

Supporting Information

Gold-Catalyzed Construction of Two Adjacent Quaternary Stereocenters via Sequential C-H Functionalization and Aldol Annulation

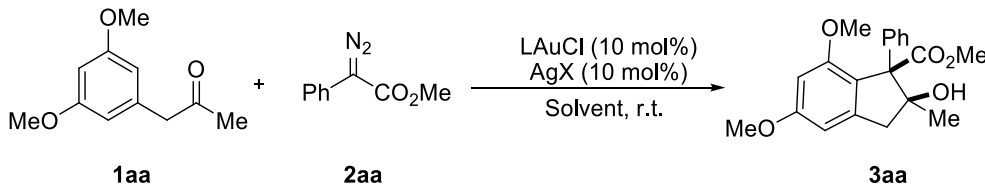
Zhunzhun Yu, Haile Qiu, Lu Liu* and Junliang Zhang*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China.

Content:

1. Table S1.....	S2
2. General Information.....	S3
3. Synthesis of 1.....	S4
4. General procedure for the cascade reactions.....	S12
5. Reaction of phenol and aniline derivatives.....	S37
6. Preliminary investigation on asymmetric catalysis.....	S38
7. Transformation of products.....	S40
8. Another proposed mechanism.....	S45
9. References.....	S46
10. Crystal structures of 7aa and 8na.....	S47
11. NMR Spectra of new compounds.....	S47

Table S1: Optimization of Reaction Conditions.^a

						
Entry	Catalyst	AgX	Solvents	Time	d.r.	Yield ^d (%)
1	PPh ₃ AuCl	AgNTf ₂	CH ₂ Cl ₂	45 min	9:1	76
2	IPrAuCl	AgNTf ₂	CH ₂ Cl ₂	45 min	> 20:1	48
3	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgNTf ₂	CH ₂ Cl ₂	45 min	12:1	81
4	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgOTf	CH ₂ Cl ₂	45 min	4:1	48
5	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgSbF ₆	CH ₂ Cl ₂	45 min	8:1	48
6	CuOTf ₂ (10 mol%)	-	CH ₂ Cl ₂	12 h	-	N.D.
7	CuOTf (10 mol%)	-	CH ₂ Cl ₂	12 h	-	N.D.
8	Rh ₂ (OAc) ₄ (10 mol%)	-	CH ₂ Cl ₂	12 h	-	N.D.
9	Pd(OAc) ₂ (10 mol%)	-	CH ₂ Cl ₂	12 h	-	N.D.
10	Pd(PPh ₃) ₄ (10 mol%)	-	CH ₂ Cl ₂	12 h	-	N.D.
11	AgNTf ₂ (10 mol%)	-	CH ₂ Cl ₂	45 min	5:1	38
12 ^b	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgNTf ₂	CH ₂ Cl ₂	45 min	11:1	68
13 ^c	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgNTf ₂	CH ₂ Cl ₂	45 min	18:1	82 (77)
14 ^c	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgNTf ₂	CH ₃ CN	45 min	> 20:1	44
15 ^c	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgNTf ₂	THF	45 min	1.5:1	30
16 ^c	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgNTf ₂	Toluene	45 min	14:1	34
17 ^c	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgNTf ₂	ClCH ₂ CH ₂ Cl	45 min	8:1	63
18 ^c	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	-	CH ₂ Cl ₂	45 min	-	N.R.

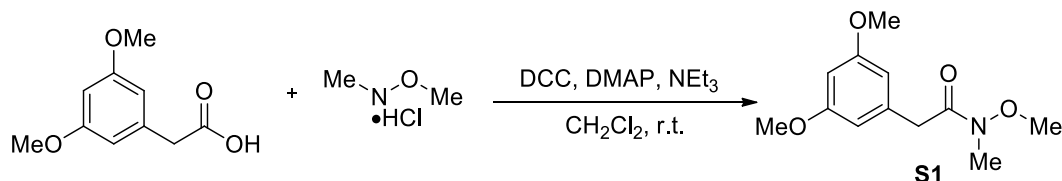
^a Unless noted, the reaction was carried out with **1aa** (0.3 mmol), **2aa** (0.2 mmol), catalyst (10 mol%) in solvent (4 mL) at room temperature. ^b Gold catalyst (5 mol%) was used. ^c 3 equiv of **1aa** and 5 mol% of catalyst were used. ^d NMR yield and the numbers in parenthesis is isolated yield.

2. General Information:

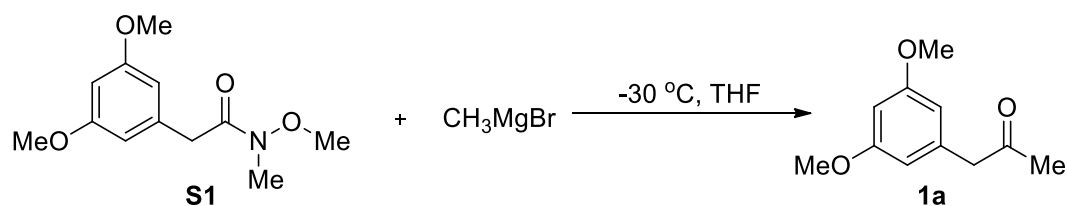
All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^1H NMR, ^{13}C NMR spectra were measured at 400 MHz and 100 MHz in CDCl_3 . Data for ^1H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CDCl_3 : 77.0 ppm). THF, toluene and ether were distilled from sodium and benzophenone prior to be used. CH_2Cl_2 , DMF was distilled from CaH_2 prior to be used.

3. Synthesis of 1.

1) Synthesis of 1-(3, 5-dimethoxyphenyl)propan-2-one (1a).



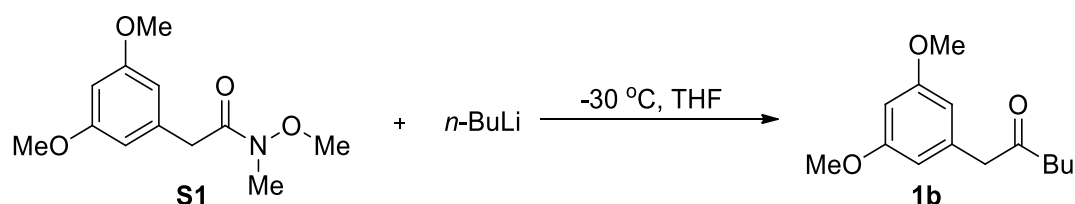
To a mixture of 2-(3,5-dimethoxyphenyl)acetic acid (1.0 g, 5.1 mmol), N,O-dimethylhydroxylamine (597 mg, 6.1 mmol) and DMAP (62 mg, 0.51 mmol) in CH_2Cl_2 (10 mL), NEt_3 (880 μL , 6.1 mmol) was added dropwise at 0 °C and then DCC (1.26 g, 6.1 mmol) was added. The reaction was stirred at 0 °C for 15 min, and then was allowed to warm to room temperature and stir for another 1 hour. The reaction was quenched with water. The solid was filtered off and washed with ethyl acetate. The filtrate was extracted with ethyl acetate for two times, and the combined organic layer was washed with brine and dried with anhydrous Na_2SO_4 . After removal of the solvent, the residue was purified by silica chromatography (PE/EtOAc = 10:1 to 5:1) to afford **S1** (830.0 mg, 68%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 6.45 (d, J = 2.0 Hz, 2H), 6.35 (t, J = 2.0 Hz, 1H), 3.77 (s, 6H), 3.70 (s, 2H), 3.61 (s, 3H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.08, 160.74, 137.02, 107.27, 98.91, 61.23, 55.21, 39.57, 32.17. MS (EI): m/z (%): 239 (M^+ , 25.69), 151 (100); HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}_4$: 239.1158, found: 239.1159.



To a solution of amide **S1** (1.0 g, 4.2 mmol) in THF (10 mL) methyl Grignard reagent (6.3 mmol, 6.3 mL, 1.0 M in THF) was added at -30 °C. After being stirred for overnight, the reaction was quenched with NH_4Cl solution. Then the resulting solution was extracted with ethyl acetate, washed with saturated brine solution and dried with anhydrous Na_2SO_4 . After being filtrated and concentrated, the residue was

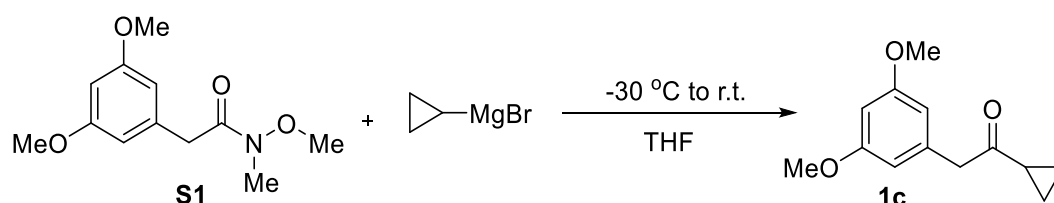
purified by silica chromatography (PE/EtOAc = 10:1) to give **1a** (0.65 g, 80%) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.37 (t, J = 2.0 Hz, 1H), 6.35 (d, J = 2.0 Hz, 2H), 3.77 (s, 6H), 3.60 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.18, 160.99, 136.34, 107.40, 99.01, 55.26, 51.27, 29.03. MS (EI): m/z (%): 194 (M^+ , 90.16), 151 (100); HRMS (EI) calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3$ 194.0943, found: 194.0945.

2) Synthesis of 1-(3, 5-dimethoxyphenyl)hexan-2-one (**1b**).



The general procedure was followed as **1a**. The residue was purified by silica chromatography (PE/EtOAc = 10:1) to give **1b** (269.5 mg, 54%) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.32-6.38 (m, 3H), 3.77 (s, 6H), 3.59 (s, 2H), 2.44 (t, J = 7.6 Hz, 2H), 1.45-1.58 (m, 2H), 1.20-1.30 (m, 2H), 0.86 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.47, 160.88, 136.48, 107.35, 98.99, 55.25, 50.39, 41.46, 25.75, 22.16, 13.79. MS (EI): m/z (%): 236 (M^+ , 6.05), 85 (100); HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_3$: 236.1412, found: 236.1415.

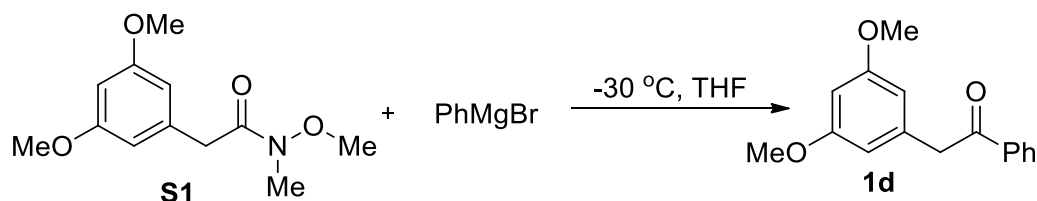
3) Synthesis of 1-cyclopropyl-2-(3, 5-dimethoxyphenyl)ethanone (**1c**).



The general procedure was followed as **1a**. The residue was purified by silica chromatography (PE/EtOAc = 10:1) to give **1c** (220.1 mg, 30%) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.36-6.42 (m, 3H), 3.78 (s, 6H), 3.74 (s, 2H), 1.92-2.02 (m, 1H), 1.00-1.05 (m, 2H), 0.80-0.85 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.28, 160.90, 136.52, 107.51, 98.90, 55.27, 50.96, 19.89, 11.44. MS (ESI): m/z (%): 243.02 ($[\text{M}+\text{Na}]^+$, 22.00), 221.05 (100); HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{16}\text{NaO}_3$ $[\text{M}+\text{Na}]$:

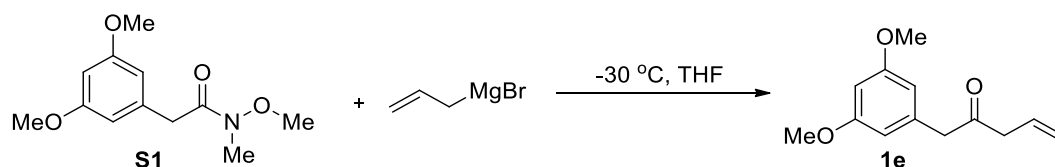
243.0092, found: 243.0984.

4) Synthesis of 2-(3, 5-dimethoxyphenyl)-1-phenylethanone (**1d**).¹



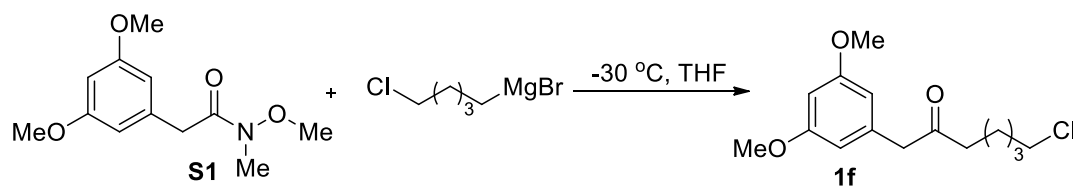
The general procedure was followed as **1a**. The residue was purified by silica chromatography (PE/EtOAc = 10:1) to give **1d** (287.5 mg, 53%) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.96-8.02 (m, 2H), 7.50-7.60 (m, 1H), 7.42-7.48 (m, 2H), 6.43 (d, $J = 2.0$ Hz, 2H), 6.35 (t, $J = 2.0$ Hz, 1H), 4.21 (s, 2H), 3.76 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.40, 160.92, 136.66, 136.54, 133.12, 128.59, 128.58, 107.49, 98.92, 55.23, 45.76. MS(EI): m/z (%): 256 (M^+ , 25.35), 105 (100), HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_3$: 256.1099, found: 256.1100.

5) Synthesis of 1-(3, 5-dimethoxyphenyl)pent-4-en-2-one (**1e**).



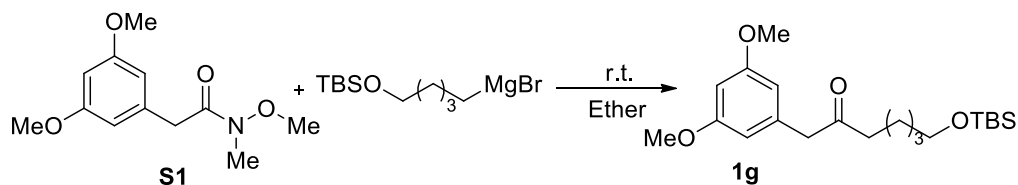
The general procedure was followed as **1a**. The residue was purified by silica chromatography (PE/EtOAc = 10:1) to give **1e** (356.3 mg, 77%) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.35-6.41 (m, 3H), 5.84-5.94 (m, 1H), 5.08-5.20 (m, 2H), 3.78 (s, 6H), 3.64 (s, 2H), 3.2 (dt, $J = 6.8$ Hz, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.99, 160.99, 136.04, 130.38, 119.01, 107.48, 99.06, 53.30, 49.84, 46.51. MS (EI): m/z (%): 220 (M^+ , 44.82), 69 (100); HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_3$: 220.1099, found: 220.1098.

6) Synthesis of 7-chloro-1-(3, 5-dimethoxyphenyl)heptan-2-one (**1f**).



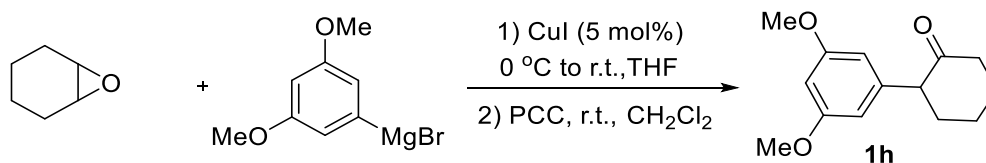
The general procedure was followed as **1a**. The residue was purified by silica chromatography (PE/EtOAc = 10:1) to give **1f** (298.0 mg, 25%) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.37 (t, J = 2.0 Hz, 1H), 6.34 (d, J = 2.0 Hz, 2H), 3.78 (s, 6H), 3.59 (s, 2H), 3.49 (t, J = 6.8 Hz, 2H), 2.46 (t, J = 7.2 Hz, 2H), 1.68-1.78 (m, 2H), 1.50-1.60 (m, 2H), 1.32-1.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 207.95, 161.01, 136.36, 107.43, 99.00, 55.31, 50.54, 44.76, 41.35, 32.30, 26.28, 22.84. MS (EI): m/z (%): 284 (M^+ , 41.64), 286 ($[\text{M}+2]^+$, 14.02), 69 (100); HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{21}\text{O}_3$: 284.1179, found 284.1180.

7) Synthesis of 7-(tert-butyldimethylsilyloxy)-1-(3,5-dimethoxyphenyl)heptan-2-one (**1g**).



The general procedure was followed as **1a** at room temperature. The residue was purified by silica chromatography (PE/EtOAc = 20:1) to give **1g** (200.0 mg, 35%) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.32-6.38 (m, 3H), 3.77 (s, 6H), 3.59 (s, 2H), 3.56 (t, J = 6.8 Hz, 2H), 2.45 (J = 7.6 Hz, 2H), 1.40-1.60 (m, 4H), 1.24-1.35 (m, 2H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.27, 160.98, 136.49, 107.43, 99.00, 62.95, 55.29, 50.46, 41.75, 32.56, 25.95, 25.36, 23.51, 18.33, -5.31. MS (ESI): m/z (%): 403.12 ($[\text{M}+\text{Na}]^+$, 84), 147.11 (100); HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{36}\text{NaO}_4\text{Si}$ $[\text{M}+\text{Na}]$: 403.2275, found: 403.2275.

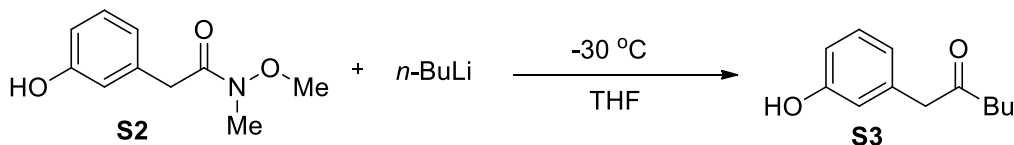
8) Synthesis of 2-(3,5-dimethoxyphenyl)cyclohexan-1-one (**1h**).



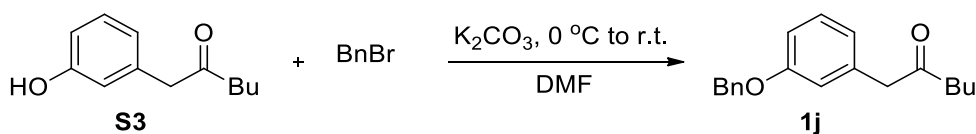
To the solution of the Grignard reagent, CuI (95 mg, 0.5 mmol) in THF at 0 °C, cyclohexene oxide was added (980 mg, 10 mmol). After being stirred for 3 h at room

temperature, the reaction was quenched with aqueous NH_4Cl solution. Then the resulting solution was extracted with ethyl acetate and dried with anhydrous Na_2SO_4 . After being filtrated and concentrated, the residue was dissolved in CH_2Cl_2 (20 mL) and silica (8.6 g) was added. Then, PCC (4.3 g, 20 mmol) was added and the resulting mixture was stirred at room temperature for another 11h. The solid was filtered off and the filtrate was concentrated. The residue was purified by silica column chromatography (PE/EtOAc = 6:1 to 3:1) to give **1h** (1.51 g, 64%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 6.37 (t, J = 2.4 Hz, 1H), 6.30 (d, J = 2.4 Hz, 2H), 3.77 (s, 6H), 3.50-3.60 (m, 1H), 2.36-2.58 (m, 2H), 2.20-2.28 (m, 1H), 1.94-2.18 (m, 3H), 1.74-1.88 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.06, 160.64, 140.97, 106.69, 98.80, 57.49, 55.22, 42.10, 34.69, 27.69, 25.14. MS(EI): m/z (%): 234 (M^+ , 100), HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3$: 234.1256, found: 234.1254.

9) Synthesis of 1-(3-(benzyloxy)phenyl)hexan-2-one (**1j**).



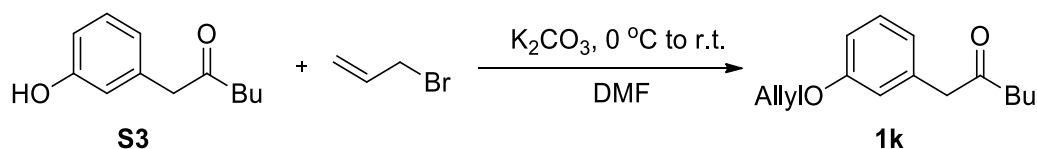
The general procedure was followed as **1a**. The residue was purified by silica chromatography (PE/EtOAc = 5:1) to give **S3** (5.81 g, 83% yield) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.18 (t, J = 8.0 Hz, 1H), 6.75 (dd, J = 8.0 Hz, 2.0 Hz, 2H), 6.70 (d, J = 2.0 Hz, 1H), 6.39 (br, 1H), 3.64 (s, 2H), 2.47 (t, J = 7.6 Hz, 2H), 1.46-1.58 (m, 2H), 1.18-1.32 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.36, 156.21, 135.52, 129.91, 121.48, 116.19, 114.27, 49.96, 41.71, 25.75, 22.14, 13.76; MS(EI): m/z (%): 192 (M^+ , 24.69), 101 (100), HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$: 192.1150, found: 192.1151.



To a mixture of ketone **S3** (1.0 g, 5.2 mmol), K_2CO_3 (857 mg, 6.2 mmol) in DMF

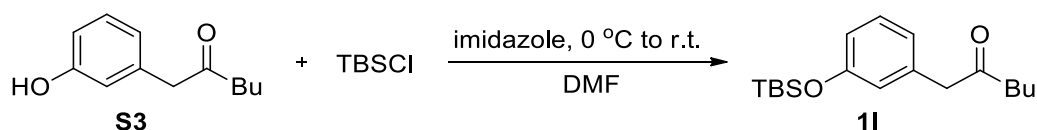
(10 mL) Benzyl bromide (736 μ L, 6.2 mmol) was added at 0 $^{\circ}$ C. The reaction was stirred for 12 h at room temperature. After being extracted with ethyl acetate and concentrated under vacuum, the residue was purified by silica column chromatography (PE/EtOAc = 50:1 to 10:1) to give **1j** (1.27 g, 87% yield) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.50 (m, 5H), 7.20-7.28 (m, 1H), 6.80-6.92 (m, 3H), 5.06 (s, 2H), 3.65 (s, 2H), 2.44 (t, J = 7.6 Hz, 2H), 1.48-1.56 (m, 2H), 1.20-1.30 (m, 2H), 0.88 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.48, 158.95, 136.84, 135.84, 129.67, 128.53, 127.93, 127.46, 121.99, 115.90, 113.29, 69.87, 50.13, 41.59, 25.76, 22.17, 13.80. MS(EI): m/z (%): 282 (M^+ , 7.54), 91 (100), HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_2$: 282.1620, found: 282.1618.

10) Synthesis of 1-(3-(allyloxy)phenyl)hexan-2-one.



The general procedure was followed as **1j**. The residue was purified by silica chromatography (PE/EtOAc = 10:1) to give **1k** (810 mg, 67% yield) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.23 (t, J = 8.0 Hz, 1H), 6.74-6.84 (m, 3H), 6.00-6.10 (m, 1H), 5.41 (d, J = 17.2 Hz, 1H), 5.28 (d, J = 10.4 Hz, 1H), 4.53 (d, J = 4.8 Hz, 2H), 3.64 (s, 2H), 2.44 (t, J = 7.6 Hz, 2H), 1.45-1.58 (m, 2H), 1.20-1.30 (m, 2H), 0.86 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.53, 158.76, 135.80, 133.14, 129.63, 121.88, 117.67, 115.78, 113.16, 68.69, 50.15, 41.59, 25.77, 22.18, 13.80. MS(EI): m/z (%): 232 (M^+ , 17.75), 85 (100), HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$: 232.1463, found: 232.1461.

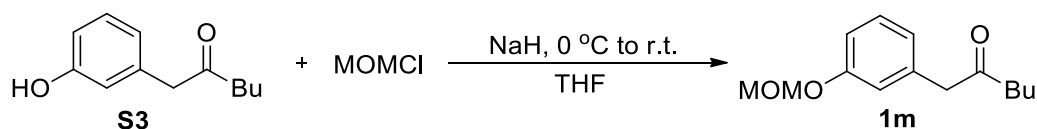
11) Synthesis of 1-(3-(tert-butyldimethylsilyloxy)phenyl)hexan-2-one (**1l**).



To a mixture of ketone **S3** (1.0 g, 5.2 mmol), imidazole (422 mg, 6.2 mmol) in

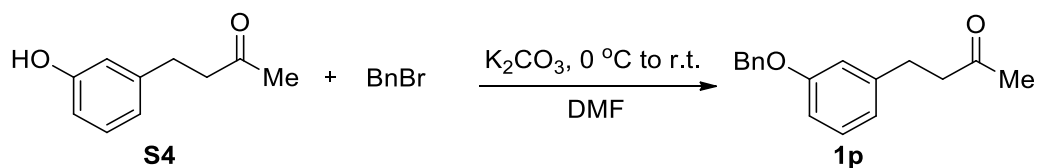
DMF (10 mL) tert-butylchlorodimethylsilane (934 mg, 6.2 mmol) was added at 0 °C. After being stirred for 12 h at room temperature, the reaction was extracted with ethyl acetate and concentrated under vacuum. The residue was purified by silica column chromatography (PE/EtOAc =50:1 to 10:1) to give **1l** (1.17 g, 73% yield) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.74 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.70 (t, *J* = 1.6 Hz, 1H), 3.60 (s, 2H), 2.42 (t, *J* = 7.6 Hz, 2H), 1.45-1.55 (m, 2H), 1.20-1.30 (m, 2H), 0.98 (s, 9H), 0.85 (t, *J* = 7.6 Hz, 3H), 0.19 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 208.59, 155.86, 135.78, 129.58, 122.37, 121.19, 118.64, 50.14, 41.49, 25.79, 25.65, 22.20, 18.17, 13.79, -4.44. MS(EI): *m/z* (%): 306 (*M*⁺, 25.46), 249 (100), HRMS (EI) calcd. for C₁₈H₃₀O₂Si: 306.2015, found: 306.2012.

12) Synthesis of 1-(3-(methoxymethoxy)phenyl)hexan-2-one (**1m**).



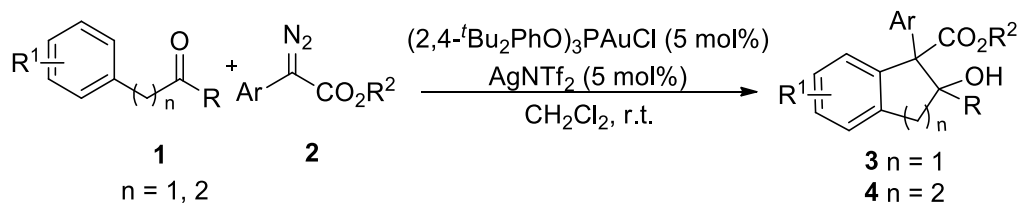
To a solution of ketone **S3** (600 mg, 3.1 mmol) in THF (6 mL) NaH (148 mg, 3.7 mmol) was added at 0 °C. After the solution was stirred for 15 min, chloro(methoxy)methane (281 μL, 3.7 mmol) was added and the reaction was allowed to warm to room temperature and stirred for another 12 h. After the resulting solution was extracted with ethyl acetate and concentrated under vacuum, the residue was purified by silica column chromatography (PE/EtOAc =50:1 to 20:1) to give **1m** (432.5 mg, 59% yield) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (t, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.17 (s, 2H), 3.65 (s, 2H), 3.47 (s, 3H), 2.45 (t, *J* = 7.6 Hz, 2H), 1.48-1.60 (m, 2H), 1.20-1.30 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.38, 157.44, 135.85, 129.64, 122.92, 117.33, 114.66, 94.37, 55.98, 50.02, 41.67, 25.77, 22.18, 13.79. MS(EI): *m/z* (%): 236 (*M*⁺, 15.88), 45 (100), HRMS (EI) calcd. for C₁₄H₂₀O₃: 236.1412, found: 236.1413.

13) Synthesis of 4-(3-(benzyloxy)phenyl)butan-2-one (**1p**).²



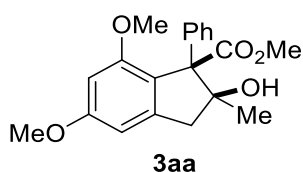
The general procedure was followed as **1j**. The residue was purified by silica chromatography (PE/EtOAc = 10:1) to give **1p** (1.05 g, 88% yield) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.50 (m, 5H), 7.15-7.20 (m, 1H), 6.76-6.84 (m, 3H), 5.05 (s, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 207.88, 158.89, 142.63, 136.98, 129.47, 128.53, 127.90, 127.46, 120.89, 115.00, 112.23, 69.85, 44.98, 30.05, 29.68.

4. General procedure for the cascade reaction:



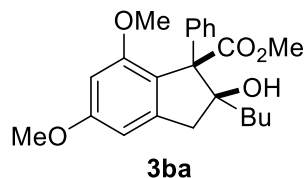
In a dried glass tube, a solution of (2,4-*t*Bu₂PhO)₃PAuCl (8.8 mg, 0.01 mmol), AgNTf₂ (3.9 mg, 0.01 mmol) in CH₂Cl₂ (3 mL) was stirred at room temperature for 15 min. Aryl ketone **1** (0.6 mmol) was added to the reaction mixture at room temperature. Then a solution of diazo compound **2** (0.2 mmol) in 1 mL of CH₂Cl₂ was introduced into the solution by a syringe in 30 min. The resulting mixture was continually stirred at room temperature for another 15-30 min and diazo compound was consumed completely determined by TLC analysis. After being filtrated through a short silica gel column and concentrated, the residue was purified by column chromatography on silica gel to afford the desired product.

1) Synthesis of methyl 2-hydroxy-5,7-dimethoxy-2-methyl-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (**3aa**).



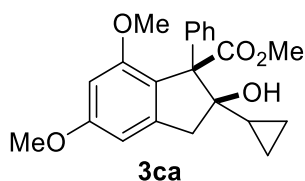
The general procedure was followed using **1a** (0.6 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3aa** (52.4 mg, 77%, d.r. = 14:1) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.20-7.30 (m, 3H), 7.10-7.18 (m, 2H), 6.44(d, *J* = 2.0 Hz, 1H), 6.39 (d, *J* = 2.0 Hz, 1H), 4.58 (s, 1H), 3.83 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.31 (d, *J* = 15.6 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 0.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.16, 161.64, 158.37, 144.80, 136.73, 128.33, 127.24, 126.77, 120.33, 101.51, 98.23, 84.62, 68.24, 55.41, 55.30, 52.31, 47.52, 25.23; MS(EI): *m/z* (%): 342 (*M*⁺, 3.83); 310 (100); HRMS (EI) calcd. for C₂₀H₂₂O₅: 342.1467, found: 342.1465.

2) Synthesis of methyl 2-butyl-2-hydroxy-5,7-dimethoxy-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3ba).



The general procedure was followed using **1b** (0.6 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ba** (48.8 mg, 64%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.16-7.28 (m, 5H), 6.46 (d, J = 2.0 Hz, 1H), 6.39 (d, J = 2.0 Hz, 1H), 3.92 (s, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.64 (s, 3H), 3.07 (d, J = 16.0 Hz, 1H), 3.00 (d, J = 16.0 Hz, 1H), 1.40-1.50 (m, 1H), 1.05-1.30 (m, 5H), 0.79 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.25, 161.57, 158.16, 144.32, 137.00, 128.55, 127.35, 126.77, 122.17, 101.33, 98.21, 87.13, 69.30, 55.42, 55.37, 52.15, 44.13, 36.14, 26.17, 23.15, 14.03; MS(EI): m/z (%): 384 (M^+ , 2.57), 352 (100), HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{28}\text{O}_5$: 384.1937, found: 384.1935.

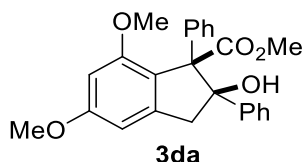
3) Synthesis of methyl 2-cyclopropyl-2-hydroxy-5,7-dimethoxy-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3ca).



The general procedure was followed using **1c** (0.6 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ca** (52.3 mg, 71%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.18-7.30 (m, 5H), 6.46 (d, J = 2.0 Hz, 1H), 6.40 (d, J = 2.0 Hz, 1H), 4.53 (s, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.05 (d, J = 15.6 Hz, 1H), 2.91 (d, J = 15.6 Hz, 1H), 0.58-0.66 (m, 1H), 0.30-0.36 (m, 1H), 0.20-0.28 (m, 1H), 0.08-0.16 (m, 1H), -0.05-0.02 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.41, 161.58, 158.06, 144.98,

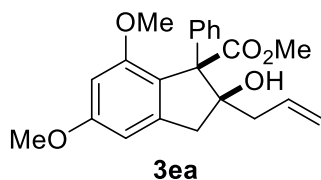
136.87, 129.17, 126.94, 126.75, 121.52, 101.54, 97.98, 85.64, 68.27, 55.43, 55.40, 52.39, 45.93, 17.41, 1.36, 1.03. MS(EI): m/z (%): 368 (M^+ , 2.00); 293 (100); HRMS (EI) calcd. for $C_{22}H_{24}O_5$: 368.1624, found: 368.1626.

4) Synthesis of methyl 2-hydroxy-5,7-dimethoxy-1,2-diphenyl-2,3-dihydro-1H-indene-1-carboxylate (3da).



The general procedure was followed using **1d** (0.6 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1), **3da** (52.6 mg, 65%, d.r. > 20:1) was obtained as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 6.96-7.15 (m, 4H), 6.85-6.95 (m, 4H), 6.59 (d, J = 1.2 Hz, 1H), 6.53 (d, J = 7.6 Hz, 2H), 6.43 (d, J = 1.2 Hz, 1H), 5.52 (s, 1H), 3.90 (s, 3H), 3.75 (s, 3H), 3.64 (s, 3H), 3.57 (d, J = 16.0 Hz, 1H), 3.35 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.24, 161.95, 158.25, 145.36, 141.97, 136.27, 128.92, 127.07, 126.98, 126.87, 126.50, 126.45, 121.27, 101.32, 98.17, 89.09, 69.85, 55.53, 55.39, 52.55, 46.11; MS(EI): m/z (%): 404 (M^+ , 0.60); 328 (100); HRMS (ESI) calcd. for $C_{25}H_{24}O_5$: 404.1624, found: 404.1626.

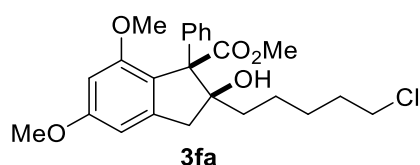
5) Synthesis of methyl 2-allyl-2-hydroxy-5,7-dimethoxy-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3ea).



The general procedure was followed using **1e** (0.6 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ea** (49.1 mg, 67%, d.r. > 20:1) was obtained as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.32 (m, 3H), 7.16-7.24 (m, 2H), 6.43 (d, J = 2.0 Hz, 1H), 6.39 (d, J = 2.0 Hz, 1H), 5.75-5.90 (m, 1H), 5.05 (d, J = 10.0 Hz, 1H), 4.92 (d, J = 17.2 Hz, 1H), 4.30 (d,

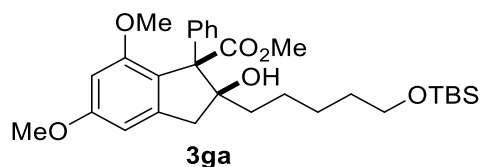
$J = 0.9$ Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.14 (d, $J = 16.0$ Hz, 1H), 3.09 (d, $J = 16.0$ Hz, 1H), 1.72-1.86 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.73, 161.64, 158.24, 144.35, 136.42, 134.41, 128.47, 127.43, 126.92, 120.77, 118.11, 101.40, 98.29, 85.91, 68.76, 55.43, 55.33, 52.31, 43.67, 41.34. MS(EI): m/z (%): 368 (M^+ , 3.52); 267 (100); HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{24}\text{O}_5$: 368.1624, found: 368.1622.

6) Synthesis of methyl 2-(5-chloropentyl)-2-hydroxy-5,7-dimethoxy-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3fa).



The general procedure was followed using **1f** (0.6 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3fa** (51.8 mg, 60%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.15-7.28 (m, 5H), 6.45 (d, $J = 2.0$ Hz, 1H), 6.39 (d, $J = 2.0$ Hz, 1H), 4.04 (d, $J = 1.2$ Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.42-3.48 (m, 2H), 3.08 (d, $J = 16.0$ Hz, 1H), 3.00 (d, $J = 16.0$ Hz, 1H), 1.60-1.70 (m, 2H), 1.42-1.50 (m, 1H), 1.18-1.32 (m, 4H), 1.05-1.12 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.36, 161.59, 158.17, 144.19, 136.76, 128.49, 127.42, 126.87, 121.76, 101.31, 98.24, 86.90, 69.13, 55.43, 55.37, 52.23, 45.05, 44.03, 36.22, 32.59, 27.31, 23.34; MS(EI): m/z (%): 432 (M^+ , 1.29), 434 ($[\text{M}+2]^+$, 0.43), 183 (100); HRMS (EI) calcd. for $\text{C}_{24}\text{H}_{29}\text{O}_5\text{Cl}$: 432.1704, found: 432.1708.

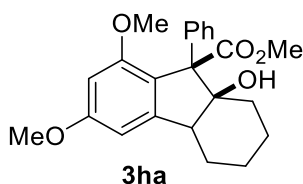
7) Synthesis of methyl 2-(5-(tert-butyldimethylsilyloxy)pentyl)-2-hydroxy-5,7-dimethoxy-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3ga).



The general procedure was followed using **1g** (0.6 mmol) and **2a** (0.2 mmol). After

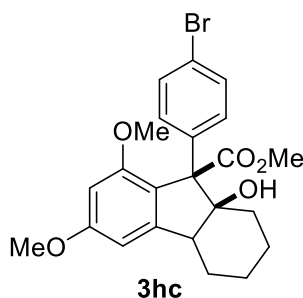
purification by column chromatography (PE/EtOAc = 20:1 to 10:1), **3ga** (63.6 mg, 58%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.18-7.32 (m, 5H), 6.45 (d, J = 2.0 Hz, 1H), 6.39 (d, J = 2.0 Hz, 1H), 3.91 (d, J = 1.2 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.64 (s, 3H), 3.51 (t, J = 6.8 Hz, 2H), 3.07 (d, J = 16.0 Hz, 1H), 2.99 (d, J = 16.0 Hz, 1H), 1.35-1.50 (m, 3H), 1.05-1.30 (m, 5H), 0.86 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.28, 161.64, 158.22, 144.33, 137.02, 128.57, 127.39, 126.81, 122.21, 101.41, 98.30, 87.12, 69.35, 63.27, 55.40, 52.15, 44.19, 36.47, 32.89, 26.30, 25.98, 23.86, 18.35, -5.27; MS(ESI): m/z (%): 551.17 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{44}\text{NaO}_6\text{Si}[\text{M}+\text{Na}]$: 551.2799, found: 551.2776.

8) Synthesis of 1,3-dimethoxy-9-((methylperoxy)-12-methyl)-9-phenyl-4b,5,6,7,8,9-hexahydro-8aH-fluoren-8a-ol (3ha).



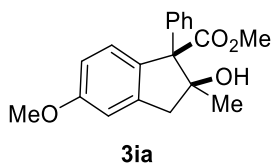
The general procedure was followed using **1h** (0.6 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ha** (37.8 mg, 49%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.32 (m, 3H), 7.05-7.15 (m, 2H), 6.43 (d, J = 1.6 Hz, 2H), 5.15 (d, J = 1.6 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.62 (s, 3H), 3.54 (d, J = 4.0 Hz, 1H), 2.06-2.15 (m, 1H), 1.92-2.05 (m, 1H), 1.35-1.50 (m, 2H), 0.90-1.30 (m, 3H), 0.35-0.45 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.02, 161.58, 158.81, 147.99, 135.20, 128.40, 126.97, 126.62, 118.01, 100.06, 97.95, 84.56, 66.81, 55.43, 55.21, 52.42, 48.26, 31.80, 22.52, 21.44, 21.21. MS(EI): m/z (%): 382 (M^+ , 2.90); 306 (100); HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{26}\text{O}_5$: 382.1780, found: 382.1782.

9) Synthesis of 9-(4-bromophenyl)-1,3-dimethoxy-9-((methylperoxy)-12-methyl)-4b,5,6,7,8,9-hexahydro-8aH-fluoren-8a-ol (3hc).



The general procedure was followed using **1h** (0.6 mmol) and **2c** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3hc** (48.6 mg, 53%, d.r. = 11:1) was obtained as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 6.41 (s, 2H), 4.99 (d, $J = 2.4$ Hz, 1H), 3.85 (s, 3H), 3.71 (s, 3H), 3.61 (s, 3H), 3.54 (s, 1H), 2.05-2.15 (m, 1H), 1.90-2.02 (m, 1H), 1.40-1.55 (m, 2H), 1.05-1.30 (m, 2H), 0.85-1.00 (m, 1H), 0.35-0.50 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.49, 161.76, 158.61, 147.98, 134.52, 130.24, 130.10, 120.74, 117.52, 100.17, 97.94, 84.51, 66.52, 55.47, 55.18, 52.51, 48.25, 31.90, 22.51, 21.42, 21.16. MS(ESI): m/z (%): 483.89 ($[\text{M}+\text{Na}]^+$, 26), 485.93 ($[(\text{M}+2+\text{Na})]^+$, 24), 483.89 (100); HRMS (EI) calcd. for $\text{C}_{23}\text{H}_{25}\text{O}_5\text{Br}$: 460.0885, found: 460.0889.

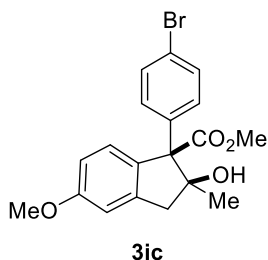
10) Synthesis of methyl 2-hydroxy-5-methoxy-2-methyl-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (**3ia**).



The general procedure was followed using **1i** (1.0 mmol), **2a** (0.2 mmol) and gold catalyst (10 mol%). After purification by column chromatography (PE/EtOAc = 20:1 to 10:1), **3ia** (33.9 mg, 54%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 8.8$ Hz, 1H), 7.27-7.36 (m, 3H), 7.12-7.18 (m, 2 H), 6.78-6.84 (m, 2 H), 5.00 (s, 1H), 3.83 (s, 3H), 3.67 (s, 3H), 3.29 (d, $J = 15.6$ Hz, 1 H), 2.95 (d, $J = 15.6$ Hz, 1 H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.75, 159.88, 144.00, 138.47, 132.08, 128.68, 128.17, 127.52, 127.28, 113.10, 109.96, 84.16, 68.43, 55.34, 52.48, 46.28, 25.41; MS(EI): m/z (%): 312 (M^+ , 7.42); 236 (100);

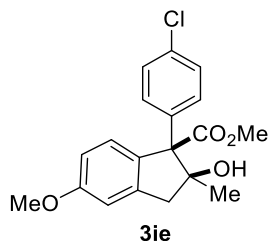
HRMS (EI) calcd. for C₁₉H₂₀O₄: 312.1362, found: 312.13585.

11) Synthesis of methyl 1-(4-bromophenyl)-2-hydroxy-5-methoxy-2-methyl-2,3-dihydro-1H-indene-1-carboxylate (3ic).



The general procedure was followed using **1i** (1.0 mmol), **2c** (0.2 mmol) and gold catalyst (10 mol%). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ic** (42.7 mg, 55%, d.r. > 20:1) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.80-6.88 (m, 2H), 4.91 (s, 1H), 3.83 (s, 3H), 3.66 (s, 3H), 3.31 (d, *J* = 15.6 Hz, 1H), 2.94 (d, *J* = 15.6 Hz, 1H), 0.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.26, 160.02, 143.94, 137.57, 131.51, 131.28, 129.30, 128.49, 121.36, 113.26, 110.07, 84.02, 68.01, 55.35, 52.59, 46.31, 25.44. MS (EI): *m/z* (%): 390 (M⁺, 5.57), 392 ([M+2]⁺, 5.25); 390 (100); HRMS (EI) calcd. for C₁₉H₁₉O₄Br: 390.0467, found: 390.0469.

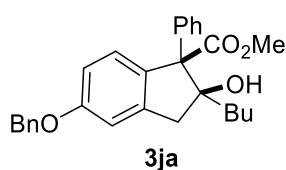
12) Synthesis of methyl 1-(4-chlorophenyl)-2-hydroxy-5-methoxy-2-methyl-2,3-dihydro-1H-indene-1-carboxylate (3ie).



The general procedure was followed using **1i** (1.0 mmol) and **2e** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ie** (41.4 mg, 60%, d.r. > 20:1) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.78-6.85 (m, 2H),

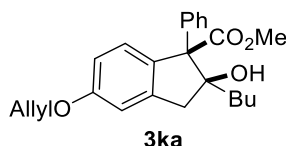
4.91 (s, 1H), 3.83 (s, 3H), 3.66 (s, 3H), 3.31 (d, $J = 15.6$ Hz, 1H), 2.94 (d, $J = 15.6$ Hz, 1H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.34, 160.02, 143.95, 137.04, 133.20, 131.60, 128.95, 128.51, 128.34, 113.26, 110.08, 84.08, 67.95, 55.36, 52.59, 46.31, 25.43. MS(EI): m/z (%): 346 (M^+ , 5.41), 348 ($[\text{M}+2]^+$, 1.85); 84 (100); HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{19}\text{O}_4\text{Cl}$: 346.0972, found: 346.0970.

13) Synthesis of methyl 5-(benzyloxy)-2-hydroxy-2-methyl-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3ja).



The general procedure was followed using **1j** (1.0 mmol), **2a** (0.2 mmol) and gold catalyst (10 mol%). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ja** (47.1 mg, 55%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.55 (m, 9H), 6.98-7.08 (m, 2H), 6.86-6.94 (m, 2H), 5.10 (s, 2H), 4.49 (s, 1H), 3.75 (s, 3H), 3.09 (d, $J = 16.0$ Hz, 1H), 2.98 (d, $J = 16.0$ Hz, 1H), 1.40-1.60 (m, 1H), 1.26-1.35 (m, 1H), 1.06-1.25 (m, 3H), 0.96-1.05 (m, 1H), 0.80 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.46, 159.08, 144.17, 138.94, 136.95, 133.23, 128.57, 128.33, 128.17, 127.97, 127.54, 127.49, 127.21, 113.77, 110.99, 86.49, 70.09, 70.03, 52.39, 42.28, 36.69, 26.01, 23.16, 14.05. MS(EI): m/z (%): 430 (M^+ , 0.81); 91 (100); HRMS (EI) calcd. for $\text{C}_{28}\text{H}_{30}\text{O}_4$: 430.2144, found: 430.2140.

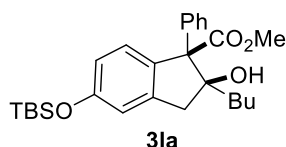
14) Synthesis of methyl 5-(allyloxy)-2-hydroxy-2-methyl-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3ka).



The general procedure was followed using **1k** (1.0 mmol), **2a** (0.2 mmol) and gold catalyst (10 mol%). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ka** (50.5 mg, 66%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400

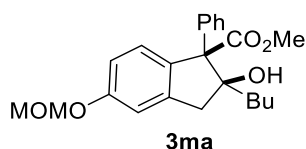
MHz, CDCl₃) δ 7.44 (d, J = 8.0 Hz, 1H), 7.22-7.30 (m, 3H), 6.95-7.05 (m, 2H), 6.80-6.85 (m, 2H), 6.02-6.15 (m, 1H), 5.44 (dd, J = 17.2 Hz, 1.6 Hz, 1H), 5.31 (dd, J = 10.4 Hz, 1.6 Hz, 1H), 4.56 (d, J = 5.2 Hz, 2H), 4.47 (s, 1H), 3.73 (s, 3H), 3.07 (d, J = 16.0 Hz, 1H), 2.95 (d, J = 16.0 Hz, 1H), 1.42-1.52 (m, 1H), 1.05-1.35 (m, 4H), 0.92-1.00 (m, 1H), 0.77 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.50, 158.87, 144.14, 138.98, 133.28, 133.13, 128.30, 128.19, 127.56, 127.23, 117.70, 113.71, 110.90, 86.50, 70.05, 68.93, 52.42, 42.30, 36.71, 26.03, 23.18, 14.06. MS(EI): m/z (%): 380 (M^+ , 5.44); 249 (100); HRMS (EI) calcd. for C₂₄H₂₈O₄ : 380.1988, found: 380.1990.

15) Synthesis of methyl 5-(tert-butyldimethylsilyloxy)-2-hydroxy-2-methyl-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3la).



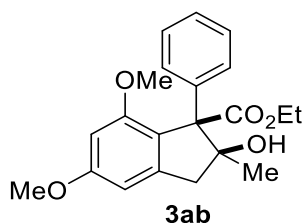
The general procedure was followed using **1l** (1.0 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3la** (40.3 mg, 44%, d.r. > 20:1) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 8.4 Hz, 1H), 7.25-7.32 (m, 3H), 6.95-7.02 (m, 2H), 6.72-6.80 (m, 2H), 4.48 (s, 1H), 3.76 (s, 3H), 3.07 (d, J = 16.0 Hz, 1H), 2.94 (d, J = 16.0 Hz, 1H), 1.40-1.52 (m, 1H), 1.24-1.34 (m, 1H), 1.06-1.23 (m, 3H), 1.02 (s, 9H), 0.92-1.02 (m, 1H), 0.80 (t, J = 7.2 Hz, 3H), 0.26 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 175.53, 155.74, 144.08, 139.07, 133.56, 128.24, 128.16, 127.56, 127.20, 118.71, 116.37, 86.47, 70.09, 52.39, 42.17, 36.76, 26.04, 25.64, 23.18, 18.14, 14.05, -4.39. MS(EI): m/z (%): 454 (M^+ , 3.79); 378 (100); HRMS (EI) calcd. for C₂₇H₃₈O₄Si : 454.2539, found: 454.2536.

16) Synthesis of methyl 2-hydroxy-5-(methoxymethoxy)-2-methyl-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3ma).



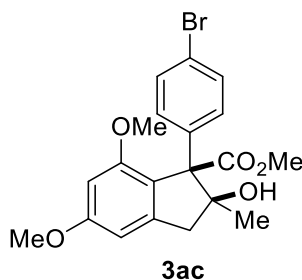
The general procedure was followed using **1m** (1.0 mmol), **2a** (0.2 mmol) and gold catalyst (10 mol%). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ma** (35.5 mg, 46%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, J = 8.5 Hz, 1H), 7.22-7.30 (m, 3H), 6.96-7.04 (m, 3H), 6.90-6.95 (m, 1H), 5.20 (dd, J = 10.0 Hz, 7.0 Hz, 2H), 4.47 (s, 1H), 3.73 (s, 3H), 3.51 (s, 3H), 3.07 (d, J = 16.0 Hz, 1H), 2.96 (d, J = 16.0 Hz, 1H), 1.44-1.52 (m, 1H), 1.23-1.32 (m, 1H), 1.05-1.22 (m, 3H), 0.92-1.01 (m, 1H), 0.77 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 175.45, 157.48, 144.19, 138.85, 134.20, 128.38, 128.20, 127.58, 127.25, 115.12, 112.51, 94.51, 86.52, 70.09, 56.08, 52.44, 42.25, 36.69, 26.00, 23.18, 14.07. MS(EI): m/z (%): 384 (M^+ , 3.93); 45 (100); HRMS (EI) calcd. for $\text{C}_{23}\text{H}_{28}\text{O}_5$: 384.1937, found: 384.1939.

17) Synthesis of ethyl 2-hydroxy-5,7-dimethoxy-2-methyl-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (3ab).



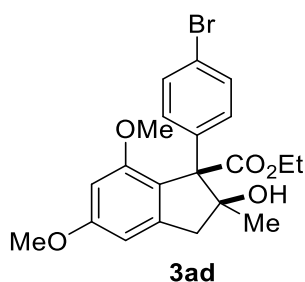
The general procedure was followed using **1a** (0.6 mmol) and **2b** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ab** (43.2 mg, 61%, d.r. = 6:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.32 (m, 3H), 7.14-7.21 (m, 2H), 6.42 (s, 1H), 6.38 (s, 1H), 4.60 (s, 1H), 4.12-4.22 (m, 2H), 3.83 (s, 3H), 3.65 (s, 3H), 3.31 (d, J = 15.6 Hz, 1H), 2.95 (d, J = 15.6 Hz, 1H), 1.13 (t, J = 7.2 Hz, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.60, 161.56, 158.38, 144.81, 136.91, 128.38, 127.14, 126.61, 120.38, 101.27, 97.98, 84.49, 68.30, 61.00, 55.41, 55.00, 47.60, 25.33, 13.86; MS(EI): m/z (%): 356 (M^+ , 4.98), 310 (100), HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_5$: 356.1624, found: 356.1627.

18) Synthesis of methyl 1-(4-bromophenyl)-2-hydroxy-5,7-dimethoxy-2-methyl-2,3-dihydro-1H-indene-1-carboxylate (3ac).



The general procedure was followed using **1a** (0.6 mmol) and **2c** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ac** (60.0 mg, 71%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.44 (d, J = 2.0 Hz, 1H), 6.39 (d, J = 2.0 Hz, 1H), 4.36 (s, 1H), 3.83 (s, 3H), 3.67 (s, 6H), 3.30 (d, J = 15.6 Hz, 1H), 2.95 (d, J = 15.6 Hz, 1H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.55, 161.80, 158.15, 144.70, 135.99, 130.33, 130.17, 120.88, 119.86, 101.58, 98.20, 84.49, 67.92, 55.41, 55.24, 52.35, 47.48, 25.24; MS(EI): m/z (%): 420 (M^+ , 2.81), 422 ($[\text{M}+2]^+$, 2.80), 388 (100); HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{21}\text{O}_5\text{Br}$: 420.0572, found: 420.0574.

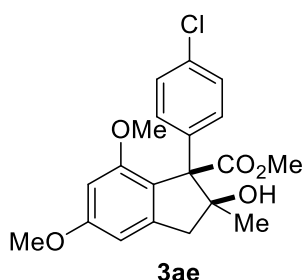
19) Synthesis of ethyl 1-(4-bromophenyl)-2-hydroxy-5,7-dimethoxy-2-methyl-2,3-dihydro-1H-indene-1-carboxylate (3ad).



The general procedure was followed using **1a** (0.6 mmol) and **2d** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ad** (56.5 mg, 65%, d.r. = 7:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.42 (d, J = 2.0 Hz, 1H), 6.37 (d, J = 2.0 Hz, 1H), 4.43 (s, 1H), 4.05-4.20 (m, 2H), 3.83 (s, 3H), 3.65 (s, 3H), 3.30 (d, J = 15.6 Hz, 1H), 2.94 (d, J = 15.6 Hz, 1H), 1.13 (t, J = 7.2 Hz, 3H), 0.85 (s, 3H); ^{13}C NMR (100

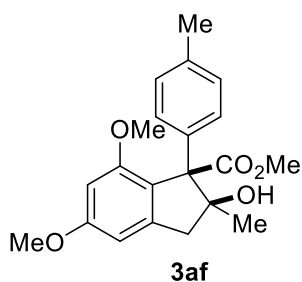
MHz, CDCl₃) δ 174.08, 161.79, 158.21, 144.78, 136.20, 130.26 (2C), 120.75, 119.96, 101.44, 98.03, 84.40, 68.03, 61.14, 55.44, 54.98, 47.61, 25.38, 13.85; MS(EI): m/z (%): 434 (M^+ , 2.69), 436 ($[M+2]^+$, 2.29), 185 (100); HRMS (EI) calcd. for C₂₁H₂₃O₅Br 434.0729, found: 434.0728.

20) Synthesis of methyl 1-(4-chlorophenyl)-2-hydroxy-5,7-dimethoxy-2-methyl-2,3-dihydro-1H-indene-1-carboxylate (3ae).



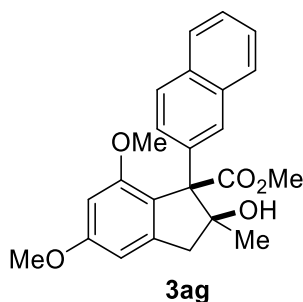
The general procedure was followed using **1a** (0.6 mmol) and **2e** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ae** (60.2 mg, 80%, d.r. = 10:1) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 6.43 (d, J = 2.0 Hz, 1H), 6.39 (d, J = 2.0 Hz, 1H), 4.34 (s, 1H), 3.83 (s, 3H), 3.670 (s, 3H), 3.667 (s, 3H), 3.30 (d, J = 15.6 Hz, 1H), 2.95 (d, J = 15.6 Hz, 1H), 0.87 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.65, 161.84, 158.20, 144.73, 135.48, 132.70, 129.82, 127.42, 120.02, 101.61, 98.25, 84.59, 67.90, 55.46, 55.27, 52.36, 47.52, 25.24; MS(EI): m/z (%): 376 (M^+ , 3.17), 378 ($[M+2]^+$, 1.12), 344 (100); HRMS (EI) calcd. for C₂₀H₂₁O₅Cl, 376.1078, found: 376.1080.

21) Synthesis of methyl 2-hydroxy-5,7-dimethoxy-2-methyl-1-p-tolyl-2,3-dihydro-1H-indene-1-carboxylate (3af).



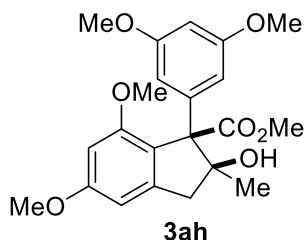
The general procedure was followed using **1a** (0.6 mmol) and **2f** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3af** (60.3 mg, 85%, d.r. = 6:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.02-7.12 (m, 4H), 6.44 (d, J = 2.0 Hz, 1H), 6.40 (d, J = 2.0 Hz, 1H), 4.54 (s, 1H), 3.83 (s, 3H), 3.677 (s, 3H), 3.676 (s, 3H), 3.29 (d, J = 15.6 Hz, 1H), 2.95 (d, J = 15.6 Hz, 1H), 2.33 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.27, 161.53, 158.33, 144.77, 136.29, 133.61, 128.17, 128.03, 120.43, 101.43, 98.17, 84.59, 67.87, 55.39, 55.29, 52.29, 47.42, 25.15, 21.00; MS(EI): m/z (%): 356 (M^+ , 5.44), 324 (100); HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_5$: 356.1624, found: 356.1627.

22) Synthesis of methyl 2-hydroxy-5,7-dimethoxy-2-methyl-1-(naphthalen-2-yl)-2,3-dihydro-1H-indene-1-carboxylate (**3ag**).



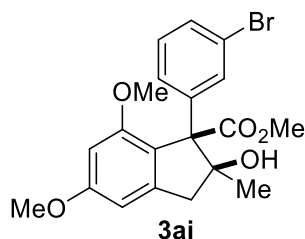
The general procedure was followed using **1a** (0.6 mmol) and **2g** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ag** (70.0 mg, 89%, d.r. = 7:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.80-7.85 (m, 1H), 7.72-7.79 (m, 2H), 7.59 (d, J = 1.2 Hz, 1H), 7.40-7.48 (m, 2H), 7.35 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 6.48 (d, J = 2.0 Hz, 1H), 6.44 (d, J = 2.0 Hz, 1H), 4.61 (s, 1H), 3.86 (s, 3H), 3.70 (s, 3H), 3.66 (s, 3H), 3.36 (d, J = 15.6 Hz, 1H), 3.01 (d, J = 15.6 Hz, 1H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.22, 161.76, 158.45, 144.92, 134.46, 132.84, 132.45, 128.28, 127.30, 127.10, 127.02, 126.40, 125.66, 125.60, 120.43, 101.62, 98.33, 84.81, 68.39, 55.47, 55.31, 52.37, 47.69, 25.44; MS(EI): m/z (%): 392 (M^+ , 2.33), 165 (100), HRMS (EI) calcd. for $\text{C}_{24}\text{H}_{24}\text{O}_5$: 392.1624, found: 392.1623.

23) Synthesis of methyl 1-(3,5-dimethoxyphenyl)-2-hydroxy-5,7-dimethoxy-2-methyl-2,3-dihydro-1H-indene-1-carboxylate (3ah).



The general procedure was followed using **1a** (0.6 mmol) and **2h** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ah** (59.4 mg, 74%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 6.35-6.45 (m, 5H), 4.46 (s, 1H), 3.82 (s, 3H), 3.73 (s, 6H), 3.71 (s, 3H), 3.68 (s, 3H), 3.27 (d, J = 15.6 Hz, 1H), 3.27 (d, J = 15.6 Hz, 1H), 2.97 (d, J = 15.6 Hz, 1H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.81, 161.63, 159.73, 158.33, 144.76, 139.01, 120.25, 107.11, 101.44, 98.71, 98.27, 84.57, 68.34, 55.41, 55.35, 55.17, 52.32, 47.49, 25.09. MS(EI): m/z (%): 402 (M^+ , 9.75), 213 (100); HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_7$: 402.1679, found: 402.1681.

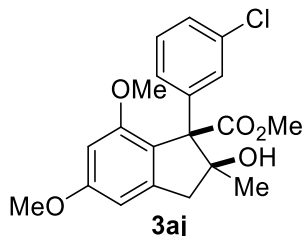
24) Synthesis of methyl 1-(3-bromophenyl)-2-hydroxy-5,7-dimethoxy-2-methyl-2,3-dihydro-1H-indene-1-carboxylate (3ai).



The general procedure was followed using **1a** (0.6 mmol) and **2i** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ai** (46.1 mg, 55%, d.r. = 7:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 7.05-7.18 (m, 2H), 6.43 (d, J = 2.0 Hz, 1H), 6.40 (d, J = 2.0 Hz, 1H), 4.45 (s, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.67 (s, 3H), 3.33 (d, J = 15.6 Hz, 1H), 2.96 (d, J = 15.6 Hz, 1H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.59, 161.83, 158.17, 144.78, 139.09, 131.57, 129.90, 128.81, 126.92, 121.50, 119.40, 101.67, 98.32, 84.55, 67.96, 55.44, 55.32, 52.47, 47.51, 25.35; MS(EI): m/z (%): 420

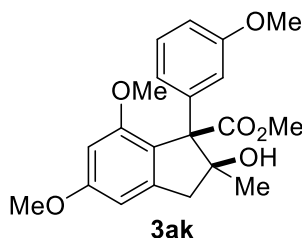
(M^+ , 2.83), 422 ($[M+2]^+$, 2.60), 388 (100); HRMS (EI) calcd. for $C_{20}H_{21}O_5Br$: 420.0572, found: 420.0569.

25) Synthesis of methyl 1-(3-chlorophenyl)-2-hydroxy-5,7-dimethoxy-2-methyl-3-dihydro-1H-indene-1-carboxylate (3aj).



The general procedure was followed using **1a** (0.6 mmol) and **2j** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3aj** (43.3 mg, 58% d.r. = 7:1) was obtained as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.15-7.30 (m, 3H), 7.05 (d, J = 7.2 Hz, 1H), 6.43 (d, J = 2.0 Hz, 1H), 6.40 (d, J = 2.0 Hz, 1H), 4.43 (s, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 3.33 (d, J = 15.6 Hz, 1H), 2.96 (d, J = 15.6 Hz, 1H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.58, 161.83, 158.18, 144.77, 138.86, 133.25, 128.69, 128.49, 126.99, 126.50, 119.50, 101.64, 98.31, 84.56, 68.01, 55.45, 55.31, 52.47, 47.51, 25.31; MS(EI): m/z (%): 376 (M^+ , 3.07), 378 ($[M+2]^+$, 1.04); 344 (100); HRMS (EI) calcd. for $C_{20}H_{21}O_5Cl$: 376.1078, found: 376.1075.

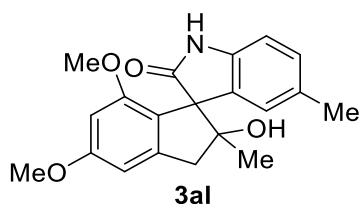
26) Synthesis of methyl 2-hydroxy-5,7-dimethoxy-1-(3-methoxyphenyl)-2-methyl-2,3-dihydro-1H-indene-1-carboxylate (3ak).



The general procedure was followed using **1a** (0.6 mmol) and **2k** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **3ak** (46.1 mg, 62%, d.r. = 5:1) was obtained as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 8.4 Hz, 1H), 7.75-7.85 (m, 3H), 6.43 (d, J = 2.0 Hz, 1H), 6.39 (d, J = 2.0 Hz, 1H),

4.49 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 3.29 (d, $J = 15.6$ Hz, 1H), 2.96 (d, $J = 15.6$ Hz, 1H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.97, 161.62, 158.70, 158.33, 144.76, 138.29, 128.13, 120.87, 120.26, 114.87, 111.83, 101.46, 98.25, 84.59, 68.21, 55.41, 55.33, 55.09, 52.32, 47.48, 25.15; MS(EI): m/z (%): 372 (M^+ , 7.94), 340 (100); HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_6$: 372.1573, found: 372.1575.

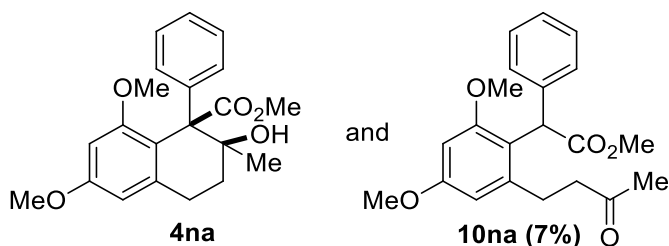
27) Synthesis of 2-hydroxy-5,7-dimethoxy-2,5'-dimethyl-2,3-dihydrospiro[indene-1,3'-indolin]-2'-one (3al**).**



The general procedure was followed using **1a** (0.6 mmol) and **2l** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 5:1 to 2:1), **3al** (54.4 mg, 80%, d.r. = 3:1) was obtained as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ [8.51 (s, 0.75 H), 7.99 (s, 0.25H)], [7.04 (d, $J = 7.6$ Hz, 0.25H), 6.53 (d, $J = 7.6$ Hz, 0.75H)], [6.98 (d, $J = 8.4$ Hz, 1H)], [6.82 (d, $J = 8.0$ Hz, 0.75H), 6.80 (d, $J = 8.0$ Hz, 0.25H)], [6.62 (d, $J = 1.6$ Hz, 0.75 H), 6.52 (d, $J = 1.6$ Hz, 0.25H)], [6.24 (d, $J = 1.6$ Hz, 1H)], [5.18 (s, 1H)], [3.810 (s, 2.25H), 3.805 (s, 0.75H)], [3.54 (s, 2.25H), 3.41 (s, 0.75H)], [3.51 (d, $J = 16.0$ Hz, 0.25H), 3.35 (d, $J = 16.0$ Hz, 0.75H)], [3.15 (d, $J = 16.0$ Hz, 0.75H), 3.08 (d, $J = 16.0$ Hz, 0.25H)], [2.28 (s, 0.25H), 2.22 (s, 2.25H)], [1.37 (s, 0.25H), 1.15 (s, 2.25H)]; ^{13}C NMR (100 MHz, CDCl_3) δ [180.60, 179.26], [161.63, 162.59], [156.37, 157.05], [145.63, 146.01], [138.06, 139.33], [132.05, 131.30], [131.49, 129.14], [128.39, 128.47], [124.44, 126.51], [123.17, 121.38], [109.87, 109.41], [102.23, 101.83], [97.57, 97.72], [85.07, 84.52], [64.00, 67.10], [55.51, 55.49], [55.45, 55.23], [48.05, 46.54], [23.18, 22.81], [21.12]; MS(EI): m/z (%): 339 (M^+ , 7.40); 49 (100); HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{21}\text{NO}_4$: 339.1471, found: 339.1468.

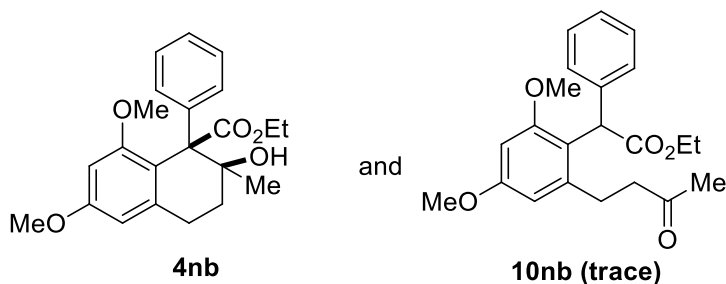
27) Synthesis of methyl 2-hydroxy-6,8-dimethoxy-2-methyl-1-phenyl-1,2,3,4-

tetrahydronaphthalene-1-carboxylate (4na).



The general procedure was followed using **1n** (0.6 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4na** (42.5 mg, 60%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.50 (m, 2H), 7.12-7.20 (m, 3H), 6.40 (d, J = 2.4 Hz, 1H), 6.30 (d, J = 2.4 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 3.44 (s, 3H), 3.27 (s, 1H), 3.12-3.25 (m, 1H), 2.65-2.76 (m, 1H), 1.52-1.64 (m, 2H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.49, 159.45, 158.95, 141.22, 138.41, 129.99, 126.72, 126.41, 120.04, 104.25, 97.98, 73.58, 60.49, 55.63, 55.21, 52.04, 31.48, 26.65, 26.08; MS(EI): m/z (%): 356 (M^+ , 5.65); 324 (100); HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_5$: 356.1624, found: 356.1627.

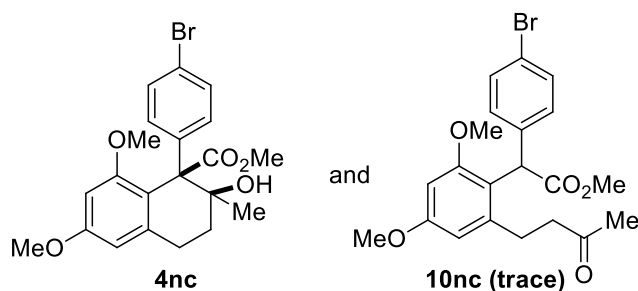
28) Synthesis of ethyl 2-hydroxy-6,8-dimethoxy-2-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (4nb).³



The general procedure was followed using **1n** (0.6 mmol) and **2n** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4nb** (56.5 mg, 76%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.50 (m, 2H), 7.10-7.25 (m, 3H), 6.39 (d, J = 2.0 Hz, 1H), 6.28 (d, J = 2.0 Hz, 1H), 4.25-4.35 (m, 1H), 4.15-4.24 (m, 1H), 3.84 (s, 3H), 3.46 (s, 1H), 3.44 (s, 3H), 3.11-3.25 (m, 1H), 2.65-2.75 (m, 1H), 1.52-1.70 (m, 2H), 1.28 (s, 3H), 1.26 (t, J = 10.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.89, 159.40, 158.88, 141.16, 138.55, 130.14, 126.64, 126.34, 119.98, 104.11, 97.68, 73.49, 61.04, 60.50, 55.33, 55.19,

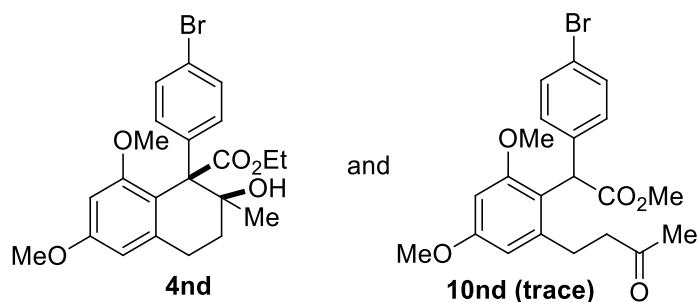
31.50, 26.62, 26.18, 14.16; MS(EI): m/z (%): 370 (M^+ , 7.25); 324 (100); HRMS (EI) calcd. for $C_{22}H_{26}O_5$: 370.1780, found: 370.1783.

29) Synthesis of methyl 1-(4-bromophenyl)-2-hydroxy-6,8-dimethoxy-2-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (4nc).



The general procedure was followed using **1n** (0.2 mmol) and **2c** (0.6 mmol). After purification by column chromatography (PE/EtOAc = 6:1), **4nc** (51.5 mg, 59%, d.r. > 20:1) was obtained as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 9.2 Hz, 2H), 7.28 (d, J = 9.2 Hz, 2H), 6.39 (d, J = 2.4 Hz, 1H), 6.29 (d, J = 2.4 Hz, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.46 (s, 3H), 3.11-3.25 (m, 1H), 3.10 (s, 1H), 2.65-2.78 (m, 1H), 1.55-1.70 (m, 2H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.03, 159.61, 158.79, 140.47, 138.19, 131.75, 129.80, 120.77, 119.45, 104.23, 97.93, 73.39, 60.08, 55.55, 55.24, 52.14, 31.53, 26.50, 25.95; MS (ESI): m/z (%): 456.97 ($[M+Na]^+$, 53.00), ($[M+2+Na]^+$, 51.00), 166.10 (100); HRMS (ESI) calcd. for $C_{21}H_{23}BrNaO_5$ $[M+Na]$: 457.0621, found 457.0607.

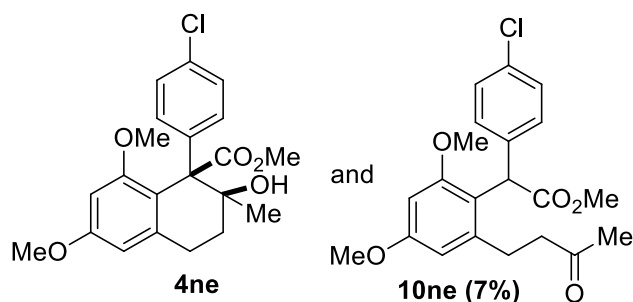
30) Synthesis of ethyl 1-(4-bromophenyl)-2-hydroxy-6,8-dimethoxy-2-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (4nd).



The general procedure was followed using **1n** (0.6 mmol) and **2d** (0.2 mmol). After

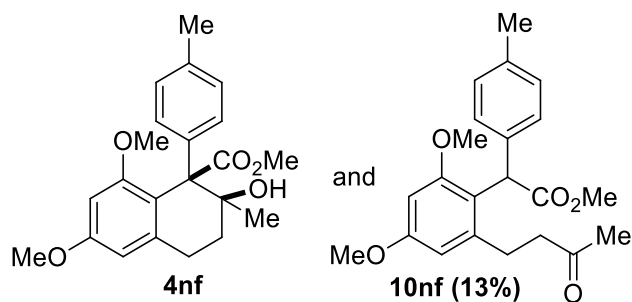
purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4nd** (59.2 mg, 66%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, J = 9.2 Hz, 2H), 7.28 (d, J = 9.2 Hz, 2H), 6.38 (d, J = 2.4 Hz, 1H), 6.27 (d, J = 2.4 Hz, 1H), 4.11-4.22 (m, 1H), 4.23-4.34 (m, 1H), 3.83 (s, 3H), 3.44 (s, 3H), 3.30 (s, 1H), 3.10-3.22 (m, 1H), 2.65-2.75 (m, 1H), 1.52-1.68 (m, 2H), 1.14-1.28 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.43, 159.56, 158.73, 140.42, 138.34, 131.89, 129.72, 120.71, 119.43, 104.12, 97.64, 73.31, 61.16, 60.12, 55.24, 55.21, 31.57, 26.48, 26.07, 14.12; MS(EI): m/z (%): 448 (M^+ , 2.28), 450 ($[\text{M}+2]^+$, 2.31), 84 (100); HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{25}\text{O}_5$: 448.0885, found: 448.0888.

31) Synthesis of methyl 1-(4-chlorophenyl)-2-hydroxy-6,8-dimethoxy-2-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (4ne).



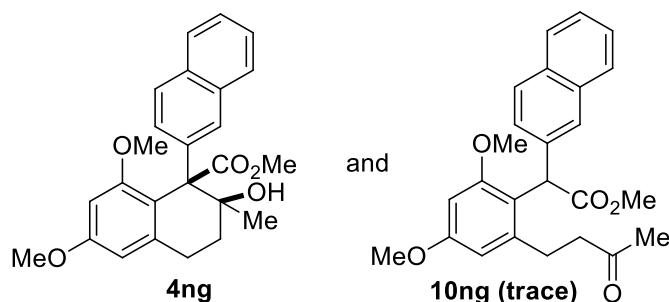
The general procedure was followed using **1n** (0.6 mmol) and **2e** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4ne** (64.8 mg, 83%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 9.2 Hz, 2H), 7.13 (d, J = 9.2 Hz, 2H), 6.39 (d, J = 2.4 Hz, 1H), 6.29 (d, J = 2.4 Hz, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.45 (s, 3H), 3.10-3.22 (m, 1H), 3.11 (s, 1H), 2.65-2.75 (m, 1H), 1.52-1.68 (m, 2H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.11, 159.62, 158.82, 139.92, 138.20, 132.42, 131.37, 126.84, 119.57, 104.26, 97.96, 73.46, 60.04, 55.56, 55.25, 52.13, 31.54, 26.51, 25.97; MS(EI): m/z (%): 390 (M^+ , 12.30); 392 ($[\text{M}+2]^+$, 4.52), 358 (100); HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{23}\text{O}_5\text{Cl}$: 390.1234, found: 390.1238.

32) Synthesis of methyl 2-hydroxy-6,8-dimethoxy-2-methyl-1-p-tolyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (4nf).



The general procedure was followed using **1n** (0.6 mmol) and **2f** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4nf** (52.3 mg, 71%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, J = 8.4, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.40 (d, J = 2.4 Hz, 1H), 6.30 (d, J = 2.4 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.47 (s, 3H), 3.38 (s, 1H), 3.11-3.24 (m, 1H), 2.64-2.74 (m, 1H), 2.28 (s, 3H), 1.54-1.66 (m, 2H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.75, 159.37, 158.90, 138.51, 138.08, 135.95, 129.96, 127.48, 120.07, 104.27, 97.92, 73.57, 60.22, 55.70, 55.19, 52.02, 31.35, 26.67, 26.09, 20.78; MS(EI): m/z (%): 370 (M^+ , 6.14); 338 (100); HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_5$: 370.1780, found: 370.1783.

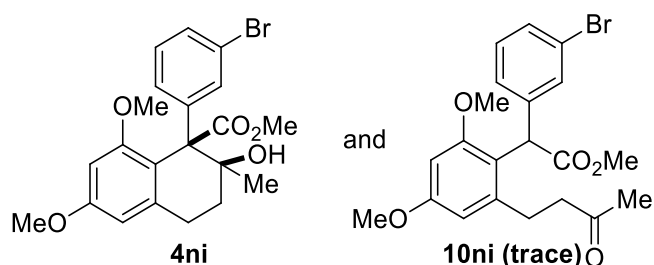
33) Synthesis of methyl 2-hydroxy-6,8-dimethoxy-2-methyl-1,2,3,4-tetrahydro-1,2'-binaphthyl-1-carboxylate (**4ng**).



