Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Boronic Acid-Catalysed Regioselective Ring-Opening of 3,4-Epoxy Alcohols with Thiols and Thiophenols

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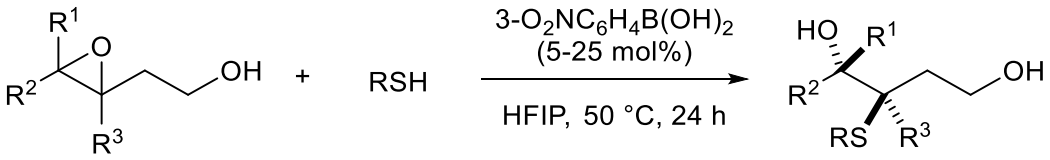
General Methods and Materials

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in $CDCl_3$, CD_3OD, benzene-d_6 or acetone-d_6 at 400 and 101 MHz. The chemical shifts are given in ppm relative to tetramethylsilane [^{1}H: δ= ($SiMe_4$)= 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^{1}H: δ=($CDCl_3$)= 7.26, ^{13}C: δ= ($CDCl_3$)= 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on Thermo UltiMate 3000. Flash chromatography was performed using 300-400 mesh silica gel with the indicated solvent system.

All racemic epoxides precursors were prepared by *m*-CPBA-mediated epoxidation. All other reagents and starting materials, unless otherwise noted, were purchased from commercial vendors and used without further purification.

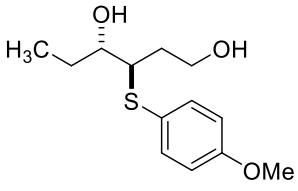
General Procedure for the Boronic Acid-catalyzed Regioselective Ring-opening of 3,4-Epoxy Alcohols.



To a suspension of the 3-nitrophenyl boronic acid (5-25 mol%, see below)[a] in 1,1,1,3,3,3-Hexafluoro-2-propanol (0.3 mL) were added 3,4-epoxy alcohols **1** (0.4 mmol) and S-nucleophiles **2** (0.6 mmol, 1.5 equiv) at room temperature. The resulting mixture was heated to 50°C and stirred at this temperature for 24 h. Then the reaction was cooled to room temperature and the solvent was removed in vacuum.[b] The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) affording the corresponding products **3**.

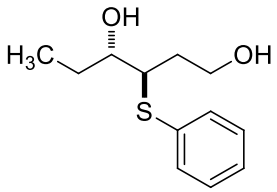
[a] Catalyst loading: 5 mol% for **3a-g**, **3i**, **3j**, **3l**, **3r-t** and **3v**; 10 mol% for **3h**, **3k**, **3m-q**, **3u**, **3w**, **3x** and **3y**; 25 mol% for **3z-ad**.

[b] In the case of **3ac**, ethylenediamine (0.4 equiv) was added to the reaction mixture after completion of the reaction and stirred for 30 min before further working up.



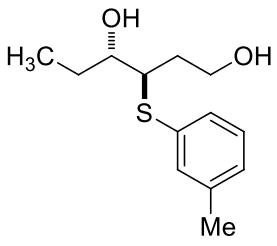
3a

(±)-erythro-3-((4-Methoxyphenyl)thio)hexane-1,4-diol (**3a**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (100 mg, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.38-7.30 (m, 2H), 6.88-6.67 (m, 2H), 3.92-3.80 (m, 1H), 3.78-3.67 (m, 1H), 3.73 (s, 3H), 3.50 (dt, *J*= 8.4, 4.2 Hz, 1H), 3.14 (dt, *J*= 7.9, 3.9 Hz, 1H), 1.92-1.83 (m, 1H), 1.82-1.71 (m, 1H), 1.59-1.37 (m, 2H), 0.86 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 159.6, 135.2 (2C), 124.5, 114.8 (2C), 73.5, 60.0, 55.4, 54.8, 31.5, 26.6, 10.6 ppm. HRMS (ESI): calcd. for $C_{13}H_{20}NaO_3S$ $[M+Na]^+$: 279.1025, found: 279.1028.



3b

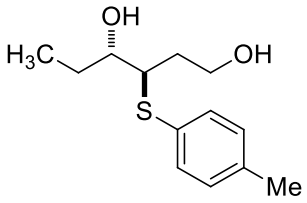
(±)-erythro-3-(Phenylthio)hexane-1,4-diol (**3b**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (86 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.44-7.31 (m, 2H), 7.27-7.12 (m, 3H), 3.95-3.79 (m, 1H), 3.79-3.68 (m, 1H), 3.59-3.49 (m, 1H), 3.35 (dt, *J*= 8.1, 4.0 Hz, 1H), 1.96-1.86 (m, 1H), 1.86-1.76 (m, 1H), 1.57-1.45 (m, 2H), 0.88 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 134.6, 131.9 (2C), 129.1, 127.2 (2C), 73.9, 59.9, 53.4, 31.7, 26.7, 10.5 ppm. HRMS (ESI): calcd. for $C_{12}H_{18}NaO_2S$ $[M+Na]^+$: 249.0920, found: 249.0920.



3c

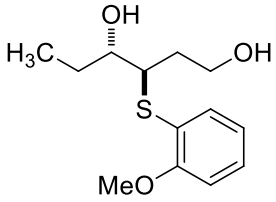
(±)-*erythro-3-(m-Tolylthio)hexane-1,4-diol* (**3c**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (89

mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.26-7.22 (m, 1H), 7.22-7.20 (m, 1H), 7.20-7.15 (m, 1H), 7.06-7.01 (m, 1H), 3.96-3.85 (m, 1H), 3.77 (ddd, *J*= 11.0, 7.3, 4.6 Hz, 1H), 3.62 (td, *J*= 6.5, 4.0 Hz, 1H), 3.39 (dt, *J*= 8.1, 4.1 Hz, 1H), 2.31 (s, 3H), 2.02-1.92 (m, 1H), 1.91-1.82 (m, 1H), 1.63-1.53 (m, 2H), 0.95 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-d) δ= 138.9, 134.4, 132.4, 129.0, 128.8, 128.1,74.0, 59.7, 53.1, 31.8, 26.8, 21.3, 10.6 ppm. HRMS (ESI): calcd. for $C_{13}H_{20}NaO_2S$ $[M+Na]^+$: 263.1076, found: 263.1078.



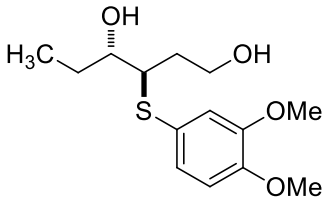
3d

(±)-erythro-3-(p-Polylthio)hexane-1,4-diol (**3d**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (90 mg, 93%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.25 (d, *J*= 7.9 Hz, 2H), 7.02 (d, *J*= 7.9 Hz, 2H), 3.90-3.78 (m, 1H), 3.75-3.65 (m, 1H), 3.56-3.47 (m, 1H), 3.28 -3.19 (m, 1H), 2.24 (s, 3H), 1.95-1.82 (m, 1H), 1.82-1.71 (m, 1H), 1.56-1.44 (m, 2H), 0.86 (t, *J*= 7.8, 6.9 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 137.5, 132.5 (2C), 130.8, 129.9 (2C), 73.8, 59.8, 53.8, 31.7, 26.7, 21.1, 10.5 ppm. HRMS (ESI): calcd. for $C_{13}H_{20}NaO_2S$ $[M+Na]^+$: 263.1076, found: 263.1078.



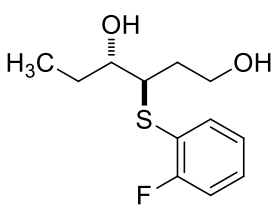
3e

(±)-erythro-3-((2-Methoxyphenyl)thio)hexane-1,4-diol (**3e**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (100 mg, 98%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.50-7.45 (m, 1H), 7.34-7.27 (m, 1H), 6.95-6.89 (m, 2H), 3.90 (s, 3H), 3.89-3.80 (m, 2H), 3.53-3.45 (m, 1H), 3.38-3.31 (m, 1H), 2.02-1.90 (m, 1H), 1.90-1.78 (m, 1H), 1.67-1.54 (m, 1H), 1.53-1.41 (m, 1H), 0.92 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 159.3, 135.5, 129.8, 121.5, 121.3, 111.2, 73.6, 60.0, 55.9, 52.3, 31.2, 26.3, 10.6 ppm. HRMS (ESI): calcd. for $C_{13}H_{20}NaO_3S$ $[M+Na]^+$: 279.1025,found:279.1029.



3f

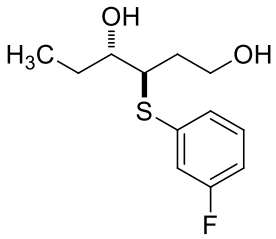
(±)-erythro-3-((3,4-Dimethoxyphenyl)thio)hexane-1,4-diol (**3f**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (100 mg, 87%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.08-7.00 (m, 1H), 6.99 (t, *J*= 2.0 Hz, 1H), 6.79 (dd, *J*= 8.3, 2.3 Hz, 1H), 3.92 (d, *J*= 6.4 Hz, 1H), 3.87 (s, 3H) 3.86 (s, 3H), 3.80 (d, *J*= 4.0 Hz, 1H), 3.29-3.11 (m, 2H), 2.01-1.90 (m, 1H), 1.89-1.75 (m, 1H), 1.66-1.50 (m, 2H), 0.94 (t, *J*= 7.4, 2.1 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 149.0, 149.0, 126.2, 125.1, 116.3, 111.5, 73.8, 59.6, 56.0, 55.9, 54.3, 31.6, 26.8, 10.6 ppm. HRMS (ESI): calcd. for $C_{14}H_{22}NaO_4S$ $[M+Na]^+$: 309.1131, found: 309.1140.



3g

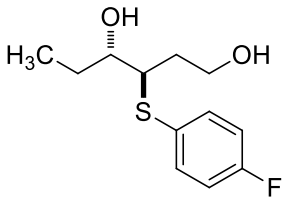
(±)-erythro-3-((2-Fluorophenyl)thio)hexane-1,4-diol (**3g**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (86 mg, 88%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.45-7.38 (m, 1H), 7.25-7.17 (m, 1H), 7.06-6.97 (m, 2H), 3.91-3.83 (m, 1H), 3.78-3.70 (m, 1H), 3.54-3.47 (m, 1H), 3.36-3.29 (m, 1H), 1.94-1.74 (m, 2H), 1.60-1.42 (m, 2H), 0.86 (t, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 162.5 (d, *J*= 245.5 Hz), 135.3 (d,

J= 1.1 Hz), 129.9 (d, *J*= 8.0 Hz), 124.7 (d, *J*= 3.8 Hz), 121.2 (d, *J*= 17.8 Hz), 116.0 (d, *J*= 23.2 Hz), 74.0, 59.7, 52.9 (d, *J*= 1.8 Hz), 31.6, 26.7, 10.5 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}FNaO_2S$ $[M+Na]^+$: 267.0825, found: 267.0829.



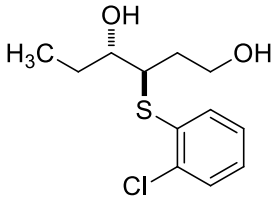
3h

(±)-erythro-3--((3-Fluorophenyl)thio)hexane-1,4-diol (**3h**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (88 mg, 90%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.29-7.21 (m, 1H), 7.20-7.16 (m, 1H), 7.16-7.11 (m, 1H), 6.95-6.88 (m, 1H), 3.96-3.88 (m, 1H), 3.82-3.75 (m, 1H), 3.68-3.61 (m, 1H), 3.46 (dt, *J*= 8.1, 4.2 Hz, 1H), 2.03-1.83 (m, 2H), 1.65-1.55 (m, 2H), 0.97 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 162.7 (d, *J*= 248.7 Hz), 137.4 (d, *J*= 7.7 Hz), 130.4 (d, *J*= 8.5 Hz), 126.6 (d, *J*= 3.0 Hz), 117.8 (d, *J*= 22.5 Hz), 113.9 (d, *J*= 21.1 Hz), 74.2, 59.5, 52.8, 31.7, 26.9, 10.6 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}FNaO_2S$ $[M+Na]^+$: 267.0825, found: 267.0829.



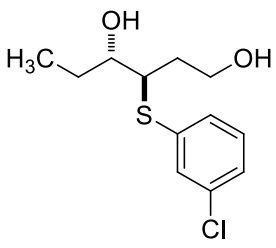
3i

(±)-erythro-3-((4-Fluorophenyl)thio)hexane-1,4-diol (**3i**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (80 mg, 82%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.48-7.40 (m, 2H), 7.05-6.96 (m, 2H), 3.97-3.88 (m, 1H), 3.84-3.74 (m, 1H), 3.62-3.56 (m, 1H), 3.29 (dt, *J*= 8.1, 4.1 Hz, 1H), 2.00-1.80 (m, 2H), 1.63-1.53 (m, 2H), 0.94 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 162.4 (d, *J*= 247.9 Hz), 134.7 (d, *J*= 8.2 Hz) (2C), 129.59 (d, *J*= 3.5 Hz), 116.27 (d, *J*= 21.8 Hz) (2C). 73.8, 59.6, 54.3, 31.6, 26.8, 10.5 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}FNaO_2S$ $[M+Na]^+$: 267.0825, found: 267.0817.



3j

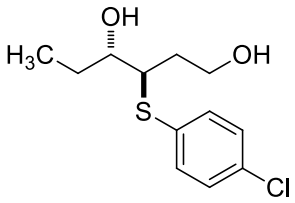
(±)-erythro-3-((2-Chlorophenyl)thio)hexane-1,4-diol (**3j**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (84 mg, 81%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.44-7.39 (m, 1H), 7.33 (dd, *J*= 7.5, 1.9 Hz, 1H), 7.17-7.08 (m, 2H), 3.91-3.83 (m, 1H), 3.76-3.68 (m, 1H), 3.57-3.50 (m, 1H), 3.45-3.39 (m, 1H), 1.97-1.77 (m, 2H), 1.60-1.44 (m, 2H), 0.87 (t, *J*= 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 136.3, 133.8, 133.1, 130.1, 128.3, 127.3, 74.0, 59.6, 52.1, 31.5, 26.8, 10.6 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}ClNaO_2S$ $[M+Na]^+$: 283.0530, found: 283.0537.



3k

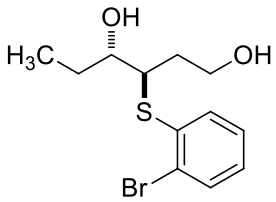
(±)-erythro-3-((3-Chlorophenyl)thio)hexane-1,4-diol (**3k**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (80 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.41 (dt, *J*= 2.4, 1.0 Hz, 1H), 7.33-7.26 (m, 1H), 7.27-7.16 (m, 2H), 3.92 (ddd, *J*= 11.0, 6.5, 4.5 Hz, 1H), 3.85–3.75 (m, 1H), 3.64 (td, *J*= 6.5, 4.0 Hz, 1H), 3.45 (dt, *J* = 8.1, 4.2 Hz, 1H), 2.04–1.82 (m, 2H), 1.66-1.54 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 137.13, 134.7, 130.9, 130.1, 129.3, 127.2, 74.1, 59.6, 53.1, 31.7, 26.8, 10.6 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}ClNaO_2S$ $[M+Na]^+$: 283.0530, found:

283.0527.



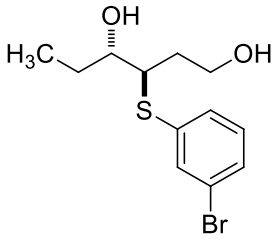
3l

(±)-erythro-3-((4-Chlorophenyl)thio)hexane-1,4-diol (**3l**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (78 mg, 75%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.36 (d, *J*= 8.6 Hz, 2H), 7.26 (d, *J*= 8.6 Hz, 2H), 4.00-3.85 (m, 1H), 3.83-3.71 (m, 1H), 3.67-3.54 (m, 1H), 3.44-3.32 (m, 1H), 2.02-1.78 (m, 2H), 1.63-1.51 (m, 2H), 0.95 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 133.3, 133.3, 133.2 (2C), 129.3 (2C), 73.9, 59.7, 53.7, 31.7, 26.7, 10.6 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}ClNaO_2S$ $[M+Na]^+$: 283.0530, found: 283.0526.



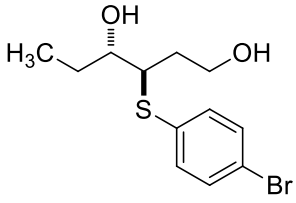
3m

(±)-erythro-3-((2-Bromophenyl)thio)hexane-1,4-diol (**3m**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (106 mg, 87%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.48 (dd, *J*= 8.0, 1.5 Hz, 1H), 7.39 (dd, *J*= 7.9, 1.6 Hz, 1H), 7.17 (td, *J*= 7.6, 1.4 Hz, 1H), 6.99 (td, *J*= 7.7, 1.6 Hz, 1H), 3.89-3.80 (m, 1H), 3.73-3.64 (m, 1H), 3.54 (m, 2H), 3.53 (brs,1H) 3.45-3.36 (m, 1H), 1.95-1.75 (m, 2H), 1.59-1.43 (m, 2H), 0.86 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 136.0, 133.4, 132.5, 128.2, 128.0, 126.7, 74.0, 59.5, 52.2, 31.45, 26.9, 10.6 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}BrNaO_2S$ $[M+Na]^+$: 327.0025, found: 327.0028.



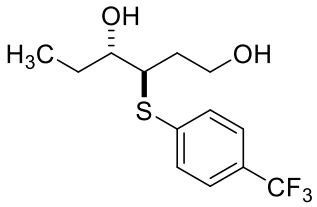
3n

(±)-erythro-3-((3-Bromophenyl)thio)hexane-1,4-diol (**3n**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (81 mg, 67%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.57 (t, *J*= 1.8 Hz, 1H), 7.38-7.31 (m, 2H), 7.15 (t, *J*= 7.9 Hz, 1H), 3.95-3.87 (m, 1H), 3.82-3.75 (m, 1H), 3.67-3.61 (m, 1H), 3.47-3.41 (m, 1H), 2.04-.82 (m, 2H), 1.66-1.54 (m, 2H), 0.97 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 137.5, 133.7, 130.4, 130.0, 129.8, 122.9, 74.1, 59.5, 53.1, 31.7, 26.9, 10.6 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}BrNaO_2S$ $[M+Na]^+$: 327.0025, found: 327.0016.



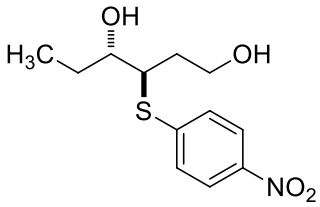
3o

(±)-erythro-3-((4-Bromophenyl)thio)hexane-1,4-diol (**3o**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (85 mg, 70%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.42 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 3.96-3.87 (m, 1H), 3.84-3.75 (m, 1H), 3.65-3.58 (m, 1H), 3.42-3.36 (m, 1H), 2.03-1.81 (m, 2H), 1.64-1.52 (m, 2H), 0.96 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 134.1, 133.2 (2C), 132.2 (2C), 121.2, 74.1, 59.5, 53.4, 31.8, 26.9, 10.5 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}BrNaO_2S$ $[M+Na]^+$: 327.0025, found: 327.0011.



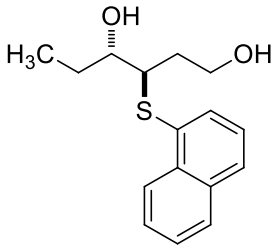
3p

(±)-erythro-3-((4-(Trifluoromethyl)phenyl)thio)hexane-1,4-diol (**3p**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (87 mg, 74%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.49-7.38 (m, 4H), 3.89-3.82 (m, 1H), 3.77-3.69 (m, 1H), 3.64-3.57 (m, 1H), 3.53-3.47 (m, 1H), 1.97-1.78 (m, 2H), 1.61-1.47 (m, 2H), 0.91 (t, *J*= 7.4 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ= 140.7, 130.0 (2C), 128.53 (q, *J*= 32.8 Hz), 125.83 (q, *J*= 3.7 Hz, 2C), 126.7 (q, *J*=272.7 Hz), 74.3, 59.5, 52.1, 31.8, 26.9, 10.5 ppm. HRMS (ESI): calcd. for $C_{13}H_{17}F_3NaO_2S$ $[M+Na]^+$: 317.0794, found: 317.0793.



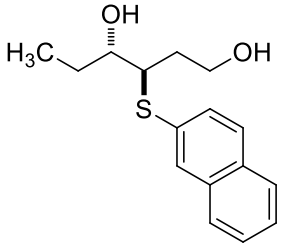
3q

(±)-erythro-3-((4-Nitrophenyl)thio)hexane-1,4-diol (**3q**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (93 mg, 86%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 8.13-8.08 (m, 2H), 7.49-7.43 (m, 2H), 3.96-3.88 (m, 1H), 3.83-3.66 (m, 3H), 2.10-1.89 (m, 2H), 1.72-1.54 (m, 2H), 1.00 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 146.4, 145.5, 128.3, 124.0, 74.7, 59.2, 51.1, 32.0, 27.0, 10.5 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}NNaO_4S$ $[M+Na]^+$: 294.0770, found: 294.0768.



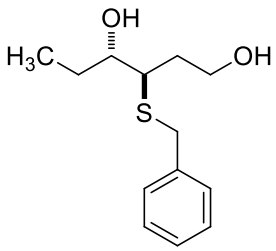
3r

(±)-erythro-3-(Naphthalen-1-ylthio)hexane-1,4-diol (**3r**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (84 mg, 76%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 8.49 (d, *J*= 8.4 Hz, 1H), 7.89-7.83 (m, 1H), 7.79 (d, *J*= 8.3 Hz, 1H), 7.71 (dd, *J*= 7.2, 1.2 Hz, 1H), 7.60-7.55 (m, 1H), 7.54-7.49 (m, 1H), 7.42-7.38 (m, 1H), 4.05-3.97 (m, 1H), 3.87-3.80 (m, 1H), 3.64-3.58 (m, 1H), 3.48-3.42 (m, 1H), 2.01-1.92 (m, 2H), 1.69-1.47 (m, 2H), 0.89 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 134.2, 134.0, 132.0, 131.5, 128.8, 128.7, 126.9, 126.4, 125.6, 125.3, 73.8, 59.8, 53.3, 31.6, 26.8, 10.6 ppm. HRMS (ESI): calcd. for $C_{16}H_{20}NaO_2S$ $[M+Na]^+$: 299.1076, found: 299.1085.



3s

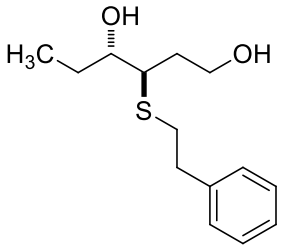
(±)-erythro-3-(Naphthalen-2-ylthio)hexane-1,4-diol (**3s**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (100 mg, 91%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.80 (t, *J*= 2.8 Hz, 1H), 7.72-7.57 (m, 3H), 7.44-7.30 (m, 3H), 3.90-3.80 (m, 1H), 3.77-3.65 (m, 1H), 3.61-3.52 (m, 1H), 3.47-3.38 (m, 1H), 1.98-1.74 (m, 2H), 1.56-1.44 (m, 2H), 0.85 (t, *J*= 7.5 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 133.7, 132.3, 132.1, 130.4, 129.2, 128.8, 127.7, 127.3, 126.7, 126.2, 74.1, 59.8, 53.1, 31.9, 26.9, 10.6 ppm. HRMS (ESI): calcd. for $C_{16}H_{20}NaO_2S$ $[M+Na]^+$: 299.1076, found: 299.1079.



3t

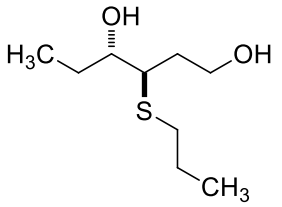
(±)-erythro-3-(Benzylthio)hexane-1,4-diol (**3t**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (84

mg, 88%).[1]H NMR (400 MHz, Chloroform-*d*) δ= 7.34-7.28 (m, 4H), 7.27-7.22 (m, 1H), 3.73 (s, 2H), 3.73-3.67 (m, 1H), 3.66-3.54 (m, 2H), 2.82-2.76 (m, 1H), 1.85-1.76 (m, 1H), 1.74-1.64 (m, 1H), 1.57-1.46 (m, 2H), 0.92 (t, *J*= 7.4 Hz, 3H) ppm.[13]C NMR (101 MHz, Chloroform-*d*) δ= 138.3, 128.9(2C), 128.6(2C), 127.3, 74.3, 59.9, 48.6, 36.0, 31.9, 26.4, 10.5 ppm. HRMS (ESI): calcd. for $C_{13}H_{20}NaO_2S$ $[M+Na]^+$: 263.1076, found: 263.1084.



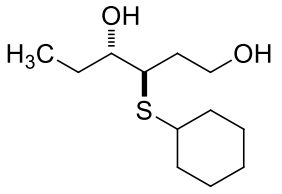
3u

(±)-erythro-3-(Phenethylthio)hexane-1,4-diol (**3u**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (96 mg, 94%).[1]H NMR (400 MHz, Chloroform-*d*) δ= 7.32-7.26 (m, 2H), 7.24-7.16 (m, 3H), 3.83-3.75 (m, 1H), 3.75-3.67 (m, 1H), 3.58 (d, *J*= 4.3 Hz, 1H), 2.91-2.83 (m, 3H), 2.83-2.75 (m, 2H), 1.92-1.81 (m, 1H), 1.79-1.68 (m, 1H), 1.58-1.48 (m, 2H), 0.96 (t, *J*= 7.4 Hz, 3H) ppm. [13]C NMR (101 MHz, Chloroform-*d*) δ= 140.3, 128.5 (4C), 126.5, 74.2, 60.0, 50.1, 36.5, 33.2, 32.2, 26.5, 10.7 ppm. HRMS (ESI): calcd. for $C_{14}H_{22}NaO_2S$ $[M+Na]^+$: 277.1233, found: 277.1230.



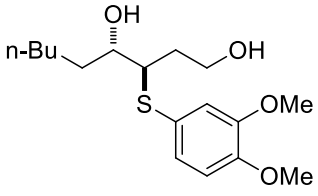
3v

(±)-erythro-3-(Propylthio)hexane-1,4-diol (**3v**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (69 mg, 90%).[1]H NMR (400 MHz, Chloroform-*d*) δ= 3.88-3.81 (m, 1H), 3.79-3.72 (m, 1H), 3.65-3.58 (m, 1H), 2.88 (dt, *J*= 8.3, 4.1 Hz, 1H), 2.56-2.49 (m, 2H), 1.96-1.85 (m, 1H), 1.82-1.73 (m, 1H), 1.66-1.52 (m, 4H), 0.93 (t, *J*= 4.0 Hz, 3H), 0.92 (t, *J*= 8.0 Hz, 3H) ppm.[13]C NMR (101 MHz, Chloroform-*d*) δ= 74.0, 60.2, 50.0, 33.8, 32.2, 26.4, 23.2, 13.5, 10.6 ppm. HRMS (ESI): calcd. for $C_9H_{20}NaO_2S$ $[M+Na]^+$: 215.1076, found: 215.1078.



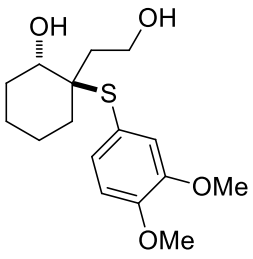
3w

(±)-erythro-3-(Cyclohexylthio)hexane-1,4-diol (**3w**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (84 mg, 91%).[1]H NMR (400 MHz, Chloroform-*d*) δ= 3.89-3.73 (m, 2H), 3.63-3.57 (m, 1H), 3.00 (dt, *J*= 8.8, 3.9 Hz, 1H), 2.74-2.62 (m, 1H), 2.05-1.92 (m, 1H), 1.94 (brs, 1H), 1.91-1.83 (m, 1H), 1.82-1.72 (m, 2H), 1.76 (brs, 1H), 1.61-1.48 (m, 2H), 1.42-1.20 (m, 6H), 1.00 (t, *J*= 7.4 Hz, 3H) ppm. [13]C NMR (101 MHz, Chloroform-*d*) δ= 74.5, 60.4, 48.4, 43.8, 34.3, 34.1, 32.5, 26.2, 26.1, 26.0, 25.7, 10.7 ppm. HRMS (ESI): calcd. for $C_{12}H_{24}NaO_2S$ $[M+Na]^+$:255.1389, found: 255.1388.



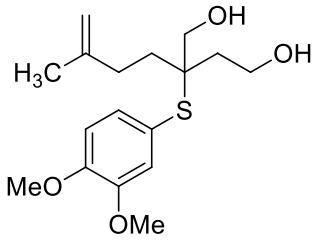
3x

(±)-erythro-3-((3,4-Dimethoxyphenyl)thio)nonane-1,4-diol (**3x**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (112 mg, 85%).[1]H NMR (400 MHz, Chloroform-*d*) δ= 6.98 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.92 (d, *J*= 2.1 Hz, 1H), 6.73 (d, *J*= 8.3 Hz, 1H), 3.89-3.82 (m, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.78-3.71 (m, 1H), 3.64-3.56 (m, 1H), 3.19 (dt, *J*= 8.0, 3.9 Hz, 1H), 1.95-1.84 (m, 1H), 1.84-1.73 (m, 1H), 1.74-1.56 (m, 1H), 1.55-1.31 (m, 3H), 1.28-1.19 (m, 4H), 0.79 (t, *J*= 4.0 Hz, 3H) ppm.[13]C NMR (101 MHz, Chloroform-*d*) δ= 149.1, 126.3, 124.9, 116.4, 111.6 (2C), 72.2, 59.9, 56.0, 55.9, 55,0, 33.6, 31.8, 31.6, 25.9 , 22.6, 14.0. ppm. HRMS (ESI): calcd. for $C_{17}H_{28}NaO_4S$ $[M+Na]^+$: 351.1601, found: 351.1608.



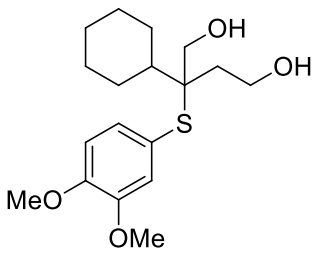
3y

(±)-erythro-2-((3,4-Dimethoxyphenyl)thio)-2-(2-hydroxyethyl)cyclohexan-1-ol (**3y**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (76 mg, 61%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.05 (dd, *J*= 8.2, 2.1 Hz, 1H), 6.96 (d, *J*= 2.0 Hz, 1H), 6.83 (d, *J*= 8.2 Hz, 1H), 4.21-4.12 (m, 1H), 3.89 (s, 6H), 3.82-3.73 (m, 1H), 3.56 (dd, *J*= 9.2, 4.0 Hz, 1H), 2.15-2.04 (m, 1H), 1.96-1.85 (m, 1H), 1.81-1.54 (m, 6H), 1.52-1.39 (m, 1H), 1.37-1.19 (m, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 150.2, 148.6, 130.9, 120.4, 120.3, 111.1, 72.4, 58.7, 58.2, 56.1, 55.9, 35.3, 35.1, 29.2, 23.5, 21.8 ppm. HRMS (ESI): calcd. for $C_{16}H_{24}NaO_4S$ $[M+Na]^+$: 335.1288, found: 335.1288.



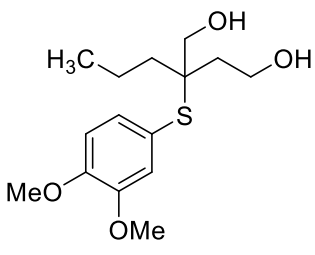
3z

2-((3,4-Dimethoxyphenyl)thio)-2-(3-methylbut-3-en-1-yl)butane-1,4-diol (**3z**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (67 mg, 51%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.01-6.97 (m, 1H), 6.89 (d, *J*= 2.1 Hz, 1H), 6.74 (d, *J*= 8.3 Hz, 1H), 4.67-4.60 (m, 2H), 3.90-3.83 (m, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.74-3.64 (m, 1H), 3.52-3.31 (m, 3H), 2.37-2.25 (m, 1H), 2.13-2.02 (m, 1H), 1.77-1.71 (m, 1H), 1.74 (brs, 1H) 1.67 (s, 3H), 1.57 (ddd, *J*= 14.2, 12.1, 4.9 Hz, 1H), 1.50-1.39 (m, 1H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 150.2, 148.6, 145.5, 130.6, 120.5, 119.9, 111.1, 109.9, 66.4, 58.6, 56.8, 56.0, 55.9, 37.5, 31.9, 31.5, 23.0 ppm. HRMS (ESI): calcd. for $C_{17}H_{26}NaO_4S$ $[M+Na]^+$: 349.1444, found: 349.1453.



3aa

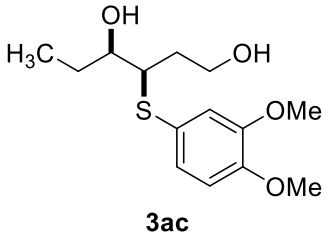
2-Cyclohexyl-2-((3,4-dimethoxyphenyl)thio)butane-1,4-diol (**3aa**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (73 mg, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 6.99 (dd, *J*= 8.3, 2.1 Hz, 1H), 6.92 (d, *J*= 2.1 Hz, 1H), 6.75 (d, *J*= 8.3 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.80-3.76 (m, 1H), 3.70-3.61 (m, 2H), 3.38 (d, *J*= 11.6 Hz, 1H), 2.10 -2.02 (m, 1H), 1.96-1.87 (m, 1H), 1.78-1.71 (m, 1H), 1.72-1.60 (m, 2H), 1.60-1.50 (m, 2H), 1.45-.34 (m, 1H), 1.23-1.15 (m, 2H), 1.13-1.01 (m, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 150.1, 148.7, 130.5, 120.6, 120.0, 111.2, 66.0, 61.0, 58.6, 56.0 , 55.9, 42.2, 37.3, 28.0, 27.4, 27.0, 26.8, 26.6. ppm. HRMS (ESI): calcd. for $C_{18}H_{28}NaO_4S$ $[M+Na]^+$: 363.1601, found: 363.1602.



3ab

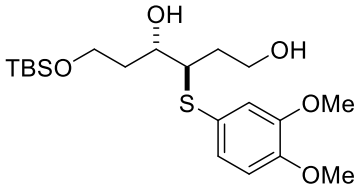
2-((3,4-Dimethoxyphenyl)thio)-2-propylbutane-1,4-diol (**3ab**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (94 mg, 78%).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 6.98 (dt, *J*= 8.3, 1.7 Hz, 1H), 6.91 (t, *J*= 1.7 Hz, 1H), 6.74 (dd, *J*= 8.2, 1.3 Hz, 1H), 3.88-3.82 (m, 1H), 3.81 (d, 6H), 3.71-3.62 (m, 1H), 3.38 (qd, *J*= 11.6, 1.2 Hz, 2H), 1.76-1.64 (m, 2H), 1.61-1.49 (m, 1H), 1.44-1.32 (m, 2H), 1.24 (ddd, *J*= 13.8, 11.8, 4.0 Hz, 1H), 0.84 (t, *J*= 7.2, 1.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 150.1, 148.6, 130.5, 120.7, 120.0, 111.2, 66.4, 58.6, 57.2, 56.0, 55.9, 37.7,

36.4, 16.8, 14.4 ppm. HRMS (ESI): calcd. for $C_{15}H_{24}NaO_4S$ $[M+Na]^+$: 323.1288, found: 323.1288.



3ac

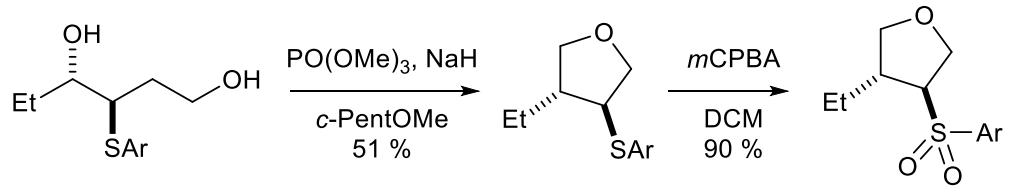
(±)-erythro-3-((3,4-Dimethoxyphenyl)thio)hexane-1,4-diol (**3ac**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a yellow syrup (58 mg, 51%). ^{1}H NMR (Mixture of two regioisomers, 400 MHz, Chloroform-*d*) δ= 7.05 (dt, *J*= 8.3, 1.9 Hz, 2H), 6.99 (dt, *J*= 6.8, 1.8 Hz, 2H), 6.82-6.76 (m, 2H), 3.99-3.89 (m, 2H), 3.86 (s, 12H), 3.83-3.71 (m, 2H), 3.62-3.44 (m, 2H), 3.25-3.19 (m, 2H), 2.88-2.78 (m, 2H), 2.01-1.82 (m, 2H), 1.82-1.66 (m, 2H), 1.64-1.34 (m, 2H), 1.17-0.87 (m, 6H) ppm. ^{13}C NMR (Mixture of two regioisomers, 101 MHz, Chloroform-*d*) δ= 149.1(2C), 149.0 (2C), 126.7, 126.2, 125.2, 124.5, 116.9, 116.6, 111.6, 115.5, 74.8, 72.6, 61.4, 60.3, 60.2, 56.0 (2 C), 55.9 (2C), 54.7, 35.2, 34.3, 26.7, 23.6, 12.0, 10.5 ppm. HRMS (ESI): calcd. for $C_{14}H_{22}NaO_4S$ $[M+Na]^+$:309.1131, found: 309.1136.



3ad

(±)-erythro-5-((tert-Butyldimethylsilyl)oxy)-3-((3,4-dimethoxyphenyl)thio)pentane-1,4-diol (**3ad**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 1:1) as a colorless syrup (32 mg, 19 %).^{1}H NMR (400 MHz, Chloroform-*d*) δ= 6.99 (dd, *J*= 8.0, 2.0 Hz, 1H), 6.96 (d, *J*= 2.0 Hz, 1H), 6.75 (d, *J*= 8.3 Hz, 1H), 3.91-3.84 (m, 2H), 3.83 (s, 6H), 3.82-3.71 (m, 3H), 3.18-3.11 (m, 1H), 1.92-1.85 (m, 1H), 1.81-1.75 (m, 1H), 1.75-1.65 (m, 2H), 0.82 (s, 9H), 0.00 (s, 6H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 149.09 (2C), 126.3, 125.2, 116.6, 111.6, 72.3, 62.0, 60.2, 55.9 (2C), 54.5, 36.0, 32.9, 25.8 (3C), 18.1, -5.55 (2C). HRMS (ESI): calcd. for $C_{20}H_{36}NaO_5SSi$ $[M+Na]^+$: 439.1945, found: 439.1940.

Experimental Procedure for Synthesis of *trans*-furans 4 and 5

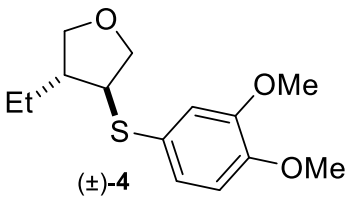


(±)-**3f** (±)-**4** (±)-**5**

Ar: 3,4-$(MeO)_2C_6H_3$

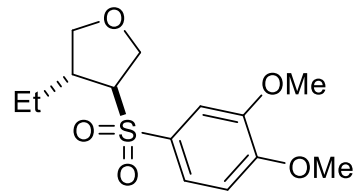
Step 1: To a solution of (±)-*erythro*-3-((3,4-dimethoxyphenyl)thio)hexane-1,4-diol (**3f**) (2.44 mmol, 700 mg) in CPME(12 mL) was added NaH at room temperature. After stirring for 10 min, trimethyl phosphate (0.7 mL, 2.5 equiv) was added. After further stirring for 6h, the mixture was quenched with H_2O, and the aqueous layer was extracted with diethyl ether. The organic layers were combined and dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was purified through column chromatography on silica gel (petroleum ether: EtOAc= 4:1) to give the product **4** (353mg, 54%) as a yellow syrup.

Step 2: To a solution of **4** (295 mg, 1.1 mmol) in methylene chloride (30 mL) was added *m*-chloroperbenzonic acid (3.0 equiv) and the resulting mixture was stirred for 2 h at room temperature, before it was quenched by adding 5% aqueous $NaHCO_3$ solution (50 mL). After stirring for 1h, the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether: EtOAc= 2:1) affording the product **5** (297 mg, 90%) as a colorless syrup.



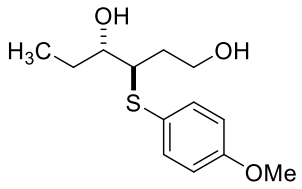
(±)-**4**

(2R,3S)-3-((3,4-Dimethoxyphenyl)thio)-2-ethyltetrahydrofuran (**4**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 4:1) as a yellow solid (320 mg, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 6.99-6.93 (m, 1H), 6.90 (dt, *J*= 4.4, 2.2 Hz, 1H), 6.75-6.69 (m, 1H), 3.84-3.66 (m, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.54 (d, *J*= 3.0 Hz, 1H), 3.12 (dd, *J*= 5.5, 2.9 Hz, 1H), 2.25-2.11 (m, 1H), 1.90-1.78 (m, 1H), 1.57-1.44 (m, 1H), 1.44-1.32 (m, 1H), 0.84 (t, *J*= 7.2, 3.0 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 149.1, 148.9, 126.3, 125.2, 116.6, 111.5, 85.5, 66.5, 55.9 (2C), 50.9, 33.8, 27.3, 10.3 ppm. HRMS (ESI): calcd. for $C_{14}H_{20}NaO_3S$ $[M+Na]^+$: 291.1025, found: 291.1029.



(±)-**5**

(2R,3S)-3-((3,4-Dimethoxyphenyl)sulfonyl)-2-ethyltetrahydrofuran (**5**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 2:1) as a colorless solid (299 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.42 (dd, *J*= 8.5, 2.2 Hz, 1H), 7.24 (d, *J*= 2.2 Hz, 1H), 6.93 (d, *J*= 8.5 Hz, 1H), 4.08 (dt, *J*= 7.0, 5.4 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.82-3.76 (m, 1H), 3.66 (td, *J*= 8.5, 6.9 Hz, 1H), 3.27 (ddd, *J*= 10.2, 5.8, 4.6 Hz, 1H), 2.33-2.22 (m, 1H), 2.12-1.96 (m, 1H), 1.44-1.30 (m, 2H), 0.78 (t, *J*= 7.4 Hz, 3H) ppm.^{13}C NMR (101 MHz, Chloroform-*d*) δ= 153.5, 149.2, 129.8, 122.7, 110.9, 110.5, 80.0, 68.0, 67.0, 56.2 (2C), 28.5, 28.0, 9.8 ppm. HRMS (ESI): calcd. for $C_{14}H_{20}NaO_5S$ $[M+Na]^+$: 323.0924, found: 323.0932.



