Supplementary Information

Copper-Catalyzed Decarboxylative Intramolecular C-O Coupling: Synthesis of 2-Arylbenzofuran from 3-Arylcoumarin

Wen-Chen Pu,[a,b] Guan-Min Mu,[a,c] Guo-Lin Zhang*[a] and Chun Wang*[a]

[a] Center for Natural Products, Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041.

[b] University of Chinese Academy of Sciences, Beijing 100049.

[c] School of Materials and Science Engineering, Southwest University of Science and Technology, Mianyang 621010, China.

Email: wangchun@cib.ac.cn; zhanggl@cib.ac.cn

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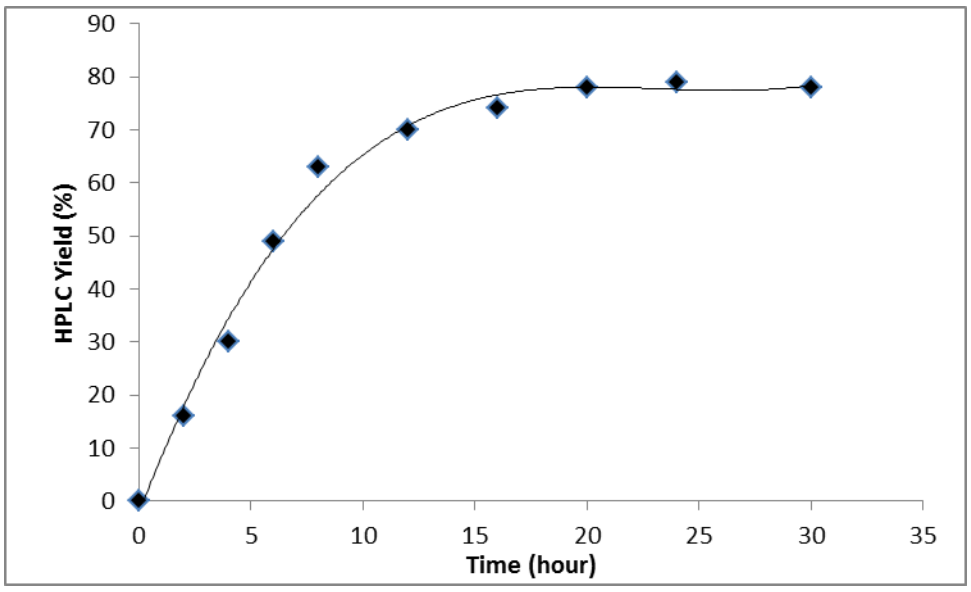
1. General Procedure under Optimized Conditions

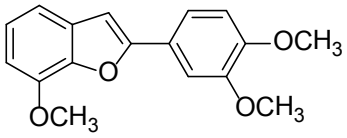
A 25 mL flask was charged with 3-arylcoumarin (1 mmol), cupric chloride (0.15 mmol), phenathroline (0.15 mmol), DMSO (10 mL) and 4 Å molecular sieve (300 mg). The reaction mixture was stirred and primarily heated to 110℃ for 1h when the color was gradually turned to dark brown. The temperature was then raised to 150℃ and maintained for 24 h. Keep the mixture exposing to air during all reaction time. After cooling to room temperature, hydrochloric acid (2 mol/L, 10 mL) and water (20 mL) were poured to terminate the reaction, which, simultaneously, brought about the generation of brown solid and bubble. The suspension was then extracted with chloroform (20 mL * 3). The combined organic layer was washed in turn with water (20 mL) and brine (20 mL), dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The solid residue obtained was purified by silica gel column chromatography.

2. Time Profile for Model Reaction



3. Experimental data

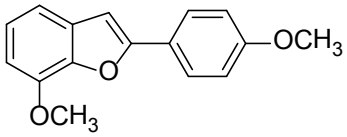
2-(3,4-Dimethoxyphenyl)-7-methoxybenzo[b]furan (2aa)



The yellow solid **2aa** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 1 : 1 as solvents with 33 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.38 (d, *J* = 1.9 Hz, 1H), 7.19 – 7.11 (m, 2H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.90 (s, 1H), 6.79 (dd, *J* = 7.3, 1.2 Hz, 1H), 4.05 (s, 3H), 3.99 (s, 3H), 3.93 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 156.19, 149.65,

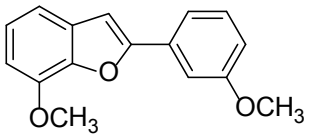
149.20, 145.22, 143.92, 131.17, 123.55, 123.47, 118.17, 113.11, 111.35, 108.29, 106.38, 100.43, 56.10, 55.99, 48.92. **HR-ESIMS**: 307.0940 $[M+Na]^+$ (calc. for $C_{17}H_{16}NaO_4$, 307.0941).

7-Methoxy-2-(4-methoxyphenyl)benzo[b]furan (2ab)



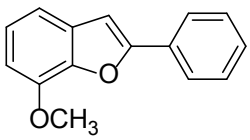
The light yellow solid **2ab** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 36 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.18 – 7.09 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.88 (s, 1H), 6.79 (dd, *J* = 7.4, 1.2 Hz, 1H), 4.05 (s, 3H), 3.86 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 160.02, 156.24, 145.23, 143.90, 131.23, 126.56, 123.48, 123.24, 114.19, 113.10, 106.40, 100.03, 56.16, 55.36. **HR-ESIMS**: 277.0831 $[M+Na]^+$ (calc. for $C_{16}H_{14}NaO_3$, 277.0835).

7-Methoxy-2-(3-methoxyphenyl)benzo[b]furan (2ac)



The light yellow solid **2ac** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 4 : 1 as solvents with 39 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.91 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.81 (dd, *J* = 7.7 Hz, 1.2 Hz, 1H), 4.06 (s, 3H), 3.89 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 159.94, 155.93, 145.35, 144.17, 131.66, 130.92, 129.79, 123.62, 117.69, 114.50, 113.37, 110.32, 106.87, 101.98, 56.18, 55.42. **HR-ESIMS**: 255.1016 $[M+H]^+$ (calc. for $C_{16}H_{15}O_2$, 255.1016).

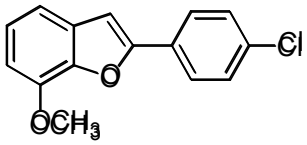
7-Methoxy-2-phenylbenzo[b]furan (2af)



The light yellow solid **2af** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 32 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 7.7 Hz, 1.1 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.37 (m, 1H), 7.19 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.02 (s, 1H), 6.82 (dd, *J* = 7.7, 1.0 Hz, 1H), 4.06 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 156.09, 145.36, 144.18, 130.96, 130.36, 128.72, 128.55, 125.06, 123.59, 113.35, 106.80, 101.63, 56.18.

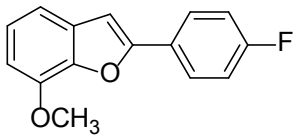
HR-ESIMS: 247.0726 $[M+Na]^+$ (calc. for $C_{15}H_{12}NaO_2$, 247.0730).

2-(4-Chlorophenyl)-7-methoxybenzo[b]furan (2ag)



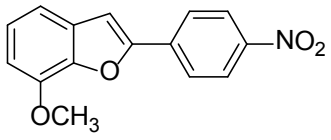
The light yellow solid **2ag** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 46 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.21 – 7.13 (m, 2H), 6.99 (s, 1H), 6.82 (dd, *J* = 7.4, 1.2 Hz, 1H), 4.05 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 154.93, 145.36, 144.21, 134.34, 130.78, 128.97, 128.86, 126.25, 123.78, 113.39, 106.93, 102.09, 56.12. **HR-ESIMS**: 281.0346 $[M+Na]^+$ (calc. for $C_{15}H_{11}{}^{35}ClNaO_2$, 281.0340), 283.0317 $[M+Na]^+$ (calc. for $C_{15}H_{11}{}^{37}ClNaO_2$, 283.0311).

2-(4-Fluorophenyl)-7-methoxybenzo[b]furan (2ah)



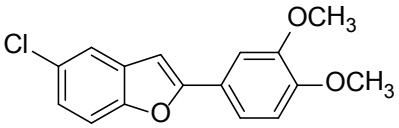
The white solid **2ah** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 42 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.91 – 7.75 (m, 2H), 7.20 – 7.06 (m, 4H), 6.94 (s, 1H), 6.81 (dd, *J* = 7.4, 1.2 Hz, 1H), 4.05 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 162.92 (d, *J* = 248.7 Hz), 155.19, 145.33, 144.13, 130.91, 126.91 (d, *J* = 8.2 Hz), 126.70 (d, *J* = 2.9 Hz), 123.70, 115.82 (d, *J* = 21.9 Hz), 113.31, 106.75, 101.36, 56.13. **HR-ESIMS**: 265.0631 $[M+Na]^+$ (calc. for $C_{15}H_{11}FNaO_2$, 265.0635).

7-Methoxy-2-(4-nitrophenyl)benzo[b]furan (2an)



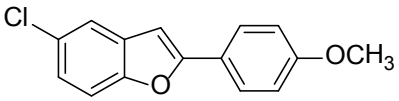
The yellow solid **2an** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 3 : 1 as solvents with 45 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 – 8.27 (m, 2H), 8.05 – 7.99 (m, 2H), 7.25 – 7.17 (m, 3H), 6.88 (dd, *J* = 7.3, 1.5 Hz, 1H), 4.06 (s, 3H). **^{13}C NMR** (100 MHz, CDCl3): δ 153.39, 147.29, 145.51, 144.87, 136.16, 130.32, 125.34, 124.27, 124.24, 113.81, 107.74, 105.41, 56.12. **HR-ESIMS**: 270.0770 $[M+H]^+$ (calc. for $C_{15}H_{12}NO_4$, 270.0761).

5-Chloro-2-(3,4-dimethoxyphenyl)benzo[b]furan (2ba)



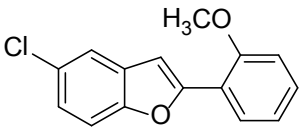
The white solid **2ba** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 4 : 1 as solvents with 87 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 1.9 Hz, 1H), 7.40 – 7.44 (m, 2H), 7.35 (d, *J* = 1.6 Hz, 1H), 7.21 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.84 (s, 1H), 3.99 (s, 3H), 3.94 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 157.49, 153.09, 149.97, 149.29, 130.85, 128.44, 123.94, 123.02, 120.11, 118.21, 111.90, 111.43, 108.19, 99.51, 56.04, 56.02. **HR-ESIMS**: 311.0445 $[M+Na]^+$ (calc. for $C_{16}H_{13}{}^{35}ClNaO_3$, 311.0445], 313.0424 $[M+Na]^+$ (calc. for $C_{16}H_{13}{}^{37}ClNaO_3$, 313.0415).

5-Chloro-2-(4-methoxyphenyl)benzo[b]furan (2bb)



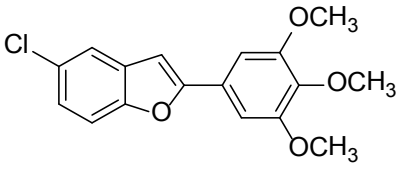
The white solid **2bb** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 85 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.19 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 1H), 3.87 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 160.33, 157.58, 153.09, 130.89, 128.37, 126.59, 123.82, 122.82, 120.08, 114.34, 111.88, 99.17, 55.39. **HR-ESIMS**: 259.0522 $[M+H]^+$ (calc. for $C_{15}H_{12}{}^{35}ClO_2$, 259.0520), 261.0500 $[M+H]^+$ (calc. for $C_{15}H_{12}{}^{37}ClO_2$, 261.0490).

5-Chloro-2-(2-methoxyphenyl)benzo[b]furan (2bd)



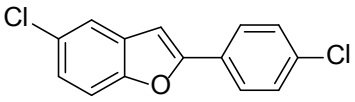
The white solid **2bd** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 63 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.29 (s, 1H), 7.22 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.07 – 7.11 (m, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 4.01 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 156.64, 153.70, 152.28, 131.20, 129.73, 128.14, 127.15, 124.19, 120.82, 120.50, 118.90, 111.75, 111.10, 105.76, 55.49. **HR-ESIMS**: 281.0346 $[M+Na]^+$ (calc. for $C_{15}H_{11}{}^{35}ClNaO_2$, 281.0340), 283.0318 $[M+Na]^+$ (calc. for $C_{15}H_{11}{}^{37}ClNaO_2$, 283.0311).

5-Chloro-2-(3,4,5-trimethoxyphenyl)benzo[b]furan (2be)



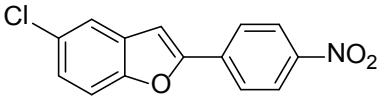
The white solid **2be** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 2 : 1 as solvents with 60 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.23 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.07 (s, 2H), 6.90 (s, 1H), 3.96 (s, 6H), 3.90 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 157.25, 153.65, 153.17, 139.14, 130.64, 128.56, 125.47, 124.32, 120.30, 112.02, 102.49, 100.49, 61.00, 56.29. **HR-ESIMS**: 341.0550 $[M+Na]^+$ (calc. for $C_{17}H_{15}{}^{35}ClNaO_4$, 341.0551), 343.0527 $[M+Na]^+$ (calc. for $C_{17}H_{15}{}^{37}ClNaO_4$, 343.0521).

5-Chloro-2-(4-chlorophenyl)benzo[b]furan (2bg)



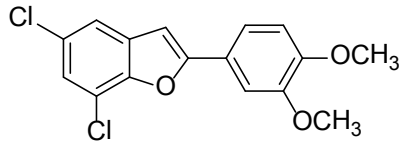
The white solid **2bg** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 78 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 1.9 Hz, 1H), 7.41 – 7.44 (m, 3H), 7.26 – 7.23 (m, 1H), 6.95 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 156.27, 153.28, 134.85, 130.43, 129.14, 128.69, 128.48, 126.27, 124.72, 120.52, 112.15, 101.22. **HR-ESIMS**: 263.0021 $[M+H]^+$ (calc. for $C_{14}H_9{}^{35}Cl_2O$, 263.0025), 264.9992 $[M+H]^+$ (cal. for $C_{14}H_9{}^{35}Cl^{37}ClO$, 264.9996), 266.9973 $[M+H]^+$ (calc. for $C_{14}H_9{}^{37}Cl_2O$, 266.9966).

5-Chloro-2-(4-nitrophenyl)benzo[b]furan (2bn)



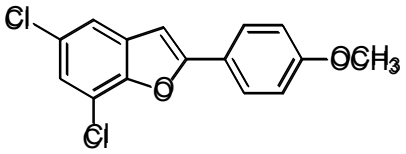
The yellow solid **2bn** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 4 : 1 as solvents with 74 % yield.**^{1}H NMR** (400 MHz, CDCl3): δ 8.39 – 8.27 (m, 2H), 8.03 – 7.94 (m, 2H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.32 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.18 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.68, 153.78, 147.56, 135.73, 129.96, 129.17, 126.02, 125.45, 124.36, 121.11, 112.51, 104.44. **HR-ESIMS**: 296.0086 $[M+Na]^+$ (calc. for $C_{14}H_8{}^{35}ClNNaO_3$, 296.0085), 298.0065 $[M+Na]^+$ (calc. for $C_{14}H_8{}^{37}ClNNaO_3$, 298.0056).

5,7-Dichloro-2-(3,4-dimethoxyphenyl)benzo[b]furan (2ca)



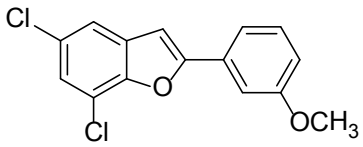
The white solid **2ca** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 4 : 1 as solvents with 90 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 1.9 Hz, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.87 (s, 1H), 3.99 (s, 3H), 3.95 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 158.30, 150.35, 149.33, 149.10, 131.81, 128.65, 123.84, 122.35, 118.72, 118.58, 116.94, 111.41, 108.32, 99.93, 56.09, 56.02. **HR-ESIMS**: 345.0064 $[M+Na]^+$ (calc. for $C_{16}H_{12}{}^{35}Cl_2NaO_3$, 345.0056), 347.0032 $[M+Na]^+$ (calc. for $C_{16}H_{12}{}^{35}Cl^{37}ClNaO_3$, 347.0027), 349.0007 $[M+Na]^+$ (calc. for $C_{16}H_{12}{}^{37}Cl_2NaO_3$, 348.9997).

5,7-Dichloro-2-(4-methoxyphenyl)benzo[b]furan (2cb)



The white solid **2cb** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 82 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 1H), 3.87 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 160.67, 158.38, 149.09, 131.86, 128.59, 126.85, 123.73, 122.16, 118.70, 116.93, 114.39, 99.57, 55.40. **HR-ESIMS**: 293.0136 $[M+H]^+$ (calc. for $C_{15}H_{11}{}^{35}Cl_2O_2$, 293.0131), 295.0105 $[M+H]^+$ (calc. for $C_{15}H_{11}{}^{35}Cl^{37}ClO_2$, 295.102), 297.0087 $[M+H]^+$ (calc. for $C_{15}H_{11}{}^{37}Cl_2O_2$, 297.0072).

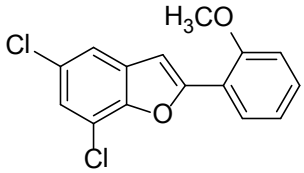
5,7-Dichloro-2-(3-methoxyphenyl)benzo[b]furan (2cc)



The white solid **2cc** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 78 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.45 – 7.48 (m, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.39 – 7.42 (m, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 1.8 Hz, 1H), 6.97 (s, 1H), 6.95 (dd, *J* = 7.9, 2.0 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 160.00, 158.03, 149.27, 131.48, 130.63, 130.02, 128.73, 124.37, 119.05, 117.85, 117.20, 115.15, 110.71, 101.53, 55.42. **HR-ESIMS**: 293.0138 $[M+H]^+$ (calc. for $C_{15}H_{11}{}^{35}Cl_2O_2$, 293.0131), 295.0098 $[M+H]^+$ (calc. for $C_{15}H_{11}{}^{35}Cl^{37}ClO_2$,

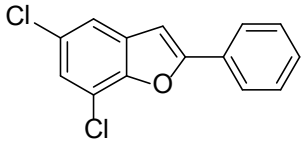
295.102), 297.0068 $[M+H]^+$ (calc. for $C_{15}H_{11}{}^{37}Cl_2O_2$, 297.0072).

5,7-Dichloro-2-(2-methoxyphenyl)benzo[b]furan (2cd)



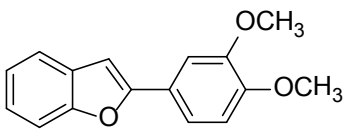
The white solid **2cd** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 68 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.31 (s, 1H), 7.26 (d, *J* = 1.8 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 4.01 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 156.72, 154.50, 148.31, 132.17, 130.20, 128.33, 127.40, 124.04, 120.90, 119.12, 118.31, 116.84, 111.08, 106.10, 55.51. **HR-ESIMS**: 293.0137 $[M+H]^+$ (calc. for $C_{15}H_{11}{}^{35}Cl_2O_2$, 293.0131), 295.0112 $[M+H]^+$ (calc. for $C_{15}H_{11}{}^{35}Cl^{37}ClO_2$, 295.102), 297.0099 $[M+H]^+$ (calc. for $C_{15}H_{11}{}^{37}Cl_2O_2$, 297.0072).

5,7-Dichloro-2-phenylbenzo[b]furan (2cf)



The white solid **2cf** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 92 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.90 – 7.87 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.43 (m, 1H), 7.28 (d, *J* = 1.9 Hz, 1H), 6.98 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 158.22, 149.30, 131.54, 129.44, 129.38, 128.91, 128.72, 125.28, 124.30, 119.04, 117.18, 101.21. **HR-ESIMS**: 263.0017 $[M+H]^+$ (calc. for $C_{14}H_9{}^{35}Cl_2O$, 263.0025), 264.9989 $[M+H]^+$ (calc. for $C_{14}H_9{}^{35}Cl^{37}ClO$, 264.9996), 266.9970 $[M+H]^+$ (calc. for $C_{14}H_9{}^{37}Cl_2O$, 266.9966).

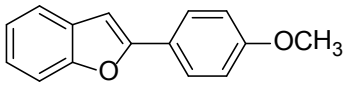
2-(3,4-Dimethoxyphenyl)benzo[b]furan (2da)



The white solid **2da** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 4 : 1 as solvents with 55 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.28 – 7.24 (m, 1H),

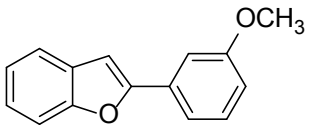
7.22 (t, J = 7.4 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 6.91 (s, 1H), 4.00 (s, 3H), 3.94 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 155.98, 154.73, 149.62, 149.25, 129.46, 123.84, 123.60, 122.88, 120.60, 117.98, 111.44, 110.99, 108.17, 100.02, 56.03, 56.01. **HR-ESIMS**: 277.0845 $[M+Na]^+$ (calc. for $C_{16}H_{14}NaO_3$, 277.0835).

2-(4-Methoxyphenyl)benzo[b]furan (2db)



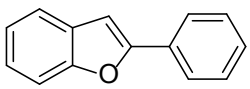
The white solid **2db** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 61 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.80 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.28 – 7.17 (m, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.89 (s, 1H), 3.87 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 160.01, 156.07, 154.72, 129.50, 126.43, 123.73, 123.38, 122.82, 120.56, 114.27, 110.98, 99.68, 55.37. **HR-ESIMS**: 225.0903 $[M+H]^+$ (calc. for $C_{15}H_{13}O_2$, 225.0910).

2-(3-Methoxyphenyl)benzo[b]furan (2dc)



The colourless liquid **2dc** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 57 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.59 (d, J = 7.4 Hz, 1H), 7.54 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.42 – 7.44 (m, 1H), 7.34 – 7.39 (m, 1H), 7.32 – 7.27 (m, 1H), 7.24 (t, J = 7.4 Hz, 1H), 7.03 (s, 1H), 6.92 (dd, J = 8.1, 1.9 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 159.99, 155.78, 154.89, 131.80, 129.87, 129.20, 124.34, 122.97, 120.95, 117.56, 114.50, 111.20, 110.20, 101.65, 55.38. **HR-ESIMS**: 225.0911 $[M+H]^+$ (calc. for $C_{15}H_{13}O_2$, 225.0910).

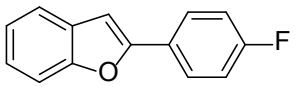
2-Phenylbenzo[b]furan (2df)



The white solid **2df** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 56 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.91 – 7.84 (m, 2H), 7.59 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.34 – 7.38 (m, 1H), 7.33 – 7.27 (m, 1H), 7.21 – 7.26 (m, 1H), 7.03 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 155.95, 154.92, 130.52, 129.24, 128.79, 128.55, 124.95, 124.26, 122.93, 120.90, 111.18, 101.30. **HR-ESIMS**: 195.0805 $[M+H]^+$ (calc. for

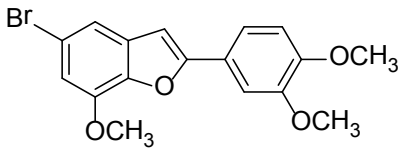
$C_{14}H_{11}O$, 195.0804).

2-(4-Fluorophenyl)benzo[b]furan (2dh)



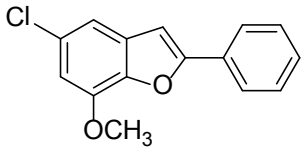
The white solid **2dh** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 72 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.82 – 7.86 (m, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.31 (m, 1H), 7.21 – 7.25 (m, 1H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.96 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 162.90 (d, *J* = 248.7 Hz), 155.04, 154.88, 129.20, 126.85, 126.78 (d, *J* = 8.2 Hz), 124.29, 123.02, 120.89, 115.89 (d, *J* = 22.0 Hz), 111.14, 101.00. **HR-ESIMS**: 213.0716 $[M+H]^+$ (calc. for $C_{14}H_{10}FO$, 213.0710).

5-Bromo-2-(3,4-dimethoxyphenyl)-7-methoxybenzo[b]furan (2ea)



The white solid **2ea** was obtained after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 63 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.29 (d, *J* = 1.6 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 1.6 Hz, 1H), 6.82 (s, 1H), 4.03 (s, 3H), 3.98 (s, 3H), 3.93 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 157.22, 149.97, 149.25, 145.48, 142.83, 132.35, 122.90, 118.36, 115.93, 115.71, 111.35, 109.91, 108.31, 99.72, 56.33, 56.10, 56.00. **HR-ESIMS**: 385.0047 $[M+Na]^+$ (calc. for $C_{17}H_{15}{}^{79}BrNaO_4$, 385.0046), 387.0029 $[M+Na]^+$ (calc. for $C_{17}H_{15}{}^{81}BrNaO_4$, 387.0025).

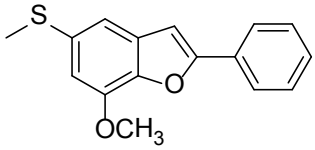
5-Chloro-7-methoxy-2-phenylbenzo[b]furan (2ef)



The white solid **2ef** was obtained from 6-bromo-8-methoxy-3-phenylcoumarin according to the general procedure after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 42 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.40 (m, 1H), 7.16 (d, *J* = 1.8 Hz, 1H), 6.94 (s, 1H), 6.78 (d, *J* = 1.8 Hz, 1H), 4.03 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.22, 145.38, 142.67, 131.41, 129.87, 128.95, 128.80, 128.70, 125.13, 112.82, 107.62, 101.15, 56.36. **HR-ESIMS**: 259.0528 $[M+H]^+$ (calc. for $C_{15}H_{12}{}^{35}ClO_2$, 259.0520), 261.0503

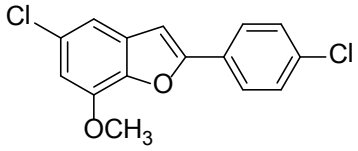
$[M+H]^+$ (calc. for $C_{15}H_{12}{}^{37}ClO_2$, 261.0491).

7-Methoxy-5-(methylthio)-2-phenylbenzo[b]furan (2ef2)



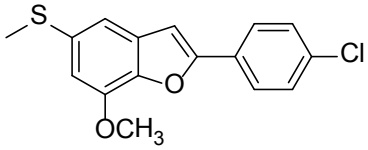
The light yellow solid **2ef2** was obtained from 6-bromo-8-methoxy-3-phenylcoumarin according to the general procedure after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 19 % yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 1.4 Hz, 1H), 6.94 (s, 1H), 6.80 (d, *J* = 1.4 Hz, 1H), 4.05 (s, 3H), 2.54 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 156.70, 145.12, 142.84, 132.87, 131.46, 130.15, 128.74, 128.70, 125.06, 112.35, 107.83, 101.14, 56.28, 17.82. **HR-ESIMS**: 271.0784 $[M+H]^+$ (calc. for $C_{16}H_{15}O_2S$, 271.0787).

5-Chloro-2-(4-chlorophenyl)-7-methoxybenzo[b]furan (2eg)



The white solid **2eg** was obtained from 6-bromo-3-(4-chlorophenyl)-8-methoxycoumarin according to the general procedure after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 38 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 – 7.72 (m, 2H), 7.47 – 7.35 (m, 2H), 7.15 (d, *J* = 1.8 Hz, 1H), 6.92 (s, 1H), 6.78 (d, *J* = 1.8 Hz, 1H), 4.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.06, 145.38, 142.70, 134.79, 131.22, 129.07, 128.89, 128.37, 126.33, 112.86, 107.79, 101.58, 56.33. **HR-ESIMS**: 314.9959 $[M+Na]^+$ (calc. for $C_{15}H_{10}{}^{35}Cl_2NaO_2$, 314.9950), 316.9925 $[M+Na]^+$ (calc. for $C_{15}H_{10}{}^{35}Cl^{37}ClNaO_2$, 316.9920), 318.9896 $[M+Na]^+$ (calc. for $C_{15}H_{10}{}^{37}Cl_2NaO_2$, 318.9891).

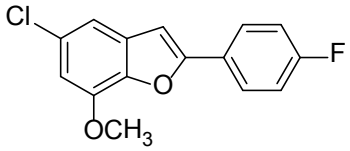
2-(4-Chlorophenyl)-7-methoxy-5-(methylthio)benzo[b]furan (2eg2)



The light yellow solid **2eg2** was obtained from 6-bromo-3-(4-chlorophenyl)-8-methoxycoumarin according to the general procedure after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 15 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 – 7.78 (m, 2H), 7.44 – 7.38 (m, 2H), 7.10 (d, *J* = 1.5 Hz, 1H), 6.93 (s, 1H), 6.79 (d, *J* = 1.5 Hz, 1H), 4.03 (s, 3H), 2.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.53, 145.10, 142.82, 134.51, 133.15, 131.27, 129.01, 128.64, 126.26, 112.17, 107.78, 101.60, 56.22, 17.73. **HR-ESIMS**: 305.0388 $[M+H]^+$ (calc. for $C_{16}H_{14}{}^{35}ClO_2S$, 305.0398),

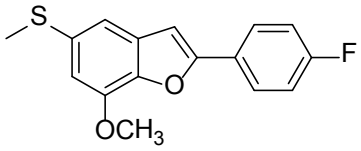
307.0357 $[M+H]^+$ (calc. for $C_{16}H_{14}{}^{37}ClO_2S$, 307.0369).

5-Chloro-2-(4-fluorophenyl)-7-methoxybenzo[b]furan (2eh)



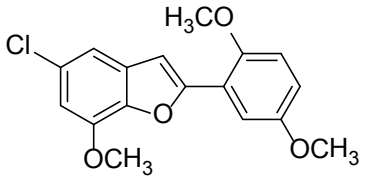
The white solid **2eh** was obtained from 6-bromo-3-(4-fluorophenyl)-8-methoxycoumarin according to the general procedure after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 46 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.20 – 7.09 (m, 3H), 6.87 (s, 1H), 6.78 (d, *J* = 1.7 Hz, 1H), 4.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.11 (d, *J* = 249.4 Hz), 156.32, 145.36, 142.62, 131.36, 128.81, 127.04 (d, *J* = 8.3 Hz), 126.21 (d, *J* = 3.3 Hz), 115.94 (d, *J* = 22.0 Hz), 112.80, 107.61, 100.88, 56.33. **HR-ESIMS**: 299.0239 $[M+Na]^+$ (calc. for $C_{15}H_{10}{}^{35}ClFNaO_2$, 299.0246), 301.0221 $[M+Na]^+$ (calc. for $C_{15}H_{10}{}^{37}ClFNaO_2$, 301.0217).

2-(4-Fluorophenyl)-7-methoxy-5-(methylthio)benzo[b]furan (2eh2)



The light yellow solid **2eh2** was obtained from 6-bromo-3-(4-fluorophenyl)-8-methoxycoumarin according to the general procedure after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 19 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 – 7.79 (m, 2H), 7.18 – 7.08 (m, 3H), 6.87 (s, 1H), 6.79 (d, *J* = 1.5 Hz, 1H), 4.03 (s, 3H), 2.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.99 (d, *J* = 249.1 Hz), 155.79, 145.09, 142.76, 133.02, 131.40, 126.94 (d, *J* = 8.2 Hz), 126.48 (d, *J* = 3.3 Hz), 115.87 (d, *J* = 22.0 Hz), 112.20, 107.66, 100.87, 56.23, 17.77. **HR-ESIMS**: 289.0690 $[M+H]^+$ (calc. for $C_{16}H_{14}FO_2S$, 289.0693).

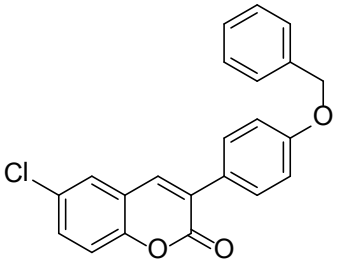
5-Chloro-2-(2,5-dimethoxyphenyl)-7-methoxybenzo[b]furan (2ek)



The light yellow solid **2ek** was obtained from 6-bromo-3-(2,5-dimethoxyphenyl)-8-methoxycoumarin according to the general procedure after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 36 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 3.0 Hz, 1H), 7.29 (s, 1H), 7.16 (d, *J* = 1.8 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.88 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.77 (d, *J* = 1.8 Hz, 1H), 4.02 (s, 3H), 3.95 (s, 3H), 3.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.68, 153.25,

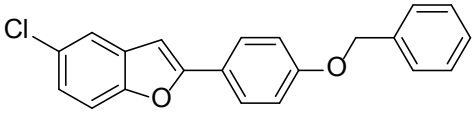
151.02, 145.21, 141.65, 132.01, 128.36, 119.37, 115.15, 113.03, 112.33, 112.26, 107.66, 106.37, 56.34, 56.01, 55.97. **HR-ESIMS**: 319.0736 $[M+H]^+$ (calc. for $C_{17}H_{16}{}^{35}ClO_4$, 319.0732), 321.0714 $[M+H]^+$ (calc. for $C_{17}H_{16}{}^{37}ClO_4$, 321.0703).

3-(4-(Benzyloxy)phenyl)-6-chlorocoumarin (1bjdb)



A 50mL round bottom flask was charged with 6-chloro-3-(4-hydroxylphenyl)coumarin (2.49 mmol), potassium carbonate (4.97 mmol), potassium iodide (0.5 mmol) and DMF (10 mL). The reaction mixture was stirred and benzyl chloride (2.98 mmol) was added dropwise at 25℃. The reaction was then conducted at 80℃ and monitored by TLC chromatogram. Hydrochloric acid (2 mol/L, 5 mL) and water (20 mL) were poured to quench the reaction, which, simultaneously, brought about the generation of solid and bubble. The suspension was then extracted with ethyl acetate (30 mL * 3). The combined organic layer was washed in turn with water (20 mL) and brine (20 mL) and concentrated under reduced pressure. The white solid **1bjdb** was obtained after recrystallization in ethanol with 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 – 7.62 (m, 3H), 7.50 (d, J = 2.3 Hz, 1H), 7.48 – 7.37 (m, 5H), 7.37 – 7.25 (m, 2H), 7.05 (d, J = 8.7 Hz, 2H), 5.12 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.18, 159.65, 151.65, 137.02, 136.66, 130.90, 129.93, 129.67, 129.00, 128.67, 128.11, 127.46, 126.87, 126.83, 120.90, 117.82, 114.94, 70.10. **HR-ESIMS**: 385.0606 $[M+Na]^+$ (calc. for $C_{22}H_{15}{}^{35}ClNaO_3$, 385.0602), 387.0574 $[M+Na]^+$ (calc. for $C_{22}H_{15}{}^{37}ClNaO_3$, 387.0573).

