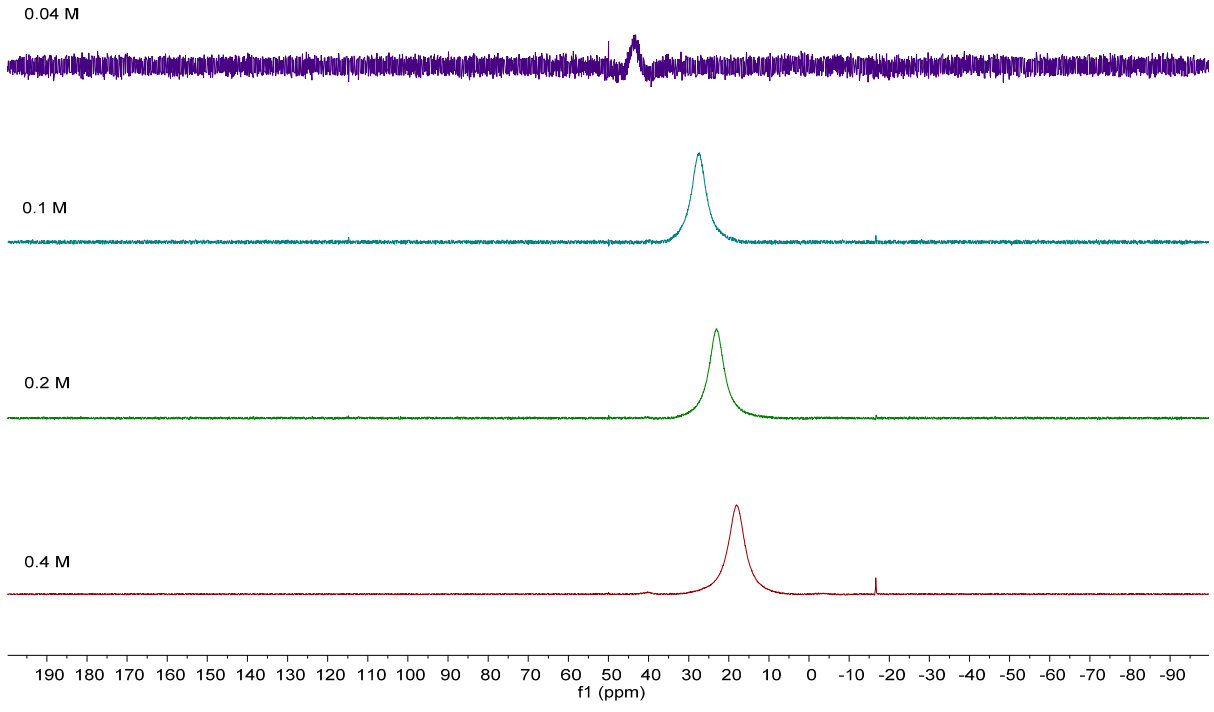
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.1 M) spectrum of **2b**.



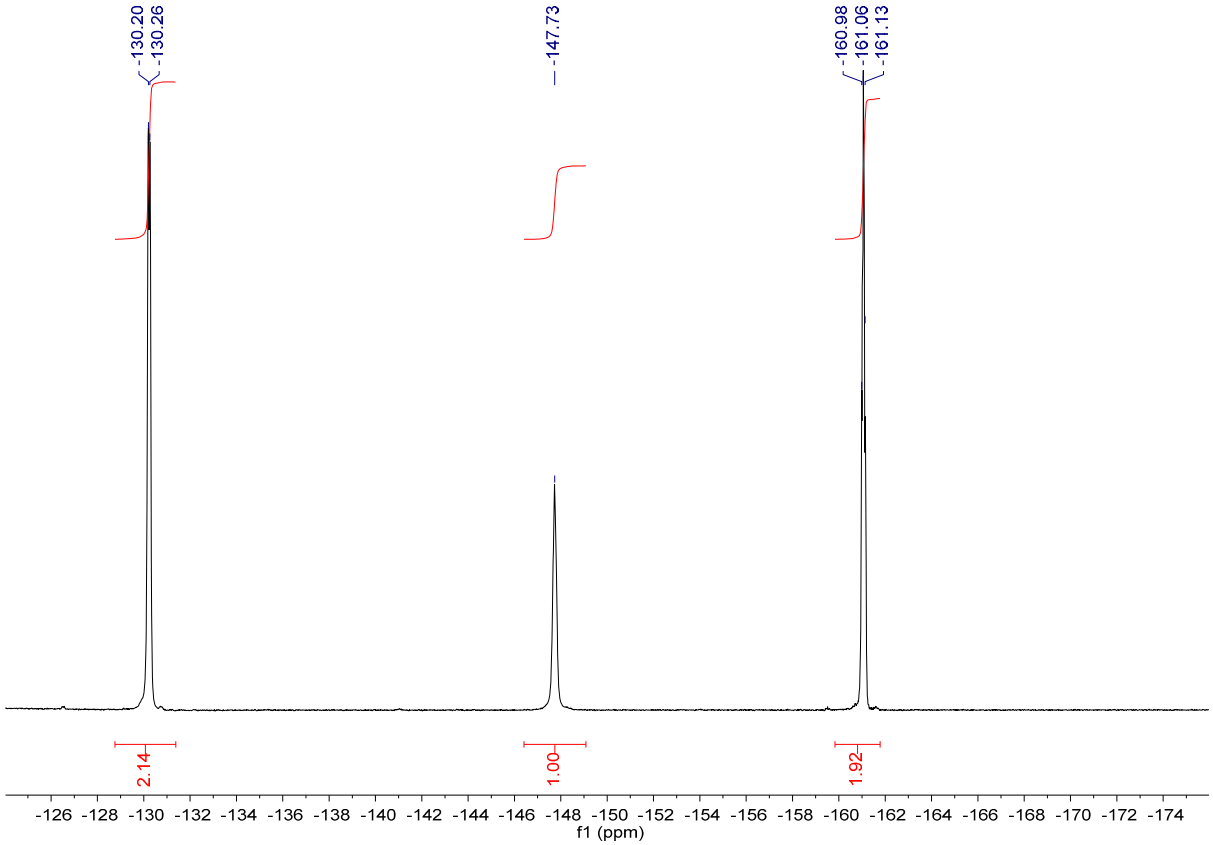
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.04 M) spectrum of **2b**.



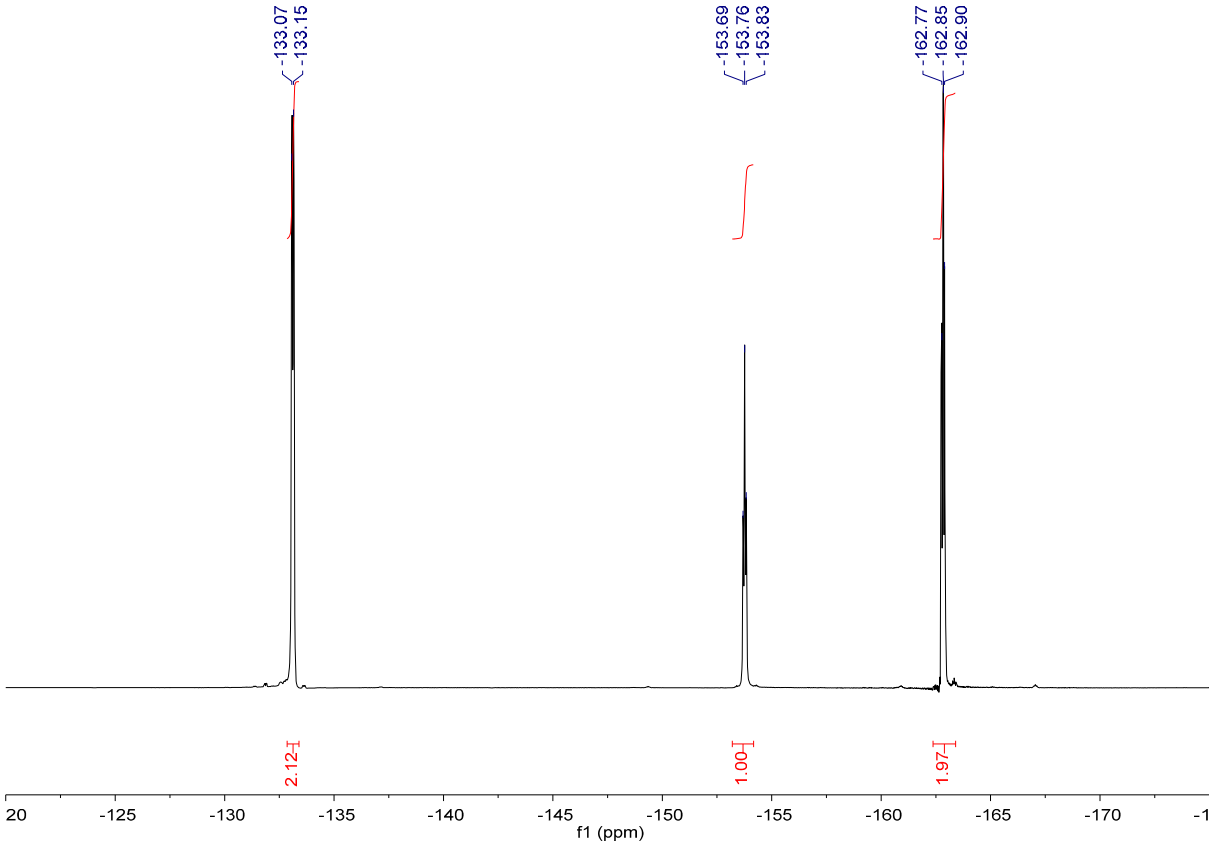
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K) spectra of **2a** across concentrations 0.04–0.4 M.



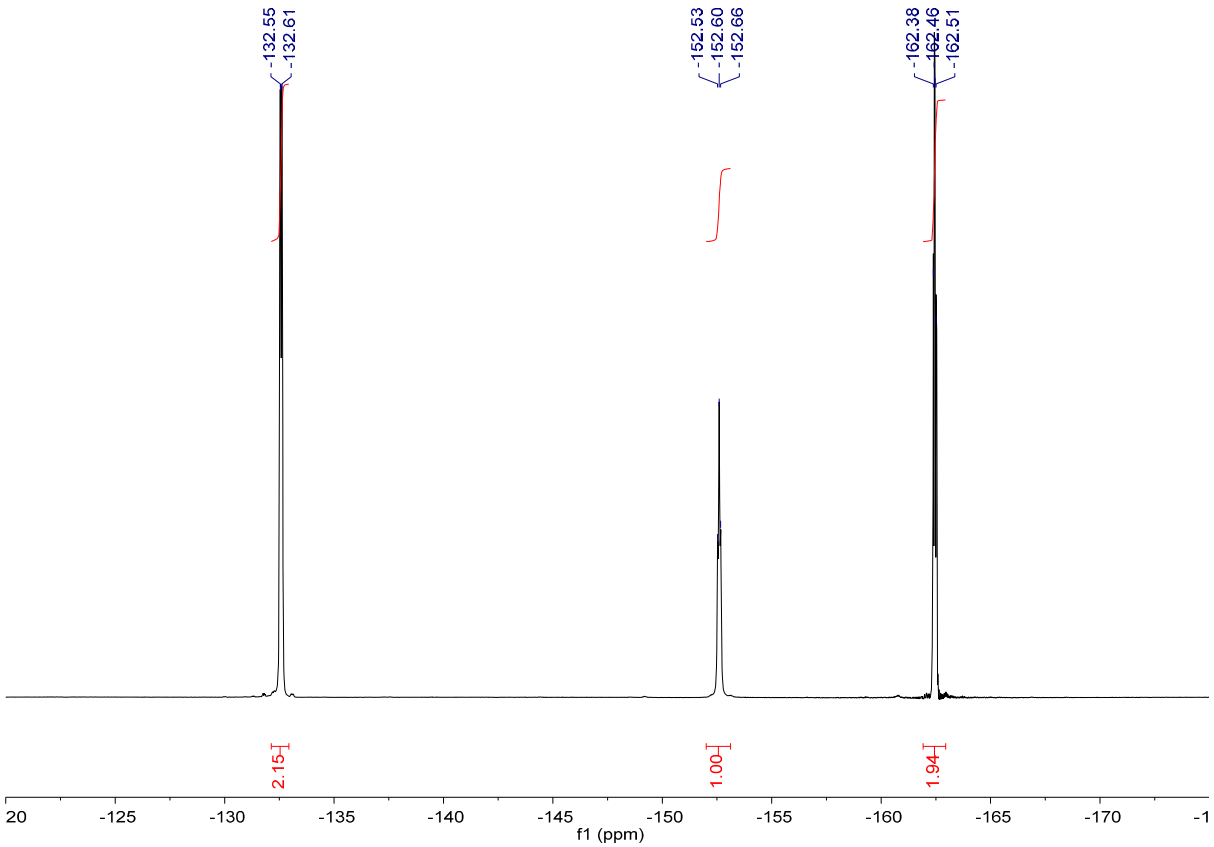
^{19}F-NMR (283 MHz, $CDCl_3$, 298 K) spectrum of **2b** crystals.