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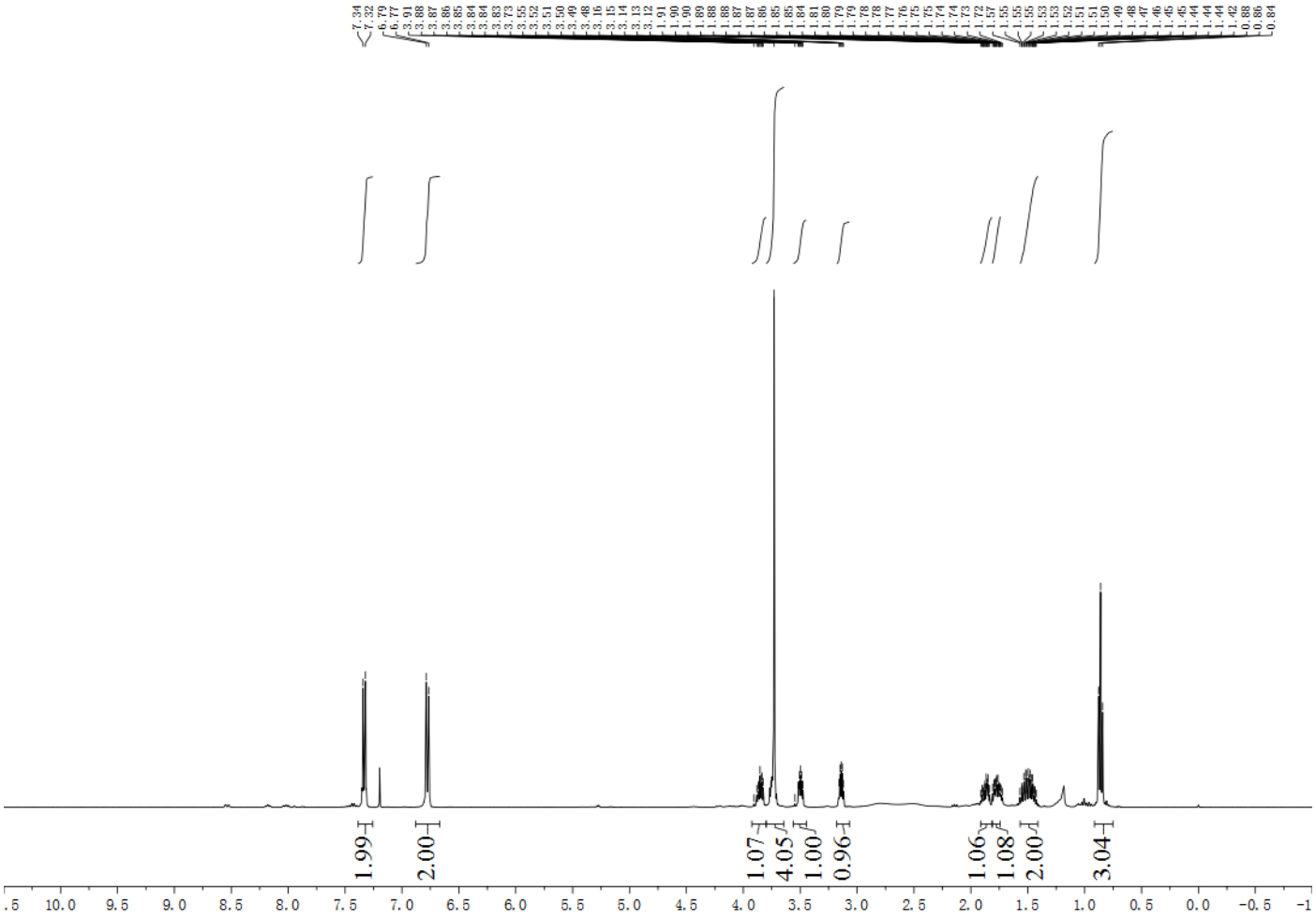

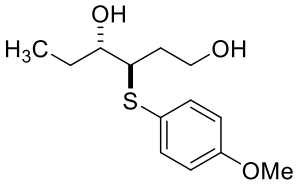
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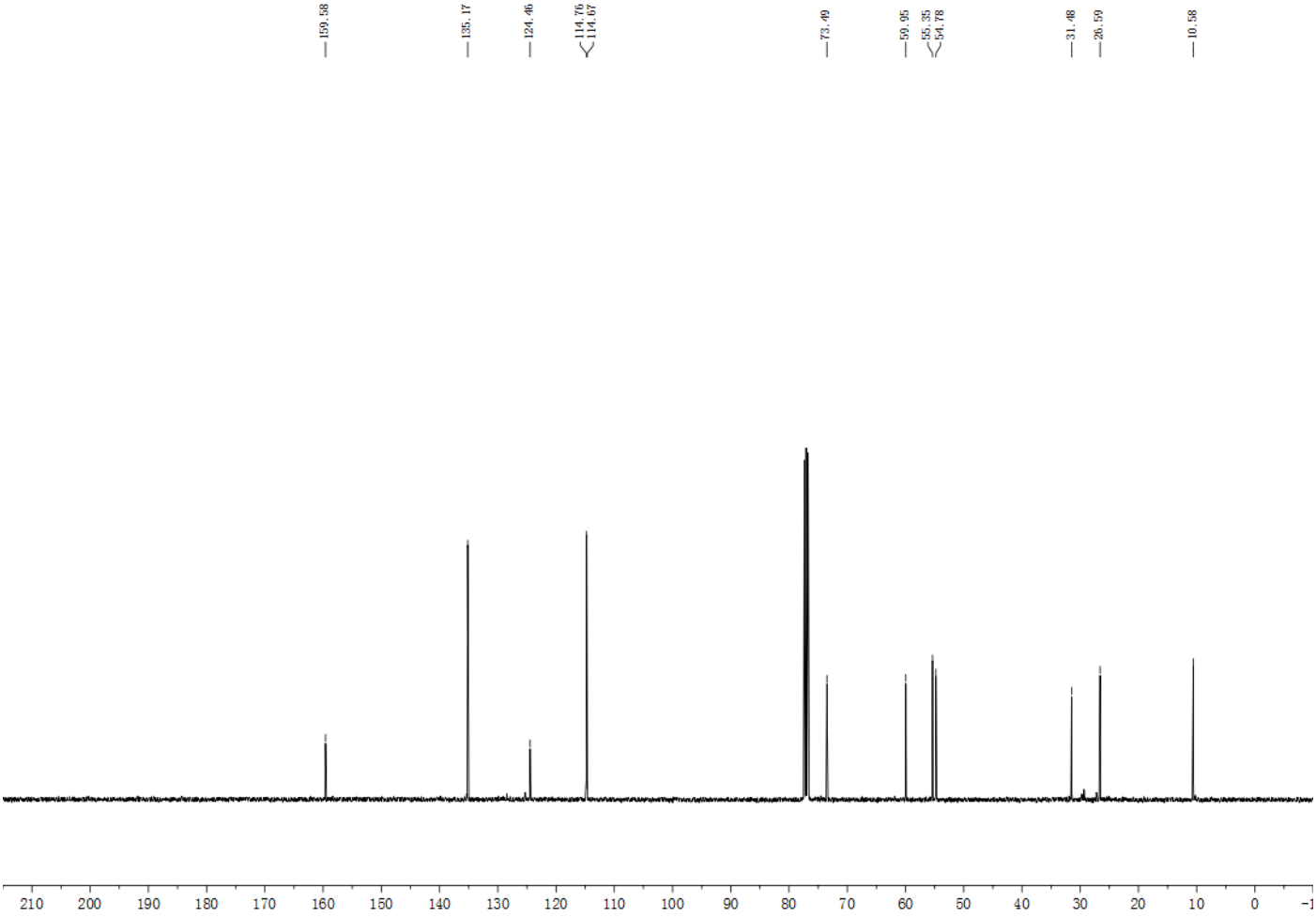
H3C
OH
S
OMe

3a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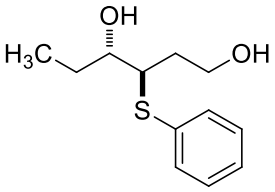

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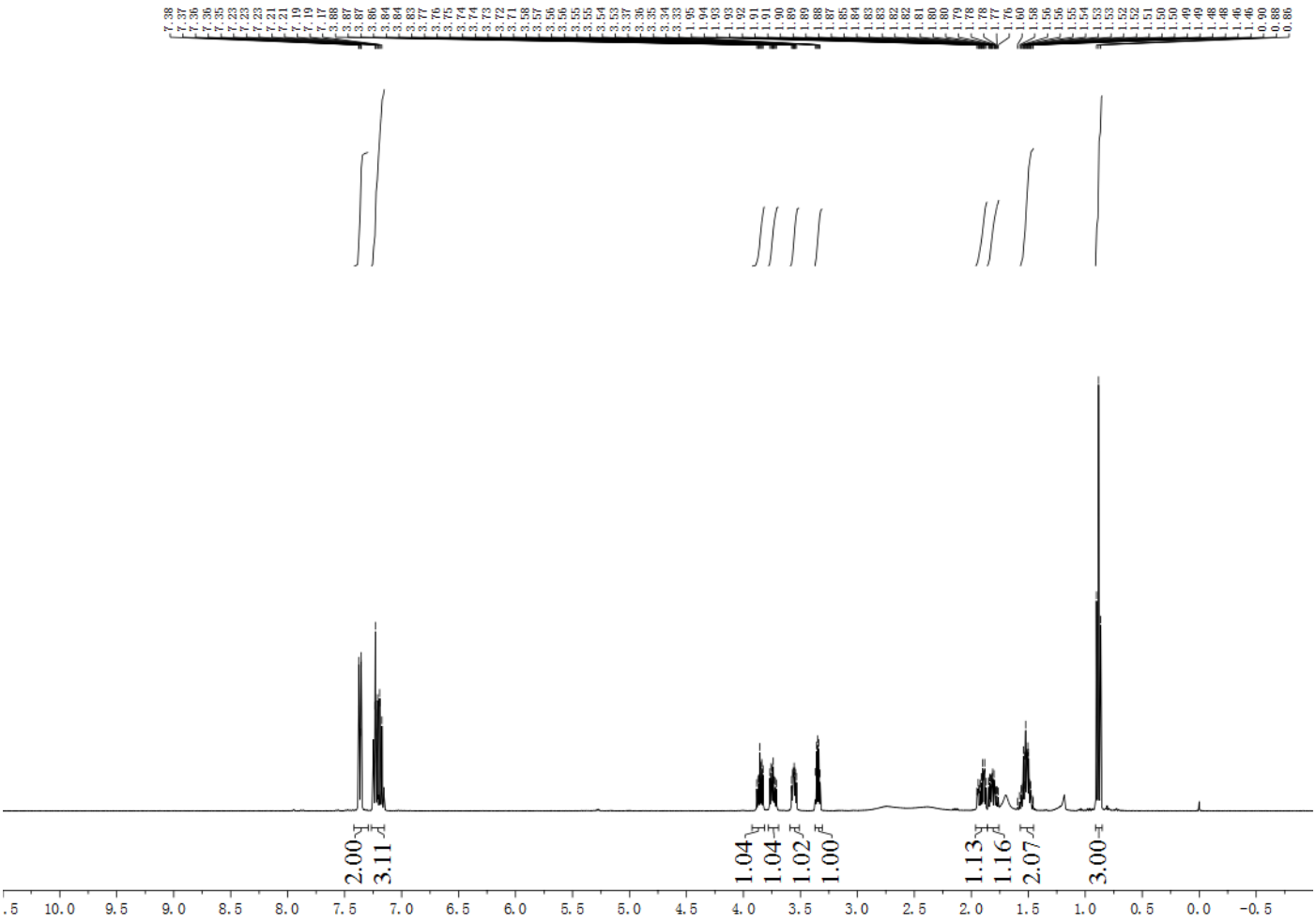

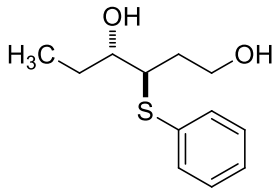
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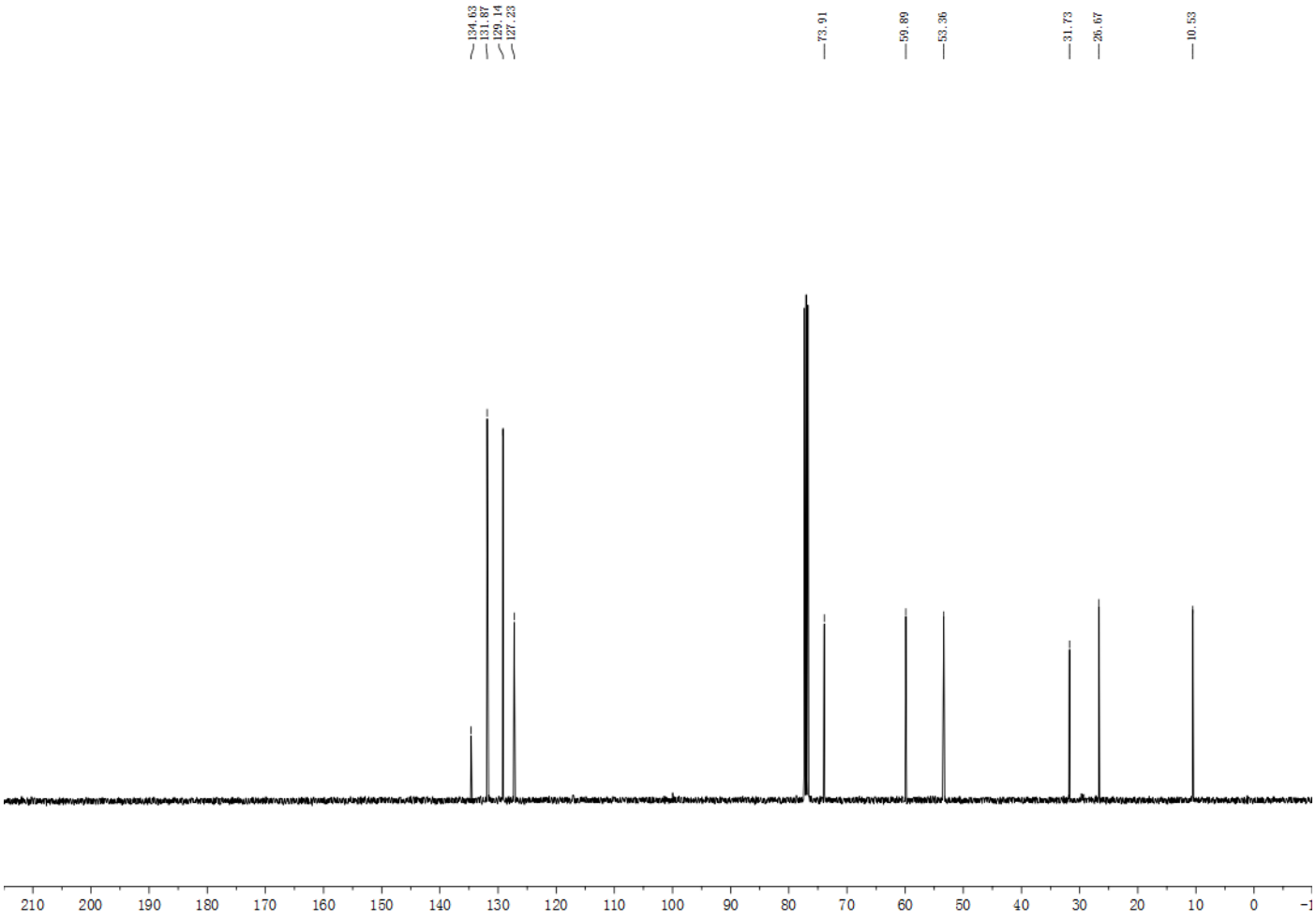
H3C
OH
S

3b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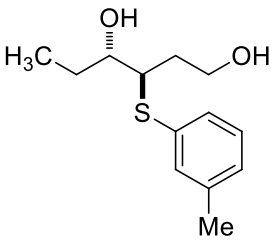

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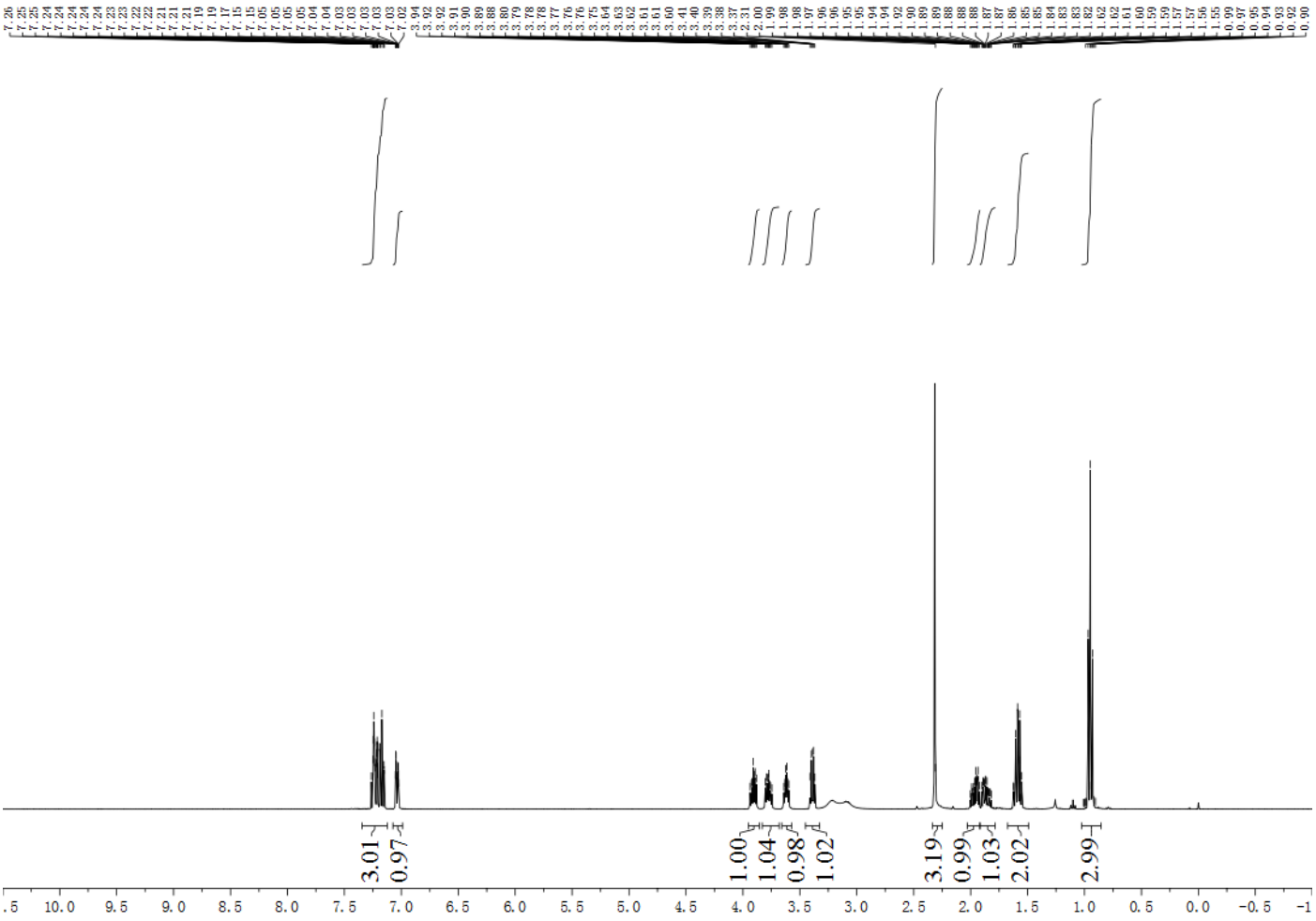

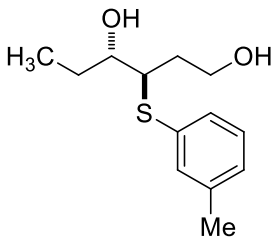
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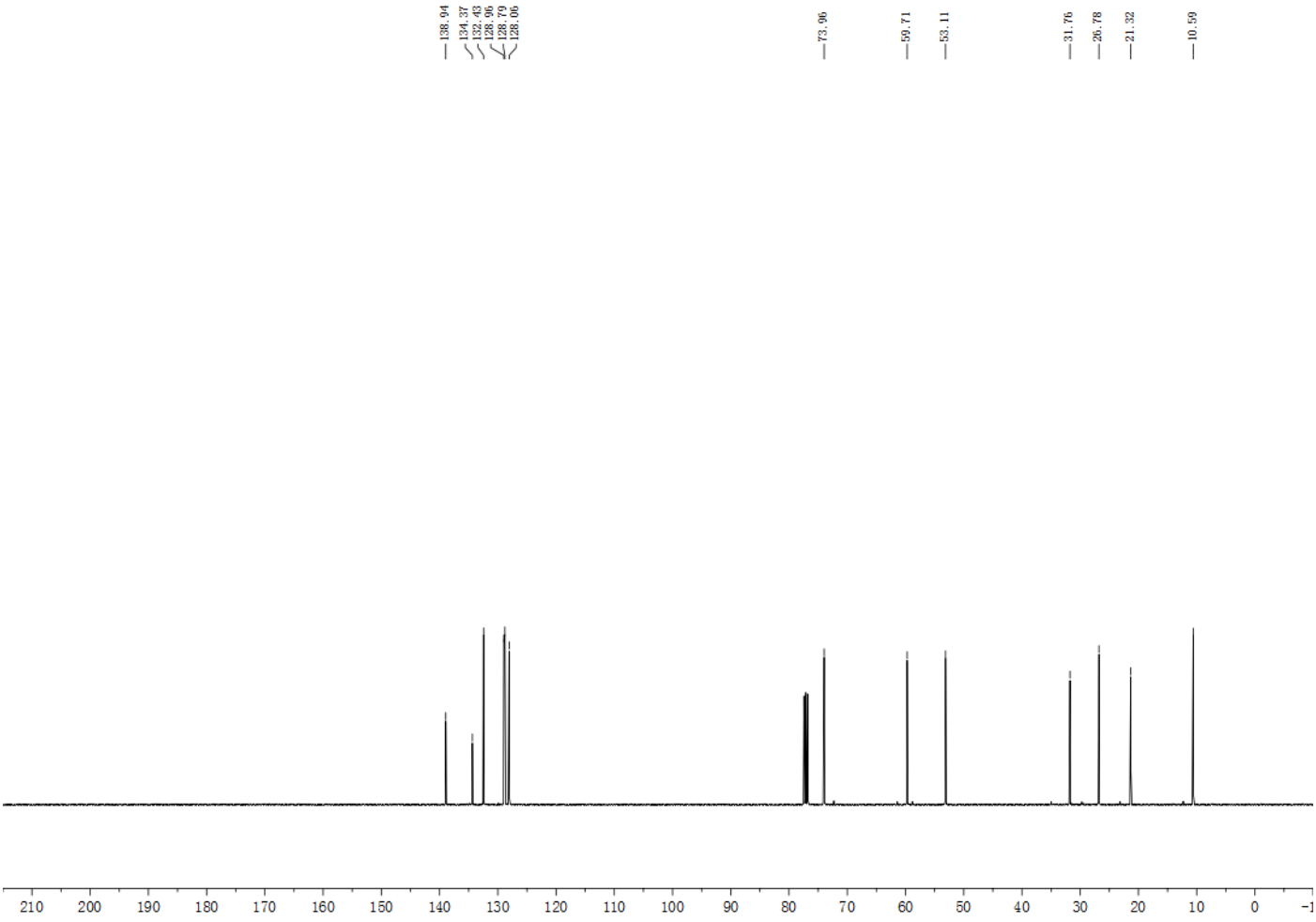
H3C
OH
S
Me

3c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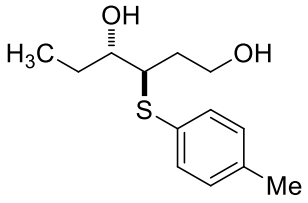
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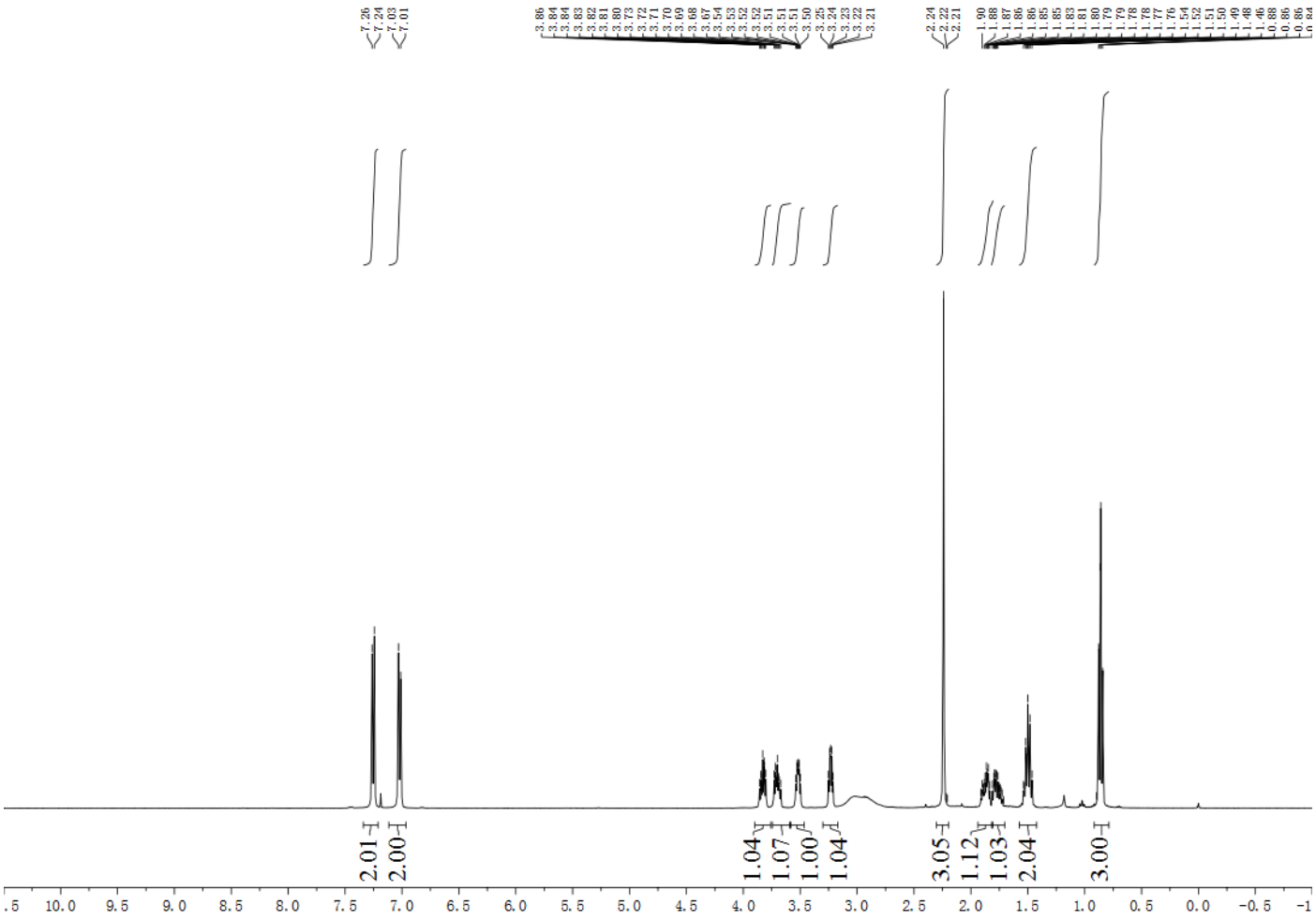
H3C
OH
S
Me

3d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1.50
1.49
1.48
1.46
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0.86
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2.00
1.04
1.07
1.00
1.04
3.05
1.12
1.03
2.04
3.00
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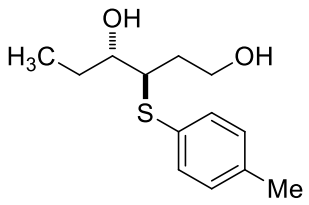
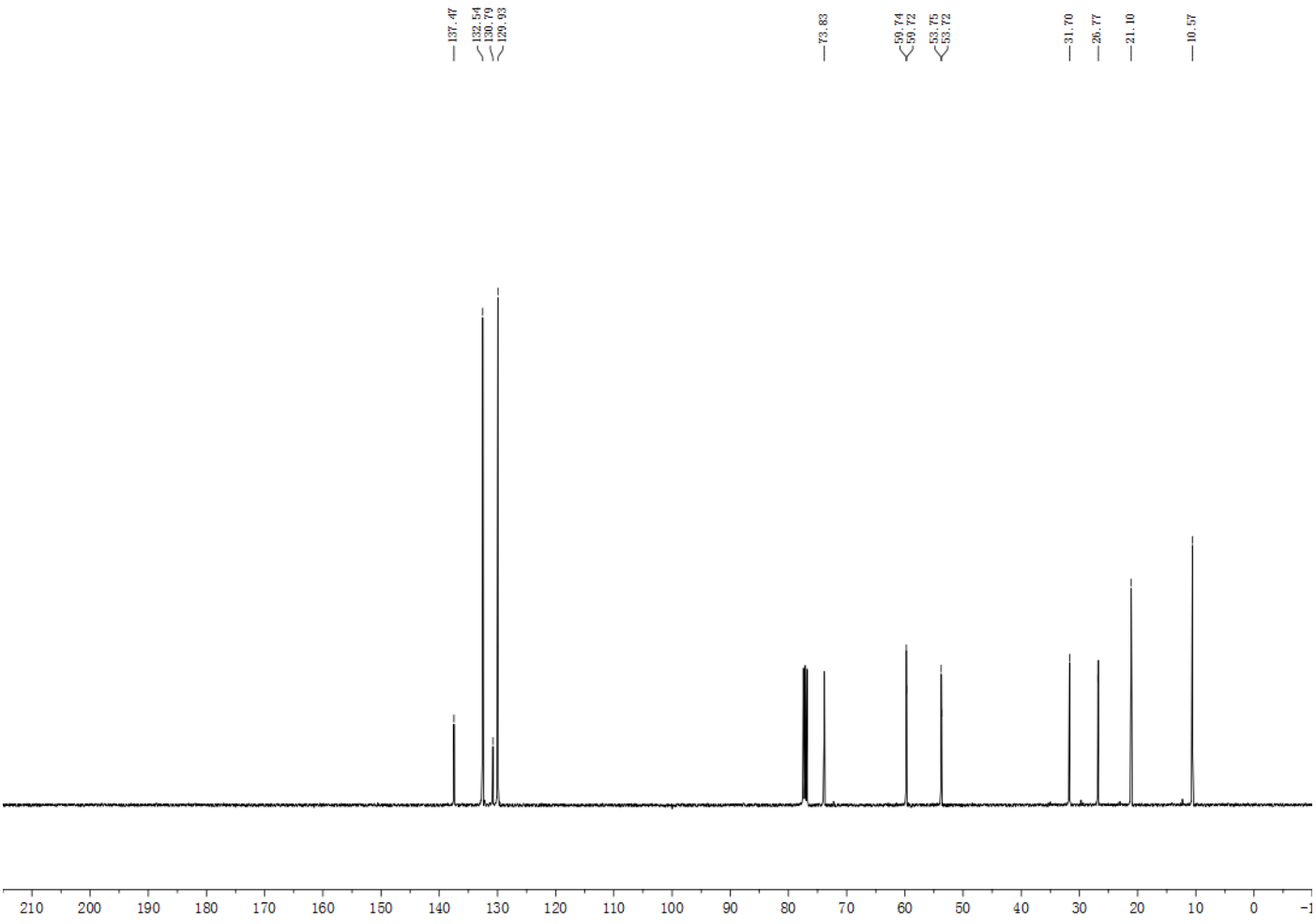

OH
H3C
OH
S
Me

3d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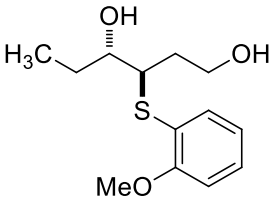

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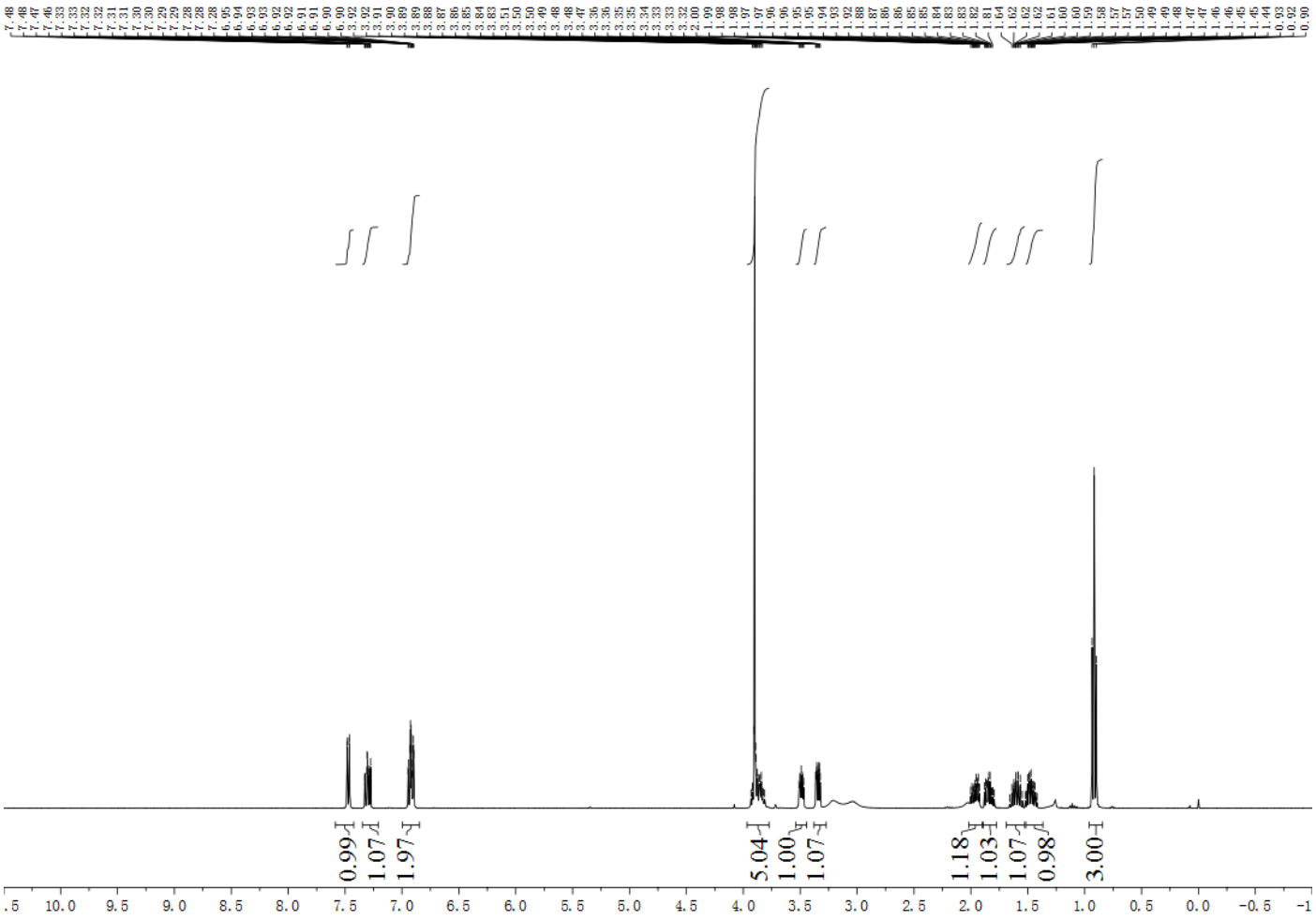

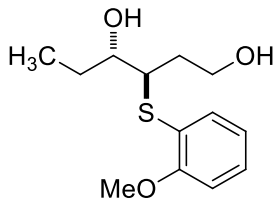
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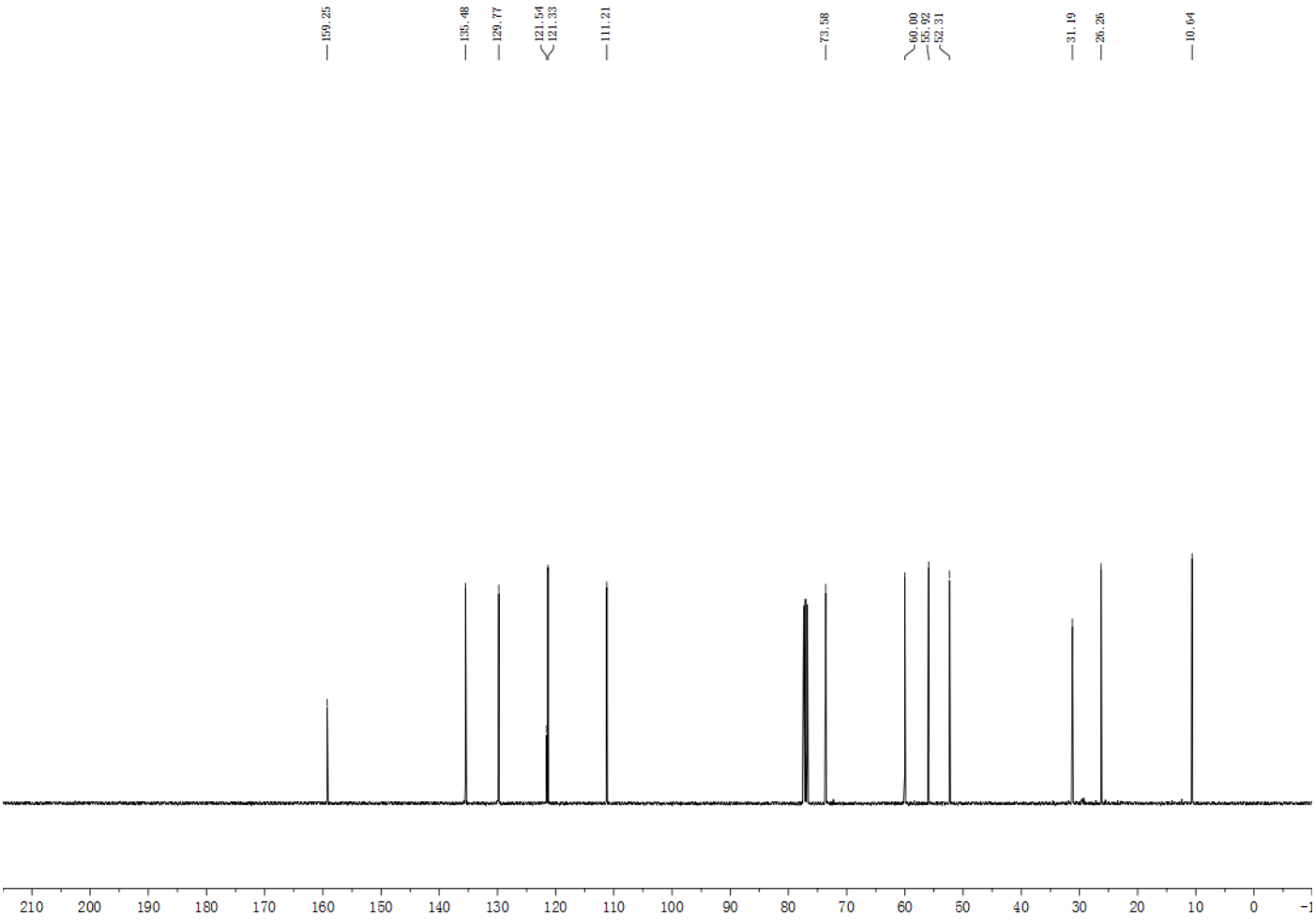
H3C
OH
S
MeO

3e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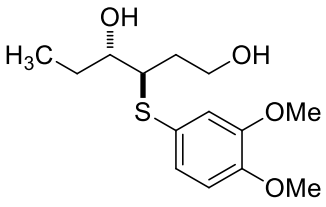
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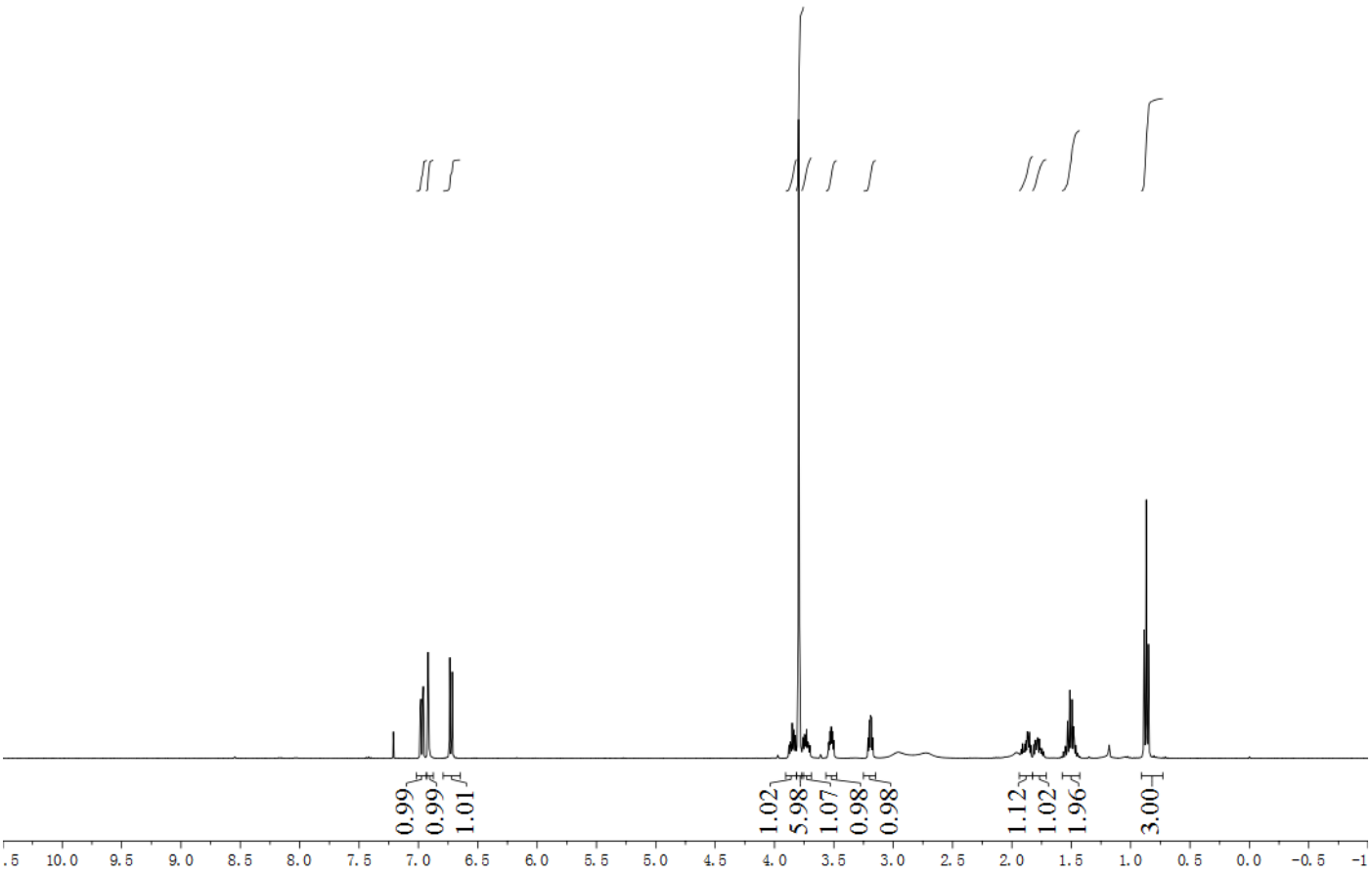
H3C
OH
S
OMe
OMe

