

Supplementary Material

PhIO-Mediated oxidative dethioacetalization/dethioketalization under water-free conditions

Zhenyang Yu,^a Yaxin Ouyang,^a Xiaofan Wang,^a Bingyue Zhao,^a Xi Wang,^a Yunfei Du,^{a,*} and Kang Zhao^{b,*}

^a Tianjin Key Laboratory for Modern Drug Delivery & High-Efficiency, School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China

^b State Key Laboratory of Microbial Technology, Institute of Microbial Technology, Shandong University, Qingdao 266237, China

Email: duyunfeier@tju.edu.cn, zhaokang@sdu.edu.cn

Table of Contents

Mechanistic Studies	S2
Data of Parent Aldehydes and Ketones.....	S4
¹ H-NMR and ¹³ C-NMR Spectra	S7

1. Mechanistic Studies

To a solution of 2,2-diphenyl-1,3-dithiolane (1 mmol) in DCM (4 mL) was added ^{18}O -labeled PhIO (1.2 mmol, $^{16}\text{O}:^{18}\text{O} = 72:28$). The mixture was stirred at room temperature until TLC revealed a complete consumption of the substrate. The solvent was removed by reduced pressure to obtain the crude products which were further purified by flash column chromatography to afford the parent aldehydes. HRMS analysis of the PhIO and aldehyde product showed that both of them had ^{18}O -labeled ingredients. The spectra diagrams are shown below.

Figure 1. HRMS spectrum of $\text{PhI}^{16/18}\text{O}$.

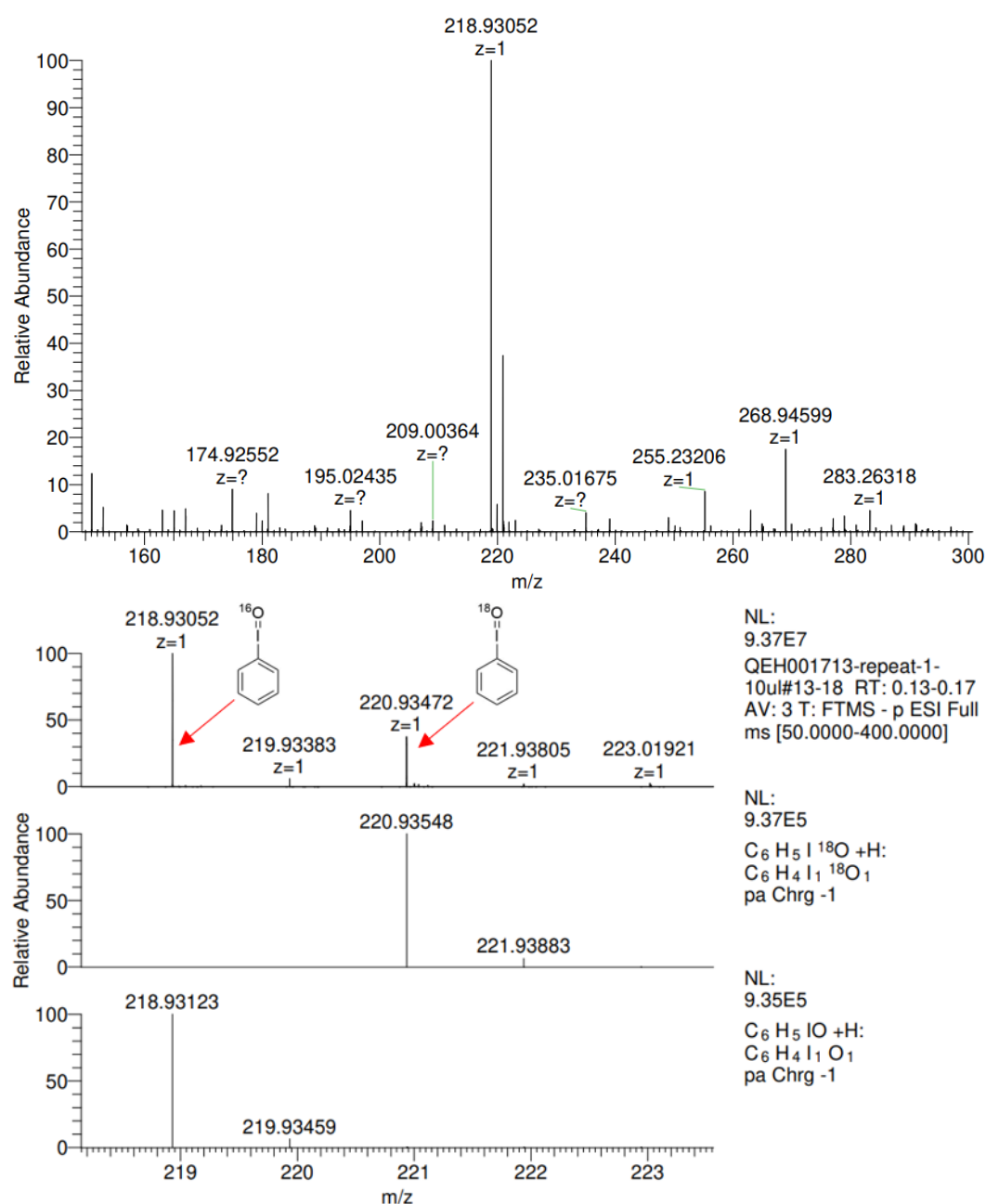
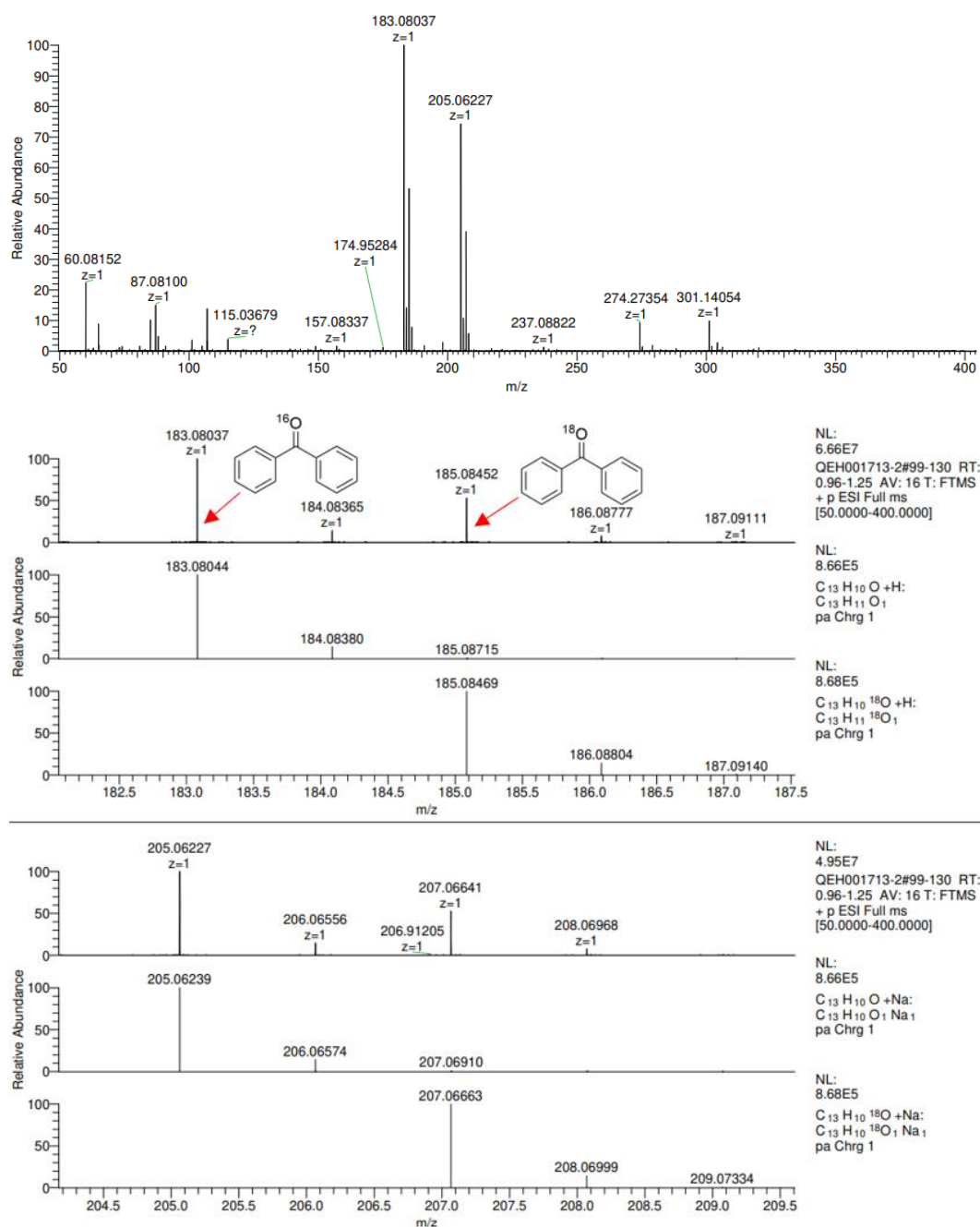


Figure 2. HRMS spectrum of product 3aa.



2. Data of parent aldehydes and ketones

Benzaldehyde (2a) Following the general procedure, **2a** was purified by silica gel chromatography (EtOAc/PE = 0/100). Yield: 153 mg, 90%, colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 10.02 (d, J = 1.7 Hz, 1H), 7.88 (dt, J = 8.2, 1.4 Hz, 2H), 7.63 (td, J = 7.3, 1.6 Hz, 1H), 7.53 (td, J = 7.7, 1.8 Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 192.3, 136.5, 134.4, 129.7, 129.0. HRMS (ESI) calcd for $\text{C}_7\text{H}_7\text{O}^+$ [$\text{M} + \text{H}^+$] 107.0491, found 107.0496.

4-Isopropylbenzaldehyde (2b) Following the general procedure, **2b** was purified by silica gel chromatography (EtOAc/PE = 2/98). Yield: 270 mg, 91%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 9.97 (s, 1H), 7.89 – 7.73 (m, 2H), 7.43 – 7.34 (m, 2H), 2.99 (p, J = 6.9 Hz, 1H), 1.28 (dd, J = 7.0, 0.8 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.1, 156.3, 134.5, 130.0, 127.2, 34.5, 23.7. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{13}\text{O}^+$ [$\text{M} + \text{H}^+$] 149.0961, found 149.0966.

4-Methoxybenzaldehyde (2c) Following the general procedure, **2c** was purified by silica gel chromatography (EtOAc/PE = 5/95). Yield: 245 mg, 90%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 9.88 (s, 1H), 7.92 – 7.73 (m, 2H), 7.00 (dt, J = 8.8, 1.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.9, 164.6, 132.0, 130.0, 114.3, 55.6. HRMS (ESI) calcd for $\text{C}_8\text{H}_9\text{O}_2^+$ [$\text{M} + \text{H}^+$] 137.0597, found 137.0592.

4-(Dimethylamino)benzaldehyde (2d) Following the general procedure, **2d** was purified by silica gel chromatography (EtOAc/PE = 2/98). Yield: 284 mg, 95%, a yellow solid, mp. 72–73 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.73 (s, 1H), 7.80 – 7.65 (m, 2H), 6.75 – 6.63 (m, 2H), 3.07 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.3, 154.3, 132.0, 125.2, 111.1, 40.1. HRMS (ESI) calcd for $\text{C}_9\text{H}_{12}\text{NO}^+$ [$\text{M} + \text{H}^+$] 150.0913, found 150.0918.

4-(Methylthio)benzaldehyde (2e) Following the general procedure, **2e** was purified by silica gel chromatography (EtOAc/PE = 5/95). Yield: 274 mg, 90%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 9.91 (s, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 2.52 (d, J = 0.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.3, 147.9, 132.9, 130.0, 125.2, 14.7. HRMS (ESI) calcd for $\text{C}_8\text{H}_9\text{OS}^+$ [$\text{M} + \text{H}^+$] 153.0369, found 153.0364.

4-(Benzyloxy)-3-methoxybenzaldehyde (2f) Following the general procedure, **2f** was purified by silica gel chromatography (EtOAc/PE = 5/95). Yield: 441 mg, 91%, a yellow solid, mp. 76–78 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.83 (s, 1H), 7.44 (dd, J = 8.2, 1.8 Hz, 3H), 7.41 – 7.35 (m, 3H), 7.35 – 7.29 (m, 1H), 6.99 (d, J = 8.2 Hz, 1H), 5.24 (s, 2H), 3.94 (d, J = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.0, 153.6, 150.1, 136.0, 130.3, 128.8, 128.2, 127.2, 126.6, 112.4, 109.3, 70.9, 56.1. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3^+$ [$\text{M} + \text{H}^+$] 243.1016, found 243.1011.

4-Formylphenyl acetate (2g) Following the general procedure, **2g** was purified by silica gel chromatography (EtOAc/PE = 5/95). Yield: 302 mg, 92%, a white solid, mp. 95–96 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.99 (s, 1H), 7.97 – 7.86 (m, 2H), 7.28 (d, J = 8.4 Hz, 2H), 2.34 (d, J = 0.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.9, 168.7, 155.4, 134.0, 131.2, 122.4, 21.2. HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{O}_3^+$ [$\text{M} + \text{H}^+$] 165.0546, found 165.0541.

3-Chlorobenzaldehyde (2h) Following the general procedure, **2h** was purified by silica gel chromatography (EtOAc/PE = 1/99). Yield: 247 mg, 88%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 9.97 (s, 1H), 7.84 (td, J = 1.9, 1.1 Hz, 1H), 7.76 (dq, J = 7.5, 1.1 Hz, 1H), 7.59 (ddt, J = 8.1, 2.2, 1.0 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.9, 137.8, 135.5, 134.4, 130.4, 129.3, 128.0. HRMS (ESI) calcd for $\text{C}_7\text{H}_6^{37}\text{ClO}^+$ [$\text{M} + \text{H}^+$] 141.0102, found 141.0107.

2-Bromobenzaldehyde (2i) Following the general procedure, **2i** was purified by silica gel chromatography (EtOAc/PE = 1/99). Yield: 315 mg, 85%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 10.36 (dd, J = 5.4, 2.6 Hz, 1H), 7.91 (ddt, J = 4.6, 2.9, 1.5 Hz, 1H), 7.64 (ddd, J = 5.9, 4.1, 2.3 Hz, 1H), 7.44 (tdd, J = 5.1, 3.8, 2.3 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.9, 135.4, 133.9, 133.5, 129.9, 127.9, 127.1. HRMS (ESI) calcd for $\text{C}_7\text{H}_6^{81}\text{BrO}^+$ [$\text{M} + \text{H}^+$] 184.9597, found 184.9592.

Methyl 2-formylbenzoate (2j) Following the general procedure, **2j** was purified by silica gel chromatography (EtOAc/PE = 2/98). Yield: 263 mg, 80%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 10.60 (d, J = 4.5 Hz, 1H), 8.01 – 7.85 (m, 2H), 7.70 – 7.56 (m, 2H), 4.01 – 3.92 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.1, 166.7, 137.0, 133.0, 132.4, 132.0, 130.4, 128.4, 52.8. HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{O}_3^+$ [$\text{M} + \text{H}^+$] 165.0546, found 165.0541.

(E)-2-Methyl-3-phenylacrylaldehyde (2k) Following the general procedure, **2k** was purified by silica gel chromatography (EtOAc/PE = 2/98). Yield: 269 mg, 92%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 9.59 (s, 1H), 7.57 – 7.51 (m, 2H), 7.49 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 7.27 (d, J = 1.6 Hz, 1H), 2.08 (d, J = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.7, 149.9, 138.4, 135.1, 130.1, 129.6, 128.7, 11.0. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{O}^+$ [$\text{M} + \text{H}^+$] 147.0804, found 147.0804.

1-Naphthaldehyde (2l) Following the general procedure, **2l** was purified by silica gel chromatography (EtOAc/PE = 2/98). Yield: 281 mg, 90%, a white solid, mp. 104-105 °C. ^1H NMR (400 MHz, CDCl_3) δ 10.14 (s, 1H), 8.30 (d, J = 1.5 Hz, 1H), 8.05 – 7.83 (m, 4H), 7.63 (ddd, J = 8.2, 6.9, 1.4 Hz, 1H), 7.57 (ddd, J = 8.2, 6.9, 1.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.3, 136.5, 134.6, 134.1, 132.6, 129.6, 129.2, 129.1, 128.1, 127.1, 122.7. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_9\text{O}^+$ [$\text{M} + \text{H}^+$] 157.0648, found 157.0643.

Furan-2-carbaldehyde (2m) Following the general procedure, **2m** was purified by silica gel chromatography (EtOAc/PE = 5/95). Yield: 163 mg, 90%, yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 9.64 (dd, J = 2.2, 1.2 Hz, 1H), 7.67 (dq, J = 1.8, 0.9 Hz, 1H), 7.24 (dq, J = 3.6, 0.9 Hz, 1H), 6.59 (ddt, J = 3.7, 1.9, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.9, 153.0, 148.1, 121.1, 112.6. HRMS (ESI) calcd for $\text{C}_5\text{H}_5\text{O}_2^+$ [$\text{M} + \text{H}^+$] 97.0284, found 97.0289.

Heptanal (2n) Following the general procedure, **2n** was purified by silica gel chromatography (EtOAc/PE = 0/100). Yield: 217 mg, 95%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 9.75 (t, J = 1.9 Hz, 1H), 2.41 (td, J = 7.4, 1.9 Hz, 2H), 1.62 (p, J = 7.4 Hz, 2H), 1.37 – 1.21 (m, 6H), 0.94 – 0.80 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 203.0, 43.9, 31.5, 28.8, 22.5, 22.0, 14.0. HRMS (ESI) calcd for $\text{C}_7\text{H}_{15}\text{O}^+$ [$\text{M} + \text{H}^+$] 115.1117, found 115.1117.

4-Hydroxy-3-methoxybenzaldehyde (2o) Following the general procedure, **2o** was purified by silica gel chromatography (EtOAc/PE = 15/85). Yield: 213 mg, 70%, a white solid, mp. 80-82 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.81 (d, J = 0.9 Hz, 1H), 7.48 – 7.35 (m, 2H), 7.03 (dd, J = 8.6, 1.3 Hz, 1H), 6.67 – 6.24 (m, 1H), 3.94 (t, J = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.0, 151.8, 147.2, 129.8, 127.6, 114.5, 108.8, 56.1. HRMS (ESI) calcd for $\text{C}_8\text{H}_9\text{O}_3^+$ [$\text{M} + \text{H}^+$] 153.0546, found 153.0551.

4-Hydroxybenzaldehyde (2p) Following the general procedure, **2p** was purified by silica gel chromatography (EtOAc/PE = 15/85). Yield: 208 mg, 85%, a pale-yellow solid, mp. 110-113 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.60 (s, 1H), 9.79 (d, J = 2.7 Hz, 1H), 8.14 – 7.62 (m, 2H), 7.32 – 6.80 (m, 2H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 191.4, 163.8, 132.6, 128.9, 116.3. HRMS (ESI) calcd for $\text{C}_7\text{H}_7\text{O}_2^+$ [$\text{M} + \text{H}^+$] 123.0441, found 123.0446.

***Tert*-butyl (4-formylphenyl) carbonate (2q)** Following the general procedure, **2q** was purified by silica gel chromatography (EtOAc/PE = 5/95). Yield: 422 mg, 95%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 9.98 (s, 1H), 7.96 – 7.84 (m, 2H), 7.41 – 7.29 (m, 2H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.9, 155.7, 150.9, 133.8, 131.2, 121.9, 84.4, 27.7. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{O}_4^+$ [$\text{M} + \text{H}^+$] 223.0965, found 223.0969.

4-((Trimethylsilyl)oxy)benzaldehyde (2r) Following the general procedure, **2r** was purified by preparative high-performance liquid chromatography (DCM/Hexane = 10/90, 10 mL/min). Yield: 369 mg, 95%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 9.89 (s, 1H), 7.88 – 7.72 (m, 2H), 7.03 – 6.86 (m, 2H), 0.31 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.7, 160.8, 131.7, 130.2, 120.1, 0.0. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{15}\text{O}_2\text{Si}^+$ [$\text{M} + \text{H}^+$] 195.0836, found 195.0833.

4-Methylbenzaldehyde (2s) Following the general procedure, **2s** was purified by silica gel chromatography (EtOAc/PE = 1/99). Yield: 221 mg, 92%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 9.92 (s, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.9, 145.5, 134.2, 129.8, 129.7, 129.7, 21.8. HRMS (ESI) calcd for $\text{C}_8\text{H}_9\text{O}^+$ [$\text{M} + \text{H}^+$] 121.0648, found 121.0643.

Benzophenone (2aa) Following the general procedure, **2aa** was purified by silica gel chromatography (EtOAc/PE = 1/99). Yield: 335 mg, 92%, a white solid, mp. 46-48 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.75 (m, 4H), 7.63 – 7.55 (m, 2H), 7.53 – 7.43 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.8, 137.6, 132.5, 130.1, 128.3. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{11}\text{O}^+$ [$\text{M} + \text{H}^+$] 183.0804, found 183.0809.

***N*-(2-Acetylphenyl)acetamide (2ab)** Following the general procedure, **2ab** was purified by silica gel chromatography (EtOAc/PE = 10/90). Yield: 314 mg, 88%, a white solid, mp. 74-76 °C. ^1H NMR (400 MHz,

CDCl_3) δ 11.69 (s, 1H), 8.72 (dt, J = 8.5, 1.5 Hz, 1H), 7.88 (dt, J = 8.1, 1.7 Hz, 1H), 7.54 (tt, J = 8.7, 1.6 Hz, 1H), 7.10 (tdd, J = 8.3, 2.4, 1.2 Hz, 1H), 2.65 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.9, 169.5, 141.0, 135.2, 131.6, 122.3, 121.7, 120.7, 28.7, 25.6. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{12}\text{NO}_2^+$ [$\text{M} + \text{H}^+$] 178.0863, found 178.0868.

1-(4-Chlorophenyl)ethan-1-one (2ac) Following the general procedure, **2ac** was purified by silica gel chromatography (EtOAc/PE = 2/98). Yield: 247 mg, 80%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.83 (m, 2H), 7.47 – 7.37 (m, 2H), 2.61 – 2.54 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.9, 139.6, 135.4, 129.7, 128.9, 26.6. HRMS (ESI) calcd for $\text{C}_8\text{H}_8^{37}\text{ClO}^+$ [$\text{M} + \text{H}^+$] 155.0258, found 155.0253.

1-(o-Tolyl)ethan-1-one (2ad) Following the general procedure, **2ad** was purified by silica gel chromatography (EtOAc/PE = 2/98). Yield: 209 mg, 78%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, J = 7.7, 1.4 Hz, 1H), 7.38 (td, J = 7.5, 1.5 Hz, 1H), 7.31 – 7.21 (m, 2H), 2.58 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.8, 138.5, 137.6, 132.1, 131.6, 129.4, 125.7, 29.6, 21.6. HRMS (ESI) calcd for $\text{C}_9\text{H}_{11}\text{O}^+$ [$\text{M} + \text{H}^+$] 135.0804, found 135.0804.

1-(3-(Trifluoromethyl)phenyl)ethan-1-one (2ae) Following the general procedure, **2ae** was purified by silica gel chromatography (EtOAc/PE = 2/98). Yield: 320 mg, 85%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (qd, J = 1.8, 1.1 Hz, 1H), 8.14 (dd, J = 7.6, 1.6 Hz, 1H), 7.86 – 7.78 (m, 1H), 7.61 (tdd, J = 7.8, 1.6, 0.8 Hz, 1H), 2.68 – 2.61 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.6, 137.5, 132.8 (q, $^2J_{\text{C-F}}$ = 38.3 Hz), 129.5 (q, $^3J_{\text{C-F}}$ = 3.8 Hz), 129.3, 125.1 (q, $^3J_{\text{C-F}}$ = 3.9 Hz), 123.7 (q, $^1J_{\text{C-F}}$ = 270.9 Hz), 119.8, 26.6. HRMS (ESI) calcd for $\text{C}_9\text{H}_8\text{F}_3\text{O}^+$ [$\text{M} + \text{H}^+$] 189.0522, found 189.0527.

4-Methylpentan-2-one (2af) Following the general procedure, **2af** was purified by silica gel chromatography (EtOAc/PE = 1/99). Yield: 186 mg, 90%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 2.24 (d, J = 7.0 Hz, 2H), 2.06 (s, 4H), 0.86 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 208.9, 52.7, 30.3, 24.6, 22.5. HRMS (ESI) calcd for $\text{C}_6\text{H}_{13}\text{O}^+$ [$\text{M} + \text{H}^+$] 101.0961, found 101.0966.

9H-fluoren-9-one (2ag) Following the general procedure, **2ag** was purified by silica gel chromatography (EtOAc/PE = 1/99). Yield: 348 mg, 95%, a yellow solid, mp. 81-82 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, J = 7.4 Hz, 2H), 7.51 – 7.41 (m, 4H), 7.29 – 7.22 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.9, 144.4, 134.7, 134.2, 129.1, 124.3, 120.3. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_9\text{O}^+$ [$\text{M} + \text{H}^+$] 181.0648, found 181.0653.

1-(Thiophen-2-yl)ethan-1-one (2ah) Following the general procedure, **2ah** was purified by silica gel chromatography (EtOAc/PE = 2/98). Yield: 207 mg, 82%, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, J = 3.7 Hz, 1H), 7.63 (d, J = 5.0 Hz, 1H), 7.12 (t, J = 4.3 Hz, 1H), 2.56 (d, J = 0.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.8, 144.6, 133.8, 132.5, 128.2, 27.0. HRMS (ESI) calcd for $\text{C}_6\text{H}_7\text{OS}^+$ [$\text{M} + \text{H}^+$] 127.0212, found 127.0217.

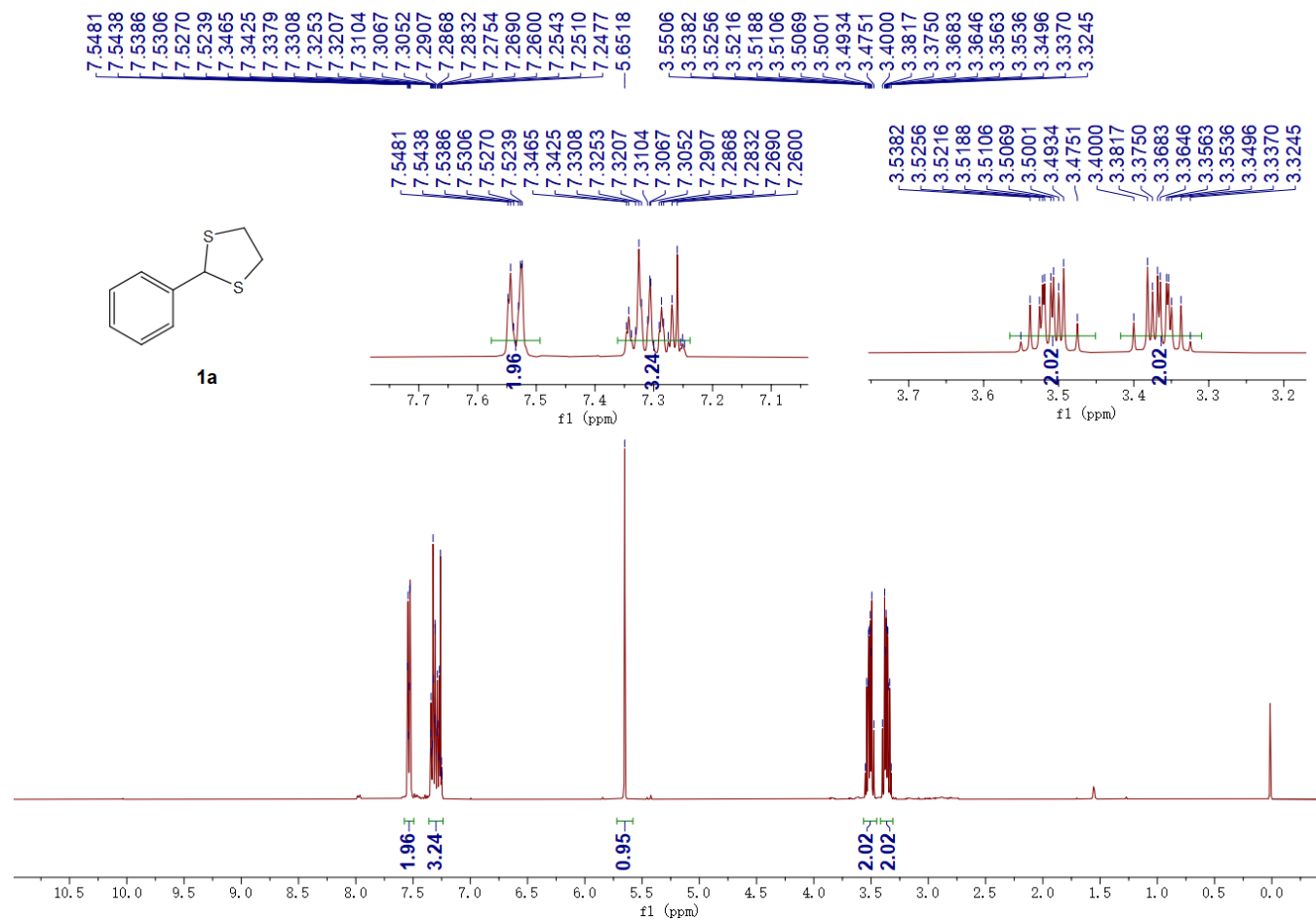
3,4-Dihydronaphthalen-1(2H)-one (2ai) Following the general procedure, **2ai** was purified by silica gel chromatography (EtOAc/PE = 1/99). Yield: 263 mg, 90%, pale-yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 2.95 (t, J = 6.1 Hz, 2H), 2.64 (t, J = 6.5 Hz, 2H), 2.13 (p, J = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.4, 144.5, 133.4, 132.6, 128.8, 127.2, 126.6, 39.2, 29.7, 23.3. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{O}^+$ [$\text{M} + \text{H}^+$] 147.0804, found 147.0809.

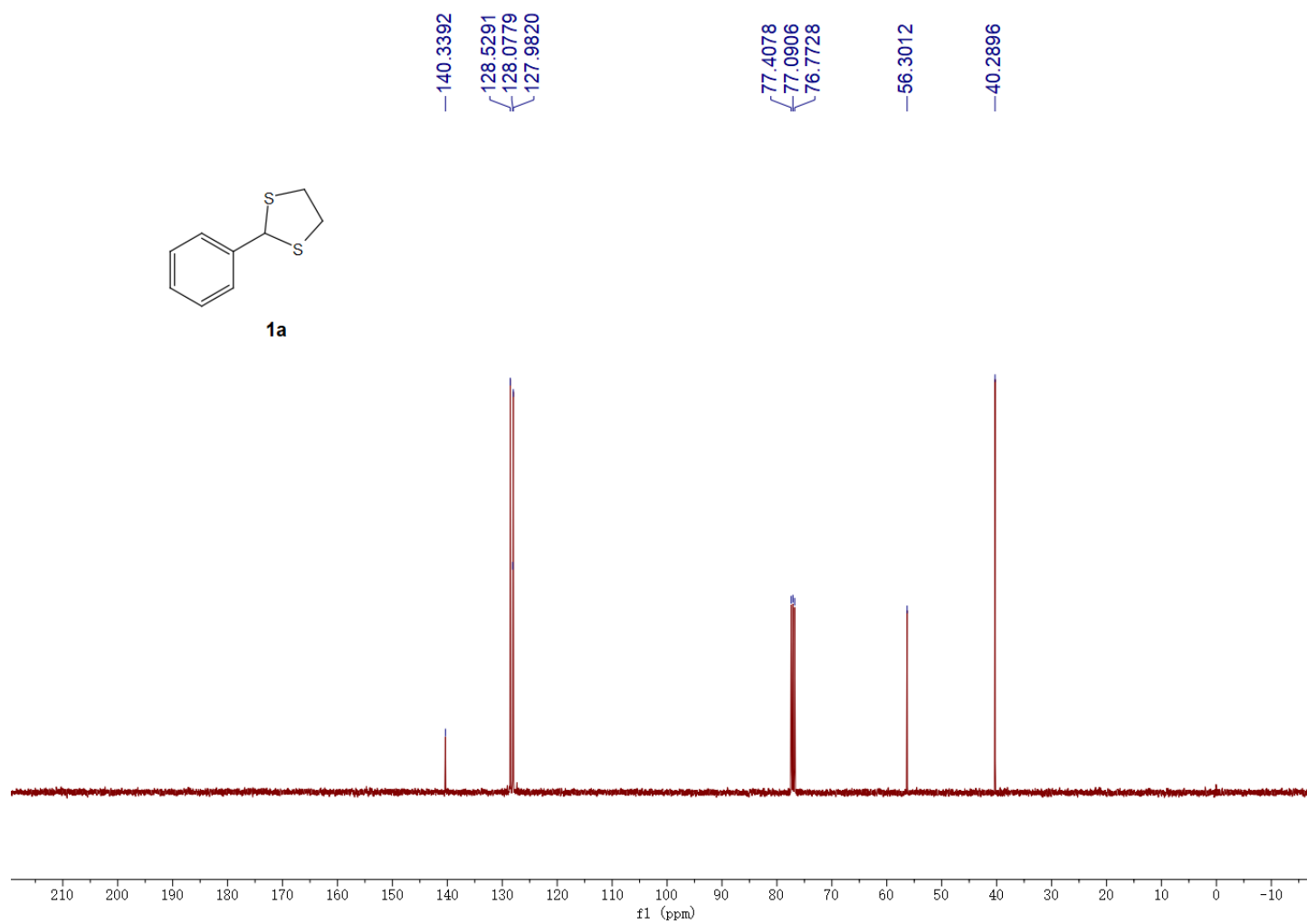
(8R,9S,13S,14S)-3-Hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-

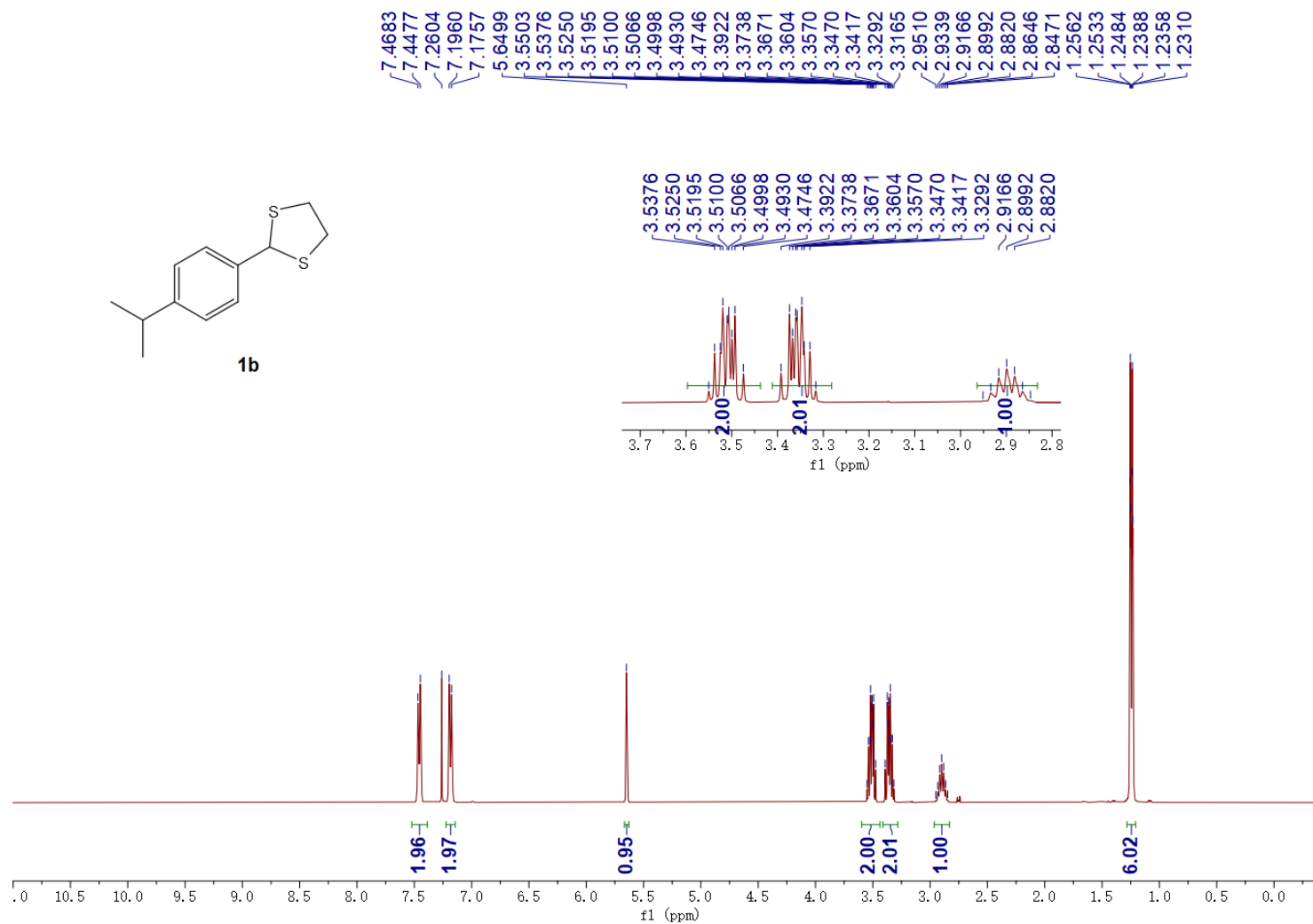
cyclopenta[*a*]phenanthren-17-one (2aj) Following the general procedure, **2aj** was purified by silica gel chromatography (MeOH/DCM = 10/90). Yield: 492 mg, 91%, a white solid, mp. 257-260 °C. ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 9.00 (s, 1H), 7.04 (d, J = 8.5 Hz, 1H), 6.51 (d, J = 8.4 Hz, 1H), 6.45 (s, 1H), 2.74 (td, J = 16.9, 6.4 Hz, 2H), 2.43 (dd, J = 18.9, 8.6 Hz, 1H), 2.30 (q, J = 6.7, 5.3 Hz, 1H), 2.13 (s, 1H), 2.06 (dt, J = 18.5, 8.9 Hz, 1H), 1.93 (ddd, J = 25.3, 13.2, 5.6 Hz, 2H), 1.74 (dd, J = 8.8, 2.6 Hz, 1H), 1.60 – 1.51 (m, 1H), 1.51 – 1.42 (m, 2H), 1.35 (t, J = 9.9 Hz, 3H), 0.82 (s, 3H). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 155.0, 137.1, 129.9, 126.0, 114.9, 112.8, 49.6, 47.3, 43.4, 39.3, 39.1, 38.0, 35.3, 31.3, 29.0, 26.1, 25.5, 21.1, 13.5. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{O}_2^+$ [$\text{M} + \text{H}^+$] 271.1693, found 271.1698.

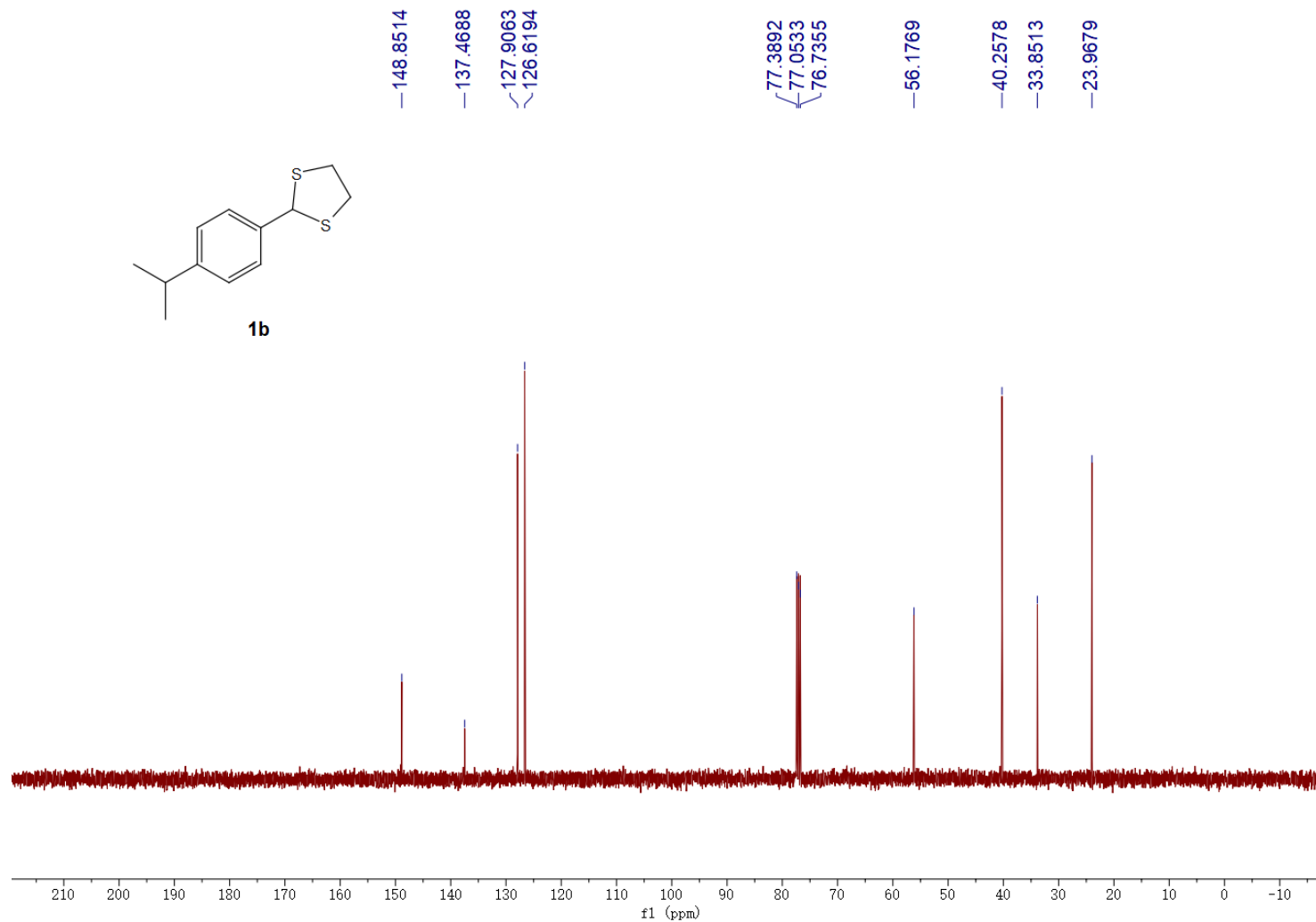
3. ^1H -NMR and ^{13}C -NMR Spectra

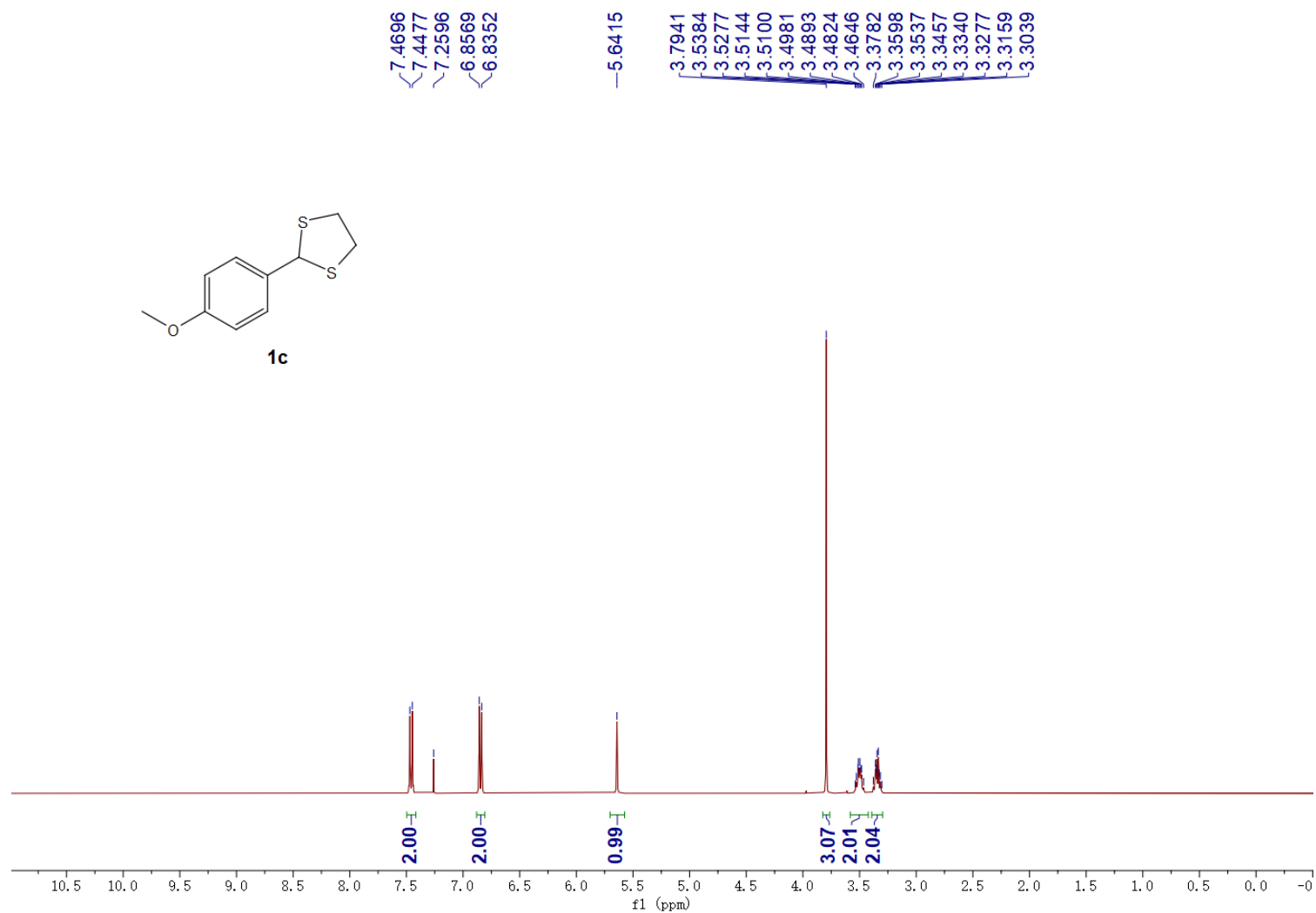
^1H -NMR Spectrum of 2-Phenyl-1,3-dithiolane (1a)

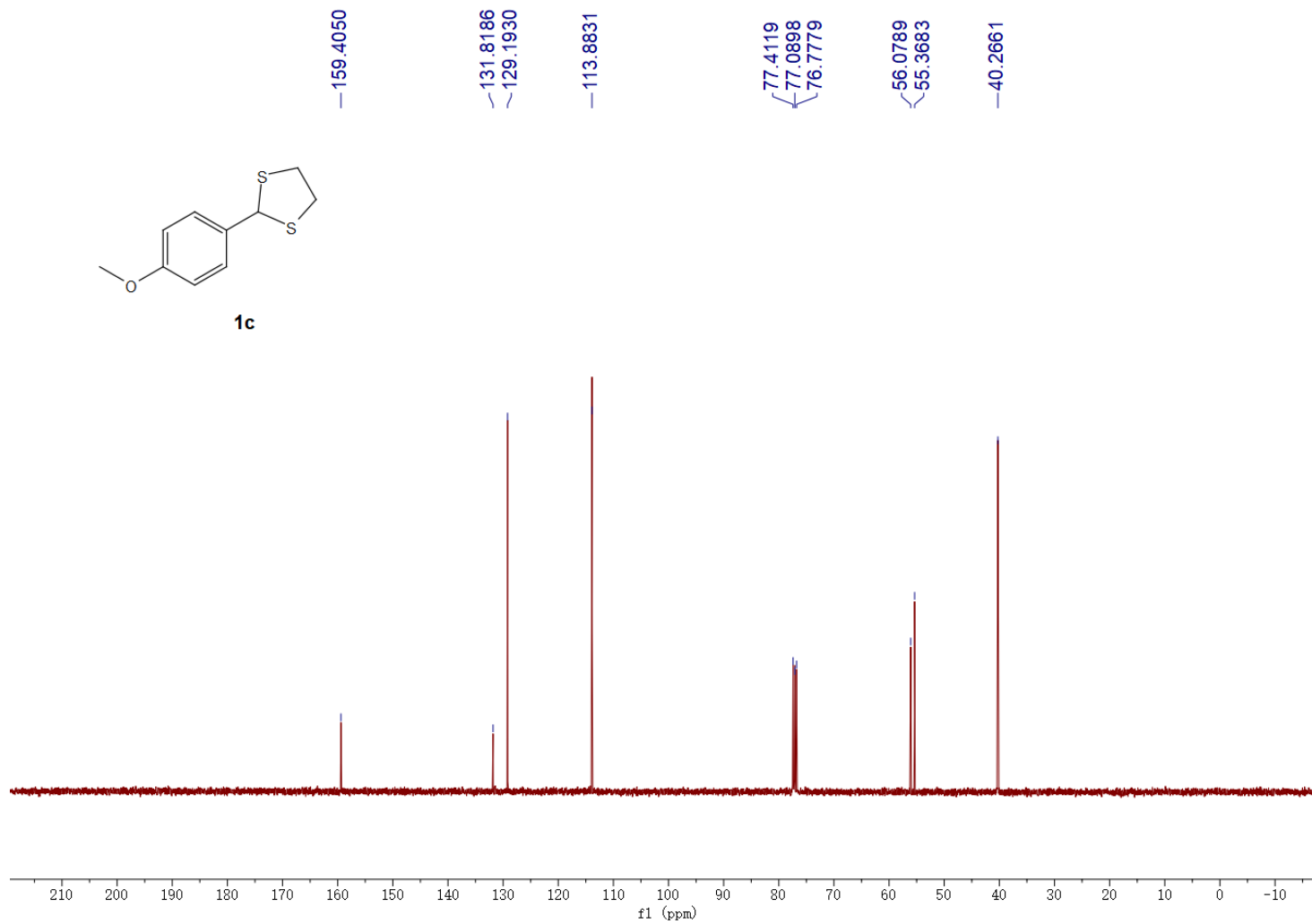


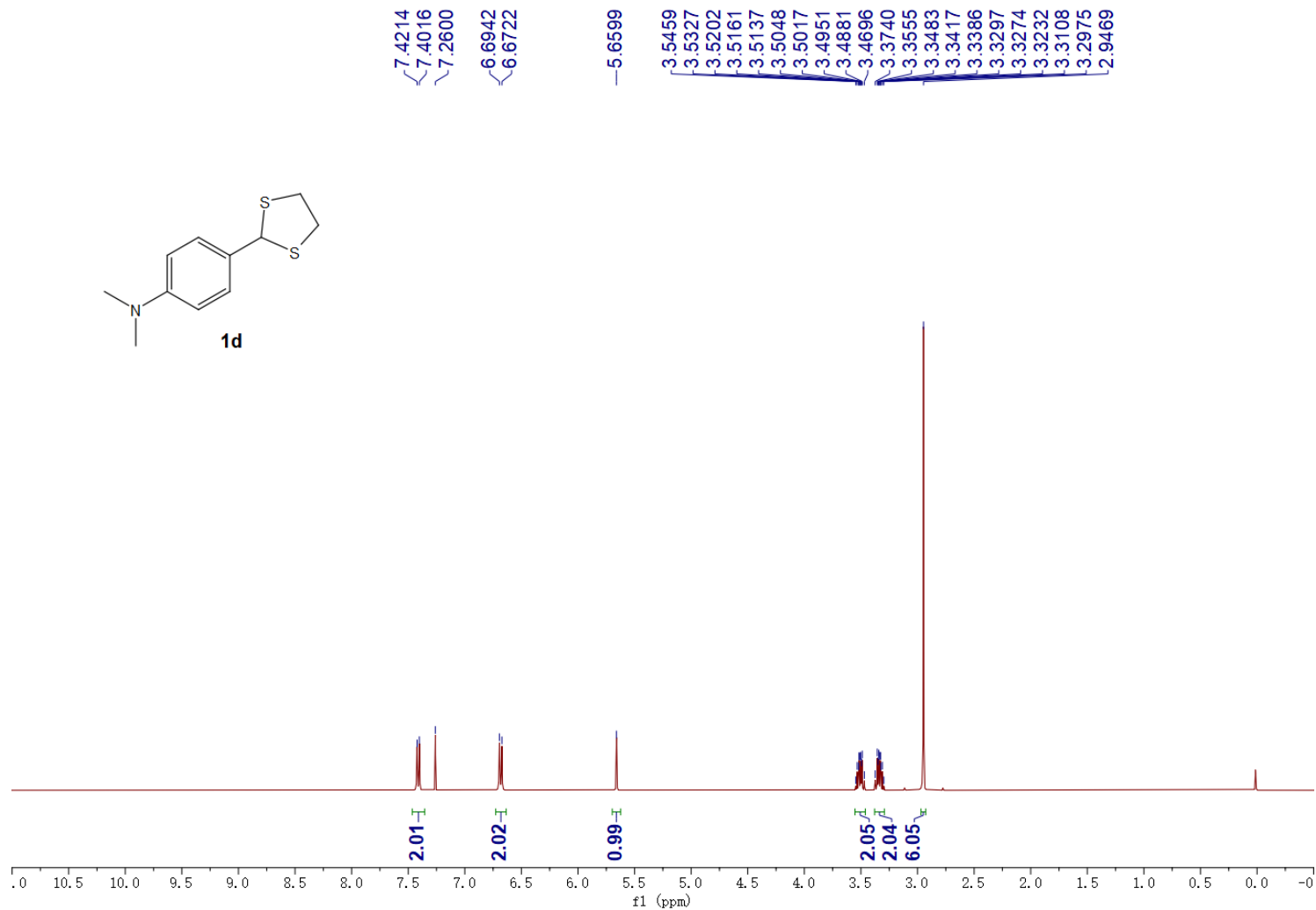
^{13}C -NMR Spectrum of 2-Phenyl-1,3-dithiolane (1a)

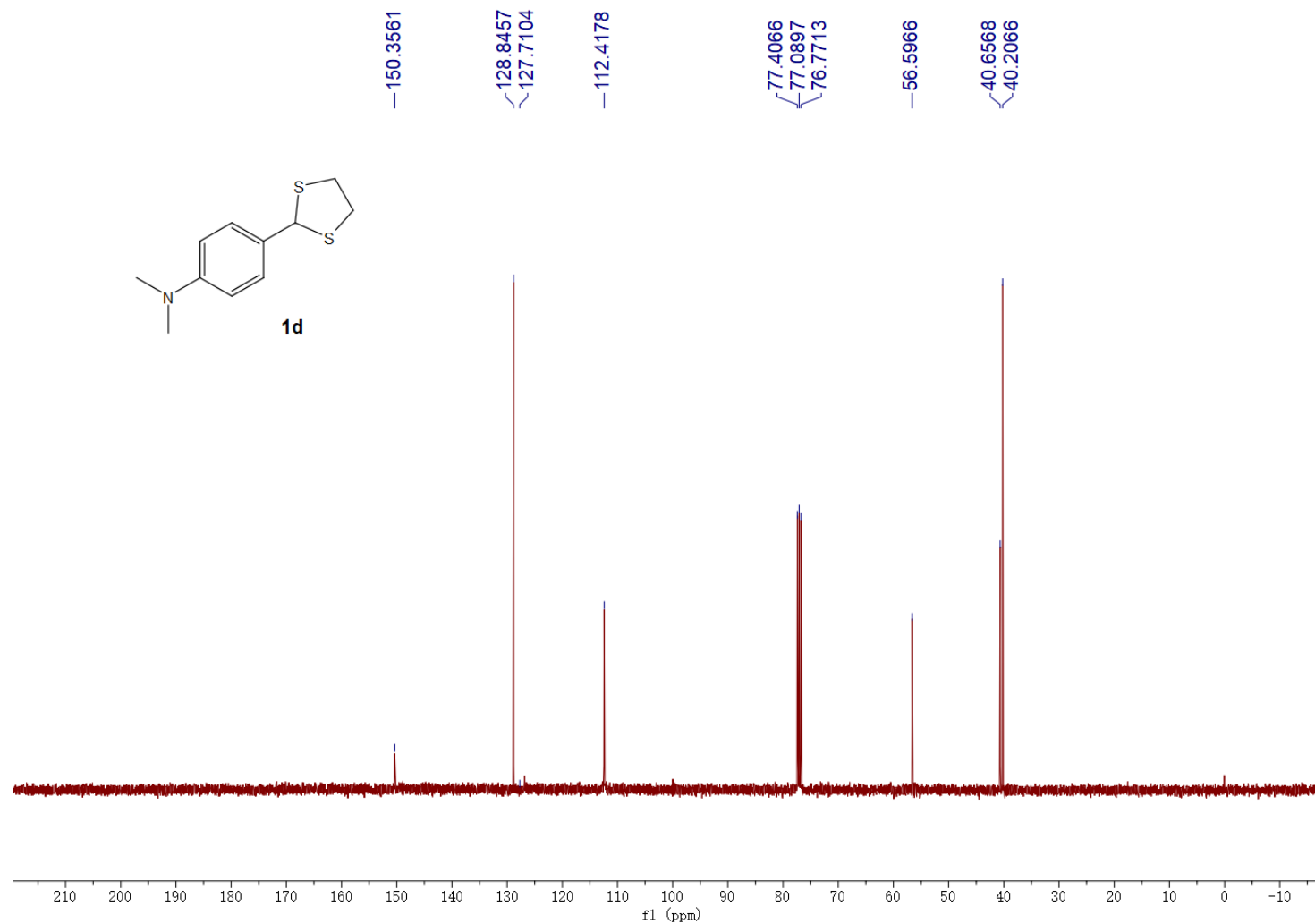
¹H-NMR Spectrum of 2-(4-Isopropylphenyl)-1,3-dithiolane (1b)

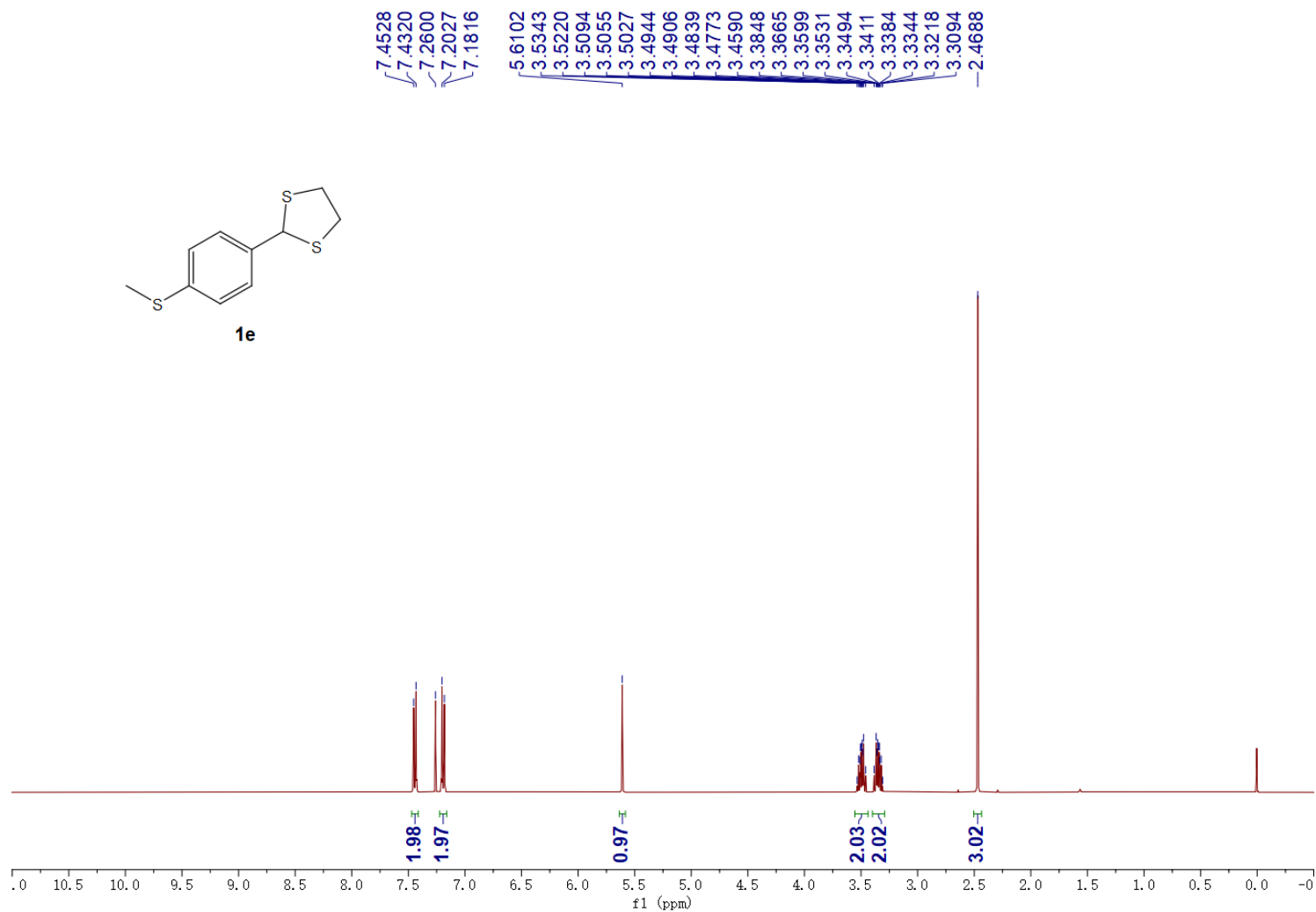
^{13}C -NMR Spectrum of 2-(4-Isopropylphenyl)-1,3-dithiolane (1b)

