

Supporting Information

Carbene-catalyzed desymmetrization of 1,3-diols: access to optically enriched tertiary alkyl chlorides

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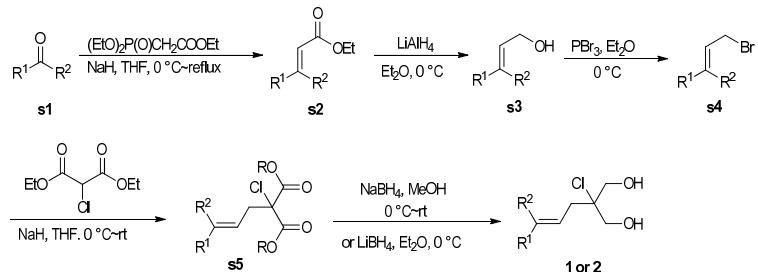
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1. General Information

All reactions were carried out under standard conditions using N₂ as shielding gas with magnetic stirring. Analytical thin layer chromatography (TLC) was performed with TLC plates. All reactions and column chromatography were monitored by thin layer chromatography with UV light at 254 nm and colorized with ethanol solution of phosphomolybdic acid, followed by heating using a heat gun. All products could be purified by column chromatography using ethyl acetate and hexane as eluent. Organic solutions were concentrated by rotary evaporation. All solvents were freshly distilled before use. ¹H and ¹³C NMR chemical shifts are reported in CDCl₃ solution of the compound by Bruker AV-300 MHz or Bruker AV-400 MHz instruments and marked in ppm relative to tetramethylsilane (TMS) (0) and CDCl₃ (77.0 ppm) as standard. The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectral analysis (HRMS) was performed on Waters Q-TOF Premier mass spectrometer. The determination of *ee* was performed *via* chiral phase HPLC analysis using Shimadzu LC-20AD HPLC workstation. Optical rotations were measured using a 1 mL cell with a 1 cm path length on a Jasco P1030 digital polarimeter and are reported as follows: [α]^D₂₀. The dr values of the products were determined by the corresponding ¹H NMR spectra. The absolute configuration of products could be confirmed according to the optical rotations of known compounds.

2. General procedure for preparation of substrates **1** and **2**

All substrates were prepared according to literature¹ (**1j**) or following general procedure (**1a-1i** and **2a-2p**) from different starting materials (the specific starting material, please see the related data part of substrate).



Under nitrogen atmosphere, to a suspension of sodium hydride (60% suspension in oil, 1.5 equiv) in THF (0.3mmol/mL) was added triethyl phosphonoacetate (1.8 equiv) dropwise at 0 °C, then the resulting mixture was stirred for 30 min at 0 °C. Ketone **s1** (1 equiv, 1 M in THF solution) was added dropwise to the resulting mixture and the reaction was allowed to reflux overnight. After cooling to room temperature, the reaction was quenched with saturated NH₄Cl, the organic phase was separated and the aqueous solution was extracted with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the corresponding (*E*)-isomer **s2**.

To a stirred suspension of LiAlH₄ (1.2 equiv) in Et₂O (3 ml per mmol) was added (*E*)-isomer **s2** (1 equiv, 1 M in Et₂O solution) dropwise at 0 °C, then the resulting mixture was stirred for 30 min at 0 °C. The reaction was then cautiously quenched with ethyl acetate at

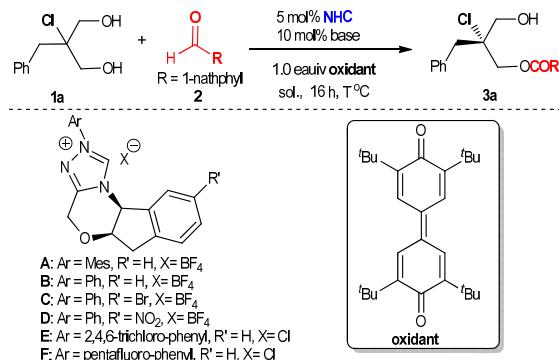
0 °C, then 15% NaOH solution (1 ml per gram of LiAlH₄) was added follow by the addition of another portion of water (1 ml per gram of LiAlH₄). The resulting mixture was allowed to stir for 1 h to form a white suspension. Anhydrous MgSO₄ was added and the suspension was stirred for another 30 min. The solid was removed by filtration using celite and the filtrate was concentrated to give the corresponding alcohol **s3** that was used without further purification.

To a stirred solution of alcohol **s3** (1 equiv) in Et₂O (1.0 mmol/mL) was added PBr₃ (0.5 equiv) dropwise at 0 °C, then the reaction was allowed to warm to room temperature and stirred. After the reaction was completed, it was cautiously treated with 20% NaOH (2 M) at 0 °C. The organic layer containing the corresponding bromide compound **s4** was separated, washed with brine, dried over anhydrous Na₂SO₄ and kept over solid sodium hydride for the next step.

To a dried flask with a magnetic stir bar was added dimethyl chloromalonate (1 equiv) and dried THF (0.3 M). The solution was cooled to 0 °C follow by the addition of sodium hydride (60% suspension in oil, 1 equiv). The resulting mixture was allowed to stir at rt for 30 min. Then bromide **s4** (1.1 equiv) was added and the reaction mixture was allowed to stir overnight at rt. The reaction mixture was quenched by saturated NH₄Cl solution, the organic phase was separated and the aqueous phase was extracted with Et₂O three times. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford diester **s5**.

To a stirred solution of diester **s5** (1 equiv) in MeOH (0.25 M) was added NaBH₄ (4 equiv), the resulting mixture of which was stirred at 0 °C for 15 min and then allowed to warm to room temperature and stirred for 6 h. After the reaction was completed, the mixture was quenched with saturated NH₄Cl, the solvent was evaporated and the aqueous solution was extracted with Et₂O. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the corresponding diol.

3. Screening of conditions and general procedure for syntheses of products 3



entry ^a	Sol.	T (°C)	base	Lewis acid	3a yield (%)	3a er (%) ^c
1	THF	0	Cs ₂ CO ₃	-	95	81:19
2	CHCl ₃	0	Cs ₂ CO ₃	-	94	65:35
3	DCM	0	Cs ₂ CO ₃	-	92	68:32
4	Tol.	0	Cs ₂ CO ₃	-	86	84:16
5	Dioxane	0	Cs ₂ CO ₃	-	70	67:33
6	1,2-DCM	0	Cs ₂ CO ₃	-	88	69:31
7	Et ₂ O	0	Cs ₂ CO ₃	-	92	77:23
8	THF	0	K ₂ CO ₃	-	<20%	-
9	THF	0	DBU	-	<20%	-
10	THF	0	Et ₃ N	-	86	50:50
11	THF	r.t.	Cs ₂ CO ₃	>90	75:25	
12	THF	-20	Cs ₂ CO ₃	>90	90:10	
13	THF	-25	Cs ₂ CO ₃	>90	92:8	
14	THF	-30	Cs ₂ CO ₃	>90	92.5:7.5	
15	THF	-35	Cs ₂ CO ₃	>90	92.5:7.5	
15	THF	-45	Cs₂CO₃	>90	95:5	
16	THF	-55	Cs ₂ CO ₃	>90 ^b	93.5:6.5	
18	THF	-65	Cs ₂ CO ₃	>90 ^b	87.5:12.5	
19	THF	-70	Cs ₂ CO ₃	>90 ^b	90:10	
20	THF	-45	Cs ₂ CO ₃	LiCl	75	79:21
21	THF	-45	Cs ₂ CO ₃	Sc(OTf) ₃	90	82:28
22	THF	-45	Cs ₂ CO ₃	Yb(OTf) ₃	92	88:26
23	THF	-45	Cs ₂ CO ₃	Cu(OTf) ₂	85	72:28
24	THF	-45	Cs ₂ CO ₃	Mg(OTf) ₂	87	87:13
25	THF	-45	Cs ₂ CO ₃	Zn(OTf) ₂	93	87:13

^aAll reactions of **1a** (0.10 mmol, 20.1 mg) with aldehyde **2** (0.2 mmol, 31.2 mg) were carried out in presence of catalyst of 5 mol%

E and Cs₂CO₃ of 10 mol% in THF (1.0 mL) for 16 h. ^bCatalyst **E** of 2 mol% and Cs₂CO₃ of 5 were used (48 h). ^cIsolated yield.

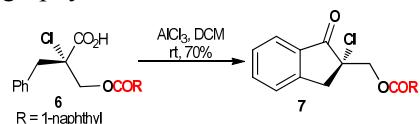
^dEr of **3a** was determined by chiral HPLC analysis.

General procedure for synthesis of product 3: Under N₂ atmosphere, oxidant (0.1 mmol), triazolium salt **A-F** (0.01 mmol) and Cs₂CO₃ (0.015 mmol, 4.9 mg) were dissolved in freshly distilled THF stirred at room temperature for 5 minutes. Then, the yellow solution was slowly added into a solution of the 1,3-diol **1** (0.10 mmol, 0.10 M) and 1-naphthaldehyde (0.15 mmol) in THF at the specified temperature (-45 °C) as shown in Chart 1 and Chart 2 in the text. The resulting mixture was stirred under constant temperature for 12 h. The solvent was removed under reduced pressure and the crude residue was purified *via* column chromatography on silica gel to afford the desired *mono*-esterification product **3**.

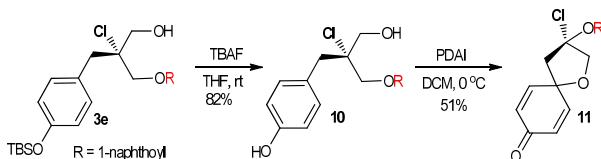
4. General procedure for the synthetic applicability



The procedure for synthesis of 6: The solution of **3a** (2.0 mmol, 1.0 equiv) in acetone was cooled to 0 °C. Jones reagent (1.6 mL, 1.67 M in water) was added dropwise and the reaction mixture was stirred at 0 °C for 2h. Then the water was added and the mixture was extracted with ether. The combined organic layers were dried with Na₂SO₄. The resulting solution was concentrated by vacuum pump. The acid **6** could be obtained in 90% yield through isolation by silica gel column chromatography.



The procedure for synthesis of 7: Under a nitrogen atmosphere, a solution of **6** (0.3 mmol, 110 mg, 1.0 equiv) in DCM (4.0 mL, 0.05 M) was added to AlCl₃ (0.6 mmol, 79 mg, 2.0 equiv) at 0 °C. After the full conversion of **6**, the reaction was quenched with H₂O. Then the organic phase was separated, and the aqueous phase was extracted with Et₂O three times. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford product **7** in 70% yield.



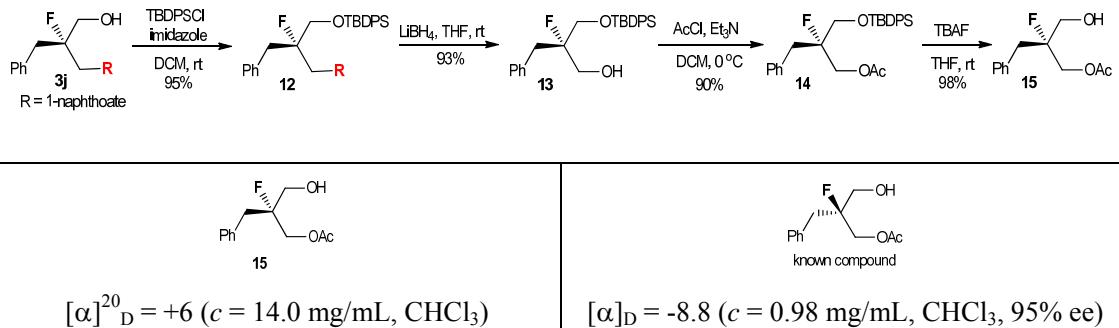
The procedure for synthesis of 11: To the solution of crude product **3e** (0.4 mmol, 194 mg, 1.0 equiv) in THF was added TBAF (105 mg, 1.0 equiv) and the reaction was treated with H₂O after full conversion of reaction by TLC monitoring. The organic phase was separated, and the aqueous phase was extracted with DCM three times. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford phenol product **10**.

To a solution of phenol **10** in DCM (0.1 M) was added PDAI (130 mg, 1 equiv) at 0 °C. After the reaction was stirred at 0 °C for 1h, the saturated Na₂S₂O₃ was added to quench reaction. The final system was quenched with ethyl acetate three times. The combined organic layers were

concentrated under vacuum and the product **11** could be obtained in 40% total yield for two steps by column chromatography.

5. Determination of the absolute configuration of the products **3** and **4**

The absolute configuration of the products **3** and **4** was determined by correlation with a known compound as follows.¹



According to the optical rotations of our synthetic compounds and the known compound, the absolute configuration of our synthetic compounds could be confirmed.

The procedure for synthesis of **12:** To a stirred solution of **3j** (0.7 mmol, 236 mg, 1 equiv) in DCM (0.5 mmol/ml) was added imidazole (, 2.2 equiv, 104.7 mg) at 0 °C. Then, TBDPSCl was added to the reaction system and the reaction was stirred for 2 h. The reaction was subsequently quenched with H₂O, the organic layer was separated and the aqueous phase was extracted with DCM. The combined organic layers were washed with brine, dried over anh. Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to give product **12** in 95% yield.

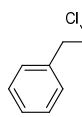
Under a nitrogen atmosphere, to a stirred solution of **12** (0.4 mmol, 230 mg, 1 equiv) in THF (0.25 mmol/ml) was added LiBH₄ (2 N in THF solution, 2.2 equiv) dropwise at 0 °C, and the reaction mixture was allowed to stir at that temperature for 12 h. Subsequently, the reaction was quenched by sat. NH₄Cl, the organic phase was separated, and the aqueous phase was extracted with Et₂O three times. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford product **13** in 89% yield.

Under a nitrogen atmosphere, to a stirred solution of **13** (0.2 mmol, 84 mg, 1 equiv) in DCM (0.5 mmol/ml) was added AcCl (2.0 equiv) dropwise at 0 °C. Subsequently, Et₃N was added to stir at that temperature for 1 h. After that, the reaction was quenched with H₂O, the organic phase was separated, and the aqueous phase extracted with DCM three times. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to afford the residue **14**.

To the solution of crude product **14** (1.0 equiv) in THF was added TBAF (1.0 equiv,) and the reaction was treated with H₂O after full conversion of reaction by TLC monitoring. The organic phase was separated, and the aqueous phase was extracted with DCM three times. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford product **15** in 81% total yield for two steps.

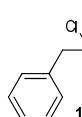
6. Characterization of key compounds 1, 2 and 3

2-benzyl-2-chloropropane-1,3-diol (1a)



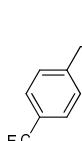
According to general procedure, the title compound (1.61 g) could be obtained in 80% yield for two steps from diethyl chloromalonate (10 mmol, 1.94 g). White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.27 (m, 5H), 3.73 (s, 2H), 3.14 (s, 2H), 2.87 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 135.0, 130.8, 128.2, 127.1, 76.6, 65.9, 41.1; HRMS (ESI) calcd. For $\text{C}_{10}\text{H}_{14}\text{ClO}_2$ $[\text{M}+\text{H}]^+$: 201.0677, Found: 201.0679. IR ν (cm^{-1}) 3269, 2947, 1455, 1119, 1074, 701.

2-chloro-2-(4-methylbenzyl)propane-1,3-diol (1b)



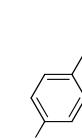
According to general procedure, the title compound (1.76 g) could be obtained in 82% yield for two steps from diethyl chloromalonate (10 mmol, 1.94 g). White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.12 (d, $J = 7.6$ Hz, 2H), 7.20 (d, $J = 7.6$ Hz, 2H), 3.74 (s, 4H), 3.14 (s, 2H), 2.34 (s, 3H), 2.29 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 136.8, 132.0, 130.6, 128.9, 66.2, 40.8, 21.1; HRMS (ESI) calcd. For $\text{C}_{11}\text{H}_{16}\text{ClO}_2$ $[\text{M}+\text{H}]^+$: 215.0833, Found: 215.0840. IR ν (cm^{-1}) 3222, 1452, 1118, 1066, 767, 699.

2-chloro-2-(4-(trifluoromethyl)benzyl)propane-1,3-diol (1c)



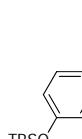
According to general procedure, the title compound (1.88 g) could be obtained in 70% yield for two steps from diethyl chloromalonate (10 mmol, 1.94 g). White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.57 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 3.77-3.68 (m, 4H), 3.20 (s, 2H), 3.13 (s, 2H), 2.87 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 139.1, 131.3, 129.5, 129.2, 125.5, 125.1, 125.0, 125.0, 125.0, 122.8, 75.7, 65.7, 40.5; HRMS (ESI) calcd. For $\text{C}_{11}\text{H}_{13}\text{ClF}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 269.0551, Found: 269.0556. IR ν (cm^{-1}) 2923, 1746, 1437, 1325.

2-chloro-2-(4-methoxybenzyl)propane-1,3-diol (1d)



According to general procedure, the title compound (1.71 g) could be obtained in 74% yield for two steps from diethyl chloromalonate (10 mmol, 1.94 g). White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.22 (d, $J = 8.4$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 3.77 (s, 3H), 3.71 (d, $J = 3.6$ Hz, 2H), 3.13 (s, 2H), 3.07 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.5, 131.8, 127.0, 113.5, 65.7, 55.1, 40.1; HRMS (ESI) calcd. For $\text{C}_{11}\text{H}_{16}\text{ClO}_3$ $[\text{M}+\text{H}]^+$: 231.0782, Found: 231.0789. IR ν (cm^{-1}) 3303, 2931, 1614, 1250, 1085, 849.

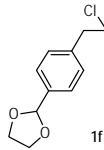
2-(4-((tert-butyldimethylsilyl)oxy)benzyl)-2-chloropropane-1,3-diol (1e)



Following the literature procedure², the corresponding (bromomethyl)benzene could be obtained. According to the general procedure, the title compound could be obtained as a white solid in 73% overall yield from (bromomethyl)benzene compound. ^1H NMR (400 MHz, CDCl_3): δ 7.16 (d, $J = 8.5$ Hz, 2H), 6.78 (d, $J = 8.5$ Hz, 2H), 3.72 (d, $J = 6.0$ Hz, 2H), 3.71 (d, $J = 6.7$ Hz, 2H), 3.10 (s, 2H), 2.41 (t, $J = 6.5$ Hz, 2H), 0.98 (s, 9H), 0.19 (s, 6H); ^{13}C NMR

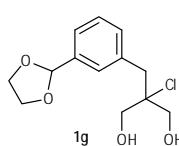
(100 MHz, CDCl₃): δ 154.9, 131.9, 127.8, 119.9, 77.6, 66.2, 40.6, 25.8, 18.3, -4.3. HRMS (ESI) calcd. For C₁₆H₂₈ClO₃Si [M+H]⁺: 331.1491, Found: 331.1497. IR ν (cm⁻¹) 2954, 1472, 1254, 1059, 778.

2-(4-(1,3-dioxolan-2-yl)benzyl)-2-chloropropane-1,3-diol (1f)



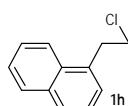
Following the literature procedure³, the corresponding (bromomethyl)benzene could be obtained. According to the general procedure, the title compound could be obtained as a white solid in 78% overall yield from the bromomethylbenzene compound. ¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.80 (s, 1H), 4.18-4.10 (m, 2H), 4.08-4.00 (m, 2H), 3.73 (d, *J* = 6.0 Hz, 2H), 3.71 (d, *J* = 6.6 Hz, 2H), 3.19 (s, 2H), 2.17 (t, *J* = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 136.8, 136.4, 131.0, 126.5, 103.7, 77.0, 66.2, 65.5, 41.0. HRMS (ESI) calcd. For C₁₃H₁₈ClO₄ [M+H]⁺: 273.0888, Found: 273.0886. IR ν (cm⁻¹) 3308, 2931, 1696, 1389, 1090, 854.

2-(3-(1,3-dioxolan-2-yl)benzyl)-2-chloropropane-1,3-diol (1g)



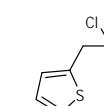
According to the procedure of **1f**, the title compound could be obtained as a white solid in 15% overall yield from the bromomethylbenzene compound. ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.38 (m, 2H), 7.36-7.32 (m, 2H), 5.80 (s, 1H), 4.18-4.09 (m, 2H), 4.08-3.99 (m, 2H), 3.72 (d, *J* = 6.0 Hz, 2H), 3.71 (d, *J* = 6.8 Hz, 2H), 3.18 (s, 2H), 2.48 (t, *J* = 6.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 137.9, 135.5, 131.9, 129.0, 128.4, 125.4, 103.8, 66.3, 65.5, 41.1. HRMS (ESI) calcd. For C₁₃H₁₈ClO₄ [M+H]⁺: 273.0888, Found: 273.0884. IR ν (cm⁻¹) 2926, 1694, 1386, 1087, 708, 583.

2-chloro-2-(naphthalen-1-ylmethyl)propane-1,3-diol (1h)



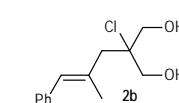
According to the general procedure, the title compound could be obtained as a white solid in 85% overall yield. ¹H NMR (400 MHz, CDCl₃): δ 7.84-7.77 (m, 4H), 7.48-7.46 (m, 3H), 3.79-3.77 (m, 4H), 3.53 (s, 2H), 2.19 (t, *J* = 2.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 133.9, 133.3, 132.7, 132.5, 129.6, 128.9, 127.7, 127.6, 126.1, 125.8, 77.4, 66.3, 41.2; HRMS (ESI) calcd. For C₁₄H₁₆ClO₂ [M+H]⁺: 251.0833, Found: 251.0842. IR ν (cm⁻¹) 3291, 2917, 1266, 1066, 1017, 754.

2-chloro-2-(thiophen-2-ylmethyl)propane-1,3-diol (1i)



The diol was obtained in 86% yield over two steps as a white solid from the bromide compound. ¹H NMR (400 MHz, CDCl₃): δ 7.22 (t, *J* = 3.3 Hz, 1H), 6.97 (d, *J* = 3.4 Hz, 2H), 3.83-3.73 (m, 4H), 3.40 (s, 2H), 2.44 (t, *J* = 6.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 136.5, 128.3, 126.9, 125.3, 76.1, 66.3, 35.6. HRMS (ESI) calcd. For C₈H₁₂ClO₂S [M+H]⁺: 207.0241, Found: 207.0247. IR ν (cm⁻¹) 3323, 1438, 1118, 1062, 710, 695.

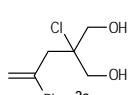
(E)-2-chloro-2-(2-methyl-3-phenylallyl)propane-1,3-diol (2b)



Following the literature procedure⁴, the corresponding

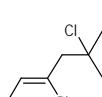
(E)-(3-bromo-2-methylprop-1-en-1-yl)benzene could be obtained. Then according to the general procedure, the diol was obtained in 81% overall yield as a white solid from bromide compound. ^1H NMR (400 MHz, CDCl_3): δ 7.36-7.31 (m, 2H), 7.28-7.21 (m, 3H), 6.44 (s, 1H), 3.86 (d, $J = 3.8$ Hz, 4H); 2.76 (s, 2H), s.45 (brs, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 137.7, 133.3, 131.2, 129.1, 128.3, 126.7, 77.0, 66.9, 46.1, 20.6. HRMS (ESI) calcd. For $\text{C}_{13}\text{H}_{18}\text{ClO}_2$ $[\text{M}+\text{H}]^+$: 241.0990, Found: 241.0990. IR v (cm^{-1}) 3319, 1494, 1124, 961, 679, 671.

2-chloro-2-(2-phenylallyl)propane-1,3-diol (2c)



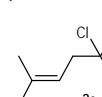
The preparation of allyl bromide followed the literature procedure⁵. The residue was purified by column chromatography to afford diol as a white solid in 76% overall yield from the allyl bromide compound. ^1H NMR (400 MHz, CDCl_3): δ 7.43-7.38 (m, 2H), 3.37-3.27 (m, 3H), 5.42 (d, $J = 1.4$ Hz, 1H), 5.31 (s, 1H), 3.64 (d, $J = 6.4$ Hz, 1H), 3.63 (d, $J = 7.0$ Hz, 1H), 3.12 (s, 2H), 2.07 (t, $J = 6.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 143, 142.1, 128.8, 128.0, 126.5, 119.7, 40.8, 77.1, 66.8. HRMS (ESI) calcd. For $\text{C}_{12}\text{H}_{15}\text{ClO}_2$ $[\text{M}+\text{H}]^+$: 226.0750, Found: 226.0755. IR v (cm^{-1}) 2933, 1624, 1431, 1071, 904, 697.

(Z)-2-chloro-2-(2-phenylbut-2-en-1-yl)propane-1,3-diol (2d)



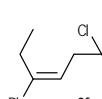
Following the literature procedure,⁵ the allyl alcohol could be obtained. According to general procedure, the diol was obtained in 78% overall yield as a white solid form the allyl bromide. ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.36 (m, 2H), 7.29-7.26 (m, 1H), 7.25-7.21 (m, 2H), 5.80 (q, $J = 7.0$ Hz, 1H), 3.57 (s, 4H), 2.98 (s, 2H), 2.08 (brs, 2H), 1.66 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 140.5, 135.2, 128.8, 128.6, 128.5, 127.2, 77.6, 66.9, 44.4, 15.1. HRMS (ESI) calcd. For $\text{C}_{13}\text{H}_{18}\text{ClO}_2$ $[\text{M}+\text{H}]^+$: 241.0990, Found: 241.0998. IR v (cm^{-1}) 3293, 2931, 1439, 1267, 1062, 703.

(E)-2-chloro-2-(3-phenylbut-2-en-1-yl)propane-1,3-diol (2e)



Following the literature procedure⁶, the allyl bromide could be obtained. Then according to general procedure the diol was obtained in 74% overall yield as a white solid from the allyl bromide. ^1H NMR (400 MHz, CDCl_3): δ 7.43-7.37 (m, 2H), 7.36-7.30 (m, 2H), 7.29-7.24 (m, 1H), 5.88 (t, $J = 7.1$ Hz, 1H), 3.84 (d, $J = 4.6$ Hz, 4H), 2.77 (d, $J = 7.4$ Hz, 2H), 2.47 (t, $J = 6.1$ Hz, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 143.6, 139.1, 128.4, 127.2, 125.9, 121.2, 77.5, 66.9, 34.7, 16.5. HRMS (ESI) calcd. For $\text{C}_{13}\text{H}_{18}\text{ClO}_2$ $[\text{M}+\text{H}]^+$: 241.0990, Found: 241.0998. IR v (cm^{-1}) 3345, 2929, 1419, 1069, 734, 695.

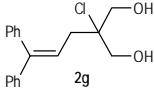
(E)-2-chloro-2-(3-phenylpent-2-en-1-yl)propane-1,3-diol (2f)



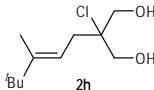
Following the literature procedure,⁷ the allyl alcohol could be obtained. Then the allyl bromide could be prepared following general procedure A. Following the general procedure B, the diol could be obtained in 72% yield overall yield as a white solid from allyl bromide. ^1H NMR (400 MHz, CDCl_3): δ 7.40-7.22 (m, 5H), 5.76-5.68 (m, 1H), 3.85 (s, 4H), 2.77 (d, $J = 6.6$ Hz, 2H).

Hz, 2H), 2.60-2.50 (m, 2H), 2.24 (brs, 2H), 1.02-0.92 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.8, 142.6, 128.4, 127.2, 126.6, 120.7, 77.2, 66.9, 34.3, 23.3, 13.4. HRMS (ESI) calcd. For $\text{C}_{14}\text{H}_{20}\text{ClO}_2$ [$\text{M}+\text{H}]^+$: 255.1146, Found: 255.1144. IR ν (cm^{-1}) 3303, 2931, 1614, 1250, 1085, 849.

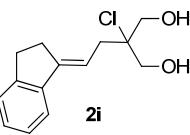
(E)-2-chloro-2-(3,3-diphenylallyl)propane-1,3-diol (2g)

 Following the literature procedure,⁸ the allyl bromide could be obtained. According to the general procedure B the diol could be obtained in 76% overall yield as a white solid from allyl bromide. ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.32 (m, 5H), 7.30-7.22 (s, 3H), 7.21-7.17 (m, 2H), 6.26 (t, $J = 7.4$ Hz, 1H), 3.74 (d, $J = 6.6$ Hz, 4H), 2.67 (d, $J = 7.3$ Hz, 2H), 2.10 (t, $J = 6.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 145.3, 142.2, 139.7, 129.8, 128.7, 128.4, 127.6, 127.4, 122.6, 76.8, 67.2, 35.0. HRMS (ESI) calcd. For $\text{C}_{18}\text{H}_{20}\text{ClO}_2$ [$\text{M}+\text{H}]^+$: 303.1146, Found: 303.1148. IR ν (cm^{-1}) 3100, 1480, 1289, 1072, 923, 626.

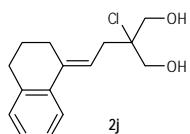
(E)-2-chloro-2-(3,4,4-trimethylpent-2-en-1-yl)propane-1,3-diol (2h)

 Following the general procedure, the diol could be obtained in 11% overall yield as a white solid from the corresponding ketone. ^1H NMR (400 MHz, CDCl_3): δ 5.33 (t, $J = 7.2$ Hz, 1H), 3.77 (d, $J = 6.5$ Hz, 4H), 2.56 (d, $J = 7.3$ Hz, 2H), 2.25 (t, $J = 6.5$ Hz, 2H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.8, 114.2, 78.1, 67.1, 36.7, 34.3, 29.2, 13.3. HRMS (ESI) calcd. For $\text{C}_{11}\text{H}_{22}\text{ClO}_2$ [$\text{M}+\text{H}]^+$: 221.1303, Found: 221.1308. IR ν (cm^{-1}) 3389, 1423, 1112, 1049, 827, 652.

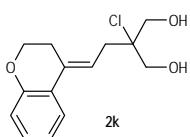
(E)-2-chloro-2-(2-(2,3-dihydro-1H-inden-1-ylidene)ethyl)propane-1,3-diol (2i)

 Following the general procedure, the diol could be obtained in 15% overall yield as a white solid from the corresponding ketone. δ 7.50-7.48 (m, 1H), 7.27-7.18 (m, 3H), 6.04-5.99 (m, 1H), 3.86-3.84 (m, 4H), 3.03-2.99 (m, 2H), 2.80-2.75 (m, 4H), 2.17-2.14 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 146.5, 141.1, 128.2, 126.6, 125.5, 120.3, 111.9, 77.8, 67.1, 35.7, 30.1, 28.3. HRMS (ESI) calcd. For $\text{C}_{14}\text{H}_{18}\text{ClO}_2$ [$\text{M}+\text{H}]^+$: 253.0990, Found: 253.0998. IR ν (cm^{-1}) 3295, 2954, 1480, 1283, 1032, 692.

(E)-2-chloro-2-(2-(3,4-dihydronaphthalen-1(2H)-ylidene)ethyl)propane-1,3-diol (2j)

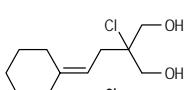
 Following the general procedure, the diol was obtained in 18% overall yield as a white solid from the corresponding ketone. ^1H NMR (400 MHz, CDCl_3): δ 7.61-7.56 (m, 1H), 7.19-7.14 (m, 2H), 7.12-7.08 (m, 2H), 6.10 (t, $J = 7.4$ Hz, 1H), 3.84 (d, $J = 5.6$ Hz, 4H), 2.82-2.75 (m, 4H), 2.54 (t, $J = 5.6$ Hz, 2H), 2.22-2.12 (m, 2H), 1.88-1.80 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 138.3, 137.7, 136.0, 129.0, 127.2, 126.2, 124.1, 117.0, 77.5, 66.9, 34.1, 30.5, 27.0, 23.3. HRMS (ESI) calcd. For $\text{C}_{15}\text{H}_{20}\text{ClO}_2$ [$\text{M}+\text{H}]^+$: 267.1146, Found: 267.1147. IR ν (cm^{-1}) 3290, 2935, 1483, 1263, 1032, 672.

(E)-2-chloro-2-(2-(chroman-4-ylidene)ethyl)propane-1,3-diol (2k)



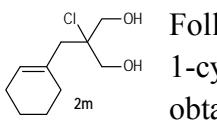
Following the general procedure, the diol was obtained in 12% overall yield as a white solid from the corresponding ketone. ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.14 (t, *J* = 7.4 Hz, 1H), 4.21 (d, *J* = 5.4 Hz, 2H), 3.84 (d, *J* = 11.8 Hz, 2H), 3.80 (d, *J* = 11.8 Hz, 2H), 2.76 (d, *J* = 7.7 Hz, 2H), 2.71 (t, *J* = 4.7 Hz, 2H), 2.05 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 154.5, 132.5, 129.1, 124.1, 122.5, 120.9, 117.6, 115.1, 77.3, 66.7, 66.4, 33.5, 26.2. HRMS (ESI) calcd. For C₁₄H₁₈ClO₃ [M+H]⁺: 269.0939, Found: 269.0935. IR ν (cm⁻¹) 3398, 1578, 1208, 1106, 905, 744.

2-chloro-2-(2-cyclohexylideneethyl)propane-1,3-diol (2l)



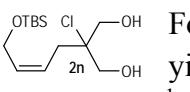
Following the general procedure, the diol was obtained in 12% overall yield as a white solid from the corresponding ketone. ¹H NMR (400 MHz, CDCl₃): δ 5.18 (t, *J* = 7.5 Hz, 1H), 3.77 (d, *J* = 5.8 Hz, 4H), 2.56 (d, *J* = 7.6 Hz, 2H), 2.21-2.18 (m, 6H), 1.57-1.49 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 144.5, 114.1, 77.8, 67.0, 37.6, 33.4, 29.2, 28.7, 27.8, 26.9. HRMS (ESI) calcd. For C₁₁H₂₀ClO₂ [M+H]⁺: 219.1146, Found: 219.1140. IR ν (cm⁻¹) 3304, 2958, 1458, 1274, 1065, 654.

2-chloro-2-(cyclohex-1-en-1-ylmethyl)propane-1,3-diol (2m)



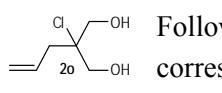
Following the general procedure, with commercially available methyl 1-cyclohexene-1-carboxylate as the starting material, the diol was obtained in 19% overall yield as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 5.61-5.57 (m, 1H), 3.77 (d, *J* = 6.5 Hz, 4H), 2.51 (s, 2H), 2.29 (t, *J* = 6.7 Hz, 2H), 2.13-2.08 (m, 2H), 2.06-2.00 (m, 2H), 1.65-1.51 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 133.0, 128.0, 77.4, 67.2, 44.1, 30.8, 25.6, 23.2, 22.2. HRMS (ESI) calcd. For C₁₀H₁₈ClO₂ [M+H]⁺: 205.0990, Found: 205.0996. IR ν (cm⁻¹) 3283, 2924, 1424, 1268, 1075, 720.

(Z)-2-((tert-butyldimethylsilyl)oxy)but-2-en-1-yl)-2-chloropropane-1,3-diol (2n)



Following the general procedure, the diol product was obtained in 21% yield over four steps as a white solid from the corresponding known allyl bromide. ¹H NMR (400 MHz, CDCl₃): δ 5.93-5.78 (m, 2H), 4.19 (d, *J* = 6.9 Hz, 2H), 3.77 (d, *J* = 7.3 Hz, 2H), 3.76 (d, *J* = 7.0 Hz, 2H), 3.26 (t, *J* = 7.1 Hz, 2H), 2.74 (d, *J* = 7.2 Hz, 2H), 0.90 (s, 9H), 0.11 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 131.1, 128.8, 75.3, 67.2, 58.5, 32.1, 26.0, 18.5, -5.1. HRMS (ESI) calcd. For C₁₃H₂₈ClO₃Si₂ [M+H]⁺: 295.1491, Found: 295.1497. IR ν (cm⁻¹) 3337, 2954, 1510, 1250, 921, 643.

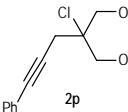
2-allyl-2-chloropropane-1,3-diol (2o)



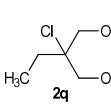
Following the general procedure, the diol could be obtained from the corresponding allyl bromide in 30% total yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 5.95-5.85 (m, 1H), 5.23 (d, *J* = 14.4 Hz, 1H), 5.18 (d, *J* = 4.4 Hz, 1H), 3.53 (s, 2H), 3.79-3.72 (dd, *J* = 12.0 Hz, 16.0 Hz, 4H), 3.42 (s, 2H), 2.57 (d, *J* = 11.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 131.1, 128.8, 75.3, 67.2, 58.5, 32.1, 26.0, 18.5, -5.1. HRMS (ESI) calcd. For C₁₀H₁₈ClO₂ [M+H]⁺: 205.0990, Found: 205.0996. IR ν (cm⁻¹) 3283, 2924, 1424, 1268, 1075, 720.

NMR (100 MHz, CDCl₃): δ 131.8, 119.5, 75.2, 66.1, 39.7; HRMS (ESI) calcd. For C₆H₁₂ClO₂ [M+H]⁺: 151.0520, Found: 151.0527. IR v (cm⁻¹) 2936, 1642, 1433, 1058, 924, 655.

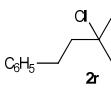
2-chloro-2-(3-phenylprop-2-yn-1-yl)propane-1,3-diol (2p)

 Following the general procedure, using 3-phenyl-2-propyl-1-ol as the starting material, the diol was obtained in 26% overall yield as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.45-7.39 (m, 2H), 7.33-7.27 (m, 2H), 3.77 (d, *J* = 4.8 Hz, 4H), 3.03 (s, 2H), 2.38 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 131.8, 128.4, 128.4, 123.0, 84.0, 83.9, 74.8, 66.8, 27.5. HRMS (ESI) calcd. For C₁₂H₁₄ClO₂ [M+H]⁺: 225.0677, Found: 225.0679. IR v (cm⁻¹) 3306, 2930, 1489, 1270, 1058, 692.

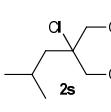
2-chloro-2-ethylpropane-1,3-diol (2q)

 Following the general procedure, using 3-phenyl-2-propyl-1-ol as the starting material, the diol was obtained in 18% overall yield as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 3.82-3.74 (m, 4H), 2.78 (s, 2H), 1.88-1.82 (dd, *J* = 7.2 Hz, 14.8 Hz, 2H), 1.06-1.02 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 177.5, 77.3, 77.0, 76.7, 66.3, 28.1, 8.0. HRMS (ESI) calcd. For C₅H₁₂ClO₂ [M+H]⁺: 139.0520, Found: 139.0526. IR v (cm⁻¹) 3304, 2958, 1274, 1065, 754.

2-chloro-2-phenethylpropane-1,3-diol (2r)

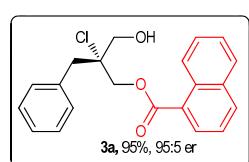
 Following the general procedure, using 3-phenyl-2-propyl-1-ol as the starting material, the diol was obtained in 20% overall yield as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.32-7.28 (m, 2H), 7.23-7.19 (m, 3H), 3.89-3.80 (m, 4H), 2.84-2.80 (m, 2H), 2.17-2.08 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 141.3, 128.6, 128.4, 77.2, 67.0, 37.3, 30.2. HRMS (ESI) calcd. For C₁₁H₁₆ClO₂ [M+H]⁺: 215.0833, Found: 215.0838. IR v (cm⁻¹) 3316, 2928, 1488, 1260, 1058, 690.

2-chloro-2-isobutylpropane-1,3-diol (2s)

 Following the general procedure, using 3-phenyl-2-propyl-1-ol as the starting material, the diol was obtained in 18% overall yield as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 3.82-3.74 (dd, *J* = 7.6 Hz, 14.8 Hz, 2H), 2.83 (s, 2H), 1.97-1.88 (m, 1H), 1.74 (d, *J* = 7.6 Hz, 2H), 1.01 (d, *J* = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 77.2, 66.8, 43.7, 24.7, 24.1. HRMS (ESI) calcd. For C₇H₁₆ClO₂ [M+H]⁺: 167.0833, Found: 167.0838. IR v (cm⁻¹) 3308, 2988, 1276, 1065, 756.

6. Characterization of products 3 and 4

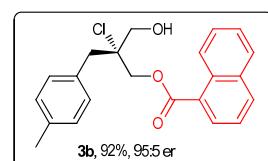
2-benzyl-2-chloro-3-hydroxypropyl 1-naphthoate (3a)



Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.95 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 6.67-6.30 (m, 1H), 7.59-7.52 (m, 2H), 7.36-7.26 (m, 5H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.59 (t, *J* = 11.6 Hz, 1H), 3.77 (d, *J* = 7.2 Hz, 2H),

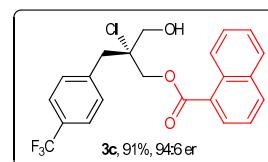
3.28 (s, 2H), 2.63 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 134.6, 134.1, 133.9, 131.5, 130.9, 130.7, 128.7, 128.3, 128.1, 127.3, 126.4, 126.1, 125.7, 124.5, 73.5, 66.2, 65.7, 41.7; HRMS (ESI) calcd. For $\text{C}_{21}\text{H}_{20}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 355.1095, Found: 355.1090. $[\alpha]^{20}_D$ = 14.0 (c = 13.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 34755, 2932, 1743, 1554, 1256, 1042. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: t_1 = 11.1 min, t_2 = 13.5 min.

2-chloro-3-hydroxy-2-(4-methylbenzyl)propyl 1-naphthoate (3b)



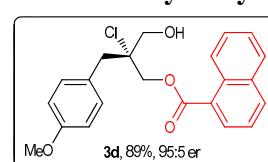
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.94 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 1.2 Hz, 1H), 8.23 (d, J = 1.2 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.93-7.62 (m, 1H), 7.57-7.50 (m, 2H), 7.24-7.21 (m, 2H), 7.13-7.11 (d, J = 7.6 Hz, 2H), 4.63 (d, J = 11.6 Hz, 1H), 4.49 (d, J = 12.0 Hz, 1H), 3.77 (d, J = 6.0 Hz, 2H), 3.23 (s, 2H), 2.56 (t, J = 7.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.20, 136.9, 134.0, 133.9, 131.4, 130.7, 130.6, 129.0, 128.6, 128.1, 126.4, 126.1, 125.7, 124.5, 73.7, 66.2, 65.7, 41.3; HRMS (ESI) calcd. For $\text{C}_{22}\text{H}_{22}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 369.1252, Found: 369.1257. $[\alpha]^{20}_D$ = 60.0 (c = 18.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 3447, 2920, 1718, 1511, 1278, 1017. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: t_1 = 11.6 min, t_2 = 13.8 min.

2-chloro-3-hydroxy-2-(4-(trifluoromethyl)benzyl)propyl 1-naphthoate (3c)



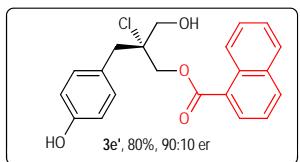
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.93 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 2.4 Hz, 1H), 8.08 (d, J = 1.2 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.67-7.25 (m, 7H), 4.66 (d, J = 11.6 Hz, 2H), 4.49 (d, J = 12.0 Hz, 2H), 3.79-3.70 (m, 2H), 3.30 (s, 2H), 2.74 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 138.6, 134.3, 133.9, 131.4, 131.3, 130.7, 128.7, 128.2, 126.5, 125.8, 125.6, 125.2, 125.2, 124.5, 72.7, 66.2, 65.4, 41.2; HRMS (ESI) calcd. For $\text{C}_{22}\text{H}_{19}\text{ClF}_3\text{O}_3$ [$\text{M}+\text{H}]^+$: 423.0969, Found: 423.0960. $[\alpha]^{20}_D$ = 40.0 (c = 11.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 3592, 1721, 1334, 1110, 1017, 784. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: t_1 = 12.3 min, t_2 = 15.3 min.

2-chloro-3-hydroxy-2-(4-methoxybenzyl)propyl 1-naphthoate (3d)



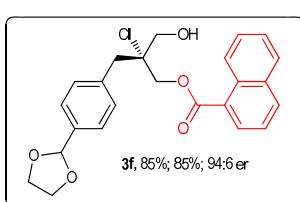
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.95 (d, J = 8.4 Hz, 1H), 8.26 (d, 0.8 Hz, 1H), 8.24 (d, J = 0.8 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.58-7.26 (m, 2H), 7.25 (d, J = 4.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 4.63 (d, J = 12.0 Hz, 1H), 4.49 (d, J = 12.0 Hz, 1H), 3.79 (s, 3H), 3.76 (d, J = 8.4 Hz, 2H), 3.21 (s, 2H), 2.66 (t, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 158.9, 134.1, 133.9, 131.9, 131.4, 130.6, 128.7, 128.1, 126.5, 126.4, 126.1, 125.7, 124.5, 113.7, 73.9, 66.2, 65.6, 55.2, 40.8; HRMS (ESI) calcd. For $\text{C}_{22}\text{H}_{22}\text{ClO}_4$ [$\text{M}+\text{H}]^+$: 385.1201, Found: 385.1208. $[\alpha]^{20}_D$ = 30.0 (c = 15.0 mg/mL, CHCl_3). The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: t_1 = 15.6 min, t_2 = 18.3 min.

2-(4-((tert-butyldimethylsilyl)oxy)benzyl)-2-chloro-3-hydroxypropyl 1-naphthoate (3e)



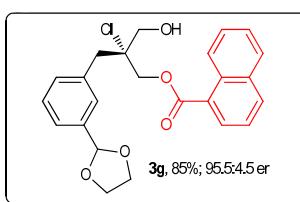
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.95 (d, $J = 8.8$ Hz, 1H), 8.25 (d, $J = 1.2$ Hz, 1H), 8.23 (d, $J = 1.2$ Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.88-7.59 (m, 1H), 7.54-7.47 (m, 2H), 7.18 (d, $J = 8.8$ Hz, 6H), 6.79 (d, $J = 8.4$ Hz, 2H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.47 (d, $J = 12.0$ Hz, 1H), 3.74 (s, 2H), 3.18 (s, 2H), 0.98 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): 8167.1, 154.8, 134.0, 133.8, 131.8, 131.4, 130.6, 128.6, 128.0, 127.1, 126.3, 126.0, 125.6, 124.5, 119.8, 73.7, 66.2, 65.6, 40.8, 25.6, 18.1; HRMS (ESI) calcd. For $\text{C}_{27}\text{H}_{34}\text{ClO}_4\text{Si}^- [\text{M}+\text{H}]^+$: 485.1909, Found: 485.1908. $[\alpha]^{20}_D = 20.0$ ($c = 4.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 1721, 1511, 1242, 1195, 1016, 782. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: $t_1 = 28.1$ min, $t_2 = 28.6$ min.

2-(4-(1,3-dioxolan-2-yl)benzyl)-2-chloro-3-hydroxypropyl 1-naphthoate (3f)



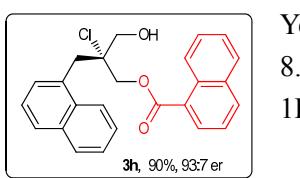
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.94 (d, $J = 8.4$ Hz, 1H), 8.25 (d, $J = 0.8$ Hz, 1H), 8.24 (d, $J = 0.8$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 7.92-7.63 (m, 1H), 7.58-7.52 (m, 2H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 5.80 (s, 1H), 4.64 (d, $J = 12.0$ Hz, 1H), 4.49 (d, $J = 12.0$ Hz, 1H), 4.15-4.05 (m, 2H), 3.75 (s, 2H), 3.28 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 137.0, 135.6, 134.1, 133.9, 131.4, 131.0, 130.7, 128.7, 128.1, 126.5, 126.4, 126.0, 125.6, 124.5, 103.5, 73.3, 66.2, 65.5, 65.3, 41.4; HRMS (ESI) calcd. For $\text{C}_{24}\text{H}_{24}\text{ClO}_5^- [\text{M}+\text{H}]^+$: 427.1307, Found: 427.1307. $[\alpha]^{20}_D = 36.0$ ($c = 8.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 2919, 1714, 1511, 1240, 1077, 781. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: $t_1 = 24.9$ min, $t_2 = 38.4$ min.

2-(3-(1,3-dioxolan-2-yl)benzyl)-2-chloro-3-hydroxypropyl 1-naphthoate (3g)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.95 (d, $J = 8.4$ Hz, 1H), 8.26 (d, $J = 7.2$ Hz, 1H), 8.10 (d, $J = 4.0$ Hz, 1H), 7.89 (d, $J = 11.6$ Hz, 1H), 7.67-7.63 (m, 1H), 7.60-7.51 (m, 2H), 7.47-7.26 (m, 1H), 5.79 (s, 1H), 4.69-4.61 (m, 1H), 4.54-4.49 (m, 1H), 4.09-4.00 (m, 4H), 3.99-3.74 (m, 2H), 3.79 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 138.1, 134.7, 134.1, 133.9, 131.8, 131.5, 130.7, 128.9, 128.7, 128.4, 128.1, 126.4, 126.0, 125.7, 125.5, 124.5, 103.5, 73.4, 66.2, 65.7, 65.3, 41.6; HRMS (ESI) calcd. For $\text{C}_{24}\text{H}_{24}\text{ClO}_5^- [\text{M}+\text{H}]^+$: 427.1307, Found: 427.1305. $[\alpha]^{20}_D = 36.0$ ($c = 9.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 2919, 1719, 1241, 1133, 1016, 782. The er value was determined by HPLC (Chiralcel ID, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: $t_1 = 43.7$ min, $t_2 = 52.2$ min.

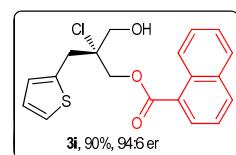
2-chloro-3-hydroxy-2-(naphthalen-1-ylmethyl)propyl 1-naphthoate (3h)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.95 (d, $J = 8.8$ Hz, 1H), 8.24 (d, $J = 0.8$ Hz, 1H), 8.22 (d, $J = 0.8$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.91-7.78 (m, 4H), 7.66-7.44 (m, 6H), 4.69 (d, $J = 11.6$ Hz, 1H),

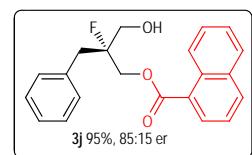
4.52 (t, $J = 12.0$ Hz, 1H), 3.80 (d, $J = 7.2$ Hz, 2H), 3.43 (s, 2H), 2.72-2.68 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.3, 134.1, 133.9, 133.2, 132.6, 132.2, 131.4, 130.7, 129.8, 128.9, 128.7, 128.1, 127.8, 127.6, 126.4, 126.1, 126.0, 125.9, 125.7, 124.5, 77.3, 77.0, 76.7, 73.7, 66.4, 65.7, 41.8; HRMS (ESI) calcd. For $\text{C}_{24}\text{H}_{24}\text{ClO}_5$ [$\text{M}+\text{H}]^+$: 427.1307, Found: 427.1304. $[\alpha]^{20}_D = 35.0$ ($c = 6.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 2923, 1510, 1241, 1195, 1133, 781. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: $t_1 = 15.7$ min, $t_2 = 18.4$ min.

2-chloro-3-hydroxy-2-(thiophen-2-ylmethyl)propyl 1-naphthoate (3i)



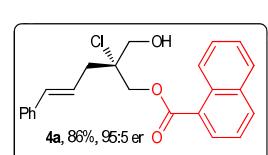
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.94 (d, $J = 8.8$ Hz, 1H), 8.27 (d, $J = 0.8$ Hz, 1H), 8.25 (d, $J = 0.8$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.91-7.62 (m, 3H), 7.57-7.51 (m, 2H), 7.25-7.01 (m, 1H), 7.00-6.97 (m, 2H), 4.65 (d, $J = 11.6$ Hz, 1H), 4.54 (d, $J = 11.6$ Hz, 1H), 3.81 (d, $J = 7.6$ Hz, 2H), 3.54-3.46 (m, 1H), 2.64 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.1, 135.8, 134.1, 133.9, 131.4, 130.7, 128.6, 128.4, 128.1, 126.9, 126.4, 126.0, 125.6, 125.3, 124.5, 72.8, 66.1, 65.8, 36.1; HRMS (ESI) calcd. For $\text{C}_{19}\text{H}_{18}\text{ClO}_3\text{S}$ [$\text{M}+\text{H}]^+$: 361.0660, Found: 361.0660. $[\alpha]^{20}_D = 30.0$ ($c = 18.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 1719, 1510, 1195, 1132, 1014, 781. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: $t_1 = 13.3$ min, $t_2 = 16.4$ min.

2-benzyl-2-fluoro-3-hydroxypropyl 1-naphthoate (3j)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.91 (d, $J = 8.8$ Hz, 1H), 8.22 (d, $J = 7.2$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.65-7.49 (m, 3H), 7.49-7.25 (m, 5H), 4.63-4.55 (dd, $J = 12.0$ Hz, 1H), 4.49-4.42 (dd, $J = 12.4$ Hz, 1H), 3.75 (d, $J = 19.2$ Hz, 2H), 3.20 (d, $J = 19.2$ Hz, 2H), 2.23 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.3, 134.6, 134.5, 134.0, 133.9, 131.4, 130.6, 130.4, 128.6, 128.5, 128.1, 127.1, 126.4, 126.2, 125.6, 124.4, 97.3, 95.5, 64.5, 64.2, 63.4, 63.1, 38.9, 38.6; HRMS (ESI) calcd. For $\text{C}_{21}\text{H}_{20}\text{FO}_3$ [$\text{M}+\text{H}]^+$: 339.1391, Found: 339.1390. $[\alpha]^{20}_D = 4.8$ ($c = 14.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 3067, 1751, 1690, 1275, 1160, 695. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: $t_1 = 24.7$ min, $t_2 = 29.2$ min.

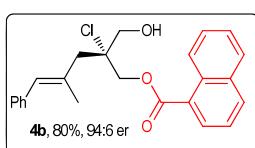
(E)-2-chloro-2-(hydroxymethyl)-5-phenylpent-4-en-1-yl 1-naphthoate (4a)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.93 (d, $J = 8.4$ Hz, 1H), 8.25 (d, $J = 7.6$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.66-7.49 (m, 3H), 7.38-7.22 (m, 5H), 6.56 (d, $J = 16.0$ Hz, 1H), 4.74 (d, $J = 12.0$ Hz, 1H), 4.62 (d, $J = 12.0$ Hz, 1H), 3.84 (d, $J = 7.2$ Hz, 2H), 2.87 (d, $J = 7.6$ Hz, 2H), 2.56 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 136.8, 134.9, 134.0, 133.8, 131.4, 130.7, 128.6, 128.6, 128.1, 127.6, 126.4, 126.3, 126.0, 125.6, 124.5, 122.8, 73.3, 66.5, 66.2, 39.6; HRMS (ESI) calcd. For $\text{C}_{23}\text{H}_{22}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 381.1252, Found: 381.1252. $[\alpha]^{20}_D = 26.0$ ($c = 5.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 3453, 2949, 1718, 1195, 1015, 782. The er value was determined

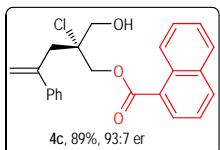
by HPLC (Chiralcel IA, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: t_1 = 21.7 min, t_2 = 25.6 min.

(E)-2-chloro-2-(hydroxymethyl)-4-methyl-5-phenylpent-4-en-1-yl 1-naphthoate (4b)



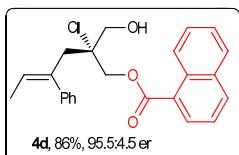
Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.92 (d, J = 8.8 Hz, 1H), 8.26 (d, J = 0.8 Hz, 1H), 8.24 (d, J = 0.8 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.91-7.49 (m, 3H), 7.34-7.21 (m, 5H), 6.47 (s, 1H), 4.76 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 11.6 Hz, 1H), 3.87-3.85 (dd, J = 2.8 Hz, 8.0 Hz, 2H), 2.90-2.81 (m, 2H), 2.66 (t, J = 7.2 Hz, 1H), 2.08 (d, J = 1.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.3, 137.5, 134.0, 133.9, 132.6, 131.6, 131.4, 130.6, 128.9, 128.6, 128.1, 128.1, 126.6, 126.4, 126.1, 125.7, 124.5, 73.5, 66.6, 66.4, 46.4, 20.6; HRMS (ESI) calcd. For C₂₄H₂₄ClO₃ [M+H]⁺: 395.1408, Found: 395.1408. $[\alpha]^{20}_D$ = 22.0 (c = 4.0 mg/mL, CHCl₃). IR ν (cm⁻¹) 3453, 2921, 1510, 1241, 1016, 782. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: t_1 = 10.6 min, t_2 = 11.8 min.

2-chloro-2-(hydroxymethyl)-4-phenylpent-4-en-1-yl 1-naphthoate (4c)



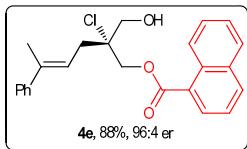
Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.87 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 0.8 Hz, 1H), 8.14 (d, J = 0.8 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.61-7.47 (m, 3H), 7.40-7.37 (m, 2H), 7.28-7.22 (m, 3H), 5.44 (d, J = 1.2 Hz, 1H), 5.33 (s, 1H), 4.50 (d, J = 11.6.0 Hz, 1H), 4.41 (d, J = 11.6 Hz, 1H), 3.70 (s, 1H), 3.27-3.18 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 142.9, 141.7, 133.9, 133.8, 131.6, 131.4, 130.6, 128.6, 128.5, 128.0, 127.8, 126.4, 126.3, 125.7, 124.4, 119.8, 73.5, 66.4, 66.3, 41.1; HRMS (ESI) calcd. For C₂₃H₂₂ClO₃ [M+H]⁺: 381.1252, Found: 381.1255. $[\alpha]^{20}_D$ = 165.0 (c = 24.0 mg/mL, CHCl₃). IR ν (cm⁻¹) 3482, 2920, 1718, 1195, 1016, 782. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: t_1 = 11.1 min, t_2 = 12.6 min.

(Z)-2-chloro-2-(hydroxymethyl)-4-phenylhex-4-en-1-yl 1-naphthoate (4d)



Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.87 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 7.2 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.64-7.48 (m, 3H), 7.30-7.17 (m, 6H), 5.83-5.80 (dd, J = 7.2 Hz, 13.6 Hz, 1H), 4.45-4.37 (dd, J = 11.6 Hz, 22.0 Hz, 2H), 3.64 (d, J = 8.8 Hz, 1H), 3.10 (d, J = 3.2 Hz, 2H), 2.22 (t, J = 7.6 Hz, 1H), 1.65 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 140.1, 134.9, 133.8, 131.4, 130.6, 128.8, 128.7, 128.6, 128.3, 127.9, 127.0, 126.3, 126.2, 125.8, 124.4, 74.2, 66.5, 66.5, 44.7, 15.0; HRMS (ESI) calcd. For C₂₄H₂₄ClO₃ [M+H]⁺: 395.1408, Found: 395.1404. $[\alpha]^{20}_D$ = 94.0 (c = 12.0 mg/mL, CHCl₃). IR ν (cm⁻¹) 1719, 1241, 1132, 780, 702. The er value was determined by HPLC (Chiralcel OD, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: t_1 = 22.2 min, t_2 = 25.3 min.

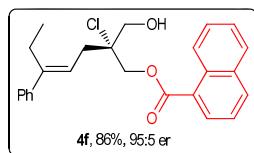
(E)-2-chloro-2-(hydroxymethyl)-5-phenylhex-4-en-1-yl 1-naphthoate (4e)



Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.93 (d, J = 8.8 Hz, 1H),

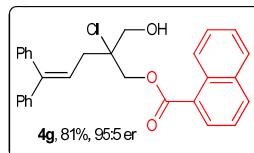
8.23 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.65-7.47 (m, 3H), 7.40-7.23 (m, 5H), 5.96 (t, J = 7.6 Hz, 1H), 4.47 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 3.85 (d, J = 6.0 Hz, 2H), 2.89-2.85 (m, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 143.4, 139.3, 134.0, 133.9, 131.4, 130.6, 128.6, 128.2, 128.1, 127.1, 126.4, 126.1, 125.8, 125.6, 124.5, 120.6, 74.0, 66.5, 66.4, 35.1, 16.5; HRMS (ESI) calcd. For $\text{C}_{24}\text{H}_{24}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 395.1408, Found: 395.1409. $[\alpha]^{20}_D$ = 74.0 (c = 15.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 3485, 2944, 1733, 1165, 1017, 782. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: t_1 = 19.0 min, t_2 = 20.1 min.

(E)-2-chloro-2-(hydroxymethyl)-5-phenylhept-4-en-1-yl 1-naphthoate (4f)



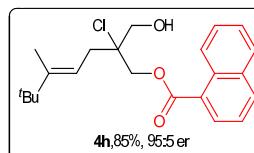
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.93 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.65-7.48 (m, 3H), 7.37-7.25 (m, 6H), 5.80 (t, J = 7.6 Hz, 1H), 4.63 (d, J = 11.6 Hz, 1H), 3.85 (d, J = 7.2 Hz, 1H), 2.90-2.87 (dd, J = 3.2 Hz, 7.6 Hz, 2H), 2.61-2.52 (m, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.3, 146.1, 142.4, 134.0, 133.9, 131.4, 130.7, 128.6, 128.3, 128.1, 127.1, 126.5, 126.4, 126.1, 125.6, 124.5, 120.1, 73.8, 66.6, 66.3, 34.7, 23.3, 13.3; HRMS (ESI) calcd. For $\text{C}_{25}\text{H}_{26}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 409.1565, Found: 409.1560. $[\alpha]^{20}_D$ = 58.0 (c = 13.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 3451, 2965, 1719, 1277, 1132, 781. The er value was determined by HPLC (Chiralcel OD-H, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: t_1 = 50.8 min, t_2 = 57.6 min.

2-chloro-2-(hydroxymethyl)-5,5-diphenylpent-4-en-1-yl 1-naphthoate (4g)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.90 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.2 Hz, 1H), 7.89 (d, J = 11.6 Hz, 1H), 7.63-7.52 (m, 2H), 7.44-7.40 (m, 1H), 7.29-7.15 (m, 10H), 6.34 (t, J = 7.2 Hz, 1H), 4.59 (s, 1H), 3.78 (d, J = 6.8 Hz, 1H), 2.82 (d, J = 6.8 Hz, 2H), 2.82 (d, J = 7.6 Hz, 3H), 2.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.9, 145.7, 142.0, 139.5, 133.9, 133.8, 131.4, 130.6, 129.7, 128.6, 128.4, 128.2, 128.0, 127.5, 127.3, 126.3, 125.8, 125.7, 124.4, 121.8, 73.7, 66.5, 66.2, 35.6; HRMS (ESI) calcd. For $\text{C}_{29}\text{H}_{26}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 457.1565, Found: 457.1565. $[\alpha]^{20}_D$ = 46.0 (c = 9.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 1720, 1242, 1195, 1139, 780. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 97:3, flow rate = 0.75 mL/min), retention time: t_1 = 29.8 min, t_2 = 33.5 min.

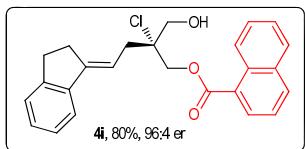
(E)-2-chloro-2-(hydroxymethyl)-5,6,6-trimethylhept-4-en-1-yl 1-naphthoate (4h)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.93 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 7.2 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.65-7.50 (m, 2H), 5.42 (d, J = 7.2 Hz, 1H), 4.67 (d, J = 11.6 Hz, 1H), 4.56 (d, J = 11.6 Hz, 1H), 3.81 (d, J = 7.2 Hz, 2H), 2.70-2.67 (m, 2H), 2.51 (t, J = 7.2 Hz, 3H), 1.65 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 148.1, 134.0, 133.9, 131.4, 130.6, 128.6, 128.0, 126.4, 126.2, 125.7, 124.5, 113.7, 74.5, 66.5, 66.4, 36.6, 34.6, 29.0, 13.3; HRMS (ESI) calcd. For $\text{C}_{22}\text{H}_{28}\text{ClO}_3$ [$\text{M}+\text{H}]^+$:

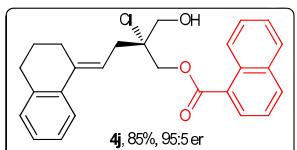
375.1721, Found: 375.1728. $[\alpha]^{20}_D = 31.0$ ($c = 10.0$ mg/mL, CHCl₃). IR ν (cm⁻¹) 2988, 1722, 1241, 781. The er value was determined by HPLC (Chiralcel ID, hexane/isopropanol = 97:3, flow rate = 0.75 mL/min), retention time: t₁ = 14.0 min, t₂ = 15.7 min.

(E)-2-chloro-4-(2,3-dihydro-1H-inden-1-ylidene)-2-(hydroxymethyl)butyl 1-naphthoate (4i)



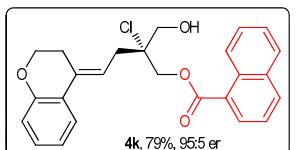
Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.97 (d, $J = 8.8$ Hz, 1H), 8.29 (d, $J = 7.6$ Hz, 1H), 8.19 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.69-7.53 (m, 4H), 7.29-7.22 (m, 3H), 6.16-6.13 (m, 1H), 4.80 (d, $J = 11.6$ Hz, 1H), 4.68 (d, $J = 11.6$ Hz, 1H), 3.90 (d, $J = 10.8$ Hz, 2H), 3.03-2.96 (m, 2H), 2.91 (d, $J = 7.2$ Hz, 2H), 2.81 (d, $J = 5.6$ Hz, 2H), 2.65-2.62 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 167.3, 146.6, 146.3, 140.9, 134.0, 133.9, 131.4, 130.6, 128.6, 128.1, 128.1, 126.5, 126.4, 126.1, 125.6, 125.3, 124.7, 124.5, 120.3, 111.3, 74.2, 66.7, 66.3, 36.1, 29.9, 28.2; HRMS (ESI) calcd. For C₂₅H₂₄ClO₃ [M+H]⁺: 407.1408, Found: 407.1400. $[\alpha]^{20}_D = 81.0$ ($c = 9.0$ mg/mL, CHCl₃). IR ν (cm⁻¹) 1719, 1459, 1241, 1194, 1132, 781. The er value was determined by HPLC (Chiralcel OD-H, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: t₁ = 30.6 min, t₂ = 42.5 min.

(E)-2-chloro-4-(3,4-dihydroronaphthalen-1(2H)-ylidene)-2-(hydroxymethyl)butyl 1-naphthoate (4j)



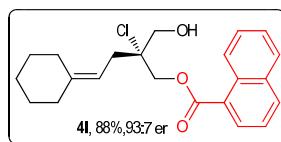
Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.97 (d, $J = 8.8$ Hz, 1H), 8.29 (d, $J = 1.2$ Hz, 1H), 8.27 (d, $J = 1.2$ Hz, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 7.95-7.20 (m, 4H), 7.15-7.12 (m, 3H), 6.23 (t, $J = 7.6$ Hz, 1H), 4.77 (d, $J = 12.0$ Hz, 1H), 4.67 (d, $J = 11.6$ Hz, 1H), 3.91-3.89 (m, 2H), 2.95-2.92 (m, 2H), 2.82-2.79 (m, 2H), 2.64-2.56 (m, 2H), 1.86-1.83 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 167.2, 138.6, 137.5, 135.8, 134.0, 133.9, 131.4, 130.6, 128.9, 128.6, 128.1, 127.2, 126.4, 126.1, 125.6, 124.5, 124.0, 116.3, 74.2, 66.6, 66.4, 34.5, 30.3, 26.9, 23.2; HRMS (ESI) calcd. For C₂₆H₂₆ClO₃ [M+H]⁺: 421.1565, Found: 421.1563. $[\alpha]^{20}_D = 80.0$ ($c = 13.0$ mg/mL, CHCl₃). IR ν (cm⁻¹) 2987, 1720, 1510, 1240, 1133, 780. The er value was determined by HPLC (Chiralcel ODH, hexane/isopropanol = 97:3, flow rate = 0.75 mL/min), retention time: t₁ = 88.9 min, t₂ = 99.3 min.

(E)-2-chloro-4-(chroman-4-ylidene)-2-(hydroxymethyl)butyl 1-naphthoate (4k)



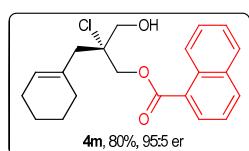
Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.92 (d, $J = 8.4$ Hz, 1H), 8.25 (d, $J = 0.8$ Hz, 1H), 8.15 (d, $J = 6.0$ Hz, 1H), 7.99 (d, $J = 5.6$ Hz, 1H), 7.17-7.13 (m, 1H), 6.91-6.83 (m, 2H), 6.22 (t, $J = 7.6$ Hz, 1H), 4.74 (d, $J = 12.0$ Hz, 1H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.16 (t, $J = 5.6$ Hz, 2H), 2.69 (t, $J = 5.6$ Hz, 2H), 2.61 (t, $J = 7.2$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 167.3, 154.4, 134.2, 133.9, 132.8, 131.4, 130.7, 129.1, 128.7, 126.5, 126.0, 125.6, 124.5, 124.0, 120.8, 117.5, 114.4, 66.6, 66.2, 35.9, 26.1; HRMS (ESI) calcd. For C₂₅H₂₄ClO₄ [M+H]⁺: 423.1358, Found: 423.1359. $[\alpha]^{20}_D = 40.0$ ($c = 5.0$ mg/mL, CHCl₃). IR ν (cm⁻¹) 2962, 1719, 1450, 1096, 1019, 801. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 97:3, flow rate = 0.75 mL/min), retention time: t₁ = 51.8 min, t₂ = 58.3 min.

2-chloro-4-cyclohexylidene-2-(hydroxymethyl)butyl 1-naphthoate (4l)



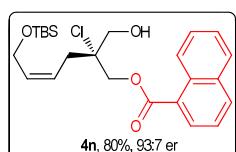
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.93 (d, $J = 9.6$ Hz, 1H), 8.24 (d, $J = 7.2$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.65-7.45 (m, 3H), 5.27 (t, $J = 7.6$ Hz, 1H), 4.65 (d, $J = 11.6$ Hz, 1H), 4.58 (d, $J = 11.6$ Hz, 1H), 3.81 (d, $J = 6.8$ Hz, 2H), 2.74-2.62 (m, 2H), 2.48 (t, $J = 7.2$ Hz, 3H), 2.17-2.14 (m, 4H), 1.57-1.48 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 144.8, 134.0, 133.9, 131.4, 130.6, 128.6, 128.0, 126.4, 126.2, 125.7, 124.5, 113.6, 74.3, 66.5, 66.4, 37.4, 33.6, 29.1, 28.6, 27.7, 26.7; HRMS (ESI) calcd. For $\text{C}_{22}\text{H}_{26}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 373.1565, Found: 373.1561. $[\alpha]^{20}_D = 35.0$ ($c = 6.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 2918, 1718, 1446, 1195, 1015, 781. The er value was determined by HPLC (Chiracel ID, hexane/isopropanol = 97:3, flow rate = 0.75 mL/min), retention time: $t_1 = 19.6$ min, $t_2 = 27.5$ min.

2-chloro-3-(cyclohex-1-en-1-yl)-2-(hydroxymethyl)propyl 1-naphthoate (4m)



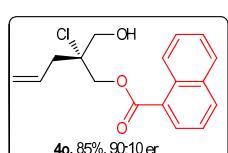
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.94 (d, $J = 8.4$ Hz, 1H), 8.24 (d, $J = 7.6$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.57-7.26 (m, 2H), 5.63 (s, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.56 (d, $J = 11.6$ Hz, 1H), 3.80-3.78 (m, 2H), 2.67-2.54 (m, 3H), 2.18-2.15 (m, 2H), 2.04 (m, 2H), 1.64-1.55 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 134.0, 133.9, 132.1, 131.4, 130.6, 128.6, 128.4, 128.0, 126.4, 126.2, 125.7, 124.5, 73.6, 66.6, 66.5, 44.2, 30.8, 25.5, 23.0, 22.0; HRMS (ESI) calcd. For $\text{C}_{21}\text{H}_{24}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 359.1408, Found: 359.1405. $[\alpha]^{20}_D = 88.0$ ($c = 18.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 3474, 1719, 1511, 1241, 1133, 1017. The er value was determined by HPLC (Chiracel IA, hexane/isopropanol = 97:3, flow rate = 0.75 mL/min), retention time: $t_1 = 21.6$ min, $t_2 = 25.9$ min.

(Z)-6-((tert-butyldimethylsilyl)oxy)-2-chloro-2-(hydroxymethyl)hex-4-en-1-yl 1-naphthoate (4n)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.95 (d, $J = 8.4$ Hz, 1H), 8.26 (d, $J = 7.2$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.89 (dd, $J = 12.0$ Hz, 15.2 Hz, 1H), 4.32-4.27 (dd, $J = 11.6$ Hz, 15.2 Hz, 1H), 4.15-4.10 (dd, $J = 12.4$ Hz, 6.0 Hz, 1H), 3.78-3.73 (m, 2H), 3.68-3.64 (m, 1H), 2.95-2.90 (dd, $J = 8.8$ Hz, 14.4 Hz, 1H), 2.66-2.61 (dd, $J = 6.4$ Hz, 14.4 Hz, 3H), 0.89 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 133.8, 132.4, 131.5, 130.6, 128.6, 128.0, 126.4, 126.3, 126.2, 125.8, 124.5, 72.6, 67.5, 64.9, 58.7, 33.0, 25.8, 18.3; HRMS (ESI) calcd. For $\text{C}_{24}\text{H}_{34}\text{ClO}_4\text{Si}$ [$\text{M}+\text{H}]^+$: 449.1909, Found: 449.1900. $[\alpha]^{20}_D = 146.0$ ($c = 13.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 3418, 2954, 1721, 1462, 1242, 837. The er value was determined by HPLC (Chiracel OD-H, hexane/isopropanol = 90:10, flow rate = 0.75 mL/min), retention time: $t_1 = 17.4$ min, $t_2 = 22.7$ min.

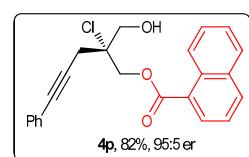
2-chloro-2-(hydroxymethyl)pent-4-en-1-yl 1-naphthoate (4o)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.23 (d, $J = 6.4$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 1.2$ Hz, 1H),

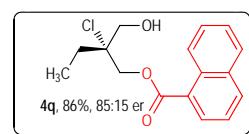
7.64-7.61 (m, 1H), 7.57-7.50 (m, 2H), 6.03-5.92 (m, 1H), 3.79 (d, J = 6.8 Hz, 2H), 2.71 (d, J = 7.2 Hz, 2H), 2.57 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 134.0, 133.9, 131.4, 130.6, 128.6, 128.1, 126.4, 126.1, 125.6, 124.5, 120.2, 72.7, 66.3, 66.2, 40.3; HRMS (ESI) calcd. For $\text{C}_{17}\text{H}_{18}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 305.0939, Found: 305.0934. $[\alpha]^{20}_D$ = 170.0 (c = 15.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 3500, 2948, 1542, 1462, 1015, 778. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: t_1 = 14.4 min, t_2 = 16.2 min.

2-chloro-2-(hydroxymethyl)-5-phenylpent-4-yn-1-yl 1-naphthoate (4p)



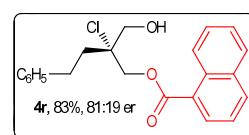
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.94 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.65-7.48 (m, 3H), 7.43-7.41 (m, 2H), 7.32-7.25 (m, 3H), 4.85 (d, J = 12.0 Hz, 1H), 4.76 (d, J = 12.0 Hz, 1H), 3.97 (d, J = 6.8 Hz, 2H), 3.02-3.11 (dd, J = 17.6 Hz, 20.0 Hz, 2H), 2.56 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.1, 134.0, 133.9, 131.7, 131.4, 130.7, 128.6, 128.3, 128.1, 126.4, 126.1, 125.7, 124.5, 122.8, 84.3, 83.2, 71.6, 66.6, 66.3, 28.2; HRMS (ESI) calcd. For $\text{C}_{23}\text{H}_{20}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 379.1095, Found: 379.1099. $[\alpha]^{20}_D$ = 104.0 (c = 12.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 1718, 1490, 1241, 1132, 1016, 781. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 97:3, flow rate = 0.75 mL/min), retention time: t_1 = 32.8 min, t_2 = 36.0 min.

(R)-2-chloro-2-(hydroxymethyl)butyl 1-naphthoate (4q)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.92 (d, J = 8.8 Hz, 1H), 8.23-8.21 (dd, J = 1.2 Hz, 7.2 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.57-7.49 (m, 2H), 4.68 (d, J = 15.6 Hz, 1H), 4.59 (d, J = 15.6 Hz, 1H), 3.80 (t, J = 1.2 Hz, 2H), 2.58-2.55 (m, 1H), 2.04-1.92 (m, 2H), 1.14-1.11 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.3, 134.0, 133.9, 131.4, 130.6, 128.6, 128.1, 126.4, 126.1, 125.6, 124.5, 74.2, 66.6, 66.4, 44.1, 24.7, 24.2; HRMS (ESI) calcd. For $\text{C}_{16}\text{H}_{18}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 293.0939, Found: 293.0938. $[\alpha]^{20}_D$ = 28.0 (c = 12.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 3420, 2964, 1728, 1442, 1245, 837. The er value was determined by HPLC (Chiralcel ID, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: t_1 = 21.1 min, t_2 = 25.9.0 min.

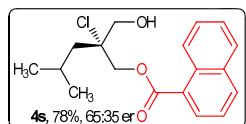
(R)-2-chloro-2-(hydroxymethyl)-4-phenylbutyl 1-naphthoate (4r)



Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.92 (d, J = 8.8 Hz, 1H), 8.21 (d, J = 6.6 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.56-7.48 (m, 2H), 7.30-7.17 (m, 5H), 4.73 (d, J = 15.6 Hz, 1H), 4.63 (d, J = 15.6 Hz, 1H), 3.83 (s, 2H), 2.92-2.88 (dd, J = 7.6 Hz, 9.2 Hz, 2H), 2.25-2.19 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 141.0, 134.3, 134.1, 133.8, 131.4, 130.6, 128.6, 128.6, 128.4, 128.1, 128.0, 126.3, 126.2, 126.0, 125.9, 125.6, 124.5, 73.5, 66.2, 66.1, 37.7, 30.0; HRMS (ESI) calcd. For $\text{C}_{22}\text{H}_{22}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 369.1252, Found: 369.1256. $[\alpha]^{20}_D$ = 24.0 (c = 18.0 mg/mL, CHCl_3). IR ν (cm^{-1}) 1718, 1470, 1261, 1156, 1043, 781. The er value was determined by HPLC (Chiralcel IA, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: t_1 = 21.2 min, t_2 = 23.0

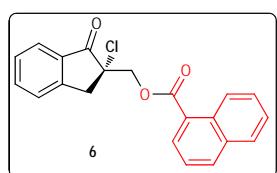
min.

(R)-2-chloro-2-(hydroxymethyl)-4-methylpentyl 1-naphthoate (4s)



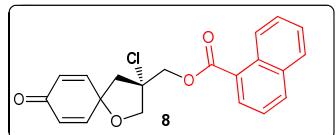
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.22 (d, $J = 1.2$ Hz, 1H), 8.21 (d, $J = 1.2$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.65-7.61 (m, 1H), 7.57-7.50 (m, 2H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.61 (d, $J = 12.0$ Hz, 1H), 3.78 (d, $J = 7.2$ Hz, 2H), 2.59 (t, $J = 7.2$ Hz, 1H), 2.01-1.99 (m, 1H), 1.86 (d, $J = 5.6$ Hz, 2H), 1.66-1.04 (dd, $J = 3.6$ Hz, 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.3, 134.0, 133.9, 131.4, 130.6, 128.6, 128.1, 126.4, 126.1, 125.6, 124.5, 74.2, 66.6, 66.4, 44.1, 24.7, 24.2; HRMS (ESI) calcd. For $\text{C}_{18}\text{H}_{22}\text{ClO}_3$ [$\text{M}+\text{H}]^+$: 321.1252, Found: 321.1258. $[\alpha]^{20}_D = 18.0$ ($c = 10.0$ mg/mL, CHCl_3). IR ν (cm^{-1}) 3418, 2954, 1721, 1462, 1242, 837. The er value was determined by HPLC (Chiralcel ID, hexane/isopropanol = 95:5, flow rate = 0.75 mL/min), retention time: $t_1 = 13.7$ min, $t_2 = 15.4$ min.

(S)-(2-chloro-1-oxo-2,3-dihydro-1H-inden-2-yl)methyl 1-naphthoate (6)



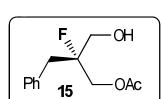
Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.80 (d, $J = 8.0$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 7.6$ Hz, 1H), 7.87-7.83 (m, 2H), 7.56-7.46 (m, 4H), 7.36 (t, $J = 7.6$ Hz, 4H), 4.96-4.79 (dd, $J = 11.2$ Hz, 32.8 Hz, 1H), 3.82 (d, $J = 11.8$ Hz, 1H), 3.63 (d, $J = 18.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 198.3, 166.2, 150.2, 136.4, 133.9, 133.7, 133.5, 131.3, 130.6, 128.5, 128.4, 128.0, 126.5, 126.3, 125.6, 125.5, 124.4, 66.9, 66.0, 41.1; HRMS (ESI) calcd. For $\text{C}_{21}\text{H}_{16}\text{ClO}_3$, $[\text{M}+\text{H}]^+$: 351.0782, Found: 351.0788.