3f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8.5
8.0
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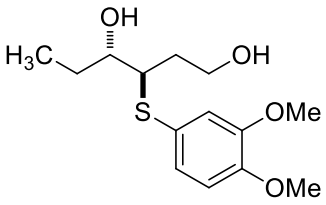
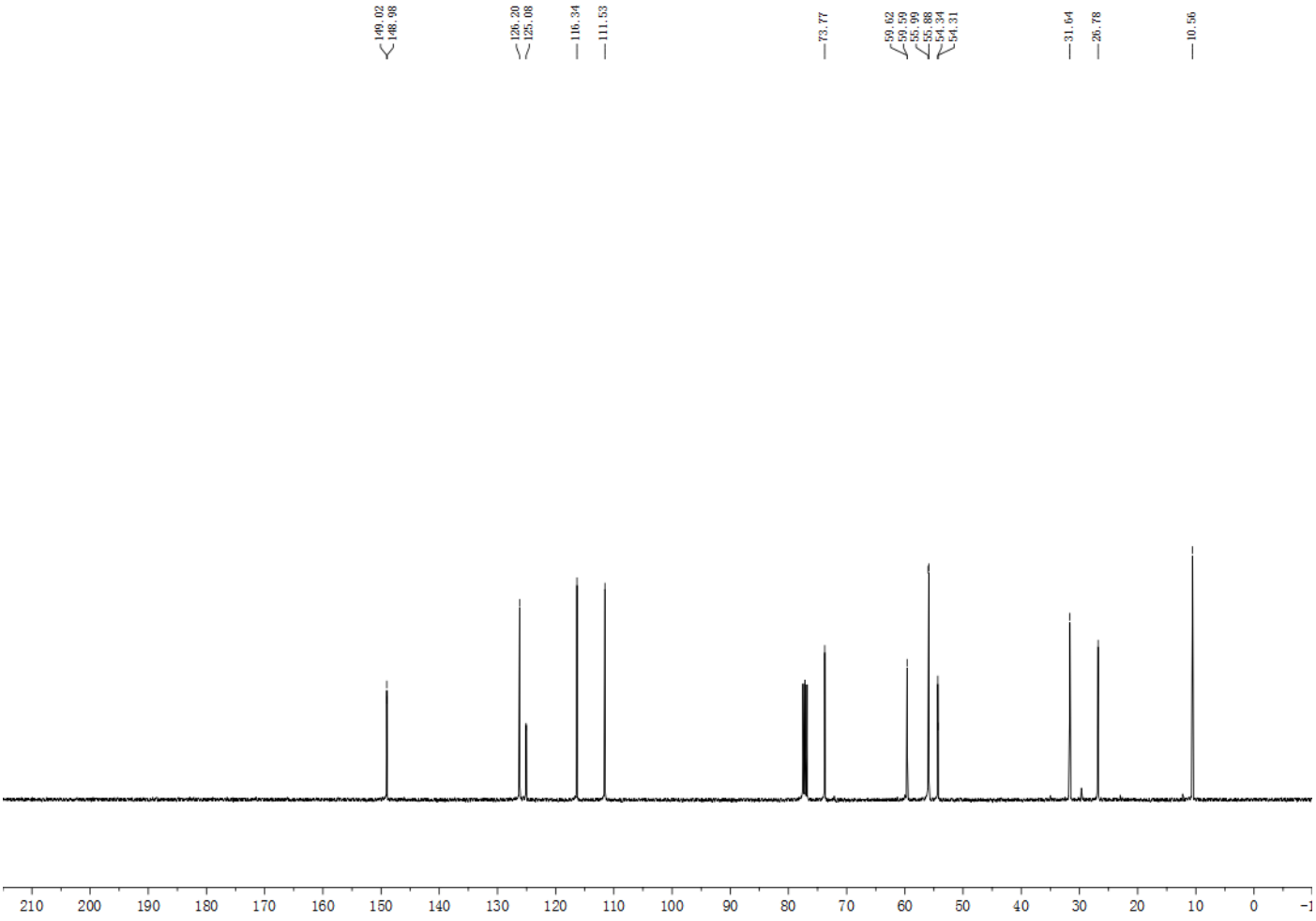

OH
H3C
OH
S
OMe
OMe

3f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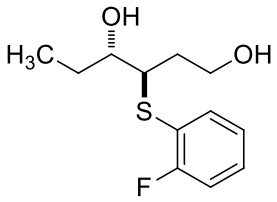

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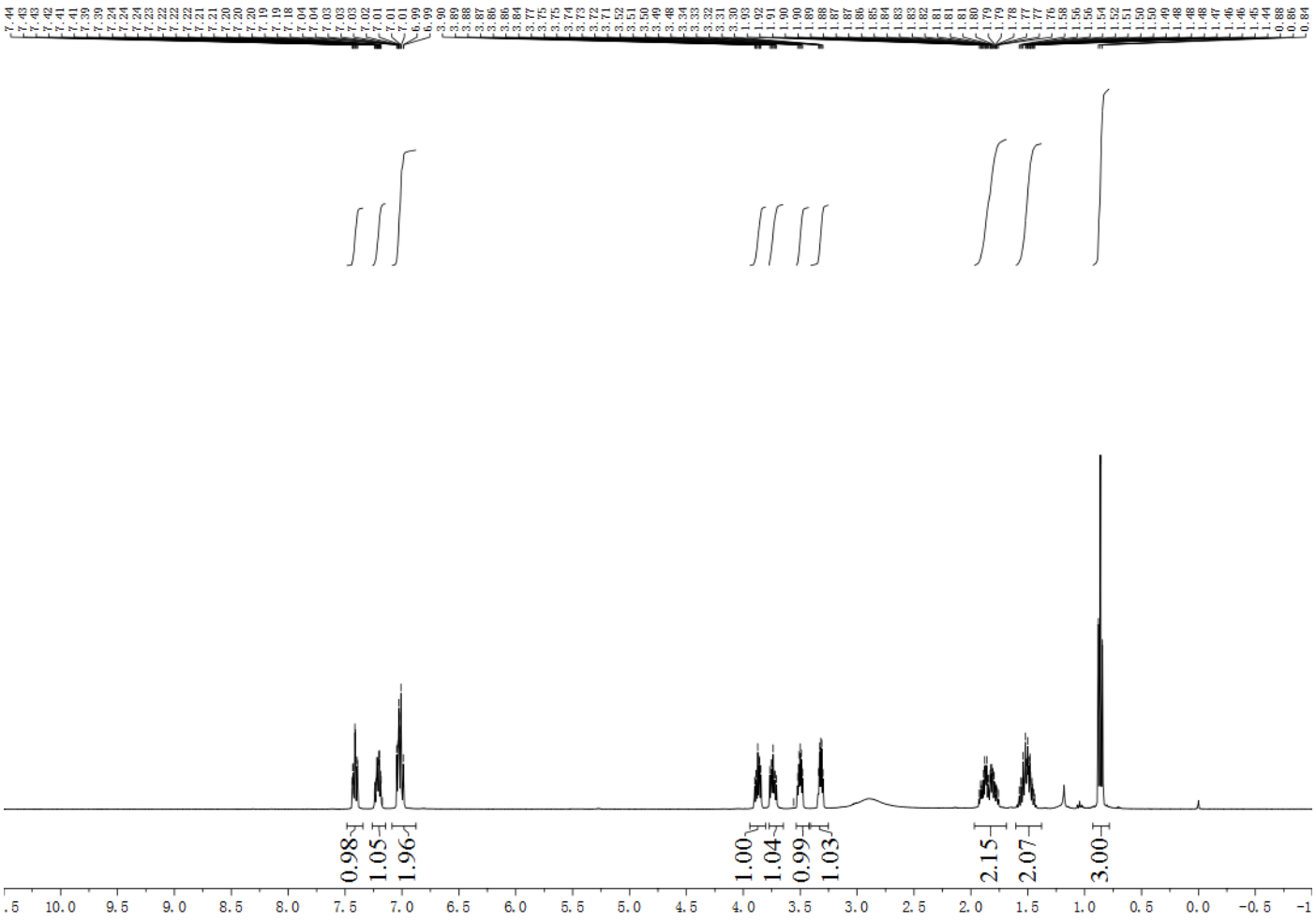
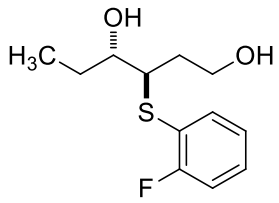
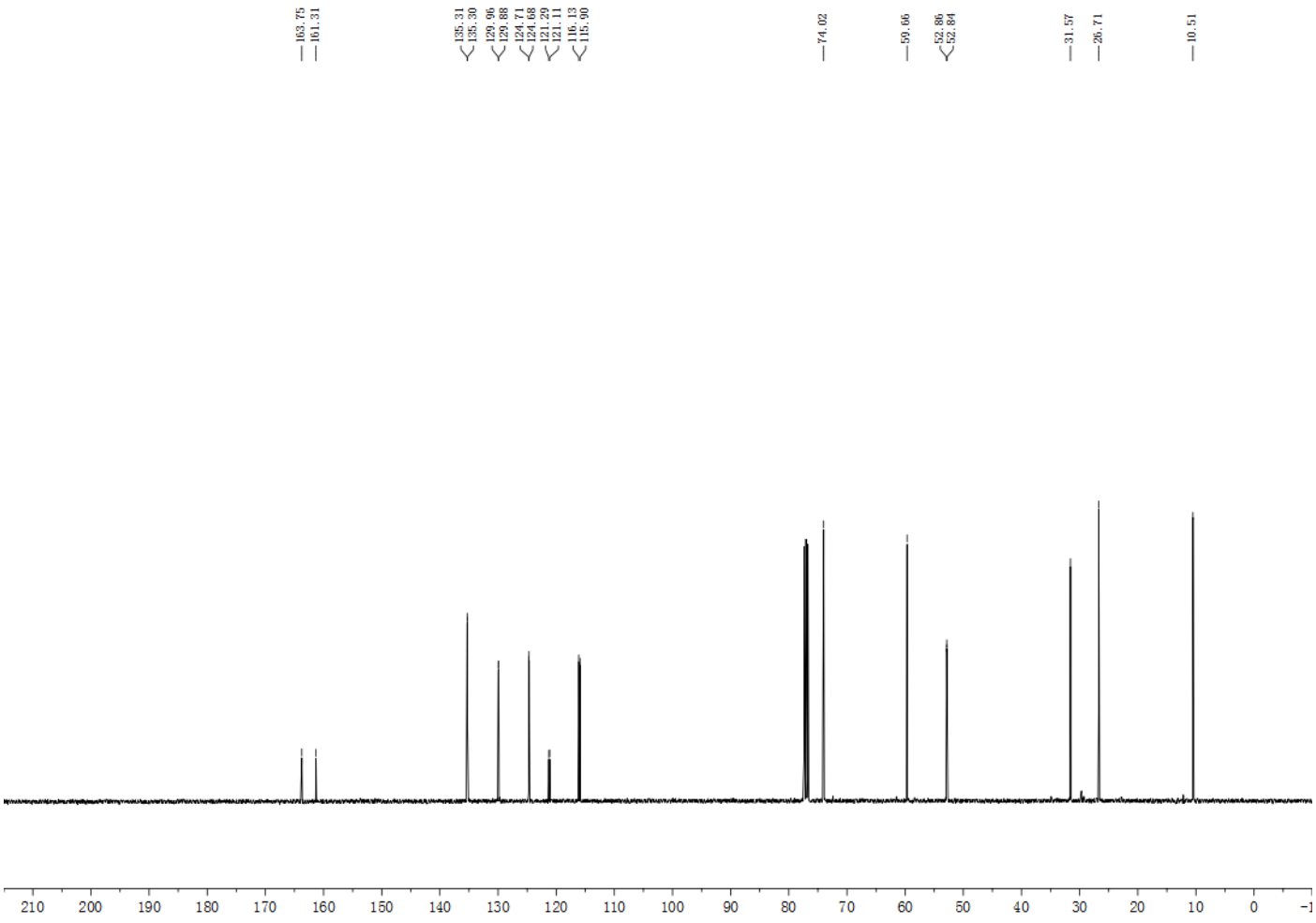



OH
H3C
OH
S
F

3g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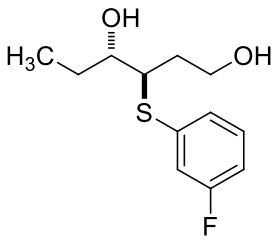
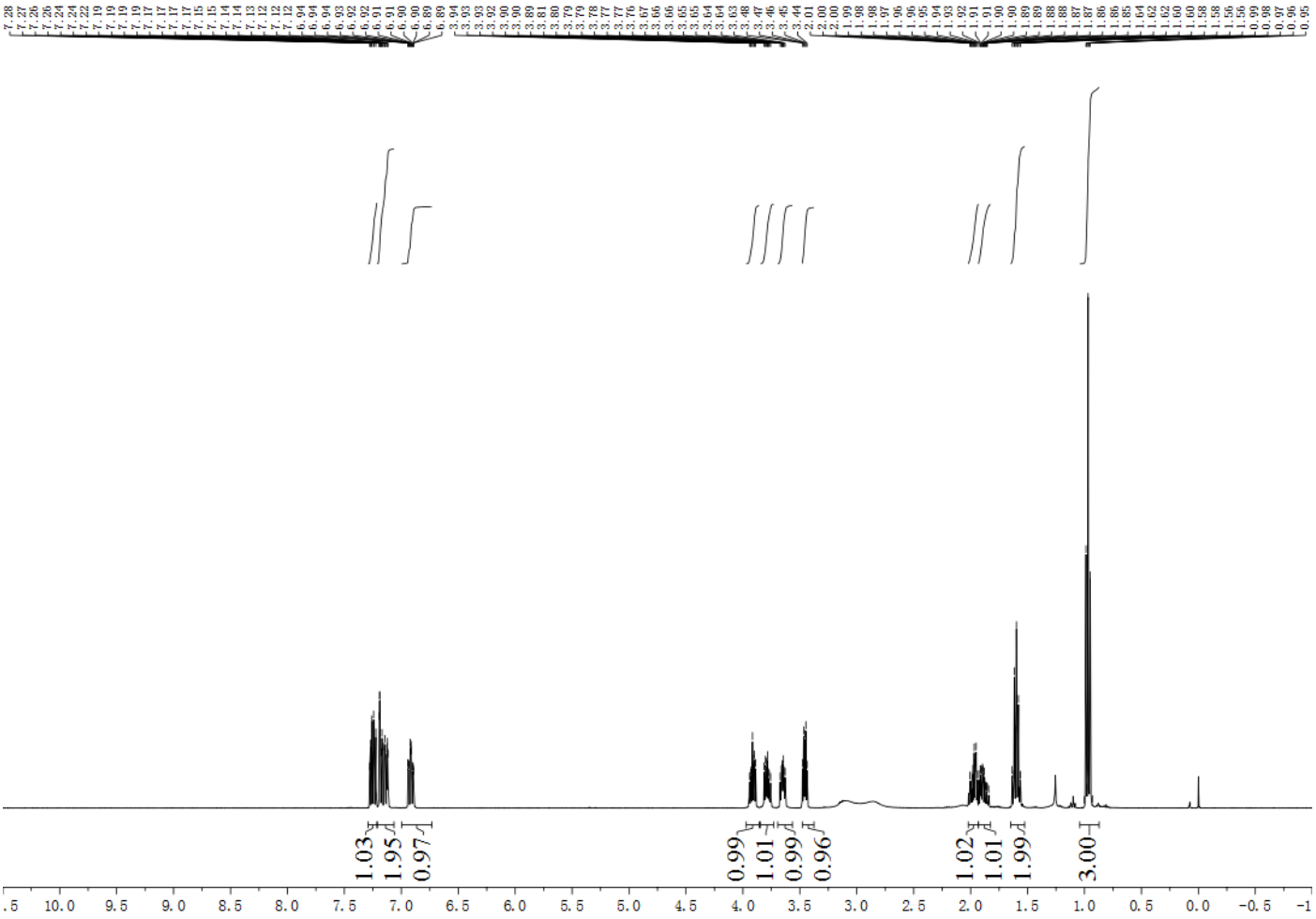
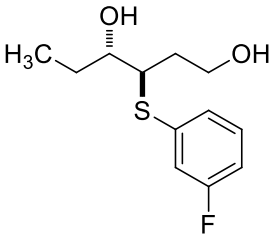
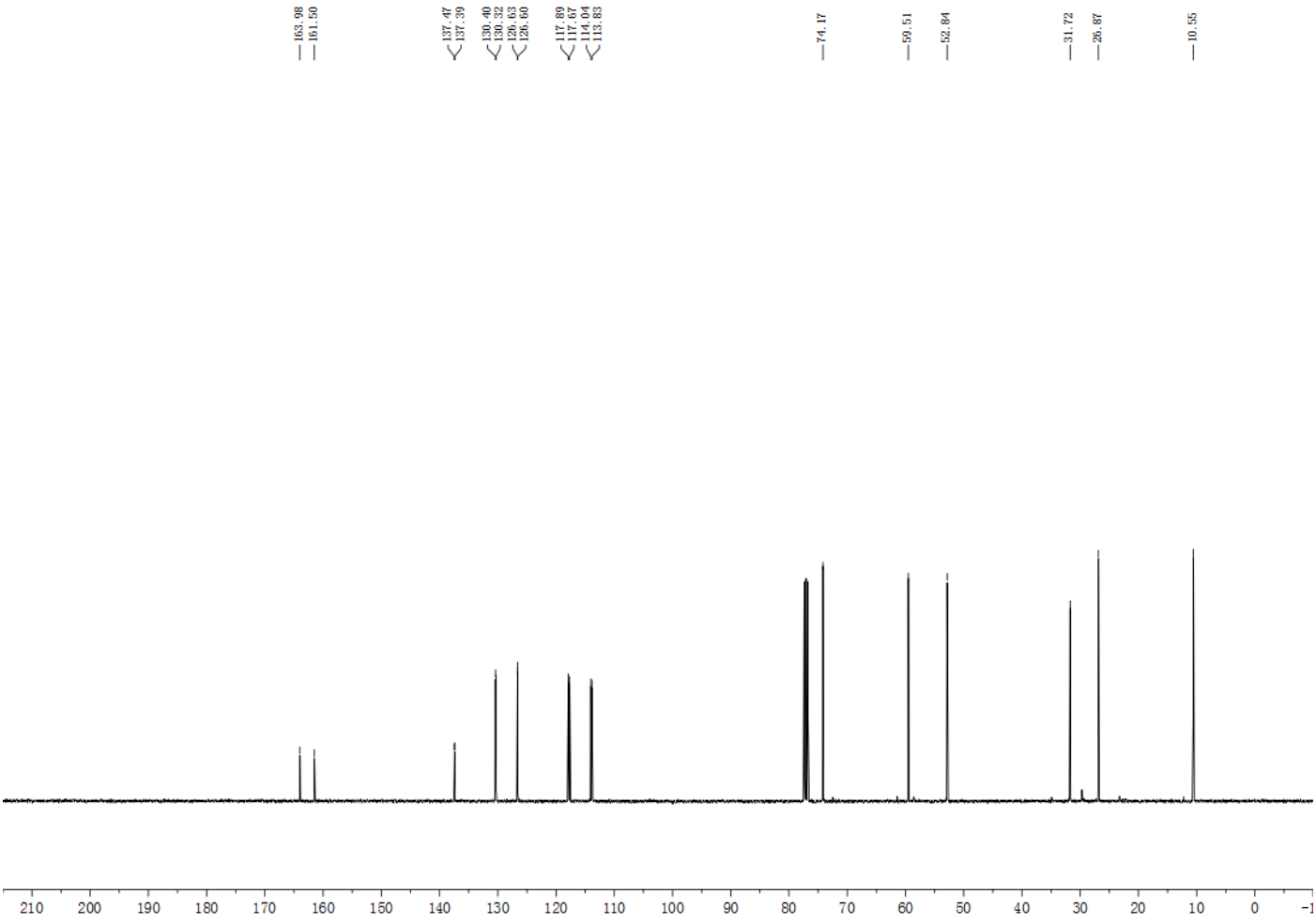


3h




OH
H3C
OH
S
F

3h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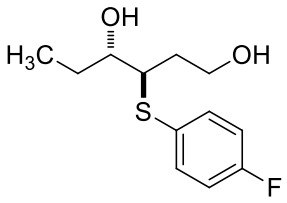
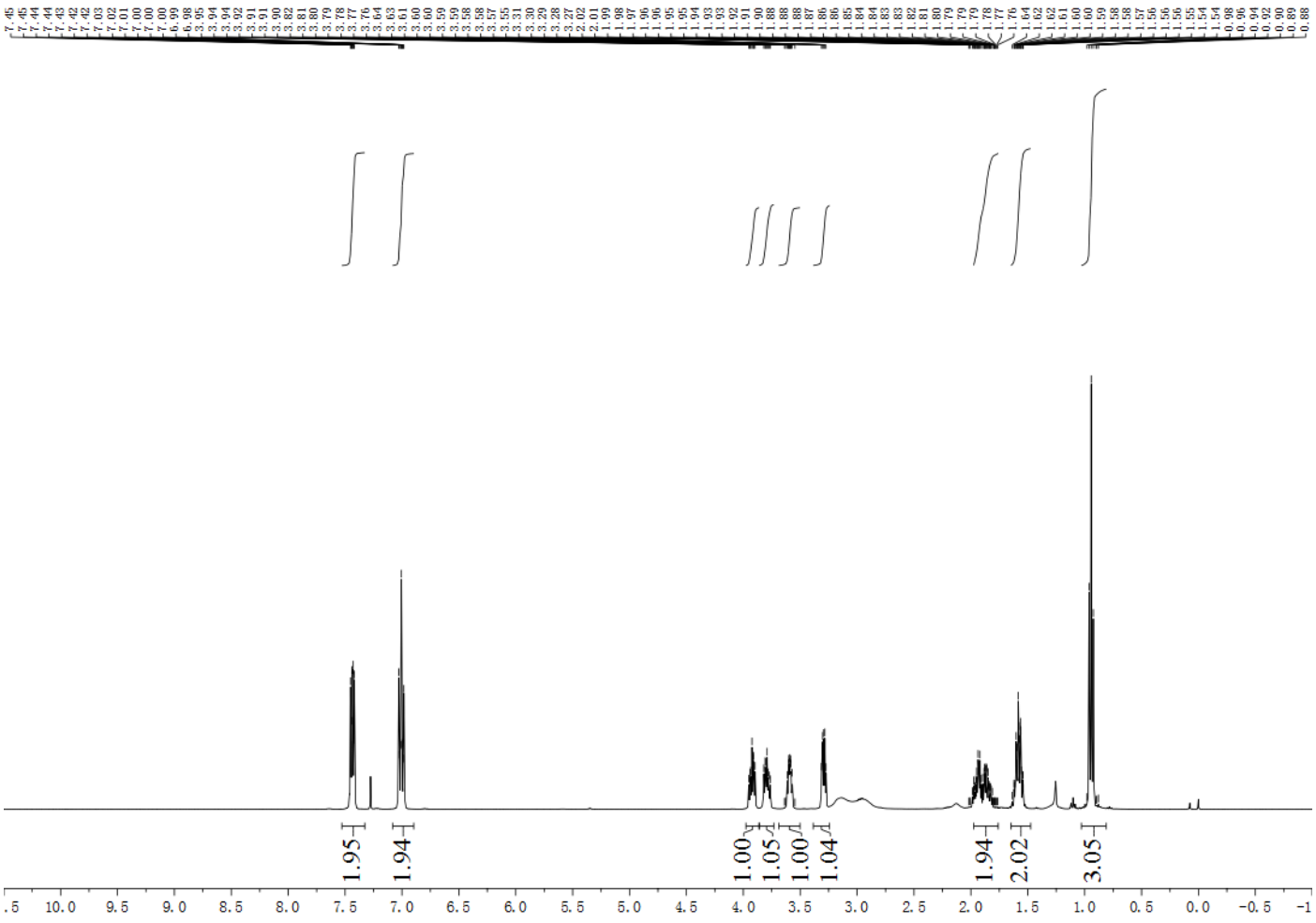
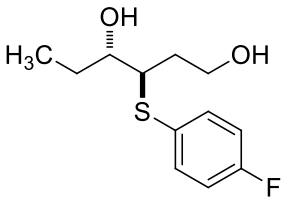


3i

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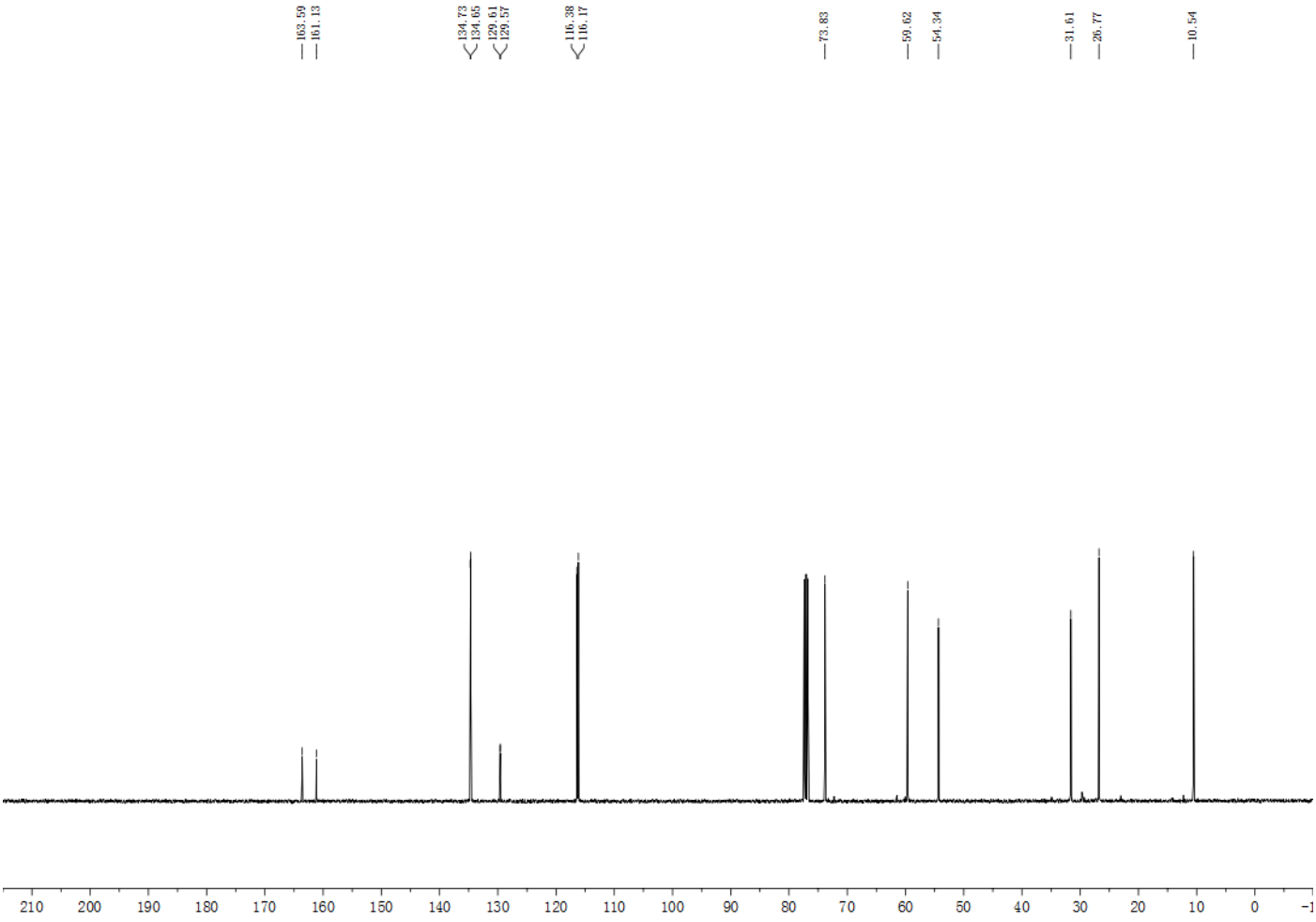
OH
S
F

3i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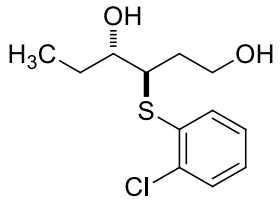

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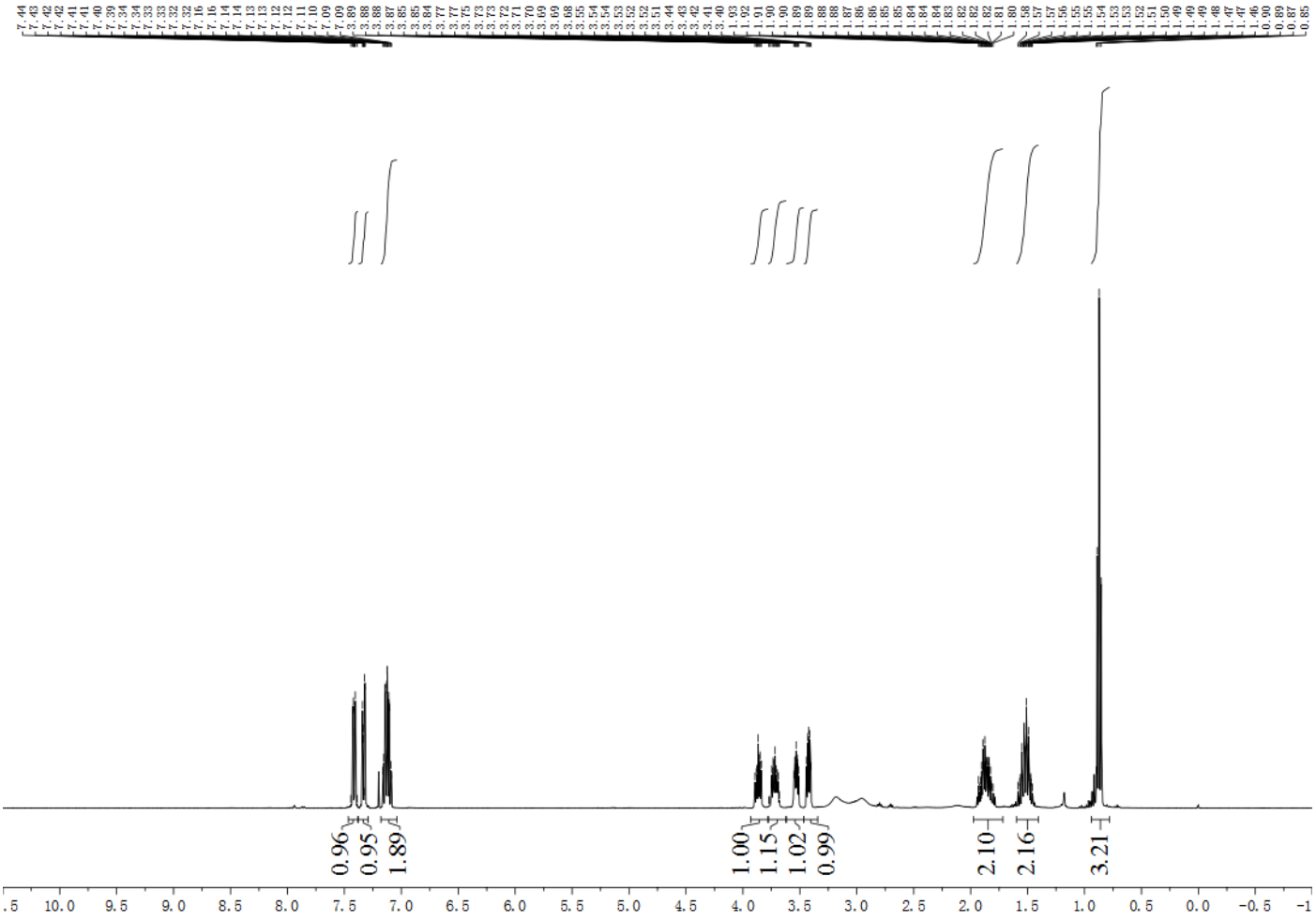

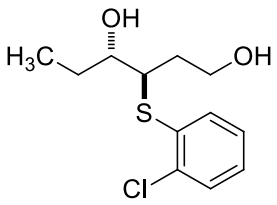
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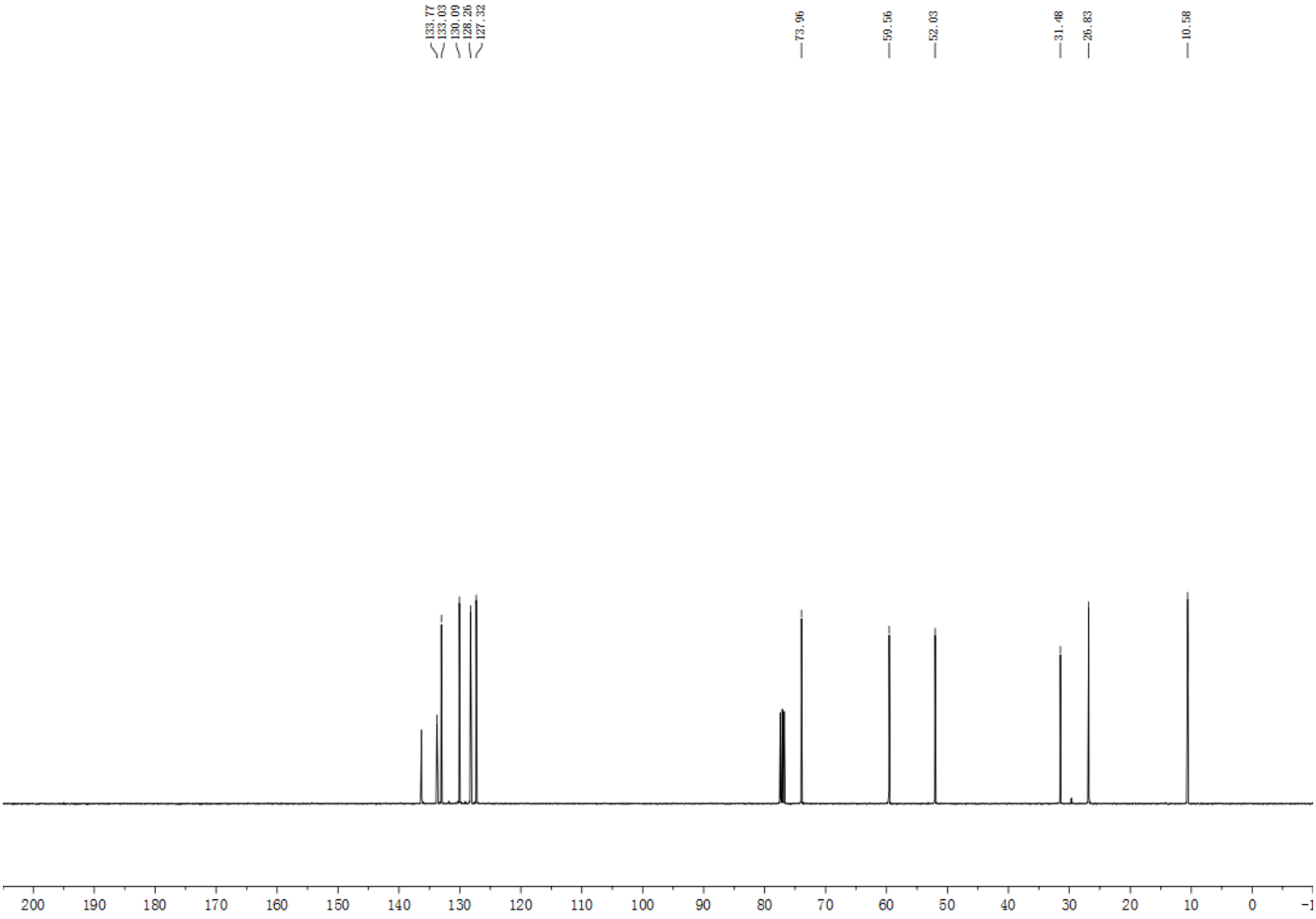
OH
S
Cl

3j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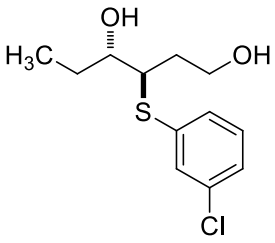
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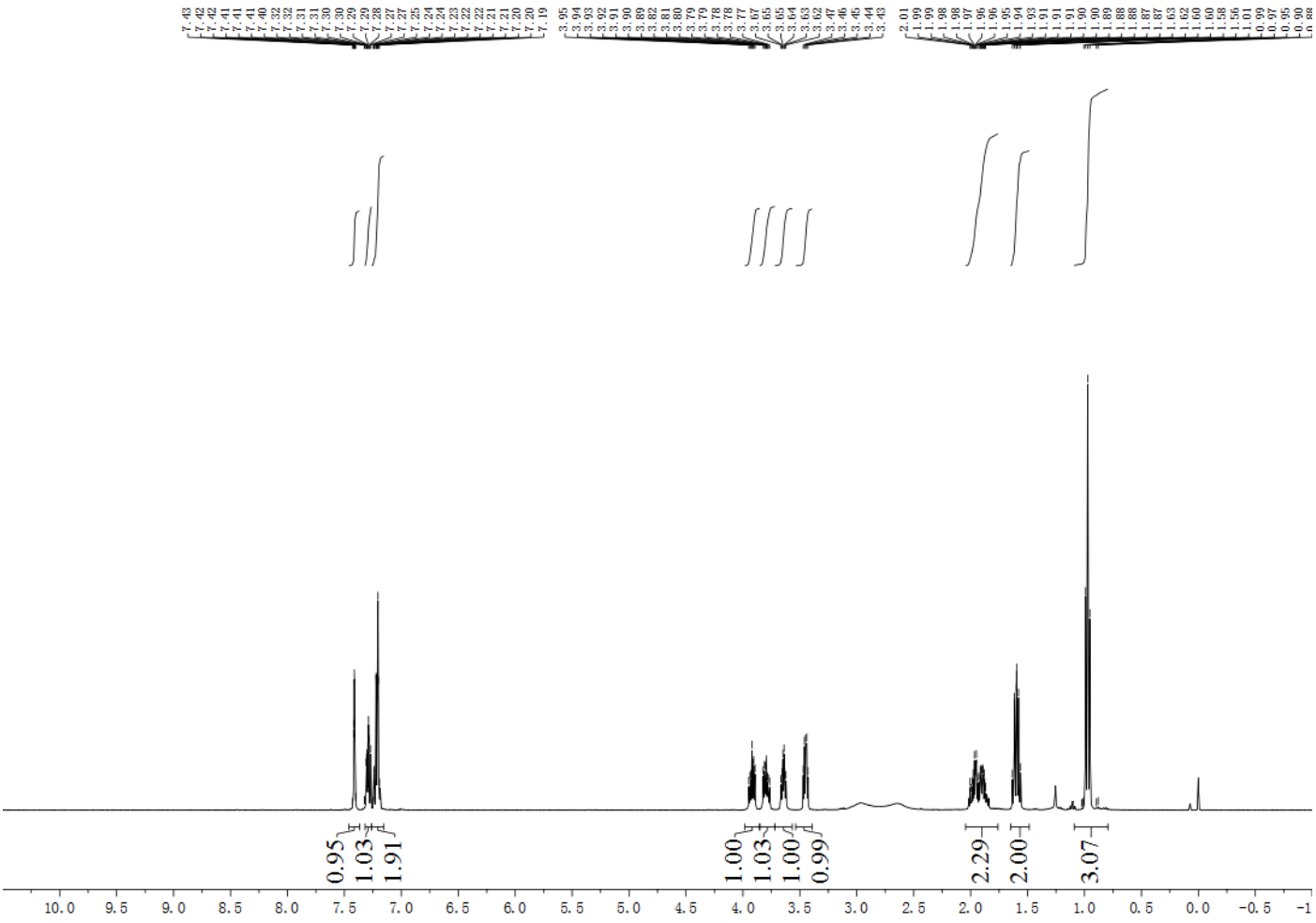
OH
S
Cl

3k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8.0
7.5
7.0
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6.0
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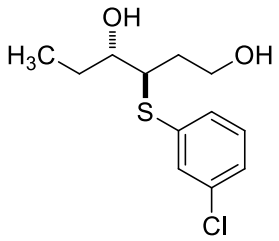
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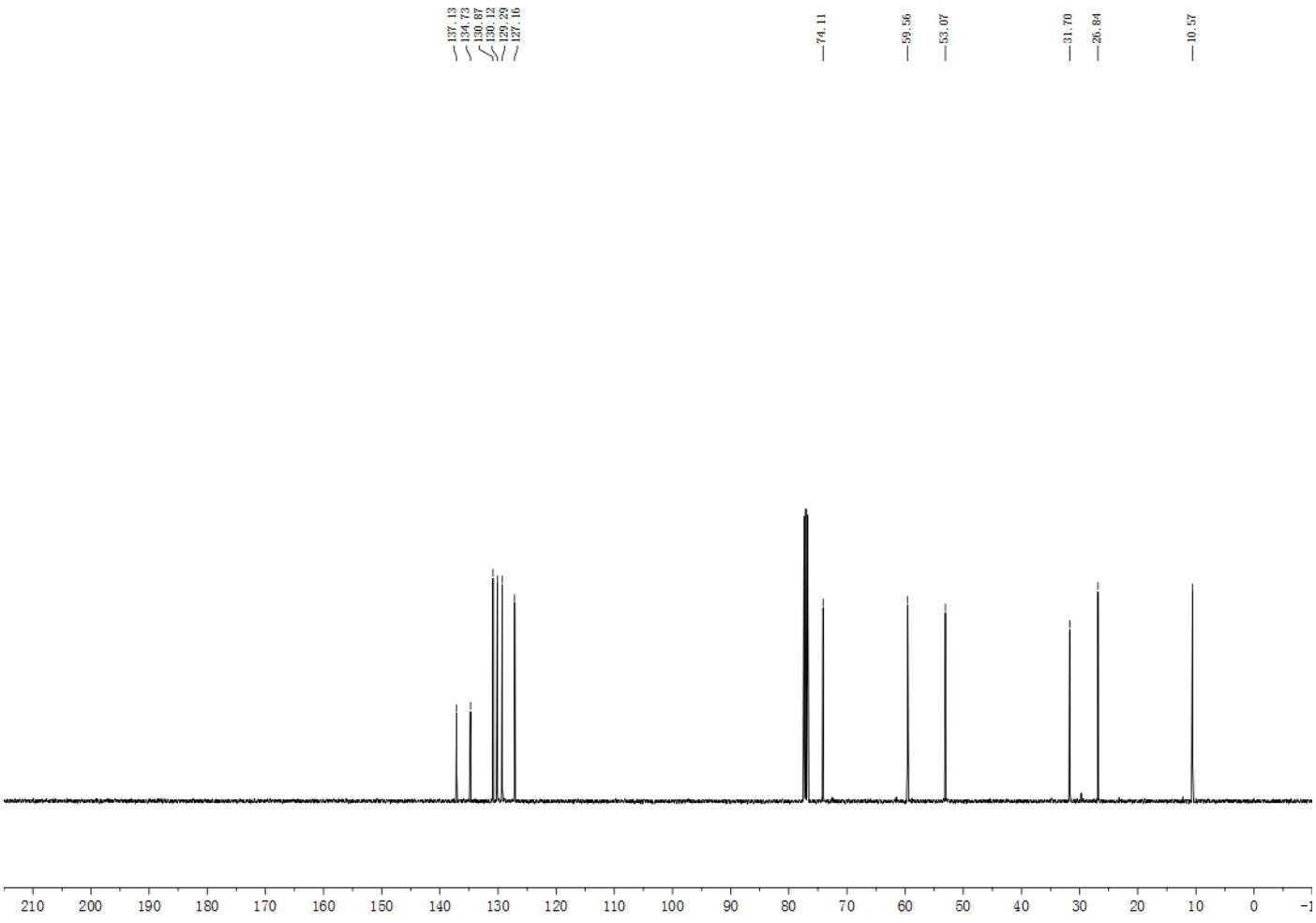
Cl

3k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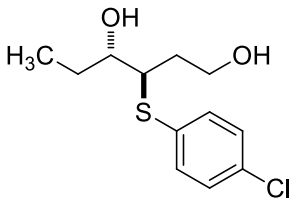