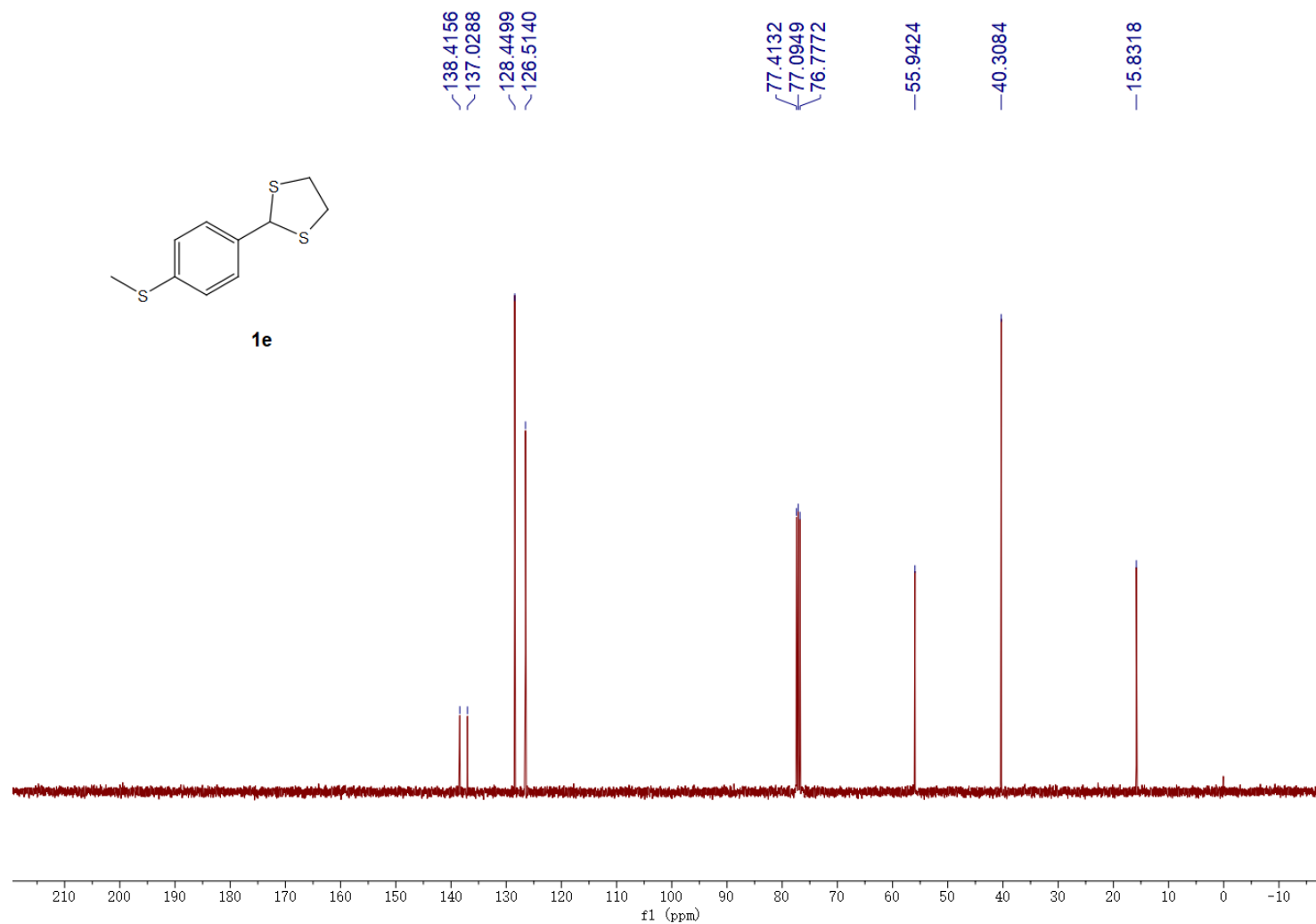
¹H-NMR Spectrum of 2-(4-Methoxyphenyl)-1,3-dithiolane (1c)

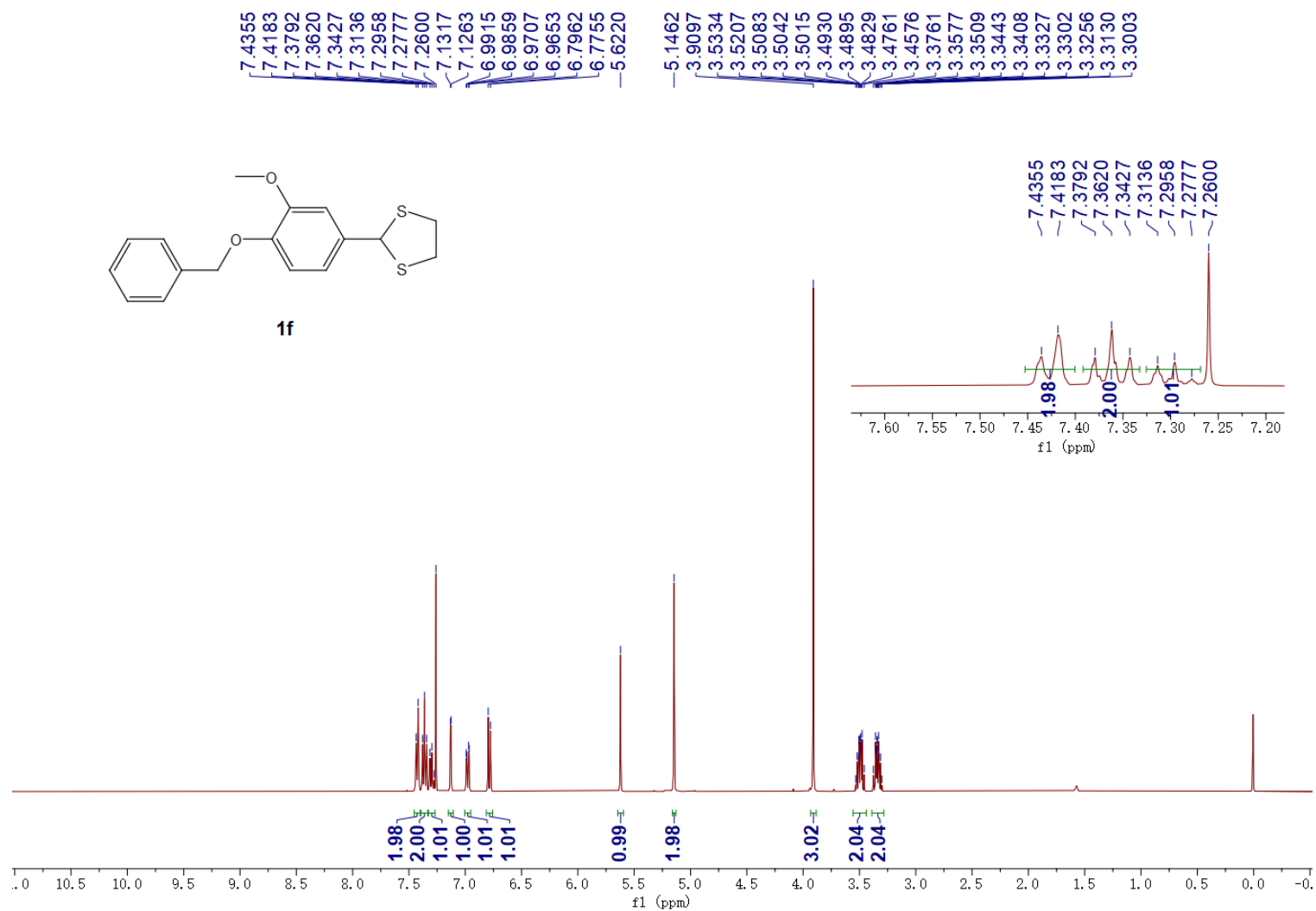
^{13}C -NMR Spectrum of 2-(4-Methoxyphenyl)-1,3-dithiolane (1c)

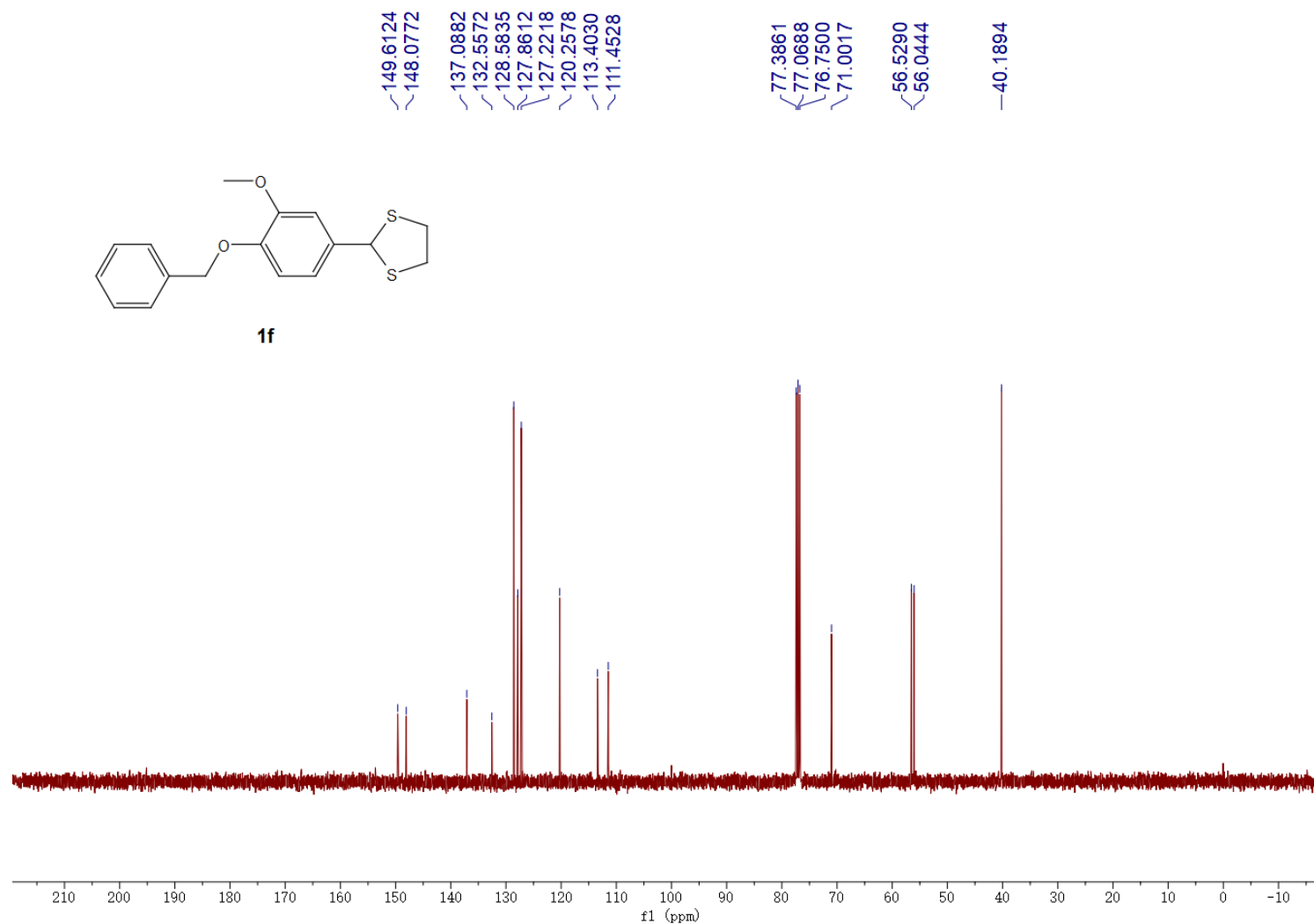
¹H-NMR Spectrum of 4-(1,3-Dithiolan-2-yl)-*N*, *N*-dimethylaniline (1d)

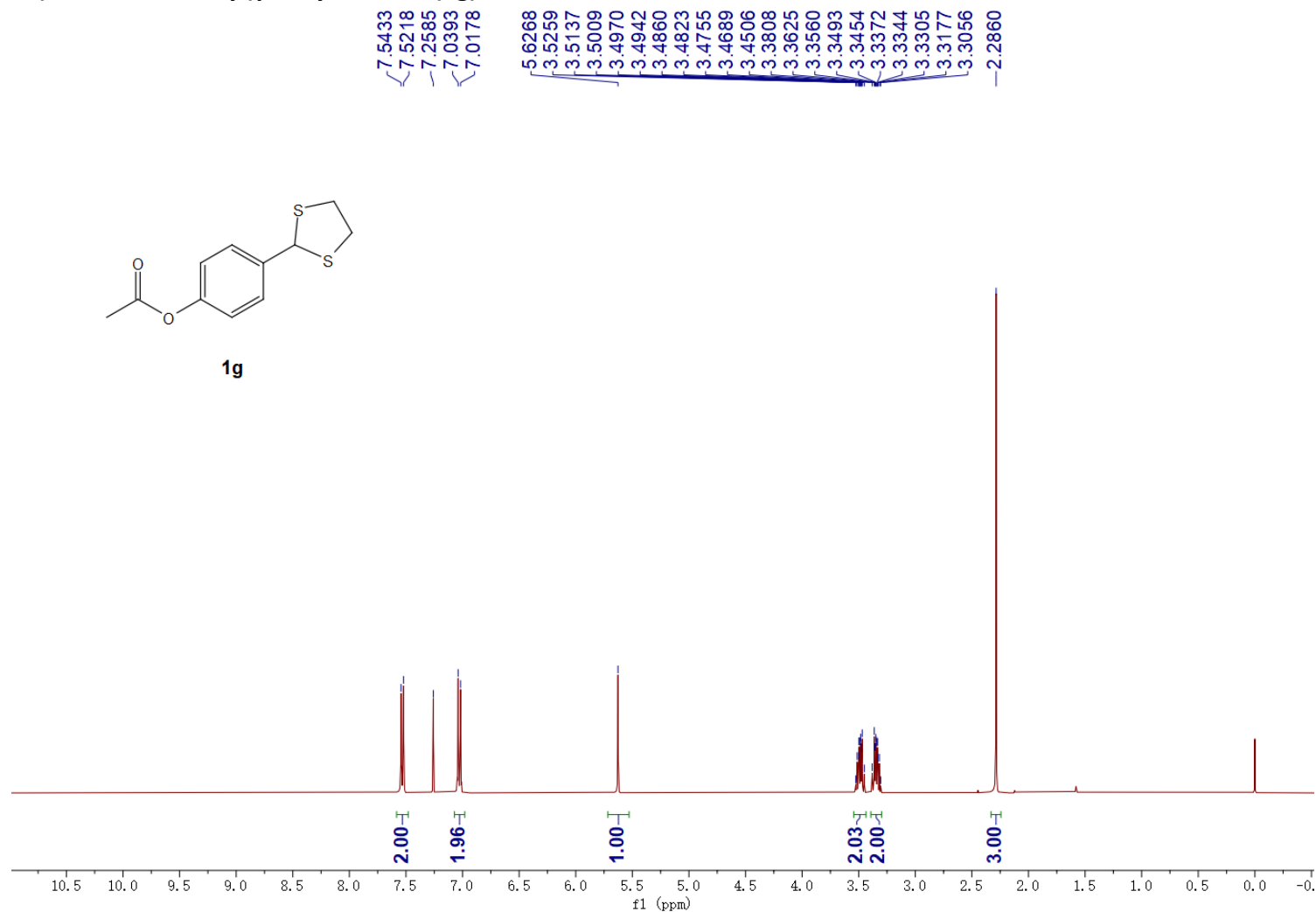
^{13}C -NMR Spectrum of 4-(1,3-Dithiolan-2-yl)-*N,N*-dimethylaniline (1d)

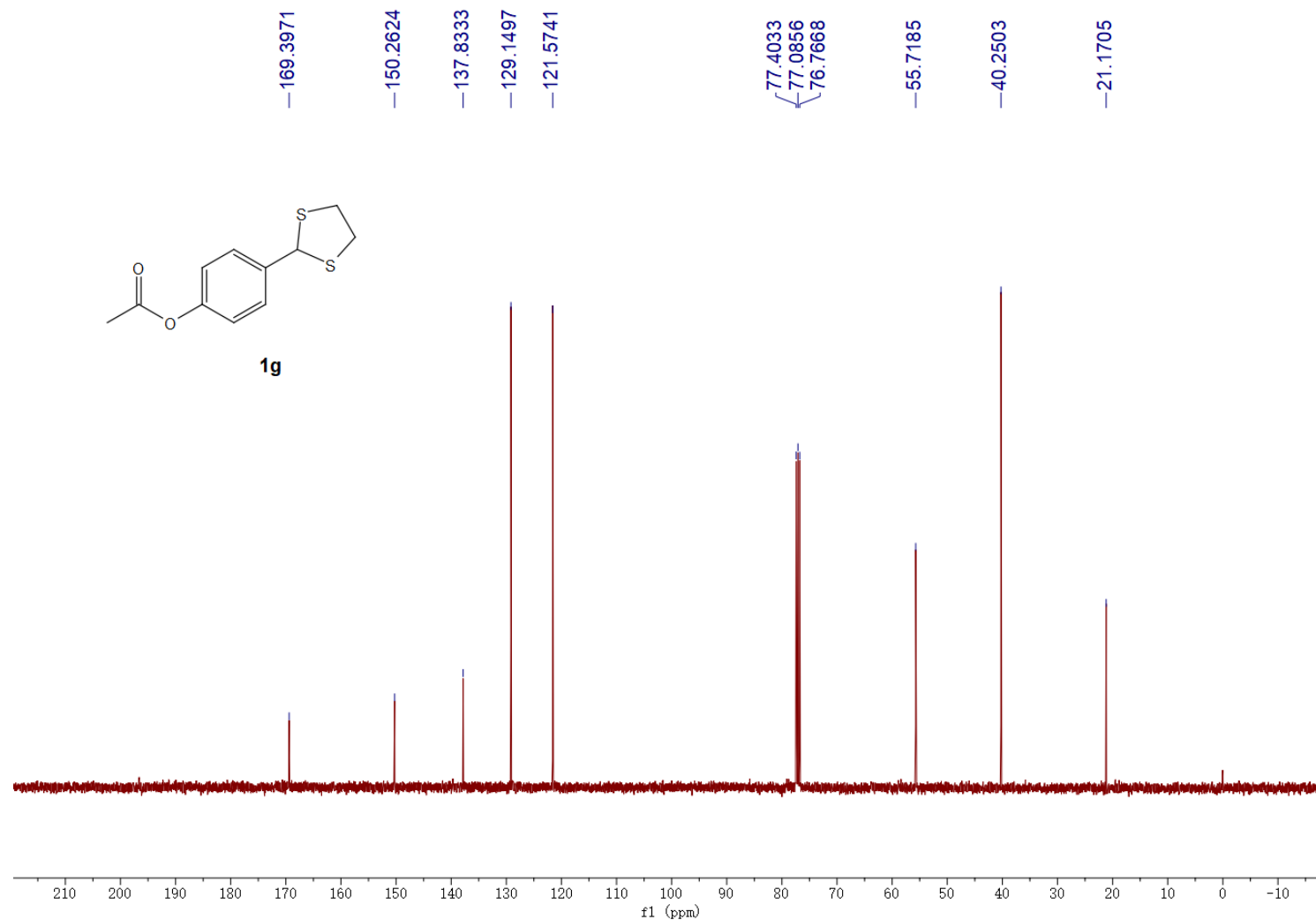
¹H-NMR Spectrum of 2-(4-(Methylthio)phenyl)-1,3-dithiolane (1e)

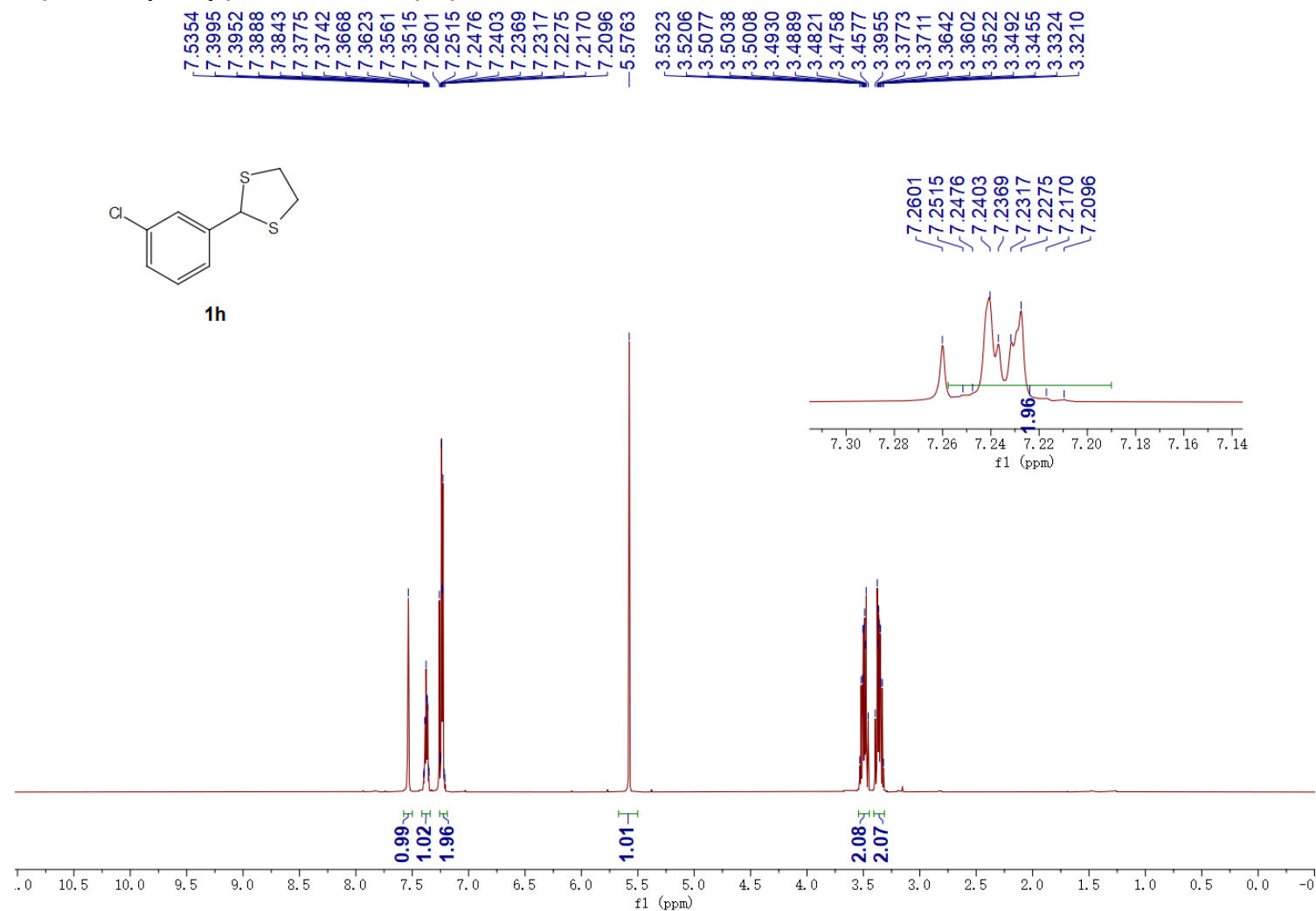
^{13}C -NMR Spectrum of 2-(4-(Methylthio)phenyl)-1,3-dithiolane (1e)

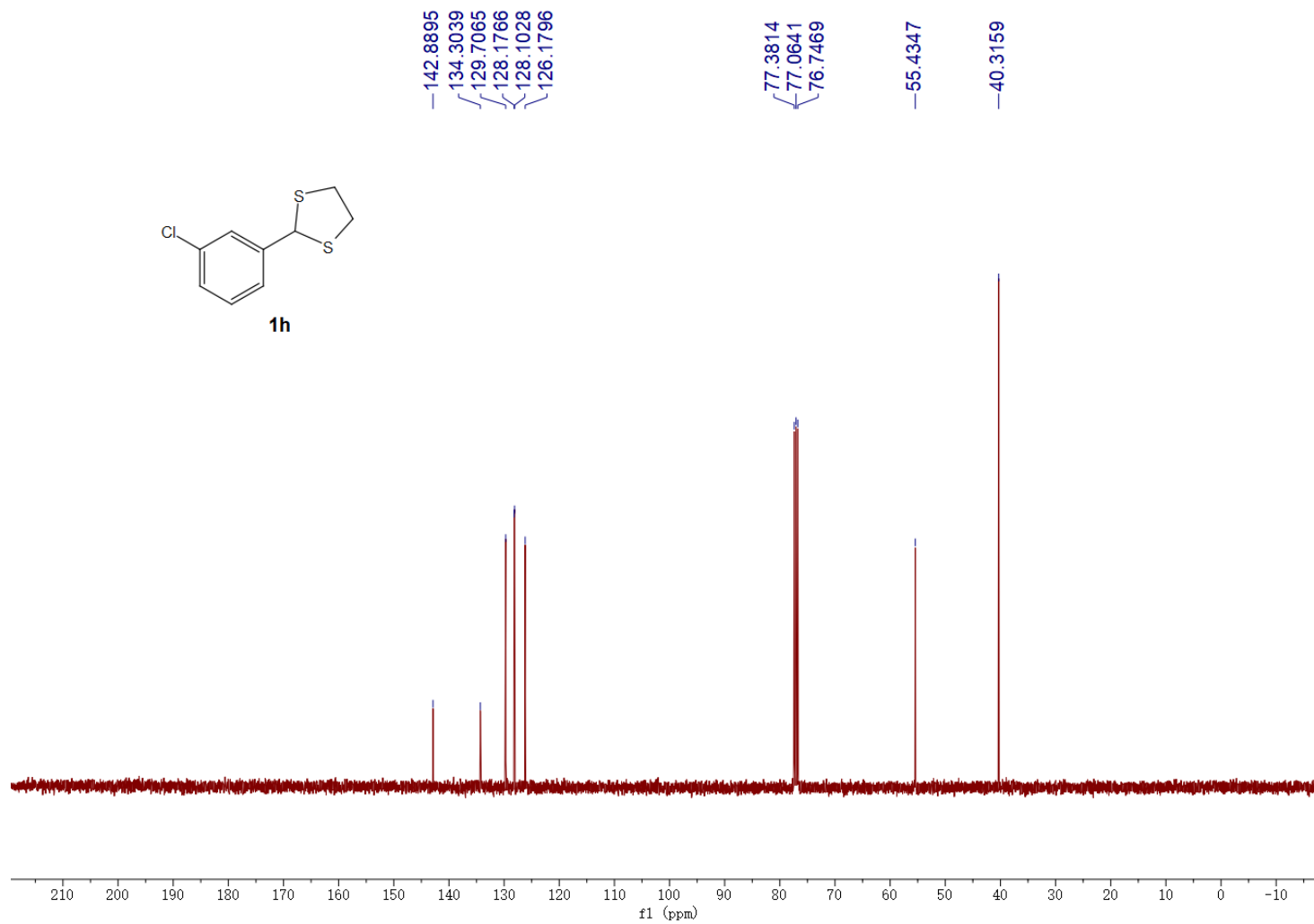
¹H-NMR Spectrum of 2-(4-(Benzyloxy)-3-methoxyphenyl)-1,3-dithiolane (1f)

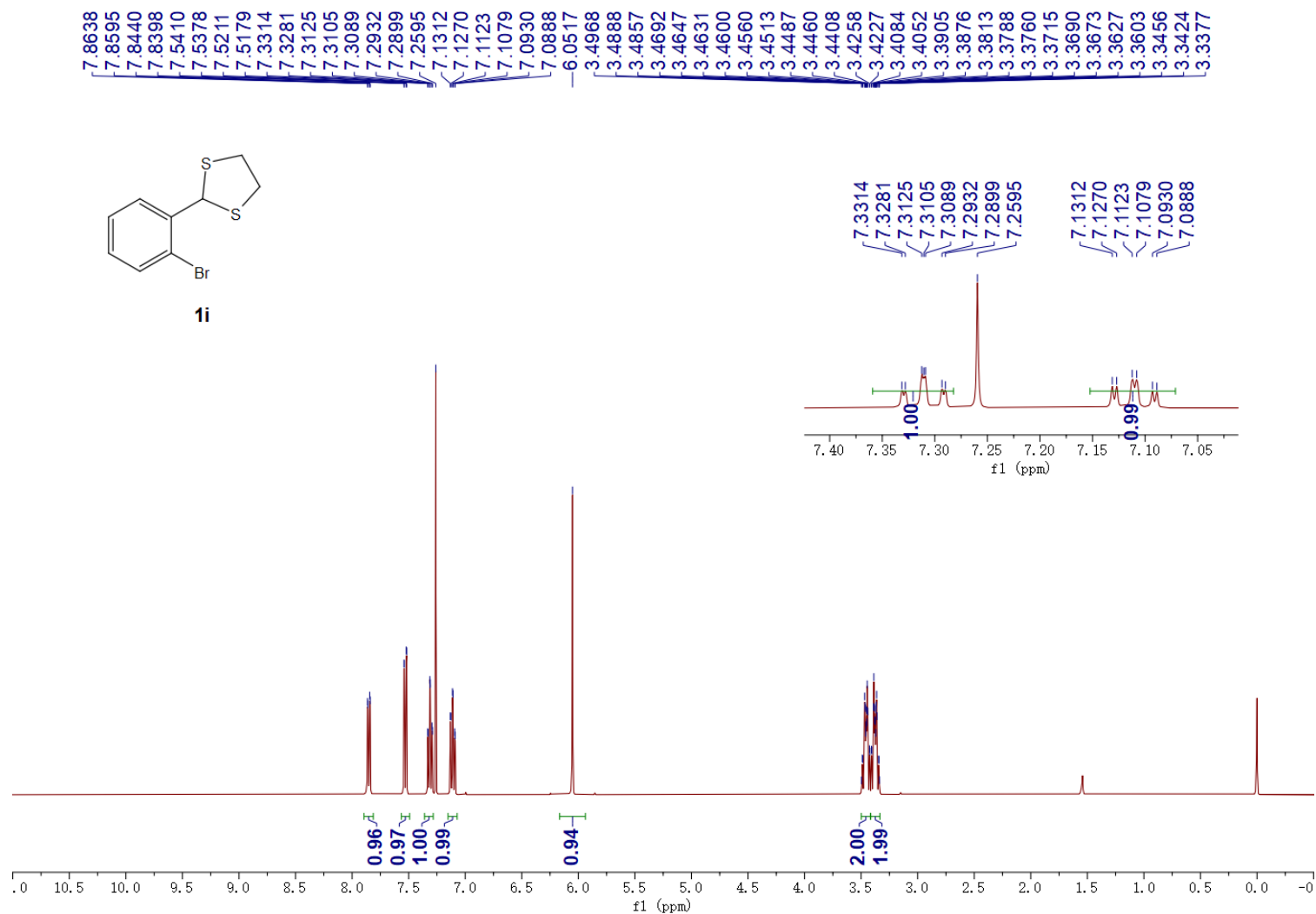
^{13}C -NMR Spectrum of 2-(4-(Benzyloxy)-3-methoxyphenyl)-1,3-dithiolane (1f)

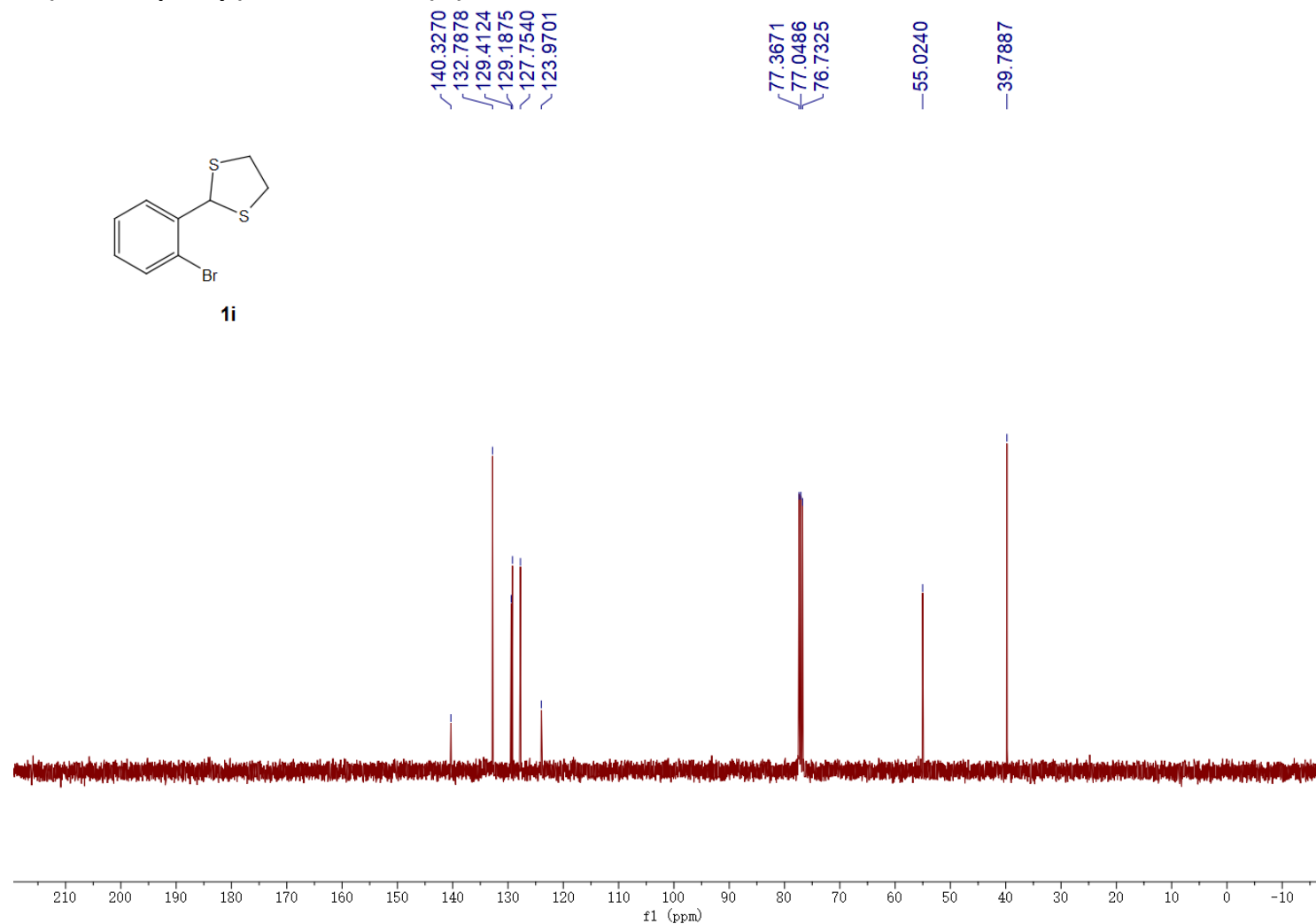
¹H-NMR Spectrum of 4-(1,3-Dithiolan-2-yl)phenyl acetate (1g)

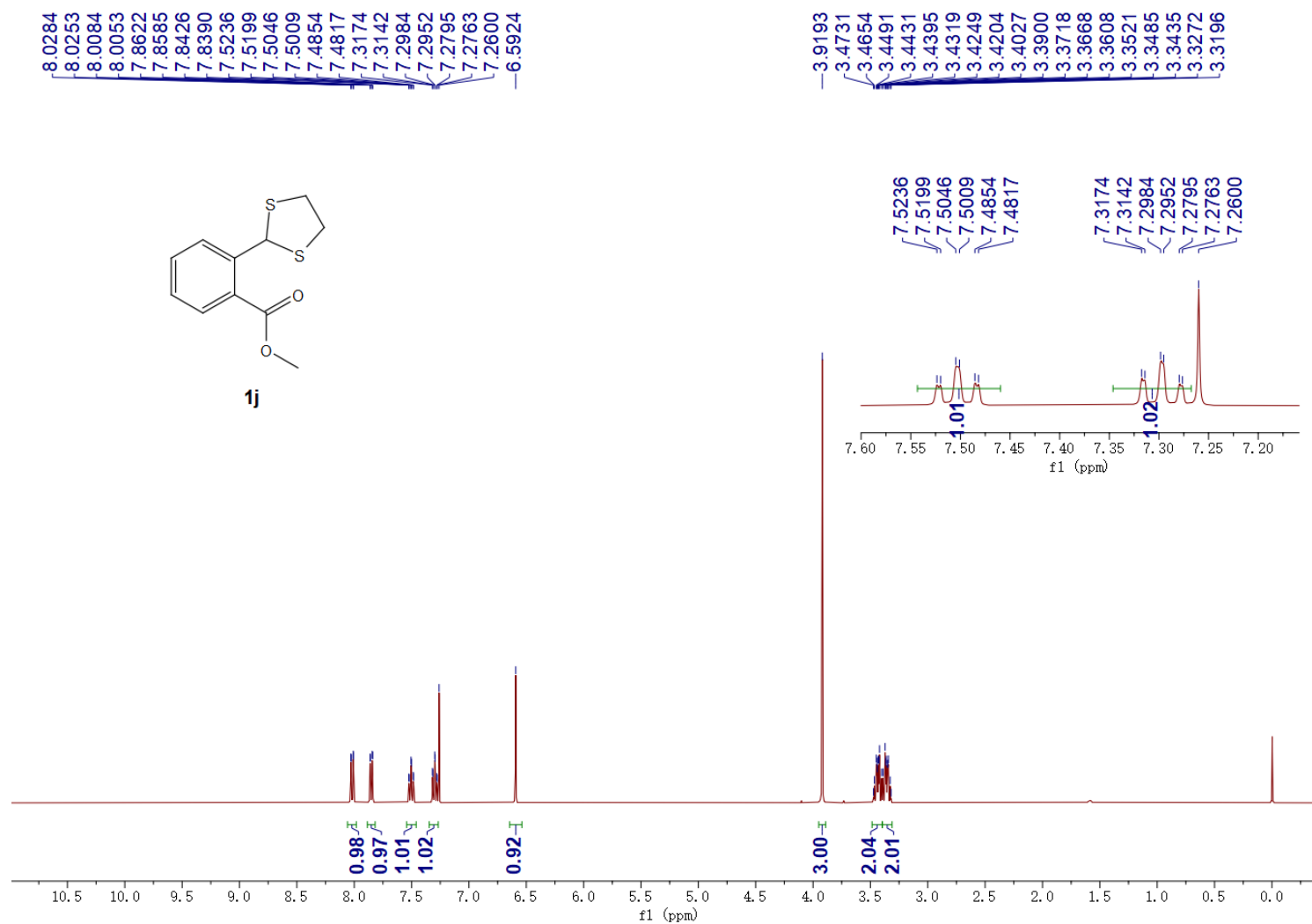
^{13}C -NMR Spectrum of 4-(1,3-Dithiolan-2-yl)phenyl acetate (1g)

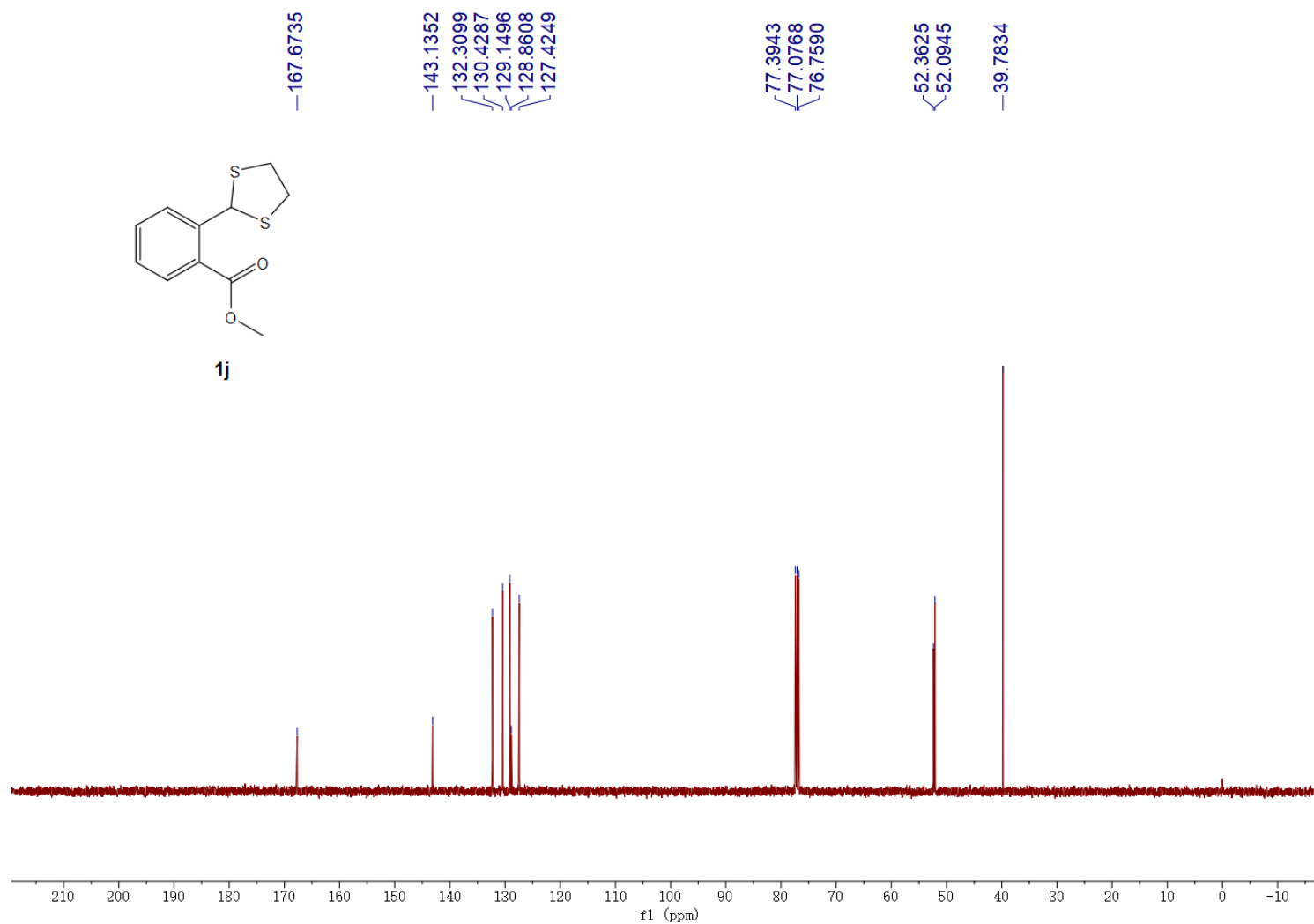
¹H-NMR Spectrum of 2-(3-Chlorophenyl)-1,3-dithiolane (1h)

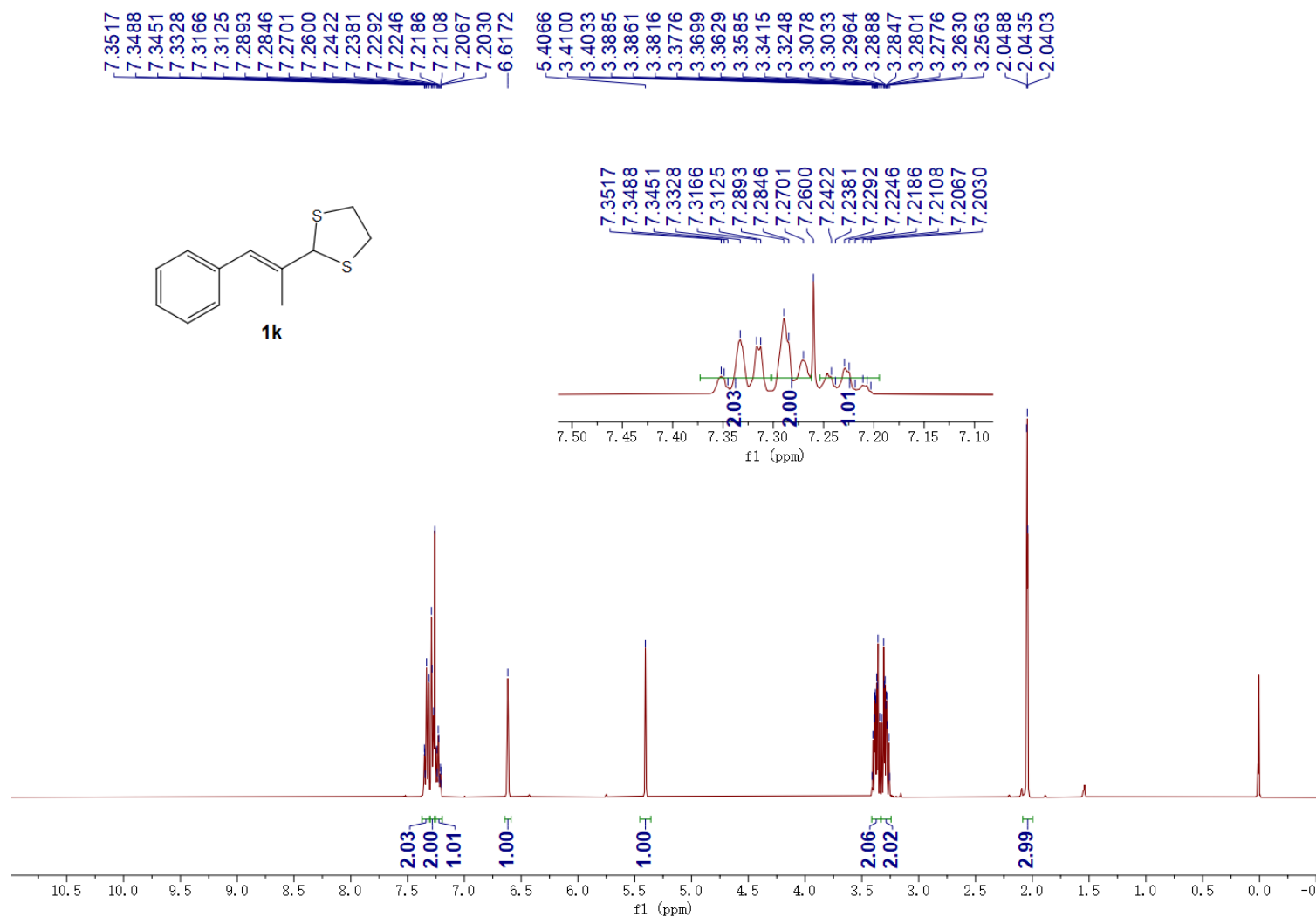
^{13}C -NMR Spectrum of 2-(3-Chlorophenyl)-1,3-dithiolane (1h)

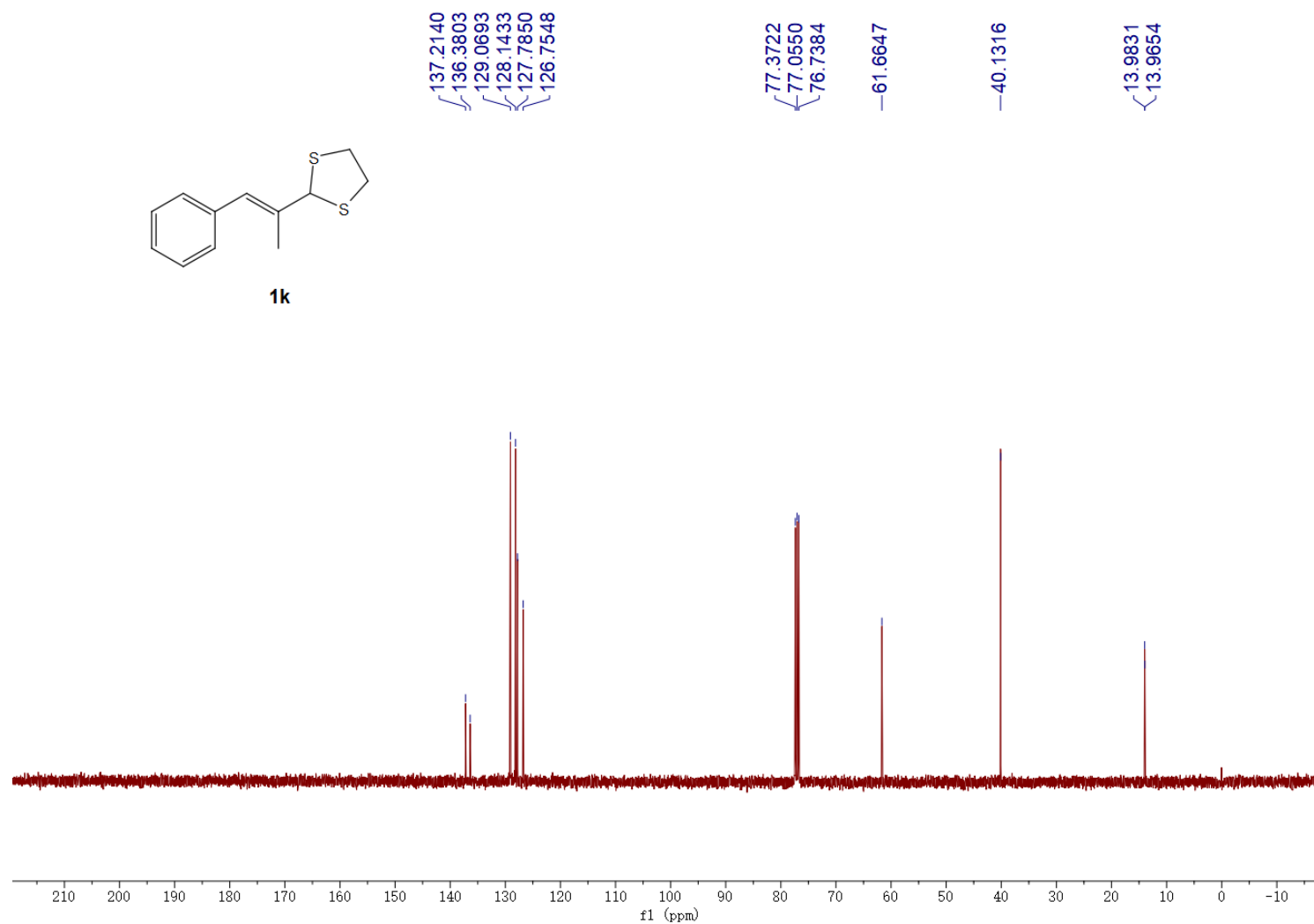
¹H-NMR Spectrum of 2-(2-Bromophenyl)-1,3-dithiolane (1i)

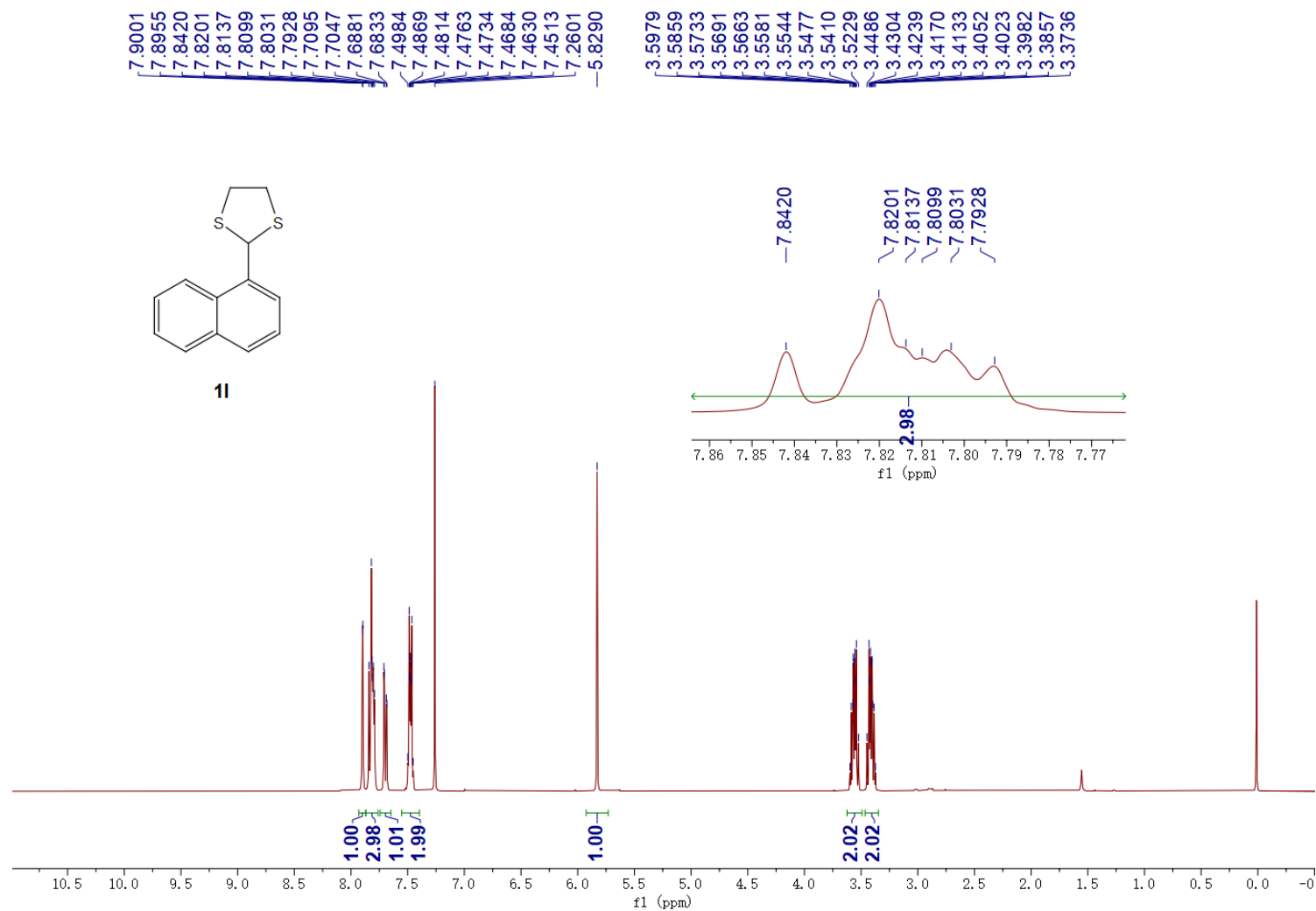
^{13}C -NMR Spectrum of 2-(2-Bromophenyl)-1,3-dithiolane (1i)

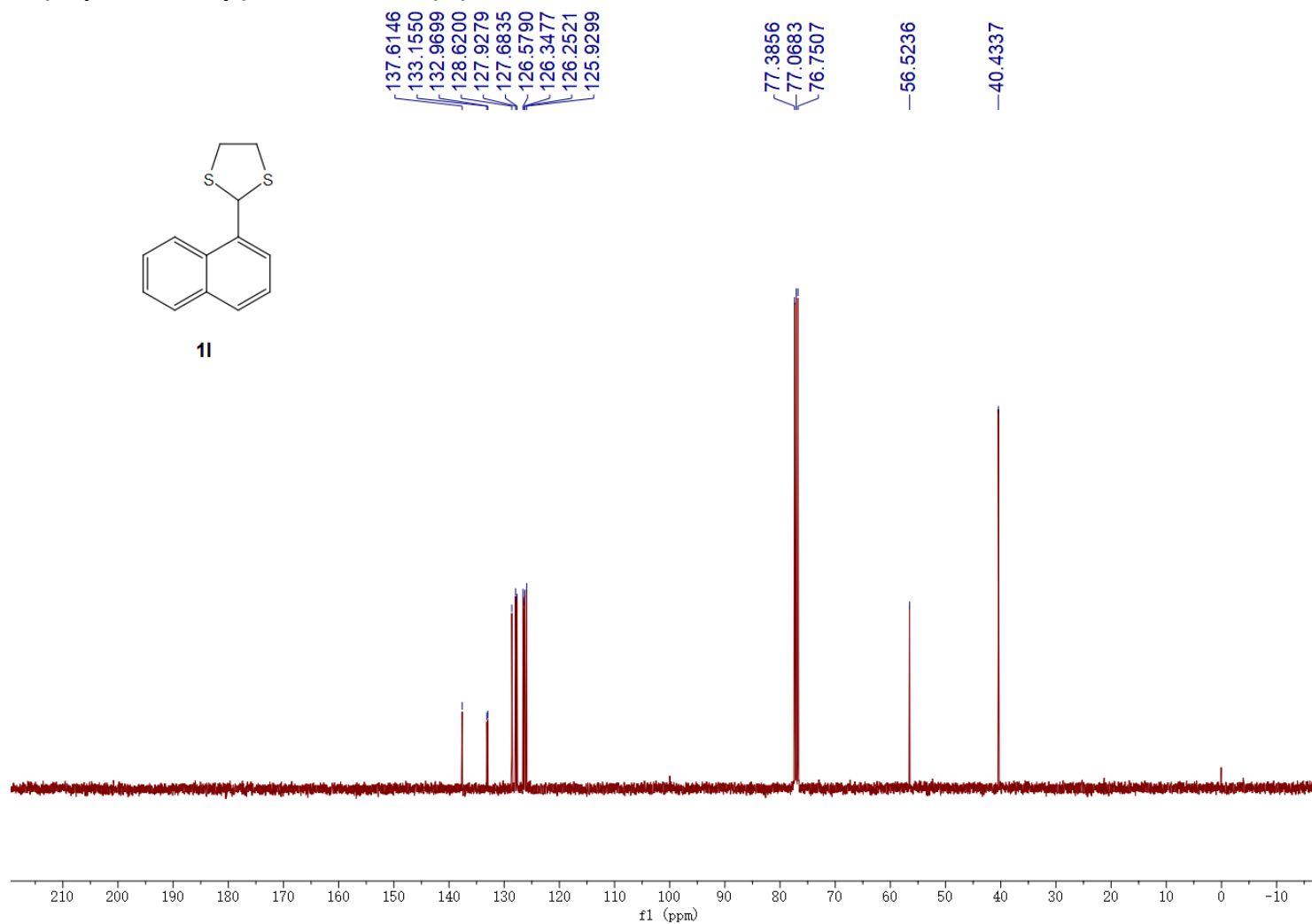
¹H-NMR Spectrum of Methyl 2-(1,3-dithiolan-2-yl)benzoate (1j)

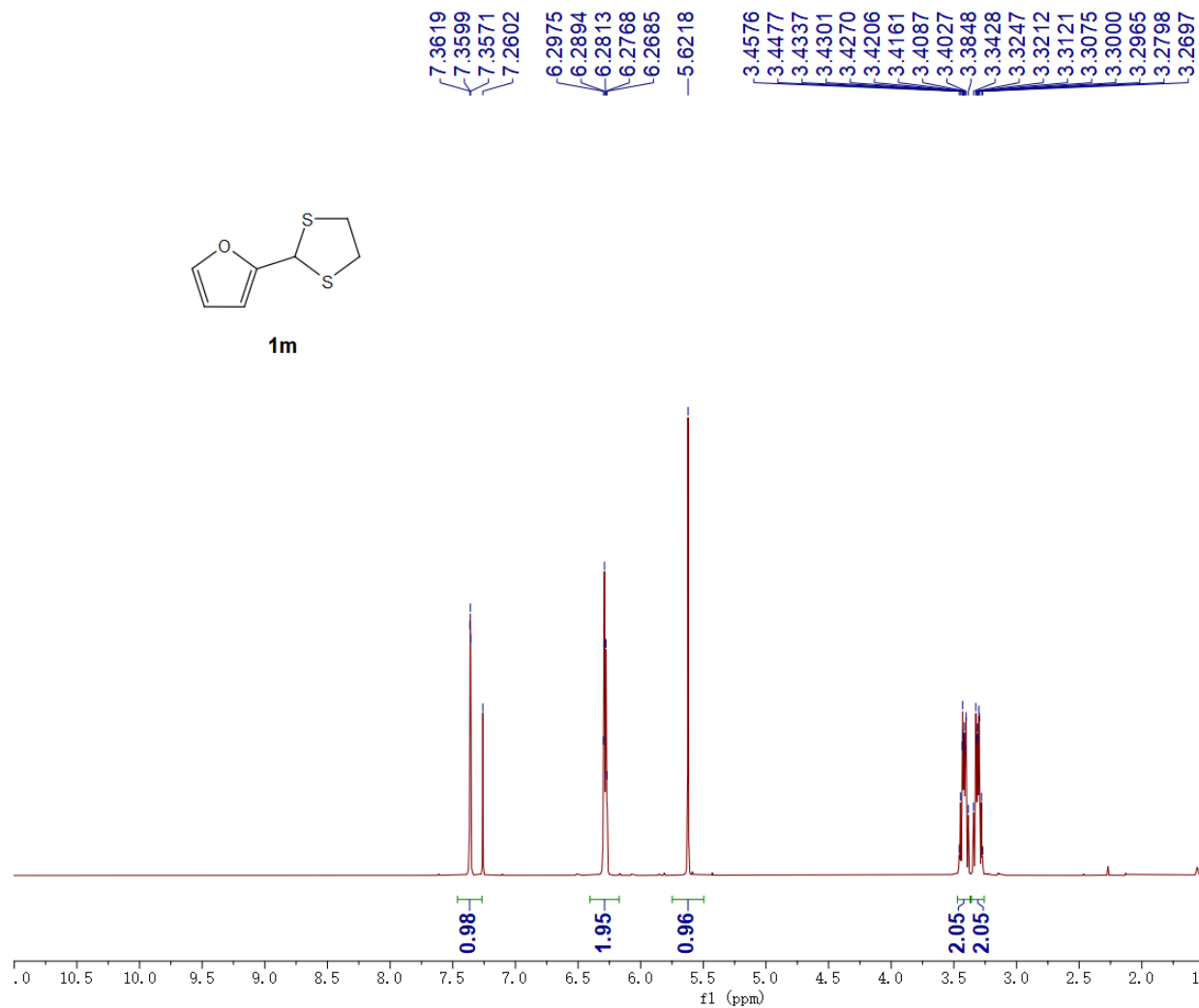
^{13}C -NMR Spectrum of Methyl 2-(1,3-dithiolan-2-yl)benzoate (1j)