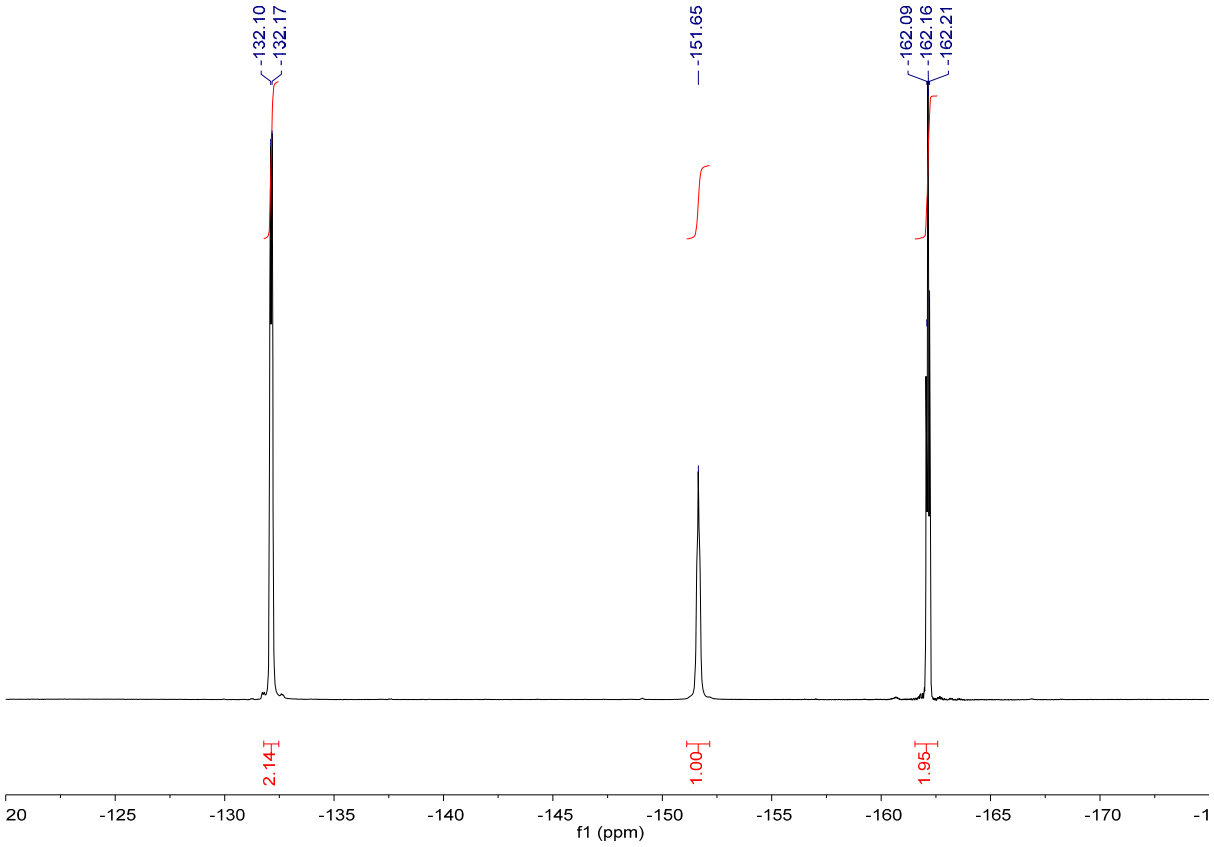
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.4 M) spectrum of **2b**.



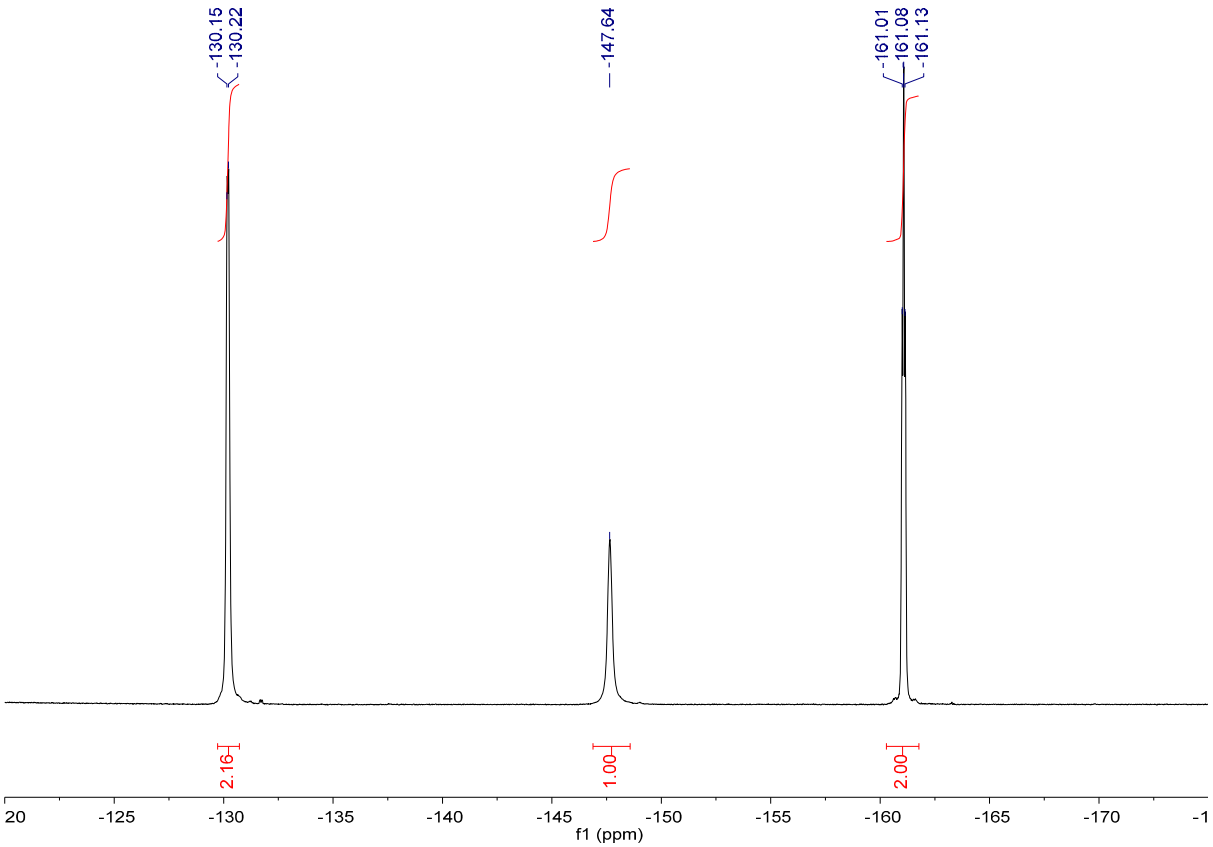
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.2 M) spectrum of **2b**.



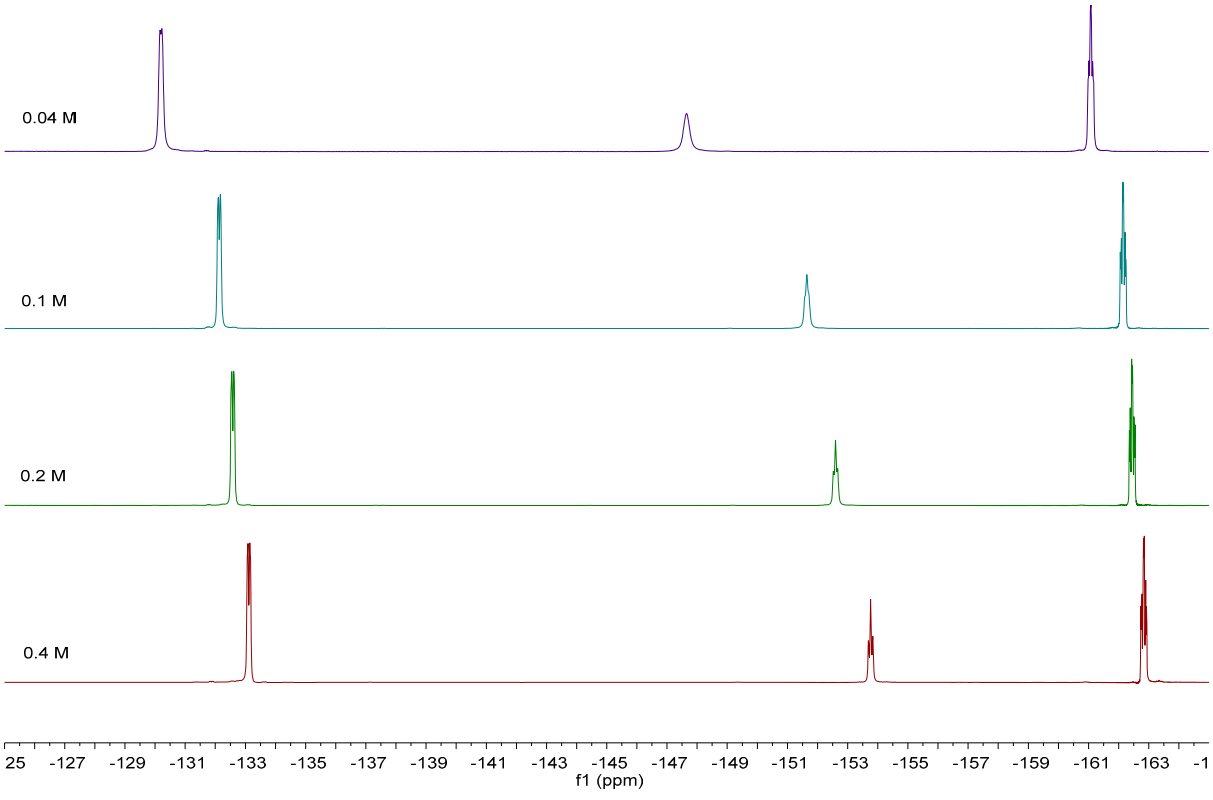
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.1 M) spectrum of **2b**.



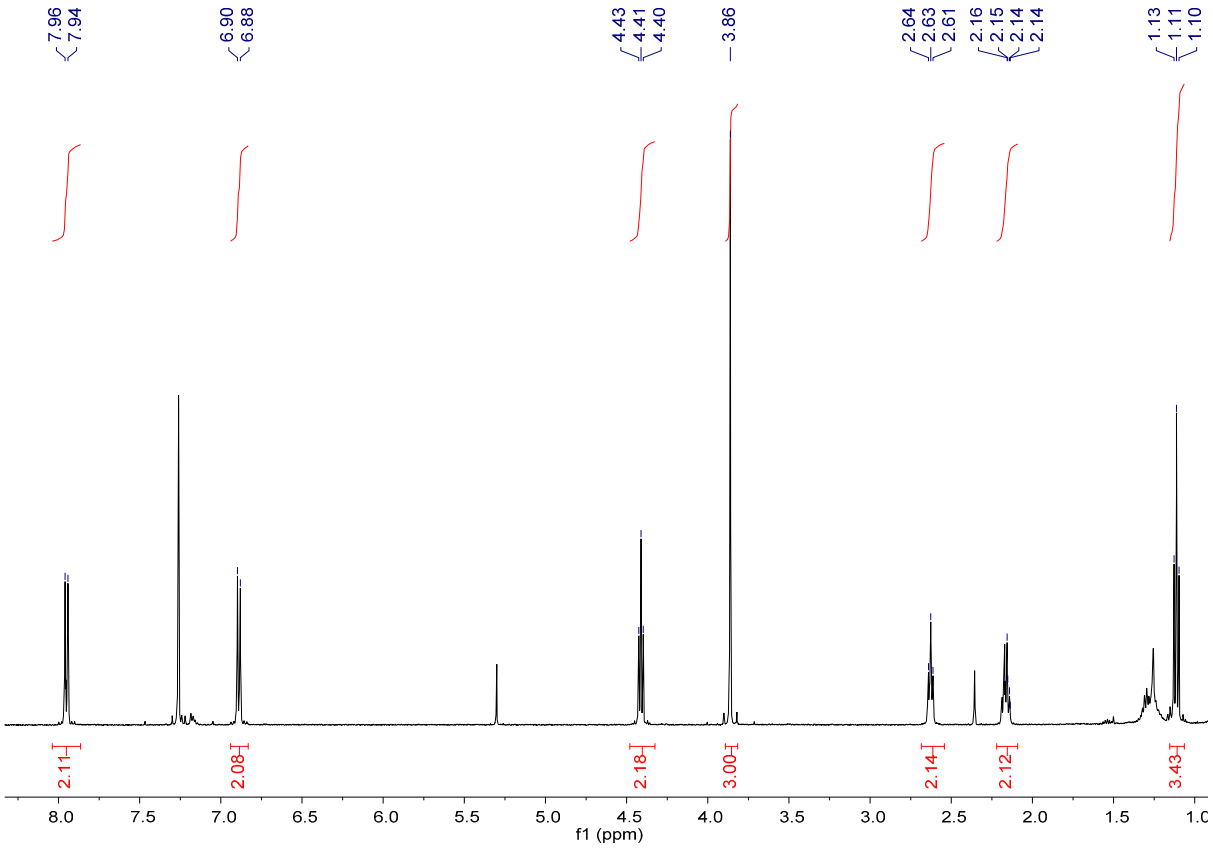
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.04 M) spectrum of **2b**.



