Supporting Information

Palladium-catalyzed Regiospecific *peri*- and *ortho*-C-H Oxygenations of Polyaromatic Rings Mediated by Tunable Directing Groups

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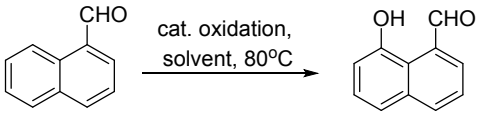
Table S1. Optimization of *peri*-oxygenation of **1a**[a]

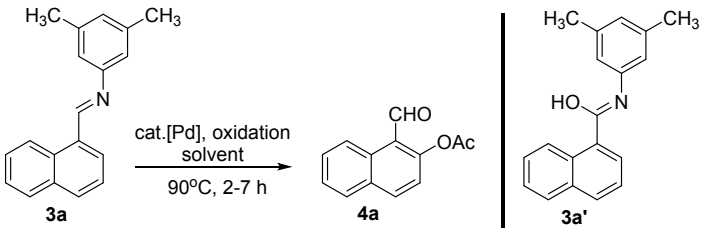


1a **2a**

entry	catalyst	oxidant	solvent	yield(%)[b]
1	$Pd(OAc)_2$	$PhI(OAc)_2$	DCE	<5
2	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	NR[c]
3	$Pd(OAc)_2$	$PhI(OTFA)_2$	DCE	42
4	$Pd(OAc)_2$	TBHP[d]	DCE	NR
5	$Pd(OAc)_2$	LPO[e]	DCE	NR
6	$Pd(OAc)_2$	DTBP[f]	DCE	NR[c]
7	$Pd(CN)_2Cl_2$	$PhI(OTFA)_2$	DCE	36
8	$Pd(OH)_2$	$PhI(OTFA)_2$	DCE	NR[c]
9	$Pd(dba)_2$	$PhI(OTFA)_2$	DCE	49
10	$Pd(OTFA)_2$	$PhI(OTFA)_2$	DCE	48
11	$RuCl_3$	$PhI(OTFA)_2$	DCE	6
12	$[Ru(p\text{-cymene})Cl_2]_2$	$PhI(OTFA)_2$	DCE	34
13	$[Cp^*RhCl_2]_2$	$PhI(OTFA)_2$	DCE	NR[c]
14	$Pd(dba)_2$	$PhI(OTFA)_2$	CCl_4	35
15	$Pd(dba)_2$	$PhI(OTFA)_2$	toluene	<5
16	$Pd(dba)_2$	$PhI(OTFA)_2$	dioxane	NR[c]
17	$Pd(dba)_2$	$PhI(OTFA)_2$	DMF	NR[c]
18	$Pd(dba)_2$	$PhI(OTFA)_2$	DMSO	NR[c]
19[g]	$Pd(dba)_2$	$PhI(OTFA)_2$	DCE	57
20[h]	$Pd(dba)_2$	$PhI(OTFA)_2$	DCE	57

[a]Reaction conditions: aldehyde 1a (1.0 mmol), oxidant (2.0 mmol), Pd catalyst (5.0 mol %), solvent (10.0 mL). [b]The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as an internal standard. [c]NR = No Reaction. [d]TBHP = *tert*-butyl hydroperoxide. [e]LPO = dilauroyl peroxide. [f]DTBP = di-*tert*-butyl peroxide. [g]DCE reduced by half. [h][Pd] (3.0 mol%), DCE (5.0 mL).

Table S2. Optimization of *ortho*-oxygenation of **3a**[a]



entry	catalyst	oxidant	solvent	yield(%)[b]
1	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	32[c]
2	$Pd(OAc)_2$	TBHP	DCE	15[c]
3	$Pd(OAc)_2$	$PhI(OTFA)_2$	DCE	74[c]
4	$Pd(OAc)_2$	IBX	DCE	46[c]
5	$Pd(OAc)_2$	$PhI(OAc)_2$	DCE	70
6	$Pd(OAc)_2$	$PhI(OAc)_2$	CCl_4	65
7	$Pd(OAc)_2$	$PhI(OAc)_2$	$CHCl_3$	55
8	$Pd(OAc)_2$	$PhI(OAc)_2$	Toluene	10
9	$Pd(OAc)_2$	$PhI(OAc)_2$	CH_3CN	20
10	$PdCl_2$	$PhI(OAc)_2$	DCE	50
11	$Pd(dba)_2$	$PhI(OAc)_2$	DCE	83
12	$Pd(CH_3CN)_2Cl_2$	$PhI(OAc)_2$	DCE	73
13	$Pd(OTFA)_2$	$PhI(OAc)_2$	DCE	51

[a]Reaction conditions: imine 3a (1.0 mmol), oxidant (2.5 mmol), Pd catalyst (5.0 mol %), solvent (10 mL). [b]All yields are reported as isolated yields. [c]yield of side oxidation product **3a'**.

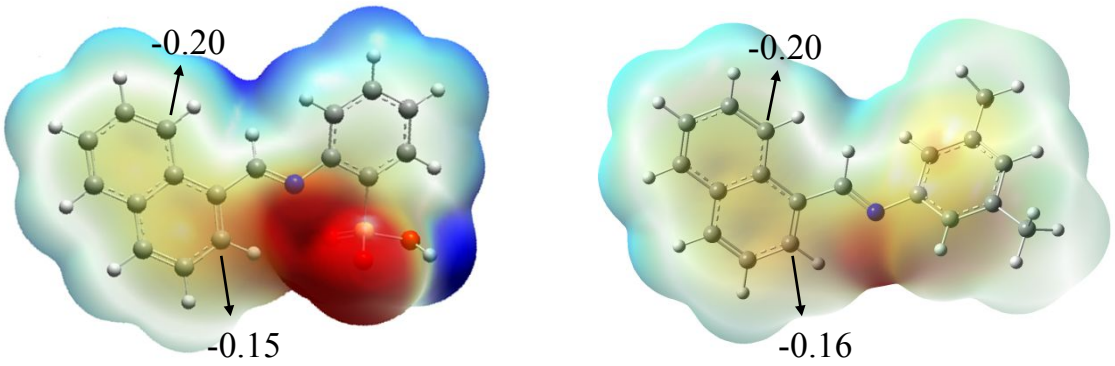


Figure S1. Calculated electrostatic potential map and the natural bond orbital (NBO) charges for the Schiff bases intermediates of **1a** (left) and **3a** (right).

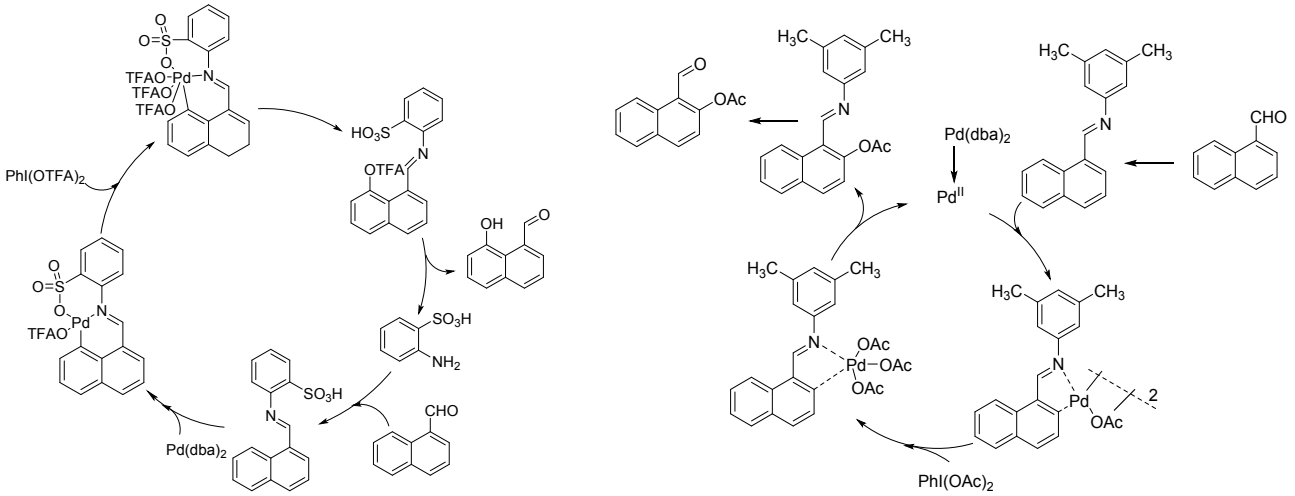


Figure S2. Proposed mechanisms for *peri*-oxygenation and *ortho*-oxygenation.

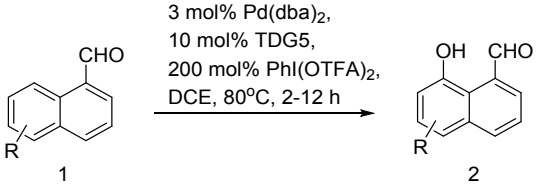
1. General materials and methods.

^{1}H (500 MHz), ^{13}C (125 MHz) and ^{19}F (470 MHz) NMR spectra were recorded at ambient temperature on Bruker AV-500, VNMRS 600 and Inova 400 instruments. The chemical shifts were reported in δ (ppm) using the δ 7.26 signal of $CDCl_3$ and δ 2.50 signal of DMSO-d_6 (^{1}H NMR), the δ 77.16 signal of $CDCl_3$ and δ 39.52 signal of DMSO-d_6 (^{13}C NMR) as internal standards. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HR-ESI-MS experiments were carried out using a Finnigan MAT 95 (EI/CI) or on a Thermo Fisher Scientific LTQ Orbitrap XL or Thermo Fisher Scientific Q Exactive Plus in the positive mode. All commercially available reagents were used without further purification, purchased from Acros or Aldrich and used without further purification unless otherwise noted. Solvents were predistilled according to standard laboratory methods. The progress of the reactions was monitored by analytical thin-layer chromatography (TLC) from Jiangyou Chemical Co., Ltd (Yantai, China). Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with basic potassium permanganate solution. And silica gel (200-300 mesh) for column chromatography was purchased from Haiyang Chemical Co., Ltd (Qingdao, China), particle size 0.040-0.063 mm (230-240 mesh, flash).

2. Computational details.

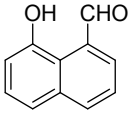
All calculations were performed with the Gaussian 16 package.[1] Geometry optimizations and vibrational frequency calculations of all stationary points were computed with the M06-2X[2] functional. Each of the species was identified to be a minimum or a transition state. The 6-31G(d,p)[3] basis set was used for H, C, N, O, Cl, and S atoms and the effective core potential LanL2DZ[4] basis set was used for Pd and I atoms. In order to get more accurate energies, single-point energies of all stationary points were computed at a larger basis set: def2-TZVP[5] for Pd and I atoms, and cc-pVTZ[6] for all other atoms. All calculations were conducted in dichloroethane solvent using the polarizable continuum model (PCM).[7] The calculated Gibbs free energies refer to 298.15 K and 1.0 atm. For each transition state, the intrinsic reaction coordinate (IRC)[8] analysis was performed to verify whether the transition state truly connects the reactant and the product.

3. Pd-catalyzed *peri*-C-H oxygenations of naphthaldehyde.

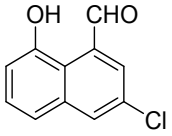


1 2

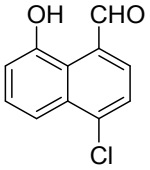
Naphthaldehyde **1** (1.0 mmol), $Pd(dba)_2$ (0.03 mmol), 2-aminobenzenesulfonic acid (TDG5) (0.1 mmol) and $PhI(OTFA)_2$ (2.0 mmol) were dissolved in DCE (5.0 mL). The reaction mixture was stirred at 80 °C by using an oil bath for 2-12 h and monitored via TLC. Upon completion, the reaction mixture was cooled to room temperature, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel using hexanes/EtOAc as the eluent to afford the desired product **2**.



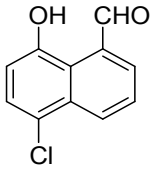
8-Hydroxy-1-naphthaldehyde (2a). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as an orange powder (151 mg, yield 88%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.70 (s, 1H), 9.86 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 7.0 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 155.3, 143.1, 139.3, 136.4, 132.5, 129.2, 124.4, 121.3, 120.6, 116.1. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_9O_2$ 173.0603, found 173.0597.



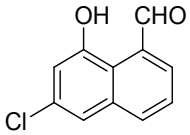
3-Chloro-8-hydroxy-1-naphthaldehyde (2b). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (169 mg, yield 82%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.40 (s, 1H), 9.84 (s, 1H), 8.10 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 2.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 155.3, 142.1, 137.3, 137.1, 134.2, 130.2, 130.1, 119.9, 119.6, 116.4. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8ClO_2$ 207.0213, found 207.0216.



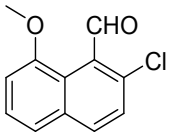
4-Chloro-8-hydroxy-1-naphthaldehyde (2c). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (171 mg, yield 83%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.73 (s, 1H), 9.83 (s, 1H), 7.96 (dd, *J* = 6.0, 0.5 Hz, 1H), 7.94 (d, *J* = 6.0 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 155.8, 143.6, 141.8, 133.4, 131.5, 130.2, 125.3, 122.3, 117.2, 116.9. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8ClO_2$ 207.0213, found 207.0207.



5-Chloro-8-hydroxy-1-naphthaldehyde (2d). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (169 mg, yield 82%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.68 (s, 1H), 9.91 (s, 1H), 8.70 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 7.0 Hz, 1H), 7.71 (t, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 154.6, 143.3, 135.3, 132.8, 132.7, 129.7, 125.5, 122.9, 122.8, 115.1. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8ClO_2$ 207.0213, found 207.0206.

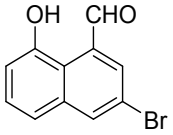


6-Chloro-8-hydroxy-1-naphthaldehyde (2e). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (167 mg, yield 81%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.96 (s, 1H), 9.85 (s, 1H), 8.04 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 2.5 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.9, 156.5, 142.9, 138.3, 136.7, 134.8, 132.6, 125.6, 120.2, 119.2, 116.5. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8ClO_2$ 207.0213, found 207.0216.

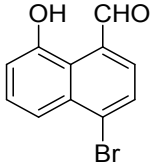


8-Methoxy-2-chloro-1-naphthaldehyde (2f). Following the the general procedure as described above to afford the corresponding hydroxylation products, in which the NMR showed a mixture with its 1,8-hemiacetal form. The mixture of hydroxylation products (1.0 equip) and K_2CO_3 (3.0 equip) in DMF (0.1 M) was treated with CH_3I (3.0 equip) with stirring at room temperature. Once the starting material was completely consumed, the reaction mixture was poured into water and extracted with EtOAc twice. The combined organic phases were washed with brine solution, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/30) to afford compound as a pale yellow powder (178 mg, yield 81%). R_f 0.60 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.46-7.43 (m,

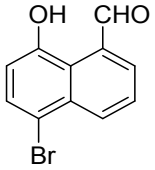
3H), 6.93-6.99 (m, 1H), 3.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 154.8, 133.4, 133.3, 130.8, 128.3, 128.2, 127.2, 123.7, 121.1, 107.1, 56.2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}ClO_2$ 221.0369, found 221.0364.



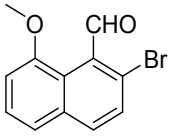
3-Bromo-8-hydroxy-1-naphthaldehyde (2g). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (212 mg, yield 85%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.40 (s, 1H), 9.83 (s, 1H), 8.28 (d, J = 2.0 Hz, 1H), 8.08 (d, J = 2.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 155.3, 144.5, 140.4, 137.5, 134.1, 130.1, 119.8, 119.7, 117.6, 116.5. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8BrO_2$ 250.9708, found 250.9707.



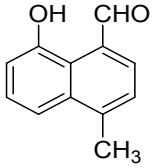
4-Bromo-8-hydroxy-1-naphthaldehyde (2h). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (200 mg, yield 80%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.71 (s, 1H), 9.86 (s, 1H), 7.98 (d, J = 4.0 Hz, 1H), 7.96 (d, J = 4.5 Hz, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.28 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 155.7, 141.8, 135.8, 134.5, 132.1, 130.4, 129.3, 122.1, 120.0, 117.2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8BrO_2$ 250.9708, found 250.9708.



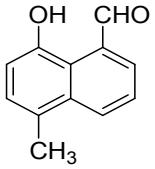
5-Bromo-8-hydroxy-1-naphthaldehyde (2i). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (200 mg, yield 80%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.73 (s, 1H), 9.90 (s, 1H), 8.68 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 7.0 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.05 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.7, 155.3, 143.4, 138.2, 133.8, 133.4, 132.8, 125.8, 123.1, 116.7, 112.9. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8BrO_2$ 250.9708, found 250.9709.



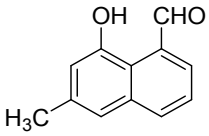
8-Methoxy-2-bromo-1-naphthaldehyde (2j). Following the the general procedure as described above to afford the corresponding hydroxylation products, in which the NMR showed a mixture with its 1,8-hemiacetal form. The mixture of hydroxylation products (1.0 equip) and K_2CO_3 (3.0 equip) in DMF (0.1 M) was treated with CH_3I (3.0 equip) with stirring at room temperature. Once the starting material was completely consumed, the reaction mixture was poured into water and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/30) to afford compound as a pale yellow powder (199 mg, yield 75%). R_f 0.60 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.47-7.43 (m, 2H), 6.92 (dd, J = 4.0, 2.0 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 154.7, 135.4, 133.7, 130.9, 130.7, 127.3, 124.0, 121.1, 116.6, 107.1, 56.2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}BrO_2$ 264.9864, found 264.9862.



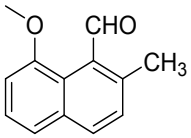
4-Methyl-8-hydroxy-1-naphthaldehyde (2k). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/40) to provide the product as a yellow powder (112 mg, yield 60%). R_f 0.40 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.87 (s, 1H), 9.77 (s, 1H), 7.93 (d, *J* = 7.0 Hz, 1H), 7.59-7.57 (m, 1H), 7.56 (q, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.19 (dd, *J* = 7.5 , 6.0 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5, 155.9, 146.9, 143.0, 135.4, 131.0, 129.0, 125.8, 121.3, 116.1, 115.9, 21.8. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O_2$ 187.0759, found 187.0759.



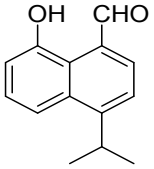
5-Methyl-8-hydroxy-1-naphthaldehyde (2l). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/40) to provide the product as a yellow powder (102 mg, yield 55%). R_f 0.40 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.41 (s, 1H), 9.89 (s, 1H), 8.35 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 7.0 Hz, 1H), 7.62 (t, *J* = 2.5 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 2.64 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 136.0, 134.9, 133.1, 131.9, 131.3, 131.1, 128.9, 127.9, 124.8, 123.0, 20.0. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O_2$ 187.0759, found 187.0754.



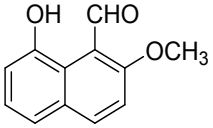
6-Methyl-8-hydroxy-1-naphthaldehyde (2m). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/40) to provide the product as a yellow powder (115 mg, yield 62%). R_f 0.40 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.63 (s, 1H), 9.81 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.20 (s, 1H), 7.03 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 154.9, 142.2, 139.5, 138.7, 136.6, 132.4, 124.4, 120.2, 119.5, 117.8, 21.4. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O_2$ 187.0759, found 187.0755.



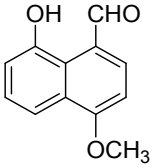
8-Methoxy-2-methyl-1-naphthaldehyde (2n). Following the the general procedure as described above to afford the corresponding hydroxylation products, in which the NMR showed a mixture with its 1,8-hemiacetal form.
The mixture of hydroxylation products (1.0 equip) and K_2CO_3 (3.0 equip) in DMF (0.1 M) was treated with CH_3I (3.0 equip) with stirring at room temperature. Once the starting material was completely consumed, the reaction mixture was poured into water and extracted with EtOAc twice. The reaction mixture was poured into water and extracted with EtOAc twice, the combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/50) to afford compound as a white powder (108 mg, yield 54%). R_f 0.50 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 3.96 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5, 155.4, 133.9, 133.6, 133.5, 130.2, 130.1, 126.0, 123.4, 121.2, 106.5, 56.1, 20.3. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O_2$ 201.0916, found 201.0914.



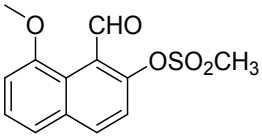
4-Isopropyl-8-hydroxy-1-naphthaldehyde (2o). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow oil (128 mg, yield 60%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.83 (s, 1H), 9.79 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.55 (q, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 3.80 (m, 1H), 1.43 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 156.9, 156.2, 143.4, 134.4, 130.6, 128.9, 122.0, 121.0, 115.8, 115.3, 30.2, 23.4×2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{14}H_{15}O_2$ 215.1072, found 215.1073.



2-Methoxy-8-hydroxy-1-naphthaldehyde (2p). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (83 mg, yield 41%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.01 (s, 1H), 10.59 (s, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 10.0 Hz, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 4.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.7, 167.2, 154.9, 142.2, 131.3, 126.9, 122.2, 120.8, 117.5, 117.3, 112.2, 57.2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O_3$ 203.0708, found 203.0704.

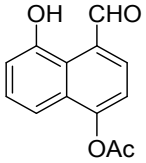


4-Methoxy-8-hydroxy-1-naphthaldehyde (2q). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (81 mg, yield 40%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.14 (s, 1H), 9.63 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.12 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.8, 163.4, 155.7, 145.8, 128.7, 128.3, 125.6, 122.6, 116.8, 113.7, 102.8, 56.4. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O_3$ 203.0708, found 203.0704.

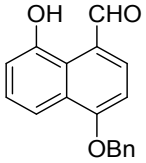


1-Formyl-8-methoxynaphthalen-2-yl methanesulfonate (2r). Following the the general procedure as described above to afford the corresponding hydroxylation products, in which the NMR showed a mixture with its 1,8-hemiacetal form.

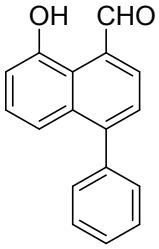
The mixture of hydroxylation products (1.0 equip) and K_2CO_3 (3.0 equip) in DMF (0.1 M) was treated with CH_3I (3.0 equip) with stirring at room temperature. Once the starting material was completely consumed, the reaction mixture was poured into water and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/7) to afford compound as a pale yellow powder (230 mg, yield 82%). R_f 0.30 (5:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.51-7.46 (m, 2H), 6.96 (dd, *J* = 6.5, 2.5 Hz, 1H), 3.97 (s, 3H), 3.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 155.6, 143.0, 133.5, 132.1, 128.0, 127.5, 123.4, 122.5, 121.2, 107.1, 56.2, 38.3. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}SO_5$ 281.0484, found 281.0477.



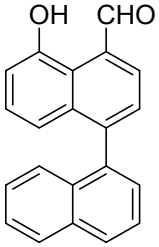
4-Formyl-5-hydroxynaphthalen-1-yl acetate (2s). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/2) to provide the product as an orange powder (133 mg, yield 58%). R_f 0.30 (2:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.82 (s, 1H), 9.83 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.57 (s, 1H), 7.56 (d, *J* = 3.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.22 (dd, *J* = 6.0, 3.0 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 168.4, 155.8, 154.1, 143.0, 130.4, 129.8, 129.7, 123.0, 117.0, 116.9, 113.2, 21.3. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_9O_3$ 189.0552, found 189.0544.



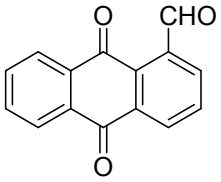
4-(Benzyloxy)-8-hydroxy-1-naphthaldehyde (2t). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/10) to provide the product as a yellow powder (192 mg, yield 69%). R_f 0.50 (5:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.15 (s, 1H), 9.62 (s, 1H), 7.95-7.93 (m, 2H), 7.52-7.48 (m, 3H), 7.45 (t, *J* = 7.0 Hz, 2H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.36 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.8, 162.3, 155.7, 145.6, 135.6, 129.0×2, 128.8, 128.7, 128.4, 127.6×2, 125.8, 122.7, 116.9, 113.9, 104.1, 71.1. HRMS (ESI) m/z [M+H]$^+$calcd for $C_{18}H_{15}O_3$ 263.1072, found 263.1063.



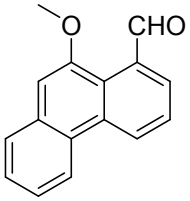
8-Hydroxy-4-phenyl-1-naphthaldehyde (6a). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (211 mg, yield 85%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.77 (s, 1H), 9.88 (s, 1H), 8.08 (d, *J* = 7.0 Hz, 1H), 7.53-7.49 (m, 4H), 7.46-7.41 (m, 4H), 7.21 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 155.5, 151.0, 142.4, 140.1, 134.9, 131.5, 129.5×2, 128.9, 128.5×2, 128.3, 125.7, 121.8, 119.0, 116.0. HRMS (ESI) m/z [M+H]$^+$calcd for $C_{17}H_{13}O_2$ 249.0916, found 249.0912.



5-Hydroxy-[1,1'-binaphthalene]-4-carbaldehyde (6b). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (238 mg, yield 80%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.78 (s, 1H), 9.95 (s, 1H), 8.16 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.64-7.59 (m, 2H), 7.50 (ddd, *J* = 13.5, 7.0, 5.5 Hz, 1H), 7.45 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.34-7.27 (m, 3H), 7.18 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.00 (dd, *J* = 8.5, 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 155.6, 149.9, 142.4, 137.8, 136.0, 133.4, 132.1, 129.1, 128.9, 128.5, 127.2, 126.8, 126.6×2, 126.3, 126.2, 125.4, 121.7, 119.6, 116.1. HRMS (ESI) m/z [M+H]$^+$calcd for $C_{21}H_{15}O_2$ 299.1072, found 299.1061.

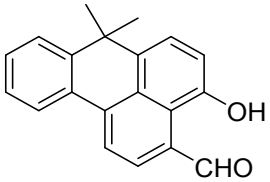


9,10-Dioxo-4a,9,9a,10-tetrahydroanthracene-1-carbaldehyde (6c). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/30) to provide the product as a yellow powder (121 mg, yield 51%). R_f 0.60 (10:1 hexane/EtOAc).^{1}H NMR (500 MHz, $CDCl_3$)) δ 10.80 (s, 1H), 8.54 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.33-8.31 (m, 1H), 8.30-8.27 (m, 1H), 8.08 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.87-7.83 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 184.7, 182.4, 139.2, 134.8, 134.7, 134.3, 134.2, 133.7, 133.6, 133.3, 133.0, 131.5, 127.6, 127.5. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{15}H_9O_3$ 237.0552, found 237.0565.



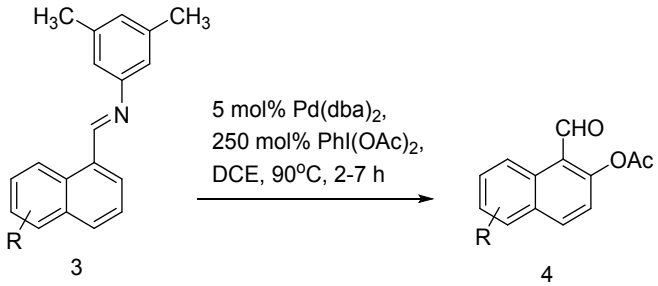
10-Methoxyphenanthrene-1-carbaldehyde (6d). Following the the general procedure as described above to afford the corresponding hydroxylation products, in which the NMR showed a mixture with its 1,8-hemiacetal form.

The mixture of hydroxylation products (1.0 equip) and K_2CO_3 (3.0 equip) in DMF (0.1 M) was treated with CH_3I (3.0 equip) with stirring at room temperature. Once the starting material was completely consumed, the reaction mixture was poured into water and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/30) to afford compound as a pale yellow powder (137 mg, yield 58%). R_f 0.60 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$)) δ 11.05 (s, 1H), 8.86 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 7.95 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.80 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.60 (td, *J* = 7.0, 1.0 Hz, 1H), 7.55 (td, *J* = 8.0, 1.5 Hz, 1H), 7.13 (s, 1H), 4.09 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.8, 154.1, 136.0, 132.7, 132.3, 127.7 , 127.6, 127.4, 127.2, 126.9, 126.5, 125.1, 125.0, 123.0, 104.9, 55.8. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{16}H_{13}O_2$ 237.0916, found 237.0923.



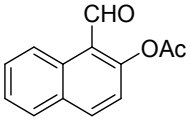
4-Hydroxy-7,7-dimethyl-7H-benzo[de]anthracene-3-carbaldehyde (6e). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/10) to provide the product as a yellow powder (196 mg, yield 68%). R_f 0.30 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.74 (s, 1H), 9.78 (s, 1H), 8.16 (d, *J* = 7.5 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.47 (t, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 1.69 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 153.7, 146.6, 143.5, 140.0, 134.6, 131.2, 130.4, 129.6, 129.2, 127.0, 126.9, 126.8, 125.2, 121.6, 118.0, 116.6, 39.1, 34.9×2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{20}H_{17}O_2$ 289.1229, found 289.1218.

4. Pd-catalyzed *ortho*-C-H oxygenations of imine.

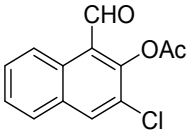


3 4

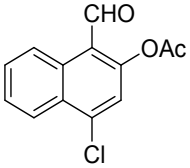
To a stirring solution of naphthaldehyde **1** (1.0 mmol) in EtOH (10 mL) at room temperature was added 3, 5-dimethylaniline (1.1 mmol) and sodium sulfate (10 mmol). The reaction mixture was refluxed by using an oil bath with stirring for 12 h. The reaction mixture was cooled and filtered. The filtrate was concentrated *in vacuo* and recrystallized with EtOH. The precipitates was filtered to give the imime substrates as yellow powders in 90-99% yields. In a sealed tube with magnetic stir bar was charged with imine substrate (0.5 mmol), $Pd(dba)_2$ (0.025 mmol), and $PhI(OAc)_2$ (1.25 mmol) in anhydrous DCE (5.0 mL). The reaction tube was sealed and heated to 90 °C by using an oil bath for 2-7 h. The reaction mixture was cooled, silica gel (100 mg) was added with stirring at 80 °C by using an oil bath for 1 h. The resulting mixture was cooled to room temperature and concentrated under vacuum. The crude reaction mixture was purified on silica gel using hexanes/EtOAc as the eluent to afford the desired product **4**.



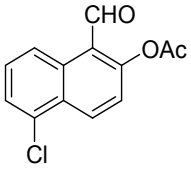
1-Formylnaphthalen-2-yl acetate (4a). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a pale yellow powder (178 mg, yield 83%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.71 (s, 1H), 9.14 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 9.0 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 9.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 169.2, 154.5, 136.6, 131.9, 131.2, 129.8, 128.6, 126.8, 125.2, 121.7, 121.5, 21.1. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_9O_2$ 173.0603, found 173.0597.



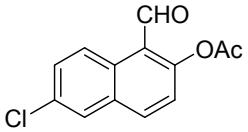
3-Chloro-1-formylnaphthalen-2-yl acetate (4b). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a pale yellow powder (104 mg, yield 42%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.63 (s, 1H), 9.05 (d, J = 8.5 Hz, 1H), 8.18 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.6, 168.6, 150.7, 135.5, 132.2, 129.9, 129.8, 127.8, 127.7, 126.1, 125.1, 123.9, 20.6. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_8ClO_2$ 207.0213, found 207.0217.



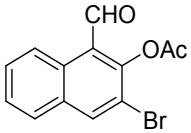
4-Chloro-1-formylnaphthalen-2-yl acetate (4c). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a pale yellow powder (174 mg, yield 70%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.66 (s, 1H), 9.18 (d, J = 8.5 Hz, 1H), 8.34 (d, J = 8.5 Hz, 1H), 7.74 (t, J = 7.0 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.44 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 169.0, 153.5, 140.1, 131.9, 130.5, 129.4, 127.8, 125.6, 125.0, 122.4, 120.7, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_8ClO_2$ 207.0213, found 207.0215.



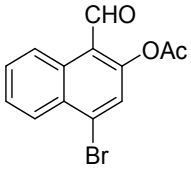
5-Chloro-1-formylnaphthalen-2-yl acetate (4d). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a pale yellow powder (184 mg, yield 74%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.69 (s, 1H), 9.08 (d, *J* = 9.0 Hz, 1H), 8.61 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 9.5 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 169.1, 154.9, 132.9, 132.7, 132.8, 129.9, 129.3, 127.3, 124.4, 122.9, 121.7, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_8ClO_2$ 207.0213, found 207.0210.



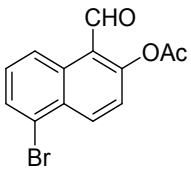
6-Chloro-1-formylnaphthalen-2-yl acetate (4e). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a pale yellow powder (191 mg, yield 77%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.66 (s, 1H), 9.13 (d, *J* = 9.5 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.86 (s, 1H), 7.61 (d, *J* = 10.5 Hz, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 169.2, 154.8, 135.5, 132.9, 132.7, 130.5, 129.4, 127.2, 127.2, 123.1, 121.6, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_8ClO_2$ 207.0213, found 207.0208.



3-Bromo-1-formylnaphthalen-2-yl acetate (4f). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (113 mg, yield 39%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.60 (s, 1H), 9.04 (d, *J* = 9.0 Hz, 1H), 8.37 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 168.7, 151.4, 139.0, 132.8, 130.3, 130.0, 127.7, 127.6, 125.0, 123.8, 115.7, 20.8. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_8BrO_2$ 250.9708, found 250.9705.

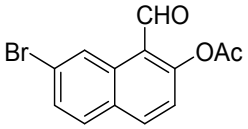


4-Bromo-1-formylnaphthalen-2-yl acetate (4g). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (169 mg, yield 58%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.67 (s, 1H), 9.16 (d, *J* = 8.5 Hz, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.68-7.65 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 169.0, 153.2, 131.7, 131.4, 130.7, 130.4, 128.0, 127.8, 126.2, 125.5, 121.2, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_8BrO_2$ 250.9708, found 250.9707.

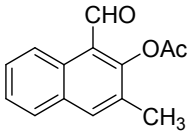


5-Bromo-1-formylnaphthalen-2-yl acetate (4h). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane

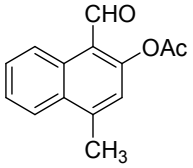
= 1/20) to provide the product as a yellow powder (204 mg, yield 70%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.68 (s, 1H), 9.14 (d, *J* = 8.5 Hz, 1H), 8.59 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 169.1, 154.9, 135.7, 132.7, 131.1, 130.4, 130.0, 125.1, 123.5, 123.1, 121.7, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_8BrO_2$ 250.9708, found 250.9706.



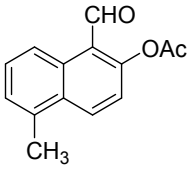
7-Bromo-1-formylnaphthalen-2-yl acetate (4i). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (198 mg, yield 68%). R_f 0.40 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.64 (s, 1H), 9.41 (d, *J* = 0.5 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.65 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.6, 169.1, 155.5, 136.4, 132.1, 130.5, 130.3, 129.9, 127.9, 125.1, 122.2, 120.6, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{11}H_8BrO_2$ 250.9708, found 250.9706.



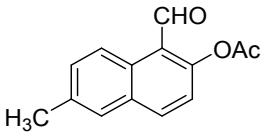
1-Formyl-3-methylnaphthalen-2-yl acetate (4j). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/30) to provide the product as a pale yellow powder (107 mg, yield 47%). R_f 0.60 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.67 (s, 1H), 9.02 (d, *J* = 8.56 Hz, 1H), 7.96 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 2.46 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 169.2, 153.9, 136.8, 132.0, 130.3, 129.8, 128.8, 127.9, 126.8, 124.6, 121.9, 20.7, 16.7. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{12}H_{11}O_2$ 187.0759, found 187.0754.



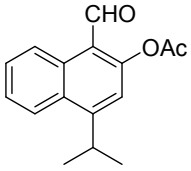
1-Formyl-4-methylnaphthalen-2-yl acetate (4k). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/30) to provide the product as a pale yellow powder (166 mg, yield 73%). R_f 0.60 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.67 (s, 1H), 9.20 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.13 (s, 1H), 2.76 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 169.4, 154.3, 144.9, 131.5, 131.2, 129.4, 126.6, 125.8, 124.5, 122.5, 120.1, 21.0, 20.5. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{12}H_{11}O_2$ 187.0759, found 187.0753.



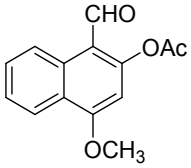
1-Formyl-5-methylnaphthalen-2-yl acetate (4l). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/30) to provide the product as a pale yellow powder (166 mg, yield 73%). R_f 0.60 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.96 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 9.0 Hz, 1H), 7.56 (dd, *J* = 8.5, 7.5 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 2.72 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 169.4, 153.9, 135.0, 132.6, 131.7, 131.1, 129.6, 127.7, 123.2, 121.9, 121.3, 21.1, 20.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{12}H_{11}O_2$ 187.0759, found 187.0754.



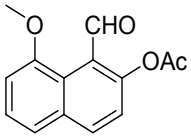
1-Formyl-6-methylnaphthalen-2-yl acetate (4m). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/30) to provide the product as a pale yellow powder (139 mg, yield 61%). R_f 0.60 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.69 (s, 1H), 9.02 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.64 (s, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 2.52 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 169.5, 153.9, 136.6, 136.0, 132.2, 132.0, 129.3, 127.6, 124.9, 121.7, 121.4, 21.5, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{12}H_{11}O_2$ 187.0759, found 187.0754.



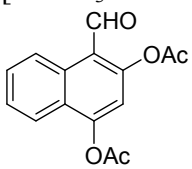
1-Formyl-4-isopropylnaphthalen-2-yl acetate (4n). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a white powder (200 mg, yield 78%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.66 (s, 1H), 9.20 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 3.85-3.77 (m, 1H), 2.44 (s, 3H), 1.42 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 169.4, 155.1, 154.7, 132.1, 130.0, 129.1, 126.5, 125.9, 123.7, 119.8, 118.1, 29.5, 23.3, 21.1×2. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{14}H_{15}O_2$ 215.1072, found 215.1071.



1-Formyl-4-methoxynaphthalen-2-yl acetate (4o). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a pale yellow powder (195 mg, yield 80%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.56 (s, 1H), 9.22 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 7.69 (t, *J* = 8.5 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 6.57 (s, 1H), 4.08 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6, 169.3, 161.9, 157.1, 132.3, 130.3, 126.2, 125.2, 124.1, 122.5, 115.2, 100.4, 56.4, 21.1. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{12}H_{11}O_3$ 203.0708, found 203.0706.

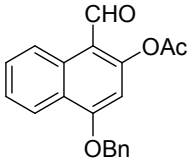


1-Formyl-8-methoxynaphthalen-2-yl acetate (4p). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a pale yellow powder (207 mg, yield 85%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.47 (t, *J* = 8.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 3.97 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 169.9, 155.8, 145.6, 133.3, 132.2, 126.8, 126.5, 123.6, 122.6, 121.3, 107.0, 56.1, 21.1. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{12}H_{11}O_3$ 203.0708, found 203.0706.

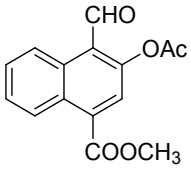


4-Formylnaphthalene-1,3-diyl diacetate (4q). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane

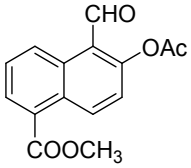
= 1/4) to provide the product as a yellow powder (122 mg, yield 45%). R_f 0.40 (2:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.65 (s, 1H), 9.21 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 2.49 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 169.0, 168.3, 154.5, 152.0, 132.2, 130.4, 127.1, 125.6, 125.4, 121.8, 119.6, 114.4, 21.3, 21.0. HRMS (ESI) m/z [M-$2CH_3CO$+3H]$^+$calcd for $C_{11}H_9O_3$ 189.0552, found 189.0544.



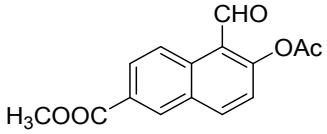
4-(Benzyloxy)-1-formylnaphthalen-2-yl acetate (4r). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/10) to provide the product as a yellow powder (192 mg, yield 60%). R_f 0.50 (5:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.57 (s, 1H), 9.23 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 8.5 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.54-7.51 (m, 3H), 7.45 (t, *J* = 7.0 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 1H), 6.68 (s, 1H), 5.29 (s, 2H), 2.44 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6, 169.3, 160.9, 156.9, 135.6, 132.3, 130.4, 129.0×2, 128.7, 127.8×2, 126.2, 125.2, 124.2, 122.7, 115.3, 101.5, 71.1, 21.1. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{18}H_{15}O_3$ 279.1021, found 279.1005.



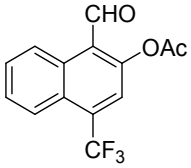
Methyl 3-acetoxy-4-formyl-1-naphthoate (4s). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/10) to provide the product as a pale yellow powder (195 mg, yield 72%). R_f 0.40 (5:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.74 (s, 1H), 9.06 (d, *J* = 8.5 Hz, 1H), 8.83 (d, *J* = 8.5 Hz, 1H), 7.88 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 4.03 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 169.2, 166.5, 152.1, 134.6, 131.9, 129.7, 129.6, 128.0, 126.3, 125.2, 125.1, 124.7, 53.0, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{13}H_{11}O_4$ 231.0657, found 231.0654.



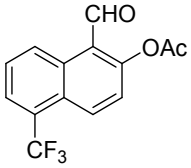
Methyl 6-acetoxy-5-formyl-1-naphthoate (4t). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/10) to provide the product as a pale yellow powder (190 mg, yield 70%). R_f 0.40 (5:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.70 (s, 1H), 9.38 (d, *J* = 8.5 Hz, 1H), 9.28 (d, *J* = 9.0 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 8.5, 7.5 Hz, 1H), 7.40 (d, *J* = 9.5 Hz, 1H), 4.01 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 169.1, 167.7, 154.6, 134.5, 131.9, 130.6, 130.1, 129.8, 128.4, 127.6, 123.4, 121.6, 52.6, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{13}H_{11}O_4$ 231.0657, found 231.0658.



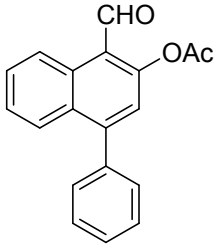
Methyl 6-acetoxy-5-formyl-2-naphthoate (4u). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/10) to provide the product as a pale yellow powder (201 mg, yield 74%). R_f 0.40 (5:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.70 (s, 1H), 9.20 (d, *J* = 9.0 Hz, 1H), 8.62 (s, 1H), 8.25 (dd, *J* = 9.0, 1.5 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 4.00 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 169.1, 166.7, 156.0, 137.6, 133.6, 131.2, 131.1, 129.0, 128.3, 125.6, 122.7, 121.6, 52.6, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{13}H_{11}O_4$ 231.0657, found 231.0654.



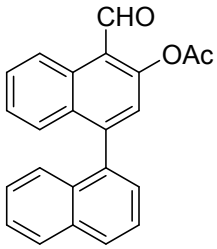
1-Formyl-4-(trifluoromethyl)naphthalen-2-yl acetate (4v). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (155 mg, yield 55%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.73 (s, 1H), 9.09 (d, *J* = 8.5 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.68 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.6, 169.1, 151.8, 143.5, 132.9 (q, *J* = 31.25 Hz), 132.0, 130.0, 128.8 (q, *J* = 192.5 Hz), 128.2, 125.6, 124.8, 124.7 (q, *J* = 2.5 Hz), 121.3 (q, *J* = 6.25 Hz) , 21.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.1 (s). HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{12}H_8F_3O_2$ 241.0476, found 241.0443.



1-Formyl-5-(trifluoromethyl)naphthalen-2-yl acetate (4w). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (113 mg, yield 40%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.71 (s, 1H), 9.39 (d, *J* = 8.5 Hz, 1H), 8.47 (d, *J* = 9.5 Hz, 1H), 7.95 (d, *J* = 7.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 9.5 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 169.1, 154.7, 132.4 (q, *J* = 2.5 Hz), 132.2, 129.8, 128.1, 127.5, 126.7 (q, *J* = 30 Hz), 125.4 (q, *J* = 6.25 Hz), 124.4 (q, *J* = 272.5 Hz), 123.6, 122.0, 21.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -58.9 (s). HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{12}H_8F_3O_2$ 241.0476, found 241.0427.

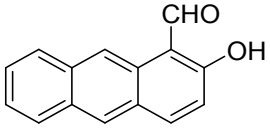


1-Formyl-4-phenylnaphthalen-2-yl acetate (7a). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (217 mg, yield 75%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.73 (s, 1H), 9.22 (d, *J* = 9.0 Hz, 1H), 8.16 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 1.5 Hz, 1H), 7.95 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.72 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 169.2, 154.4, 140.1, 139.3, 136.6, 132.2, 130.2, 129.2, 129.0×2, 127.8, 127.4×2, 126.0, 125.6, 122.0, 121.3, 20.9. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{17}H_{13}O_2$ 249.0916, found 249.0913.

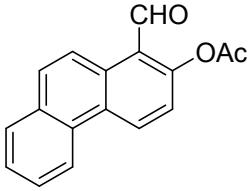


4-Formyl-[1,1'-binaphthalen]-3-yl acetate (7b). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a yellow powder (238 mg, yield 71%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.80 (s, 1H), 9.26 (d, *J* = 9.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H),

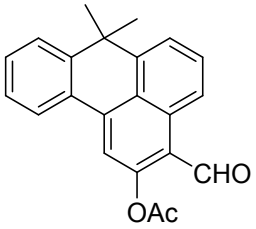
7.67 (t, J = 7.0 Hz, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.52-7.46 (m, 3H), 7.39-7.34 (m, 3H), 7.32 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 169.3, 153.8, 147.7, 136.5, 133.6, 132.2, 131.6, 131.5, 129.6, 128.9, 128.4, 127.7, 127.3, 126.8, 126.7, 126.3, 126.2, 125.4, 125.3, 123.8, 121.2, 21.0. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{21}H_{15}O_2$ 299.1072, found 299.1072.



2-Hydroxyanthracene-1-carbaldehyde (7c). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/50) to provide the product as a pale yellow powder (46 mg, yield 21%). R_f 0.60 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.76 (s, 1H), 10.92 (s, 1H), 8.80 (s, 1H), 8.37 (s, 1H), 8.14 (d, J = 9.0 Hz, 1H), 7.99 (dd, J = 7.5, 2.0 Hz, 2H), 7.56 (t, J = 7.0 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 9.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 166.7, 140.2, 133.5, 130.6, 129.9, 128.9, 128.3, 127.9, 127.3, 127.1, 125.6, 120.3, 116.6, 110.1. HRMS (ESI) m/z [M+H]$^+$calcd for $C_{15}H_{11}O_2$ 223.0759, found 223.0759.

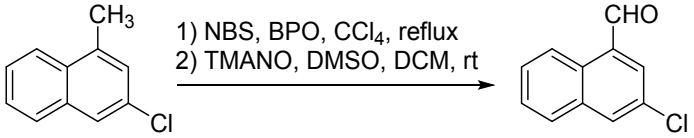


1-Formylphenanthren-2-yl acetate (7d). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/20) to provide the product as a pale yellow powder (147 mg, yield 56%). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.78 (s, 1H), 8.99 (d, J = 4.5 Hz, 1H), 8.98 (d, J = 4.5 Hz, 1H), 8.65 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 9.5 Hz, 1H), 7.94 (dd, J = 9.0, 3.0 Hz, 1H), 7.73-7.69 (m, 1H), 7.68-7.64 (m, 1H), 7.46 (d, J = 9.0 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 169.4, 153.7, 131.7, 131.4, 131.1, 130.3, 129.8, 128.9, 128.8, 127.6, 127.4, 122.8, 122.5, 122.4, 121.7, 21.1. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{15}H_{11}O_2$ 223.0759, found 223.0749.



3-Formyl-7,7-dimethyl-7H-benzo[de]anthracen-2-yl acetate (7e). The title compound was prepared according to the general procedure. The crude compound was purified by flash column chromatography over silica gel (EtOAc/n-hexane = 1/10) to provide the product as a yellow powder (118 mg, yield 36%). R_f 0.60 (5:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.68 (s, 1H), 9.11 (dd, J = 7.0, 2.5 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H), 7.75 (s, 1H), 7.74 (d, J = 4.5 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 2.49 (s, 3H), 1.74 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 169.5, 155.1, 145.9, 143.8, 138.7, 132.3, 130.3, 129.9, 128.9, 127.3, 126.9, 125.3, 124.6, 124.2, 123.0, 120.3, 114.5, 39.2, 35.1×2, 21.2. HRMS (ESI) m/z [M-CH_3CO+2H]$^+$calcd for $C_{20}H_{17}O_2$ 289.1229, found 289.1227.

5. Preparation of substrates.

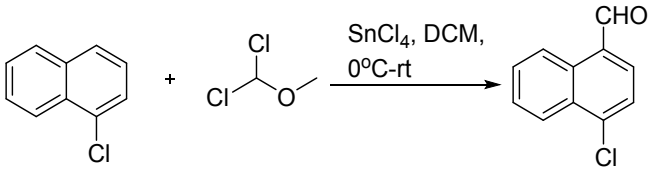


1b

3-Chloro-1-naphthaldehyde (1b). The NBS (1.1 mmol) and benzoylperoxide (0.2 mmol) was added to a solution

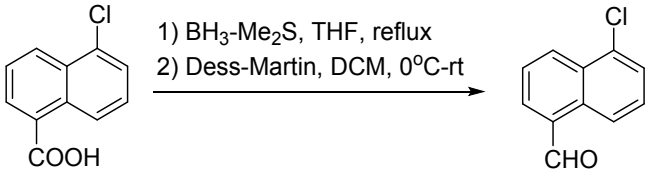
of 3-chloro-1-methylnaphthalene (1.0 mmol) in CCl_4 (2.0 mL) at room temperature and the reaction mixture was heated to reflux by using an oil bath for 12 h. After cooled to room temperature, the mixture was filtered off and the filtrate was concentrated under reduced pressure to afford the corresponding benzyl bromide.

A mixture of benzyl bromide (1.0 mmol) in a mixture of DMSO (2.0 mL) and DCM (1.0 mL) was treated with trimethylamine N-oxide dehydrate (3.0 mmol) at room temperature with stirring for 6 h. The reaction mixture was poured into water and extracted with DCM twice, the combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/50) to afford compound **1b** as a white solid (161 mg, 0.85 mmol, 85 % yield). R_f 0.30 (50:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 9.14 (d, J = 8.5 Hz, 1H), 8.05 (s, 1H), 7.91 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 7.0 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 136.3, 134.8, 133.6, 132.9, 131.0, 129.3, 129.0, 128.1, 127.8, 125.0. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8ClO$ 191.0264, found 191.0256.



1c

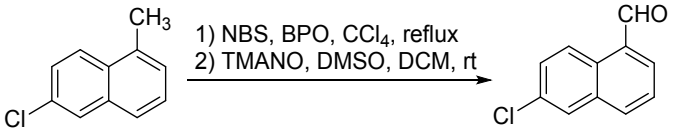
4-Chloro-1-naphthaldehyde (1c). A solution of α,α-dichloromethyl methyl ether (1.3 mmol) in DCM (2.6 mL) was cooled in an ice bath and then treated dropwise with $SnCl_4$ (1.3 mmol). After stirring for 45 minutes, a solution of 1-chloronaphthalene (1.0 mmol) in DCM (1.0 mL) was added. The mixture was allow to slowly warm to room temperature with stirring overnight. The mixture was poured into ice water and extracted with DCM twice. The combined organics were washed with H_2O, brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/50) to give the desired product **1c** as a white solid (158 mg, 0.83 mmol, 83 % yield). R_f 0.30 (50:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 9.30 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.78-7.70 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 139.8, 136.2, 131.7, 131.1, 130.5, 130.0, 128.2, 125.7, 125.3, 125.1. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8ClO$ 191.0264, found 191.0261.



1d

5-Chloro-1-naphthaldehyde (1d). 5-Chloronaphthalene-1-Carboxylic Acid[9] (1.0 mmol) was dissolved in anhydrous THF (3.0 mL) under N_2 atmosphere. Borane-methyl sulfide complex (2.0 M, 1.0 mmol) was added by syringe slowly. The resulting mixture was refluxed for 3 h. After cooled down to the room temperature, the mixture was poured into 2N NaOH solution and stirred for 0.5 h. The mixture was extracted with EtOAc twice. The combined organic phases were washed with brine solution, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford the corresponding benzyl alcohol without further purification.

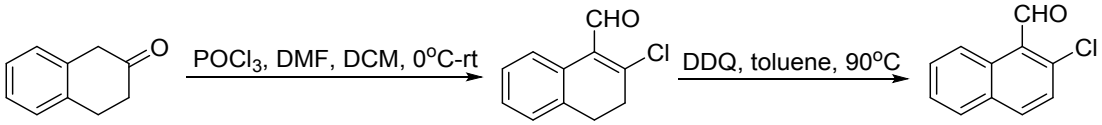
To a solution of above benzyl alcohol (1.0 mmol) in CH_2Cl_2 (2.0 mL) was added Dess-Martin periodinane (1.1 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. The reaction was quenched with $Na_2S_2O_3$ solution, washed with saturated $NaHCO_3$ solution and extracted with DCM. The collected organic phase was washed with brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/50) to afford compound **1d** as a white solid (180 mg, 0.95 mmol, 95 % yield). R_f 0.30 (50:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 9.22 (d, J = 8.5 Hz, 1H), 8.62 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 7.0 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 137.3, 132.68, 132.0, 131.7, 131.6, 131.3, 129.1, 127.6, 126.1, 124.2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8ClO$ 191.0264, found 191.0256.



1e

6-Chloro-1-naphthaldehyde (1e). NBS (1.1 mmol) and benzoyl peroxide (0.2 mmol) was added to a solution of 6-chloro-1-methylnaphthalene (1.0 mmol) in CCl_4 (2.0 mL) at room temperature and the reaction mixture was heated to reflux by using an oil bath for 12 h. After cooled to room temperature, the mixture was filtered off and the filtrate was concentrated under reduced pressure to afford the corresponding benzyl bromide.

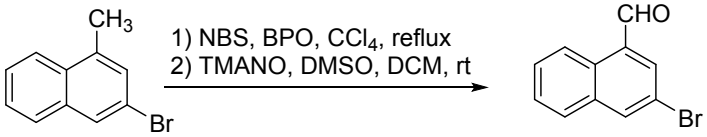
A mixture of benzyl bromide (1.0 mmol) in a mixture of DMSO (2.0 mL) and DCM (1.0 mL) was treated with trimethylamine N-oxide dehydrate (3.0 mmol) at room temperature with stirring for 6 h. The reaction mixture was poured into water and extracted with DCM twice. The collected organic phase was washed with brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/50) to afford compound **1e** as a white solid (129 mg, 0.68 mmol, 68 % yield). R_f 0.30 (50:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 9.24 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 7.0 Hz, 1H), 7.91 (d, J = 2.5 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.63 (dd, J = 9.0, 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 137.0, 134.7, 134.3, 133.2, 131.7, 130.0, 128.8, 127.2, 127.0, 126.2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8ClO$ 191.0264, found 191.0254.



1f

2-Chloro-1-naphthaldehyde (1f). To a solution of DMF (3.5 mmol) was added $POCl_3$ (4.0 mmol) dropwise at 0 °C with stirring for 0.5 h. The resulting mixture was diluted by the addition of DCM (20.0 mmol) and allowed to stir at room temperature for 2 h. A solution of 3, 4-dihydro-1H-naphthalen-2-one (1.0 mmol) in DCM (1.0 mL) was added to the mixture and kept stiriring for another 12 h. The reaction was quenched with H_2O and extracted with DCM twice. The combined organic layers were collected, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated to afford the corresponding aldehyde.

The mixture of above aldehyde (1.0 mmol) and DDQ (1.05 mmol) in toluene (10 mL) was stirred at 90 °C by using an oil bath for 12 h. Additional 1 equivalent of DDQ was added to the mixture at times and the reaction was monitored by TLC. Once the starting material was completely consumed, the resulting mixture was cooled and filtered. The filtrate was collected, concentrated, and purified by silica gel column chromatography (EtOAc/n-hexane = 1/60) to afford compound **1f** as a white solid (161 mg, 0.85 mmol, 85 % yield). R_f 0.60 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.92 (s, 1H), 9.15 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 8.5, Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.51 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8, 140.94, 135.8, 132.6, 131.6, 130.0, 128.5, 127.9, 127.2, 127.1, 125.1. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8ClO$ 191.0264, found 191.0259.

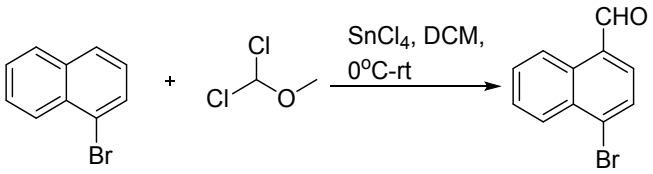


1g

3-Bromo-1-naphthaldehyde (1g). NBS (1.1 mmol) and benzoyl peroxide (0.2 mmol) was added to a solution of 3-bromo-1-methylnaphthalene (1.0 mmol) in CCl_4 (2.0 mL) at room temperature and the reaction mixture was heated to reflux by using an oil bath for 12 h. After cooled to room temperature, the mixture was filtered off and the filtrate was concentrated under reduced pressure to afford the corresponding benzyl bromide.

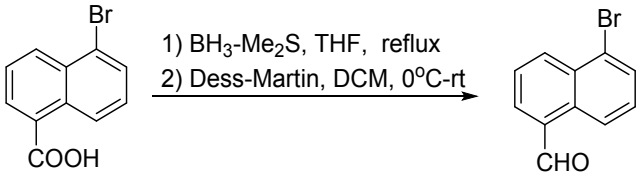
A mixture of benzyl bromide (1.0 mmol) in a mixture of DMSO (2.0 mL) and DCM (1.0 mL) was treated with trimethylamine N-oxide dehydrate (3.0 mmol) at room temperature with stirring for 6 h. The reaction mixture was poured into water and extracted with DCM twice. The collected organic phase was washed with brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/50) to afford compound **1g** as a yellow solid (142 mg, 0.61 mmol, 61%

yield). R_f 0.50 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.34 (s, 1H), 9.14 (d, J = 8.5 Hz, 1H), 8.23 (s, 1H), 8.03 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 138.8, 136.9, 135.2, 132.9, 129.4, 129.1, 128.1, 127.7, 125.0, 118.7. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8BrO$ 234.9759, found 234.9750.



1h

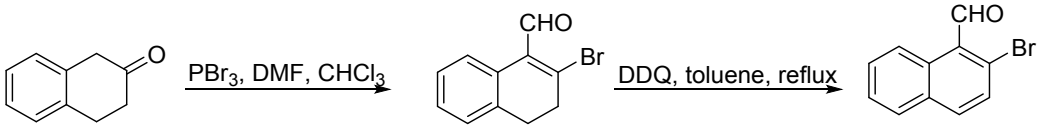
4-Bromo-1-naphthaldehyde (1h). A solution of α,α-dichloromethyl methyl ether (1.3 mmol) in DCM (2.6 mL) was cooled in an ice bath and then treated dropwise with $SnCl_4$ (1.3 mmol). After stirring for 45 minutes, a solution of 1-bromonaphthalene (1.0 mmol) in DCM (1.0 mL) was added. The mixture was allow to slowly warm to room temperature with stirring overnight. The mixture was poured into ice water and extracted with DCM twice. The combined organics were washed with H_2O, brine, dried over anhydrous Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/50) to give the desired product **1h** as a brown solid (171 mg, 0.73 mmol, 73 % yield). R_f 0.50 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 9.28 (d, J = 8.5 Hz, 1H), 8.36 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.72 (td, J = 8.0, 1.0 Hz, 1H), 7.70 (td, J = 8.0, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8, 136.3, 132.3, 131.6, 131.5, 131.1, 130.0, 129.5, 128.4, 127.9, 125.3. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8BrO$ 234.9759, found 234.9754.



1i

5-Bromo-1-naphthaldehyde (1i). 5-Bromonaphthalene-1-carboxylic Acid (1.0 mmol) was dissolved in anhydrous THF (3.0 mL) under N_2 atmosphere. Borane-methyl sulfide complex (2.0 M, 1.0 mmol) was added by syringe slowly. The resulting mixture was refluxed by using an oil bath for 3 h. After cooled down to the room temperature, the mixture was poured into 2N NaOH solution and stirred for 0.5 h. The mixture was extracted with EtOAc twice. The combined organic phases were washed with brine solution, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford the corresponding benzyl alcohol without further purification.

To a solution of above benzyl alcohol (1.0 mmol) in CH_2Cl_2 (2.0 mL) was added Dess-Martin periodinane (1.1 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. The reaction was quenched with $Na_2S_2O_3$ solution, washed with saturated $NaHCO_3$ solution and extracted with DCM. The collected organic phase was washed with brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/50) to afford compound **1i** as a yellow solid (220 mg, 0.94 mmol, (94 % yield). R_f 0.50 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.27 (d, J = 9.0 Hz, 1H), 8.58 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 7.0 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 137.4, 134.4, 132.4, 132.1, 131.7, 131.4, 129.5, 126.4, 124.9, 123.5. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8BrO$ 234.9759, found 234.9751.

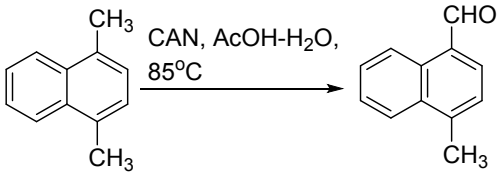


1j

2-Bromo-1-naphthaldehyde (1j). To a solution of DMF (3.0 mmol) in dry chloroform (5.0 mL) at 0 °C was added PBr_3 (2.5 mmol) dropwise at 0 °C with stirring for 1 h. A solution of 3,4-dihydro-1H-naphthalen-2-one (1.0 mmol) in dry chloroform (10.0 mL) was added to the mixture and raise the temperature to reflux for another 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$, and extracted with DCM twice. The combined organic layers were collected, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, filtered, and

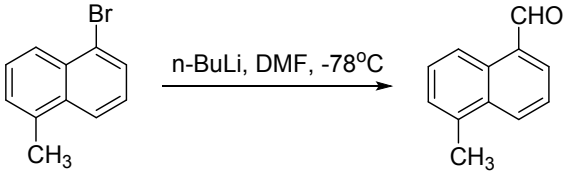
concentrated to afford the corresponding aldehyde.

The mixture of above aldehyde (1.0 mmol) and DDQ (1.05 mmol) in toluene (10 mL) was stirred at 90 °C by using an oil bath for 72 h. Additional 1 equivalent of DDQ was added to the mixture at times and the reaction was monitored by TLC. Once the starting material was completely consumed, the resulting mixture was cooled and filtered. The filtrate was collected, concentrated, and purified by silica gel column chromatography (EtOAc/n-hexane = 1/60) to afford compound **1j** as a yellow solid (150 mg, 0.64 mmol, 64 % yield). R_f 0.50 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.77 (s, 1H), 9.11 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.0, 135.5, 133.1, 131.9, 130.9, 130.6, 129.8, 128.5, 127.3×2, 124.8. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8BrO$ 234.9759, found 234.9754.



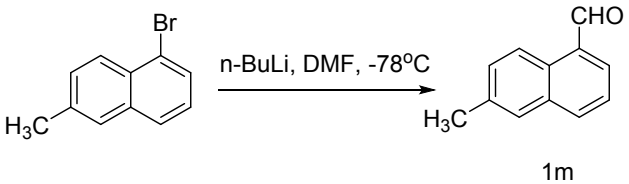
1k

4-Methyl-1-naphthaldehyde (1k). To a solution of CAN (3.5 mmol) in 50% acetic acid (100 mL) at 85 °C by using an oil bath was dropwisely added 1,4-dimethylnaphthalene (1.0 mmol). Once the starting material was completely consumed as monitored by TLC, the reaction mixture was cooled and poured into water. The product was extracted with EtOAc twice, the combined organic phases were washed with water, brine solution, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by column chromatography (EtOAc/n-hexane = 1/100) to afford compound **1k** as a yellow oil (49 mg, 0.29 mmol, 29 % yield). R_f 0.60 (50:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1H), 9.33 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.0 Hz, 1H), 7.70 (t, *J* = 7.0 Hz, 1H), 7.63 (t, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 143.0, 137.0, 132.9, 130.7, 130.2, 128.8, 126.9, 126.1, 125.6, 124.5, 20.6. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O$ 171.0810, found 171.0811.



1l

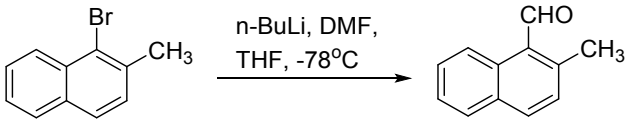
5-Methyl-1-naphthaldehyde (1l). To a solution of 1-bromo-5-methylnaphthalene[10] (1.0 mmol) in anhydrous THF at -78 °C under N_2 atomosphere was dropwisely added n-butyl lithium solution (1.6 M in hexane, 1.5 mmol). The resulting reaction mixture was stirred at -78 °C for 20 minutes, and then treated with anhydrous DMF (1.2 mmol) for another 15 minutes. After warmed to room temperature, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/100) to afford compound **1l** as a white solid (127 mg, 0.75 mmol, 75% yield). R_f 0.60 (50:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 9.12 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.43 (d, *J* = 6.5 Hz, 1H), 2.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 136.0, 134.9, 133.1, 131.9, 131.3, 131.1, 128.9, 127.9, 124.8, 122.9, 20.0. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O$ 171.0810, found 171.0809.



1m

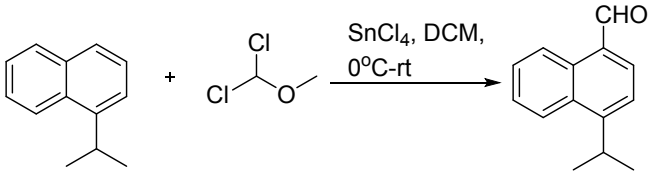
6-Methyl-1-naphthaldehyde (1m). To a solution of 1-bromo-6-methylnaphthalene (1.0 mmol) in anhydrous THF at -78 °C under N_2 atomosphere was dropwisely added n-butyl lithium solution (1.6 M in hexane, 1.5 mmol). The resulting reaction mixture was stirred at -78 °C for 20 minutes, and then treated with anhydrous DMF (1.2

mmol) for another 15 minutes. After warmed to room temperature, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/100) to afford compound **1m** as a white solid (144 mg, 0.85 mmol, 85 % yield). R_f 0.60 (50:1 hexane/EtOAc). ^1H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 9.14 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.0 Hz, 1H), 7.69 (s, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.53 (dd, *J* = 8.5, 1.5 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 136.9, 135.9, 134.8, 134.2, 131.5, 131.4, 128.8, 127.6, 125.0, 124.8, 21.7. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O$ 171.0810, found 171.0808.



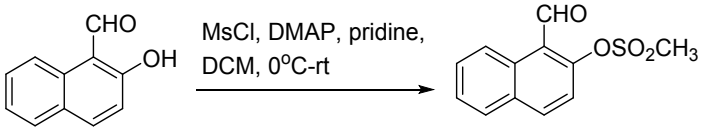
1n

2-Methyl-1-naphthaldehyde (1n). To a solution of 1-bromo-2-methylnaphthalene (1.0 mmol) in anhydrous THF at -78 °C under N_2 atomosphere was dropwisely added n-butyl lithium solution (1.6 M in hexane, 1.5 mmol). The resulting reaction mixture was stirred at -78 °C for 20 minutes, and then treated with anhydrous DMF (1.2 mmol) for another 15 minutes. After warmed to room temperature, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/100) to afford compound **1n** as a white solid (127 mg, 0.75 mmol, 75 % yield). R_f 0.60 (50:1 hexane/EtOAc). ^1H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 8.97 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 142.7, 134.5, 132.6, 131.6, 129.9, 128.9×2, 128.5, 126.1, 124.5, 20.2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O$ 171.0810, found 171.0812.



1o

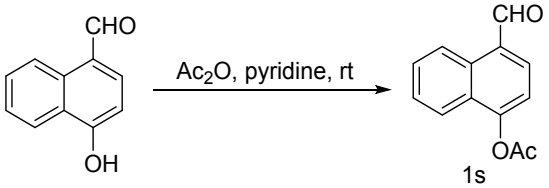
4-Isopropyl-1-naphthaldehyde (1o). A solution of α,α-dichloromethyl methyl ether (1.3 mmol) in DCM (2.6 mL) was cooled in an ice bath and then treated dropwise with $SnCl_4$ (1.3 mmol). After stirring for 45 minutes, a solution of 1-isopropylnaphthalene (1.0 mmol) in DCM (1.0 mL) was added. The mixture was allow to slowly warm to room temperature with stirring overnight. The mixture was poured into ice water and extracted with DCM twice. The combined organics were washed with H_2O, brine, dried over anhydrous Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/50) to give compound **1o** as a colorless solid (148 mg, 0.75 mmol, 75 % yield). R_f 0.50 (20:1 hexane/EtOAc). ^1H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 9.36 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 3.86-3.81 (m, 1H), 1.44 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 153.1, 137.2, 131.7, 131.2, 129.8, 128.5, 126.9, 125.8, 123.7, 121.2, 29.4, 23.5×2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{14}H_{15}O$ 199.1123, found 199.1125.



1r

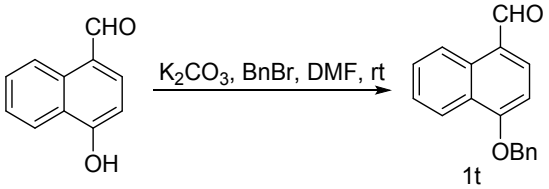
1-Formylnaphthalen-2-yl methanesulfonate (1r). 2-Hydroxy-1-naphthaldehyde (1.0 mmol) and DMAP (0.1 mmol) were dissolved in DCM (5.0 mL) under N_2 atmosphere. Pyridine (0.4 mL) and methanesulfonyl chlorideand (0.12 mL) were successively added by syringe slowly at 0 °C and stirred until naphthol was all consumed. The reaction was quenched with aqueous HCl and extracted with DCM twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by column chromatography (EtOAc/n-hexane = 1/10) to afford compound **1r** as a yellow

solid (237 mg, 0.95 mmol, 95 % yield). R_f 0.20 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.80 (s, 1H), 9.18 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 151.9, 136.9, 132.4, 131.1, 130.2, 128.6, 127.5, 125.6, 123.3, 121.2, 38.6. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}SO_4$ 251.0378, found 251.0377.



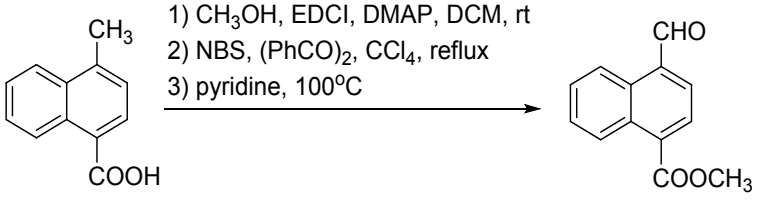
1s

4-Formylnaphthalen-1-yl acetate (1s). 4-Hydroxy-1-naphthaldehyde (1.0 mmol) was dissolved in pyridine (2.0 mL). Ac_2O (1.5 mmol) was added at room temperature and stirred until naphthol was all consumed. The reaction was quenched with aqueous HCl and extracted with DCM twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by column chromatography (EtOAc/n-hexane = 1/5) to afford compound **1s** as a yellow solid (209 mg, 0.98 mmol, 98 % yield). R_f 0.30 (5:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 9.31 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 8.5 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 168.8, 151.8, 137.0, 132.2, 129.8, 129.6, 127.6, 127.2, 125.3, 121.8, 117.5, 21.3. HRMS (ESI) m/z $[M-CH_3CO+2H]^+$calcd for $C_{11}H_9O_2$ 173.0603, found 173.0595.



1t

4-(Benzyloxy)-1-naphthaldehyde (1t). 4-Hydroxy-1-naphthaldehyde (1.0 mmol) and K_2CO_3 (2.0 mmol) were dissolved in DMF (10 mL). BnBr (1.5 mmol) was added at room temperature and stirred until naphthol was all consumed. The reaction mixture was poured into water and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by column chromatography (EtOAc/n-hexane = 1/20) to afford compound **1t** as a yellow oil (248 mg, 0.95 mmol, 95 % yield). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.21 (s, 1H), 9.32 (d, *J* = 8.5 Hz, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.36 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 159.9, 139.6, 136.1, 132.1, 129.7, 128.9×2, 128.5, 127.6×2, 126.6, 125.8, 125.3, 125.0, 122.7, 104.3, 70.7. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{15}O_2$ 263.1072, found 263.1055.

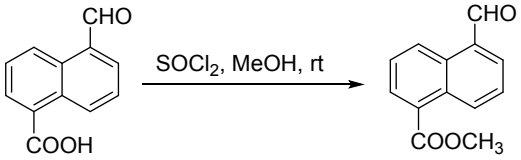


1u

Methyl 4-formyl-1-naphthoate (1u). A mixture of 4-methyl-1-naphthoic acid (1.0 mmol), MeOH (1.5 mmol), 1-(3-dimethlyaminopropyl)-3-ethylcarbodiimide hydrochloride (1.1 mmol), N,N-dimethyl-4-aminopyridine (0.25 mmol) were dissolved in CH_2Cl_2 (2.0 mL) and stirred overnight. The reaction was quenched with saturated aqueous $NaHCO_3$ and extracted three times with DCM. The combined organic layers were dried over Na_2SO_4, filtrated and concentrated *in vacuo* to afford the corresponding methyl ester without further purification.

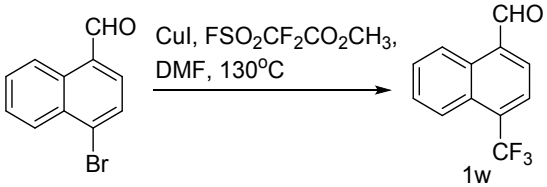
To a solution of crude methyl ester (1.0 mmol) in CCl_4 (2.0 mL) was added NBS (2.0 mmol) followed by benzoylperoxide (0.15 mmol). After refluxed by using an oil bath for 8 h, the resulting mixture was cooled to room temperature and filtered to remove succinimide. The residue was dissolved in anhydrous pyridine (2 mL)

and heated to 100 °C by using an oil bath for 6 h. The reaction mixture was poured into ice-water and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/20) to afford compound **1s** as a white solid (182 mg, 0.81 mmol, 81 % yield). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.47 (s, 1H), 9.24 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 7.0 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.70 (dt, *J* = 17.0, 6.5 Hz, 2H), 4.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 167.5, 134.1, 134.0, 133.7, 131.6, 131.1, 129.2, 128.4, 128.1, 126.2, 124.9, 52.8. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{11}O_3$ 215.0708, found 215.0705.



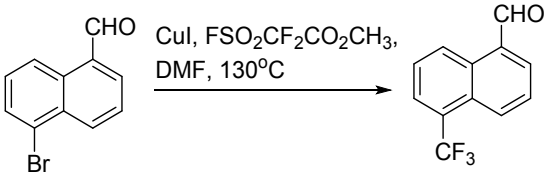
1v

Methyl 5-formyl-1-naphthoate (1v). To a solution of 5-formyl-1-naphthoic acid (1.0 mmol) in dry MeOH (2.0 mL) at 0 °C was dropwisely added thionyl chloride (1.3 mmol). The mixture was stirred at room temperature for 1 h and extracted with EtOAc twice. The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (EtOAc/n-hexane = 1/20) to give compound **1t** as a white solid (171 mg, 0.8 mmol, 80 % yield). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.39 (s, 1H), 9.53 (d, *J* = 8.5 Hz, 1H), 9.24 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 7.0 Hz, 1H), 8.05 (d, *J* = 7.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 167.9, 137.2, 132.9, 131.7, 131.6, 131.1, 130.9, 130.0, 127.8, 127.7, 126.8, 52.6. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{11}O_3$ 215.0708, found 215.0704.



1w

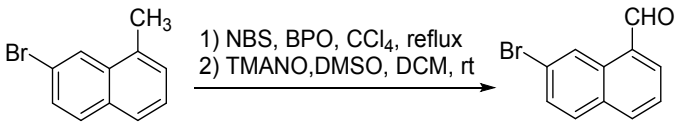
4-(Trifluoromethyl)-1-naphthaldehyde (1w). 4-bromo-1-naphthaldehyde (1.0 mmol) and CuI (1.5 mmol) were dissolved in anhydrous DMF (10 mL) under N_2 atmosphere. $FSO_2CF_2CO_2CH_3$ (10 mmol) was added by syringe slowly at room temperature and the reaction mixture was stirred at 130 °C by using an oil bath for 16 h. The reaction mixture was cooled and poured into water and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by column chromatography (EtOAc/n-hexane = 1/50) to afford compound **1r** as a pink oil (123 mg, 0.55 mmol, 55 % yield). R_f 0.50 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 9.30 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.03 (s, 2H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.8, 134.5, 133.9, 131.8 (q, *J* = 30 Hz), 131.2, 129.6, 128.6, 125.4, 124.7 (q, *J* = 3.75 Hz), 124.1 (q, *J* = 272.5 Hz), 124.8 (q, *J* = 6.25 Hz), 123.8 (q, *J* = 6.25 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -59.9 (s). HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_8F_3O$ 225.0527, found 225.0541.



1x

5-(Trifluoromethyl)-1-naphthaldehyde (1x). 5-bromo-1-naphthaldehyde (1.0 mmol) and CuI (1.5 mmol) were dissolved in anhydrous DMF (10 mL) under N_2 atmosphere. $FSO_2CF_2CO_2CH_3$ (10 mmol) was added by syringe slowly at room temperature and the reaction mixture was stirred at 130 °C by using an oil bath for 16 h. The reaction mixture was cooled and poured into water and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by reversed-phase column chromatography with gradient CH_3CN/H_2O eluent to afford compound

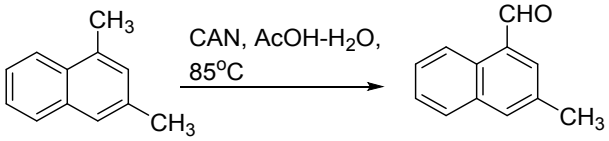
as a white solid (74 mg, 0.33 mmol, 33 % yield). R_f 0.50 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.54 (d, *J* = 8.5 Hz, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 7.0 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.81 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 137.1, 131.8, 131.2, 131.0 (q, *J* = 2.5 Hz), 130.2 (q, *J* = 200 Hz), 129.6, 127.5, 126.8, 126.6 (q, *J* = 30 Hz), 125.7 (q, *J* = 6.25 Hz), 123.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -59.0 (s). HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_8F_3O$ 225.0527, found 225.0529.



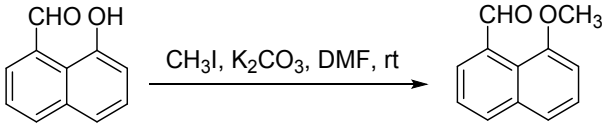
1y

7-Bromo-1-naphthaldehyde (1y). NBS (1.1 mmol) and benzoyl peroxide (0.2 mmol) was added to a solution of 7-bromo-1-methylnaphthalene[11] (1.0 mmol) in CCl_4 (2.0 mL) at room temperature and the reaction mixture was heated to reflux by using an oil bath for 12 h. After cooled to room temperature, the mixture was filtered off and the filtrate was concentrated under reduced pressure to afford the corresponding benzyl bromide.

A mixture of benzyl bromide (1.0 mmol) in a mixture of DMSO (2.0 mL) and DCM (1.0 mL) was treated with trimethylamine N-oxide dehydrate (3.0 mmol) at room temperature with stirring for 6 h. The reaction mixture was poured into water and extracted with DCM twice. The collected organic phase was washed with brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/40) to afford compound as a yellow solid (182 mg, 0.78 mmol, 78 % yield). R_f 0.60 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.31 (s, 1H), 9.49 (d, *J* = 2.0 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.99 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.68 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.65 (dd, *J* = 8.0, 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 137.8, 135.2, 132.3, 131.4, 130.7, 130.6, 129.9, 127.7, 125.4, 124.3. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_8BrO$ 234.9759, found 234.9753.

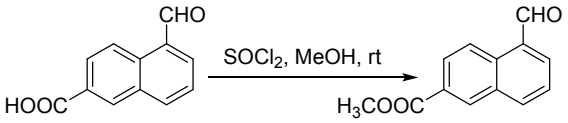


3-Methyl-1-naphthaldehyde. To a solution of CAN (3.5 mmol) in 50% acetic acid (100 mL) at 85 °C by using an oil bath was dropwisely added 1,3-dimethylnaphthalene (1.0 mmol). Once the starting material was completely consumed as monitored by TLC, the reaction mixture was cooled and poured into water. The product was extracted with EtOAc twice. The combined organic phases were washed with water, brine solution, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by column chromatography (EtOAc/n-hexane = 1/100) to afford compound as a yellow oil (65 mg, 0.38 mmol, 38 % yield). R_f 0.50 (50:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.38 (s, 1H), 9.17 (d, *J* = 8.5 Hz, 1H), 7.87 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 1H), 7.63 (t, *J* = 7.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 138.9, 134.7, 134.4, 134.3, 131.4, 129.1, 128.2, 127.9, 127.1, 124.8, 21.4. HRMS (ESI) m/z [M+H]+calcd for $C_{12}H_{11}O$ 171.0810, found 171.0811.

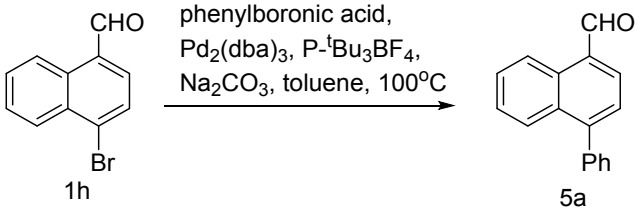


2a

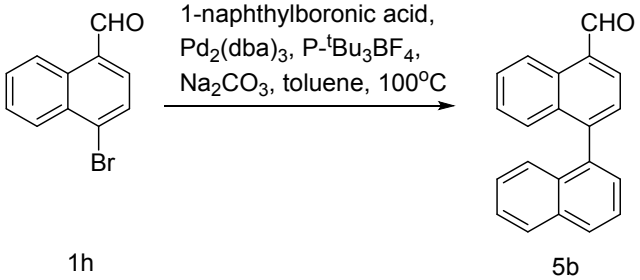
8-Methoxy-1-naphthaldehyde. To a solution of compound **2a** (1.0 mmol) and K_2CO_3 (3.0 mmol) in DMF (10 mL) at room temperature, CH_3I (3.0 mmol) was added dropwise. The mixture was stirred at room temperature for 6 h. Upon completion, the mixture was poured into water and extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (EtOAc/n-hexane = 1/50) to give compound as a pale yellow solid (176 mg, 0.95 mmol, 95 % yield). R_f 0.40 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.10 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 7.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.8, 156.4, 135.46, 135.2, 133.3, 127.4, 126.7, 125.9, 123.5, 121.7, 106.9, 55.8. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O_2$ 187.0759, found 187.0759.



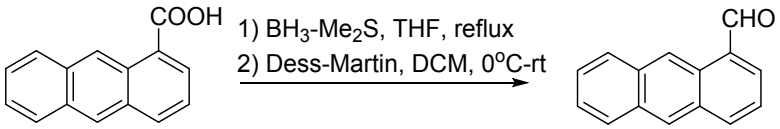
Methyl 5-formyl-2-naphthoate. To a solution of 5-formyl-2-naphthoic acid (1.0 mmol) in dry MeOH (2.0 mL) at 0 °C, thionyl chloride (1.3 mmol) was added dropwise. The mixture was stirred at room temperature for 1 h. Upon completion, aqueous $NaHCO_3$ solution was added to the mixture and extracted with EtOAc twice. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (EtOAc/n-hexane = 1/20) to give compound as a white solid (186 mg, 0.87 mmol, 87 % yield). R_f 0.50 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.42 (s, 1H), 9.31 (d, *J* = 9.0 Hz, 1H), 8.67 (s, 1H), 8.26 (d, *J* = 10.5 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 7.0 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 4.0 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 166.9, 138.5, 136.5, 133.2, 132.8, 131.6, 131.3, 128.60, 128.53, 125.91, 125.40, 52.57. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{11}O_3$ 215.0708, found 215.0705.



4-Phenyl-1-naphthaldehyde (5a). A Schlenk tube with a magnetic stir bar was charged with $Pd_2(dba)_3$ (0.02 mmol), P-^{t}Bu$_3$BF$_4$ (0.06 mmol), Na_2CO_3 (1.0 mol/L in water, 2.6 mL), compound **1h** (1.0 mmol), phenylboronic acid (2.0 mmol) and dry toluene (3.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at room temperature for 10 min and then heated at 100 °C by using an oil bath for 12 h. After cooling down to the room temperature, water was added and the mixture extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/40) to afford compound **5a** as a white solid (176 mg, 0.76 mmol, 76 % yield). R_f 0.40 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.45 (s, 1H), 9.37 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.56-7.50 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 147.6, 140.0, 136.3, 132.2, 131.2, 130.7, 129.9×2, 129.0, 128.6×2, 128.2, 127.1, 126.9, 126.2, 125.2. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{17}H_{13}O$ 233.0966, found 233.0967.



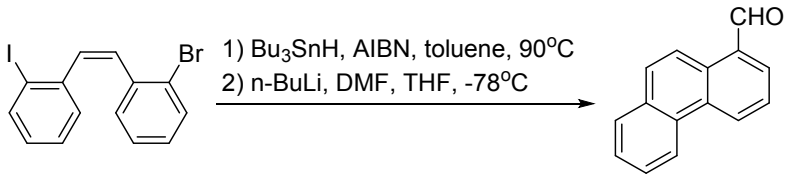
[1,1'-Binaphthalene]-4-carbaldehyde (5b). A Schlenk tube with a magnetic stir bar was charged with $Pd_2(dba)_3$ (0.02 mmol), P-^{t}Bu$_3$BF$_4$ (0.06 mmol), Na_2CO_3 (1.0 mol/L in water, 2.6 mL), compound **1h** (1.0 mmol), 1-naphthylboronic acid (2.0 mmol), dry toluene (3.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at room temperature for 10 min and then at 100 °C by using an oil bath for 12 h. After cooling down to the room temperature, water was added and the mixture extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/40) to afford compound **5b** as a white solid (225 mg, 0.8 mmol, 80 % yield). R_f 0.40 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.50 (s, 1H), 9.40 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 7.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.71-7.68 (m, 1H), 7.68-7.66 (m, 1H), 7.62 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.53-7.47 (m, 3H), 7.40 (ddd, *J* = 14.5, 7.0, 1.5 Hz, 1H), 7.33-7.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 146.2, 137.6, 136.2, 133.6, 133.4, 132.4, 131.2, 130.9, 129.1, 128.7, 128.4, 127.6, 127.4, 127.2, 127.1, 126.5, 126.3, 126.2, 125.4, 125.1. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{21}H_{15}O$ 283.1123, found 283.1114.



5c

Anthracene-1-carbaldehyde (5c). 1-anthroic acid (1.0 mmol) was dissolved in anhydrous THF (3.0 mL) under N_2 atmosphere. Borane-methyl sulfide complex (2.0 M, 1.0 mmol) was added by syringe slowly. The resulting mixture was refluxed by using an oil bath for 3 h. After cooling down to the room temperature, the mixture was poured into 2N NaOH solution and stirred for 0.5 h. The mixture was extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford the corresponding anthryl alcohol without further purification.

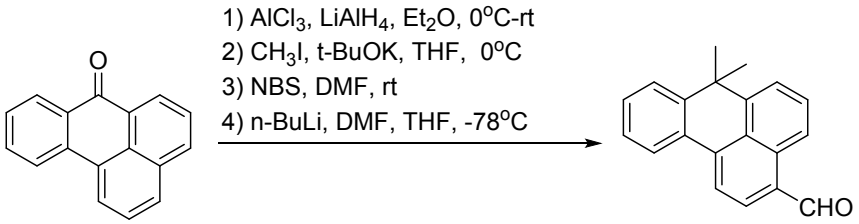
To a solution of above anthryl alcohol (1.0 mmol) in CH_2Cl_2 (2.0 mL) was added Dess-Martin periodinane (1.1 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. The reaction was quenched with $Na_2S_2O_3$ solution, washed with saturated $NaHCO_3$ solution and extracted with DCM twice. The collected organic phases were washed with brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/50) to afford compound **5c** as a yellow solid (187 mg, 0.91 mmol, 91 % yield). R_f 0.50 (20:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 9.91 (s, 1H), 8.45 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.13 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.00 (dd, *J* = 9.5, 9.0 Hz, 1H), 7.95 (d, *J* = 7.0 Hz, 1H), 7.59-7.51 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 139.1, 136.2, 133.6, 131.9, 131.8, 131.7, 129.3, 128.1, 127.4, 127.3, 126.6, 126.5, 125.0, 124.0. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{15}H_{11}O$ 207.0810, found 207.0815.



5d

Phenanthrene-1-carbaldehyde (5d). To a solution of (Z)-1-bromo-2-(2-iodostyryl)-benzene (1.0 mmol) in toluene (25 mL), Bu_3SnH (1.2 mmol) and AIBN (0.2 mmol) were added at room temperature. The mixture was stirred at 90 °C for 12 h. Second batch of Bu_3SnH (1.2 mmol) and AIBN (0.2 mmol) were added with continuing heating at 90 °C by using an oil bath for 6 h. After cooling down to the room temperature, water was added and the mixture was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford the corresponding bromophenylanthrene.

To a solution of bromophenylanthrene in anhydrous THF (0.3 M) was added n-butyl lithium solution (1.6 M in hexane, 1.5 mmol) at -78 °C under an atmosphere of N_2. The resulting mixture was kept stirring at -78 °C for 20 minutes. Anhydrous DMF (1.2 mmol) was added to the reaction and stirred at -78 °C for another 15 minutes. The reaction was allowed to warm to room temperature and then quenched with aqueous NH_4Cl solution. The resulting mixture was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/30) to afford compound **5d** as a white solid (154 mg, 0.75 mmol, 75 % yield). R_f 0.60 (10:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.52 (s, 1H), 9.15 (d, *J* = 9.5 Hz, 1H), 8.99 (d, *J* = 8.5 Hz, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 7.0 Hz, 1H), 7.96 (t, *J* = 9.0 Hz, 2H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 135.3, 131.9, 131.8, 131.0, 130.6, 130.4, 129.9, 129.2, 128.8, 127.4, 127.3, 125.8, 123.0, 122.3. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{15}H_{11}O$ 207.0810, found 207.0812.



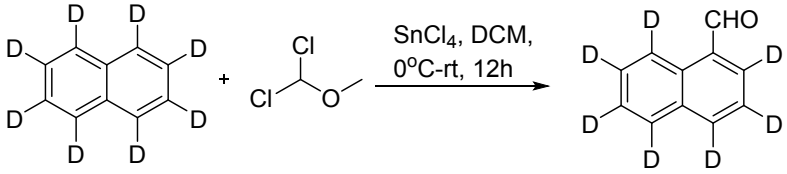
5e

7,7-Dimethyl-7H-benzo[de]anthracene-3-carbaldehyde (5e). To a solution of the 7H-benzo[de]anthracen-7-one (1.0 mmol) in Et_2O (5.0 mL), $AlCl_3$ (1.2 mmol) and $LiAlH_4$ (1.5 mmol) were added slowly at 0 °C. The the reaction was allowed to warm to room temperature with stirring for 6 h. Aqueous HCl was added and the resulting mixture was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum to afford the corresponding benzo[de]anthracene without further purification.

To a solution of above benzo[de]anthracene (~1.0 mmol) and t-BuOK (2.0 mmol) in THF (10 mL) at 0 °C, excess CH_3I (3.0 mmol) was added and stirred for 1 h. Upon completion, aqueous HCl was added and the resulting mixture was extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was recrystallizated by hot EtOH. The precipitates was filtered to give the 7,7-Dimethyl-7H-benzo[de]anthracene.

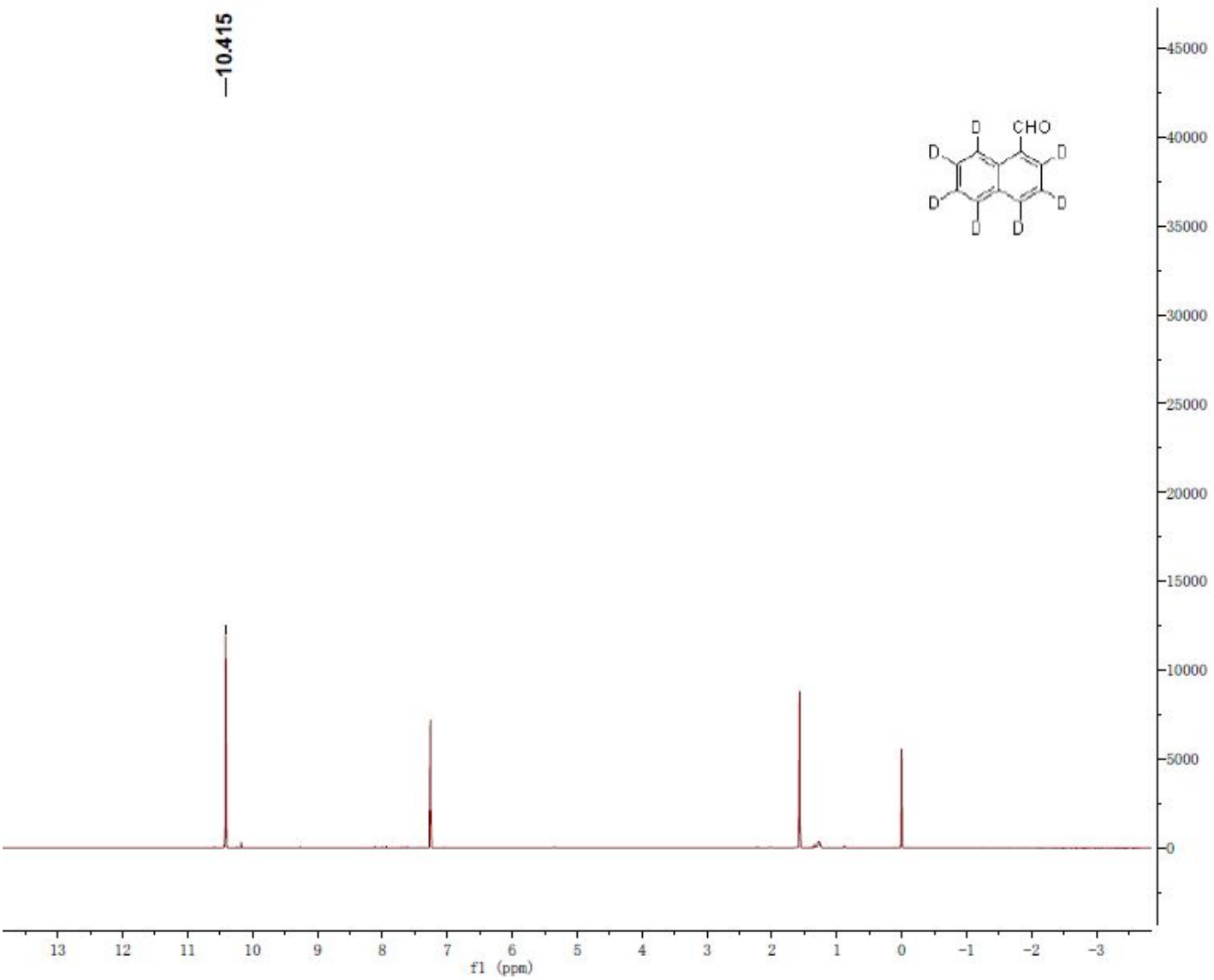
The crude 7,7-Dimethyl-7H-benzo[de]anthracene and NBS (1.0 mmol) was dissolved in DMF (10 mL) with stirring for 1 h. Once the substrate was completely consumed as monitored by TLC, water was added and the mixture was extracted with EtOAc twice. The combined organic layers were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford the corresponding brominated intermediate, which was dissolved in anhydrous THF (0.3 M) and treated with n-butyl lithium solution (1.6 M in hexane, 1.5 mmol) at -78 °C under an atmosphere of N_2. The resulting mixture was kept stirring at -78 °C for 20 minutes. Anhydrous DMF (1.2 mmol) was added to the reaction and stirred at -78 °C for another 15 minutes. The reaction was allowed to warm to room temperature and then quenched with aqueous NH_4Cl solution. The resulting mixture was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography (EtOAc/n-hexane = 1/20) to afford compound **5e** as a white solid (136 mg, 0.5 mmol, 50 % yield). R_f 0.50 (10:1 hexane/EtOAc). ^1H NMR (500 MHz, $CDCl_3$) δ 10.38 (s, 1H), 9.23 (d, J = 9.0 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 7.5 Hz, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.80 (d, J = 6.5 Hz, 1H), 7.78-7.74 (m, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.46 (t, J = 7.0 Hz, 1H), 7.40 (t, J = 7.0 Hz, 1H), 1.75 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 145.8, 143.7, 137.3, 136.6, 131.3, 130.5, 129.8, 129.6, 129.2, 127.3, 127.0, 126.9, 124.5×2, 122.8, 118.1, 39.2×2, 35.1. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{20}H_{17}O$ 273.1279, found 273.1280.

