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Supporting Information

Synthesis of Functional Catechols as Monomers of Mussel-Inspired Biomimetic Polymers

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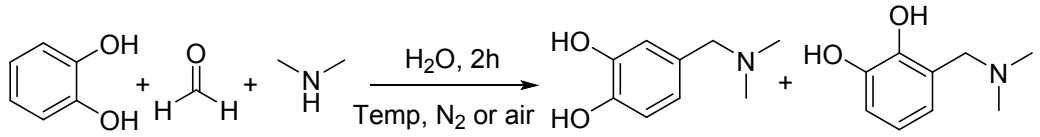
1. Additional Data for Optimization of Mannich Reaction Conditions[a]



2a-4 **2a**-3

entry	atmosphere	temperature	conversion (%)[b]	yield of **2a**-4/**2a**-3 (%)[c]
1	N_2	25 °C	88	68 / 12
2	air	25 °C	51	32 / 10
3	N_2	40 °C	90	24 / 60
4	N_2	5 °C	26	26 / trace
5	air	40 °C	35	10 /18
6	air	5 °C	21	18 / trace

[a]Reaction conditions: catechol (0.02 mol), dimethylamine (0.02 mol, 33 wt % aqueous), formaldehyde (0.02 mol, 37 wt % aqueous), water (30 mL). [b]The conversion rate of catechol was calculated based on the recovered amount of catechol; [c]The yield of isolated product.

2. Ten-fold scale-up synthesis of 2b-4 and 2c-4.

To the solution of a secondary amine (0.2 mol) in distilled water (50 mL), formaldehyde (0.2 mol, 37 wt % aqueous) was added, and the mixture was stirred at room temperature for 1 h. Then a solution catechol in water (0.2 mol, 50 mL) was added dropwise under N2 and the resultant solution was stirred for another 4 h. After that, dilute hydrochloric acid was added to the solution and the solution acidity was adjusted to about pH 2. After extraction with ethyl acetate for three times to recover completely the unreacted catechol residue, the acidity of the aqueous phase was adjusted to pH 8.1 with aqueous NaOH, and extracted using 250 mL ethyl acetate for 5 times. The combined organic phase was dried over anhydrous Na_2SO_4 and evaporated to afford a residue, which was dissolved in a 150 mL acetonitrile for recrystallization and the **2b**-4 and **2c**-4 was obtained in 60% (13.6 g) and 71% (13.8 g) yield, respectively.

3. NMR spectra of DEPU and DEPA

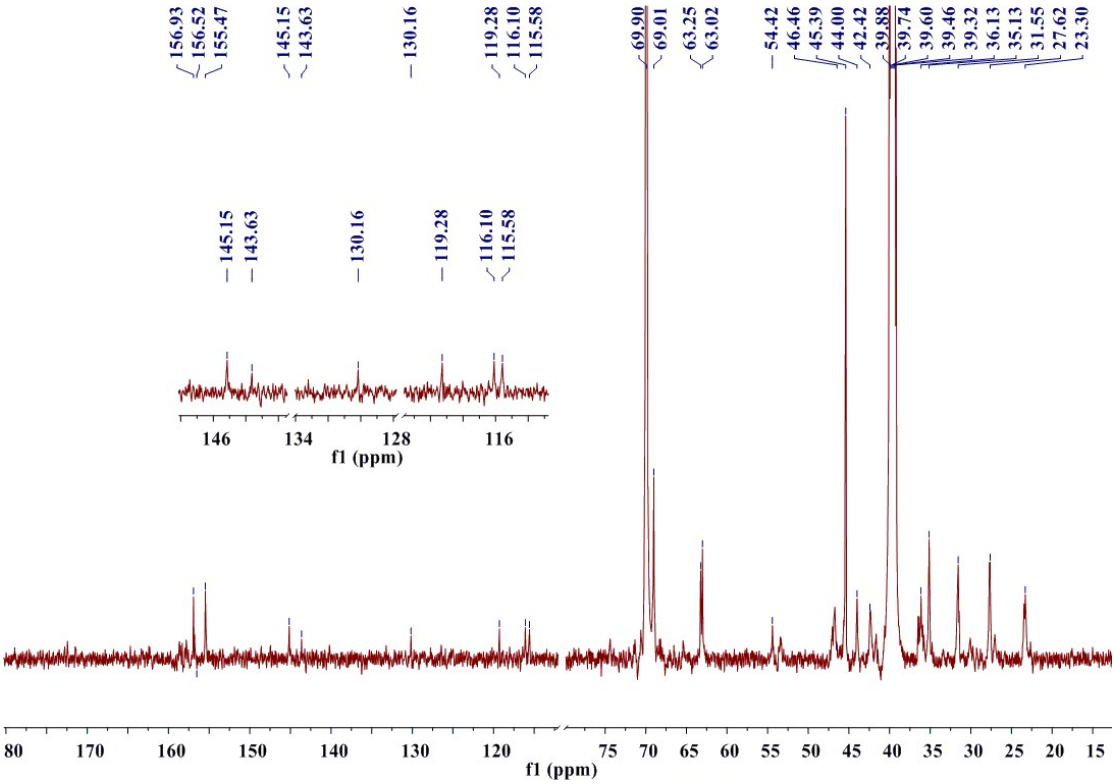


Figure S1. ^{13}C NMR spectrum of DEPU (DMSO-*d6*, 600 MHz).

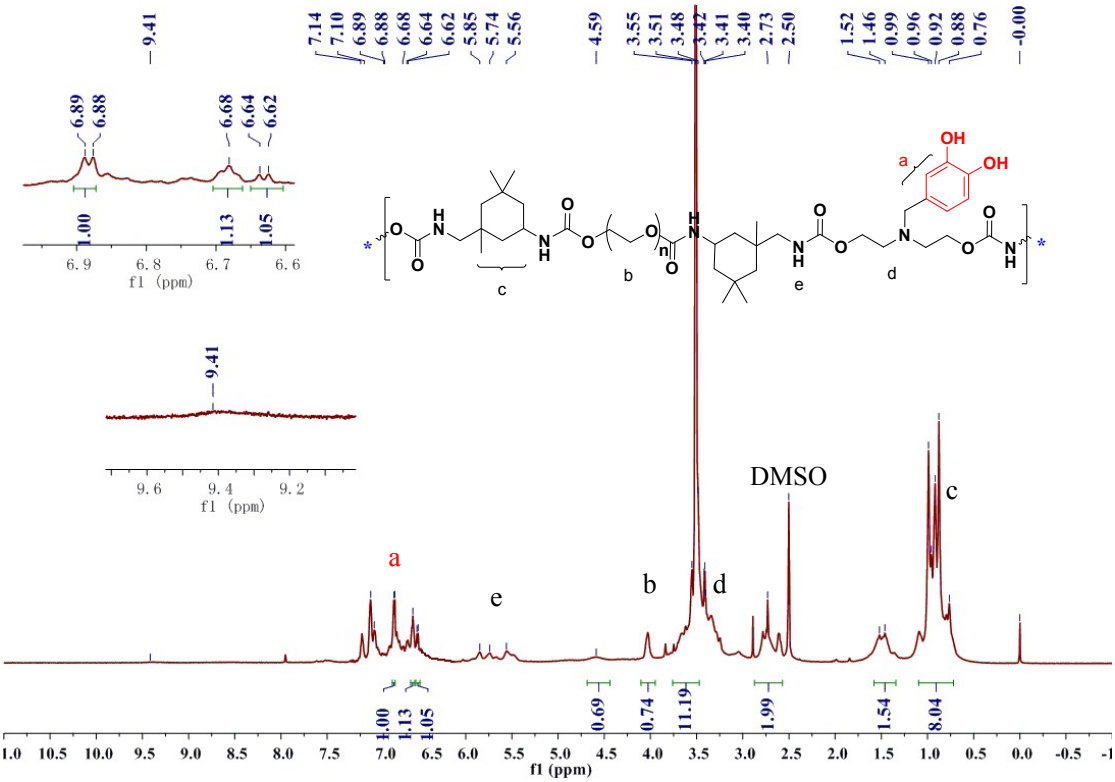


Figure S2. ^{1}H NMR spectrum of DEPU (DMSO-*d6*, 600 MHz).

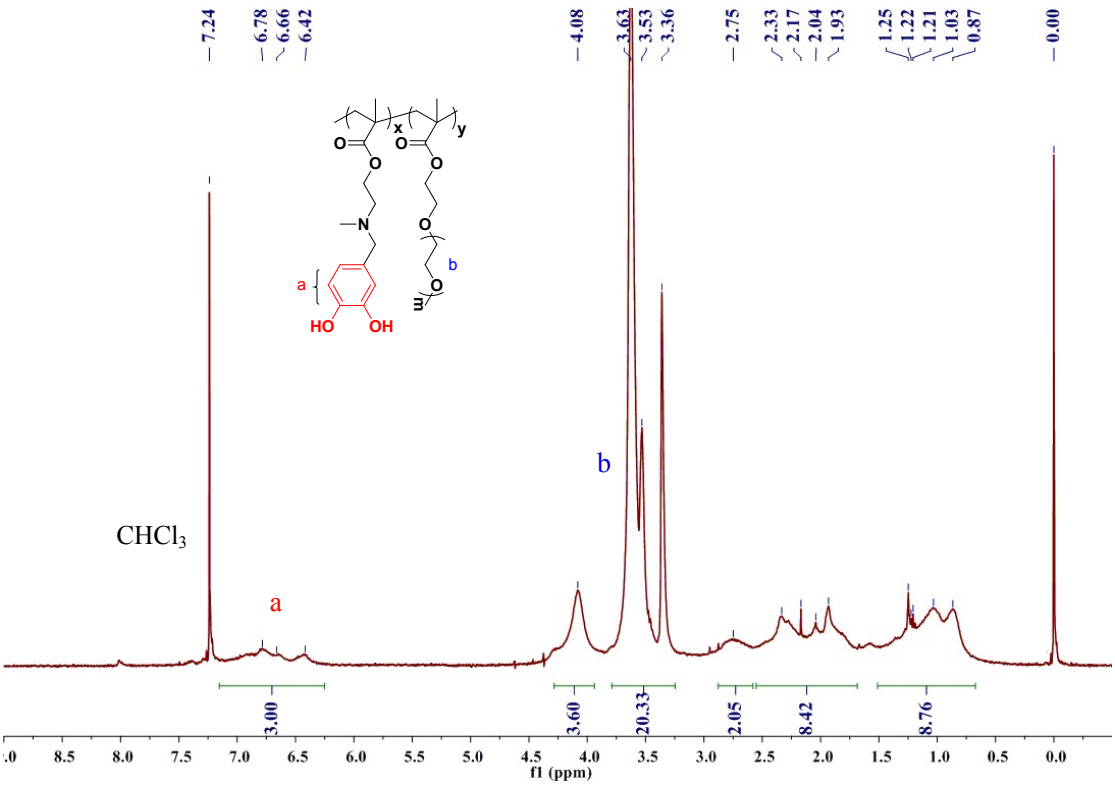


Figure S3. ^{1}H NMR spectrum of catechol-containing polymethacrylate DEPA ($CDCl_3$, 600 MHz).

4. GPC analysis of polymers DEPA and DEPU

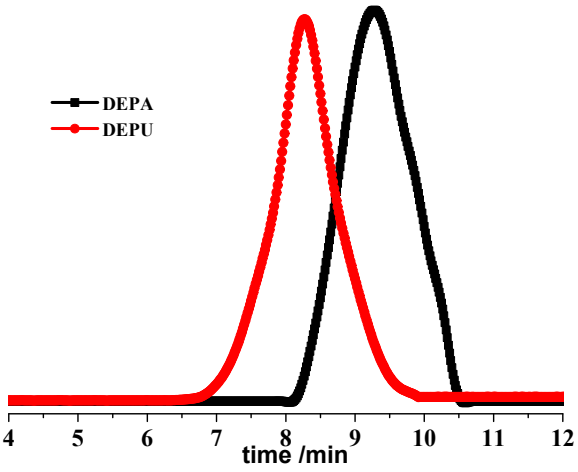


Figure S4.GPC elution profiles for polymers DEPA (black line) and DEPU (red line) using THF as eluent.