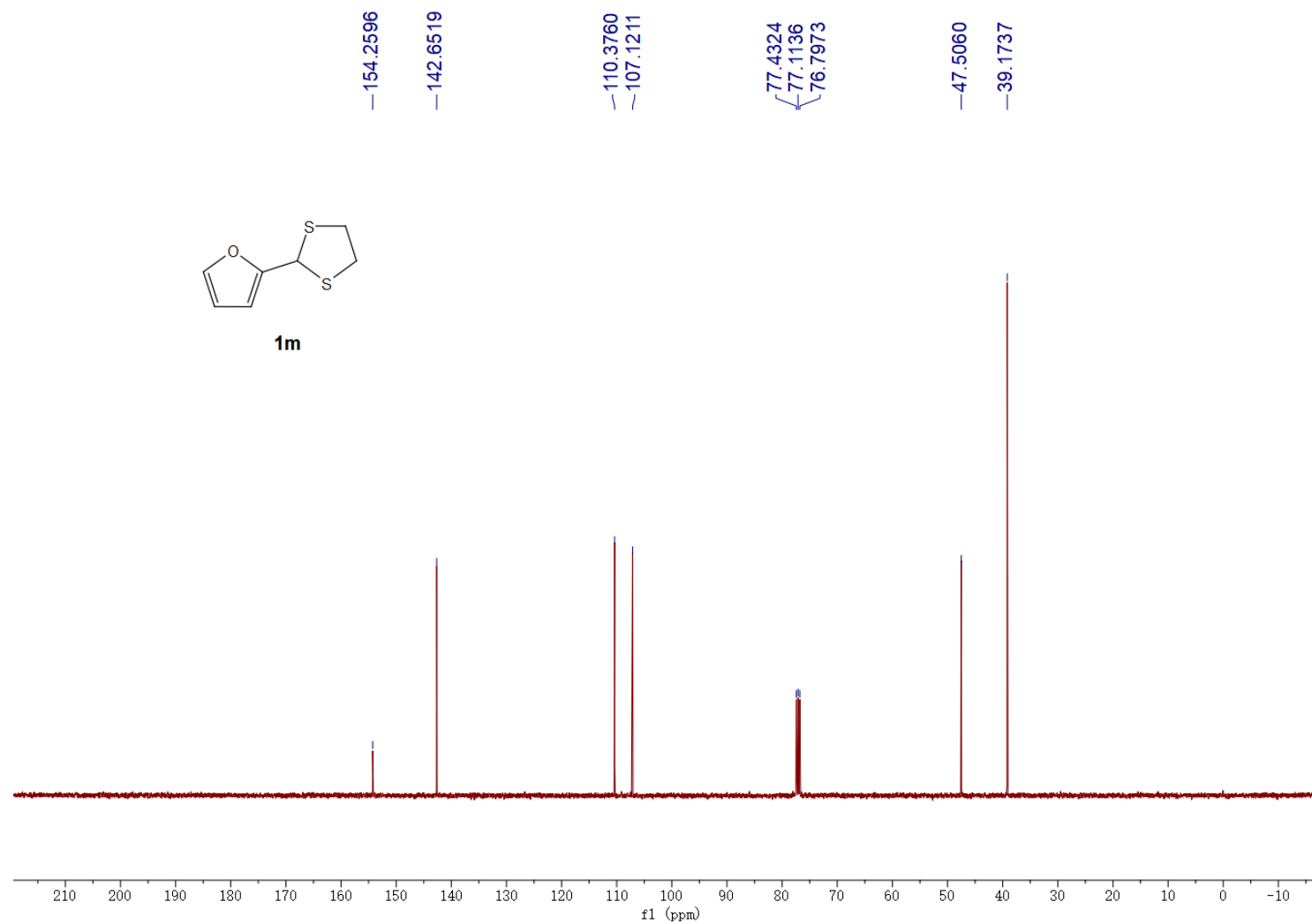
¹H-NMR Spectrum of (*E*)-2-(1-Phenylprop-1-en-2-yl)-1,3-dithiolane (1k)

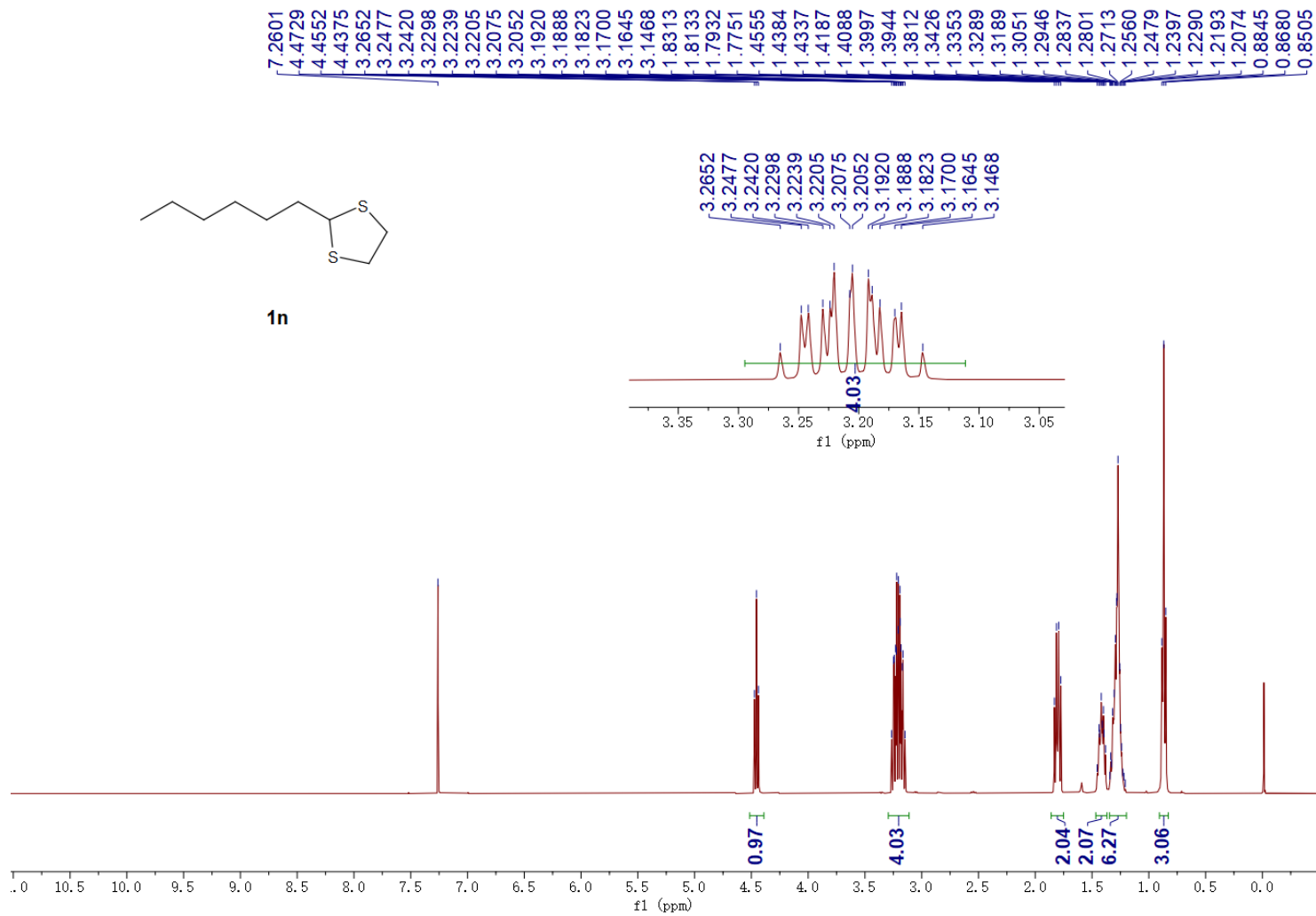
^{13}C -NMR Spectrum of (*E*)-2-(1-Phenylprop-1-en-2-yl)-1,3-dithiolane (1k)

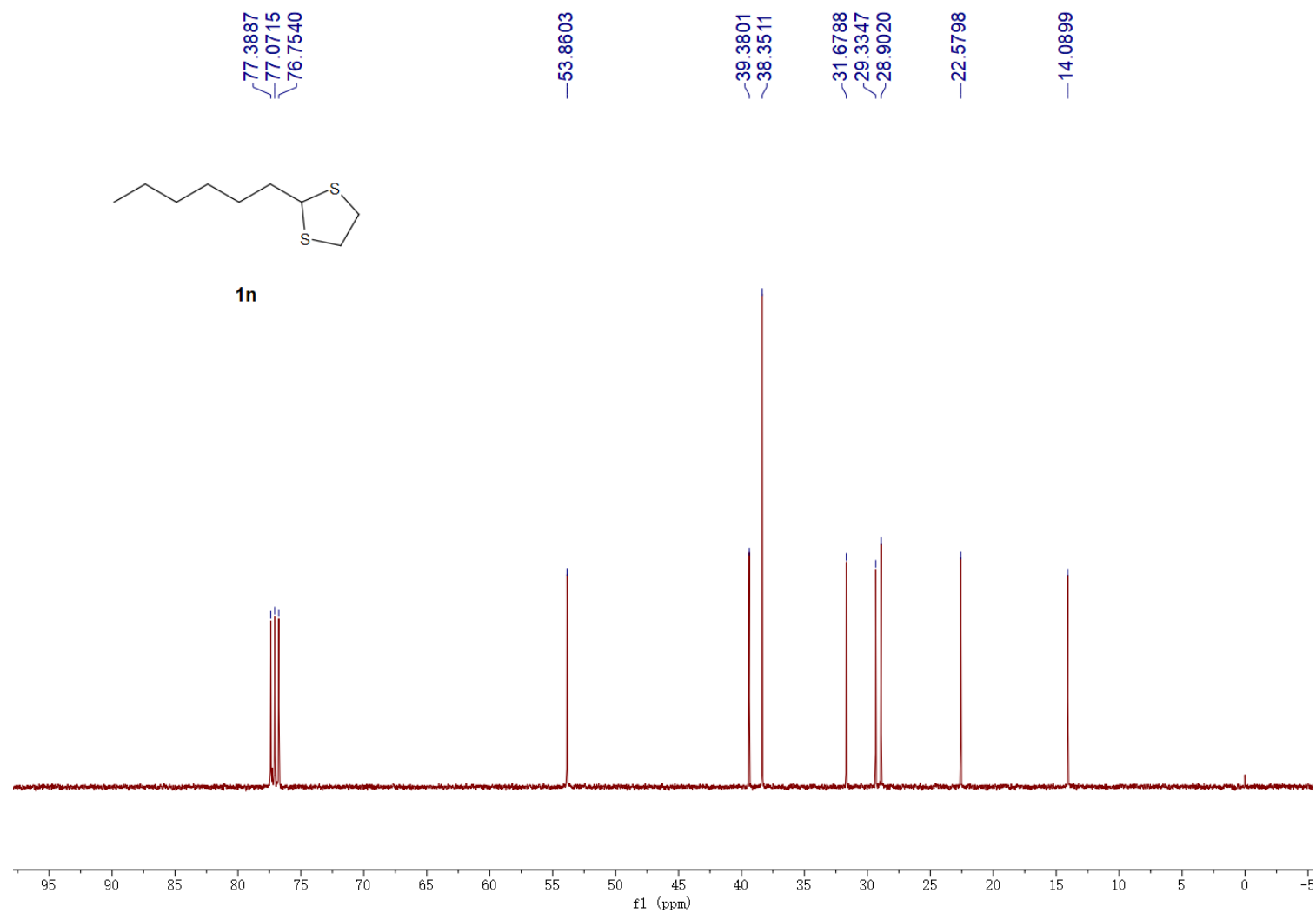
¹H-NMR Spectrum of 2-(Naphthalen-1-yl)-1,3-dithiolane (1I)

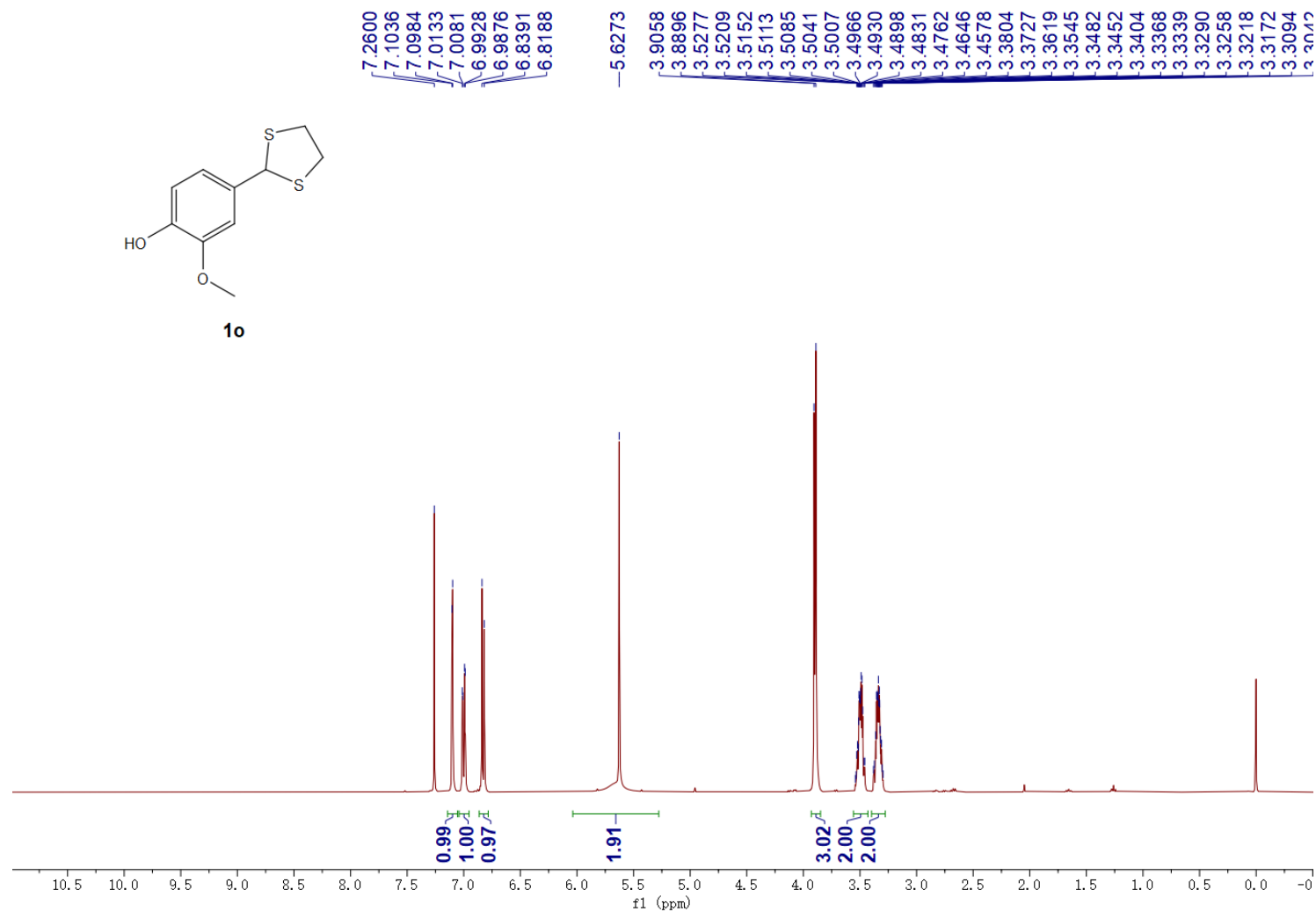
^{13}C -NMR Spectrum of 2-(Naphthalen-1-yl)-1,3-dithiolane (1I)

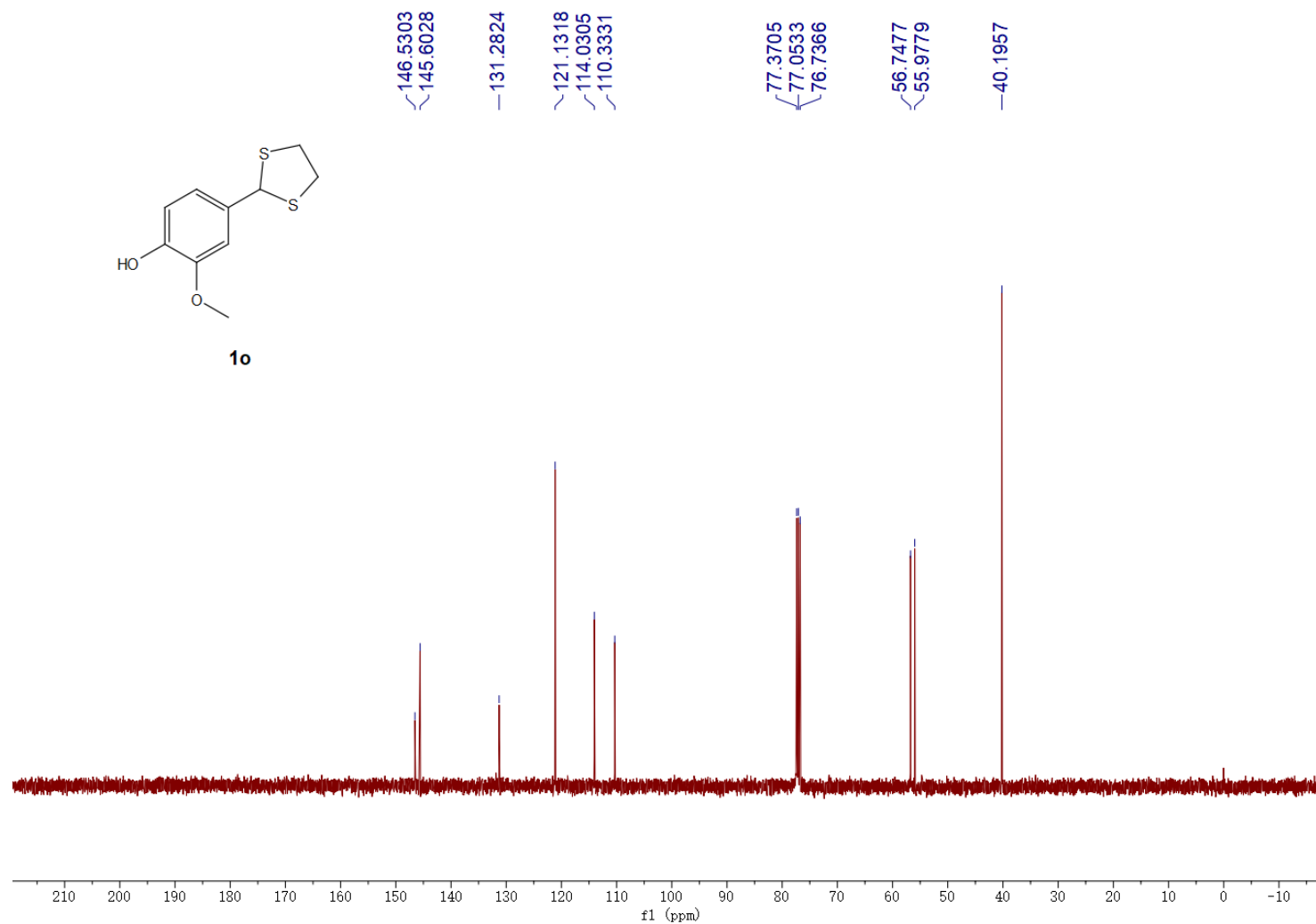
^1H -NMR Spectrum of 2-(1,3-Dithiolan-2-yl)furan (1m)

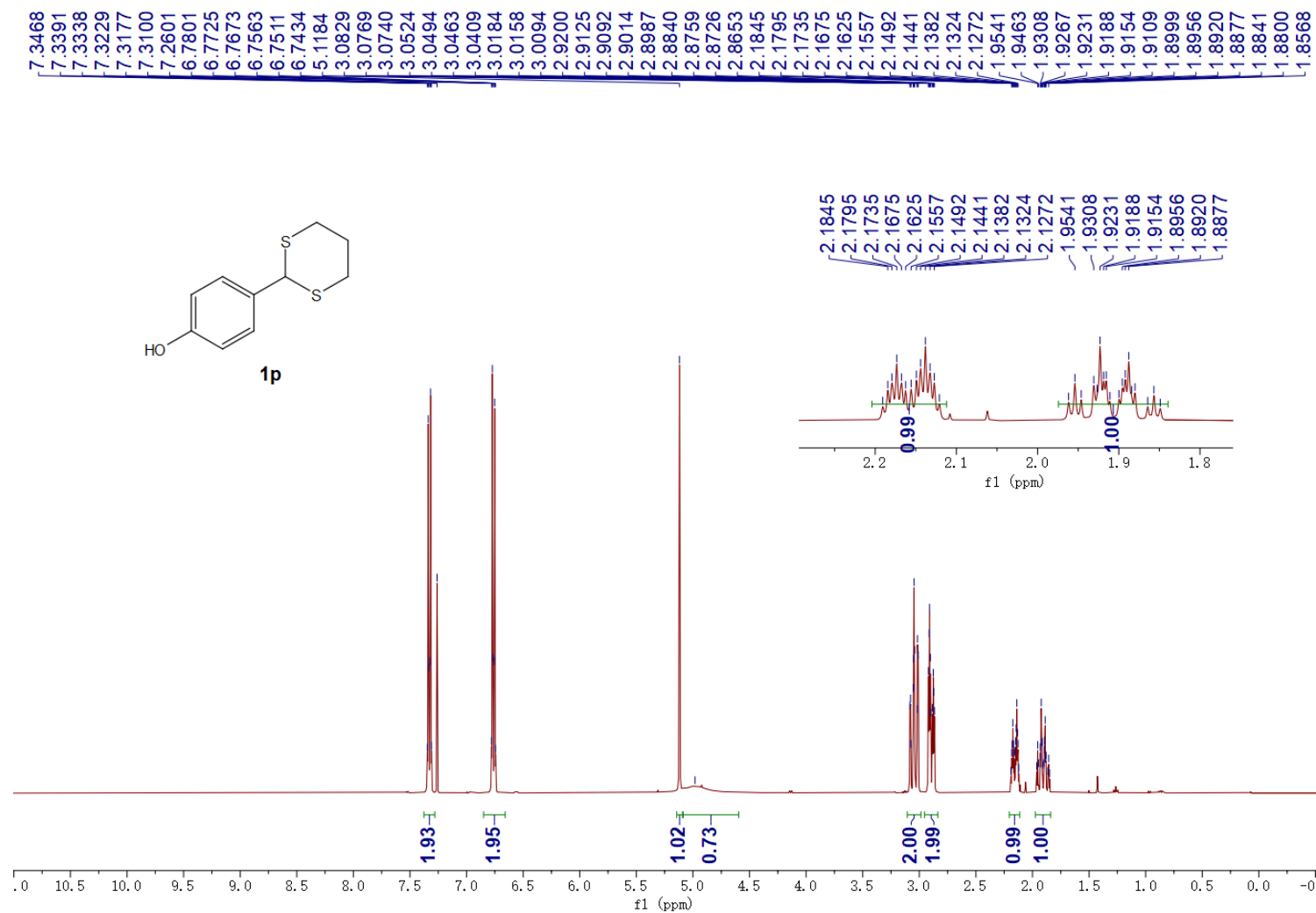
^{13}C -NMR Spectrum of 2-(1,3-Dithiolan-2-yl)furan (1m)

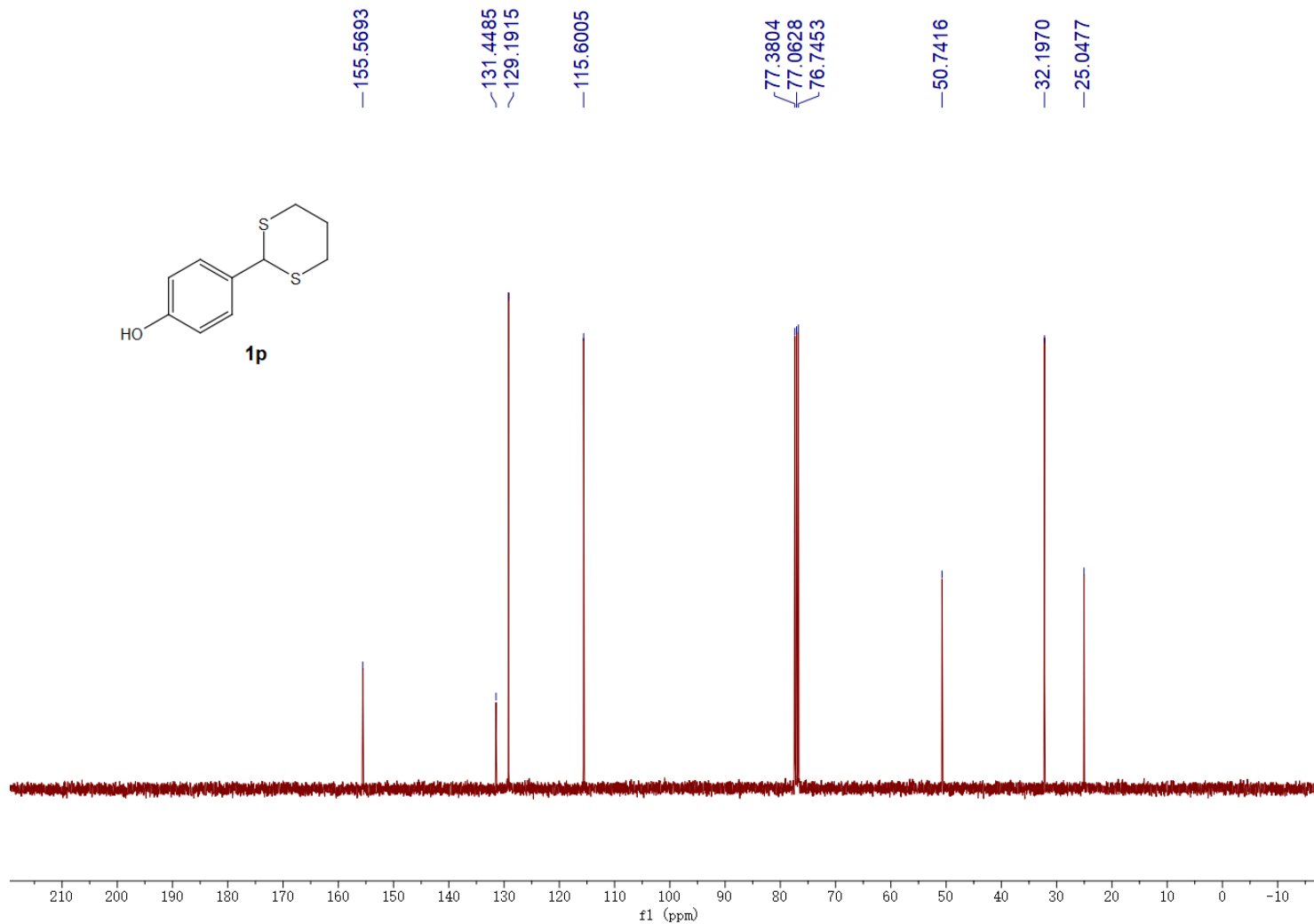
¹H-NMR Spectrum of 2-Hexyl-1,3-dithiolane (1n)

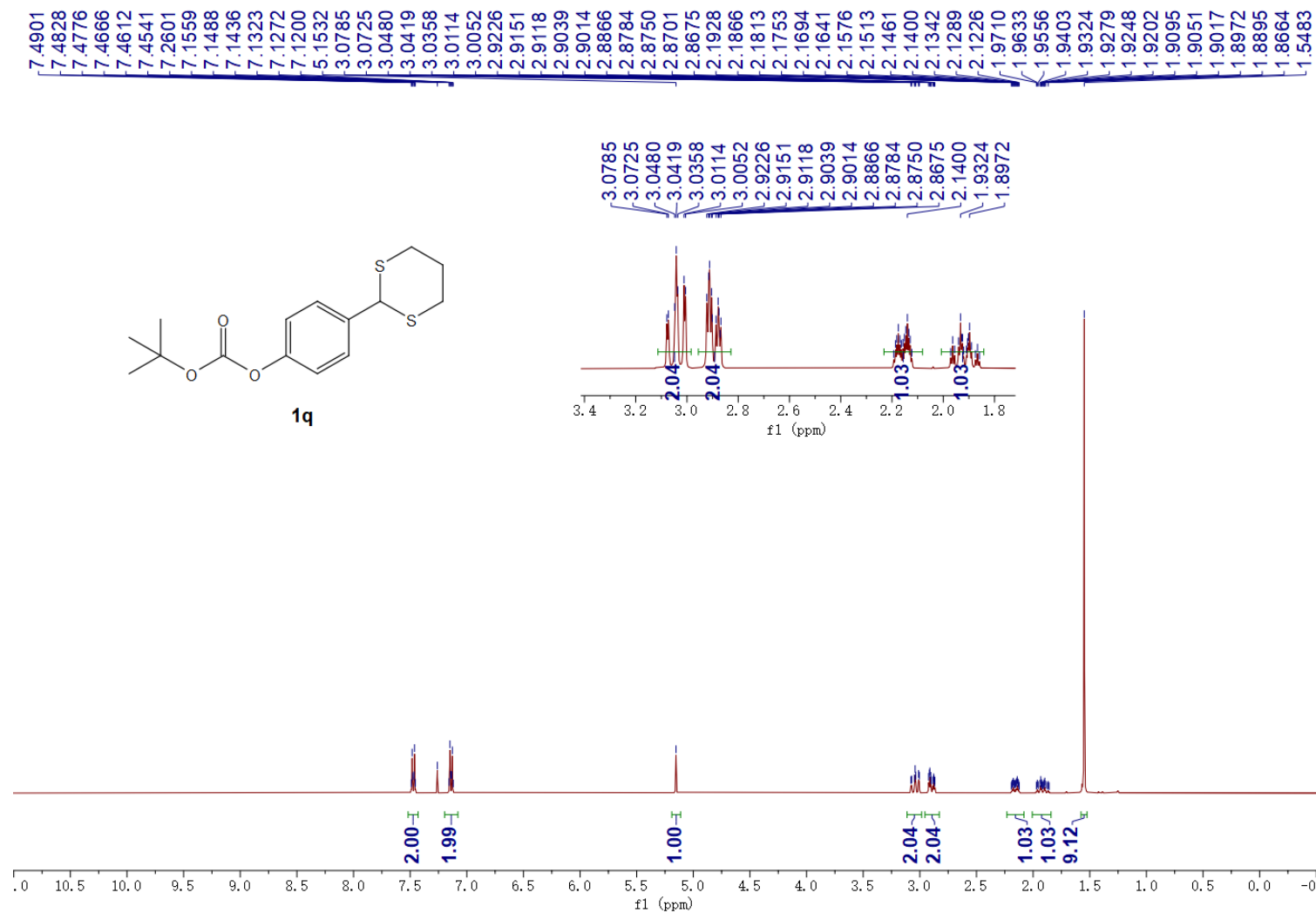
^{13}C -NMR Spectrum of 2-Hexyl-1,3-dithiolane (1n)

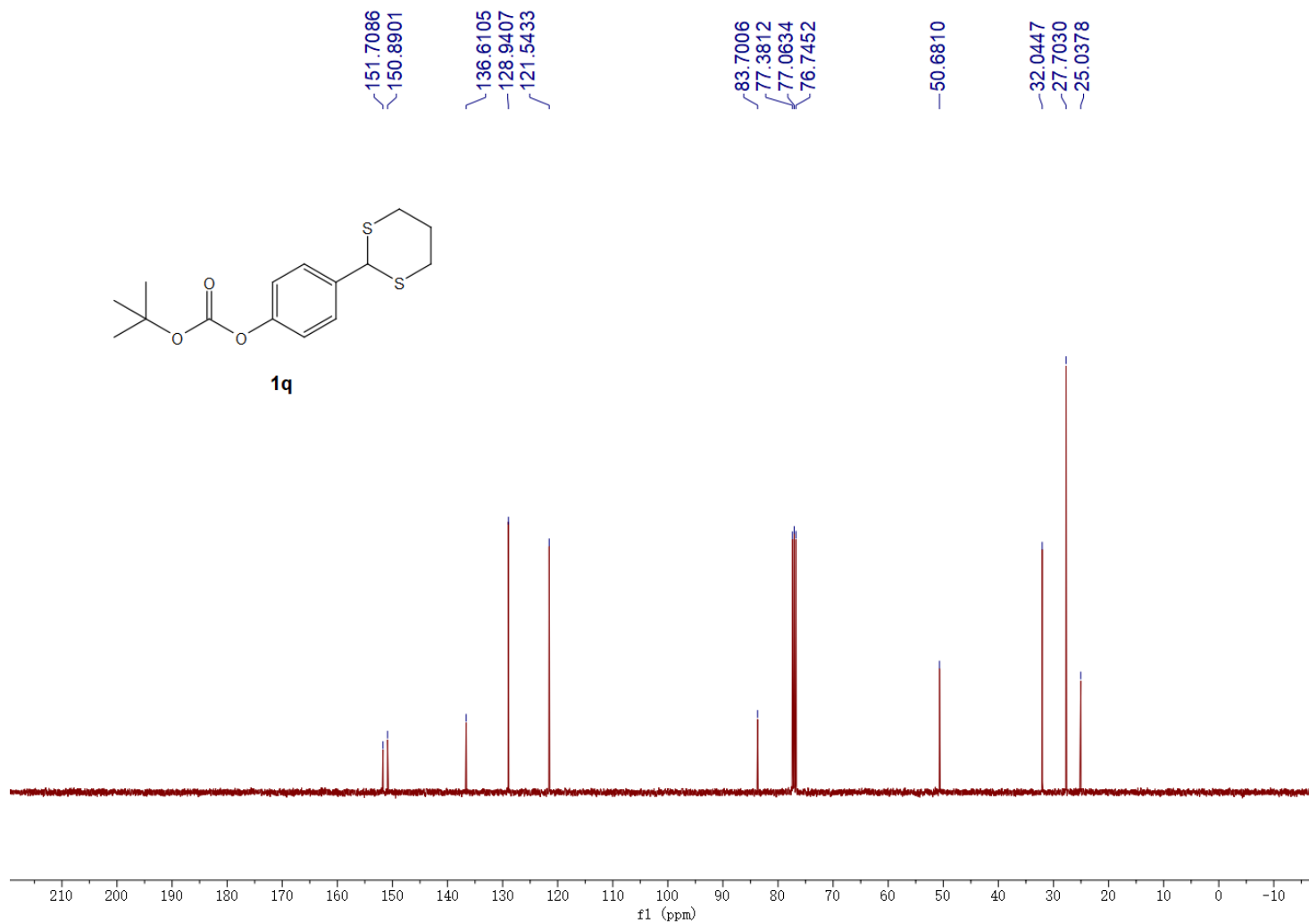
¹H-NMR Spectrum of 4-(1,3-Dithiolan-2-yl)-2-methoxyphenol (1o)

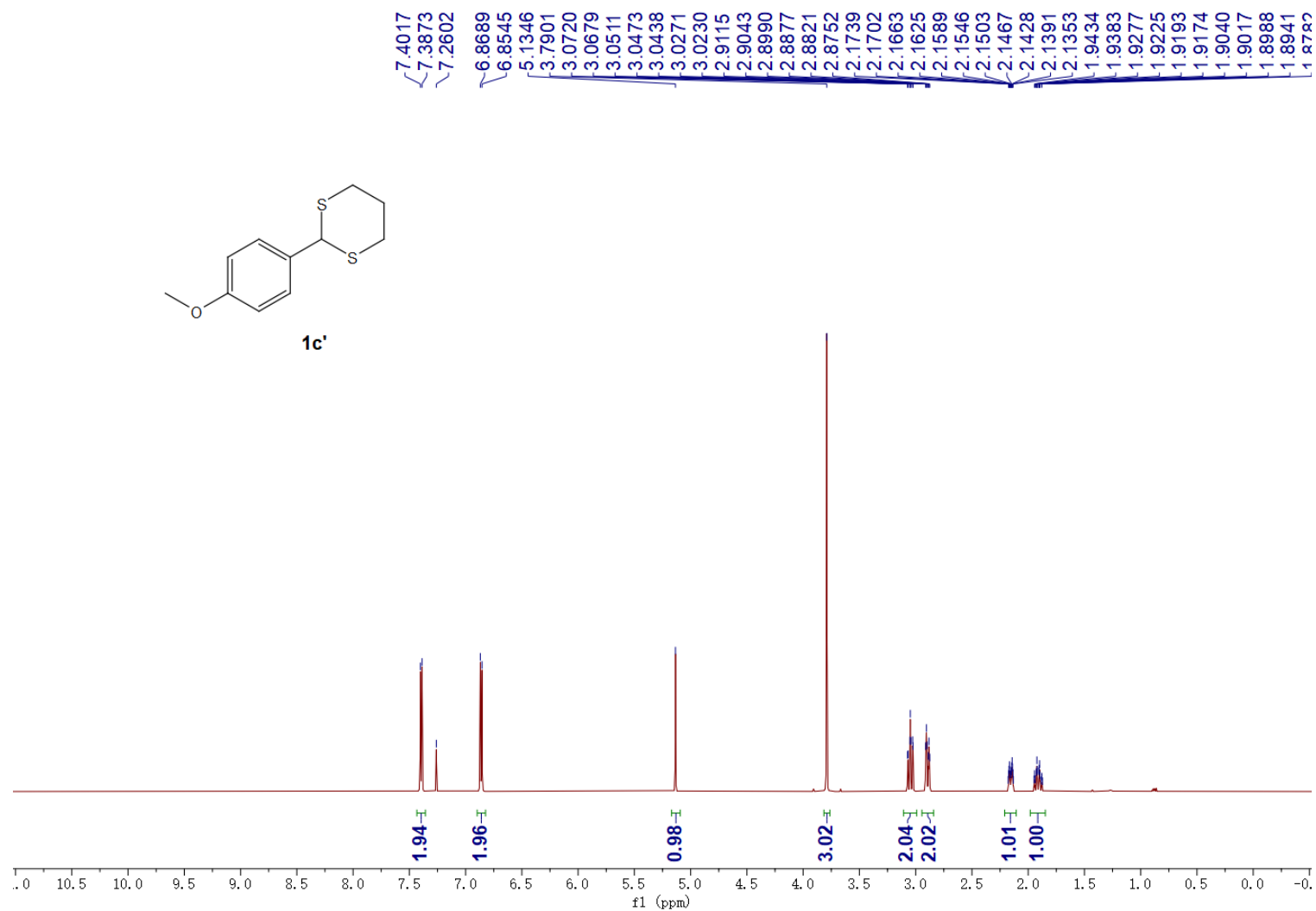
^{13}C -NMR Spectrum of 4-(1,3-Dithiolan-2-yl)-2-methoxyphenol (1o)

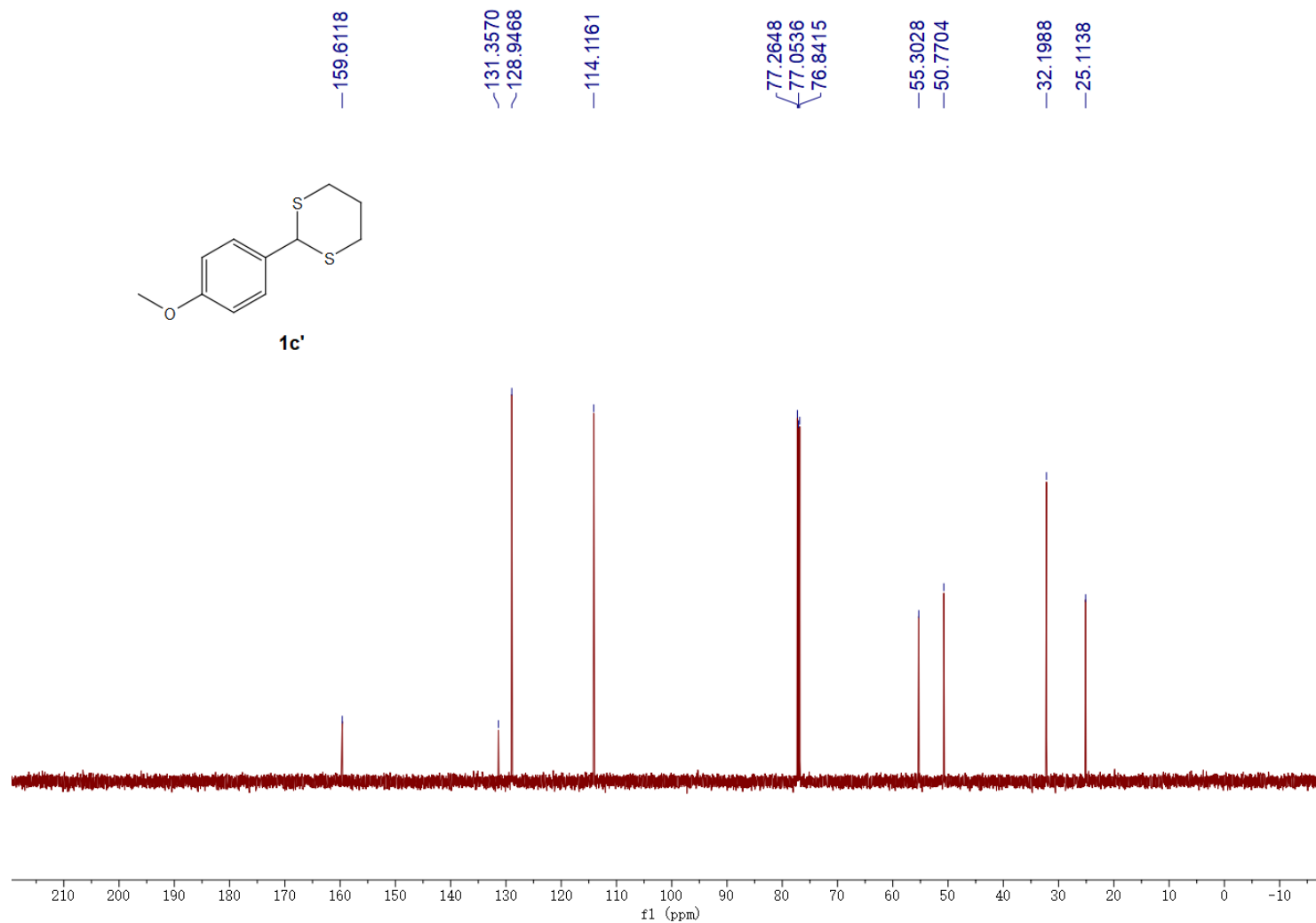
¹H-NMR Spectrum of 4-(1,3-Dithian-2-yl)phenol (1p)

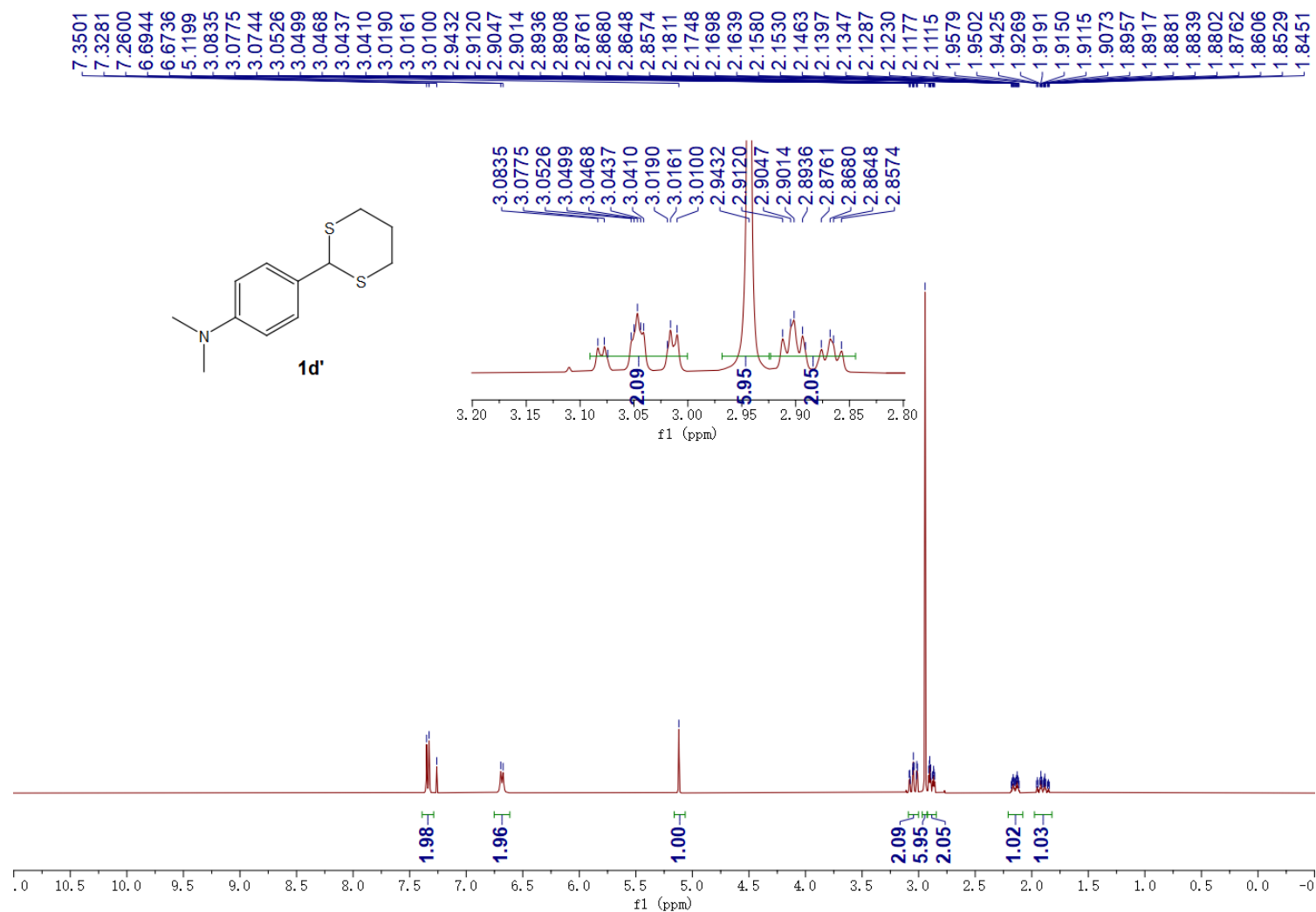
^{13}C -NMR Spectrum of 4-(1,3-Dithian-2-yl)phenol (1p)

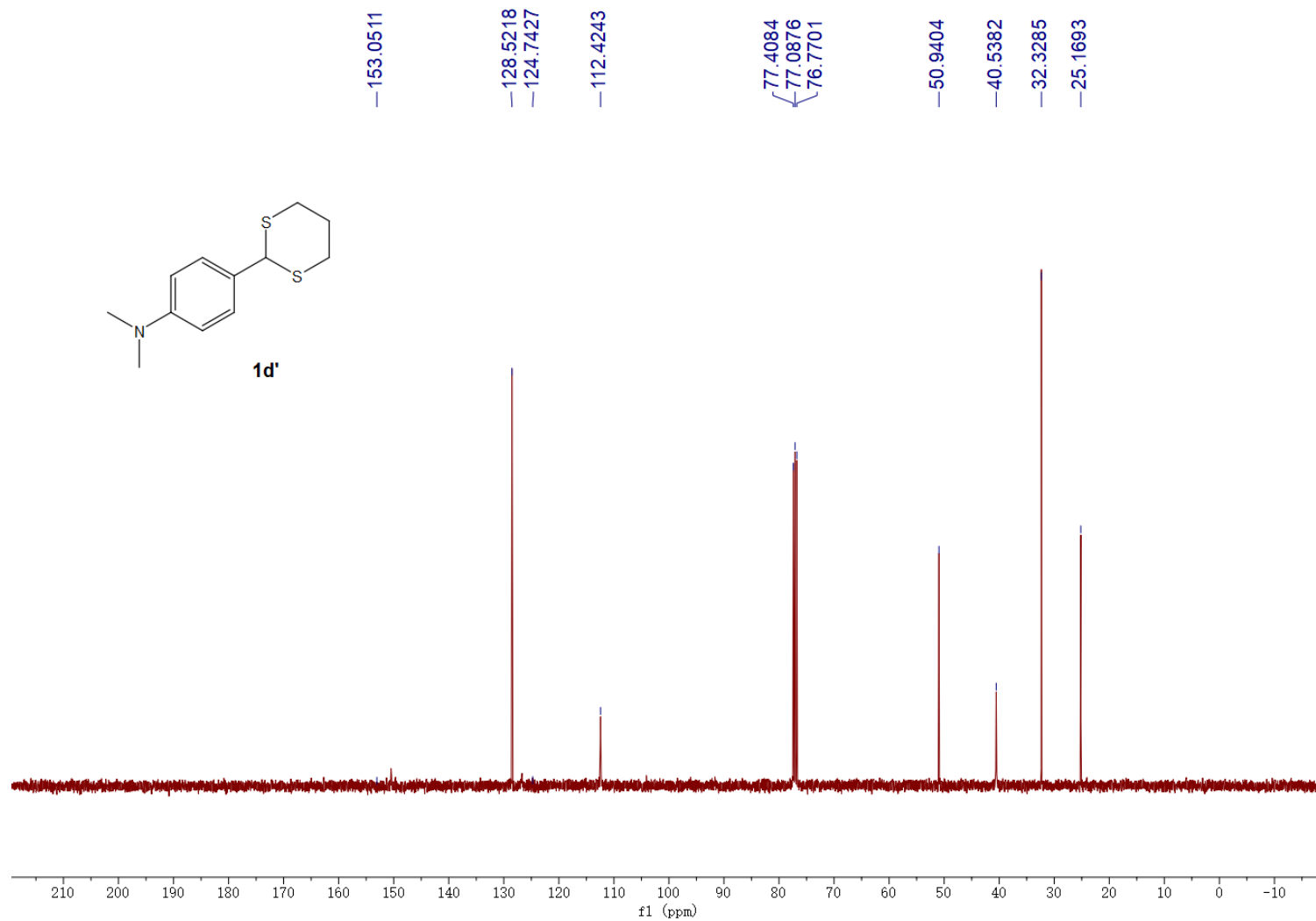
¹H-NMR Spectrum of 4-(1,3-Dithian-2-yl)phenyl *tert*-butyl carbonate (1q)

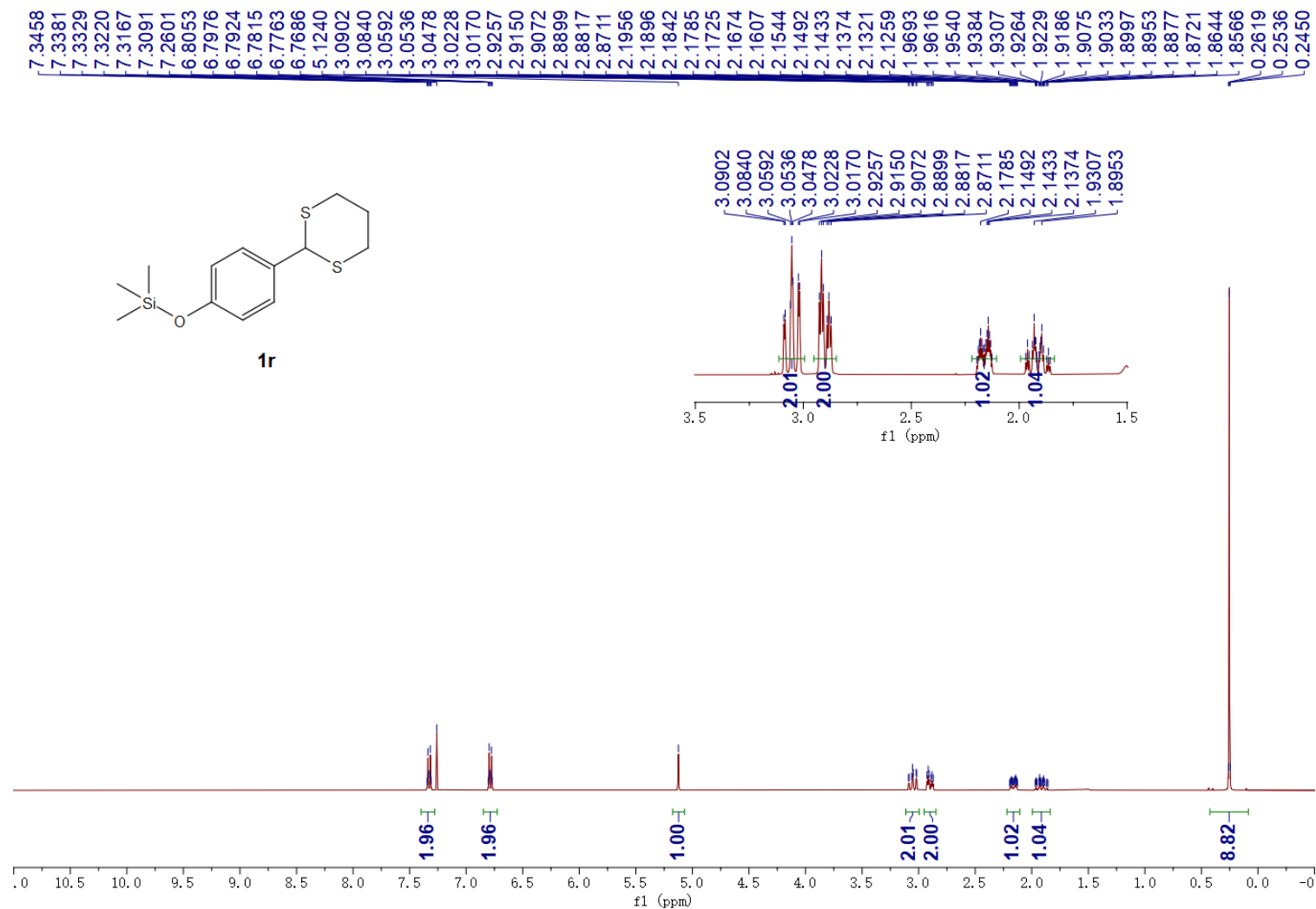
^{13}C -NMR Spectrum of 4-(1,3-Dithian-2-yl)phenyl *tert*-butyl carbonate (1q)

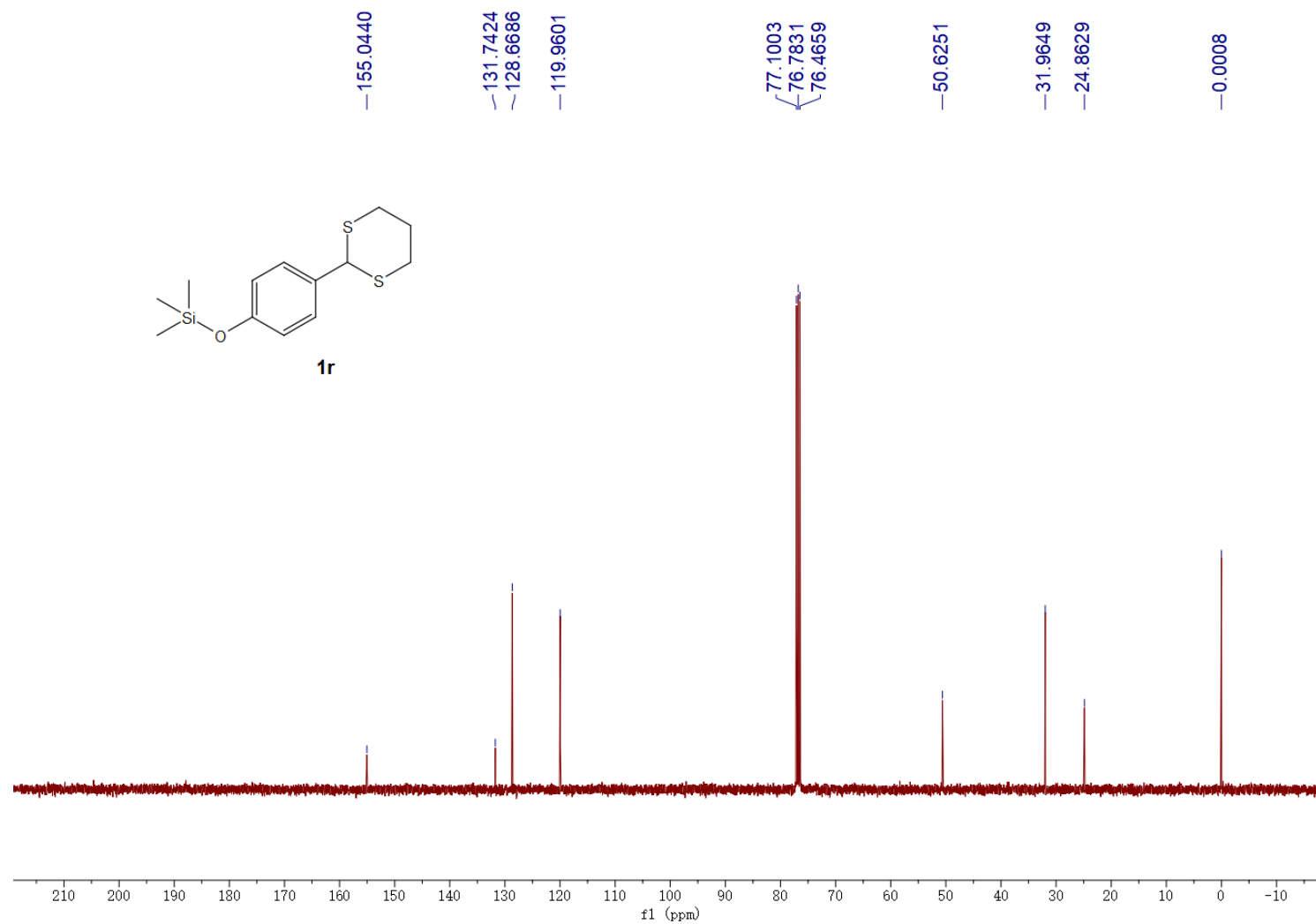
¹H-NMR Spectrum of 2-(4-Methoxyphenyl)-1,3-dithiane

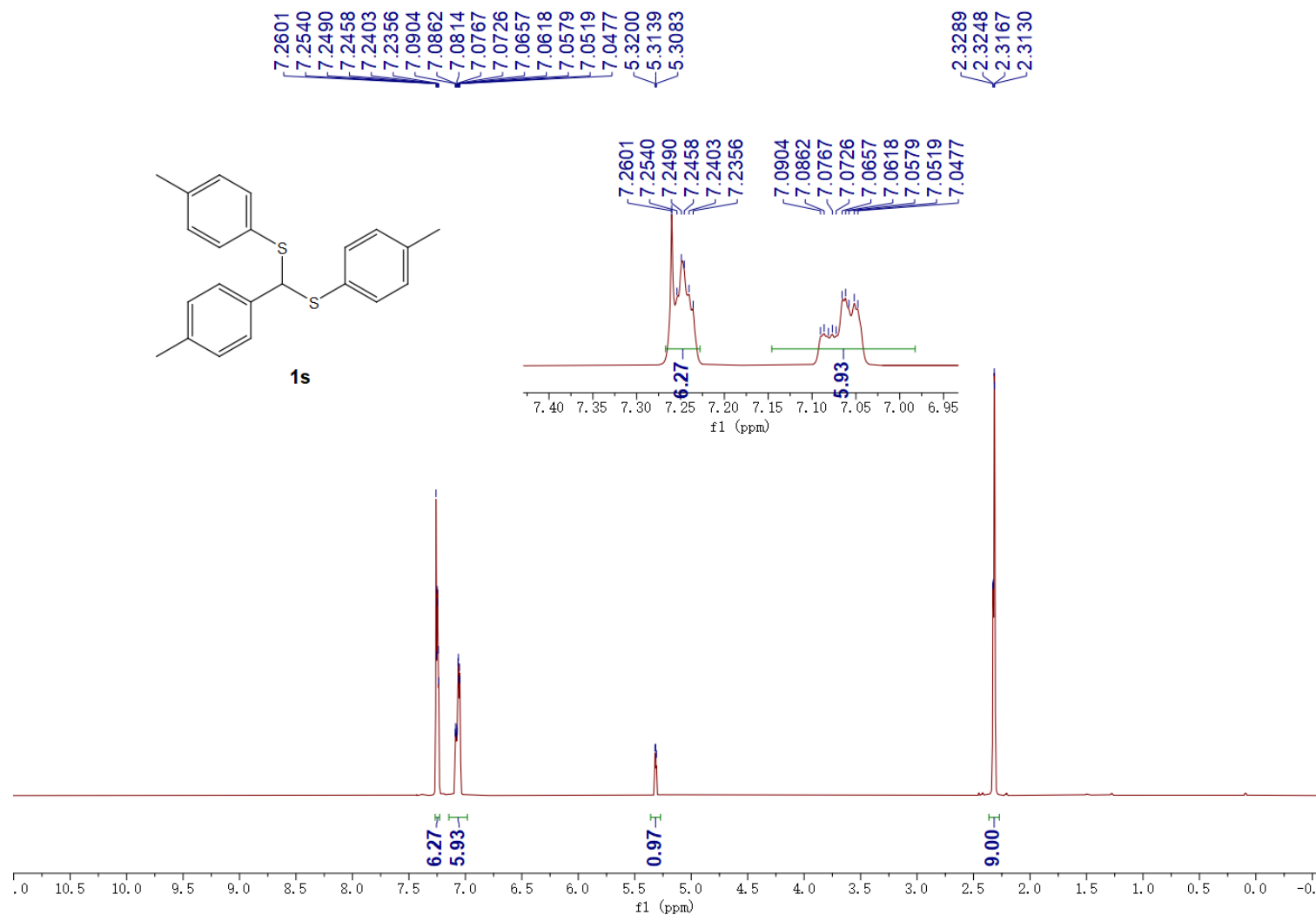
^{13}C -NMR Spectrum of 2-(4-Methoxyphenyl)-1,3-dithiane

