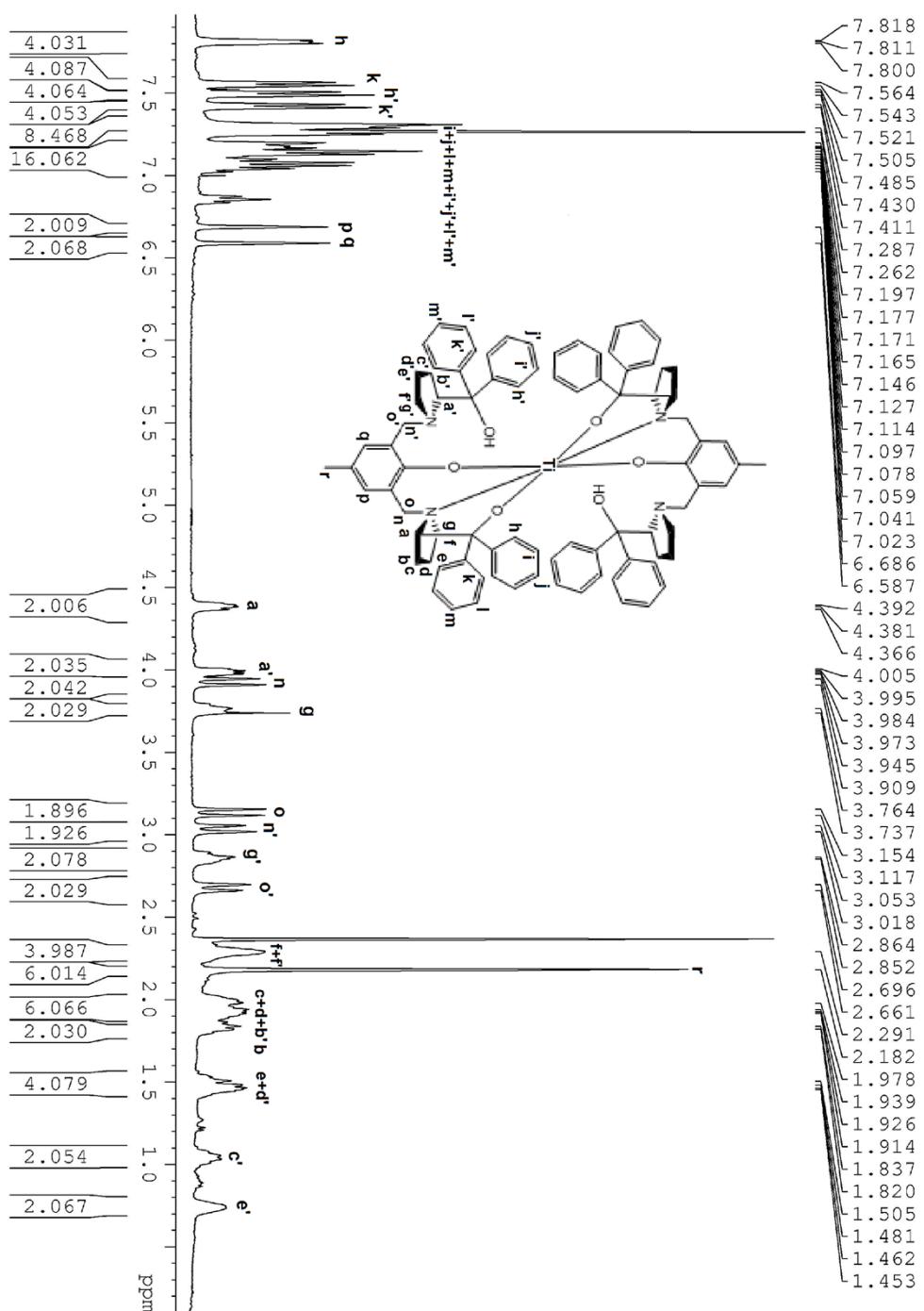
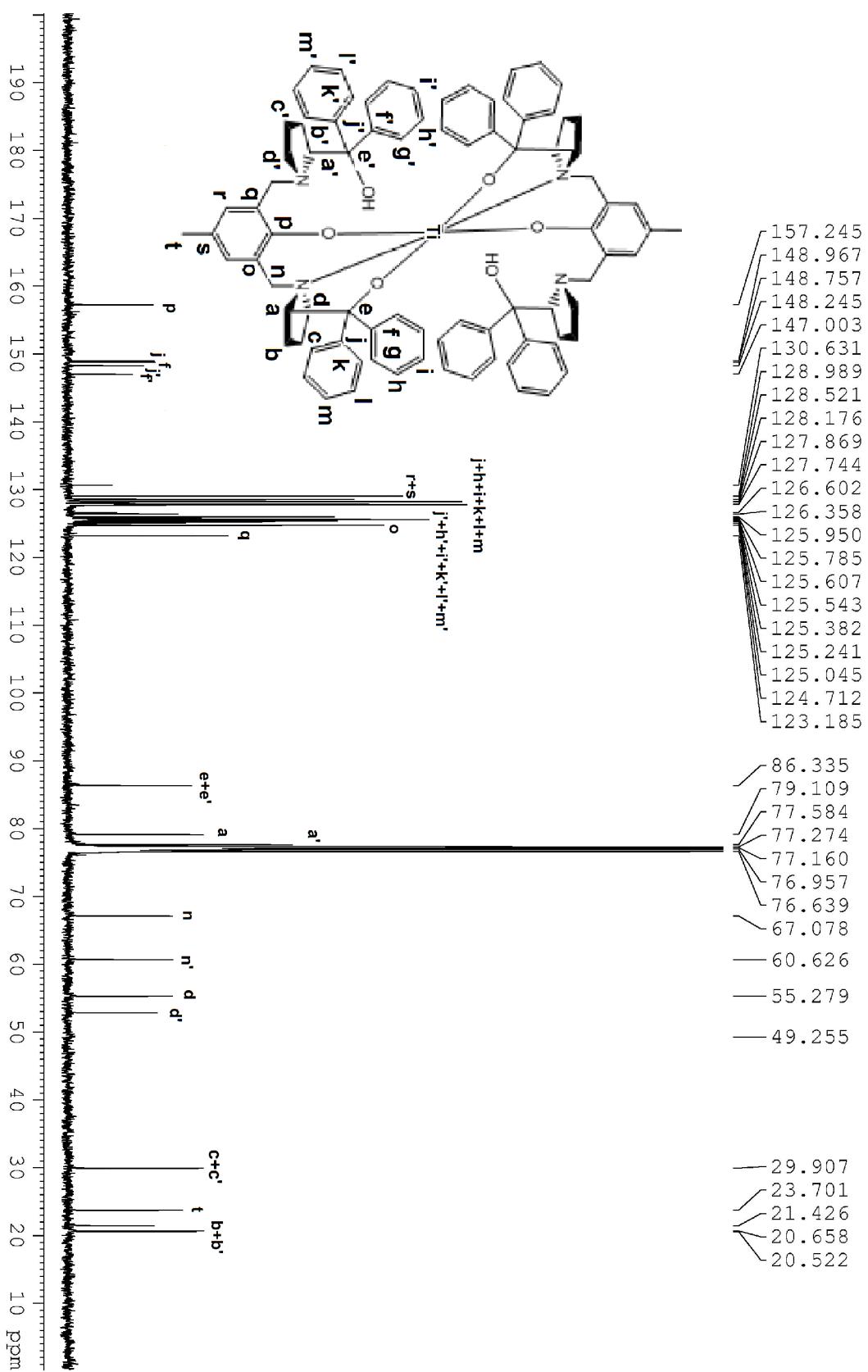