(3-chloro-8-oxo-1-oxaspiro[4.5]deca-6,9-dien-3-yl)methyl 1-naphthoate (8)



Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.93 (d, $J = 8.4$ Hz, 1H), 8.24 (d, $J = 7.2$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.67-7.53 (m, 3H), 7.34-7.26 (m, 1H), 6.80-6.77 (dd, $J = 2.8$ Hz, 10.0 Hz, 1H), 6.22-6.17 (m, 2H), 4.77 (d, $J = 11.6$ Hz, 1H), 4.70 (d, $J = 12.0$ Hz, 1H), 4.43-4.36 (dd, $J = 7.6$ Hz, 16.0 Hz, 2H), 2.70-2.61 (dd, $J = 14.8$ Hz, 20.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): 8185.0, 166.5, 148.0, 147.6, 134.3, 133.9, 131.4, 130.6, 128.7, 128.2, 128.1, 127.4, 126.5, 125.7, 125.5, 124.5, 78.2, 78.0, 72.6, 67.8, 48.8; HRMS (ESI) calcd. For $\text{C}_{21}\text{H}_{18}\text{ClO}_4$ $[\text{M}+\text{H}]^+$: 369.0888, Found: 369.0889. $[\alpha]^{20}_D = 20.0$ ($c = 4.0$ mg/mL, CHCl_3).

(R)-2-benzyl-2-fluoro-3-hydroxypropyl acetate (15)



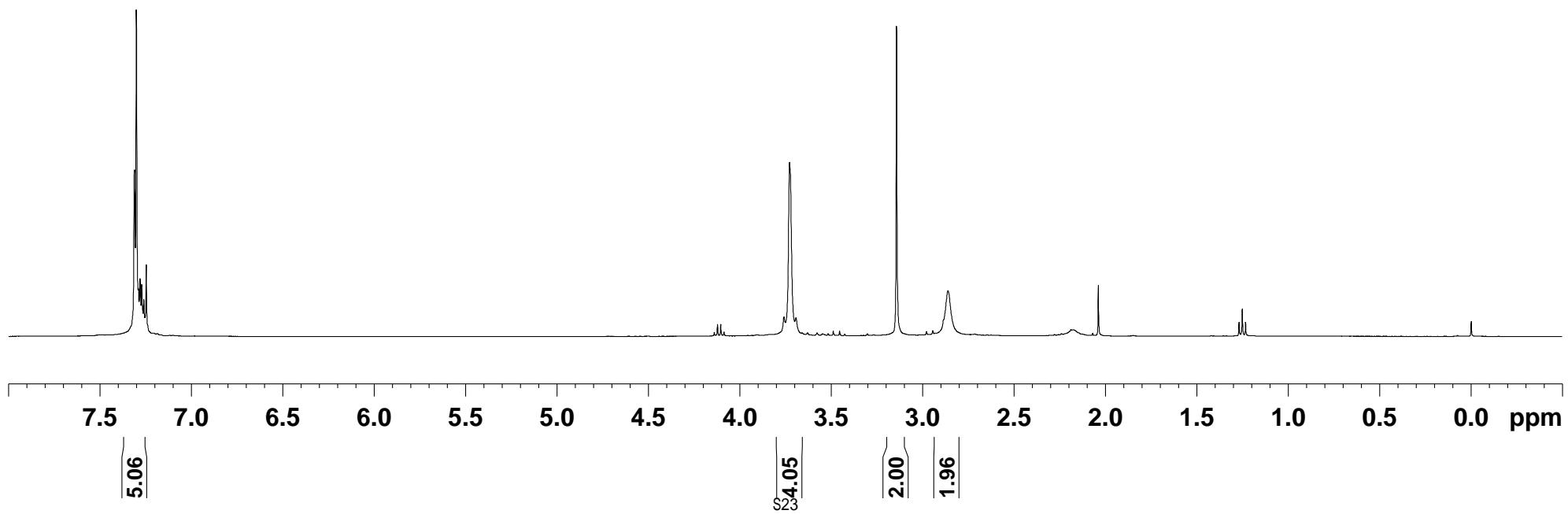
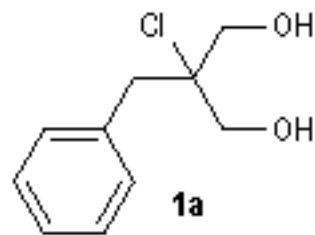
Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.23 (m, 5H), 4.28-4.09 (m, 2H), 3.64-3.59 (dd, $J = 3.6$ Hz, 12.4 Hz, 1H), 3.05 (d, $J = 21.2$ Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 1171.0, 134.5, 134.5, 130.3, 128.4, 127.0, 97.0, 95.3, 64.1, 63.8, 63.1, 62.8, 38.57, 38.4, 20.7; HRMS (ESI) calcd. For $\text{C}_{11}\text{H}_{14}\text{ClO}_3$ $[\text{M}+\text{H}]^+$: 229.0626, Found: 229.0629. $[\alpha]^{20}_D = 6.0$ ($c = 14.0$ mg/mL, CHCl_3).

7. References

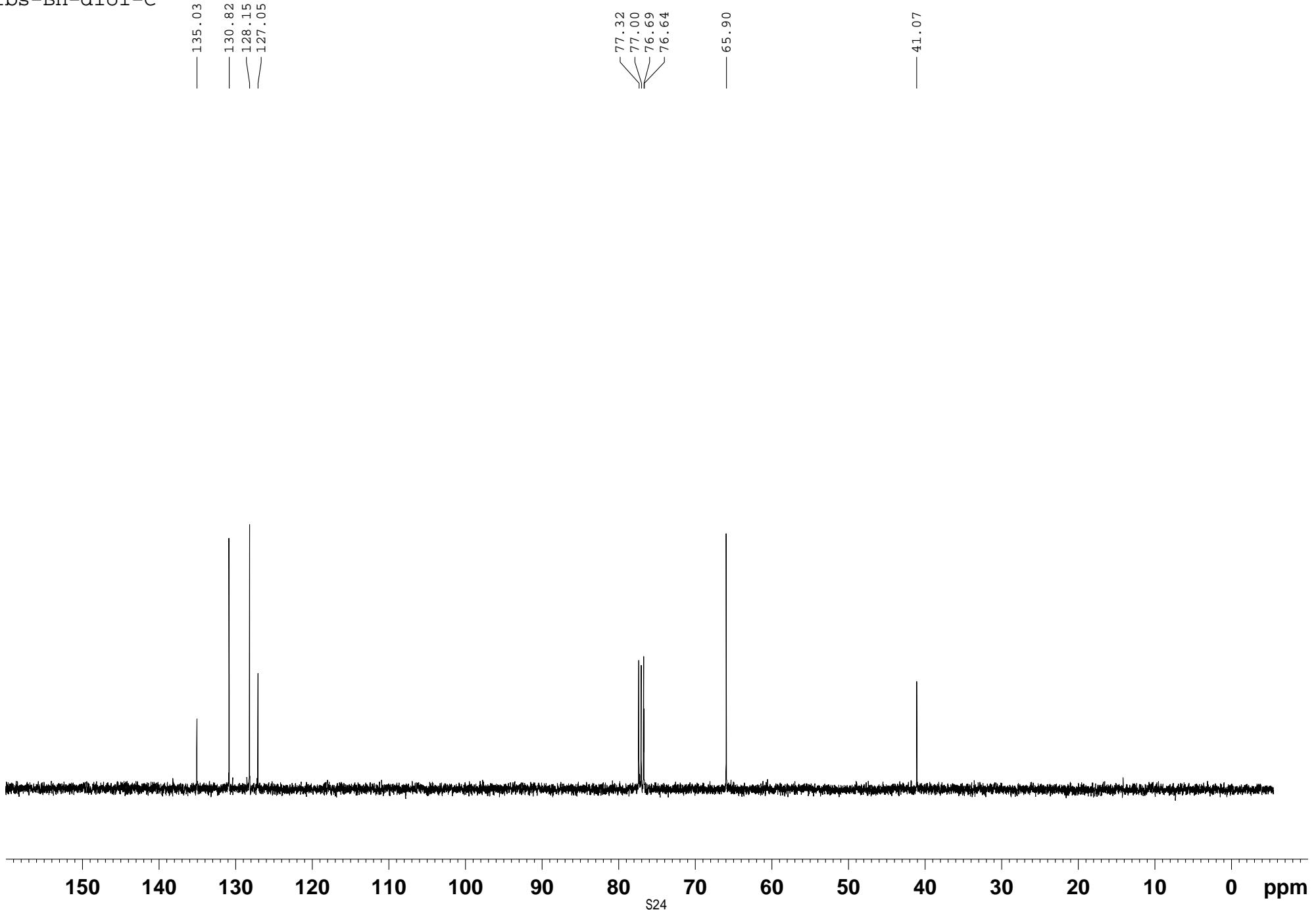
1. C. Yokoyama, R. Hyodo, A. Nakadat, S. Yamaguchit, Y. Hirail, T. Kometani, M. Goto, N. Shibata and Y. Takeuehi, *Tetrahedron Lett.* 1998, **39**, 7741.
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3. O. Iliashevsky, L. Amir, R. Glaser, R. S. Mark and N. G. Lemcoff, *J. Mater. Chem.* 2009, **19**, 6616.
4. K. D. Reichl, N. L. Dunn, N. J. Fastuca and A. T. Radosevich, *J. Am. Chem. Soc.* 2015, **137**, 5292.
5. K. Hirano, A. T. Biju, I. Piel and F. Glorius, *J. Am. Chem. Soc.* 2009, **131**, 14190.
6. M. A. Ischay, Z. Lu and T. P. Yoon, *J. Am. Chem. Soc.* 2010, **132**, 8572.
7. H. Zheng, M. Lejkowski and D. G. Hall, *Chem. Sci.* 2011, **2**, 1305.
8. K. D. Reichl, N. L. Dunn, N. J. Fastuca and A. T. Radosevich, *J. Am. Chem. Soc.* 2015, **137**, 5292.

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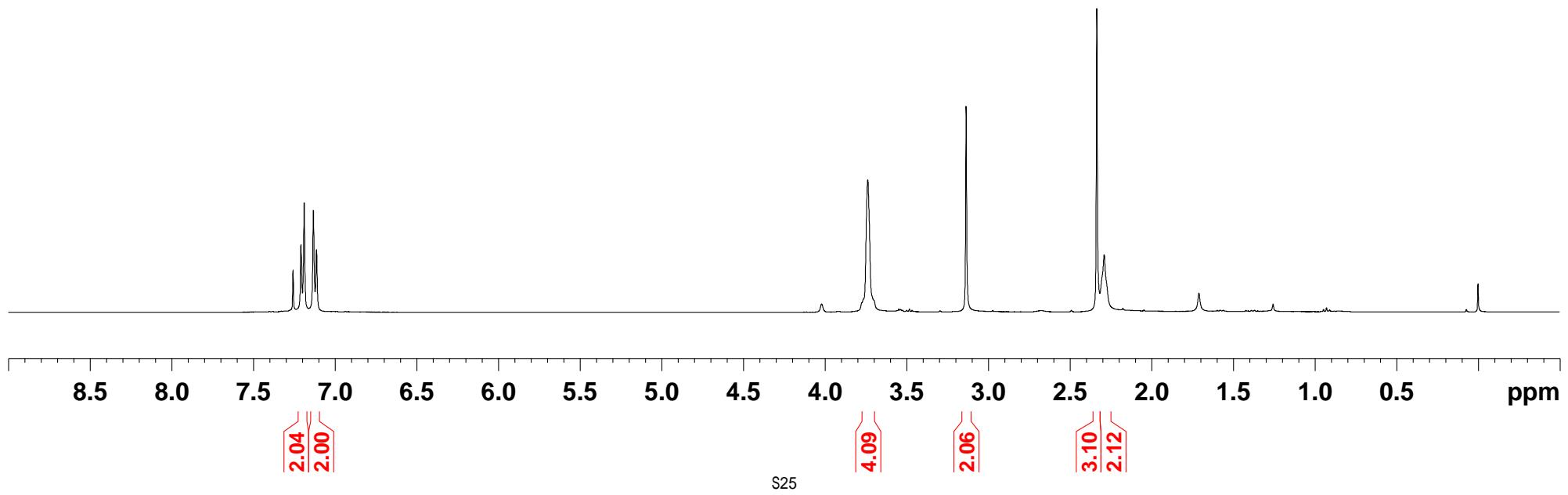
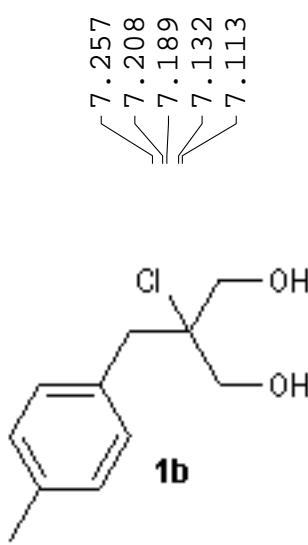
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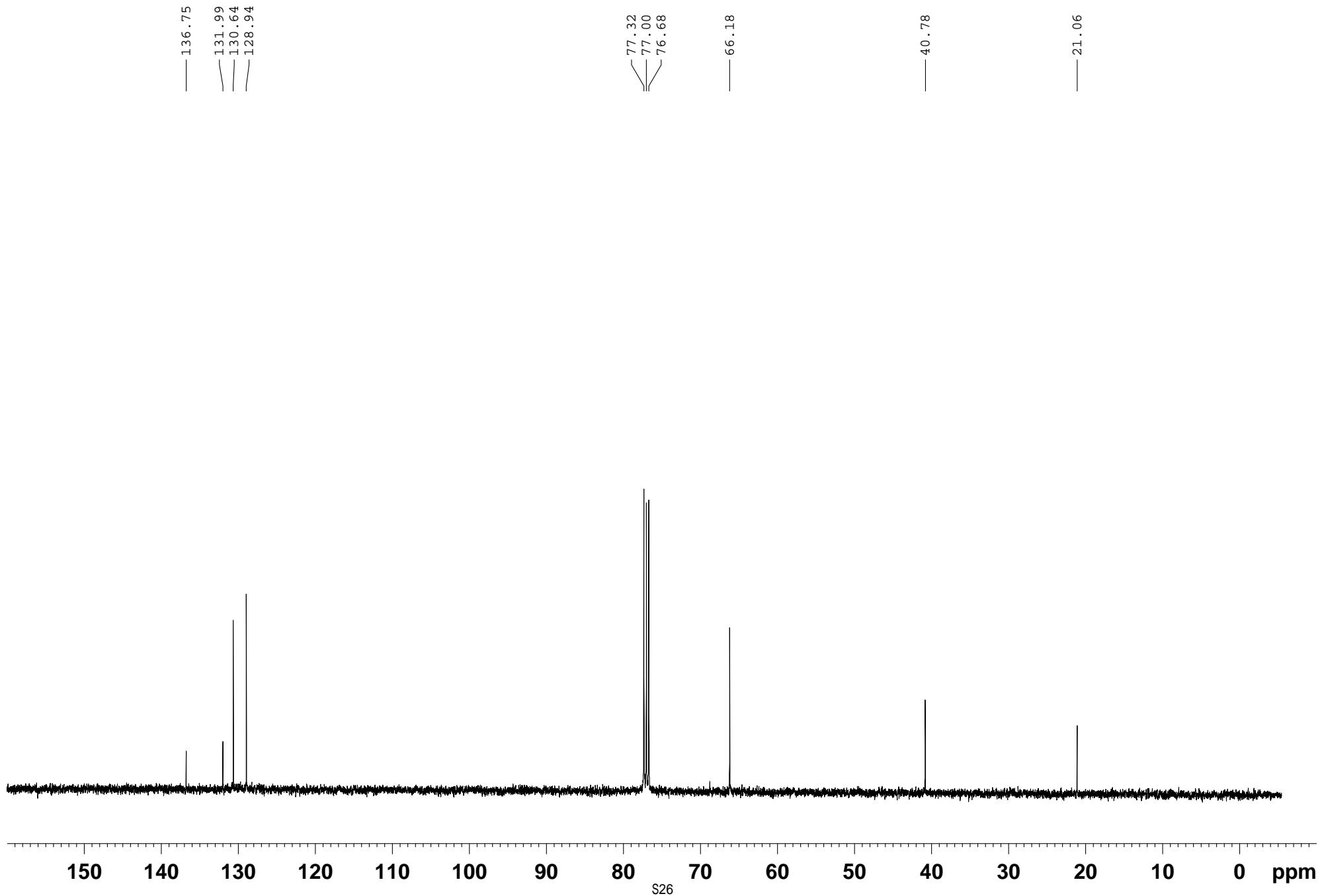
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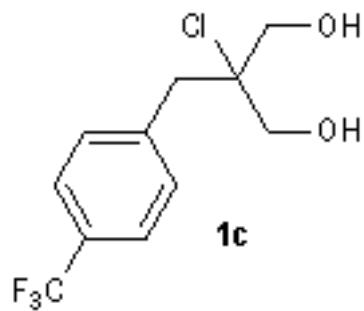


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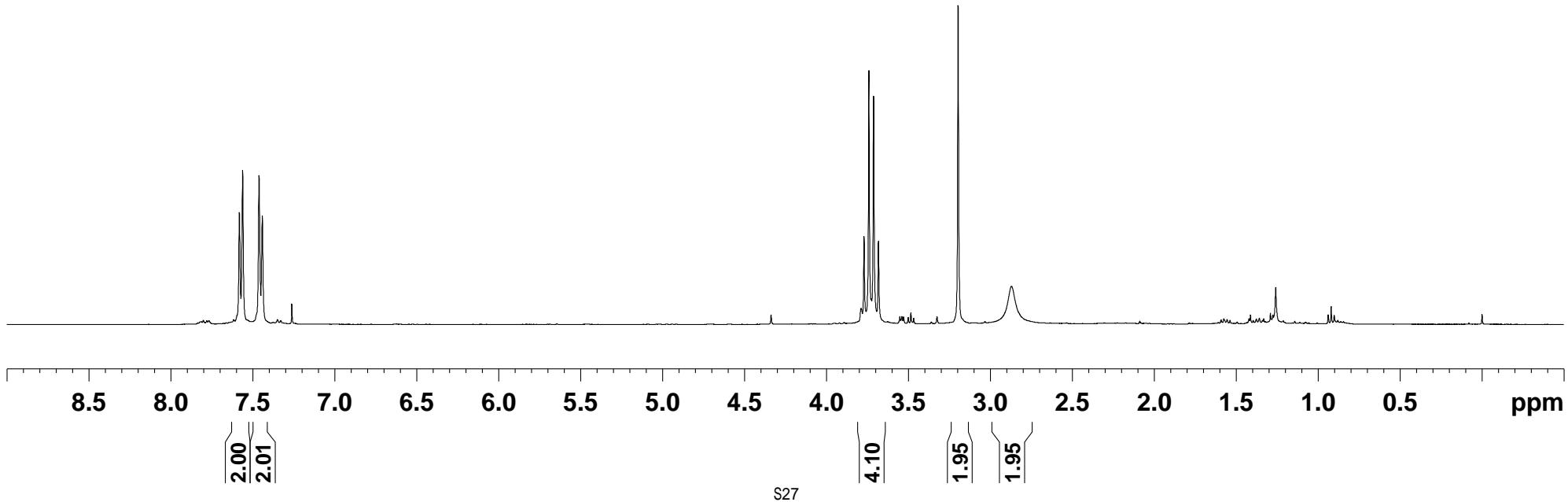


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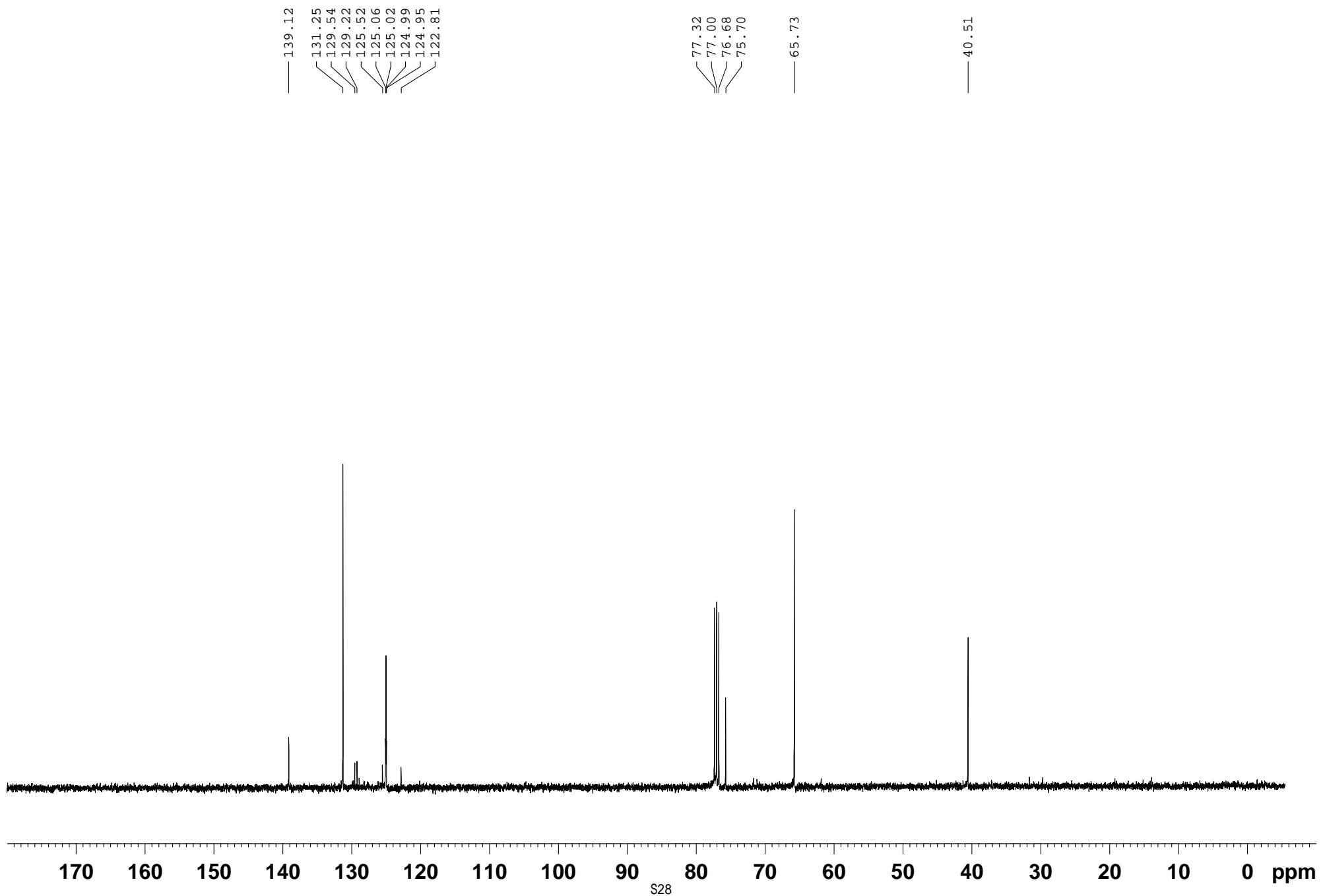
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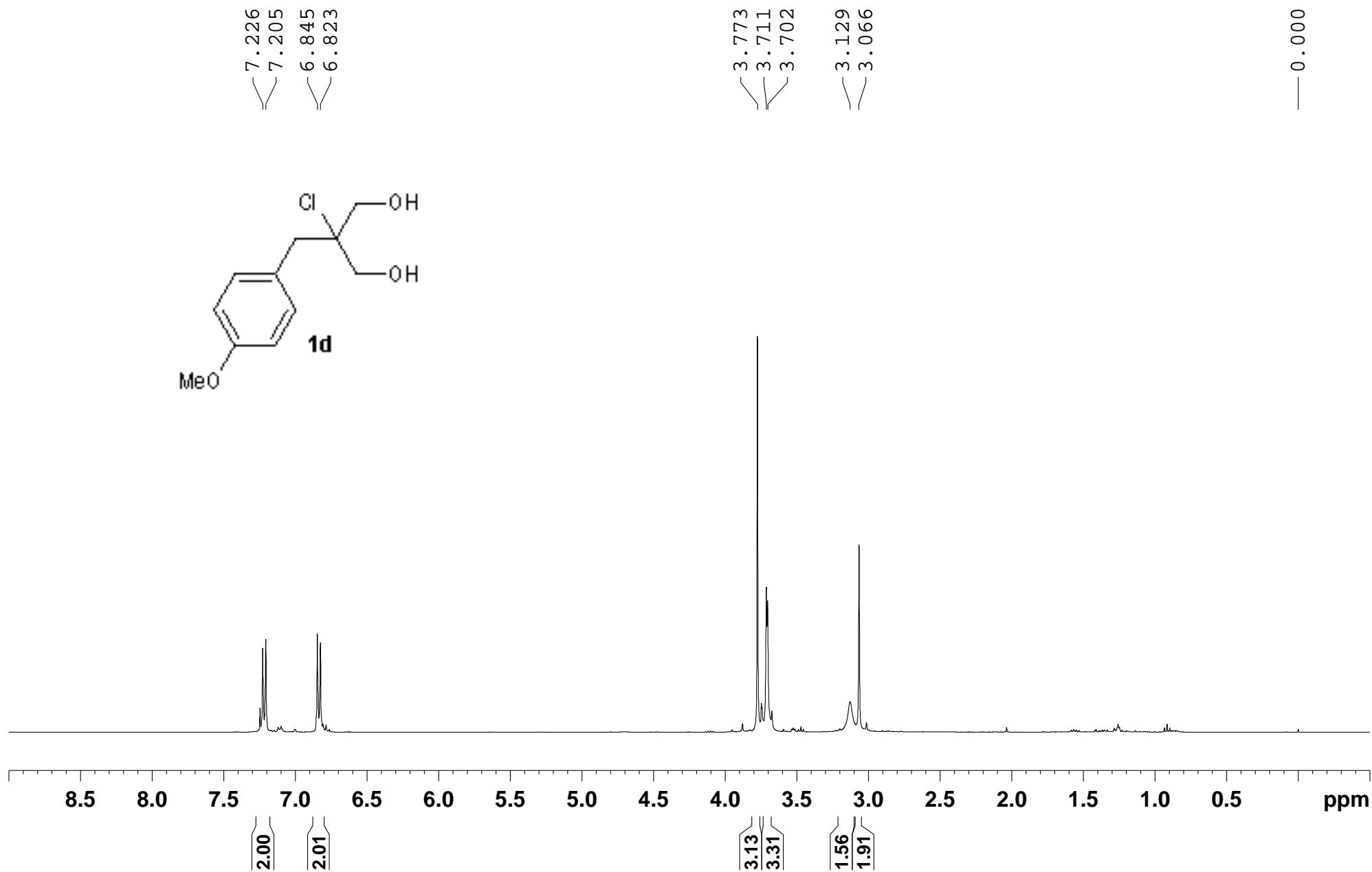
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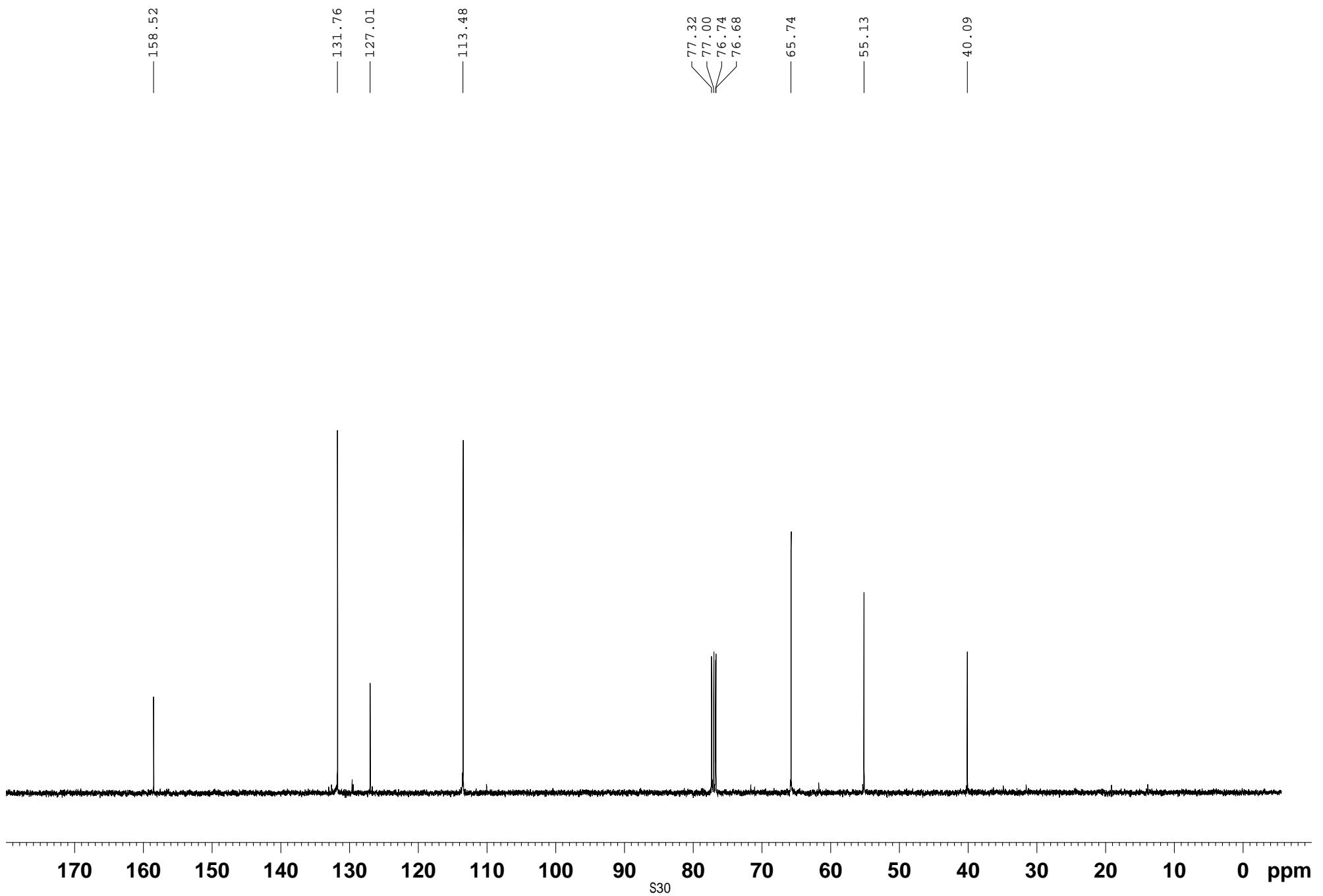
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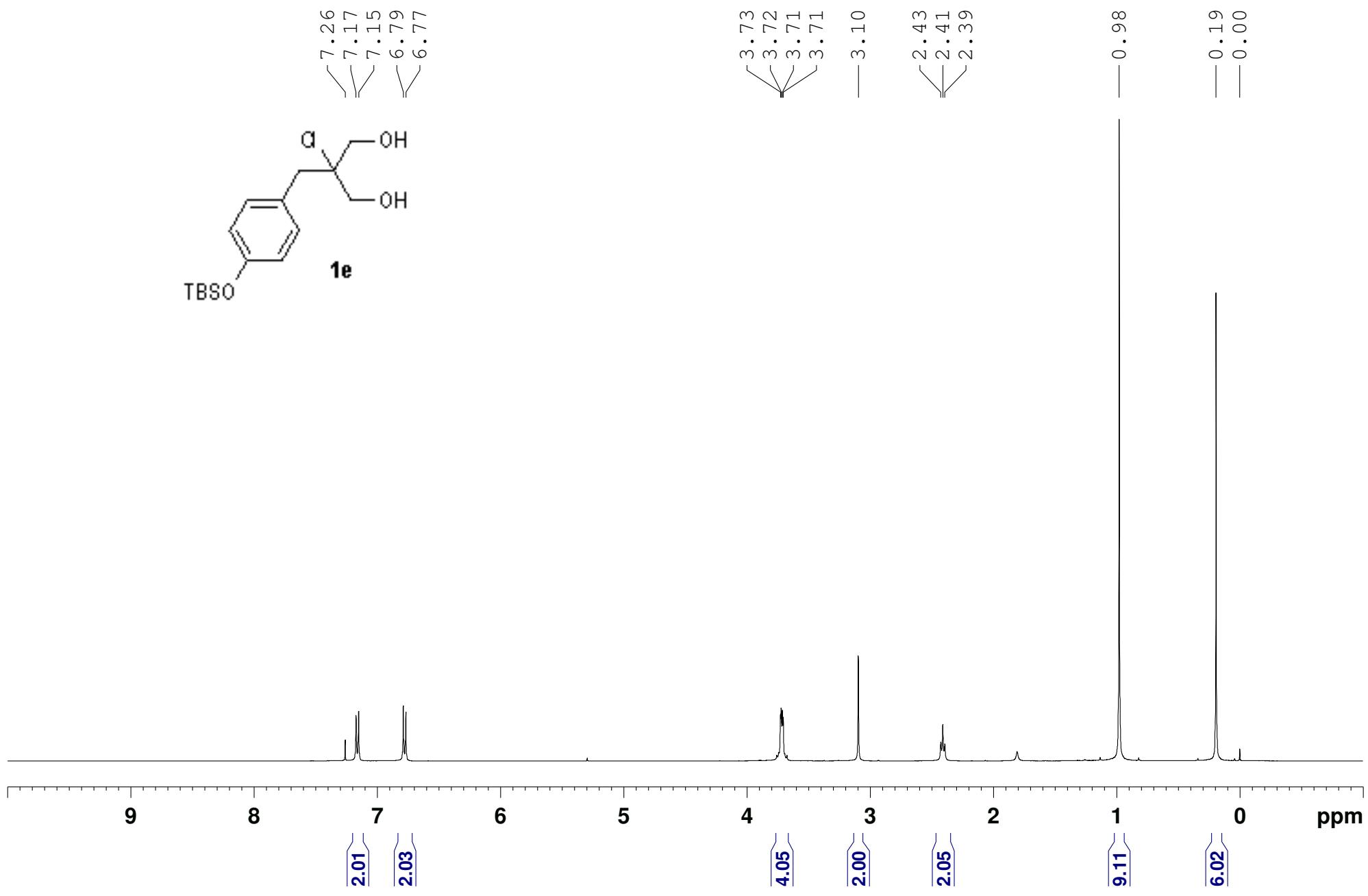


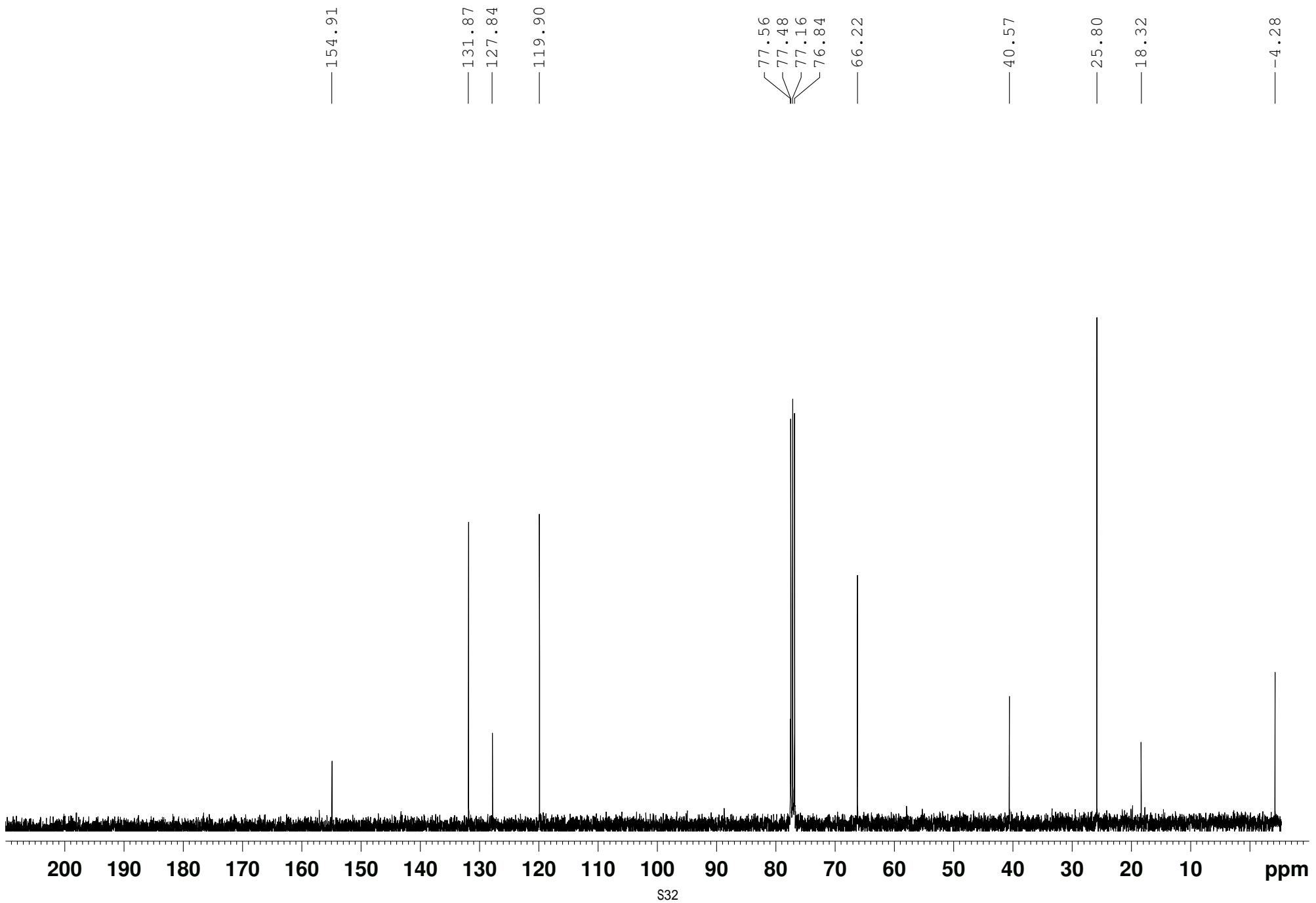
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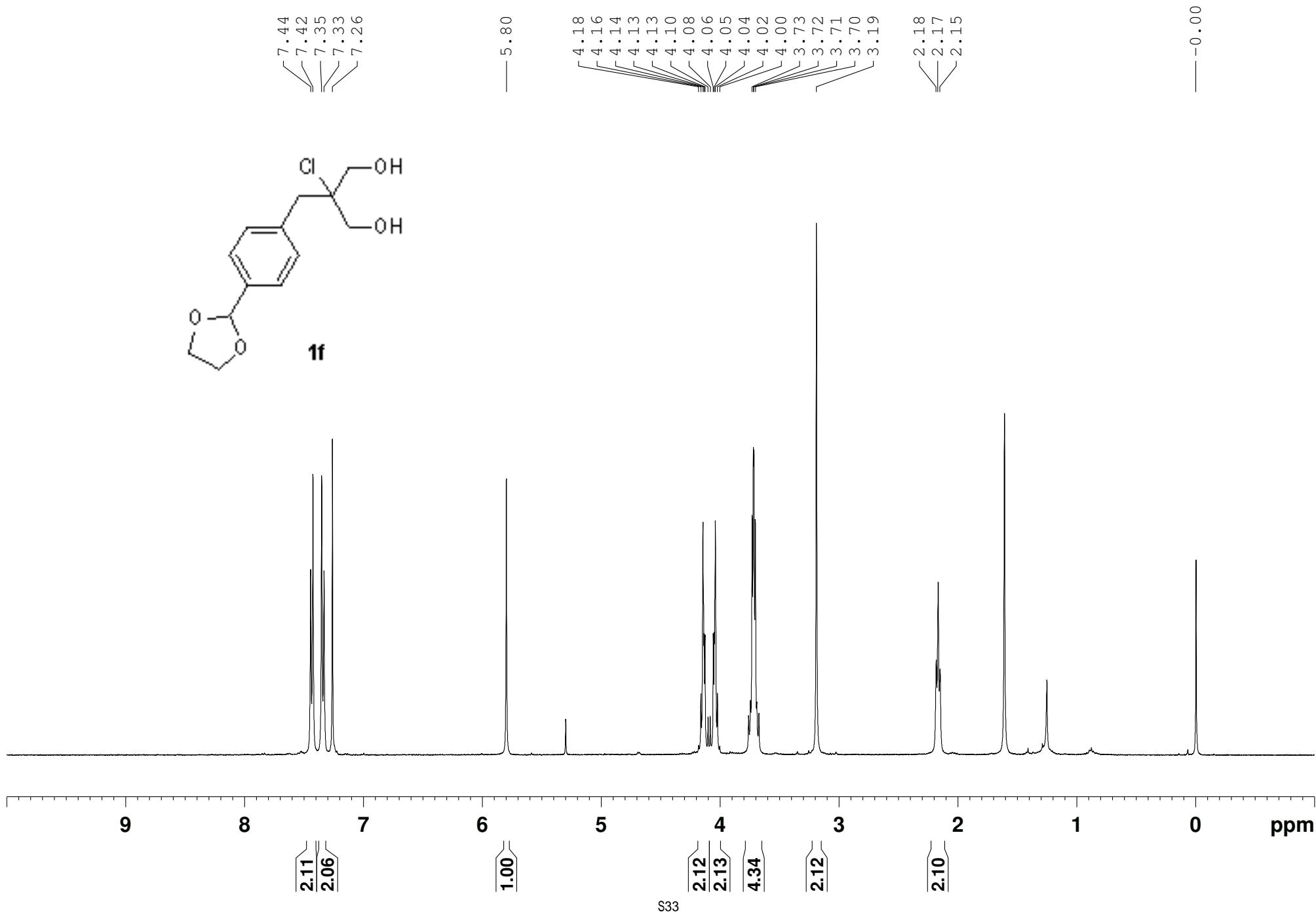


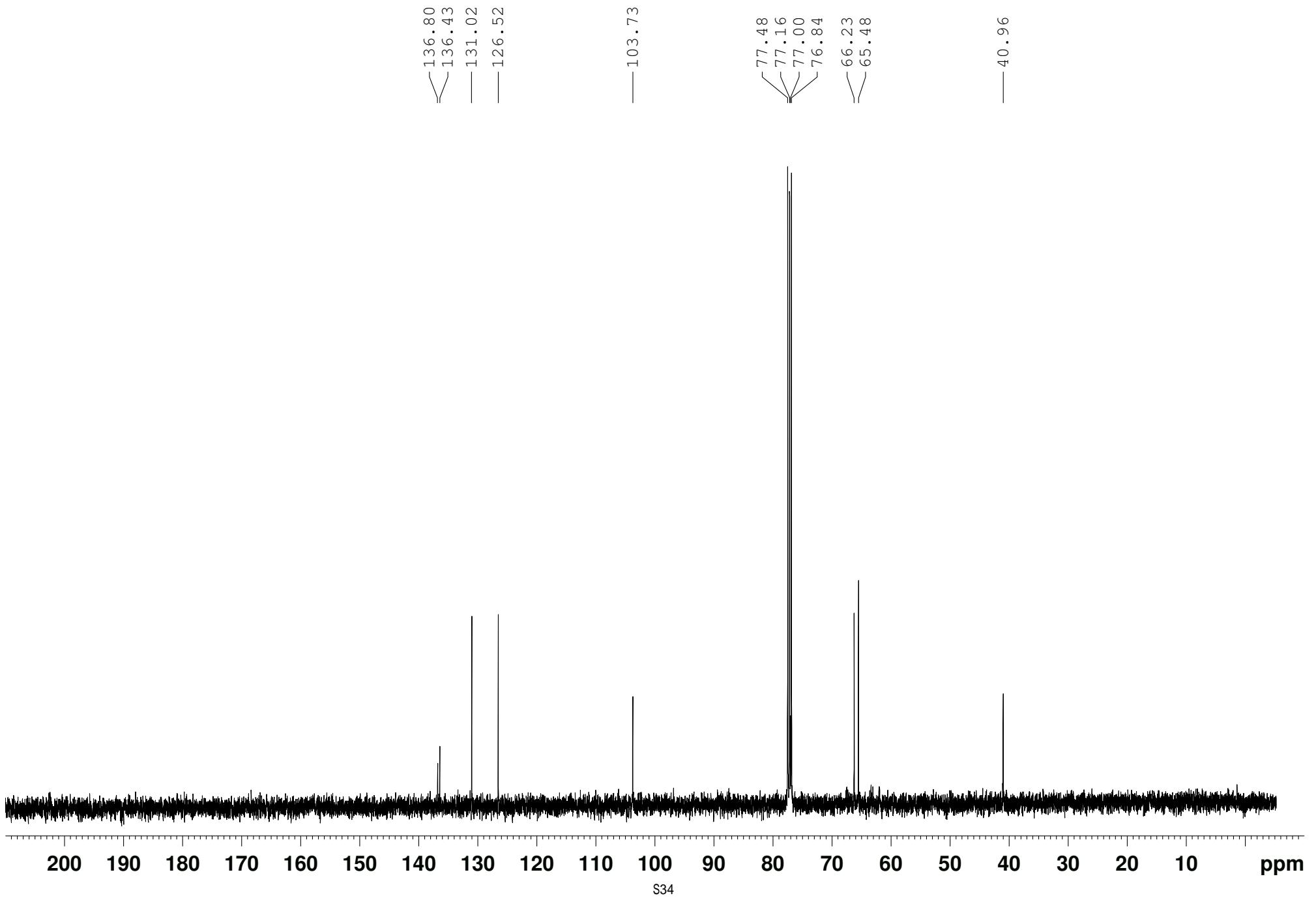
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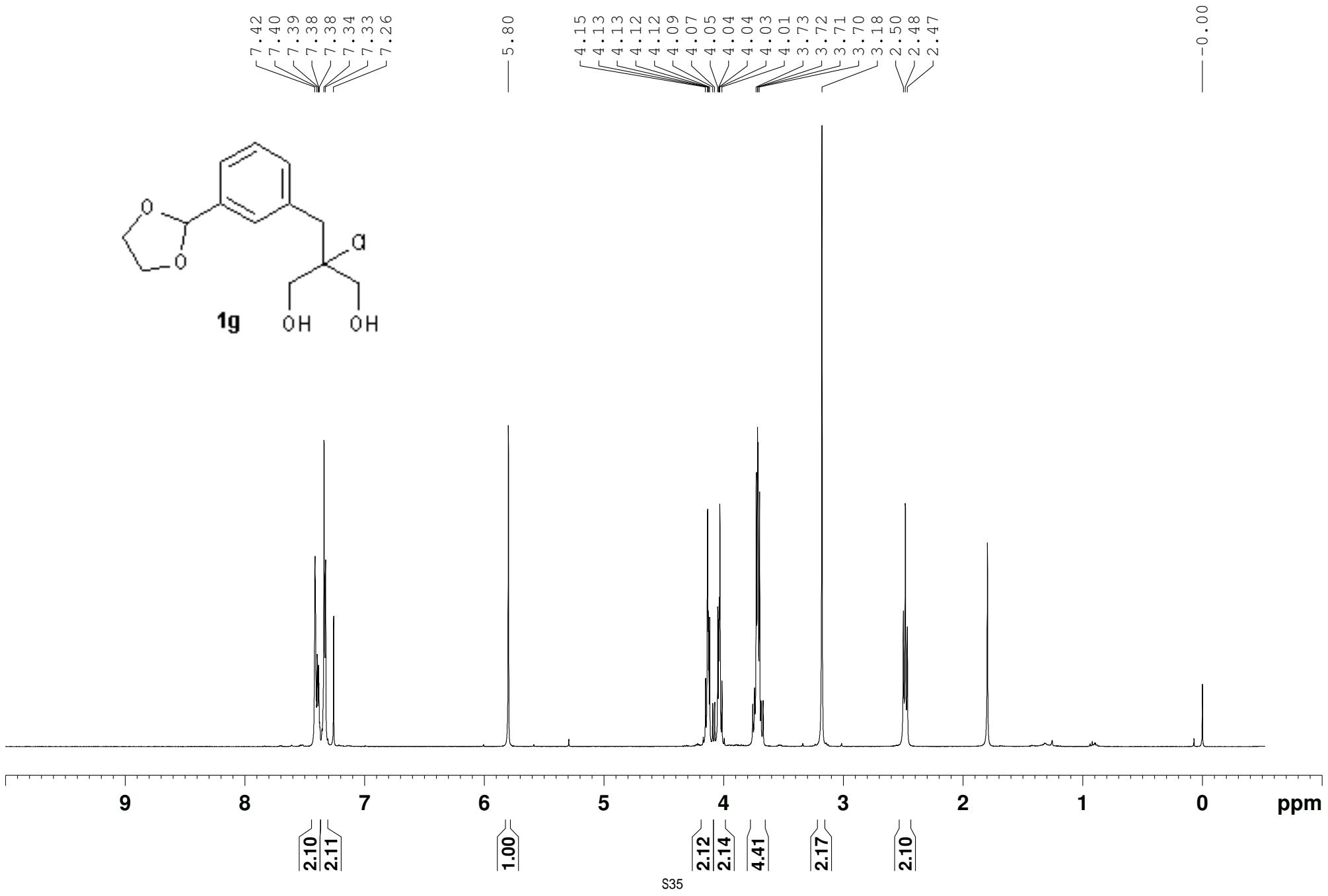
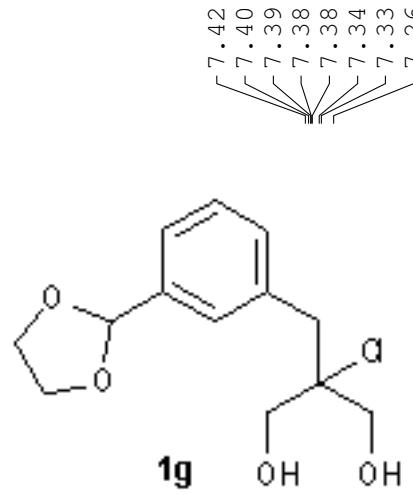


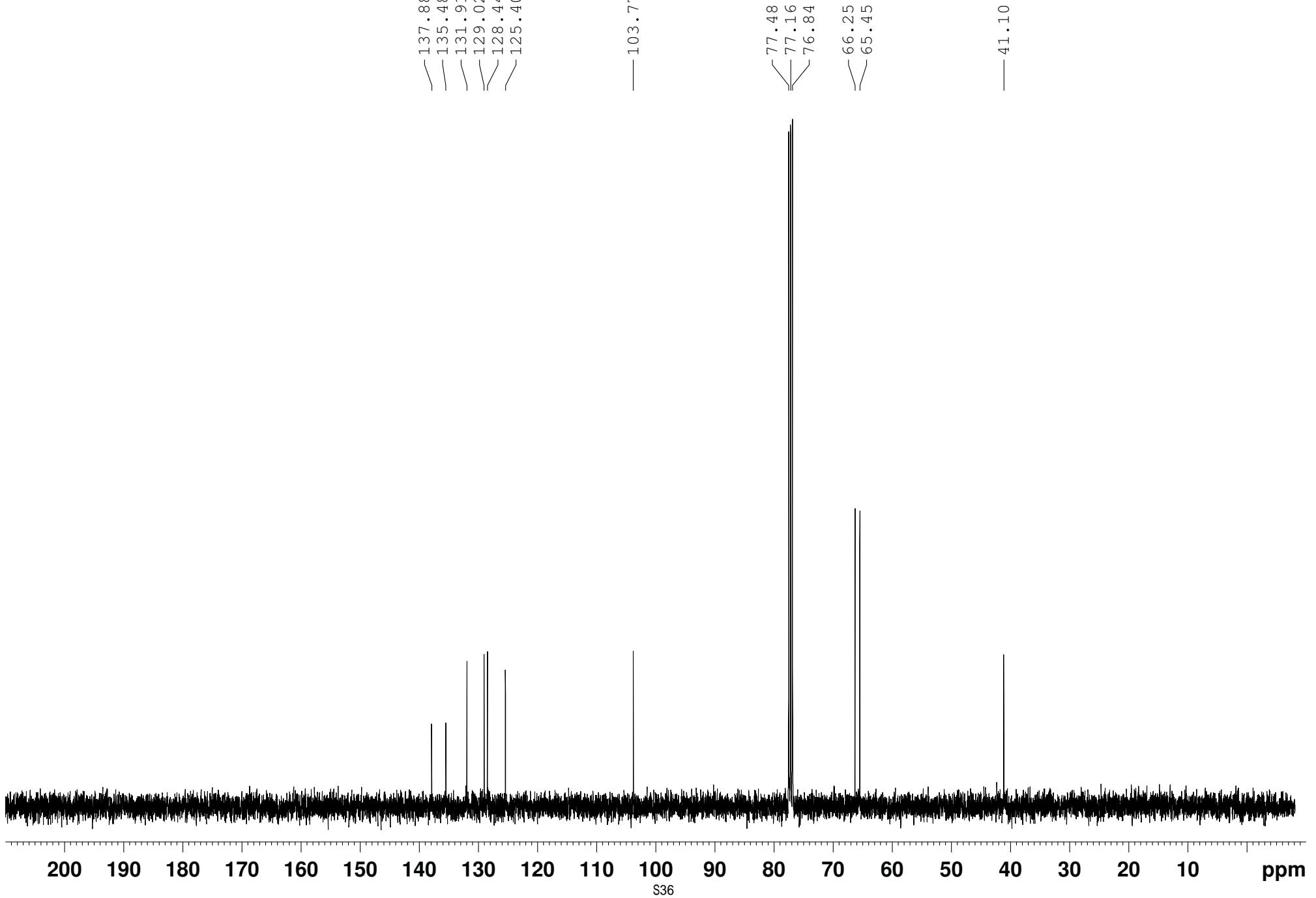






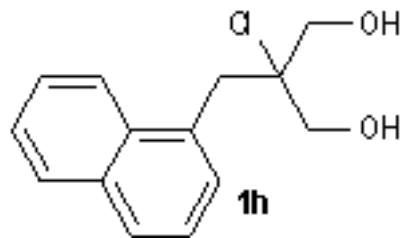






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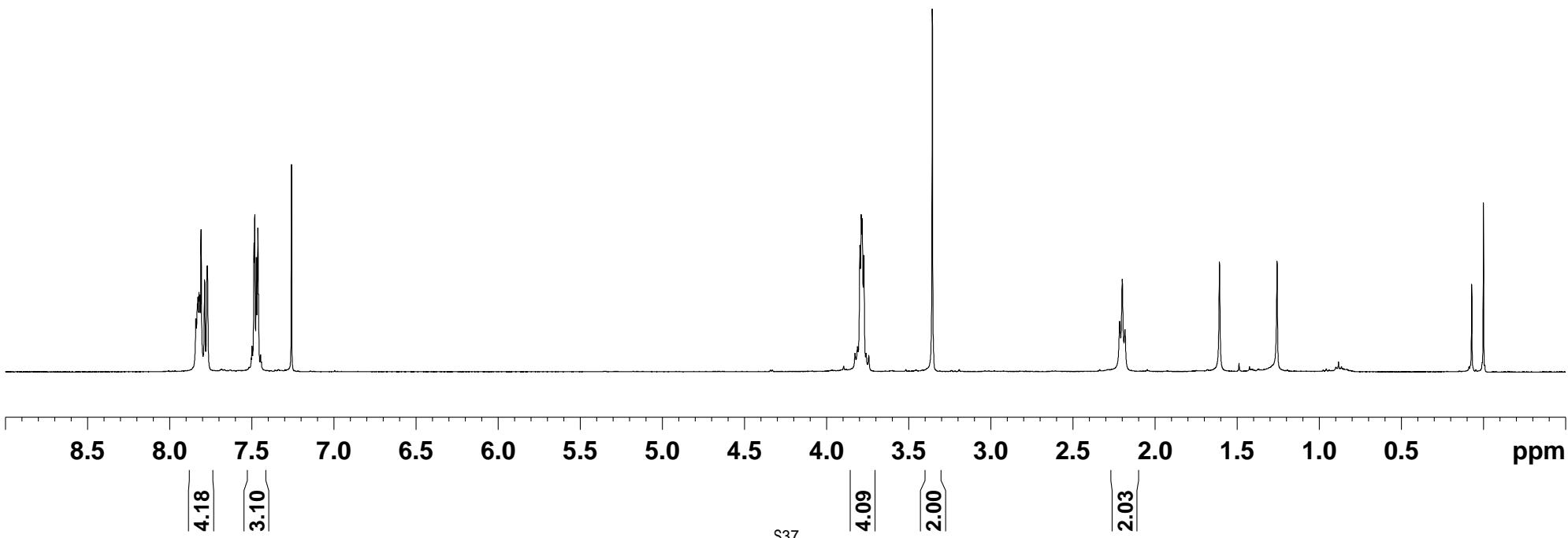
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7.460
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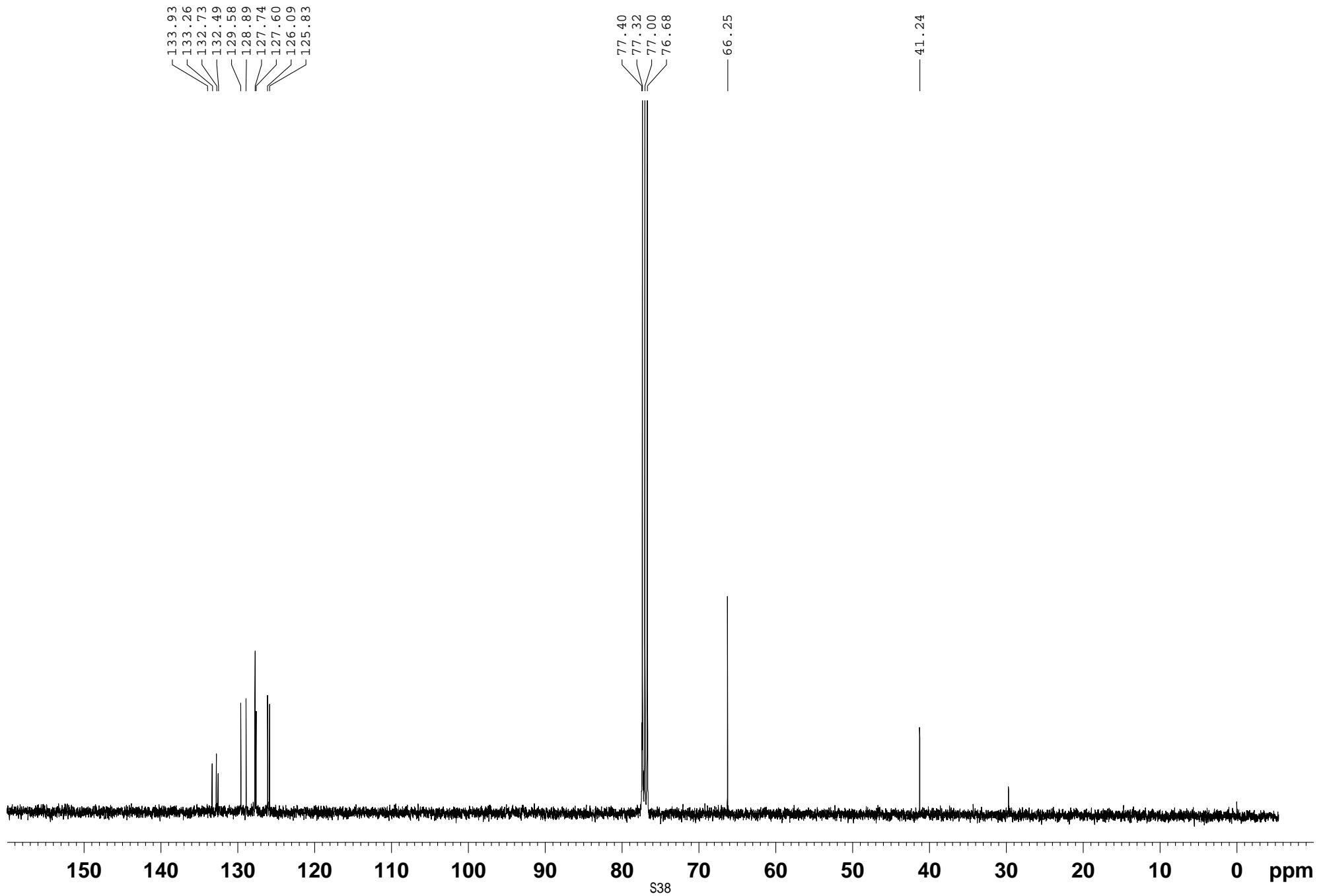
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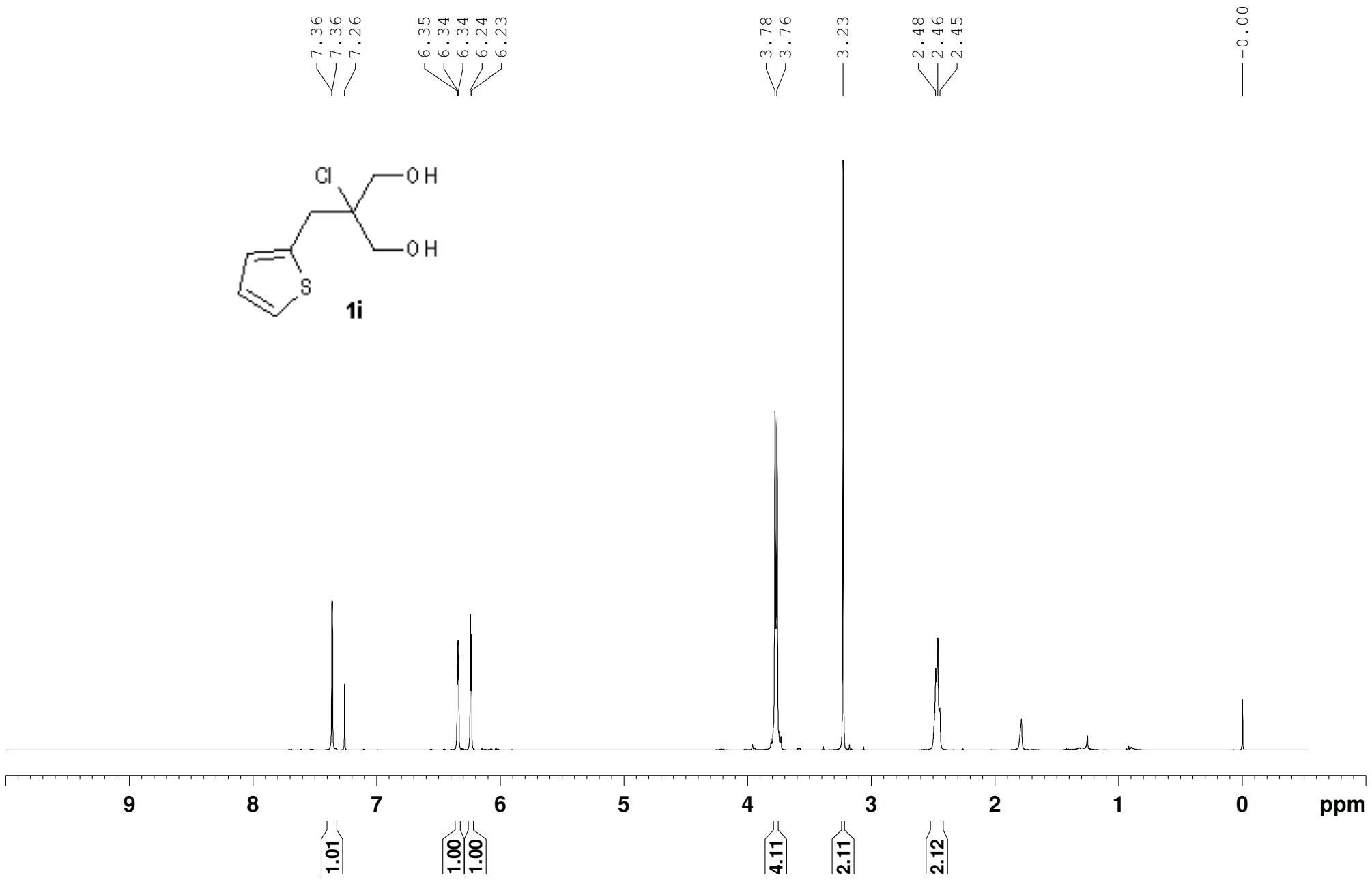
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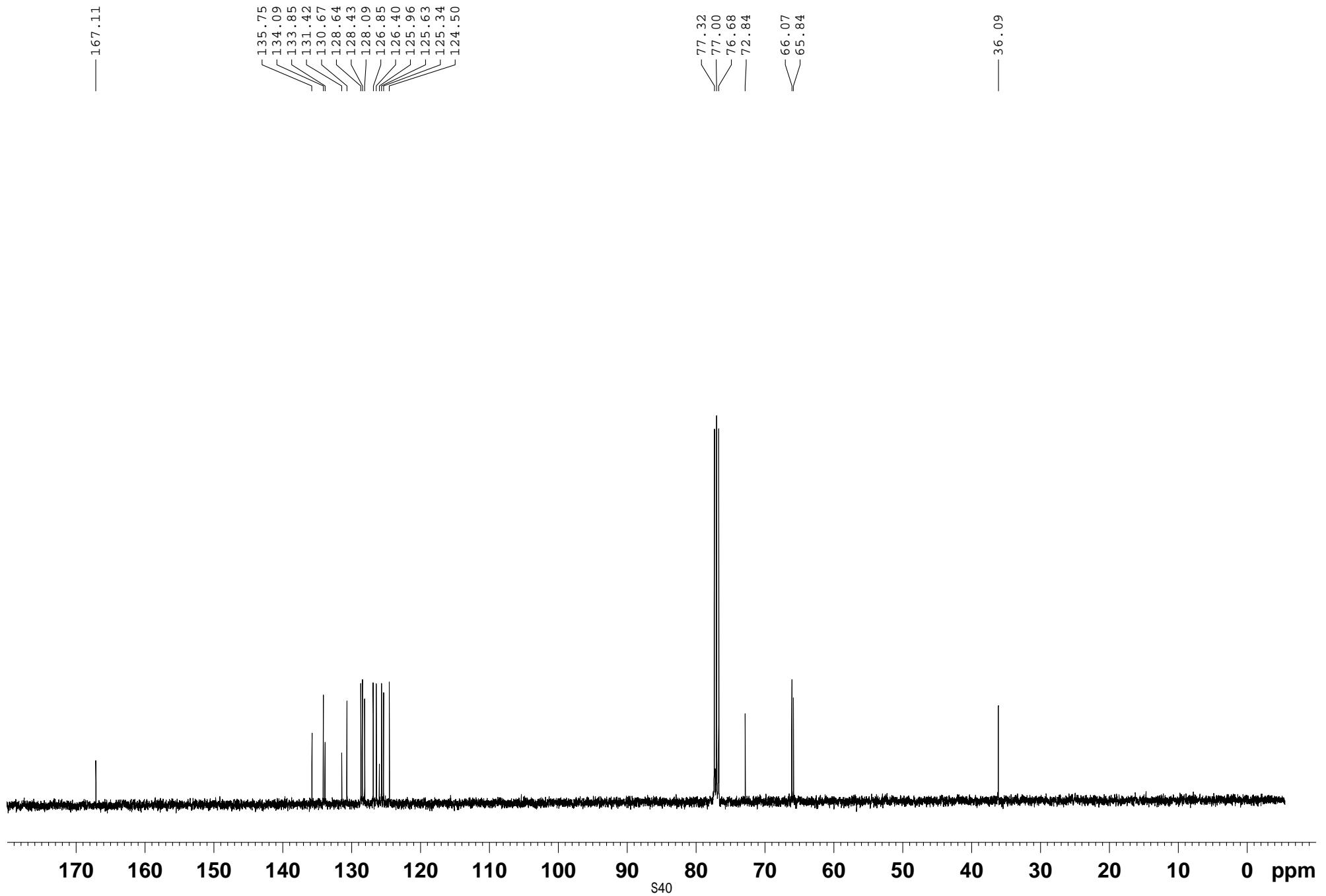


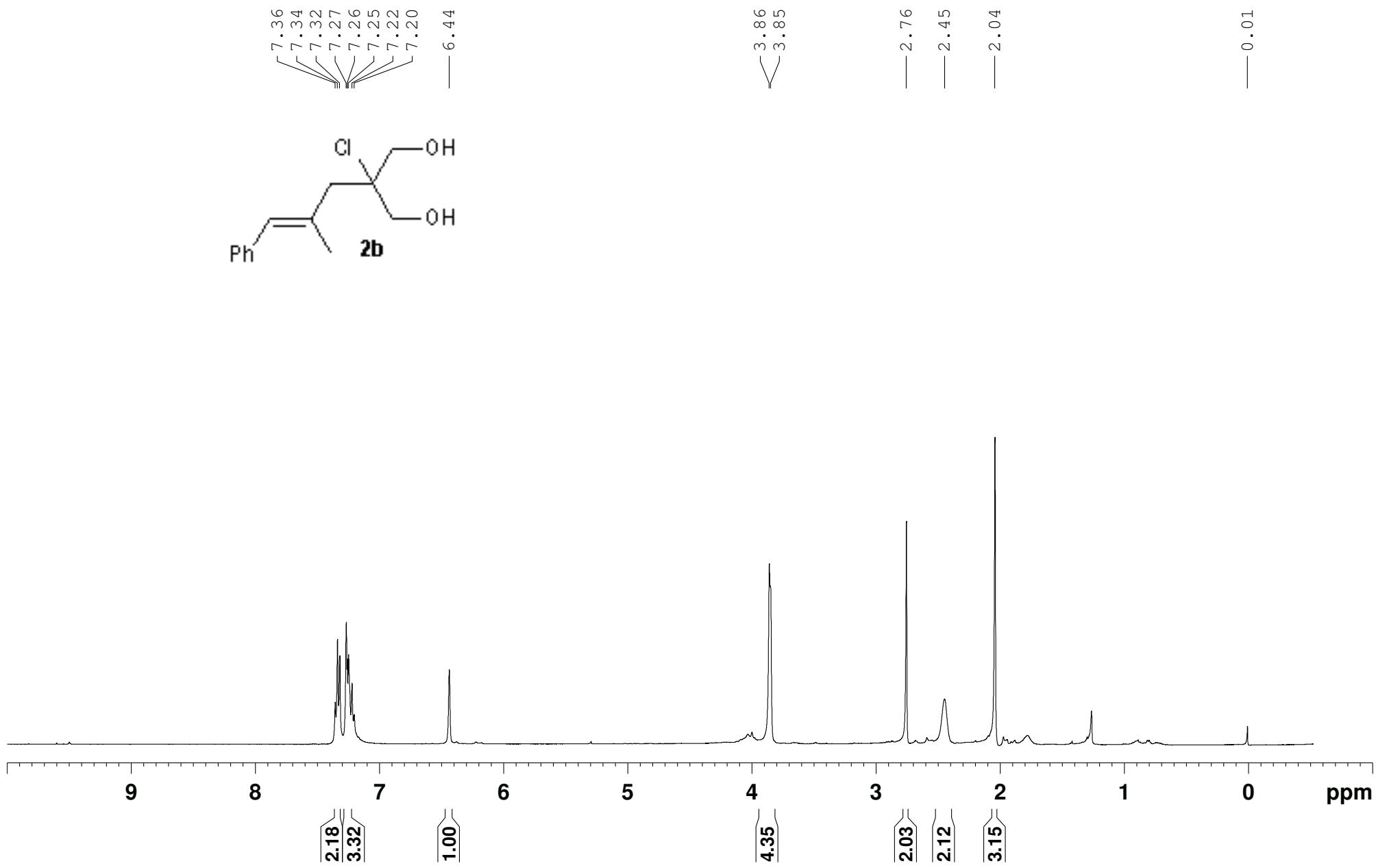
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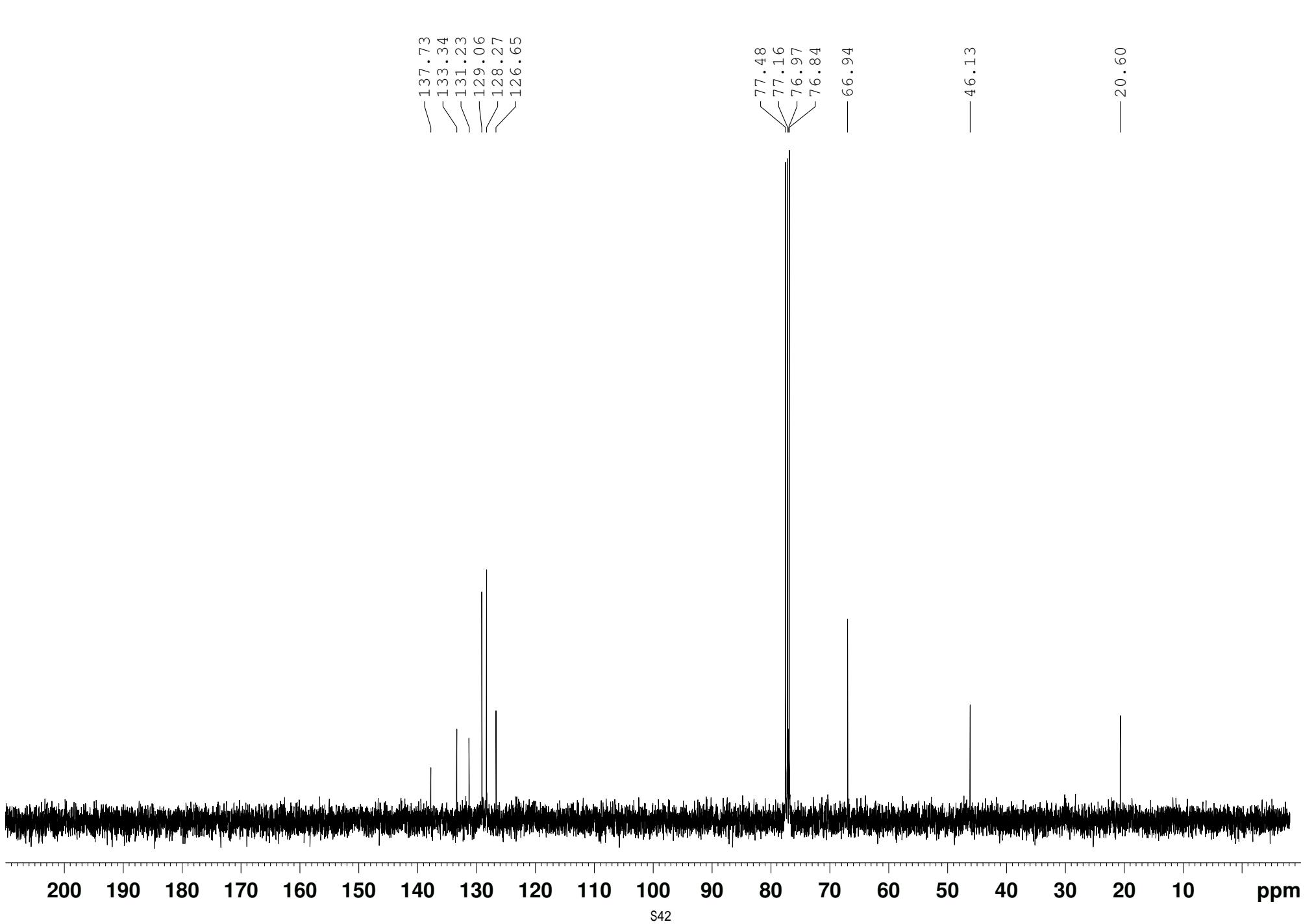


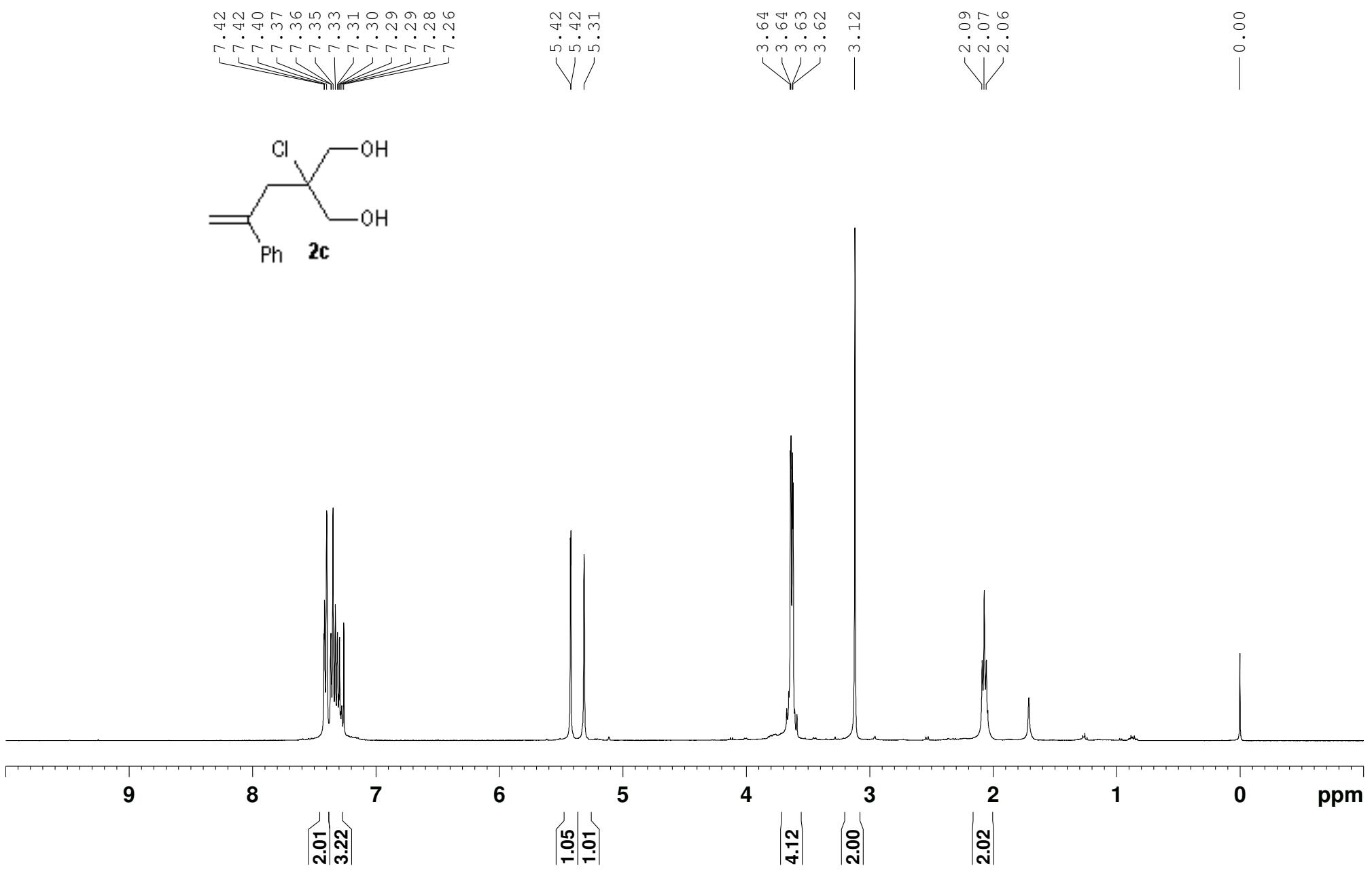


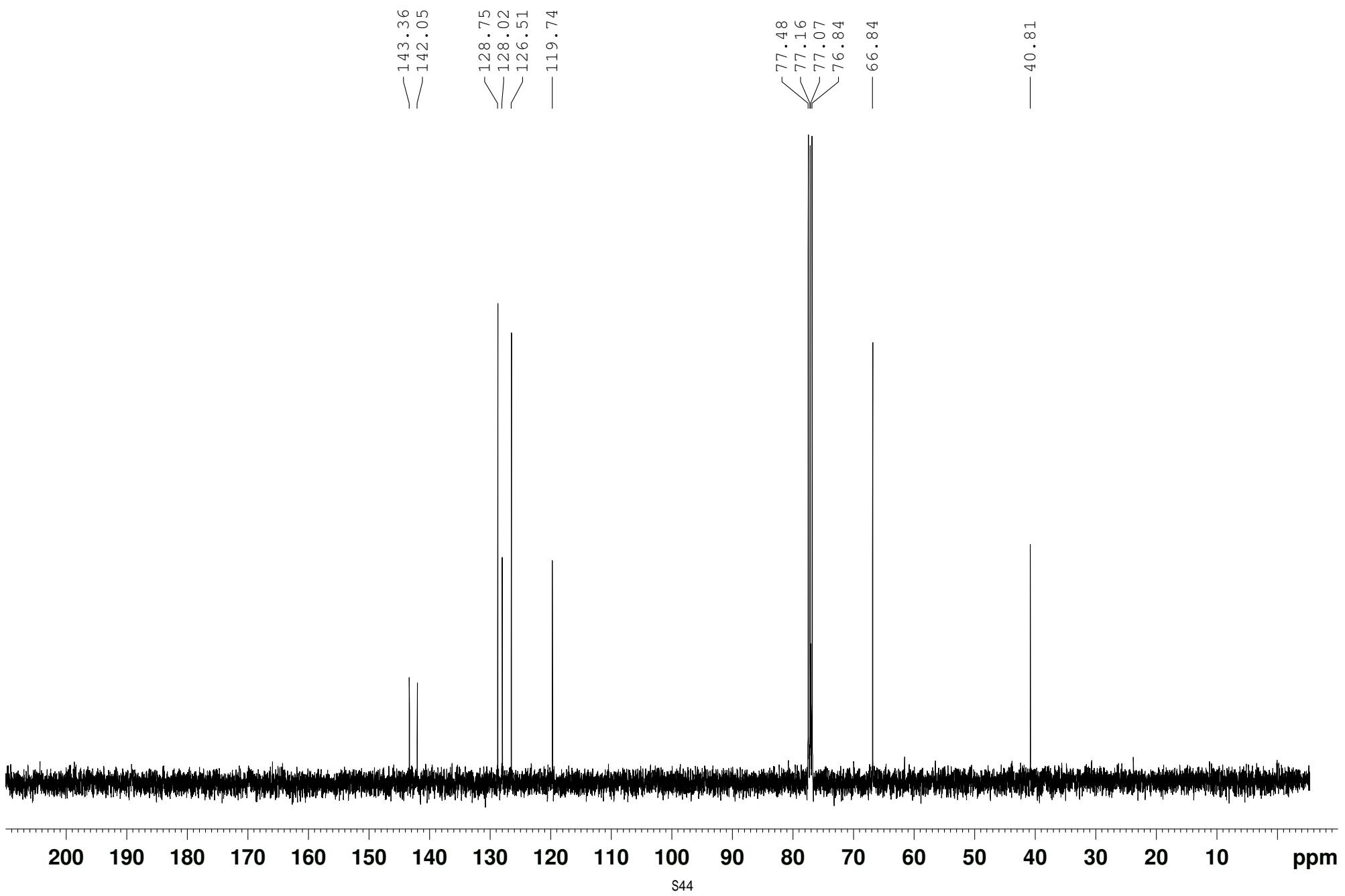
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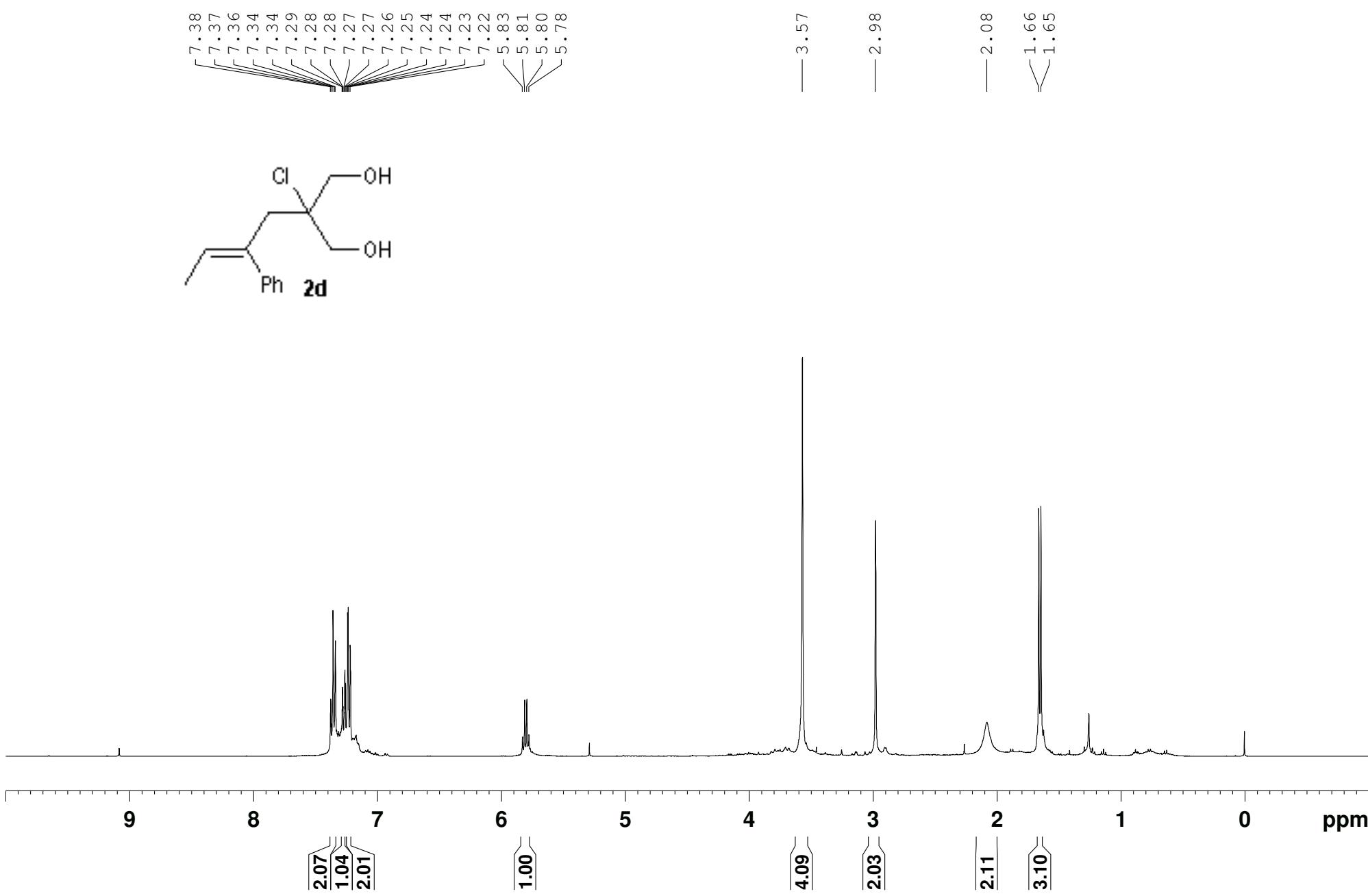