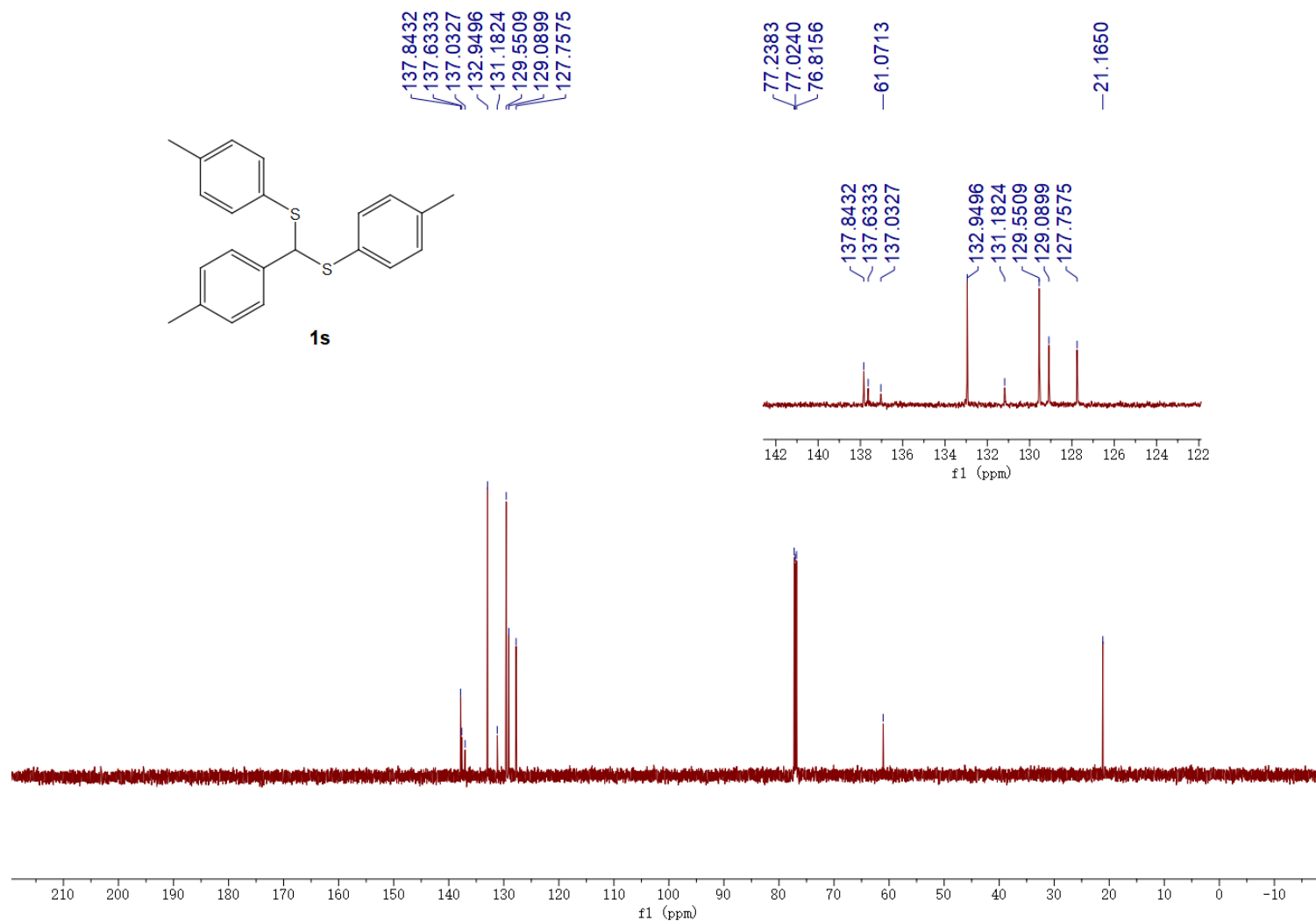
¹H-NMR Spectrum of 4-(1,3-Dithian-2-yl)-*N*, *N*-dimethylaniline (1d')

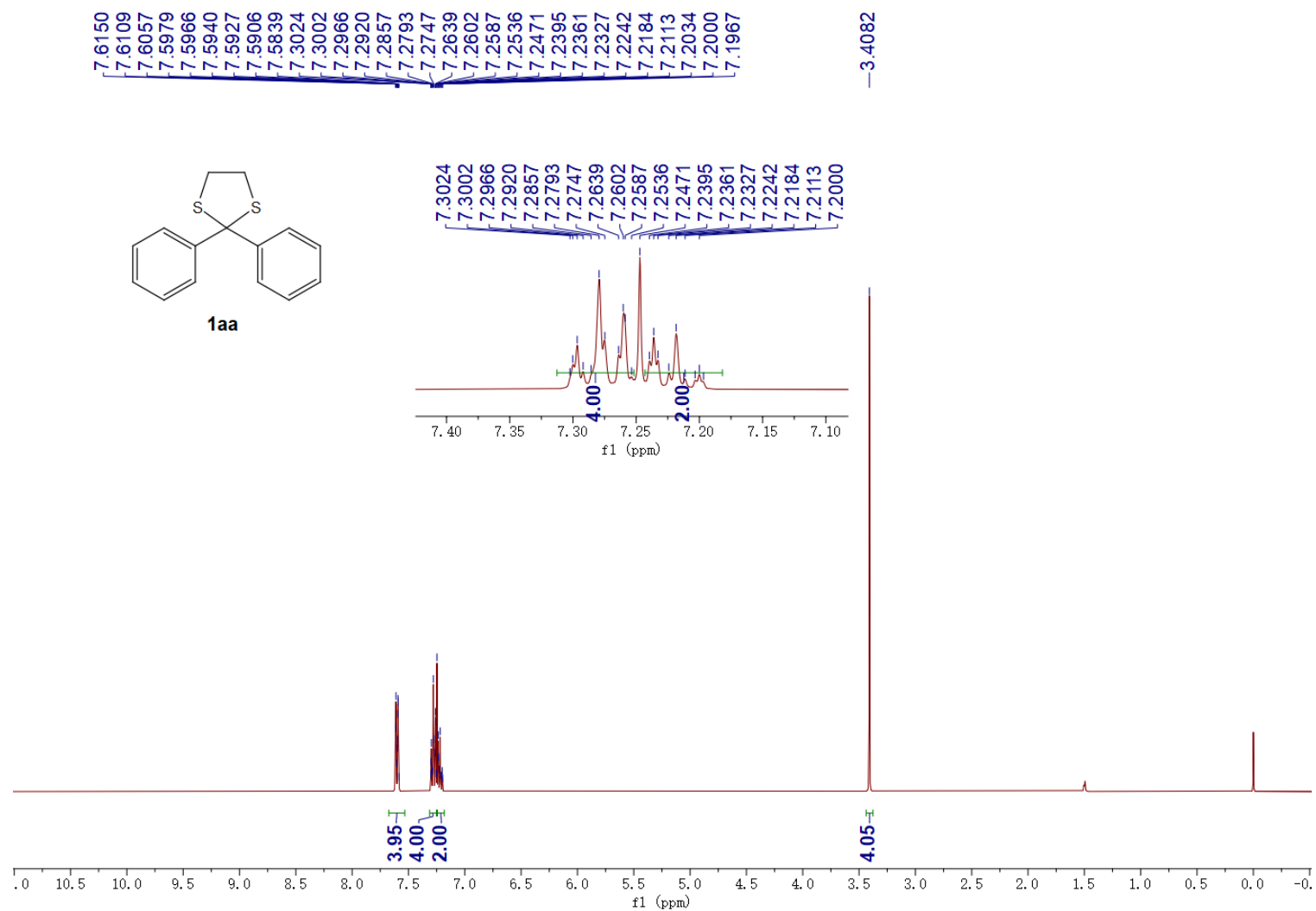
^{13}C -NMR Spectrum of 4-(1,3-Dithian-2-yl)-*N,N*-dimethylaniline (1d')

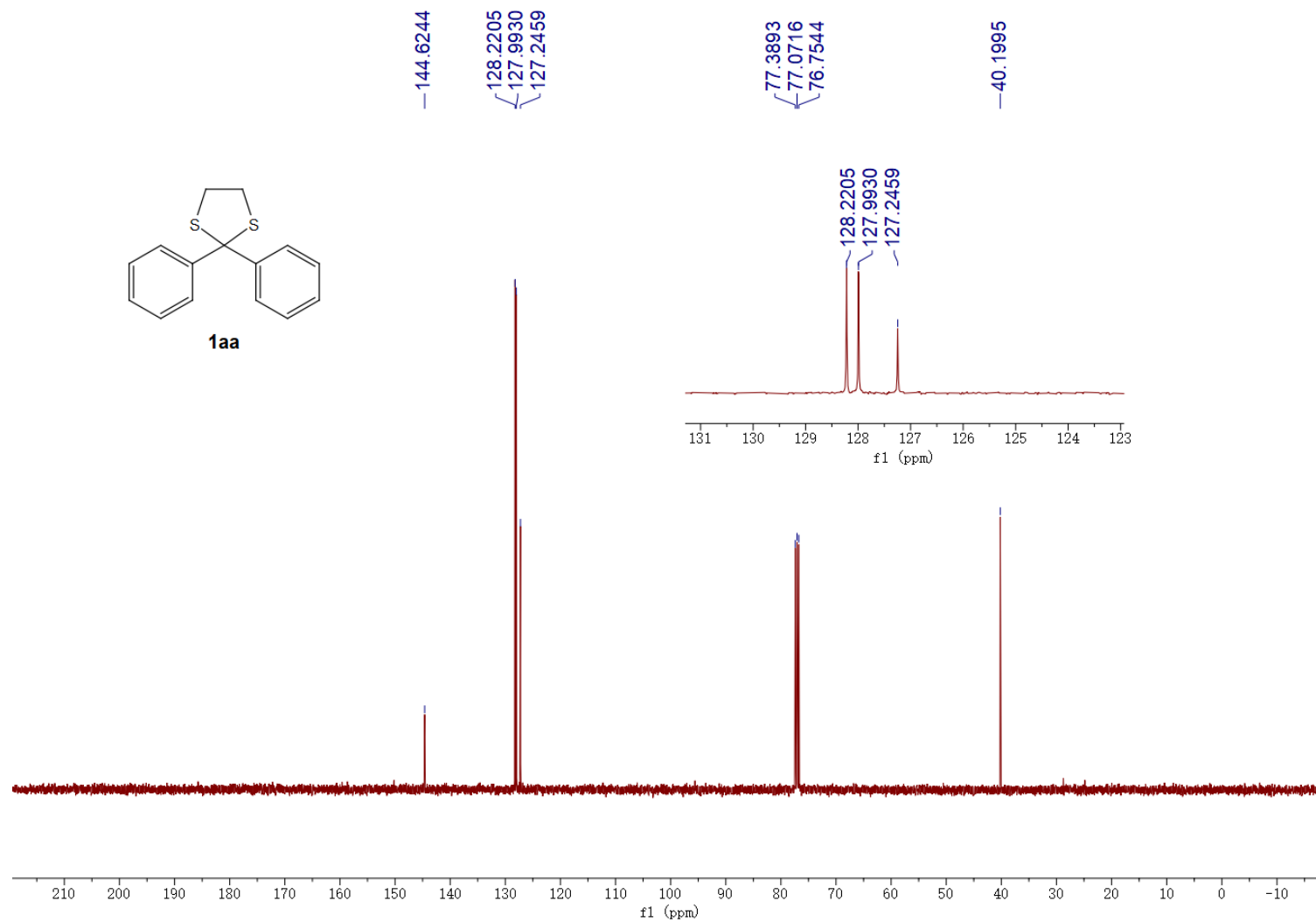
¹H-NMR Spectrum of (4-(1,3-dithian-2-yl)phenoxy)trimethylsilane (1r)

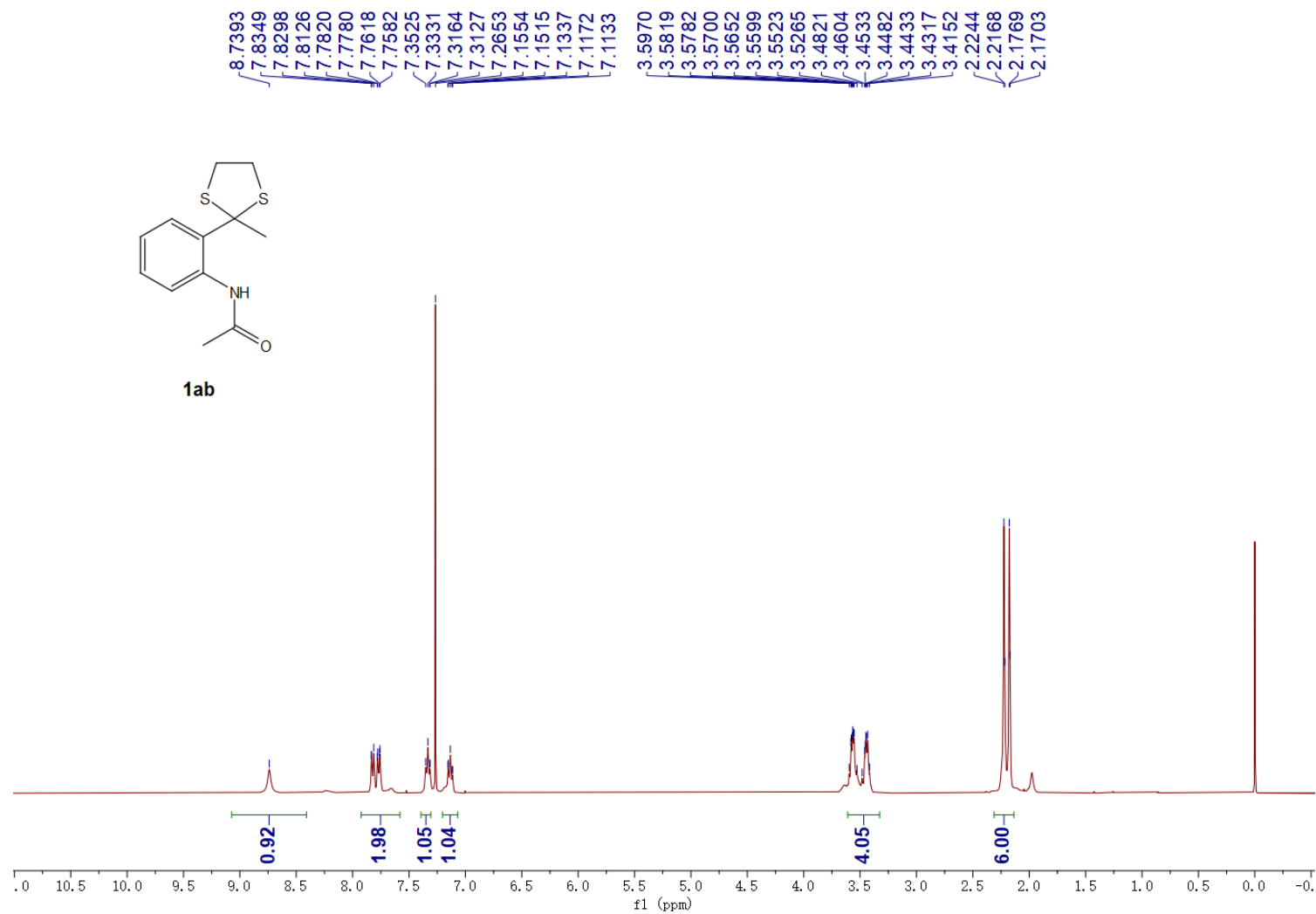
^{13}C -NMR Spectrum of (4-(1,3-dithian-2-yl)phenoxy)trimethylsilane (1r)

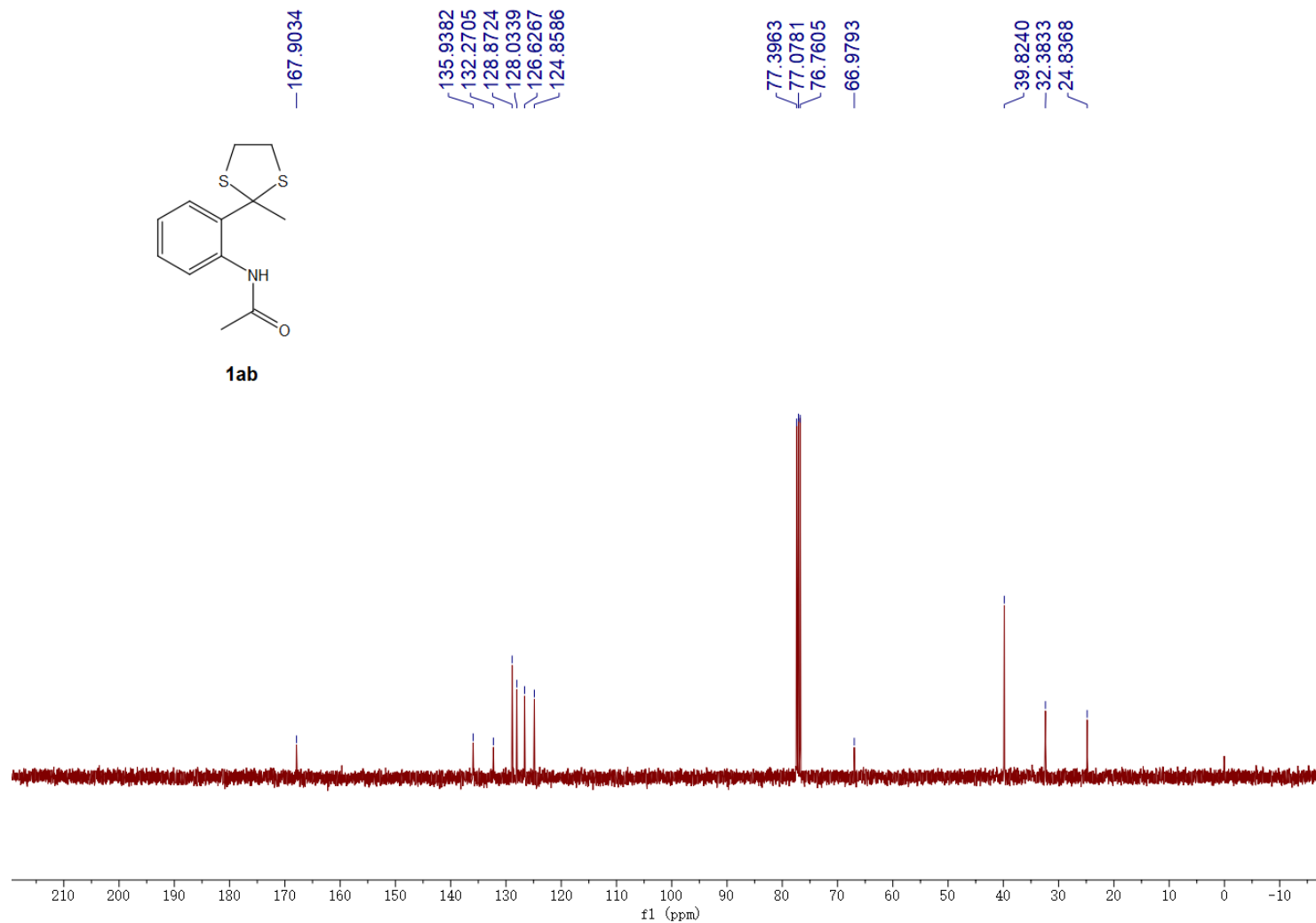
^1H -NMR Spectrum of (*p*-Tolylmethylene)bis(*p*-tolylsulfane) (1s**)**

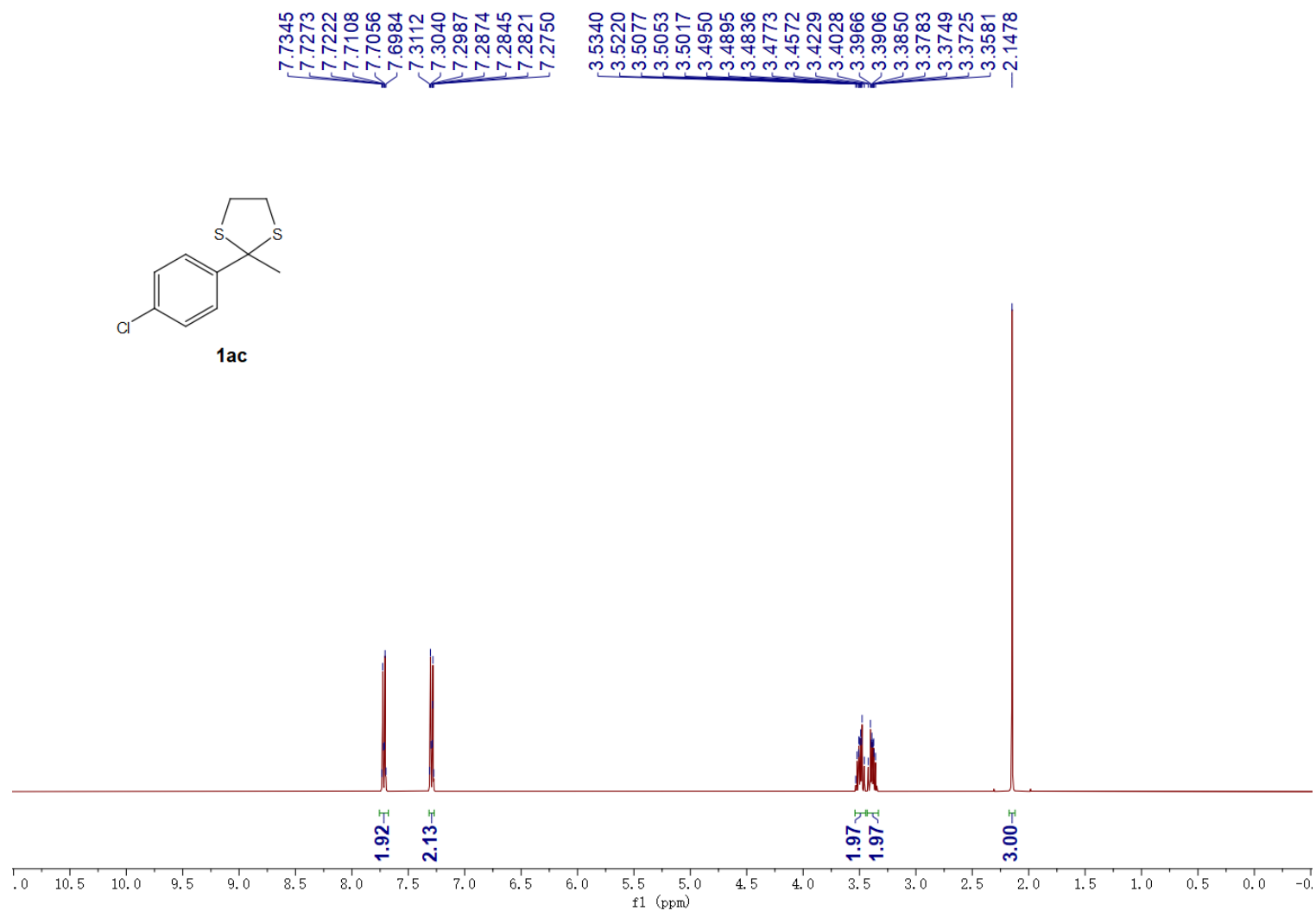
^{13}C -NMR Spectrum of (*p*-Tolylmethylene)bis(*p*-tolylsulfane) (1s**)**

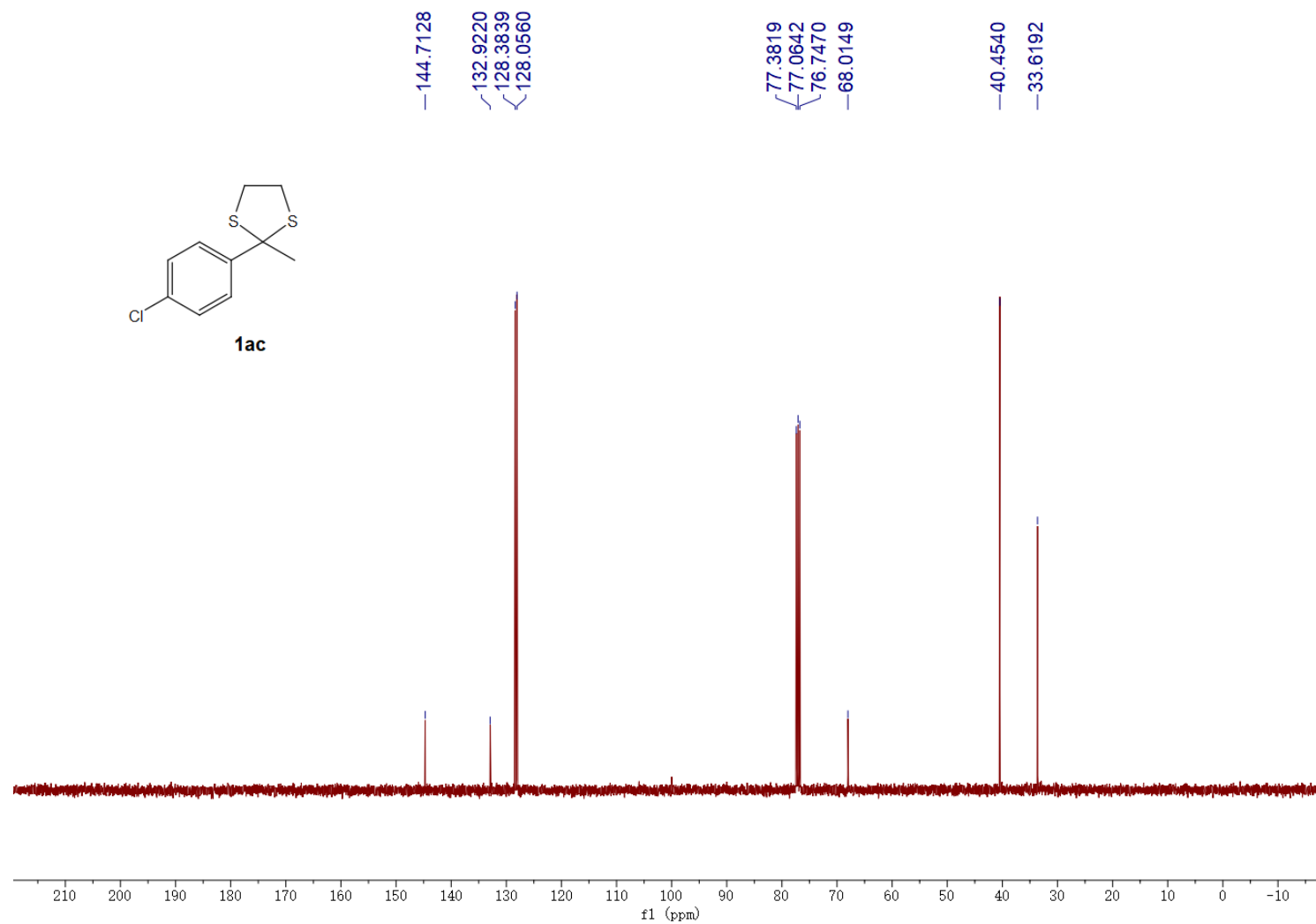
¹H-NMR Spectrum of 2,2-Diphenyl-1,3-dithiolane (1aa)

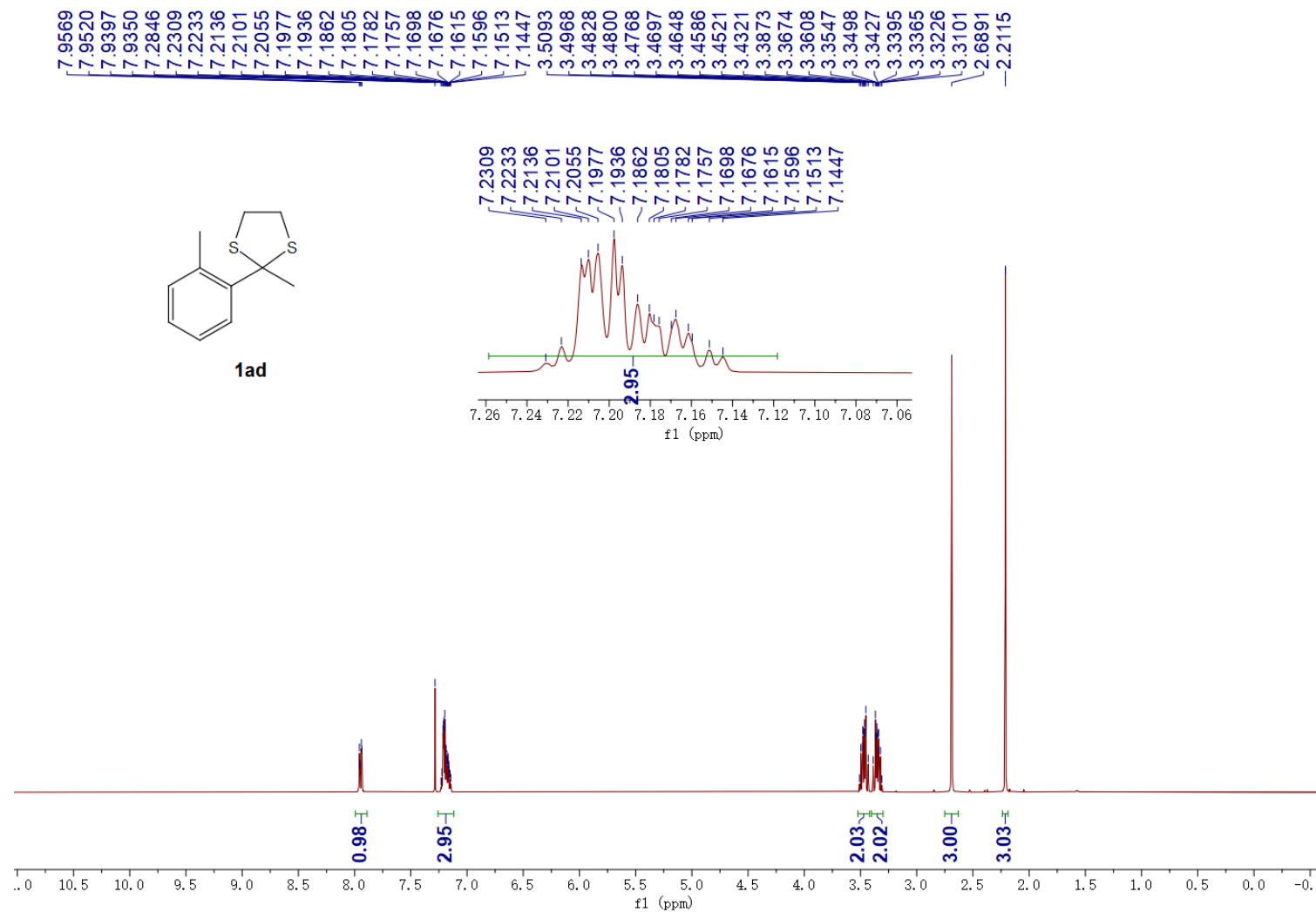
^{13}C -NMR Spectrum of 2,2-Diphenyl-1,3-dithiolane (1aa)

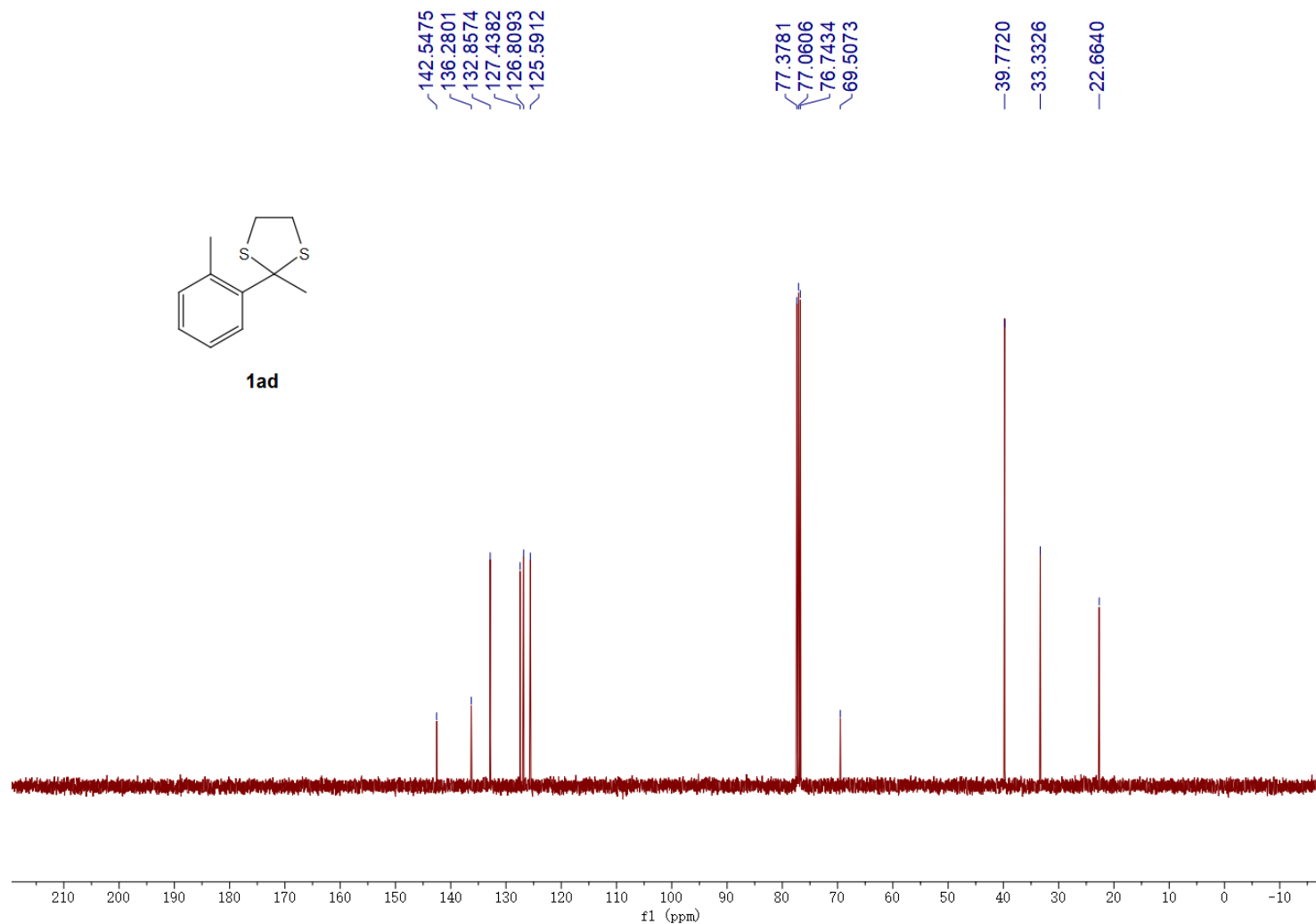
¹H-NMR Spectrum of *N*-(2-(2-Methyl-1,3-dithiolan-2-yl)phenyl)acetamide (1ab)

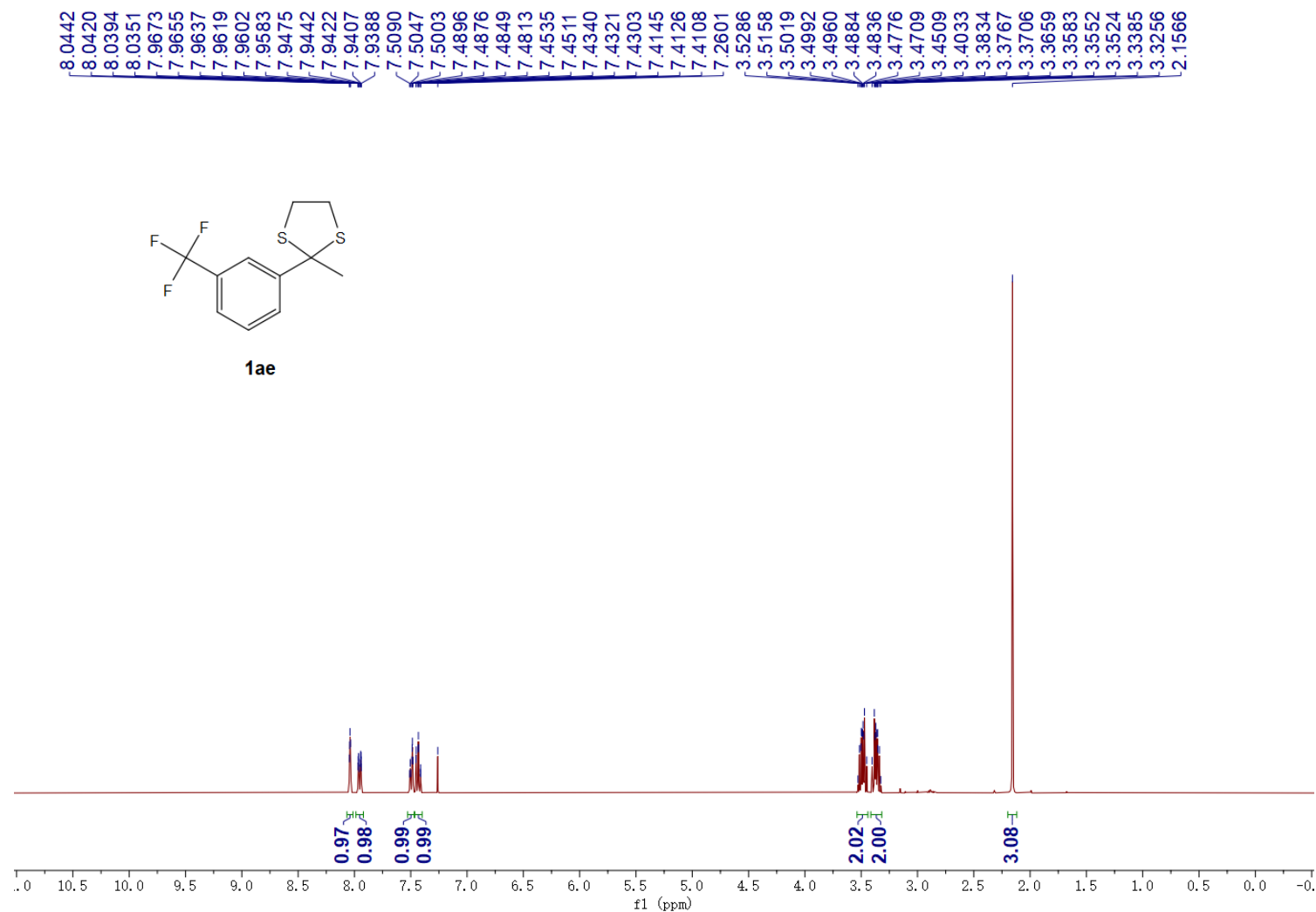
^{13}C -NMR Spectrum of *N*-(2-(2-Methyl-1,3-dithiolan-2-yl)phenyl)acetamide (1ab)

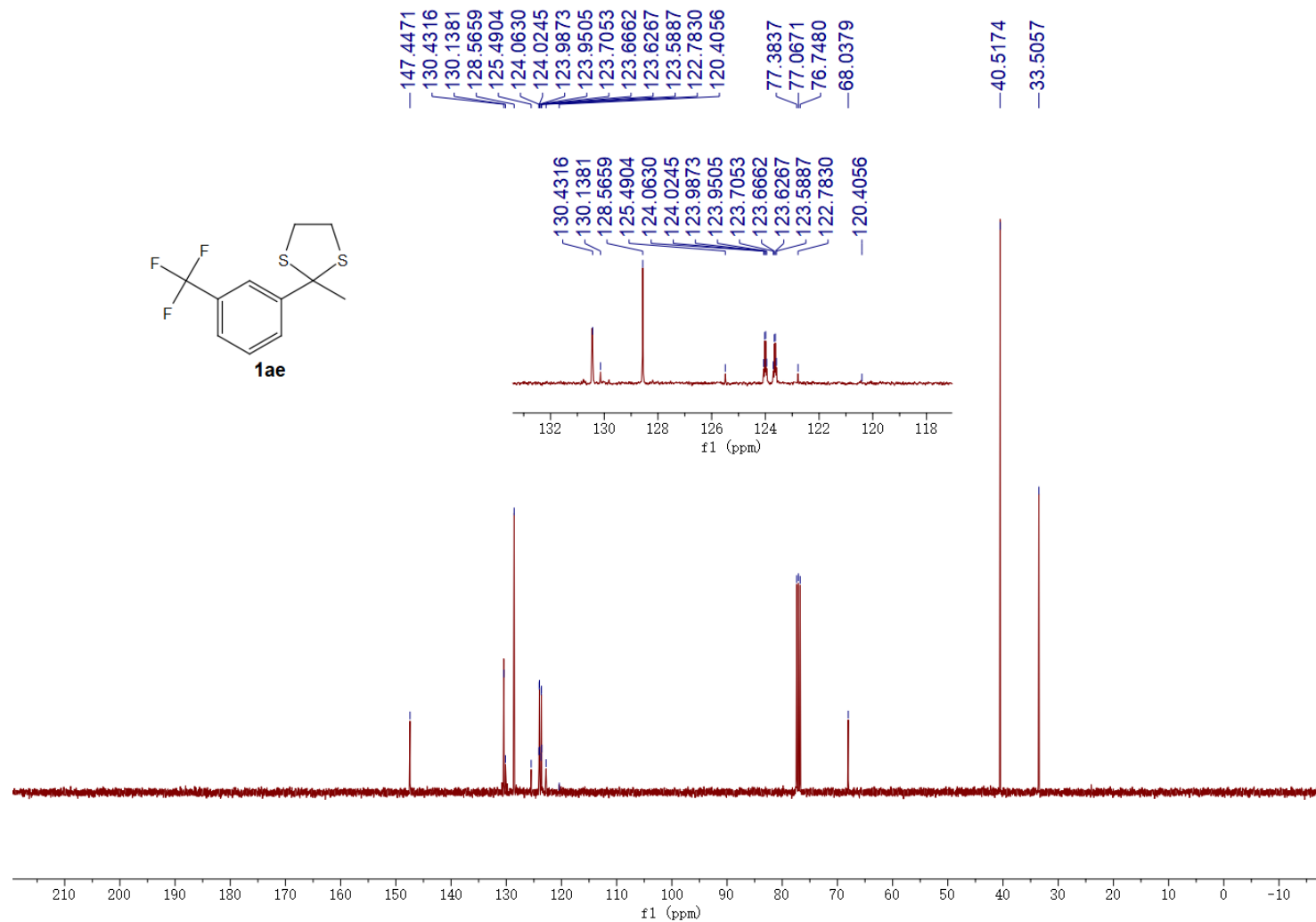
¹H-NMR Spectrum of 2-(4-Chlorophenyl)-2-methyl-1,3-dithiolane (1ac)

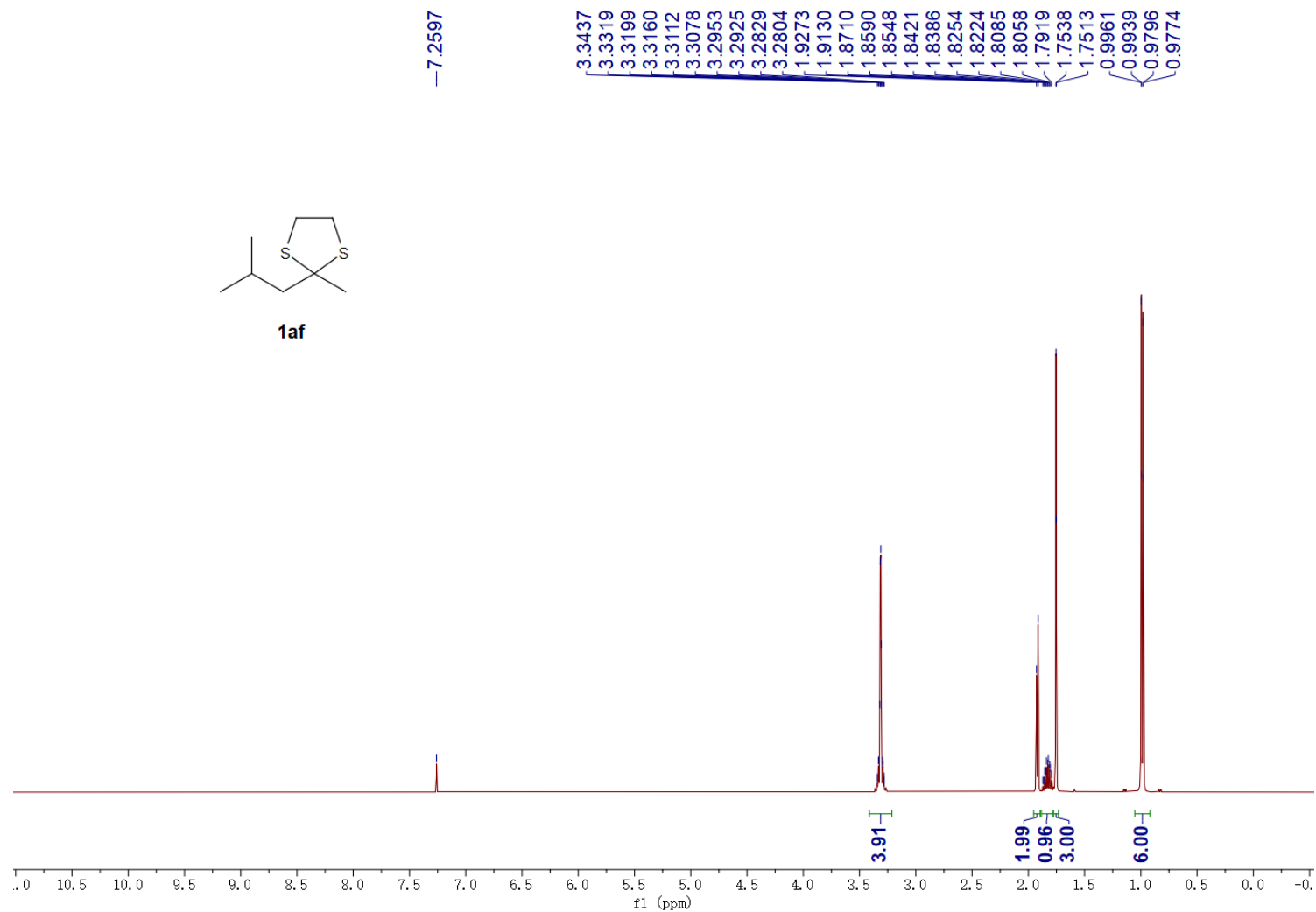
^{13}C -NMR Spectrum of 2-(4-Chlorophenyl)-2-methyl-1,3-dithiolane (1ac)

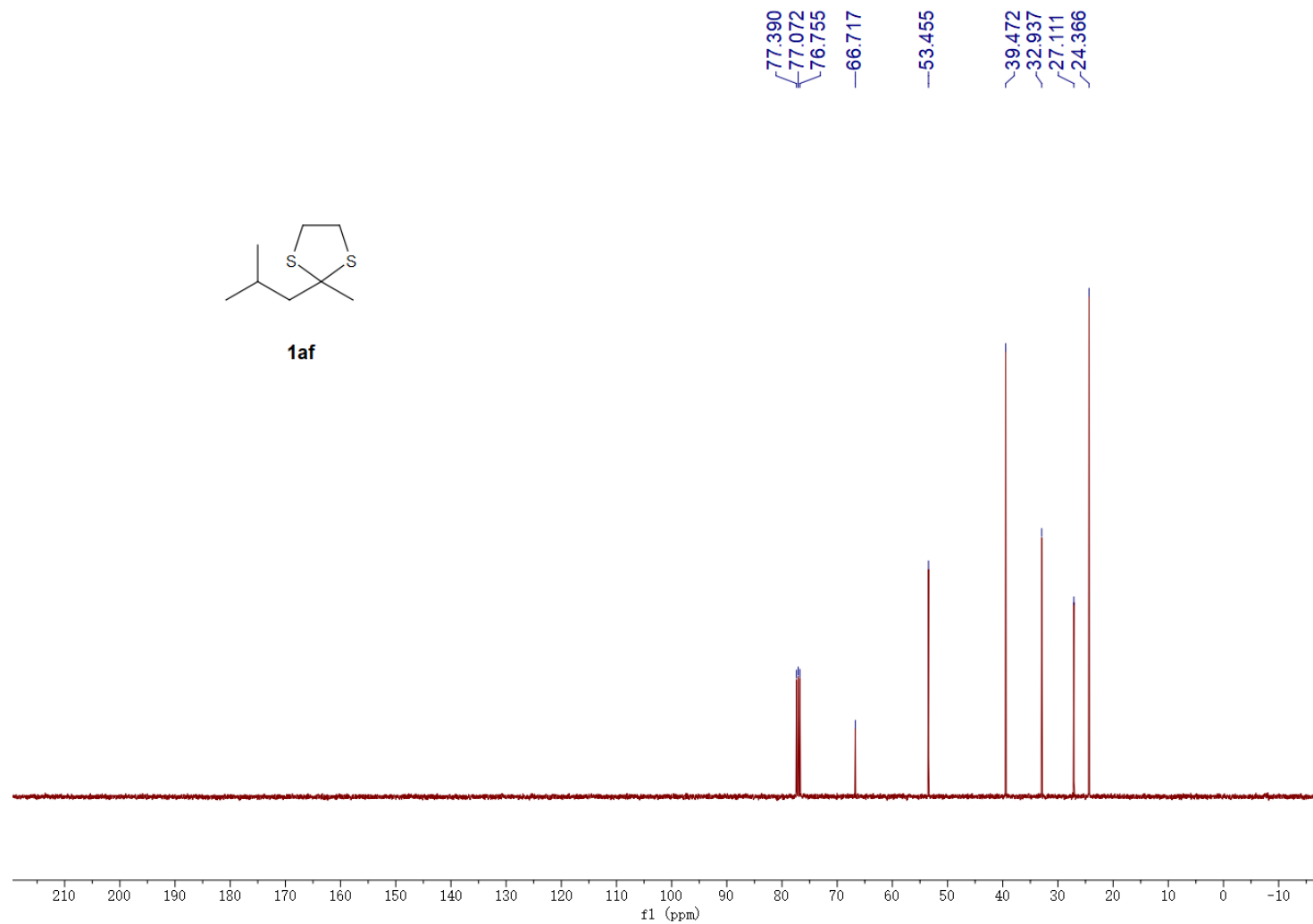
¹H-NMR Spectrum of 2-Methyl-2-(o-tolyl)-1,3-dithiolane (1ad)

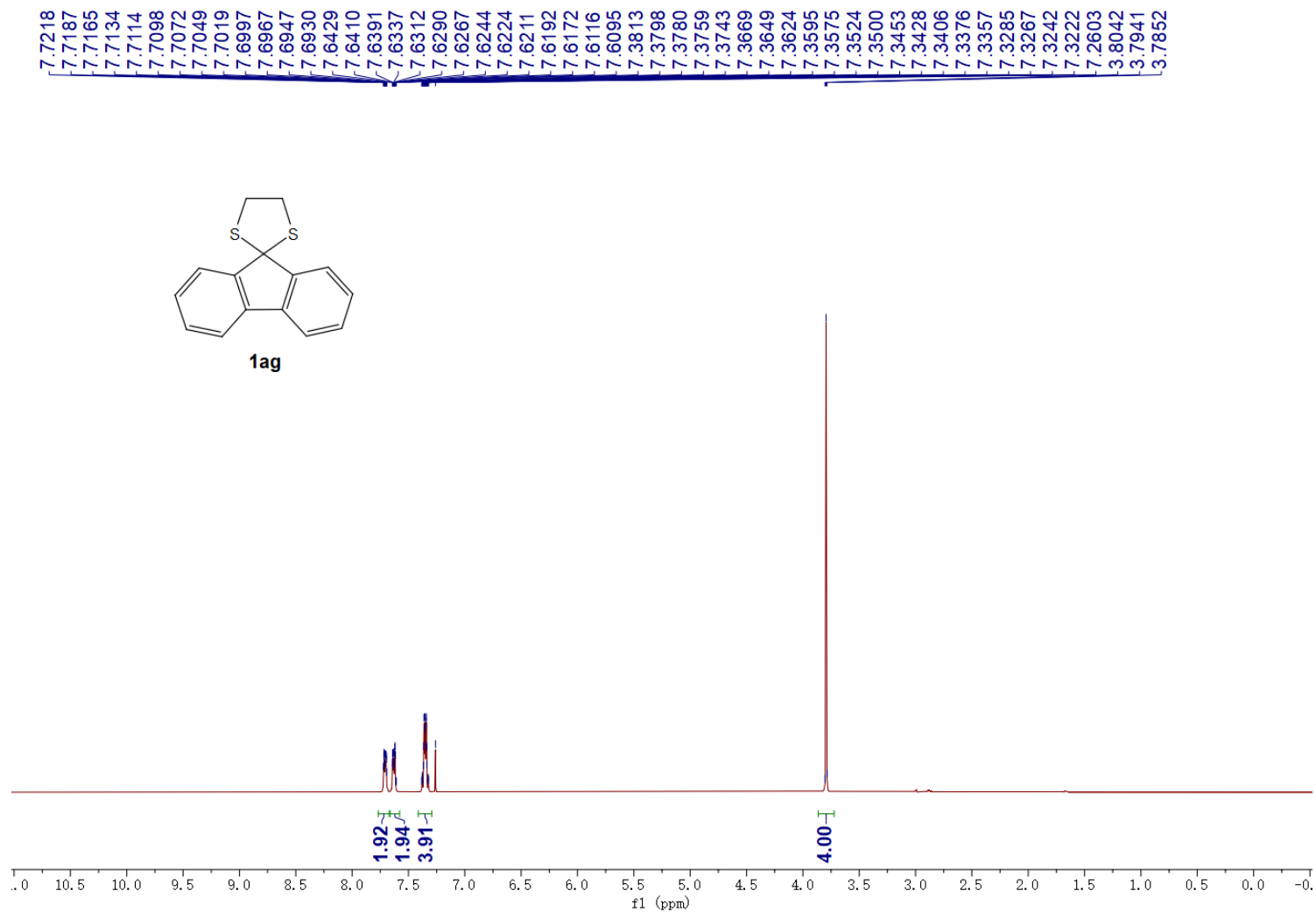
^{13}C -NMR Spectrum of 2-Methyl-2-(o-tolyl)-1,3-dithiolane (1ad)

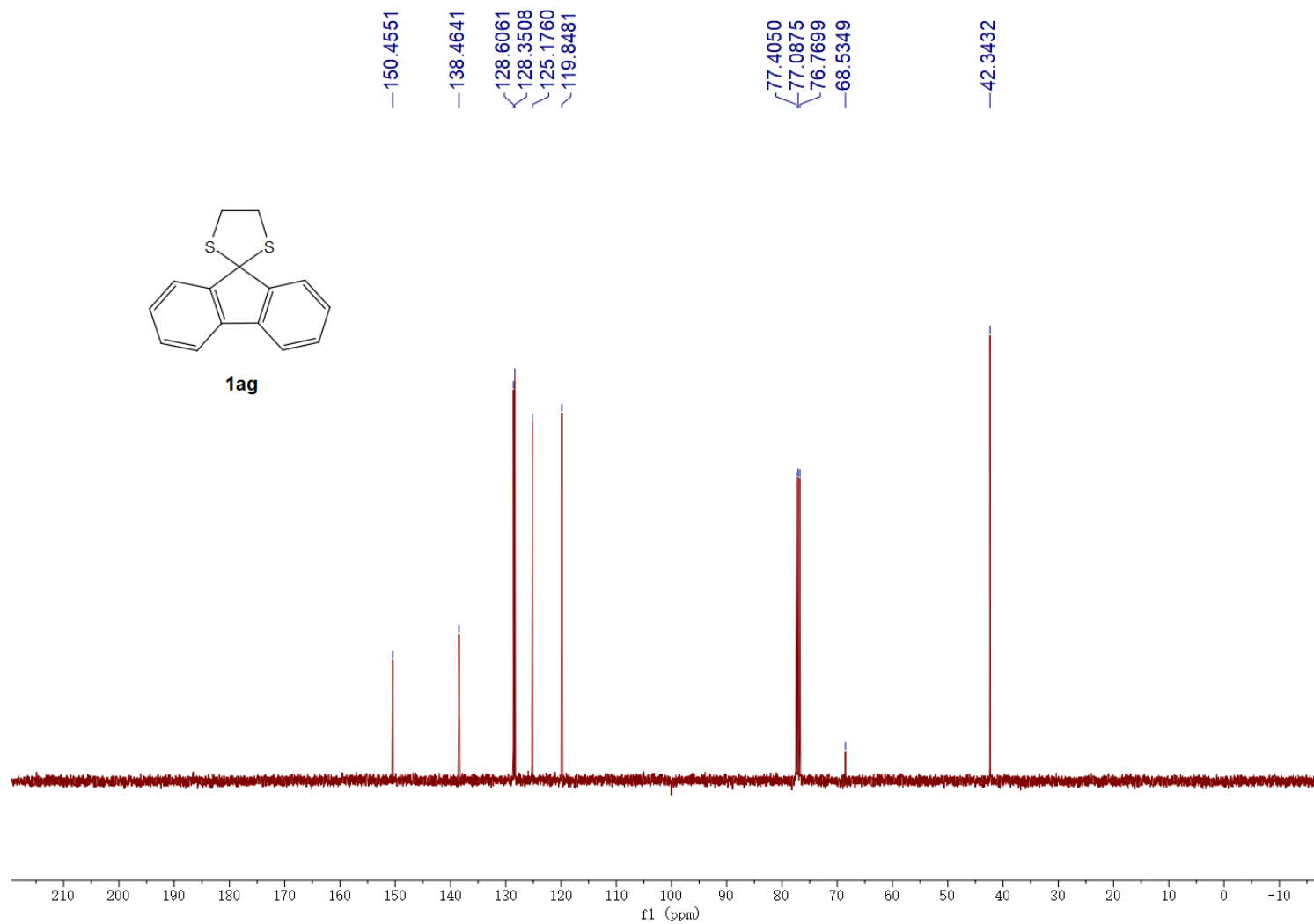
¹H-NMR Spectrum of 2-Methyl-2-(3-(trifluoromethyl)phenyl)-1,3-dithiolane (1ae)

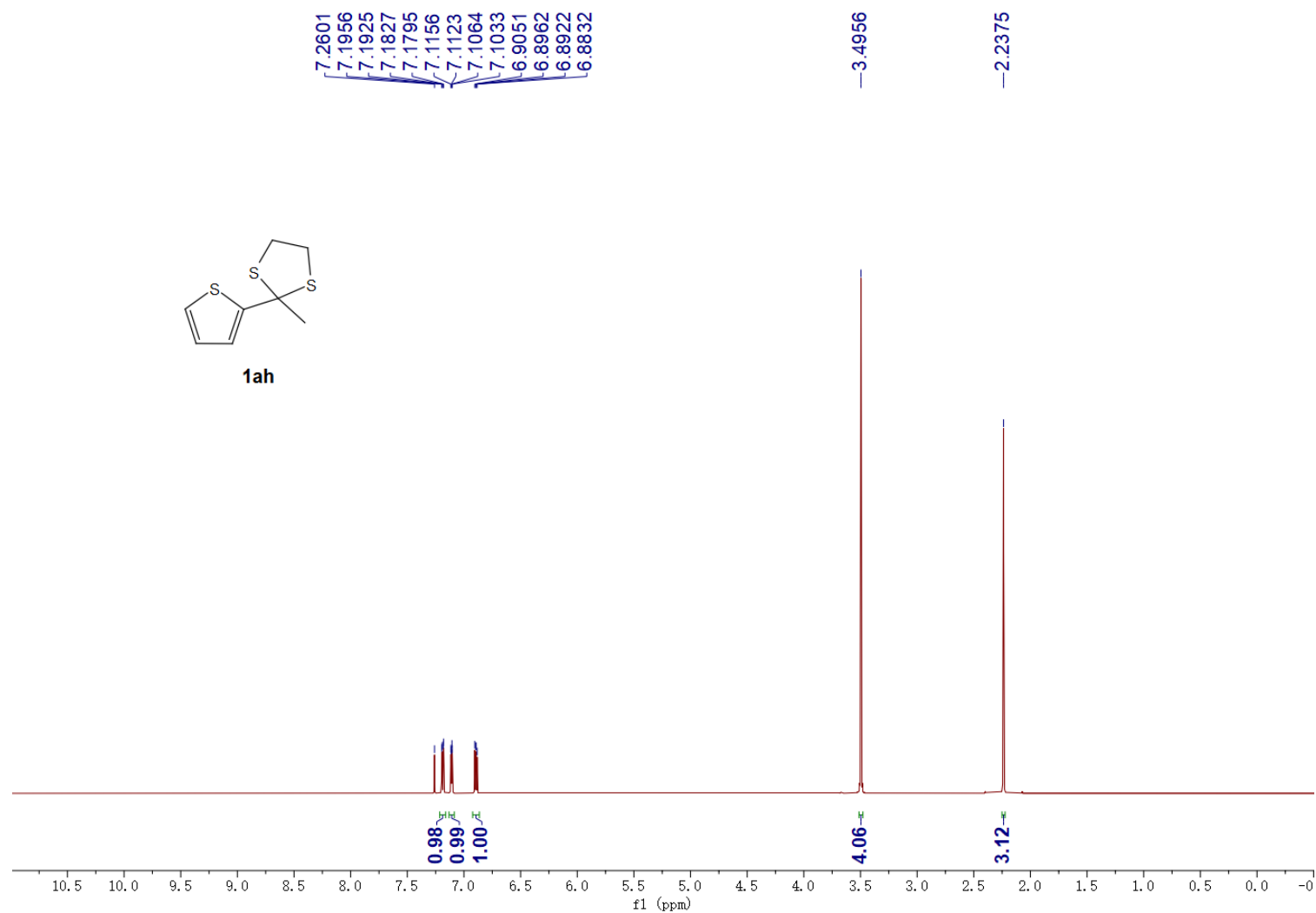
^{13}C -NMR Spectrum of 2-Methyl-2-(3-(trifluoromethyl)phenyl)-1,3-dithiolane (1ae)