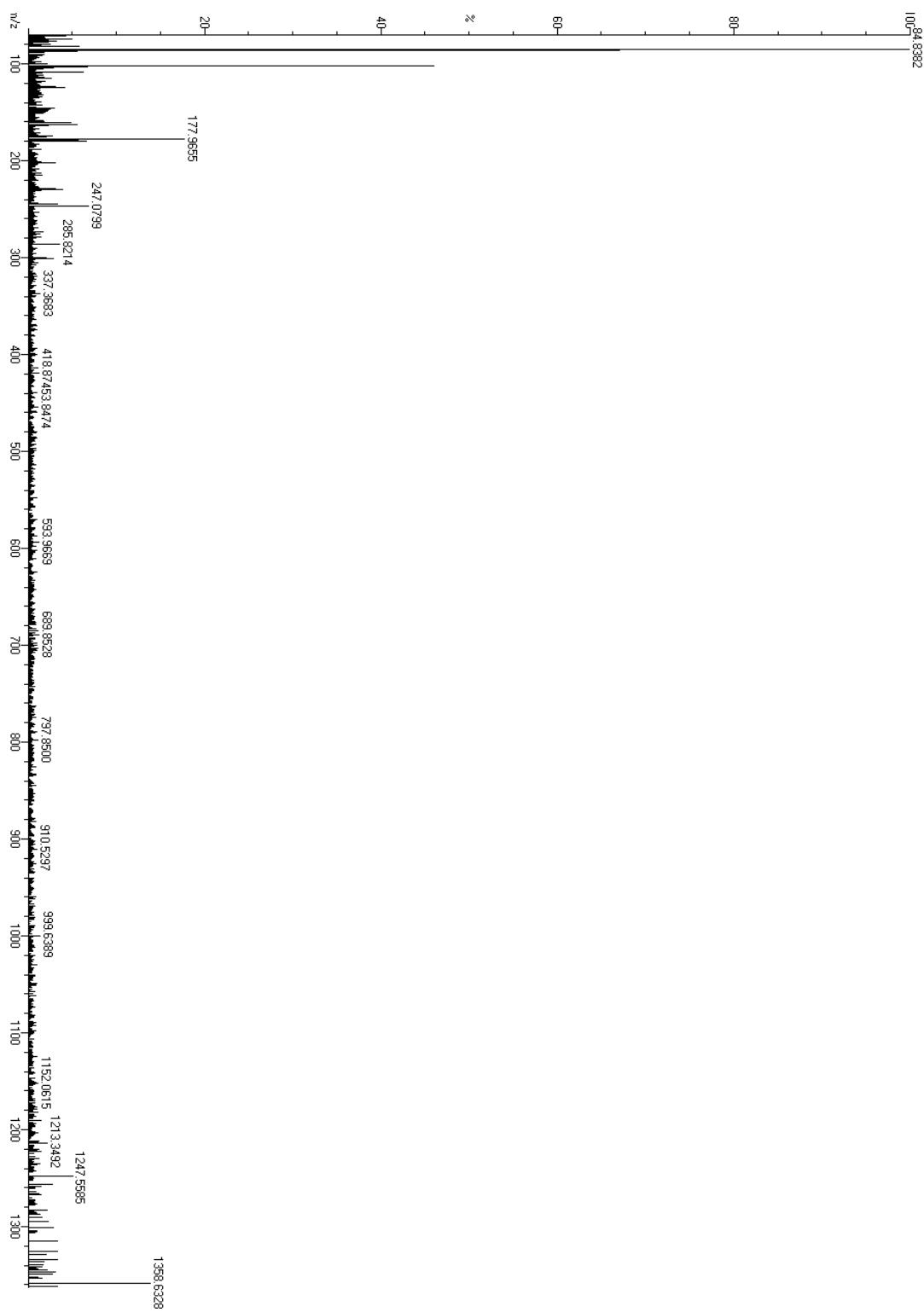
## Supporting Information



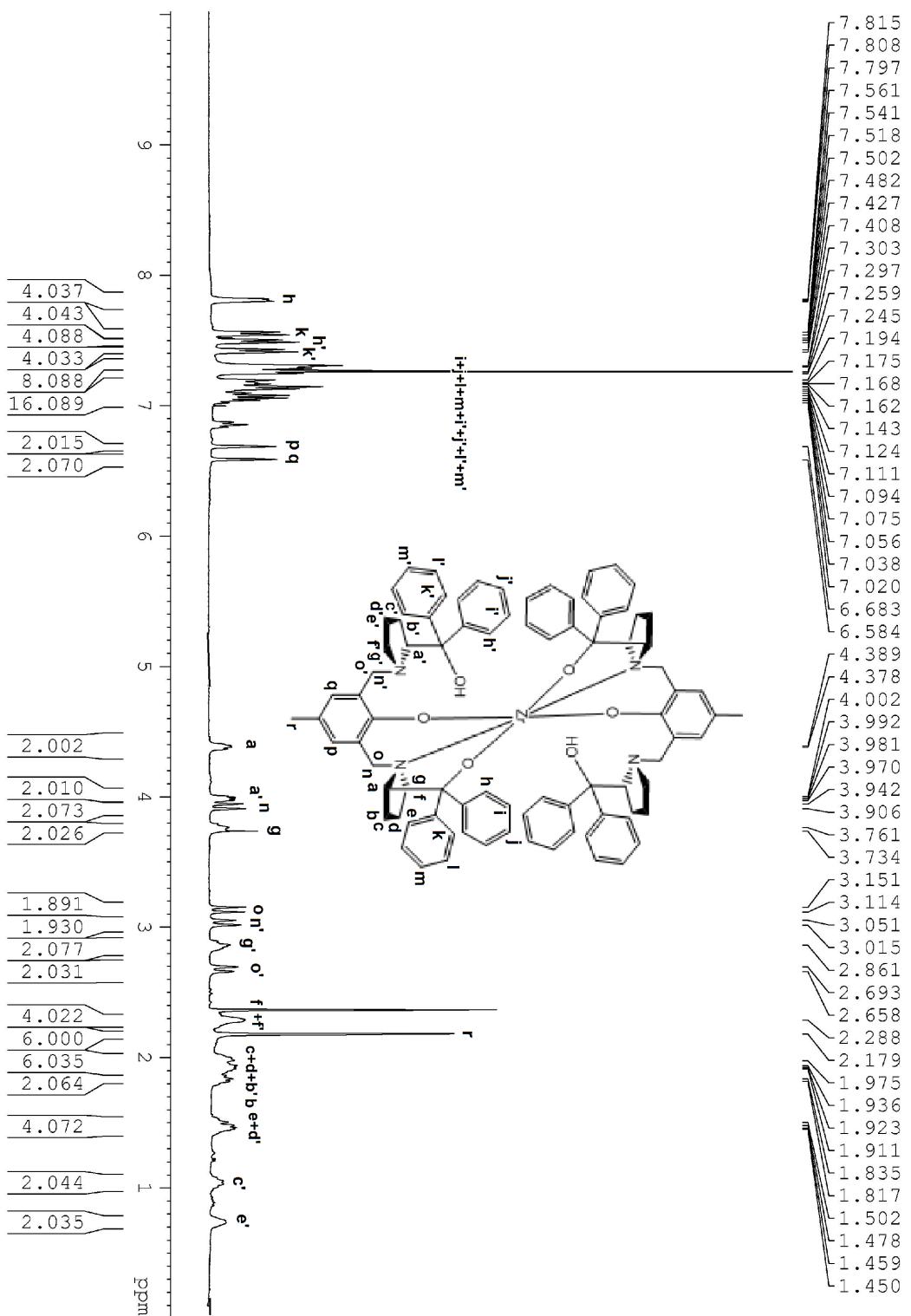
**Fig. 1**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **1**.