5. SEM images of the Coatings morphologies on silicon

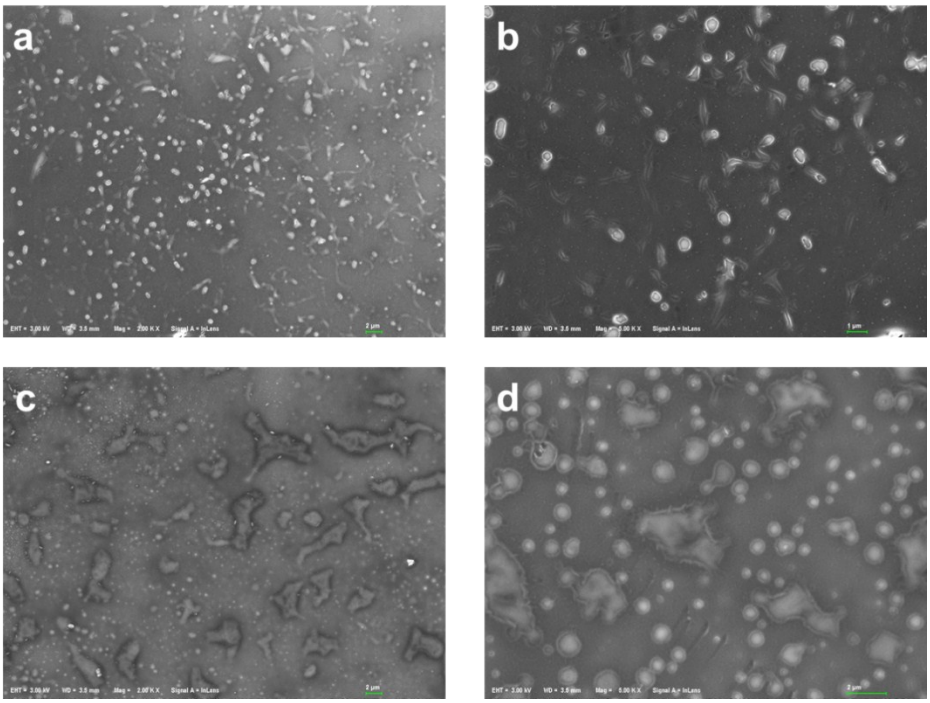
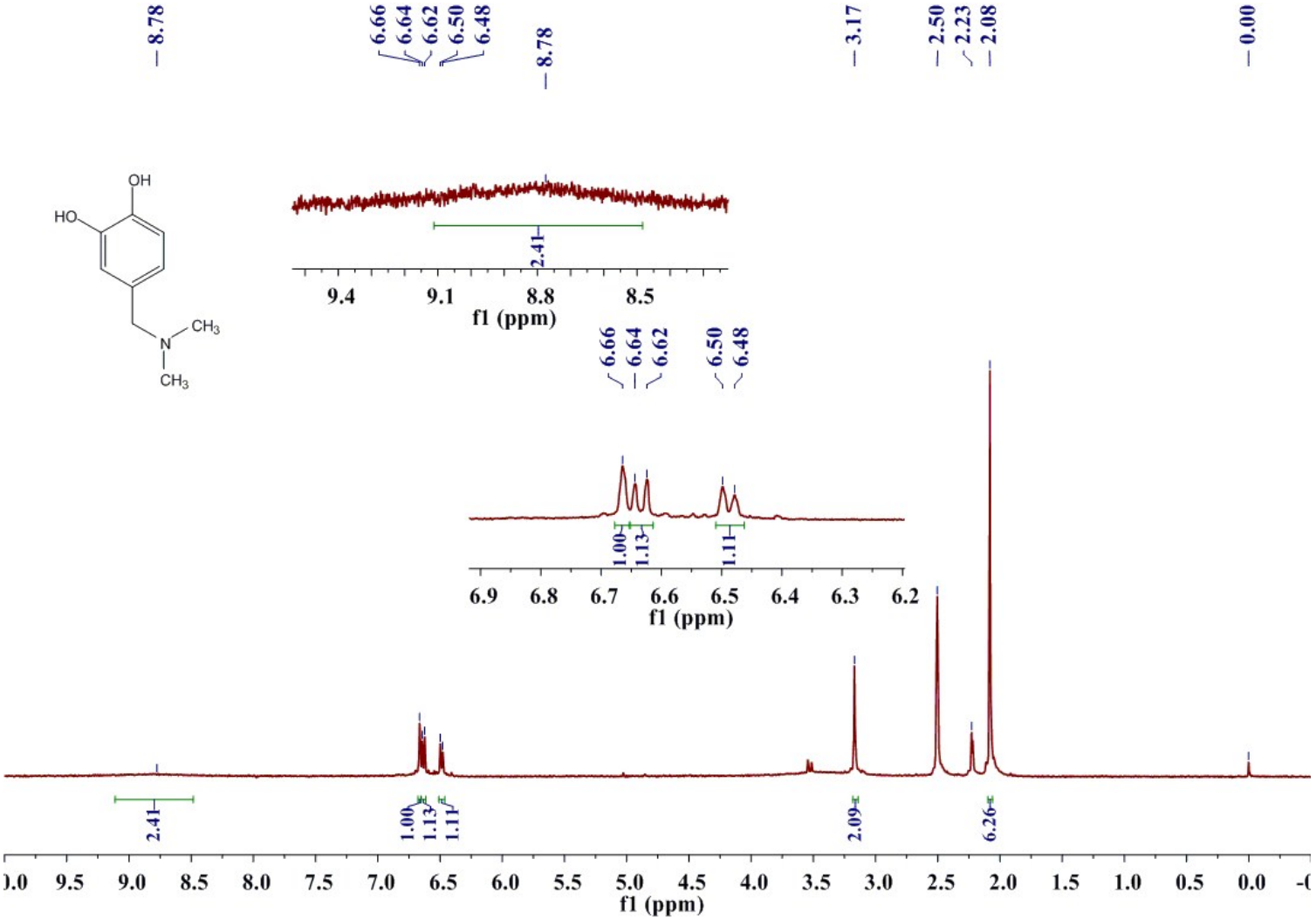


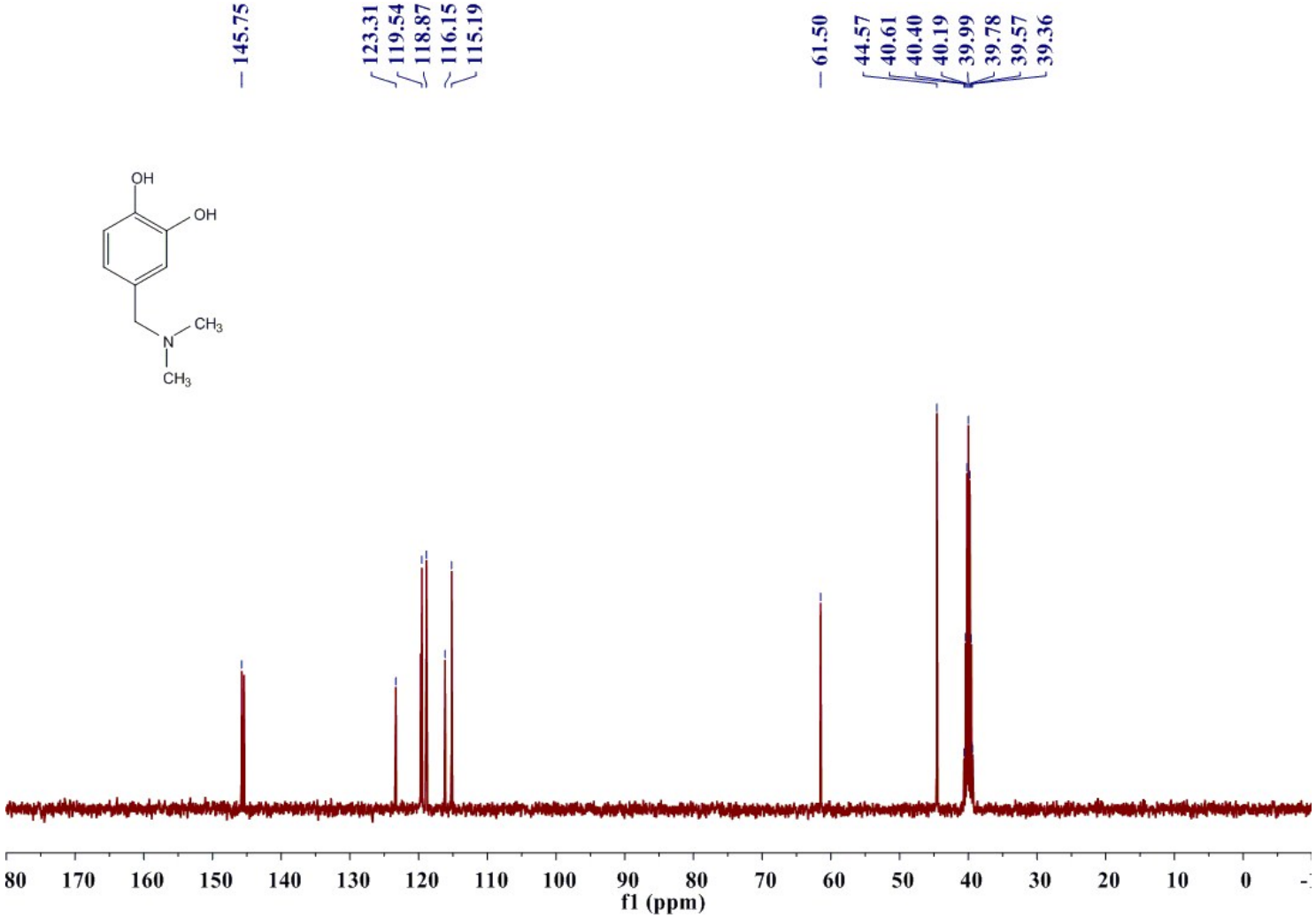
Figure S5. Scanning electron microscopy (SEM) images of (a-b) DEPU and (c,d) DEPA on silicon (magnification 2000× (a, c) and 5000× (c, d)).

6. Copies of ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of 2a~l-4 and 2a~j-3, methacrylated 2c-4

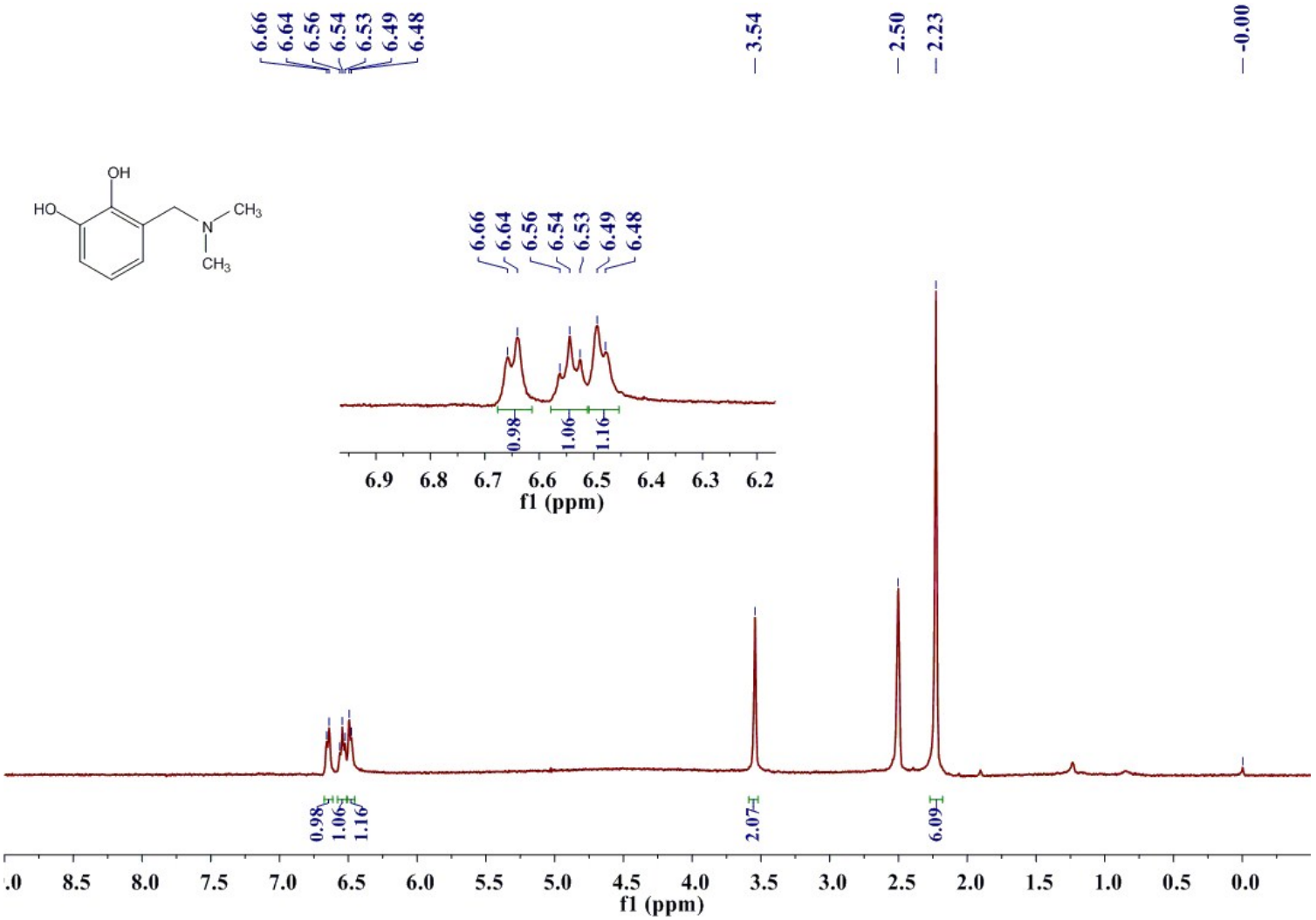
Compound **2a**-4 (^{1}H NMR, 400 MHz, DMSO-*d6*)