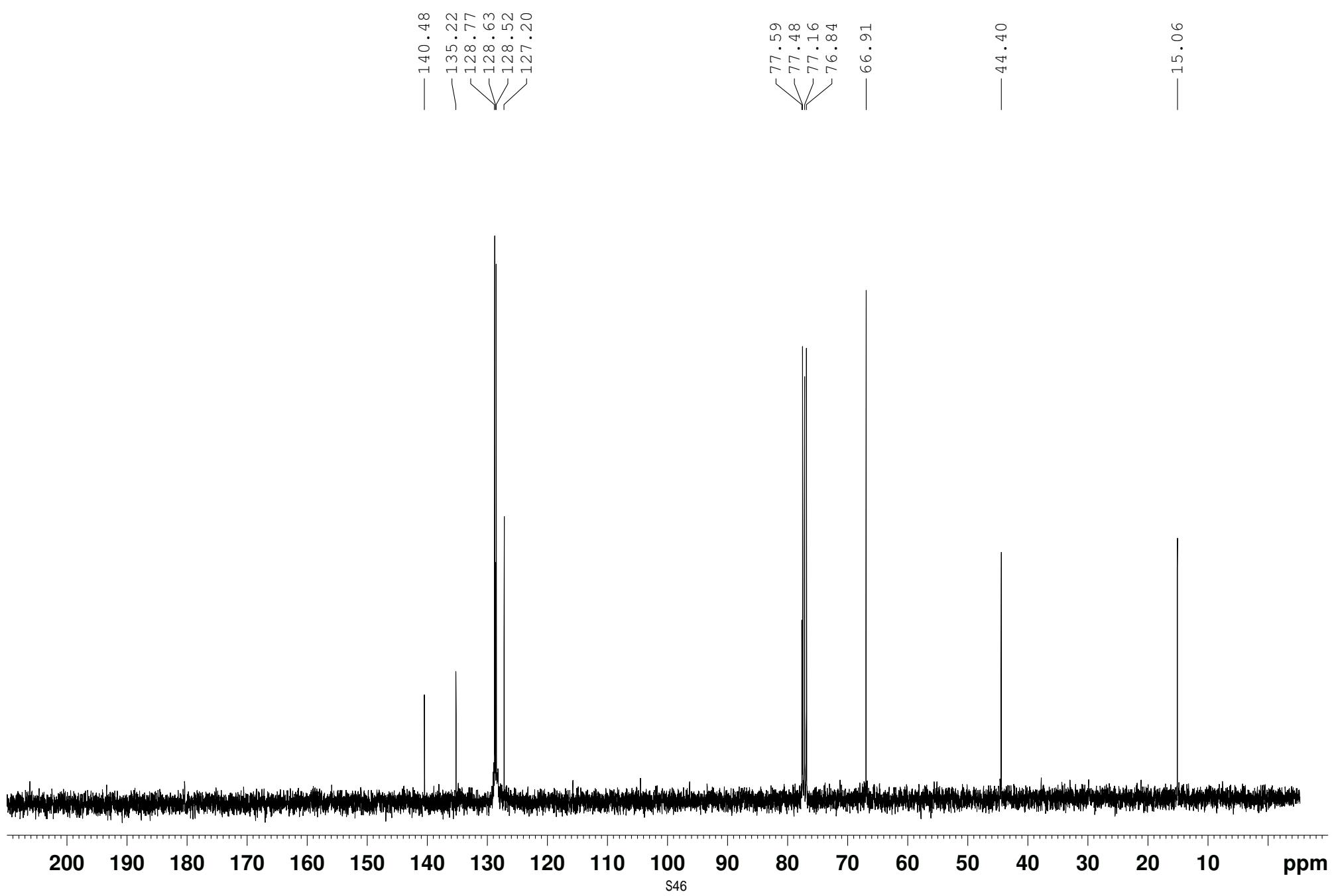


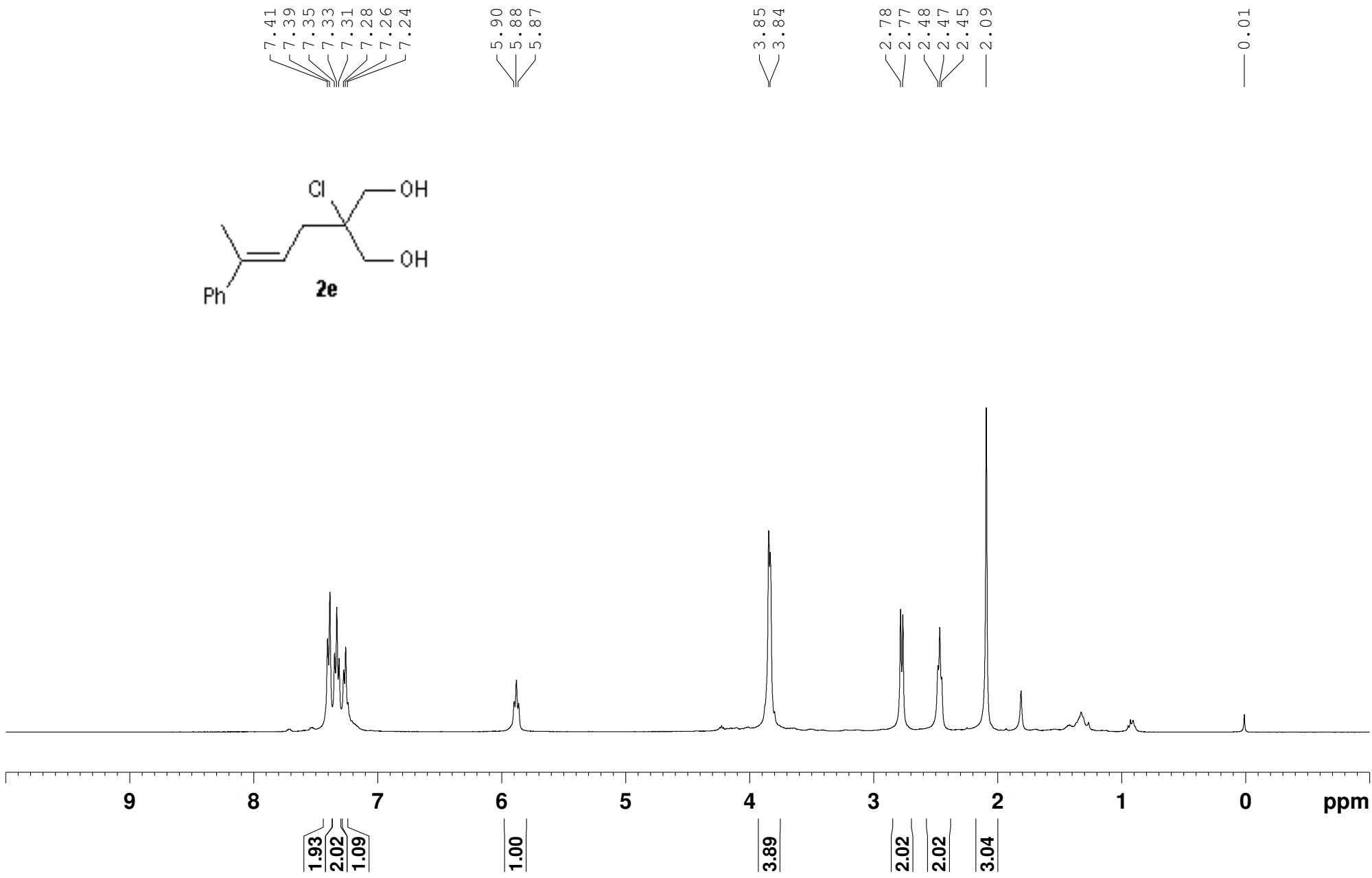
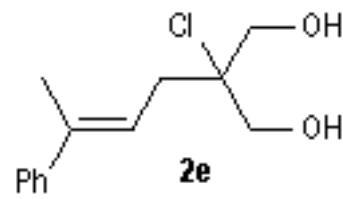
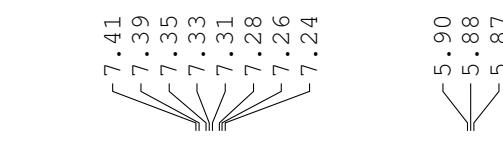


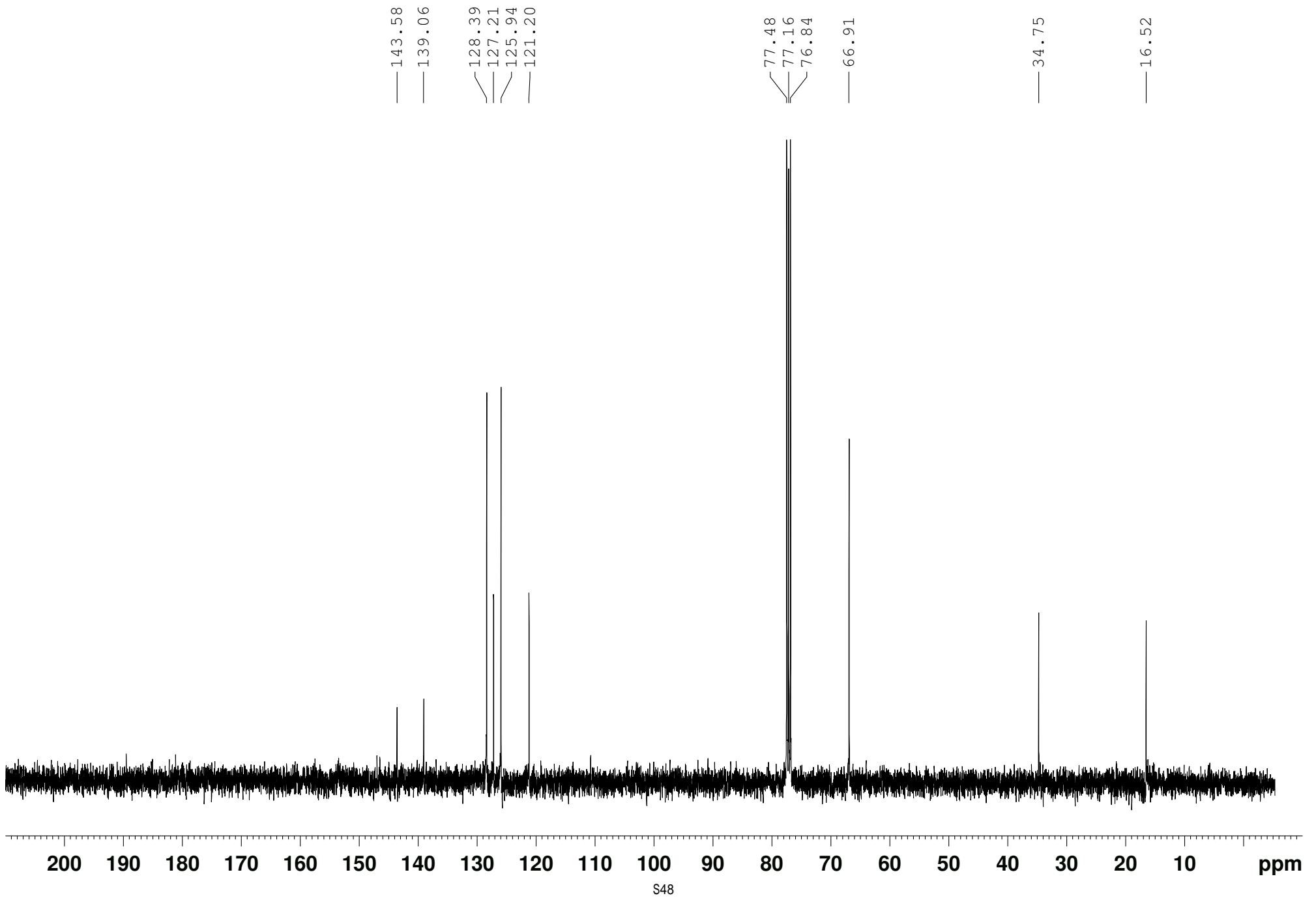


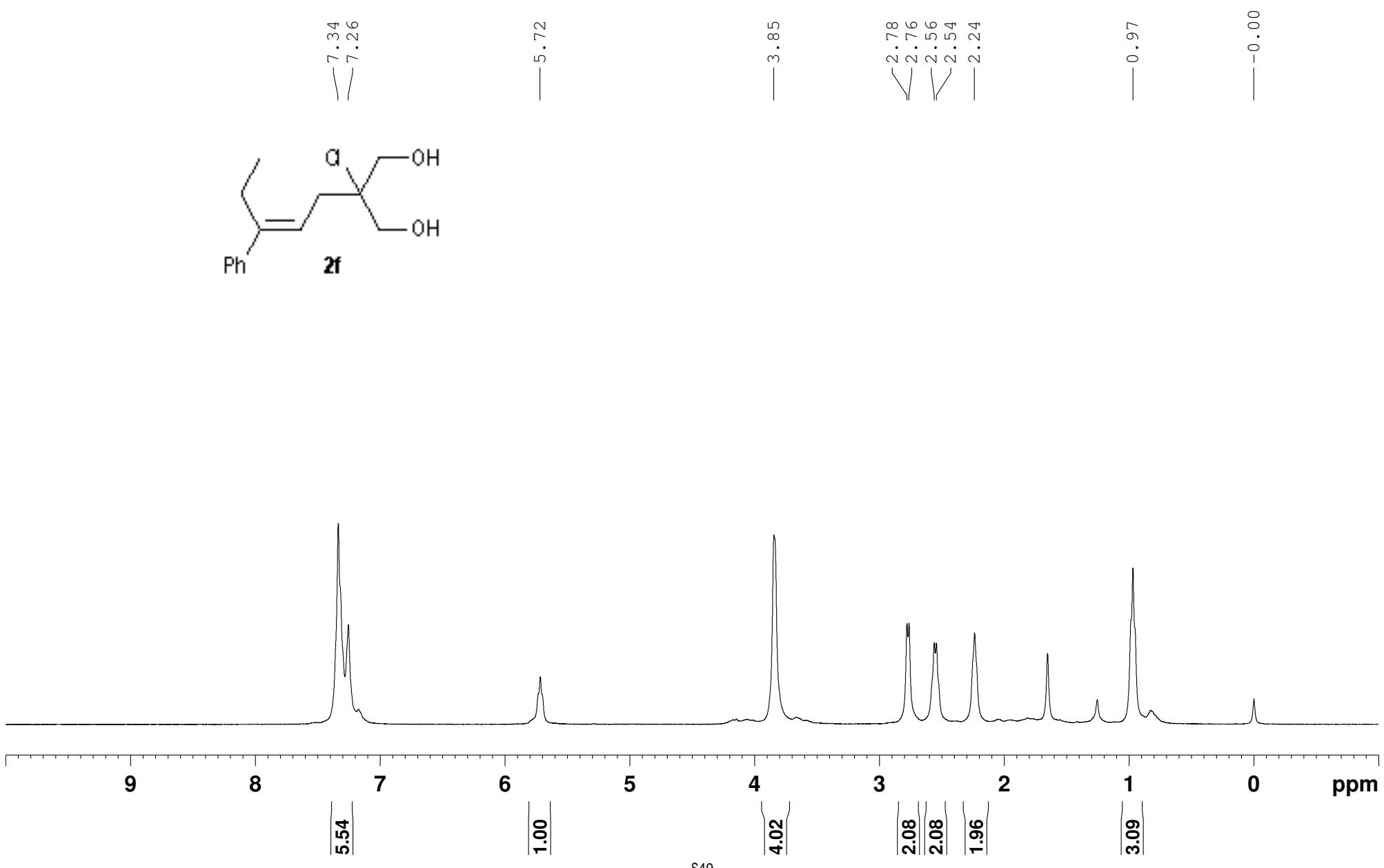


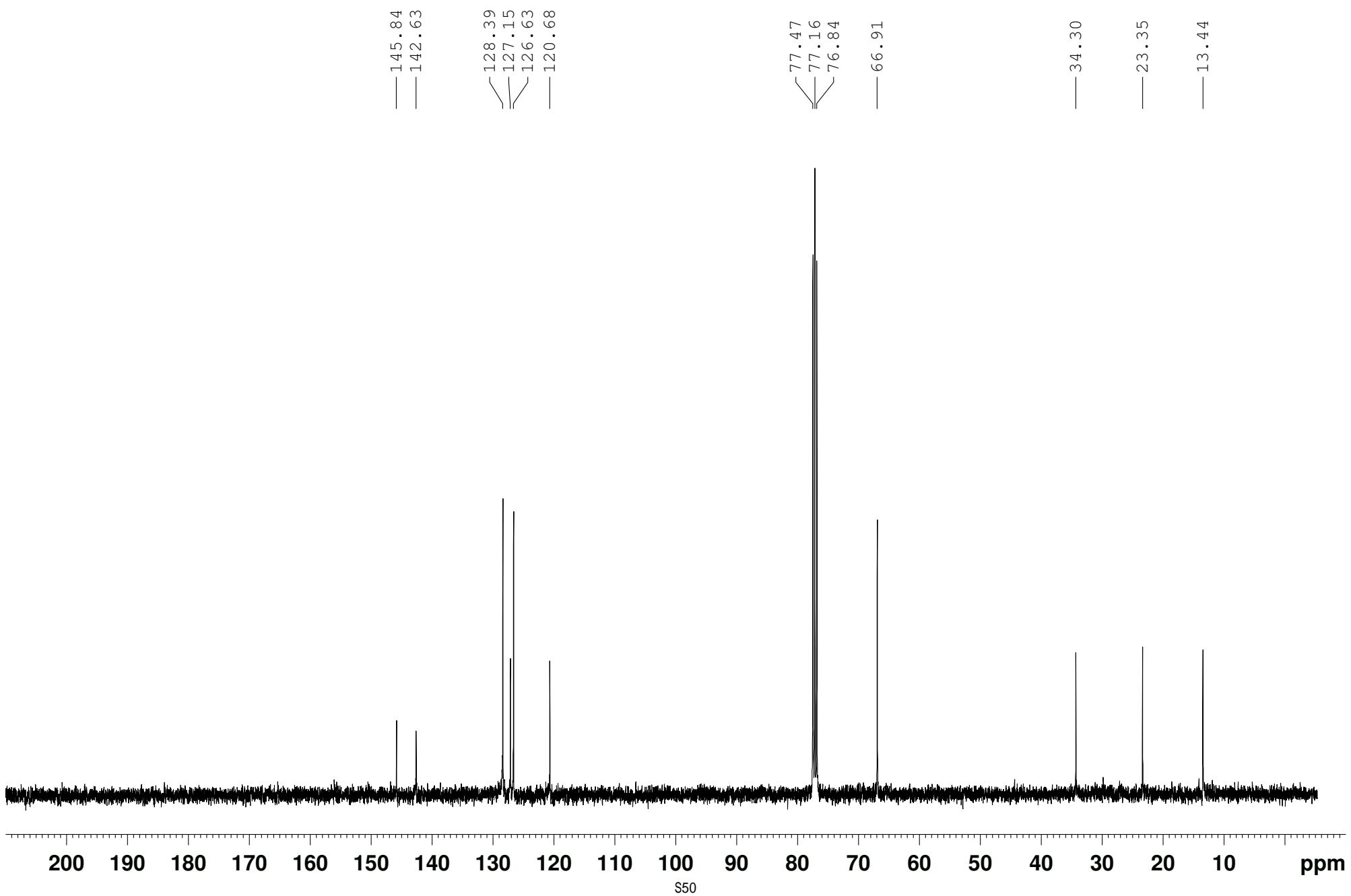


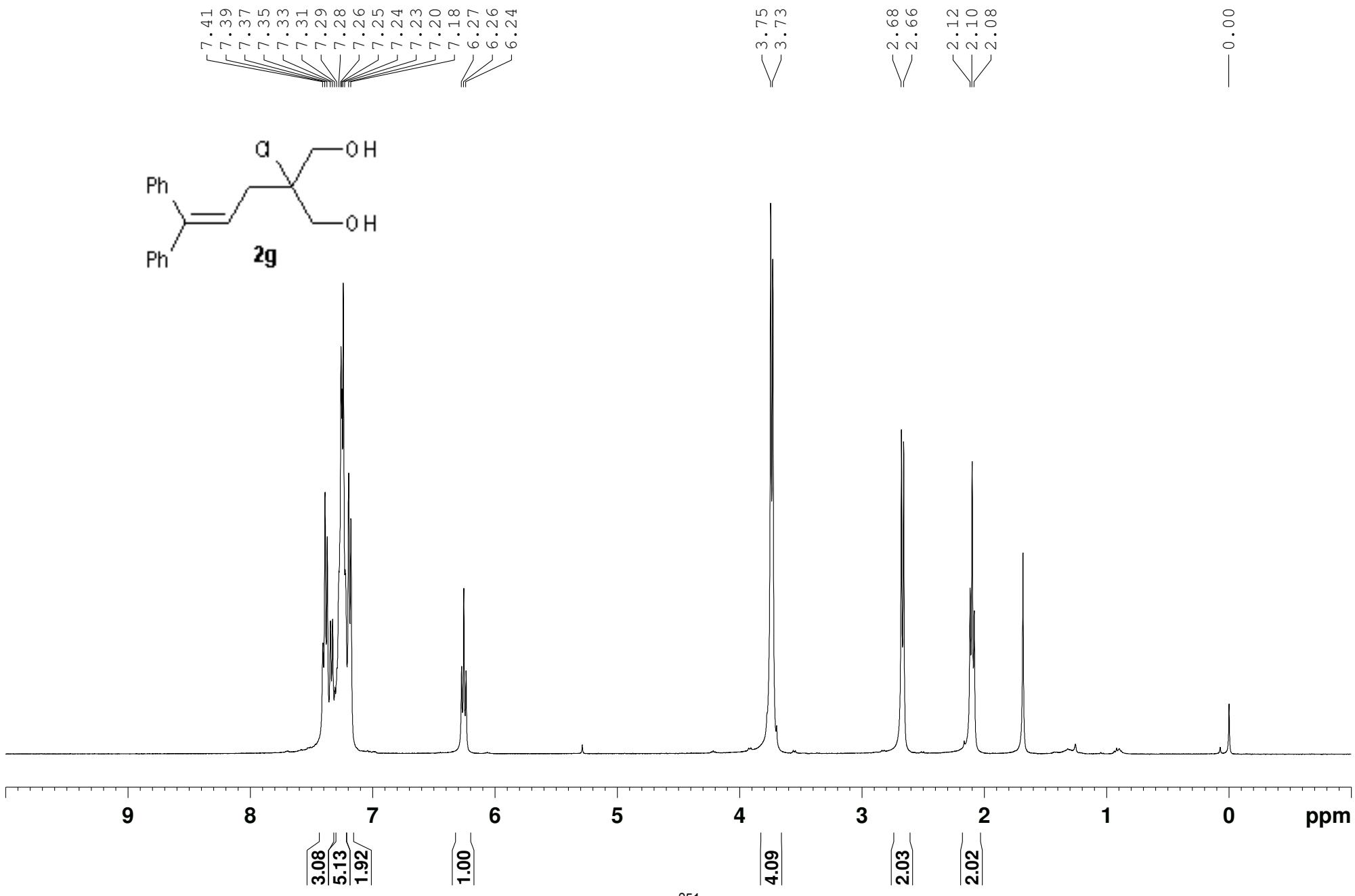


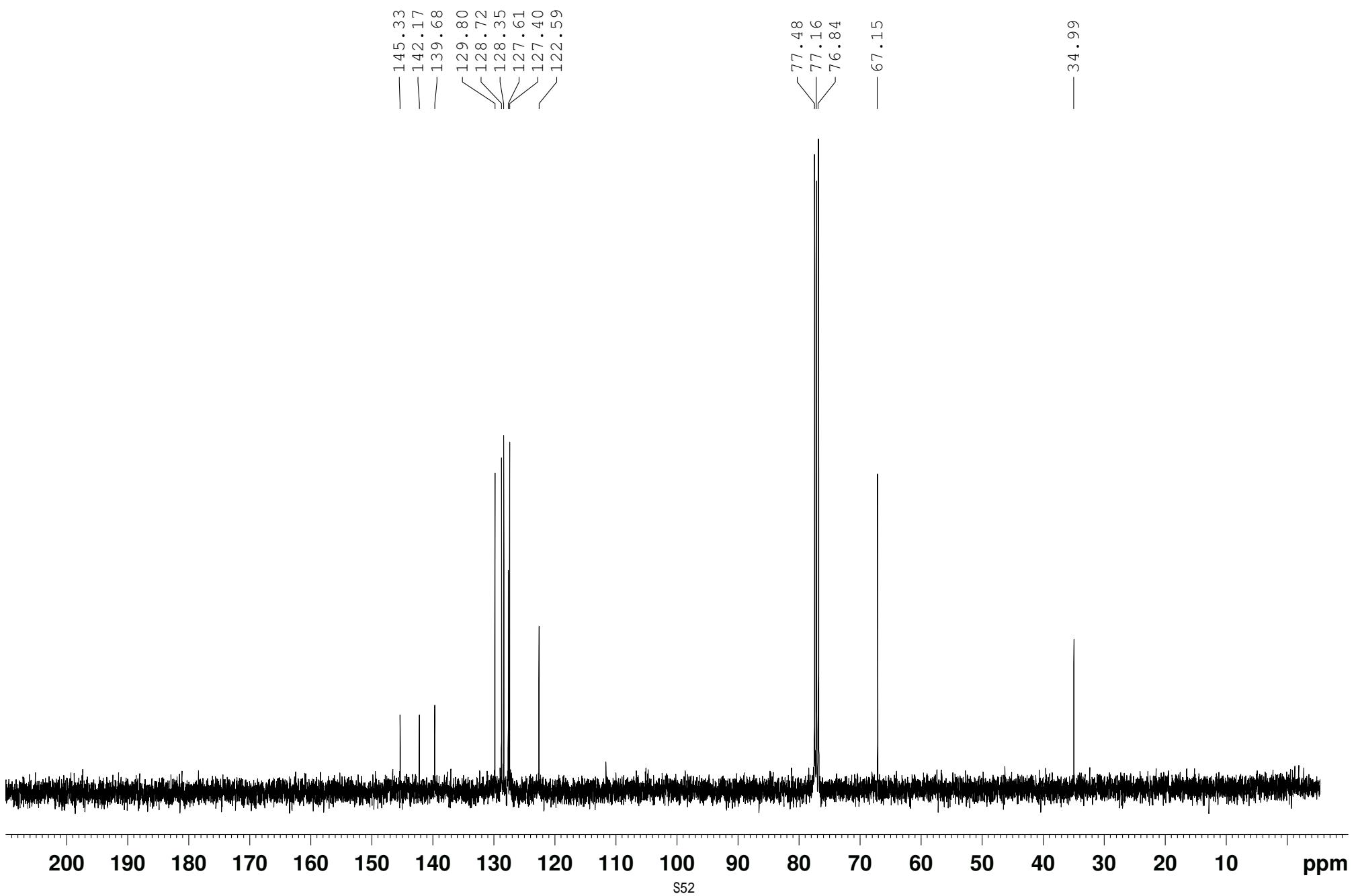


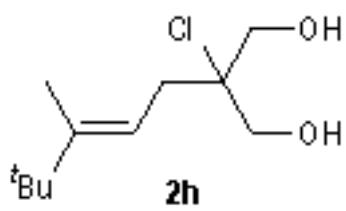












— 7.26

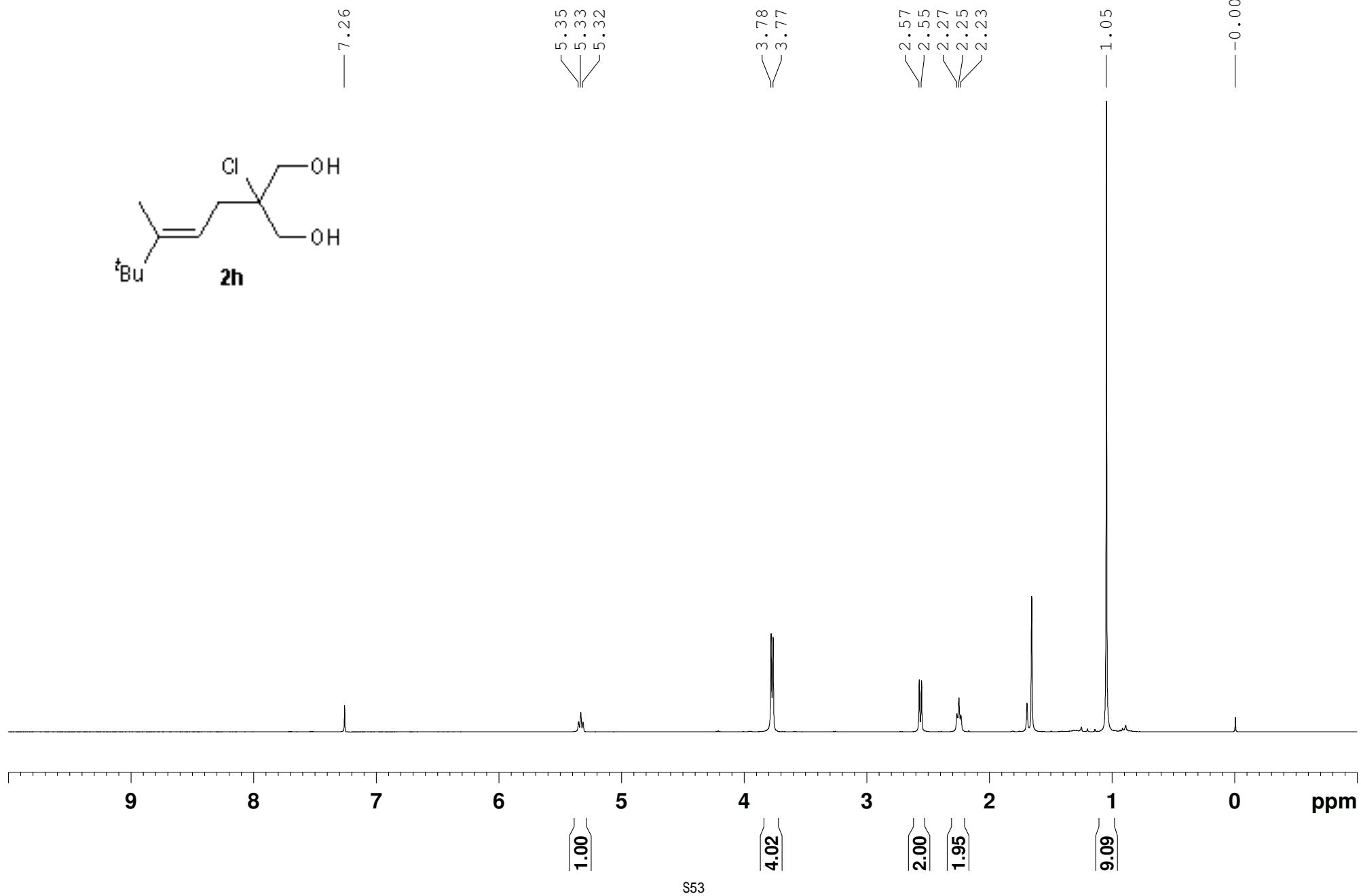
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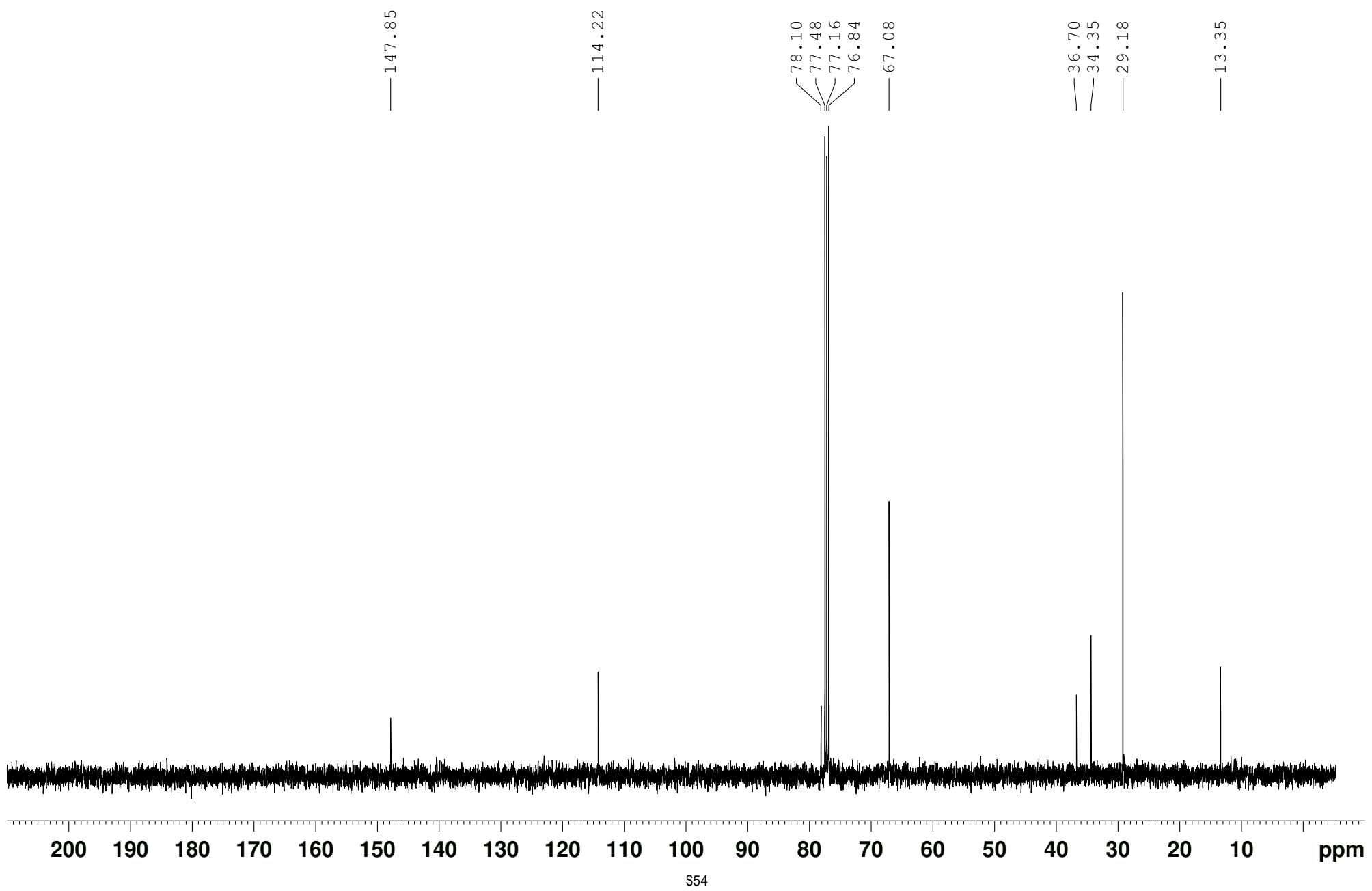
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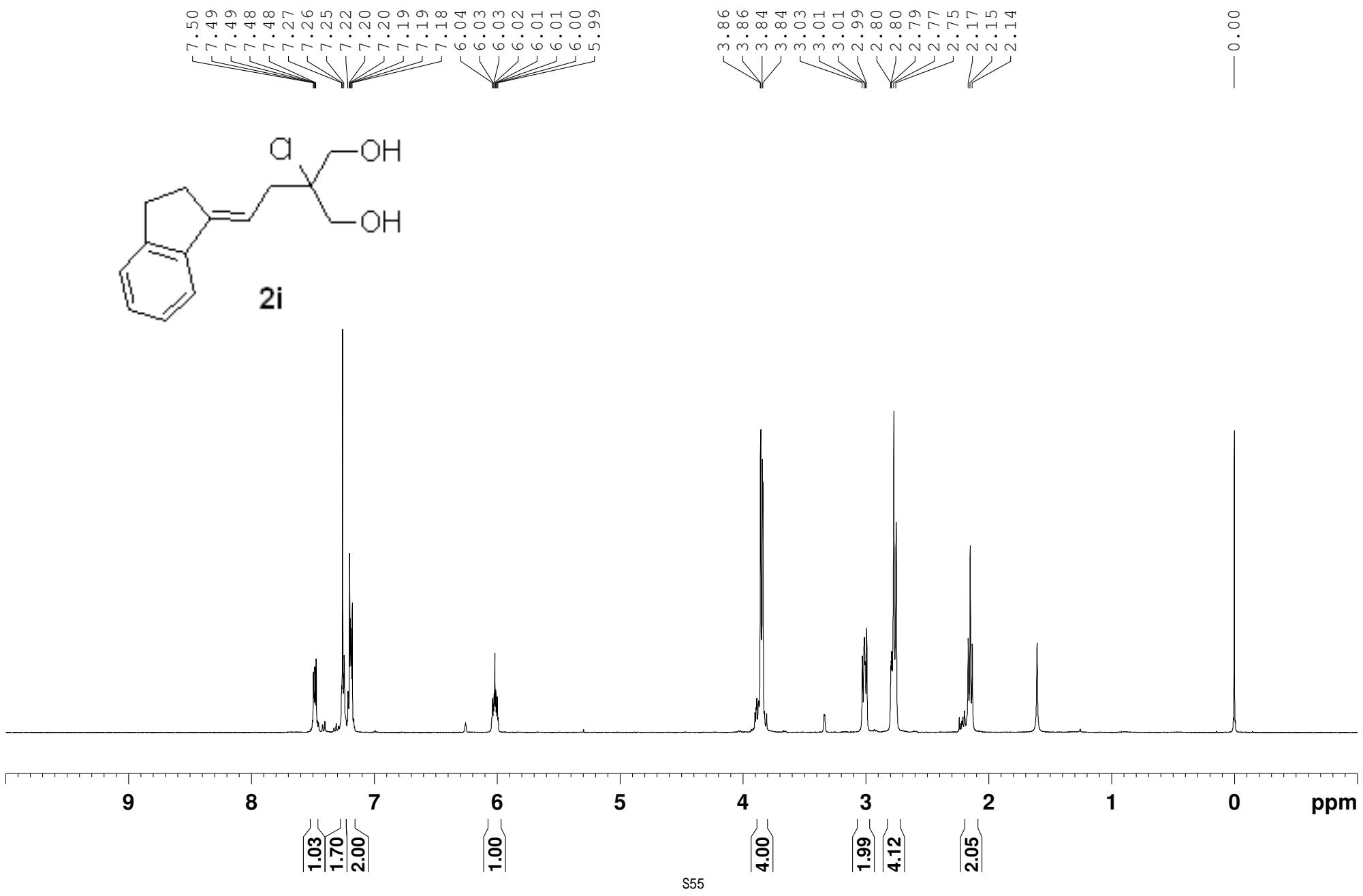
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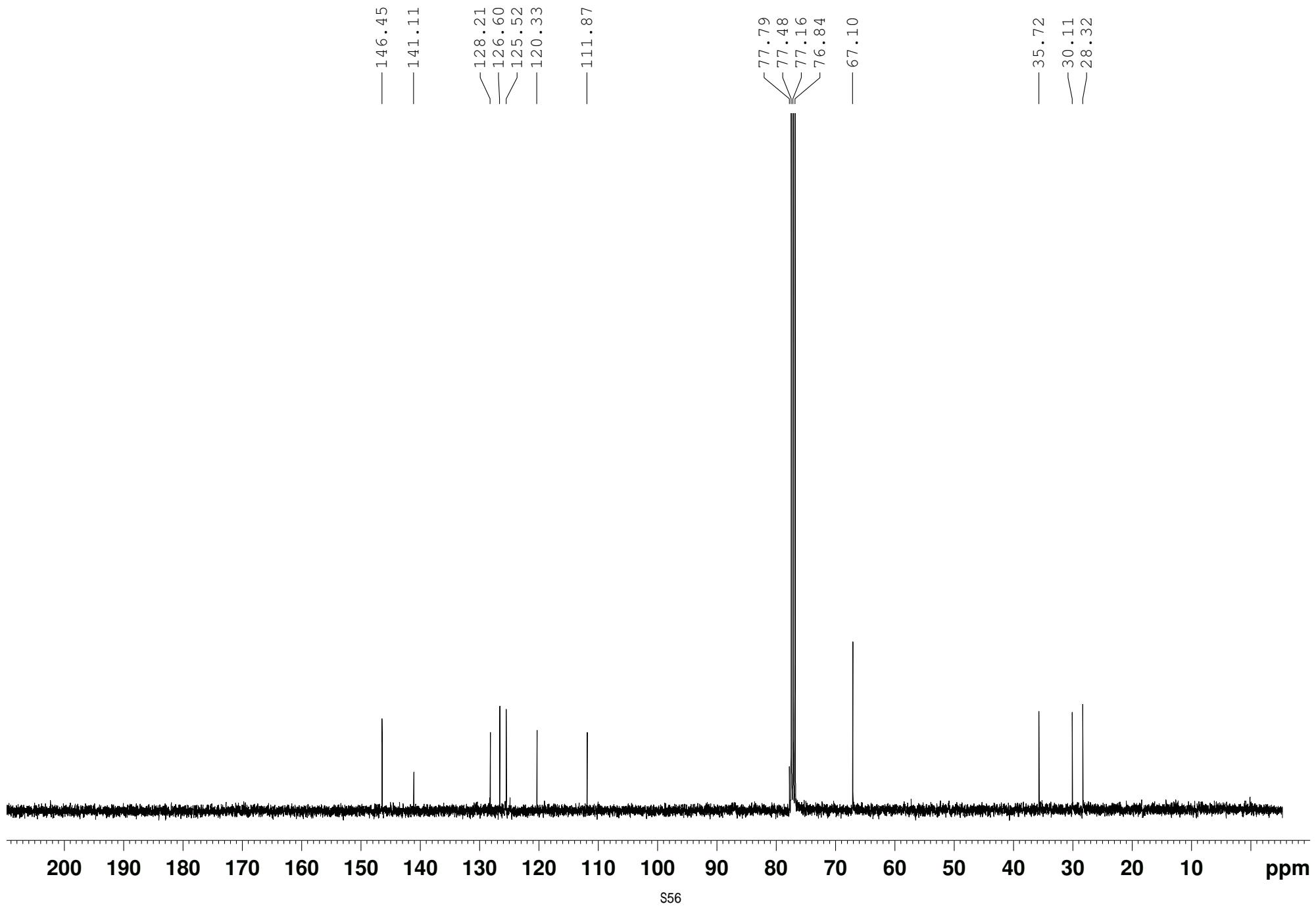
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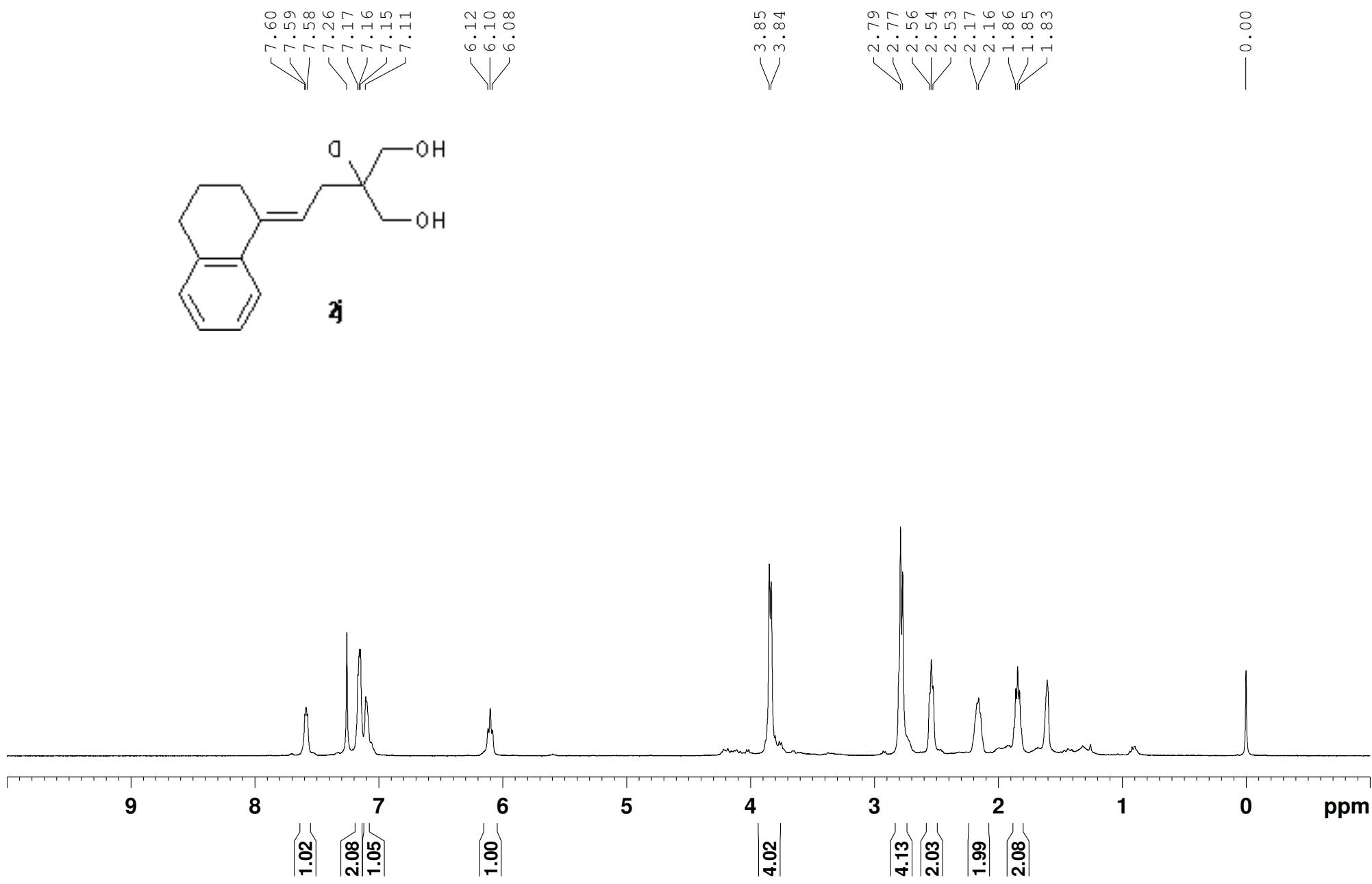
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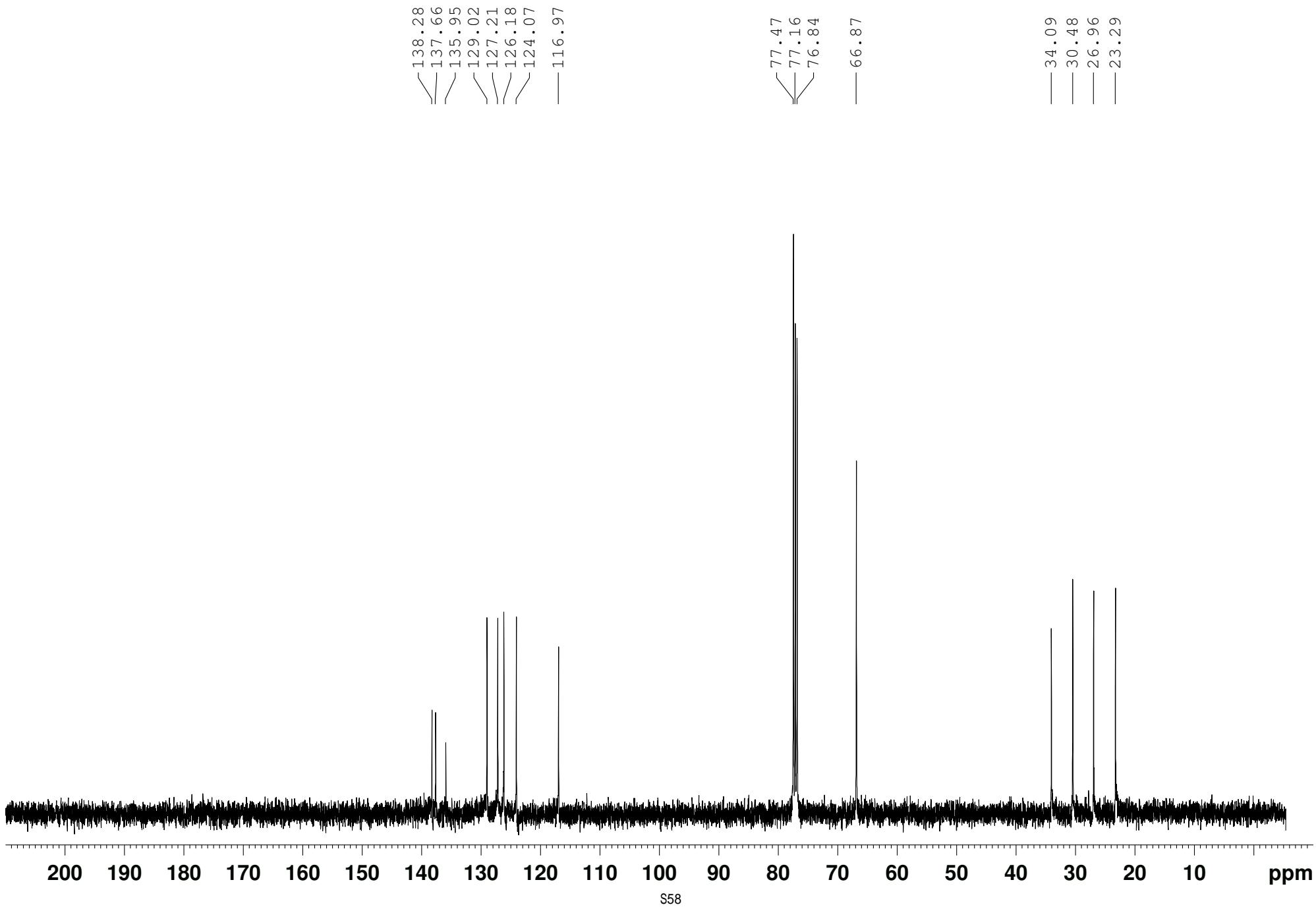


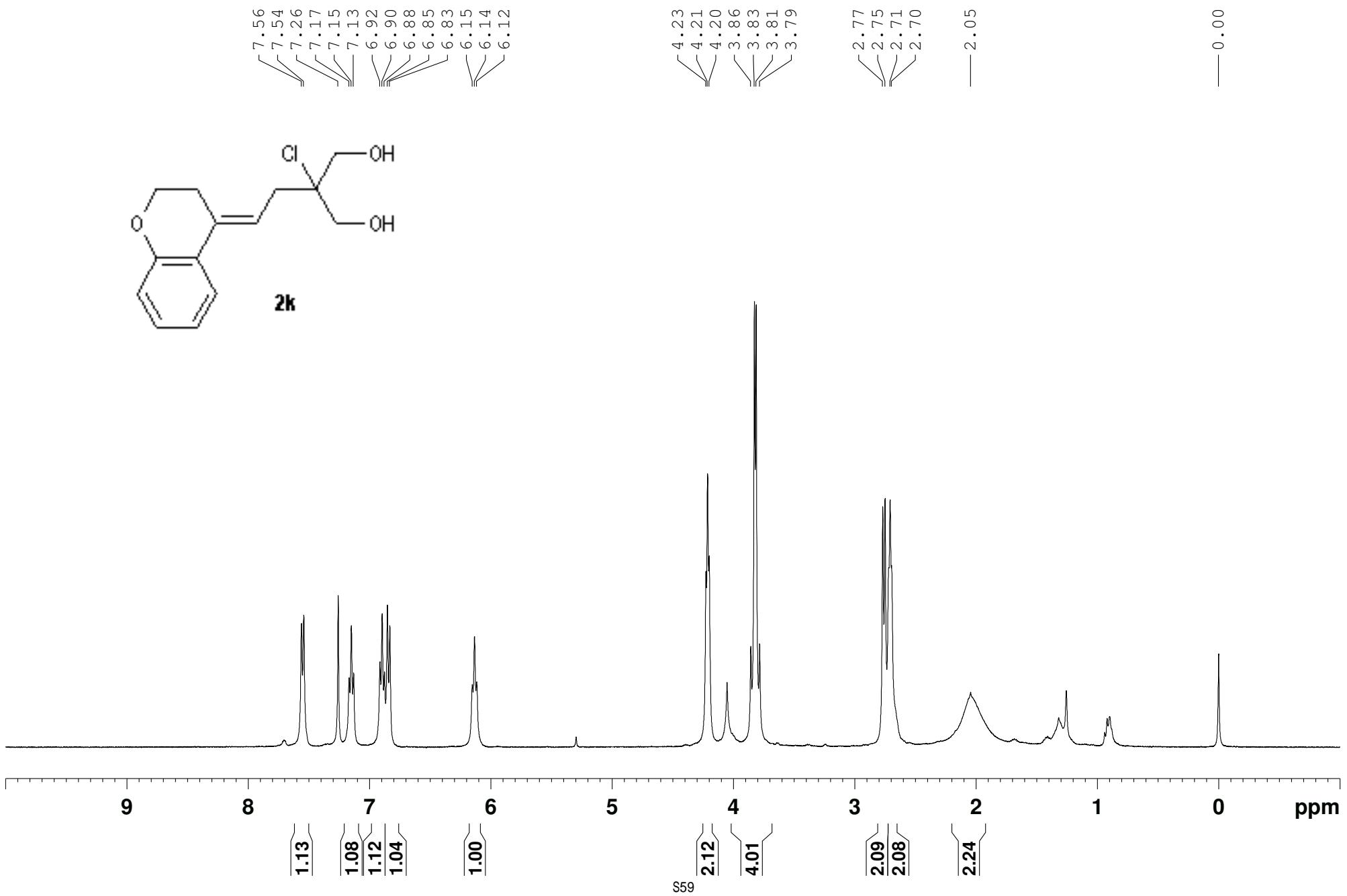
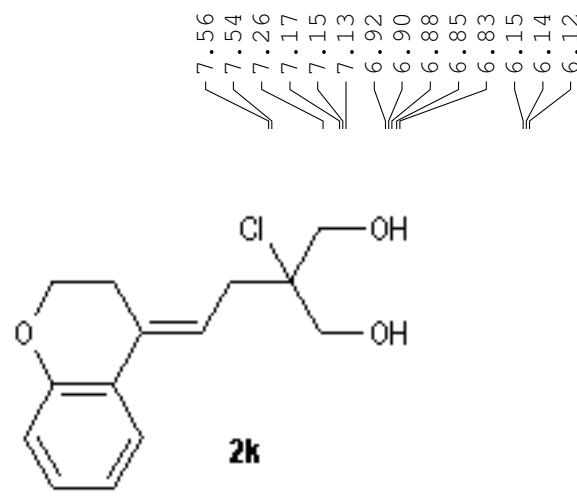


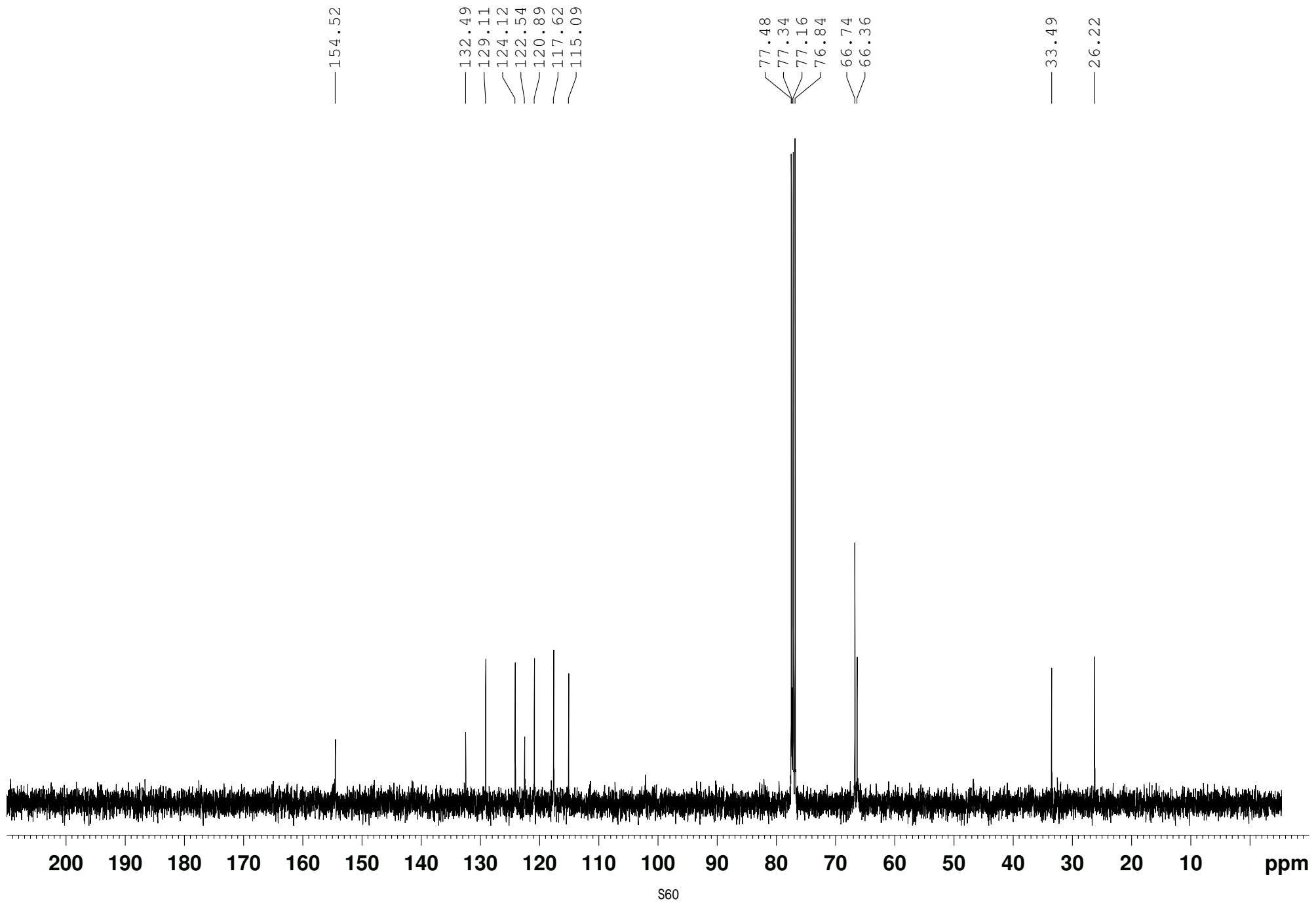


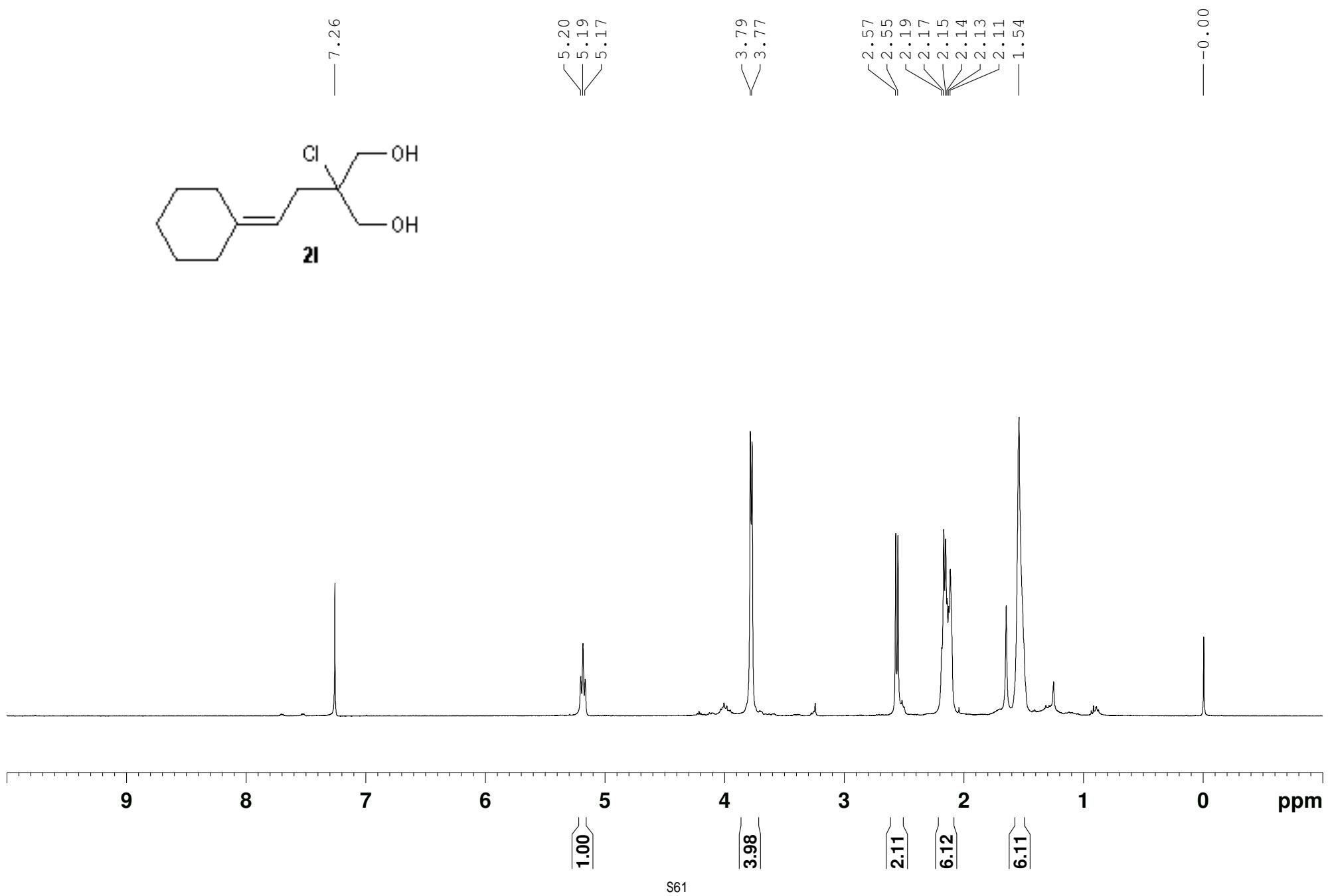


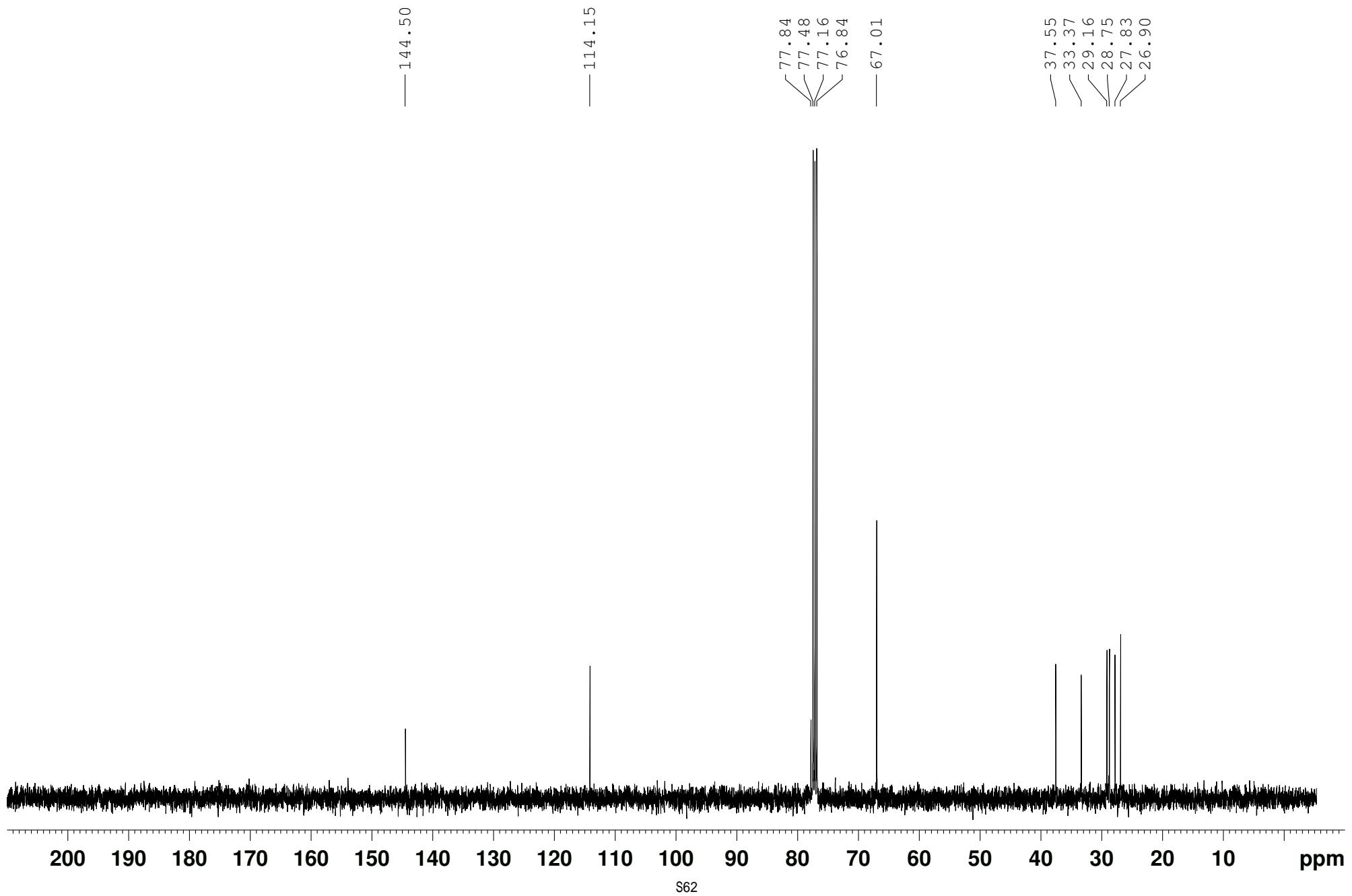


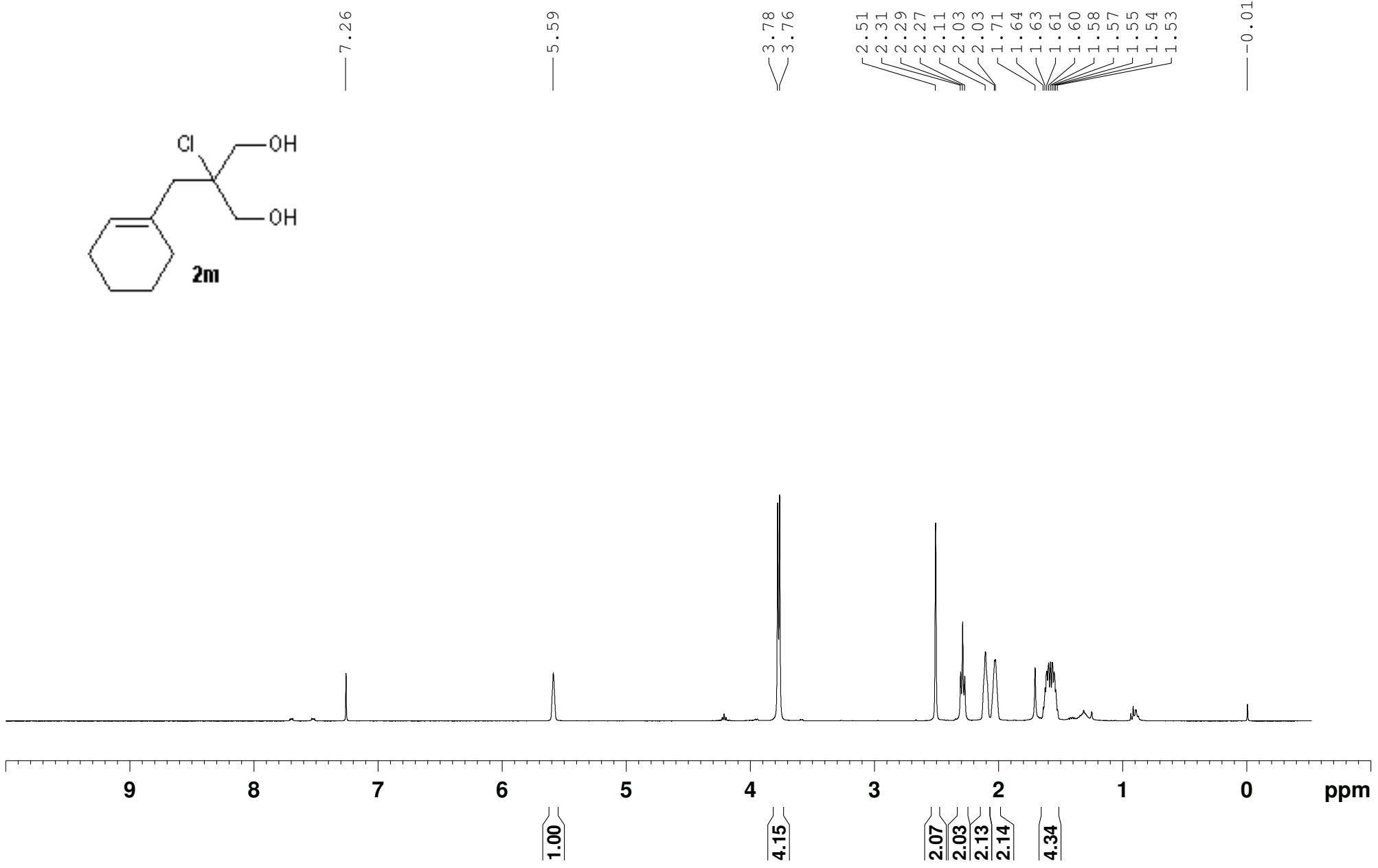
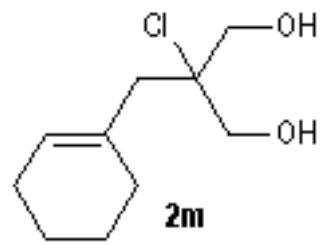