6. Preliminary mechanistic experiments.

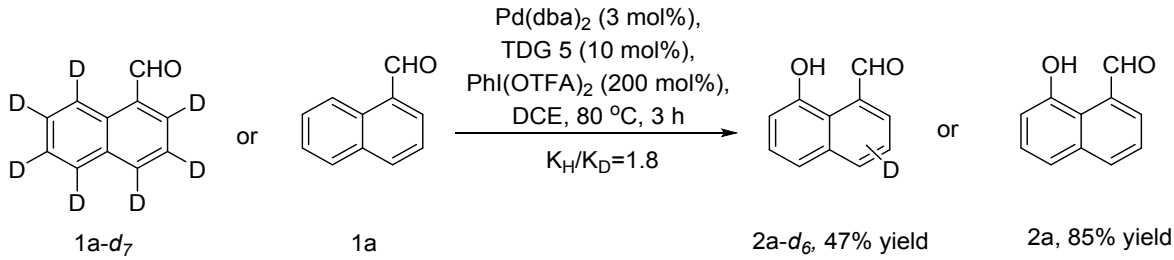


1a-d_7

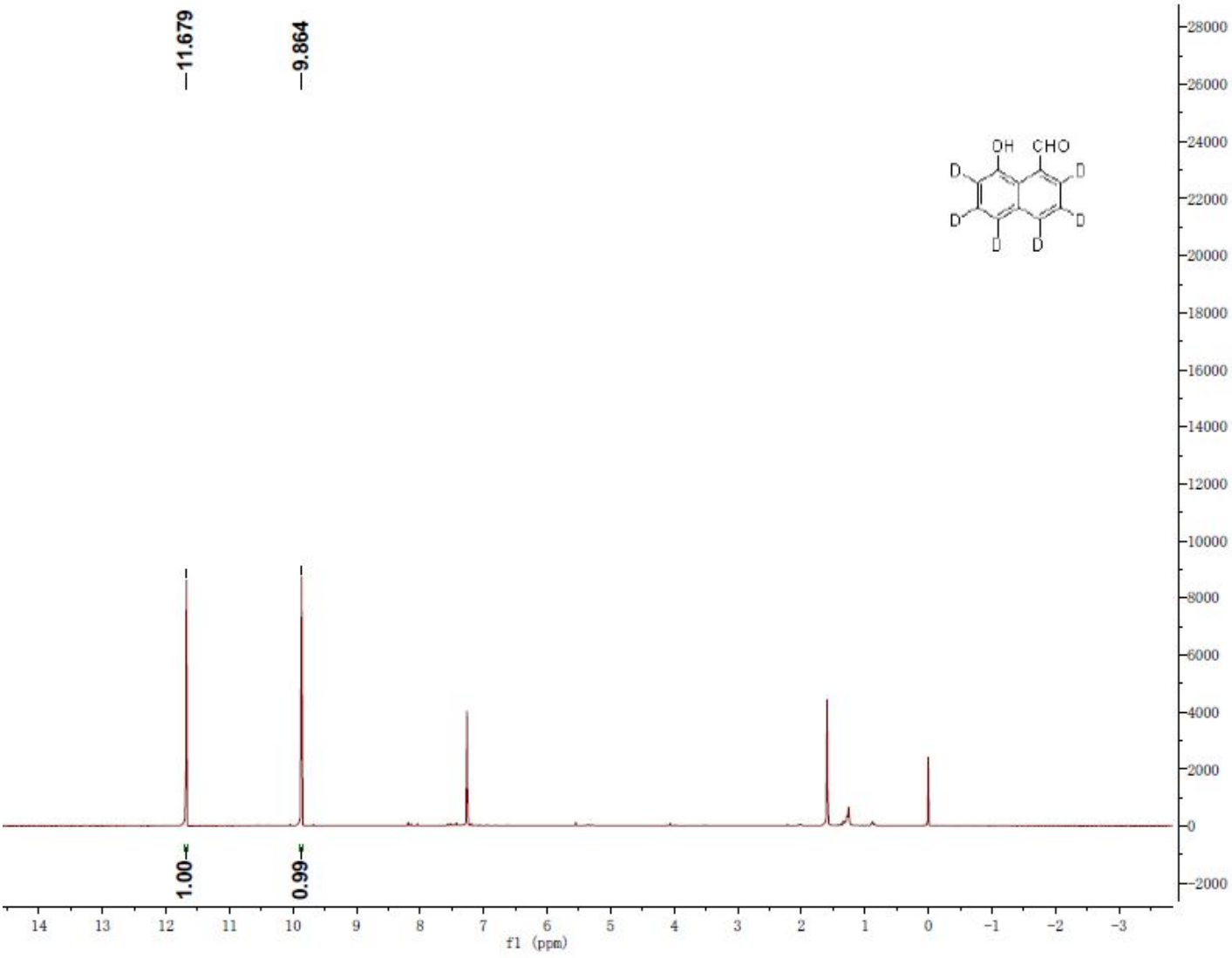
1-Naphthaldehyde-2,3,4,5,6,7,8-d$_7$ (1a-*d$_7$*). A solution of α,α-dichloromethyl methyl ether (1.3 mmol) in DCM (2.6 mL) was treated with $SnCl_4$ (1.3 mmol) dropwisely at 0 °C. After stirring for 45 min, a solution of 1-chloronaphthalene (1.0 mmol) in DCM (1.0 mL) was added. The reaction was stirred at room temperatue overnight. Upon completion, the mixture was poured into ice water and extracted with DCM twice. The combined organics were washed with H_2O, brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography (EtOAc/n-hexane = 1/50) to give **1a-*d$_7$*** as a colorless oil (130 mg, 0.8 mmol, 80 % yield). R_f 0.50 (20:1 hexane/EtOAc). HRMS (ESI) m/z $[M+H]^+$calcd for $C_{11}H_2D_7O$ 164.1093, found 164.1090.

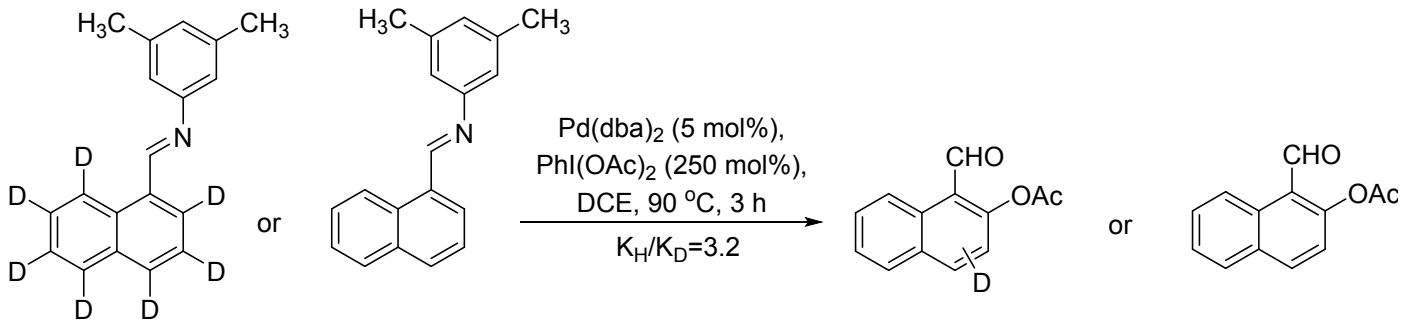


a) Parellel kinetic isotope effect.



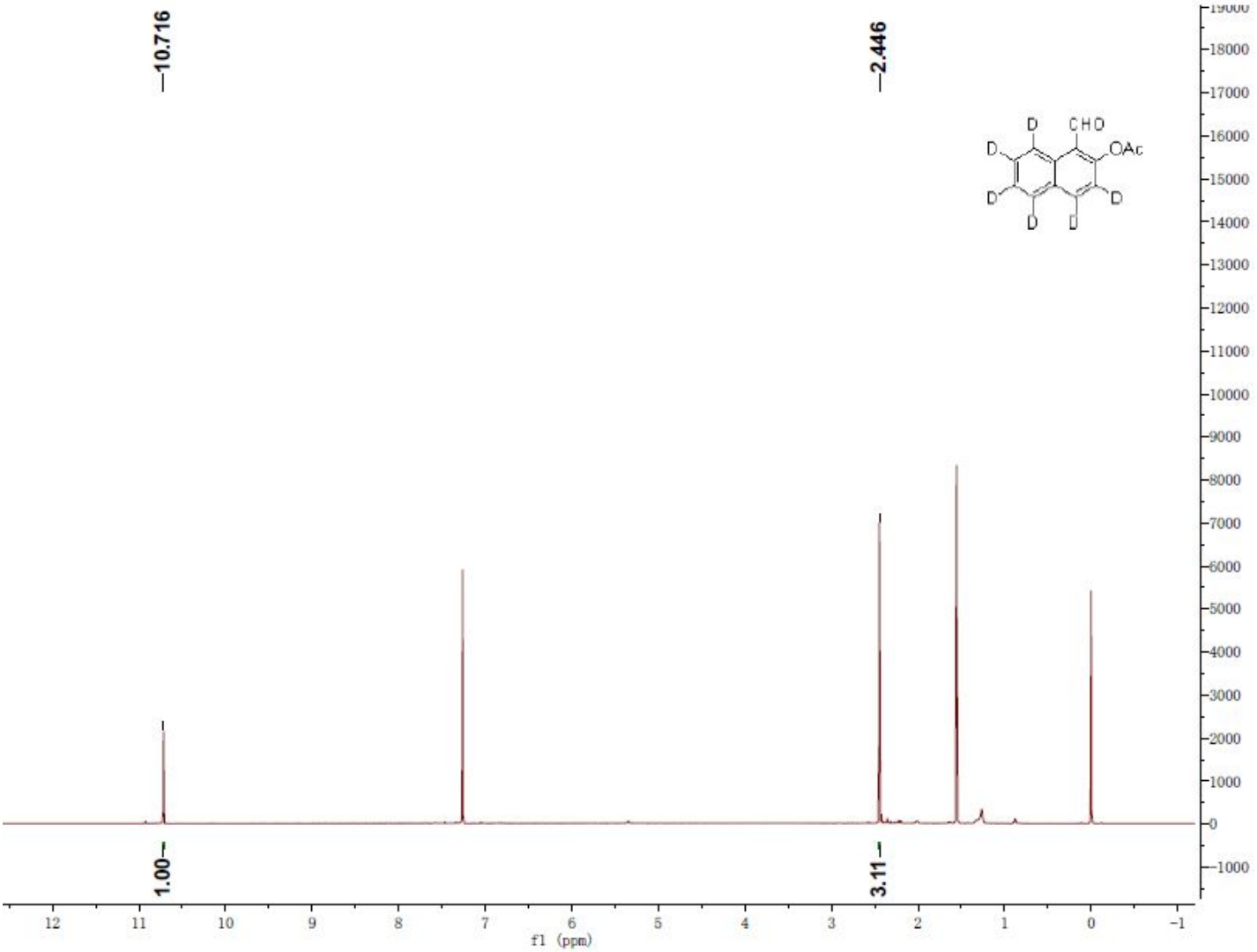
One mixture of 1-naphthaldehyde **1a** (0.1 mmol), 2-aminobenzenesulfonic acid (TDG) (0.01 mmol), $Pd(dba)_2$ (0.003 mmol), $PhI(OTFA)_2$ (0.2 mmol) were dissolved in DCE (0.5 mL). The other mixture of 1-naphthaldehyde **1a-*d*$_7$**, 2-aminobenzenesulfonic acid (TDG) (0.01 mmol), $Pd(dba)_2$ (0.003 mmol), $PhI(OTFA)_2$ (0.2 mmol) were dissolved in DCE (0.5 mL).The reaction mixtures were stirred at 80 °C by using an oil bath for 3 h. Upon completion, the reaction mixtures were cooled to room temperature, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (EtOAc/n-hexane = 1/20) to give the products **2a** as an organe powder (14 mg, 81% yield) or **2a-*d*$_6$** as an organe powder (8 mg, 45% yield). By the yield of the product, KIE=85%/47%=1.8.



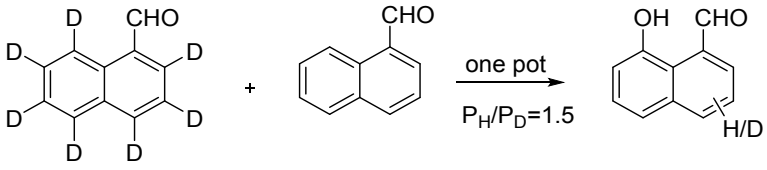


3a-d_7 3a 4a-d_6, 15% yield 4a, 48% yield

One mixture of imine **3a** (0.1 mmol), $Pd(dba)_2$ (0.005 mmol), $PhI(OAc)_2$ (0.25 mmol) were dissolved in anhydrous DCE (1.0 mL) in a sealed tube. The other mixture of imine **3a-*d*$_7$** (0.1 mmol), $Pd(dba)_2$ (0.005 mmol), $PhI(OAc)_2$ (0.25 mmol) were dissolved in anhydrous DCE (1.0 mL) in a sealed tube. The reactions were heated to 90 °C by using an oil bath for 3 h and cooled down to the room temperature, silica gel (50 mg) was added separately with stirring at 80 °C by using an oil bath for another 1 h. The resulting mixtures were cooled to room temperature and concertrated under vacuum. The crude reaction mixtures were purified by flash column chromatography (EtOAc/n-hexane = 1/20) to give the products **4a** as a pale yellow powder (10 mg, 48% yield) or **4a-*d*$_6$** as a pale yellow powder (3 mg, 15% yield). By the yield of the product, KIE=48%/15%=3.2.

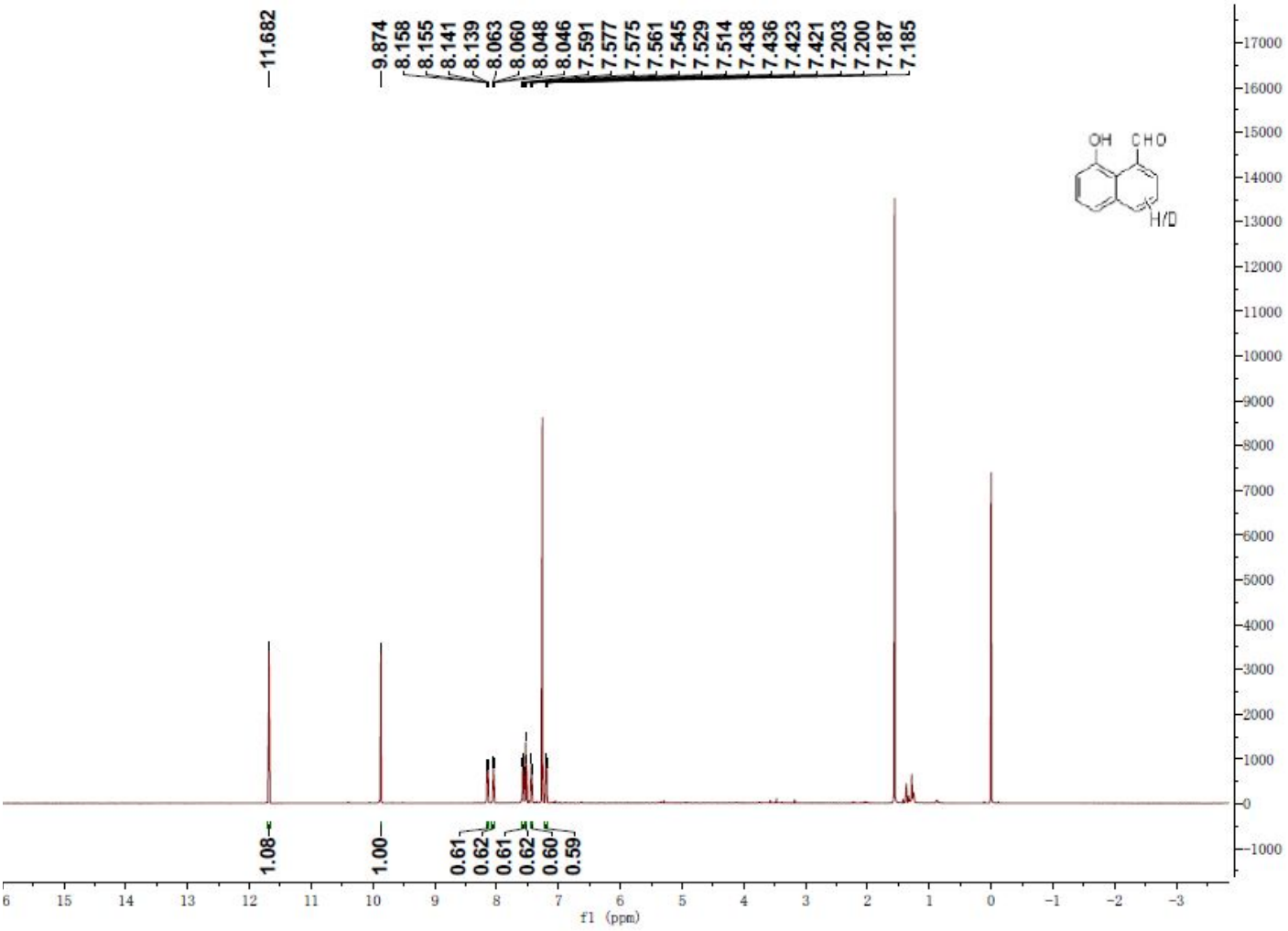


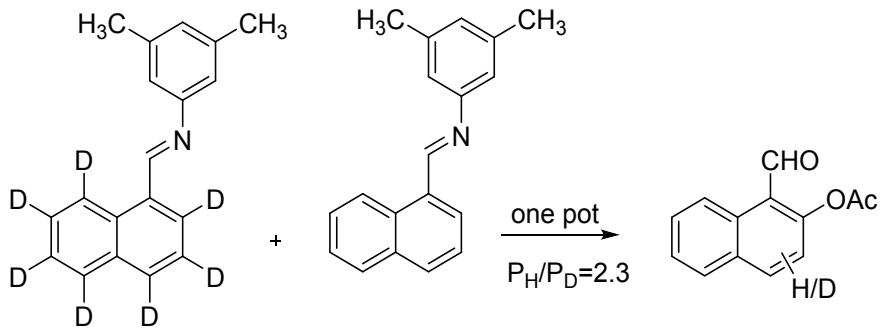
b) Intermoleculr kinetic isotope effect.



1a-d_7 1a 2a/2a-d_6 (mix)

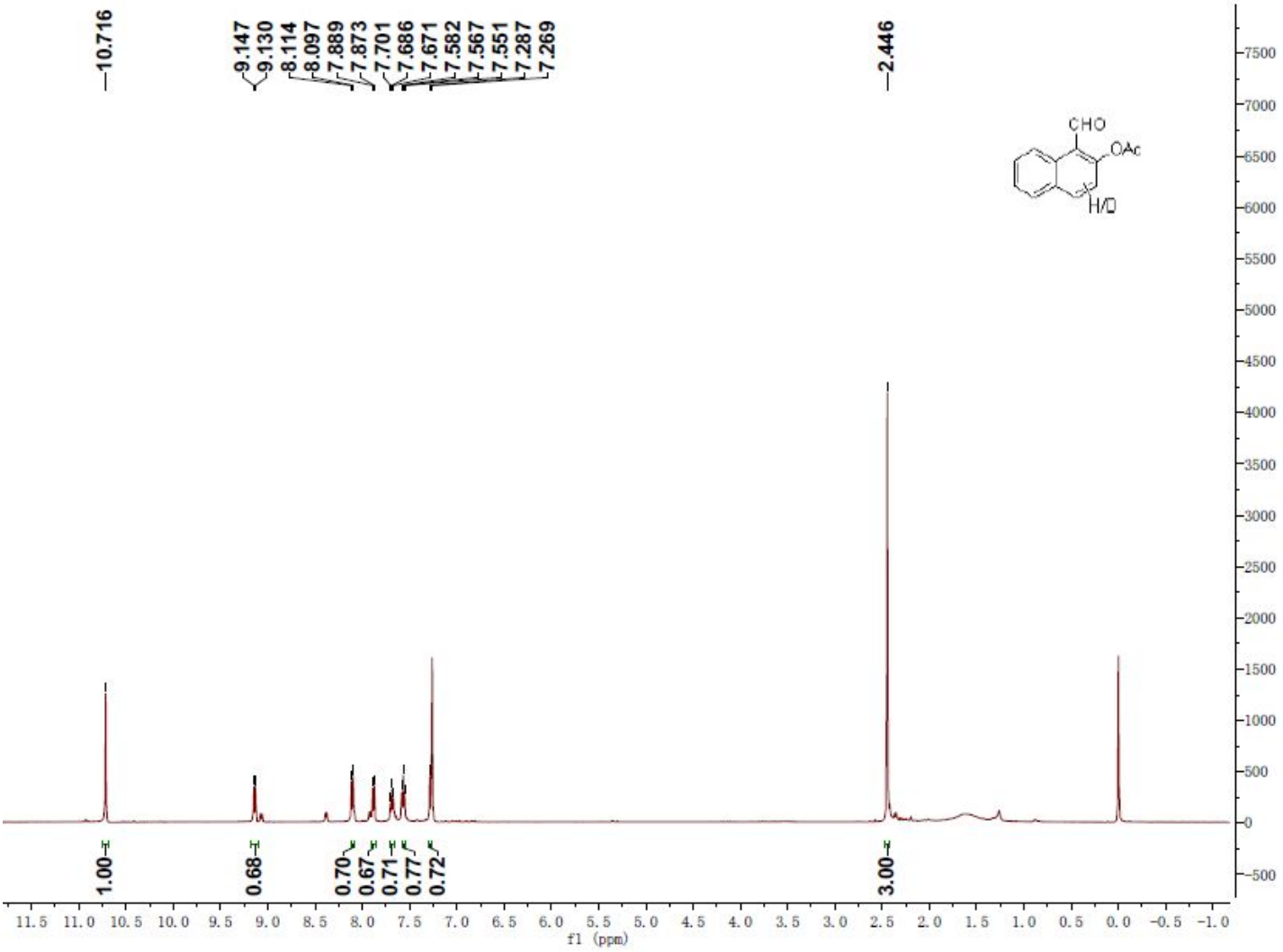
A mixture of 1-naphthaldehyde **1a** (0.1 mmol), naphthaldehyde **1a-*d*$_7$** (0.1 mmol), 2-aminobenzenesulfonic acid (TDG) (0.02 mmol), $Pd(dba)_2$ (0.006 mmol), $PhI(OTFA)_2$ (0.4 mmol) were dissolved in DCE (1.0 mL). The reaction mixture was was stirred at 80 °C by using an oil bath for 3 h. Upon completion, the reaction mixture was cooled to room temperature, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (EtOAc/n-hexane = 1/20) to give a mixture of products **2a** and **2a-*d*$_6$**. The proton NMR analysis of **2a**/**2a-*d*$_6$ (mix)** as shown below indicates a KIE value of 1.5 (0.61/0.39 = 1.5).



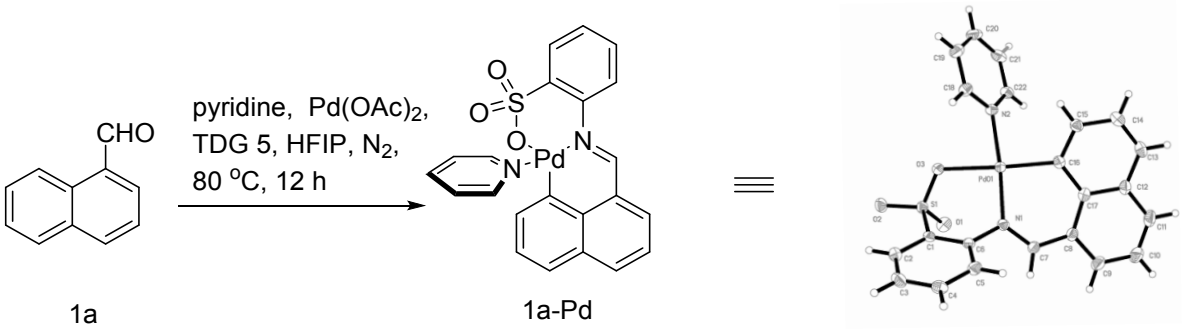


3a-d_7 3a 4a/4a-d_6 (mix)

In a sealed tube with magnetic stir bar was charged with imine **3a** (0.1 mmol), imine **3a-*d*$_7$** (0.1 mmol), $Pd(dba)_2$ (0.01 mmol), $PhI(OAc)_2$ (0.5 mmol) were dissolved in anhydrous DCE (2.0 mL). The reaction tube was sealed and heated to 90 °C by using an oil bath for 3 h. The reaction mixture was cooled, silica gel (100 mg) was added with stirring at 80 °C by using an oil bath for 1 h. The resulting mixture was cooled to room temperature and concertrated under vacuum. The crude reaction mixture was purified by flash column chromatography (EtOAc/n-hexane = 1/20) to give a mixture of products **4a** and **4a-*d*$_6$**. The proton NMR analysis of **4a**/**4a-*d*$_6$ (mix)** as shown below indicates a KIE value of 2.3 (0.70/0.30 = 2.3).

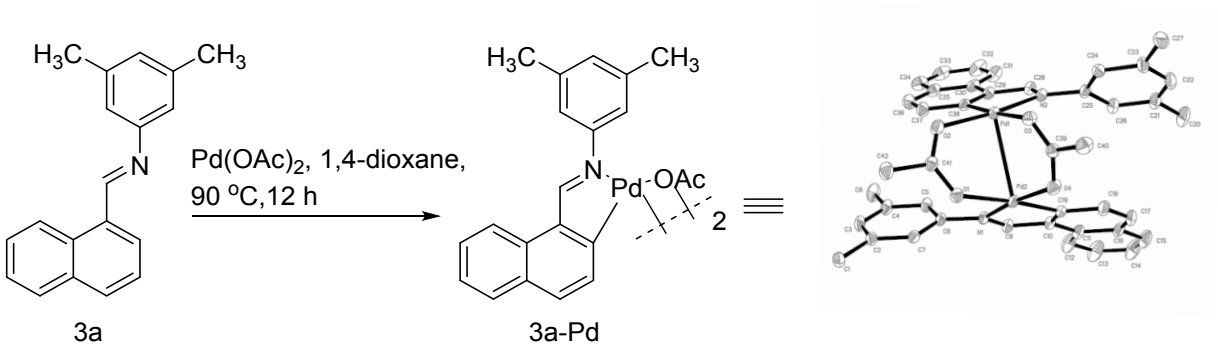


c) Synthetic and isolation of palladacycle.



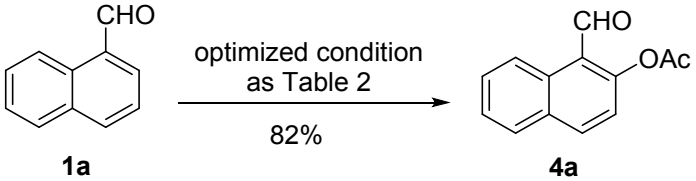
1a 1a-Pd

A sealed tube equipped with a stir bar was charged with $Pd(OAc)_2$ (112 mg, 0.5 mmol), 2-aminobenzenesulfonic acid (86.5 mg, 0.5 mmol), pyridine (39.5 mg, 0.5 mmol) and HFIP (0.1 M, 5 mL). The sealed tube was stirred at 80 °C by using an oil bath for 12 h. After cooling to room temperature, the reaction was filtered through a pad of Celite, washed off with DCM, and concentrated *in vacuo*. The residue was purified by column chromatography (MeOH/DCM = 1/10) to afford the desired palladacycle **1a-Pd** as a yellow powder (98 mg, 0.2 mmol, 40 % yield). R_f 0.20 (10:1 DCM/MeOH). The crystal was grown from a mixture of $CHCl_3$/hexane (1:1) with slow volatization. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.94 (s, 1H), 8.58 (d, J = 4.0 Hz, 2H), 8.37 (d, J = 7.0 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.10 (t, J = 5.0 Hz, 1H), 7.88 (dd, J = 12.5, 1.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.64-7.55 (m, 4H), 7.32 (d, J = 7.5 Hz, 1H), 7.17 (t, J = 9.0 Hz, 1H), 6.60 (t, J = 3.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.6, 153.0, 152.4×2, 147.3, 139.5, 139.4, 138.6, 137.7, 137.6, 137.3, 133.5, 132.2, 132.1, 128.1, 126.3, 125.9, 125.8, 125.7, 125.5, 125.4, 125.1.

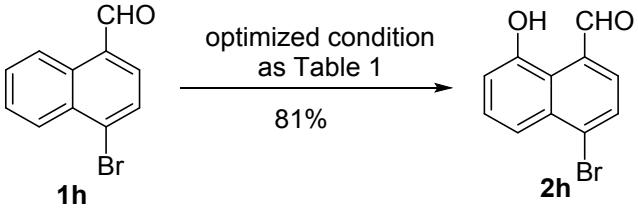


A sealed tube equipped with a stir bar was charged with $Pd(OAc)_2$ (112 mg, 0.5 mmol), compound **3a** (130 mg, 0.5 mmol) and 1,4-dioxane (0.1 M, 5 mL). The sealed tube was stirred at 90 °C by using an oil bath for 12 h. After cooling to room temperature, the reaction was filtered through a pad of Celite, washed off with DCM, and concentrated *in vacuo*. The residue was purified by column chromatography (MeOH/DCM = 1/10) to afford the desired palladacycle **3a-Pd** as a yellow powder (165 mg, 0.2 mmol, 41 % yield). R_f 0.20 (10:1 DCM:MeOH). The crystal was grown from a mixture of $CHCl_3$/hexane/MeOH (1:1:1) with slow volatization. ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.40 (t, *J* = 6.5 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.90 (s, 1H), 6.44 (s, 2H), 2.26 (s, 6H), 1.923 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.7, 169.2, 162.0, 147.9, 139.2, 137.7, 137.7, 131.2, 131.0, 129.3, 129.2, 127.2, 124.6, 122.2, 121.1×2, 24.2, 21.3×2.

7. Gram-scale reaction.



1-Formylnaphthalen-2-yl acetate (4a). To a stirring solution of naphthaldehyde **1a** (1.56 g, 10 mmol) in EtOH (100 mL) at room temperature was added 3, 5-dimethylaniline (1.33 g, 11 mmol) and sodium sulfate (14.2 g, 100 mmol). The reaction mixture was refluxed by using an oil bath with stirring for 12 h. The reaction mixture was cooled and filtered. The filtrate was concentrated *in vacuo* and recrystallized with EtOH. The precipitates was filtered to give the imime intermediate as yellow powders. In a sealed tube with magnetic stir bar was charged with the imine intermediate (2.59 g, 10 mmol), $Pd(dba)_2$ (287 mg, 0.5 mmol), and $PhI(OAc)_2$ (8.05 g, 25 mmol) in anhydrous DCE (0.1 M, 100 mL). The reaction tube was sealed and heated to 90 °C by using an oil bath for 6 h. The reaction mixture was then treated with silica gel (3 g, 200-300 mesh) with stirring at 80 °C by using an oil bath for 1 h. The resulting mixture was cooled to room temperature and concentrated under vacuum. The crude reaction mixture was purified on silica gel using 20:1 hexanes/EtOAc as the eluent to afford the desired product **4a** (1.75 g, 8.2 mmol, 82%). R_f 0.50 (10:1 hexane/EtOAc).



4-Bromo-8-hydroxy-1-naphthaldehyde (2h). 4-bromo-1-naphthaldehyde (2.34 g, 10 mmol), $Pd(dba)_2$ (173 mg, 0.3 mmol), 2-aminobenzenesulfonic acid (TDG5) (173 mg, 1.0 mmol) and $PhI(OTFA)_2$ (8.6 g, 20 mmol) were dissolved in DCE (0.2 M, 50 mL) and the reaction mixture was at 80 °C by using an oil bath with stirring for 12 h. Upon completion, the reaction mixture was cooled to room temperature, concentrated *in vacuo*. The crude reaction mixture was purified on silica gel using 20:1 hexanes/EtOAc as the eluent to afford the desired product **2h** (2.02 g, 8.1 mmol, 81%). R_f 0.40 (10:1 hexane/EtOAc).

8. The deposition information of crystal structures.

The CIF data of three crystal structures were deposited to the Cambridge Crystallographic Data Centre with following deposition numbers, compound **2a** (CCDC2024937), compound **1a-Pd** (CCDC2024933), and compound **3a-Pd** (CCDC2024936), respectively.

9. Supplemental references.

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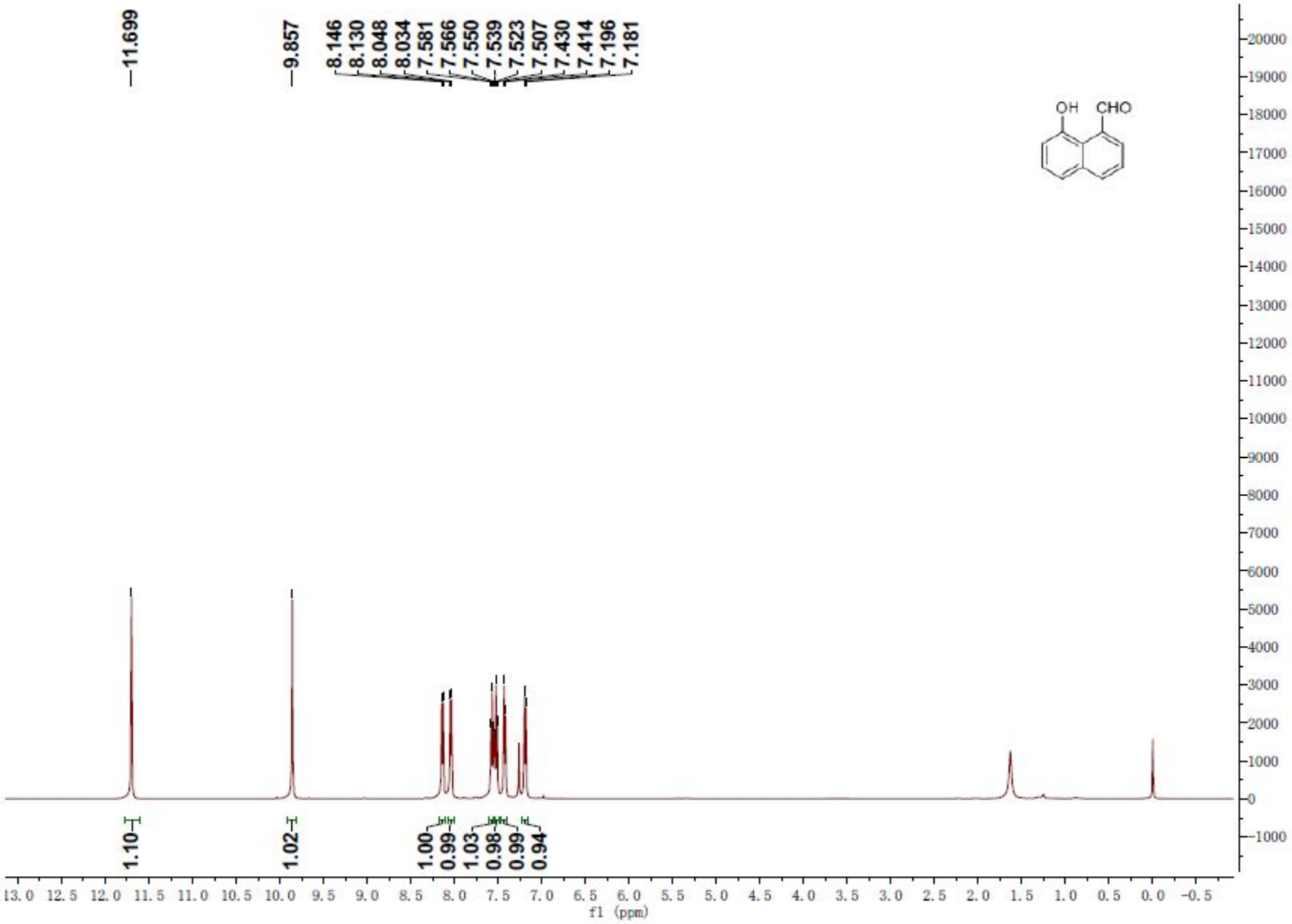
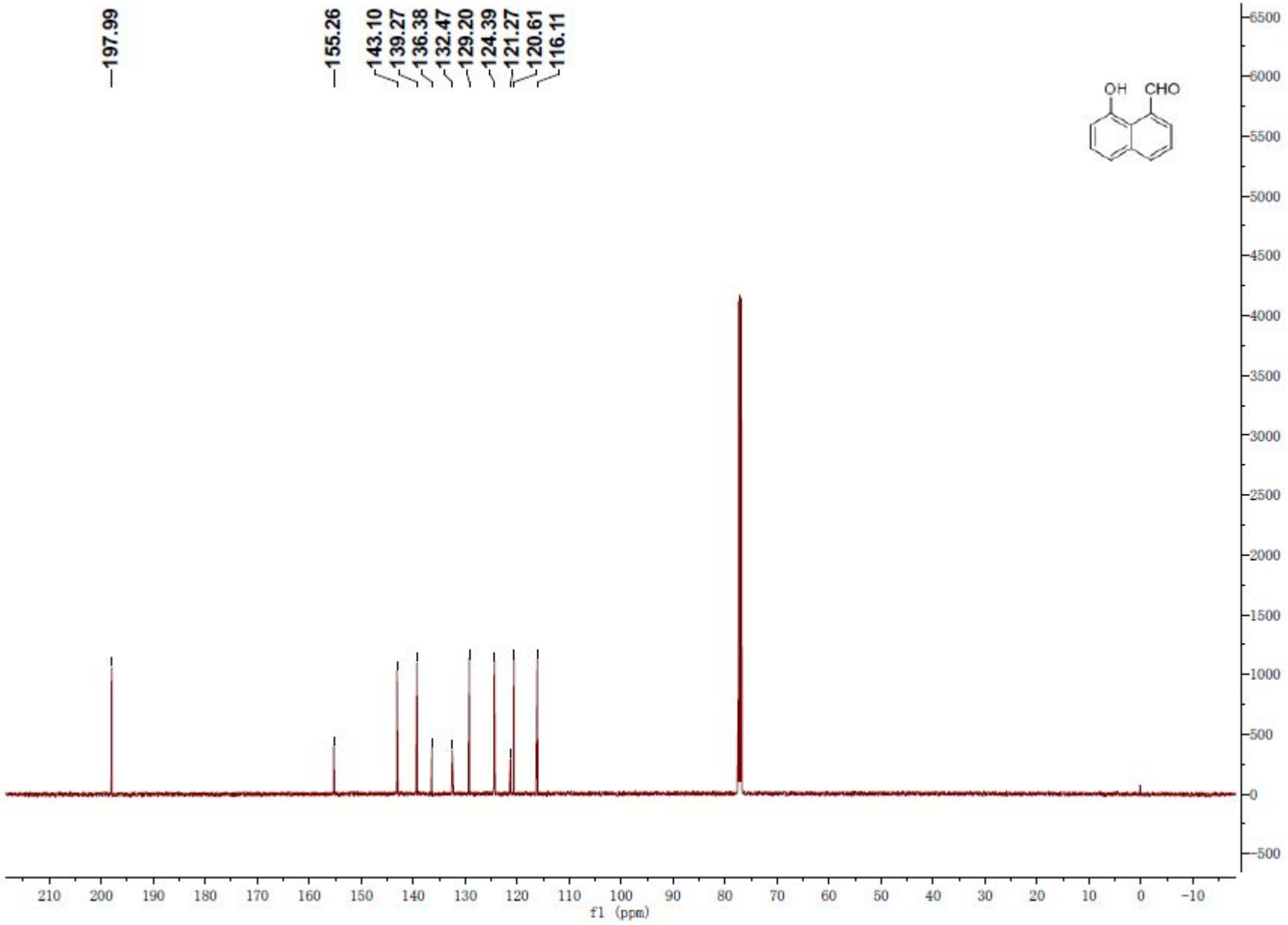
10. ^{1}H NMR and ^{13}C NMR Spectra

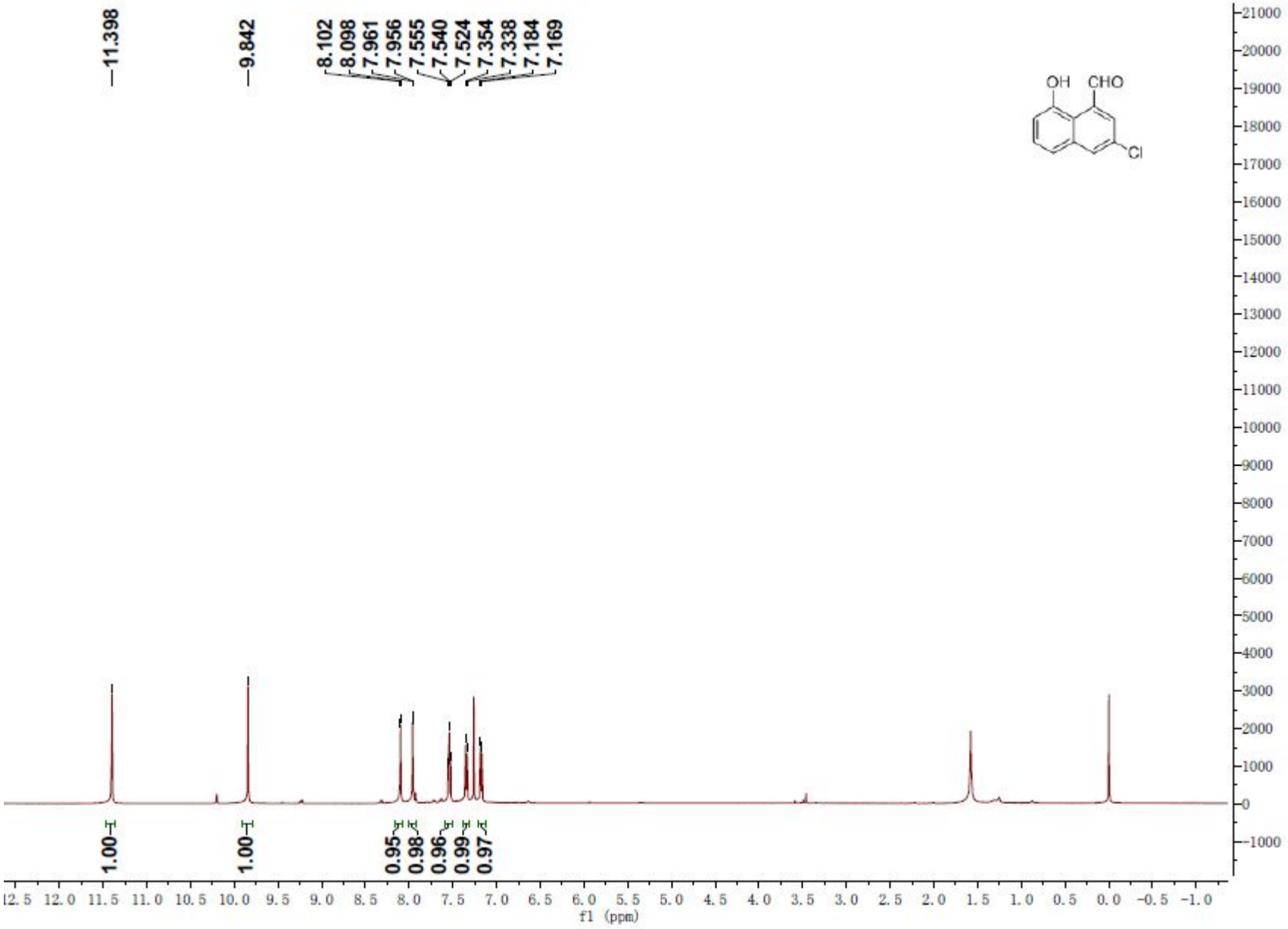
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 8-hydroxy-1-naphthaldehyde (2a)



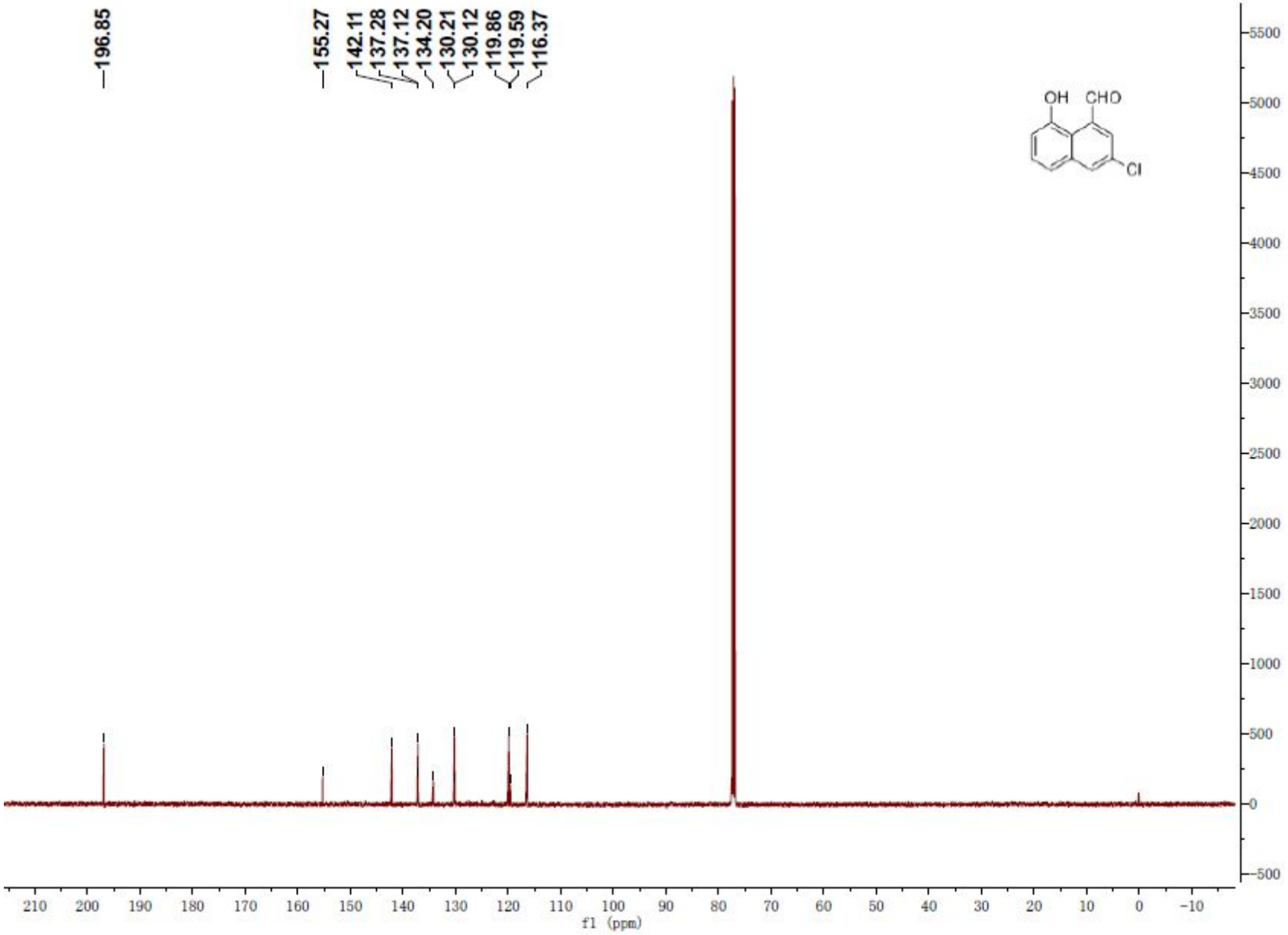
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 8-hydroxy-1-naphthaldehyde (2a)



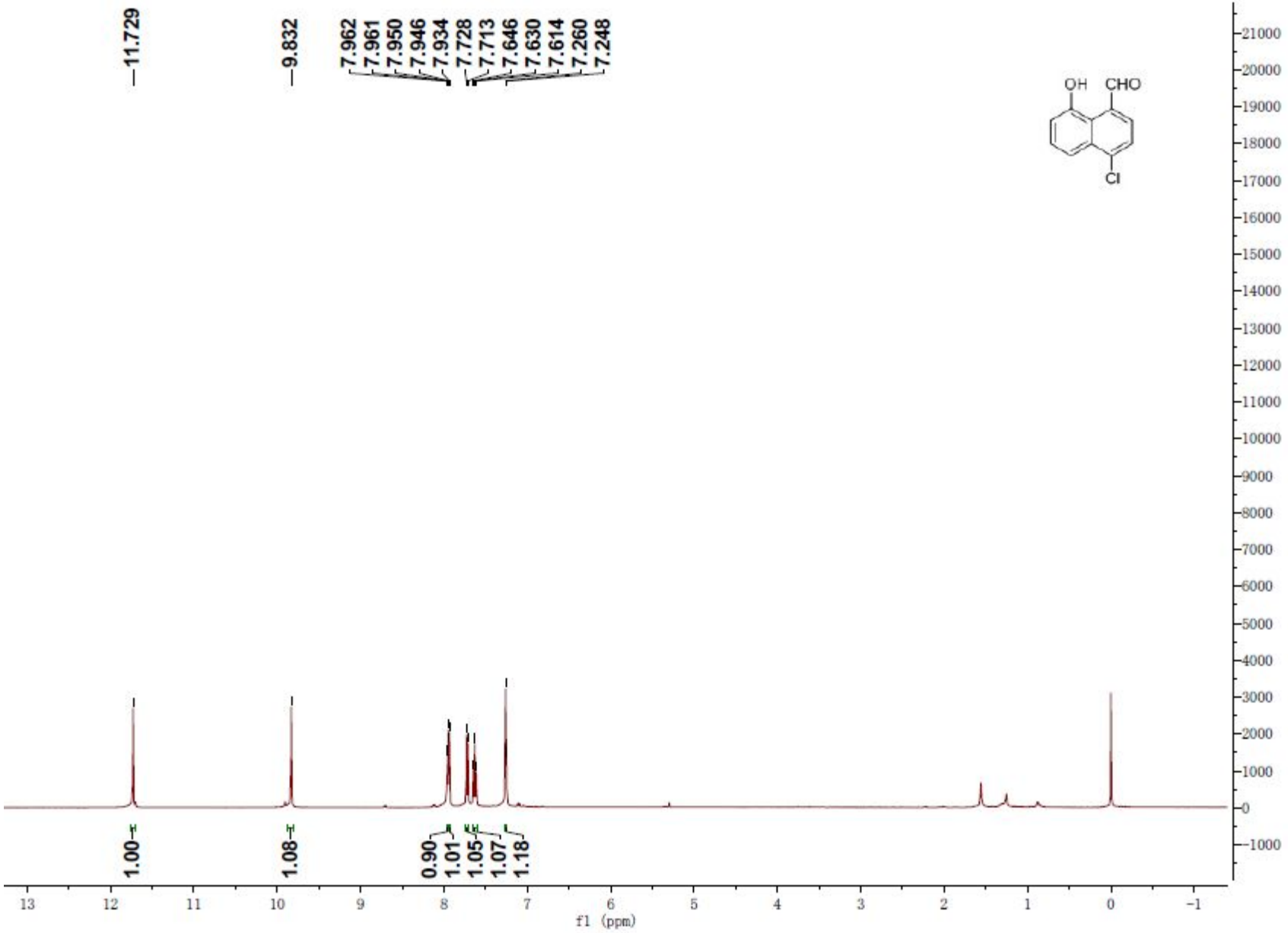
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3-chloro-8-hydroxy-1-naphthaldehyde (2b)



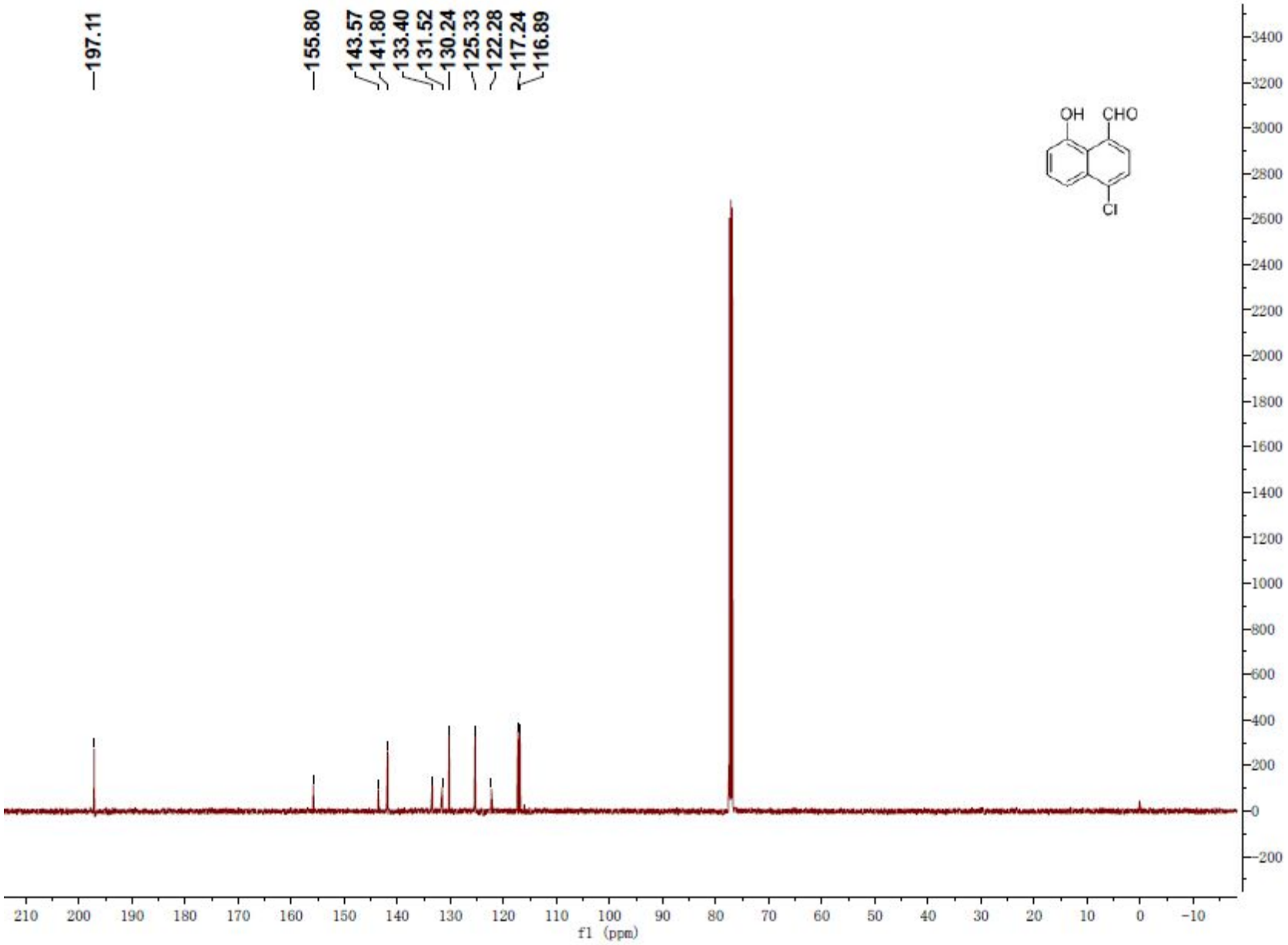
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 3-chloro-8-hydroxy-1-naphthaldehyde (2b)



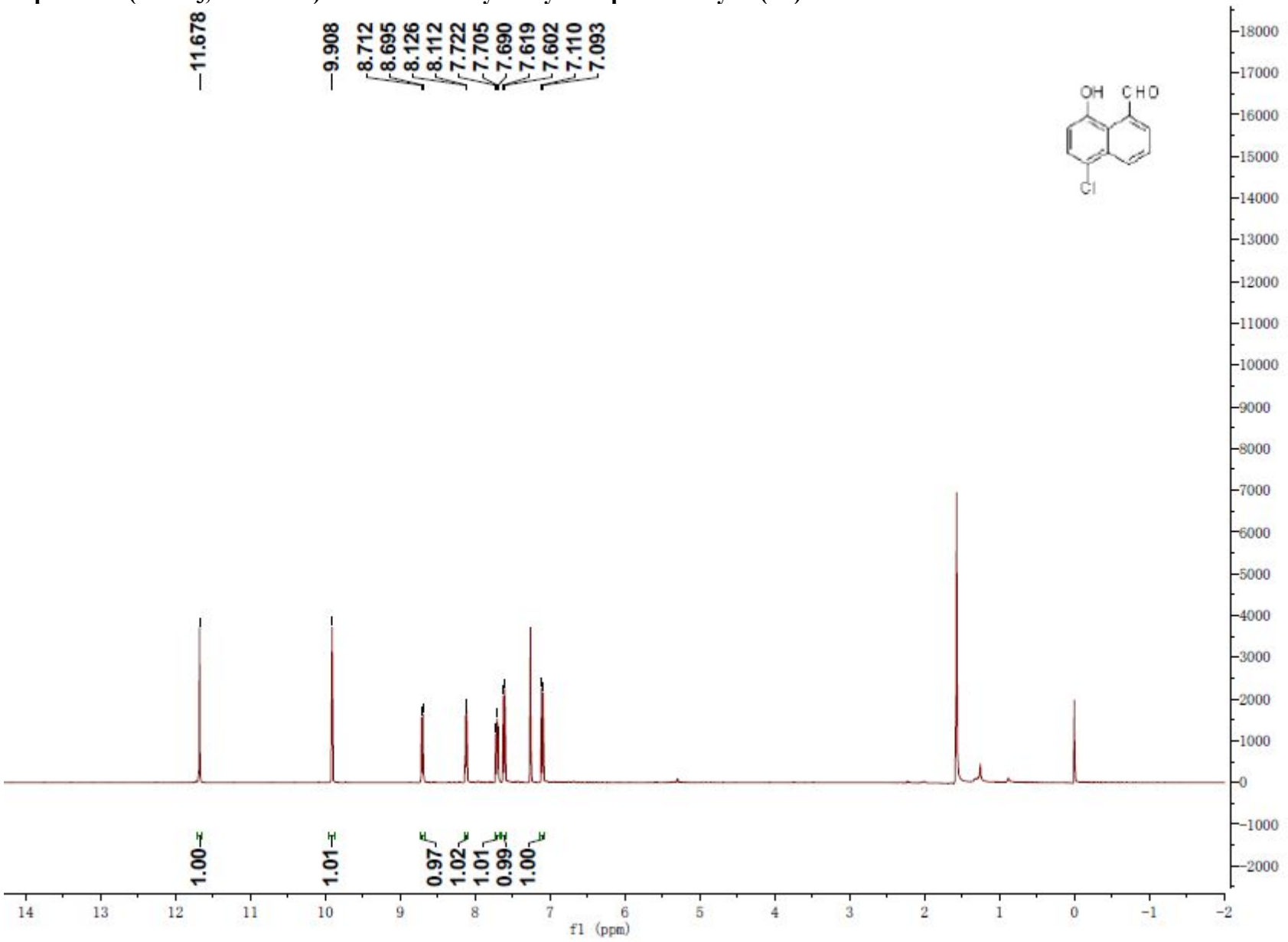
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-chloro-8-hydroxy-1-naphthaldehyde (2c)



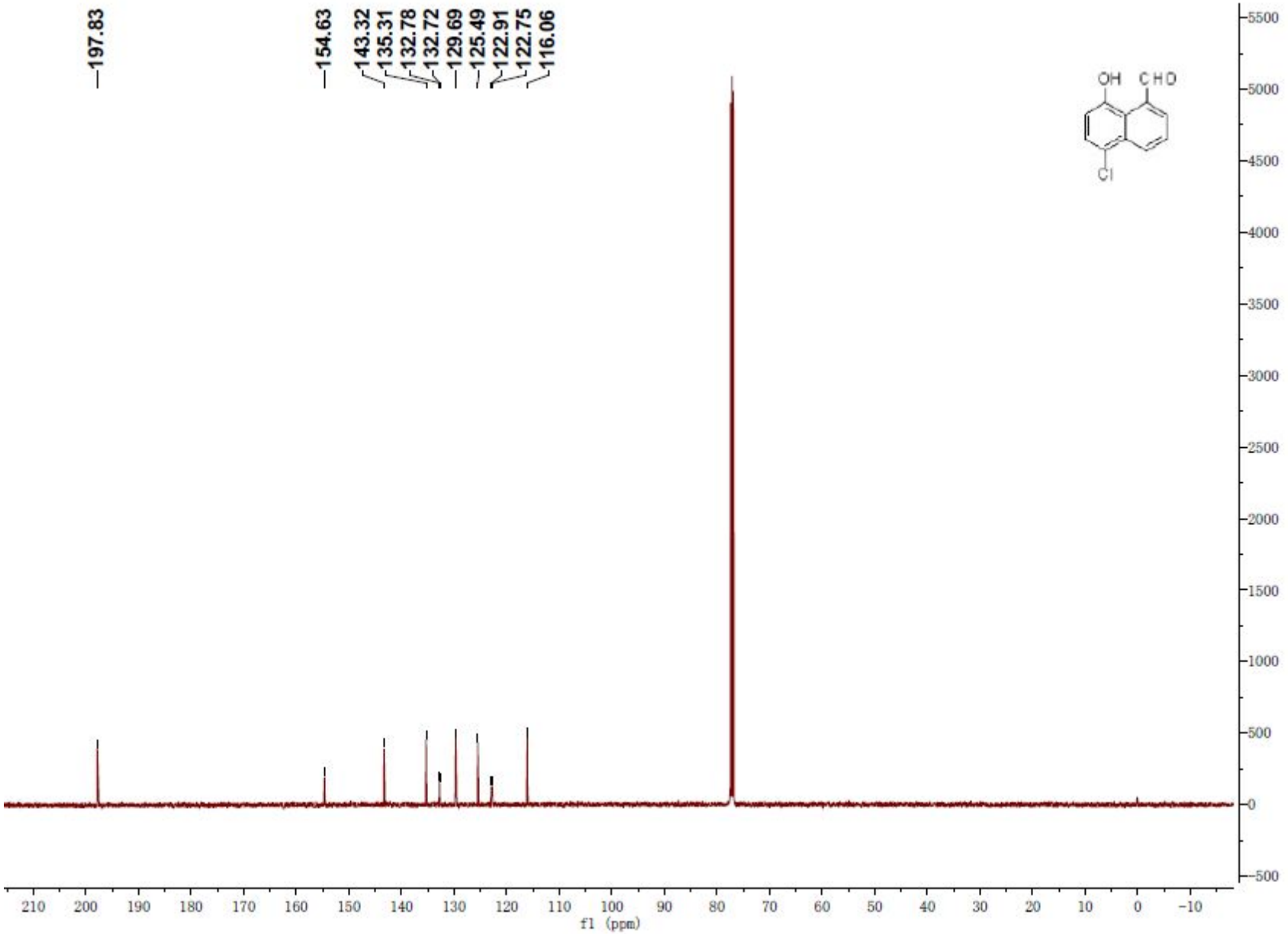
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-chloro-8-hydroxy-1-naphthaldehyde (2c)



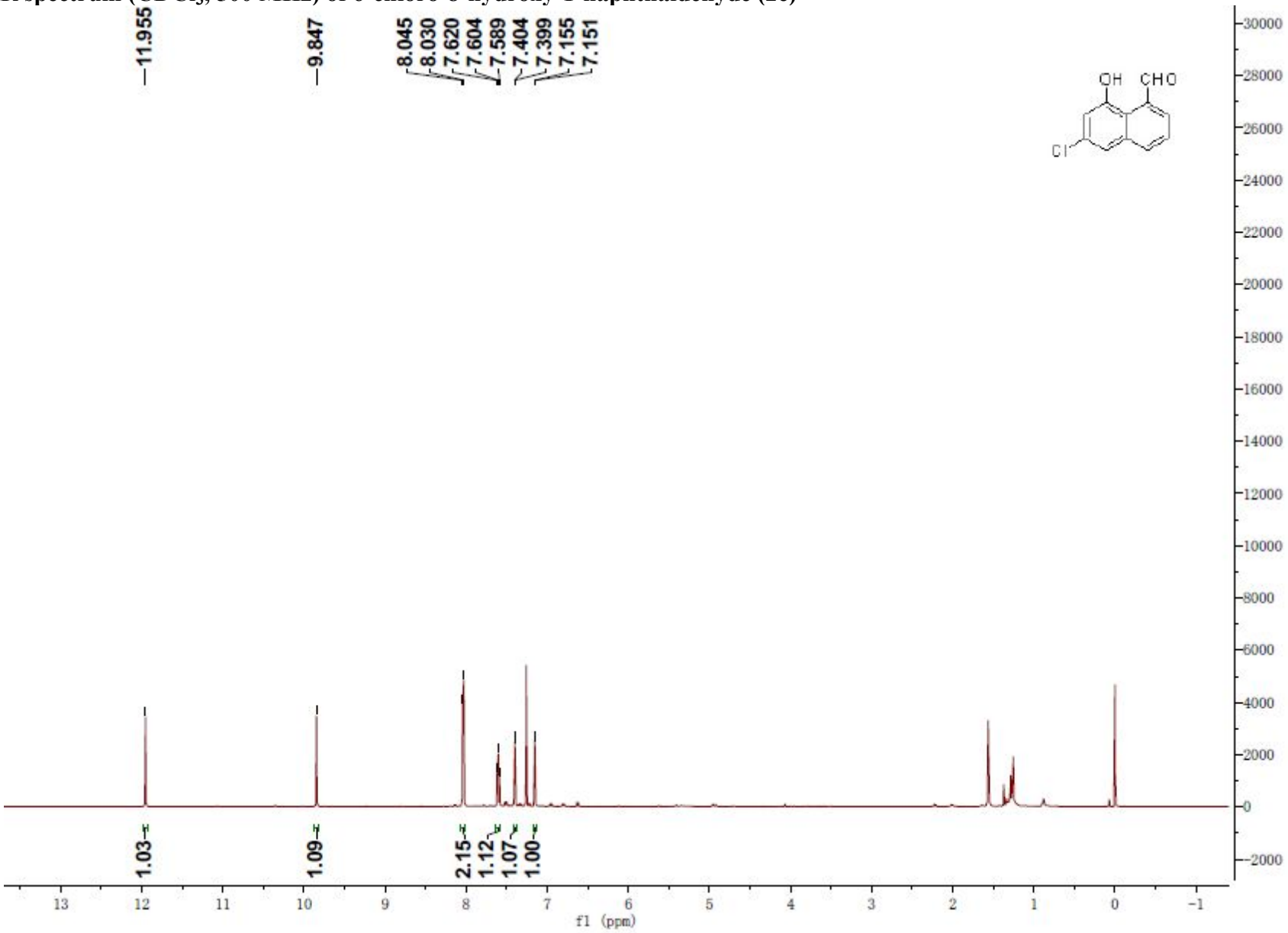
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-chloro-8-hydroxy-1-naphthaldehyde (2d)



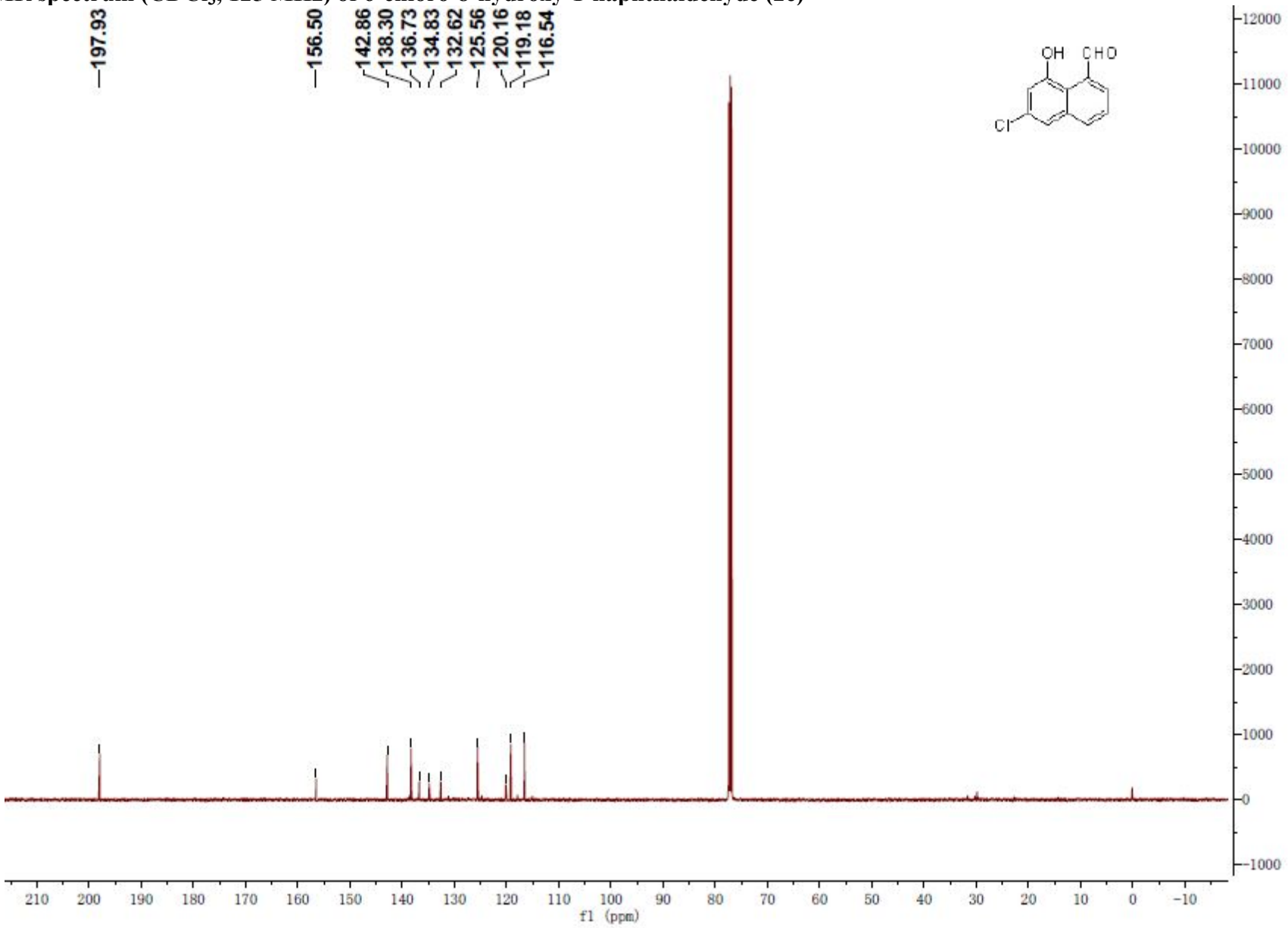
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-chloro-8-hydroxy-1-naphthaldehyde (2d)



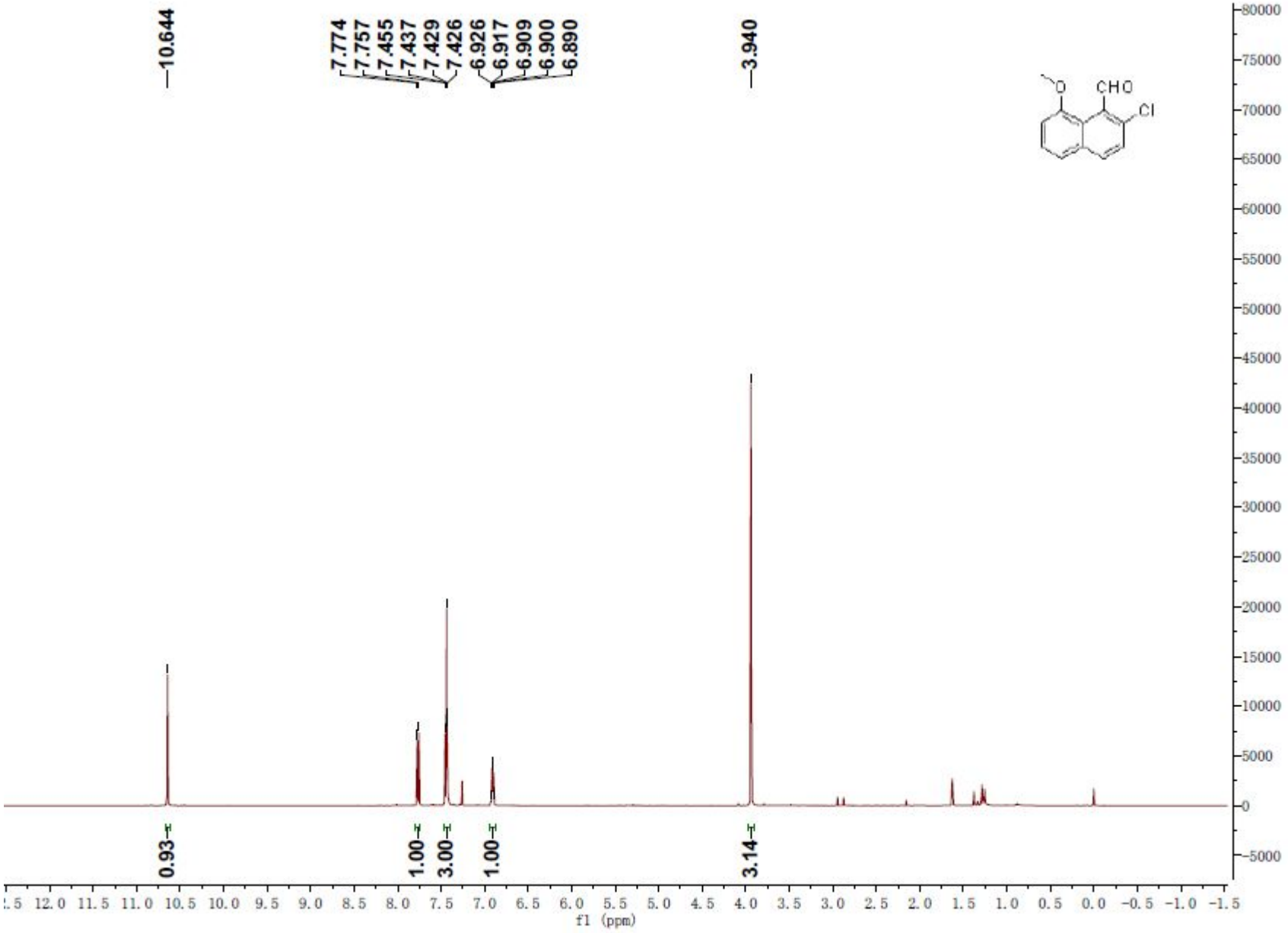
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 6-chloro-8-hydroxy-1-naphthaldehyde (2e)



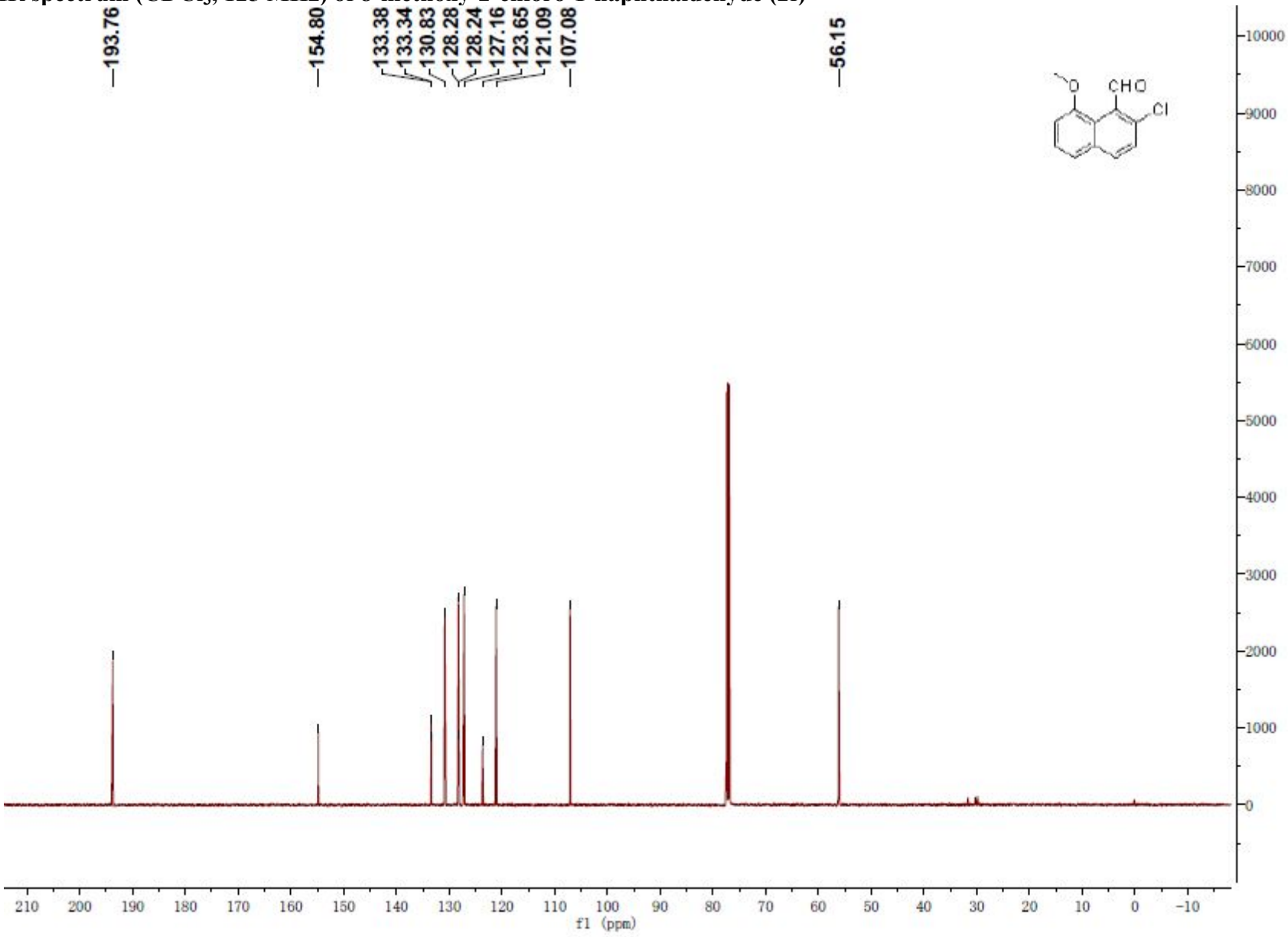
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 6-chloro-8-hydroxy-1-naphthaldehyde (2e)



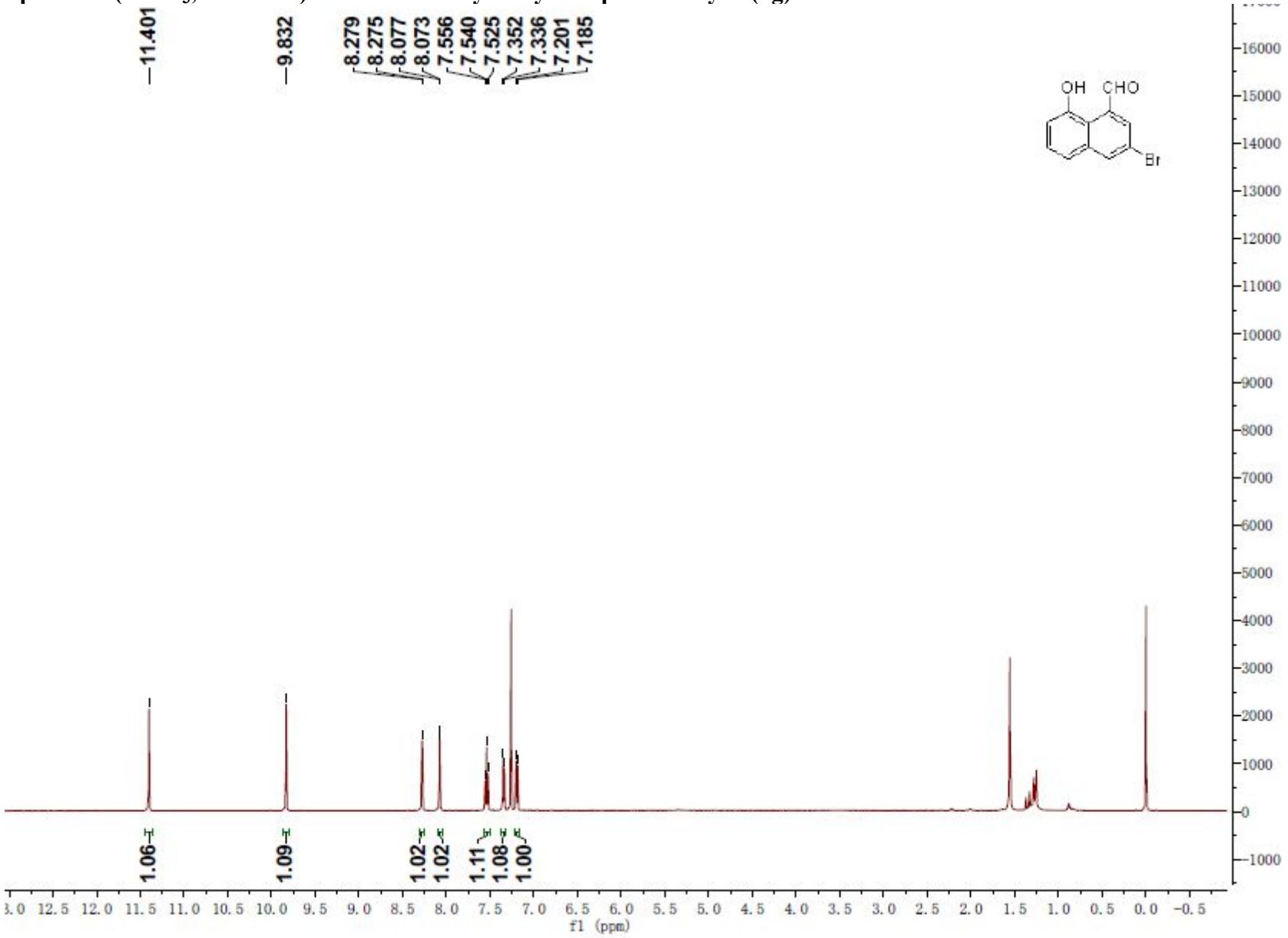
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 8-methoxy-2-chloro-1-naphthaldehyde (2f)



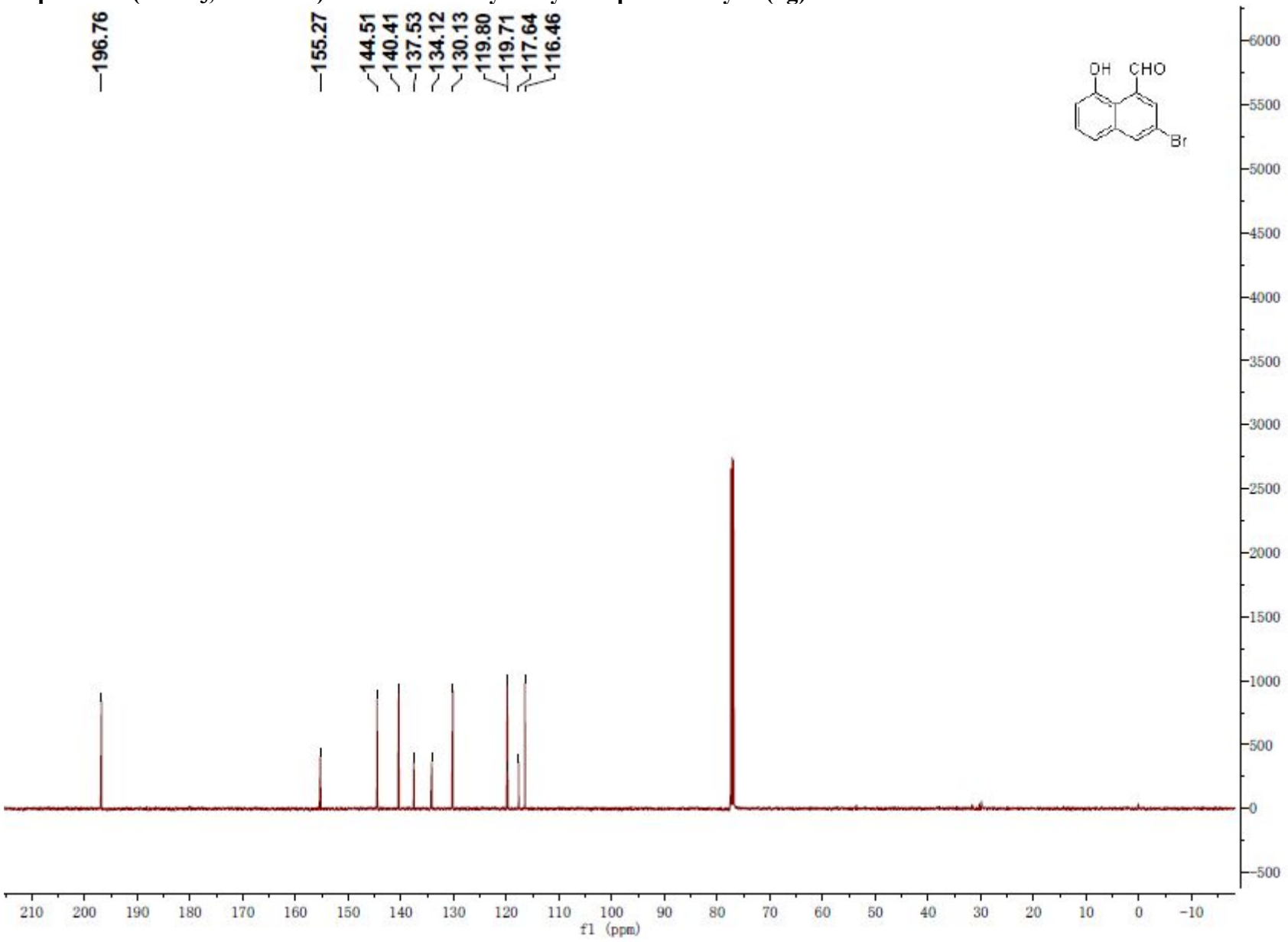
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 8-methoxy-2-chloro-1-naphthaldehyde (2f)



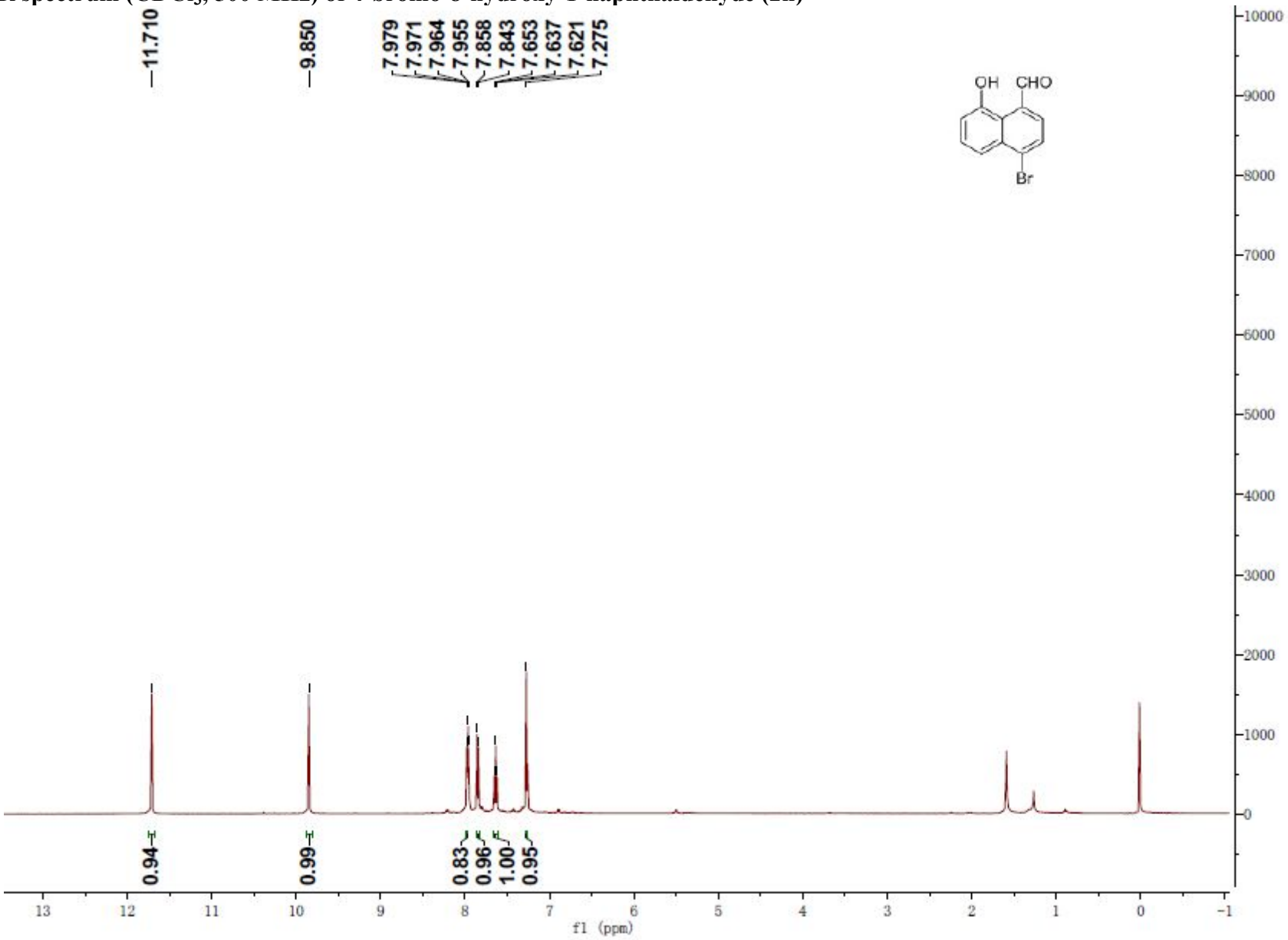
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3-bromo-8-hydroxy-1-naphthaldehyde (2g)



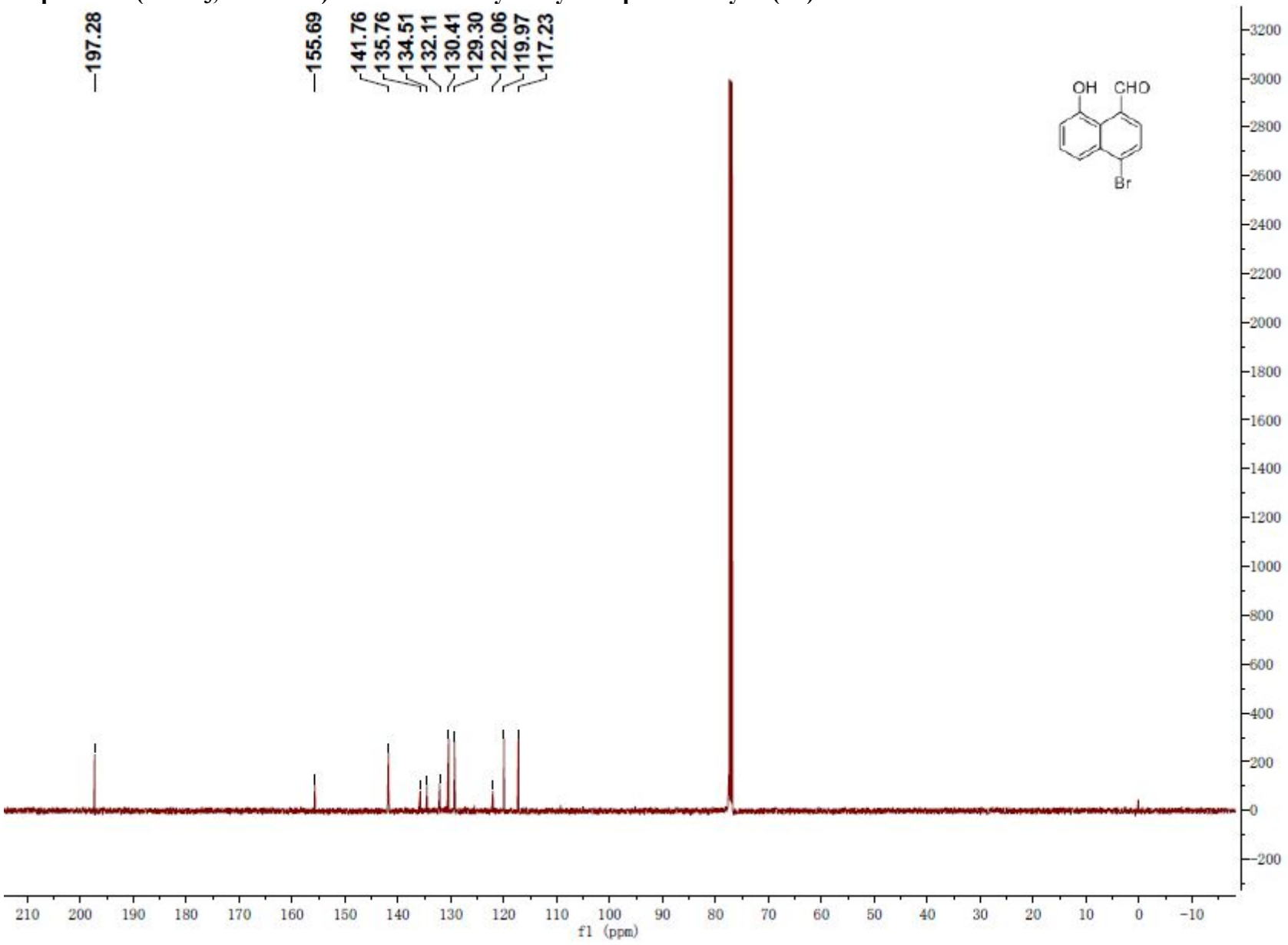
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 3-bromo-8-hydroxy-1-naphthaldehyde (2g)



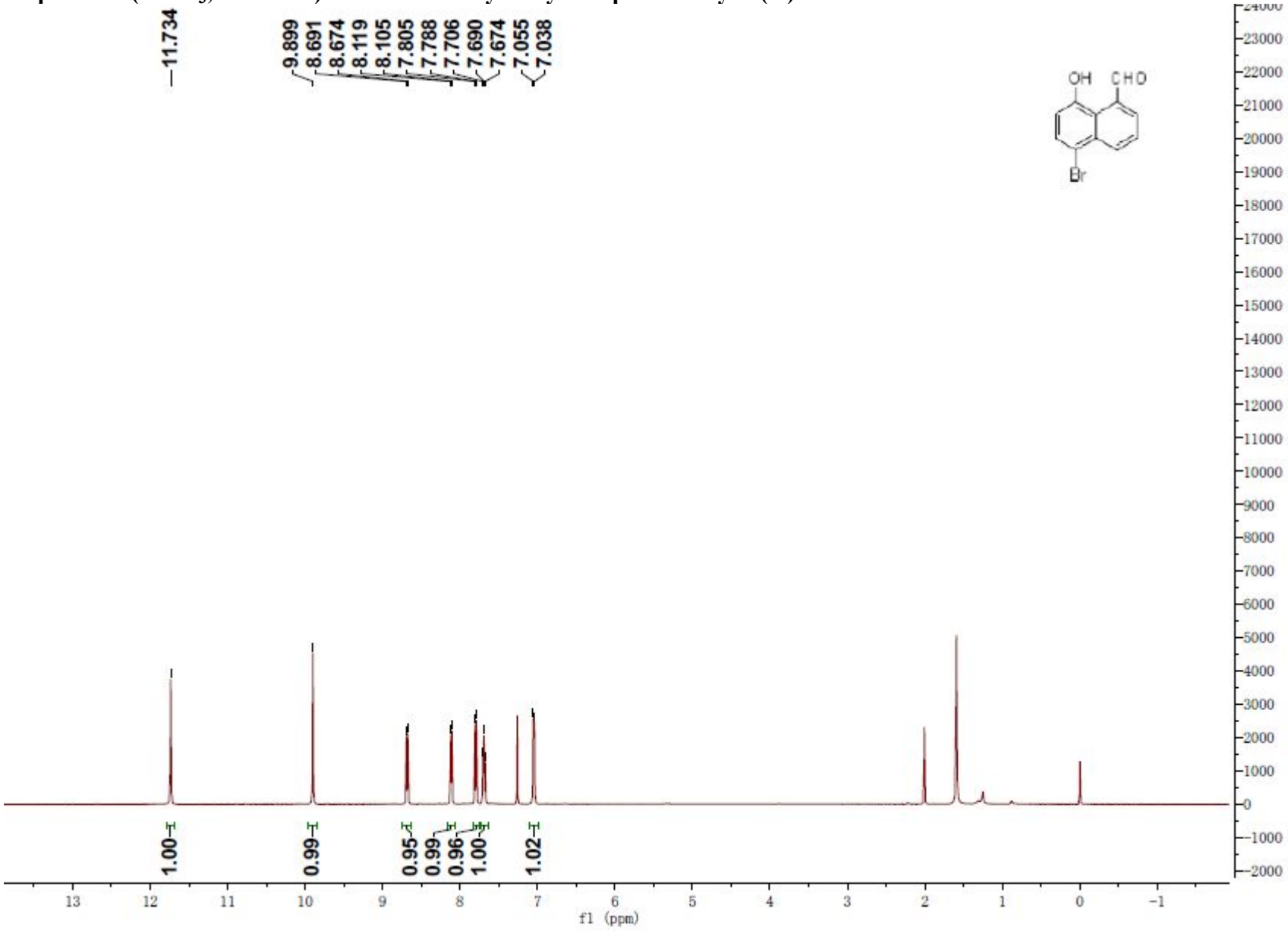
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-bromo-8-hydroxy-1-naphthaldehyde (2h)



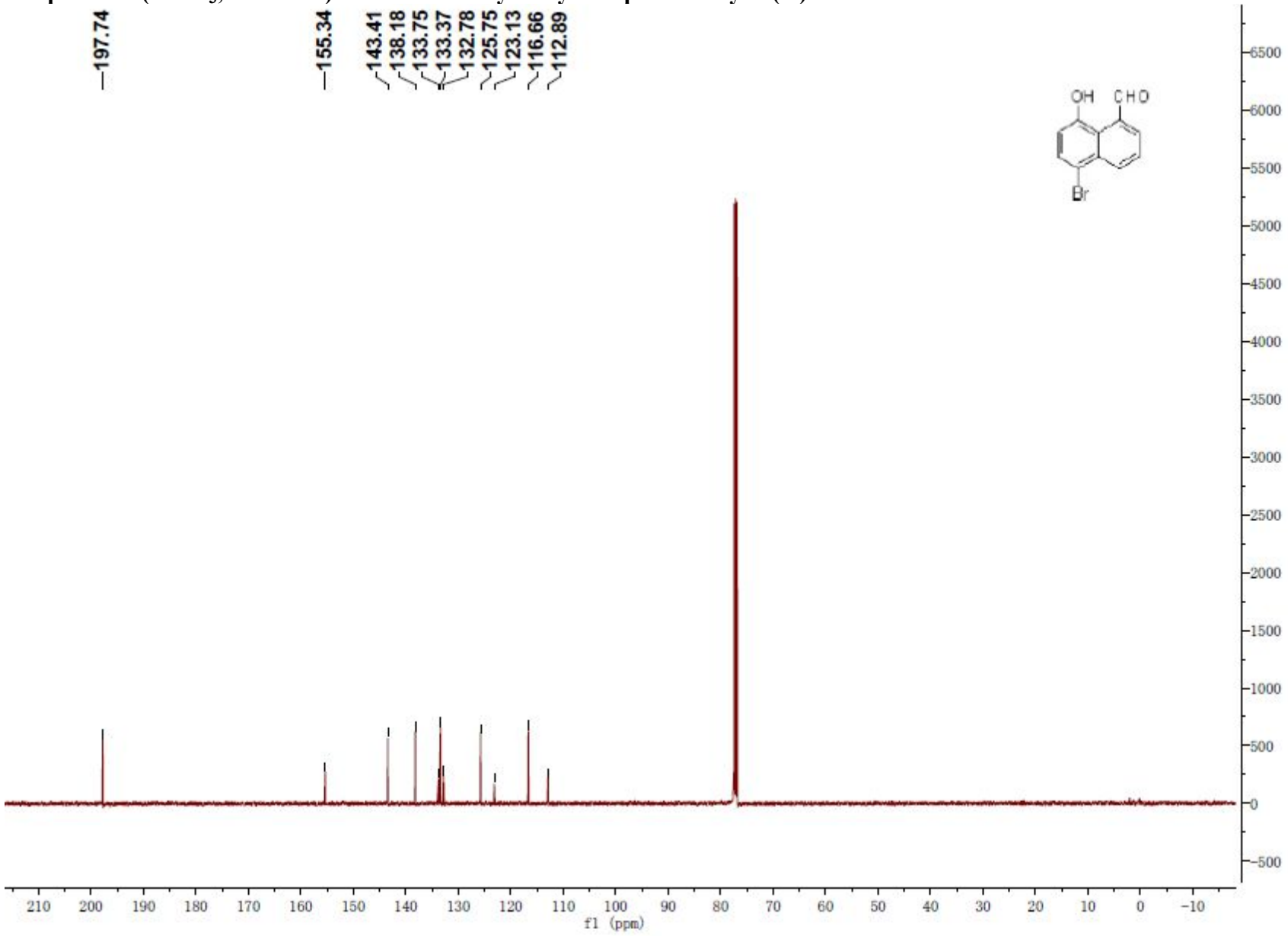
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-bromo-8-hydroxy-1-naphthaldehyde (2h)