**Fig. 2**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **1**



**Fig. 3** ESI-MS spectrum of **1**



**Fig. 4**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **2**.

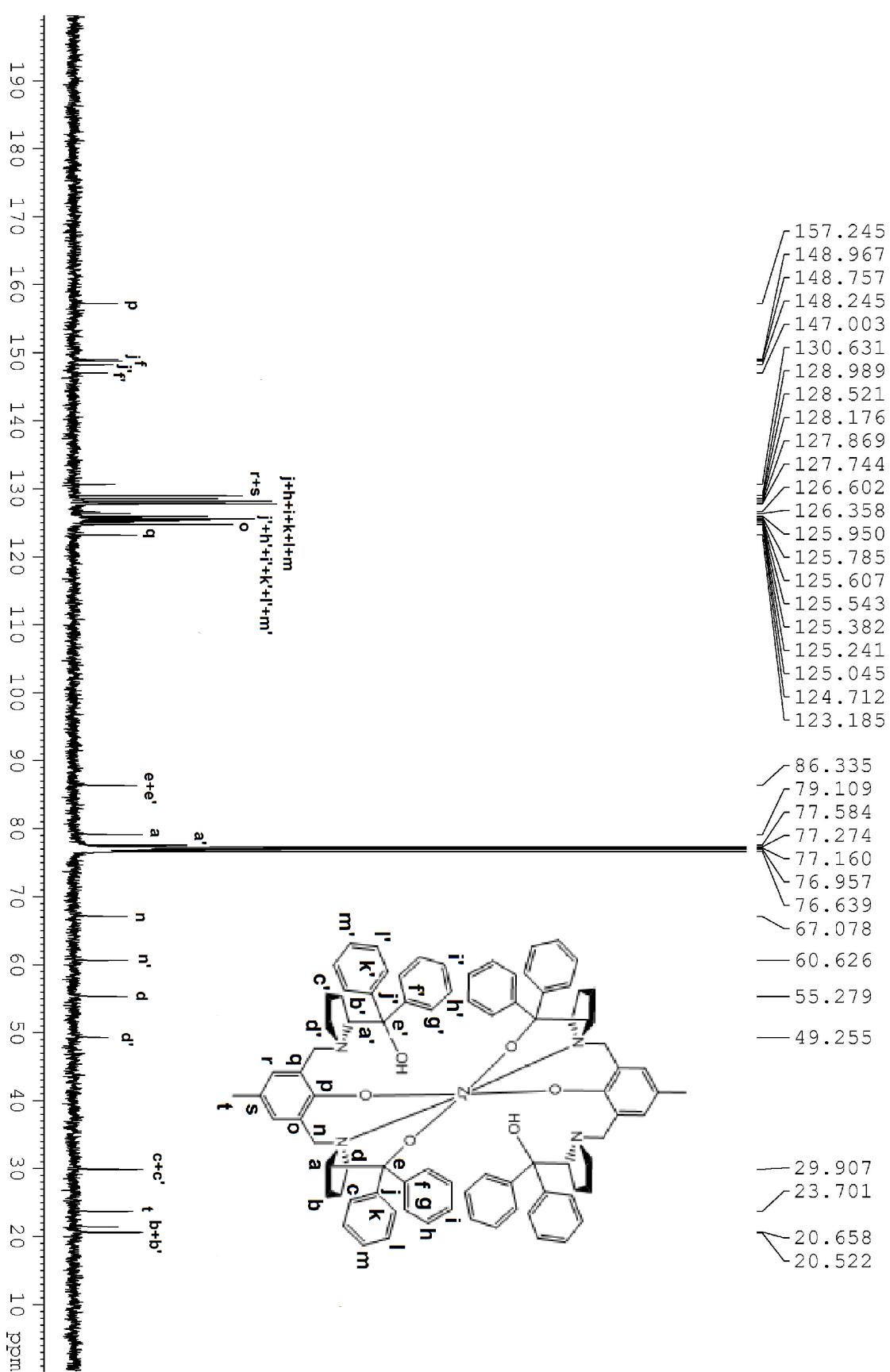
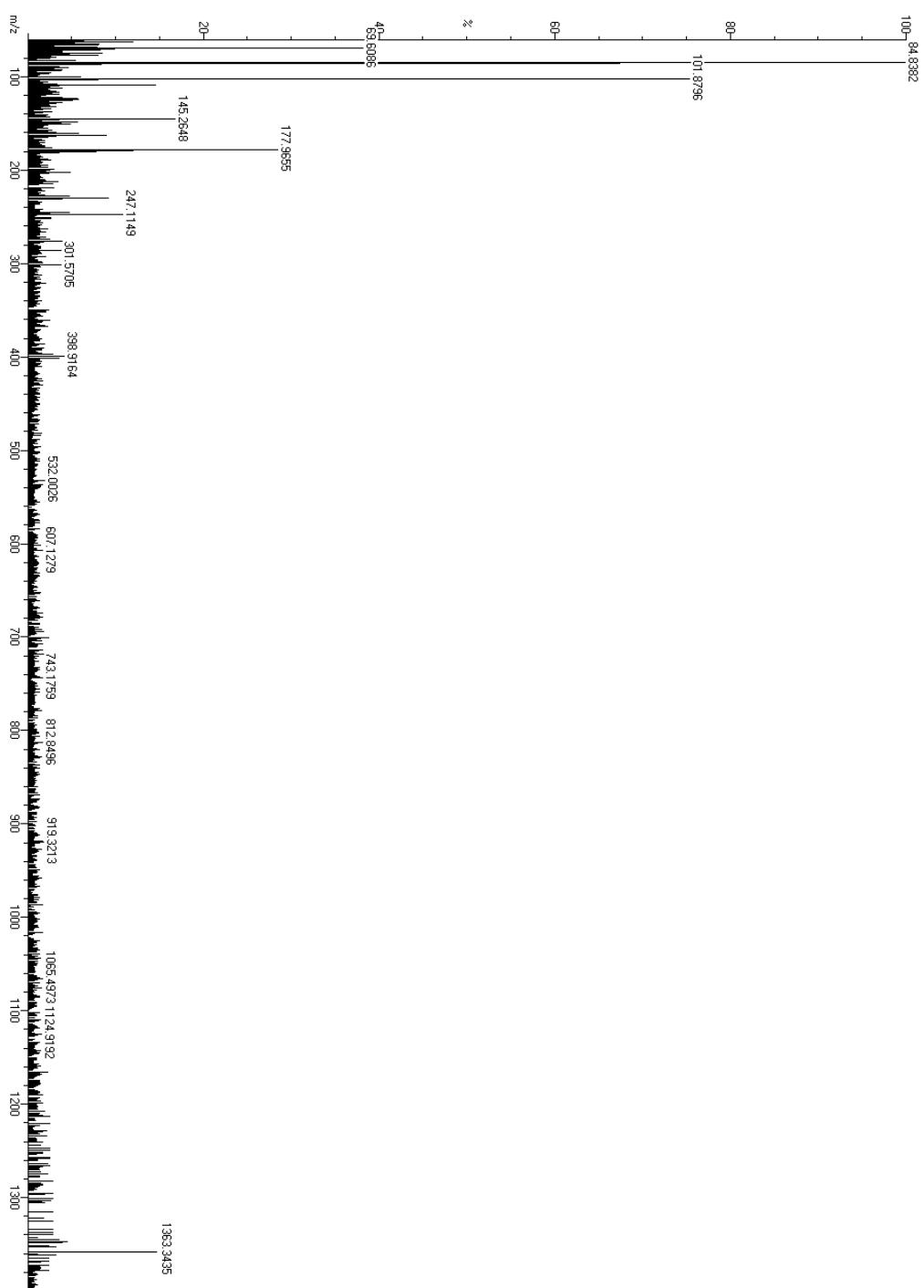
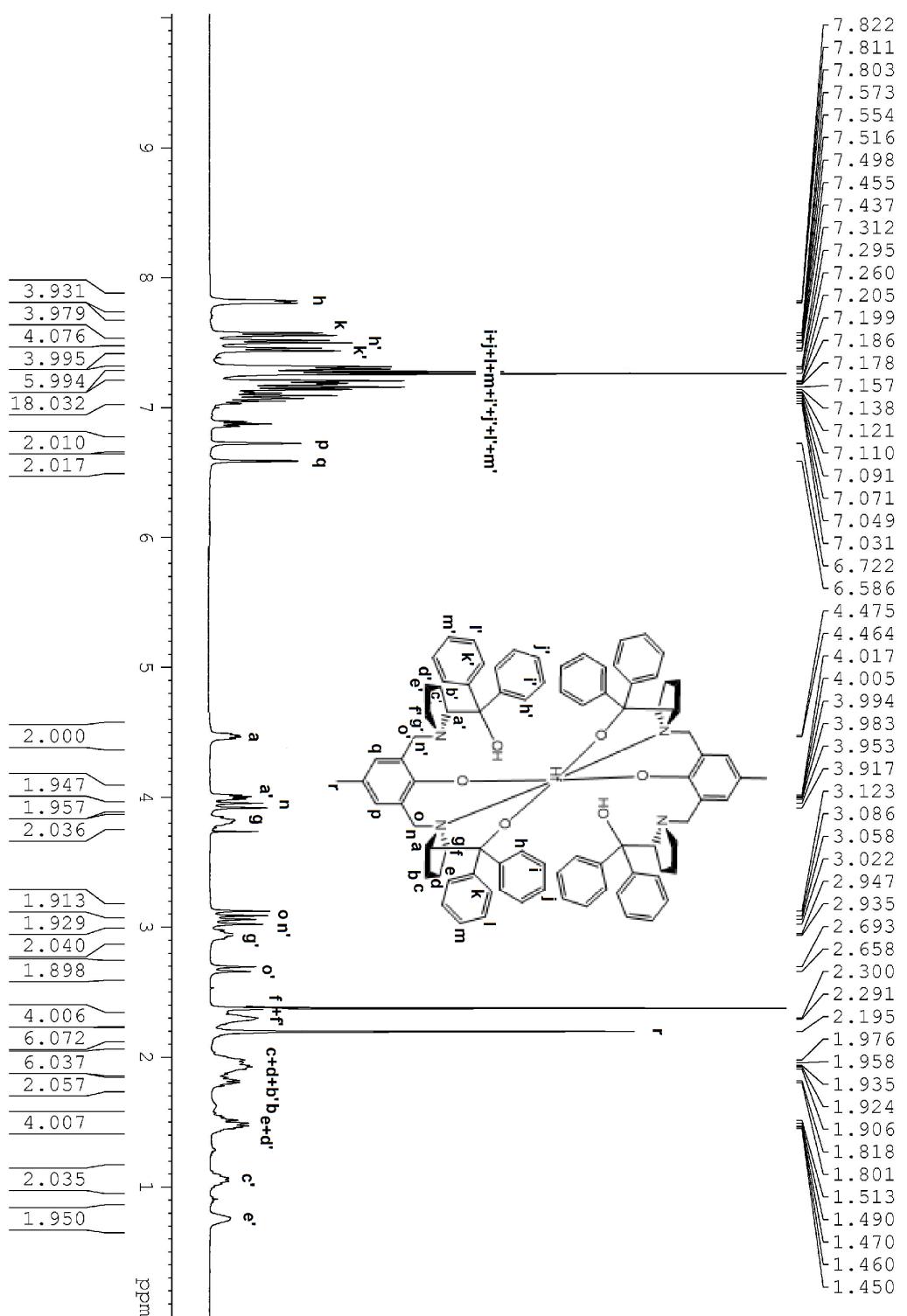