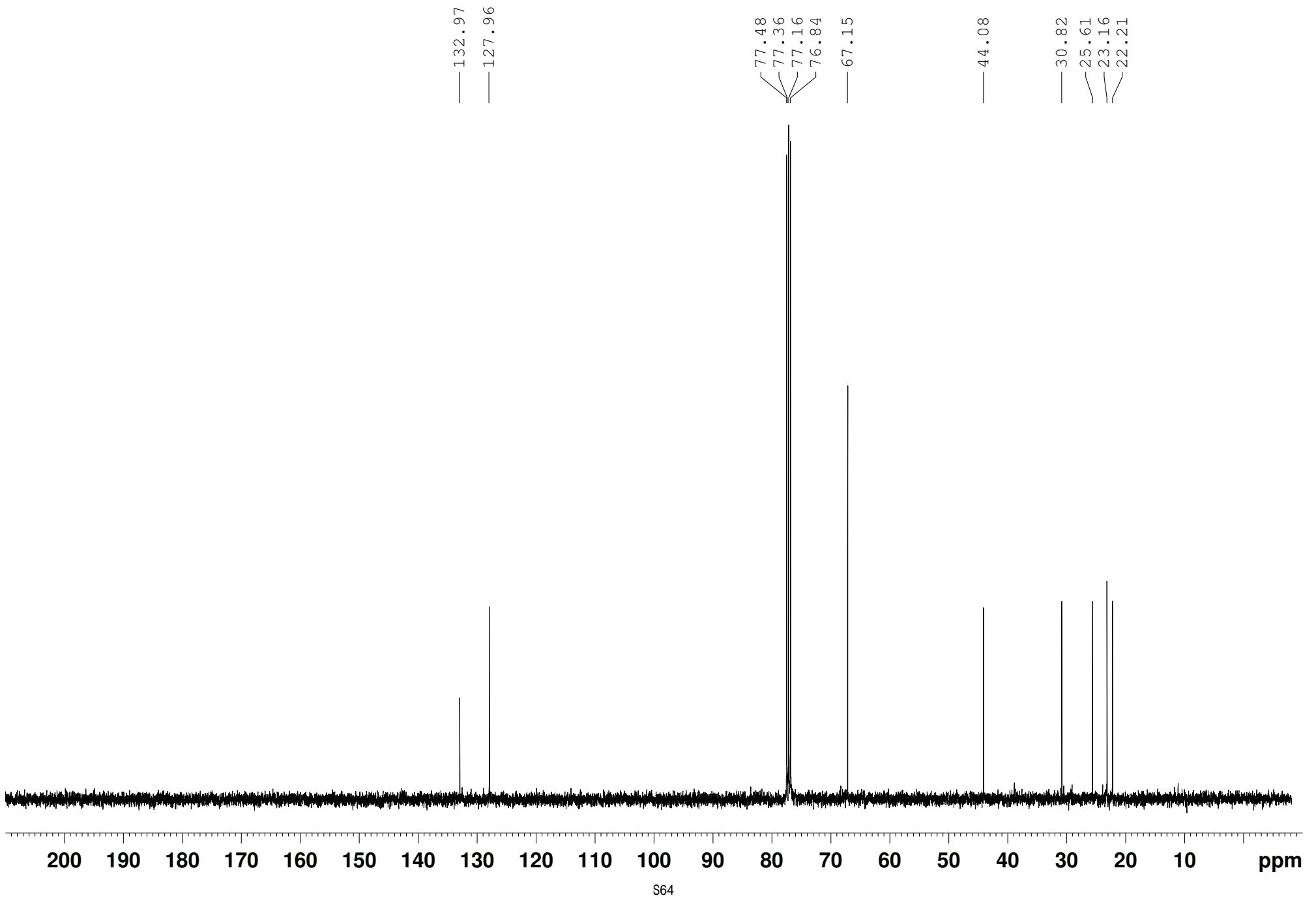


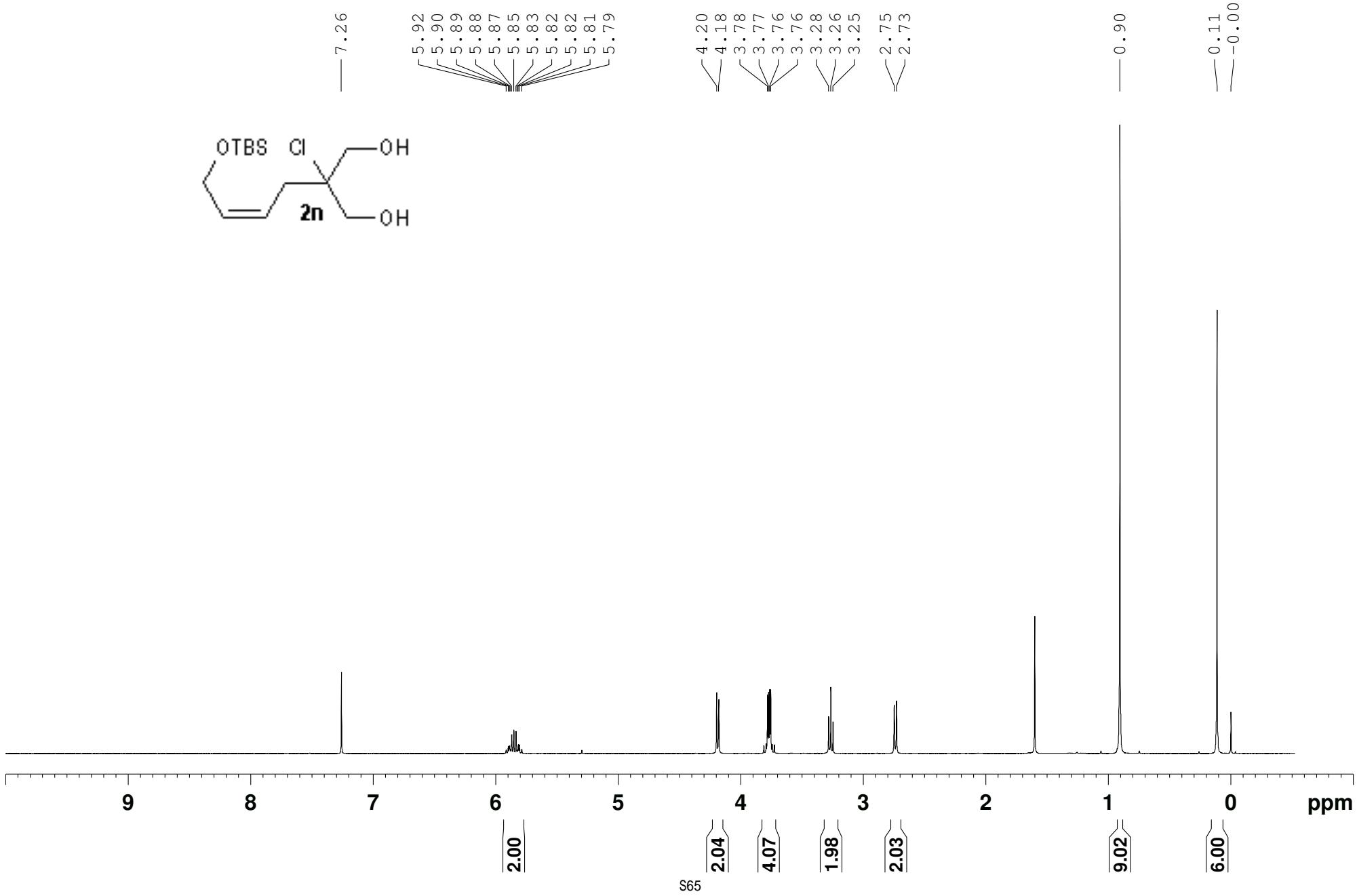


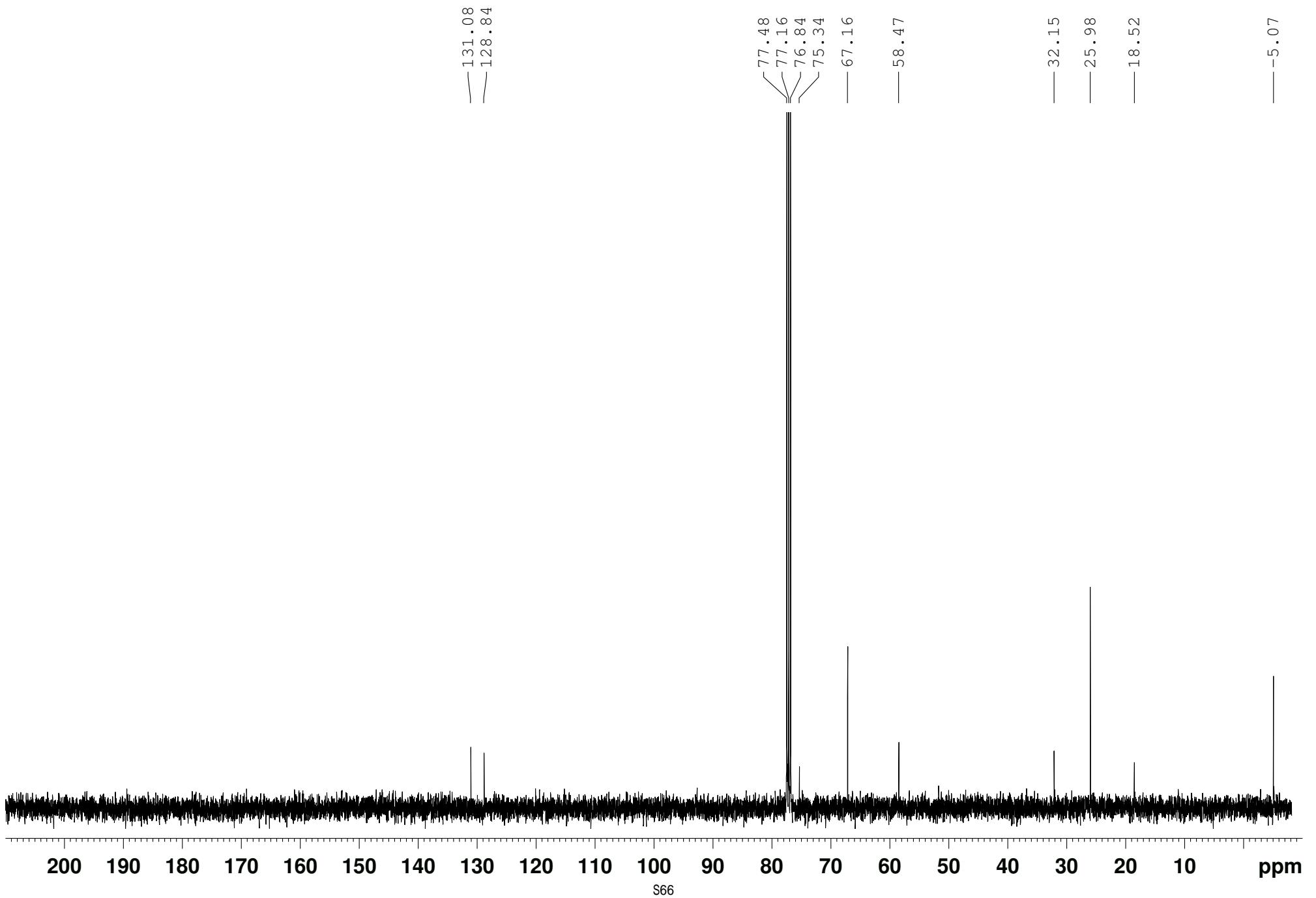




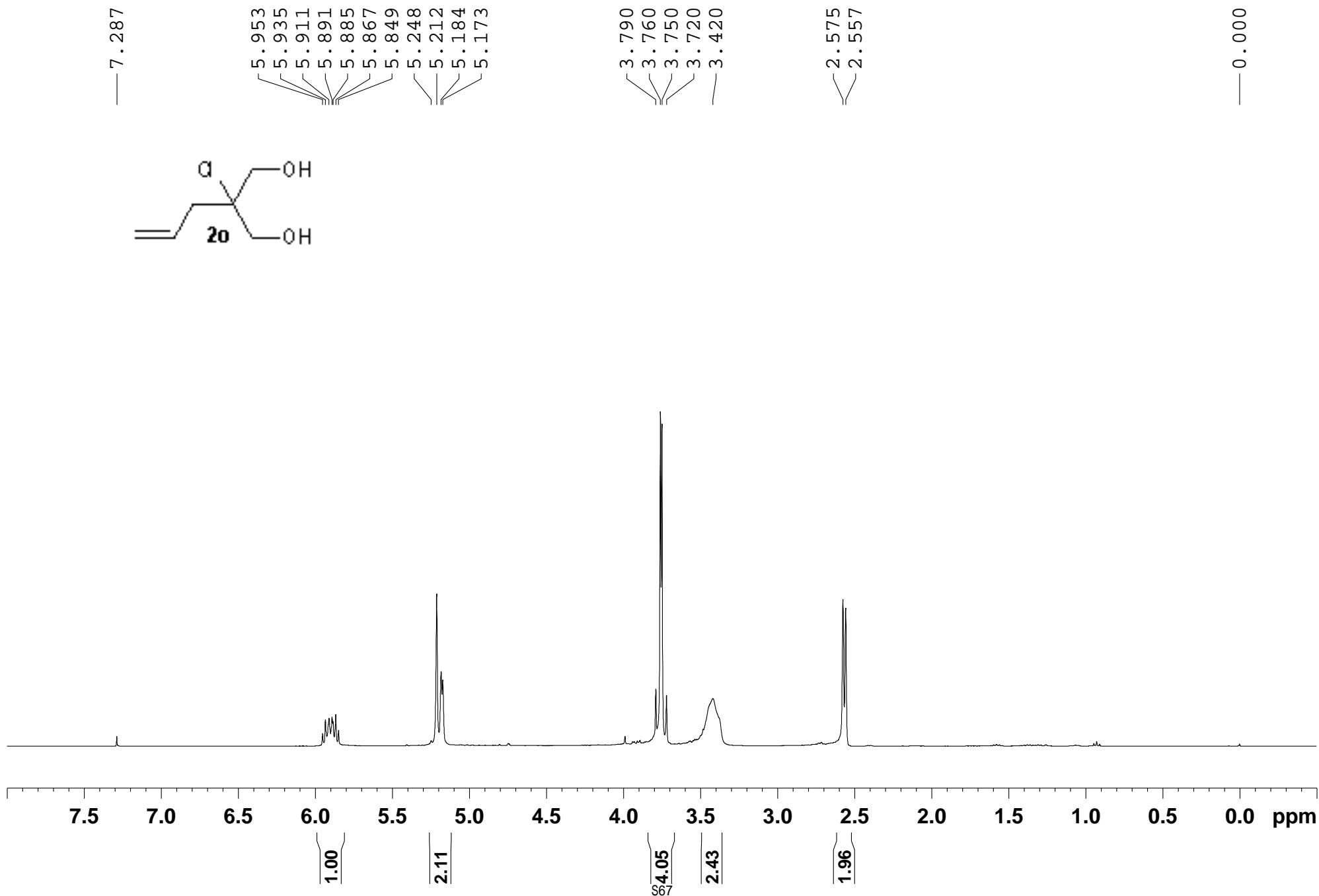




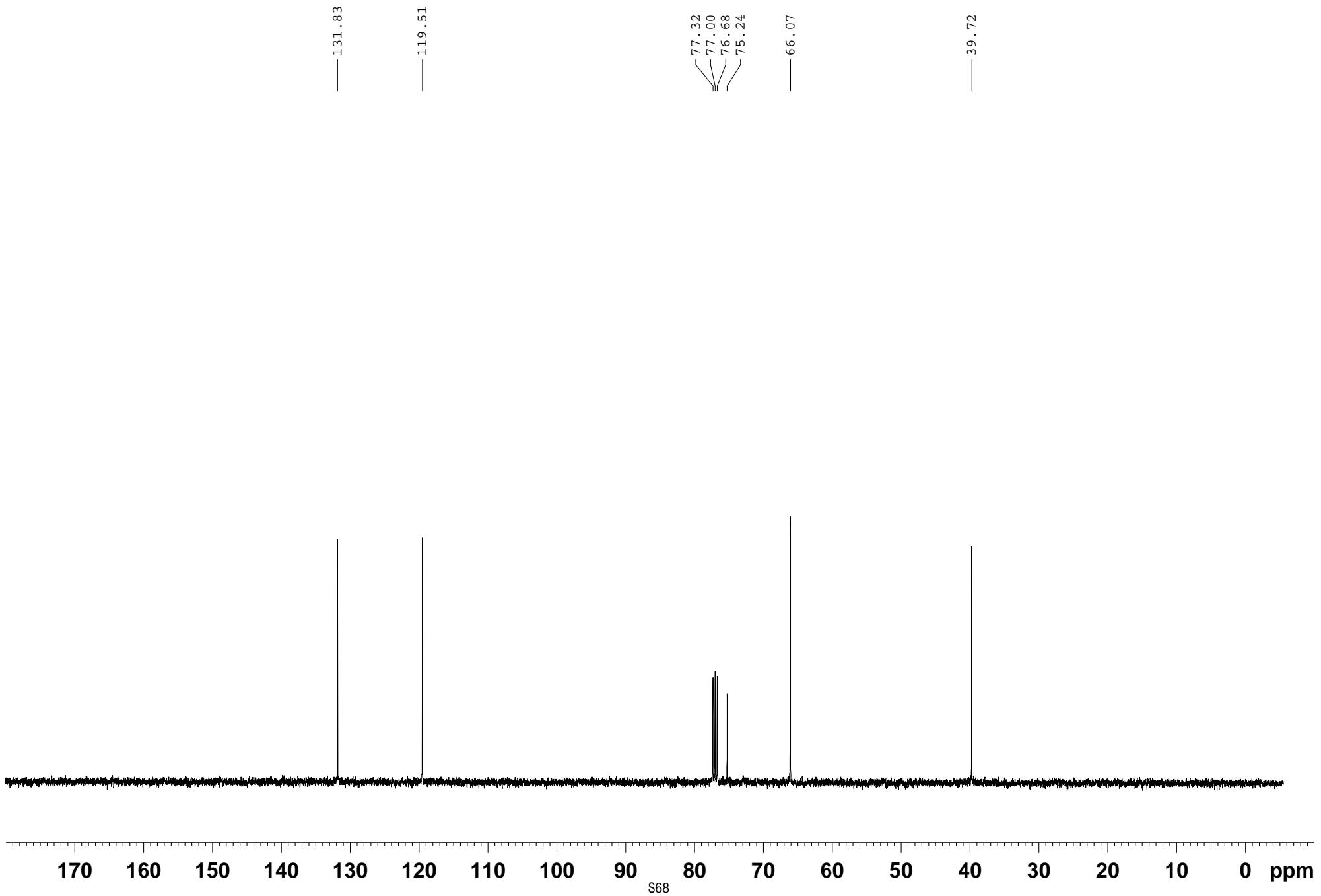


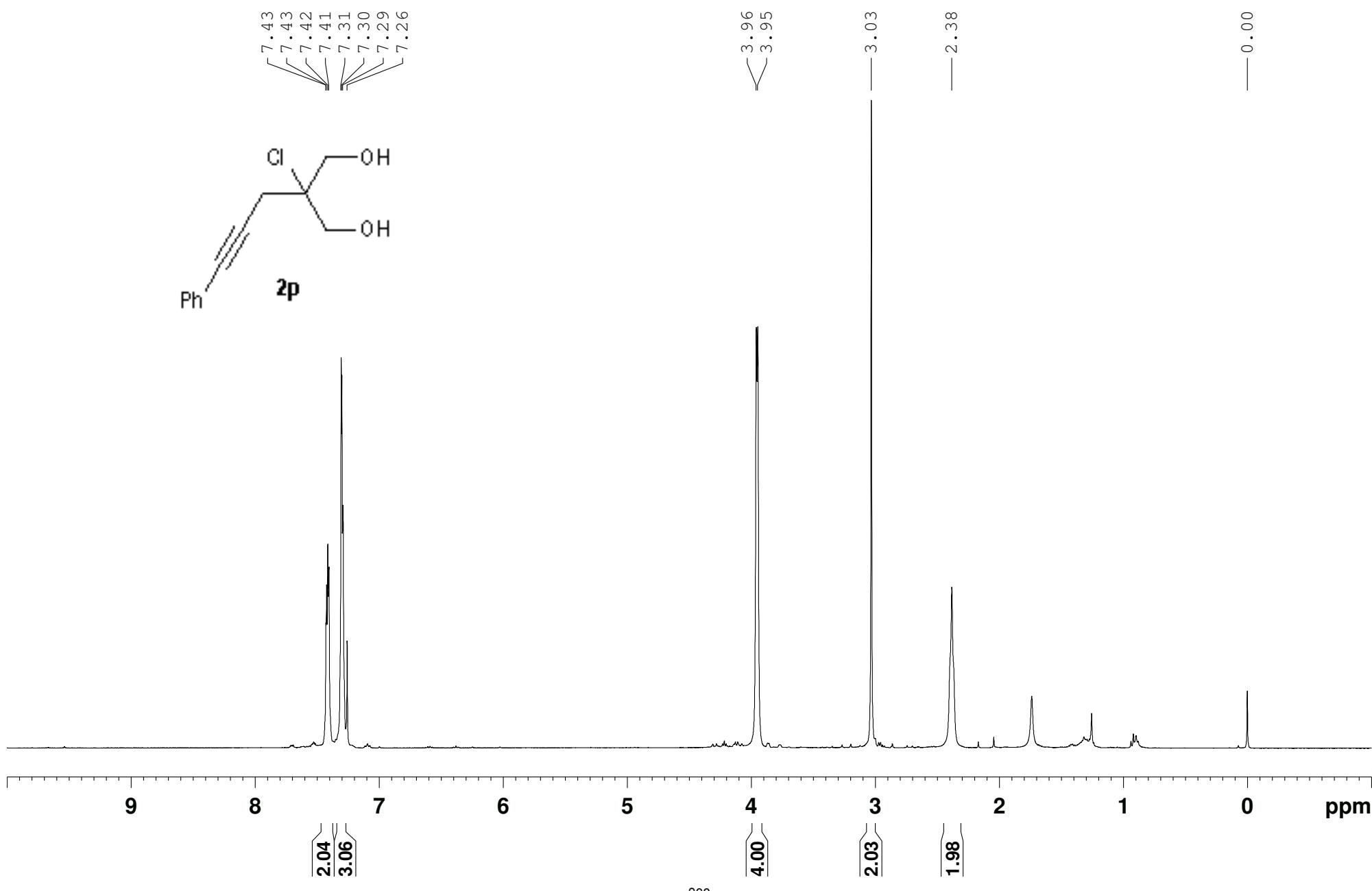


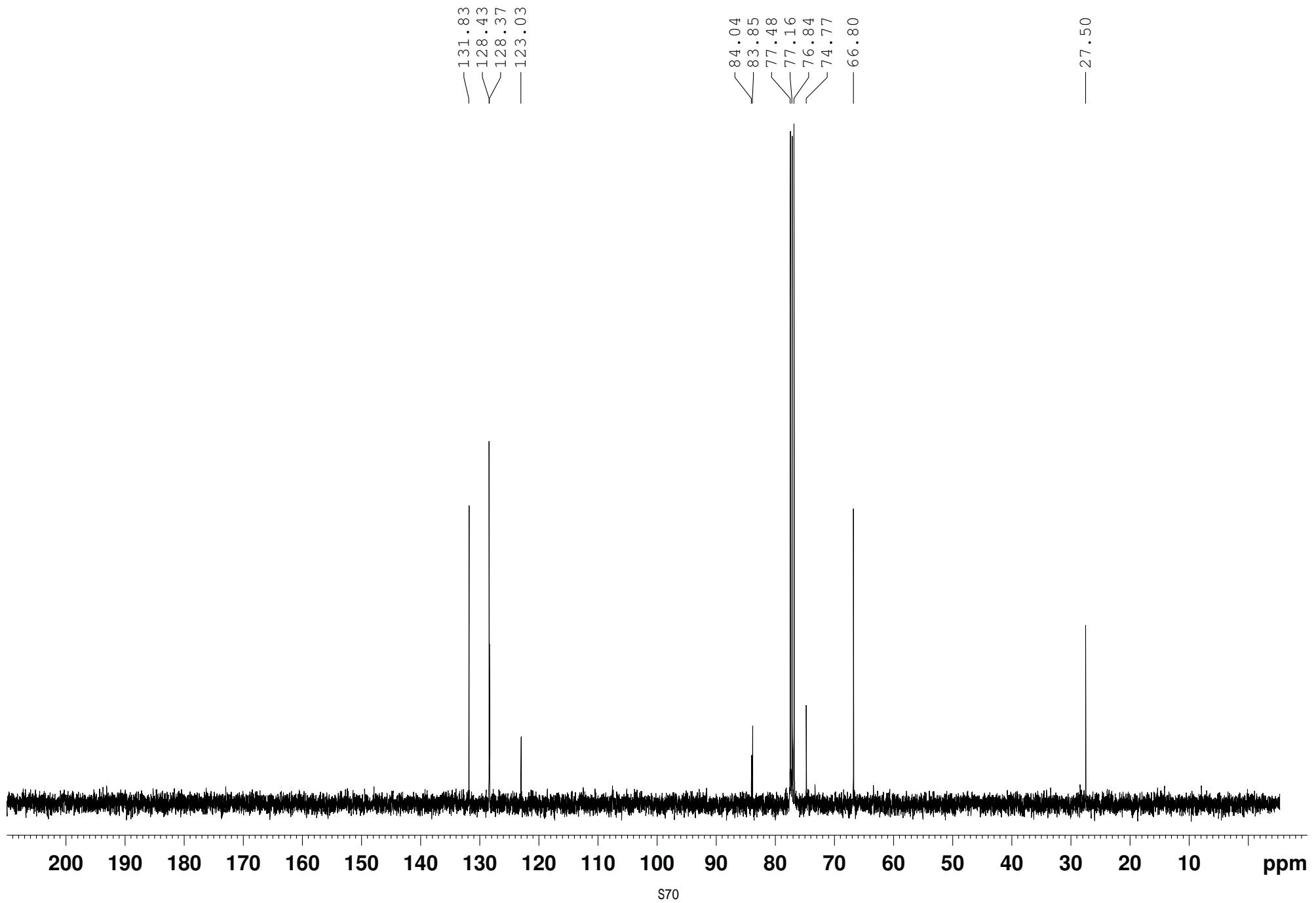
lbs-allyl-diol-H6



lbs-allyl-diol-C6

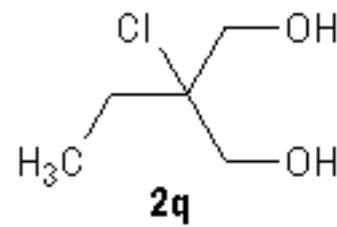






lbs-Et-Diol-H

— 7.271



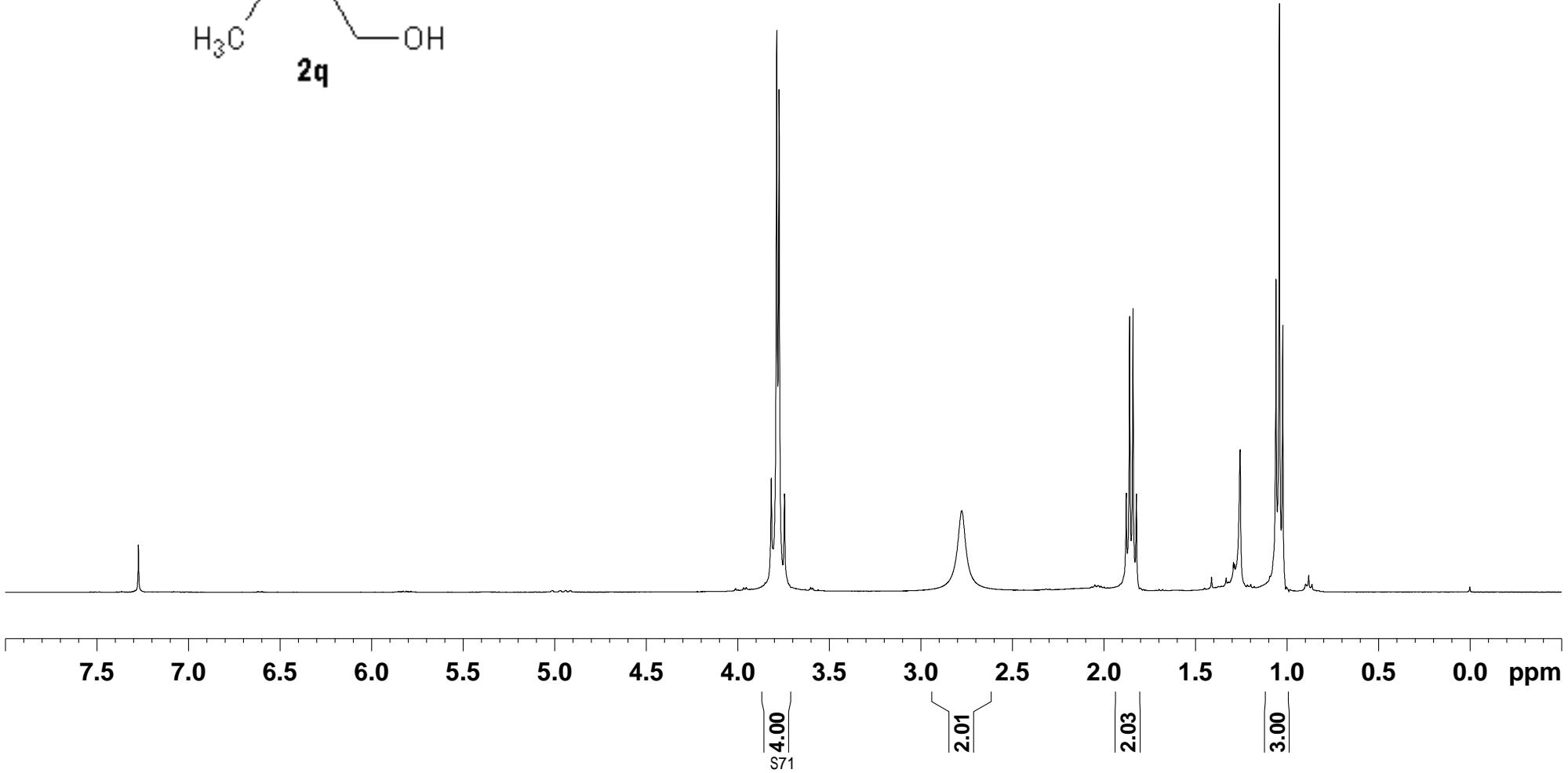
3.816
3.787
3.774
3.744

— 2.776

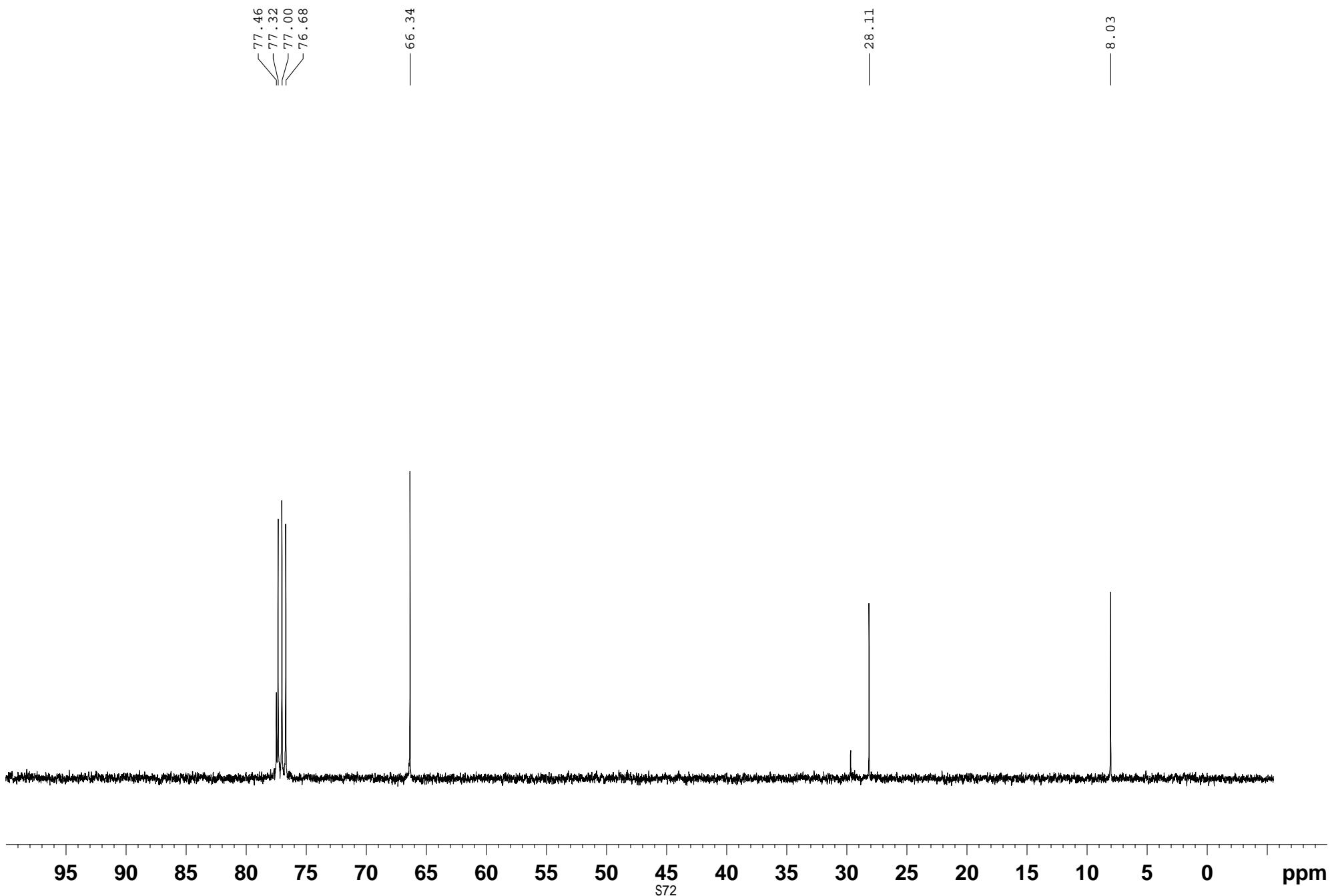
1.877
1.859
1.840
1.822

1.059
1.041
1.022

— 0.000



lbs-Et-Diol-C

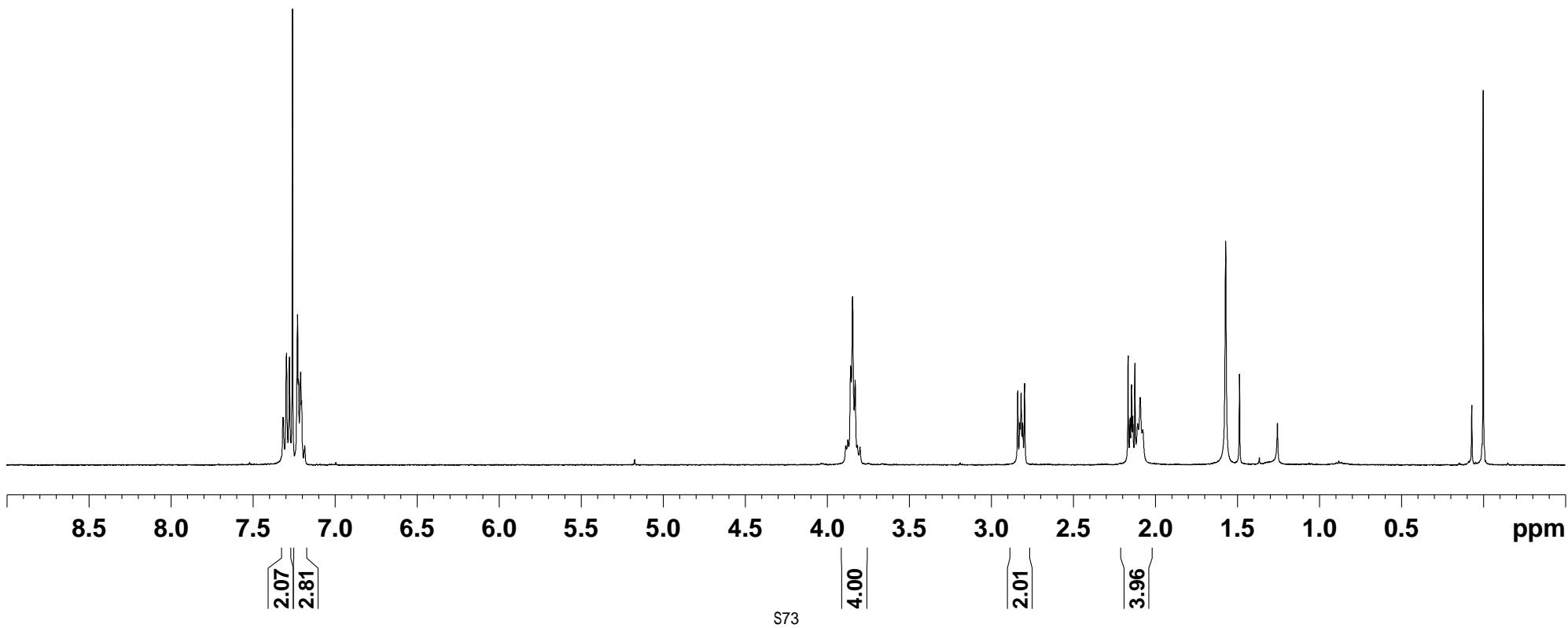
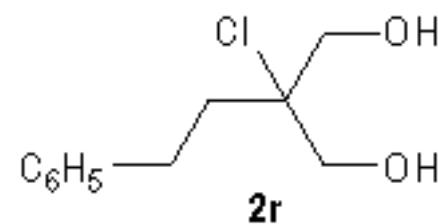


1bs-PhCH₂CH₂-diol-H

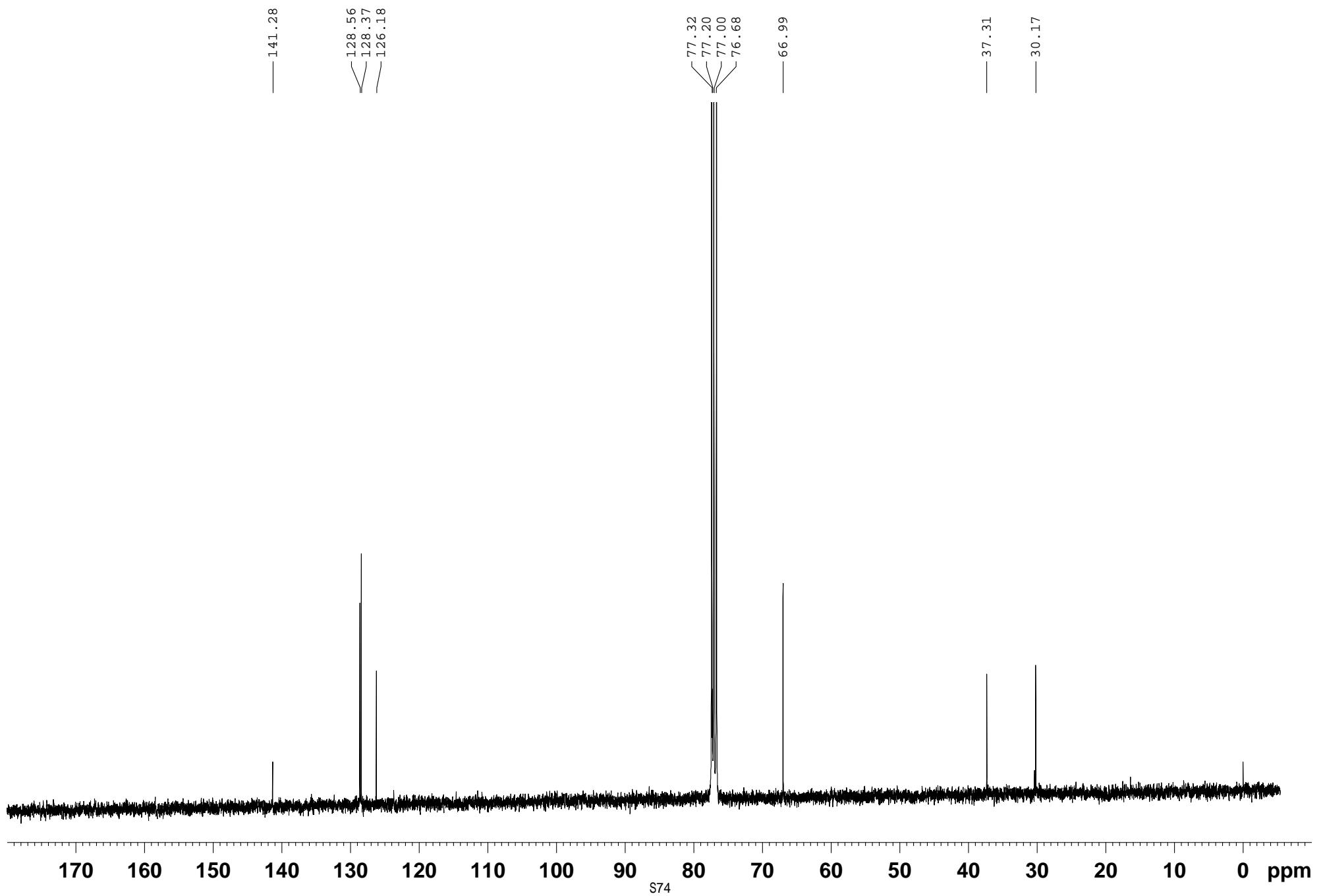
7.315
7.296
7.283
7.278
7.260
7.229
7.223
7.210
7.204
7.185

3.886
3.874
3.857
3.845
3.829
3.816
3.799
2.838
2.825
2.817
2.809
2.796
2.165
2.152
2.144
2.137
2.123
2.107
2.091
2.075

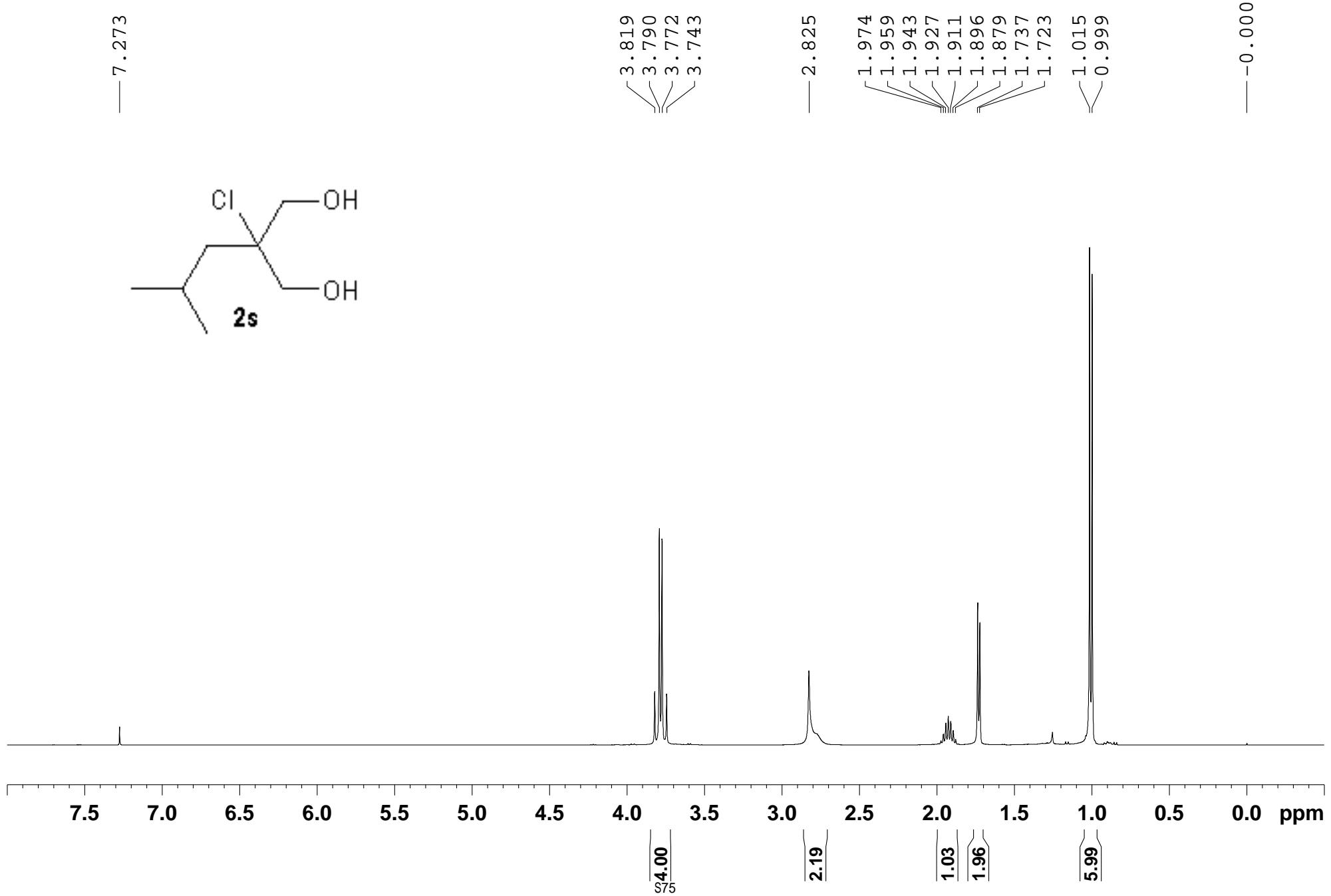
— 0.000



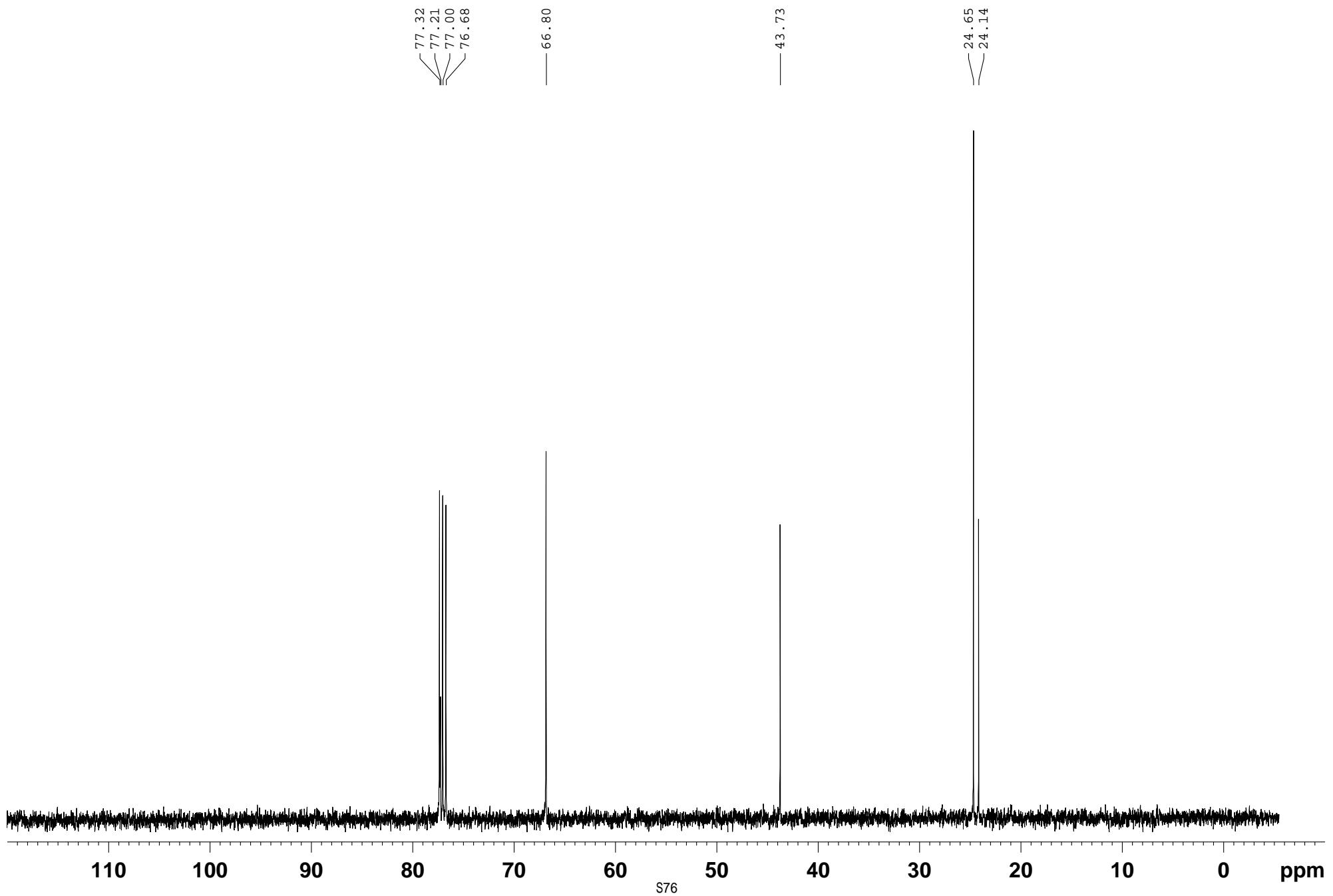
lbs-PhCH₂CH₂-diol-C



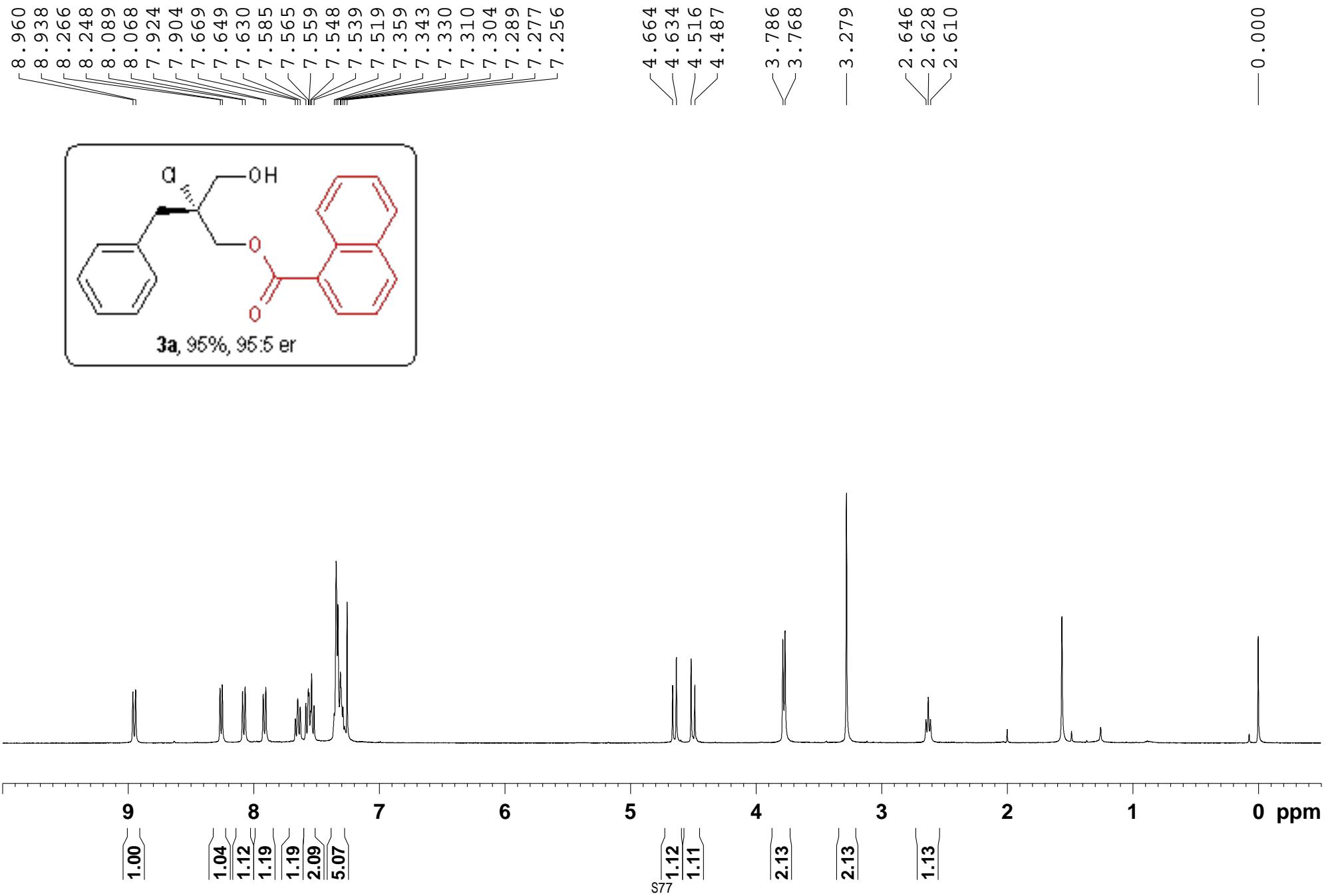
lbs-ipr-diol-H



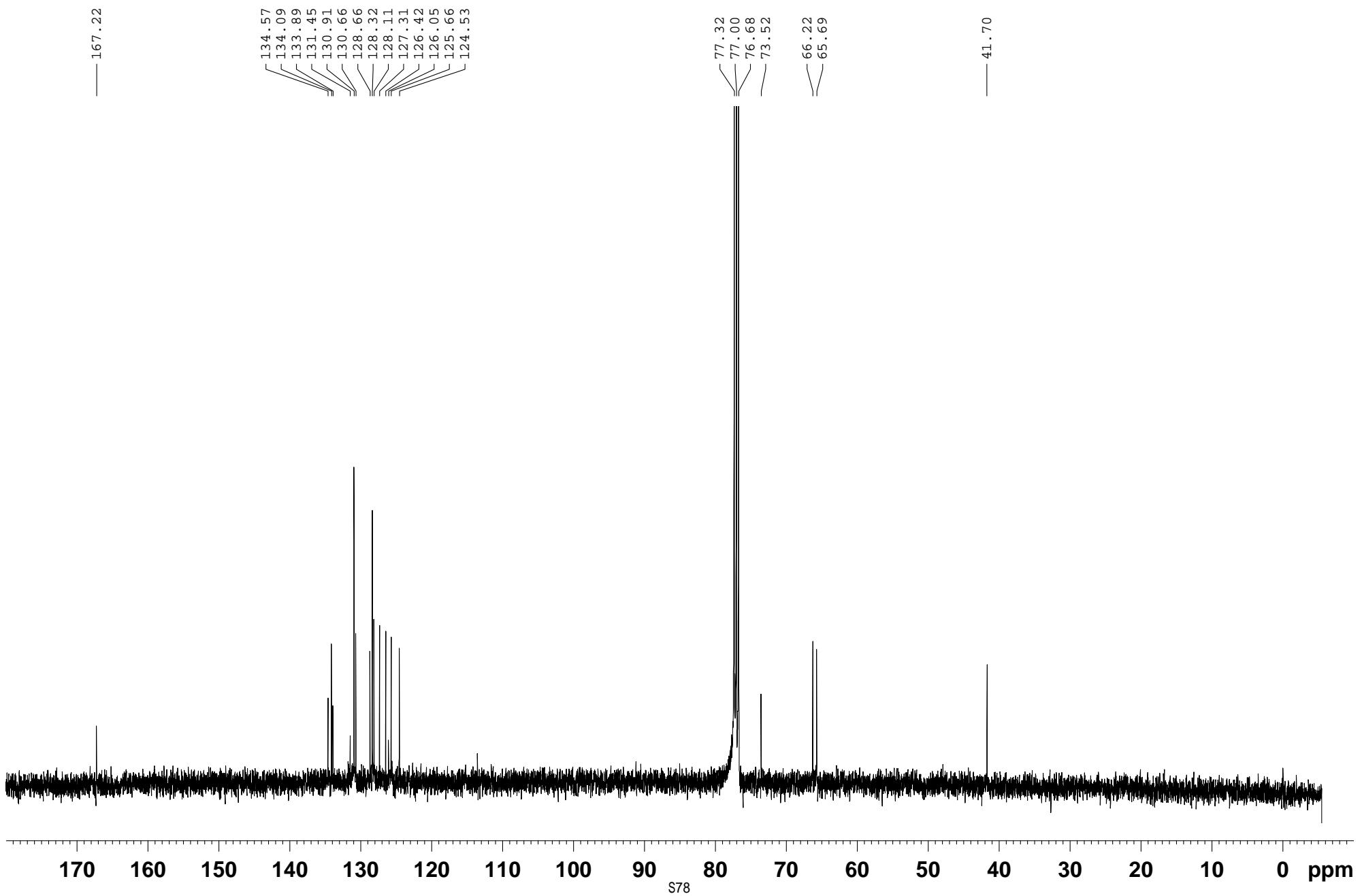
lbs-ipr-diol-C



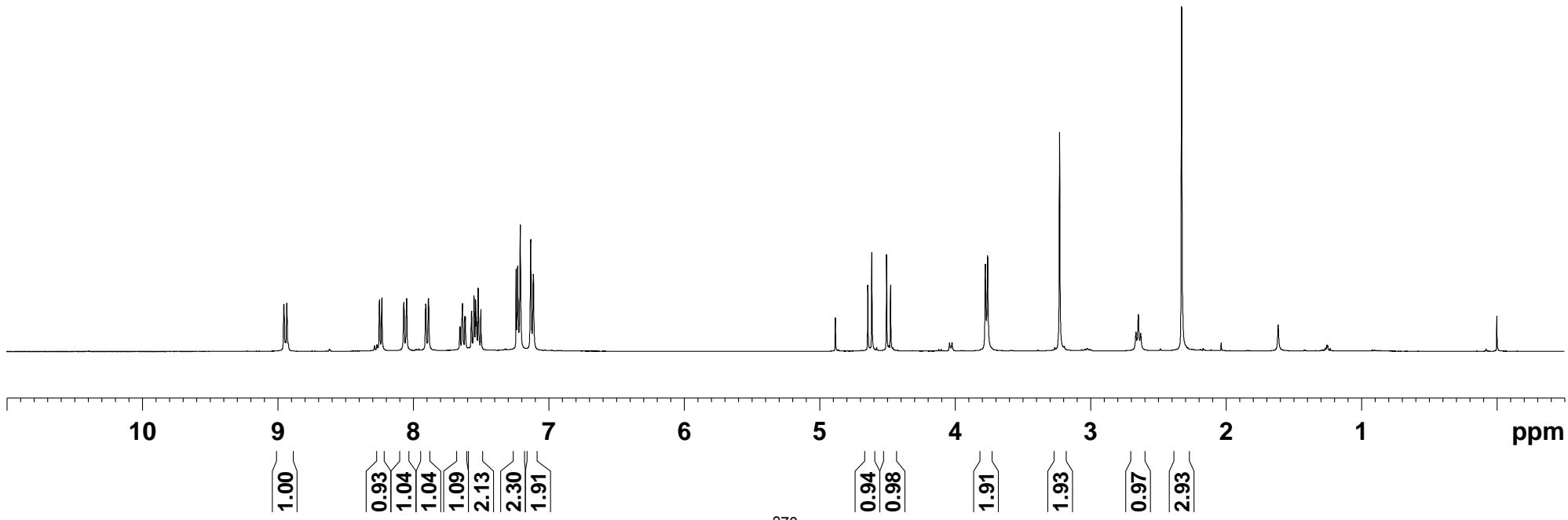
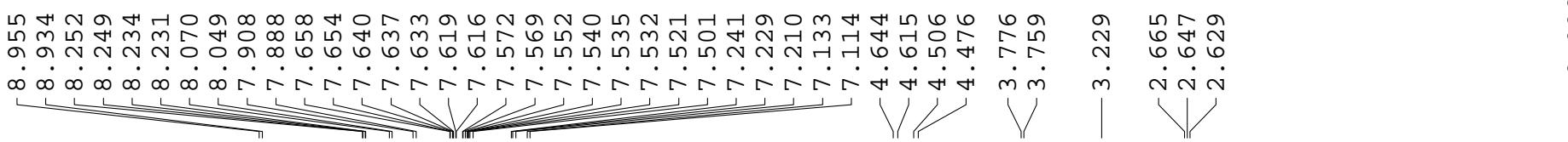
lbs-Bn-Cl-H



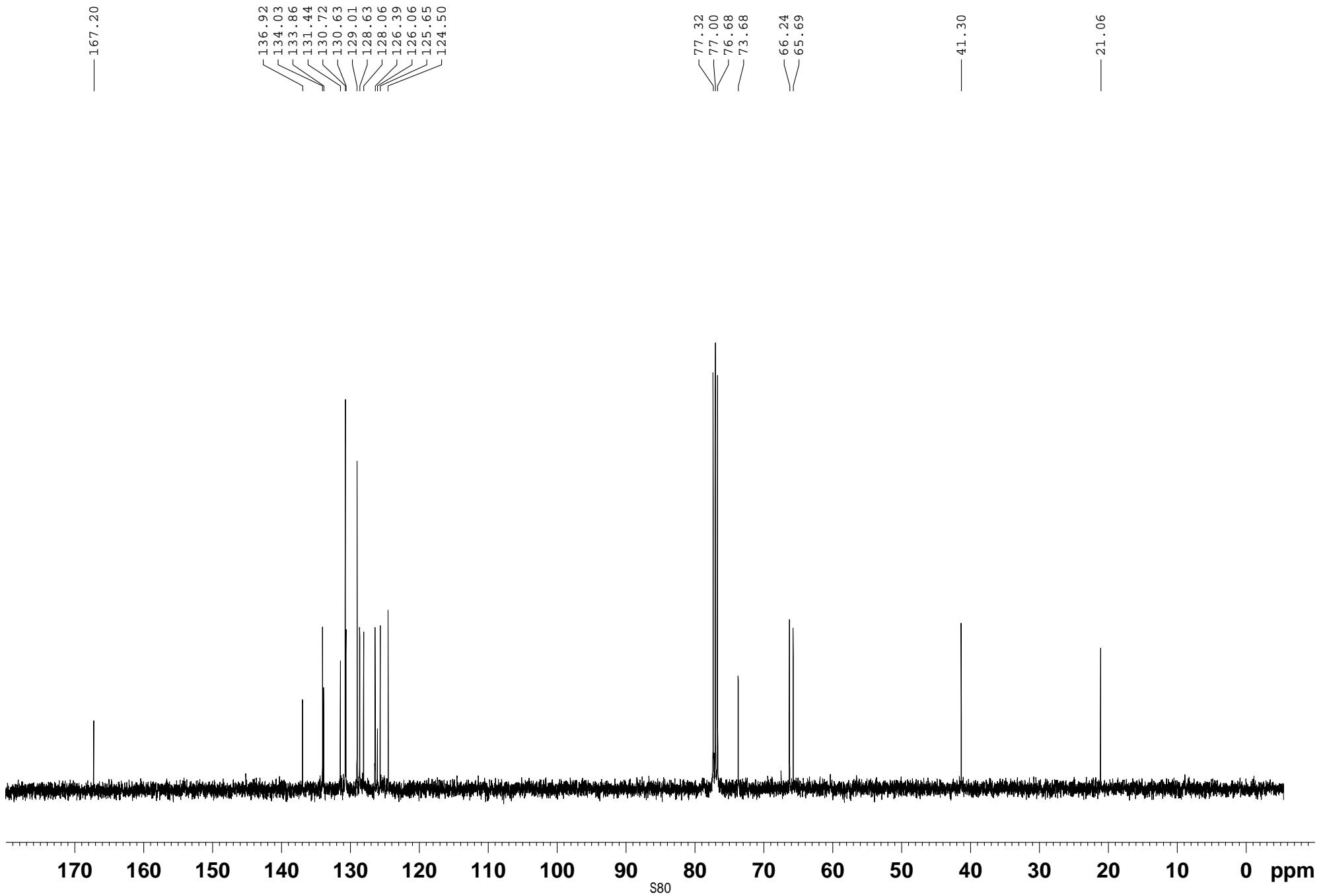
lbs-Bn-Cl-C



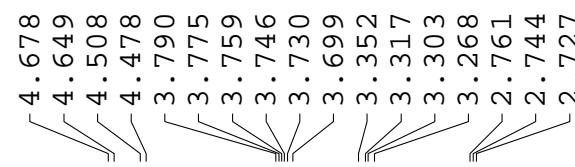
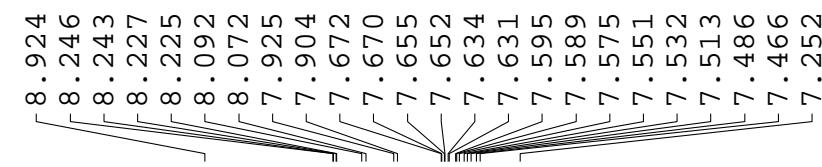
1bs-4-Me-Cl-H