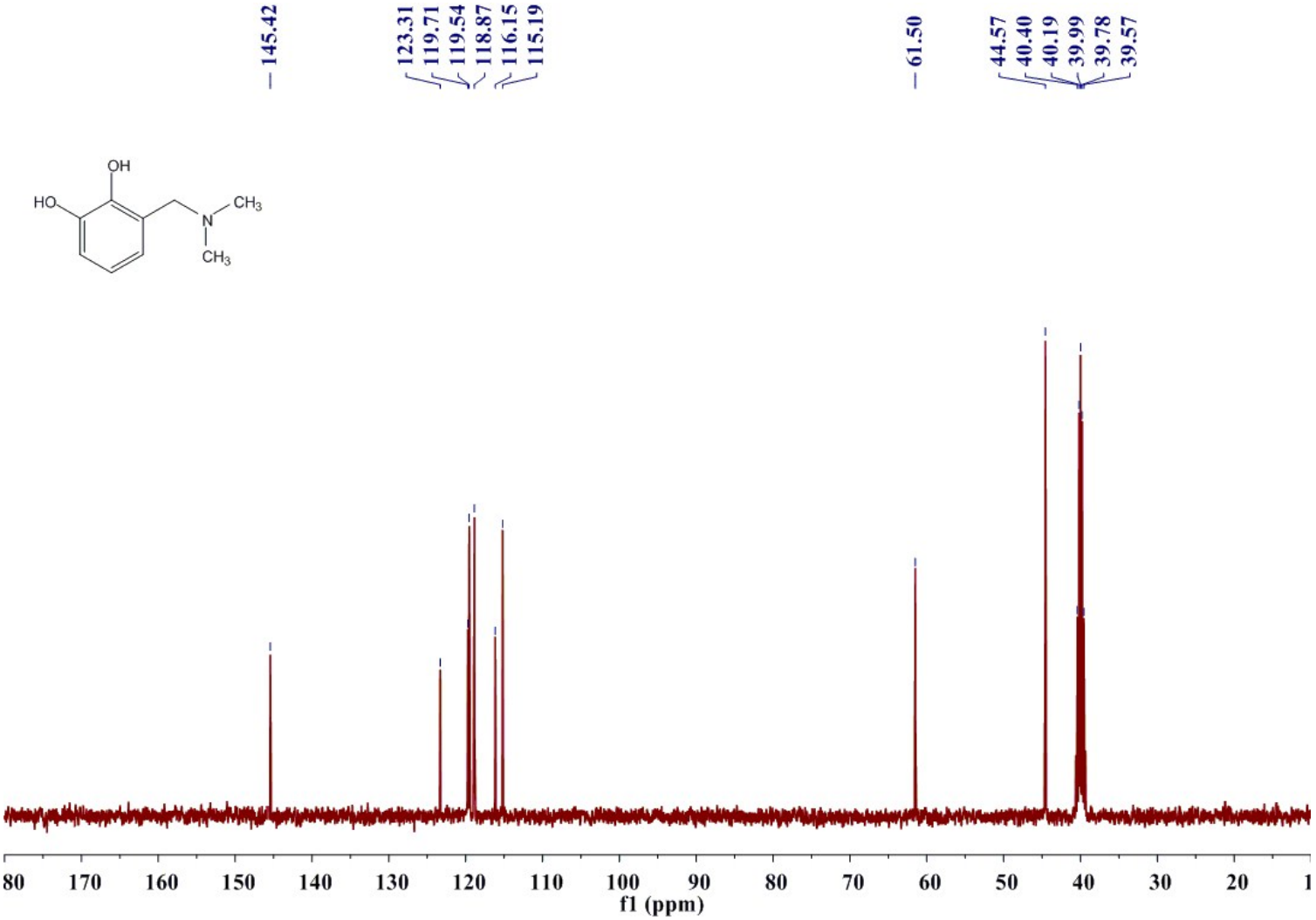
Compound **2a**-4 (^{13}C NMR, 400 MHz, DMSO-*d6*)



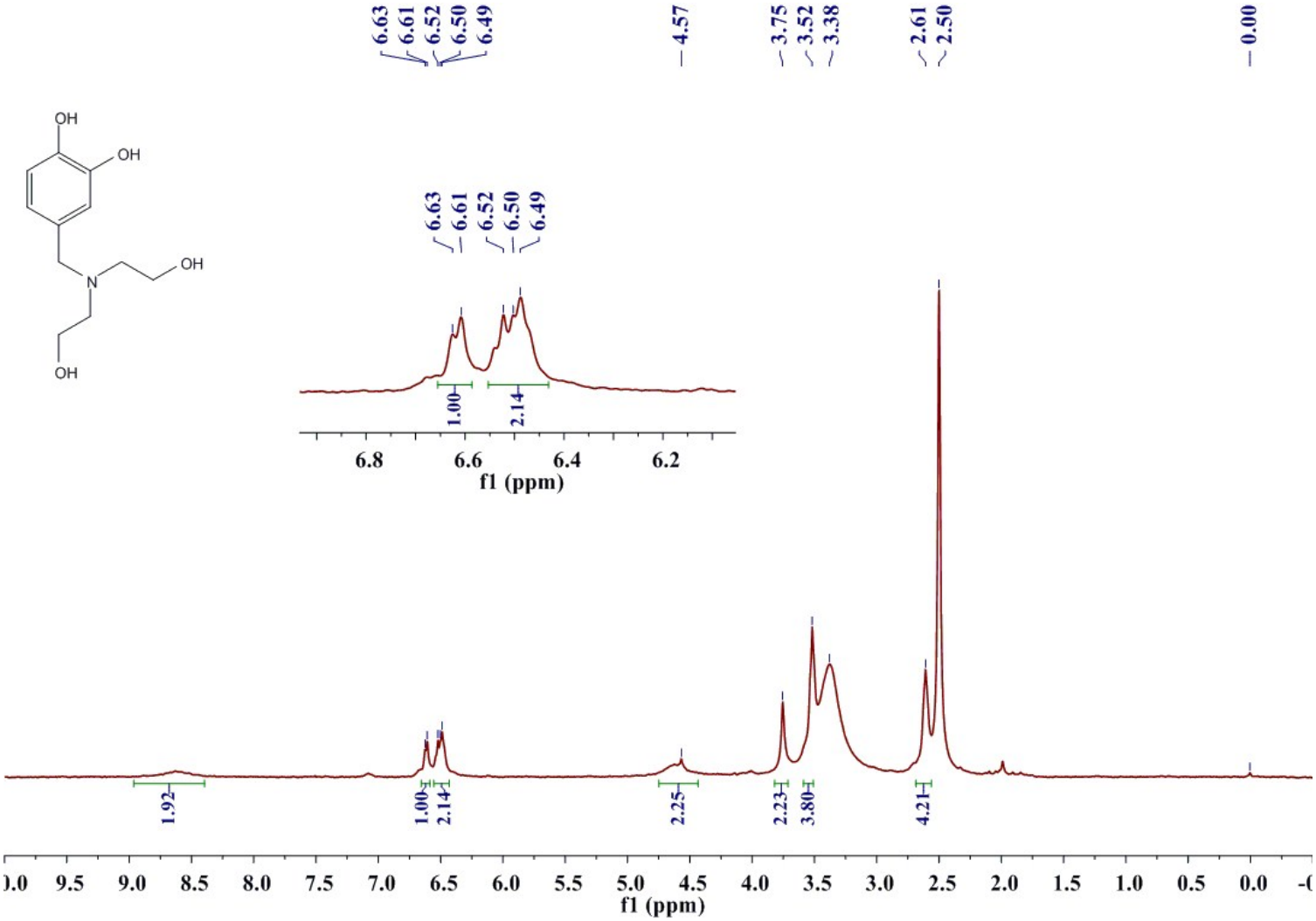
Compound **2a**-3 (^{1}H NMR, 400 MHz, DMSO-*d6*)



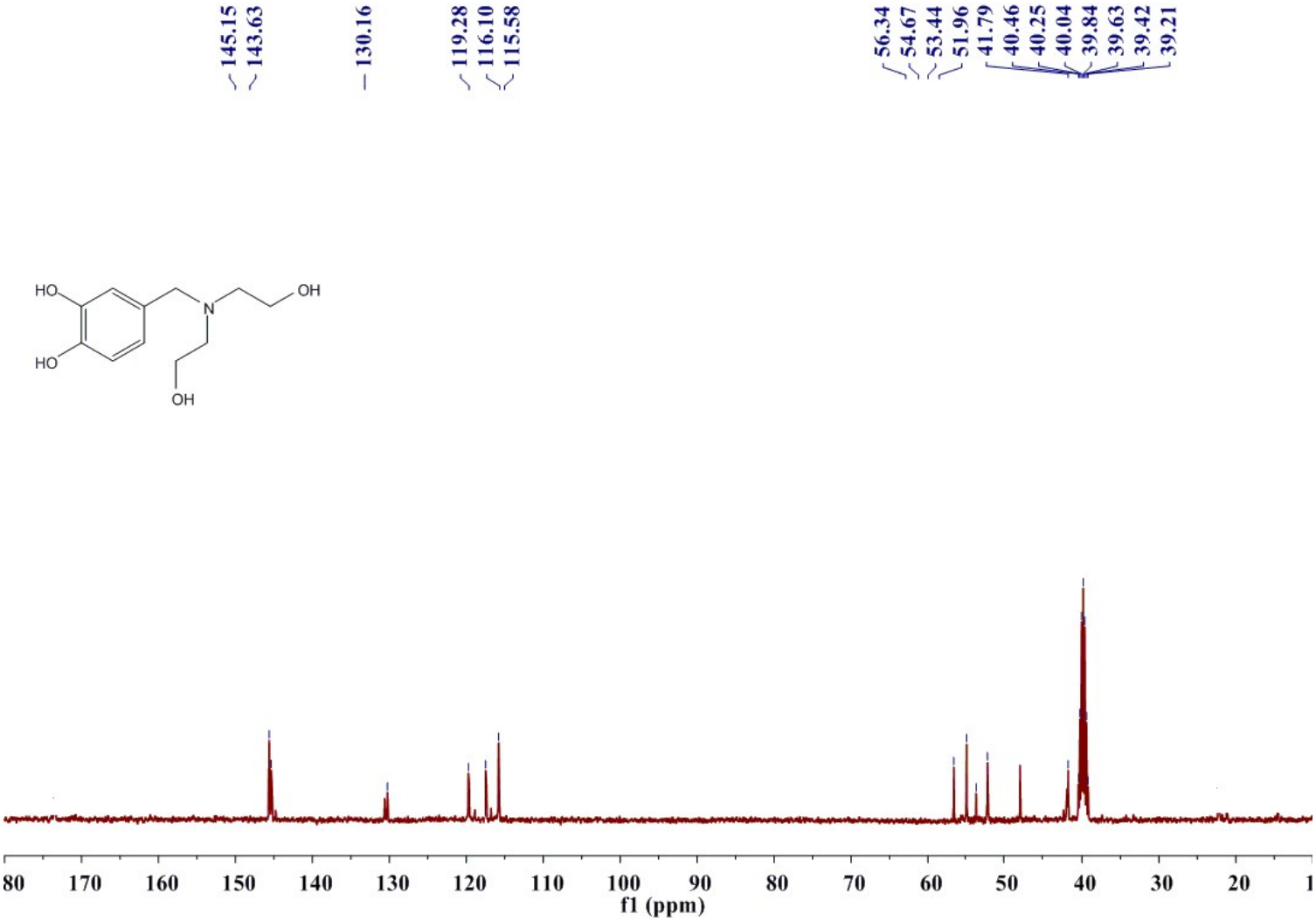
Compound **2a**-3 (^{13}H NMR, 400 MHz, DMSO-*d6*)