The general procedure was followed using **1n** (0.6 mmol) and **2g** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4ng** (50.8 mg, 63%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.65-8.00 (m, 5H), 7.35-7.48 (m, 2H), 6.45 (d, J = 2.4 Hz, 1H), 6.32 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 3.41 (s, 3H), 3.32 (s, 1H), 3.15-3.30 (m, 1H), 2.72-2.84 (m, 1H), 1.58-1.72 (m, 2H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ

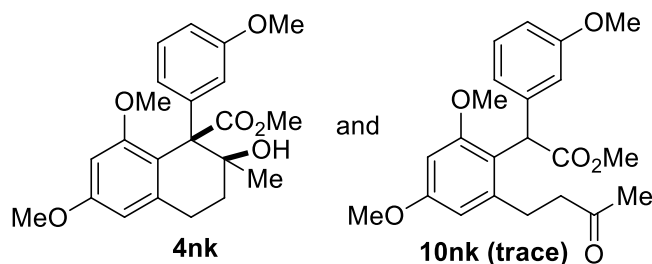
174.58, 159.51, 158.98, 138.86, 138.41, 132.44, 131.96, 129.16, 128.66, 128.32, 126.94, 125.77, 125.64, 125.35, 119.96, 104.29, 97.92, 73.81, 60.57, 55.59, 55.24, 52.10, 31.59, 26.79, 26.12; MS(ESI): m/z (%): 406 (M^+ , 18.67), 374 (100); HRMS (ESI) calcd. for $C_{25}H_{26}O_5$: 406.1780, found: 406.1783.

34) Synthesis of methyl -1-(3-bromophenyl)-2-hydroxy-6,8-dimethoxy-2-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (4ni).



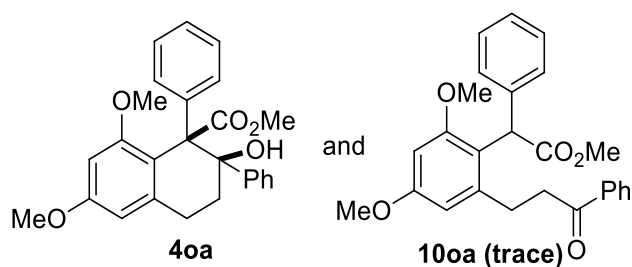
The general procedure was followed using **1n** (0.6 mmol) and **2i** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4ni** (51.1 mg, 59%, d.r. > 20:1) and **4ah'** (14.0 mg, 16%) were obtained as colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.26-7.34 (m, 2H), 7.02 (t, J = 8.0 Hz, 1H), 6.38 (d, J = 2.4 Hz, 1H), 6.29 (d, J = 2.4 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.45 (s, 3H), 3.10-3.22 (m, 1H), 3.06 (s, 1H), 2.66-2.78 (m, 1H), 1.55-1.70 (m, 2H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.85, 159.65, 158.82, 143.80, 138.14, 132.95, 129.54, 128.44, 128.17, 121.18, 119.33, 104.30, 98.02, 73.53, 60.23, 55.55, 55.23, 52.16, 31.65, 26.52, 25.95; MS(ESI): m/z (%): 457.09 ($[M+Na]^+$, 96.00); 459.09 ($[M+Na+2]^+$, 100); HRMS (EI) calcd. for $C_{21}H_{23}O_5Br$: 434.0729, found: 434.0731.

35) Synthesis of methyl 2-hydroxy-6,8-dimethoxy-1-(3-methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (4nk).



The general procedure was followed using **1n** (0.6 mmol) and **2k** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4nk** (44.4 mg, 57%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.15 (s, 1H), 7.08 (t, $J = 8.0$ Hz, 1H), 6.97 (d, $J = 8.0$ Hz, 1H), 6.70-6.74 (m, 1H), 6.38 (d, $J = 2.4$ Hz, 1H), 6.29 (d, $J = 2.4$ Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 3.46 (s, 3H), 3.22 (s, 1H), 3.12-3.20 (m, 1H), 2.65-2.75 (m, 1H), 1.58-1.70 (m, 2H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.39, 159.45, 158.96, 158.19, 142.94, 138.26, 127.36, 122.72, 120.04, 116.96, 111.16, 104.24, 97.99, 73.62, 60.42, 55.68, 55.20, 55.06, 52.05, 31.50, 26.70, 26.03; MS(EI): m/z (%): 386 (M^+ , 9.99); 354 (100); HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_6$: 386.1729, found: 386.1731.

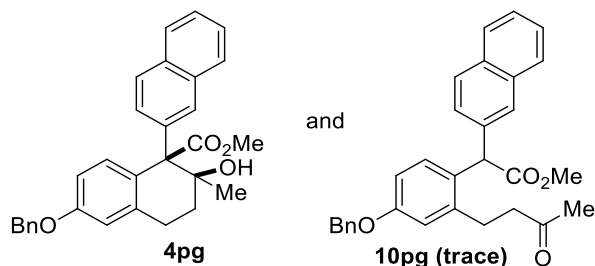
36) Synthesis of methyl 2-hydroxy-6,8-dimethoxy-1,2-diphenyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (**4oa**).⁴



The general procedure was followed using **1o** (0.6 mmol) and **2a** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4oa** (50.0 mg, 60%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.32 (m, 3H), 7.05-7.15 (m, 1H), 6.90-7.02 (m, 4H), 6.46-6.58 (m, 3H), 6.34 (d, $J = 2.8$ Hz, 1H), 5.17 (s, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 3.49 (s, 3H), 3.38-3.45 (m, 1H), 2.80-2.92 (m, 1H), 2.14-2.24 (m, 1H), 1.80-1.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.47, 159.57, 158.73, 144.12, 139.34, 138.77, 131.44, 127.78, 127.41,

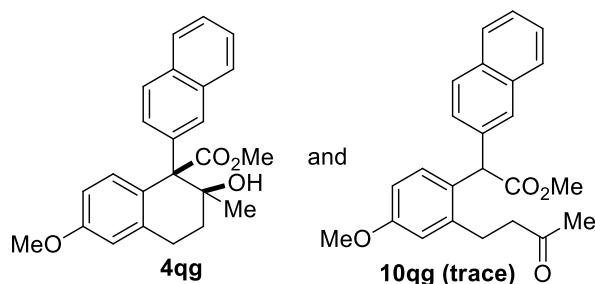
126.95, 126.64, 125.78, 120.02, 104.52, 97.77, 76.62, 62.26, 55.69, 55.25, 52.22, 29.76, 26.57; MS(EI): m/z (%): 418 (M^+ , 1.79); 105 (100); HRMS (ESI) calcd. for $C_{26}H_{26}O_5$: 418.1780, found: 418.1777.

37) Synthesis of methyl 6-(benzyloxy)-2-hydroxy-2-methyl-1,2,3,4-tetrahydro-1,2'-binaphthyl-1-carboxylate (4pg).



The general procedure was followed using **1p** (1.0 mmol), **2g** (0.2 mmol) and gold catalyst (10 mol%). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4pg** (42.9 mg, 47%, d.r. > 20:1) was obtained as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.84 (m, 1H), 7.70-7.77 (m, 2H), 7.25-7.55 (m, 10H), 6.78-6.84 (m, 2H), 5.08 (s, 2H), 4.63 (s, 1H), 3.71 (s, 3H), 2.95-3.05 (m, 2H), 2.44-2.56 (m, 1H), 1.84-1.94 (m, 1H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.58, 157.85, 138.82, 138.21, 136.85, 134.25, 132.25, 132.17, 129.05, 128.60, 128.27, 128.25, 128.04, 127.58, 127.27, 126.21, 126.02, 125.85, 113.44, 112.93, 73.76, 69.88, 64.19, 52.65, 34.53, 28.51, 24.74. MS(EI): m/z (%): 452 (M^+ , 1.01); 91 (100); HRMS (ESI) calcd. for $C_{30}H_{28}O_4$: 452.1988, found: 452.1989.

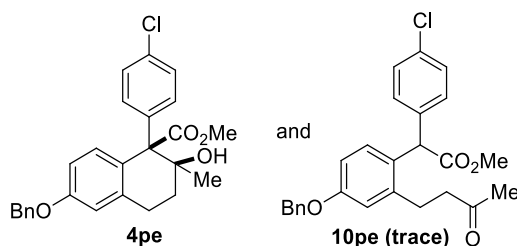
38) Synthesis of methyl 2-hydroxy-6-methoxy-2-methyl-1,2,3,4-tetrahydro-1,2'-binaphthyl-1-carboxylate (4qg).⁵



The general procedure was followed using **1q** (1.0 mmol), **2g** (0.2 mmol) and gold

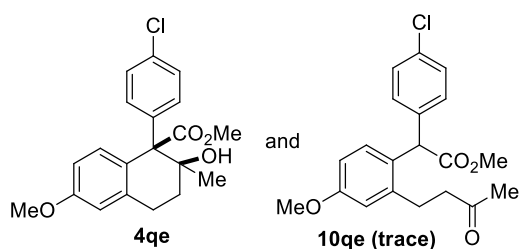
catalyst (10 mol%). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4qg** (31.7 mg, 42%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.80-7.85 (m, 1H), 7.72-7.79 (m, 2H), 7.42-7.52 (m, 3H), 7.26-7.36 (m, 2H), 6.70-6.75 (m, 2H), 4.63 (s, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 2.96-3.04 (m, 2H), 2.44-2.54 (m, 1H), 2.85-2.93 (m, 1H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.61, 158.53, 138.77, 138.22, 134.21, 132.35, 132.17, 129.04, 128.27, 128.25, 127.75, 127.27, 126.20, 126.02, 125.84, 112.49, 112.29, 73.76, 64.17, 55.17, 52.64, 34.54, 28.51, 24.72; MS(EI): m/z (%): 376 (M^+ , 5.67); 299 (100); HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{24}\text{O}_4$: 376.1675, found: 376.1679.

39) Synthesis of methyl 6-(benzyloxy)-1-(4-chlorophenyl)-2-hydroxy-2-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (4pe).



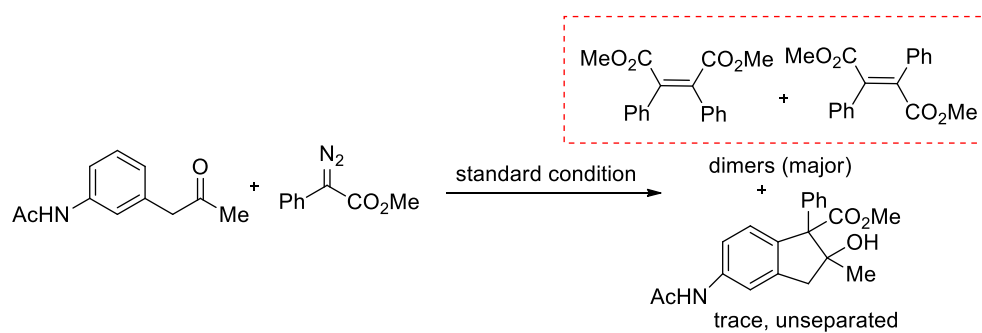
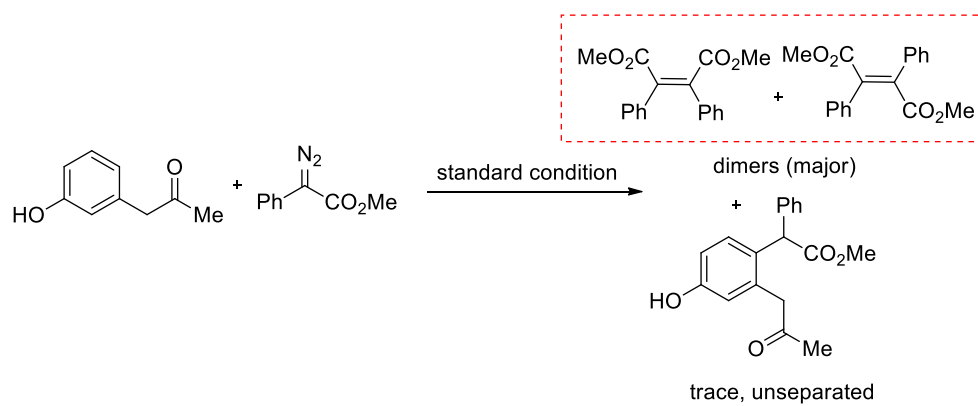
The general procedure was followed using **1p** (1.0 mmol), **2e** (0.2 mmol) and gold catalyst (10 mol%). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4pe** (36.1 mg, 41%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.46 (m, 5H), 7.20-7.29 (m, 3H), 7.03 (d, J = 8.8 Hz, 2H), 7.72-7.82 (m, 2H), 5.05 (s, 2H), 4.42 (s, 1H), 3.67 (s, 3H), 2.90-2.98 (m, 2H), 2.42-2.54 (m, 1H), 1.80-1.88 (m, 1H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.12, 157.92, 139.20, 138.75, 136.80, 134.01, 132.81, 131.35, 128.60, 128.04, 127.58, 127.53, 127.21, 113.50, 113.04, 73.43, 69.88, 63.69, 52.66, 34.40, 28.44, 24.52. MS(EI): m/z (%): 436 (M^+ , 0.28); 438 ($[\text{M}+2]^+$, 0.09), 91 (100); HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{25}\text{O}_4\text{Cl}$: 436.1441, found: 436.1445.

40) Synthesis of methyl 1-(4-chlorophenyl)-2-hydroxy-6-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (4qe).



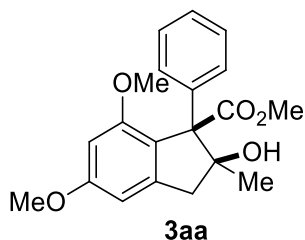
The general procedure was followed using **1q** (1.0 mmol) and **2e** (0.2 mmol). After purification by column chromatography (PE/EtOAc = 10:1 to 5:1), **4qe** (34.5 mg, 48%, d.r. > 20:1) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.32 (m, 3H), 7.04 (d, J = 8.4 Hz, 2H), 6.64-6.76 (m, 2H), 4.42 (s, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 2.89-3.02 (m, 2H), 2.42-2.55 (m, 1H), 1.80-1.88 (m, 1H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.13, 158.62, 139.23, 138.69, 133.95, 132.80, 131.36, 127.30, 127.20, 112.56, 112.39, 73.43, 63.68, 55.15, 52.63, 34.42, 28.43, 24.52. MS(EI): m/z (%): 360 (M^+ , 5.22); 362 ($[\text{M}+2]^+$, 1.75), 284 (100); HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{21}\text{O}_4\text{Cl}$: 360.1128, found: 360.1129.

5. Reactions of phenol and aniline derivatives:



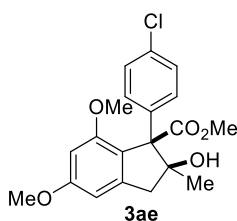
6. Preliminary investigation on asymmetric catalysis.

1) Procedure for **3aa**



In a dried glass tube, a solution of (R)-MeO-DTBM-PIPHEP (11.5 mg, 0.01 mmol) and AuCl Me₂S (5.9 mg, 0.02 mmol) in CH₂Cl₂ (2 mL) was stirred at room temperature for 2 h. Then, the solvent was removed in reduced pressure. AgNTf₂ (7.8 mg, 0.02 mmol) and CH₂Cl₂ (3 mL) was added in the residue and the resulting solution was stirred at room temperature for 15 min. Aryl ketone (39mg, 0.2 mmol) was added to the reaction mixture at room temperature. Then a solution of diazo compound (106 mg, 0.6 mmol) in CH₂Cl₂ (1 mL) was introduced into the reaction mixture by a syringe in 30 min at -40 °C. The resulting mixture was continually stirred at -40 °C for 24 h and aryl ketone compound was consumed completely determined by TLC analysis. After being filtrated through a short silica gel column and concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (PE / EtOAc = 5:1 to 2:1) to afford the desired product (57.4 mg, 84%, d.r. = 8:1, 58% ee) as a colorless oil. HPLC analysis Daicel chiralpak AD-H, hexane/*i*-PrOH = 80/20, 0.8 mL/min, 210 nm. *t*_R (minor) = 12.7 min, *t*_R (major) = 24.8 min; [α]_D²⁵ = 37.7 (*c* = 0.2, CHCl₃).

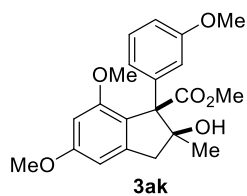
2) For **3ae**



The procedure was followed as **3aa**. The desired product **3ae** was obtained (64.3 mg, 86%, d.r. = 9:1, 67% ee) as a colorless oil. HPLC analysis Daicel chiralpak AD-H, hexane/*i*-PrOH = 80/20, 0.8 mL/min, 210 nm. *t*_R (minor) = 17.5 min, *t*_R (major) = 31.8

min; $[\alpha]_{\text{D}}^{25} = 45.8$ ($c = 0.2$, CHCl_3).

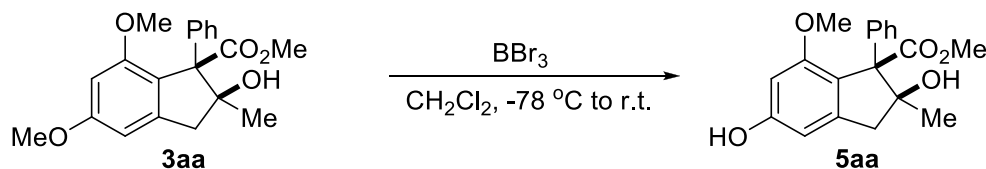
3) For **3ak**



The procedure was followed as **3aa**. The desired product **3ak** was obtained (54.5 mg, 72%, d.r. = 5:1, 59% ee) as a colorless oil. HPLC analysis Daicel chiralpak AD-H, hexane/*i*-PrOH = 80/20, 0.8 mL/min, 210 nm. t_{R} (minor) = 9.2 min, t_{R} (major) = 13.9 min; $[\alpha]_{\text{D}}^{25} = 31.0$ ($c = 0.2$, CHCl_3).

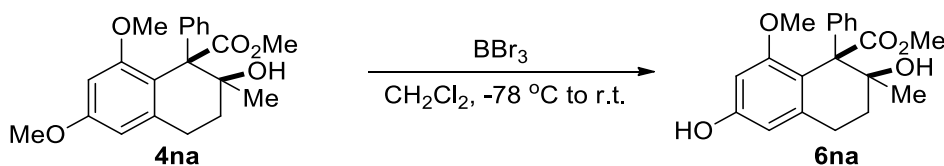
7. Transformations of products.

1) Synthesis of methyl 2,5-dihydroxy-7-methoxy-2-methyl-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (**5aa**)



To a solution of compound **3aa** (51 mg, 0.15 mmol) in CH_2Cl_2 (5 mL), the solution of BBr_3 (56 μL , 0.6 mmol) in CH_2Cl_2 (1 mL) was added at -78°C . After being stirred for 15 min at room temperature, the reaction was quenched with saturated NaHCO_3 solution. After being extracted with ethyl acetate, washed with brine solution and dried with Na_2SO_4 , the solid was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by silica chromatography (PE/EtOAc = 2:1 to 1:1) to give **5aa** (25.2 mg, 51%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.31 (m, 3H), 7.12-7.24 (m, 2H), 6.33 (d, $J = 4.0$ Hz, 2H), 5.77 (s, 1H), 4.81 (s, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.27 (d, $J = 15.6$ Hz, 1H), 2.91 (d, $J = 15.6$ Hz, 1H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.46, 158.47, 157.78, 144.88, 136.51, 128.33, 127.28, 126.87, 119.73, 104.27, 98.56, 84.77, 68.04, 55.31, 52.46, 47.12, 25.18; MS(EI): m/z (%): 328 (M^+ , 4.48); 296 (100); HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_5$: 328.1311, found: 328.1309

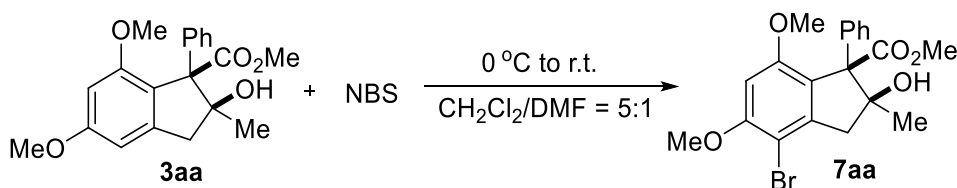
2) Synthesis of methyl 2,6-dihydroxy-8-methoxy-2-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (**6na**).



The procedure was followed as **5aa**. The corresponding residue was purified by silica chromatography (PE/EtOAc = 2:1 to 1:1) to get desired product **6na** (32.3 mg, 63%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.46 (m, 2H), 7.12-7.20 (m, 3H), 6.29 (d, $J = 2.4$ Hz, 1H), 6.24 (d, $J = 2.4$ Hz, 1H), 5.81 (s, 1H), 3.75 (s, 3H), 3.62 (s, 1H), 3.42 (s, 3H), 3.04-3.15 (m, 1H), 2.58-2.66 (m, 1H), 1.52-1.64 (m, 2H),

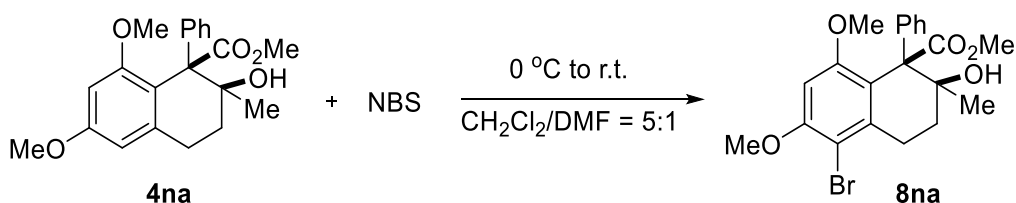
1.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.04, 158.96, 155.74, 140.93, 138.73, 130.06, 126.77, 126.51, 119.43, 107.19, 98.28, 73.91, 60.52, 55.64, 52.19, 31.26, 26.69, 25.70; MS(EI): m/z (%): 342 (M^+ , 6.00), 310 (100); HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_5$: 342.1467, found: 342.1470.

3) Synthesis of methyl 4-bromo-2-hydroxy-5,7-dimethoxy-2-methyl-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (7aa).



To a solution of compound **3aa** (110 mg, 0.32 mmol) in CH_2Cl_2 (5.0 mL), the solution of NBS (113 mg, 0.96 mmol) in DMF (1 mL) was added at 0 °C. After was stirred for 1 hour at r.t., the solution was quenched with saturated Na_2SO_3 solution. After the mixture was extracted with ethyl acetate, washed with brine solution, dried with Na_2SO_4 and concentrated, the residue was purified by silica chromatography (PE/EtOAc = 5:1) to get desired product **7aa** (131.8 mg, 98%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.32 (m, 3H), 7.12-7.20 (m, 2H), 6.44 (s, 1H), 4.31 (s, 1H), 3.94 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 3.31 (d, J = 16.4 Hz, 1H), 3.09 (d, J = 16.4 Hz, 1H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.44, 157.34, 157.18, 144.83, 136.52, 128.13, 127.32, 126.90, 121.58, 100.14, 96.17, 83.78, 69.65, 56.45, 55.65, 52.34, 48.71, 25.31; MS(EI): m/z (%): 420 (M^+ , 5.56), 422 ($[\text{M}+2]^+$, 5.36); 346 (100); HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{21}\text{O}_5\text{Br}$: 420.0572, found: 420.0570.

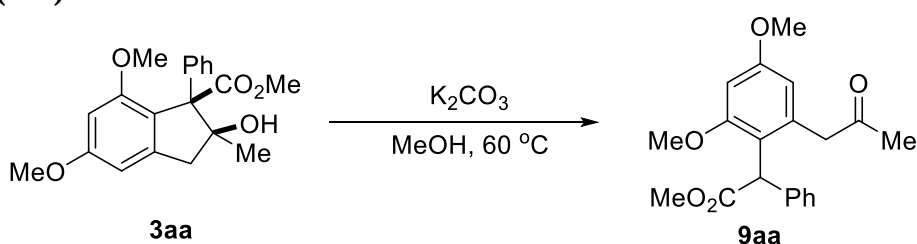
4) Synthesis of methyl 5-bromo-2-hydroxy-6,8-dimethoxy-2-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (8na).



The procedure was followed as **7aa**. The corresponding residue was purified by silica chromatography (PE/EtOAc = 5:1 to 2:1) to get desired product **8na** (50.5 mg,

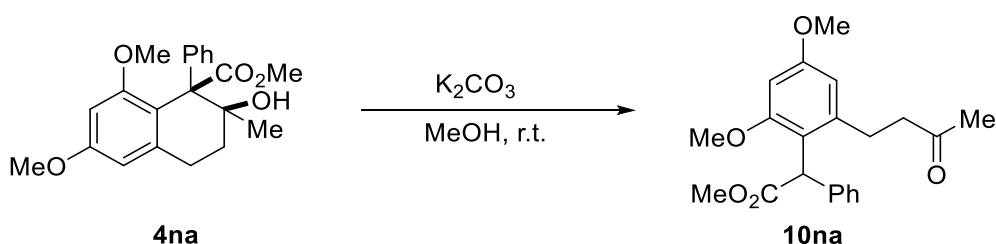
97%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.50 (m, 2H), 7.15-7.22 (m, 3H), 6.40 (s, 1H), 3.93 (s, 3H), 3.74 (s, 3H), 3.48 (s, 3H), 3.19 (s, 1H), 2.95-3.08 (m, 1H), 2.82-2.94 (m, 1H), 1.55-1.75 (m, 2H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.22, 157.74, 155.64, 140.88, 138.05, 129.88, 126.84, 126.59, 121.76, 105.27, 95.63, 73.24, 60.86, 56.31, 55.97, 52.14, 31.46, 27.64, 26.45; MS(EI): m/z (%): 434 (M^+ , 0.76), 436 ($[\text{M}+2]^+$, 0.77), 151 (100); HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{23}\text{O}_5\text{Br}$: 434.0729, found: 434.0728.

5) Synthesis of methyl 2-(2,4-dimethoxy-6-(2-oxopropyl)phenyl)-2-phenylacetate (9aa).



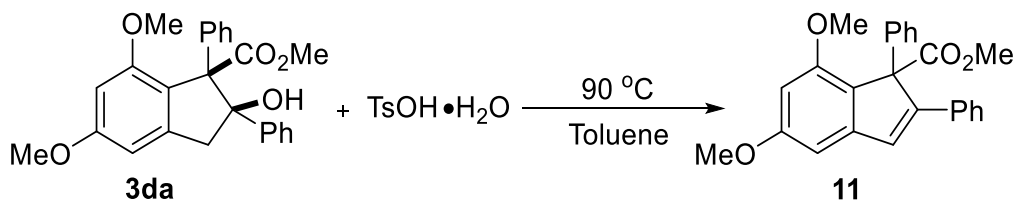
The mixture of compound **3aa** (34 mg, 0.1 mmol), K_2CO_3 (14 mg, 0.1 mmol) in MeOH (5 mL) was heated to 60 $^\circ\text{C}$ and for 45 mins. The resulting solution was quenched with H_2O and extracted with CH_2Cl_2 . After the combined organic layer was dried with Na_2SO_4 and concentrated, the residue was purified by silica chromatography (PE/EtOAc = 1:1) to give **9aa** (33.9 mg, 99%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.12-7.35 (m, 5H), 6.51 (d, J = 2.4 Hz, 1H), 6.35 ((d, J = 2.4 Hz, 1H), 5.13 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.68 (s, 3H), 3.59 (s, 2H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.17, 173.54, 159.70, 158.50, 137.51, 135.58, 128.85, 128.17, 126.84, 119.42, 107.96, 98.02, 55.66, 55.23, 52.09, 49.09, 48.52, 28.98; MS(EI): m/z (%): 342 (M^+ , 2.51), 310 (100); HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_5$: 342.1467, found: 342.1464.

6) Synthesis of methyl 2-(2,4-dimethoxy-6-(3-oxobutyl)phenyl)-2-phenylacetate (10na).



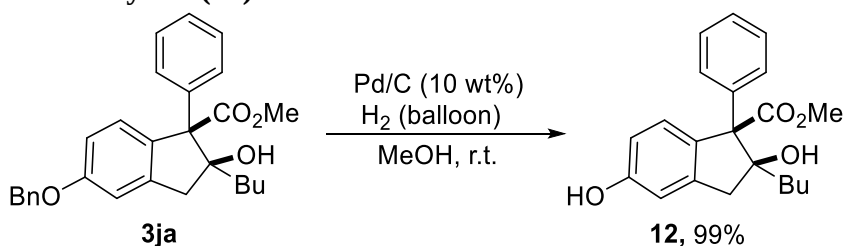
The procedure was followed as **9aa** at room temperature. The crude product was purified by silica chromatography (PE/EtOAc = 1:1) to get desired product **10na** (33.9 mg, 99%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.12-7.28 (m, 5H), 6.41 (d, $J = 2.4$ H, 1H), 6.33 (d, $J = 2.4$ H, 1H), 5.03 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.67 (s, 3H), 2.72-2.88 (m, 2H), 2.30-2.52 (m, 2H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 207.45, 173.72, 159.67, 158.33, 141.76, 138.14, 129.02, 128.11, 126.77, 118.86, 106.45, 97.12, 55.54, 55.17, 52.01, 48.81, 44.27, 29.77, 27.49; MS(EI): m/z (%): 356 (M^+ , 5.61); 91 (100); HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_5$: 356.1624, found: 356.1621.

7) Synthesis of 5,7-dimethoxy-1-(methylperoxymethyl)-1,2-diphenyl-1H-indene (**11**).

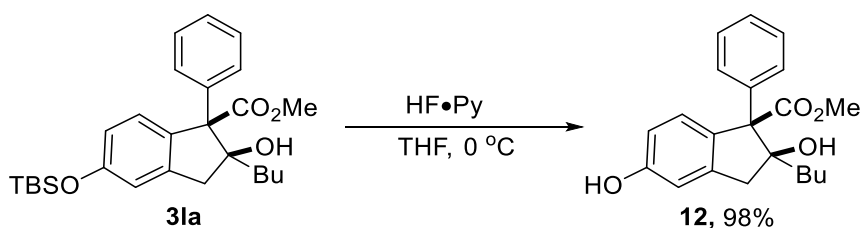


The solution of compound **3da** (410 mg, 1 mmol), $\text{TsOH} \cdot \text{H}_2\text{O}$ (19 mg, 0.1 mmol) in toluene (10 mL) was heated to 90 $^\circ\text{C}$ for 2 hours. After the resulting solution was extracted with ether, dried with Na_2SO_4 and concentrated, the residue was purified by silica chromatography (PE/EtOAc = 20:1 to 10:1) to give **11** (241.0 mg, 62%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.54 (m, 2H), 7.41-7.48 (m, 2H), 7.35 (s, 1H), 7.14-7.28 (m, 6H), 6.62 (d, $J = 2.0$ Hz, 1H), 6.27 (d, $J = 2.0$ Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.12, 161.51, 154.89, 150.82, 144.53, 137.04, 133.55, 129.89, 129.55, 128.21, 128.19, 127.75, 127.62, 127.25, 126.73, 99.15, 97.42, 67.01, 55.50, 55.40, 52.42; MS(EI): m/z (%): 386 (M^+ , 44.65); 327 (100); HRMS (EI) calcd. for $\text{C}_{25}\text{H}_{24}\text{O}_4$: 386.1518, found: 386.1517.

8) Synthesis of methyl 2-butyl-2,5-dihydroxy-1-phenyl-2,3-dihydro-1H-indene-1-carboxylate (12**).**

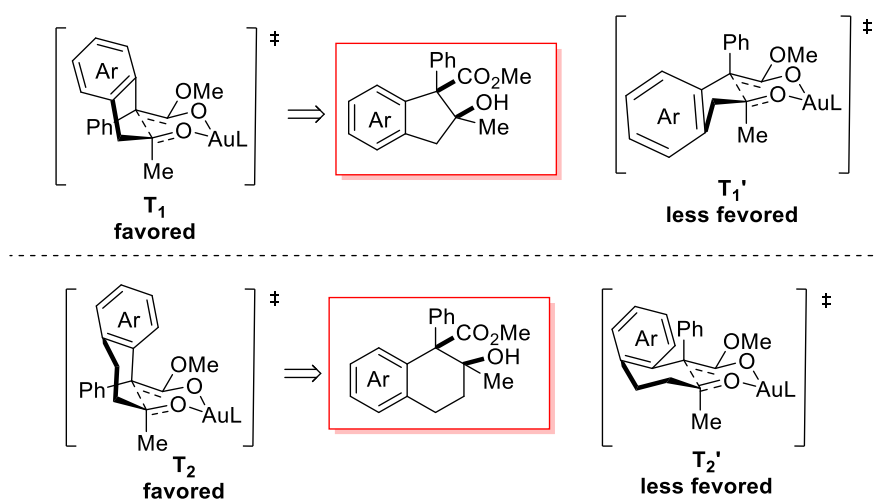


Pd/C (10 mg) was added to the solution of **3ja** (43 mg, 0.1 mmol) in MeOH (5 mL). The mixture was stirred at room temperature for 12 h under H₂ balloon. After the solution was filtered and concentrated, **12** was obtained (34.0 mg, 99%) as a colorless oil.



To a solution of **3la** (43 mg, 0.1 mmol) in THF (2 mL) HF·Py (0.5 mL) was added at 0 °C. After being stirred for 12 h under N₂ atmosphere, the reaction was quenched with saturated NaHCO₃ solution. The resulting mixture was extracted with ethyl acetate and the combined organic layer was concentrated. The residue was purified by silica chromatography directly (PE/EtOAc = 5:1 to 2:1) to afford **12** (33.2 mg, 98%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, *J* = 8.4 Hz, 1H), 7.22-7.35 (m, 3H), 6.88-7.02 (m, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.65 (s, 1H), 6.33 (s, 1H), 4.78 (s, 1H), 3.82 (s, 3H), 3.01 (d, *J* = 16.2 Hz, 1H), 2.86 (d, *J* = 16.2 Hz, 1H), 1.40-1.65 (m, 2H), 0.95-1.34 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 175.67, 156.13, 144.14, 139.19, 132.90, 128.20, 128.14, 127.56, 127.28, 114.52, 112.24, 87.11, 70.24, 52.43, 42.01, 36.81, 26.05, 23.14, 13.98. MS(EI): *m/z* (%): 340(M⁺, 7.00), 44 (100), HRMS (EI) calcd. for C₂₁H₂₄O₄: 340.1675, found: 340.1673.

8. Another proposed Mechanism.

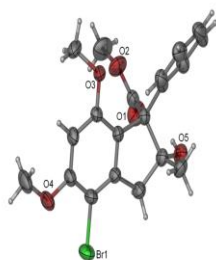


The excellent diastereoselectivity of this reaction may be attributed to the stereocontrol of the intramolecular aldol reaction step. The cis-fused transition state T_1 , T_2 is favored over the trans-fused one T_1' , T_2' , leading to the formation of the product with hydroxyl group and ester group having cis-configuration.

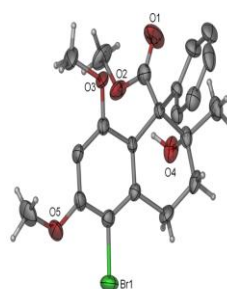
9. References:

- (1) Preparation of **S1**, see: Kumbe, T.; Maruyama, T.; Nakai, Y.; Oida, H.; Maruyama, T.; Abe, N. Nishiura, A.; Naki, H.; Toda, M. *Bioorg. Med. Chem.* **2012**, *20*, 3502.
- (2) Preparation of **S4**, see: Acton, III, J. F.; Black, R. M.; Jones, B.; Moller, D. E.; Colwell, L.; Doebber, T. W.; Macnaul, K. L.; Bergerb, J.; Wood, H. B. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 357.
- (3) Preparation of **1n**, see: Pharma, S. A. C.; Daria, Z.; Joanna, L.; Maciej, W.; Karolina, D.; Abdellah, Y.; Krzysztof, D.; Monika, L.-P.; Paulina, G.; Aleksandra, S. *WO2014/141015 A1*, **2014**.
- (4) Preparation of **1n**, see: Corrie, J. E. T. *Tetrahedron* **1998**, *54*, 5407.
- (5) Preparation of **1q**, see: Conrad, J. C.; Kong, J.; Laforteza, B. N.; Macmillan, D. W. C. *J. Am. Chem. Soc.* **2009**, *131*, 11640.

10. Crystal structures of 7aa and 8na.



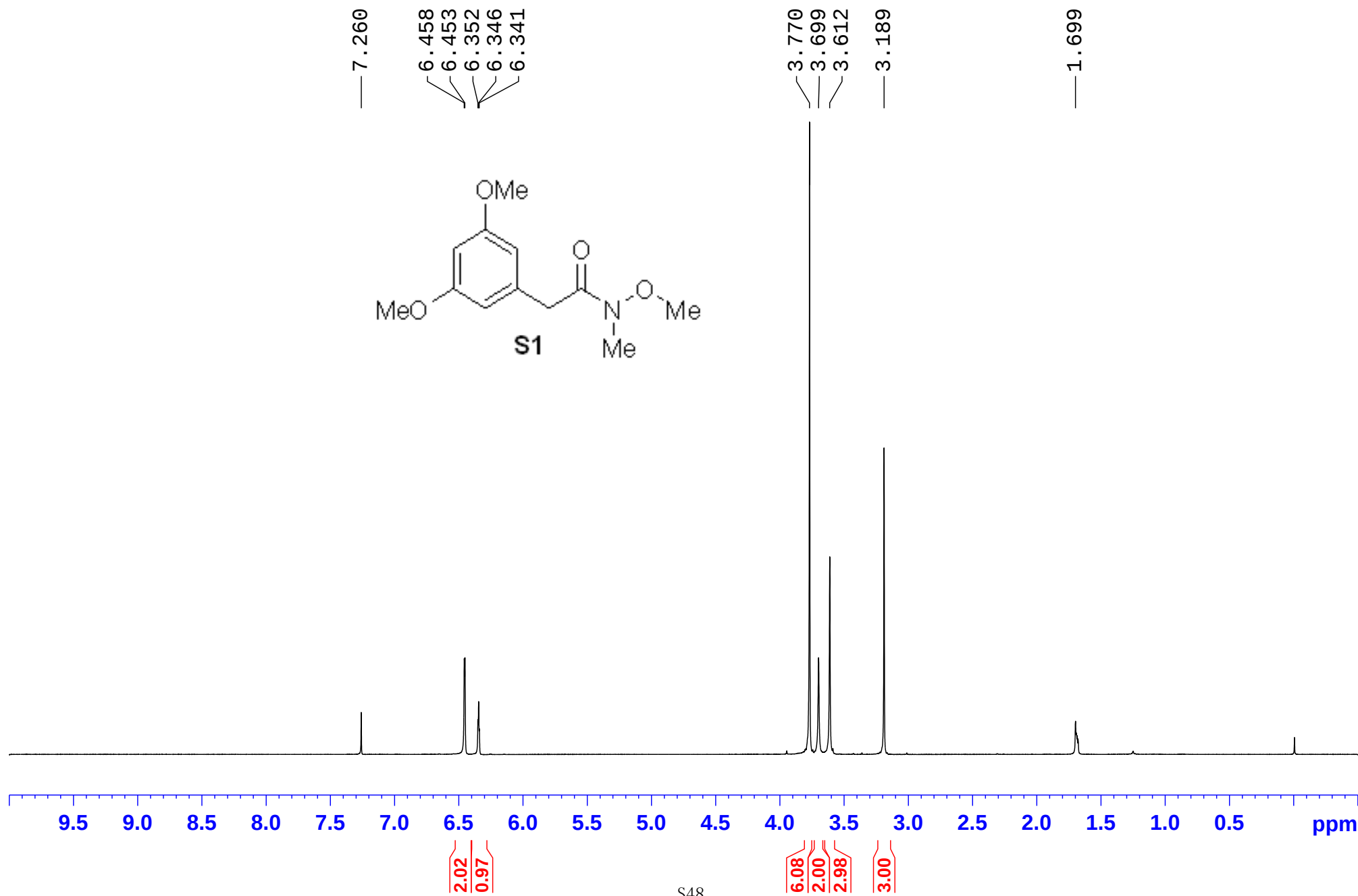
7aa



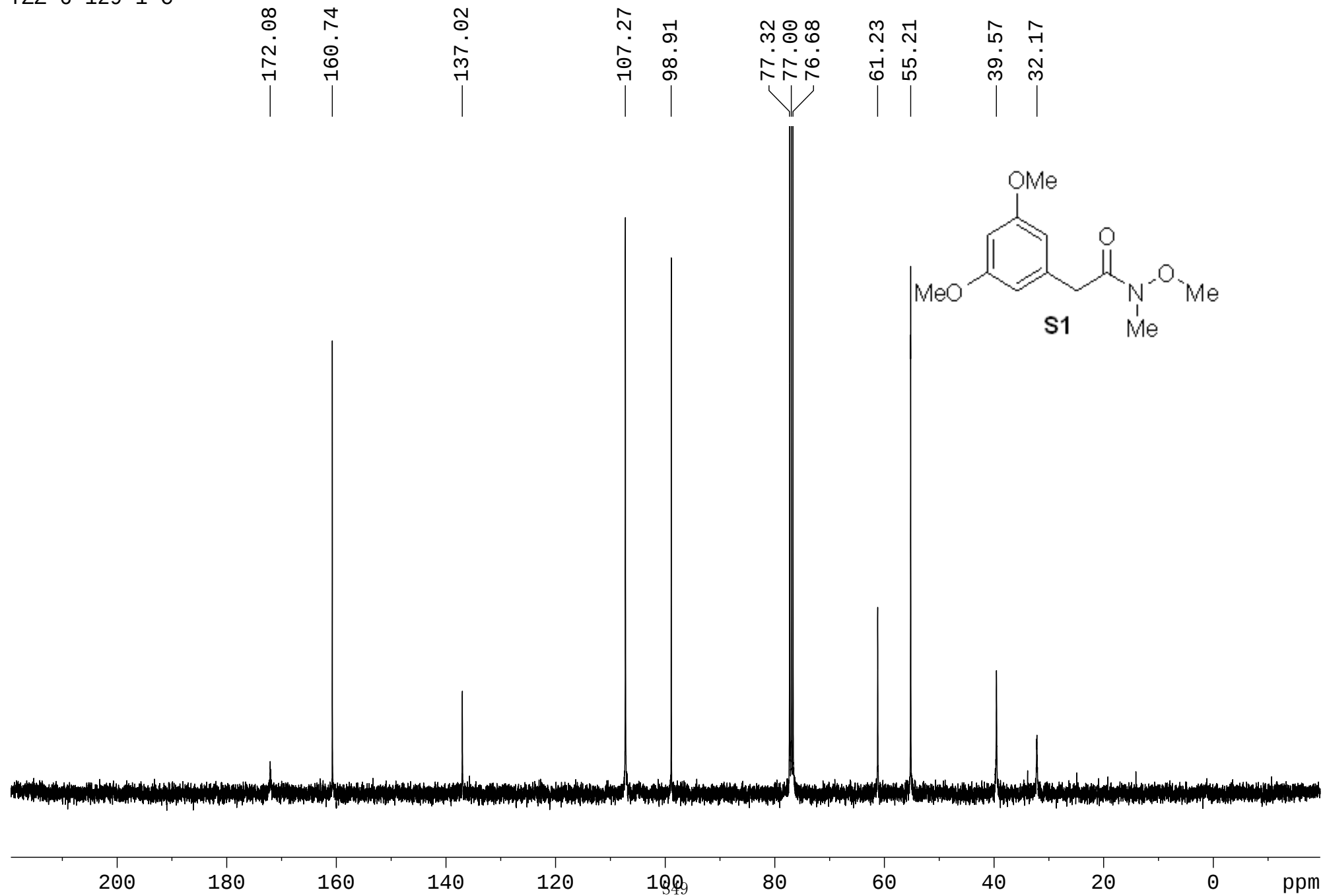
8na

11. NMR Spectra of new compounds

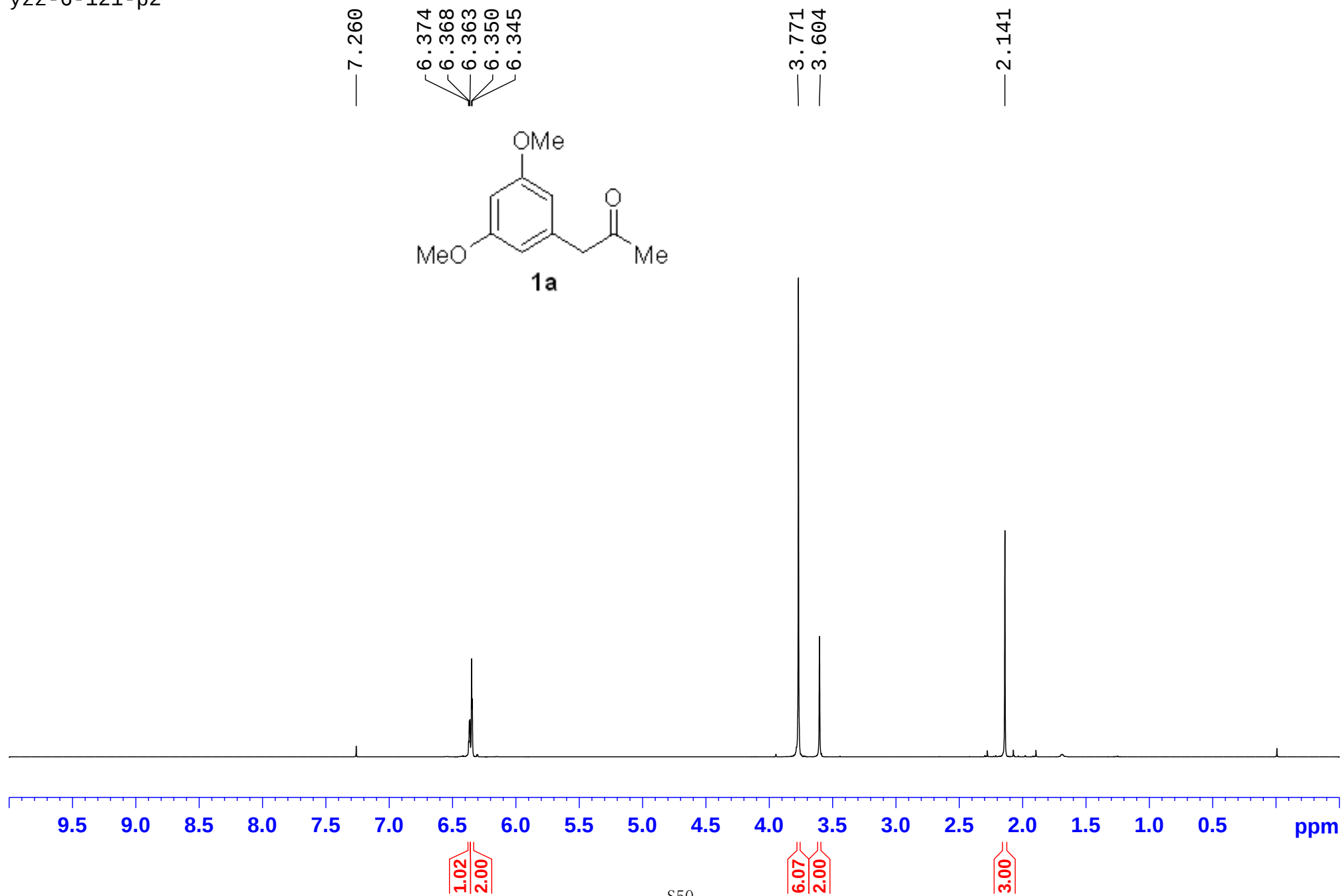
yyy-7-126-1



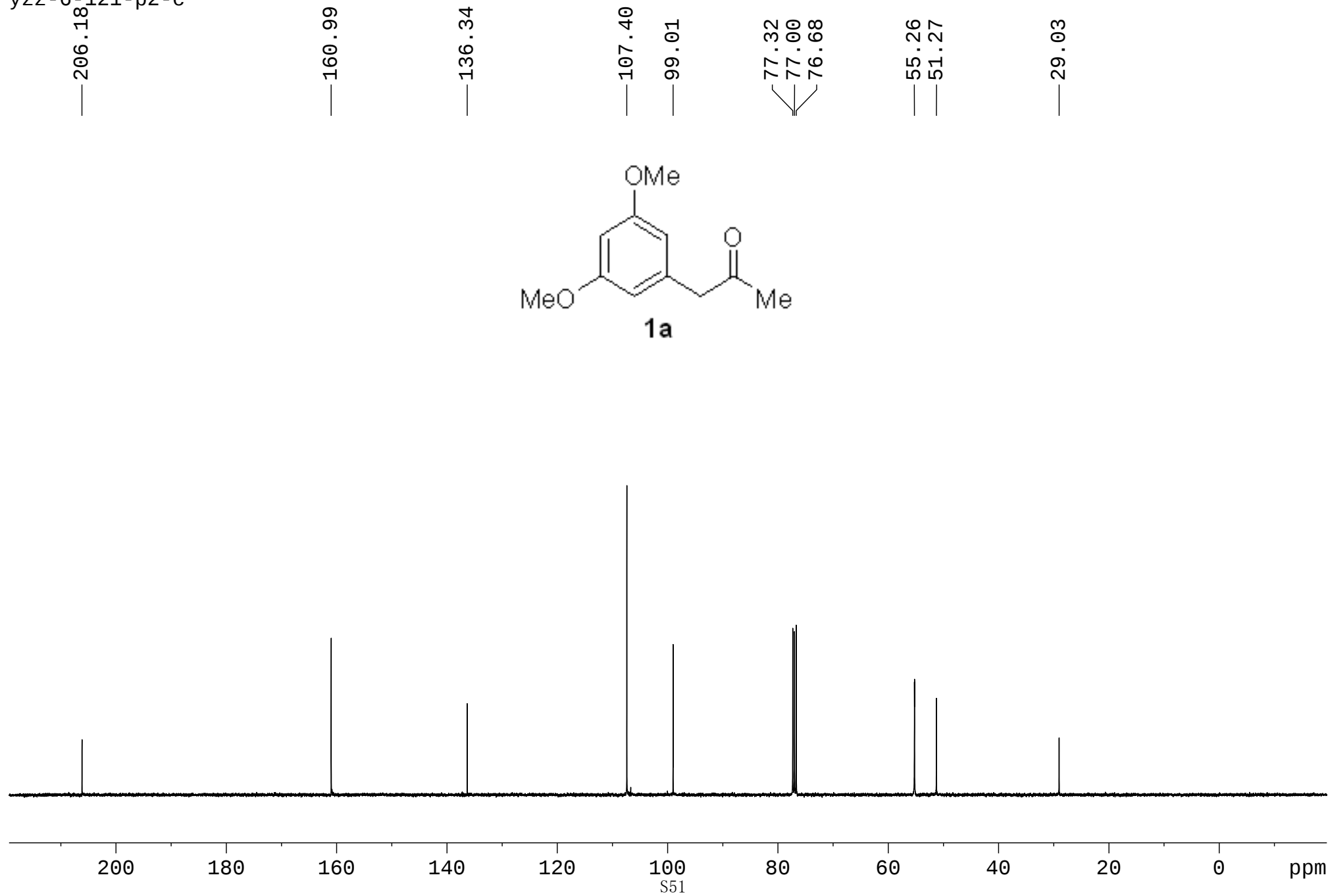
YZZ-6-129-1-C

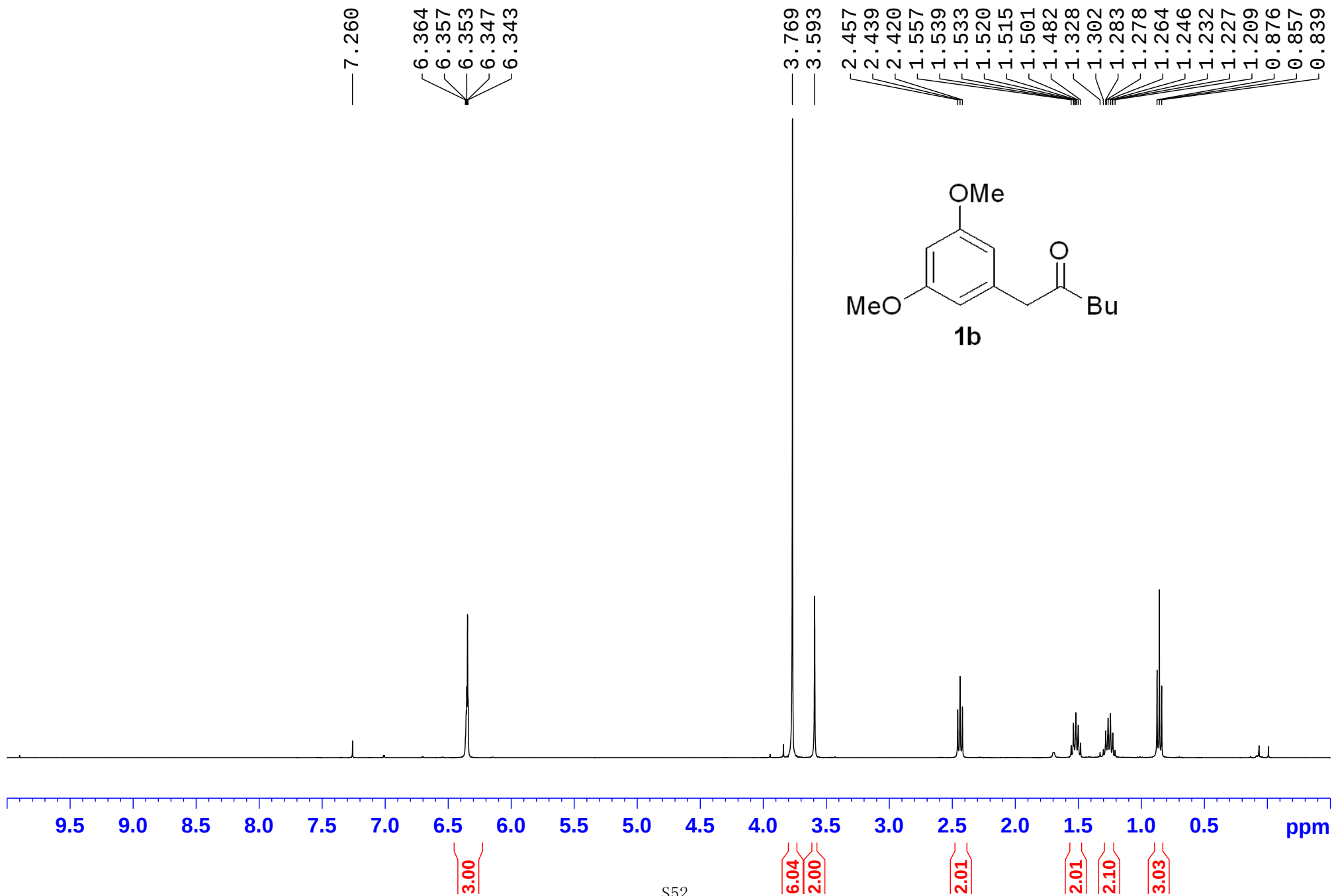


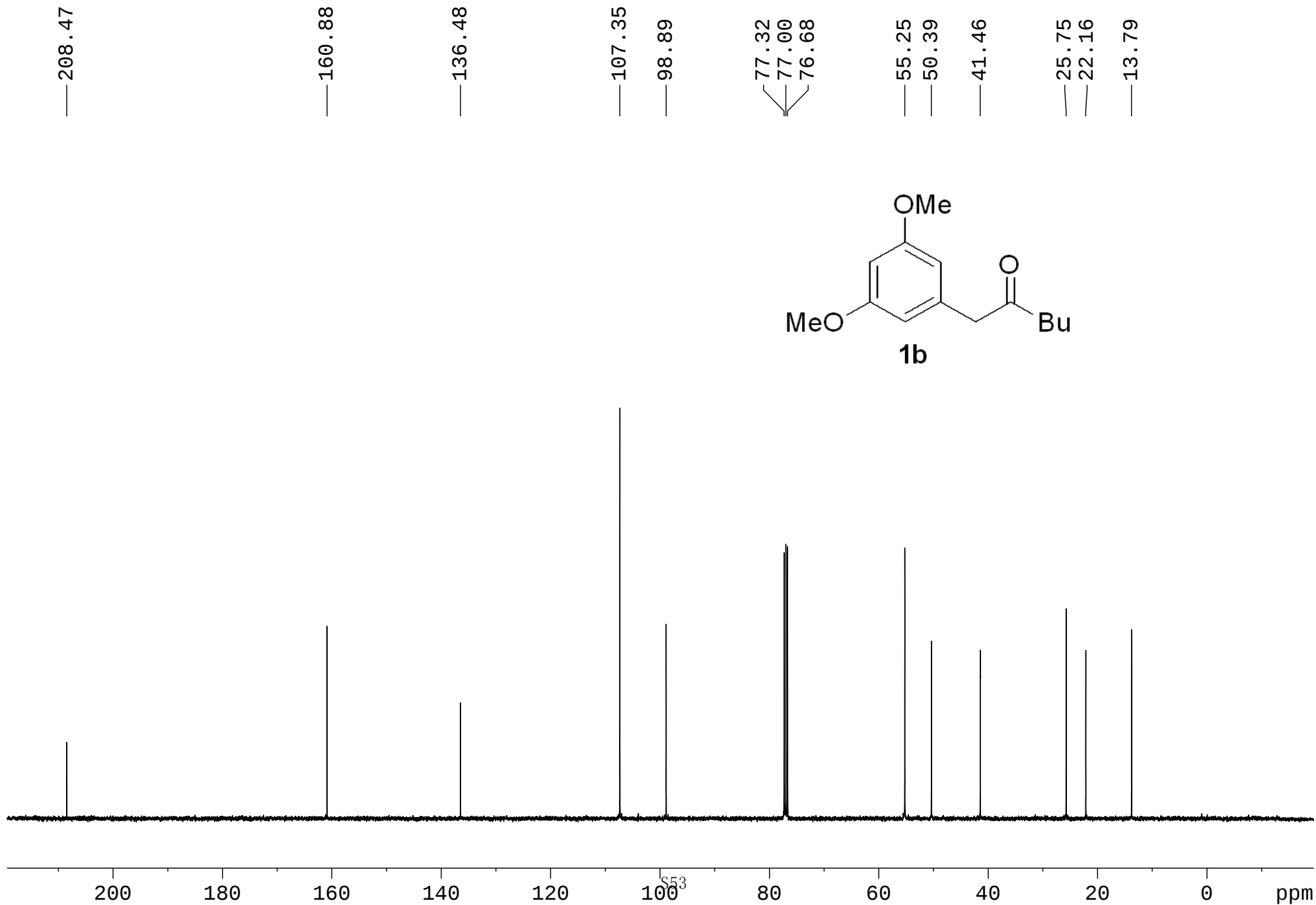
yyy-6-121-p2



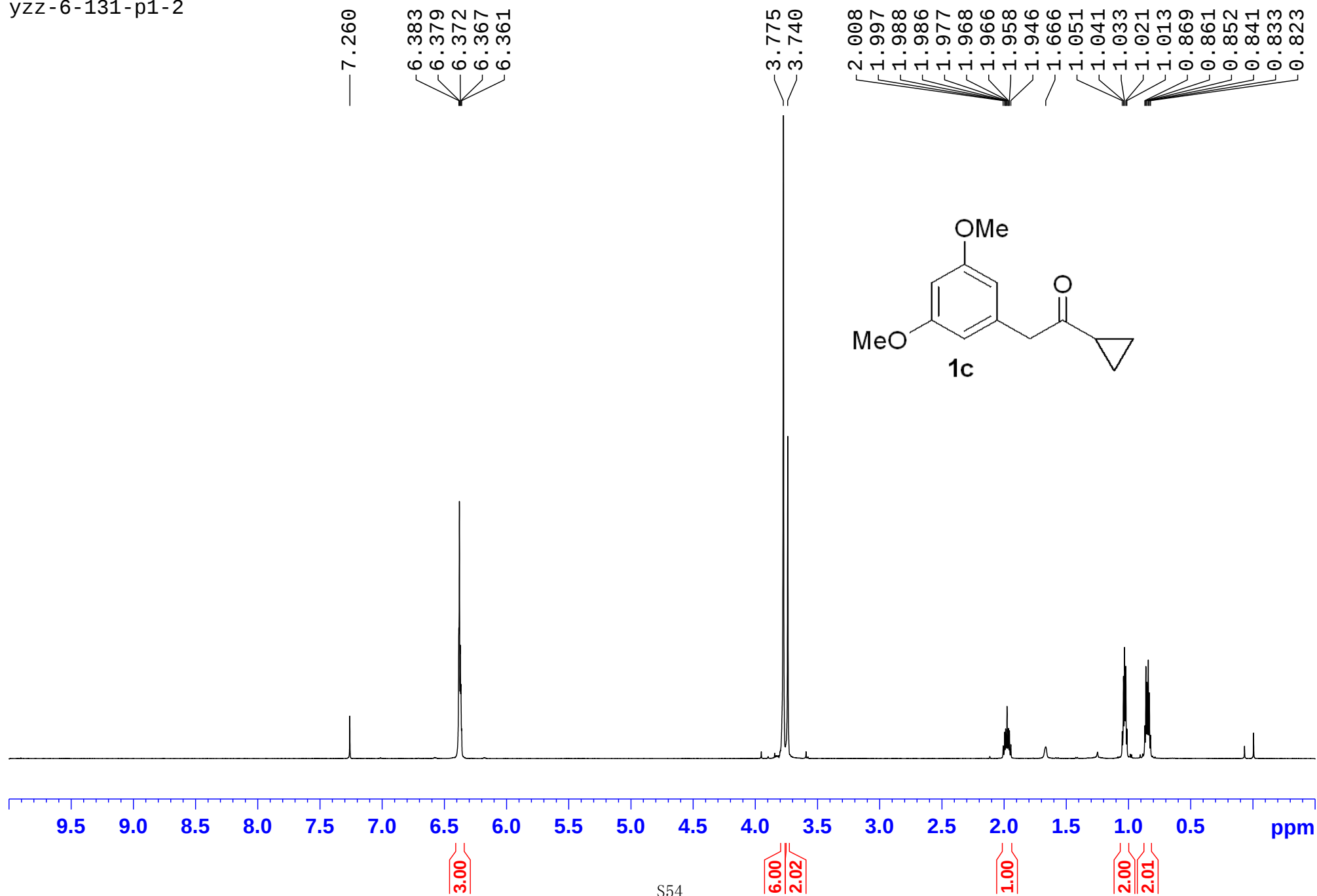
yyy-6-121-p2-c



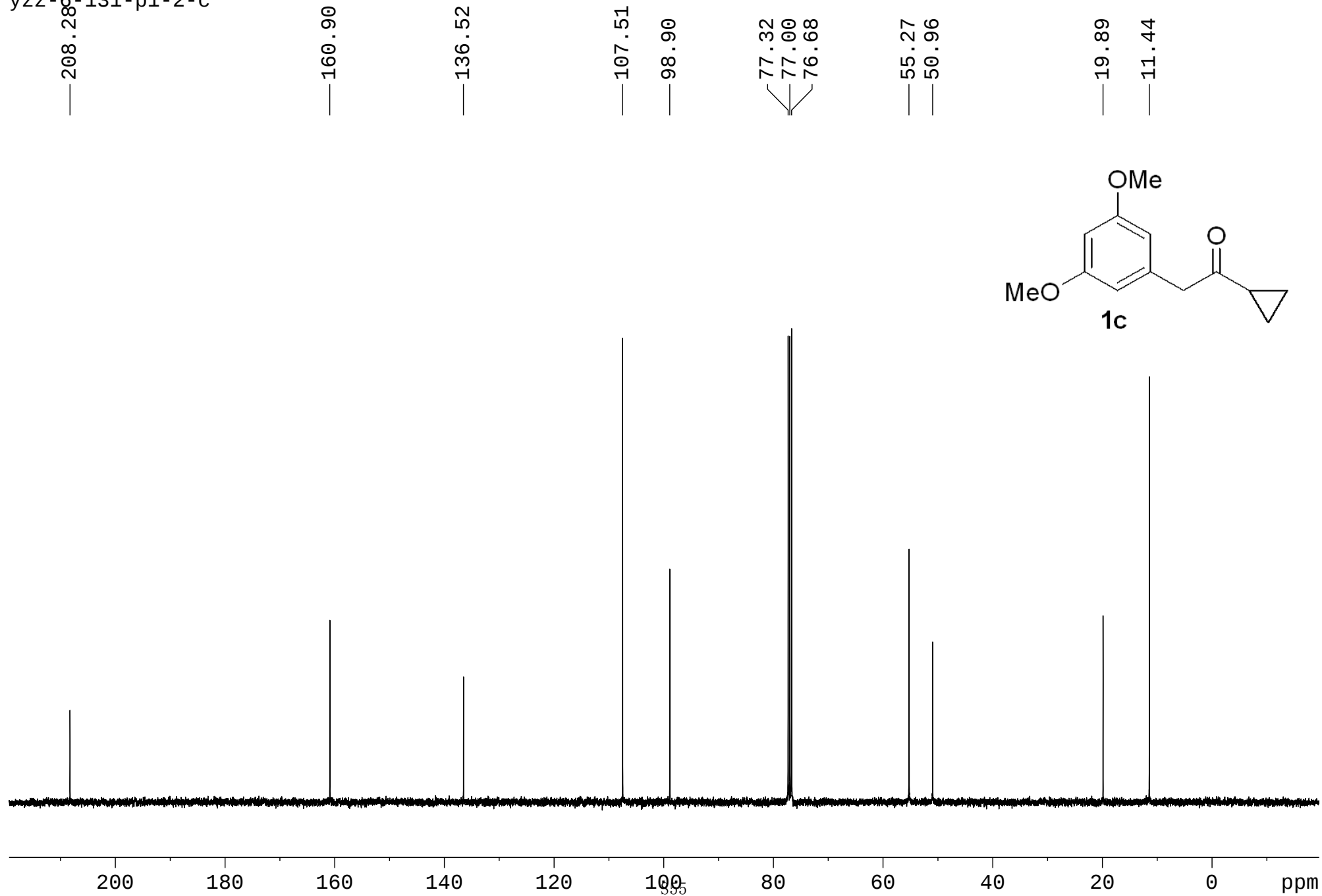




yyy-6-131-p1-2



yzzz-6-131-p1-2-c



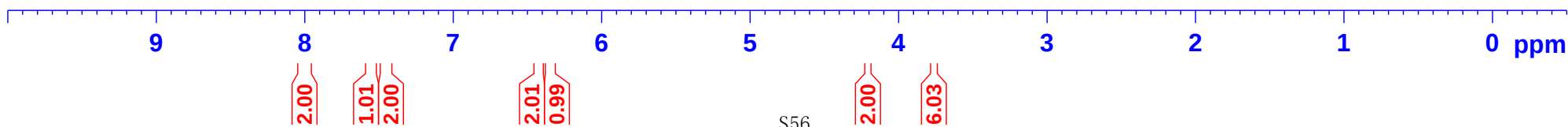
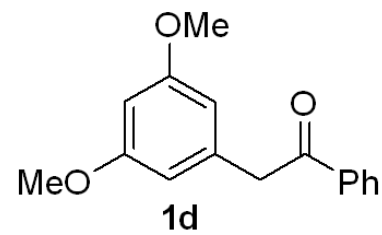
yyy-7-013-1

8.013
7.995
7.992
7.570
7.567
7.552
7.547
7.537
7.534
7.531
7.471
7.451
7.433
7.260
6.428
6.423
6.357
6.352
6.346

4.207

3.762

1.572



yz-z-7-012-p2-2-c

—197.40

—160.92

136.66

136.54

133.12

128.59

128.58

—107.49

—98.92

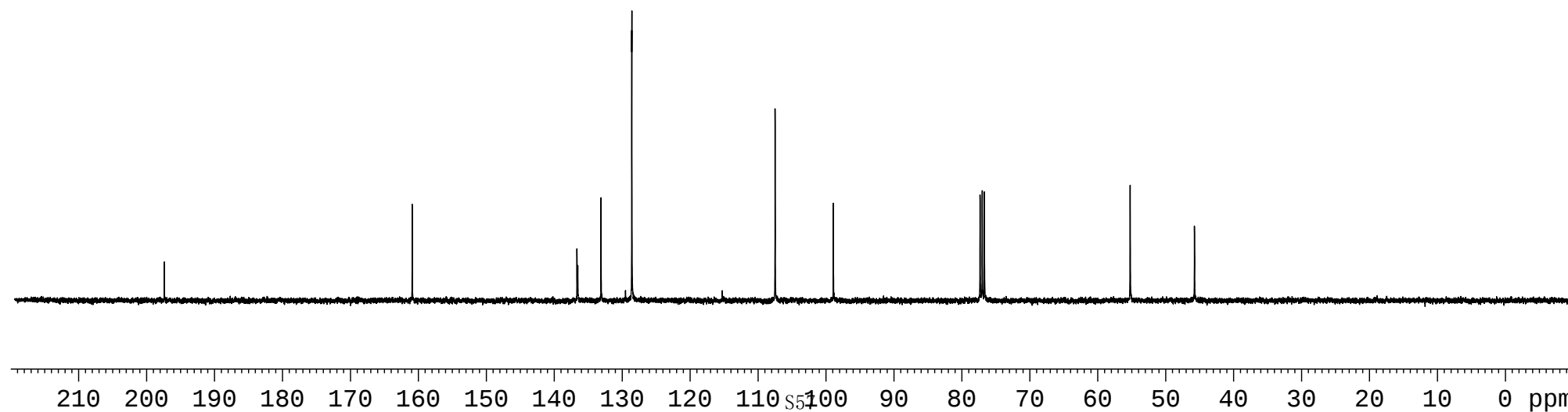
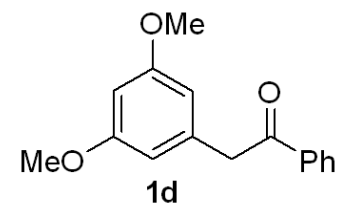
77.32