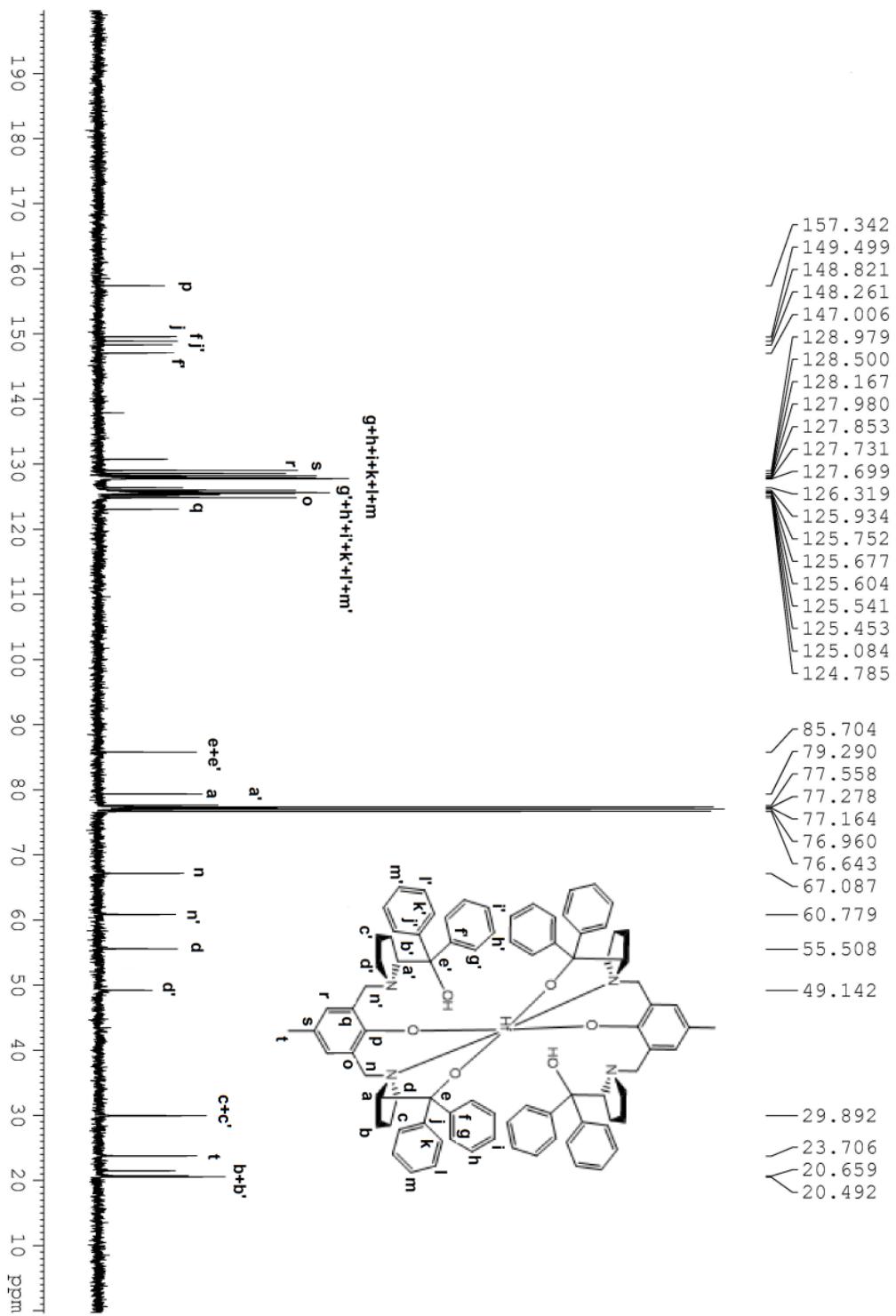
Fig. 5  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 2.