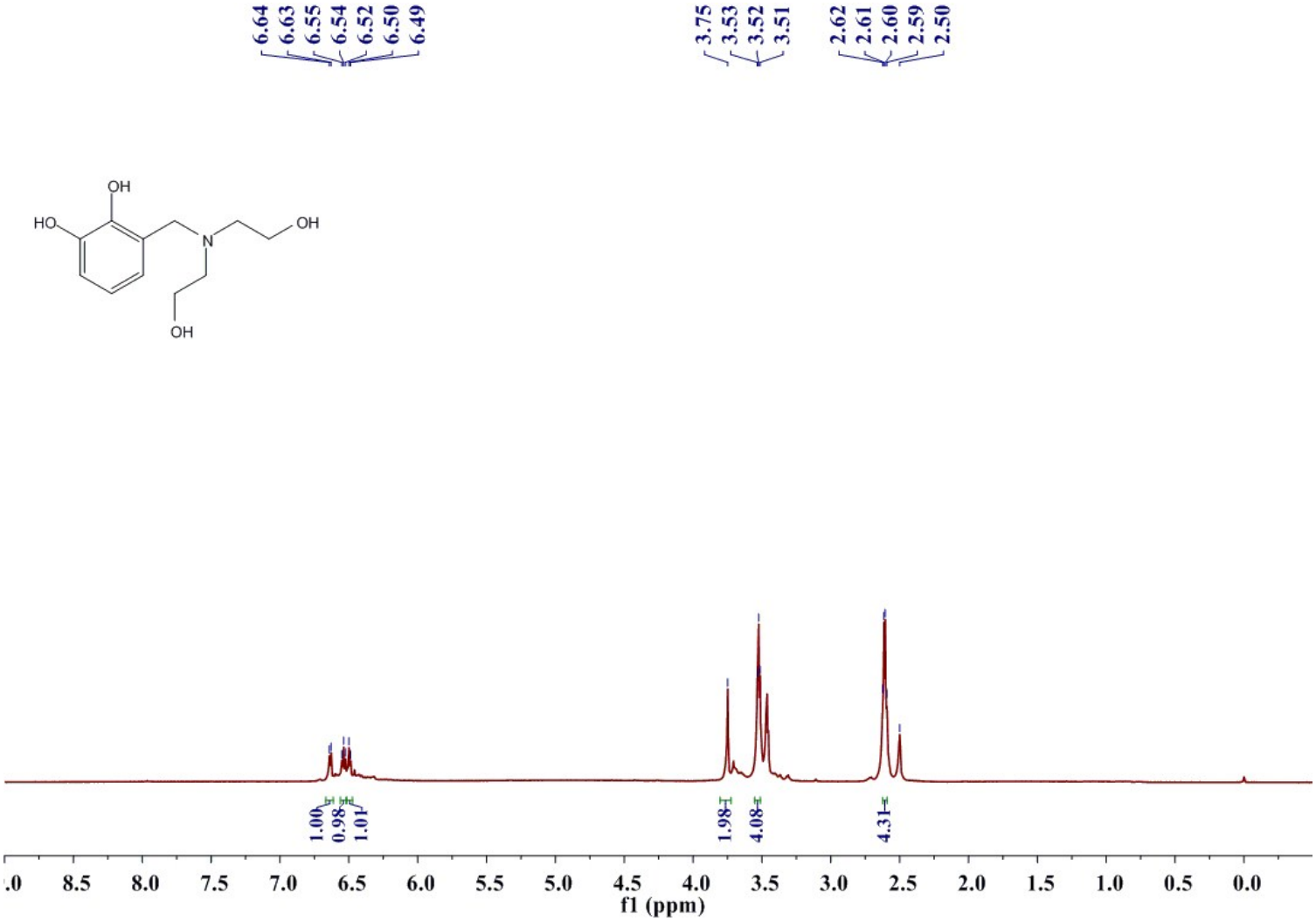
Compound **2b**-4 (^{1}H NMR, 600 MHz, DMSO-*d6*)



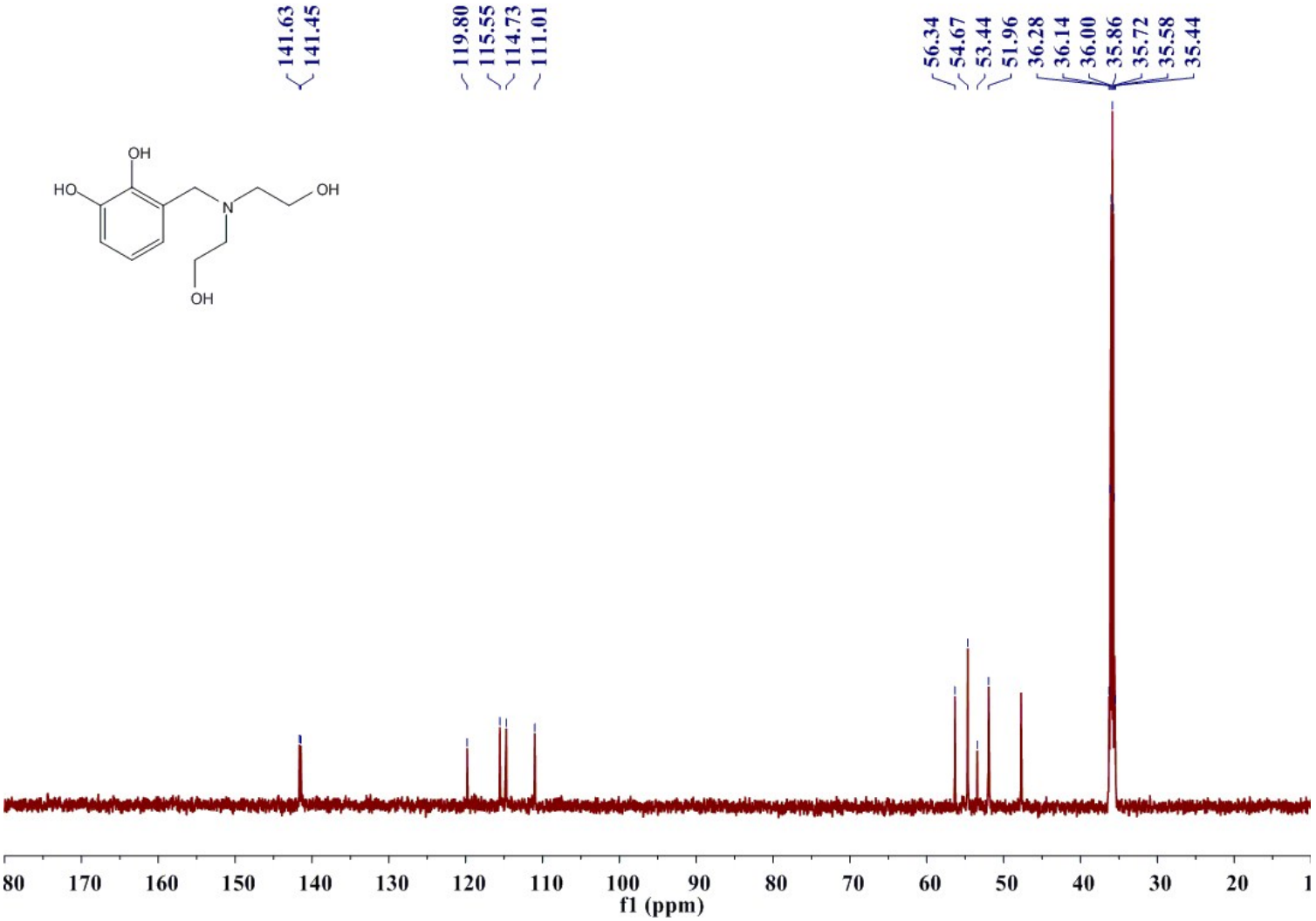
Compound **2b**-4 (^{13}C NMR, 151 MHz, DMSO-*d6*)



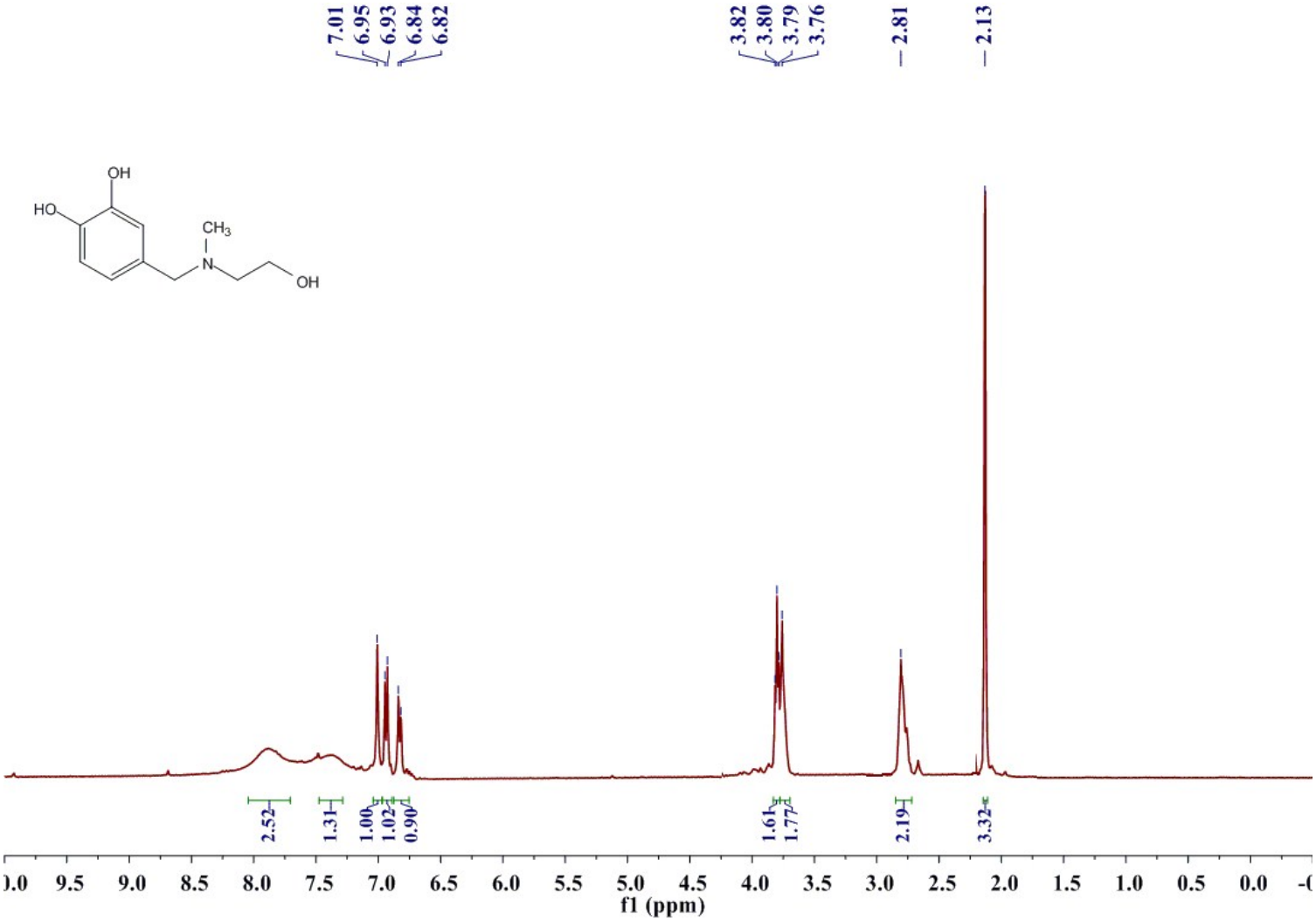
Compound **2b**-3 (^{1}H NMR, 400 MHz, DMSO-*d6*)