77.00

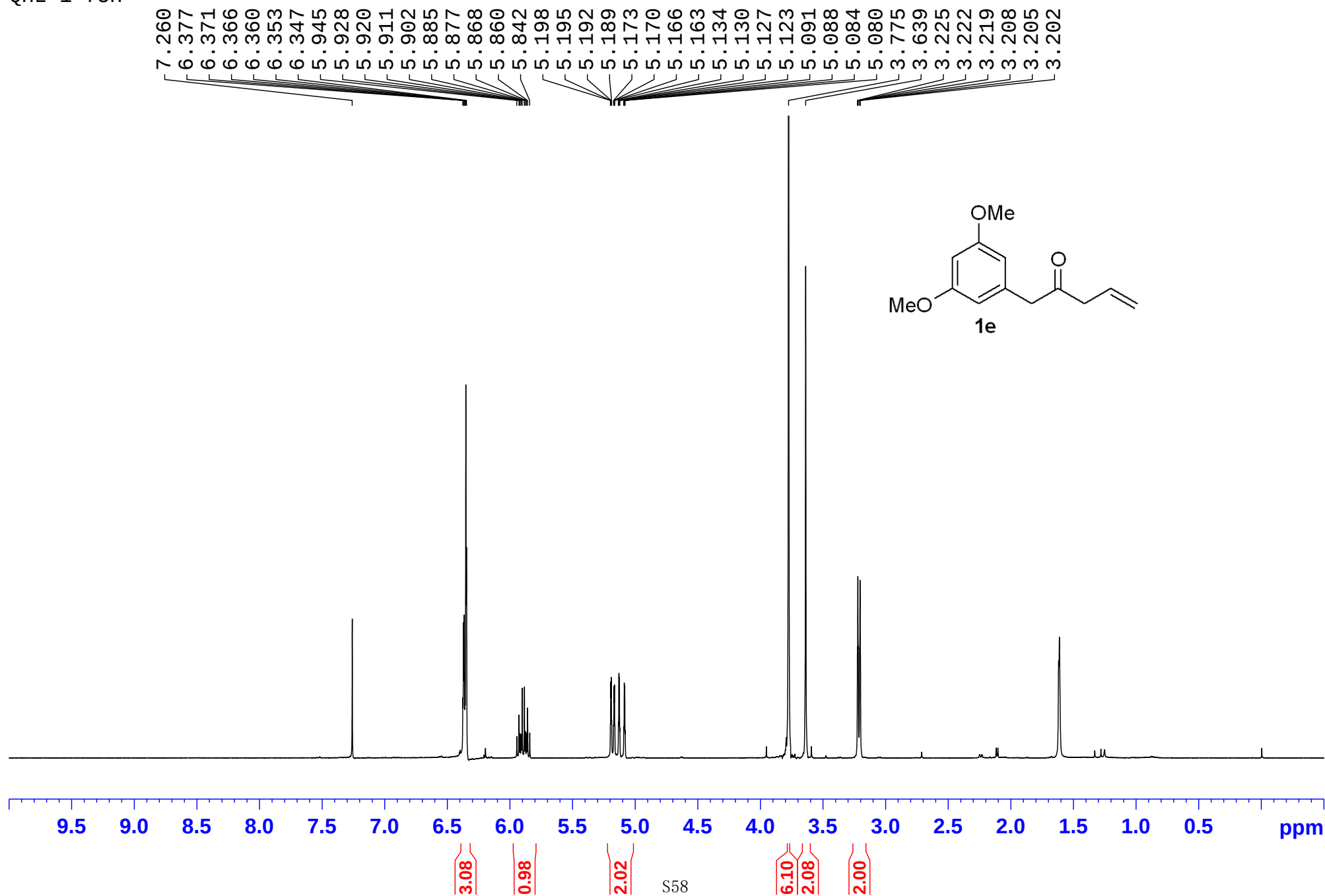
76.68

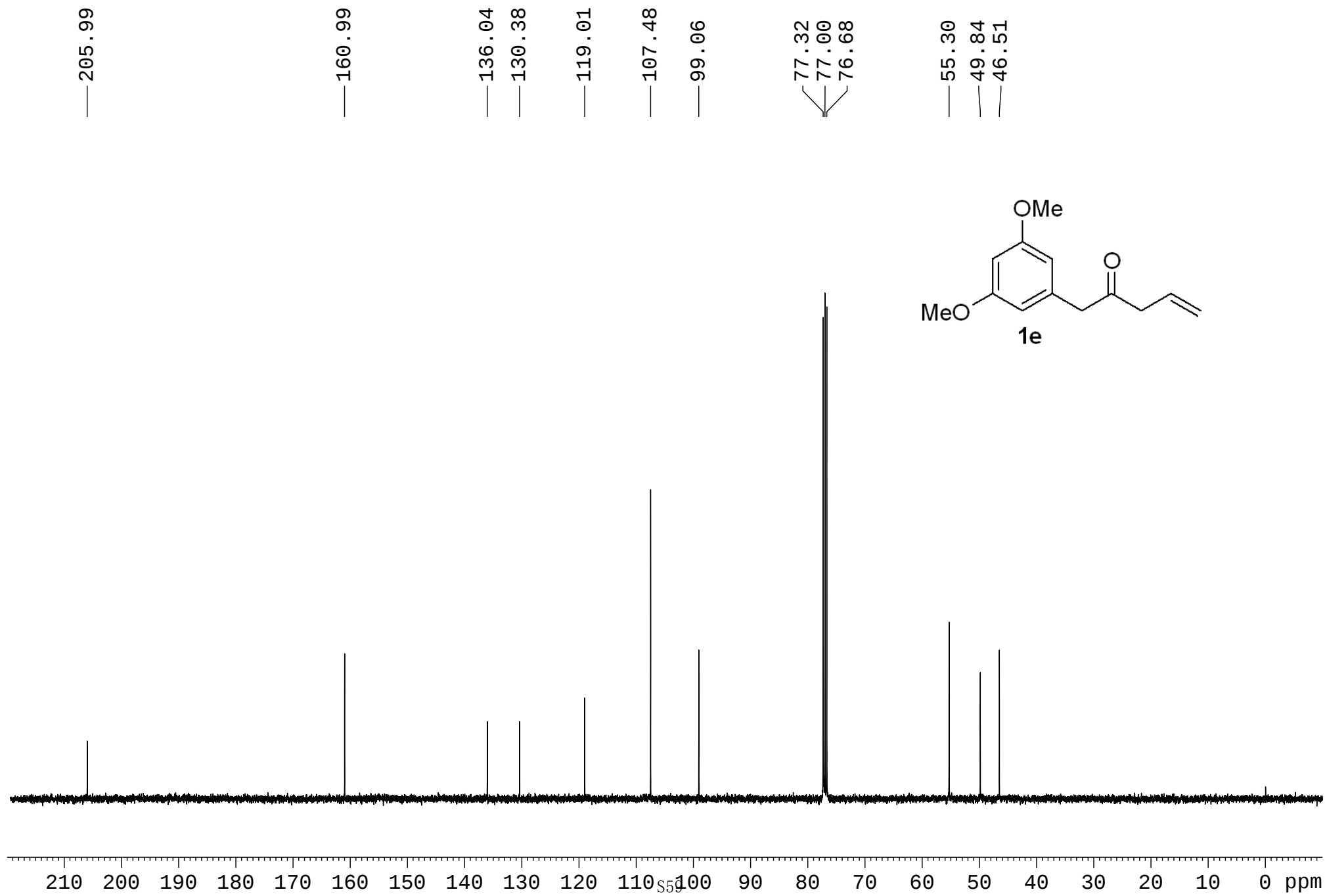
—55.23

—45.76

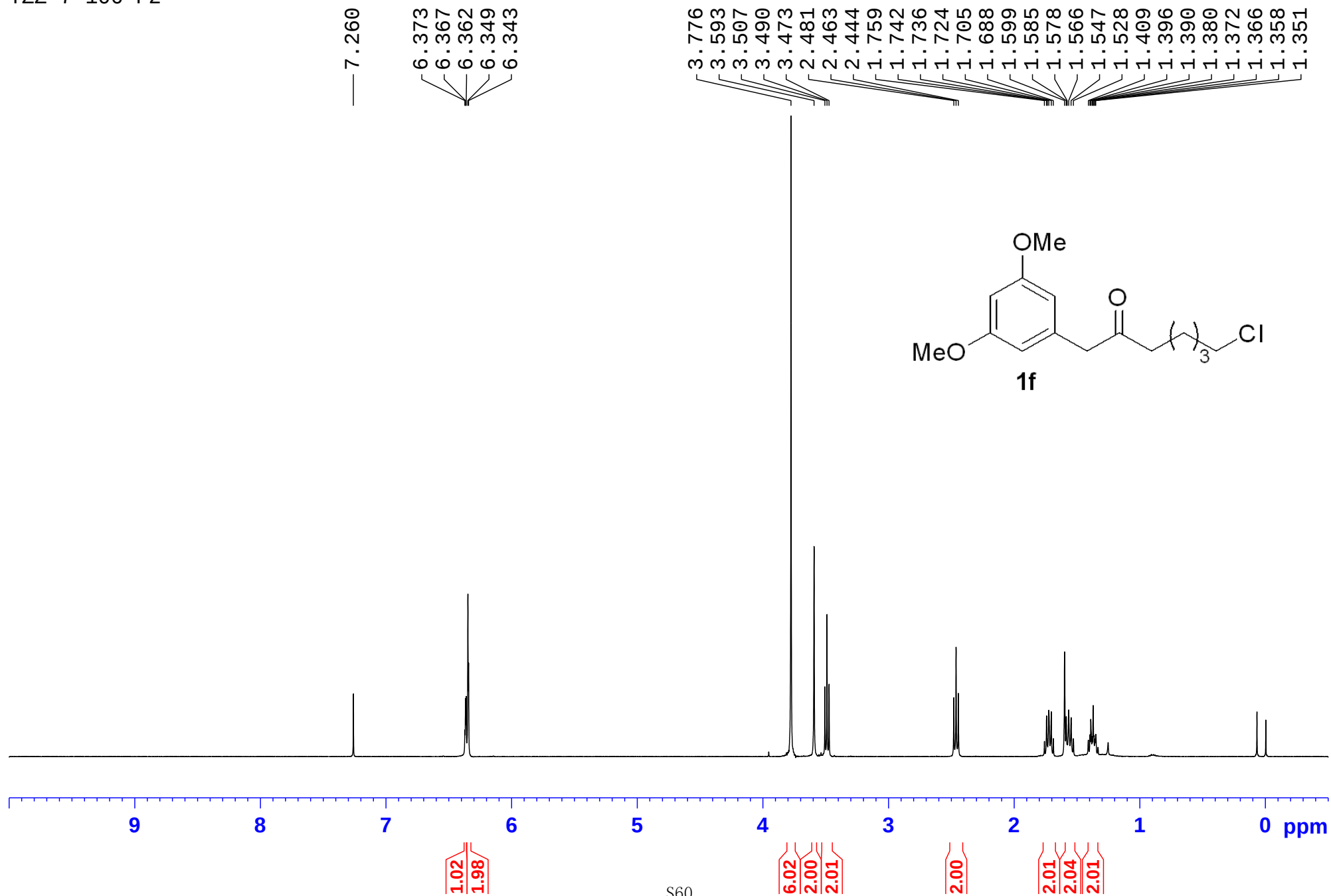


QHL-1-75H

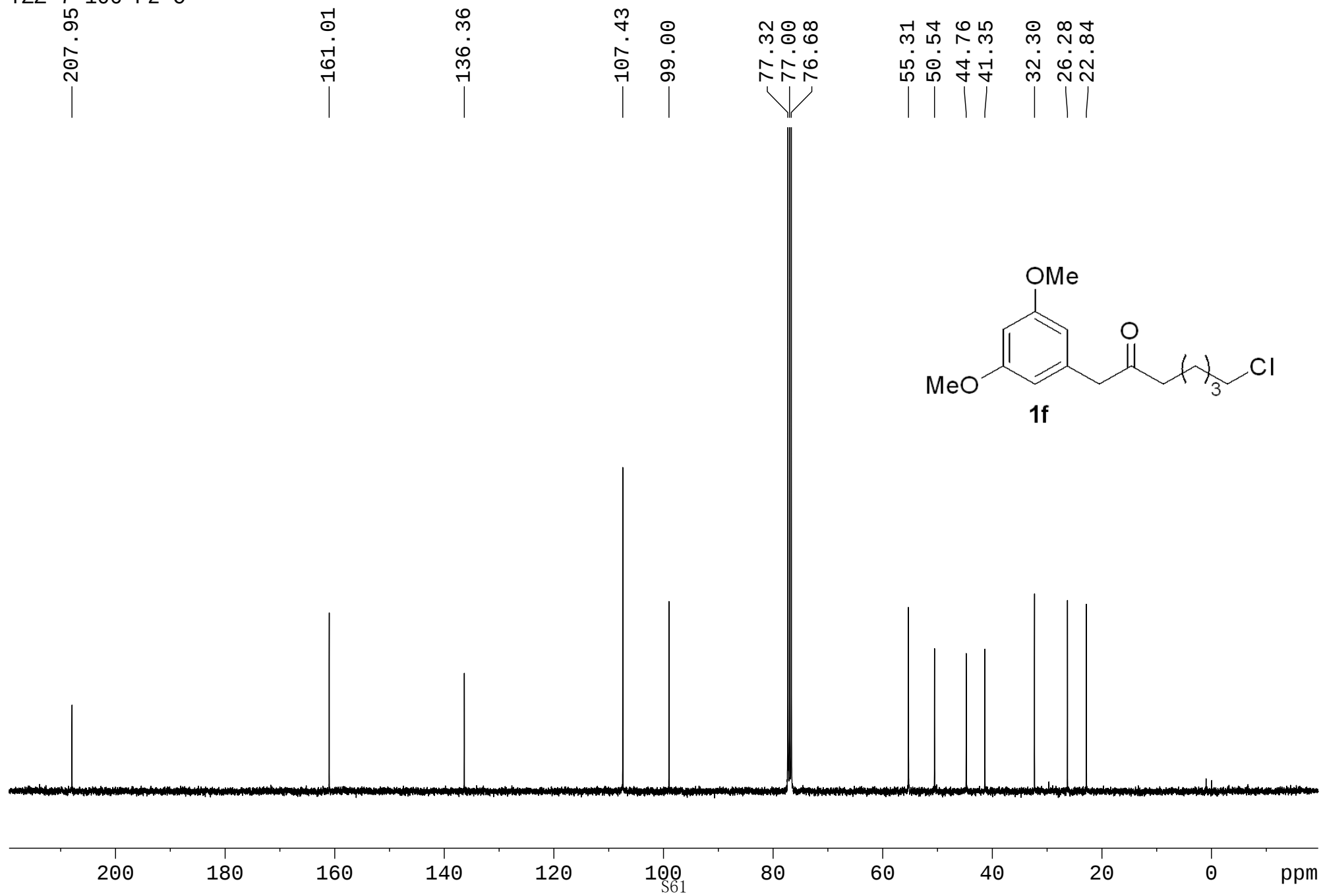




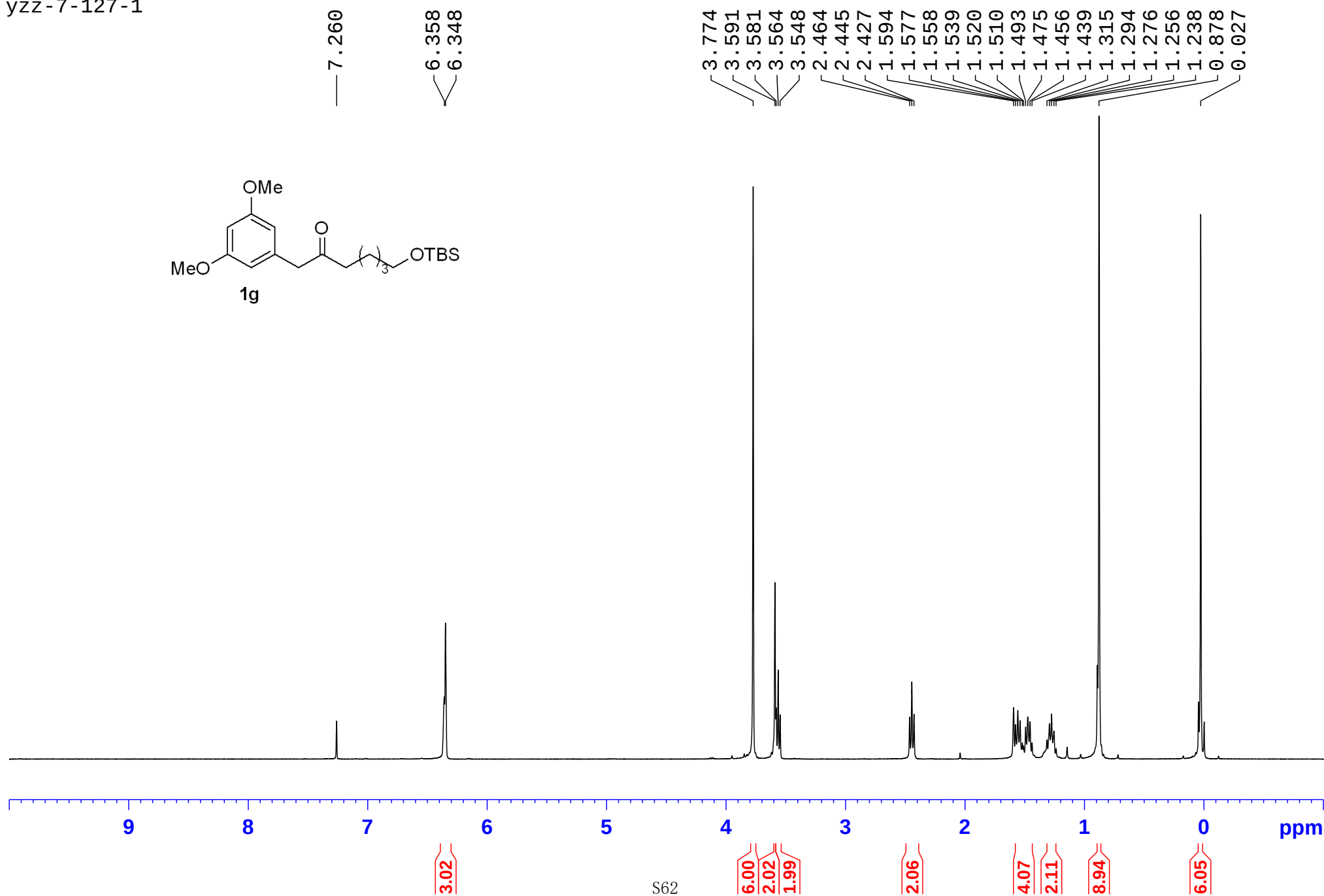
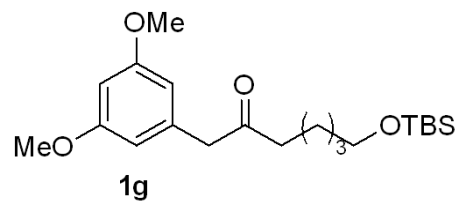
YZZ-7-106-P2



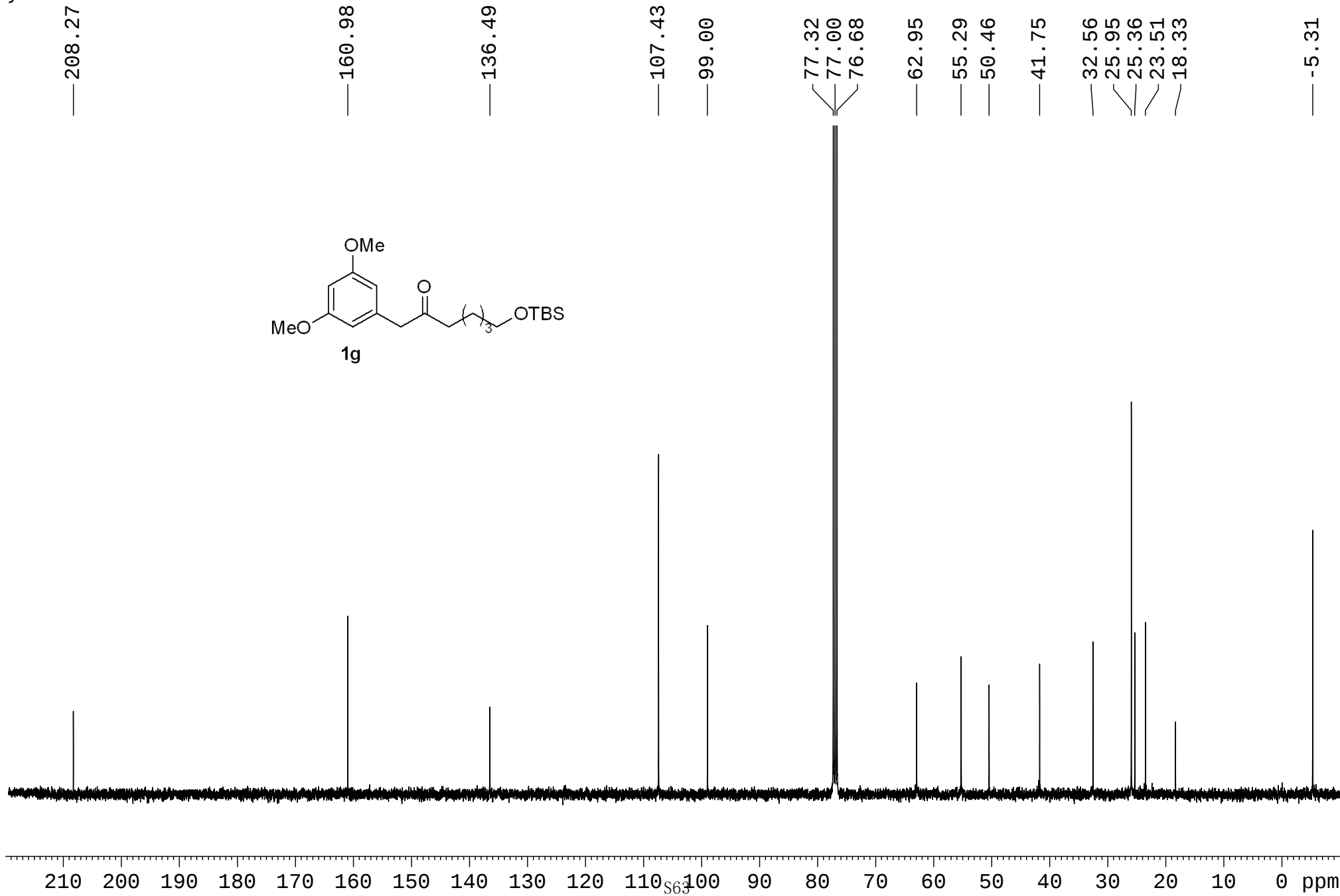
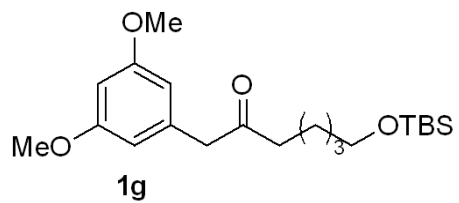
YZZ-7-106-P2-C



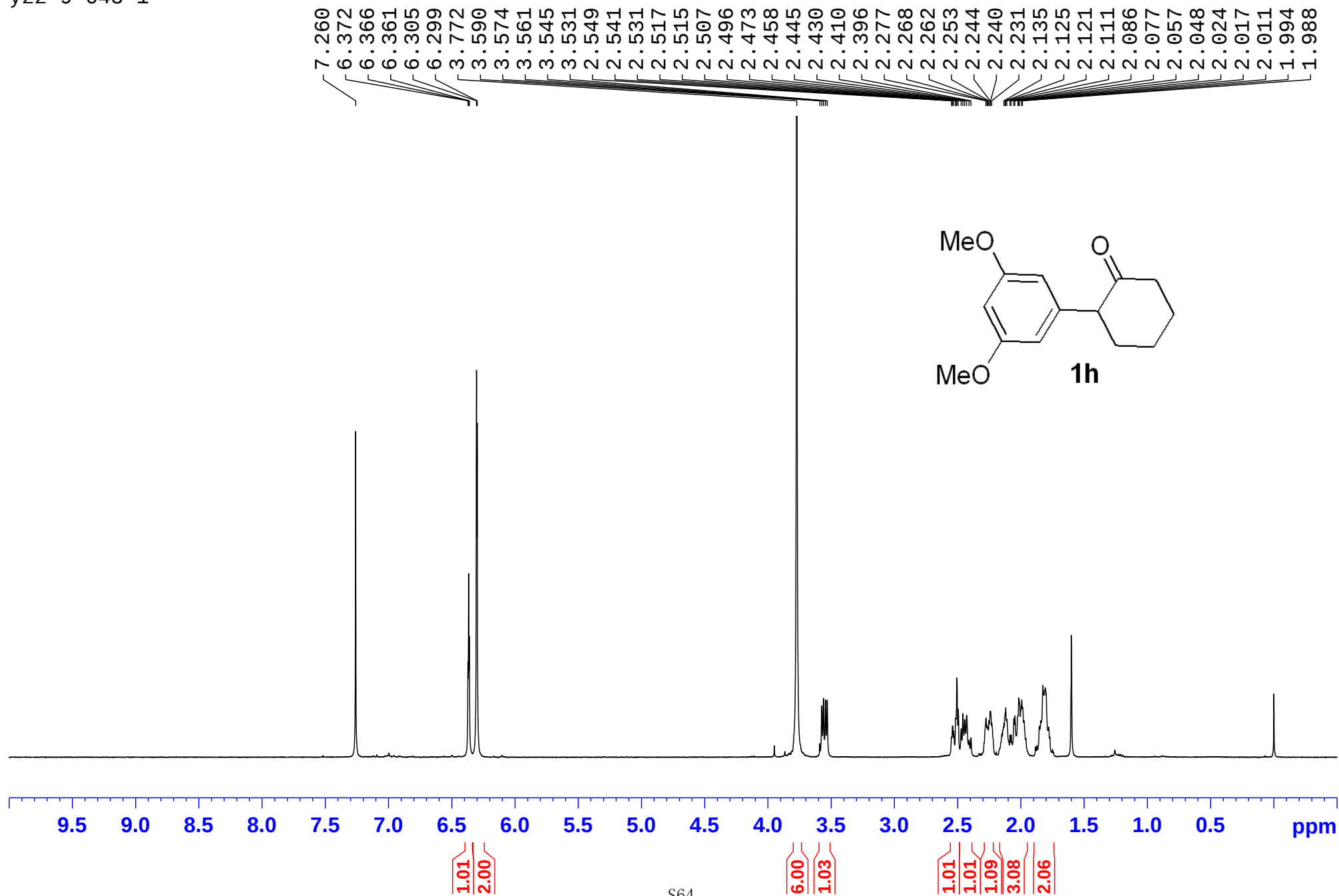
yyy-7-127-1



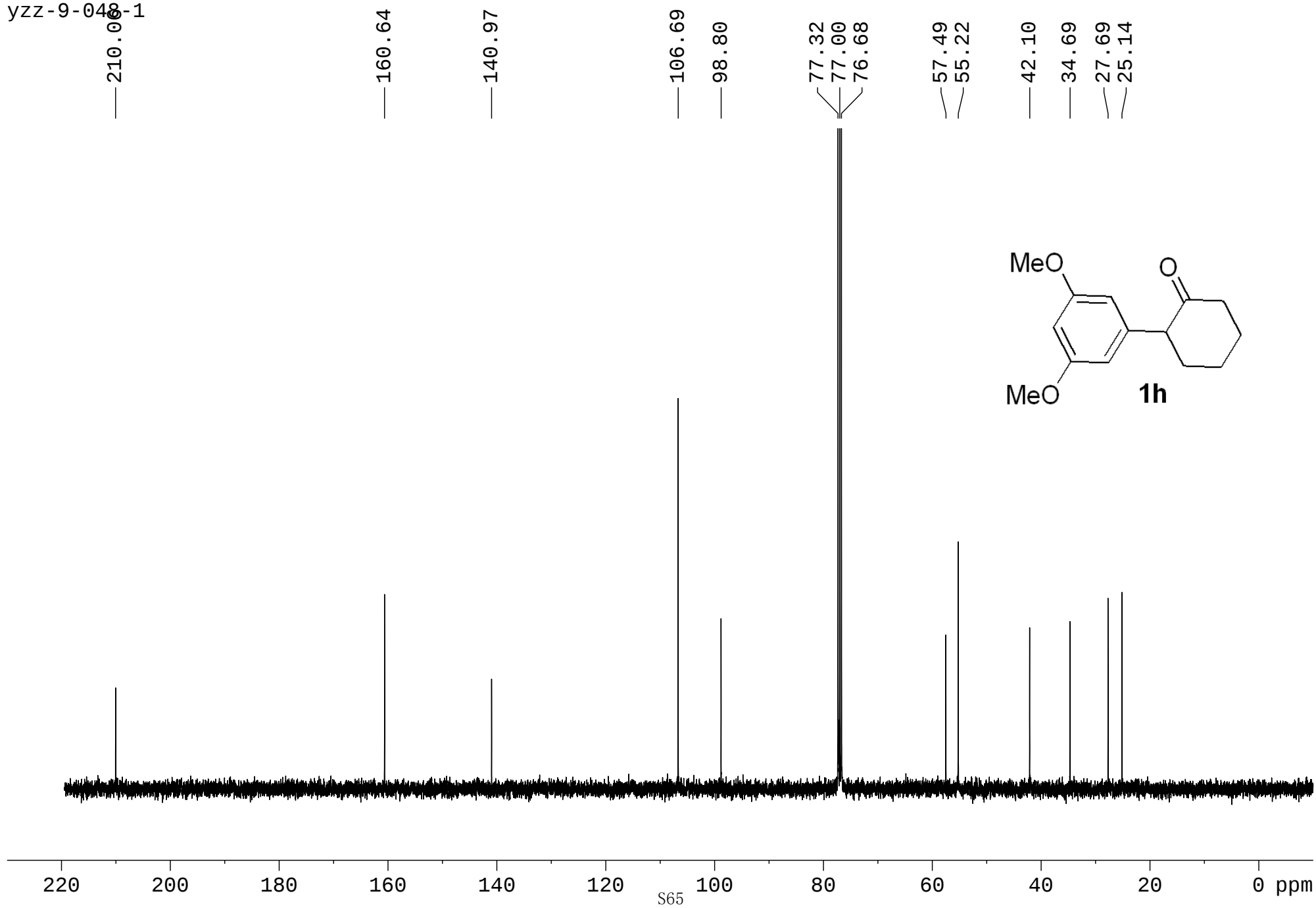
yyy-7-127-1-c



yyy-9-048-1



yyy-9-048-1

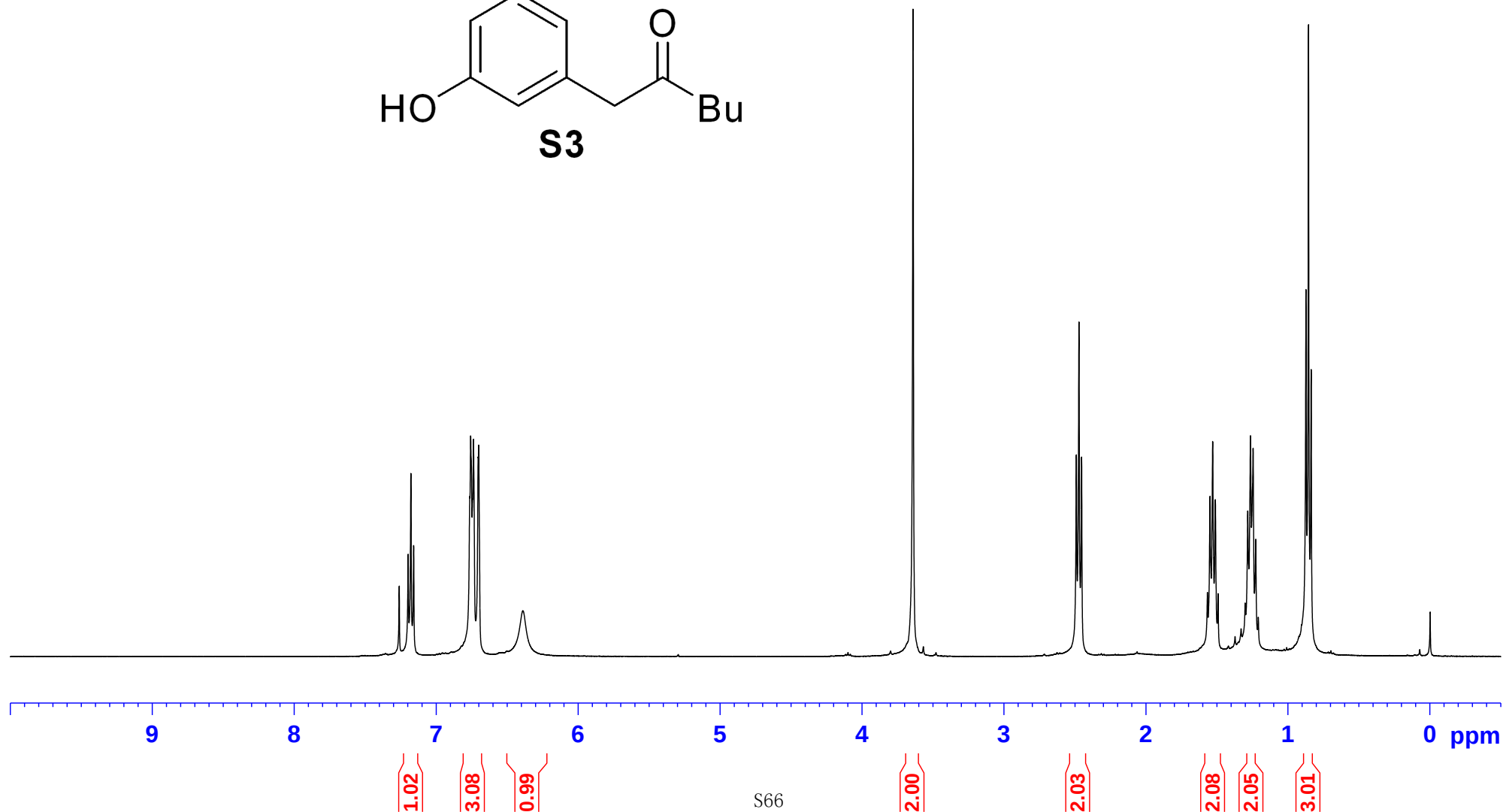
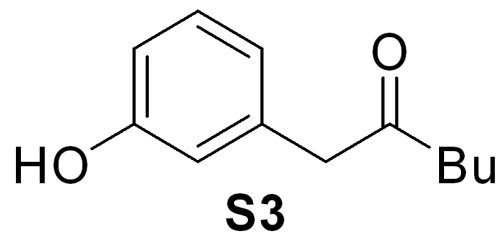


yyy-8-075-1

7.260
7.197
7.178
7.158
6.763
6.757
6.742
6.737
6.704
6.700
6.388

3.641

2.491
2.472
2.454
1.567
1.549
1.530
1.512
1.492
1.301
1.283
1.264
1.245
1.227
1.209
0.873
0.855
0.837



yyy-8-075-1-c

— 210.36

— 156.21

— 135.52

— 129.91

— 121.48

— 116.19

— 114.27

77.32

77.00

76.68

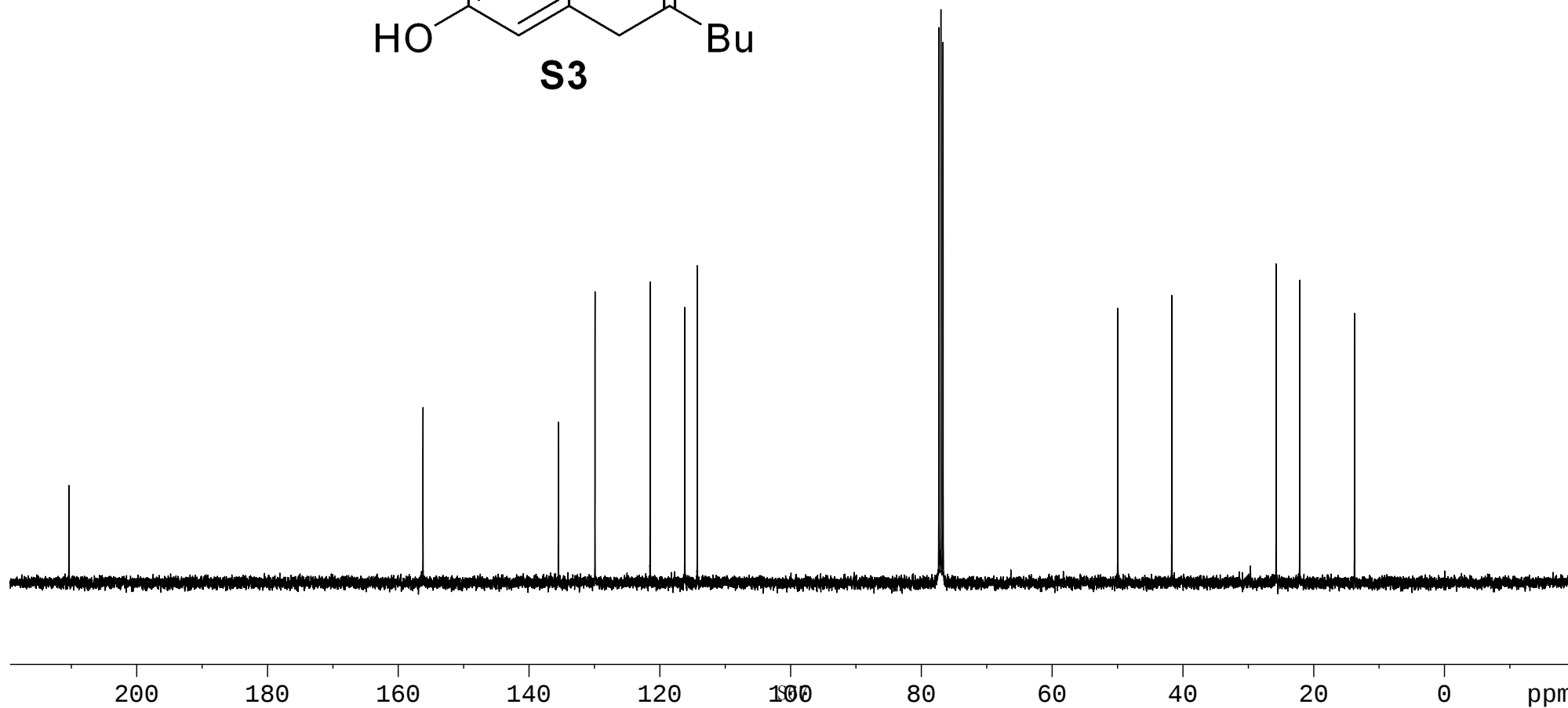
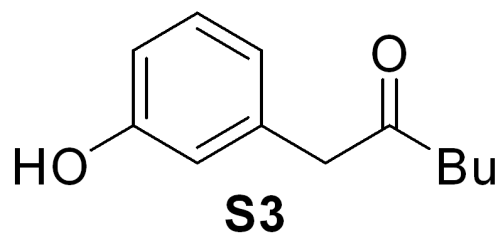
— 49.96

— 41.71

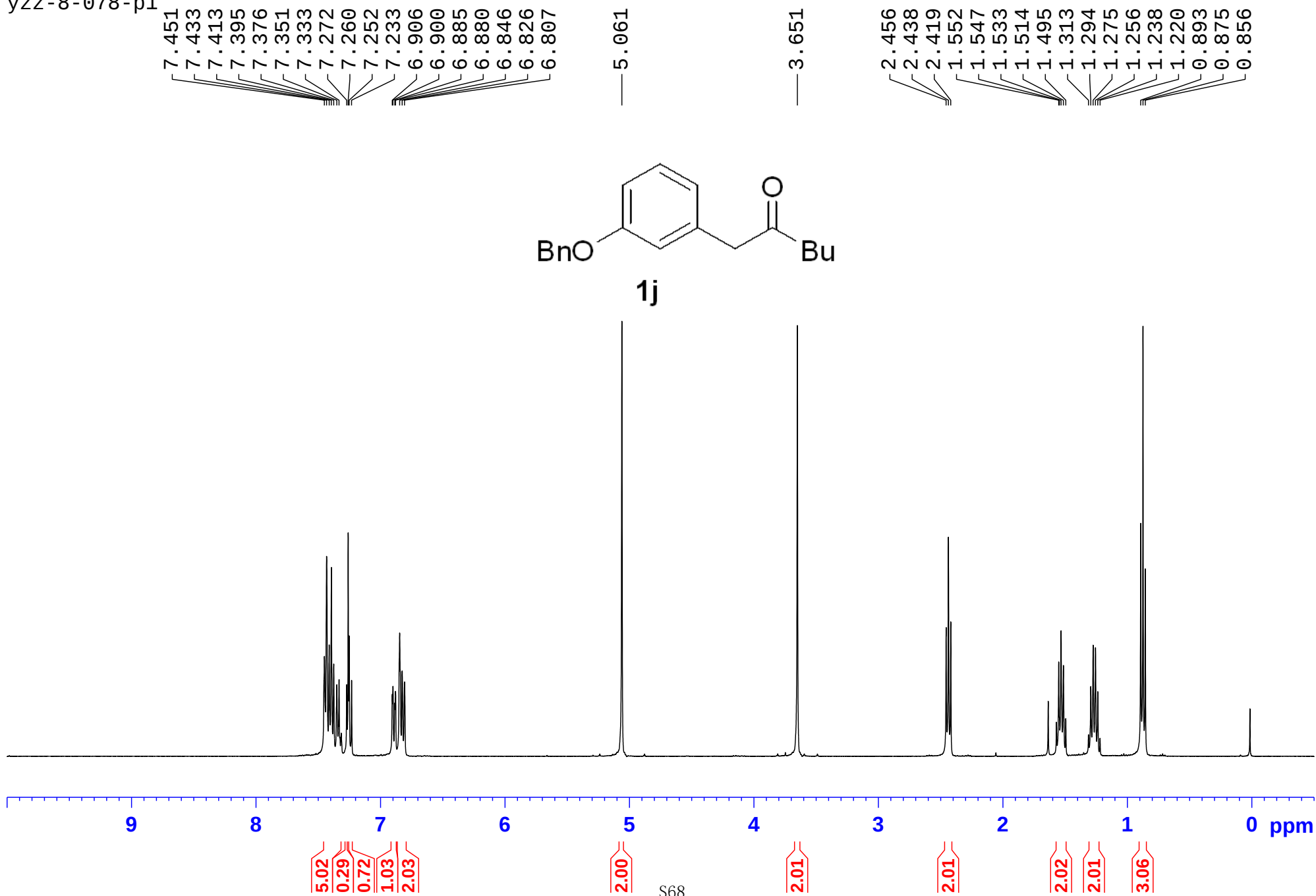
— 25.75

— 22.14

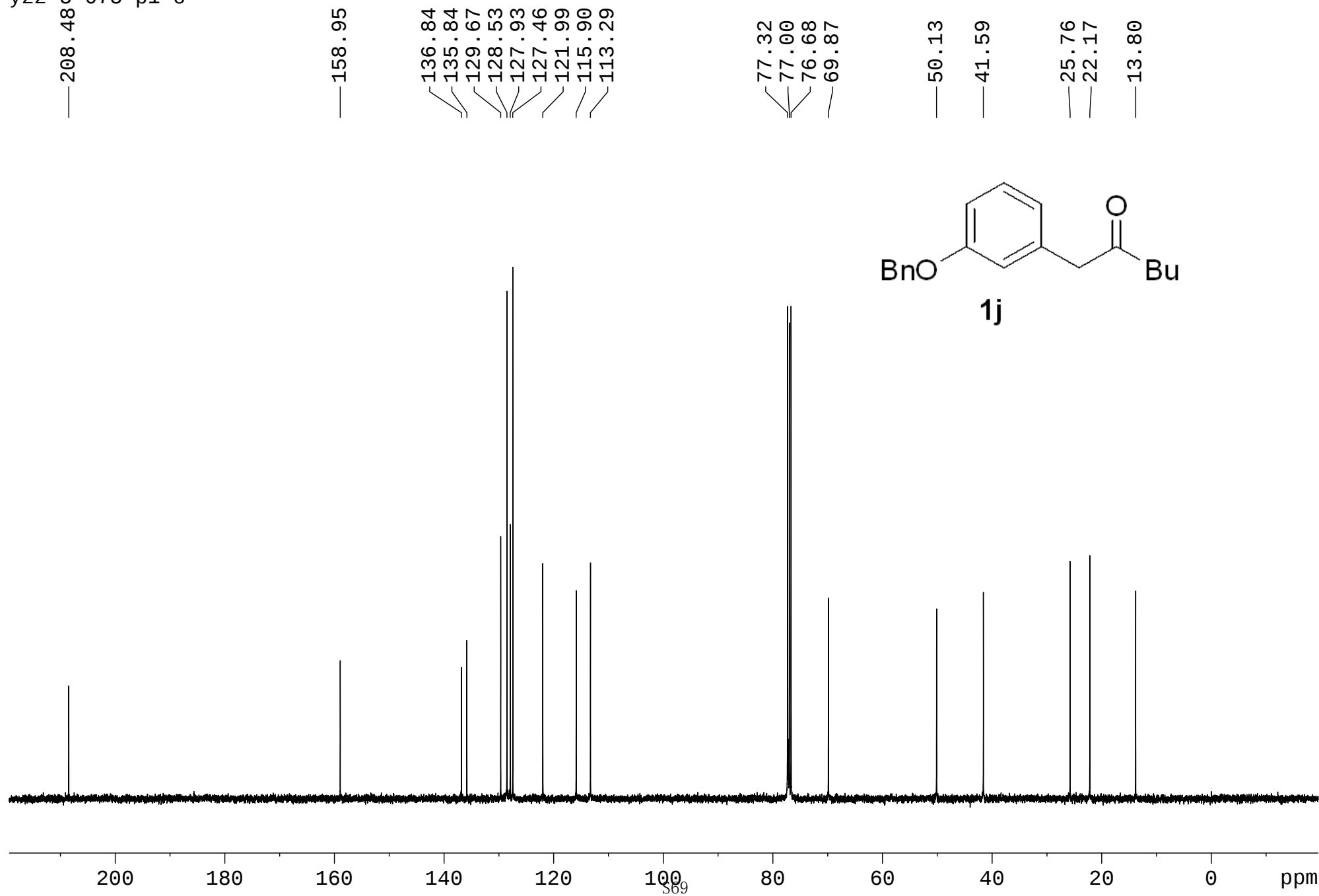
— 13.76



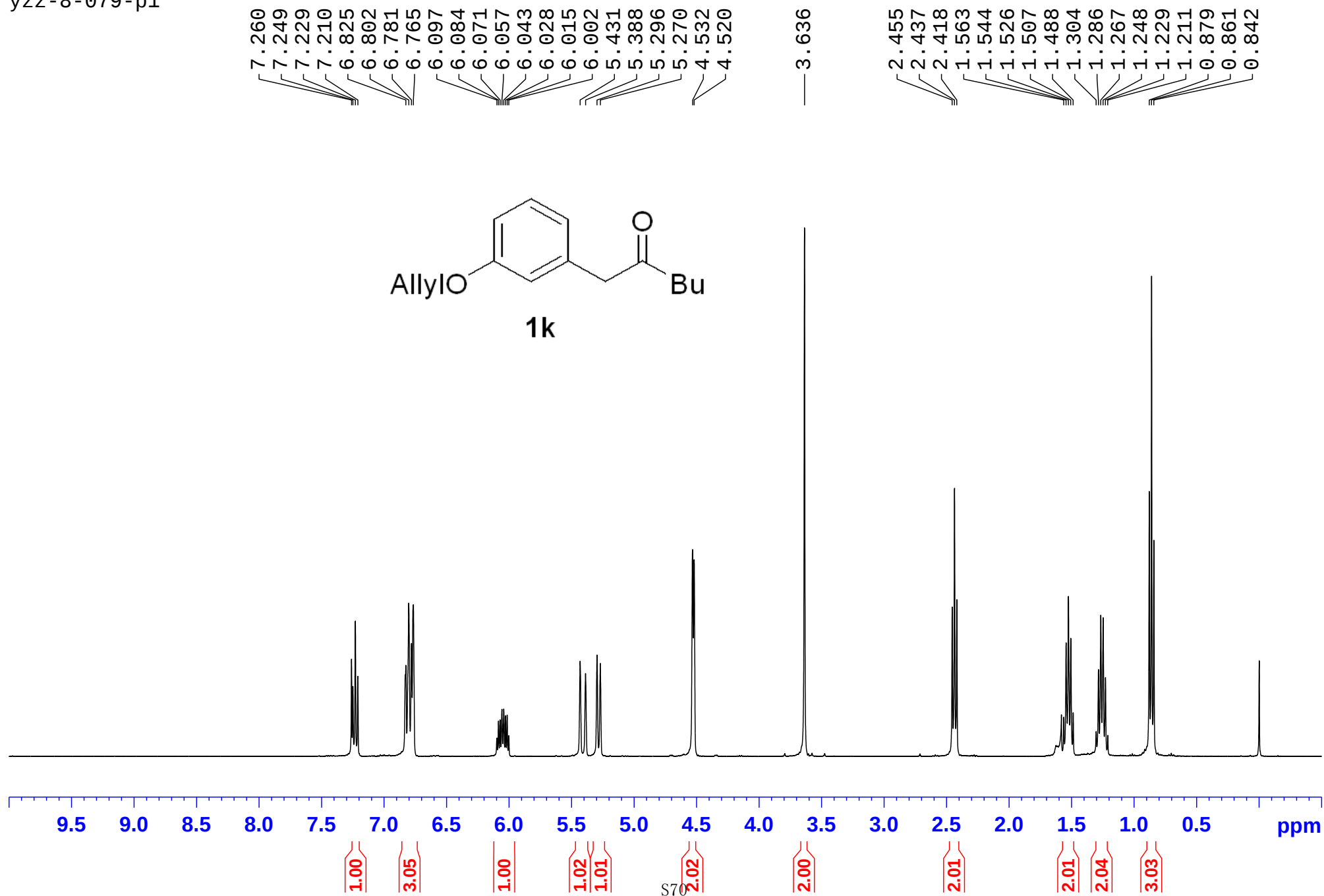
yyy-8-078-p1



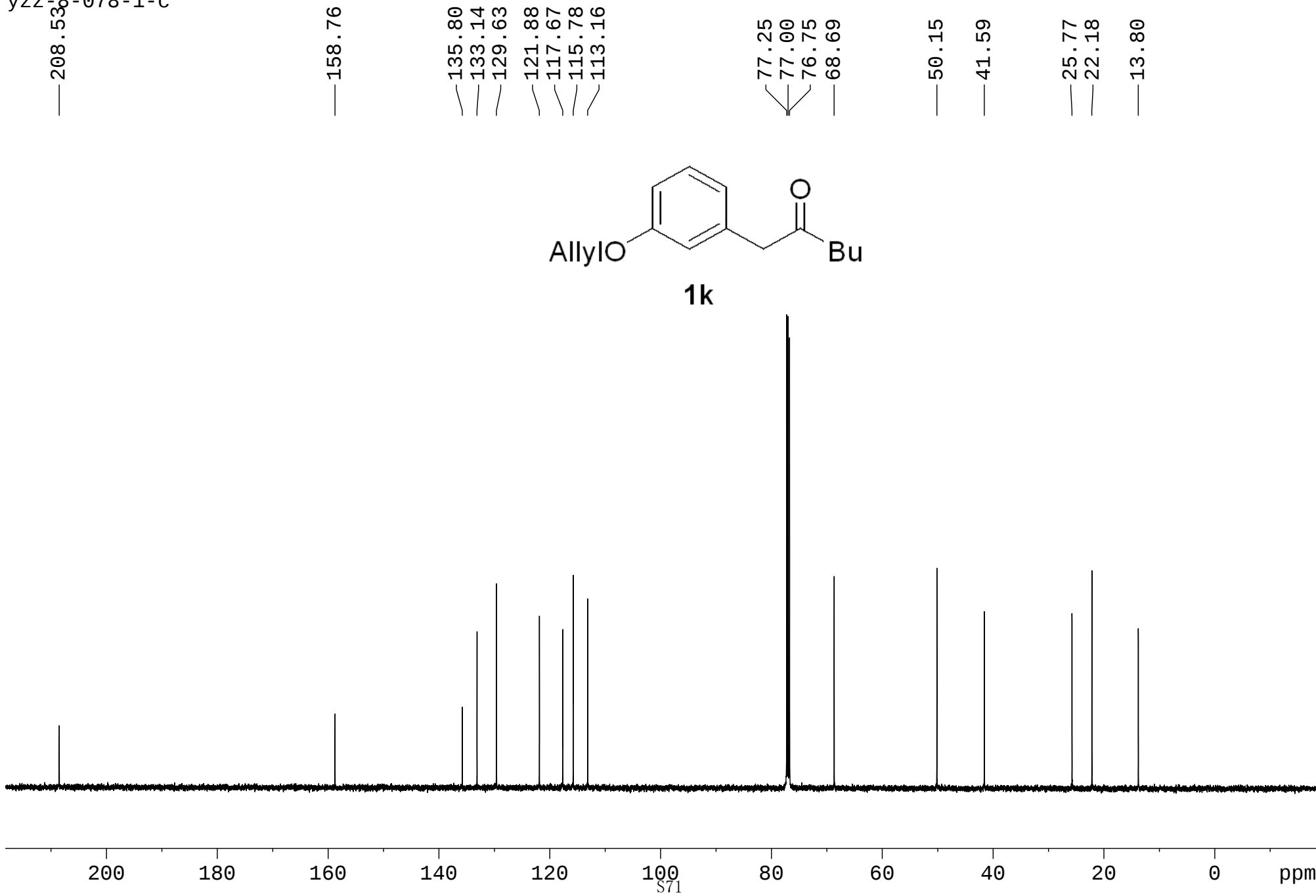
yyy-8-078-p1-c



yyy-8-079-p1



yzzz-078-1-c

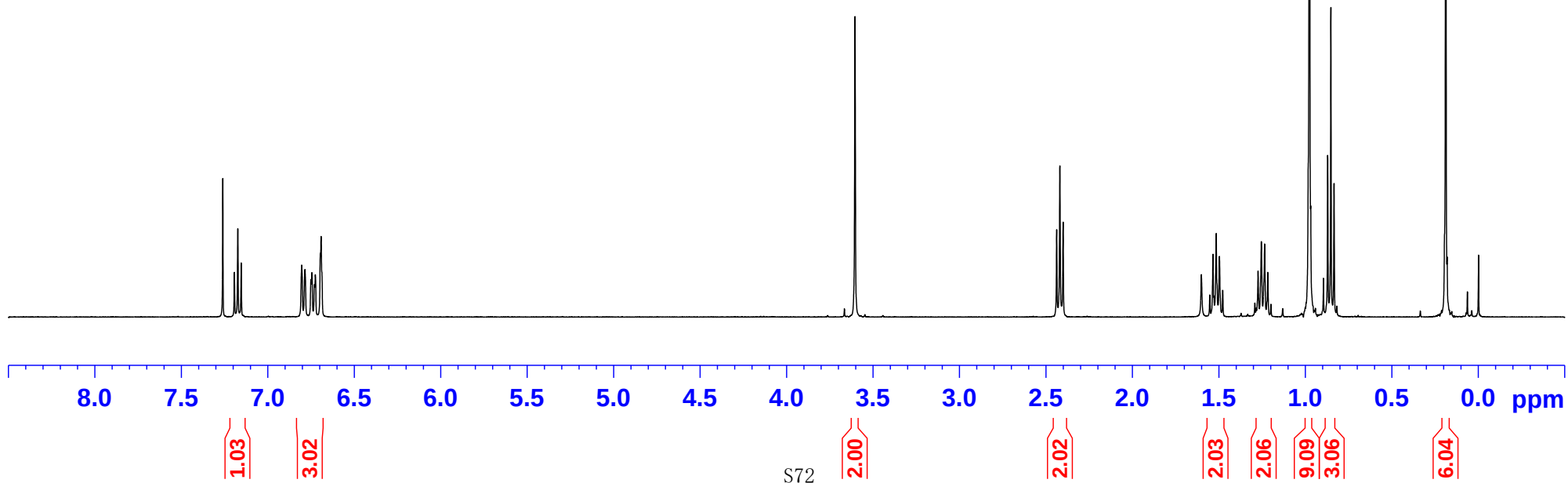
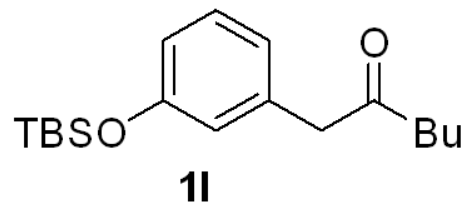


yz-z-8-080-p1

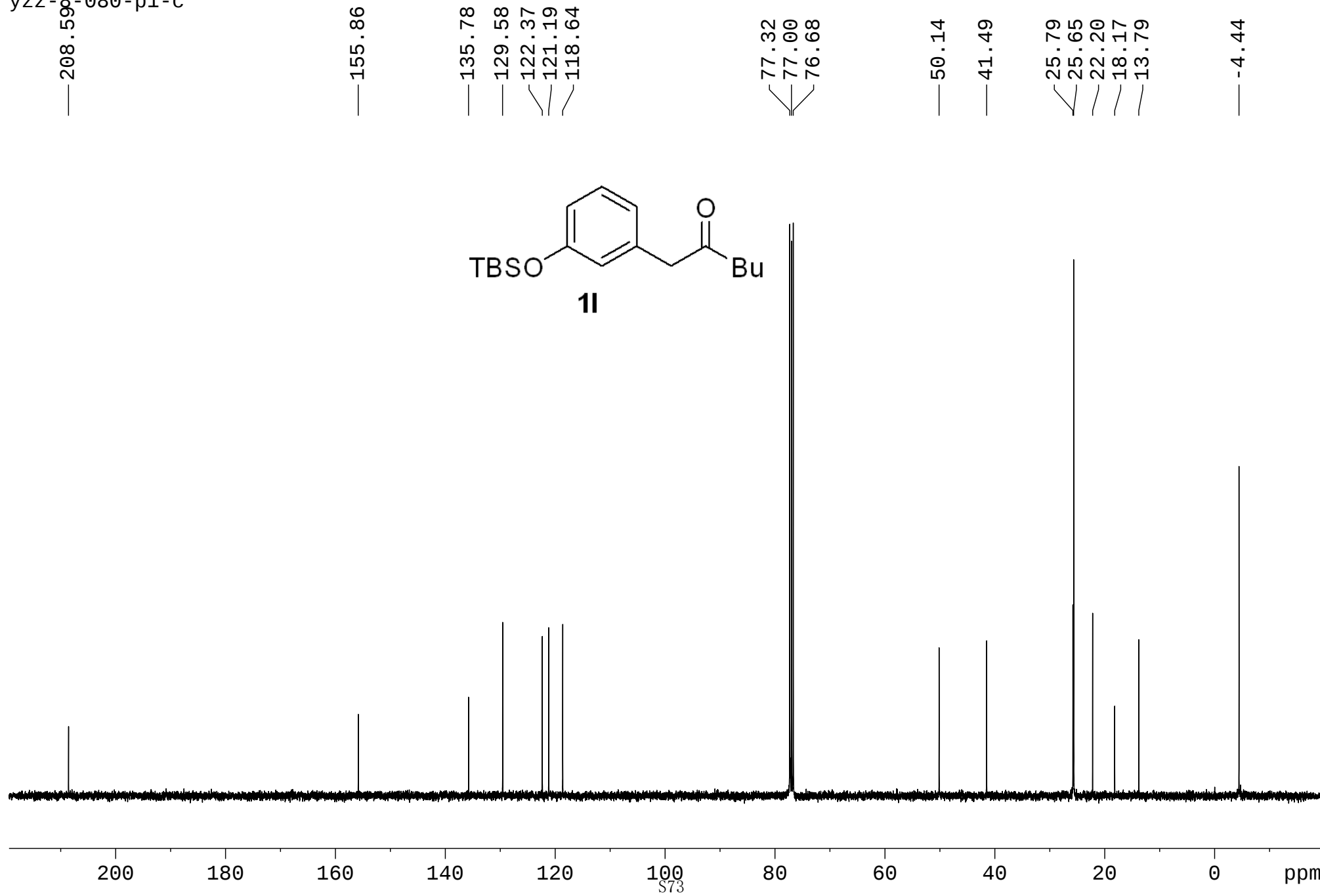
7.260
7.193
7.173
7.154
6.804
6.785
6.750
6.745
6.729
6.725
6.696
6.692

3.604

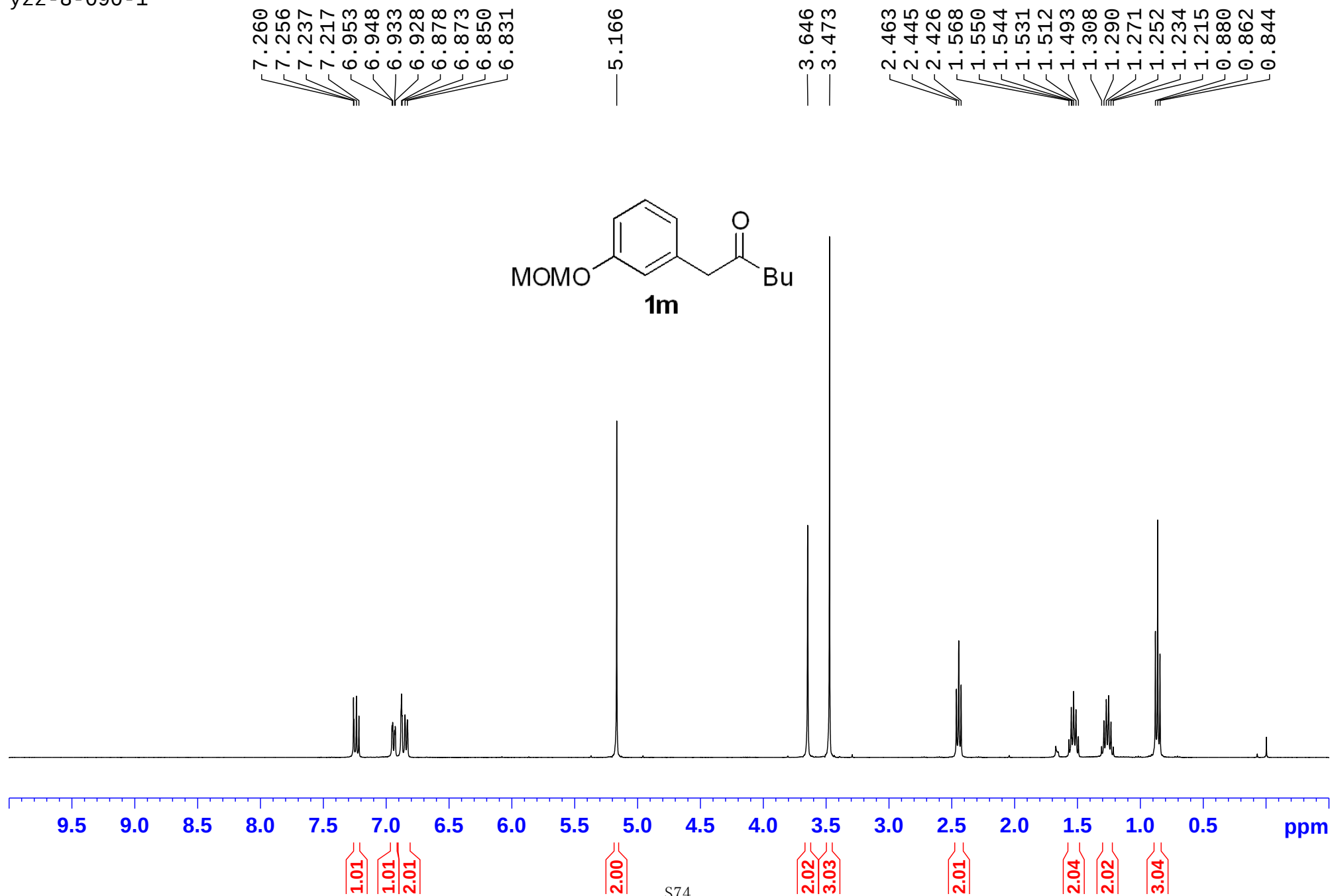
2.438
2.420
2.401
1.601
1.553
1.534
1.529
1.516
1.497
1.478
1.292
1.285
1.274
1.255
1.236
1.217
1.199
0.977
0.871
0.852
0.834
0.188



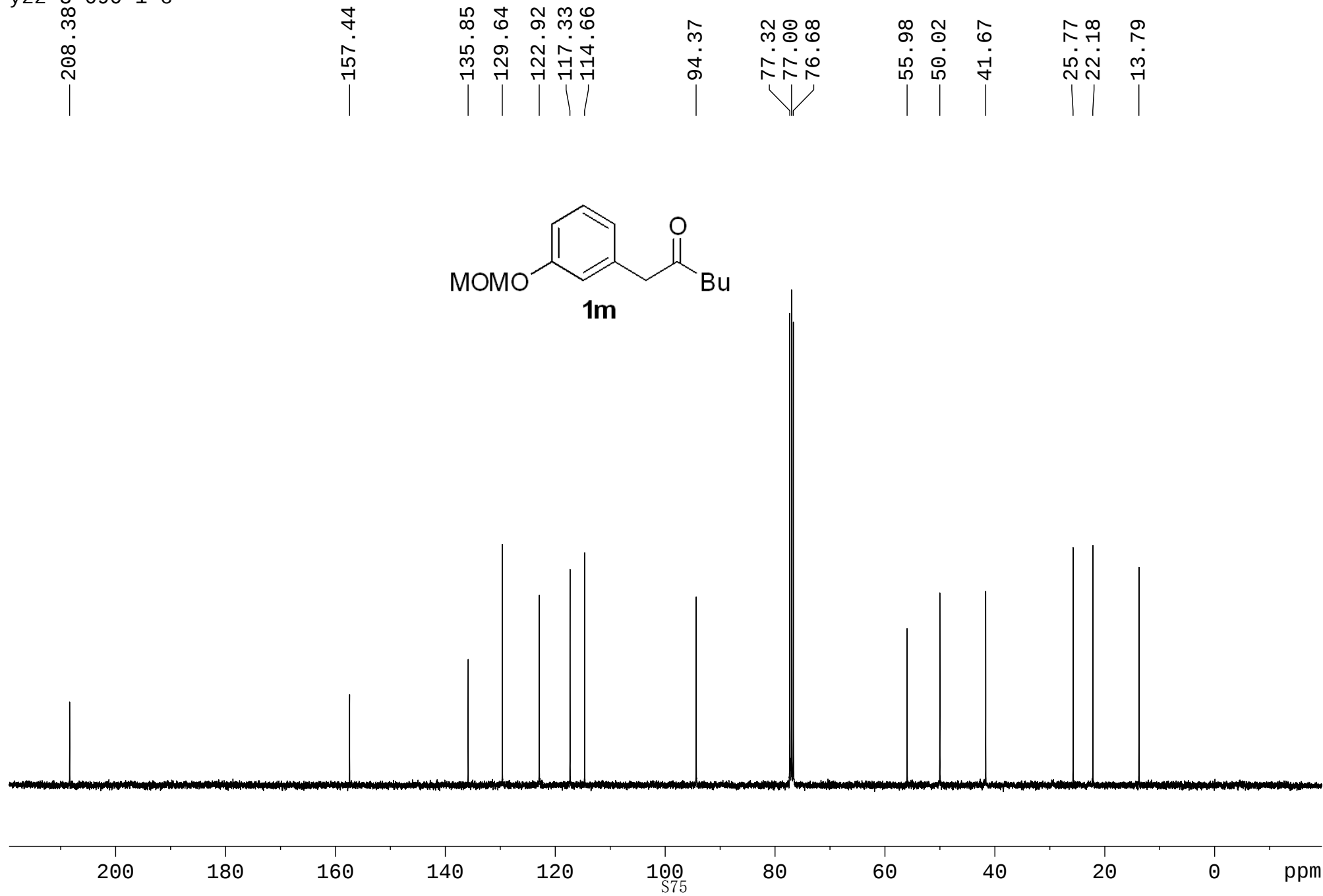
yzzz-0080-p1-c



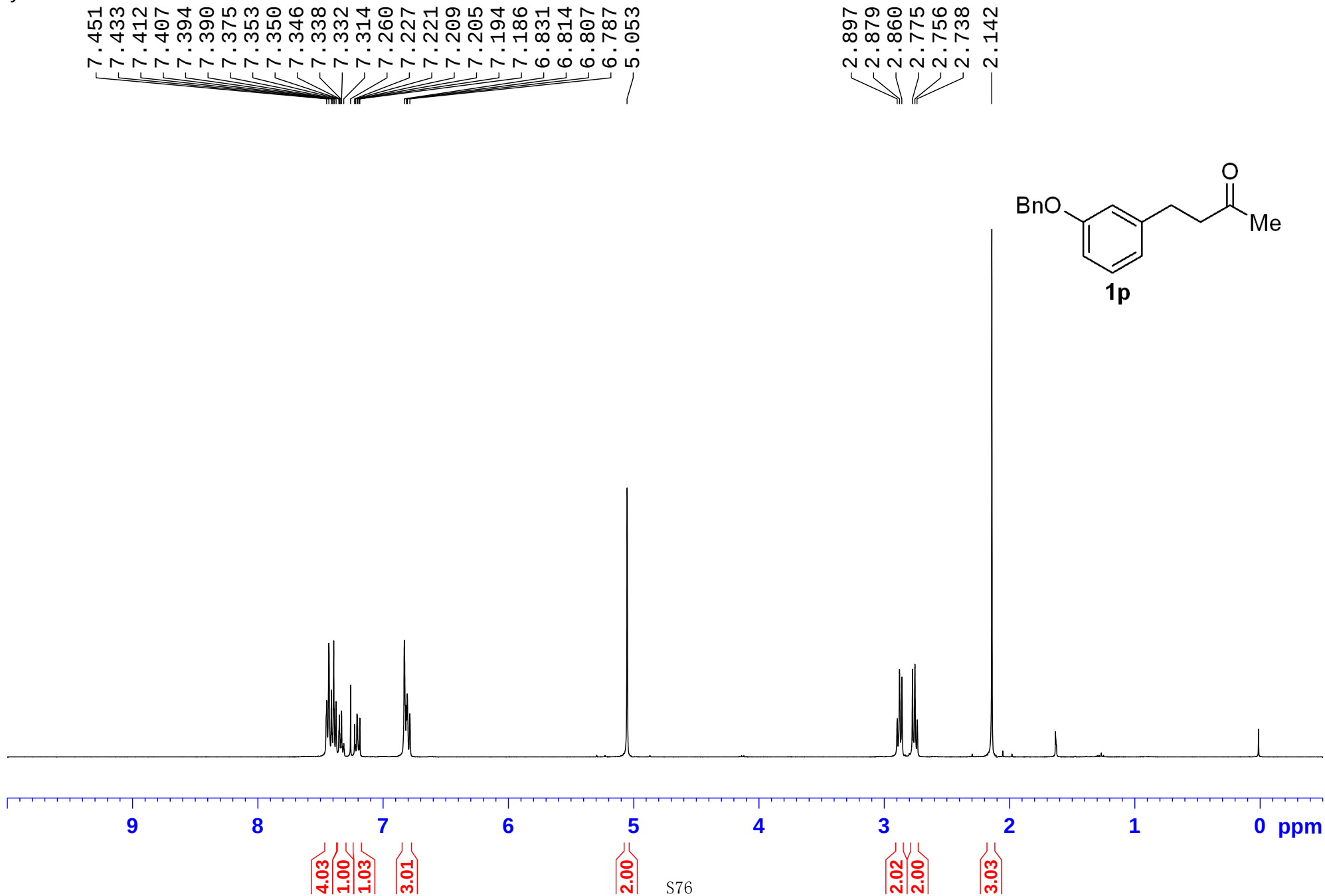
yyy-8-090-1



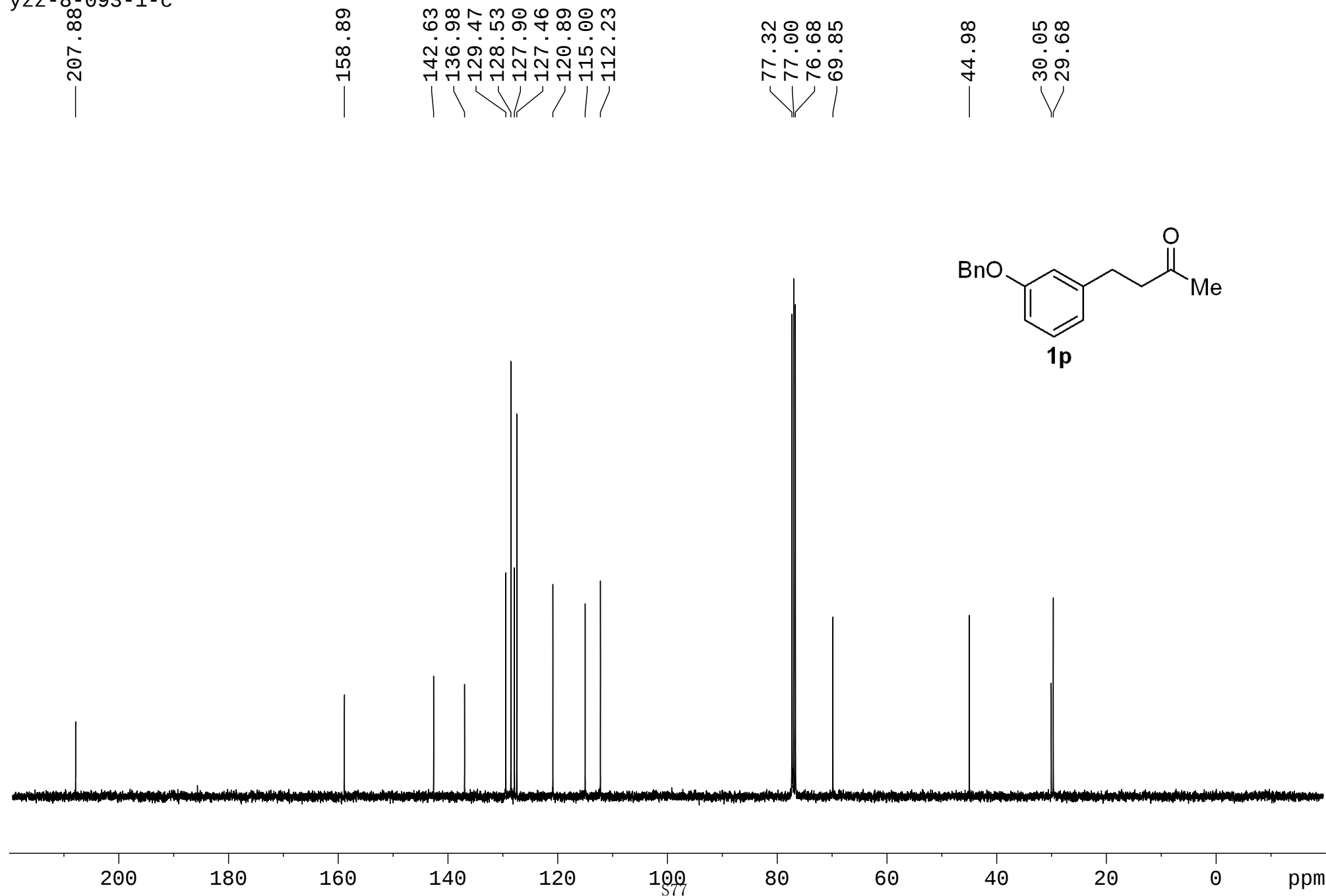
yyy-8-090-1-c



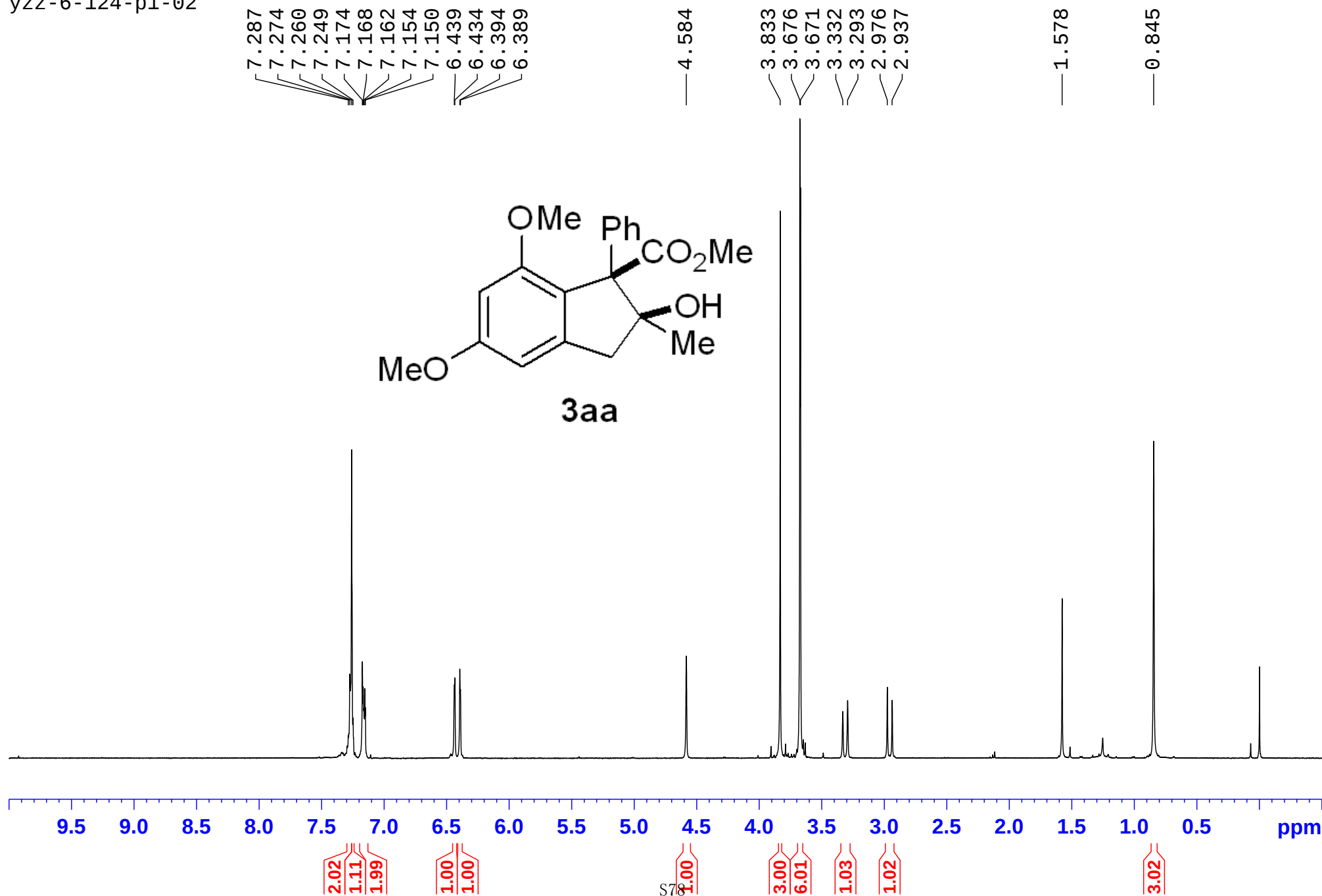
yzz-8-093-1



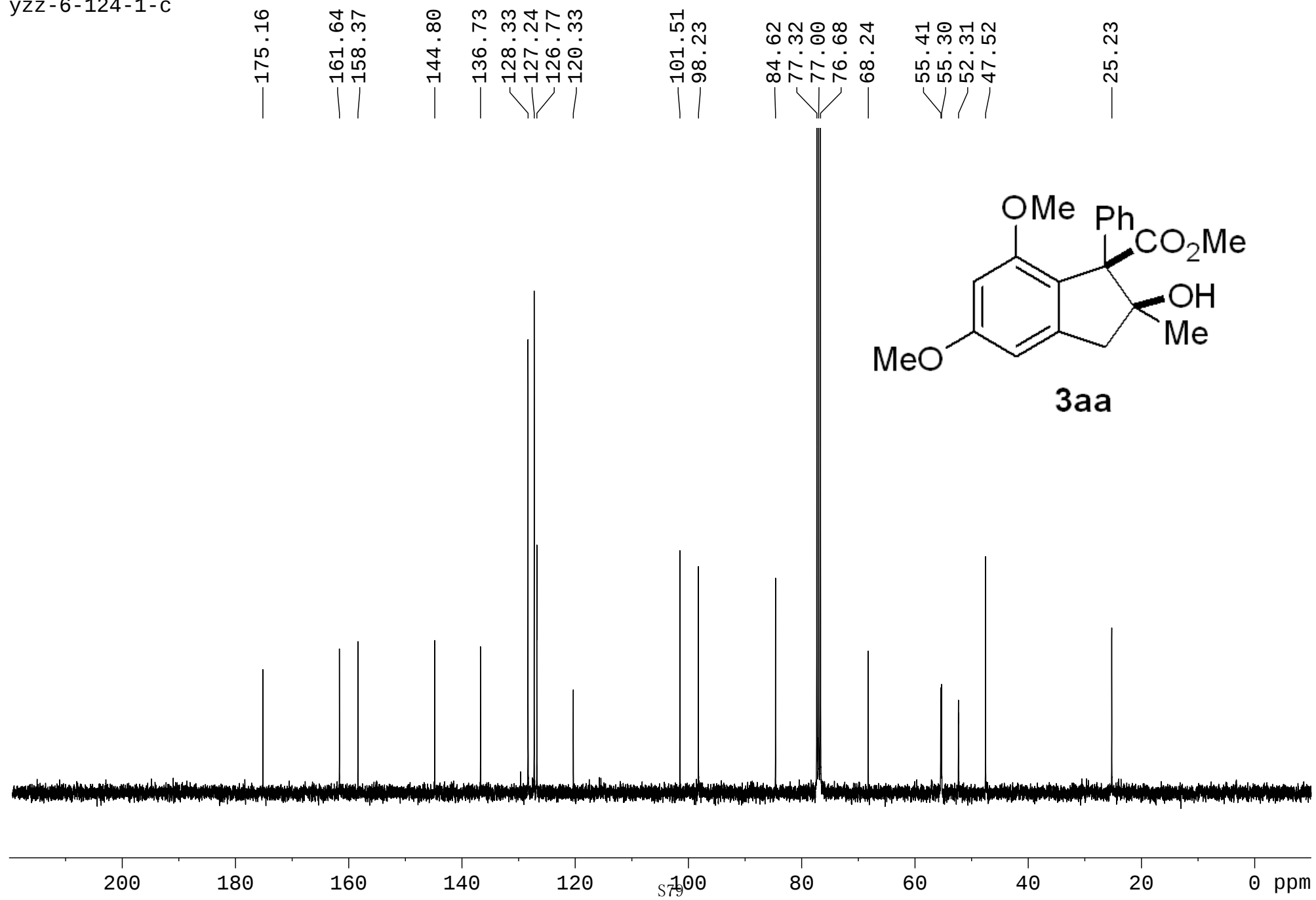
yzzz-8-093-1-c



yyy-6-124-p1-02



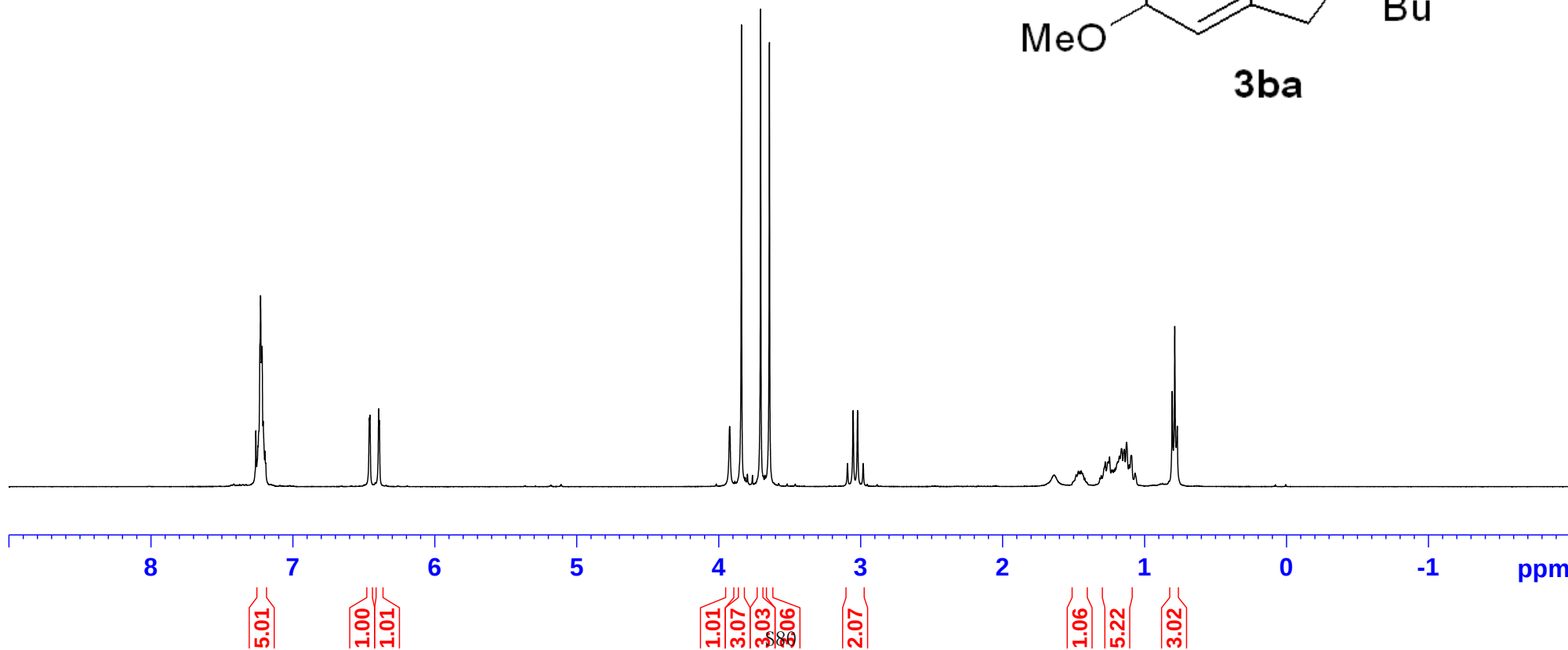
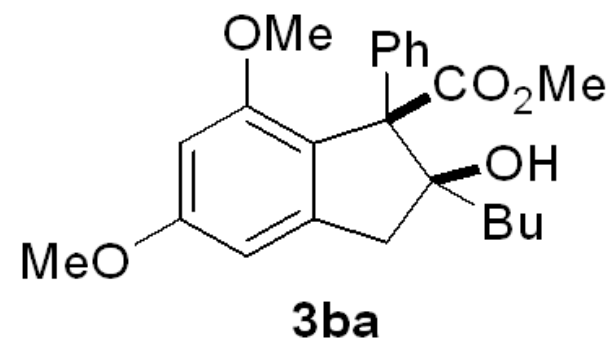
yyy-6-124-1-c