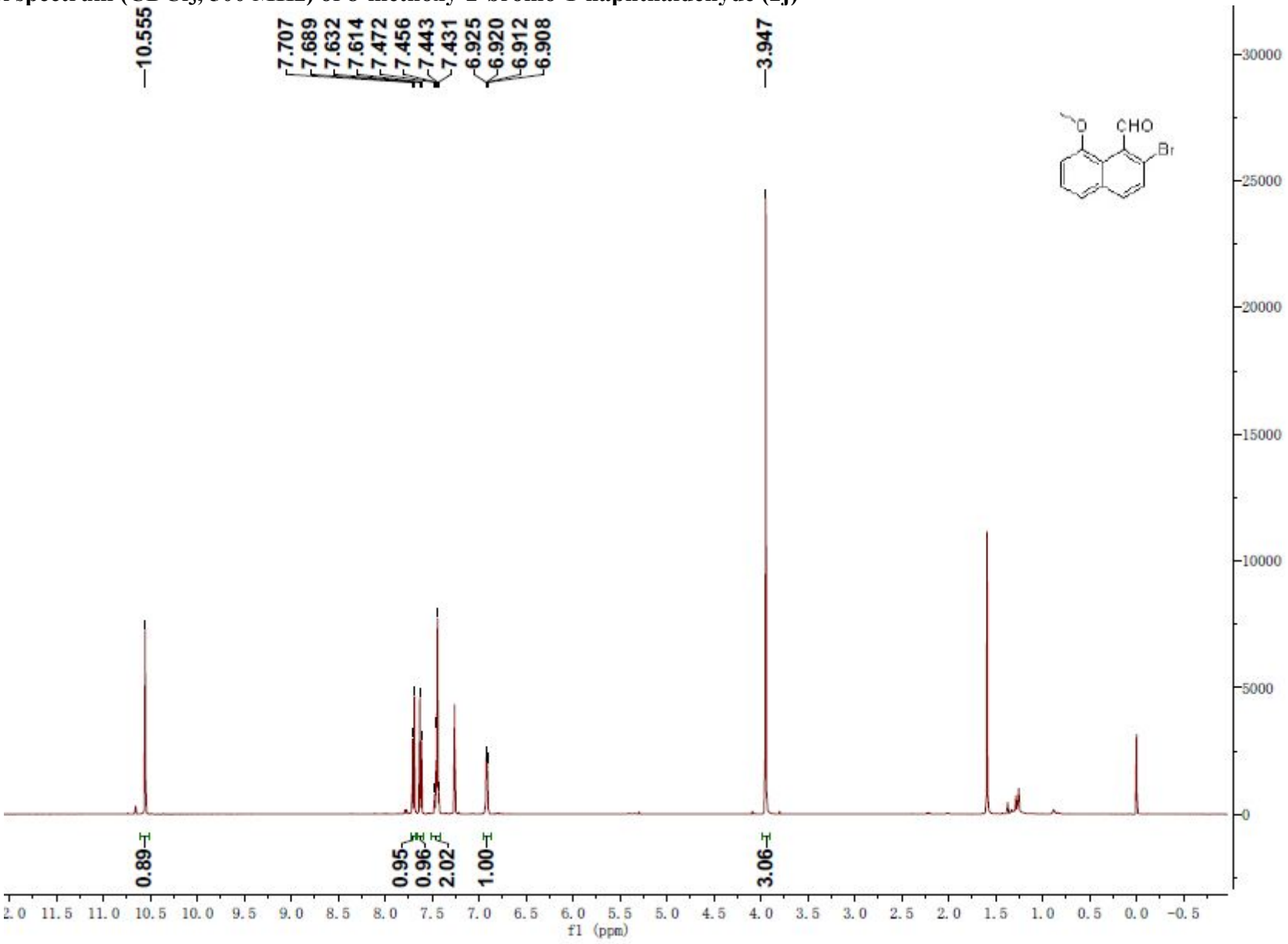
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-bromo-8-hydroxy-1-naphthaldehyde (2i)



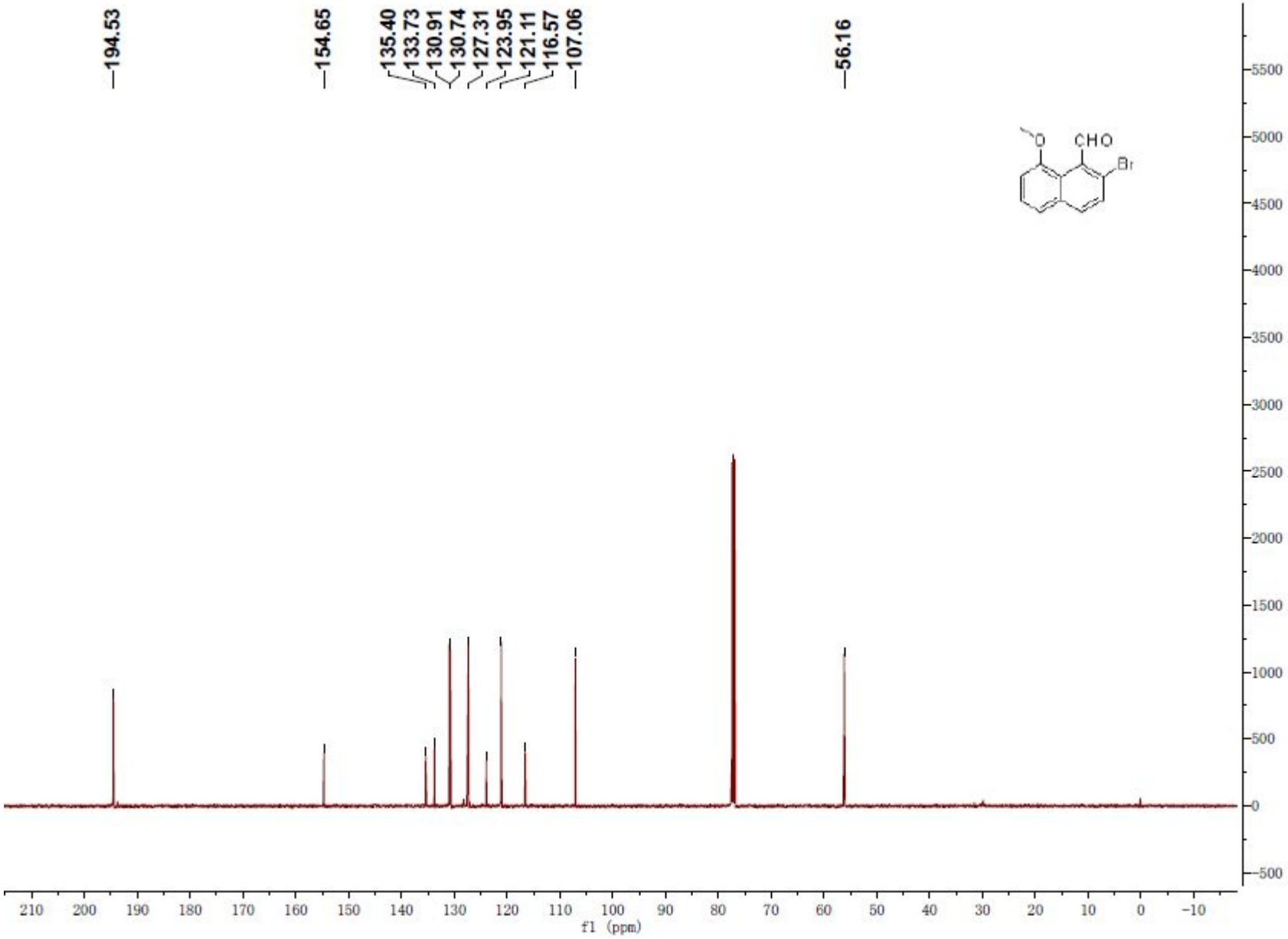
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-bromo-8-hydroxy-1-naphthaldehyde (2i)



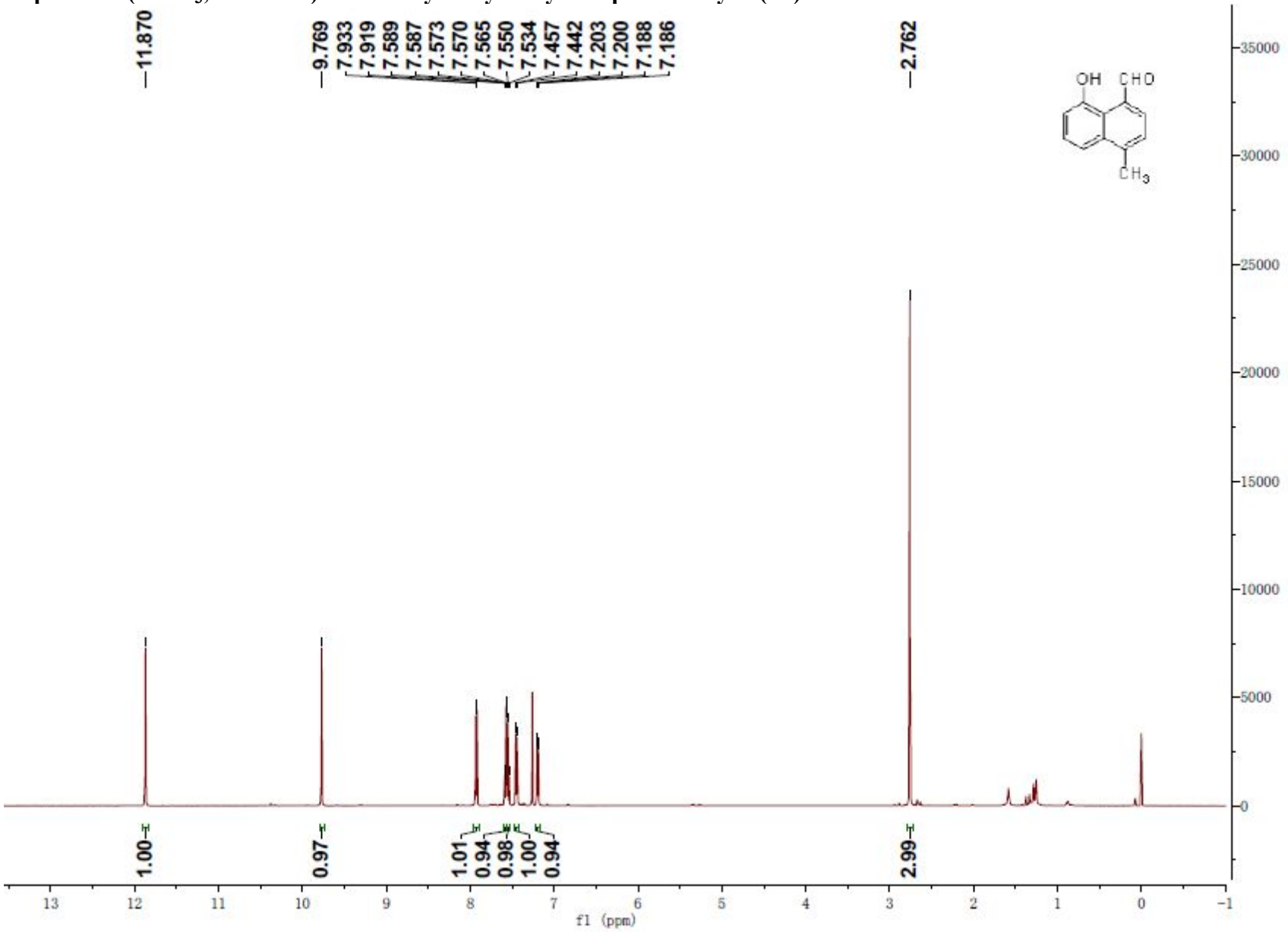
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 8-methoxy-2-bromo-1-naphthaldehyde (2j)



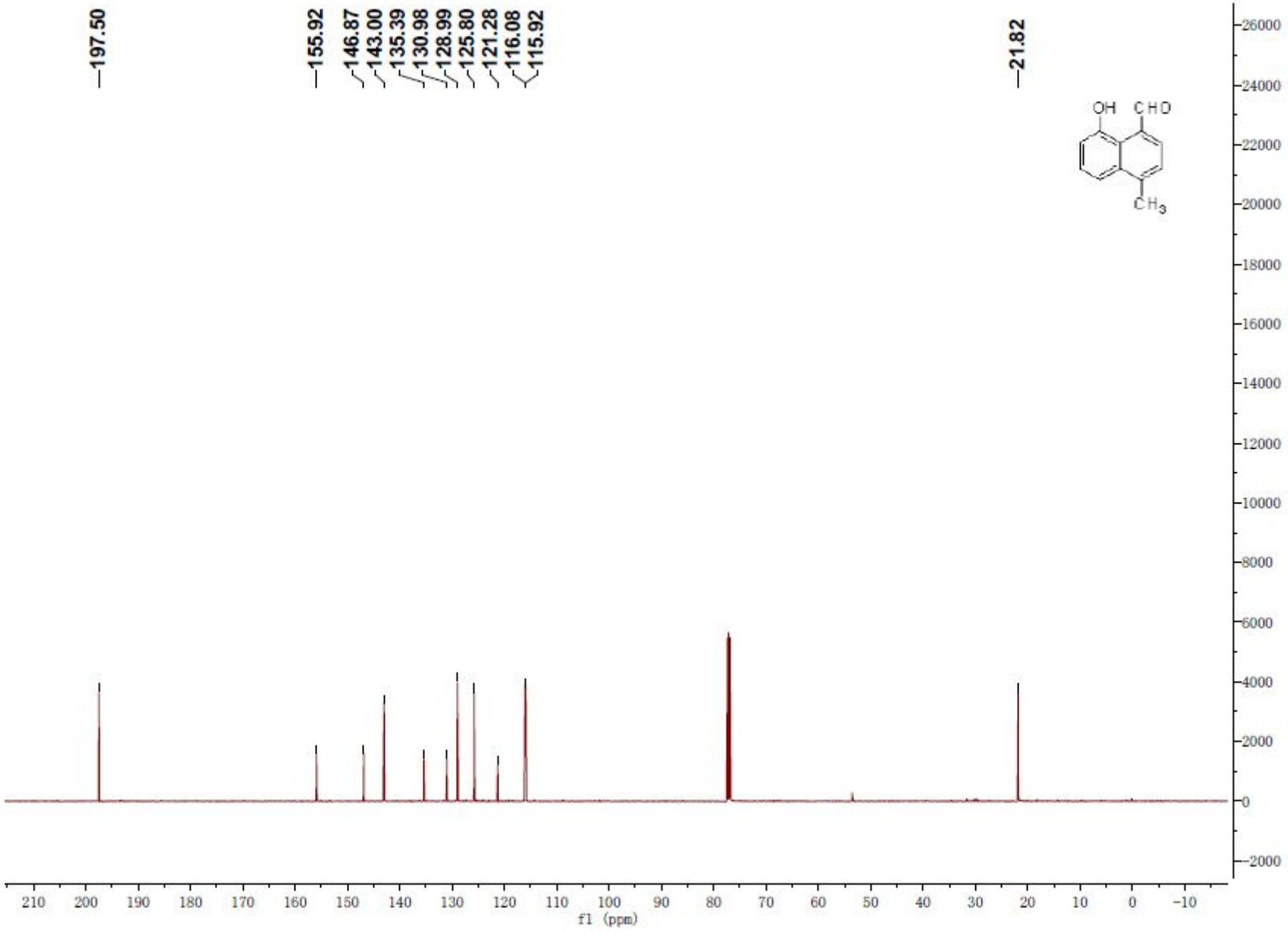
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 8-methoxy-2-bromo-1-naphthaldehyde (2j)



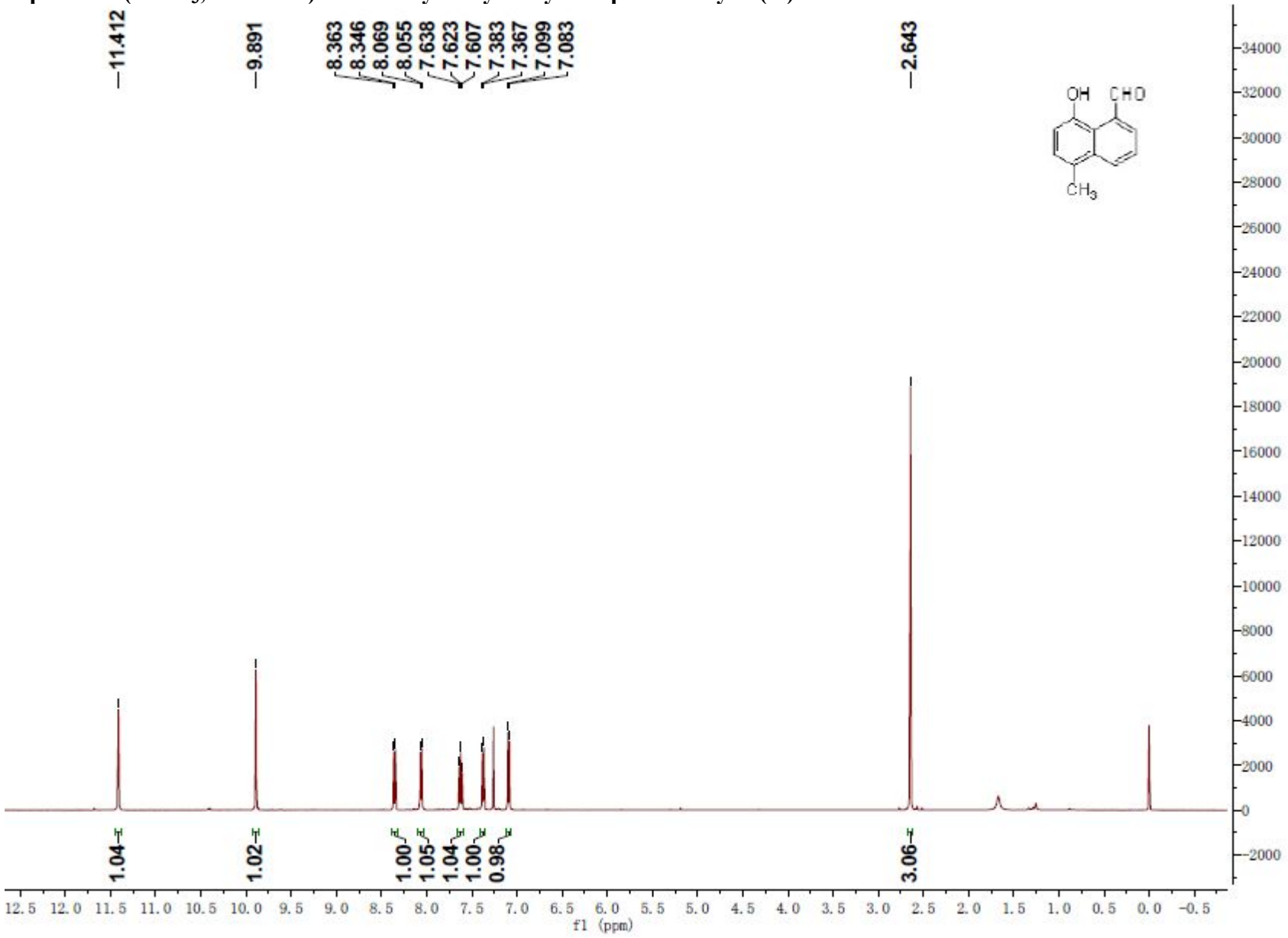
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-methyl-8-hydroxy-1-naphthaldehyde (2k)



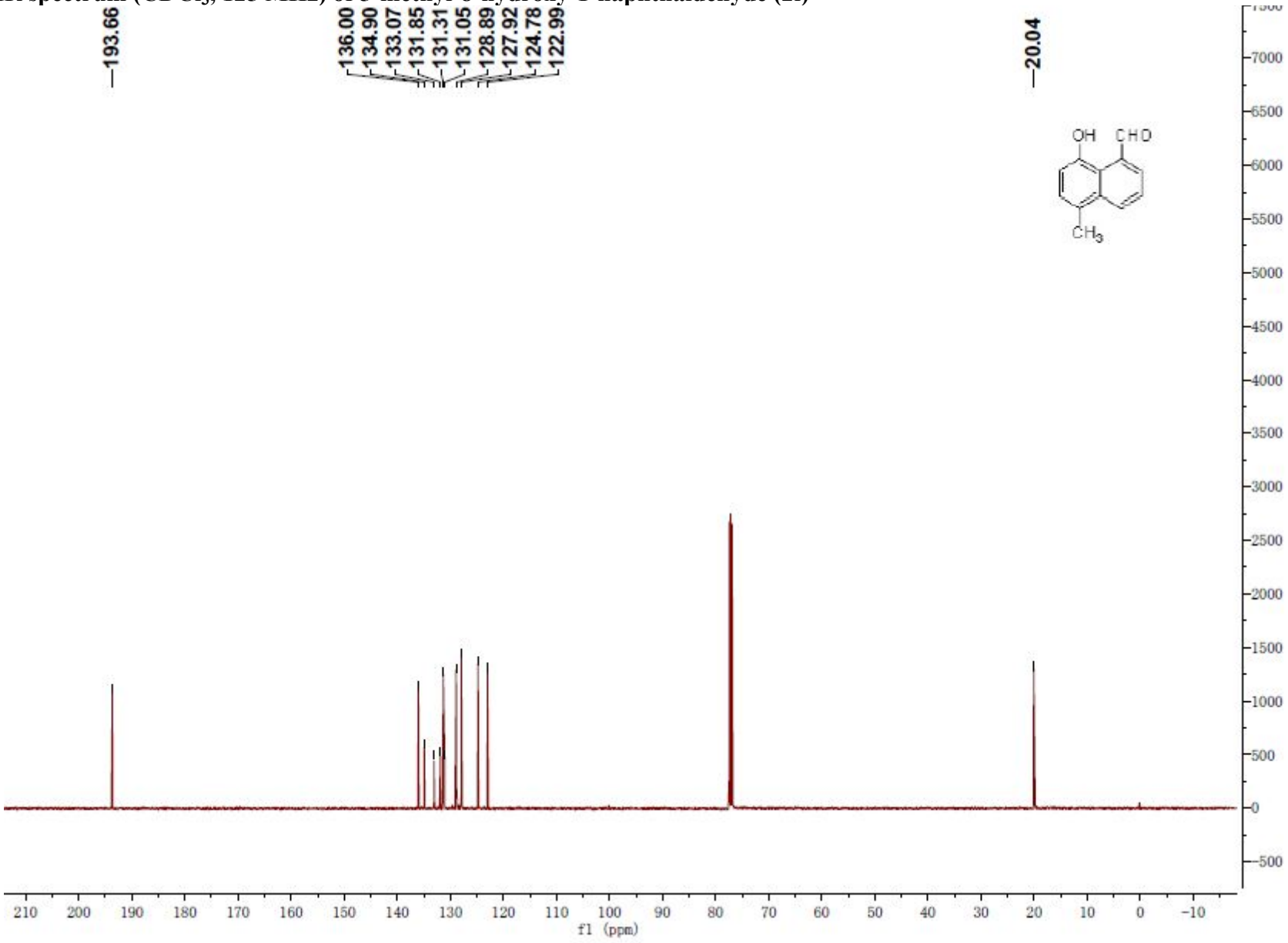
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-methyl-8-hydroxy-1-naphthaldehyde (2k)



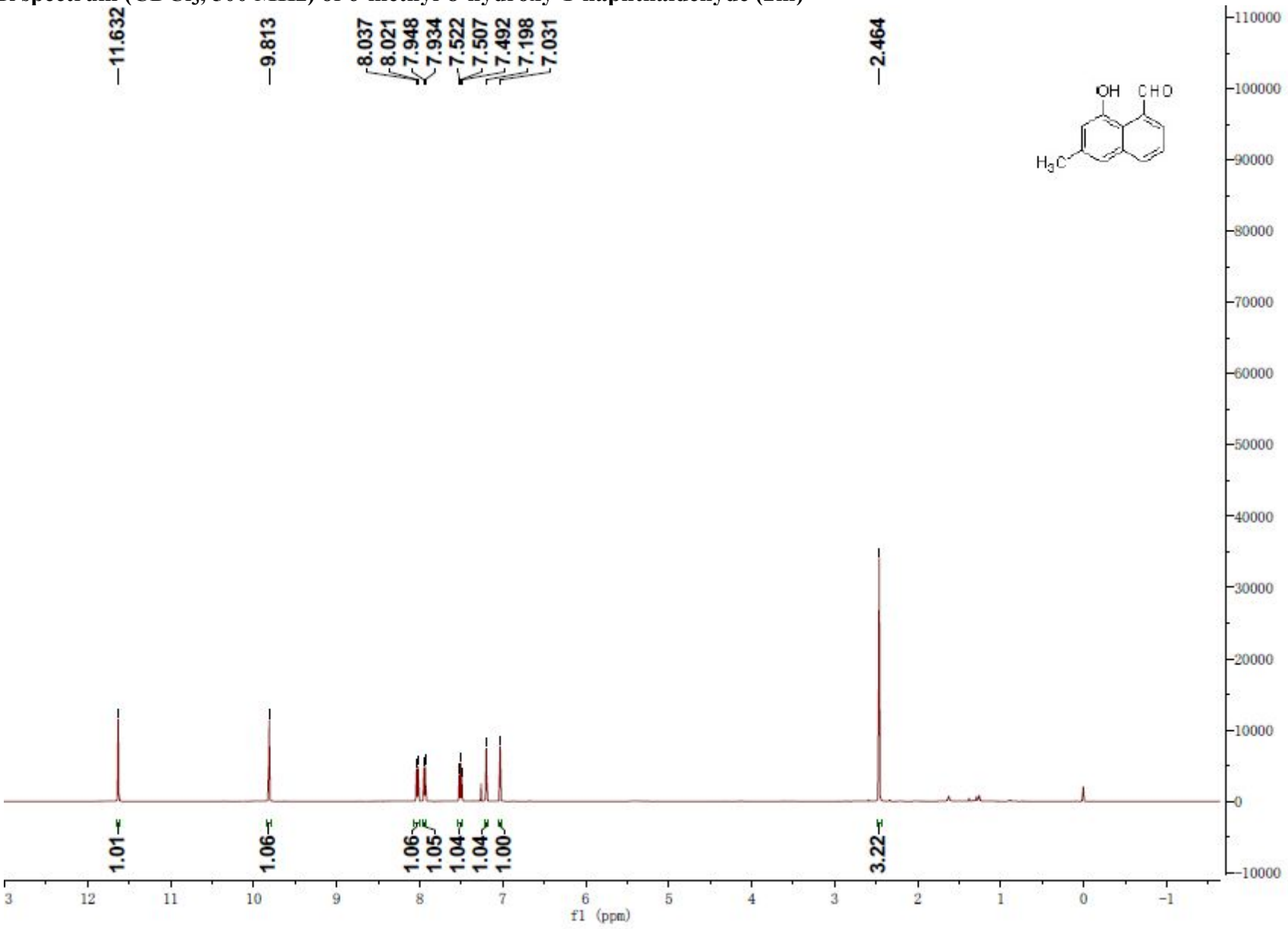
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-methyl-8-hydroxy-1-naphthaldehyde (2l)



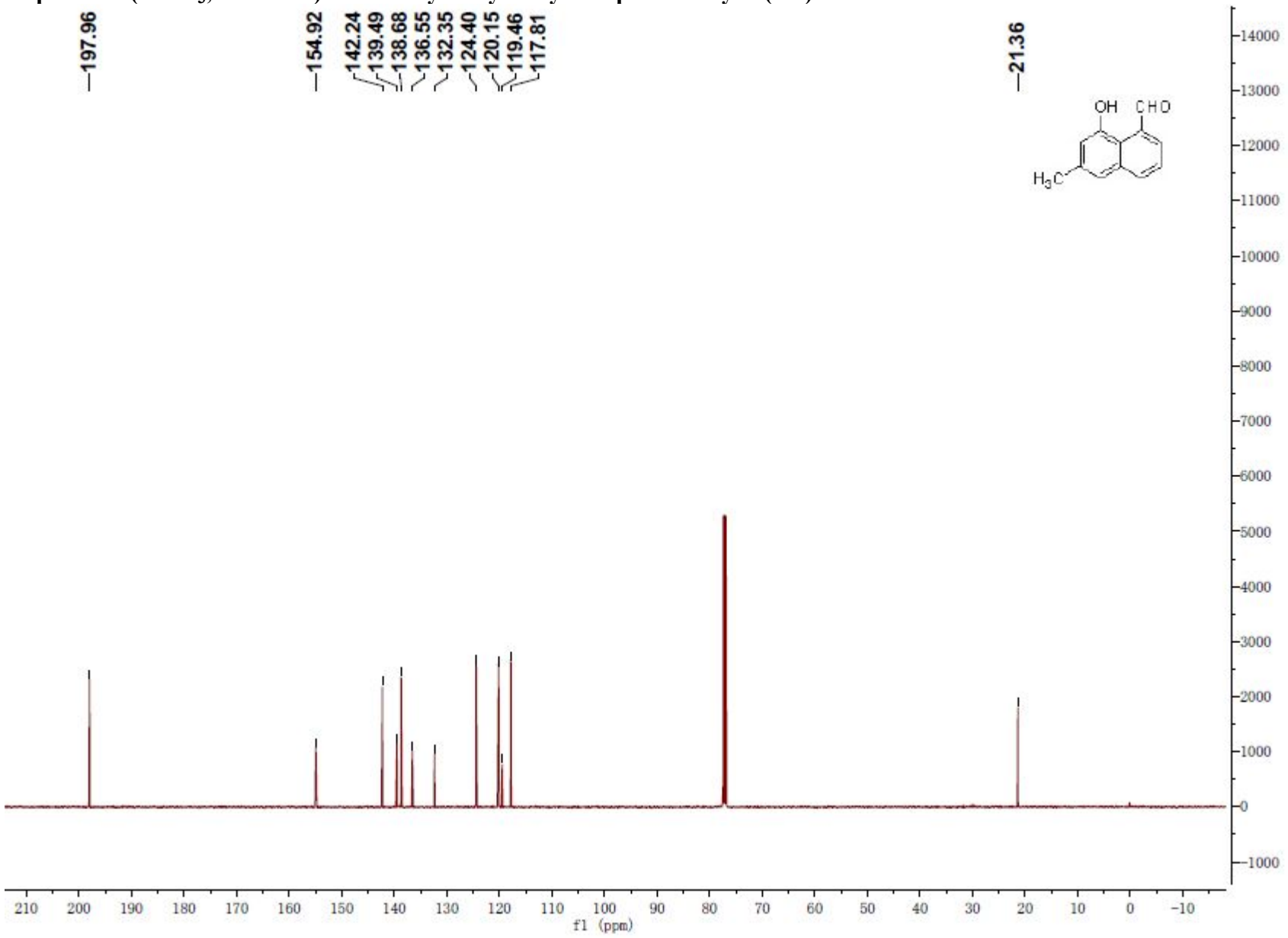
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-methyl-8-hydroxy-1-naphthaldehyde (2l)



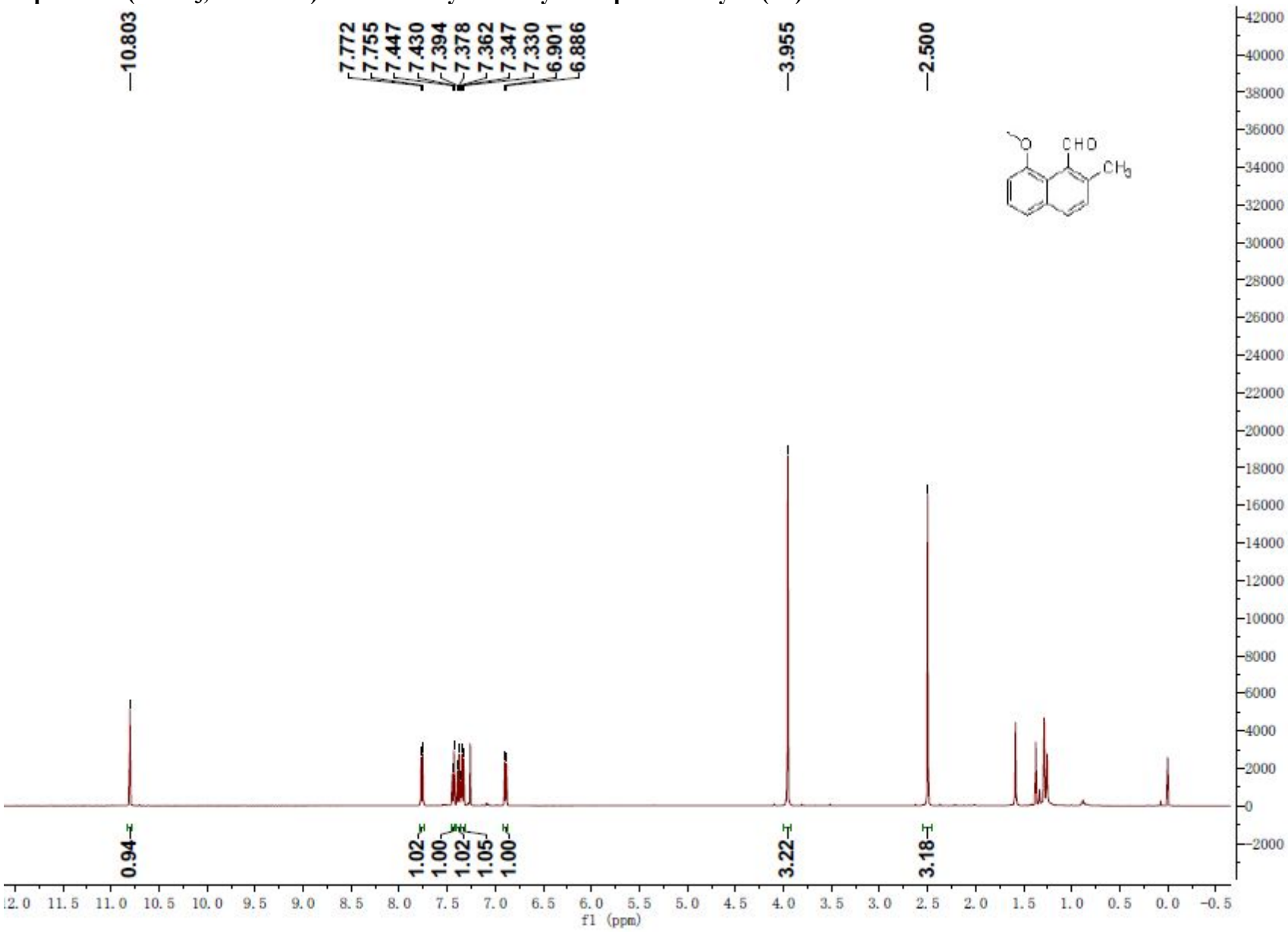
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 6-methyl-8-hydroxy-1-naphthaldehyde (2m)



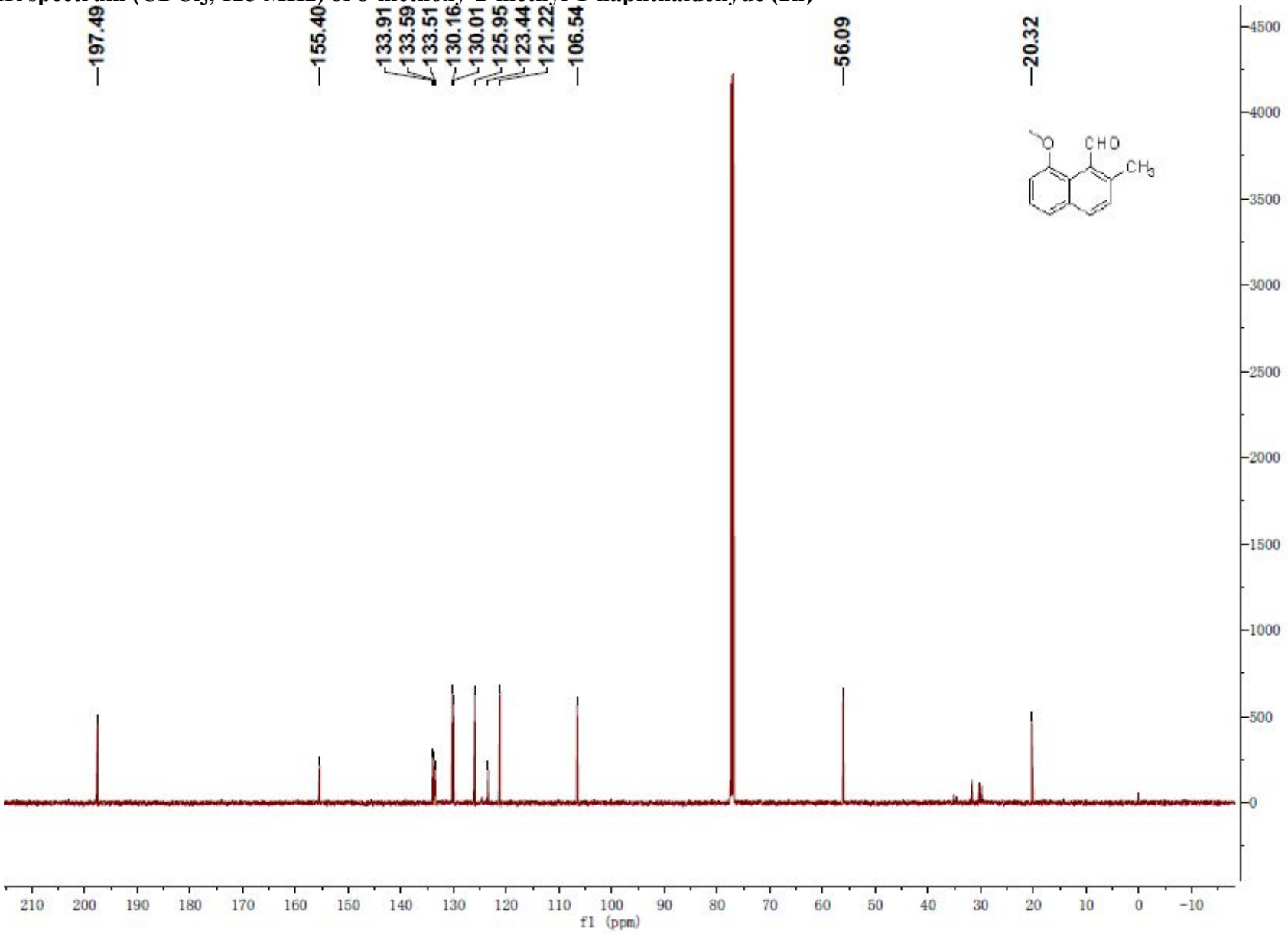
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 6-methyl-8-hydroxy-1-naphthaldehyde (2m)



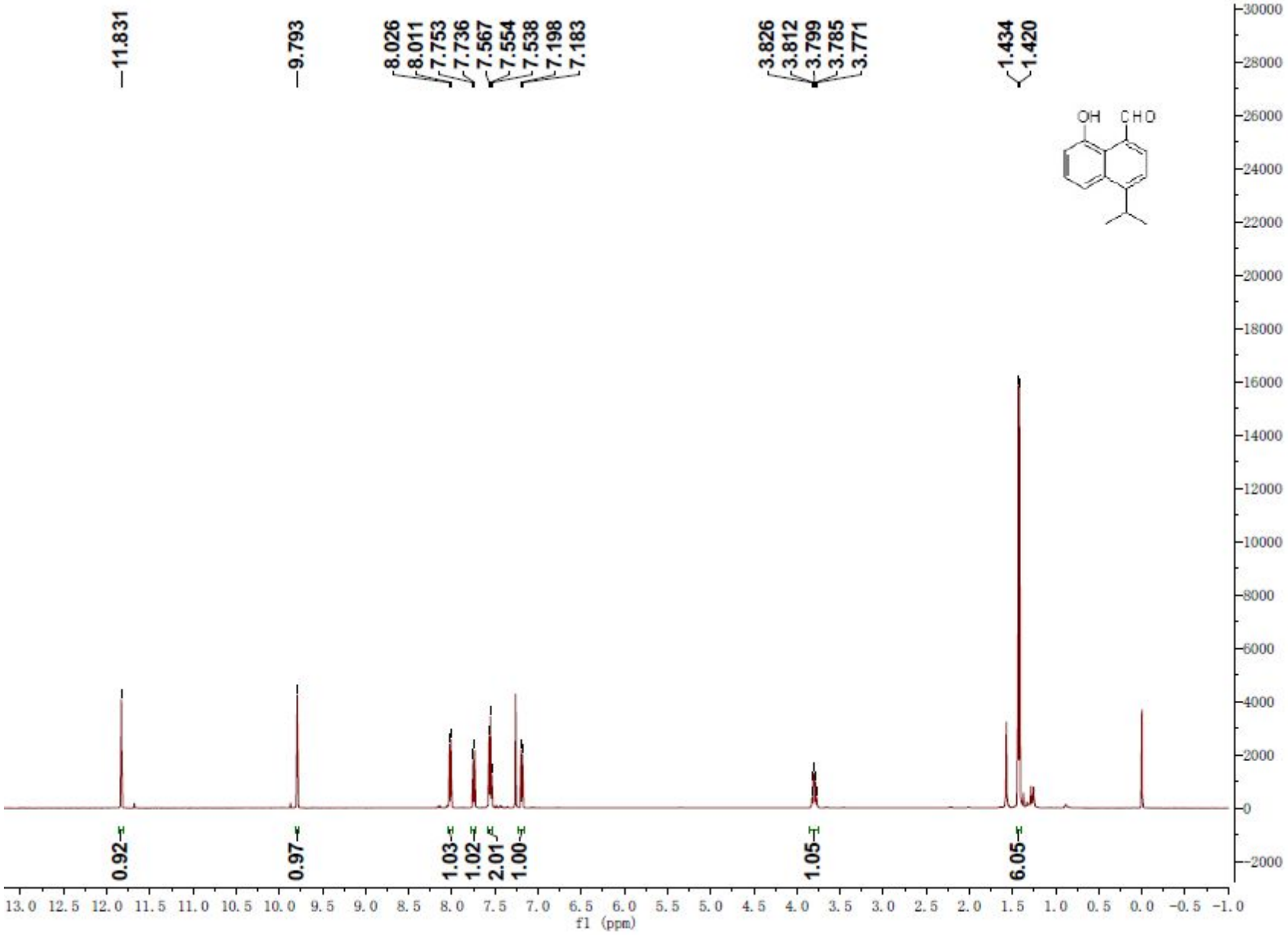
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 8-methoxy-2-methyl-1-naphthaldehyde (2n)



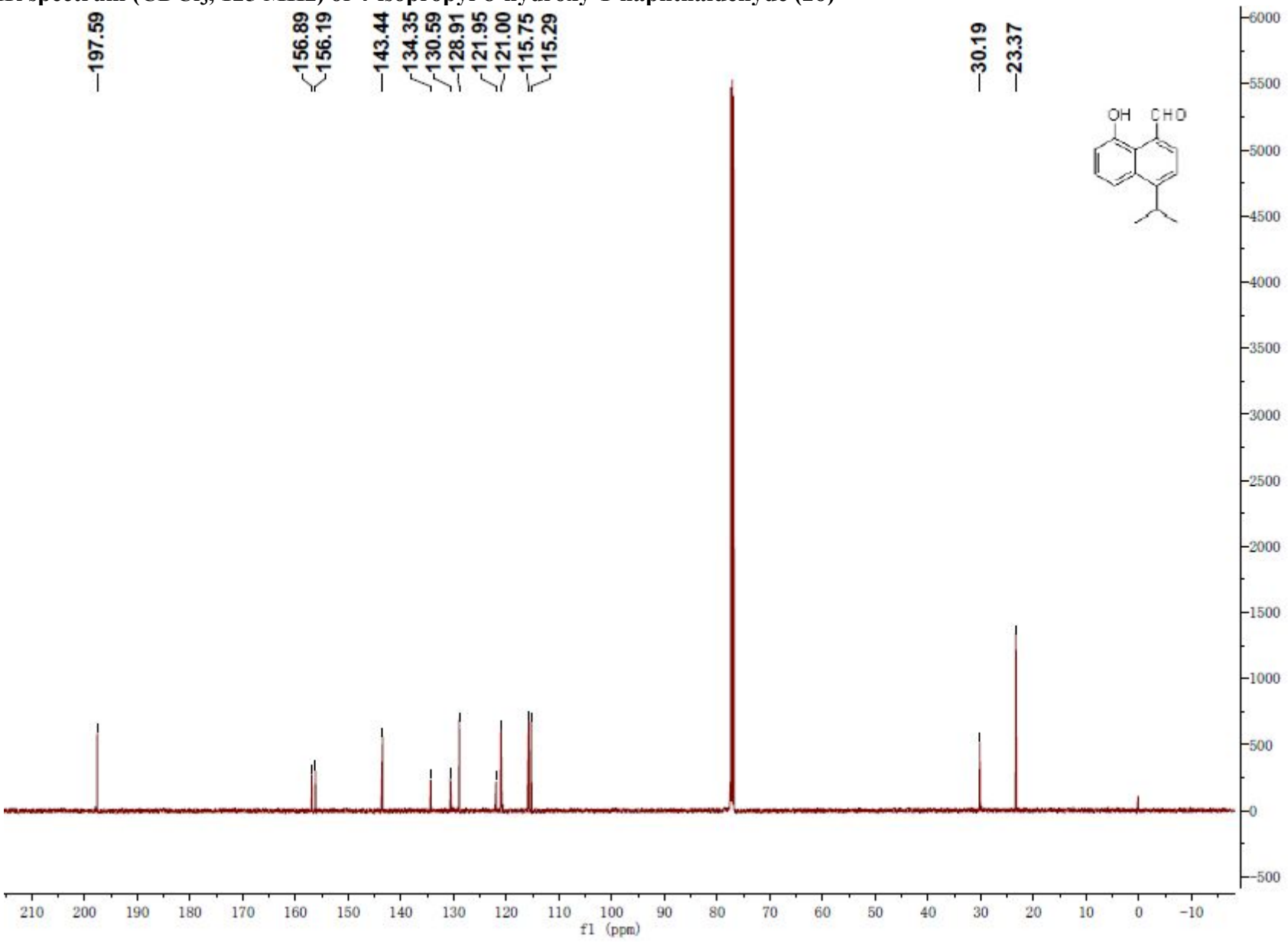
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 8-methoxy-2-methyl-1-naphthaldehyde (2n)



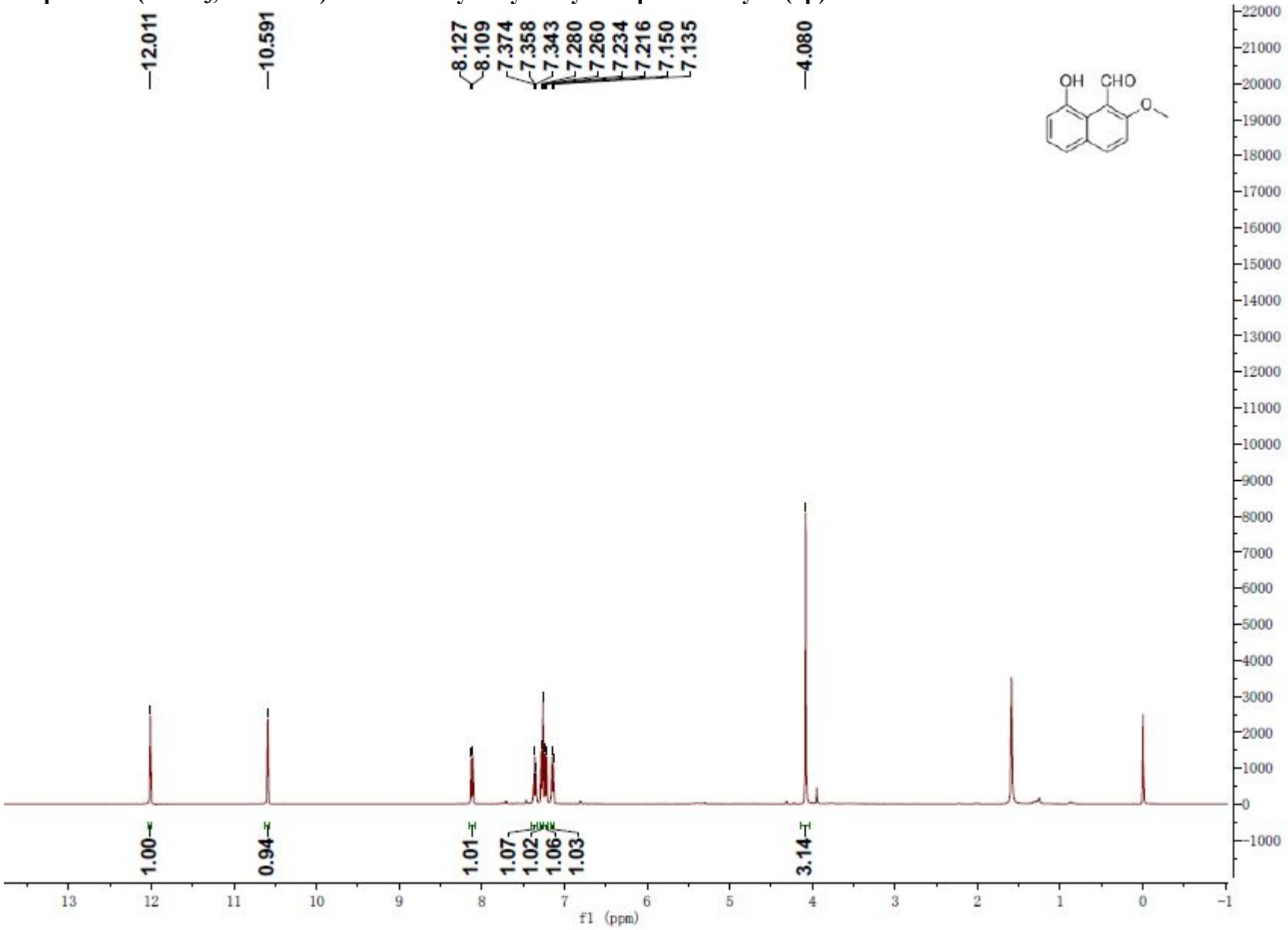
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-isopropyl-8-hydroxy-1-naphthaldehyde (2o)



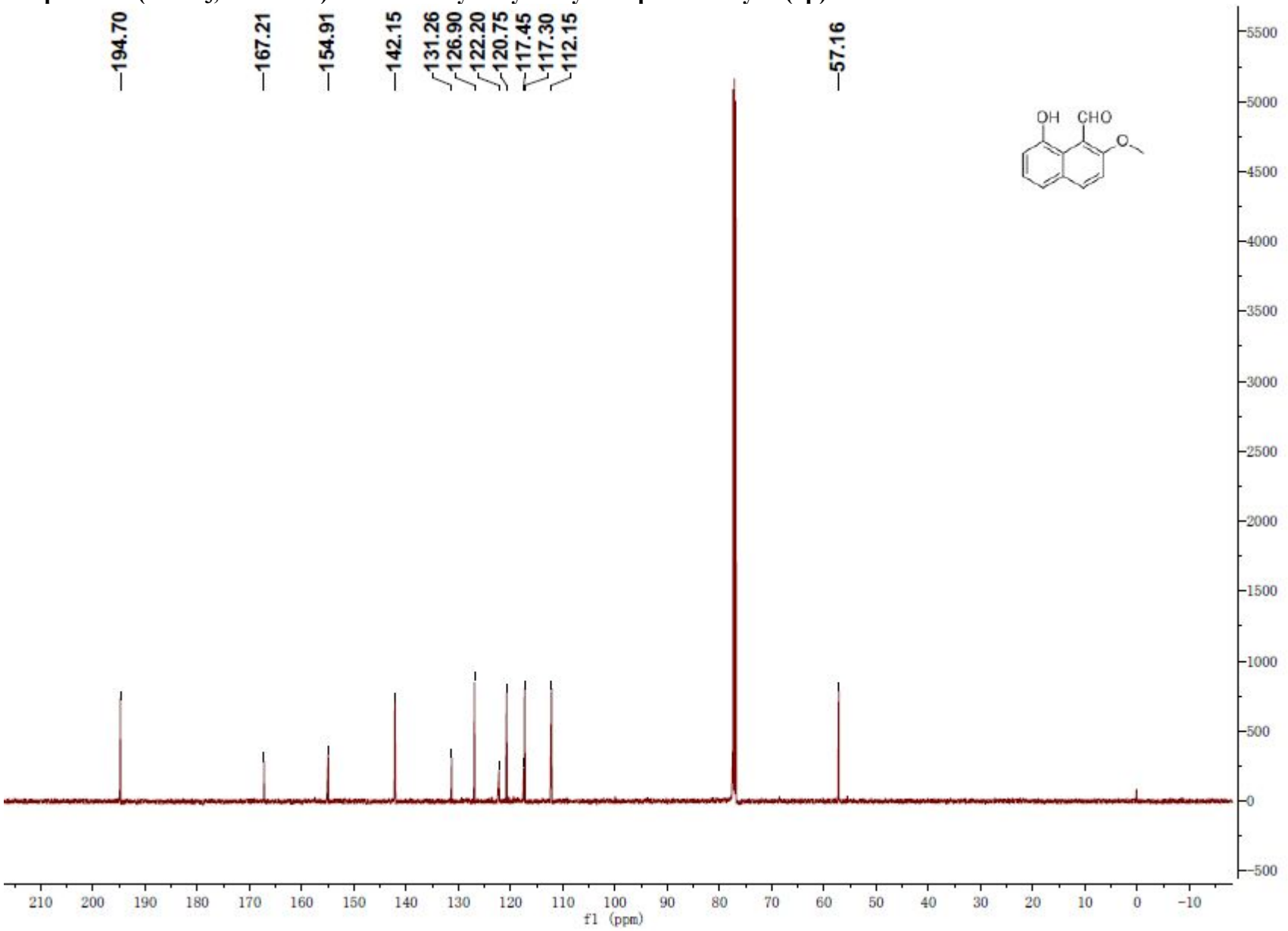
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-isopropyl-8-hydroxy-1-naphthaldehyde (2o)



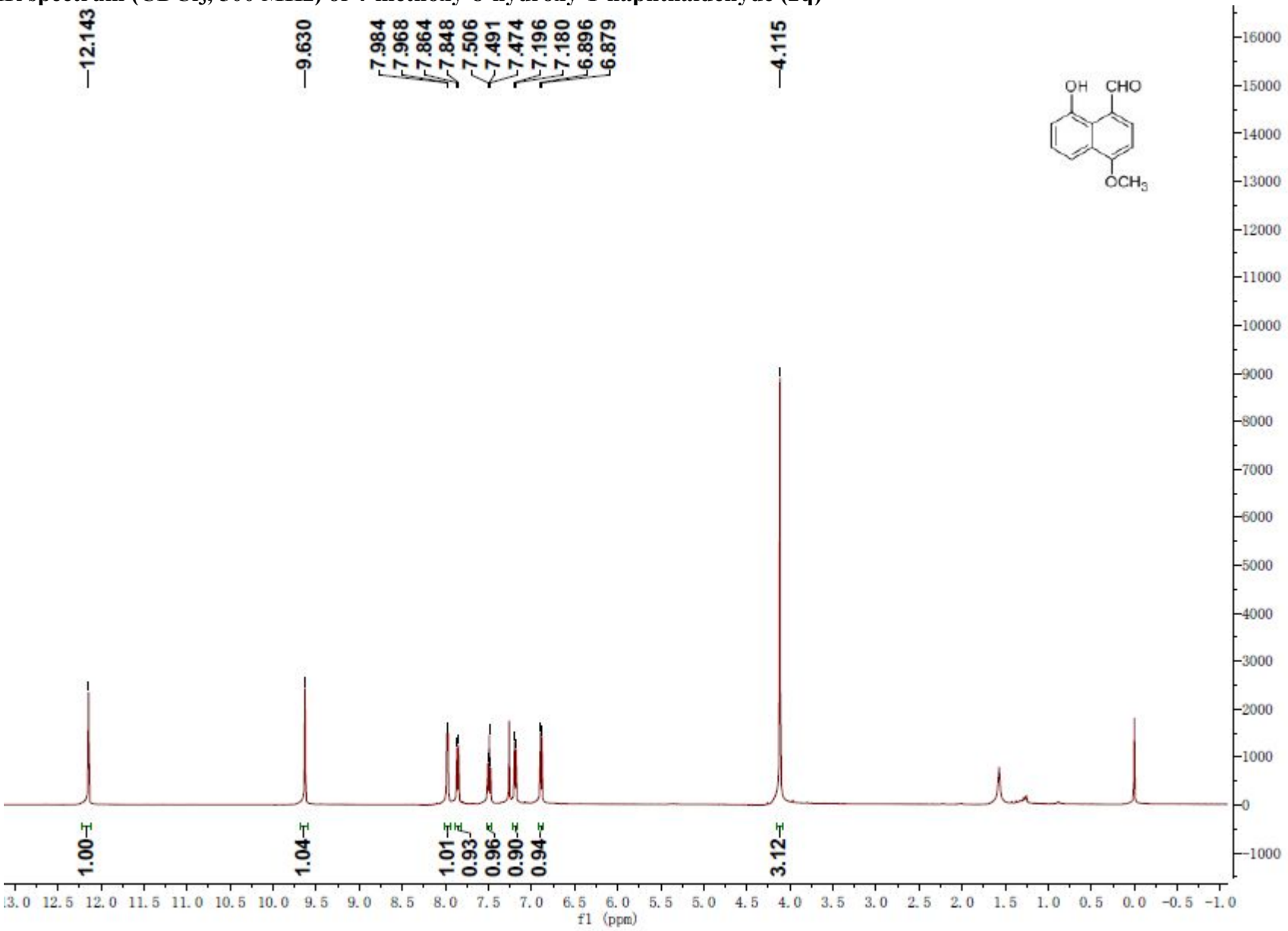
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2-methoxy-8-hydroxy-1-naphthaldehyde (2p)



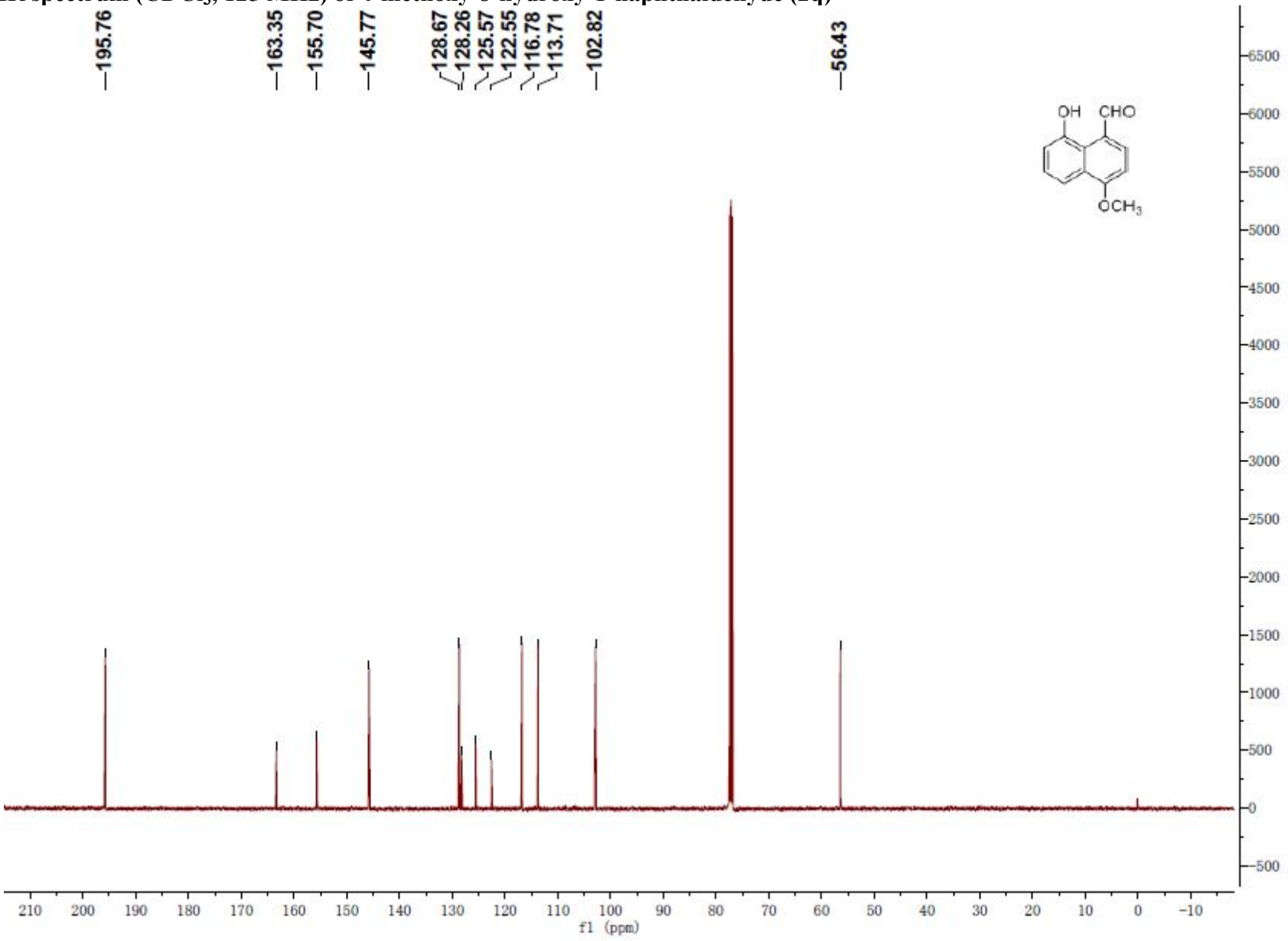
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 2-methoxy-8-hydroxy-1-naphthaldehyde (2p)



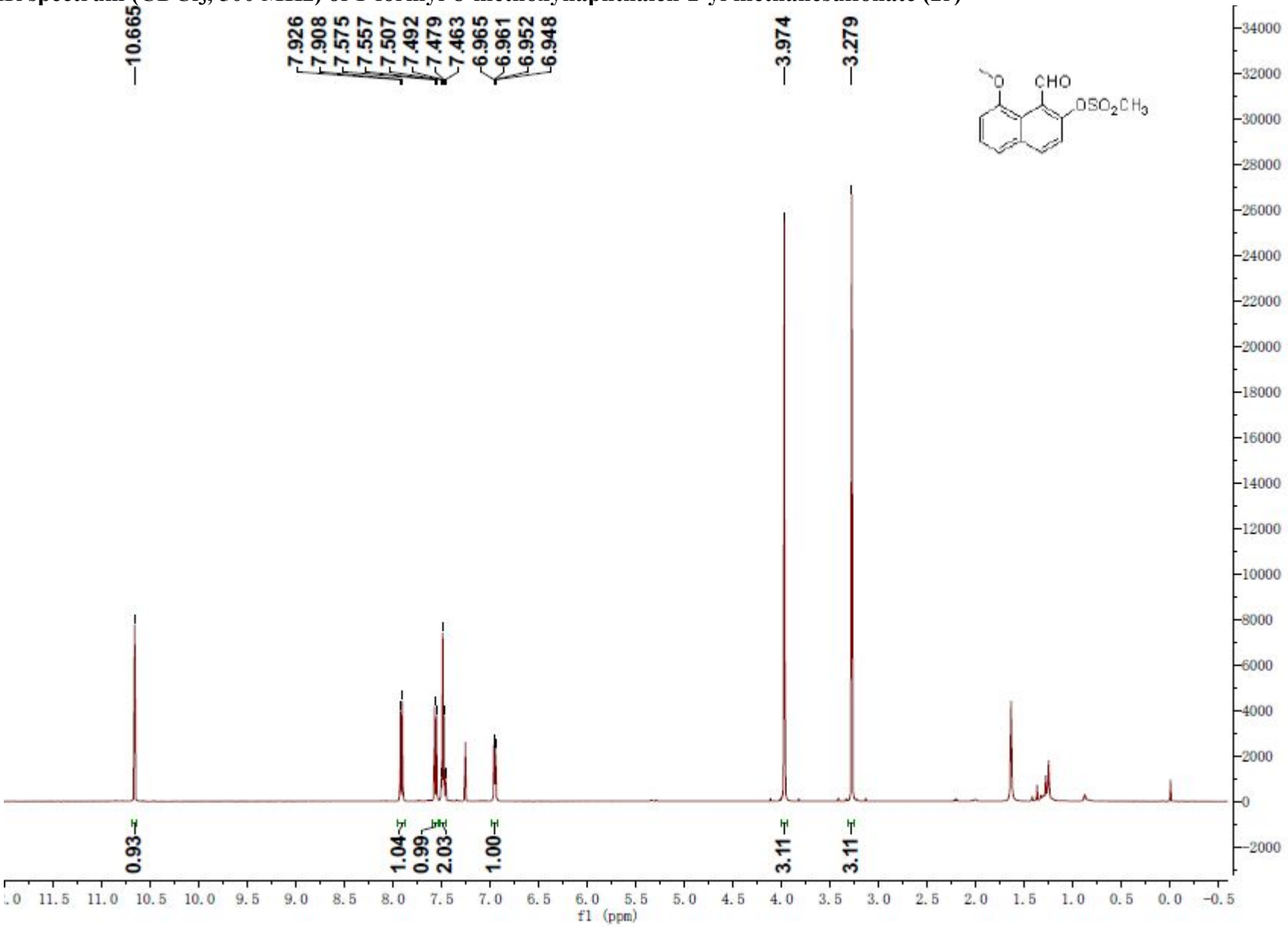
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-methoxy-8-hydroxy-1-naphthaldehyde (2q)



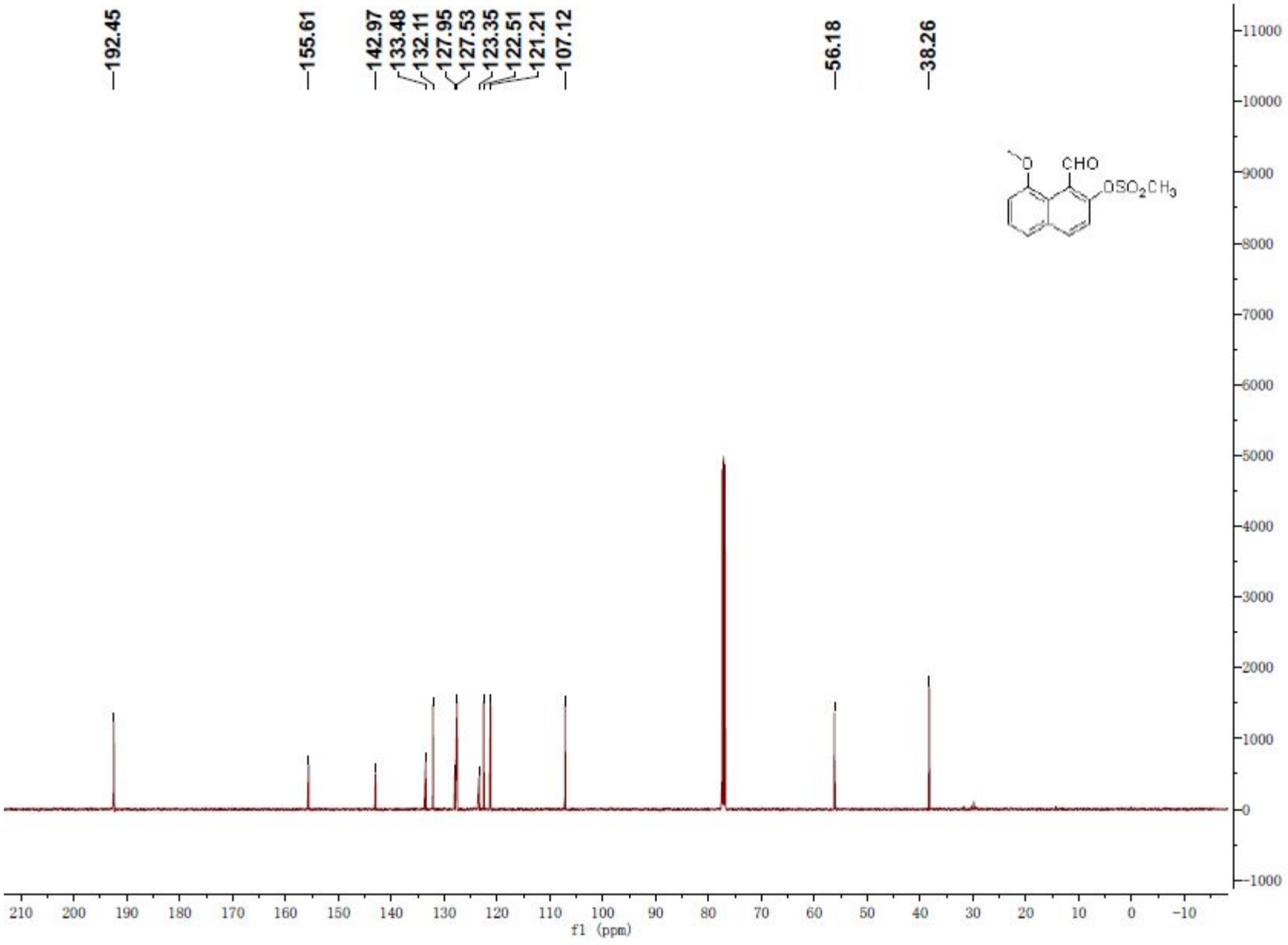
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-methoxy-8-hydroxy-1-naphthaldehyde (2q)



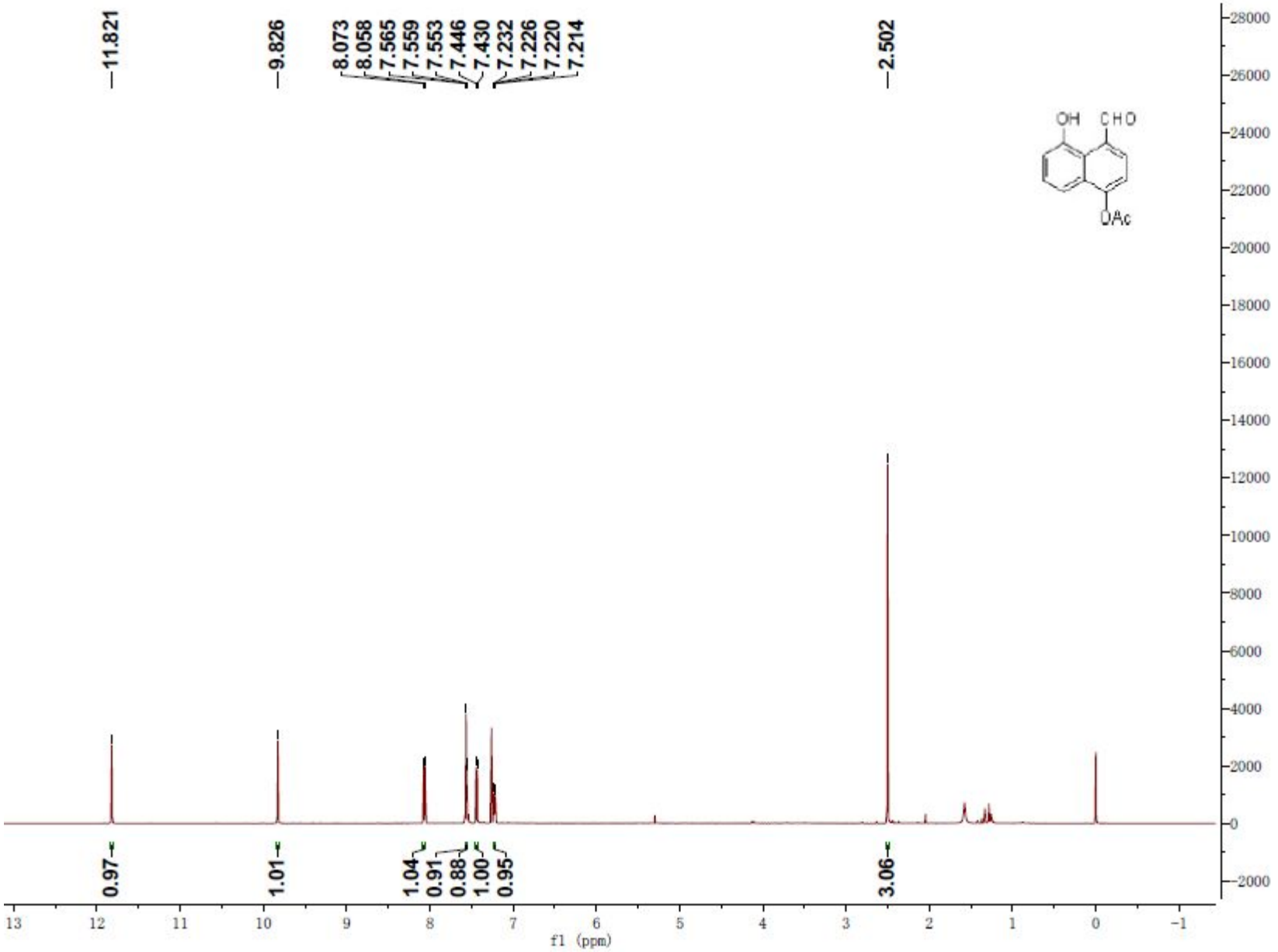
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-8-methoxynaphthalen-2-yl methanesulfonate (2r)



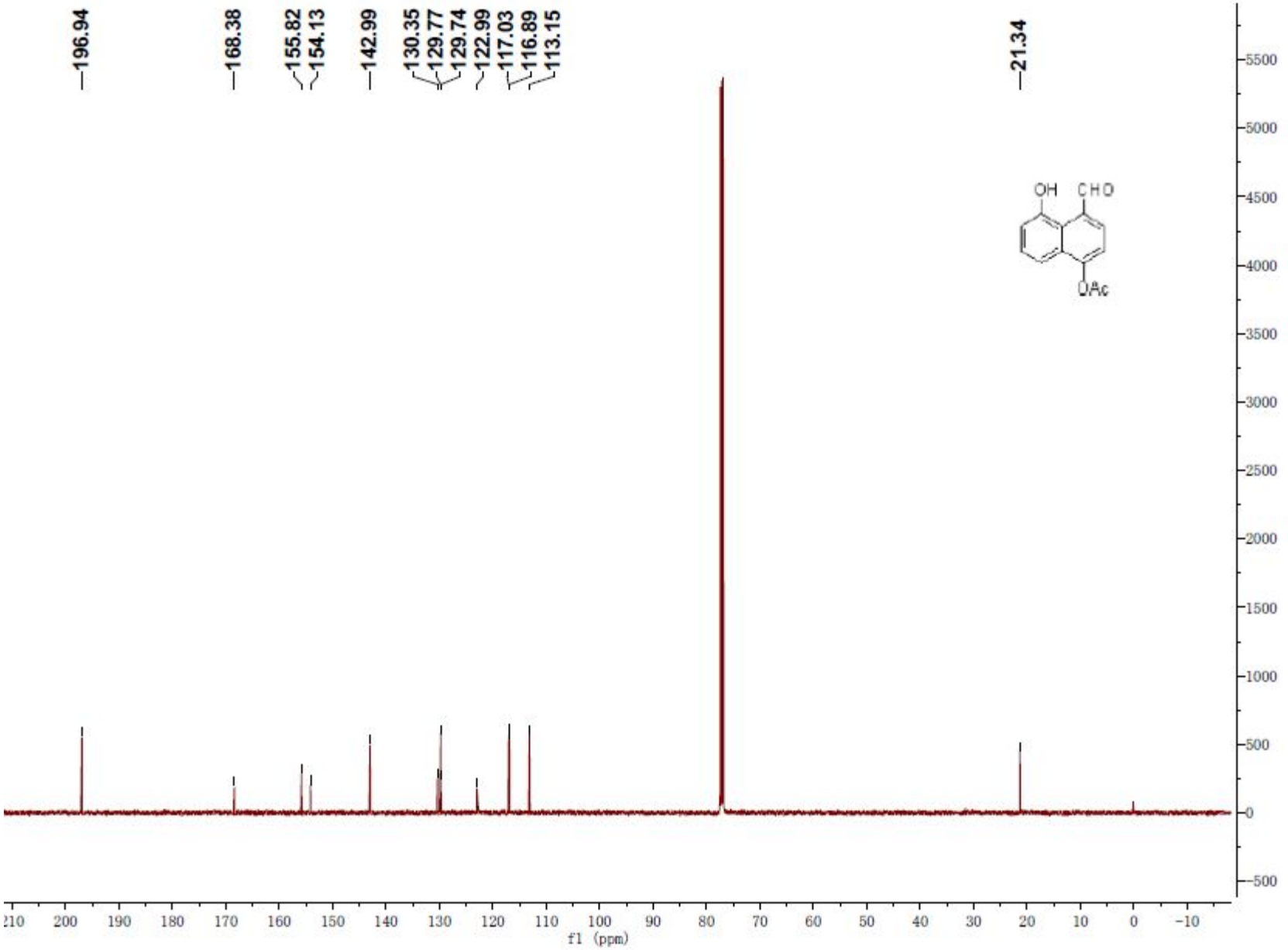
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-8-methoxynaphthalen-2-yl methanesulfonate (2r)



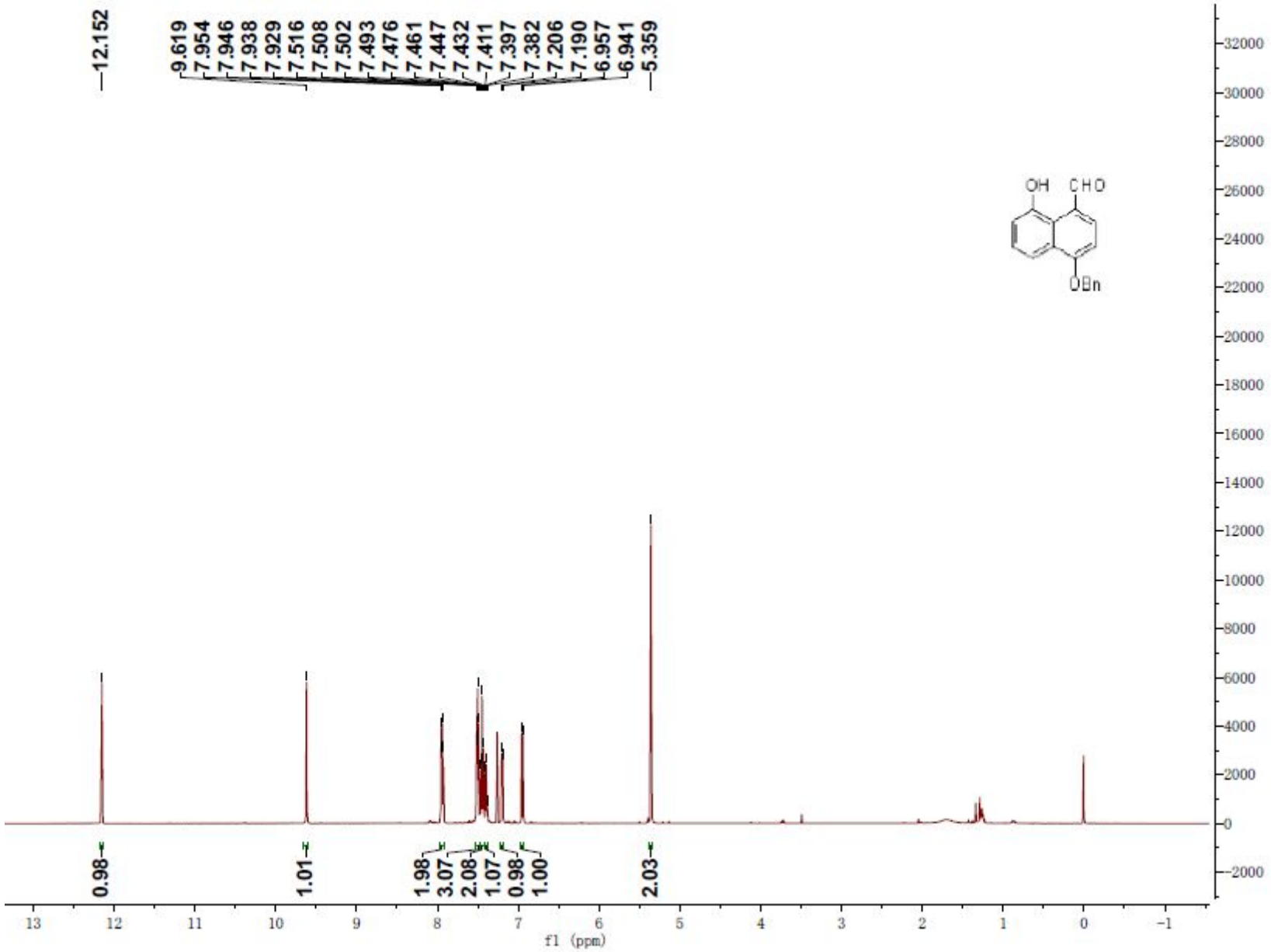
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-formyl-5-hydroxynaphthalen-1-yl acetate (2s)



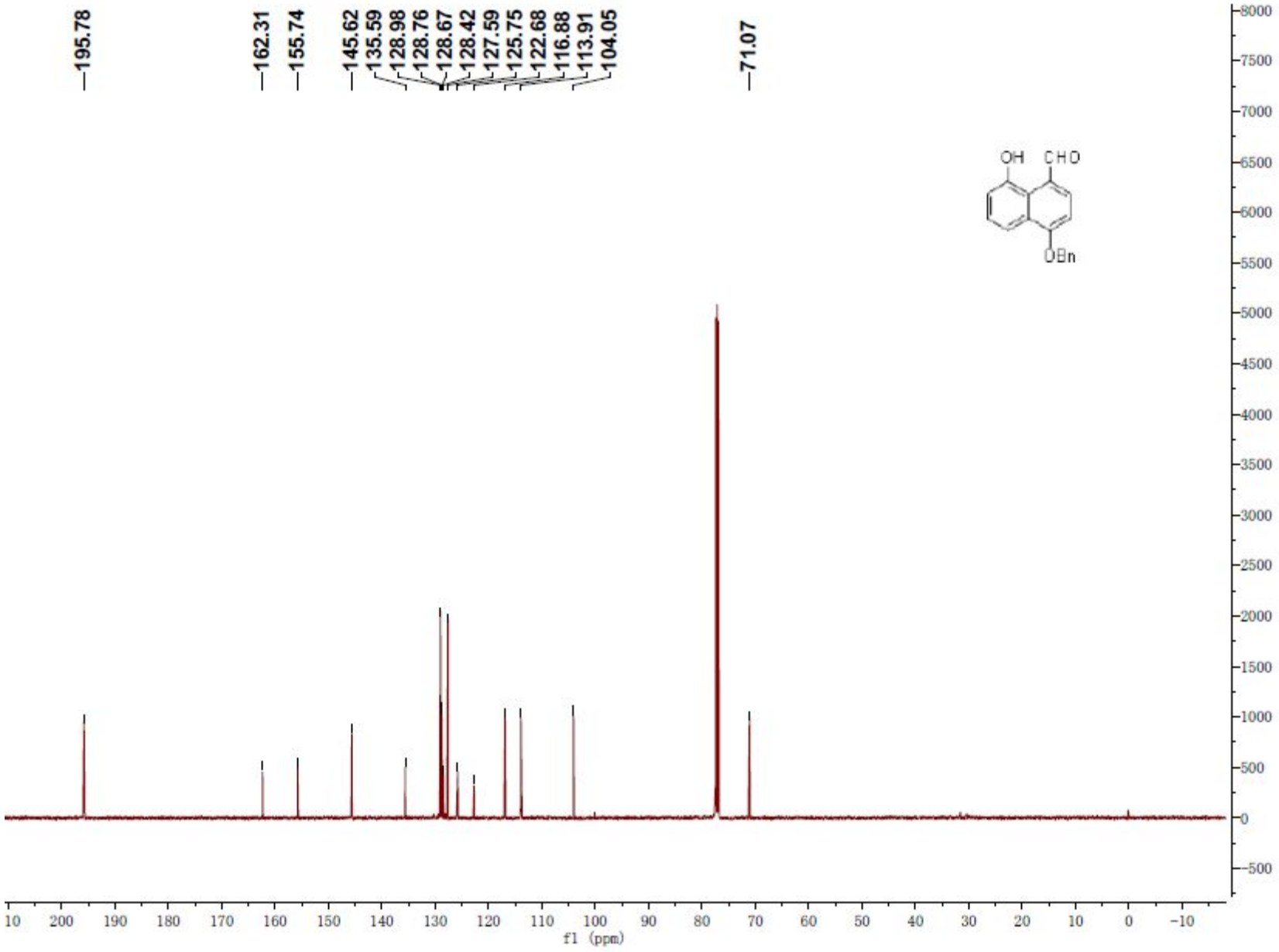
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-formyl-5-hydroxynaphthalen-1-yl acetate (2s)



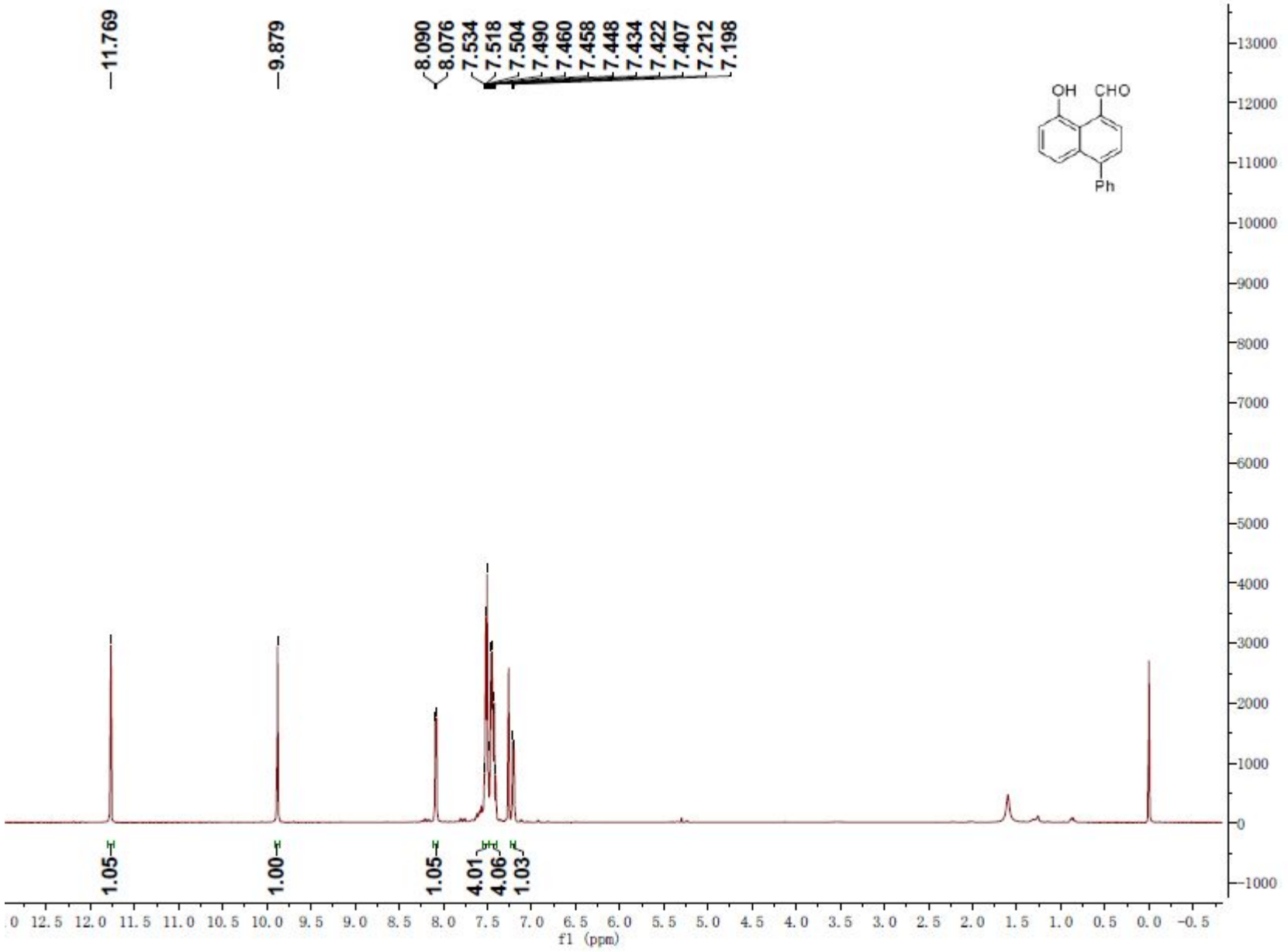
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-(benzyloxy)-8-hydroxy-1-naphthaldehyde (2t)



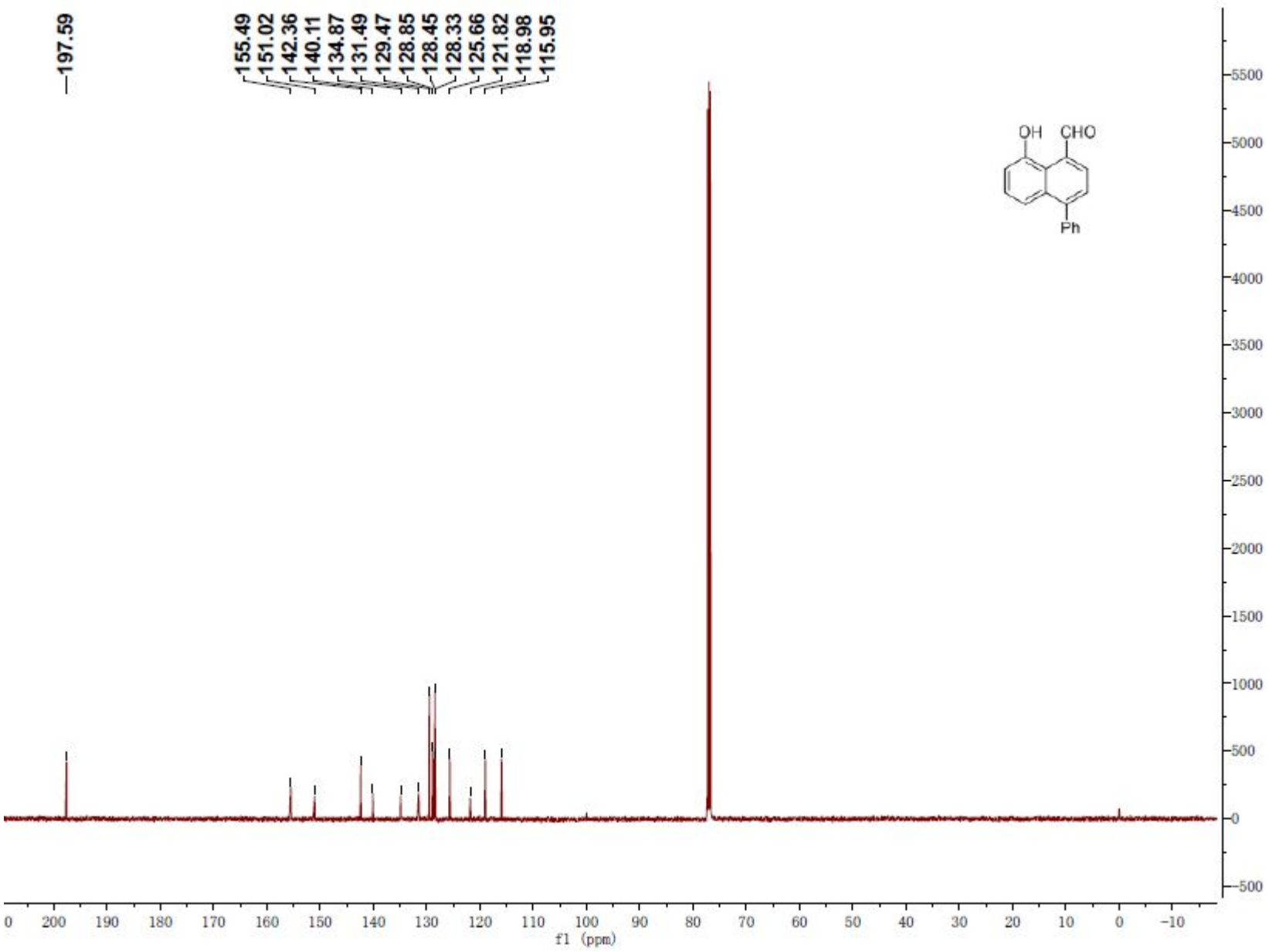
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-(benzyloxy)-8-hydroxy-1-naphthaldehyde (2t)



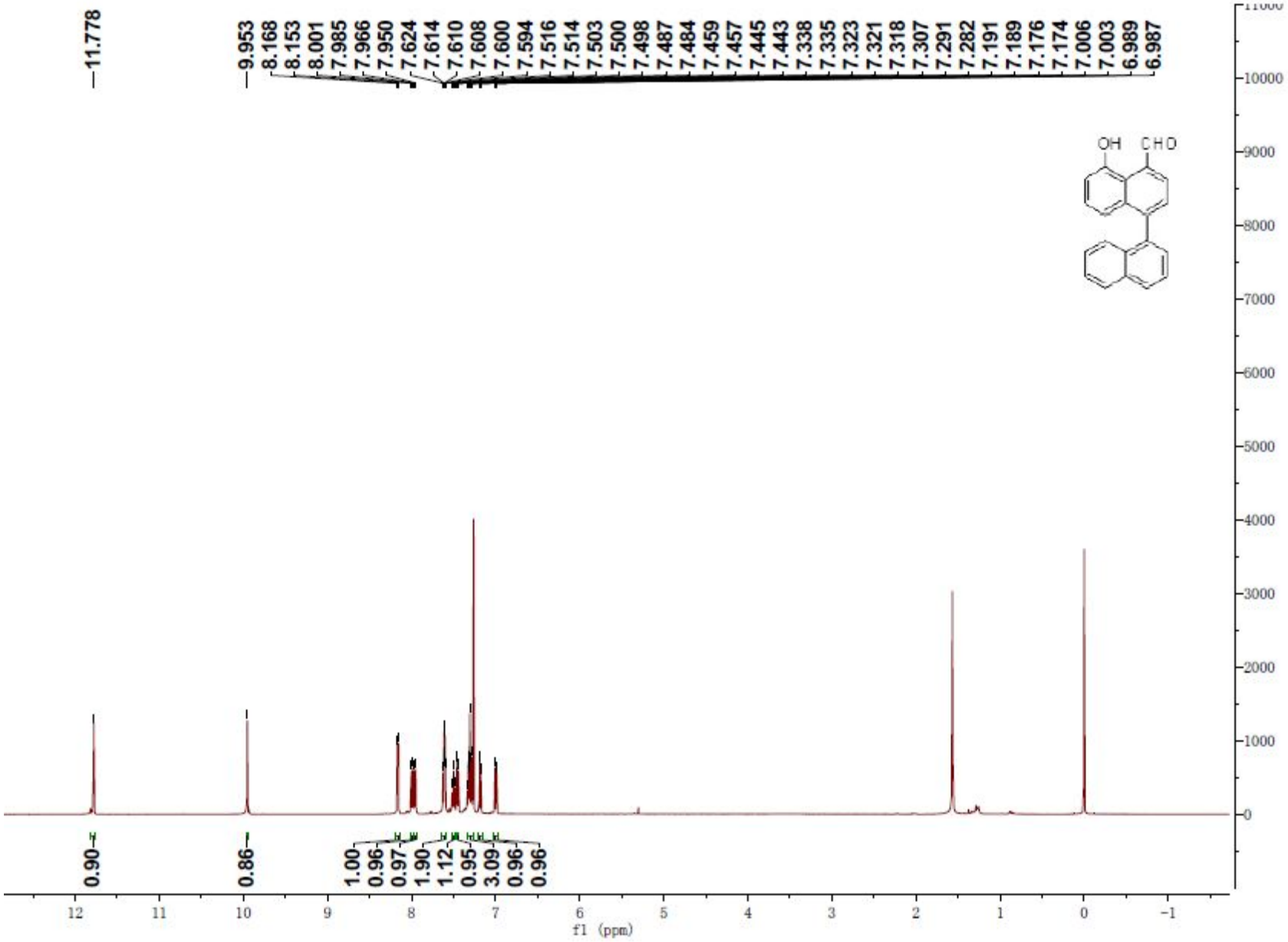
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 8-hydroxy-4-phenyl-1-naphthaldehyde (6a)