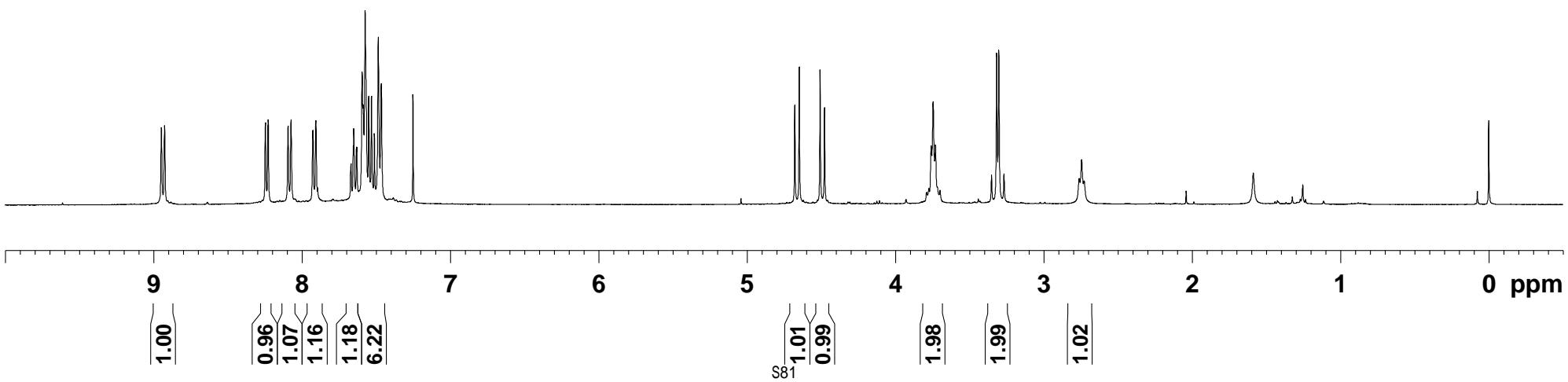
lbs-4-Me-Cl-C



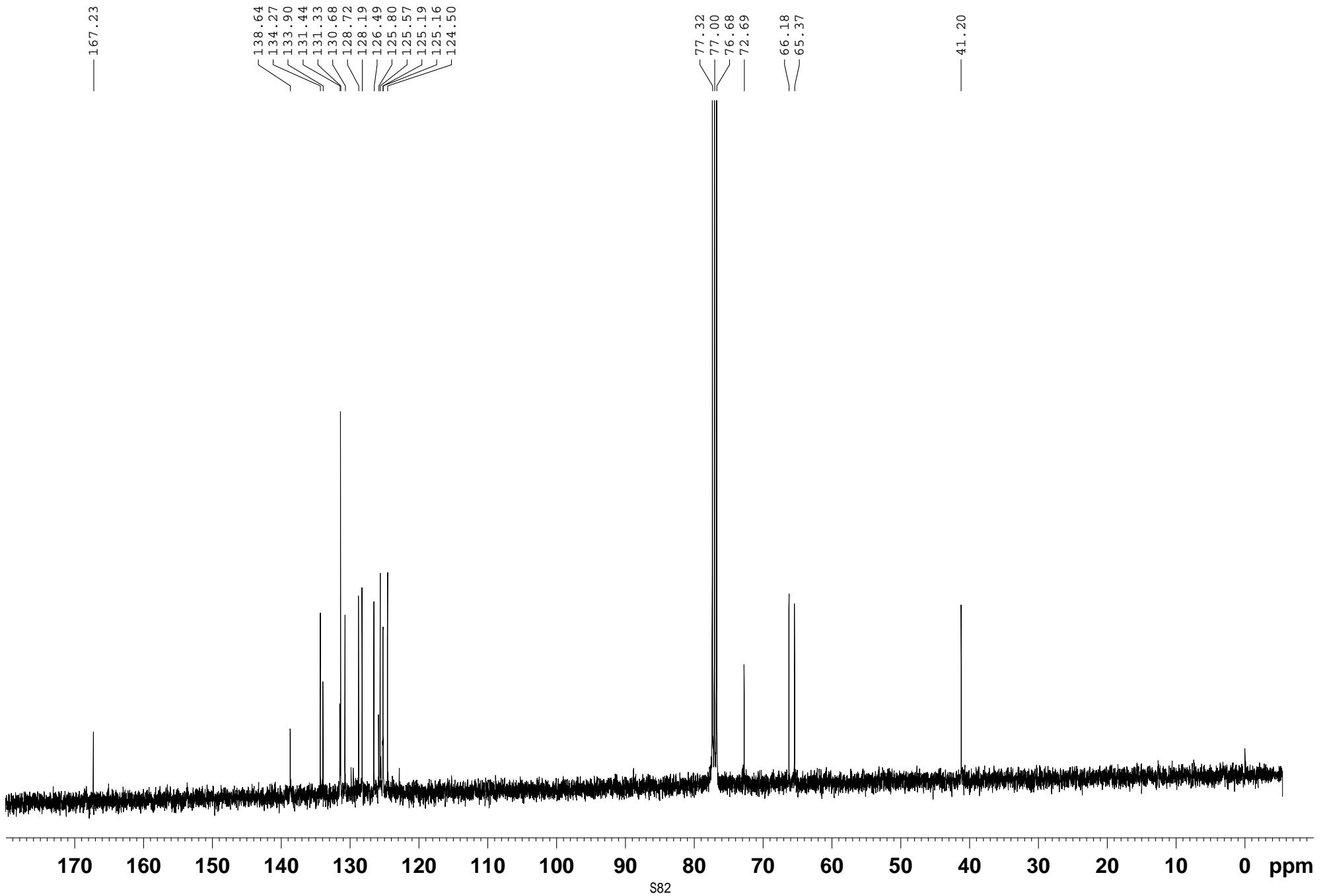
lbs-4-CF₃-Cl-H



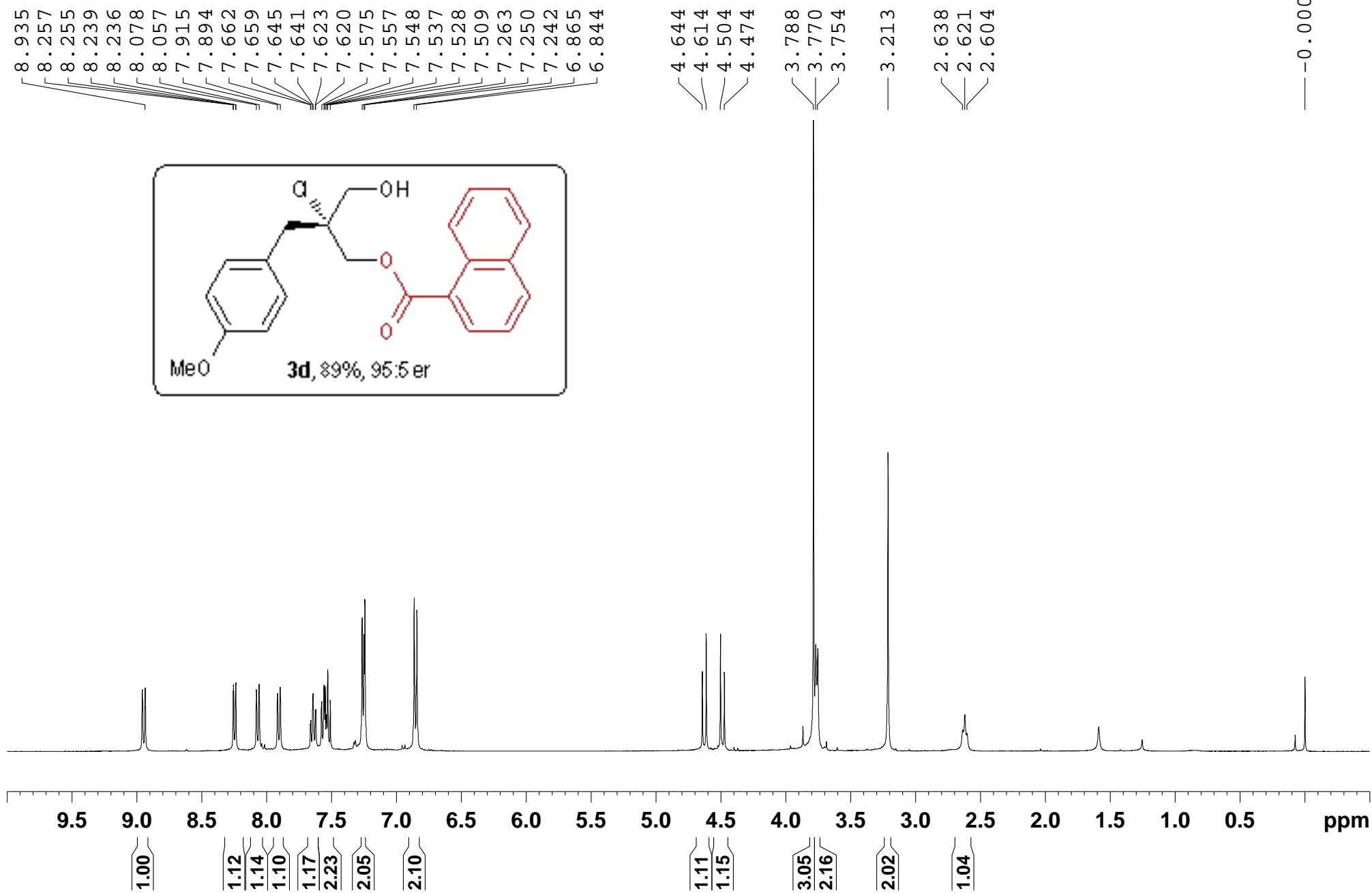
— 0.000



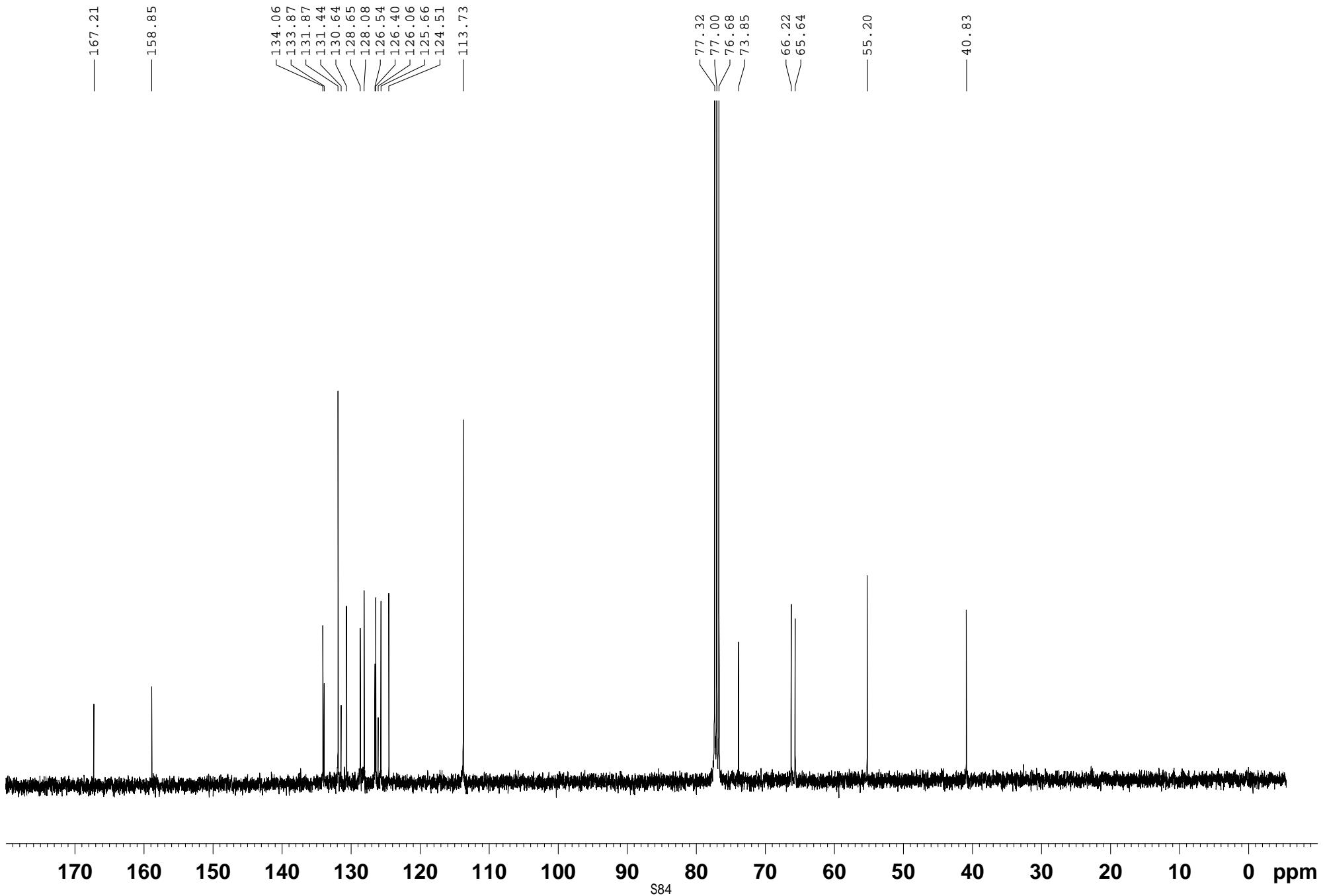
lbs-4-CF₃-Cl-C



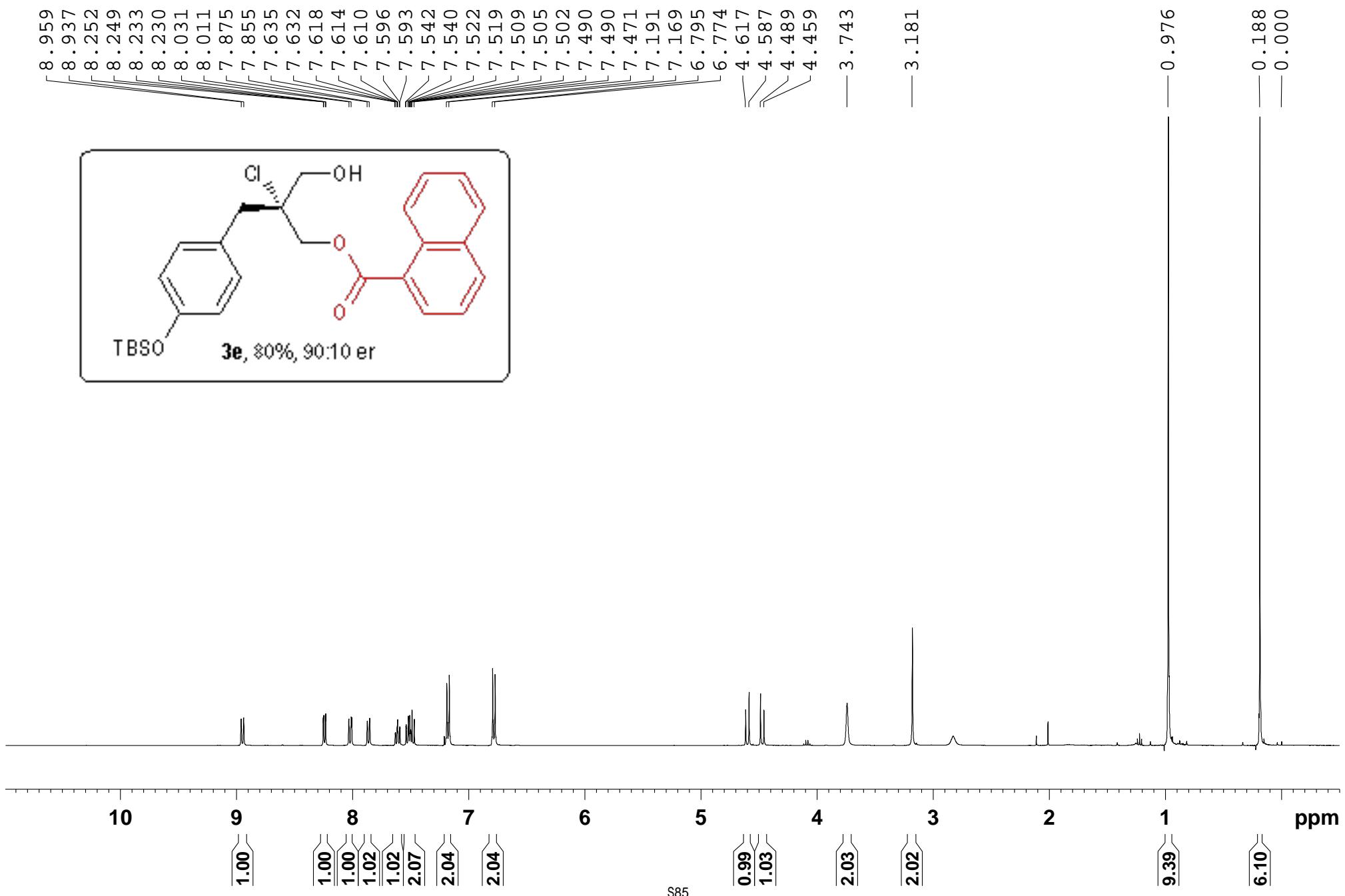
1bs-OMe-desymmetrization-H



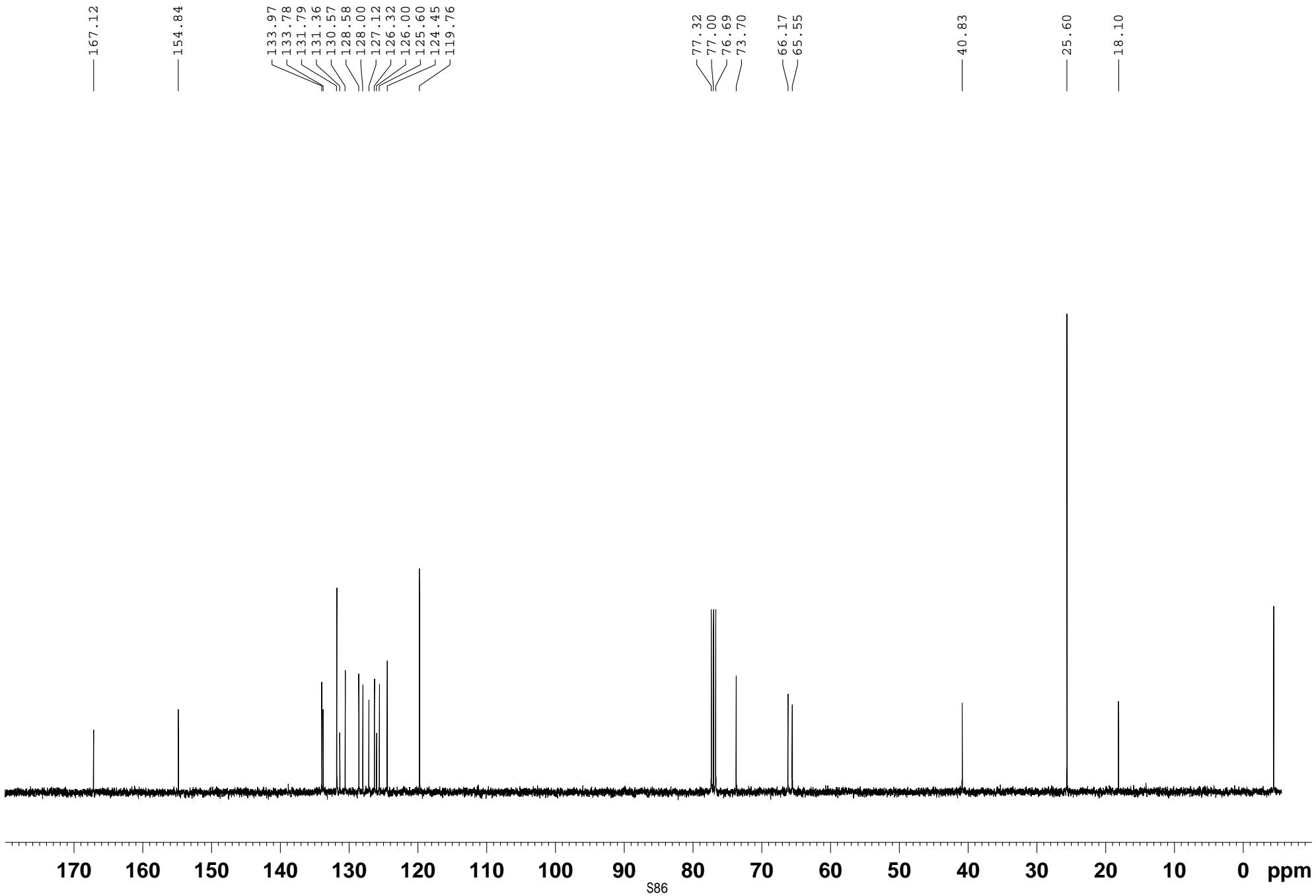
lbs-OMe-desymmetrization-C1



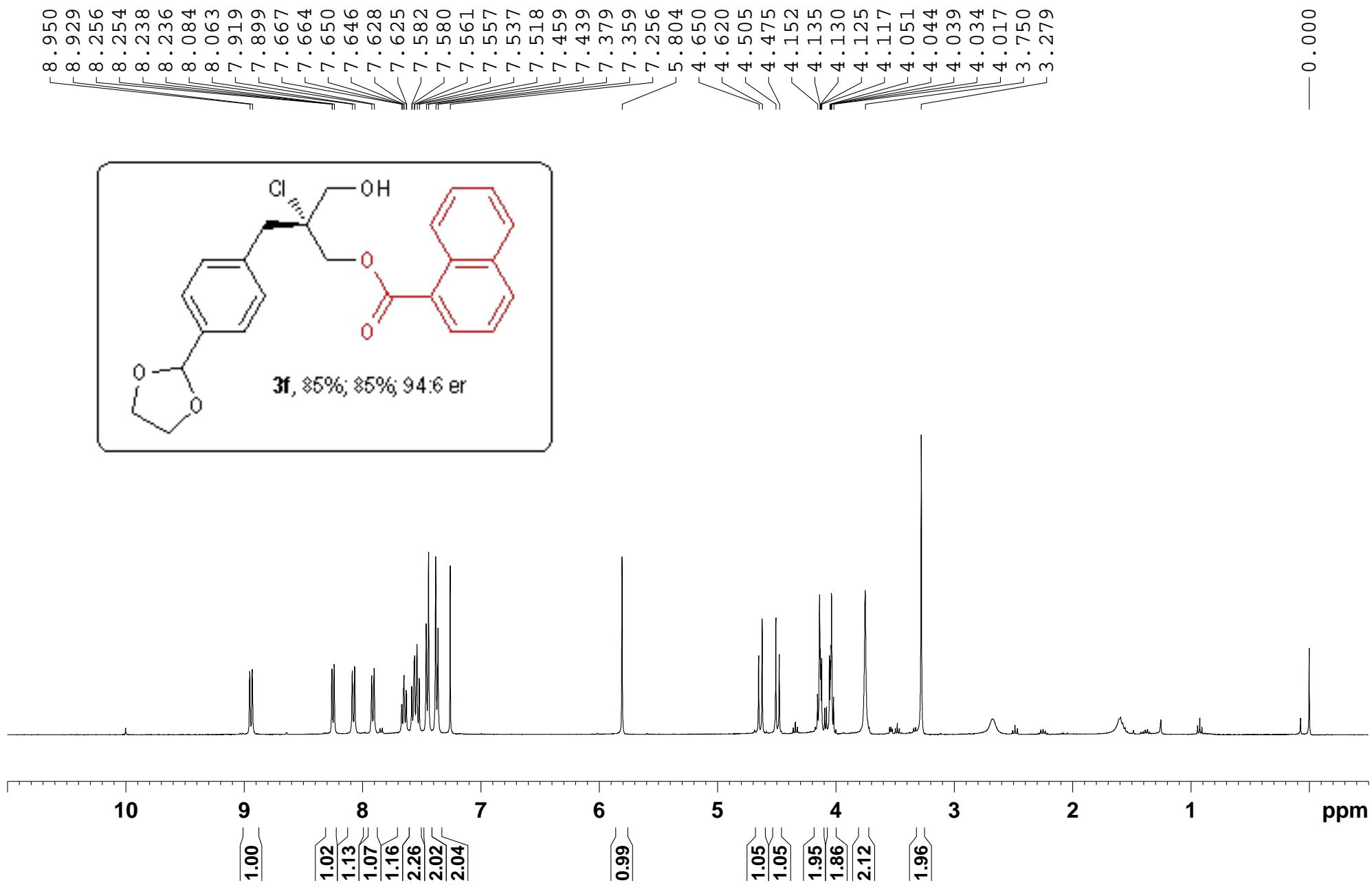
lbs-TBS-Cl-H



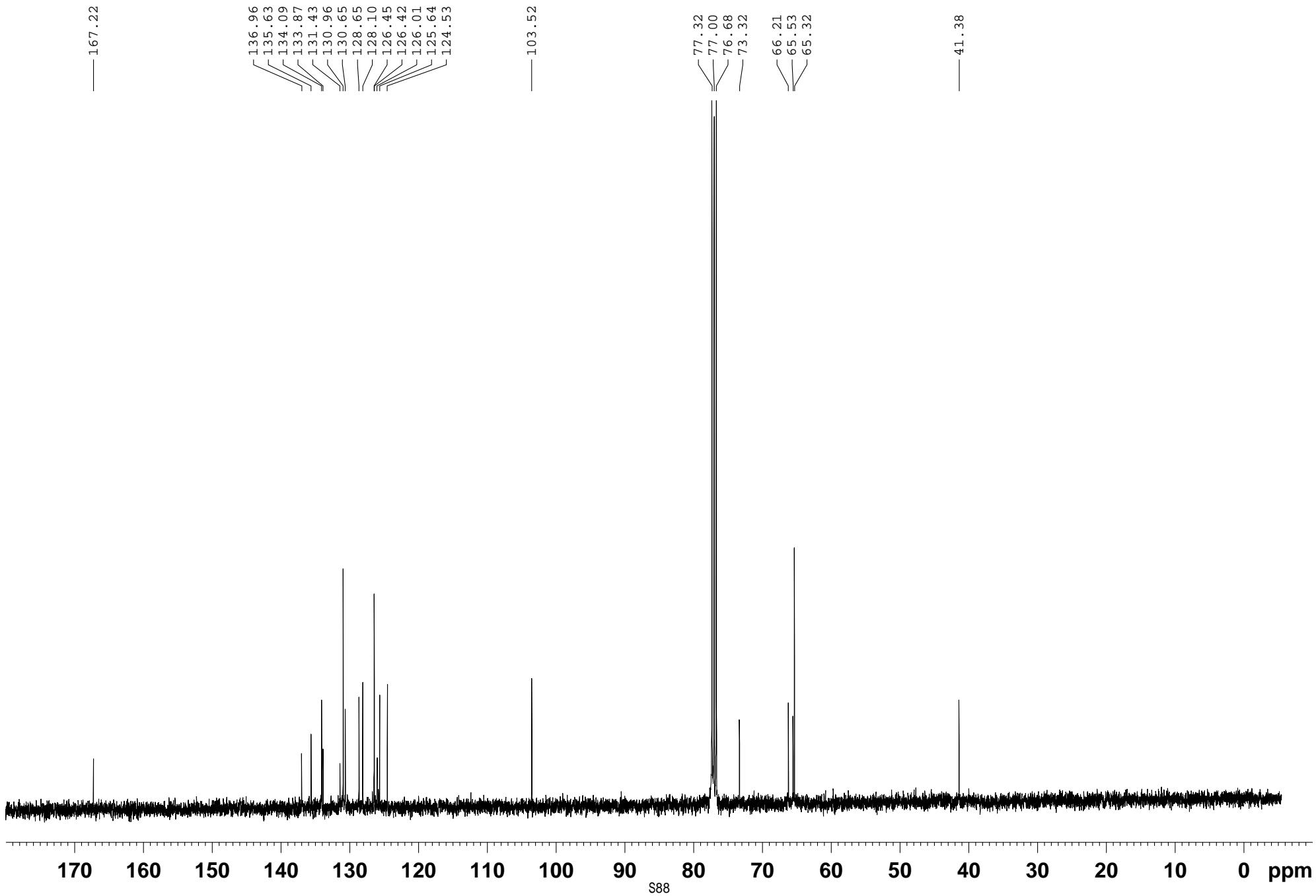
lbs-TBS-C1-C1



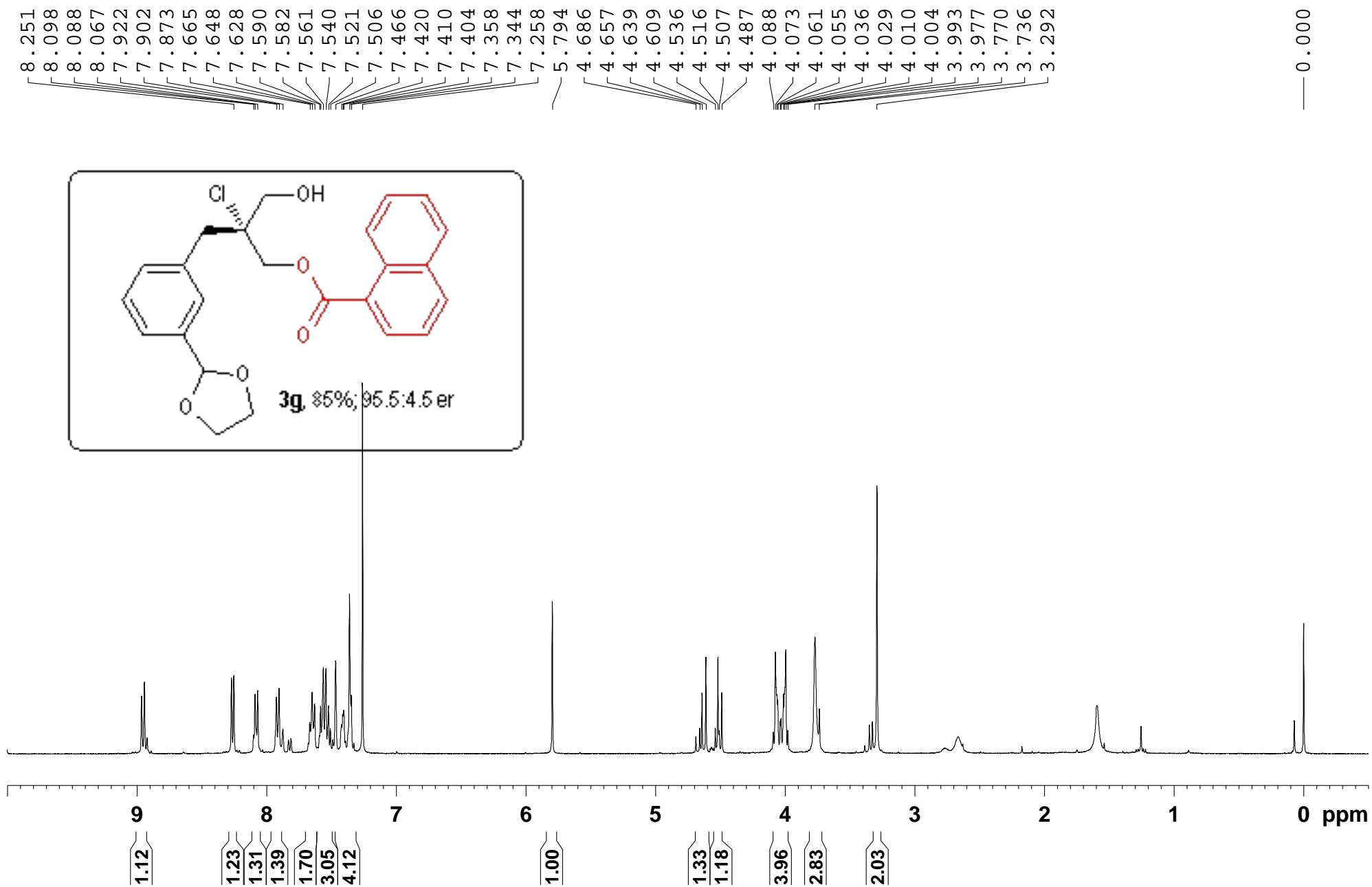
1bs-4-protecting-ethyl-ol-H1



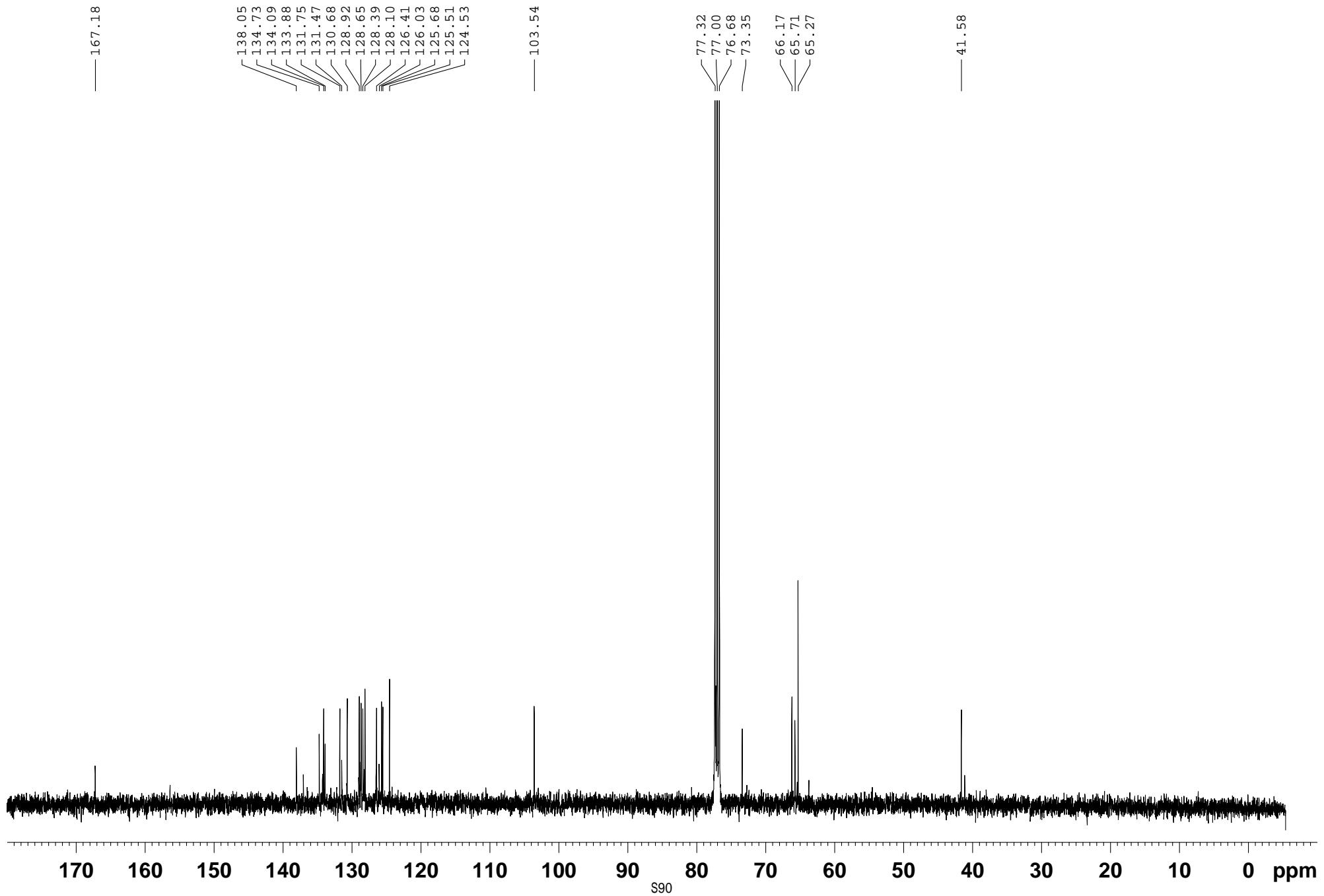
lbs-4-protecting-ethyl-ol-C



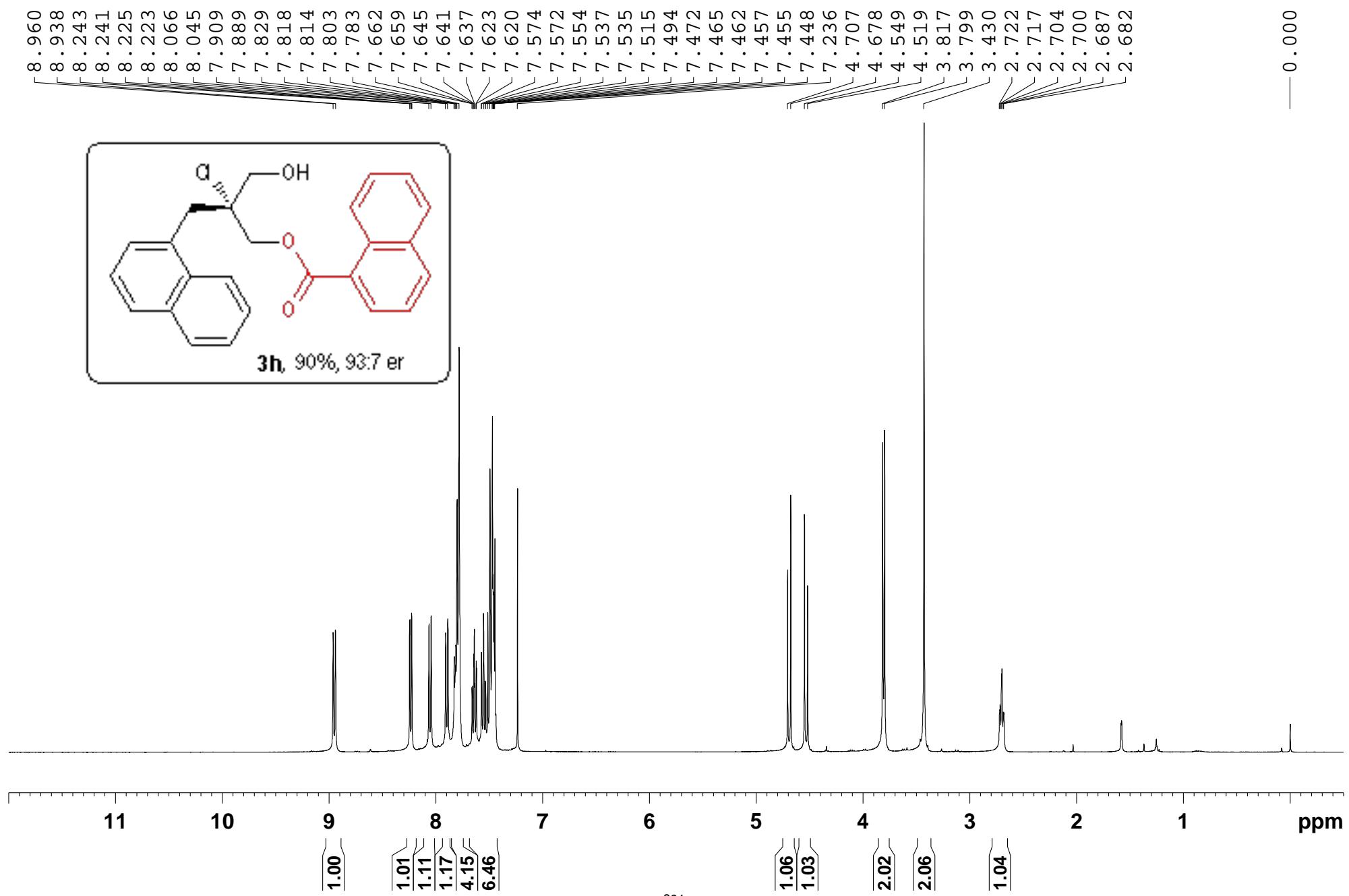
lbs-m-protecting-H



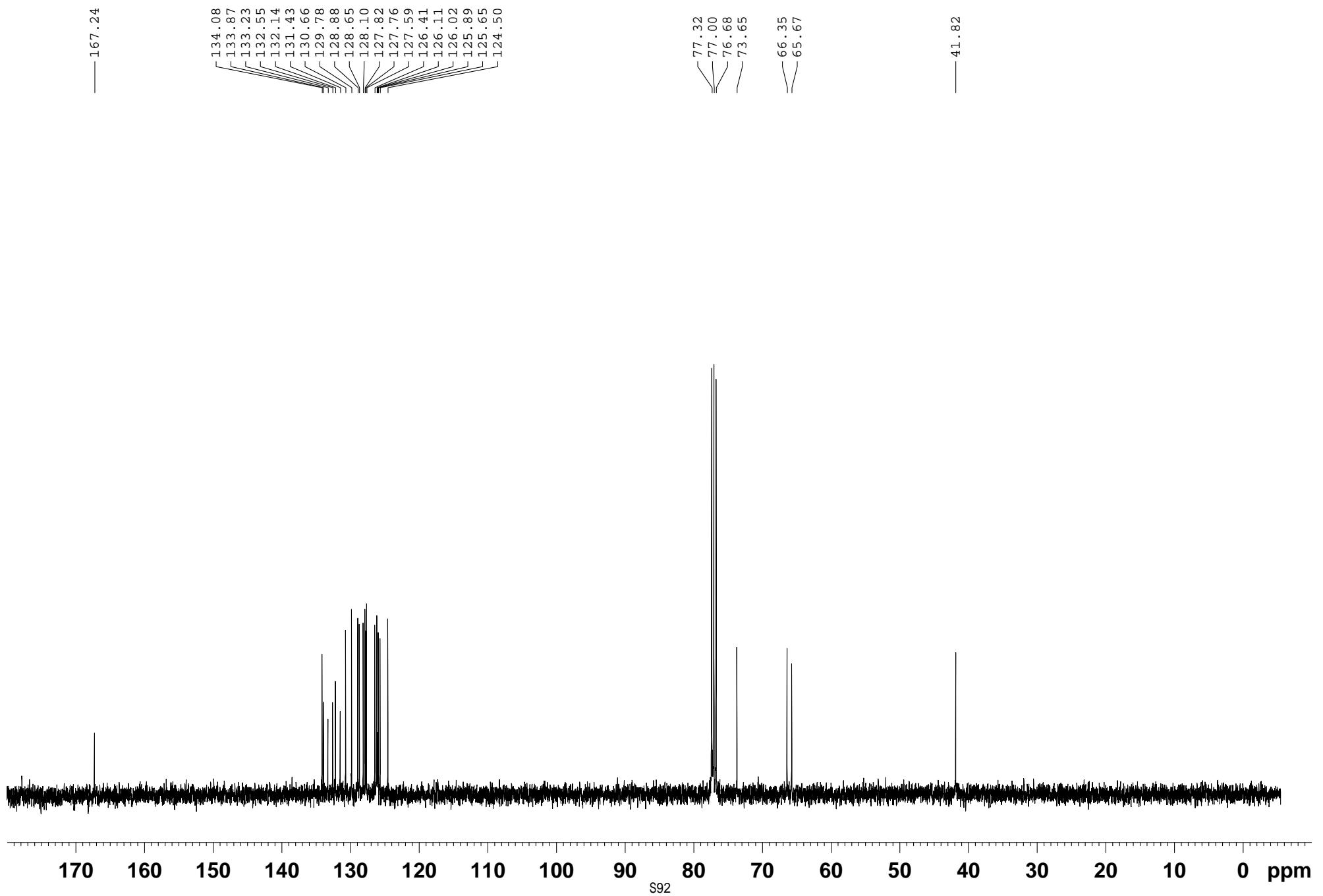
lbs-m-protecting-C



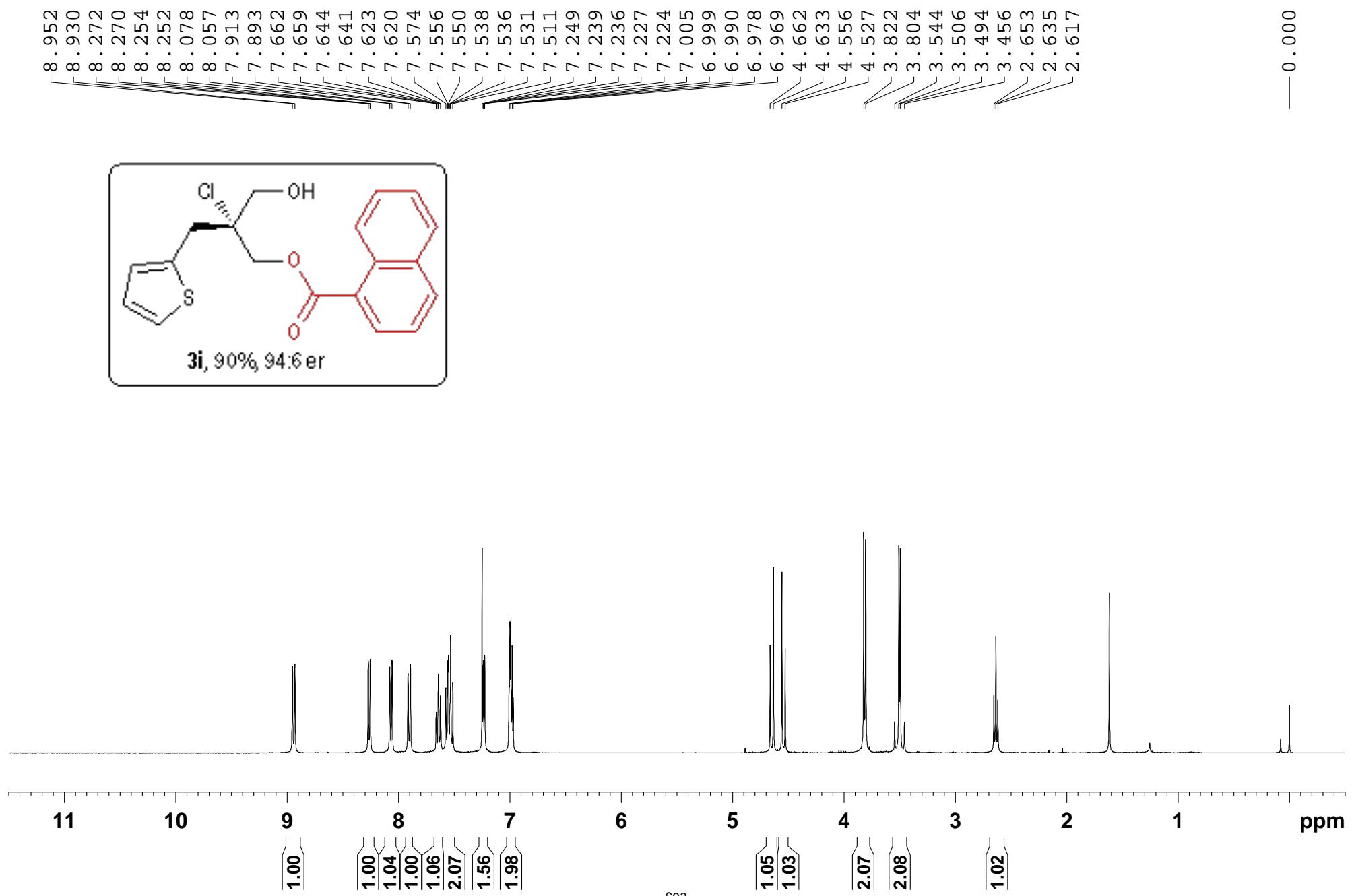
lbs-NAP-C1-H1



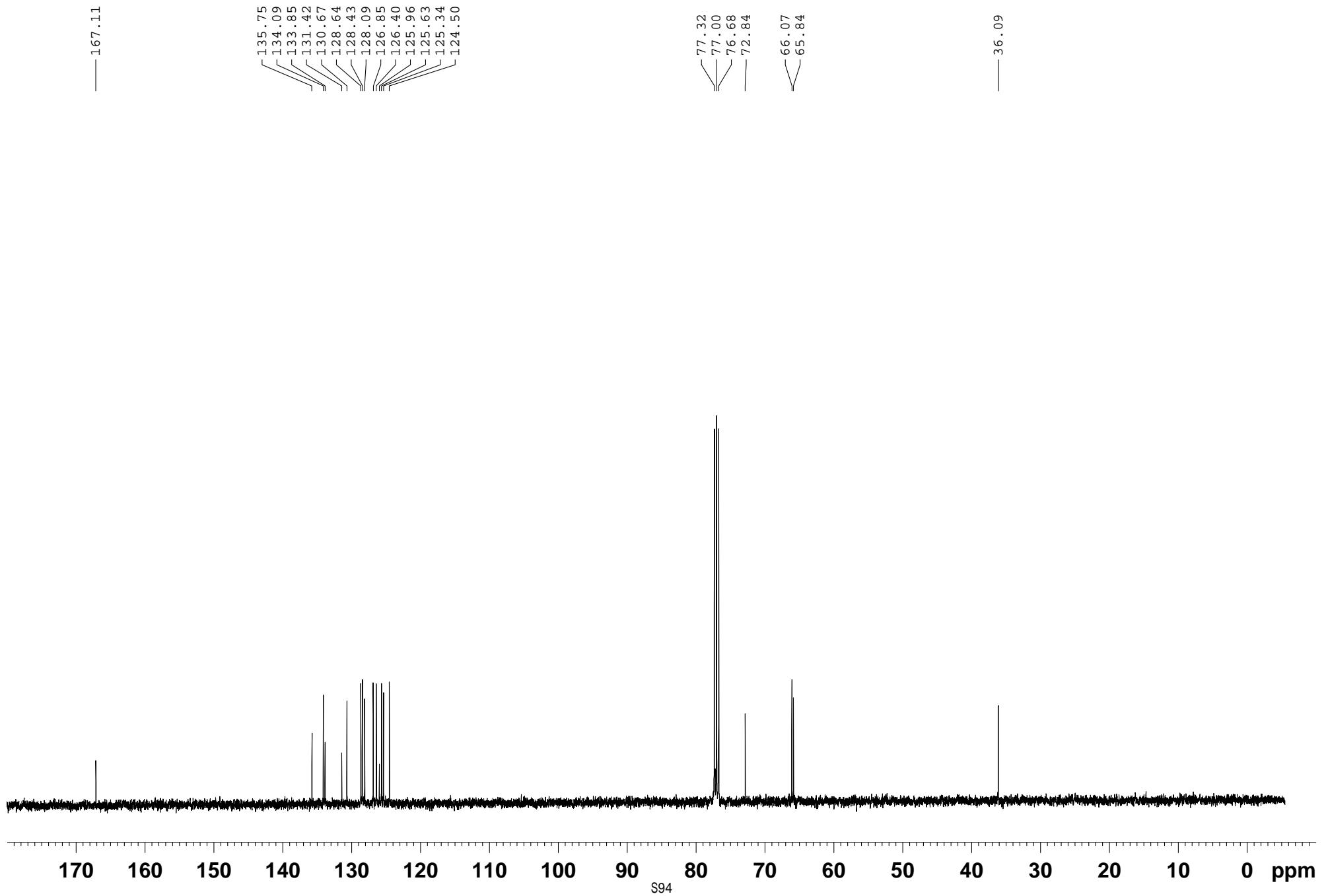
lbs-NAP-C1-C1



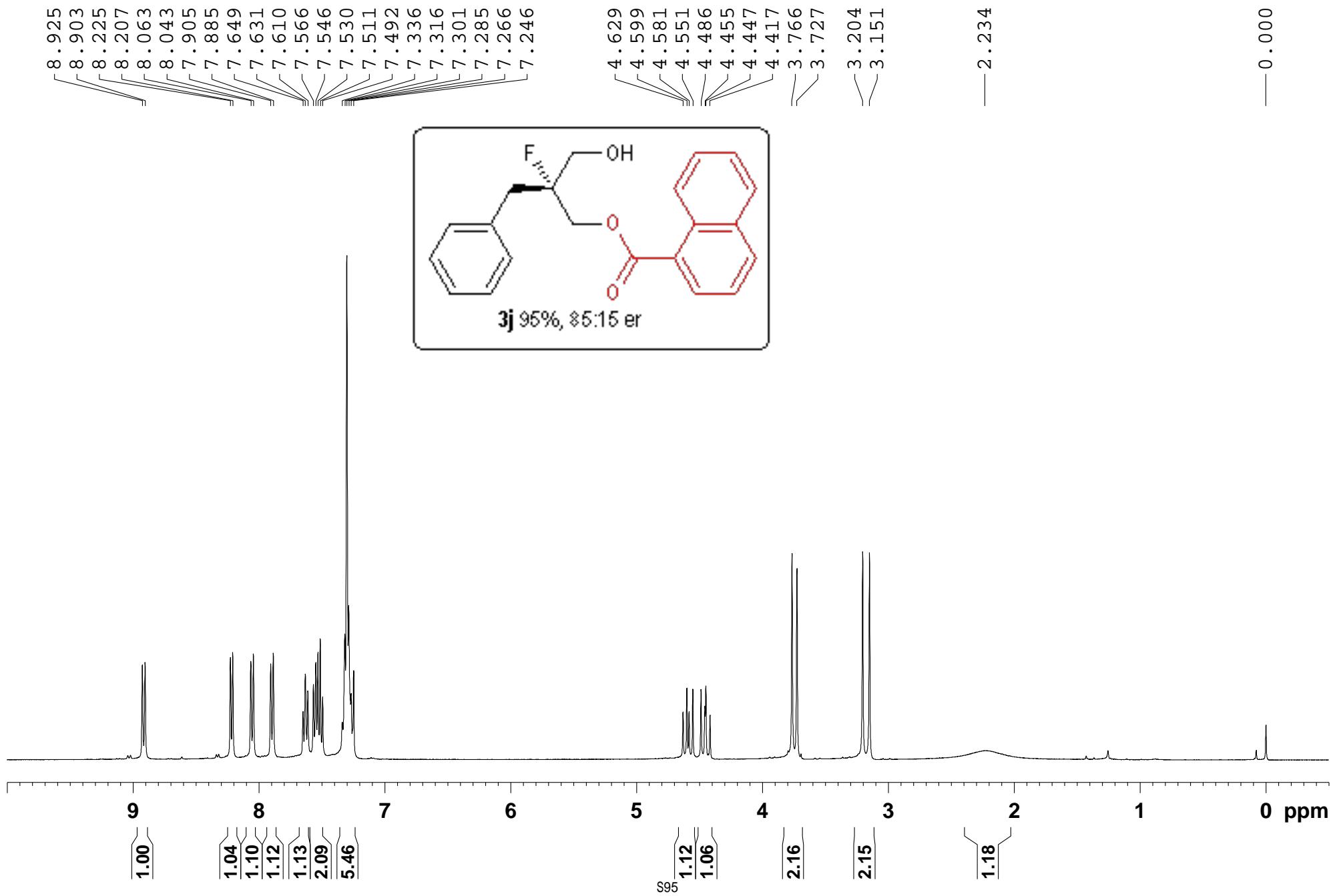
2-Cl-thiol-H



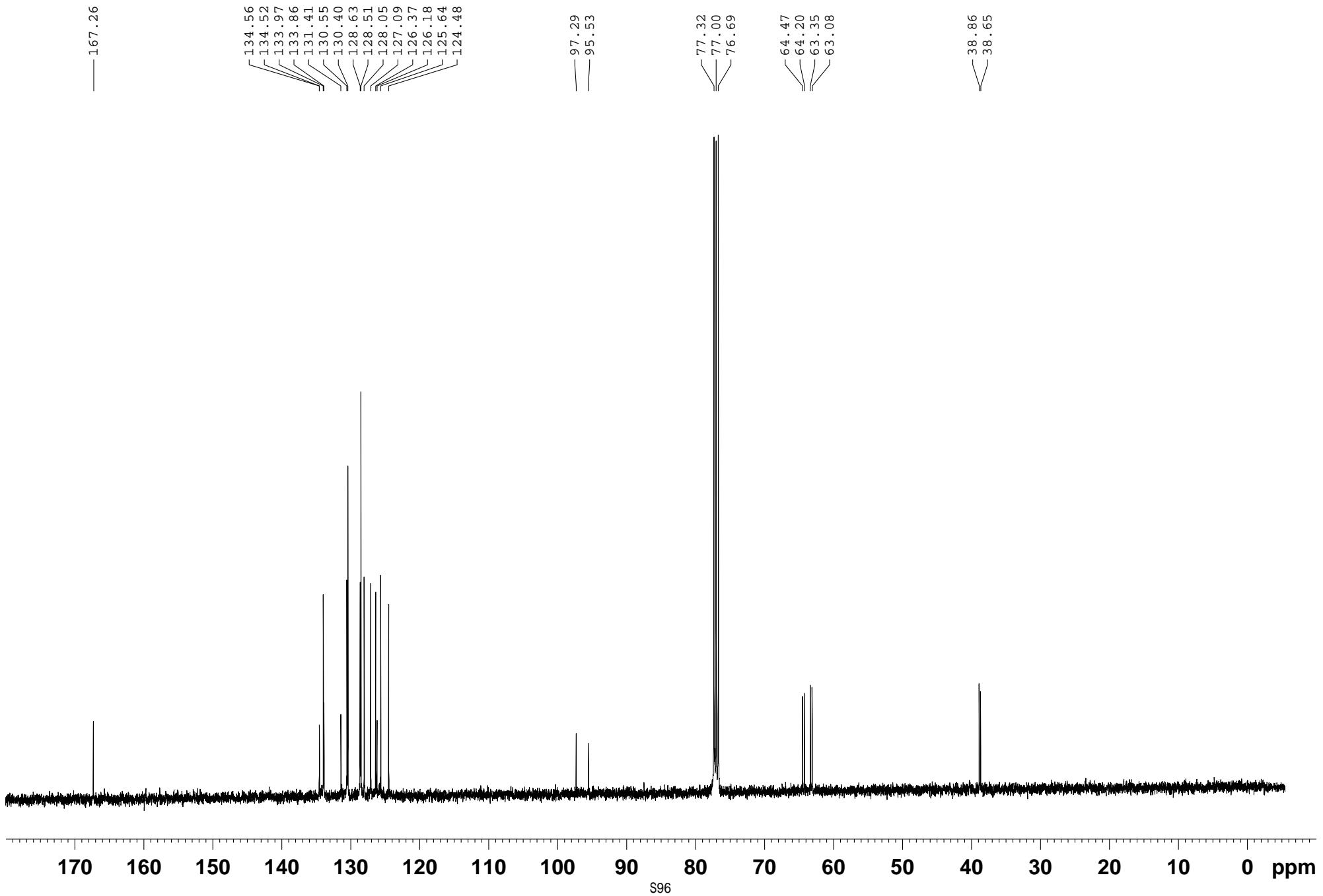
2-Cl-thiol-C



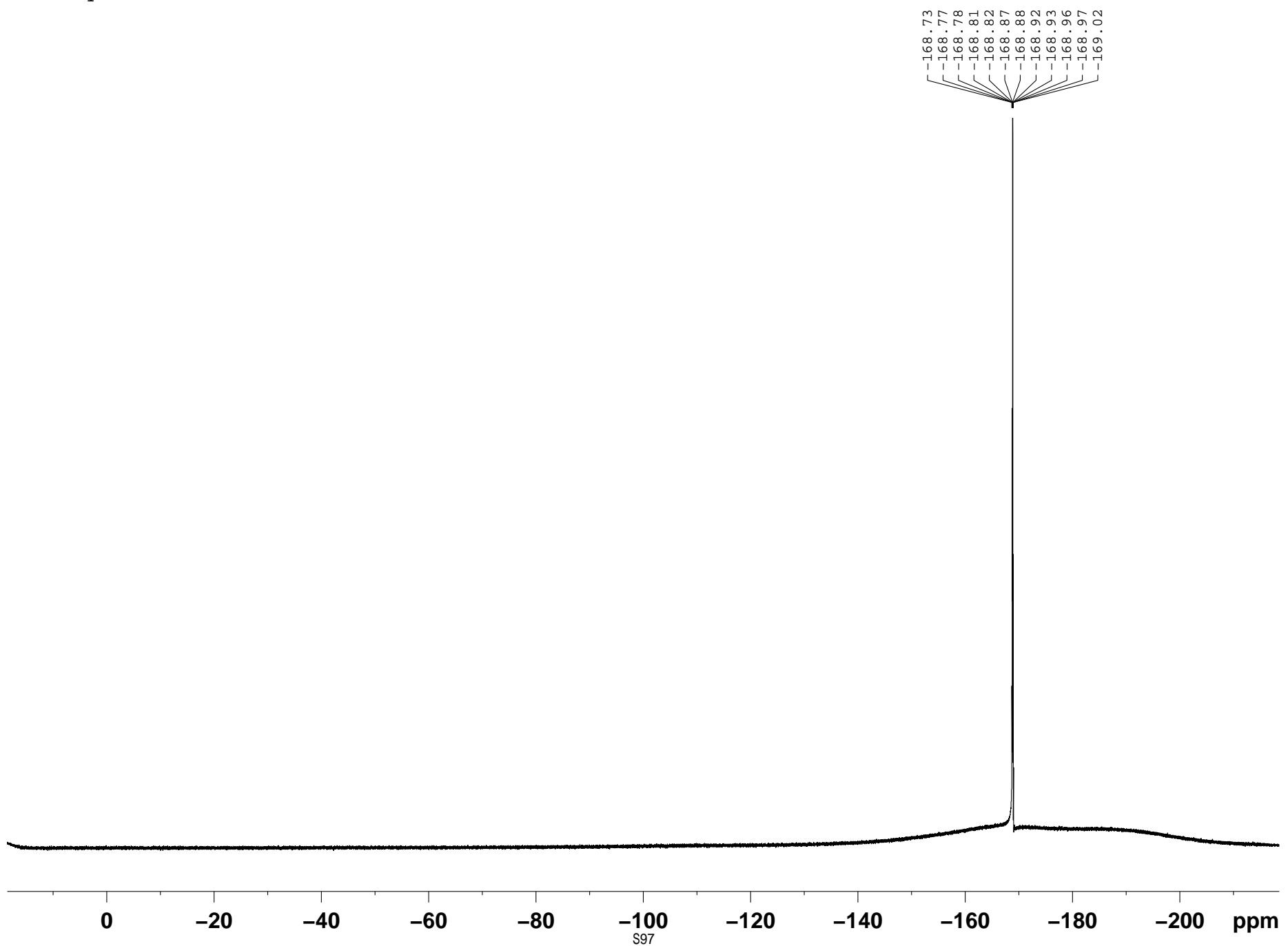
lbs-desymmetrization-F-H



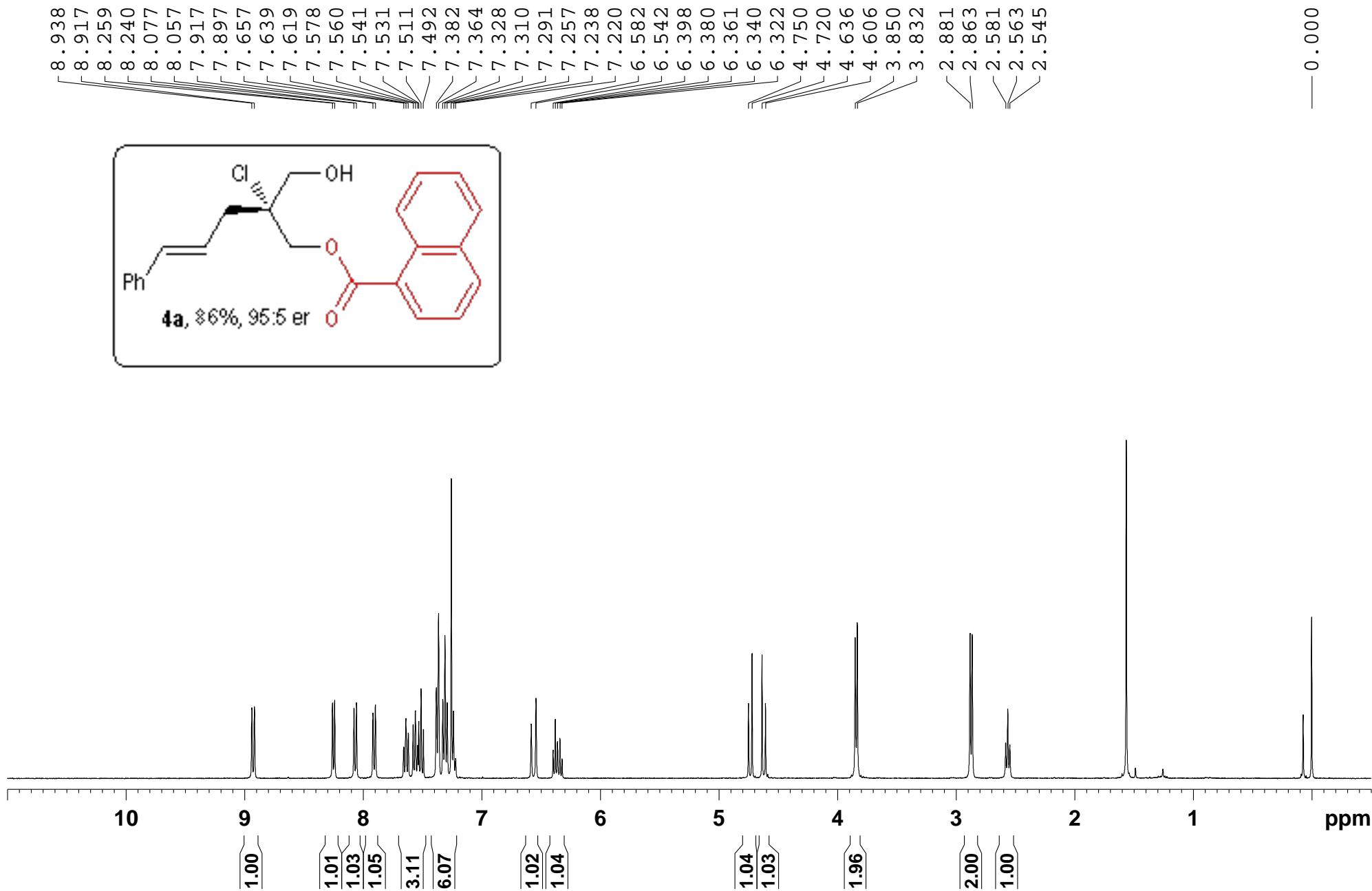
lbs-desymmetrization-F-C1



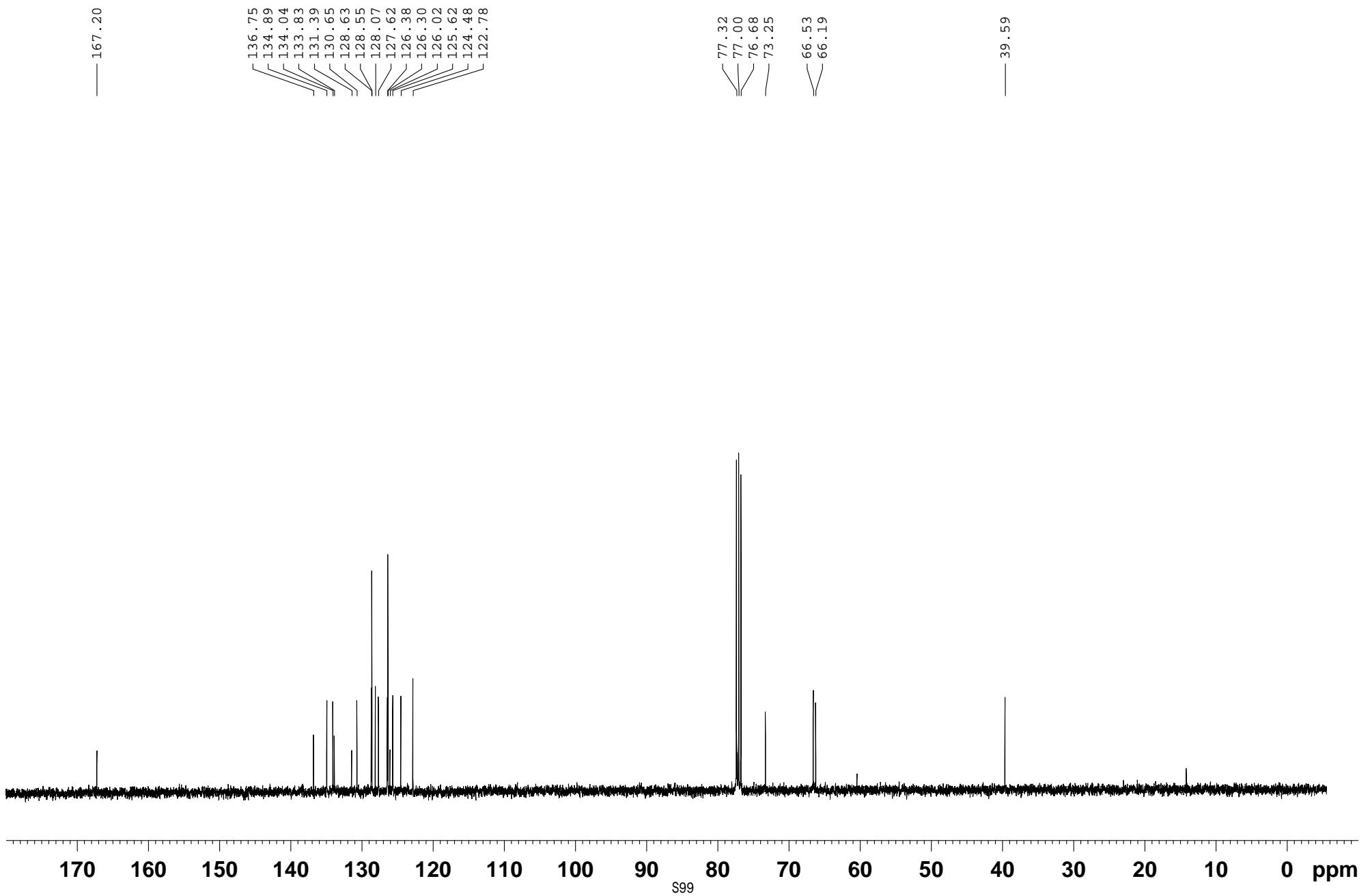
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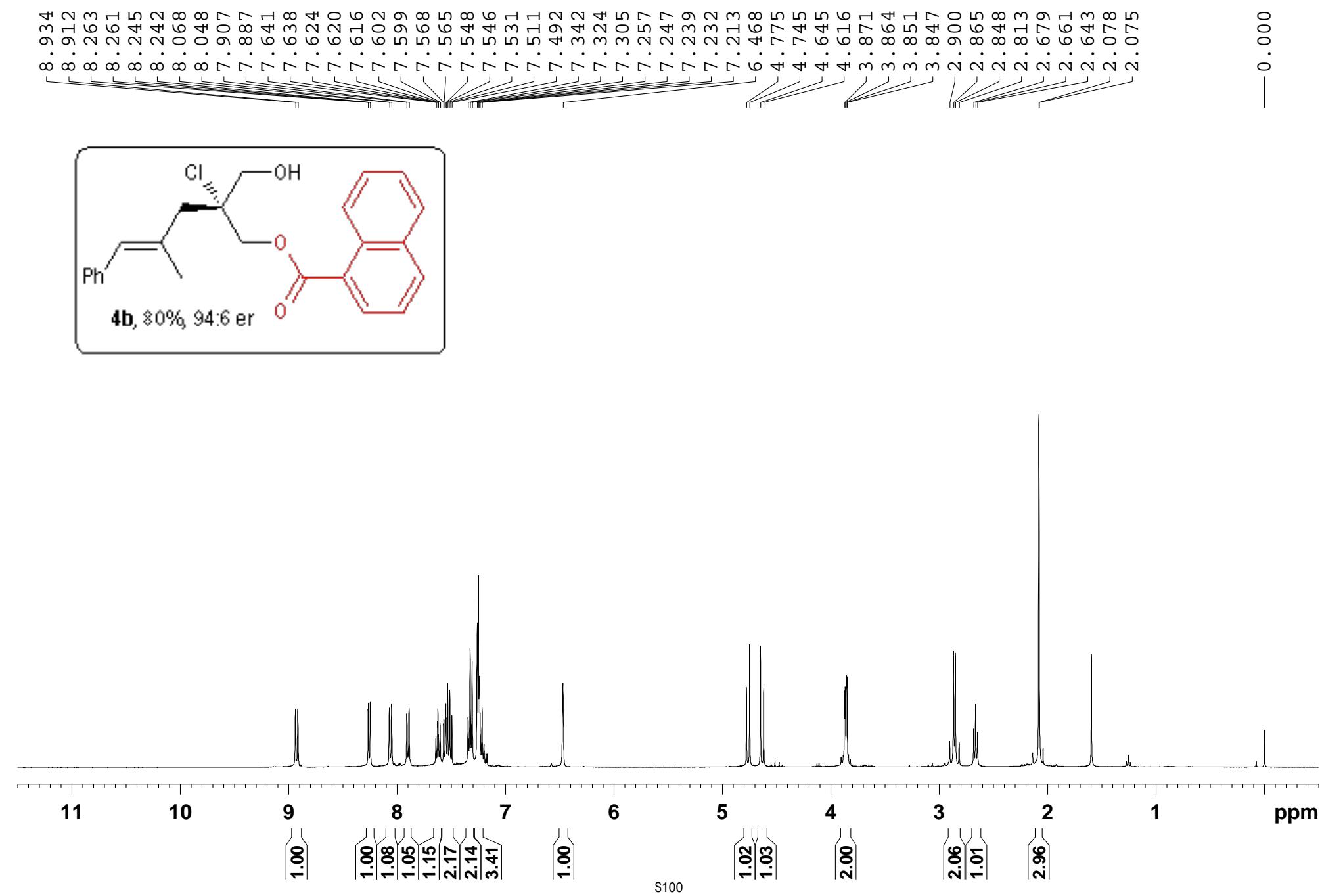
lbs-styrene-CH₂-H1



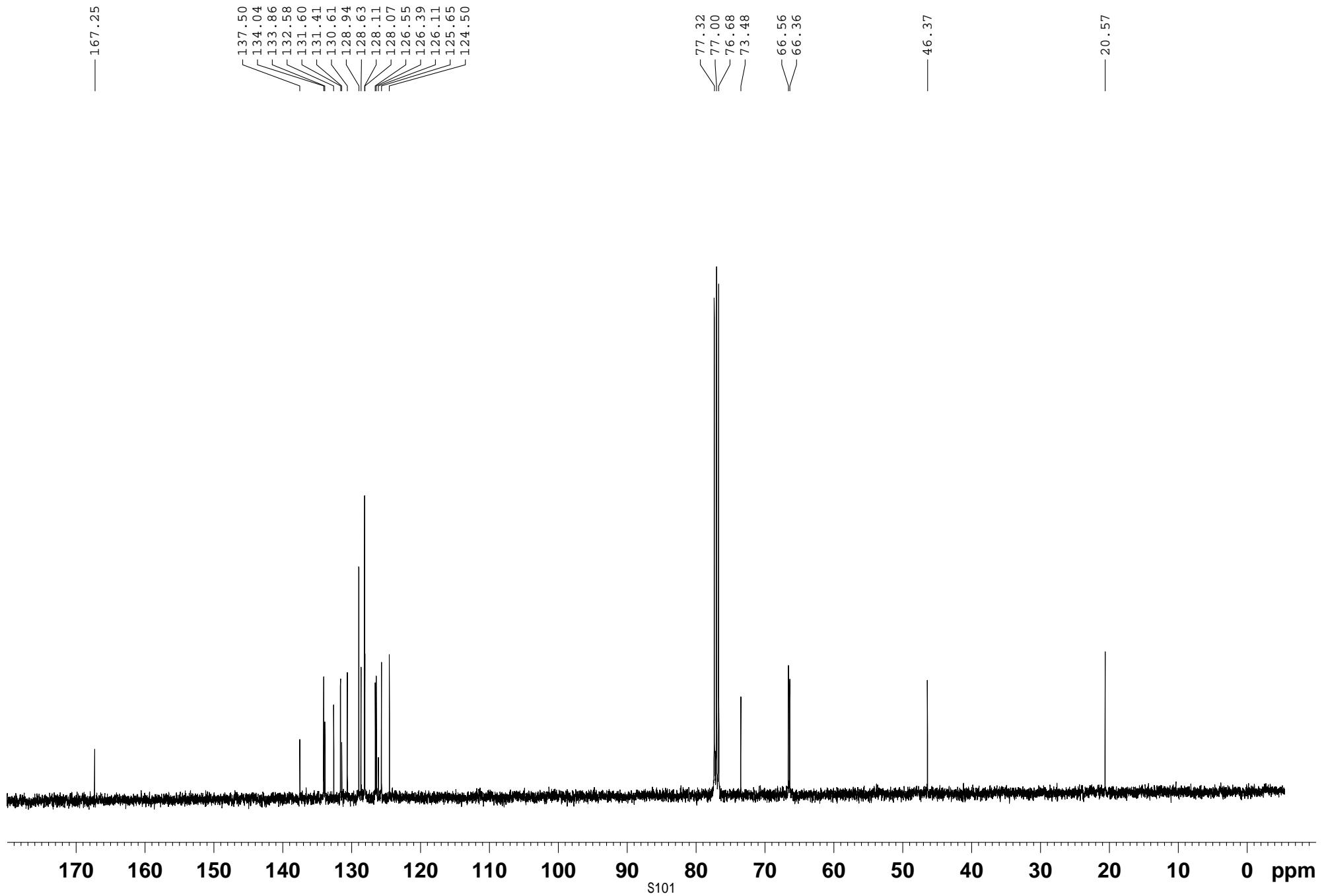
2-Cl-styrene-C



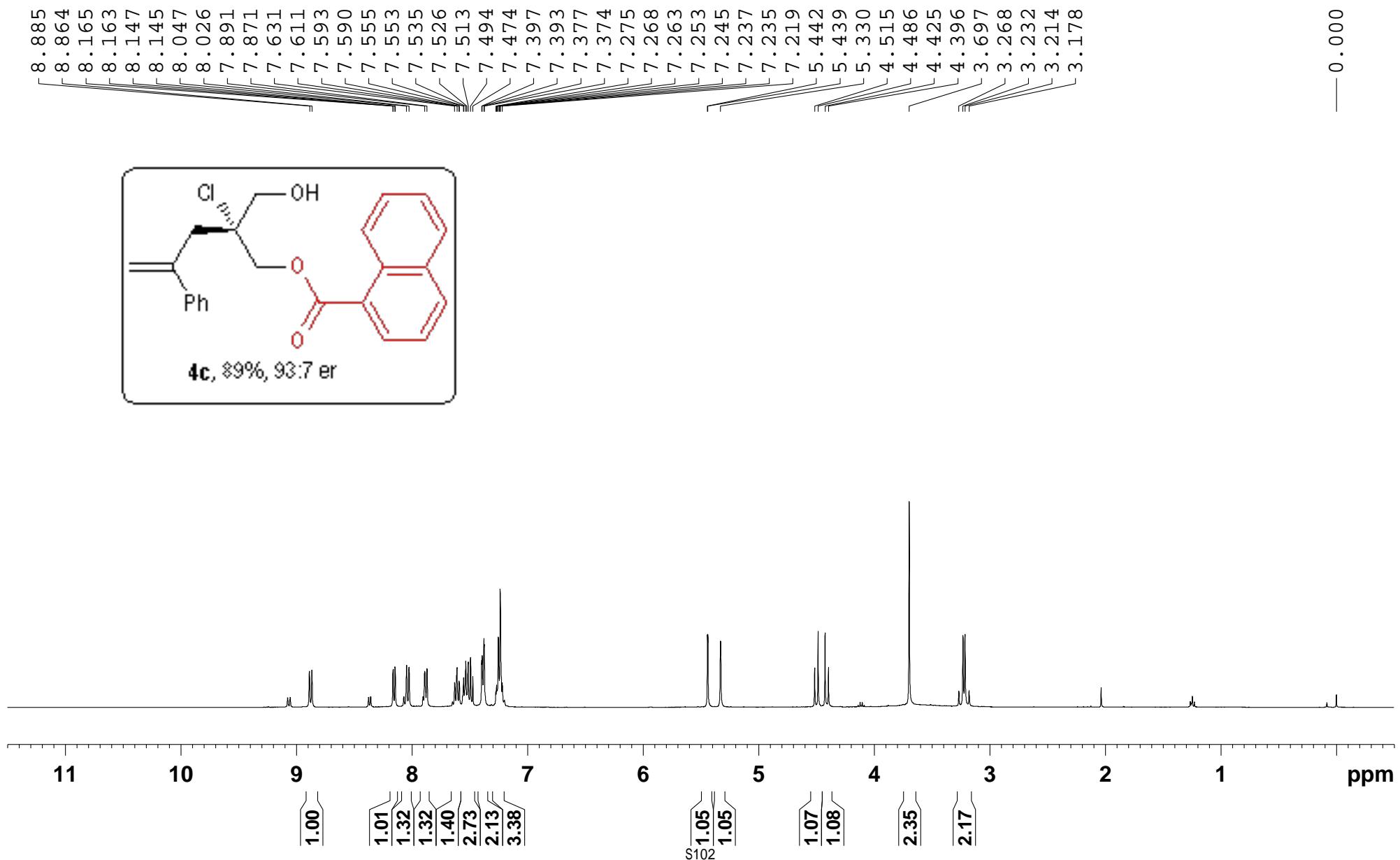
lbs-styrene-a-me-H2



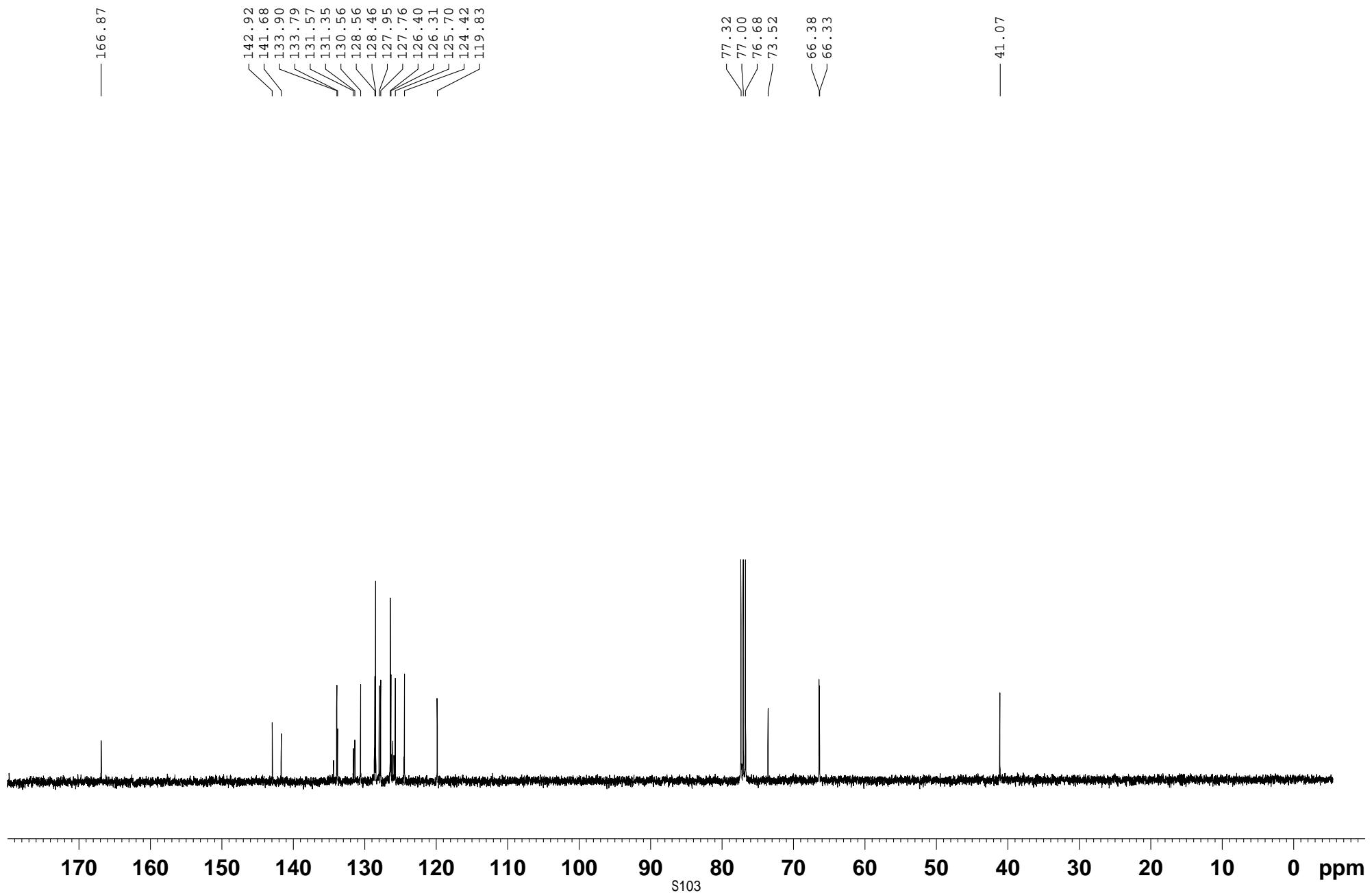
lbs-styrene-a-me-C1



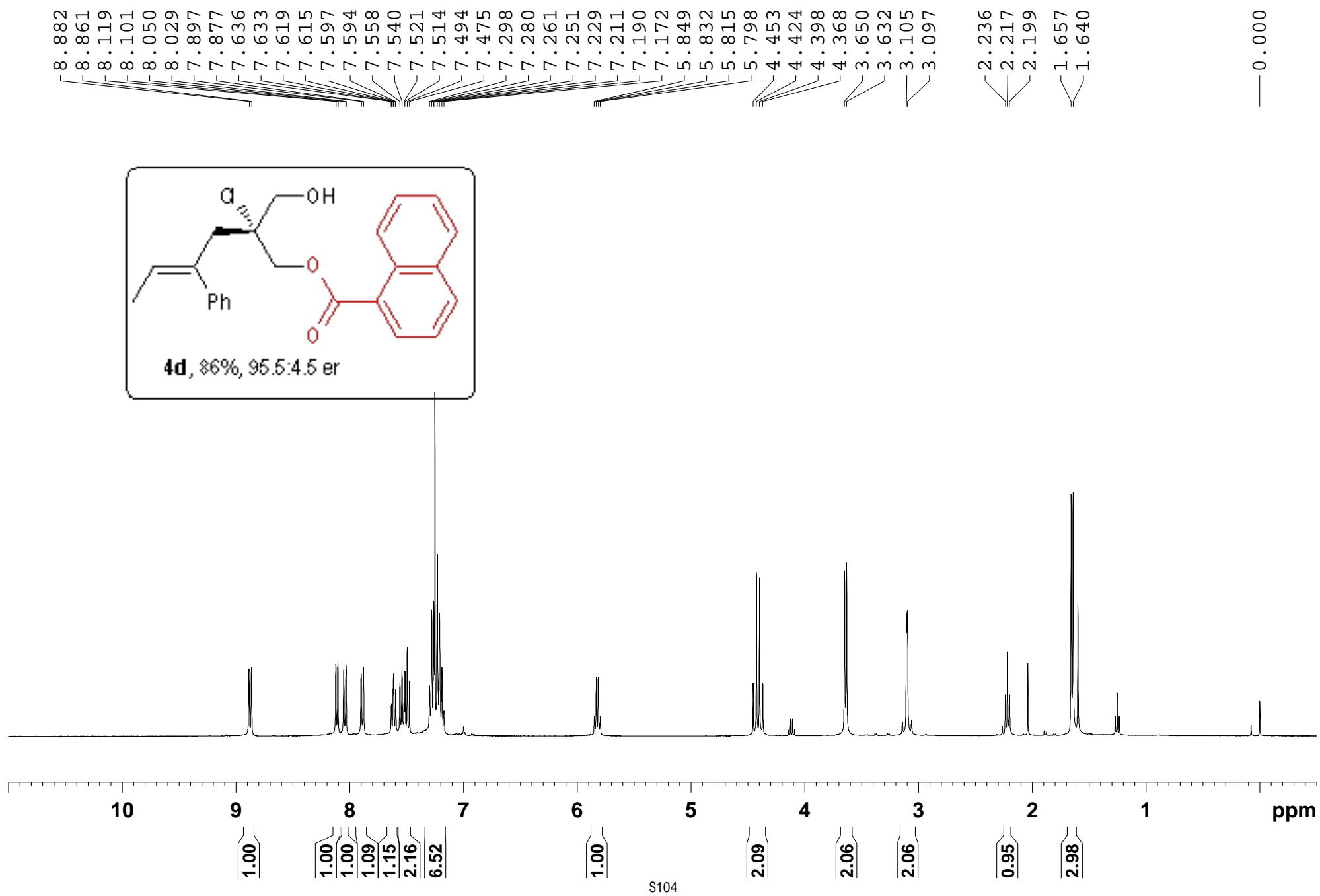
1bs-2-styrene-2'-2-Cl-H



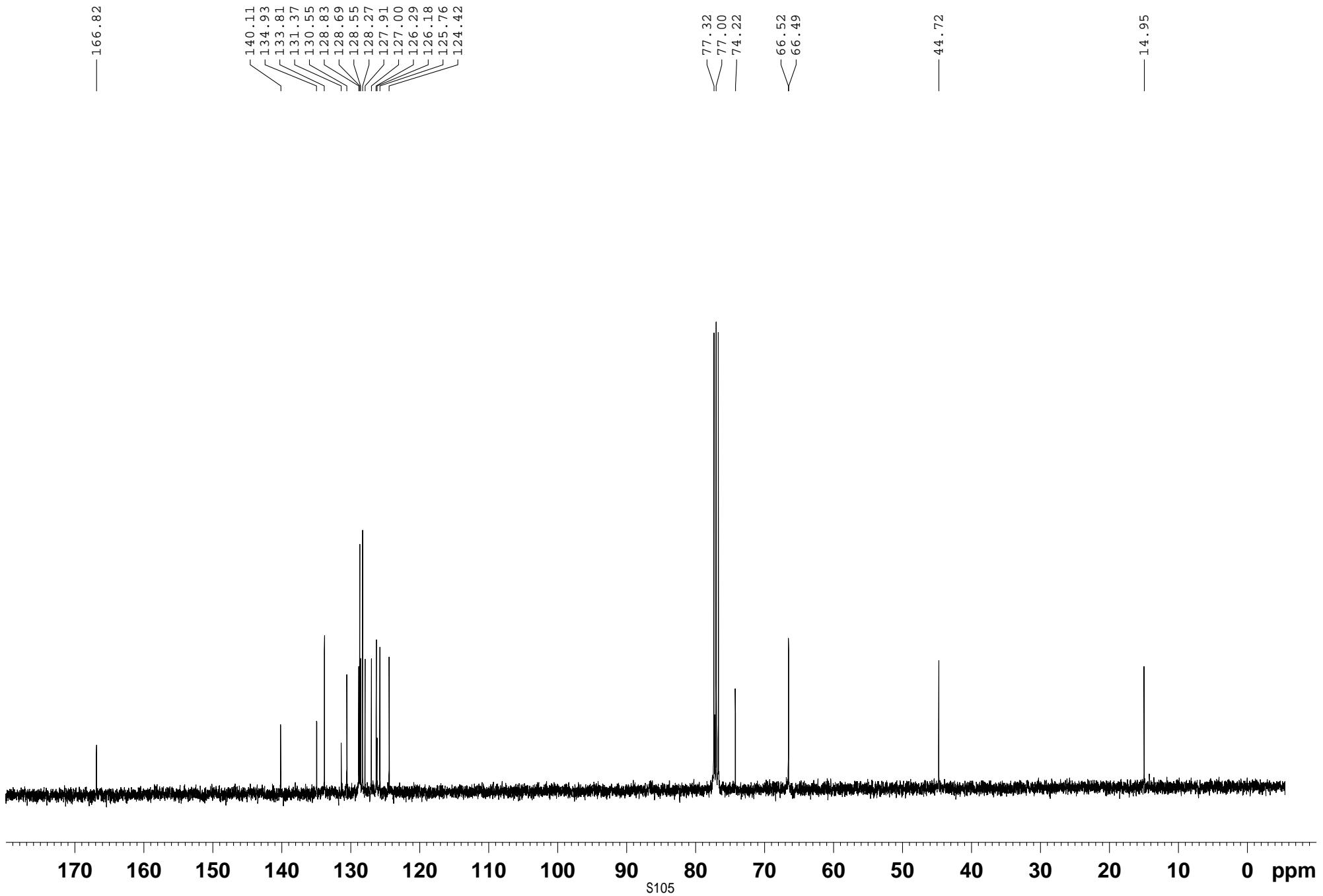
lbs-2-styrene-2'-2-Cl-C



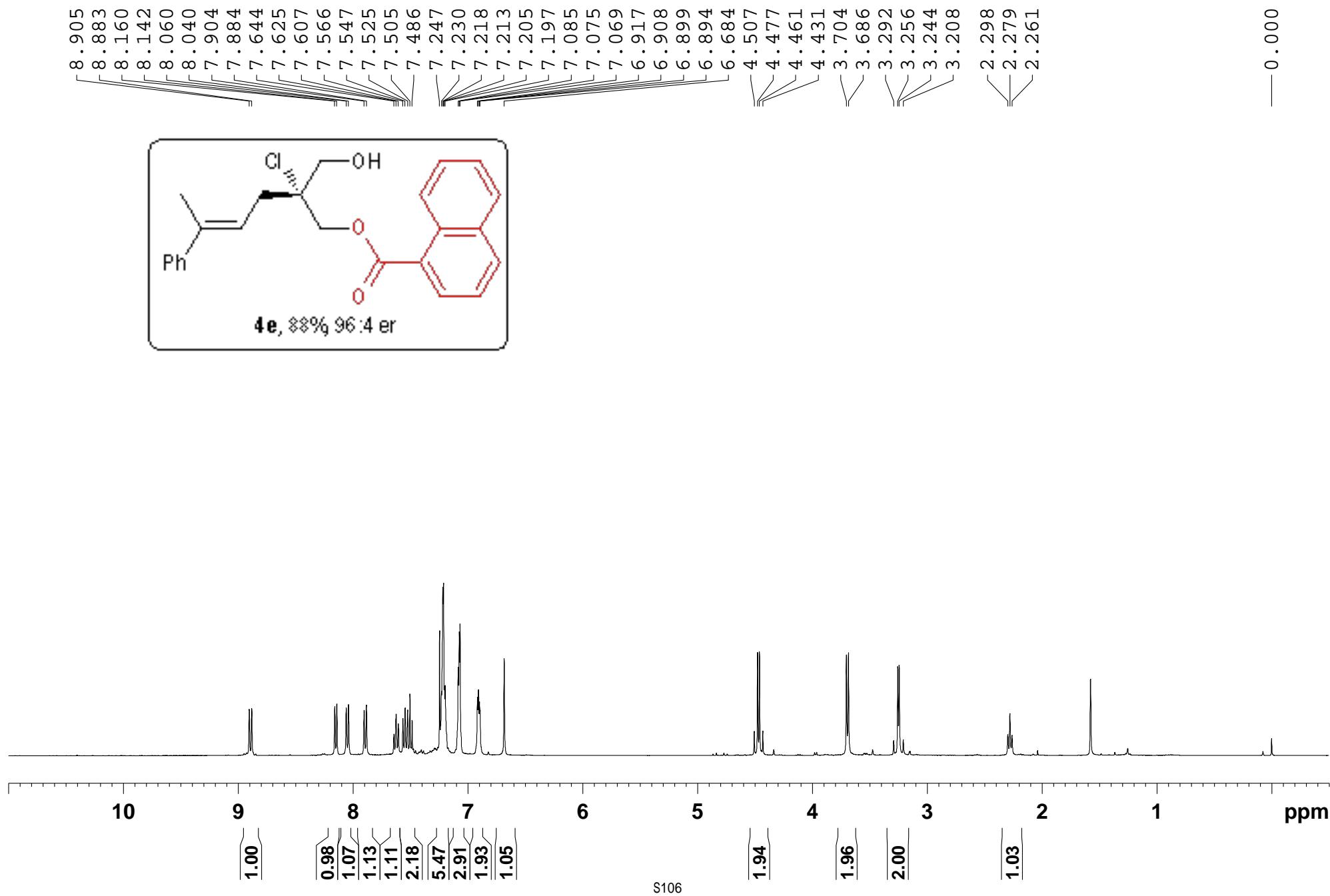
lbs-a-styrene-b'-Me-H1



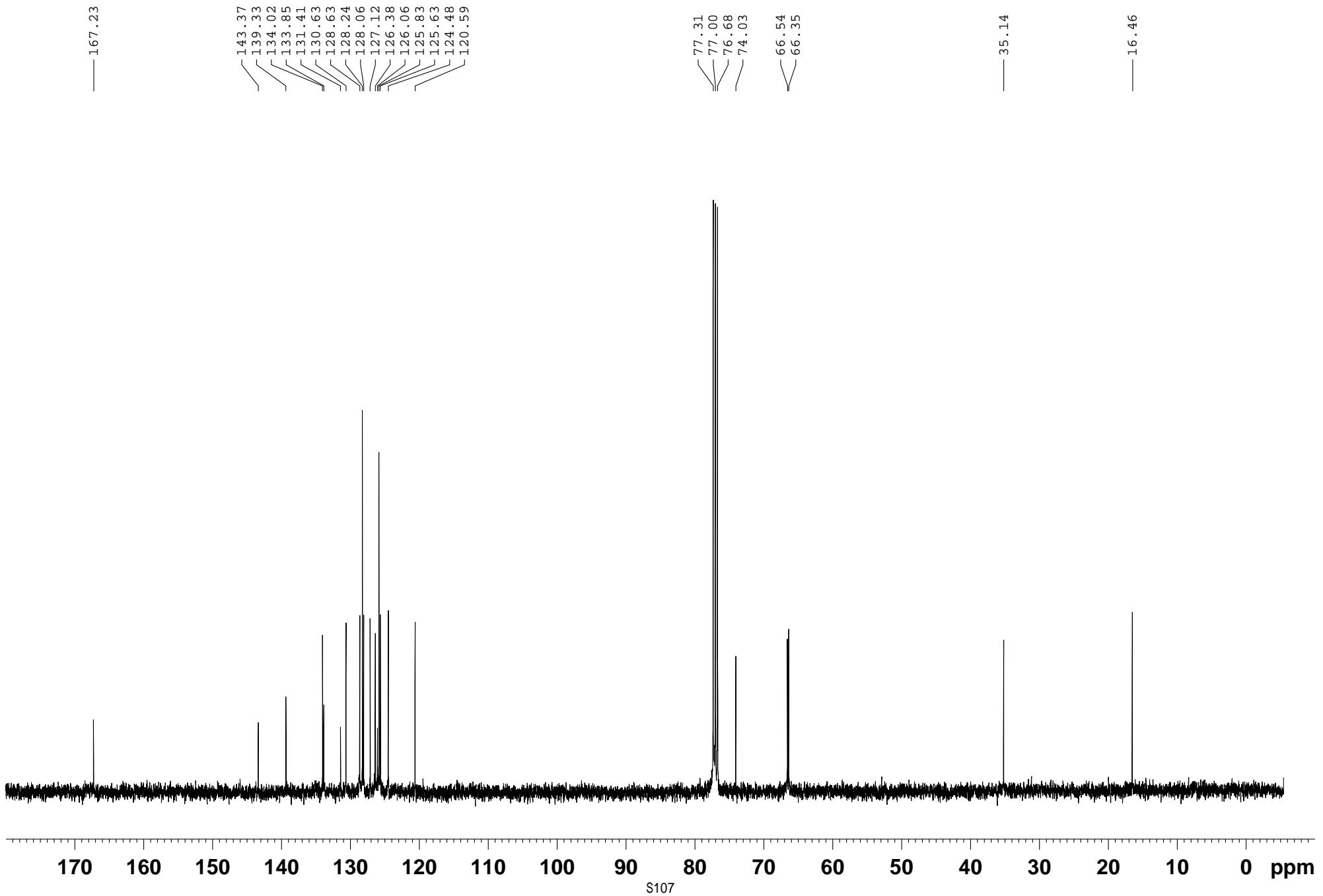
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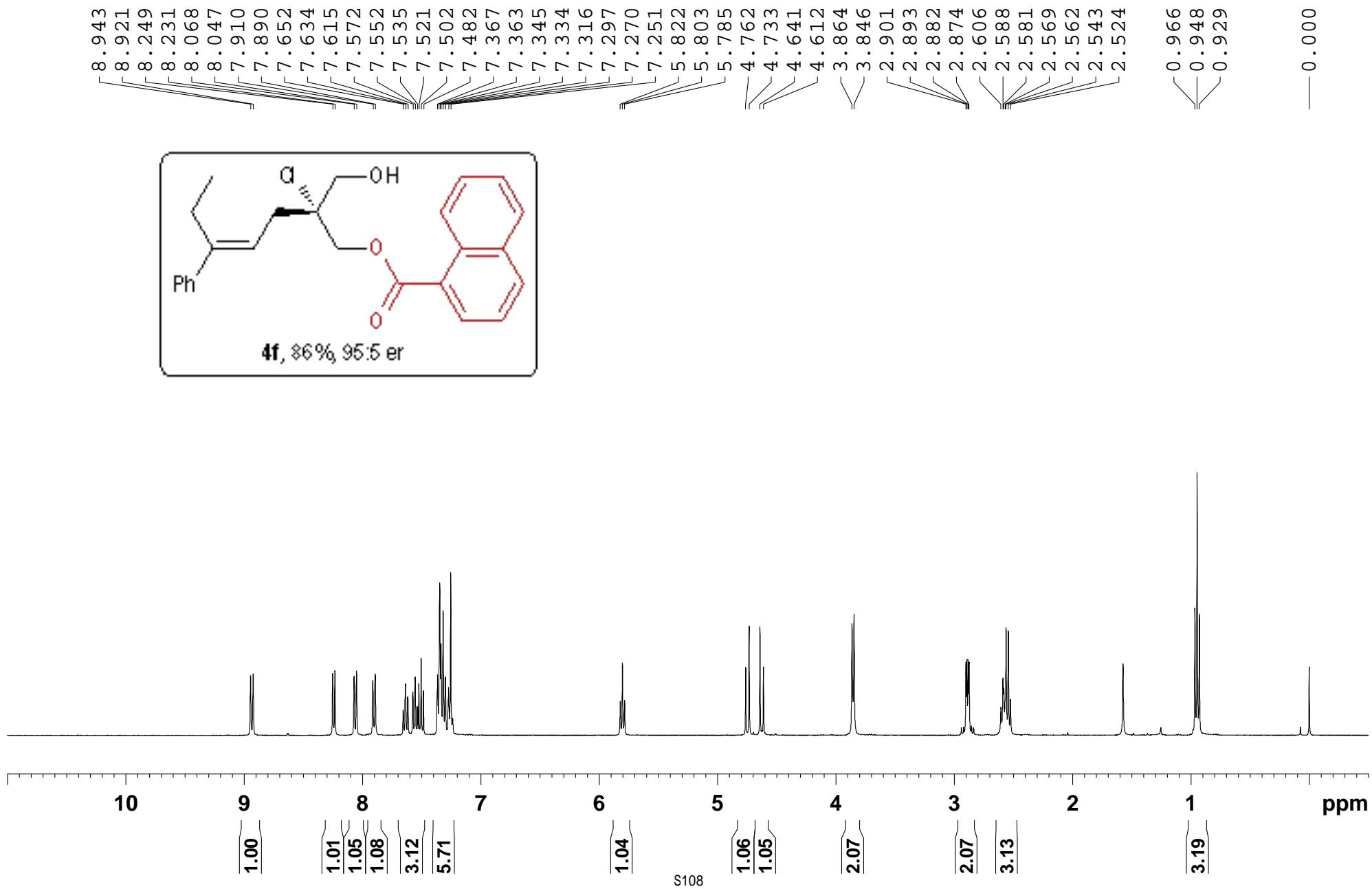
lbs-styrene-5-Ph-6-Ph-H