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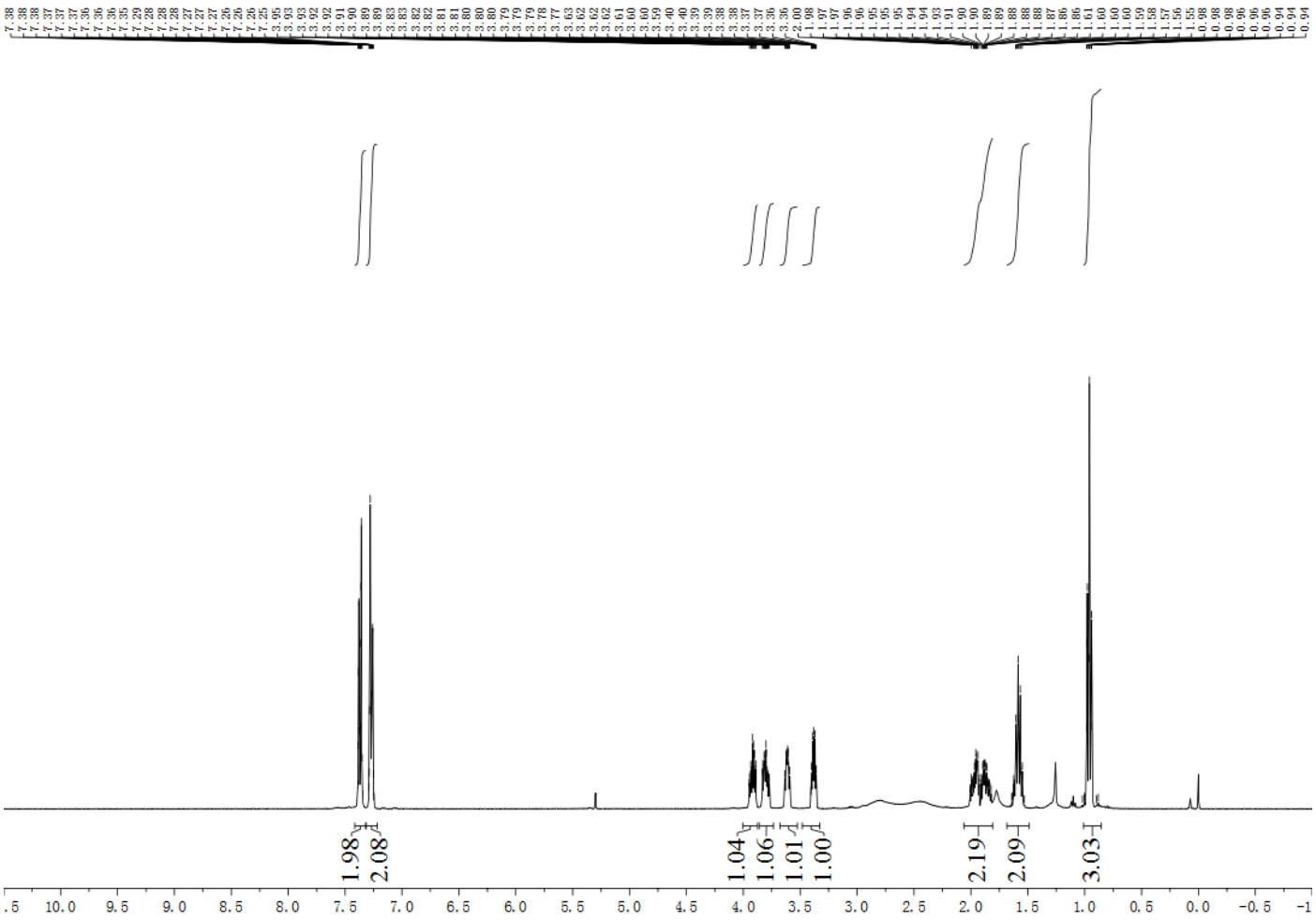

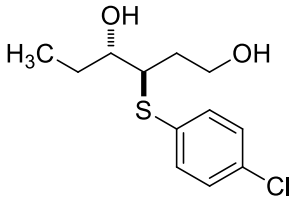
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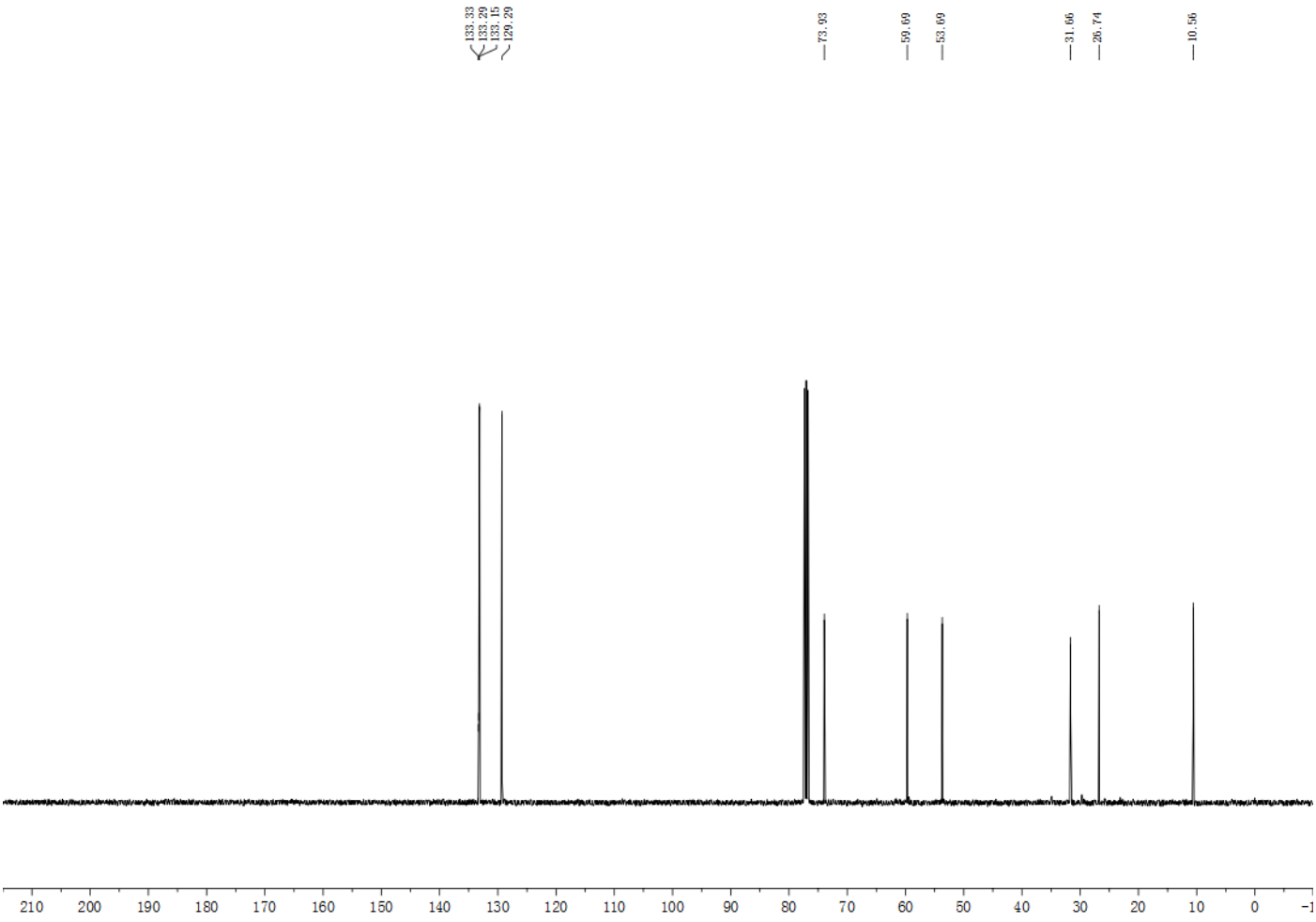
H3C
OH
S
Cl

3l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10.56
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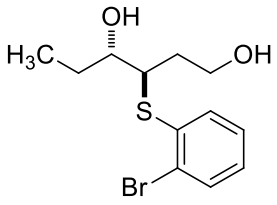

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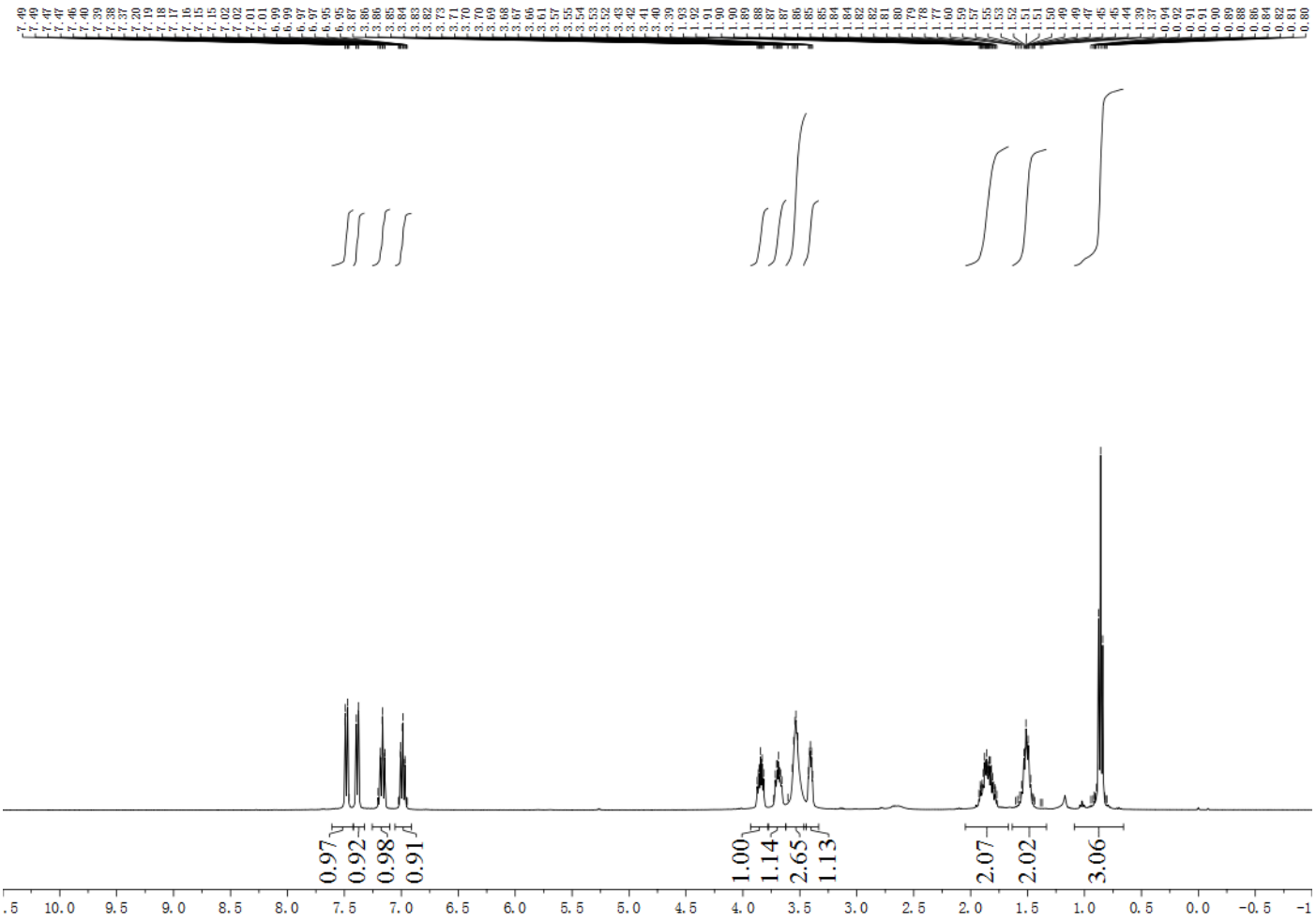
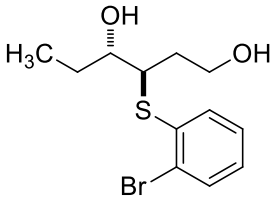
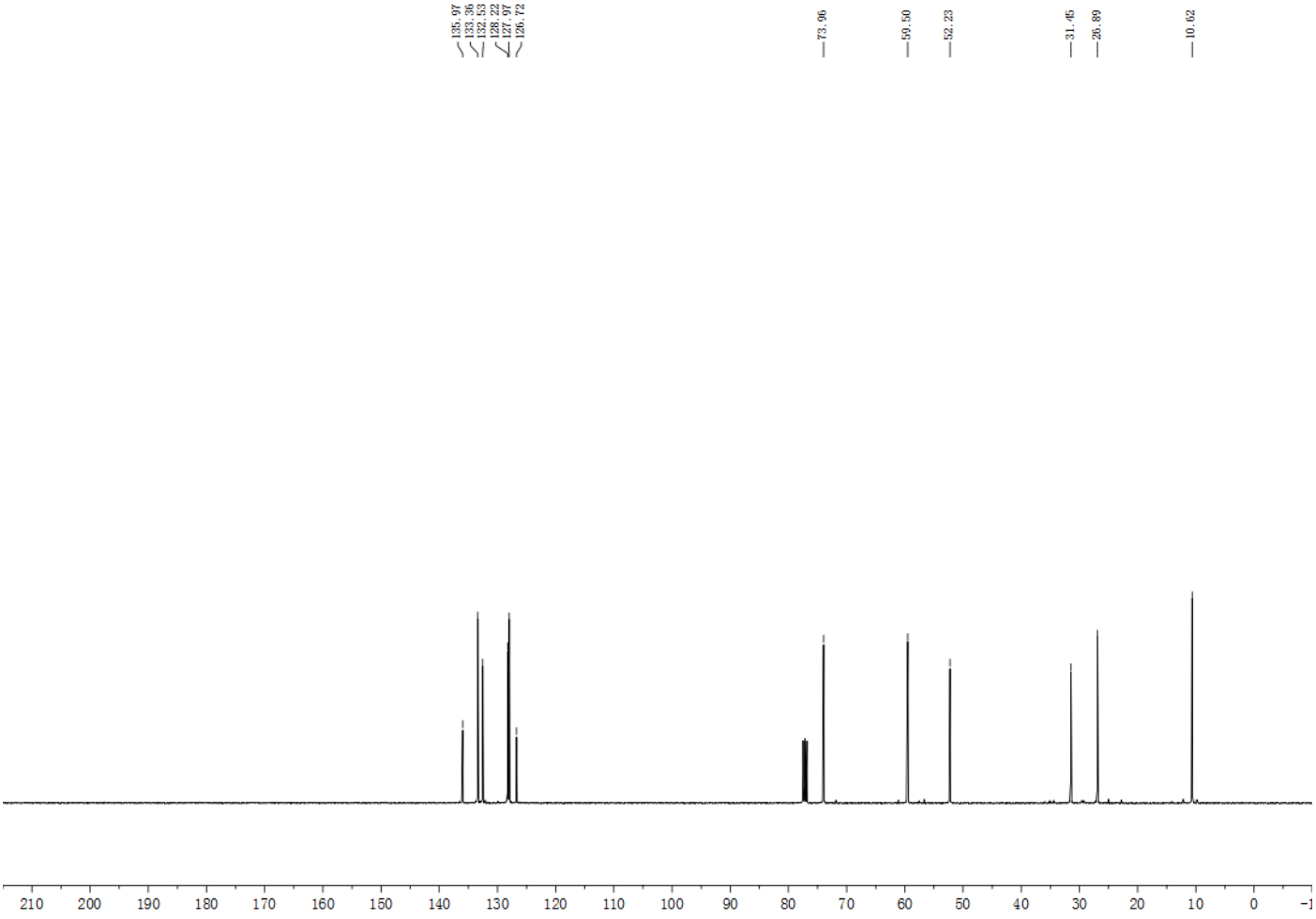



OH
H3C
OH
S
Br

3m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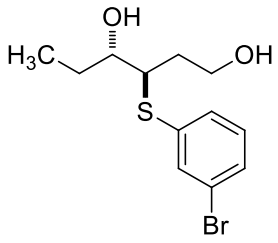

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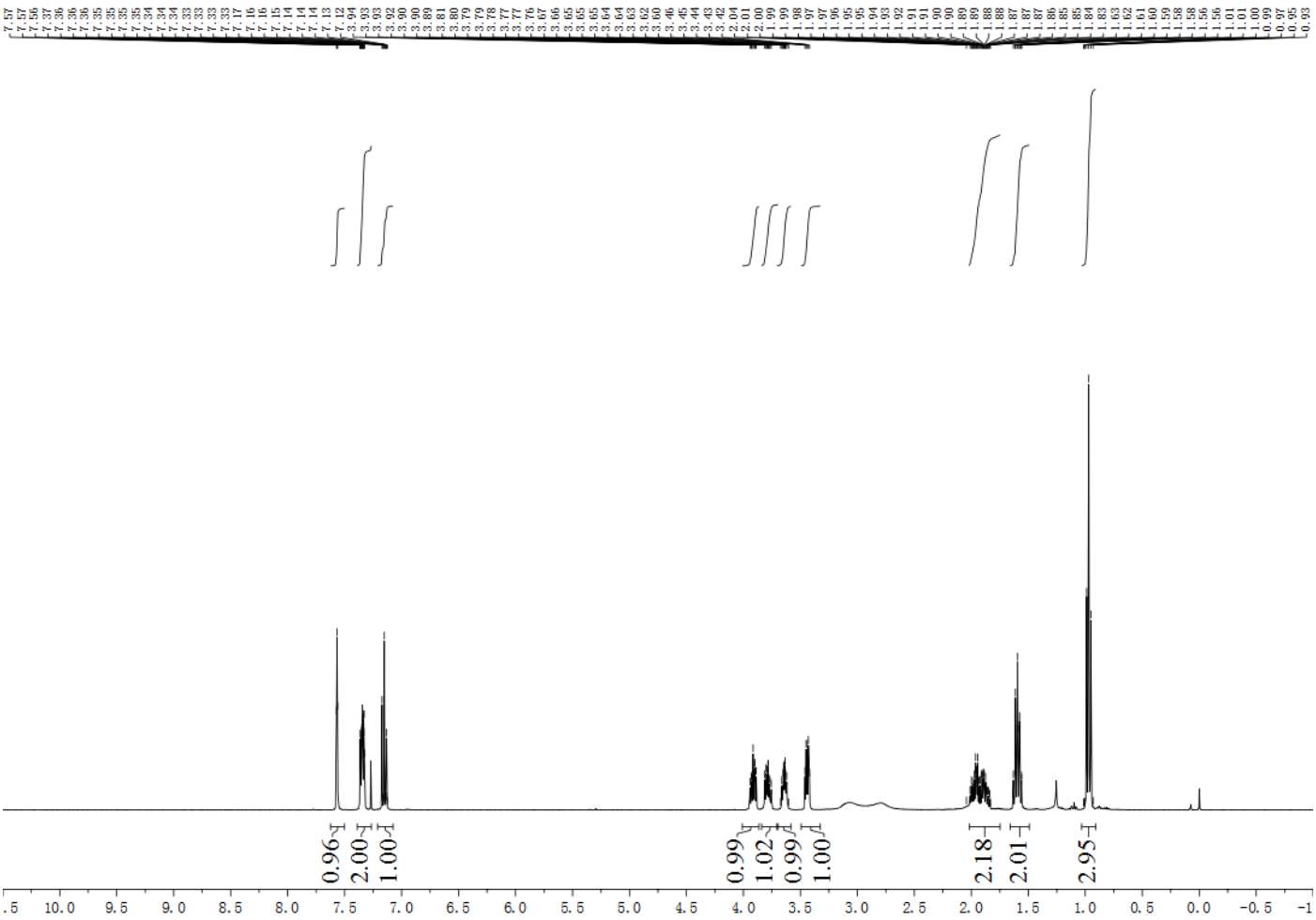
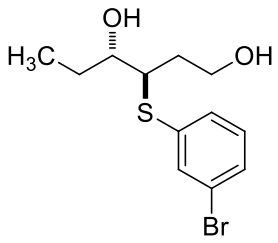
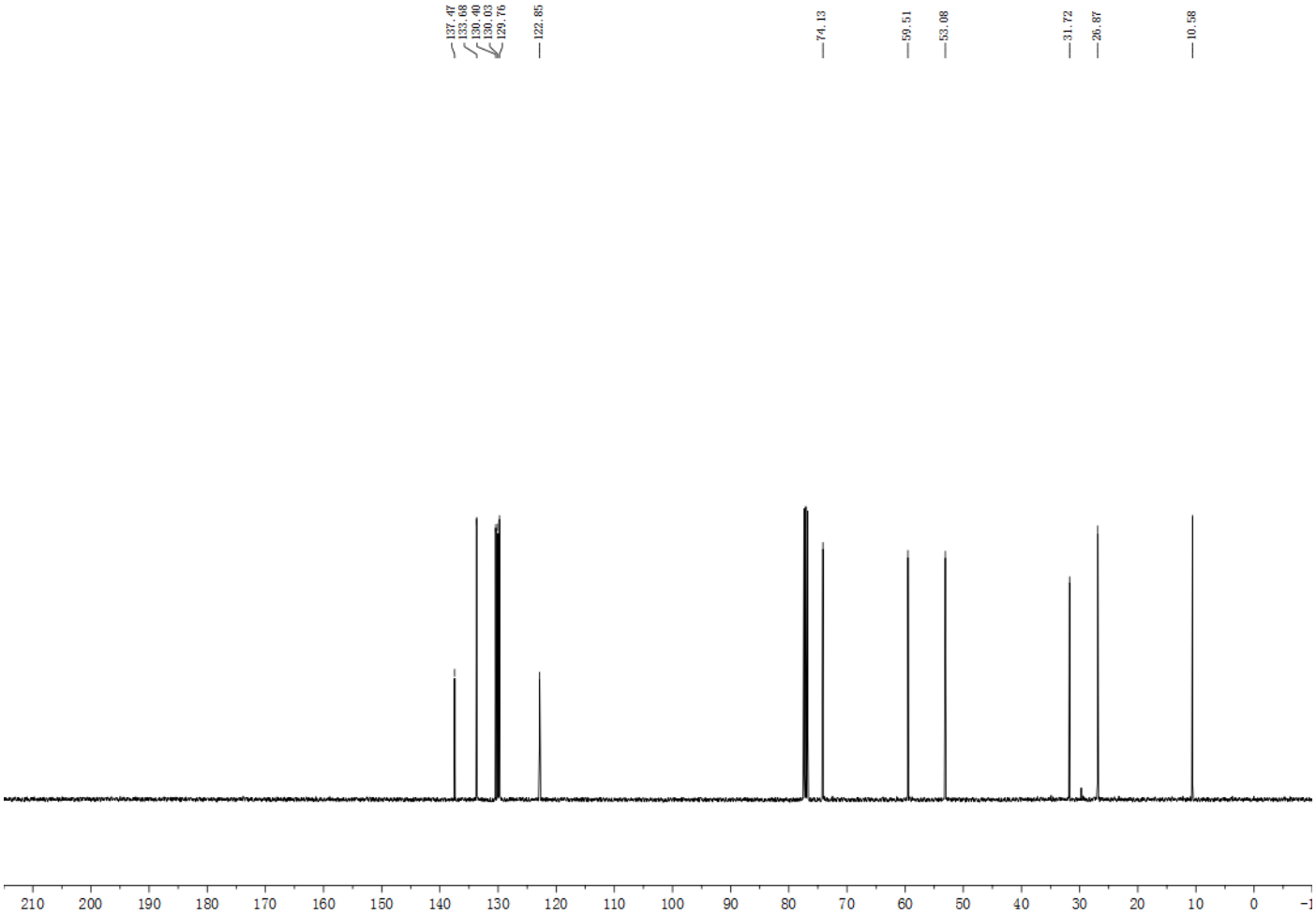



OH
H3C
OH
S
Br

3n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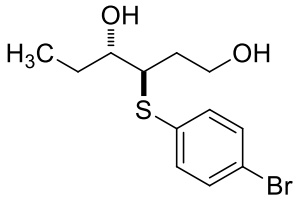

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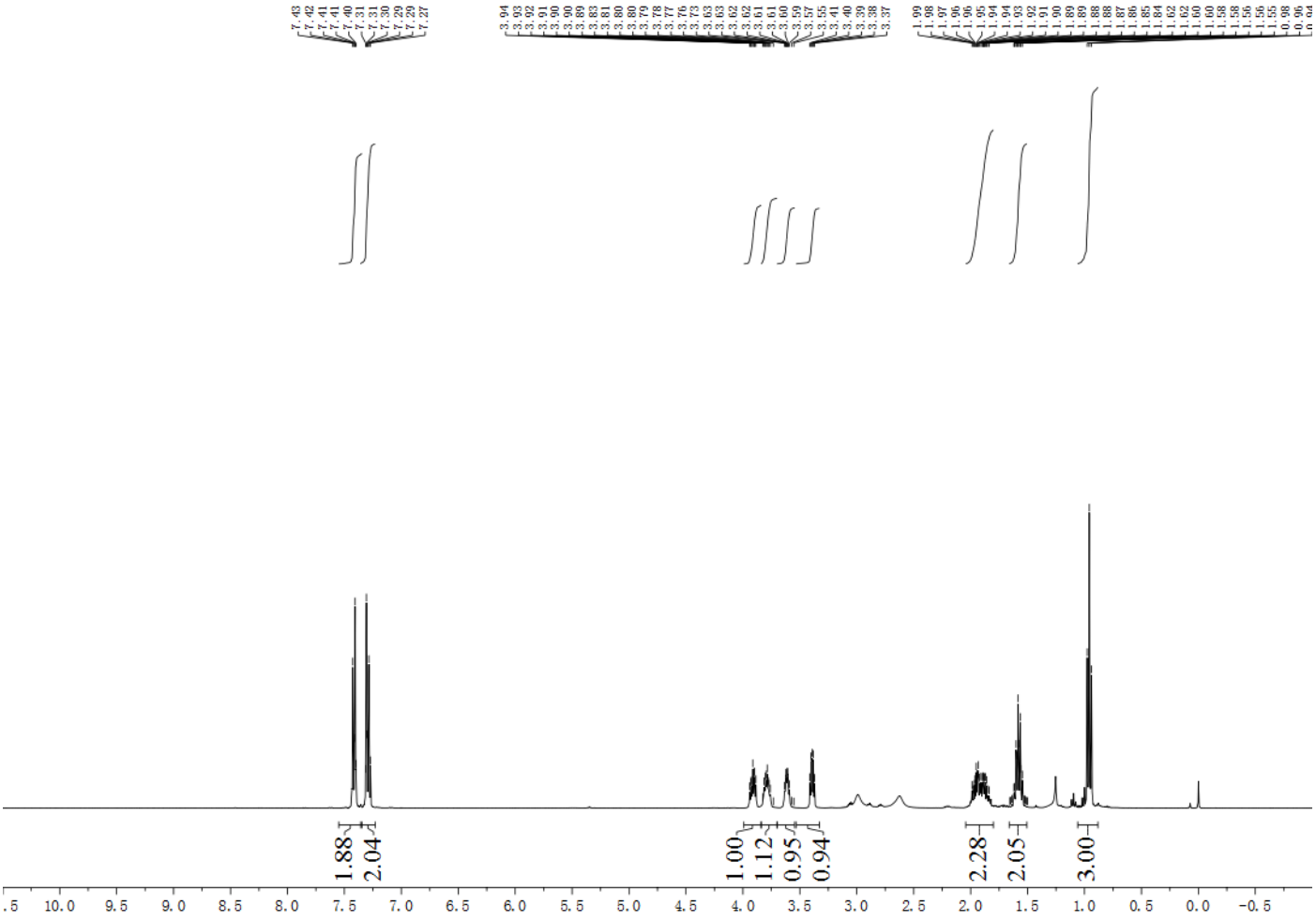

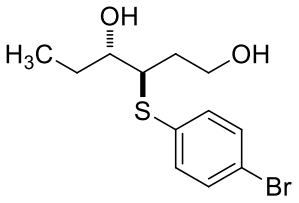
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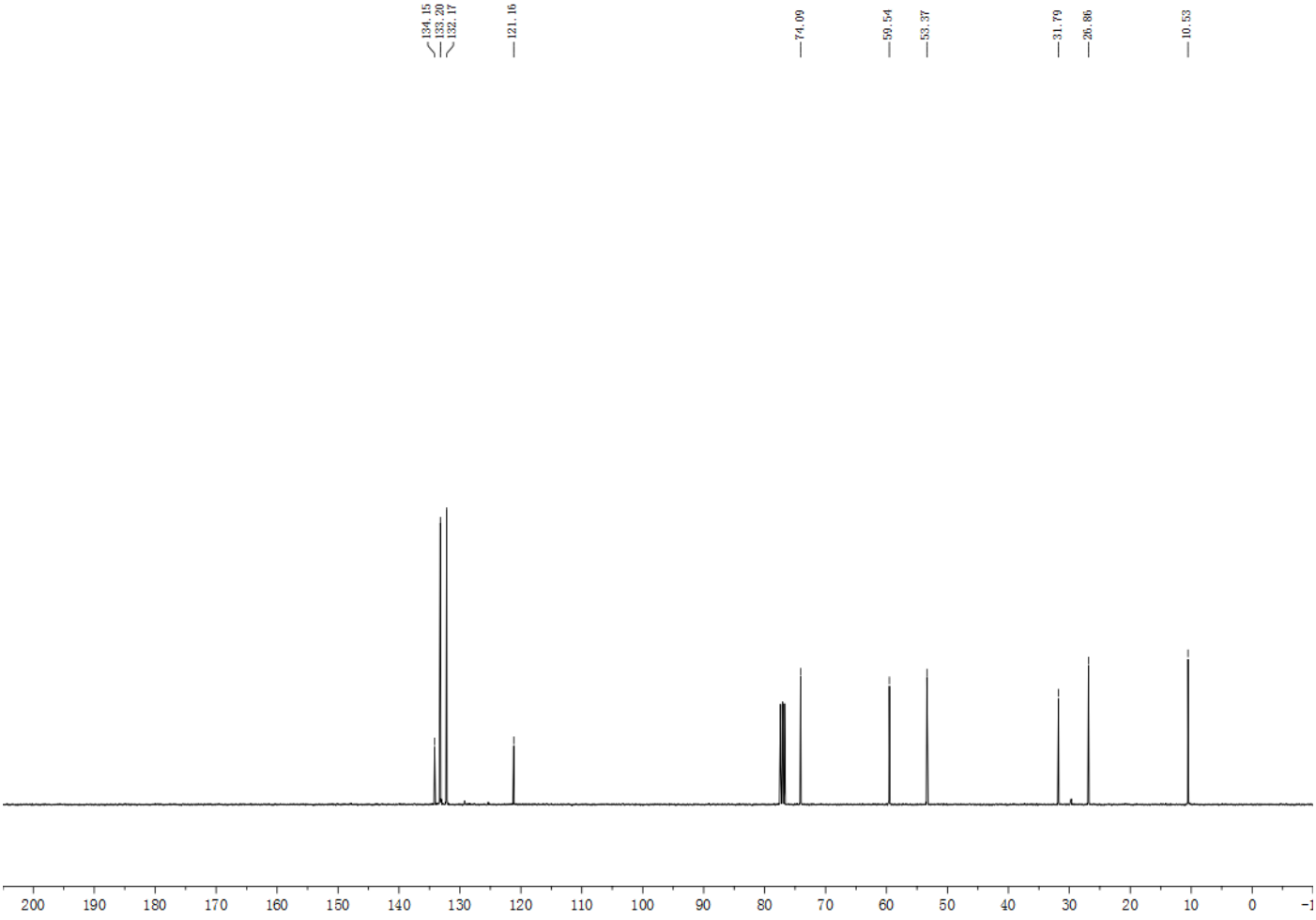
H3C
OH
S
Br

3o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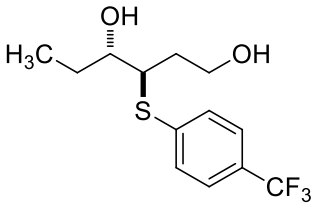

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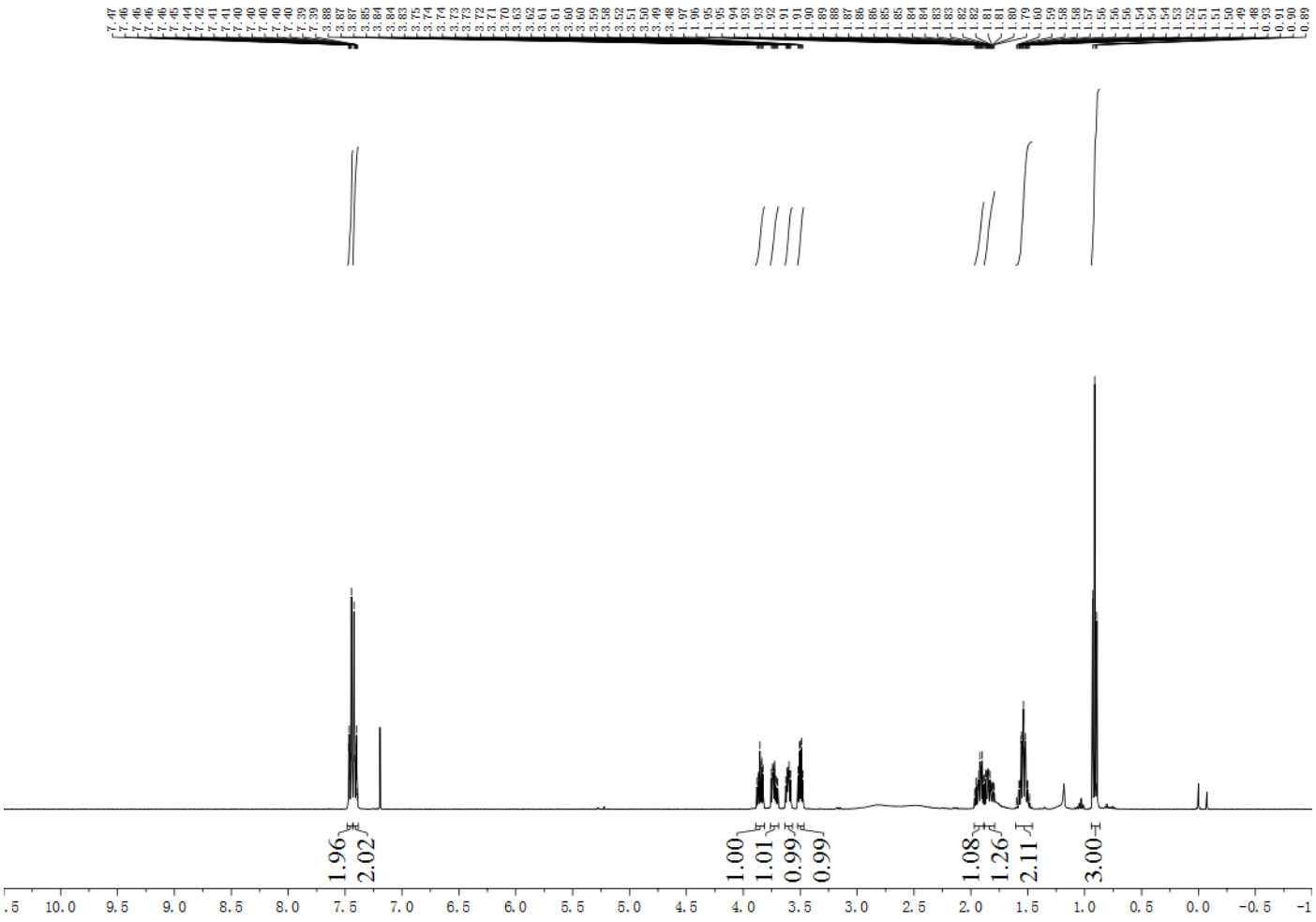

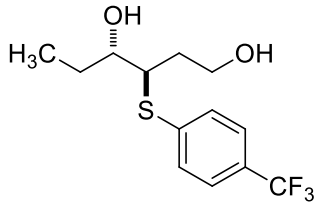
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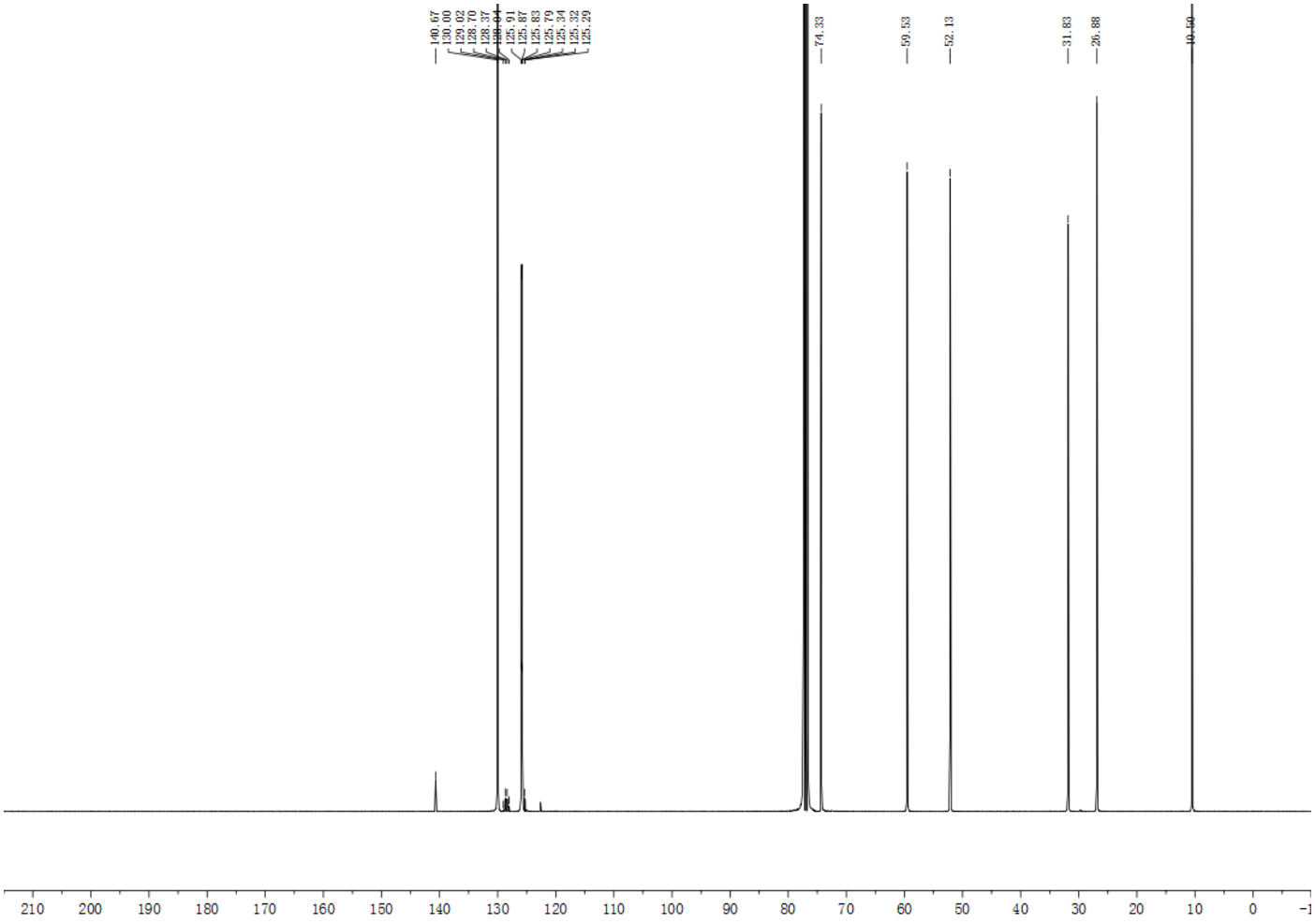
OH
S
CF3

3p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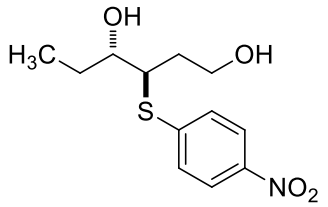
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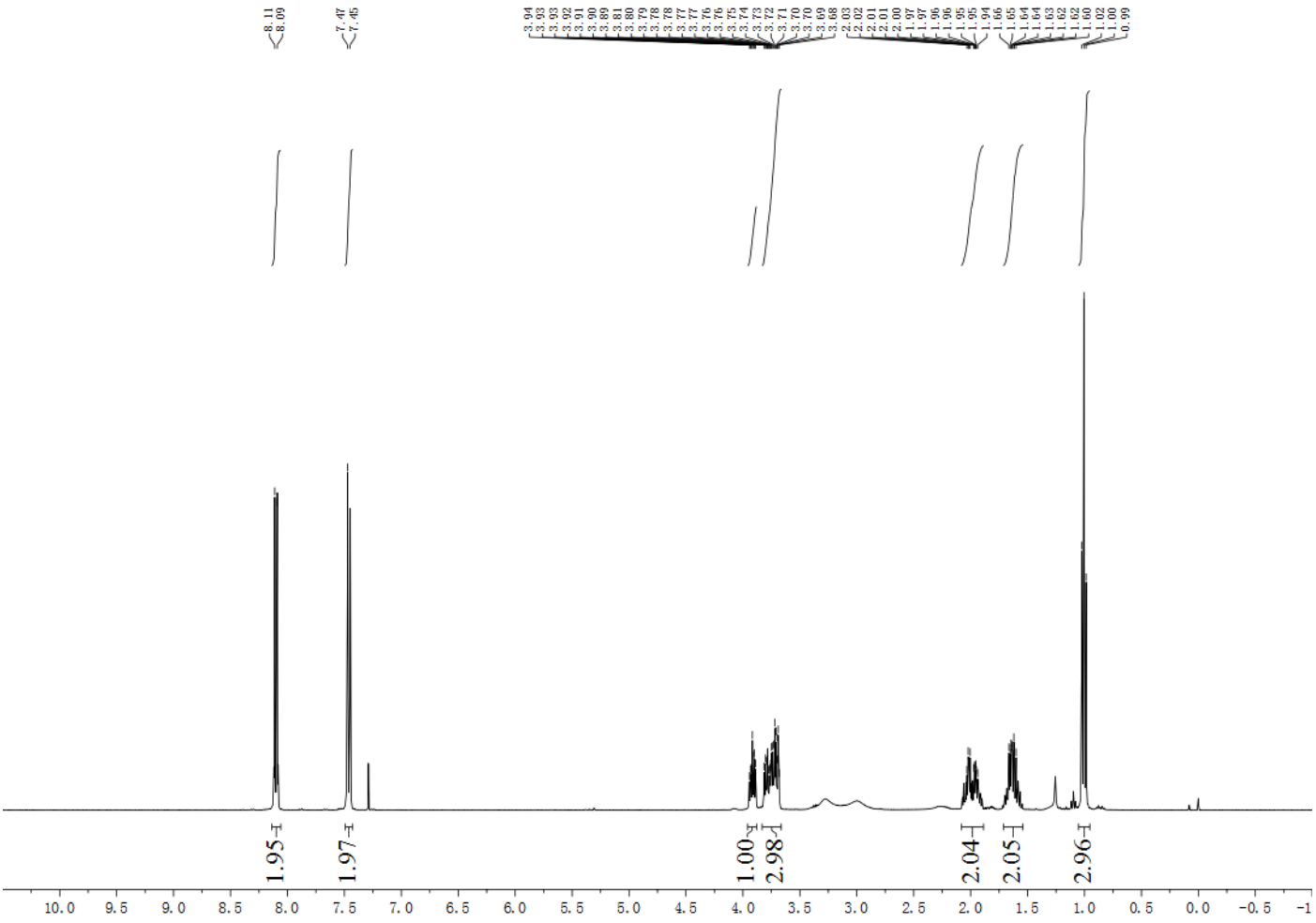
OH
S
NO2