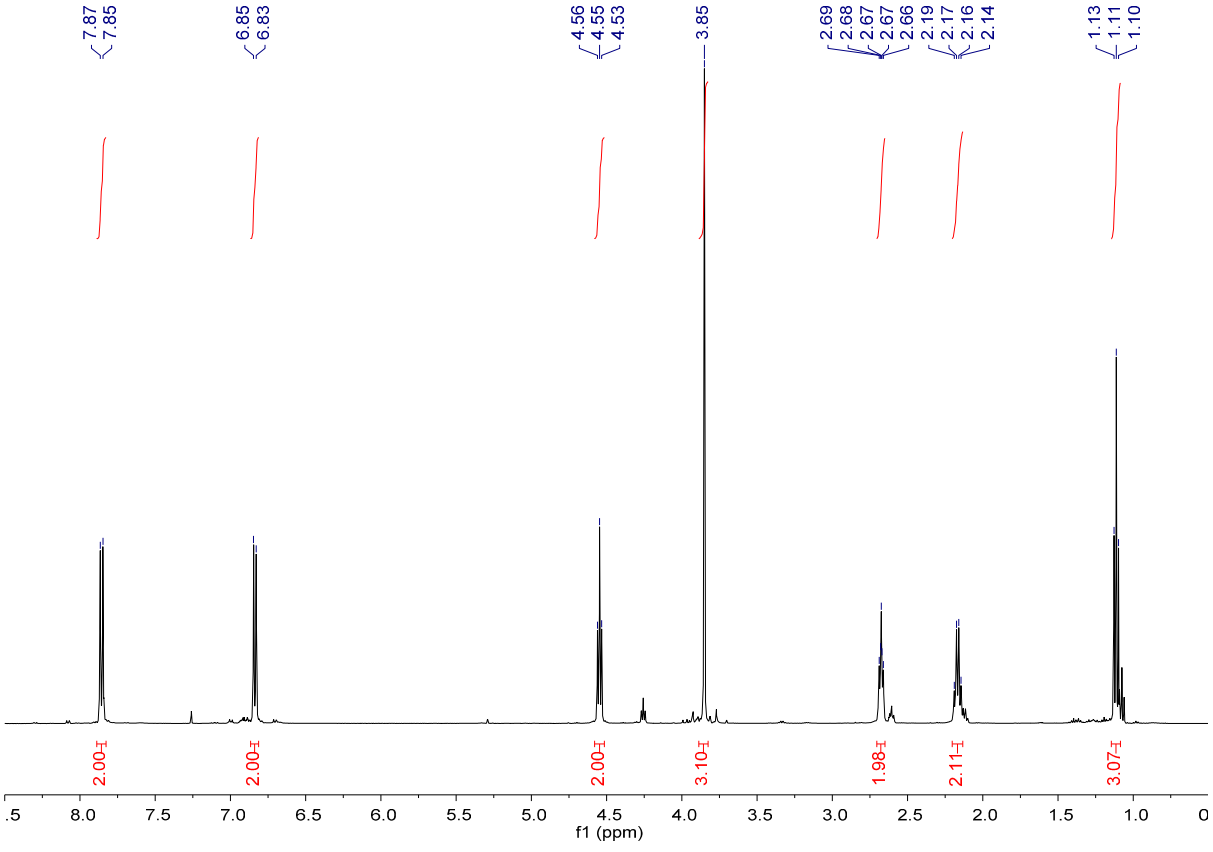
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K) spectra of **2b** across concentrations 0.04–0.4 M



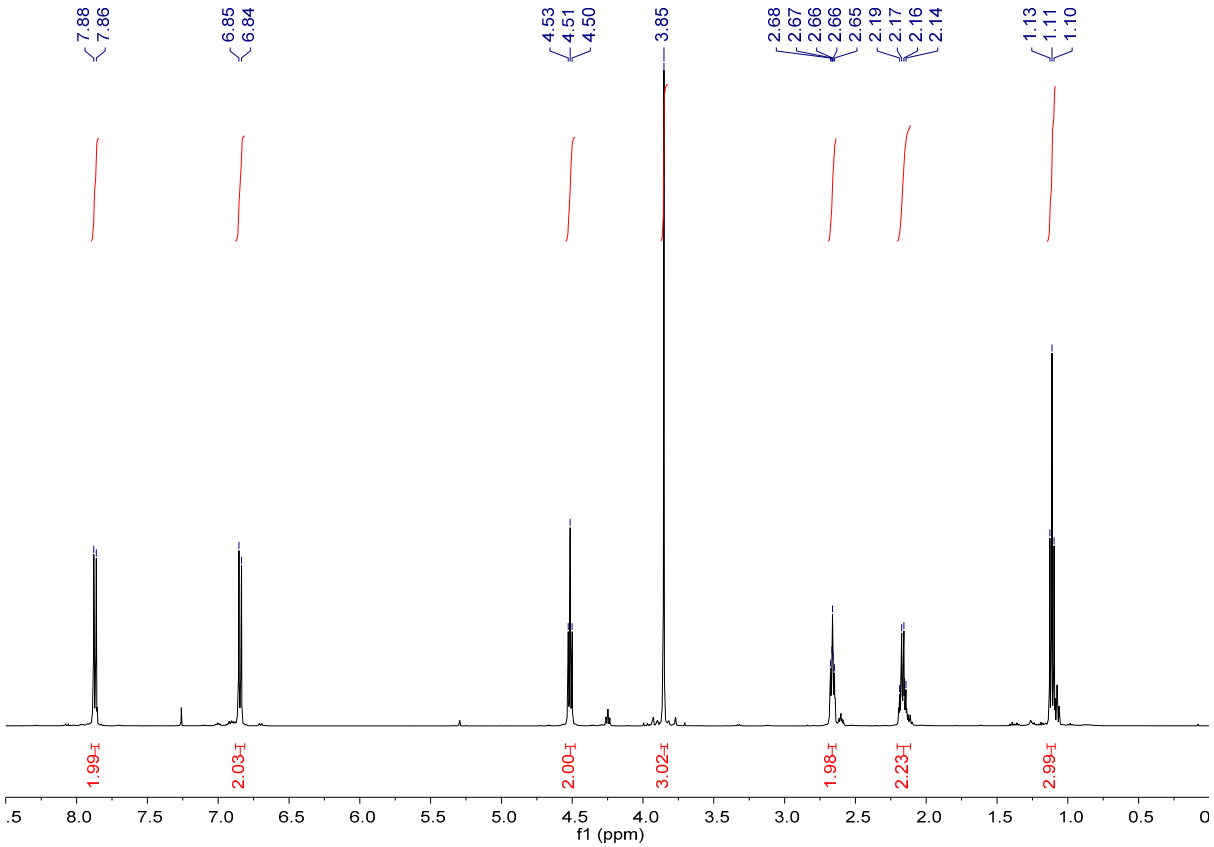
^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectrum of **2c** crystals.



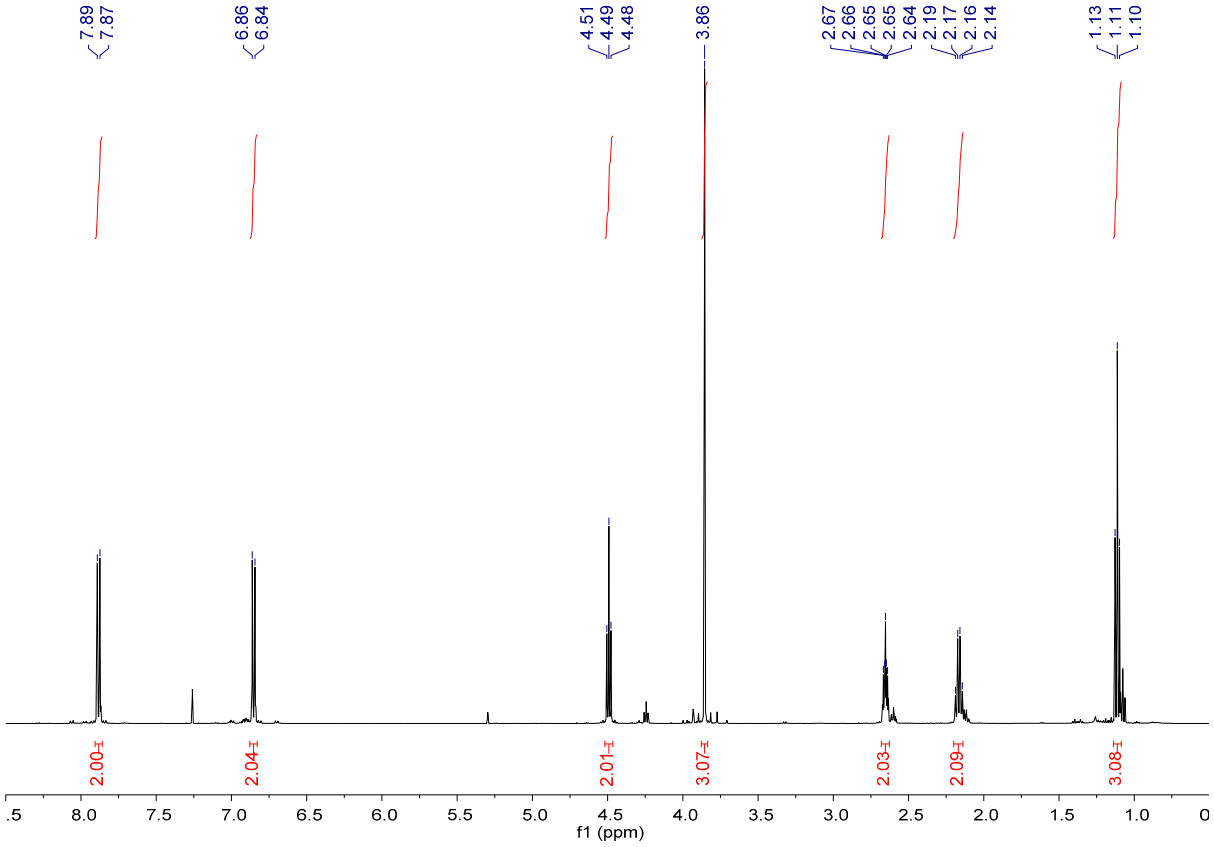
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.4 M) spectrum of **2c**.



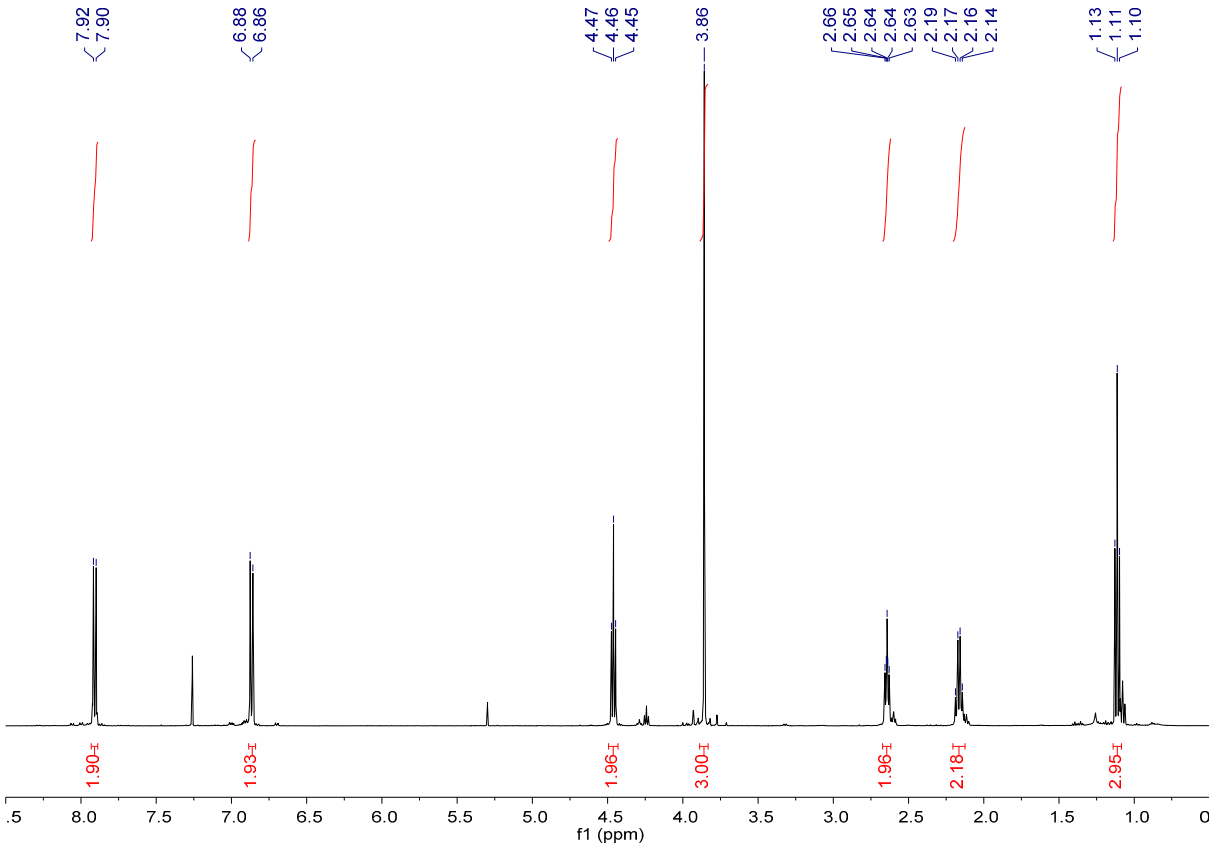
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.2 M) spectrum of **2c**.



