Supplementary Information

Iodine-catalyzed tandem synthesis of terminal acetals and glycol mono esters from olefins

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1. General information

All chemicals used were reagent grade and used as received without further purification. ^{1}H NMR spectra were recorded at 300, 400 and 500 MHz and ^{13}C NMR spectra 75 MHz in $CDCl_3$ or DMSO-D_6. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR spectra. Coupling constants (*J*) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet). Column chromatography was carried out using silica gel (100-200 mesh).

2. General procedure for the synthesis of acetals/ glycol mono esters

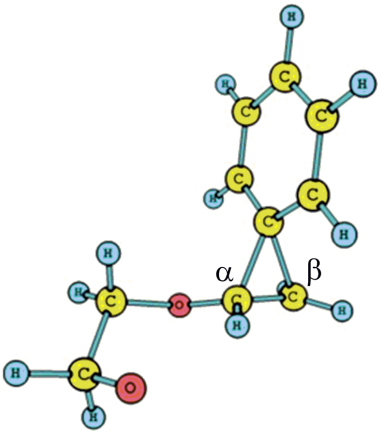
Oxone (1.5 mmol for acetal/ 3 mmol for glycol mono ester) was slowly added to a well stirred solution of olefine (2 mmol) and I_2 (0.1 mmol) in ethylene glycol (2 ml), then the reaction mixture was stirred at room temperature for the time shown in Table 2 and 3. After completion of the reaction (as indicated by TLC), the reaction mixture was quenched with aqueous sodium thiosulfate and extracted with DCM (3×20 ml). Finally, the combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude reaction mixture was further purified by column chromatography using silica gel (100-200 mesh) afforded the pure products.

3. General procedure for the synthesis of acetals from various diols

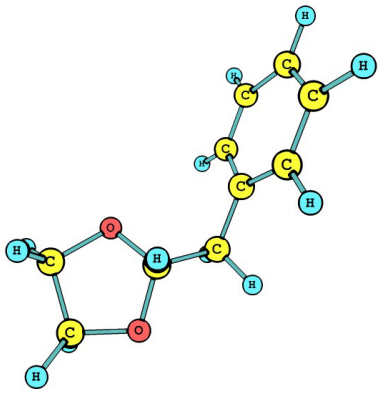
Oxone (1.5 mmol) was slowly added to a well stirred solution of styrene (2 mmol), I_2 (0.1 mmol) and diol (8 mmol) in $CHCl_3$ (5 ml) and the reaction mixture was allowed to stir at reflux temperature for 24 h (Table S2). Then the reaction mixture was quenched with aqueous sodium thiosulfate and extracted with DCM (3×20 ml). Finally, the combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude reaction mixture was further purified by column chromatography using silica gel (100-200 mesh) afforded the pure products.

4. Computational study

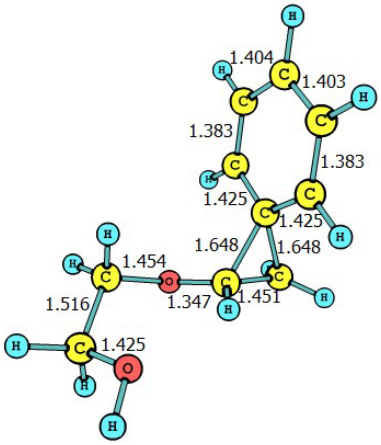
Formation of acetal (**3a**) from styrene (**1a**) proceeds through the phenonium ion intermediate (**2A**), which is confirmed by the *in situ* mass studies (Figure S3). However one can ask a question that why O^- attacks on α-C rather than on β-C, if the reaction goes through phenonium ion intermediate. So, to understand the feasibility of O^- attack, we have carried out the quantum chemical calculations at B3LYP/6-31G* level of theory. The full optimization of the phenonium ion (**2A**) leads to the *anti*-markovnikov product (**3a**) (Figure S1). Thus we have done the constrained geometry optimization of phenonium ion intermediate (the terminal negative ion saturated with hydrogen to avoid the ring opening). The charge on the atoms provides the straight forward answer for the propensity of O^- attack on α-C rather than on β-C. Compared to β-C (0.18 a.u), α-C (0.44 a.u) posses higher positive charge (Figure S1) hence, the attack by O^- is more favorable at α-C than β-C. To get further insights, we have also modeled the various derivatives of the phenonium ion intermediate and done full optimization at B3LYP/6-31G* level of theory (Figure S2). Interestingly all the structures are minima in the potential energy surface (PES). A cursory look at the Figure S2, one can understand that the substituent ($-CH_3$, -OH, -Cl, -Br and $-OCH_2CH_2OH$) at α-C weakens the bond between α-C and aromatic carbon. Thus, the computations provide definitive evidence that the $-OCH_2CH_2OH$ substitution at α-C of phenonium ion intermediate weakens the bond between the α-C and aromatic carbon. These results clearly shows that why O^- attacks on α-C rather than on β-C in the phenonium ion intermediate. All the geometry optimization and the frequency calculations have been done using Gaussian 09 program package.[S1]

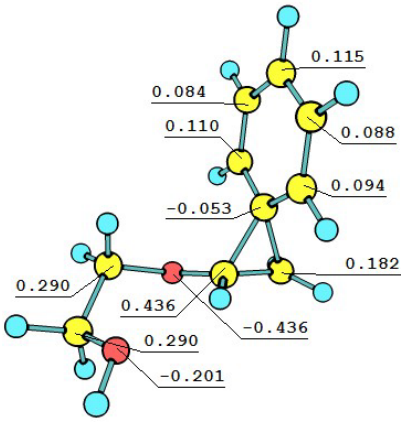


Phenonium ion (**2A**)
(I)



Anti-markovnikov's product (**3a**)
(II)





Phenonium ion intermediate
(III)

Figure S1. (I) The initial guess of the neutral phenonium-ion intermediate. (II) The structure obtained by the full optimization of phenonium ion. (III) The structure of phenonium ion intermediate obtained by the constrained geometry optimization at B3LYP/6-31G* level of theory.

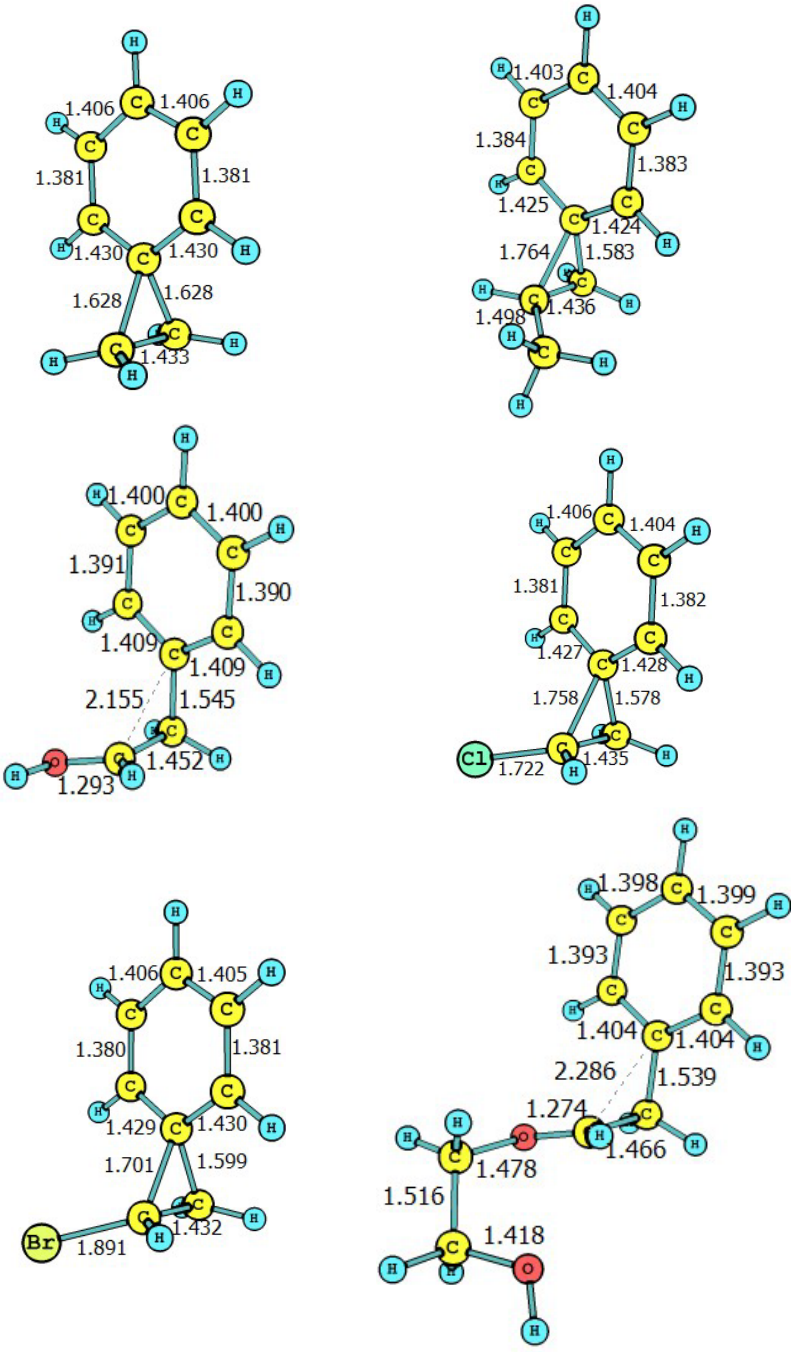


Figure S2. The derivatives of the Phenonium ion intermediate optimized at the B3LYP/6-31G* level of theory without any constraint.

5. *In Situ* ESI-MS experiments

(5a) Experimental

The *in situ* Electrospray ionization mass spectrometry (ESI-MS) experiments were performed using a quadrupole time-of-flight mass spectrometer (Q-Star XL, Applied Biosystems/MDS Sciex, Foster city, CA, USA). The typical positive ESI conditions were capillary voltage 5 kV, declustering potential 60 V and focusing potential 220 V; and negative ESI conditions were capillary voltage -4.5 kV, declustering potential -60 V, focusing potential -230 V. The instrument mass resolution was 10000 (FWHM). All the tandem mass spectrometry (MS/MS) were recorded at different collision energies (CE=10, 15 and 20) using nitrogen as the collision gas. The reaction mixture was collected at different time intervals (0, 30, 60 and 90 min) and diluted with two volumes of acetonitrile before introducing into the ESI source through flow injection (10 µl loop; methanol was used as the mobile phase at a flow rate of 30 µL/min).

(5b) Results

The detected peaks of *in situ* ESI mass spectra were identified based on accurate mass measurements (elemental composition), isotope distribution patterns and tandem MS data. The positive and negative ion ESI mass spectra of the reaction mixture at 60 min were shown in Figure S3. The positive ion spectrum showed the ion at *m/z* 105 corresponding to $[M+H]^+$ ion of styrene (**1a**; Scheme 2). The intermediate **1A**, a preformed ion, was detected in the positive ion spectrum at *m/z* 231 (the positive counterpart). The structure of this species was confirmed by MS/MS, where it showed loss of iodine. The ion *m/z* 331 correspond to the potassium adduct of intermediate, $[\mathbf{2a}+K]^+$ and as expected its MS/MS spectrum K^+ as the product ion. The intermediate **2A** was detected as protonated, sodiated and potassiated heterodimers with ethylene glycol (*m/z* 227, 249 and 265, respectively). The MS/MS of *m/z* 227 showed the loss of 62 unit (ethylene glycol). The reaction product **3a** was detected at *m/z* 165 as the protonated molecule, whose structure was confirmed by its MS/MS that showed loss of C_2H_4O from acetal moiety. The abundances of the detected peaks due to **1A**, **2a** and **2A** were decreased as the reaction progressed.

The negative ion spectral data are in support with the positive ion results. The intermediate **1A** was detected as a sulphate (SO_4^{-2}) adduct ion in the negative ion spectrum at

m/z 327. The structure of this species was confirmed by MS/MS, where it showed the sulphate anion (*m/z* 96) as a product ion. The intermediate **2A** was also detected as sulphate adduct (*m/z* 261) in negative mode.

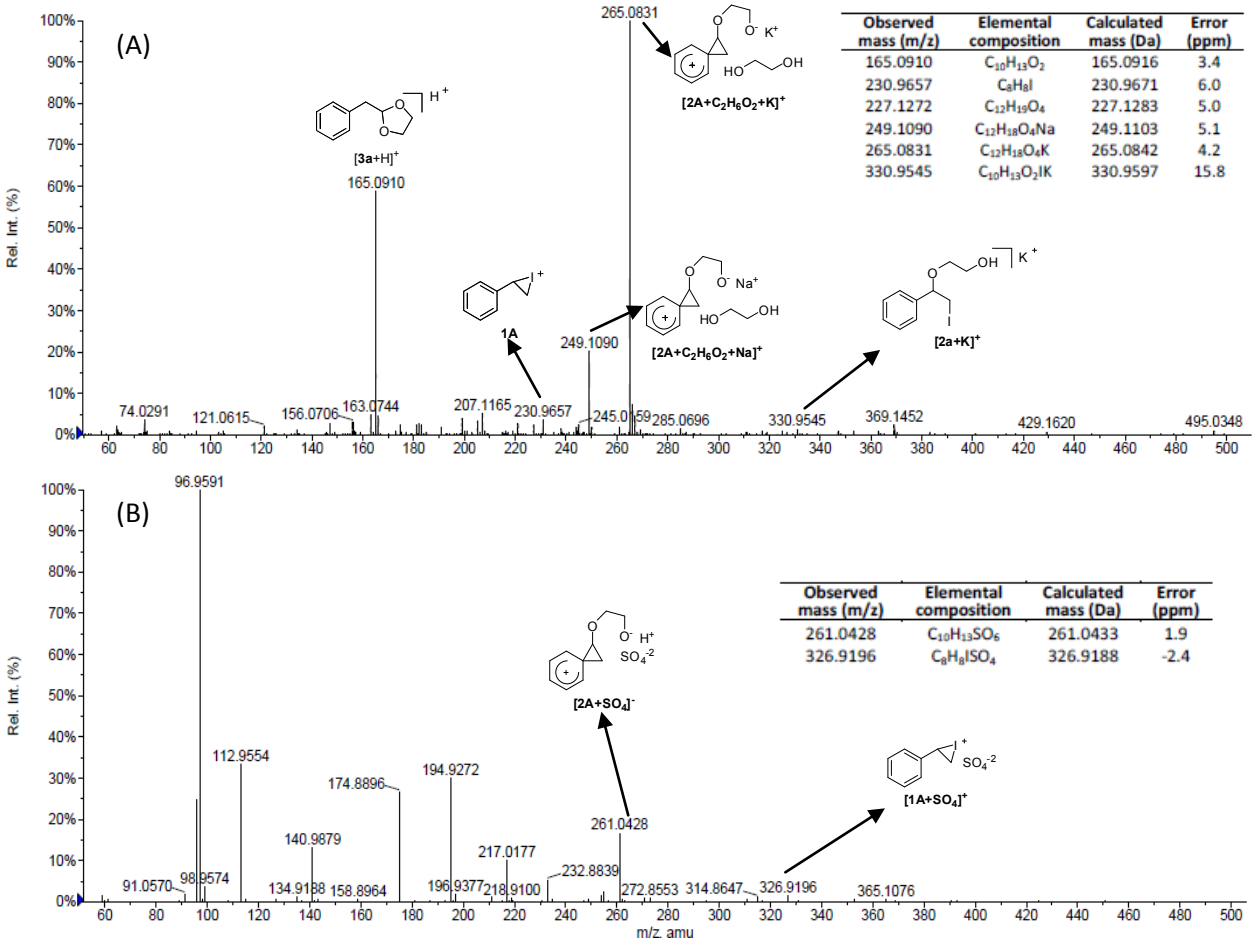
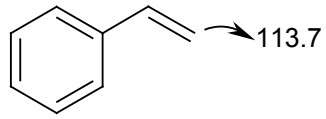


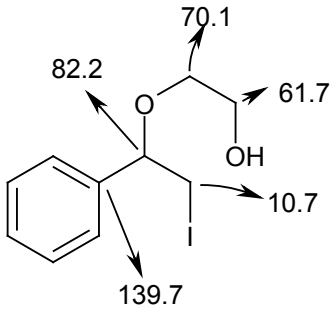
Figure S3. *In situ* ESI mass spectra of the reaction mixture at 60 min (synthesis of **3a** from **1a**); (A) Positive ion (B) Negative ion. HRMS data of the assigned ions were given in insets.