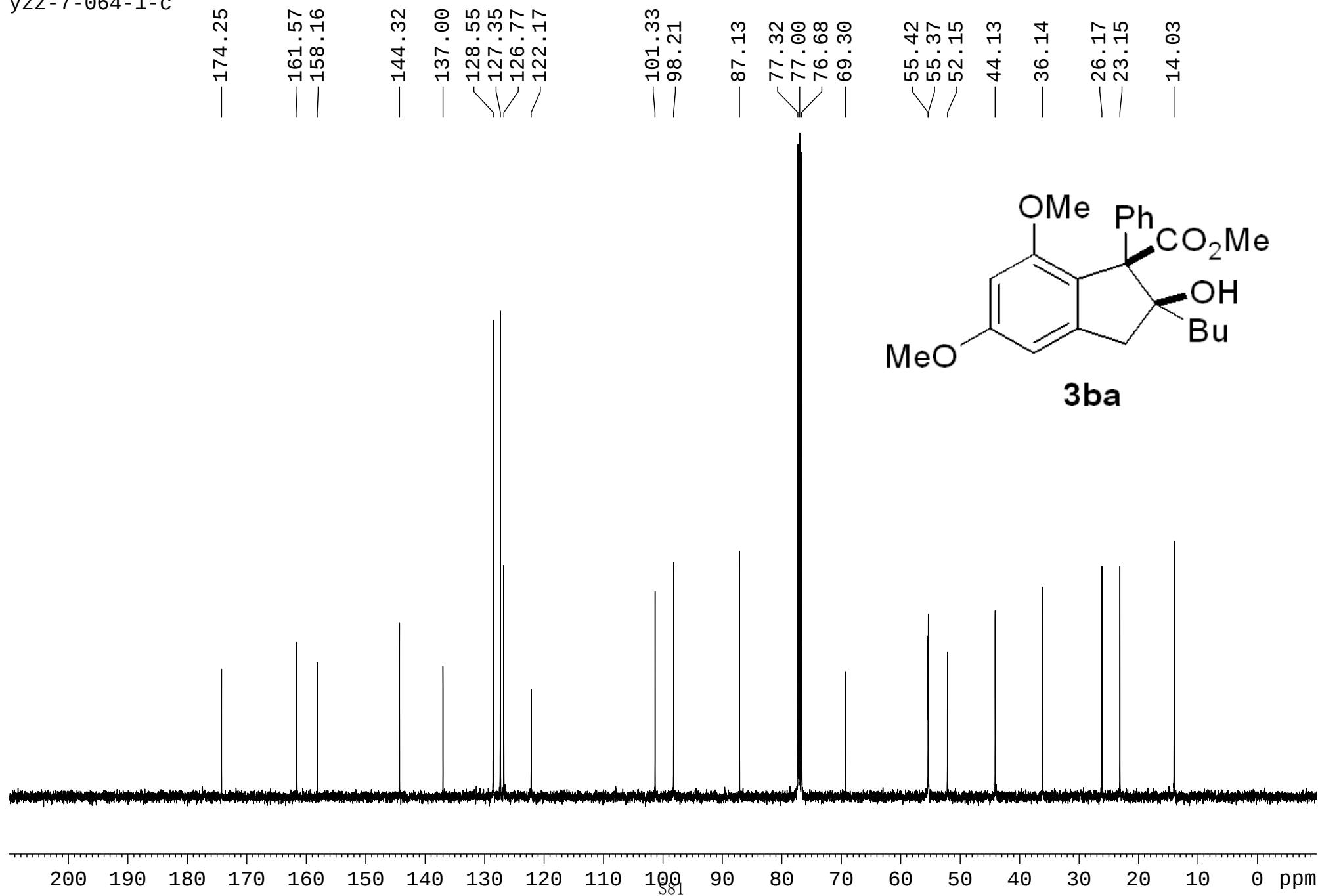
yyy-7-064-1

7.260
7.246
7.232
7.227
7.221
7.216
7.209
7.196
7.191
6.461
6.456
6.395
6.390

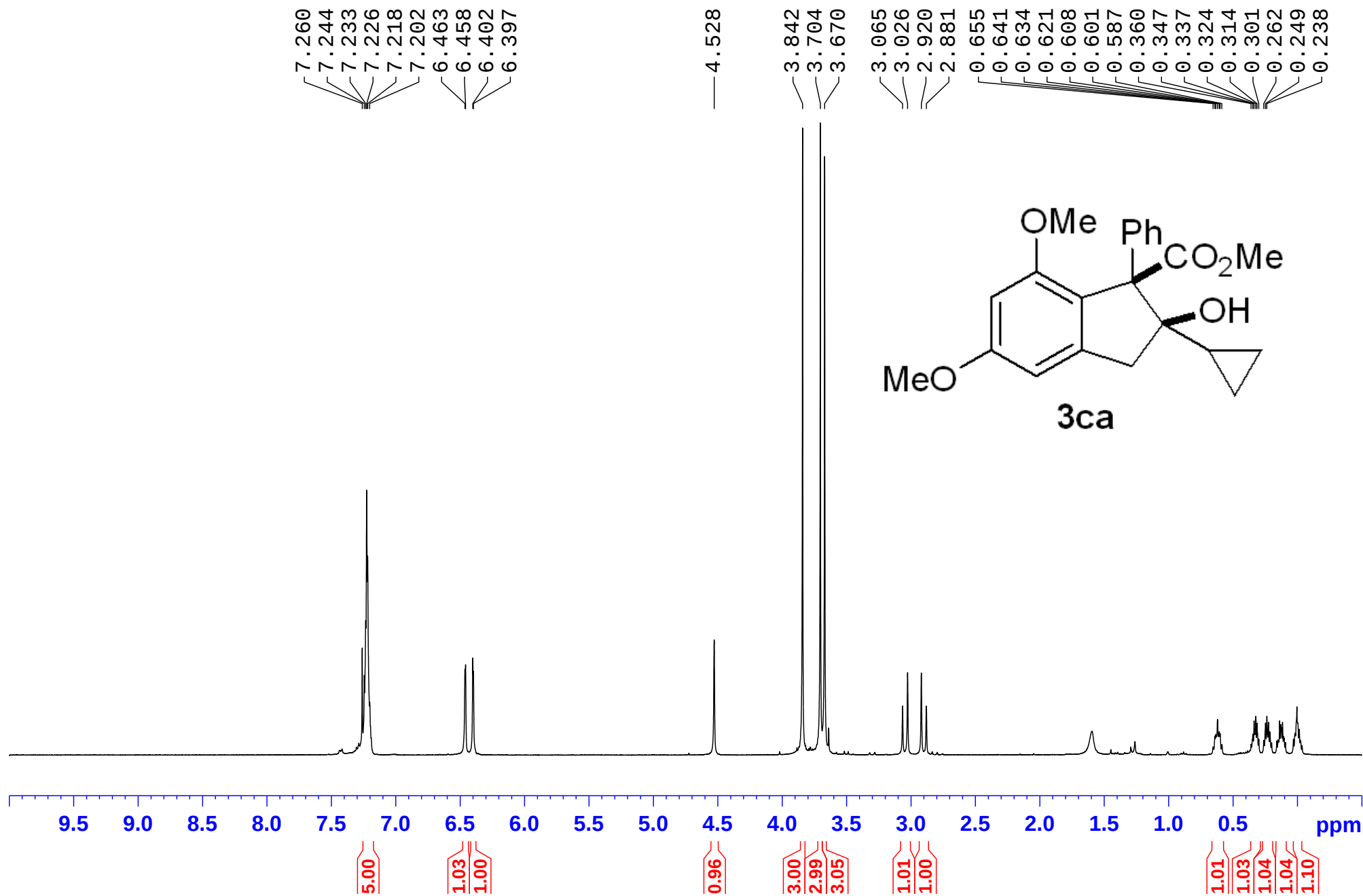
3.923
3.840
3.705
3.643
3.093
3.053
3.022
2.982
1.482
1.466
1.460
1.454
1.446
1.440
1.437
1.431
1.421
1.277
1.260
1.256
1.247
1.234
1.230
1.222
1.216
1.207
1.190
1.178
1.163
1.161
1.142
1.128
1.108
1.096
1.091
1.067
0.805
0.787
0.770

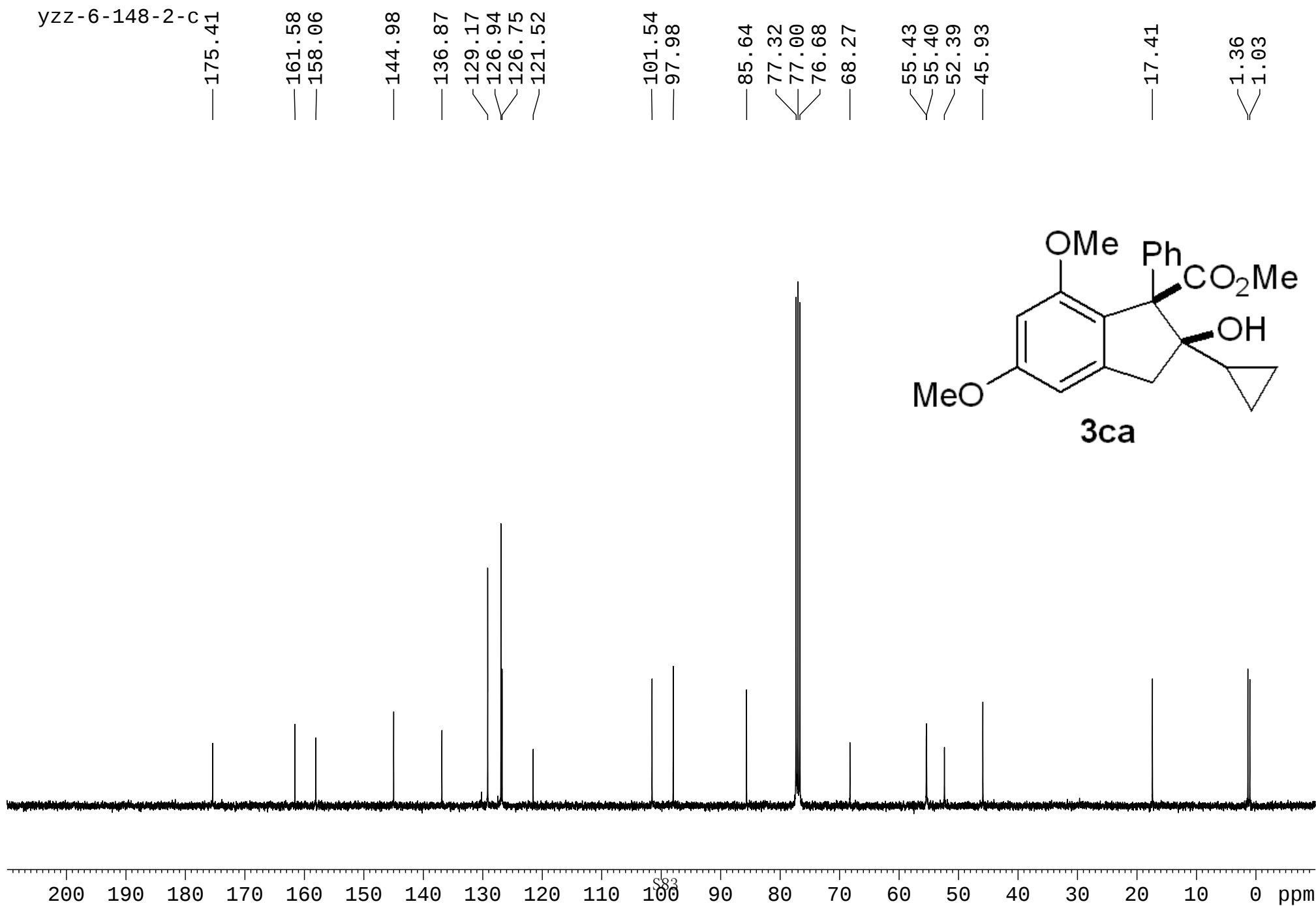


yyy-7-064-1-c



YZZ-6-148-1



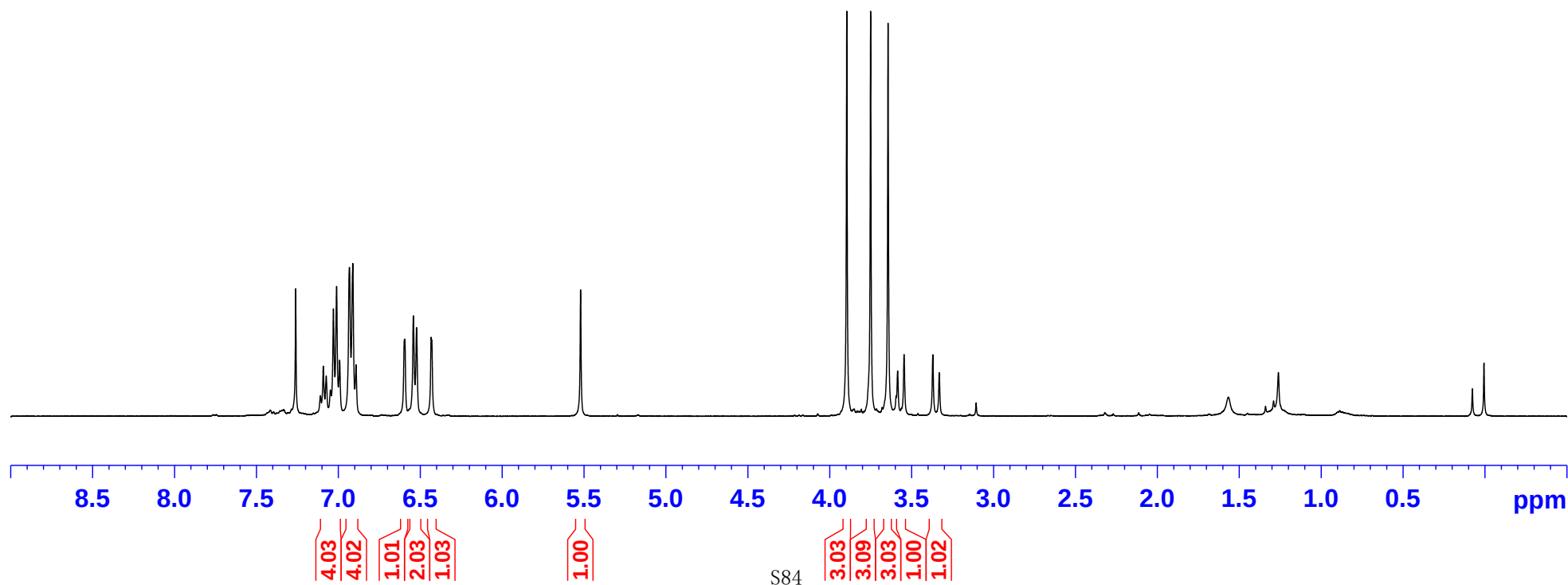
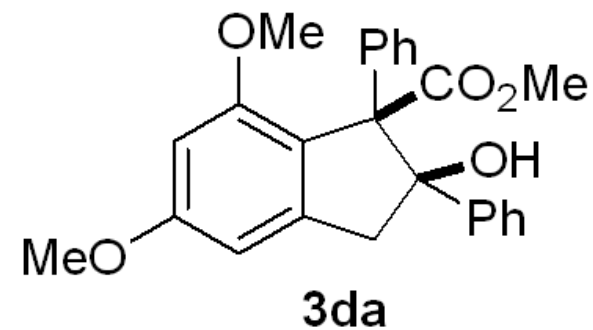


yyy-7-017-p1-1

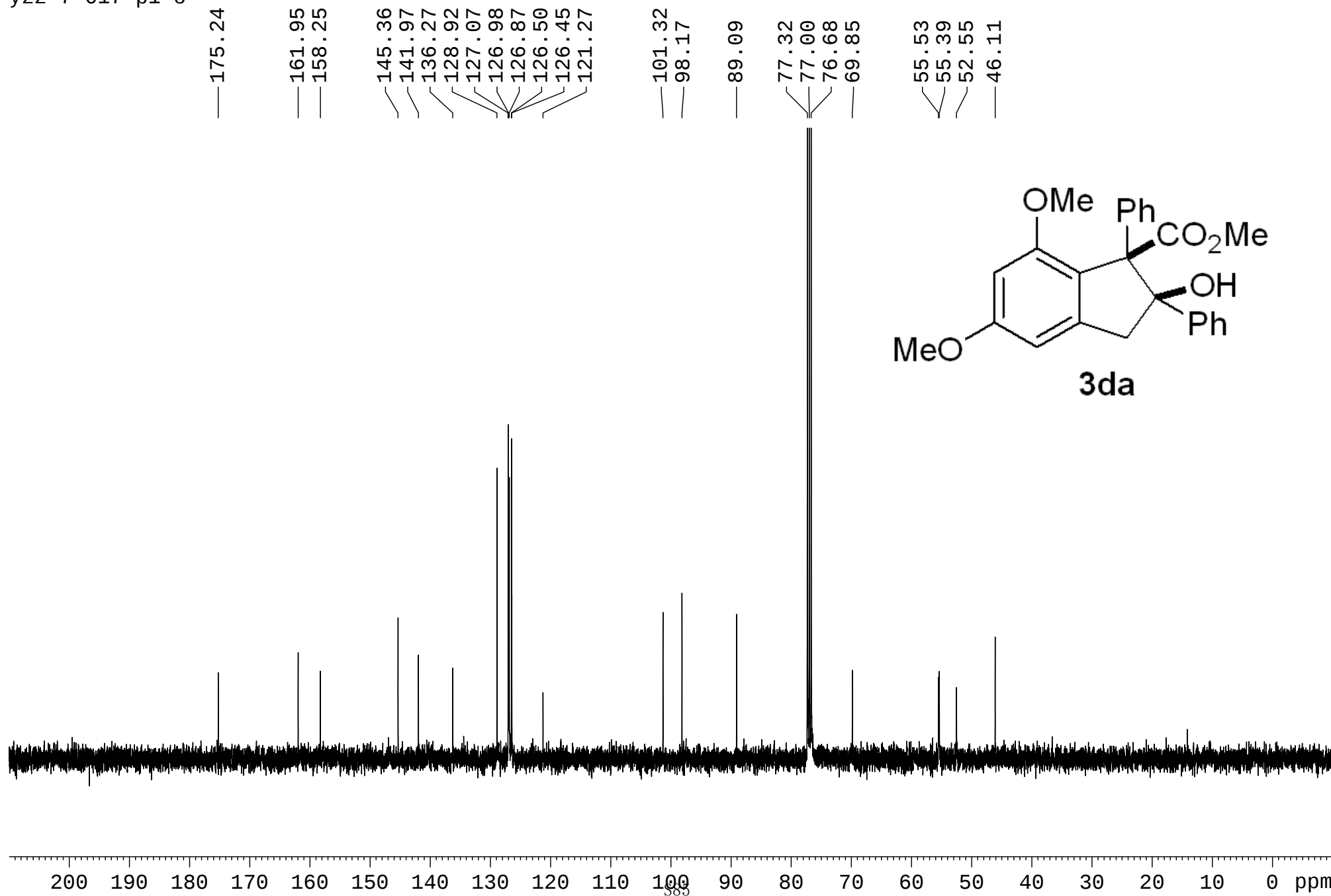
7.260
7.109
7.092
7.074
7.048
7.030
7.010
6.992
6.932
6.911
6.892
6.594
6.542
6.523
6.433
6.430
5.521

3.896
3.751
3.644
3.586
3.546
3.371
3.332

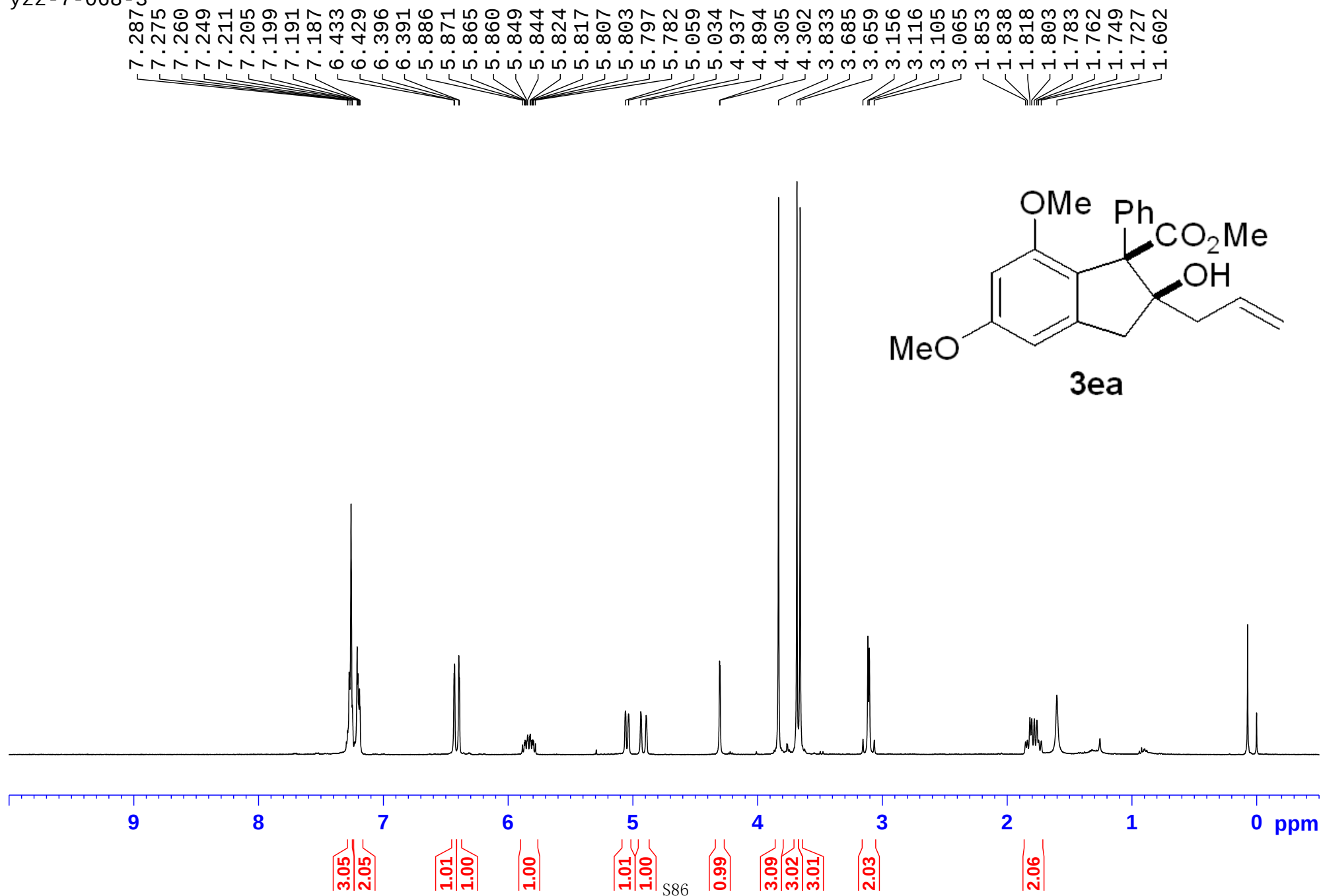
1.567



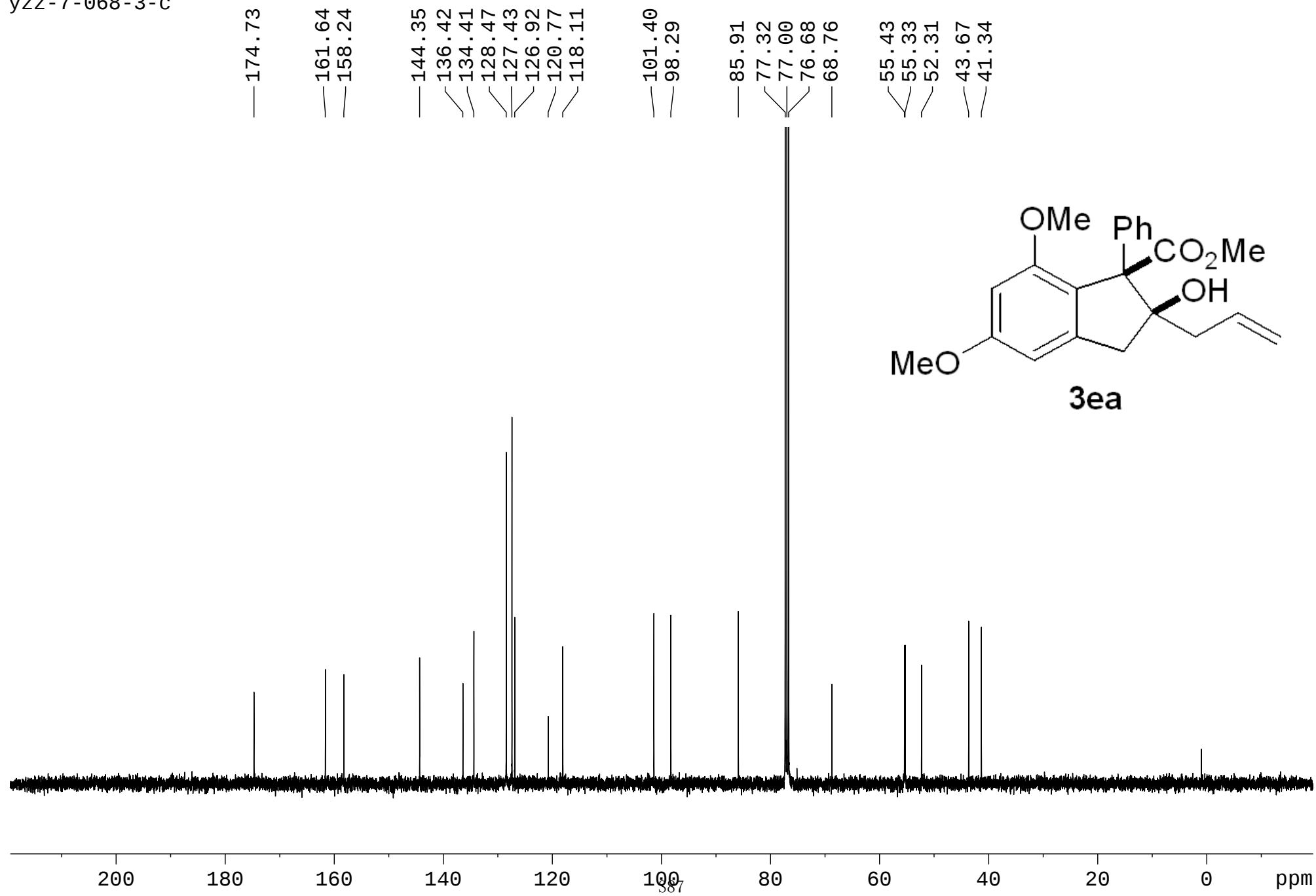
yyy-7-017-p1-c



yyy-7-068-3



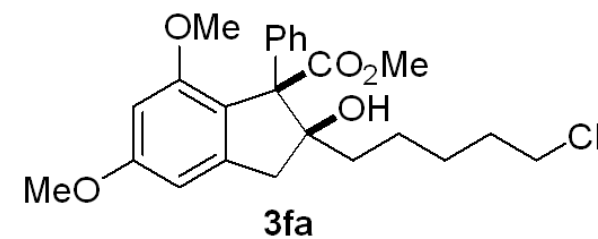
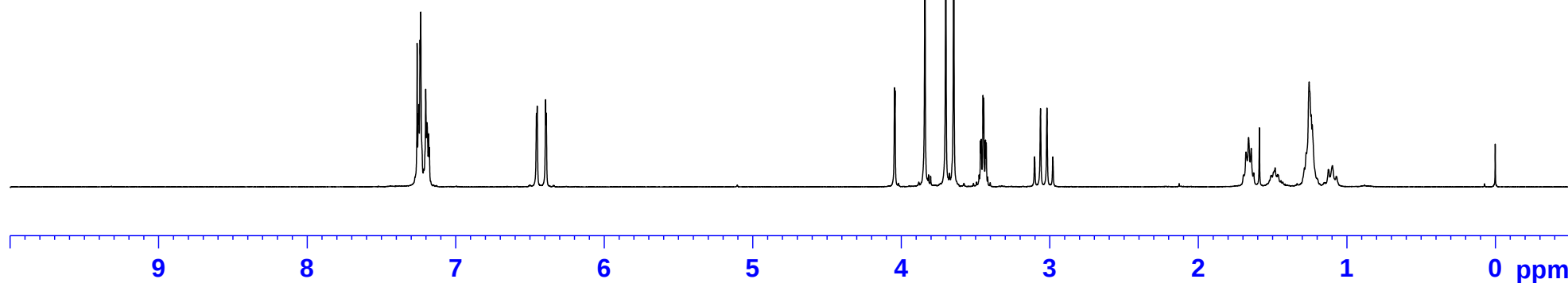
yyy-7-068-3-c



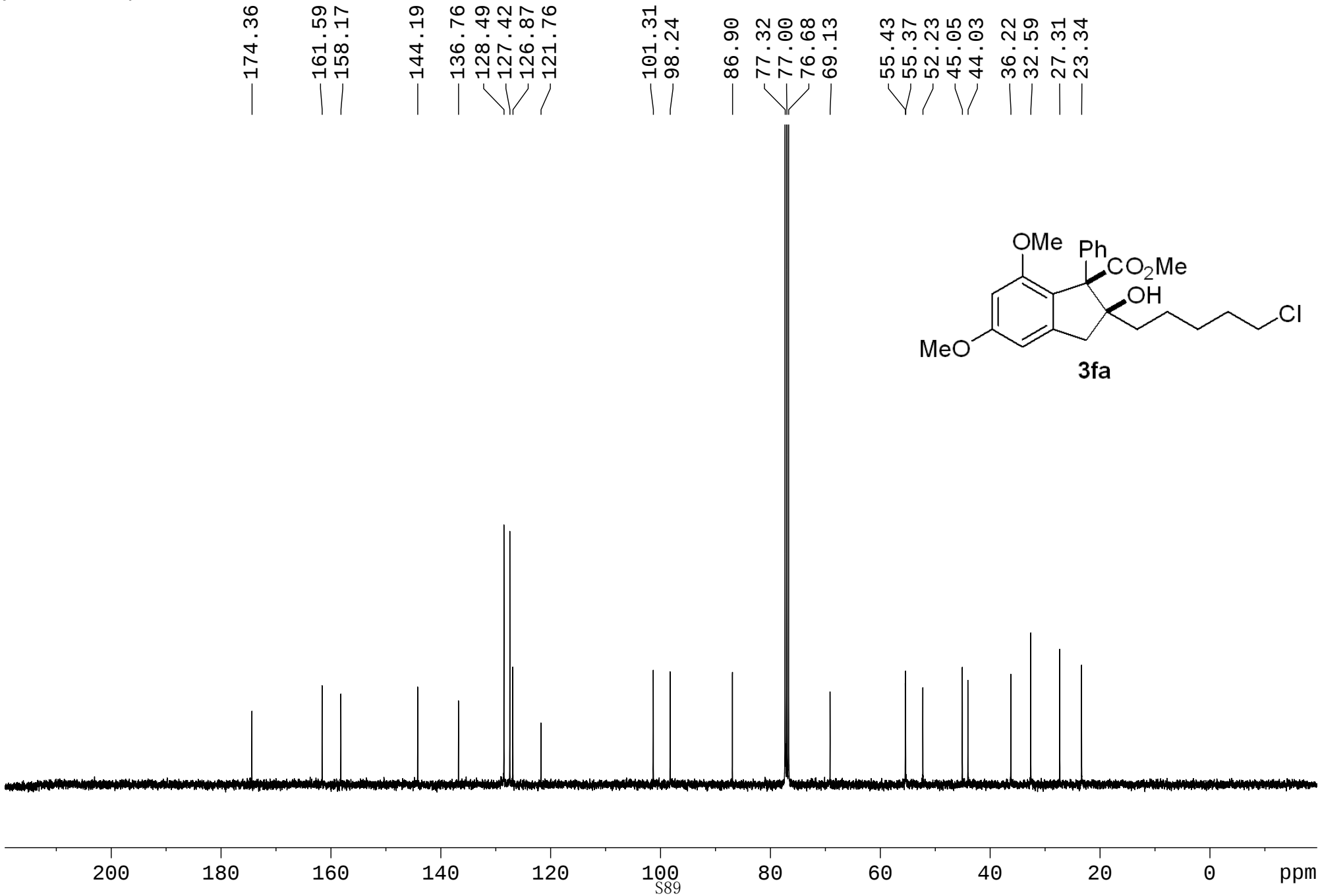
yyy-7-118-p1-01

7.260
7.253
7.249
7.240
7.235
7.202
7.194
7.183
7.177
6.457
6.452
6.395
6.390

4.046
4.042
3.841
3.701
3.647
3.467
3.462
3.450
3.445
3.433
3.428
3.103
3.063
3.019
2.980
1.679
1.662
1.644
1.589
1.509
1.495
1.483
1.473
1.466
1.462
1.254
1.250
1.240
1.233
1.125
1.121



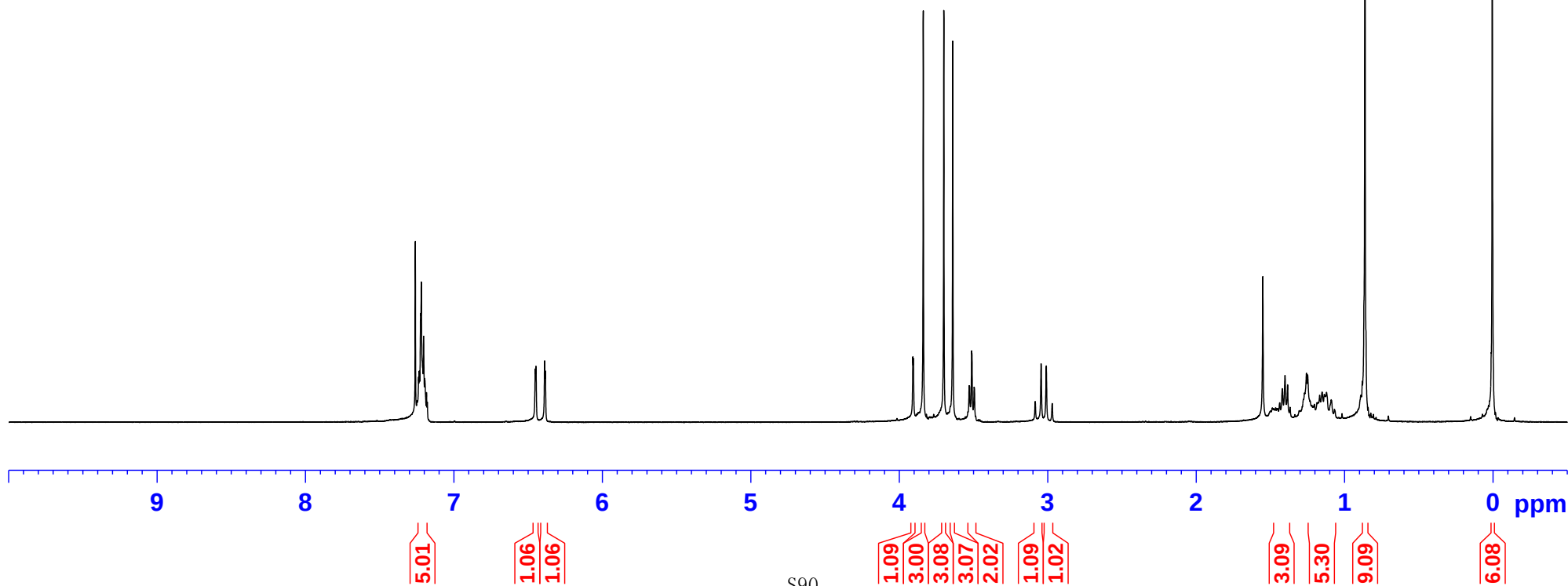
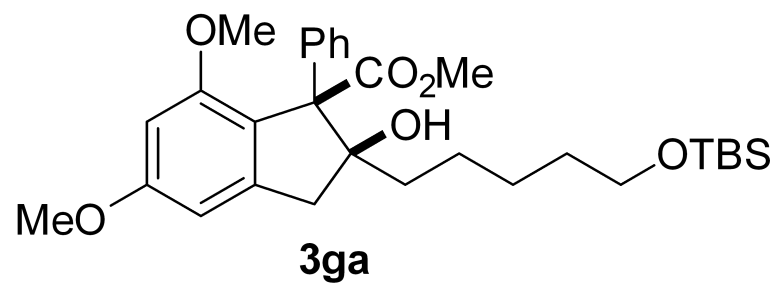
yyy-7-118-p1-01



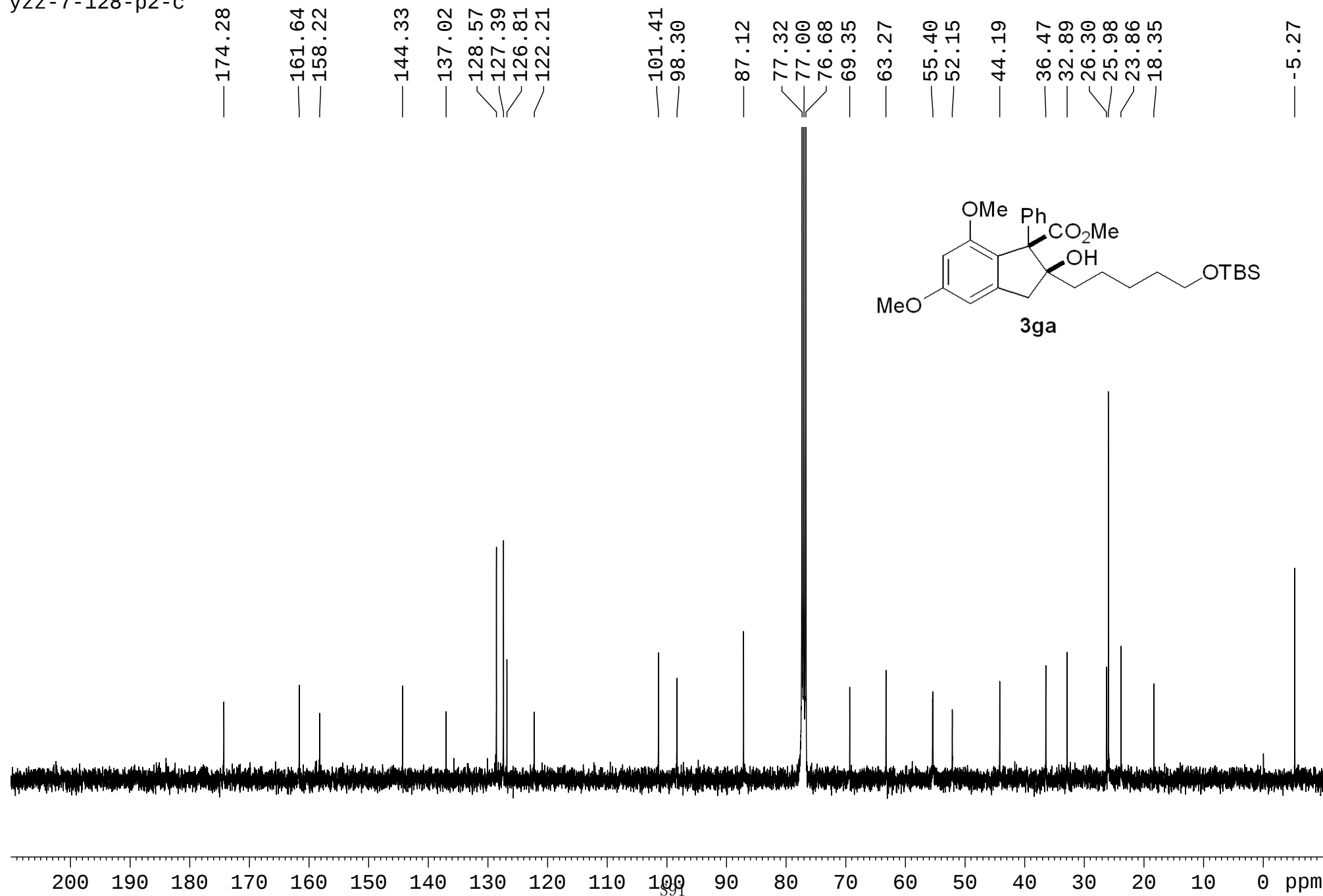
yyy-7-128-p2

7.260
7.249
7.239
7.234
7.224
7.220
7.205
7.197
7.185
7.179
6.453
6.448
6.390
6.385

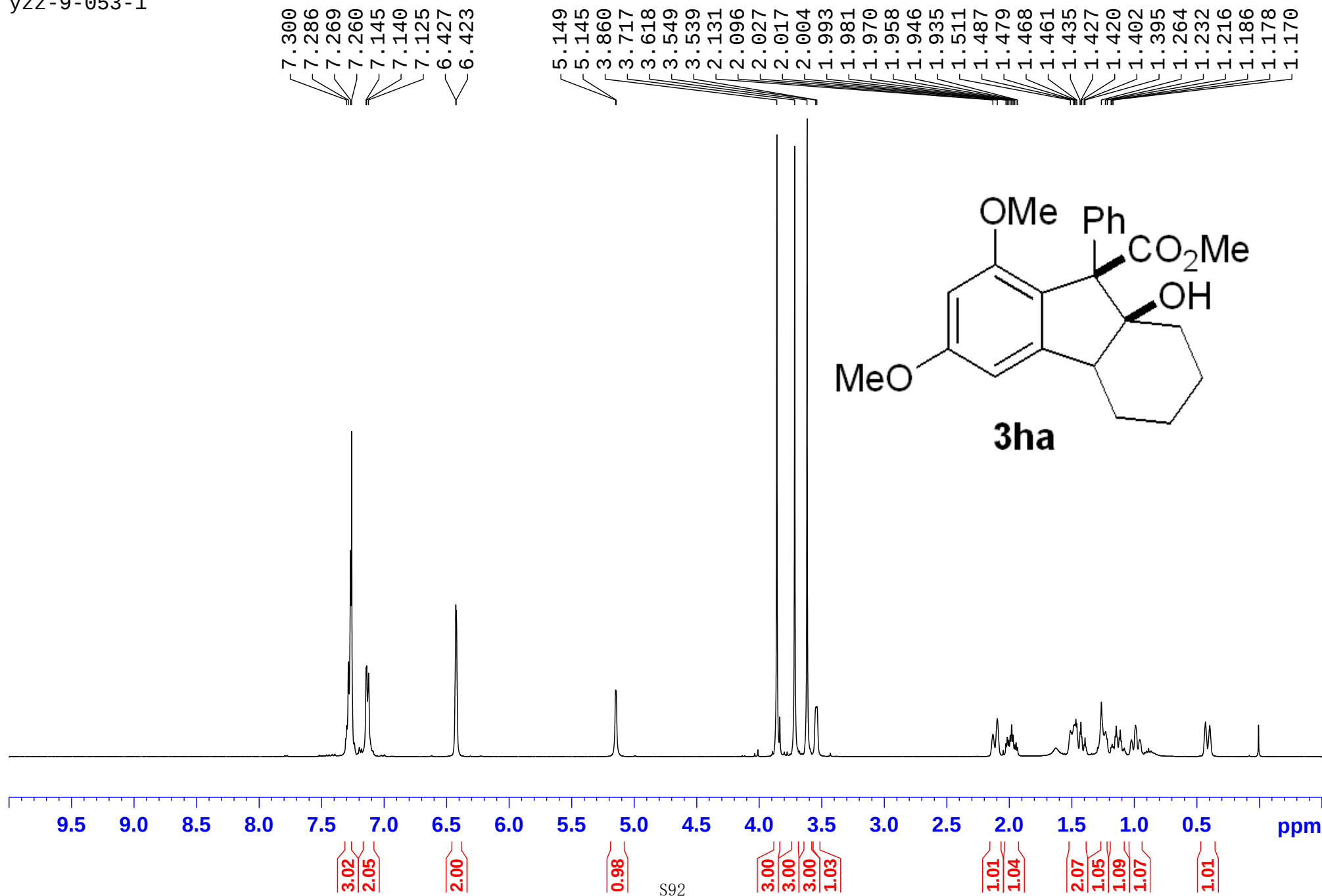
3.909
3.905
3.839
3.701
3.640
3.530
3.528
3.513
3.496
3.085
3.045
3.010
2.971
1.552
1.438
1.420
1.385
1.271
1.258
1.250
1.169
1.152
1.137
1.122
0.863
0.006



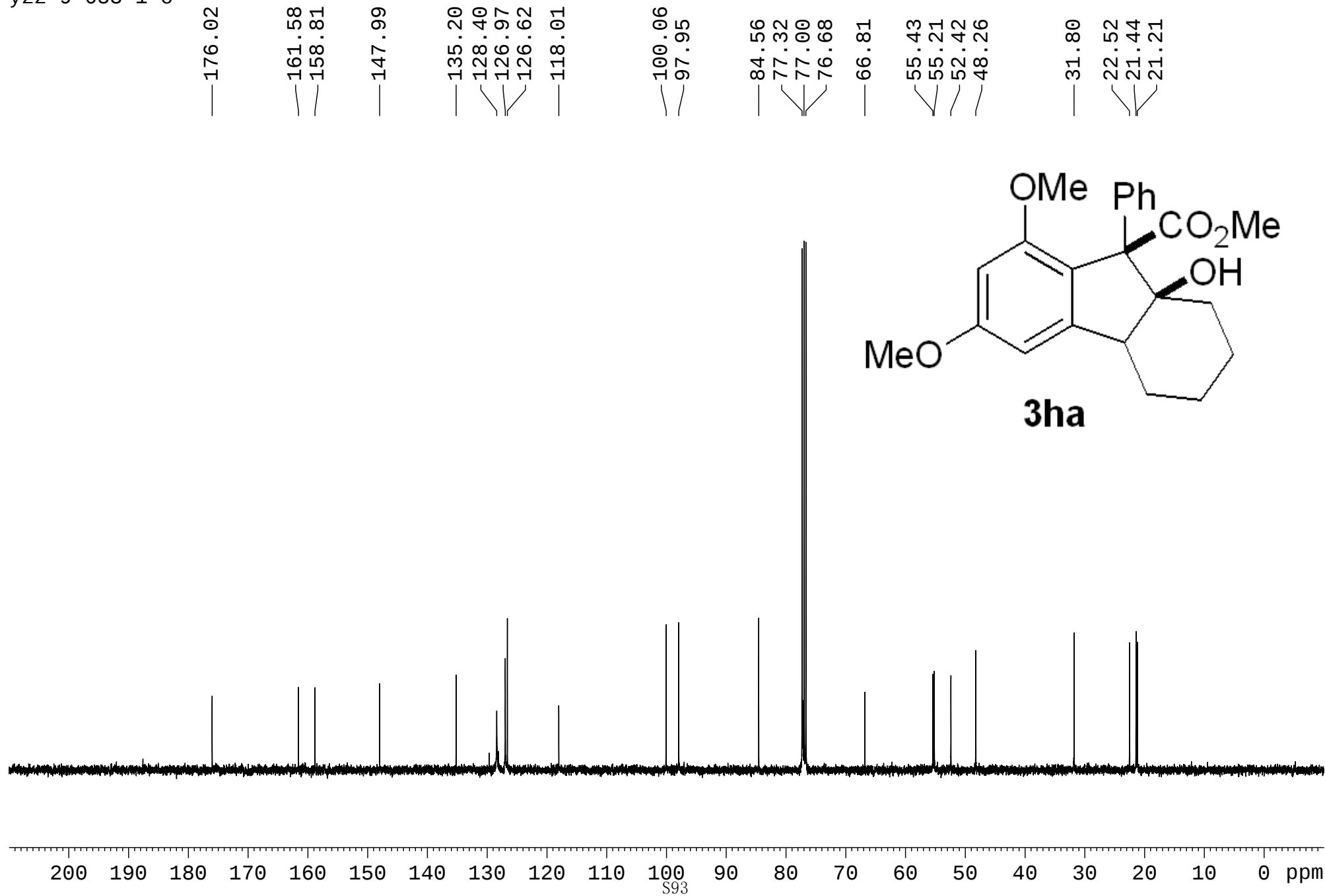
yyy-7-128-p2-c



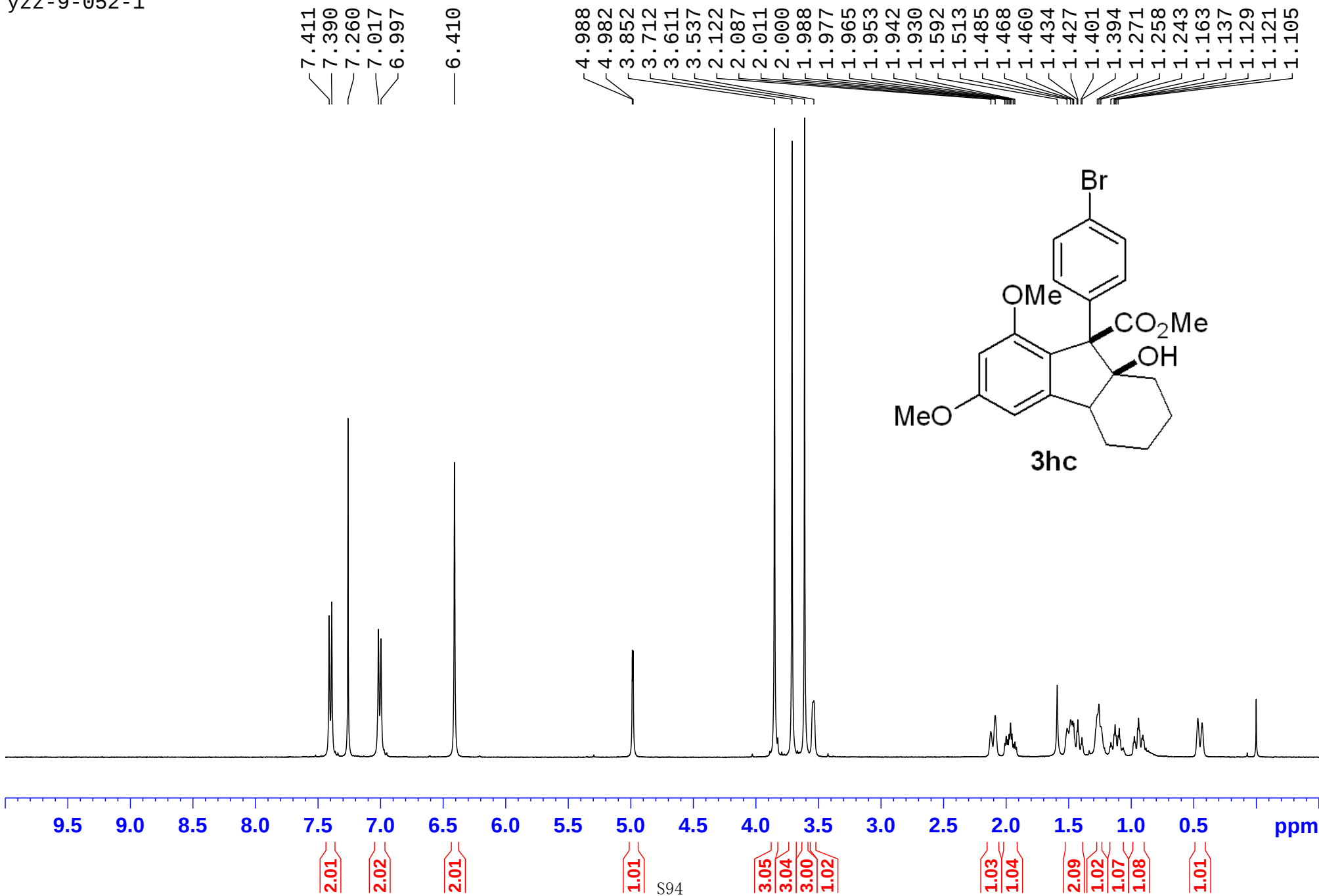
yzz-9-053-1



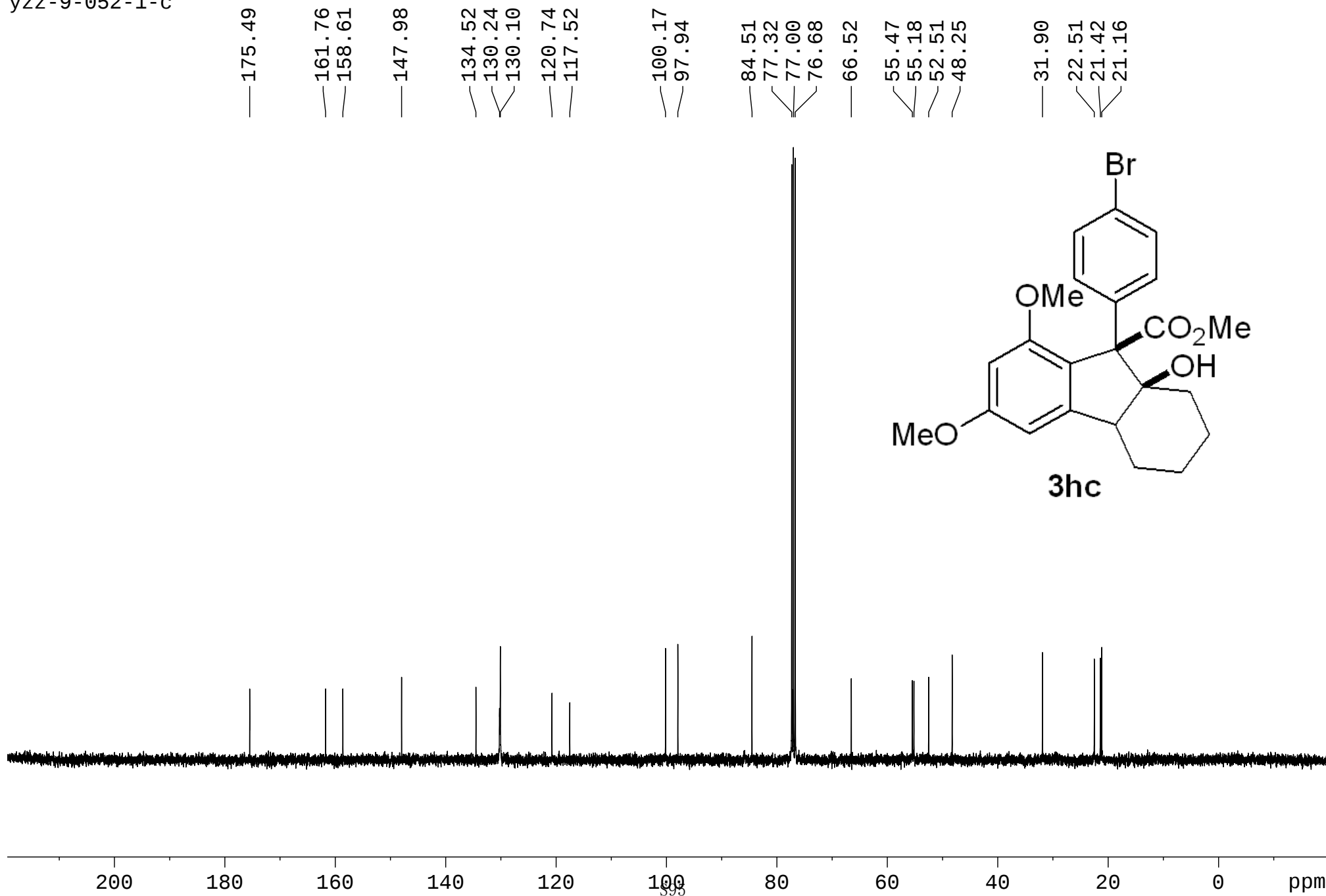
yyy-9-053-1-c



yyy-9-052-1



yyy-9-052-1-c



yyy-8-044-p1-1

7.422
7.400
7.328
7.311
7.298
7.260
7.151
7.146
7.131
7.127
6.845
6.839
6.820

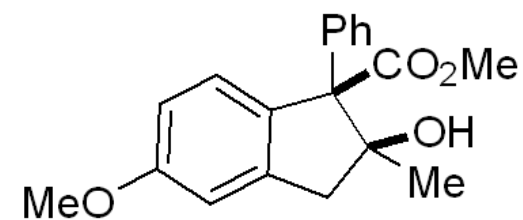
— 4.996

— 3.831
— 3.671

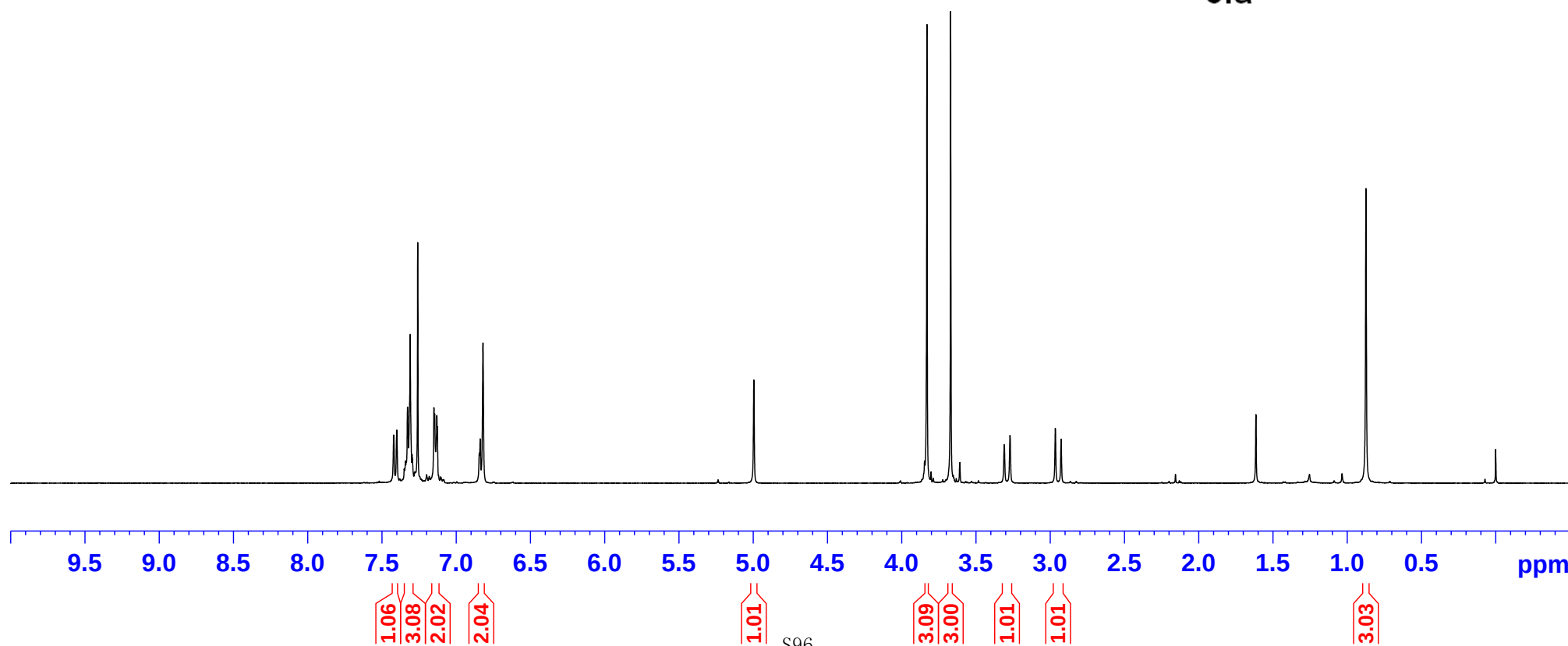
3.310
3.271
2.966
2.927

— 1.615

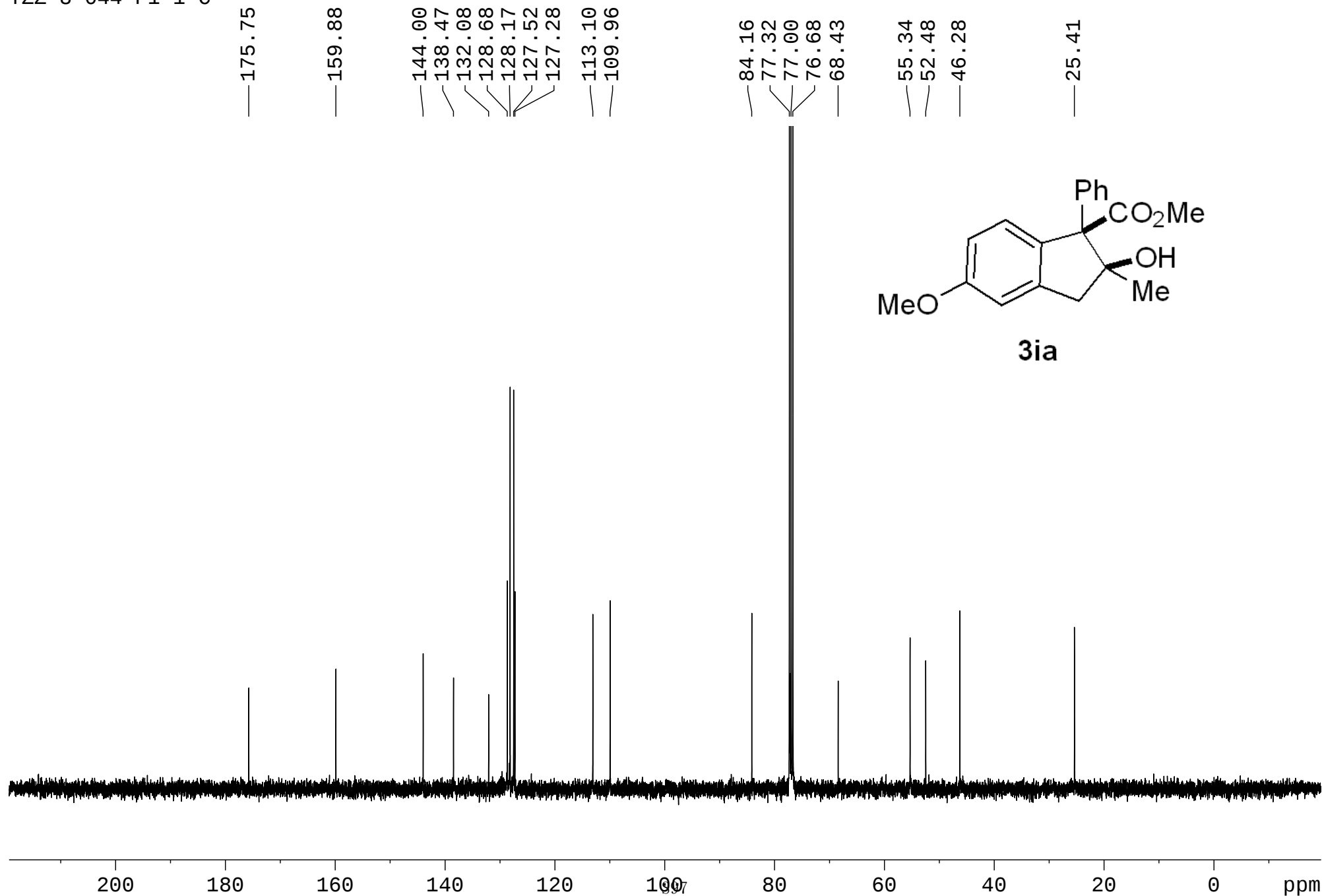
— 0.874



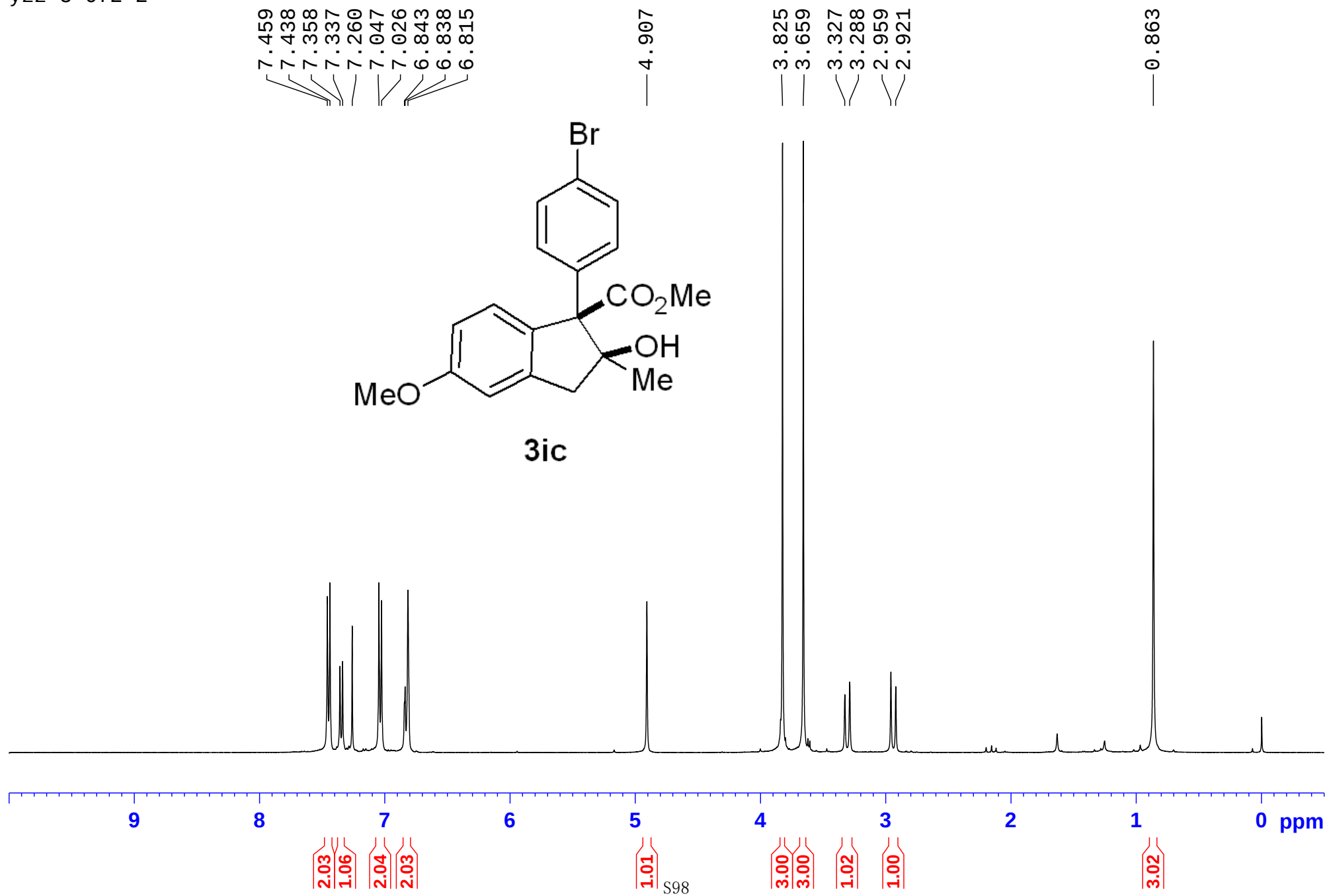
3ia



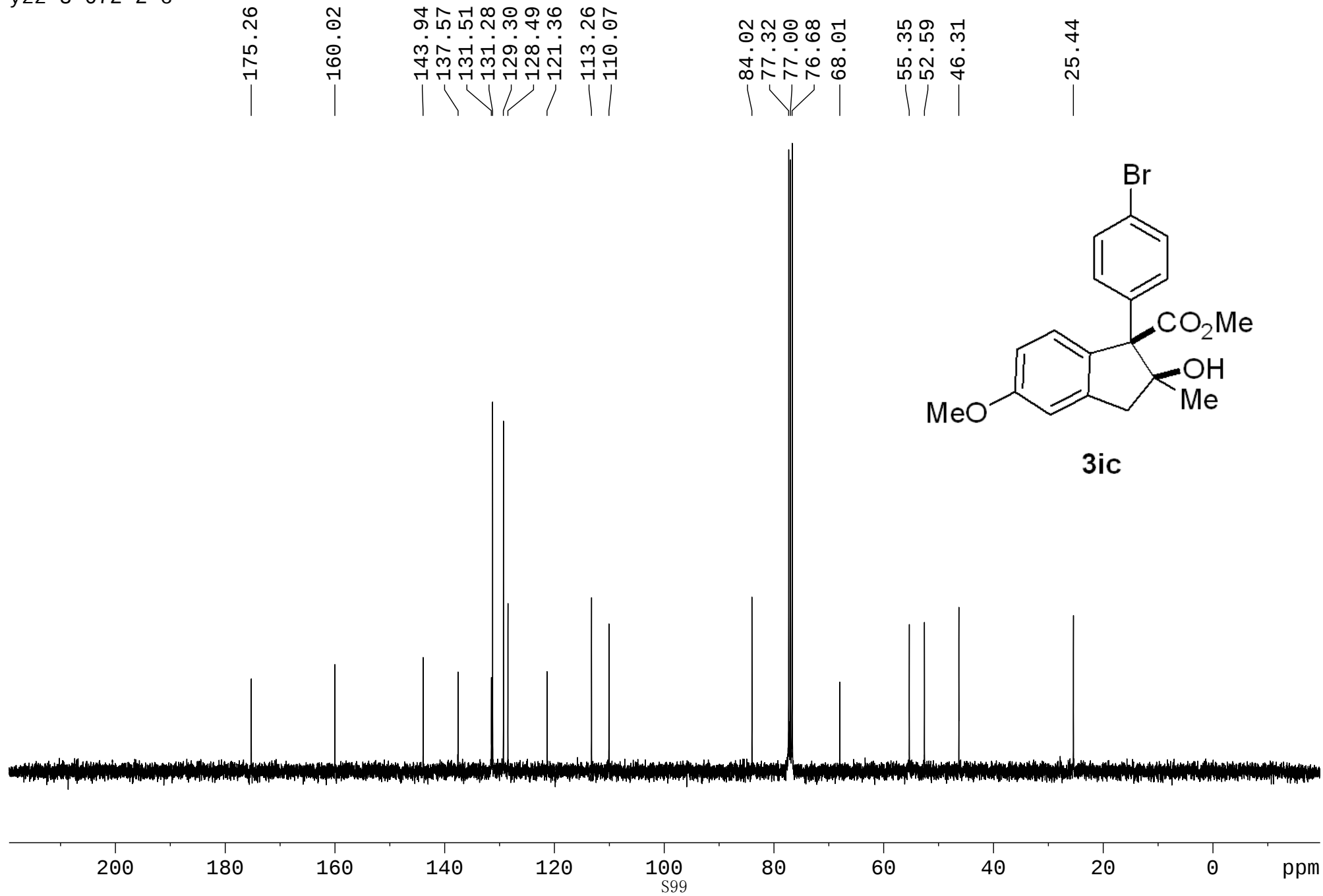
YZZ-8-044-P1-1-C



yyy-8-072-2



yyy-8-072-2-c



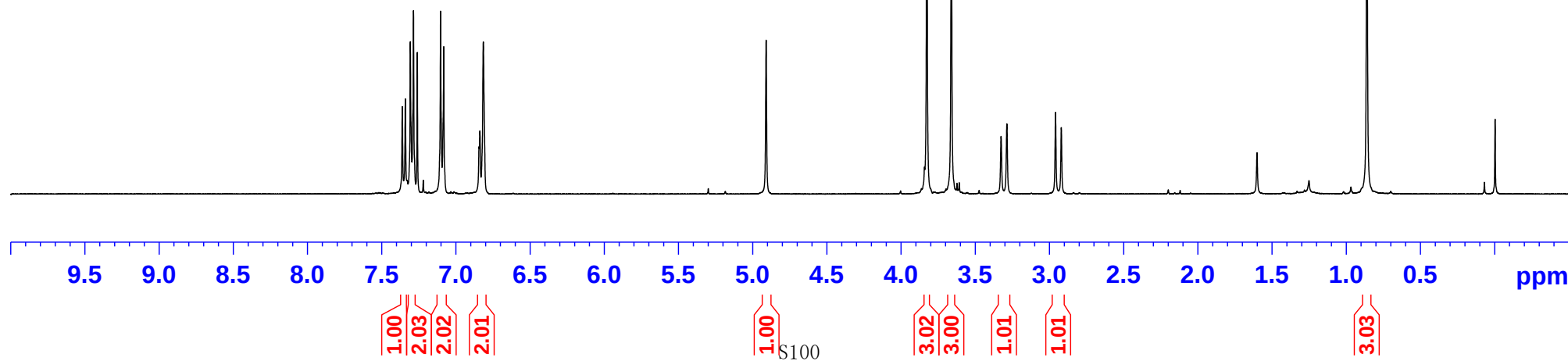
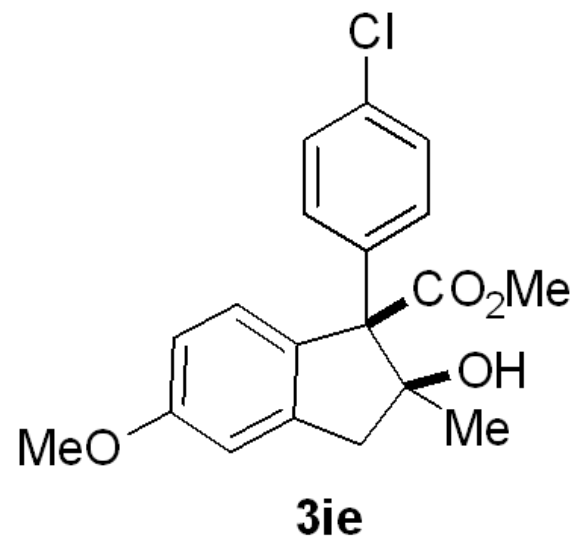
yyy-8-071-2