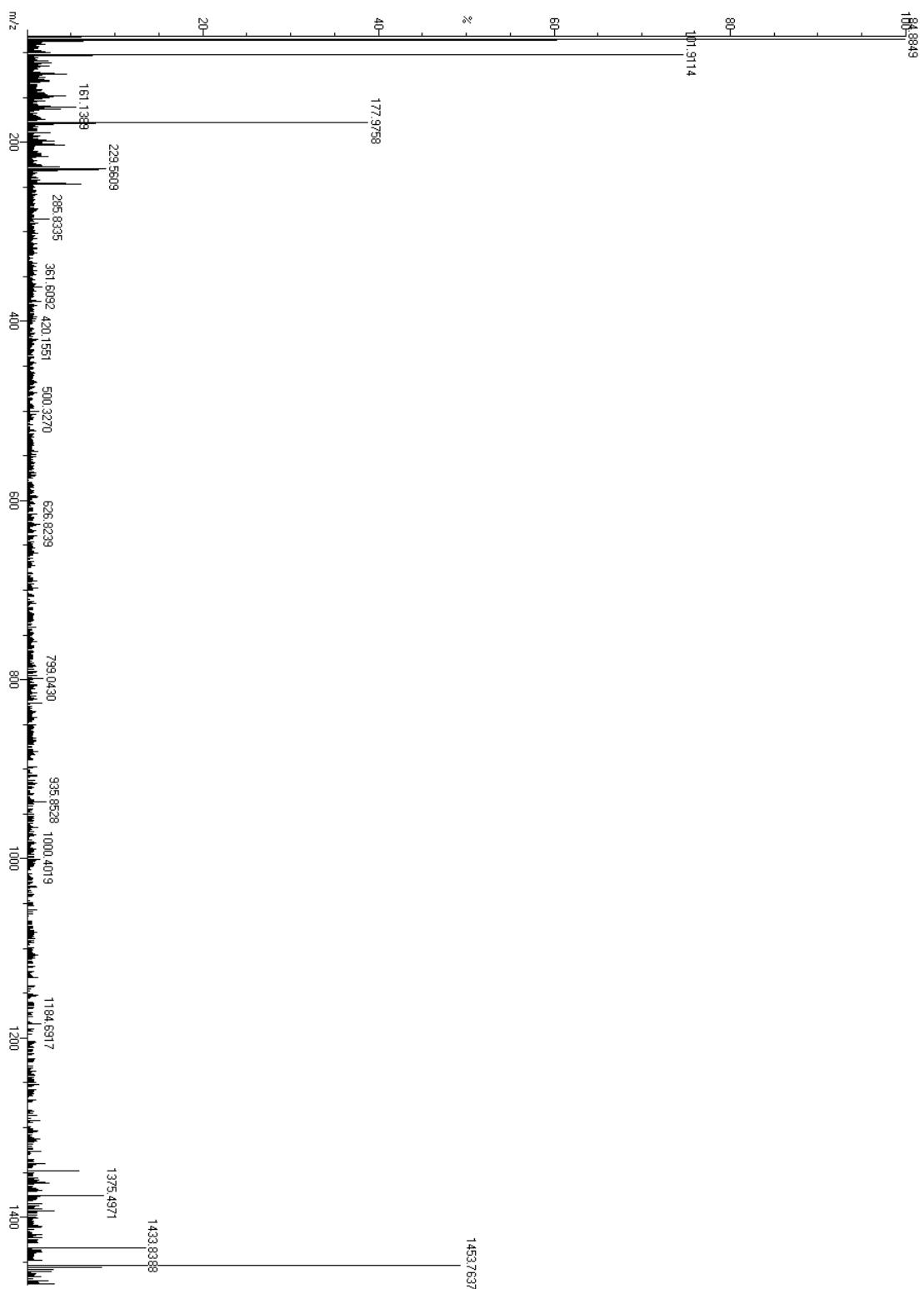
**Fig. 6** ESI-MS spectrum of **2**.



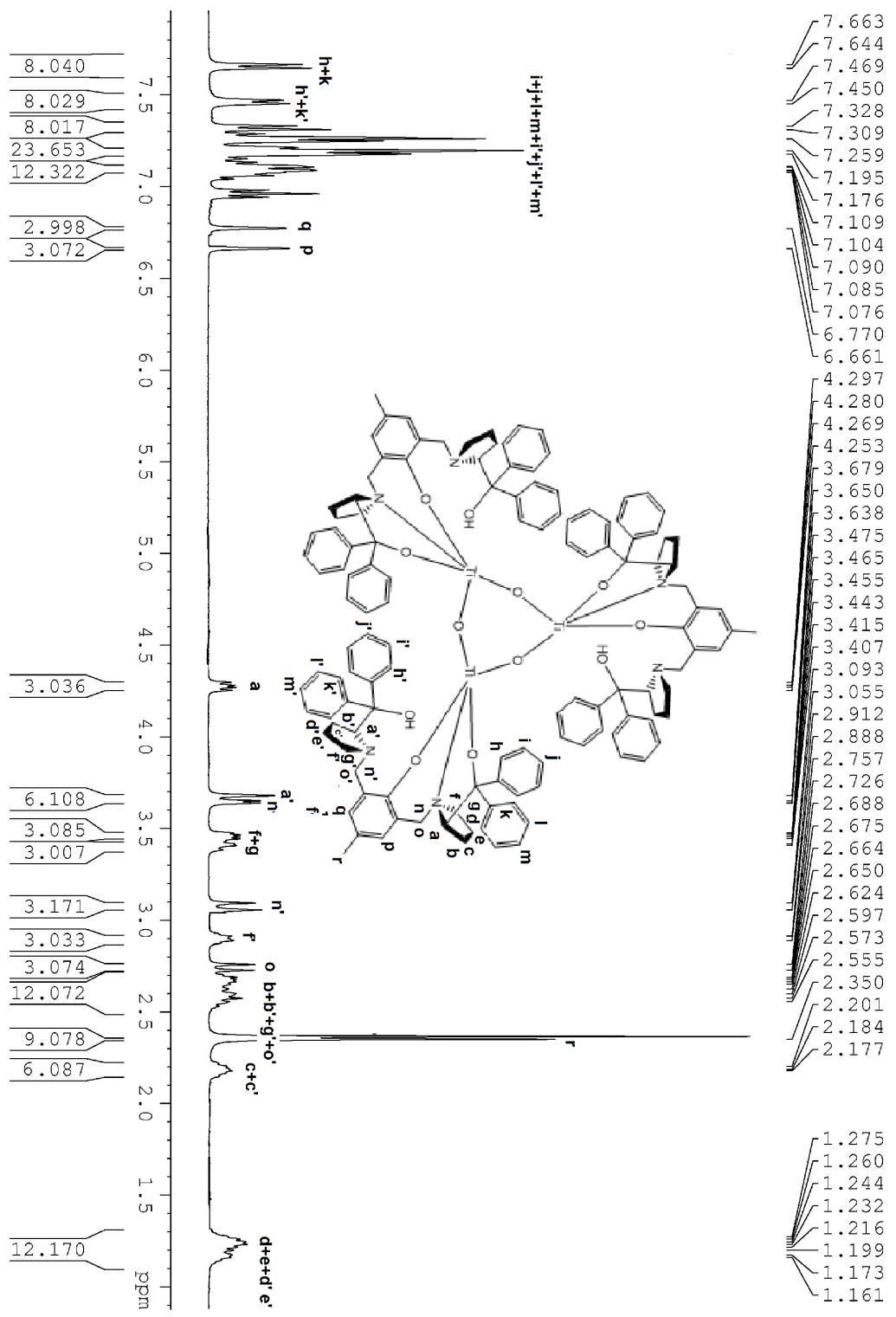
**Fig. 7**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **3**.