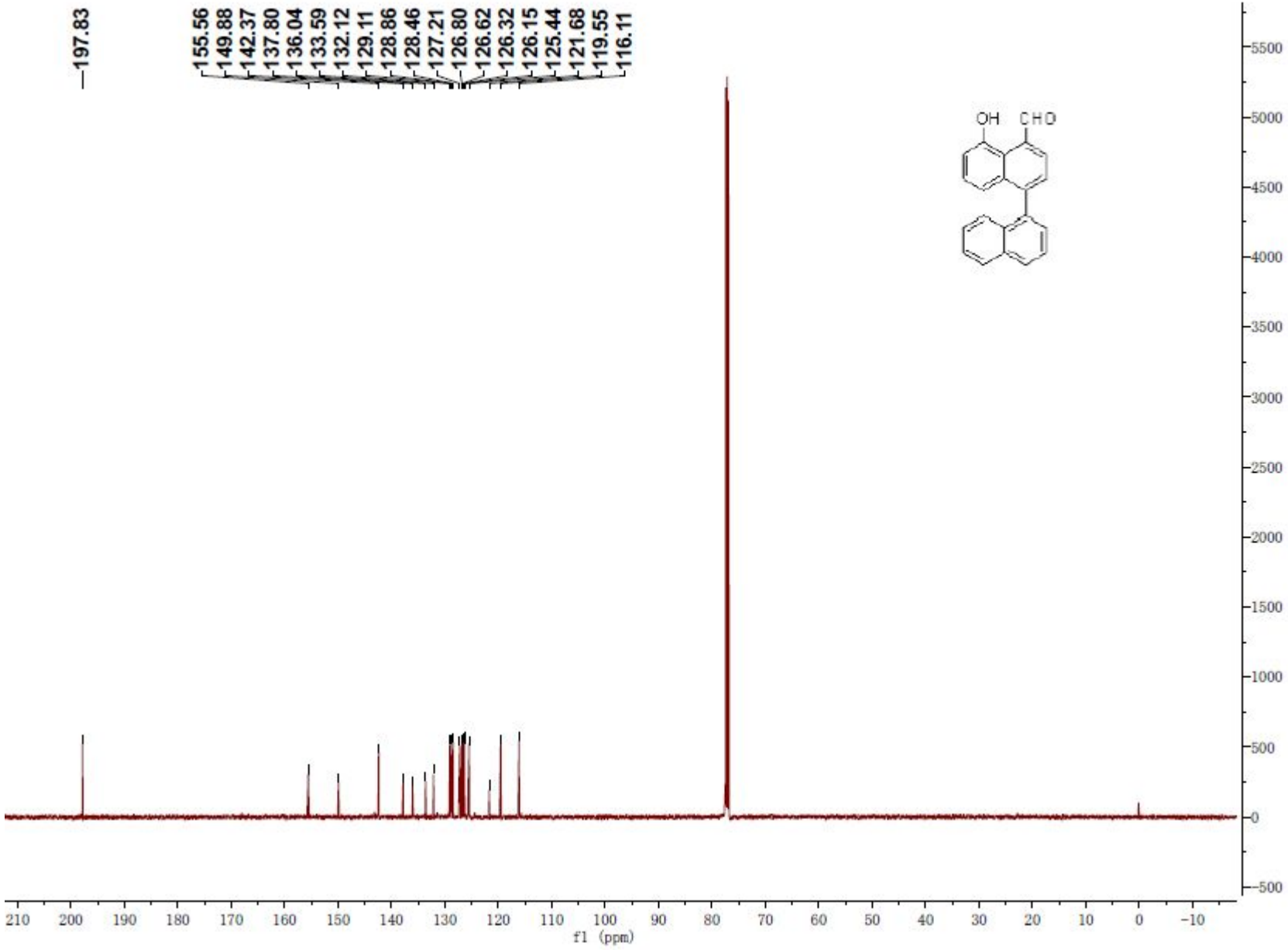
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 8-hydroxy-4-phenyl-1-naphthaldehyde (6a)



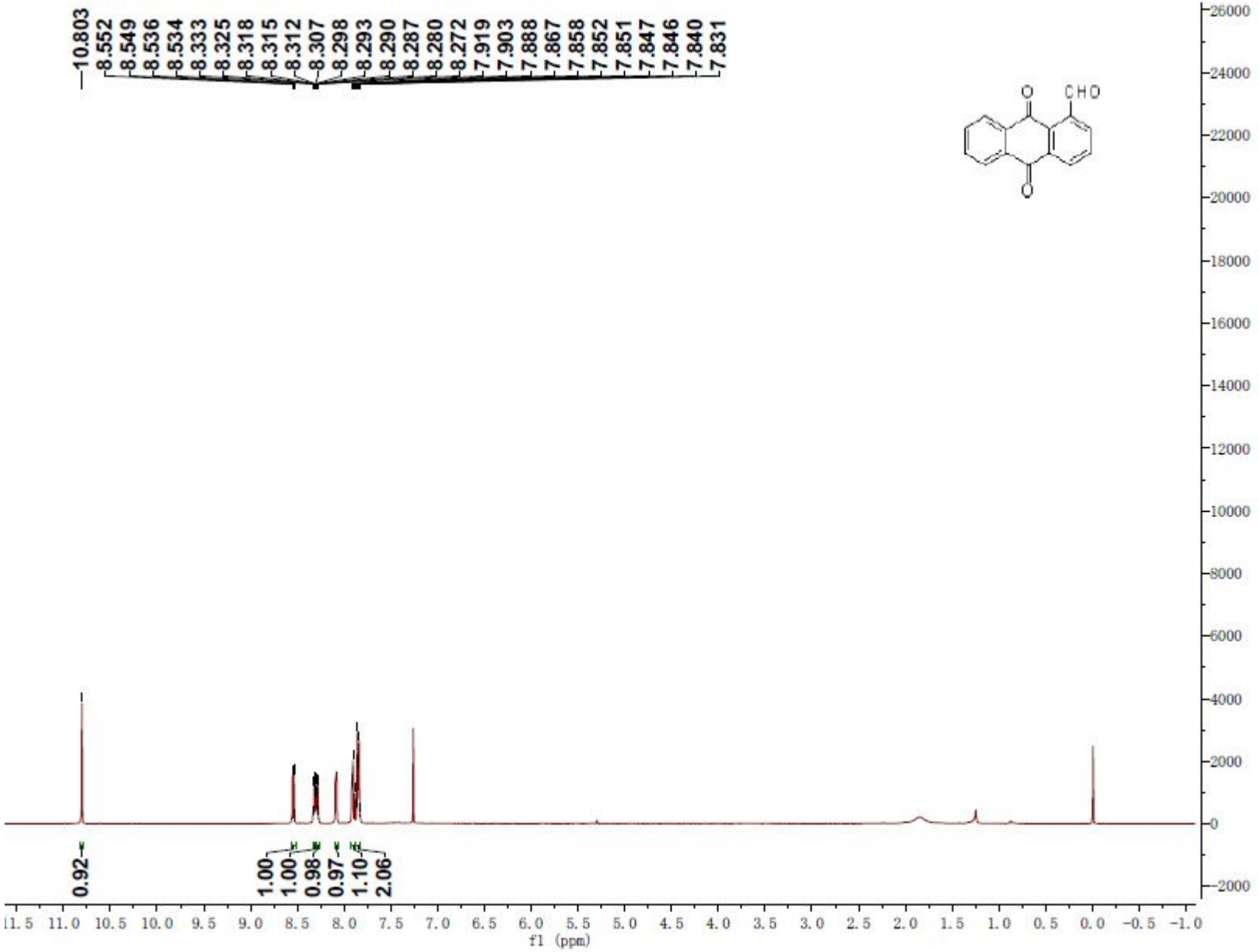
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-hydroxy-[1,1'-binaphthalene]-4-carbaldehyde (6b)



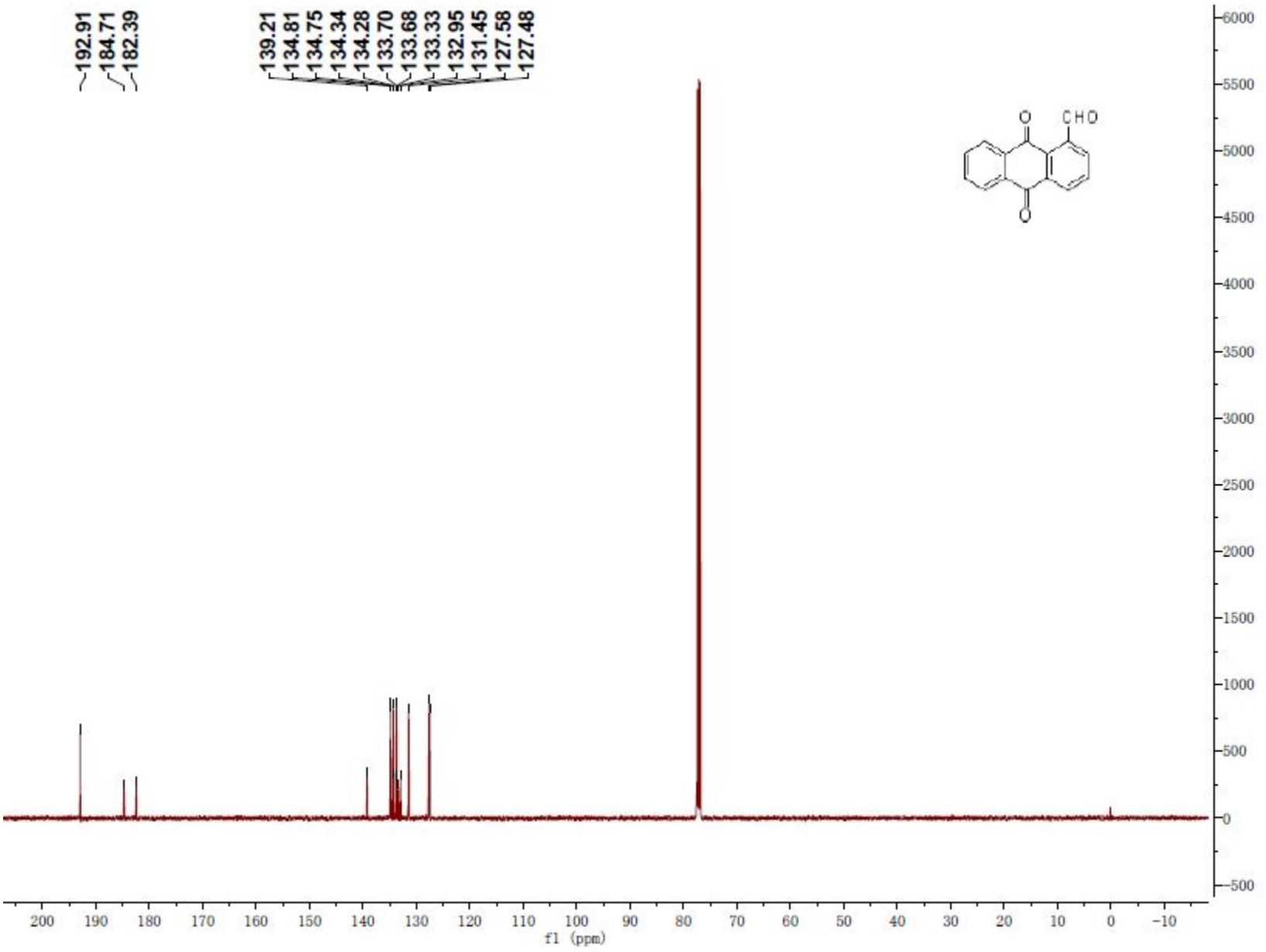
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-hydroxy-[1,1'-binaphthalene]-4-carbaldehyde (6b)



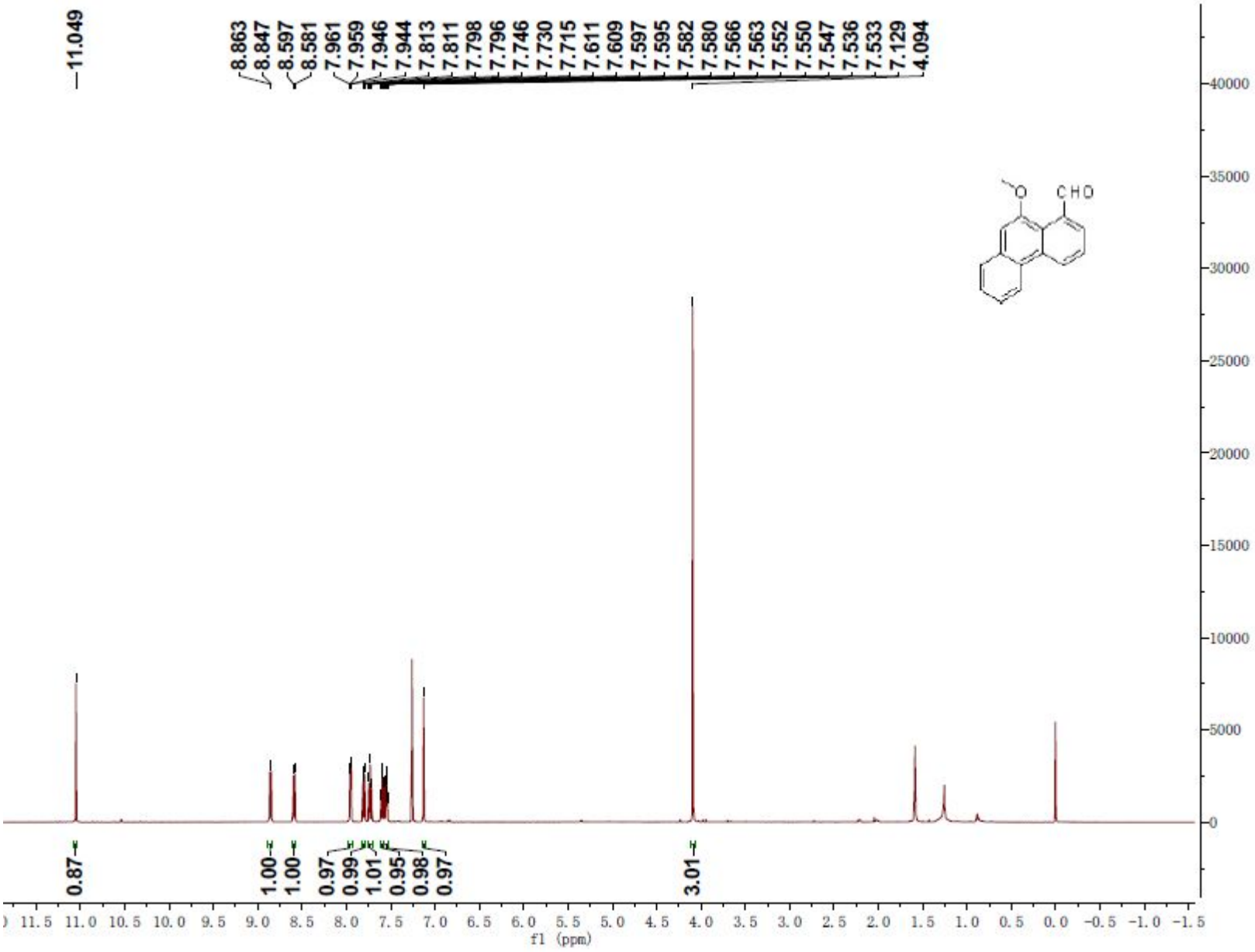
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 9,10-dioxo-4a,9,9a,10-tetrahydroanthracene-1-carbaldehyde (6c)



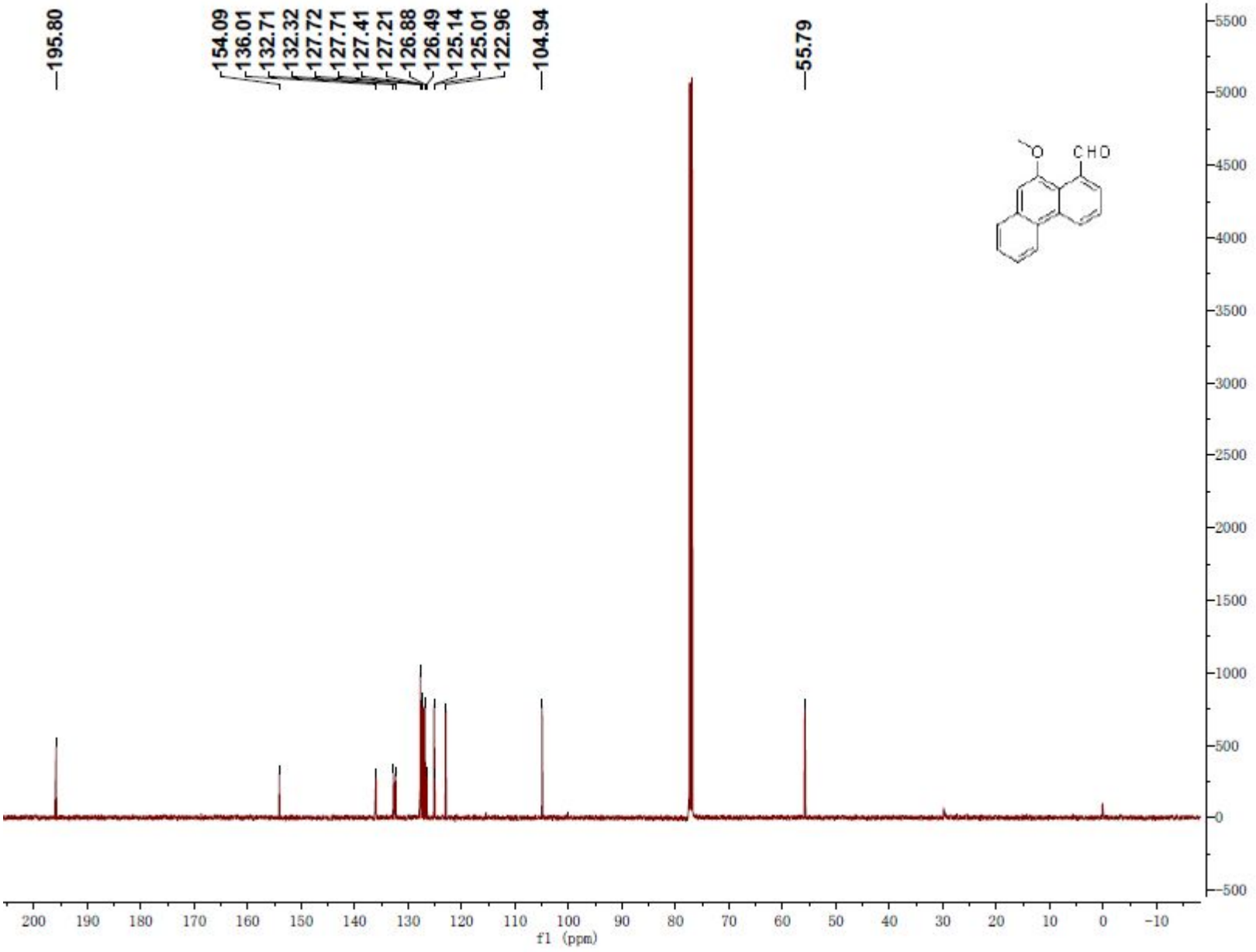
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 9,10-dioxo-4a,9,9a,10-tetrahydroanthracene-1-carbaldehyde (6c)



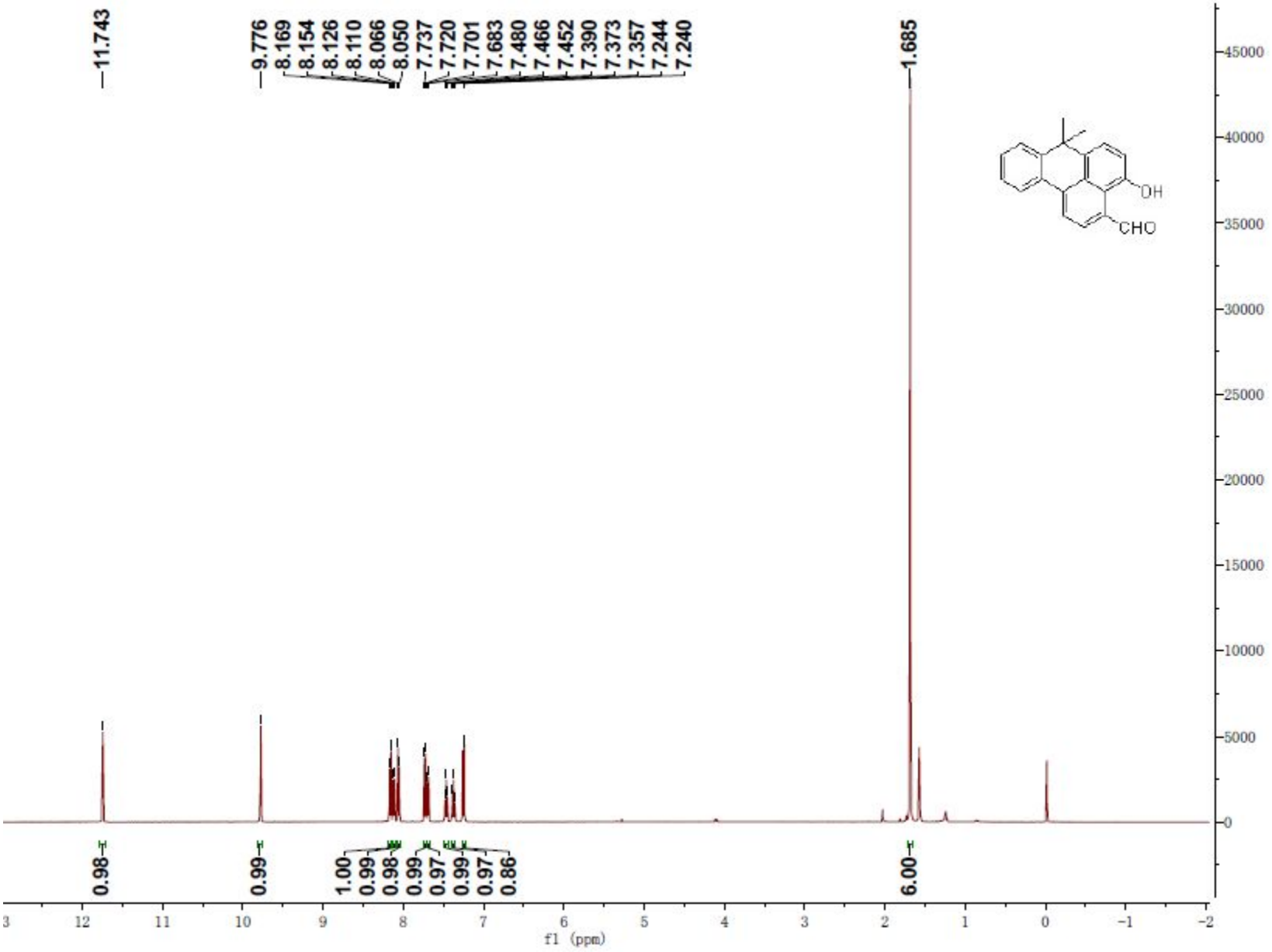
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 10-methoxyphenanthrene-1-carbaldehyde (6d)



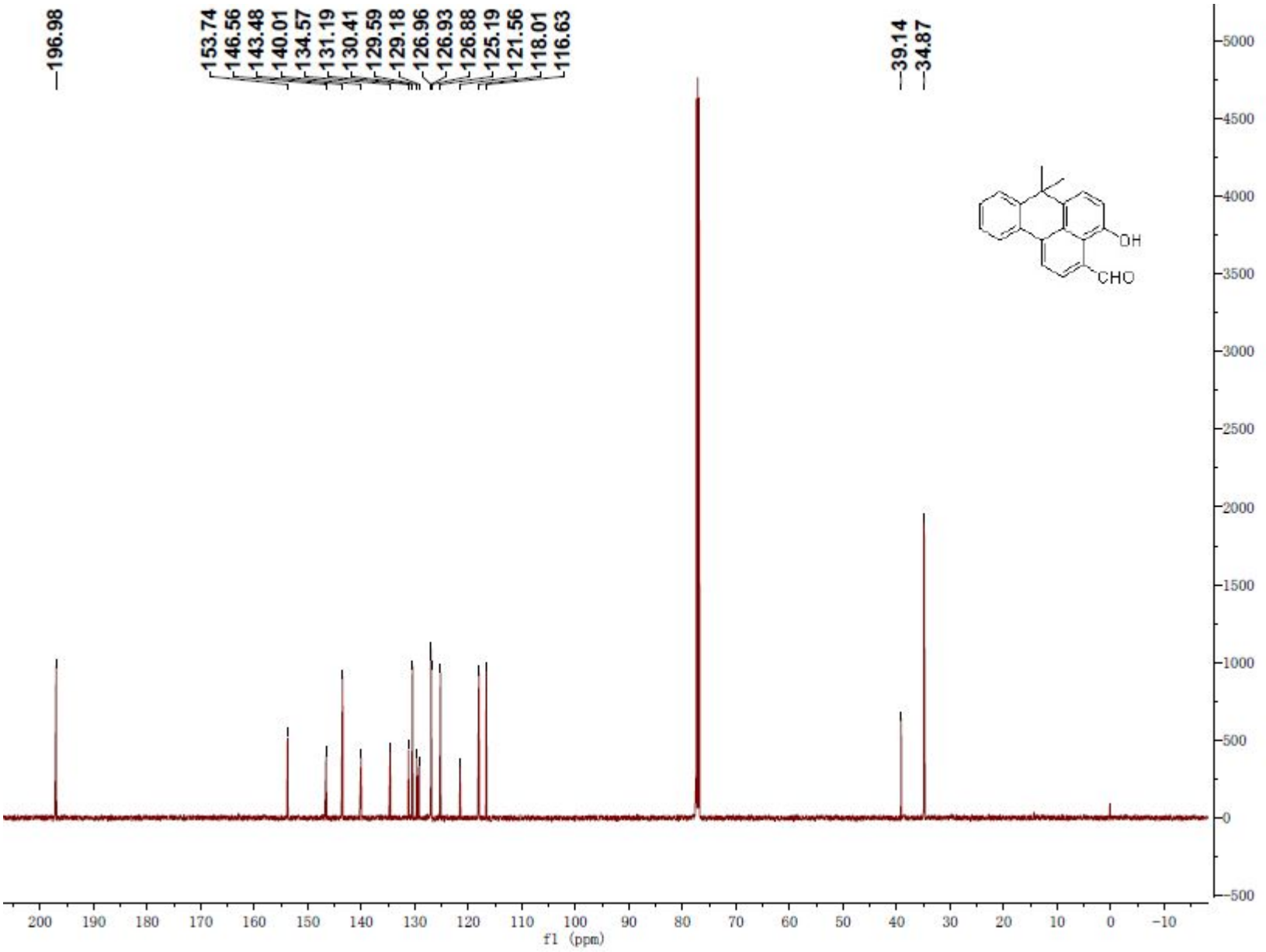
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 10-methoxyphenanthrene-1-carbaldehyde (6d)



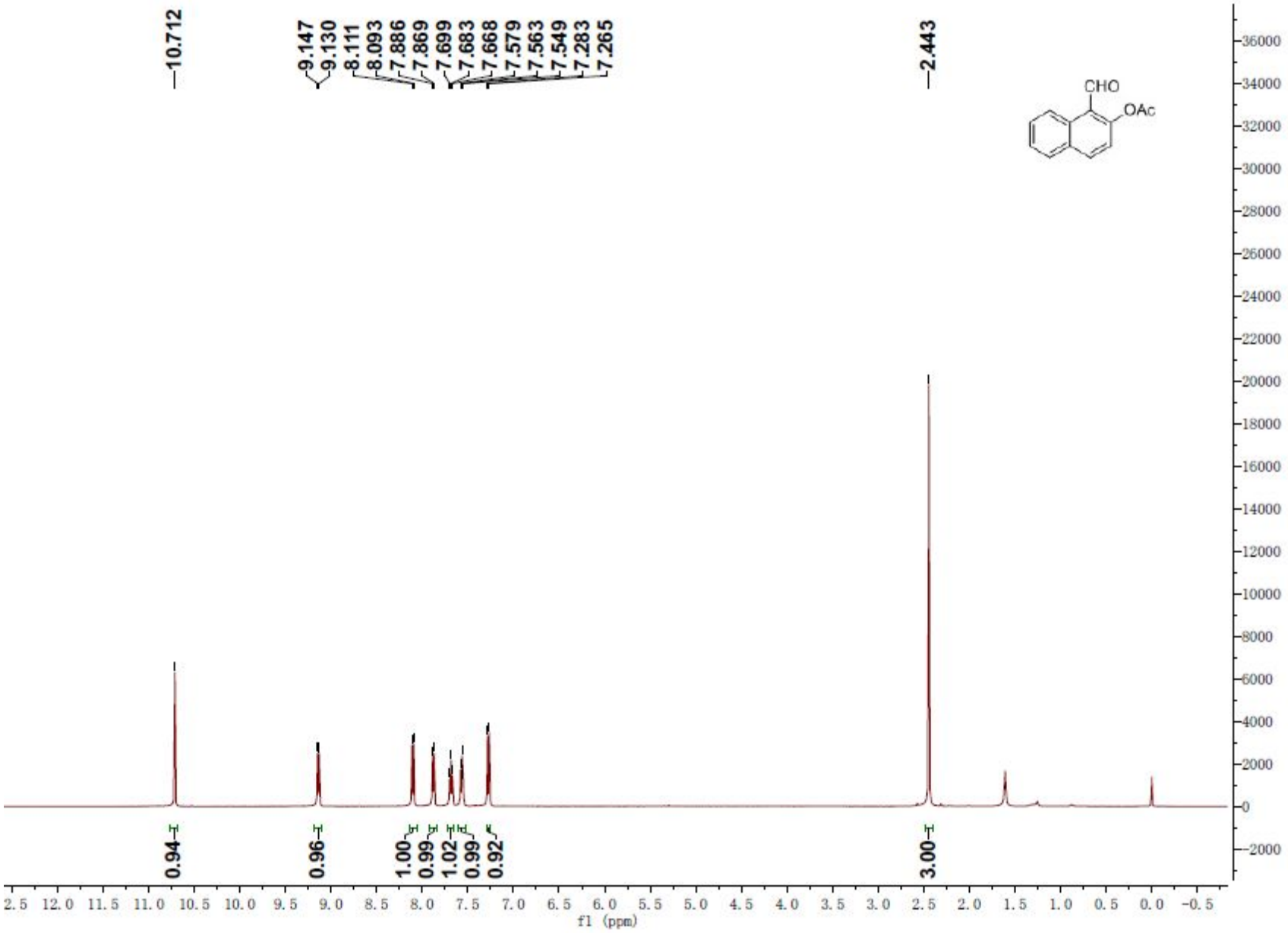
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-hydroxy-7,7-dimethyl-7H-benzo[de]anthracene-3-carbaldehyde (6e)



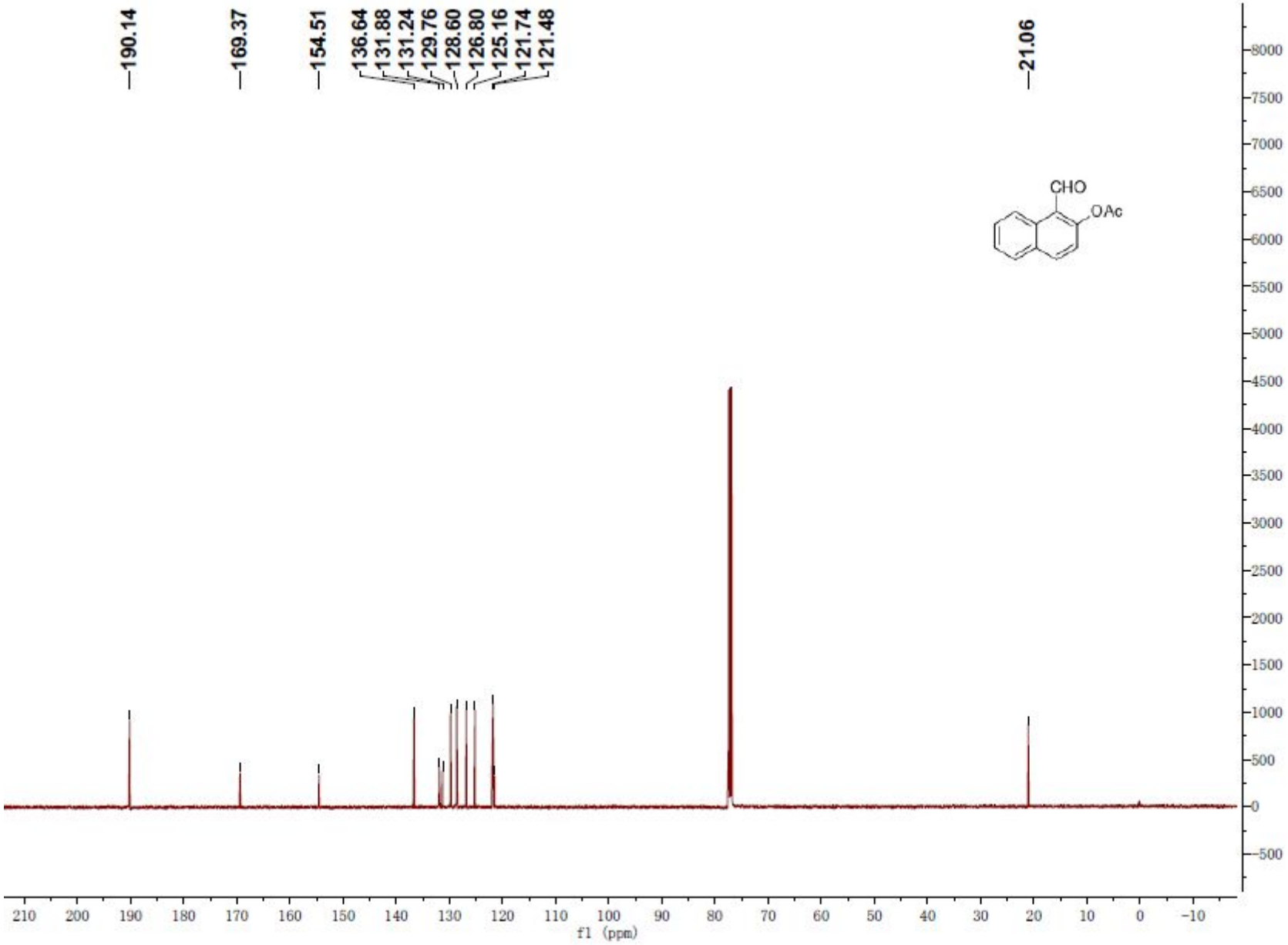
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-hydroxy-7,7-dimethyl-7H-benzo[de]anthracene-3-carbaldehyde (6e)



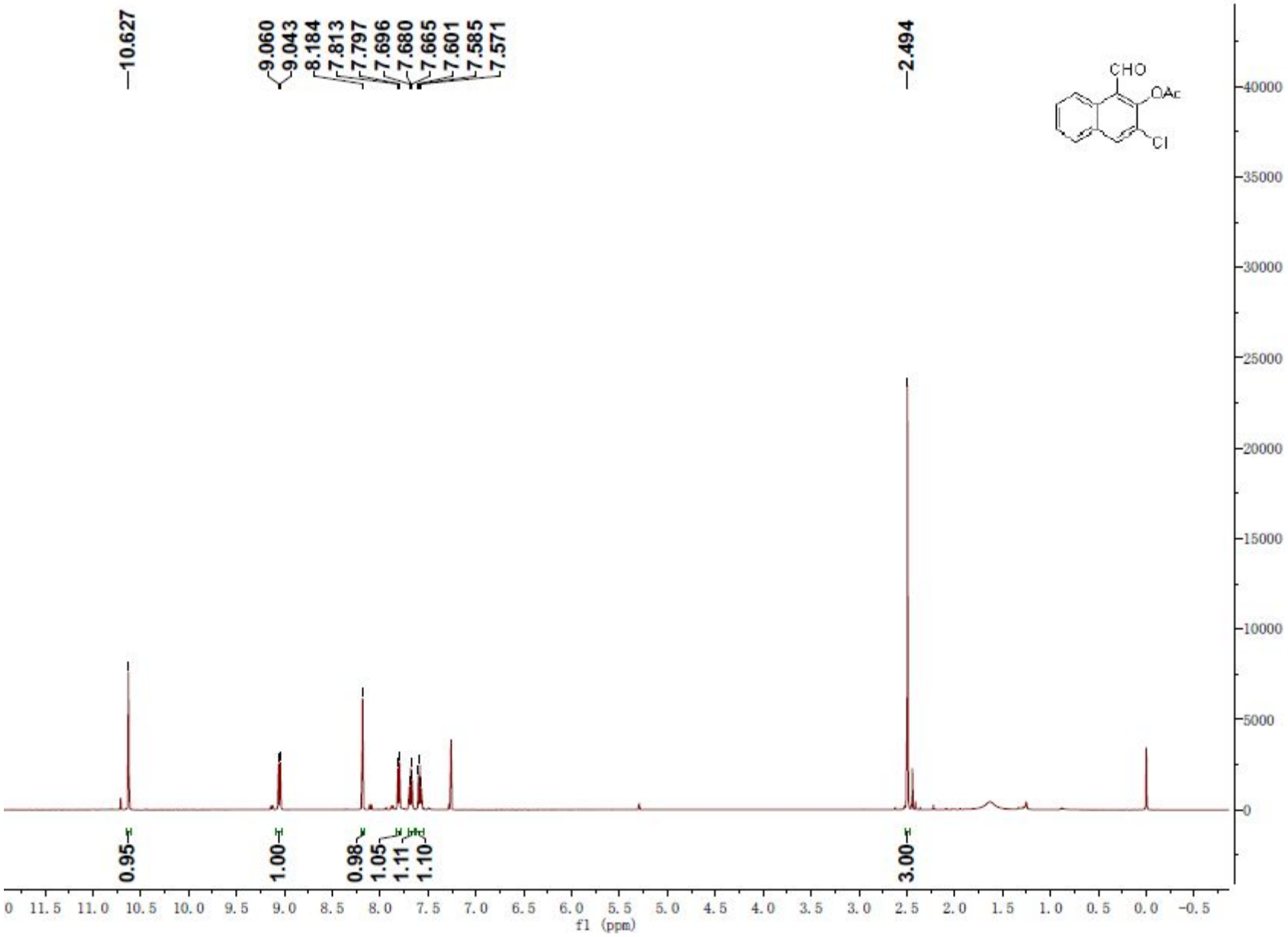
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formylnaphthalen-2-yl acetate (4a)



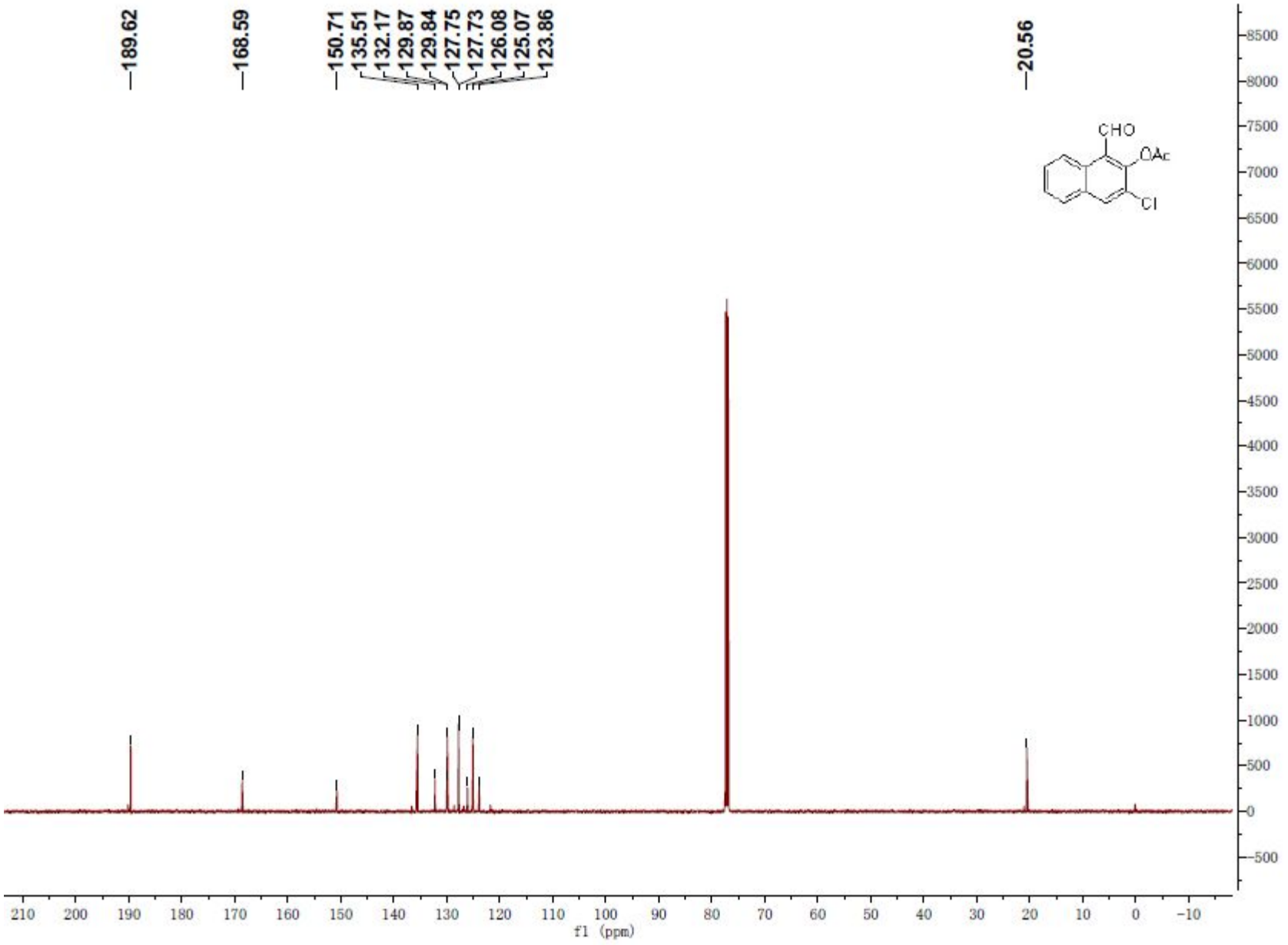
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formylnaphthalen-2-yl acetate (4a)



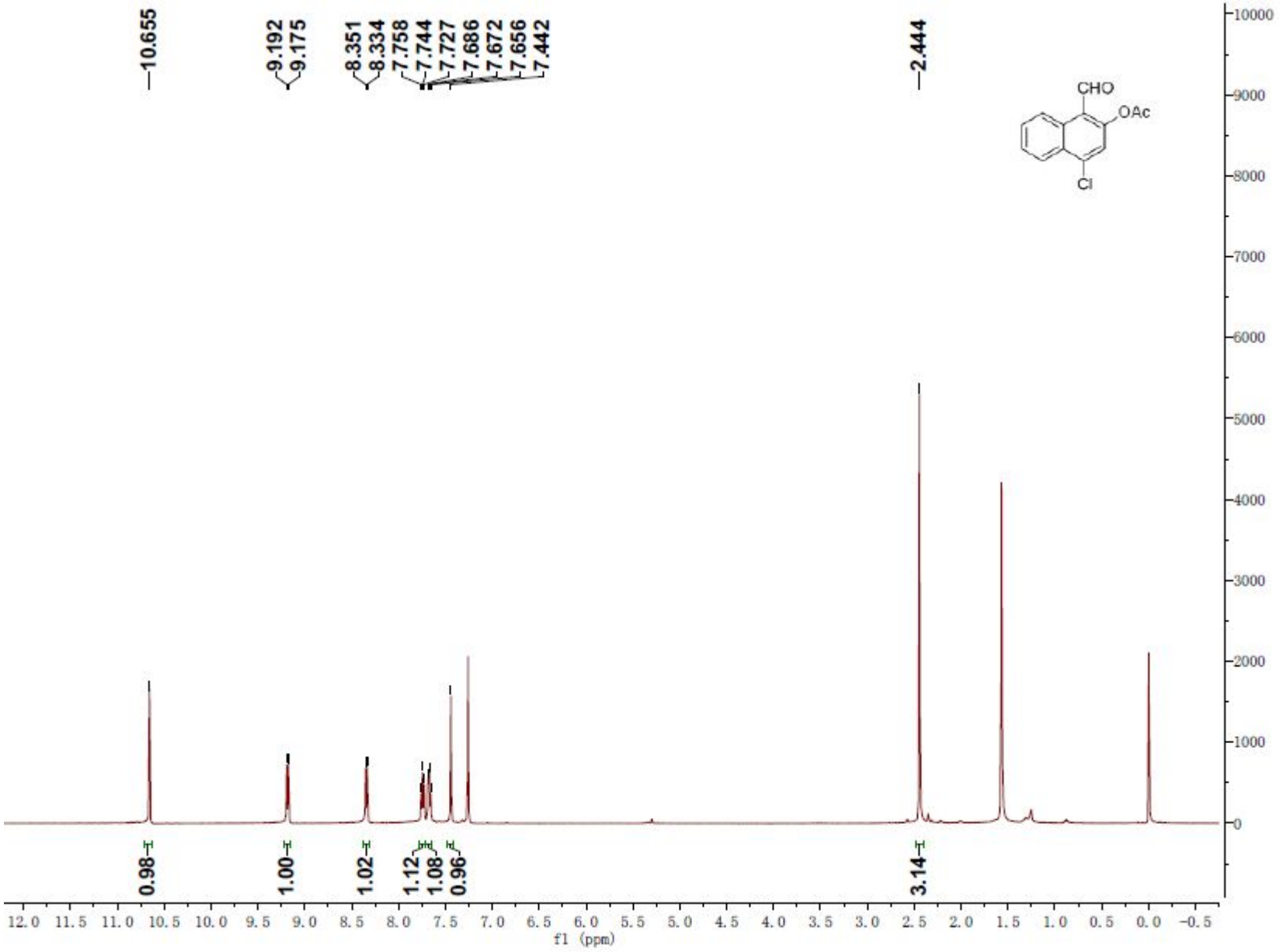
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3-chloro-1-formylnaphthalen-2-yl acetate (4b)



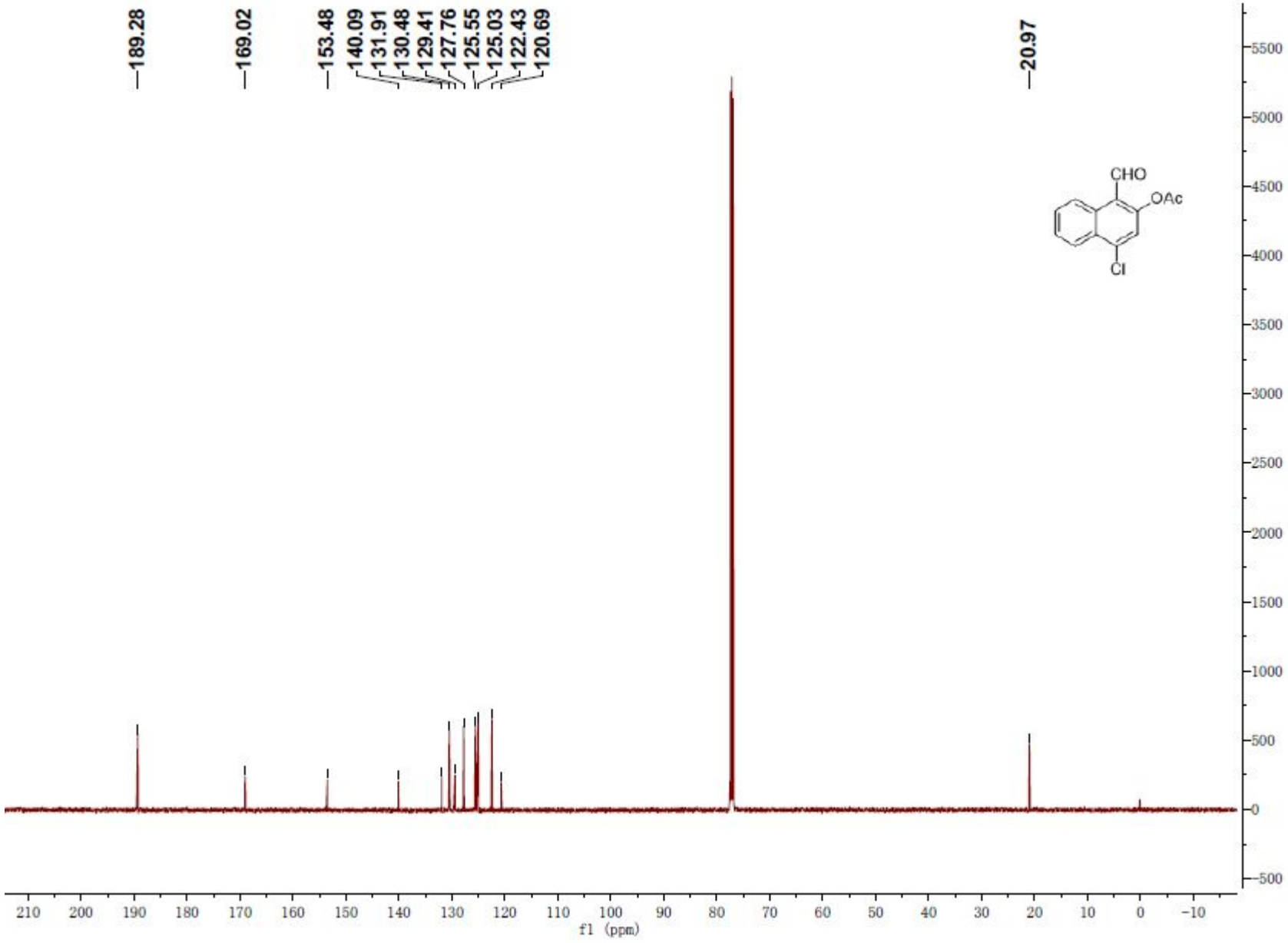
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 3-chloro-1-formylnaphthalen-2-yl acetate (4b)



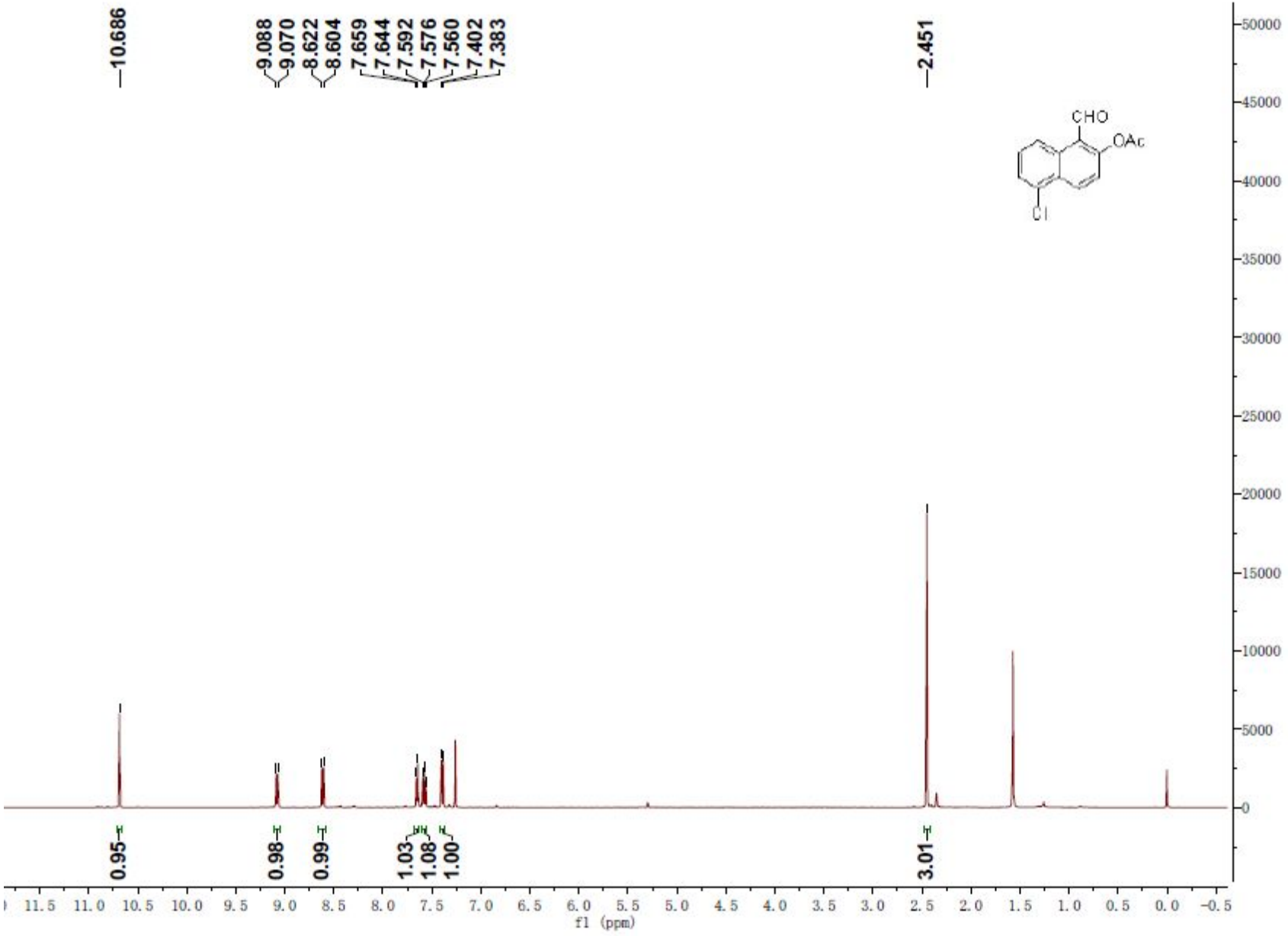
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-chloro-1-formylnaphthalen-2-yl acetate (4c)



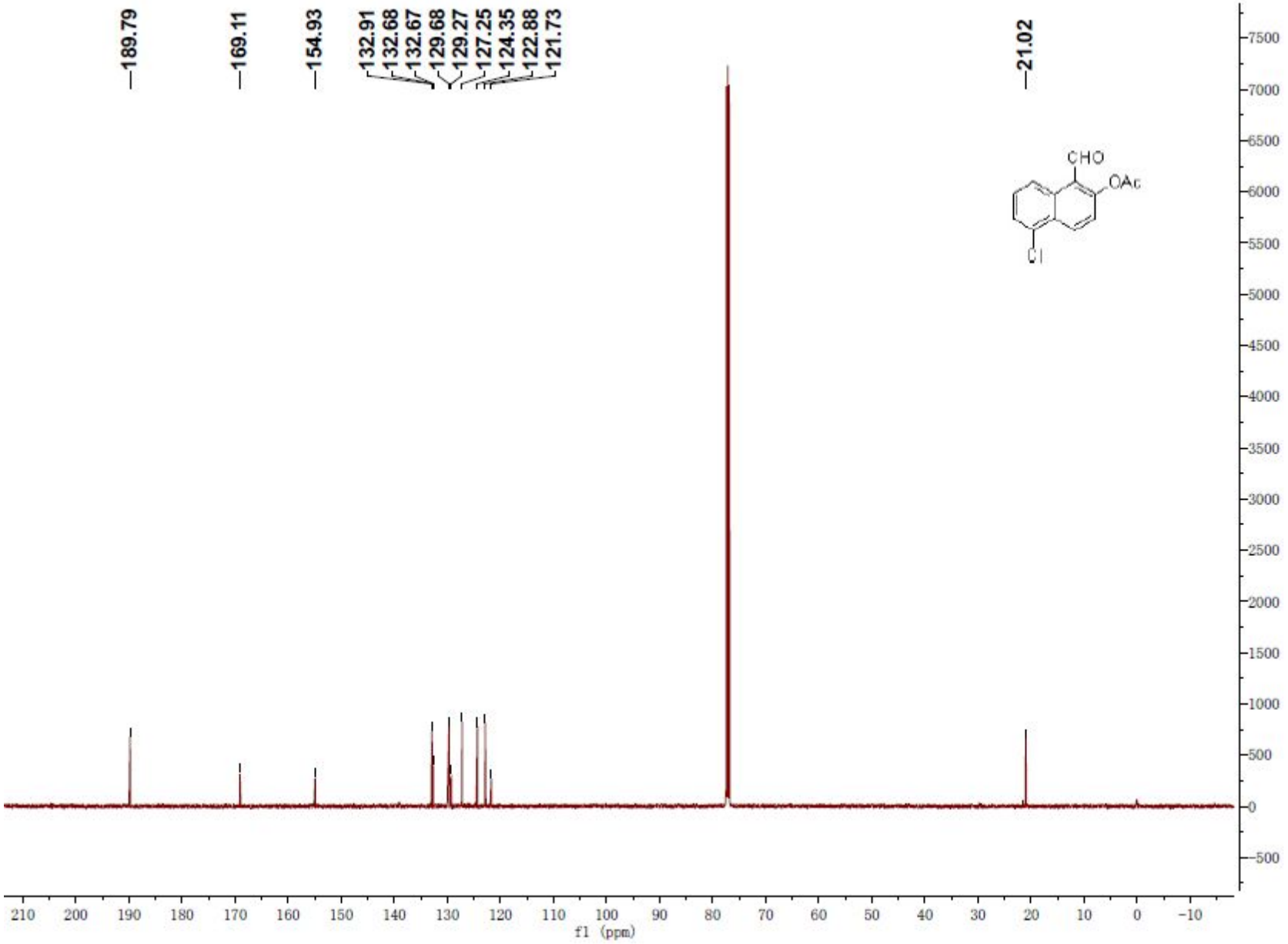
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-chloro-1-formylnaphthalen-2-yl acetate (4c)



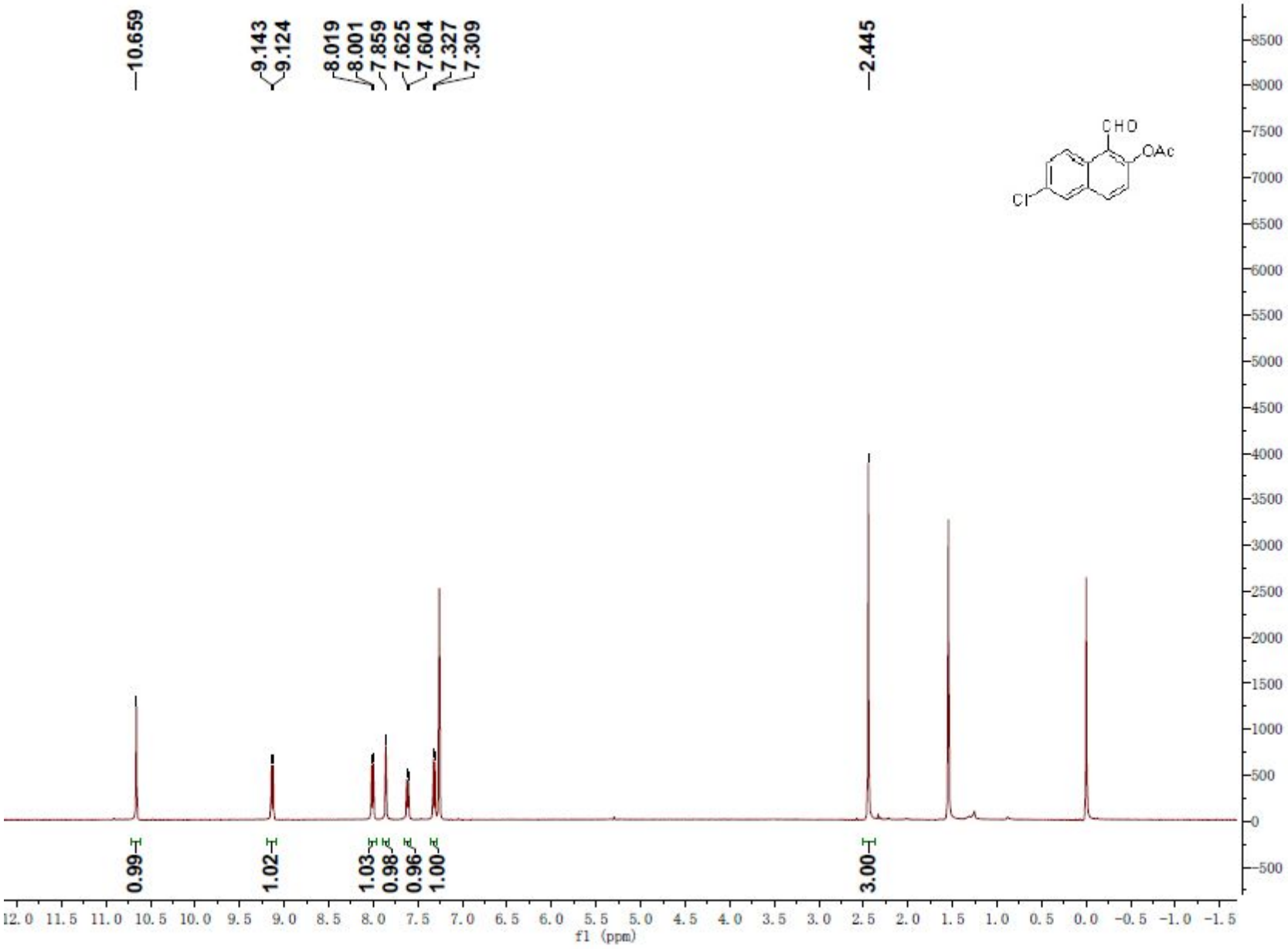
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-chloro-1-formylnaphthalen-2-yl acetate (4d)



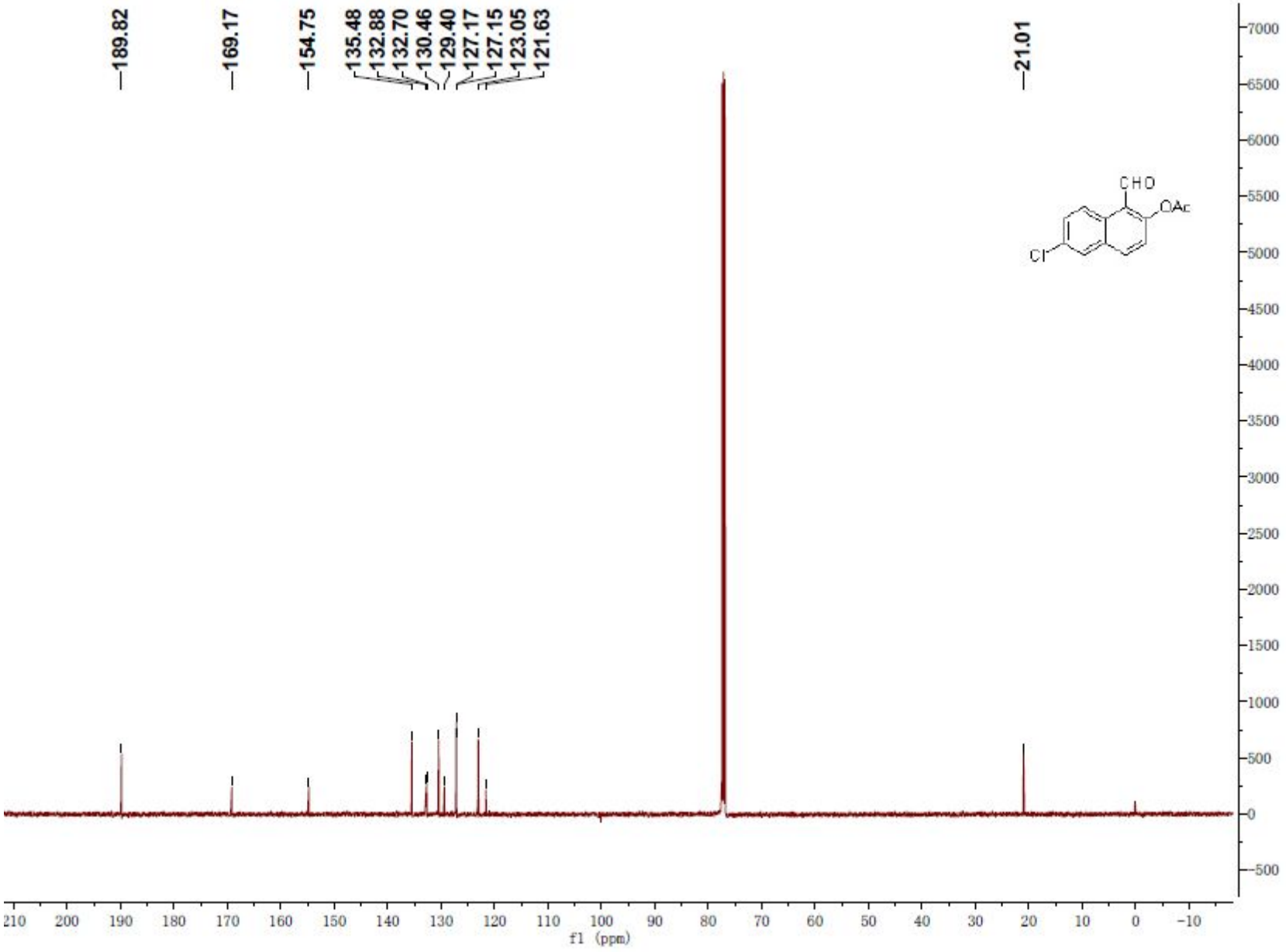
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-chloro-1-formylnaphthalen-2-yl acetate (4d)



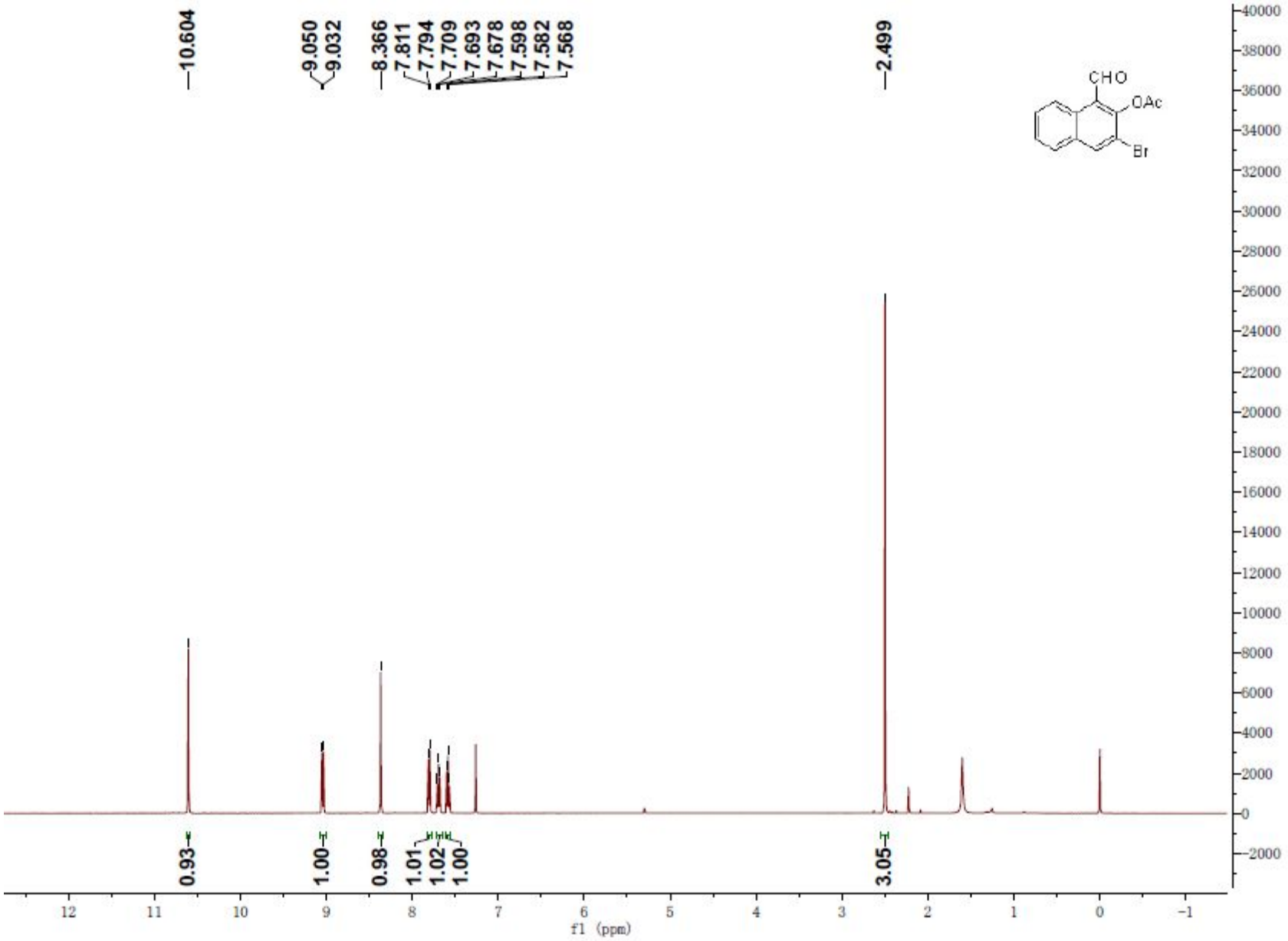
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 6-chloro-1-formylnaphthalen-2-yl acetate (4e)



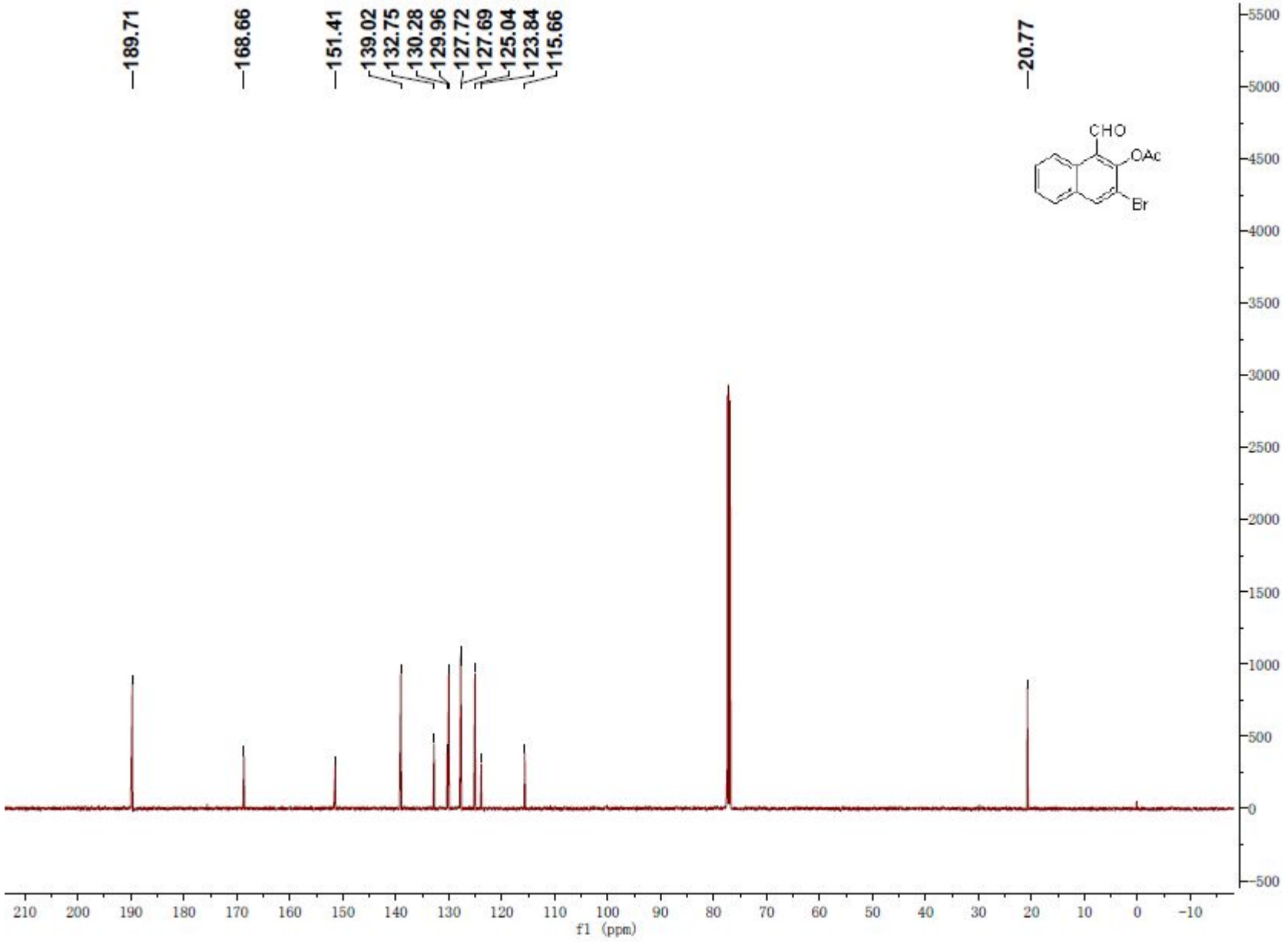
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 6-chloro-1-formylnaphthalen-2-yl acetate (4e)



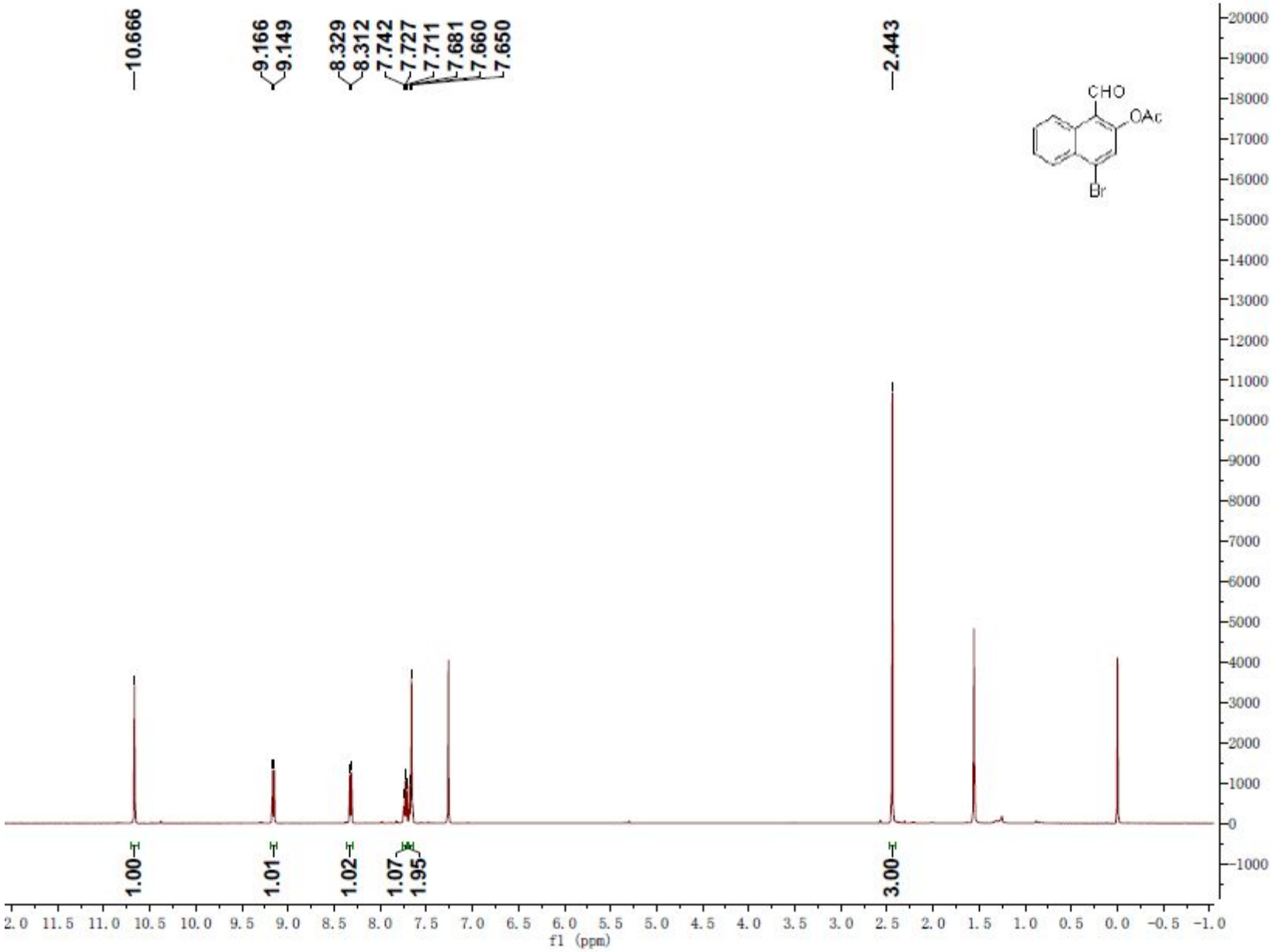
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3-bromo-1-formylnaphthalen-2-yl acetate (4f)



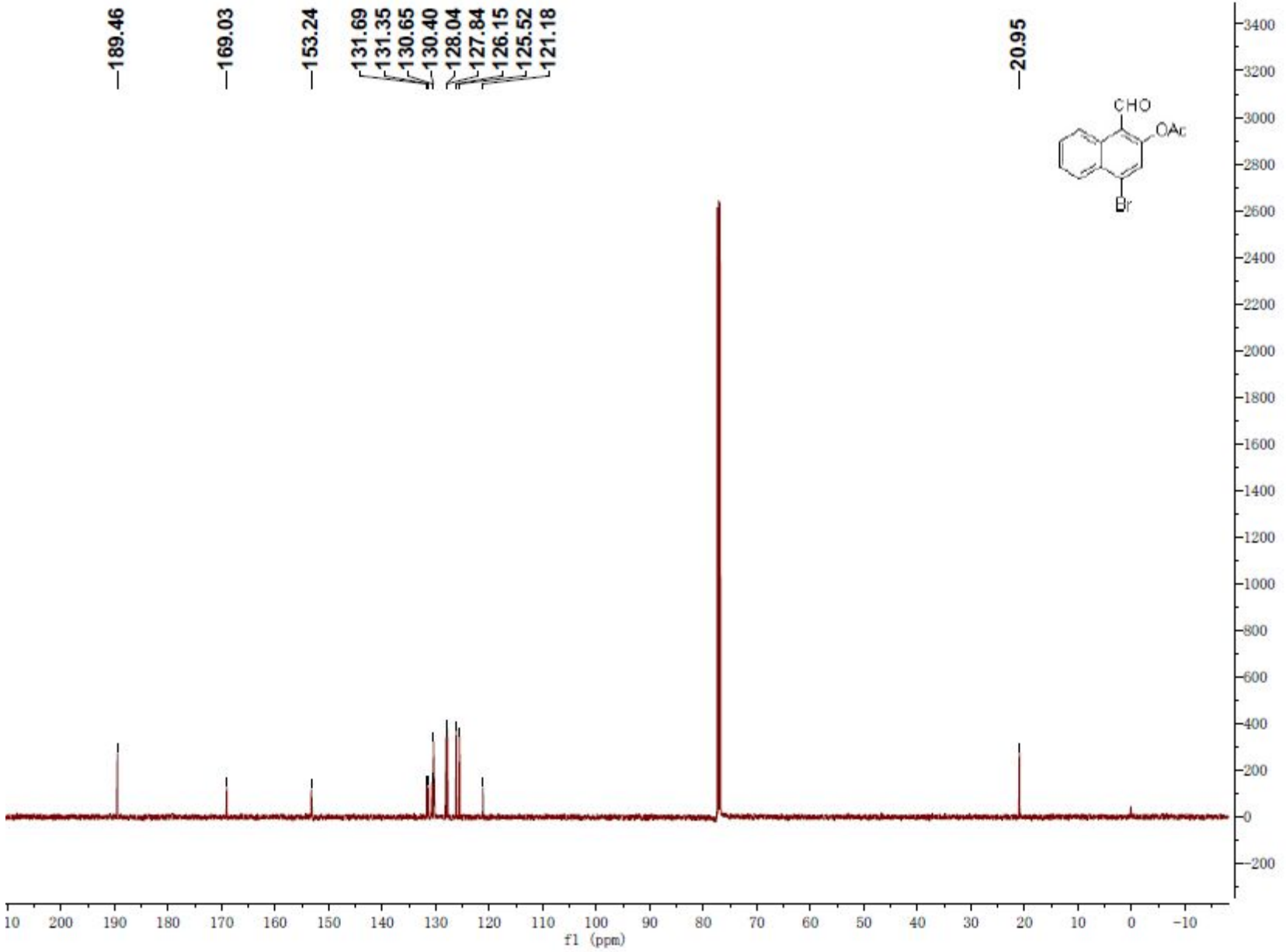
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 3-bromo-1-formylnaphthalen-2-yl acetate (4f)



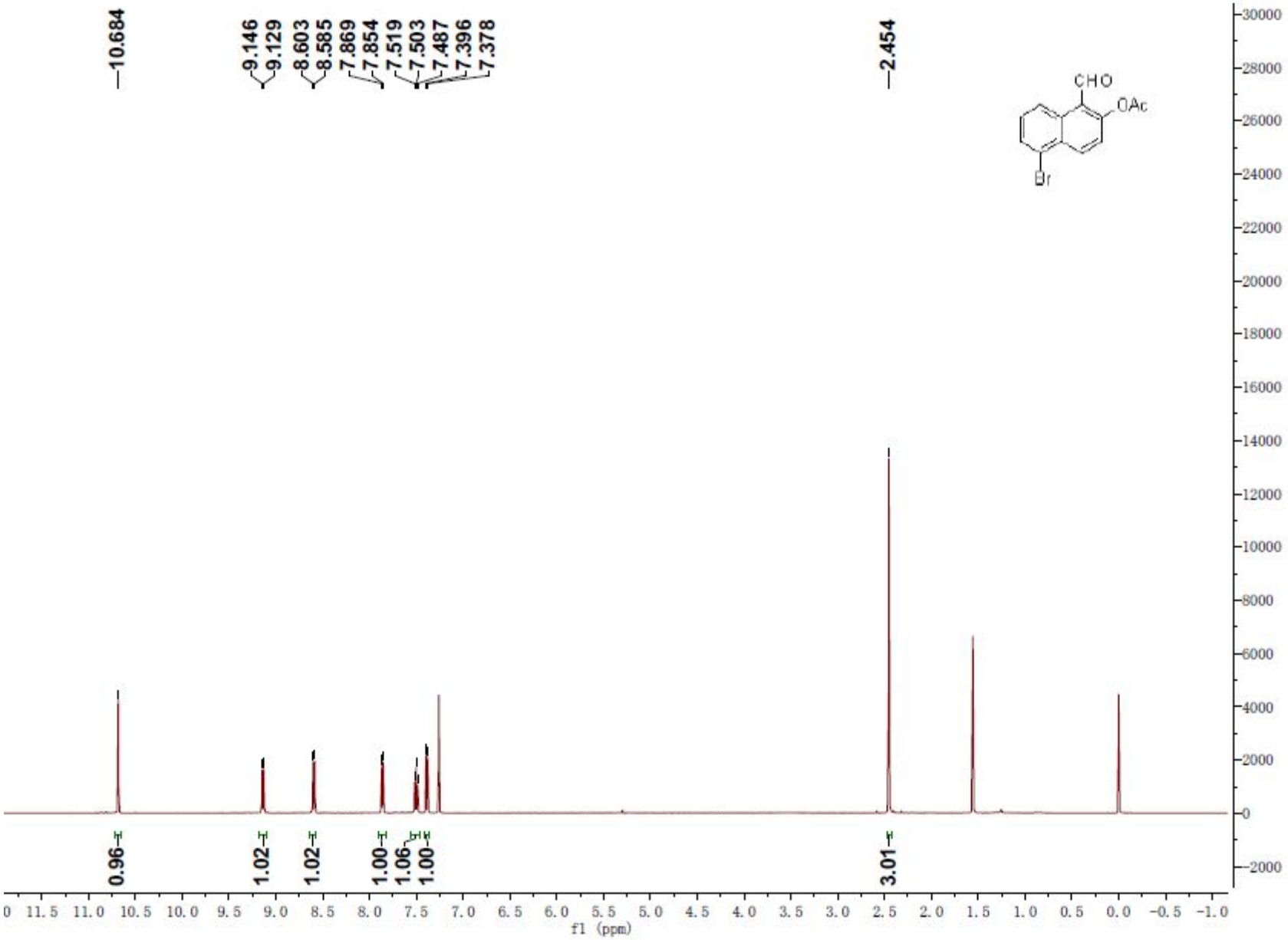
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-bromo-1-formylnaphthalen-2-yl acetate (4g)



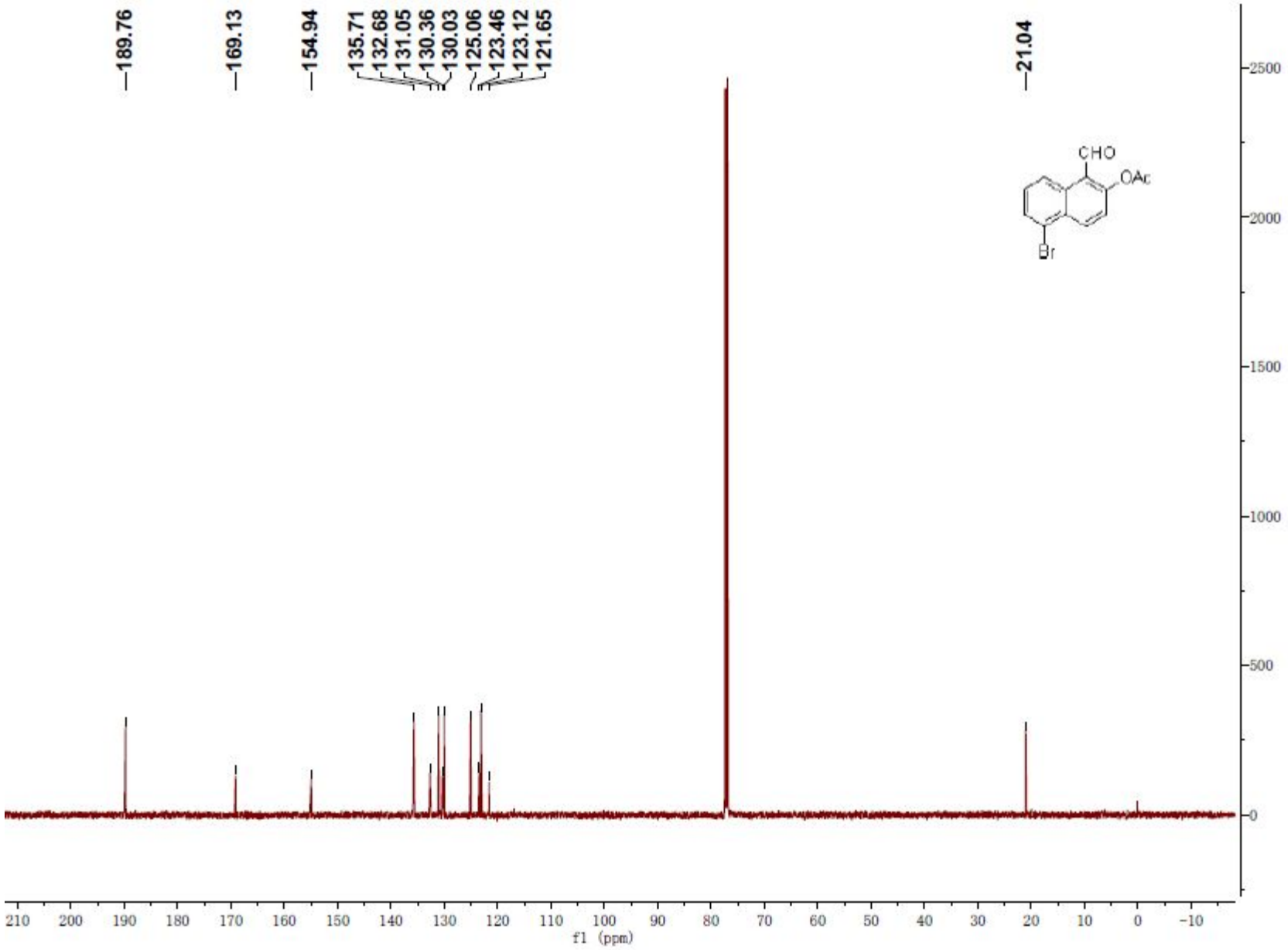
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-bromo-1-formylnaphthalen-2-yl acetate (4g)



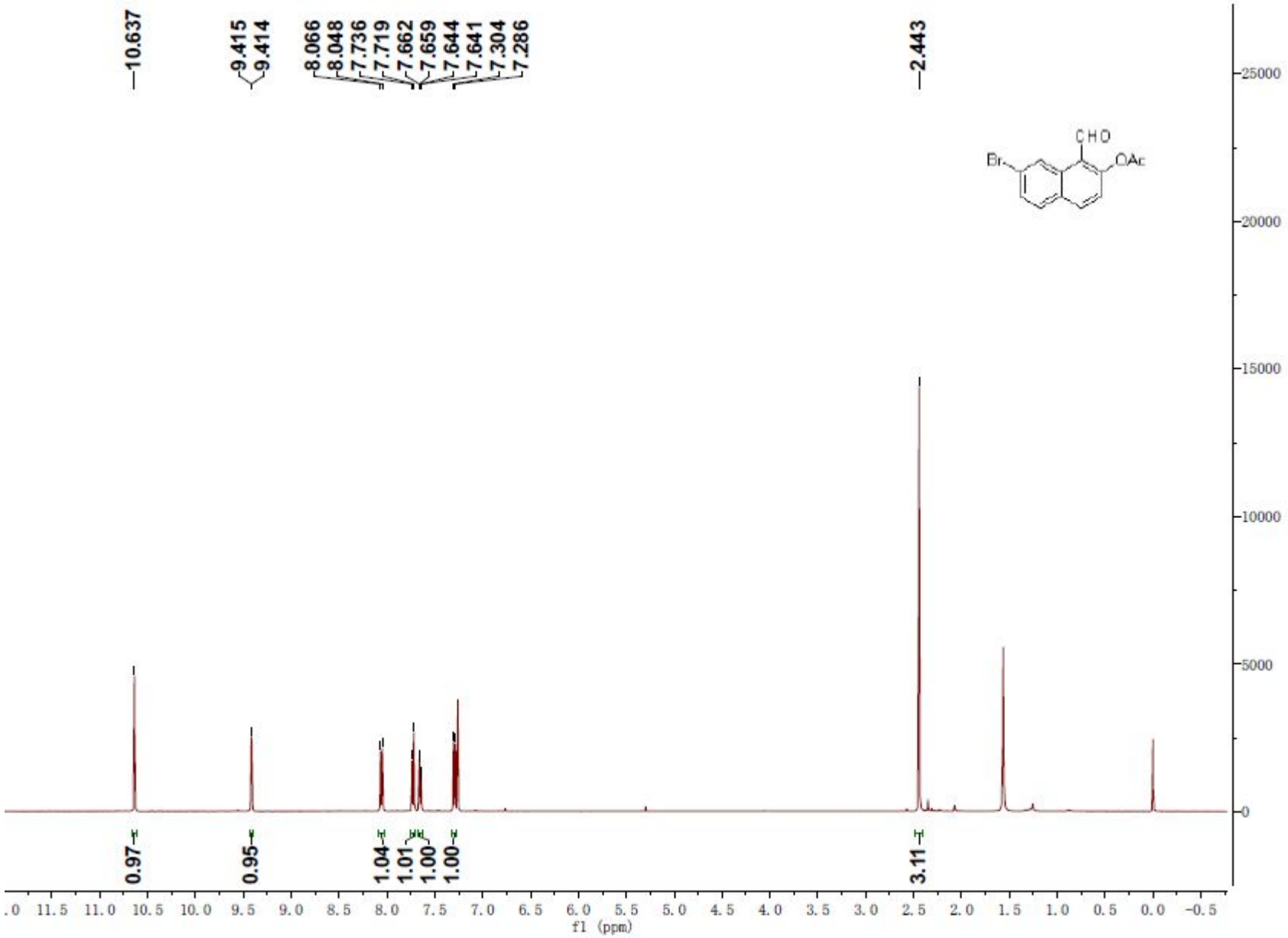
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-bromo-1-formylnaphthalen-2-yl acetate (4h)



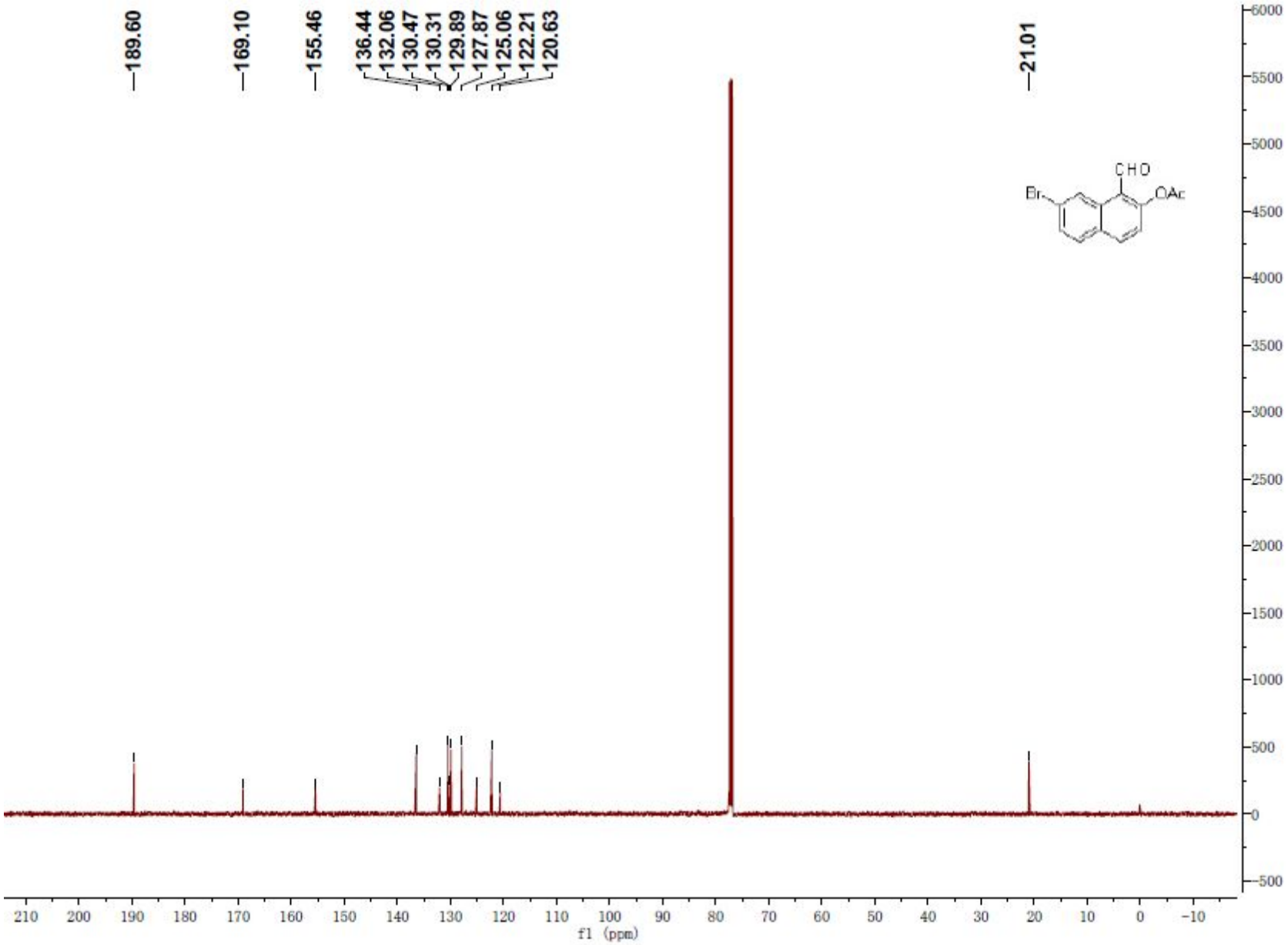
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-bromo-1-formylnaphthalen-2-yl acetate (4h)



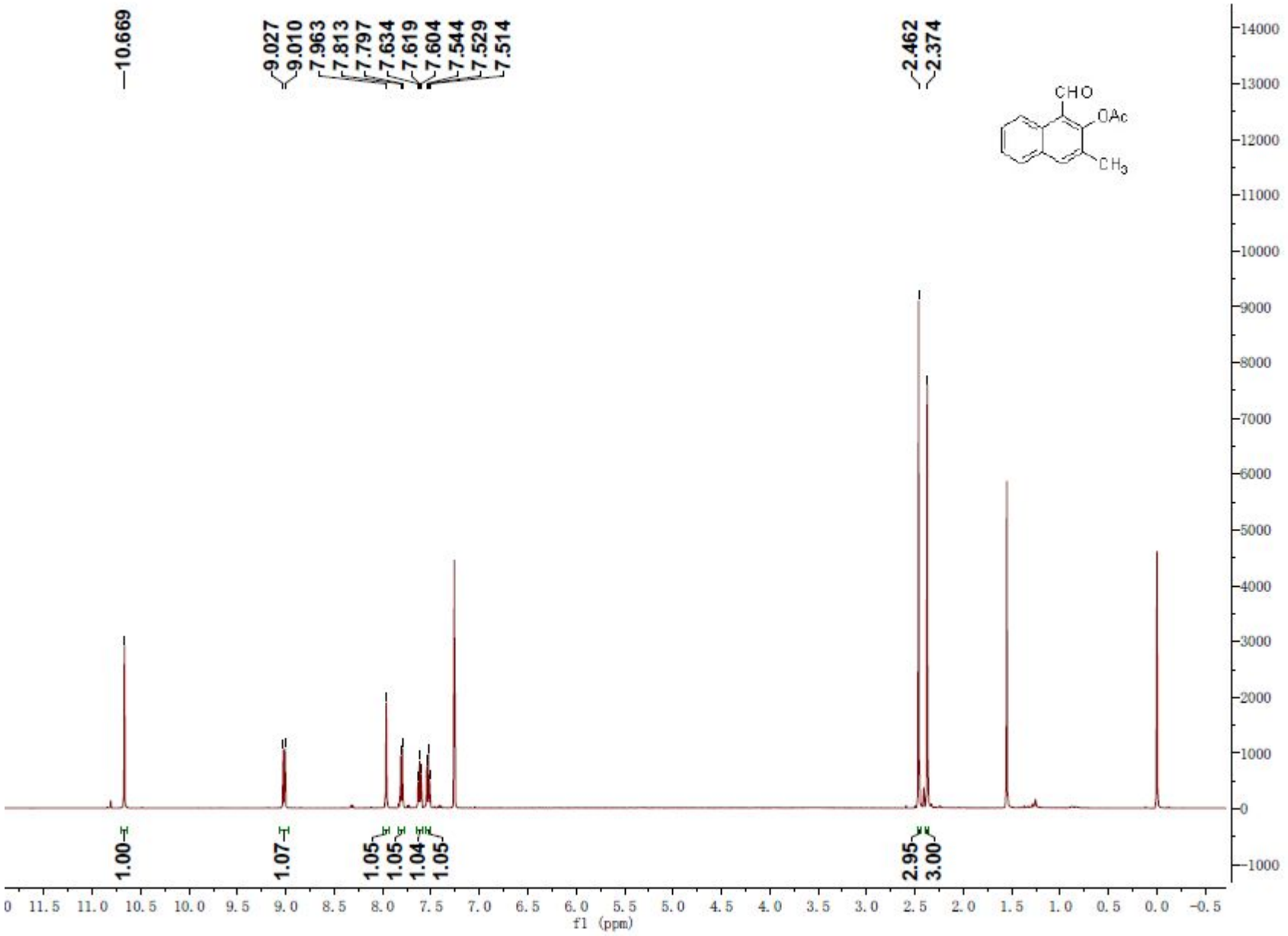
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 7-bromo-1-formylnaphthalen-2-yl acetate (4i)