7.361
7.341
7.307
7.285
7.260
7.103
7.082
6.844
6.838
6.815

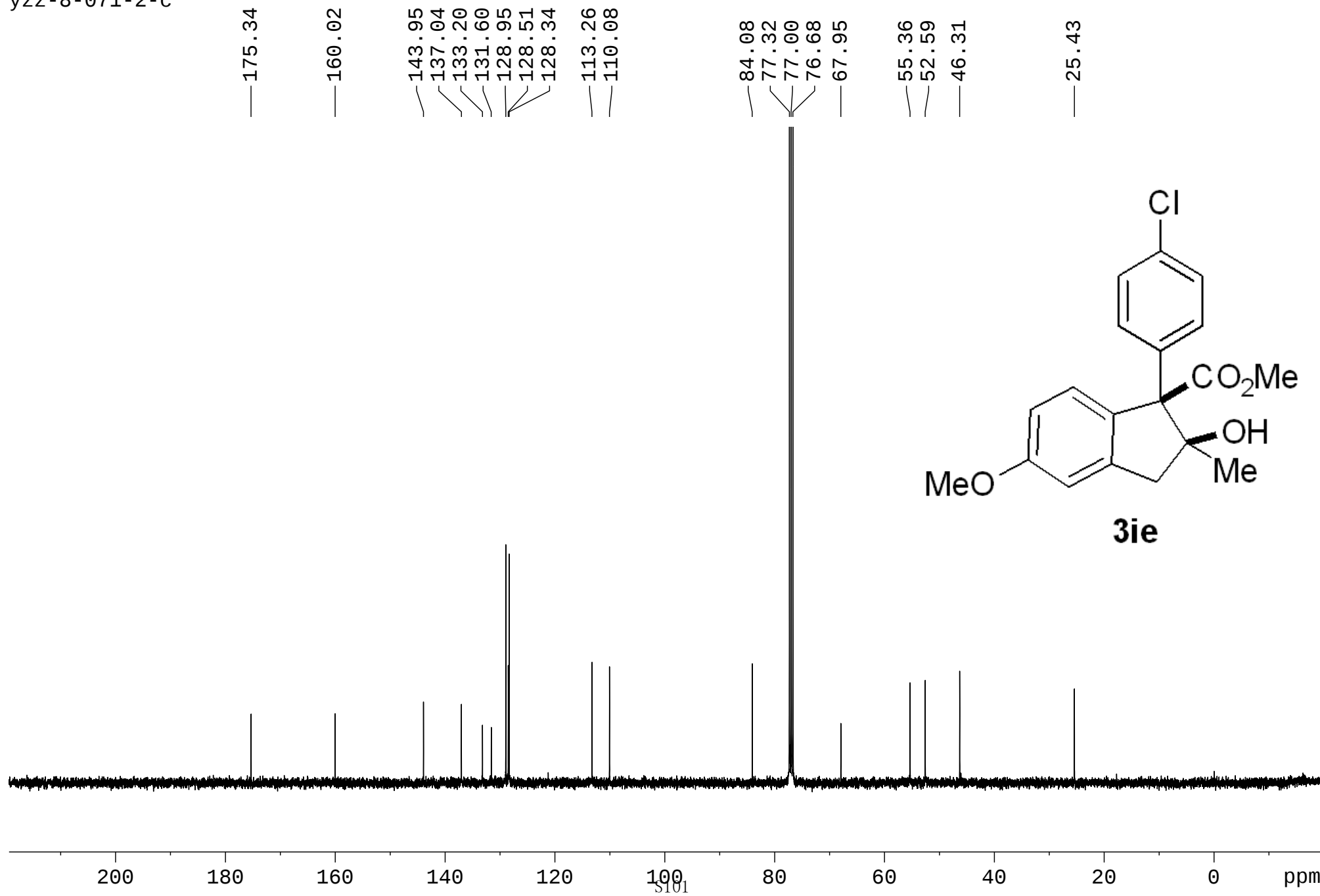
— 4.909

— 3.826
— 3.661
— 3.326
— 3.287
— 2.959
— 2.920

— 0.862

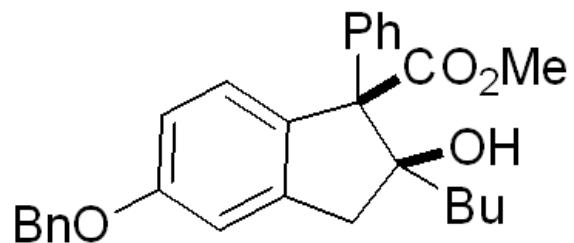


yyy-8-071-2-c

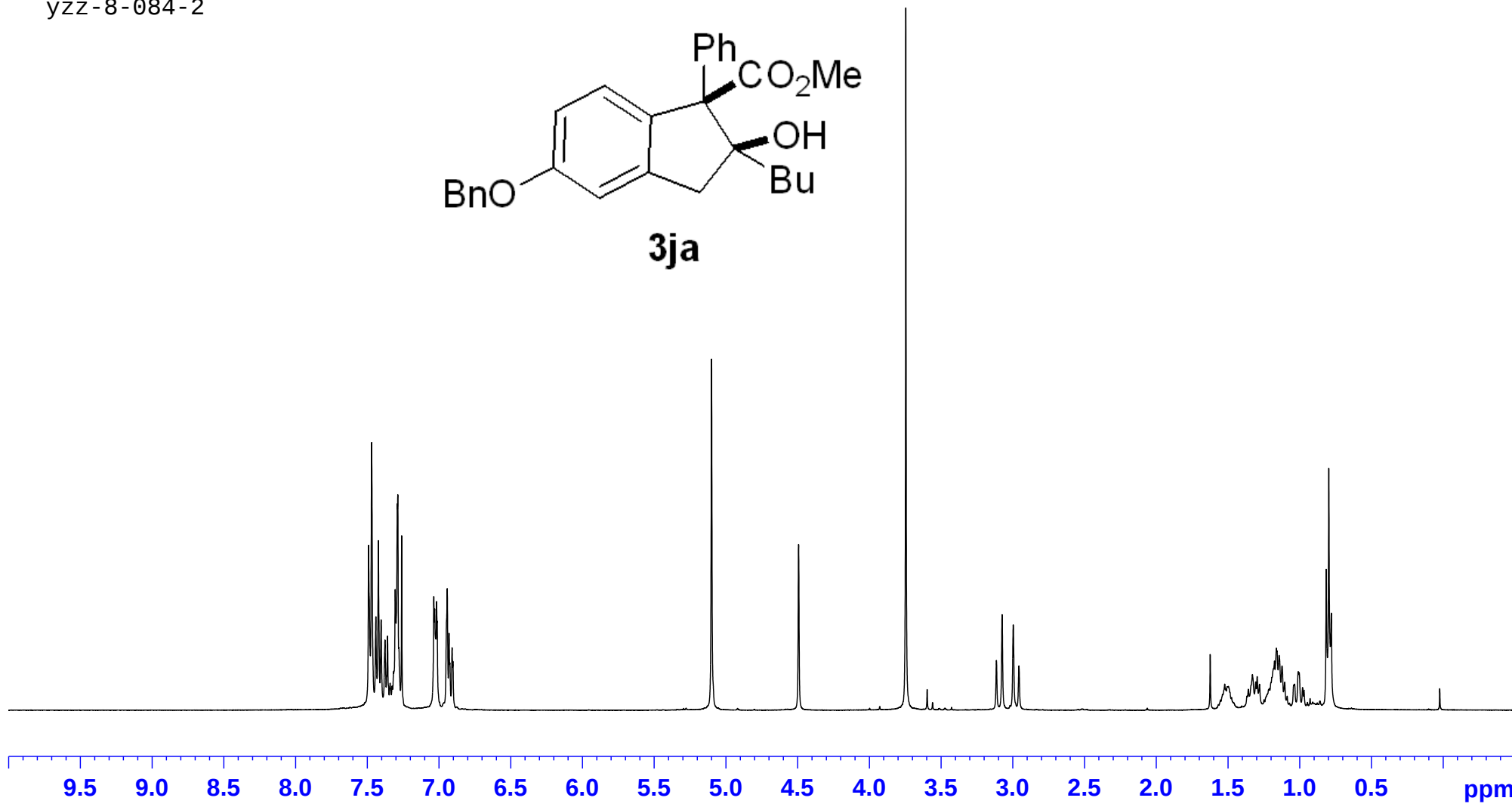


7.491
7.469
7.440
7.422
7.403
7.377
7.359
7.341
7.328
7.317
7.305
7.290
7.287
7.280
7.260
7.036
7.030
7.022
7.016
7.013
6.942
6.930
6.924
6.909
6.903
5.100
4.493
3.746
3.114
3.074
2.997
2.958
1.624
1.523
1.516
1.506
1.497
1.359
1.330
1.307
1.297
1.281
1.218
1.213
1.201
1.176
1.163
1.159
1.144
1.124
1.105
1.042
1.036
1.011
1.004
0.981
0.816
0.798
0.780

yyy-8-084-2



3ja



3.05
2.08
1.06
3.03
2.03
2.01

2.02

1.00

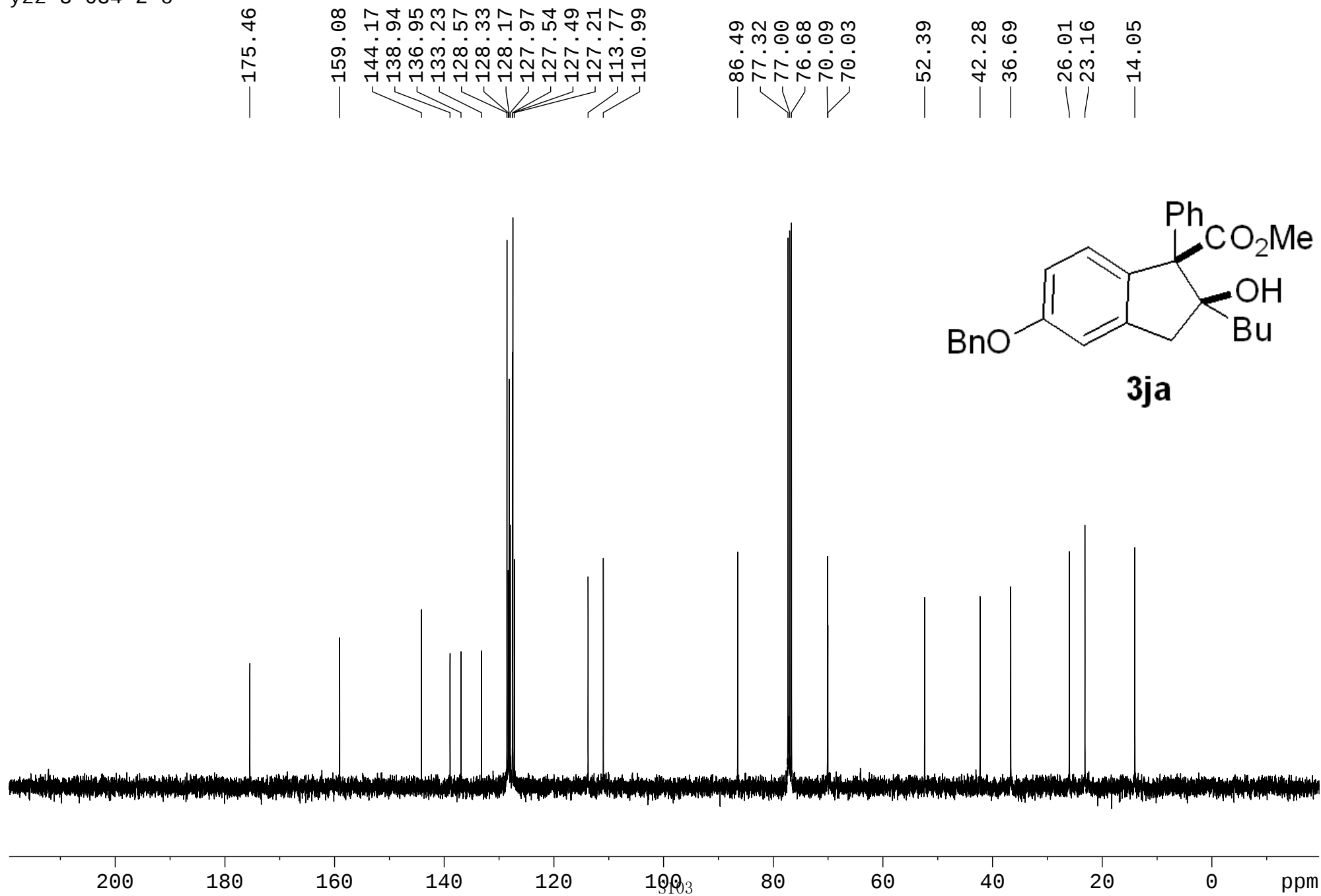
3.00

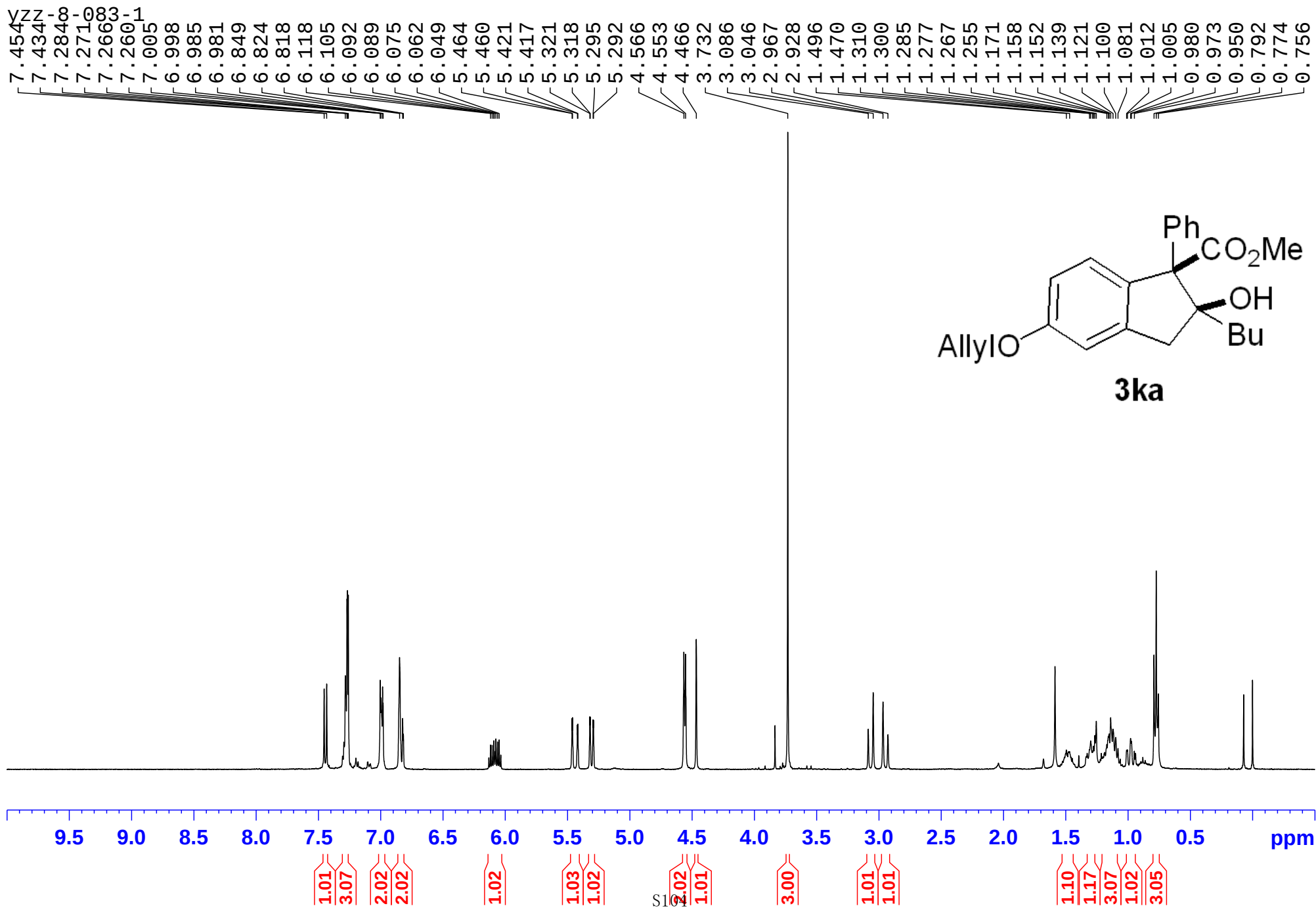
1.02
1.02

1.07
1.17
3.08
1.03
3.03

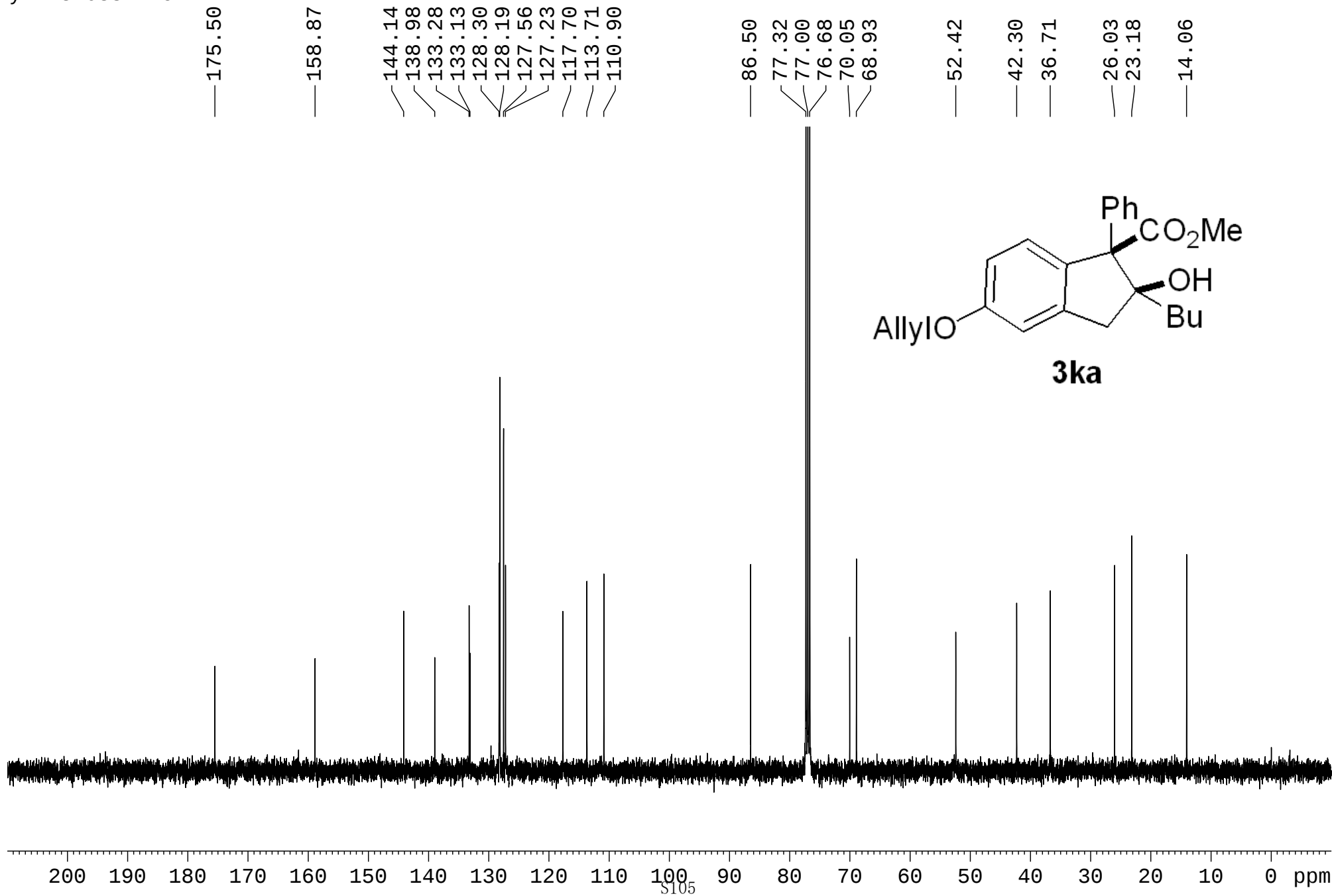
S102

yyy-8-084-2-c

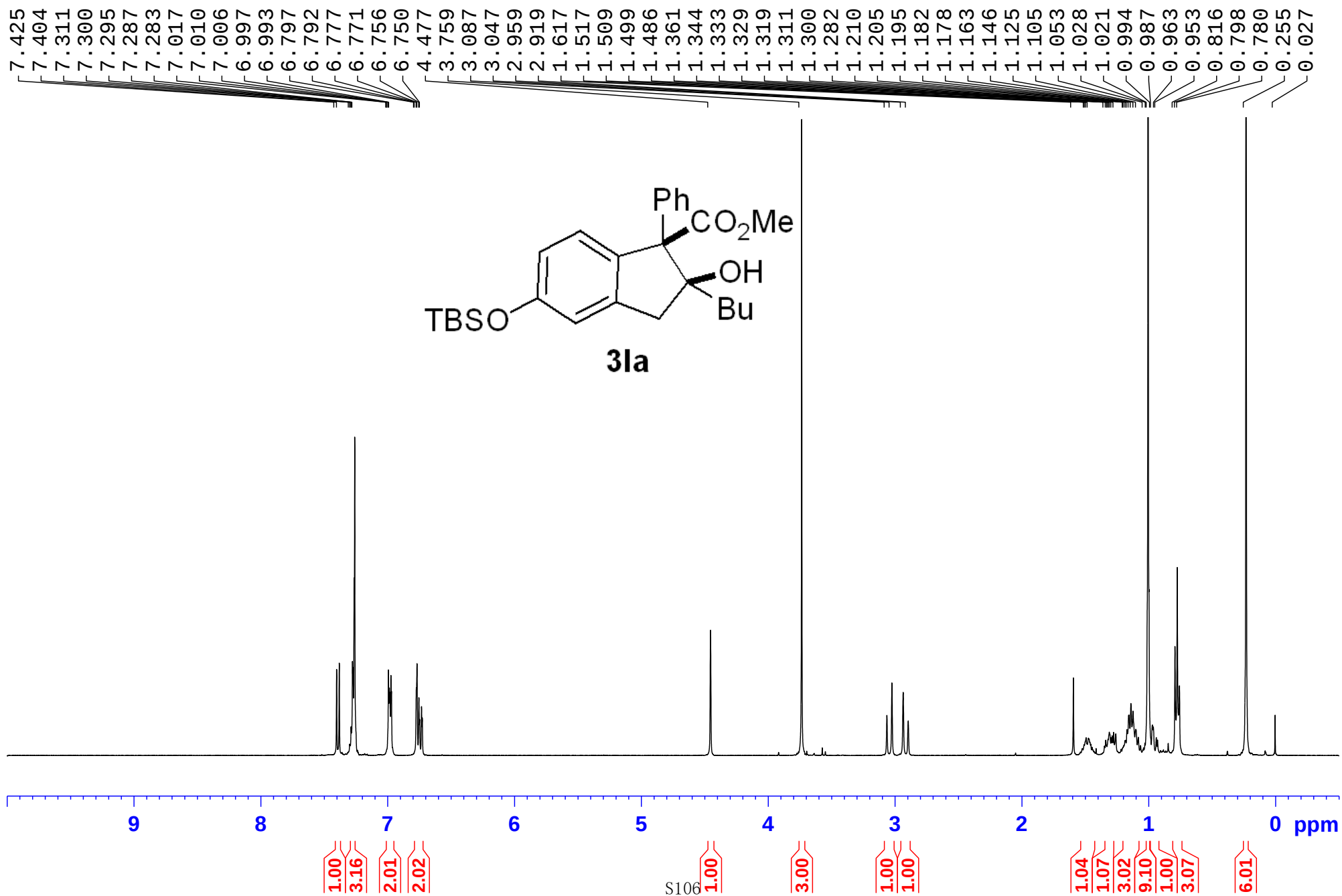




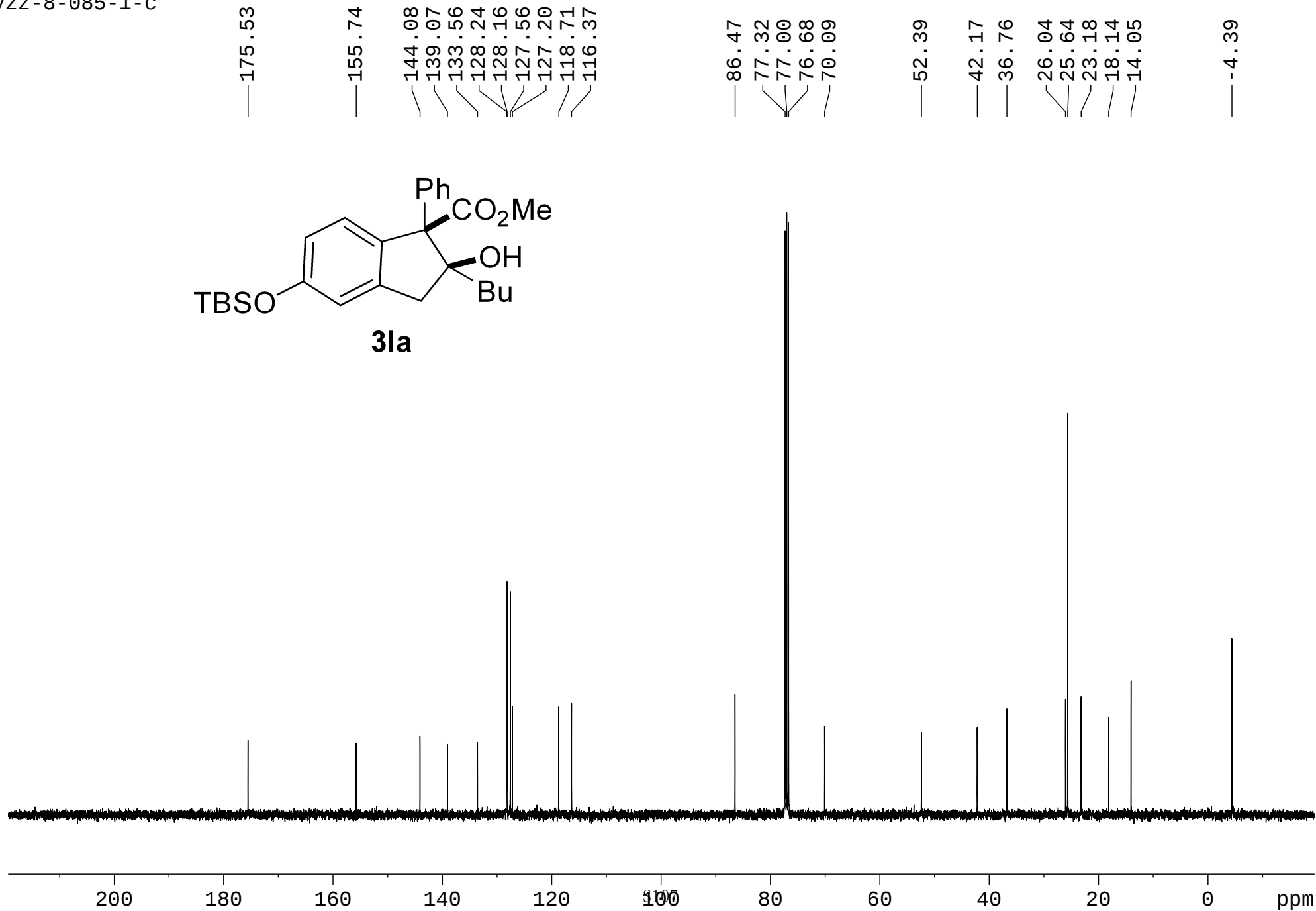
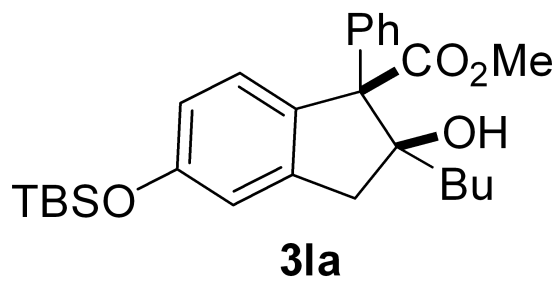
yyy-8-083-1-c



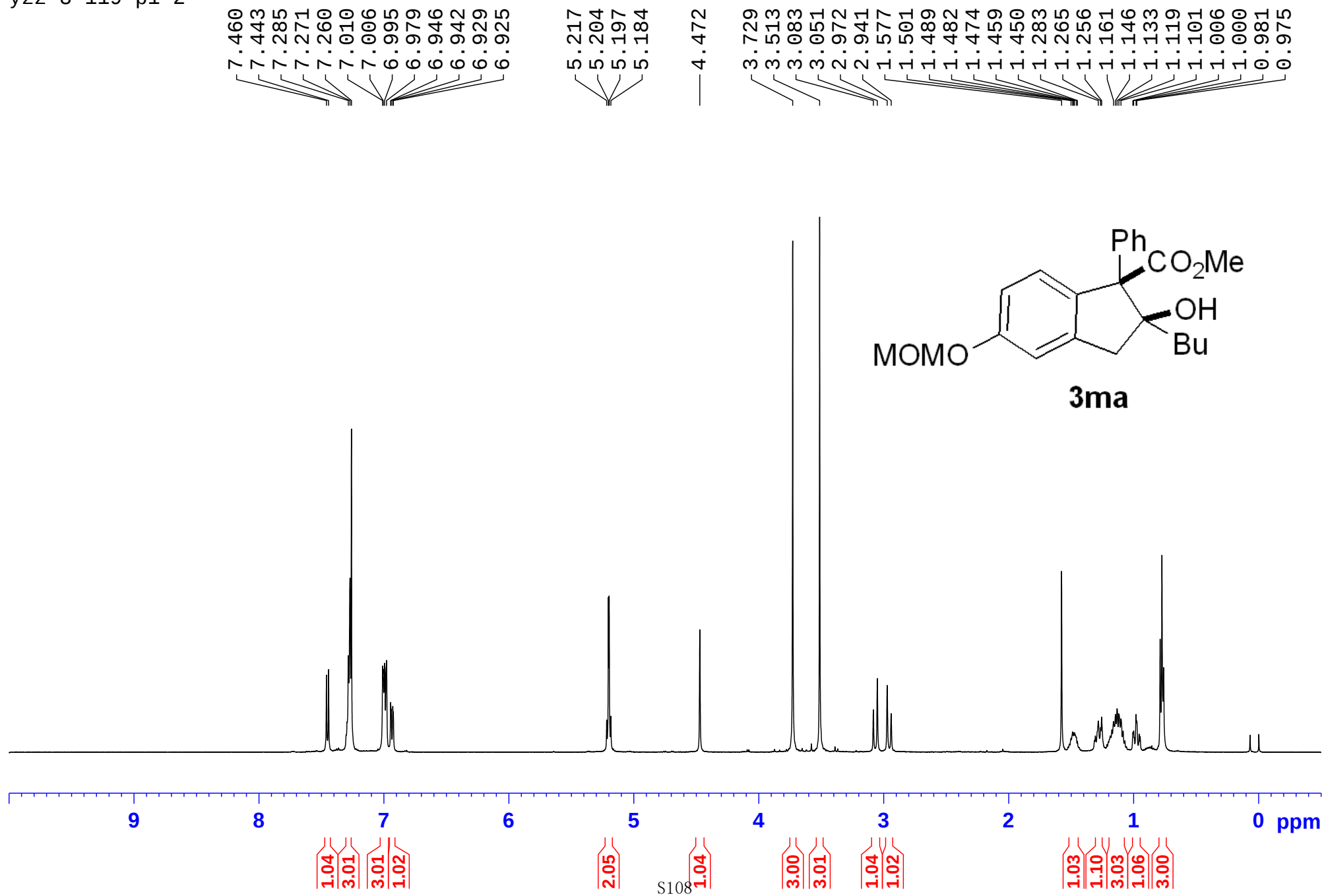
yyy-8-085-1-h



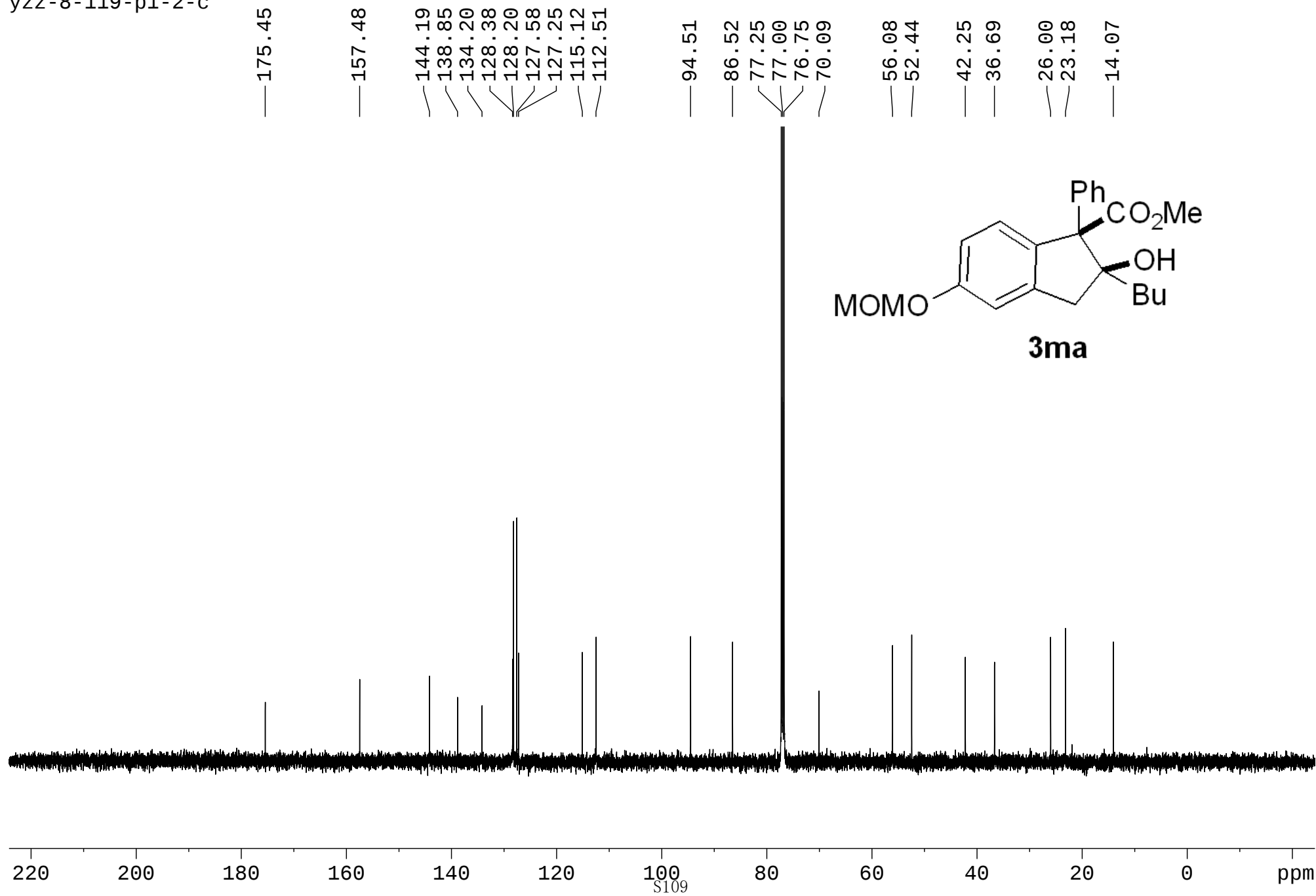
yyy-8-085-1-c



yyy-8-119-p1-2



yyy-8-119-p1-2-c

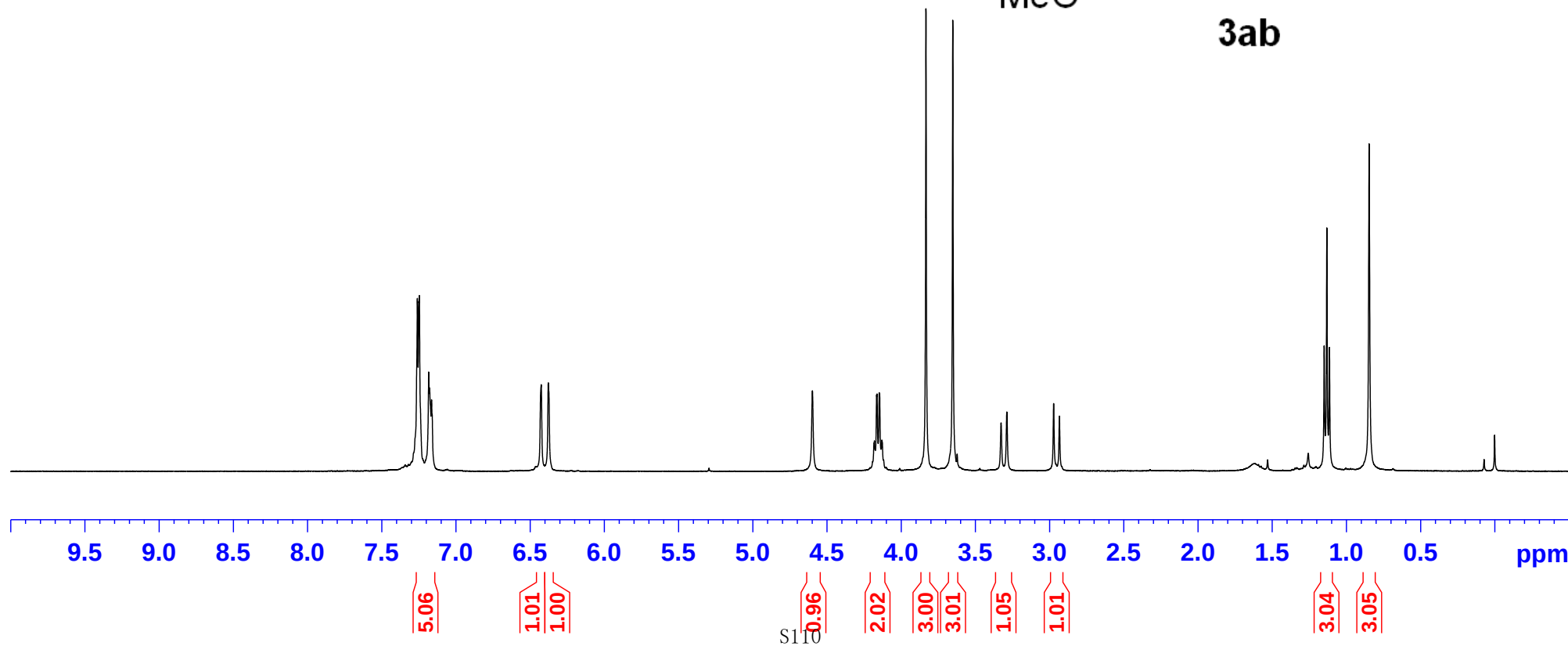
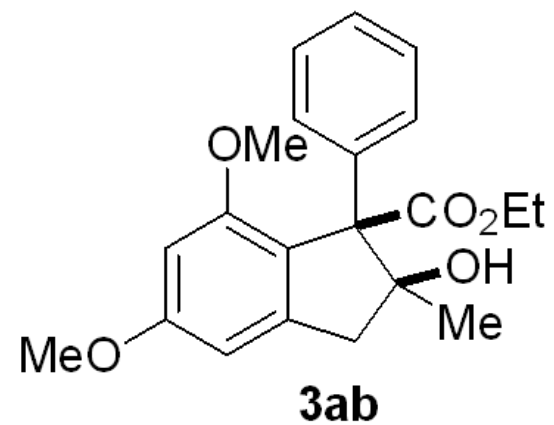


yyy-7-032-02

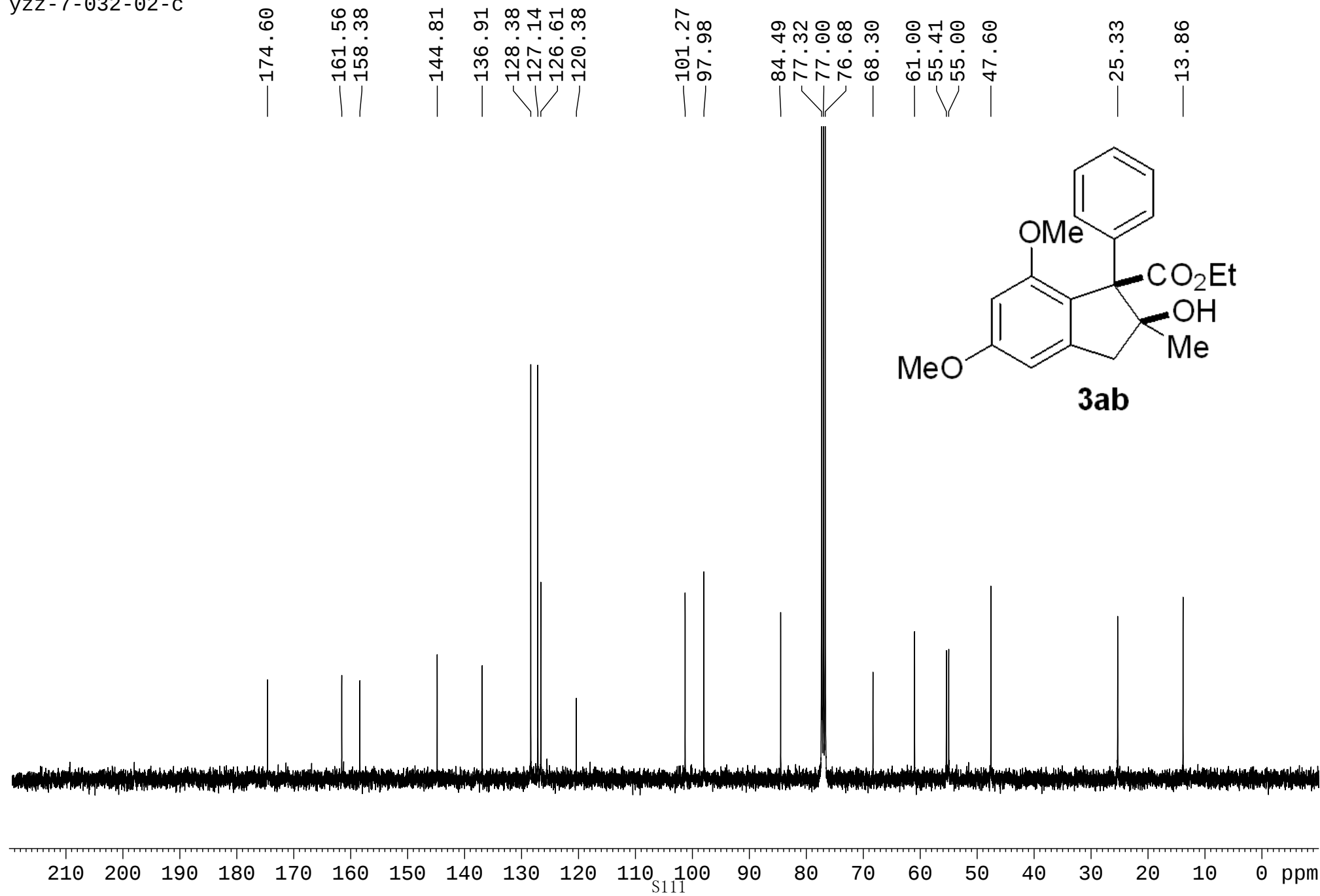
7.260
7.250
7.247
7.184
7.177
7.164
6.426
6.378

4.598
4.180
4.166
4.163
4.148
4.145
4.130
3.833
3.652
3.327
3.288
2.973
2.934

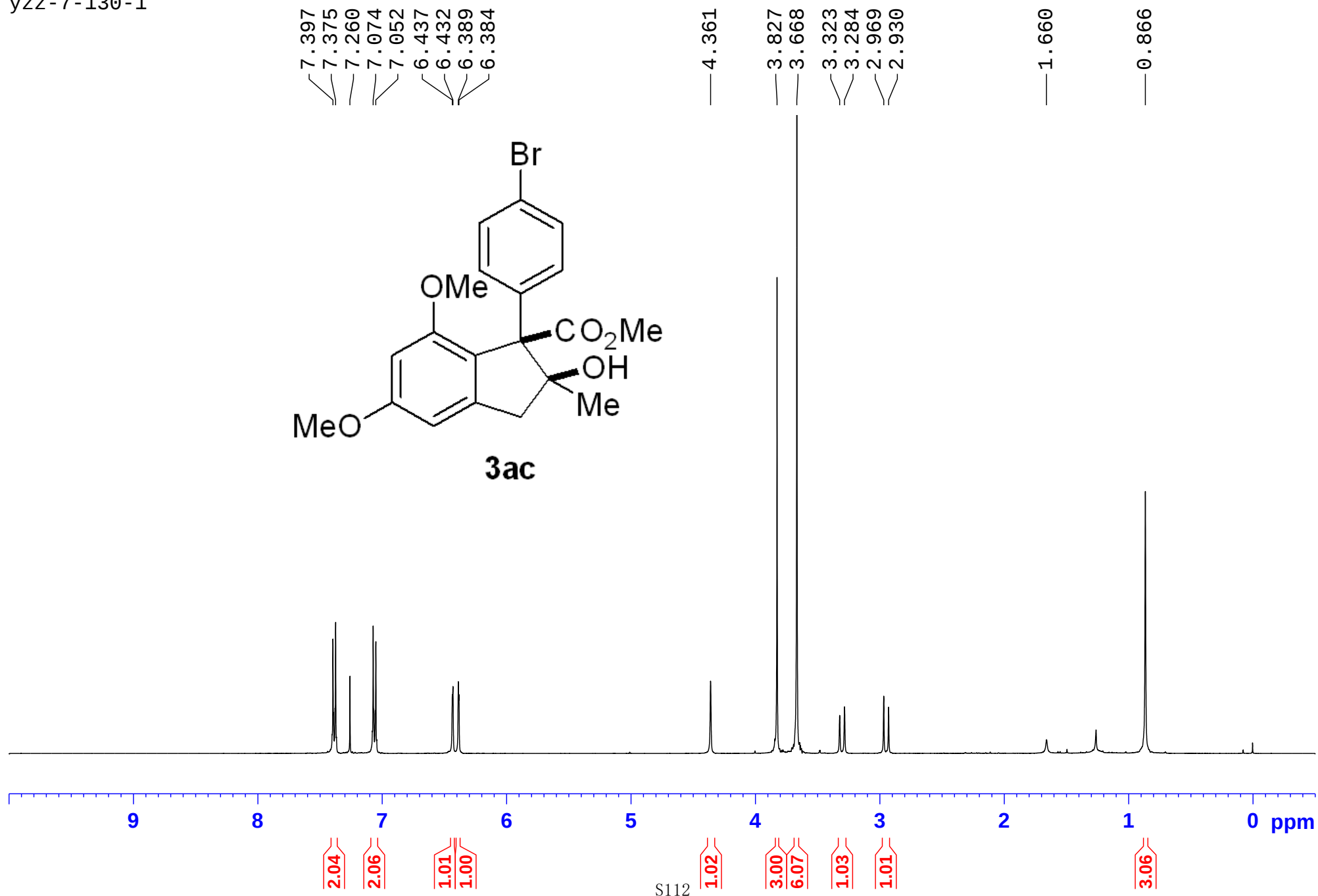
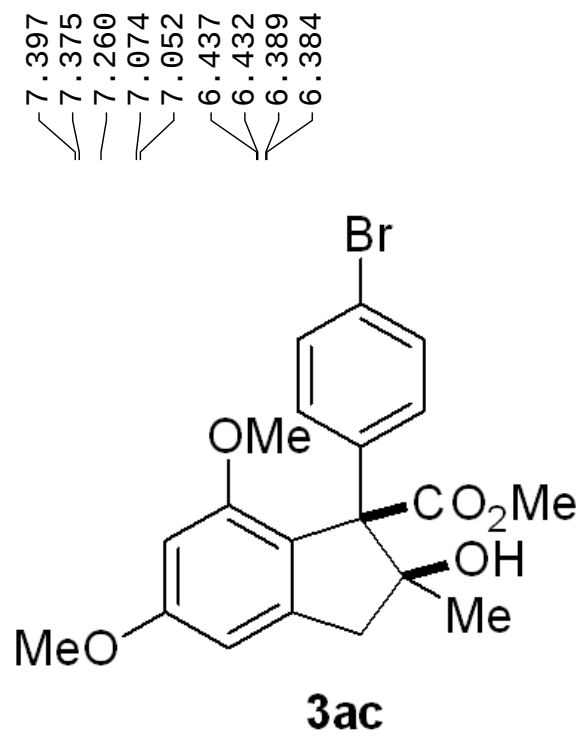
1.150
1.132
1.114
0.847



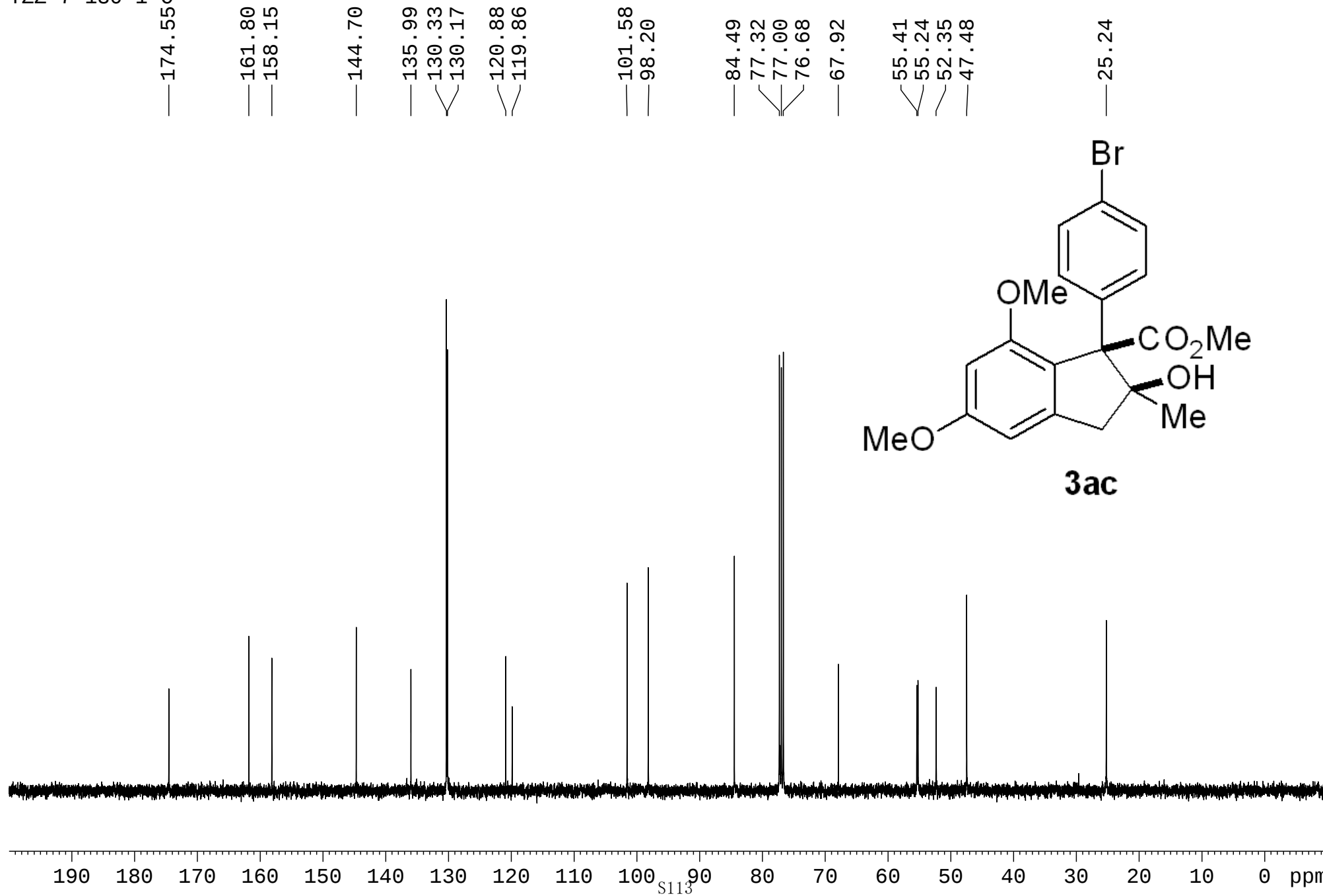
yyy-7-032-02-c



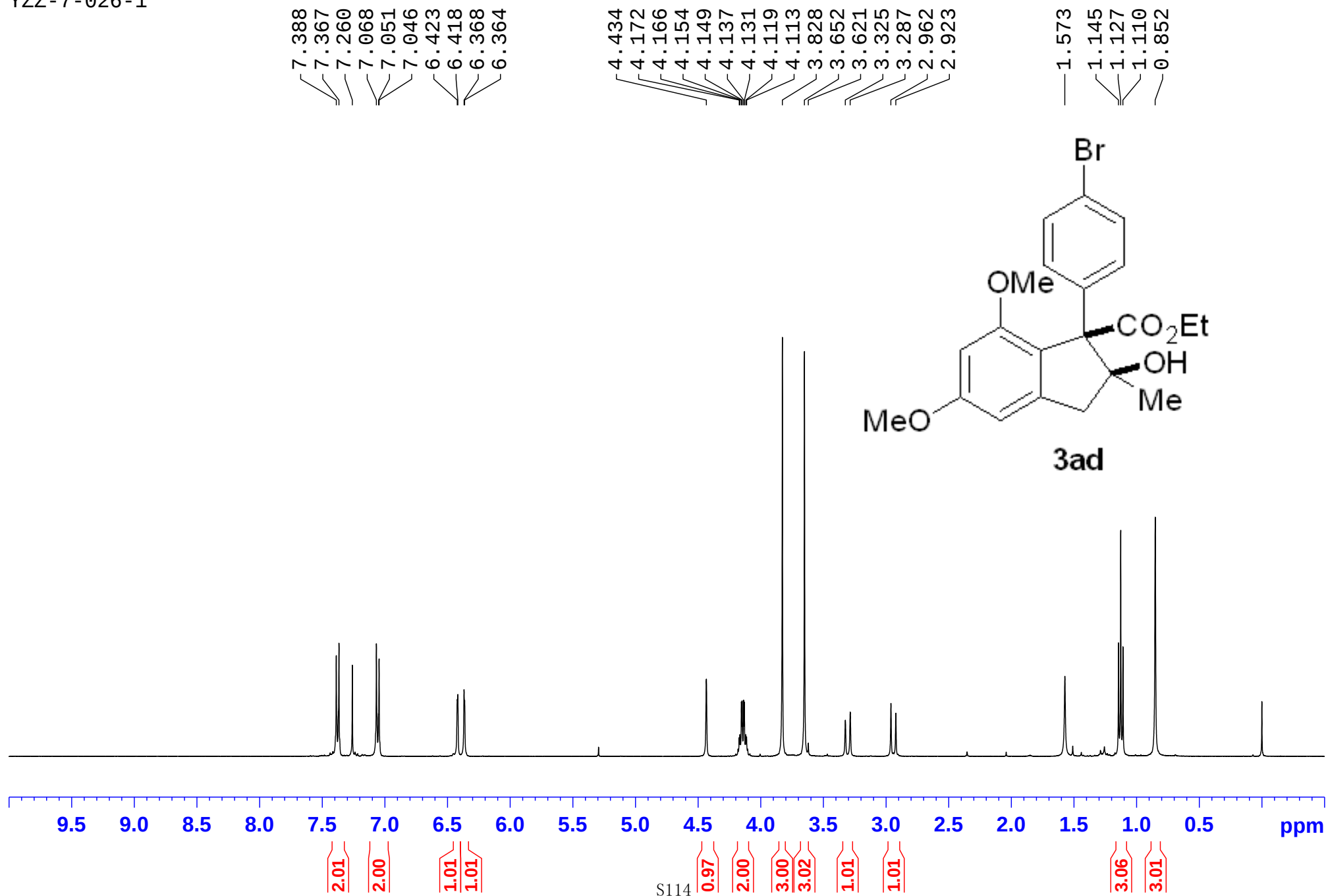
yyy-7-130-1



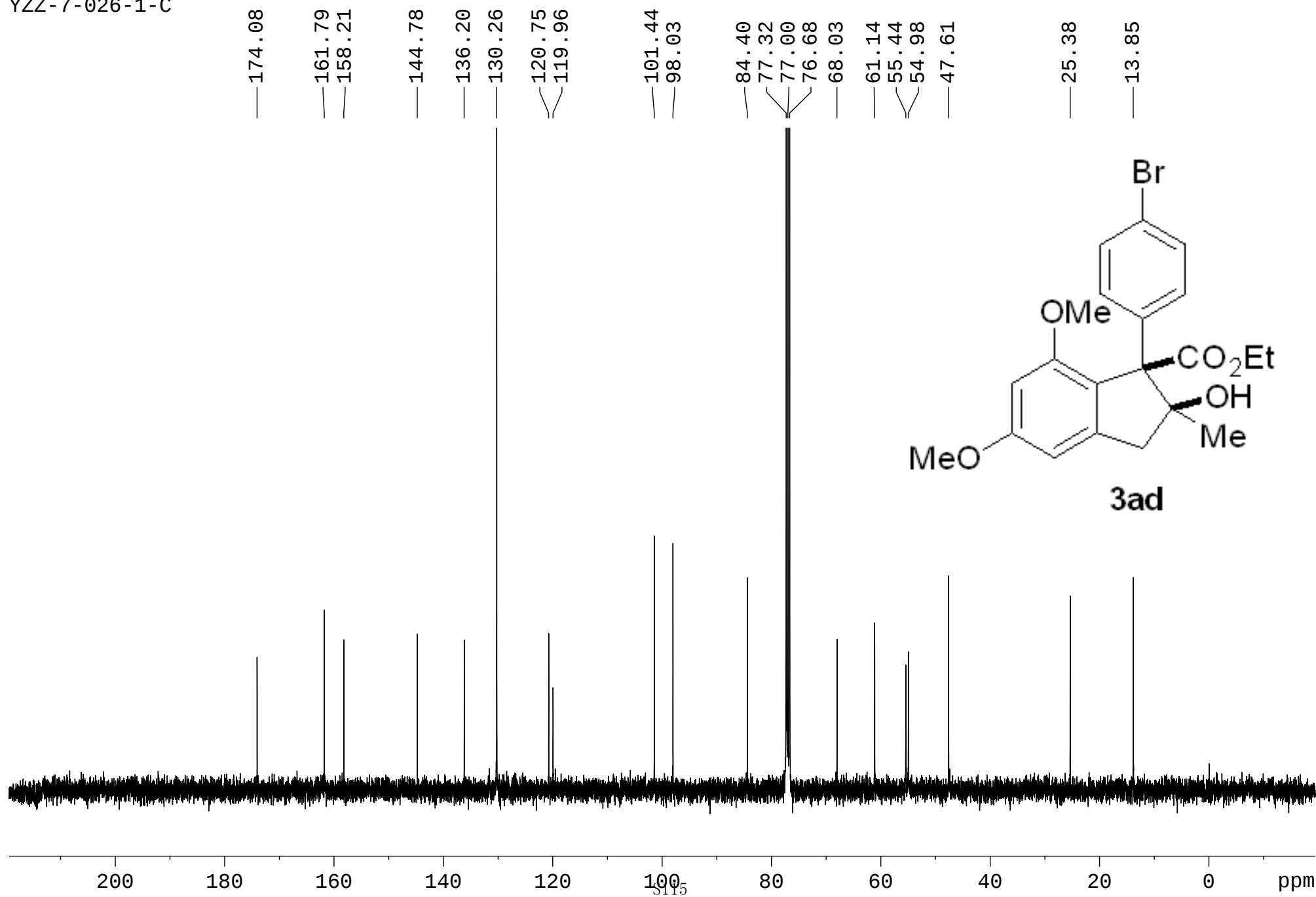
YZZ-7-130-1-C



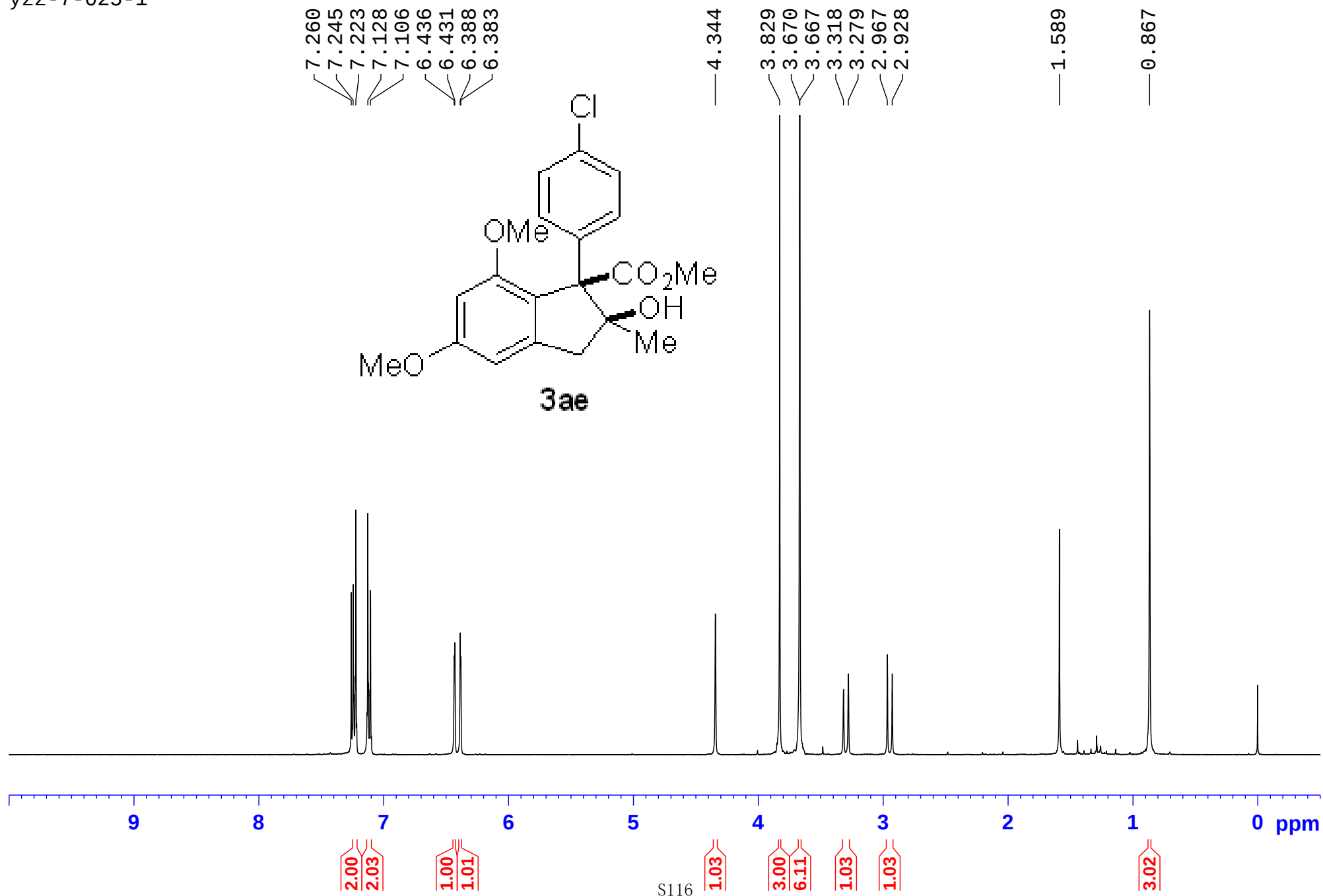
YZZ-7-026-1



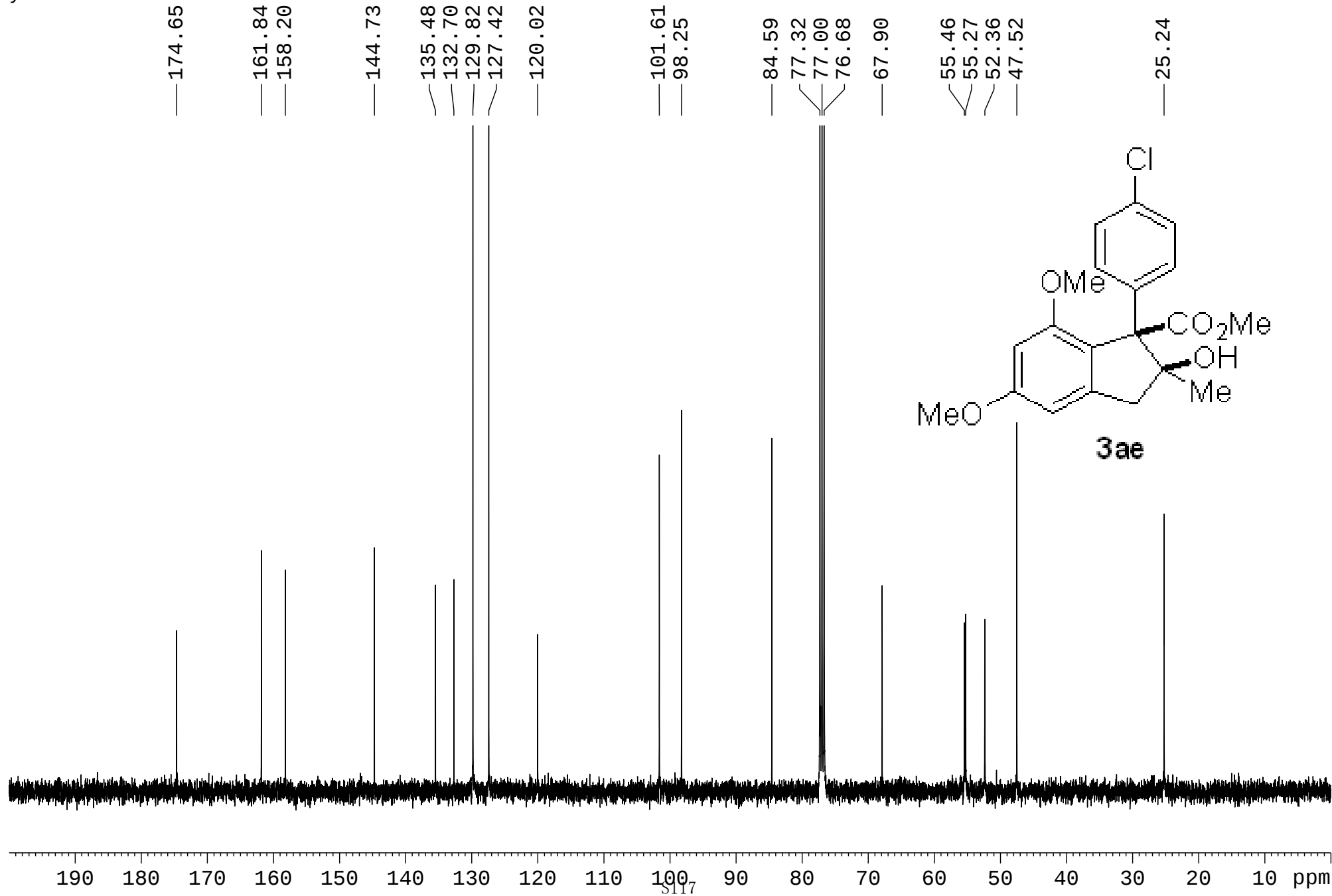
YZZ-7-026-1-C



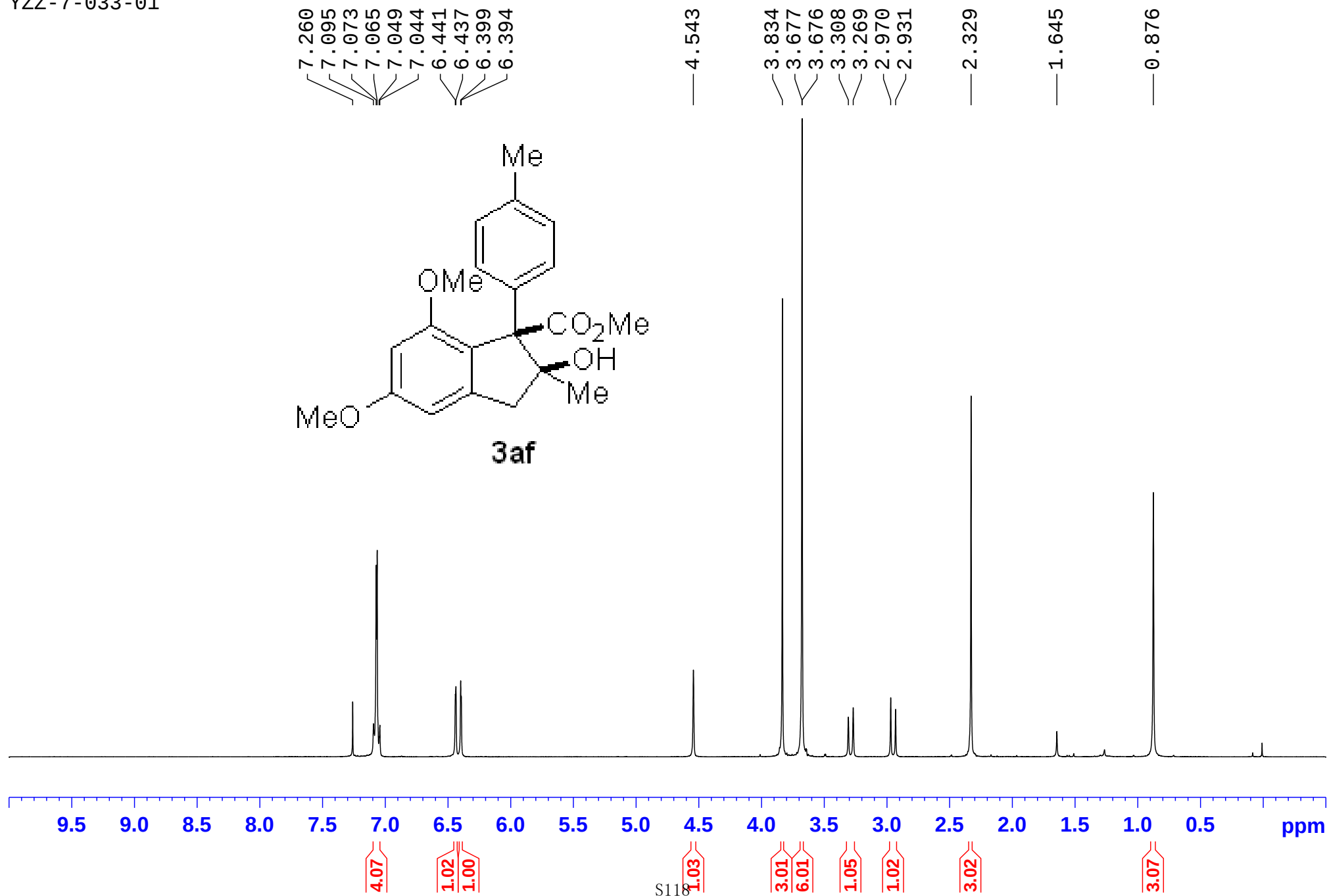
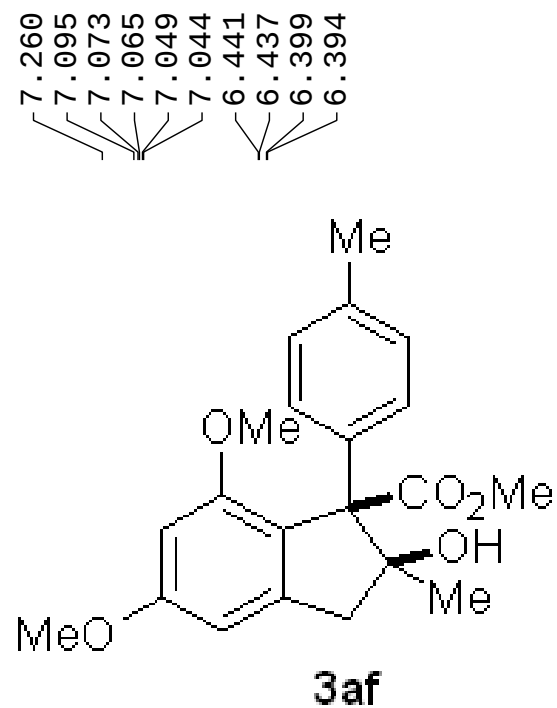
yyy-7-025-1



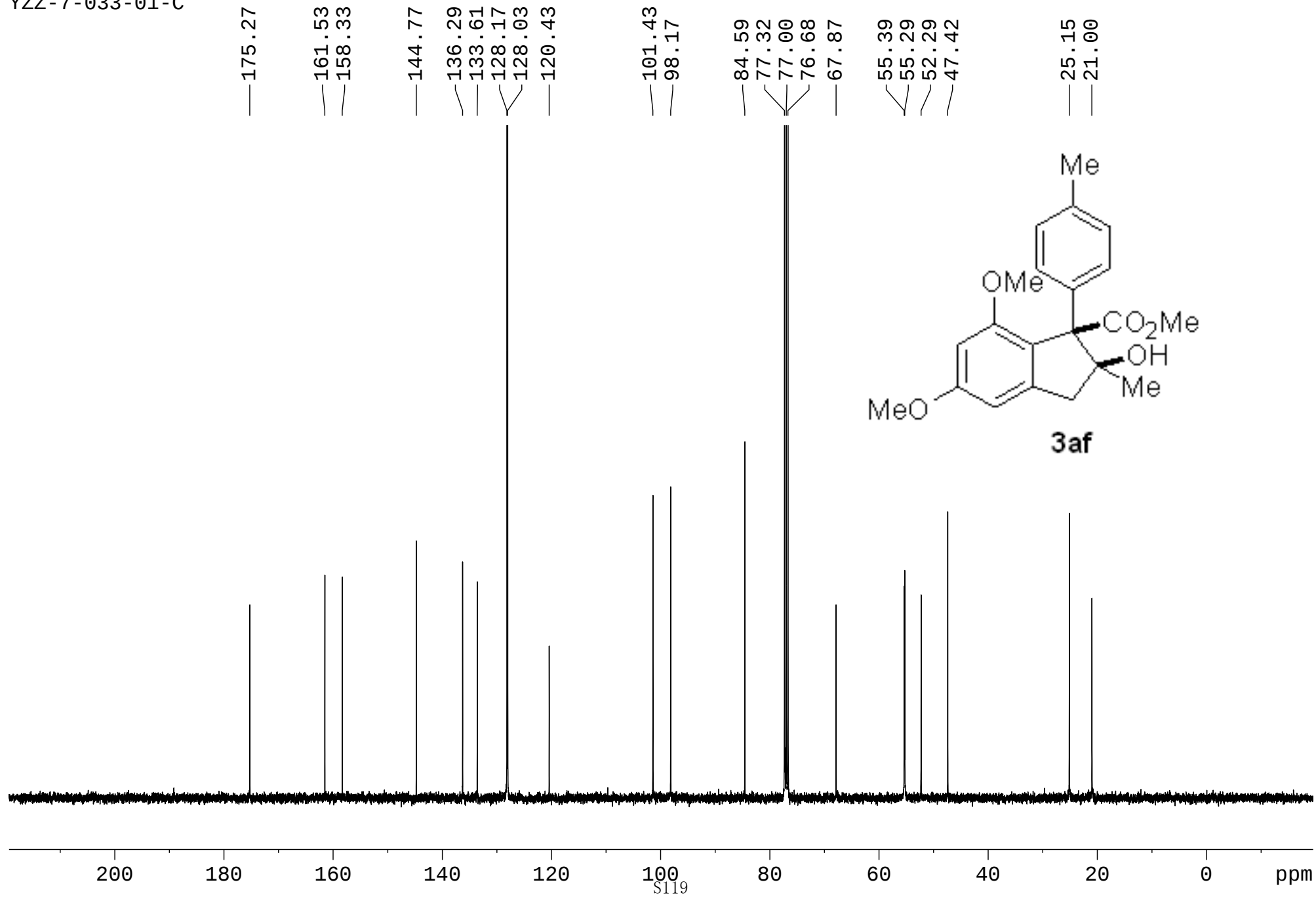
yyy-7-025-1-c



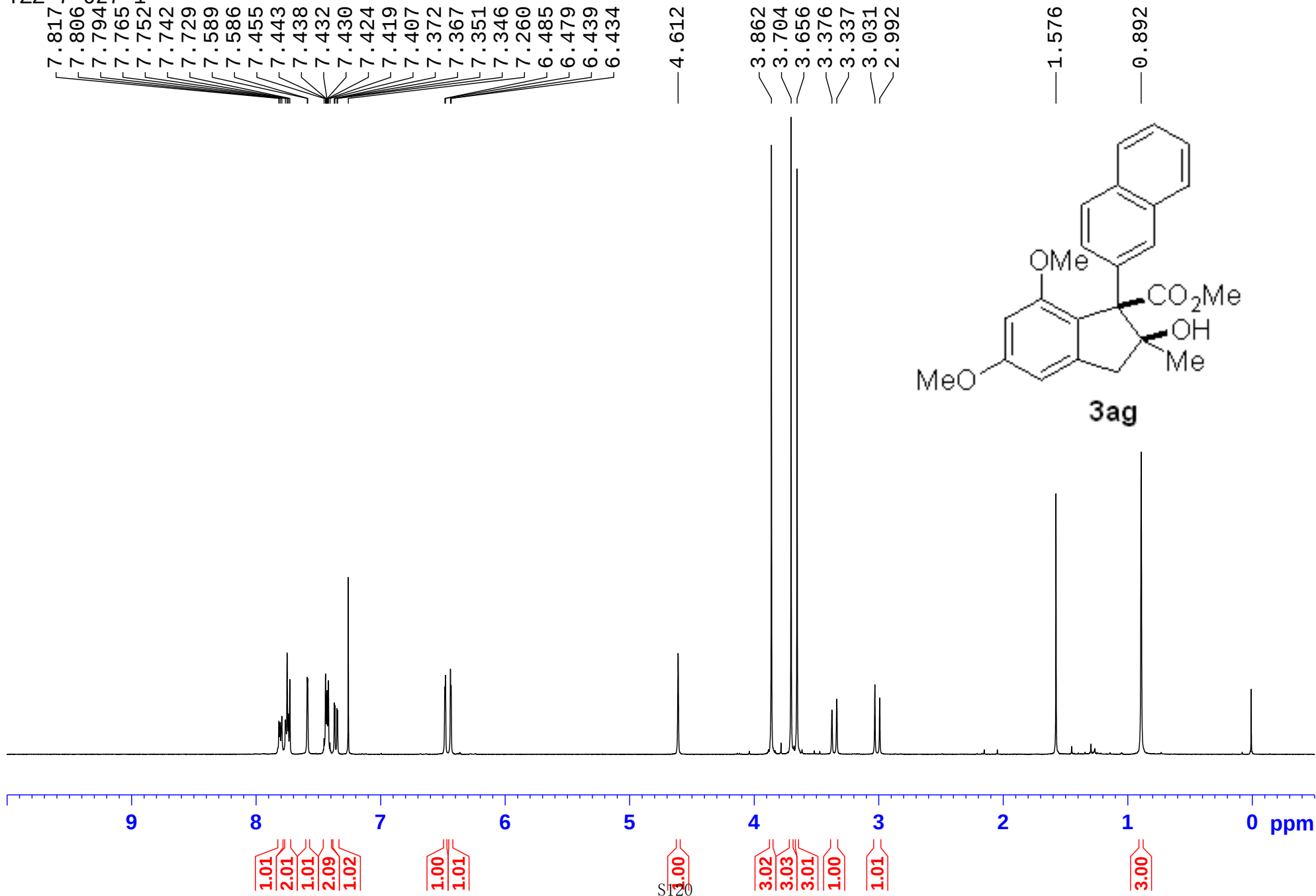
YZZ-7-033-01



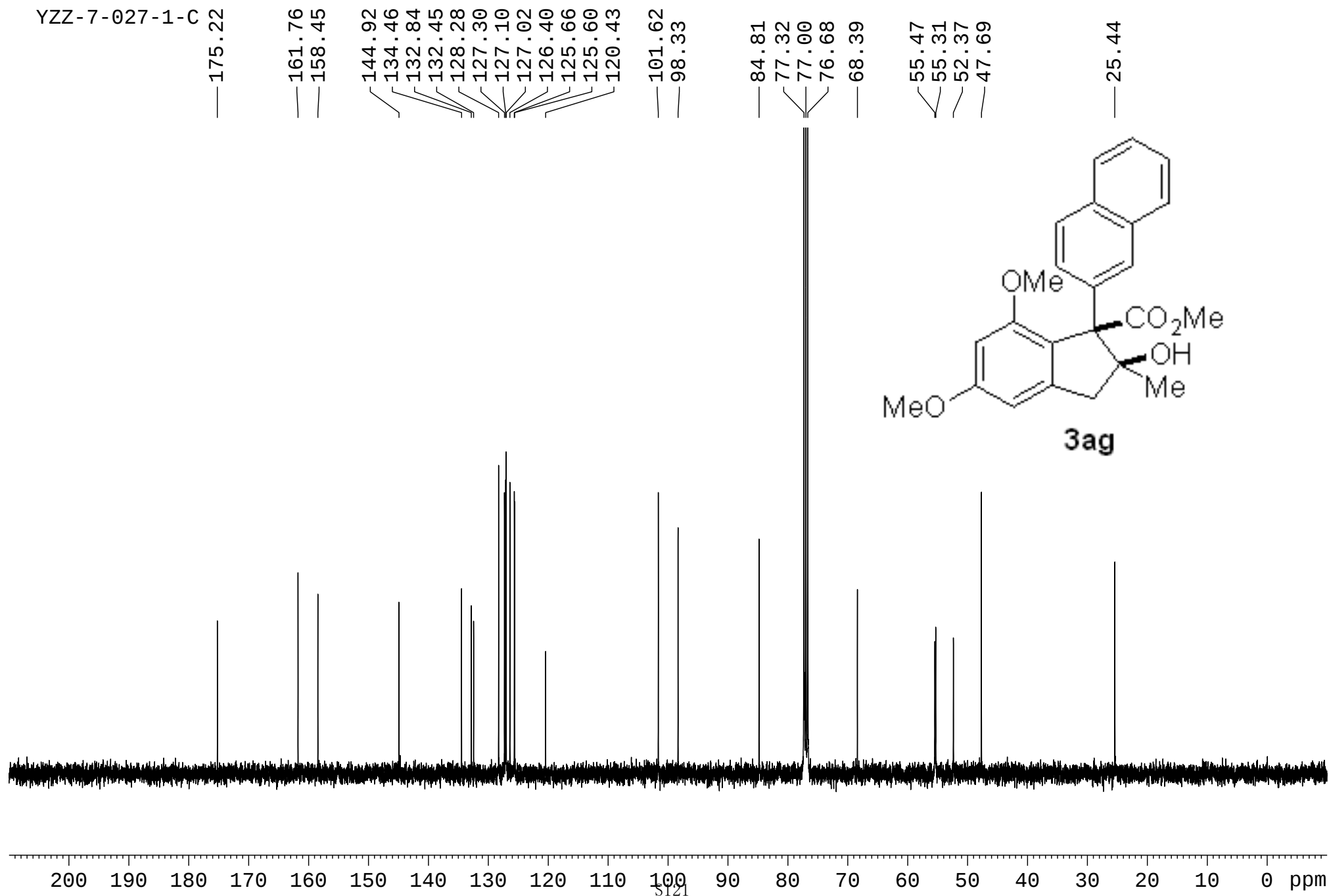
YZZ-7-033-01-C



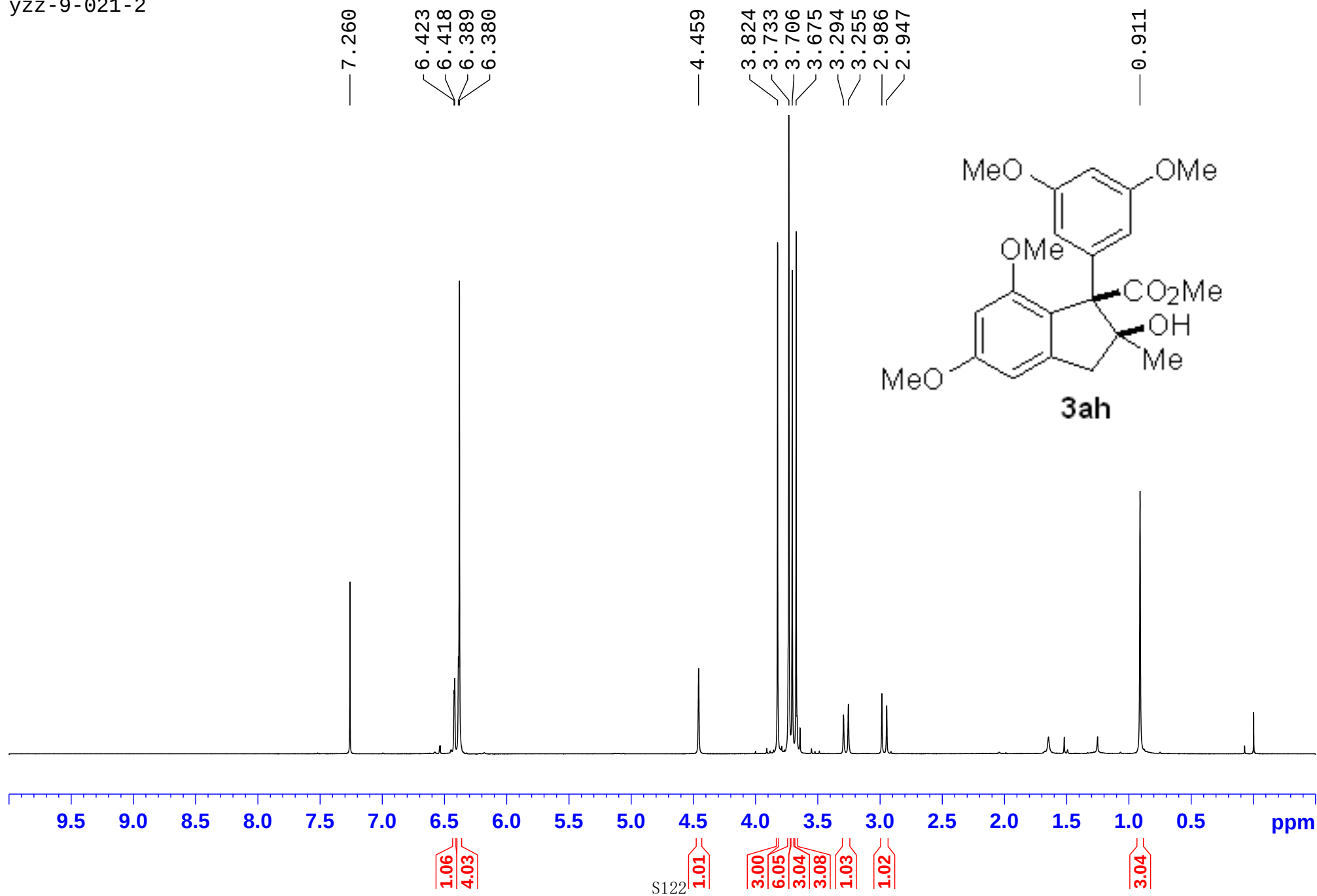
YZZ-7-027-1



YZZ-7-027-1-C

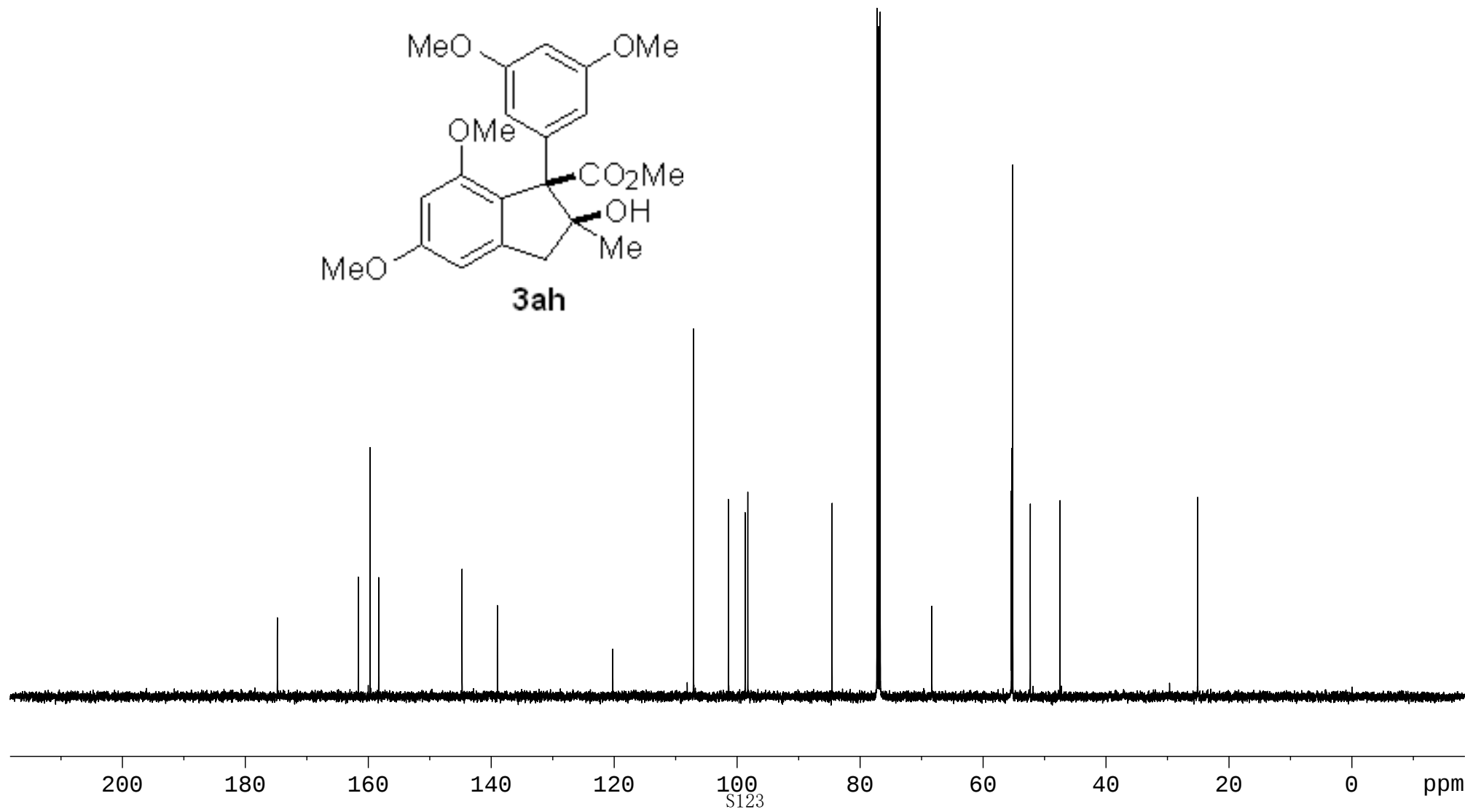
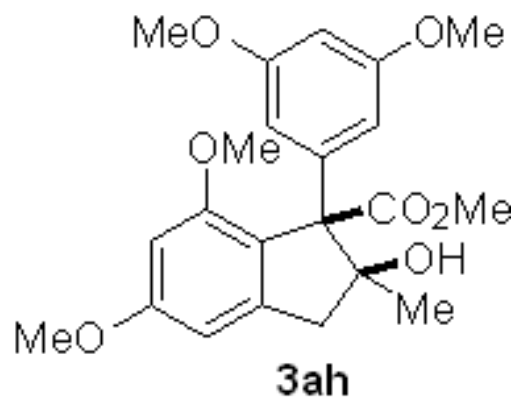


yyy-9-021-2



yyy-9-021-1-c

—174.81
161.63
159.73
158.33
—144.76
—139.01
—120.25
107.11
101.44
98.71
98.27
84.57
77.25
77.00
76.75
68.34
55.41
55.35
55.17
52.32
47.49
—25.09



yyy-7-060-p1-1

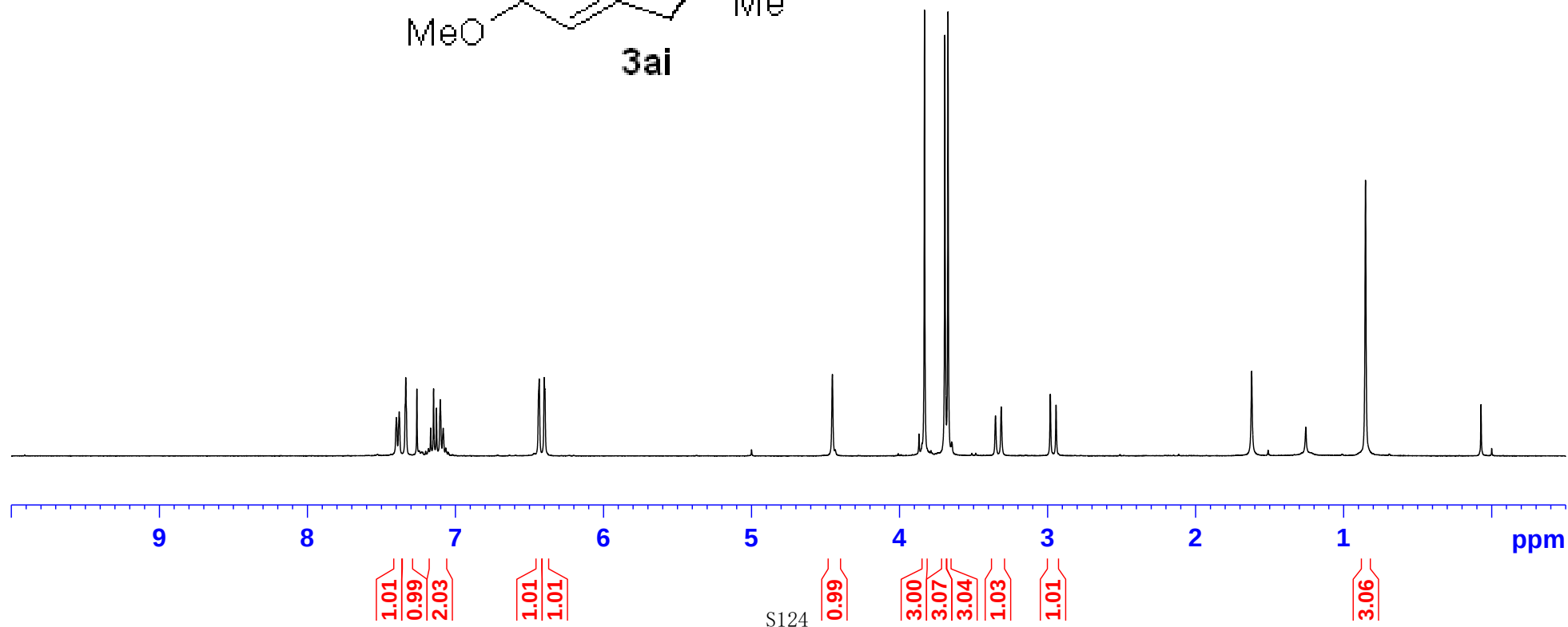
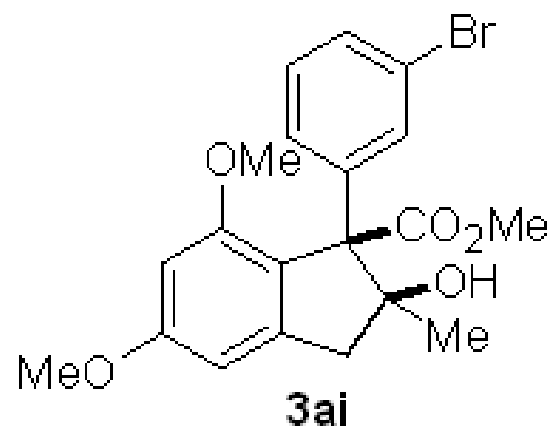
7.399
7.379
7.335
7.260
7.167
7.147
7.128
7.102
7.082
7.065
6.434
6.400
6.395