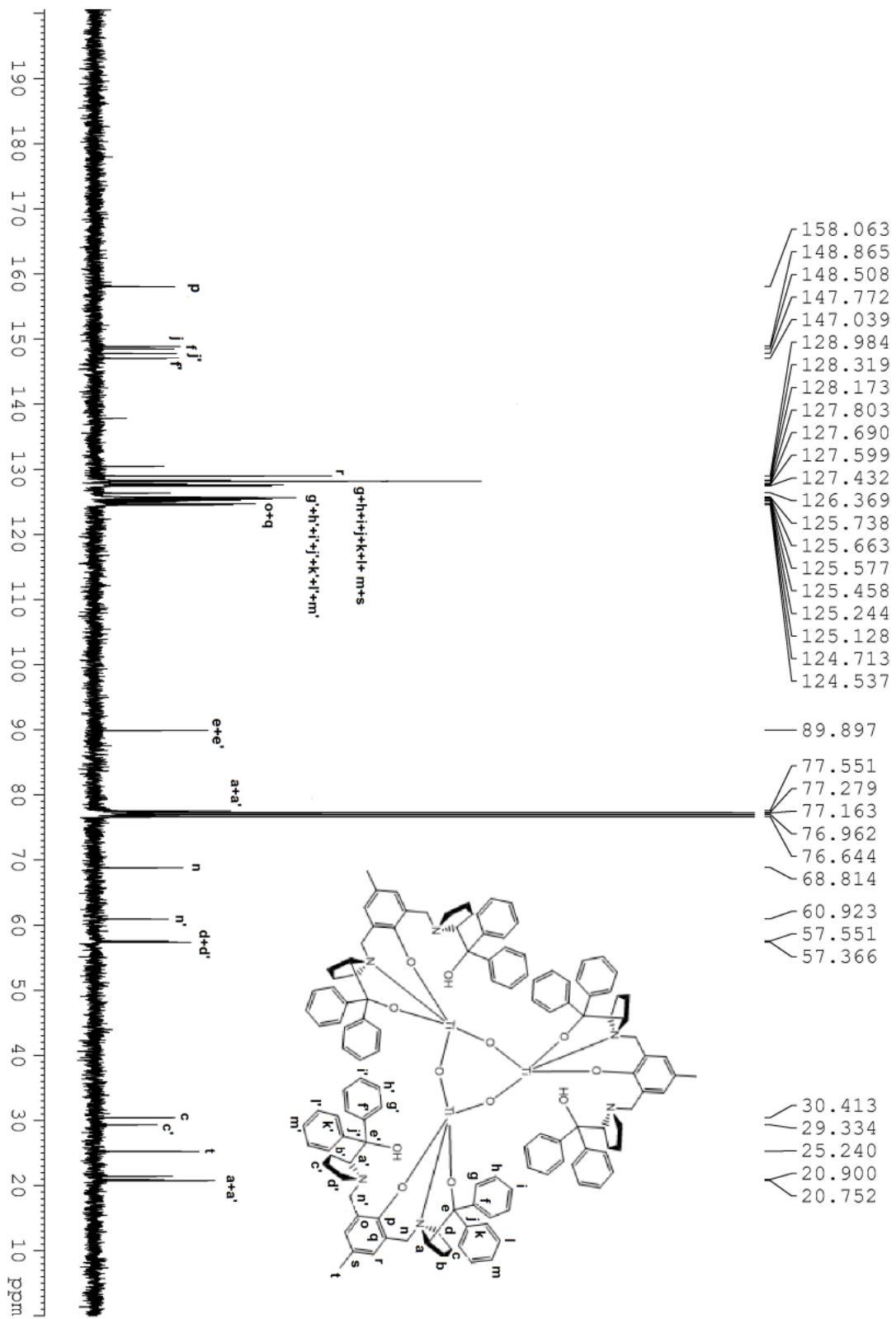
**Fig. 8**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **3**.