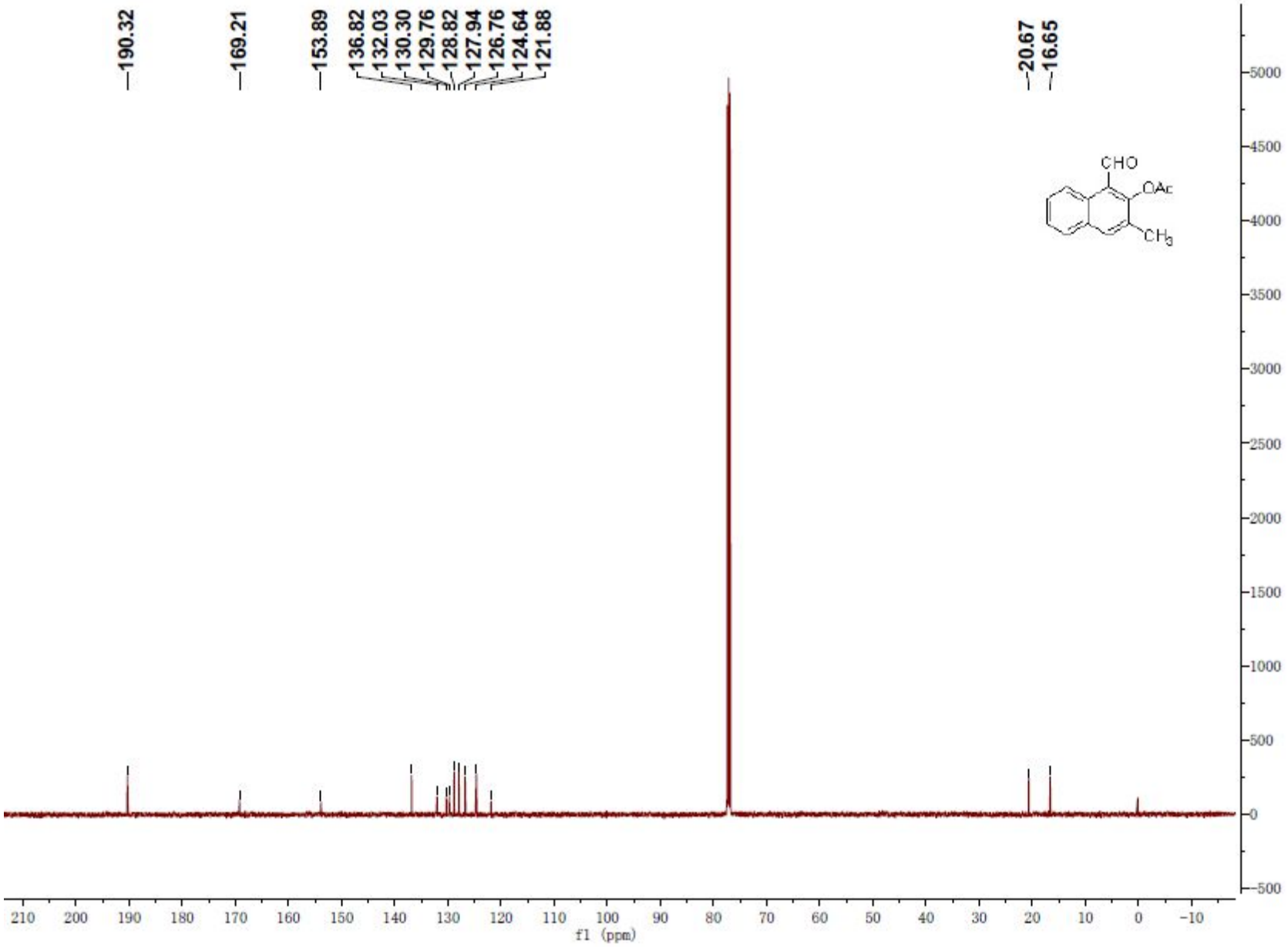
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 7-bromo-1-formylnaphthalen-2-yl acetate (4i)



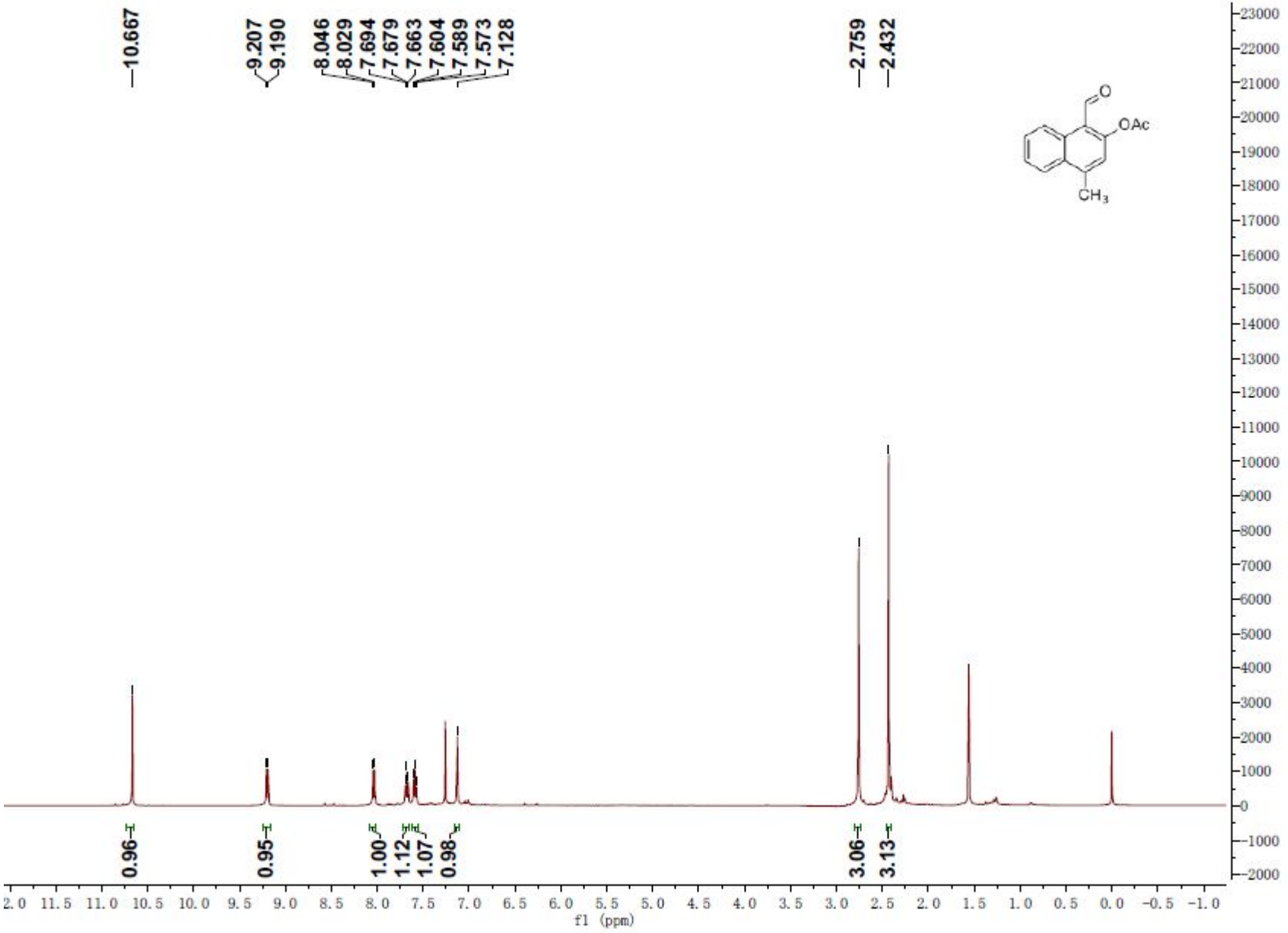
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-3-methylnaphthalen-2-yl acetate (4j)



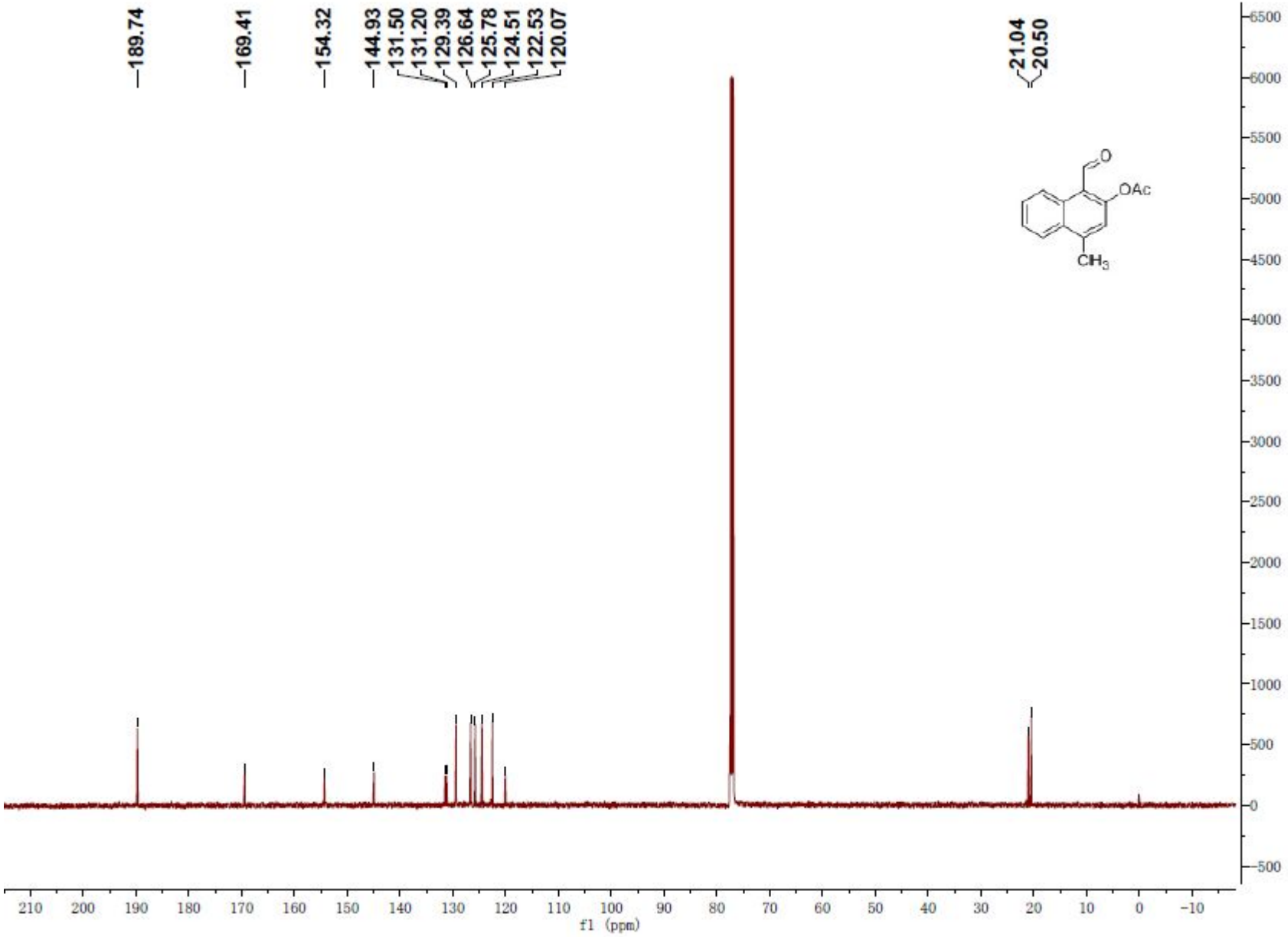
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-3-methylnaphthalen-2-yl acetate (4j)



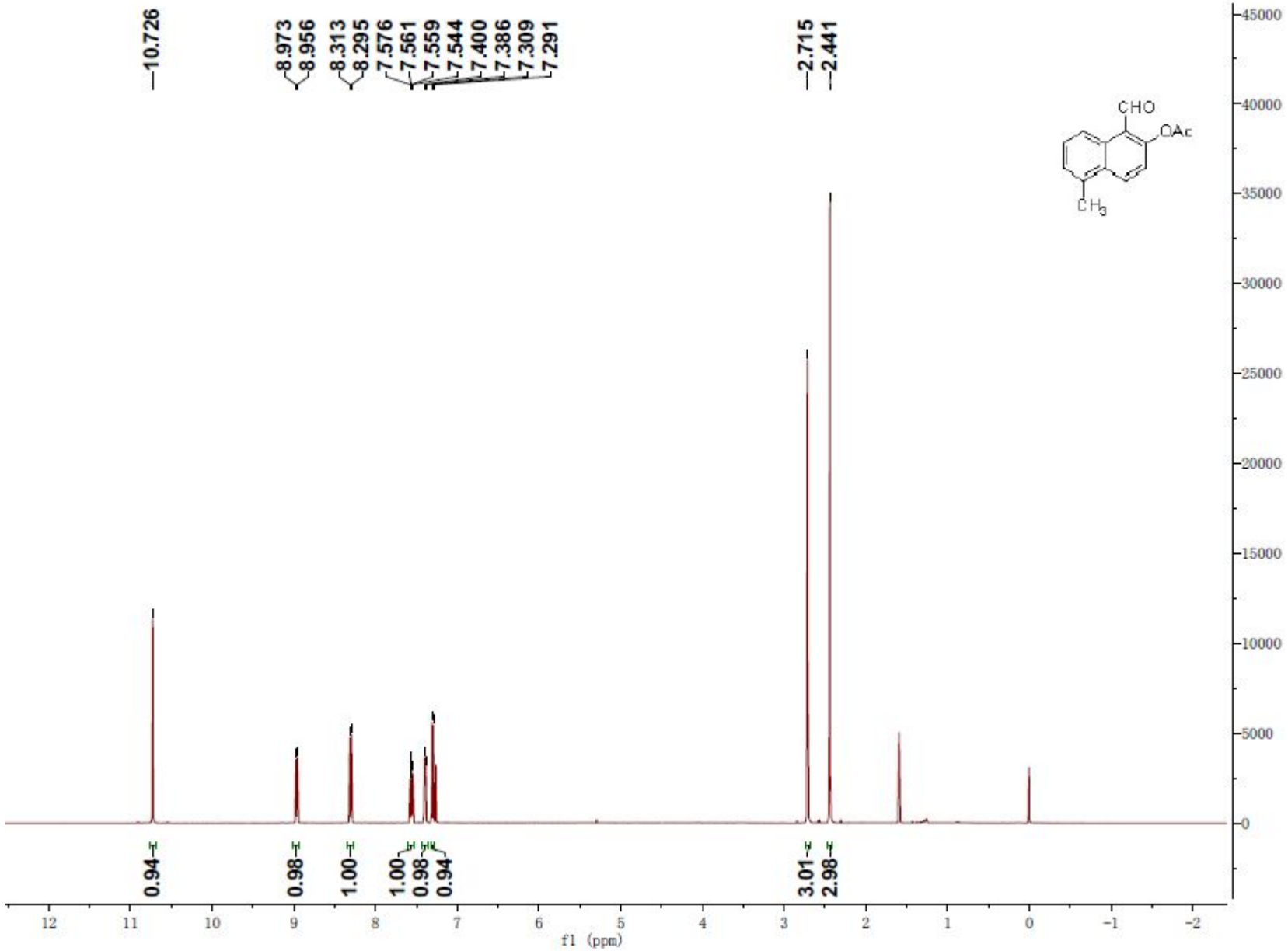
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-4-methylnaphthalen-2-yl acetate (4k)



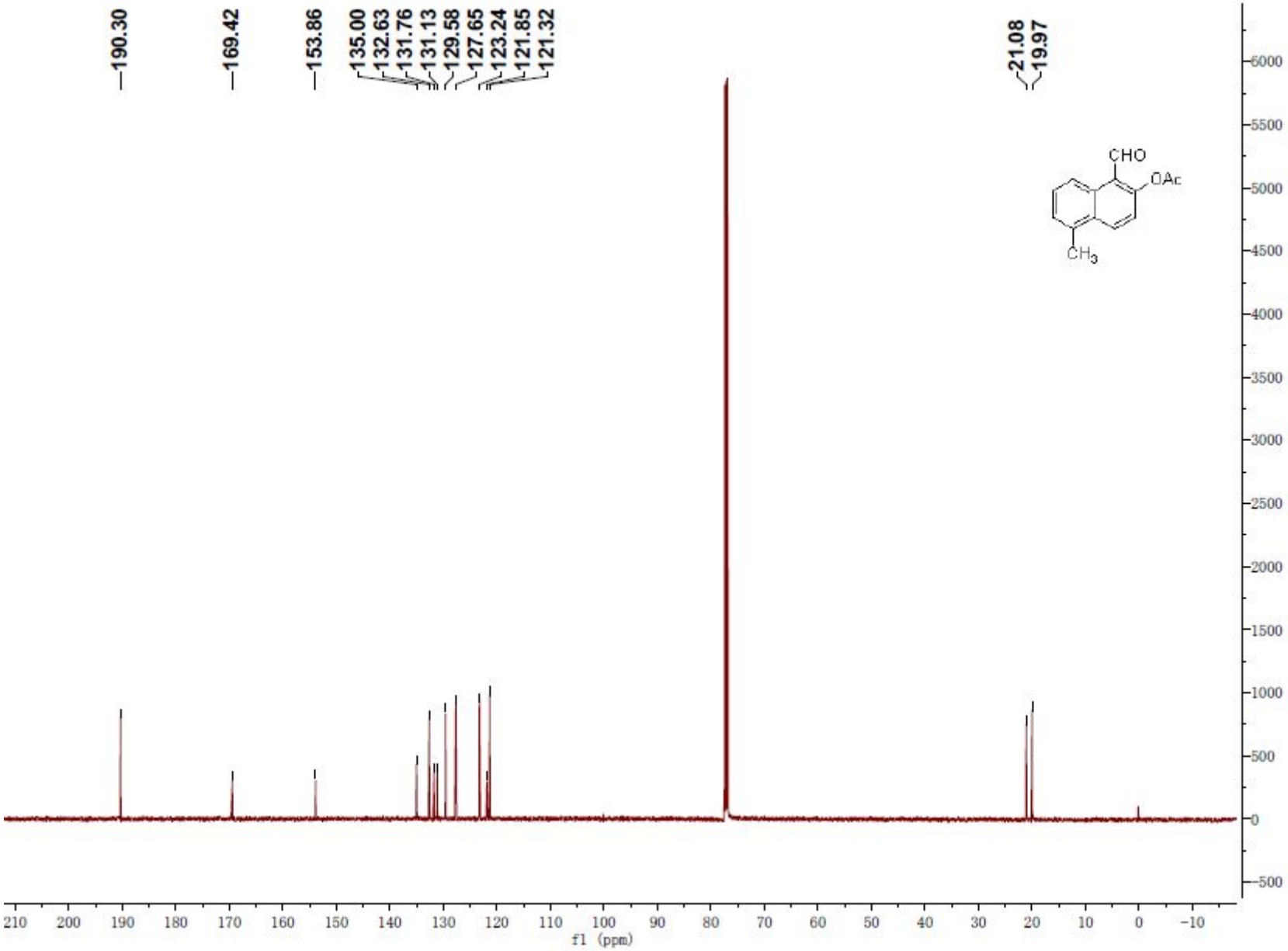
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-4-methylnaphthalen-2-yl acetate (4k)



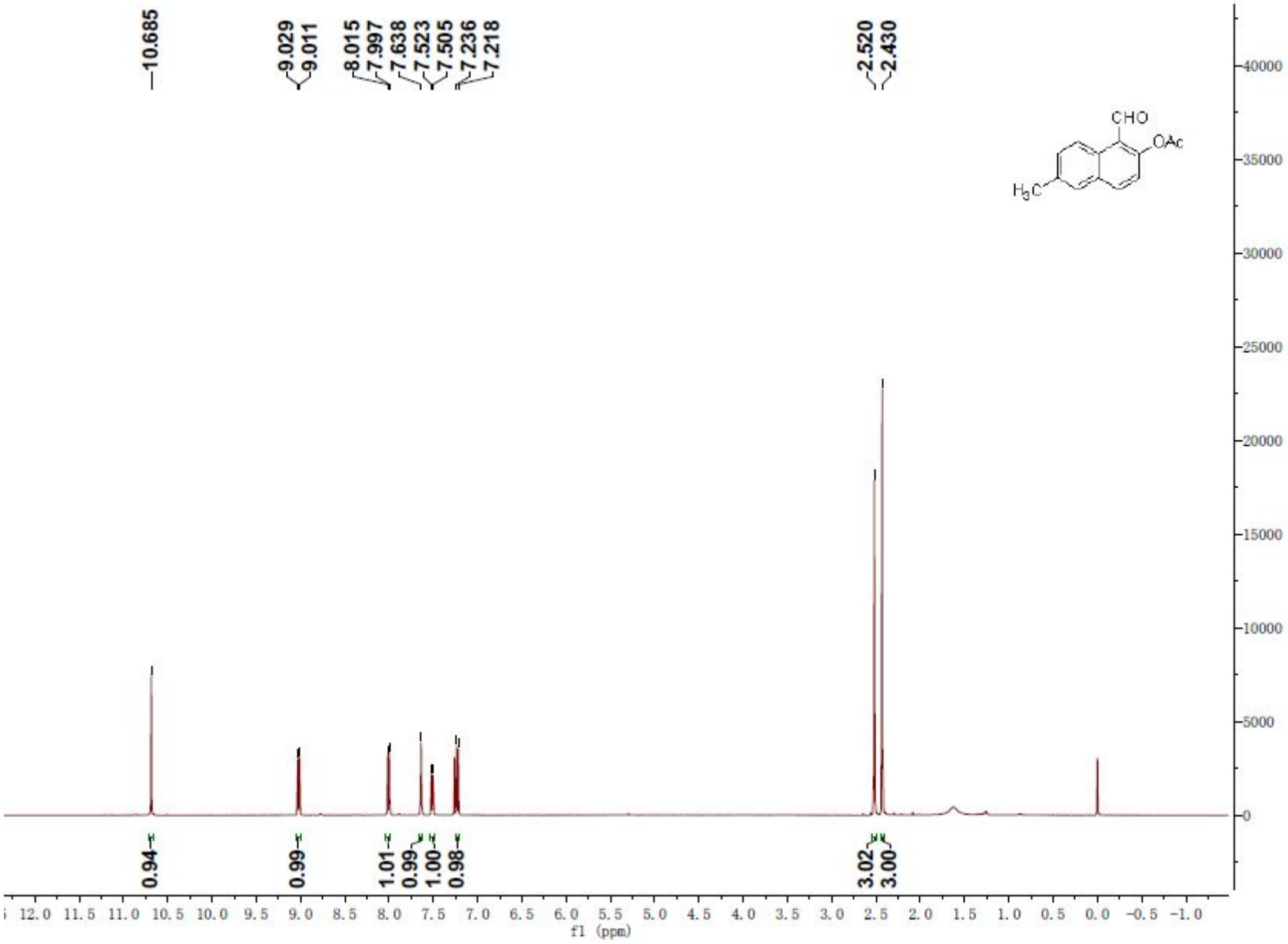
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-5-methylnaphthalen-2-yl acetate (4l)



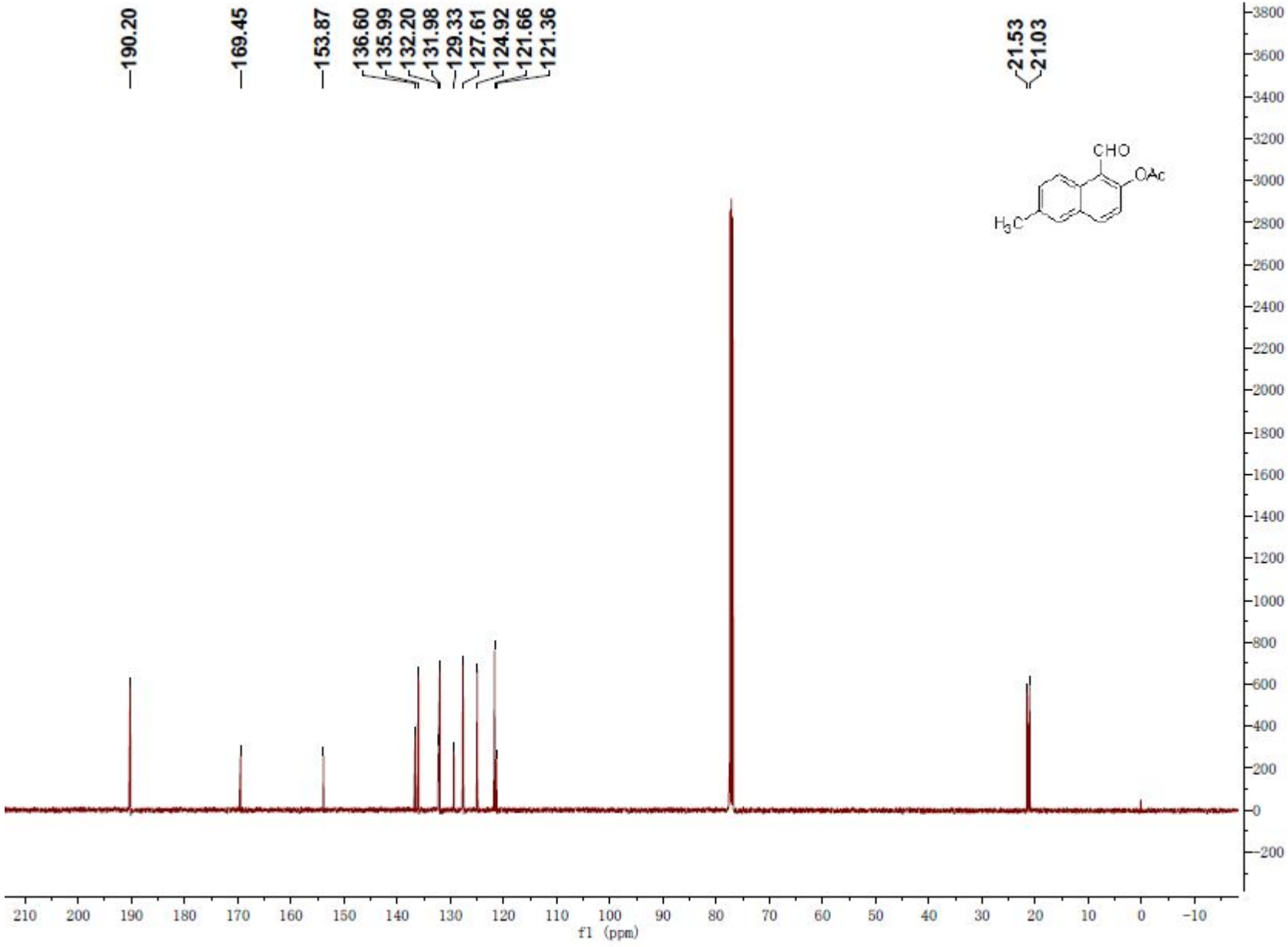
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-5-methylnaphthalen-2-yl acetate (4l)



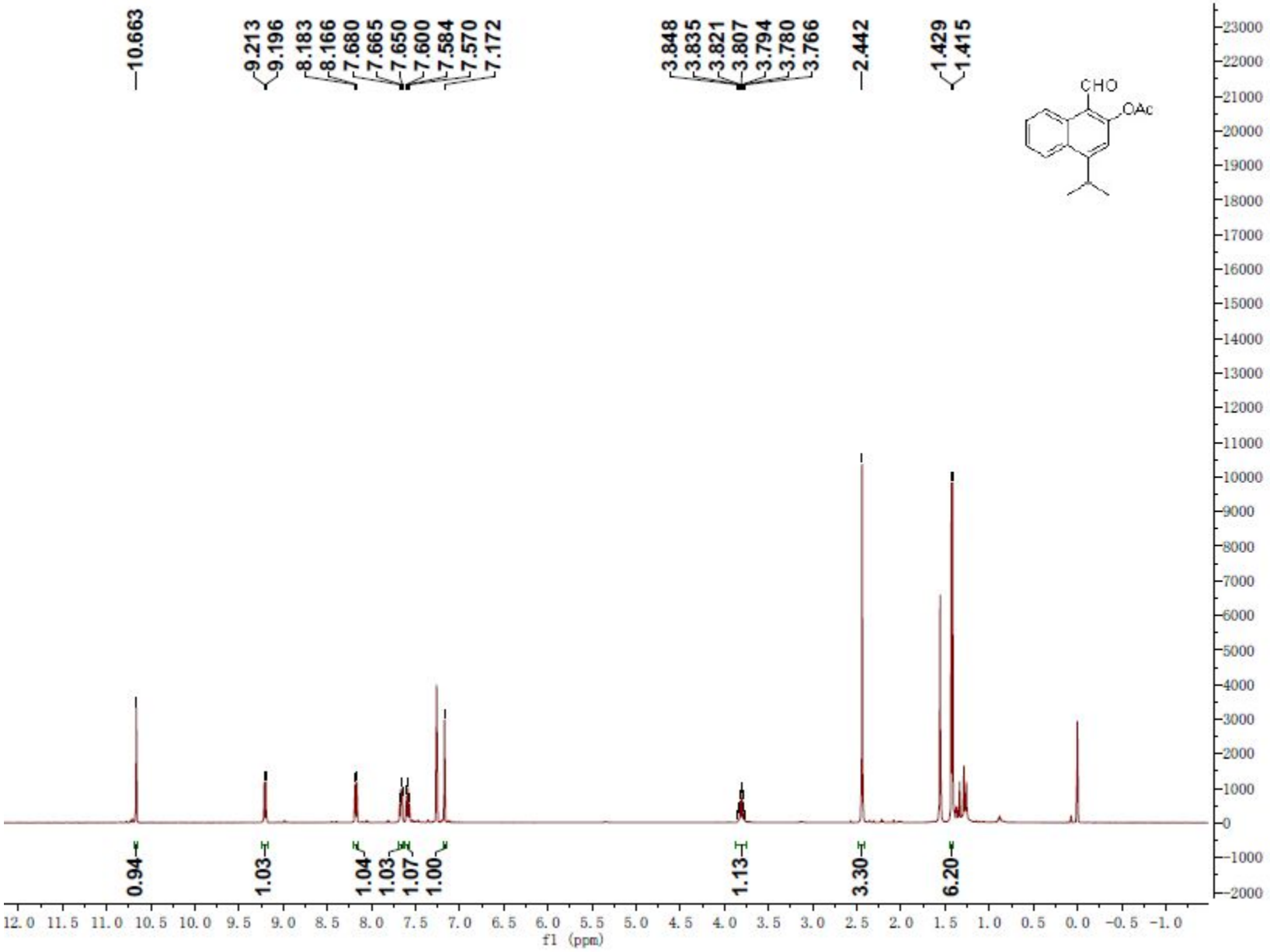
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-6-methylnaphthalen-2-yl acetate (4m)



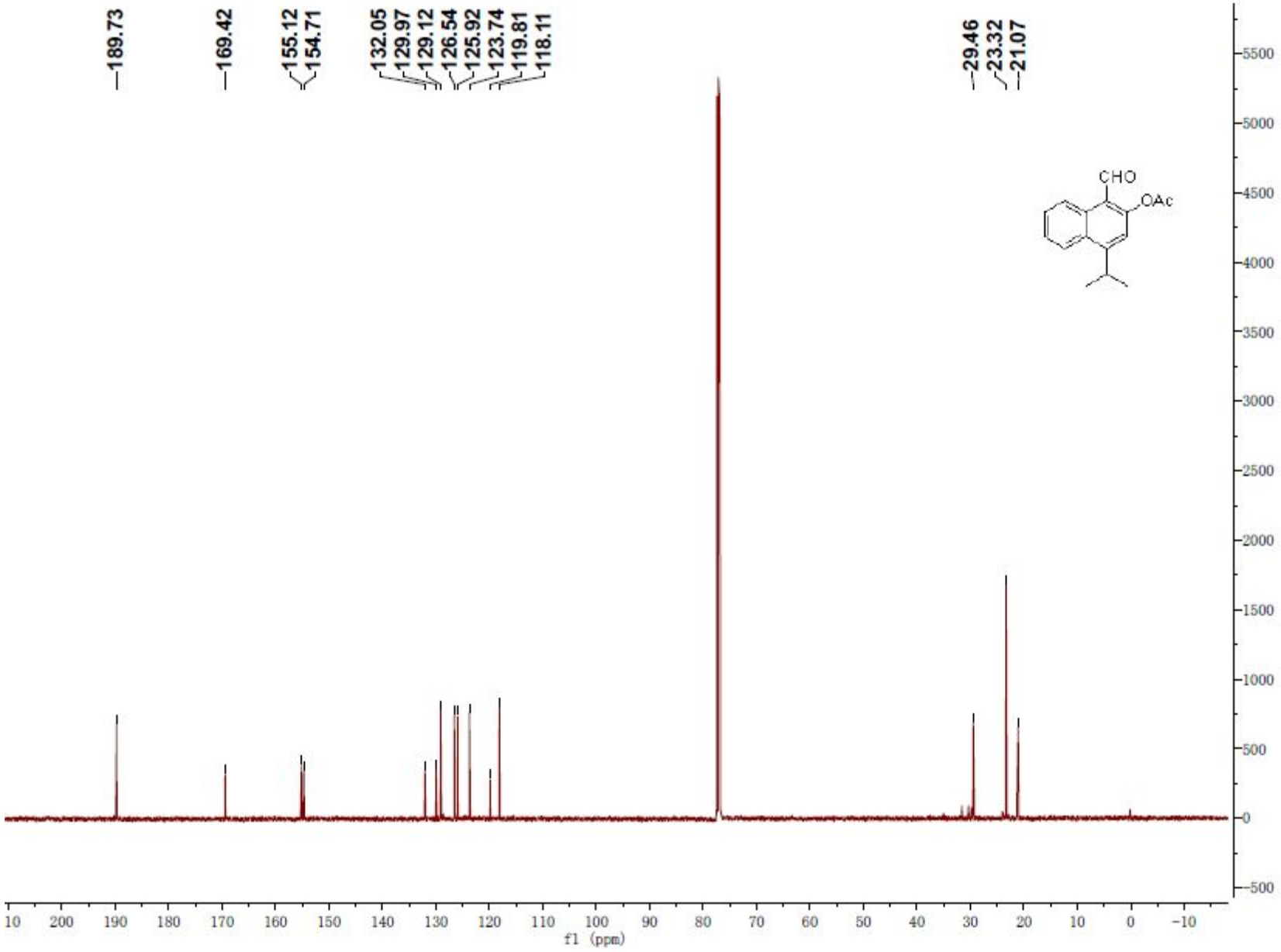
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-6-methylnaphthalen-2-yl acetate (4m)



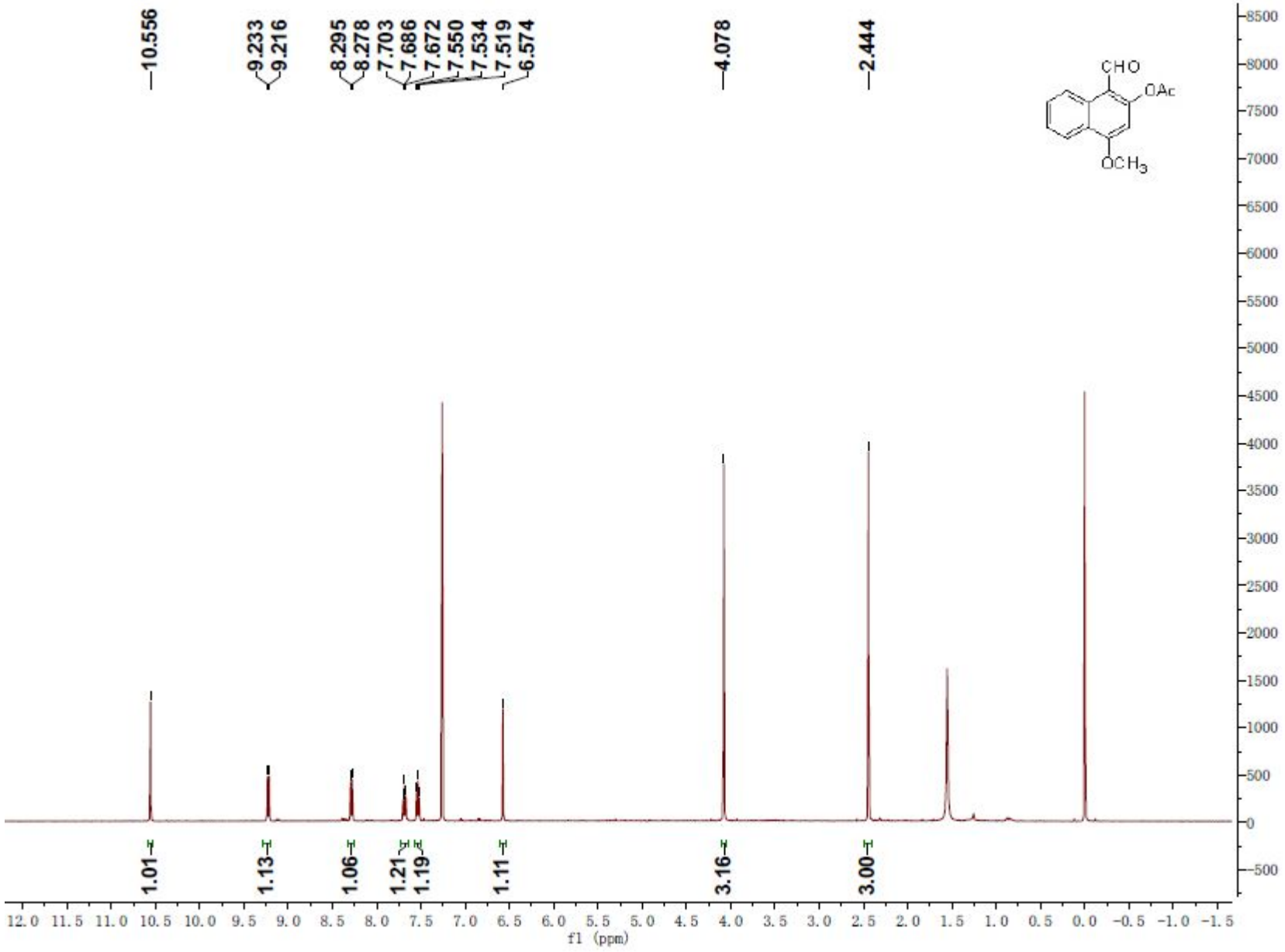
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-4-isopropylnaphthalen-2-yl acetate (4n)



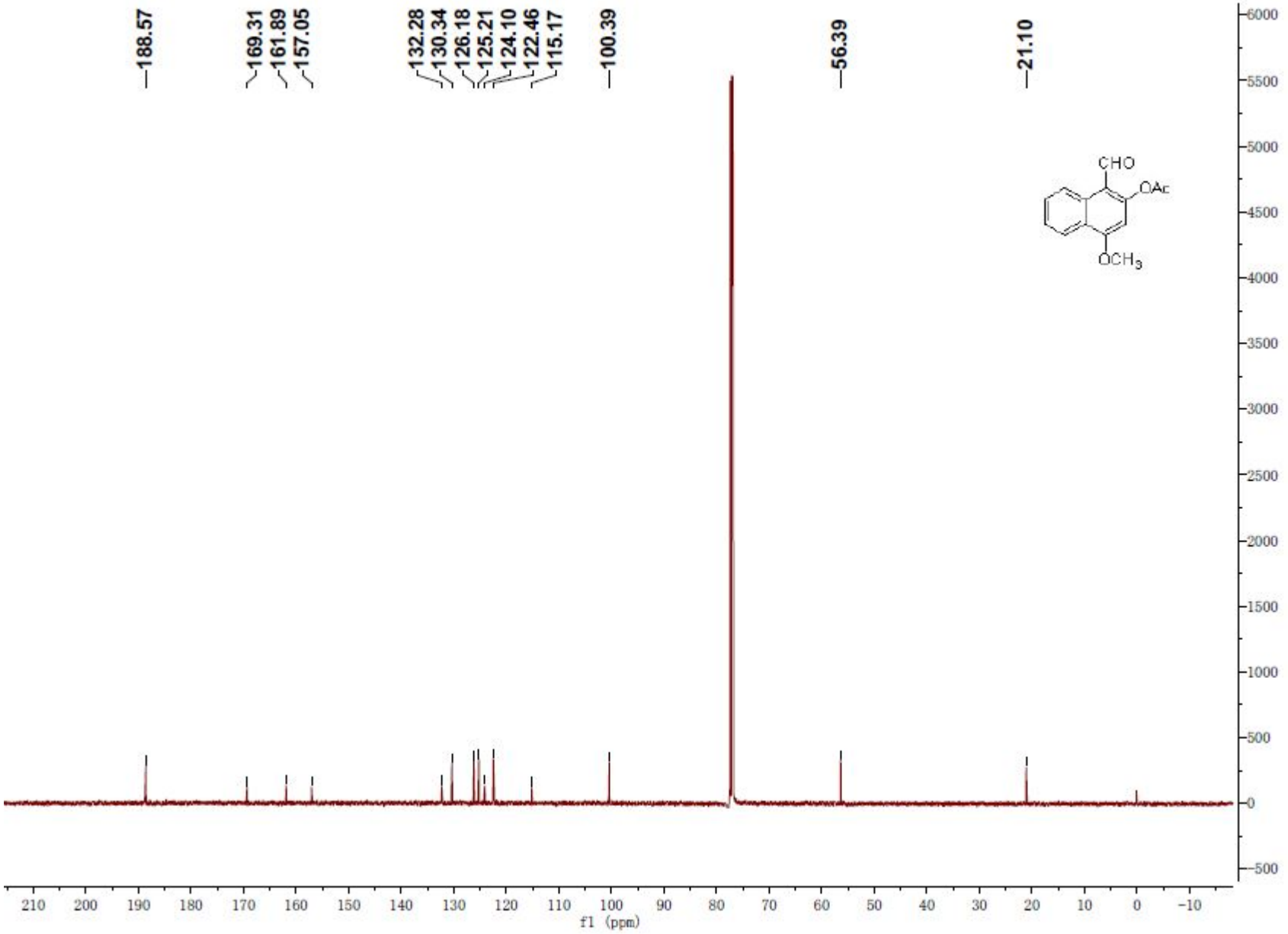
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-4-isopropylnaphthalen-2-yl acetate (4n)



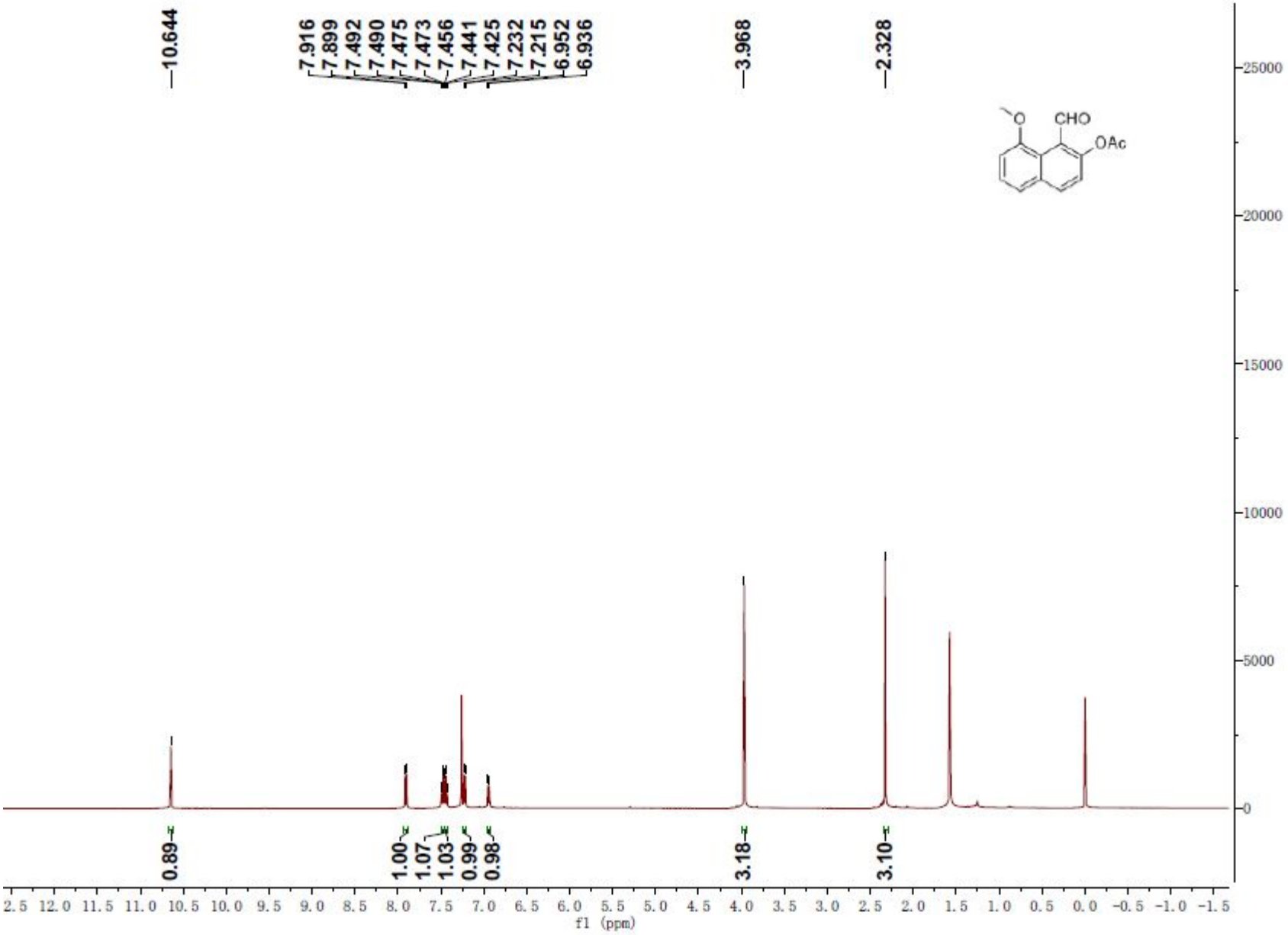
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-4-methoxynaphthalen-2-yl acetate (4o)



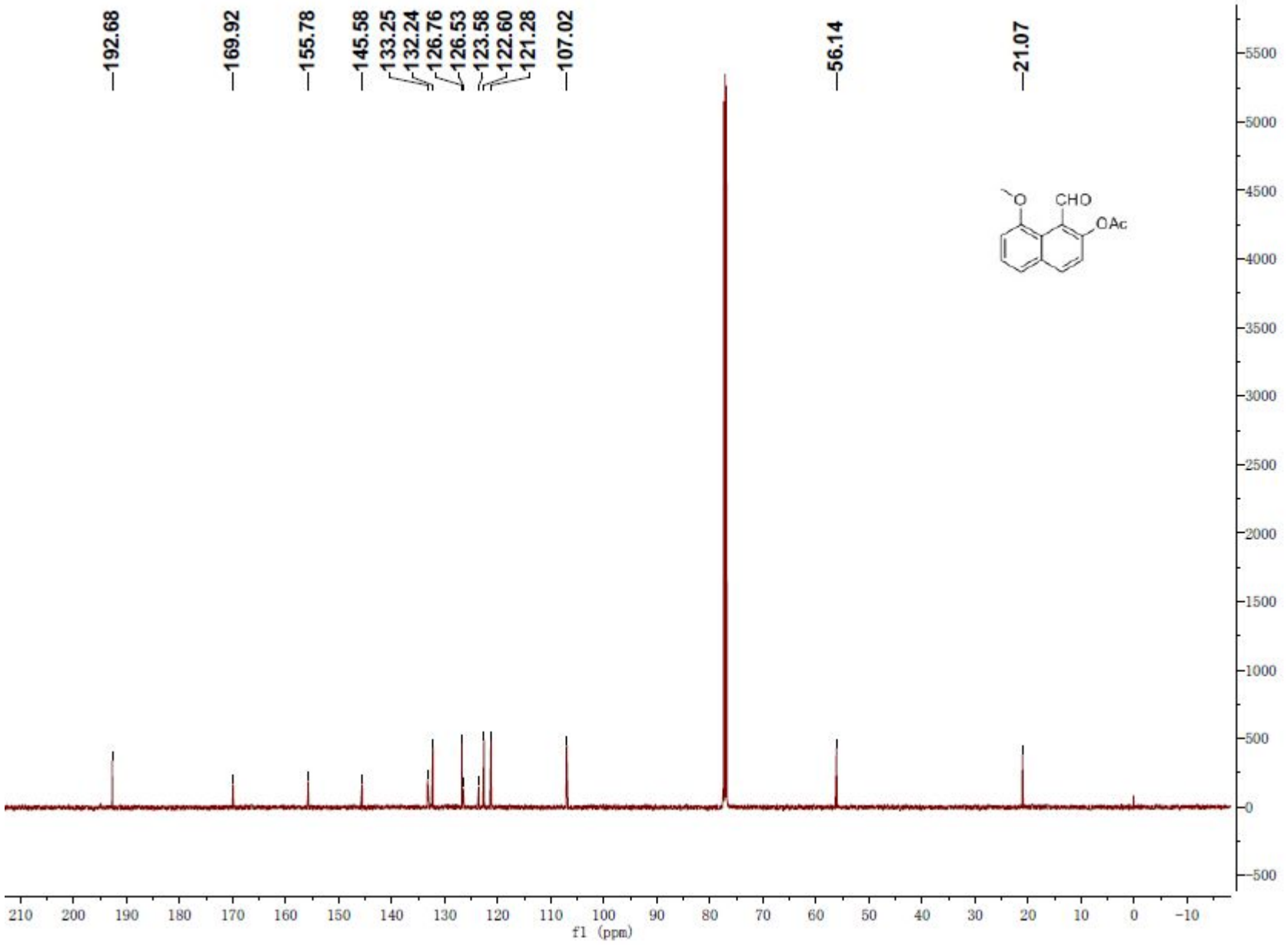
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-4-methoxynaphthalen-2-yl acetate (4o)



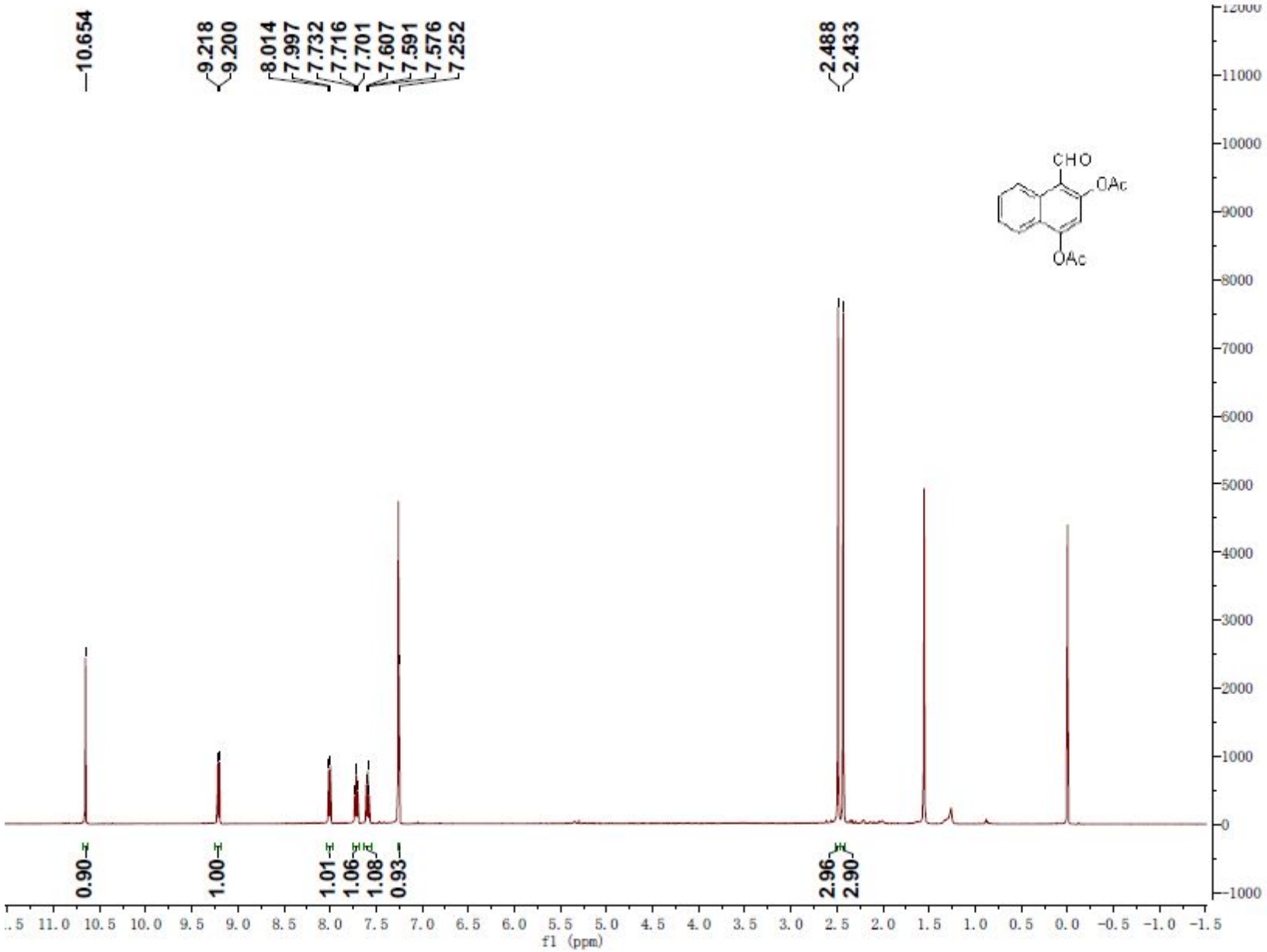
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-8-methoxynaphthalen-2-yl acetate (4p)



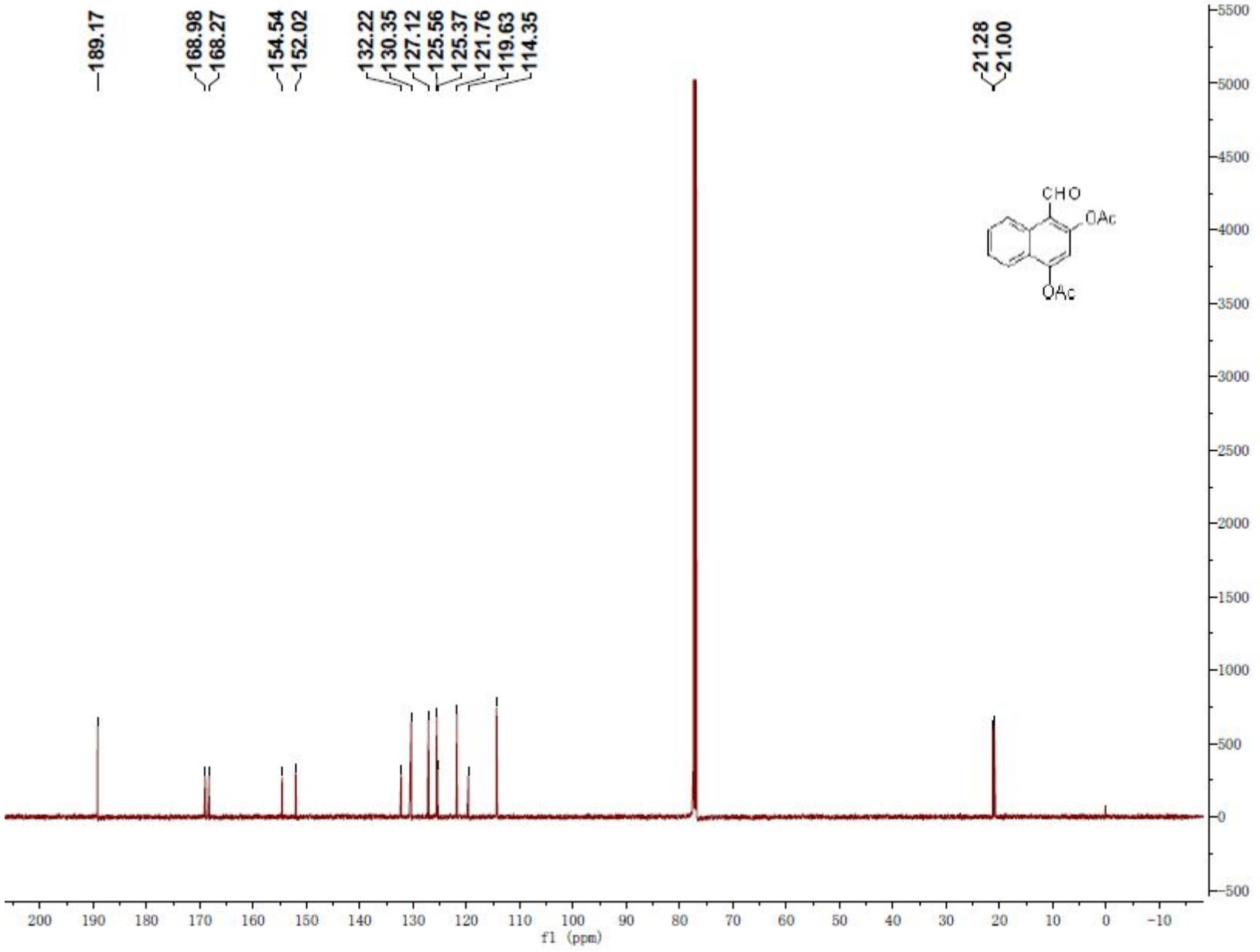
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-8-methoxynaphthalen-2-yl acetate (4p)



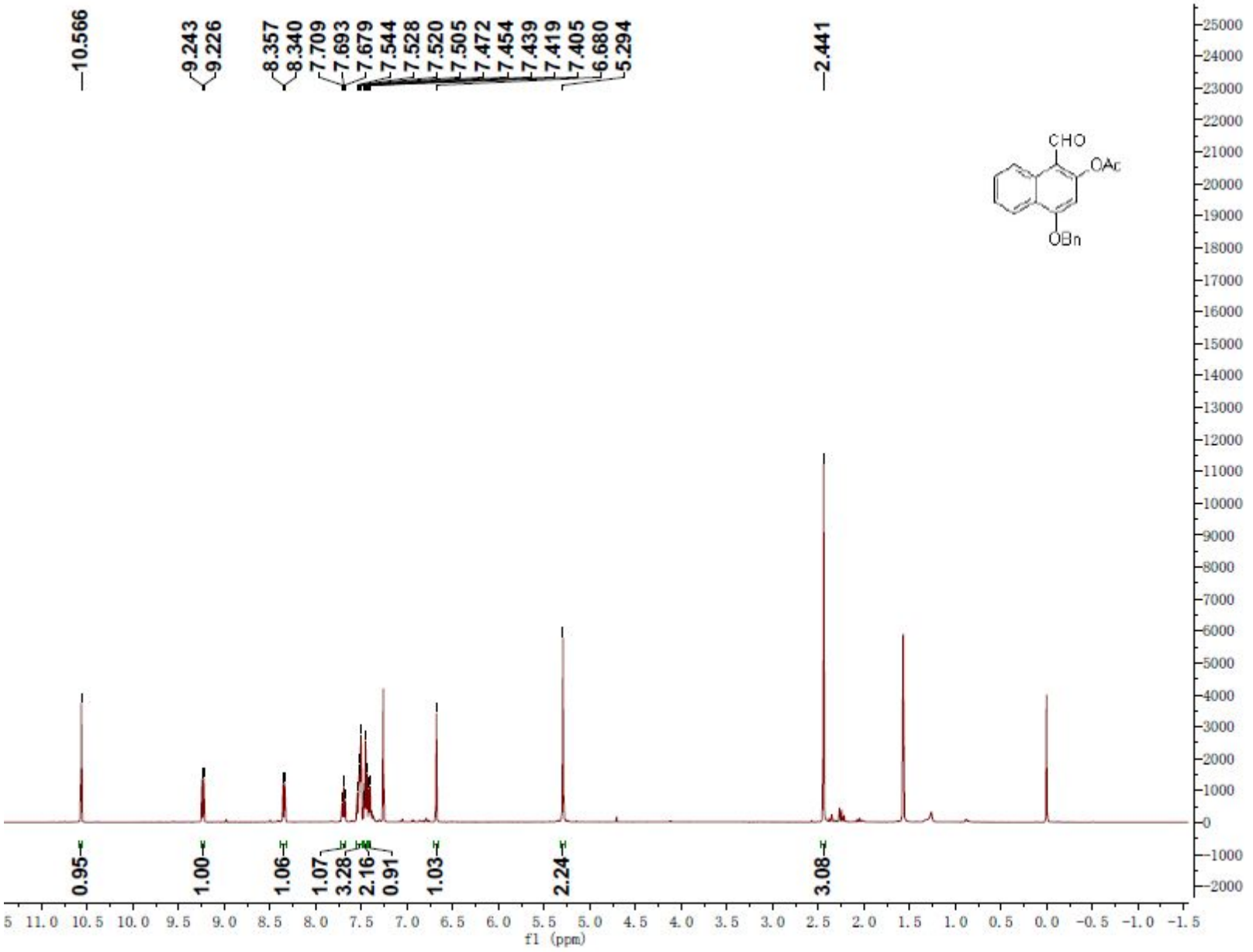
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-formylnaphthalene-1,3-diyl diacetate (4q)



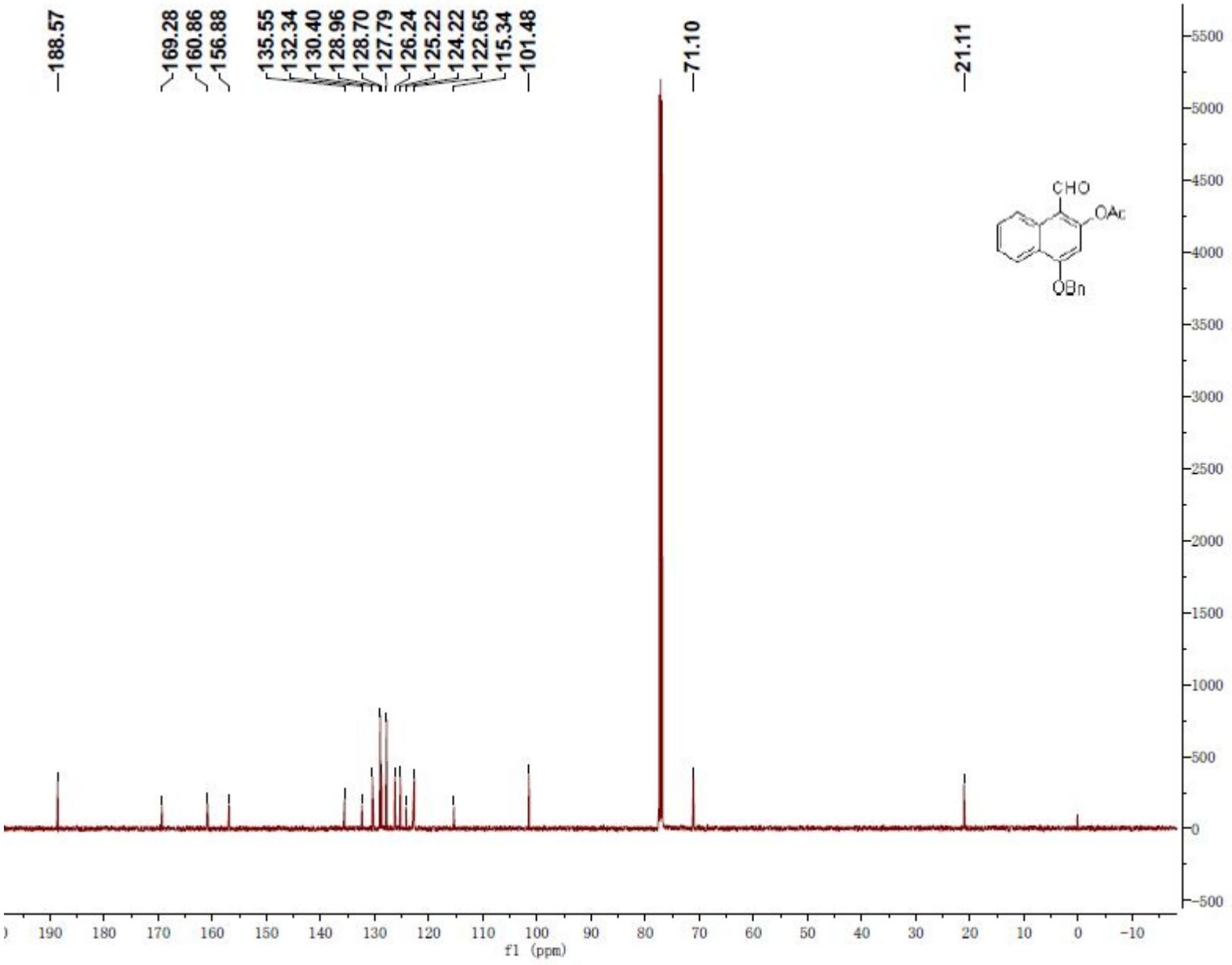
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-formylnaphthalene-1,3-diyl diacetate (4q)



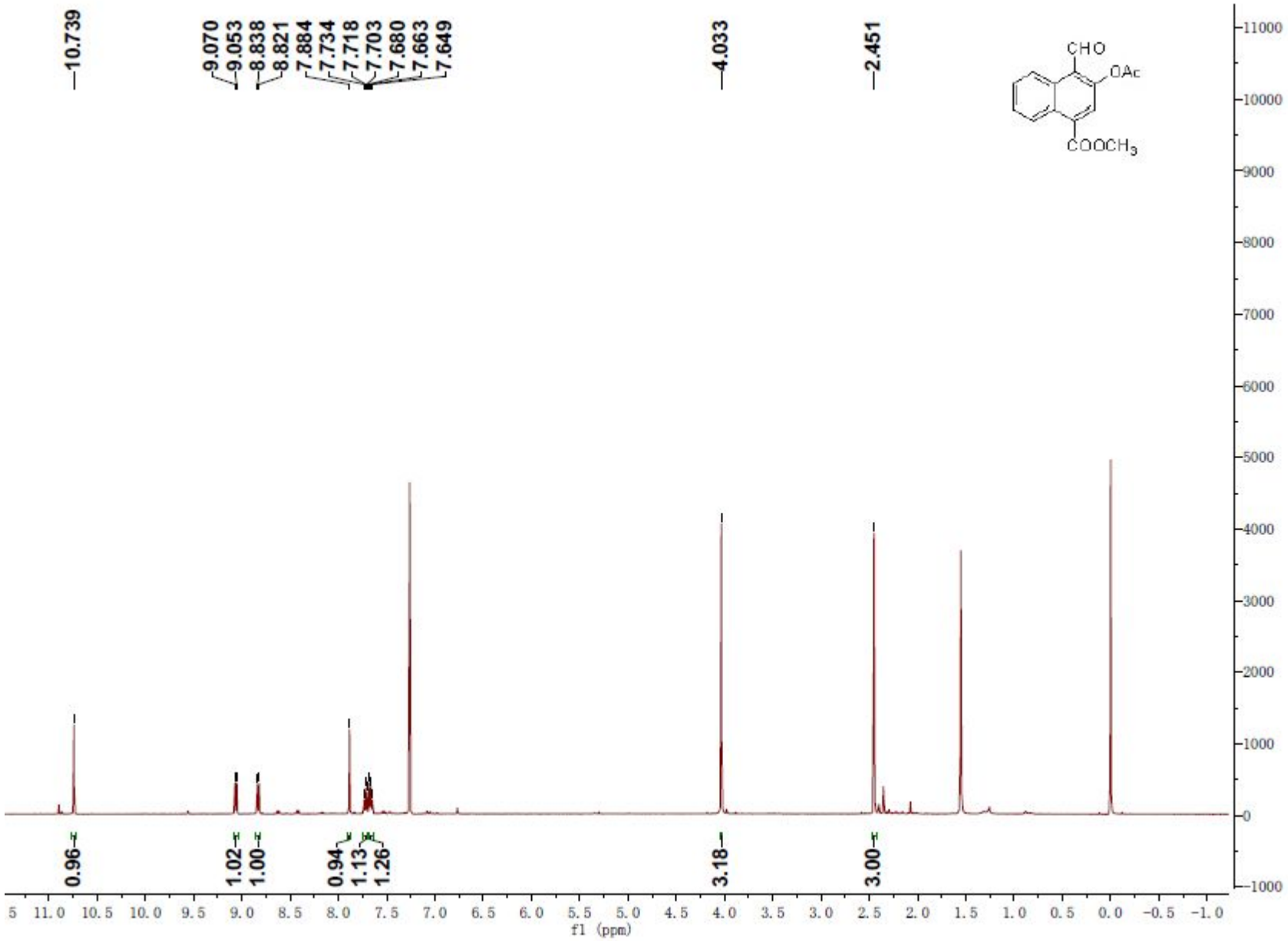
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-(benzyloxy)-1-formylnaphthalen-2-yl acetate (4r)



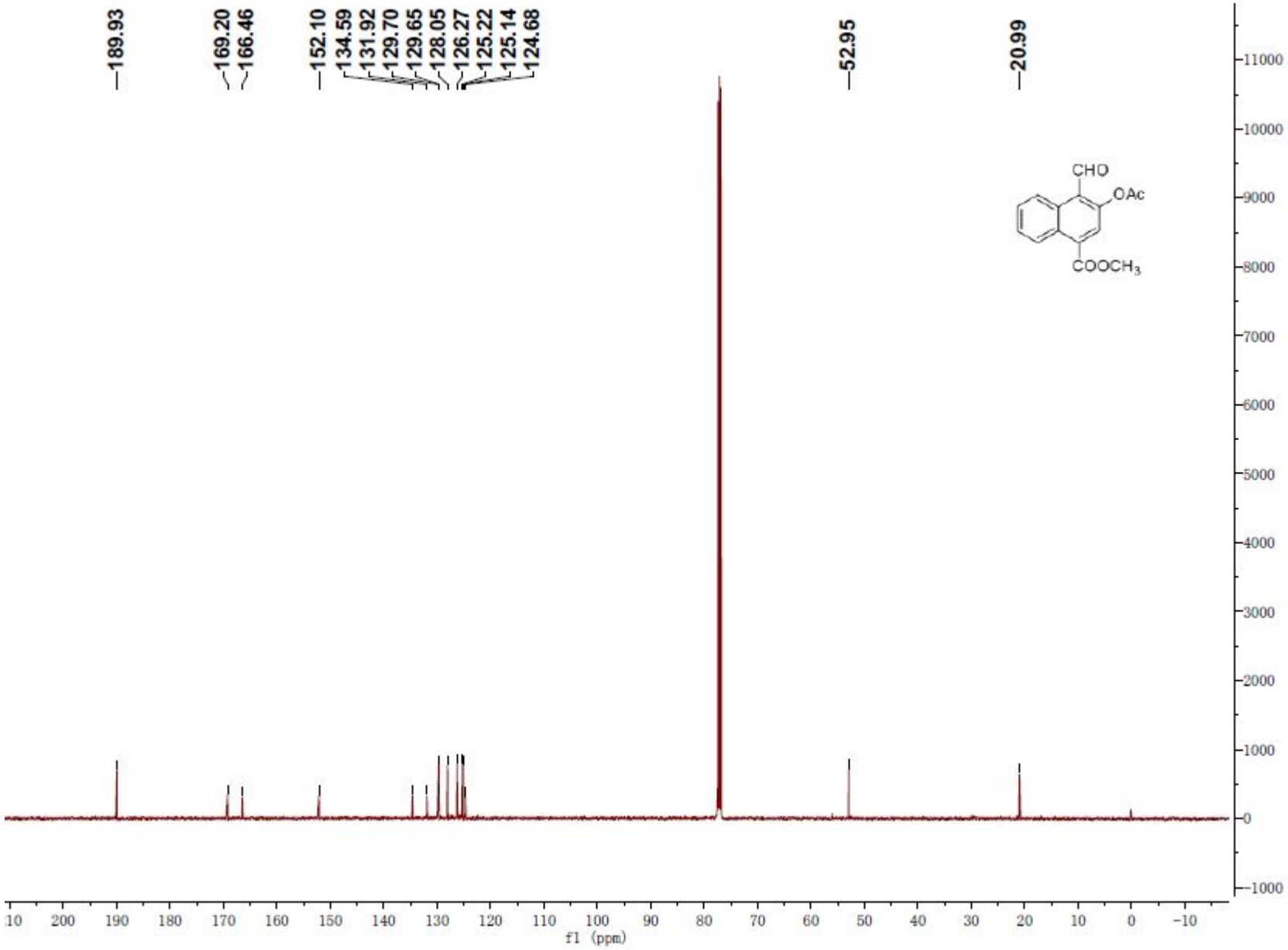
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-(benzyloxy)-1-formylnaphthalen-2-yl acetate (4r)



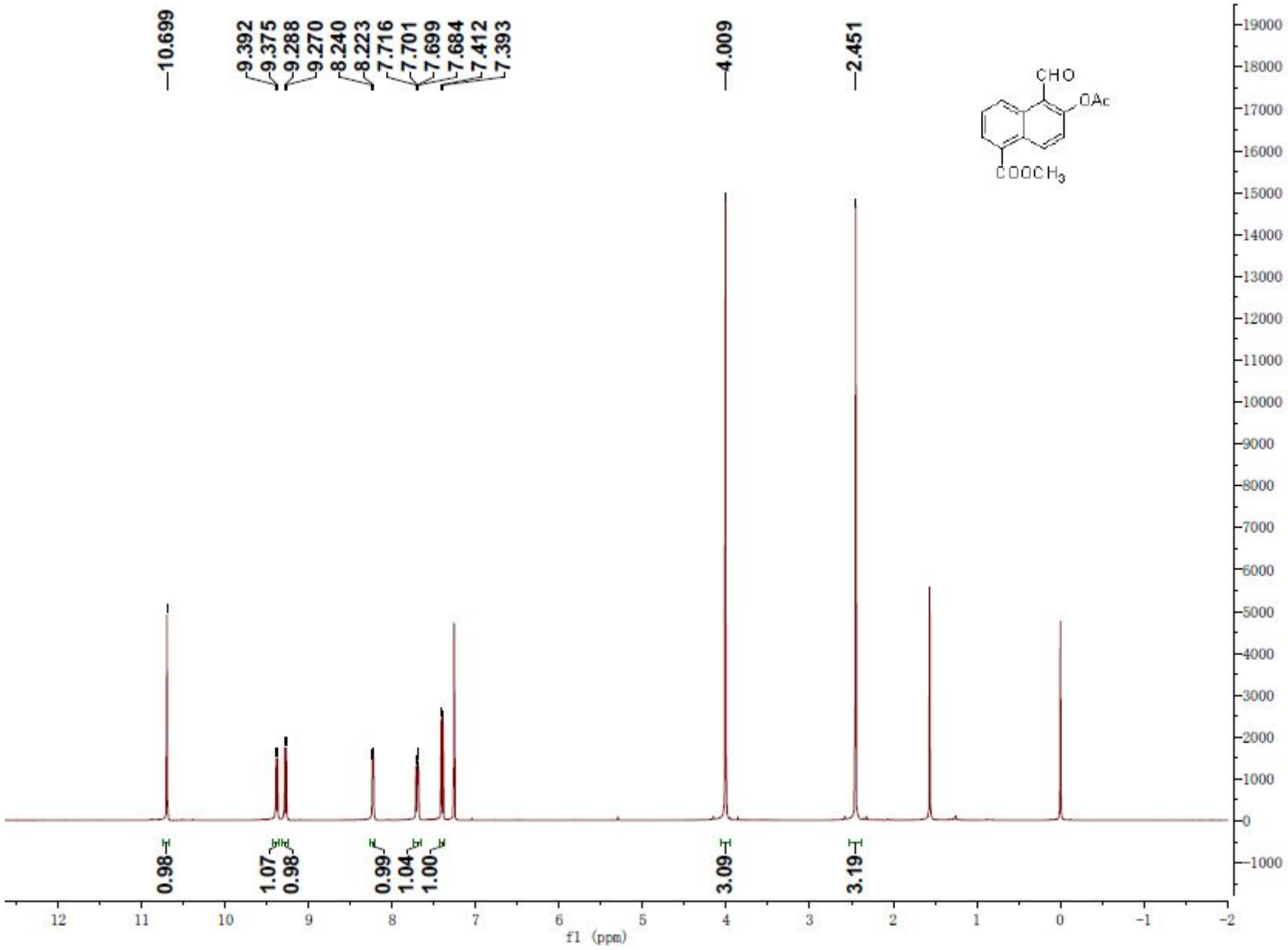
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of methyl 3-acetoxy-4-formyl-1-naphthoate (4s)



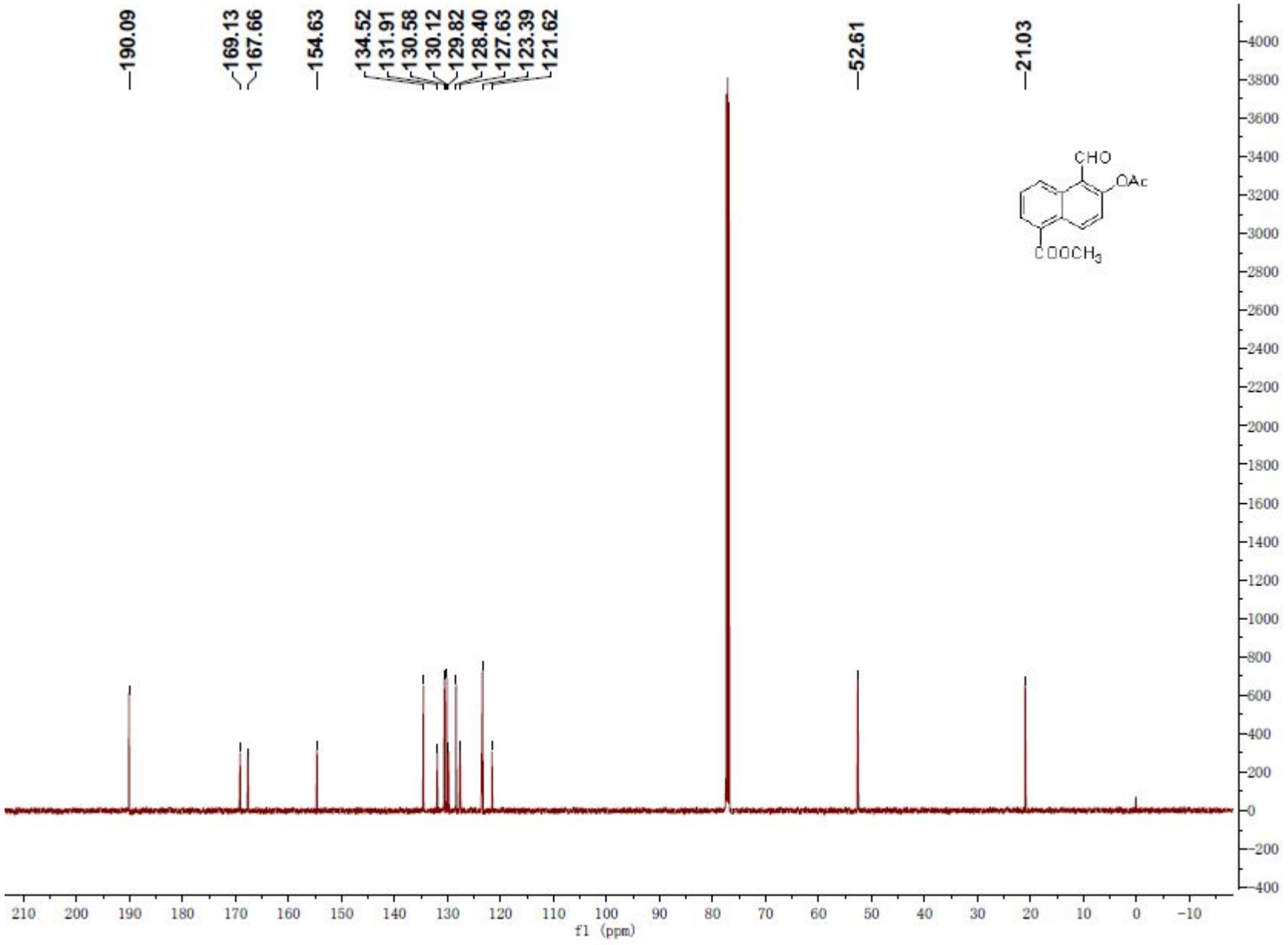
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of methyl 3-acetoxy-4-formyl-1-naphthoate (4s)



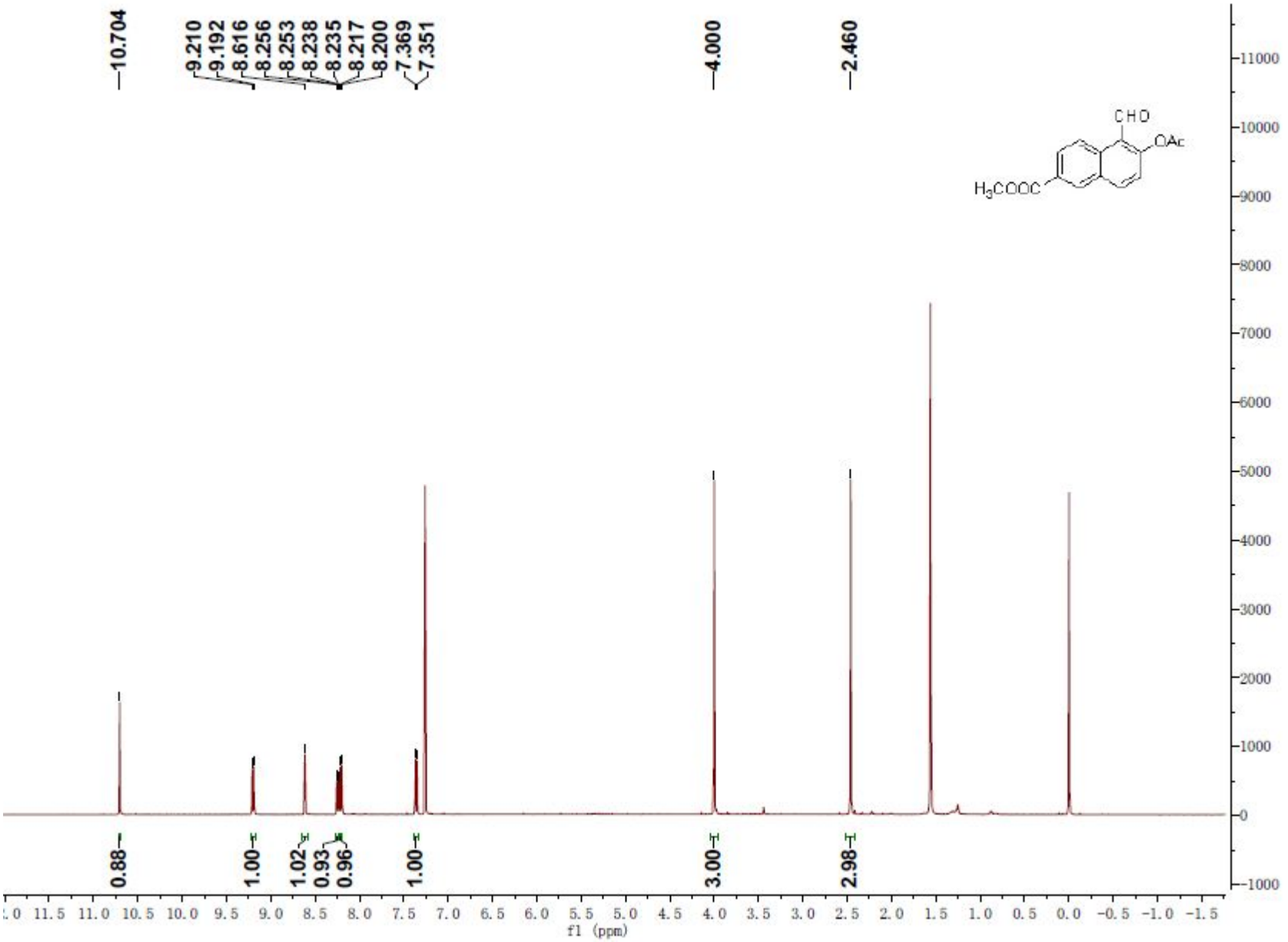
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of methyl 6-acetoxy-5-formyl-1-naphthoate (4t)



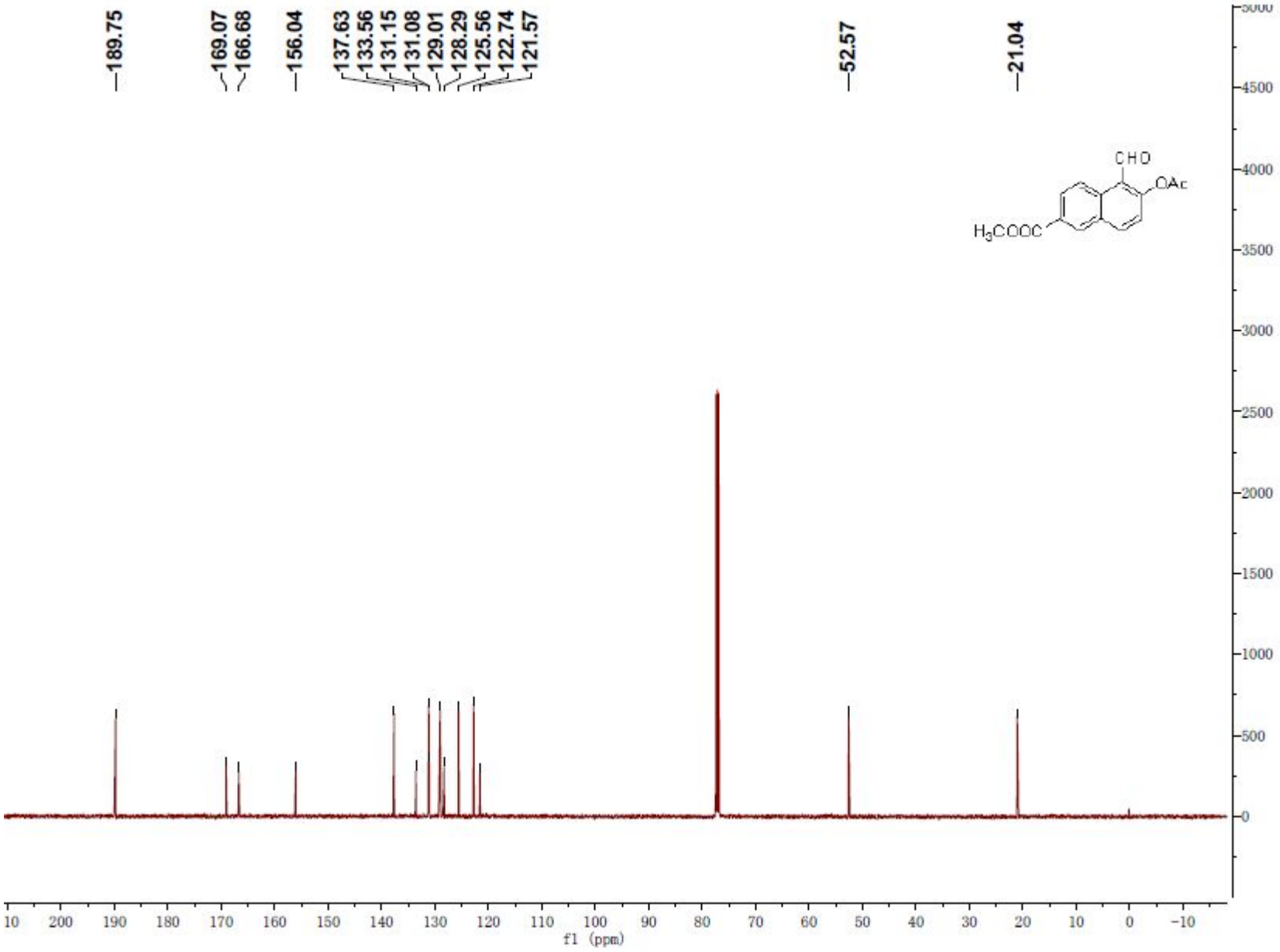
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of methyl 6-acetoxy-5-formyl-1-naphthoate (4t)



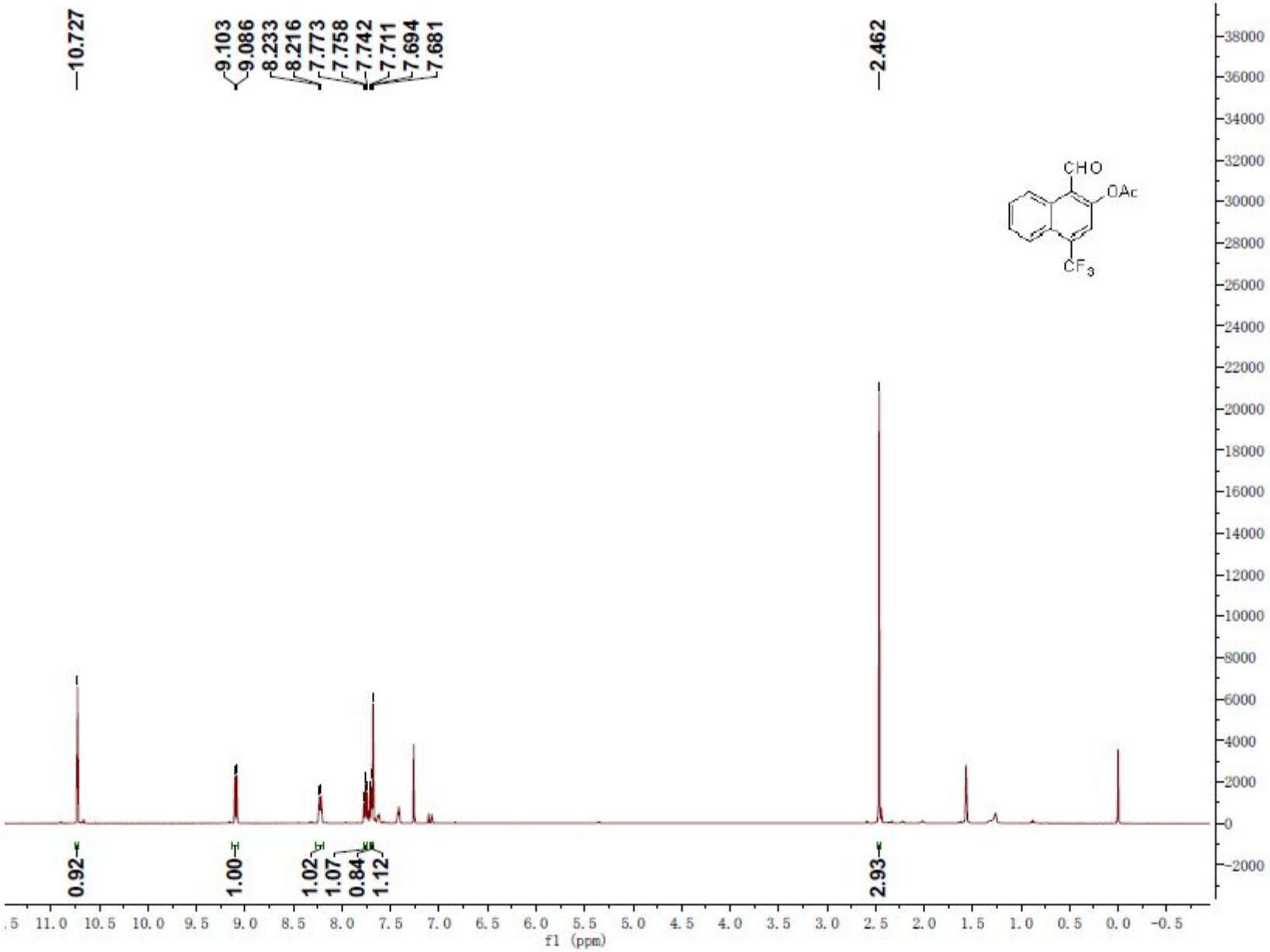
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of methyl 6-acetoxy-5-formyl-2-naphthoate (4u)



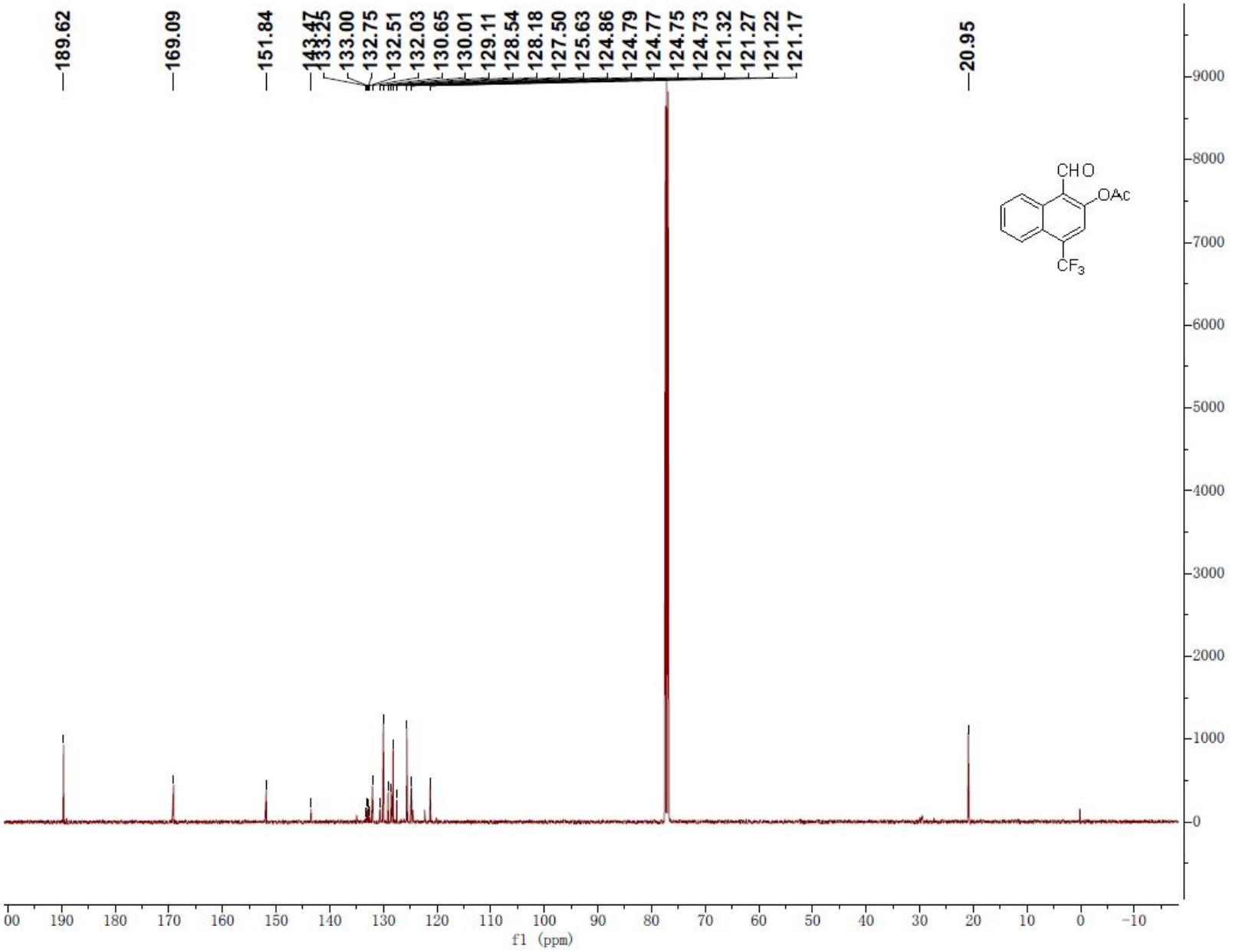
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of methyl 6-acetoxy-5-formyl-2-naphthoate (4u)



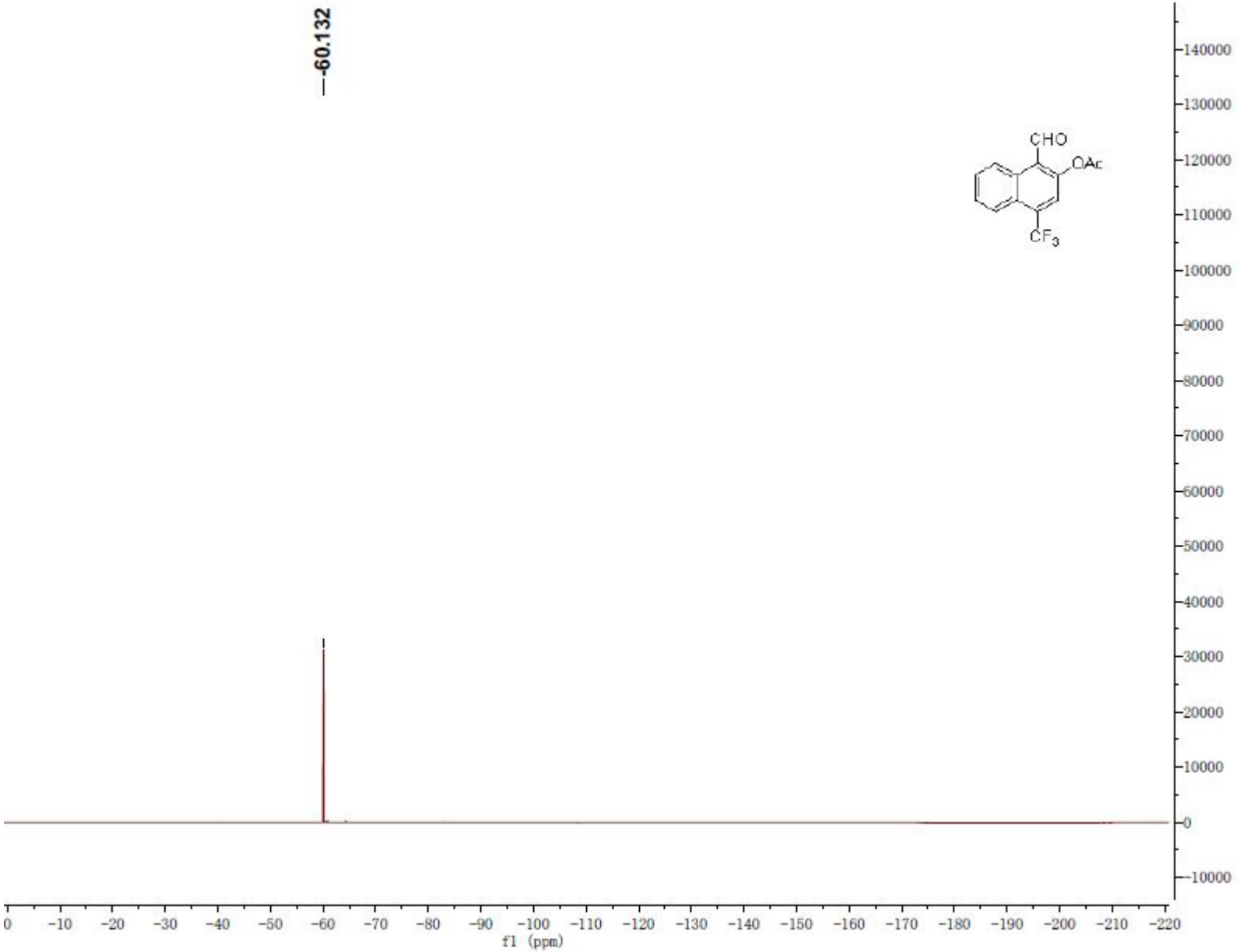
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-4-(trifluoromethyl)naphthalen-2-yl acetate (4v)