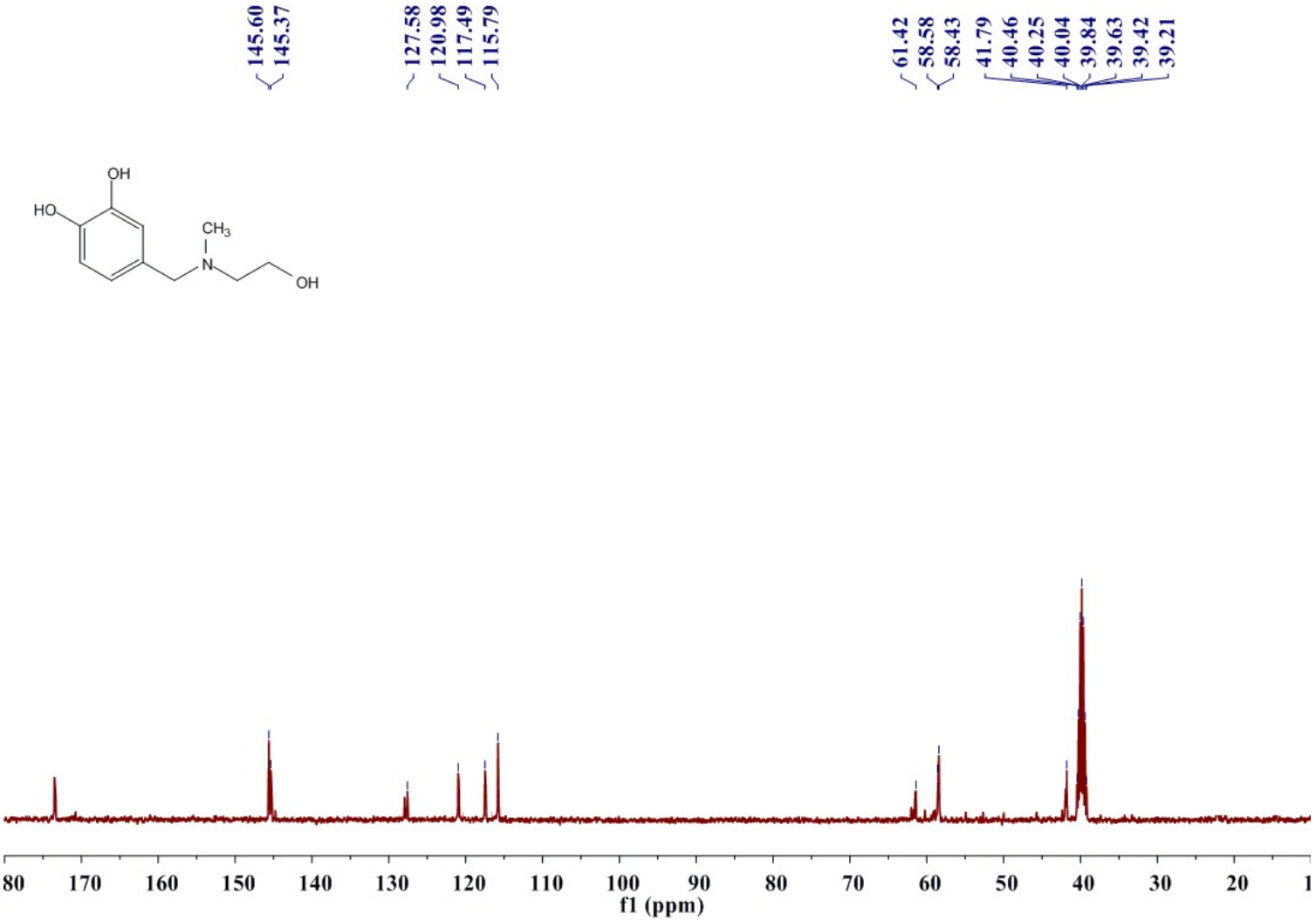
Compound **2b**-3 (^{13}C NMR, 101 MHz, DMSO-*d6*)



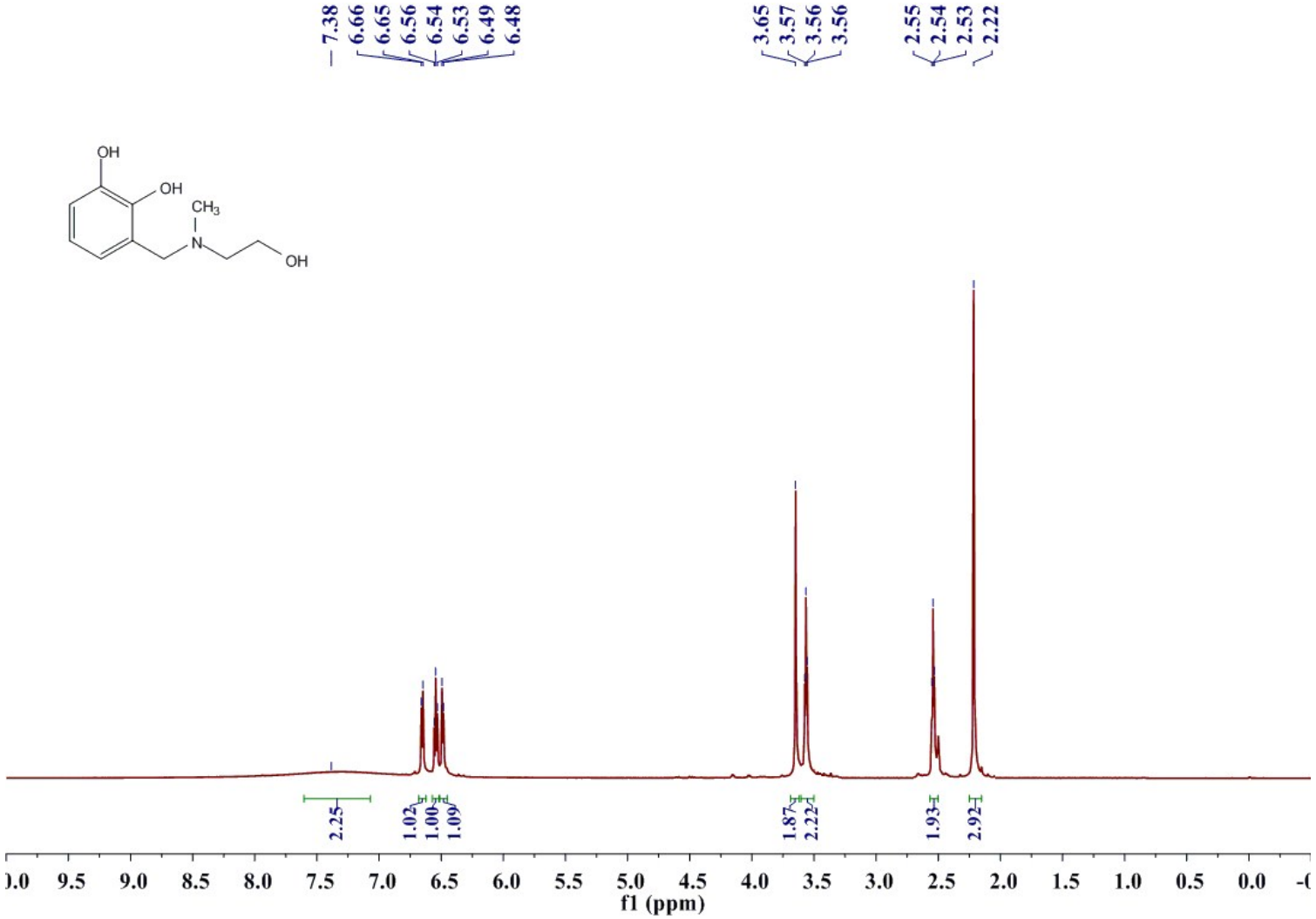
Compound **2c**-4 (^{1}H NMR, 400 MHz, DMSO-*d6*)



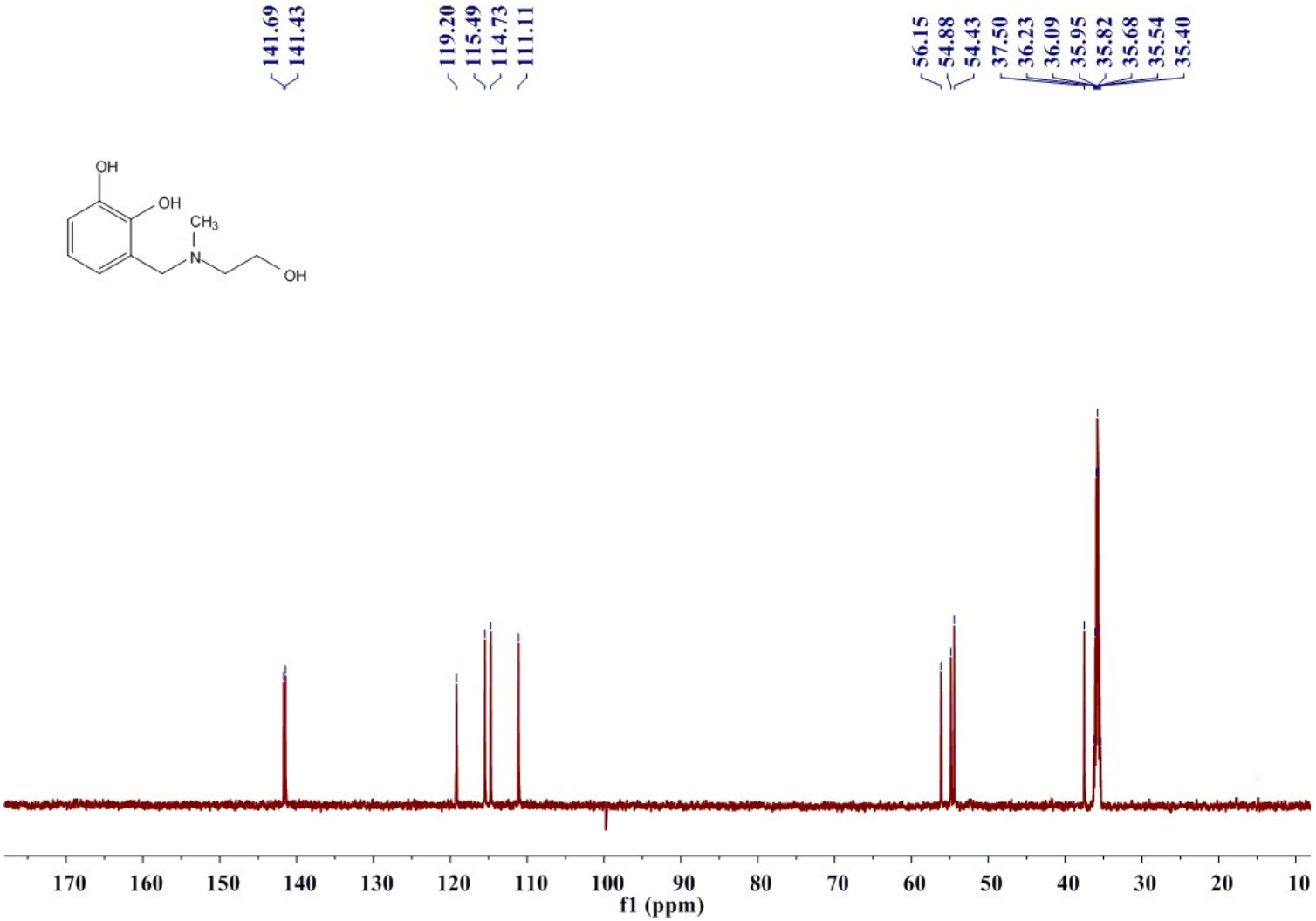
Compound **2c**-4 (^{13}C NMR, 101 MHz, DMSO-*d6*)