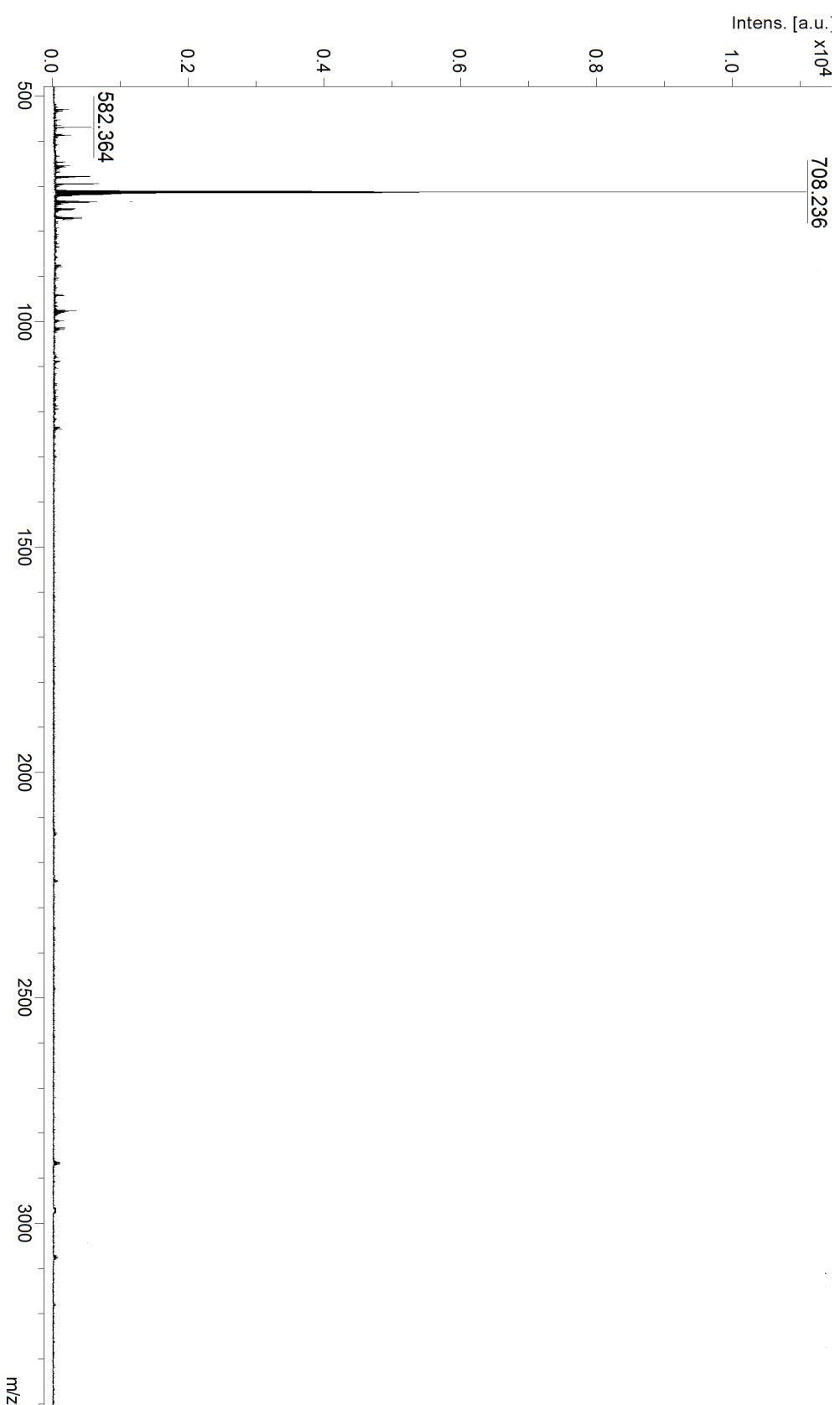
**Fig. 9** ESI-MS spectrum of **3**.



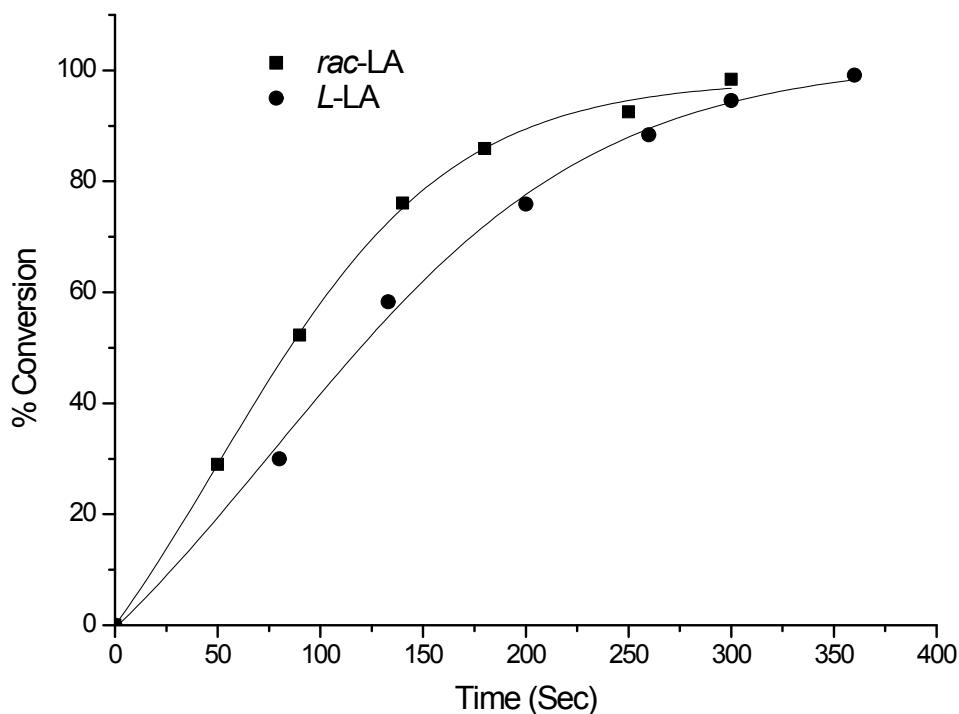
**Fig. 10**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 4.



**Fig. 11**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **4**.

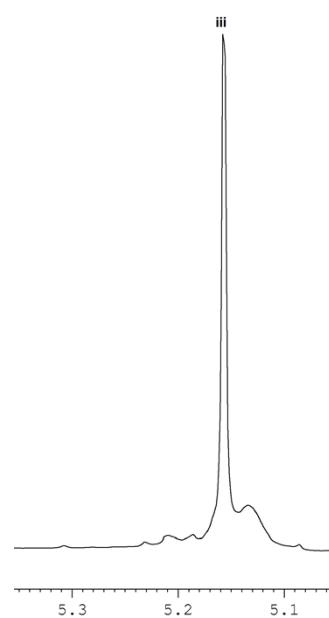


**Fig. 12** ESI-MS spectrum of **4**.



**Fig. 13** *rac*-LA and *L*-LA conversion vs. time plot using 2:  $[M]_0/[I]_0 = 200$  at 140 °C.

### Microstructural analysis



**Fig.14** Methine region of homonuclear decoupled  $^1\text{H}$  NMR spectra of isotactic PLA obtained from *L*-LA polymerization initiated by 2 ( $\text{CDCl}_3$ , 500 MHz).