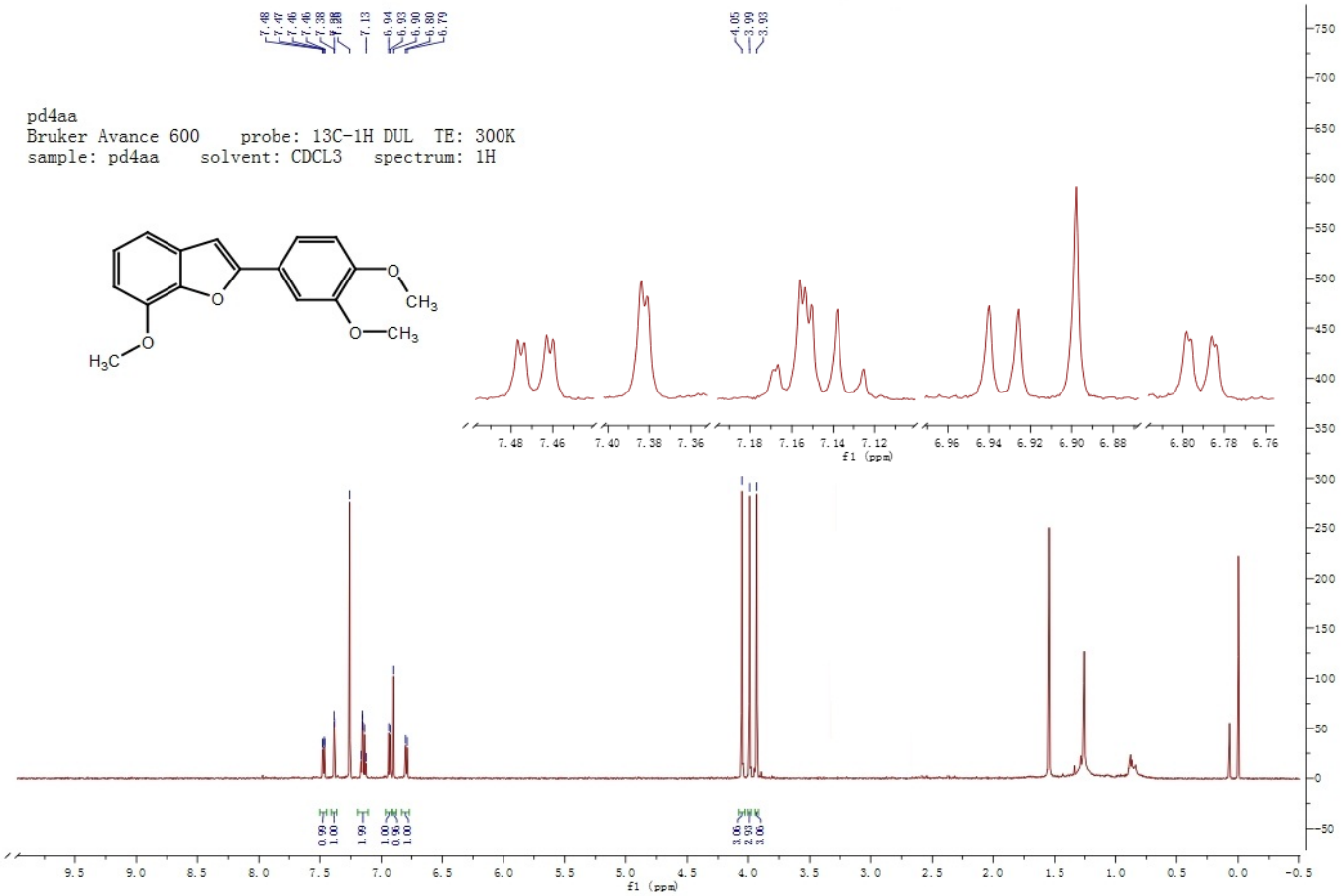
2-(4-(Benzyloxy)phenyl)-5-chlorobenzo[b]furan (2bjdb)

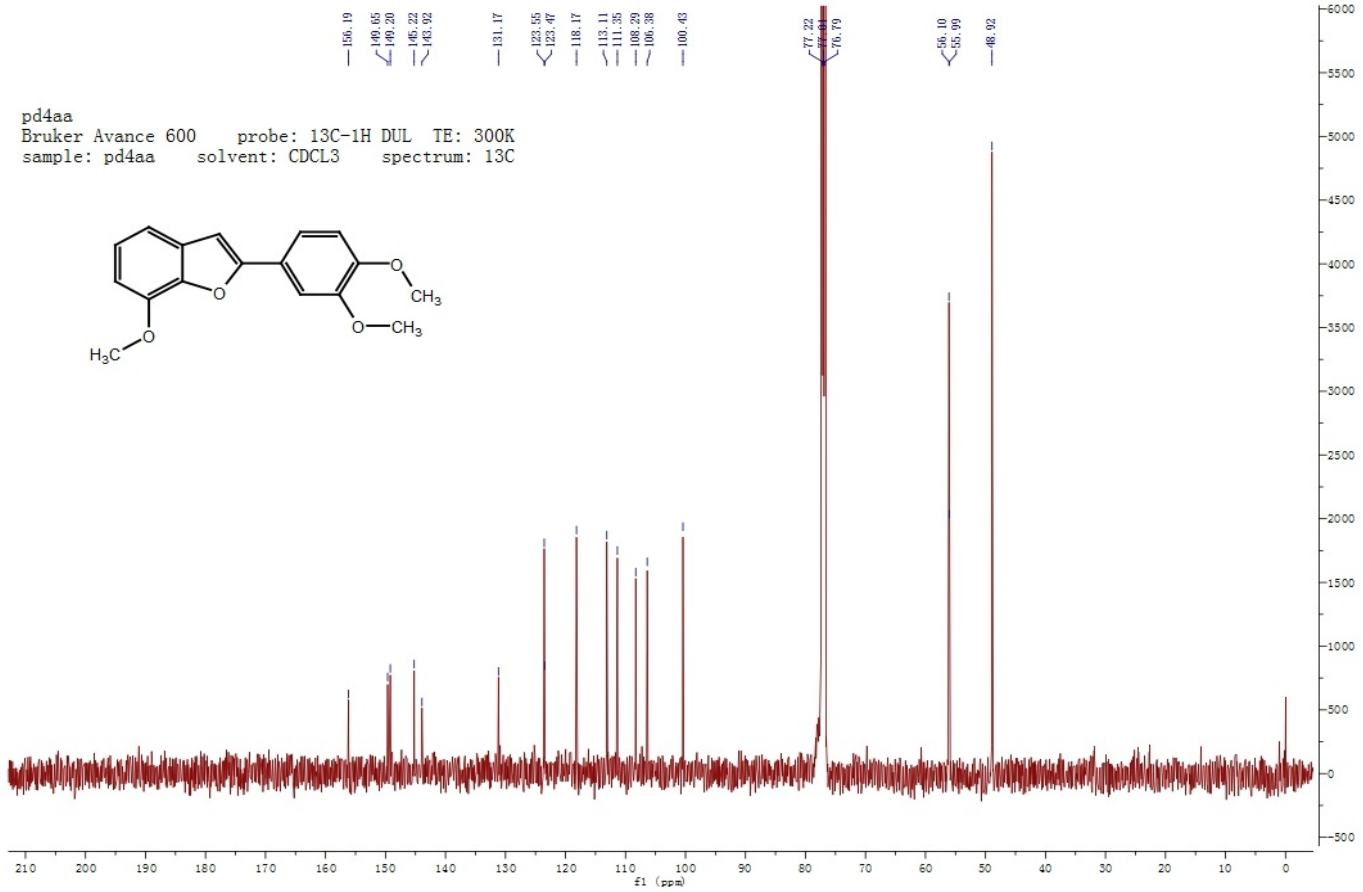


The white solid **2bjdb** was obtained from **1bjdb** according to the general procedure after purification by silica gel column chromatography using petroleum ether / chloroform = 5 : 1 as solvents with 69 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 – 7.75 (m, 2H), 7.51 (d, J = 2.1 Hz, 1H), 7.49 – 7.31 (m, 6H), 7.20 (dd, J = 8.7, 2.1 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.82 (s, 1H), 5.13 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.50, 157.51, 153.10, 136.61, 130.87, 128.67, 128.38, 128.13, 127.49, 126.60, 123.86, 123.05, 120.11, 115.26, 111.90, 99.27, 70.13. **HR-ESIMS**: 335.0832 $[M+H]^+$ (calc. for $C_{21}H_{16}{}^{35}ClO_2$, 335.0833), 337.0807 $[M+H]^+$ (calc. for $C_{21}H_{16}{}^{37}ClO_2$, 337.0803).

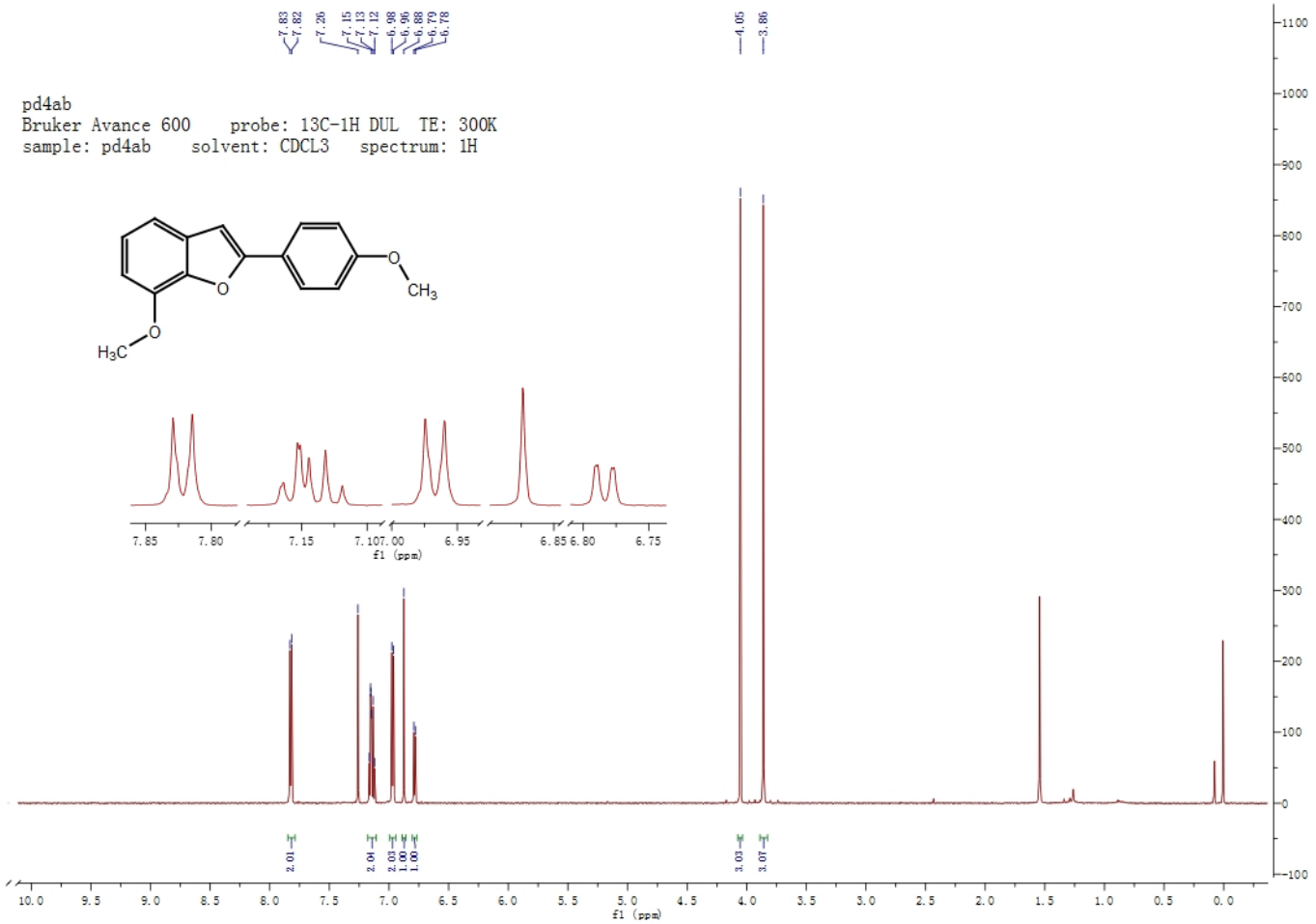
4. Copies of ^{1}H NMR and ^{13}C NMR spectra

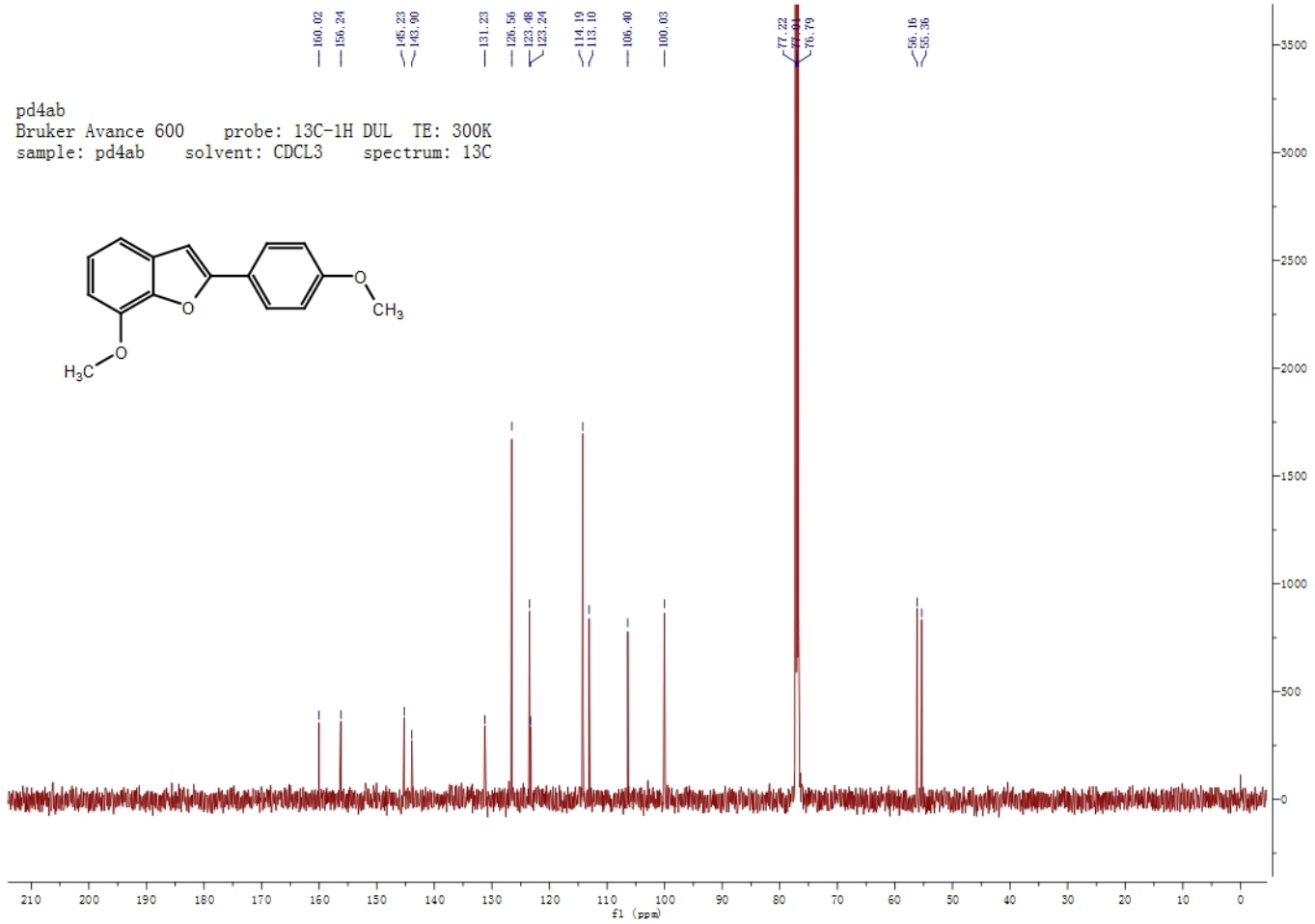
Compound 2aa:



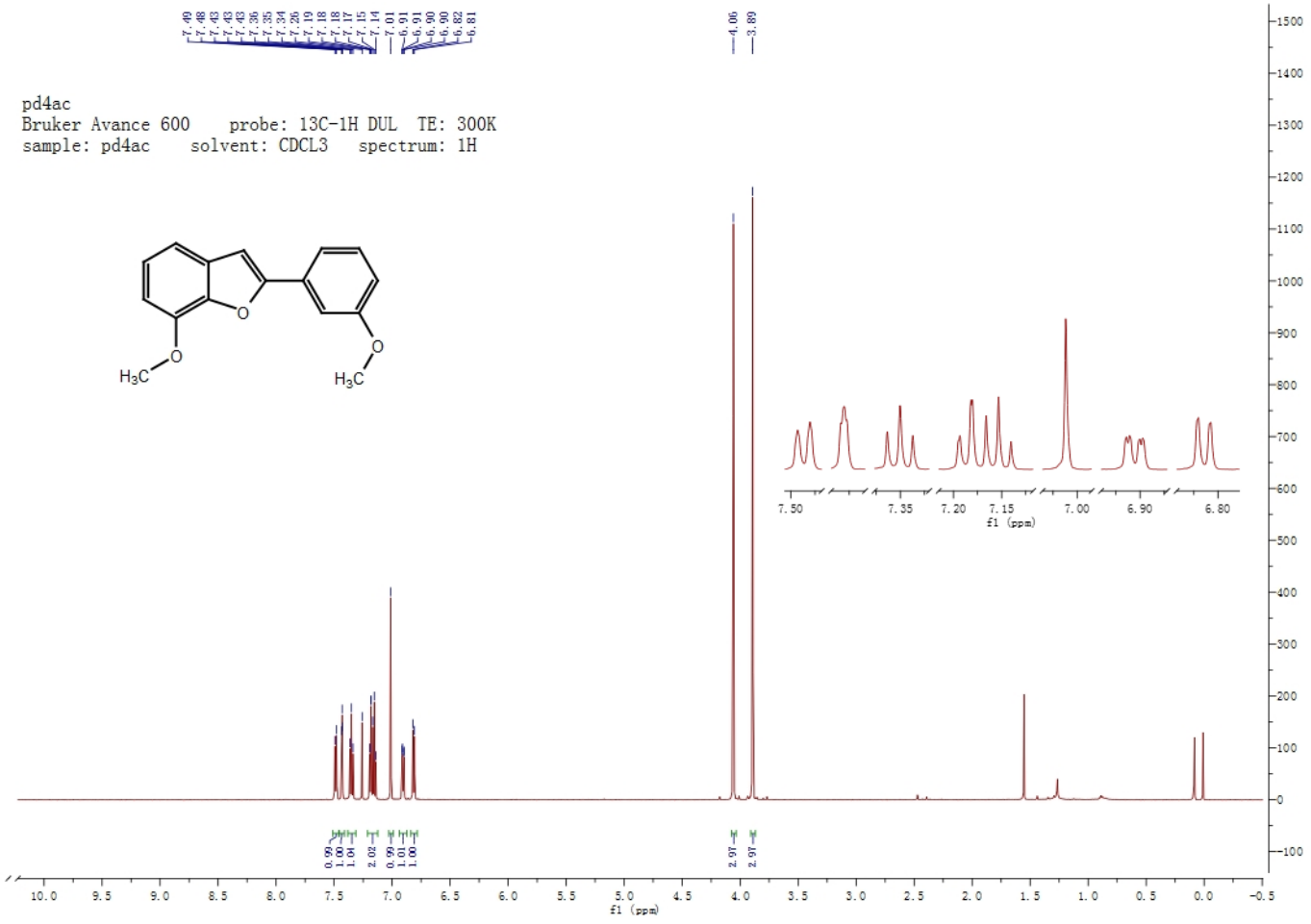


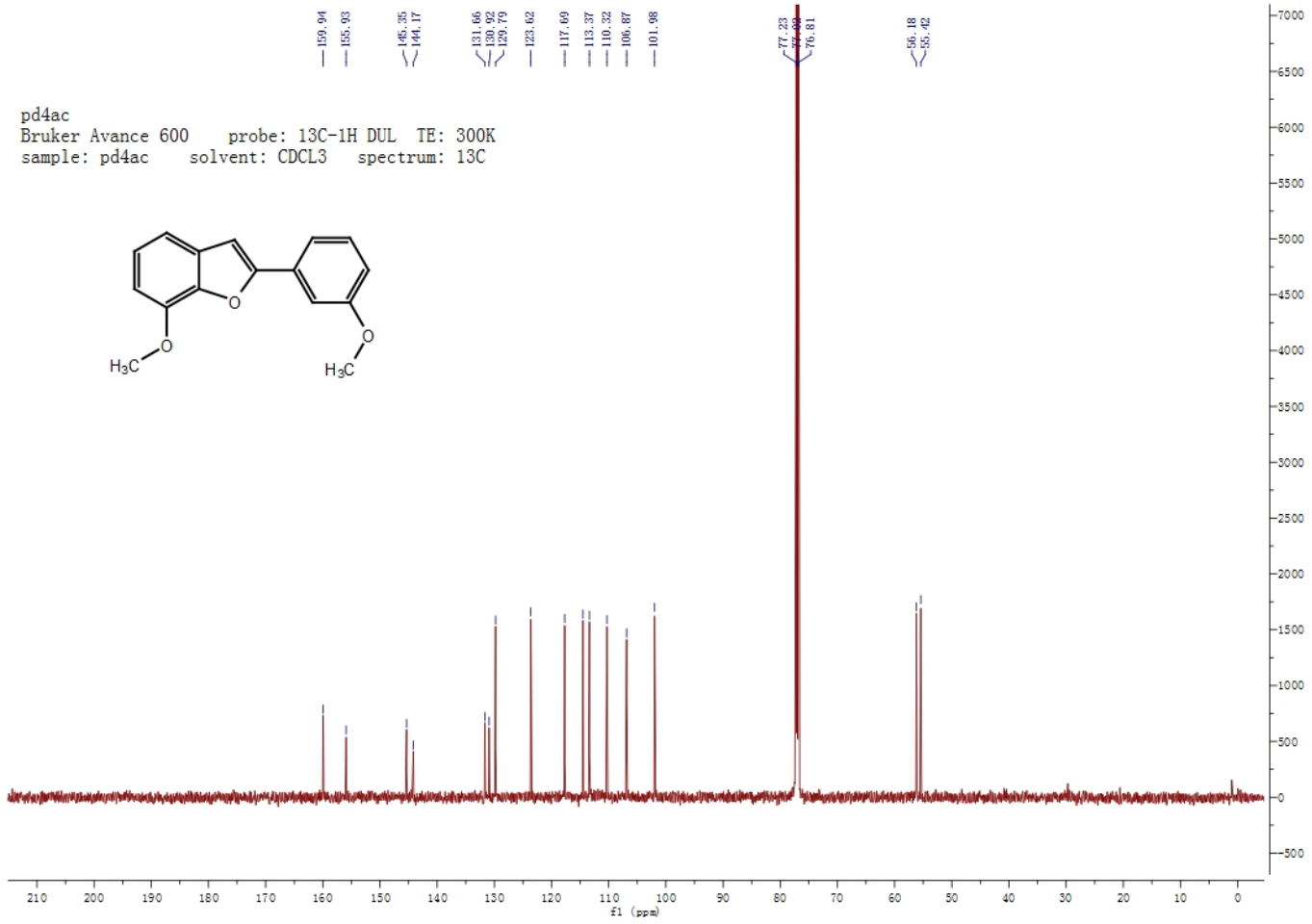
Compound 2ab:





Compound 2ac:





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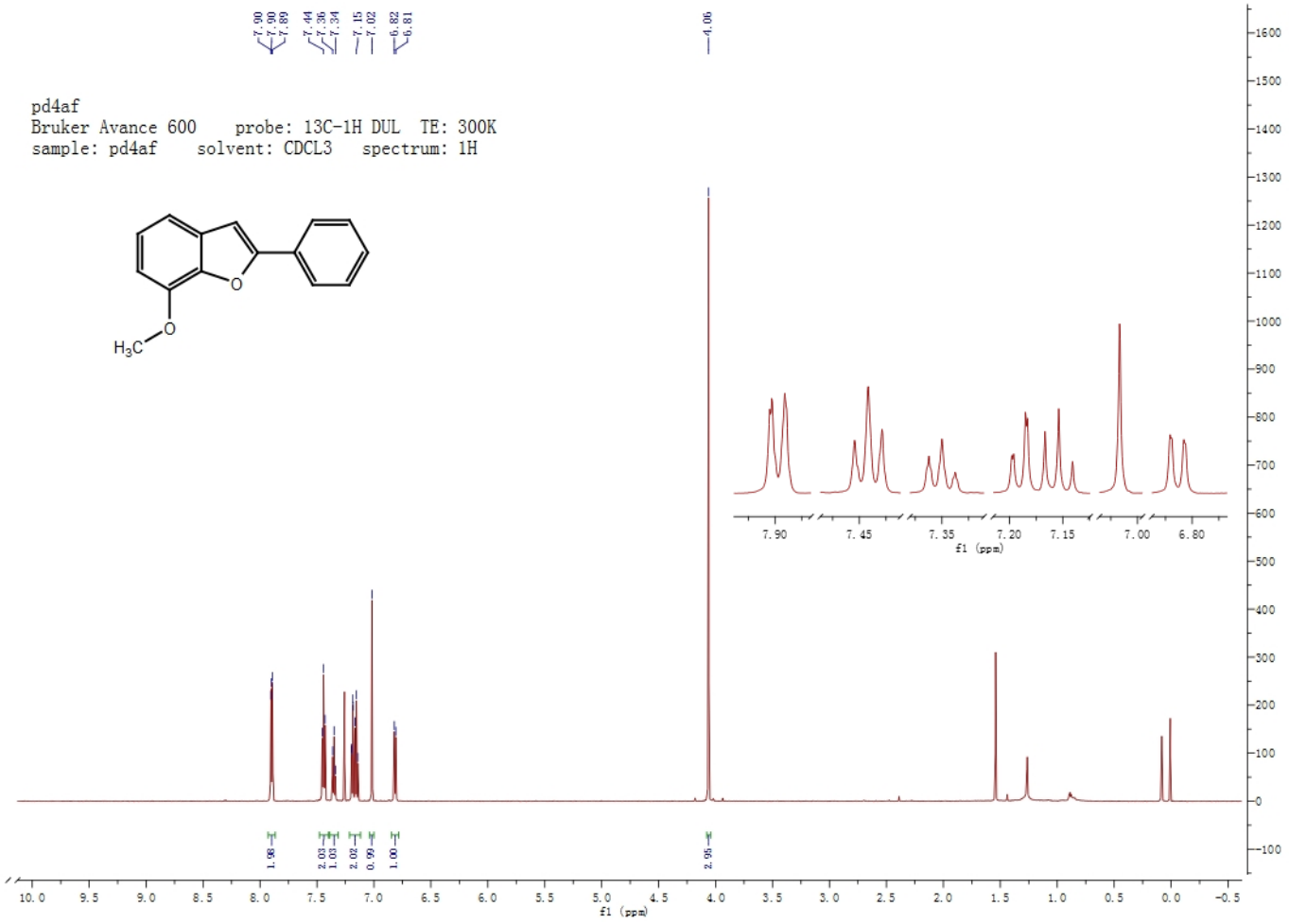
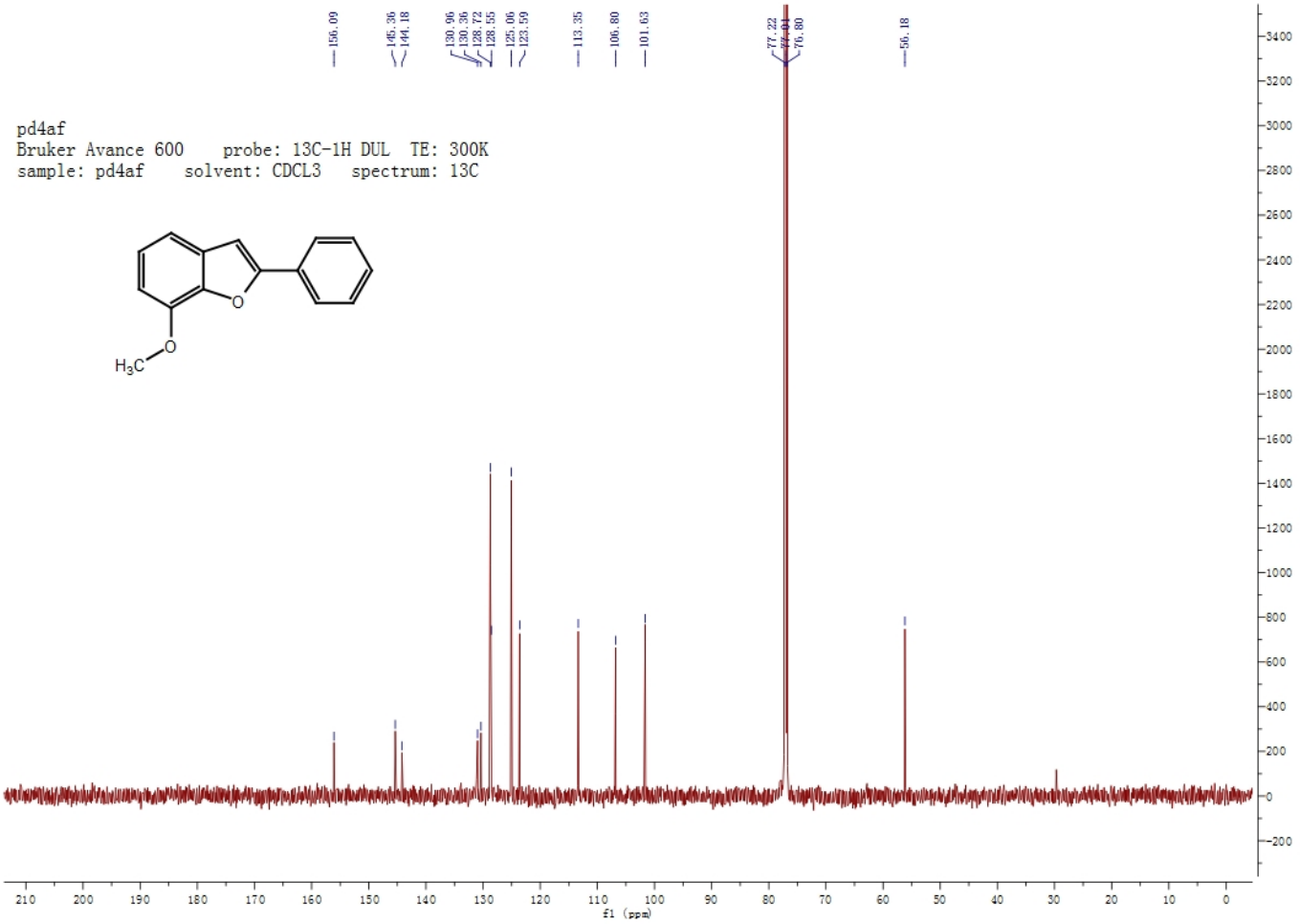
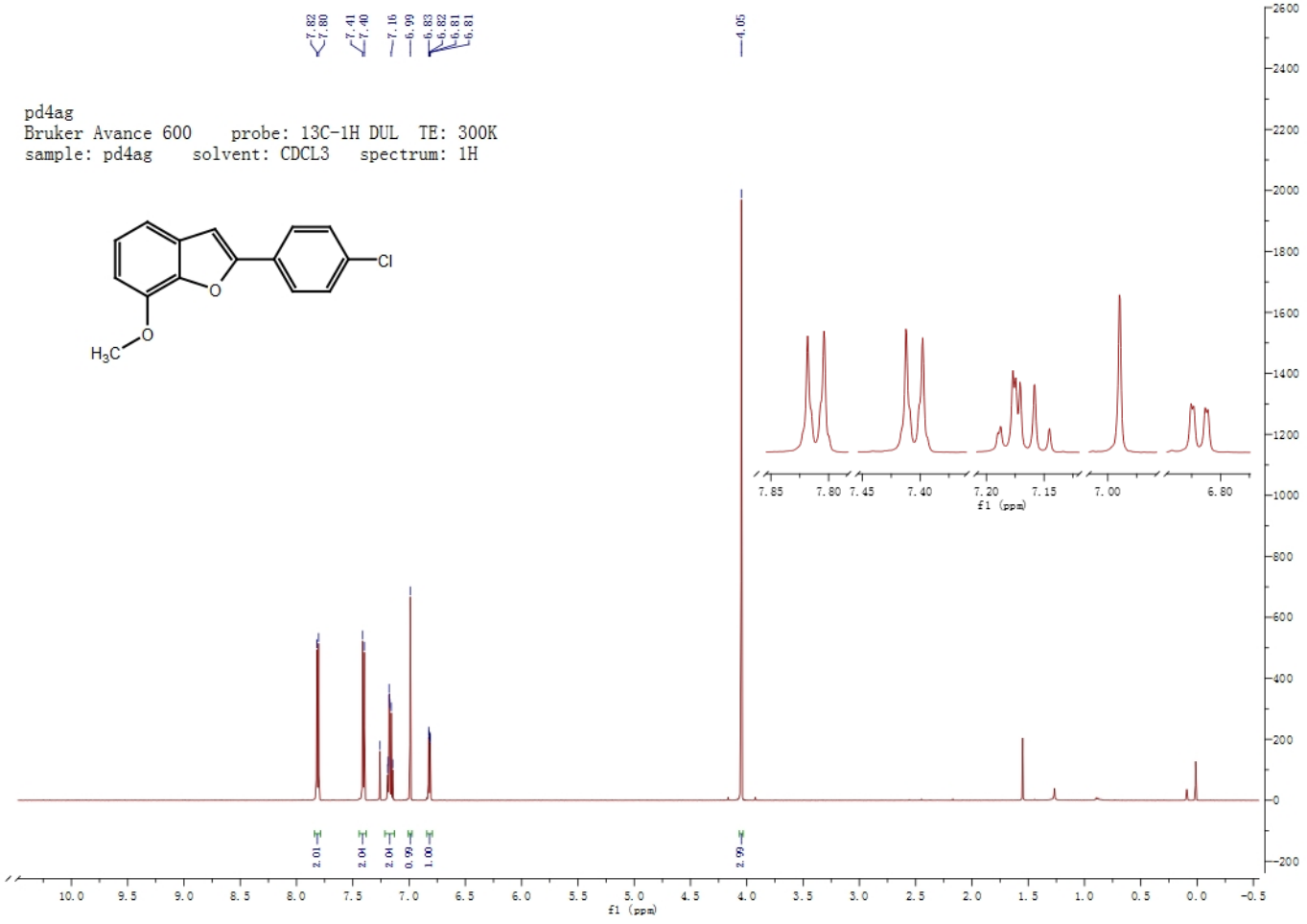
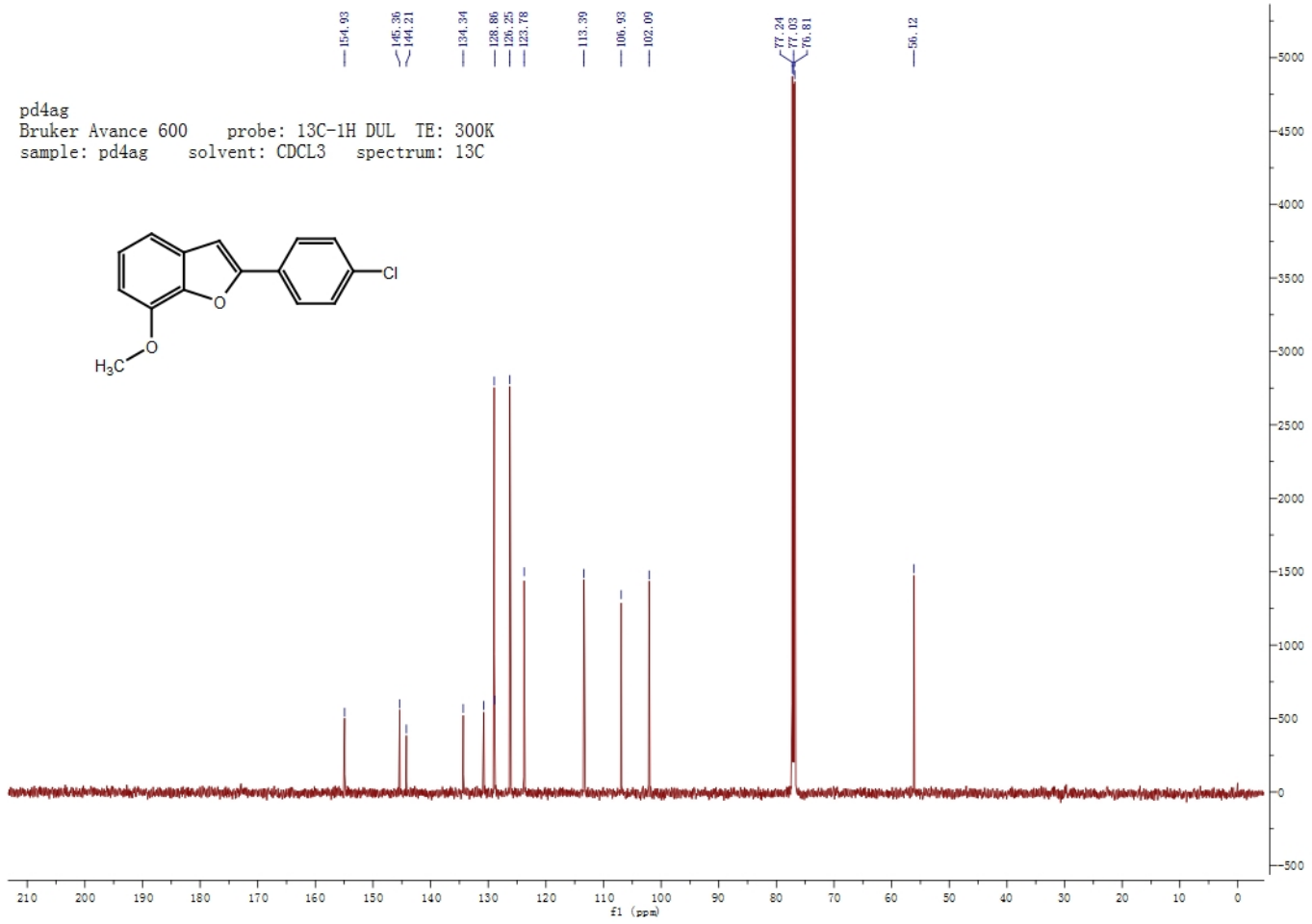