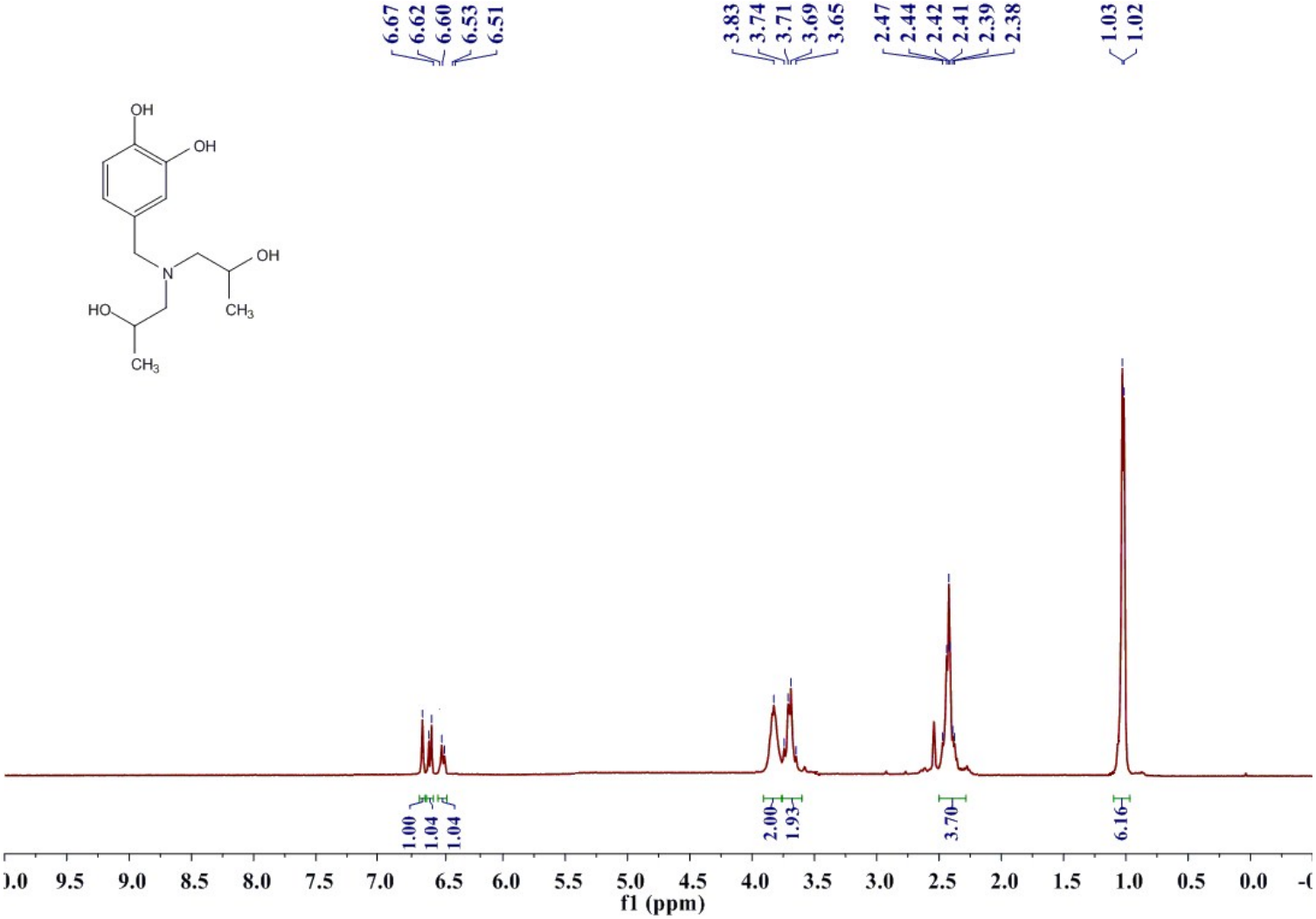
Compound **2c**-3 (^{1}H NMR, 600 MHz, DMSO-*d6*)



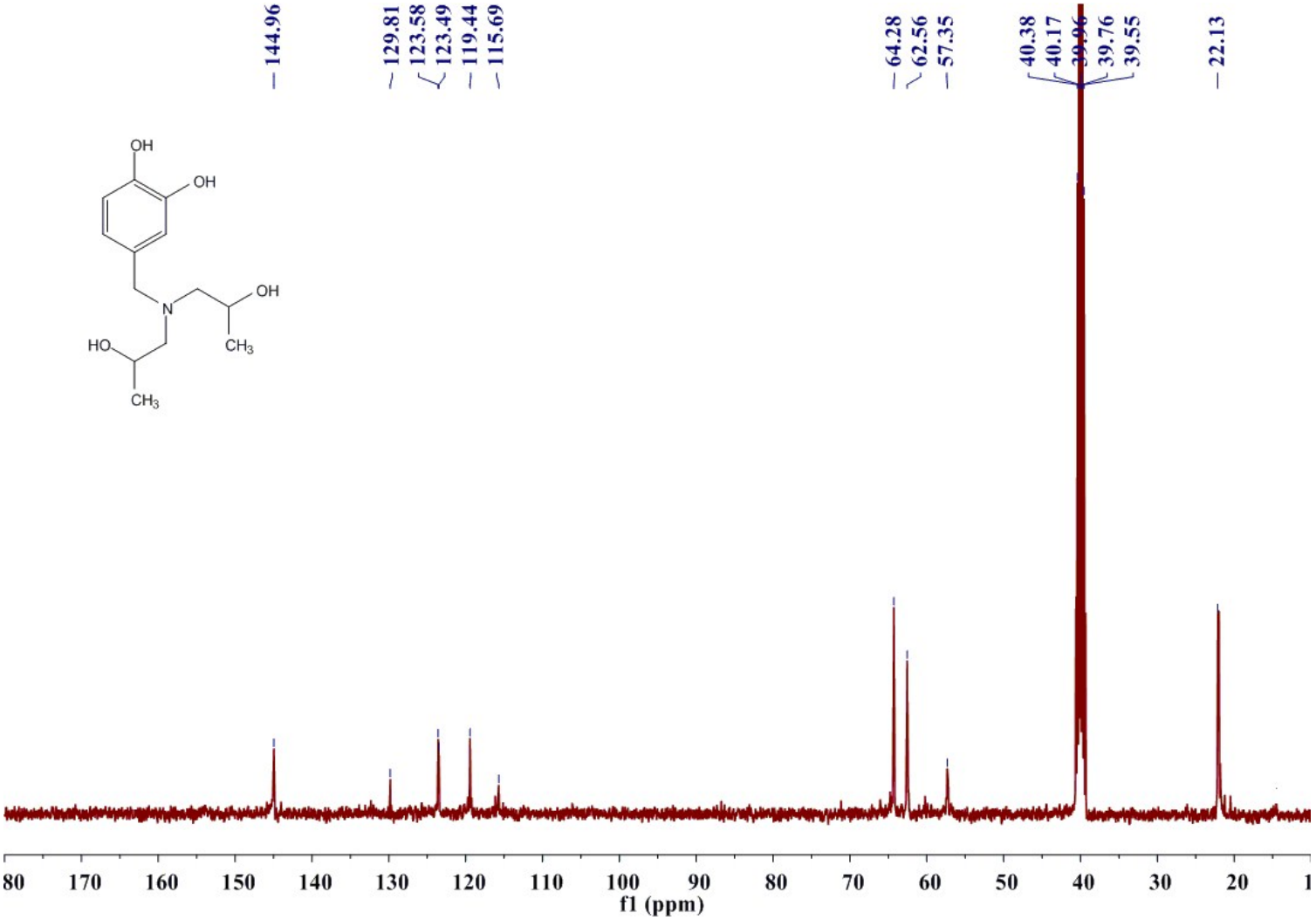
Compound **2c**-3 (^{13}C NMR, 101 MHz, DMSO-*d6*)



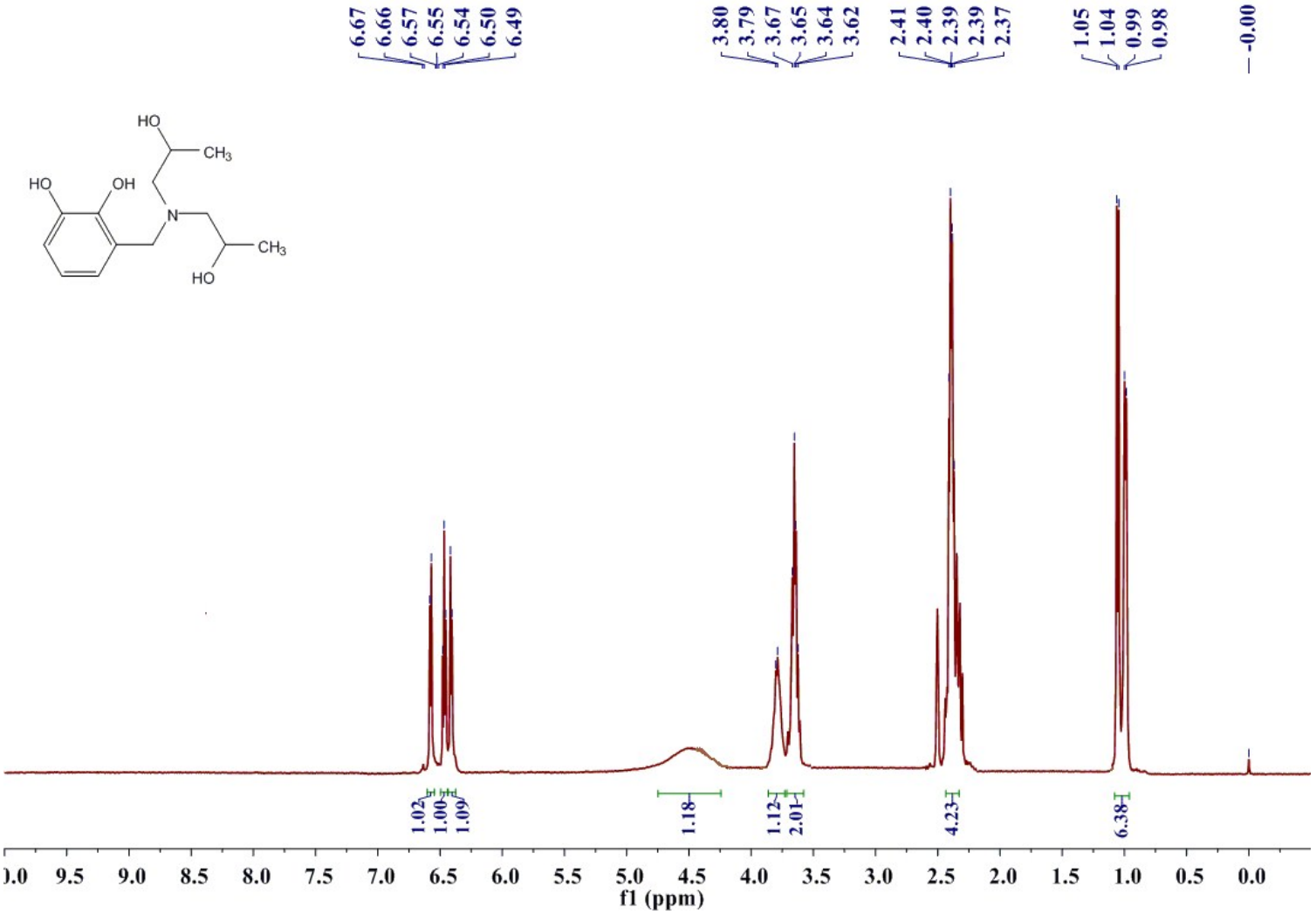
Compound **2d**-4 (^{1}H NMR, 400 MHz, DMSO-*d6*)



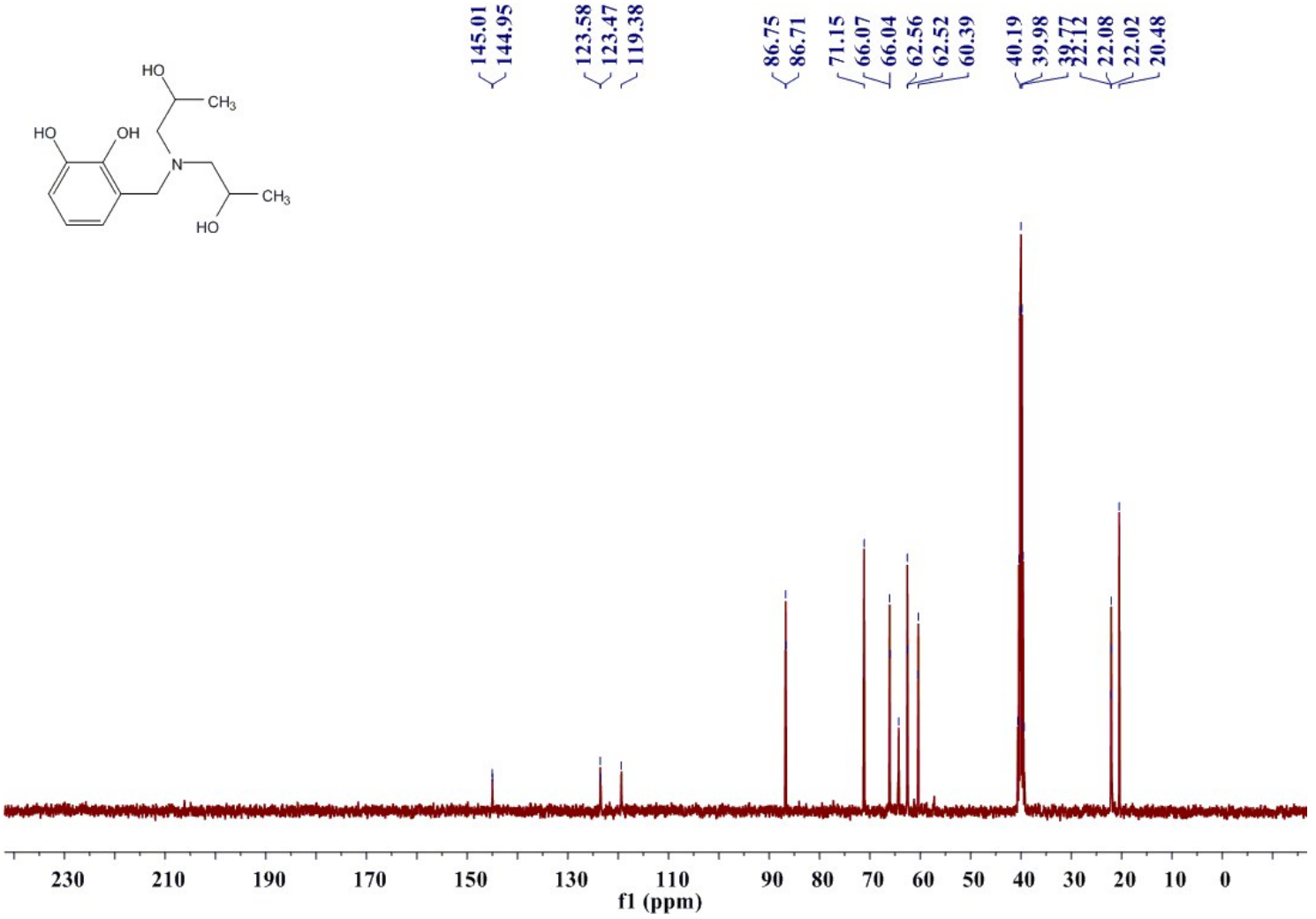
Compound **2d**-4 (^{13}C NMR, 101 MHz, DMSO-*d6*)