3q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9.0
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8.0
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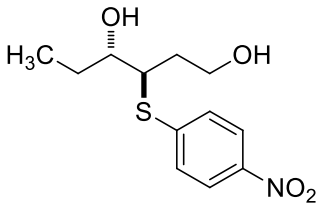
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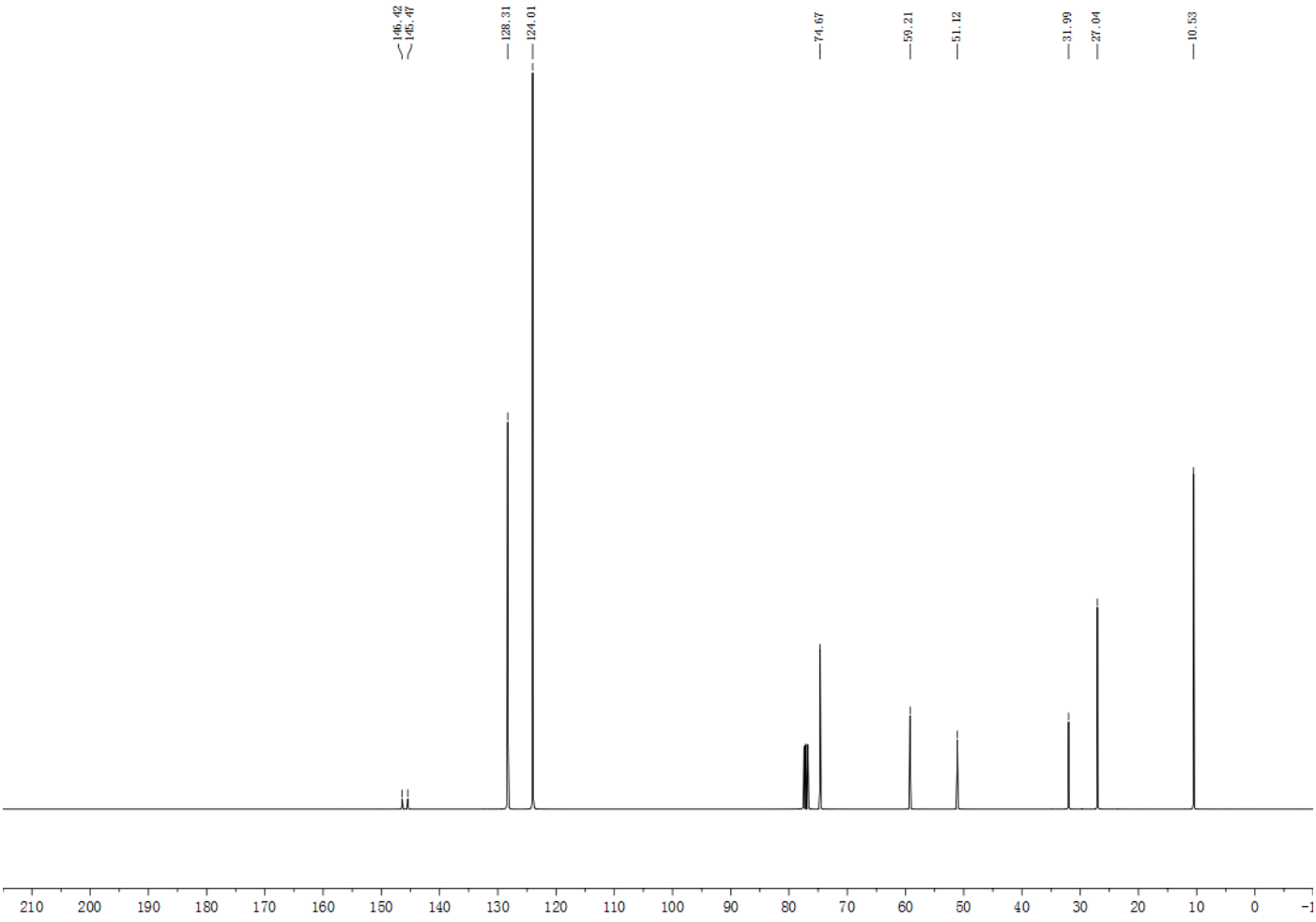
OH
S
NO2

3q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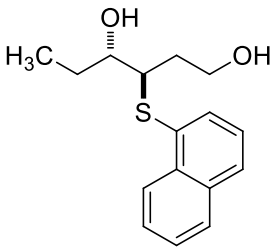

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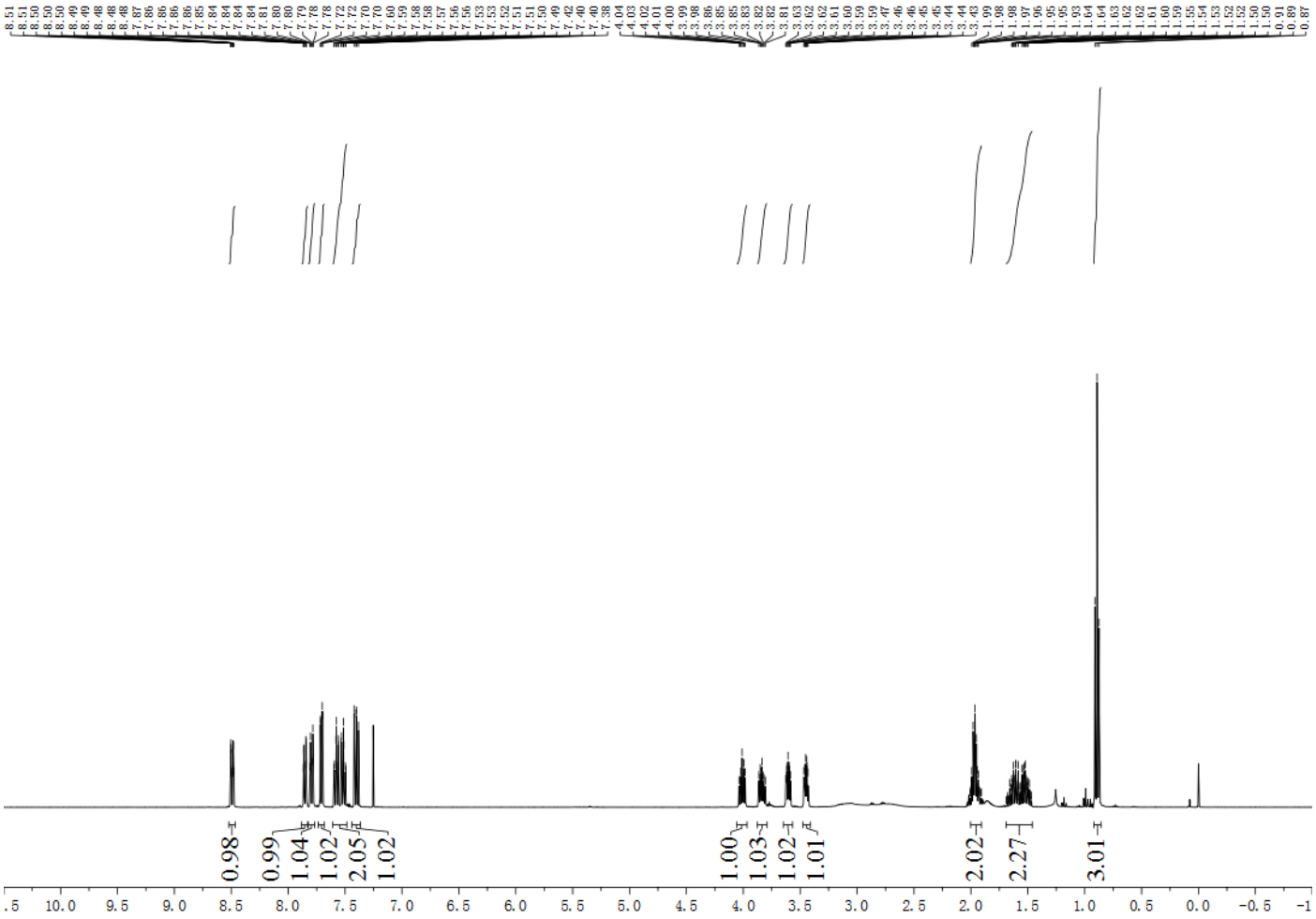

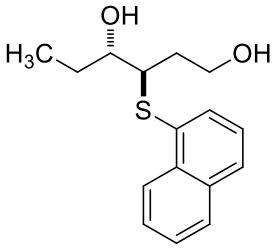
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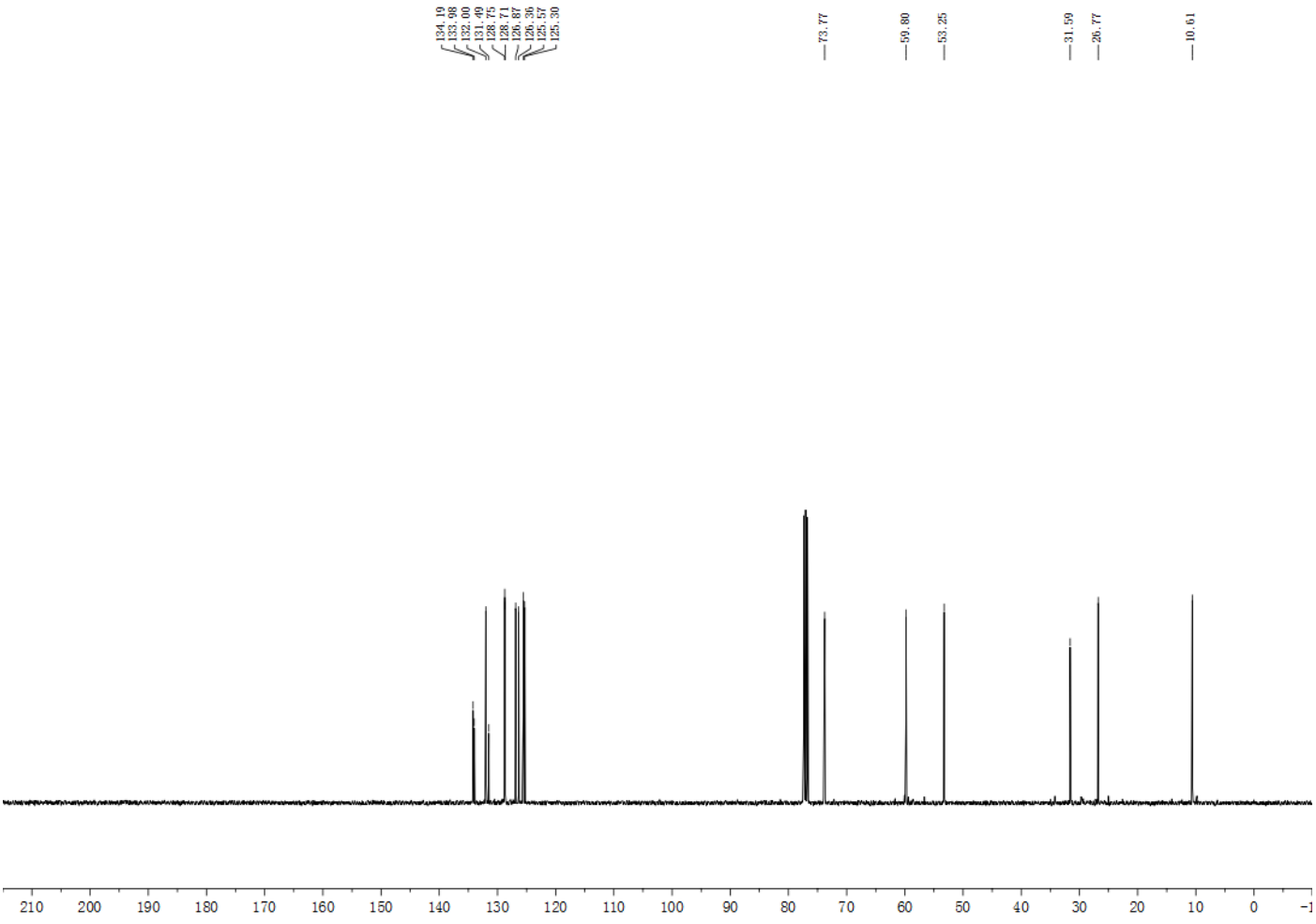
H3C
OH
S

3r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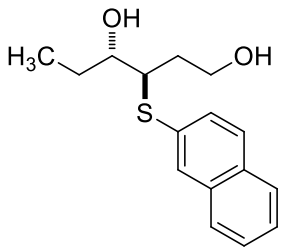

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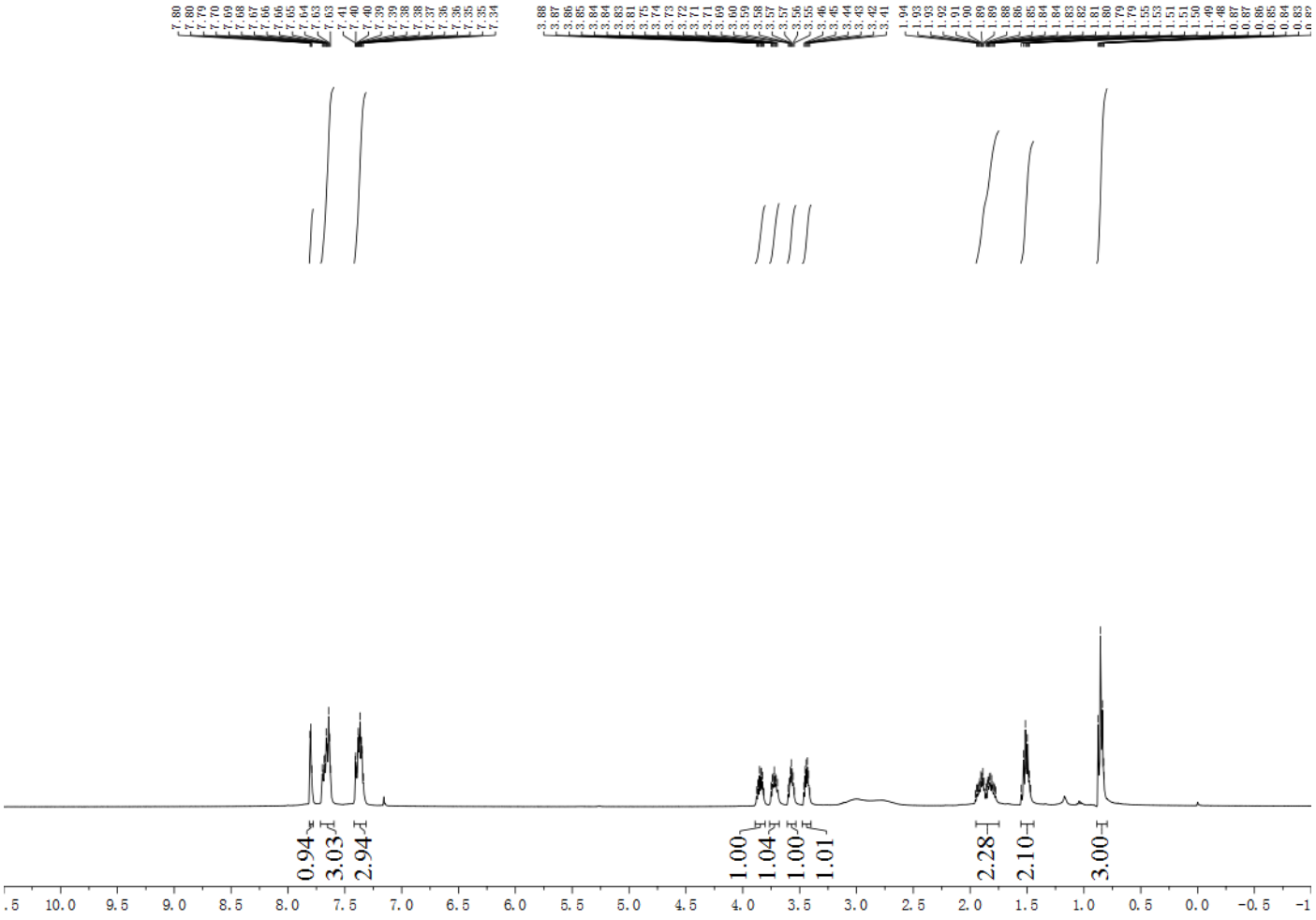

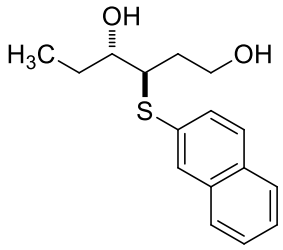
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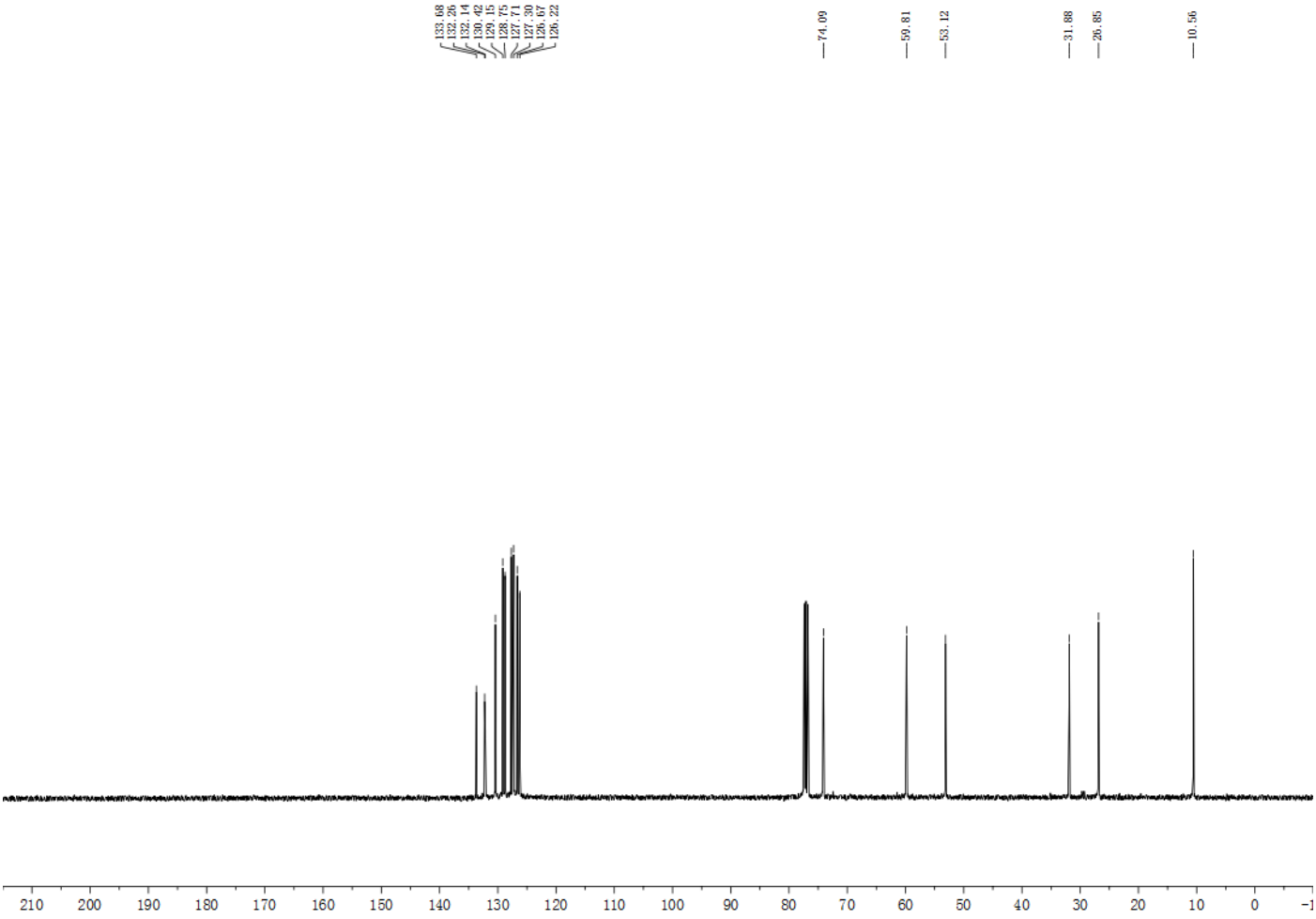
H3C
OH
S

3s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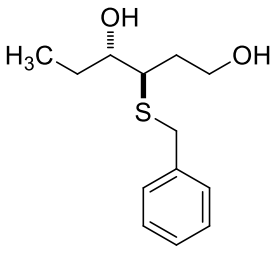
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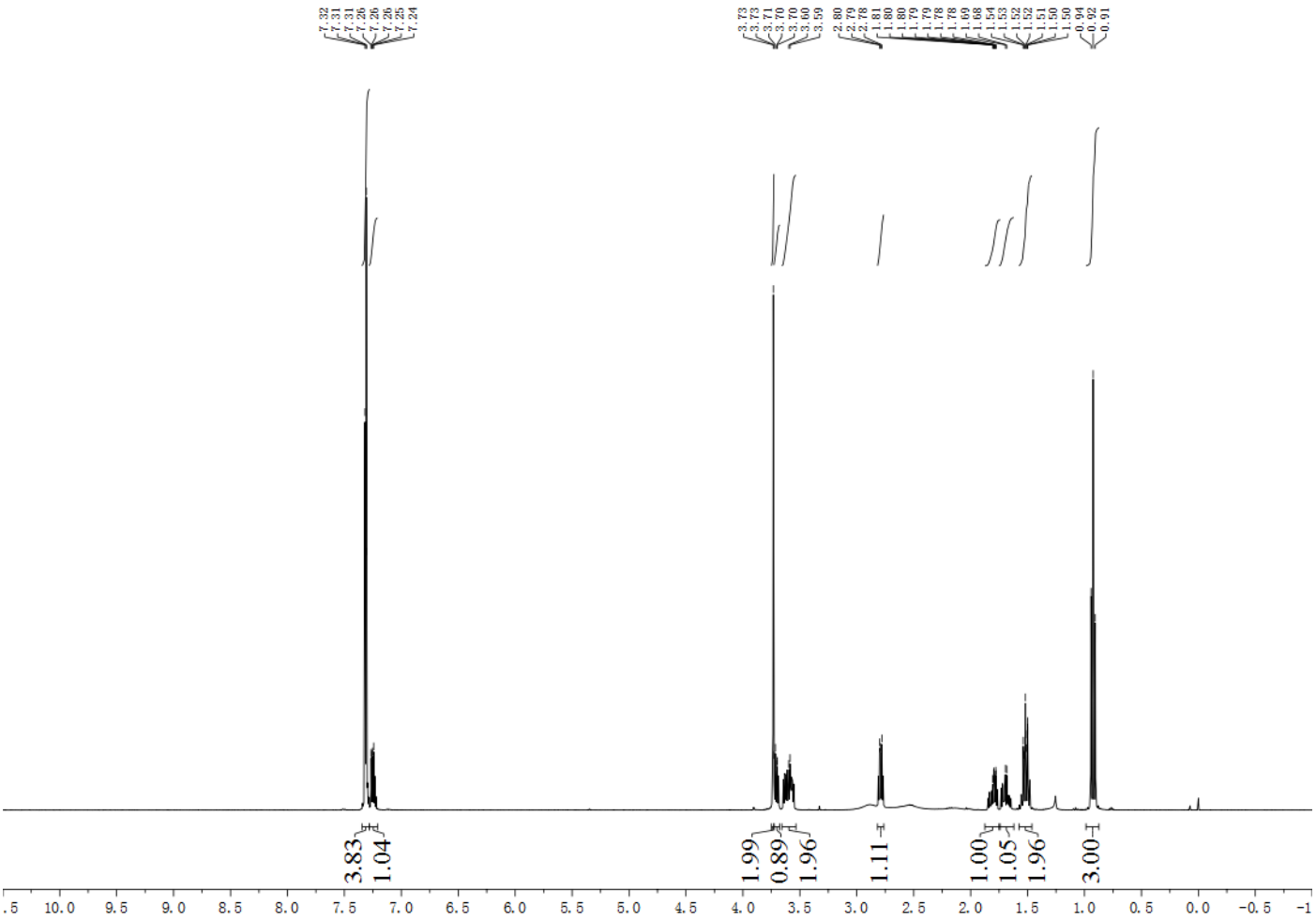
H3C
OH
S

3t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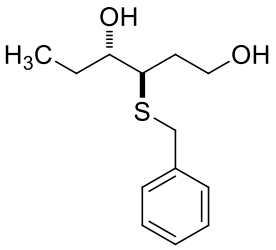
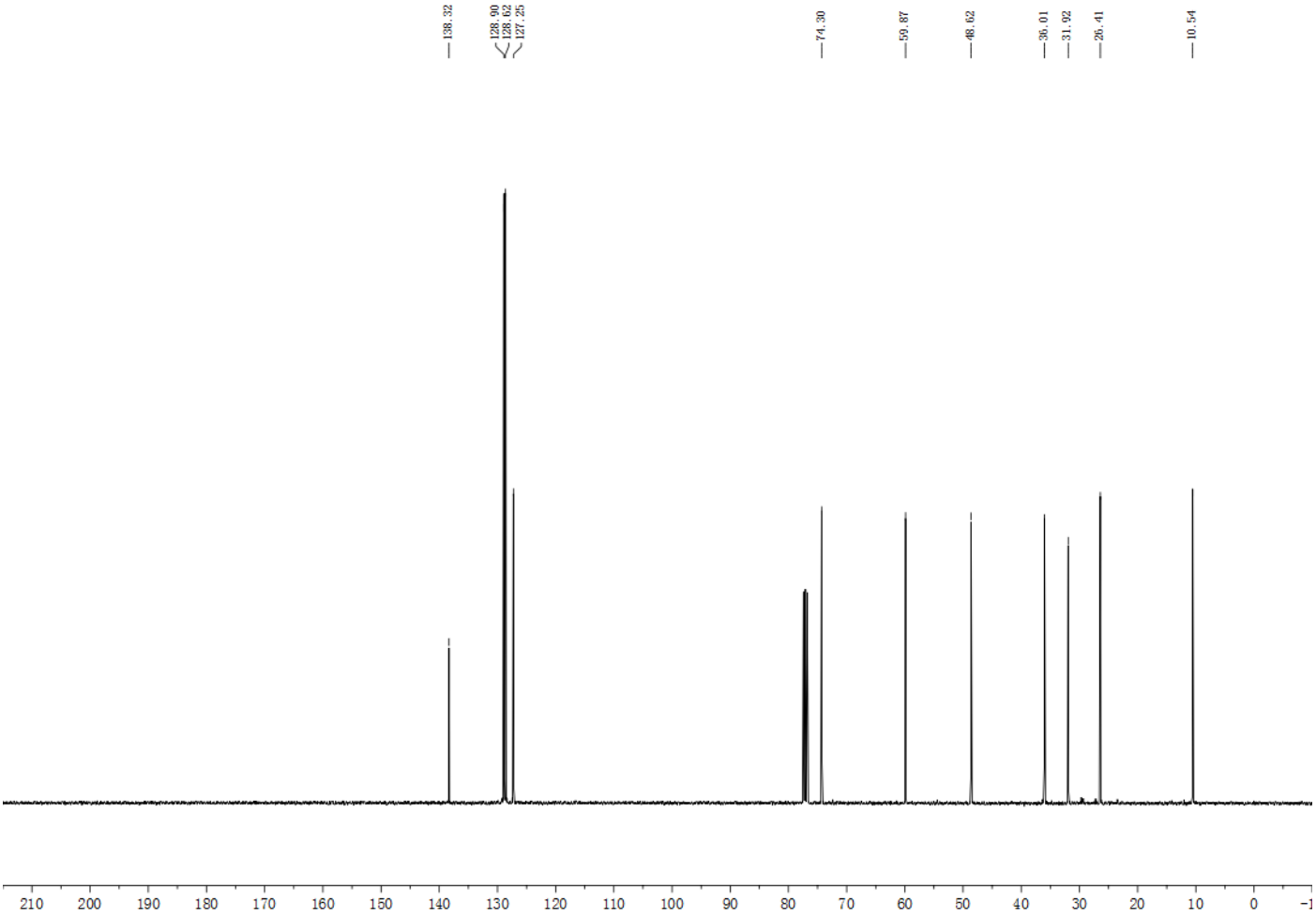
3.00


OH
H3C
OH
S

3t


138.32
128.90
128.62
127.25
74.30
59.87
48.62
36.01
31.92
26.41
10.54
210
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150
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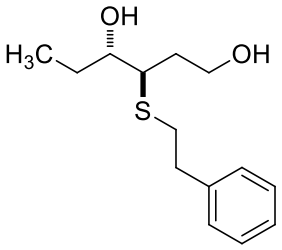
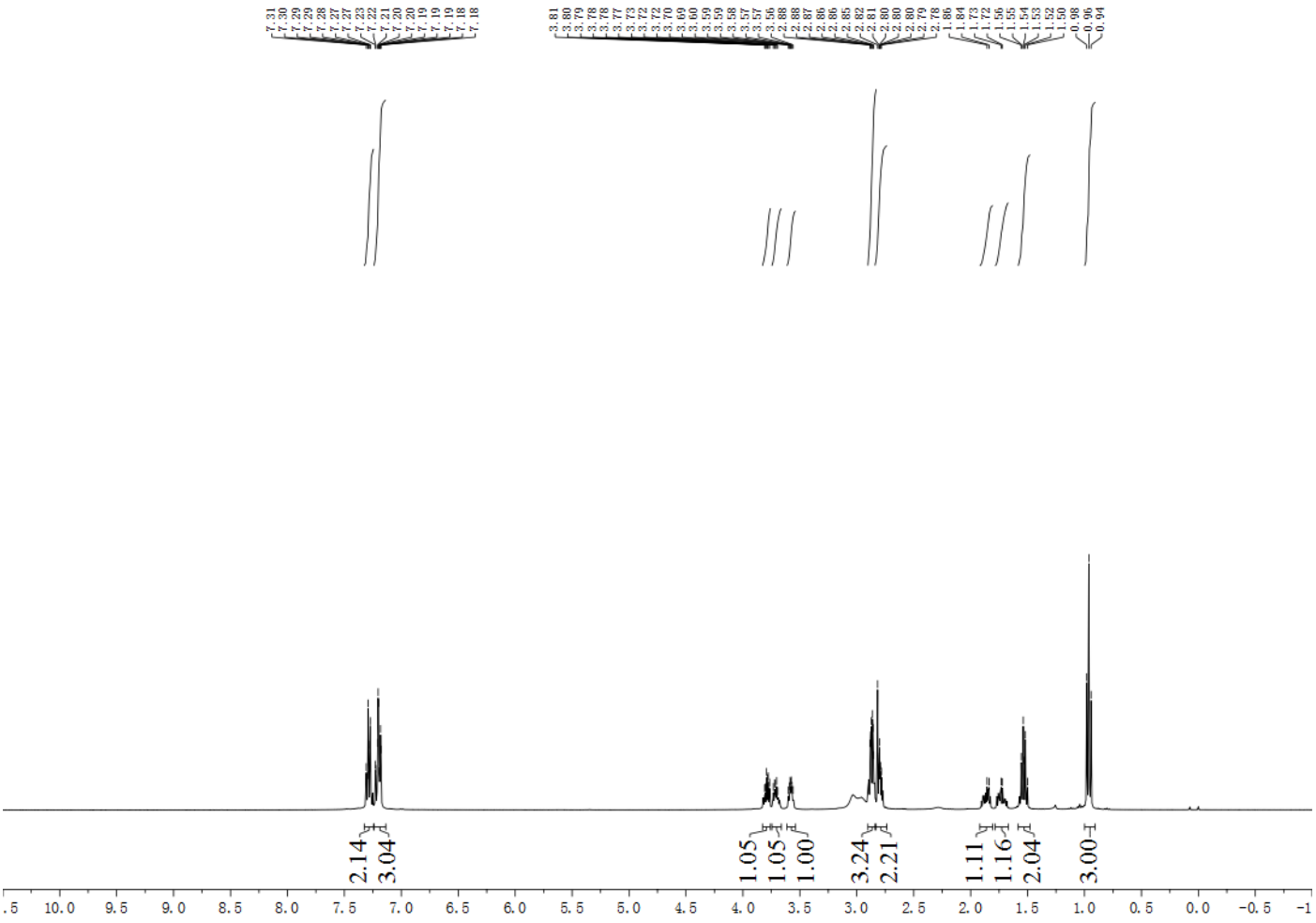
30
20
10
0


OH
H3C
OH
S

3u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7.27
7.23
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.18
3.81
3.80
3.79
3.78
3.78
3.77
3.73
3.72
3.72
3.70
3.69
3.60
3.59
3.59
3.58
3.57
3.57
3.56
2.88
2.87
2.86
2.86
2.85
2.82
2.81
2.80
2.80
2.80
2.79
2.78
1.86
1.84
1.73
1.72
1.56
1.55
1.54
1.53
1.52
1.50
0.98
0.96
0.94
2.14
3.04
1.05
1.05
1.00
3.24
2.21
1.11
1.16
2.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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1.0
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0.0
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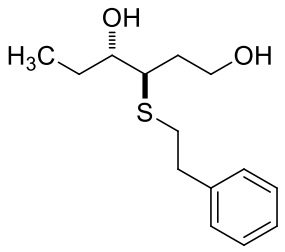
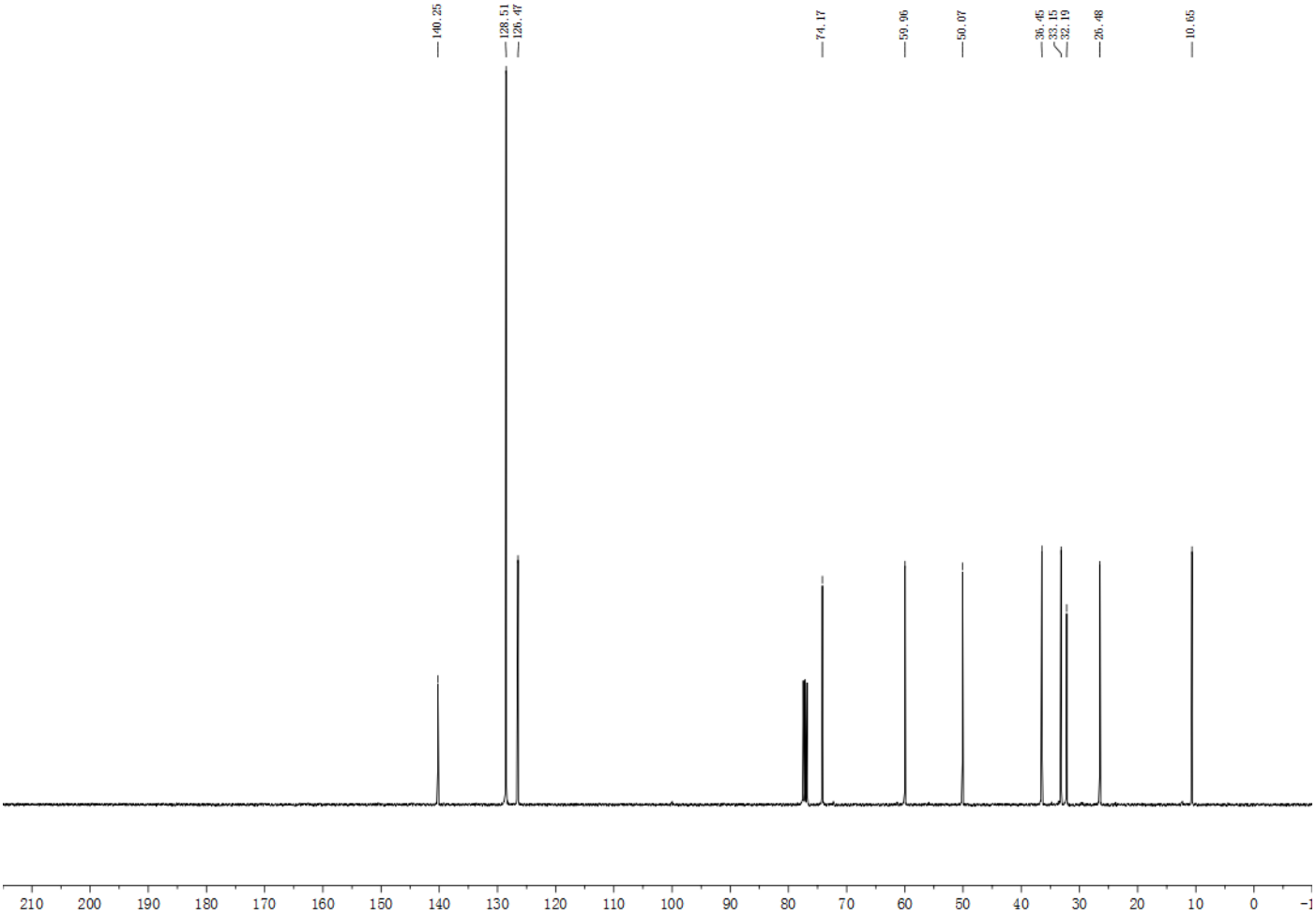
-1


OH
H3C
OH
S

3u


140.25
128.51
126.47
74.17
59.96
50.07
36.45
33.15
32.19
26.48
10.65
210
200
190
180
170
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150
140
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110
100
90
80
70
60
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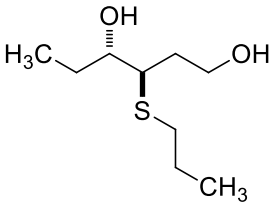
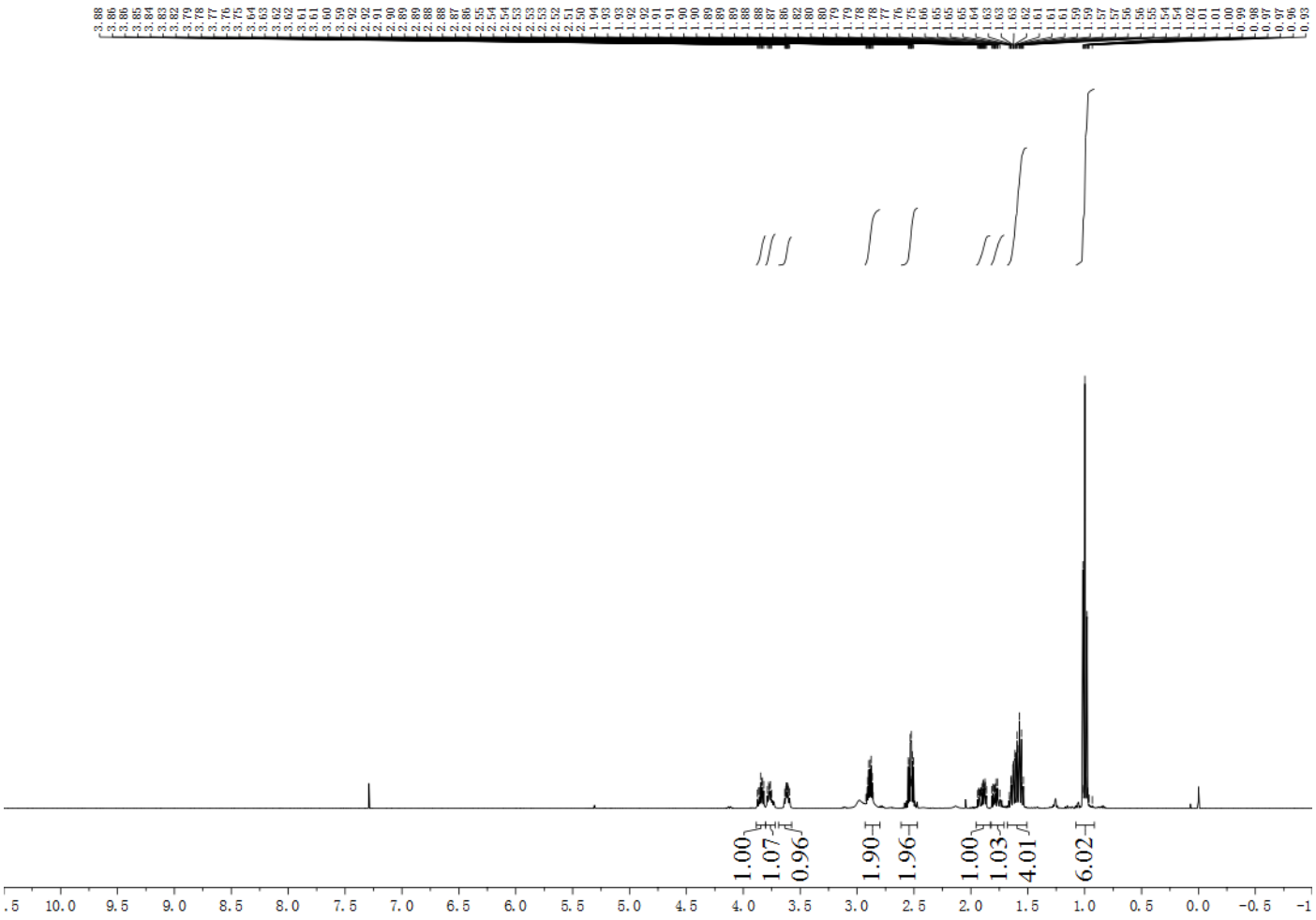
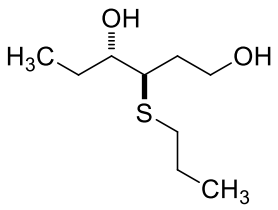
40
30
20
10
0