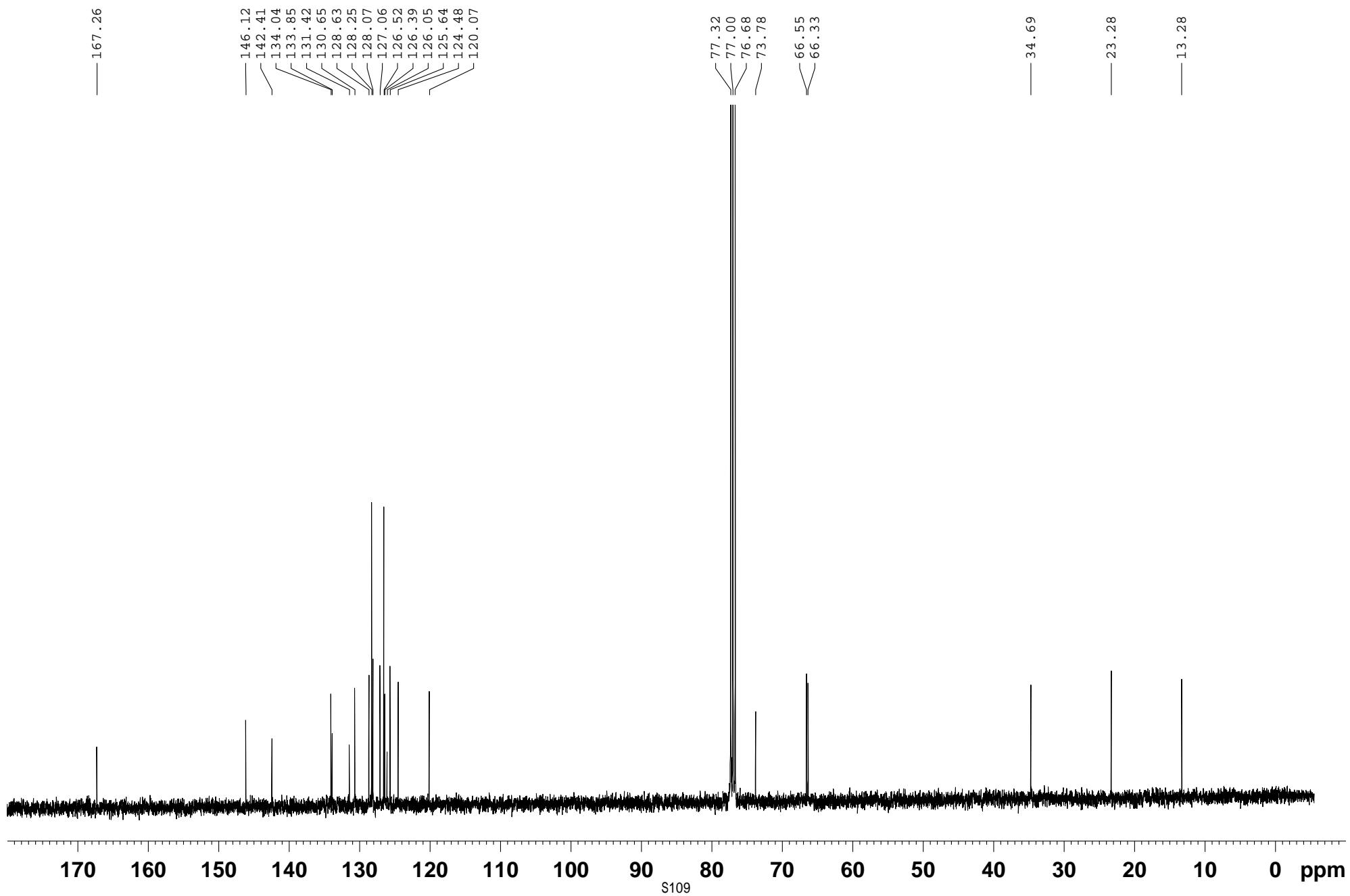
lbs-styrene-5-Me-5-Ph-C



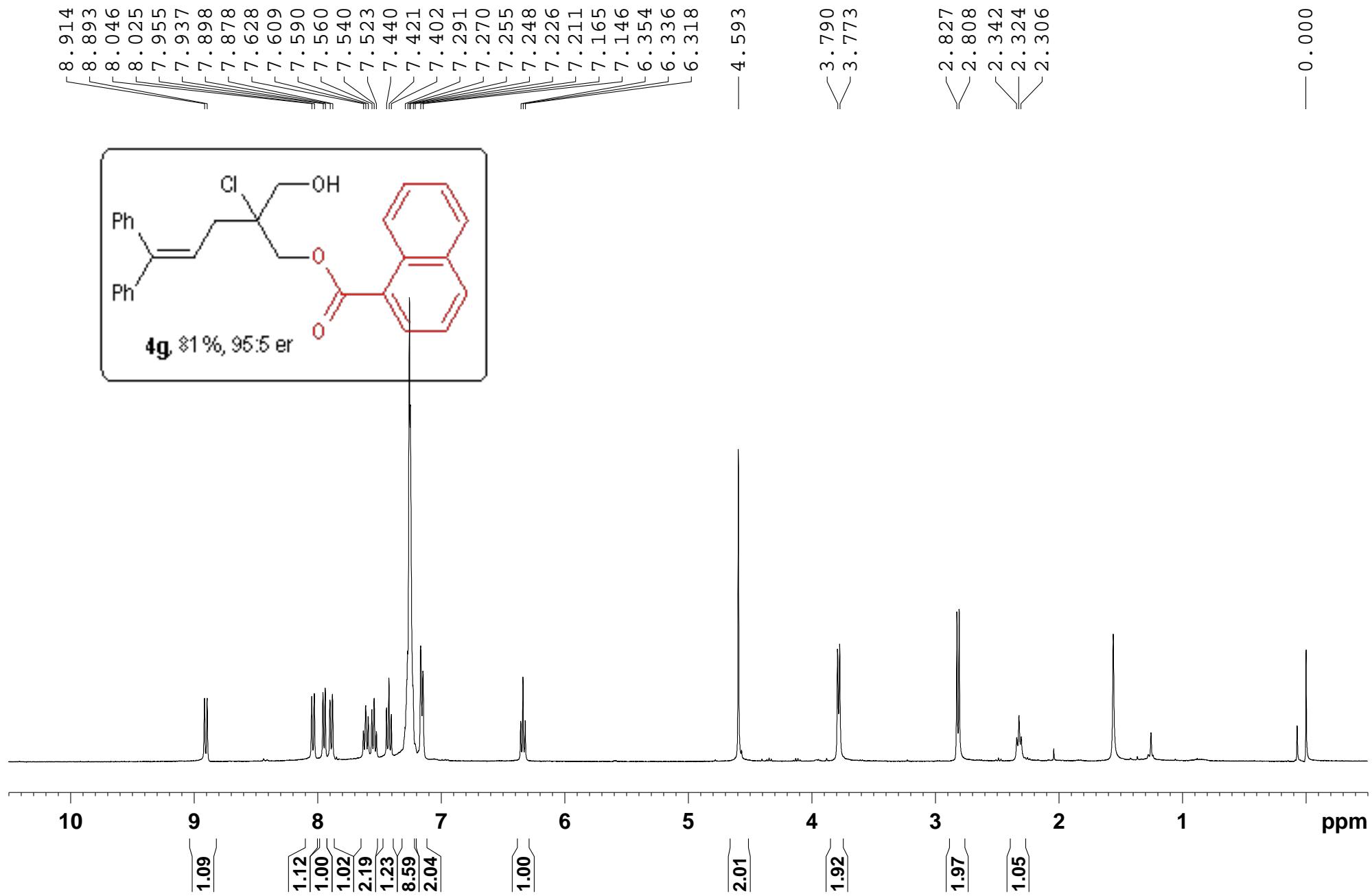
lbs-5-Et-5-Ph-H



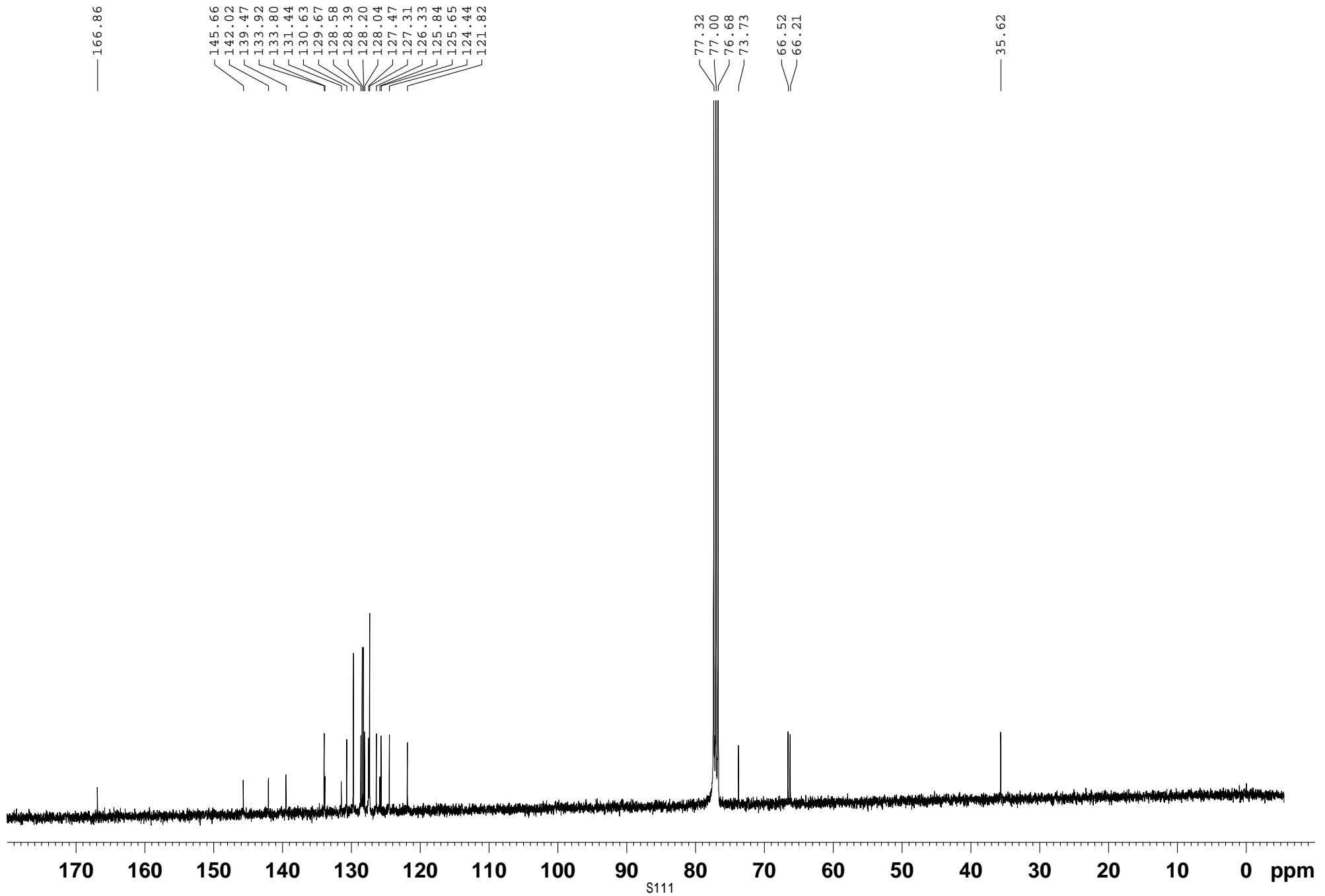
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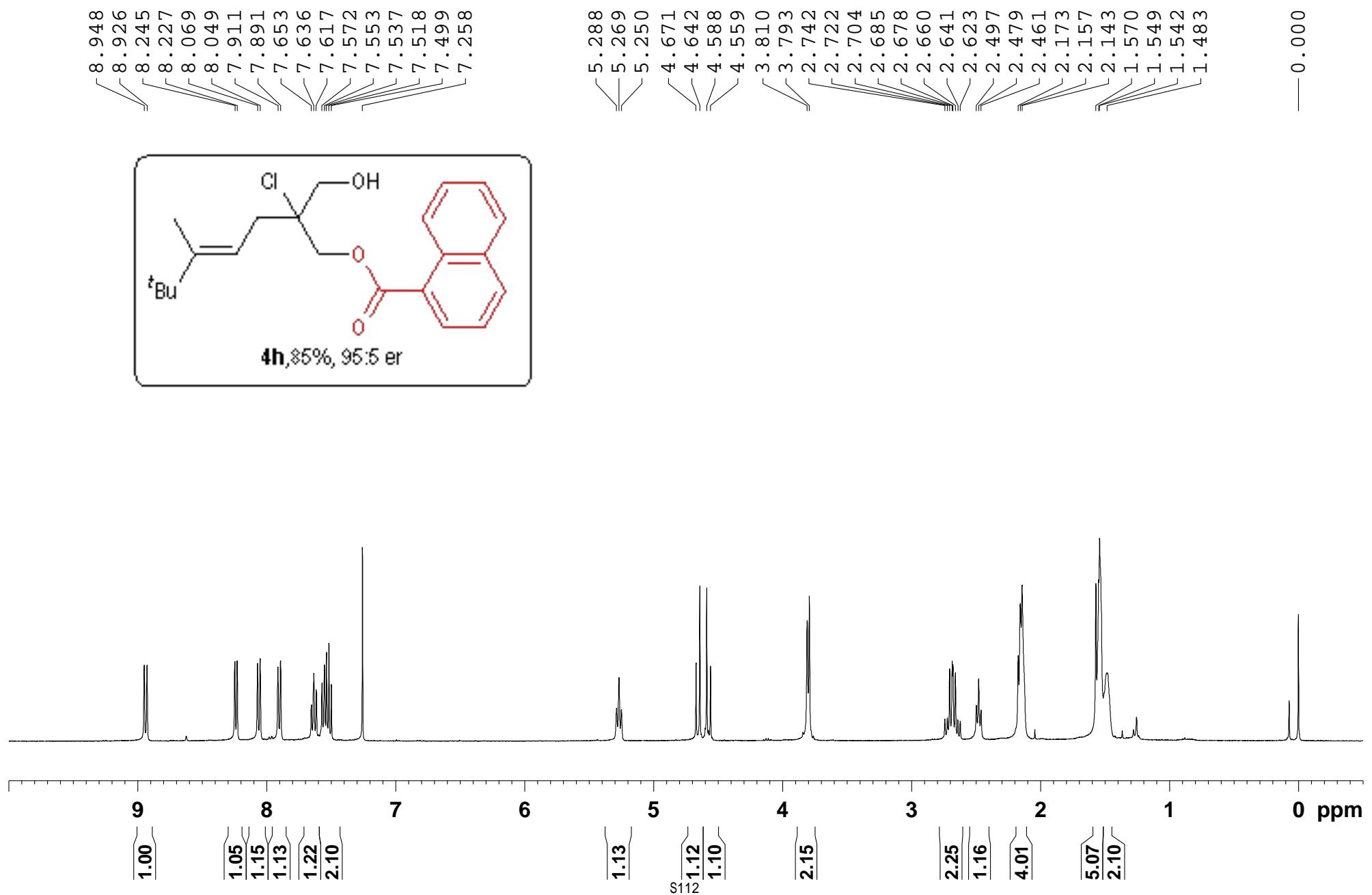
1bs-5-diphenyl-H



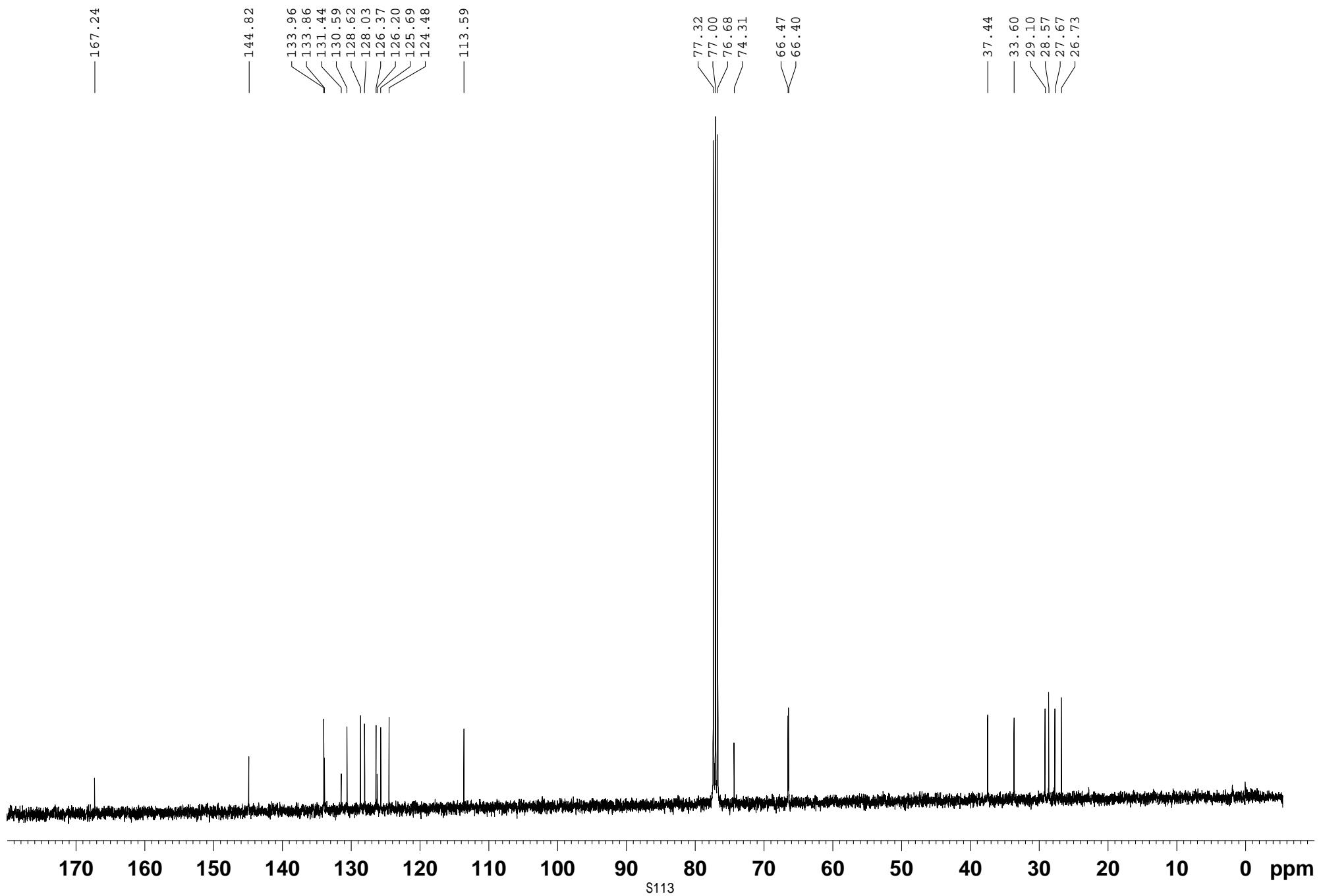
1bs-5-diphenyl-C



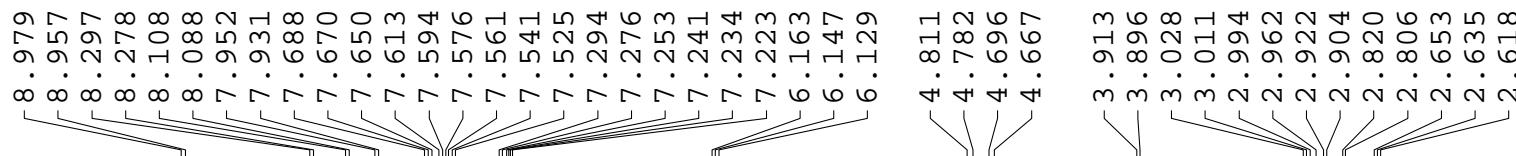
1bs-5-tBu-5-Me-H



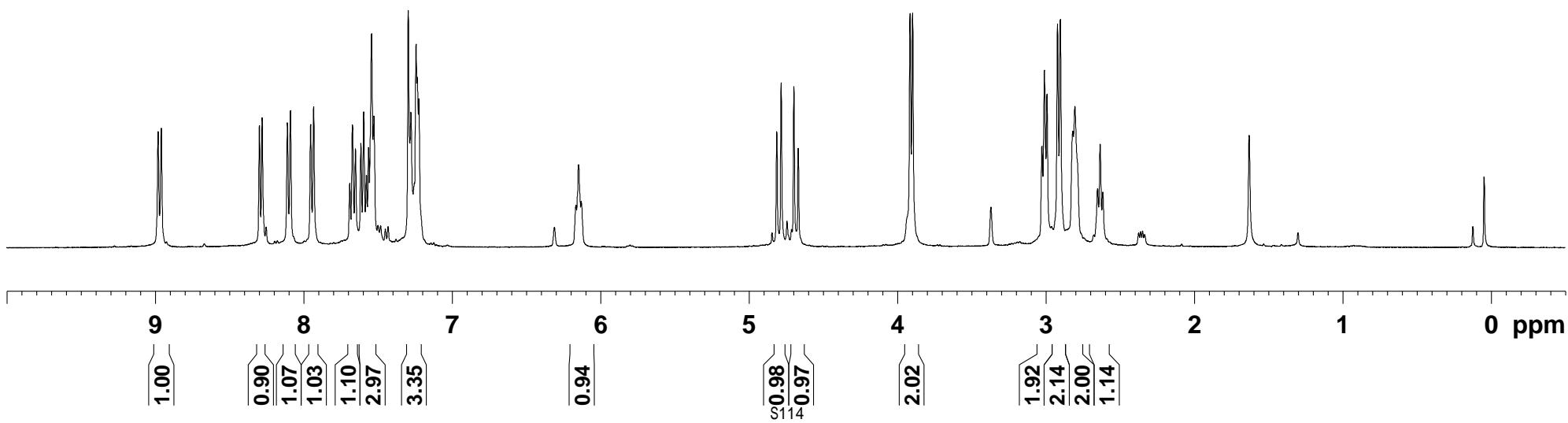
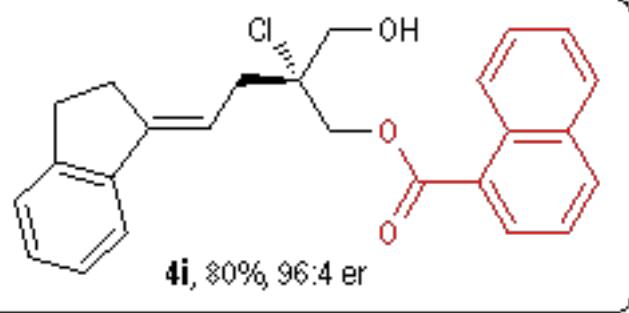
lbs-5-tBu-5-Me-C



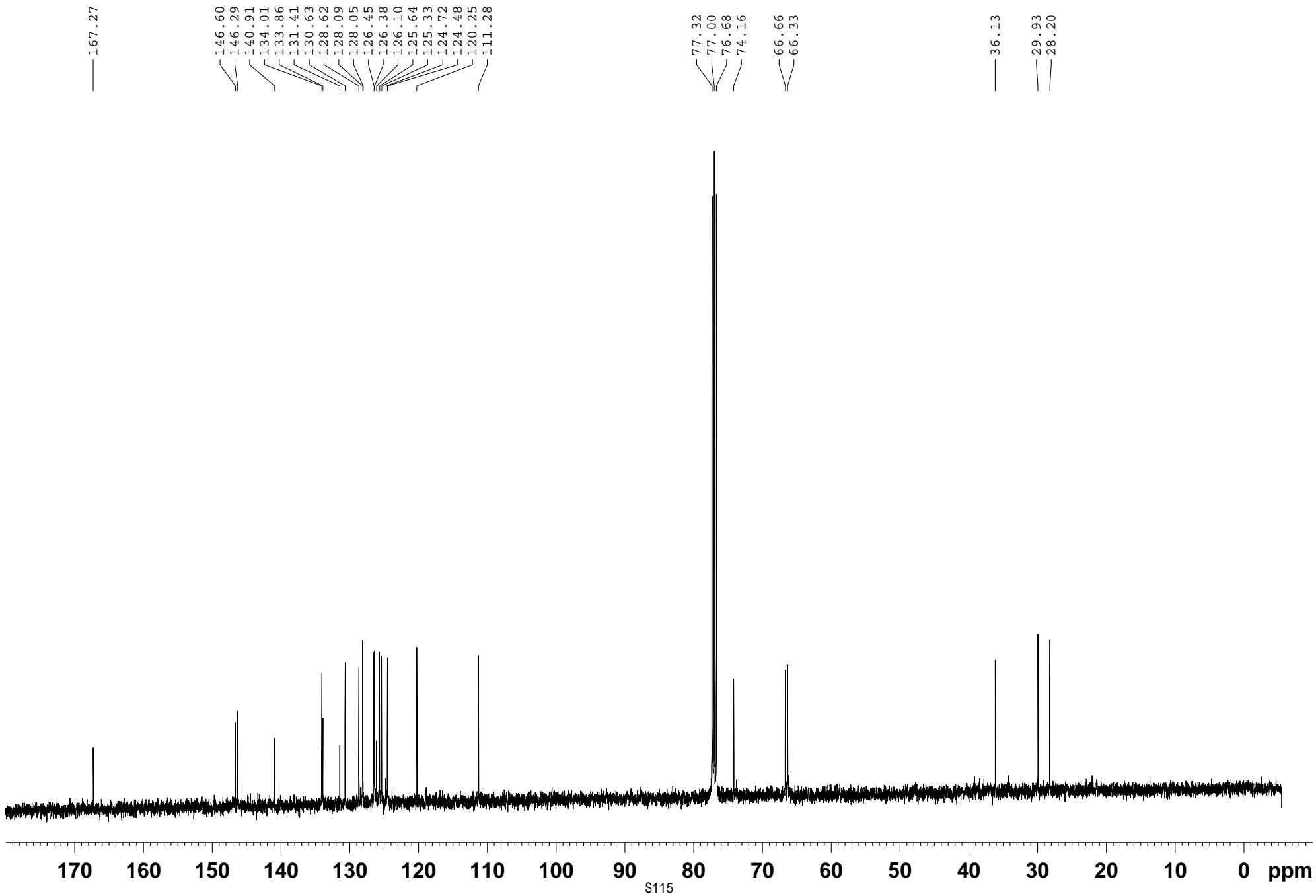
1bs-benzenecyclopentane-H1

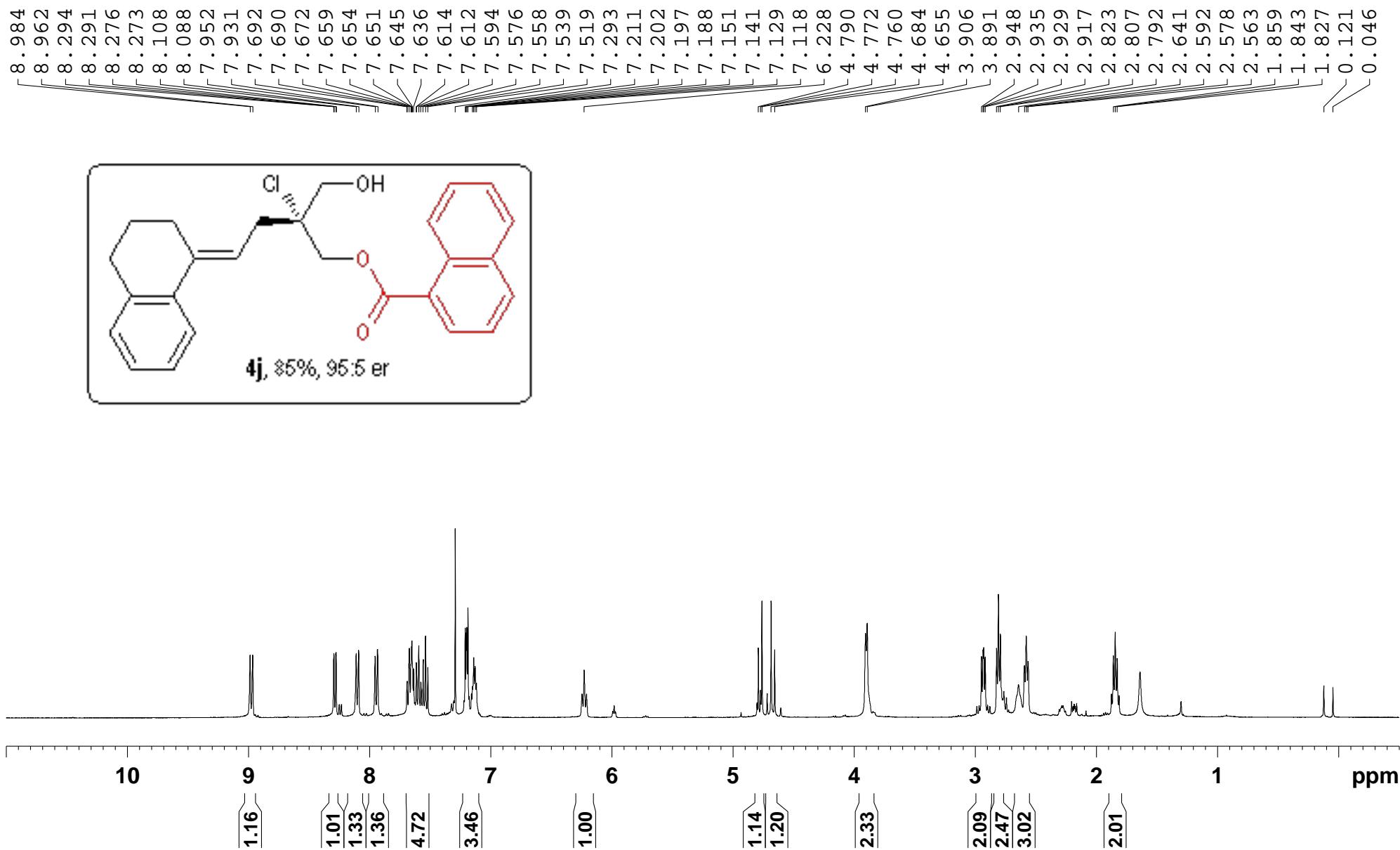


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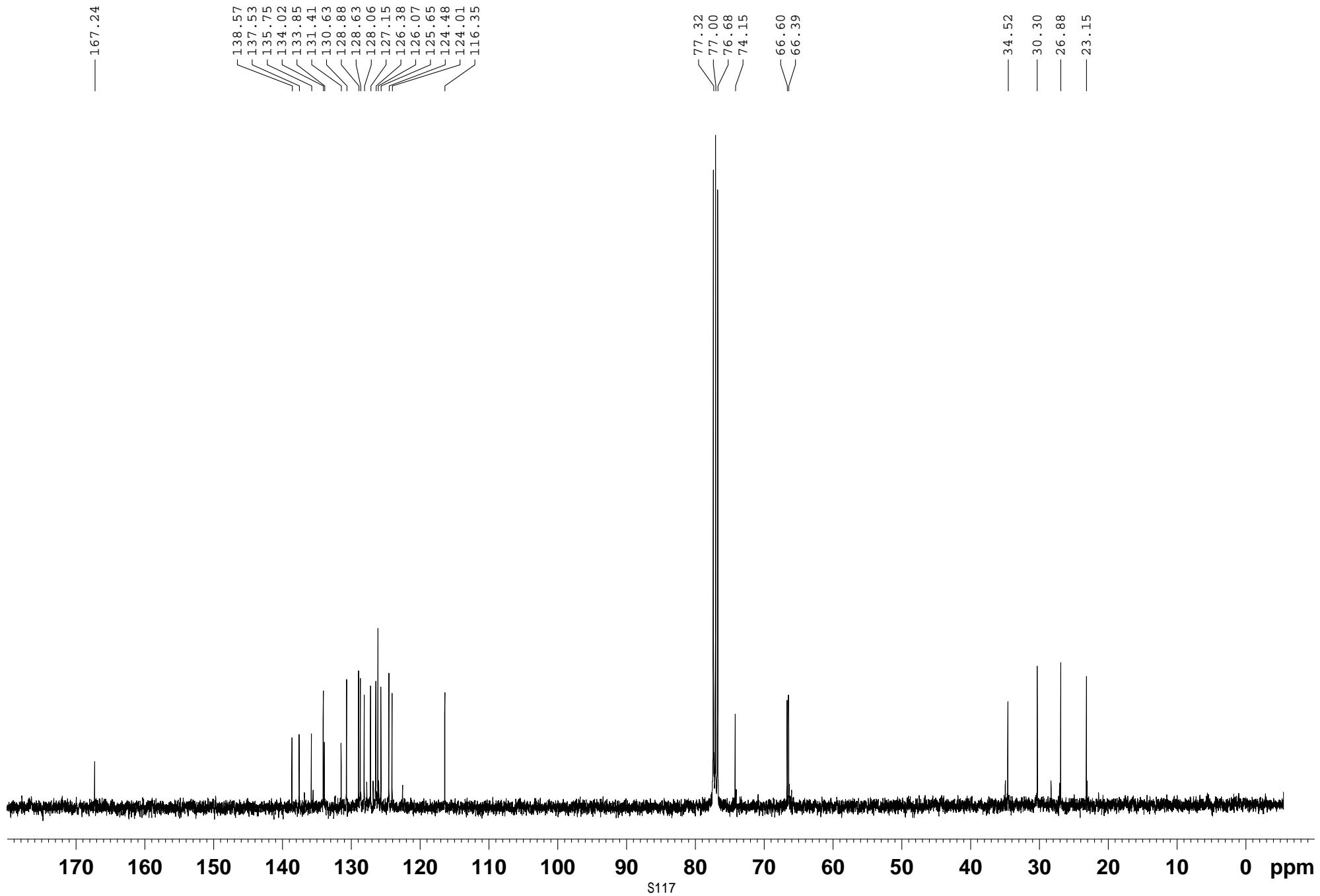


lbs-benzenecyclopentane-C

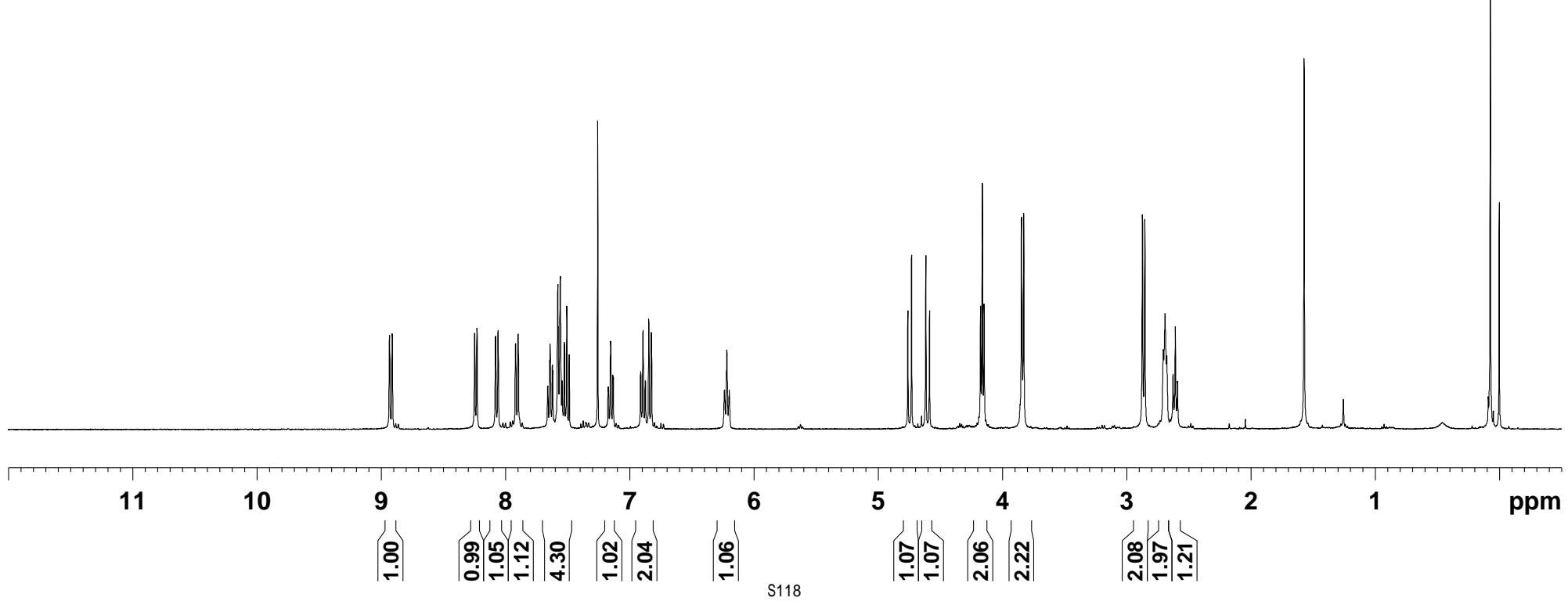
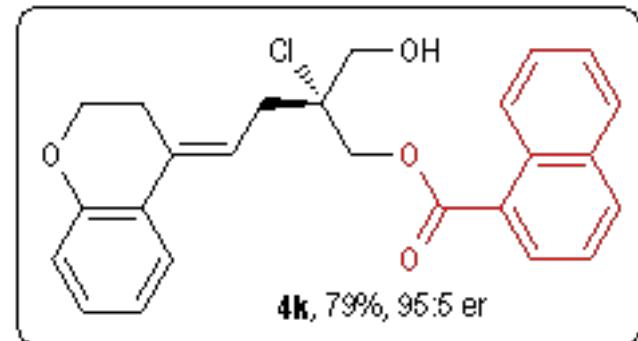
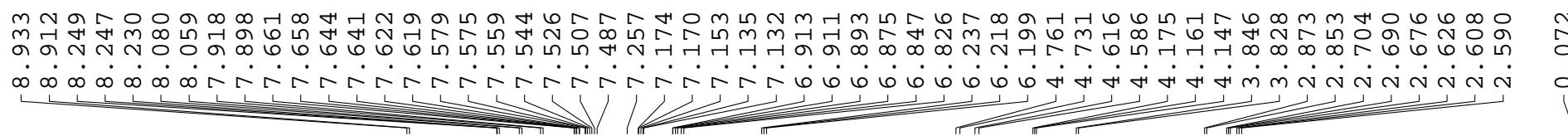




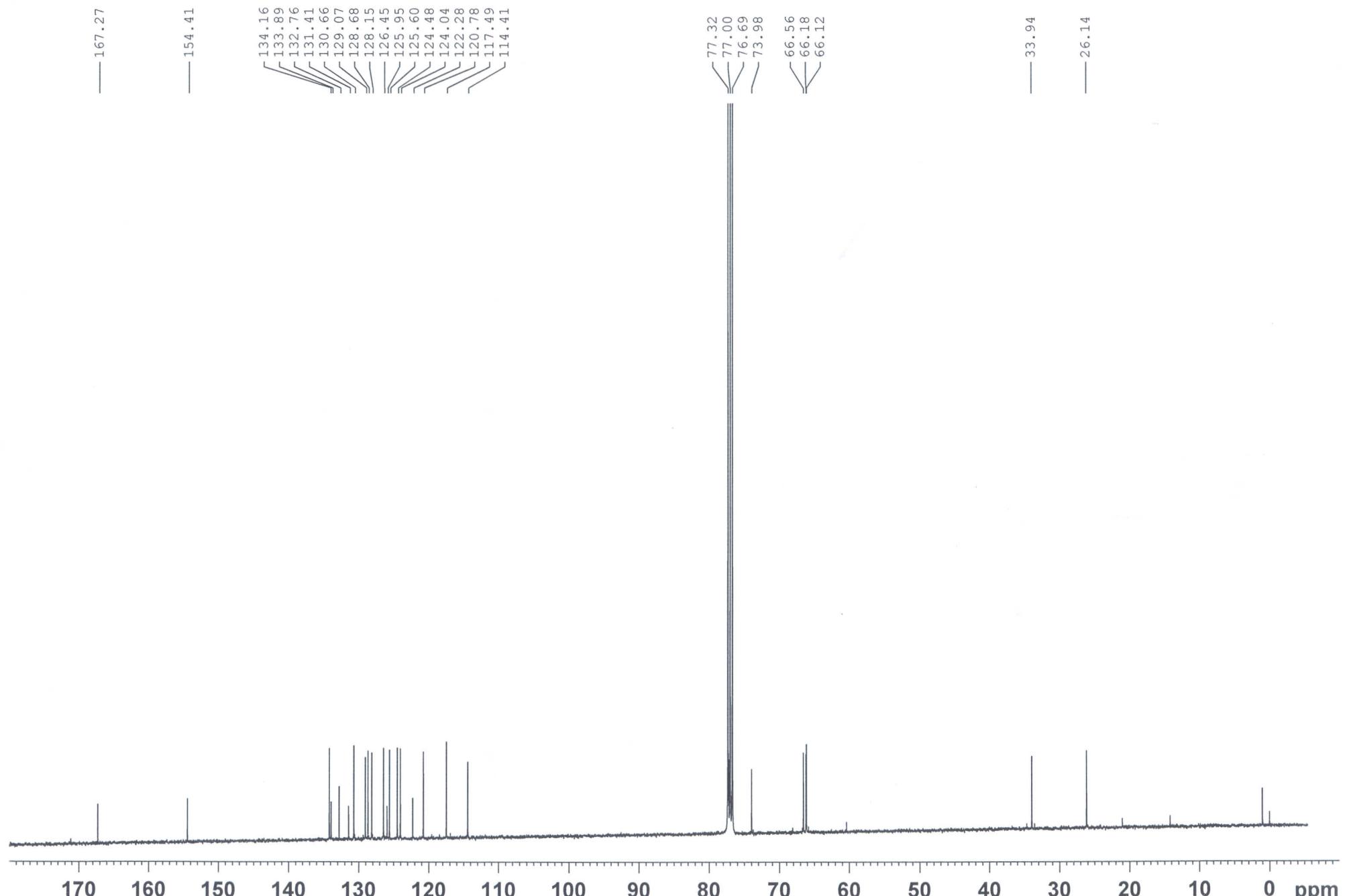
lbs-benezocyclohexane-C



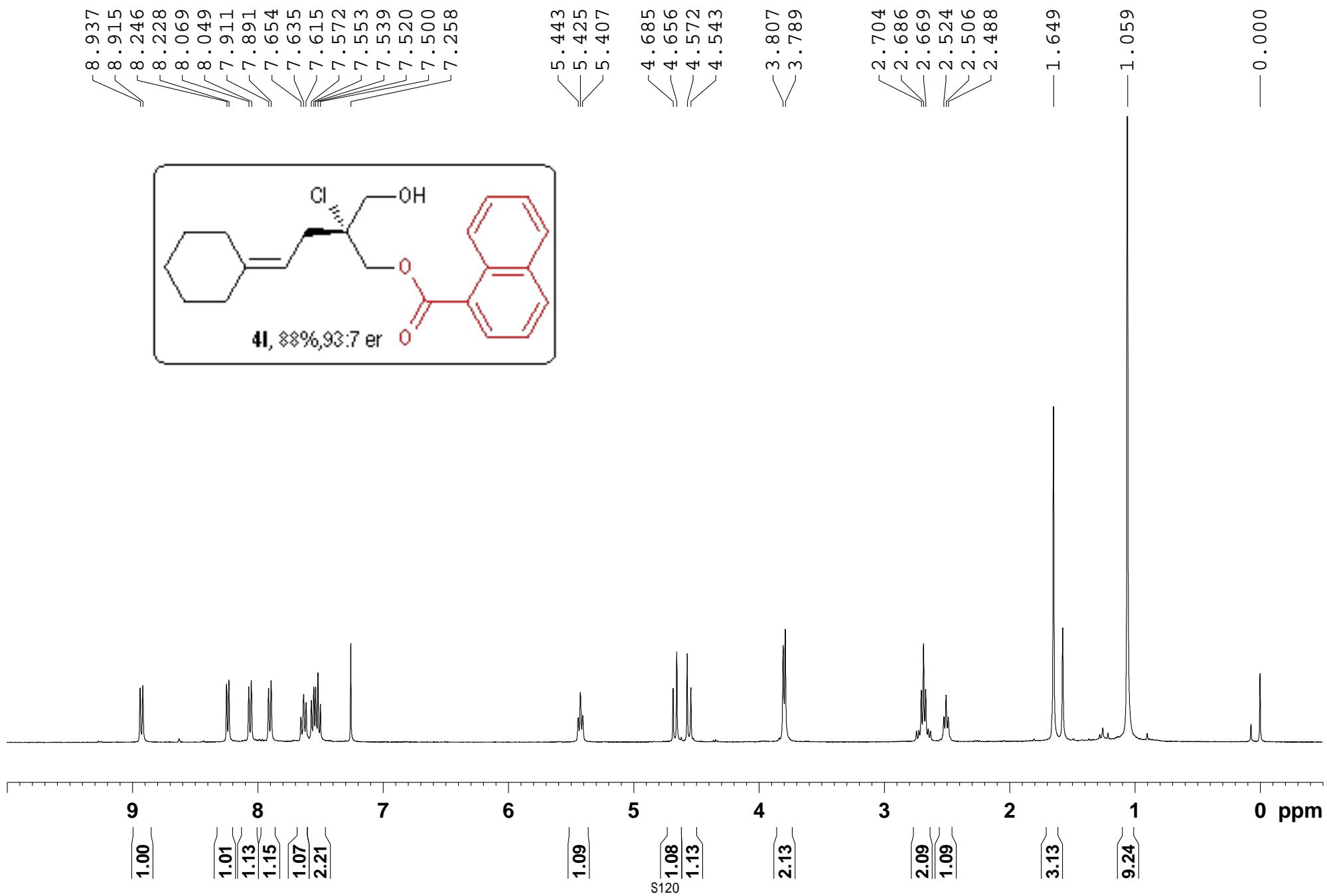
lbs-benzopyran-H4



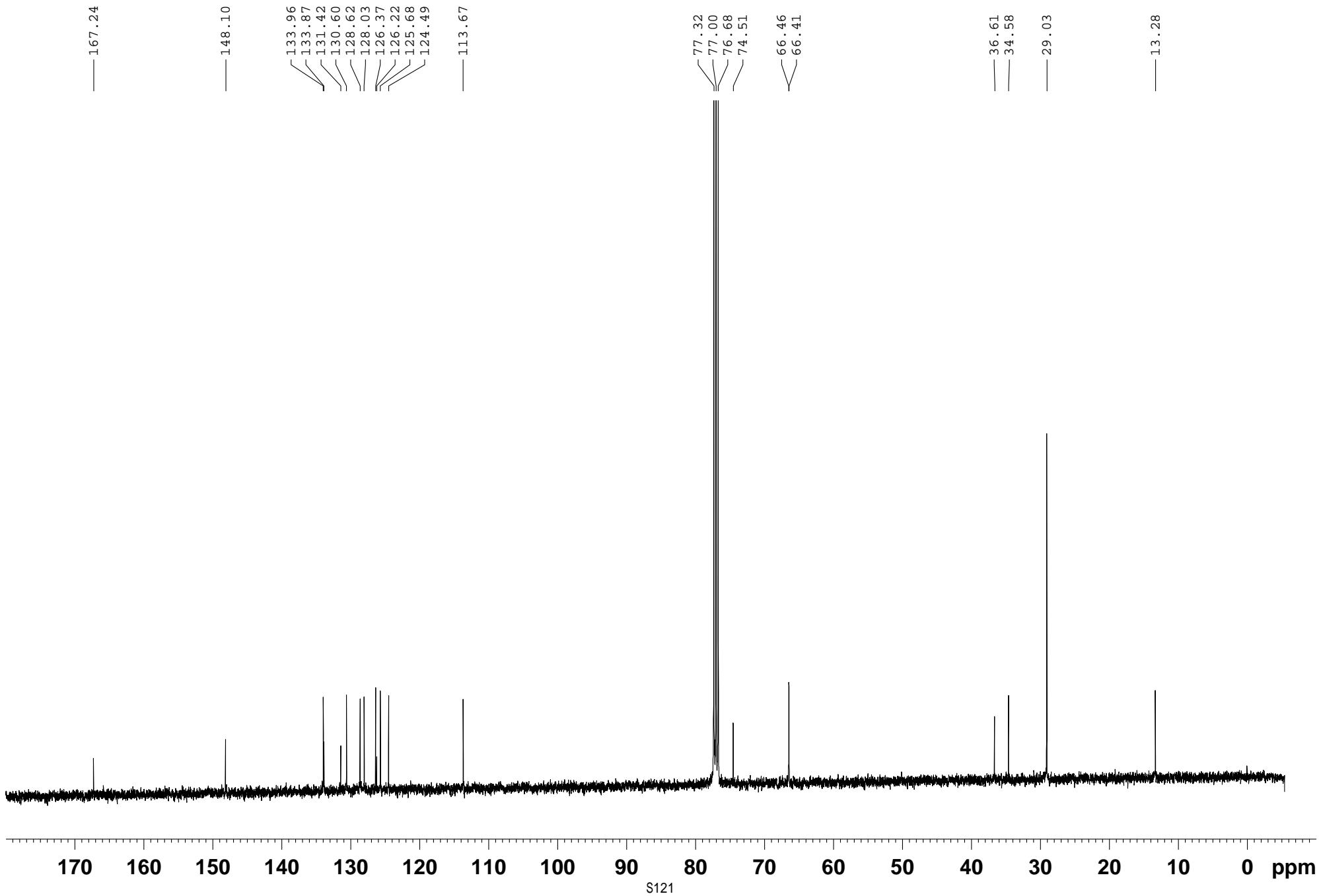
1bs-benzopyran-C3



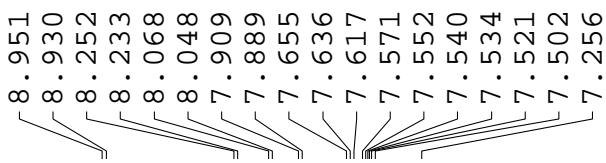
1bs-5-cyclohexane-H



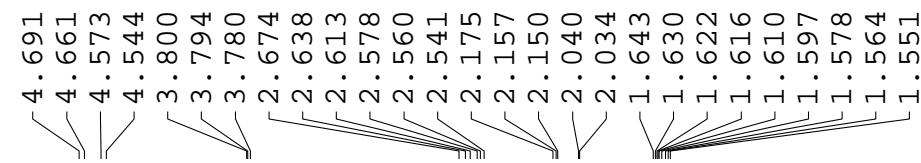
lbs-5-cyclohexane-C



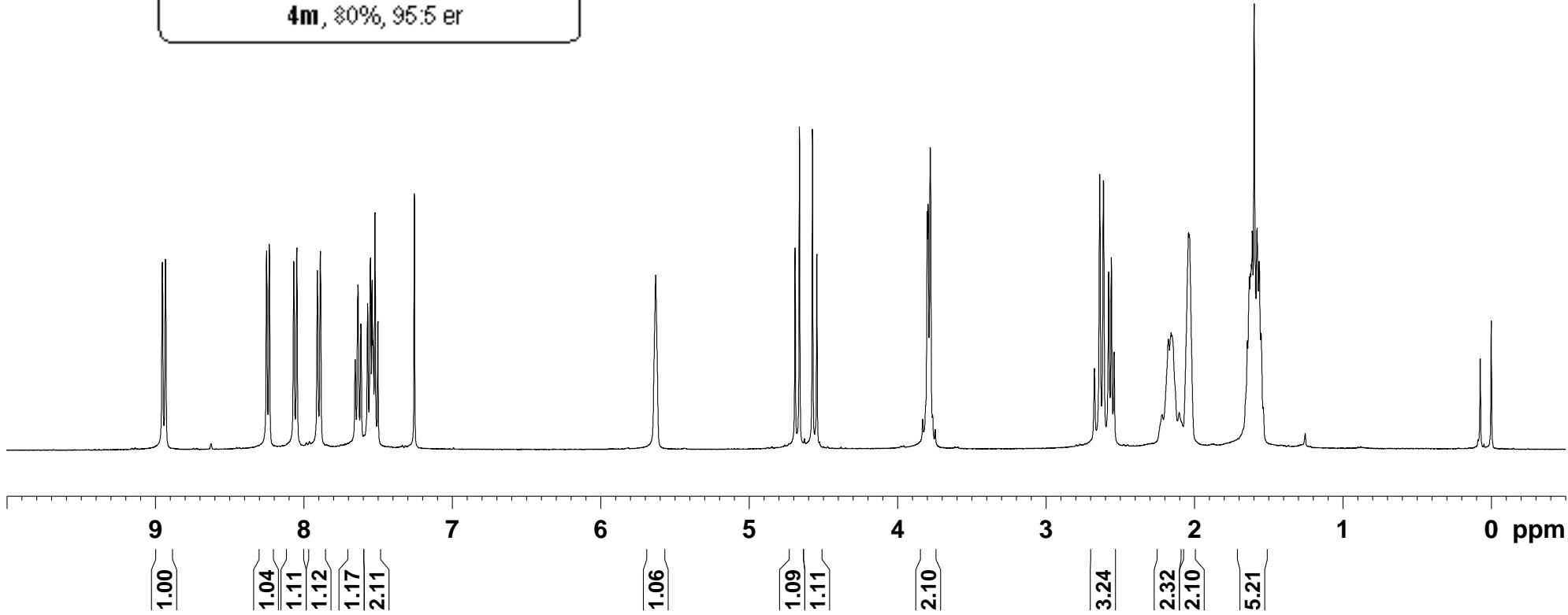
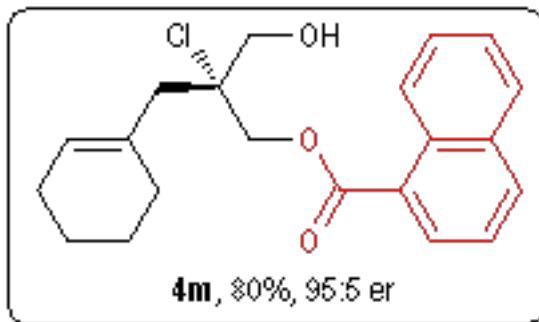
lbs-cyclohexene-H



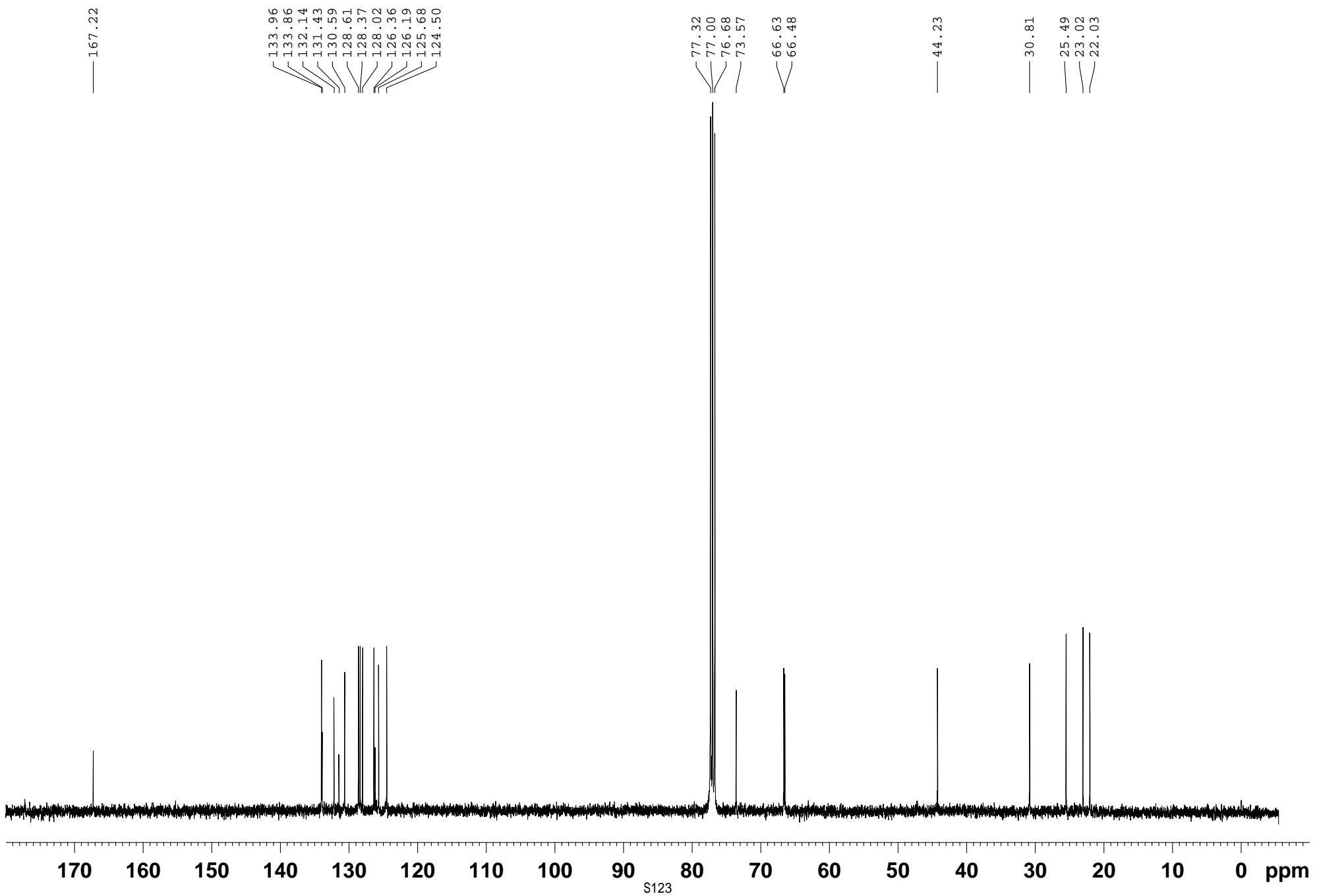
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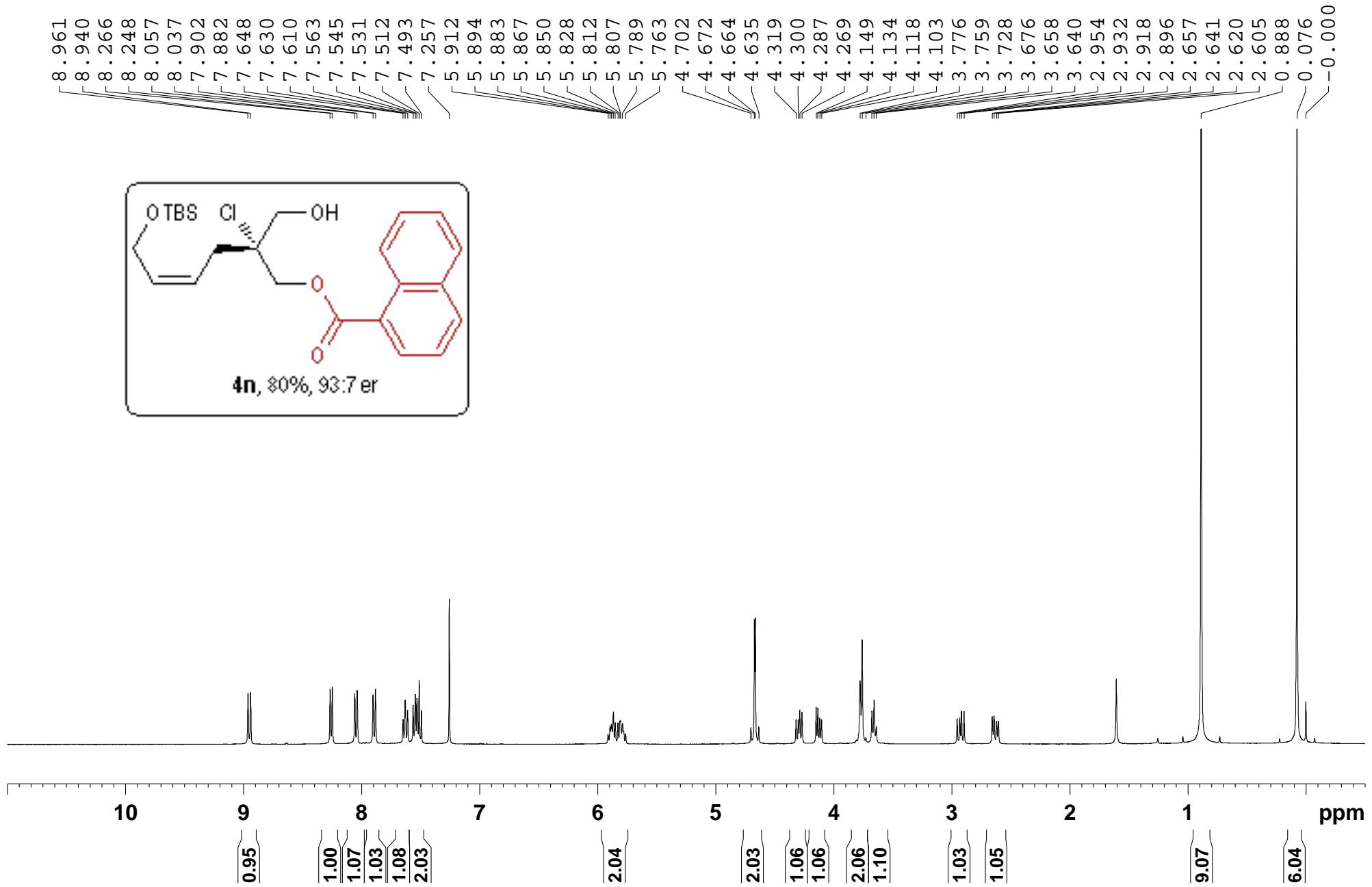
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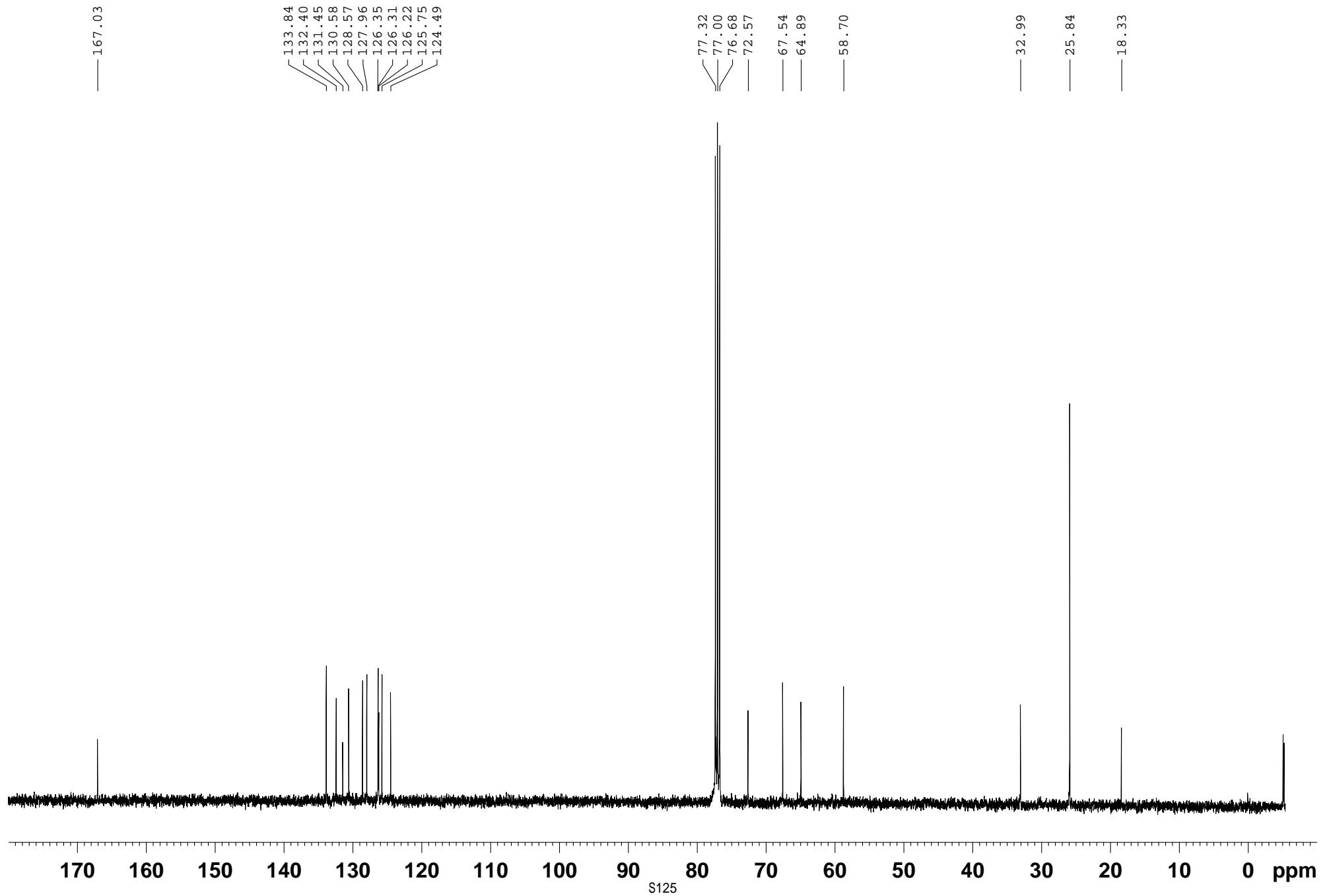
lbs-cyclohexene-C