6. *In Situ* ^{13}C NMR experiments

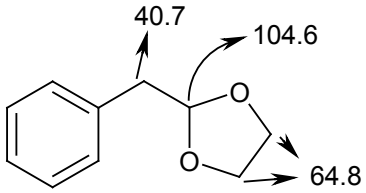
^{13}C NMR experiments were performed on a Bruker AVANCE 500 MHz NMR spectrometer at 25°C. The experiment was started with the reaction mixture containing 14 µl of styrene, 1.58 mg of I_2, 57.63 mg of oxone and 125 µl of ethylene glycol. A series of ^{13}C spectra were acquired to monitor the progress of the reaction. These spectra were overlaid to identify the signals from intermediates and final product. Initially the ^{13}C signals corresponding to the stable intermediate (**2a**) were starting to show up and these signals were present throughout the reaction. After sometime we could identify the signals from product (**3a**). For better signal to noise a ^{13}C spectrum with more number of scans is acquired to clearly display the signals of intermediates and product. Only the signals from **2a** and **3a** along with the starting material **1a** were identified and these signals were labeled on the spectrum (Figure S4). During the course of the reaction we were unable to detect the unstable intermediates **1A** and **2A** on the NMR time scale, whereas all the intermediates and product could be detected in *in situ* MS.



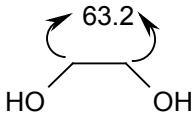
1a



2a



3a



A

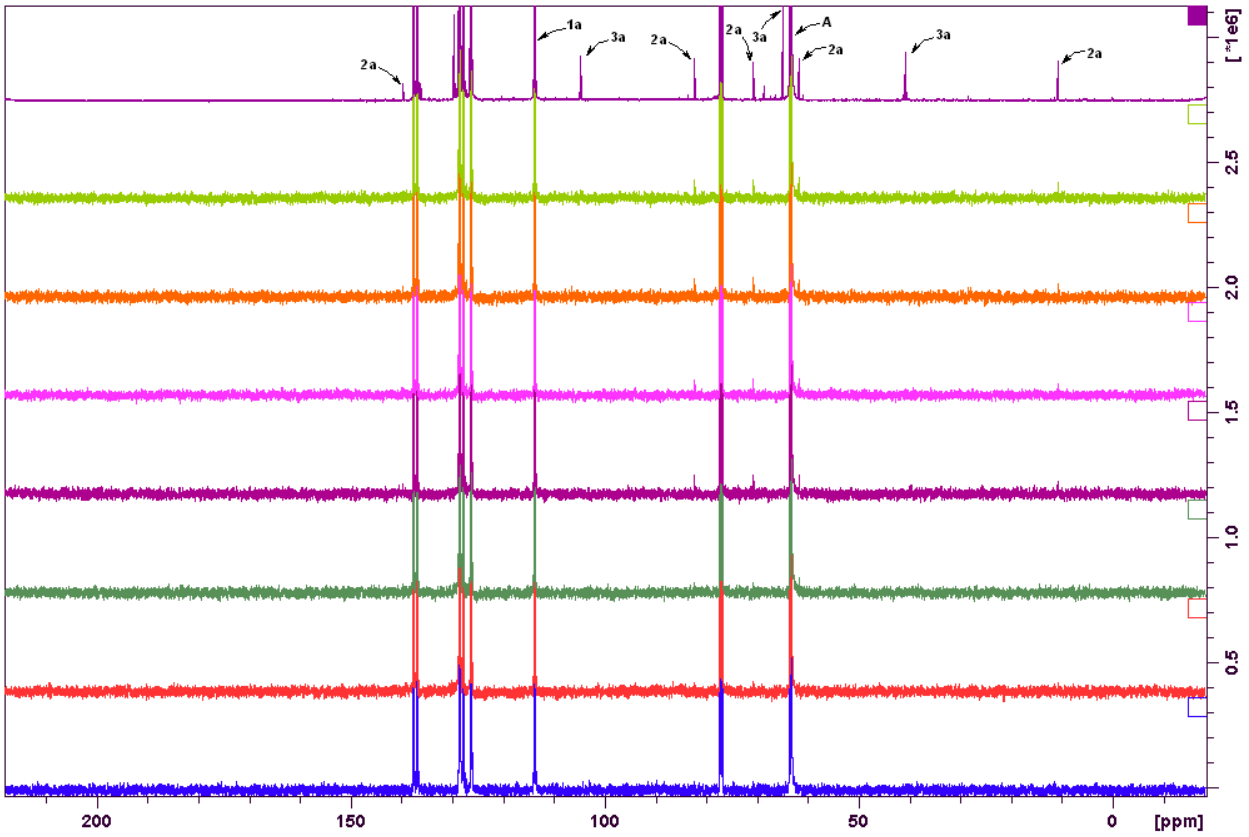
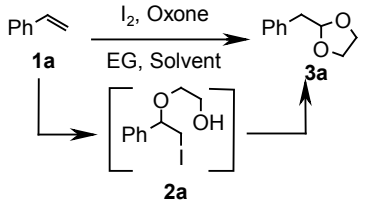


Figure S4. *In situ* ^{13}C NMR spectra of reaction mixture (synthesis of **3a** from **1a**).

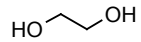
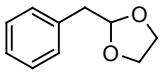
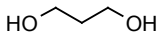
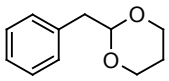
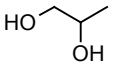
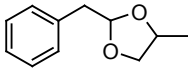
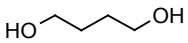
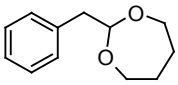
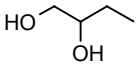
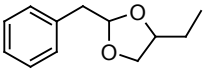
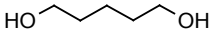
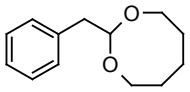
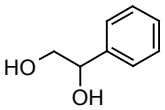
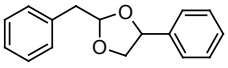
7. Table S1 Acetalization of styrene - effect of solvent[a]



Entry	EG (mmol)	Solvent (5 ml)	Temp	Time (h)	Yield[b] (%) **2a**	**3a**
1	8	CH_3CN	rt	24	06	07
2	,,	THF	,,	,,	07	-
3	,,	Acetone	,,	,,	-	-
4	,,	DME	,,	,,	-	-
5	,,	DCE	,,	,,	06	22
6	,,	$CHCl_3$	,,	,,	05	16
7	,,	DCM	,,	,,	03	33
8	,,	CCl_4	,,	,,	02	11
9	,,	DCE	reflux	,,	09	37
10	**,,**	**$CHCl_3$**	**,,**	**,,**	**08**	**69**
11	,,	DCM	,,	,,	07	46
12	,,	CCl_4	,,	,,	07	36
13	,,	$CHCl_3$	,,	48	09	70
14	2	,,	,,	24	03	14
15	4	,,	,,	,,	05	32
16	6	,,	,,	,,	07	45
17	10	,,	,,	,,	08	73

[a] Styrene (2 mmol), I_2 (0.1 mmol), Oxone (1.5 mmol). [b] Products were characterized by NMR, mass spectra and quantified by GC

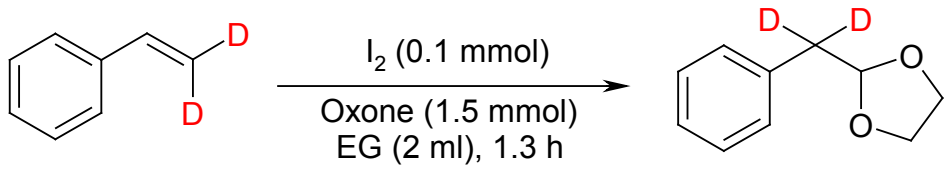
8. Table S2 Acetalization of styrene with various diols using $CHCl_3$ as solvent[a]

Entry	Diol	Product	Yield[b] (%)
1		 **3a**	69
2		 **5**	49
3		 **6**	52[c]
4		 **7**	10
5		 **8**	53[c]
6		 **9**	-
7		 **10**	46[c]

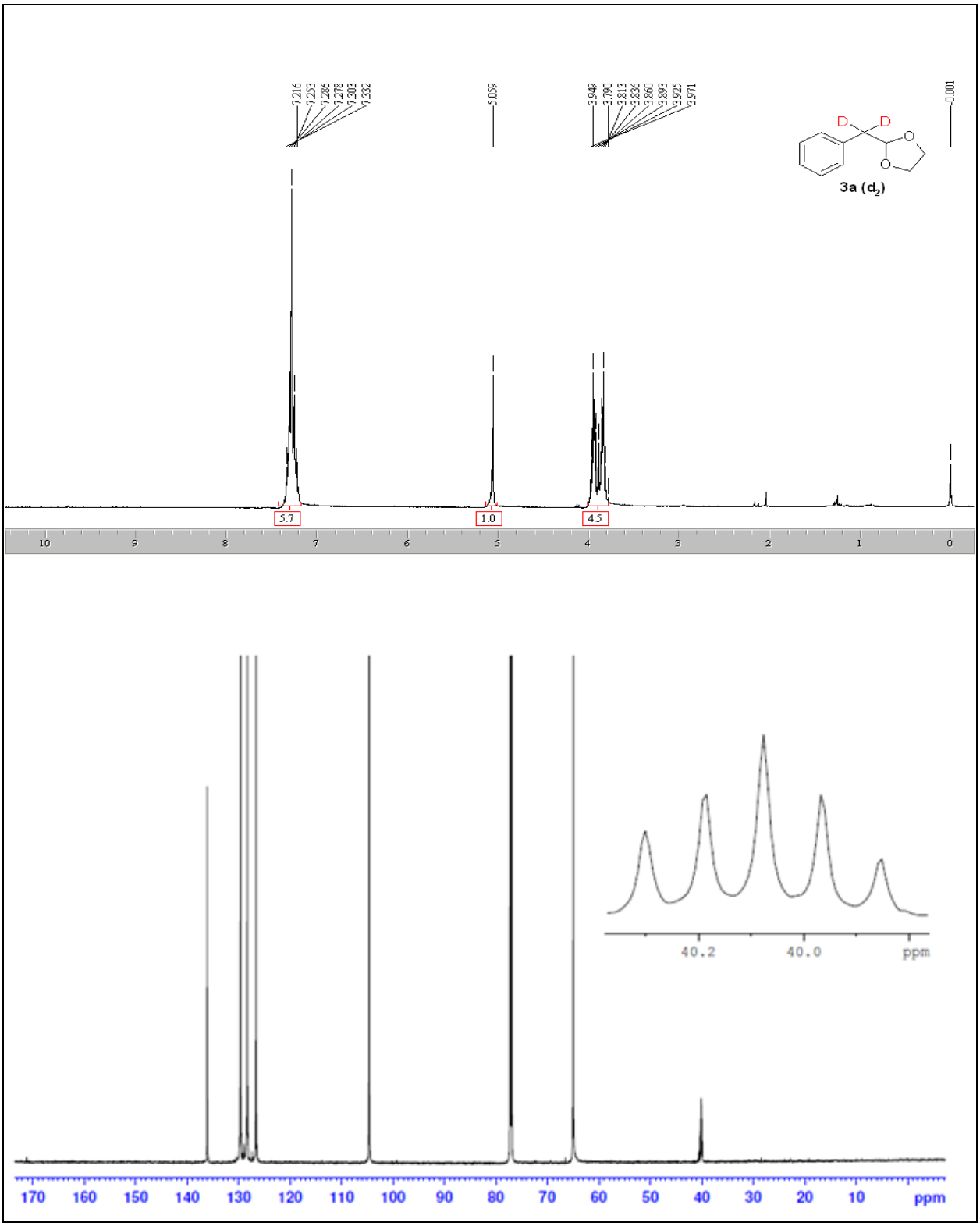
[a] Styrene (2 mmol), I_2 (0.1 mmol), Oxone (1.5 mmol), Diol (8 mmol), $CHCl_3$ (5 ml), Reflux temperature, 24 h. [b] Products were characterized by NMR, mass spectra and quantified by GC. [c] Mixture of diastereoisomers .

9. Aectalization of Styrene-*β*,*β*-*d*$_2$

Oxone (1.5 mmol) was slowly added to a well stirred solution of styrene-*β*,*β*-*d*2 (98%) (2 mmol) and I_2 (0.1 mmol) in ethylene glycol (2 ml), then the reaction mixture was stirred at room temperature. After completion of the reaction (as indicated by TLC), the reaction mixture was quenched with aqueous sodium thiosulfate and extracted with DCM (3×20 ml). Finally, the combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude reaction mixture was further purified by column chromatography using silica gel (100-200 mesh) afforded the pure product.

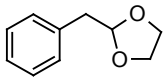


1a (d_2) **3a (d_2)**: 92%


7.216
7.253
7.286
7.278
7.303
7.332
5.059
3.949
3.790
3.813
3.836
3.860
3.893
3.925
3.971
0.001
D
D
O
O
3a (d2)
5.7
1.0
4.5
10
9
8
7
6
5
4
3
2
1
0
40.2
40.0
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

10. Spectral data

2-(Benzyl)-1,3-dioxolane (3a)[S2]

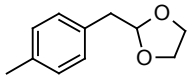


^{1}H NMR (500 MHz, $CDCl_3$): 2.91 (d, 2H, *J* = 5 Hz), 3.75-3.91 (m, 4H), 4.99 (t, 1H, *J* = 5 Hz), 7.14-7.26 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): 40.7, 64.9, 104.6, 126.5, 128.3, 129.6, 136.1.

Anal.Calcd for $C_{10}H_{12}O_2$ C, 73.15; H, 7.37; Found: C, 73.21; H, 7.34.

2-(4-Methylbenzyl)-1,3-dioxolane (3b)[S2]

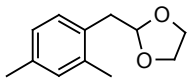


^{1}H NMR (300 MHz, $CDCl_3$): 2.31 (s, 3H), 2.88 (d, 2H, *J* = 4.53 Hz), 3.74-3.94 (m, 4H), 4.96 (t, 1H, *J* = 4.53 Hz), 7.04 (d, 2H, *J* = 8.3 Hz), 7.1 (d, 2H, *J* = 8.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): 21.0, 40.2, 64.8, 104.8, 128.9, 129.4, 132.9, 136.

Anal.Calcd for $C_{11}H_{14}O_2$ C, 74.13; H, 7.92; Found: C, 74.17; H, 7.87.

2-(2,4-Dimethylbenzyl)-1,3-dioxolane (3c)

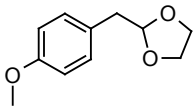


^{1}H NMR (300 MHz, $CDCl_3$): 2.27 (s, 3H), 2.3 (s, 3H), 2.9 (d, 2H, *J* = 5 Hz), 3.74-3.93 (m, 4H), 4.97 (t, 1H, *J* = 5 Hz), 6.88-6.93 (m, 2H), 7.05 (d, 1H, *J* = 8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): 19.7, 20.9, 37.4, 64.8, 104.4, 126.5, 130.2, 130.9, 131.4, 136.1, 136.5.

Anal.Calcd for $C_{12}H_{16}O_2$ C, 74.97; H, 8.39; Found: C, 74.90; H, 8.42.

2-(4-Methoxybenzyl)-1,3-dioxolane (3d)[S3]

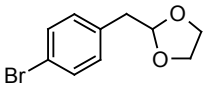


^{1}H NMR (300 MHz, $CDCl_3$): 2.86 (d, 2H, *J* = 4.53 Hz), 3.75-3.92 (m, 7H), 4.95 (t, 1H, *J* = 4.53 Hz), 6.78 (d, 2H, *J* = 8.3 Hz), 7.13 (d, 2H, *J* = 8.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): 39.8, 55.1, 64.9, 104.7, 113.7, 128.1, 130.5, 158.3.

Anal.Calcd for $C_{11}H_{14}O_3$ C, 68.02; H, 7.27; Found: C, 67.93; H, 7.25.

2-(4-Bromobenzyl)-1,3-dioxolane (3e)

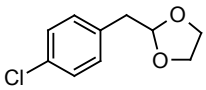


^{1}H NMR (500 MHz, $CDCl_3$): 2.87 (d, 2H, J = 4.94 Hz), 3.75-3.89 (m, 4H), 4.97 (t, 1H, J = 4.94 Hz), 7.11 (d, 2H, J = 7.91 Hz), 7.38 (d, 2H, J = 7.91 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): 40.0, 64.9, 104.1, 120.5, 131.3, 131.4, 135.

Anal.Calcd for $C_{10}H_{11}BrO_2$ C, 49.41; H, 4.56; Found: C, 49.44; H, 4.59.

2-(4-Chlorobenzyl)-1,3-dioxolane (3f)

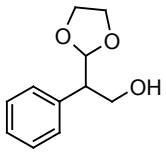


^{1}H NMR (500 MHz, $CDCl_3$): 2.93 (d, 2H, J = 4.94 Hz), 3.79-3.95 (m, 4H), 5.04 (t, 1H, J = 4.94 Hz), 7.2 (d, 2H, J = 7.91 Hz), 7.26 (d, 2H, J = 7.91 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): 39.9, 64.9, 104.1, 128.4, 128.7, 130.6, 131.0

Anal.Calcd for $C_{10}H_{11}ClO_2$ C, 60.46; H, 5.58; Found: C, 60.38; H, 5.51.