Compound 2ag:





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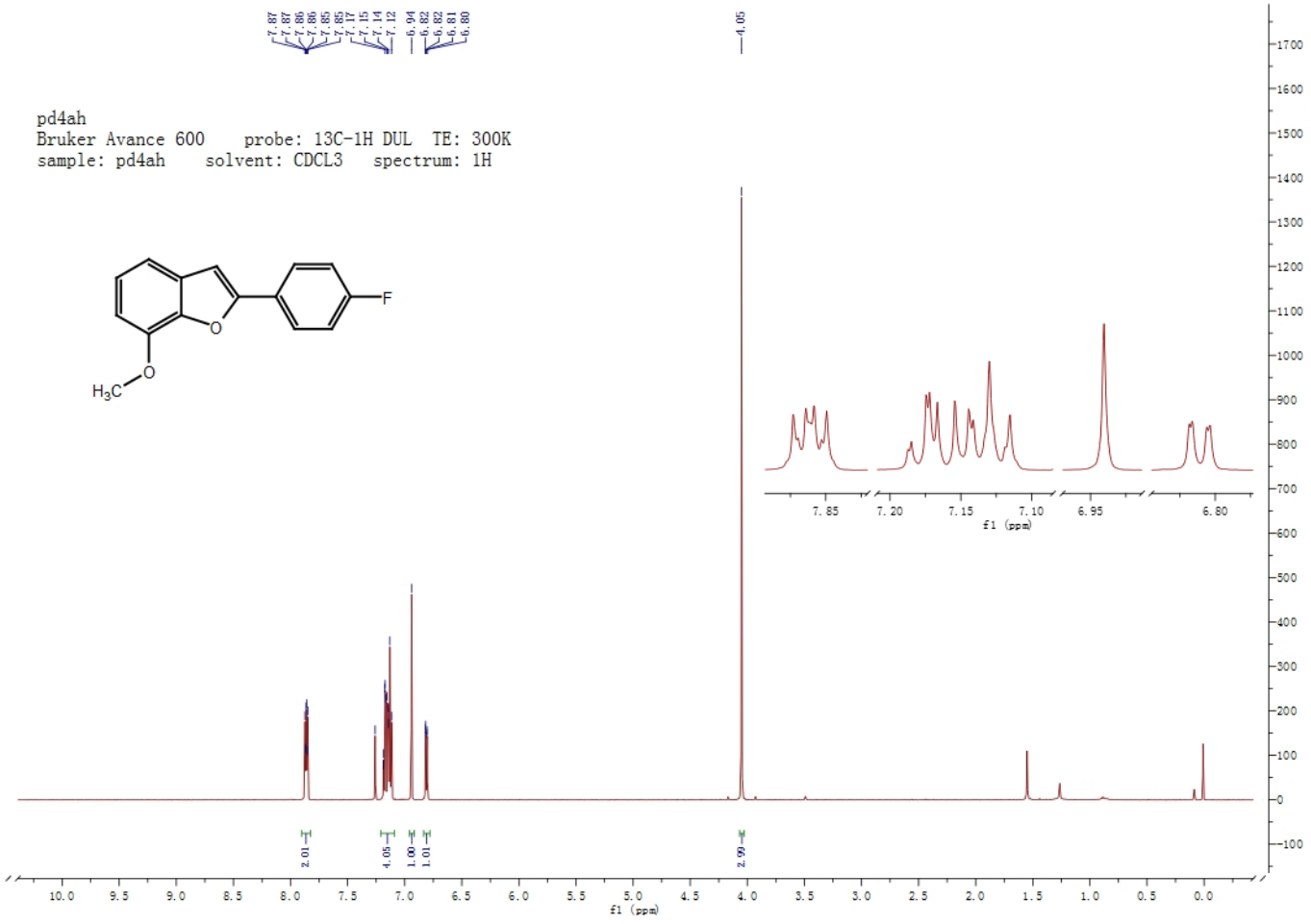

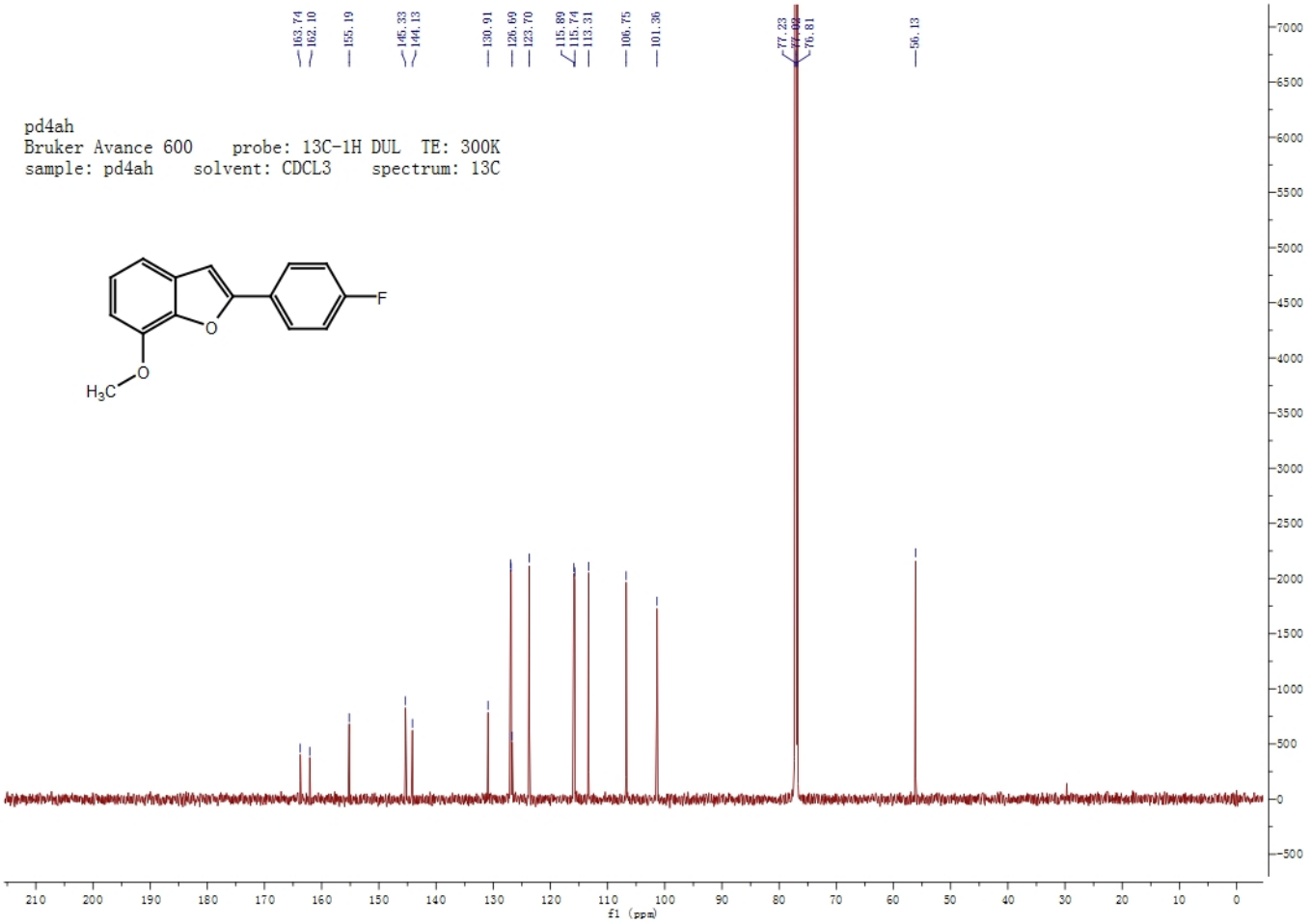

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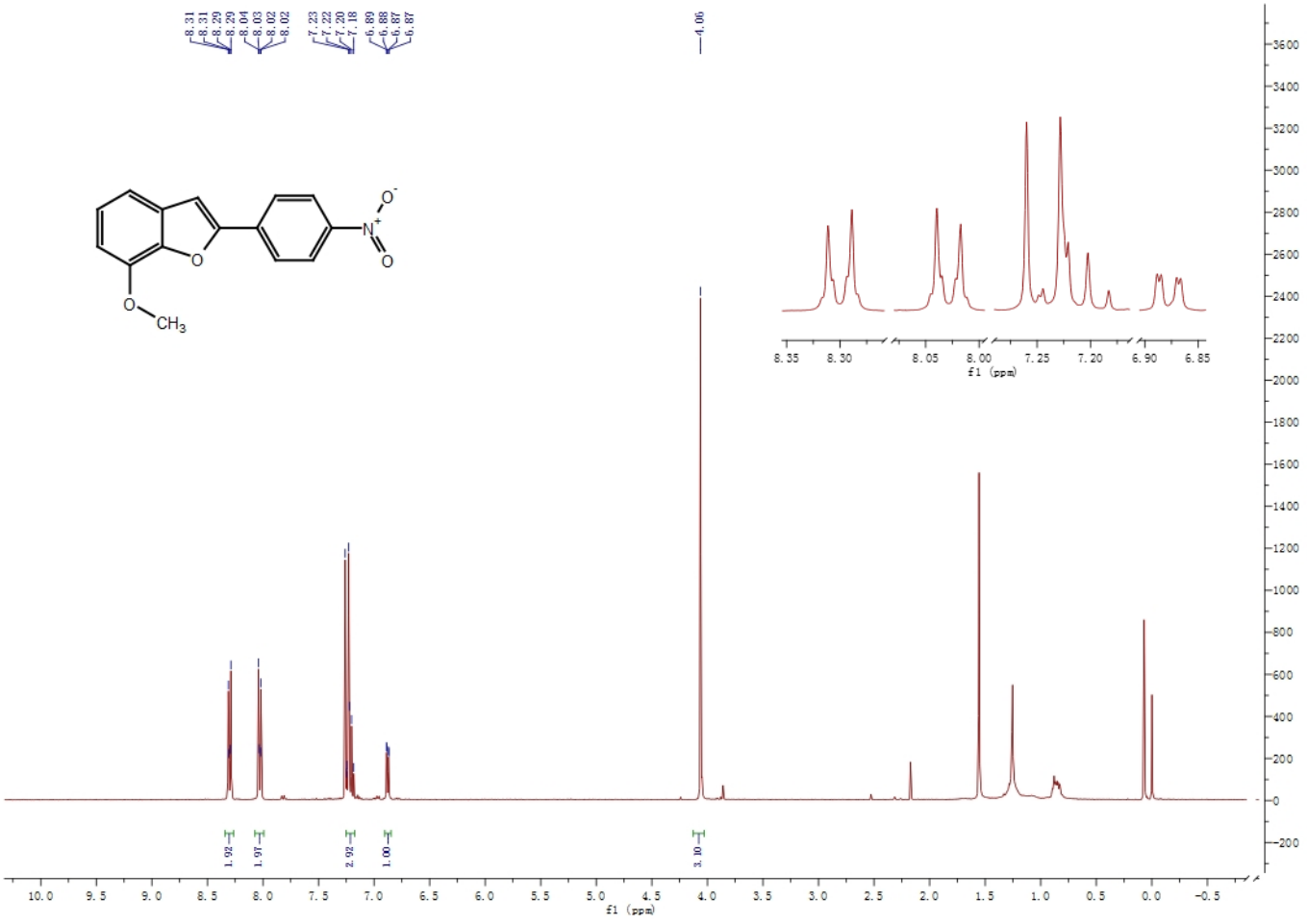

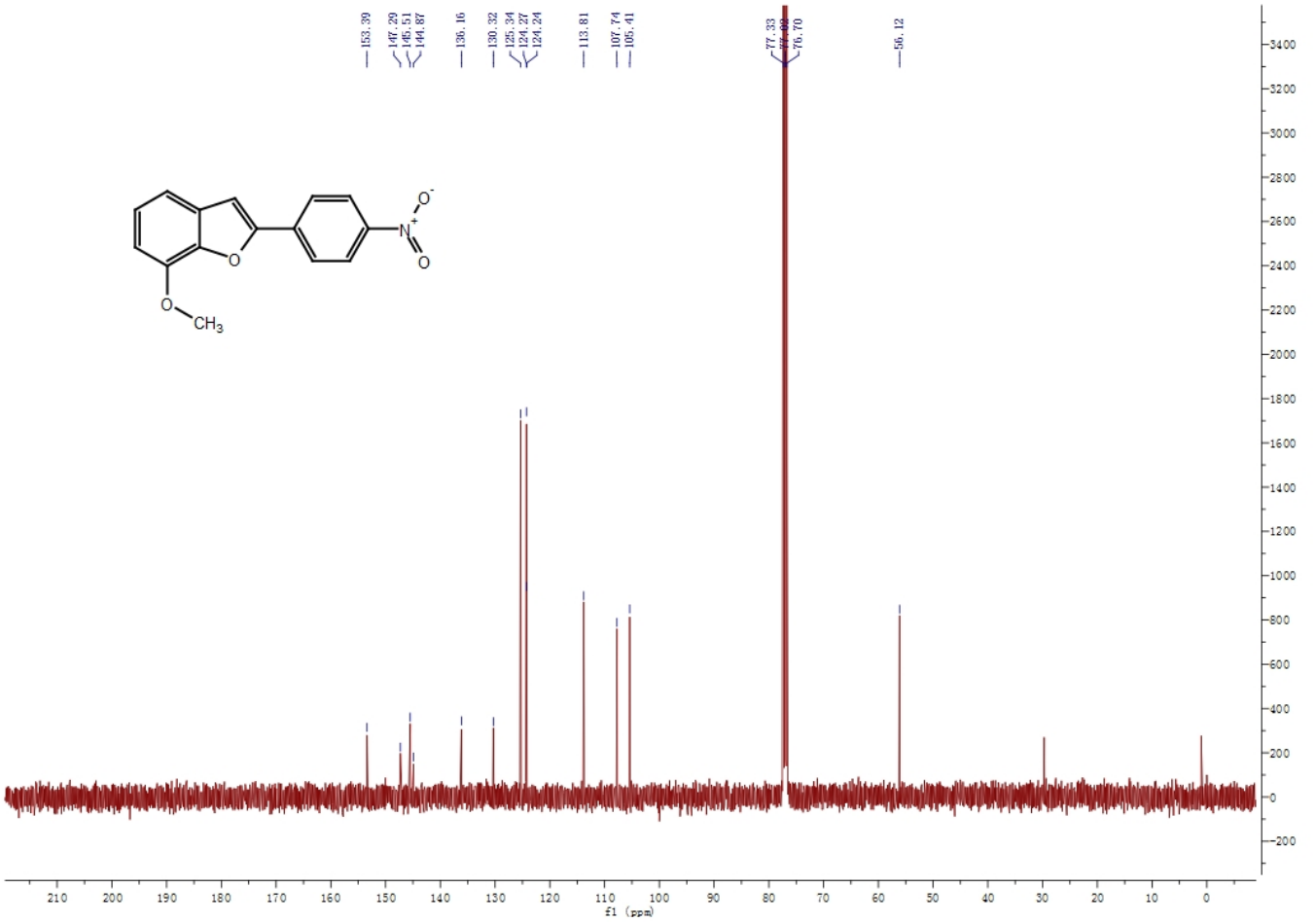

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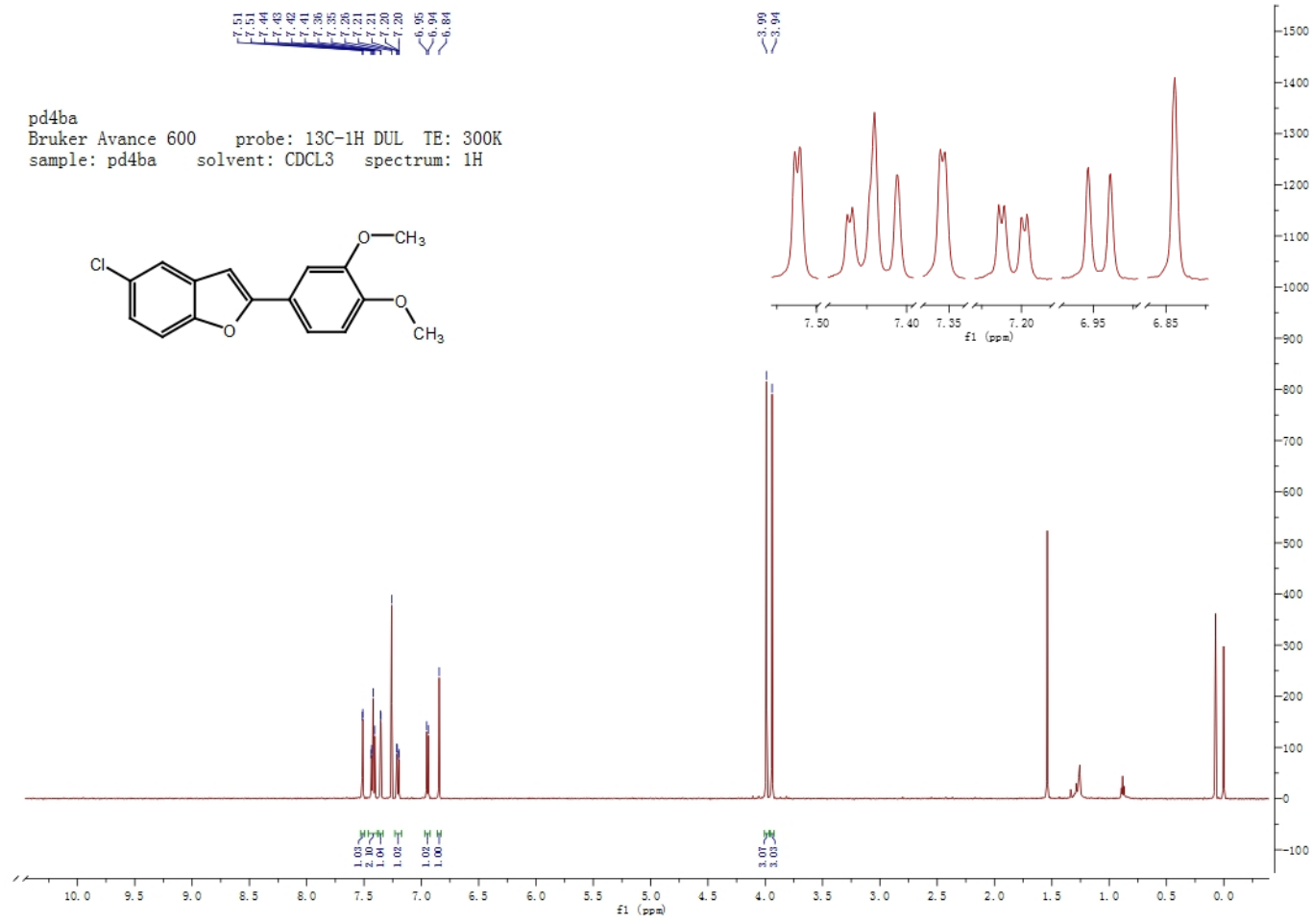

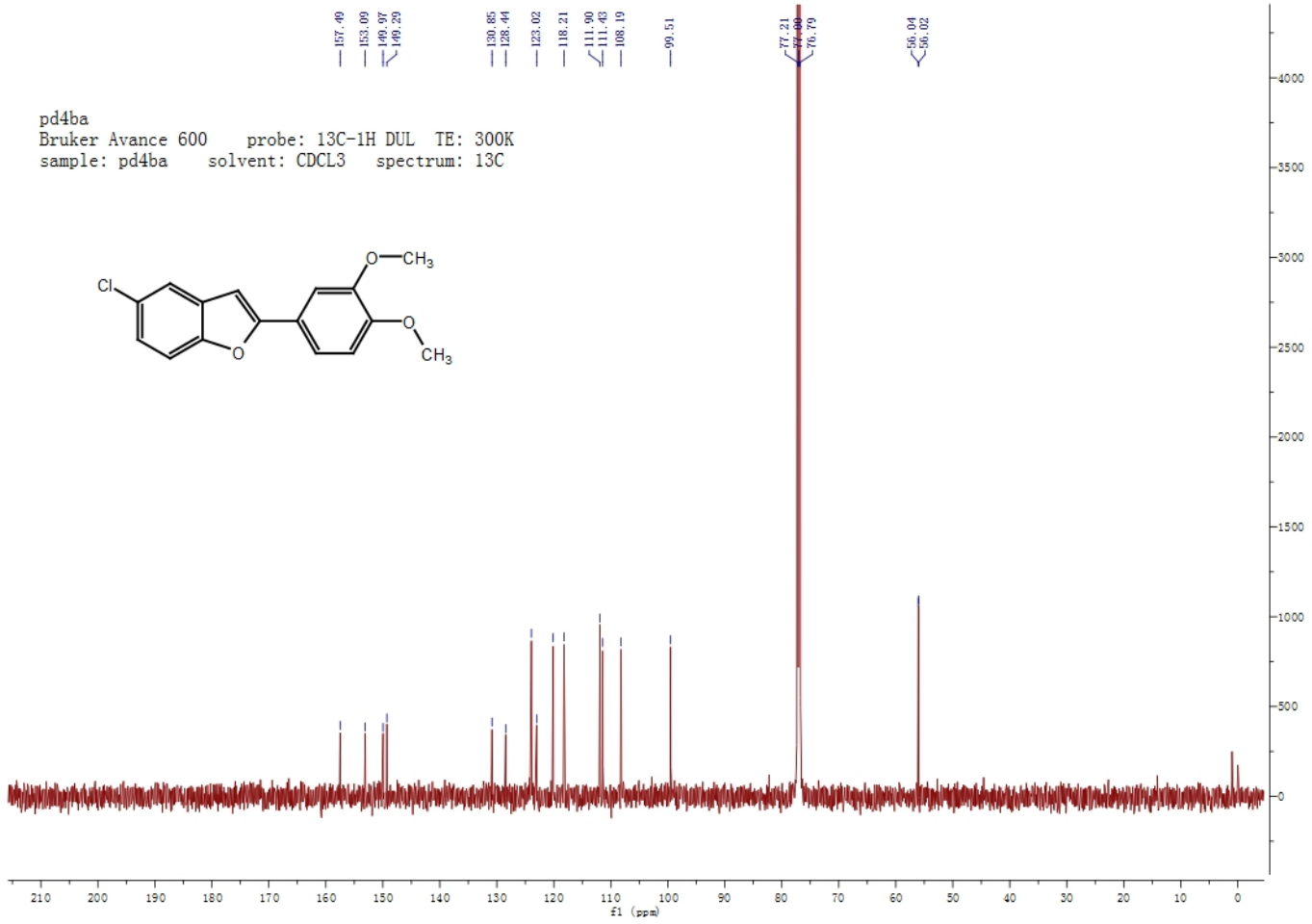

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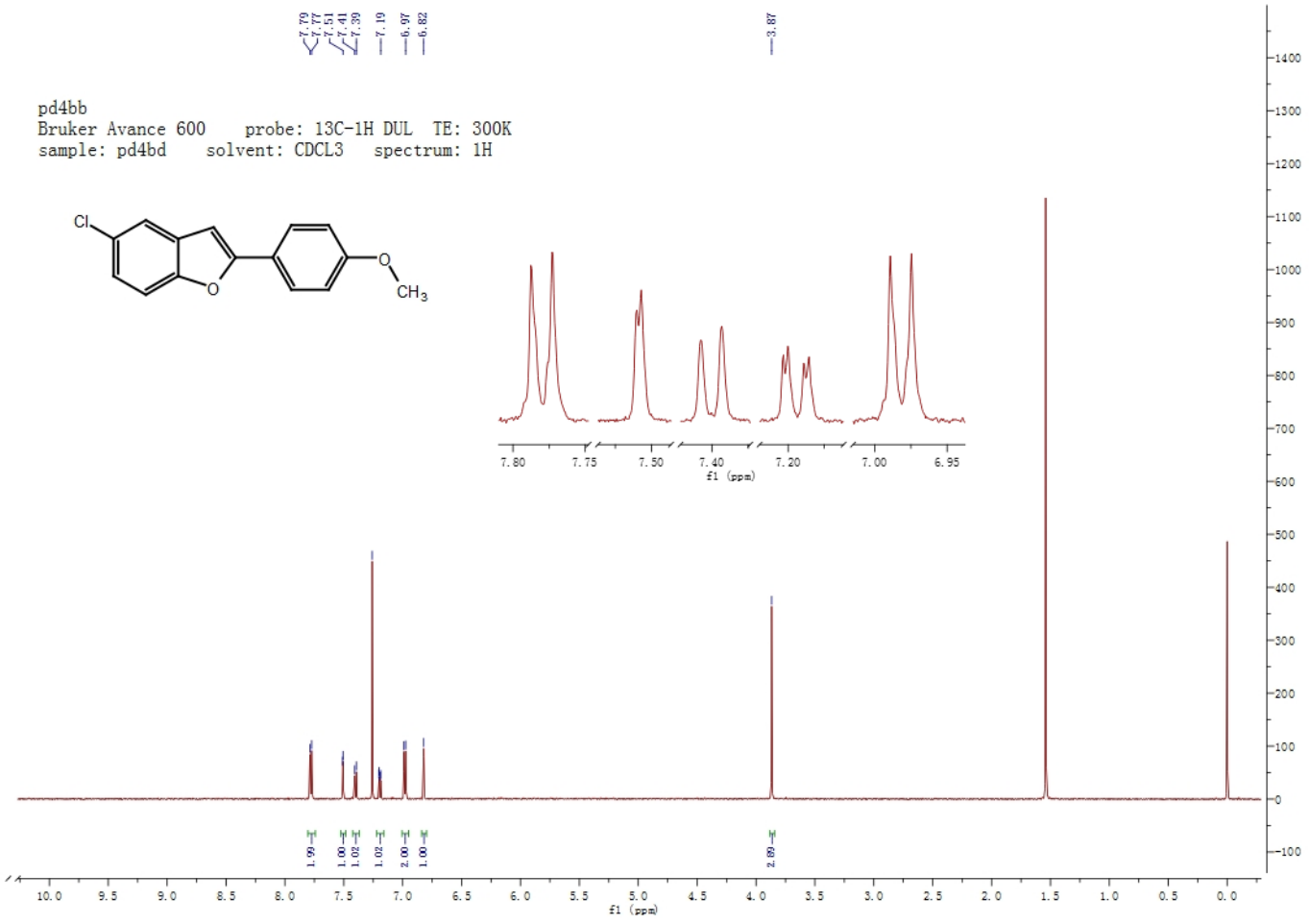

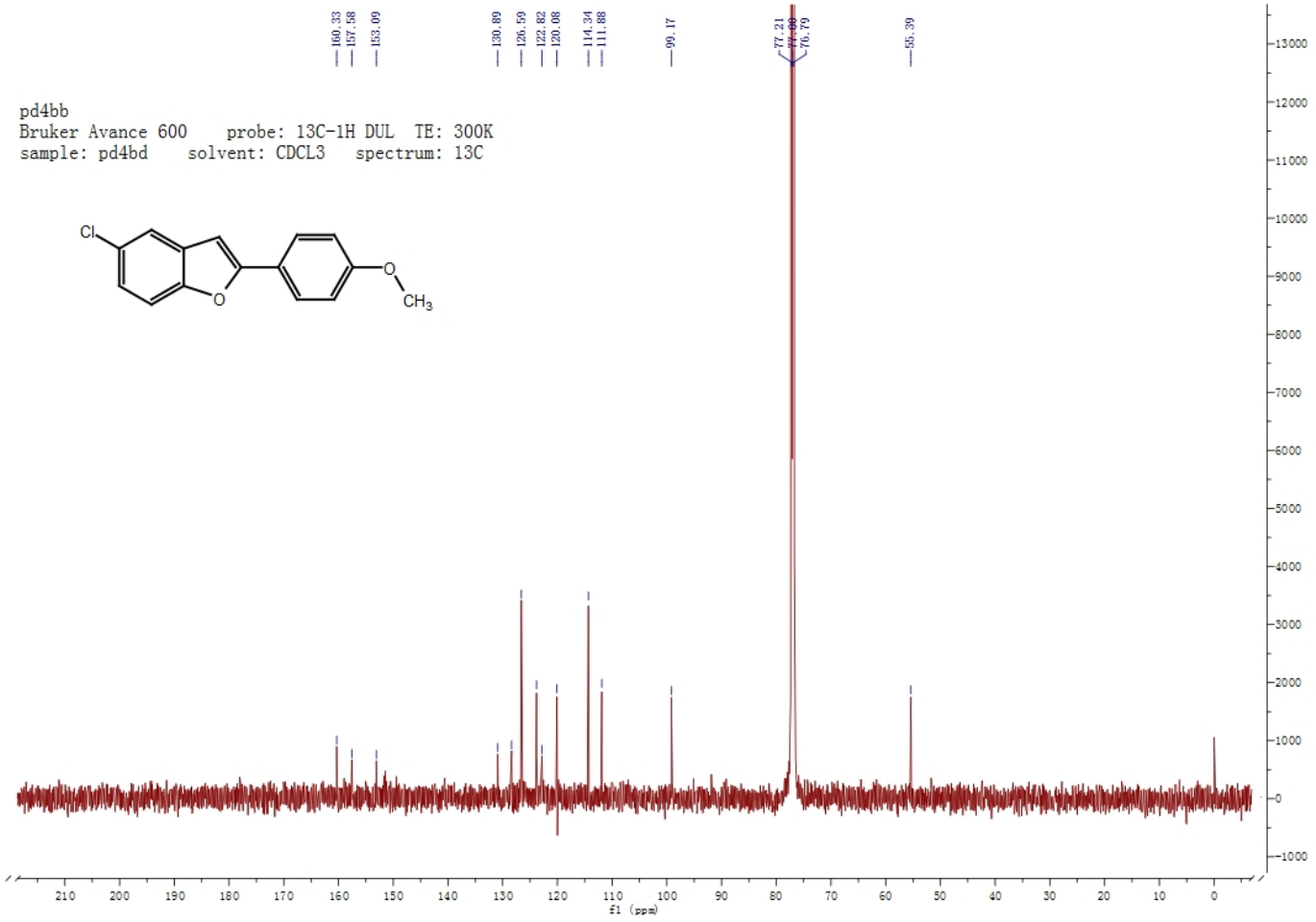

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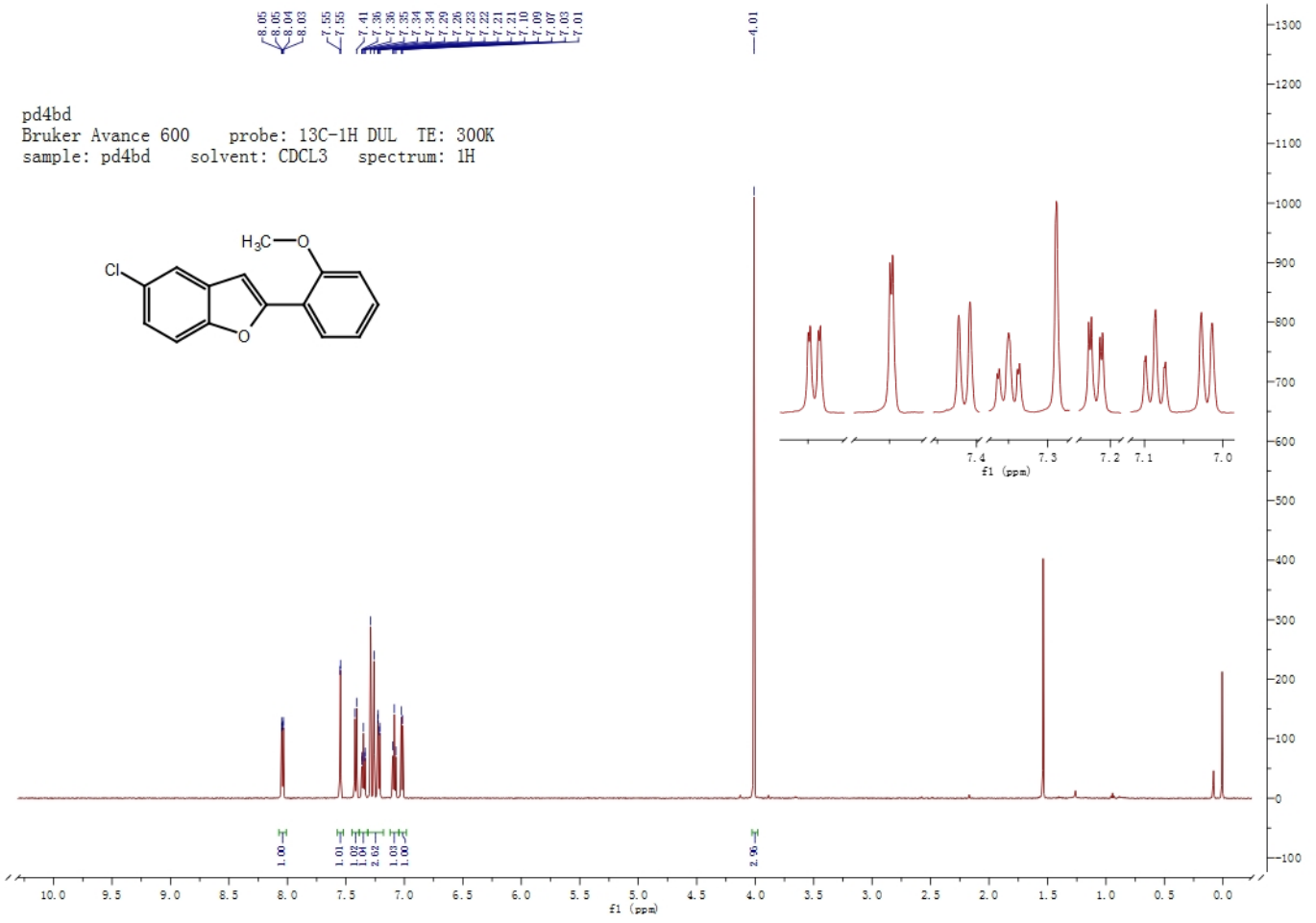