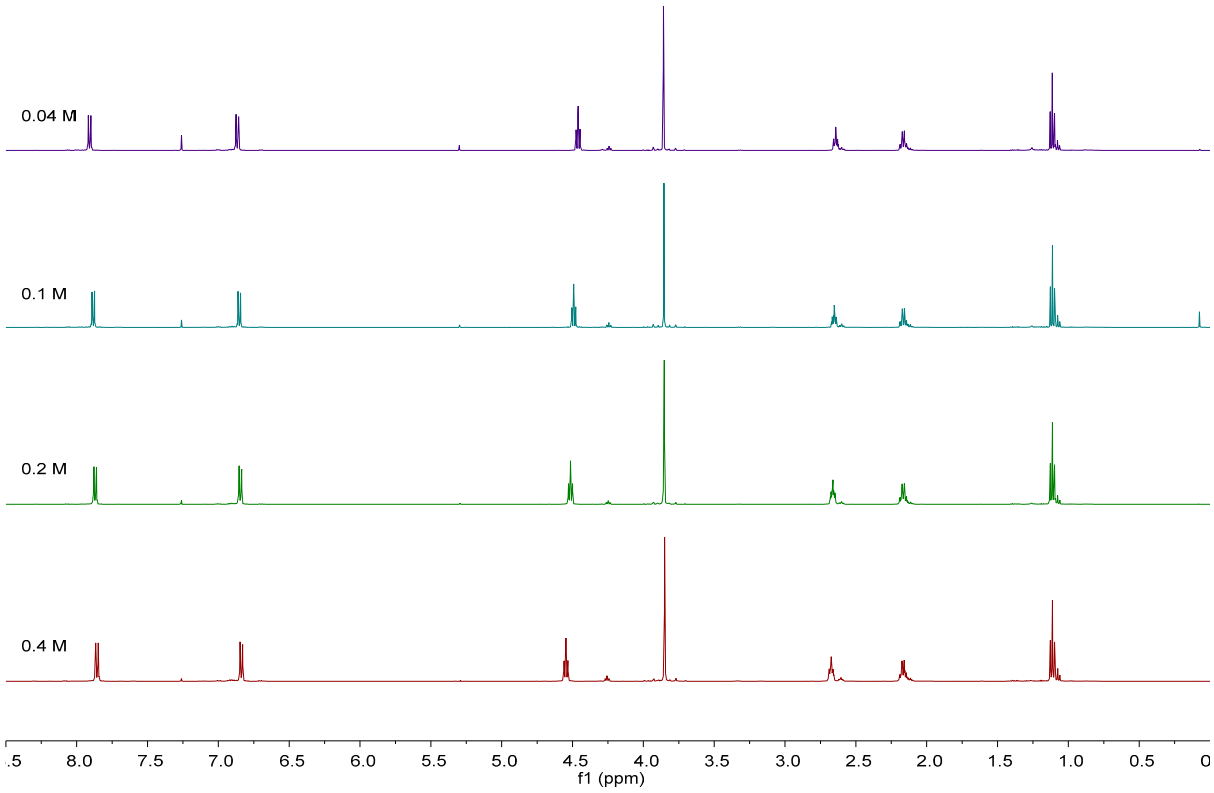
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.1 M) spectrum of **2c**.



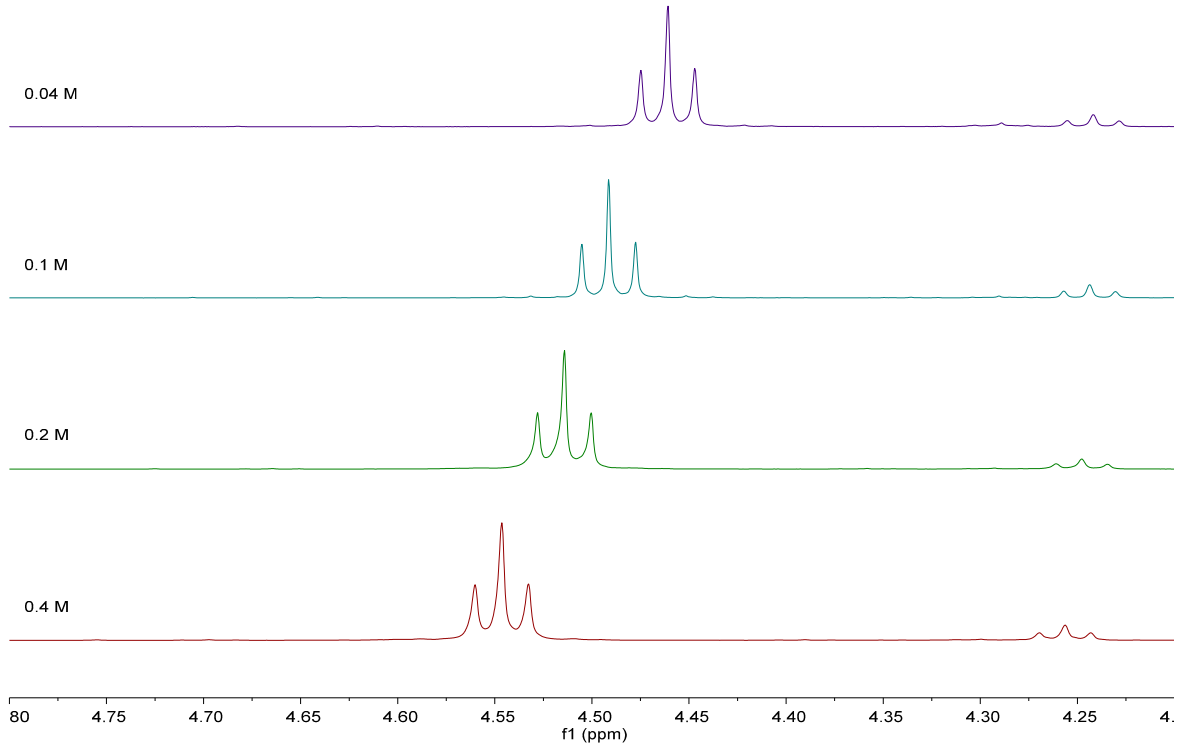
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K, 0.04 M) spectrum of **2c**.



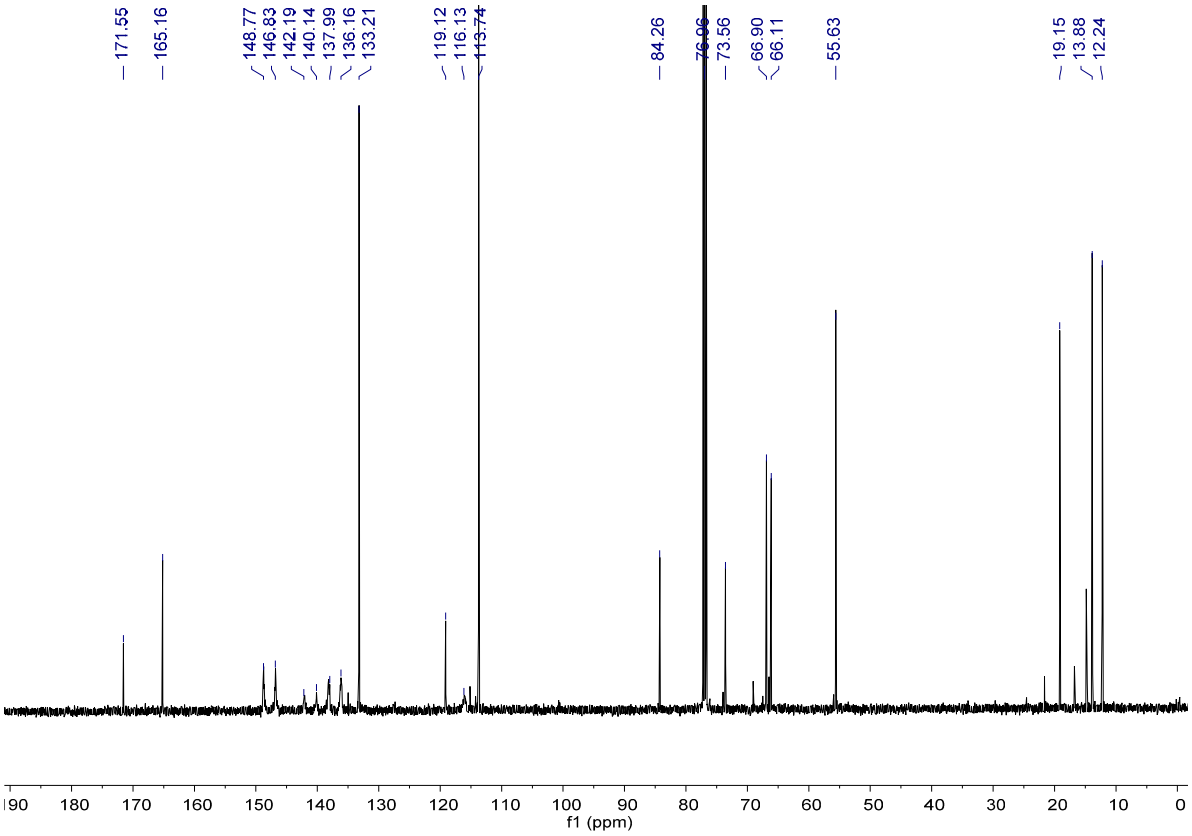
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectra of **2c** across concentrations 0.04–0.4 M.



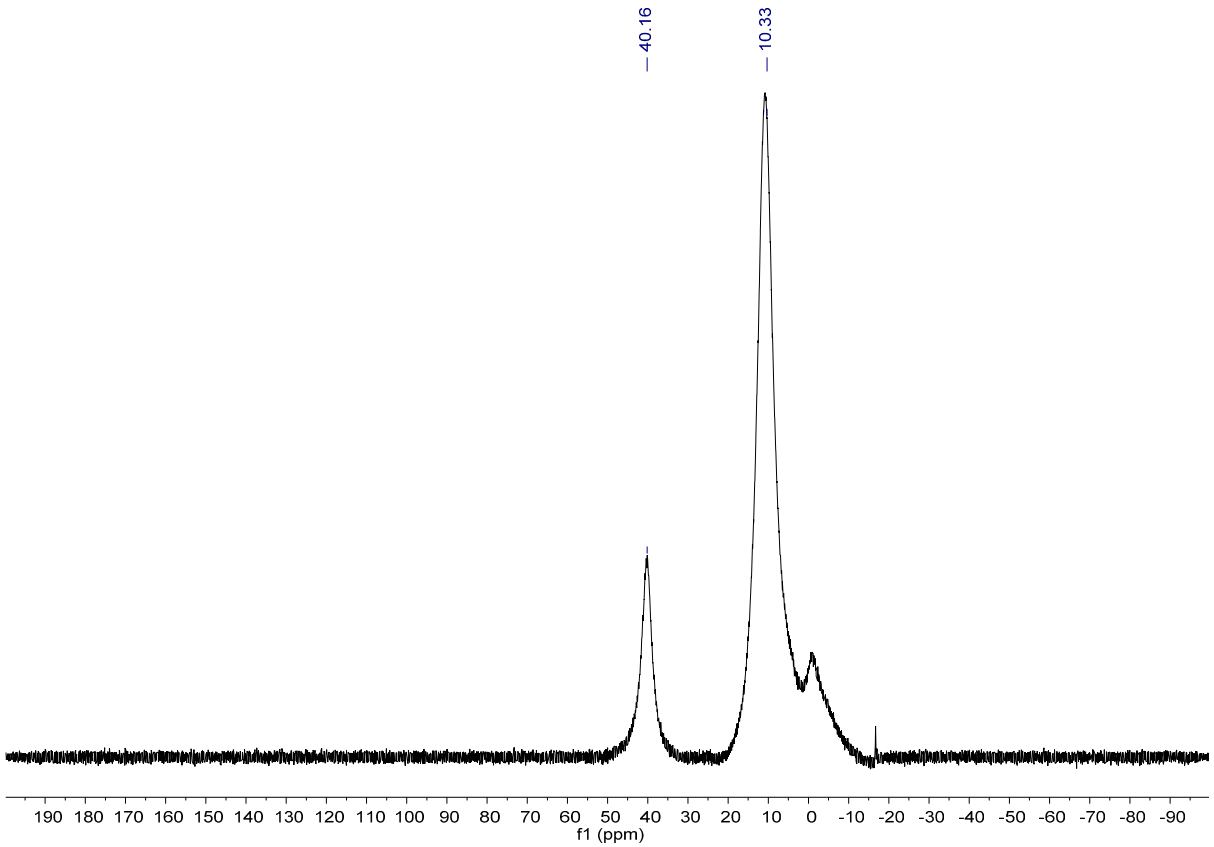
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectra of **2c,** expansion of $C\underline{H_2}O(CO)$-) across concentrations 0.04 –0.4 M.