2-(1,3-Dioxolan-2-yl)-2-phenylethanol (3g)

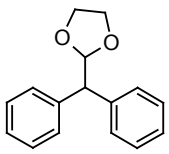


^{1}H NMR (500 MHz, $CDCl_3$): 2.18 (bs, 1H), 3.03-3.09 (m, 1H), 3.75-4.05 (m, 6H), 5.09 (d, 1H, J = 5 Hz), 7.19-7.3 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): 51.4, 63.5, 64.6, 65.1, 106.1, 127.2, 128.5, 128.5, 137.8.

Anal.Calcd for $C_{11}H_{14}O_3$ C, 68.02; H, 7.27; Found: C, 68.17; H, 7.22.

2-Diphenylmethyl-1,3-dioxolane (3h)[S4]

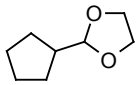


^{1}H NMR (400 MHz, $CDCl_3$): 3.68-3.86 (m, 4H), 4.2 (d, 1H, J = 4.67 Hz), 5.5 (d, 1H, J = 4.67 Hz), 7.14-7.36 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): 55.4, 65.2, 105.6, 126.6, 128.2, 129, 140.2.

Anal.Calcd for $C_{16}H_{16}O_2$ C, 79.97; H, 6.71; Found: C, 79.91; H, 6.77.

2-Cyclopentyl-1,3-dioxolane (3i)[S2]

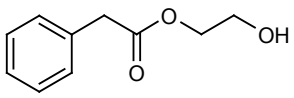


^{1}H NMR (300 MHz, $CDCl_3$): 1.38-1.69 (m, 6H), 1.7-1.82 (m, 2H), 2.04-2.19 (m, 1H), 3.8-4.03 (m, 4H), 4.7 (d, 1H, J = 5.28 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): 25.8, 27.6, 43.0, 65.0, 107.7.

Anal.Calcd for $C_8H_{14}O_2$ C, 67.57; H, 9.92; Found: C, 67.60; H, 9.99.

2-Hydroxyethyl-2-phenylacetate (4a)[S5]

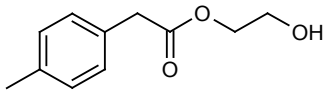


^{1}H NMR (500 MHz, $CDCl_3$): 2.09 (bs, 1H), 3.62 (s, 2H), 3.74 (t, 2H, J = 5 Hz), 4.18 (t, 2H, J = 5 Hz), 7.21-7.32 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): 41.1, 60.9, 66.3, 127.1, 128.6, 129.1, 133.7, 171.9.

Anal.Calcd for $C_{10}H_{12}O_3$ C, 66.65; H, 6.71; Found: C, 66.60; H, 6.63.

2-Hydroxyethyl-2-*p*-tolylacetate (4b)

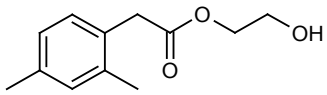


^{1}H NMR (300 MHz, $CDCl_3$): 1.96 (bs, 1H), 2.33 (s, 3H), 3.63 (s, 2H), 3.8 (t, 2H, J = 4.53 Hz), 4.22 (t, 2H, J = 4.53 Hz), 7.08-7.21 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): 21.0, 40.7, 61.0, 66.3, 129.0, 129.3, 130.7, 136.7, 172.1

Anal.Calcd for $C_{11}H_{14}O_3$ C, 68.02; H, 7.27; Found: C, 67.88; H, 7.31.

2-Hydroxyethyl-2-(2,4-dimethylphenyl)acetate (4c)

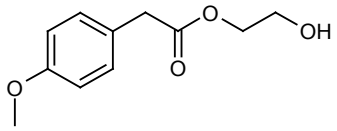


^{1}H NMR (300 MHz, $CDCl_3$): 2.03 (bs, 1H), 2.23-2.38 (m, 6H), 3.64 (s, 2H), 3.78 (t, 2H, J = 4.53 Hz), 4.21 (t, 2H, J = 4.53 Hz), 6.94-7.12 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 19.4, 21.0, 38.6, 61.0, 66.3, 126.8, 129.4, 129.9, 131.1, 136.5, 137.0, 172.0

Anal.Calcd for $C_{12}H_{16}O_3$ C, 69.21; H, 7.74; Found: C, 69.35; H, 7.71.

2-Hydroxyethyl-2-(4-methoxyphenyl)acetate (4d)

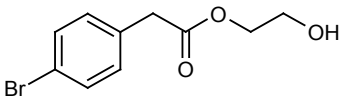


^{1}H NMR (300 MHz, $CDCl_3$): 2.1 (bs, 1H), 3.61 (s, 2H), 3.73-3.84 (m, 5H), 4.22 (t, 2H, J = 4.72 Hz), 6.86 (d, 2H, J = 8.3 Hz), 7.2 (d, 2H, J = 8.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): 40.2, 55.2, 61.0, 66.3, 114.0, 125.8, 130.2, 158.7, 172.2.

Anal.Calcd for $C_{11}H_{14}O_4$ C, 62.85; H, 6.71; Found: C, 62.80; H, 6.66.

2-Hydroxyethyl-2-(4-bromophenyl)acetate (4e)

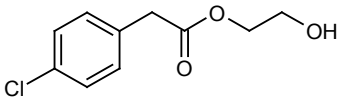


^{1}H NMR (300 MHz, $CDCl_3$): 2.17 (bs, 1H), 3.62 (s, 2H), 3.81 (t, 2H, J = 4.53 Hz), 4.23 (t, 2H, J = 4.53 Hz), 7.16 (d, 2H, J = 8.3 Hz), 7.45(d, 2H, J = 8.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): 40.4, 60.9, 66.4, 121.2, 130.9, 131.6, 132.6, 171.4.

Anal.Calcd for $C_{10}H_{11}BrO_3$ C, 46.36; H, 4.28; Found: C, 46.42; H, 4.35.

2-Hydroxyethyl-2-(4-chlorophenyl)acetate (4f)

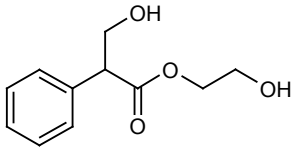


^{1}H NMR (300 MHz, $CDCl_3$): 2.15 (bs, 1H), 3.64 (s, 2H), 3.81 (t, 2H, J = 4.53 Hz), 4.23 (t, 2H, J = 4.53 Hz), 7.19-7.32 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): 40.3, 60.9, 66.4, 128.7, 130.5, 133.1, 171.5.

Anal.Calcd for $C_{10}H_{11}ClO_3$ C, 55.96; H, 5.17; Found: C, 56.02; H, 5.05.

2-Hydroxyethyl-3-hydroxy-2-phenylpropanoate (4g)

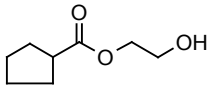


^{1}H NMR (300 MHz, $CDCl_3$): 2.47 (bs, 1H), 3.58 (bs, 1H), 3.71-3.81 (m, 3H), 3.83-3.91 (m, 1H), 4.07-4.18 (m, 2H), 4.3-4.4 (m, 1H), 7.21-7.34 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): 54.3, 60.4, 64.5, 66.3, 127.8, 128.1, 128.8, 135.2, 173.3.

Anal.Calcd for $C_{11}H_{14}O_4$ C, 62.85; H, 6.71; Found: C, 62.91; H, 6.67.

2-Hydroxyethyl cyclopentanecarboxylate (4i)

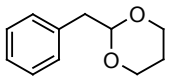


^{1}H NMR (300 MHz, $CDCl_3$): 1.5-1.99 (m, 8H), 2.21 (bs, 1H), 2.71-2.84 (m, 1H), 3.83 (t, 2H, J = 4.53 Hz), 4.21 (t, 2H, J = 4.53 Hz,).

^{13}C NMR (75 MHz, $CDCl_3$): 25.7, 30.0, 43.6, 61.1, 65.9, 177.3.

Anal.Calcd for $C_8H_{14}O_3$ C, 60.74; H, 8.92; Found: C, 60.83; H, 8.99.

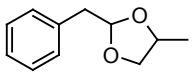
2-(Benzyl)-1,3-dioxane (5)[S6]



^{1}H NMR (500 MHz, $CDCl_3$): 1.26-1.35 (m, 1H), 2.03-2.15 (m, 1H), 2.9 (d, 2H, J = 5.0 Hz), 3.68-3.76 (m, 2H), 4.06-4.13 (m, 2H), 4.69 (t, 1H, J = 5.0 Hz), 7.18-7.32 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$):25.6, 41.9, 66.9, 102.6, 126.3, 128.1, 129.5, 136.5.

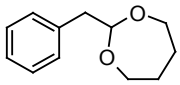
2-(Benzyl)-4-methyl-1,3-dioxolane (6)[S7]**[Mixture of diastereoisomers]**



^{1}H NMR (300 MHz, $CDCl_3$): 1.23 (d, 3H, J = 6.04 Hz), 1.26 (d, 3H, J = 6.04 Hz), 2.91-2.99 (m, 4H), 3.33-3.4 (m, 2H), 3.89 (m, 1H), 4.05-4.22 (m, 3H), 5.1 (t, 1H, J = 4.53 Hz), 5.23 (t, 1H, J = 5.28 Hz), 7.19-7.33 (m, 10 H).

^{13}C NMR (75 MHz, $CDCl_3$): 18.2, 18.5, 41.1, 41.2, 70.9, 71.7, 71.9, 72.8, 103.9, 104.7, 126.4, 126.5, 128.1, 128.2, 129.6, 129.7, 136.1, 136.2.

2-(Benzyl)-1,3-dioxepane (7)

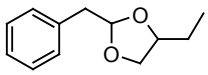


^{1}H NMR (300 MHz, $CDCl_3$): 1.62-1.82 (m, 4H), 2.88 (d, 2H, J = 6.04 Hz), 3.56-3.68 (m, 2H), 3.87-3.98 (m, 2H), 4.87 (t, 1H, J = 6.04 Hz), 7.18-7.33 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): 29.2, 41.0, 65.7, 103.0, 126.2, 128.2, 129.5, 137.2.

Anal.Calcd for $C_{12}H_{16}O_2$ C, 74.97; H, 8.39; Found: C, 74.82; H, 8.49.

2-(Benzyl)-4-ethyl-1,3-dioxolane (8) [Mixture of diastereoisomers]

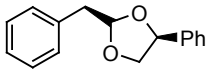


^{1}H NMR (300 MHz, $CDCl_3$): 0.93 (t, 6H, *J* = 7.55 Hz), 1.41-1.7 (m, 4H), 2.86-3.05 (m, 4H), 3.4-3.52 (m, 2H), 3.85-4.03 (m, 3H), 4.04-4.12 (m, 1H), 5.09 (t, 1H, *J* = 4.72 Hz), 5.19 (t, 1H, J = 5.09 Hz), 7.18-7.35 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): 9.7, 26.0, 26.3, 40.9, 41.0, 69.2, 70.0, 77.3, 77.8, 104.0, 104.5, 126.4, 128.0, 128.1, 129.6, 129.7, 136.1, 136.2.

Anal.Calcd for $C_{12}H_{16}O_2$ C, 74.97; H, 8.39; Found: C, 74.92; H, 8.45.

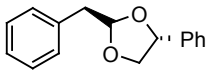
***cis*-2-(Benzyl)-4-phenyl-1,3-dioxolane (10a)**[S8]



^{1}H NMR (300 MHz, $CDCl_3$): 2.98-3.13 (m, 2H), 3.66 (t, 1H, *J* = 8.43 Hz), 4.35 (dd, 1H, *J* = 2.20 Hz, 6.23 Hz), 4.97 (dd, 1H, *J* = 1.10 Hz, 6.60 Hz), 5.47 (t, 1H, *J* = 4.76 Hz), 7.09-7.44 (m, 10 H).

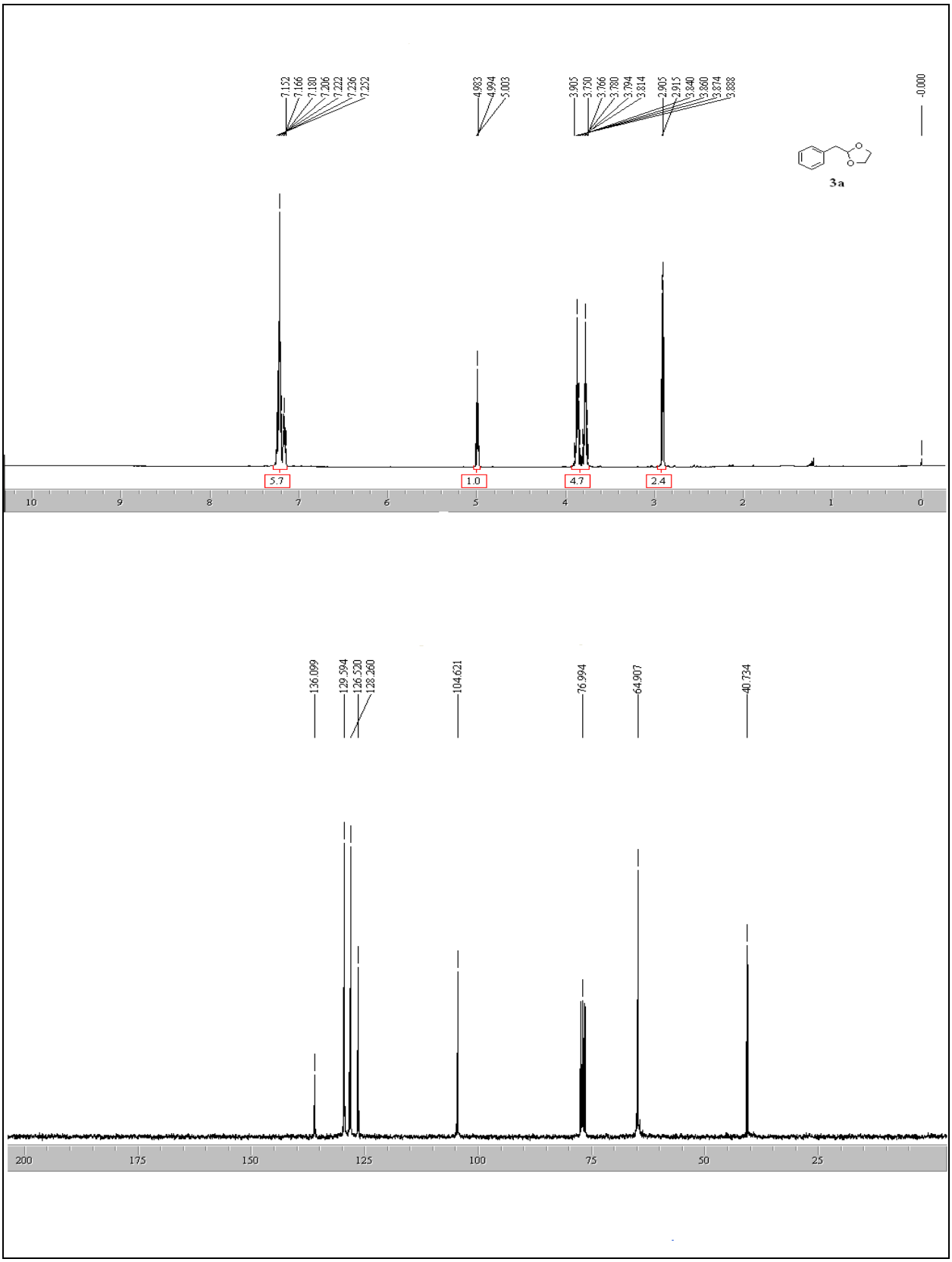
^{13}C NMR (100 MHz, $CDCl_3$): 41.2, 72.7, 77.7, 105.7, 125.9, 126.6, 127.9, 128.3, 128.5, 129.8, 136.0, 139.5

***trans*-2-(Benzyl)-4-phenyl-1,3-dioxolane (10b)**[S8]



^{1}H NMR (300 MHz, $CDCl_3$): 3.06-3.20 (m, 2H), 3.69 (dd, 1H, *J* = 1.51 Hz, 6.79 Hz), 4.17 (dd, 1H, *J* = 0.75 Hz, 6.79 Hz), 5.0 (t, 1H, *J* = 6.79 Hz), 5.29 (t, 1H, *J* = 4.53 Hz), 7.21-7.38 (m, 10 H).