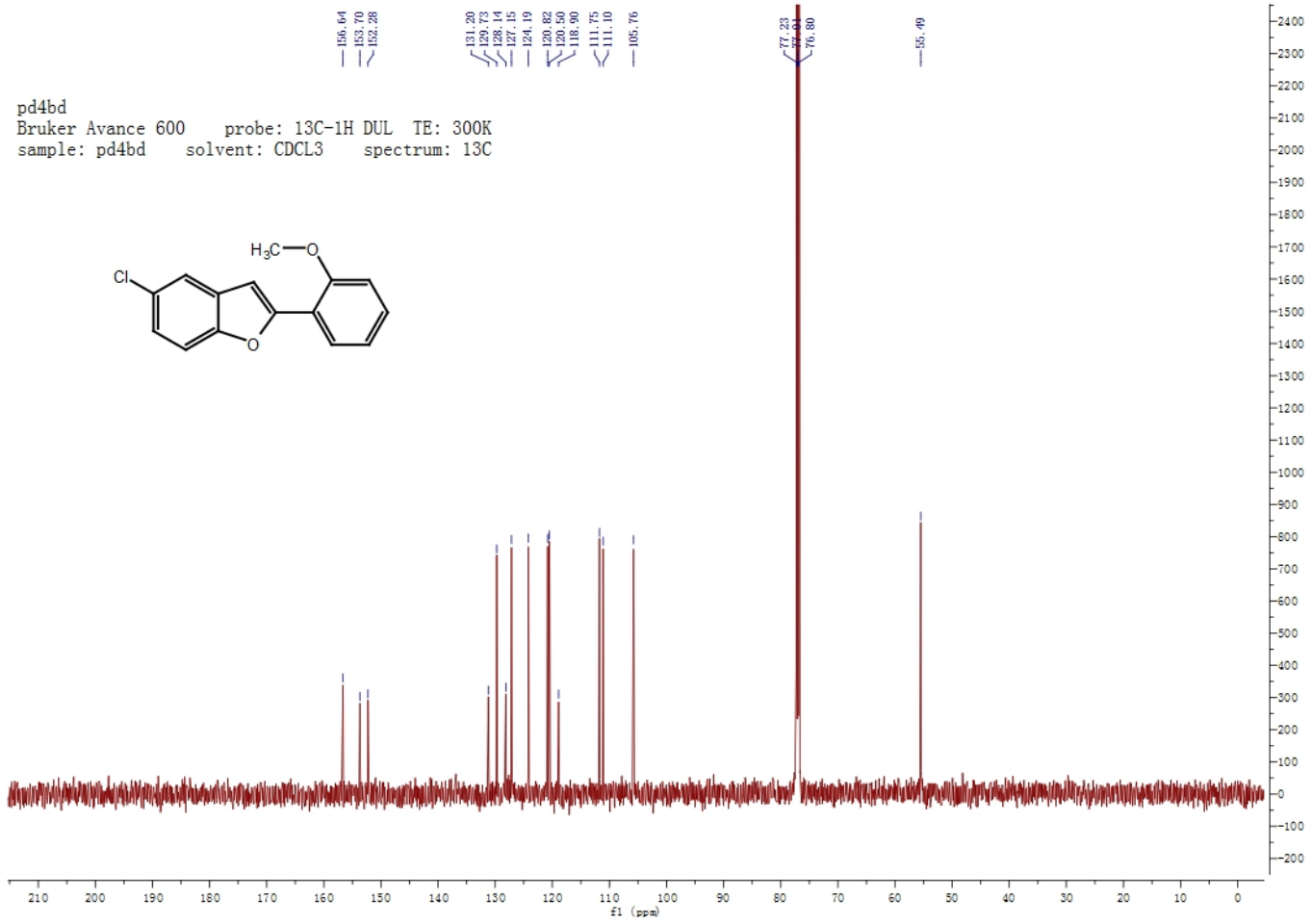

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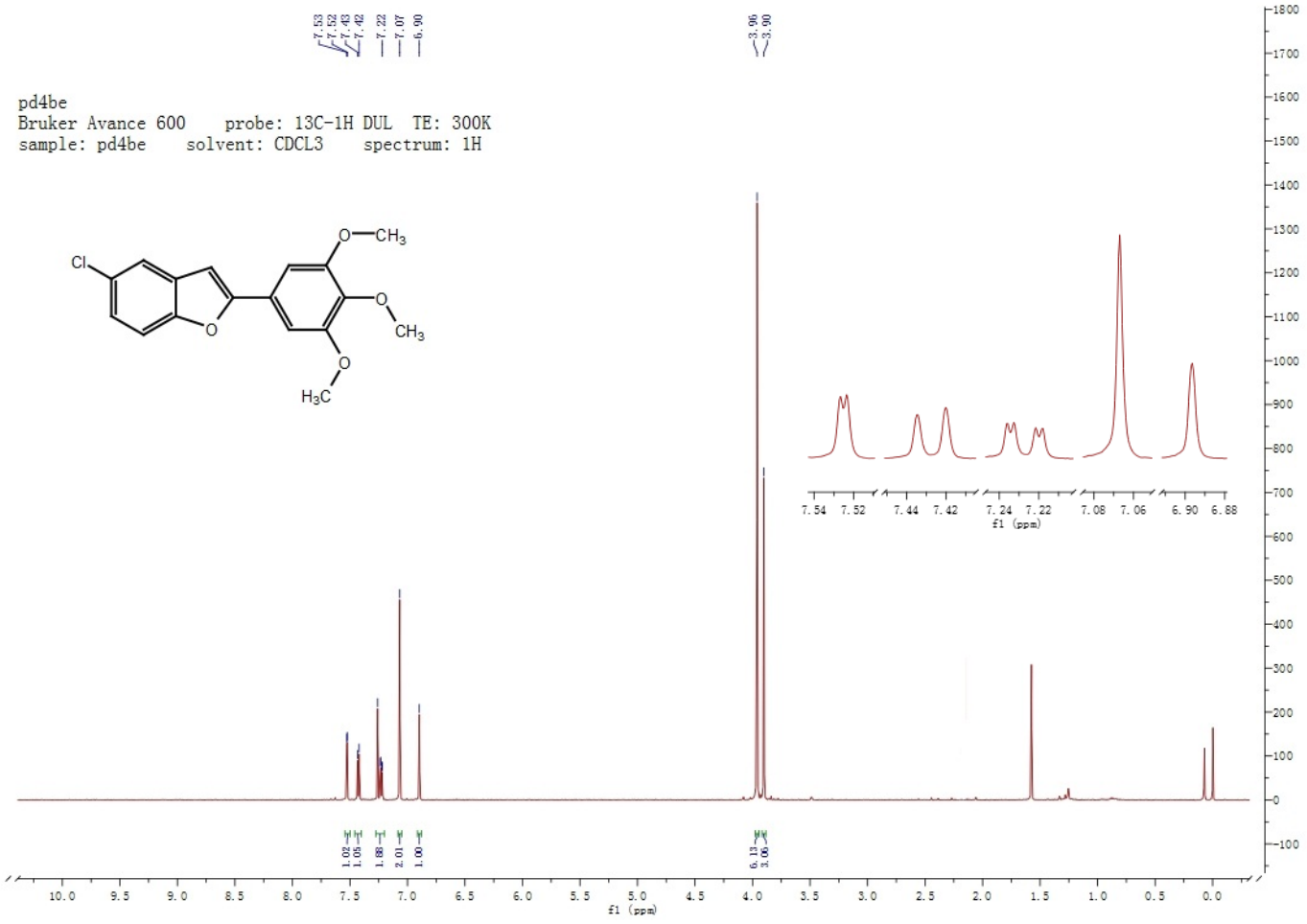

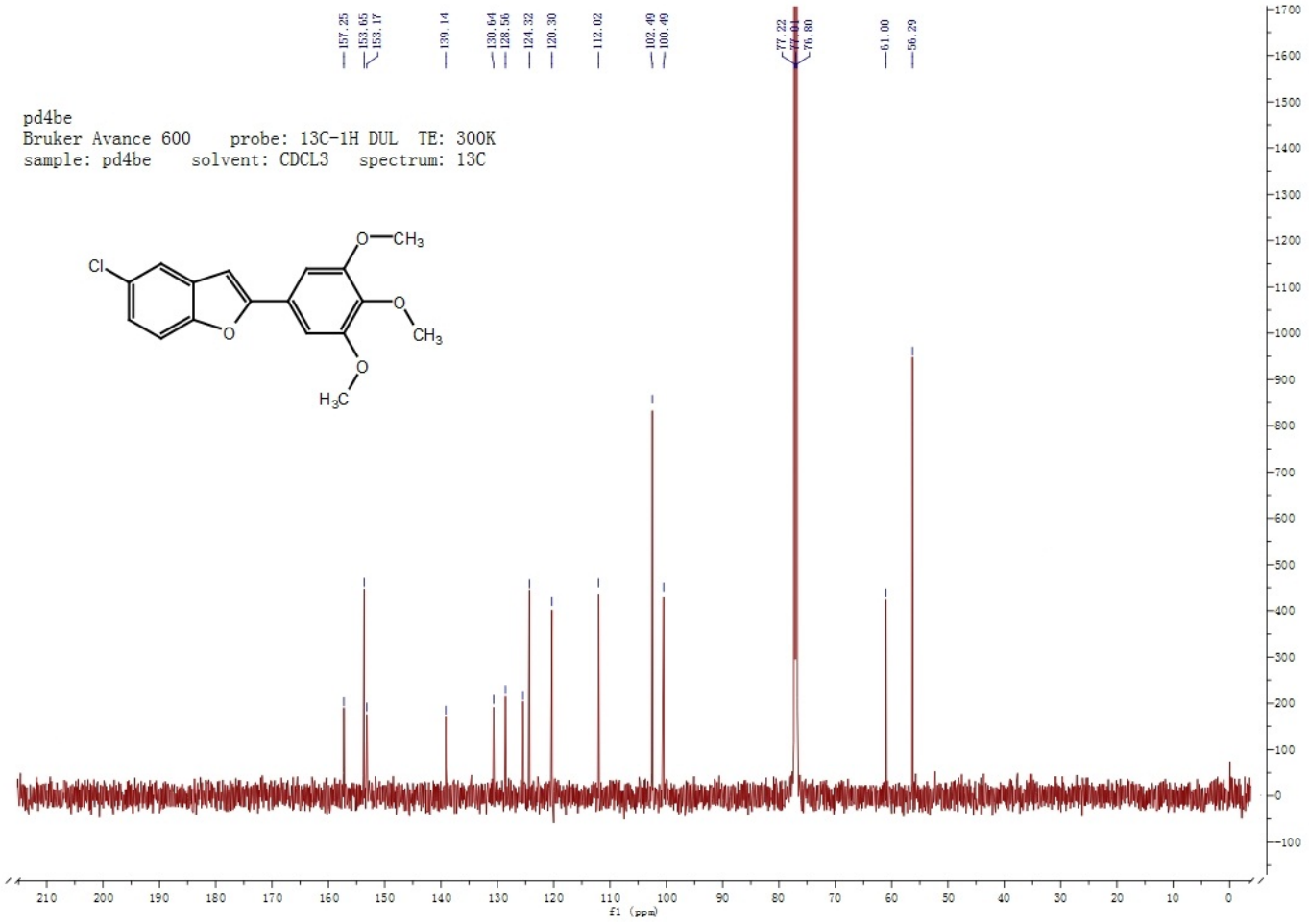

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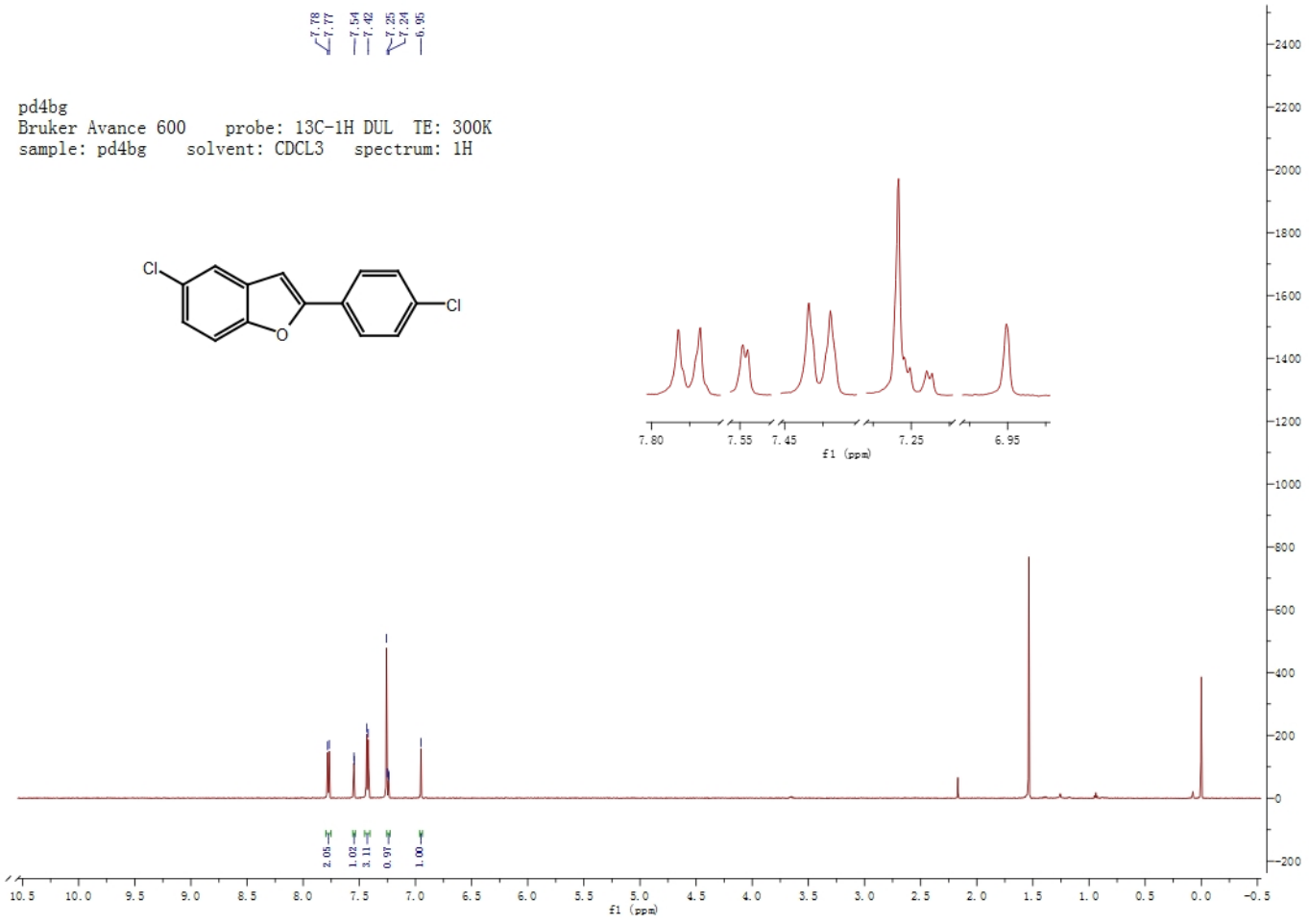

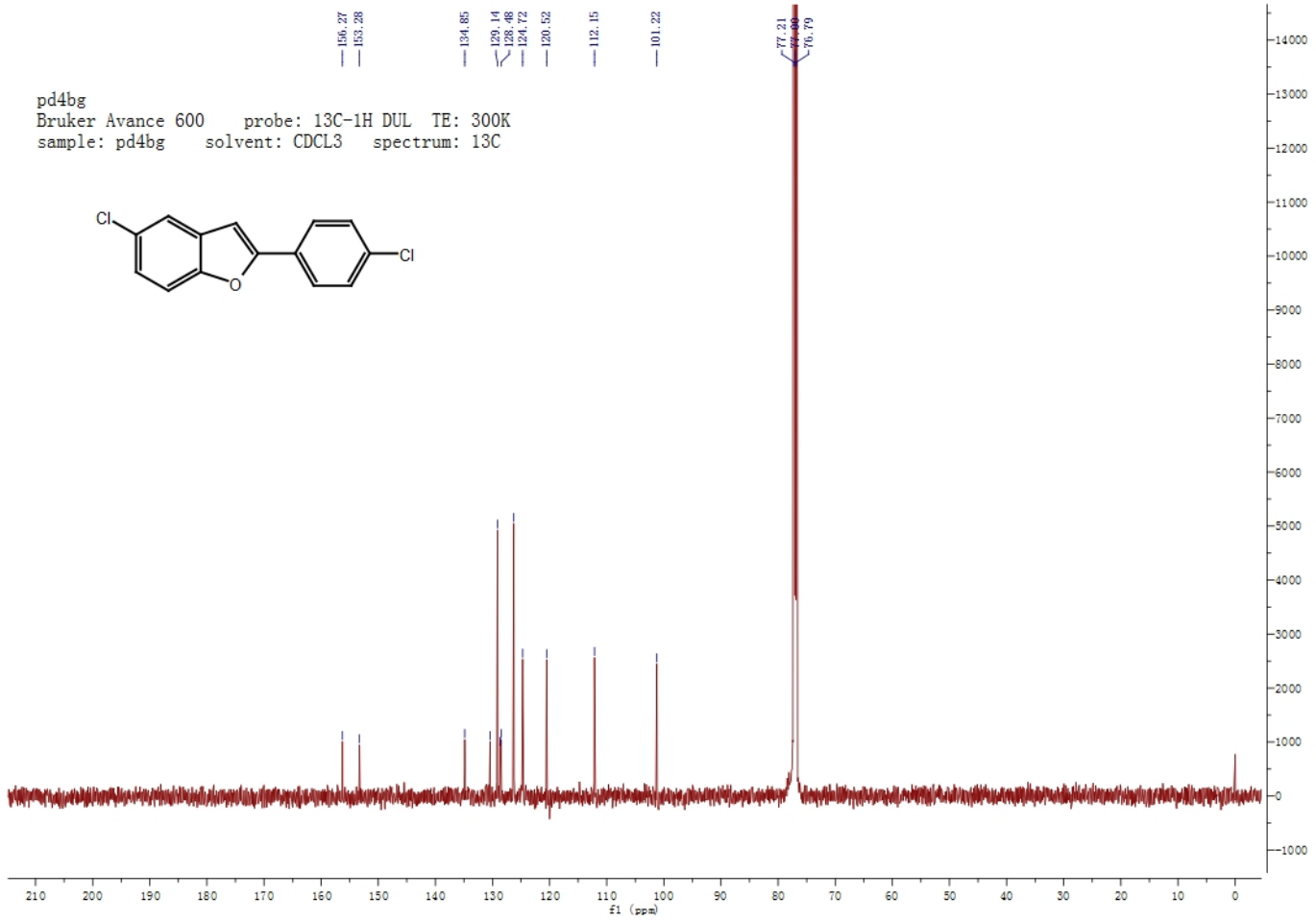

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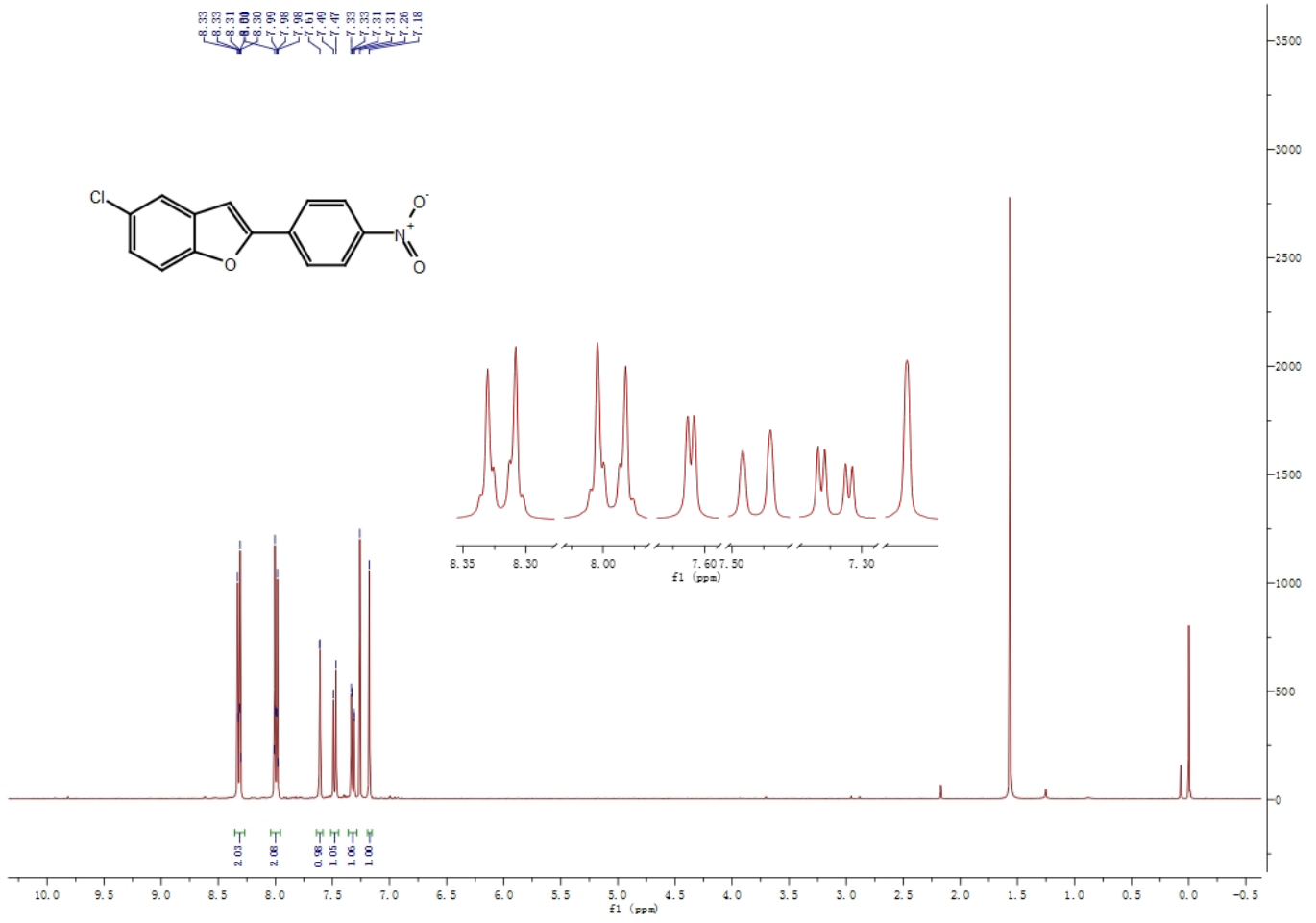

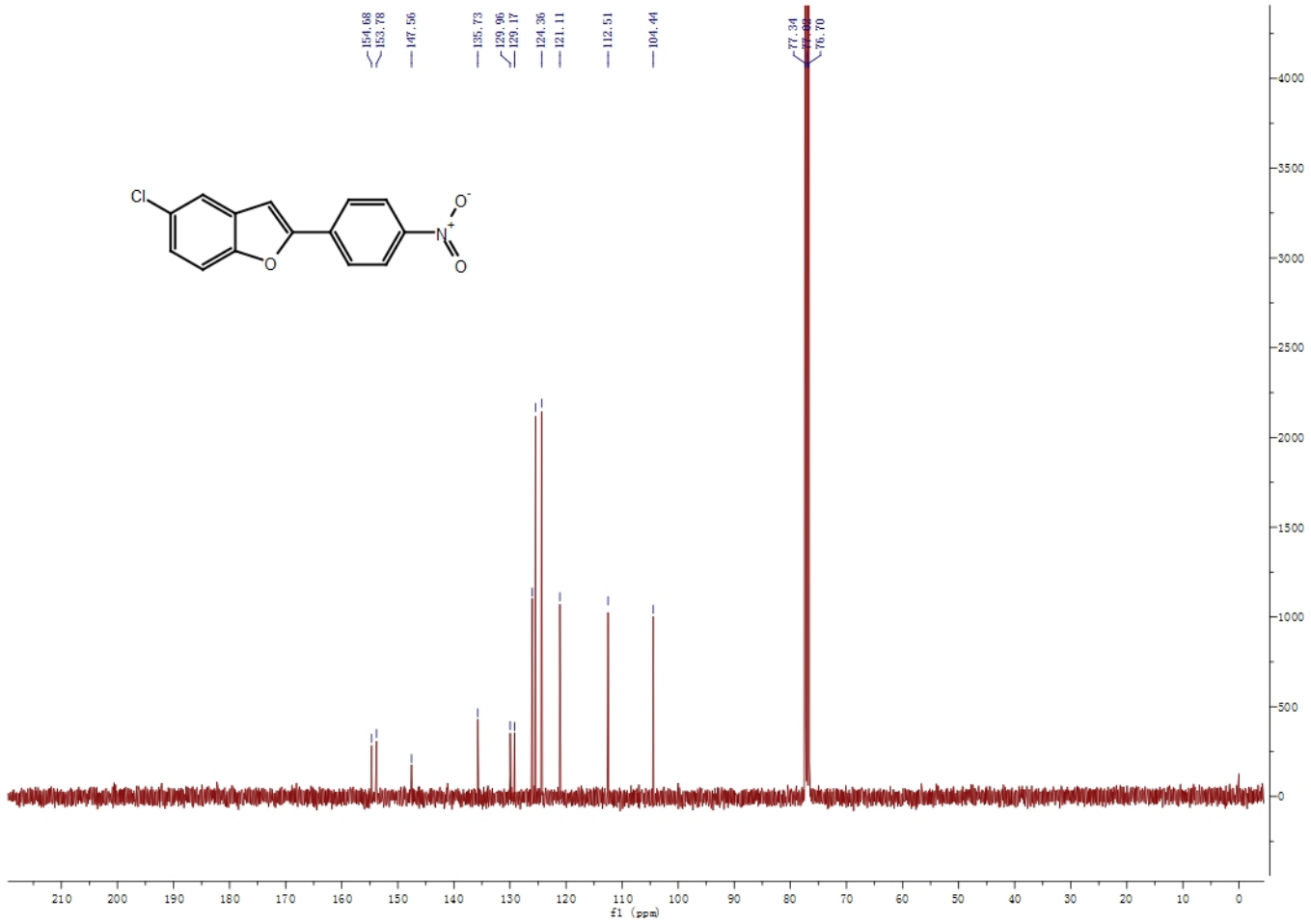

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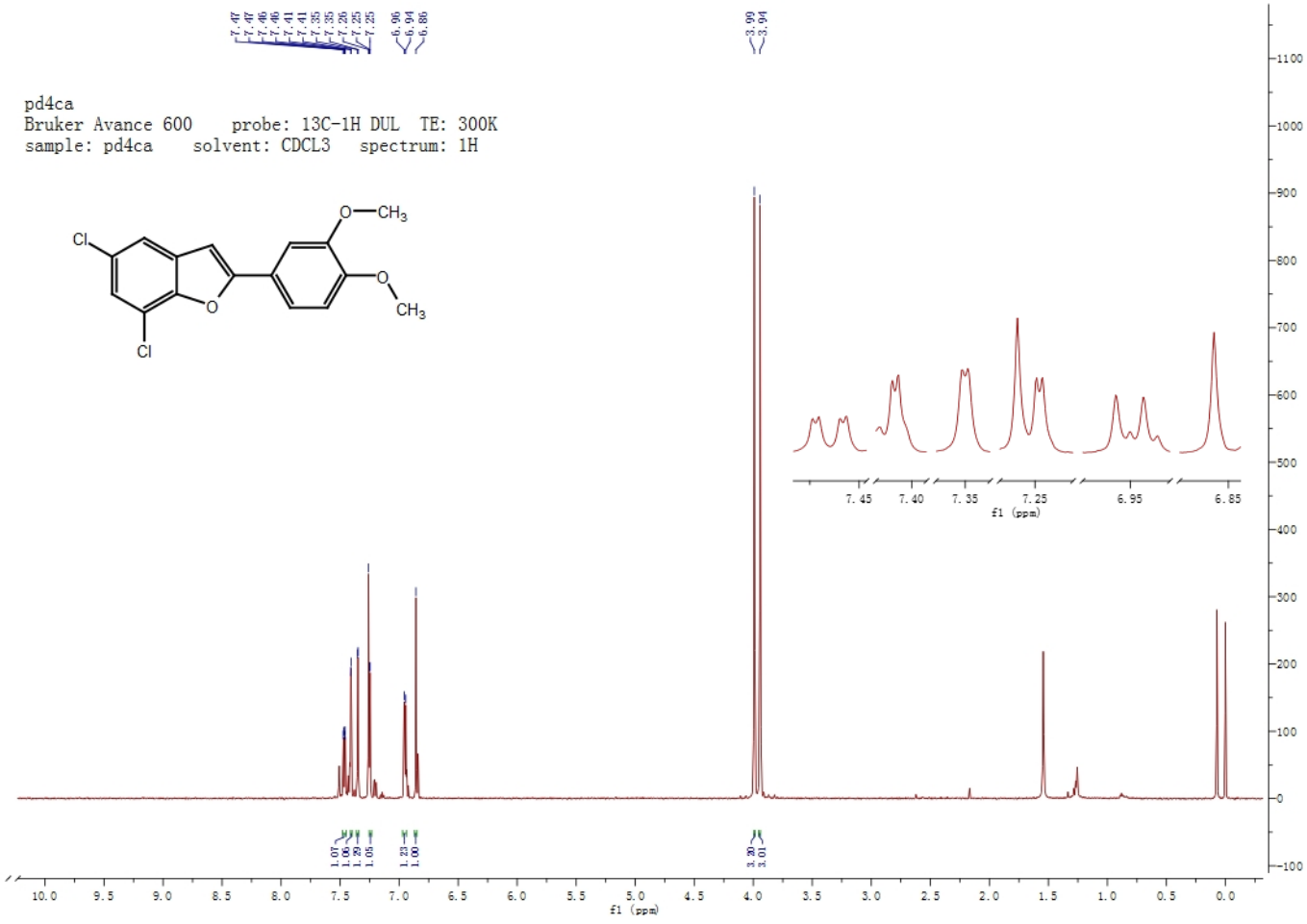