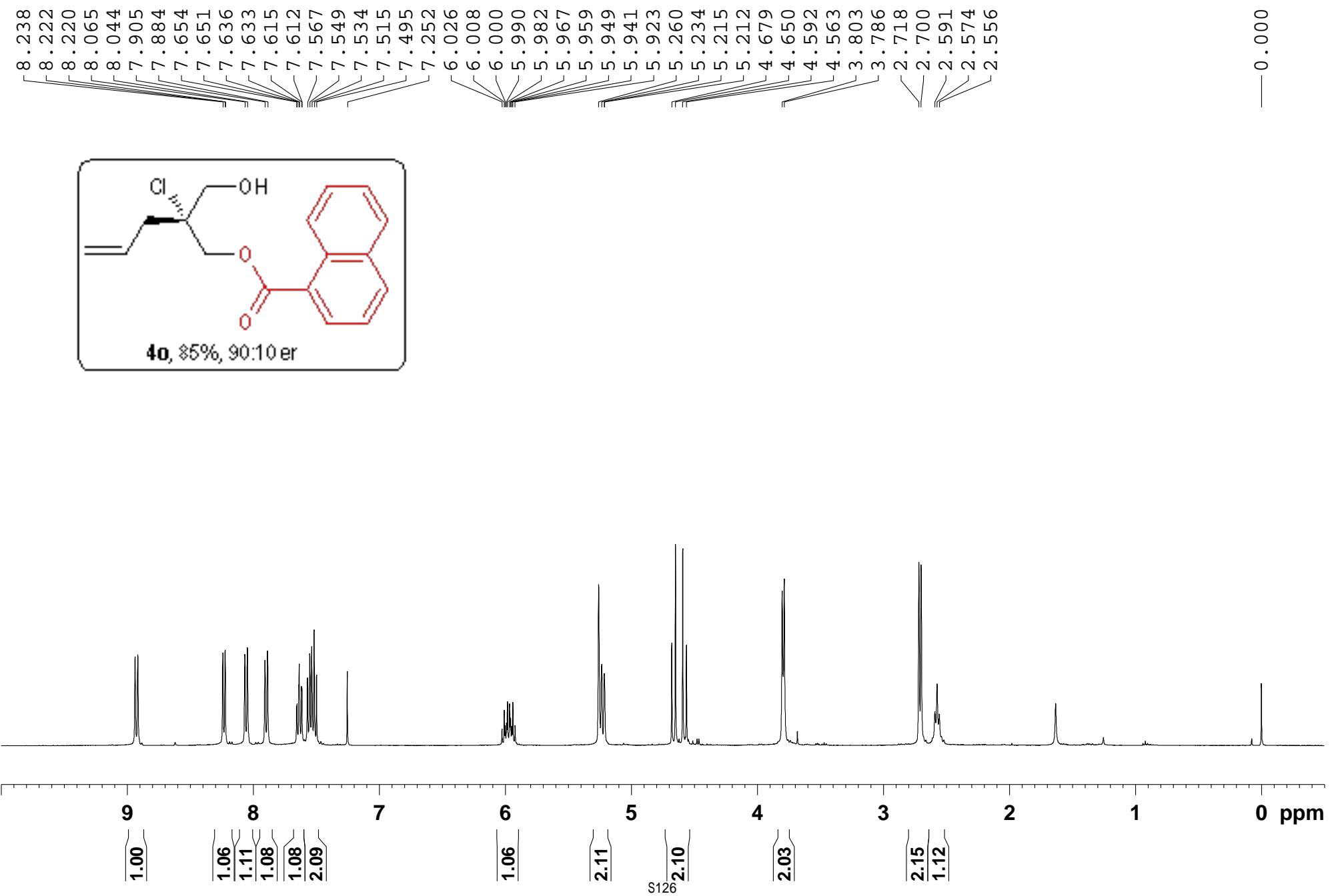
lbs-cis-olefin-OTBS-H



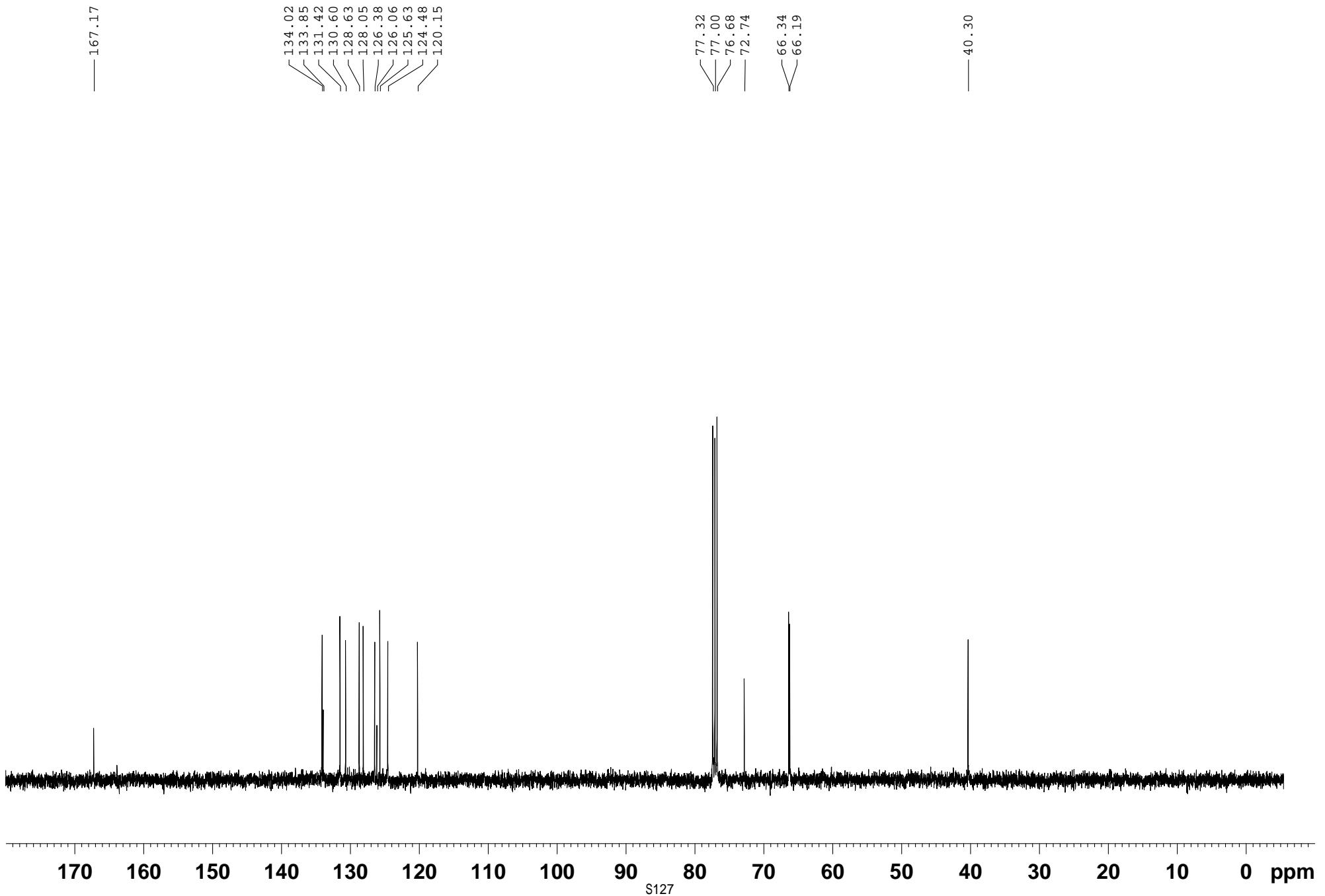
lbs-cis-olefin-OTBS-C



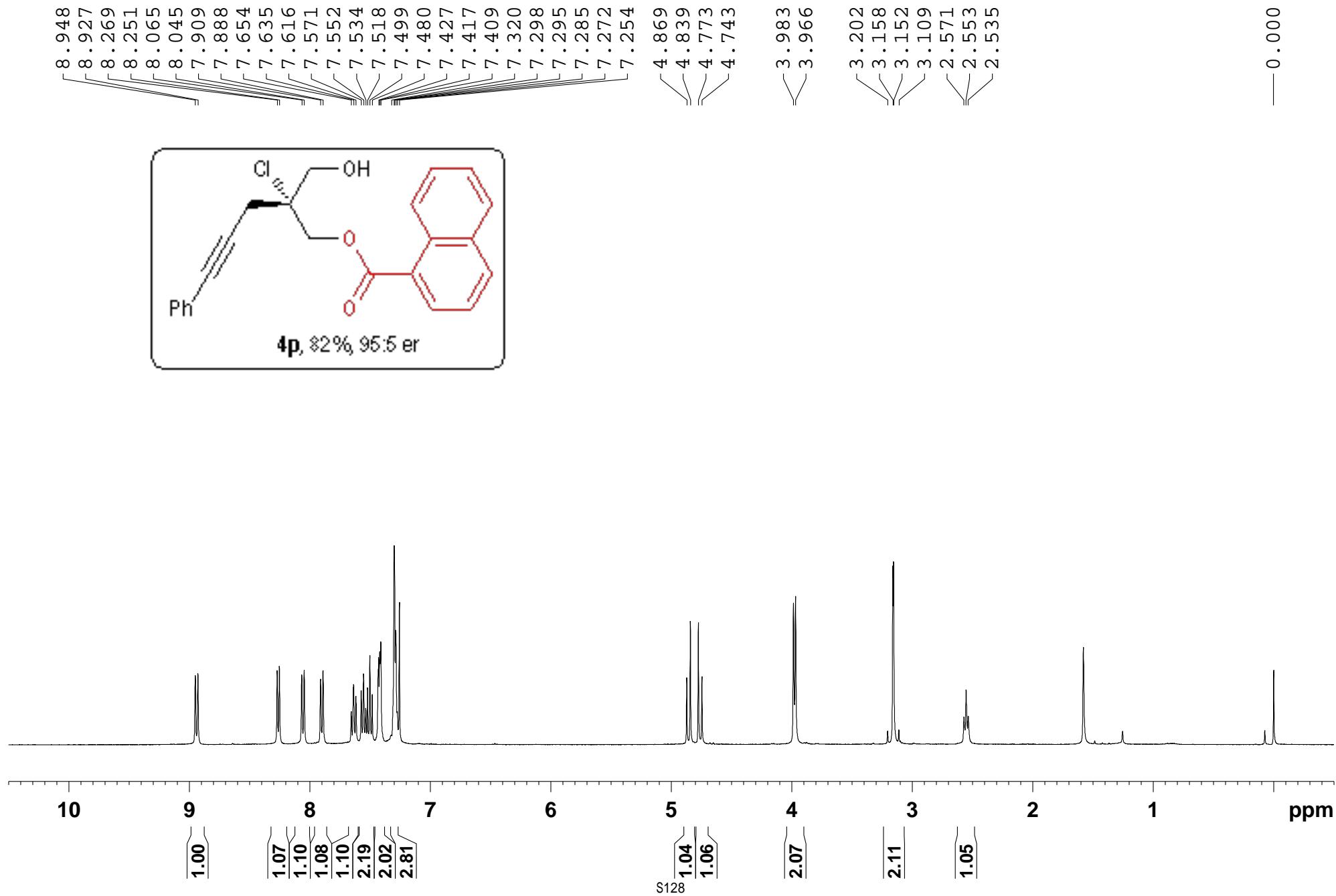
lbs-allyl-Cl-H



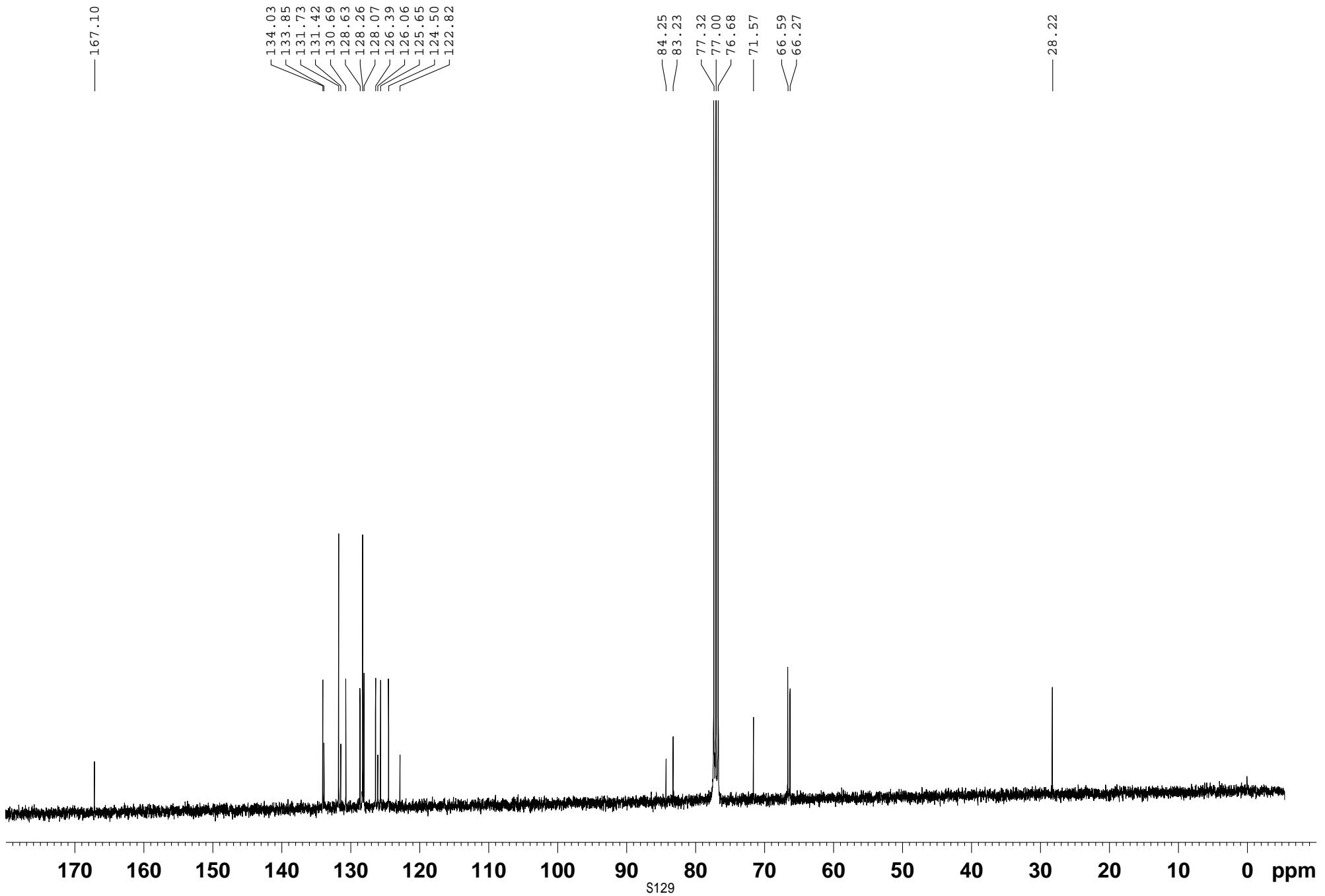
lbs-allyl-Cl-C



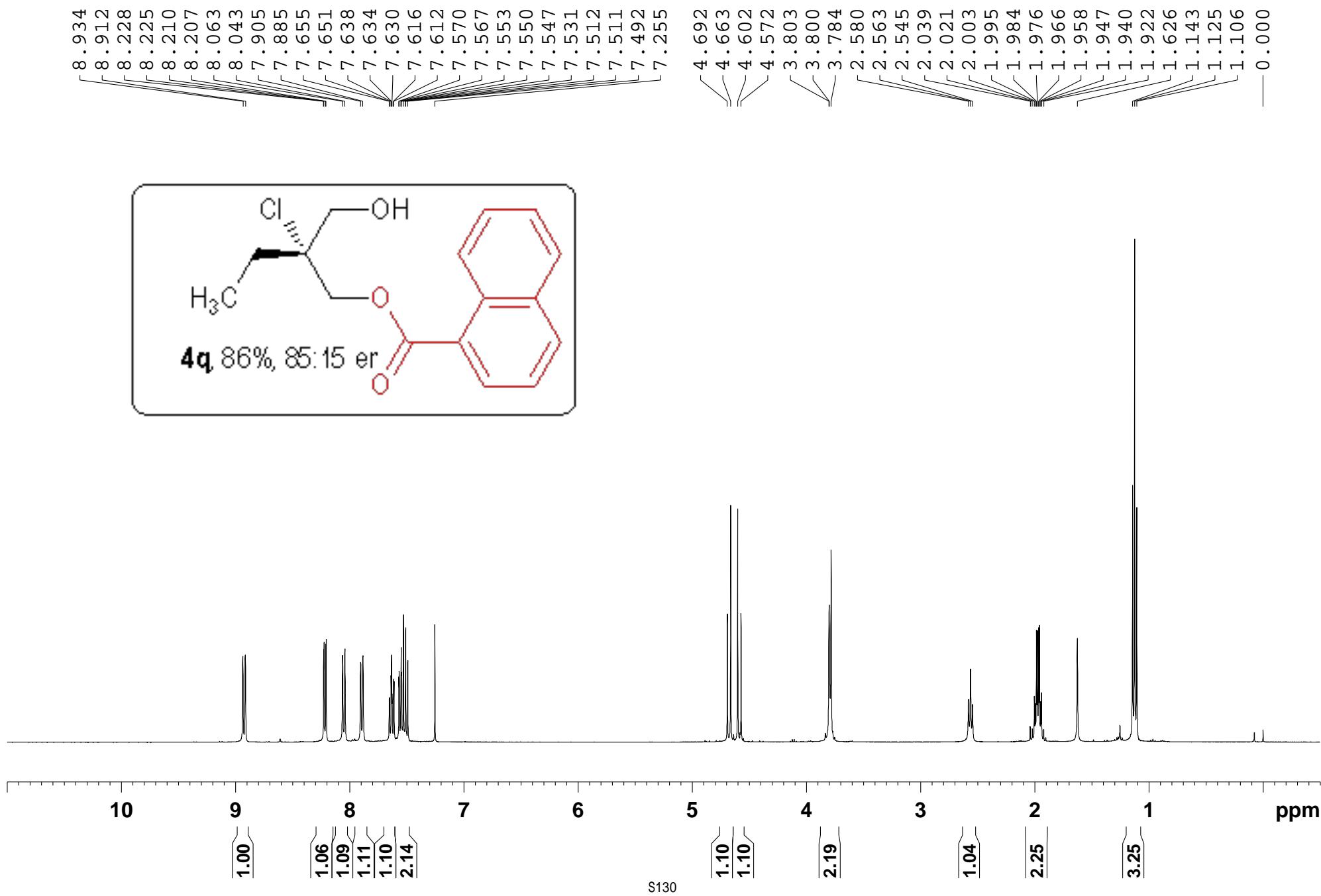
lbs-phenylacetate-Cl-H



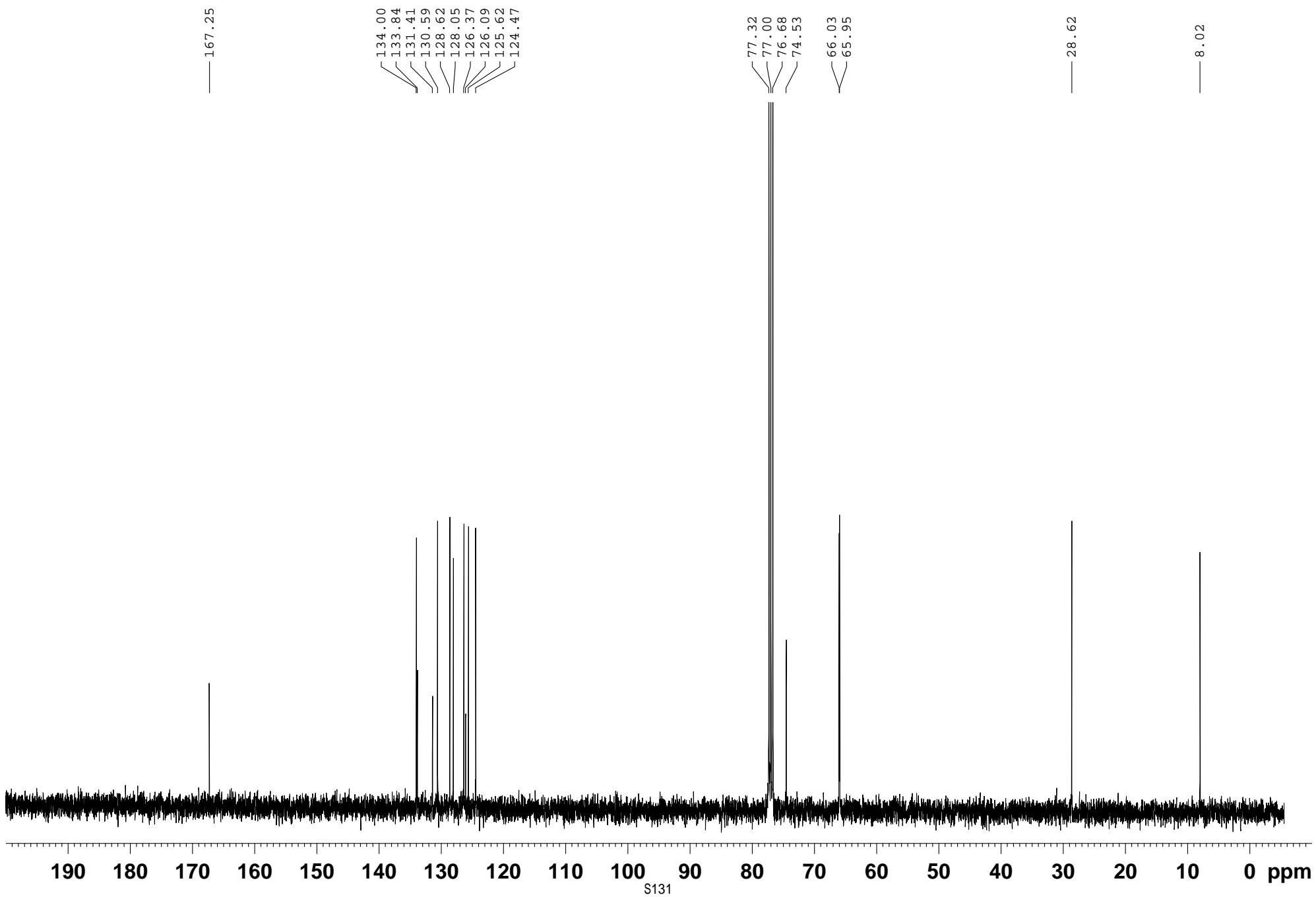
lbs-phenylacetate-Cl-C



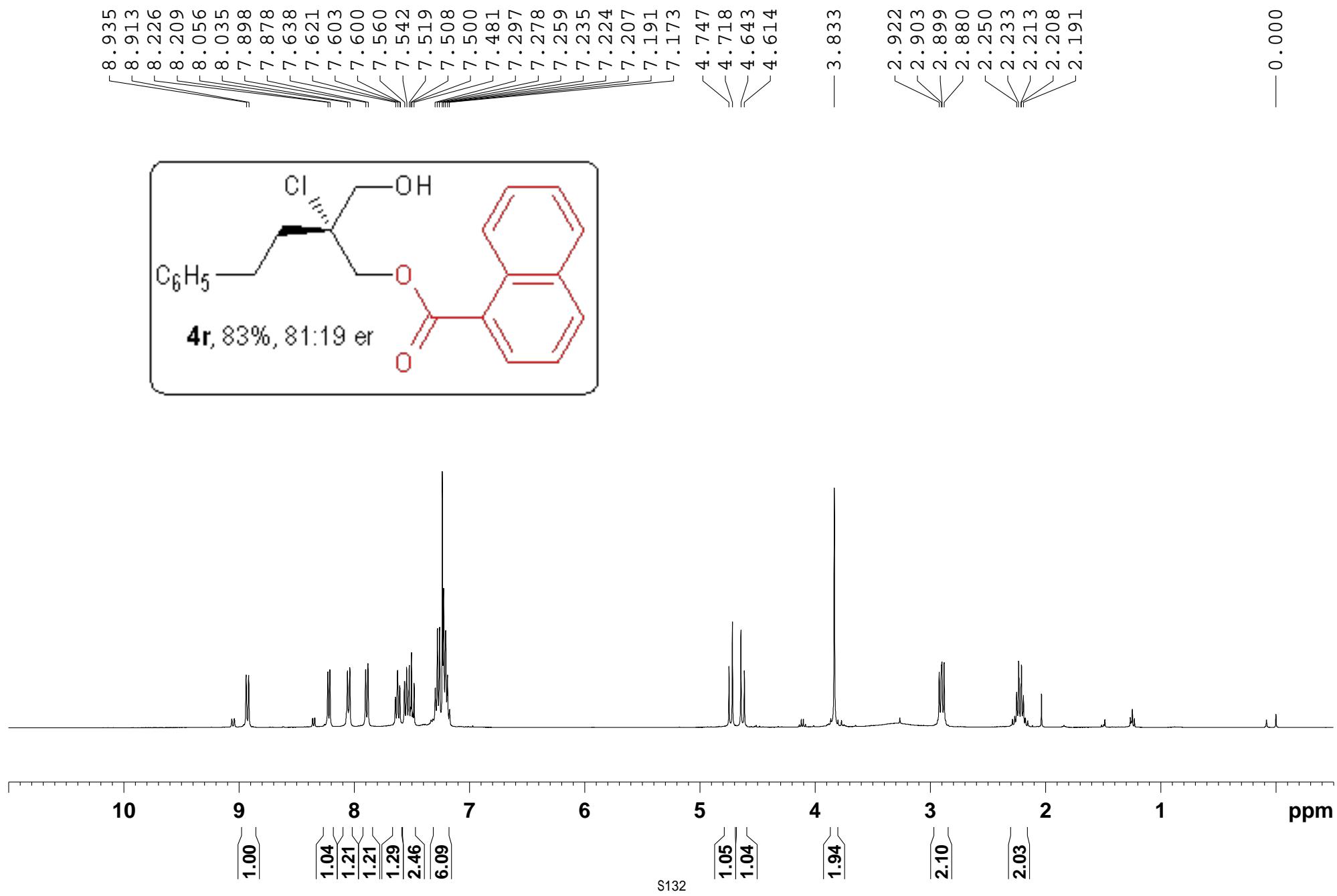
lbs-Et-monoester-H



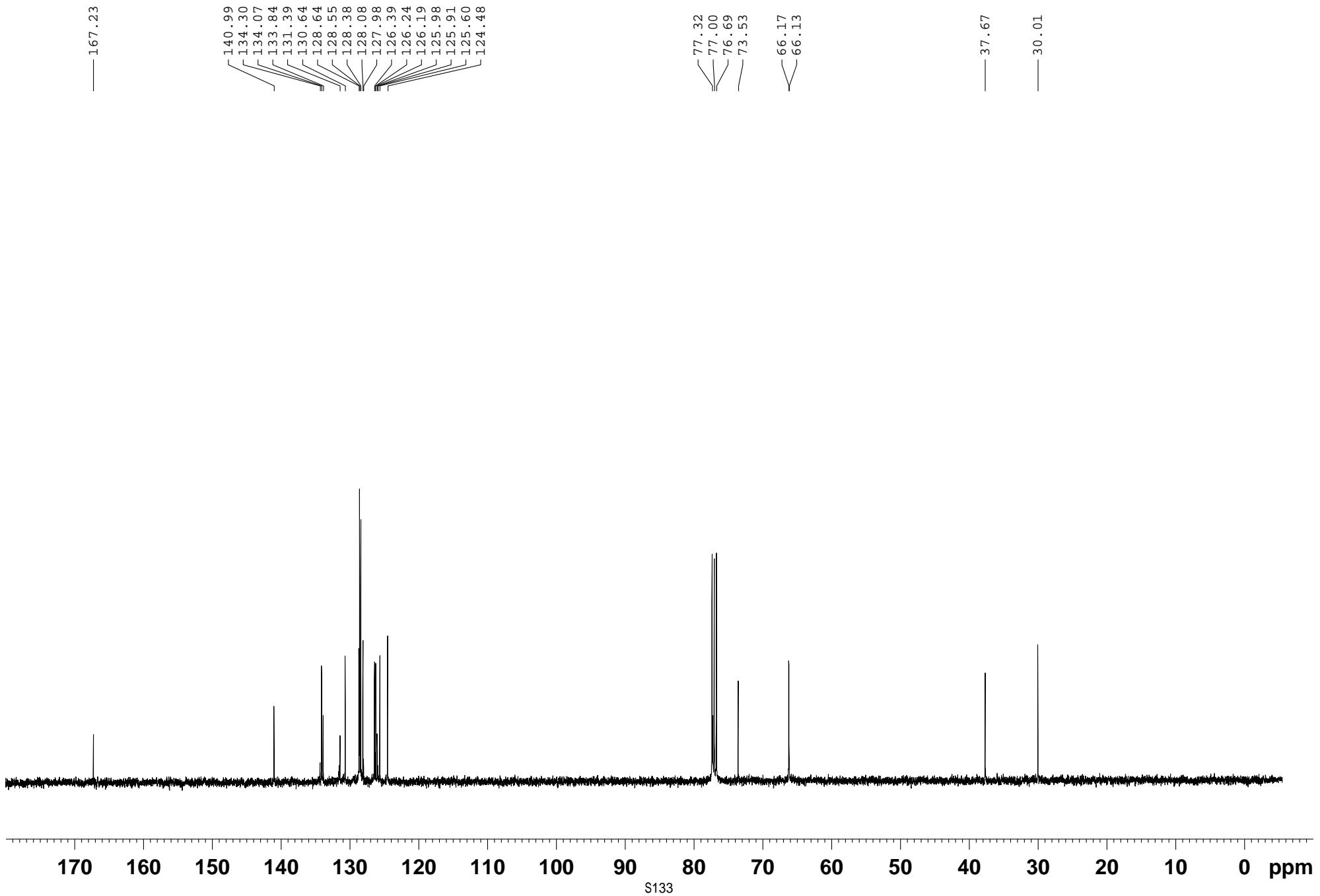
lbs-Et-monoester-C



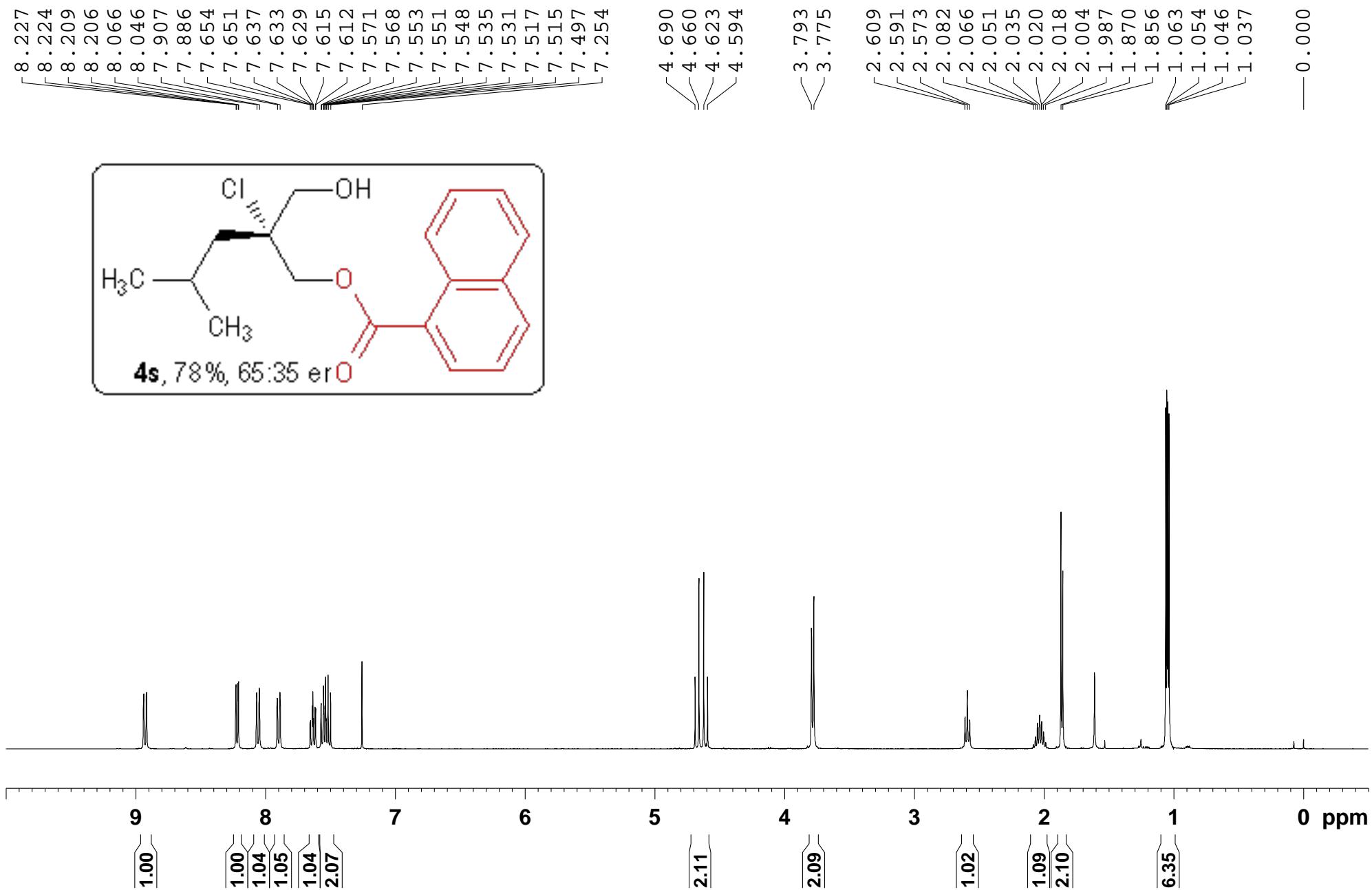
1bs-2-Bn-CH2-2-Cl-H



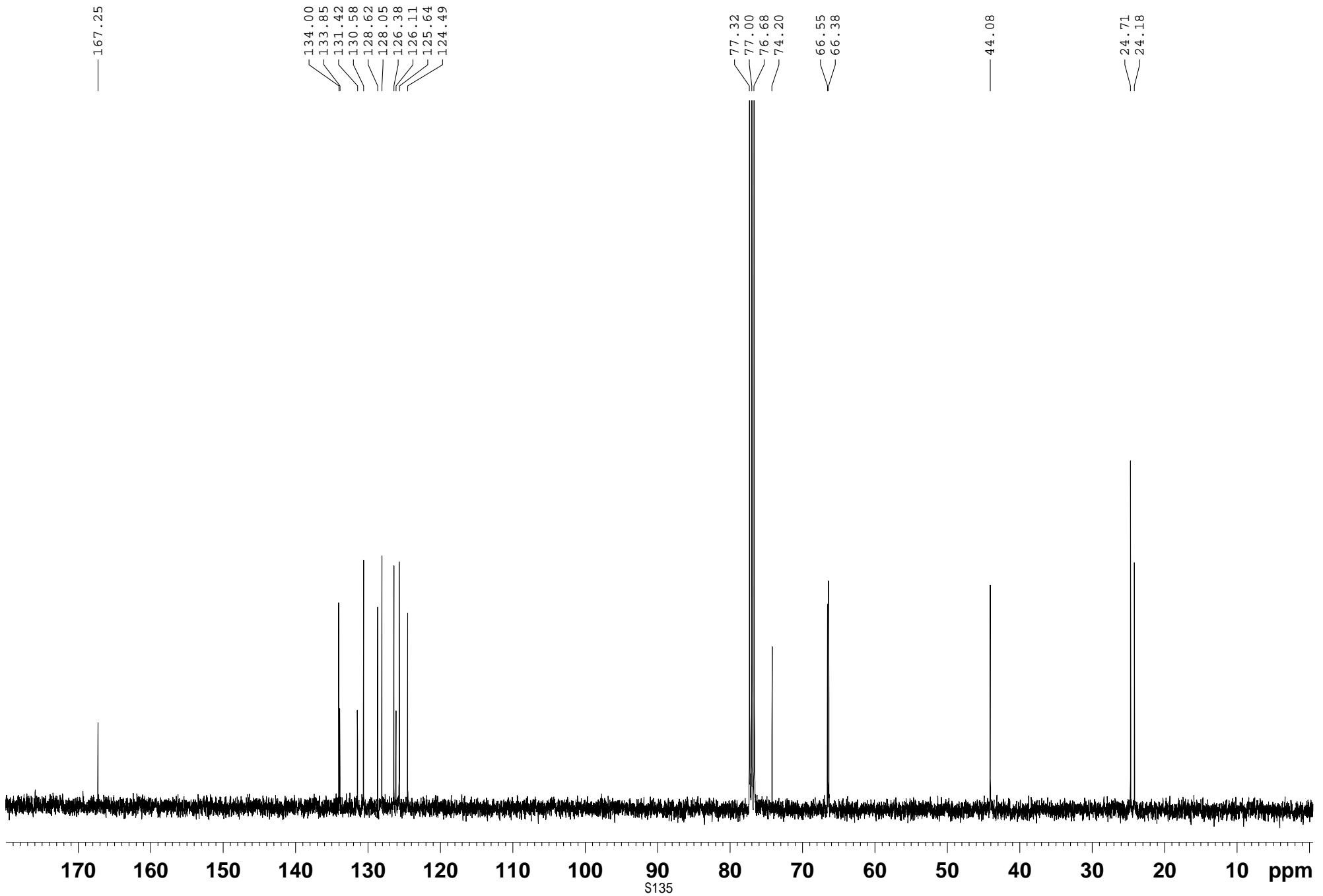
lbs-2-Bn-CH2-2-Cl-C



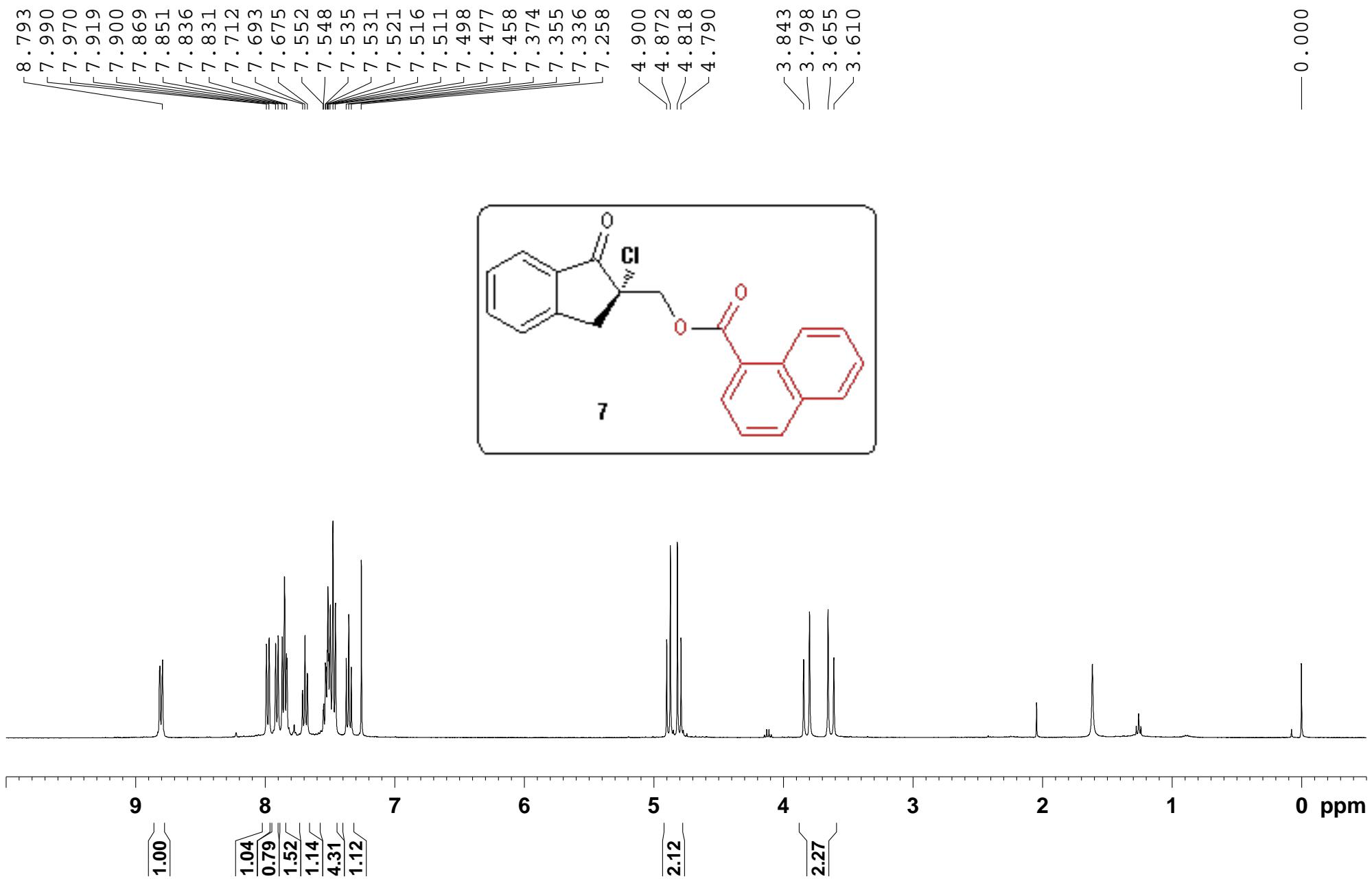
lbs-ipr-monoester-H



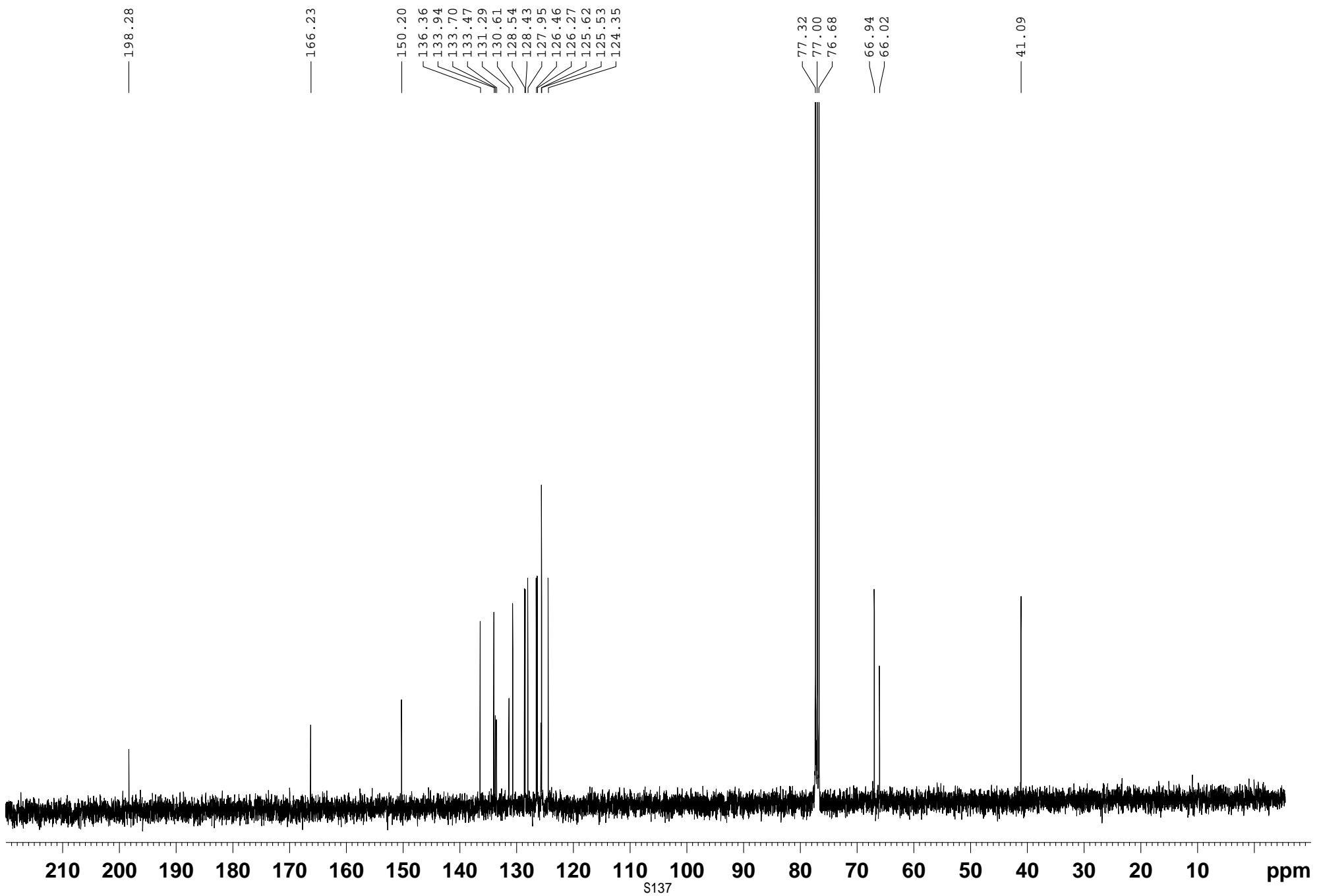
lbs-ipr-monoester-C



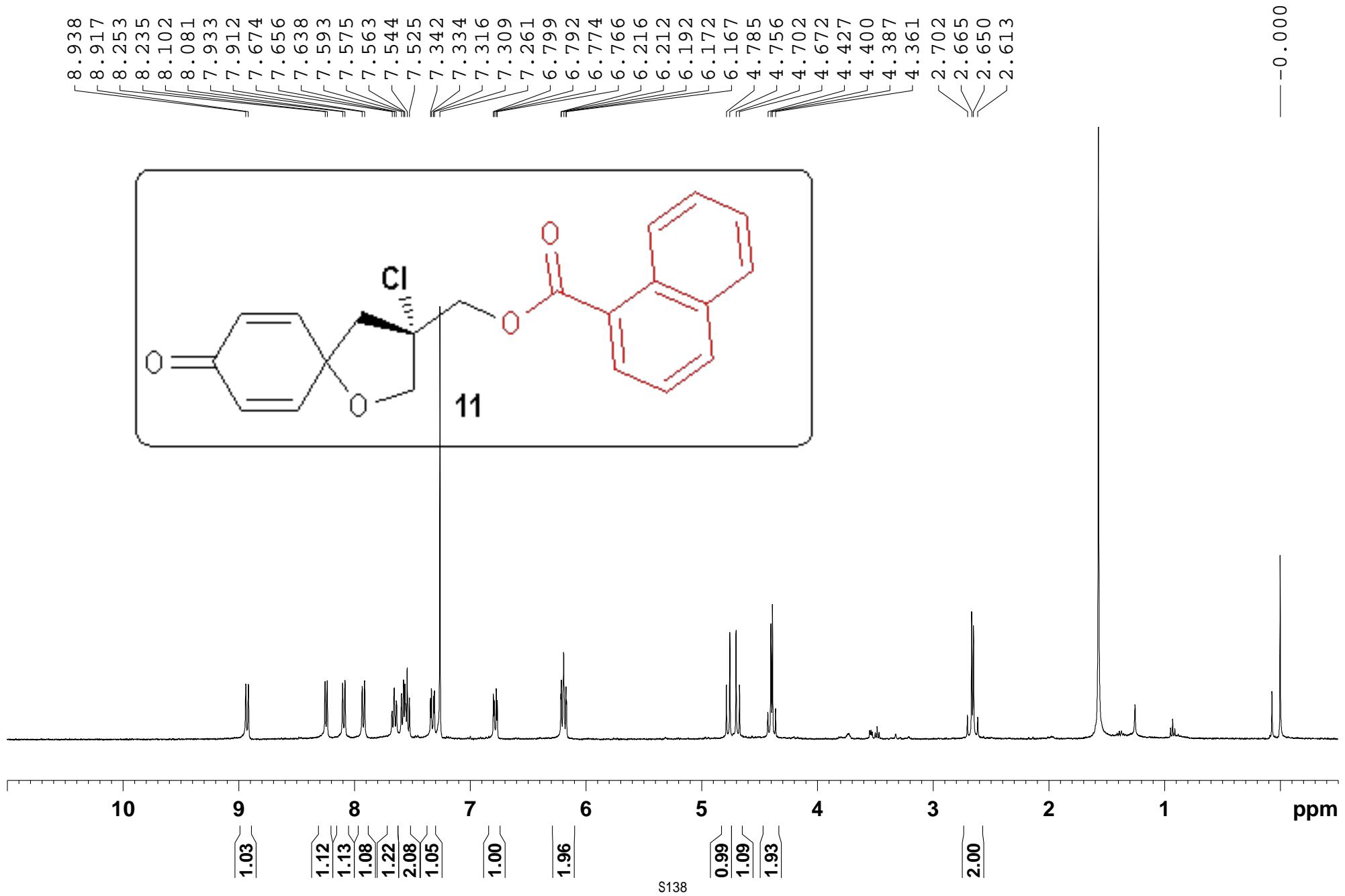
LBS-indanol-ester-H



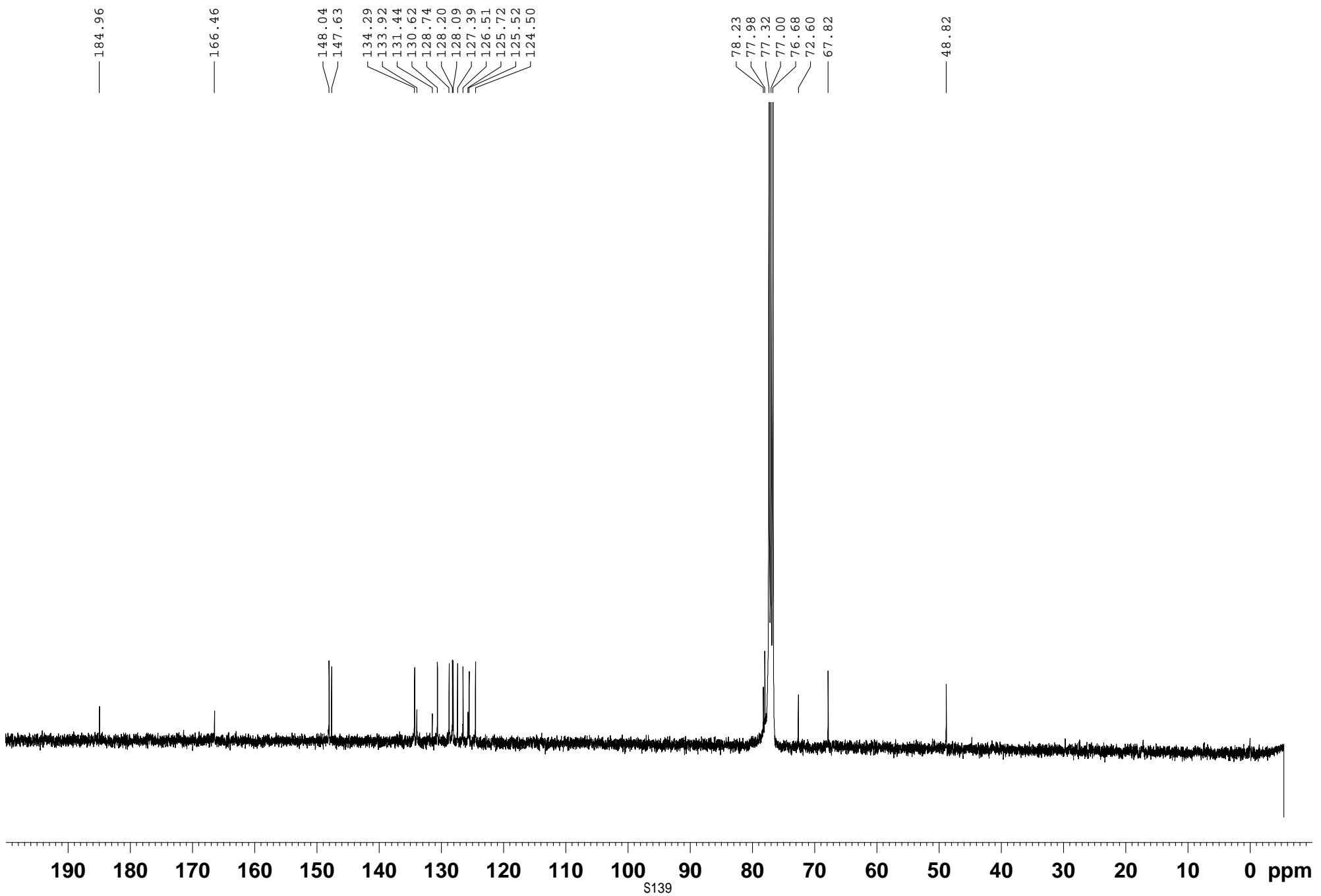
LBS-indanol-ester-C



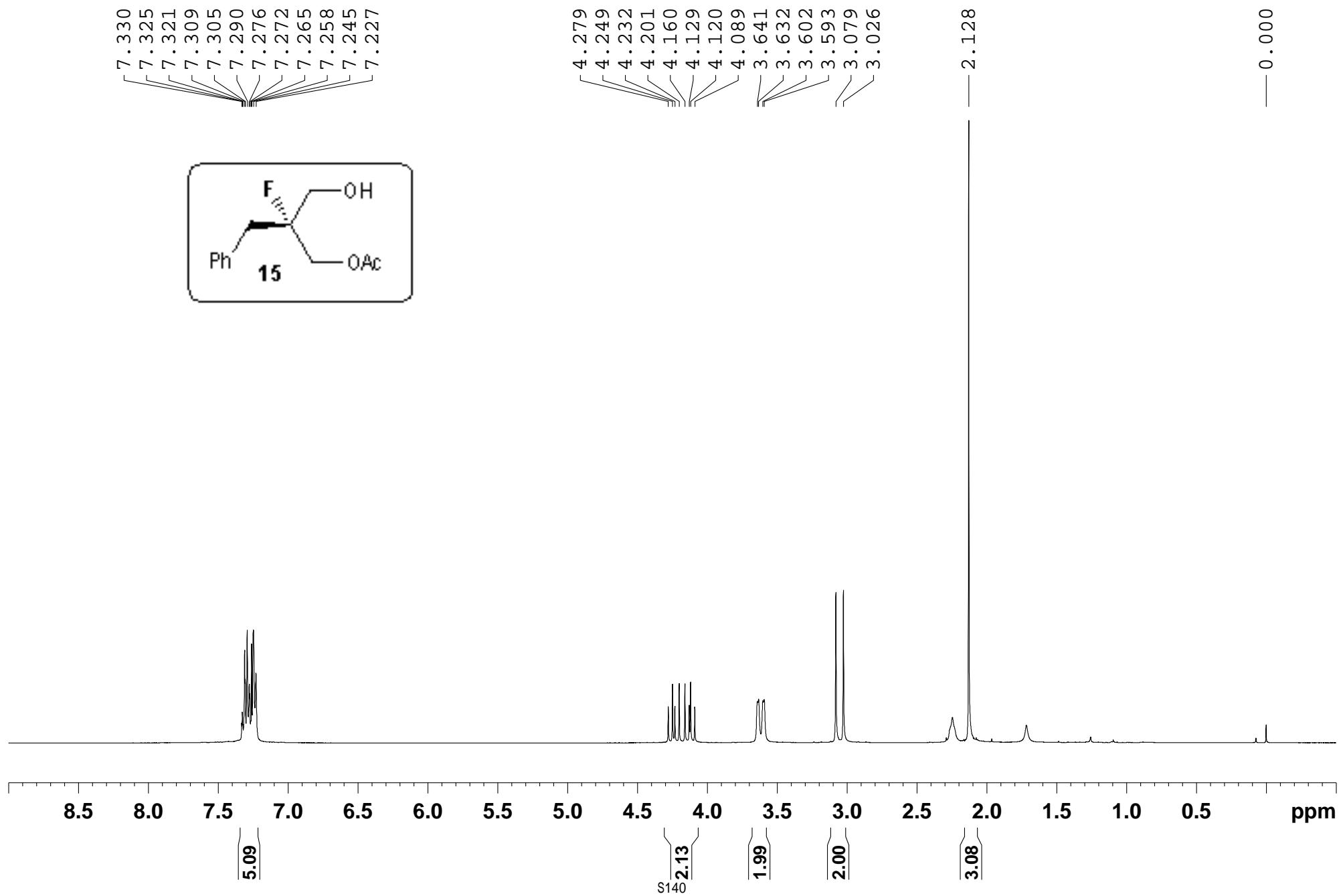
lbs-oxidation-H



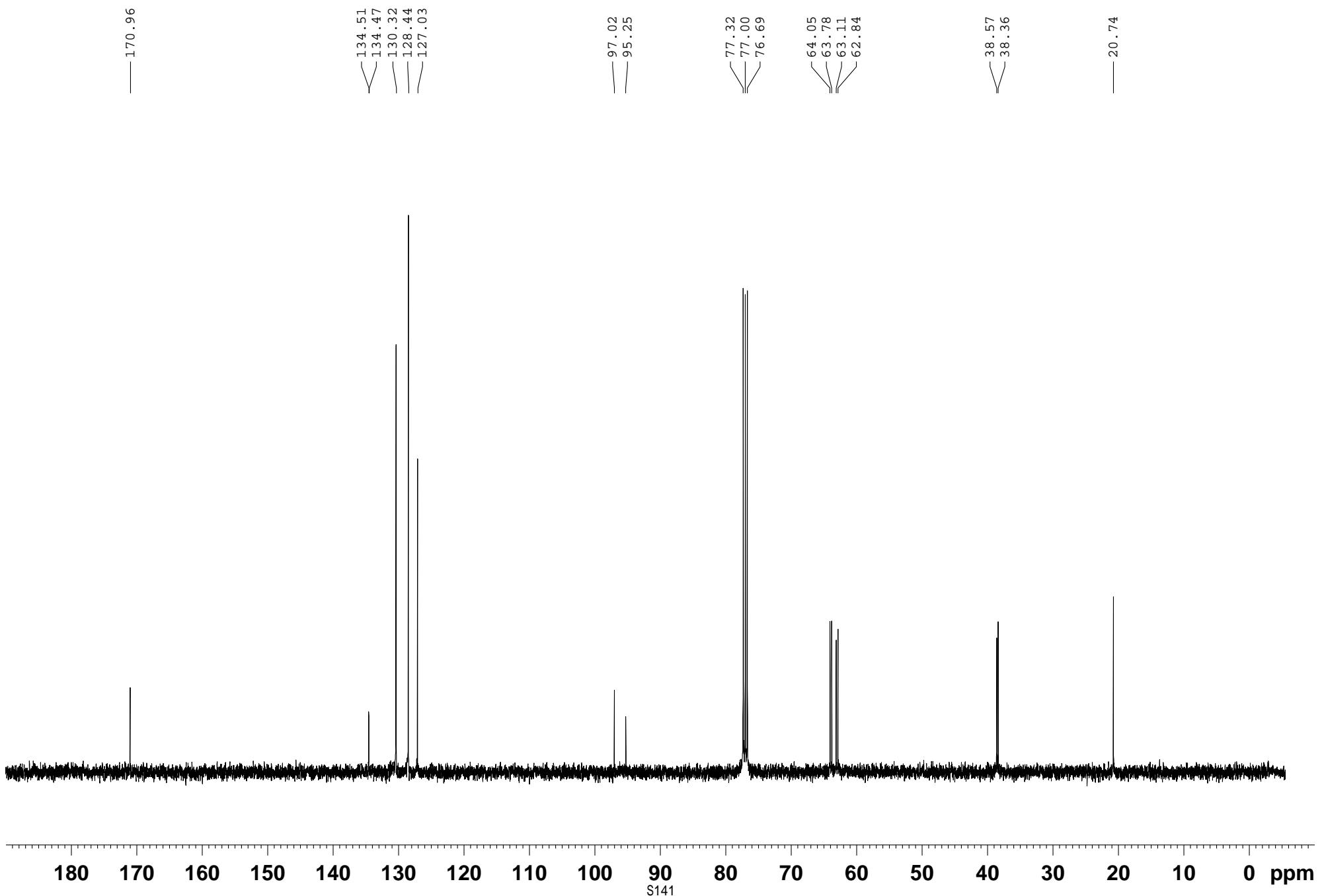
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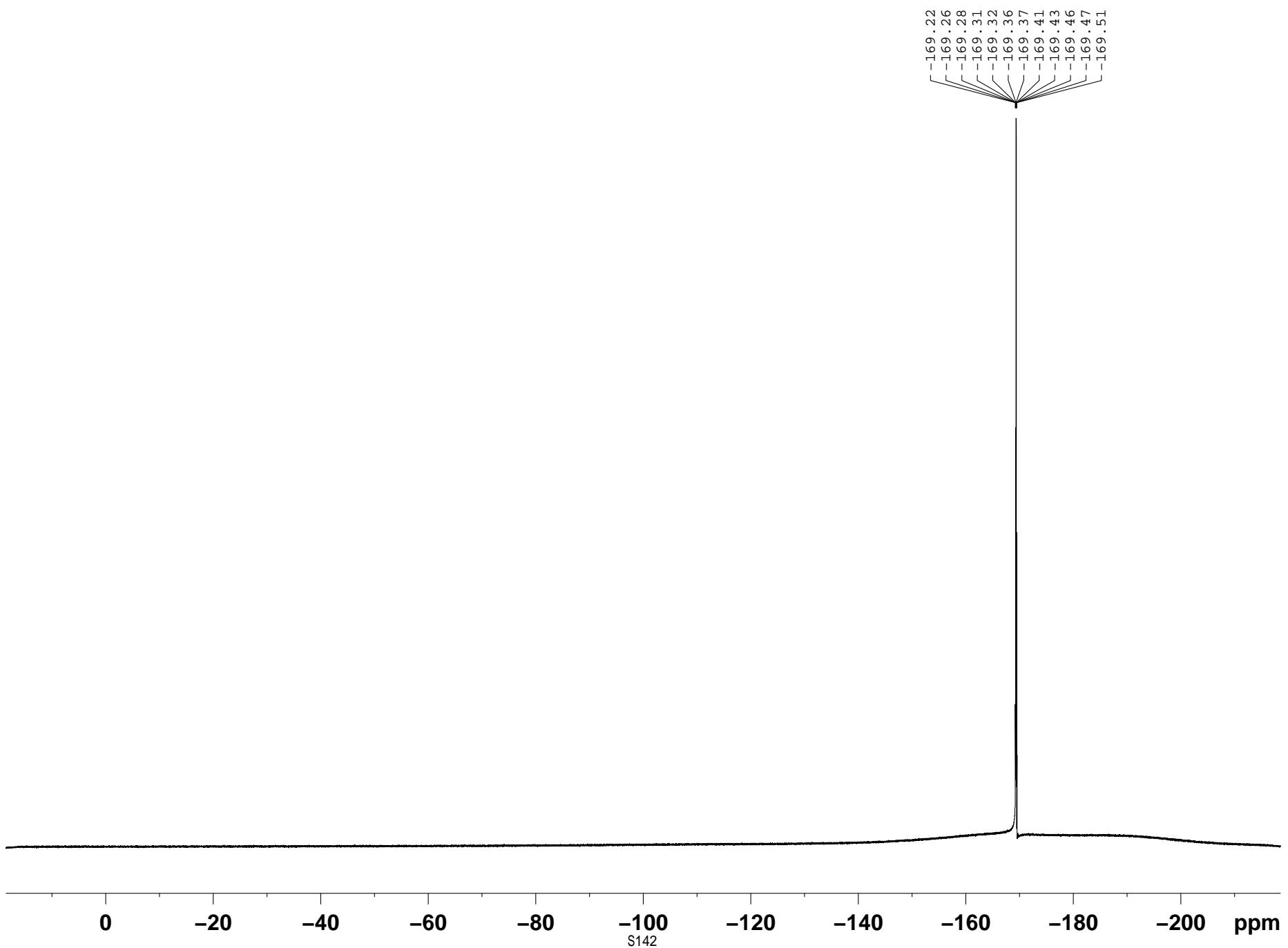
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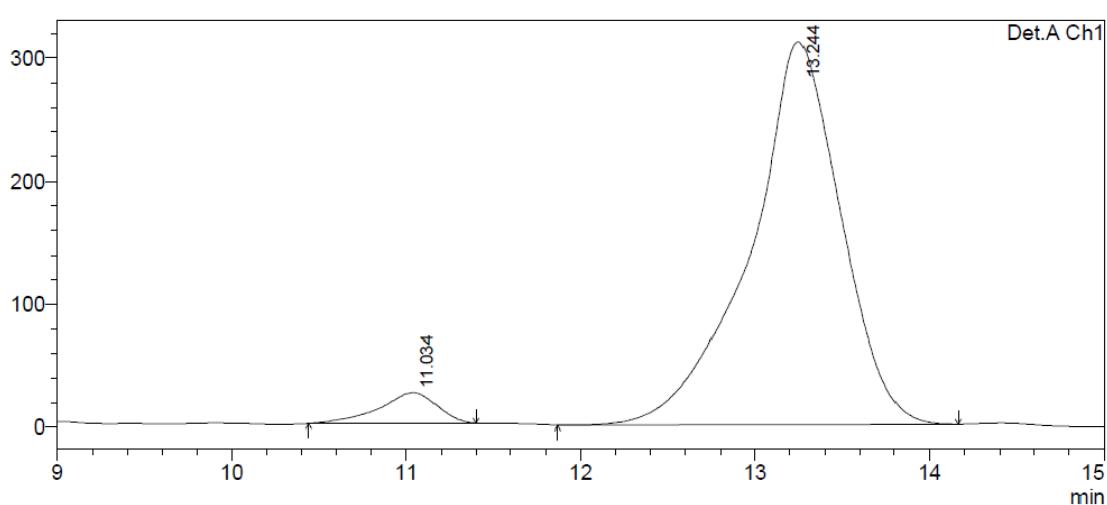
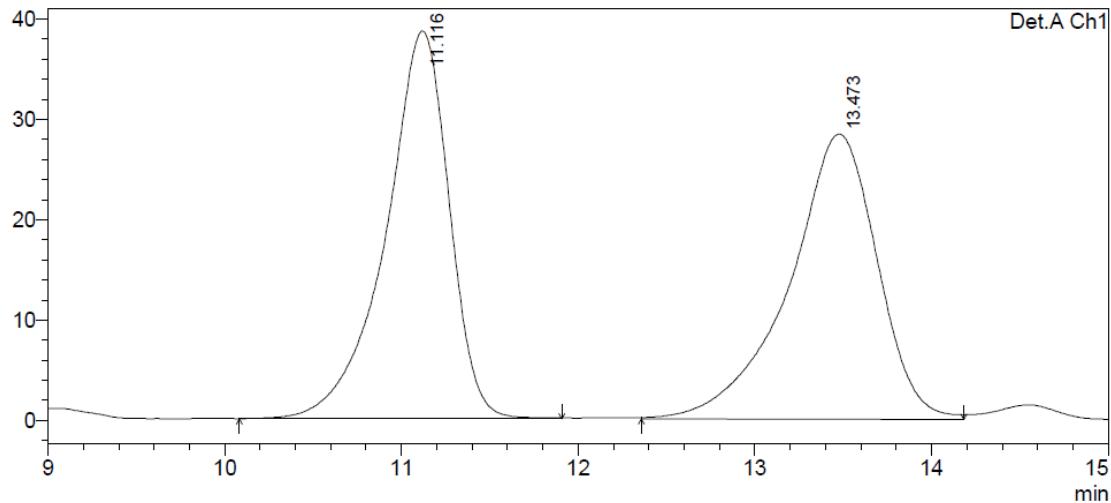
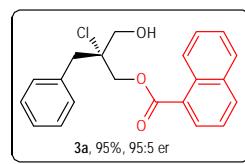


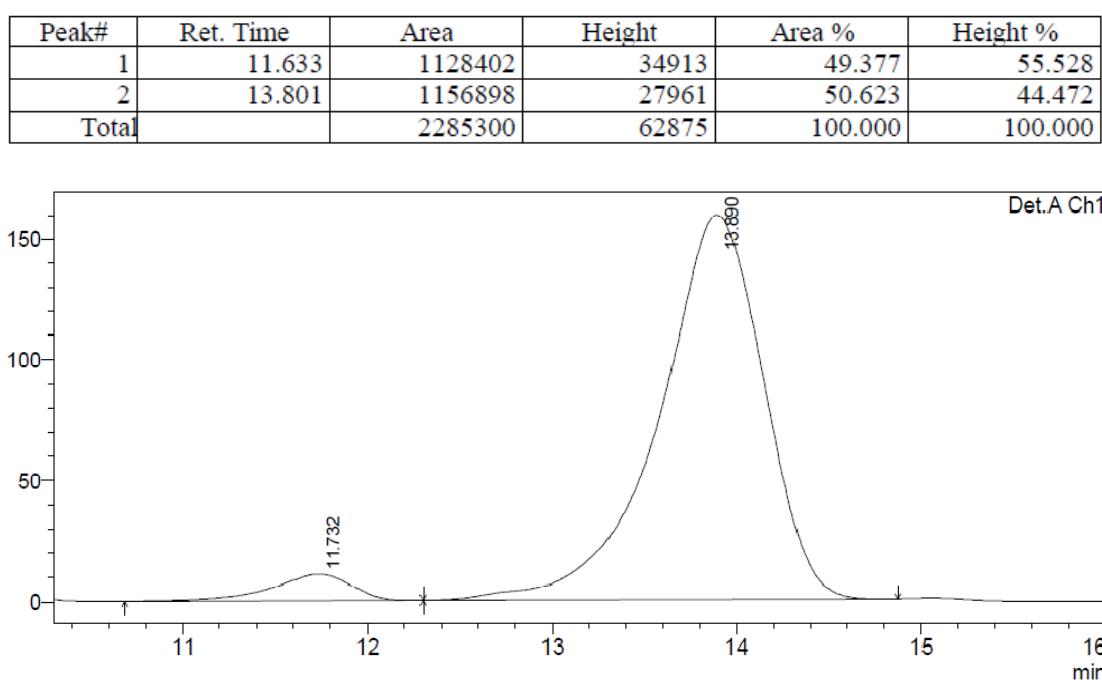
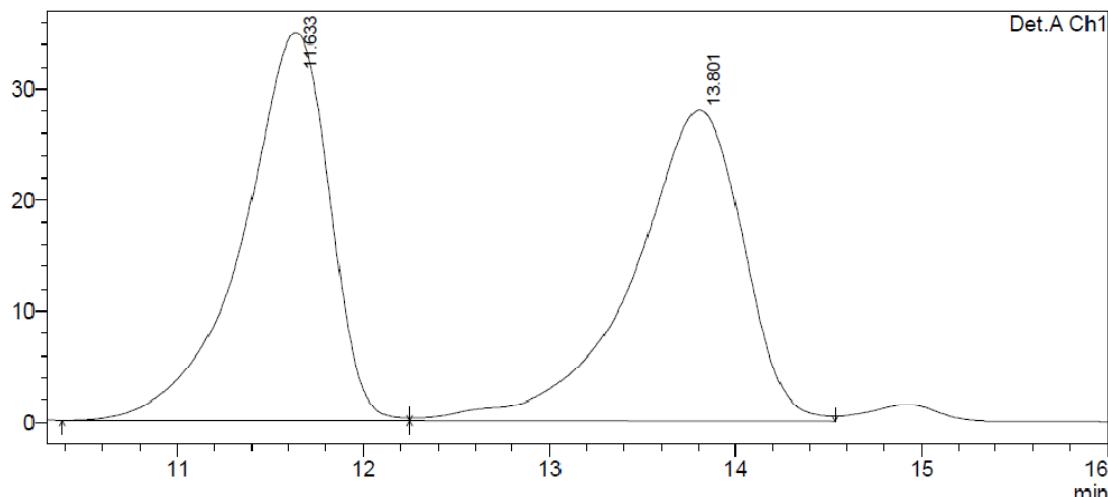
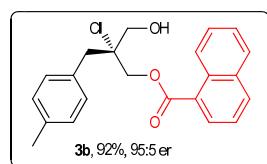
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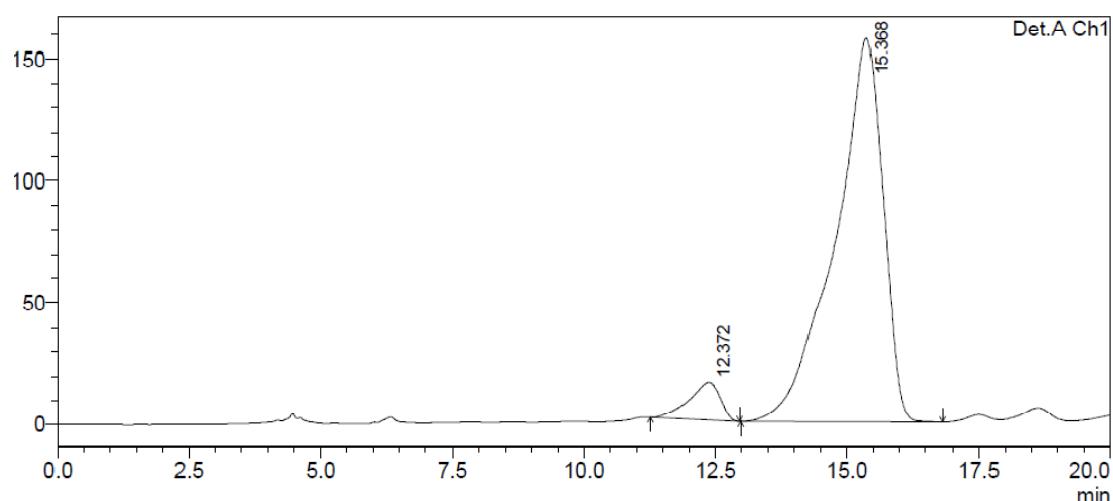
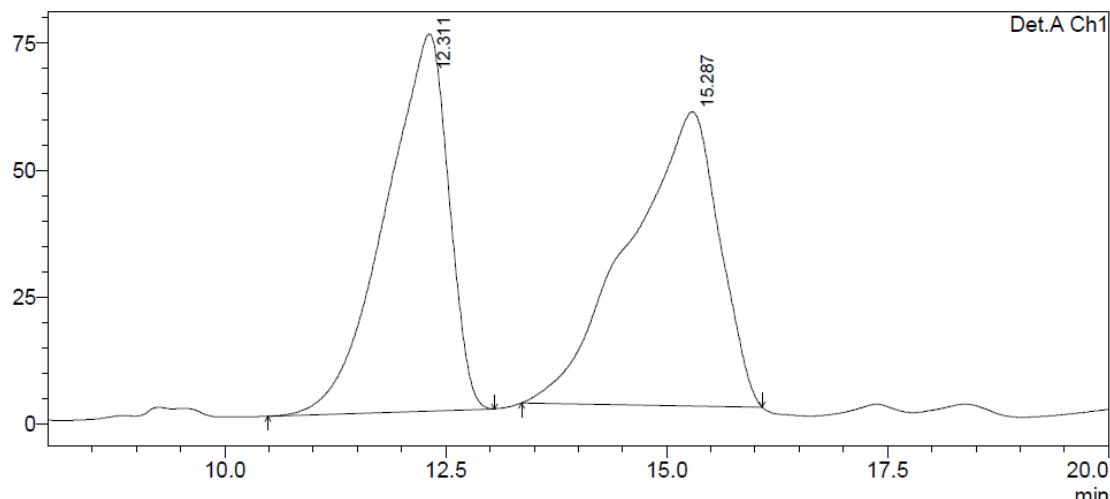
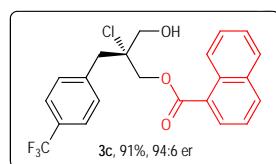


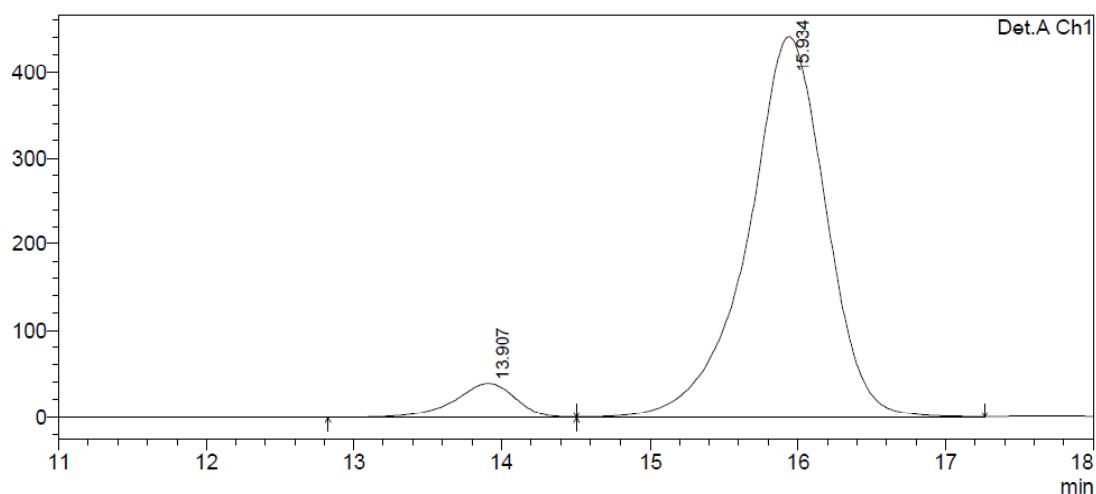
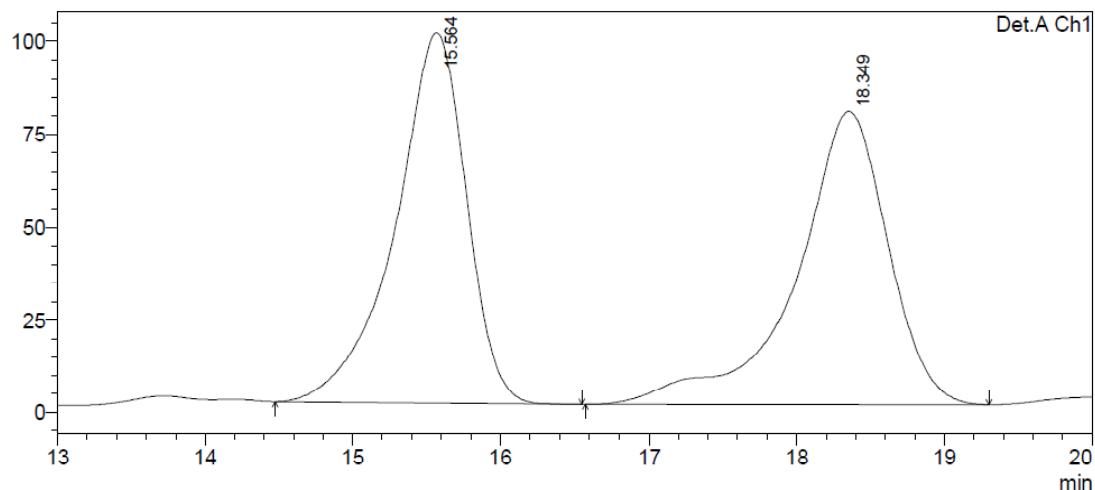
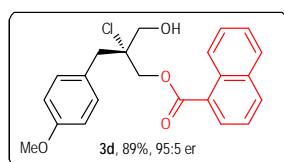
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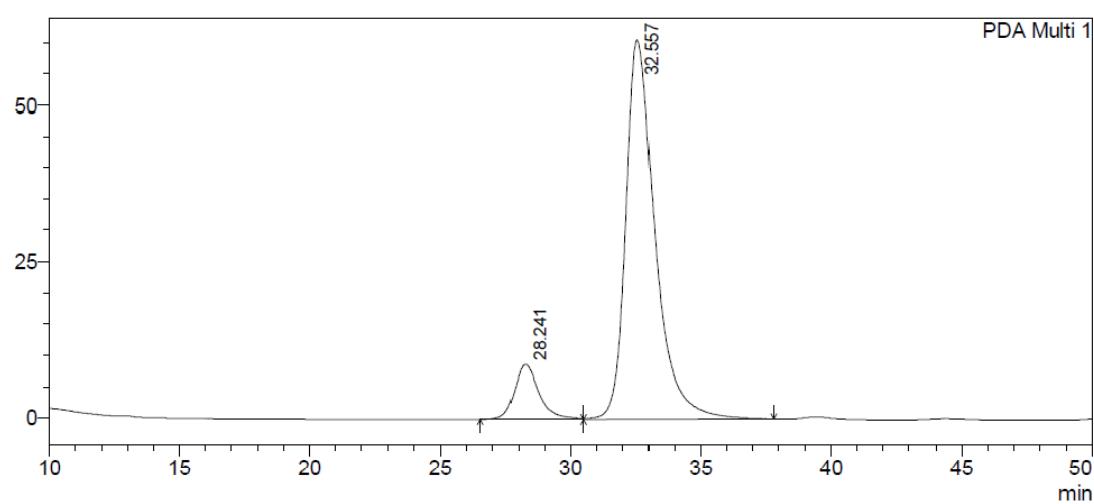
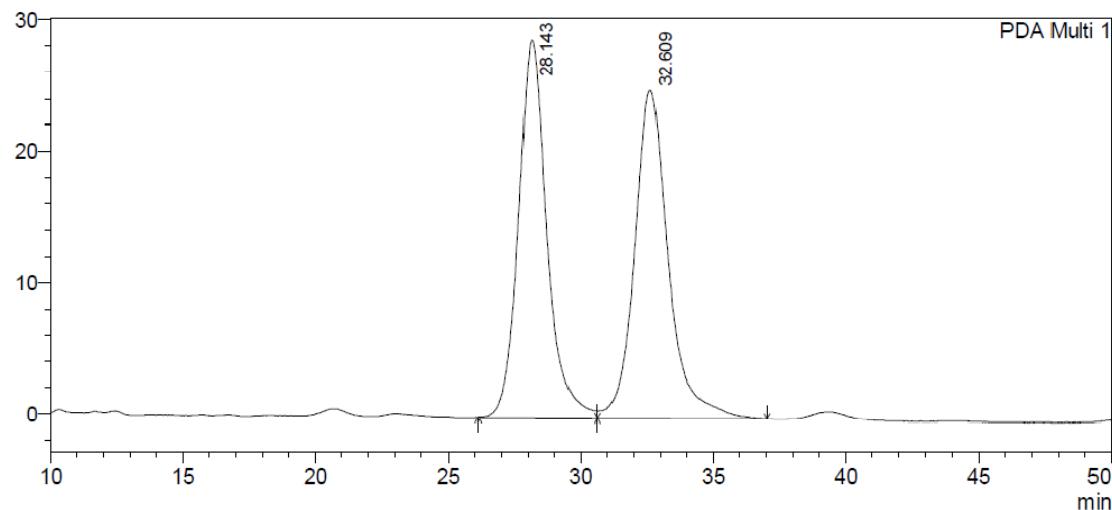
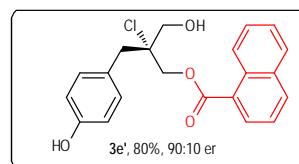


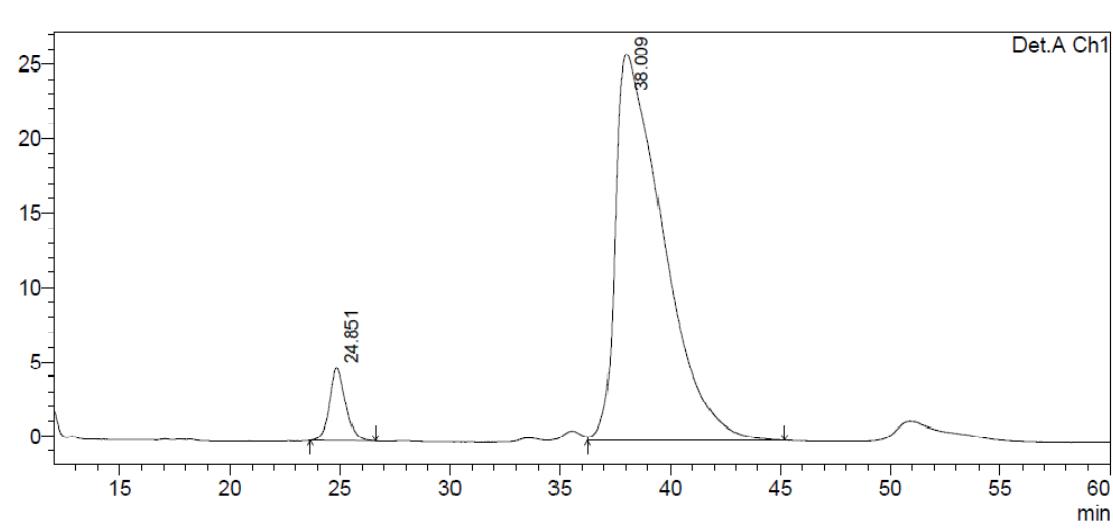
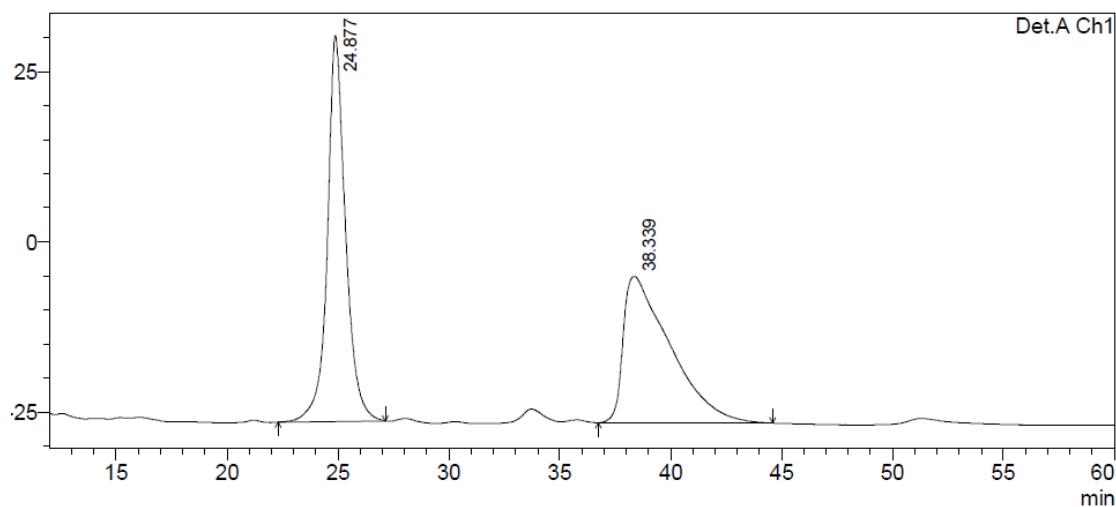
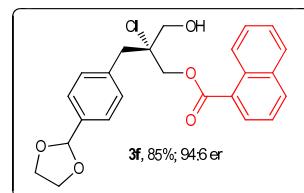


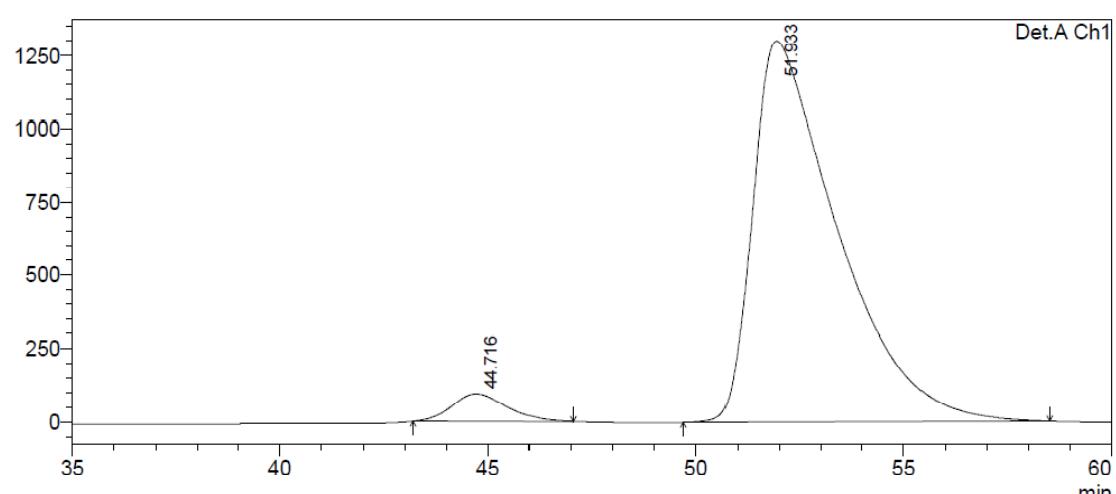
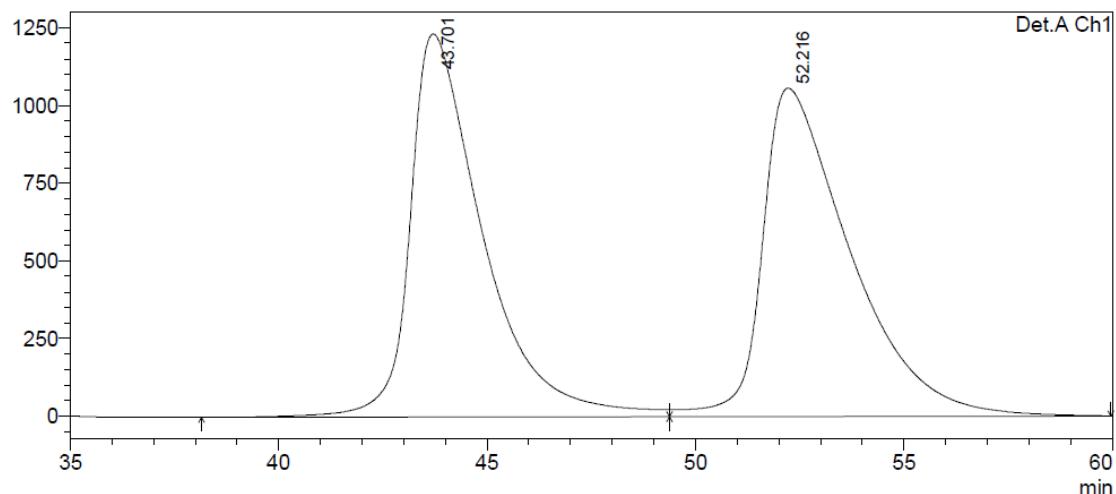
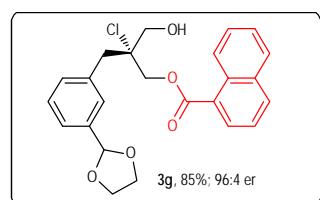


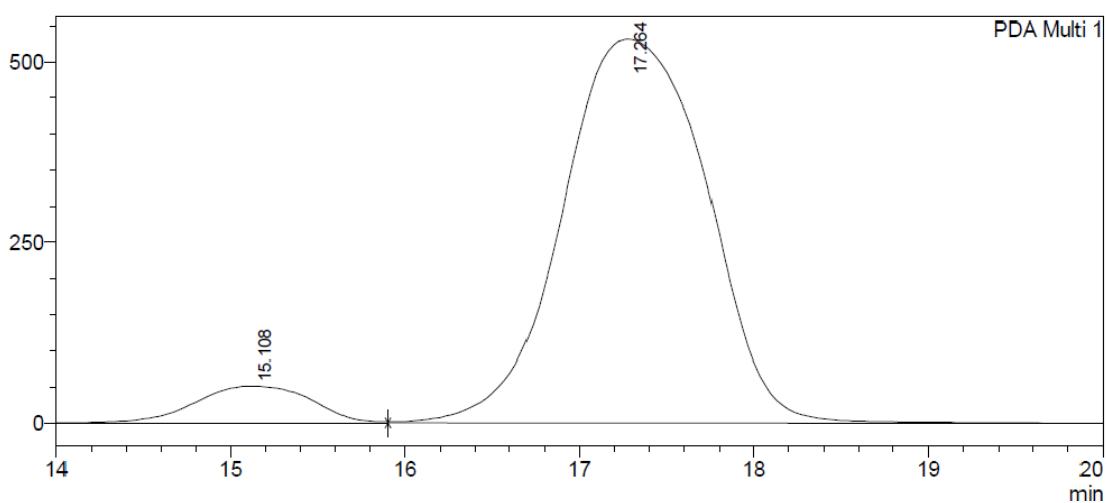
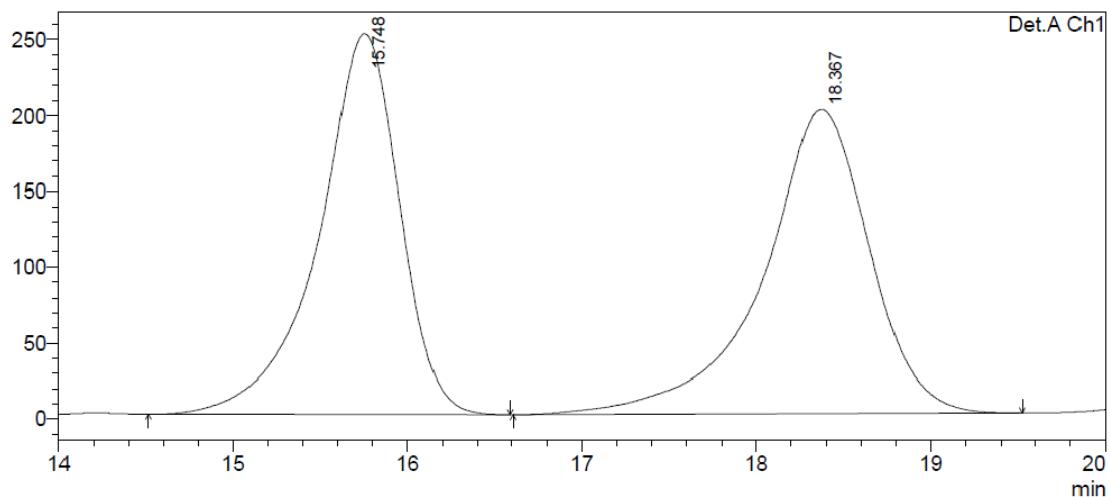
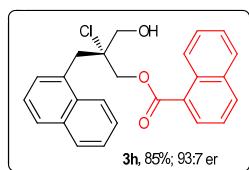


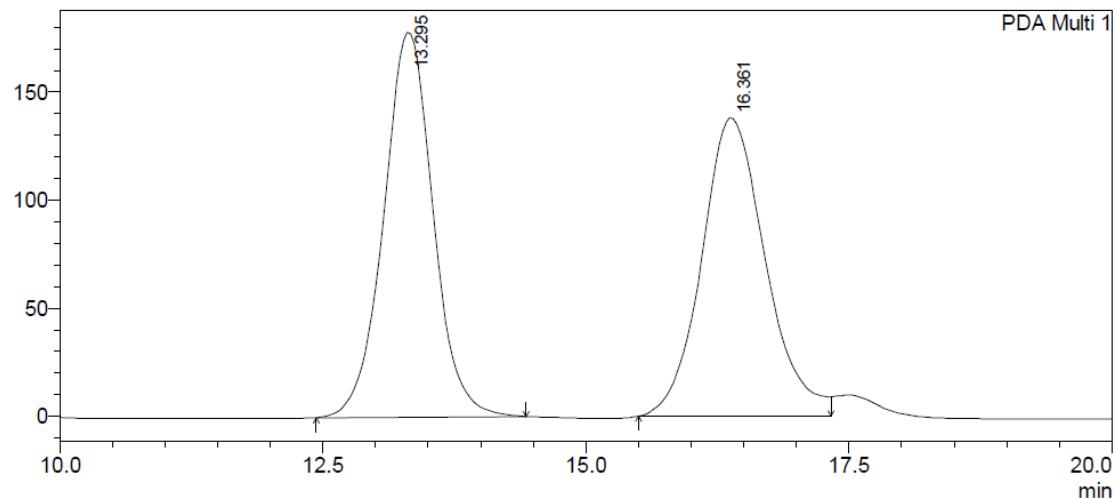
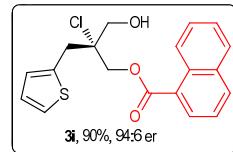




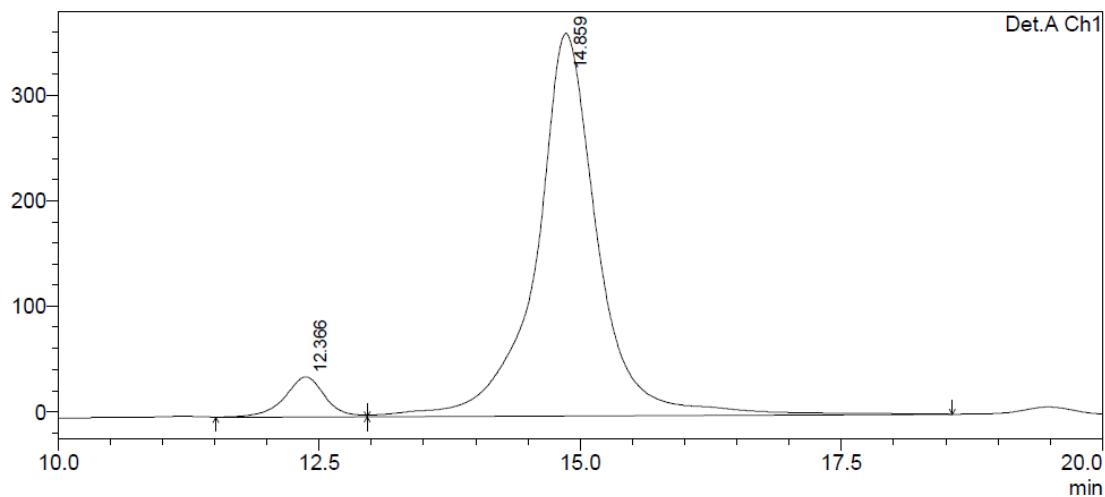




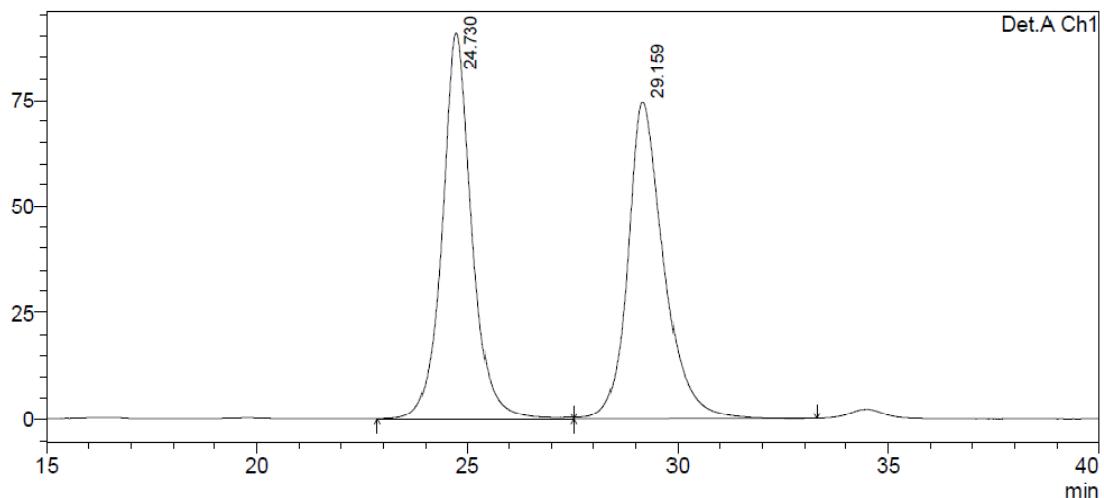
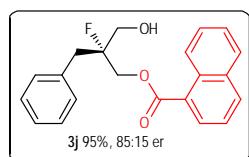