^{13}C NMR (75 MHz, $CDCl_3$): 40.8, 72.0, 78.4, 105.3, 126.3, 126.6, 128.1, 128.3, 128.5, 129.9, 135.9, 139.4.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5.003
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3.766
3.780
3.794
3.814
2.905
2.915
3.840
3.860
3.874
3.888
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4.7
2.4
10
9
8
7
6
5
4
3
2
1
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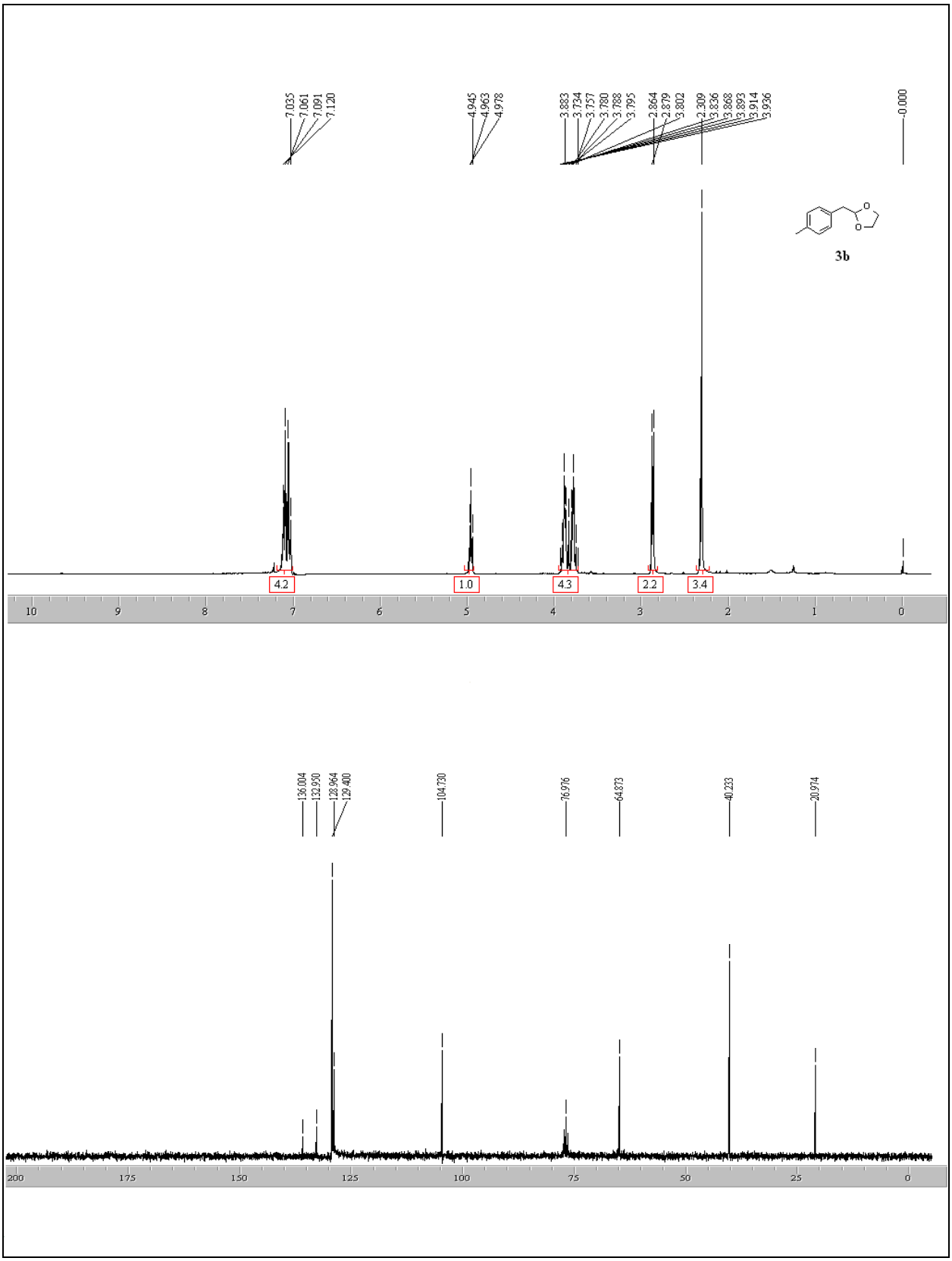
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3.4