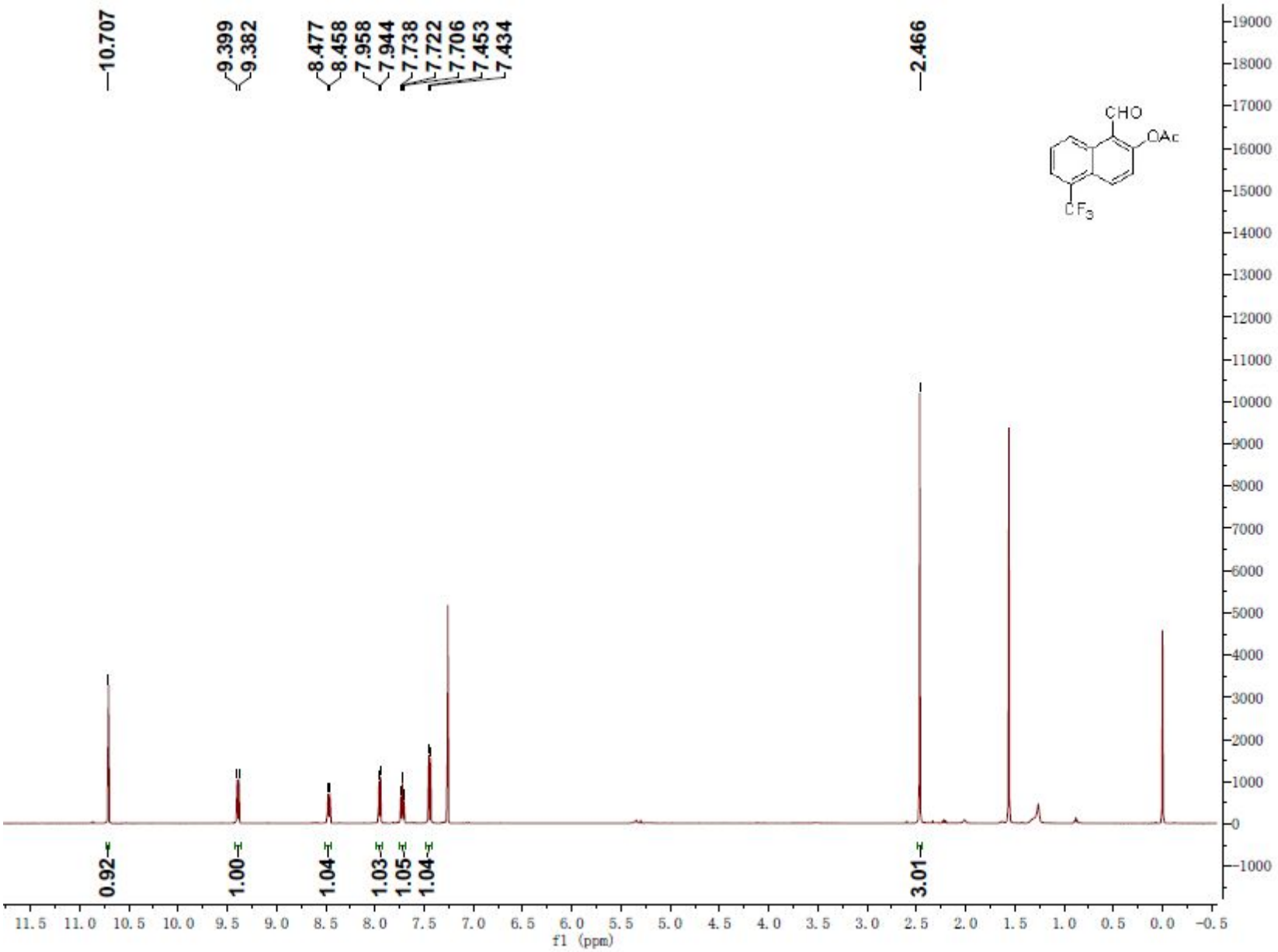
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-4-(trifluoromethyl)naphthalen-2-yl acetate (4v)



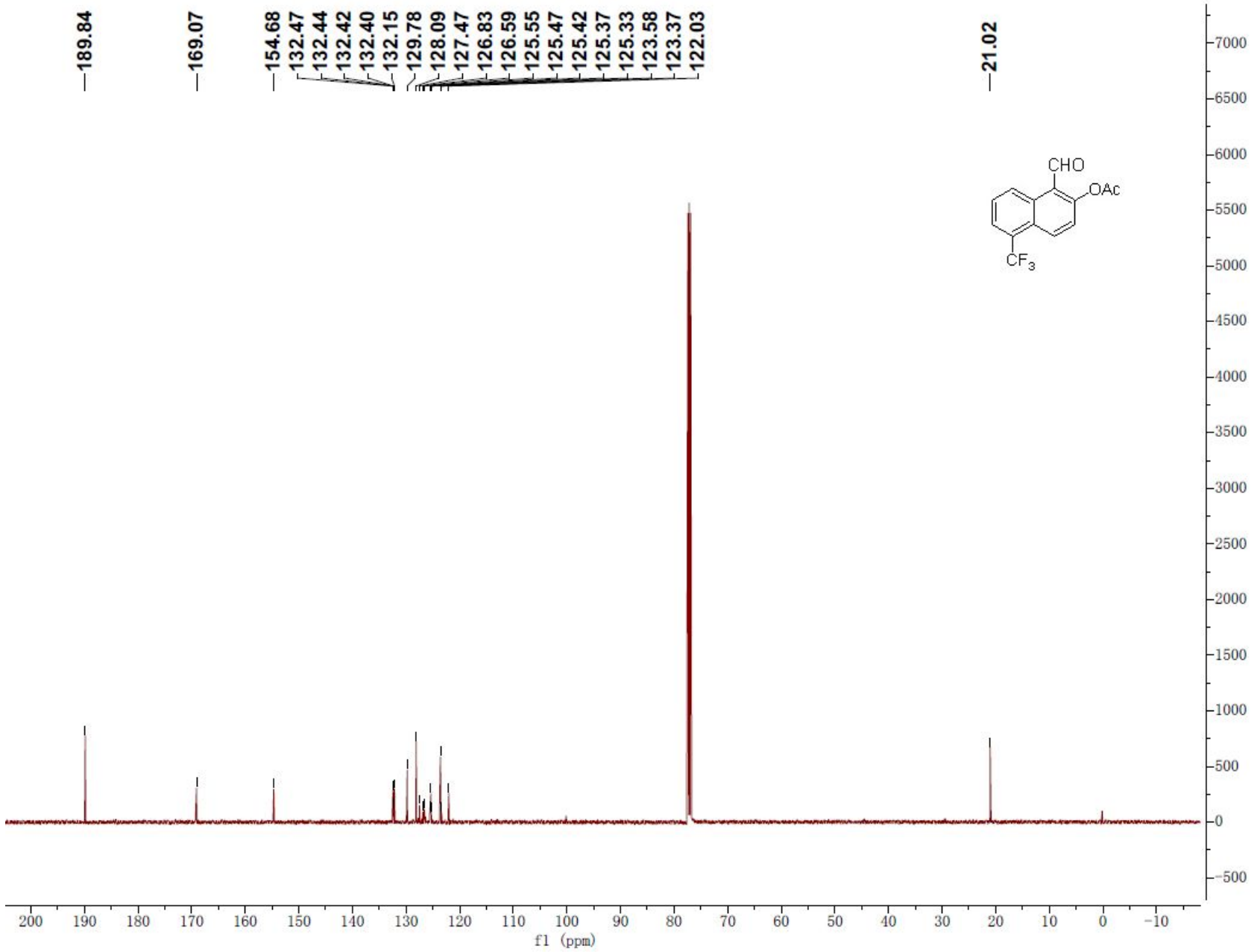
^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of 1-formyl-4-(trifluoromethyl)naphthalen-2-yl acetate (4v)



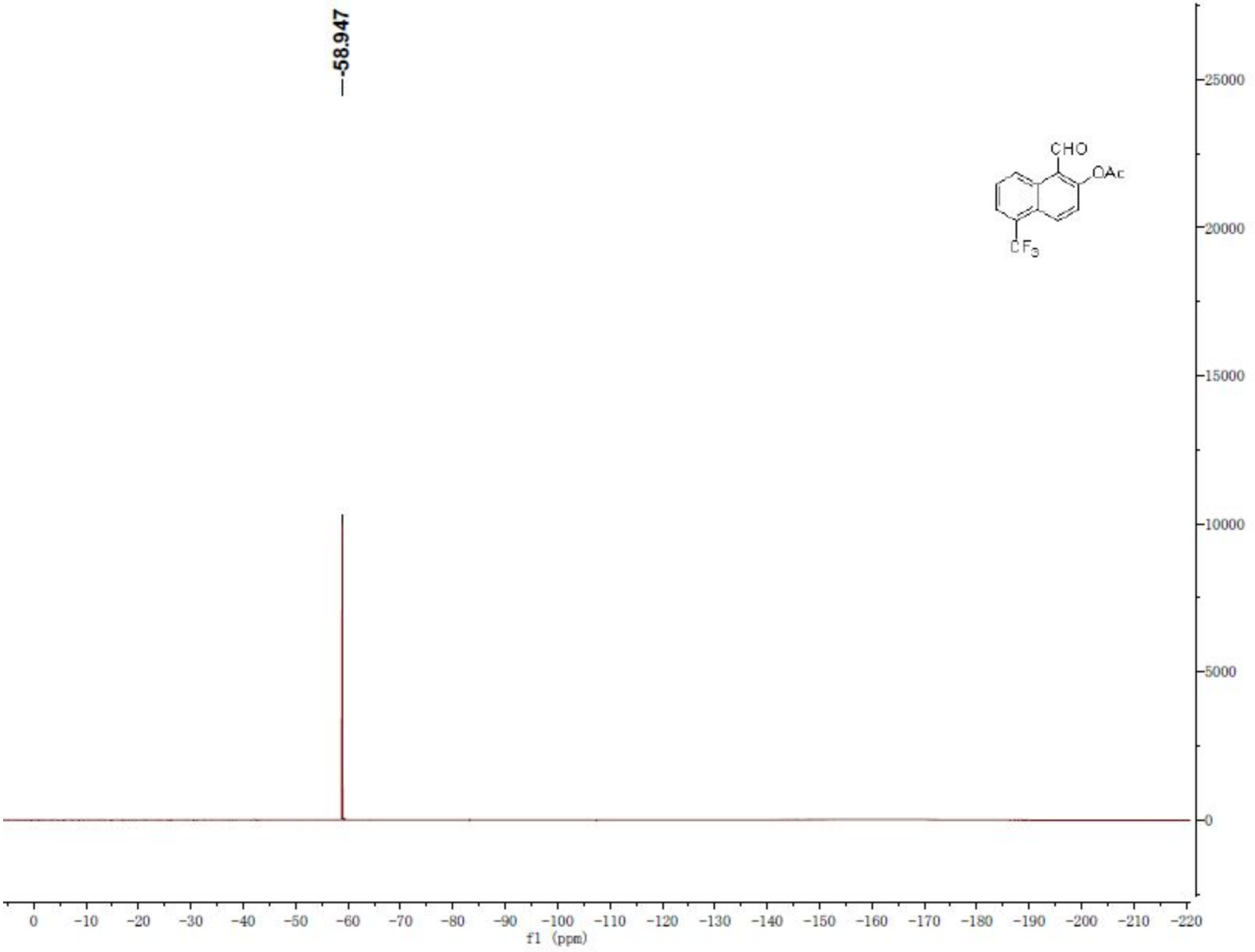
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-5-(trifluoromethyl)naphthalen-2-yl acetate (4w)



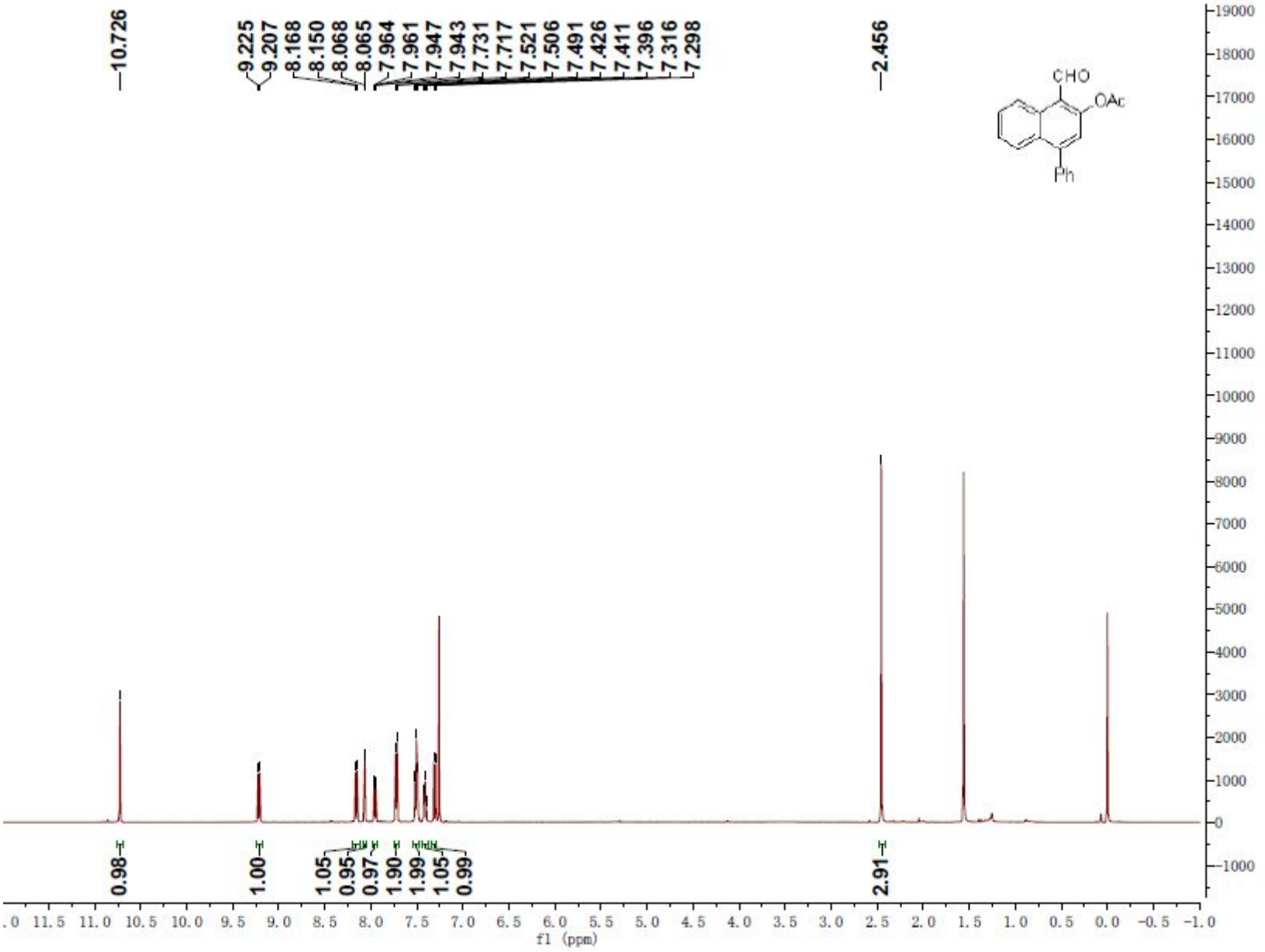
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-5-(trifluoromethyl)naphthalen-2-yl acetate (4w)



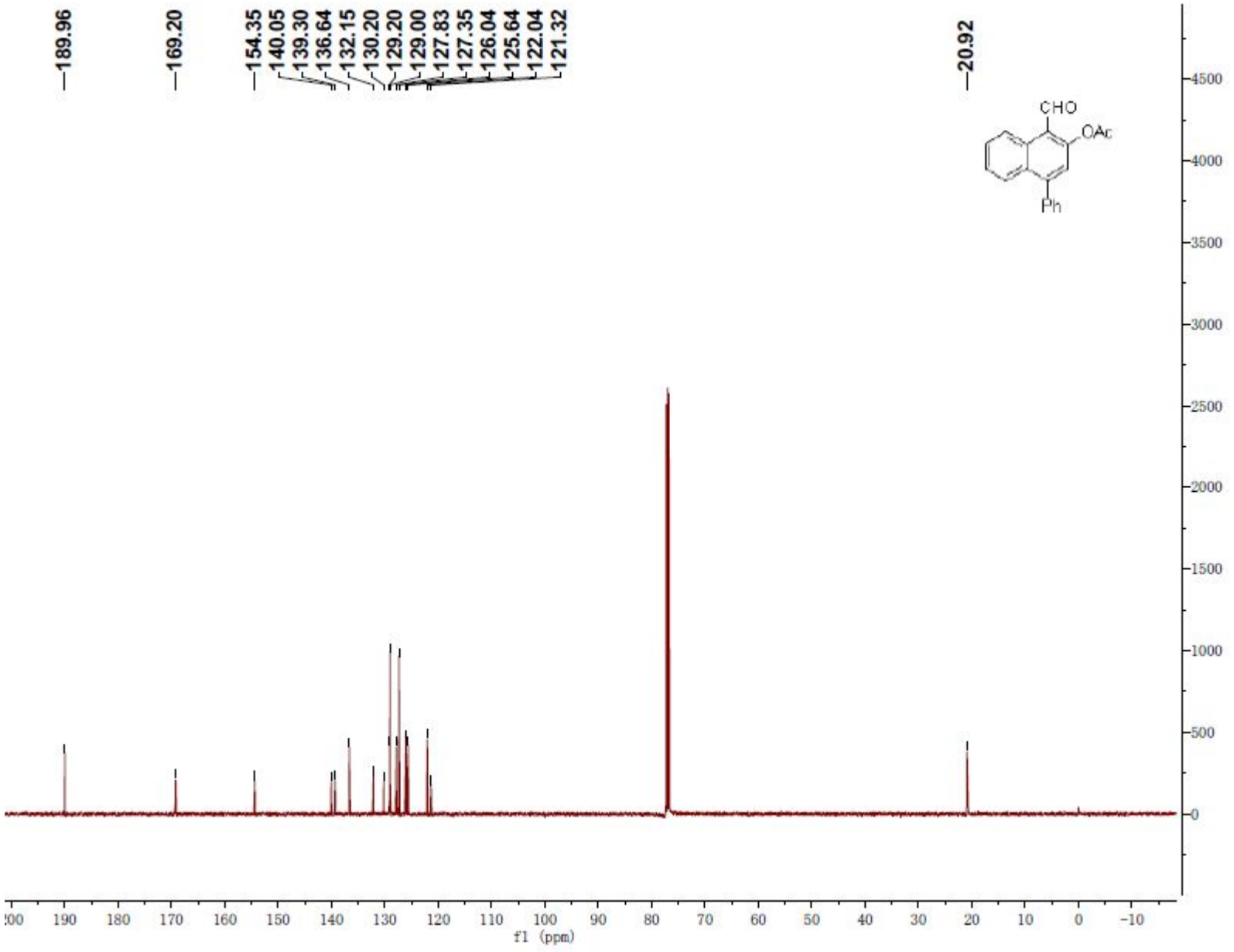
^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of 1-formyl-5-(trifluoromethyl)naphthalen-2-yl acetate (4w)



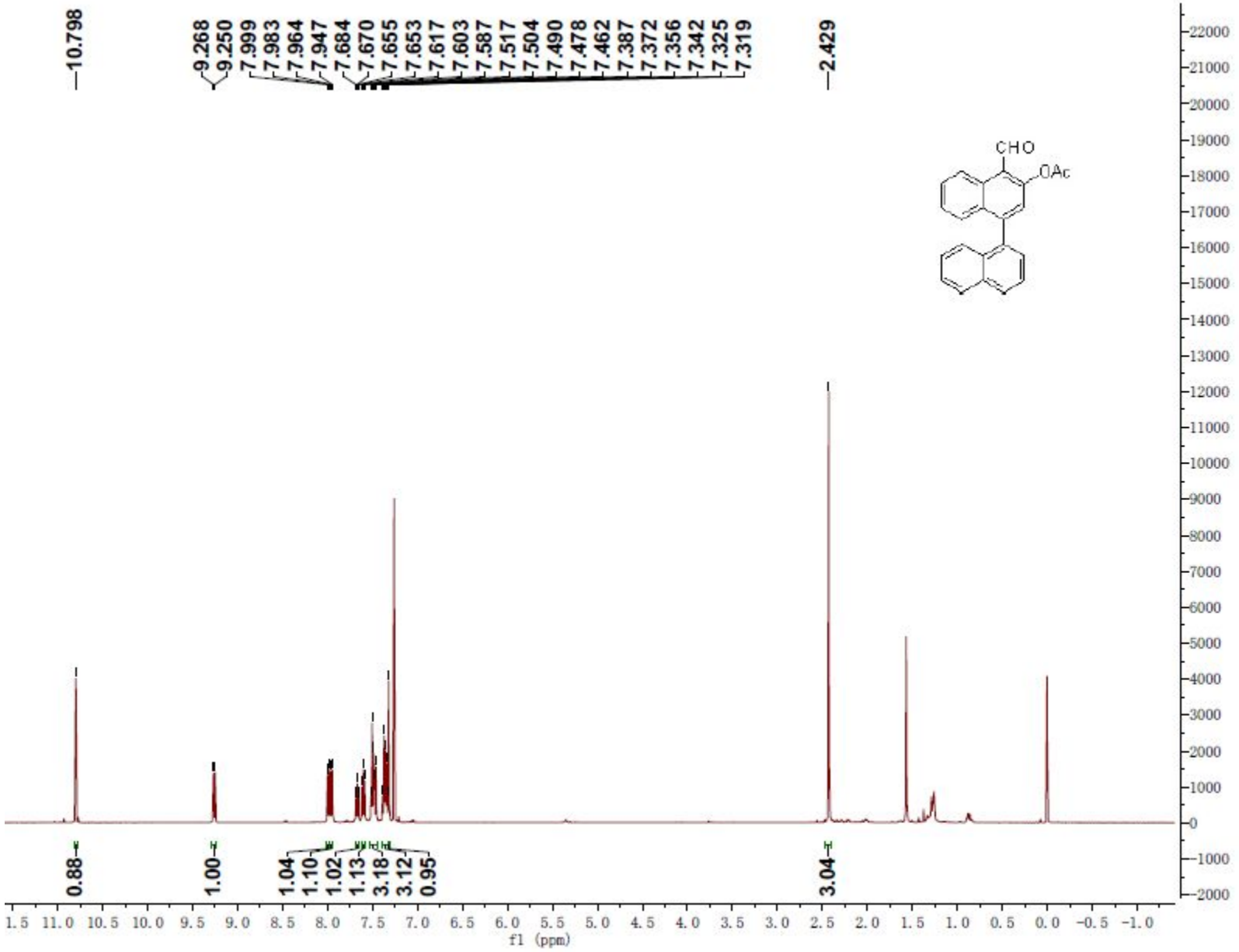
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formyl-4-phenylnaphthalen-2-yl acetate (7a)



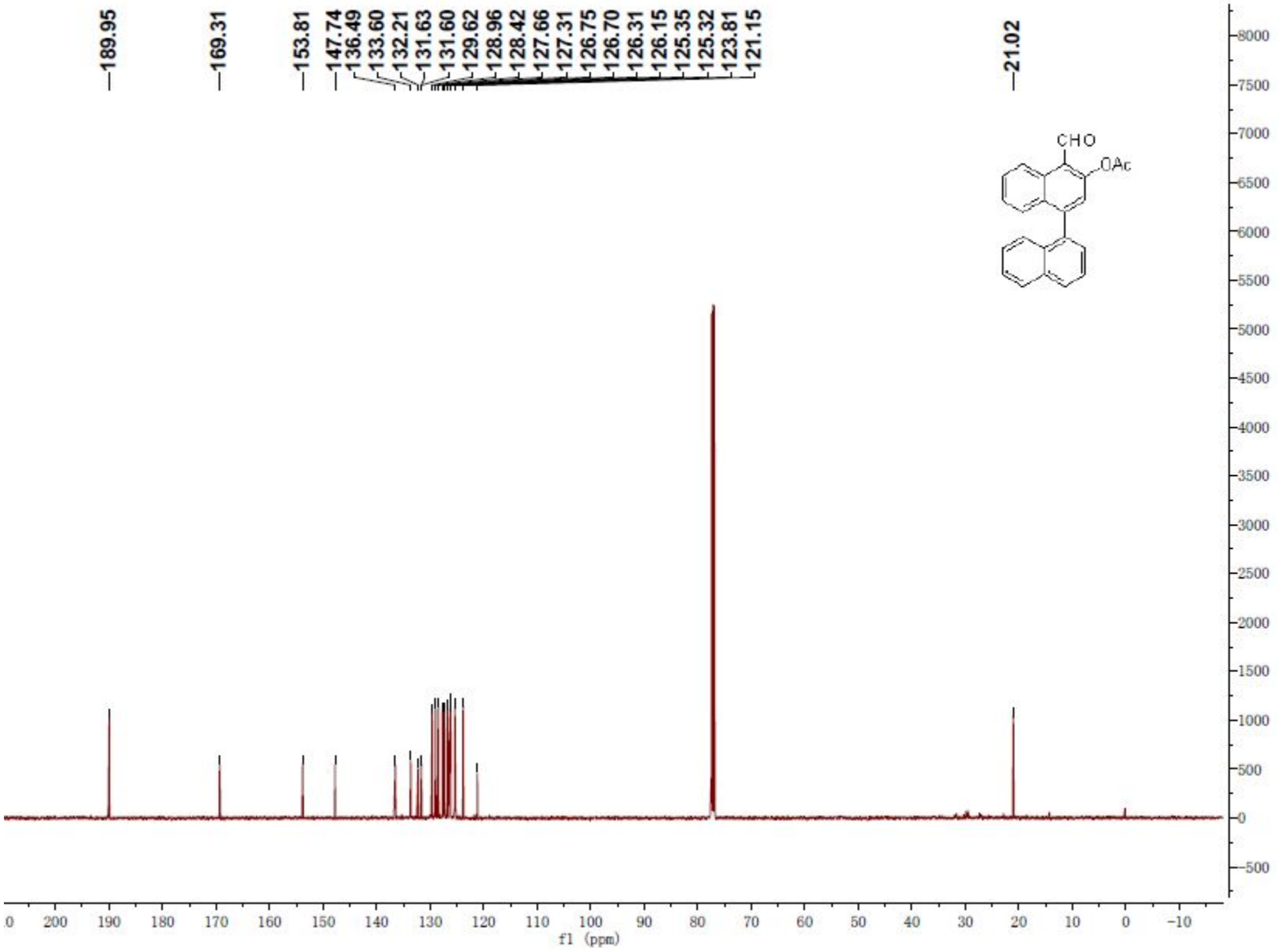
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formyl-4-phenylnaphthalen-2-yl acetate (7a)



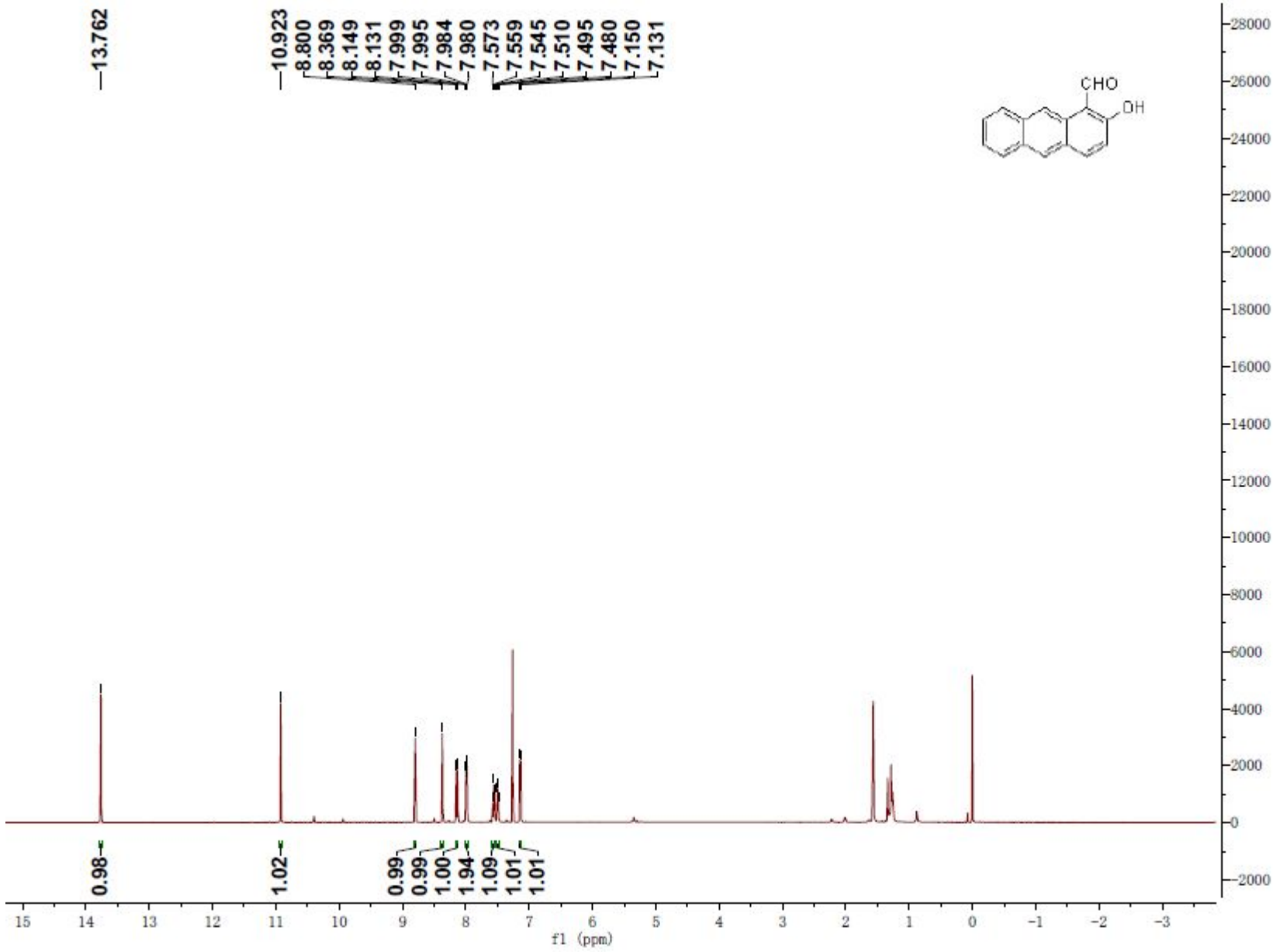
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-formyl-[1,1'-binaphthalen]-3-yl acetate (7b)



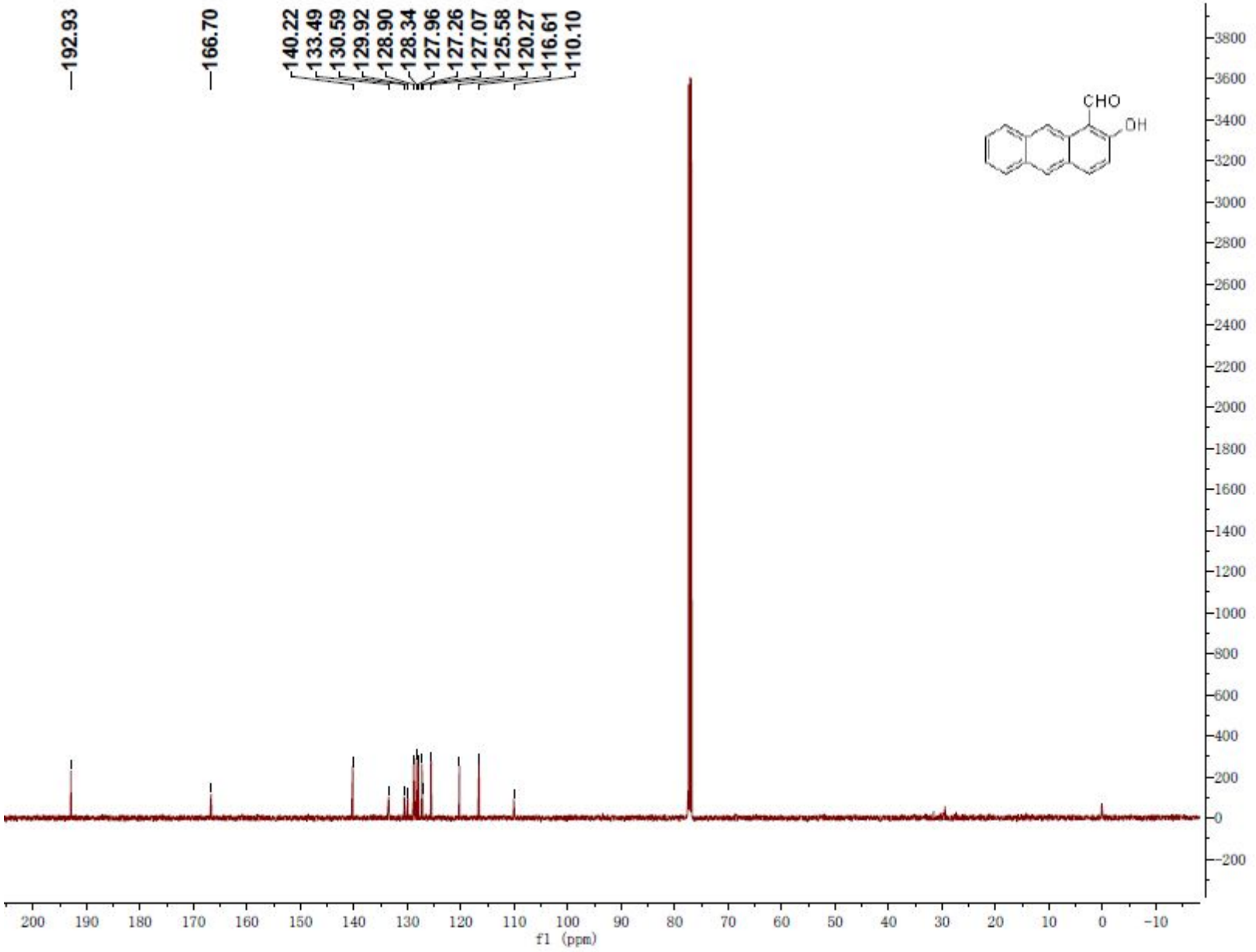
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-formyl-[1,1'-binaphthalen]-3-yl acetate (7b)



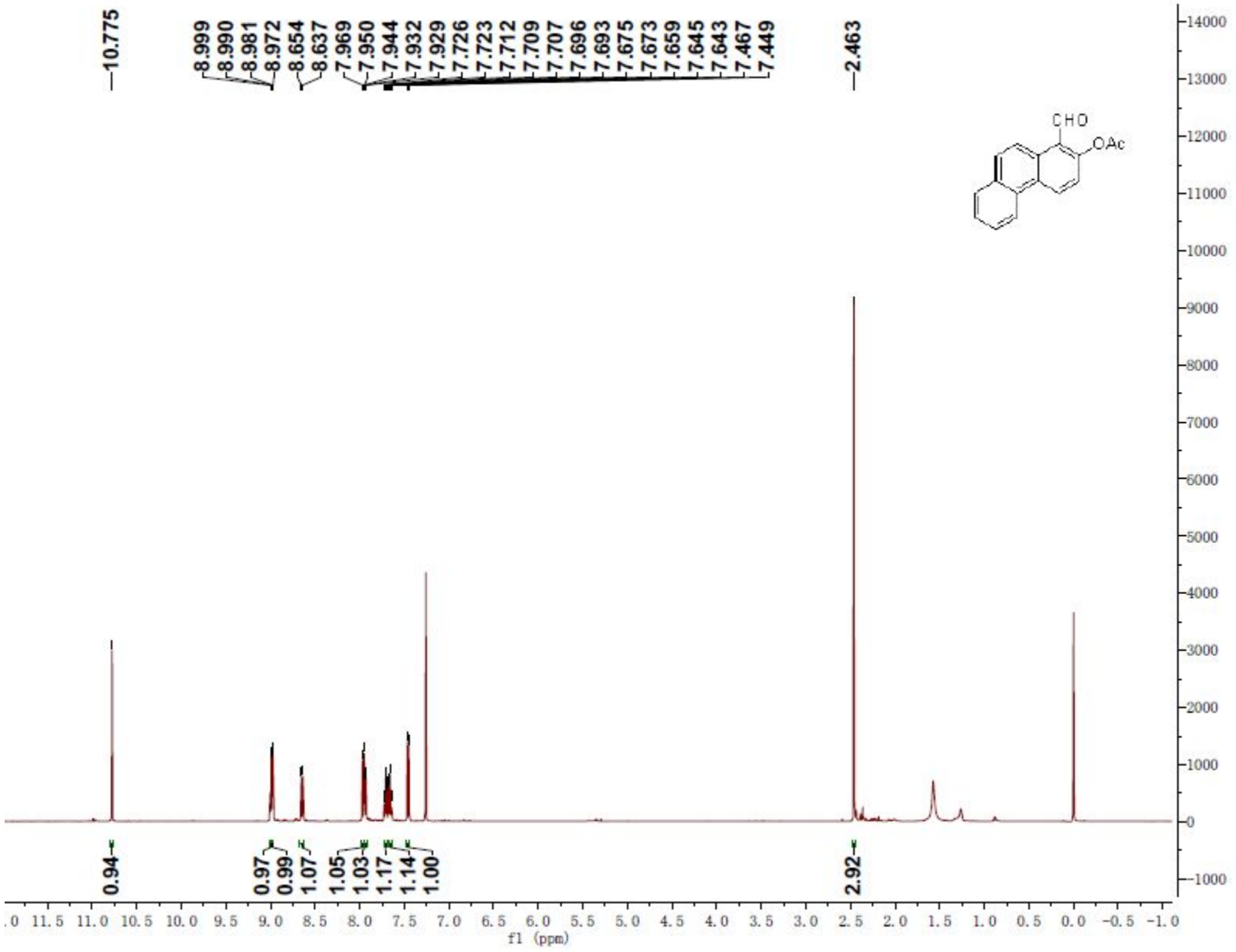
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2-hydroxyanthracene-1-carbaldehyde (7c)



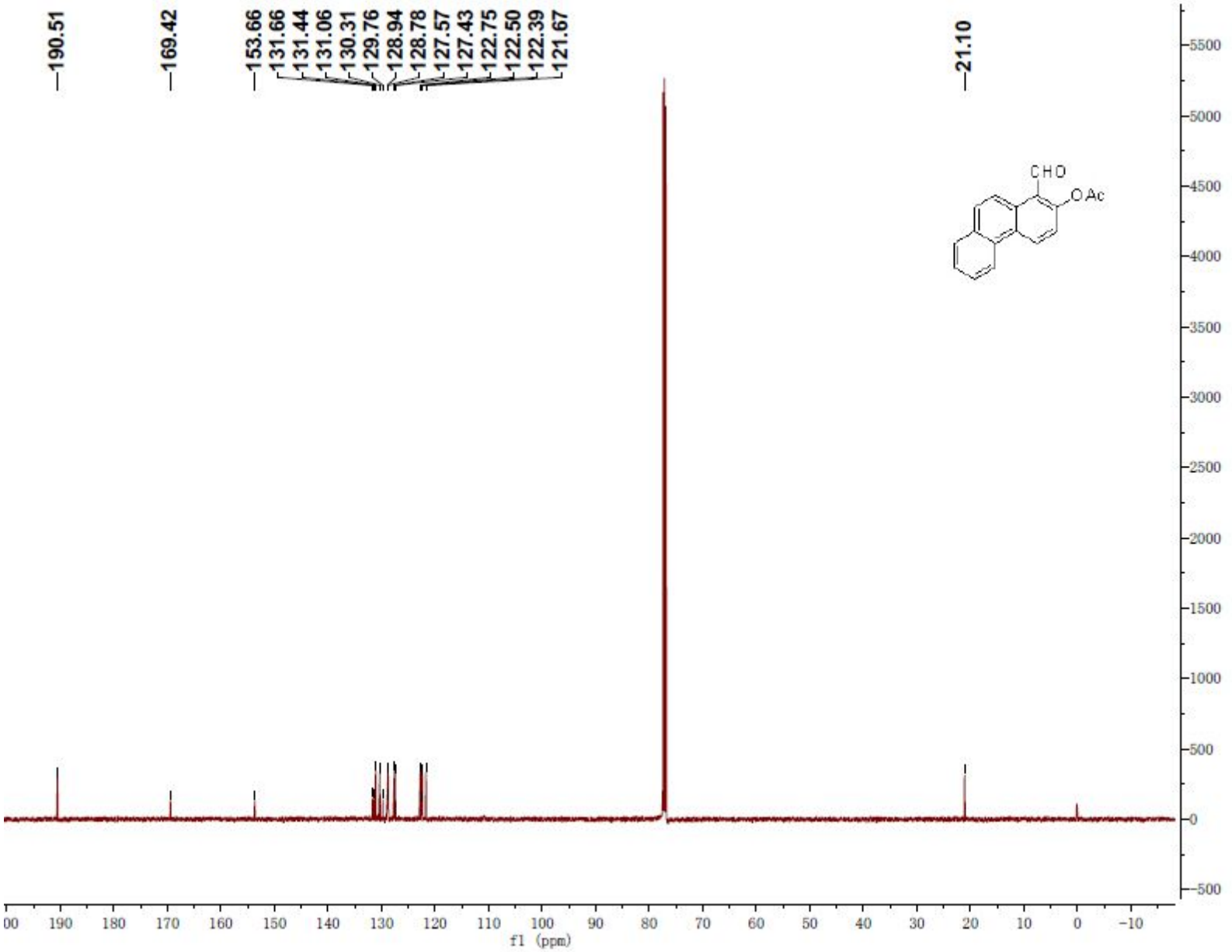
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 2-hydroxyanthracene-1-carbaldehyde (7c)



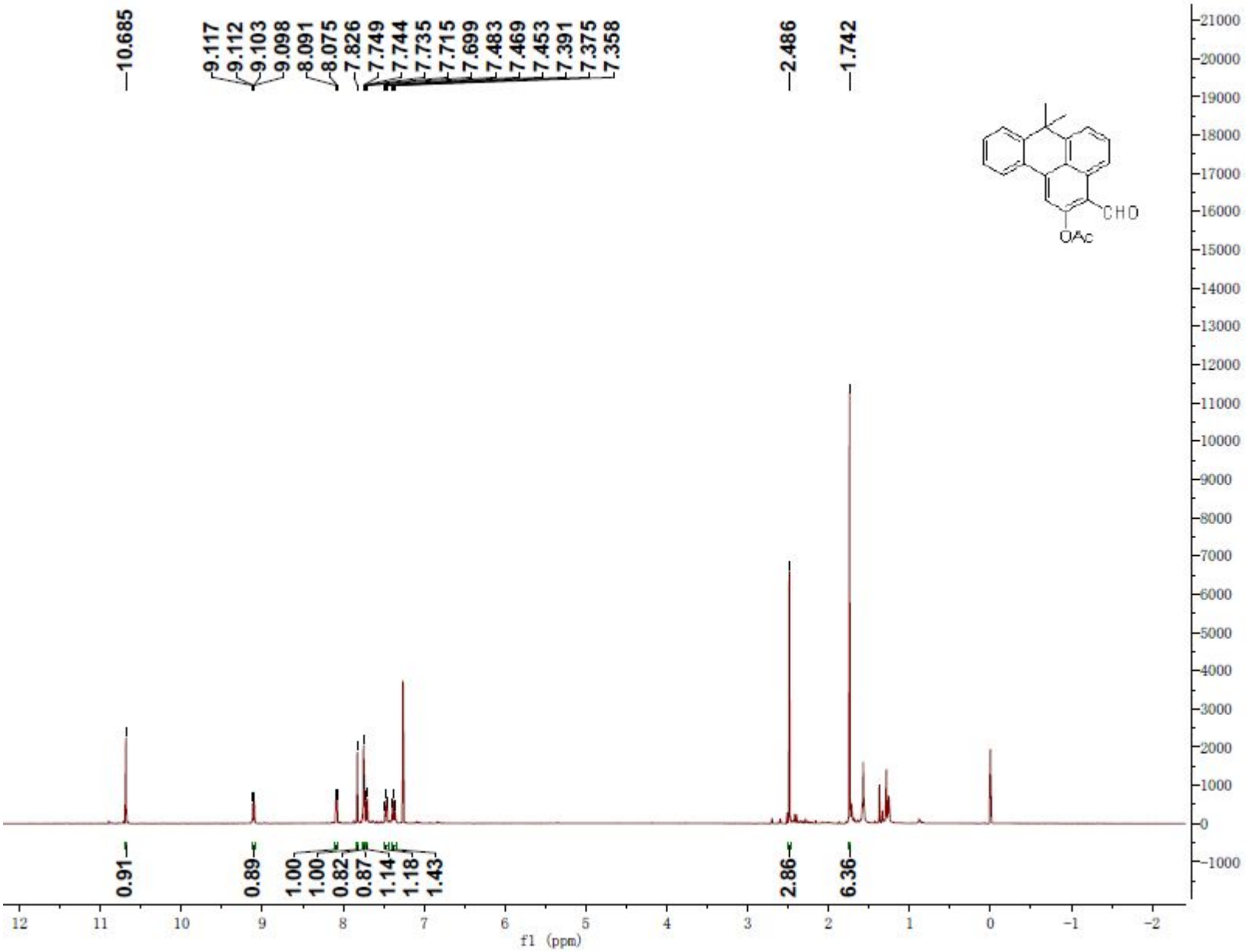
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formylphenanthren-2-yl acetate (7d)



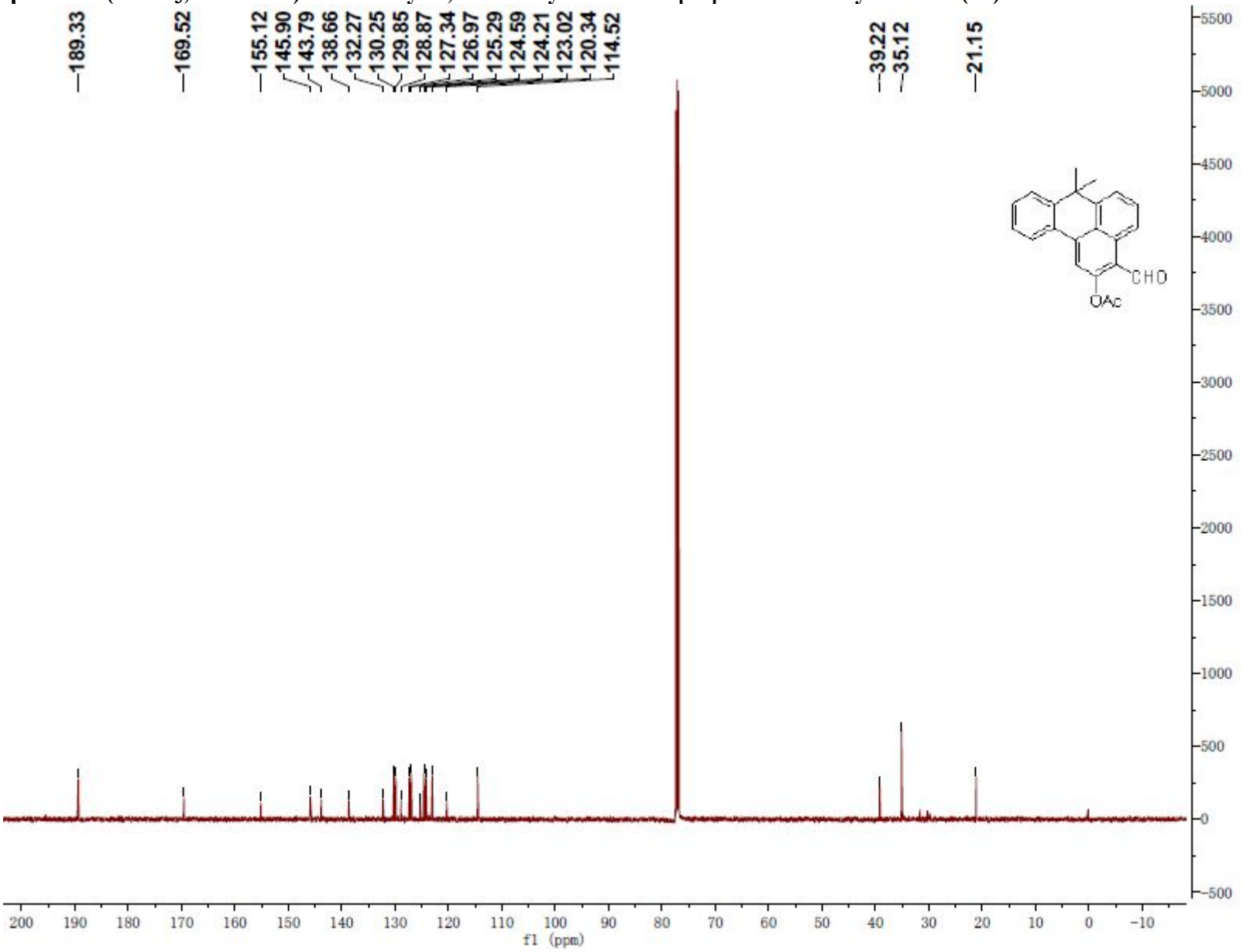
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formylphenanthren-2-yl acetate (7d)



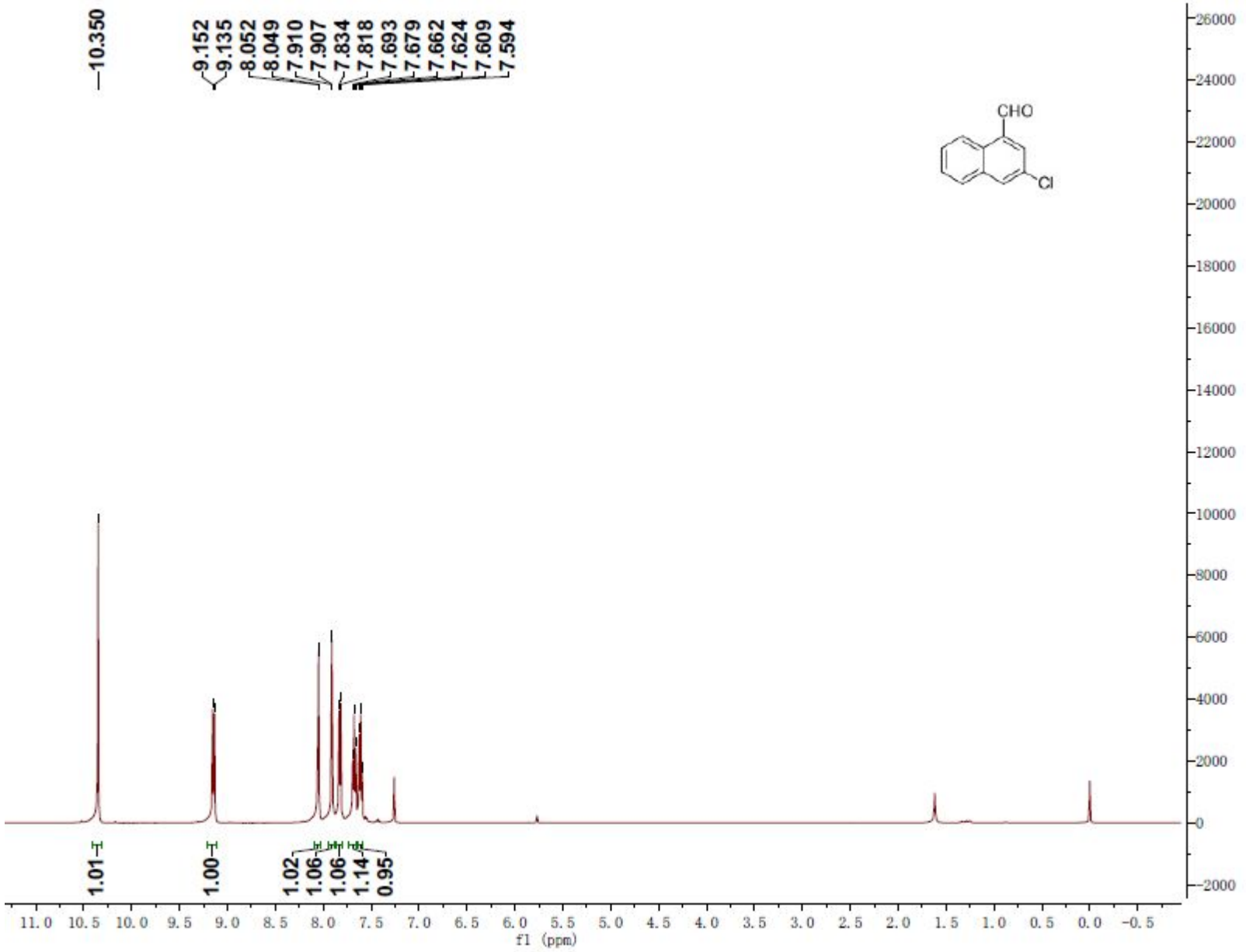
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3-formyl-7,7-dimethyl-7H-benzo[de]anthracen-2-yl acetate (7e)



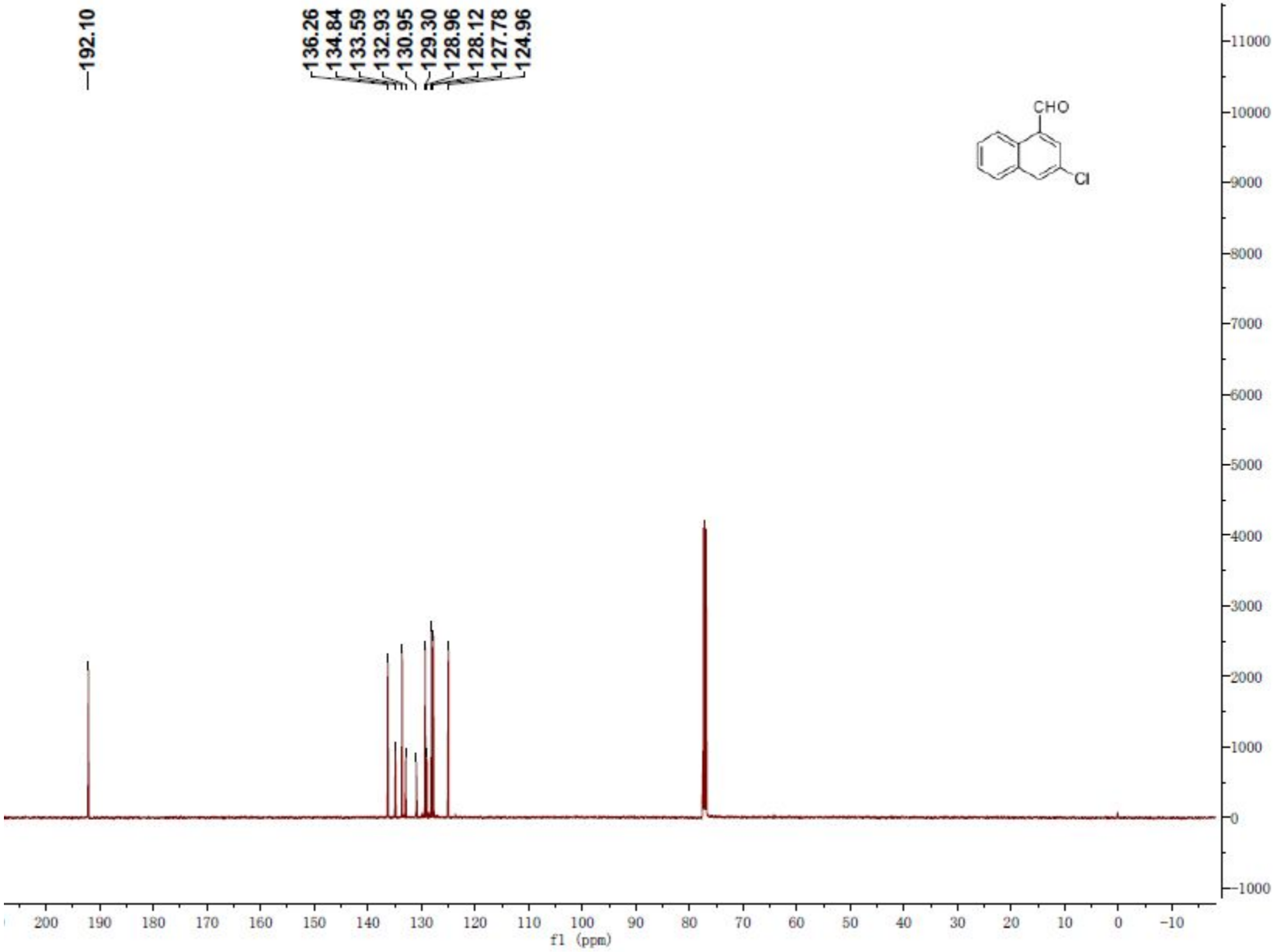
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 3-formyl-7,7-dimethyl-7H-benzo[de]anthracen-2-yl acetate (7e)



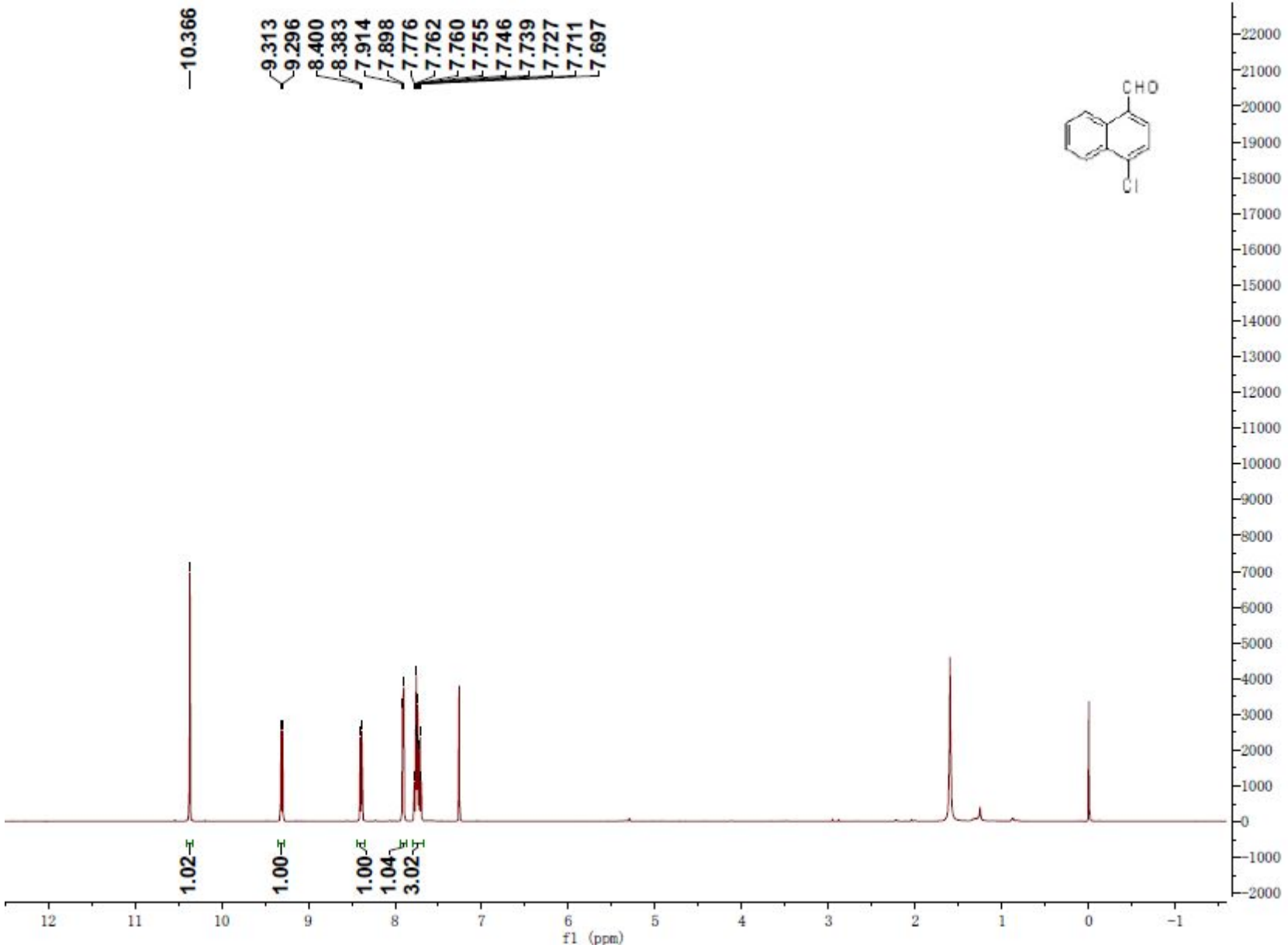
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3-chloro-1-naphthaldehyde (1b)



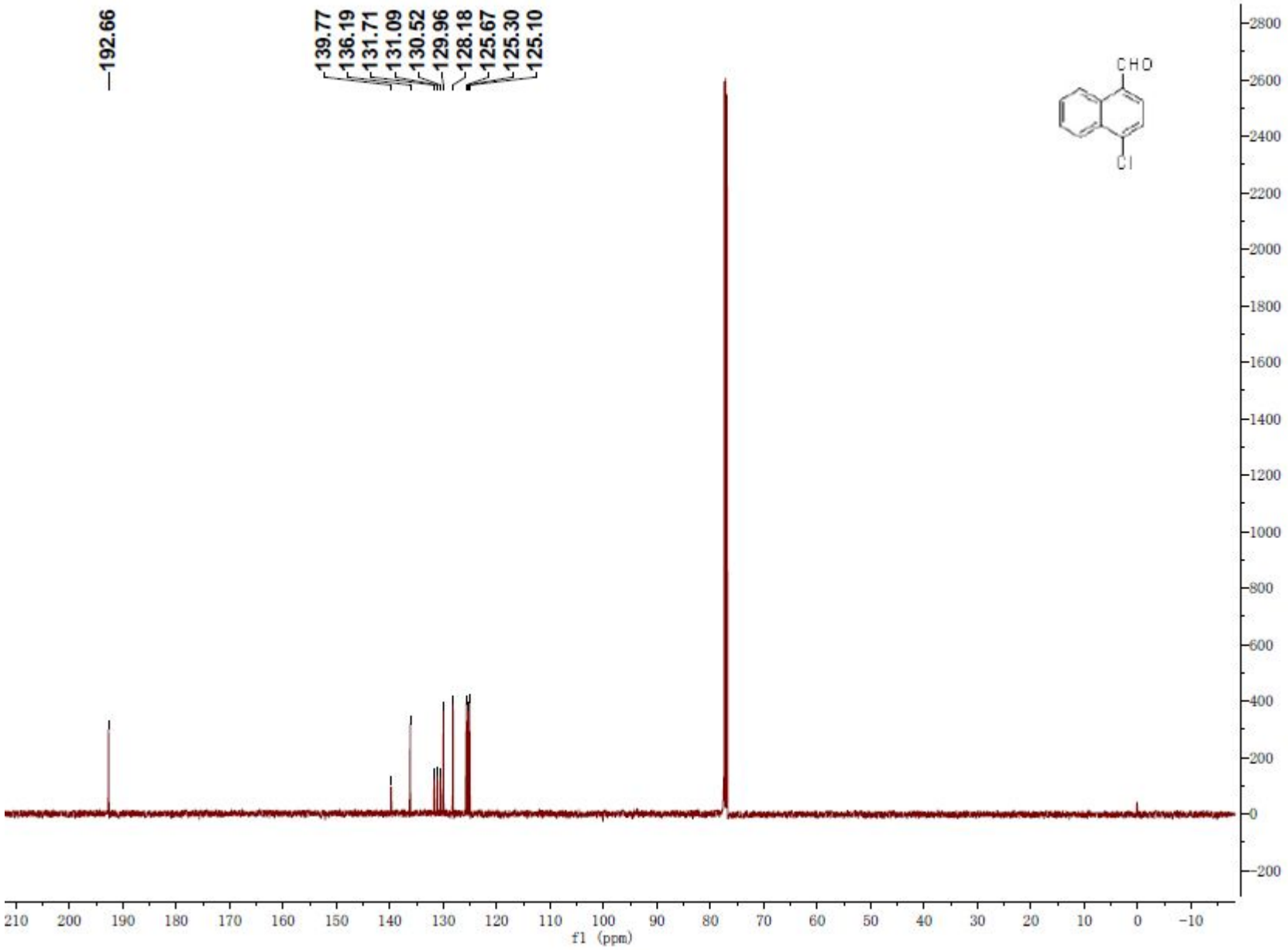
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 3-chloro-1-naphthaldehyde (1b)



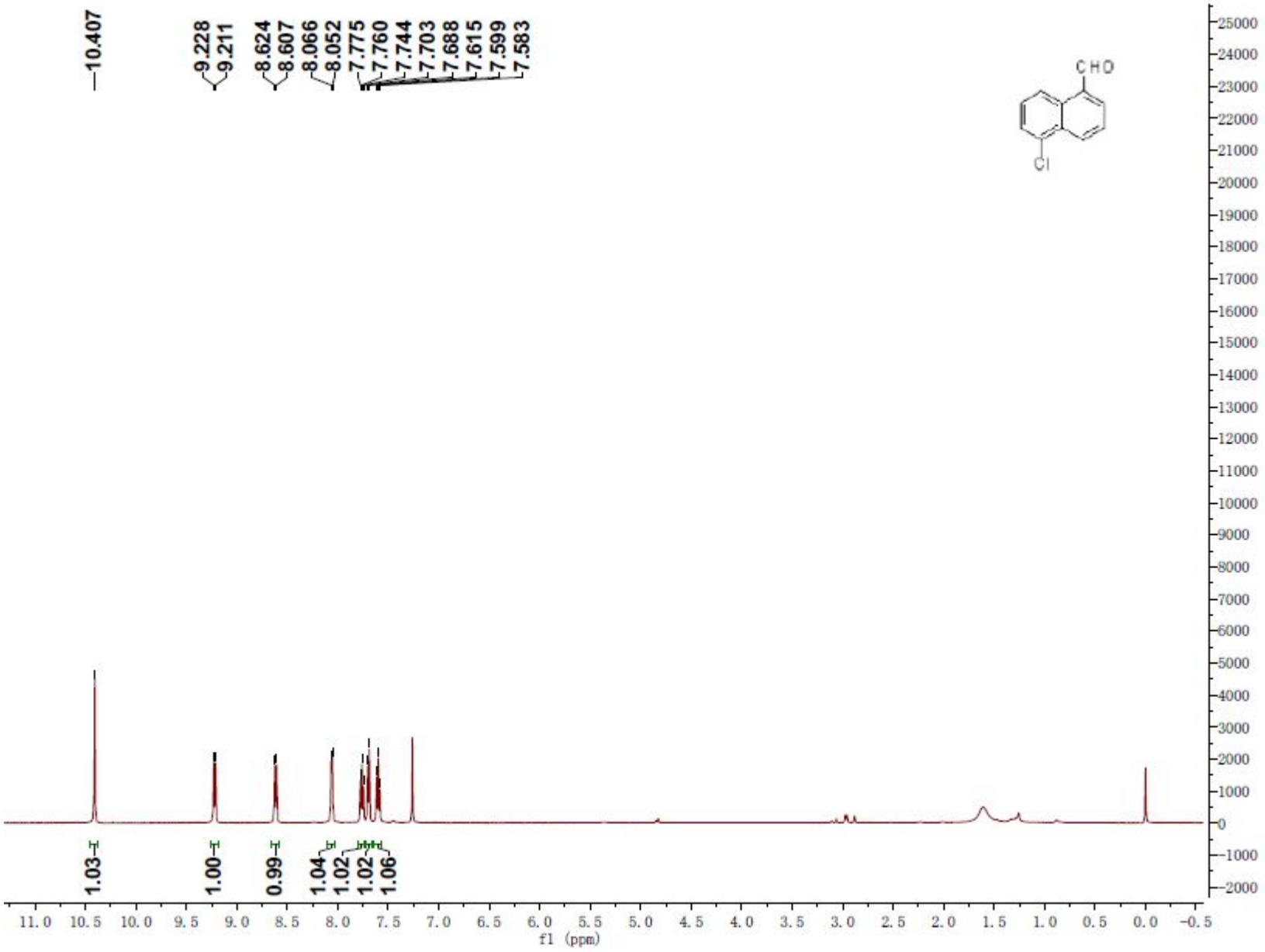
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-chloro-1-naphthaldehyde (1c)



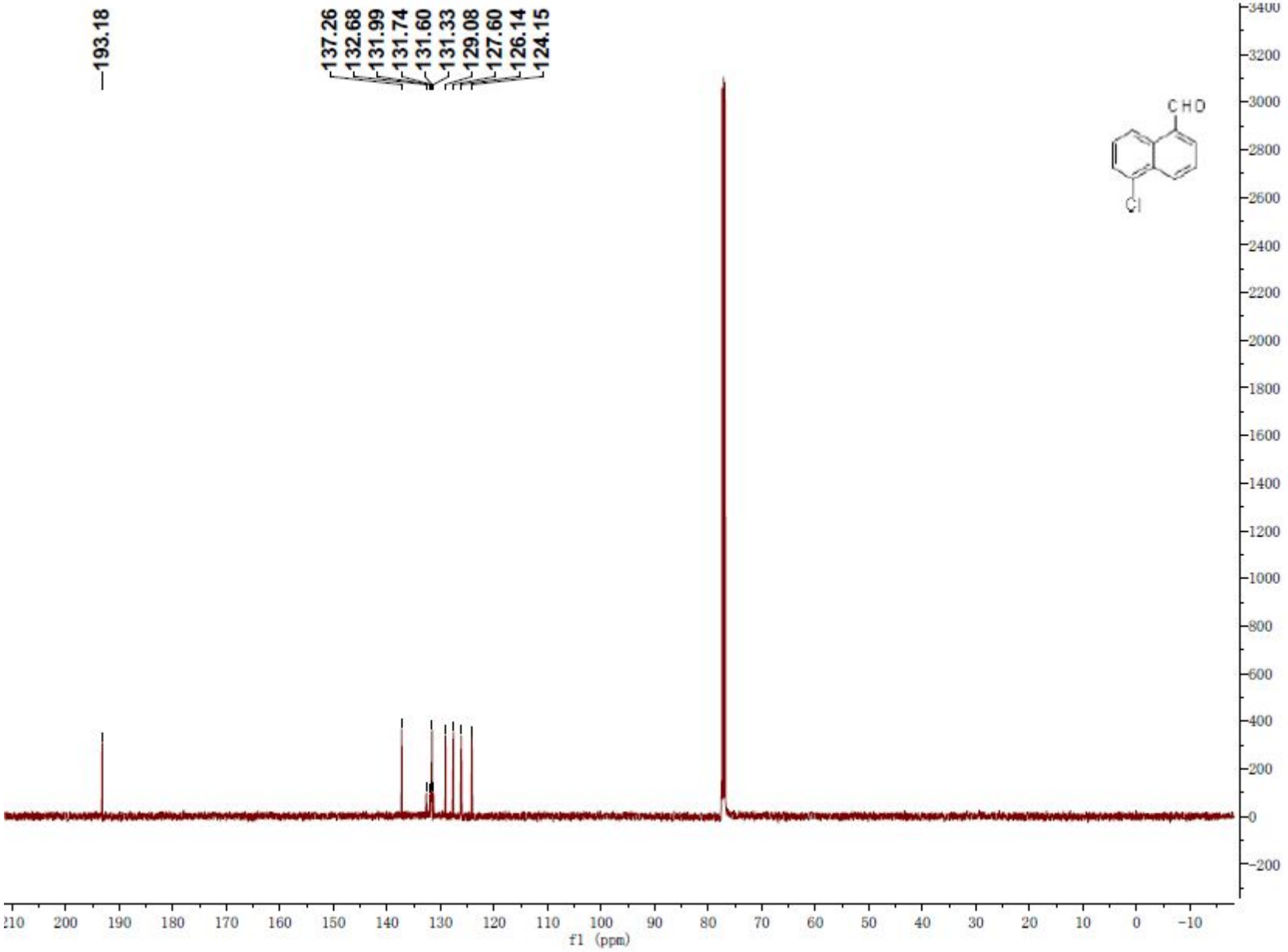
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-chloro-1-naphthaldehyde (1c)



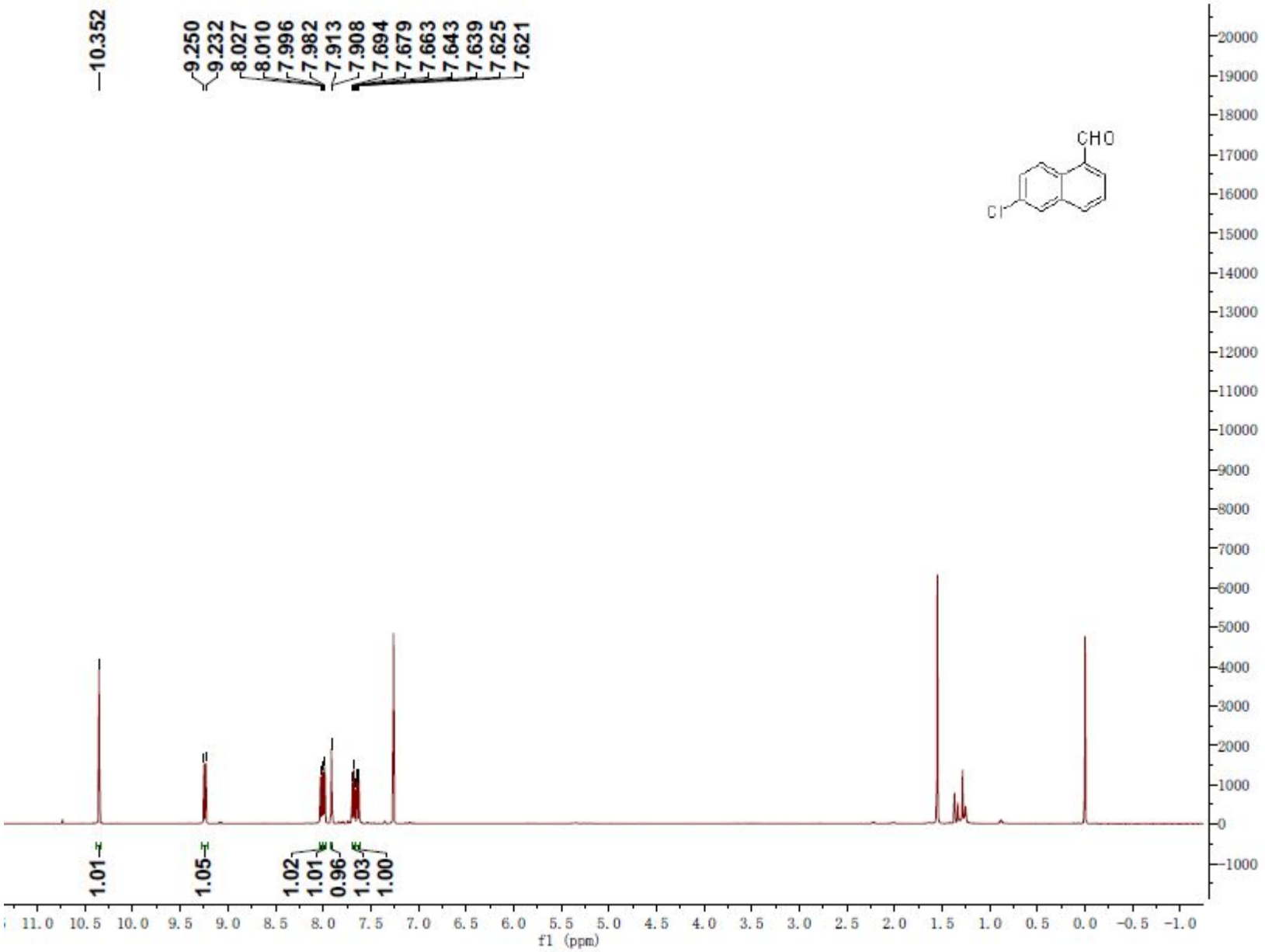
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-chloro-1-naphthaldehyde (1d)



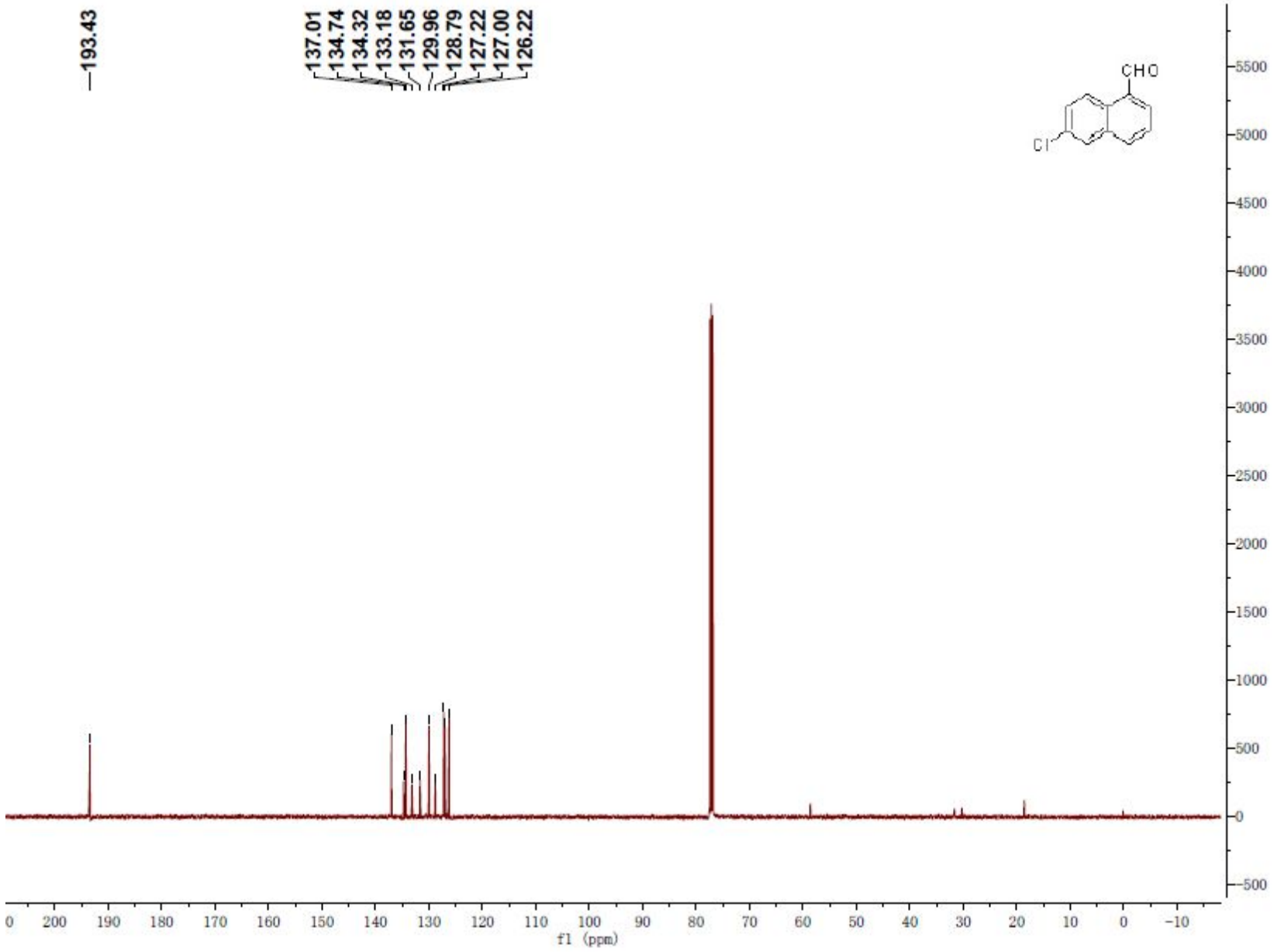
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-chloro-1-naphthaldehyde (1d)



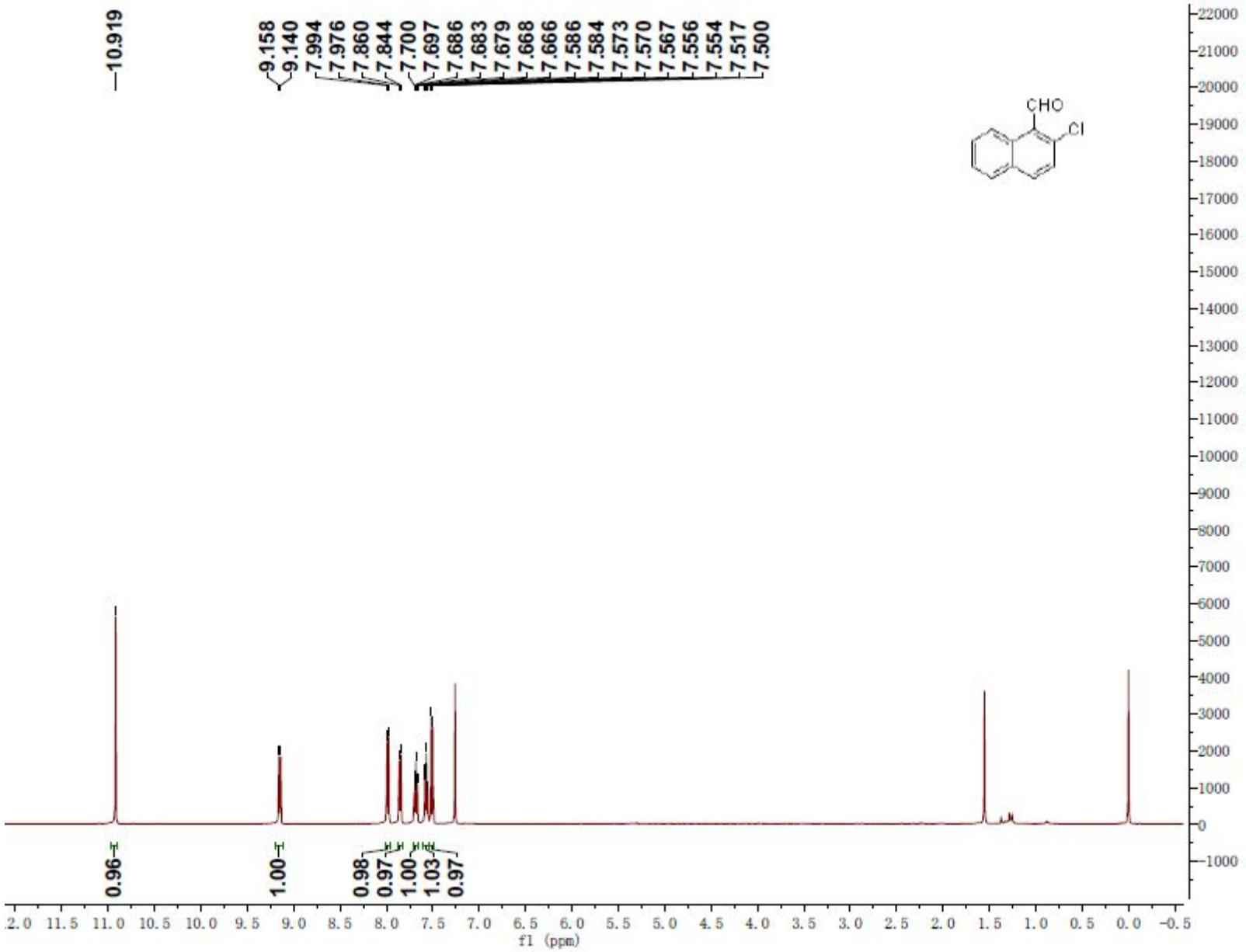
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 6-chloro-1-naphthaldehyde (1e)



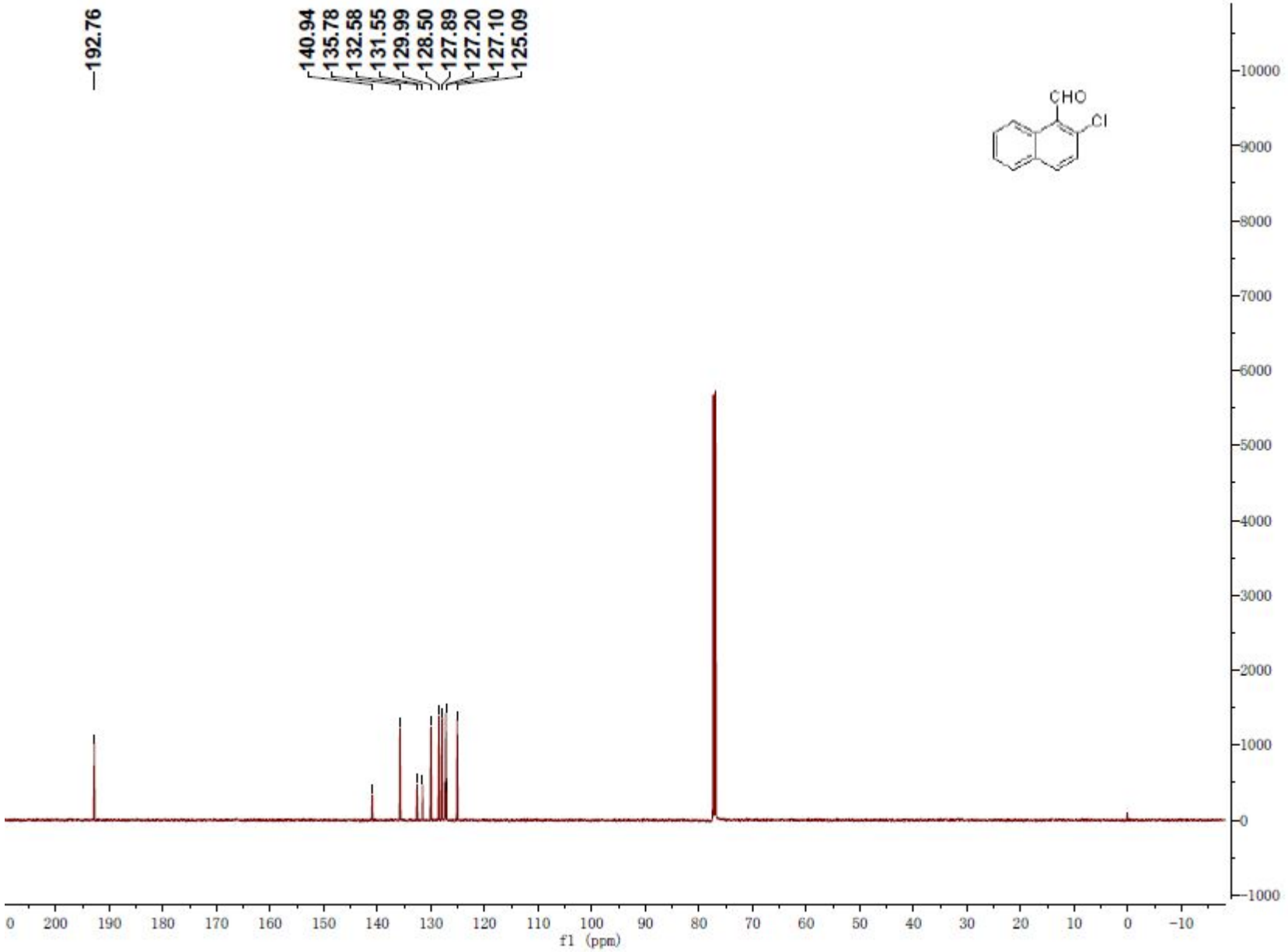
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 6-chloro-1-naphthaldehyde (1e)



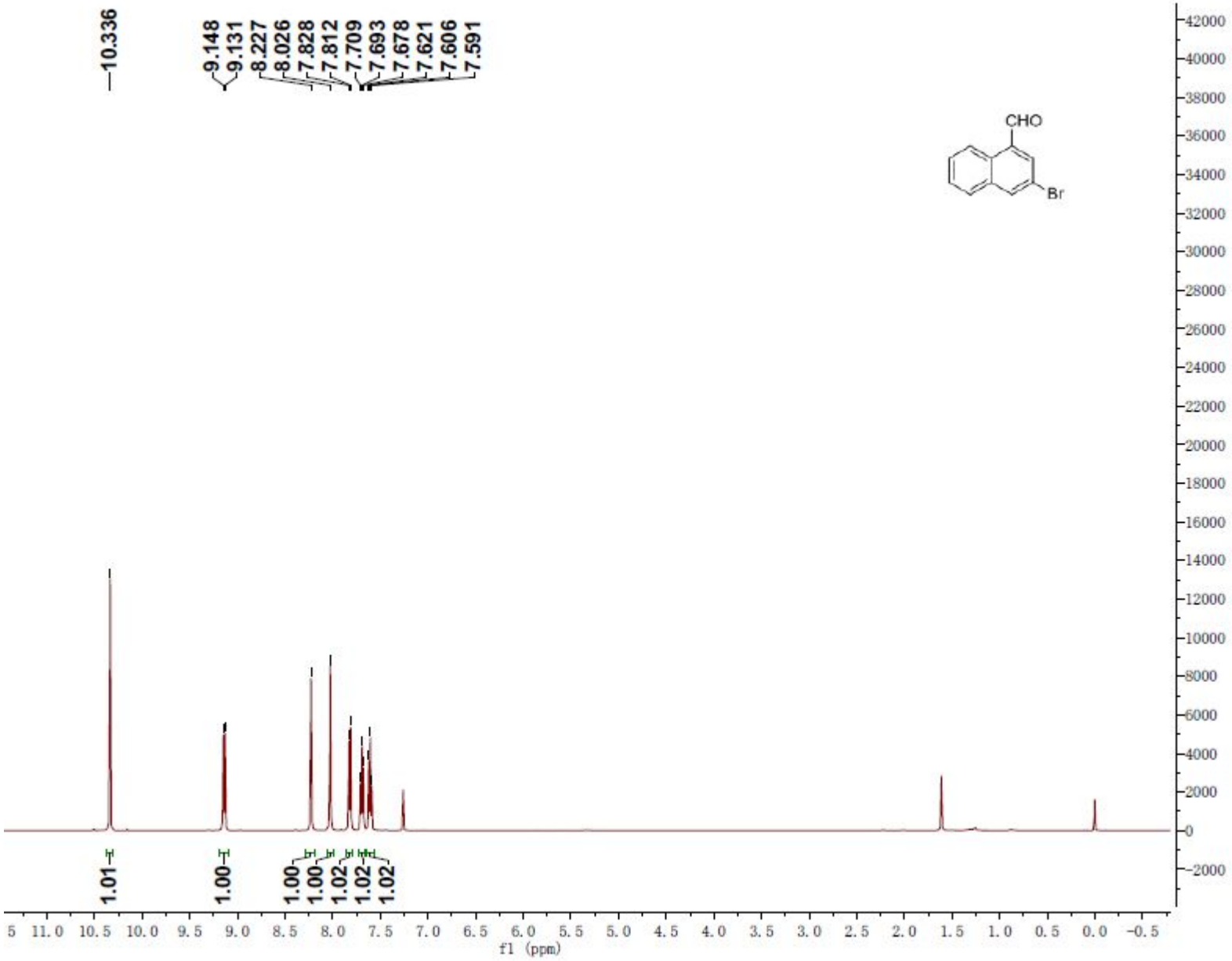
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2-chloro-1-naphthaldehyde (1f)



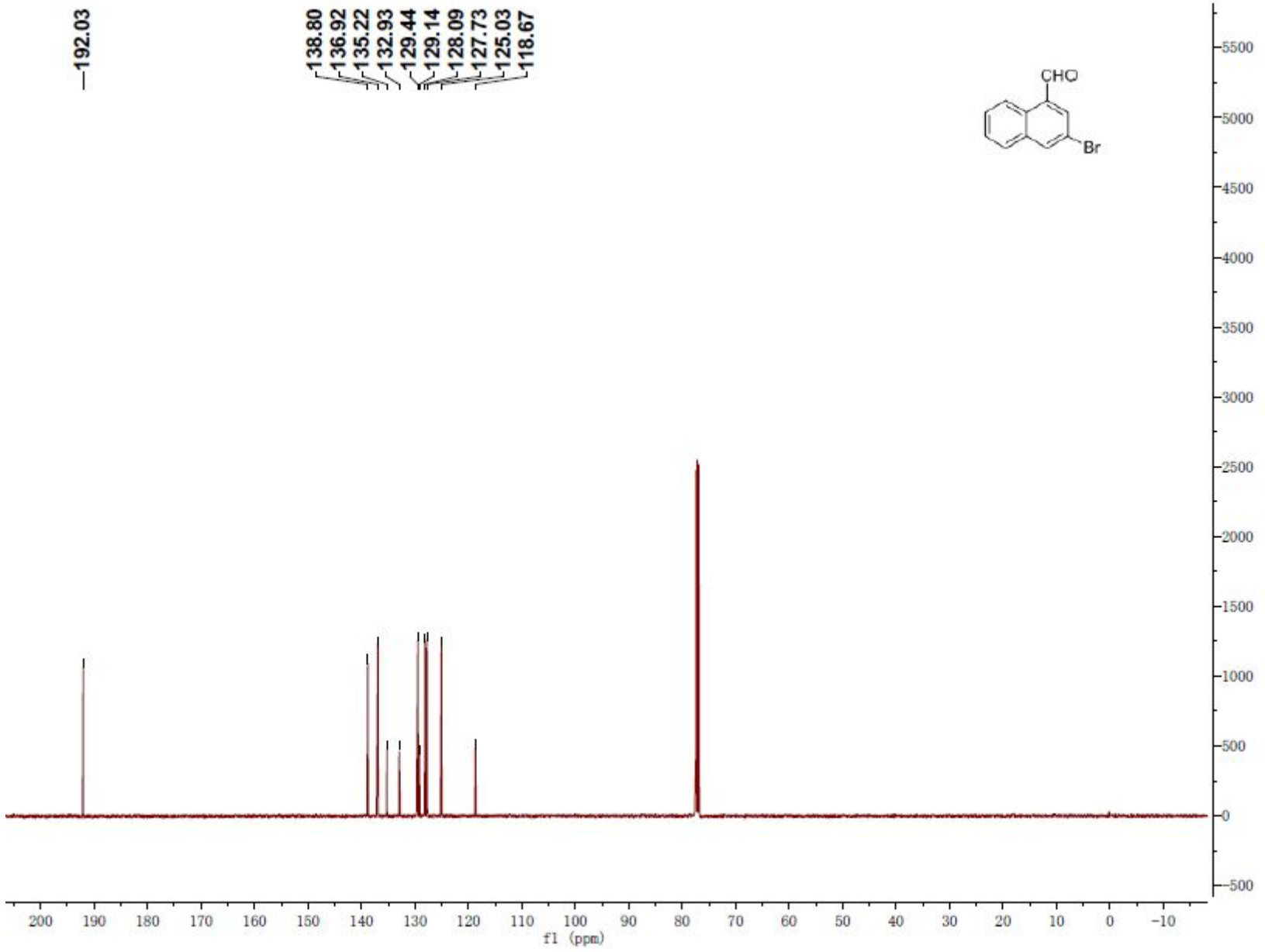
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 2-chloro-1-naphthaldehyde (1f)



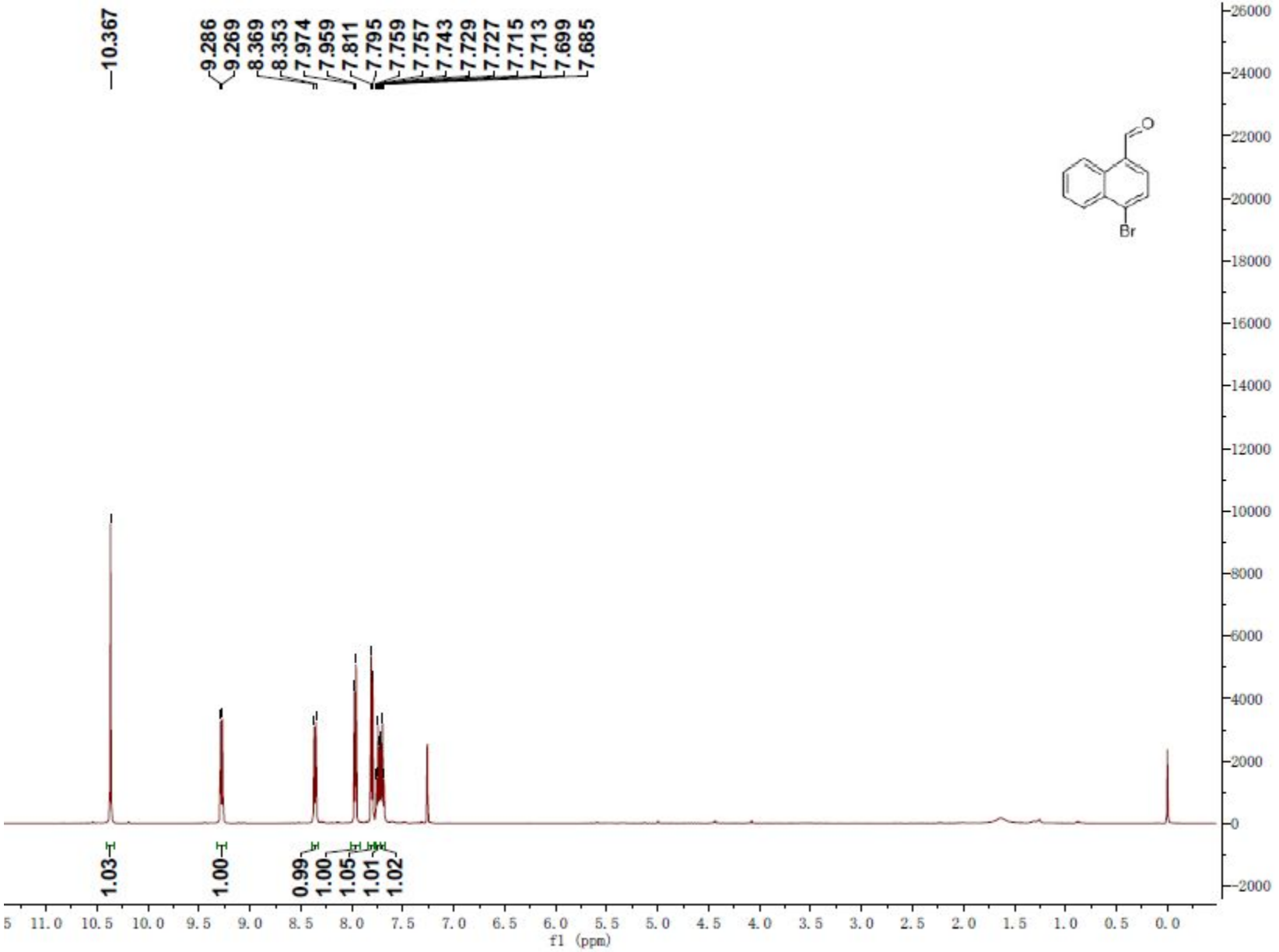
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3-bromo-1-naphthaldehyde (1g)