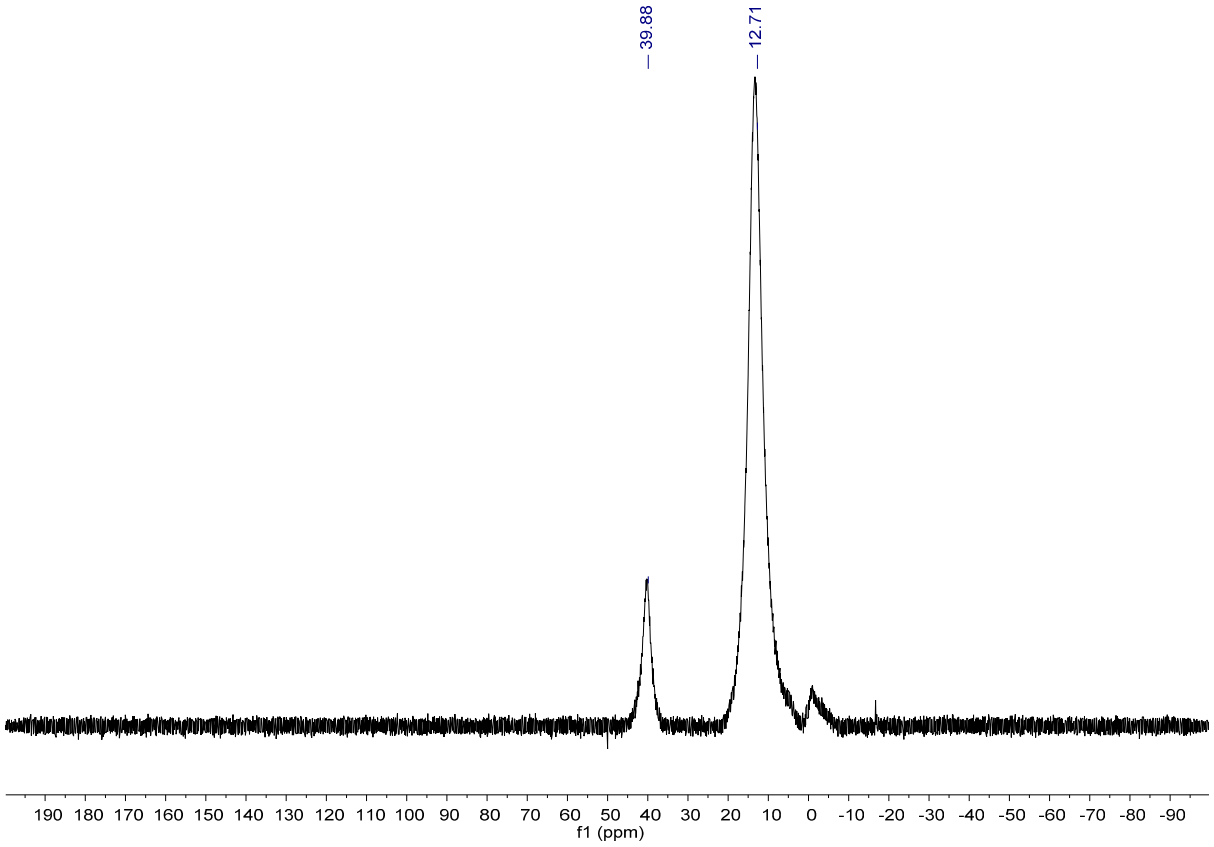
In situ ^{13}C-NMR (125 MHz, $CDCl_3$, 298K, 0.2 M) spectrum of **2c**



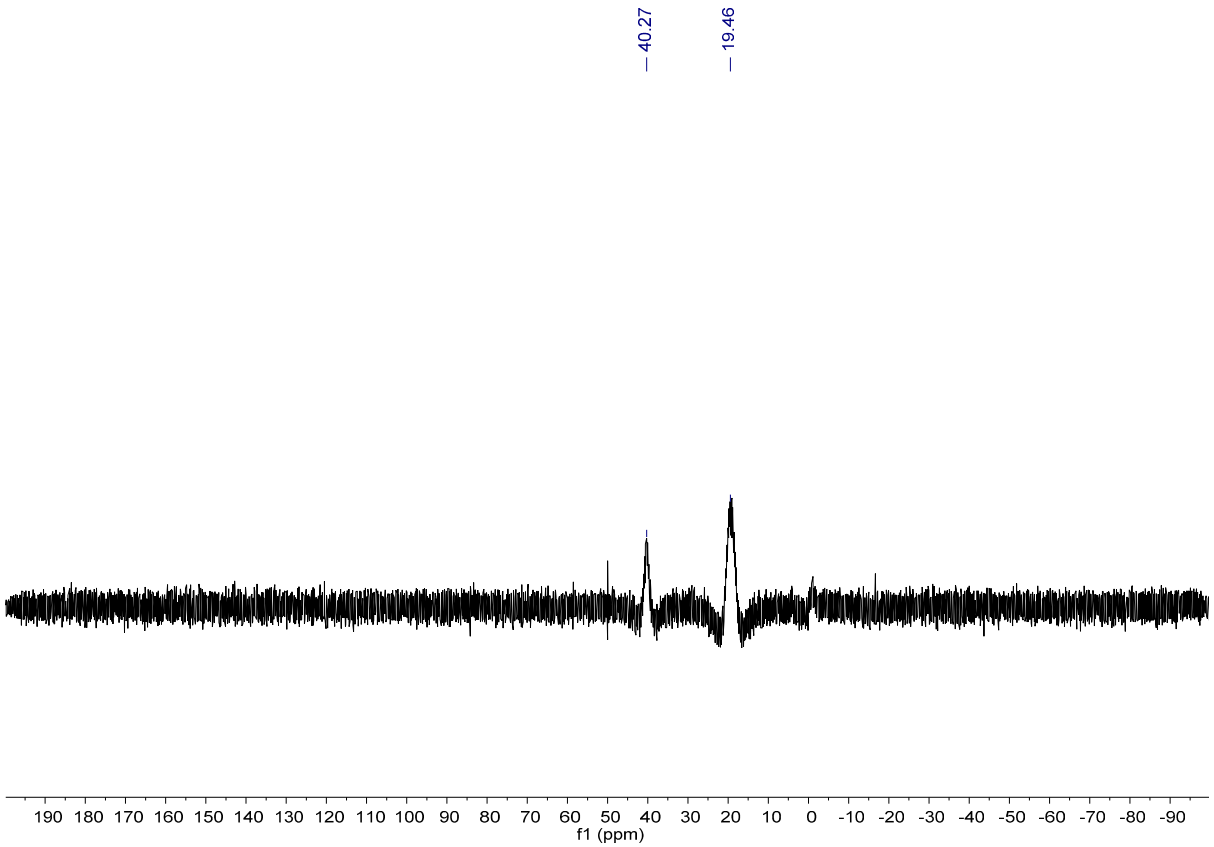
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.4 M) spectrum of **2c**.



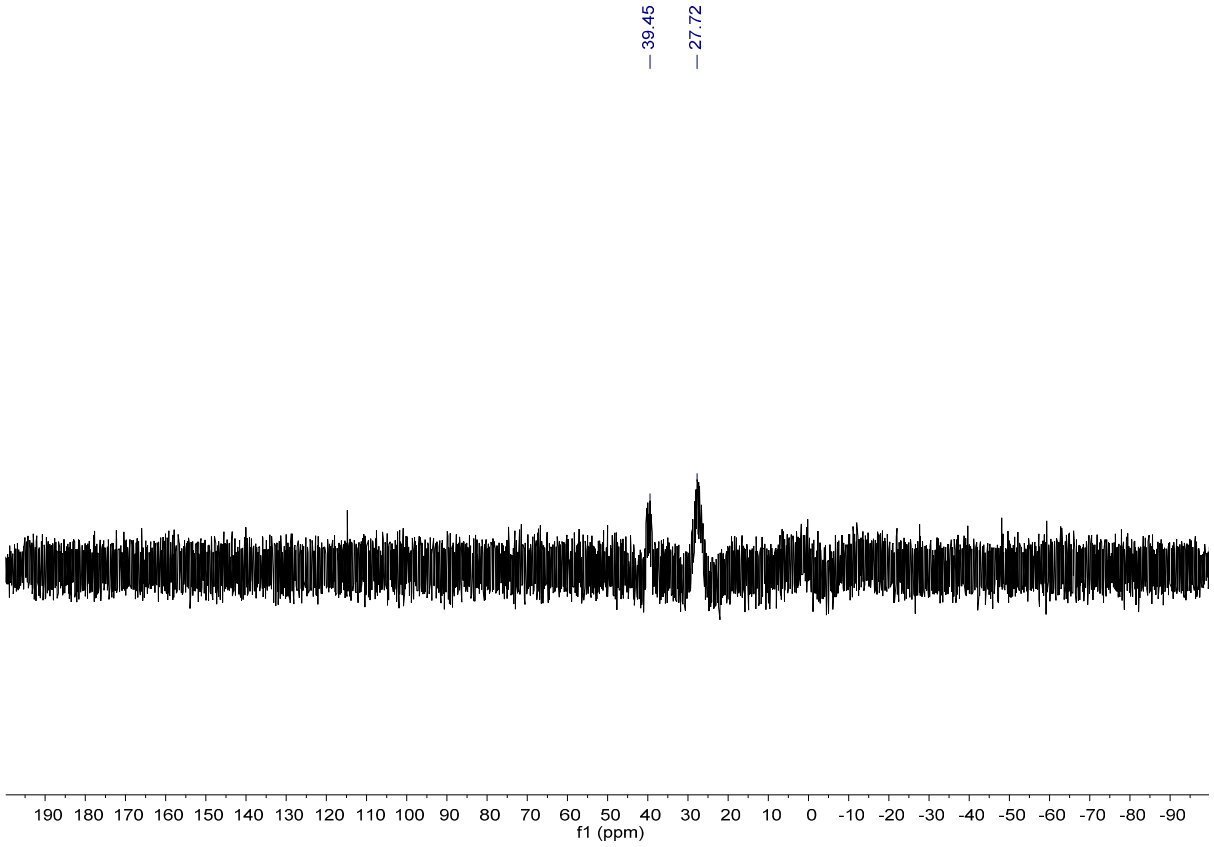
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.2 M) spectrum of **2c**.



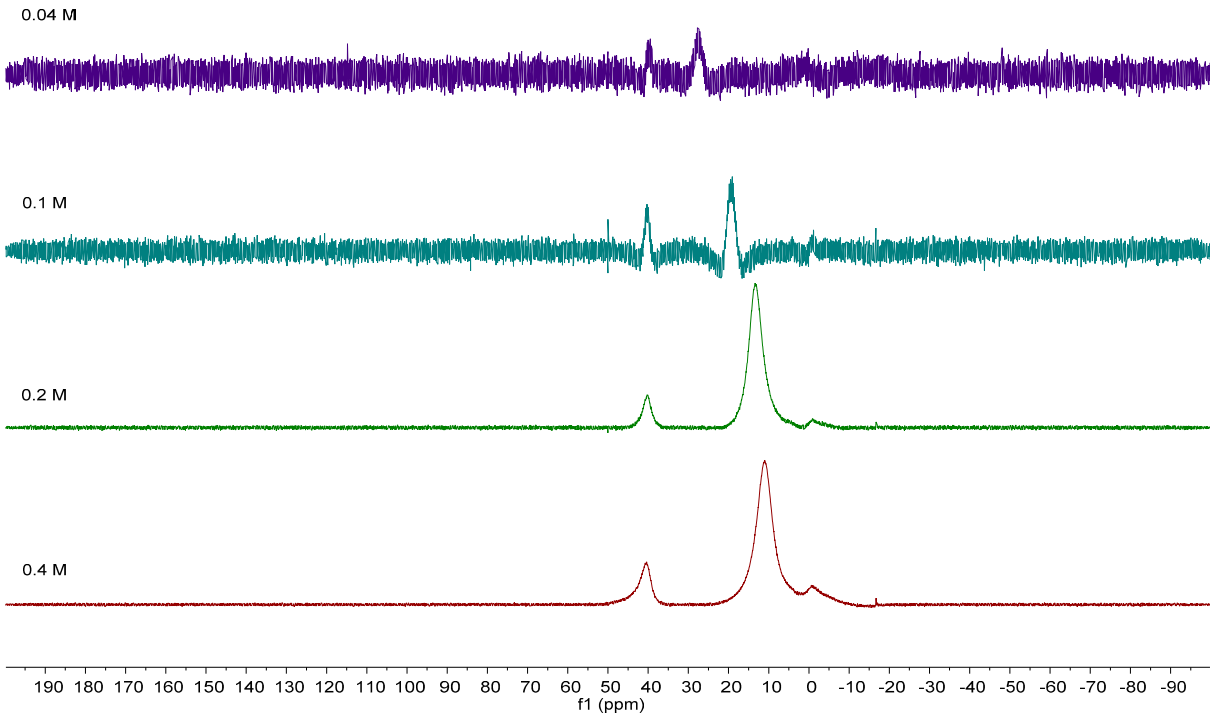
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.1 M) spectrum of **2c**.