— 4.454

3.832
3.694
3.673
3.352
3.313
2.982
2.943

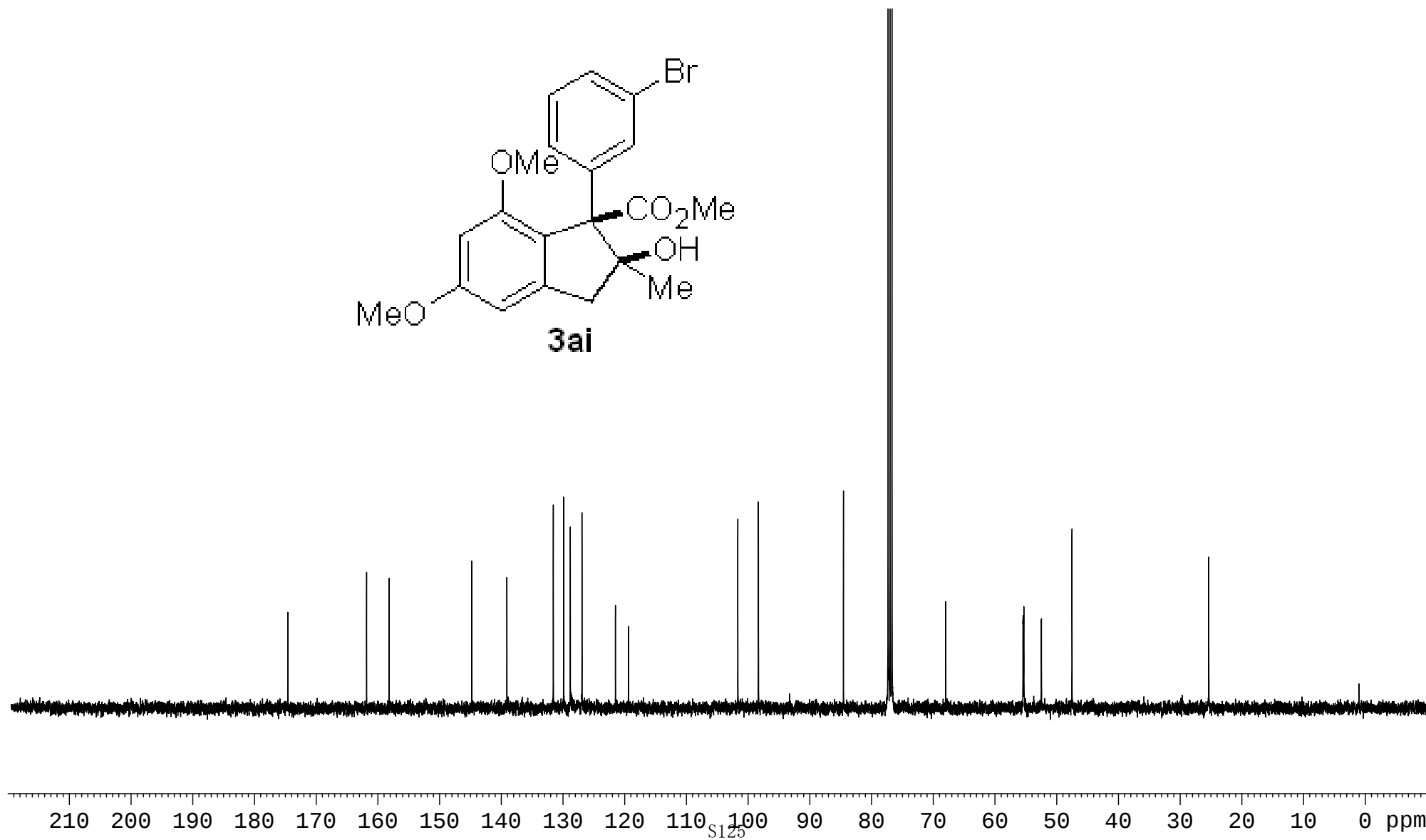
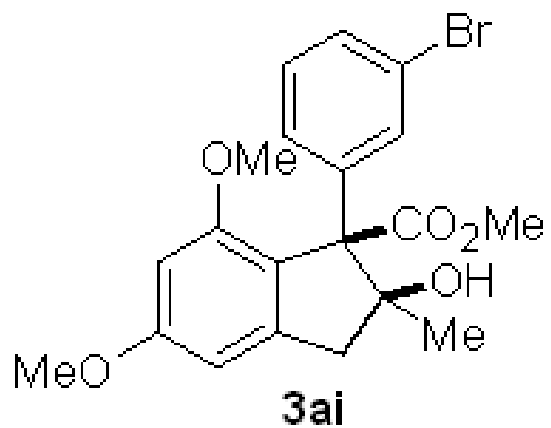
— 1.621

— 0.852

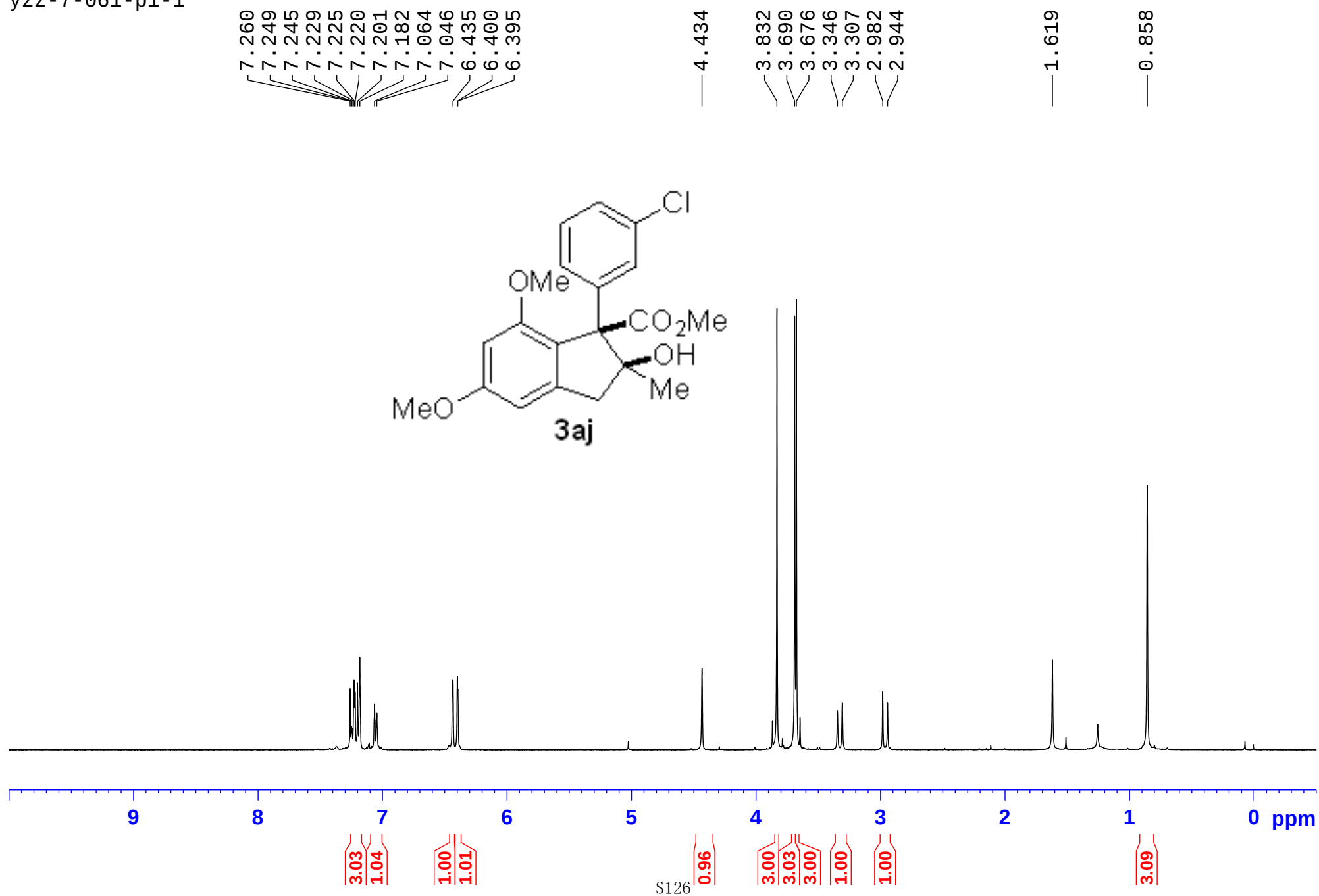


YZZ-7-060-P1-C

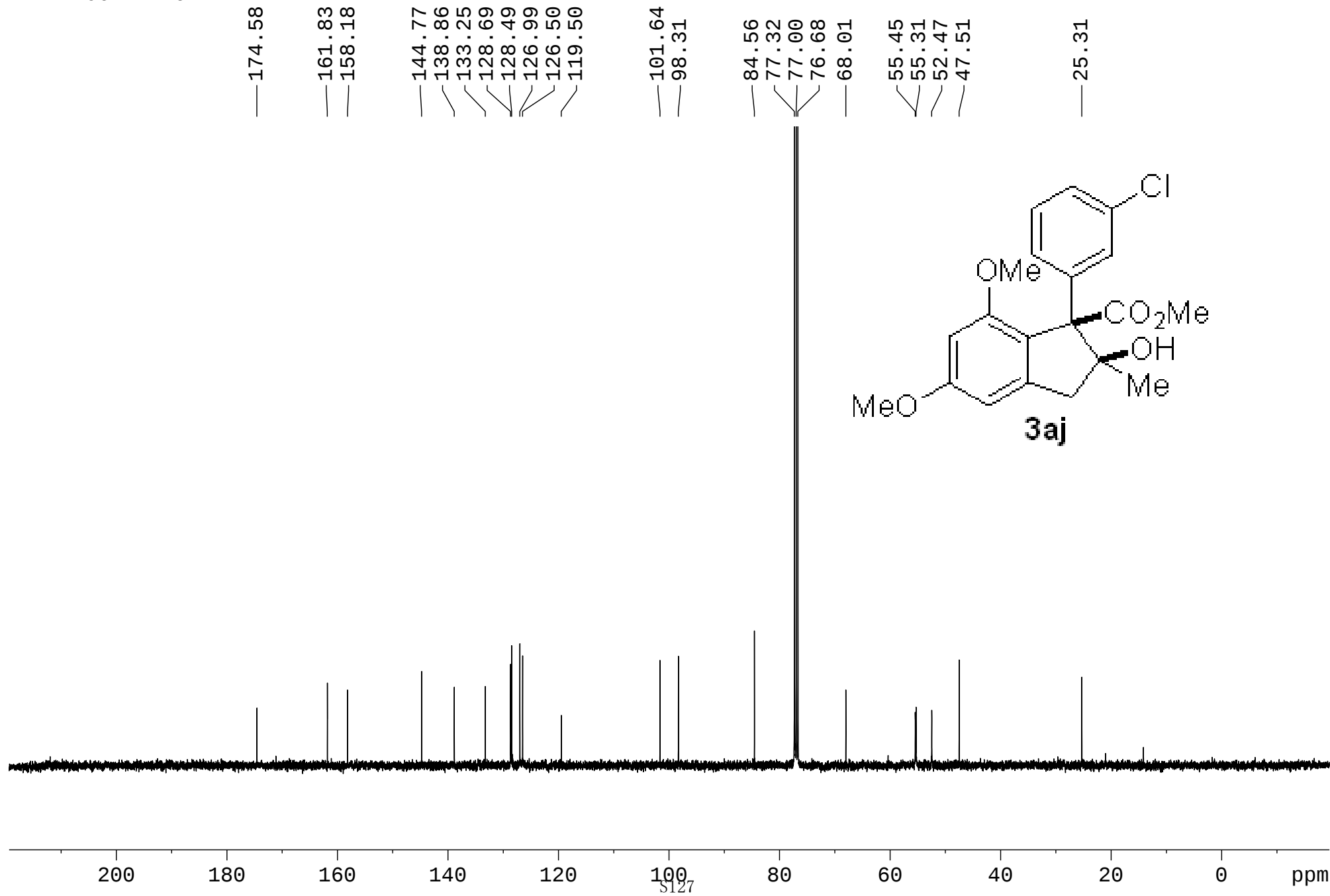
—174.59
—161.83
—158.17
—144.78
—139.09
—131.57
—129.90
—128.81
—126.92
—121.50
—119.40
—101.67
—98.32
—84.55
77.32
77.00
76.68
—67.96
55.44
55.32
52.47
47.51
—25.35



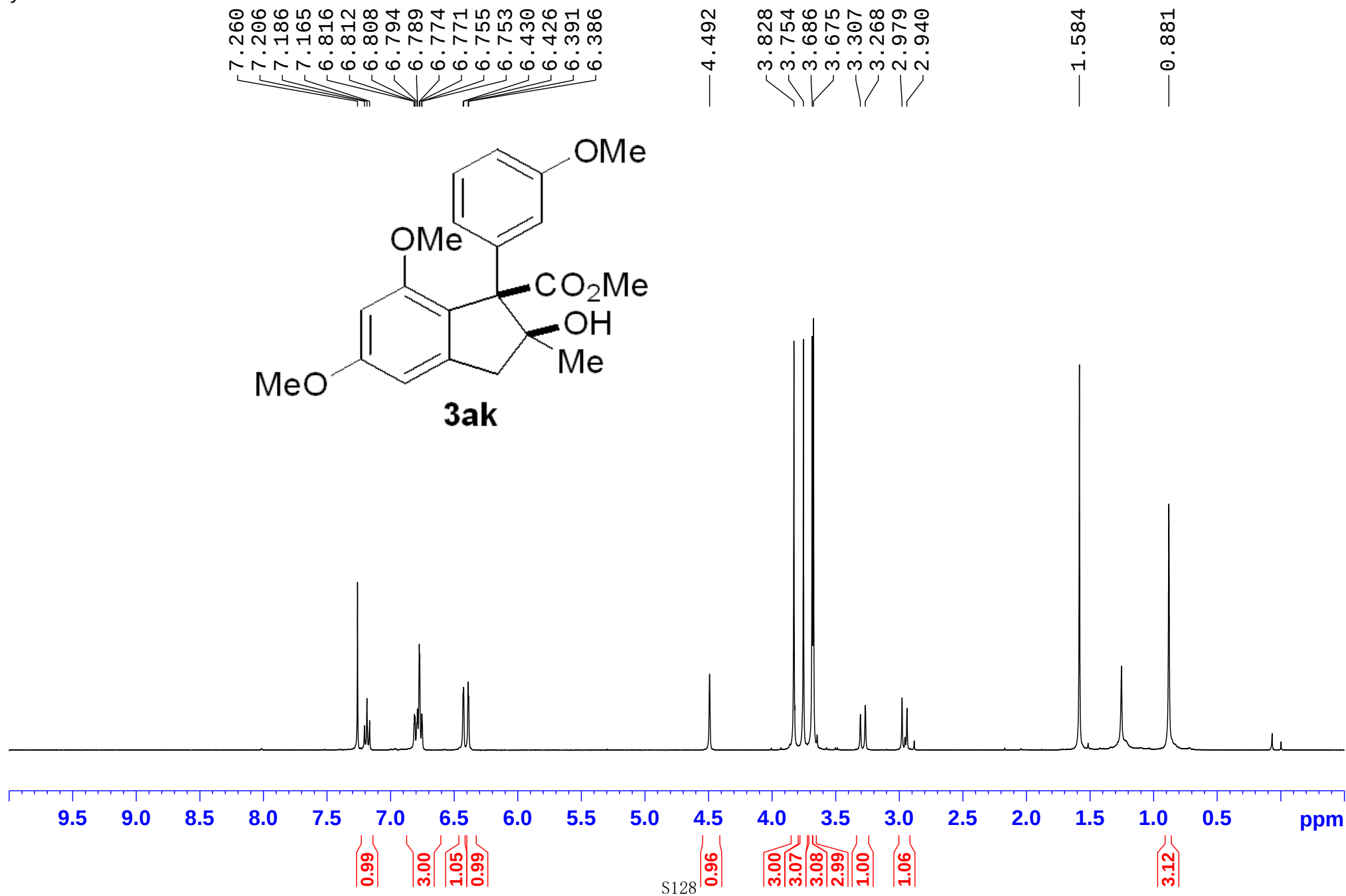
yyy-7-061-p1-1



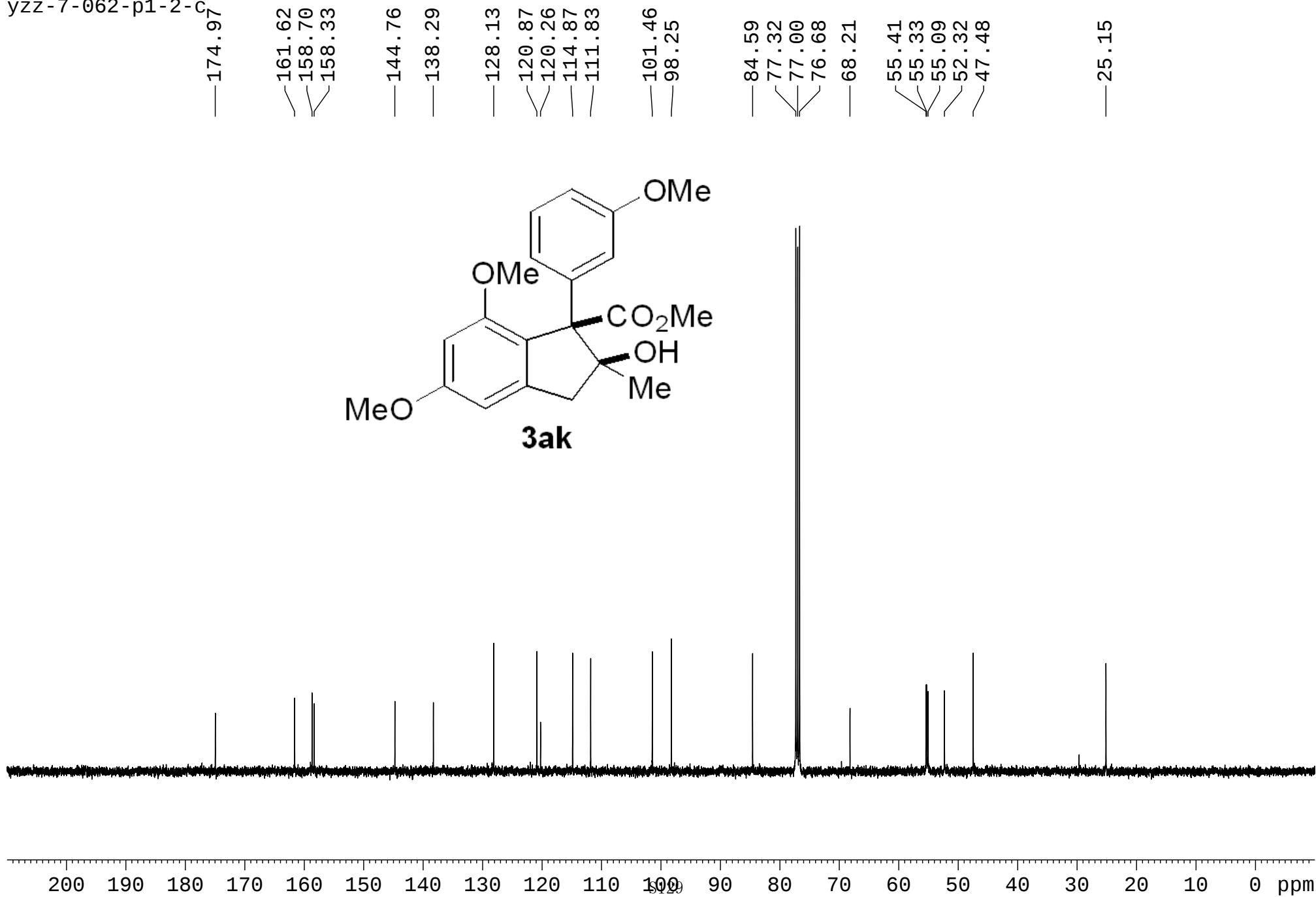
YZZ-7-061-P1-C



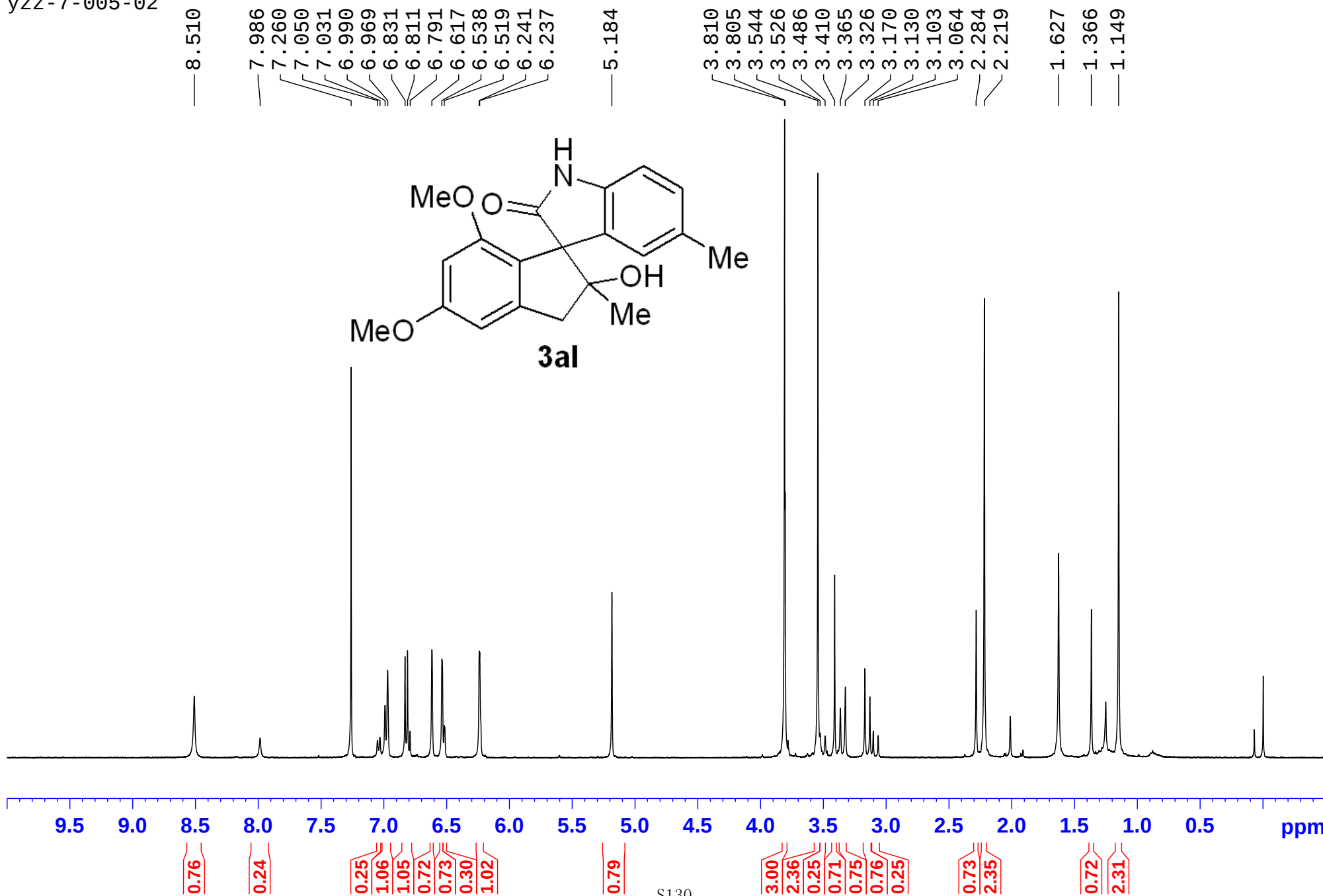
yyy-7-062-1



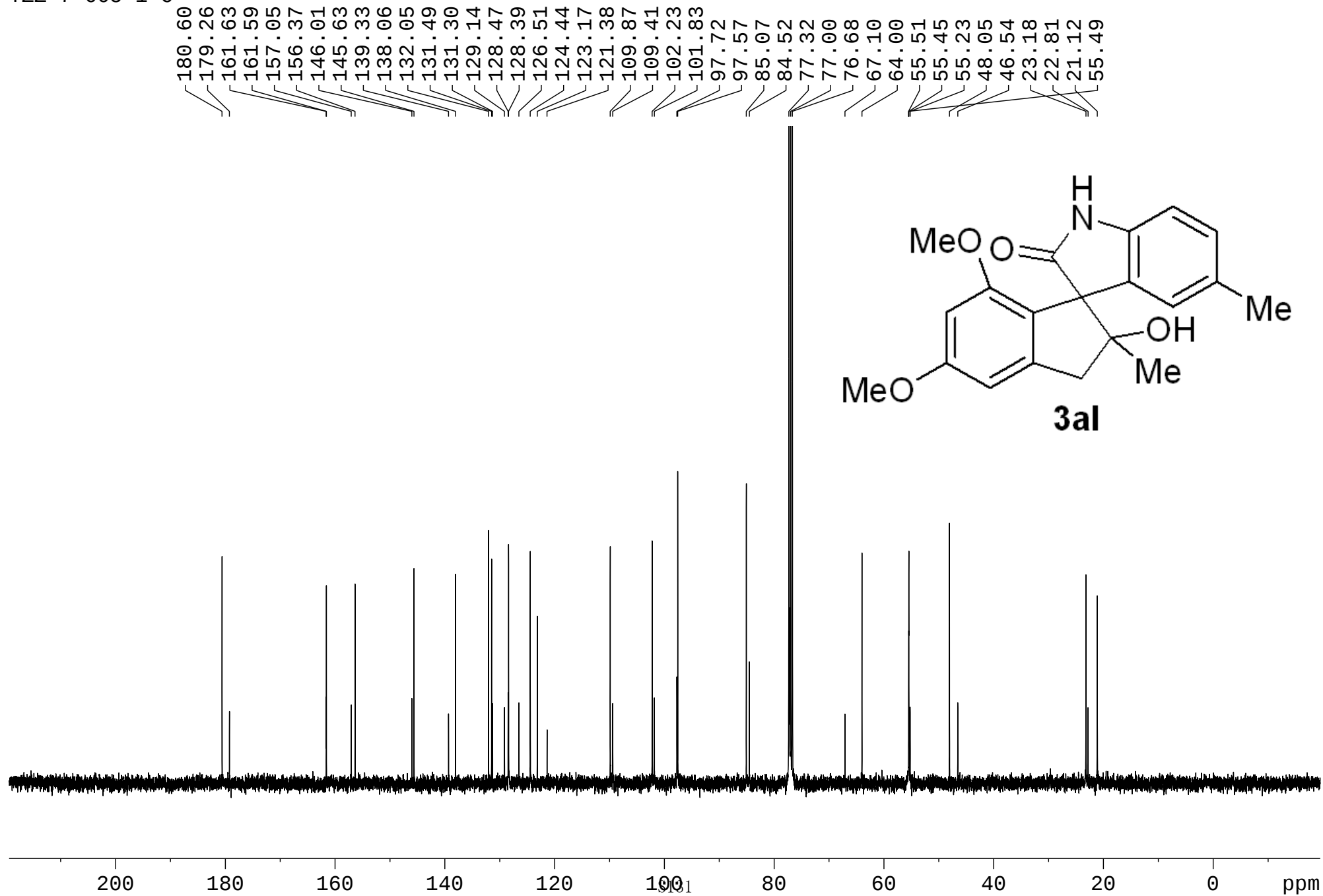
yyy-7-062-p1-2-c



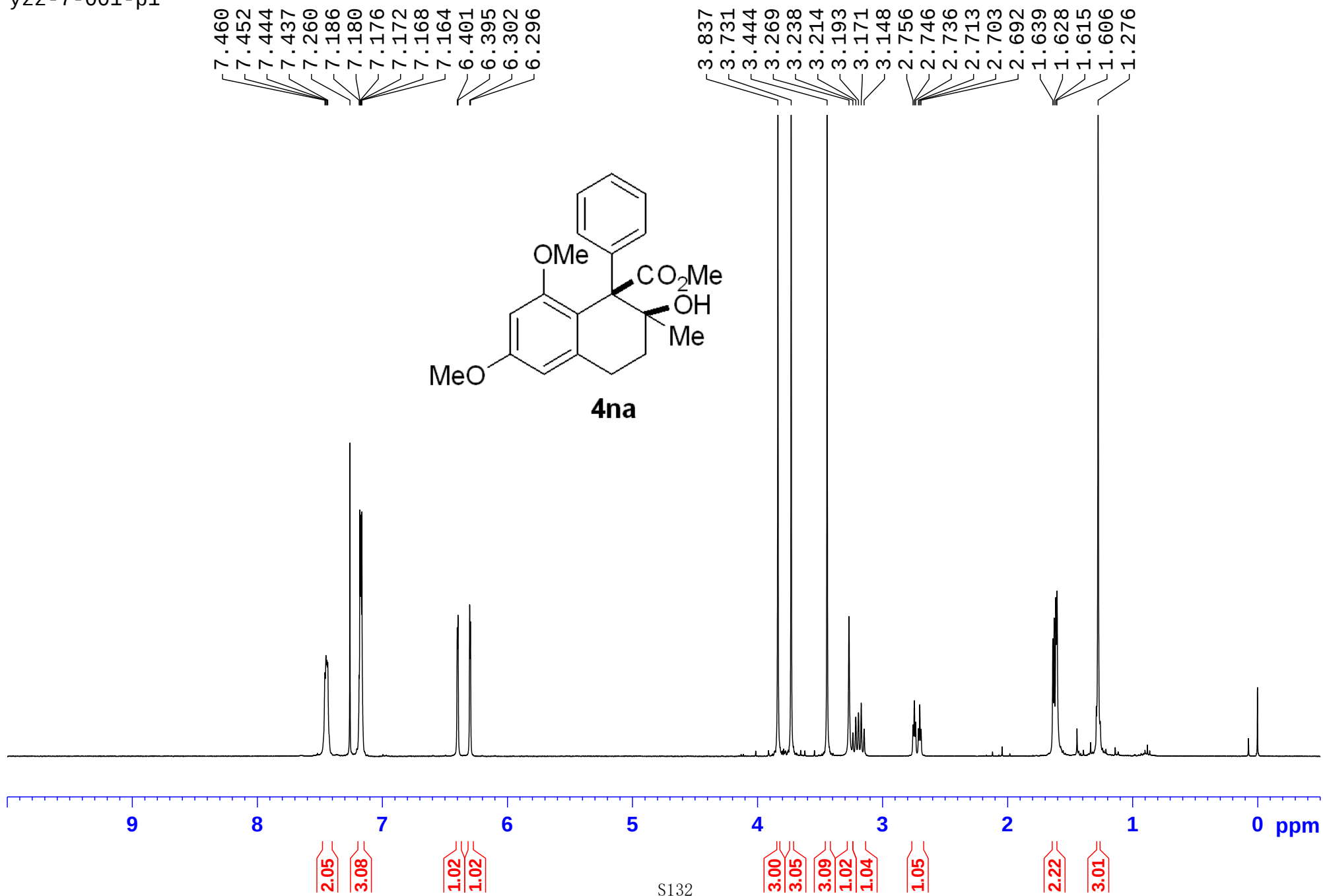
yyy-7-005-02



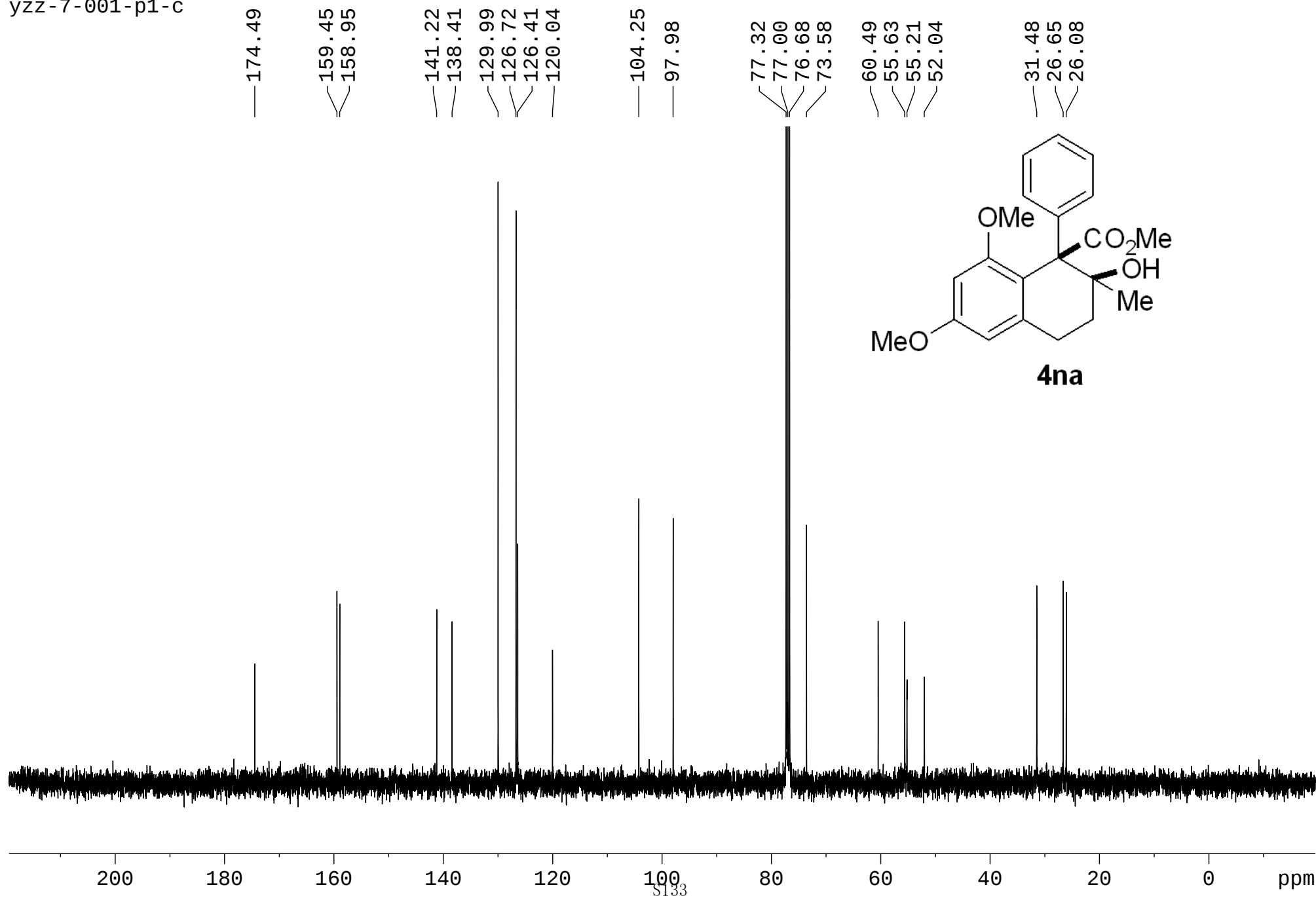
YZZ-7-005-1-C



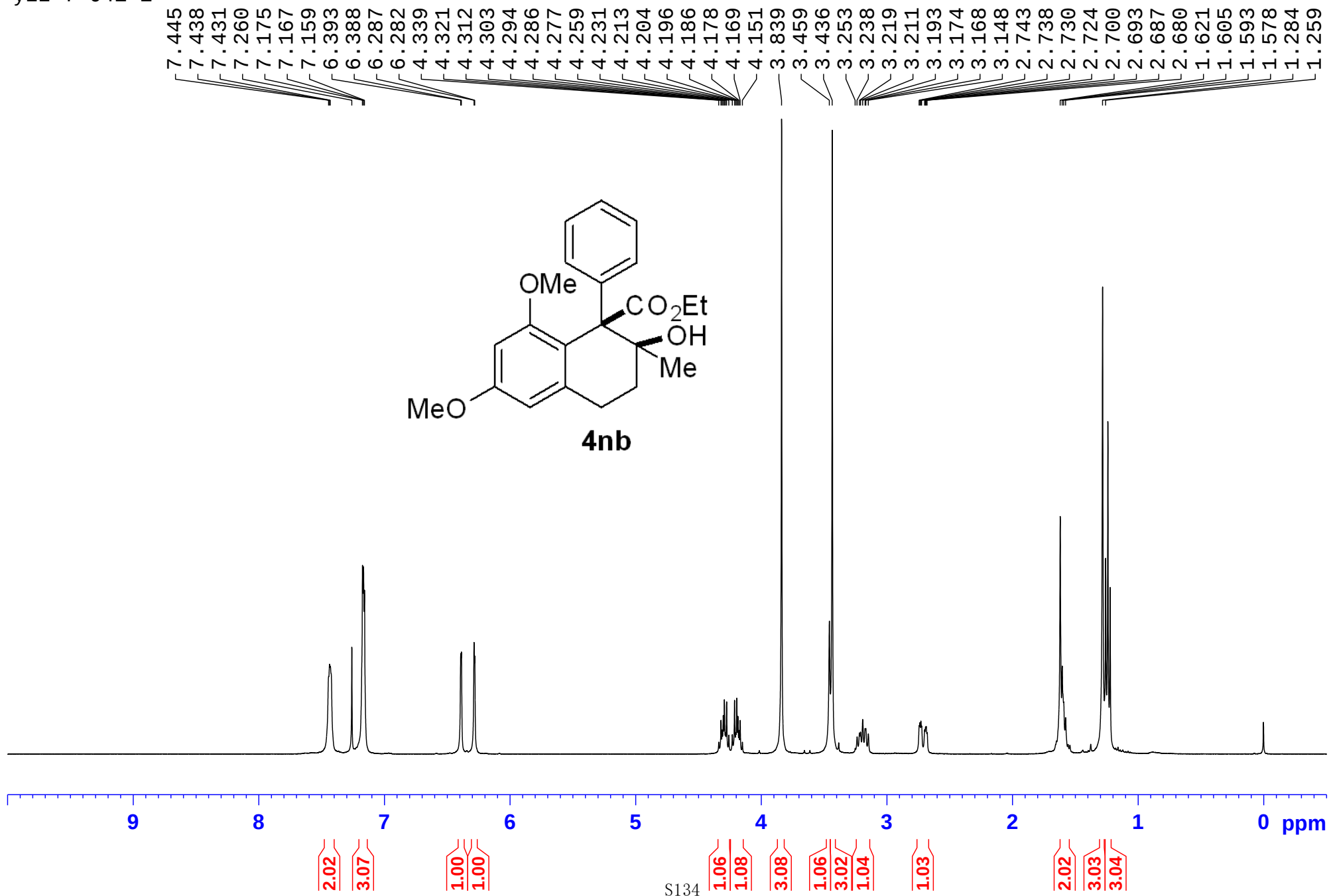
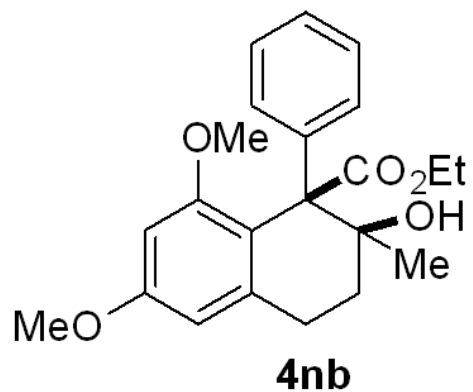
yyy-7-001-p1



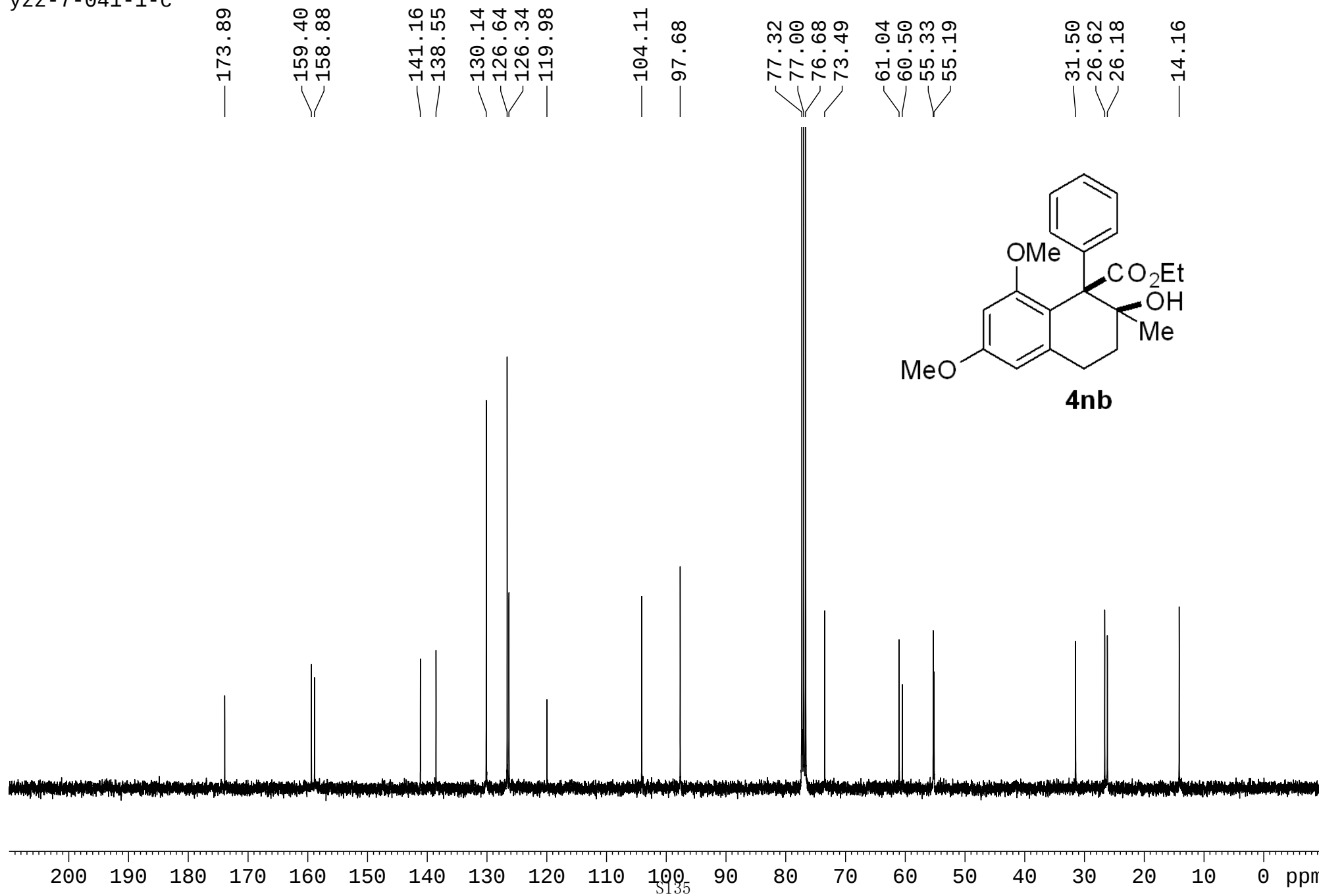
yyy-7-001-p1-c

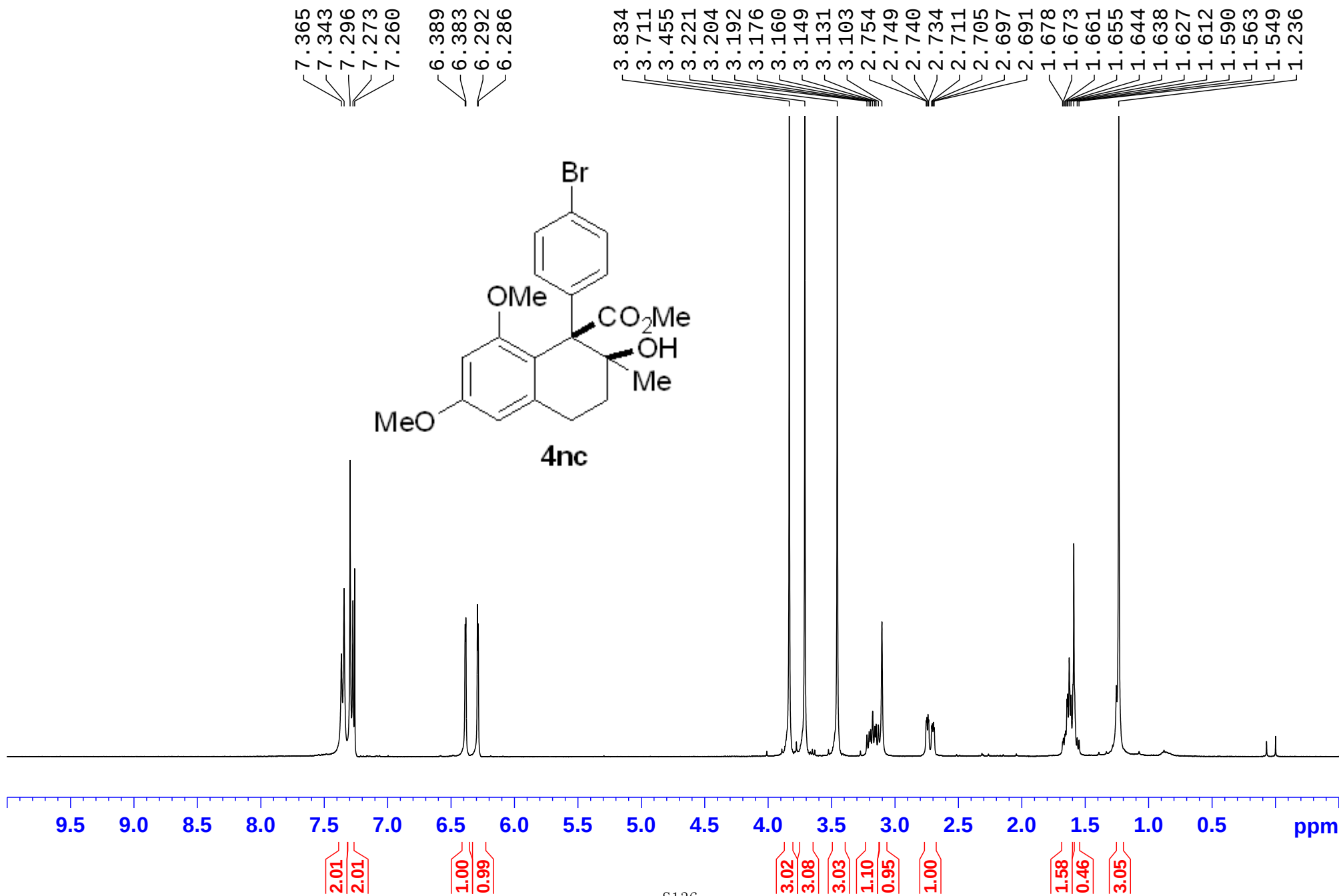


yyy-7-041-1

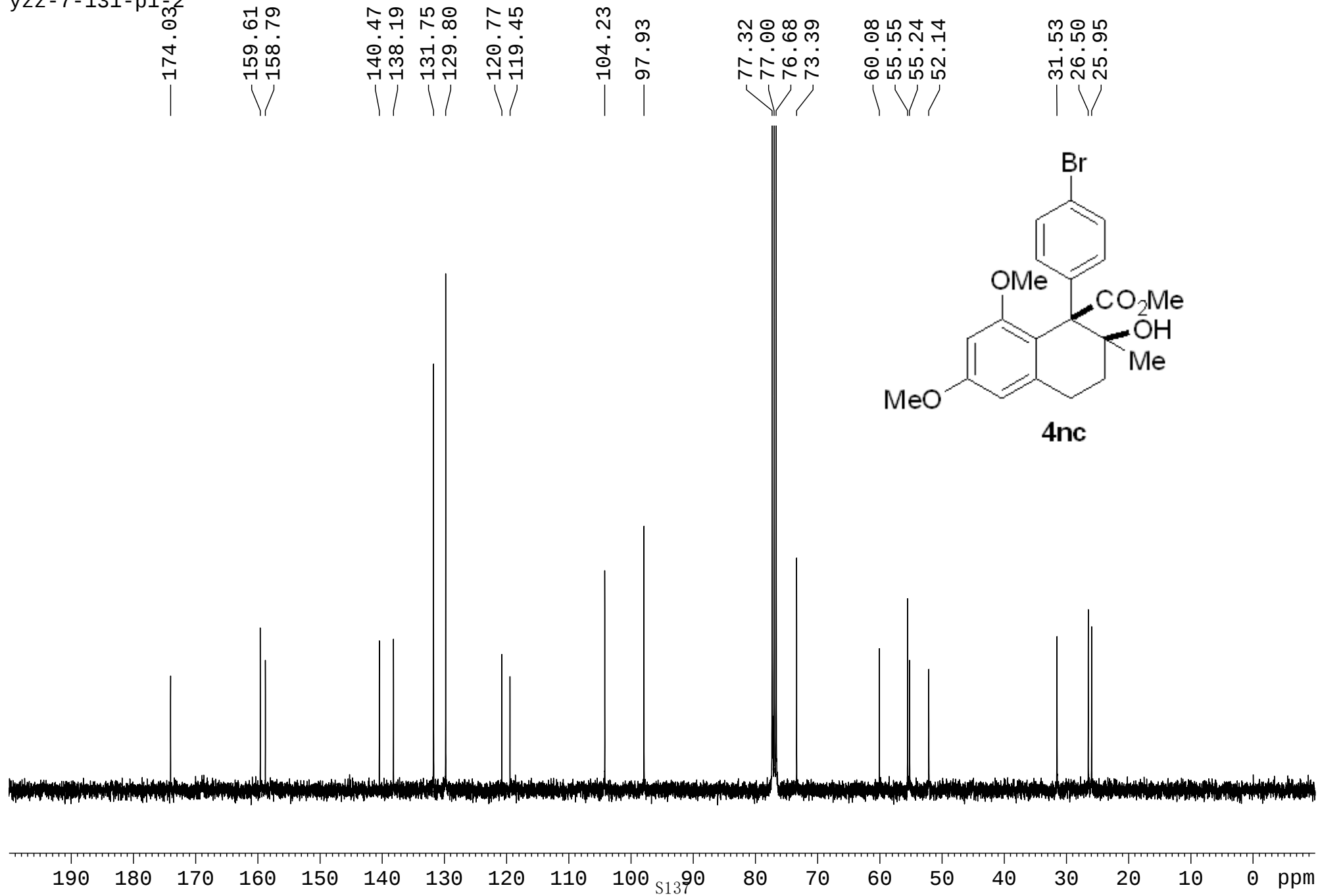


yyy-7-041-1-c

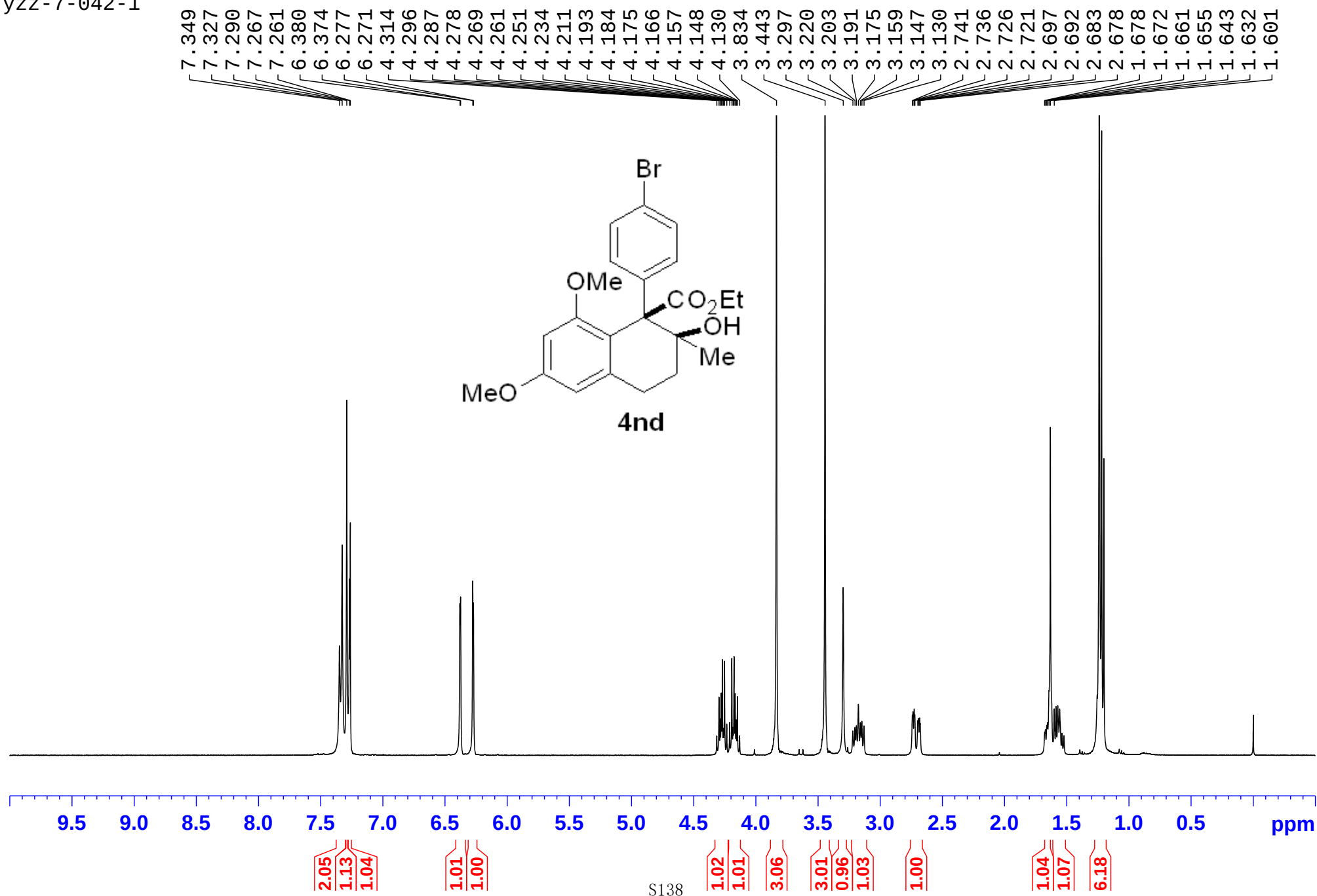




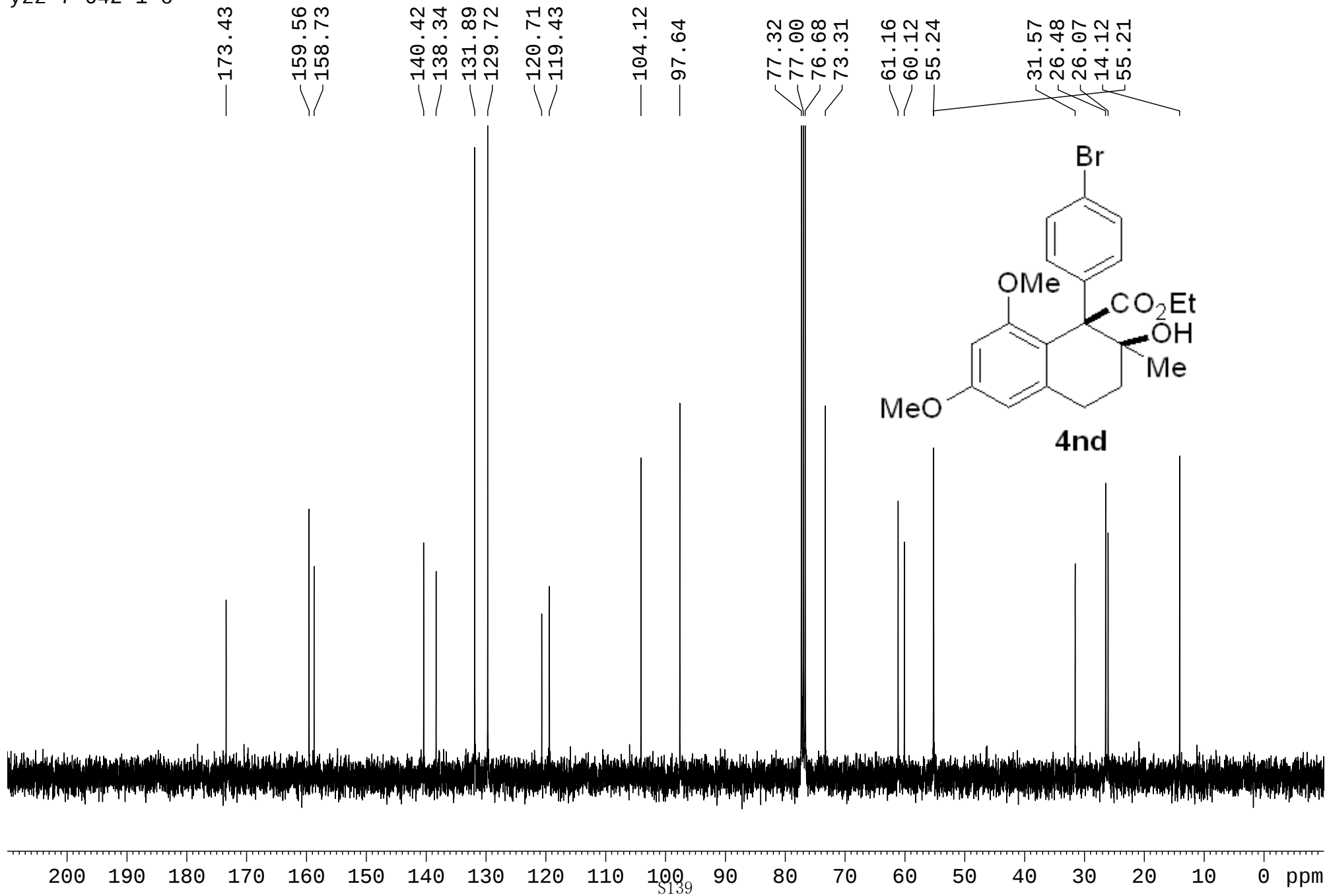
yyy-7-131-p1_2



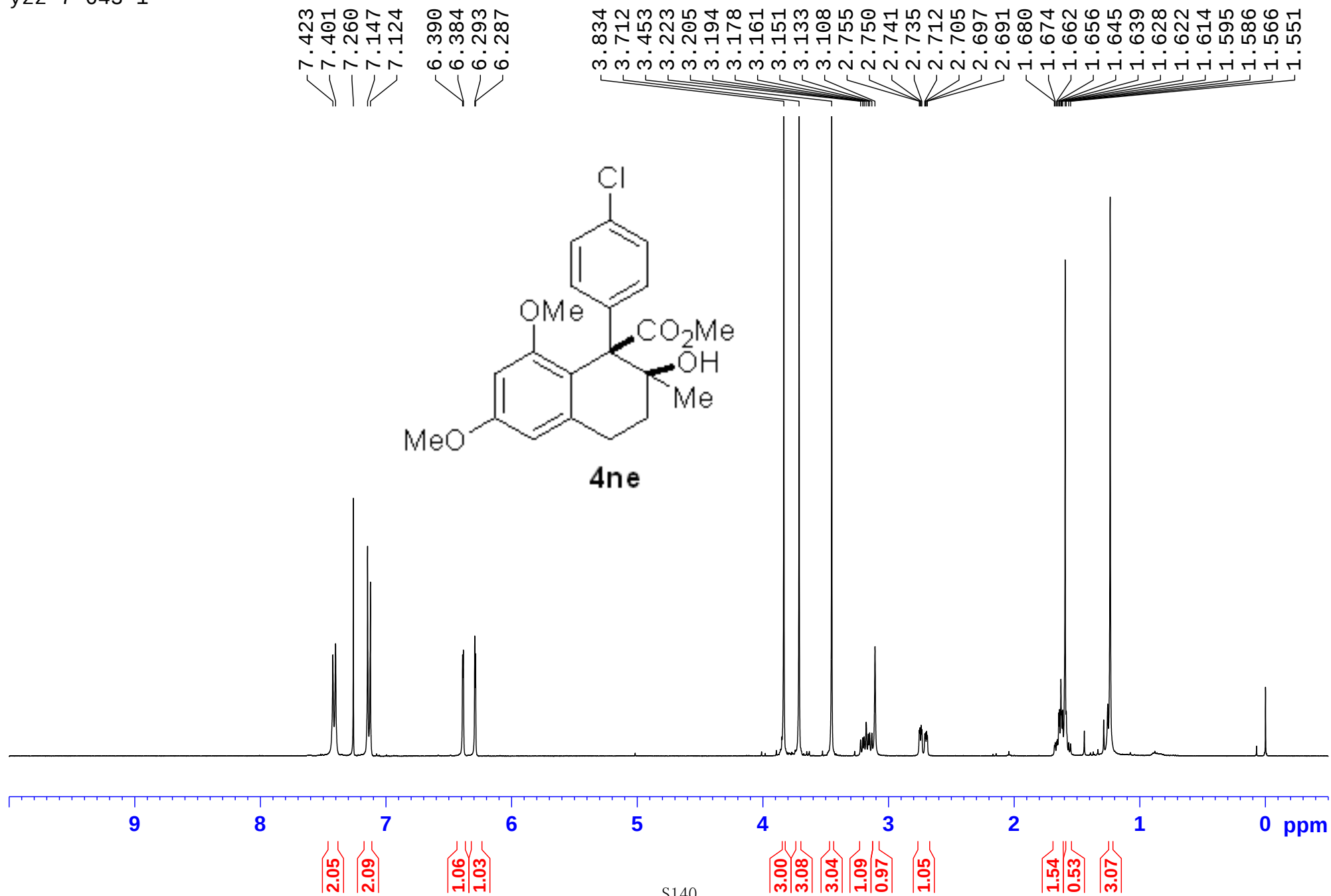
yyy-7-042-1



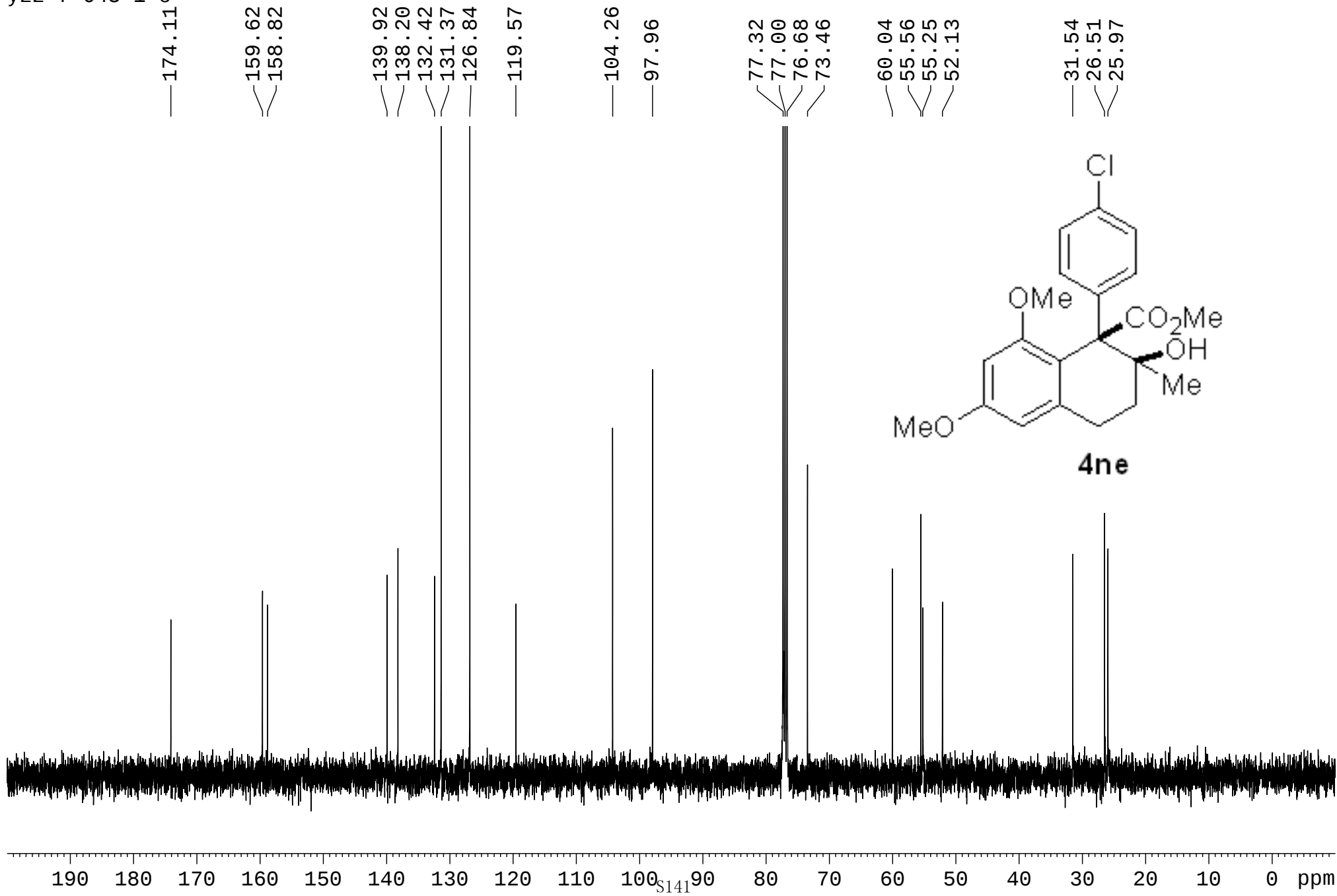
yyy-7-042-1-c



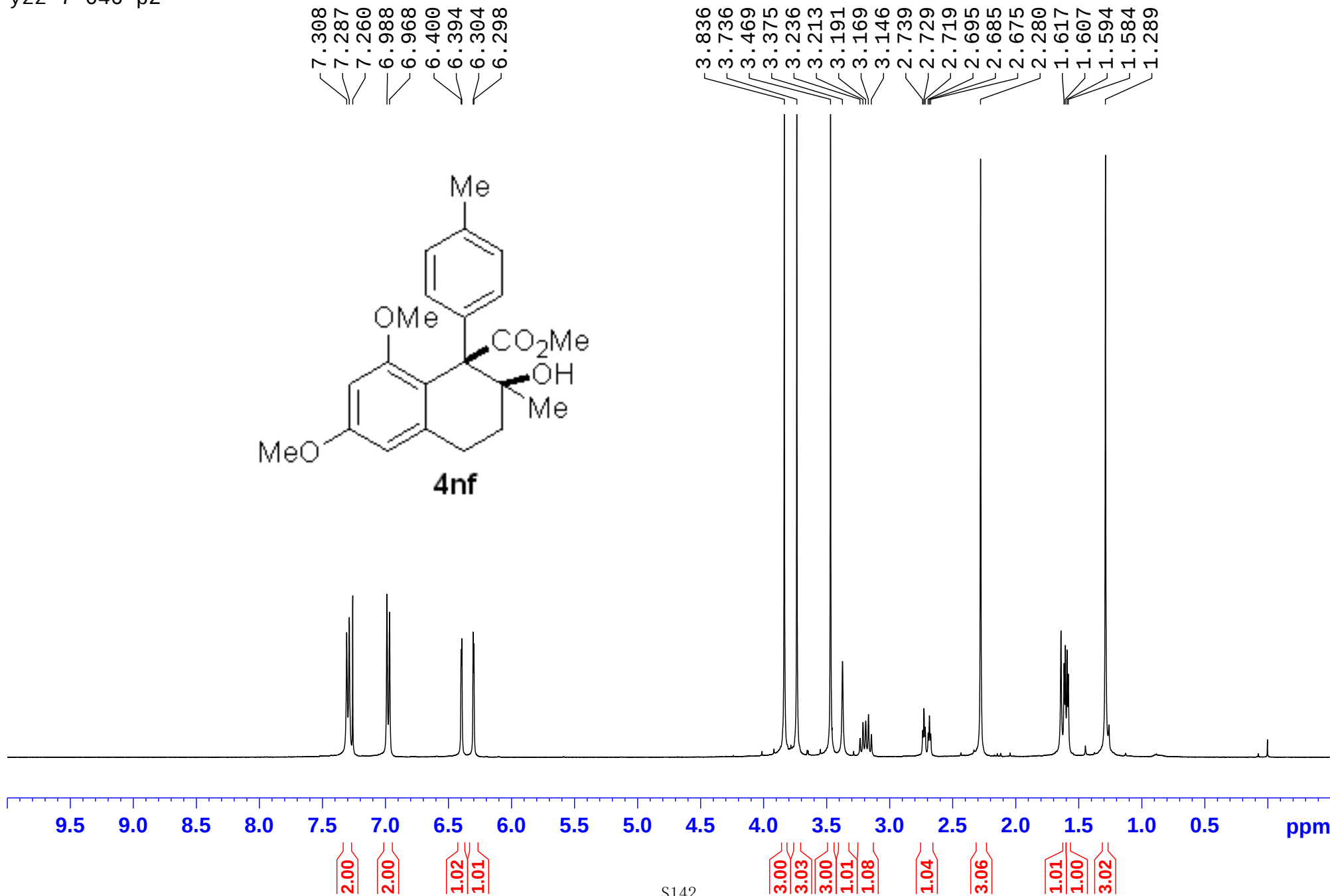
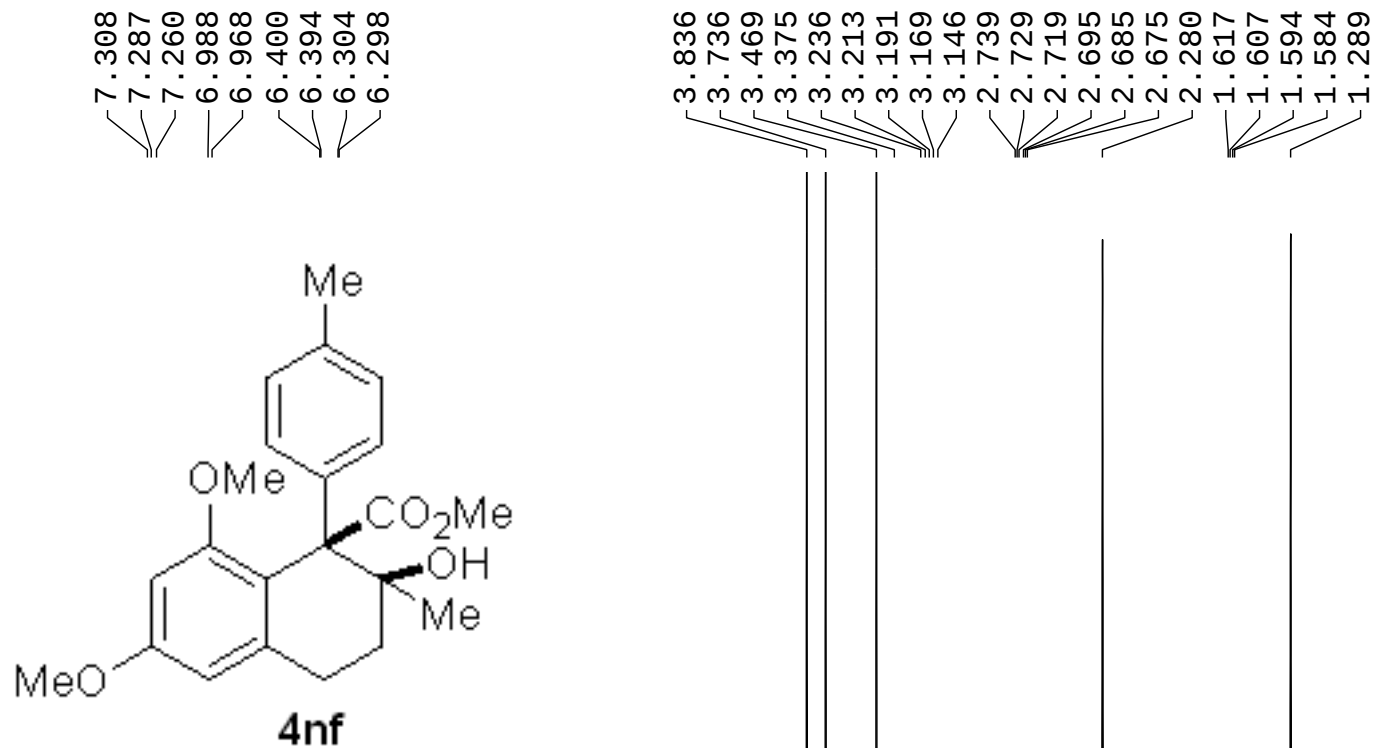
yyy-7-043-1