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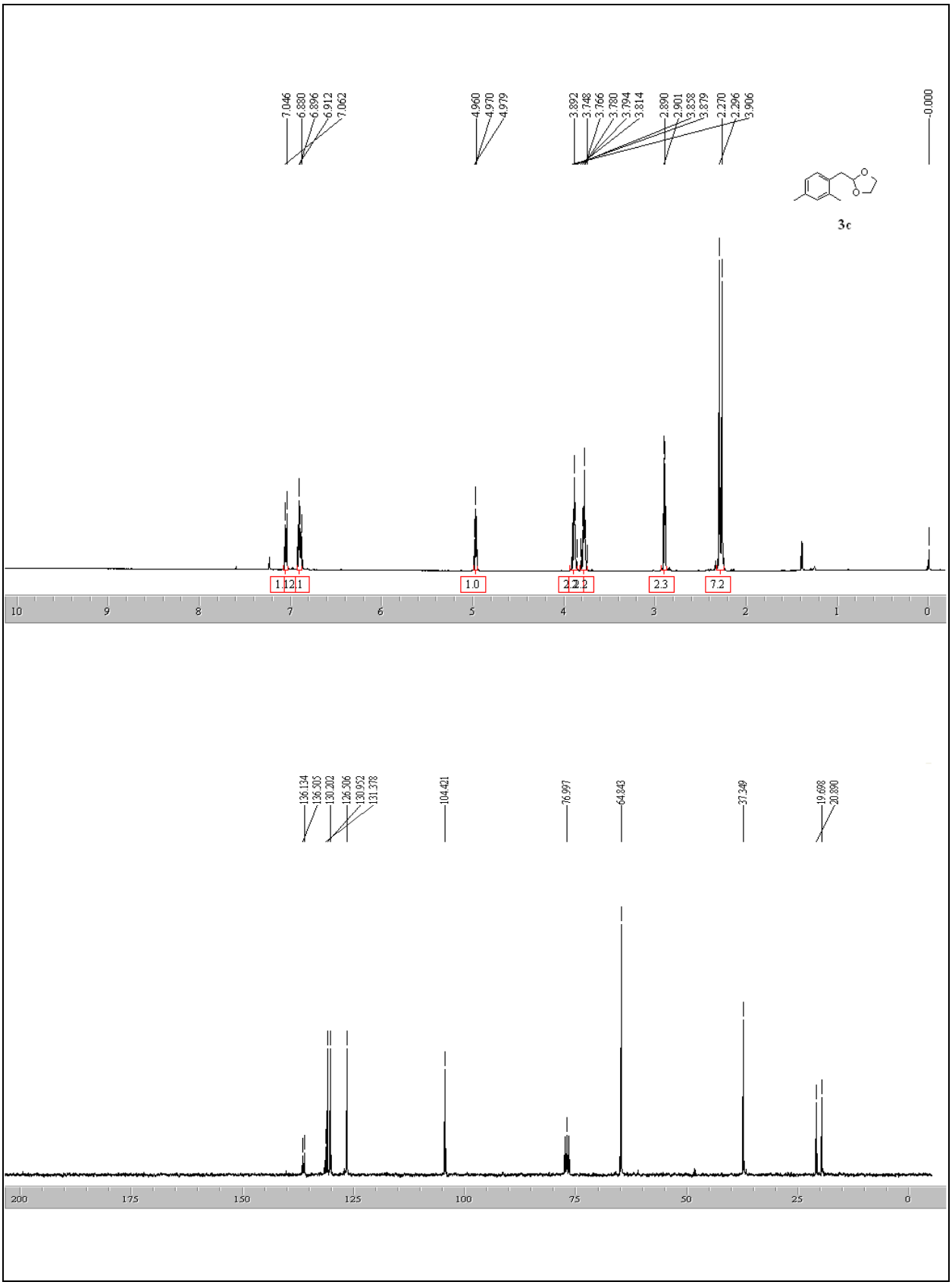
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2.3
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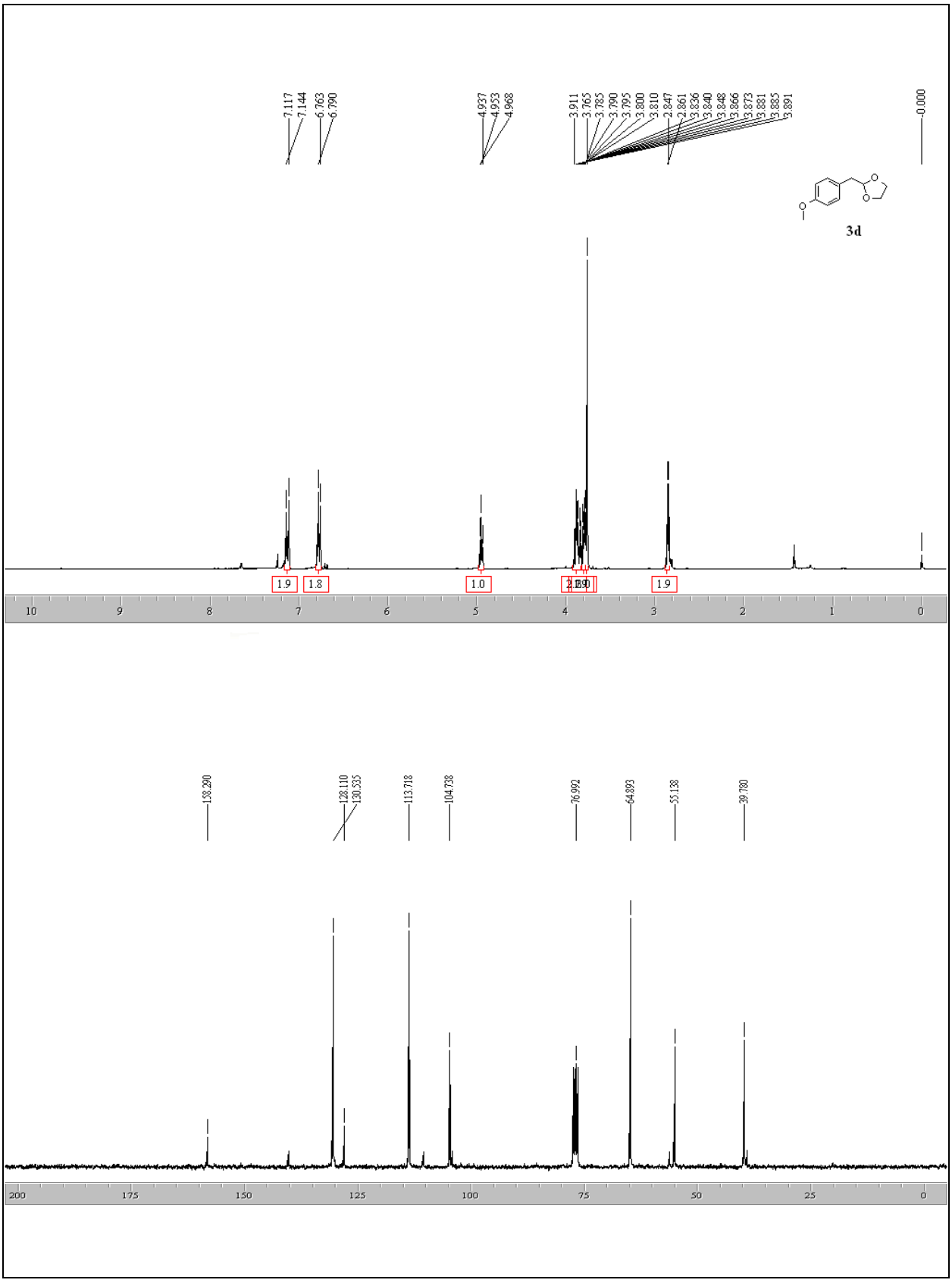
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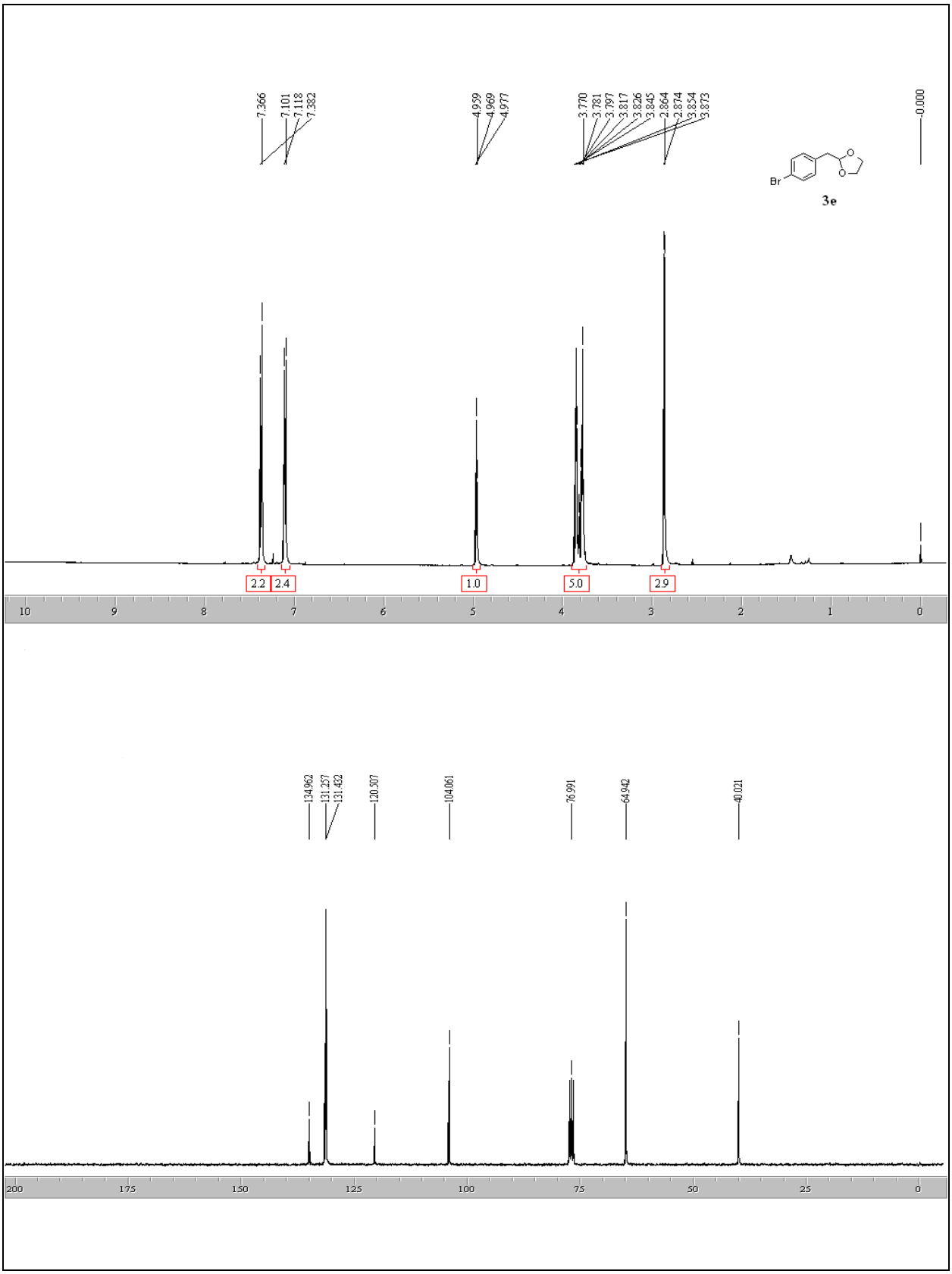
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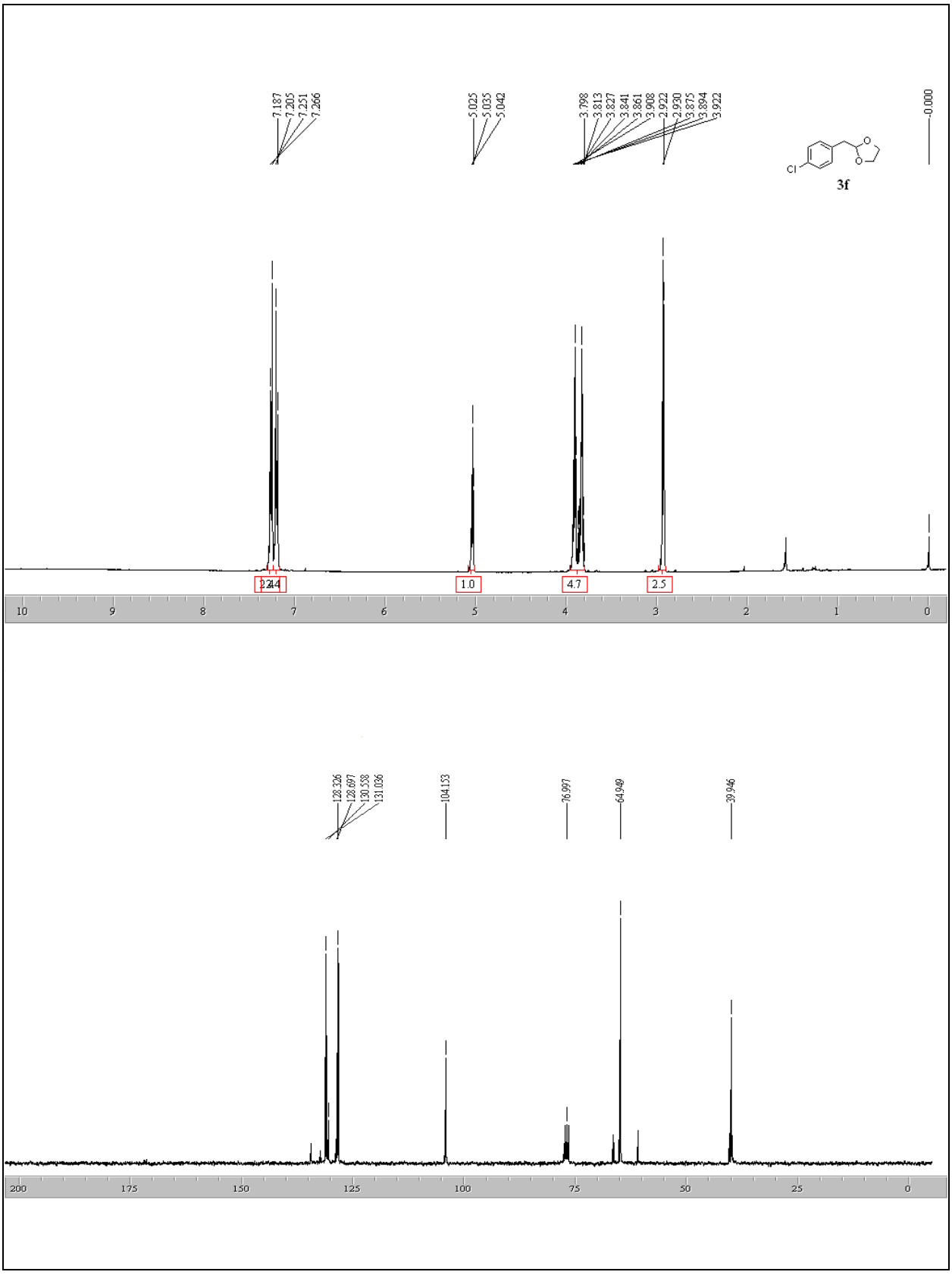
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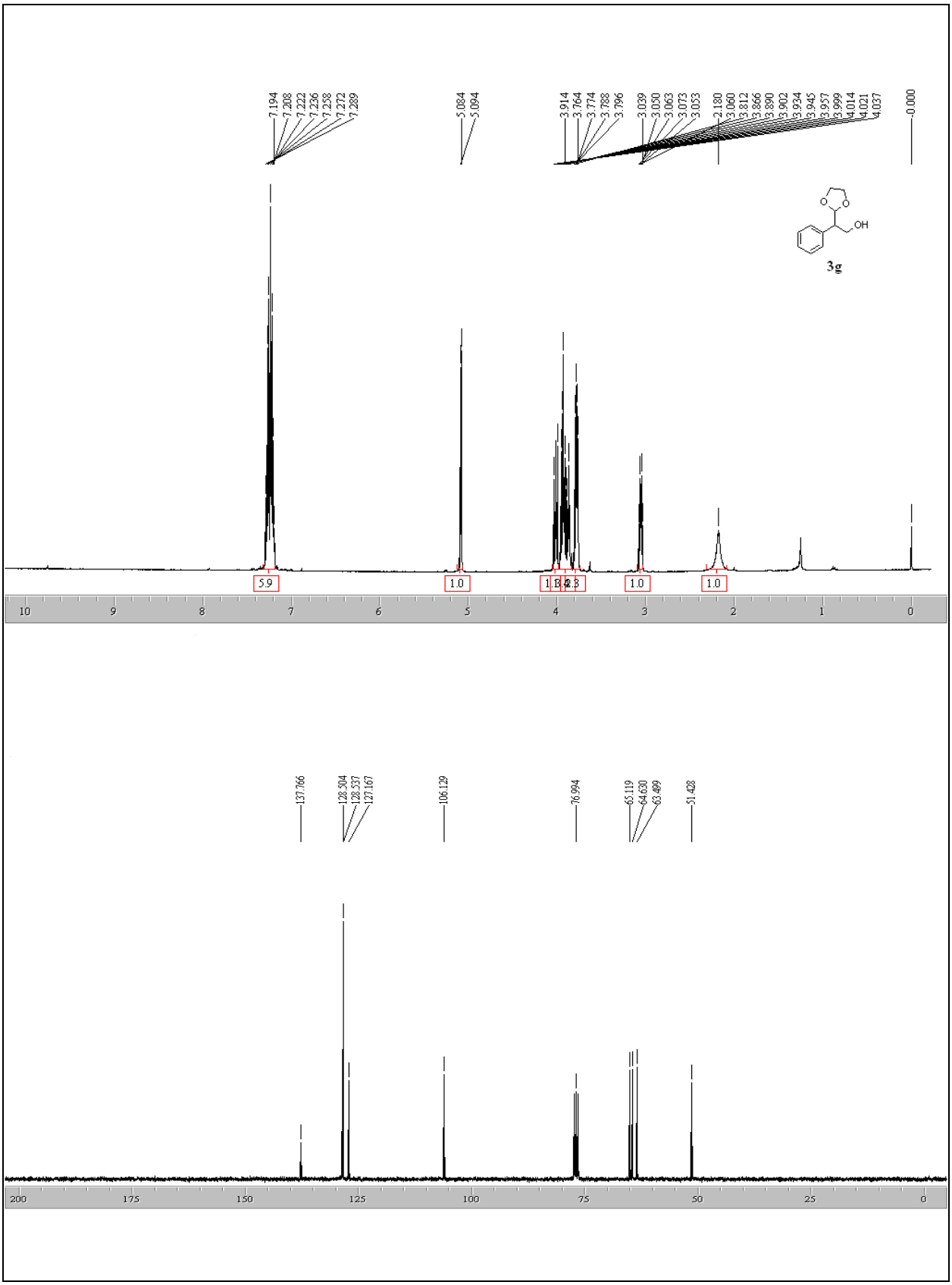