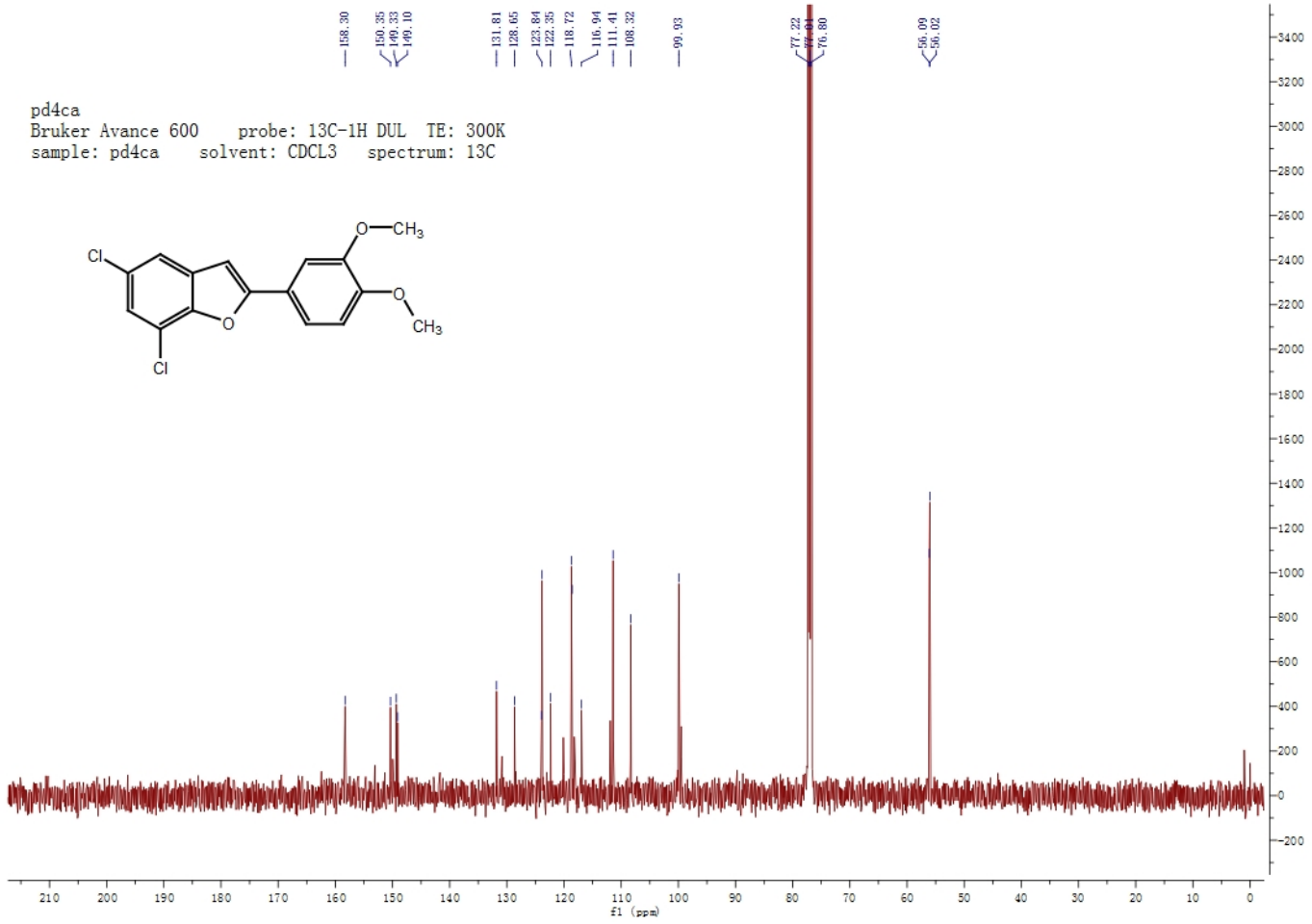

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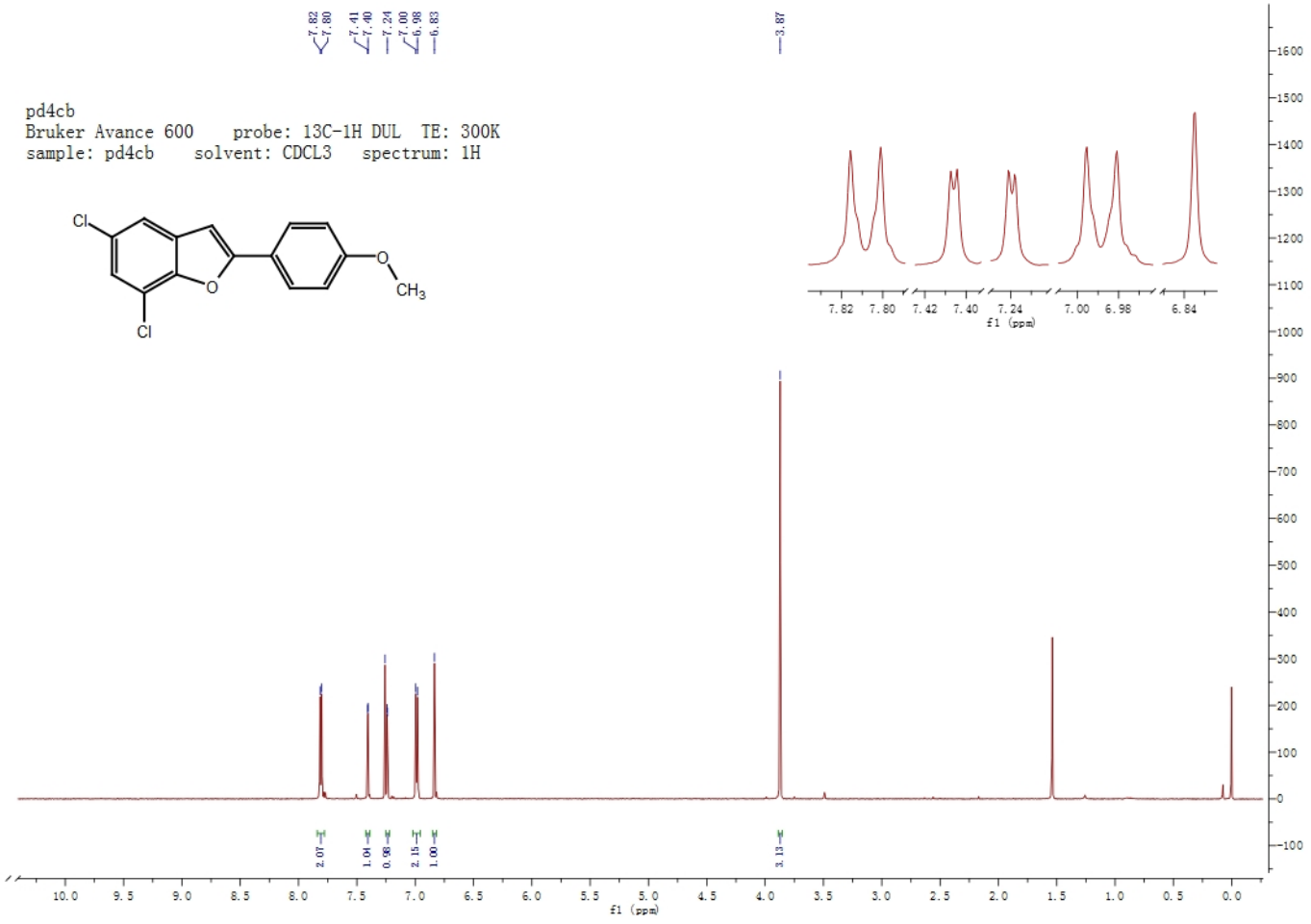

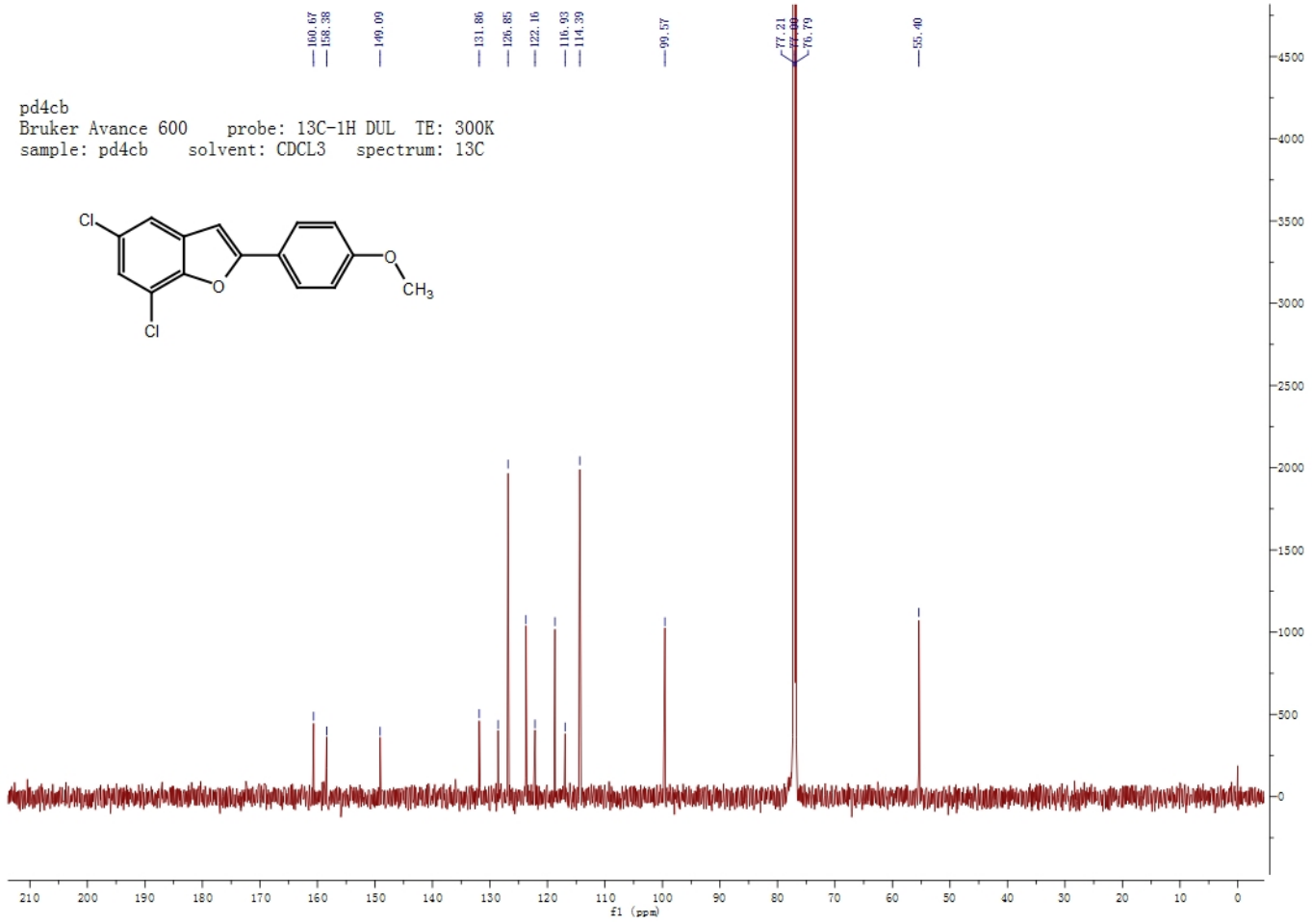

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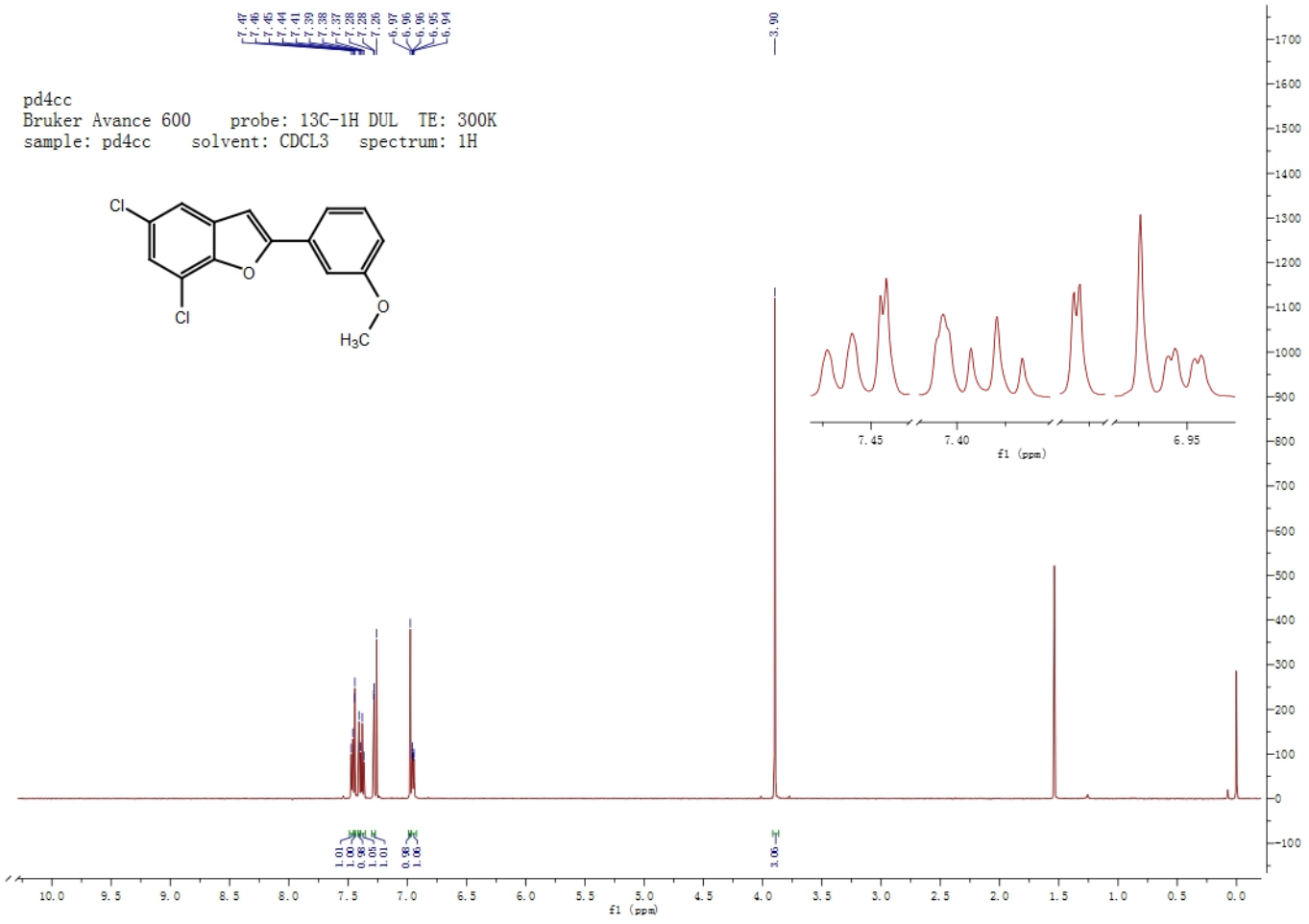

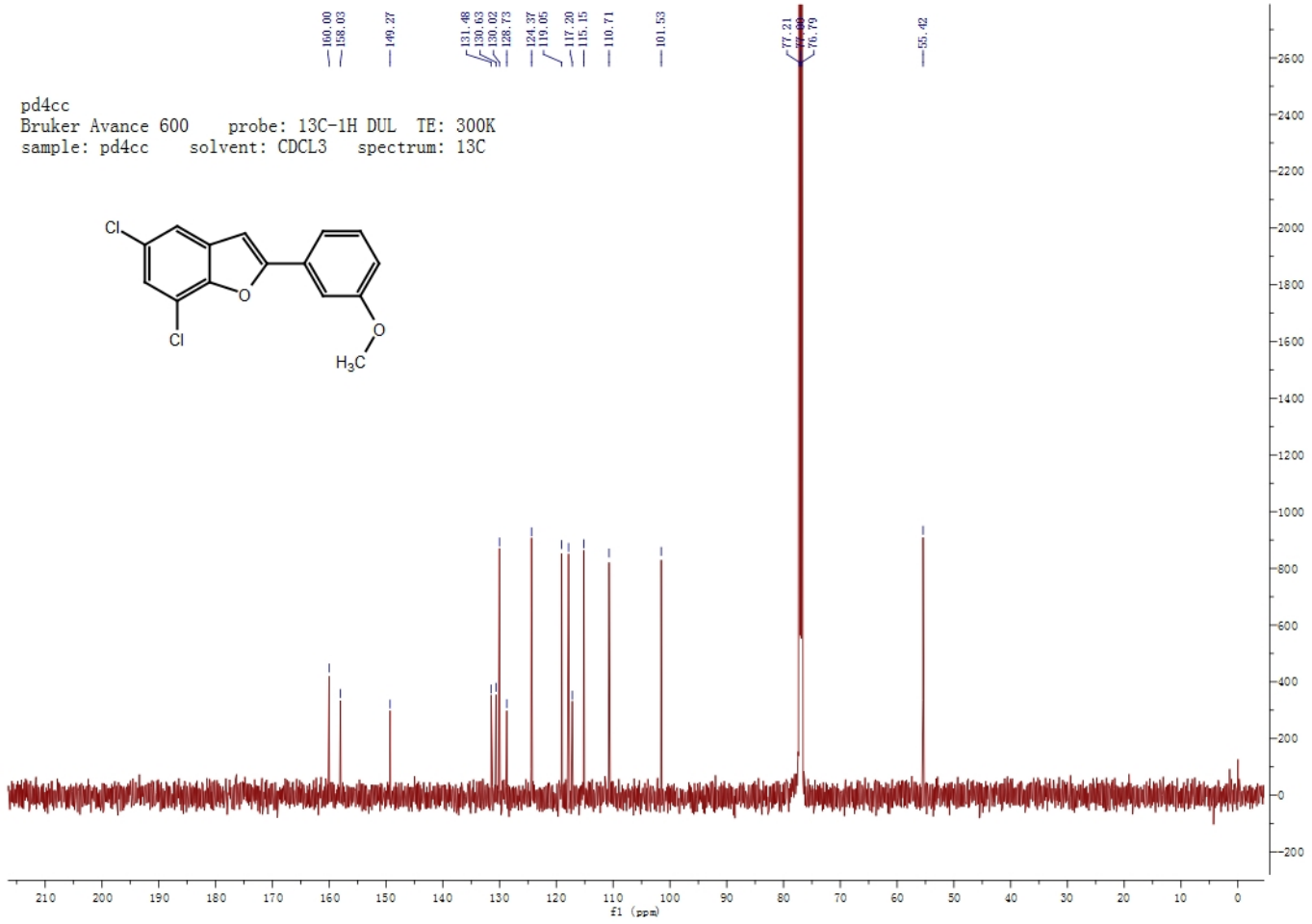

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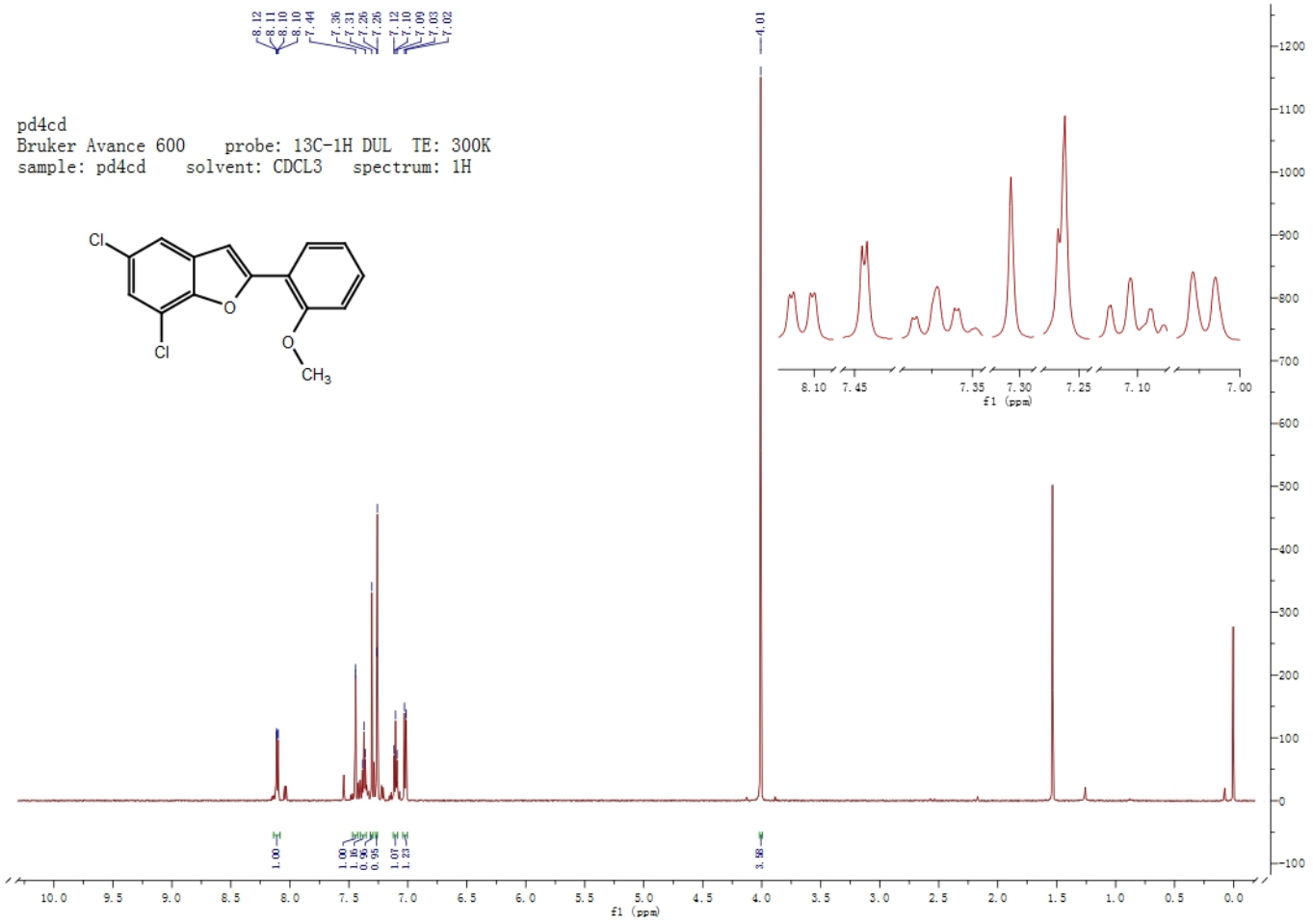

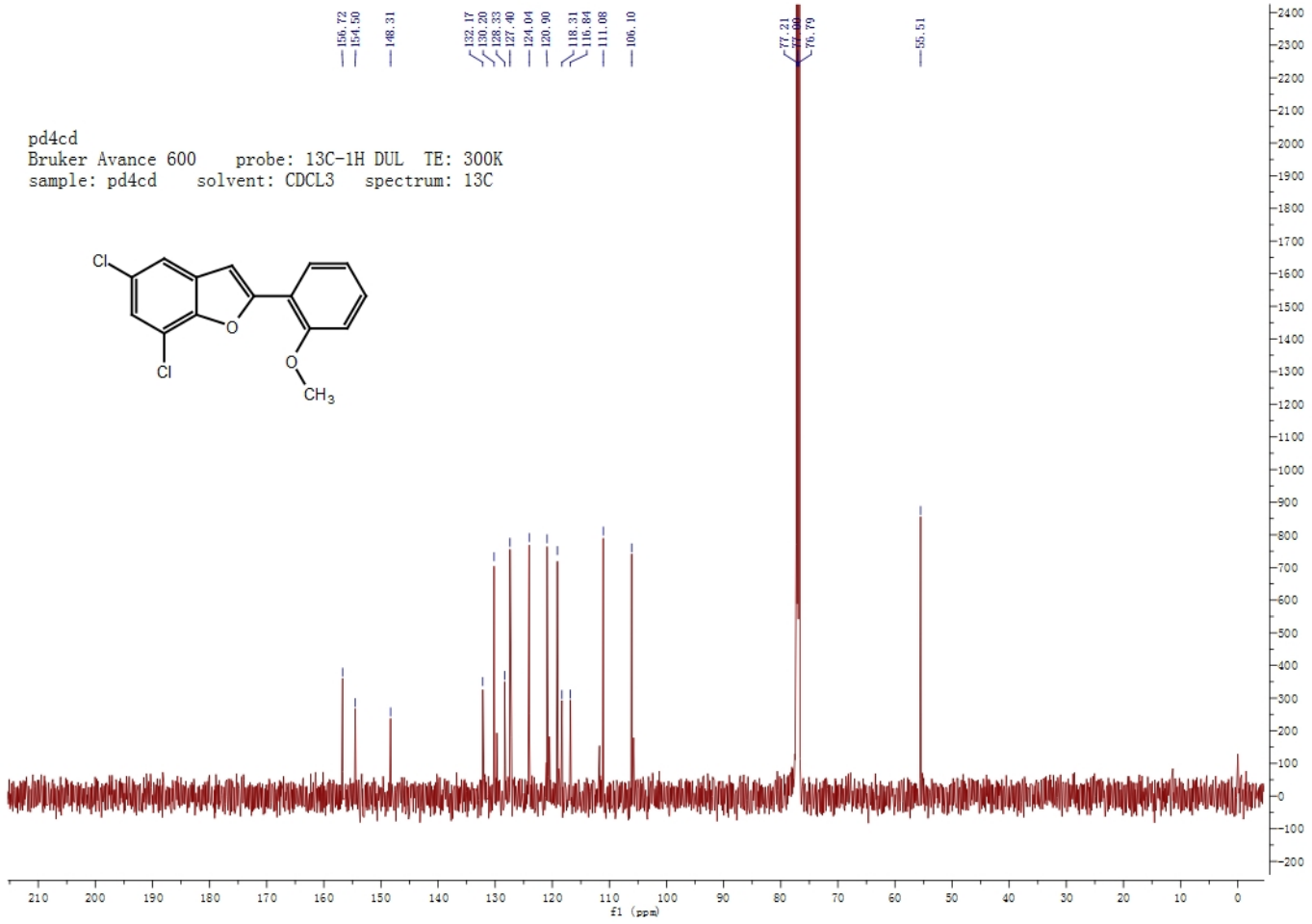

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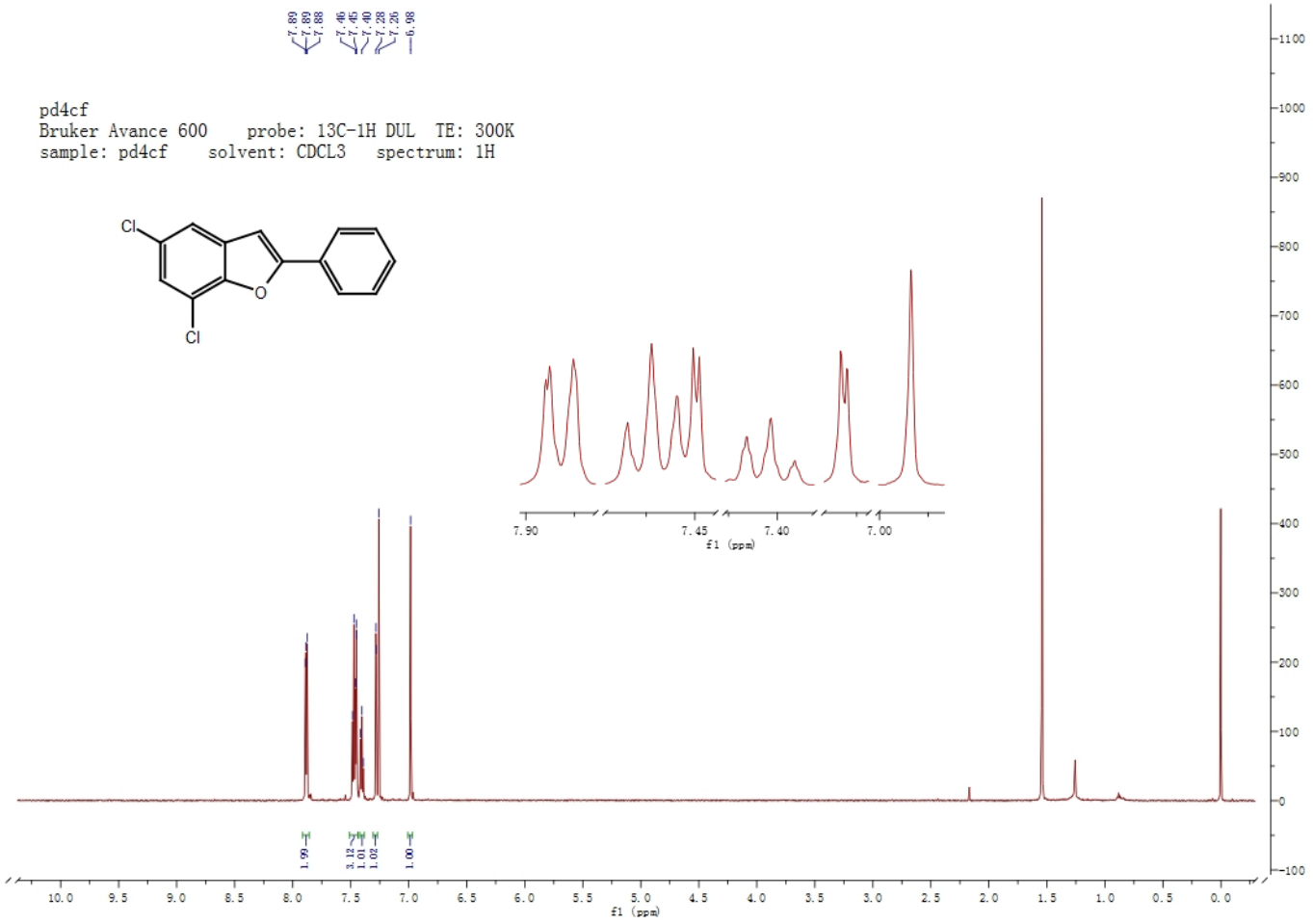

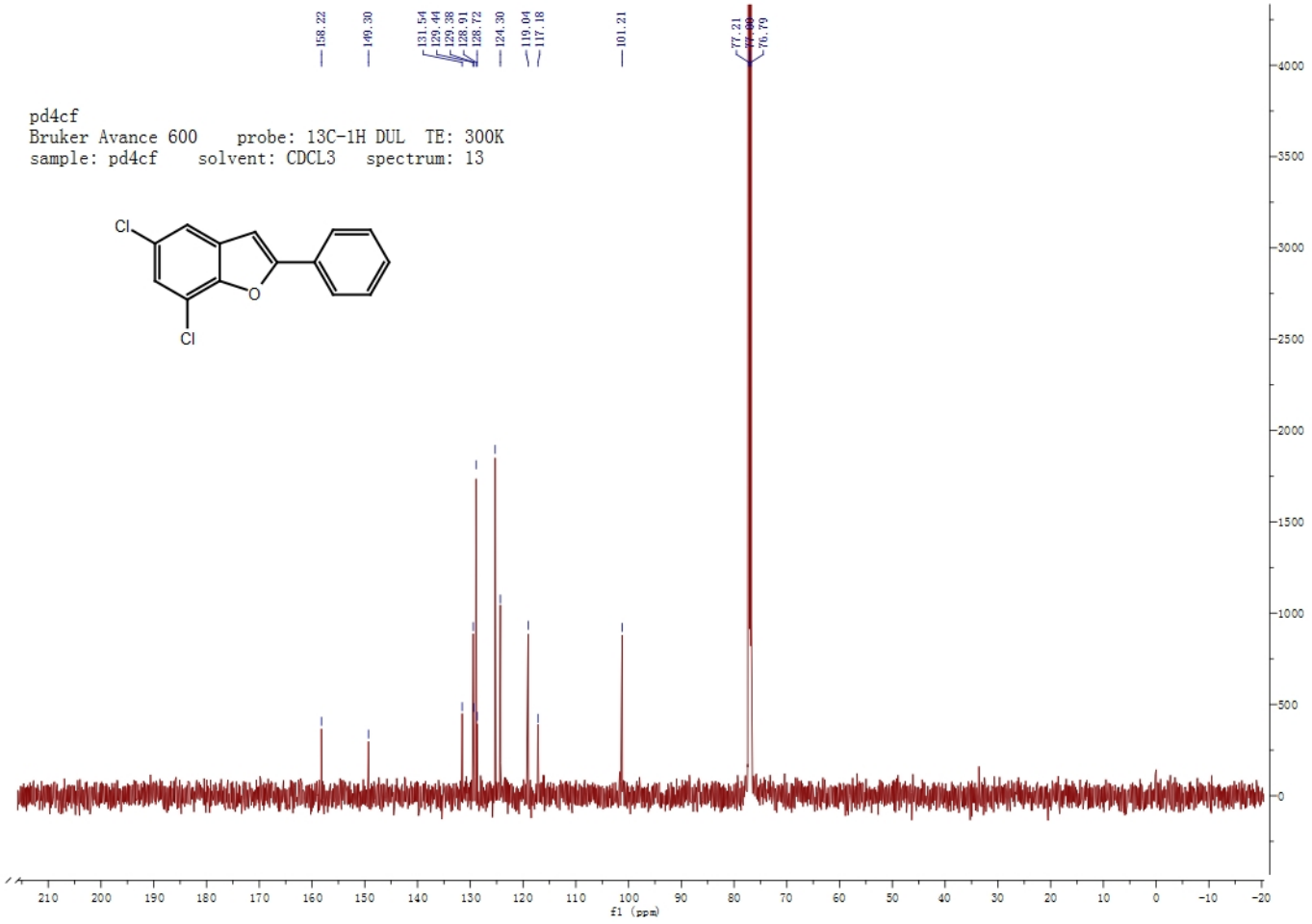

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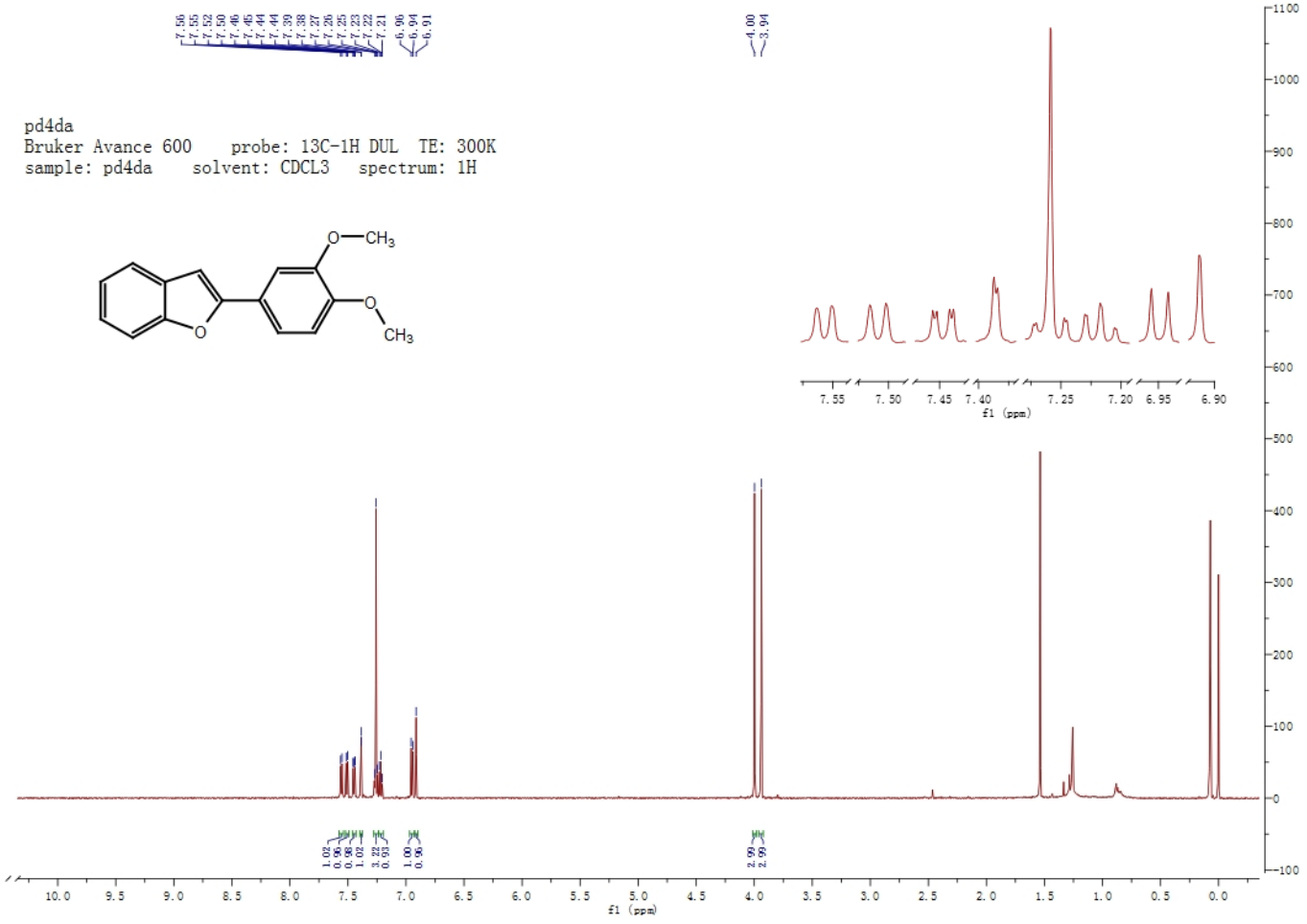