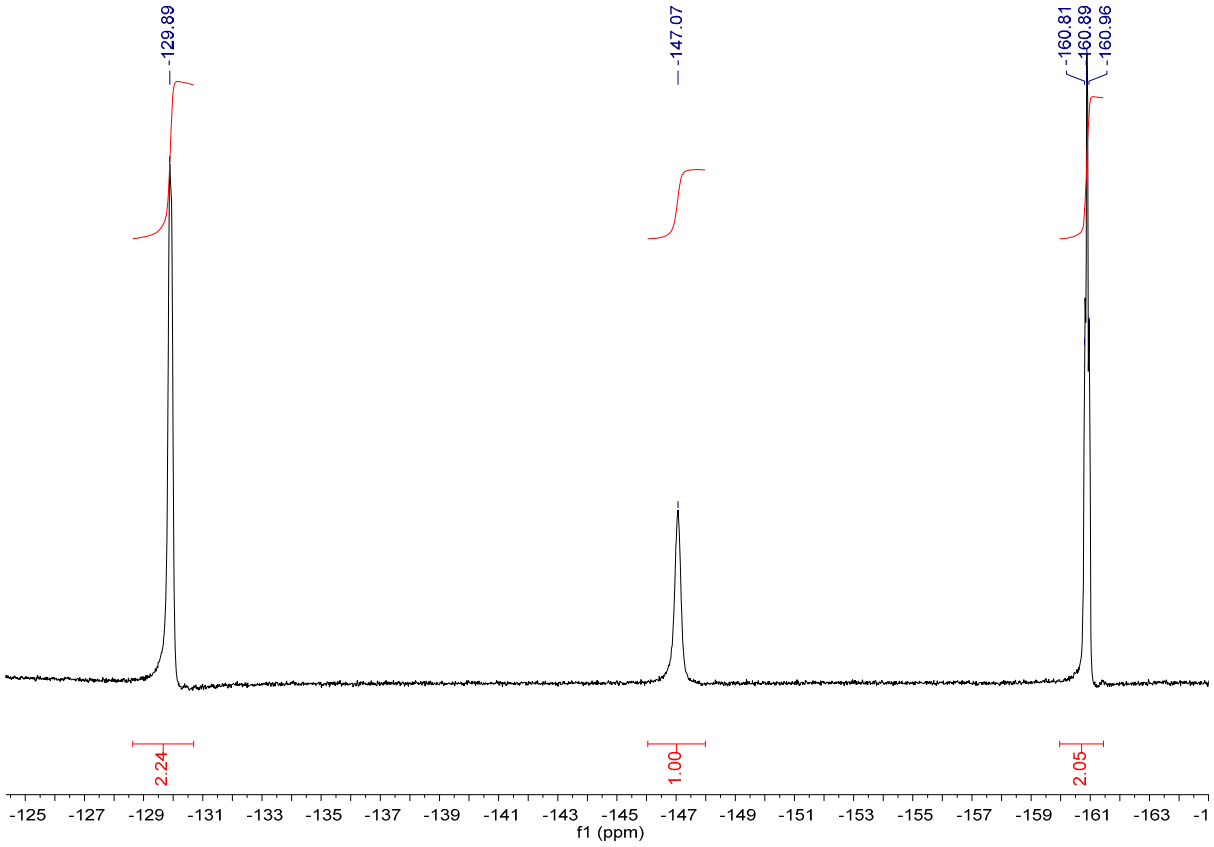
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K, 0.04 M) spectrum of **2c**.



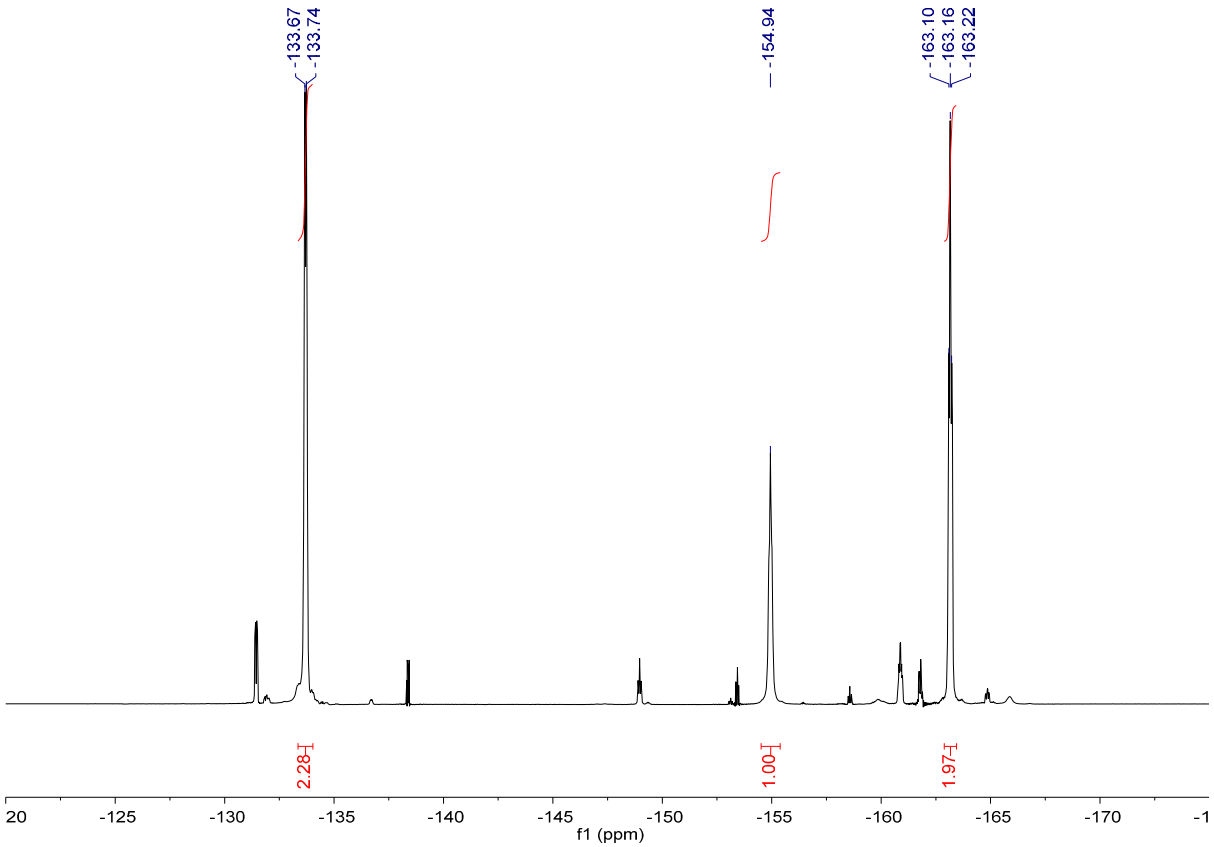
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K) spectrum of **2c** across concentrations 0.04–0.4 M.



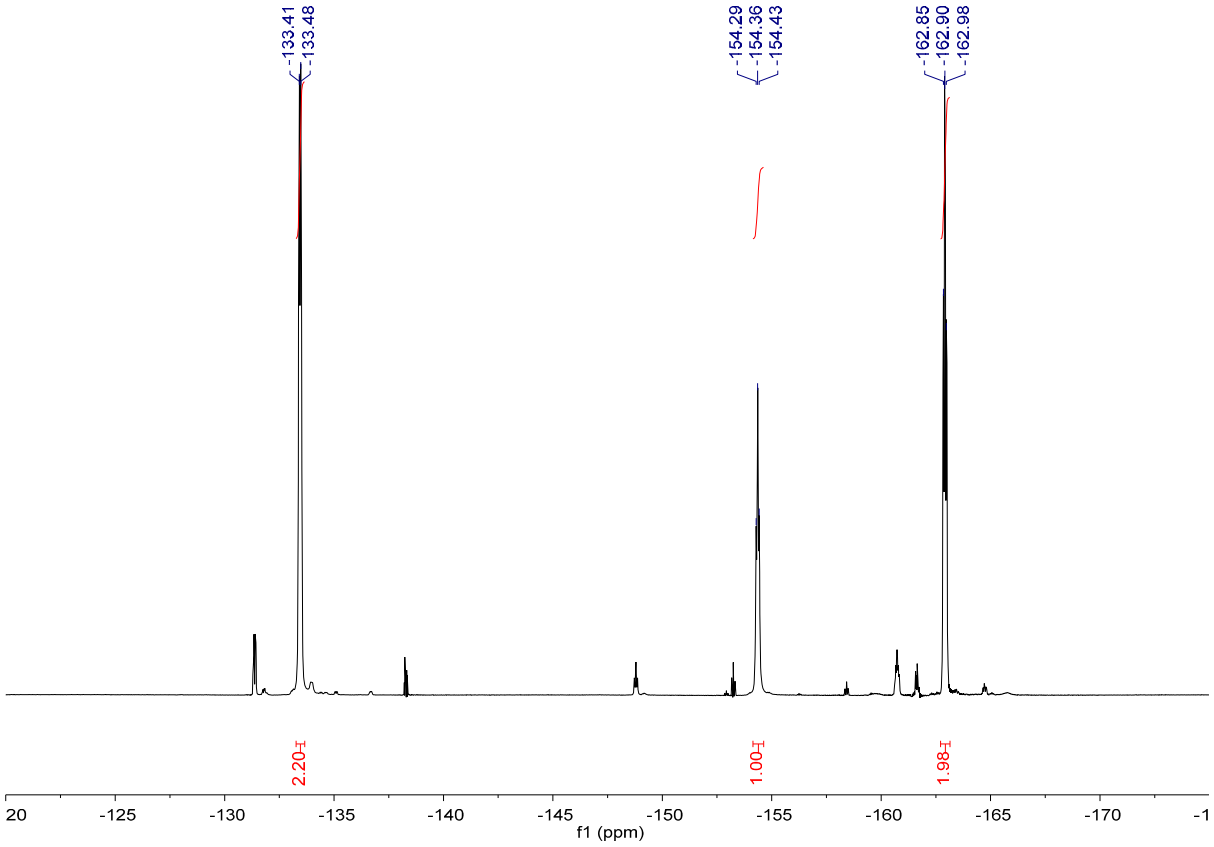
^{19}F-NMR (283 MHz, $CDCl_3$, 298 K) spectrum of **2c** crystals.