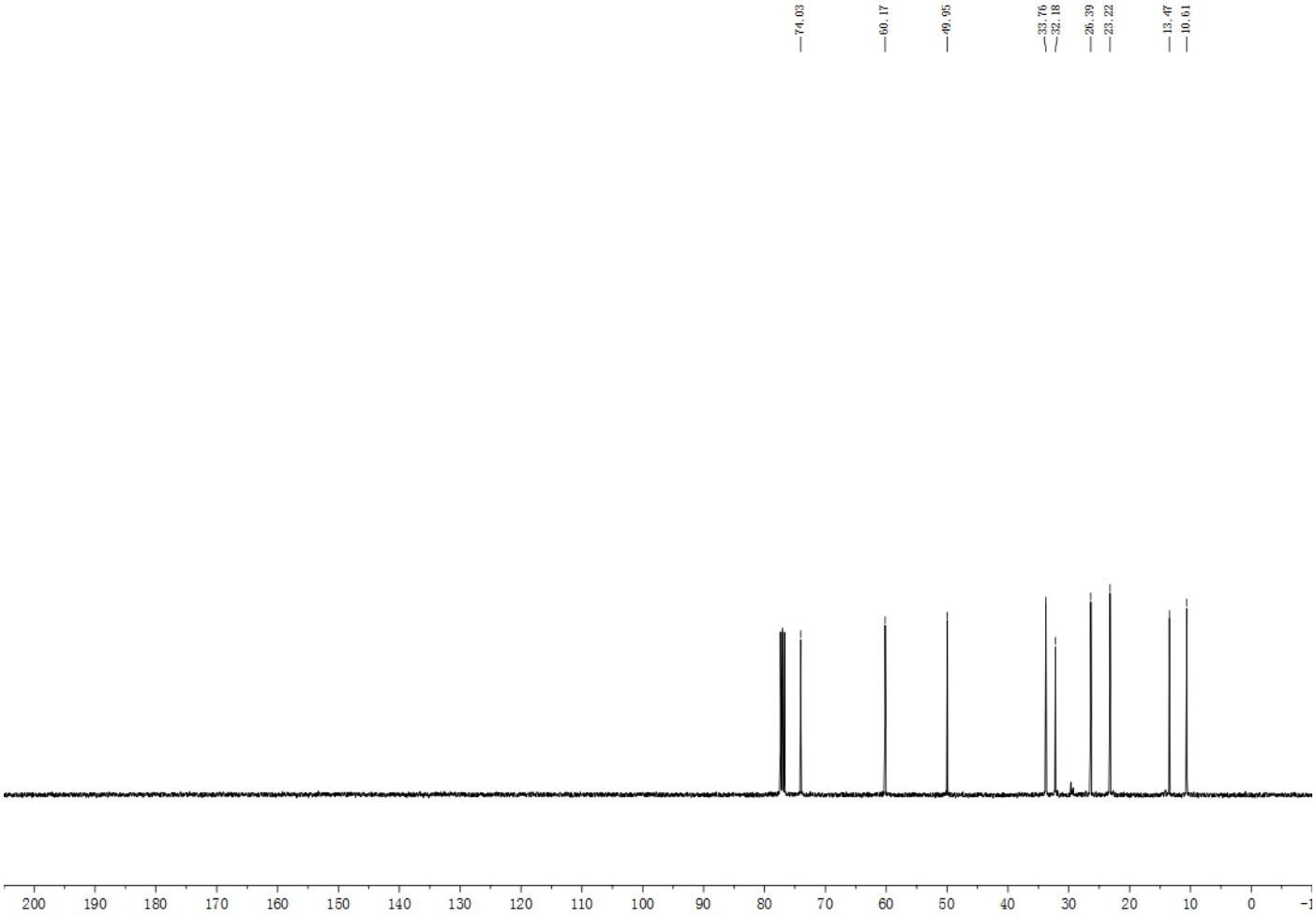


3v




OH
H3C
OH
S
CH3

3v


74.03
60.17
49.95
33.76
32.18
26.39
23.22
13.47
10.61
200
190
180
170
160
150
140
130
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110
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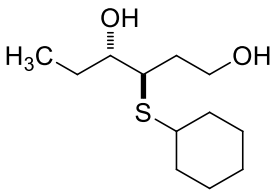
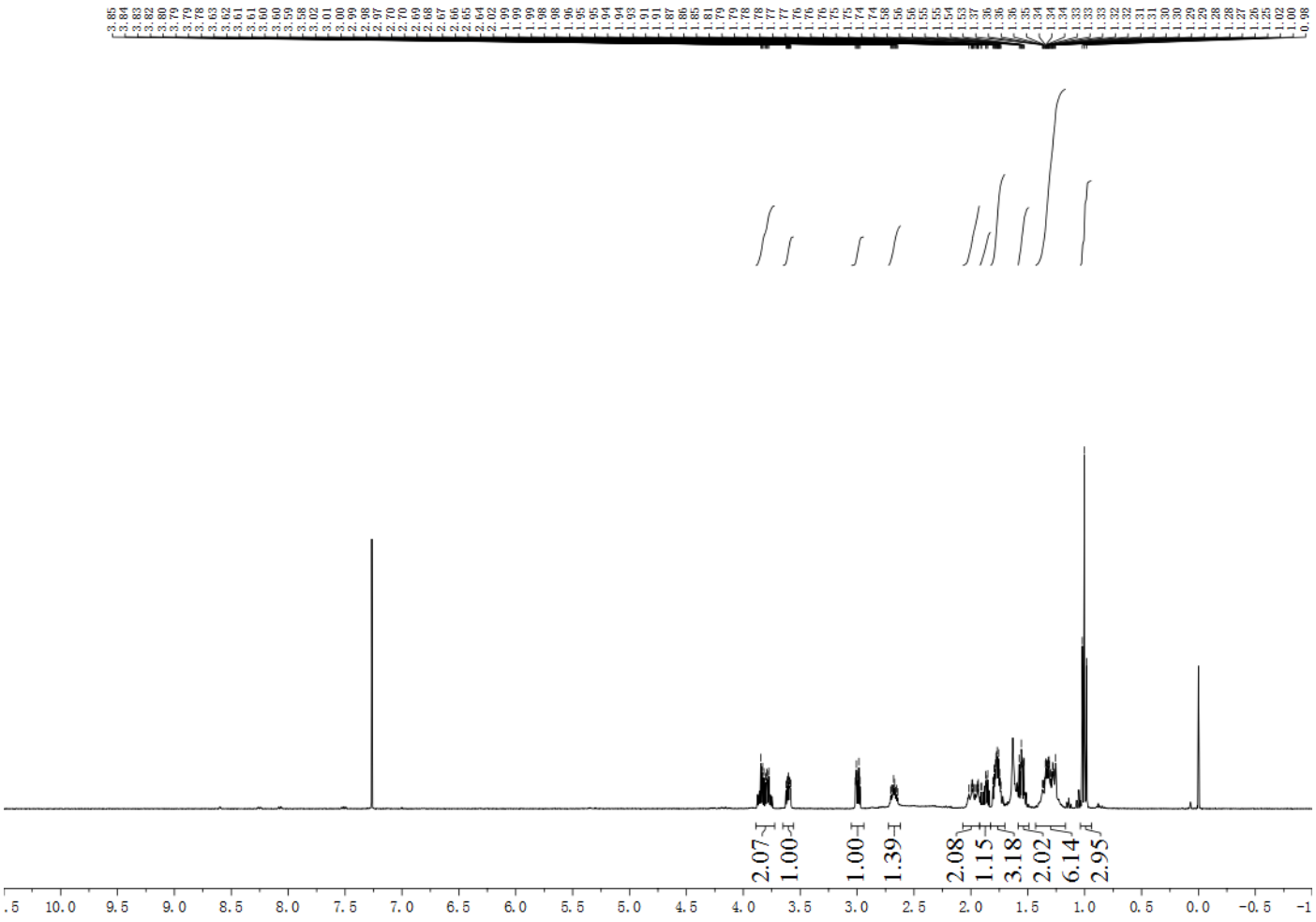
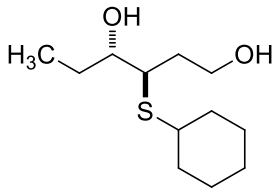
40
30
20
10
0

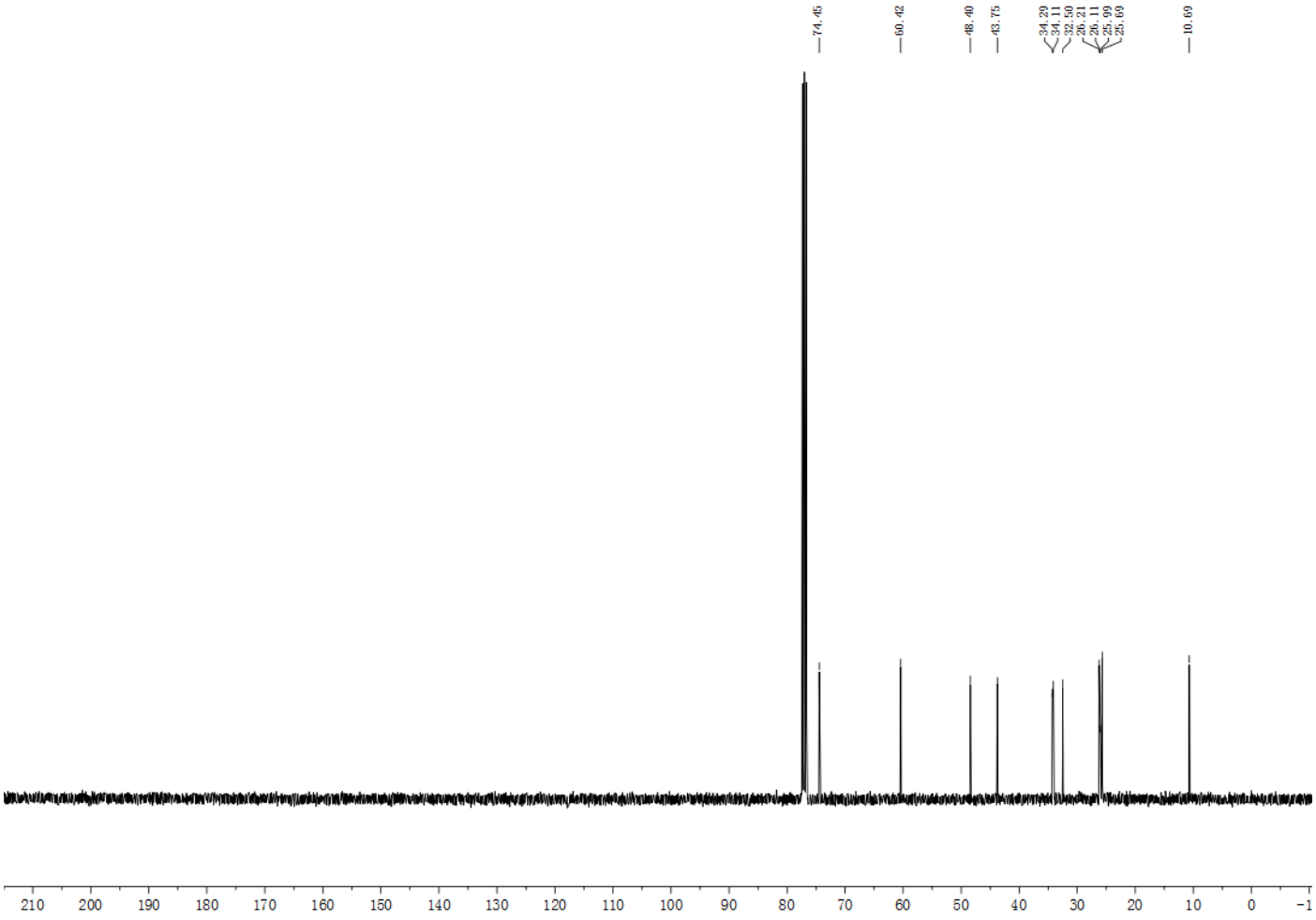


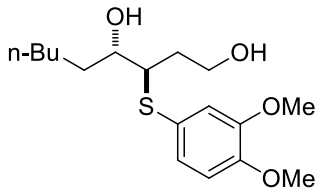
3w



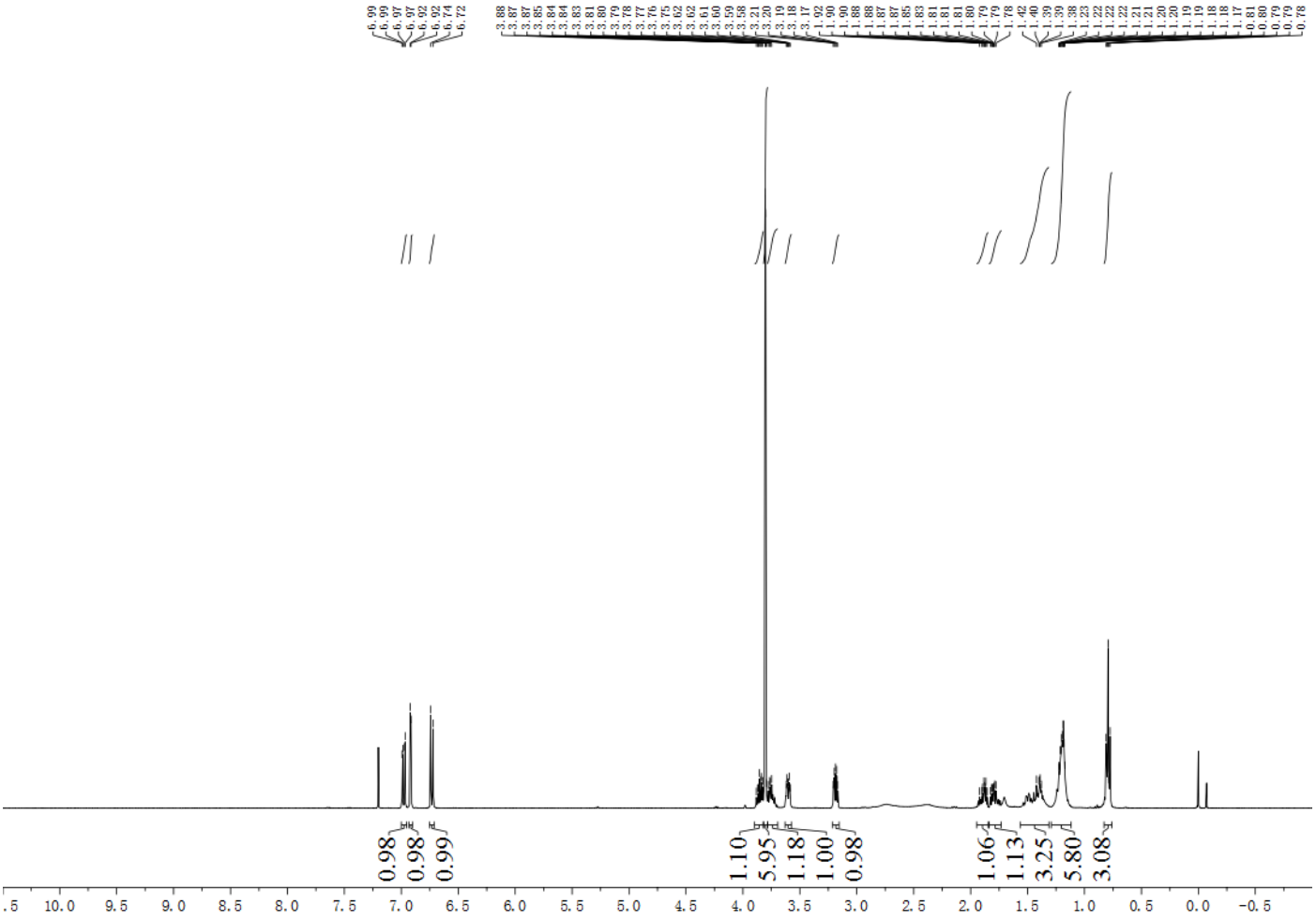

OH
H3C
OH
S

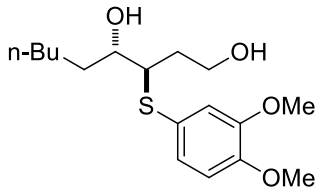
3w


74.45
60.42
48.40
43.75
34.29
34.11
32.50
26.21
26.11
25.99
25.69
10.69
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

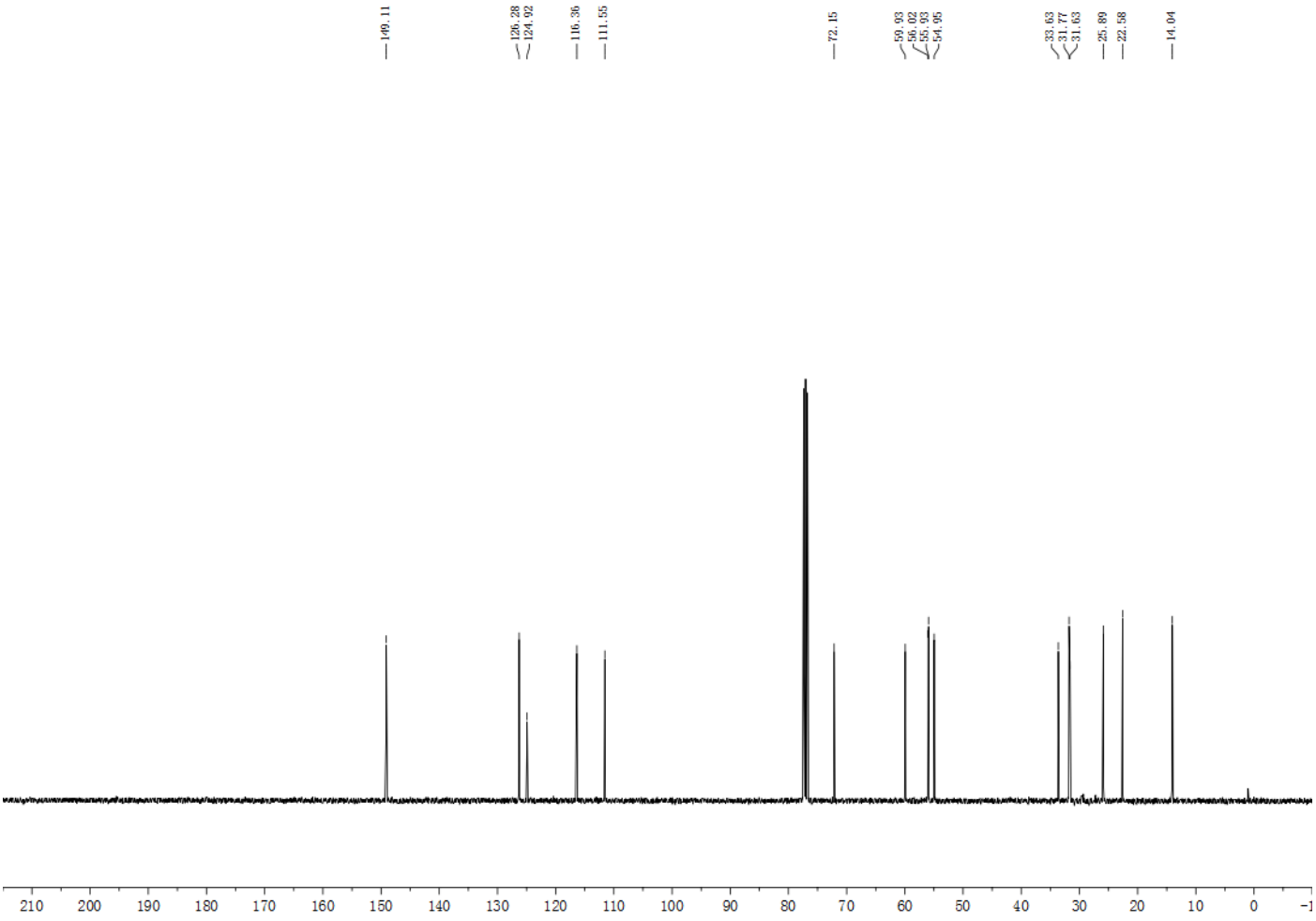

OH
n-Bu
OH
S
OMe
OMe

3x


0.98
0.98
0.99
1.10
5.95
1.18
1.00
0.98
1.06
1.13
3.25
5.80
3.08


OH
n-Bu
OH
S
OMe
OMe

3x


149.11
126.28
124.92
116.36
111.55
72.15
59.93
56.02
55.93
54.95
33.63
31.77
31.63
25.89
22.58
14.04
210
200
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150
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110
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70
60
50
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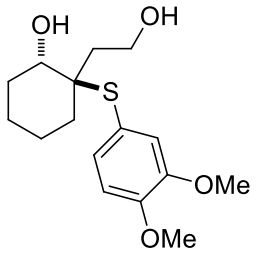
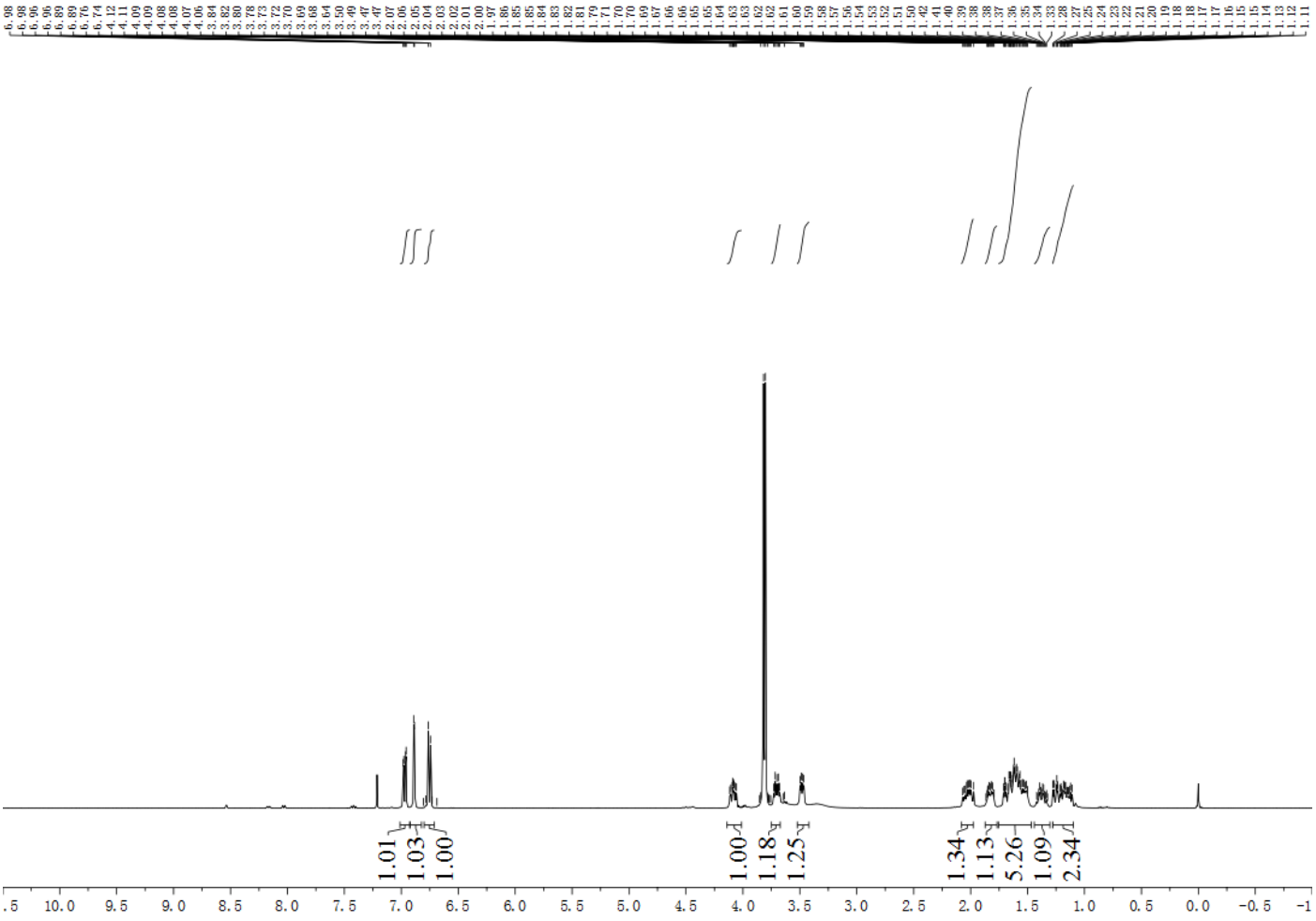
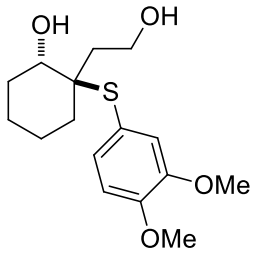
30
20
10
0

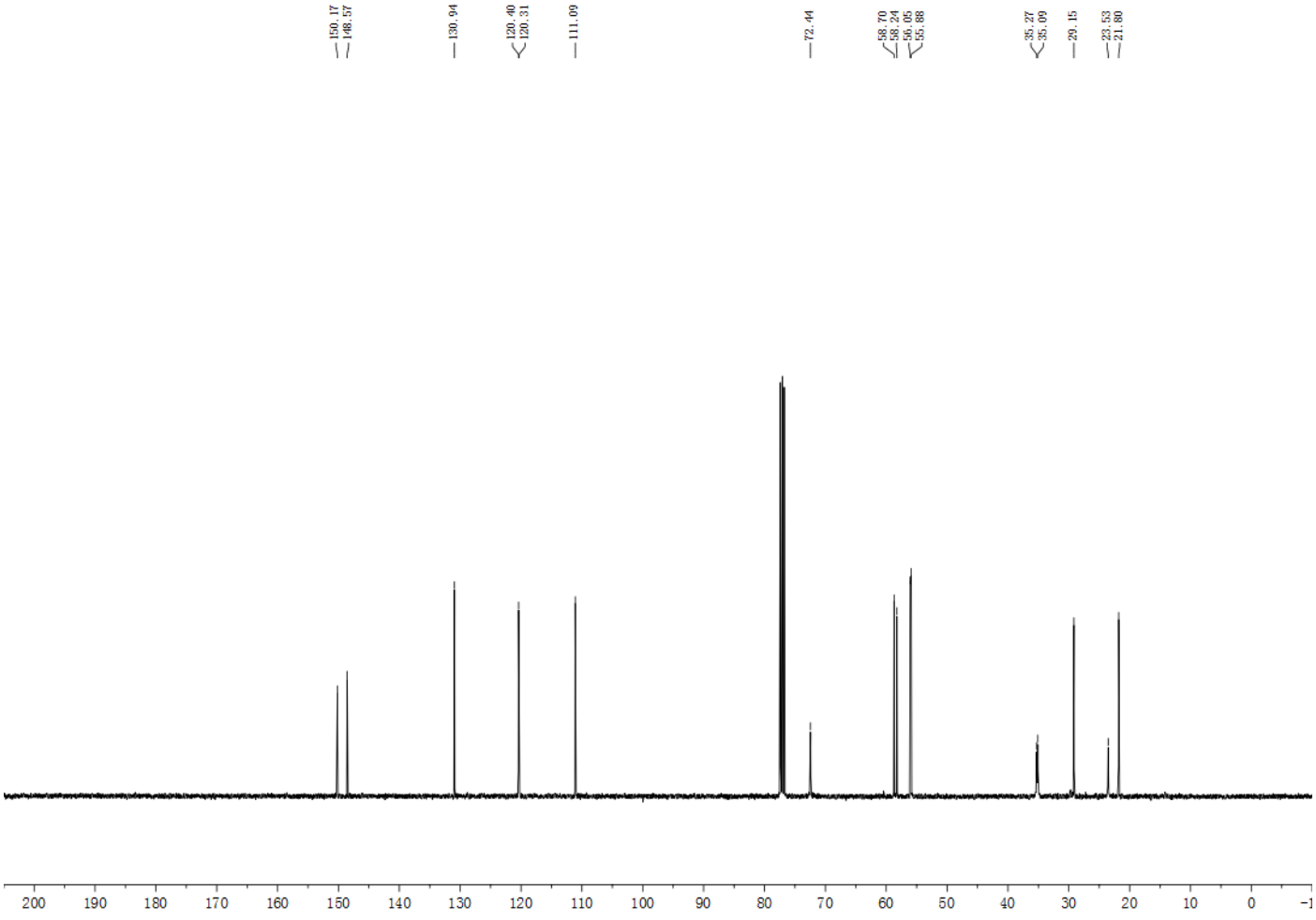


3y

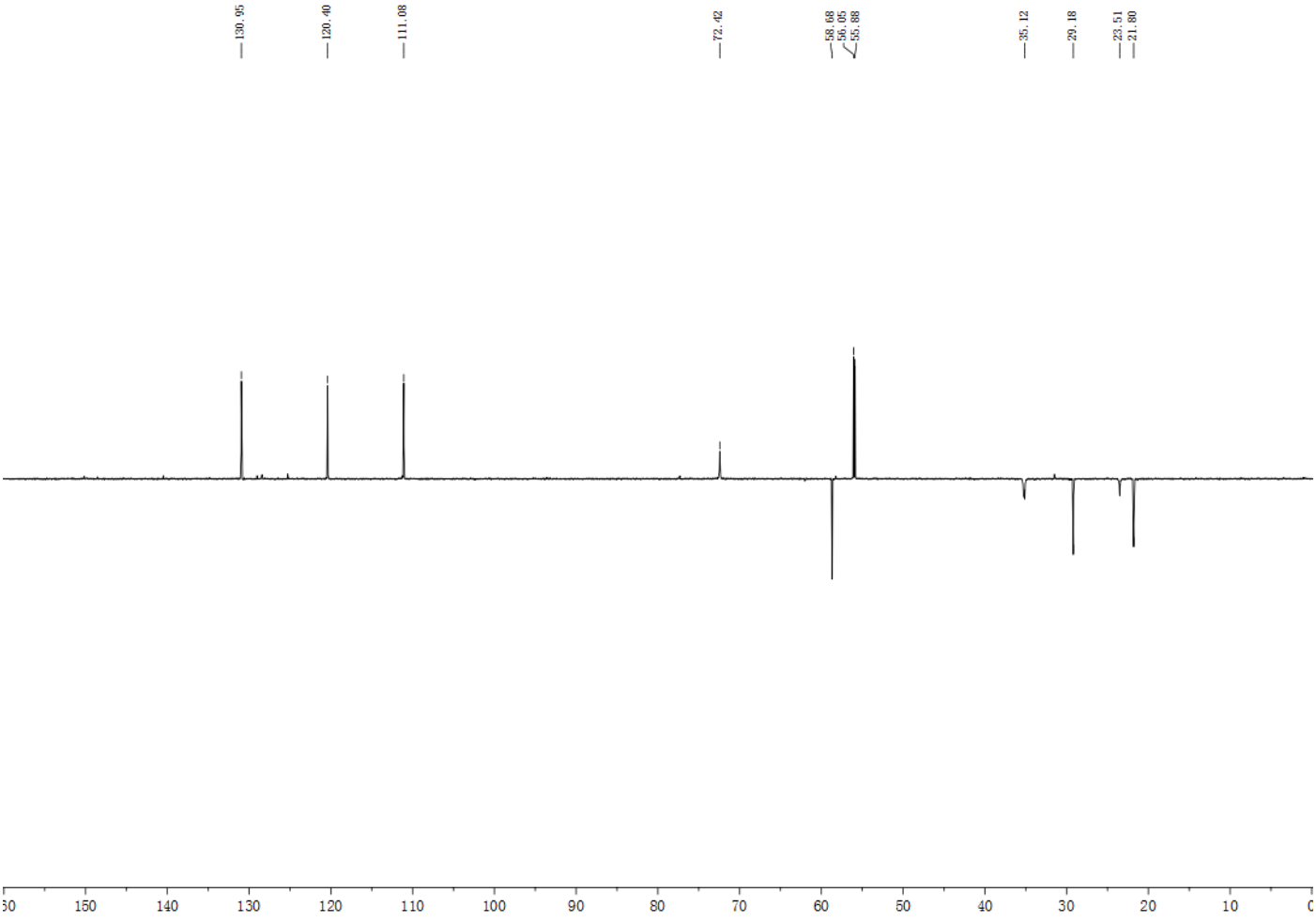


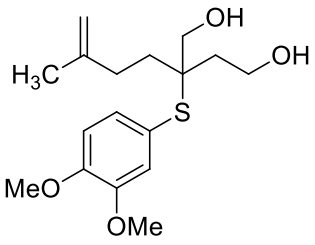

OH
OH
S
OMe
OMe

3y

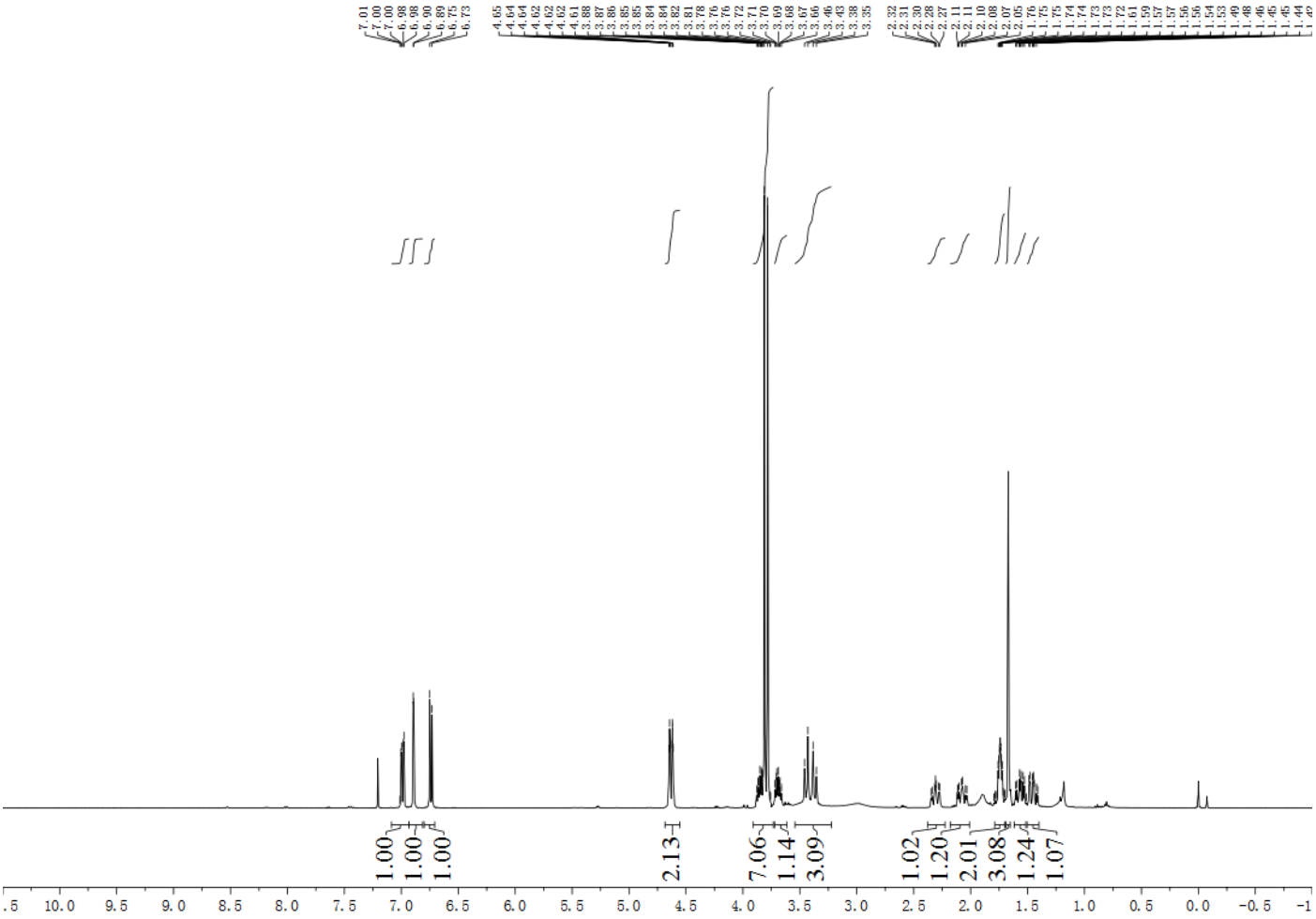

150.17
148.57
130.94
120.40
120.31
111.09
72.44
58.70
58.24
56.05
55.88
35.27
35.09
29.15
23.53
21.80
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

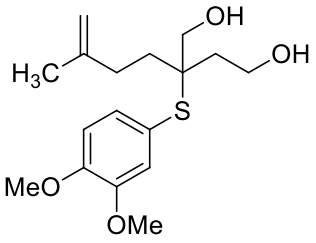
DEPT 135° spectrum of 3y



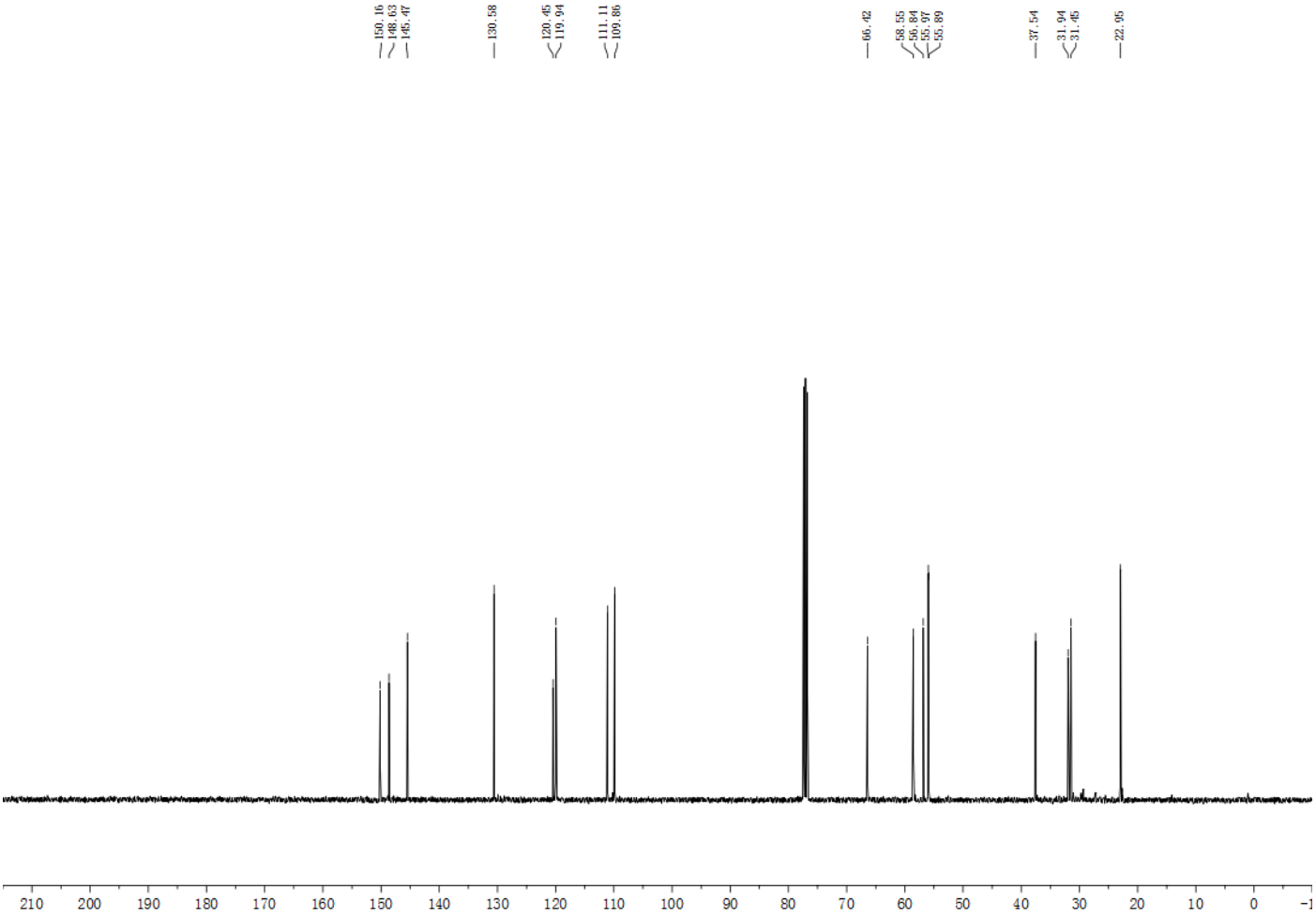

OH
OH
H_3C
S
MeO
OMe

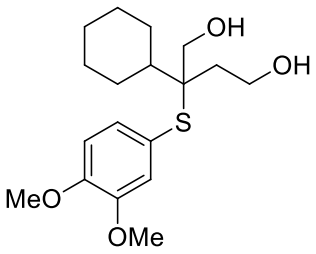
3z


1.00
1.00
1.00
2.13
7.06
1.14
3.09
1.02
1.20
2.01
3.08
1.24
1.07

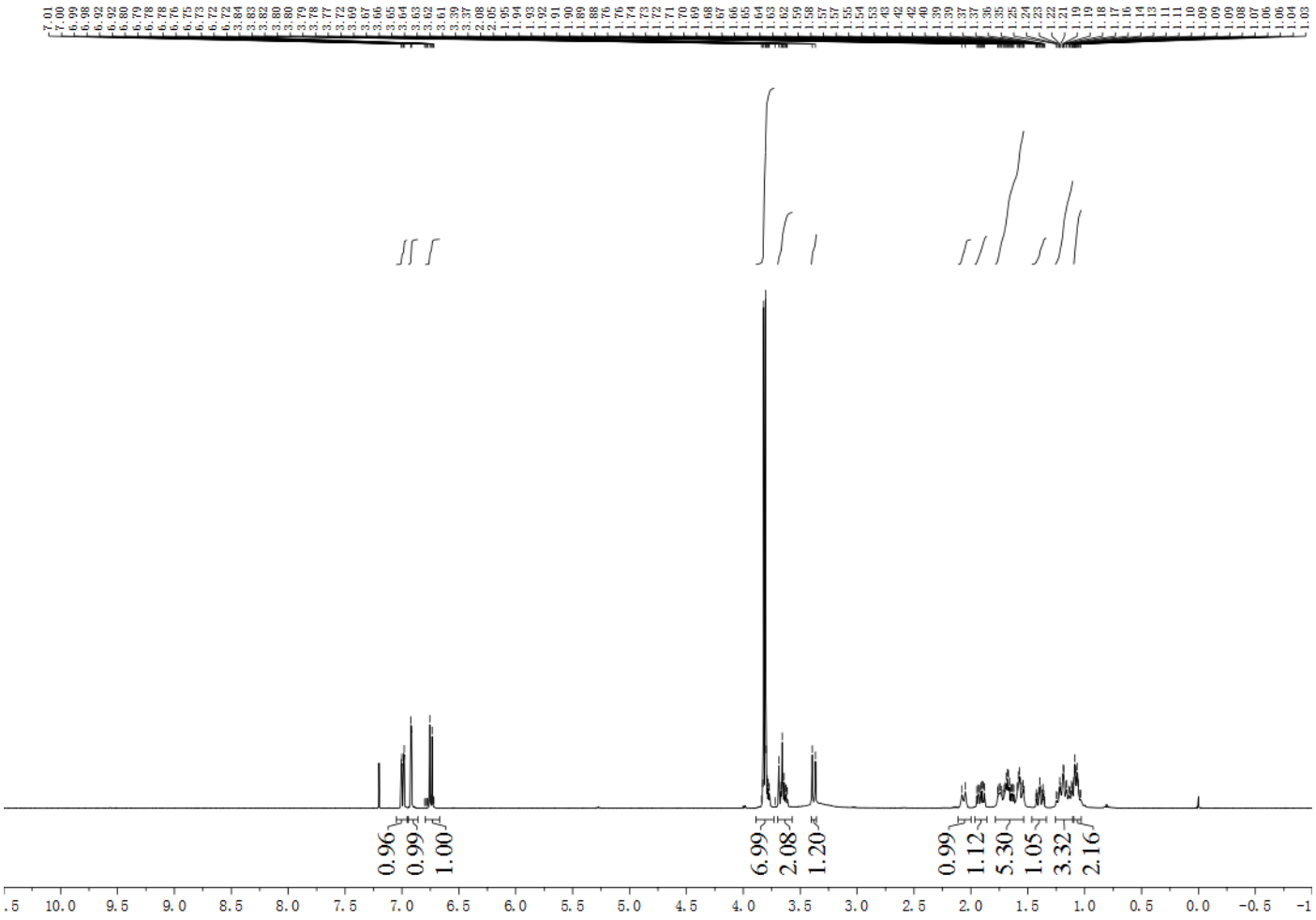

OH
H3C
OH
S
MeO
OMe

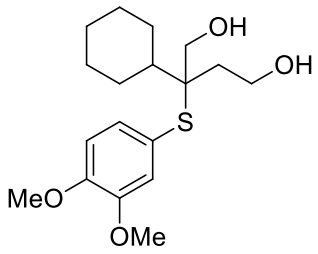
3z


150.16
148.63
145.47
130.58
120.45
119.94
111.11
109.86
66.42
58.55
56.84
55.97
55.89
37.54
31.94
31.45
22.95
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