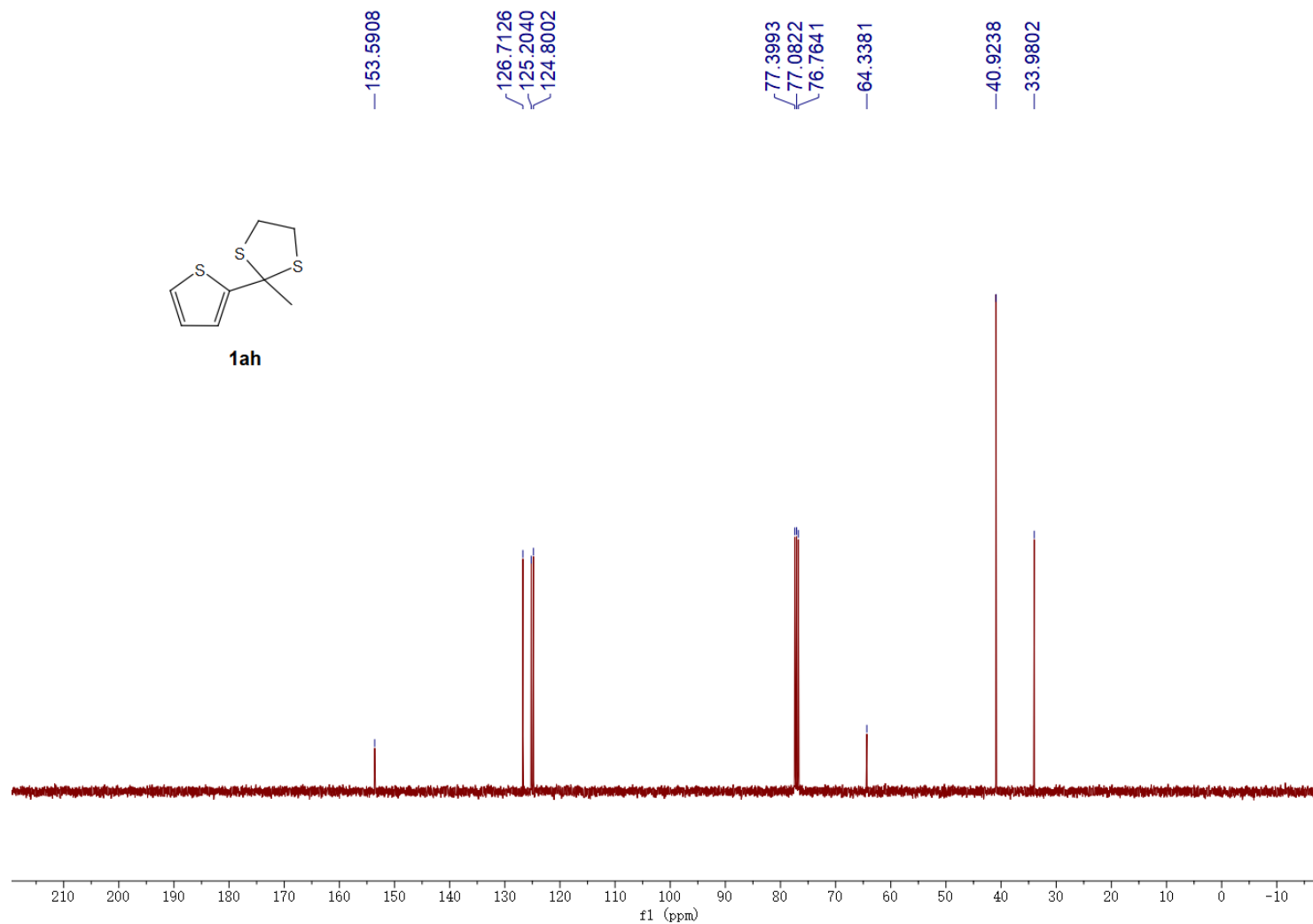
¹H-NMR Spectrum of 2-Isobutyl-2-methyl-1,3-dithiolane (1af)

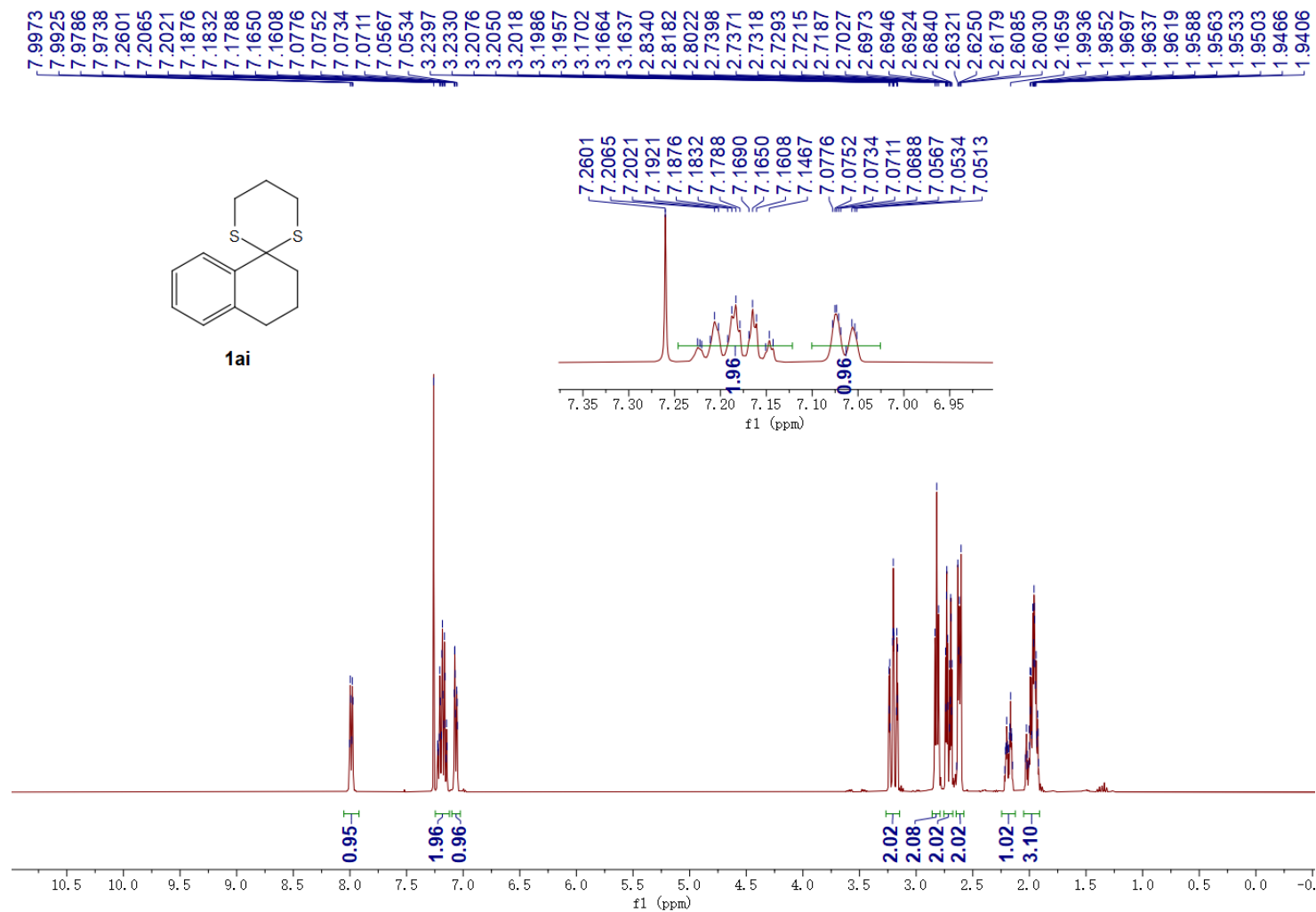
^{13}C -NMR Spectrum of 2-Isobutyl-2-methyl-1,3-dithiolane (1af)

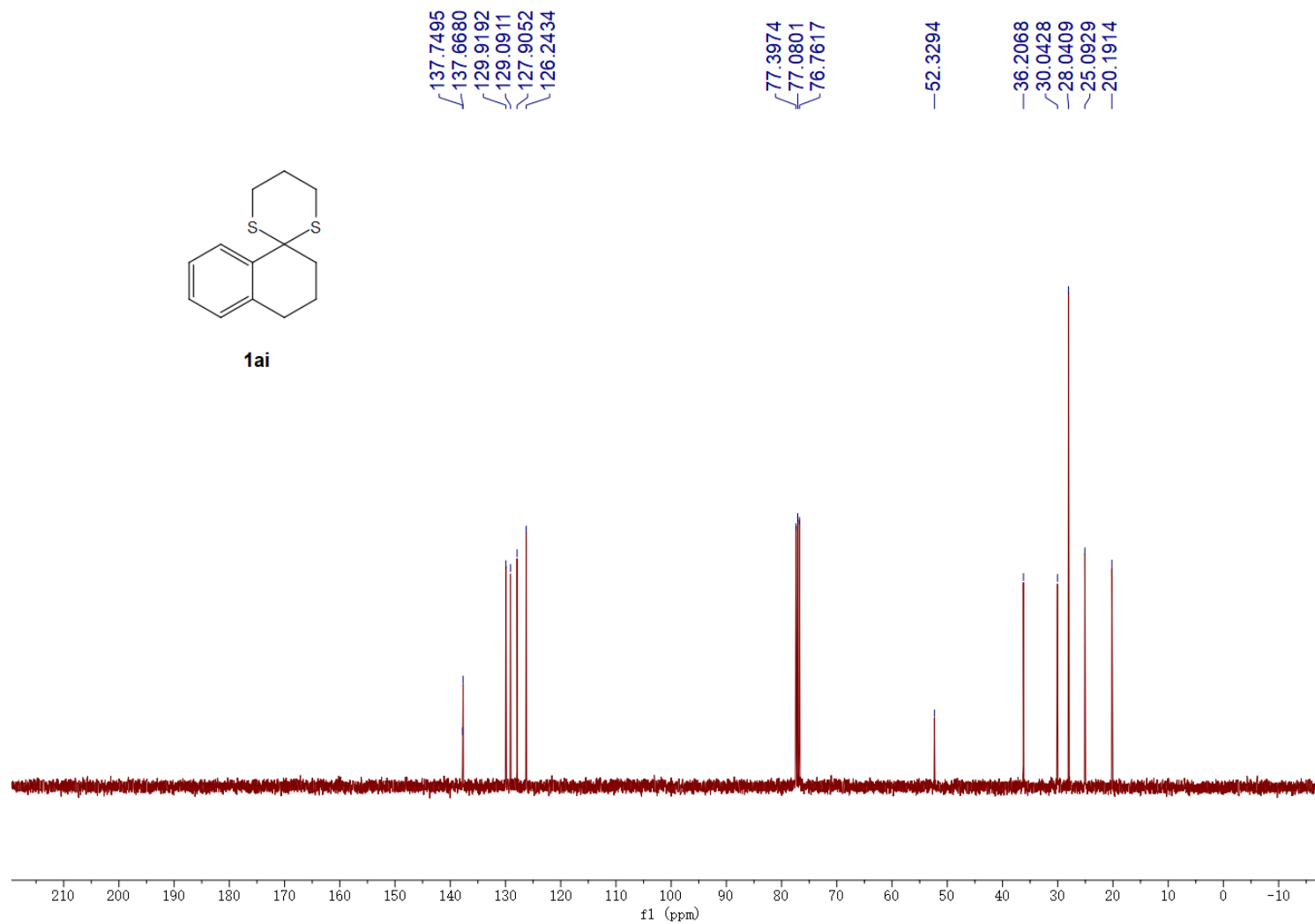
¹H-NMR Spectrum of Spiro[fluorene-9,2'-[1,3]dithiolane] (1ag)

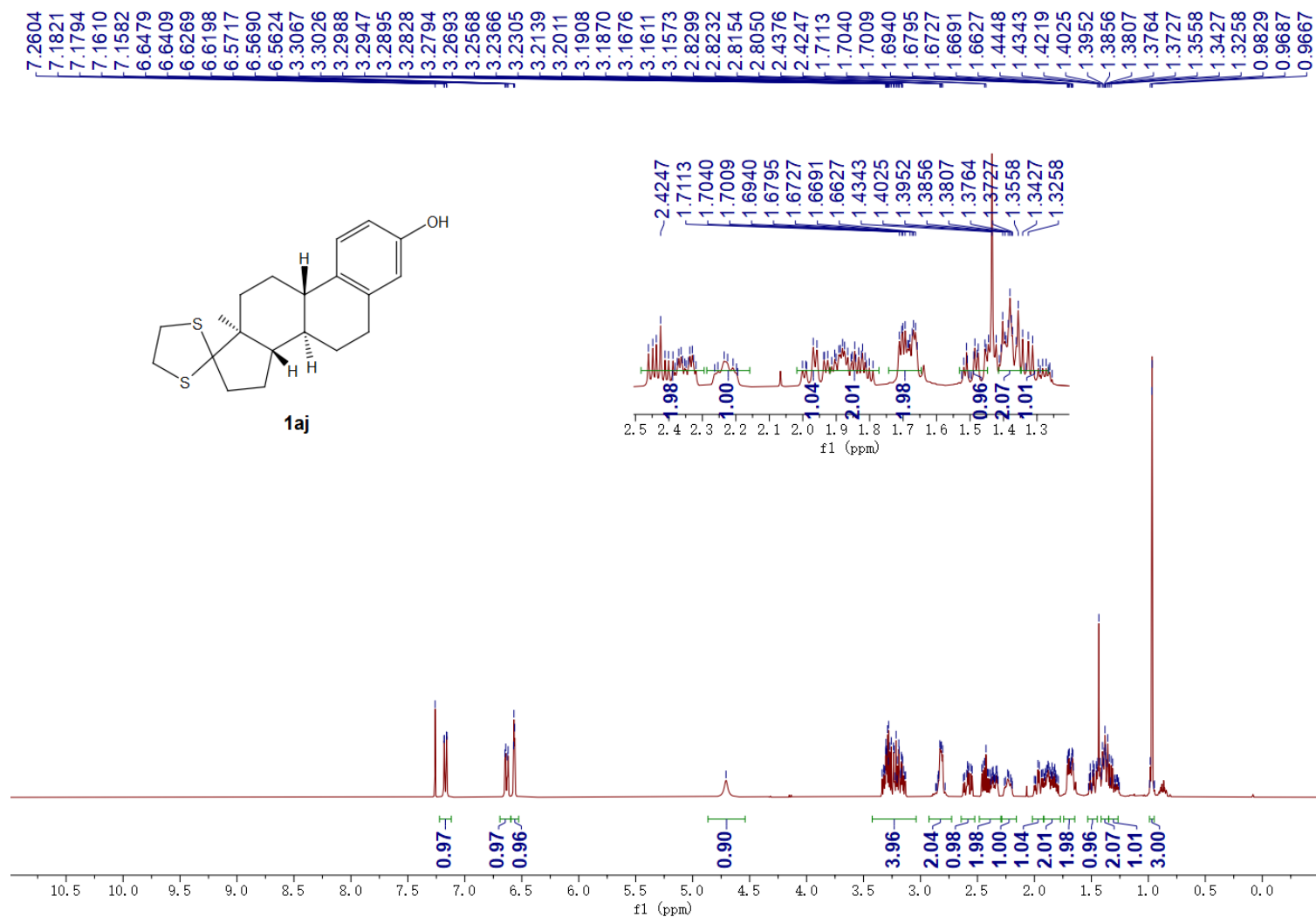
^{13}C -NMR Spectrum of Spiro[fluorene-9,2'-[1,3]dithiolane] (1ag)

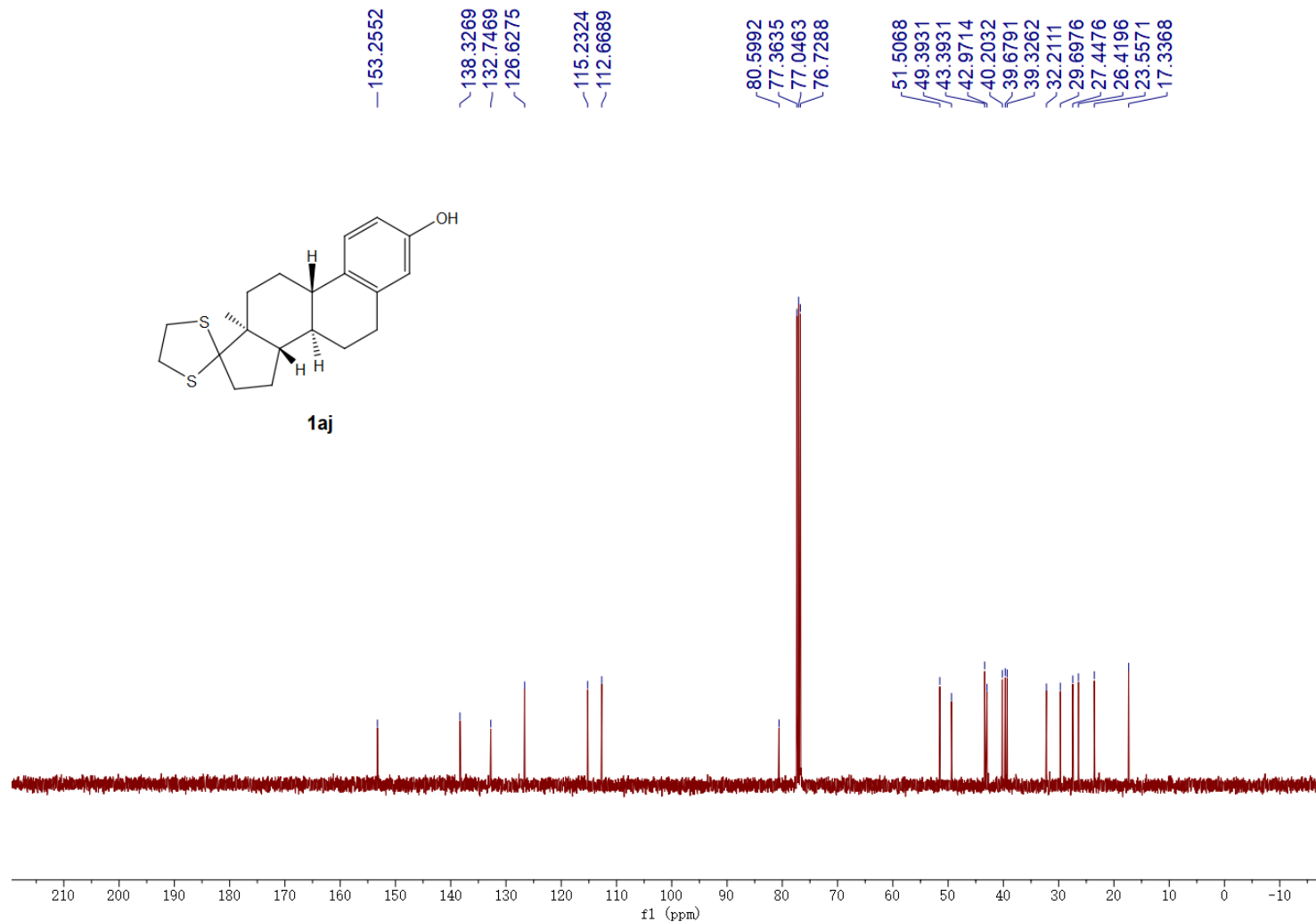
¹H-NMR Spectrum of 2-Methyl-2-(thiophen-2-yl)-1,3-dithiolane (1ah)

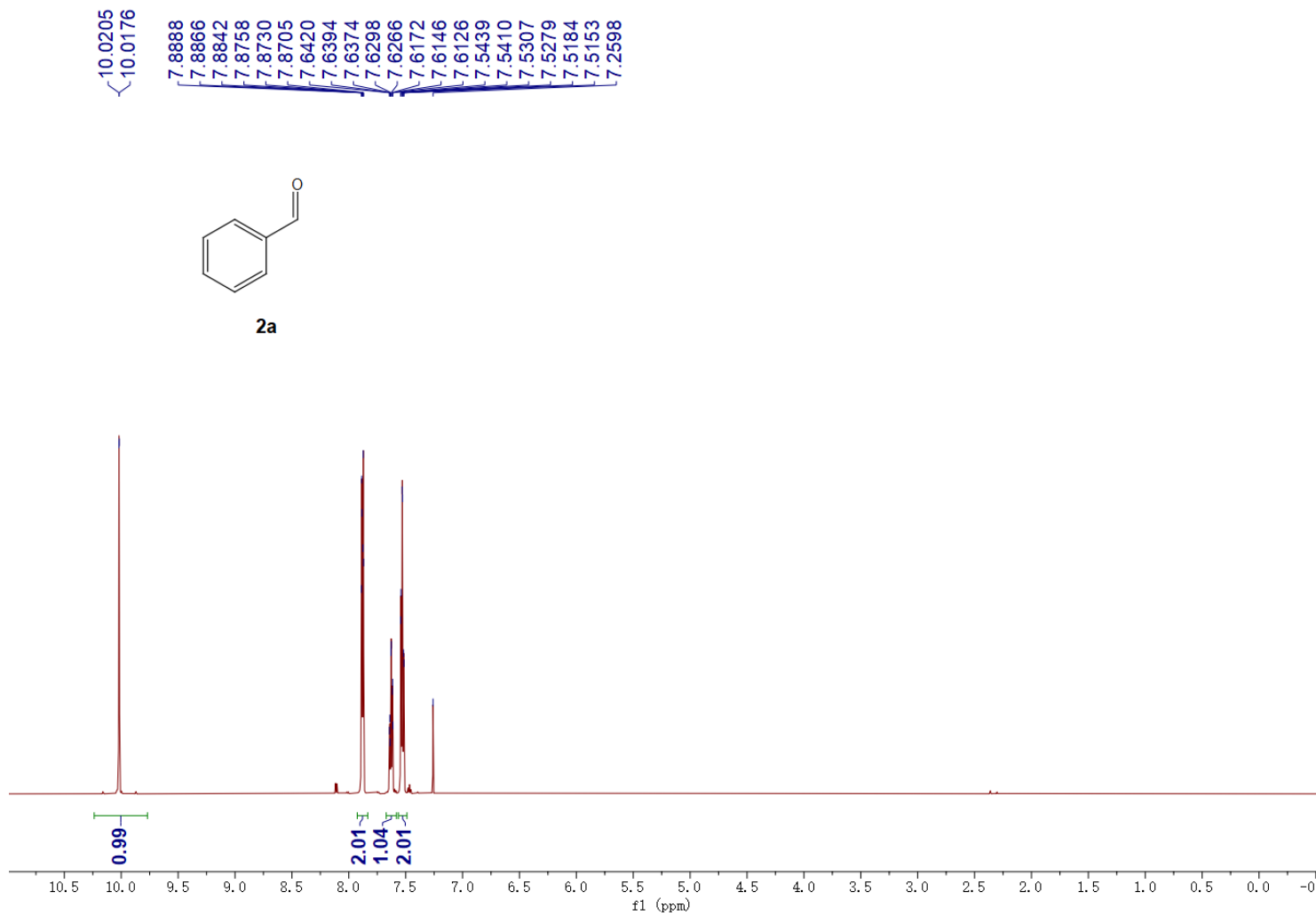
^{13}C -NMR Spectrum of 2-Methyl-2-(thiophen-2-yl)-1,3-dithiolane (1ah)

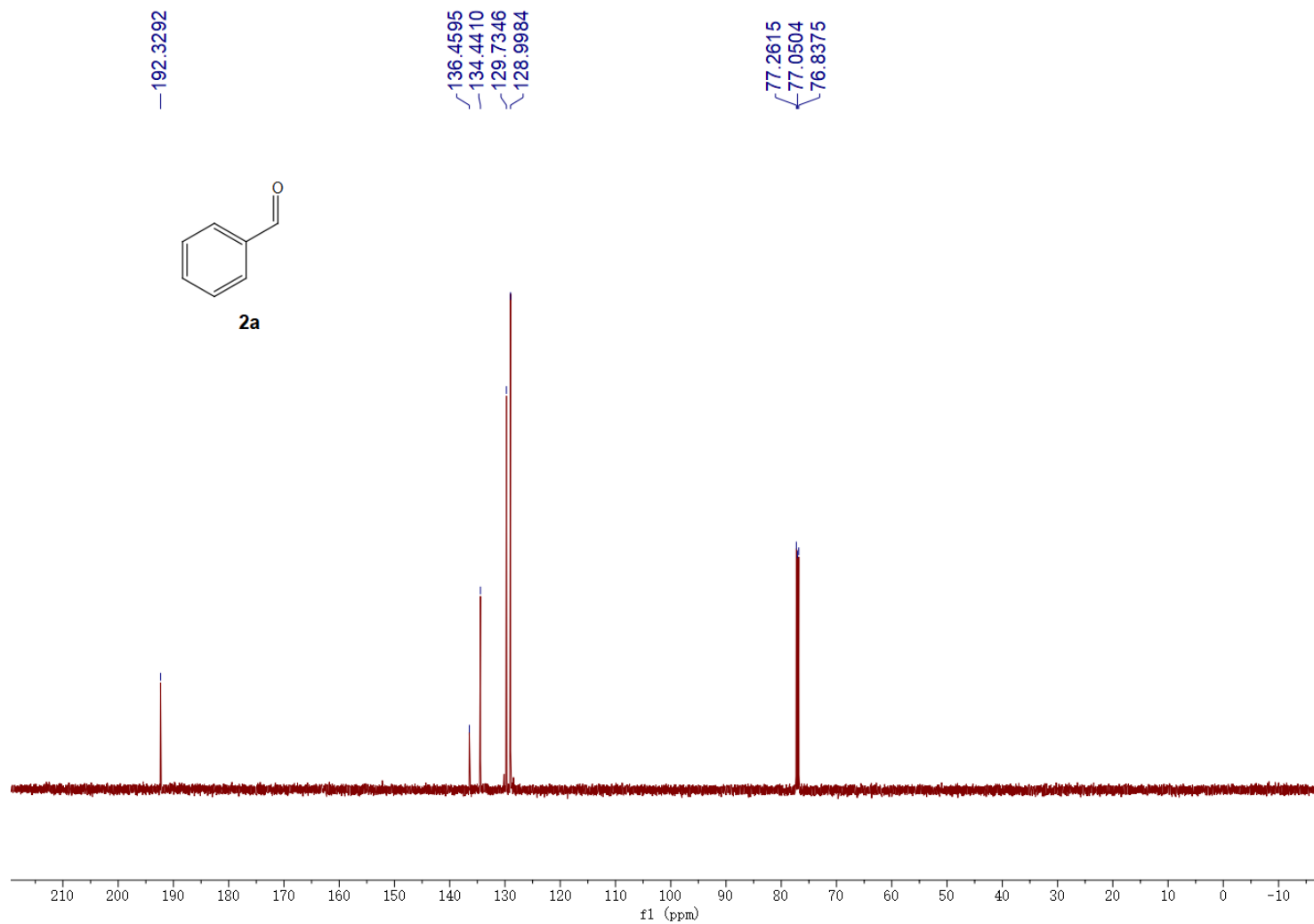
¹H-NMR Spectrum of 3,4-Dihydro-2H-spiro[naphthalene-1,2'-[1,3]dithiane] (1ai)

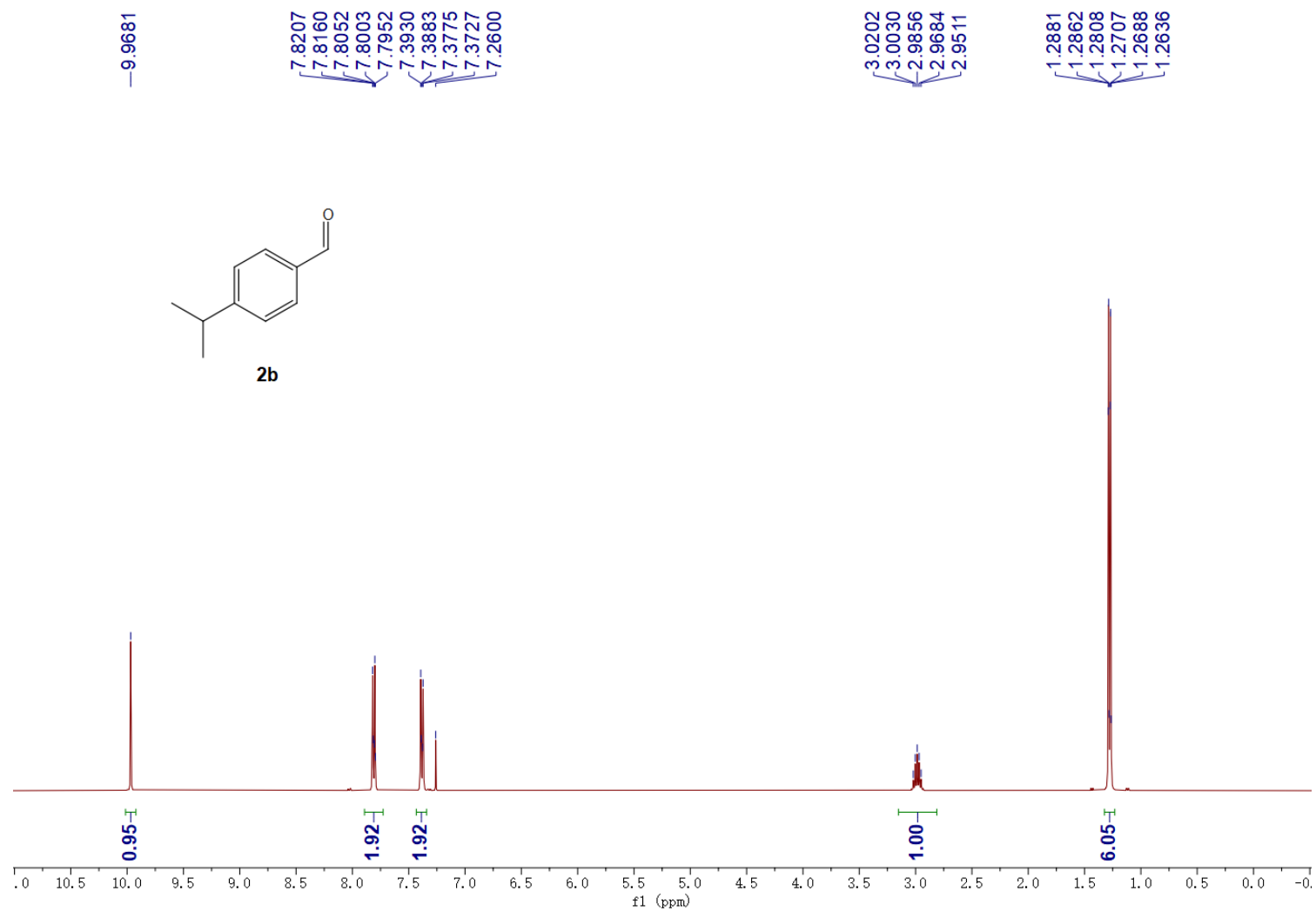
^{13}C -NMR Spectrum of 3,4-Dihydro-2H-spiro[naphthalene-1,2'-[1,3]dithiane] (1ai)

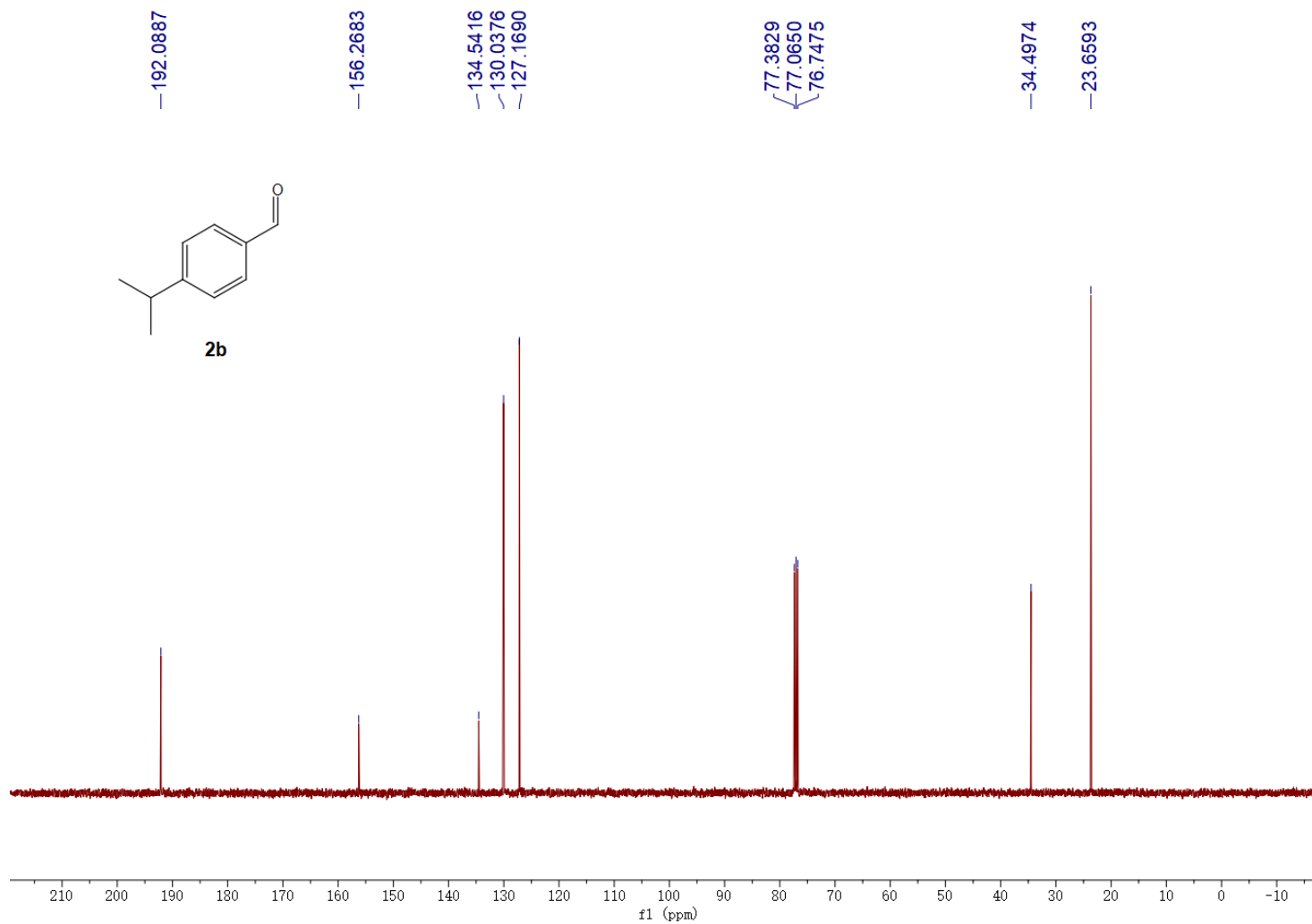
¹H-NMR Spectrum of (8*R*,9*S*,13*S*,14*S*)-13-Methyl-6,7,8,9,11,12,13,14,15,16 decahydrospiro[cyclopenta-[a]phenanthrene-17,2'-[1,3]dithiolan]-3-ol (1aj)

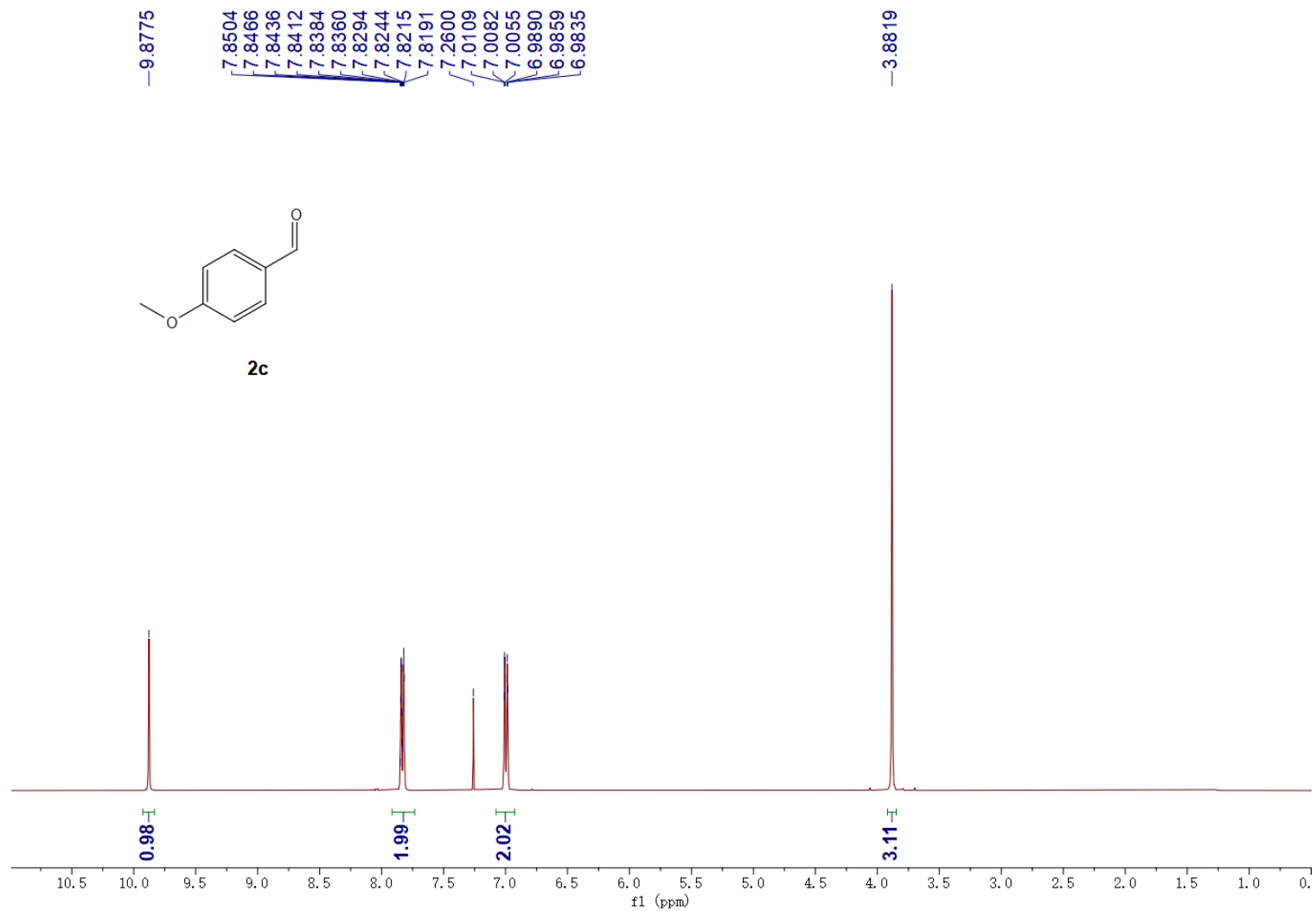
^{13}C -NMR Spectrum of (8*R*,9*S*,13*S*,14*S*)-13-Methyl-6,7,8,9,11,12,13,14,15,16 decahydrospiro[cyclopenta-[a]phenanthrene-17,2'-[1,3]dithiolan]-3-ol (1aj)

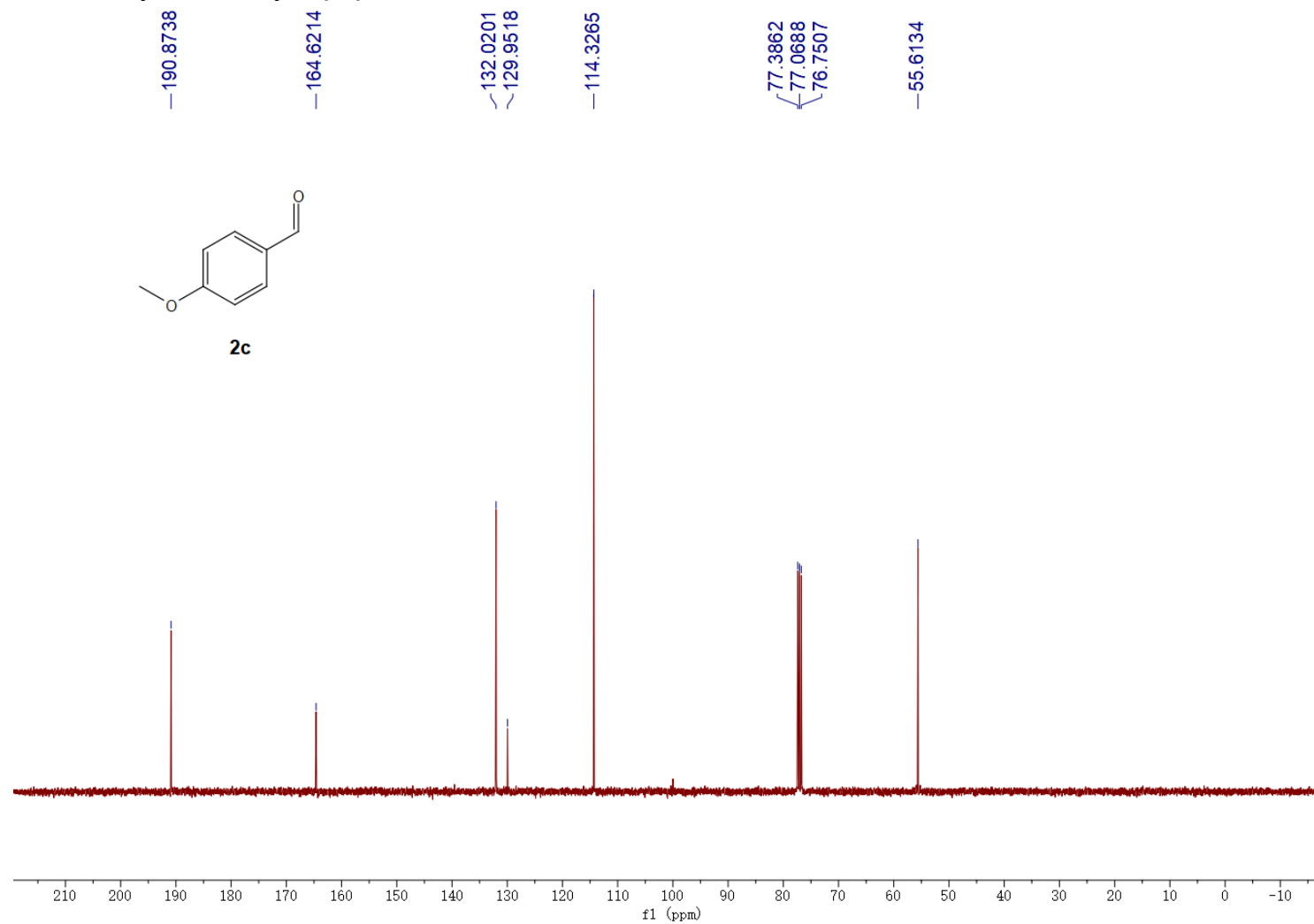
¹H-NMR Spectrum of Benzaldehyde (2a)

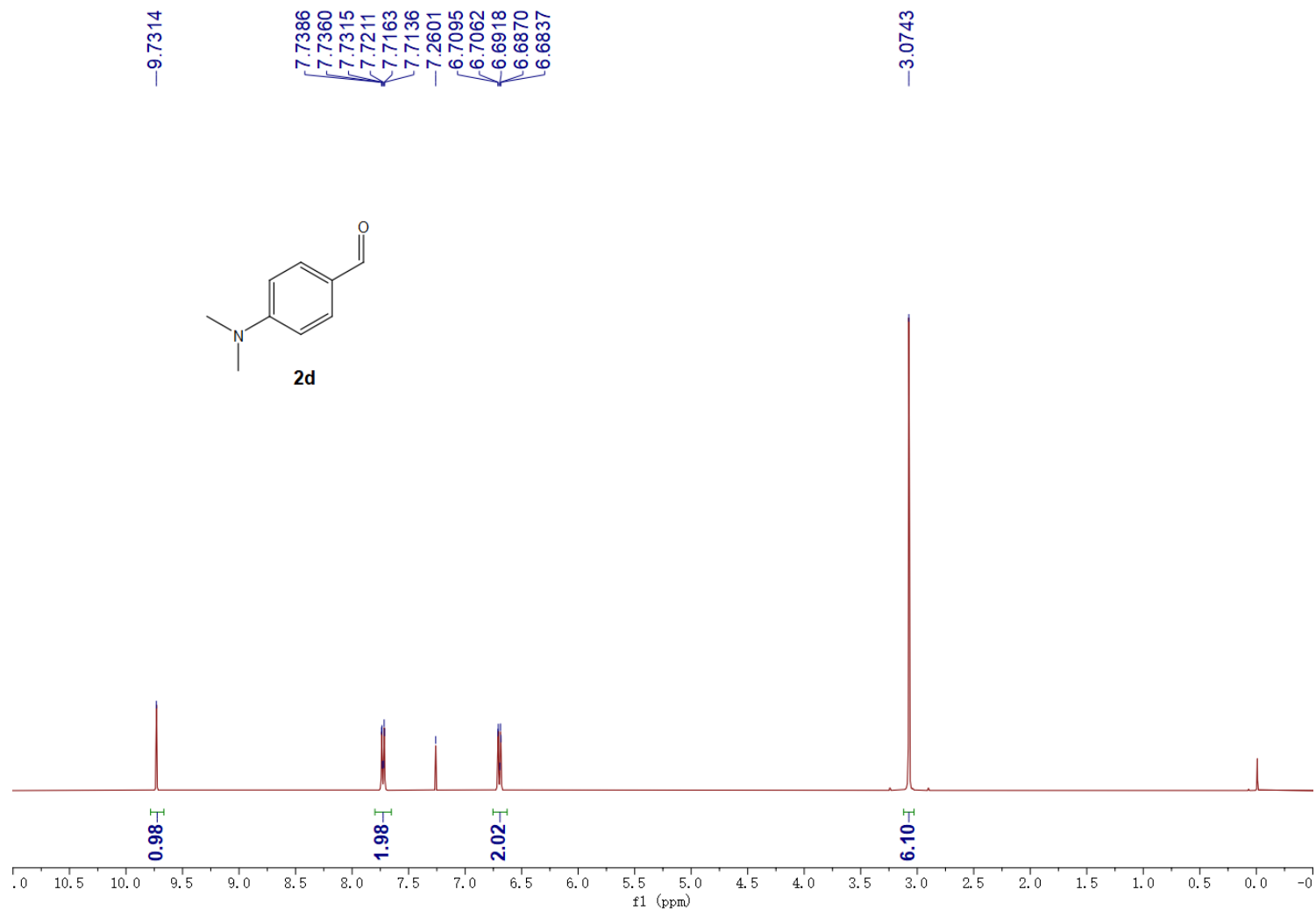
^{13}C -NMR Spectrum of Benzaldehyde (2a)

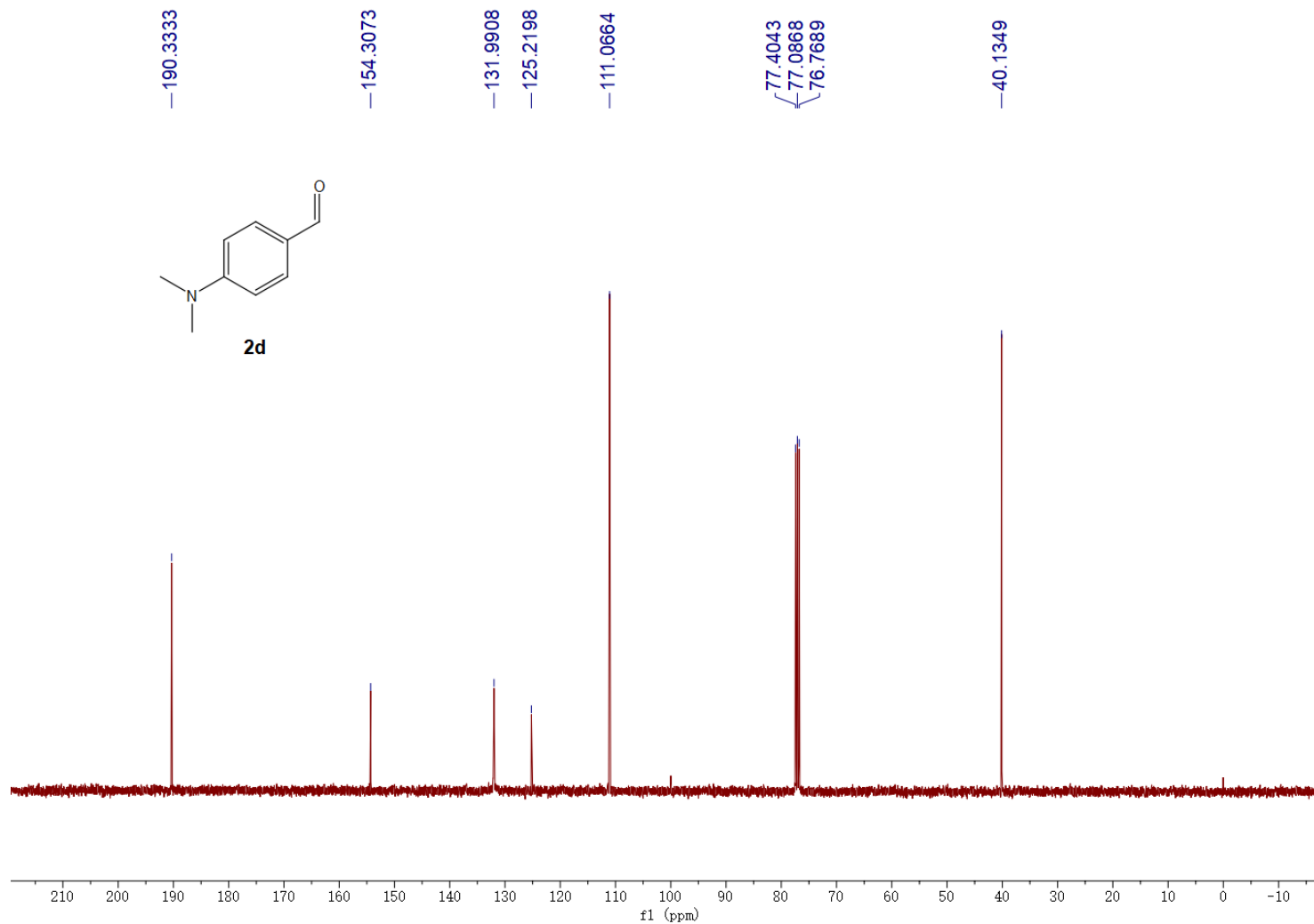
¹H-NMR Spectrum of 4-Isopropylbenzaldehyde (2b)

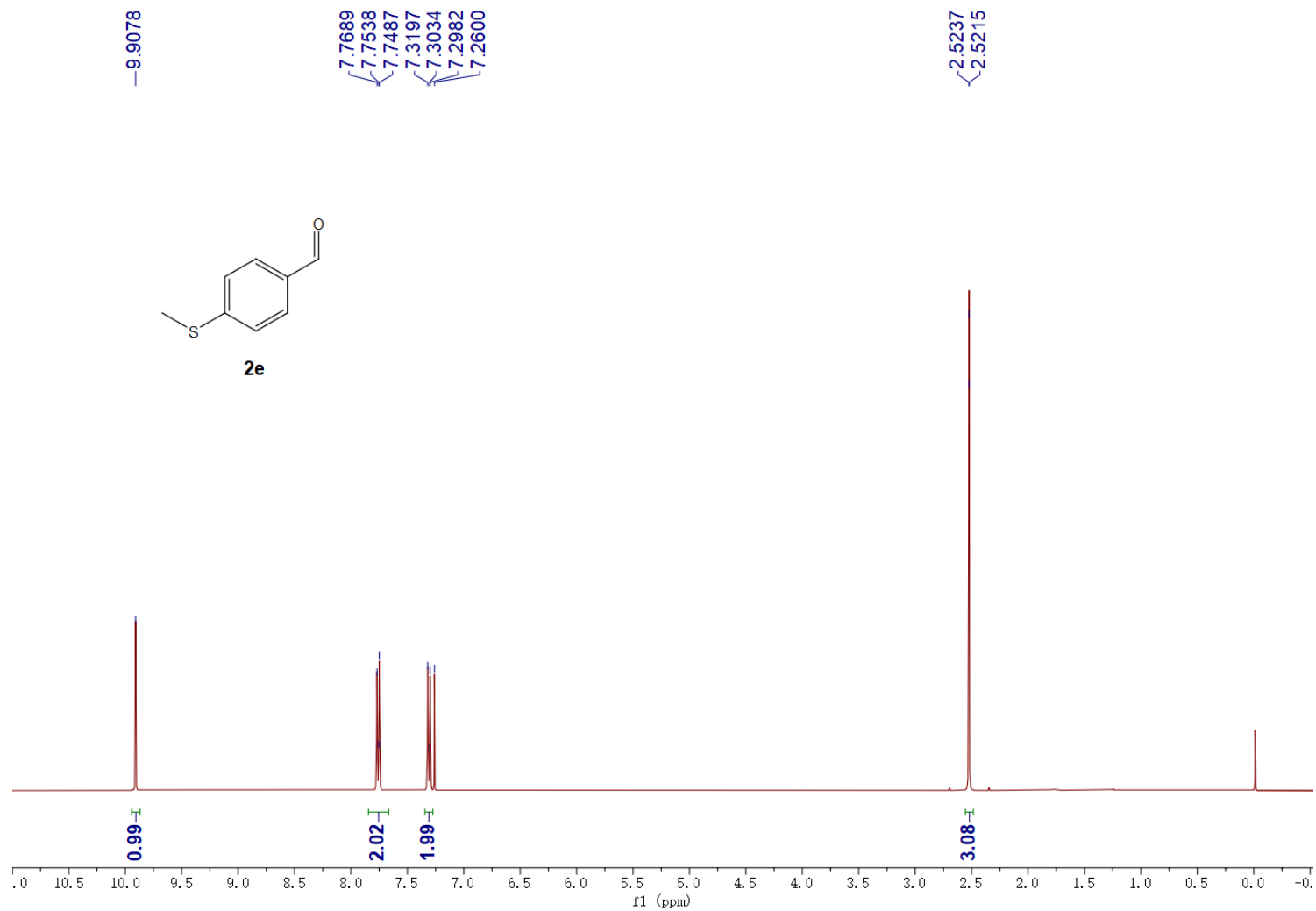
^{13}C -NMR Spectrum of 4-Isopropylbenzaldehyde (2b)

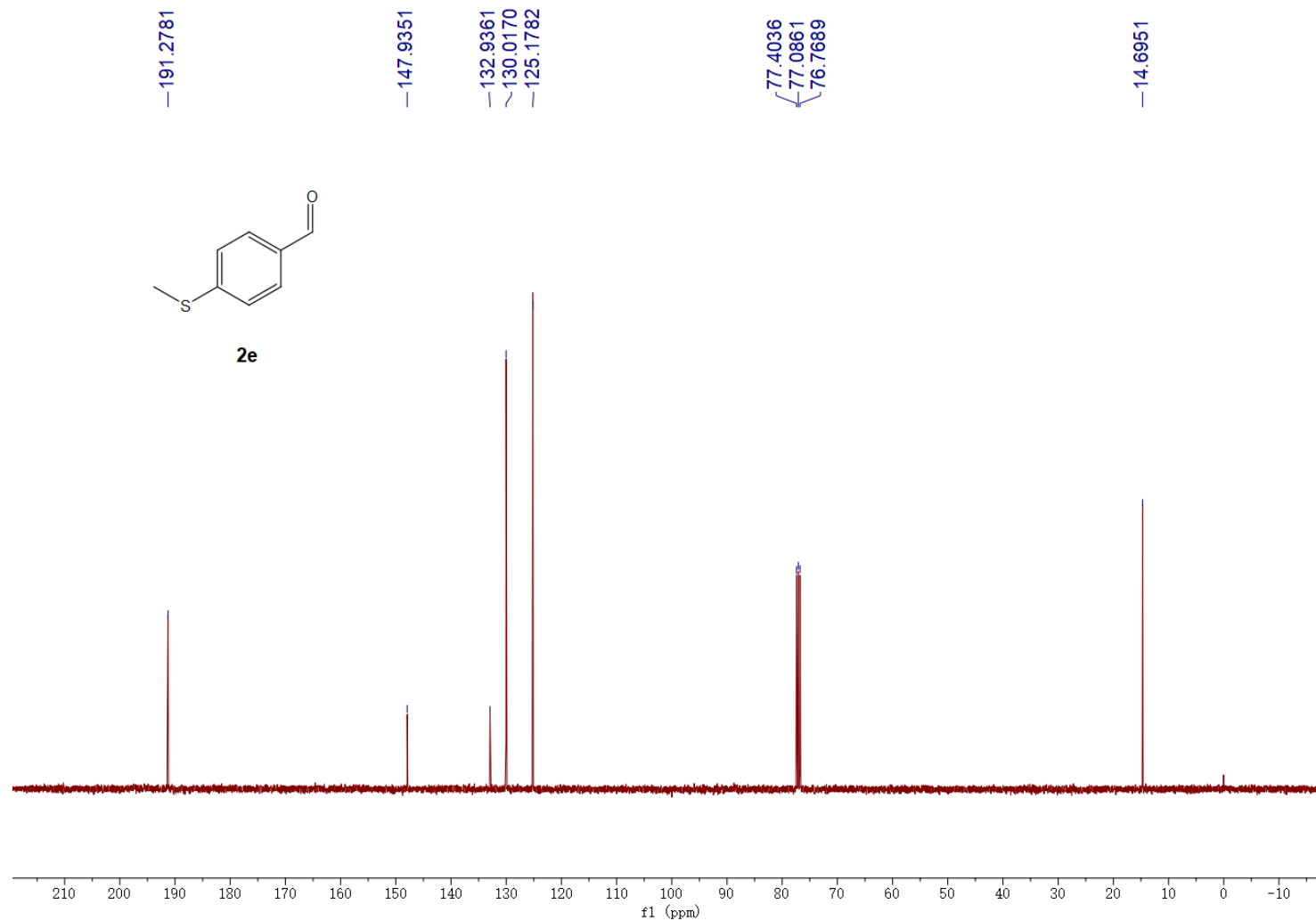
¹H-NMR Spectrum of 4-Methoxybenzaldehyde (2c)

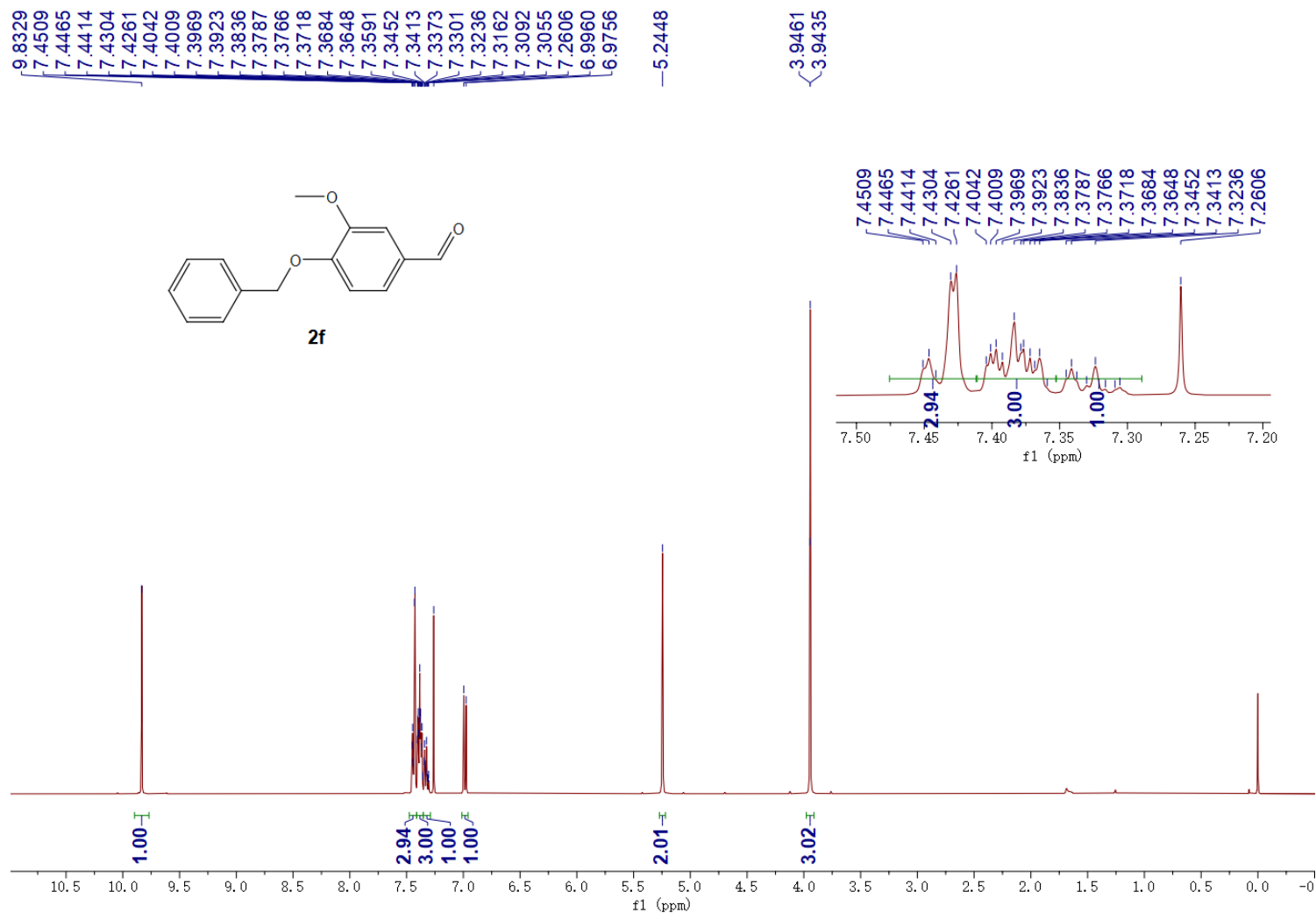
^{13}C -NMR Spectrum of 4-Methoxybenzaldehyde (2c)