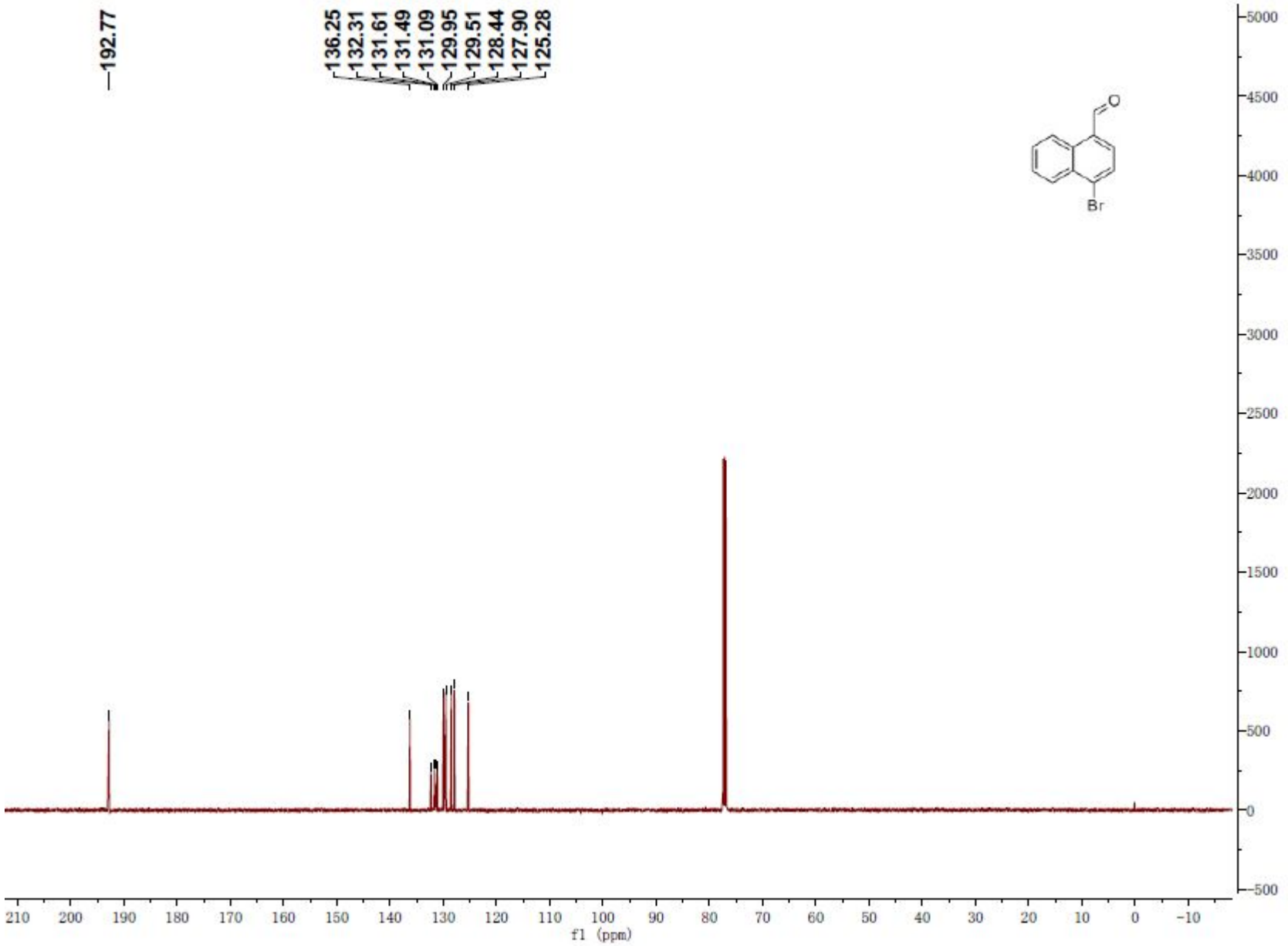
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 3-bromo-1-naphthaldehyde (1g)



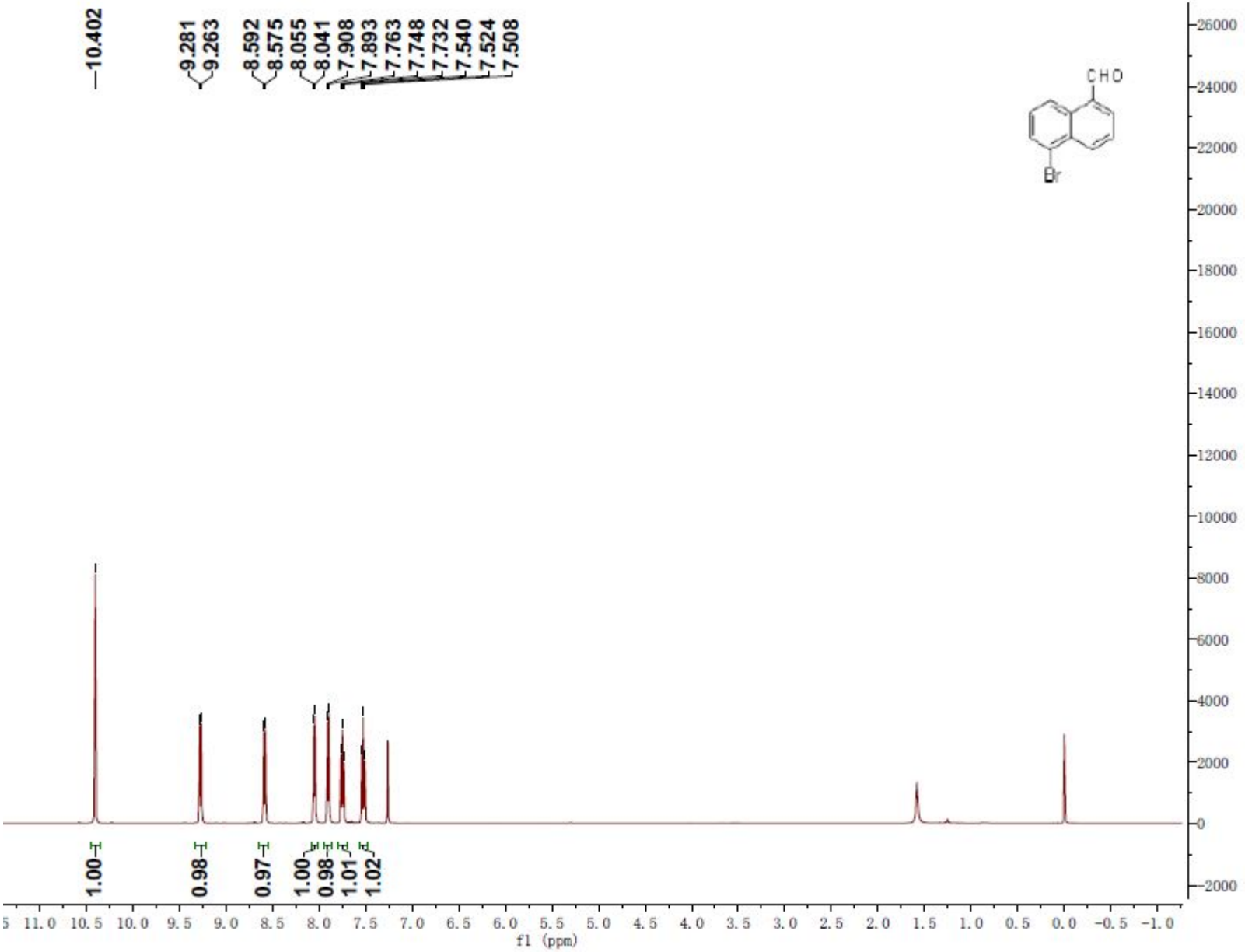
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-bromo-1-naphthaldehyde (1h)



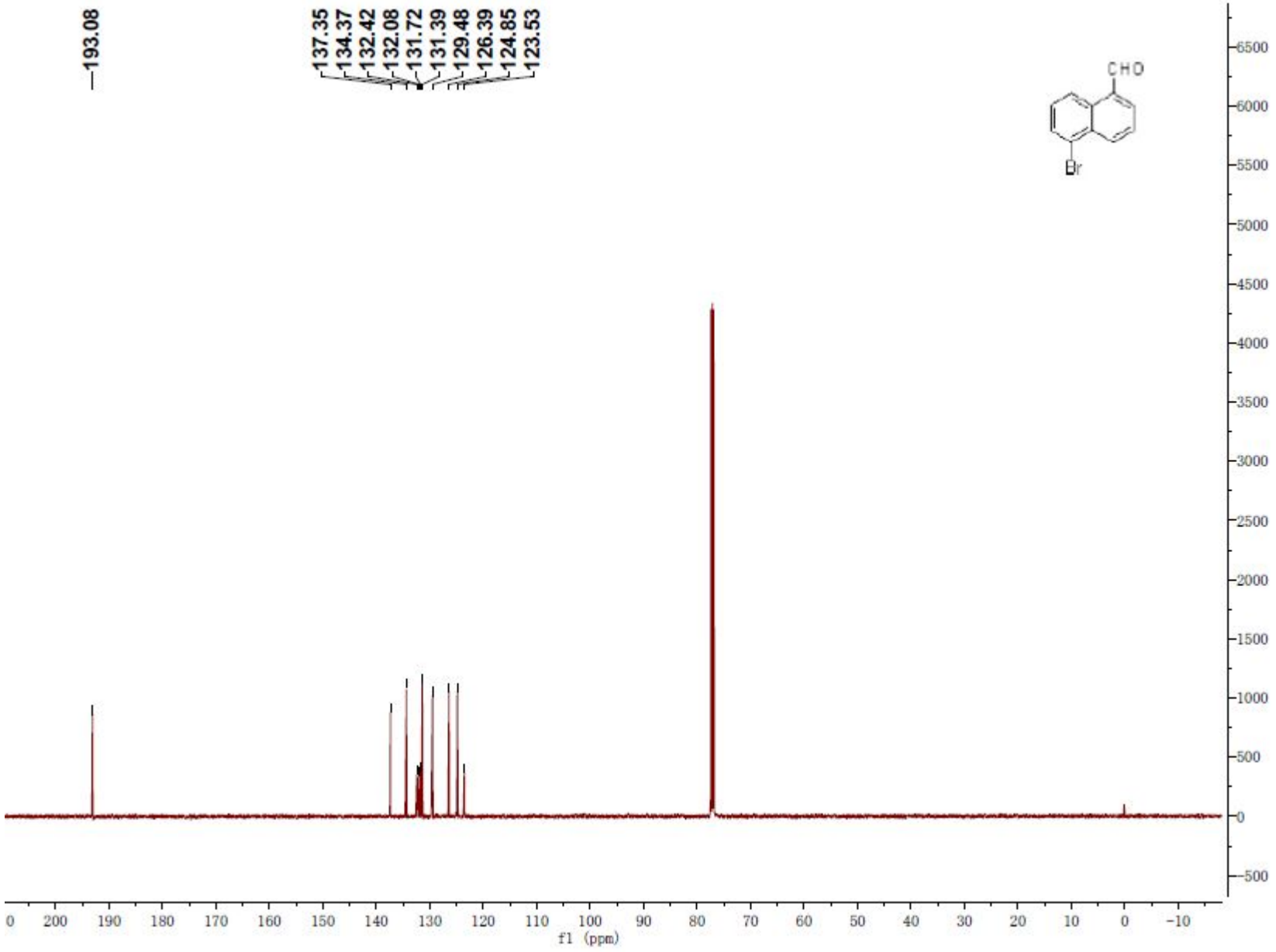
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-bromo-1-naphthaldehyde (1h)



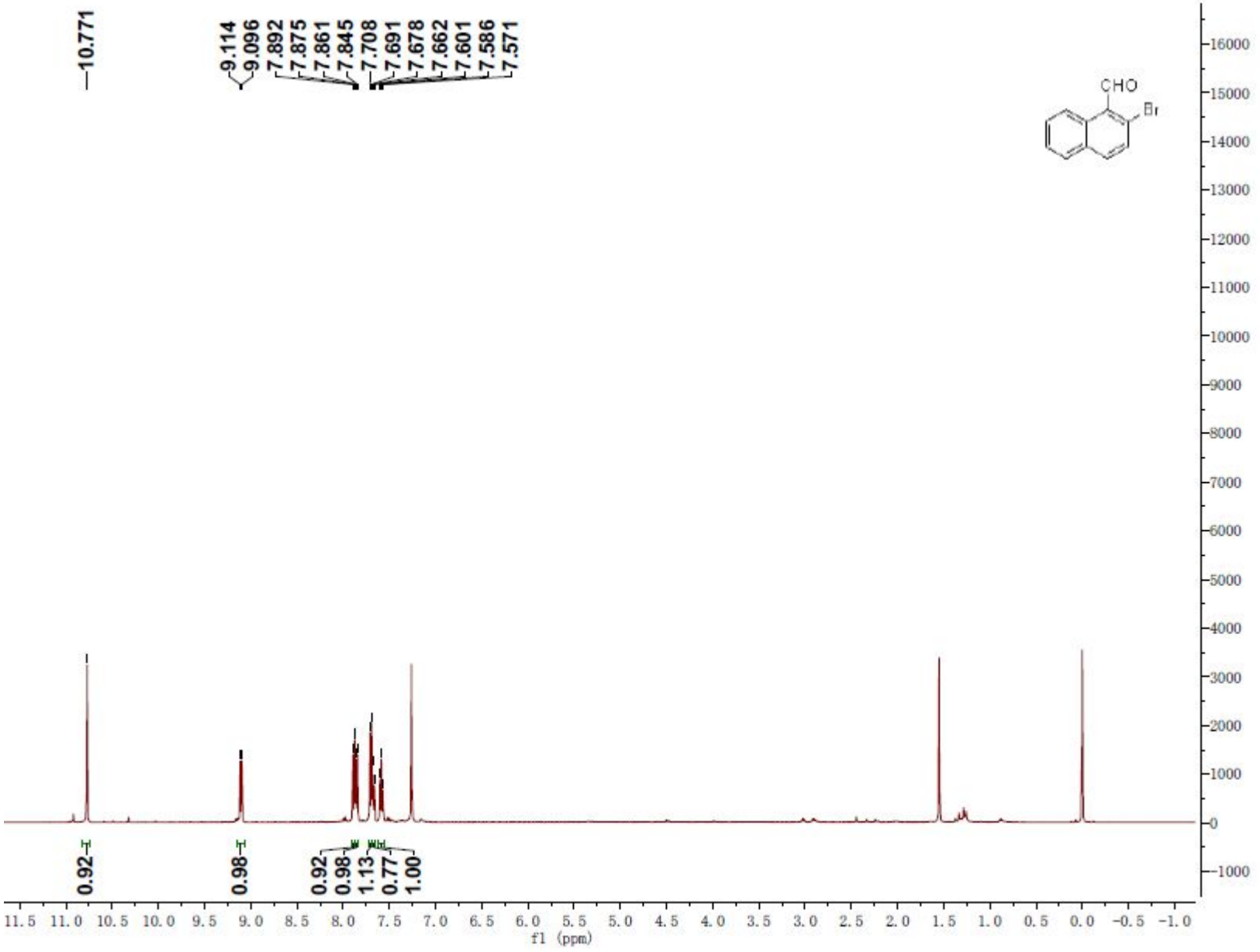
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-bromo-1-naphthaldehyde (1i)



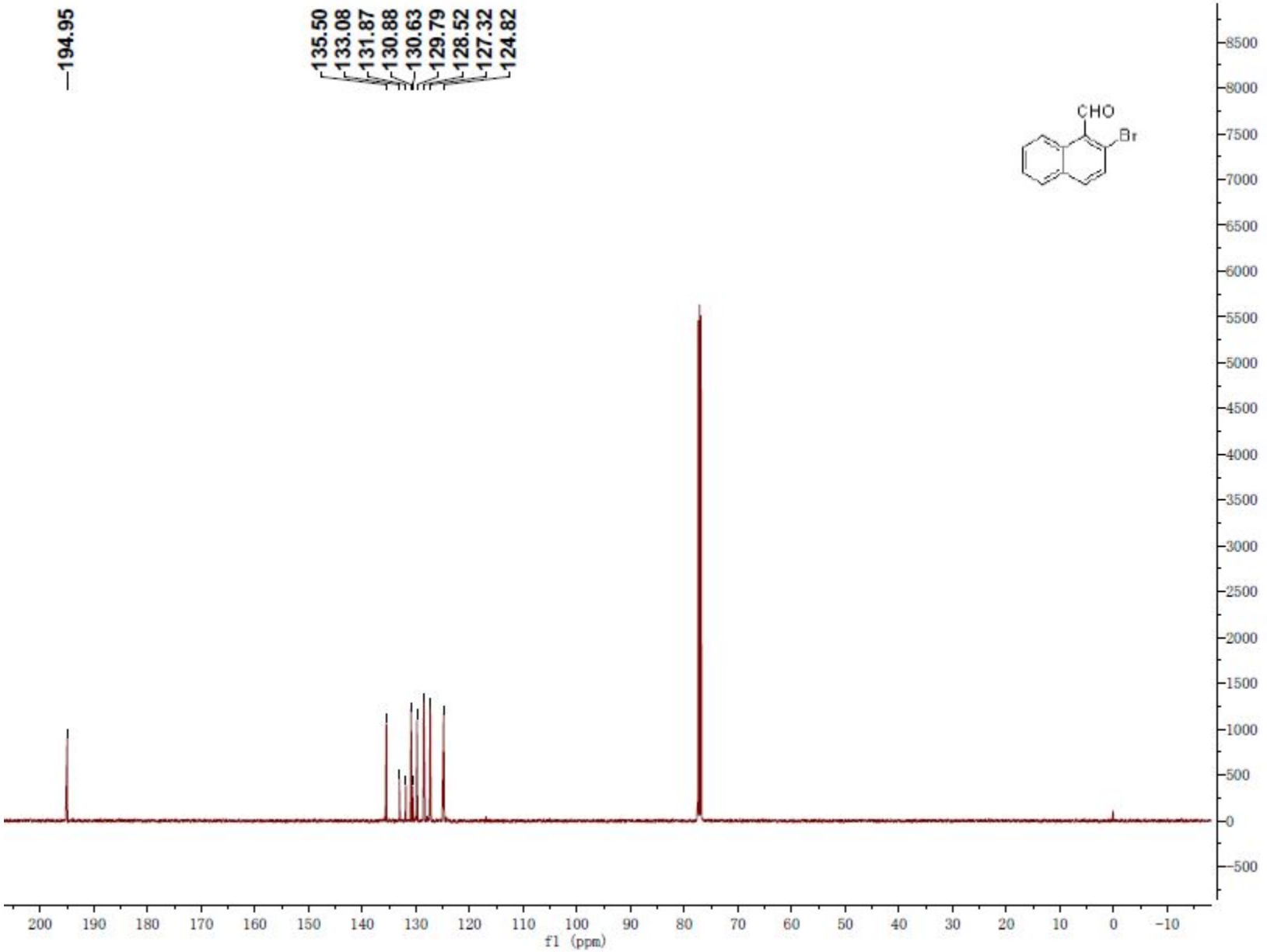
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-bromo-1-naphthaldehyde (1i)



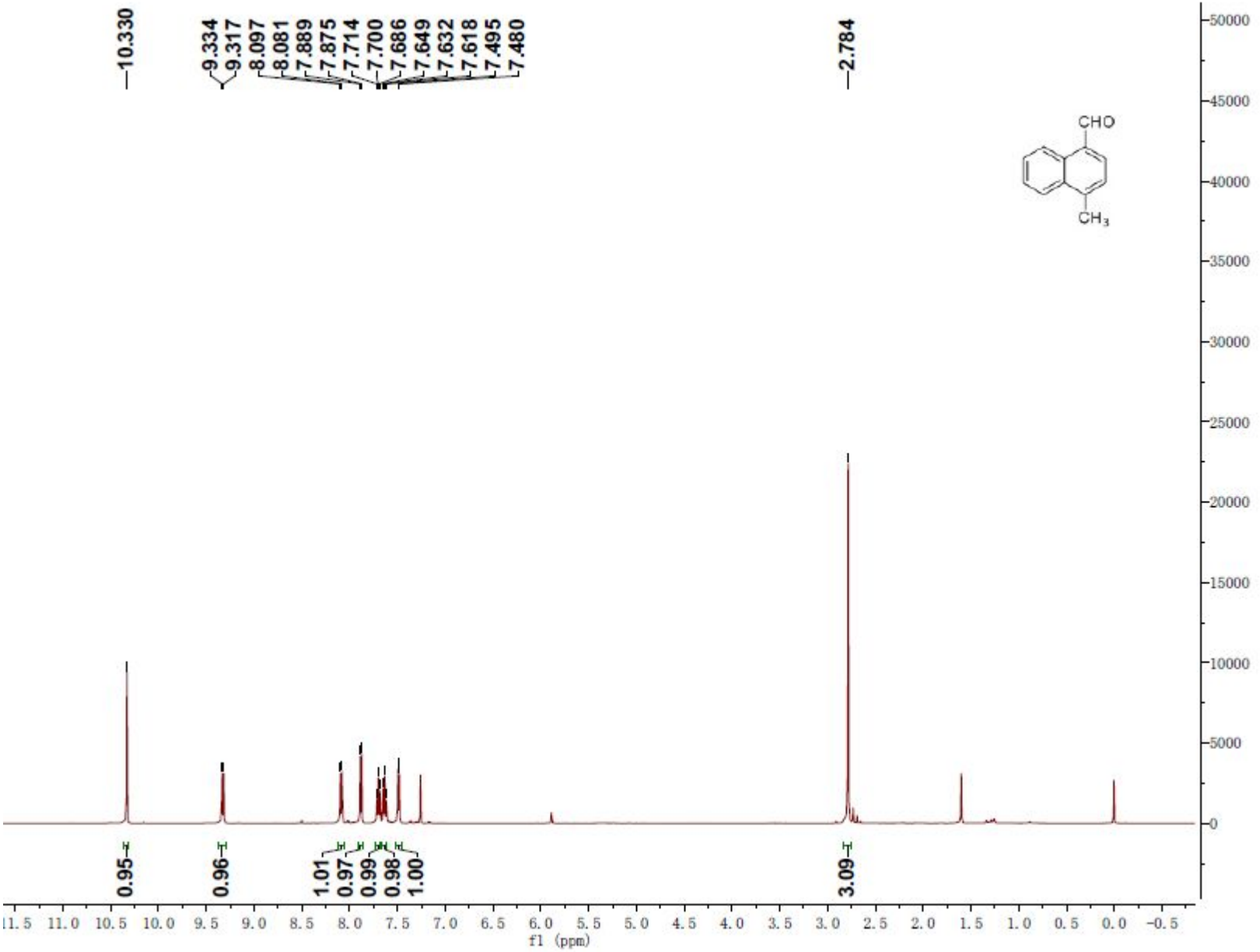
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2-bromo-1-naphthaldehyde (1j)



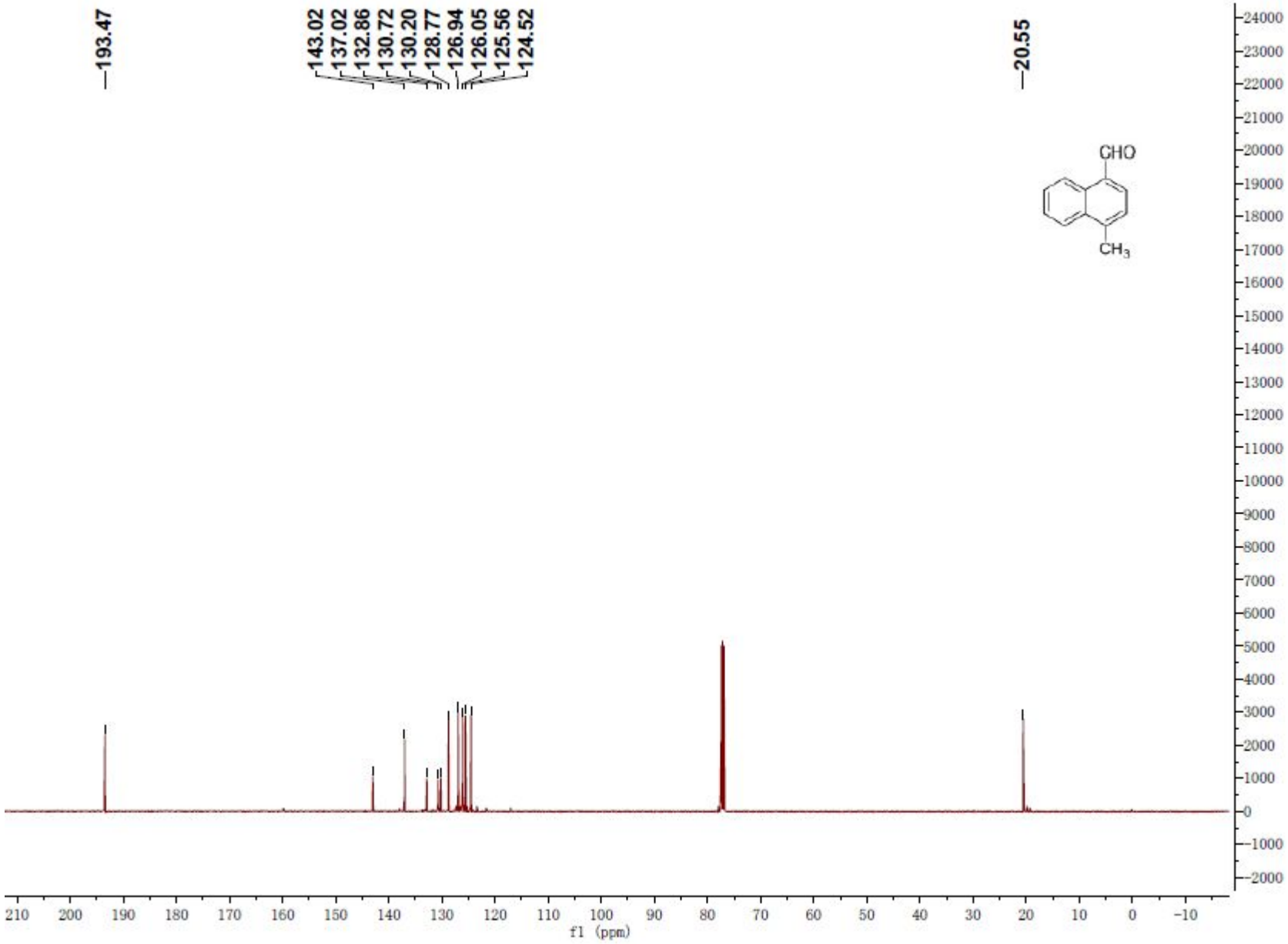
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 2-bromo-1-naphthaldehyde (1j)



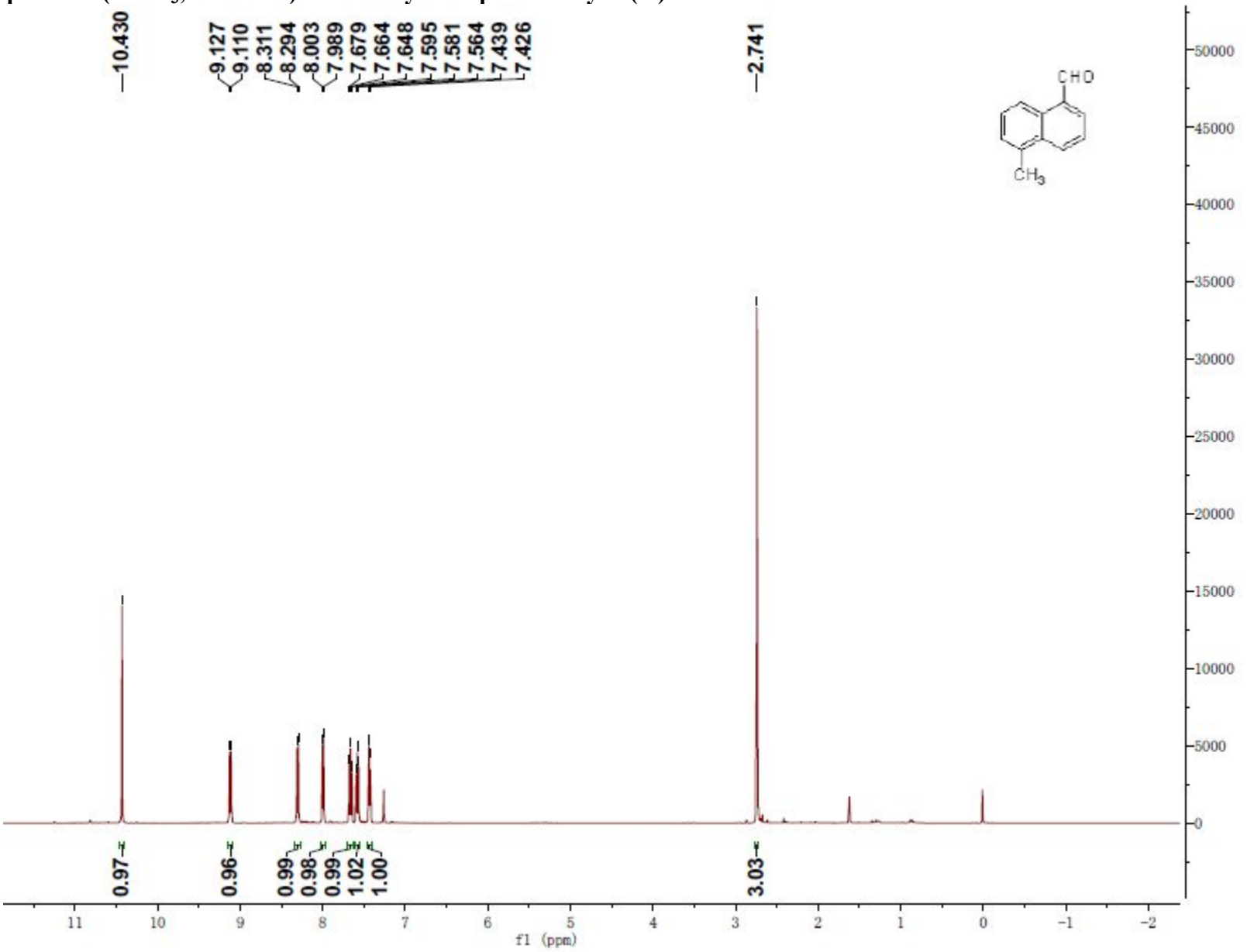
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-methyl-1-naphthaldehyde (1k)



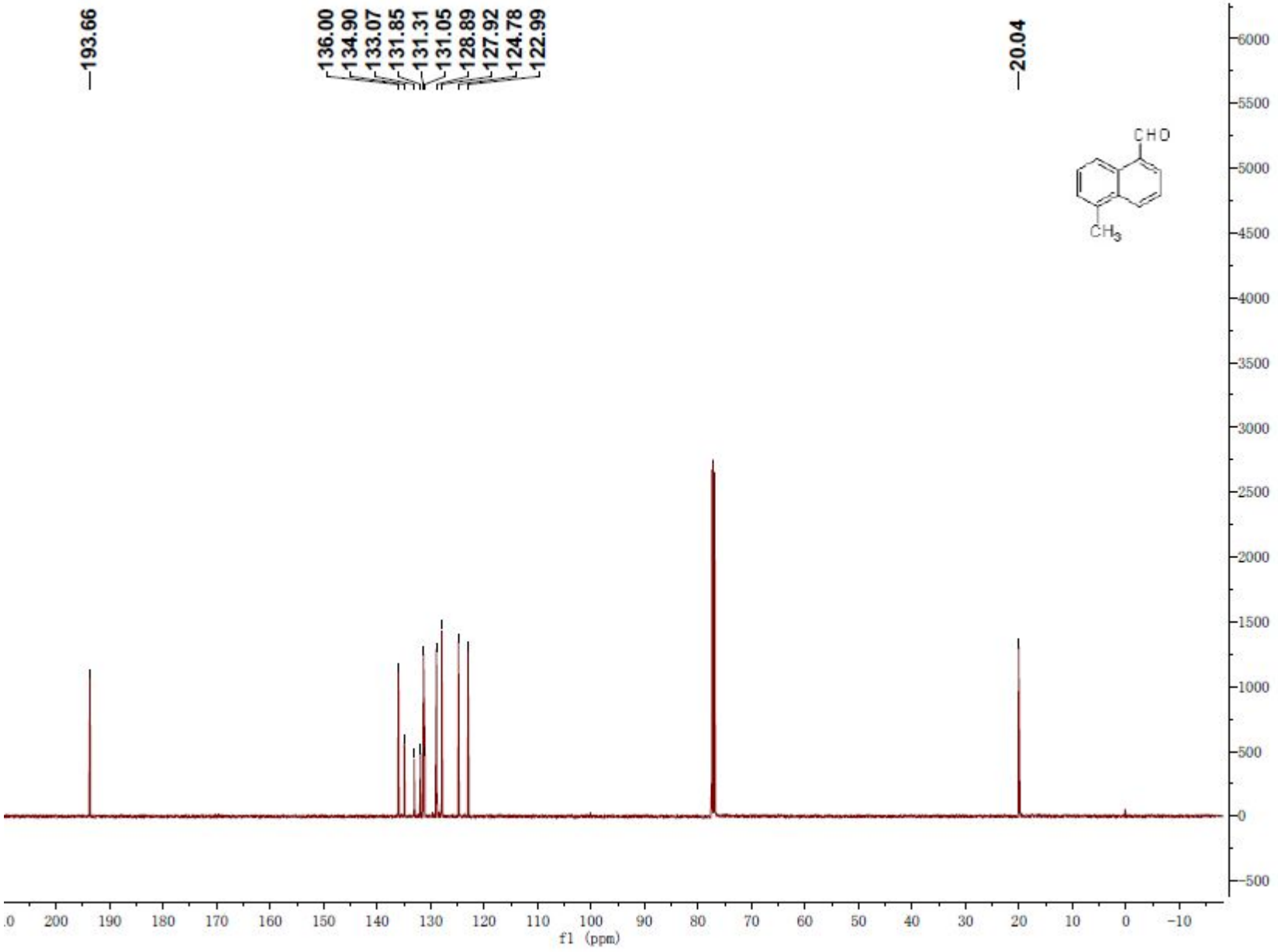
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-methyl-1-naphthaldehyde (1k)



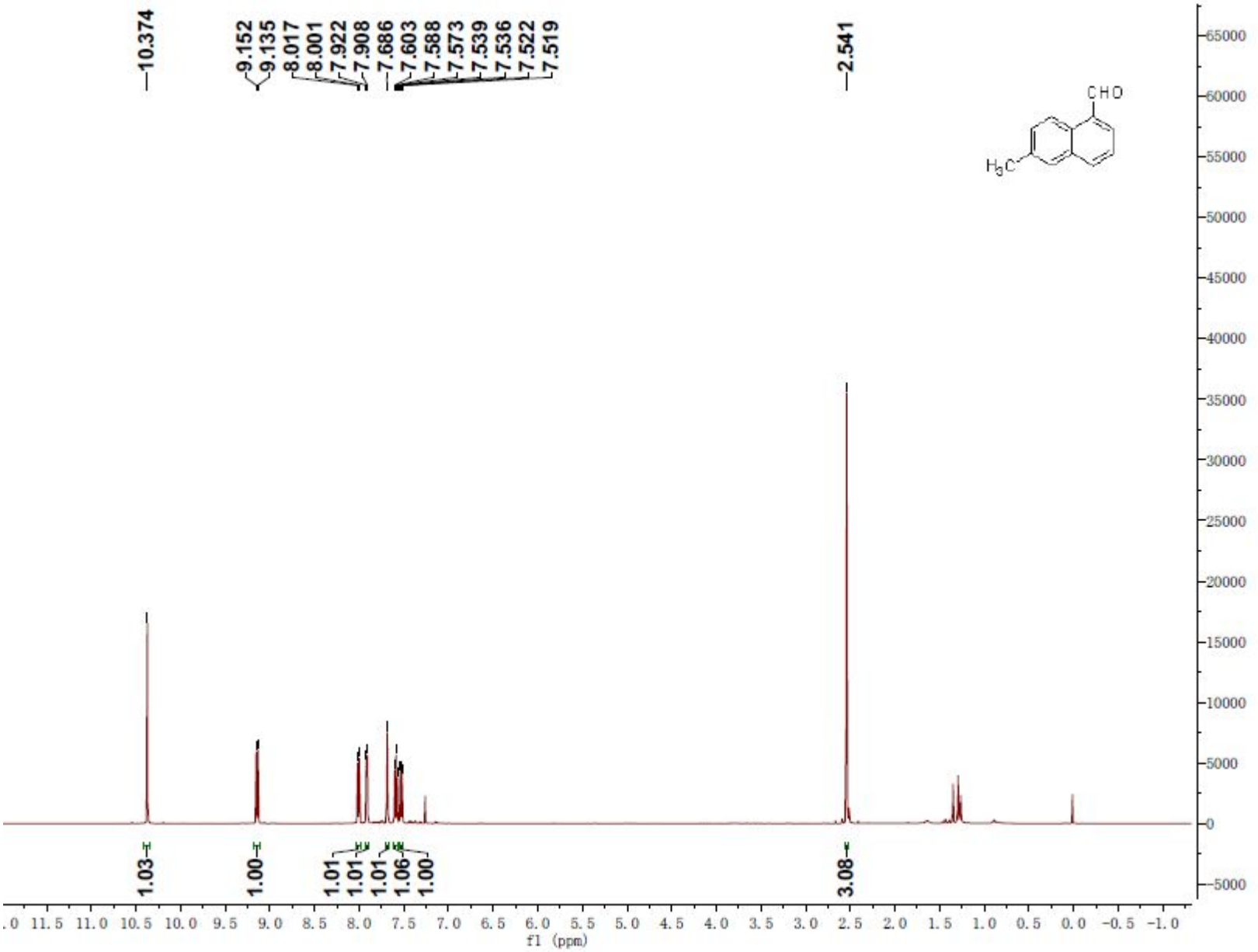
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-methyl-1-naphthaldehyde (1l)



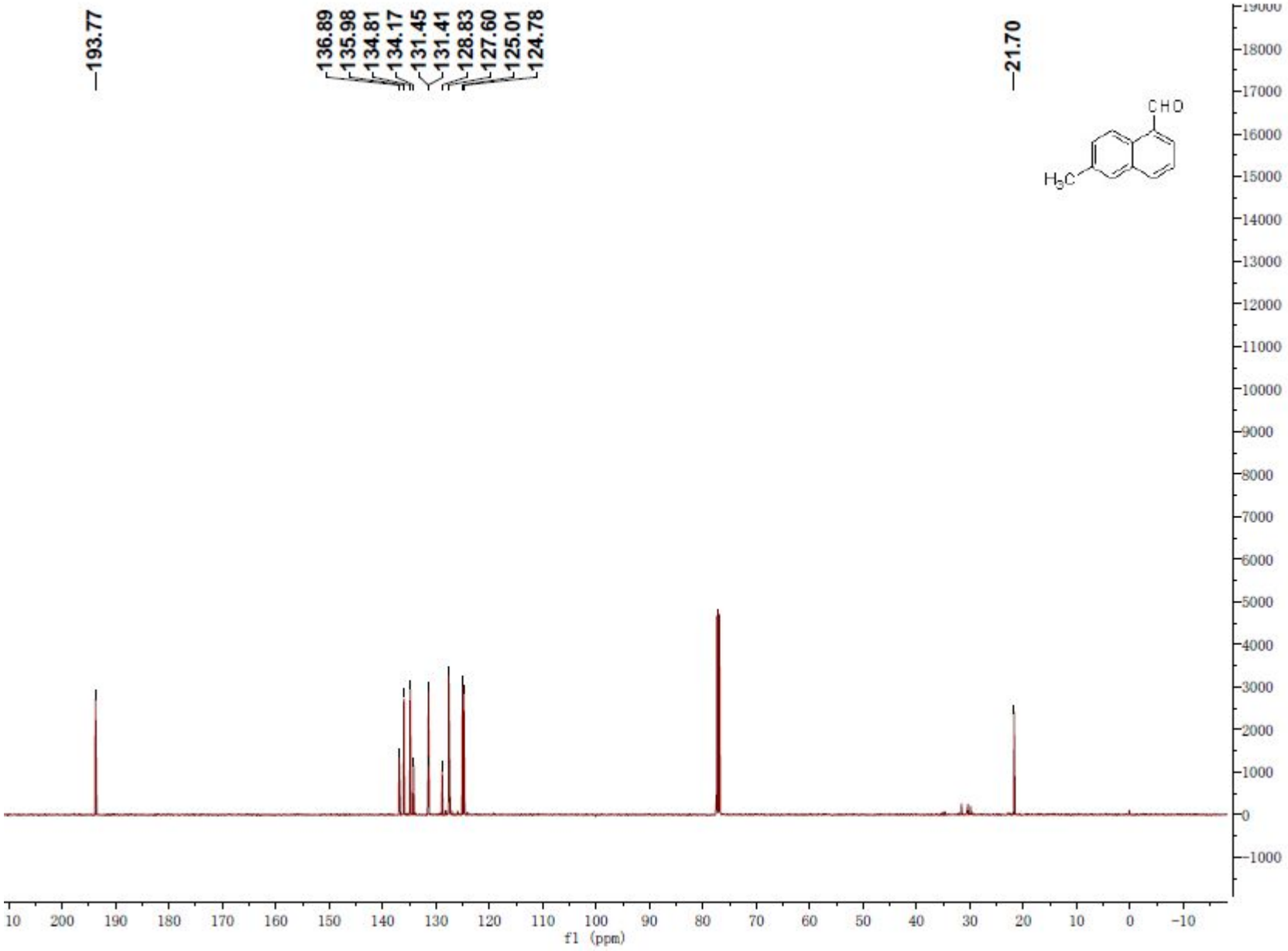
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-methyl-1-naphthaldehyde (1l)



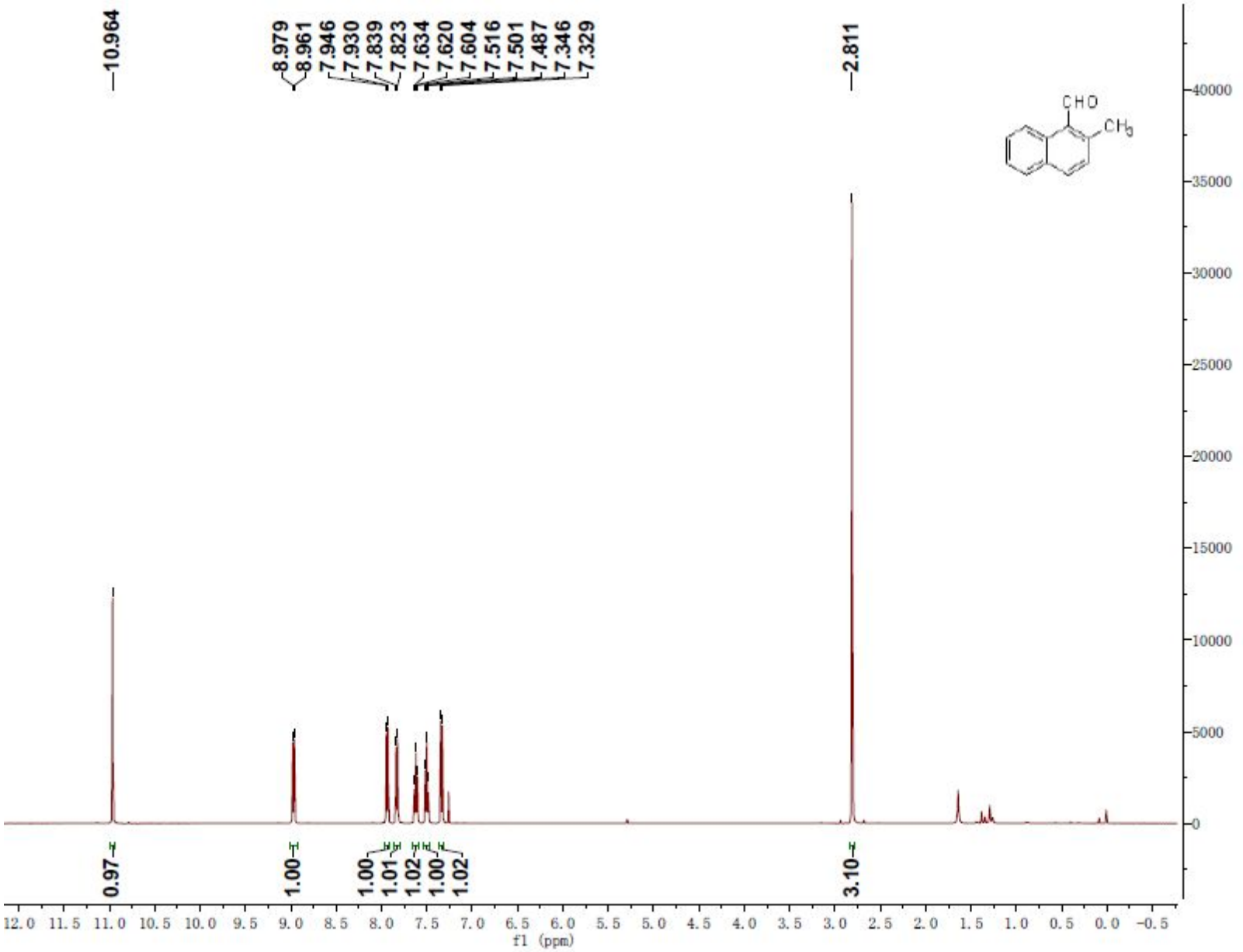
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 6-methyl-1-naphthaldehyde (1m)



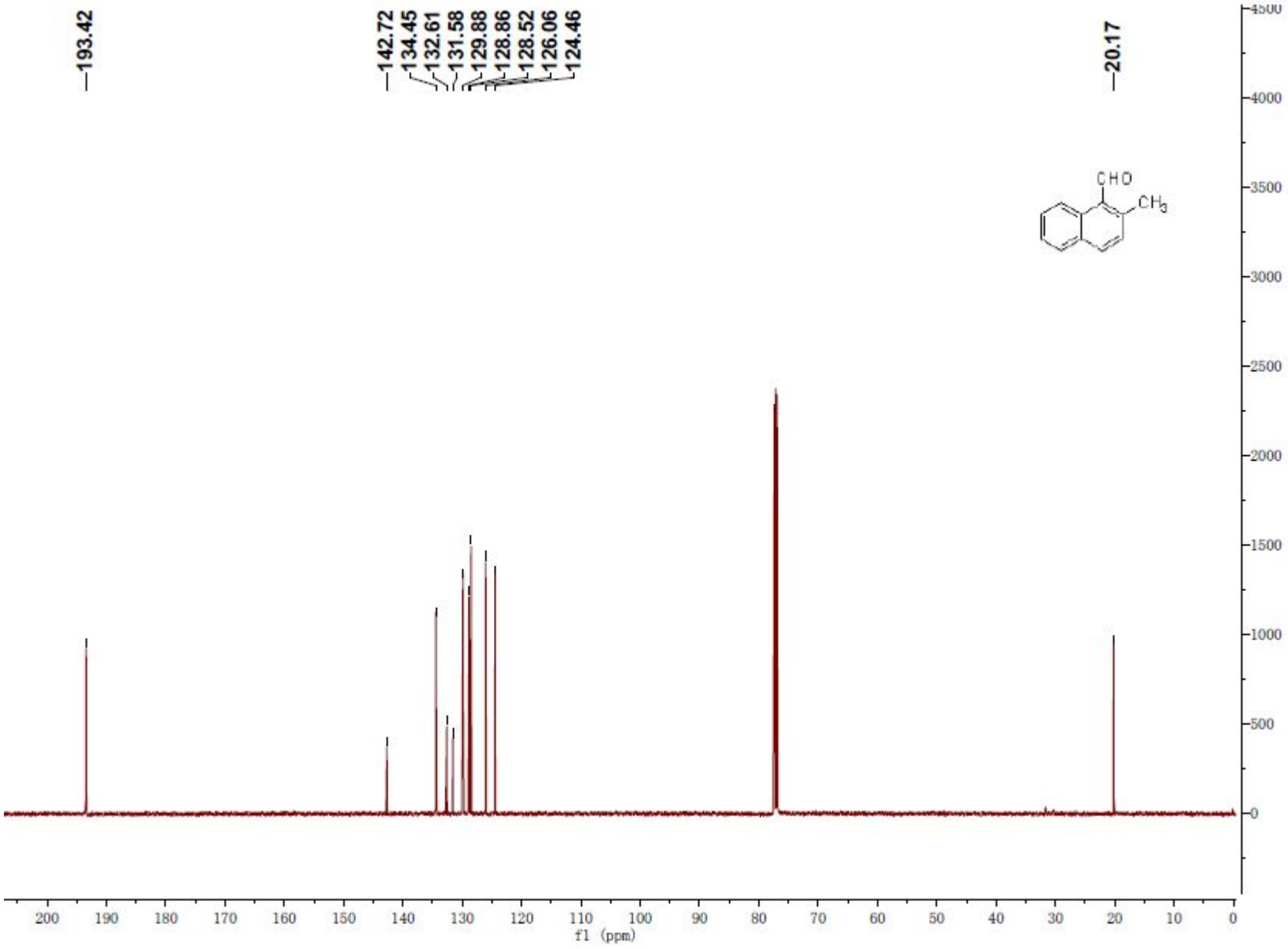
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 6-methyl-1-naphthaldehyde (1m)



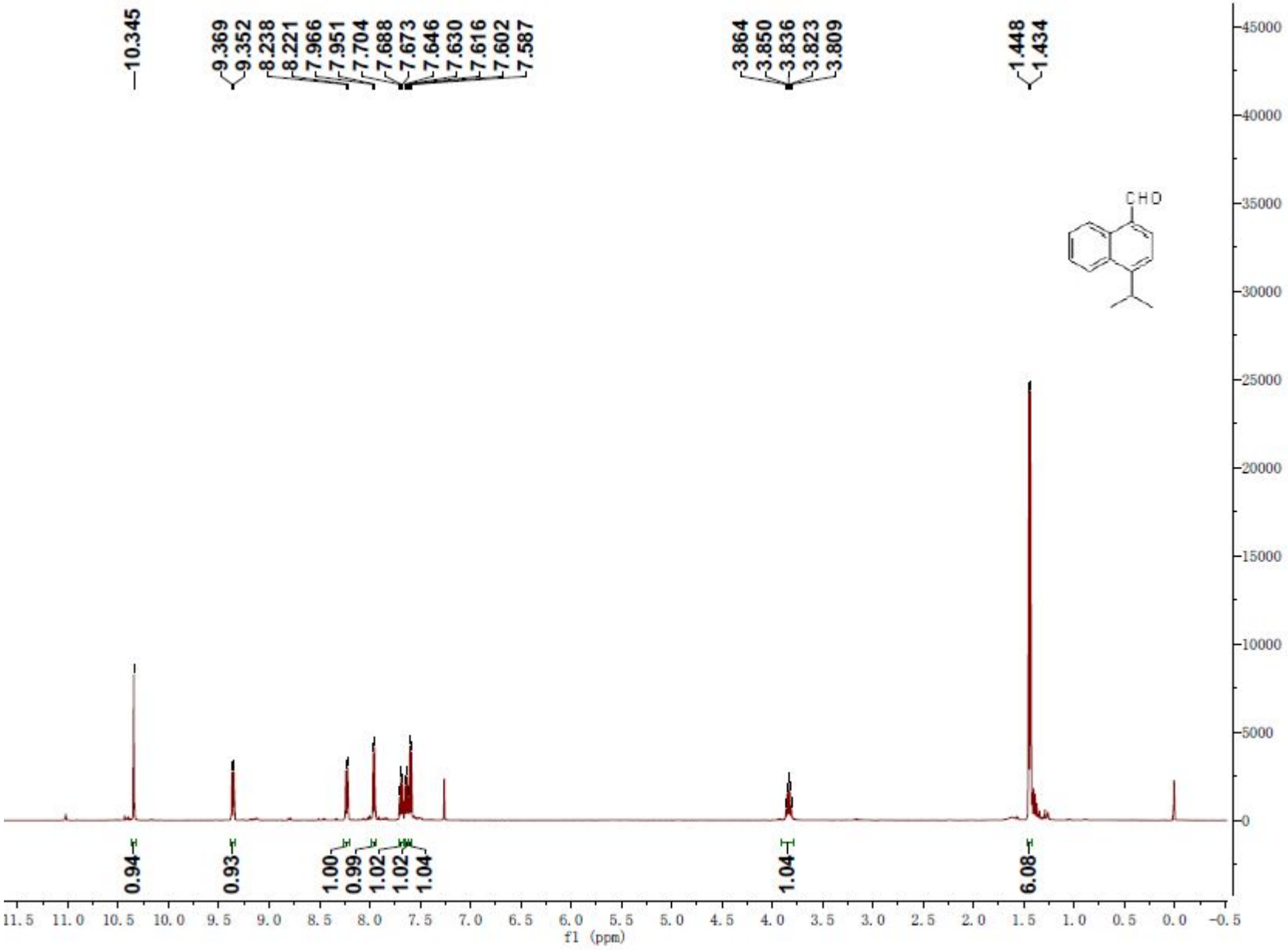
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2-methyl-1-naphthaldehyde (1n)



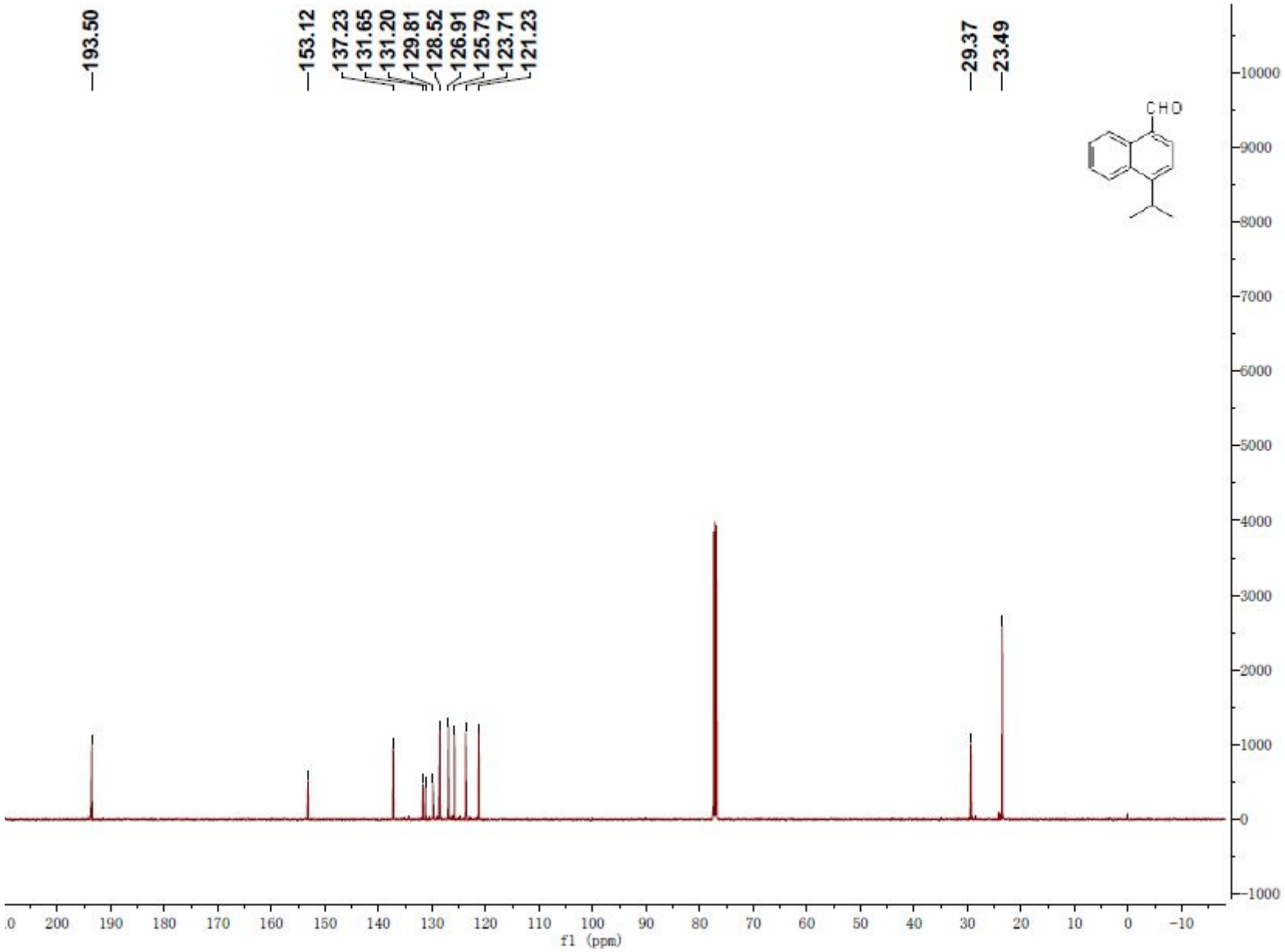
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 2-methyl-1-naphthaldehyde (1n)



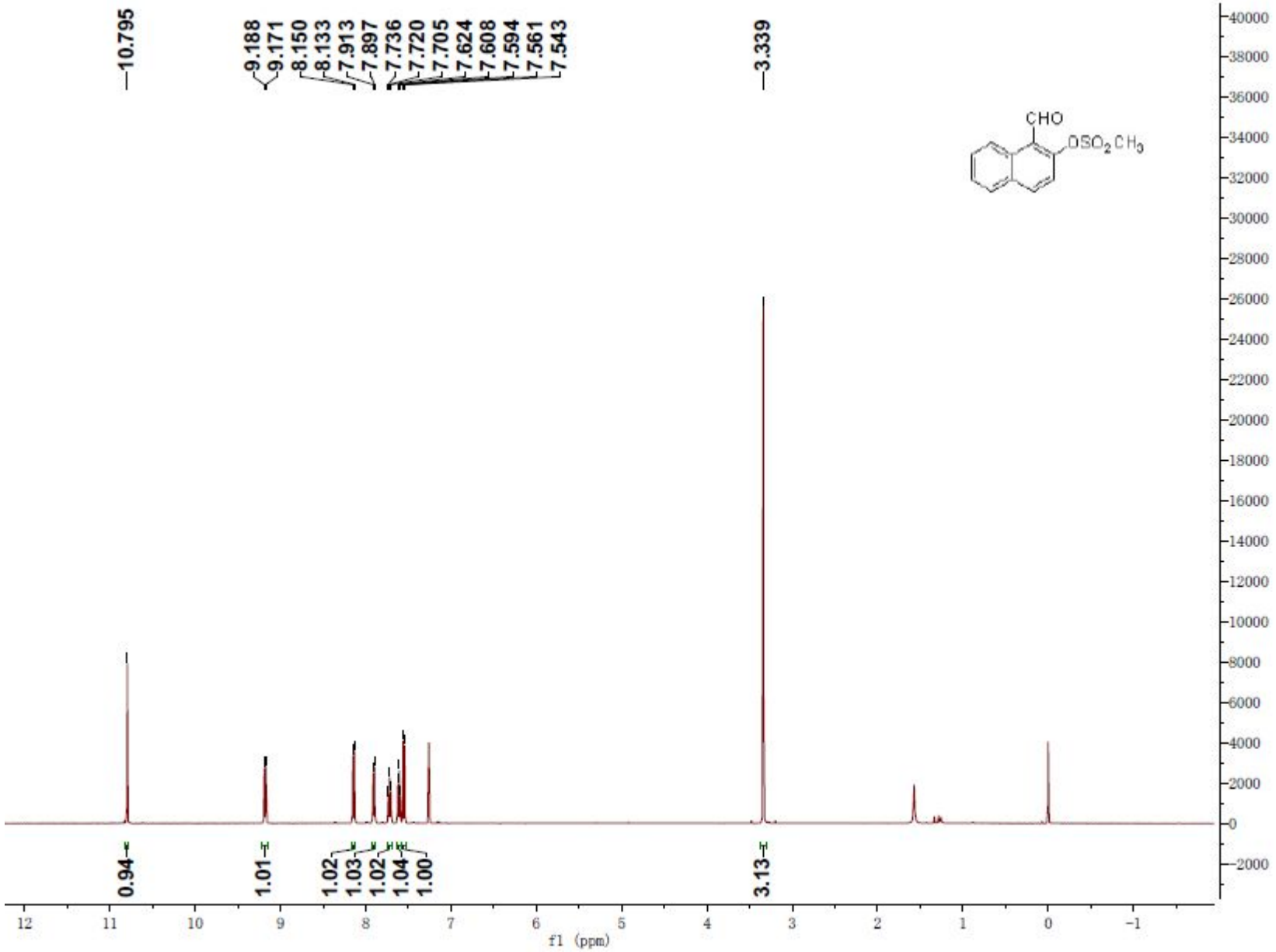
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-isopropyl-1-naphthaldehyde (1o)



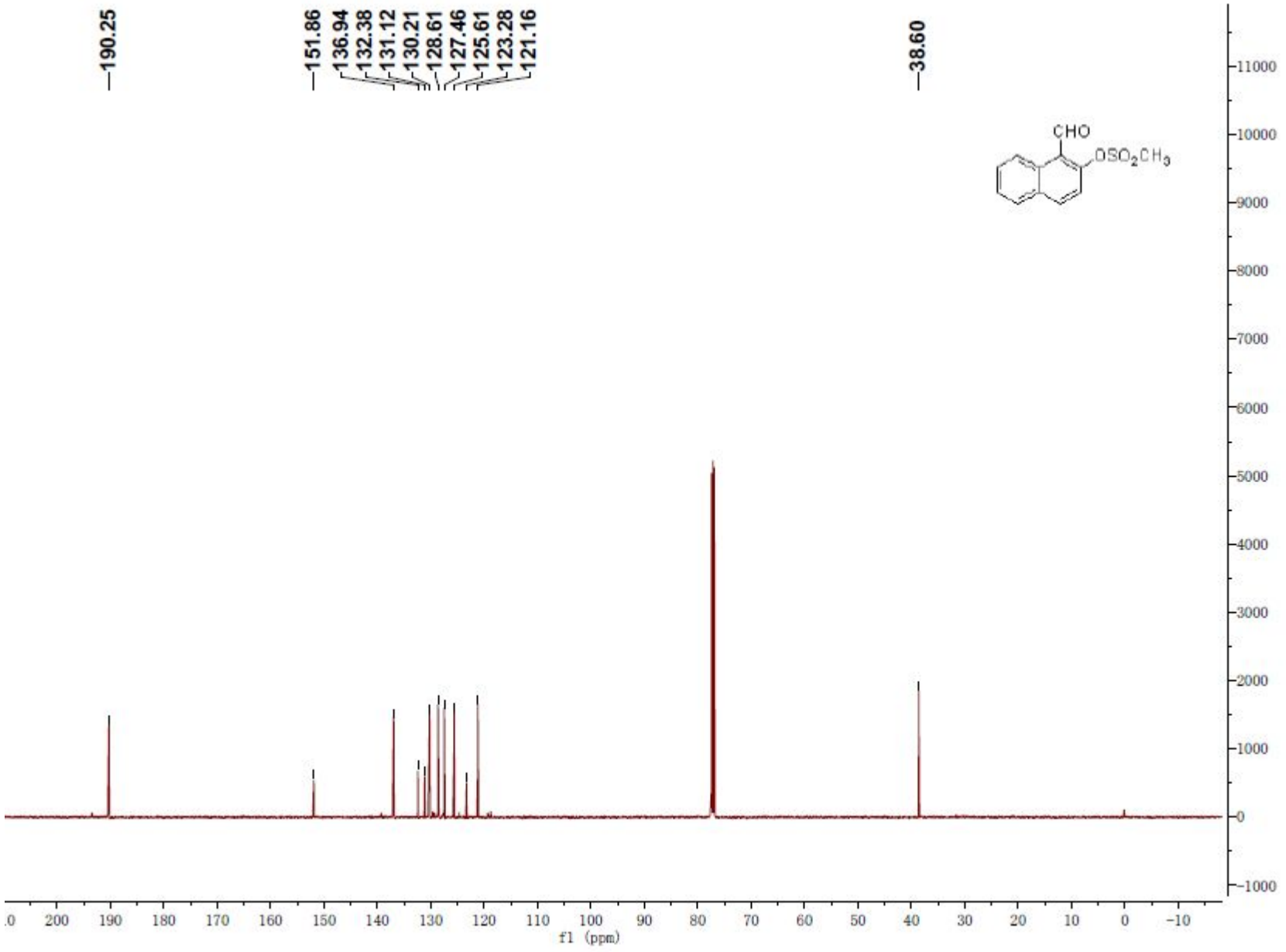
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-isopropyl-1-naphthaldehyde (1o)



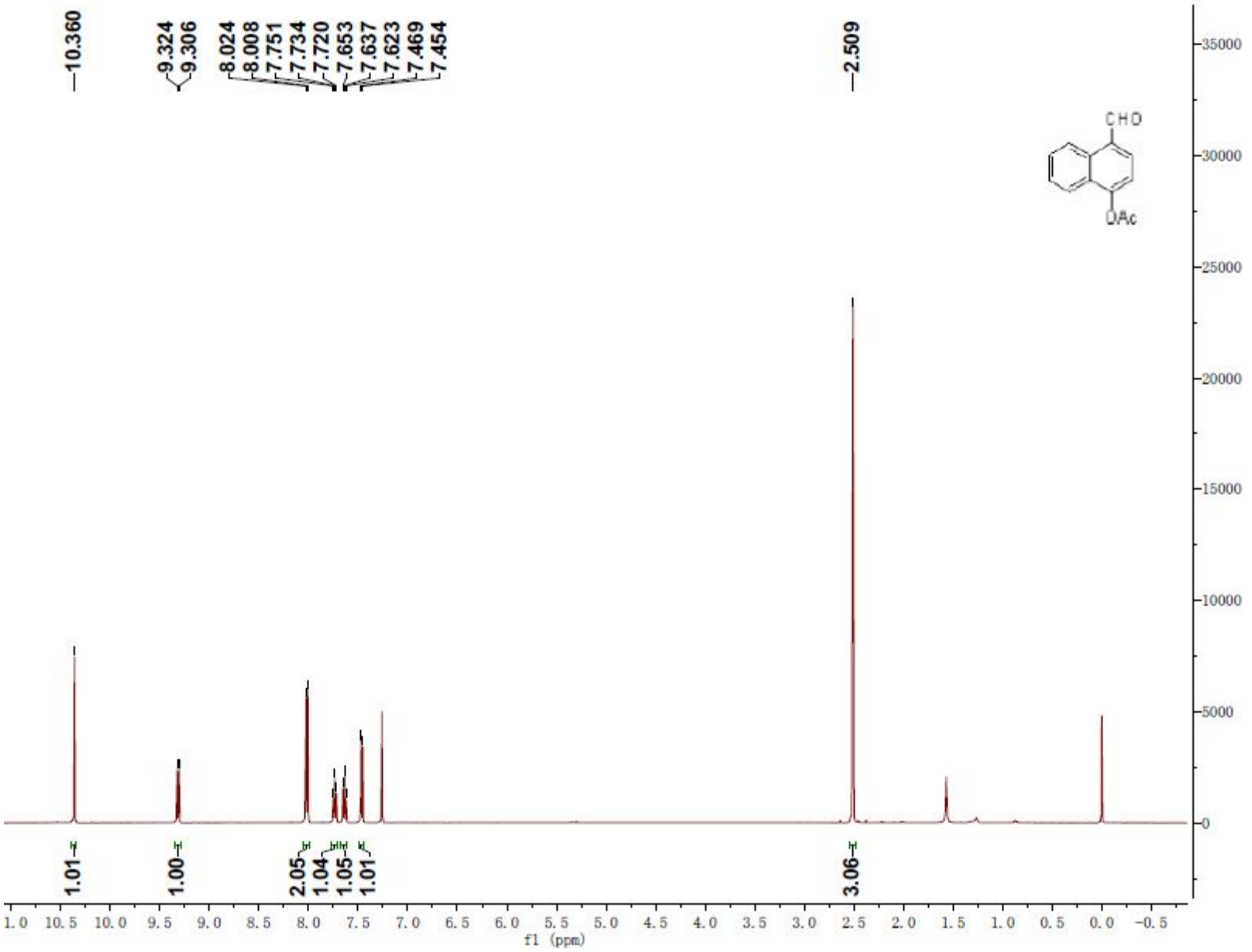
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1-formylnaphthalen-2-yl methanesulfonate (1r)



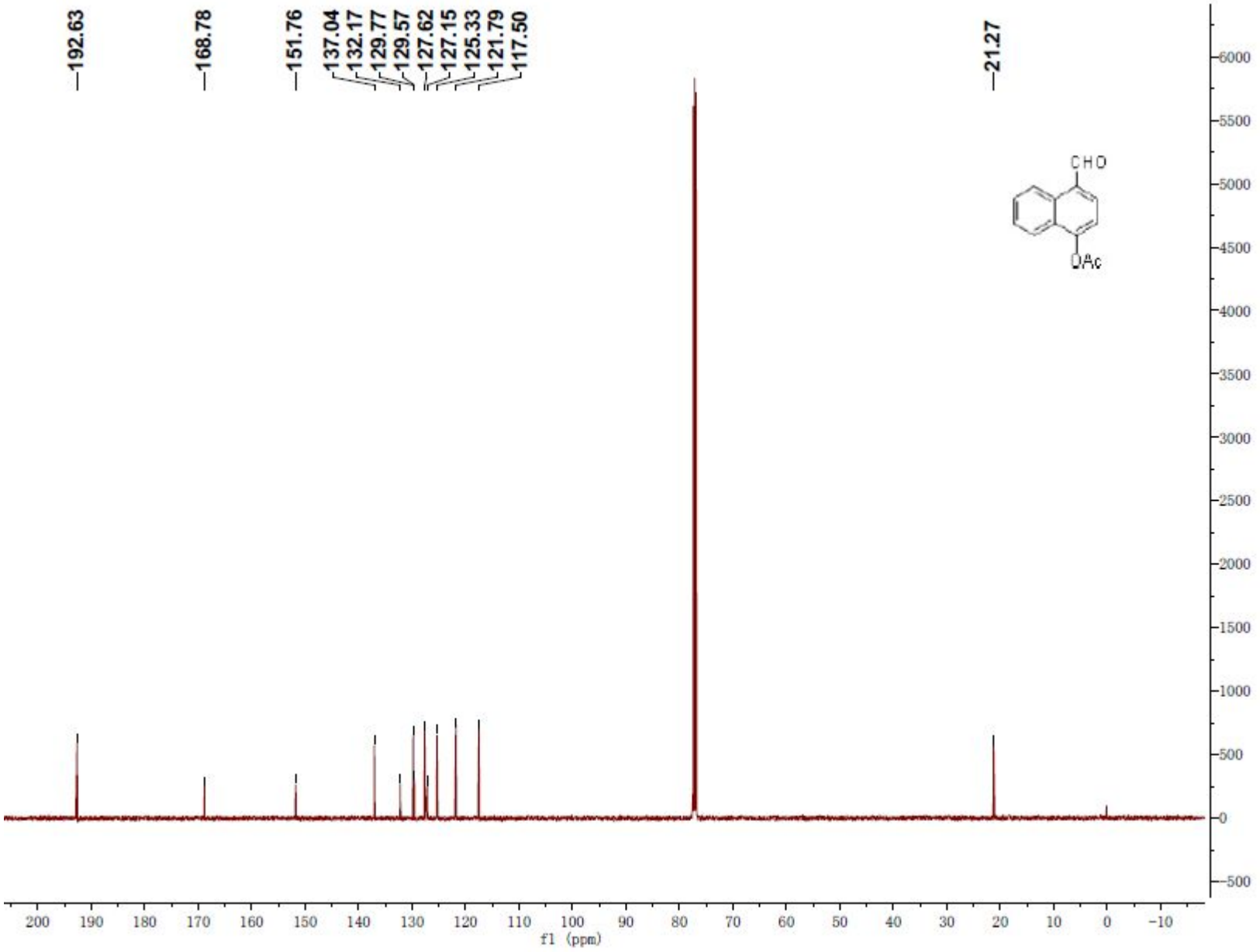
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 1-formylnaphthalen-2-yl methanesulfonate (1r)



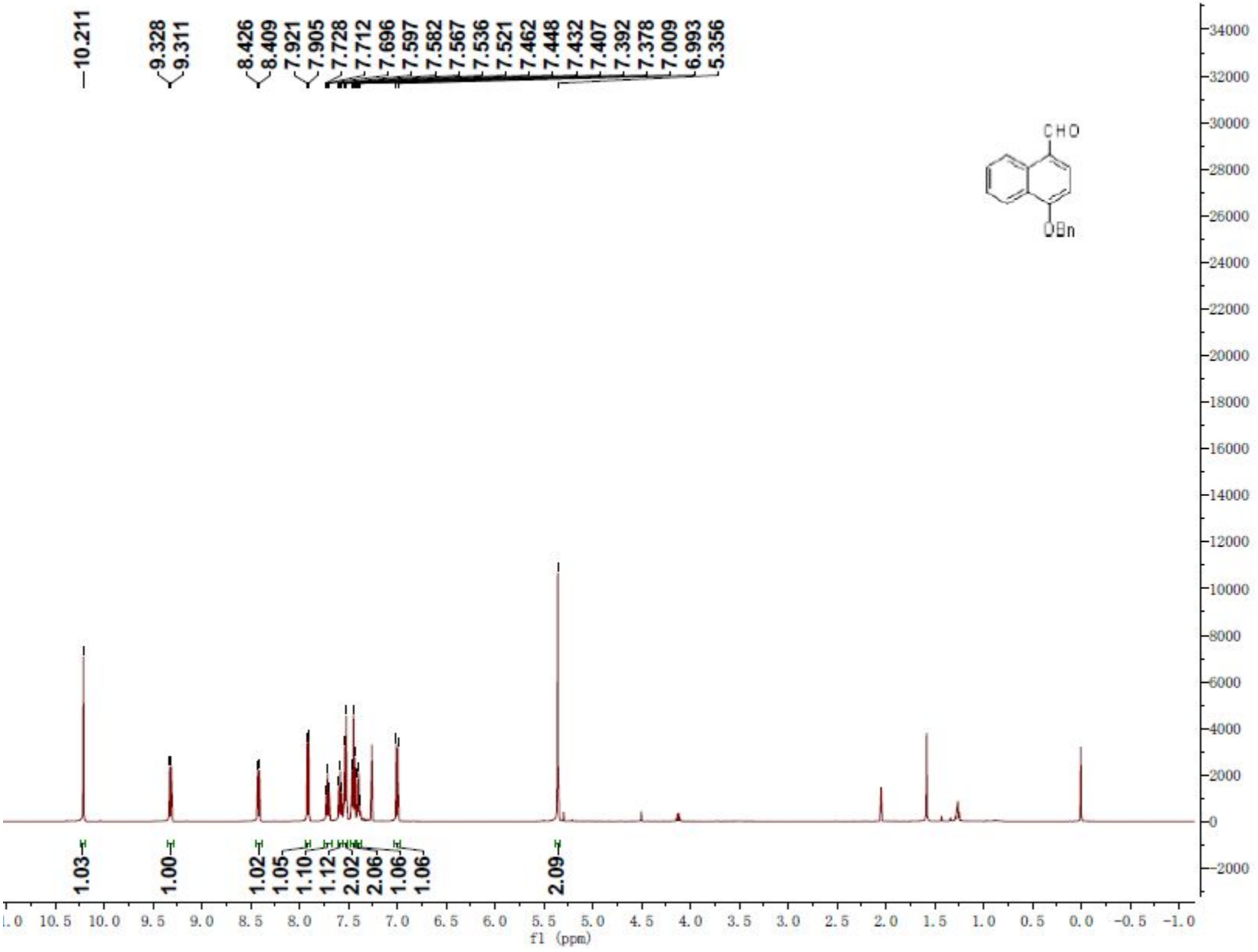
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-formylnaphthalen-1-yl acetate (1s)



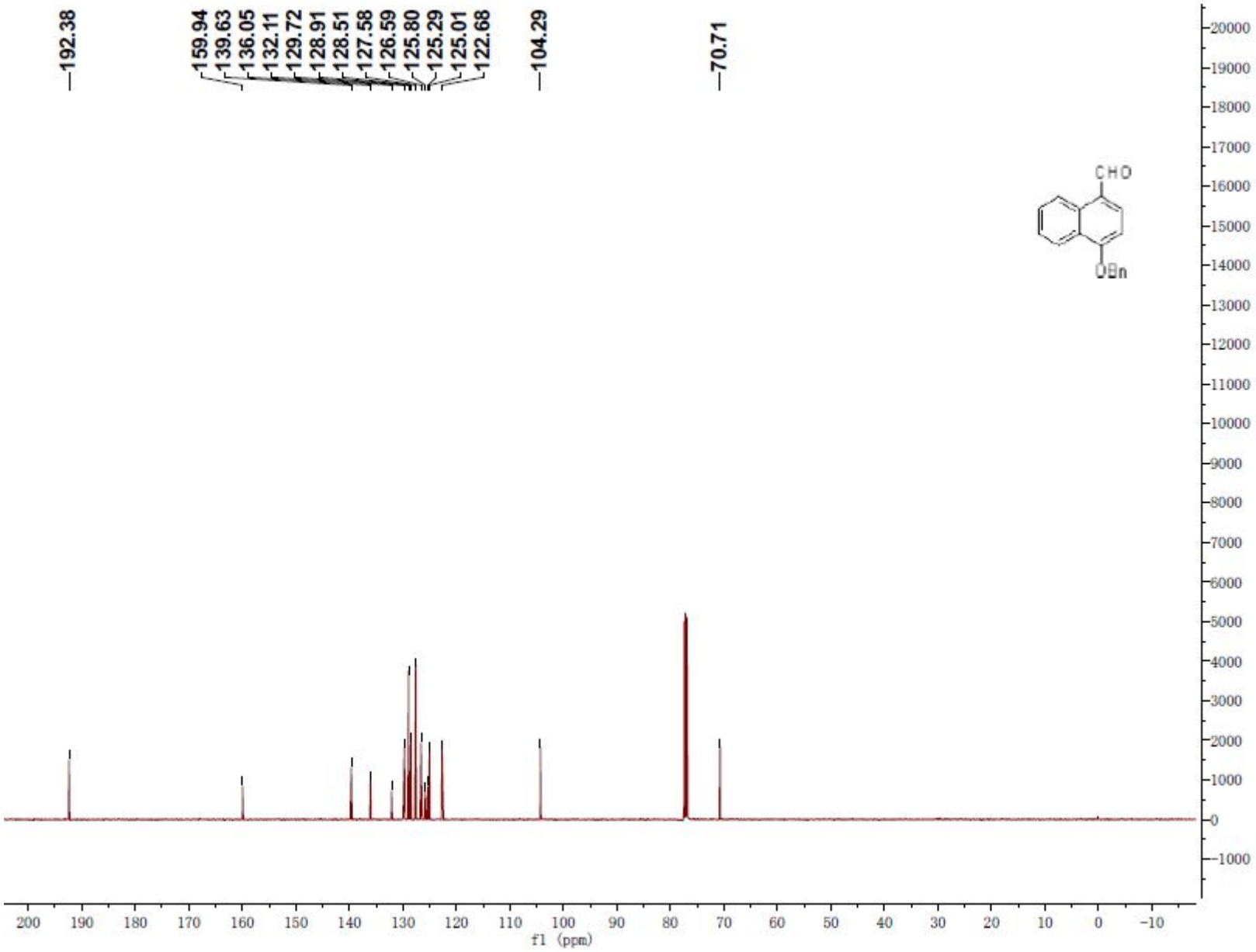
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-formylnaphthalen-1-yl acetate (1s)



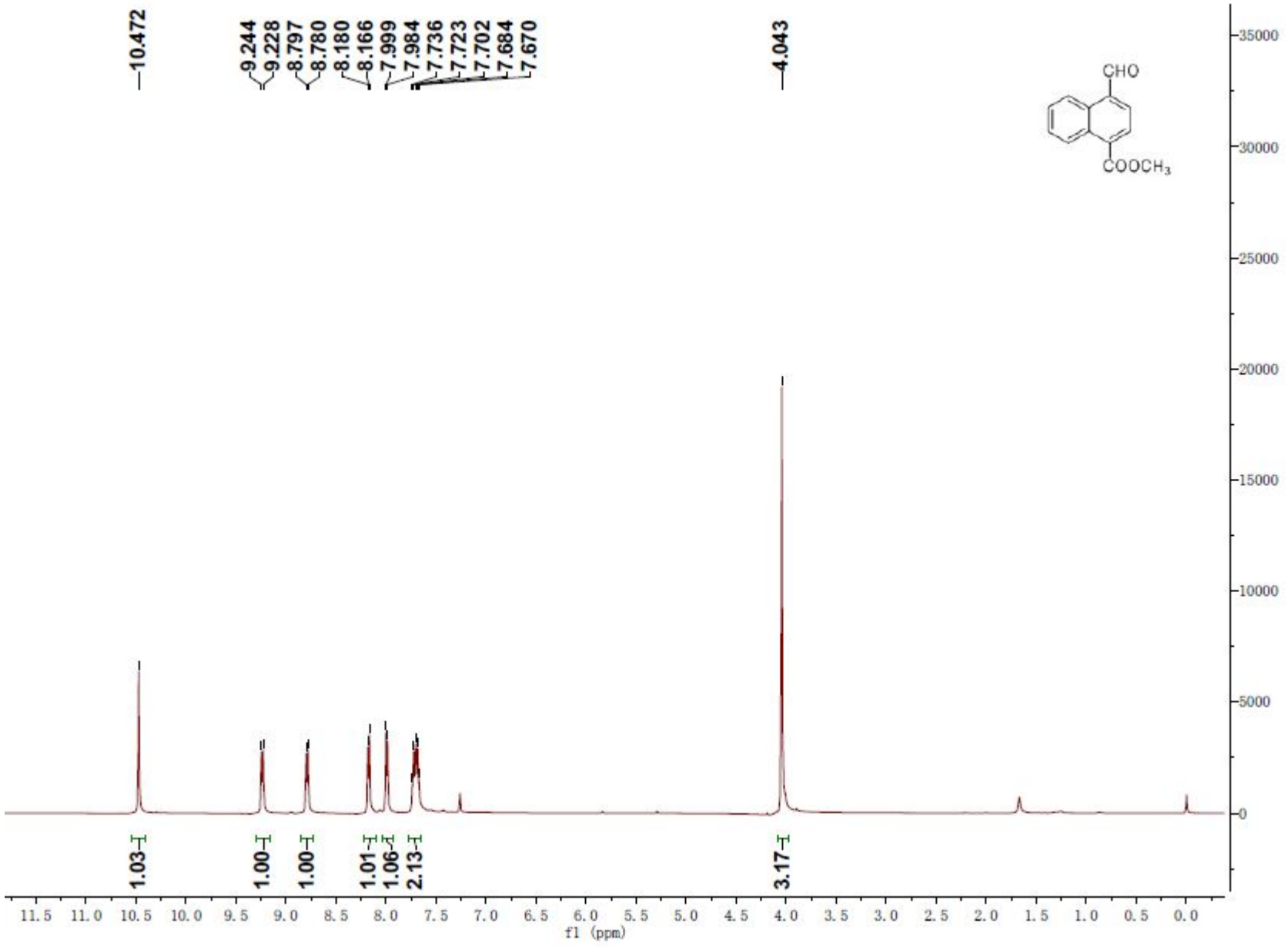
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-(benzyloxy)-1-naphthaldehyde (1t)



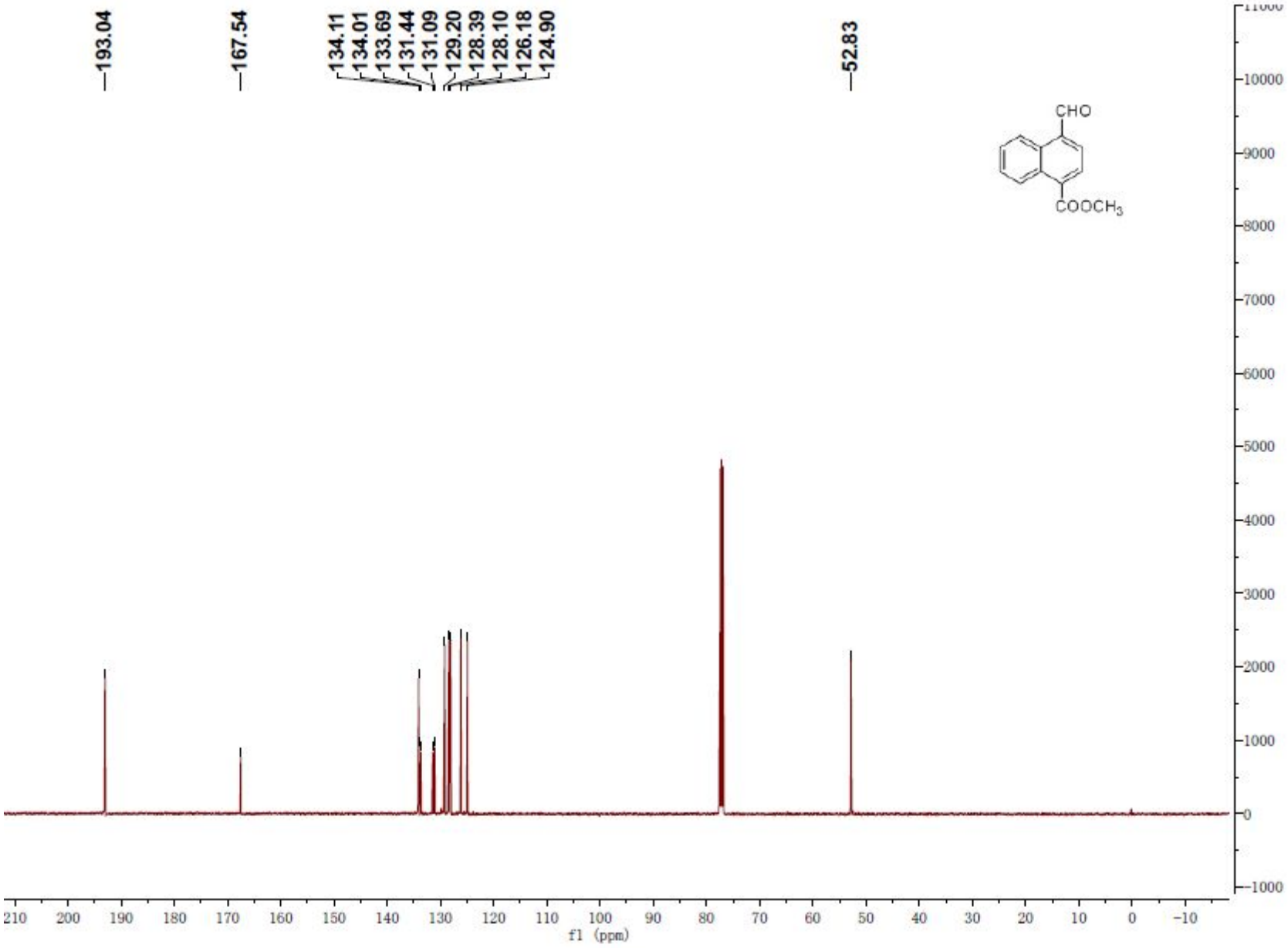
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-(benzyloxy)-1-naphthaldehyde (1t)



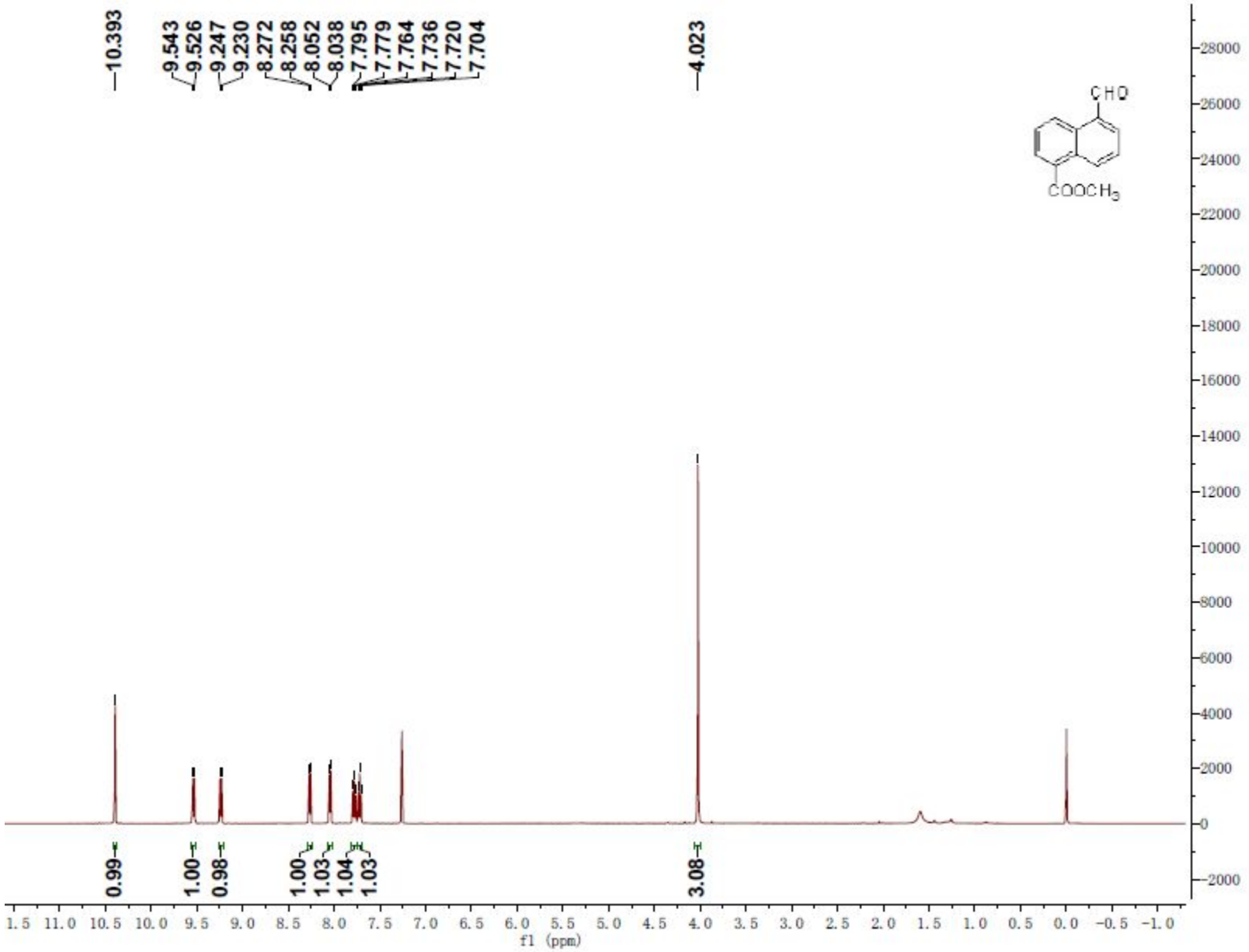
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of methyl 4-formyl-1-naphthoate (1u)



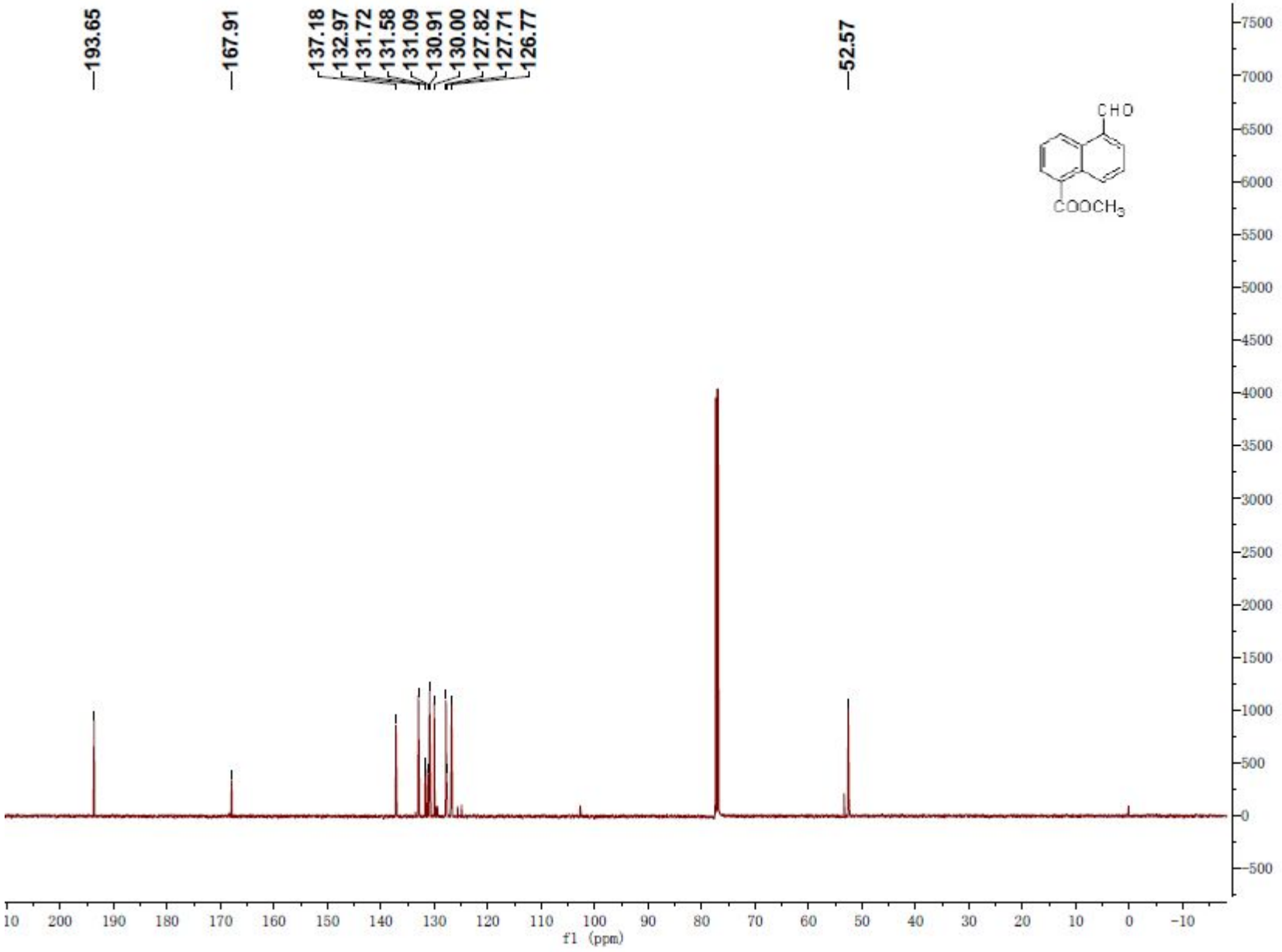
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of methyl 4-formyl-1-naphthoate (1u)



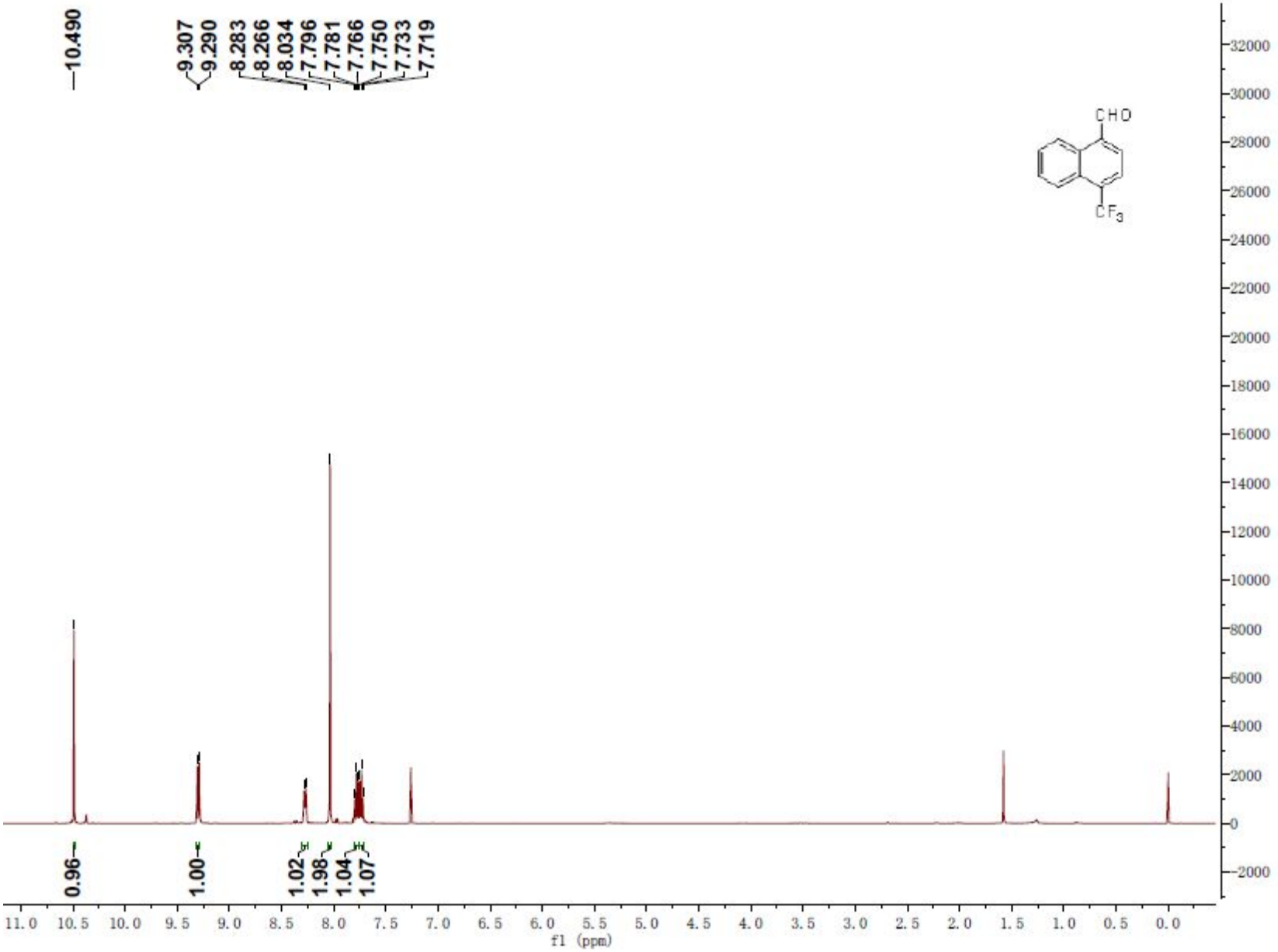
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of methyl 5-formyl-1-naphthoate (1v)