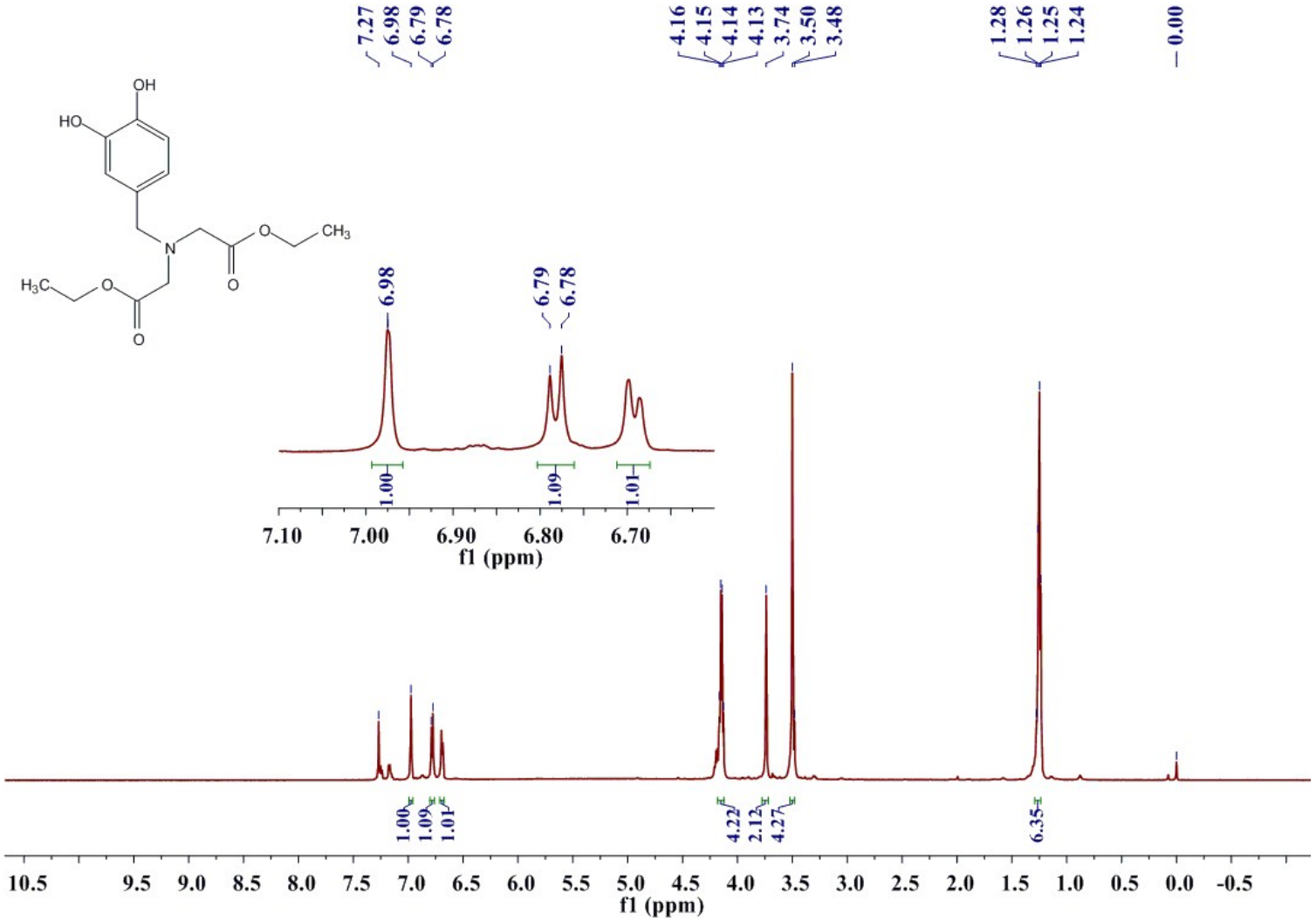
Compound **2d**-3 (^{1}H NMR, 400 MHz, DMSO-*d6*)



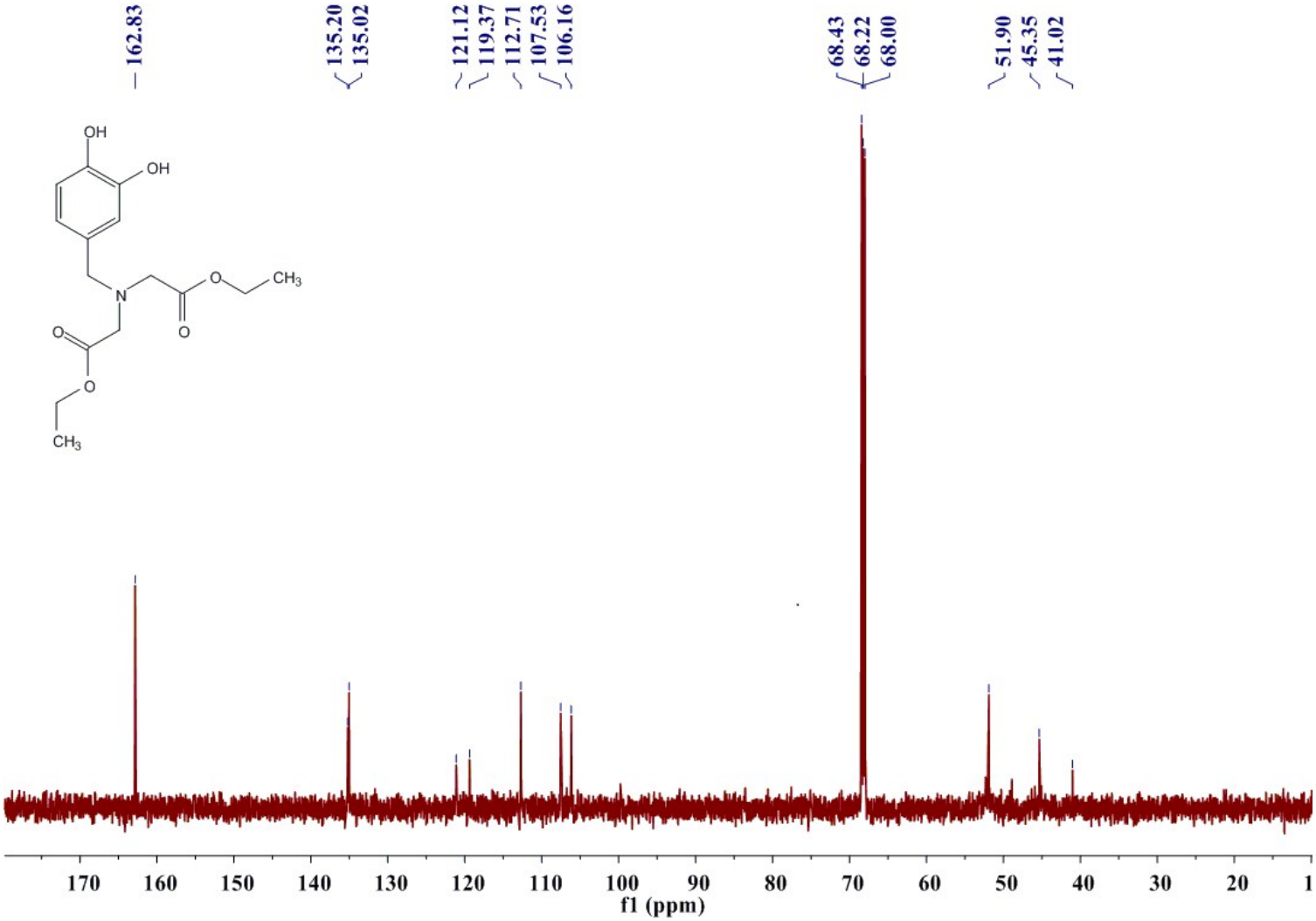
Compound **2d**-3 (^{13}C NMR, 101 MHz, DMSO-*d6*)



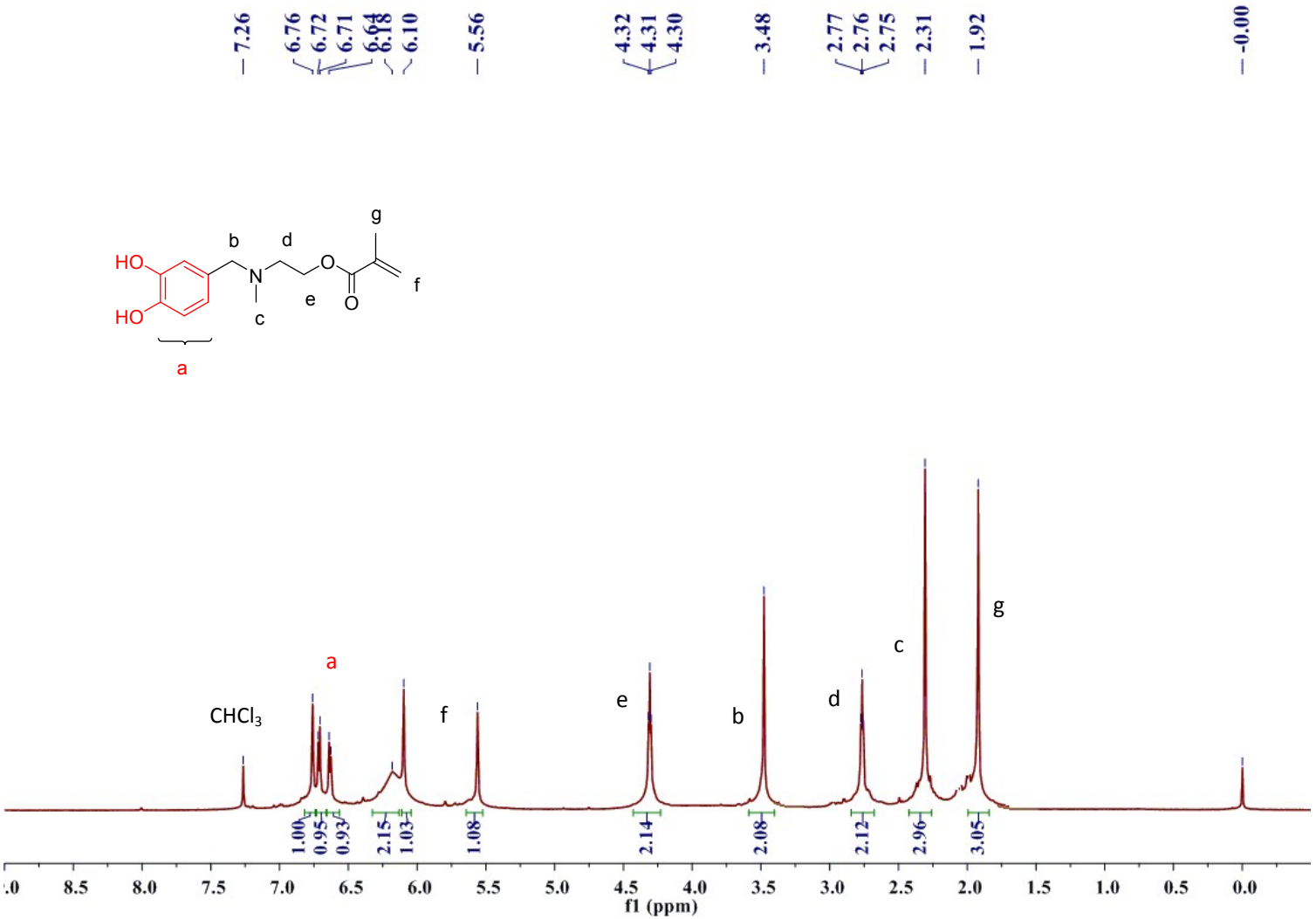
Compound **2e**-4 (^{1}H NMR, 400 MHz, $CDCl_3$)