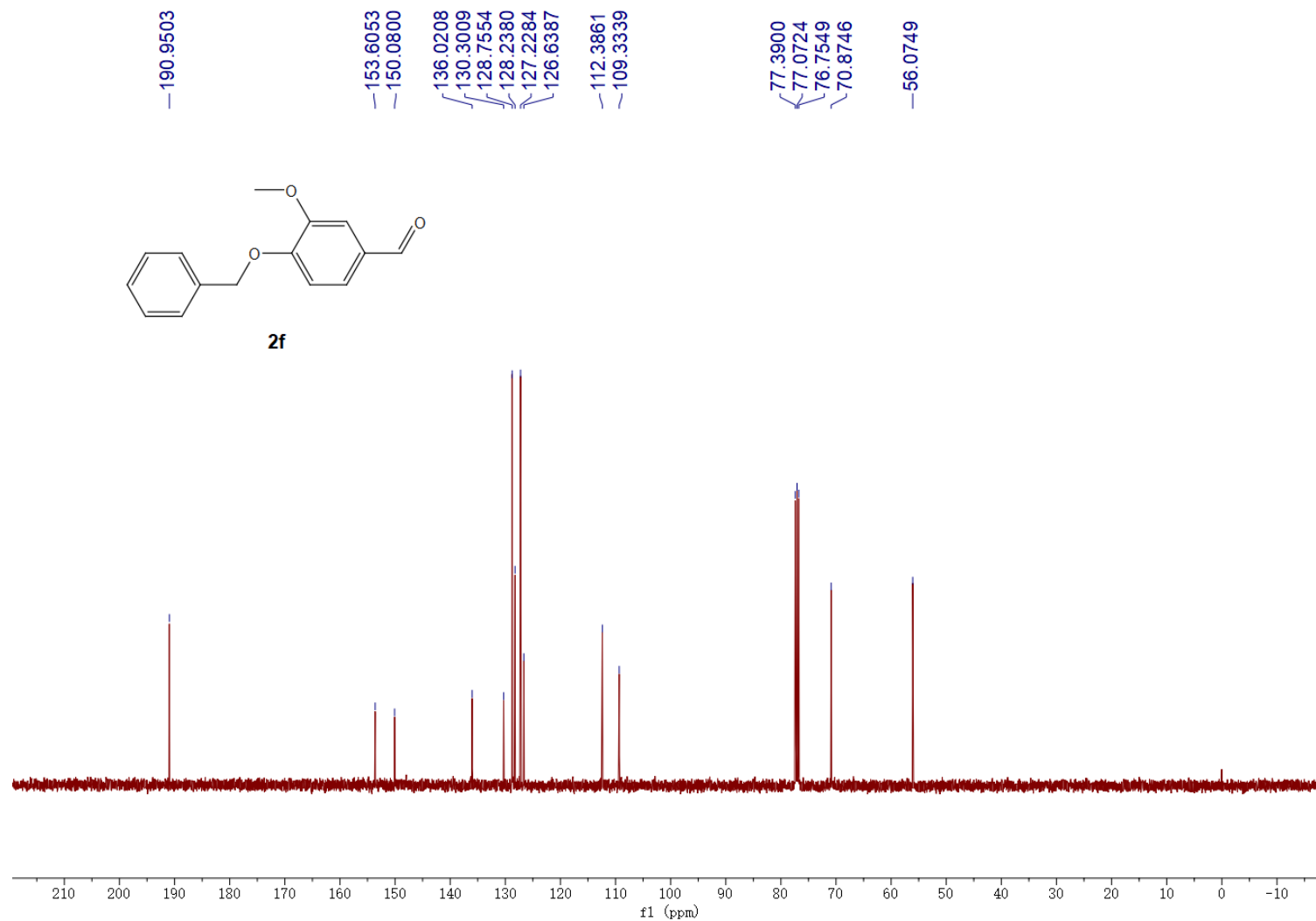
¹H-NMR Spectrum of 4-(Dimethylamino)benzaldehyde (2d)

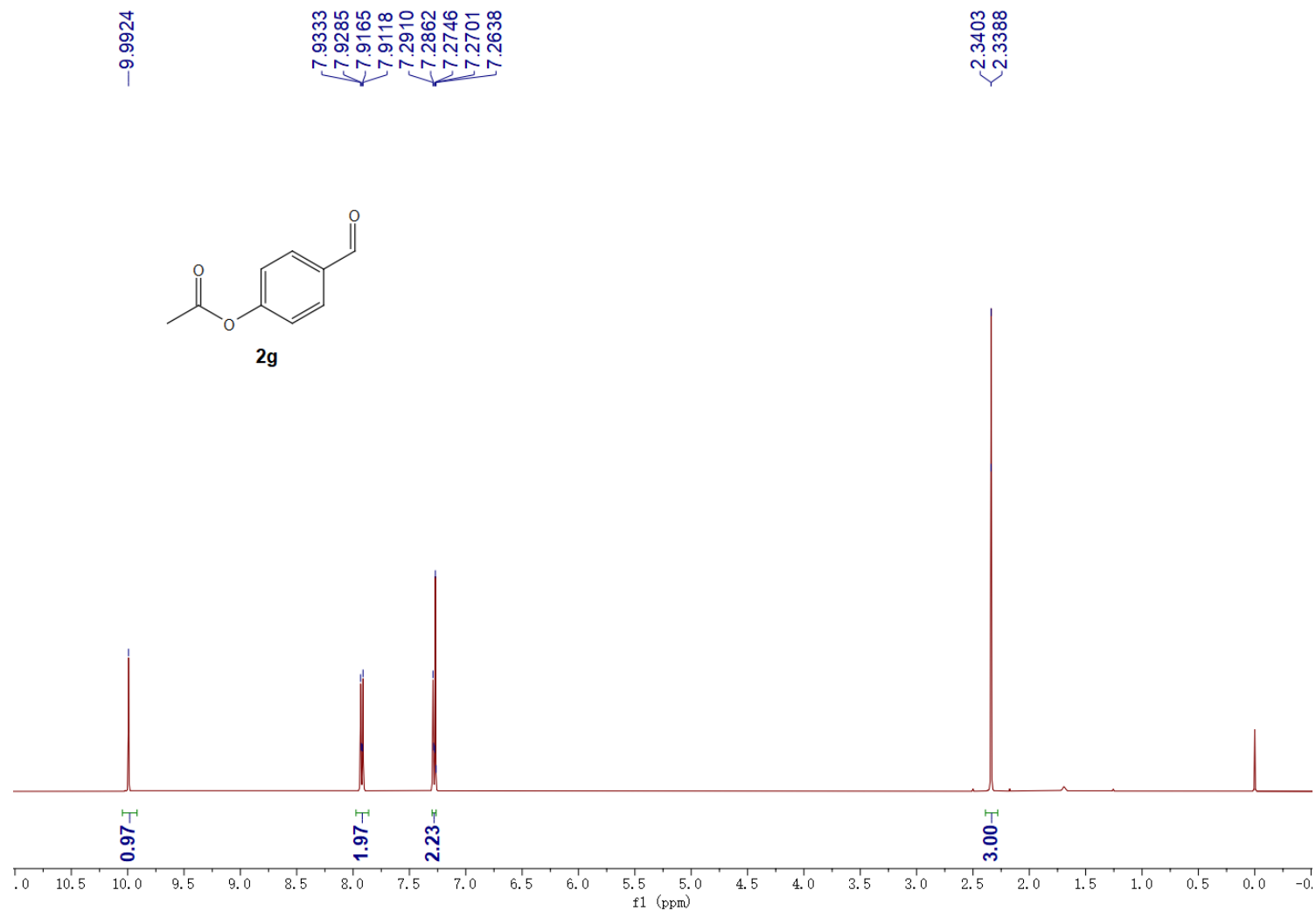
^{13}C -NMR Spectrum of 4-(Dimethylamino)benzaldehyde (2d)

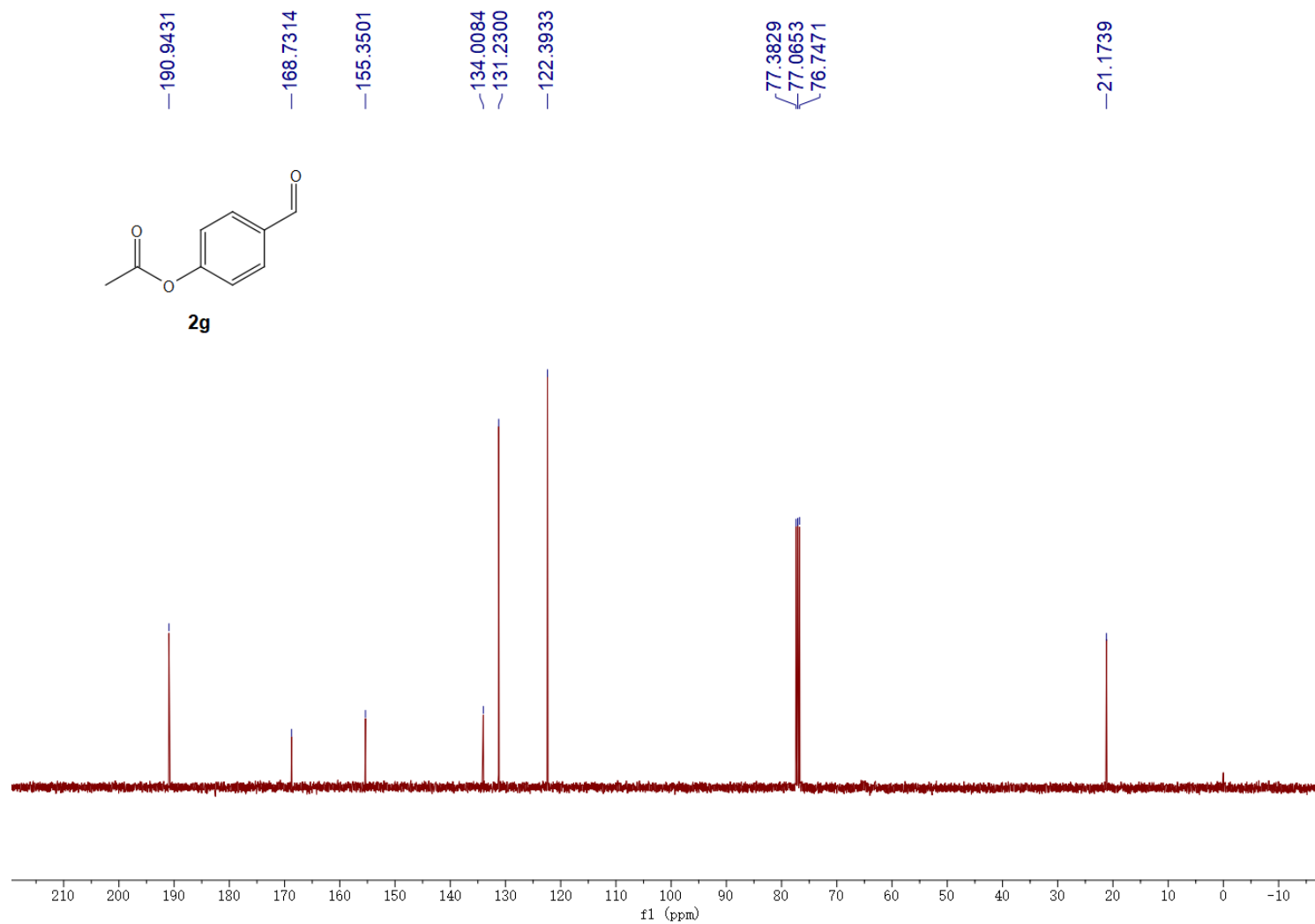
^1H -NMR Spectrum of 4-(Methylthio)benzaldehyde (2e)

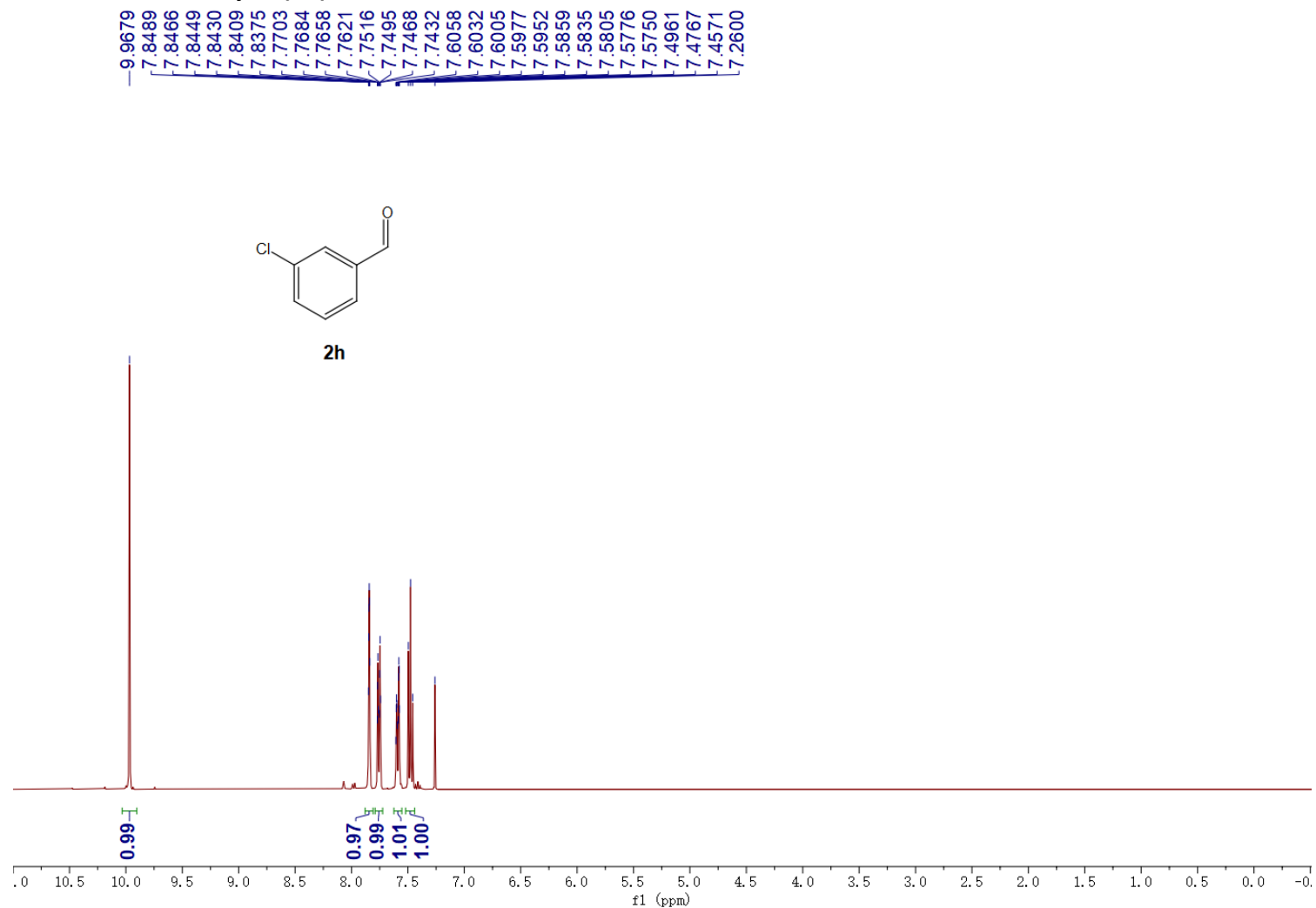
^{13}C -NMR Spectrum of 4-(Methylthio)benzaldehyde (2e)

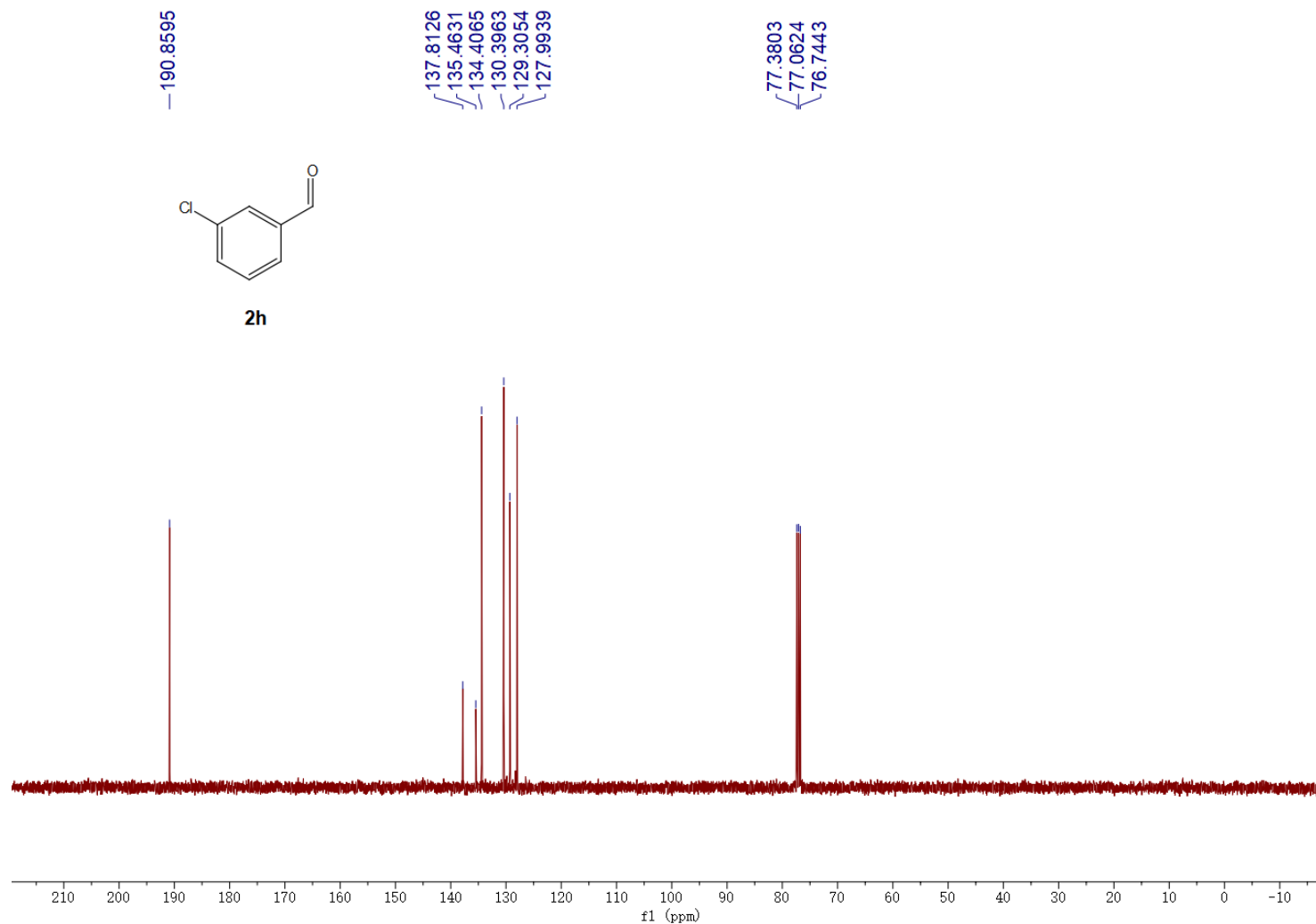
¹H-NMR Spectrum of 4-(Benzyloxy)-3-methoxybenzaldehyde (2f)

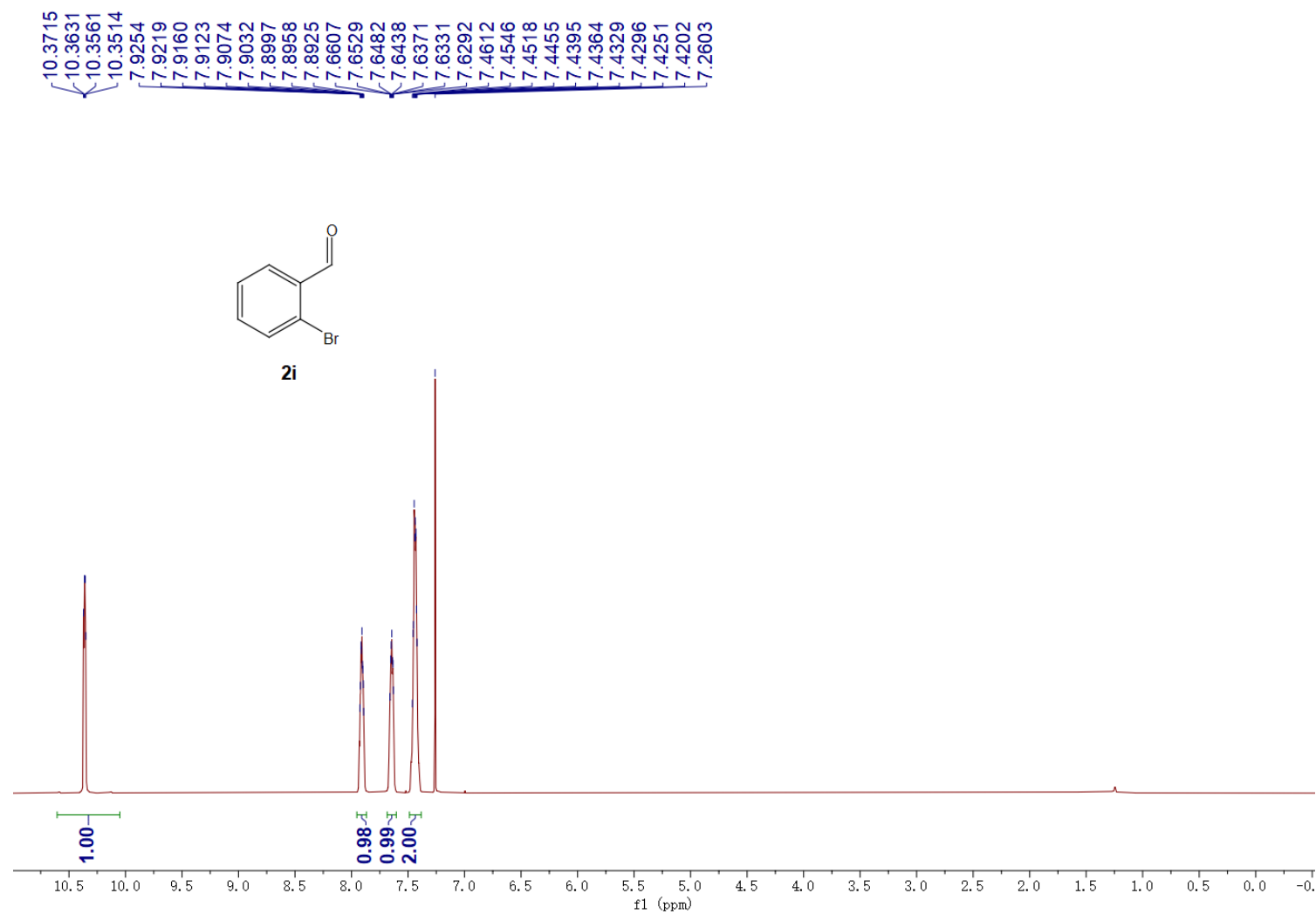
^{13}C -NMR Spectrum of 4-(Benzyloxy)-3-methoxybenzaldehyde (2f)

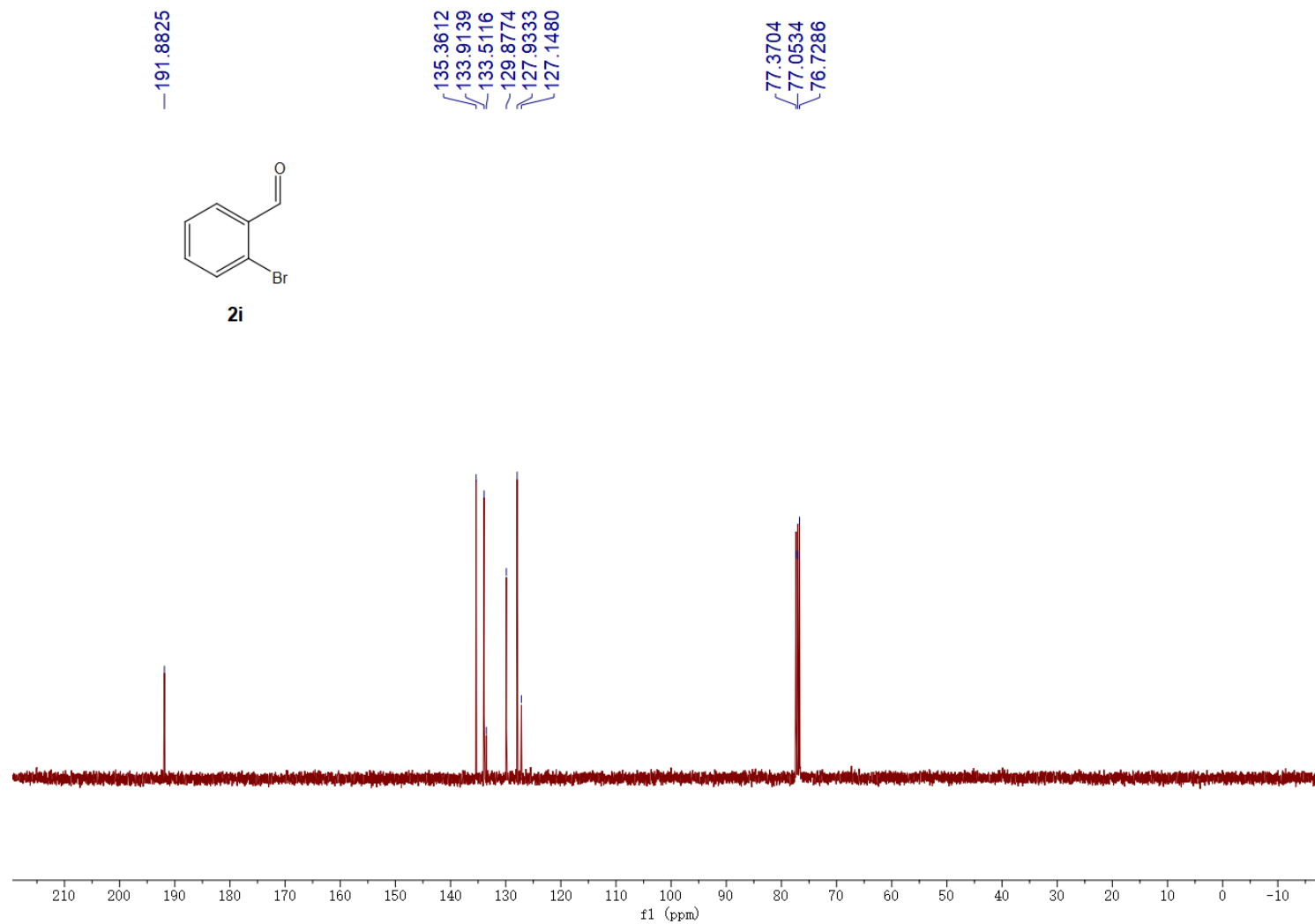
^1H -NMR Spectrum of 4-Formylphenyl acetate (2g)

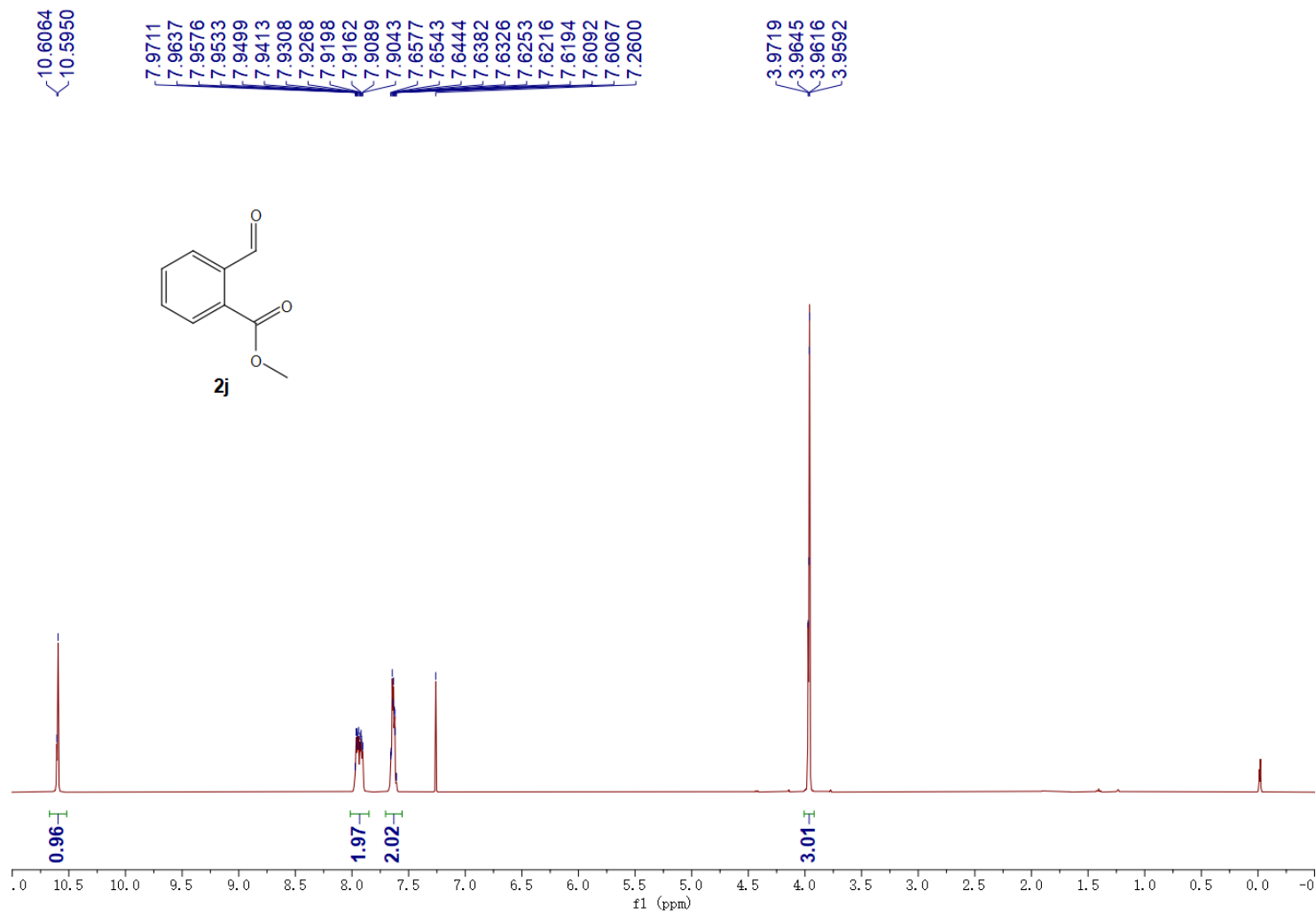
^{13}C -NMR Spectrum of 4-Formylphenyl acetate (2g)

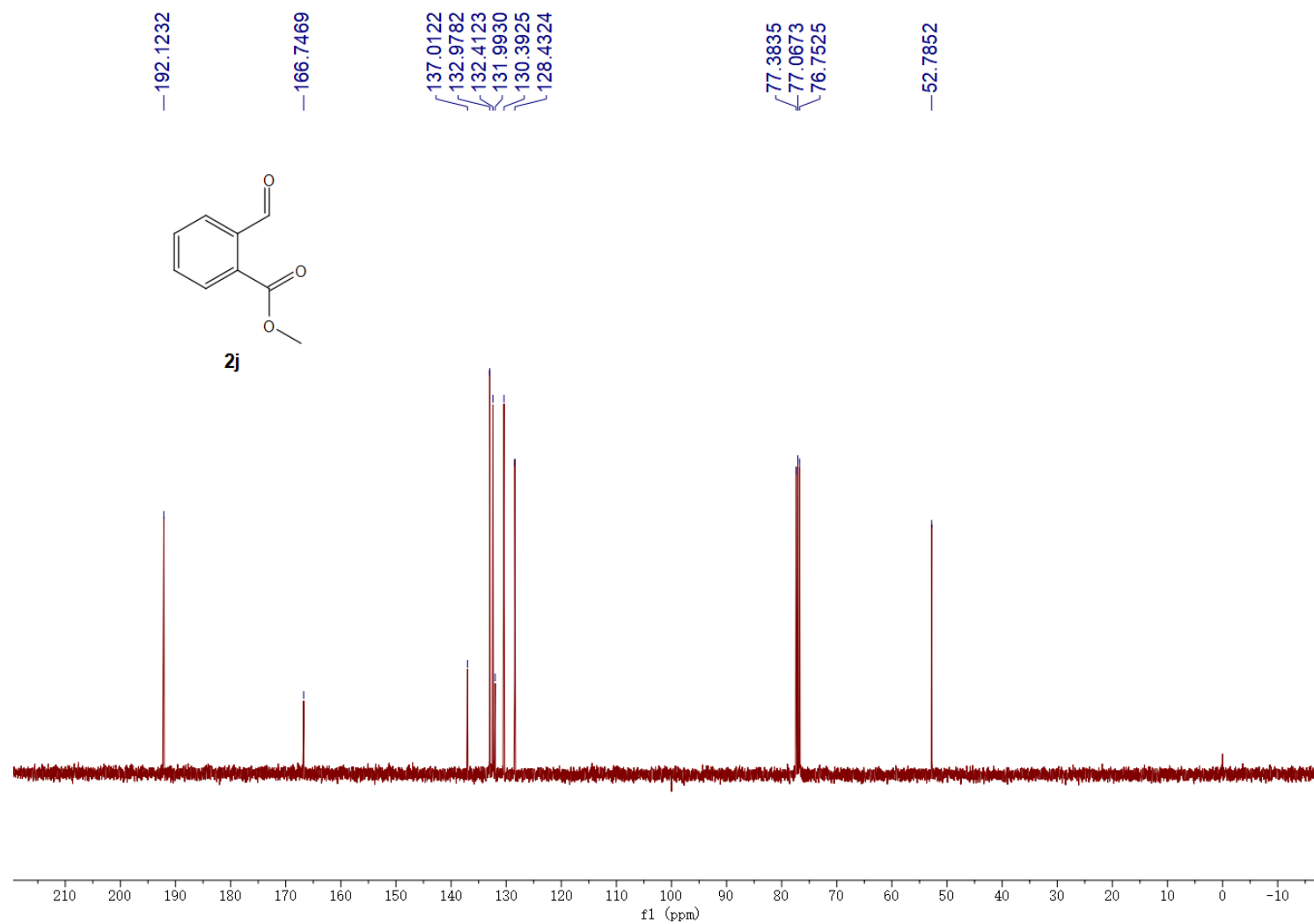
¹H-NMR Spectrum of 3-Chlorobenzaldehyde (2h)

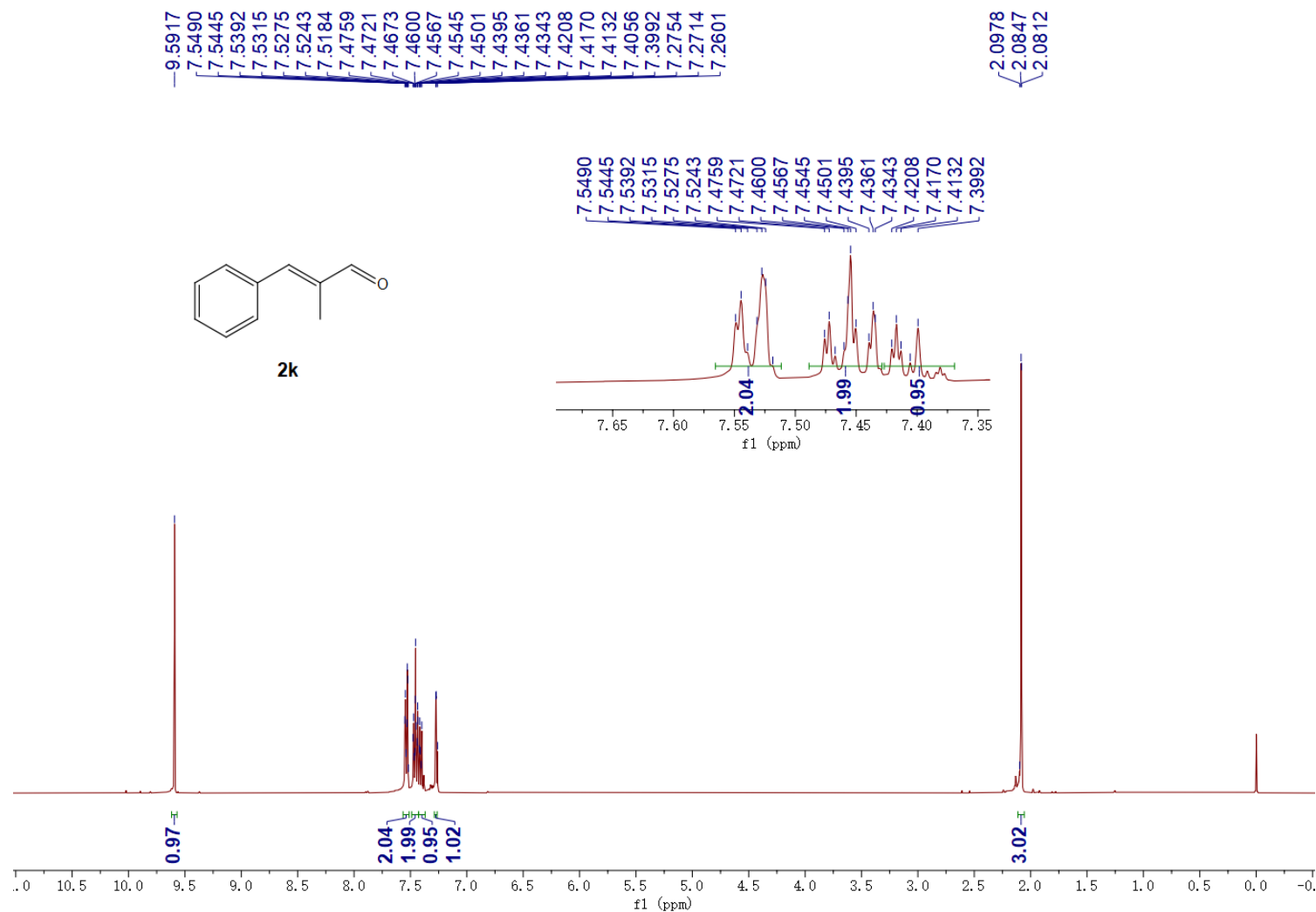
^{13}C -NMR Spectrum of 3-Chlorobenzaldehyde (2h)

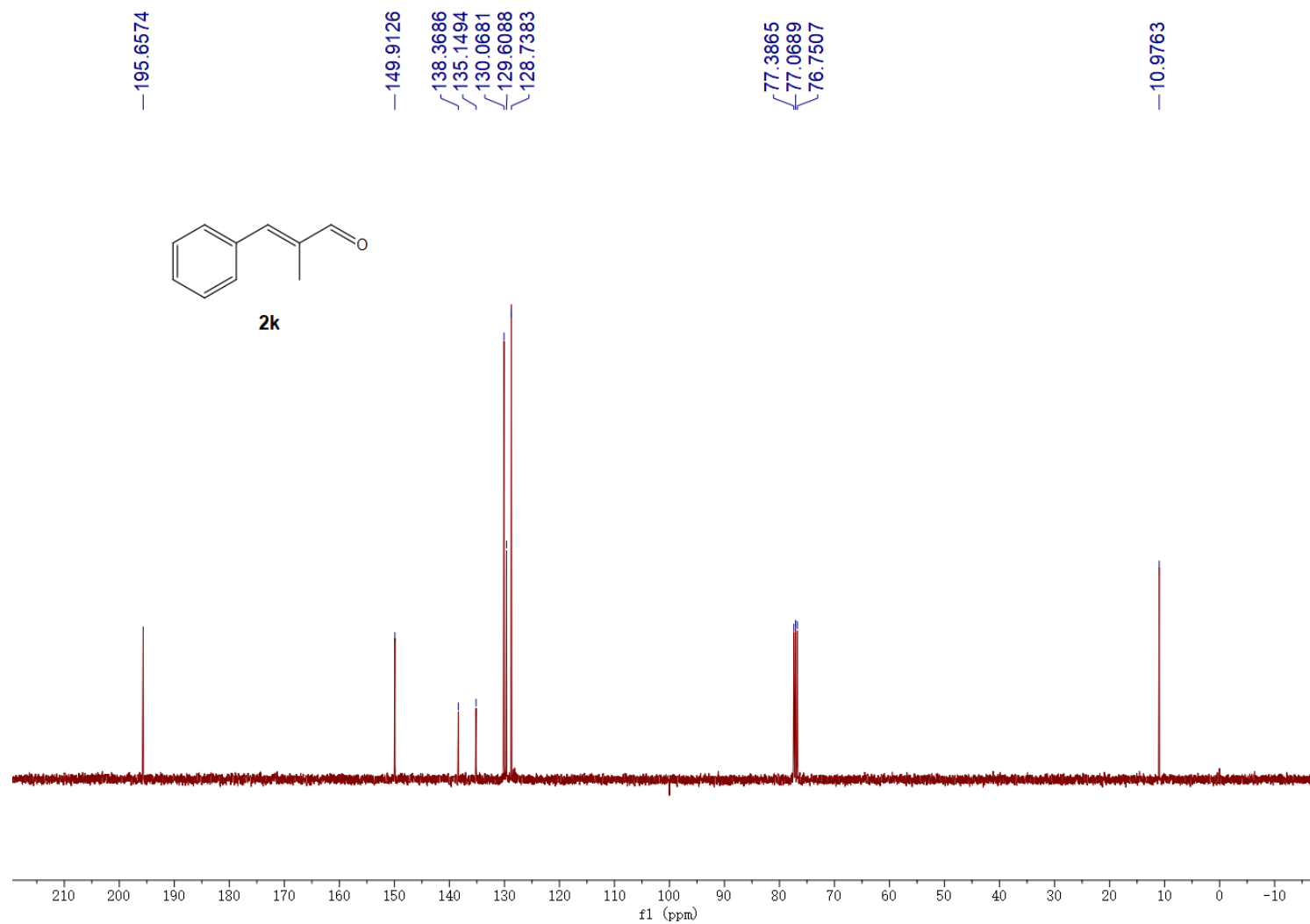
¹H-NMR Spectrum of 2-Bromobenzaldehyde (2i)

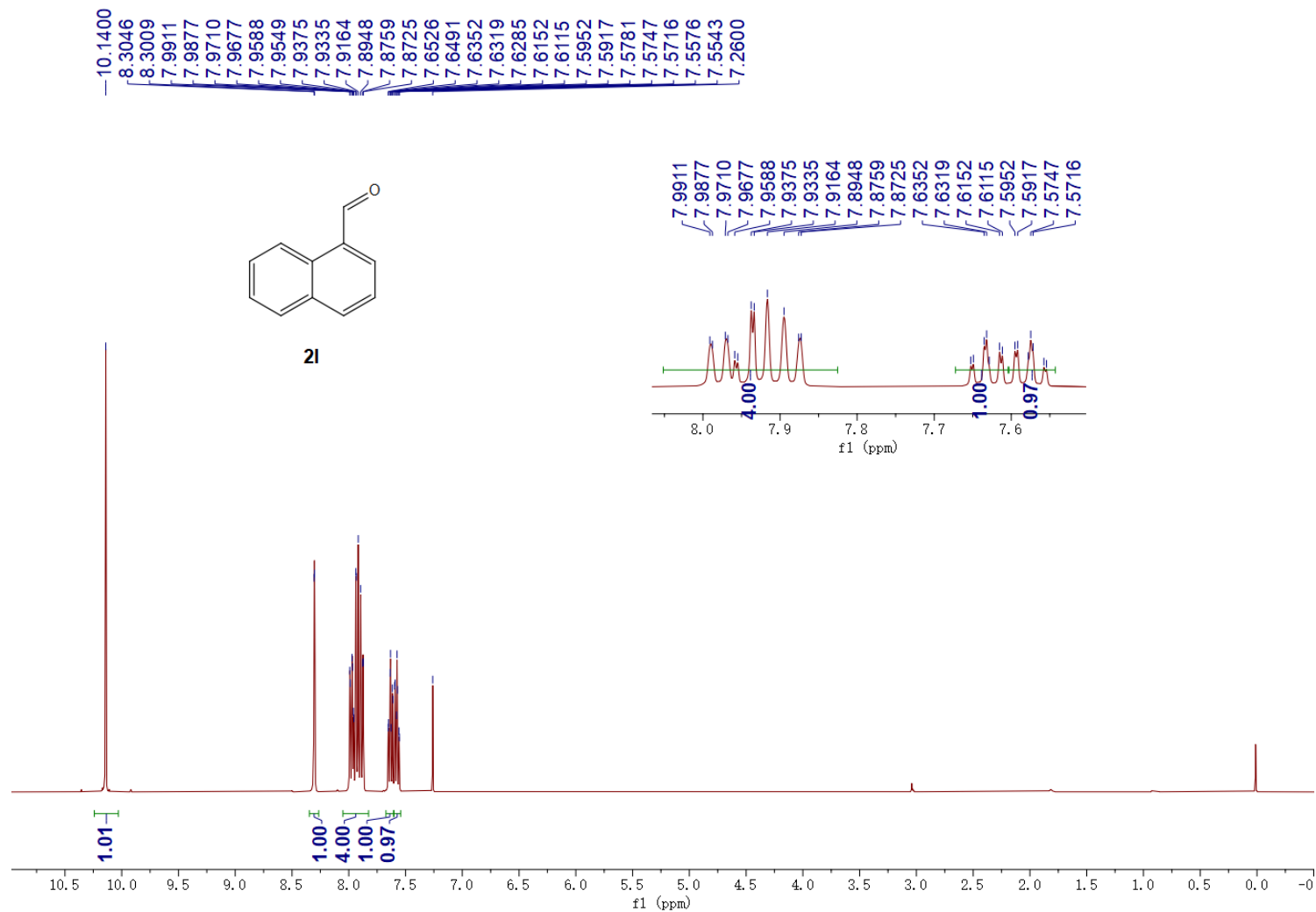
^{13}C -NMR Spectrum of 2-Bromobenzaldehyde (2i)

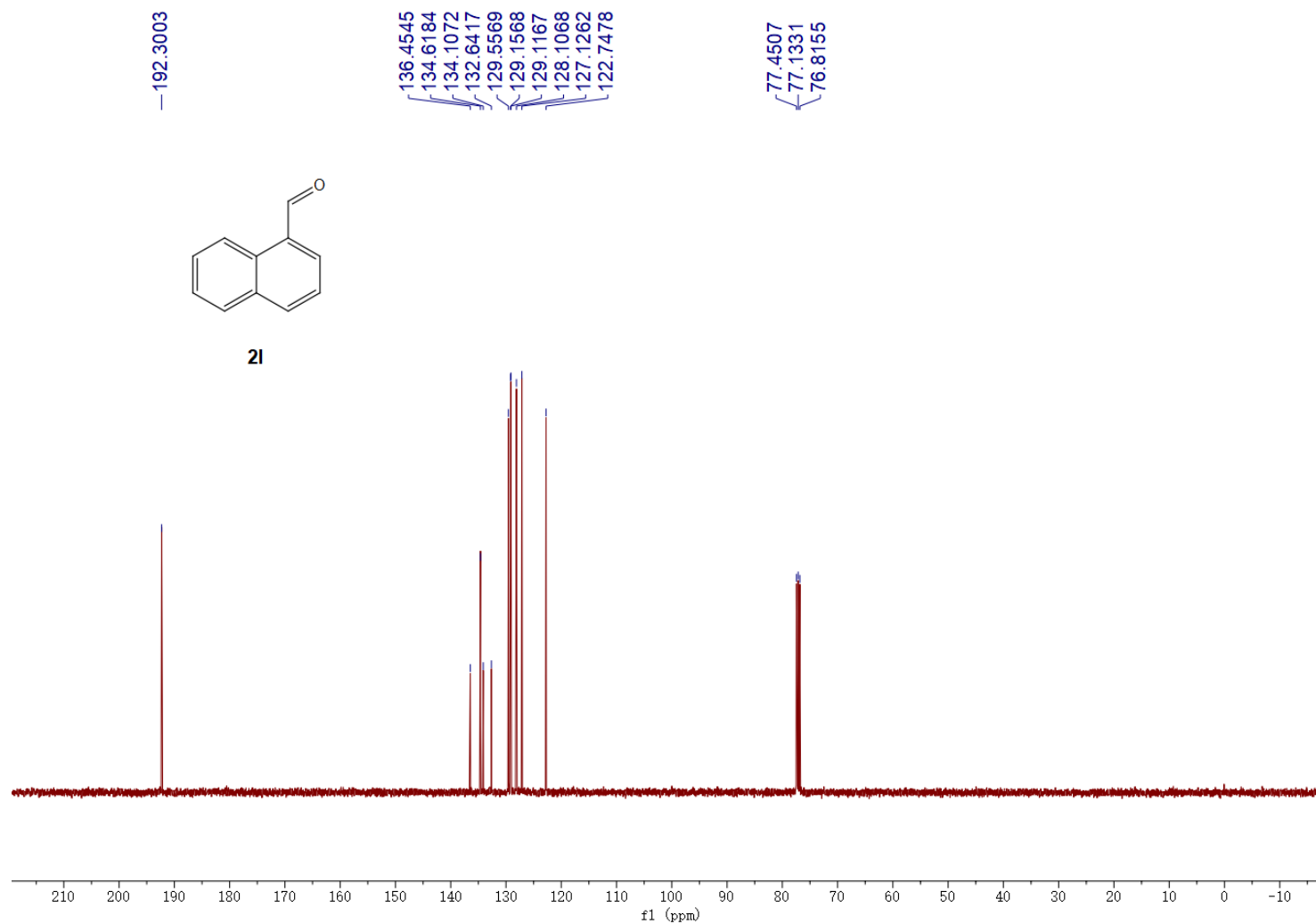
¹H-NMR Spectrum of Methyl 2-formylbenzoate (2j)

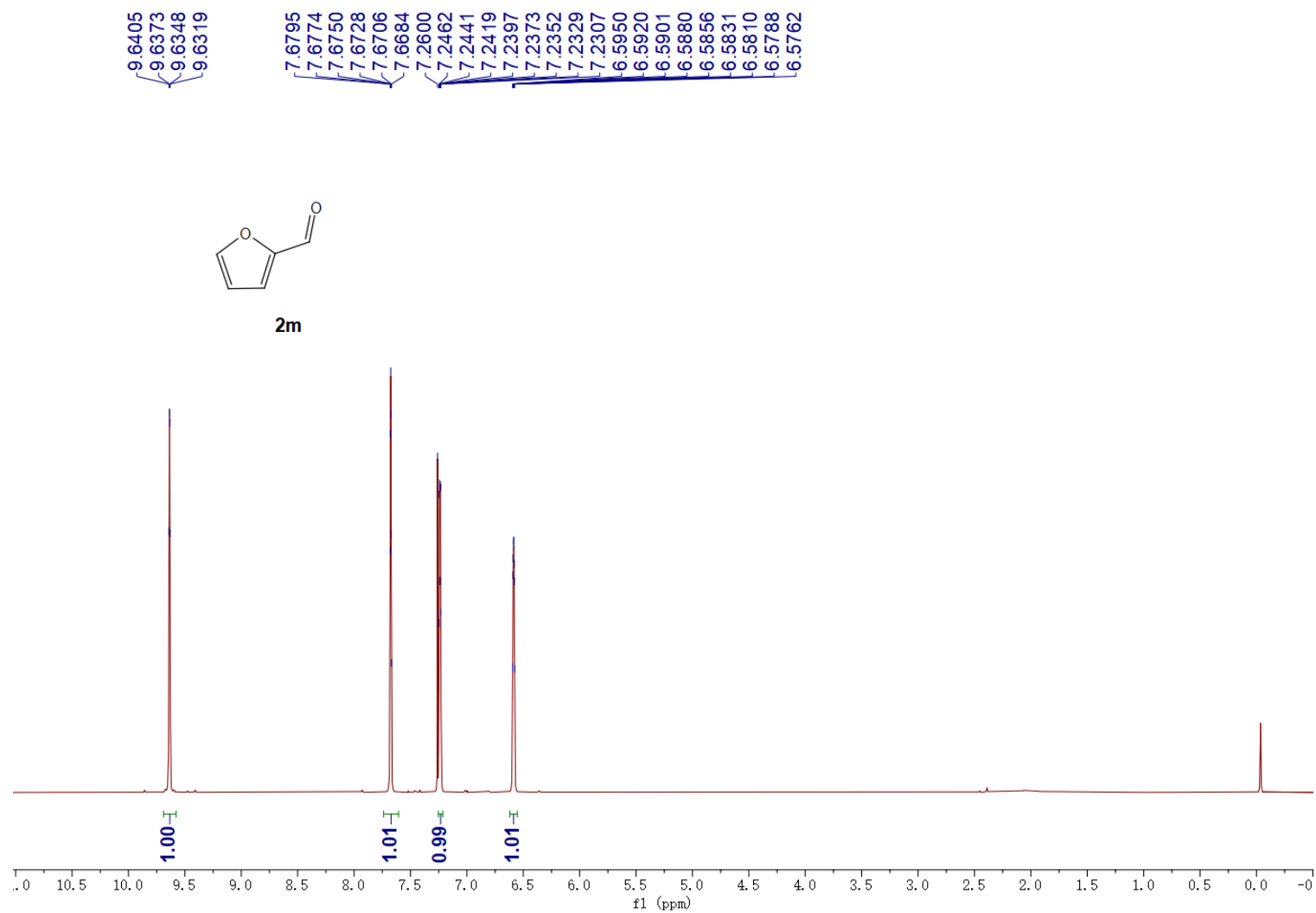
^{13}C -NMR Spectrum of Methyl 2-formylbenzoate (2j)

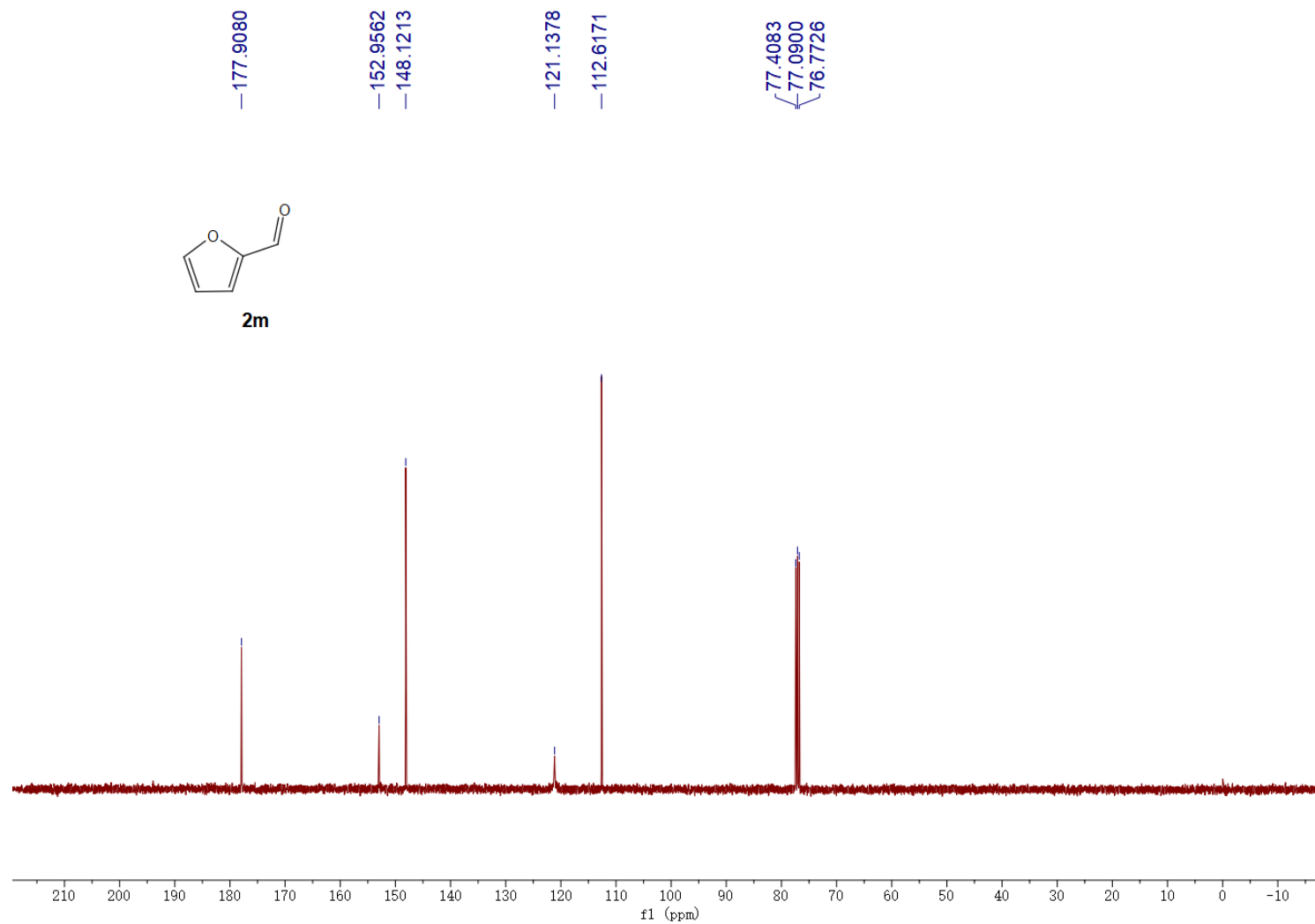
¹H-NMR Spectrum of (*E*)-2-Methyl-3-phenylacrylaldehyde (2k)

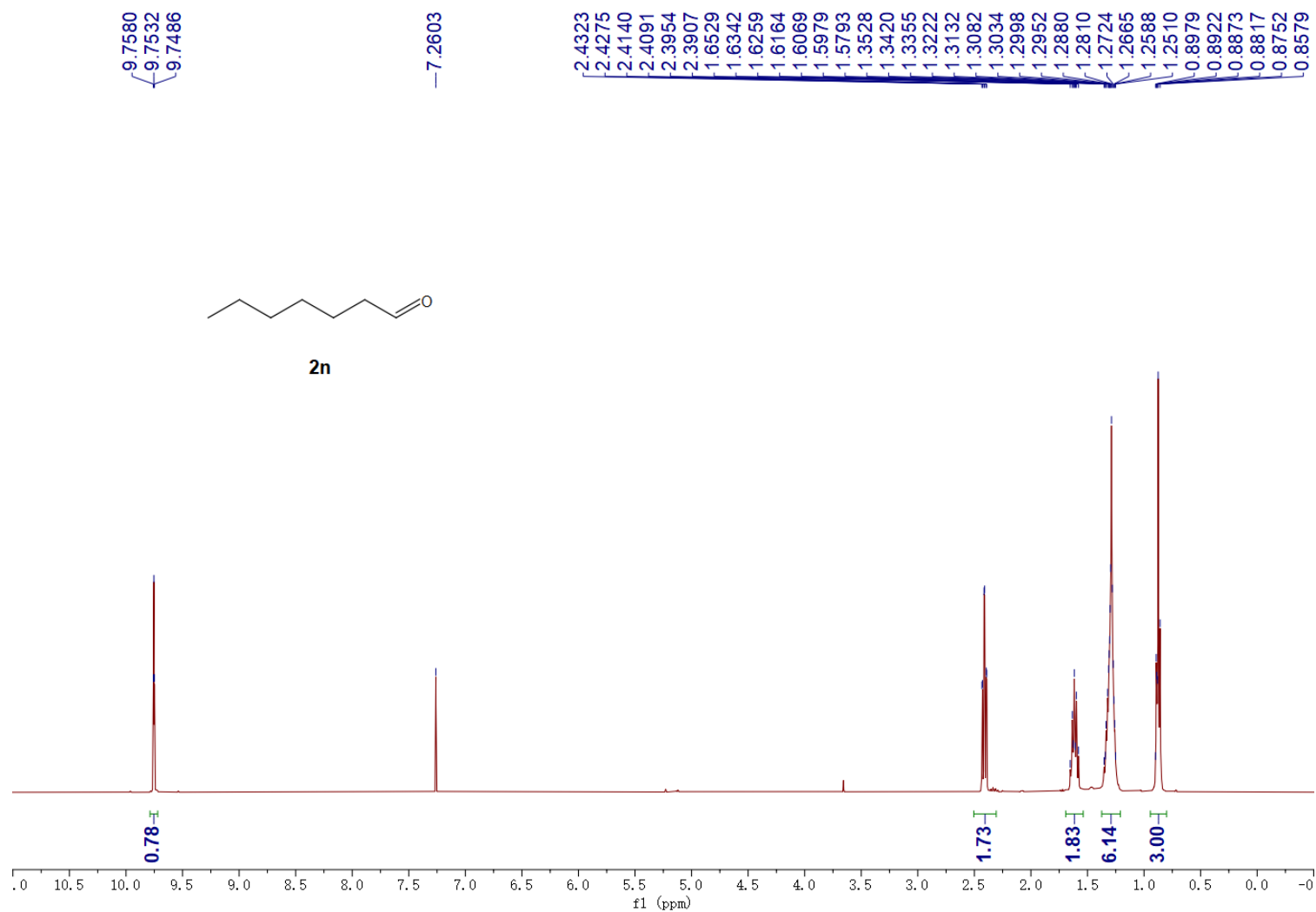
^{13}C -NMR Spectrum of (*E*)-2-Methyl-3-phenylacrylaldehyde (2k)