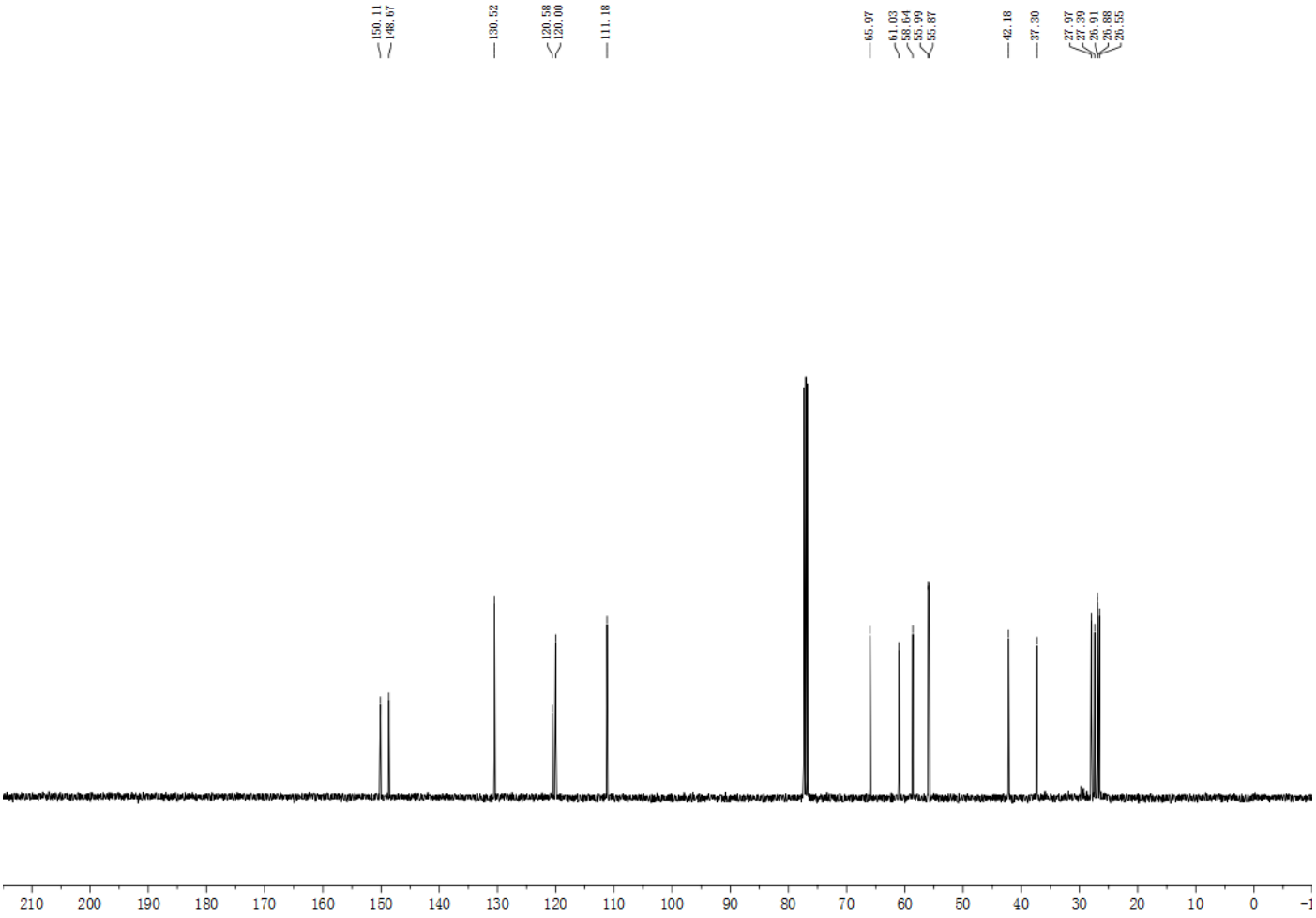


3aa

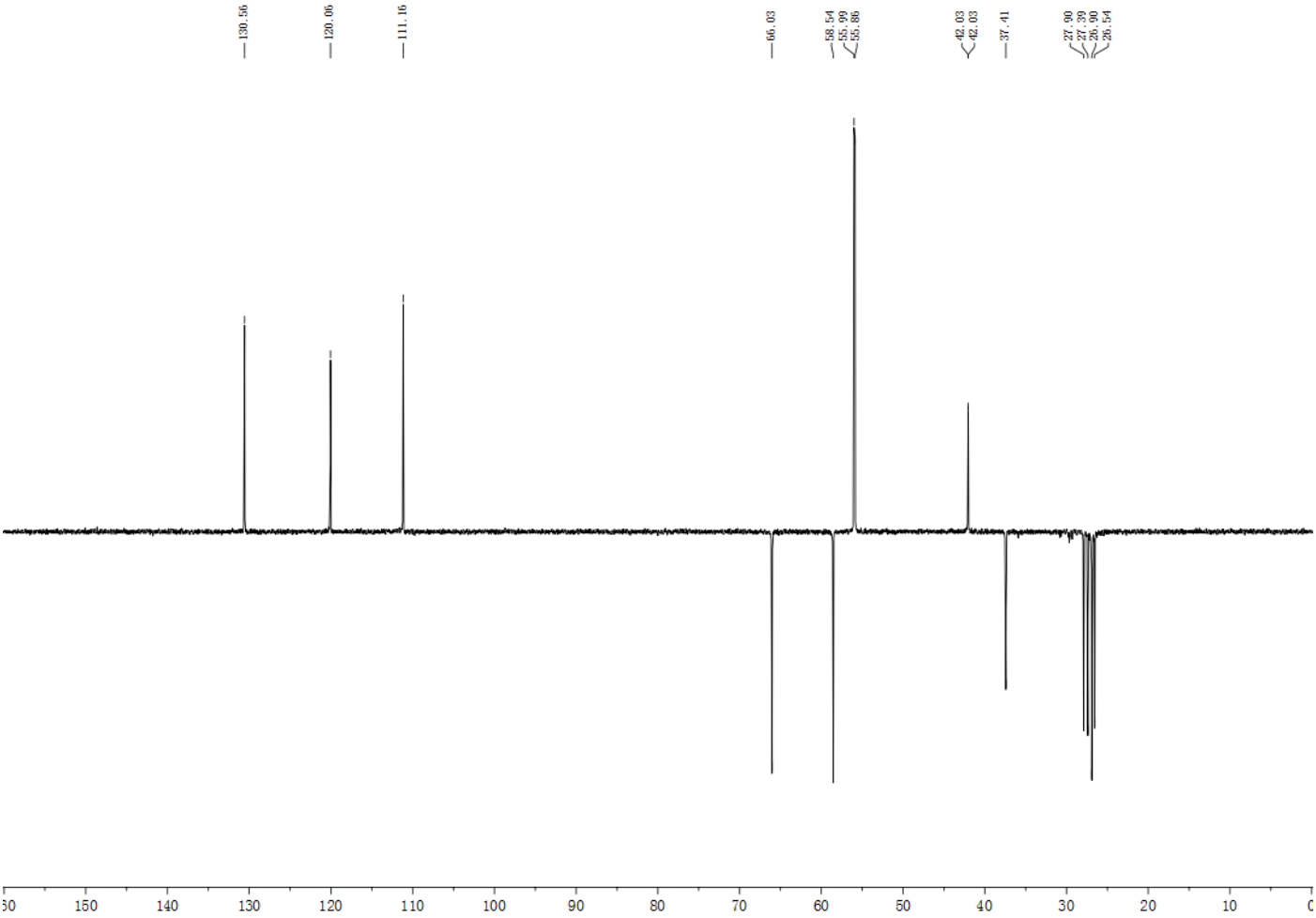


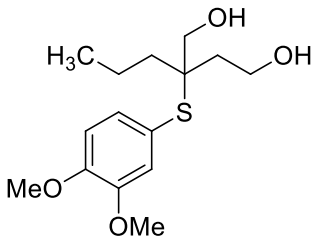

OH
OH
S
MeO
OMe

3aa

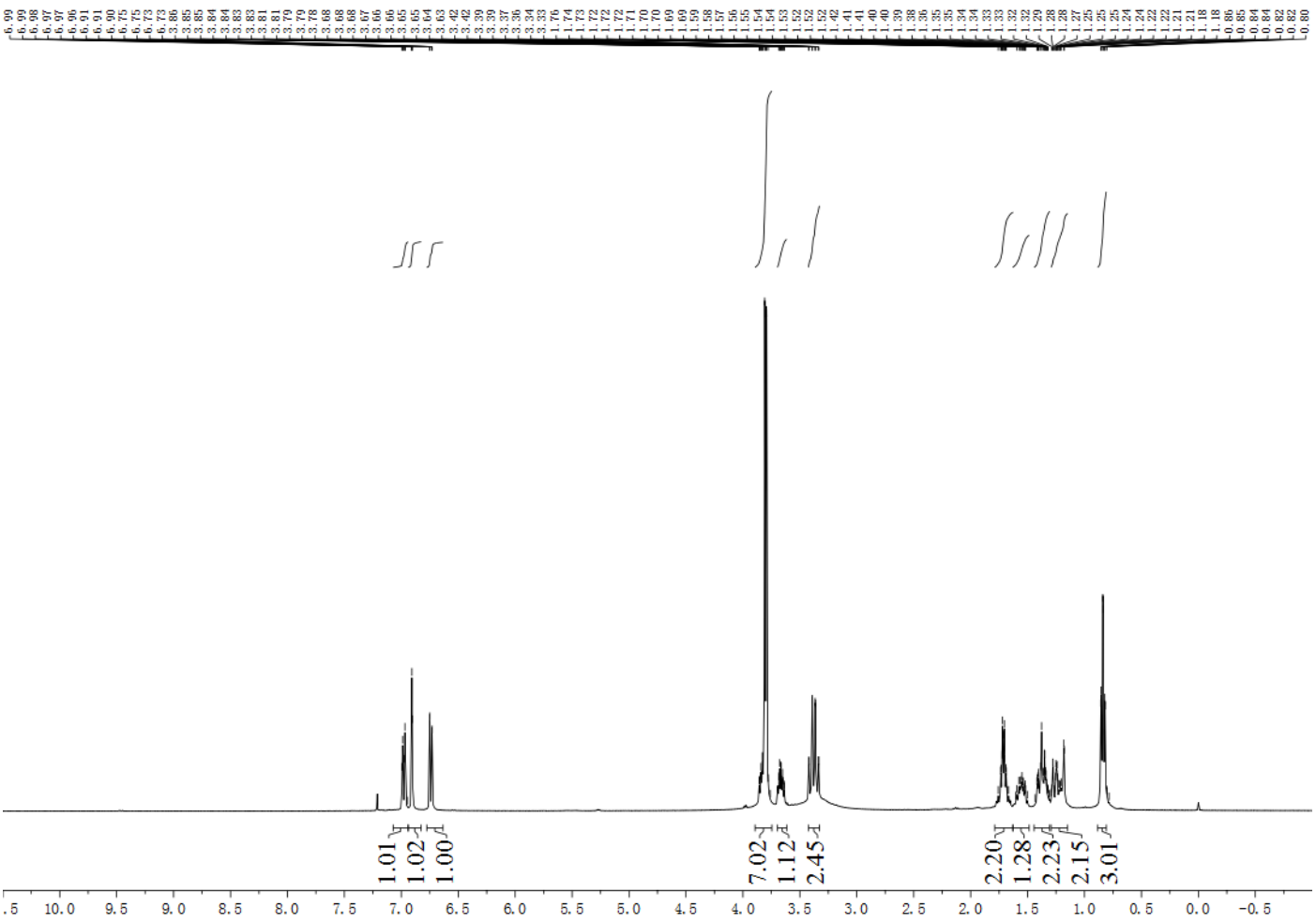

150.11
148.67
130.52
120.58
120.00
111.18
65.97
61.03
58.64
55.99
55.87
42.18
37.30
27.97
27.39
26.91
26.88
26.55
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

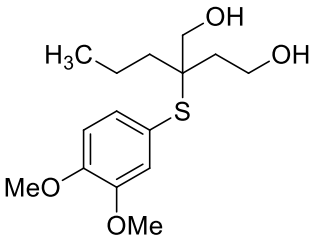
DEPT 135° spectrum of 3aa



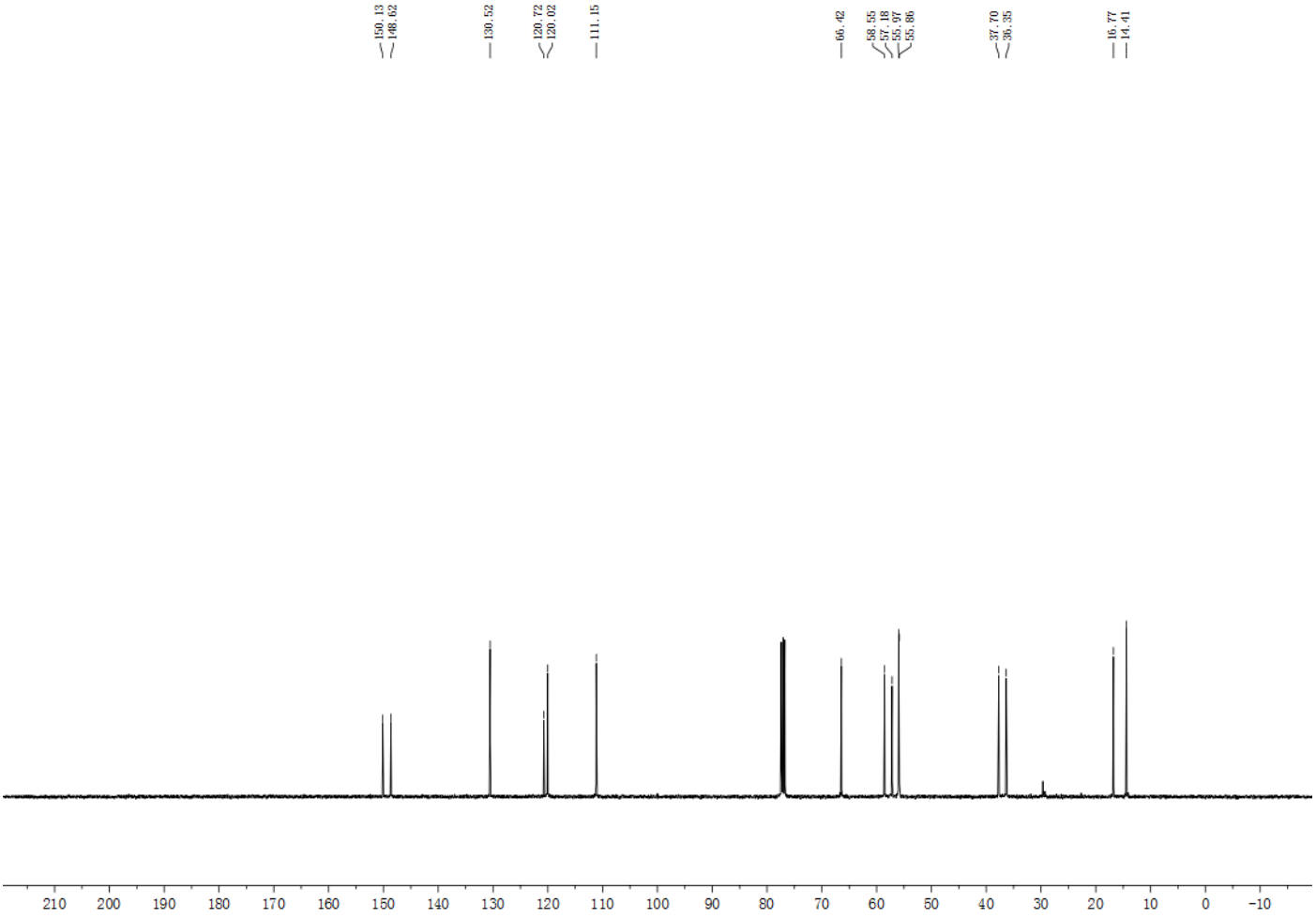


3ab




OH
H3C
OH
S
MeO
OMe

3ab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148.62
130.52
120.72
120.02
111.15
66.42
58.55
57.18
55.97
55.86
37.70
36.35
16.77
14.41
210
200
190
180
170
160
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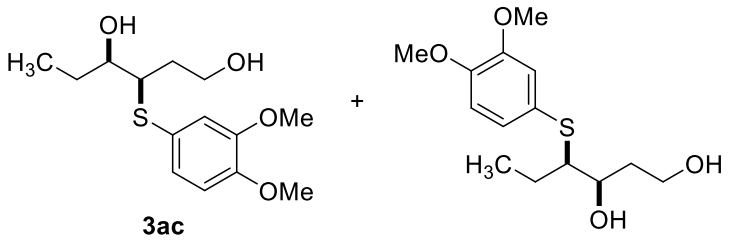
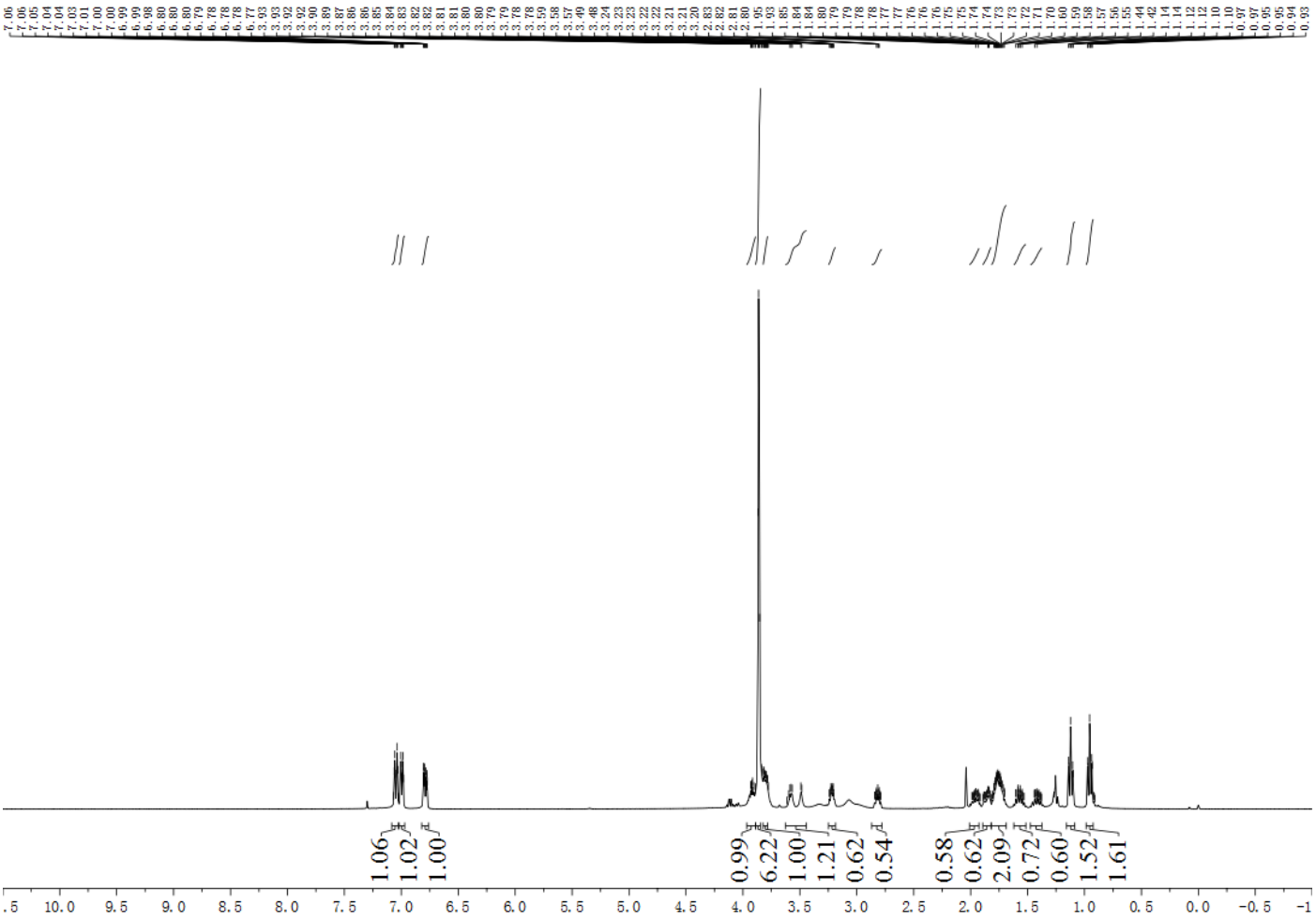
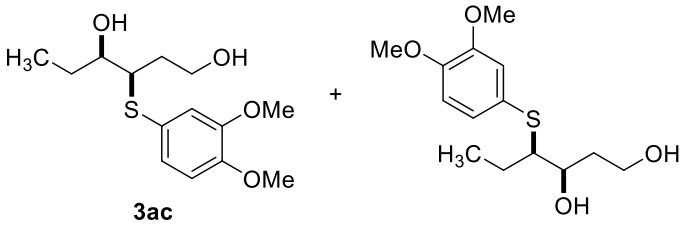
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


OH
H3C
OH
S
OMe
OMe
+
OMe
MeO
S
H3C
OH
OH

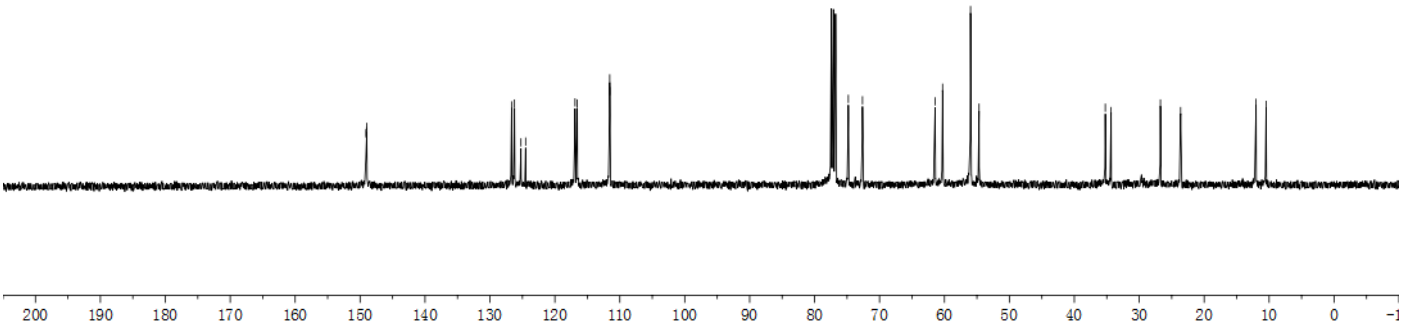
3ac

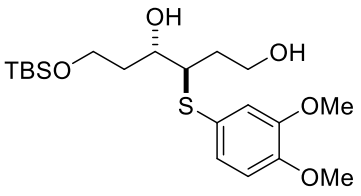

1.06
1.02
1.00
0.99
6.22
1.00
1.21
0.62
0.54
0.58
0.62
2.09
0.72
0.60
1.52
1.61



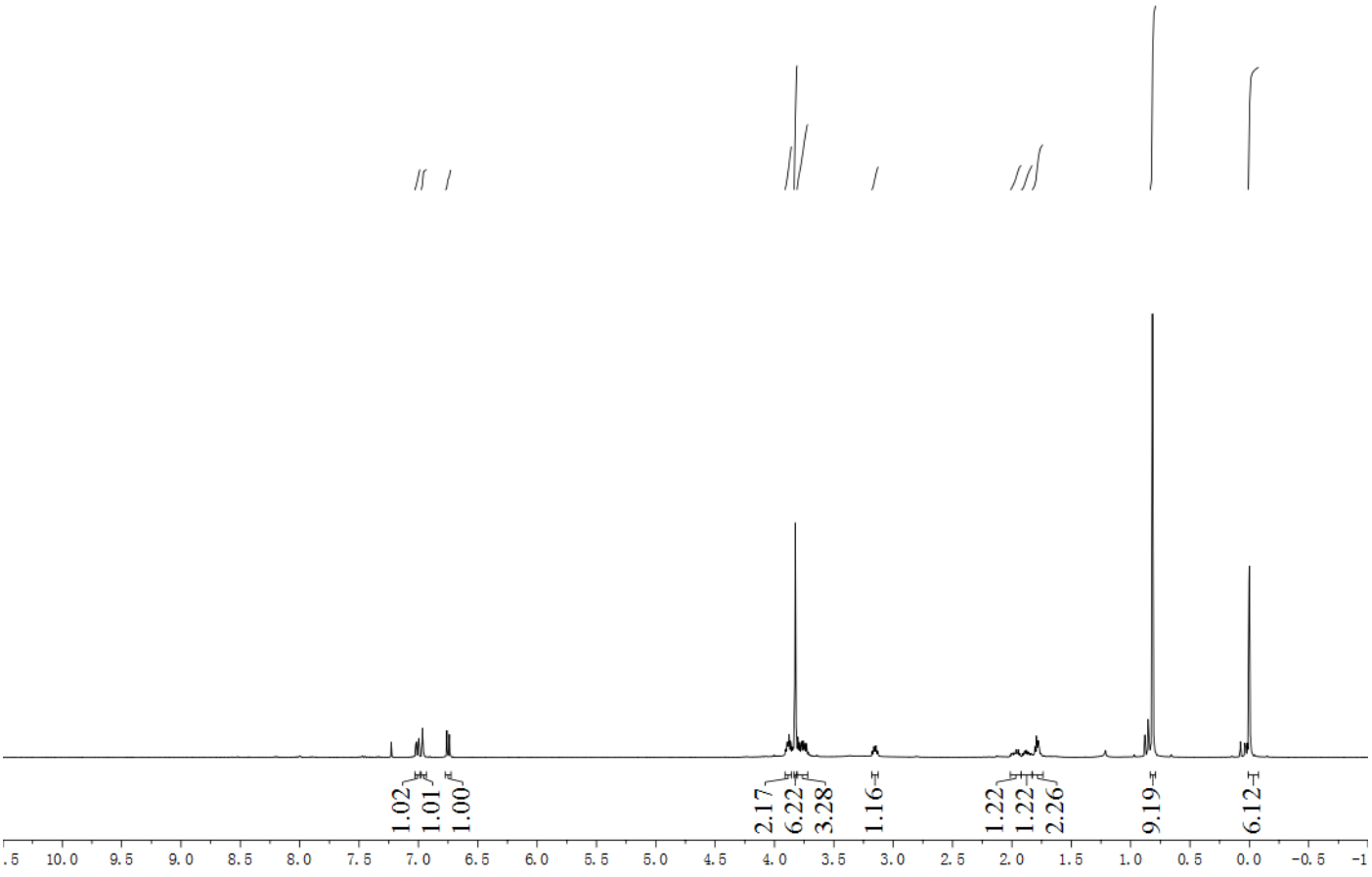
3ac

149.10
149.01
148.97
126.67
126.23
125.23
124.51
116.90
116.55
111.55
111.53
74.80
72.62
61.44
60.29
60.23
55.98
55.90
54.67
35.23
34.34
26.74
23.63
12.01
10.46




OH
TBSO
OH
S
OMe
OMe

3ad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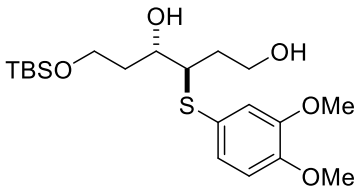
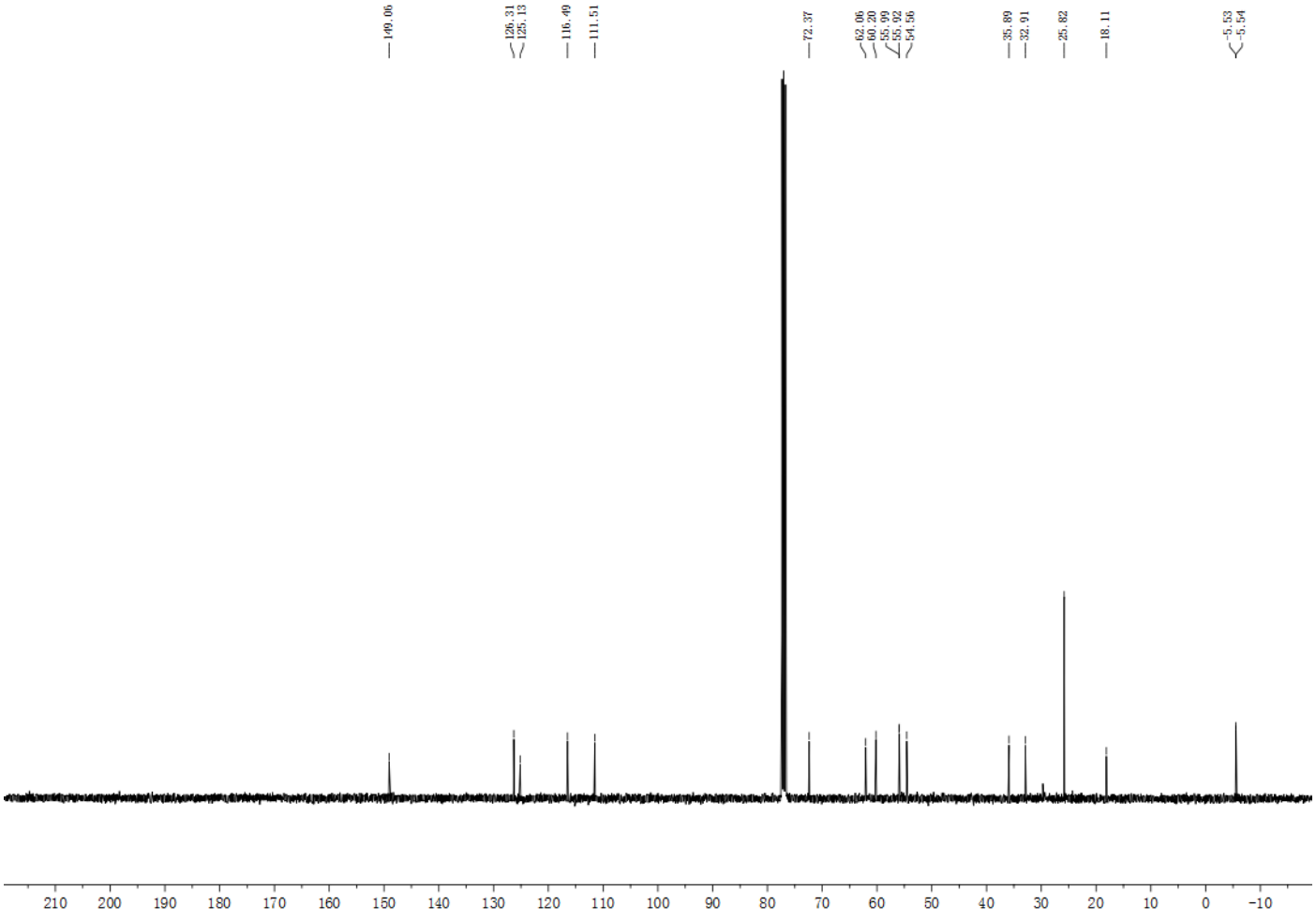
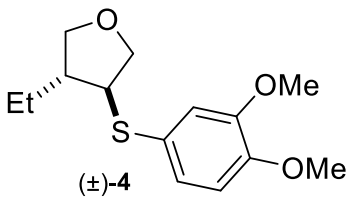
2.17
6.22
3.28
1.16
1.22
1.22
2.26
9.19
6.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

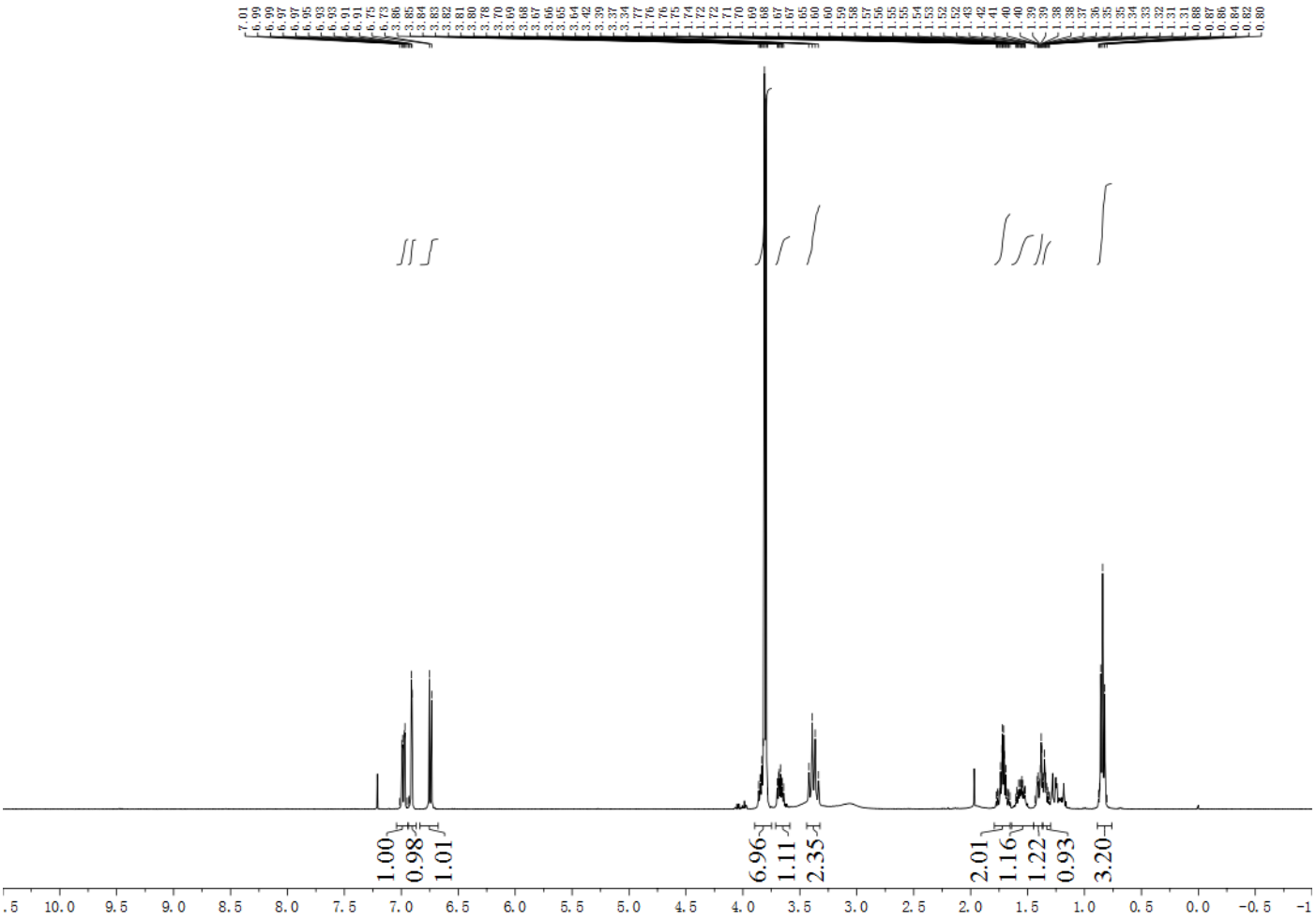

OH
TBSO
OH
S
OMe
OMe

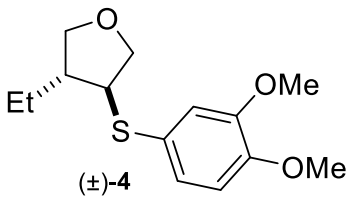
3ad


149.06
126.31
125.13
116.49
111.51
72.37
62.06
60.20
55.99
55.92
54.56
35.89
32.91
25.82
18.11
-5.53
-5.54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

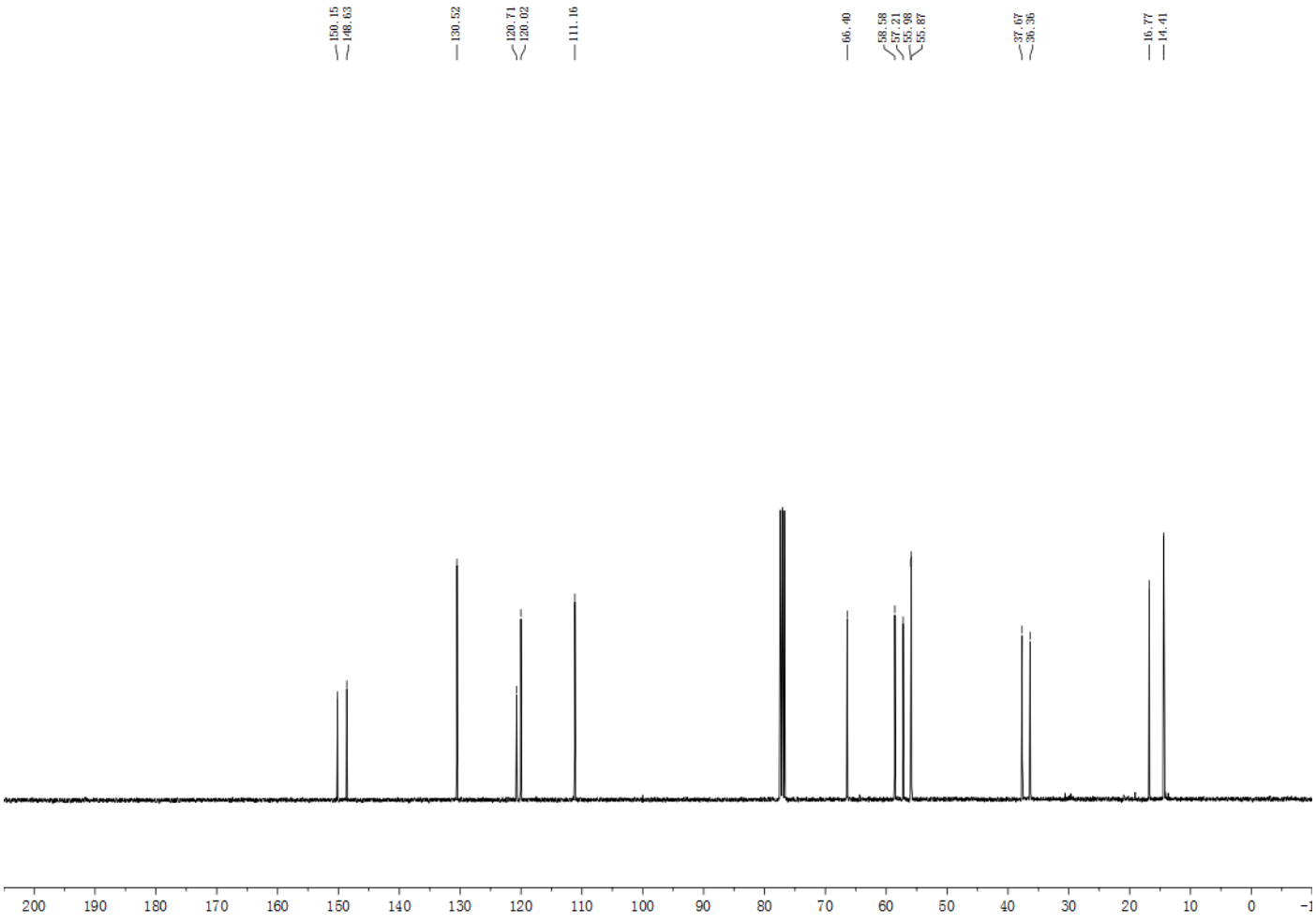


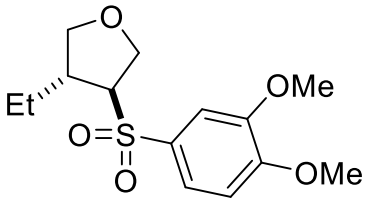
(±)-**4**



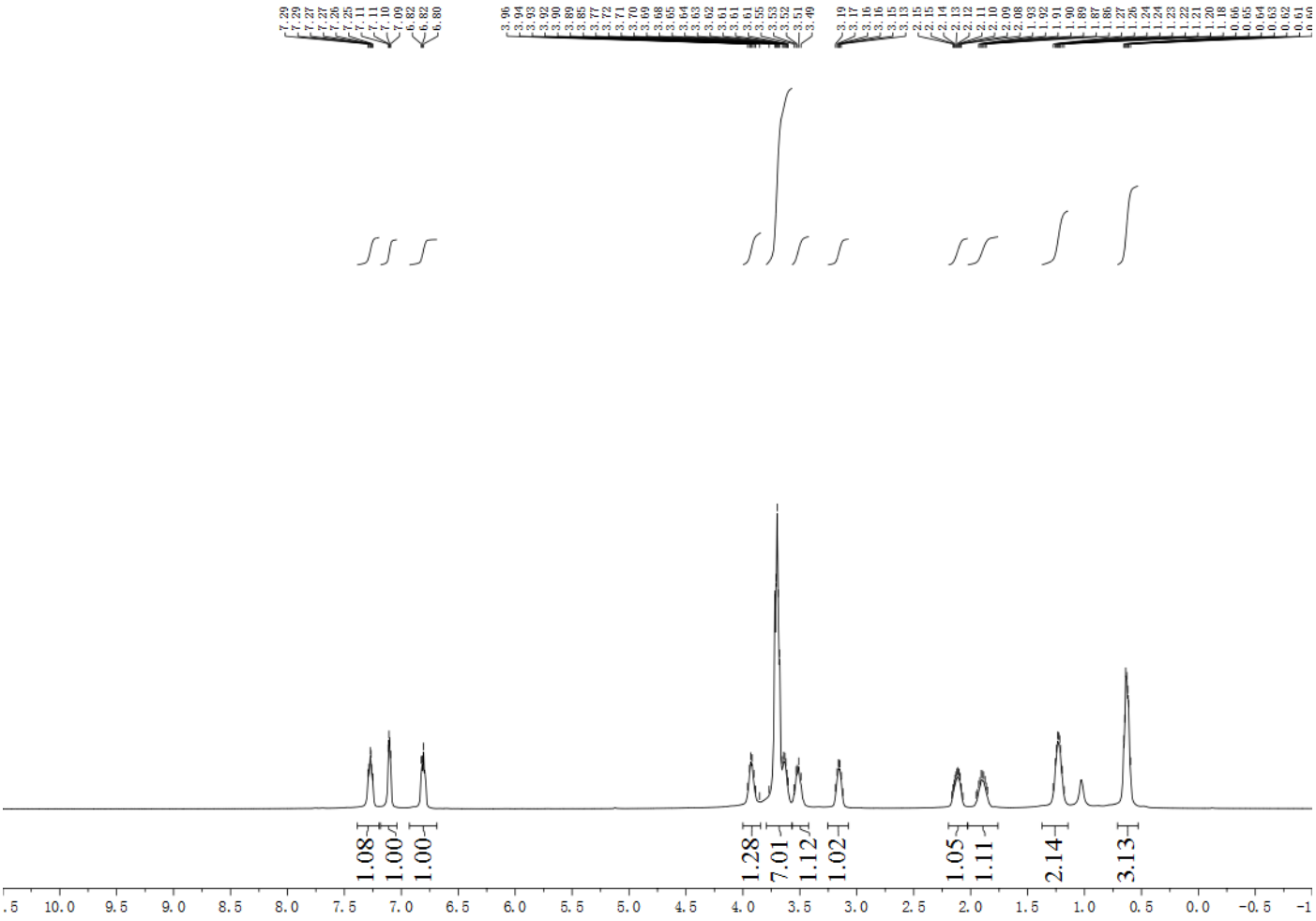

O
Et
S
OMe
OMe

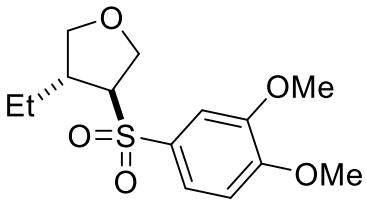
(±)-**4**


150.15
148.63
130.52
120.71
120.02
111.16
66.40
58.58
57.21
55.98
55.87
37.67
36.36
16.77
14.41
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