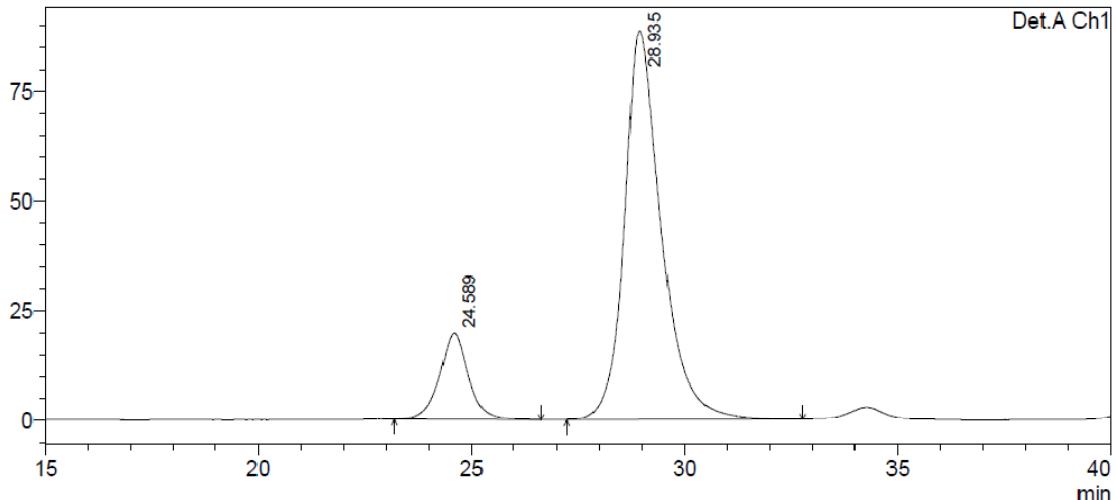
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.295	5833308	178159	50.013	56.327
2	16.361	5830246	138136	49.987	43.673
Total		11663554	316295	100.000	100.000



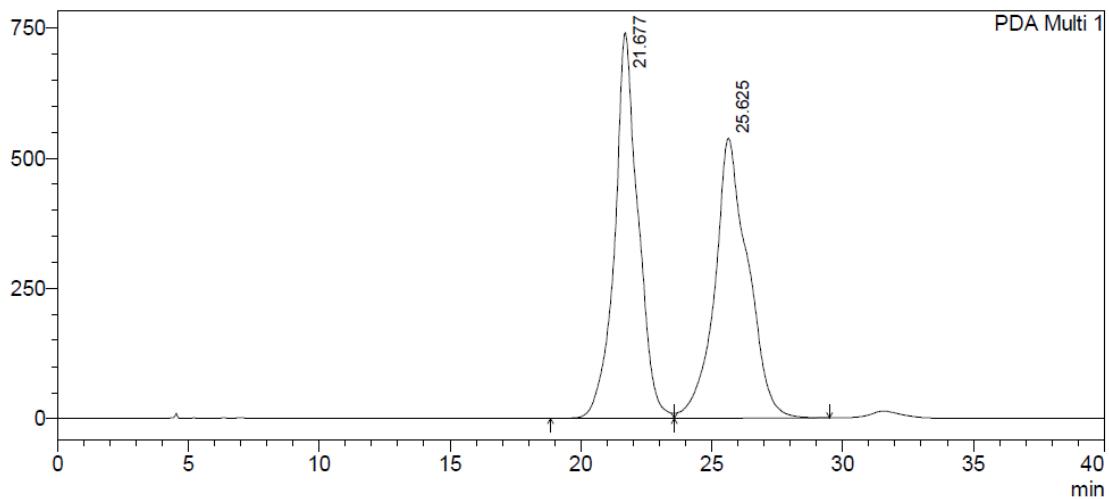
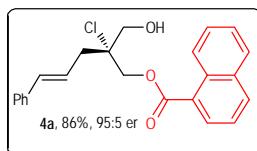
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.366	1011367	37821	6.352	9.461
2	14.859	14910607	361927	93.648	90.539
Total		15921974	399748	100.000	100.000



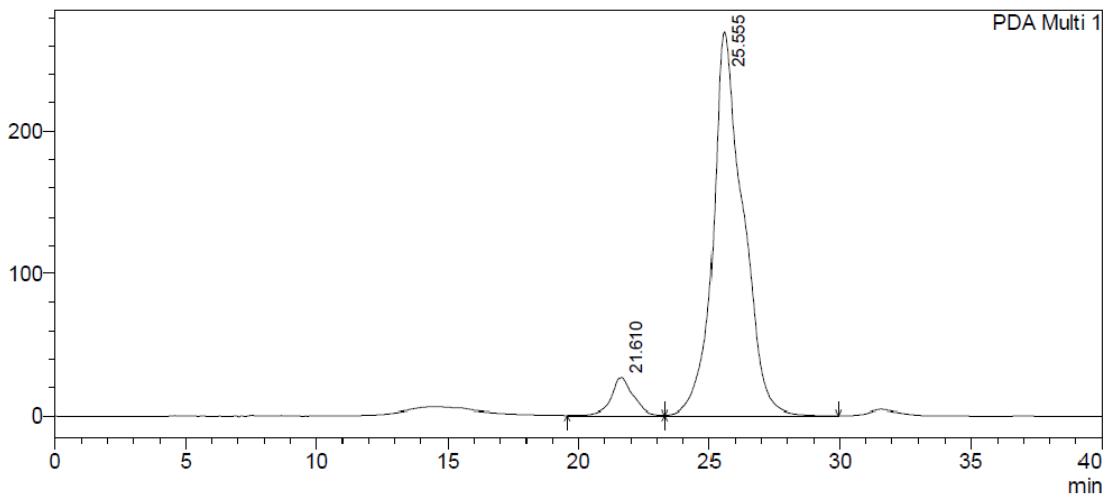
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.730	4485804	90592	50.132	54.885
2	29.159	4462148	74466	49.868	45.115
Total		8947952	165058	100.000	100.000



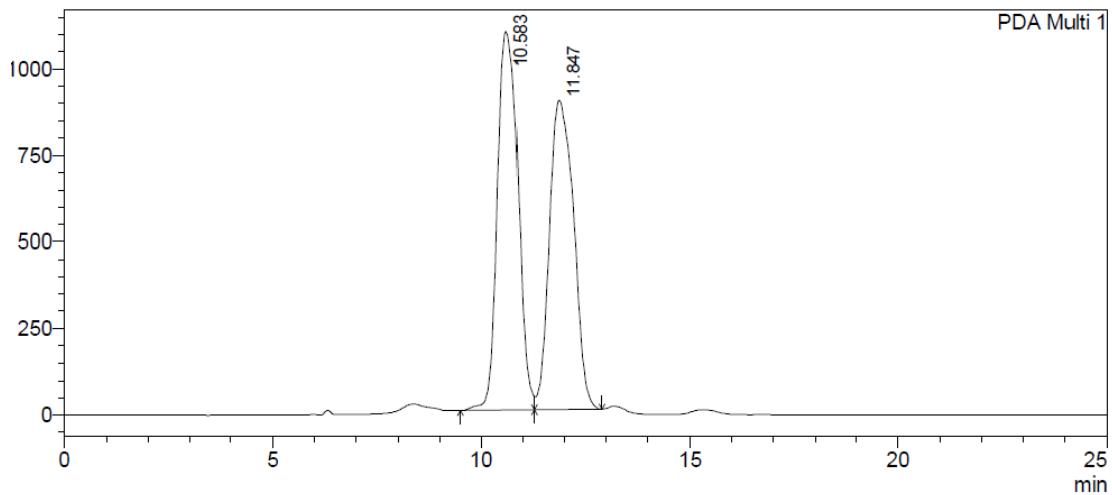
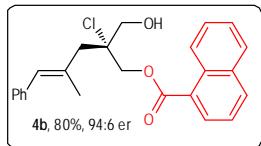
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.589	931865	19725	14.836	18.199
2	28.935	5349184	88662	85.164	81.801
Total		6281049	108387	100.000	100.000



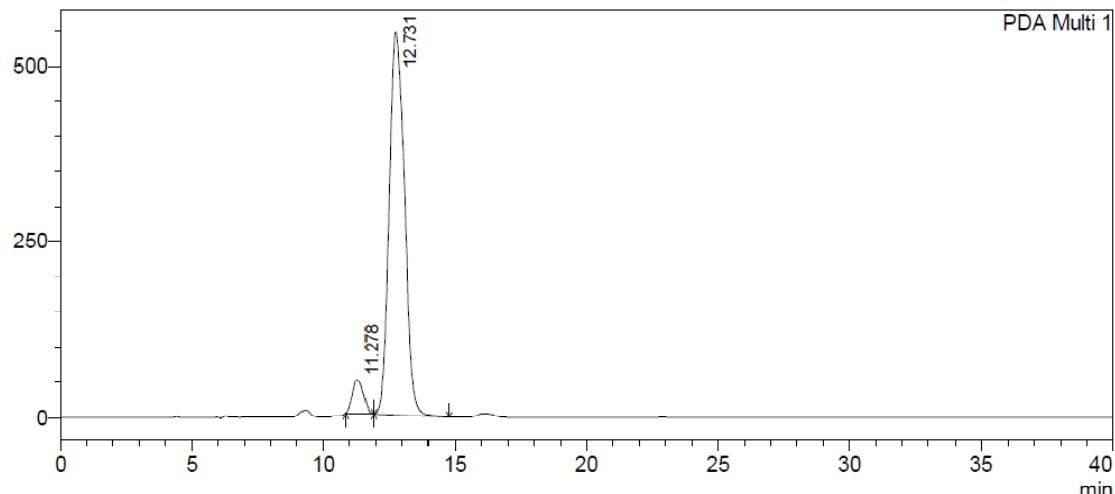
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.677	46469444	740442	49.390	57.932
2	25.625	47617304	537689	50.610	42.068
Total		94086748	1278131	100.000	100.000



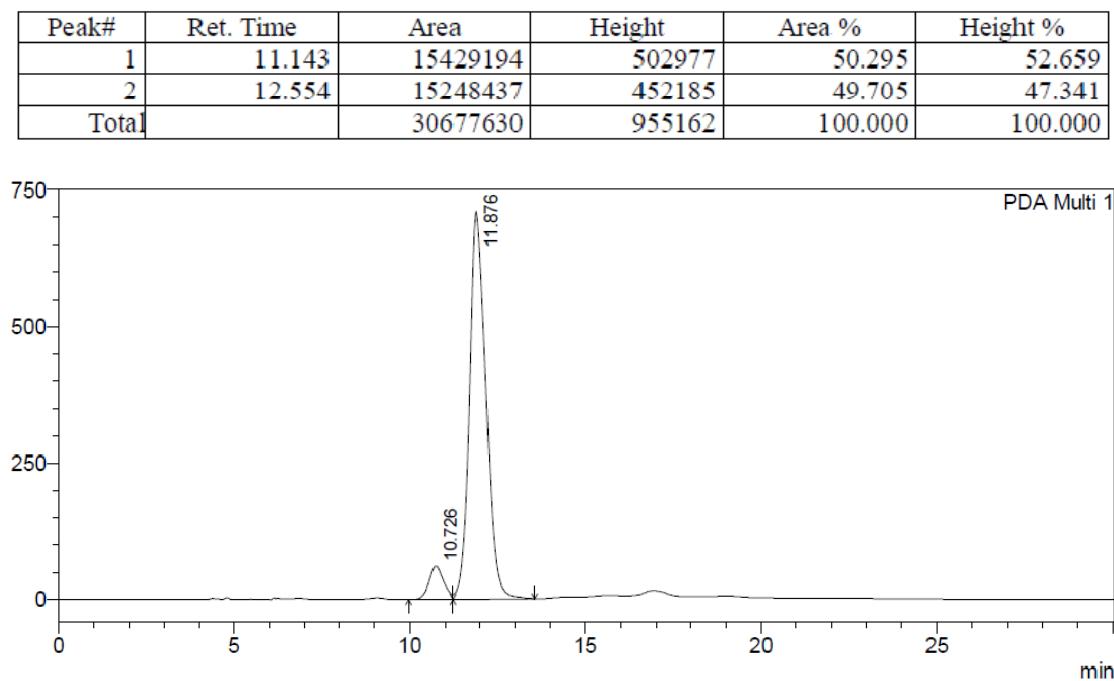
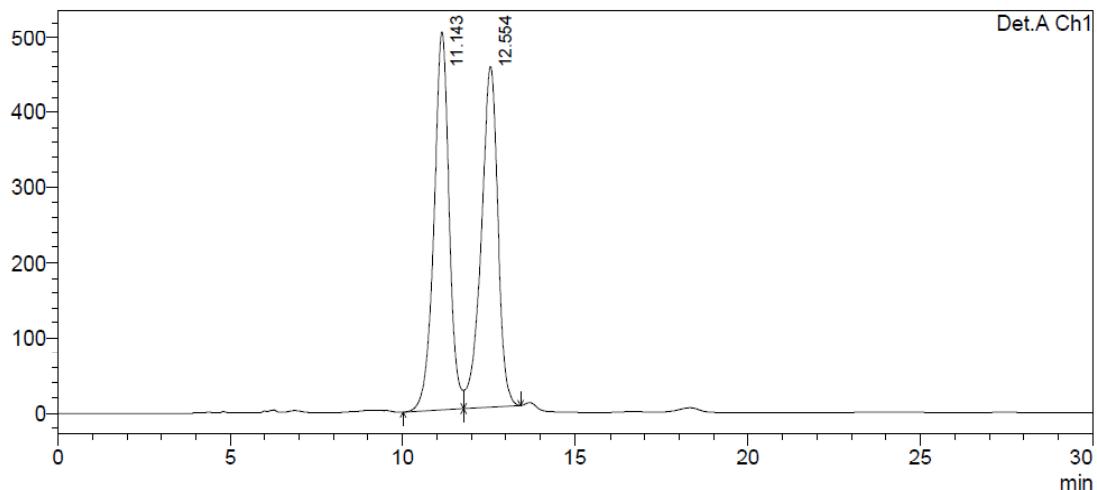
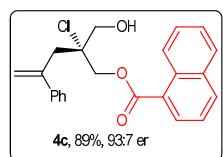
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.610	1136152	24356	5.023	8.279
2	25.555	21482018	269847	94.977	91.721
Total		22618171	294204	100.000	100.000

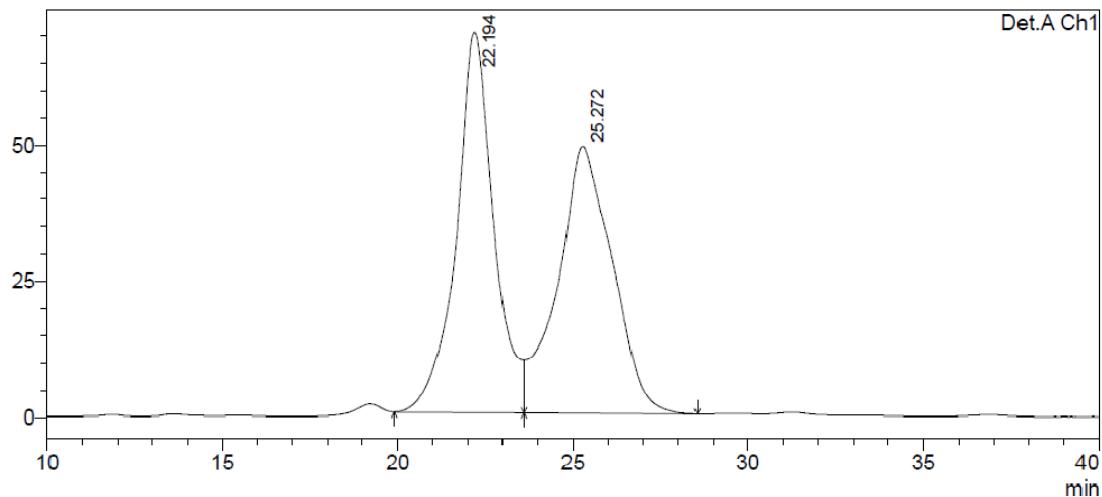
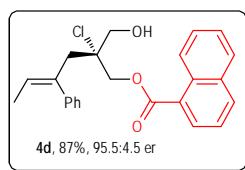


Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.583	37153493	1094179	50.519	55.075
2	11.847	36389383	892514	49.481	44.925
Total		73542876	1986692	100.000	100.000

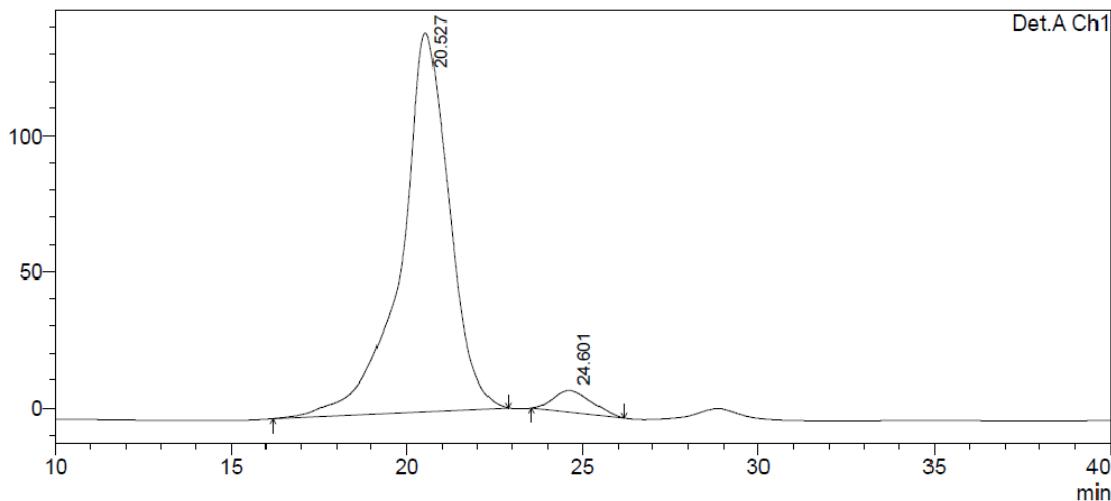


Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.278	1428360	48149	5.989	8.129
2	12.731	22420193	544193	94.011	91.871
Total		23848553	592342	100.000	100.000

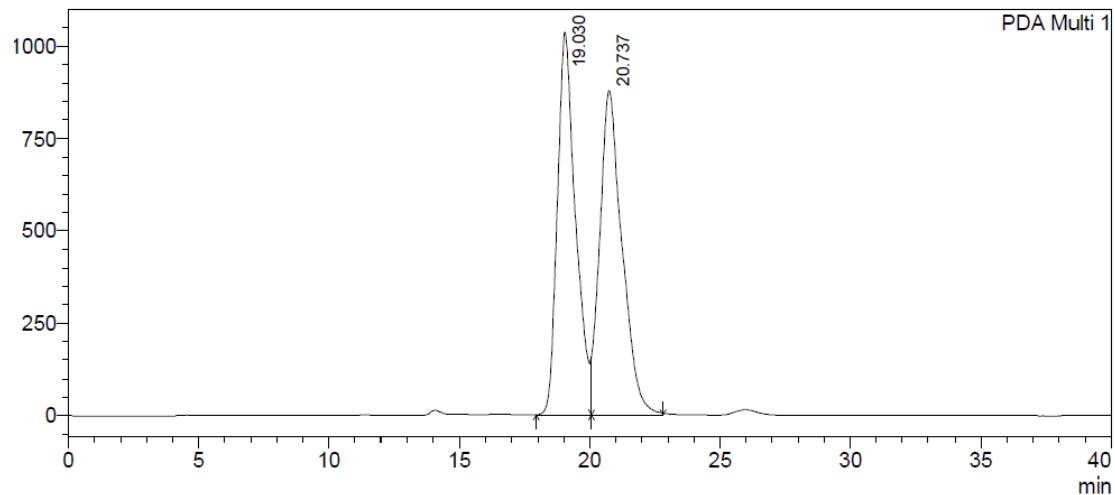
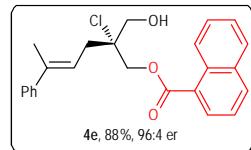




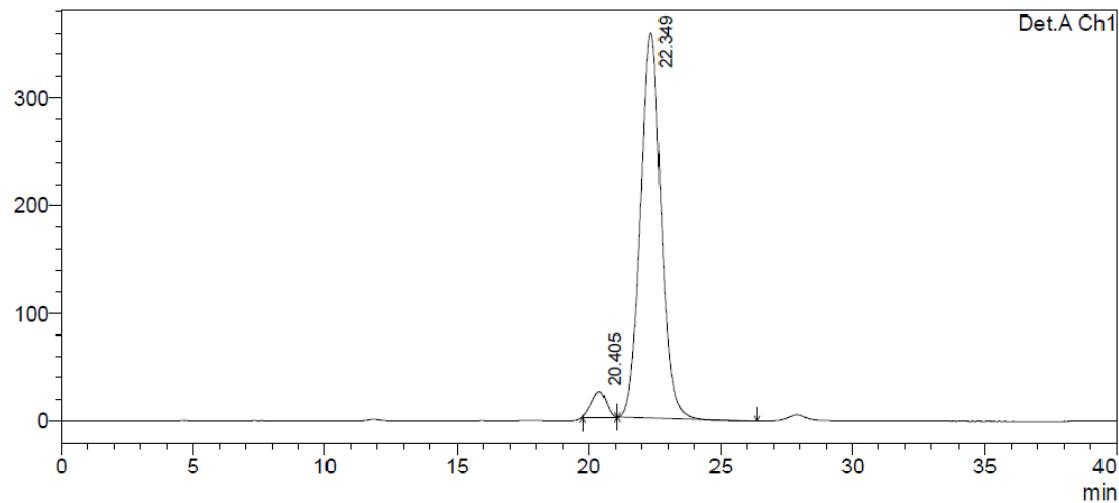
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.194	5229238	69942	49.591	58.759
2	25.272	5315485	49090	50.409	41.241
Total		10544724	119031	100.000	100.000



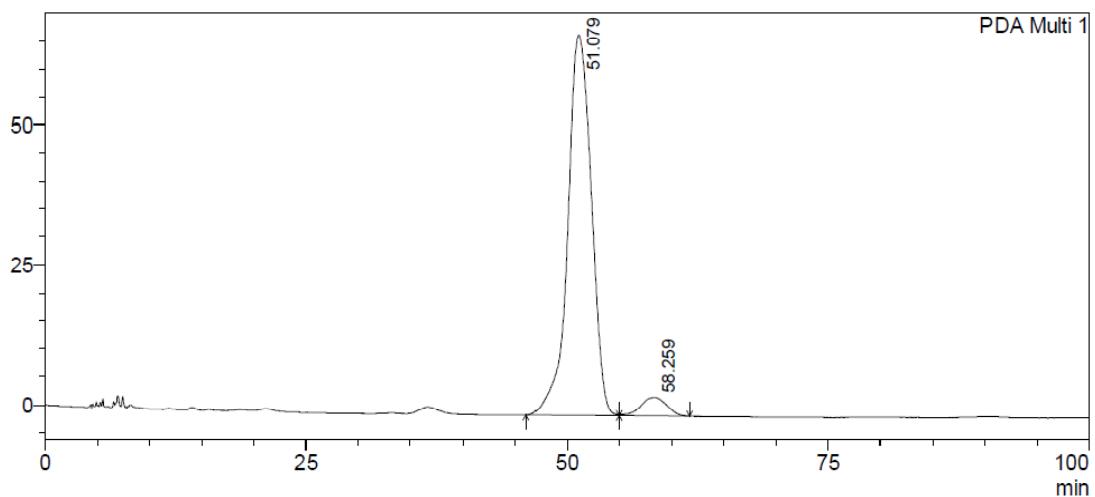
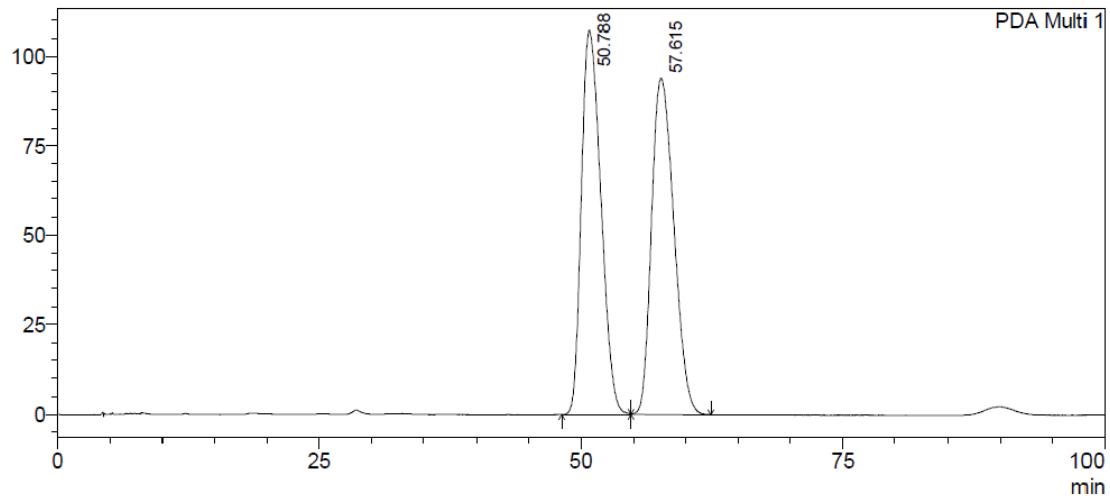
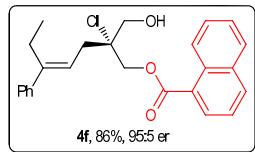
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.527	13190383	139147	95.527	94.496
2	24.601	617617	8105	4.473	5.504
Total		13807999	147252	100.000	100.000

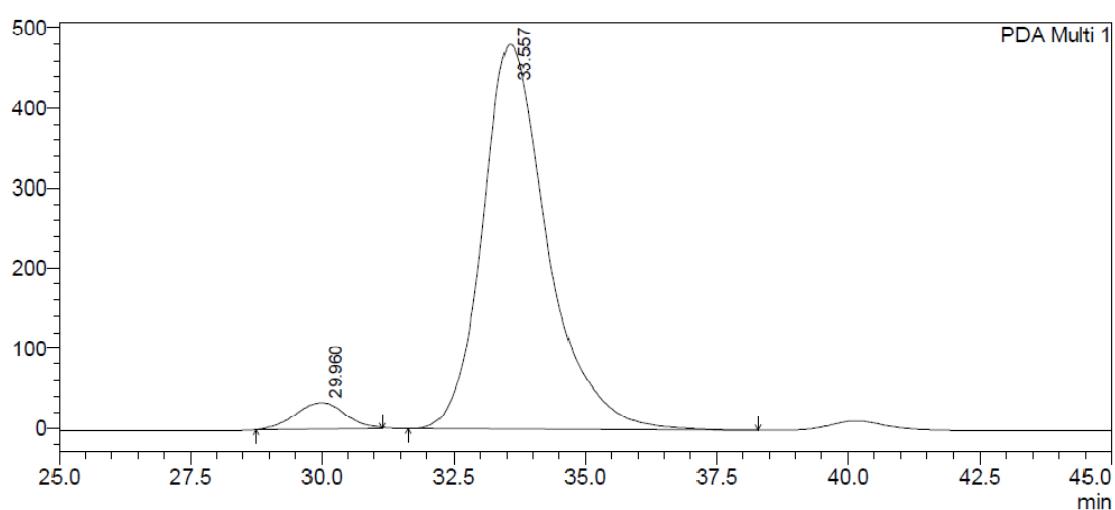
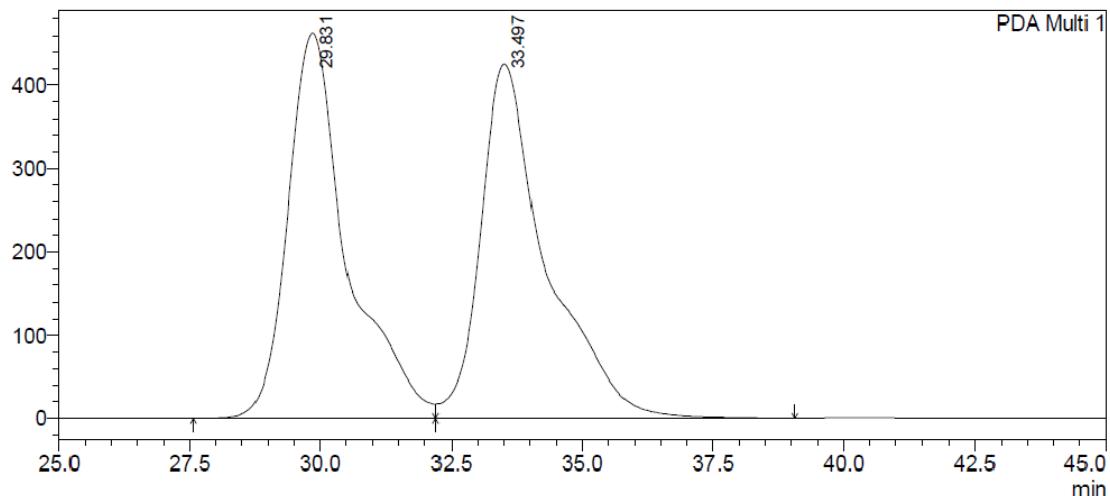
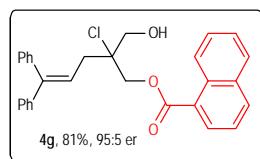


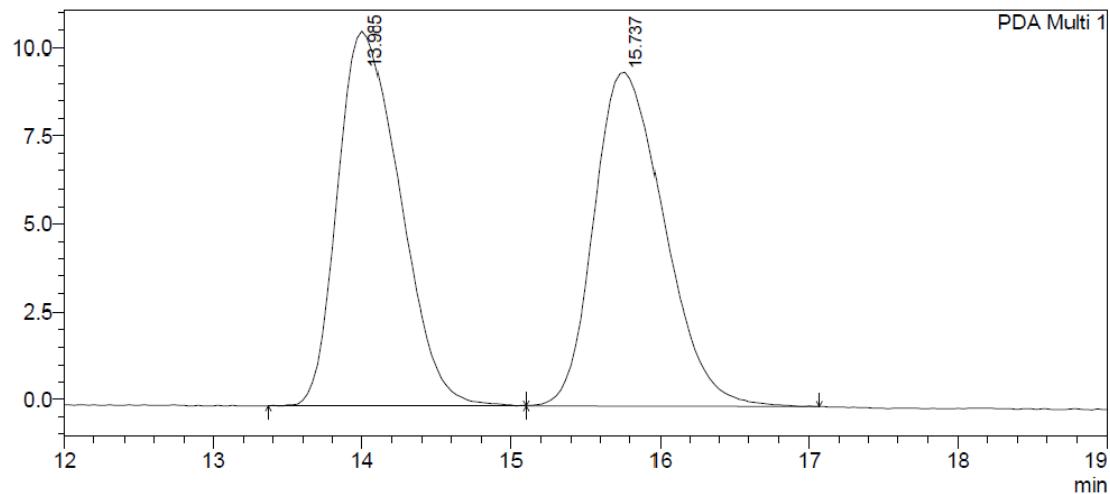
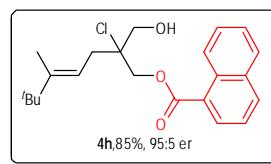
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.030	51005927	1036004	49.356	54.165
2	20.737	52336100	876684	50.644	45.835
Total		103342026	1912688	100.000	100.000



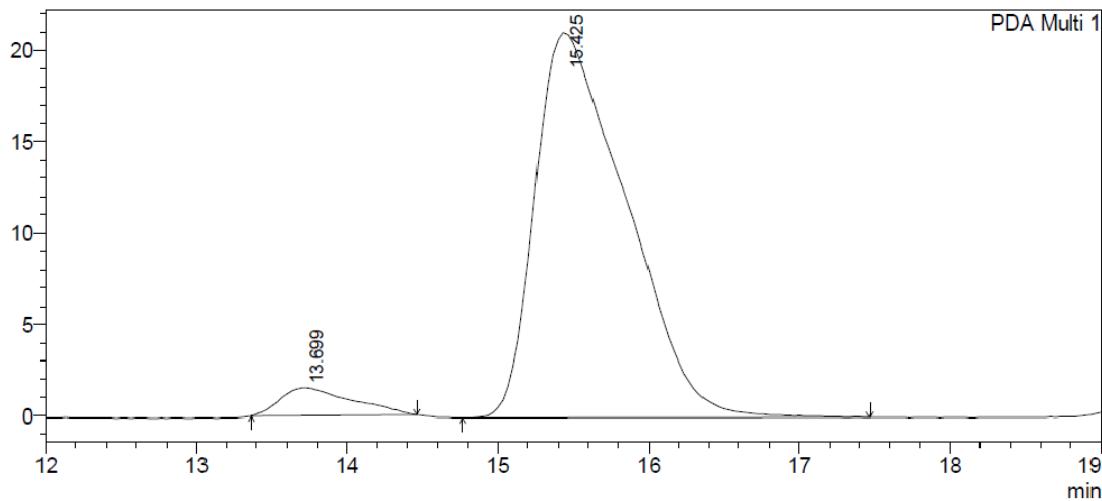
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.405	824007	22730	4.092	5.974
2	22.349	19311532	357760	95.908	94.026
Total		20135540	380491	100.000	100.000



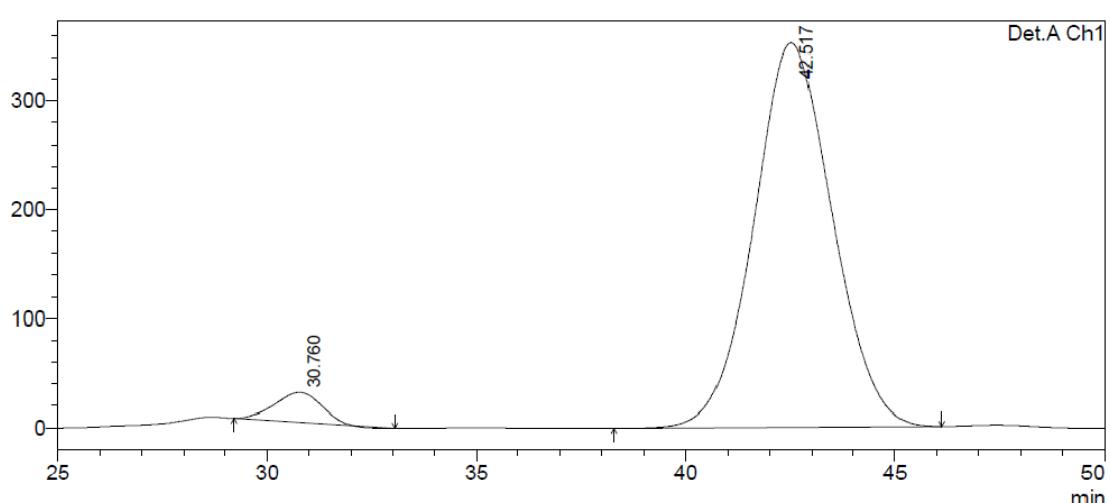
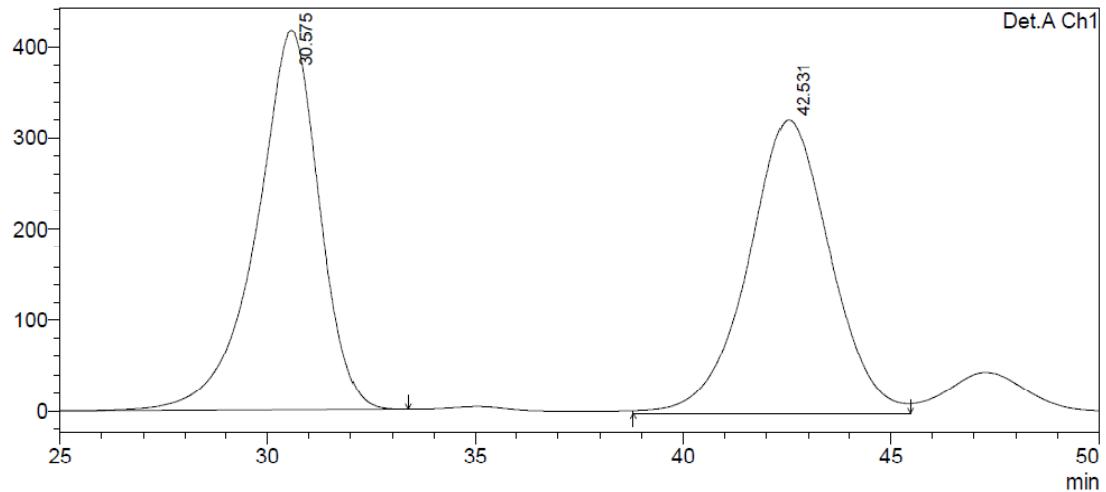
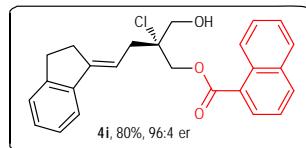


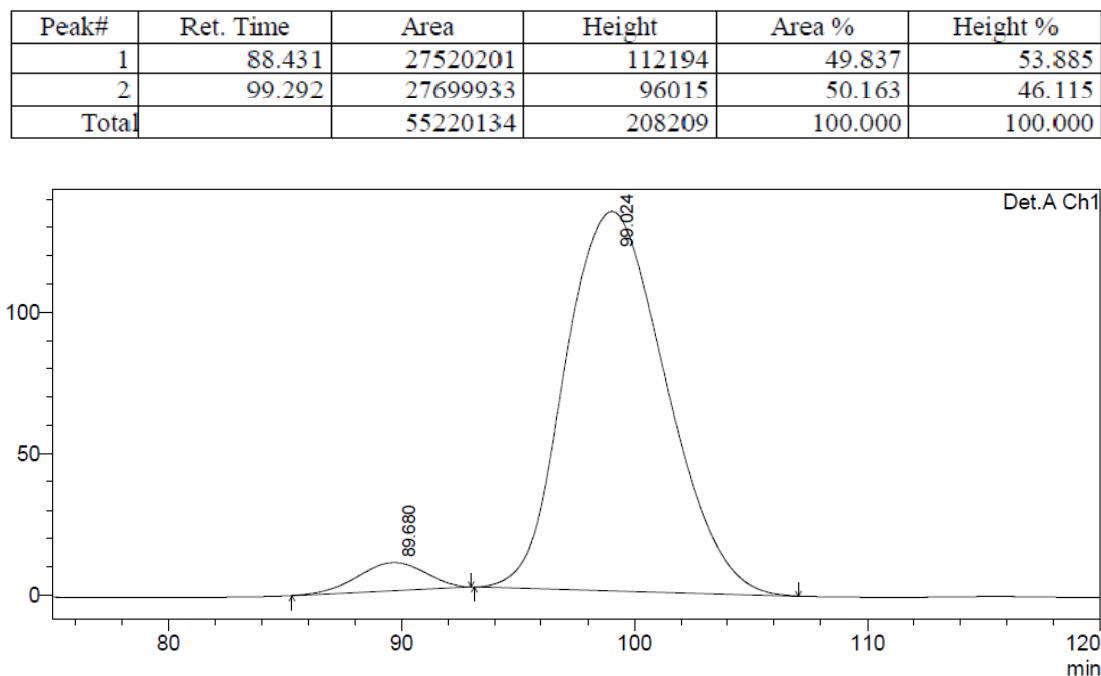
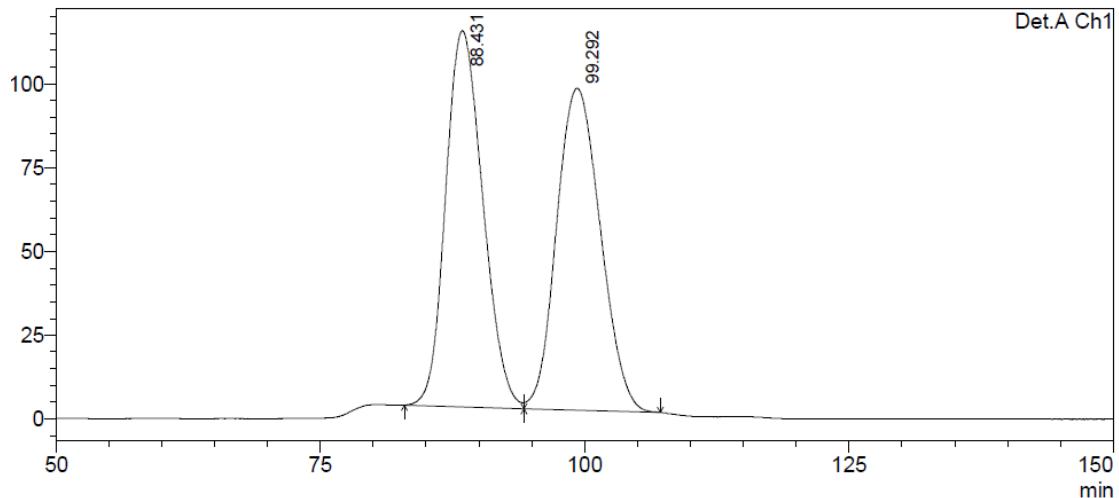
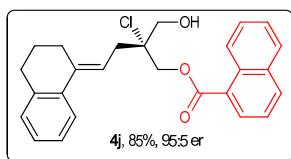


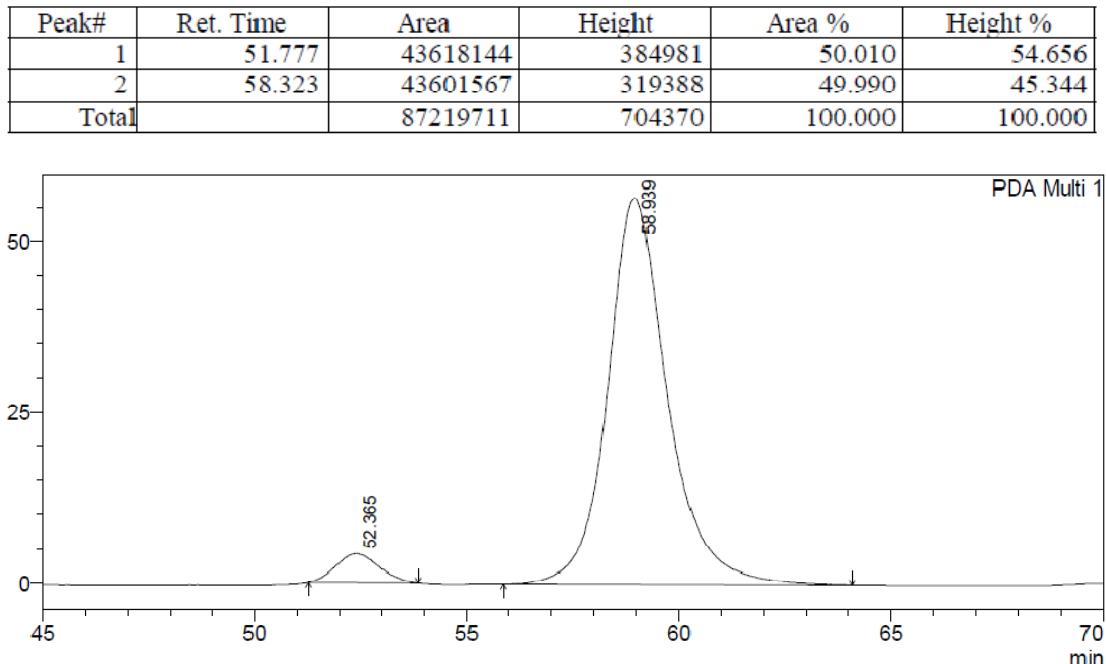
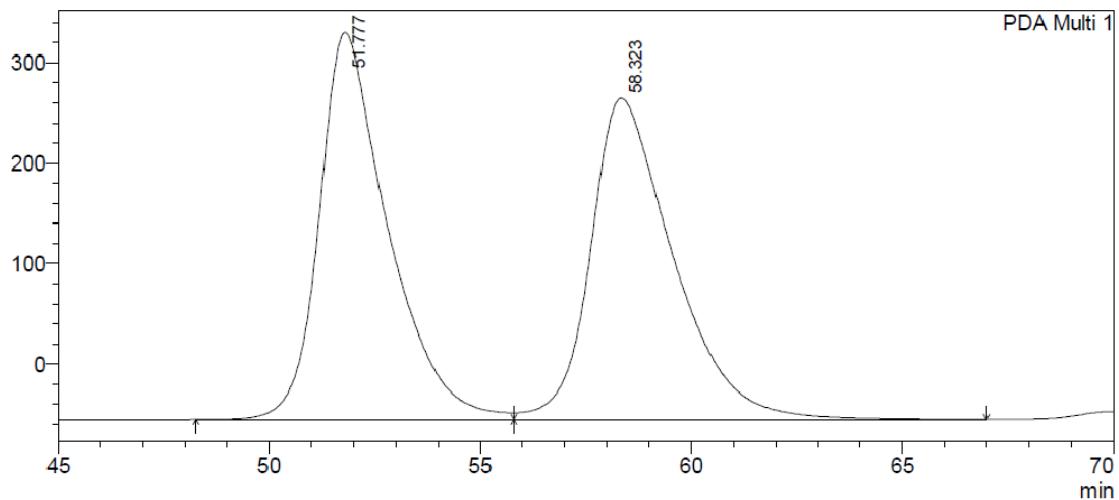
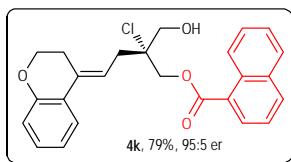
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.985	309490	10646	49.781	52.793
2	15.737	312217	9520	50.219	47.207
Total		621707	20166	100.000	100.000

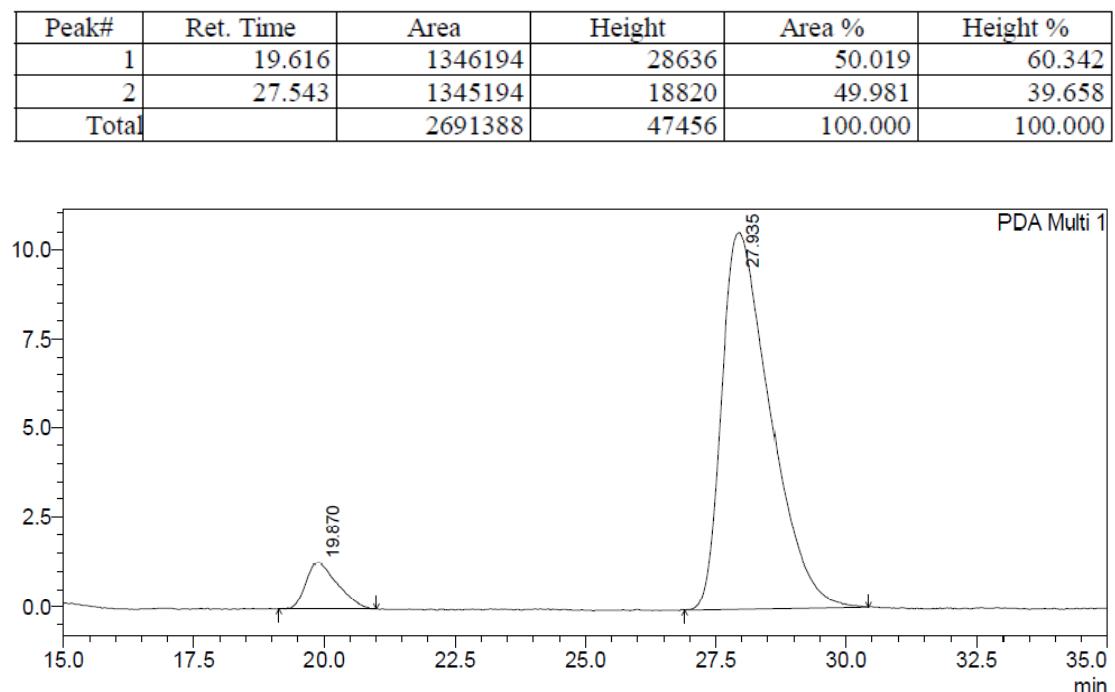
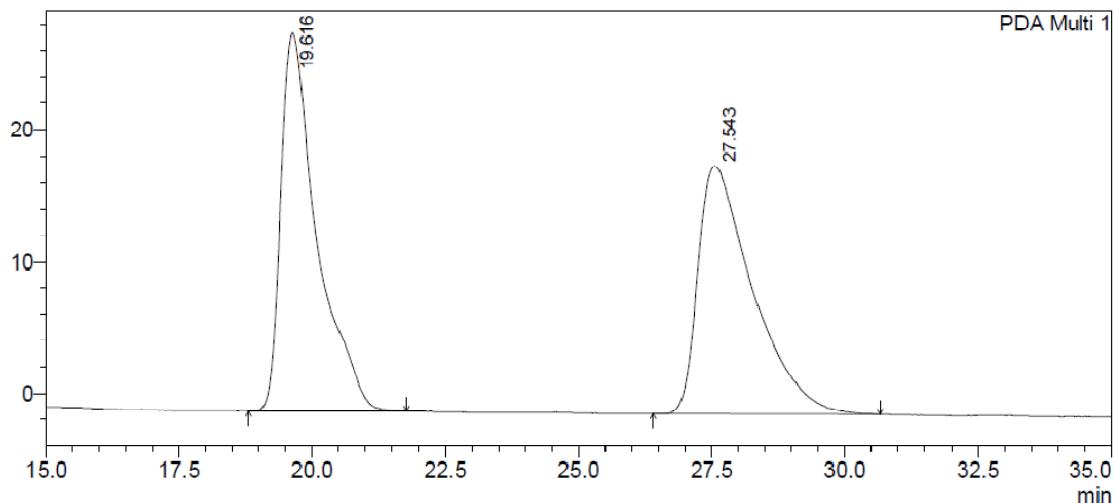
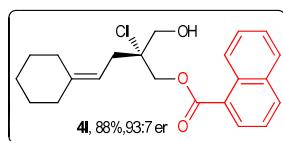


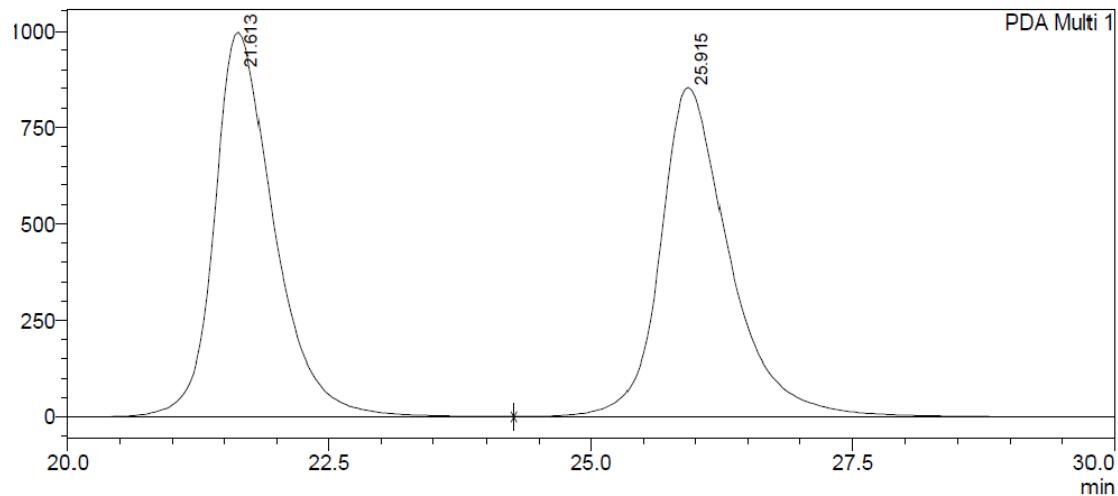
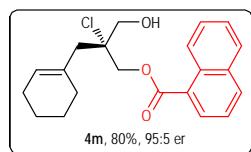
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.699	50300	1528	5.387	6.770
2	15.425	883467	21041	94.613	93.230
Total		933767	22569	100.000	100.000



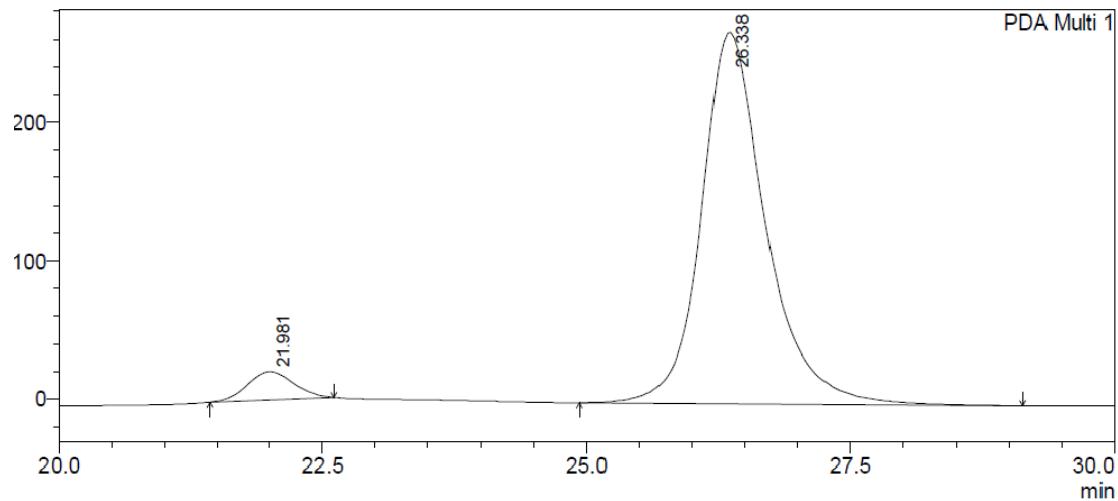




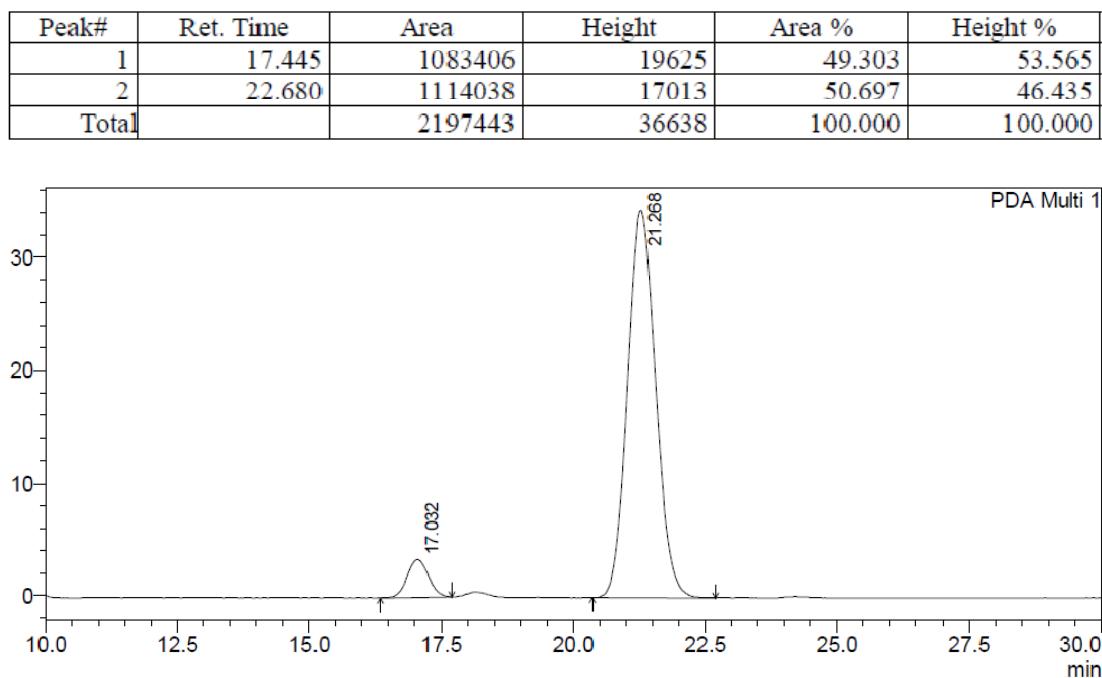
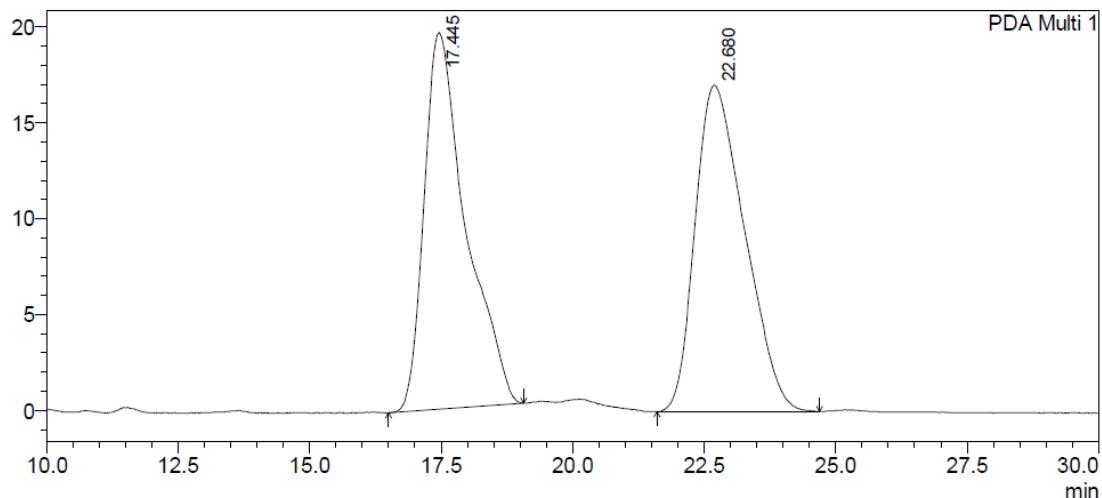
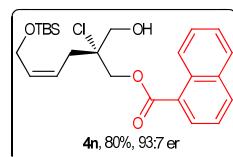


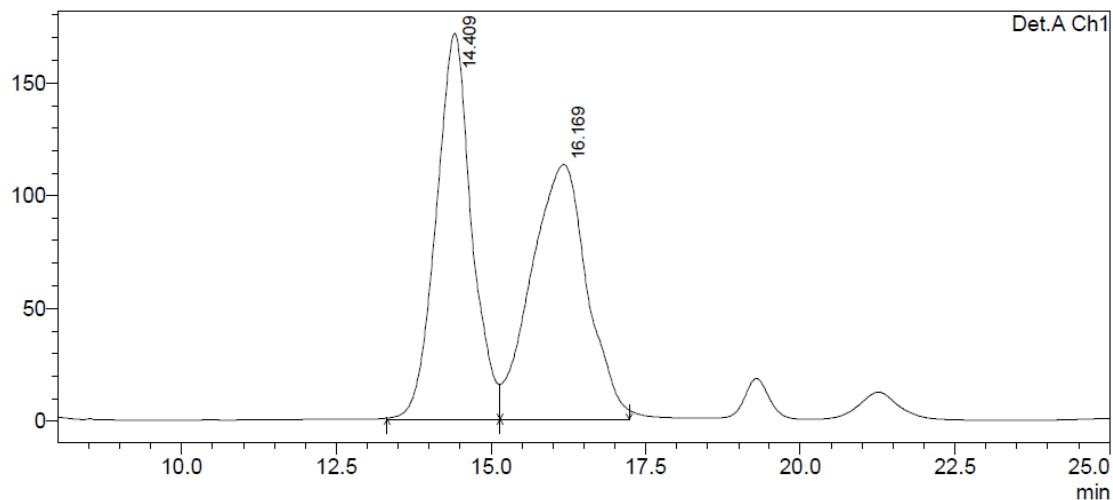
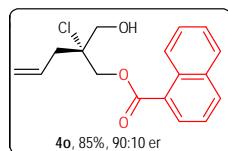


Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.613	39654722	998094	49.934	53.895
2	25.915	39759997	853842	50.066	46.105
Total		79414719	1851936	100.000	100.000

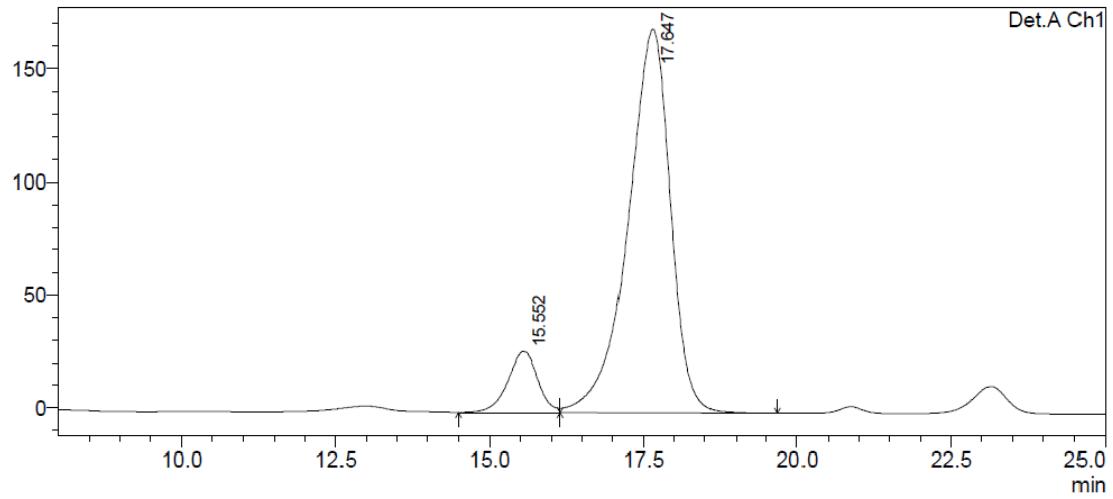


Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.981	630859	20697	5.222	7.151
2	26.338	11449229	268746	94.778	92.849
Total		12080088	289444	100.000	100.000

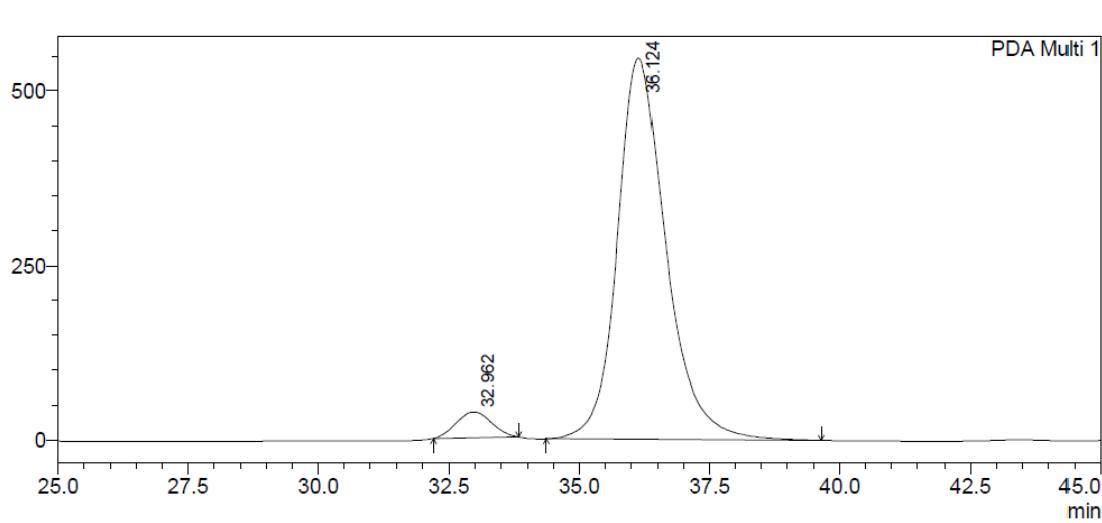
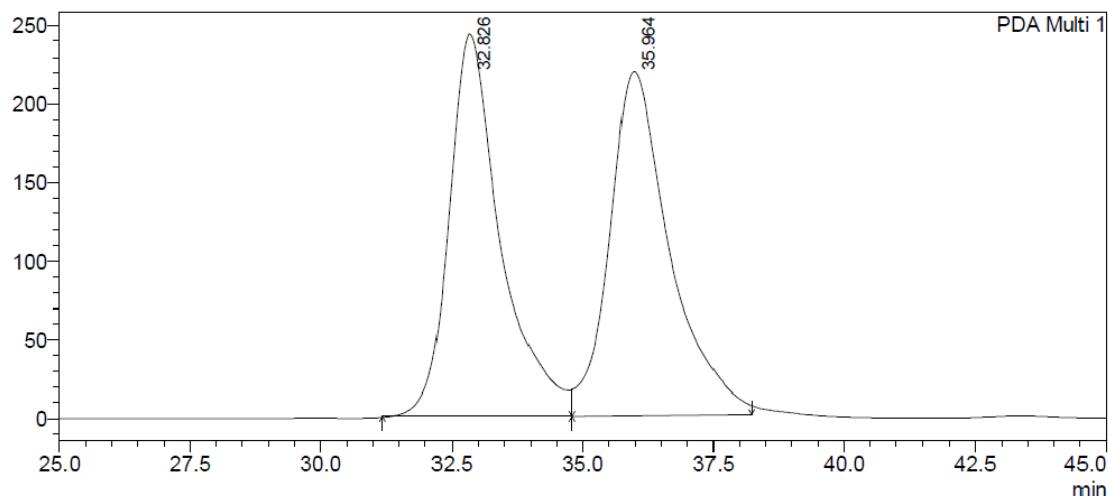
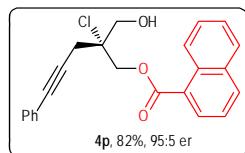


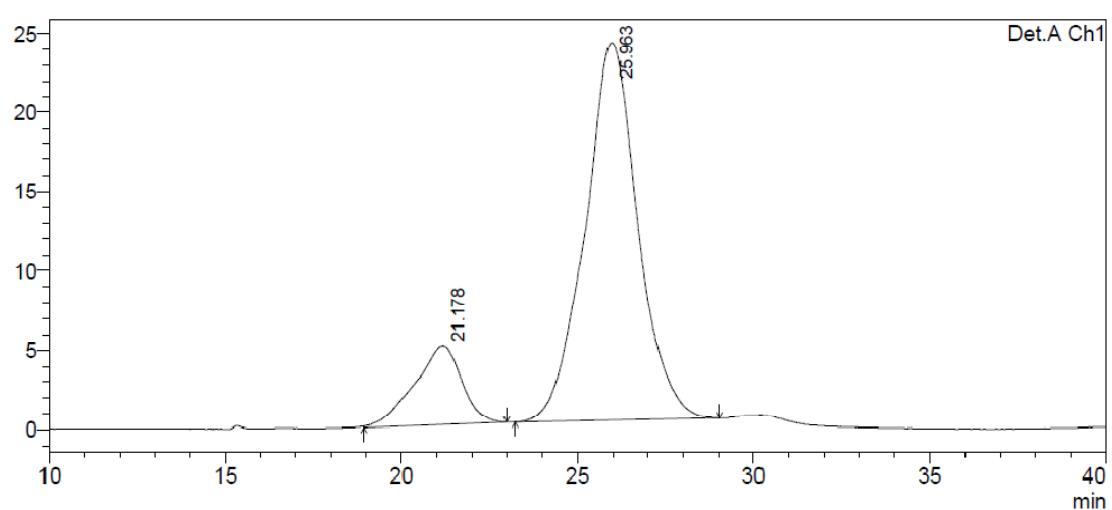
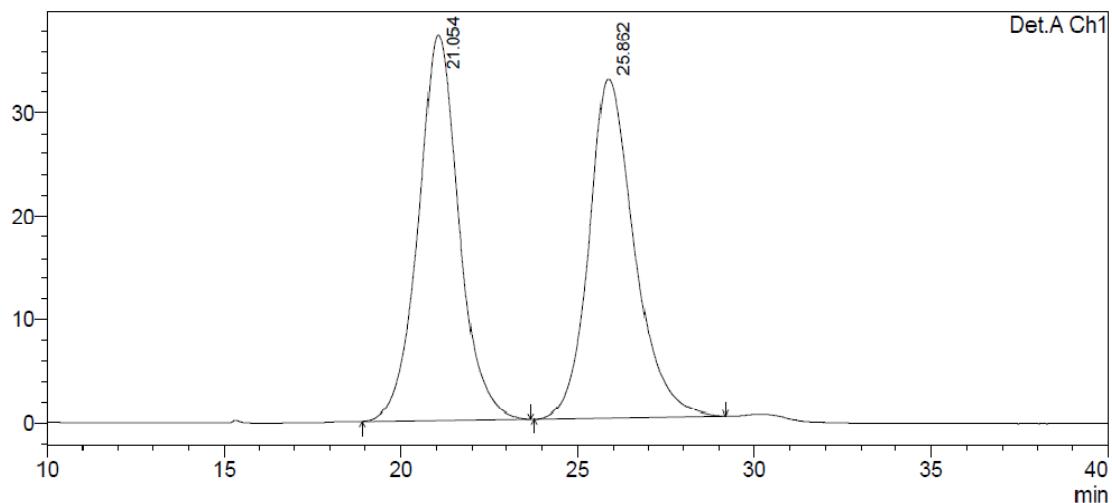
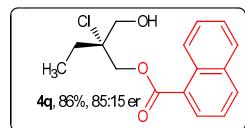


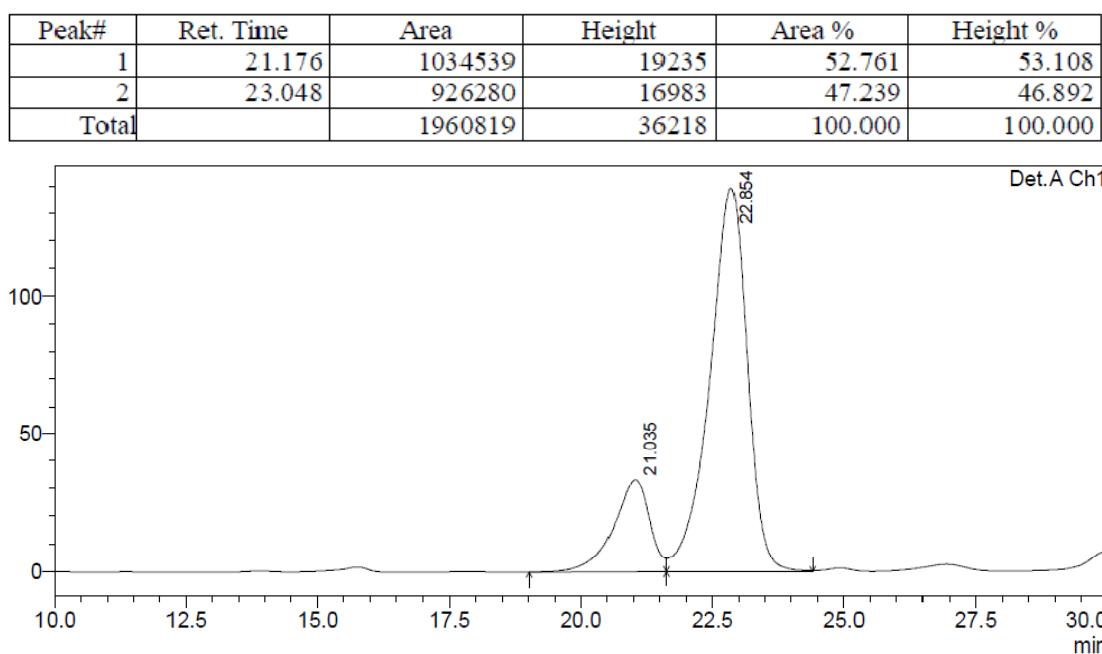
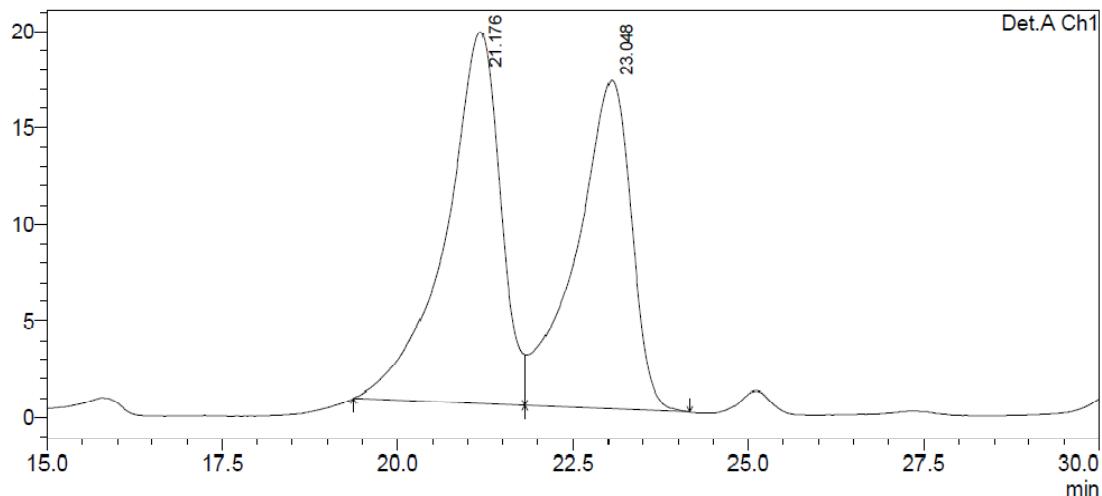
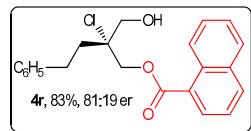
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.409	6815592	171008	49.104	60.243
2	16.169	7064303	112857	50.896	39.757
Total		13879895	283865	100.000	100.000

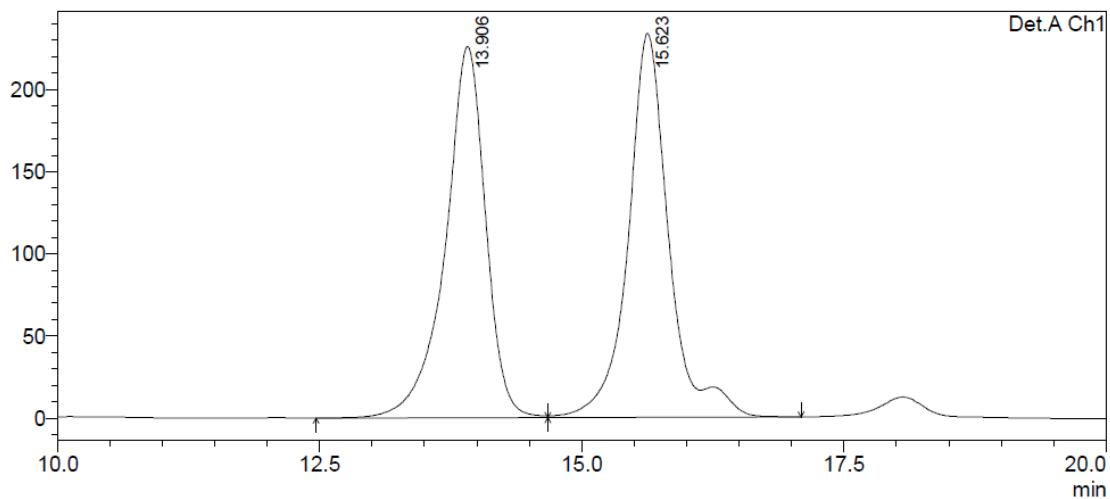
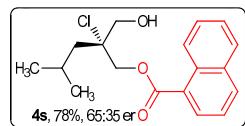


Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.552	898657	26967	9.892	13.712
2	17.647	8186349	169706	90.108	86.288
Total		9085006	196673	100.000	100.000

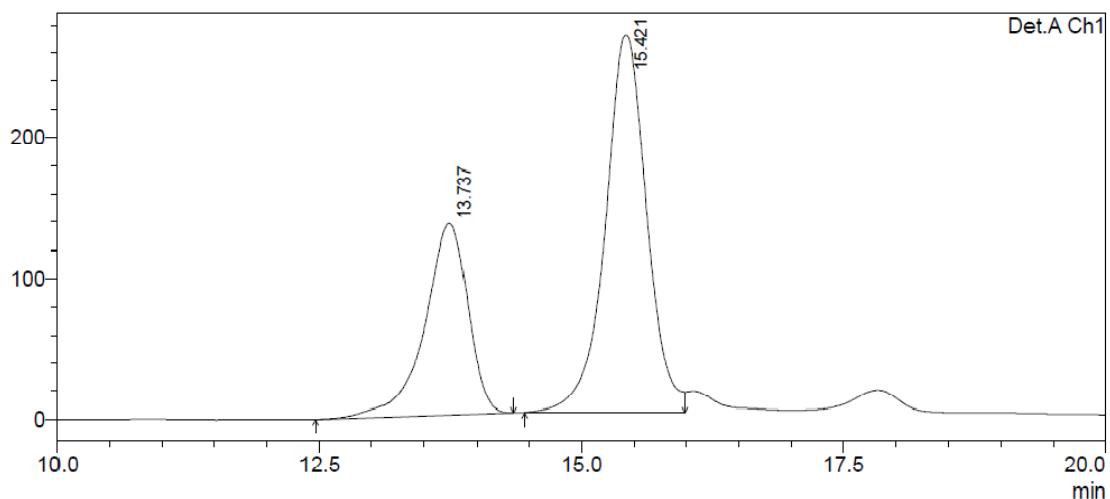




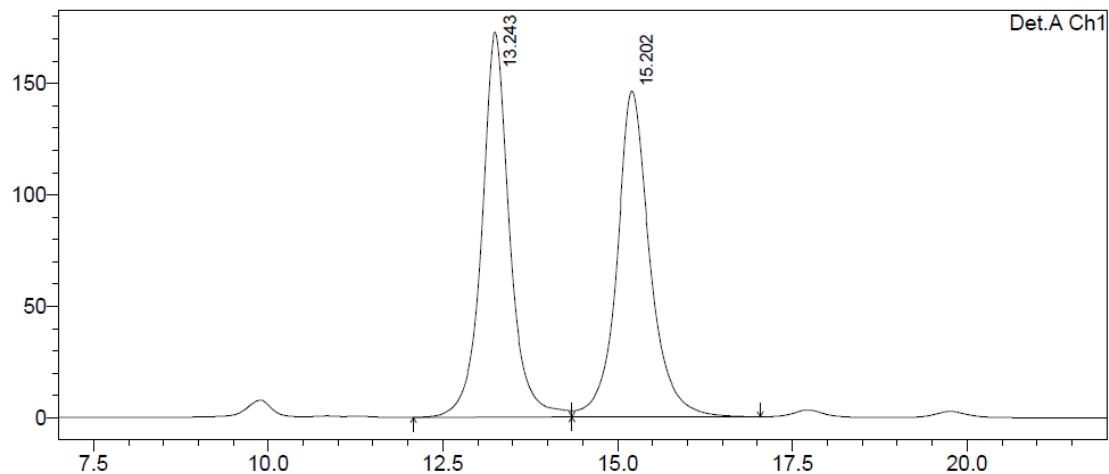
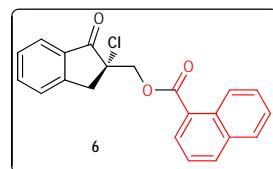




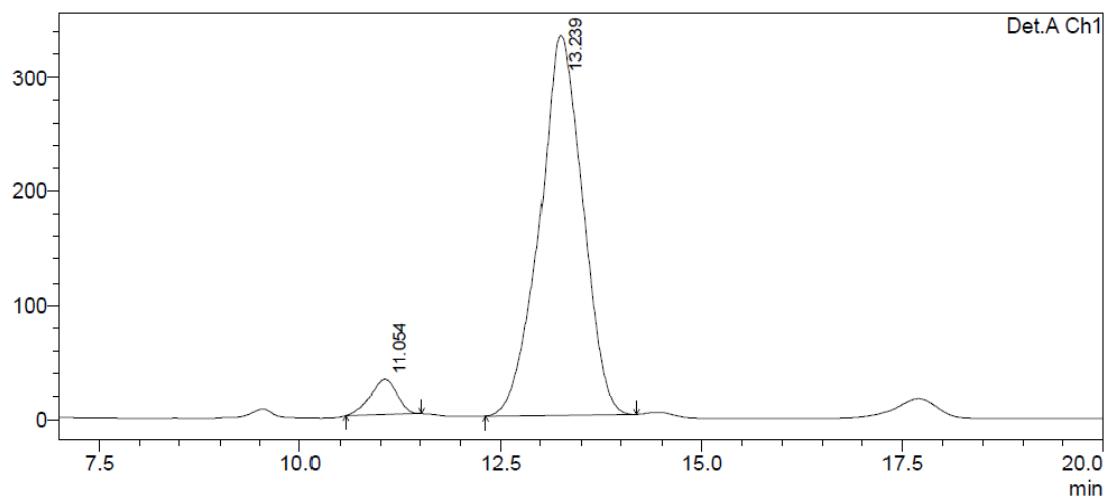
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.906	6059630	226287	49.230	49.176
2	15.623	6249251	233867	50.770	50.824
Total		12308882	460154	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.737	3909018	135853	34.717	33.596
2	15.421	7350544	268525	65.283	66.404
Total		11259562	404378	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.243	4819732	172834	50.018	54.157
2	15.202	4816297	146303	49.982	45.843
Total		9636029	319138	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.054	720628	30655	5.505	8.434
2	13.239	12370017	332829	94.495	91.566
Total		13090645	363483	100.000	100.000