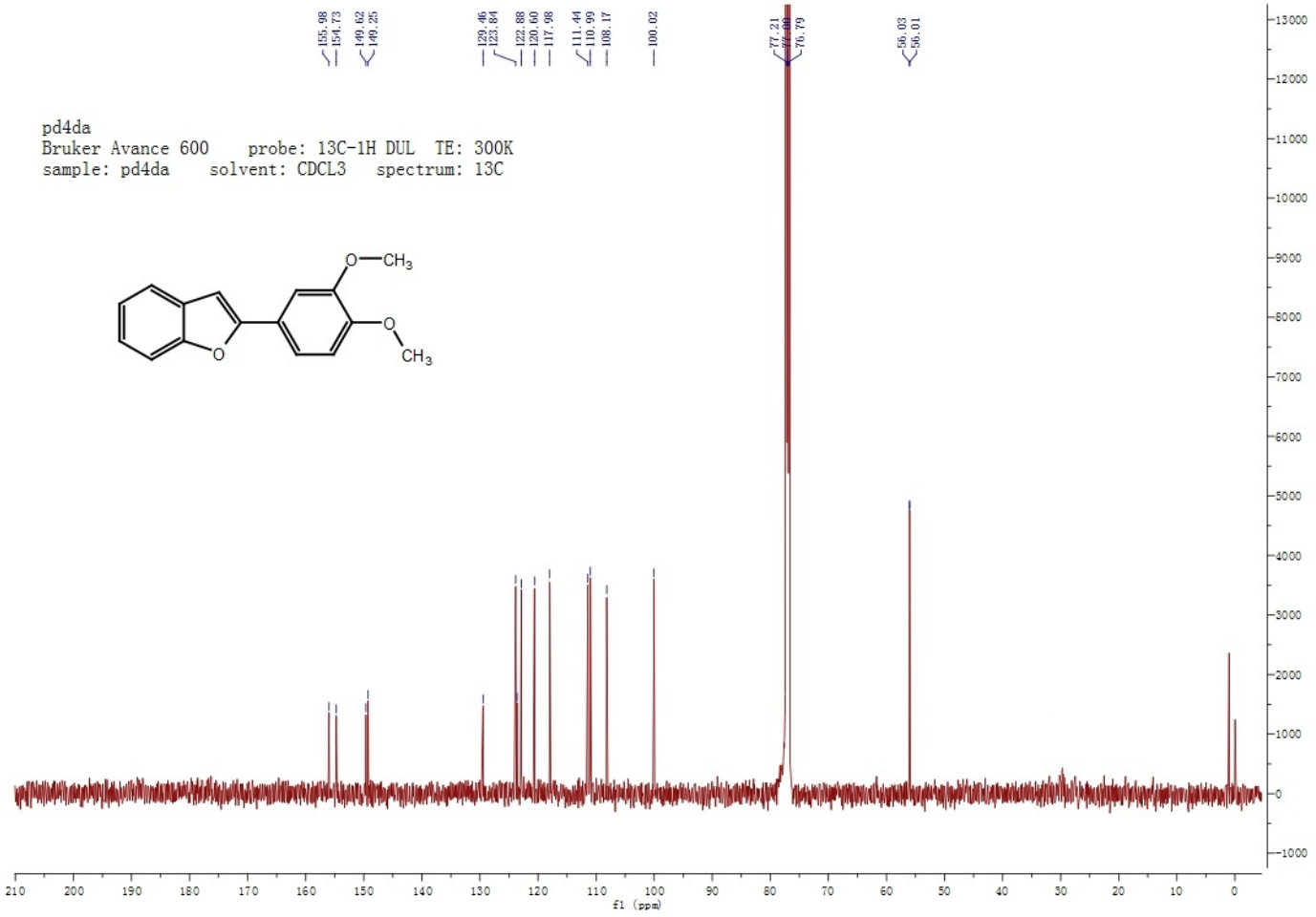

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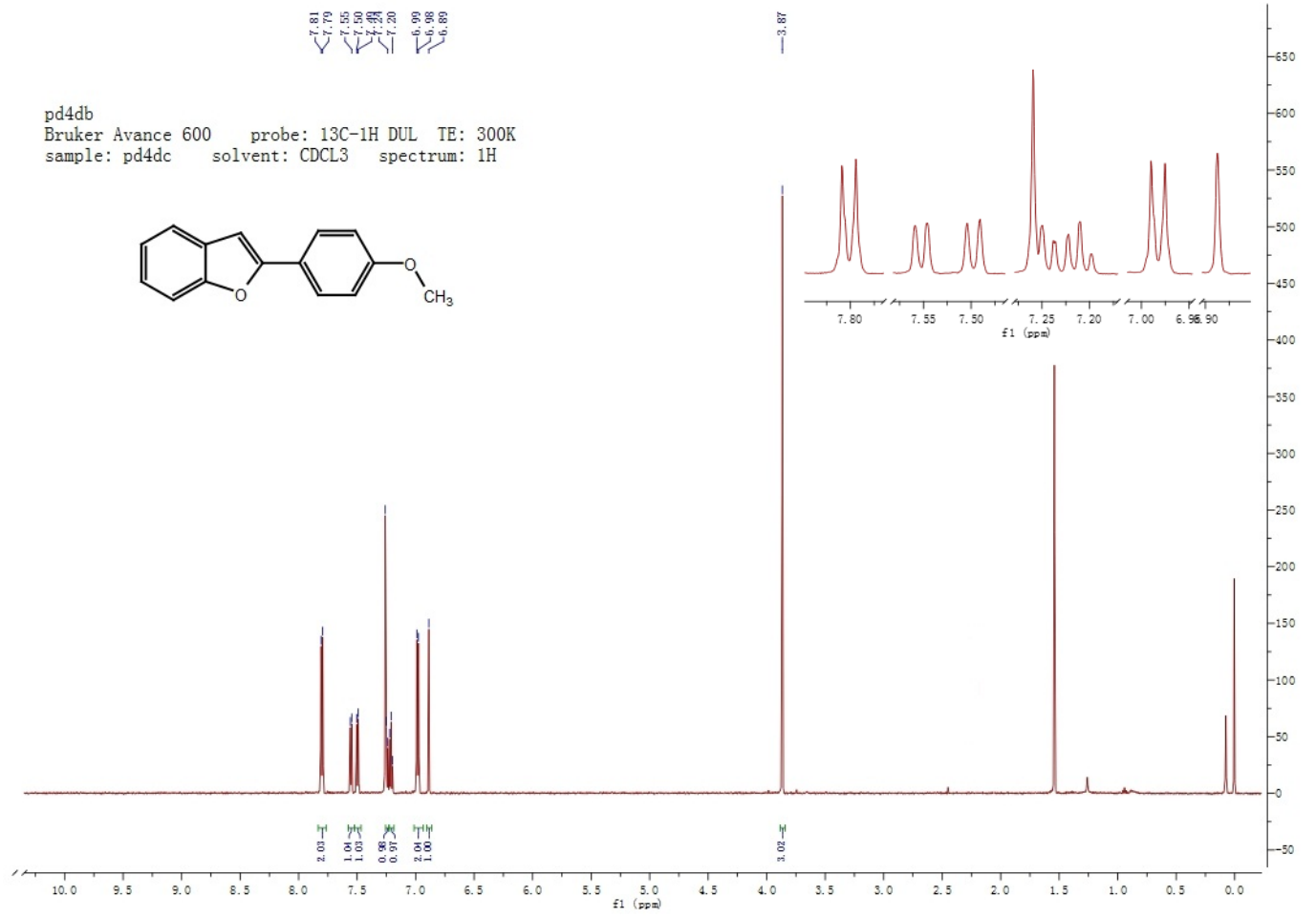

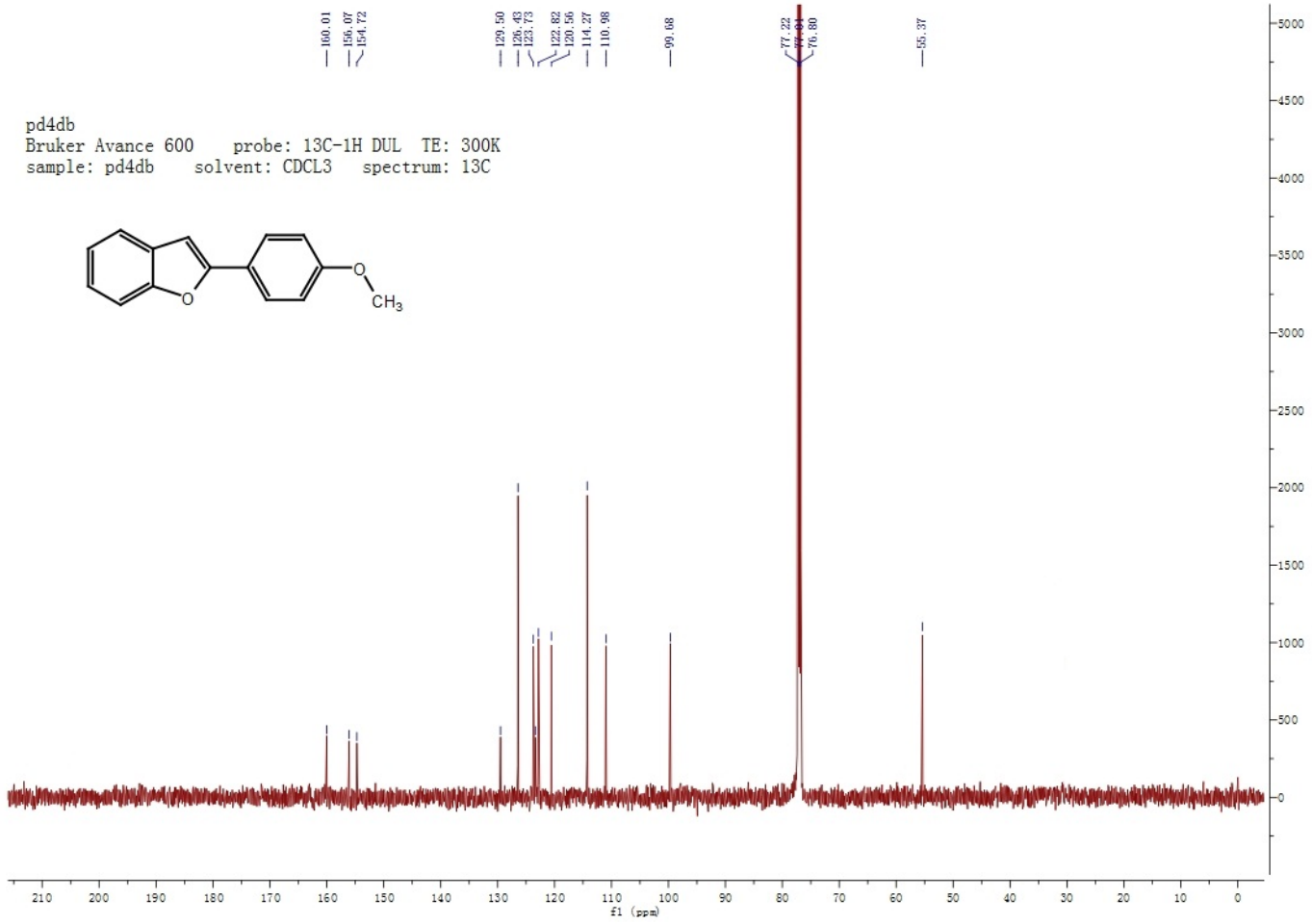

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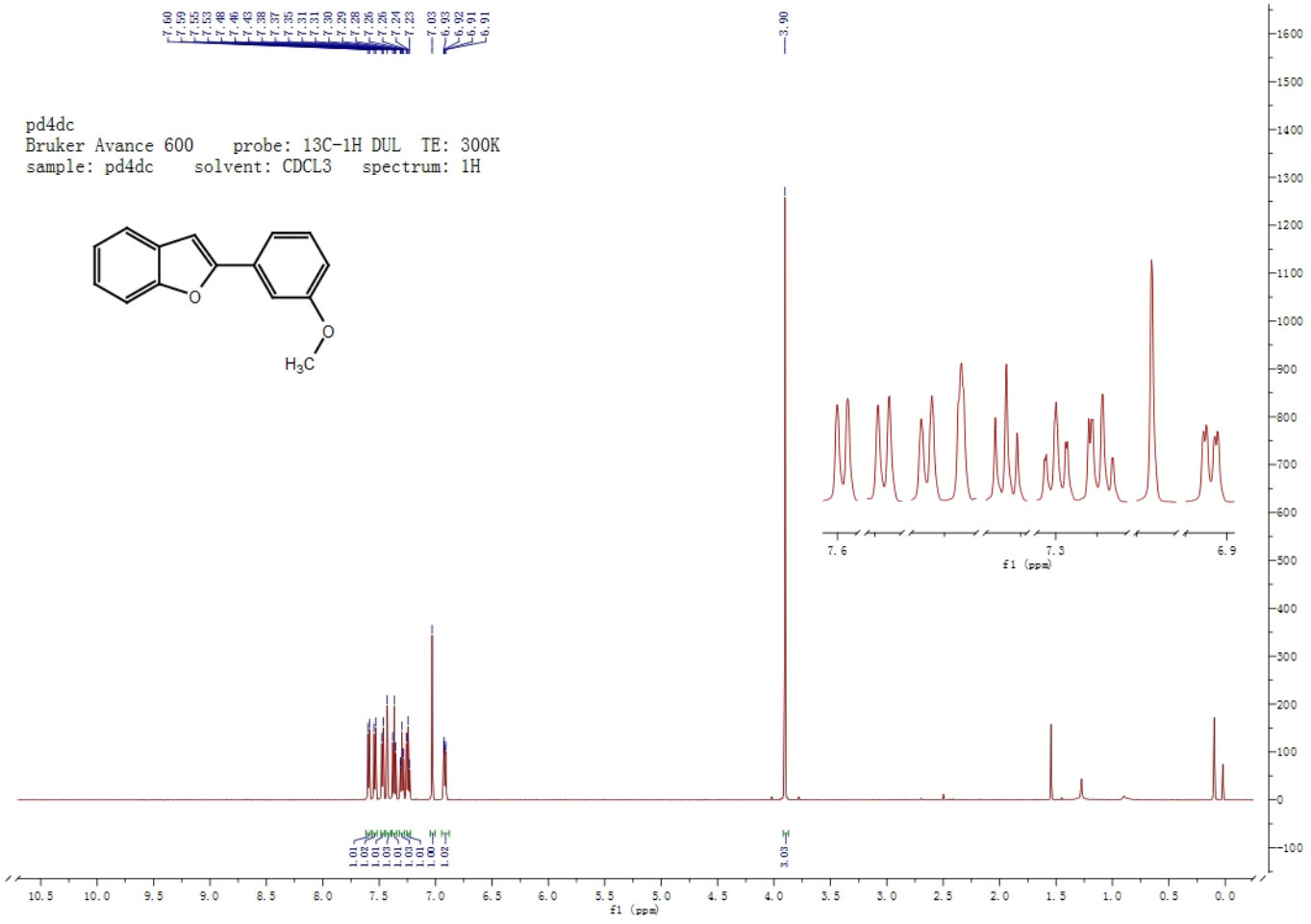

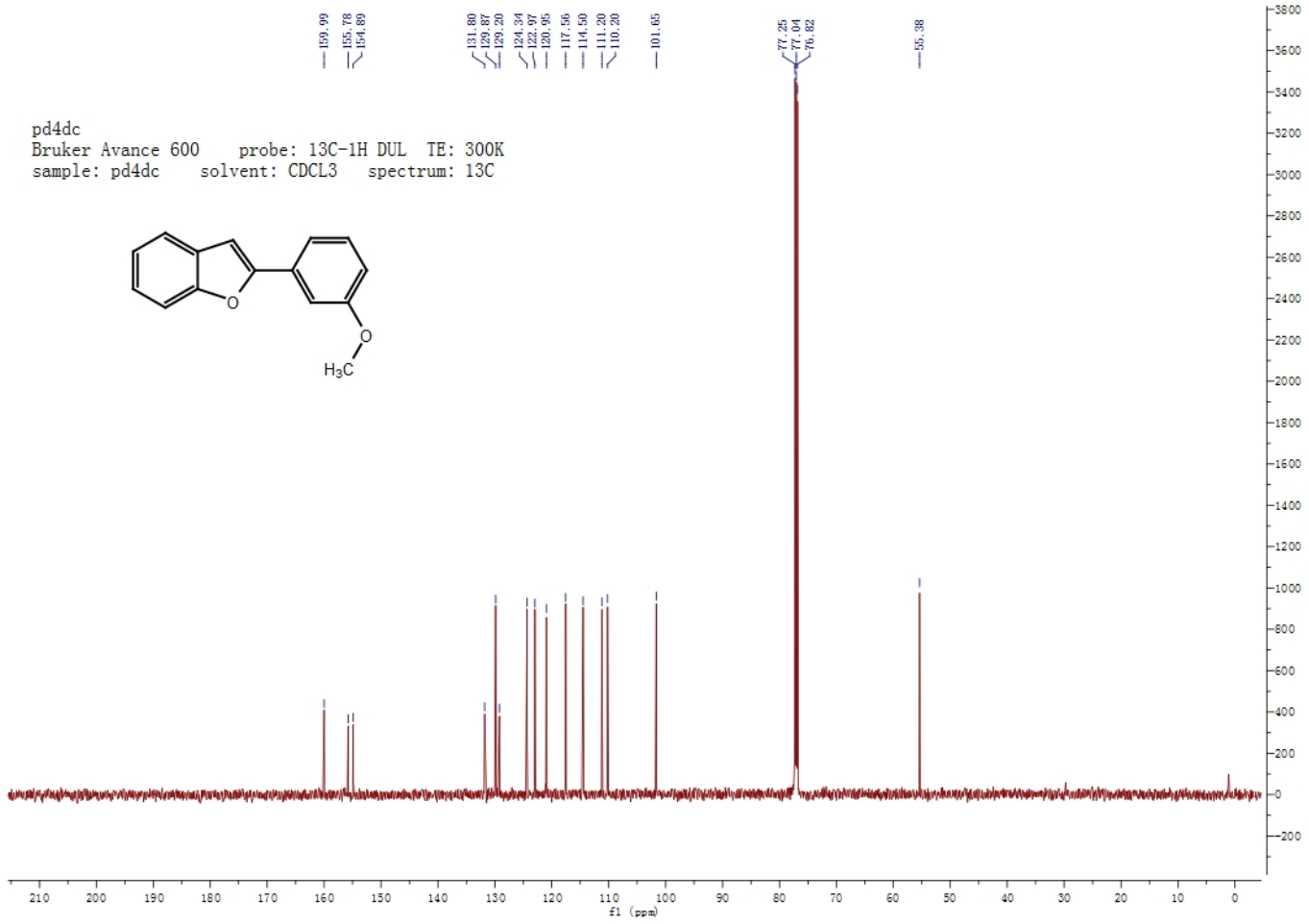

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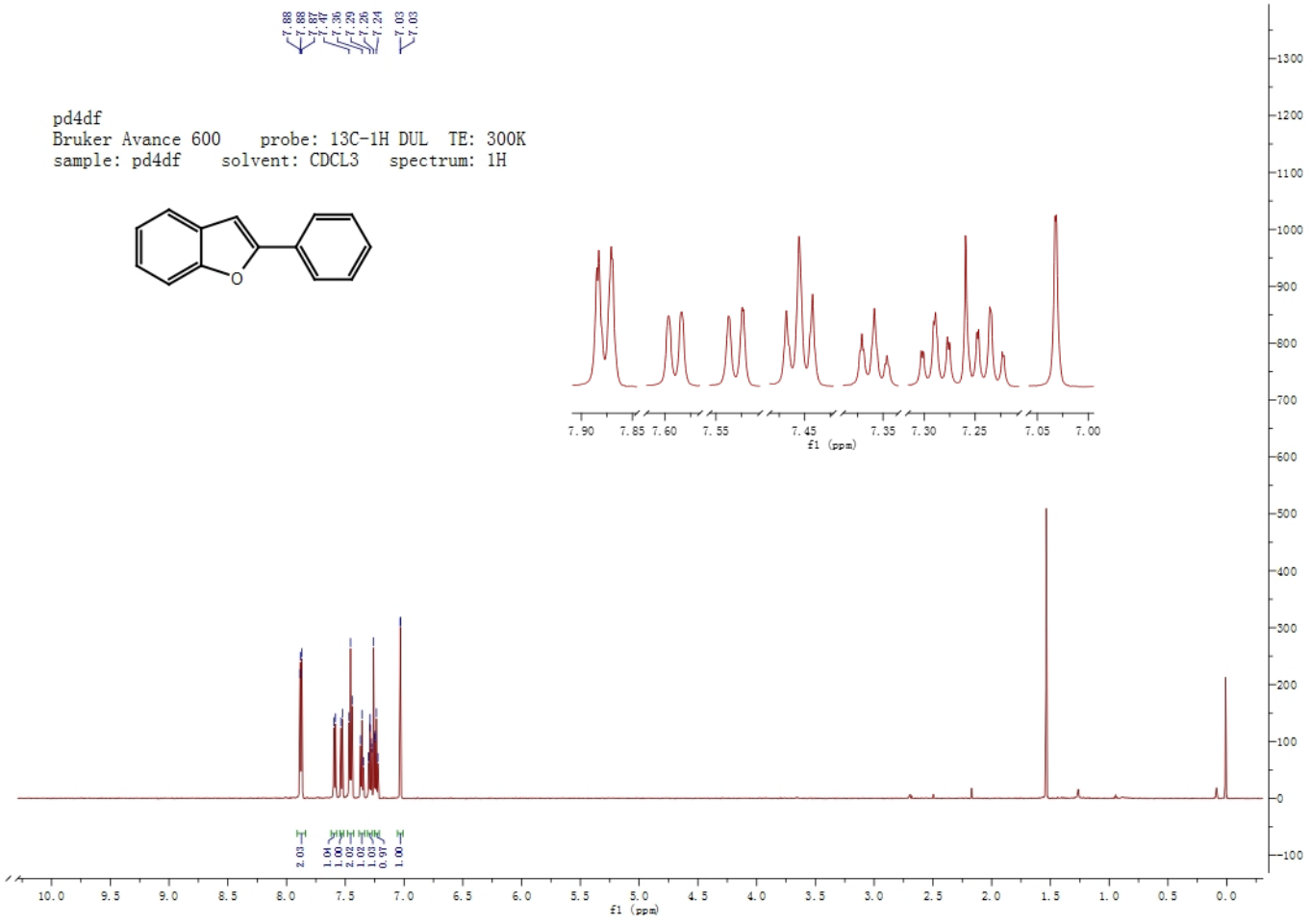

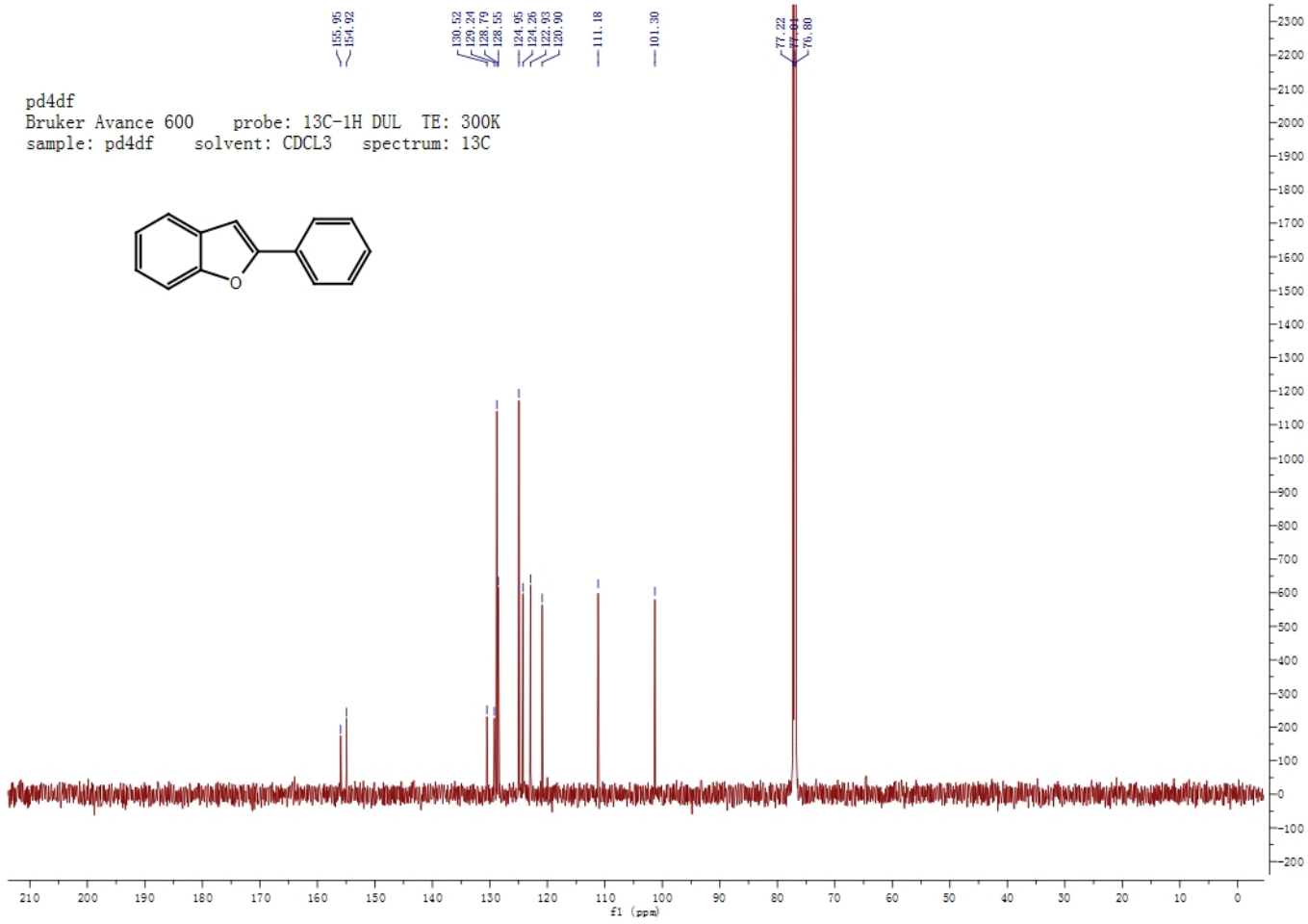

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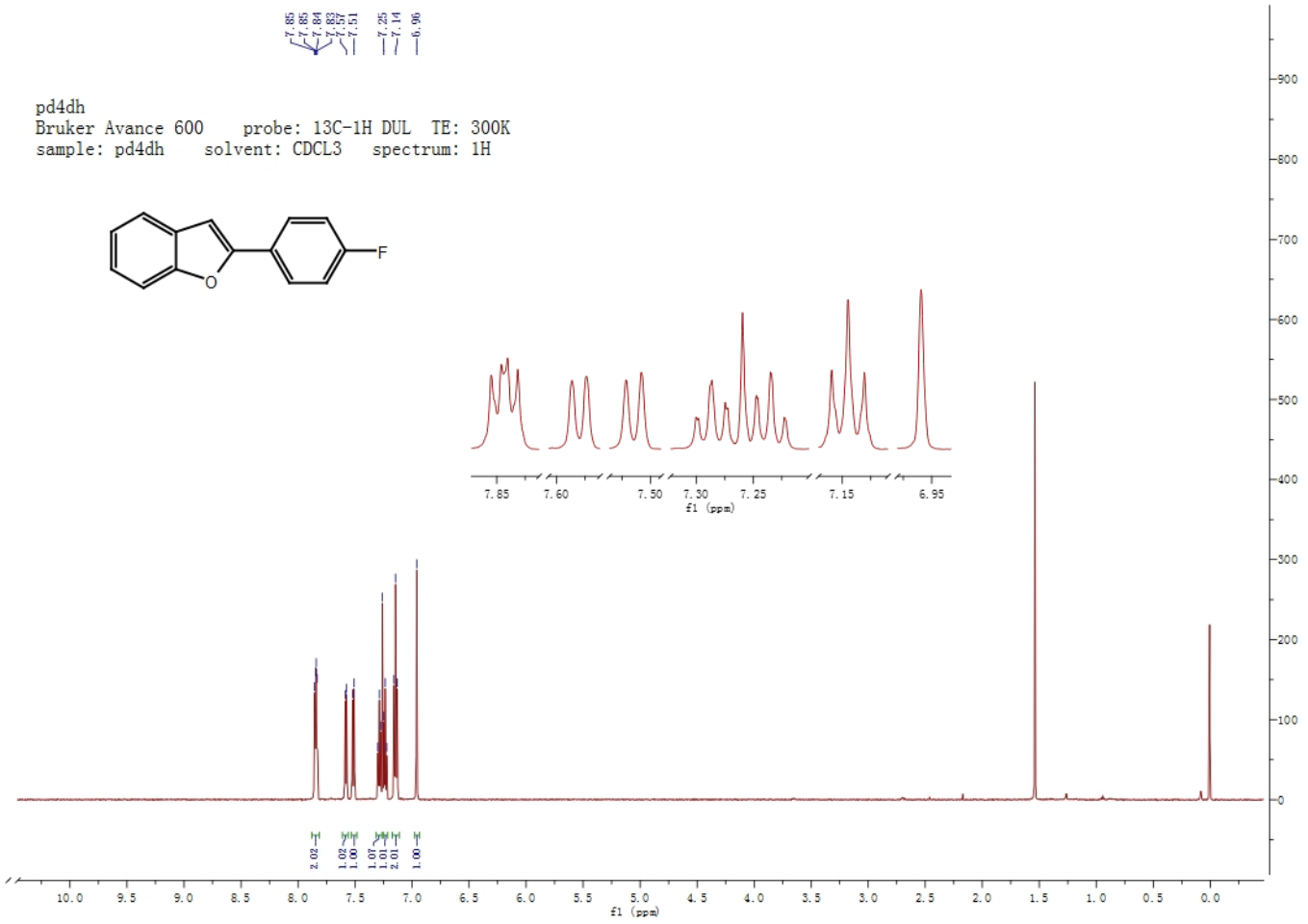