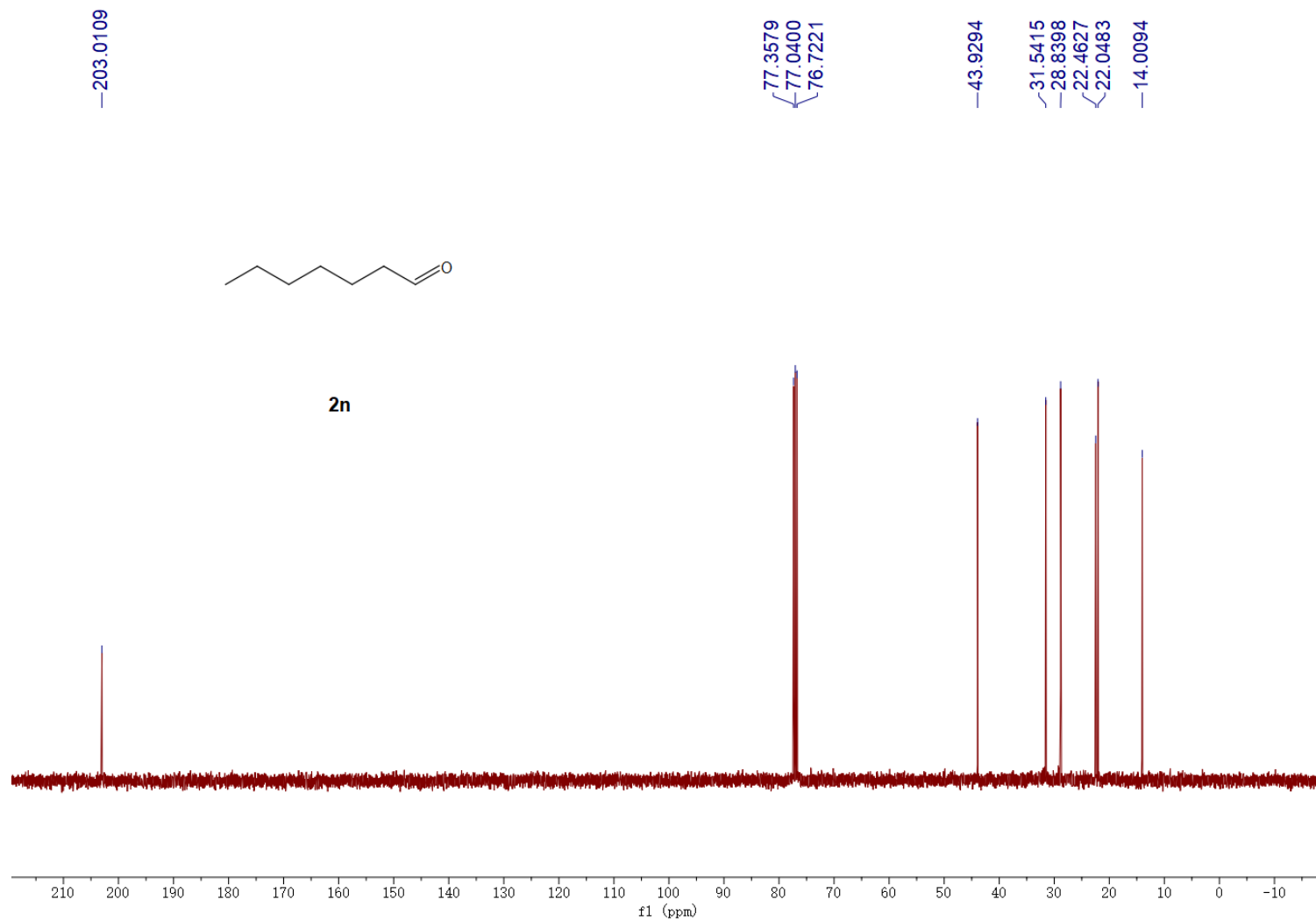
¹H-NMR Spectrum of 1-Naphthaldehyde (2I)

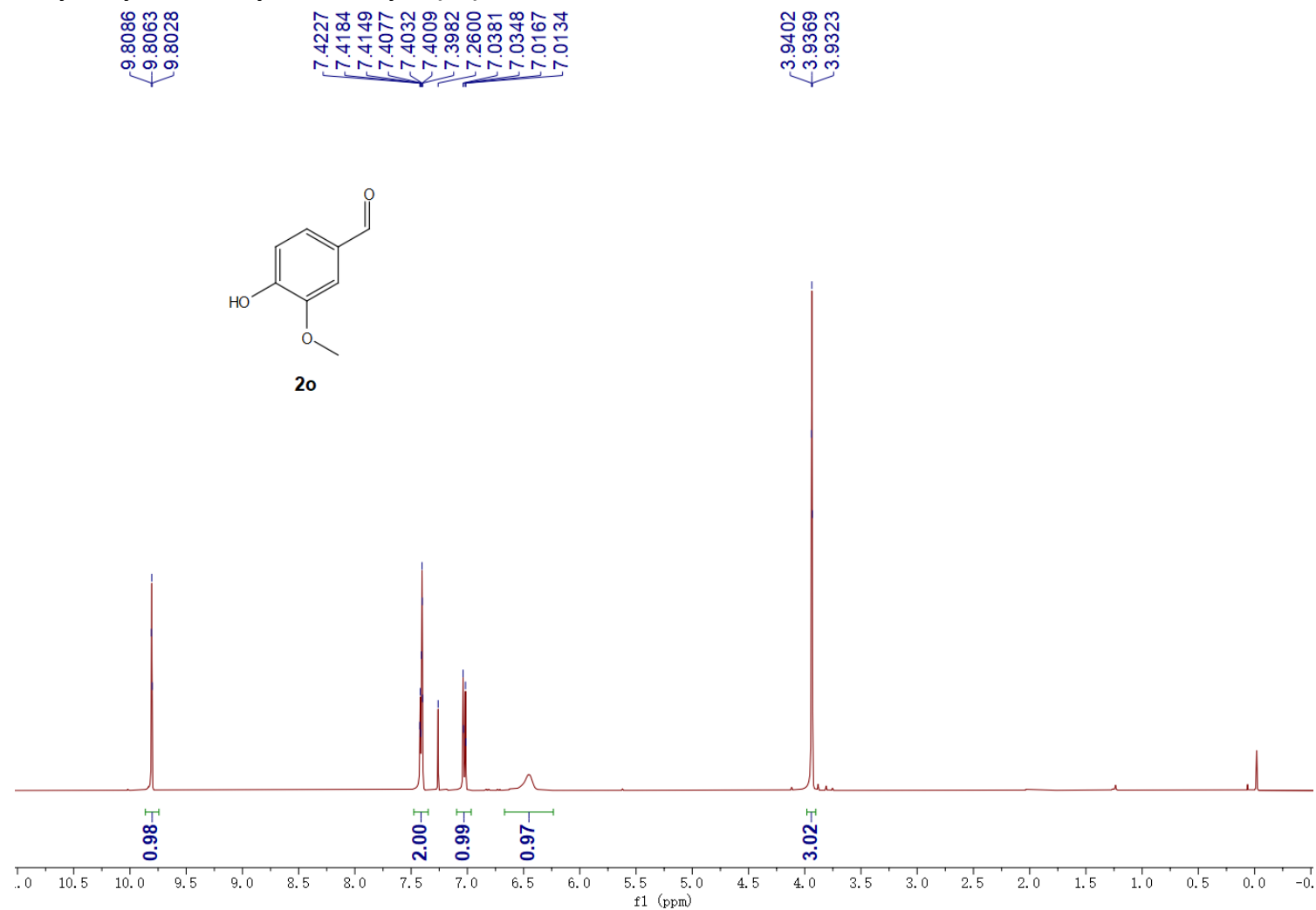
^{13}C -NMR Spectrum of 1-Naphthaldehyde (2I)

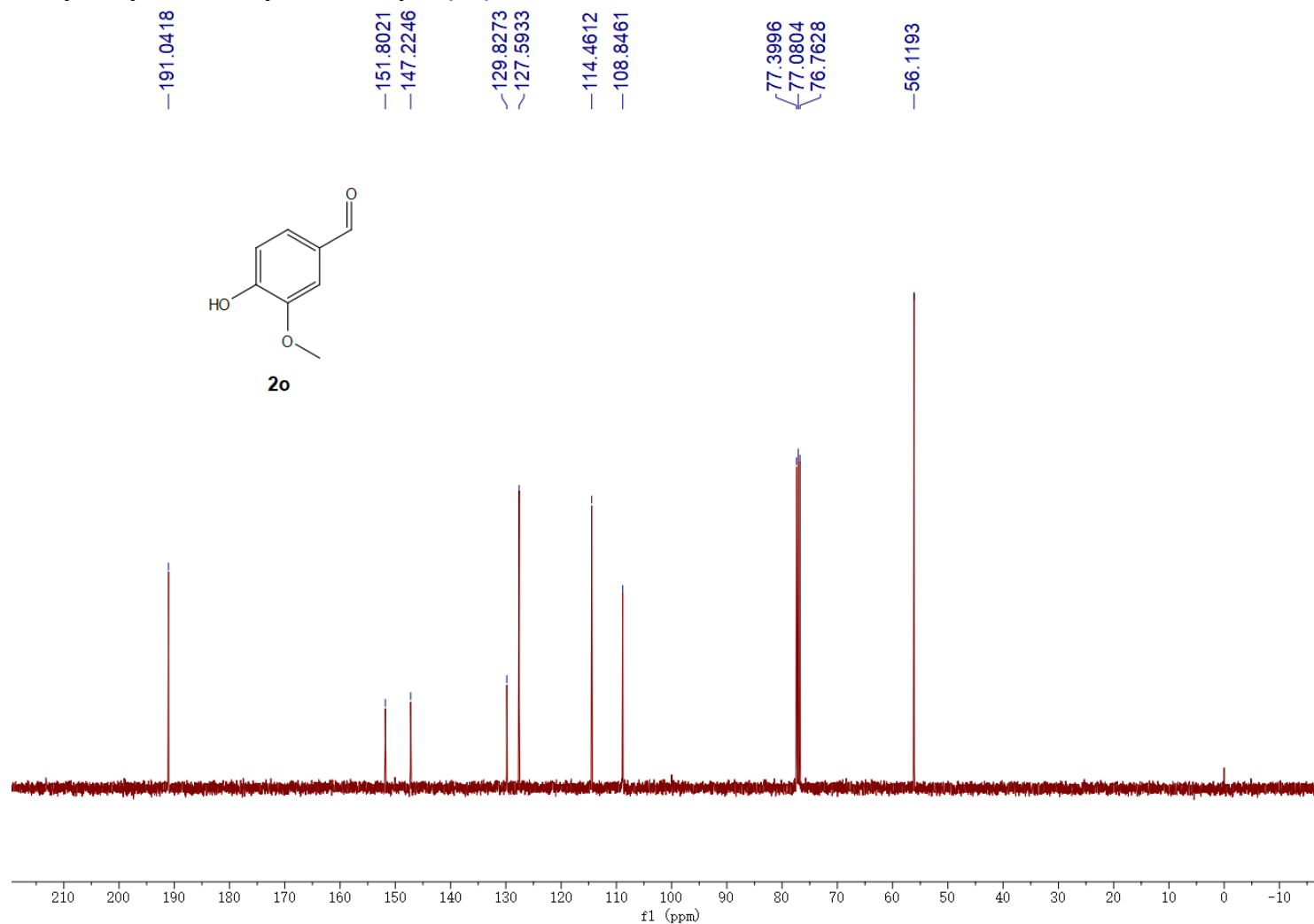
¹H-NMR Spectrum of Furan-2-carbaldehyde (2m)

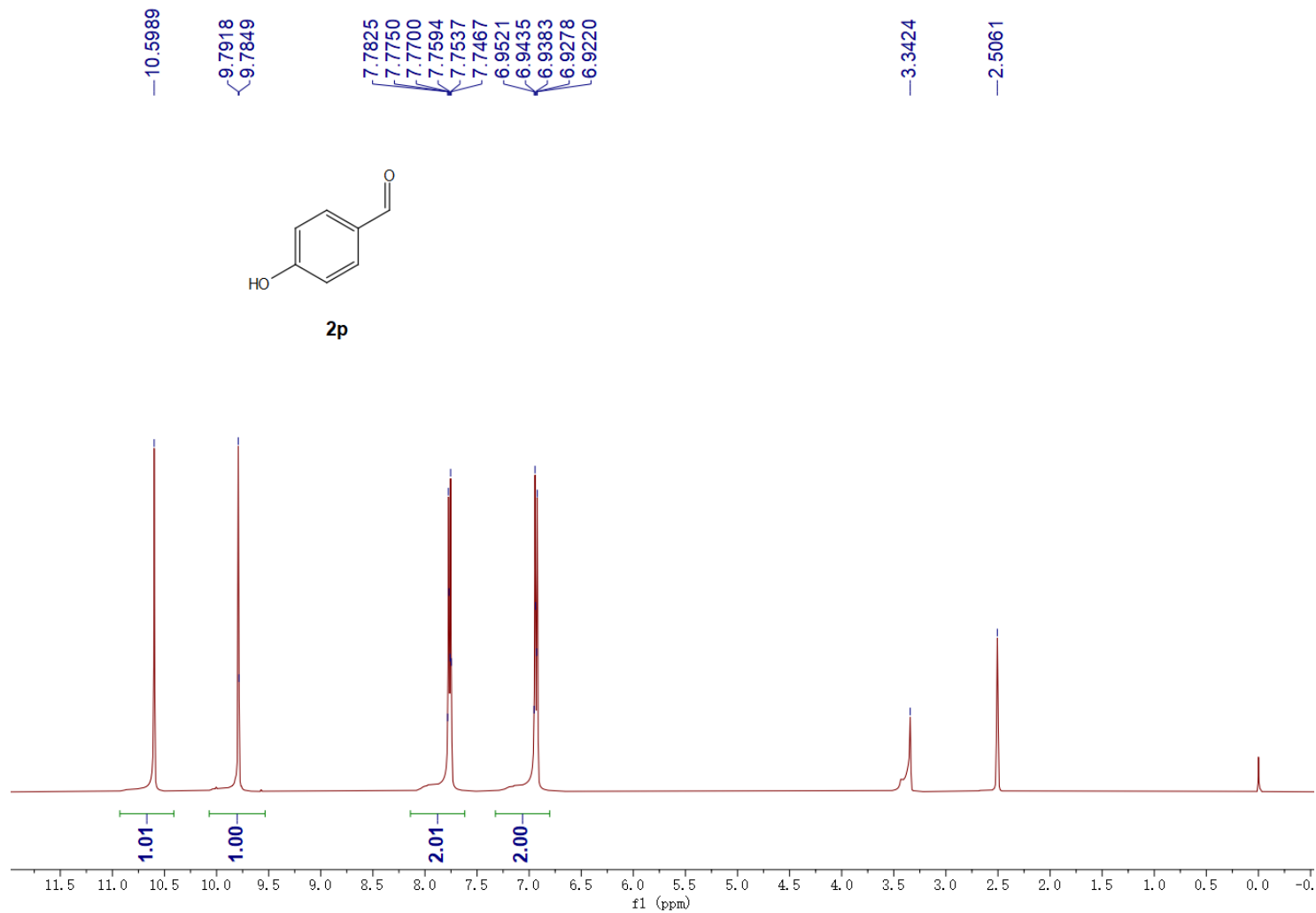
^{13}C -NMR Spectrum of Furan-2-carbaldehyde (2m)

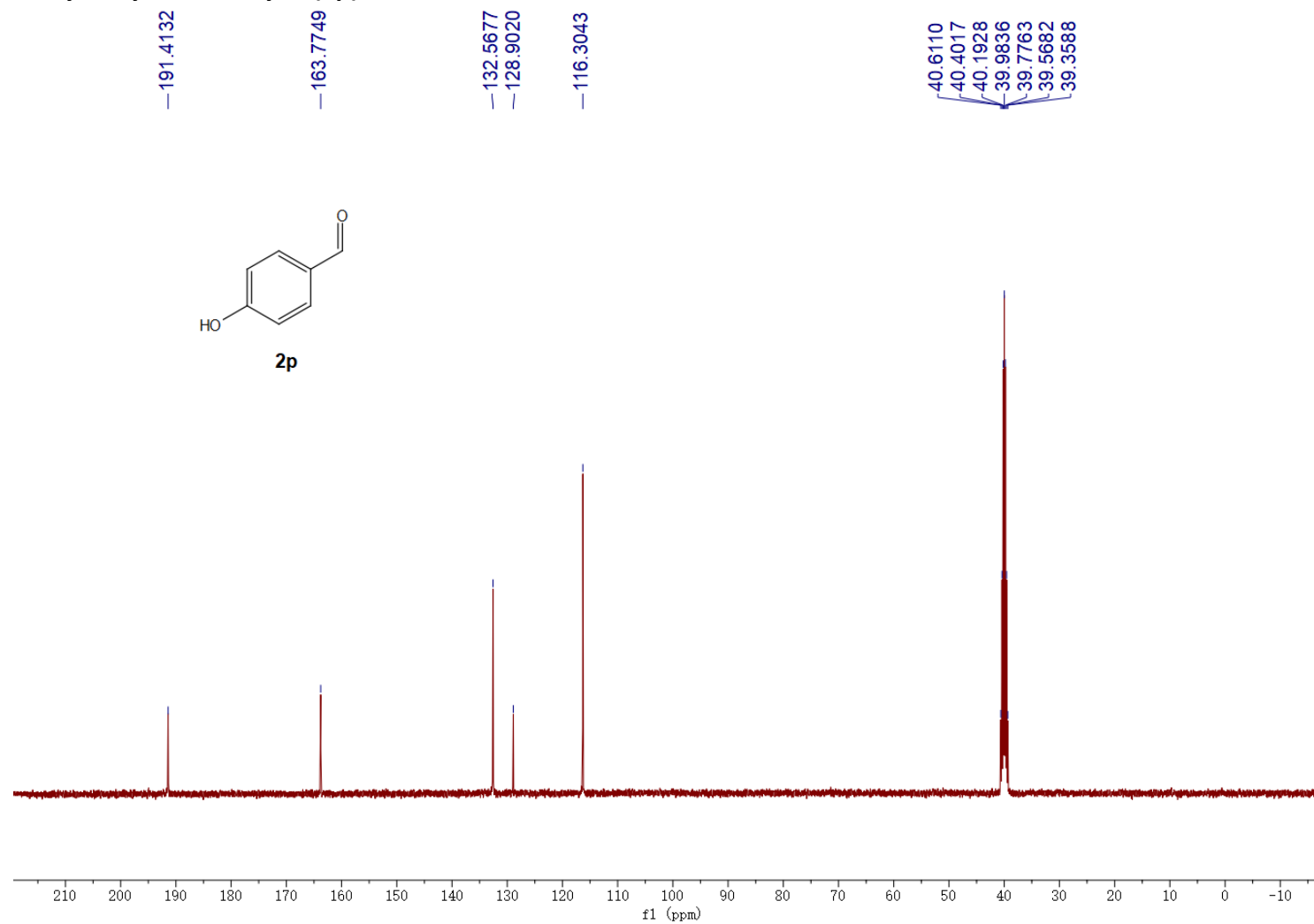
¹H-NMR Spectrum of Heptanal (2n)

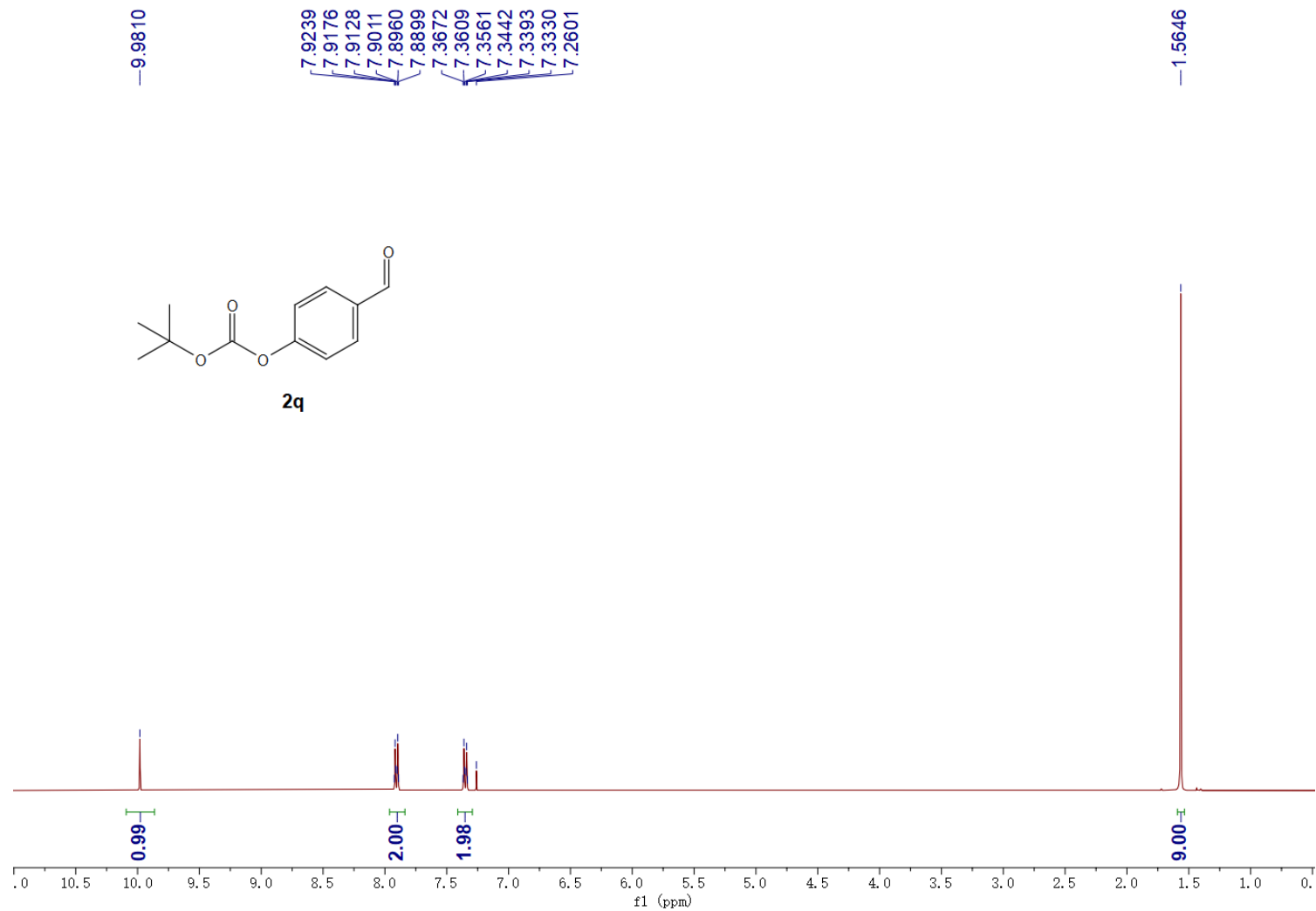
^{13}C -NMR Spectrum of Heptanal (2n)

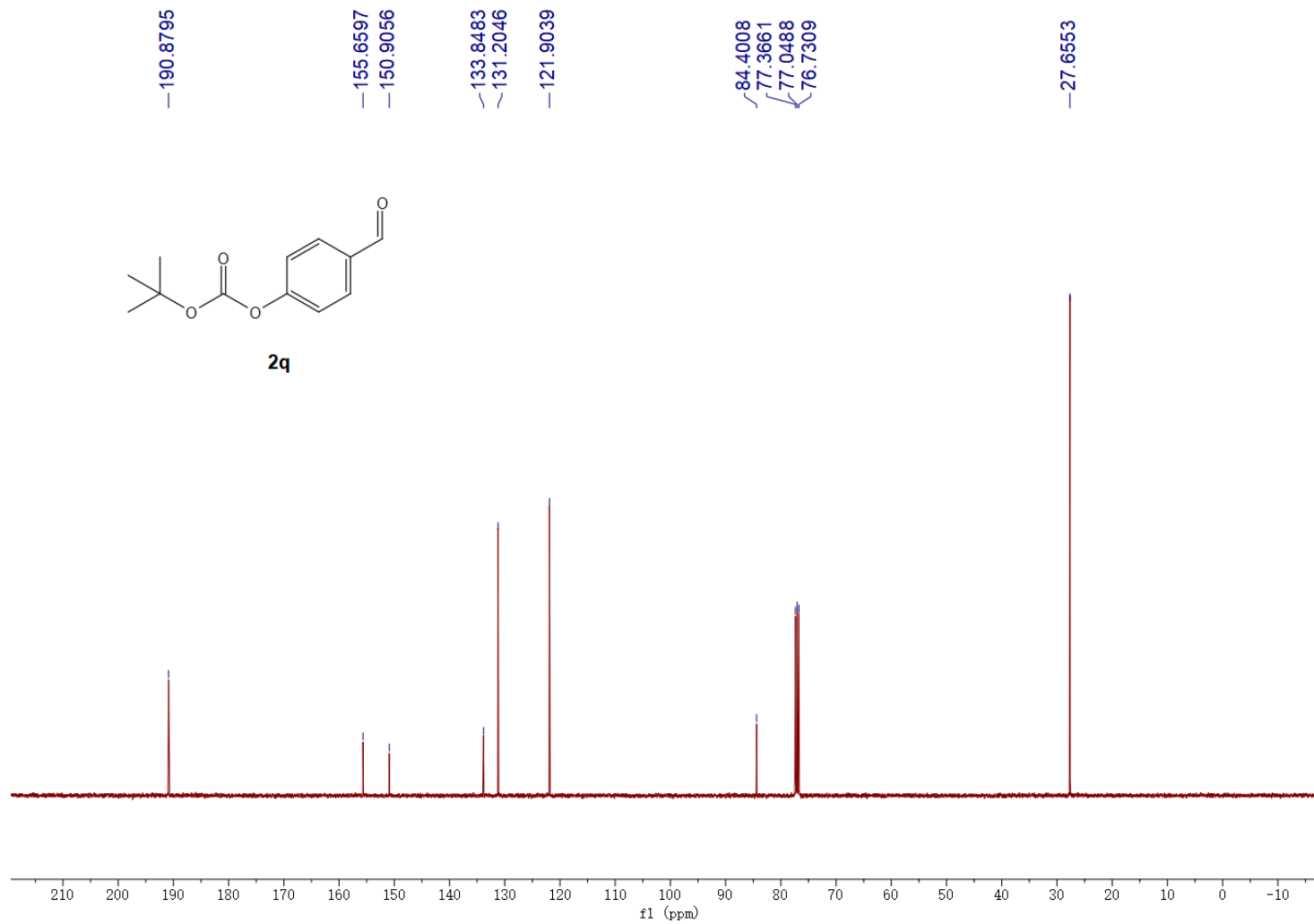
¹H-NMR Spectrum of 4-Hydroxy-3-methoxybenzaldehyde (2o)

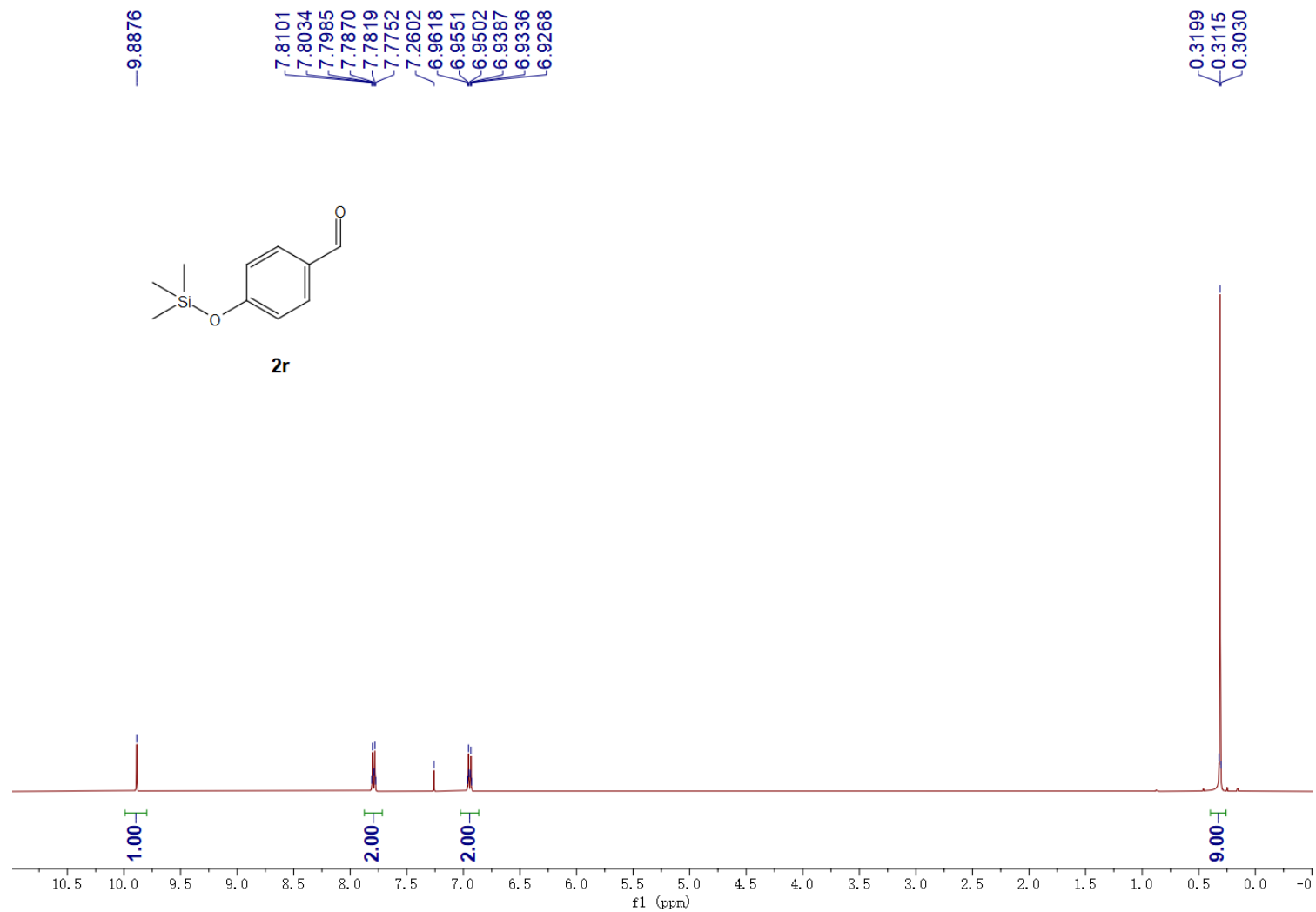
^{13}C -NMR Spectrum of 4-Hydroxy-3-methoxybenzaldehyde (2o)

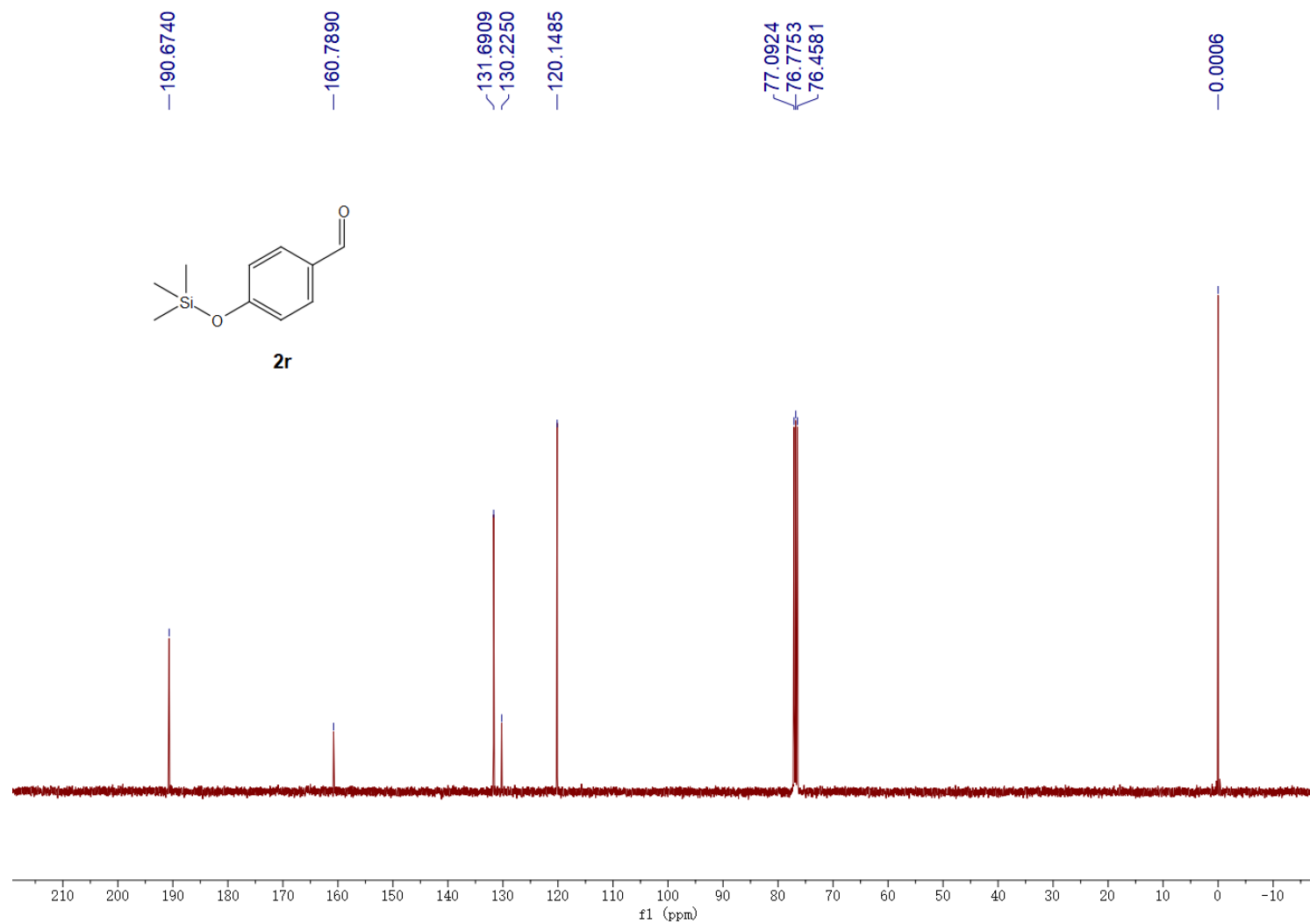
¹H-NMR Spectrum of 4-Hydroxybenzaldehyde (2p)

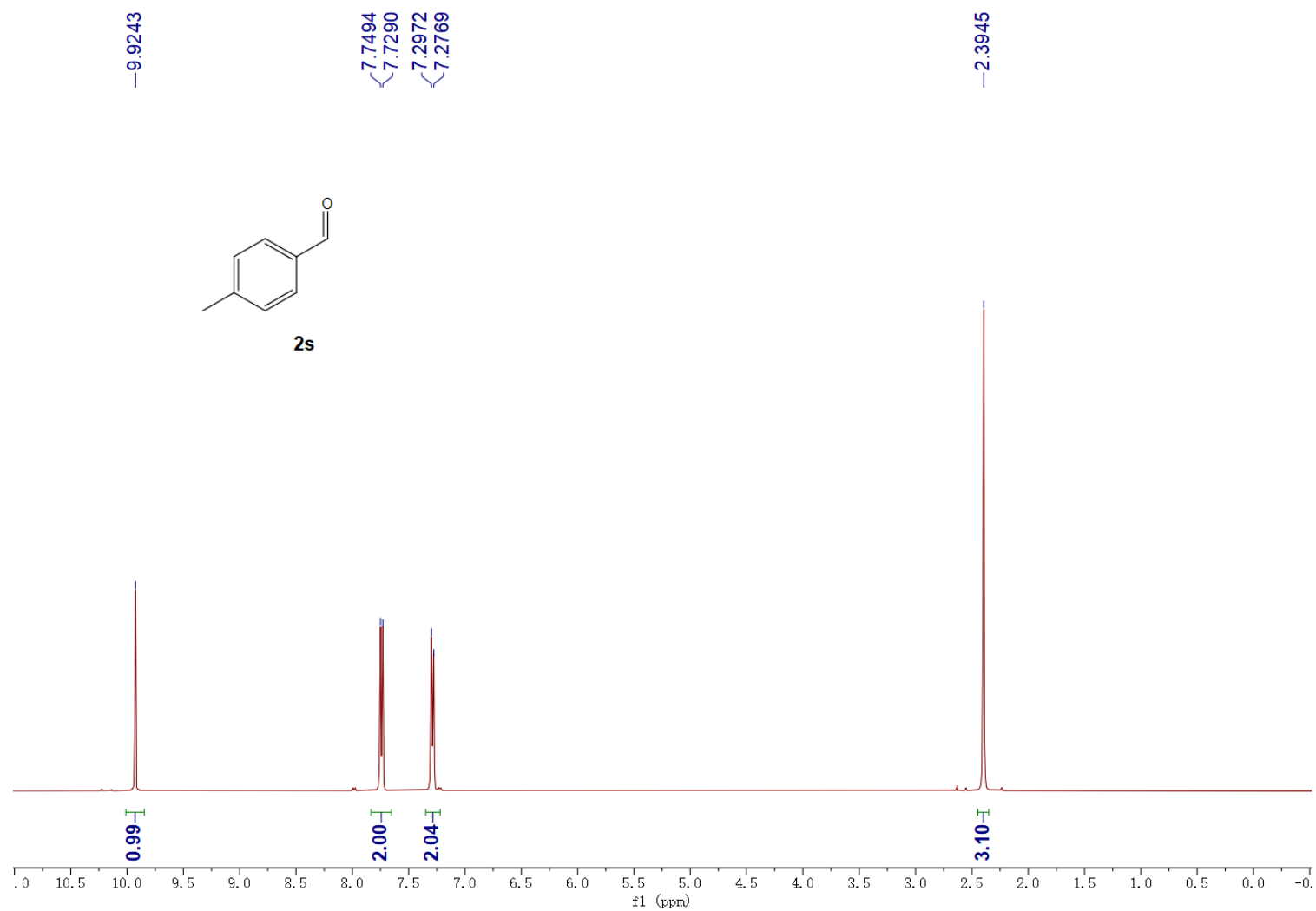
^{13}C -NMR Spectrum of 4-Hydroxybenzaldehyde (2p)

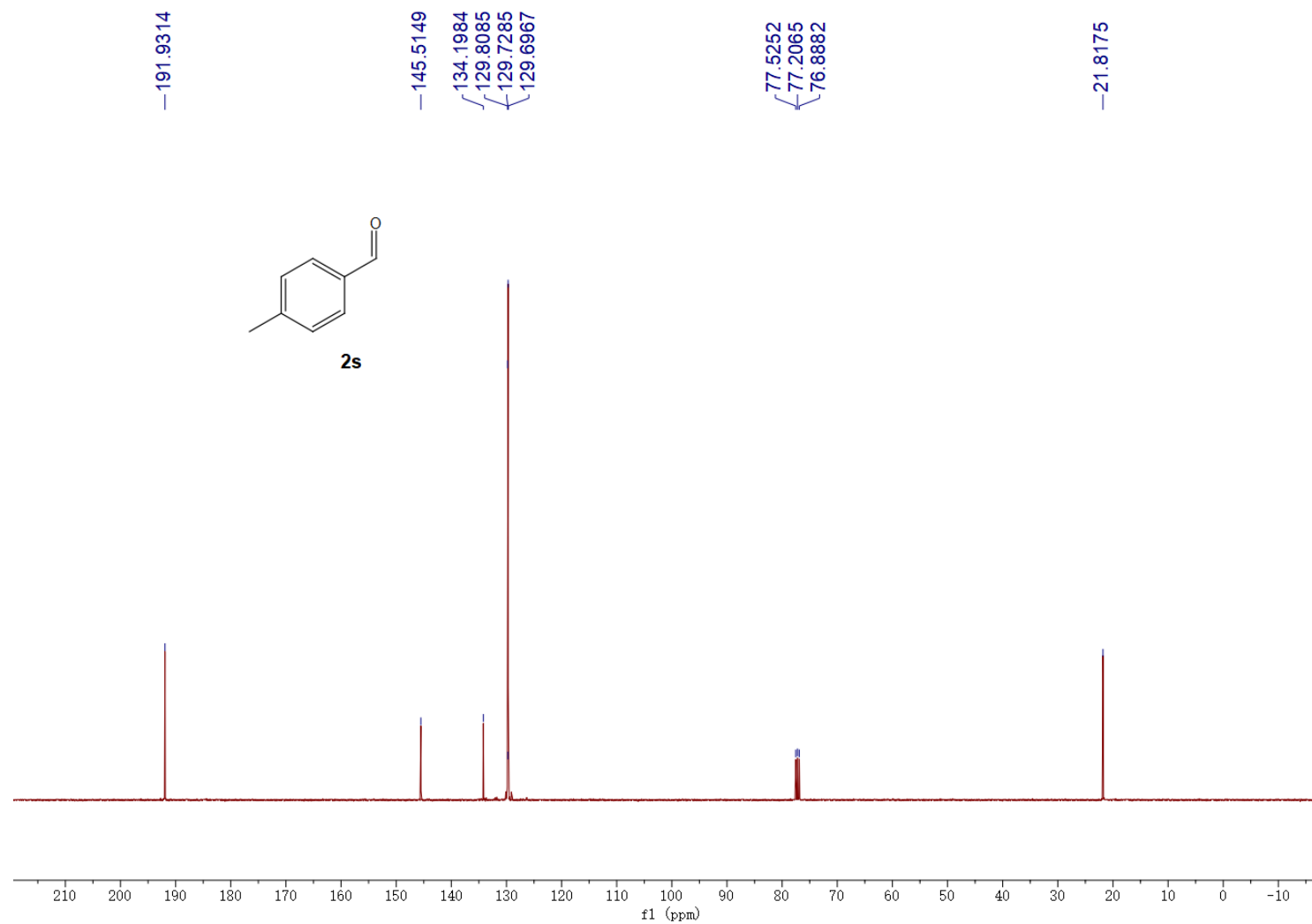
¹H-NMR Spectrum of *Tert*-butyl (4-formylphenyl) carbonate (2q)

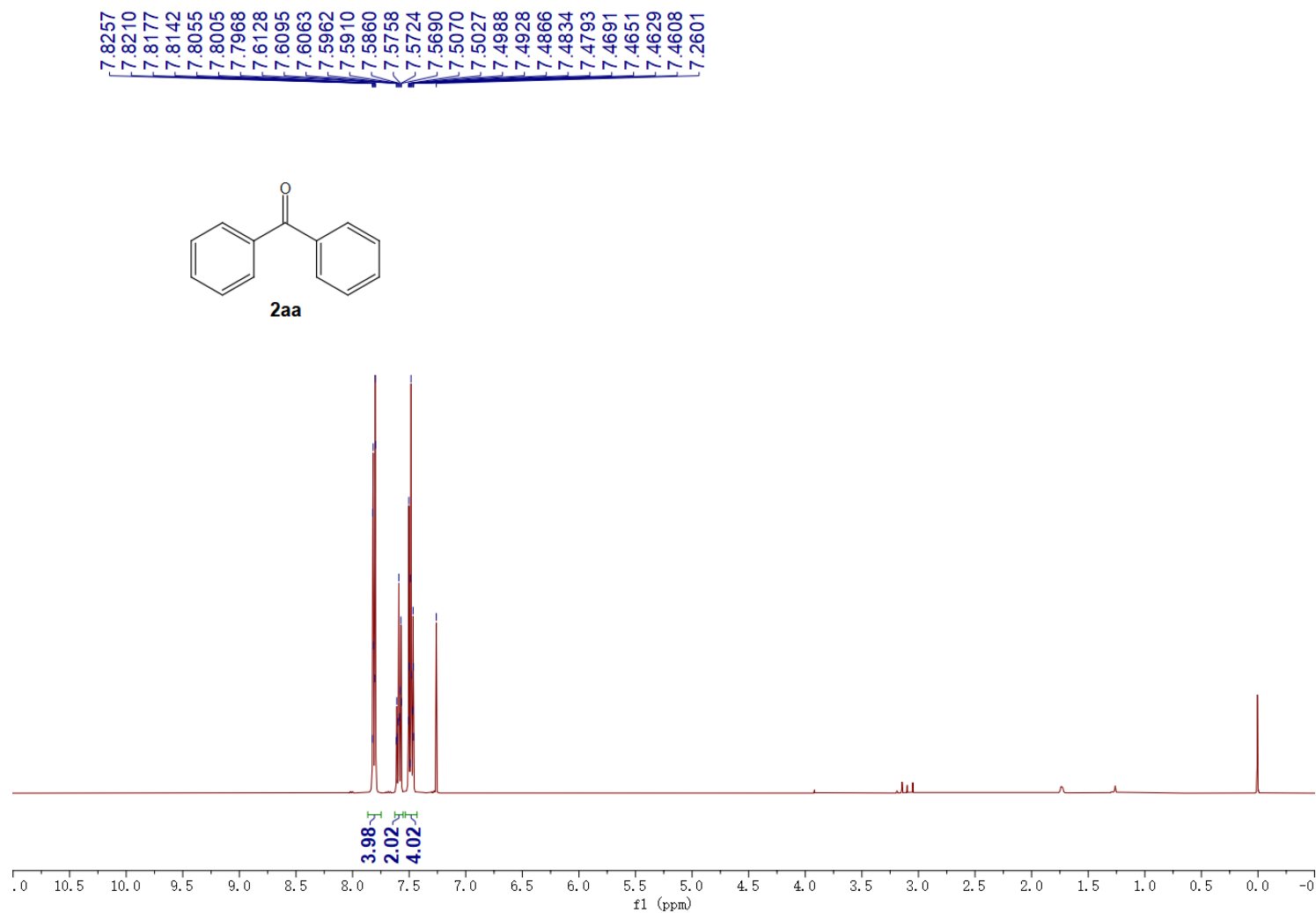
^{13}C -NMR Spectrum of *Tert*-butyl (4-formylphenyl) carbonate (2q)

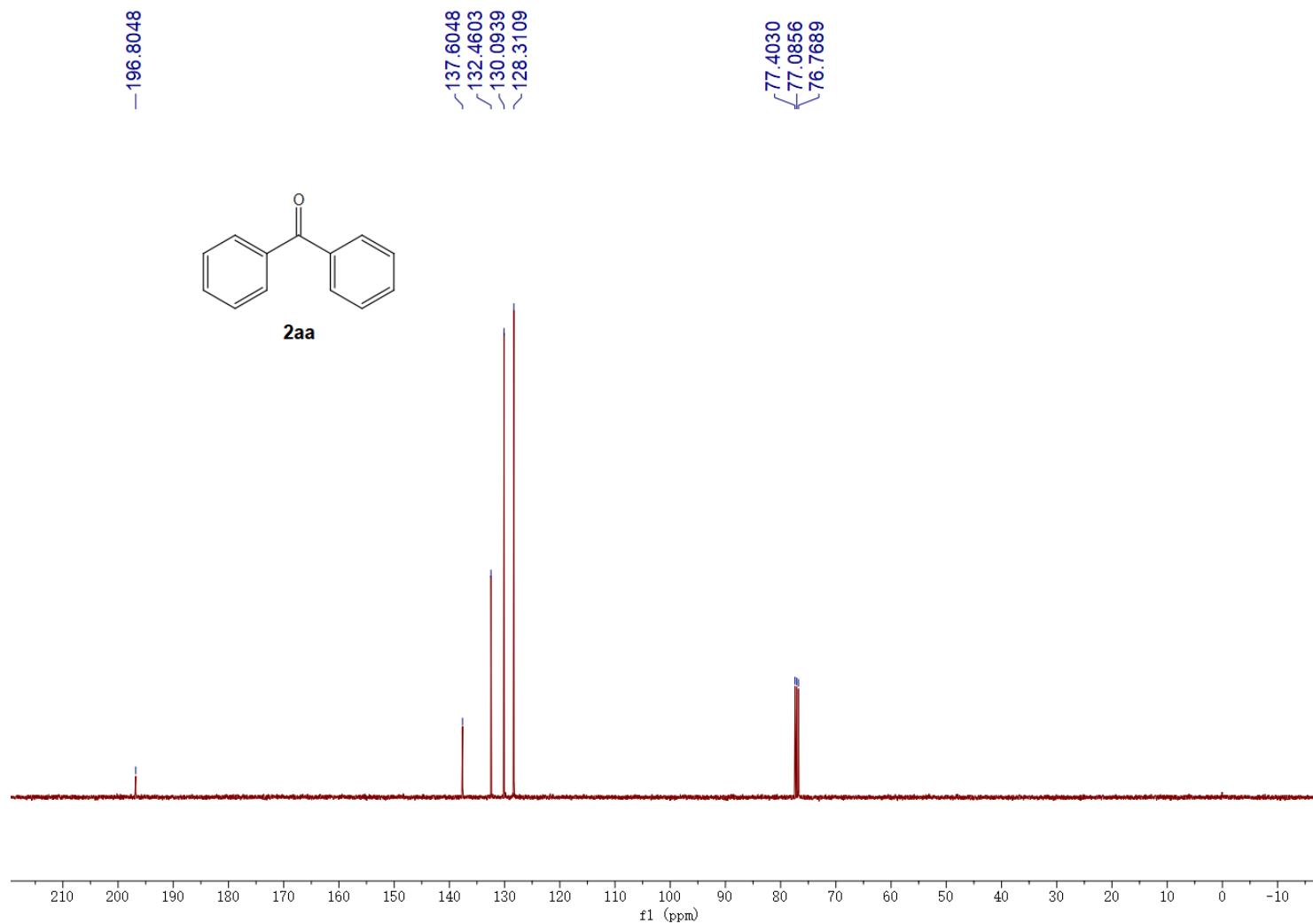
¹H-NMR Spectrum of 4-((Trimethylsilyl)oxy)benzaldehyde (2r)

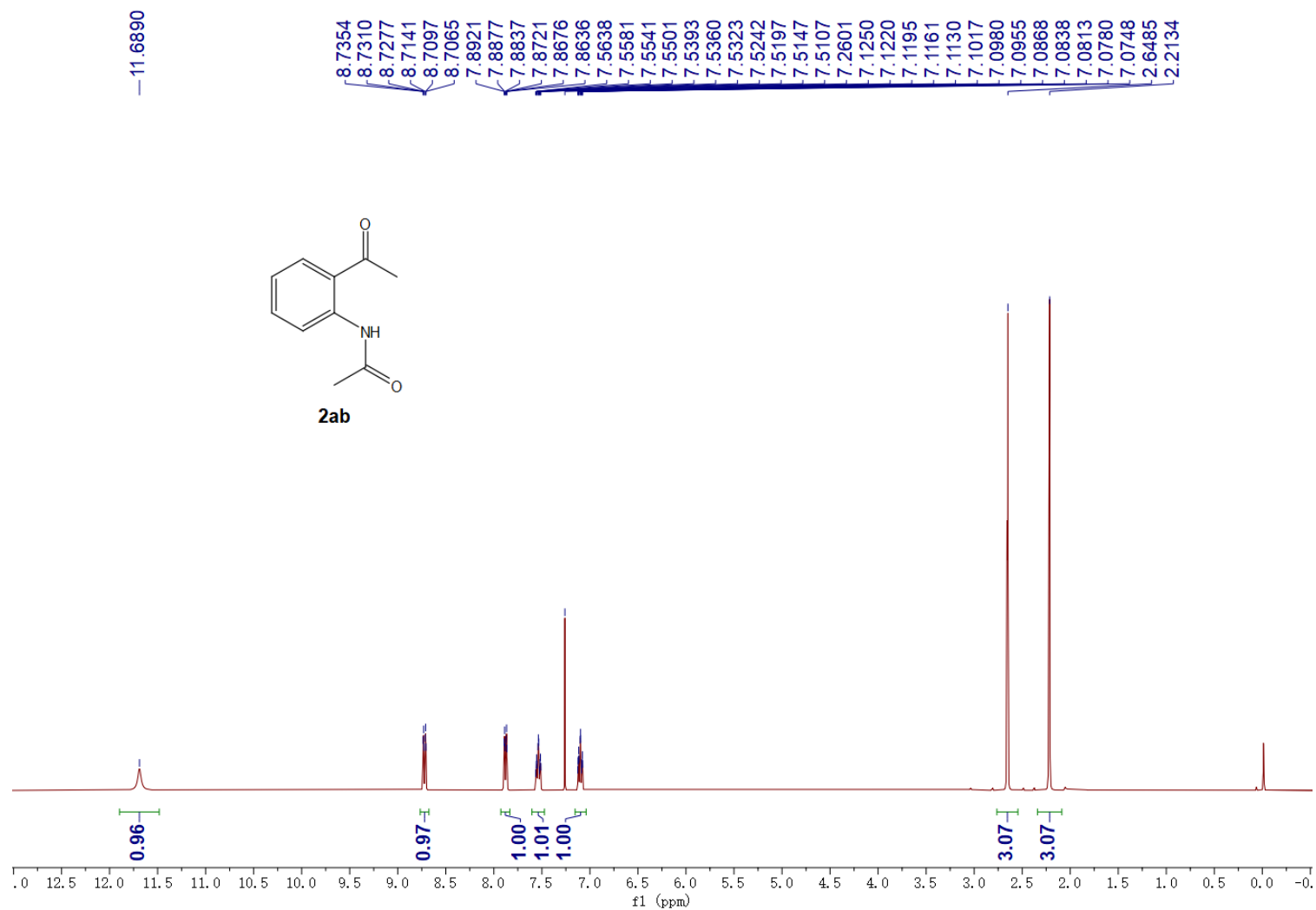
^{13}C -NMR Spectrum of 4-((Trimethylsilyl)oxy)benzaldehyde (2r)

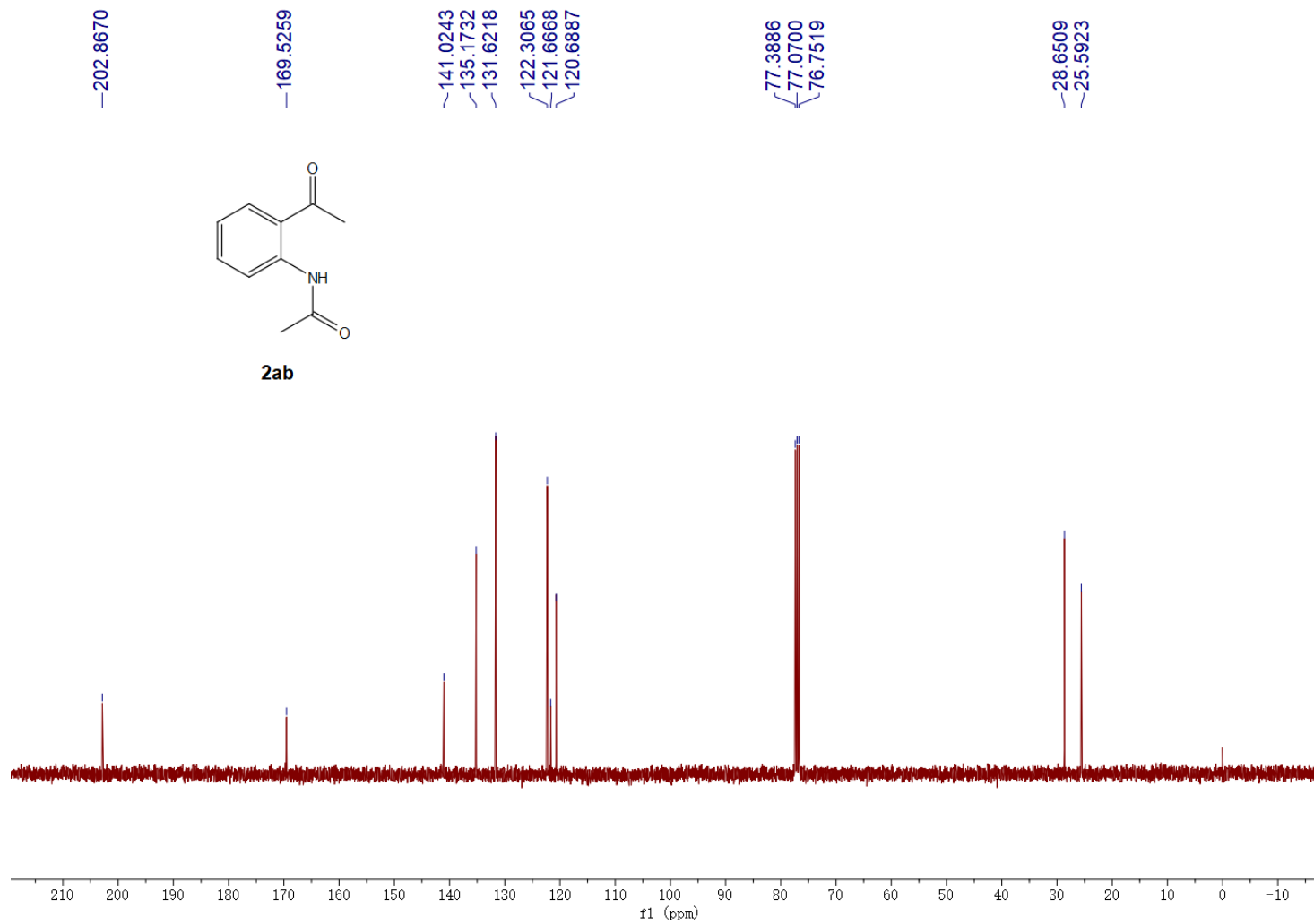
¹H-NMR Spectrum of 4-Methylbenzaldehyde (2s)

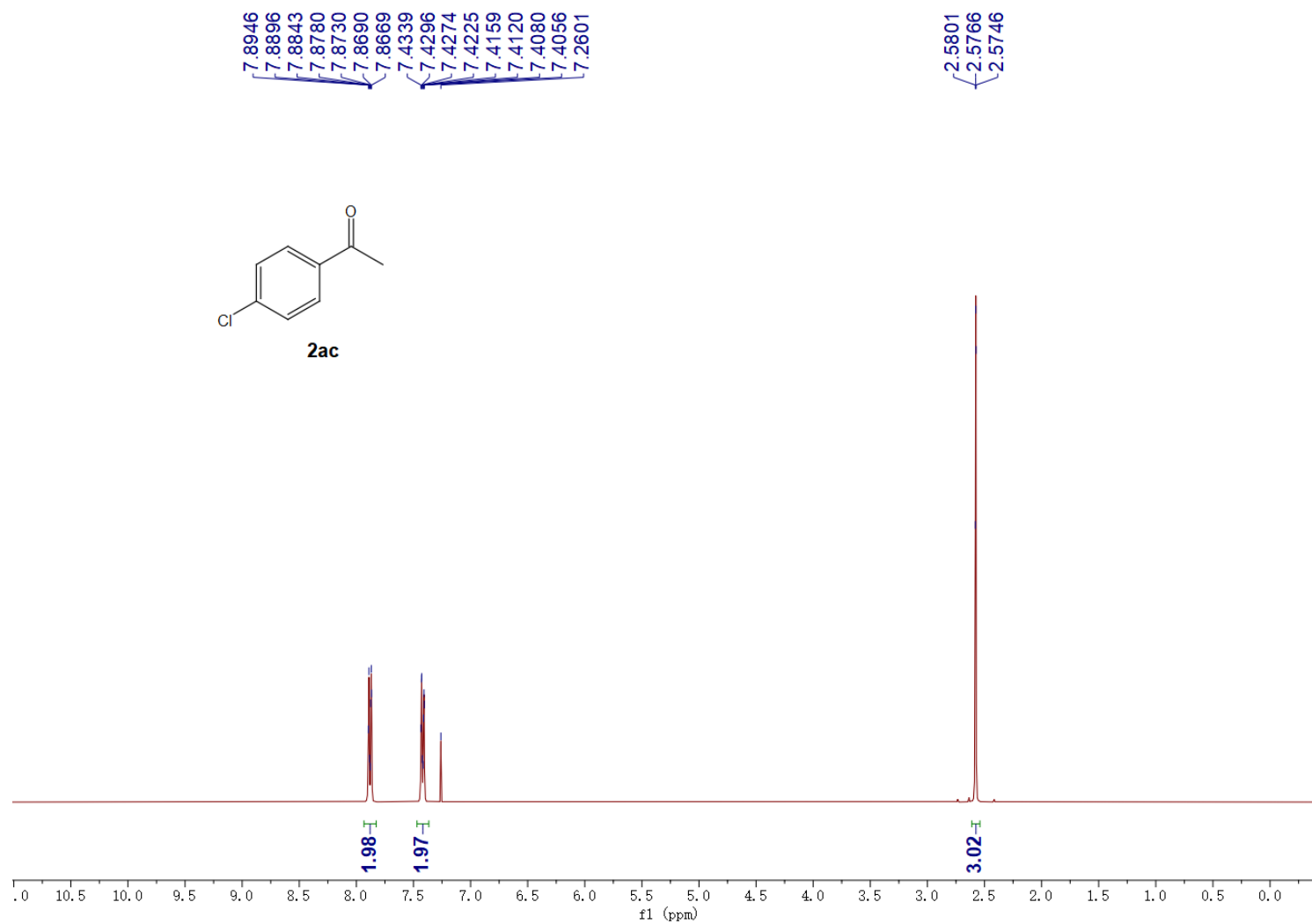
^{13}C -NMR Spectrum of 4-Methylbenzaldehyde (2s)