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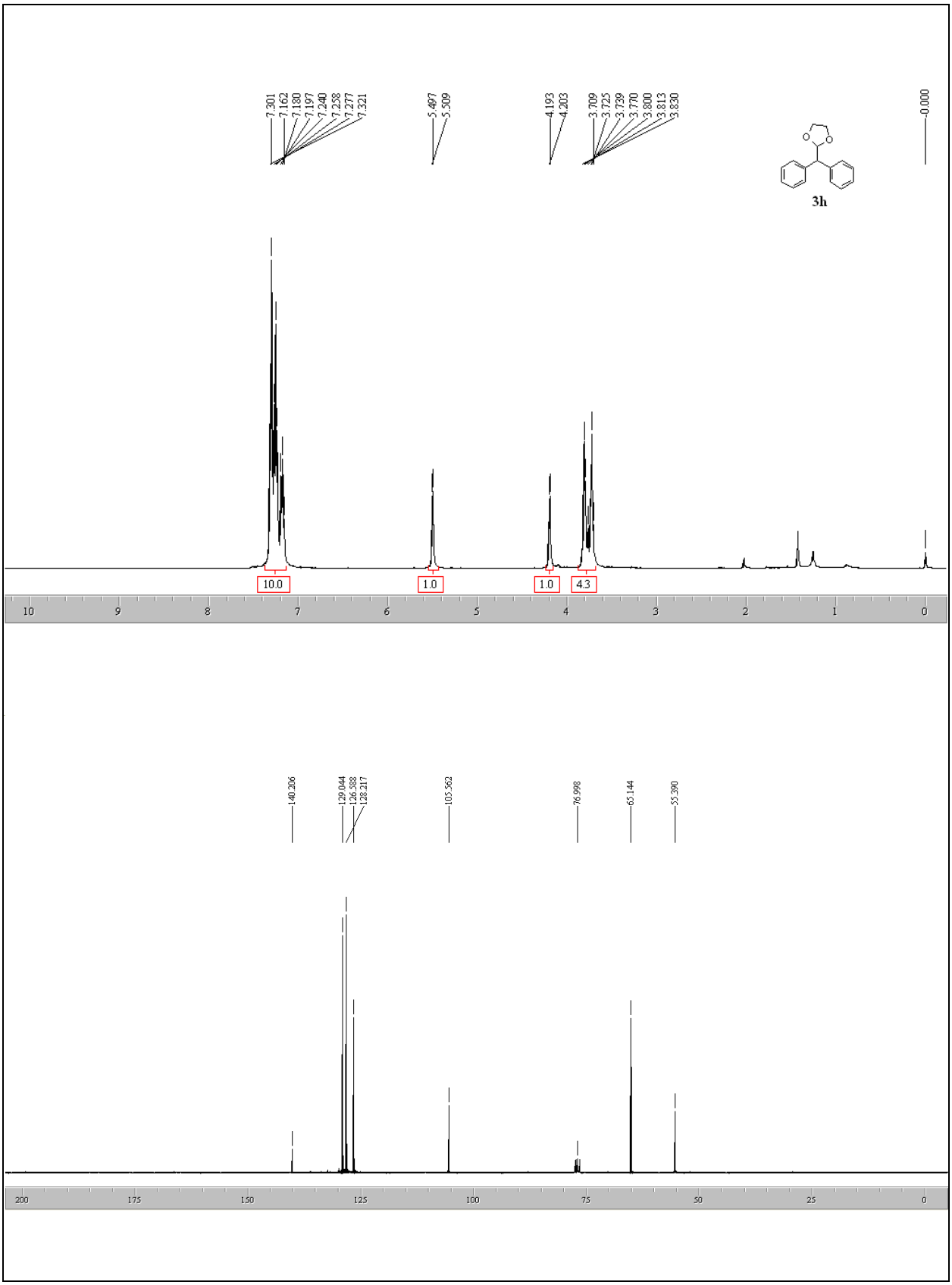
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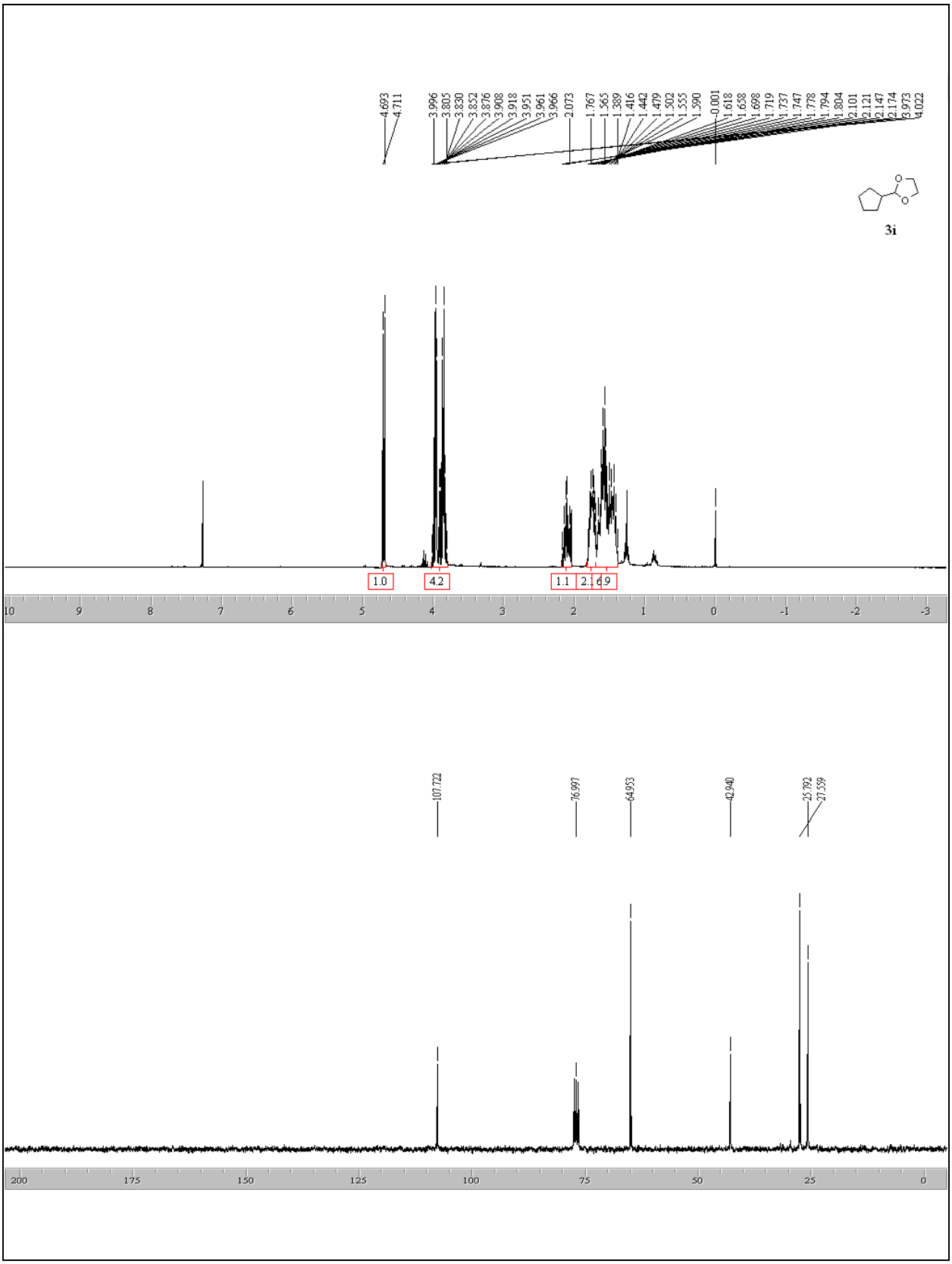
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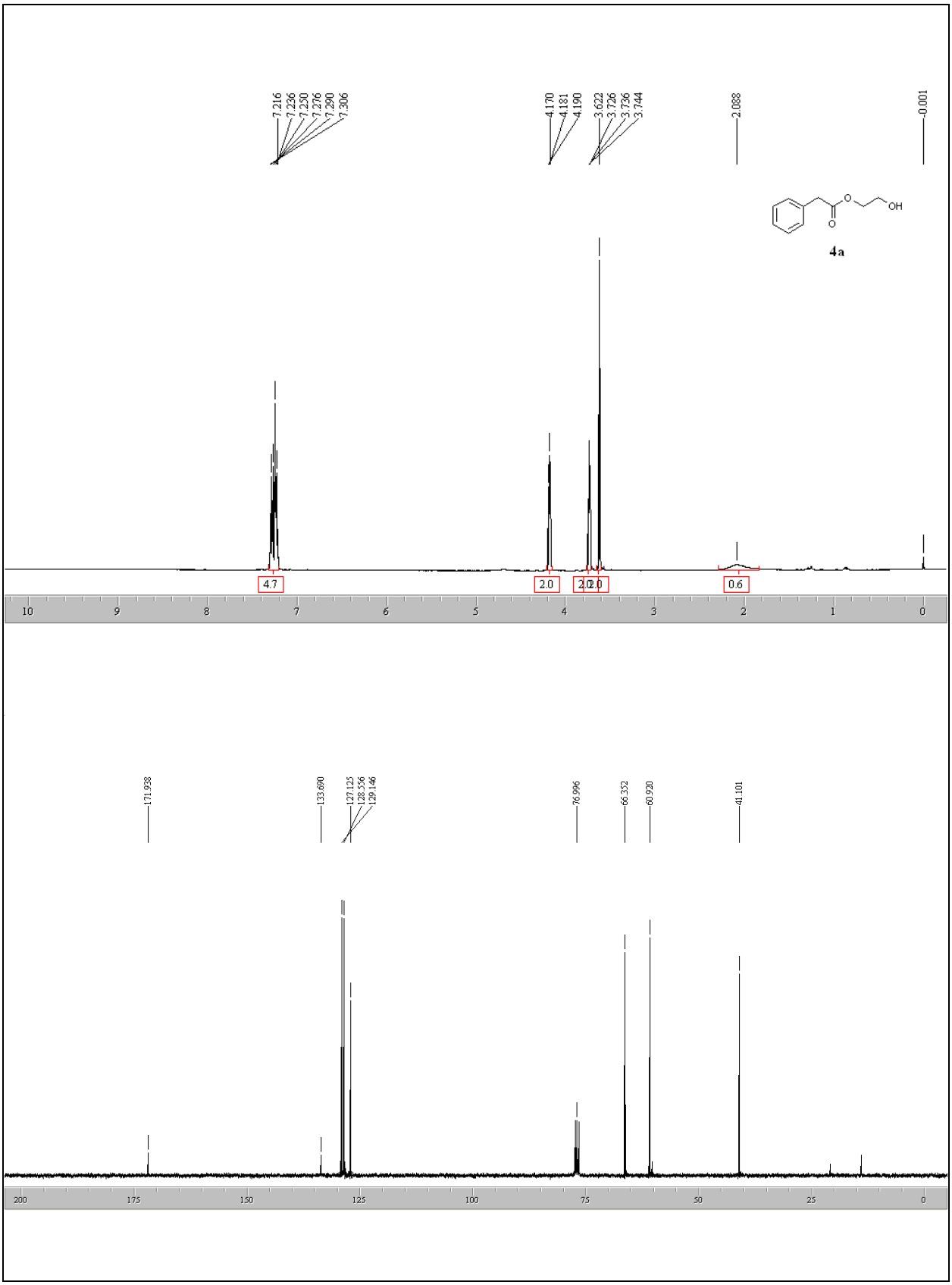
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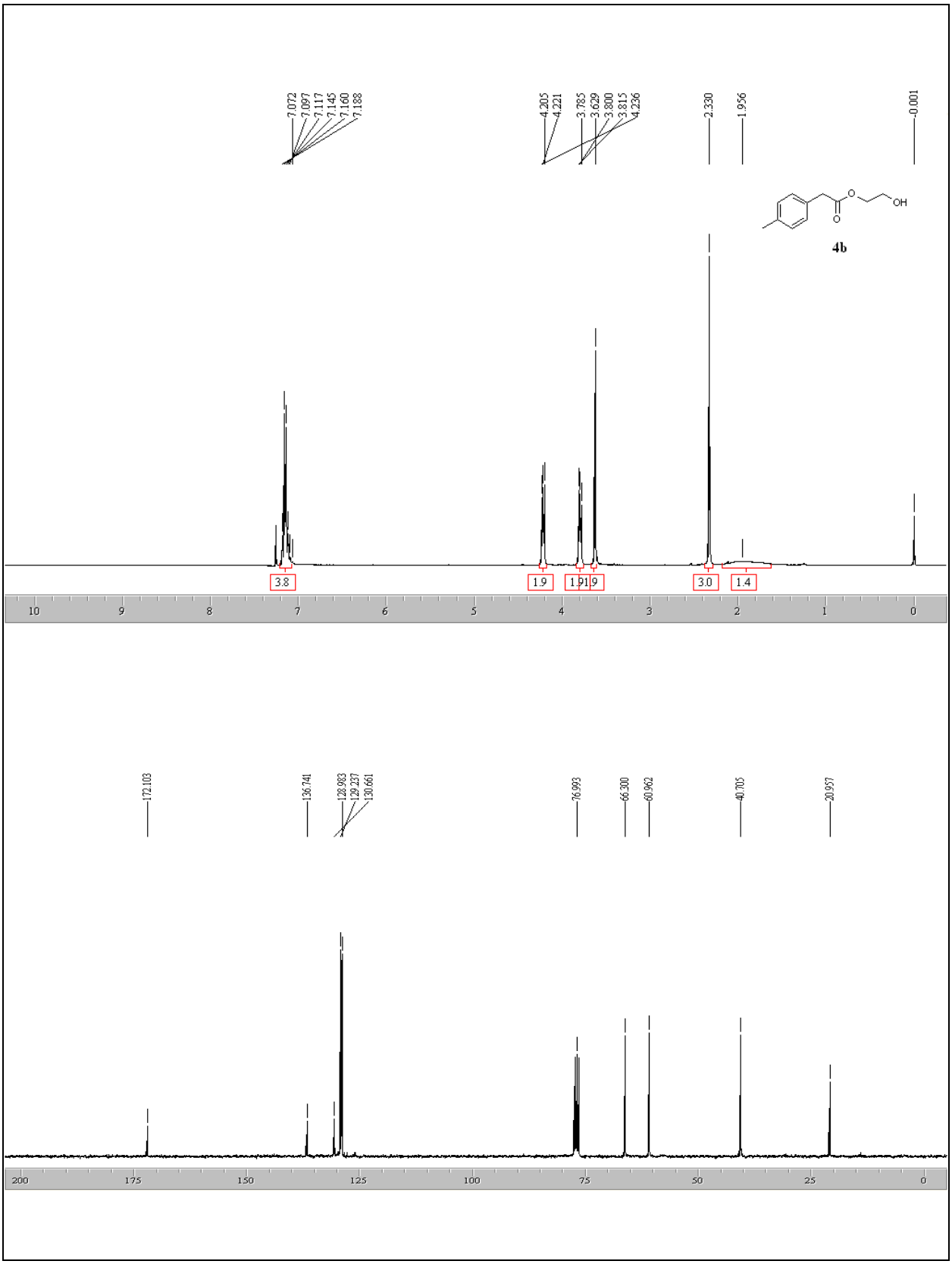
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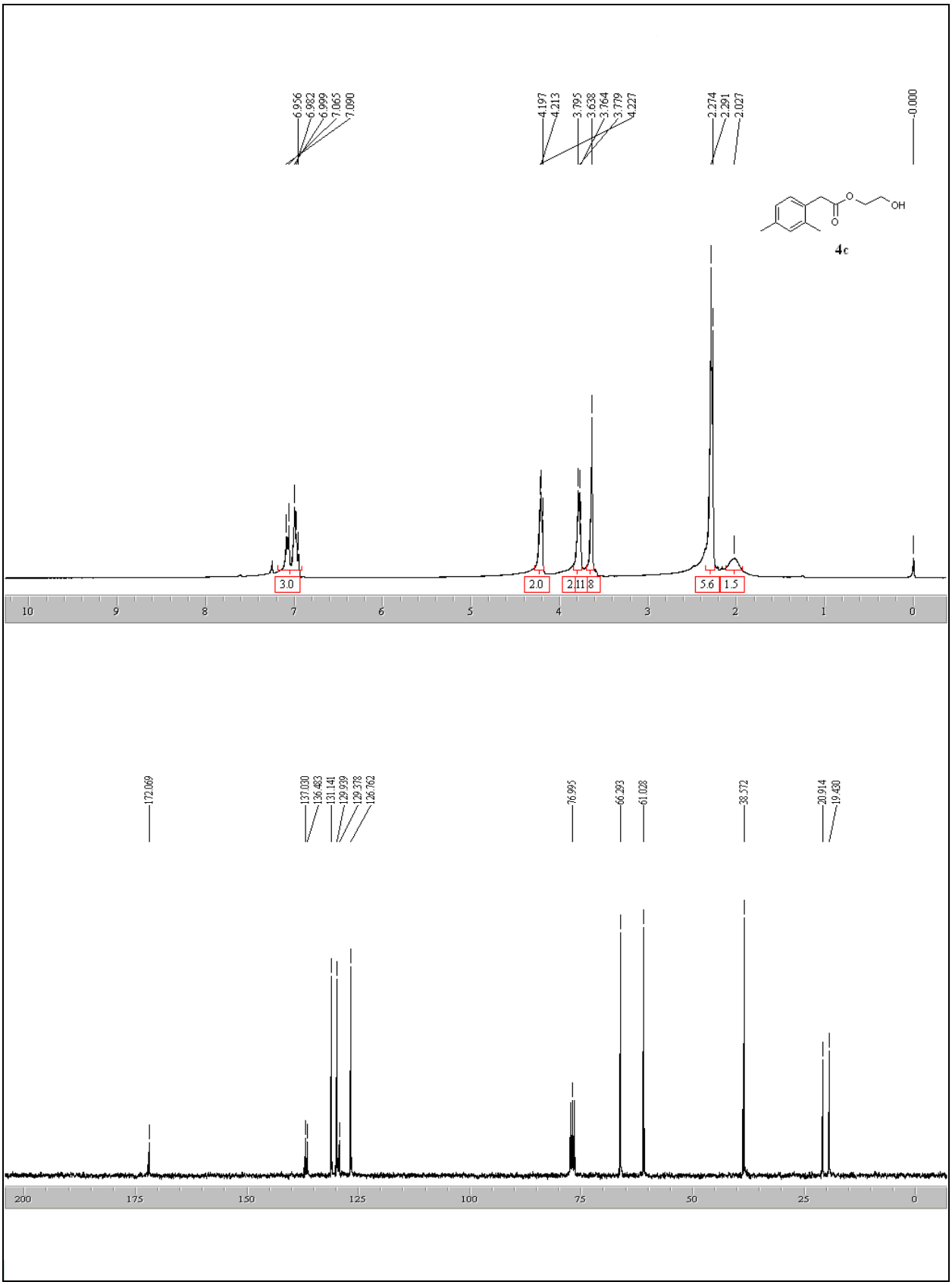
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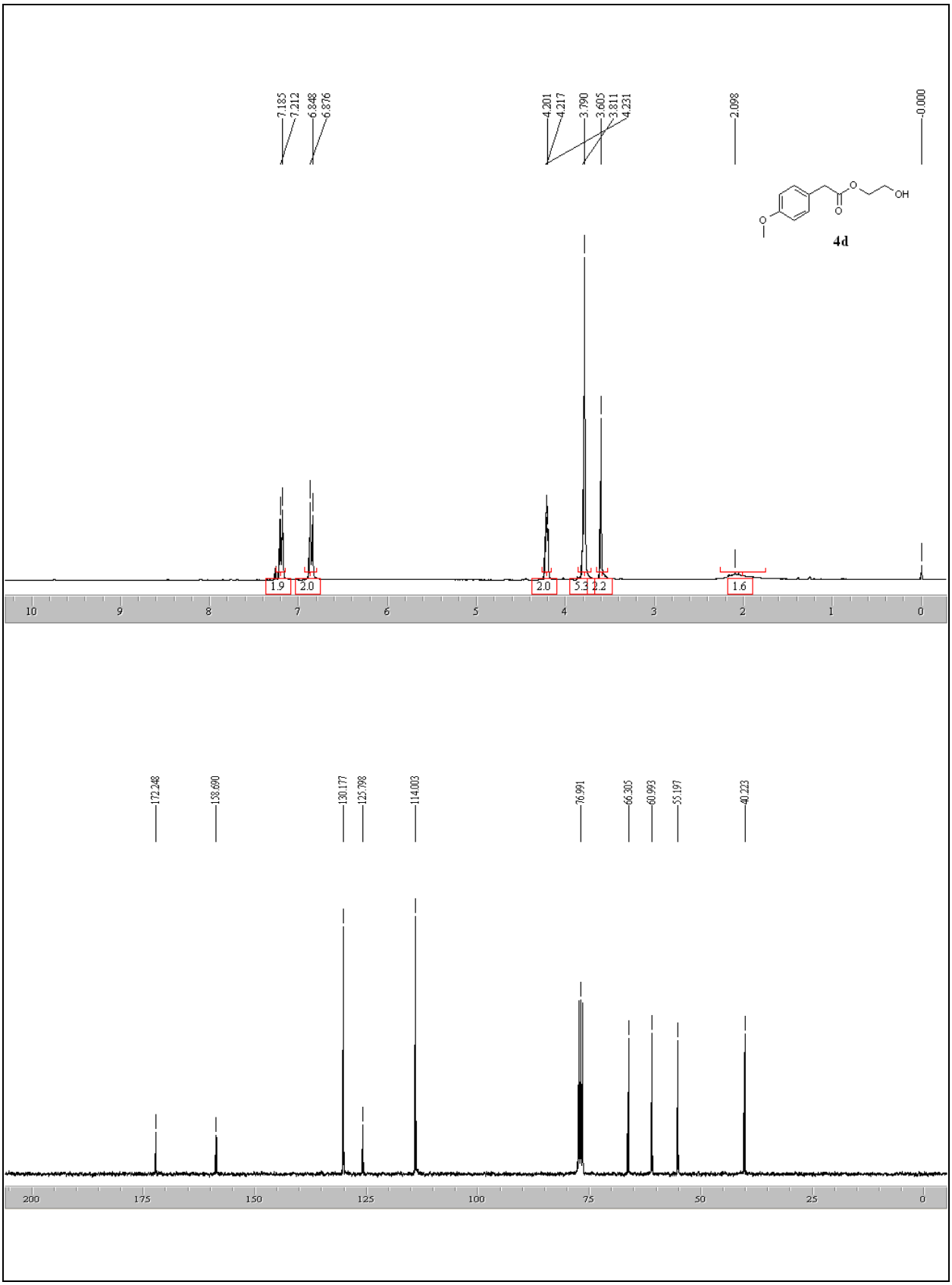