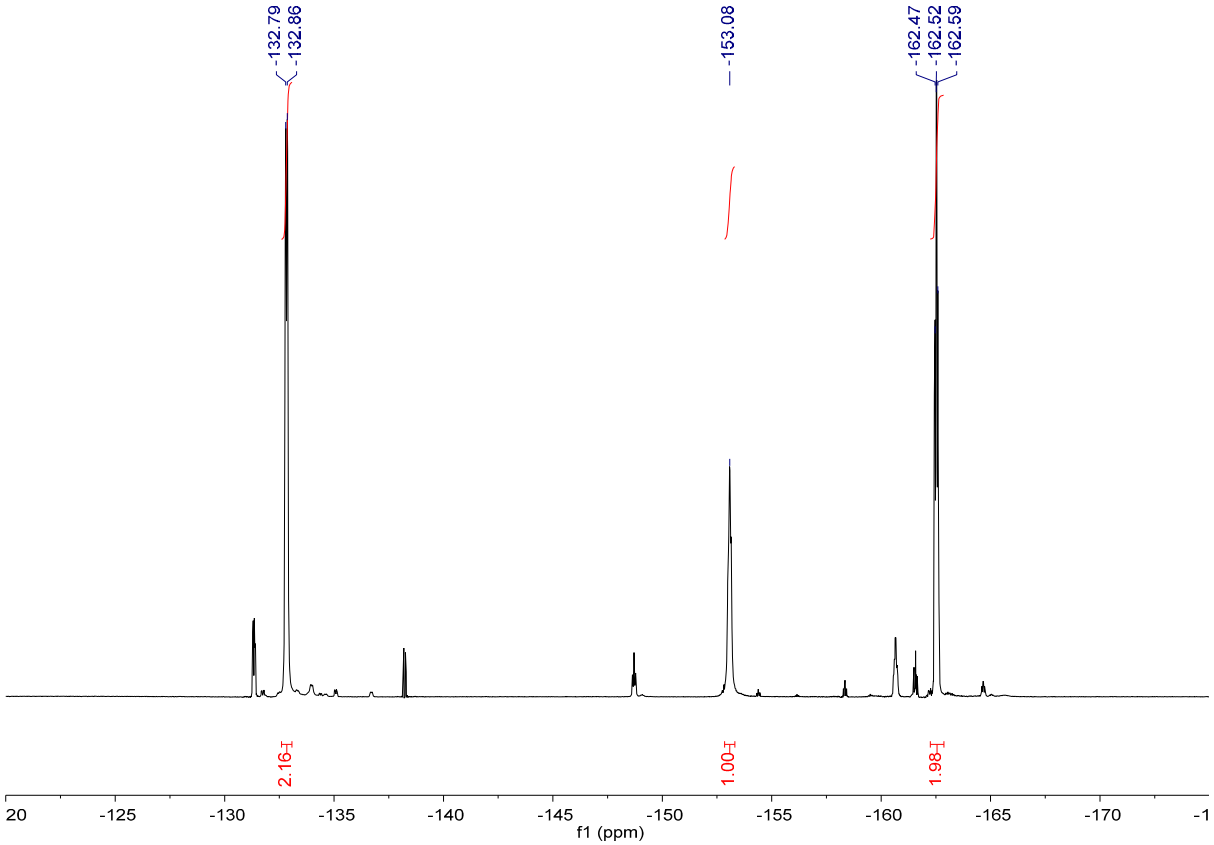
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.4 M) spectrum of **2c**.



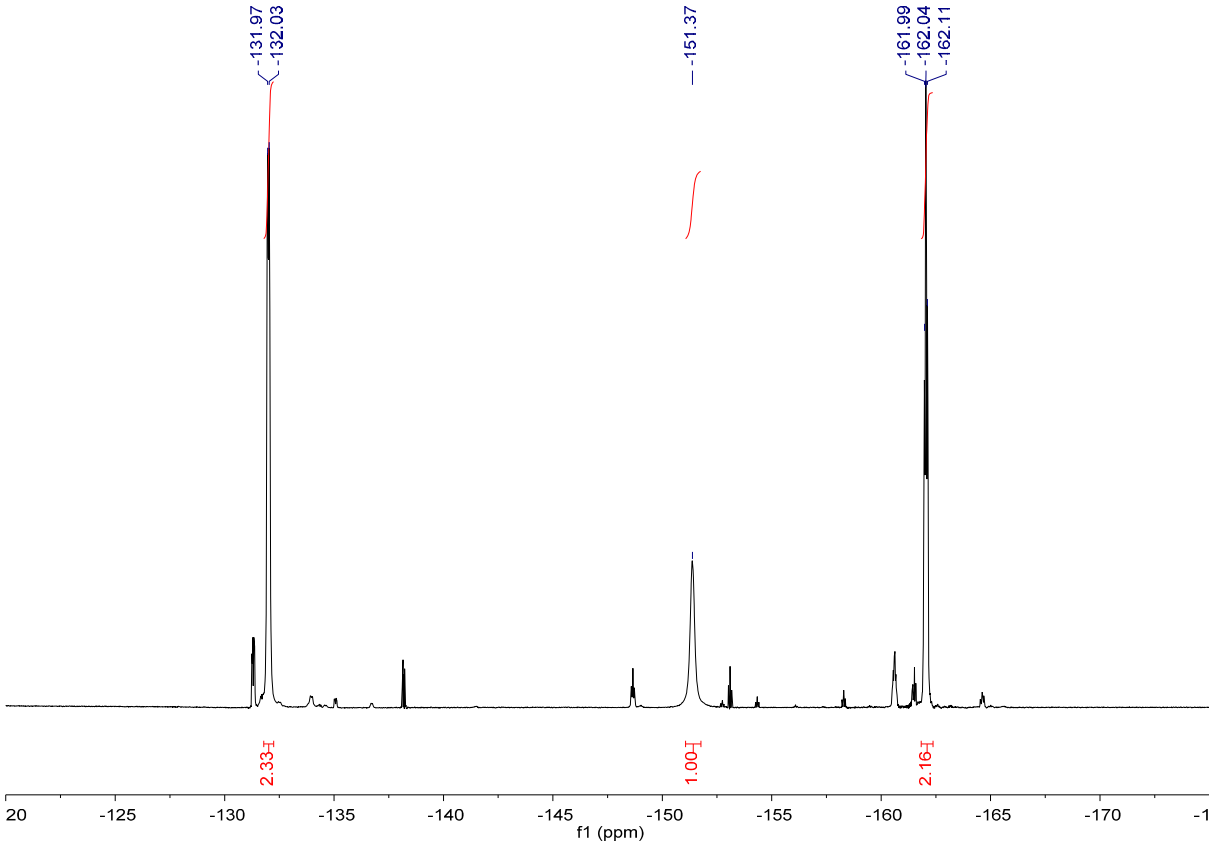
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.2 M) spectrum of **2c**.



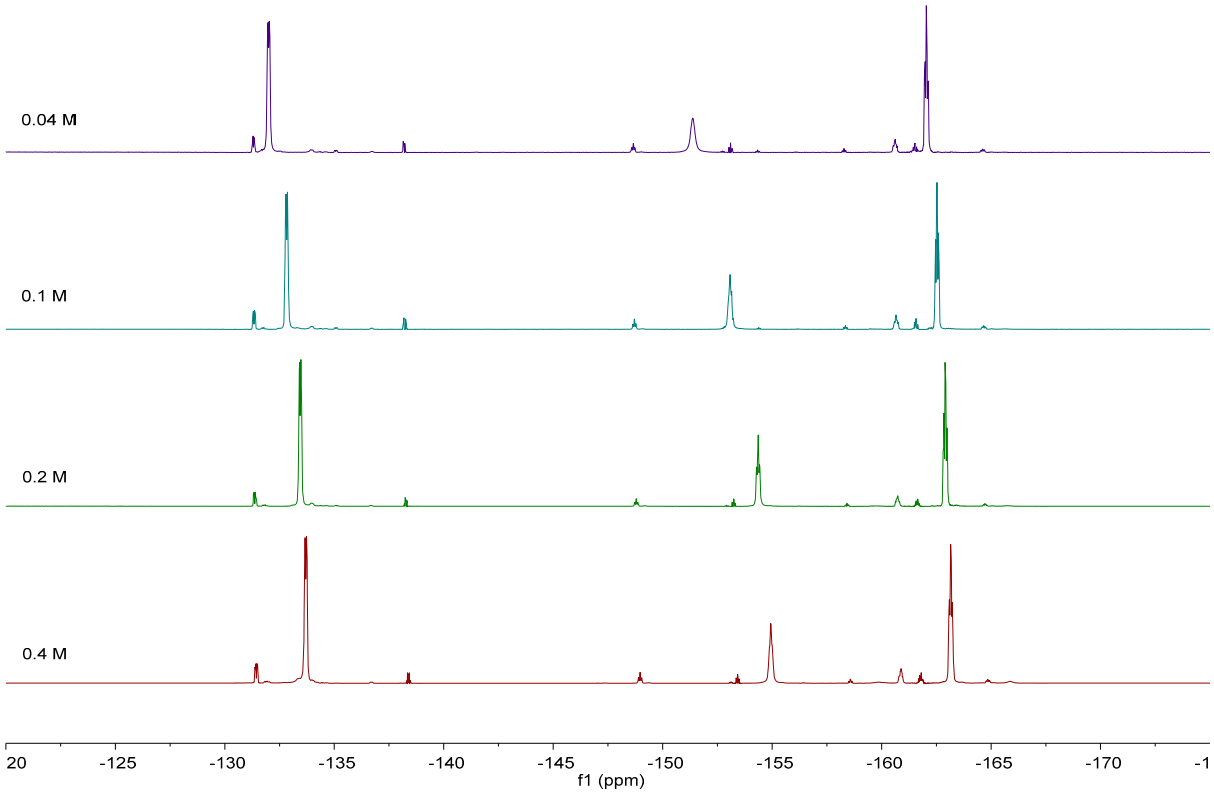
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.1 M) spectrum of **2c**.



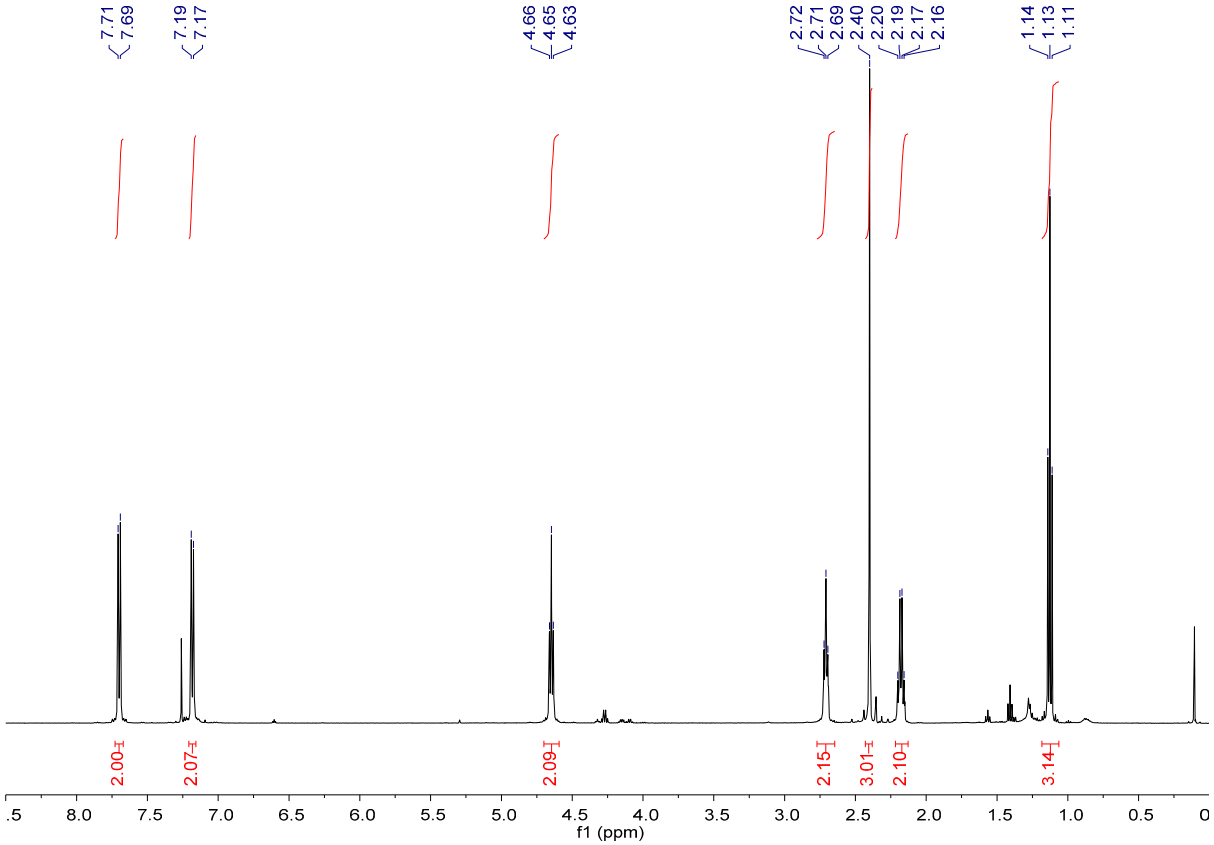
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K, 0.04 M) spectrum of **2c**.