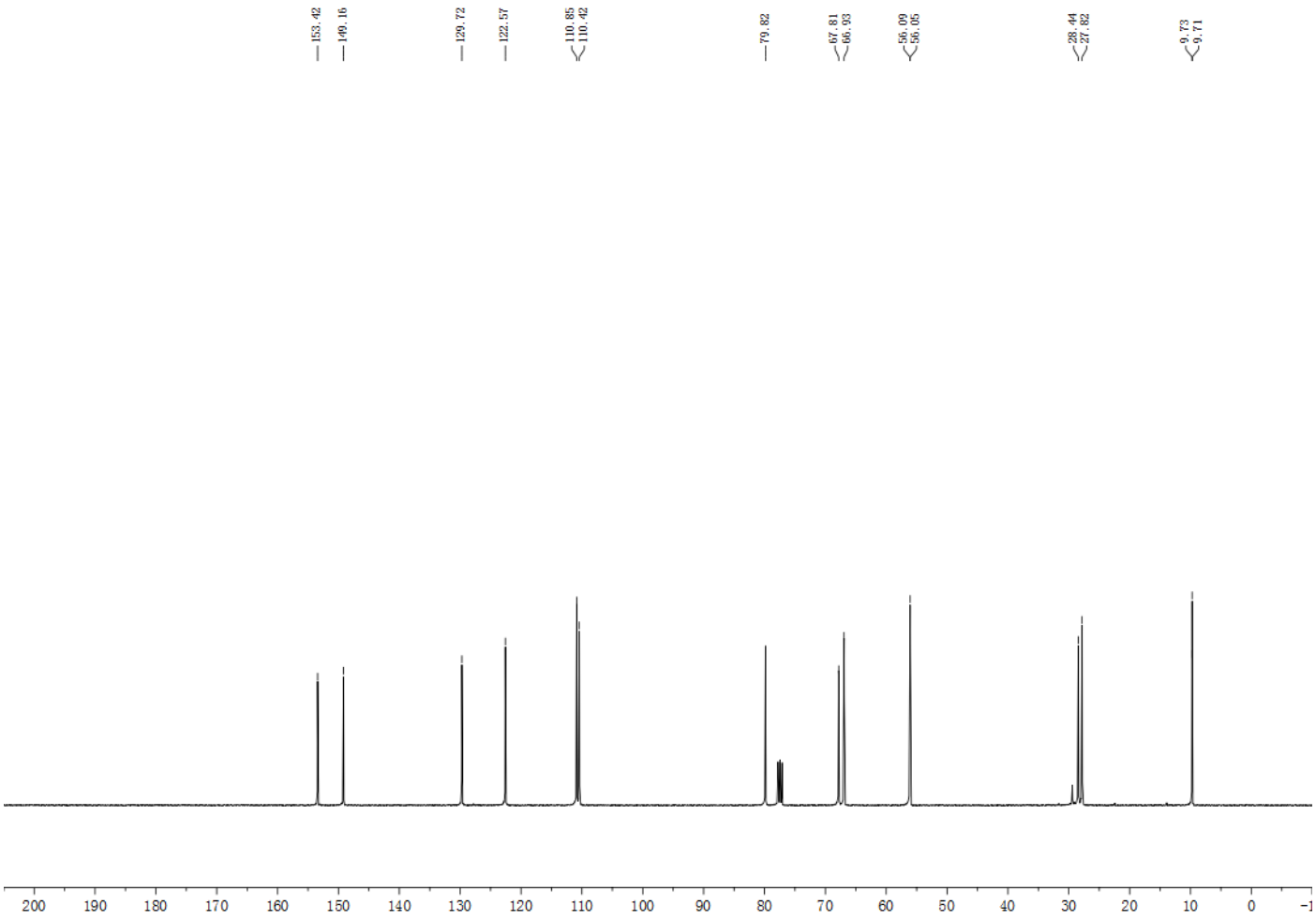


(±)-**5**




O
Et
O=S
O
OMe
OMe

(±)-**5**


153.42
149.16
129.72
122.57
110.85
110.42
79.82
67.81
66.93
56.09
56.05
28.44
27.82
9.73
9.71
200
190
180
170
160
150
140
130
120
110
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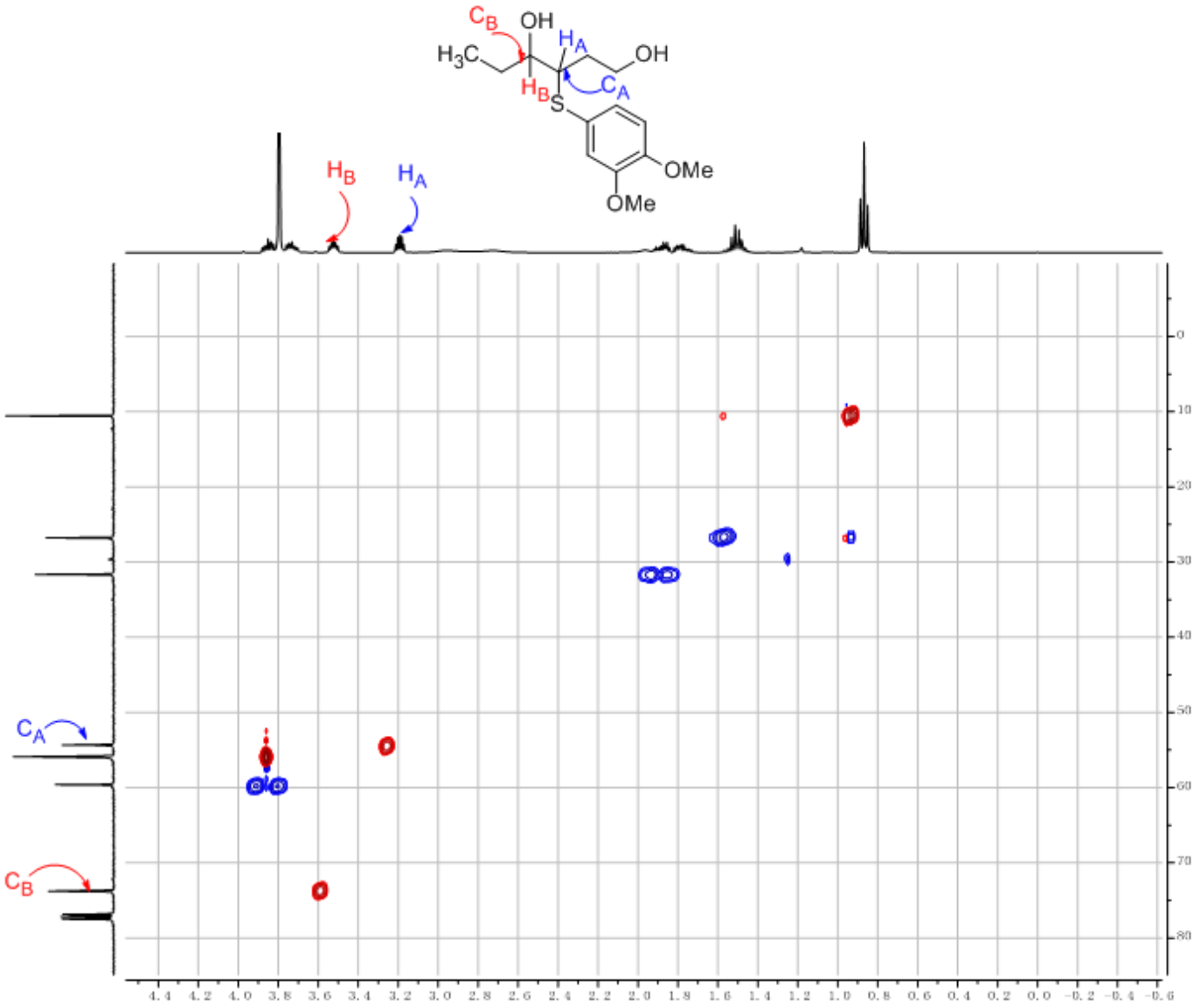
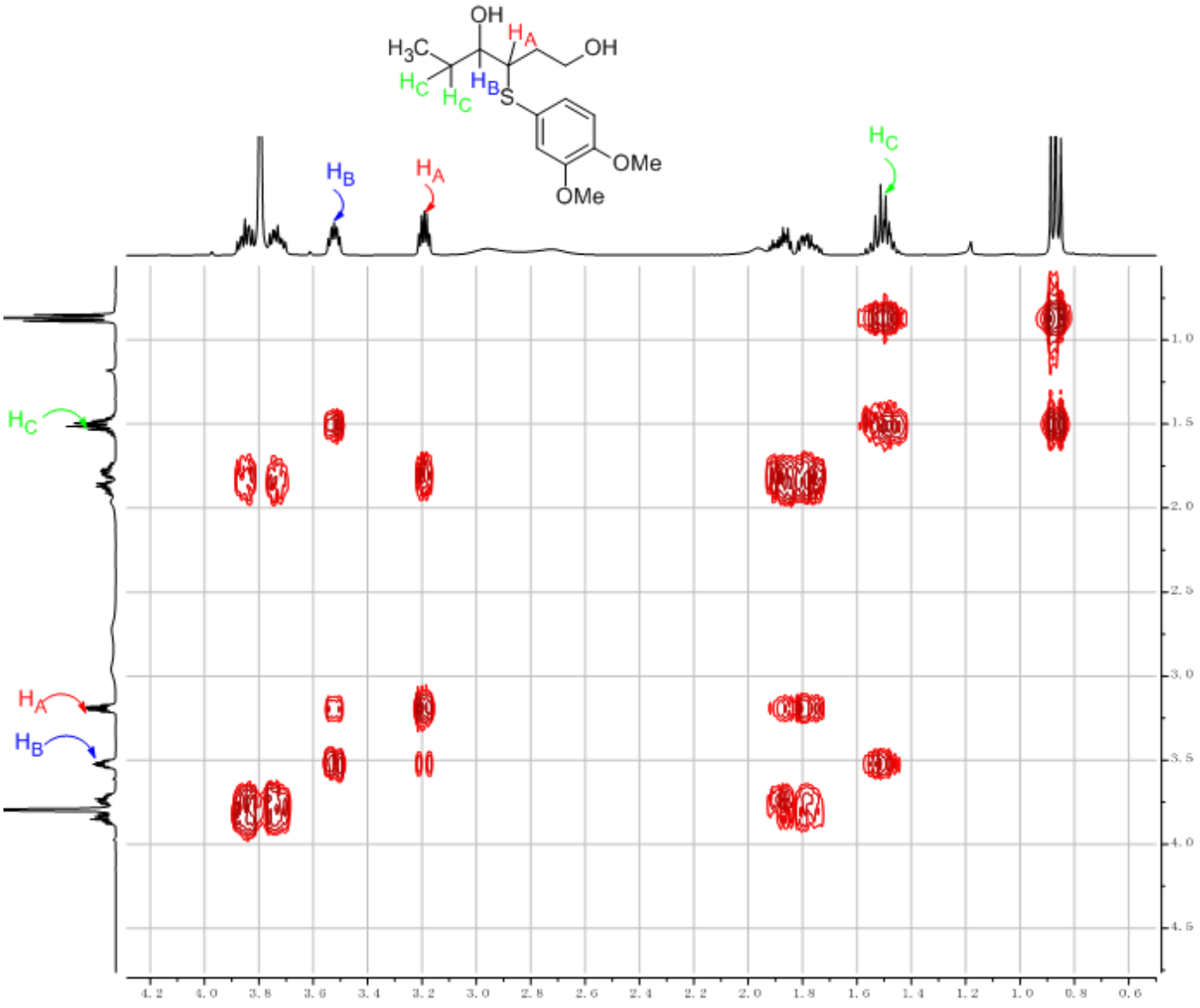
90
80
70
60
50
40
30
20
10
0

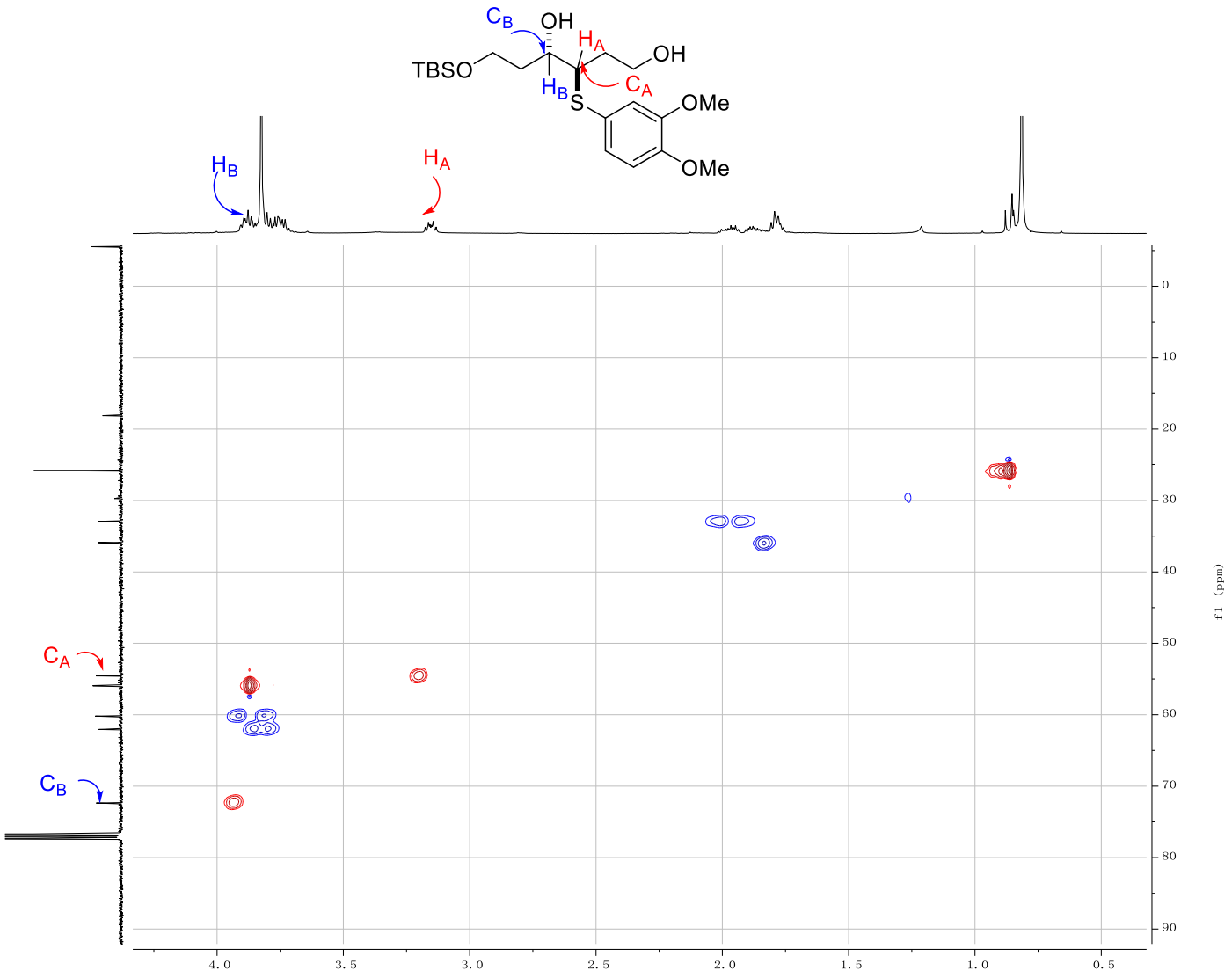
HSQC spectrum of 3f



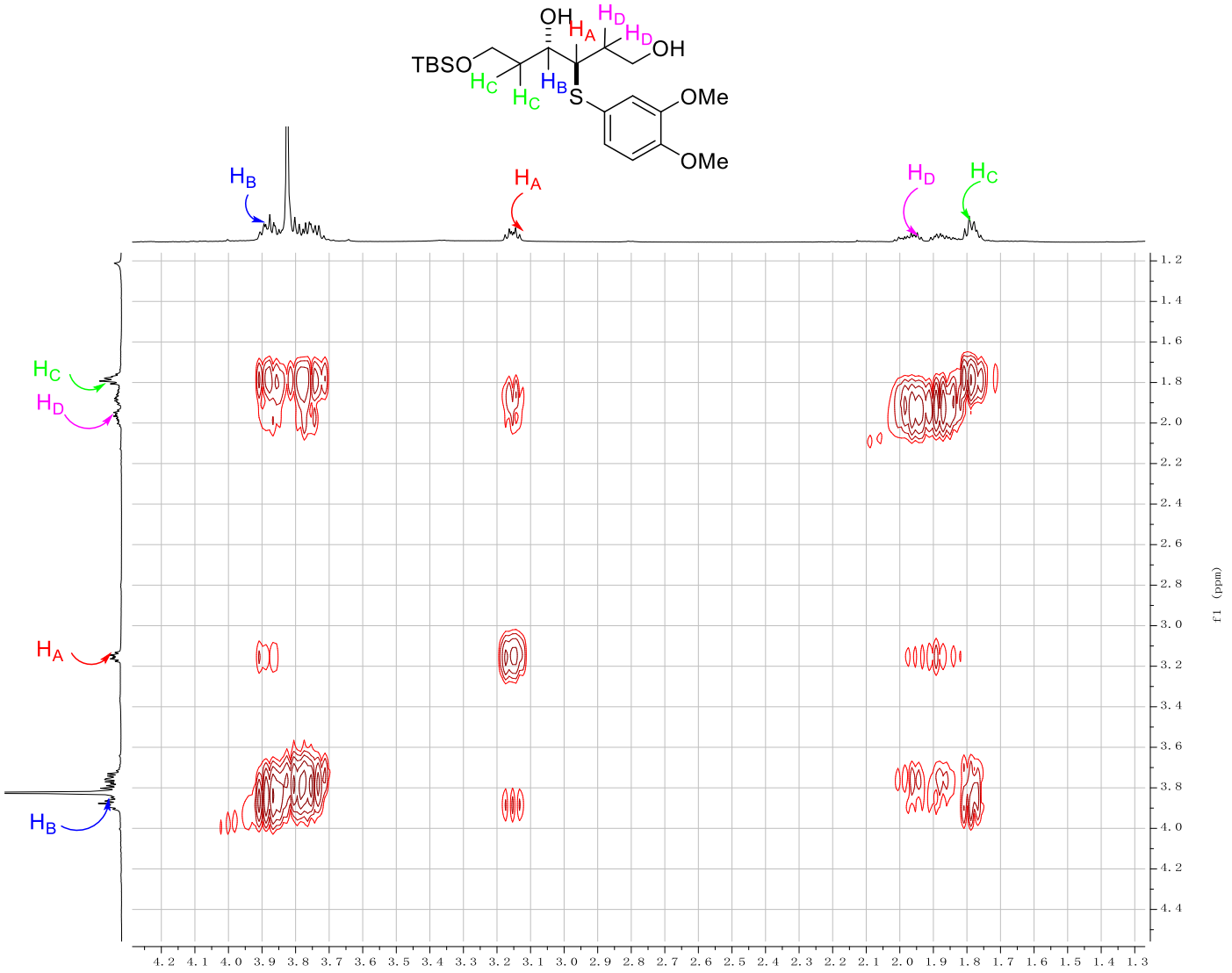
COSY spectrum of 3f



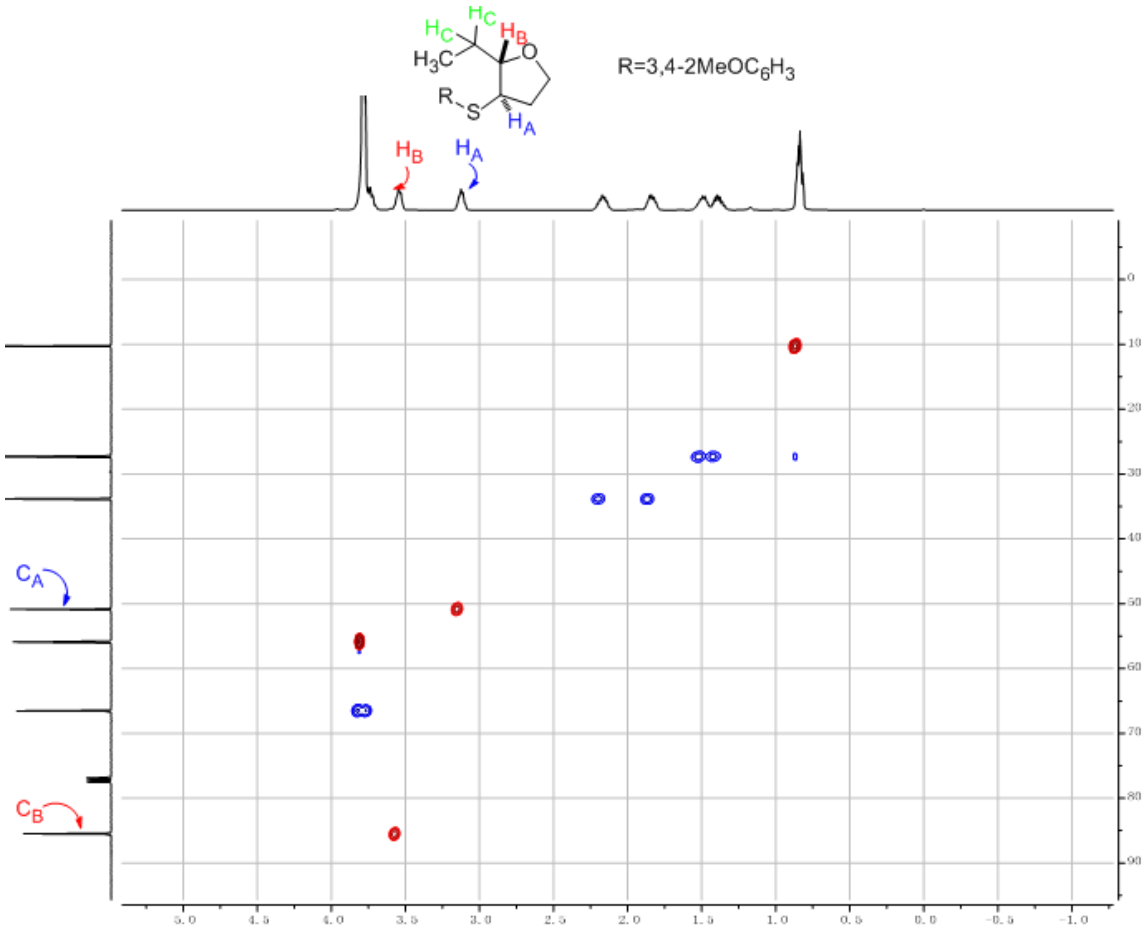
HSQC spectrum of 3ad



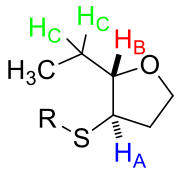
COSY spectrum of 3ad



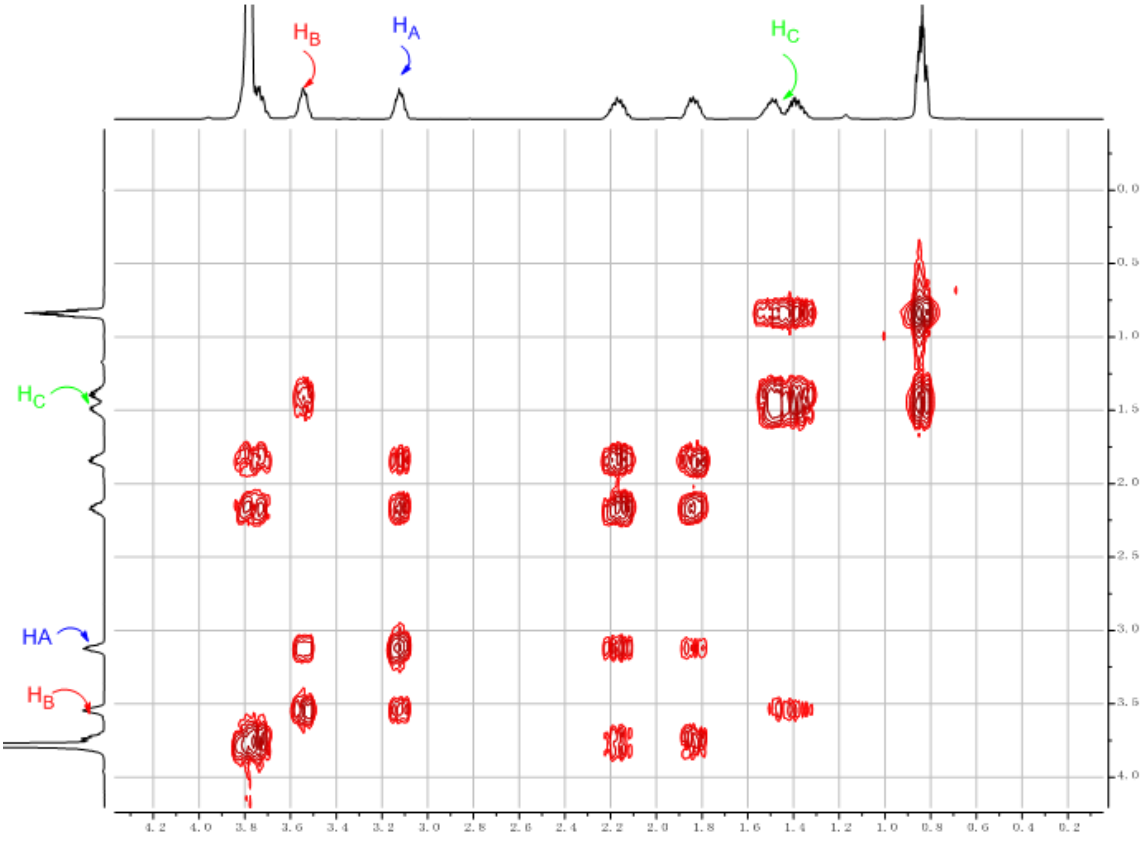
HSQC spectrum of 5



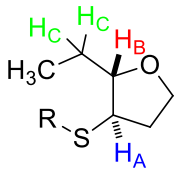
COSY spectrum of 5



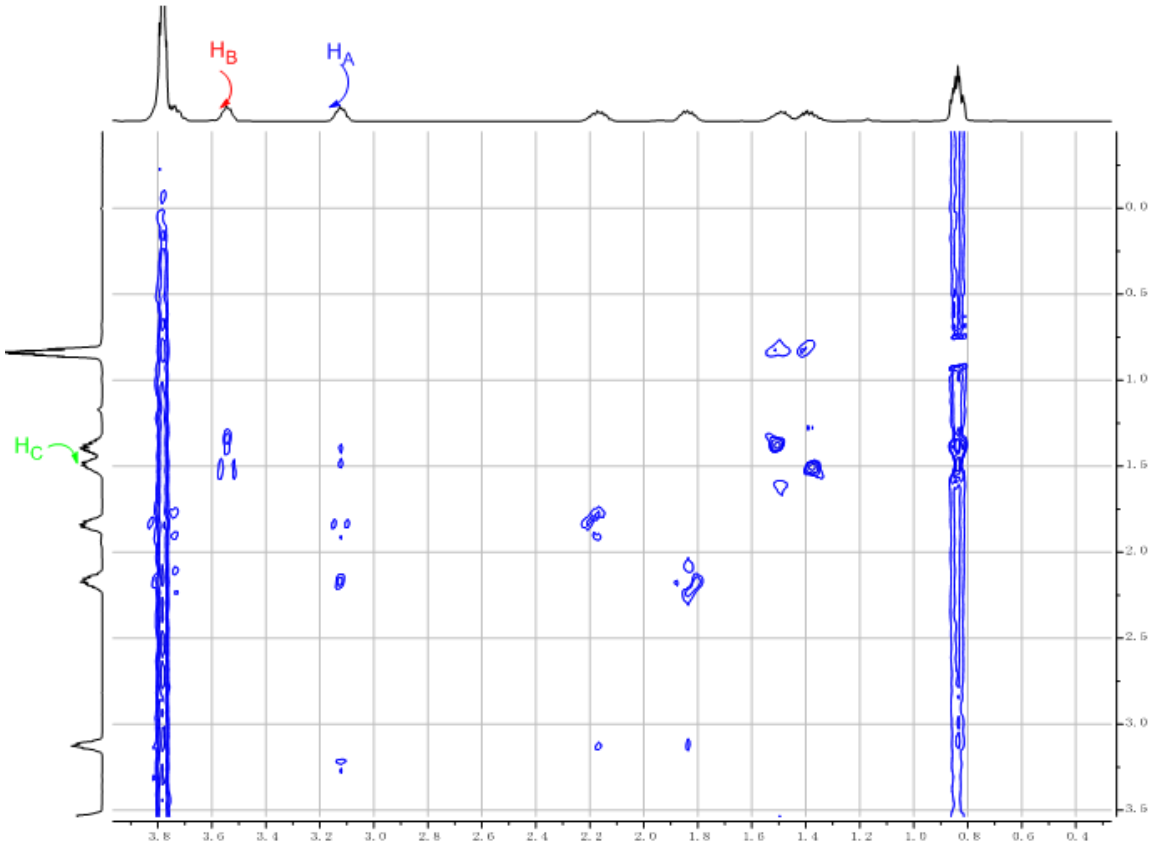
R=3,4-2-MeOC$_6$H$_3$



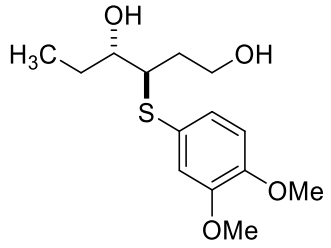
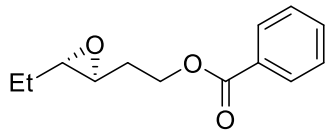
2D-NOE spectrum of 5

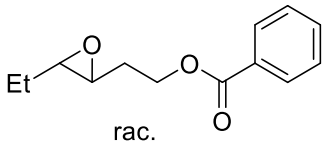


R=3,4-2-MeOC$_6$H$_3$



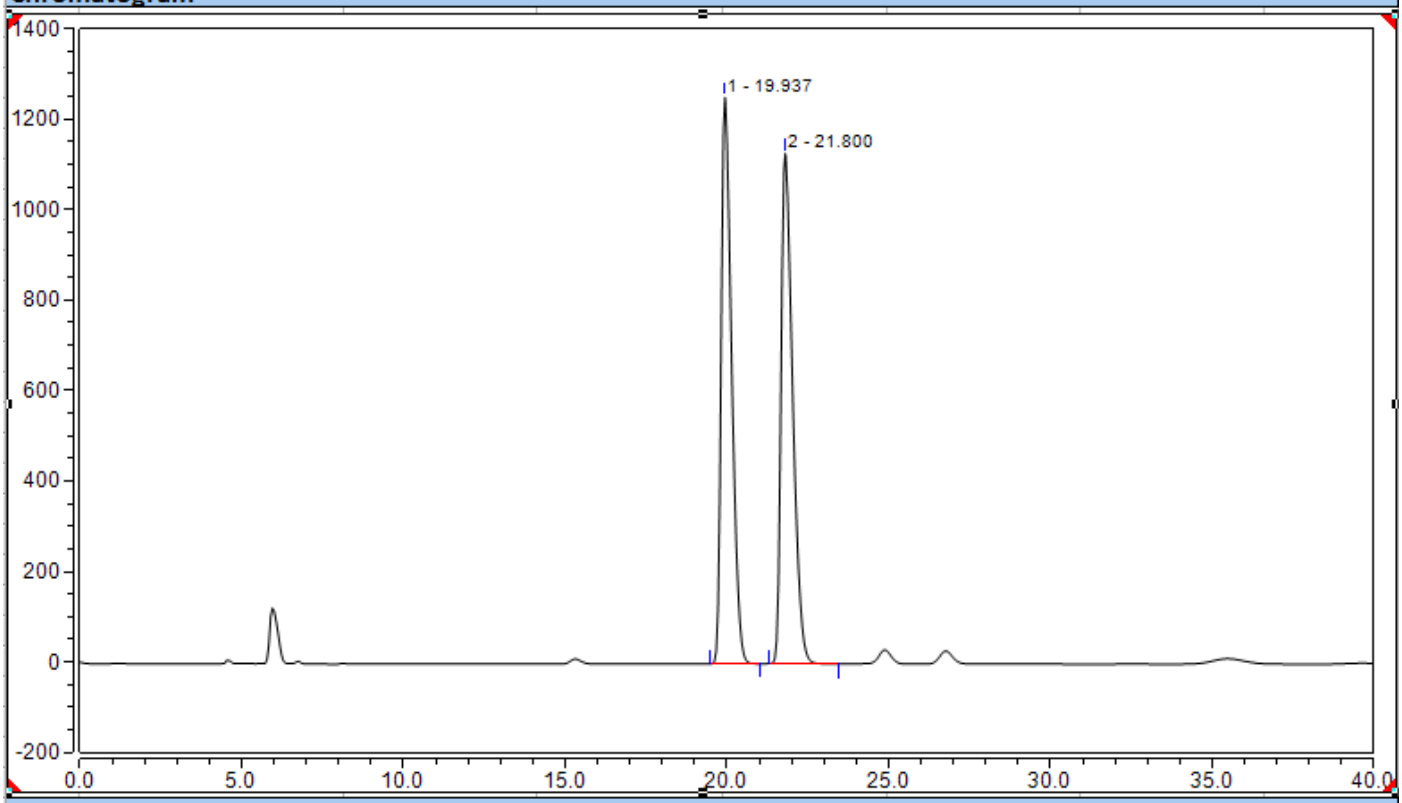
HPLC Data and Spectra

Product	conditions
	HPLC (Chiralpak IB): Condition: 80:20 Hexanes/2-Propanol, flow rate 0.75mL/min; result: 12.7 min (minor), 14.0 min (major).
	HPLC (Chiralcel OJ-H): Condition: 99:1 Hexanes/2-Propanol, flow rate 0.75 mL/min; result: 19.9 min (major), 22.1 min (minor)



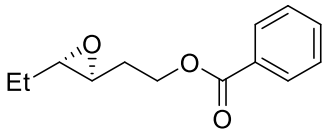
rac.

Chromatogram

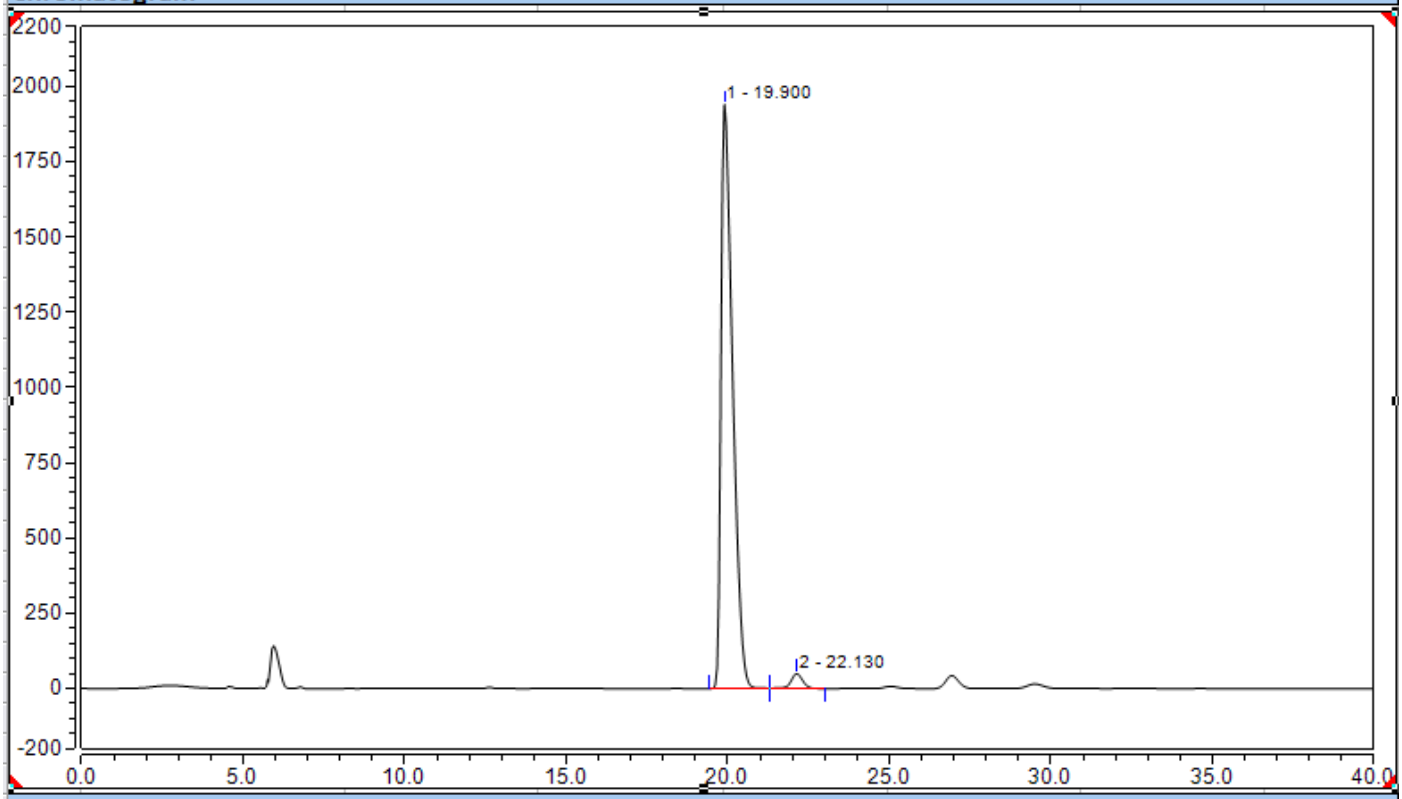


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.937	466.165	1252.006	50.01	52.61	n.a.
2		21.800	465.923	1127.987	49.99	47.39	n.a.
Total:			**932.087**	**2379.993**	**100.00**	**100.00**	

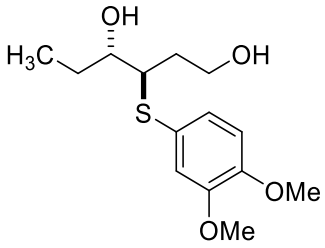


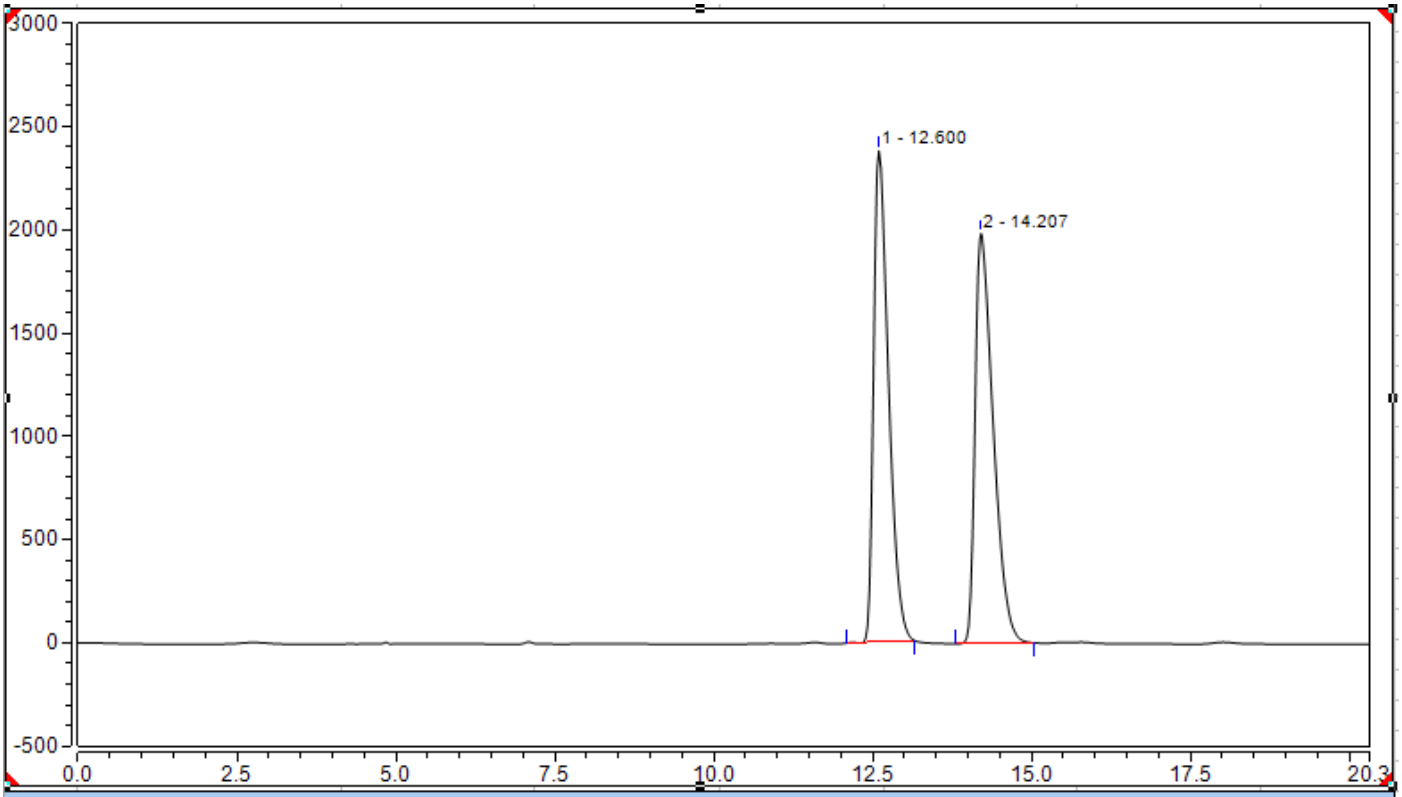
Chromatogram



Integration Results

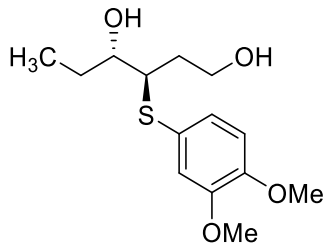
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.900	807.624	1941.129	97.42	97.50	n.a.
2		22.130	21.396	49.847	2.58	2.50	n.a.
Total:			**829.021**	**1990.977**	**100.00**	**100.00**	

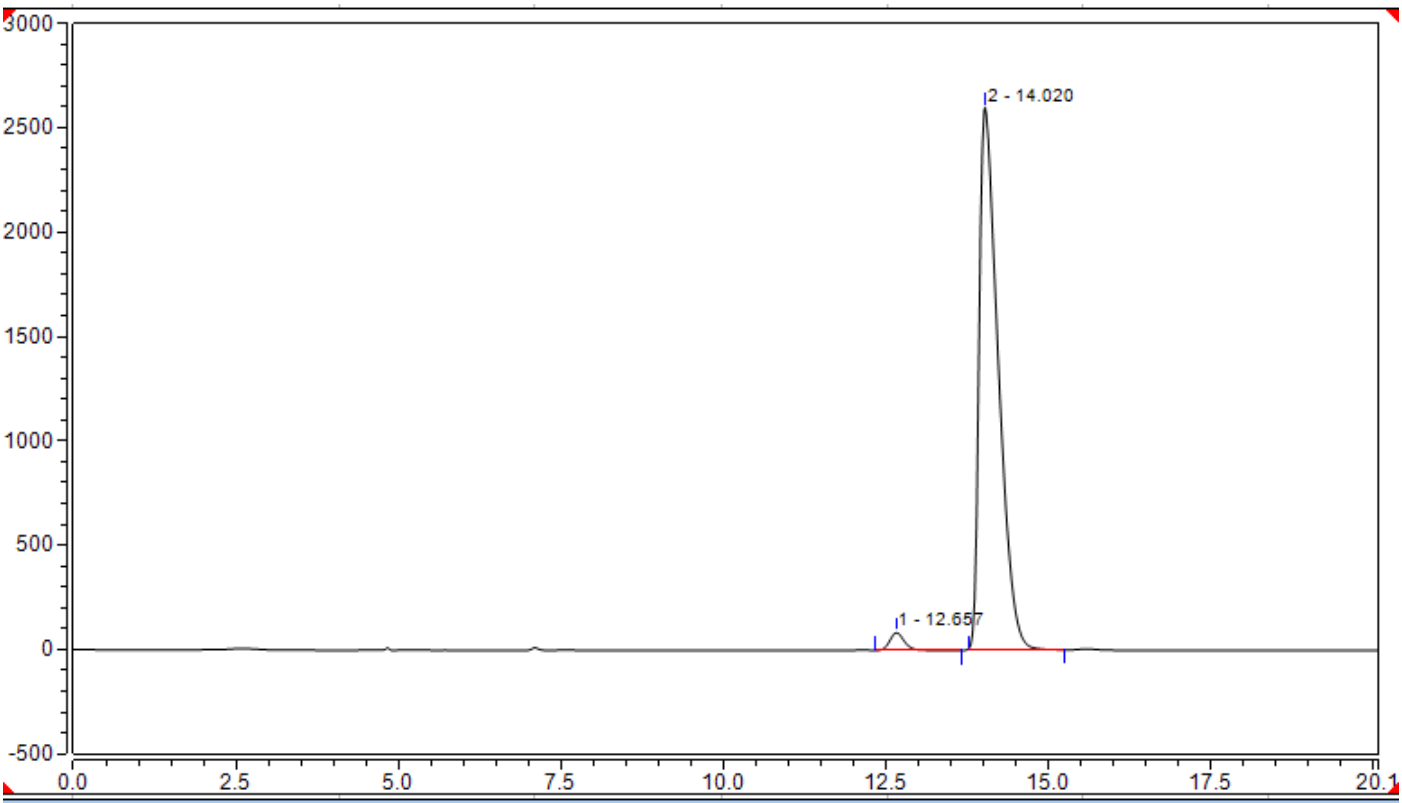




Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.600	644.101	2377.563	49.59	54.50	n.a.
2		14.207	654.841	1985.187	50.41	45.50	n.a.
Total:			**1298.942**	**4362.750**	**100.00**	**100.00**	





Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.657	21.897	84.930	2.43	3.17	n.a.
2		14.020	880.684	2597.753	97.57	96.83	n.a.
Total:			**902.581**	**2682.683**	**100.00**	**100.00**	