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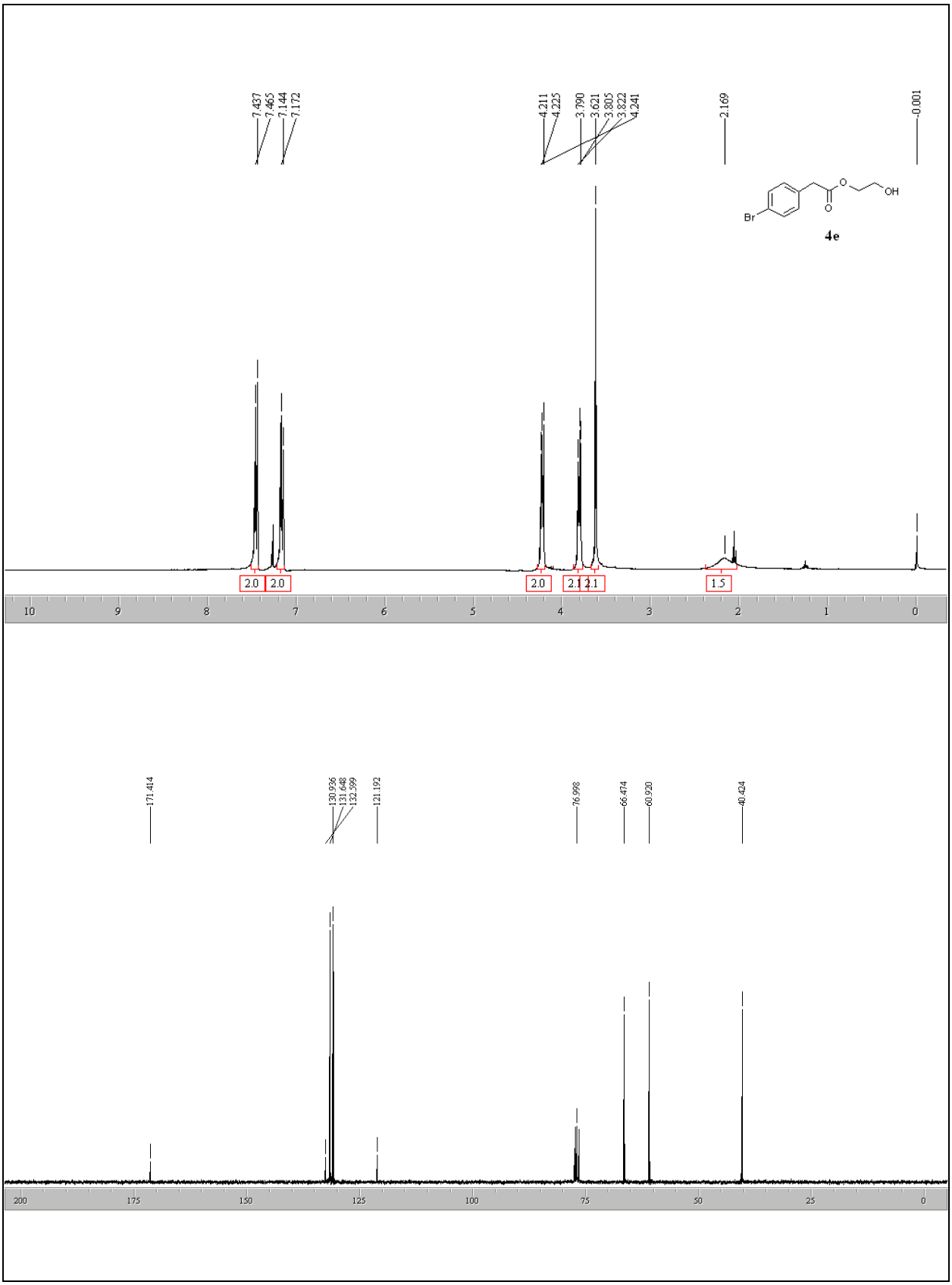
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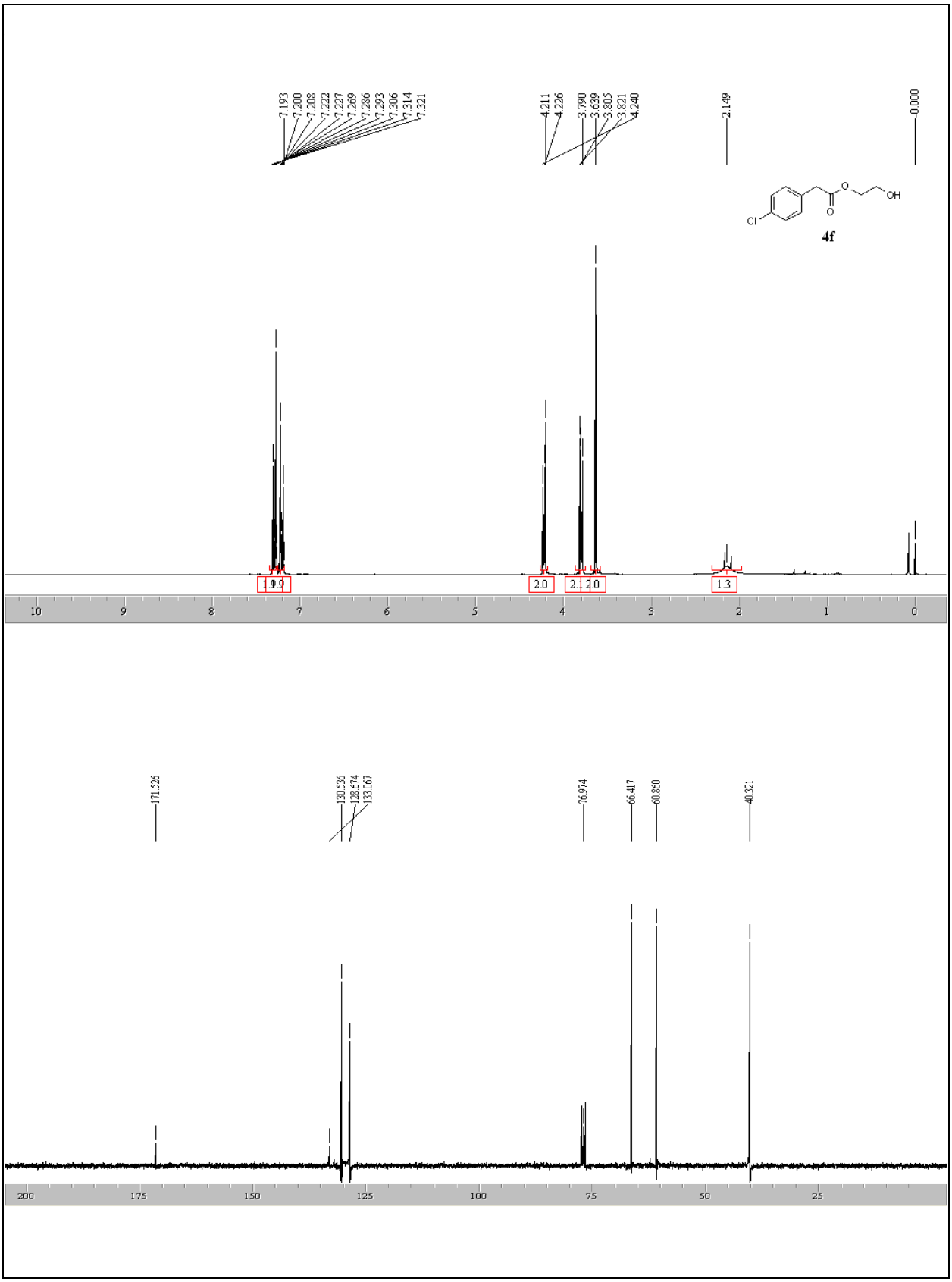
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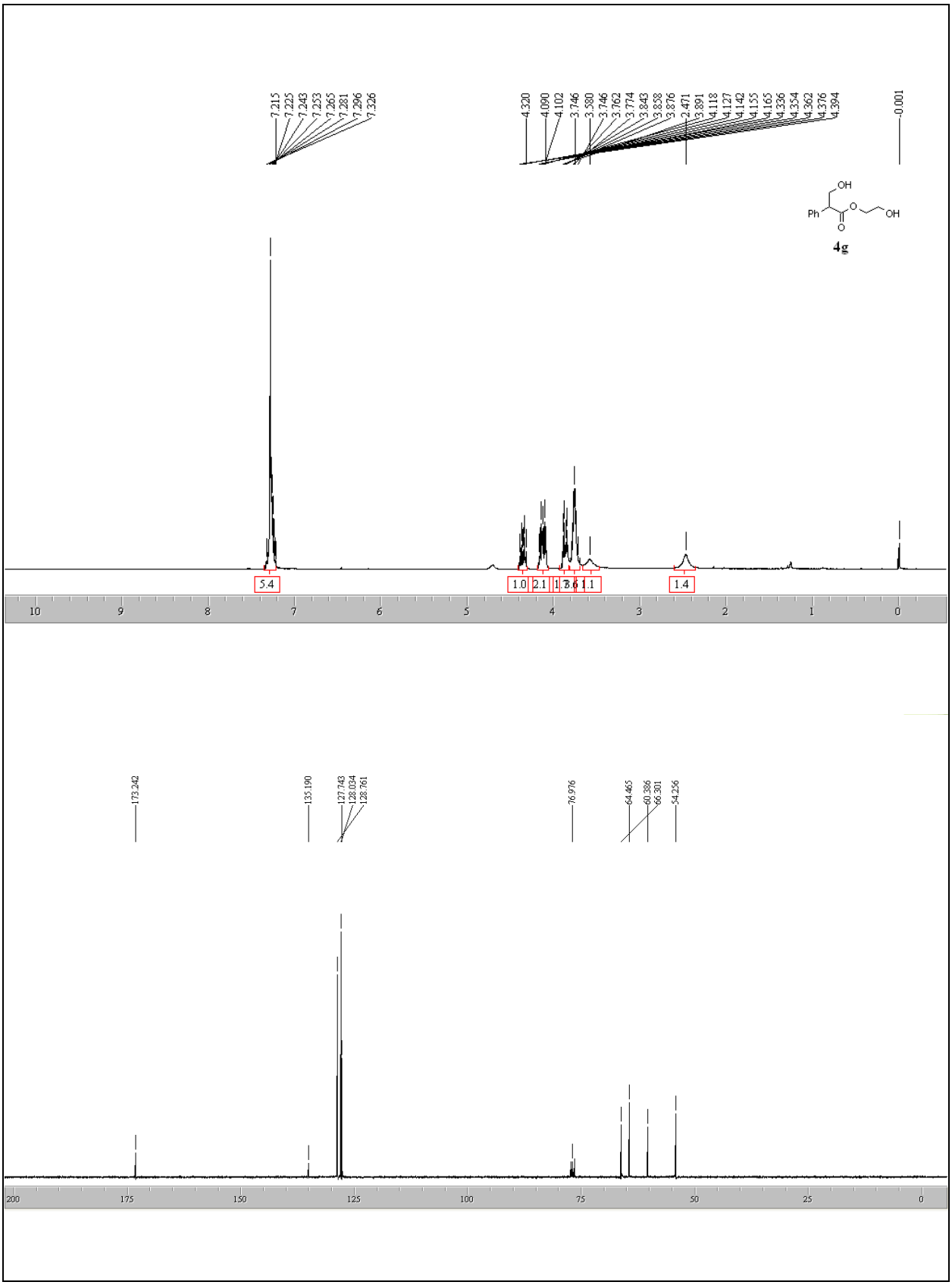
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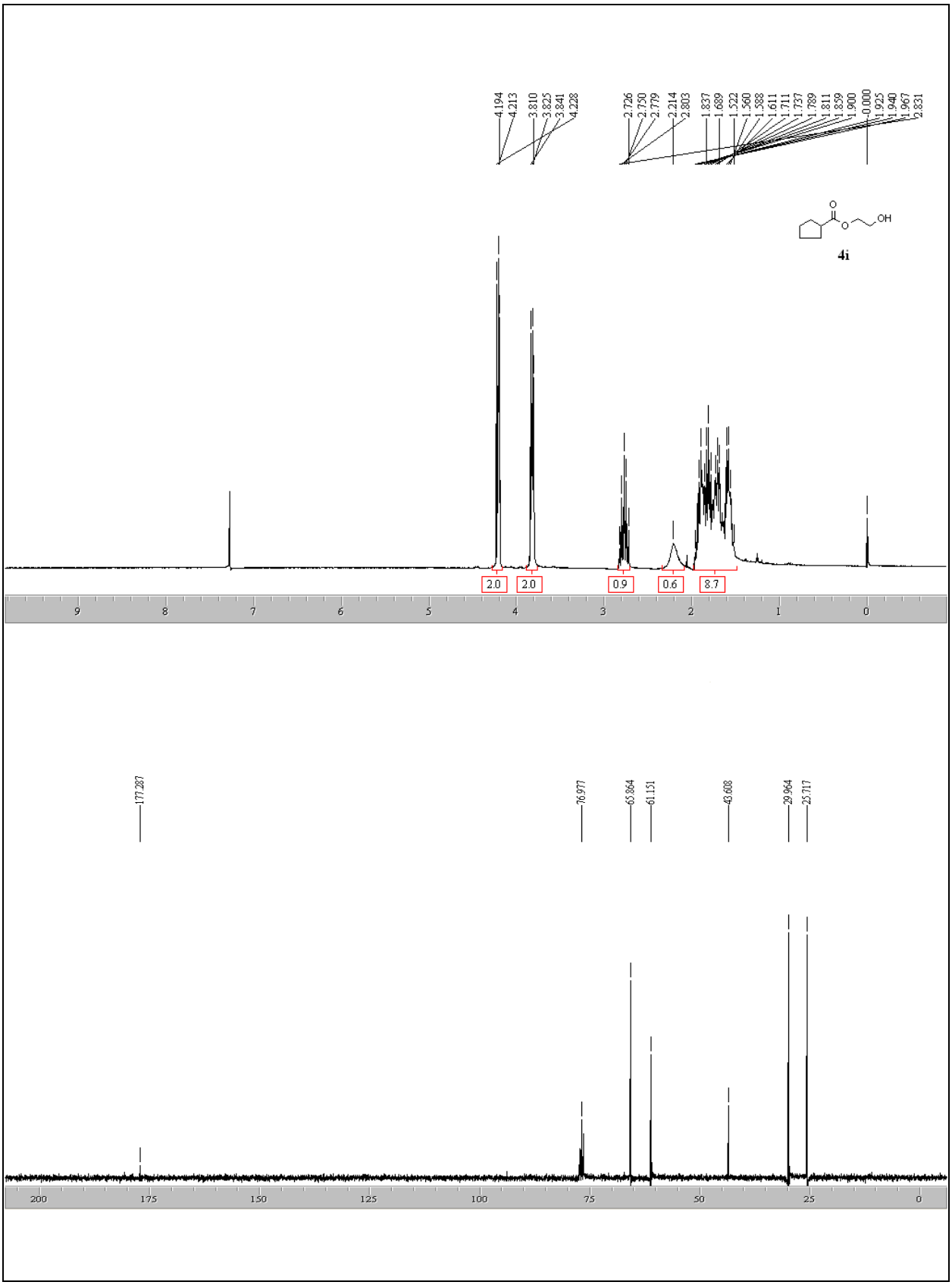
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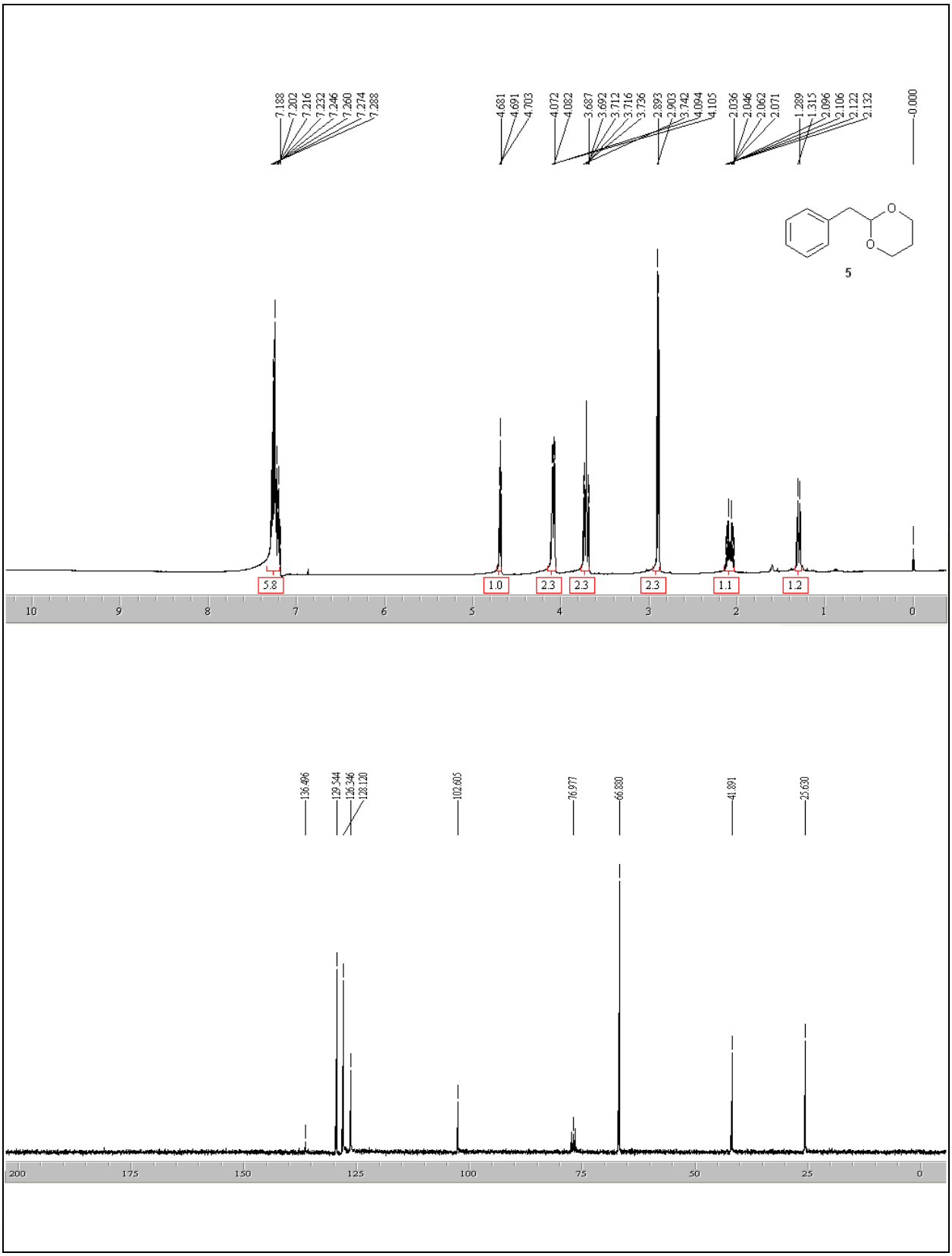
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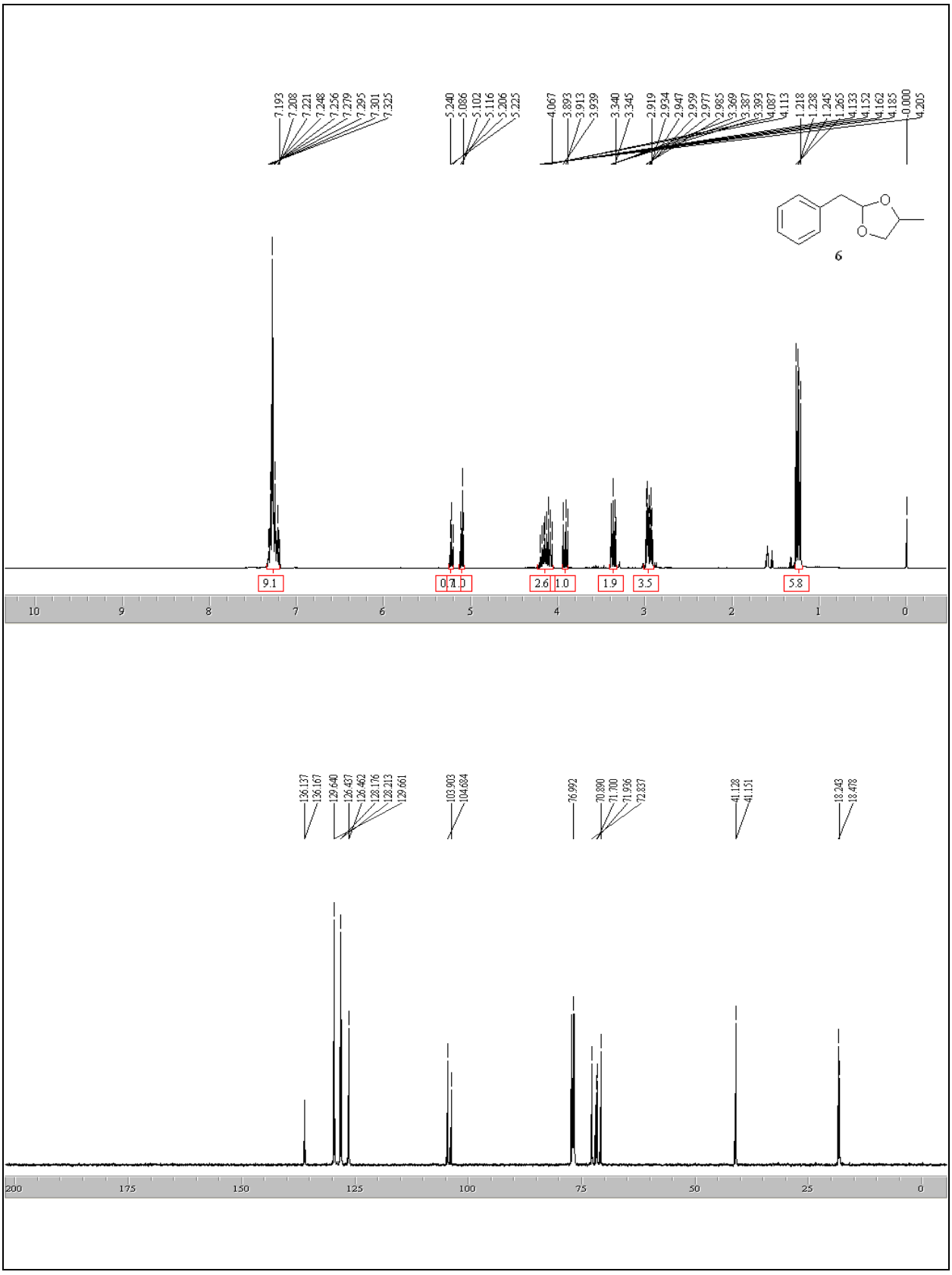