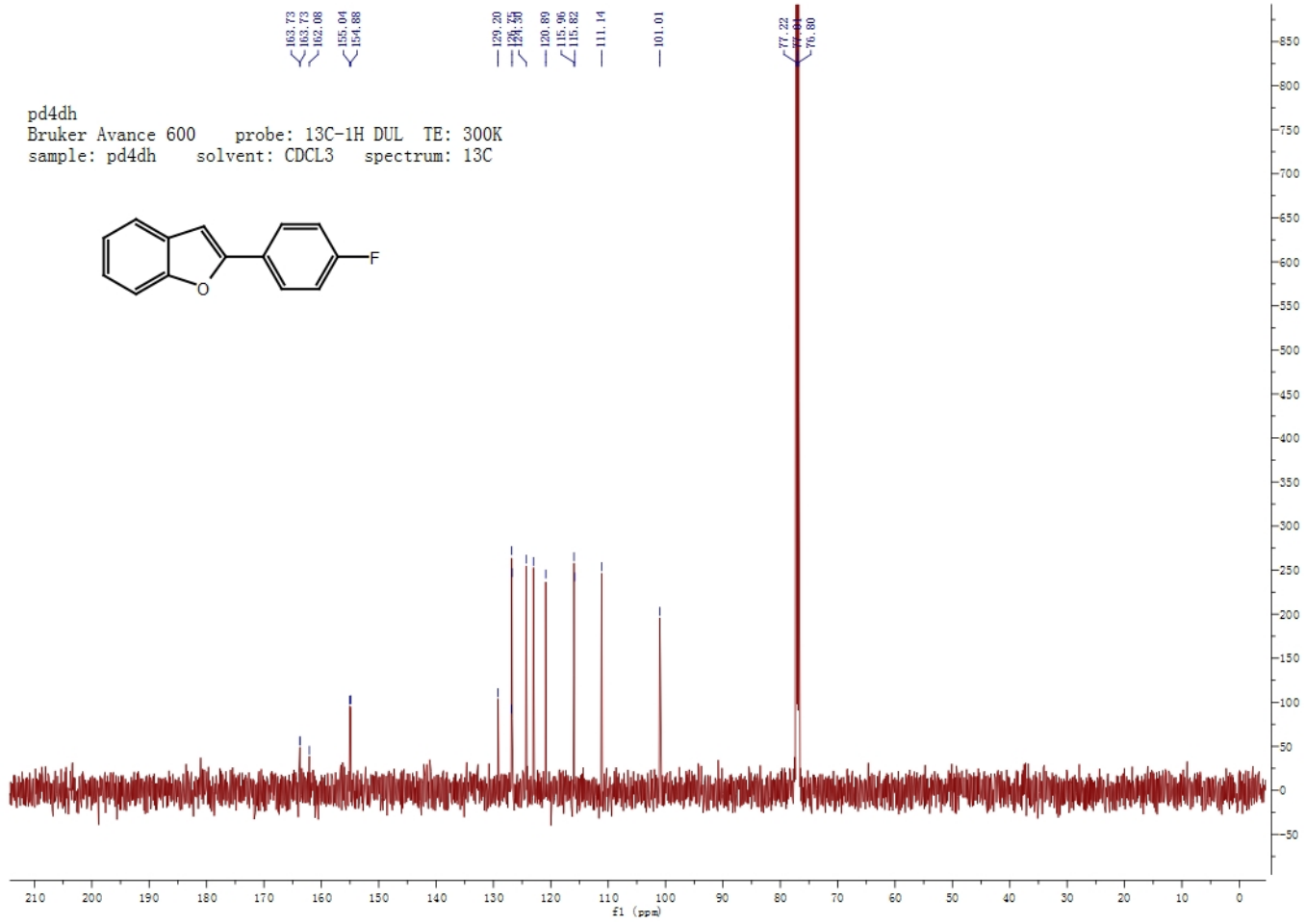

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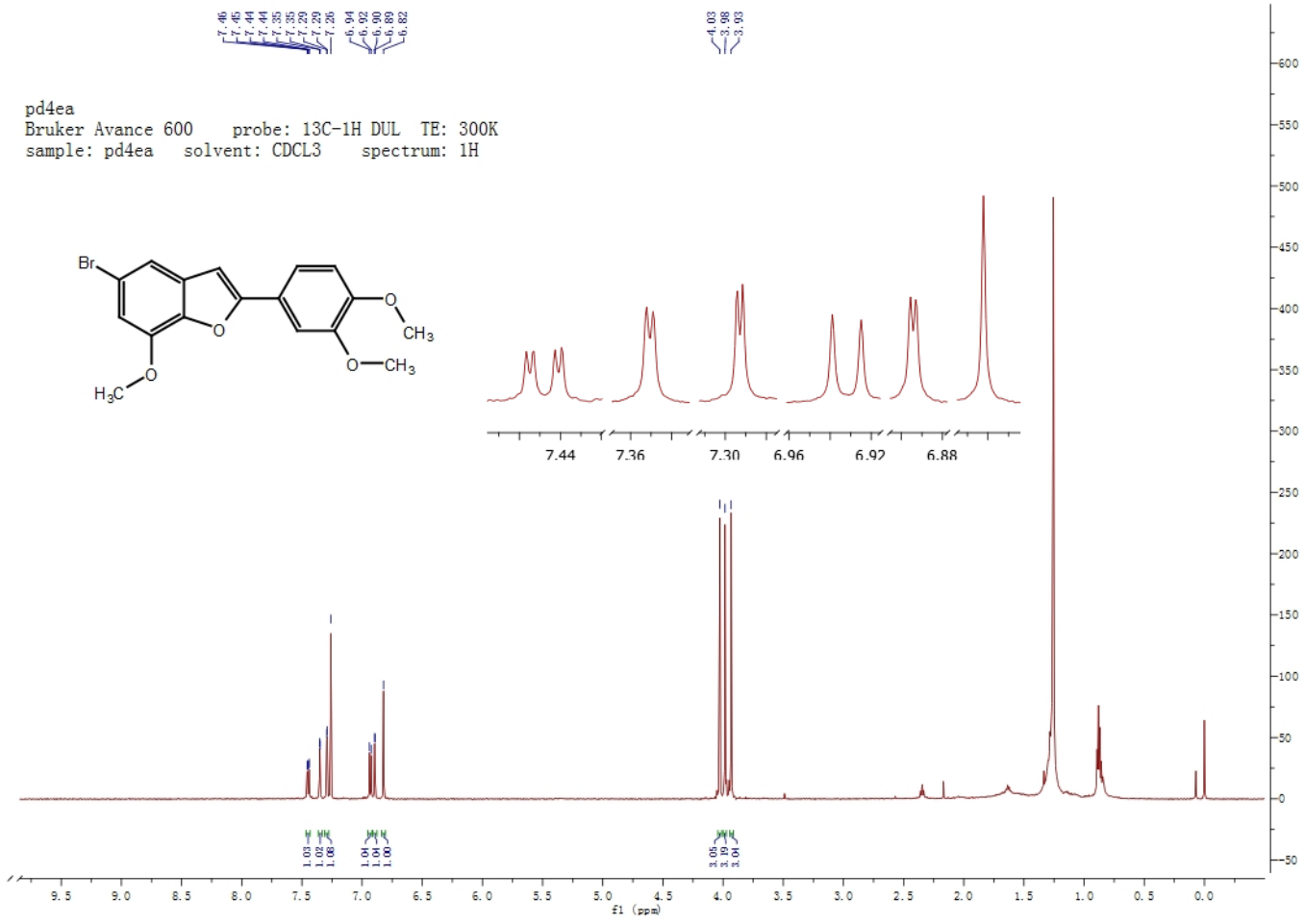

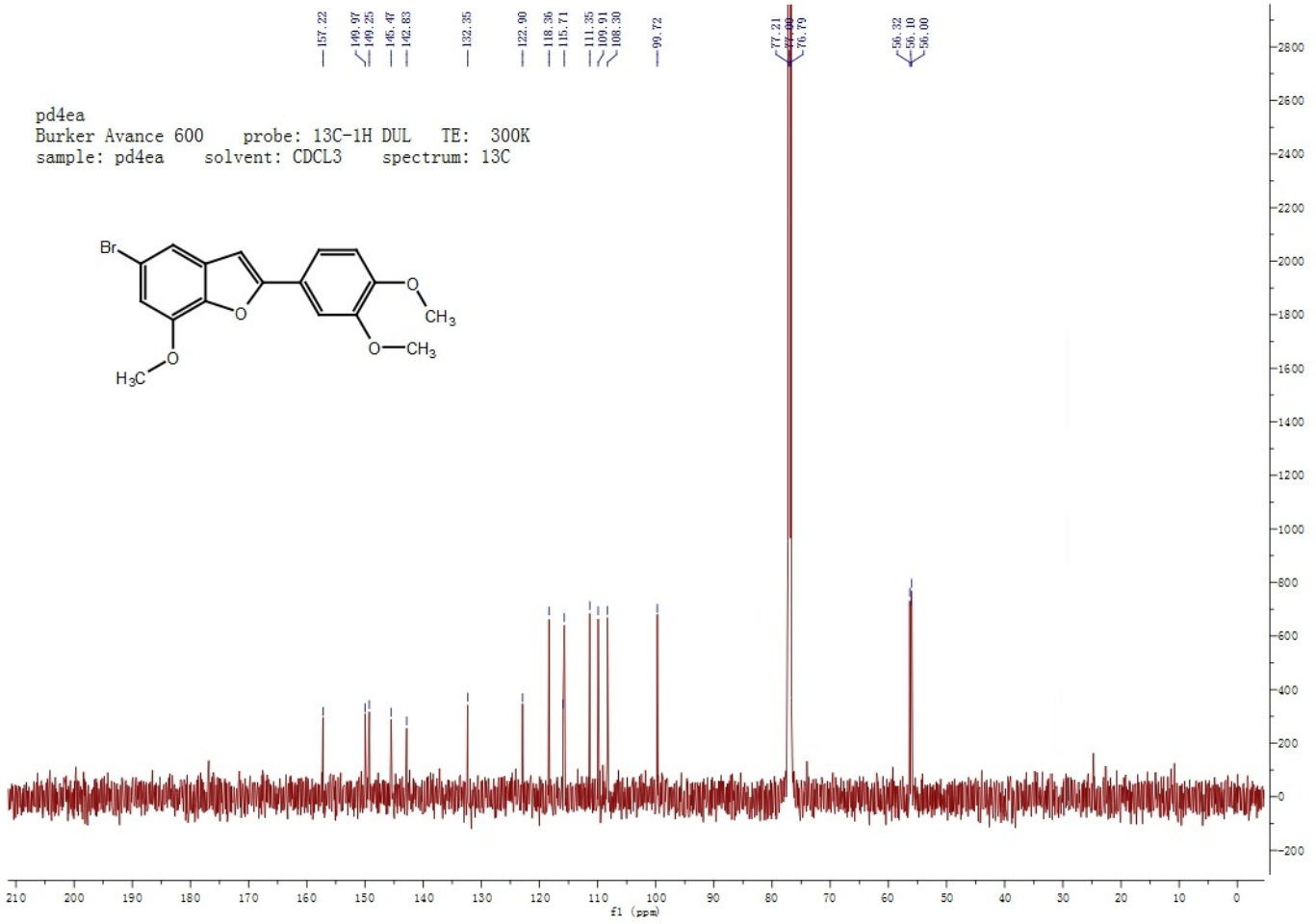

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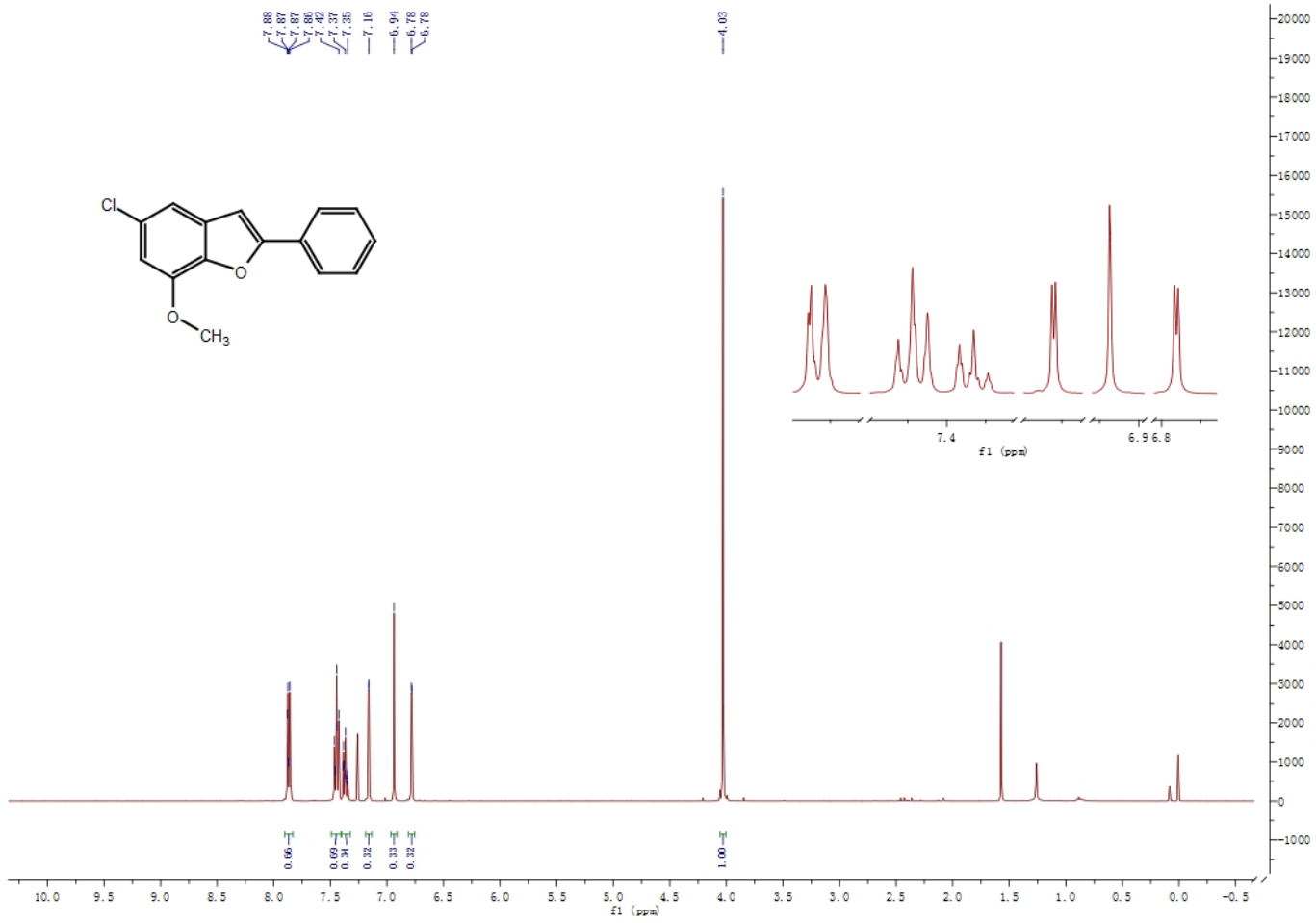

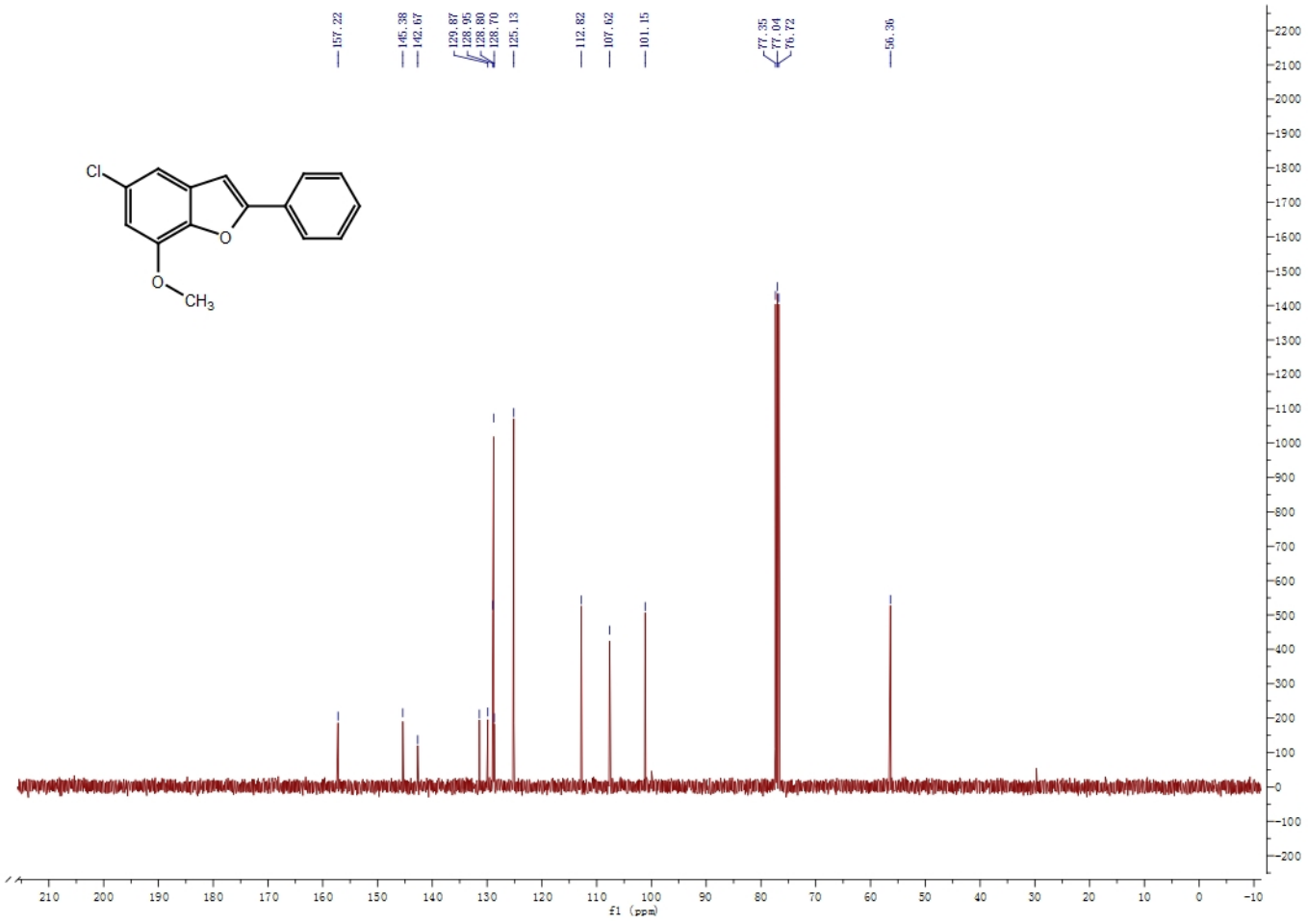

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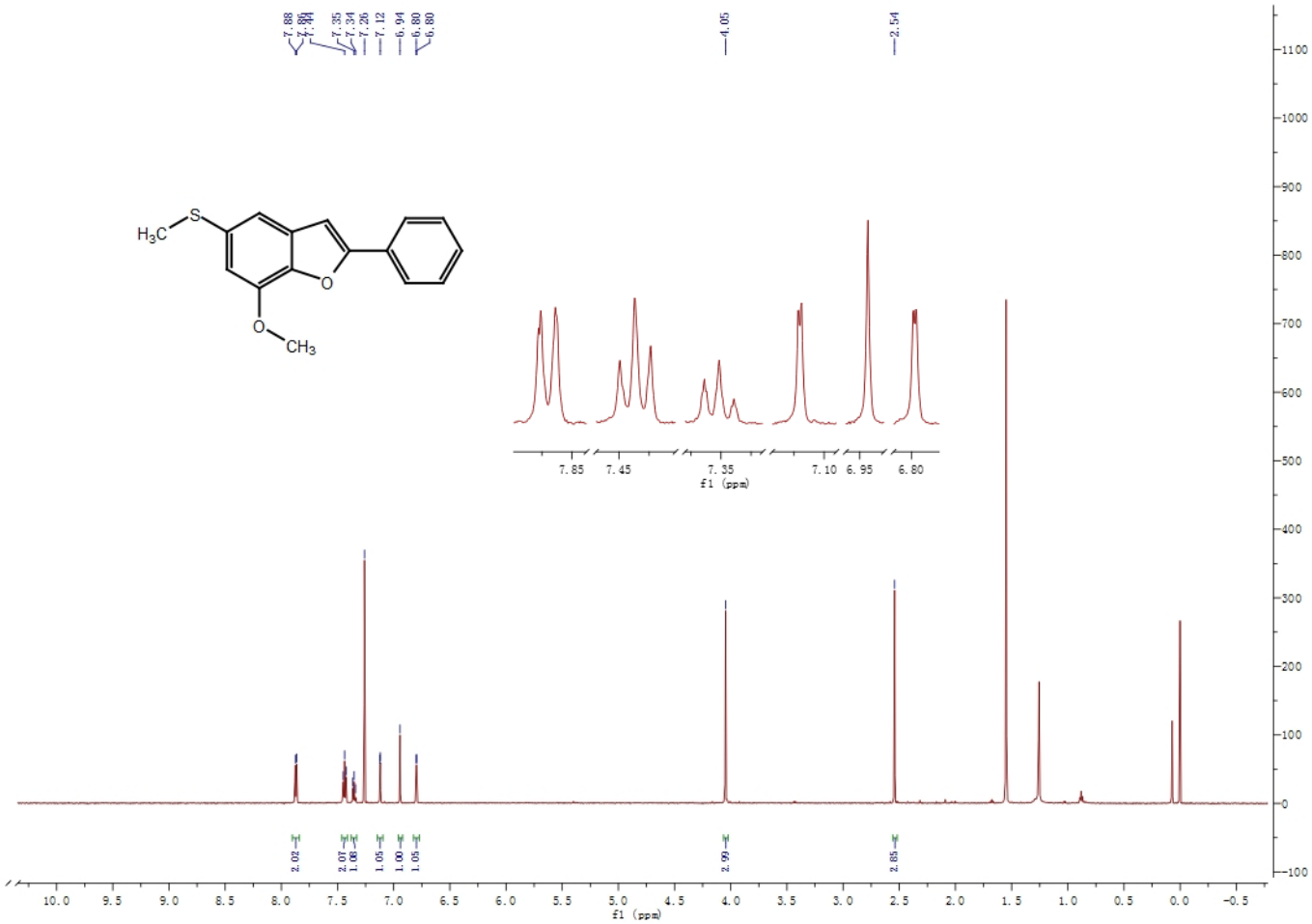

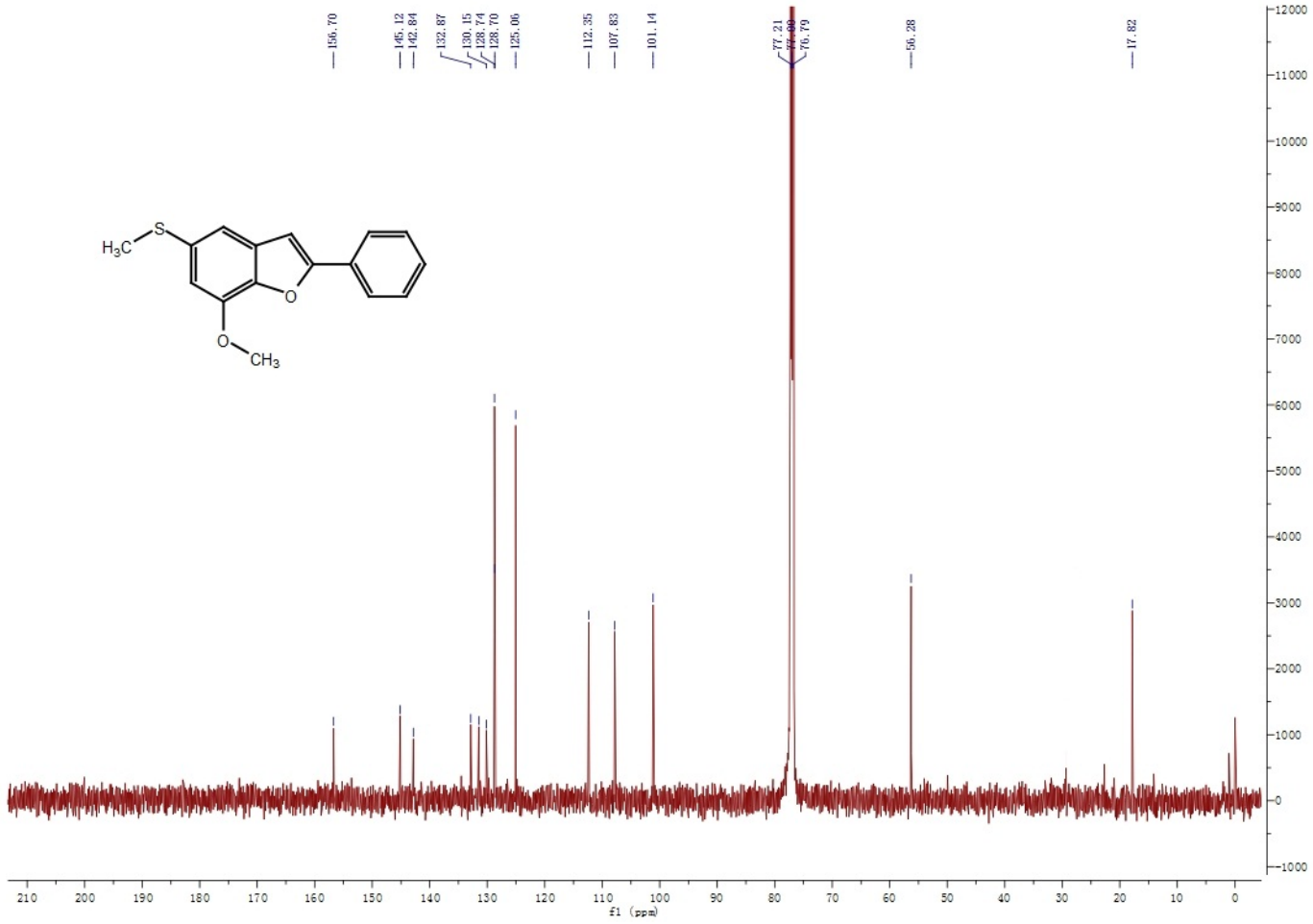

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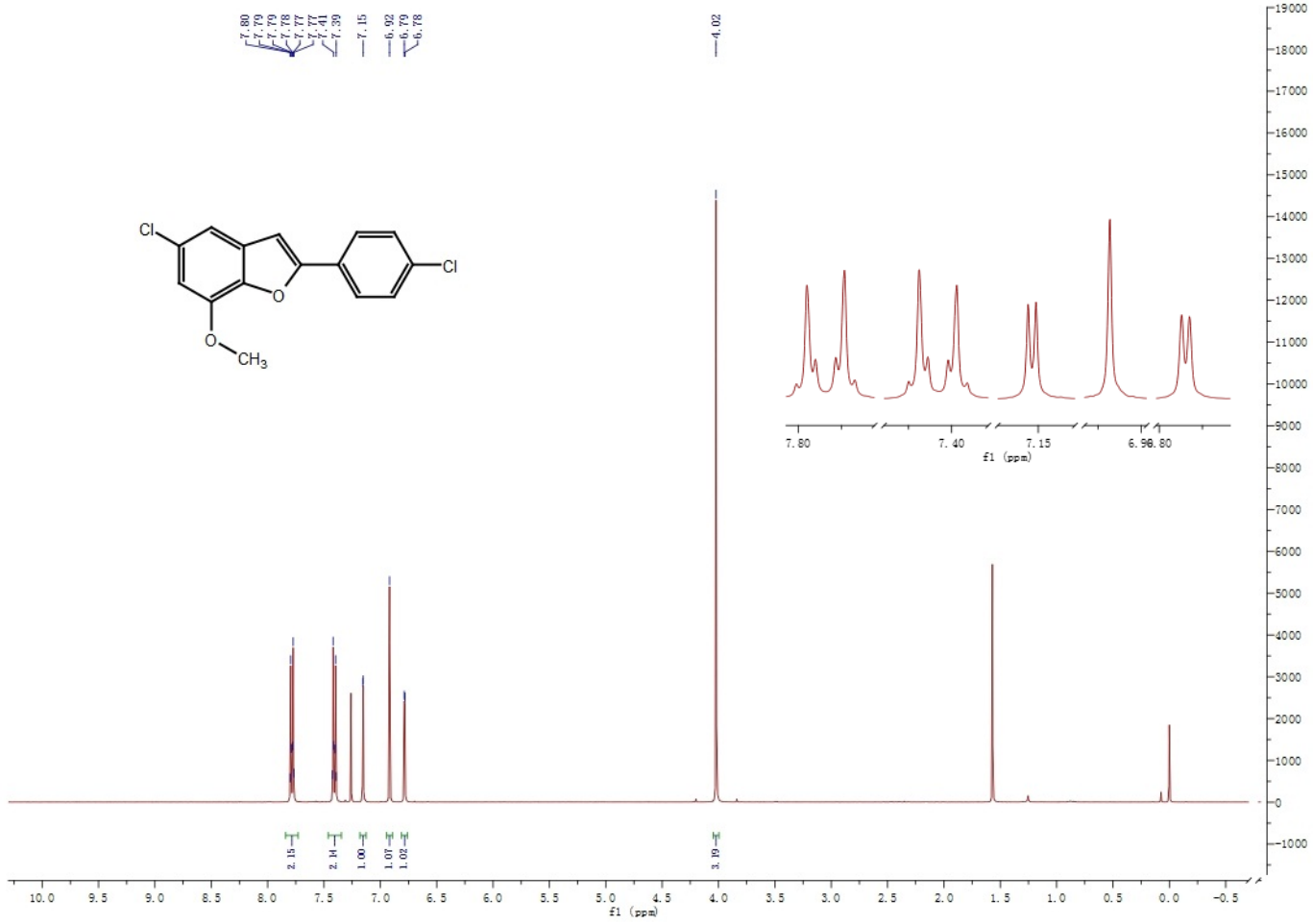

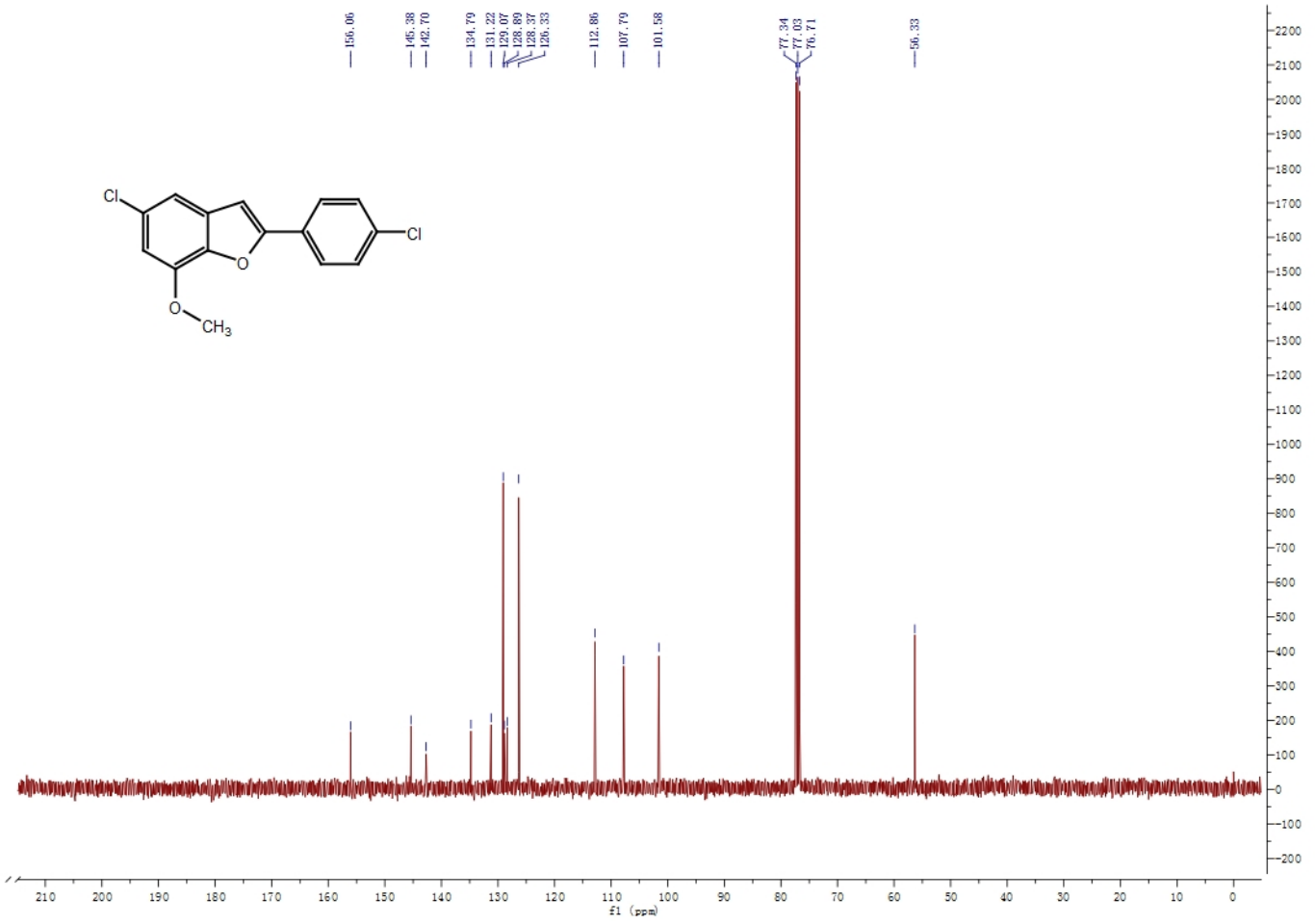

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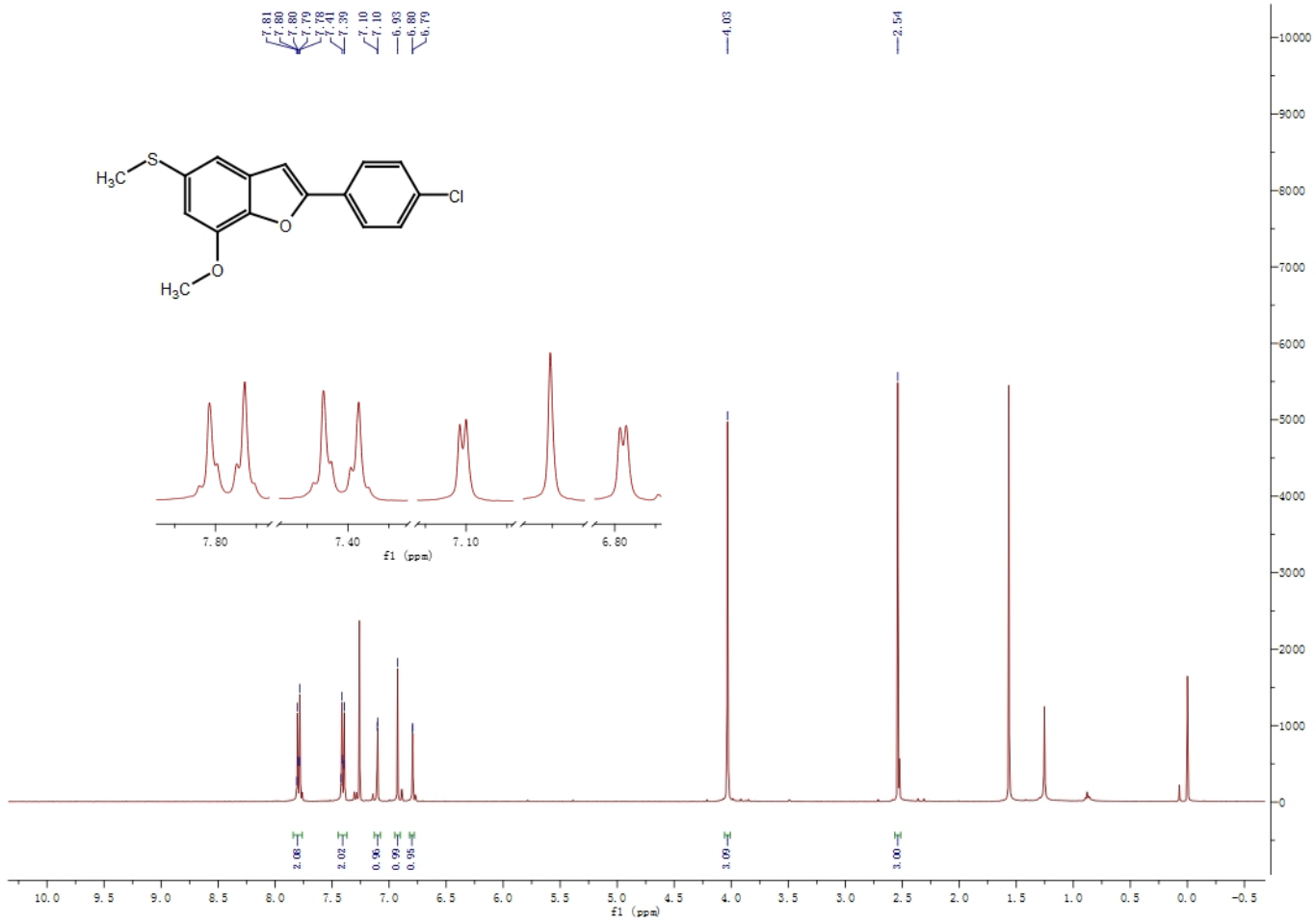