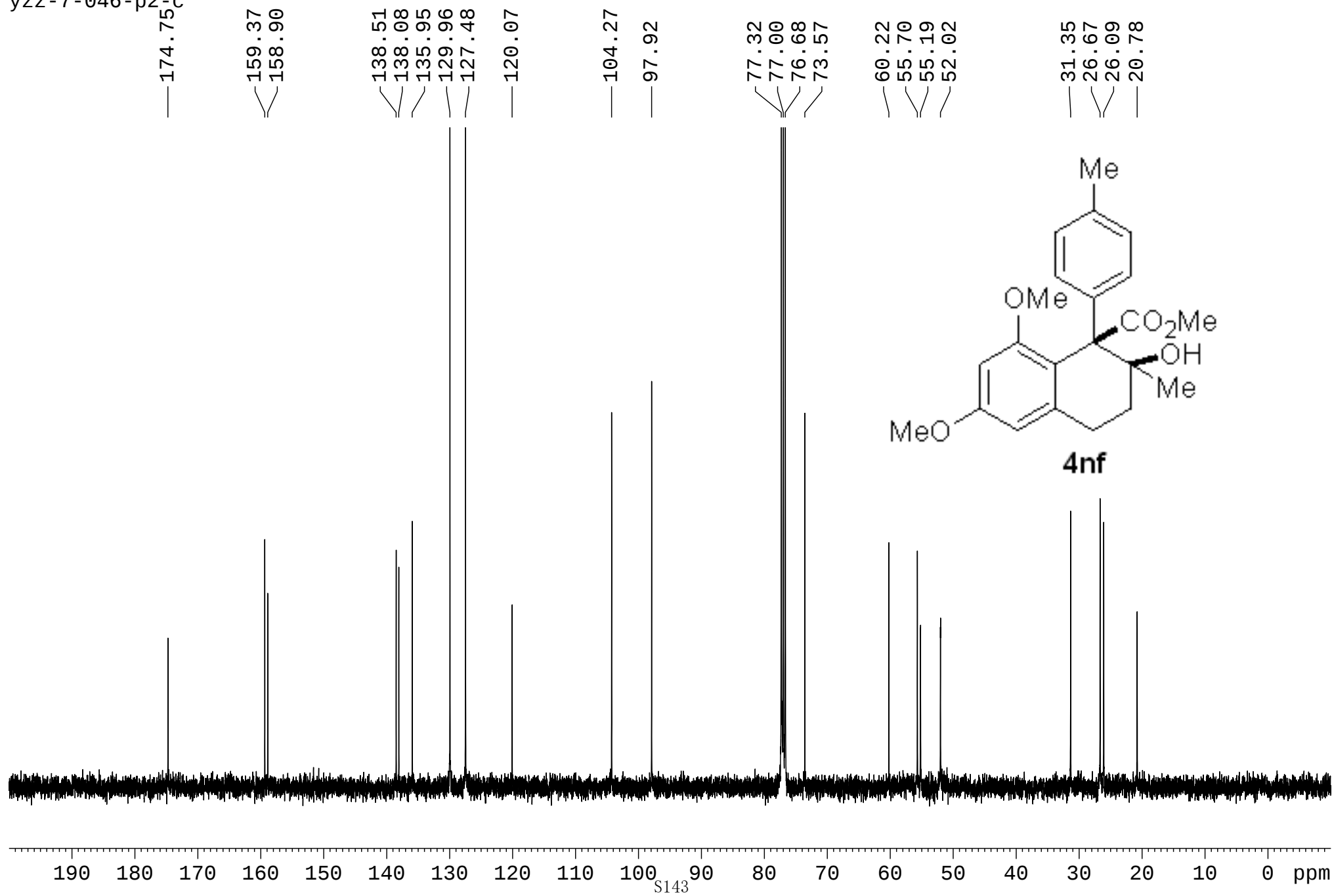
yyy-7-043-1-c



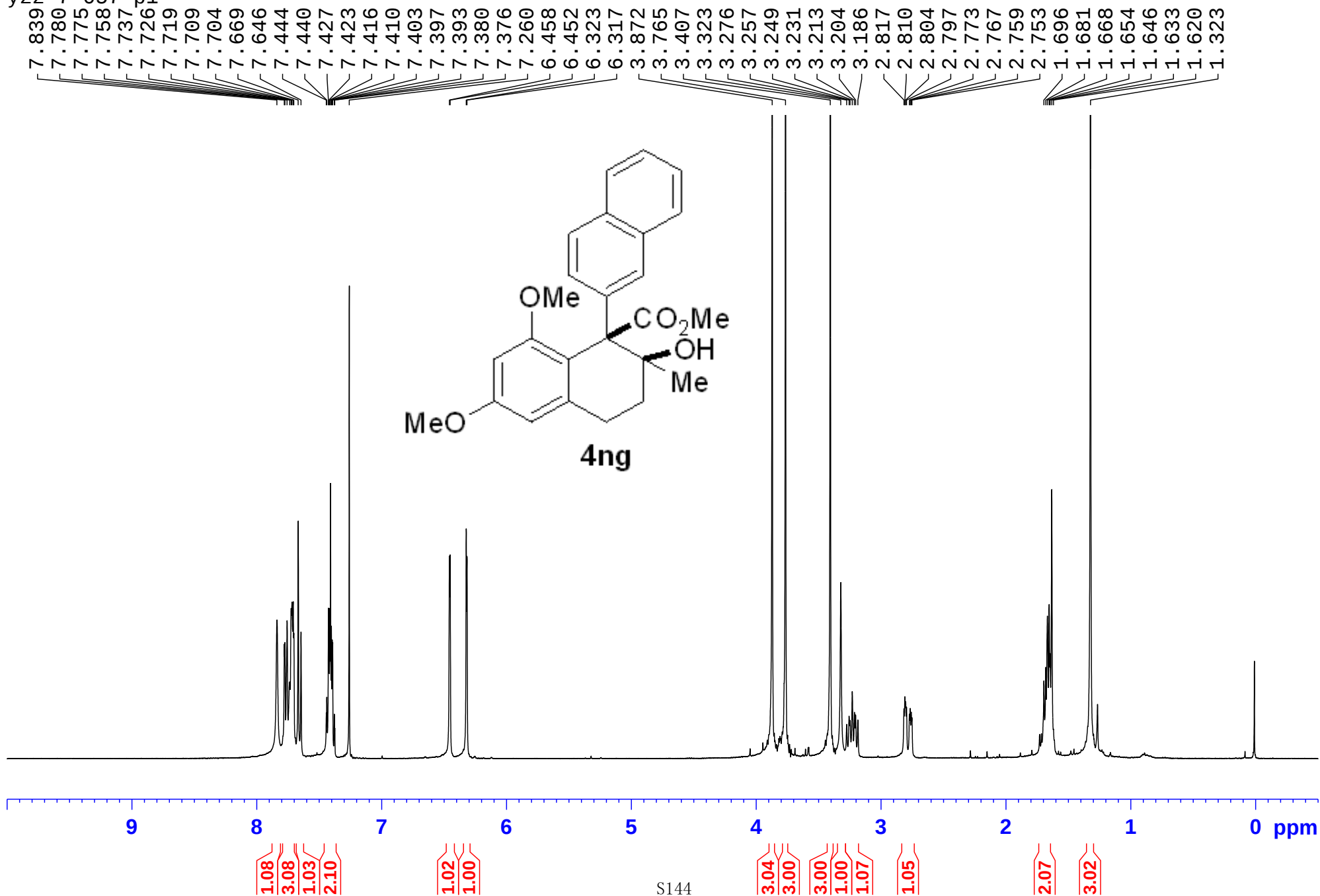
yyy-7-046-p2



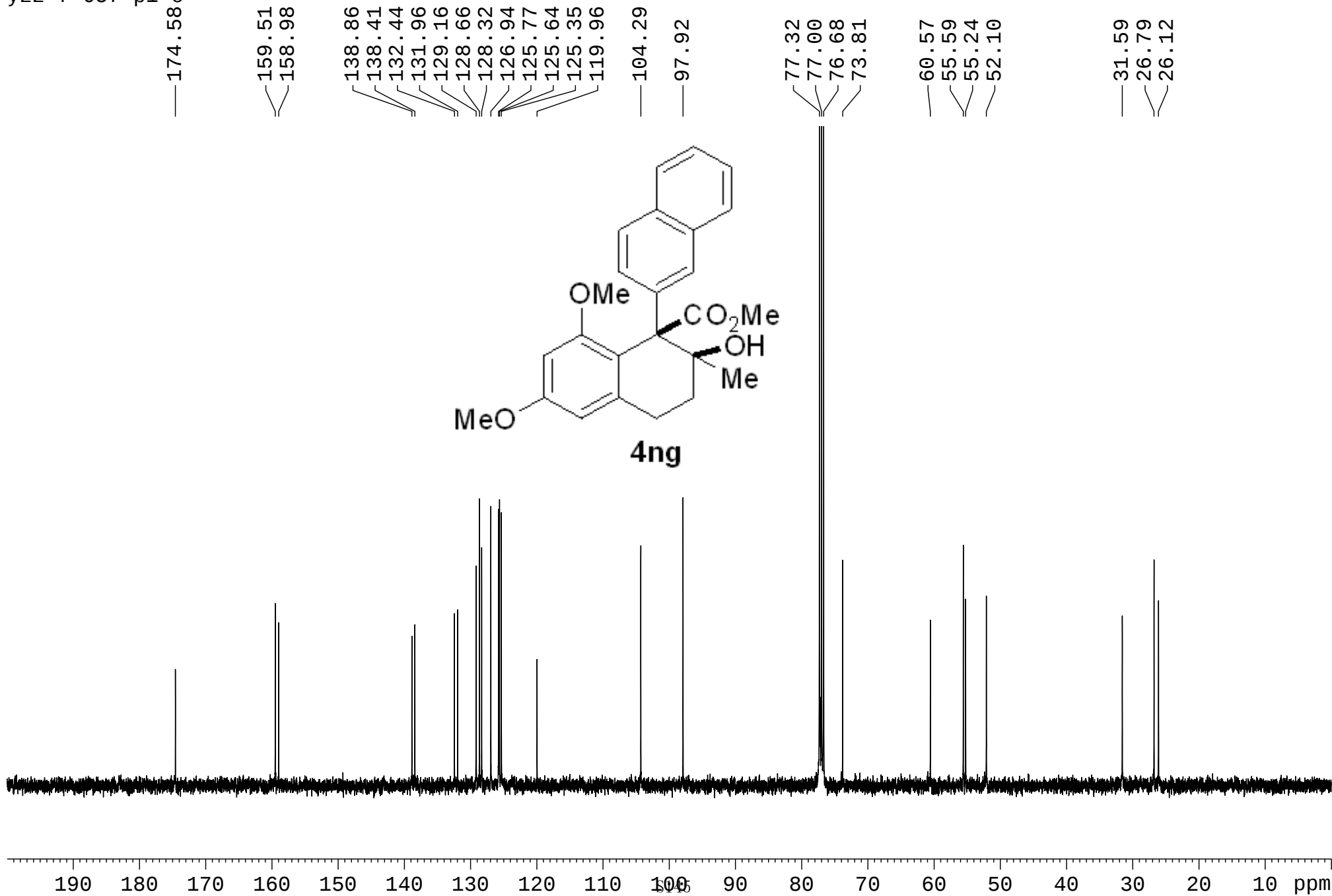
yyy-7-046-p21c



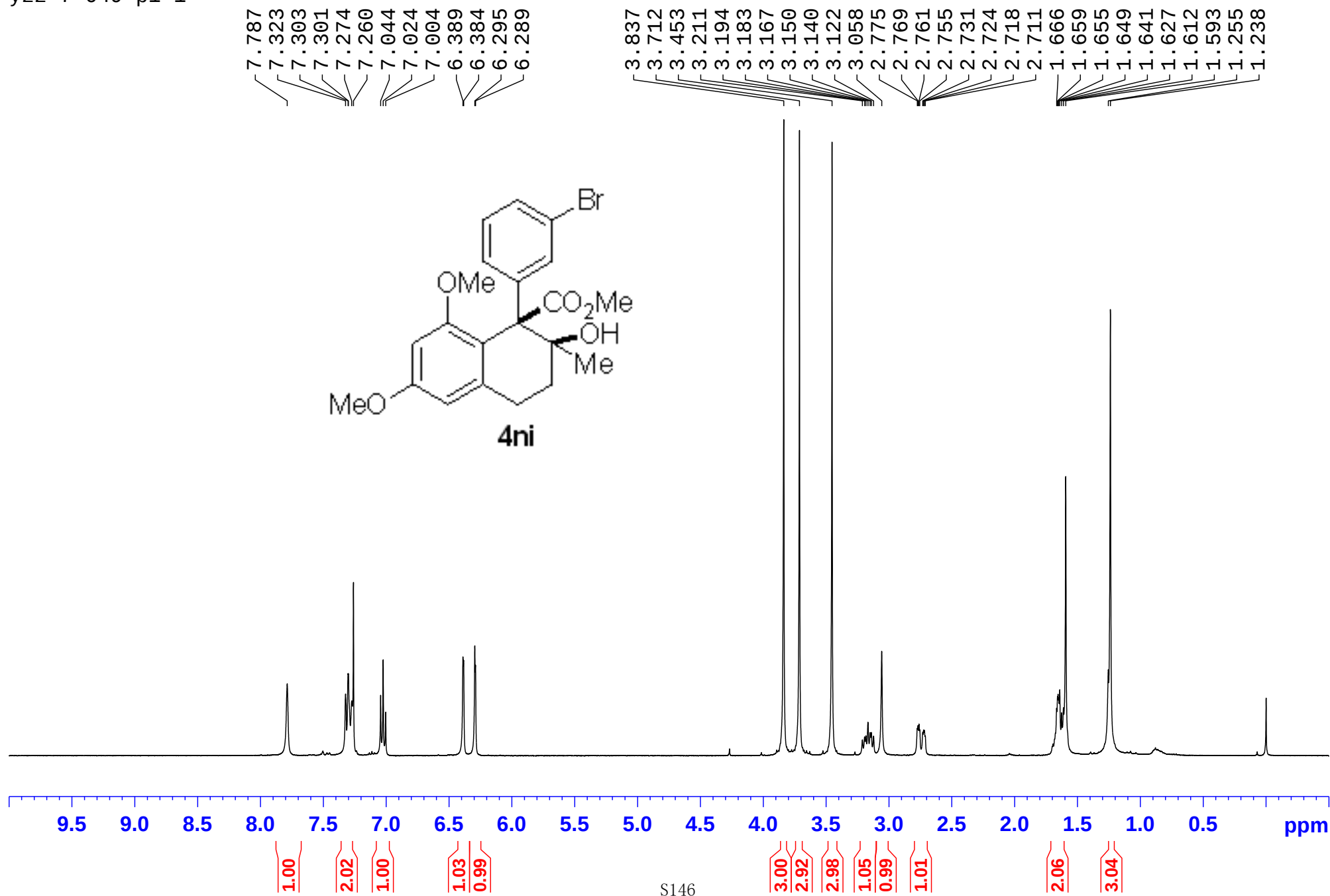
yz-z-7-057-p1



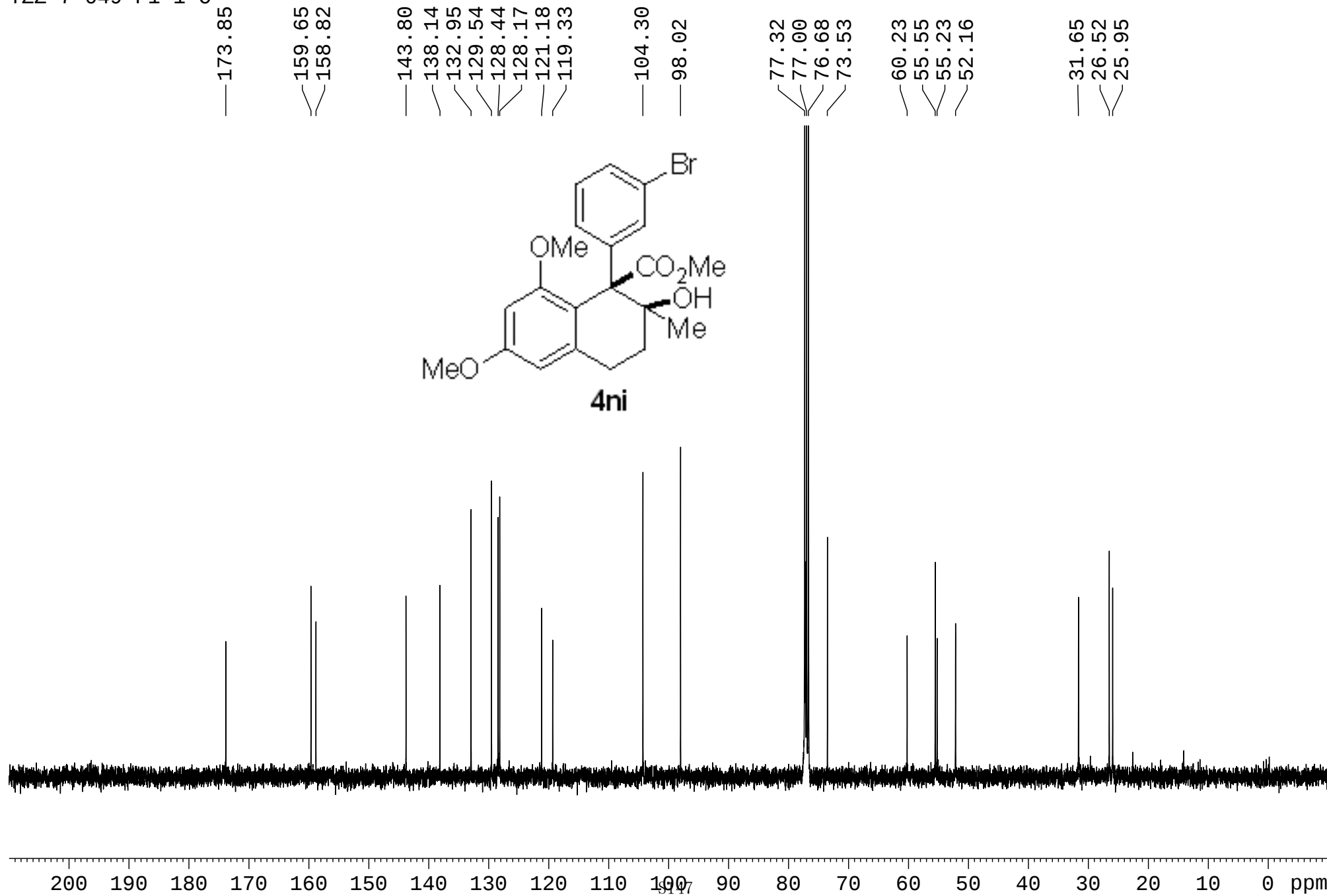
yyy-7-057-p1-c



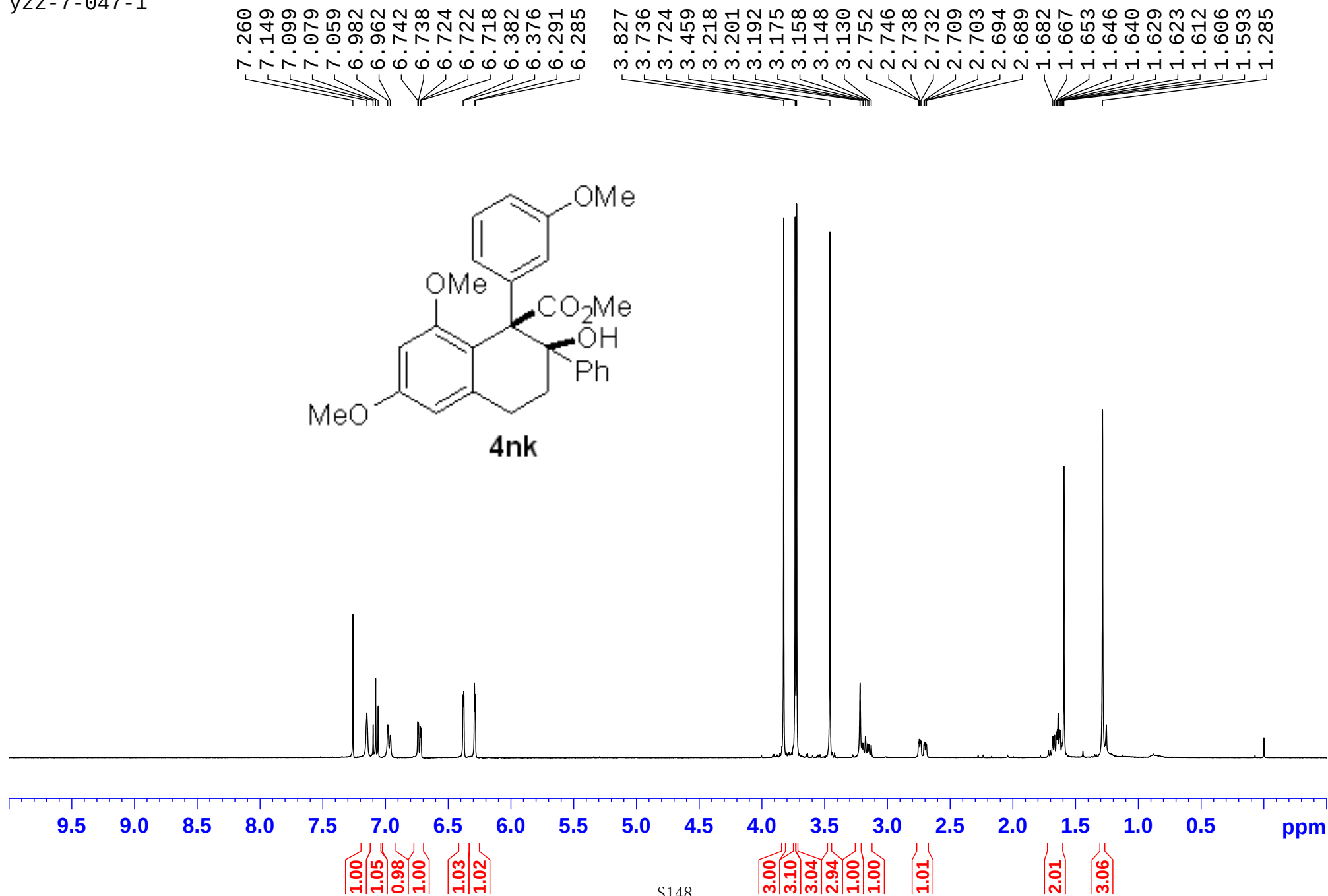
yyy-7-049-p1-1



YZZ-7-049-P1-1-C

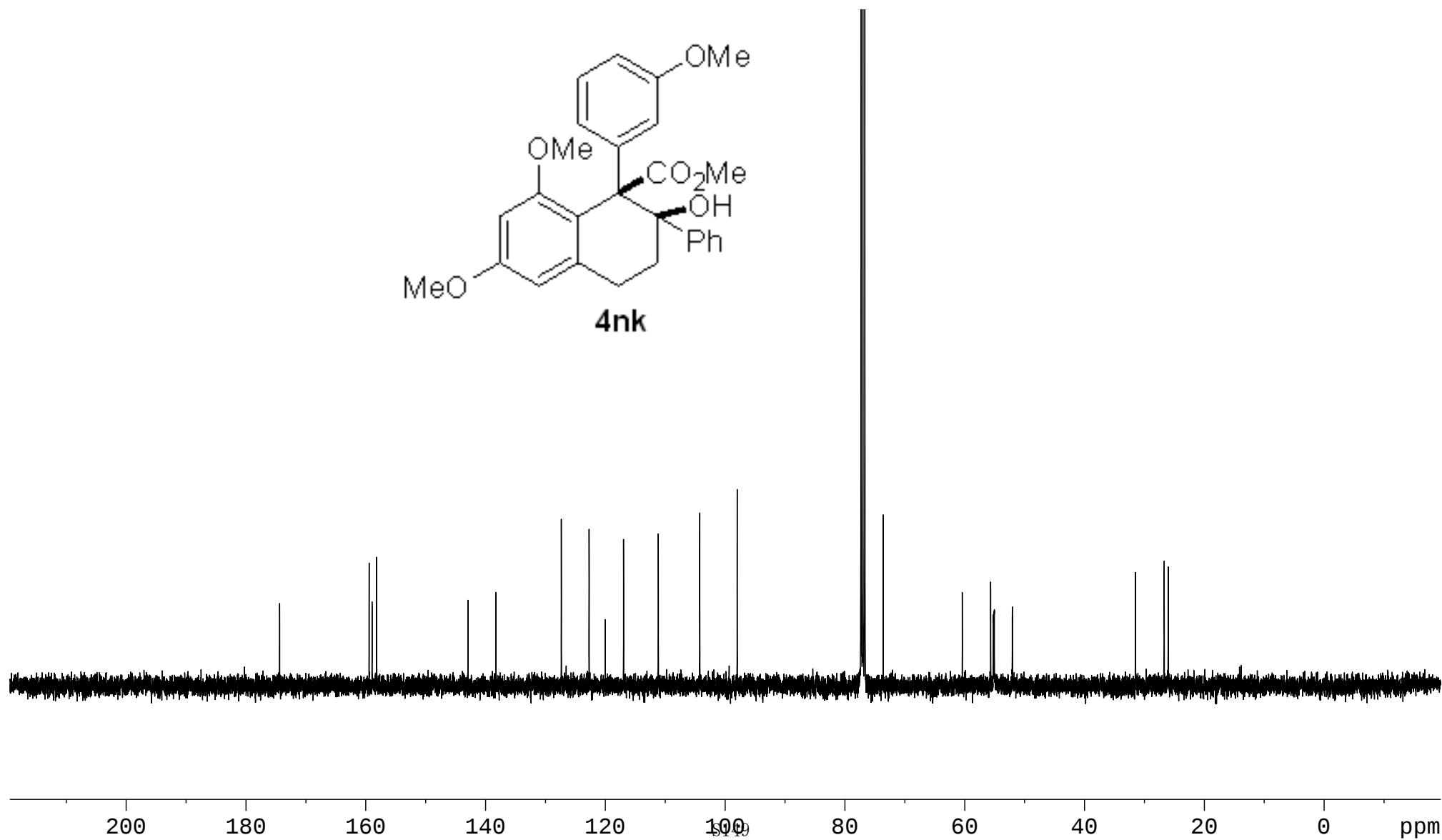
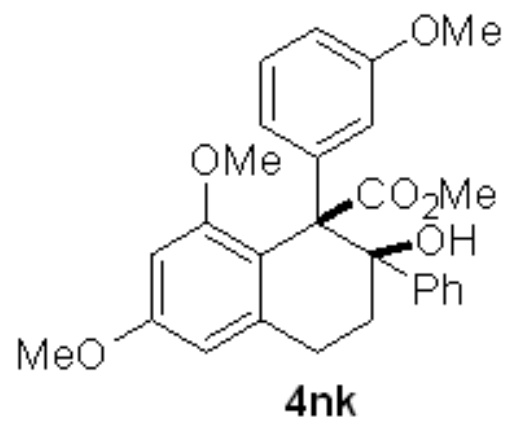


yyy-7-047-1

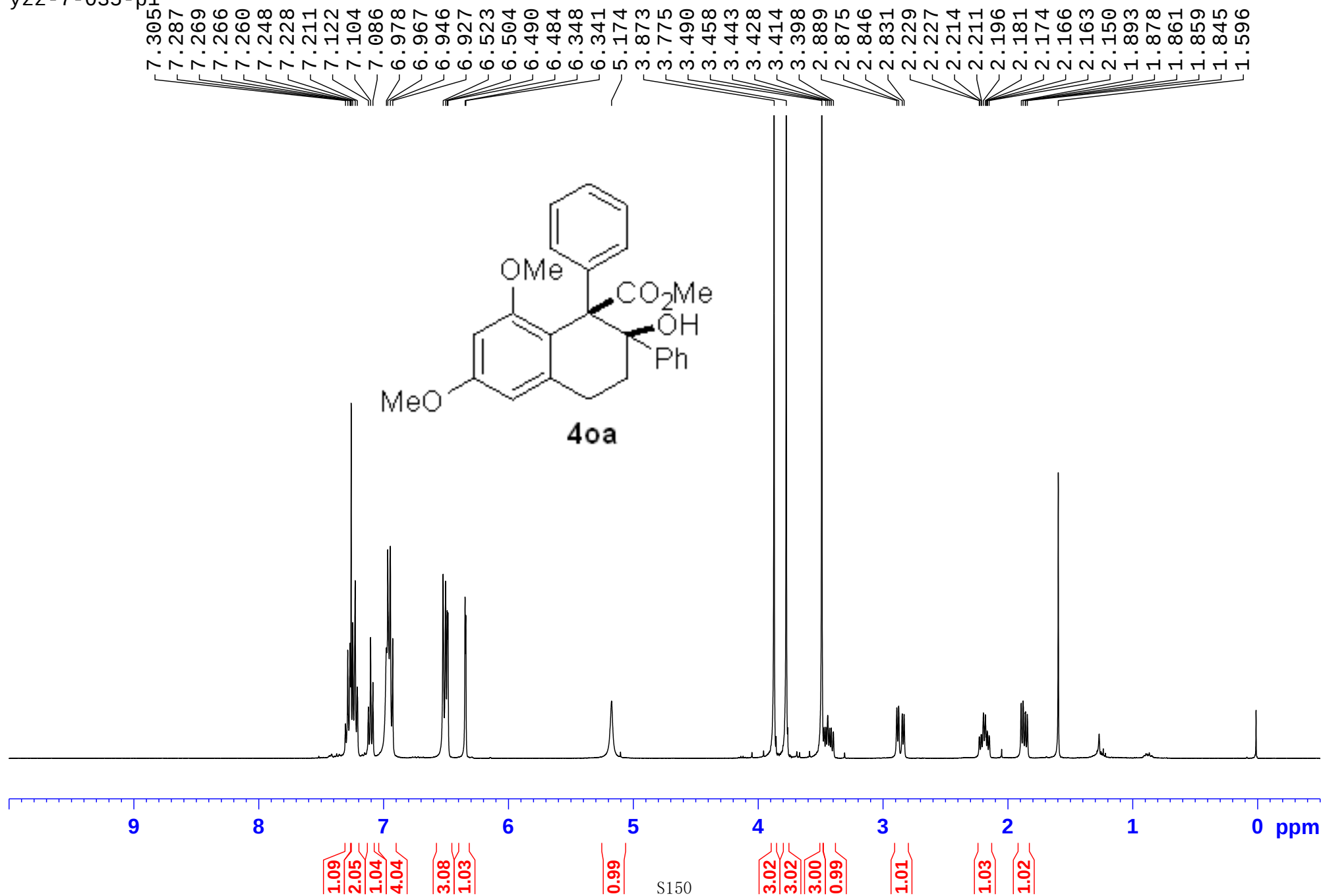


yyy-7-047-1-c

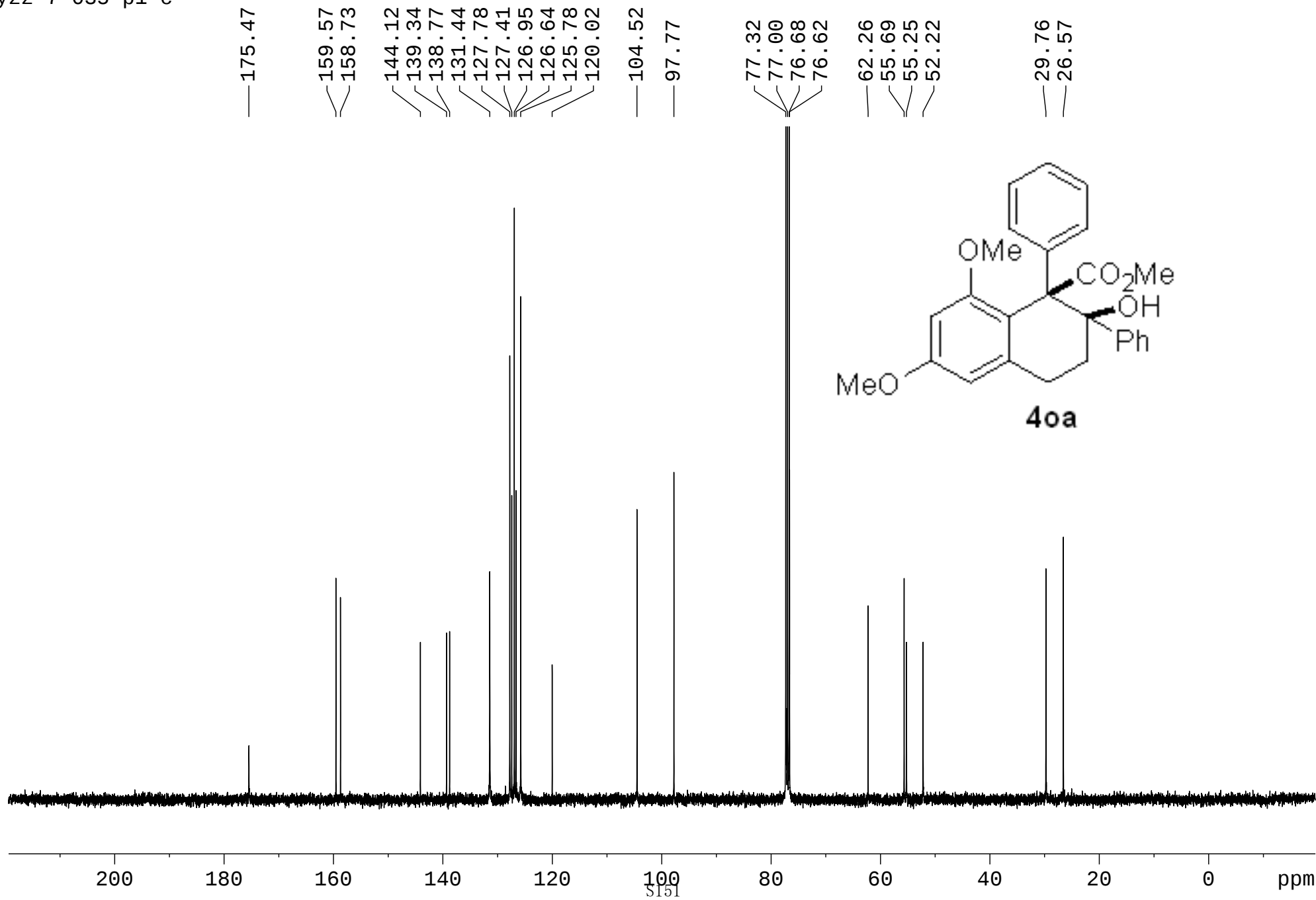
174.39
159.45
158.96
158.19
142.94
138.26
127.36
122.72
120.04
116.96
111.16
104.24
97.99
77.32
77.00
76.68
73.62
60.42
55.68
55.20
55.06
52.05
31.50
26.70
26.03



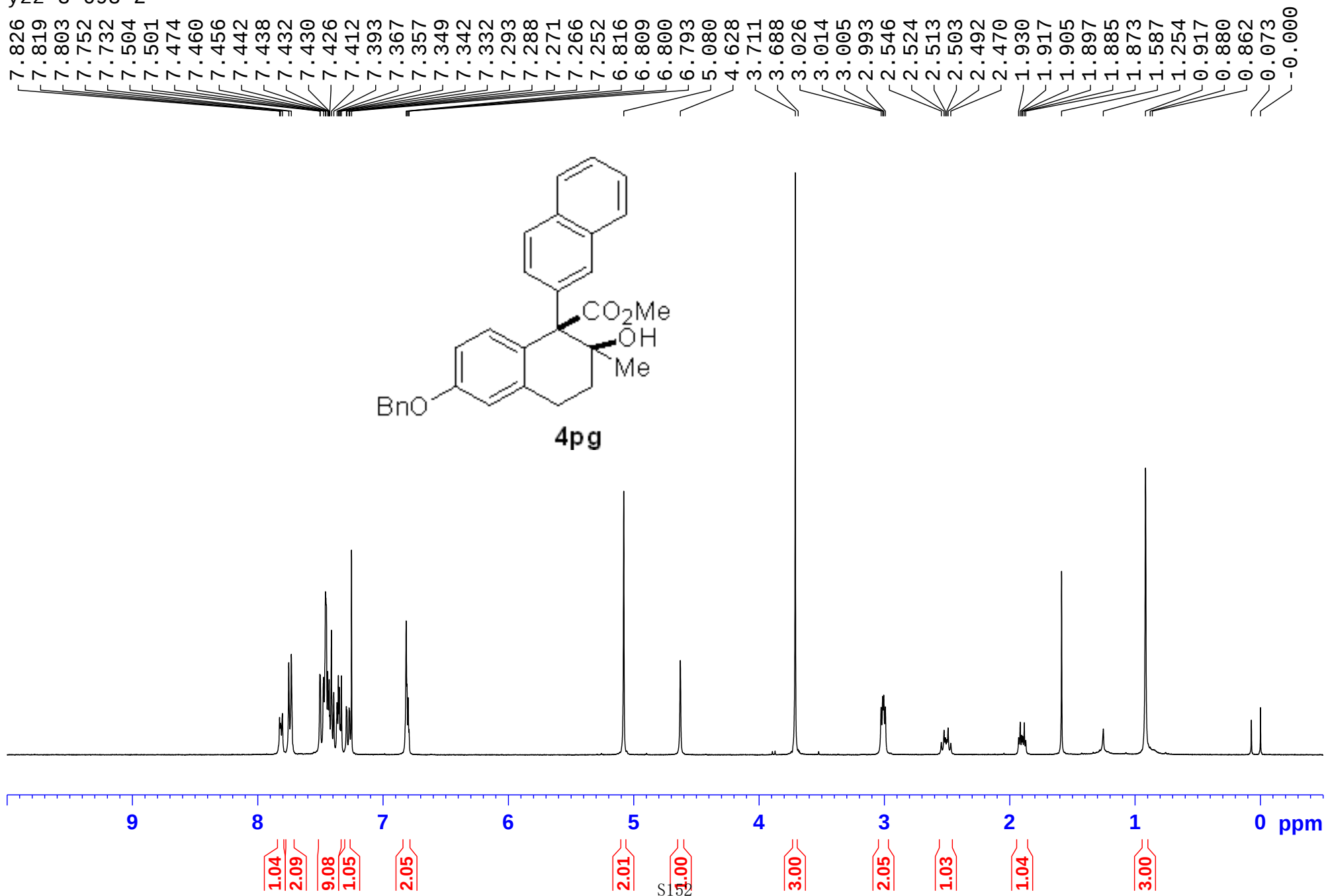
yyy-7-035-p1



yyy-7-035-p1-c



yyy-8-098-2



yyy-8-098-2-

—176.58

157.85

138.82

138.21

136.85

134.25

132.35

132.17

129.05

128.60

128.27

128.25

128.04

127.58

127.27

126.21

126.02

125.85

113.44

112.93

77.32

77.00

76.68

73.76

69.88

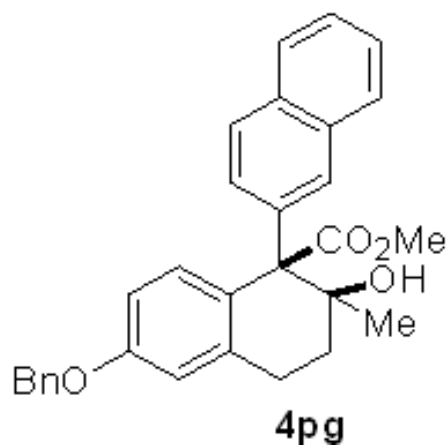
64.19

—52.65

—34.53

—28.51

—24.74



180

160

140

120

100

80

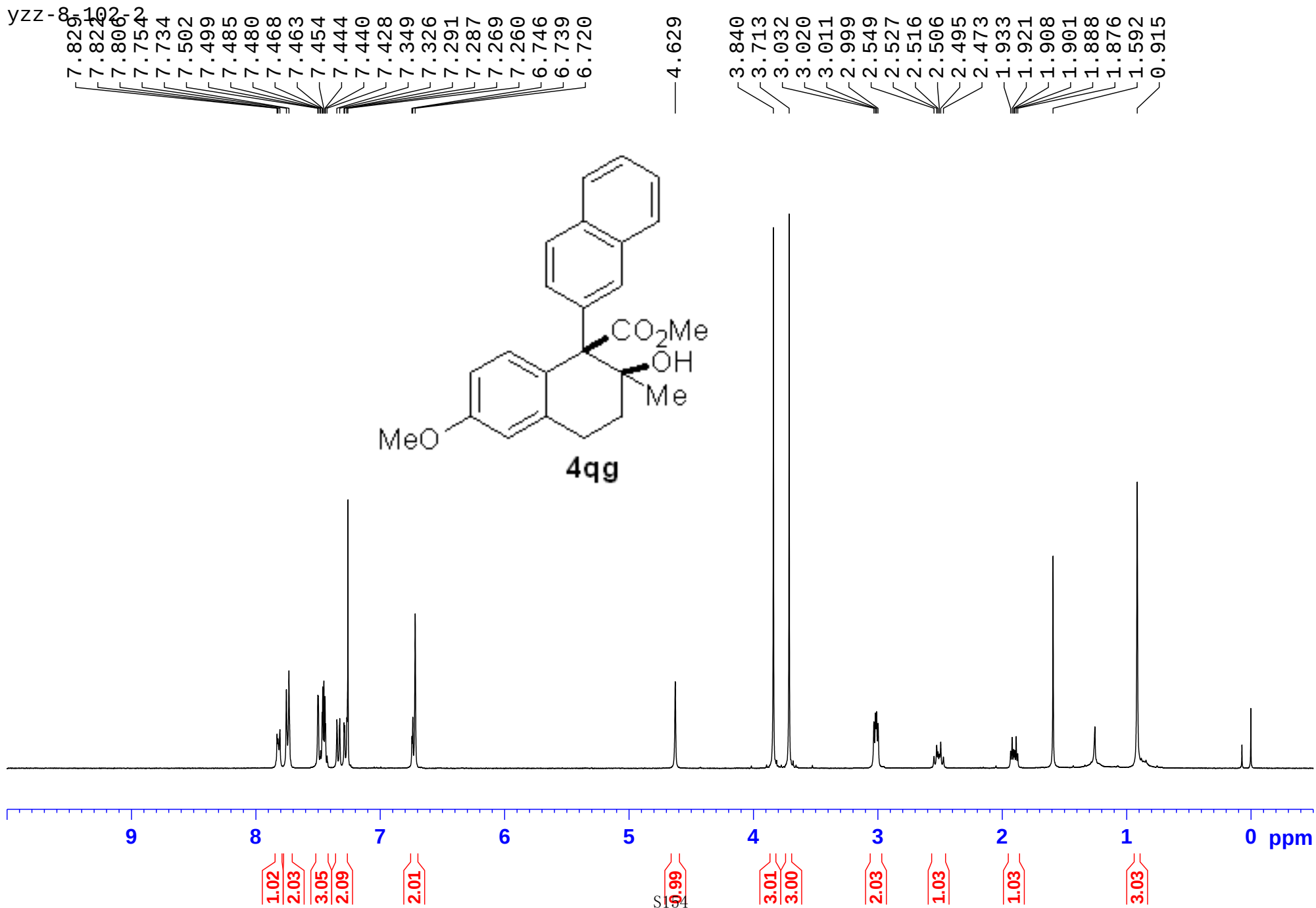
60

40

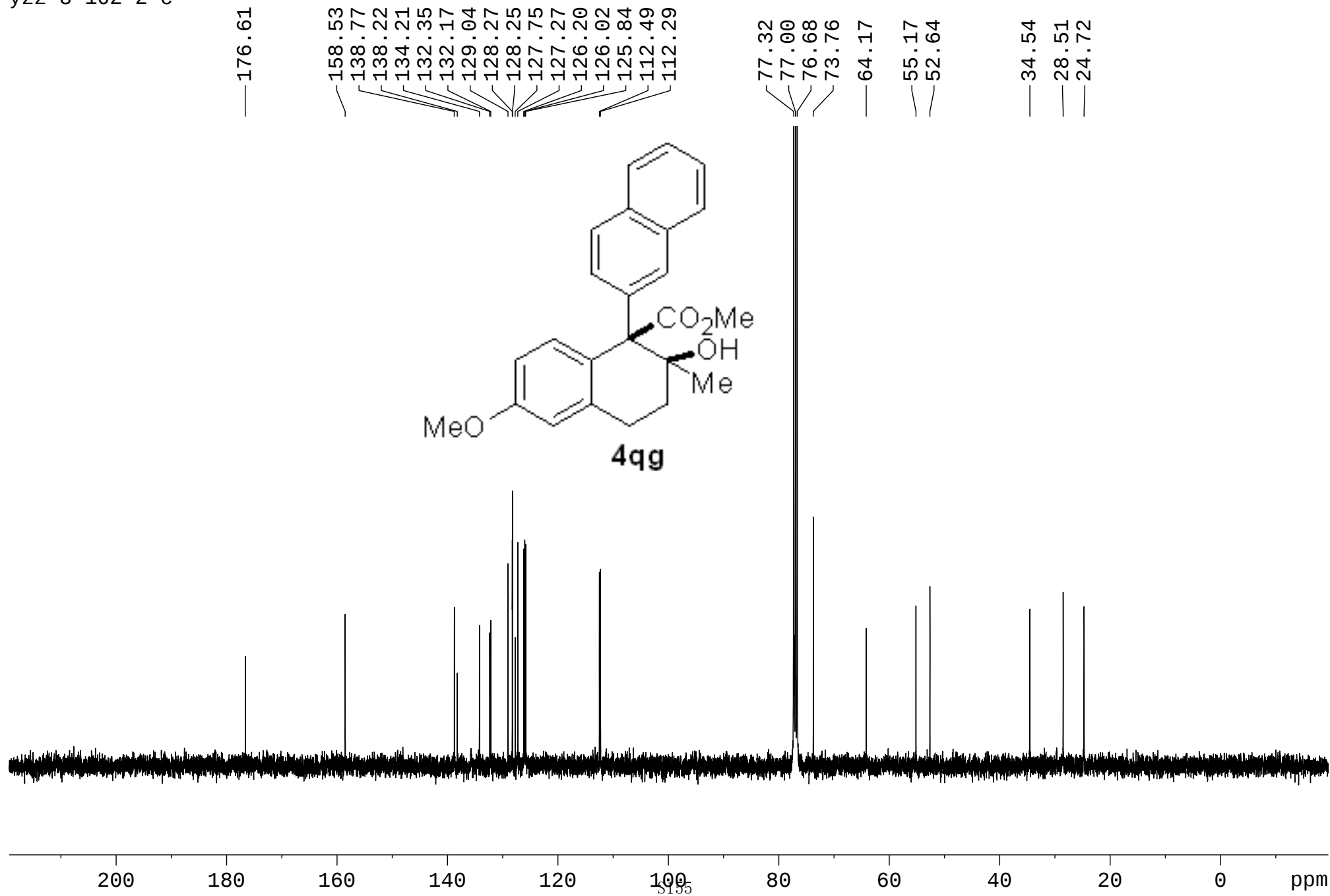
20

ppm

S153



yyy-8-102-2-c

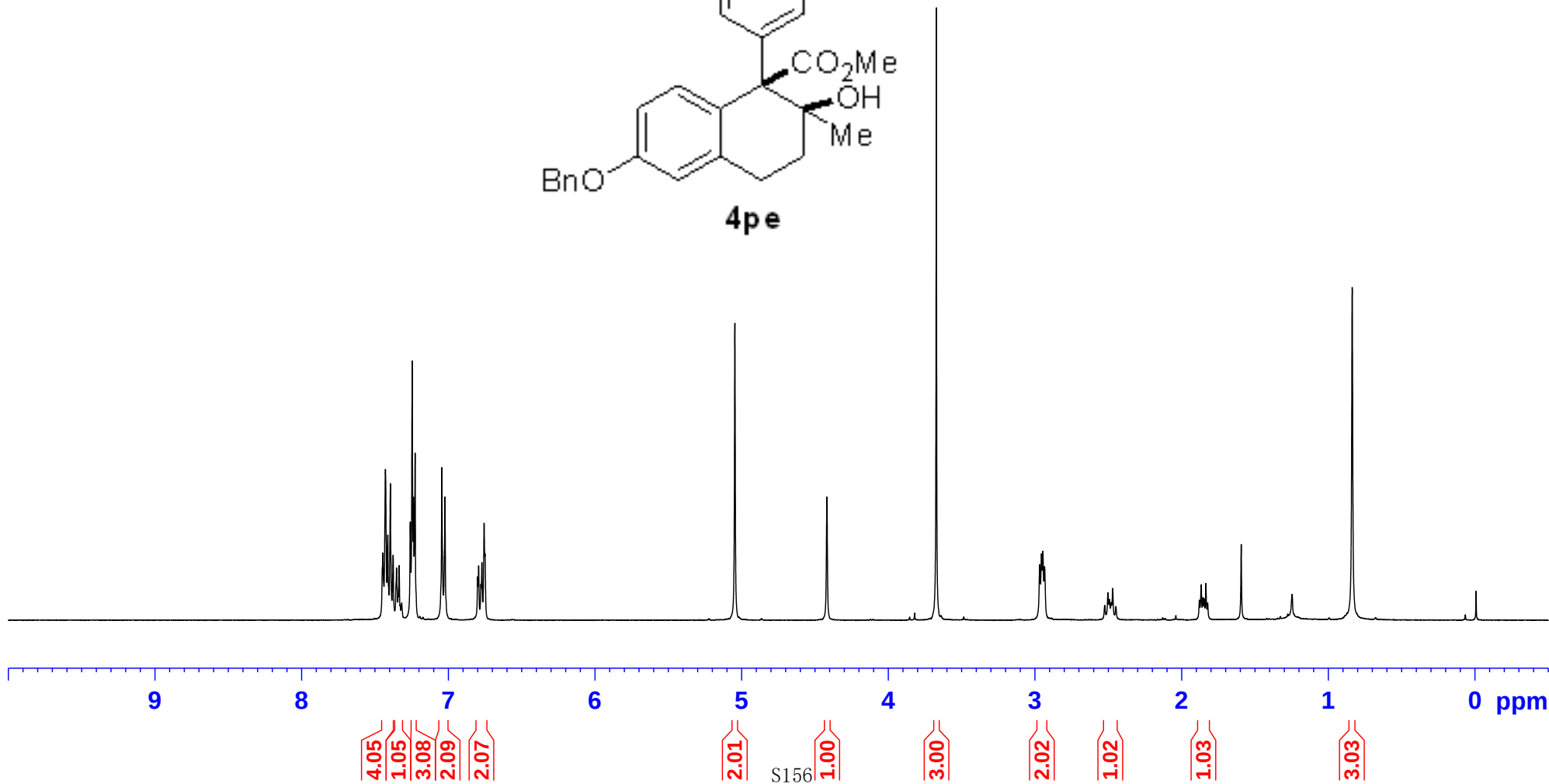
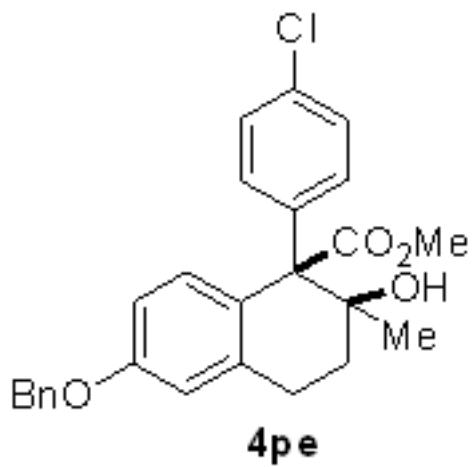


yyy-8-097-1

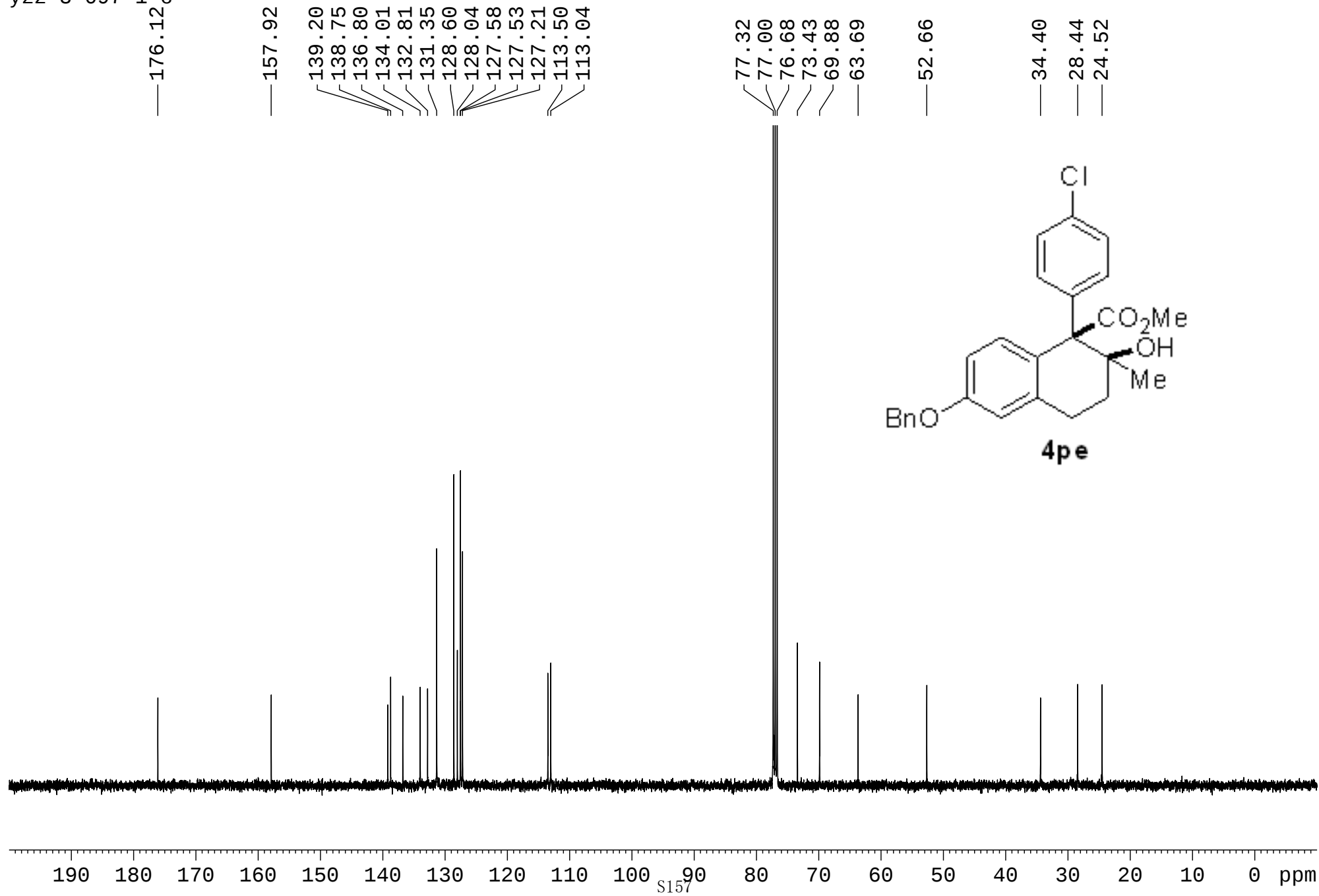
7.447
7.430
7.413
7.396
7.377
7.354
7.342
7.336
7.329
7.318
7.260
7.247
7.238
7.227
7.045
7.023
6.801
6.794
6.778
6.772
6.757
6.750
— 5.047

— 4.419

3.673
2.968
2.956
2.946
2.935
2.525
2.503
2.492
2.481
2.470
2.449
1.879
1.867
1.855
1.847
1.835
1.823
1.594
0.837



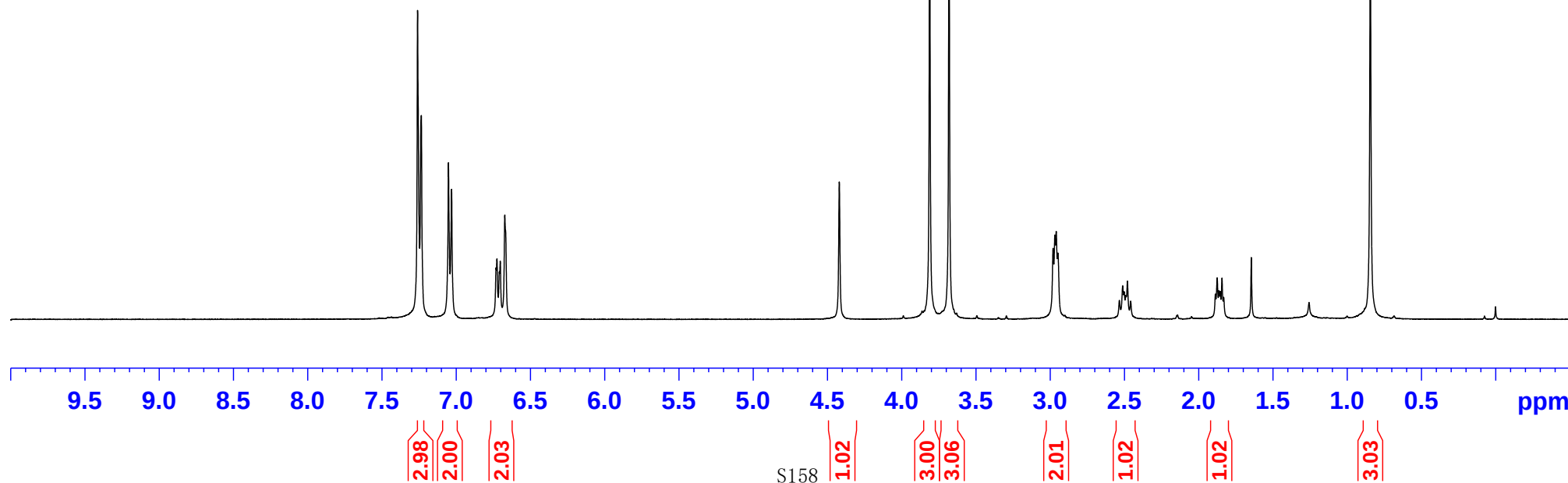
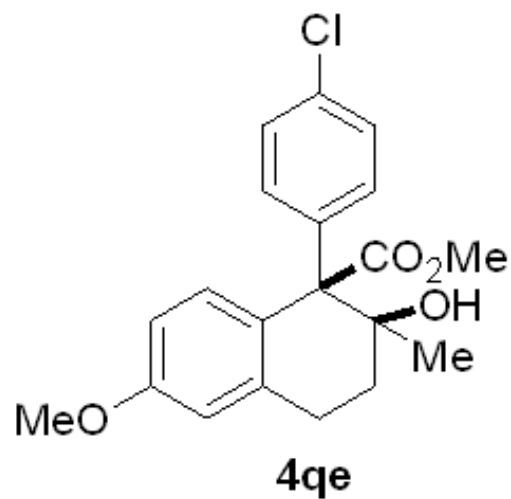
yyy-8-097-1-c



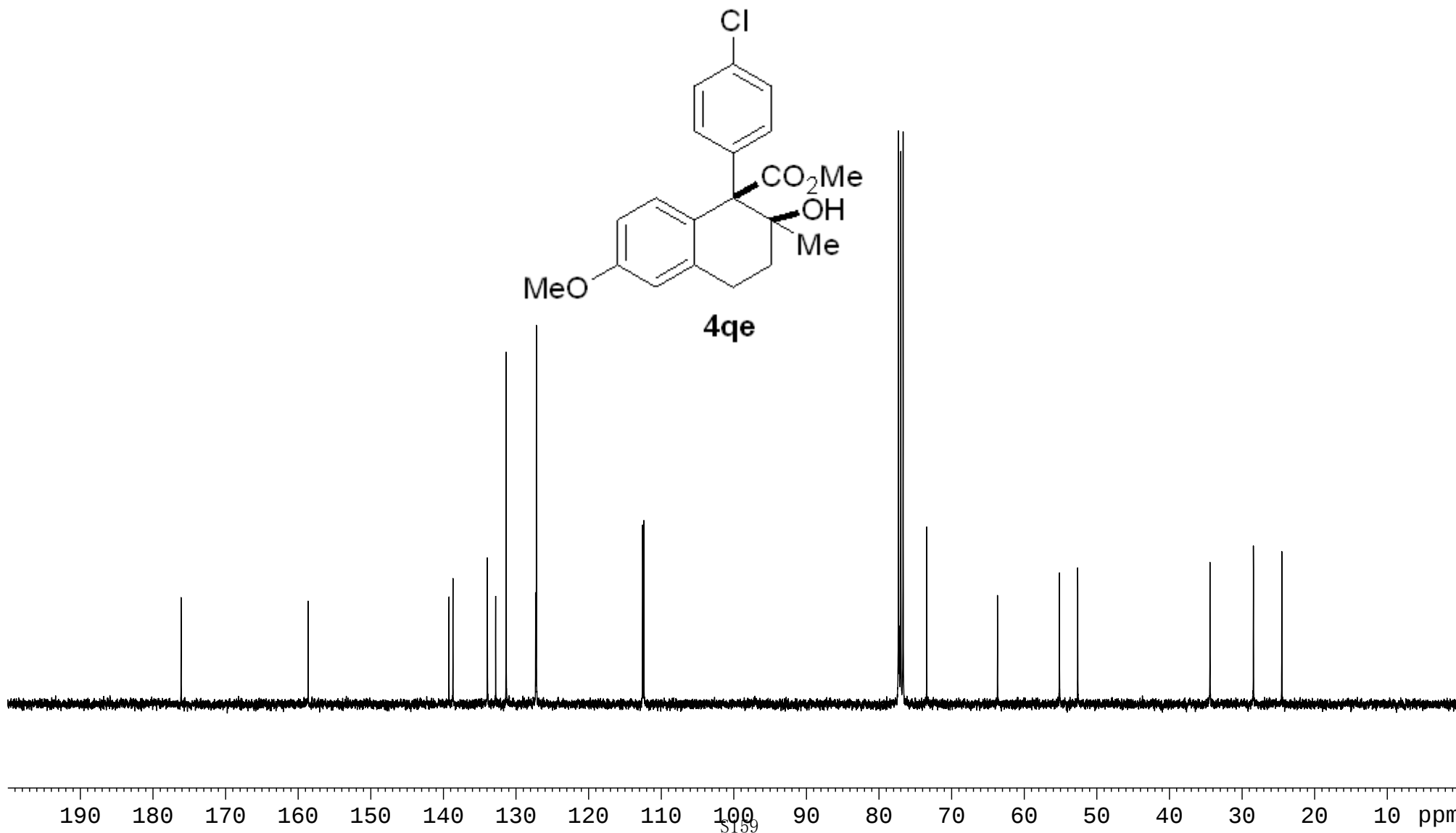
yyy-8-101-1

7.260
7.235
7.052
7.031
6.732
6.726
6.710
6.703
6.673

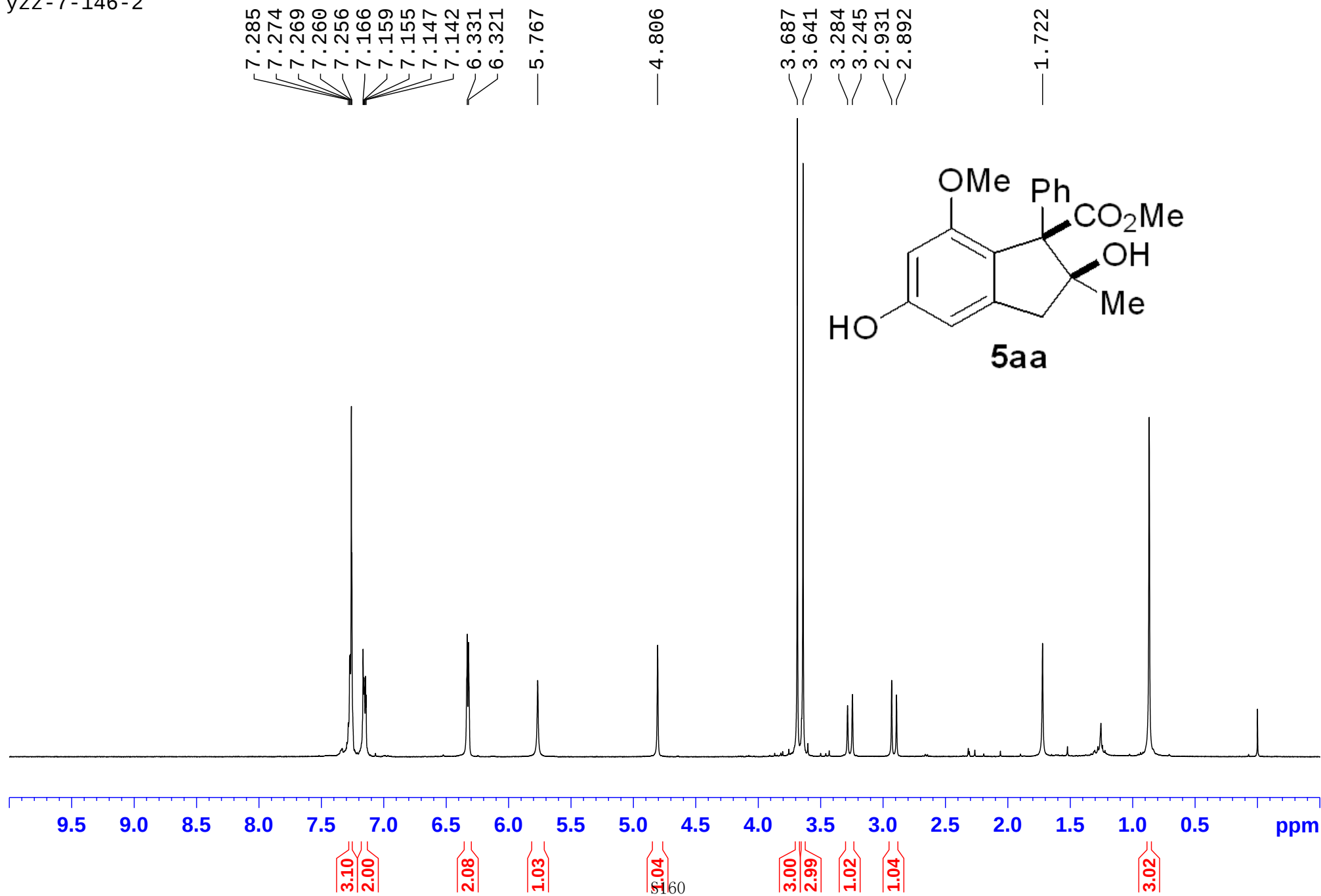
— 4.421
3.812
3.682
2.981
2.969
2.960
2.949
2.535
2.513
2.503
2.491
2.480
2.458
1.888
1.876
1.864
1.856
1.844
1.832
1.646
0.845