Compound **2e**-4 (^{13}C NMR, 151 MHz, $CDCl_3$)

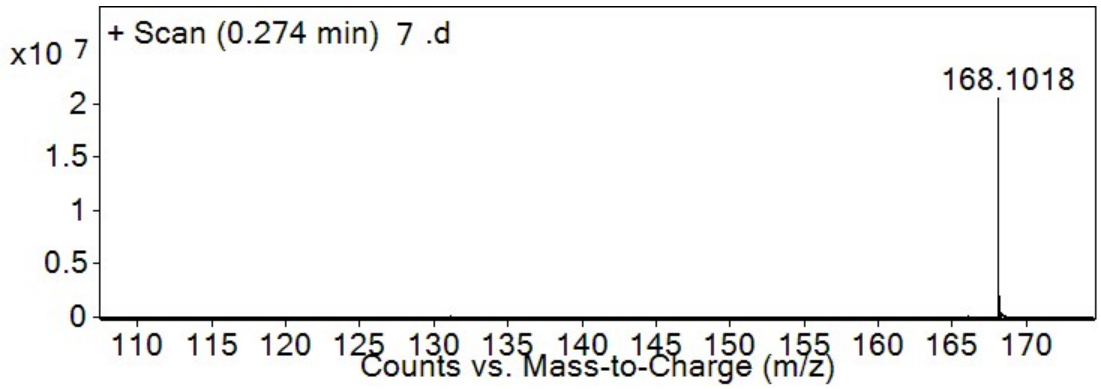


Compound methacrylated **2c**-4 (^{1}H NMR, 600 MHz, $CDCl_3$)

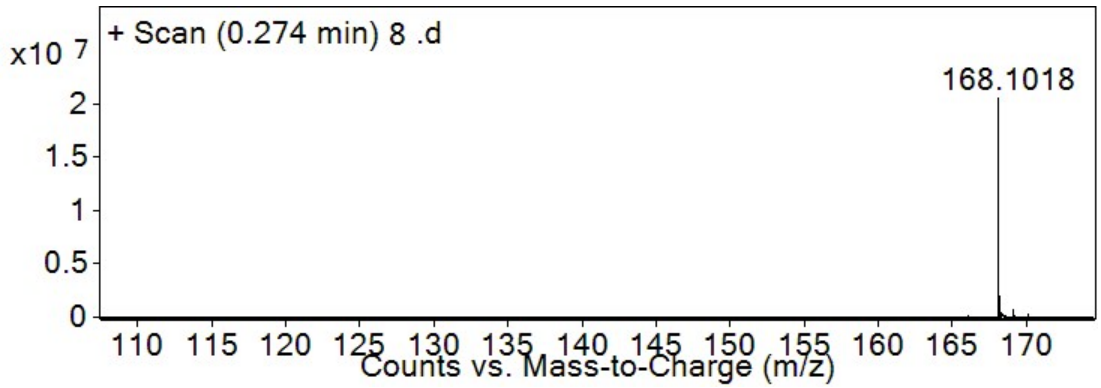


7. Copies of HRMS (ESI-TOF) spectra：

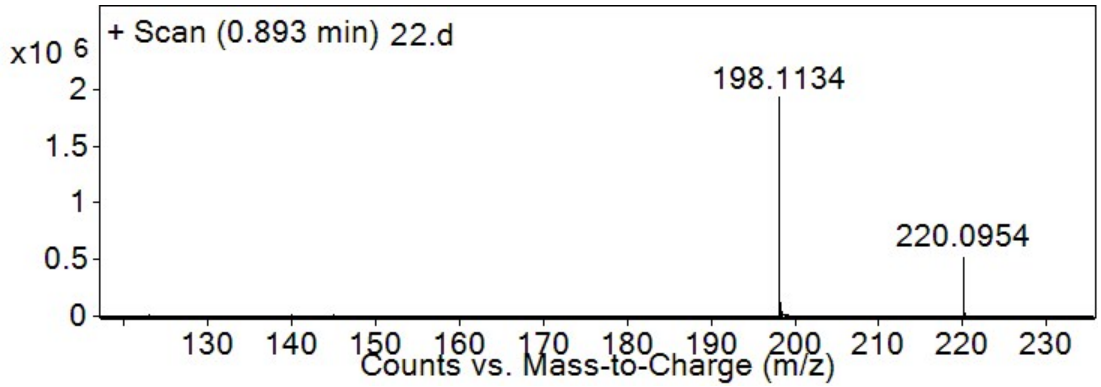
Compound **2a**-4



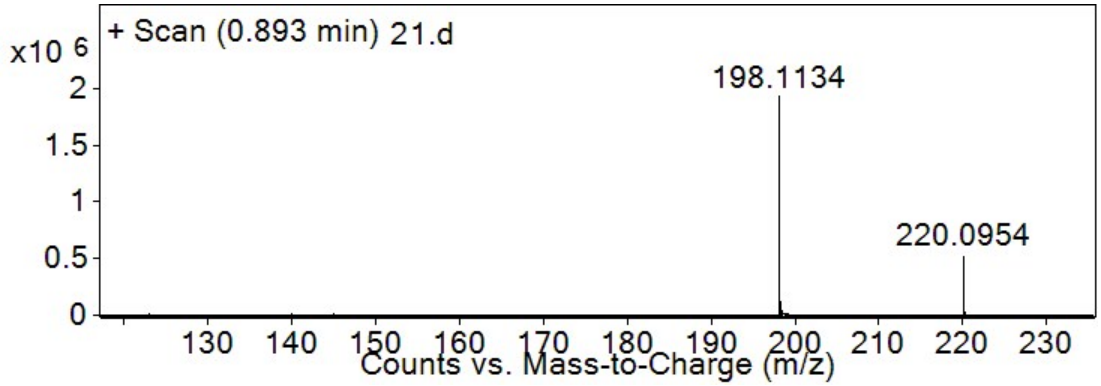
Compound **2a**-3



Compound **2b**-4



Compound **2b**-3



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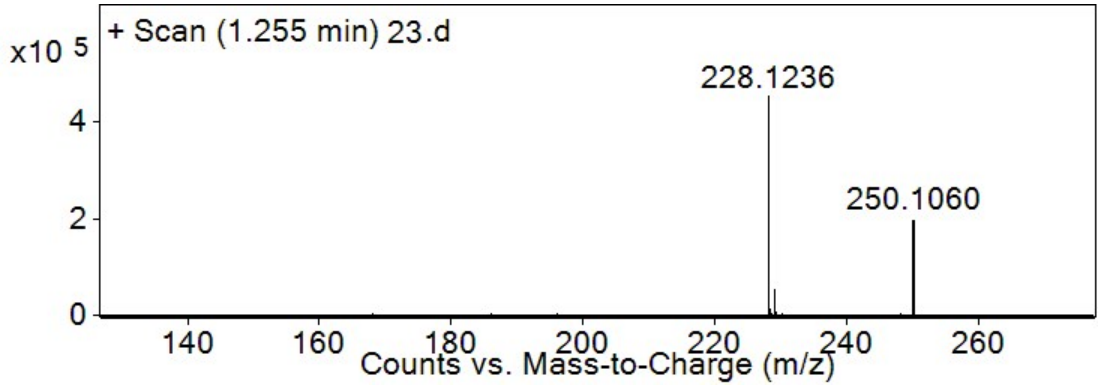
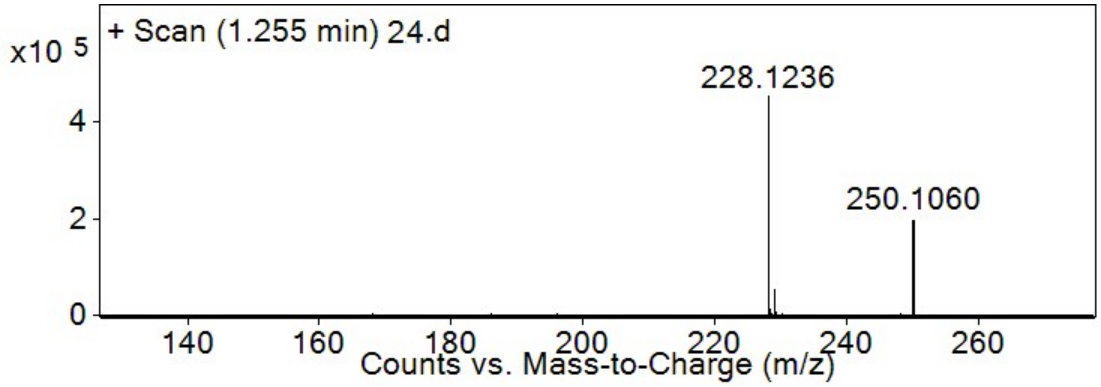
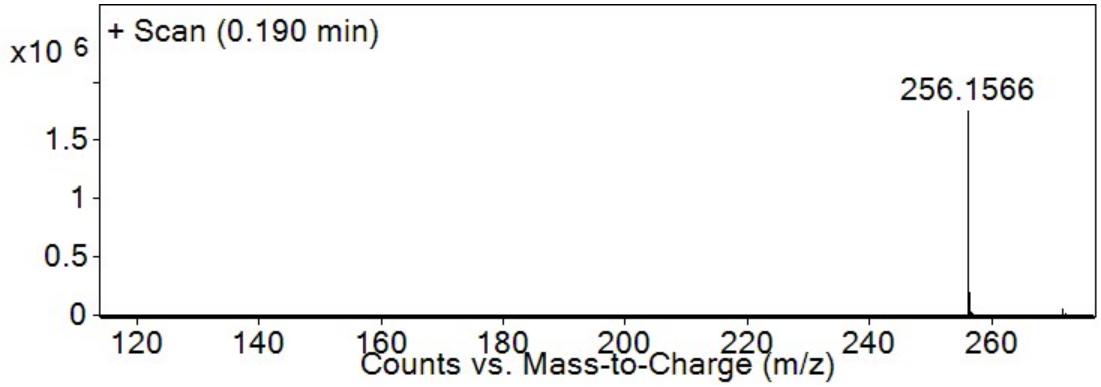


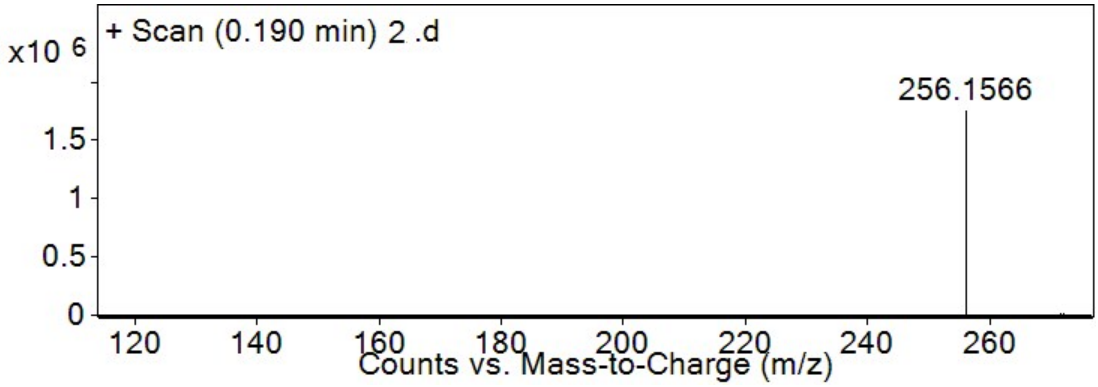
Compound **2c**-3



Compound **2d**-4



Compound **2d**-3



Compound **2e**-4