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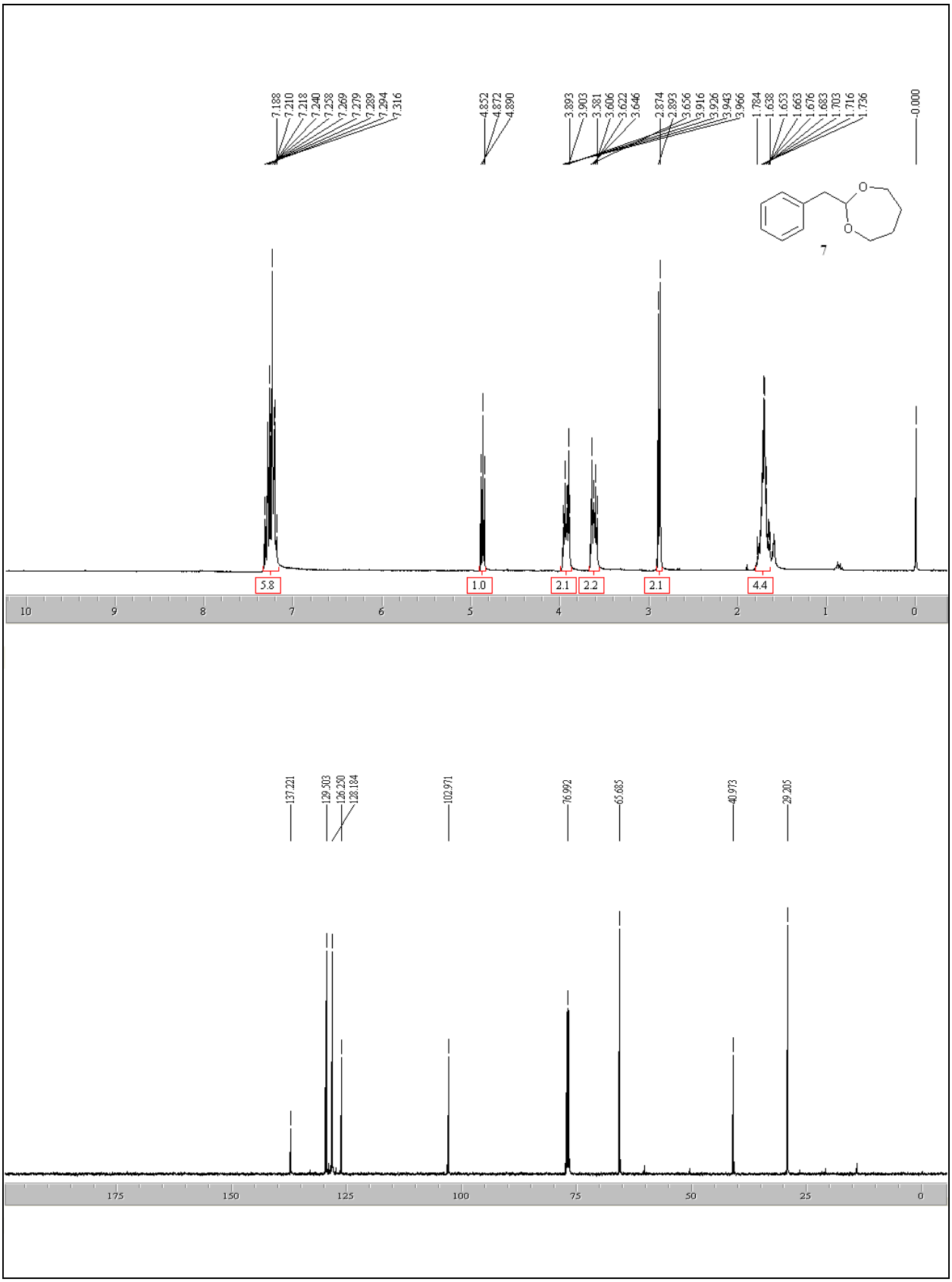
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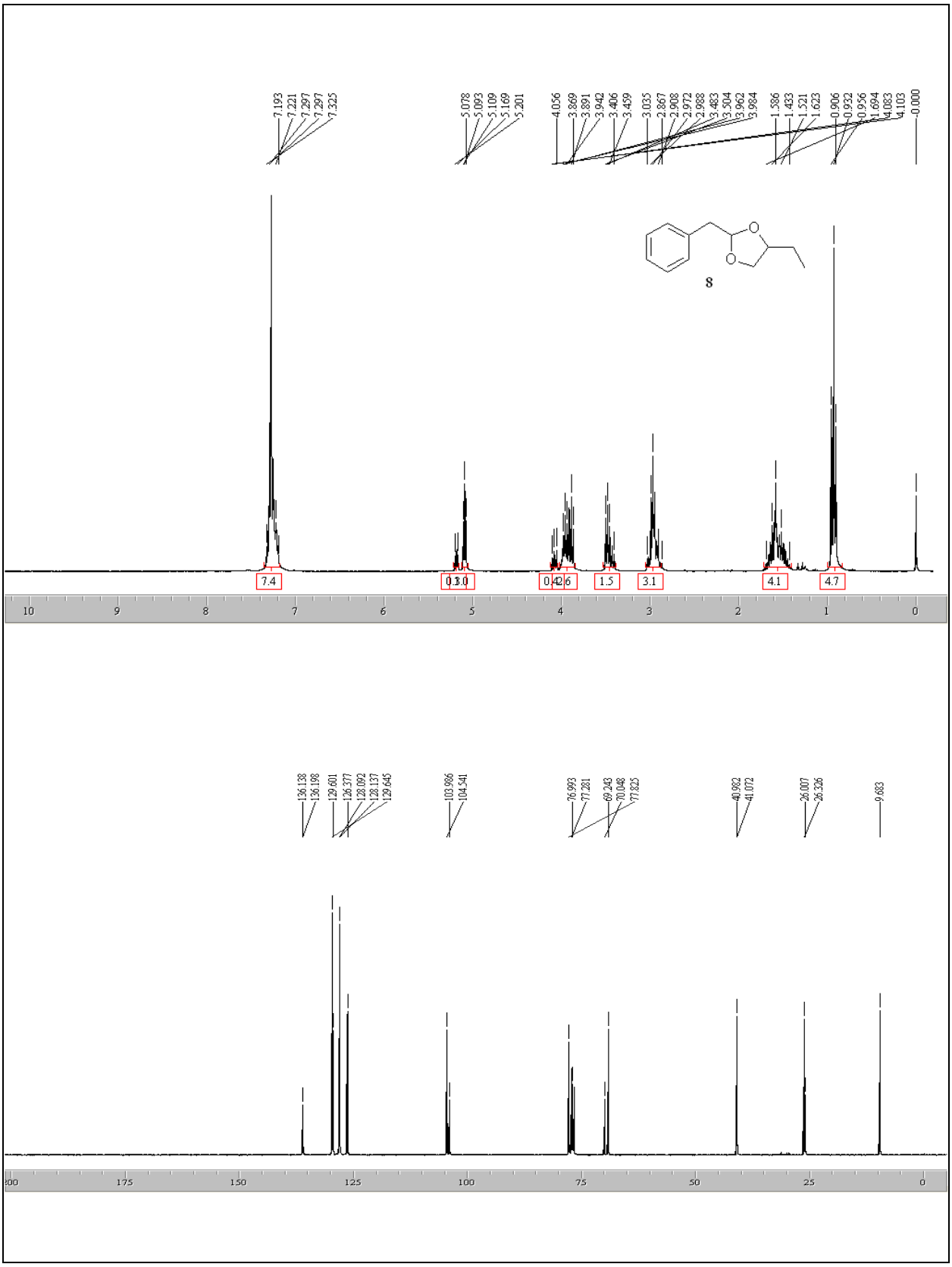
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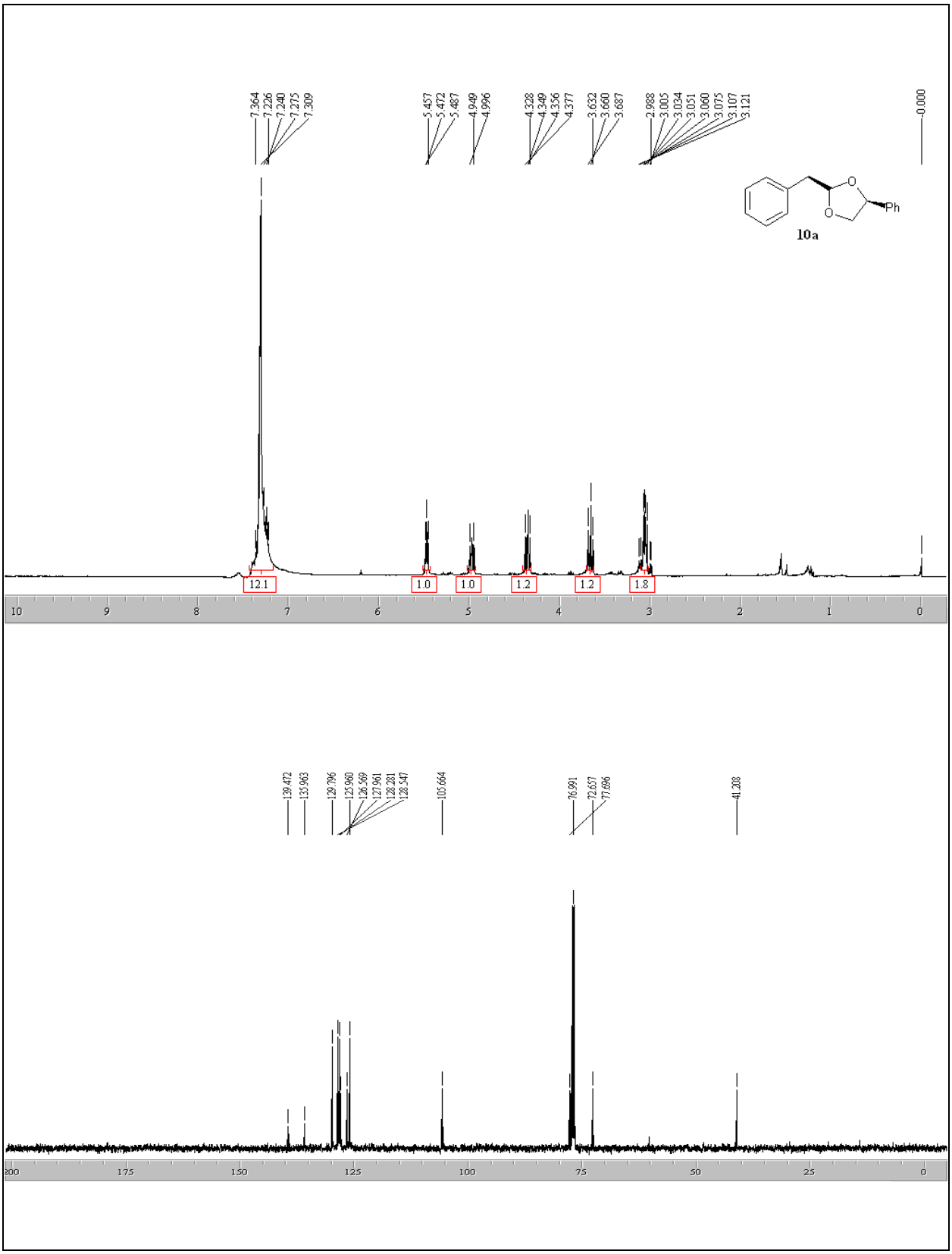
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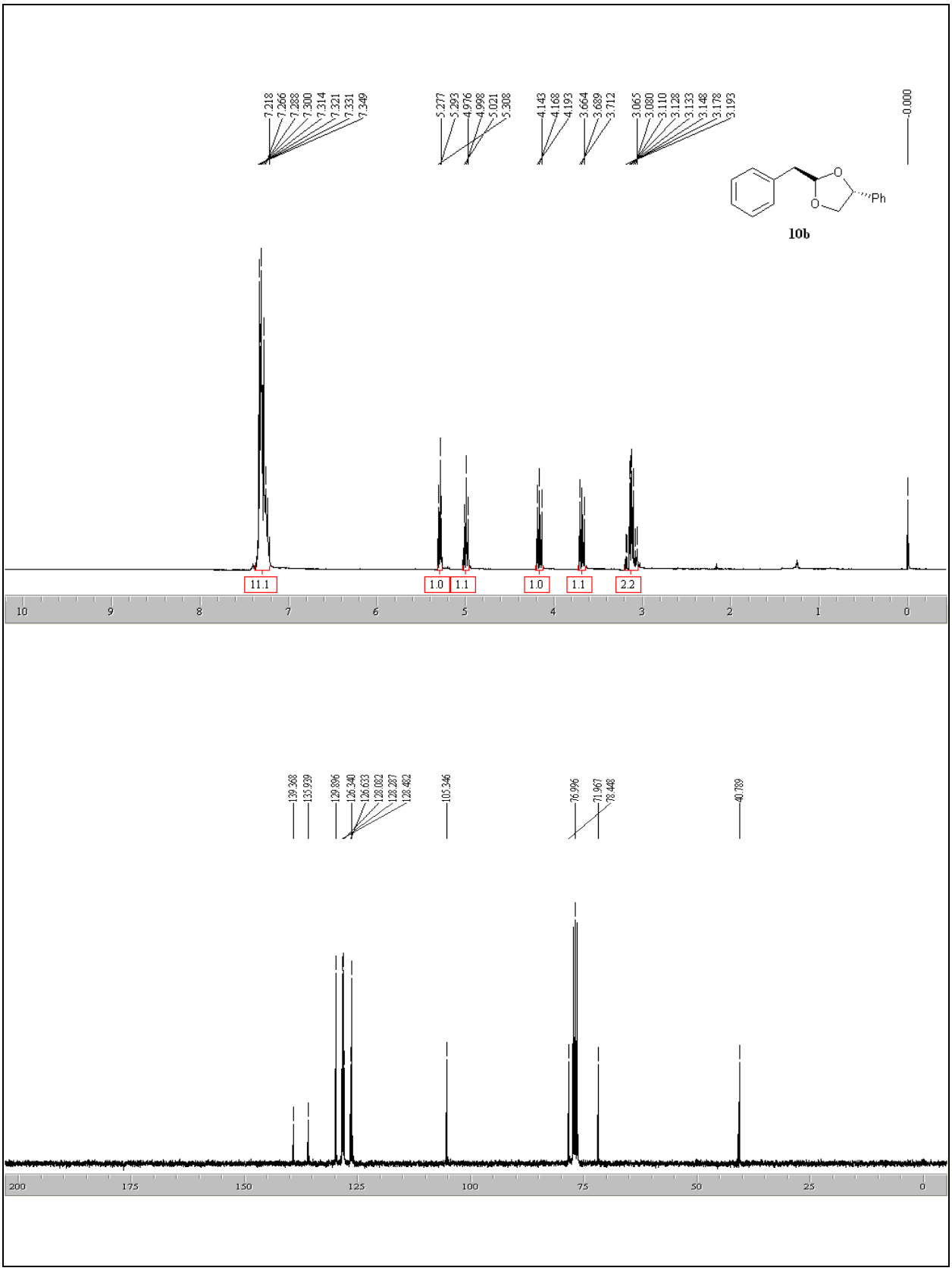
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12. Notes and references

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