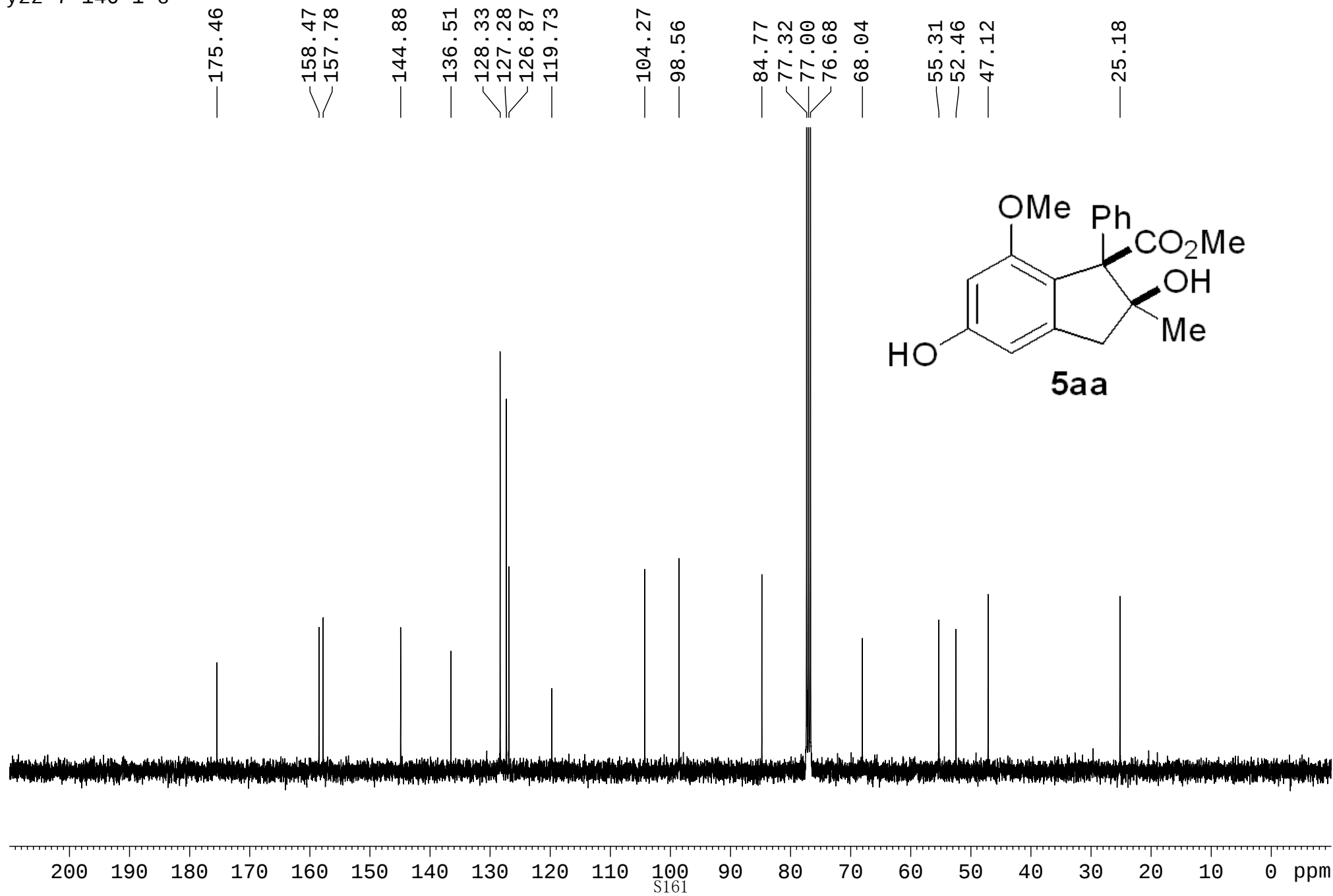
yyy-8-101-1-

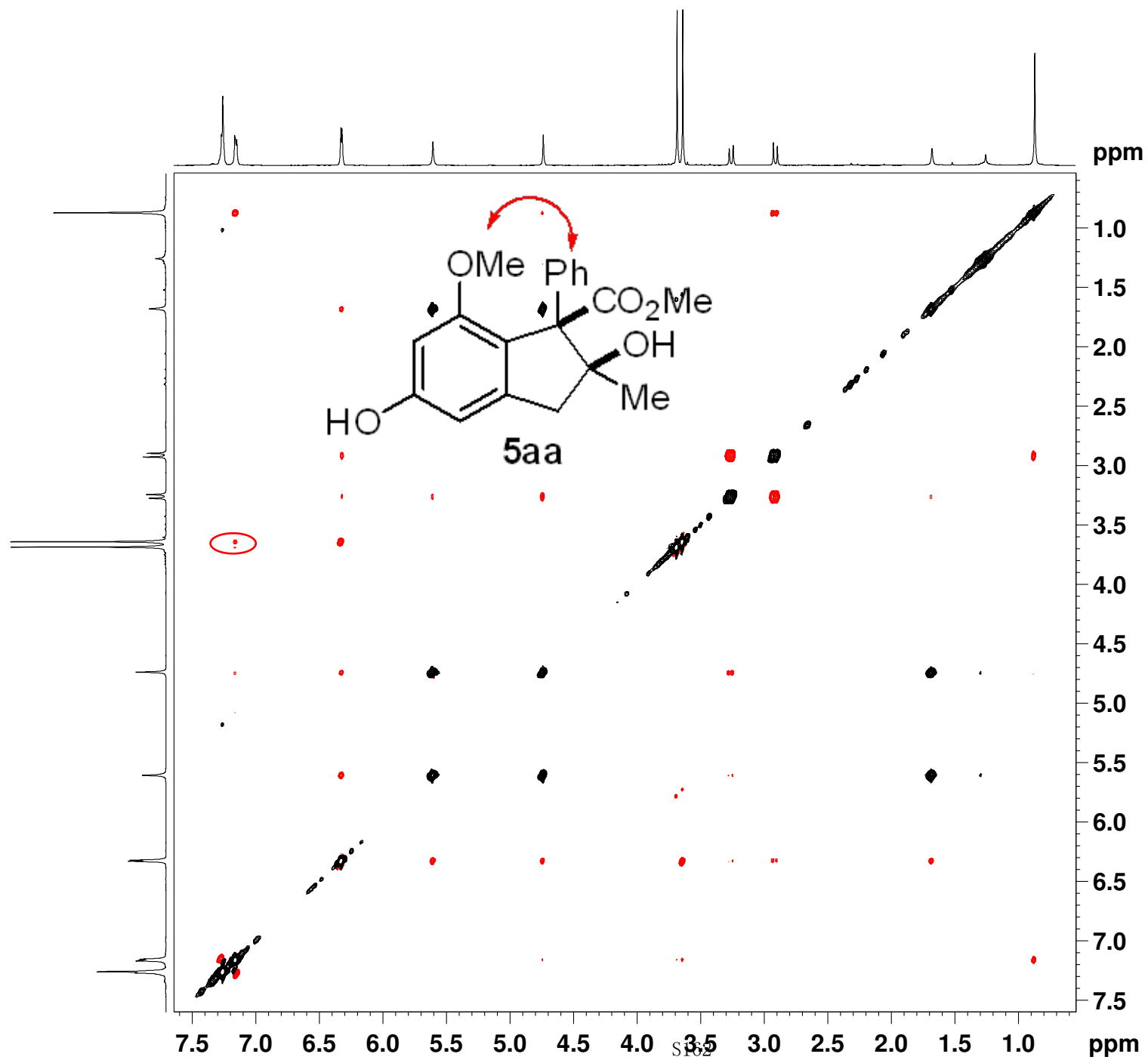


yyy-7-146-2

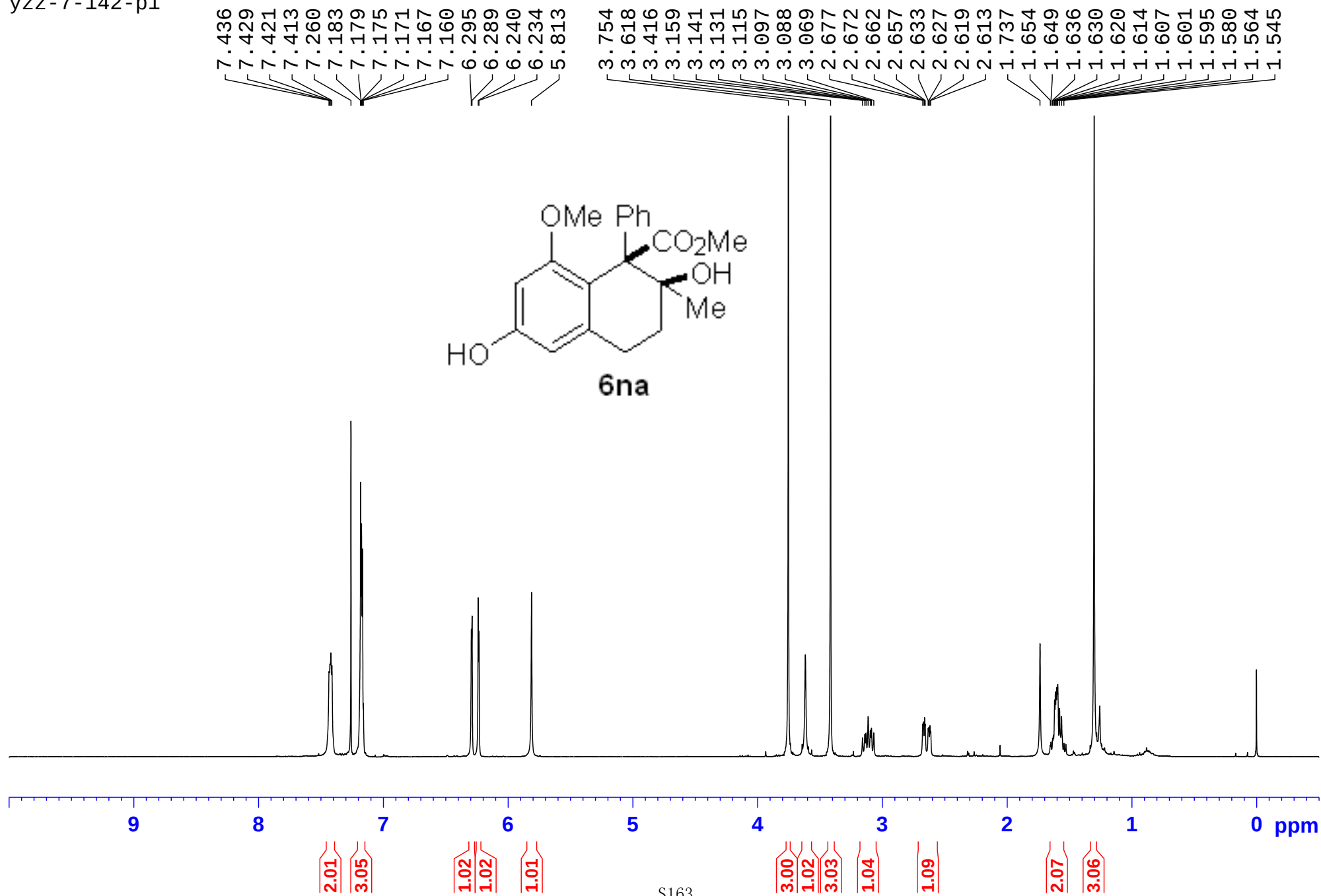


yyy-7-146-1-c

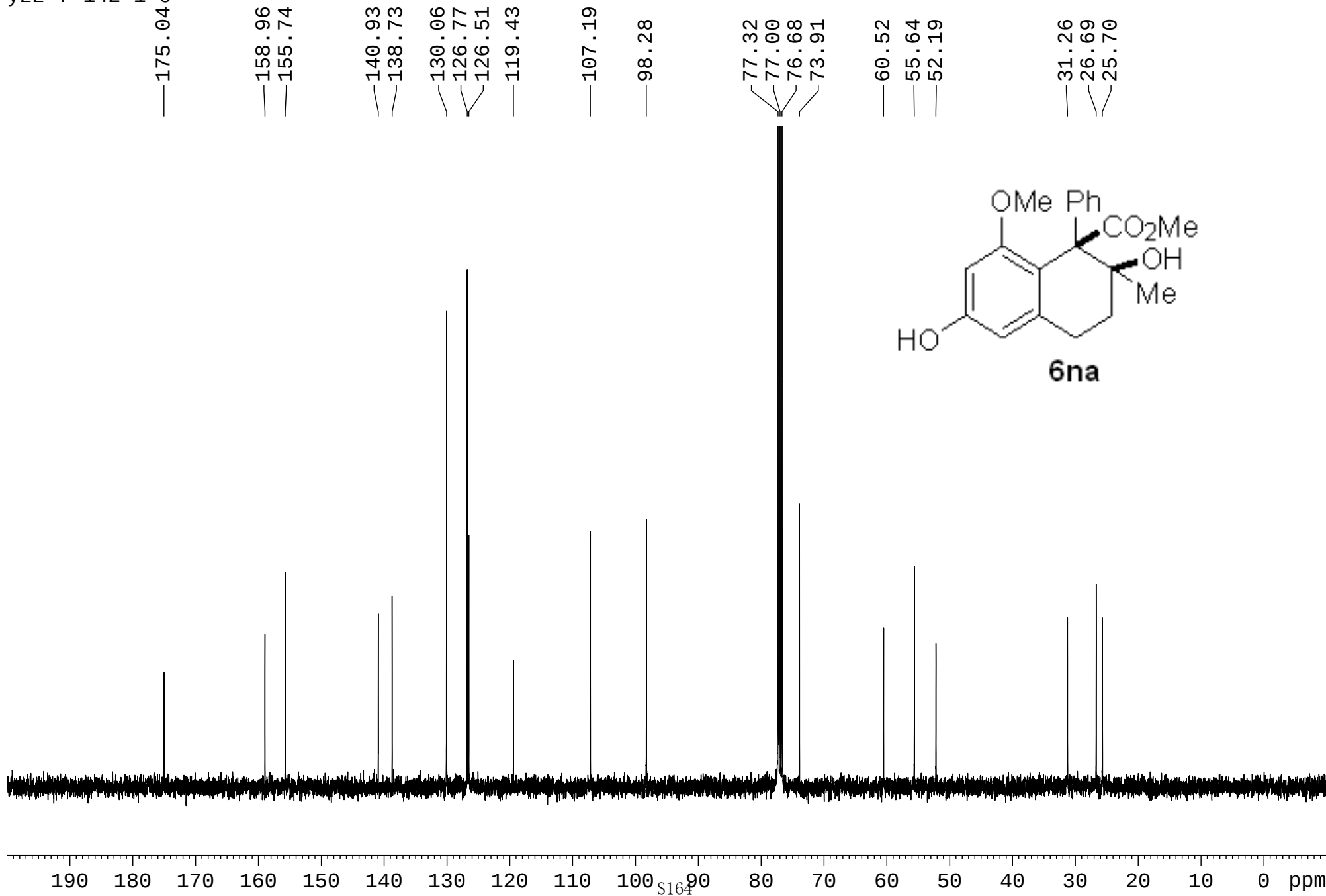


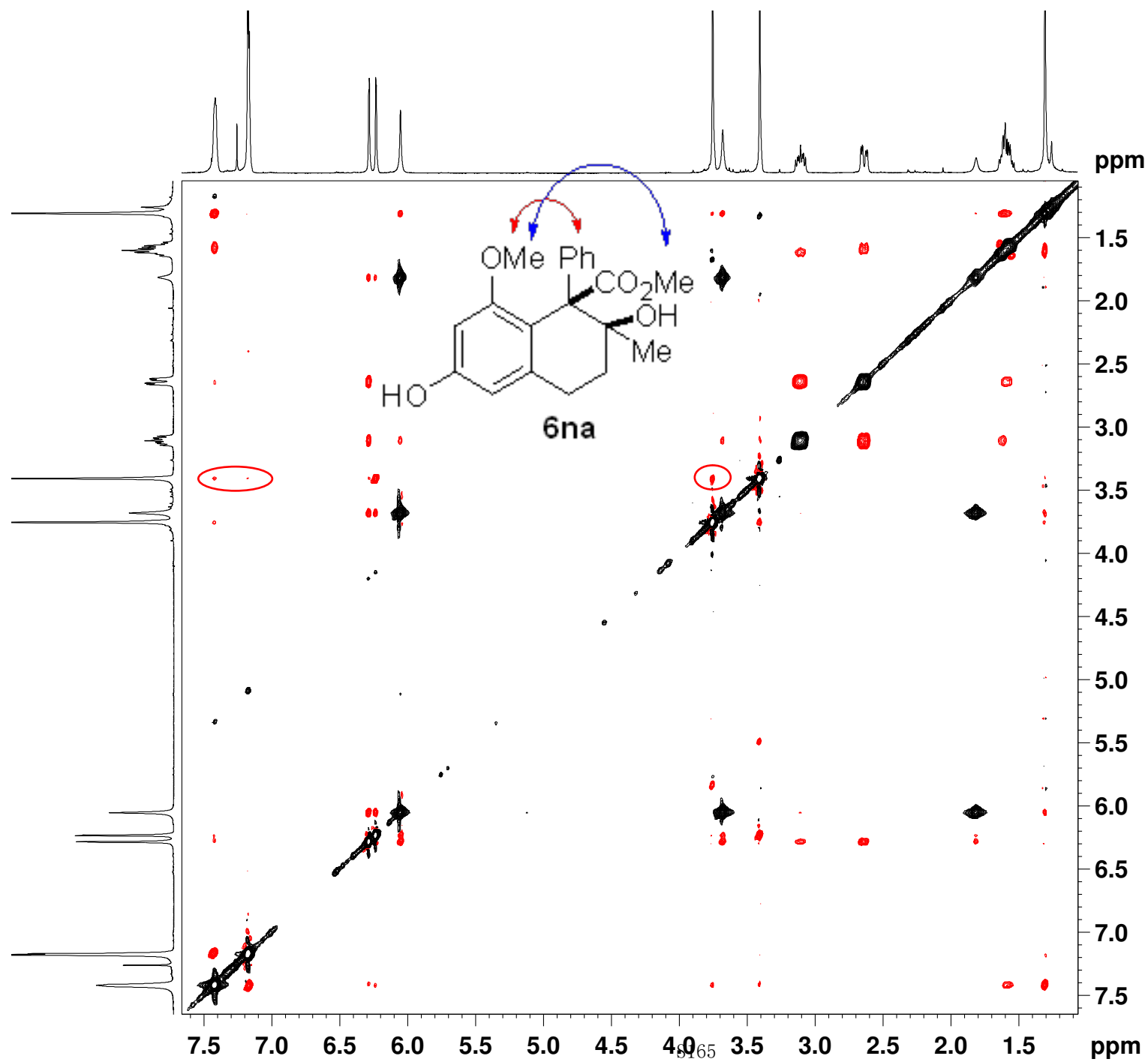


yyy-7-142-p1



yzzz-7-142-1-c





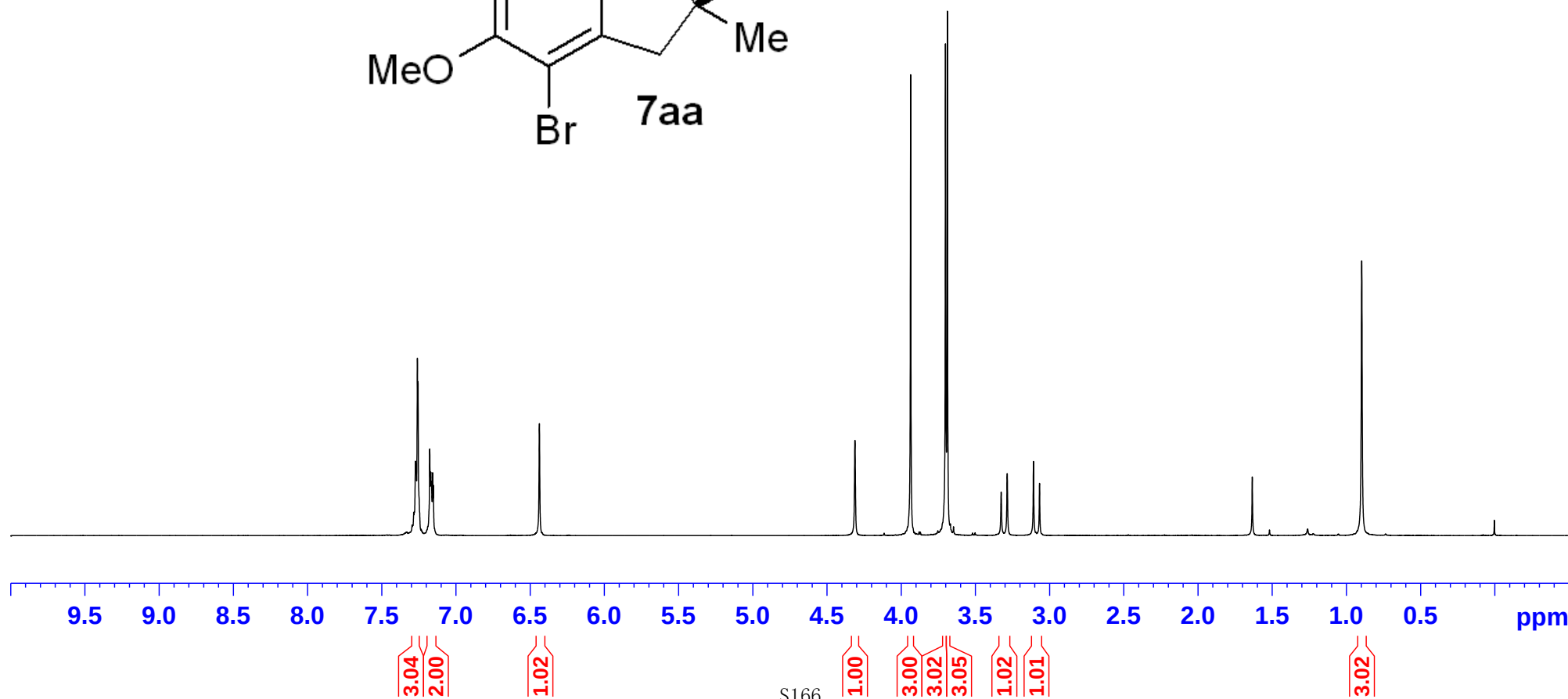
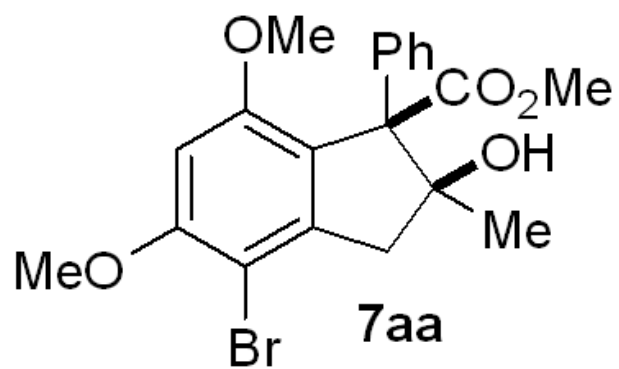
yyy-7-040-1

7.273
7.268
7.260
7.255
7.176
7.170
7.165
7.157
7.152
6.438

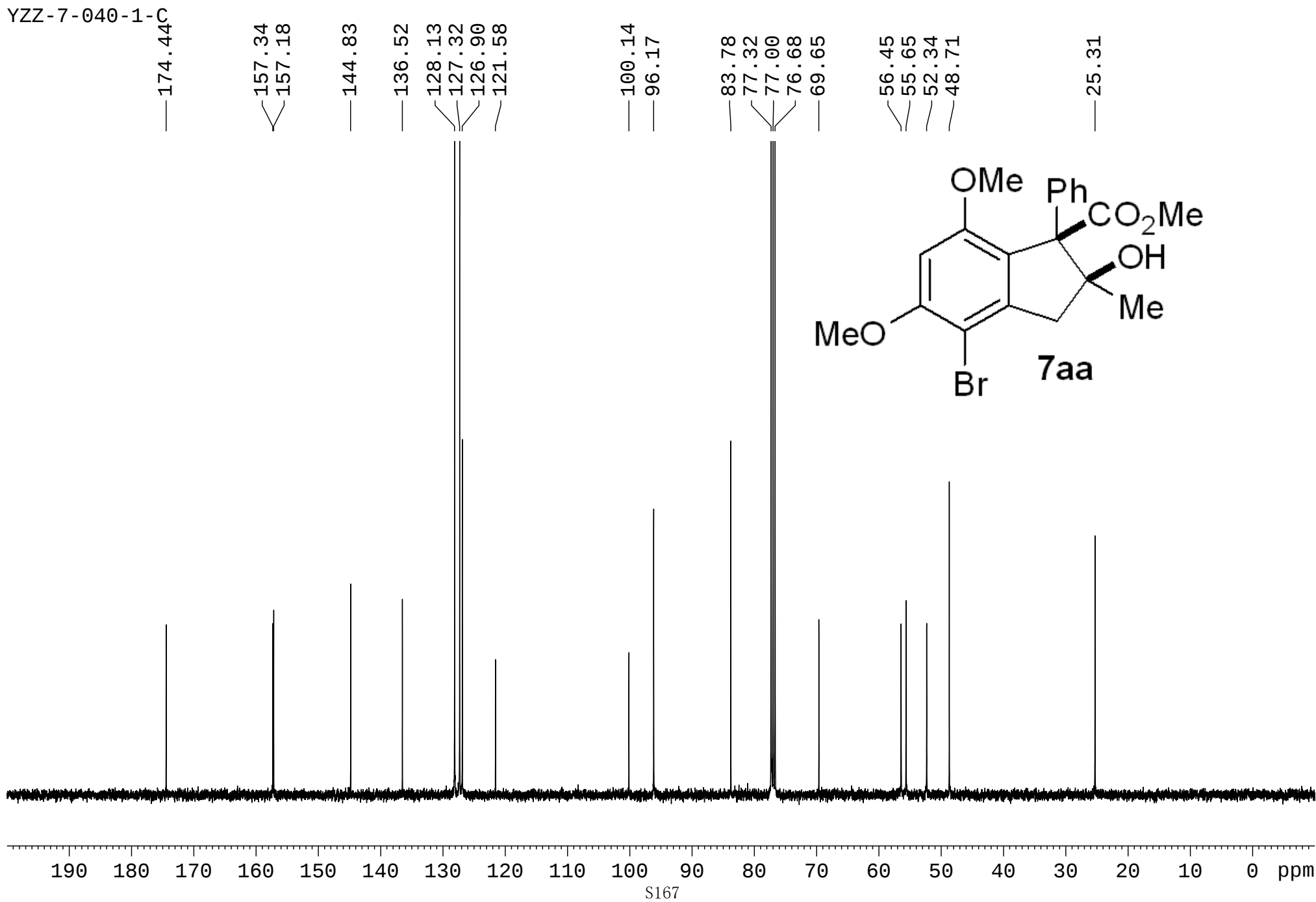
4.311
3.937
3.701
3.689
3.326
3.285
3.108
3.068

1.634

0.897

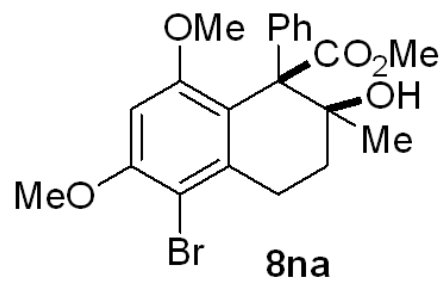


YZZ-7-040-1-C

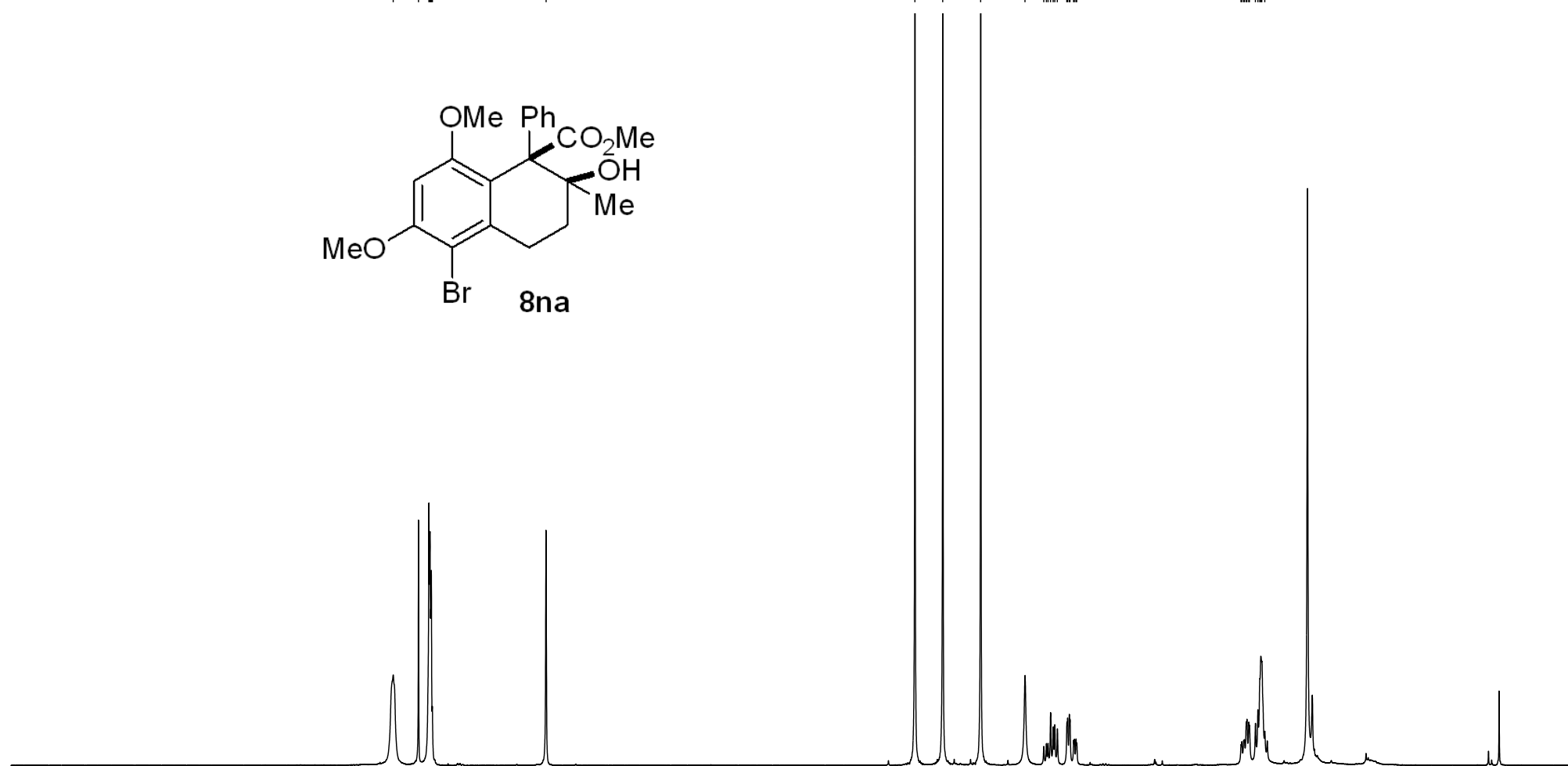


yyy-7-066-1

7.430
7.260
7.190
7.183
7.177
7.174
7.167
— 6.403



3.925
3.737
3.483
3.185
3.059
3.041
3.030
3.013
2.995
2.985
2.967
2.903
2.899
2.888
2.882
2.858
2.853
2.842
2.837
1.733
1.728
1.716
1.711
1.698
1.694
1.681
1.677
1.637
1.620
1.607
1.600
1.593
1.574



9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

2.01

3.02

1.01

3.00

2.98

2.97

0.99

1.02

1.02

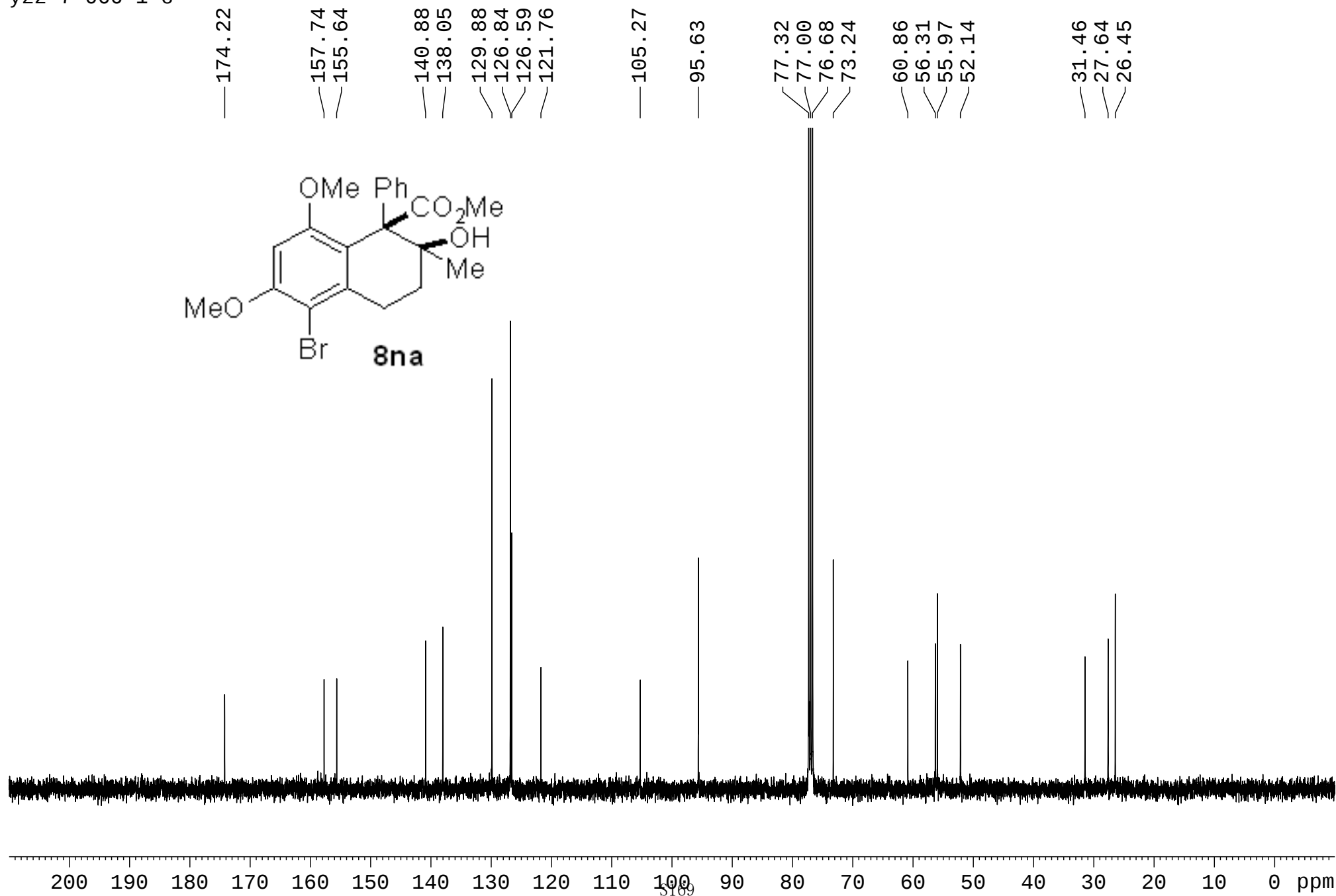
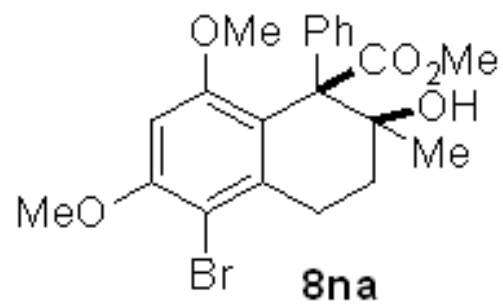
1.03

0.68

0.38

3.06

yyy-7-066-1-c

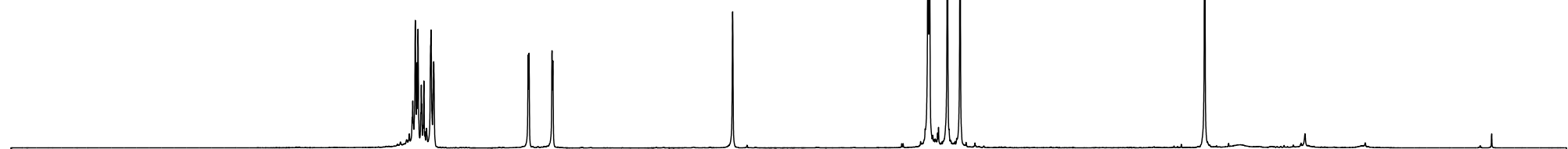
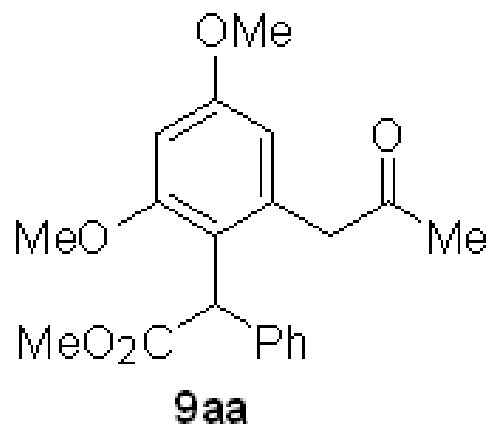


yyy-7-144-p2

7.311
7.291
7.288
7.284
7.271
7.266
7.260
7.252
7.233
7.230
7.226
7.218
7.212
7.205
7.197
7.194
7.164
7.146
6.509
6.503
6.348
6.342
5.129

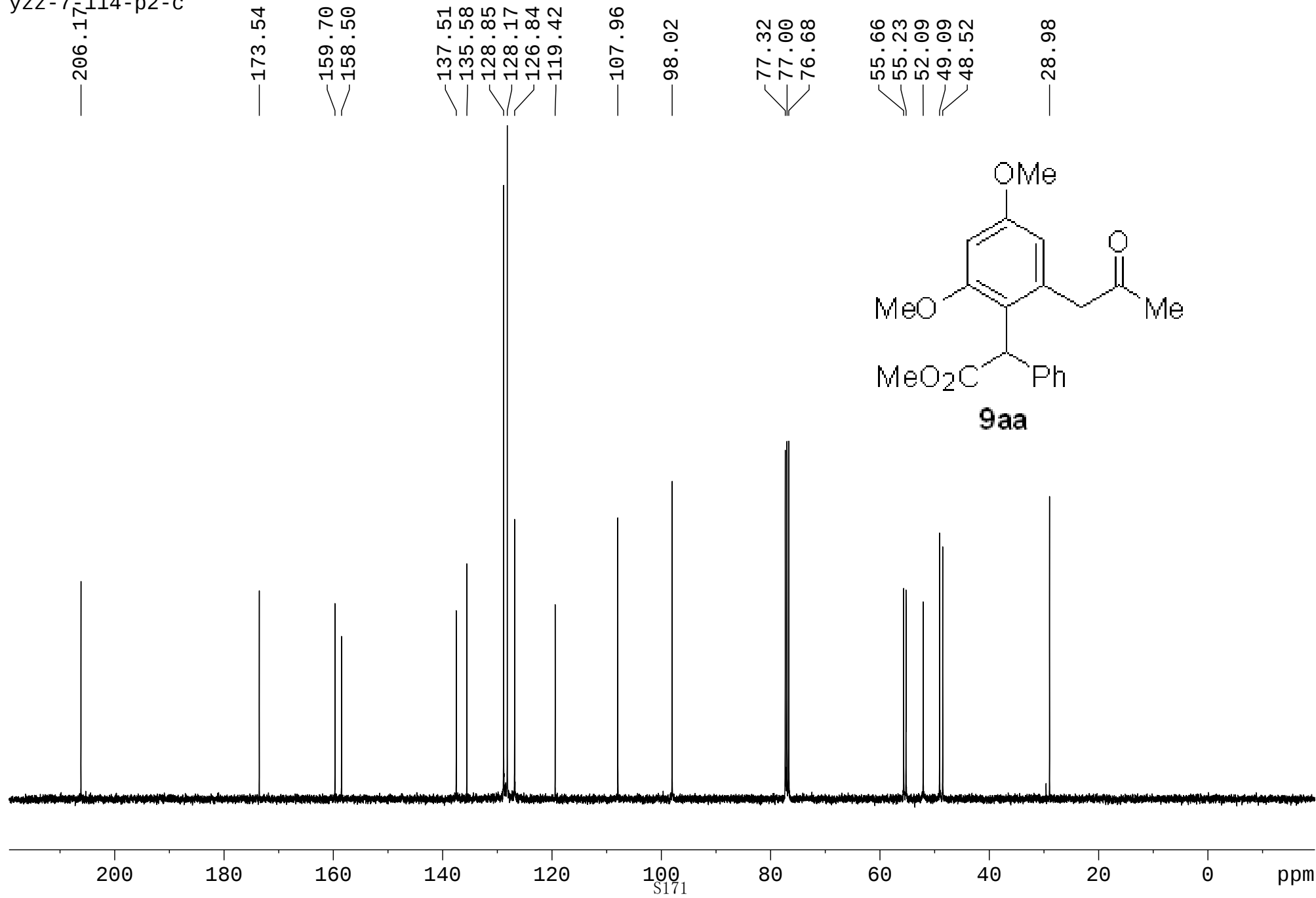
3.811
3.800
3.680
3.594

1.944

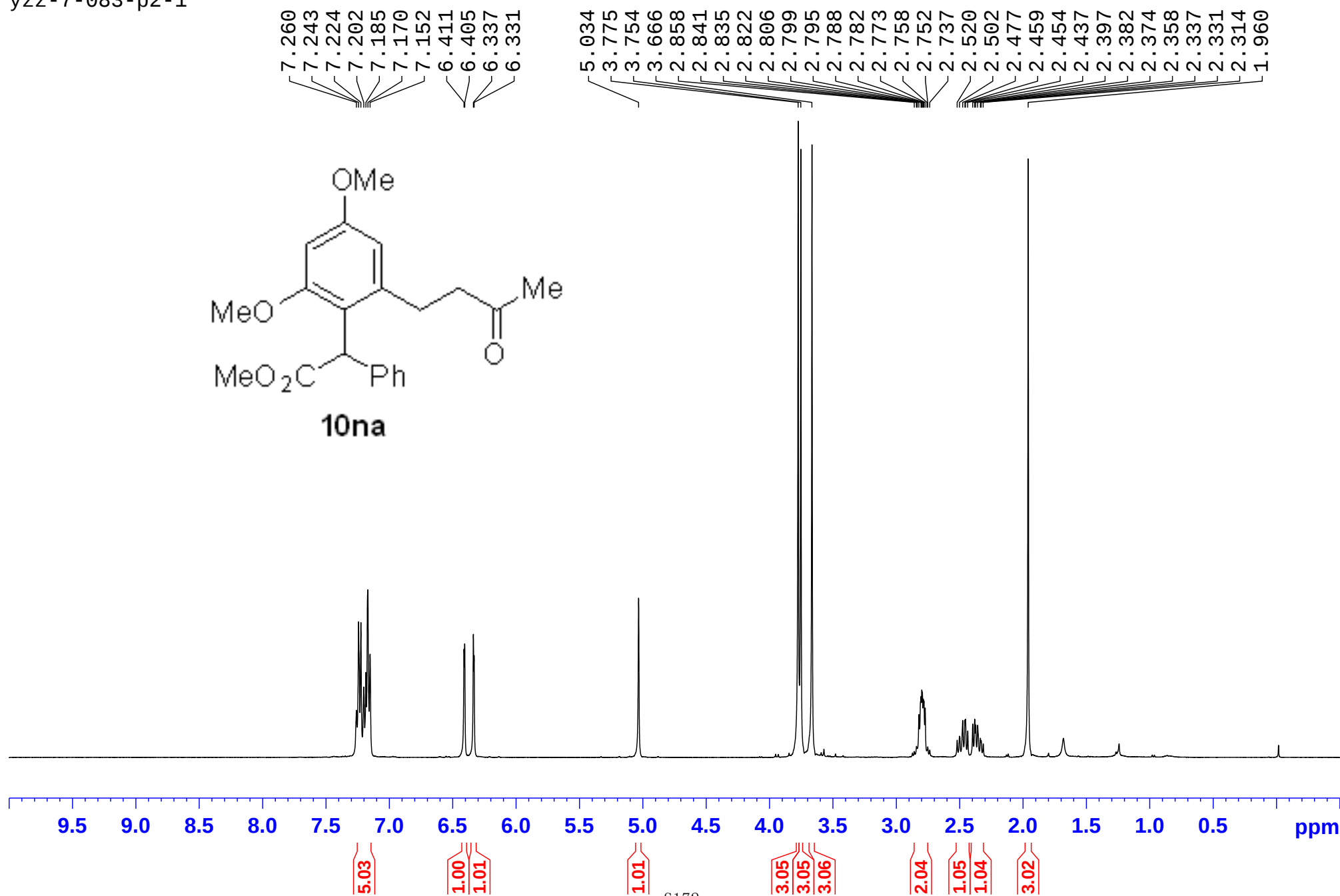


9 8 7 6 5 4 3 2 1 0 ppm

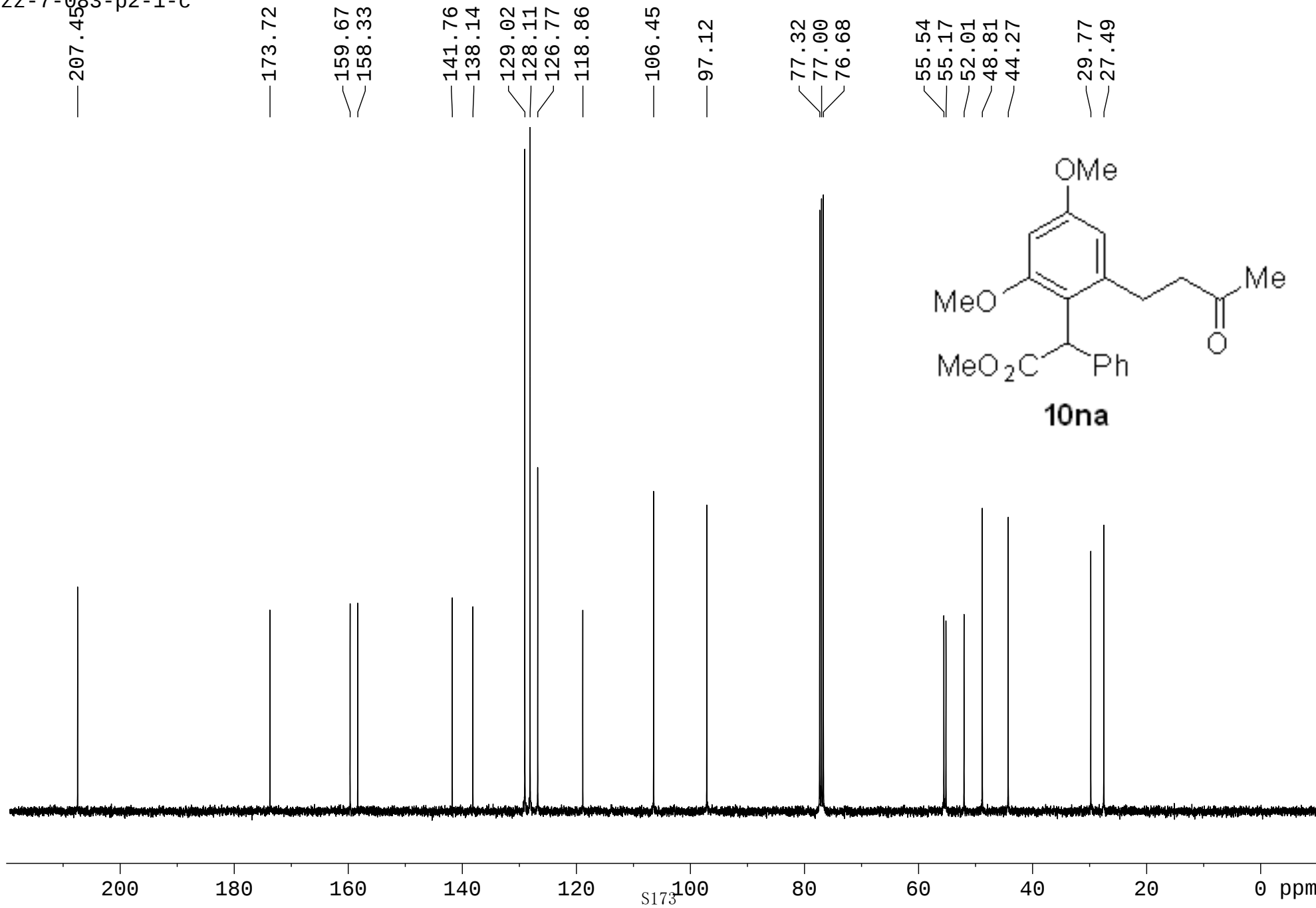
yyy-7,114-p2-c



yyy-7-083-p2-1



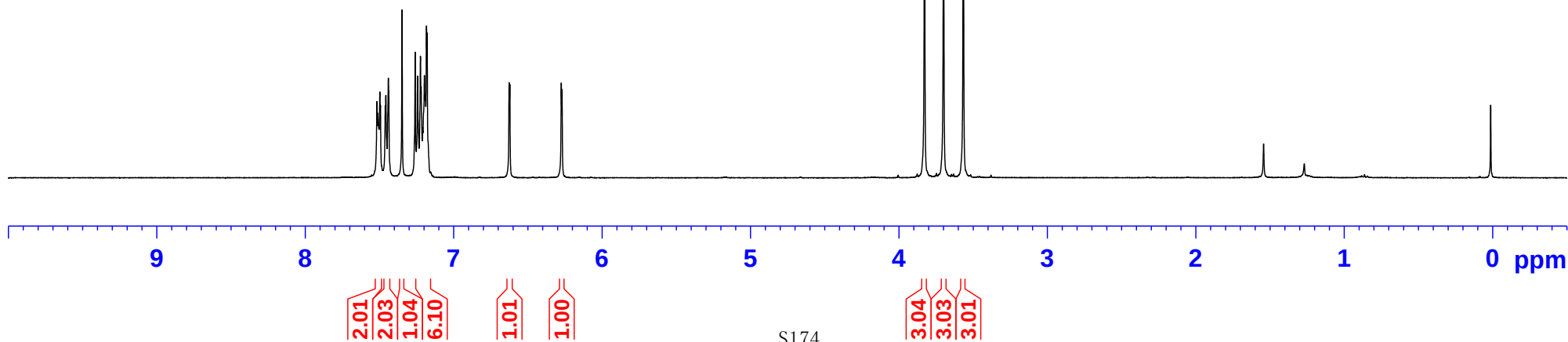
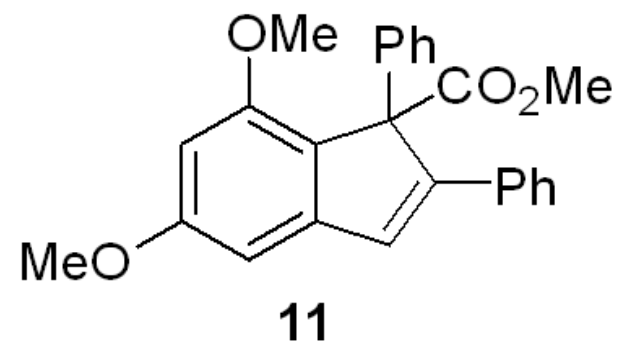
yyy-7-083-p2-1-c



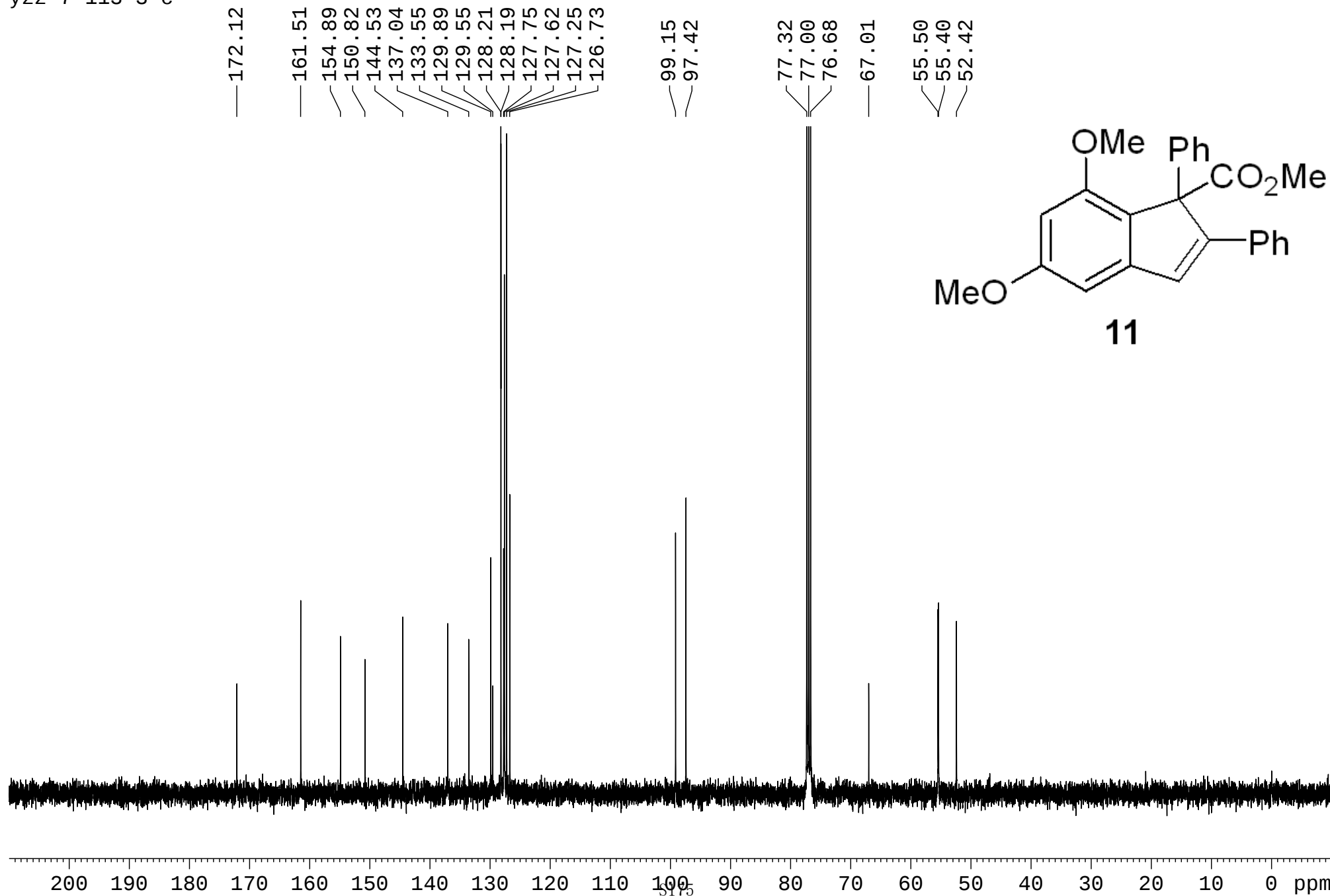
yyy-7-113

7.518
7.511
7.503
7.498
7.493
7.461
7.457
7.440
7.437
7.348
7.260
7.243
7.224
7.219
7.209
7.197
7.193
7.190
7.183
7.179
6.627
6.622
6.275
6.270

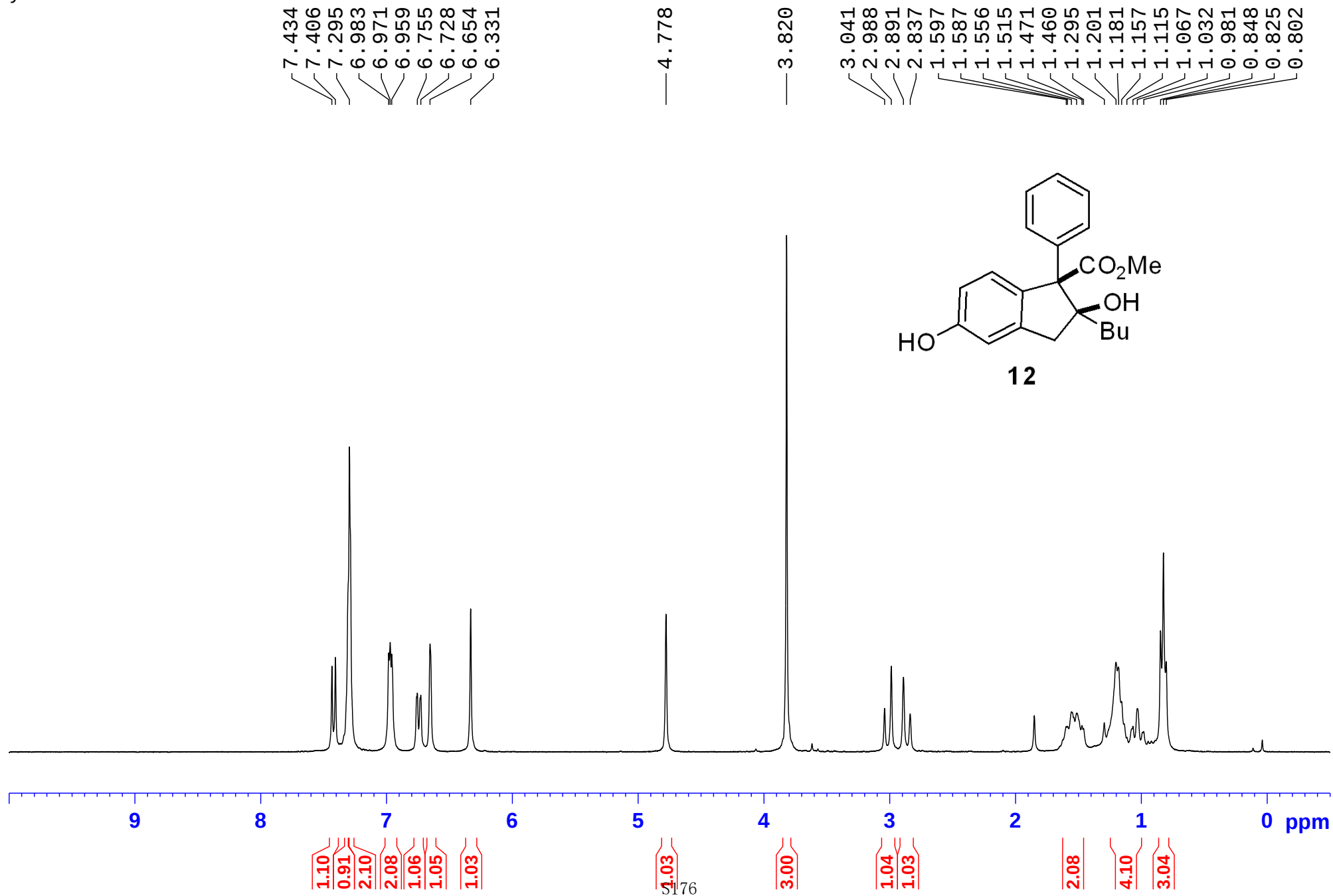
3.828
3.700
3.566



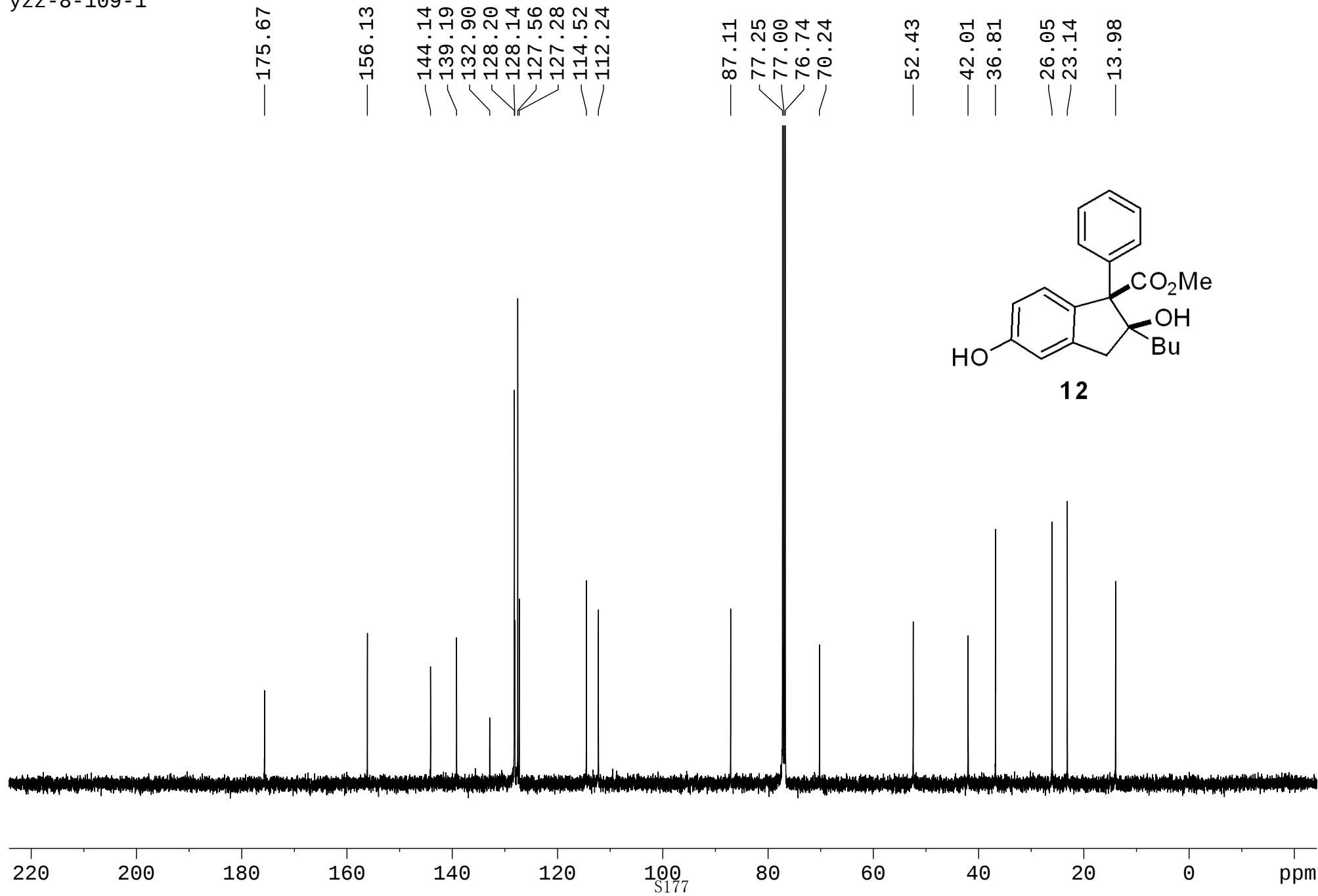
yyy-7-113-3-c



yyy-8-109-1

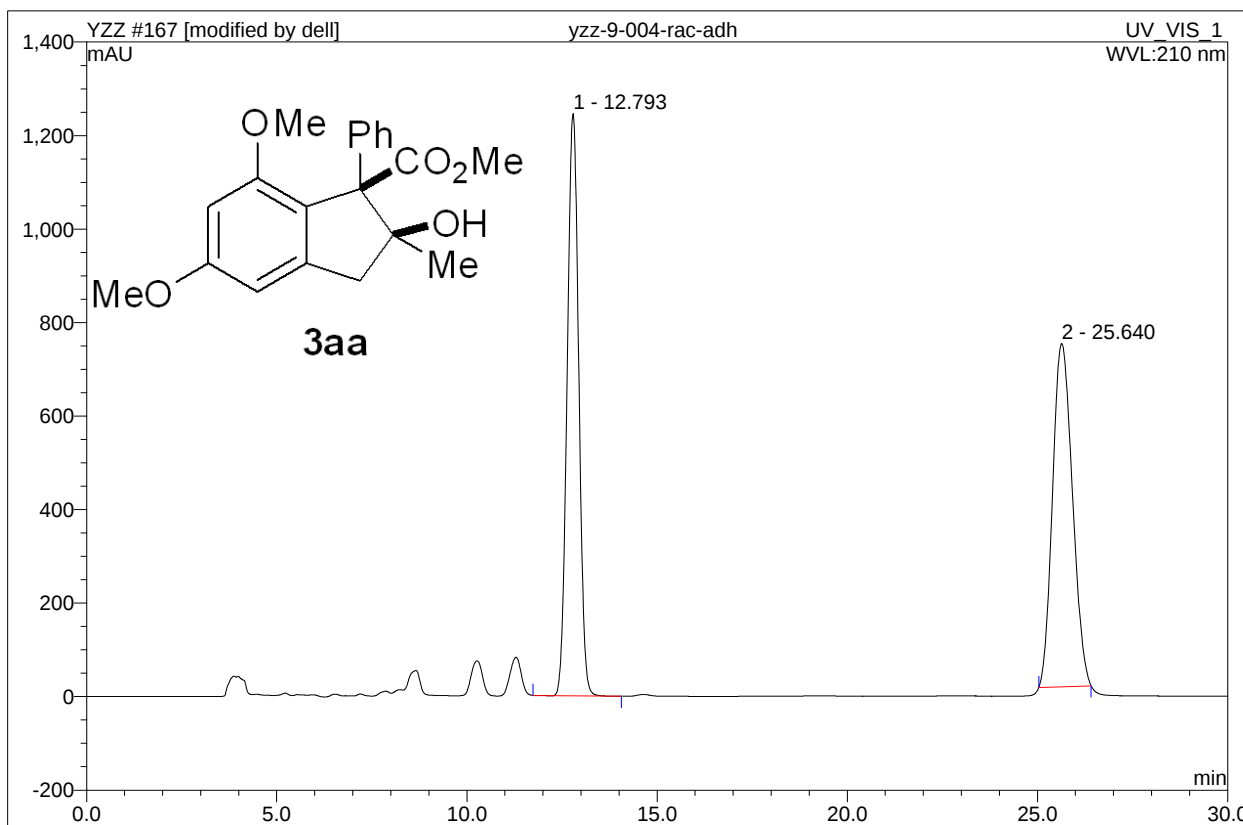


yyy-8-109-1



167 yzz-9-004-rac-adh

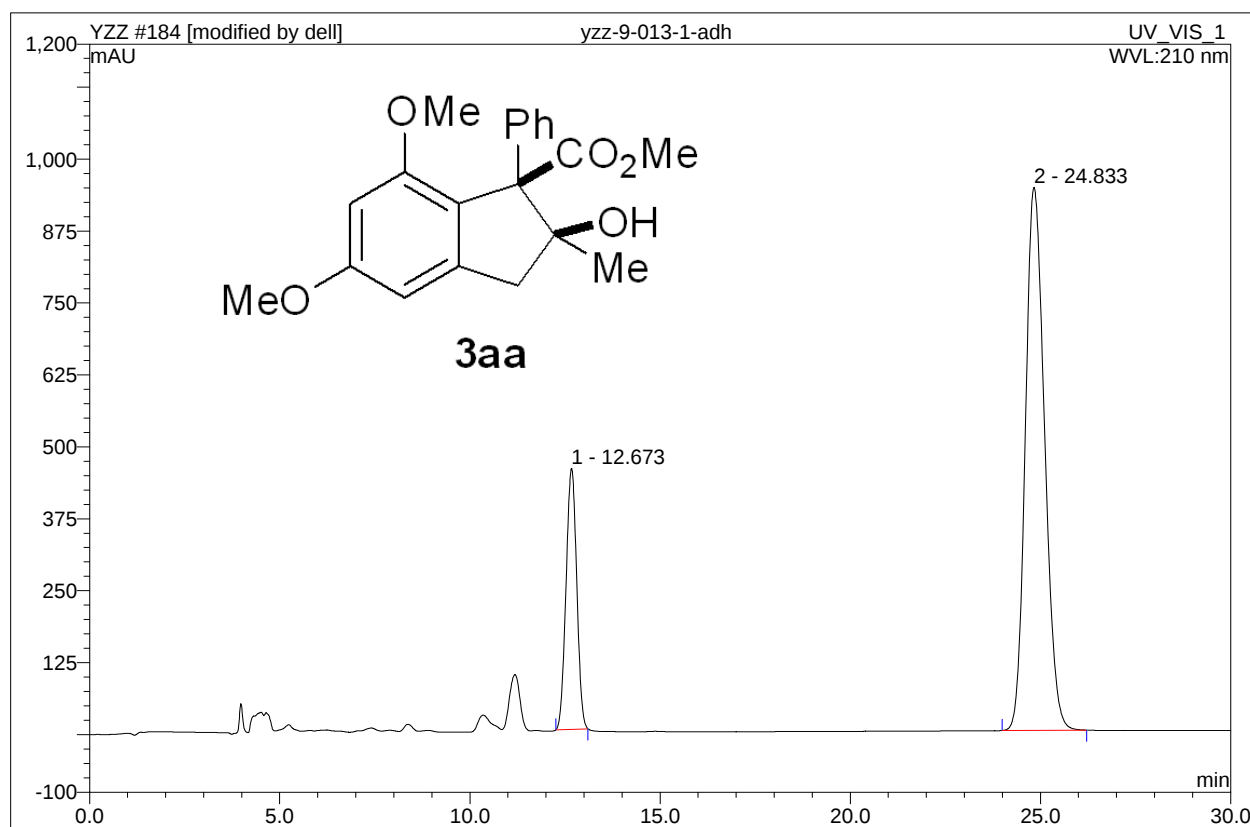
样品名:	yzz-9-004-rac-adh	进样量:	20.0
瓶序号:	169	通道:	UV_VIS_1
样品类型:	unknown	波长:	210
控制程序:	程序文件-公用-08	带宽:	n.a.
定量方法:	方法-公用	稀释因子:	1.0000
记录时间:	2015-3-26 16:17	样品重量:	1.0000
运行时间(min):	30.00	样品量:	1.0000



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	12.79	n.a.	1245.367	438.580	49.73	n.a.	BMB*
2	25.64	n.a.	734.540	443.298	50.27	n.a.	BMB*
总和:			1979.907	881.878	100.00	0.000	

184 yzz-9-013-1-adh

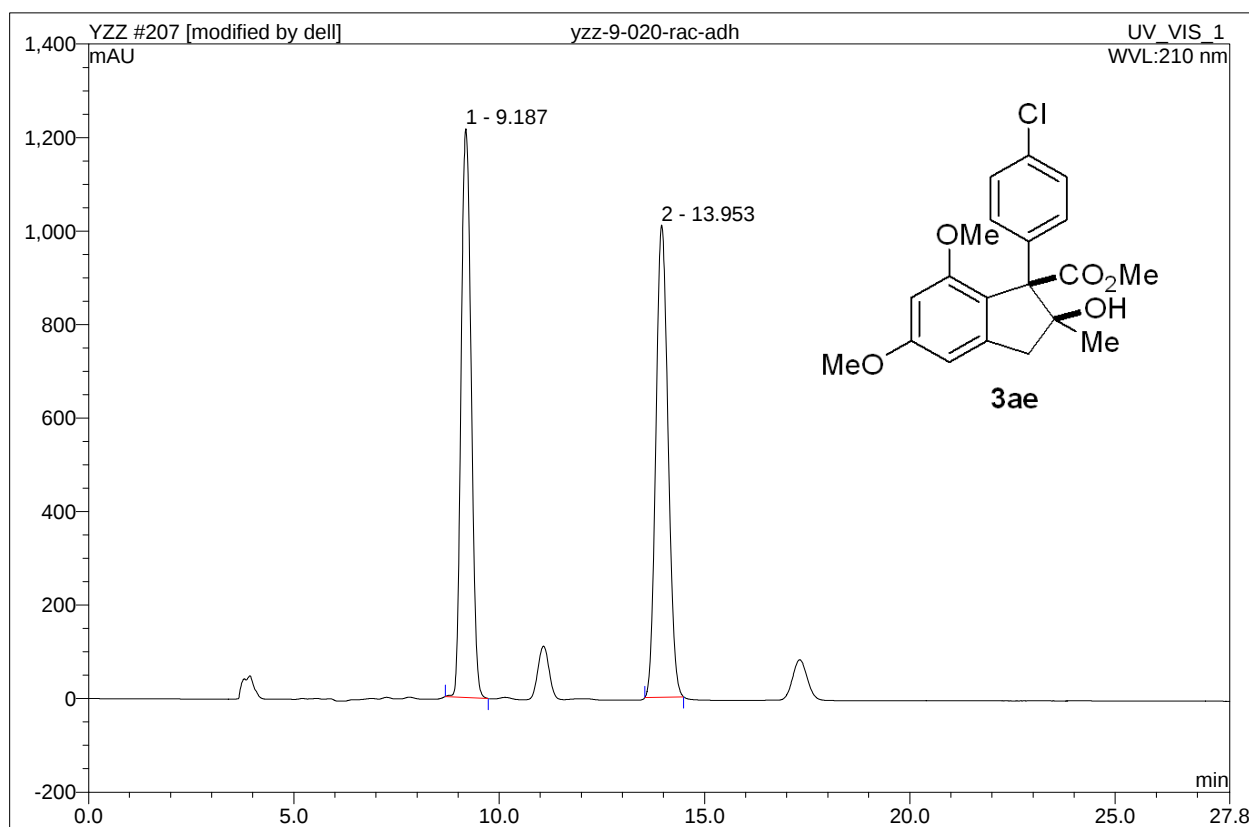
样品名:	yyz-9-013-1-adh	进样量:	20.0
瓶序号:	186	通道:	UV_VIS_1
样品类型:	unknown	波长:	210
控制程序:	程序文件-公用-08	带宽:	n.a.
定量方法:	方法-公用	稀释因子:	1.0000
记录时间:	2015-4-1 22:46	样品重量:	1.0000
运行时间(min):	30.00	样品量:	1.0000



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	12.67	n.a.	453.667	147.163	21.06	n.a.	BMB*
2	24.83	n.a.	944.082	551.673	78.94	n.a.	BMB*
总和:			1397.749	698.837	100.00	0.000	

207 yzz-9-020-rac-adh

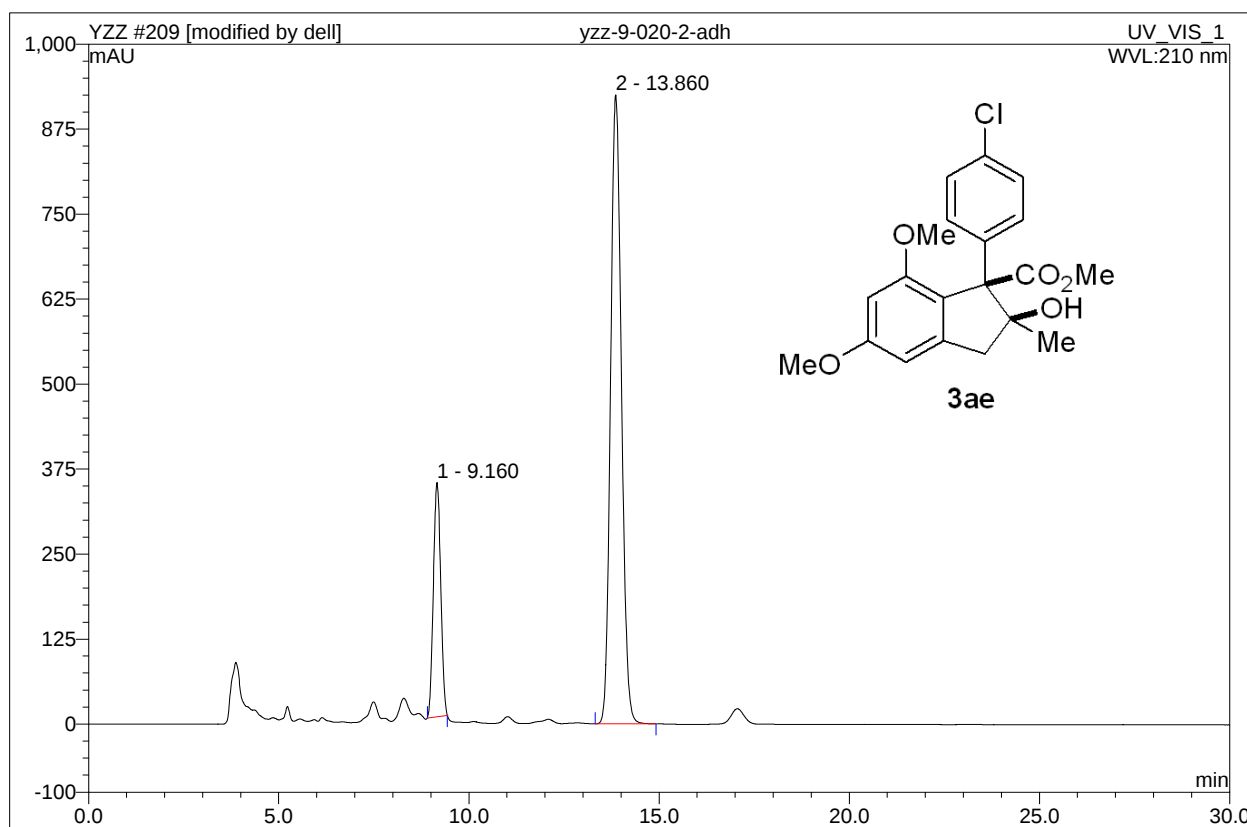
样品名:	yyz-9-020-rac-adh	进样量:	20.0
瓶序号:	209	通道:	UV_VIS_1
样品类型:	unknown	波长:	210
控制程序:	程序文件-公用-1	带宽:	n.a.
定量方法:	方法-公用	稀释因子:	1.0000
记录时间:	2015-5-13 13:08	样品重量:	1.0000
运行时间(min):	27.79	样品量:	1.0000



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	9.19	n.a.	1216.822	345.627	49.97	n.a.	BMB*
2	13.95	n.a.	1010.679	346.059	50.03	n.a.	BMB*
总和:			2227.502	691.686	100.00	0.000	

209 yzz-9-020-2-adh

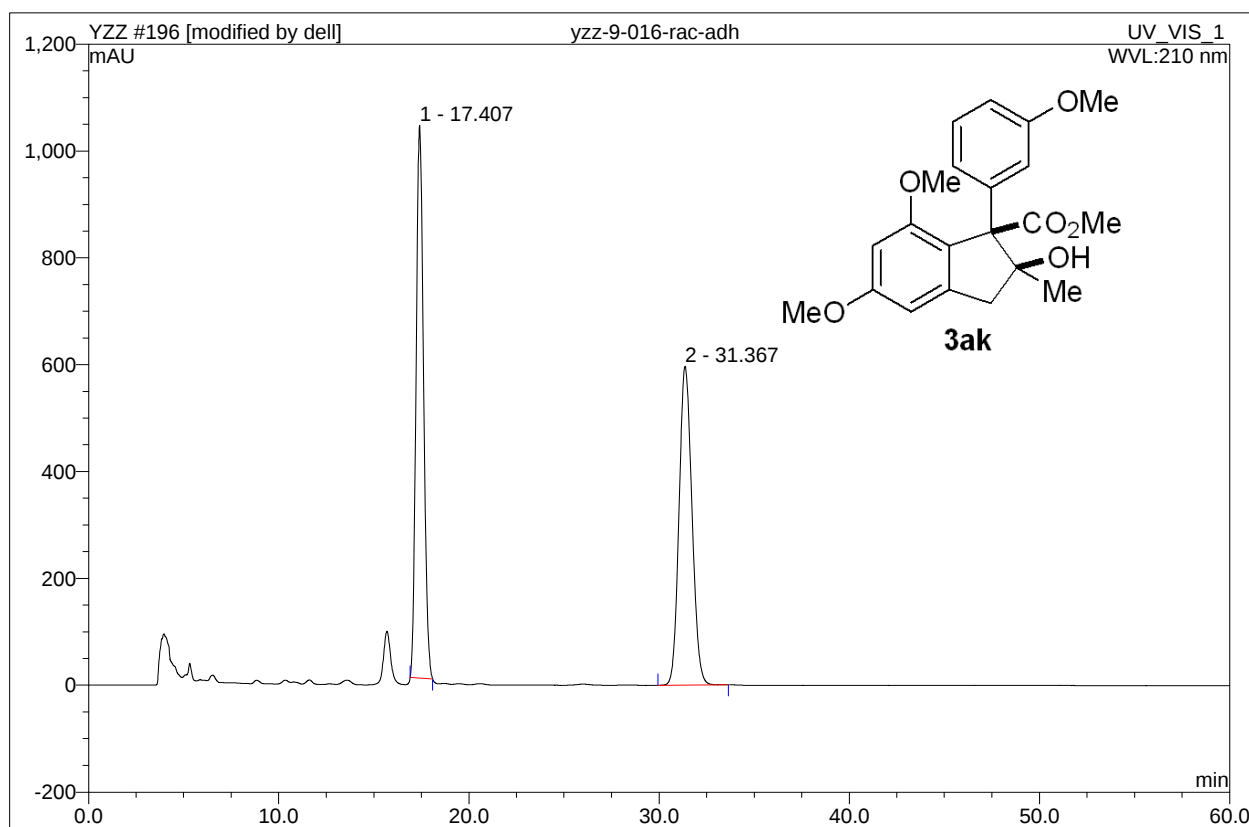
样品名:	yyz-9-020-2-adh	进样量:	20.0
瓶序号:	211	通道:	UV_VIS_1
样品类型:	unknown	波长:	210
控制程序:	程序文件-公用-1	带宽:	n.a.
定量方法:	方法-公用	稀释因子:	1.0000
记录时间:	2015-5-13 14:16	样品重量:	1.0000
运行时间(min):	30.00	样品量:	1.0000



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	9.16	n.a.	344.345	77.563	20.35	n.a.	BMB*
2	13.86	n.a.	925.204	303.587	79.65	n.a.	BMB*
总和:			1269.549	381.150	100.00	0.000	

196 yzz-9-016-rac-adh

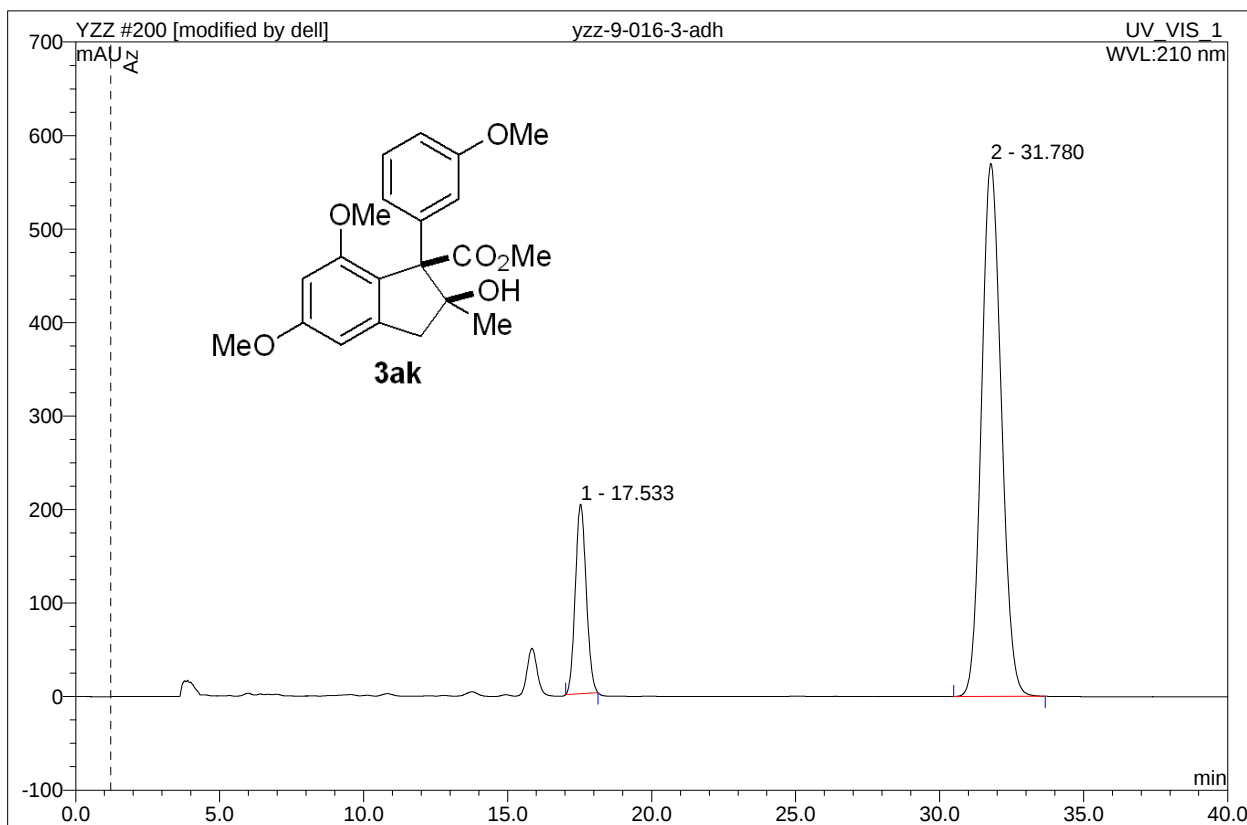
样品名:	yyz-9-016-rac-adh	进样量:	20.0
瓶序号:	198	通道:	UV_VIS_1
样品类型:	unknown	波长:	210
控制程序:	程序文件-公用-08	带宽:	n.a.
定量方法:	方法-公用	稀释因子:	1.0000
记录时间:	2015-4-6 16:38	样品重量:	1.0000
运行时间(min):	60.00	样品量:	1.0000



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	17.41	n.a.	1033.940	468.884	50.02	n.a.	BMB*
2	31.37	n.a.	596.860	468.436	49.98	n.a.	BMB*
总和:			1630.800	937.320	100.00	0.000	

200 yzz-9-016-3-adh

样品名:	yyz-9-016-3-adh	进样量:	20.0
瓶序号:	202	通道:	UV_VIS_1
样品类型:	unknown	波长:	210
控制程序:	程序文件-公用-08	带宽:	n.a.
定量方法:	方法-公用	稀释因子:	1.0000
记录时间:	2015-4-7 15:17	样品重量:	1.0000
运行时间(min):	40.00	样品量:	1.0000



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	17.53	n.a.	202.594	88.792	16.32	n.a.	BMB*
2	31.78	n.a.	570.067	455.419	83.68	n.a.	BMB*
总和:			772.661	544.211	100.00	0.000	