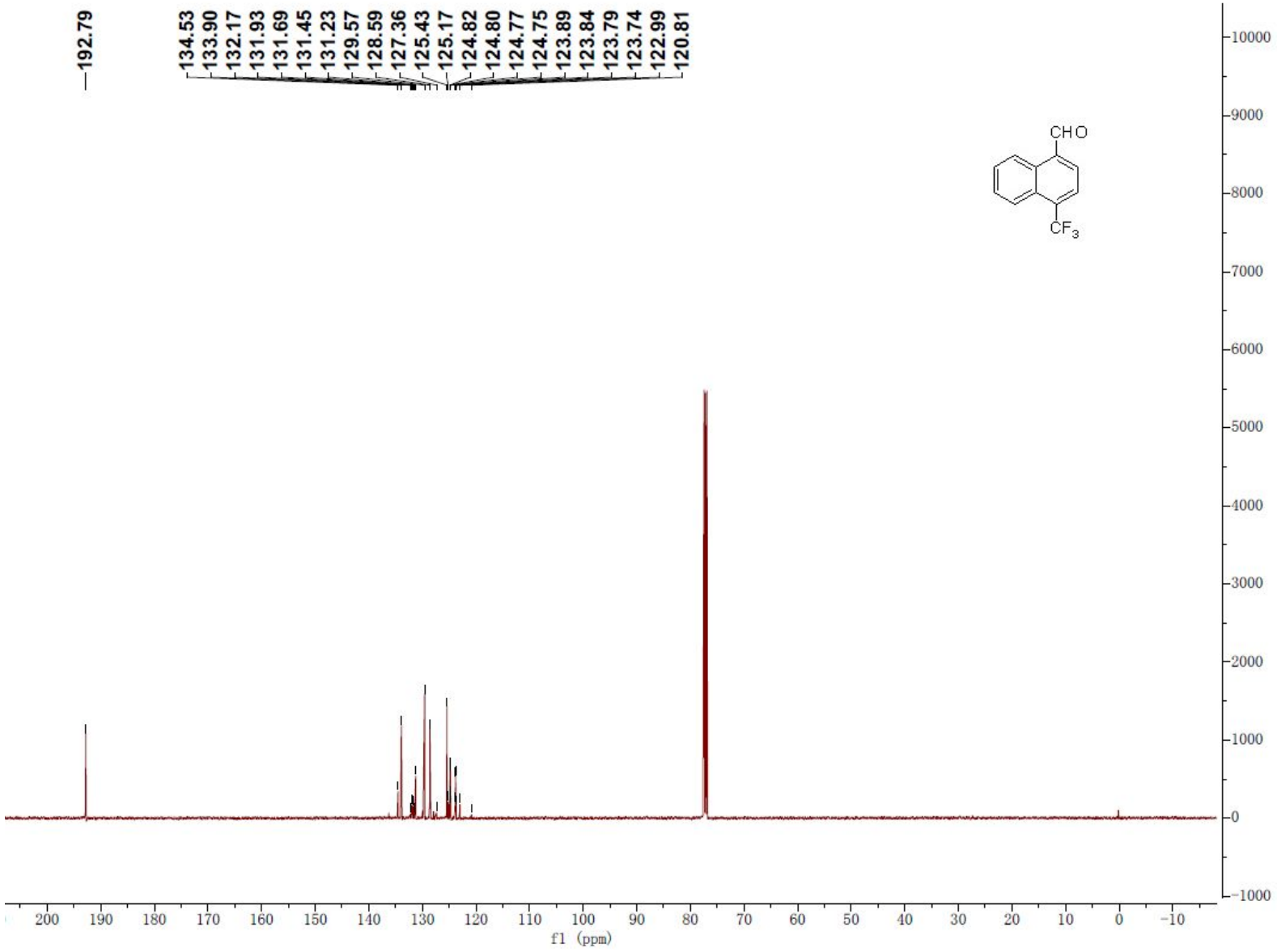
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of methyl 5-formyl-1-naphthoate (1v)



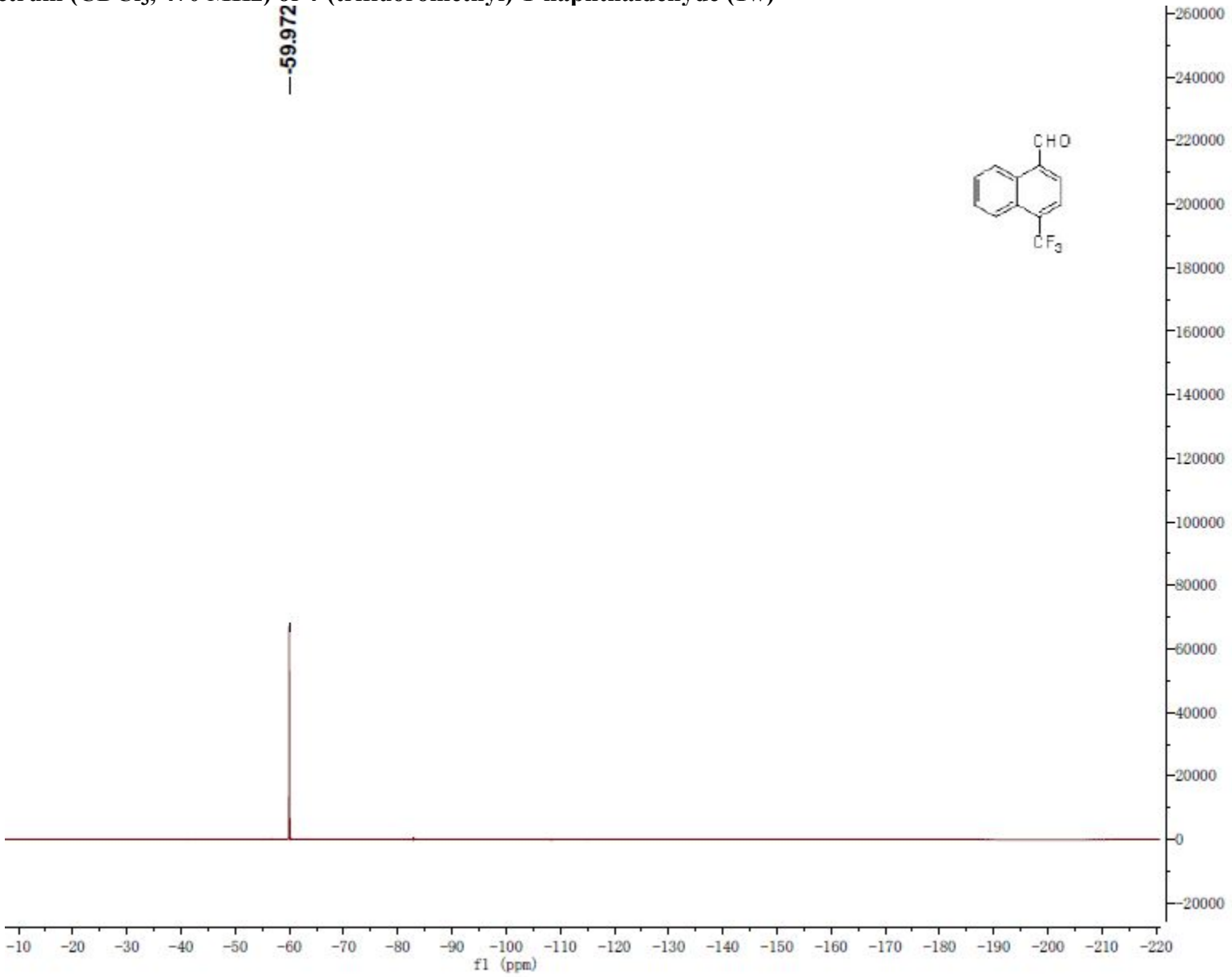
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-(trifluoromethyl)-1-naphthaldehyde (1w)



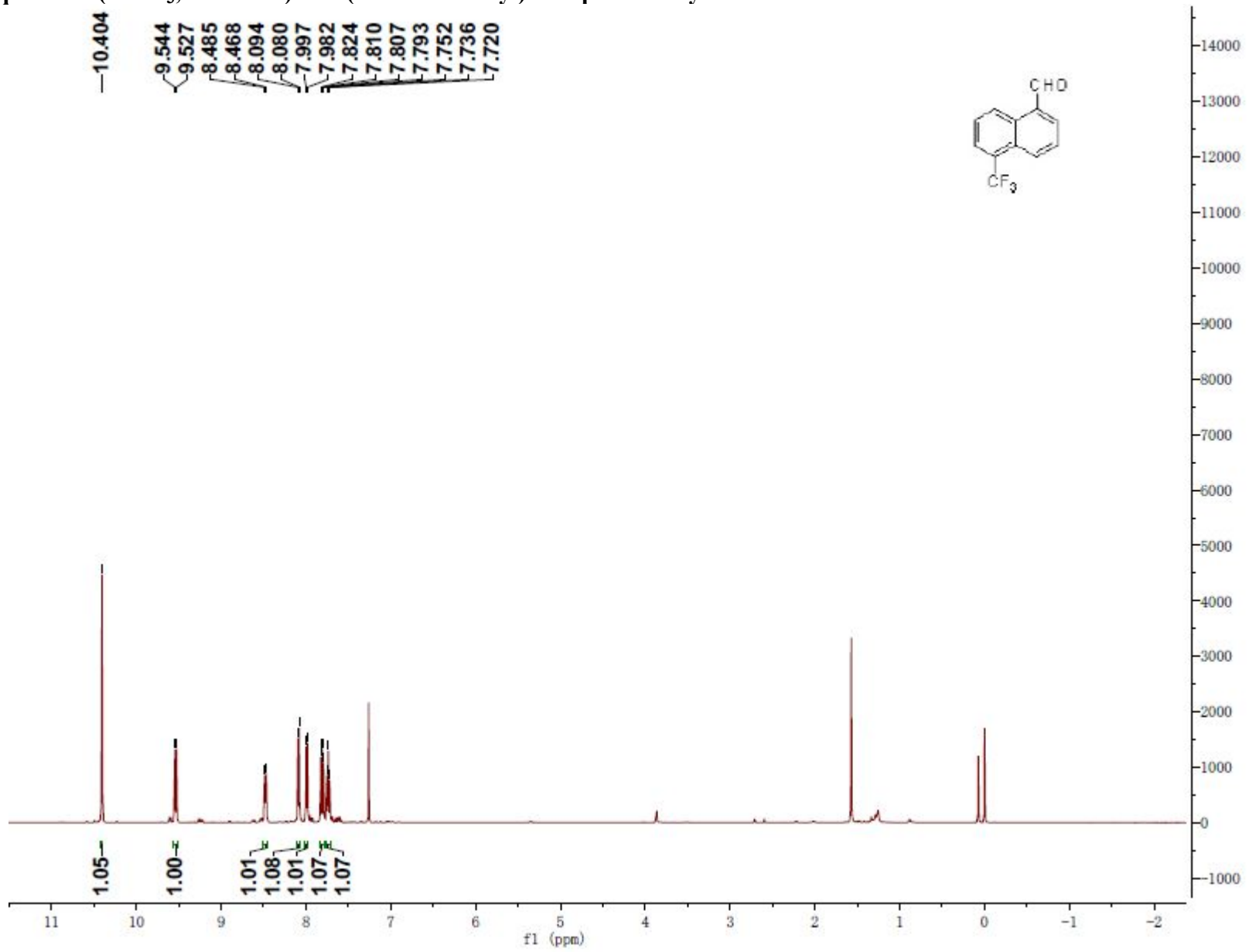
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-(trifluoromethyl)-1-naphthaldehyde (1w)



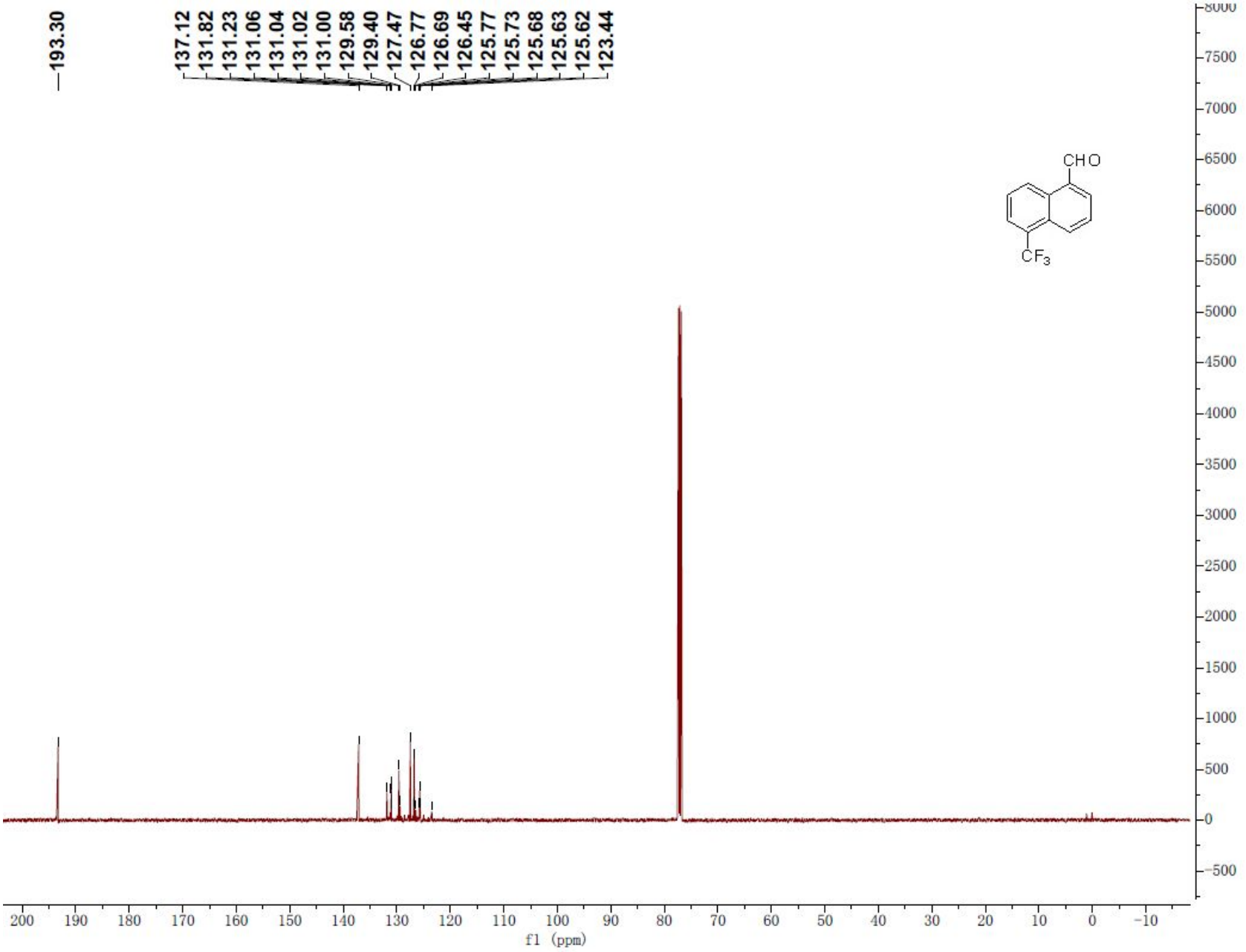
^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of 4-(trifluoromethyl)-1-naphthaldehyde (1w)



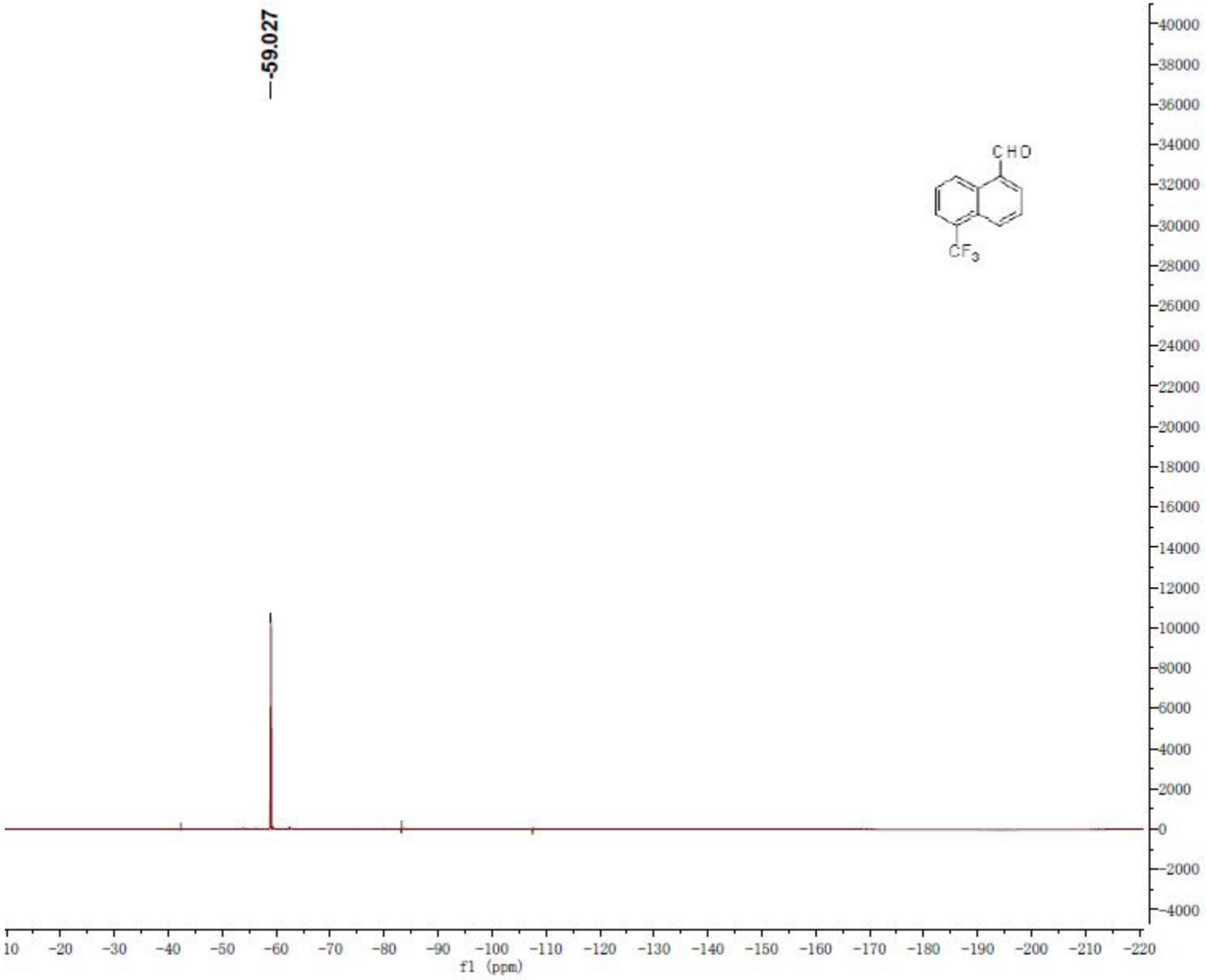
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 5-(trifluoromethyl)-1-naphthaldehyde



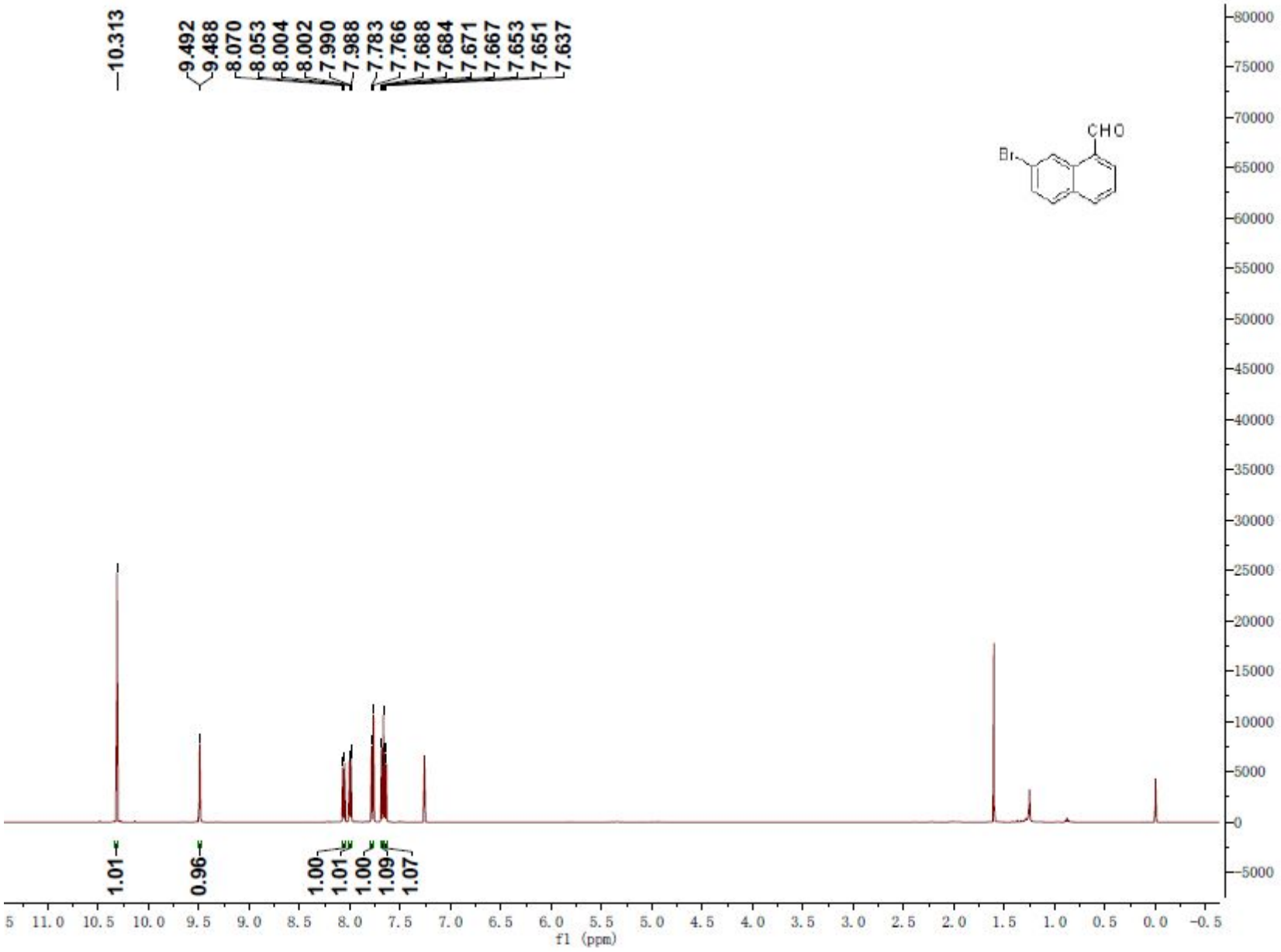
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 5-(trifluoromethyl)-1-naphthaldehyde



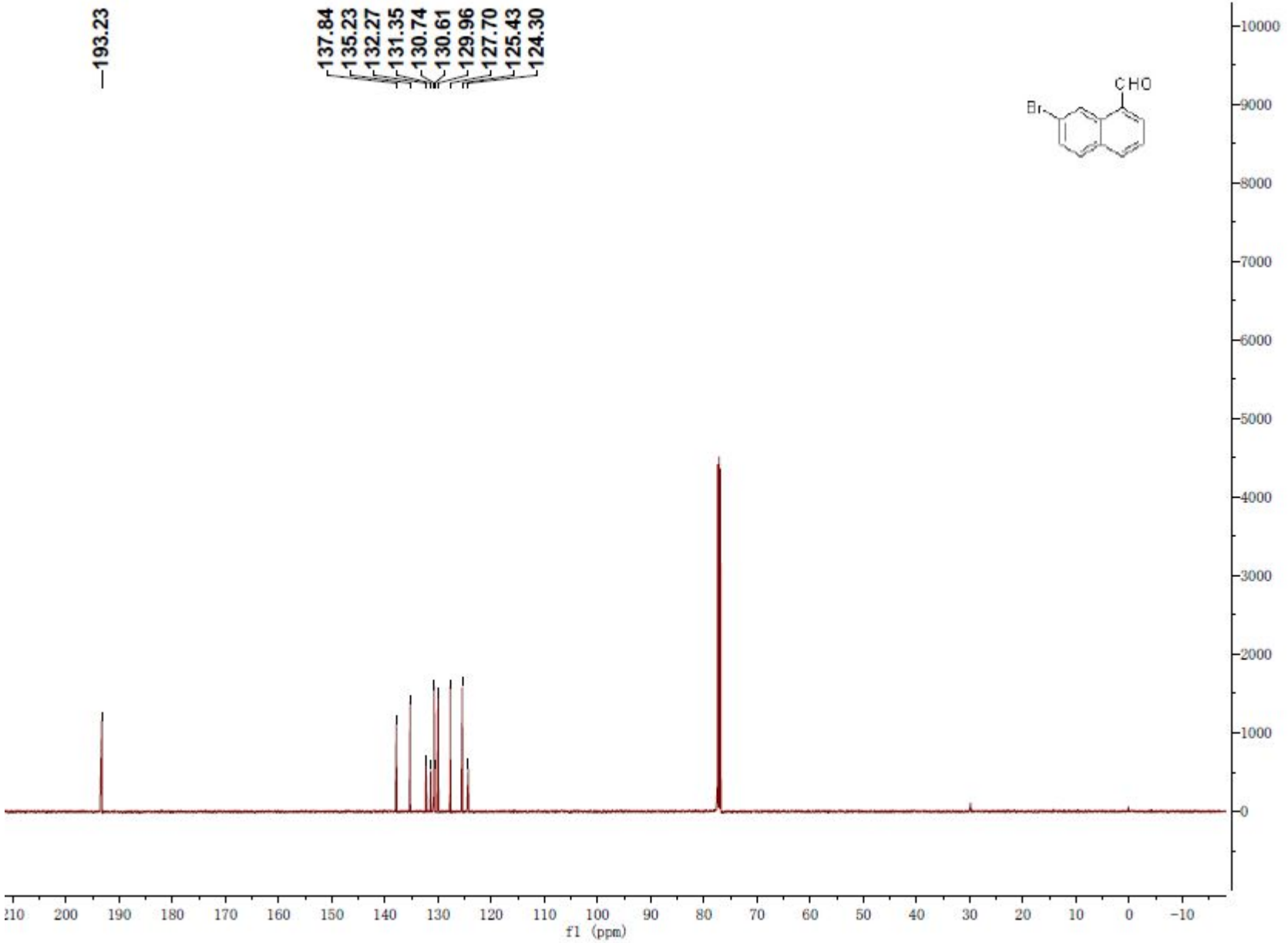
^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of 5-(trifluoromethyl)-1-naphthaldehyde



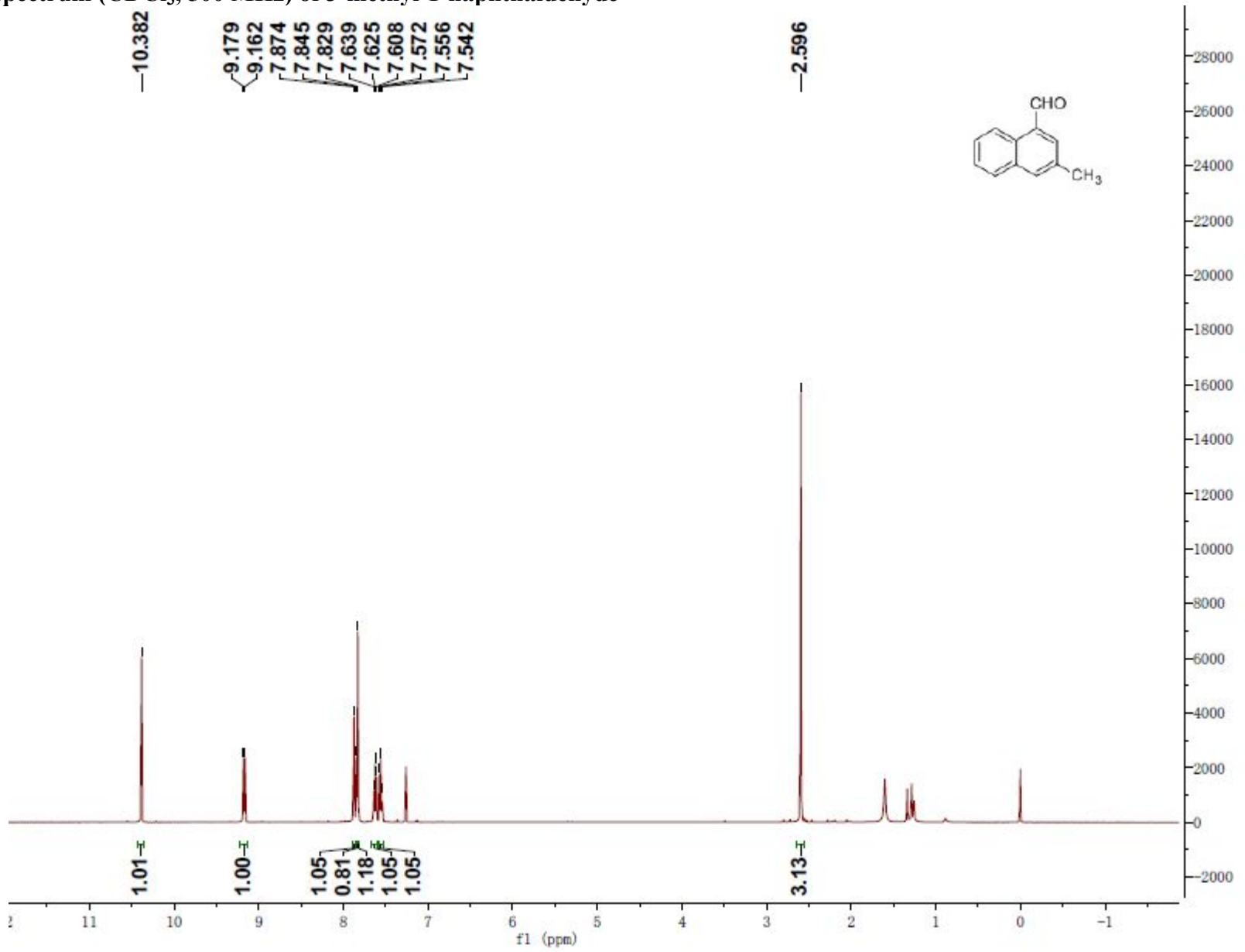
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 7-bromo-1-naphthaldehyde



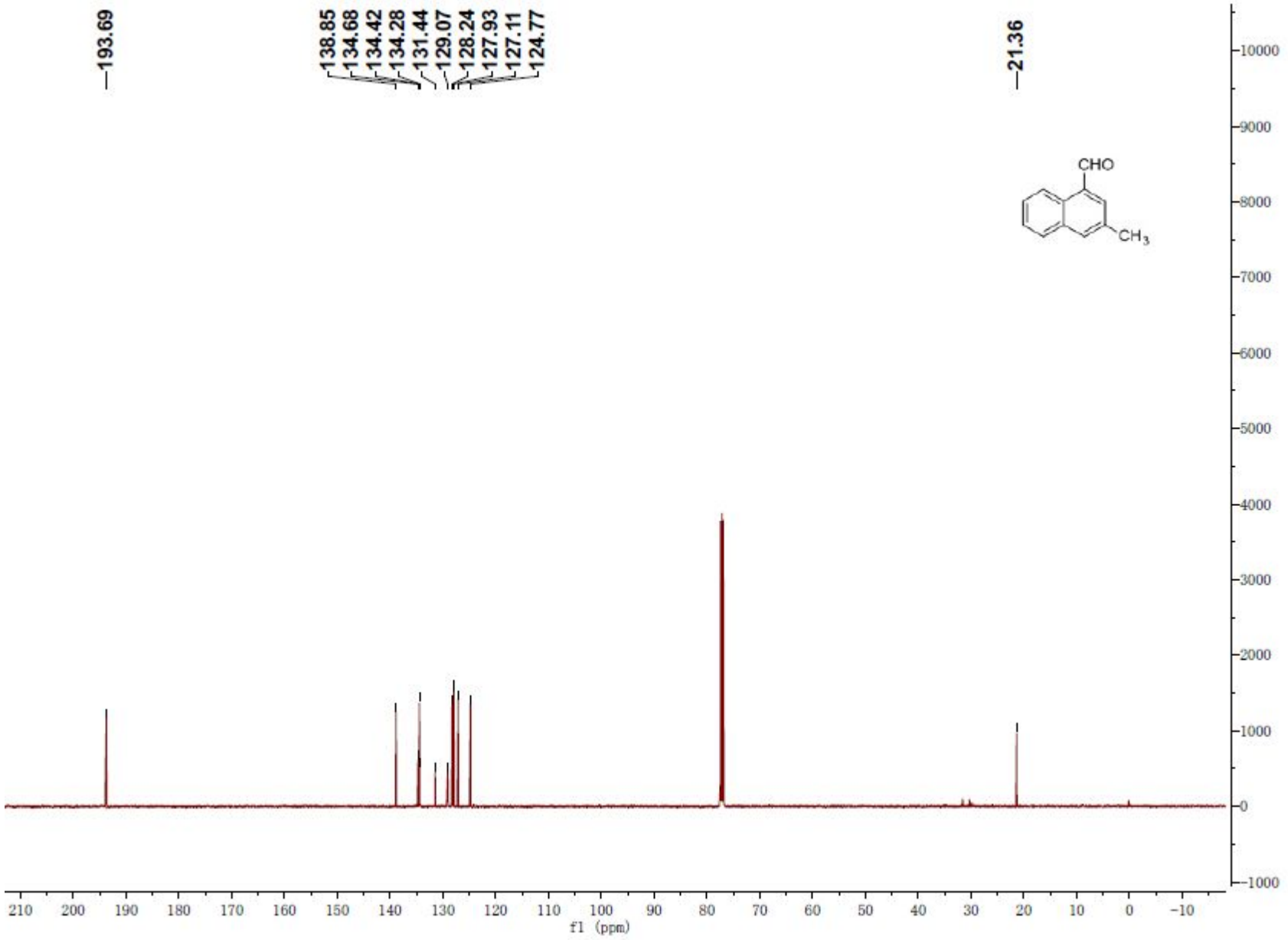
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 7-bromo-1-naphthaldehyde



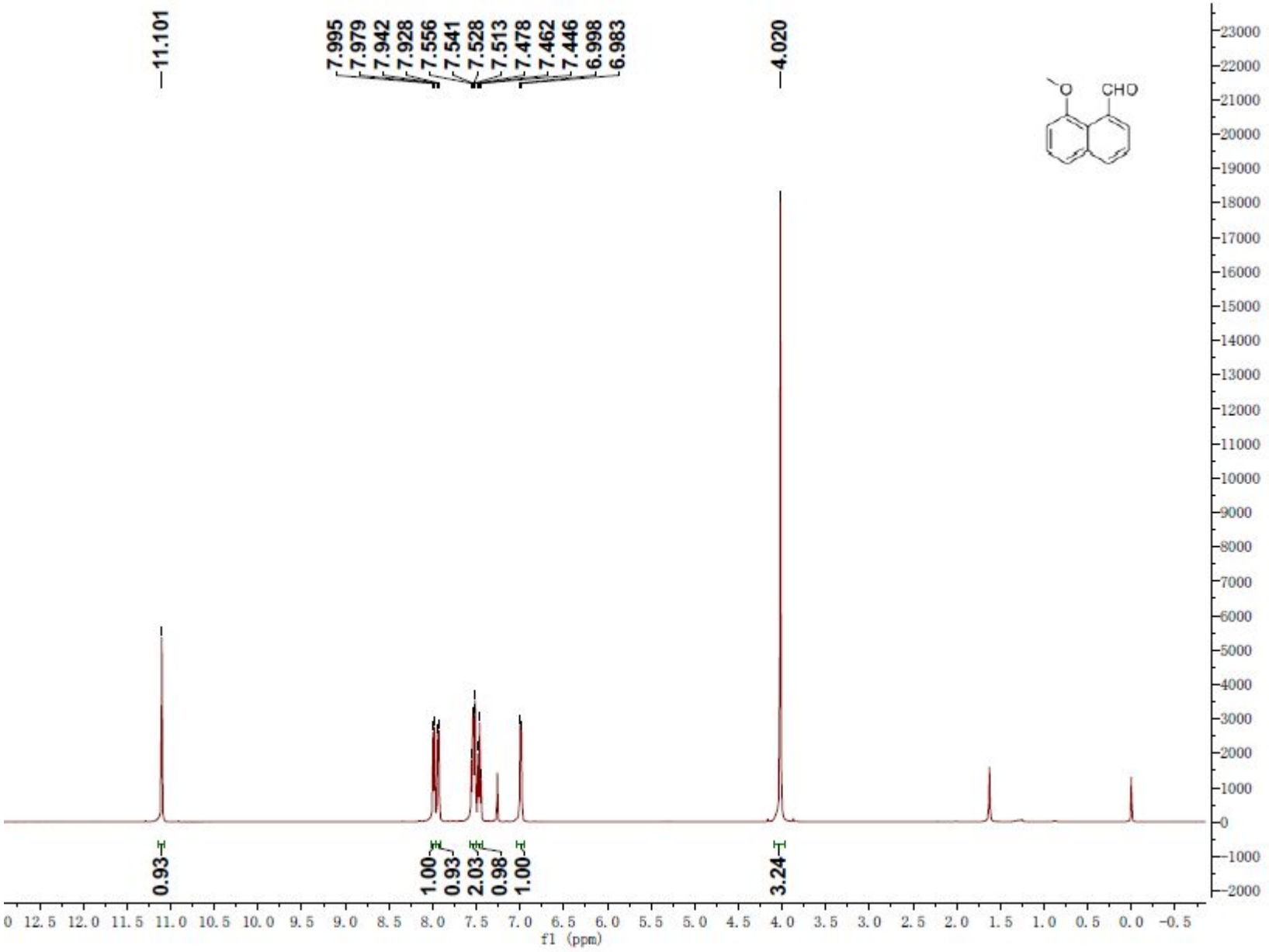
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3-methyl-1-naphthaldehyde



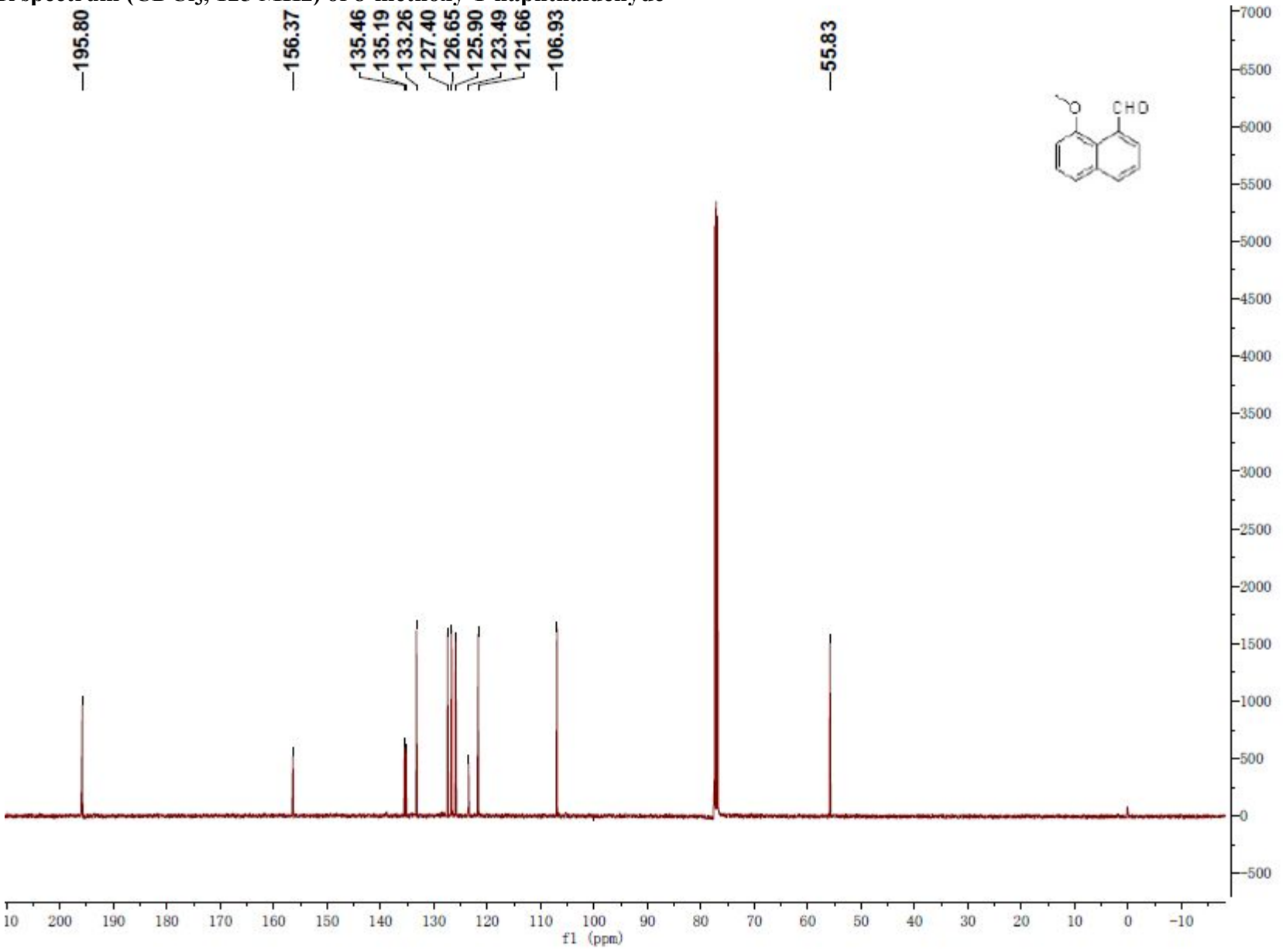
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 3-methyl-1-naphthaldehyde



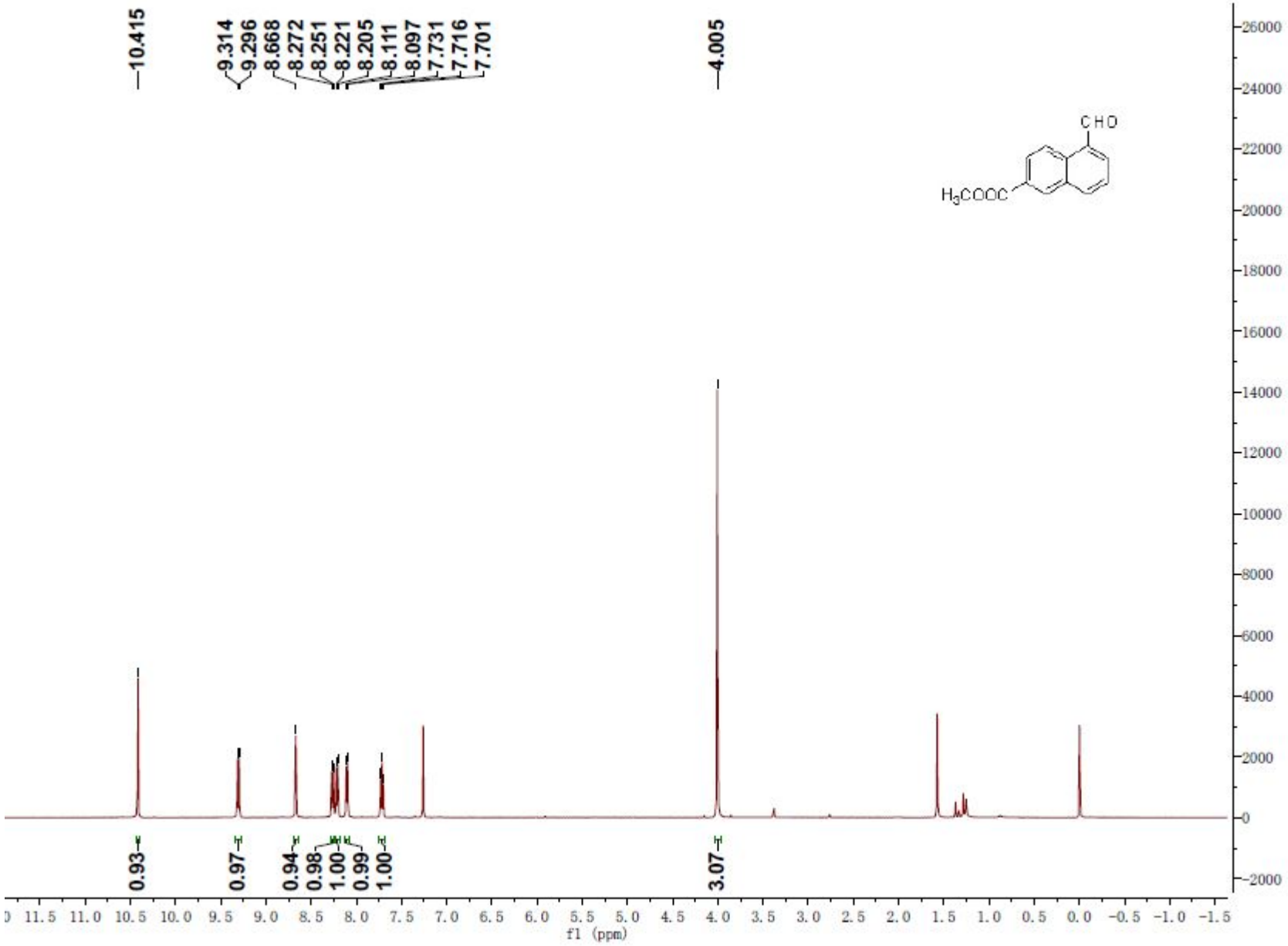
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 8-methoxy-1-naphthaldehyde



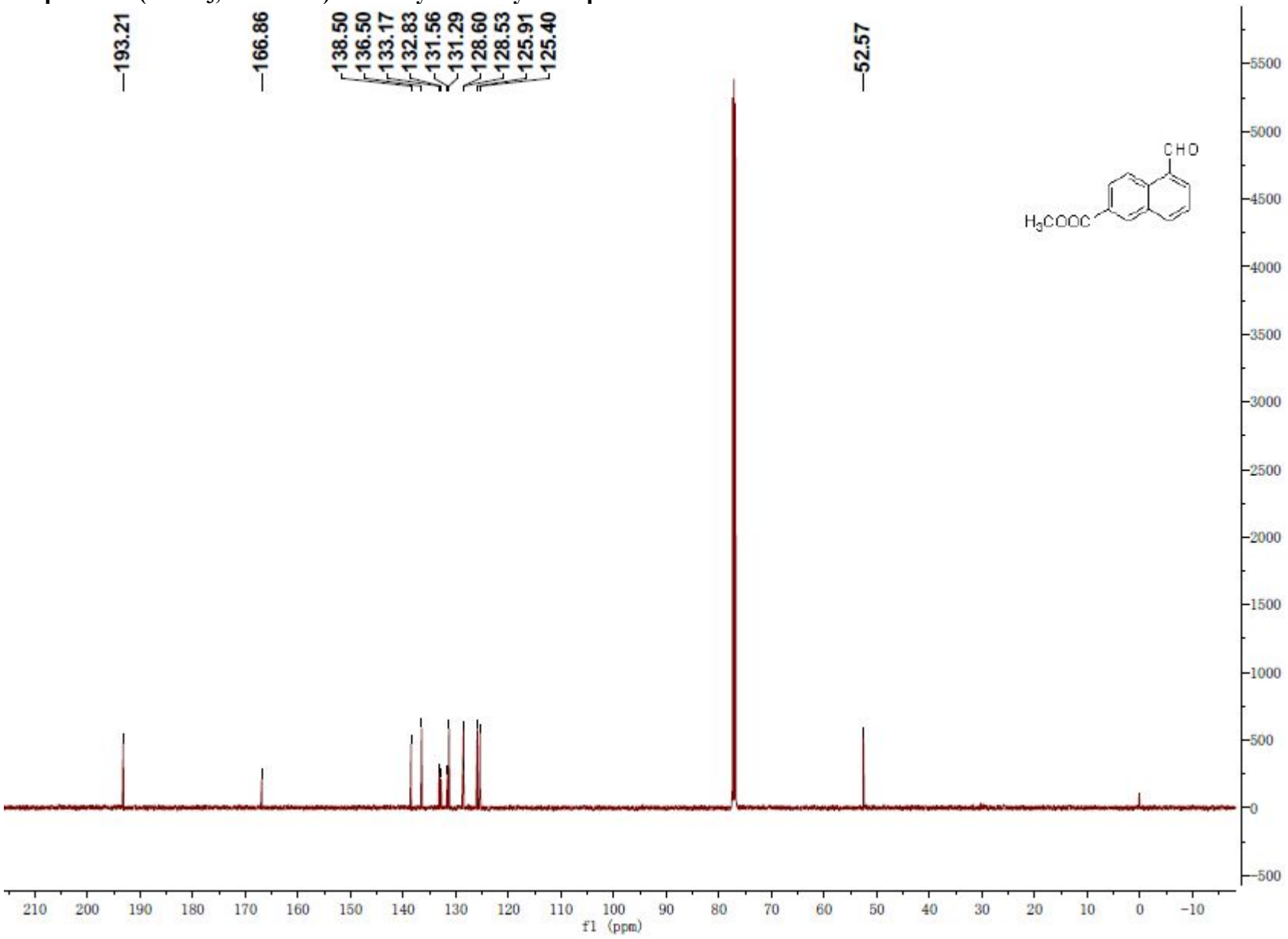
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 8-methoxy-1-naphthaldehyde



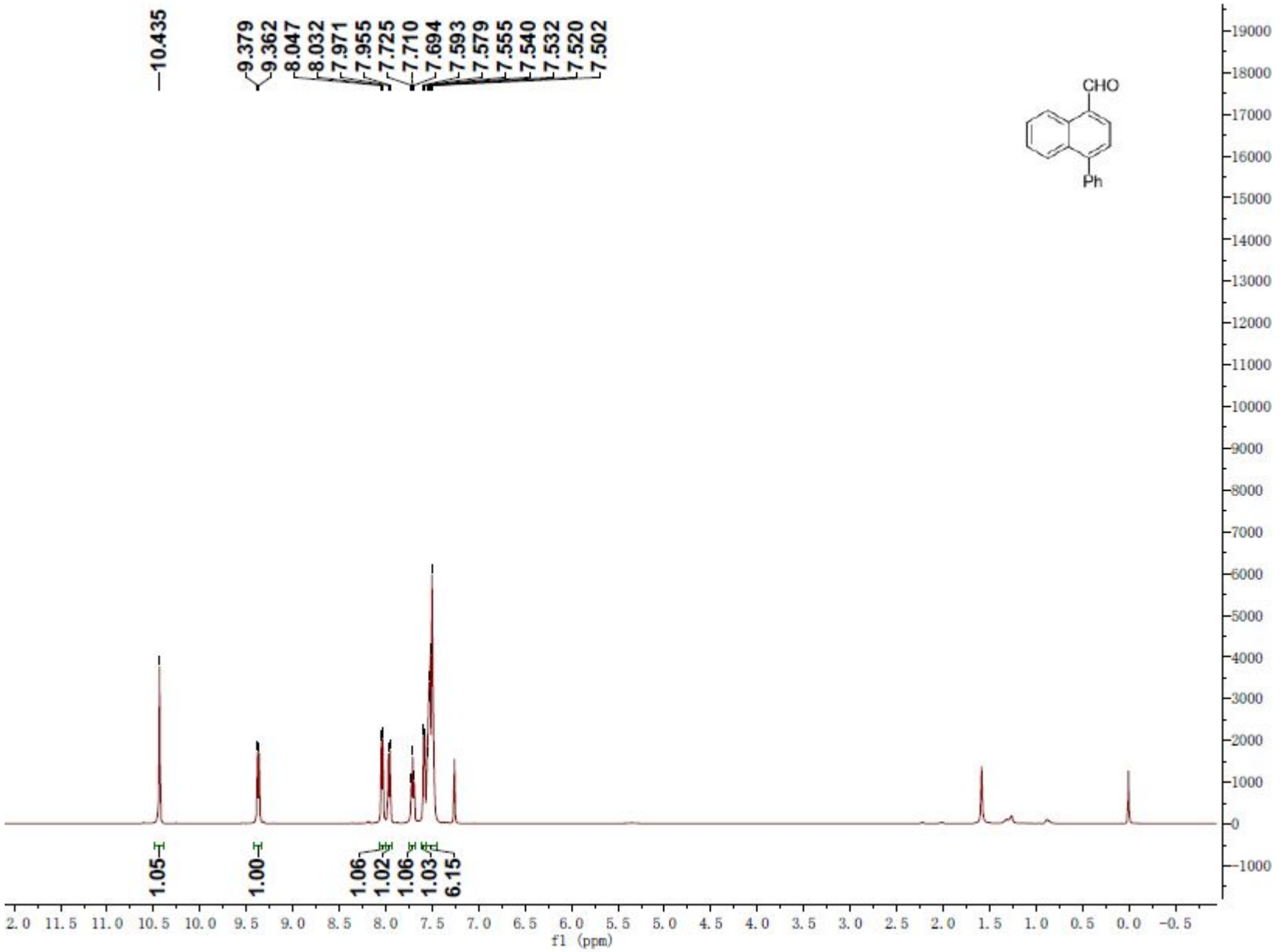
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of methyl 5-formyl-2-naphthoate



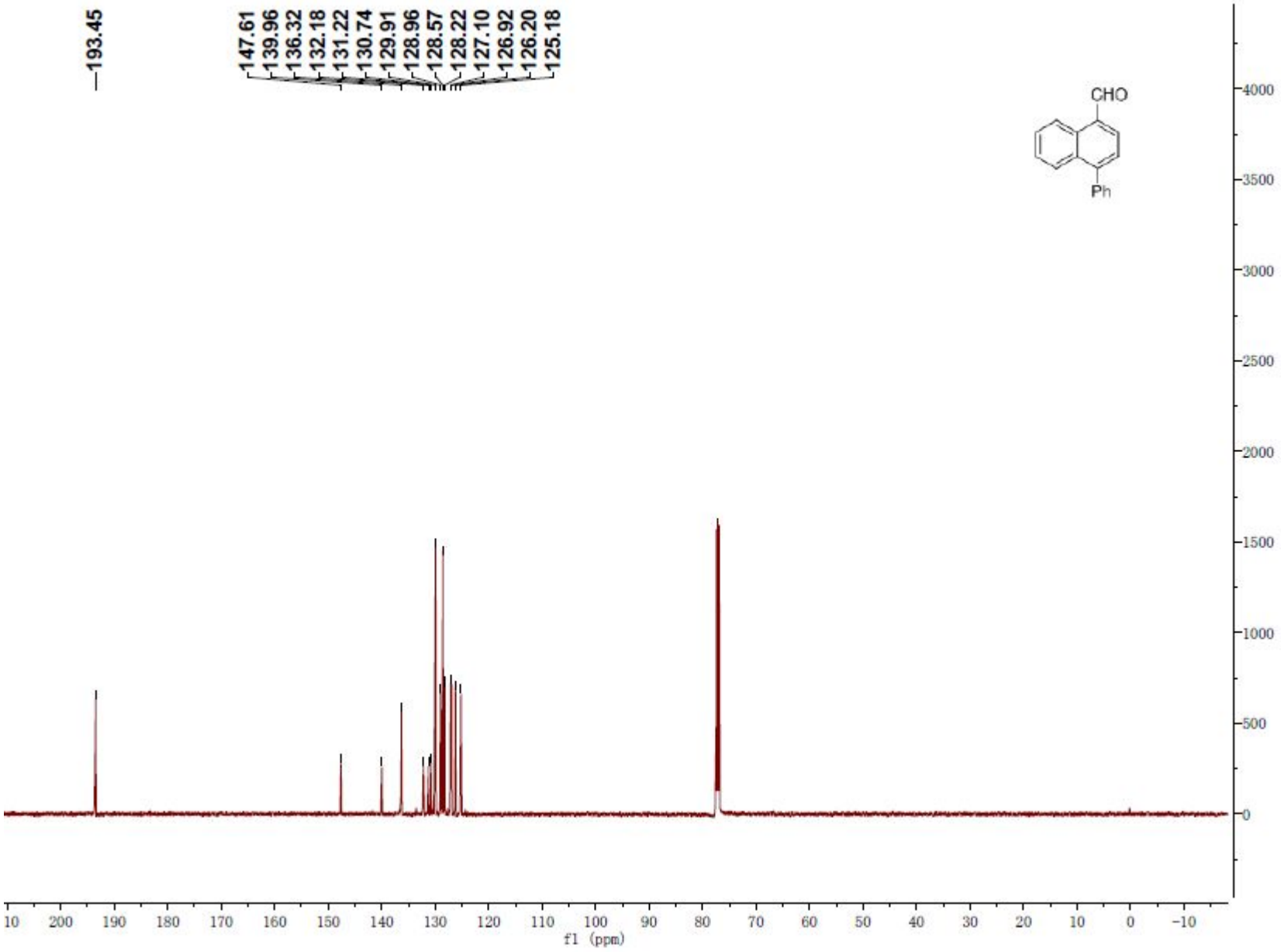
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of methyl 5-formyl-2-naphthoate



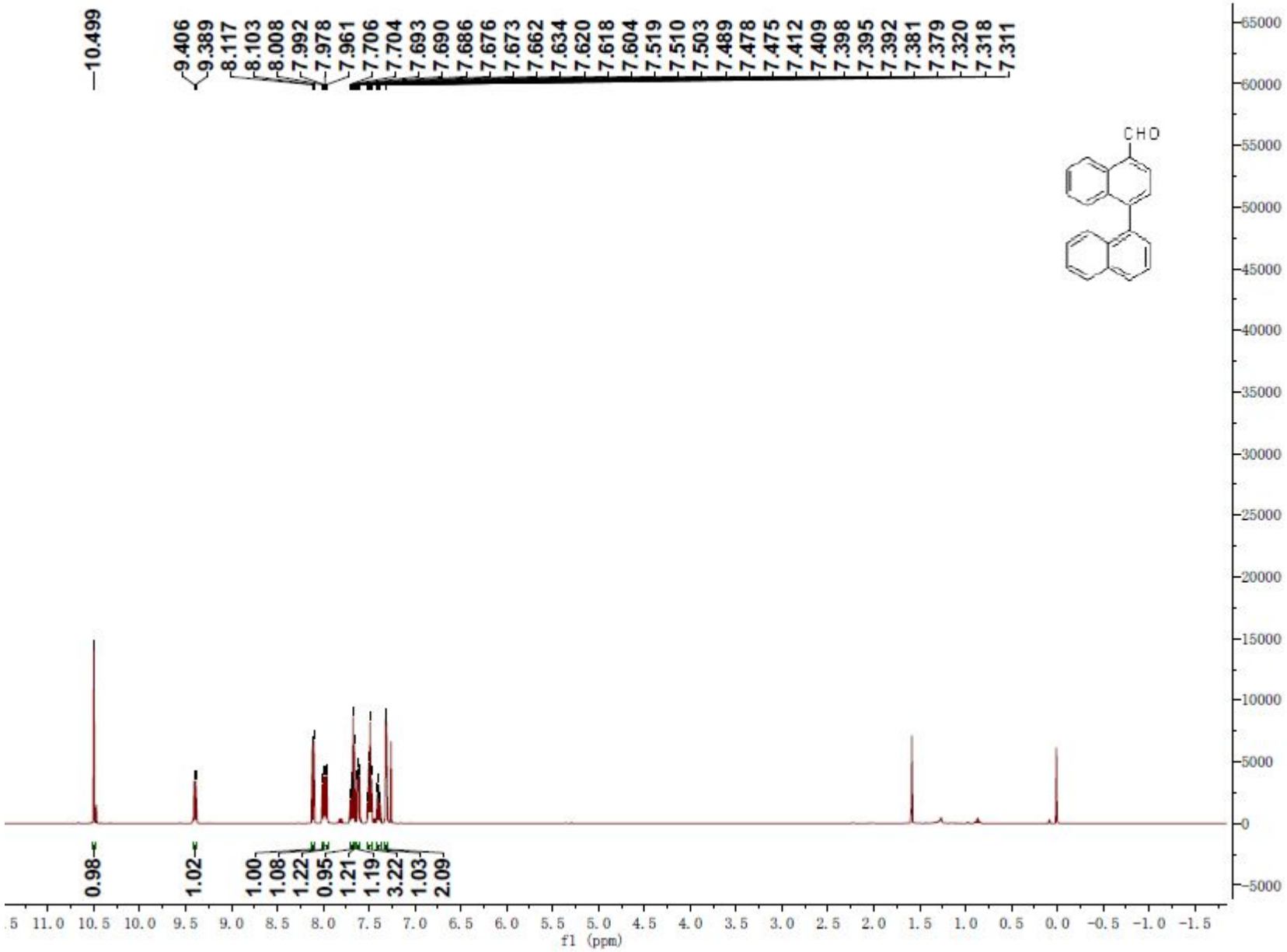
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4-phenyl-1-naphthaldehyde (5a)



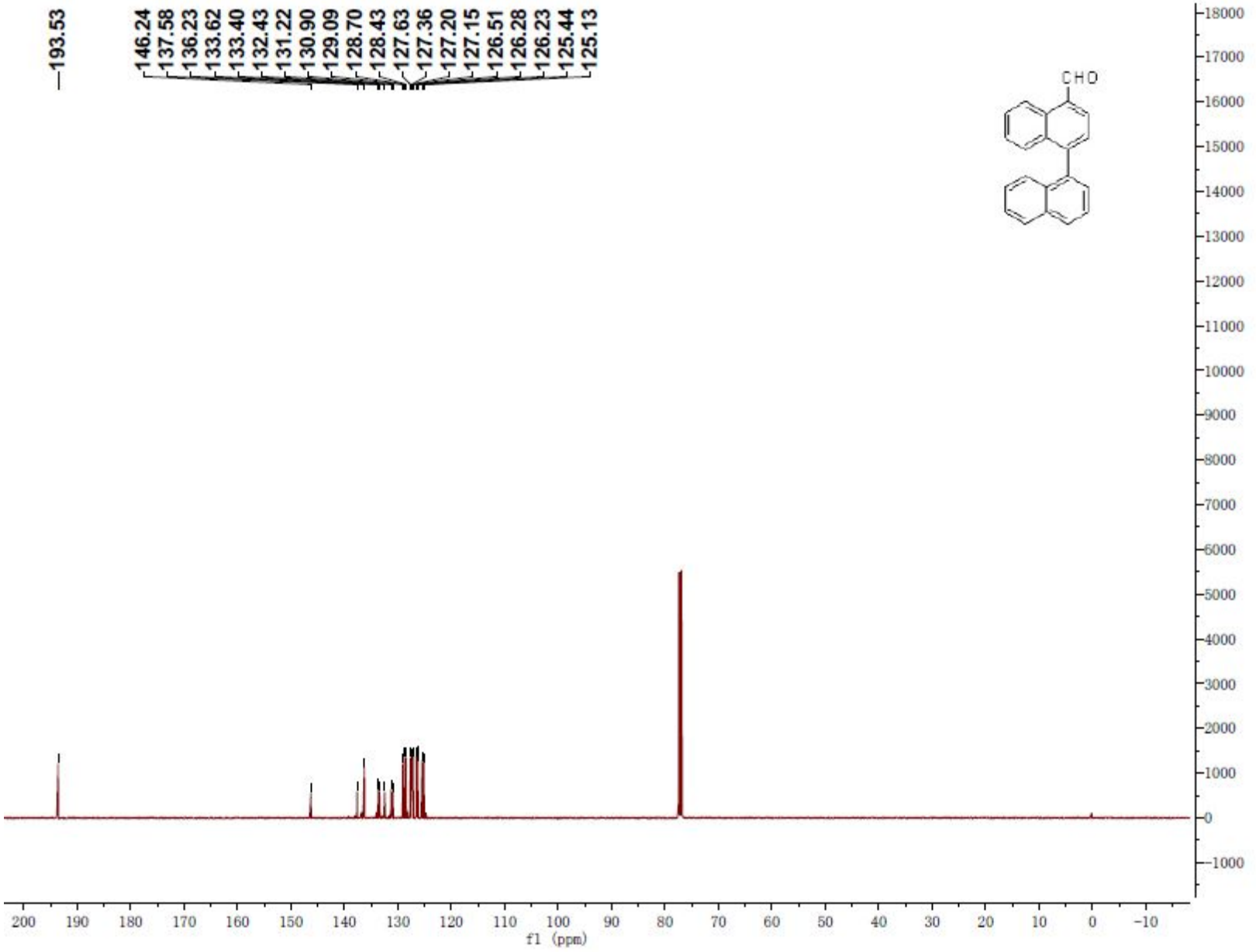
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4-phenyl-1-naphthaldehyde (5a)



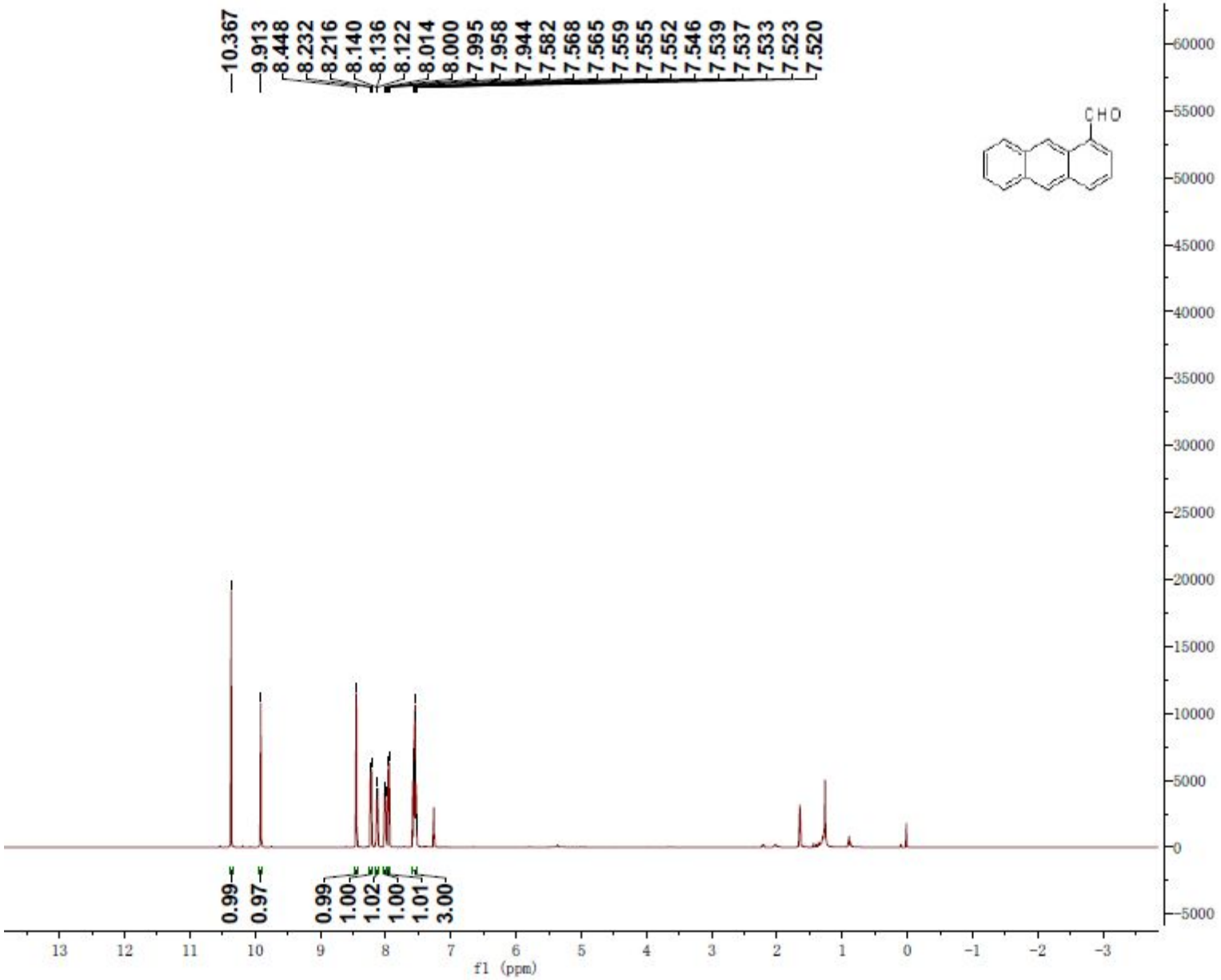
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of [1,1'-binaphthalene]-4-carbaldehyde (5b)



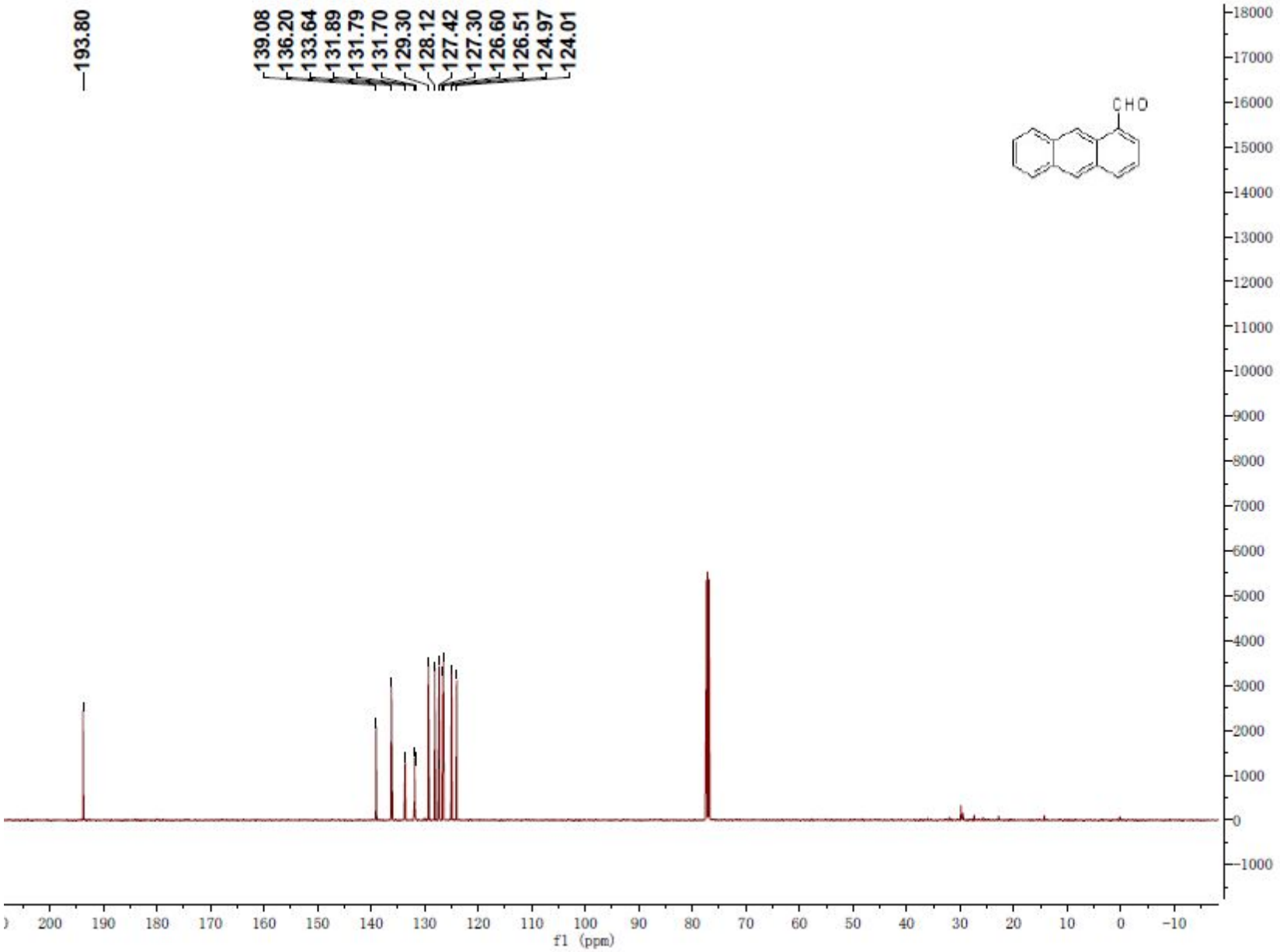
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of [1,1'-binaphthalene]-4-carbaldehyde (5b)



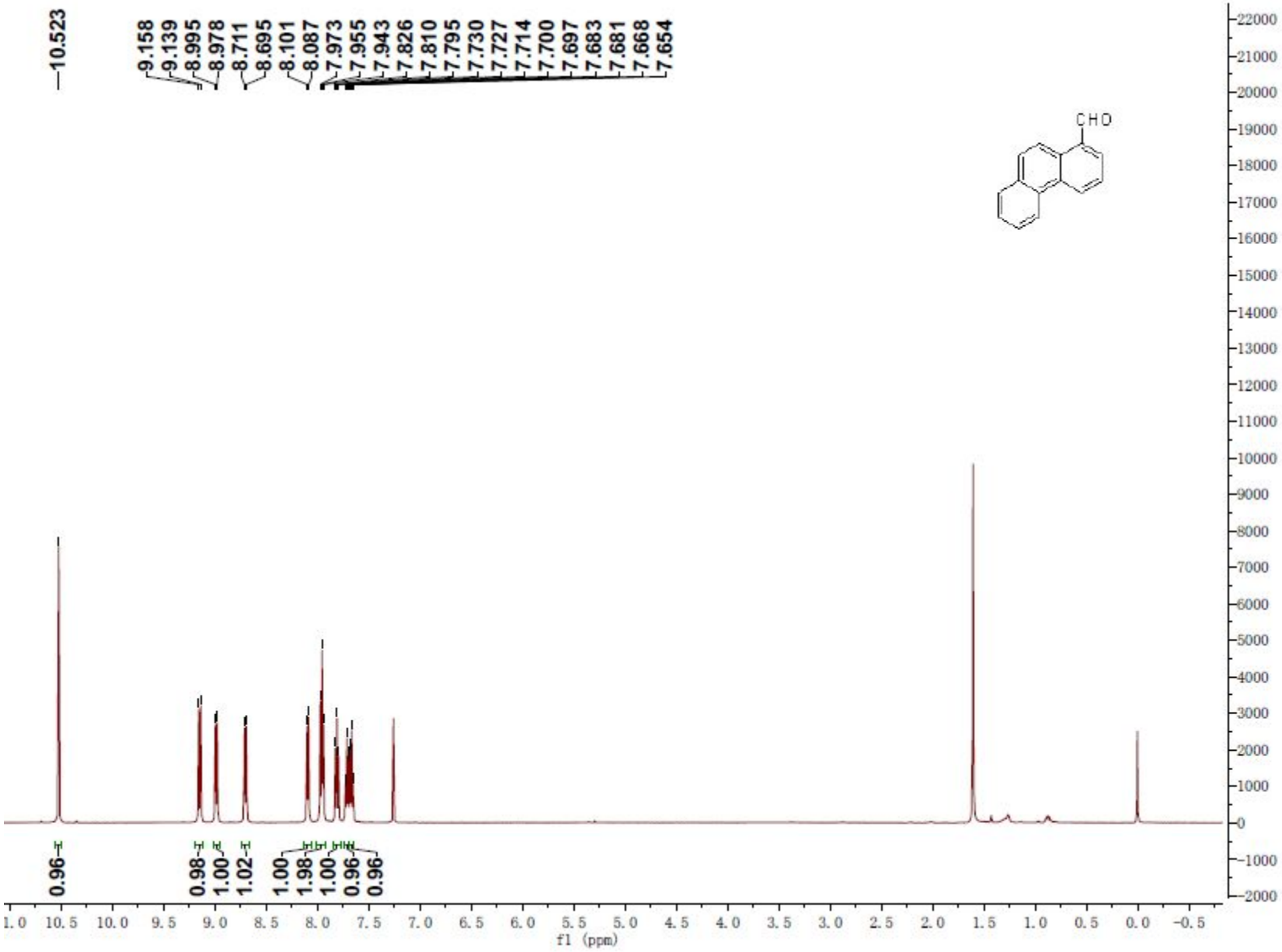
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of anthracene-1-carbaldehyde (5c)



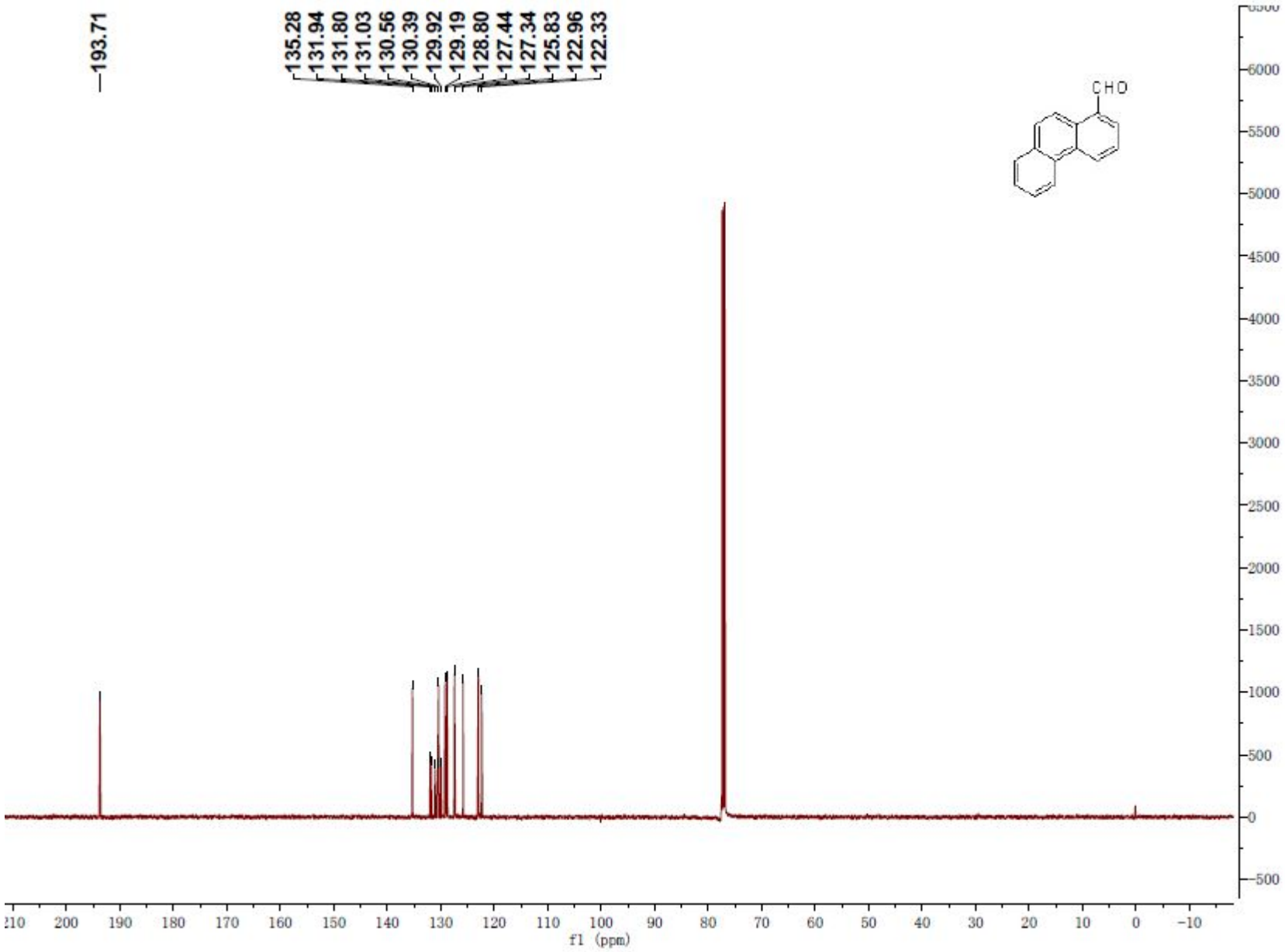
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of anthracene-1-carbaldehyde (5c)



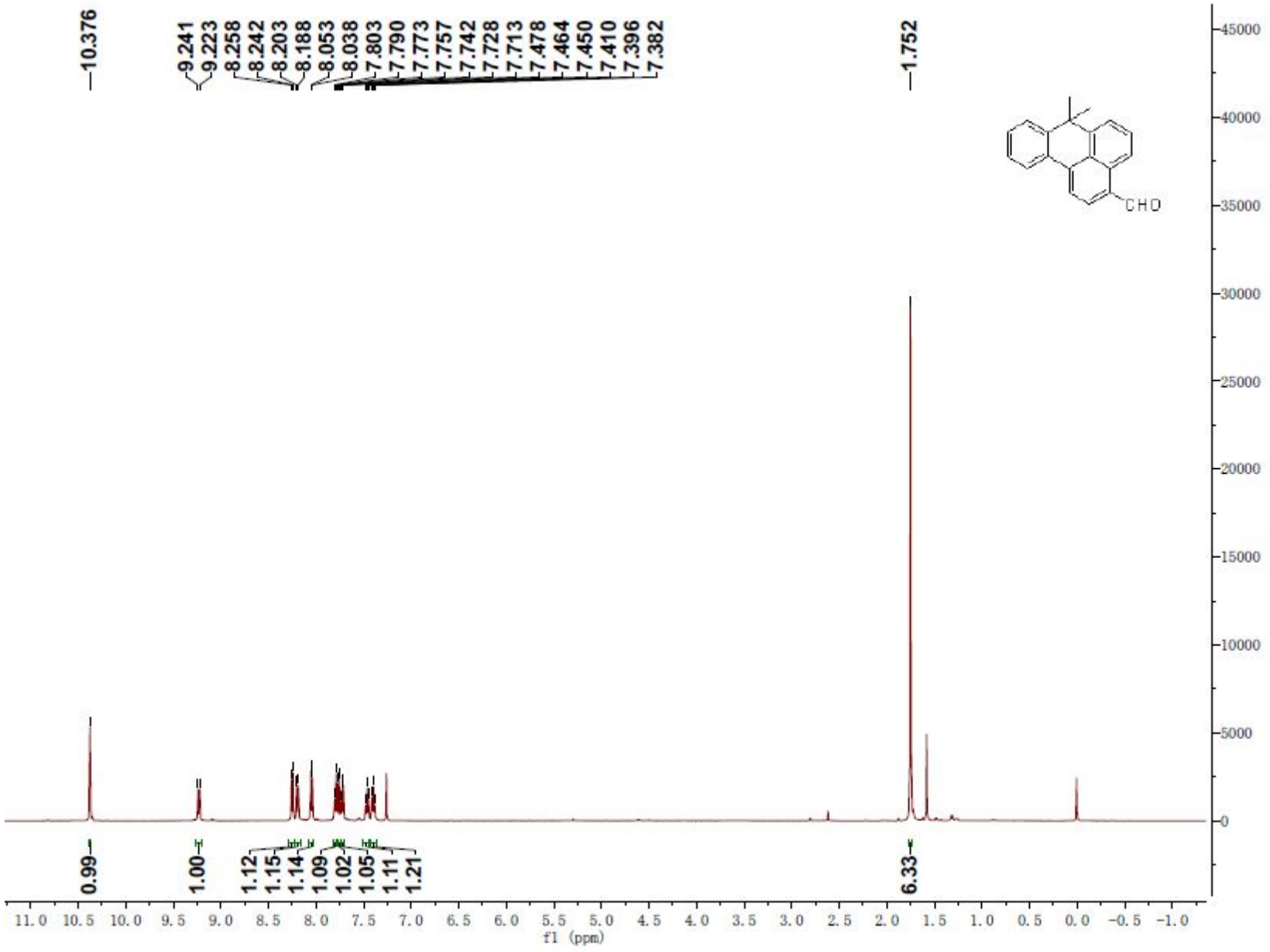
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of phenanthrene-1-carbaldehyde (5d)



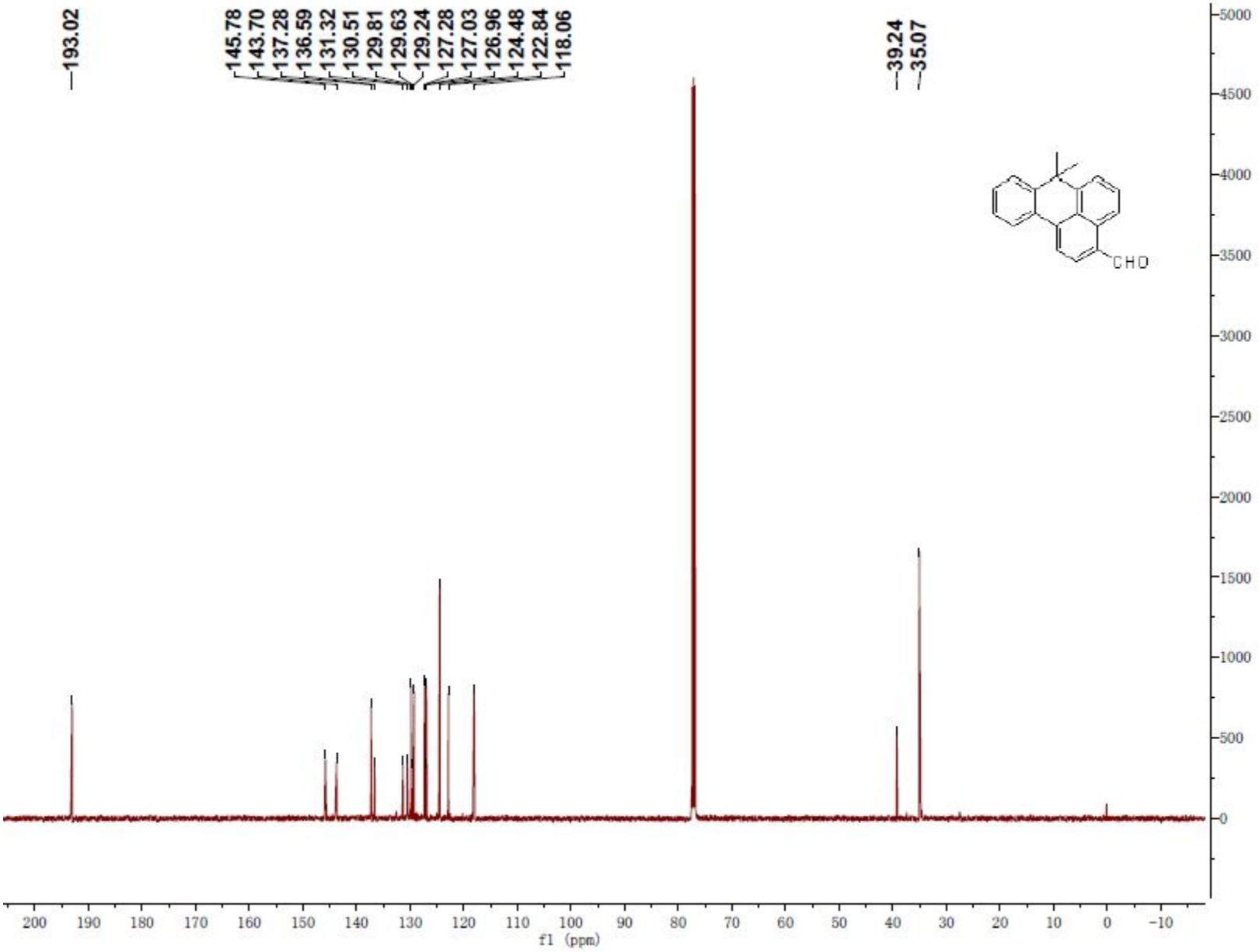
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of phenanthrene-1-carbaldehyde (5d)



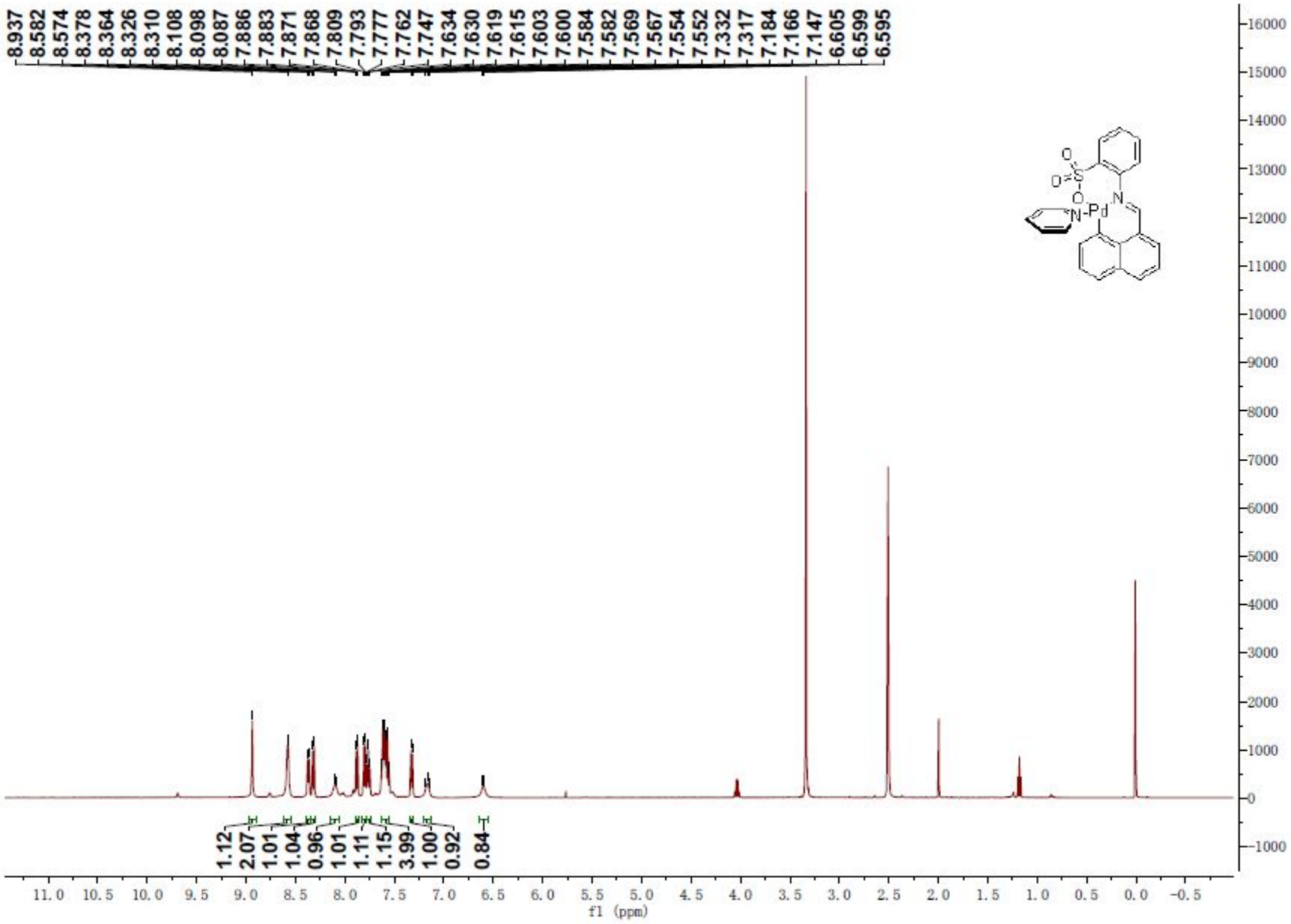
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 7,7-dimethyl-7H-benzo[de]anthracene-3-carbaldehyde (5e)



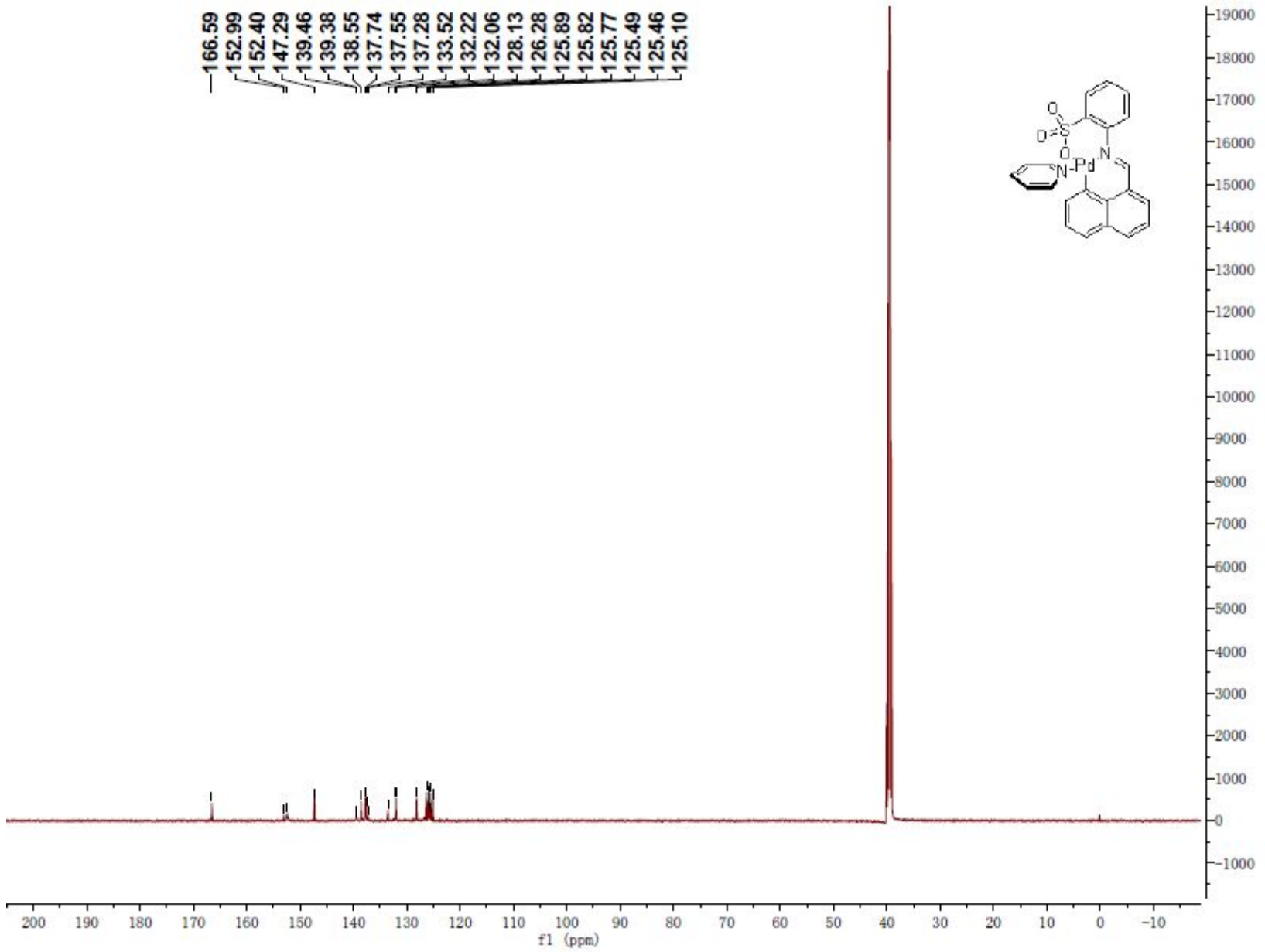
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 7,7-dimethyl-7H-benzo[de]anthracene-3-carbaldehyde (5e)



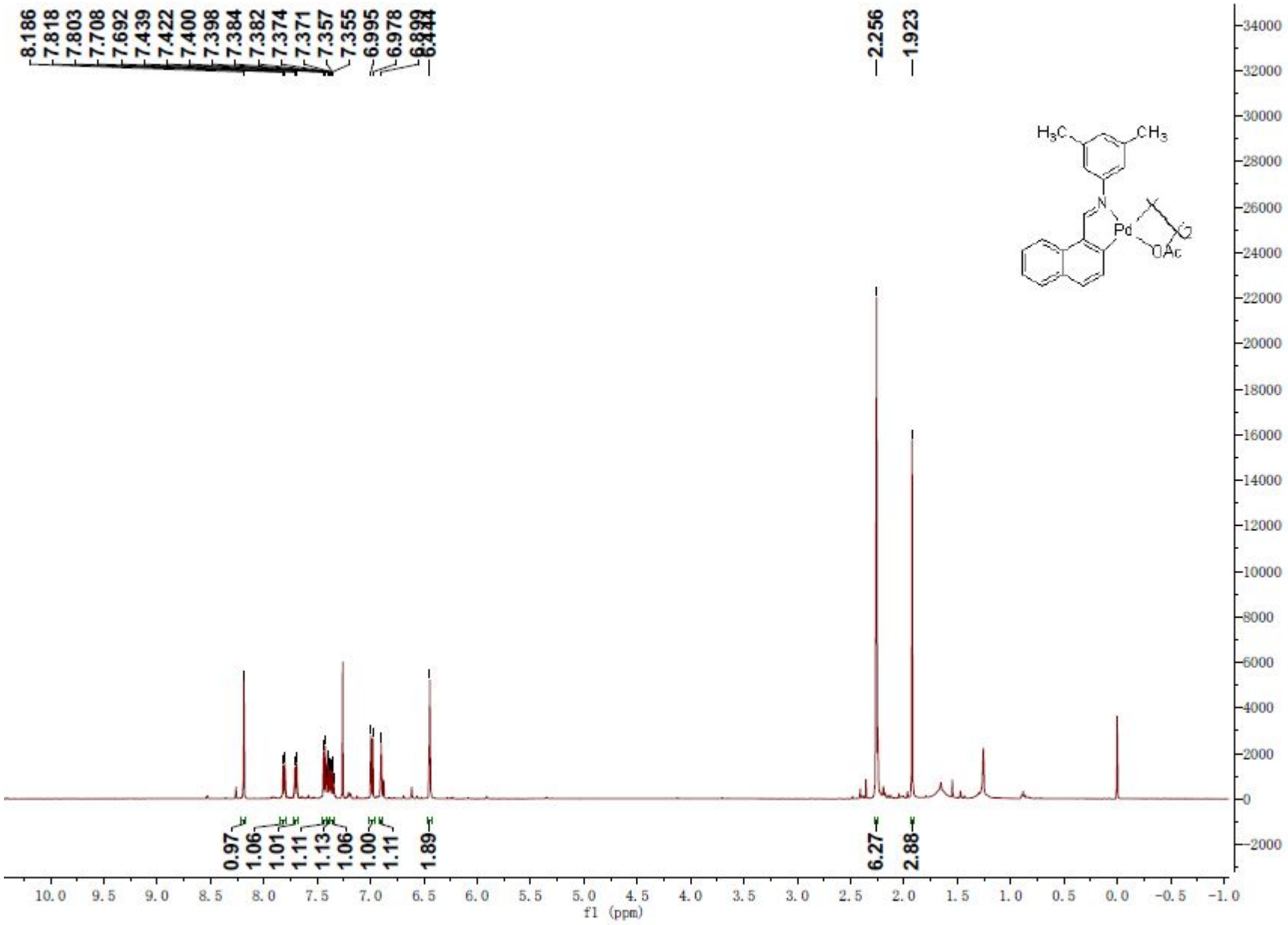
^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of palladacycle (1a-Pd)



^{13}C NMR spectrum (DMSO-d_6, 125 MHz) of palladacycle (1a-Pd)



^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of palladacycle (3a-Pd)



^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of palladacycle (3a-Pd)