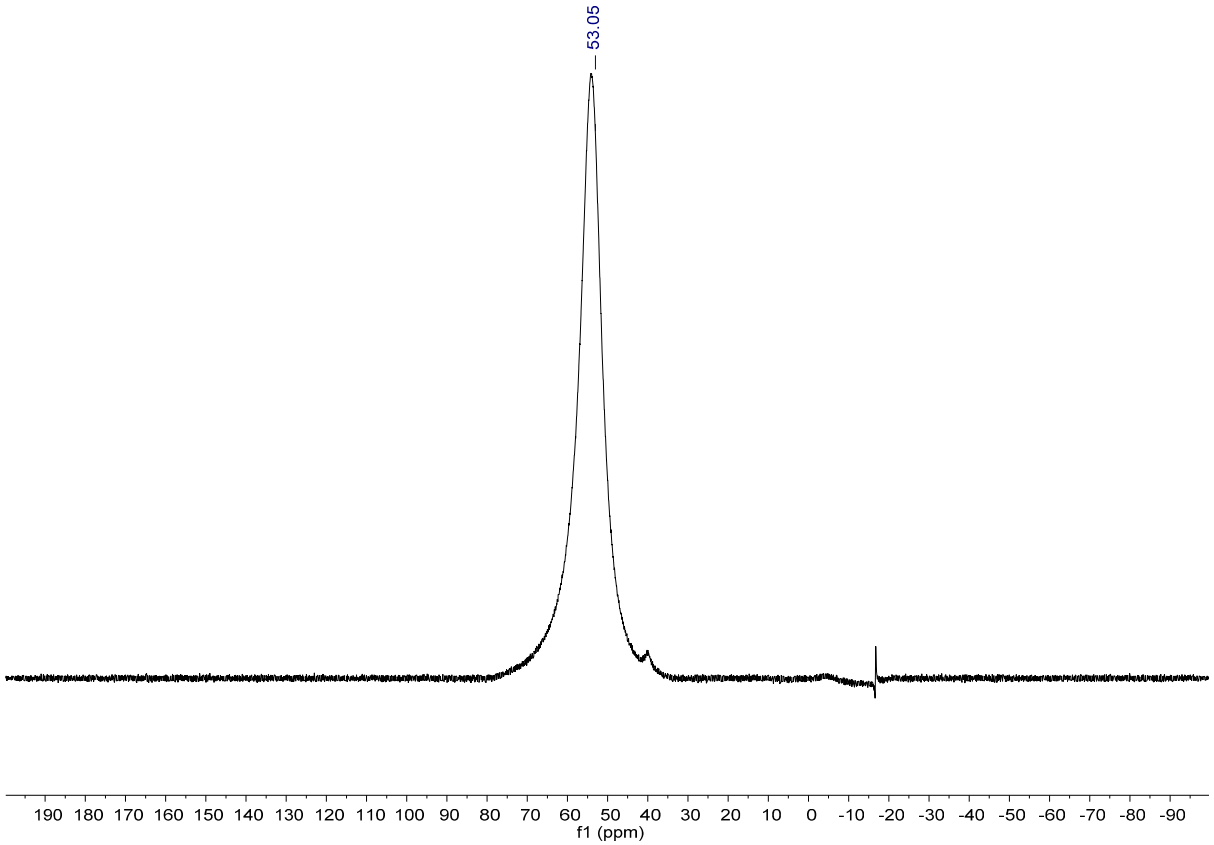
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K) spectra of **2c** across concentrations 0.04–0.4 M



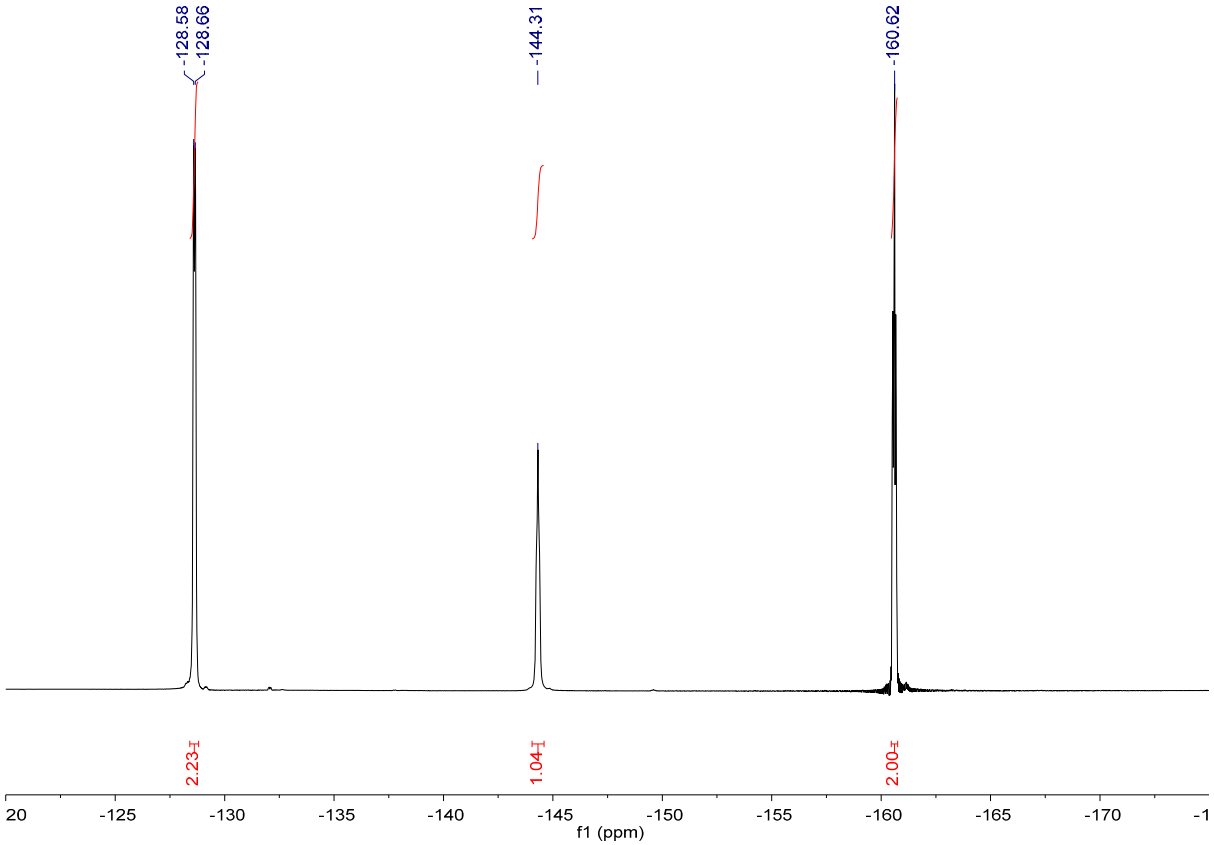
In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectrum of excess $B(C_6F_5)_3$.



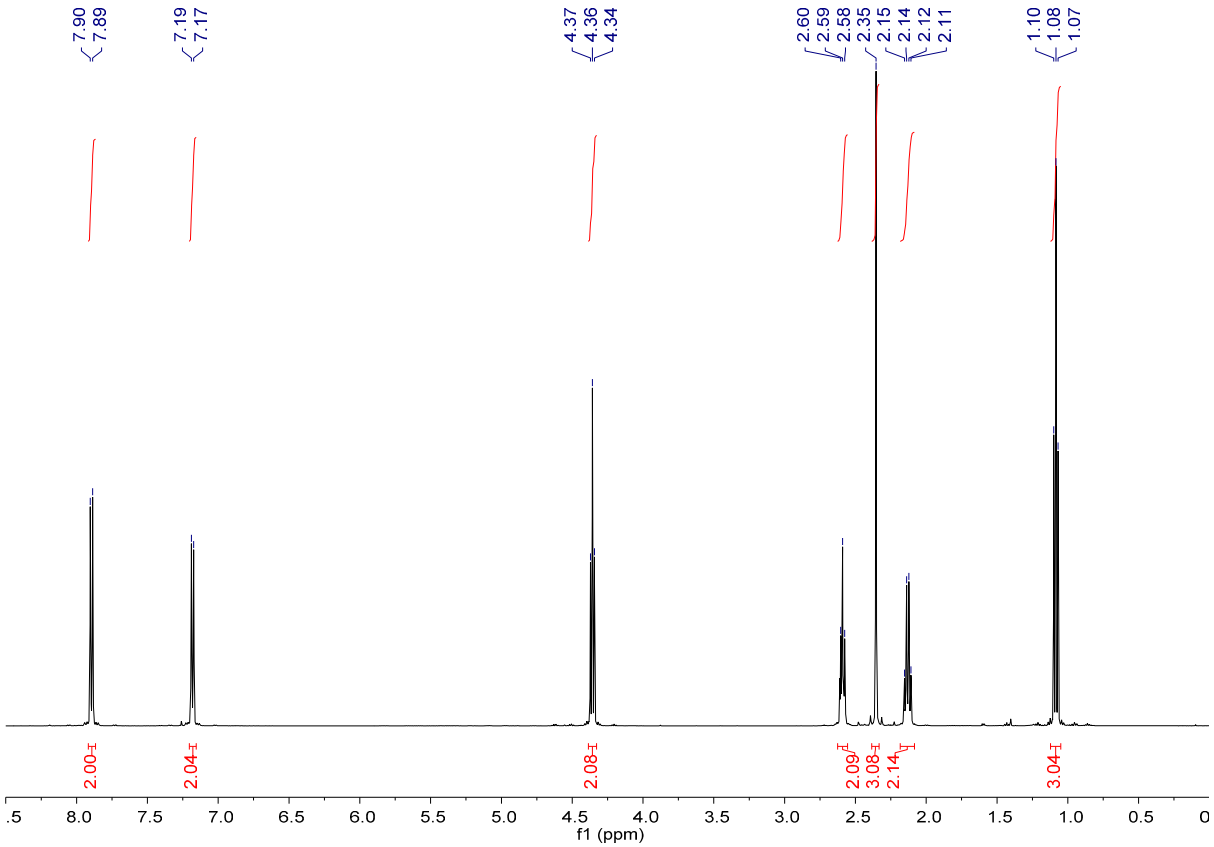
In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K) spectrum of excess $B(C_6F_5)_3$.



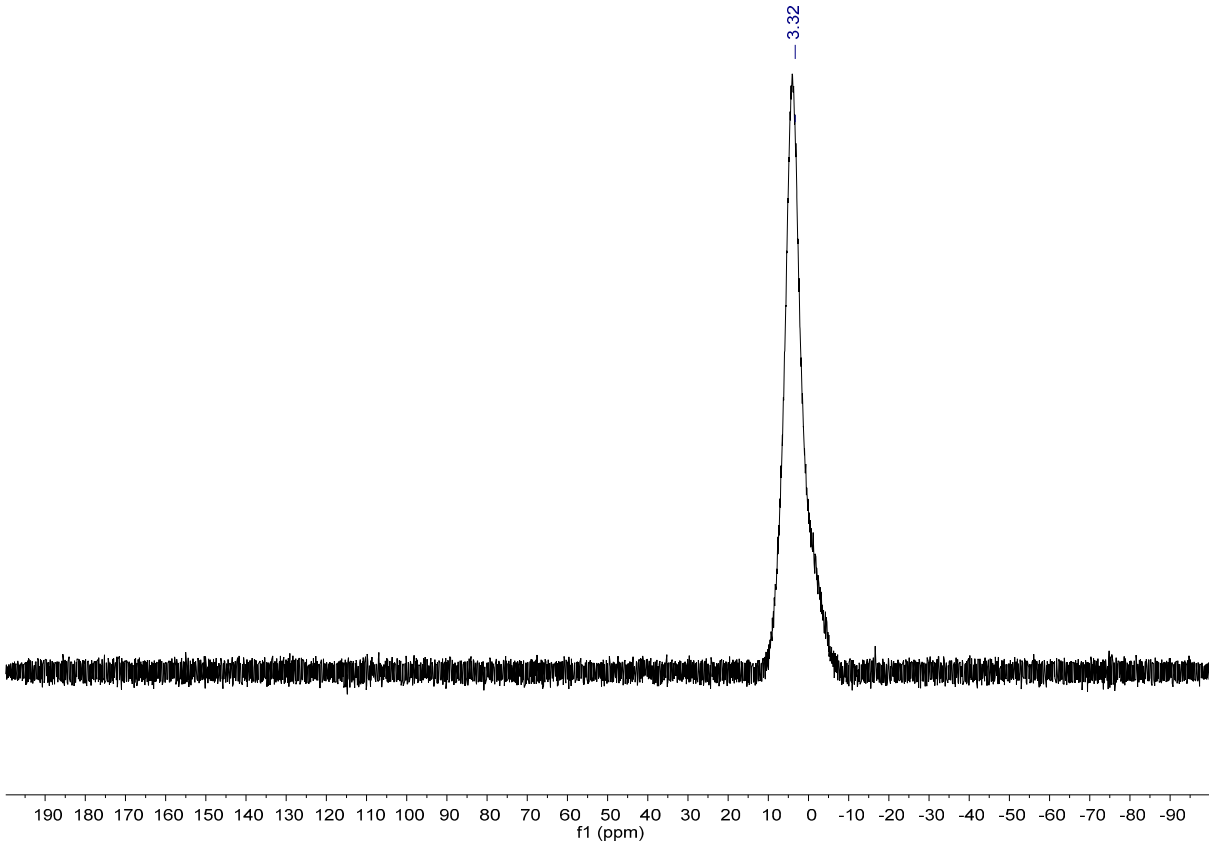
In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K) spectrum of excess $B(C_6F_5)_3$.



In situ ^{1}H-NMR (500 MHz, $CDCl_3$, 298K) spectrum of excess **2b**.



In situ ^{11}B-NMR (160 MHz, $CDCl_3$, 298 K) spectrum of excess **2b**.



In situ ^{19}F-NMR (283 MHz, $CDCl_3$, 298 K) spectrum of excess **2b**.