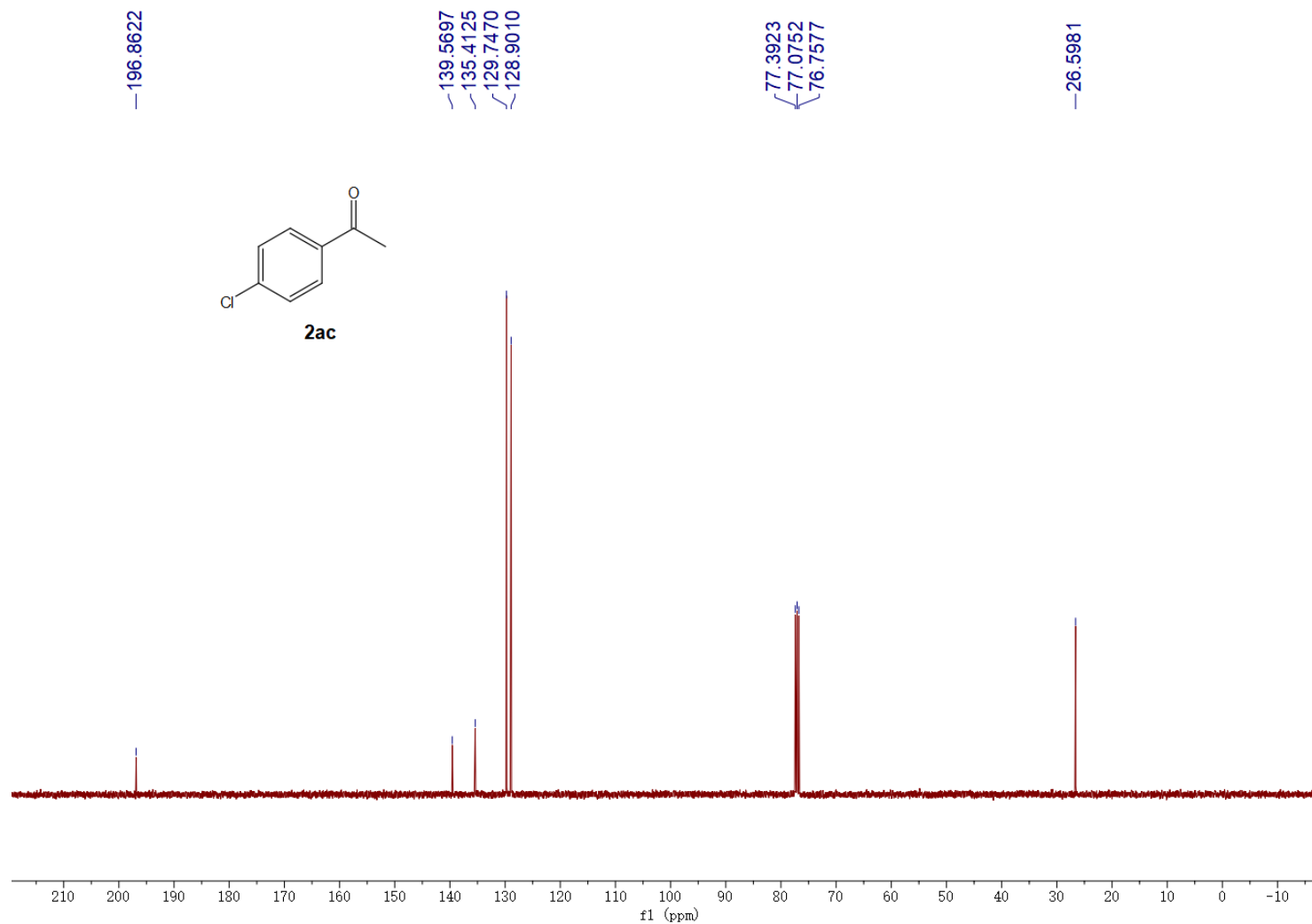
¹H-NMR Spectrum of Benzophenone (2aa)

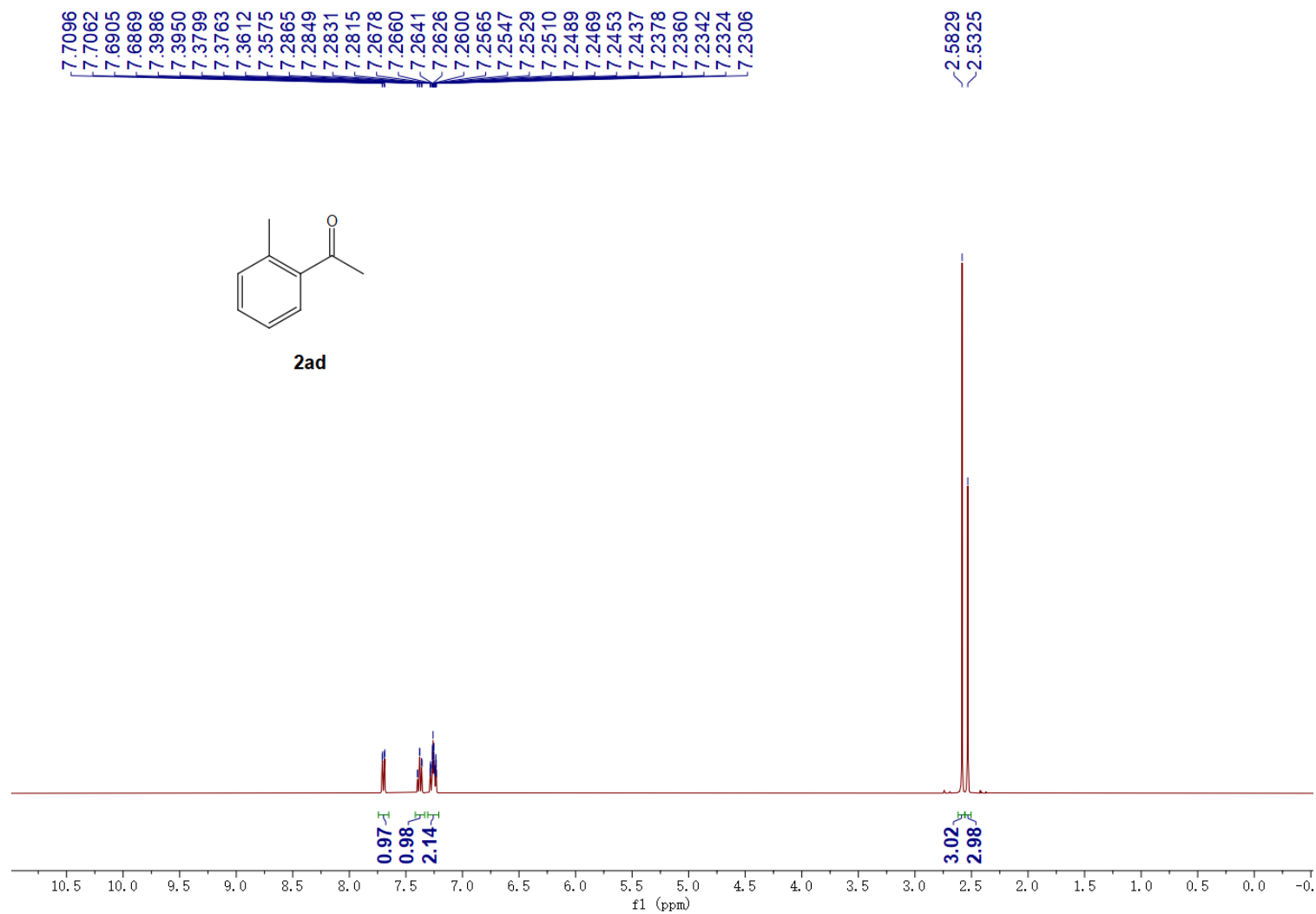
^{13}C -NMR Spectrum of Benzophenone (2aa)

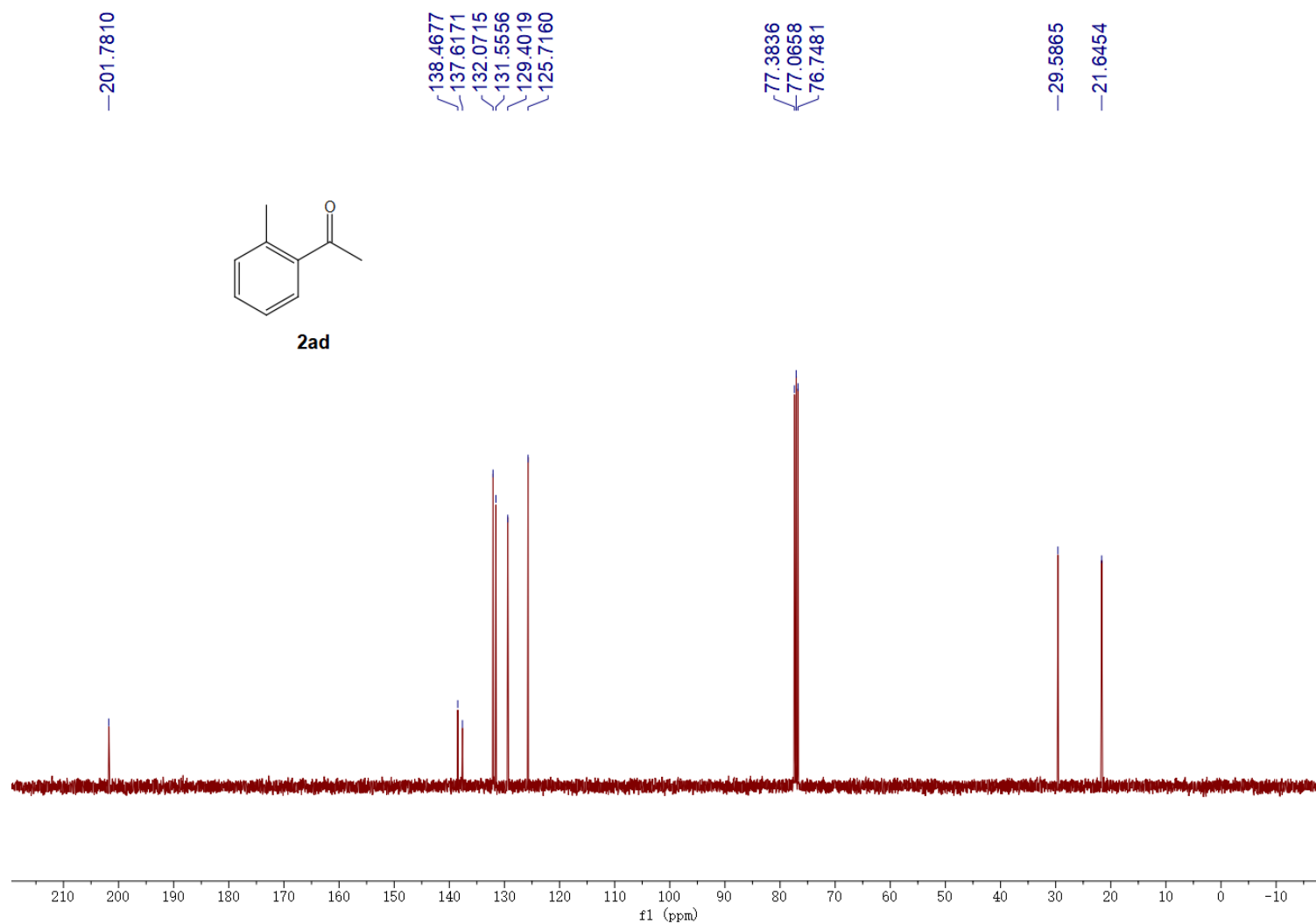
¹H-NMR Spectrum of *N*-(2-Acetylphenyl)acetamide (2ab)

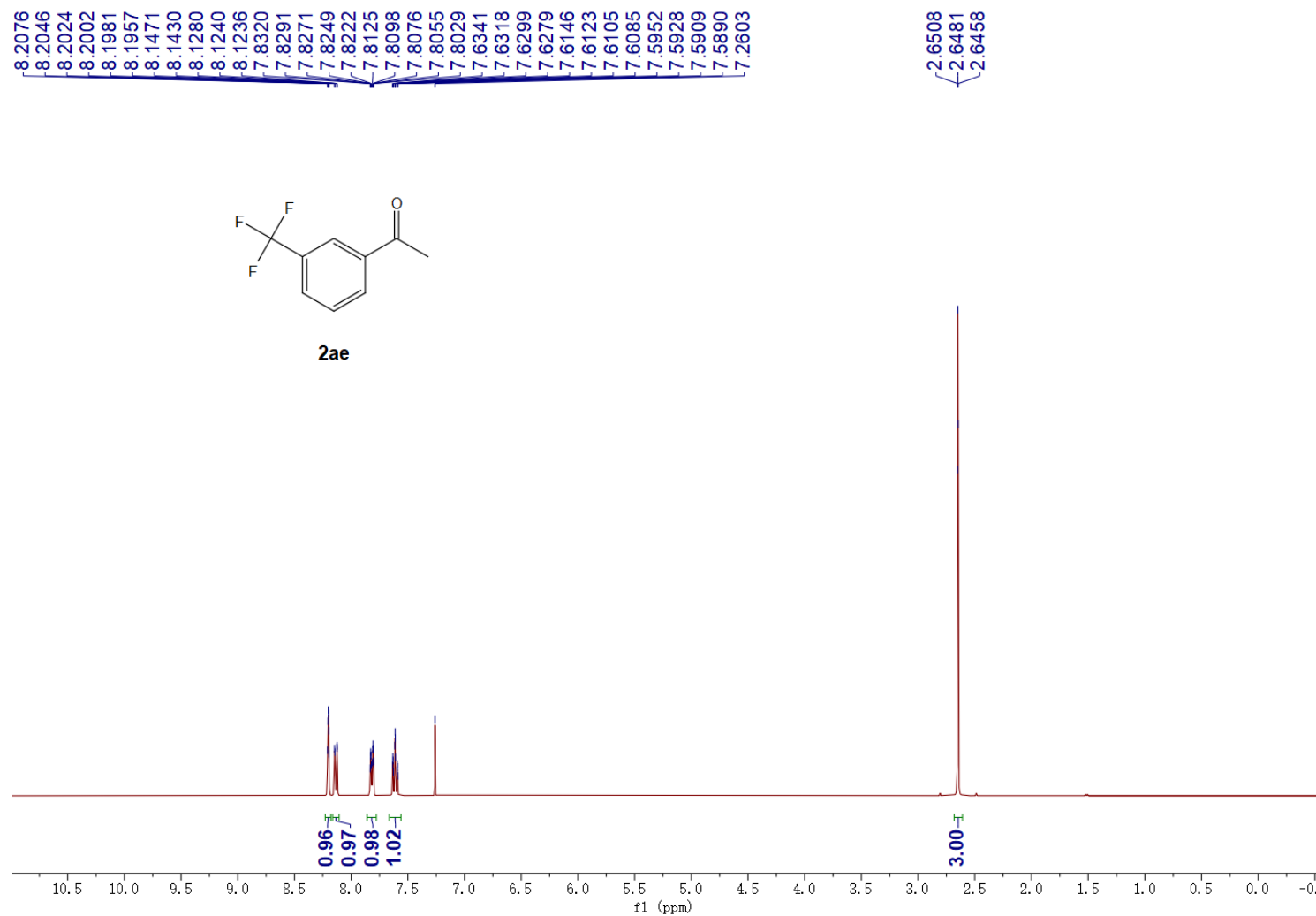
^{13}C -NMR Spectrum of *N*-(2-Acetylphenyl)acetamide (2ab)

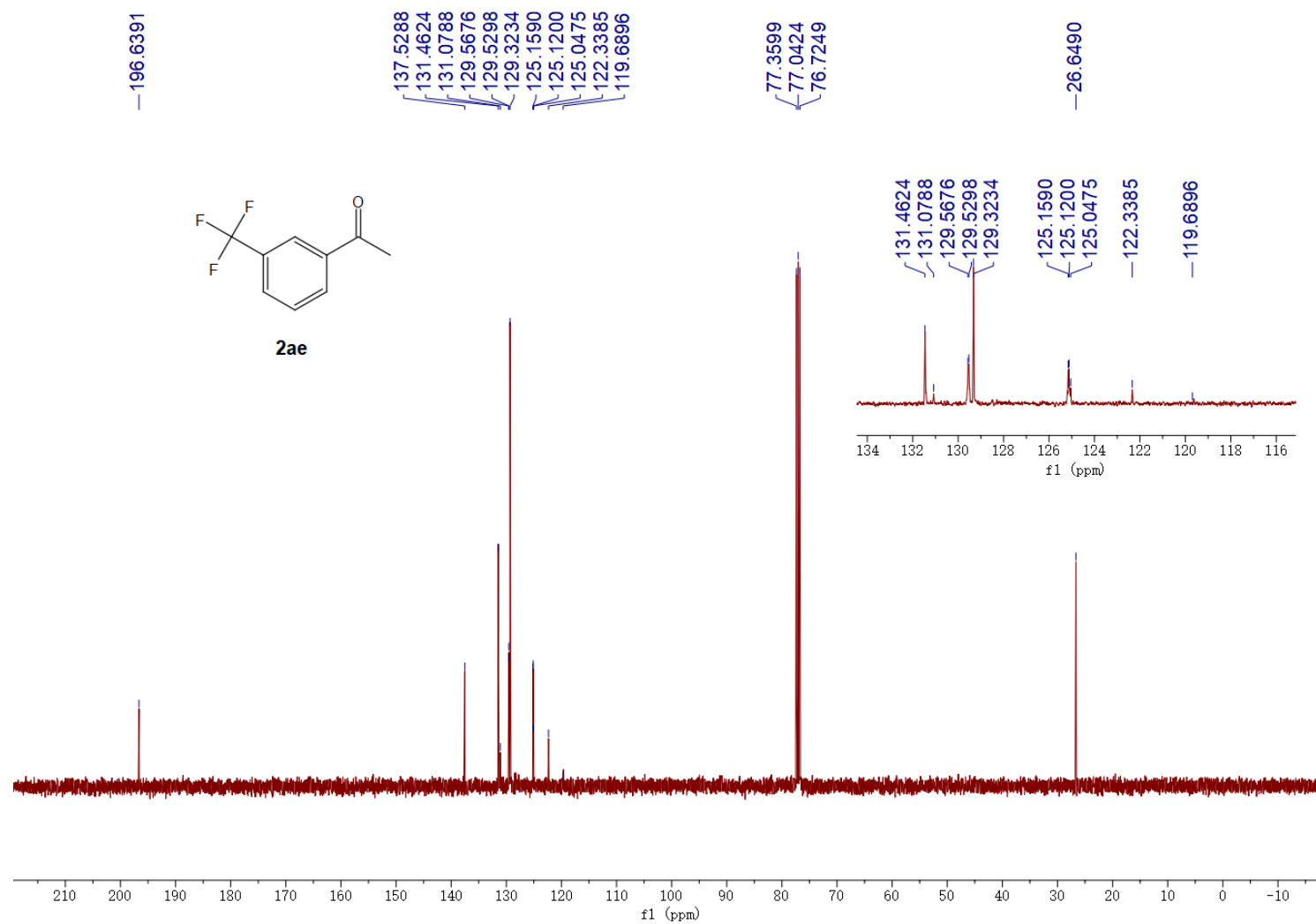
¹H-NMR Spectrum of 1-(4-Chlorophenyl)ethan-1-one (2ac)

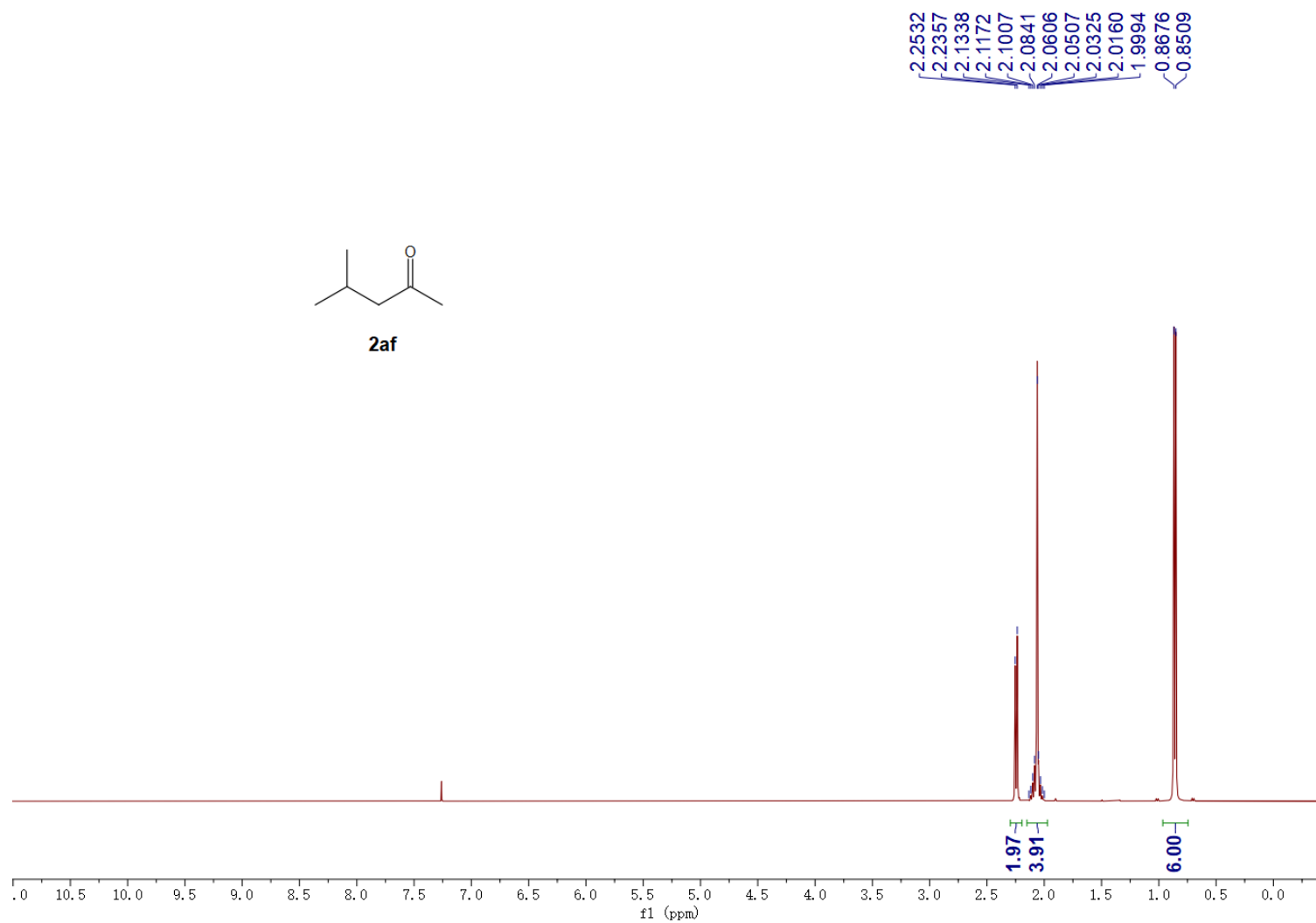
^{13}C -NMR Spectrum of 1-(4-Chlorophenyl)ethan-1-one (2ac)

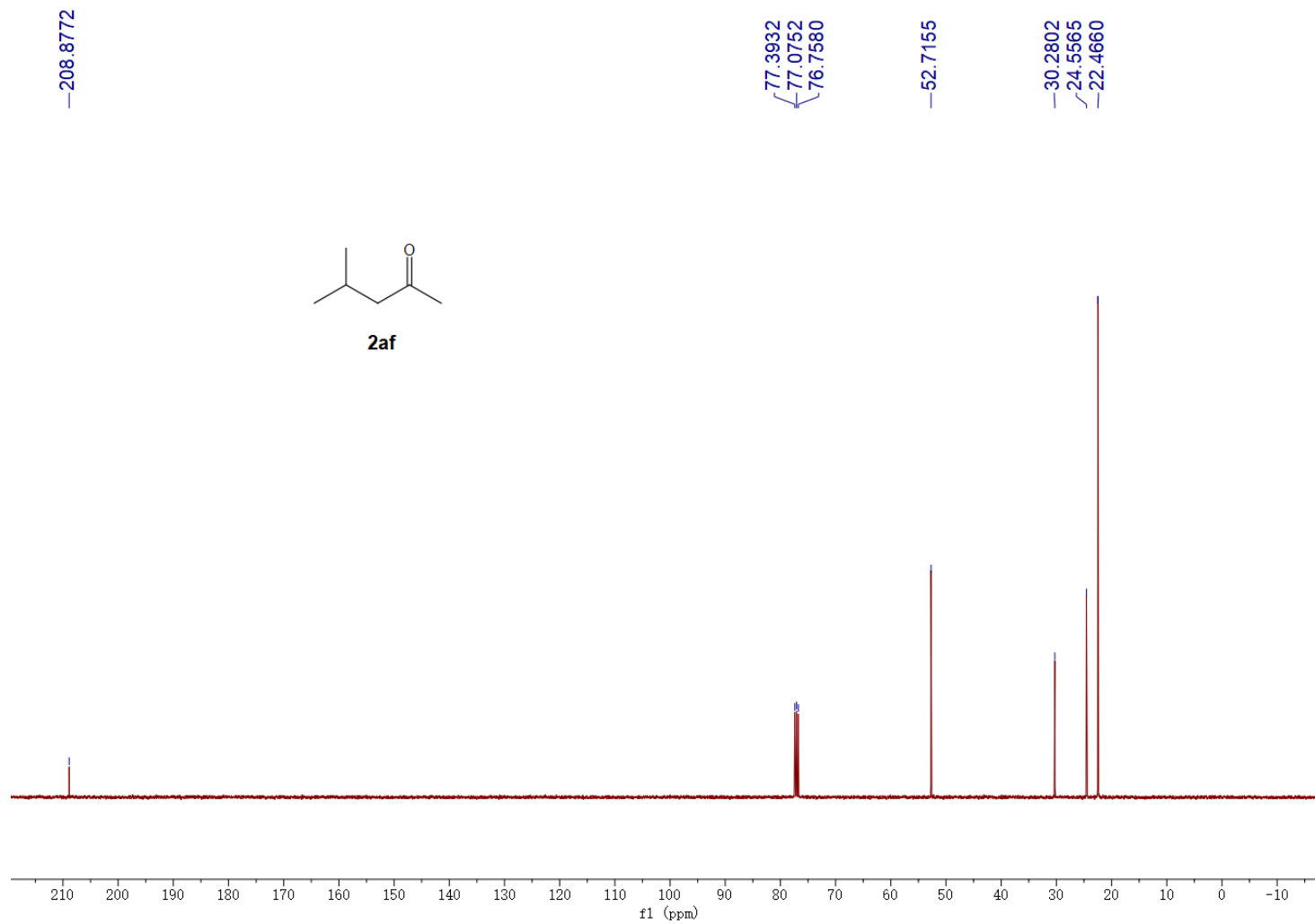
¹H-NMR Spectrum of 1-(*o*-Tolyl)ethan-1-one (2ad)

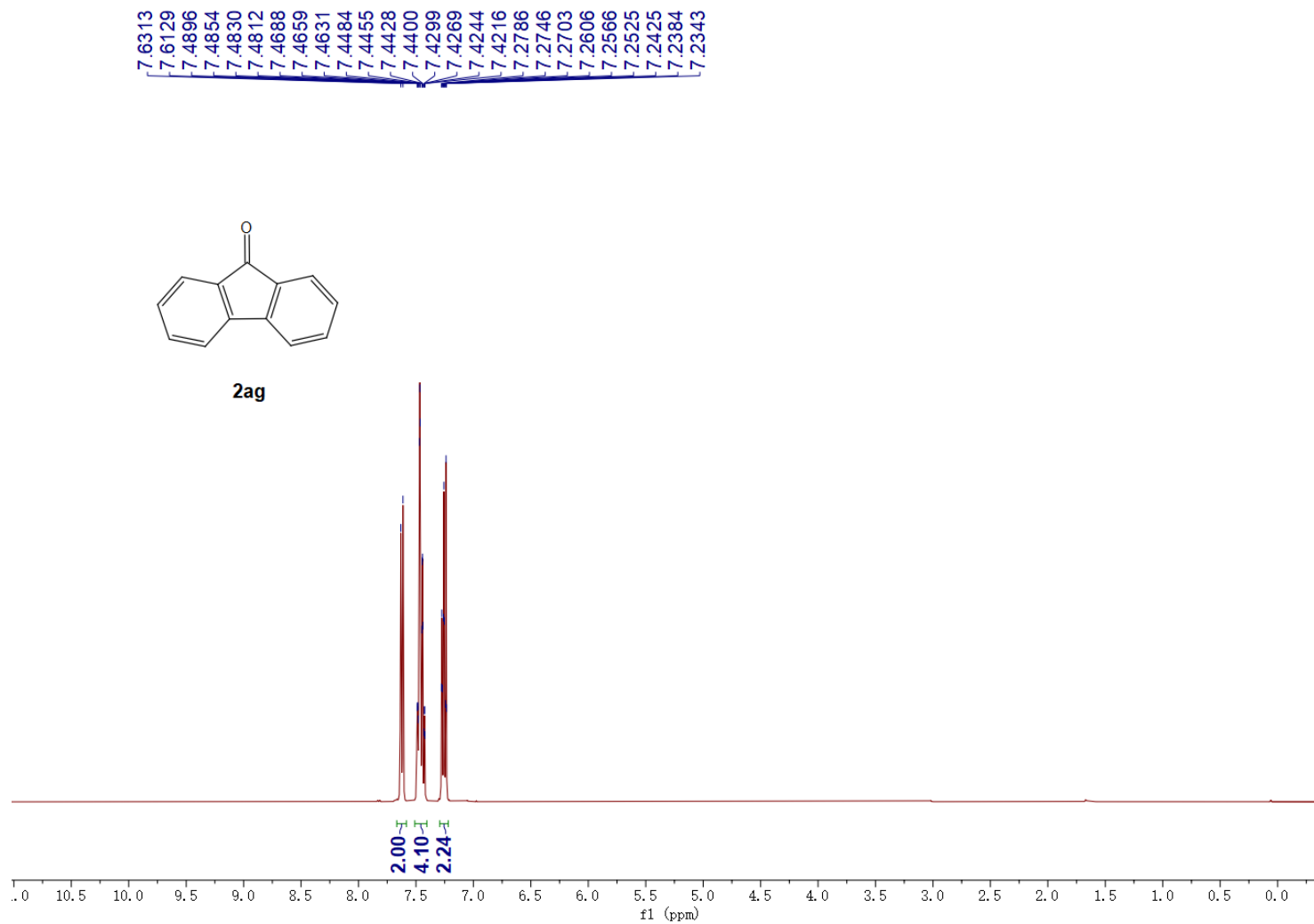
^{13}C -NMR Spectrum of 1-(*o*-Tolyl)ethan-1-one (2ad)

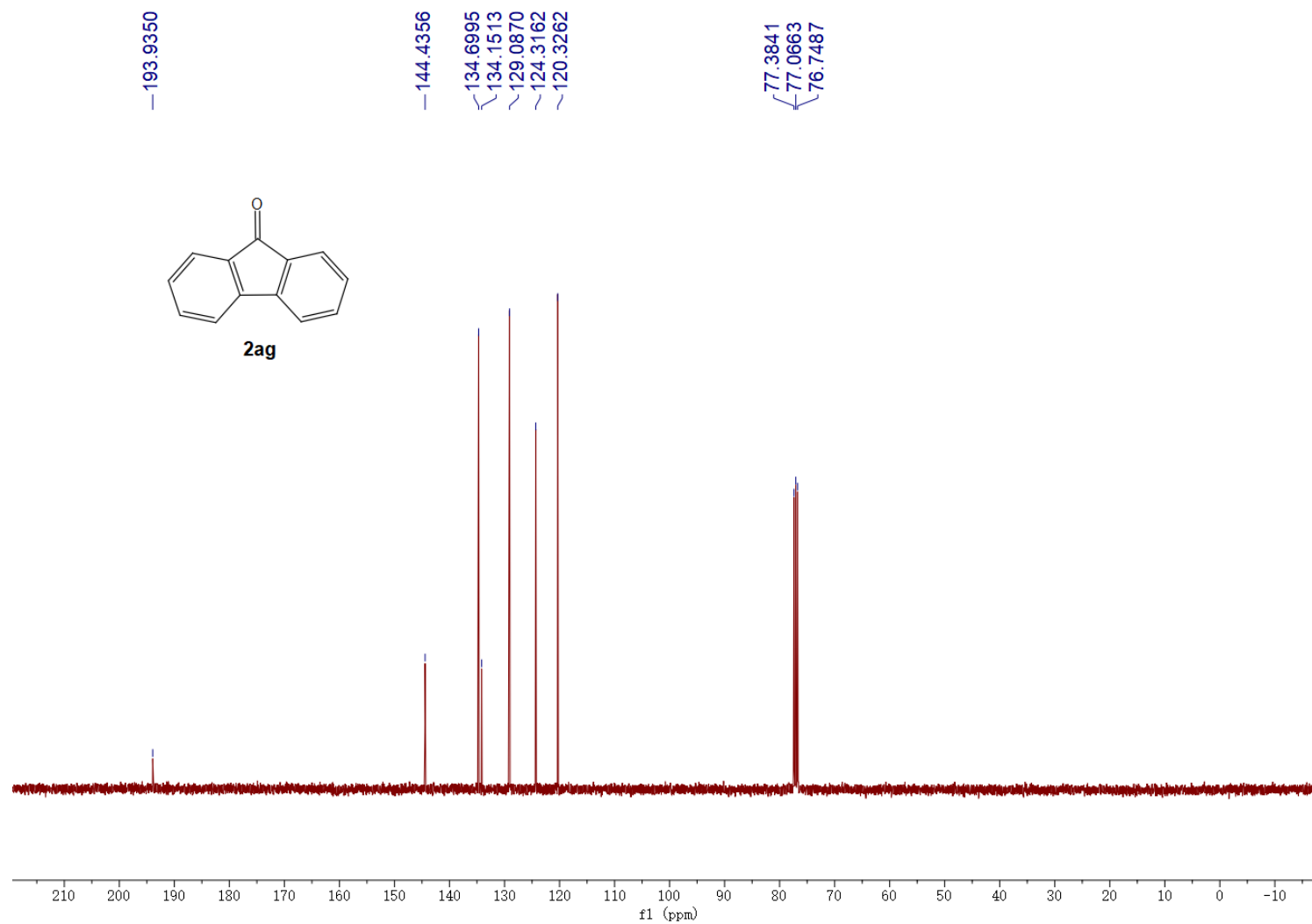
¹H-NMR Spectrum of 1-(3-(Trifluoromethyl)phenyl)ethan-1-one (2ae)

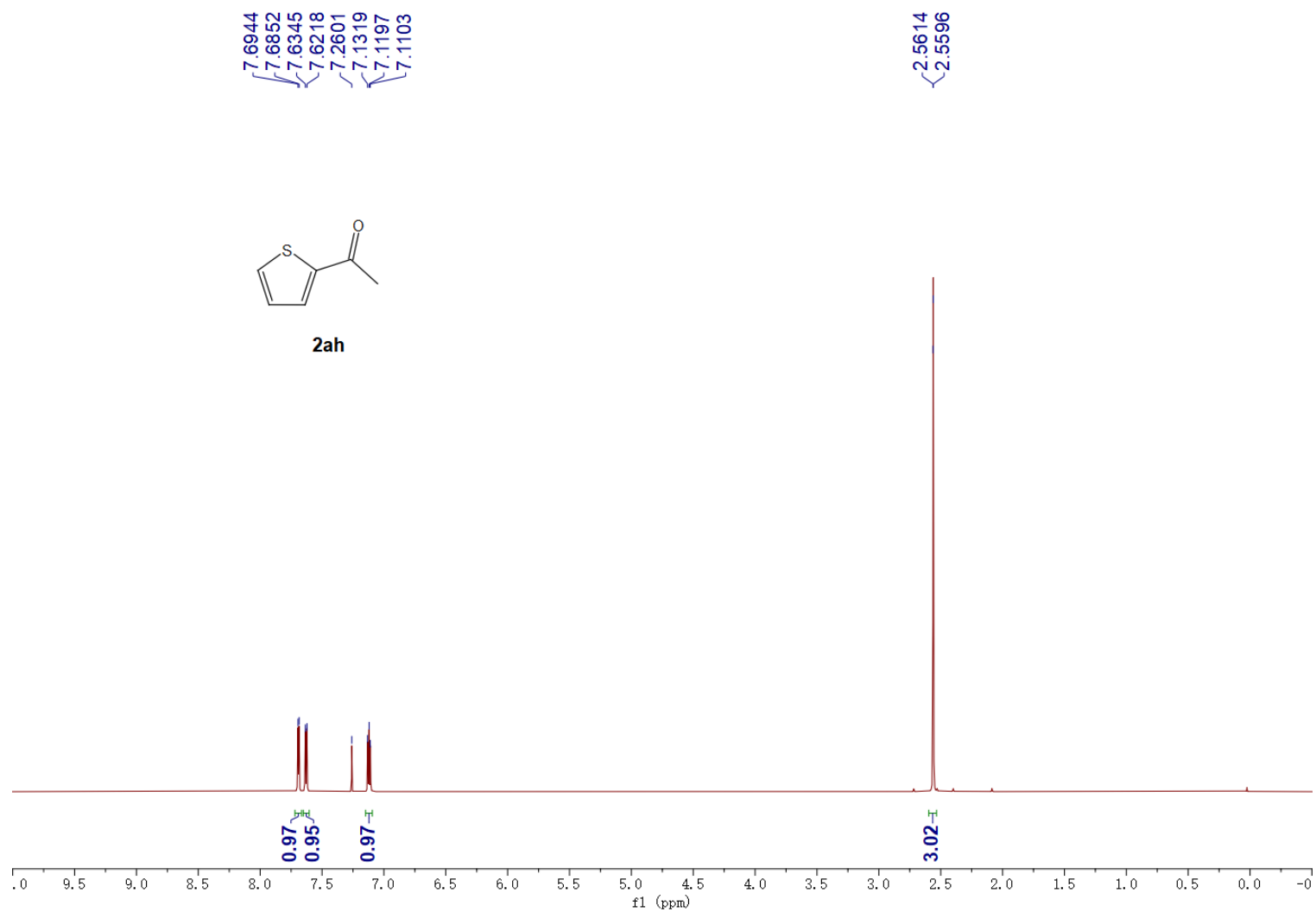
^{13}C -NMR Spectrum of 1-(3-(Trifluoromethyl)phenyl)ethan-1-one (2ae)

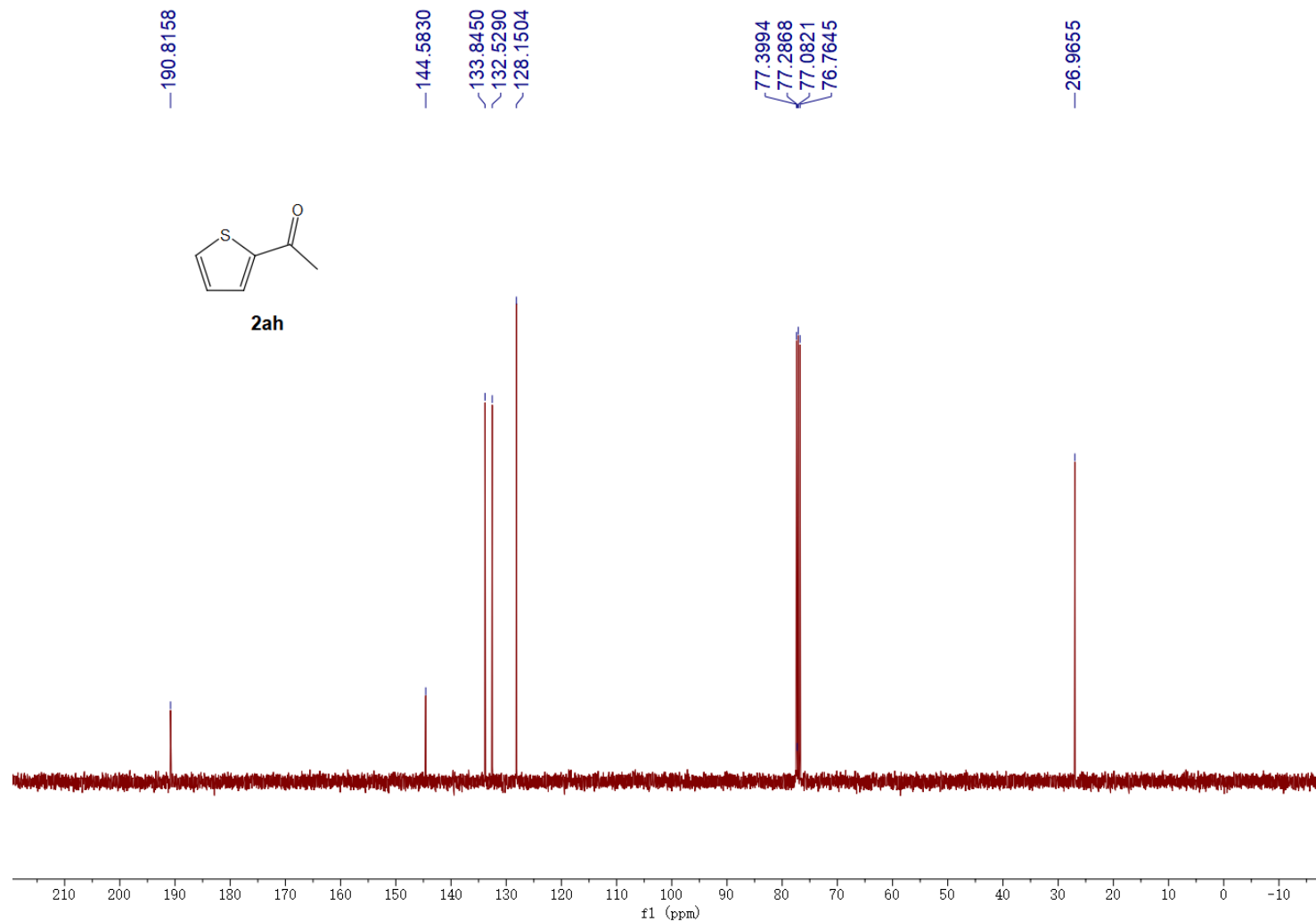
¹H-NMR Spectrum of 4-Methylpentan-2-one (2af)

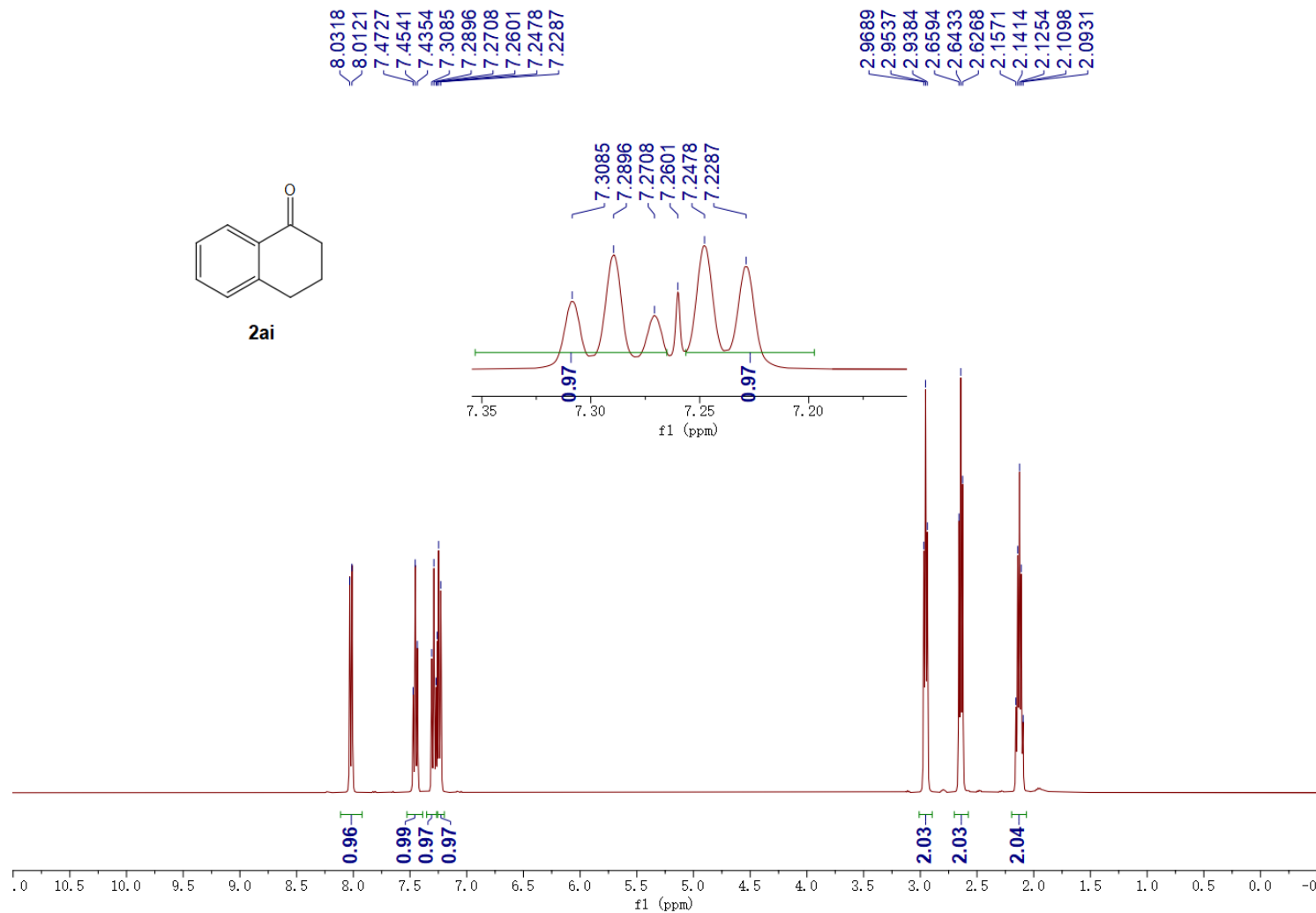
^{13}C -NMR Spectrum of 4-Methylpentan-2-one (2af)

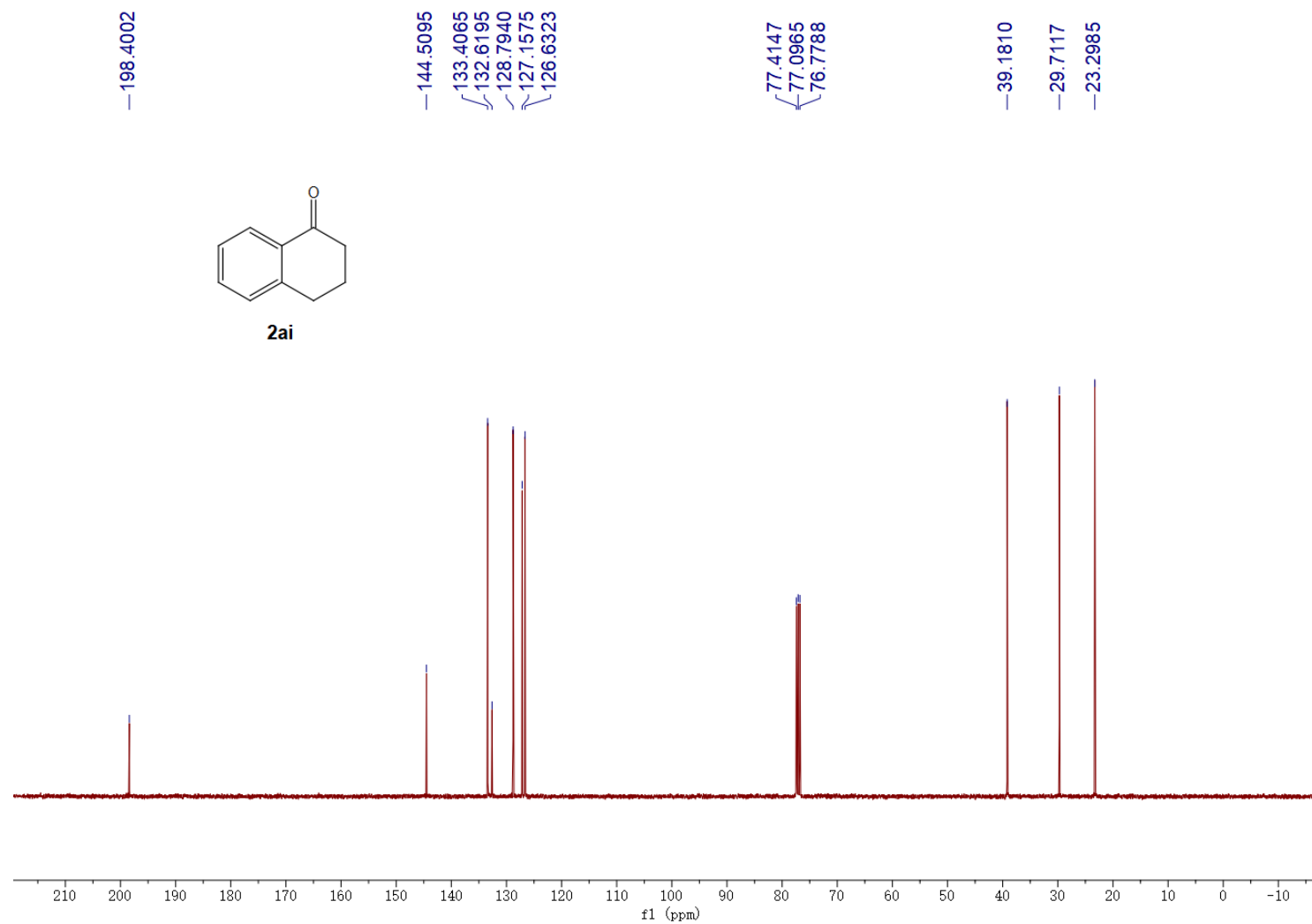
¹H-NMR Spectrum of 9H-fluoren-9-one (2ag)

^{13}C -NMR Spectrum of 9H-fluoren-9-one (2ag)

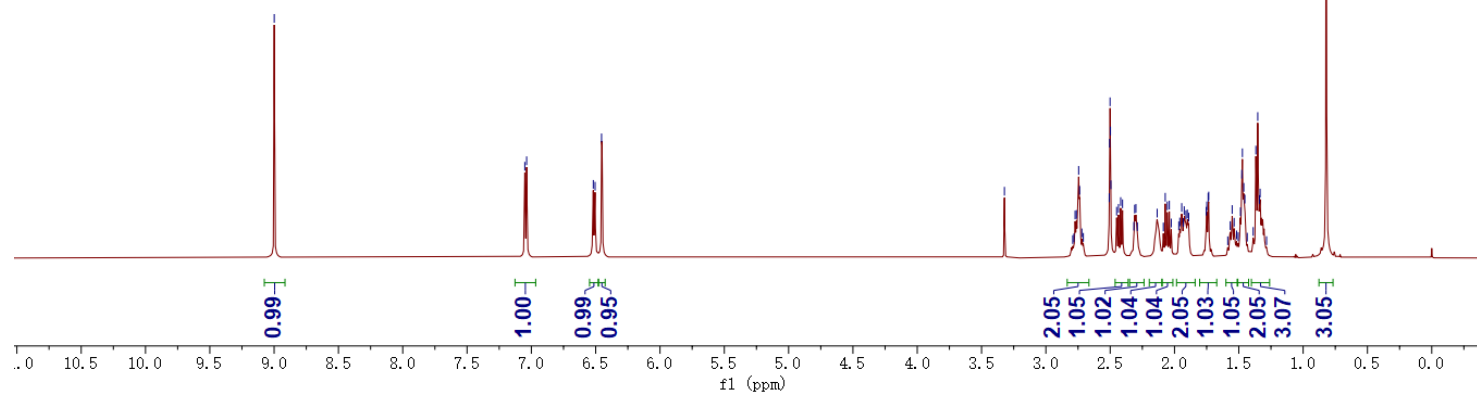
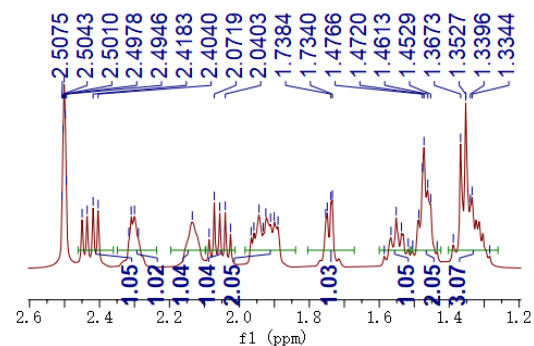
¹H-NMR Spectrum of 1-(Thiophen-2-yl)ethan-1-one (2ah)

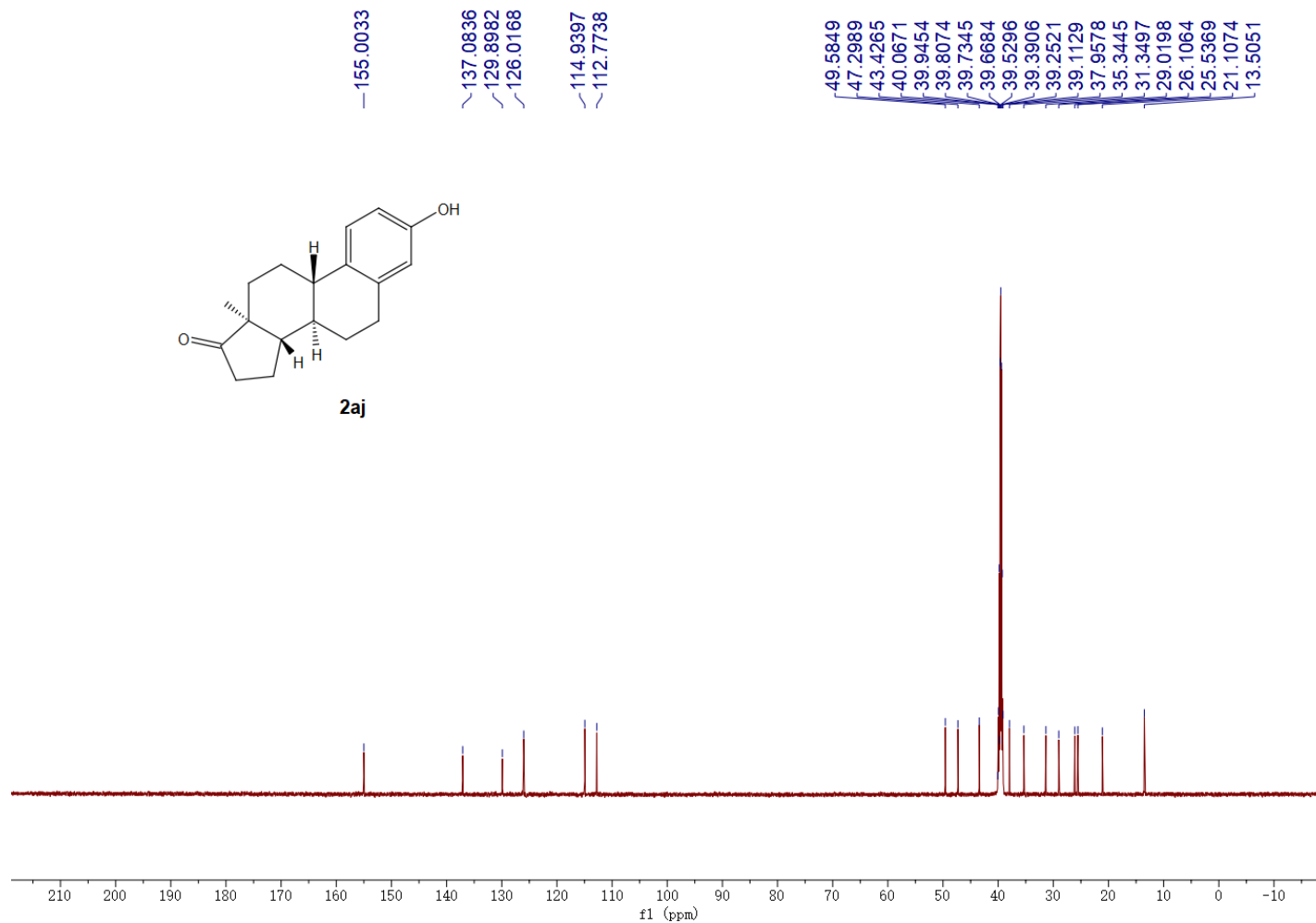
^{13}C -NMR Spectrum of 1-(Thiophen-2-yl)ethan-1-one (2ah)

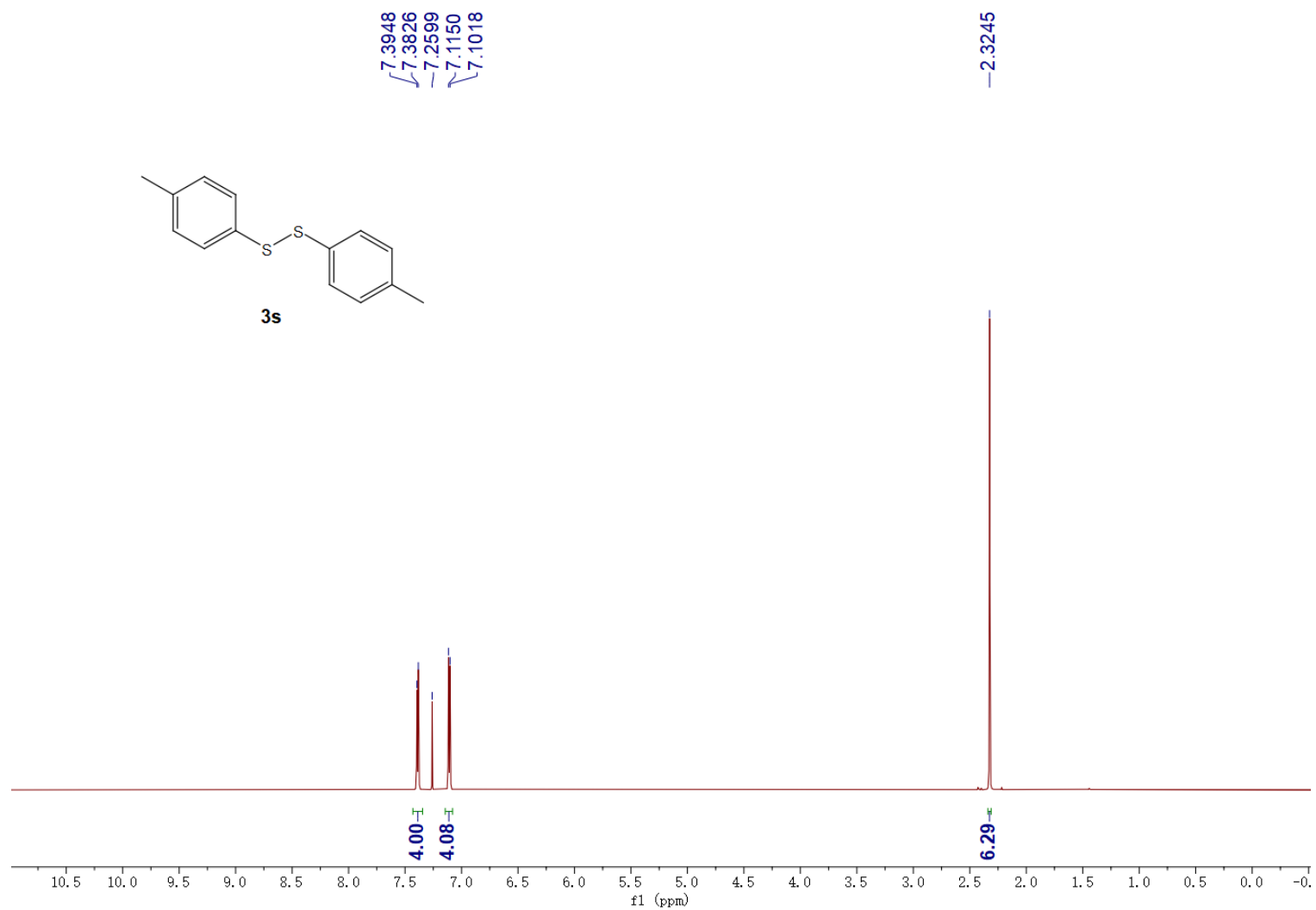
¹H-NMR Spectrum of 3,4-Dihydronaphthalen-1(2H)-one (2ai)

^{13}C -NMR Spectrum of 3,4-Dihydronaphthalen-1(2*H*)-one (2ai)

8.9991	7.0509	7.0368	6.5184	6.5045	6.4543	3.3222	2.7728	2.7629	2.7450	2.7376	2.7204	2.5075	2.5043	2.5010	2.4978	2.4946	2.4498	2.4354	2.4183	2.4040	2.3161	2.3095	2.3000	2.2887	2.1347	2.0865	2.0719	2.0563	2.0403	2.0254	1.9665	1.9586	1.9439	1.9318	1.9244	1.9110	1.9005	1.8896	1.8896	1.7532	1.7487	1.7384	1.7340	1.5664	1.5516	1.5364	1.5172	1.5045	1.4868	1.4766	1.4720	1.4613	1.4529	1.3883	1.3673	1.3527	1.3364	1.3346	0.8205
--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------



^{13}C -NMR Spectrum of (8*R*,9*S*,13*S*,14*S*)-3-Hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (2aj)

¹H-NMR Spectrum of 1,2-Di-*p*-tolyldisulfane (3s)

^{13}C -NMR Spectrum of 1,2-Di-*p*-tolylidysulfane (3s)