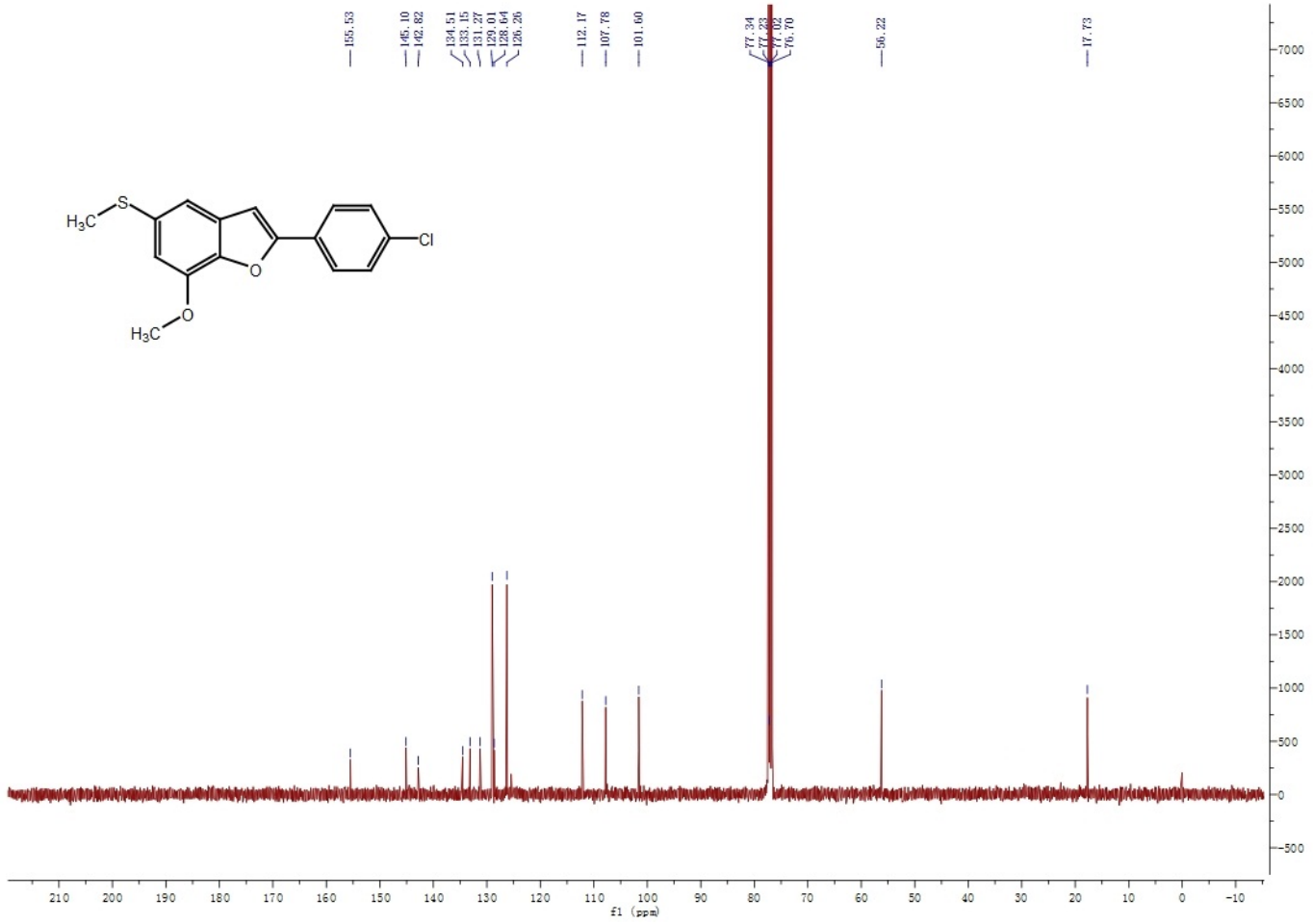

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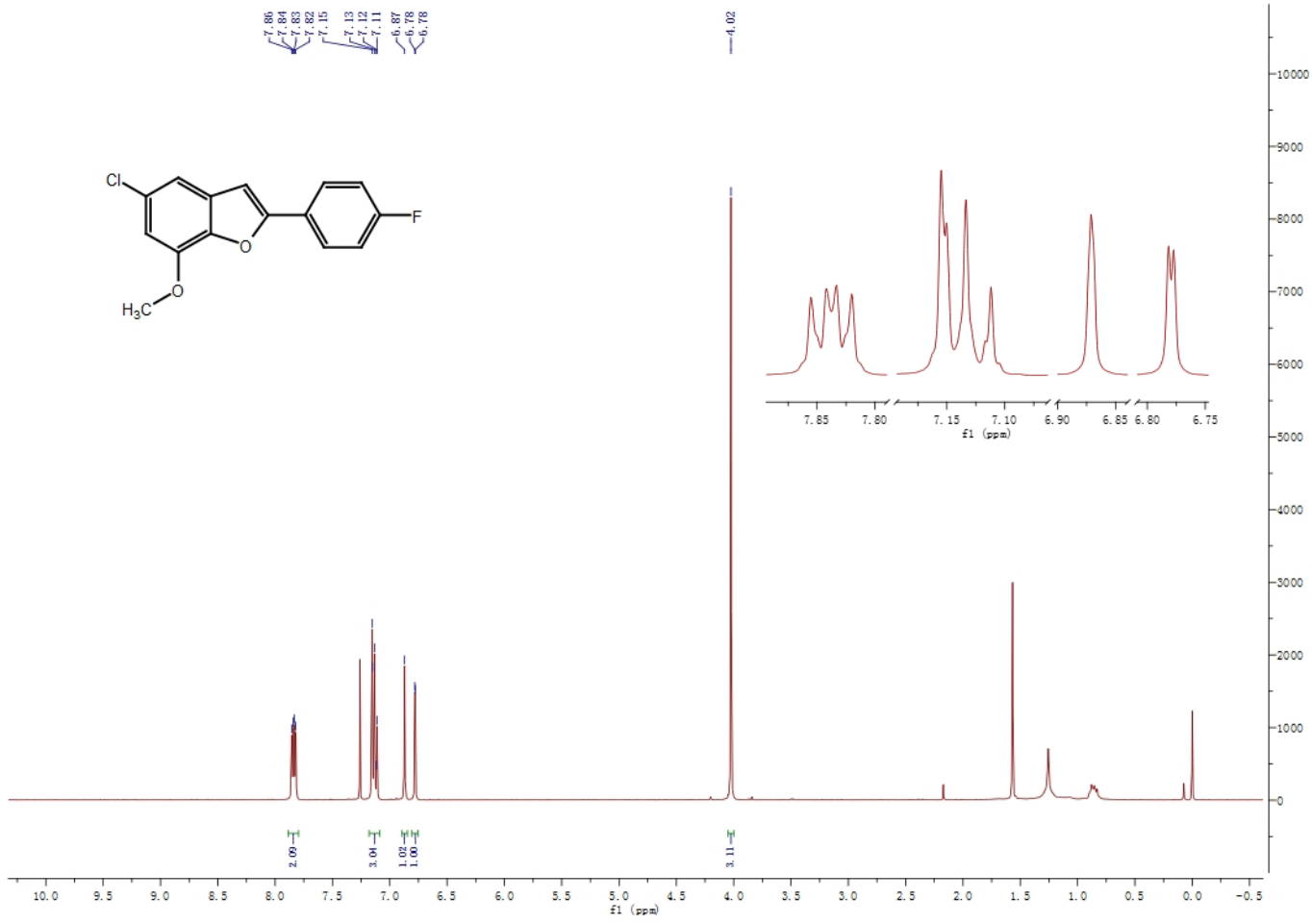

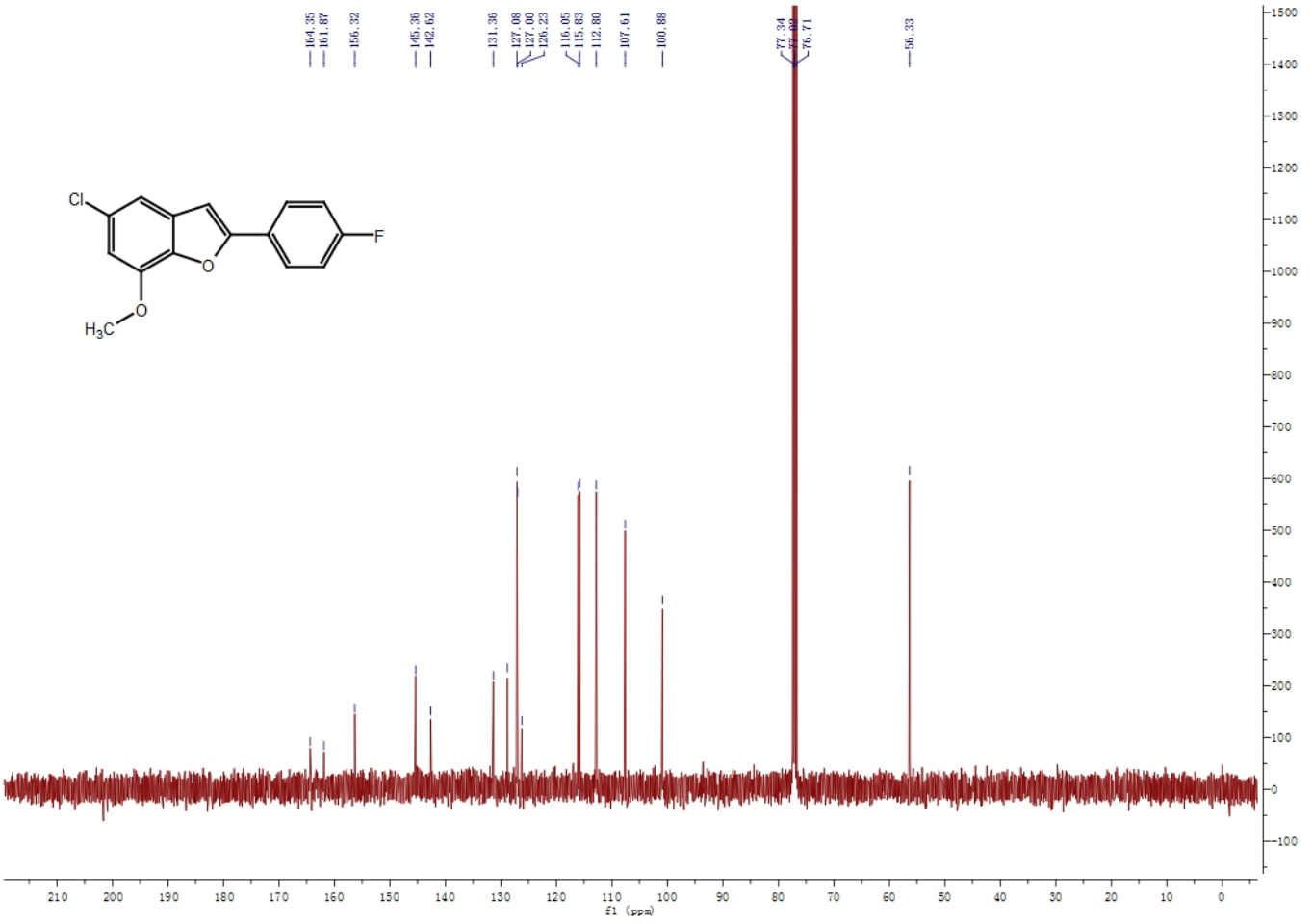

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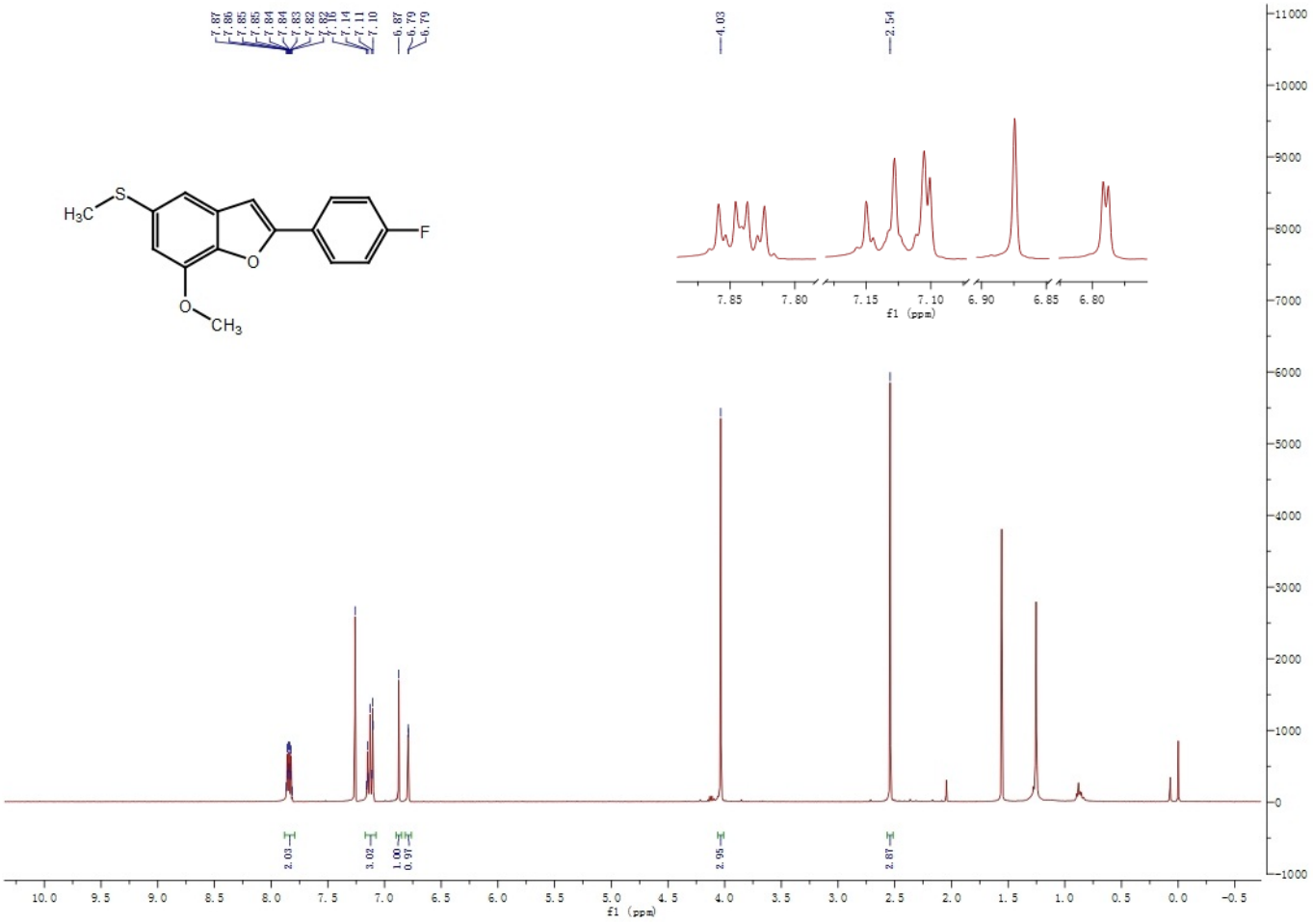

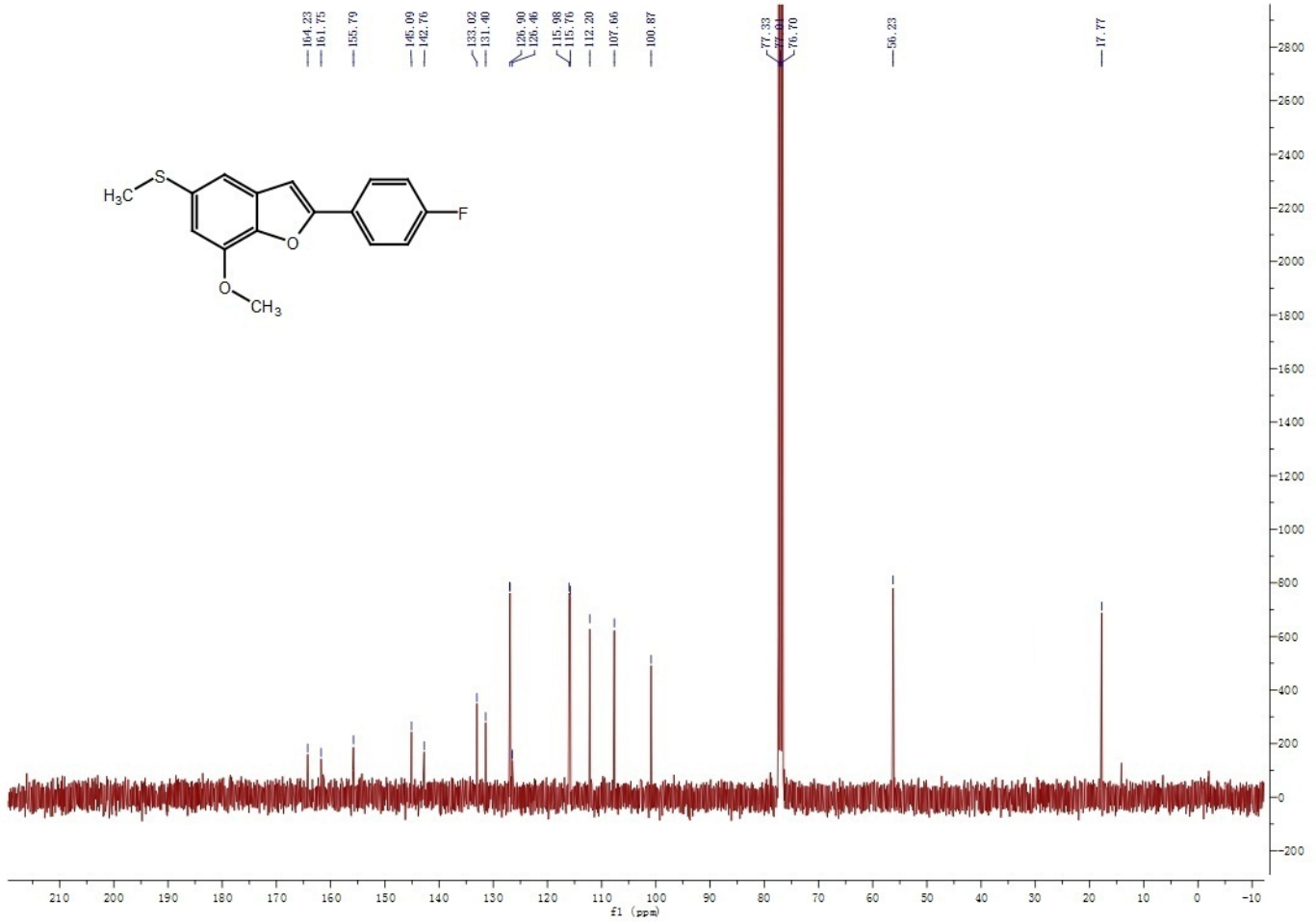

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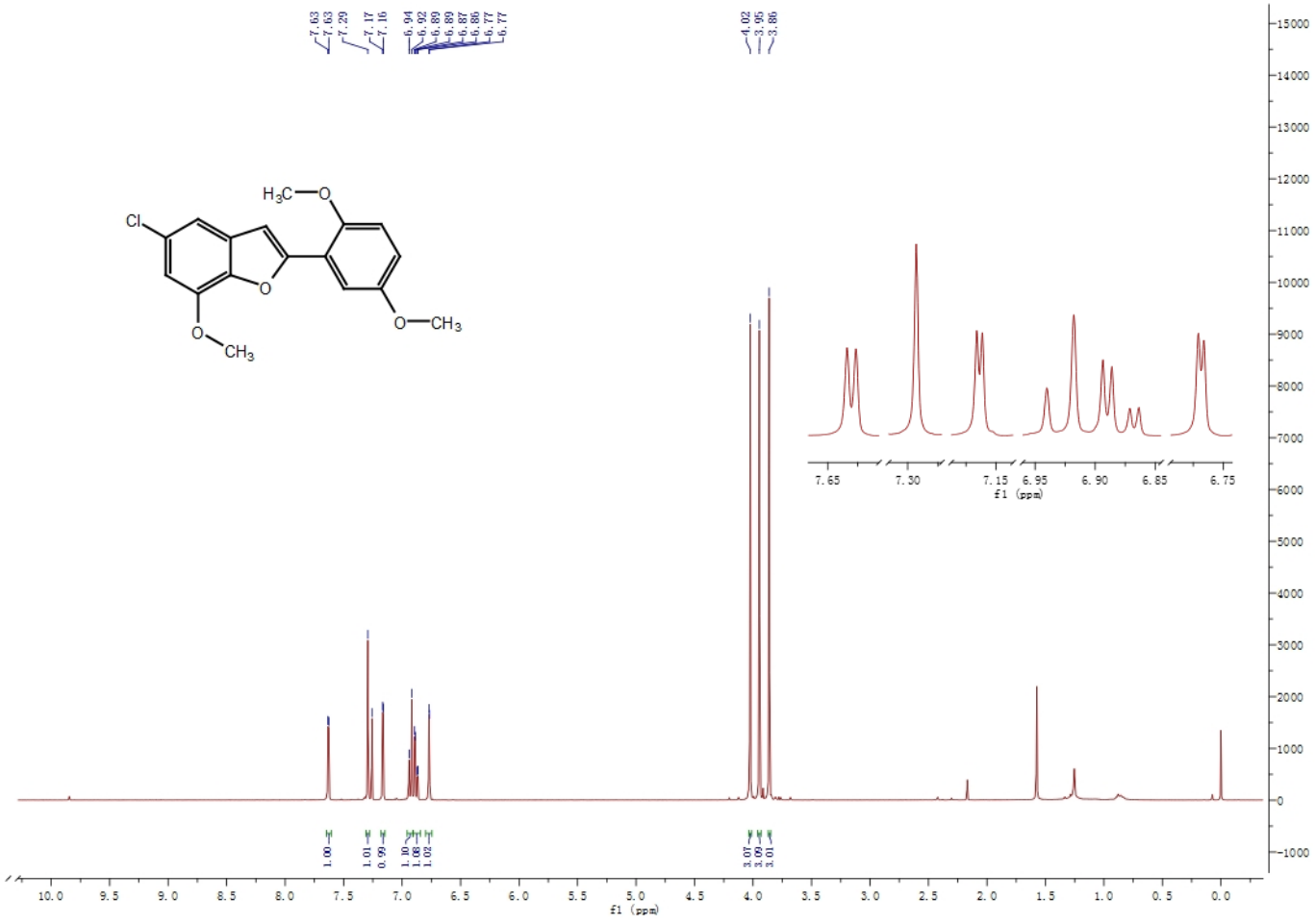

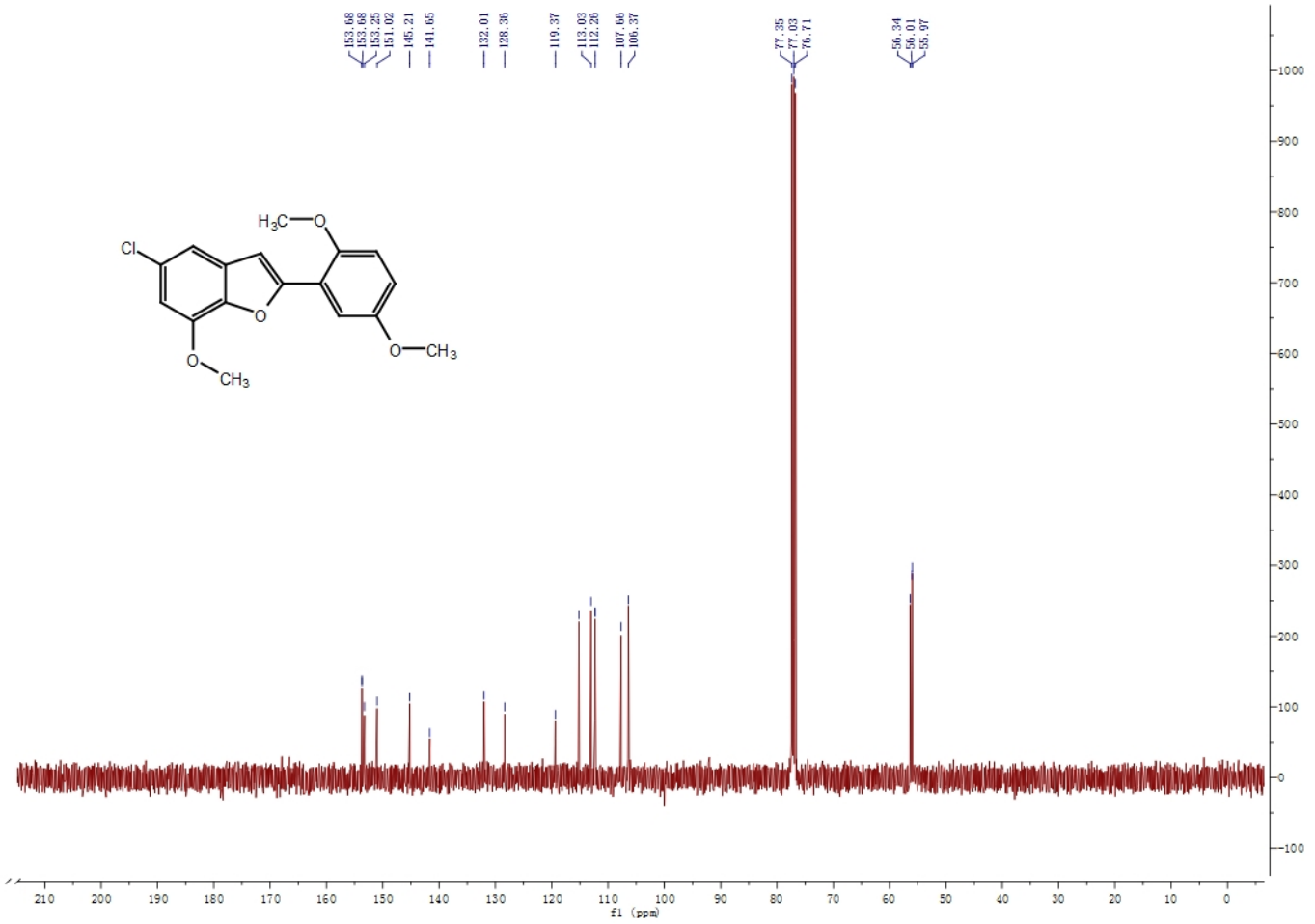

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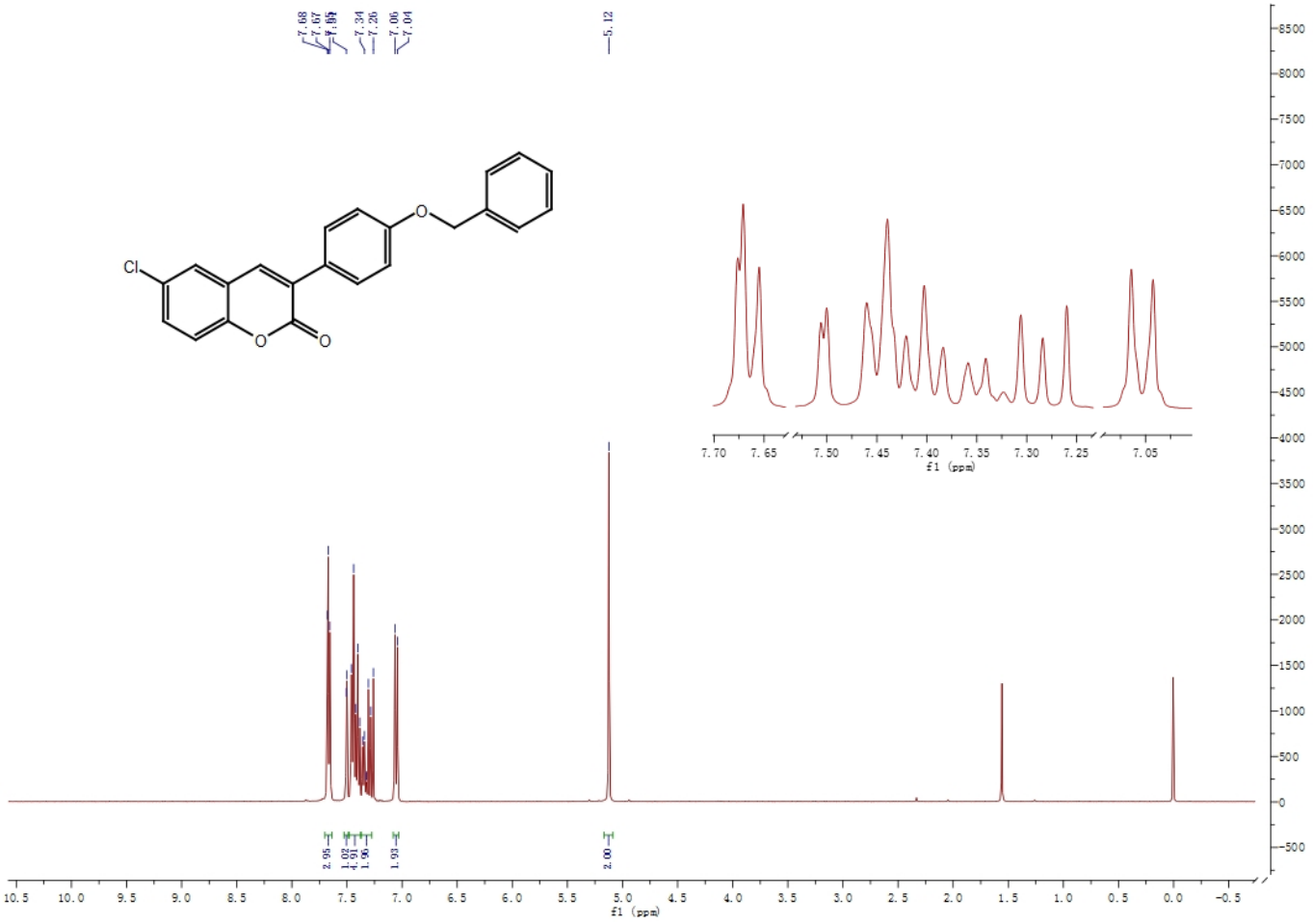

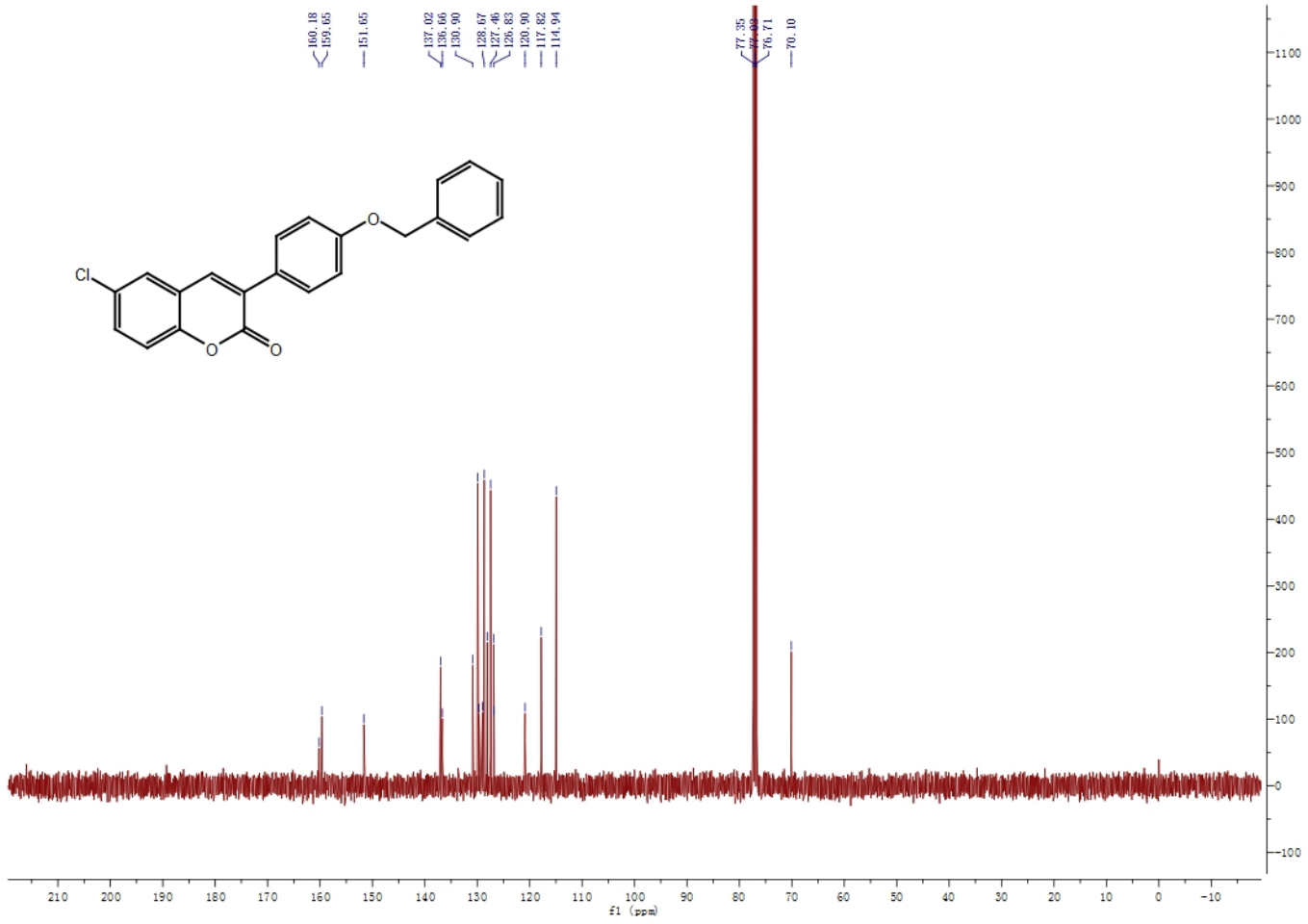

Compound 2bjdb: