Electronic Supplementary Material (ESI) for Chemical Science
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Palladium-Catalyzed Cascade Reactions of 3-Iodochromones with Aryl Iodides and Norbornadiene Leading to Annulated Xanthones

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Supporting Information

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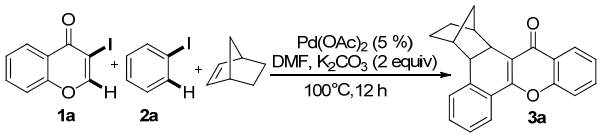
General Information:

Unless otherwise noted, all materials were used as received from commercial sources without further purification. All reactions were performed under nitrogen atmosphere and were heated with oil baths calibrated to an external thermometer. Prior to starting experiments, the oil bath was allowed to equilibrate to the desired temperature over 20 minutes. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz. High resolution mass spectra were recorded on a Finnigan MAT 95 mass spectrometer (ESI). Column chromatography was performed with 200-300 mesh silica gel using flash column techniques. Melting points are uncorrected.

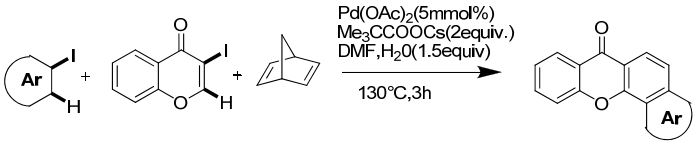
Experimental:

Procedure A: Synthesis of compound 3a



To a 50 mL flask, were added 3-iodochromone (100 mg, 0.37 mmol), Iodobenzene (40 μL, 0.37mmol), norbornene (70 mg, 0.74 mmol), $Pd(OAc)_2$ (4 mg,0.018 mmol), K_2CO_3 (101 mg,0.74 mmol) and DMF(15 mL).The reaction mixture were stirred under nitrogen at 100 ^{o}C for 12 h. At the end of this time the reaction was allowed to cool to room temperature, diluted with DCM, filtered through a short pad of Celite, washed with DCM, and concentrated in vacuo. The resulting residue was purified by column chromatography to afford compound **3a** in 82% yield.

Procedure B: Synthesis of benzoxanthone derivatives



Typically, 3-iodochromone (100 mg, 0.37 mmol), $Pd(OAc)_2$ (4 mg, 0.018 mmol), $Me_3CCOOCs$ (172 mg, 0.74 mmol), norbornadiene(220 μL, 2.2 mmol) and aryl iodine (0.74 mmol) (if a solid) were weighed into an oven-dried 50-mL flask. The flask was then evacuated and back-filled with argon, and water (1.5 equiv.) in DMF (15 mL) was added under an argon atmosphere. The reaction mixture was then stirred in a preheated oil bath at 130 °C (or 90 °C as indicated) for 3 hours. At the end of this time the flask was removed from the bath, allowed to cool to room temperature, the contents diluted with DCM (20 mL), and the mixture filtered through a short pad of Celite, washed with DCM, and concentrated in vacuo. The residue was purified by column chromatography to afford desired product.

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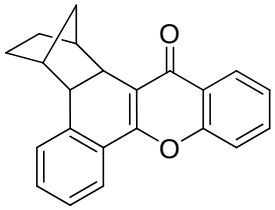
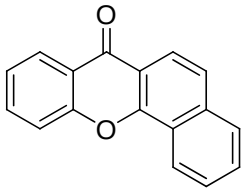
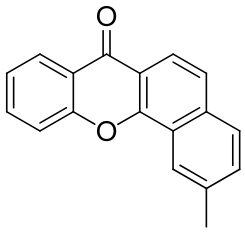
Characterization Data:



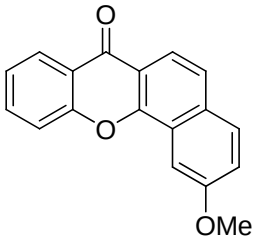
Compoud **3a:** White solid: m.p. 192-193 ^{O}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.30 (m, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 3.24 (dd, *J* = 26.9, 10.1 Hz, 2H), 2.49 (s, 1H), 2.34 (s, 1H), 1.84 – 1.54 (m, 4H), 1.35 (d, *J* = 9.8 Hz, 1H), 1.10 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 156.5, 155.3, 141.5, 133.1, 131.3, 129.4, 126.7, 126.4, 125.6, 124.6, 123.7, 123.2, 117.8, 117.0, 49.2, 45.5, 44.6, 40.0, 33.8, 30.4, 29.9; HRMS calcd for $C_{22}H_{19}O_2$: 315.1385, found: 315.1381.



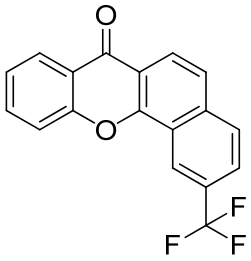
7H-benzo[c]xanthen-7-one (4a): White solid: m.p.152-153 ^{O}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.6 Hz, 1H), 8.37 (d, *J* = 7.9 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.76-7.60 (m, 5H), 7.41 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 155.7, 153.6, 136.5, 134.3, 129.6, 128.1, 126.9, 126.5, 124.4, 124.0, 122.9, 122.4, 121.4, 118.1, 117.5; HRMS calcd for $C_{17}H_{11}O_2$: 247.0759, found: 247.0771.



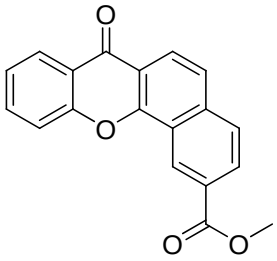
2-methyl-7H-benzo[c]xanthen-7-one (4b): White solid: m.p.184-185 ^{O}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.7 Hz, 1H), 8.24 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.44-7.36 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 155.7, 153.1, 136.9, 134.6, 134.2, 131.6, 127.8, 126.5, 124.3, 124.0, 123.7, 122.3, 121.8, 120.4, 118.0, 117.6, 21.9; HRMS calcd for $C_{18}H_{13}O_2$: 261.0916, found: 261.0914.



2-methoxy-7H-benzo[c]xanthen-7-one (4c):Yellow solid: m.p.169-171 ^{O}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.81-7.71 (m, 3H), 7.69 – 7.58 (m, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.34 – 7.25 (m, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 158.5, 155.7, 152.7, 134.3, 131.8, 129.6, 126.6, 125.1 124.3, 123.7, 122.3, 121.6, 119.1, 118.0, 101.6, 55.6; HRMS calcd for $C_{18}H_{12}O_3Na$: 299.0684, found: 299.0695.



2-(trifluoromethyl)-7H-benzo[c]xanthen-7-one (4d): White solid: m.p.196-197 ^{O}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.32 (t, *J* = 9.3 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.87 – 7.74 (m, 2H), 7.73-7.63 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 155.6, 153.6, 137.7, 134.8, 129.2, 128.8 (q, *J* = 32.4 Hz, 1C), 126.6, 125.2 (q, *J* = 3.0 Hz, 1C), 124.9, 124.1, 124.1 (q, *J* = 275.0 Hz, 1C), 123.6, 123.3, 122.3, 120.7 (q, *J* = 4.4 Hz, 1C), 118.3, 118.2; HRMS calcd for $C_{18}H_9O_2NaF_3$: 337.0452, found: 337.0462.



Methyl 7-oxo-7H-benzo[c]xanthene-2-carboxylate (4e) : White solid: m.p.204-206 ^{O}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ 9.33 (s, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 8.27 (d, *J* = 8.6 Hz, 1H),7.95 (d, *J* = 8.5 Hz, 1H), 7.85 – 7.71 (m, 3H), 7.47 (t, *J* = 7.4 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 166.2, 155.2, 153.6, 138.2, 134.2, 128.6, 127.9, 126.1, 125.2, 124.3, 123.7, 123.2, 123.1, 121.9, 117.8, 117.6, 52.1; HRMS calcd for $C_{19}H_{12}O_4Na$: 327.0633, found: 327.0628.

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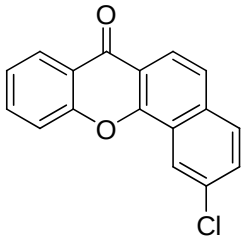
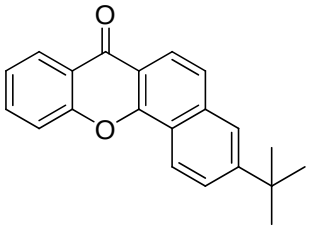
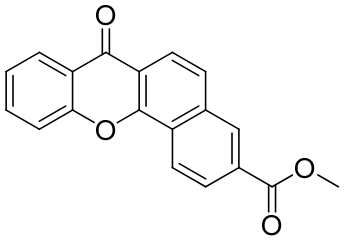


2-chloro-7H-benzo[c]xanthen-7-one (4f): Yellow solid: m.p.204-205 ^{O}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 7.86-7.72 (m, 2H), 7.70-7.53 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 155.7, 152.6, 134.7, 134.7, 133.1, 130.3, 129.7, 126.7, 124.9, 124.7, 123.8, 123.7, 122.4 122.1, 122.0, 118.2, 118.1; HRMS calcd for $C_{17}H_9O_2NaCl$: 303.0189, found: 303.0184



3-tert-butyl-7H-benzo[c]xanthen-7-one (4g): White solid: m.p.153-154 ^{O}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.8 Hz, 1H), 8.40 (d, *J* = 7.0 Hz, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 7.86 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.79-7.69 (m, 2H), 7.45-7.34 (m,1H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 155.8, 153.7, 153.0, 136.8, 134.2, 126.6, 125.7, 124.3, 124.2, 123.5, 122.7, 122.5, 122.0, 121.4, 118.1, 117.2, 35.2, 31.2; HRMS calcd for $C_{21}H_{18}O_2Na$: 325.1204, found: 325.1215.



methyl 7-oxo-7H-benzo[c]xanthene-3-carboxylate (4h): Yellow solid: m.p.205-206^{O}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.7 Hz, 1H), 8.63 (s, 1H), 8.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.32 (d, *J* = 8.7 Hz, 1H), 8.25 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.46 (s, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 166.6, 155.8, 153.2, 135.8, 134.7, 130.7, 130.6, 126.7, 126.4, 126.4, 124.9, 124.7, 123.3, 122.5, 122.4, 119.0, 118.1, 52.6; HRMS calcd for $C_{19}H_{12}O_4Na$: 327.0633, found: 327.0624.

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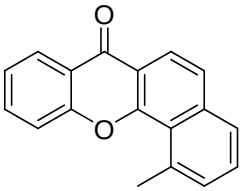
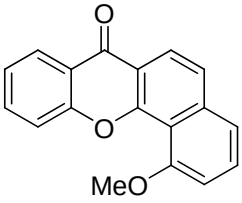
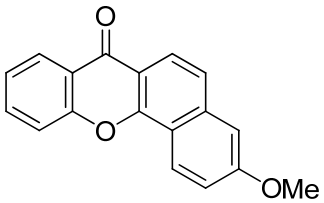


1-methyl-7H-benzo[c]xanthen-7-one (4i) : White solid: m.p.175-175 ^{O}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.7 Hz, 1H), 7.82 – 7.67 (m, 3H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (m, 2H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 155.3, 155.0, 137.7, 135.9, 133.8, 129.9, 128.7, 126.4, 126.0, 124.6, 124.0, 123.0, 121.5, 121.0, 117.9, 117.5, 25.0; HRMS calcd for $C_{18}H_{12}O_2Na$: 283.0735, found: 283.0742.



1-methoxy-7H-benzo[c]xanthen-7-one (4j):White solid: m.p.215-216 ^{O}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.31 (d, *J* = 8.7 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.66-7.72 (m, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.46-7.43 (m, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 4.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 160.7, 155.8, 154.0, 138.7, 134.2, 126.6, 124.7, 124.3, 123.2, 122.5, 122.4, 119.0, 118.7, 118.0, 116.3, 106.9, 55.6; HRMS calcd for $C_{18}H_{12}O_3$:2 77.0865, found: 277.0877.



3-methoxy-7H-benzo[c]xanthen-7-one (4j′): White solid: m.p.208-209 ^{O}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 9.1 Hz, 1H), 8.40 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.70-7.56 (m, 2H), 7.48 – 7.41 (m, 1H), 7.32 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 158.3, 155.8, 155.1, 139.2, 134.2, 130.1, 126.2, 124.3, 124.2, 122.4, 122.1, 120.8, 118.6, 118.2, 115.5, 107.8, 56.3; HRMS calcd for $C_{18}H_{12}O_3$: 277.0865, found: 277.0867.

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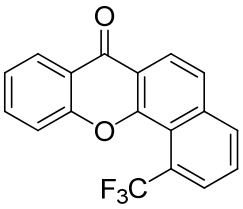
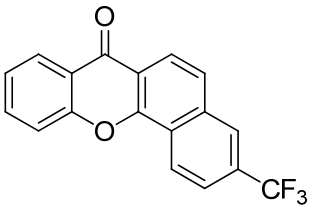
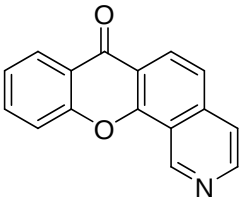


1-(trifluoromethyl)-7H-benzo[c]xanthen-7-one (4k): Yellow solid: m.p.183-185 ^{O}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.6 Hz, 1H), 8.46 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.94 – 7.78 (m, 4H), 7.58 – 7.51 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 155.5, 152.1, 138.1, 134.9, 133.4, 127.9, 127.8 (q, *J* = 7.5 Hz, 1C), 126.3, 125.9 (q, *J* = 31.3 Hz, 1C), 124.9, 124.7, 124.6 (q, *J* = 31.3 Hz, 1C), 123.2, 121.9, 120.7, 119.6, 118.2; HRMS calcd for $C_{18}H_9O_2NaF_3$: 337.0452, found: 337.0446.



3-(trifluoromethyl)-7H-benzo[c]xanthen-7-one (4k′): Yellow solid: m.p.135-137 ^{O}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.5 Hz, 1H), 8.35 (dd, *J* = 22.3, 8.1 Hz, 2H), 8.18 (s, 1H), 7.88 – 7.73 (m, 3H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.46 (q, *J* = 7.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 155.7, 153.0, 135.5, 134.8, 131.2 (q, *J* = 32.5 Hz, 1C), 126.7, 125.6, 125.6 (q, *J* = 5.0 Hz, 1C), 124.8, 124.3, 124.1,124.0 (q, *J* = 271.3 Hz, 1C),123.1, 122.6 (q, *J* = 3.75 Hz, 1C), 122.3, 118.9, 118.1; HRMS calcd for $C_{18}H_9O_2NaF_3$: 337.0452, found: 337.0455.



7H-chromeno[3,2-h]isoquinolin-7-one (4l): Yellow solid: m.p.213-214 ^{O}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.80 (d, *J* = 5.6 Hz, 1H), 8.49 (d, *J* = 8.7 Hz, 1H), 8.41 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.84 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.80 – 7.70 (m, 3H), 7.50 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 155.5, 153.9, 147.7, 146.9, 139.4, 134.9, 126.6, 126.6, 125.0, 122.4, 122.4, 120.5, 119.4, 118.5, 118.2; HRMS calcd for $C_{16}H_{10}NO_2$: 248.0712, found: 277.0712.

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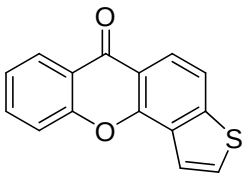
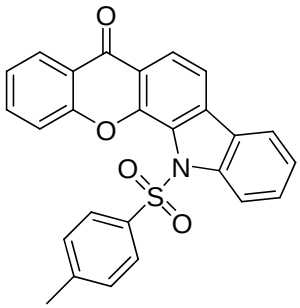
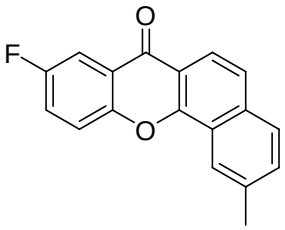


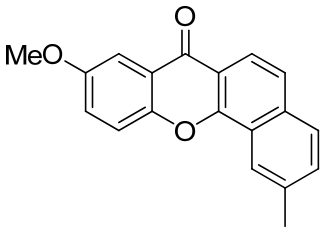
6H-thieno[2,3-c]xanthen-6-one (4m): White solid: m.p.211-212 ^{O}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.9 Hz, 1H), 8.24 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 5.5 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.75 (m,1H), 7.63 – 7.55 (m, 2H), 7.45 – 7.37 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 155.7, 151.9, 146.4, 134.5, 129.2, 127.3, 126.7, 124.3, 122.2, 121.7, 120.8, 118.4, 118.0, 117.6; HRMS calcd for $C_{15}H_9O_2S$: 253.0323, found: 277.0319.



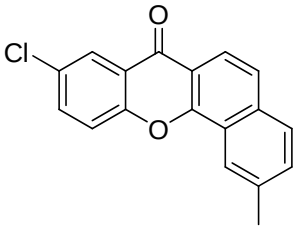
13-tosylchromeno[2,3-a]carbazol-7(13H)-one (4n): Yellow solid: m.p.200-201 ^{O}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, *J* = 9.3 Hz, 1H), 8.32 (s, 2H), 7.97 (d, *J* = 6.6 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.75 (m, 1H), 7.64-7.50 (m, 4H), 7.48 – 7.35 (m, 2H), 7.09 (d, *J* = 7.3 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 155.4, 145.8, 144.8, 142.3, 136.2, 135.0, 134.9, 134.0, 129.7, 129.0, 126.6, 126.3, 125.9, 124.8, 124.4, 123.2, 121.6, 120.9, 120.6, 117.9, 117.7, 115.4, 21.6; HRMS calcd for $C_{26}H_{17}NO_4NaS$: 462.0776, found: 462.0786



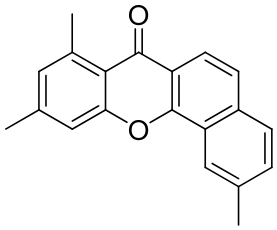
9-fluoro-2-methyl-7H-benzo[c]xanthen-7-one (4o): Yellow solid: 185-186 ^{O}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 8.03 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.71 (dd, *J* = 9.0, 3.5 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.54 – 7.46 (m, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 159.0(d, *J* = 244.4 Hz, 1C), 153.3, 151.9, 137.1, 134.8, 131.8, 128.0, 124.1, 124.0, 123.3 (d, *J* = 8.9 Hz, 1C), 122.4 (d, *J* = 31.5 Hz, 1C), 121.9, 120.2, 120.0 (d, *J* = 9.8 Hz, 1C), 116.9, 111.3 (d, *J* = 29.3 Hz, 1C), 22.0; HRMS calcd for $C_{18}H_{12}O_2F$: 279.0821, found: 279.0833



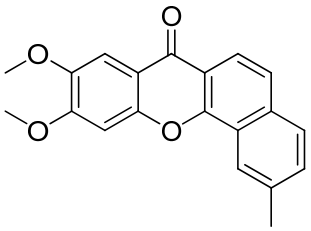
9-methoxy-2-methyl-7H-benzo[c]xanthen-7-one (4p): Yellow solid: 161-162 ^{O}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 2.6 Hz, 1H), 7.72-7.60 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.44-7.33 (m, 1H), 3.95 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 156.2, 153.2, 150.5, 136.8, 134.5, 131.5, 127.9, 124.3, 124.1, 123.6, 122.7, 121.9, 120.4, 119.4, 117.0, 105.5, 55.9, 21.9; HRMS calcd for $C_{19}H_{14}O_3Na$: 313.0841, found: 313.0844.



9-chloro-2-methyl-7H-benzo[c]xanthen-7-one (4q): Yellow solid: 187-189 ^{O}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 2.4 Hz, 1H), 8.22 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.55 – 7.44 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 153.9, 153.1, 137.1, 134.8, 134.3, 131.8, 130.1, 127.9, 125.8, 124.1, 123.8, 123.1, 121.8, 120.2, 119.7, 117.3, 21.9; HRMS calcd for $C_{18}H_{11}O_2NaCl$: 317.0345, found: 317.0359.



2,8,10-trimethyl-7H-benzo[c]xanthen-7-one (4r): Yellow solid: 226-227 ^{O}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 7.99 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.39 (s, 1H), 2.67 (s, 3H), 2.61 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 152.8, 152.2, 136.7, 136.4, 134.5, 133.4, 131.3, 127.8, 127.0, 124.2, 123.4, 123.3, 121.7, 121.7, 120.5, 117.2, 22.0, 20.8, 15.8; HRMS calcd for $C_{20}H_{16}O_2Na$: 311.1048, found: 311.1042.



9,10-dimethoxy-2-methyl-7H-benzo[c]xanthen-7-one (4s): Yellow solid: 203-204 ^{O}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.73 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.14 (s, 1H), 4.09 (s, 3H), 4.03 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 154.9, 153.0, 151.9, 147.0, 136.7, 134.3, 131.3, 127.9, 124.1, 123.6, 121.7, 120.5, 117.3, 115.5, 105.1, 99.7, 56.5, 56.3, 21.9; HRMS calcd for $C_{20}H_{16}O_4Na$: 343.0946, found: 343.0932.

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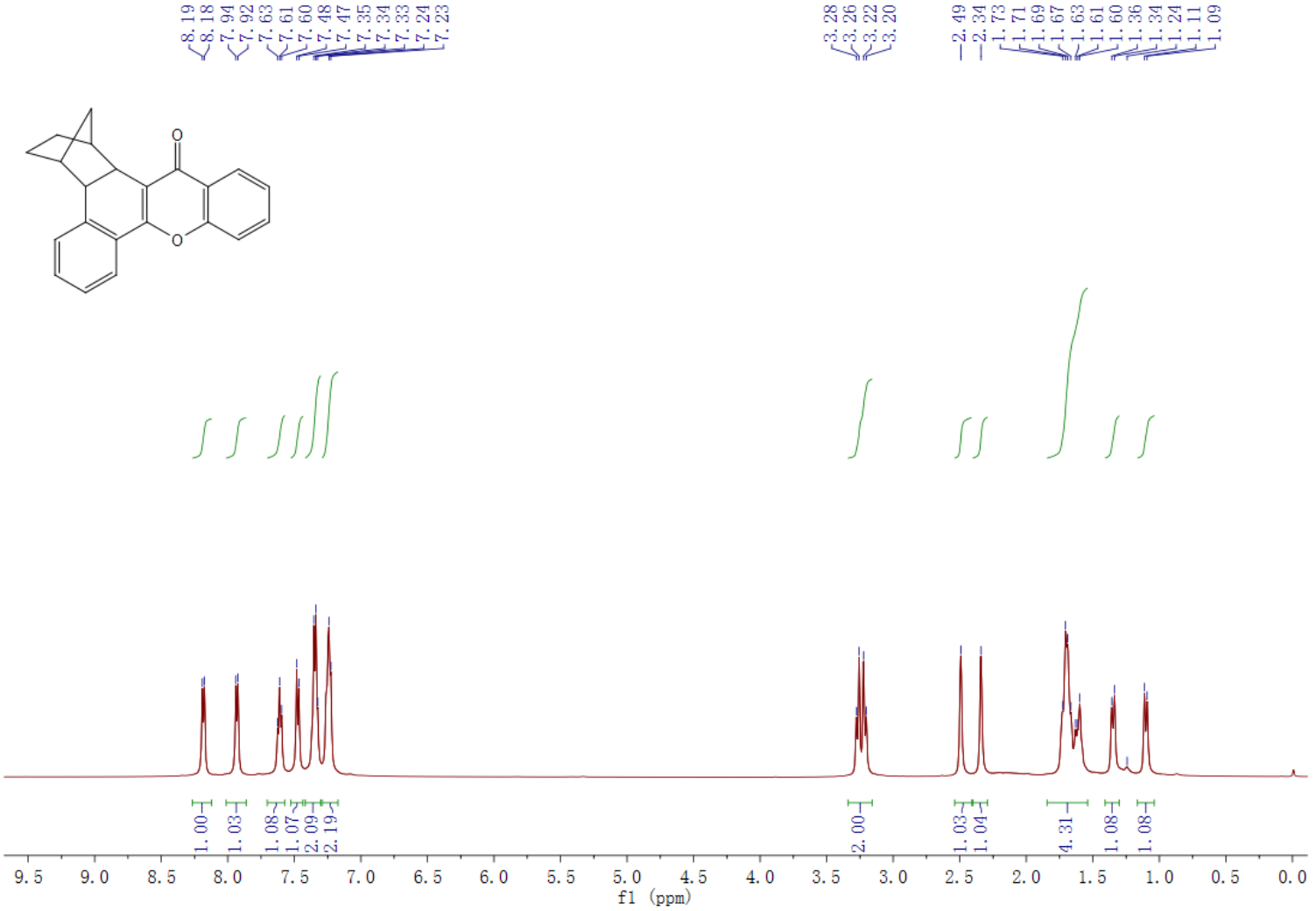
^{1}H NMR Spectra of 3a



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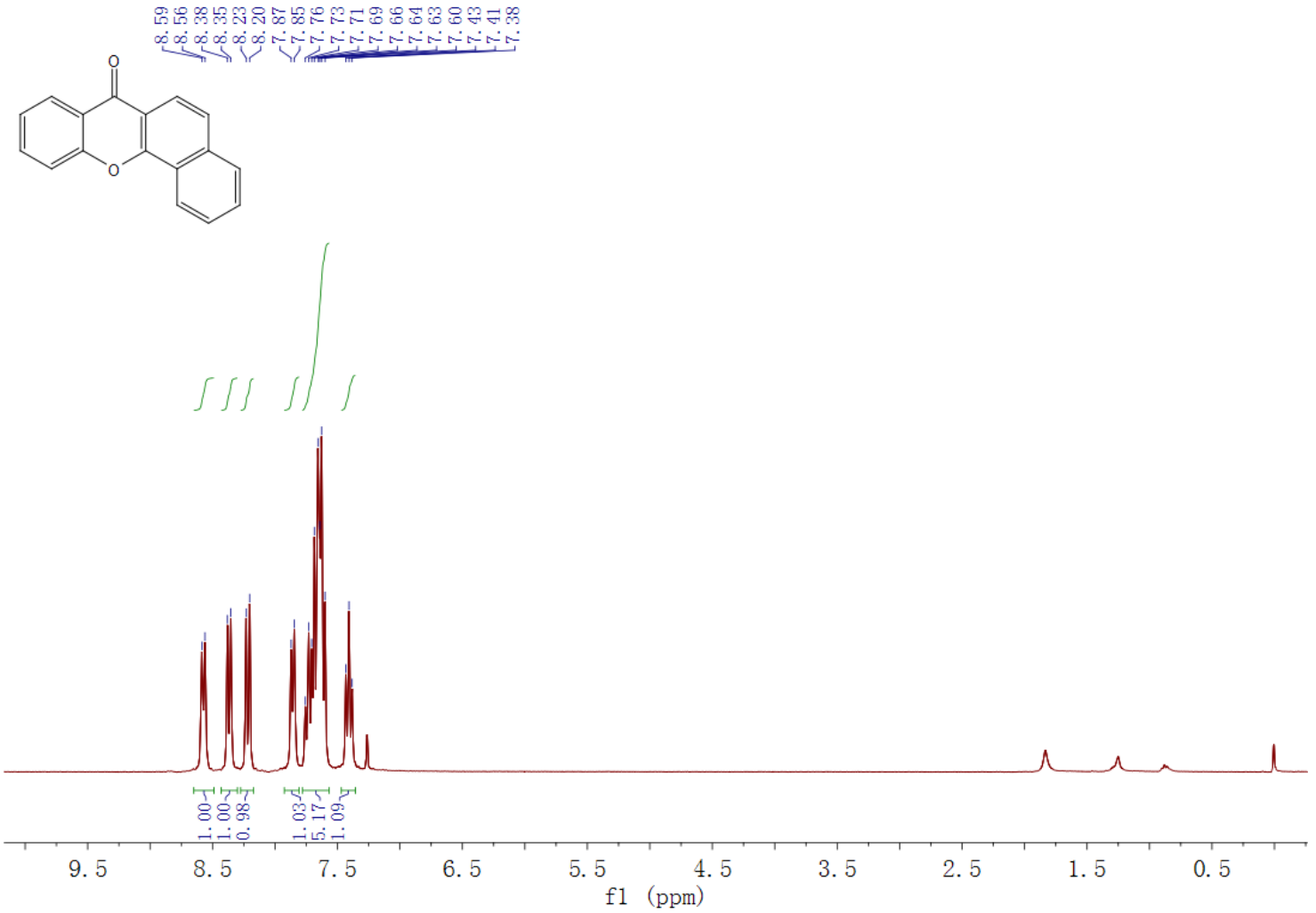
^{1}H NMR Spectra of 4a



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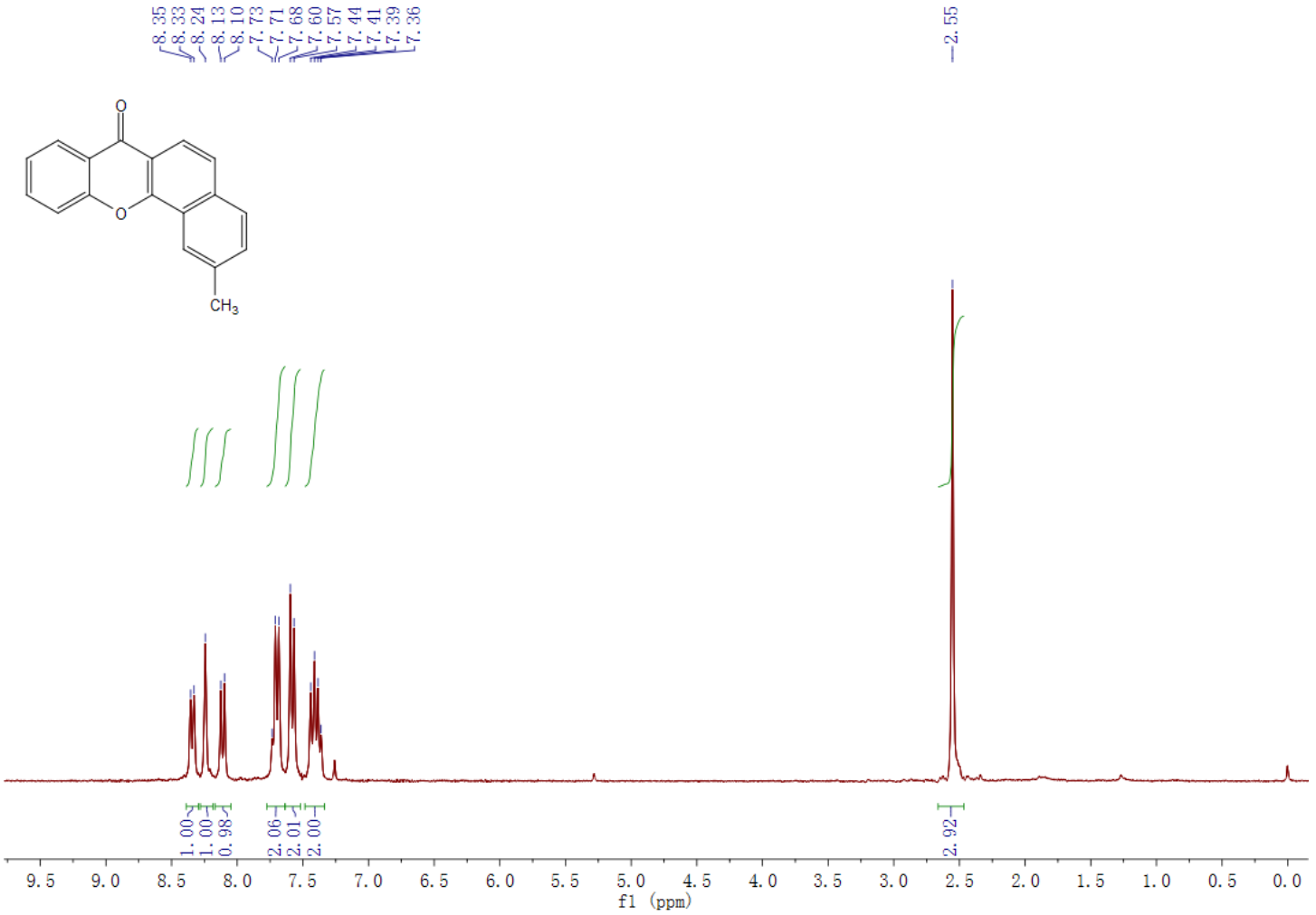
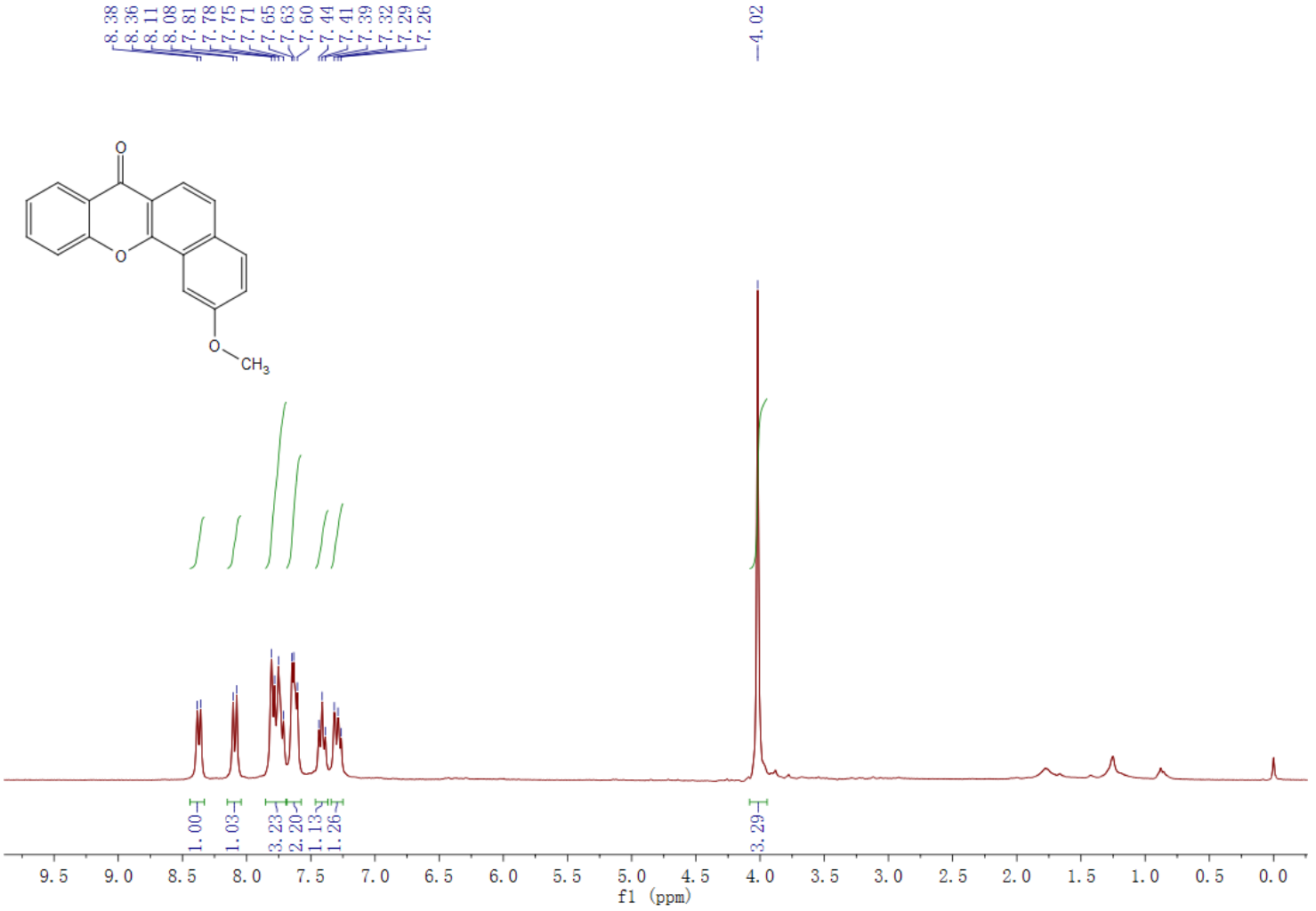
^{1}H NMR Spectra of 4b



^{1}H NMR Spectra of 4c



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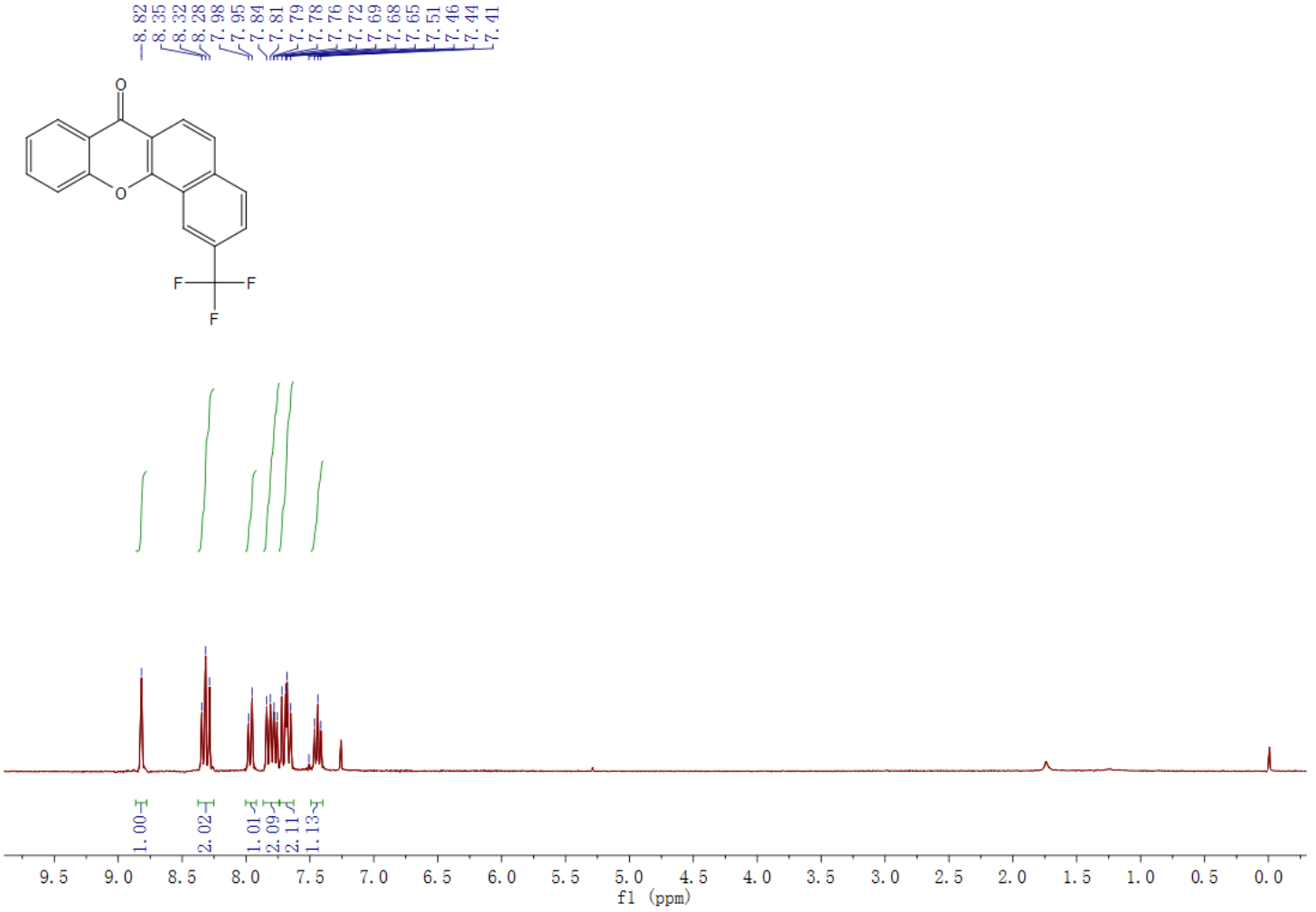
^{1}H NMR Spectra of 4d



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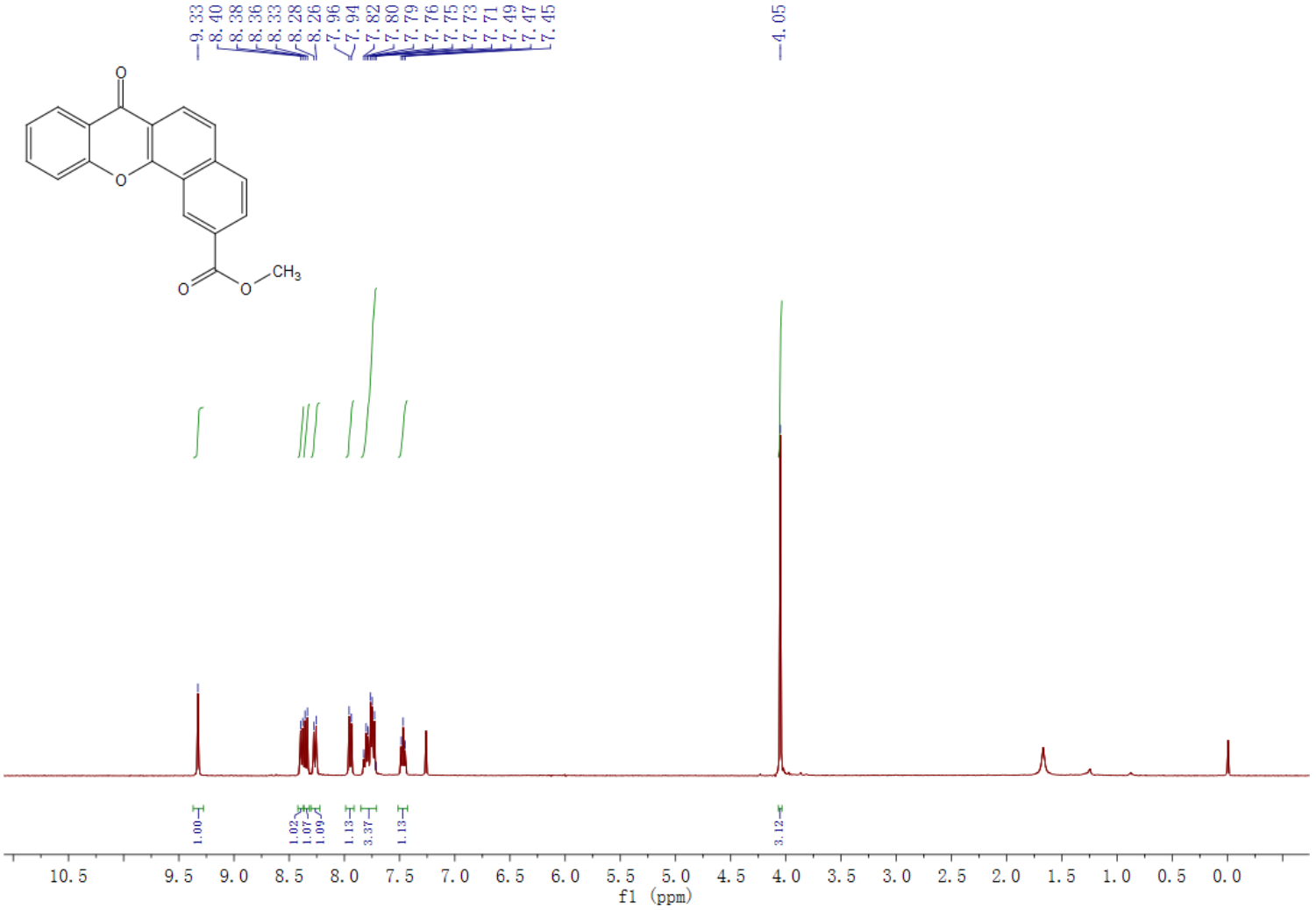
^{1}H NMR Spectra of 4e



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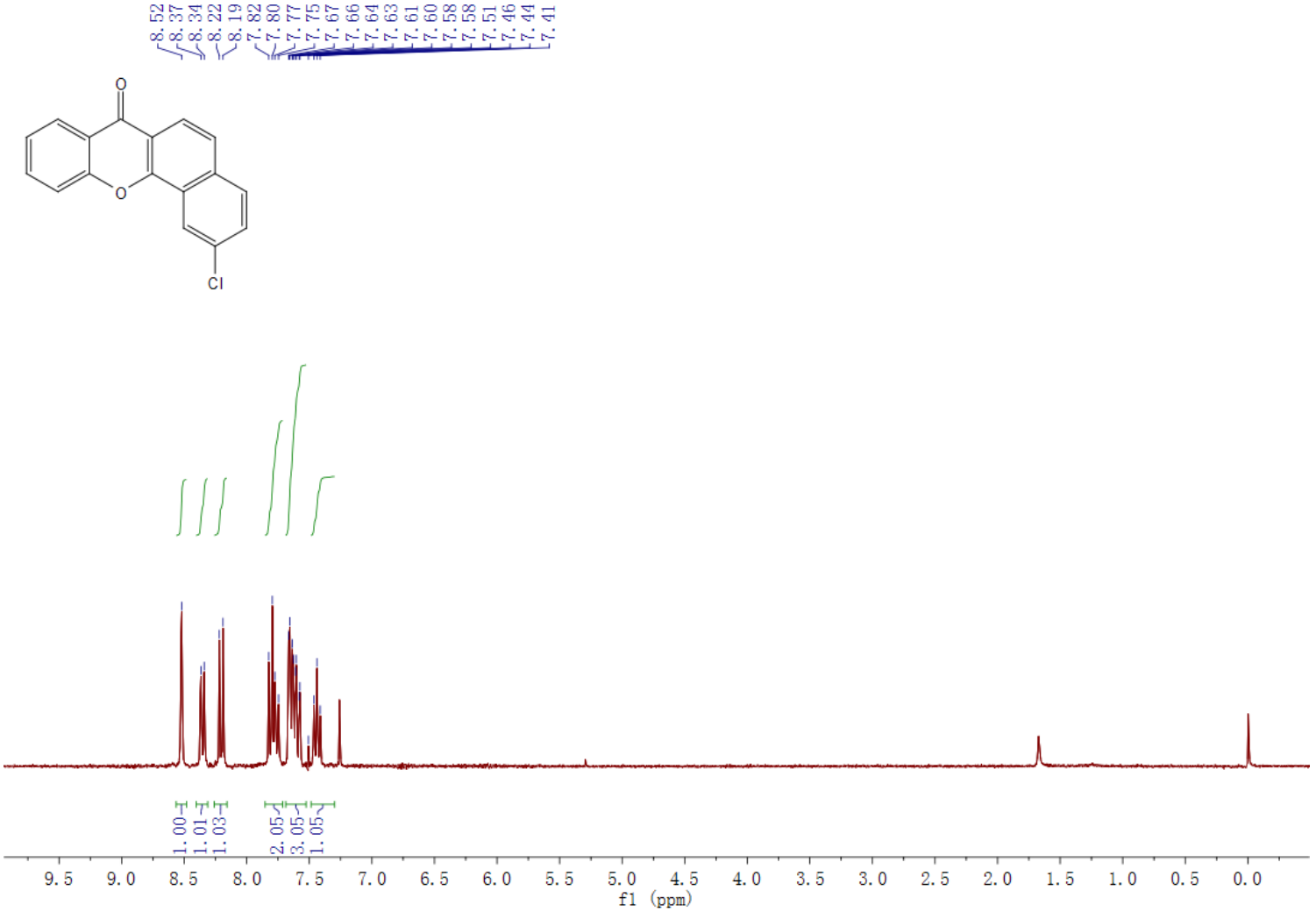
^{1}H NMR Spectra of 4f



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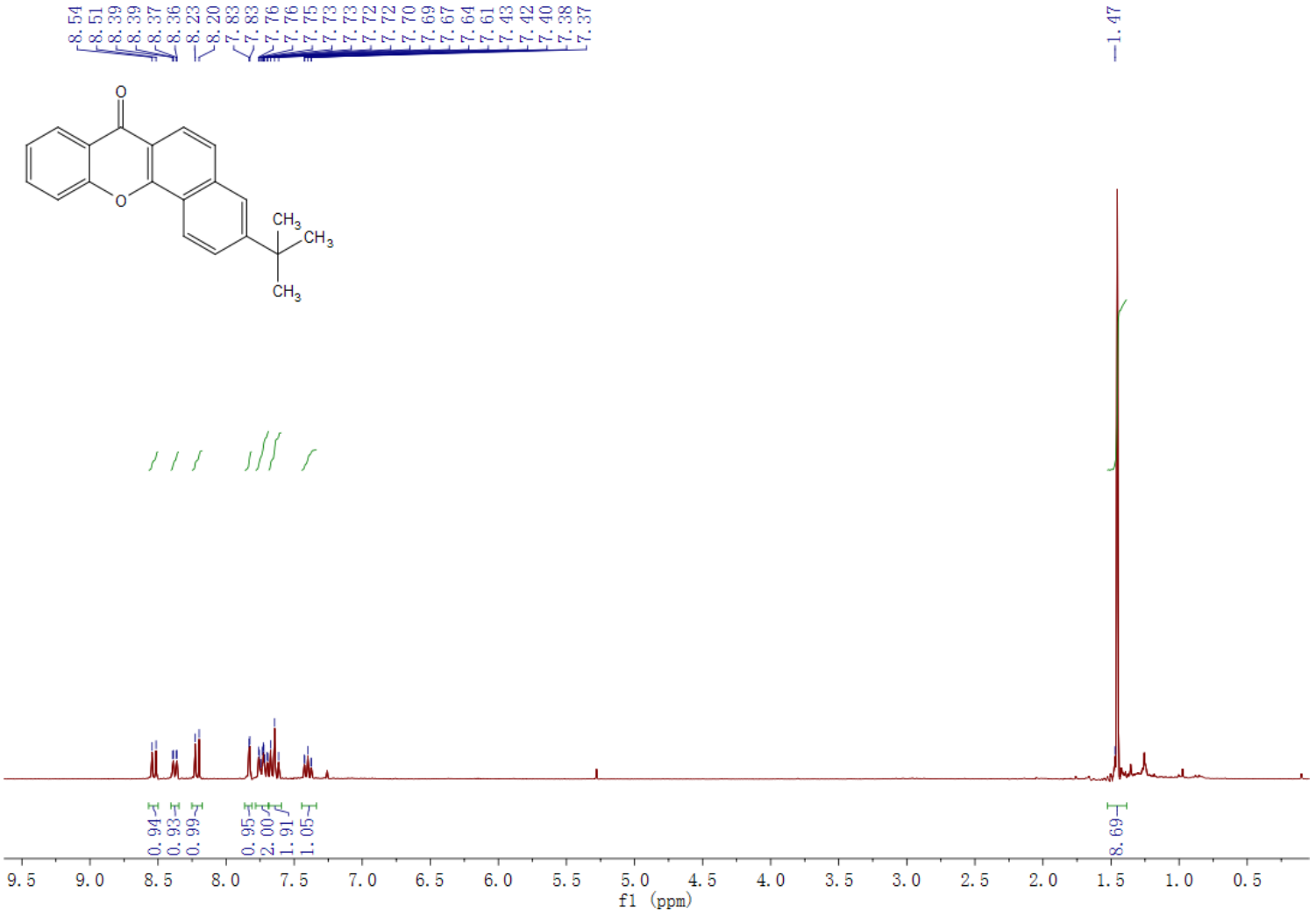
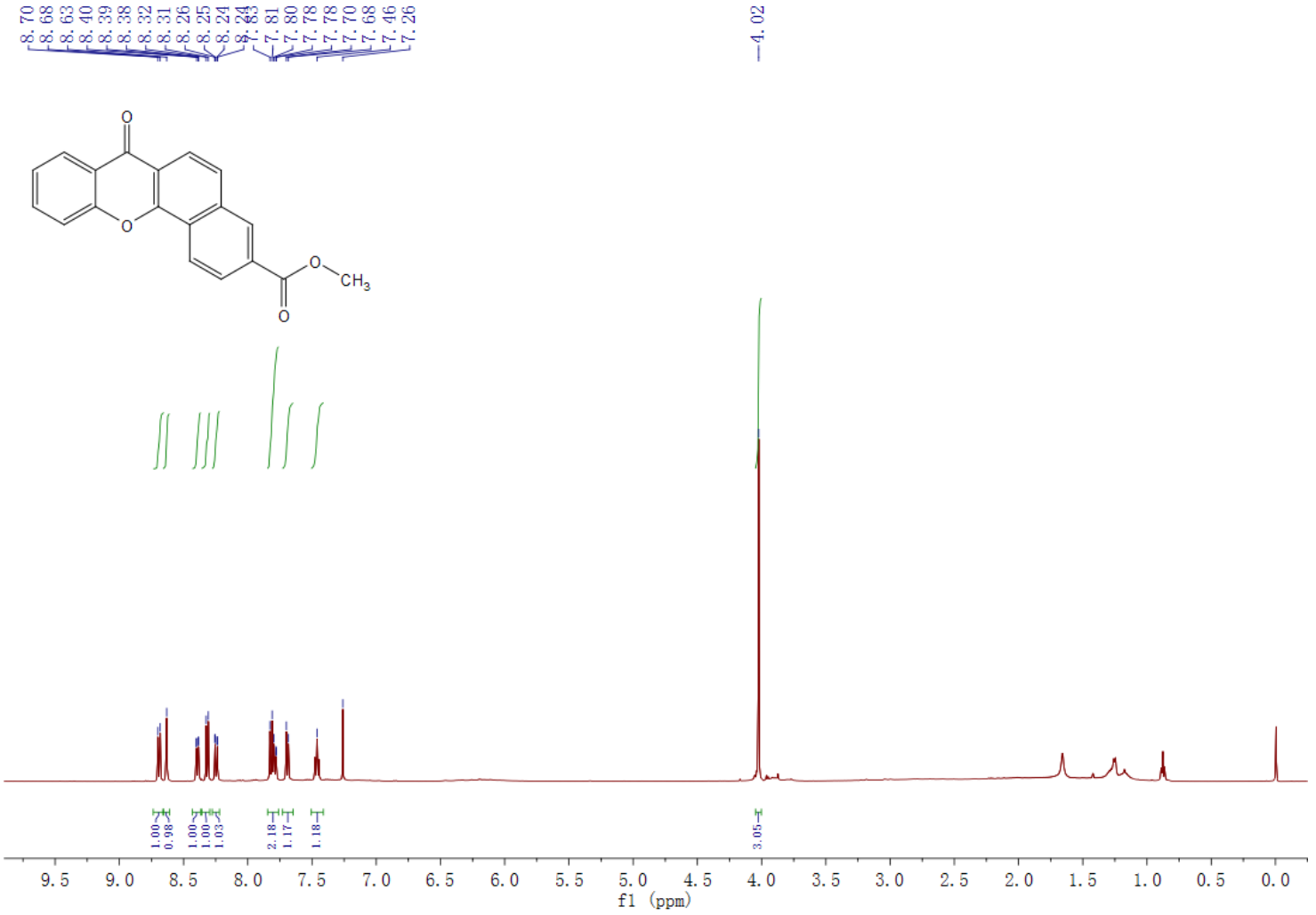
^{1}H NMR Spectra of 4g



^{1}H NMR Spectra of 4h



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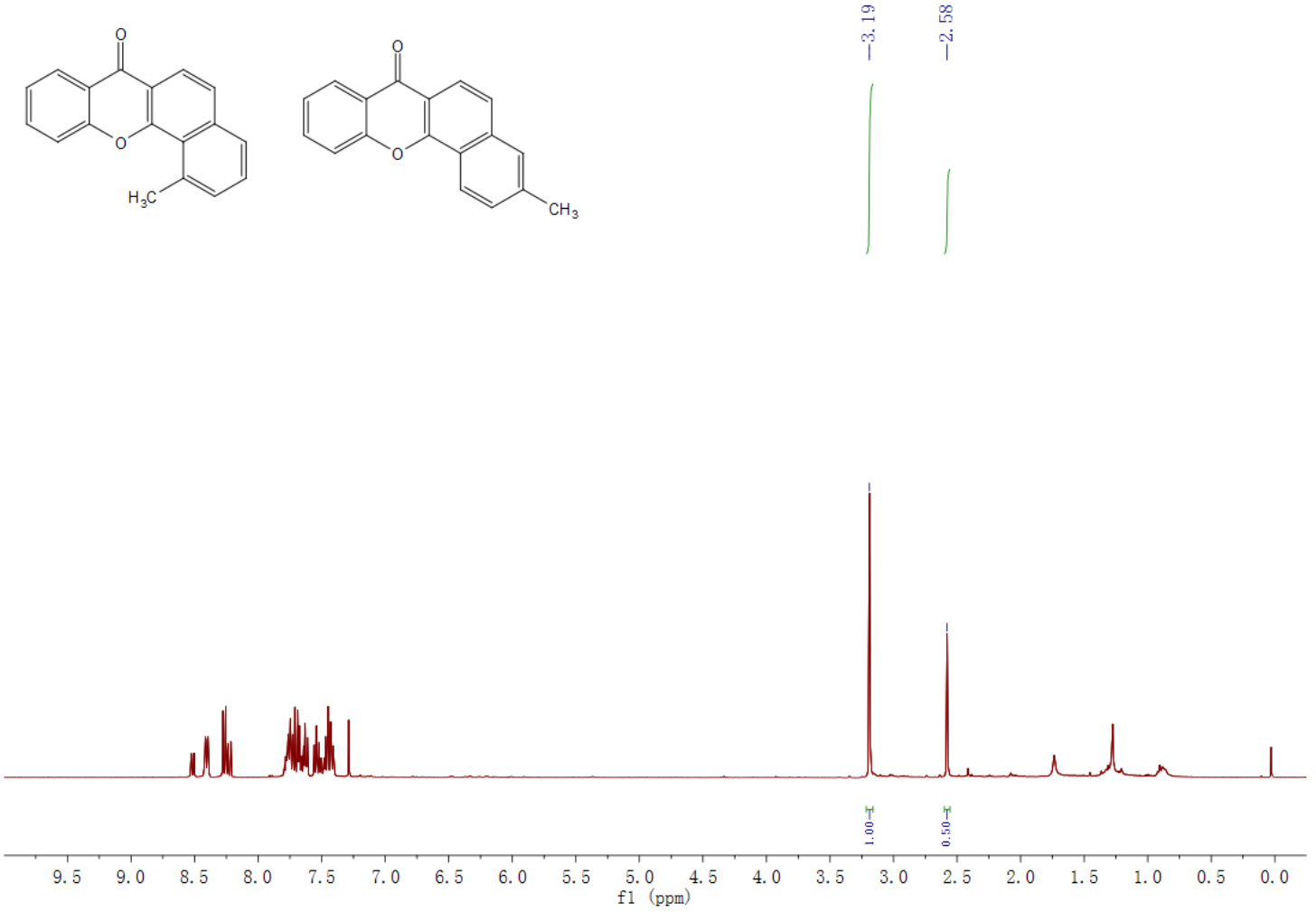
^{1}H NMR Spectra of 4i and 4i′



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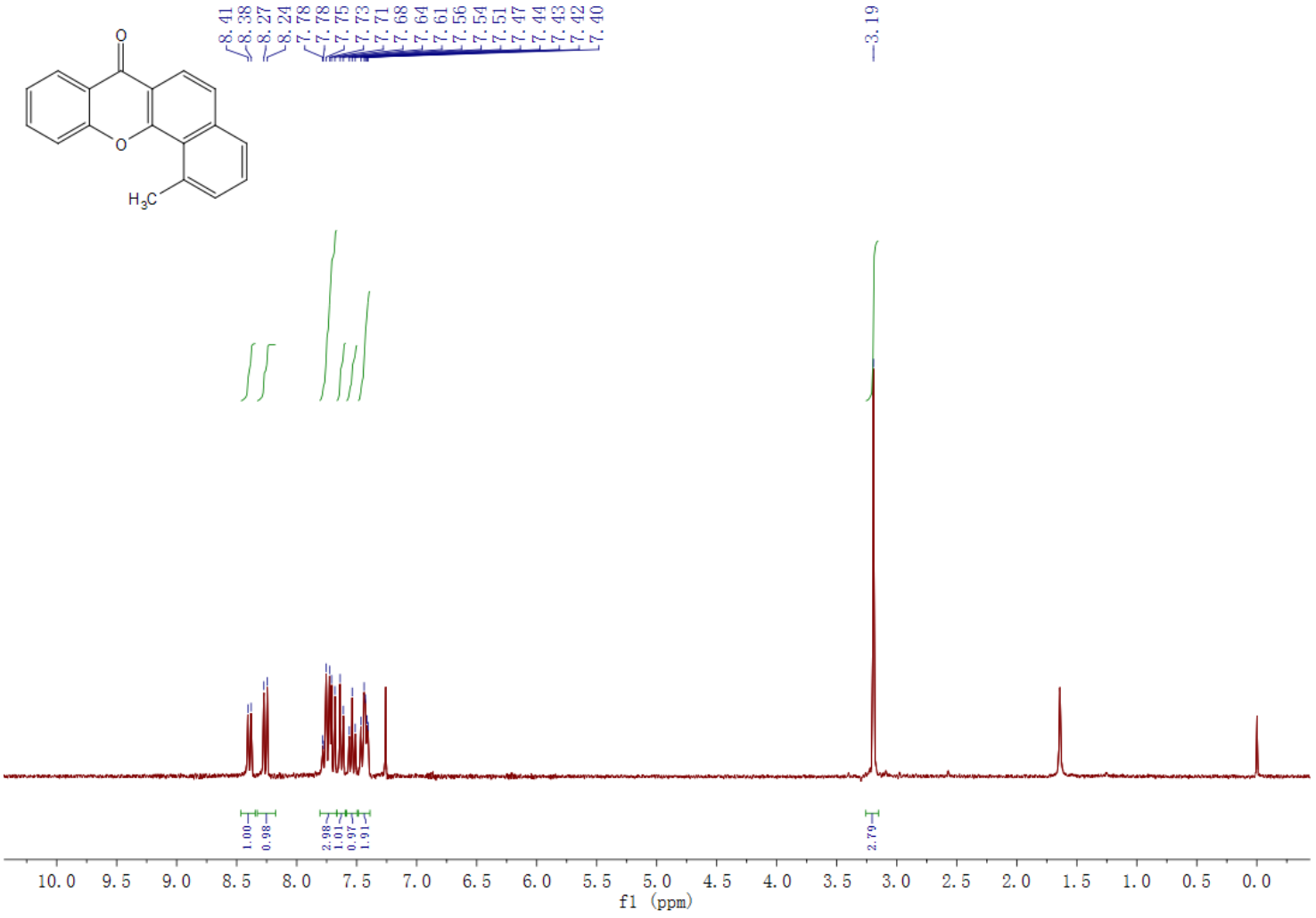
^{1}H NMR Spectra of 4i



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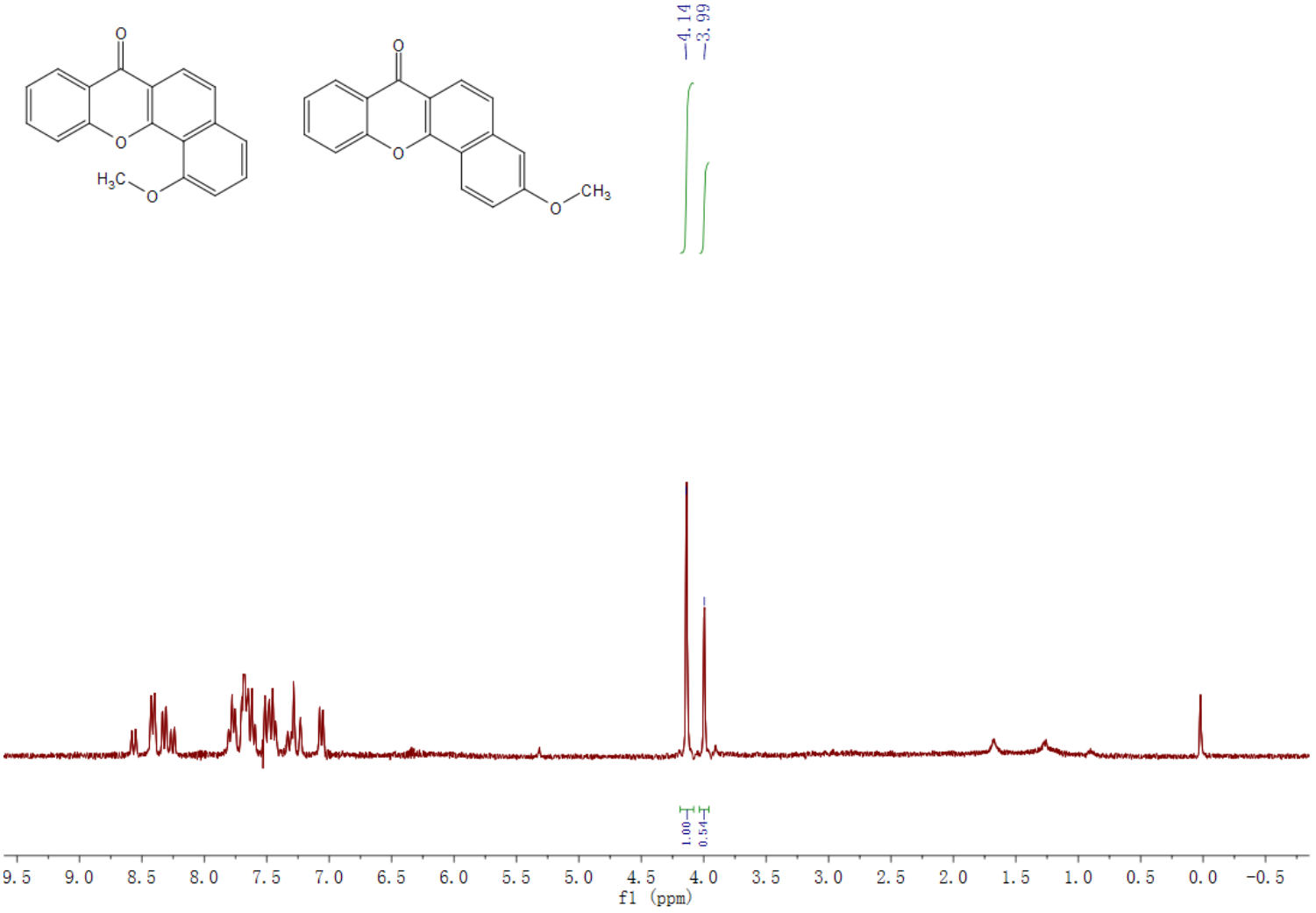
^{1}H NMR Spectra of 4j and 4j′



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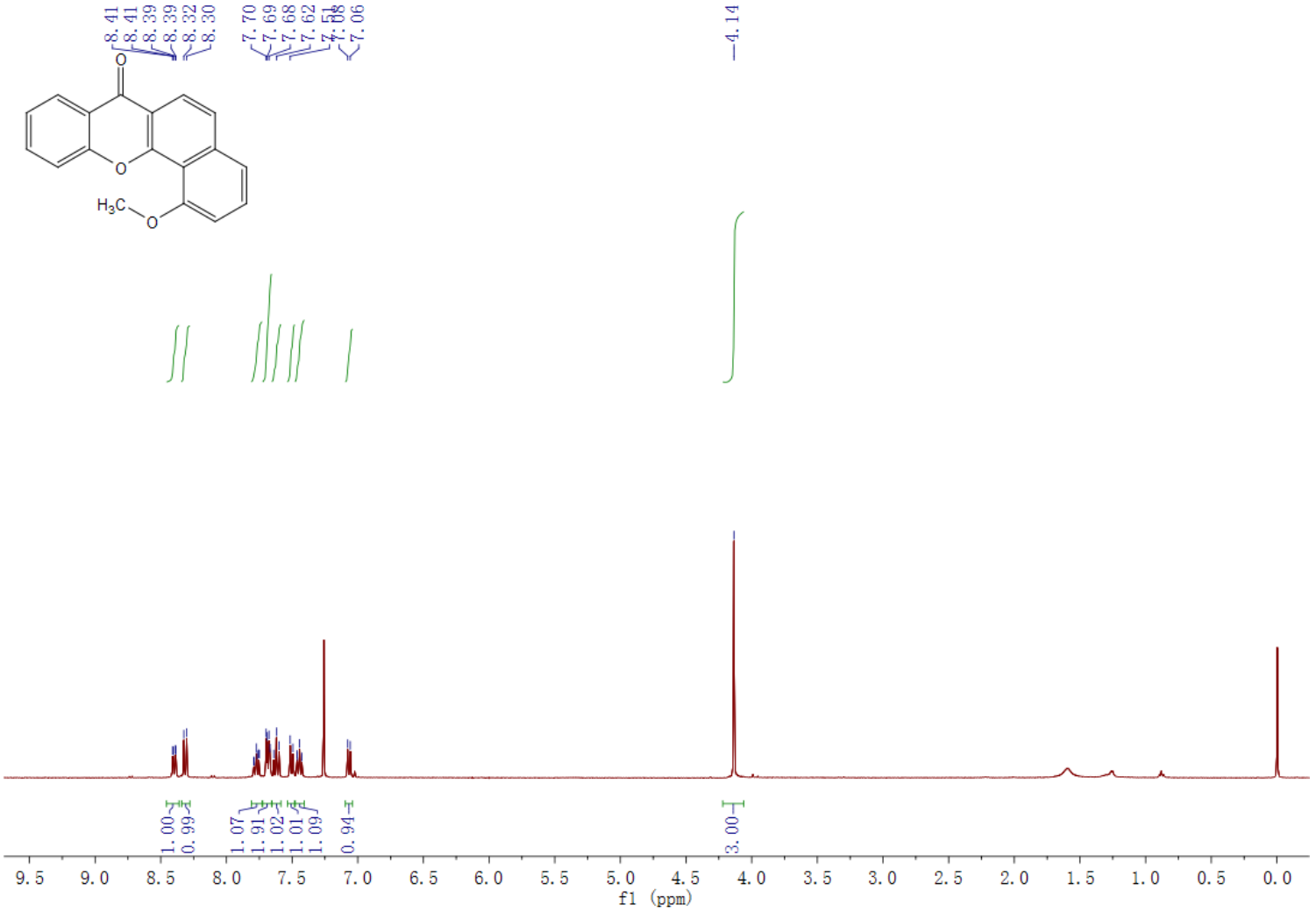
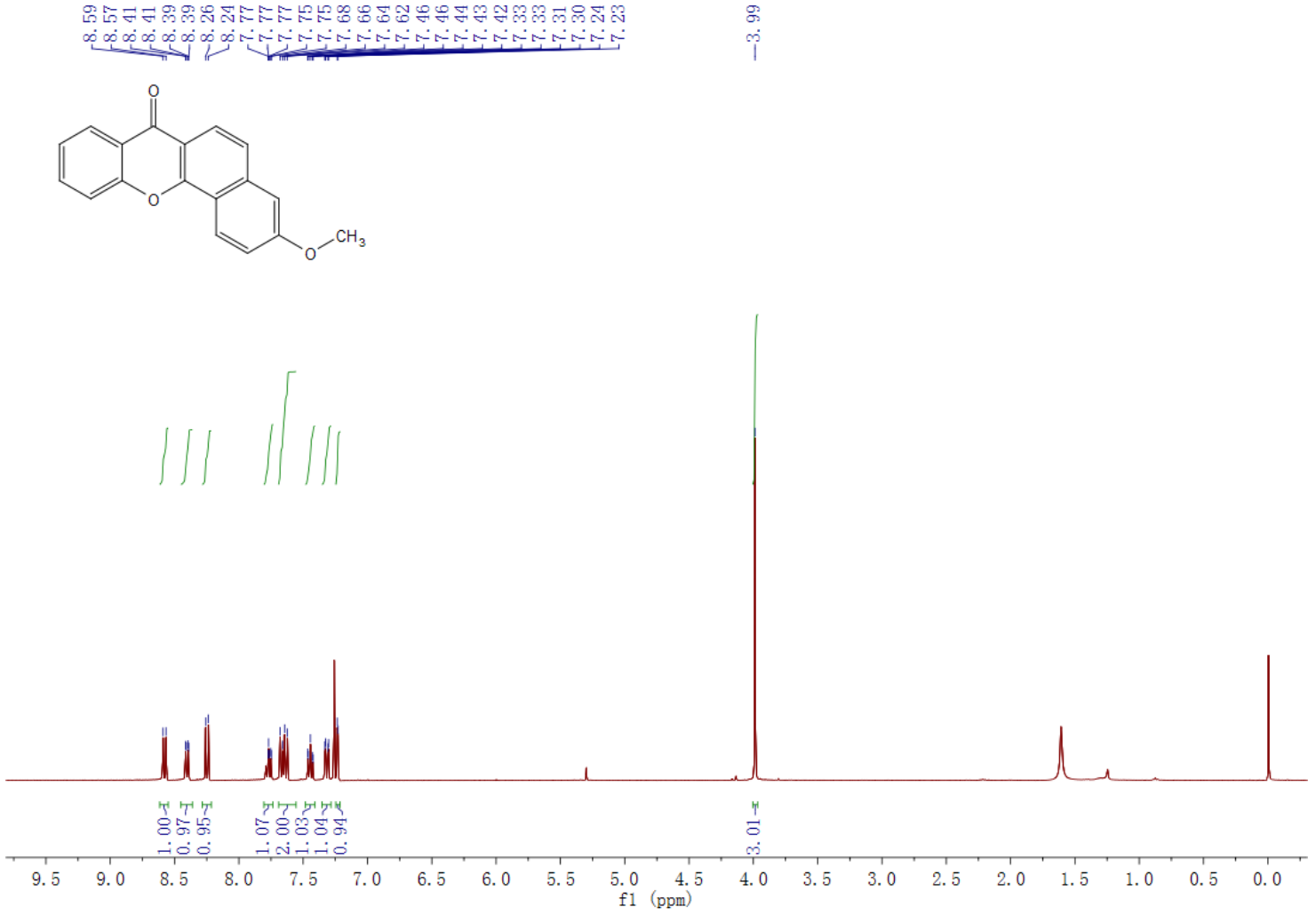
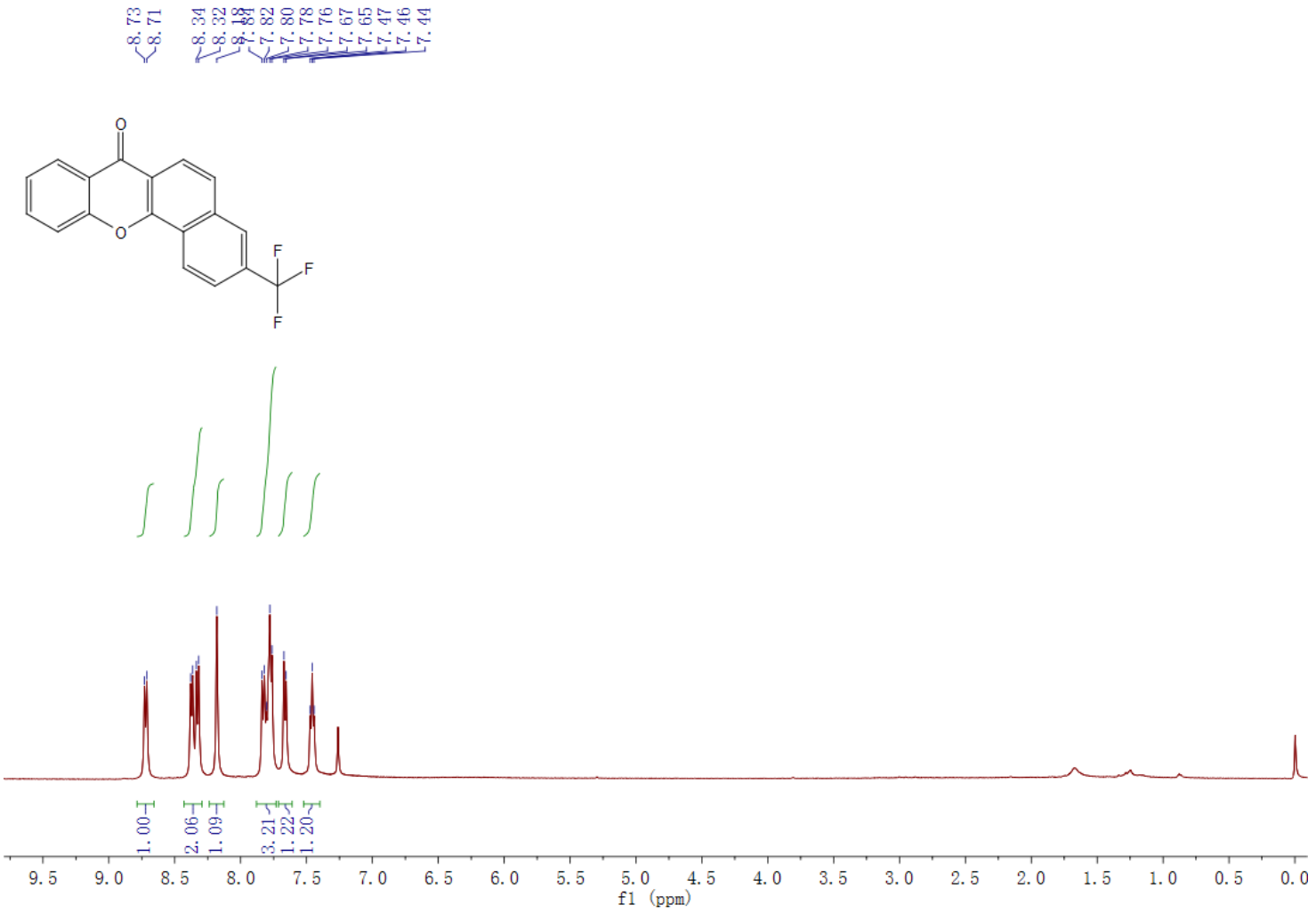
^{1}H NMR Spectra of 4j



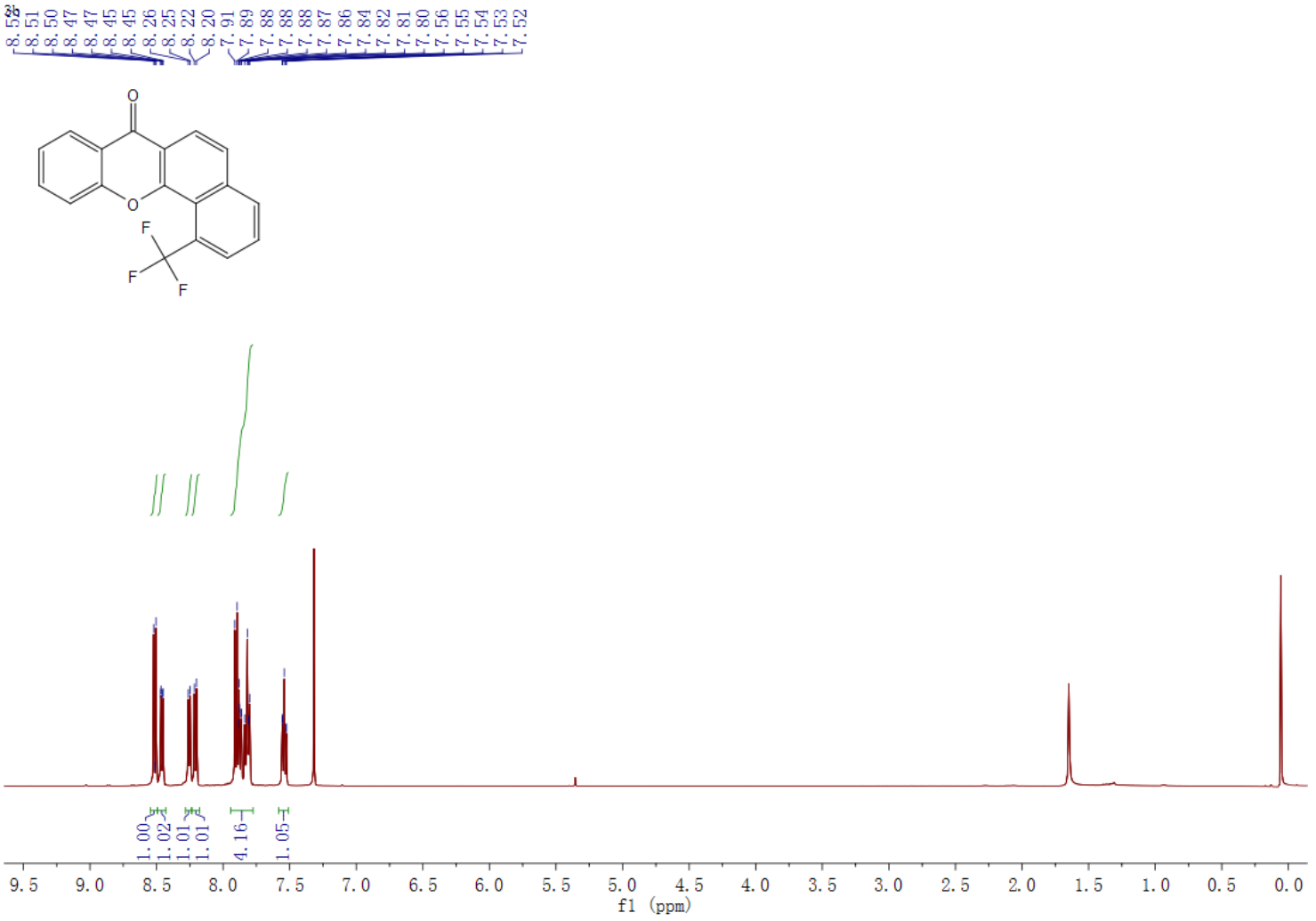
^{1}H NMR Spectra of 4j′



^{1}H NMR Spectra of 4k



^{1}H NMR Spectra of 4k′



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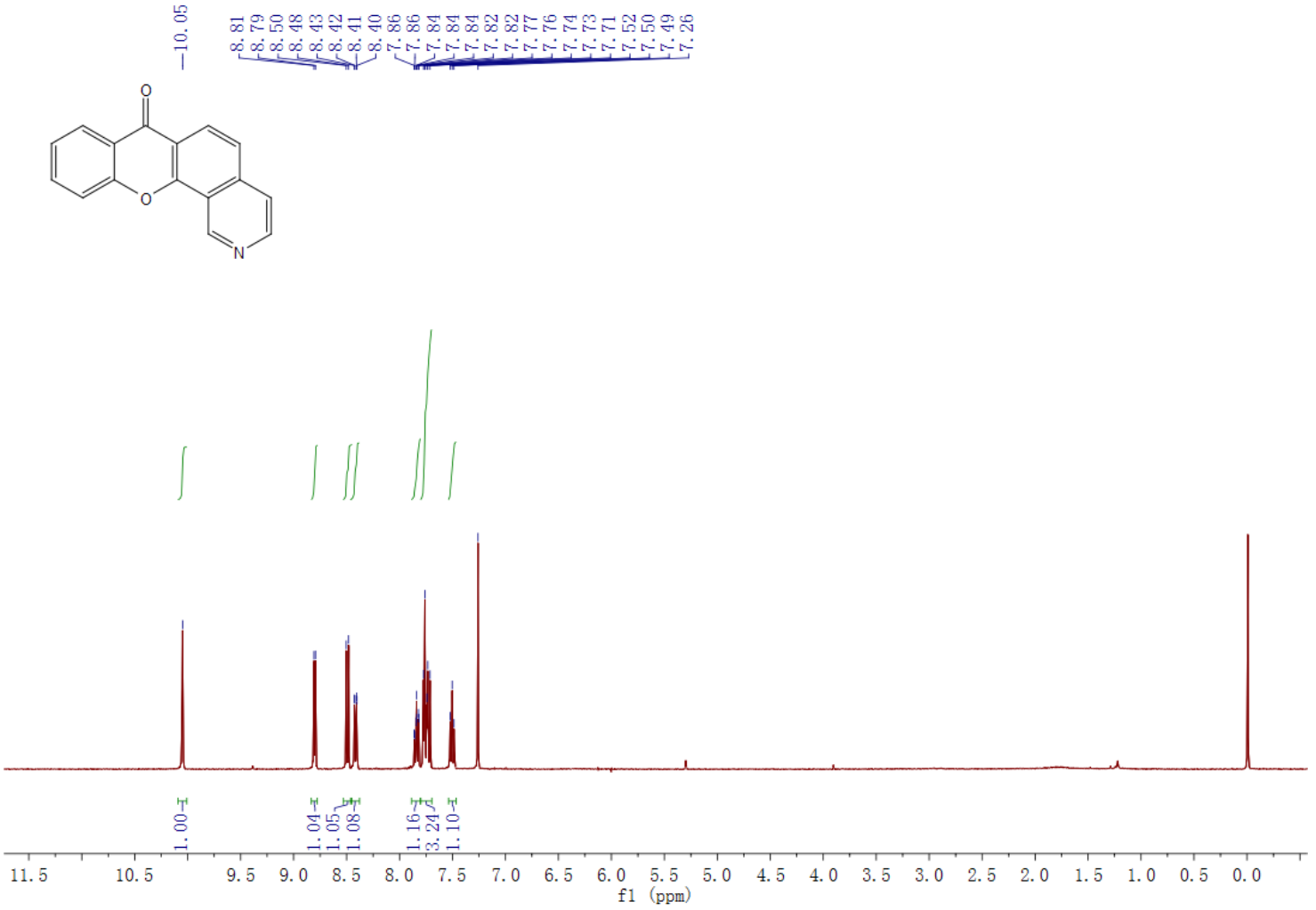
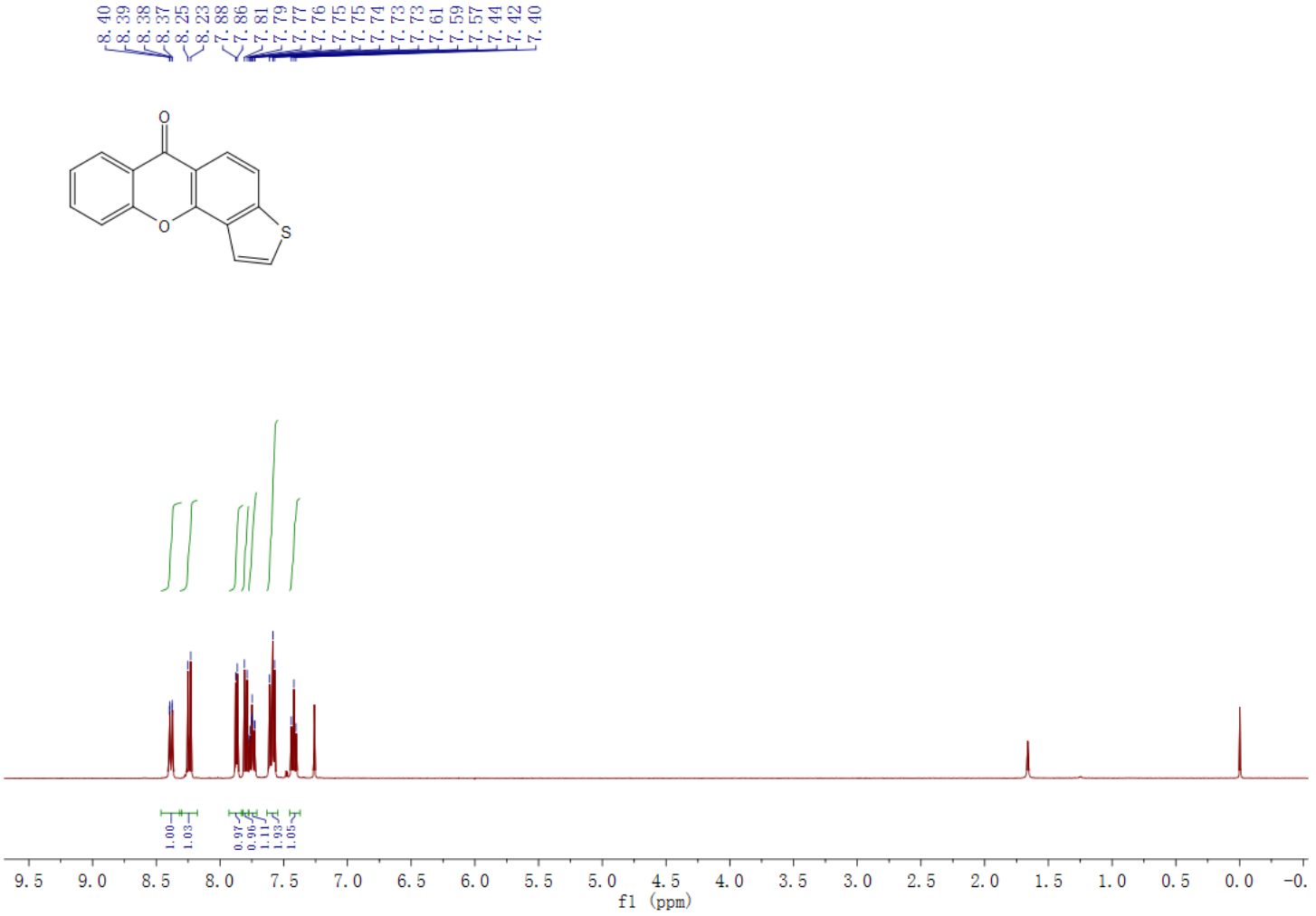
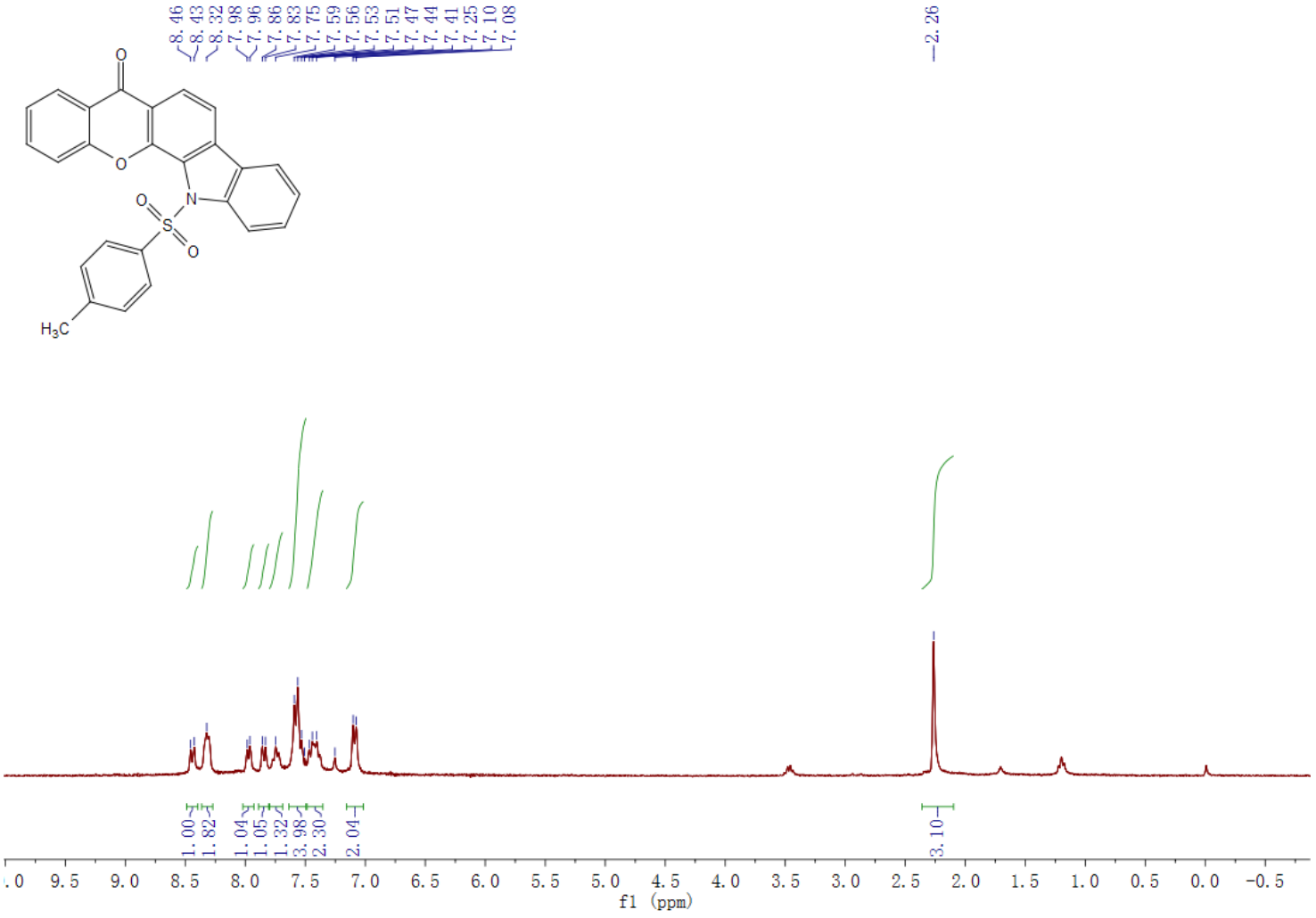
^{1}H NMR Spectra of 4l



^{1}H NMR Spectra of 4m



^{1}H NMR Spectra of 4n



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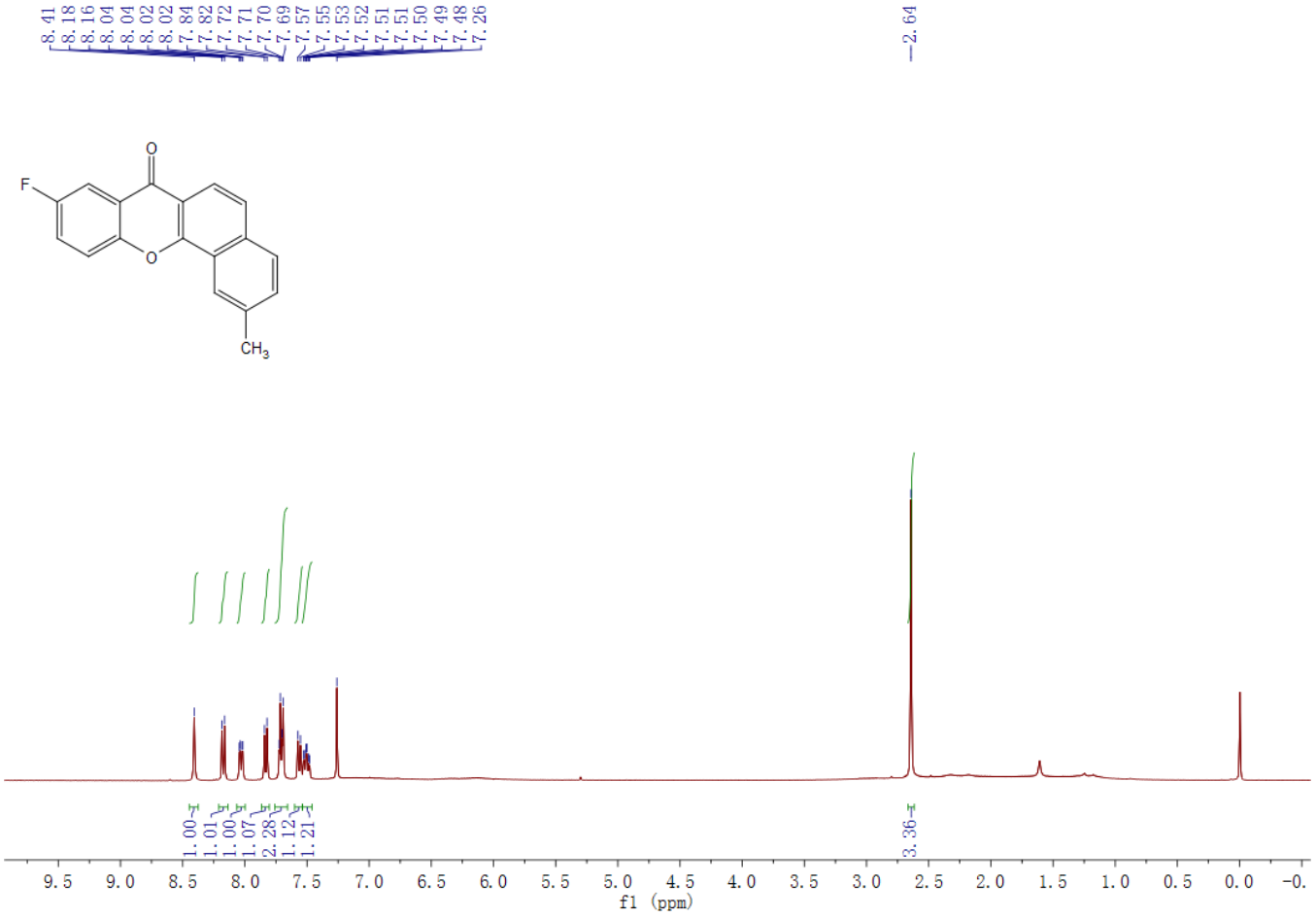
^{1}H NMR Spectra of 4o



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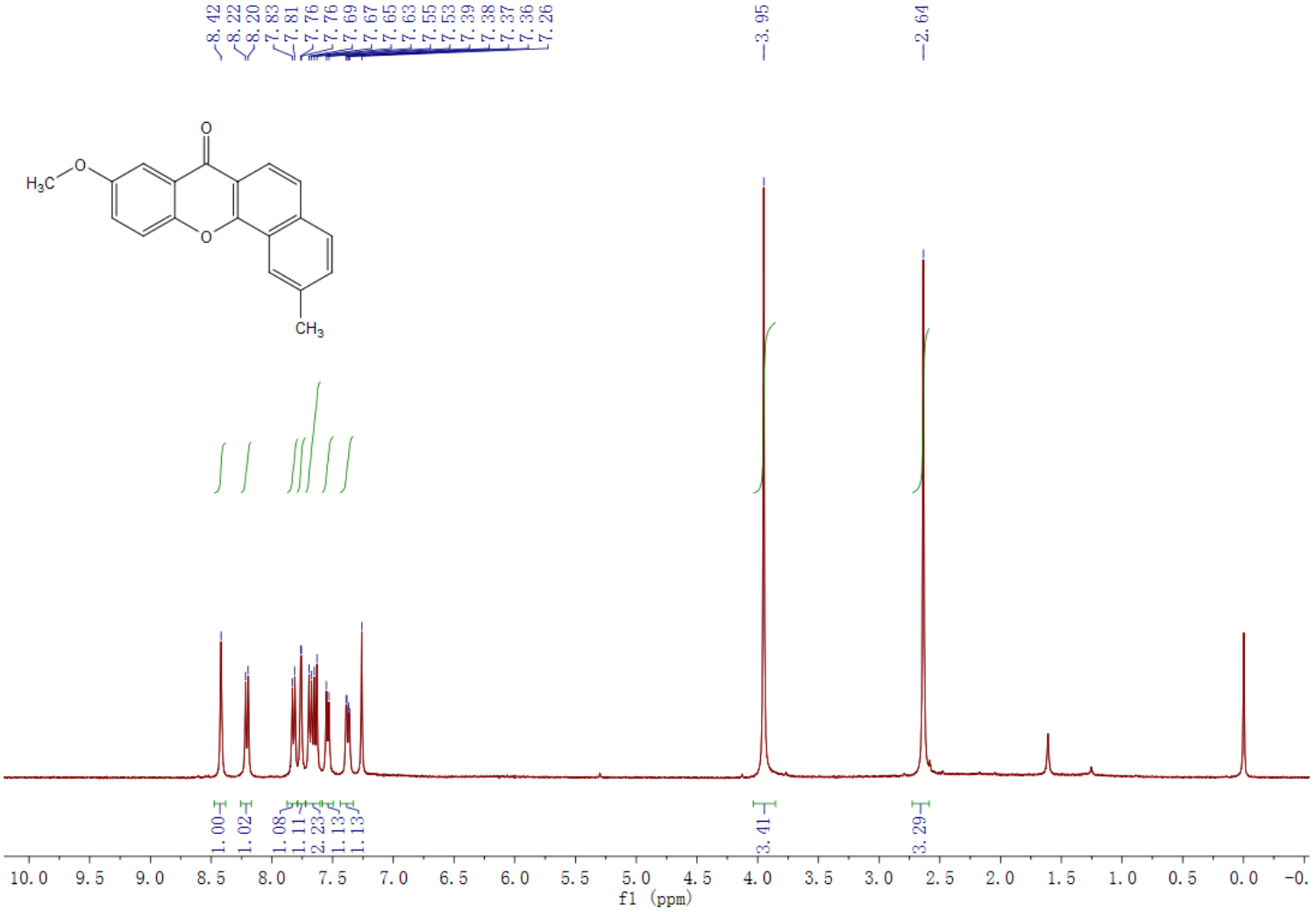
^{1}H NMR Spectra of 4p



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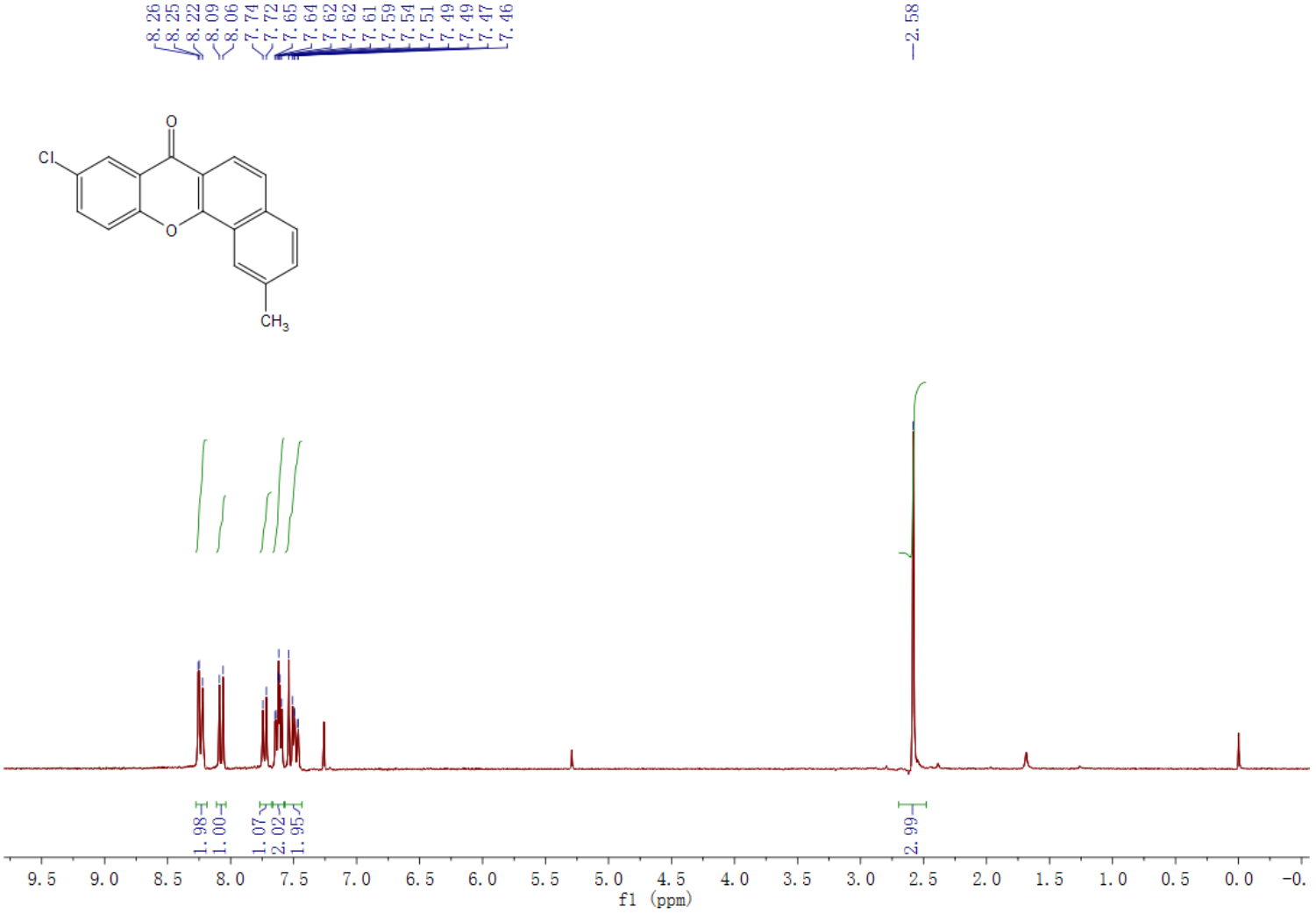
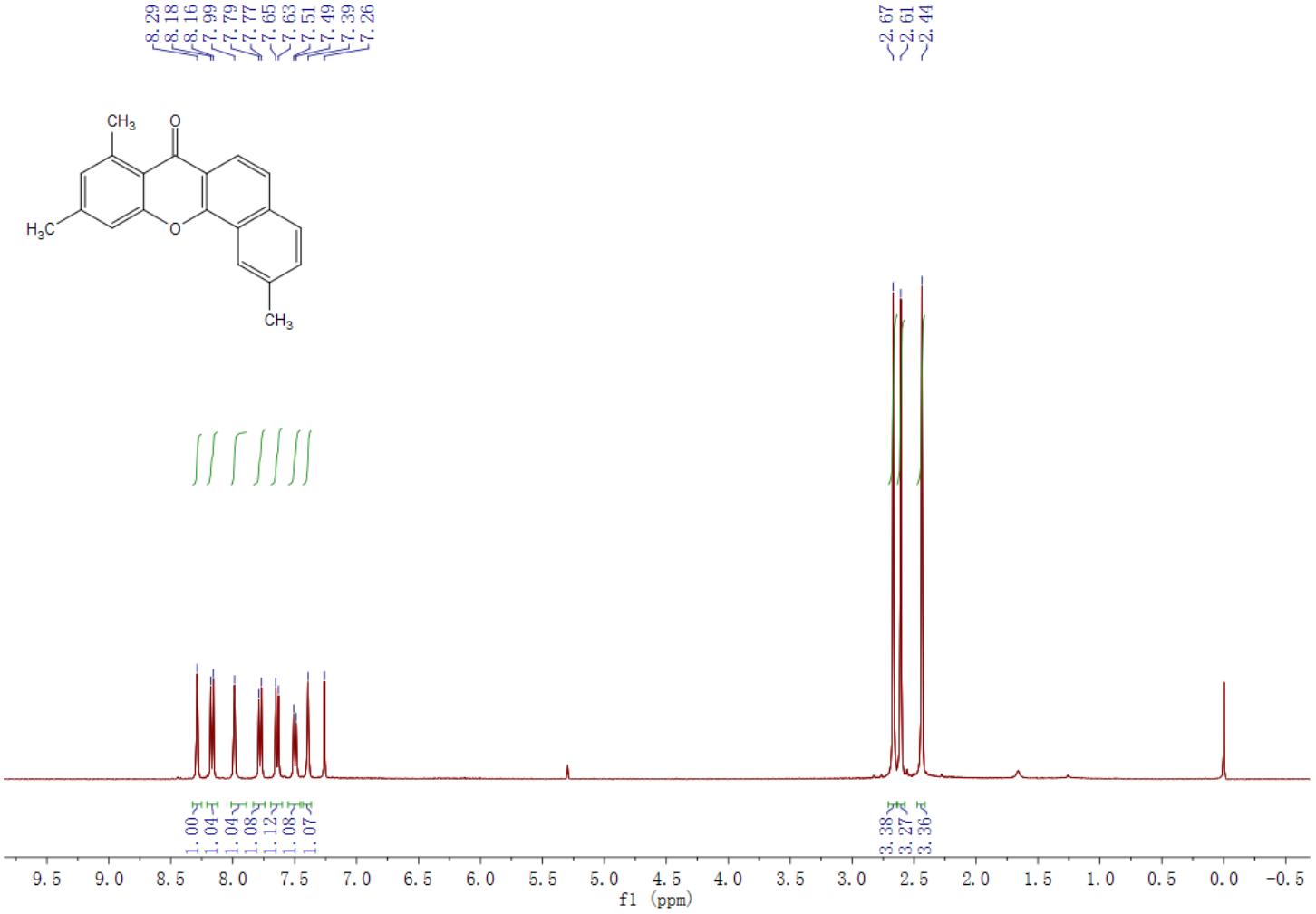
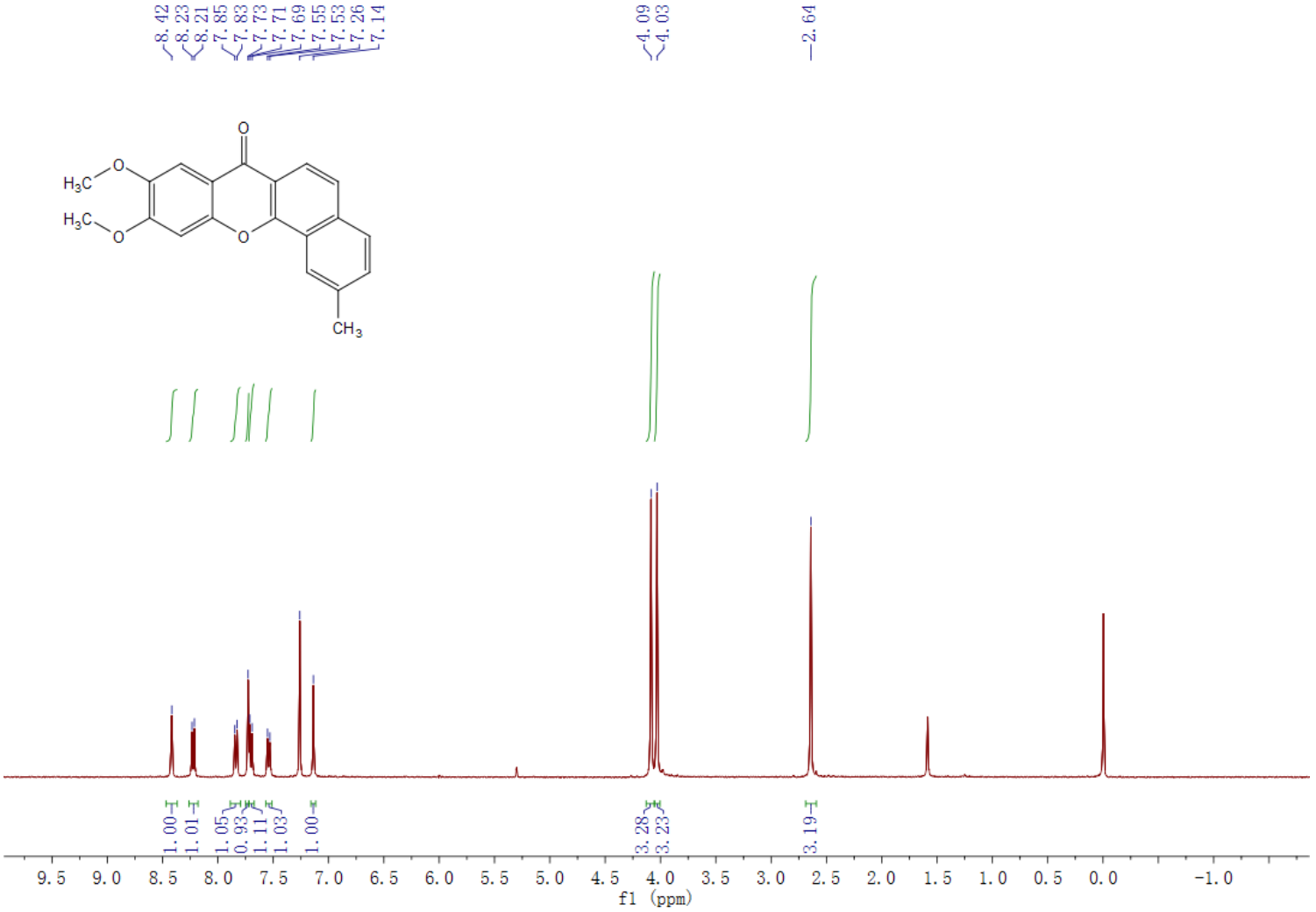
^{1}H NMR Spectra of 4q



^{1}H NMR Spectra of 4r



^{1}H NMR Spectra of 4s



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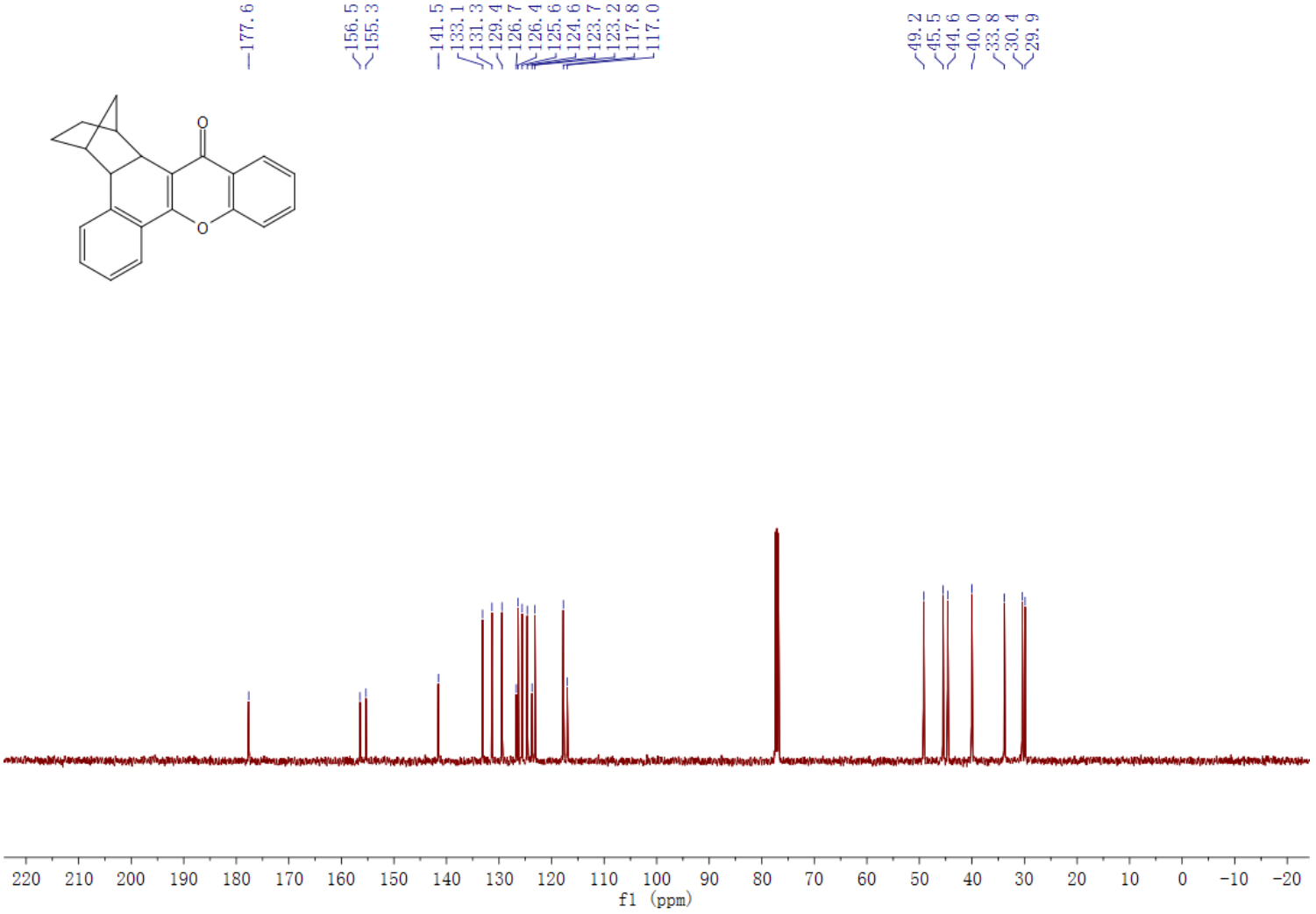
^{13}C NMR Spectra of 3a



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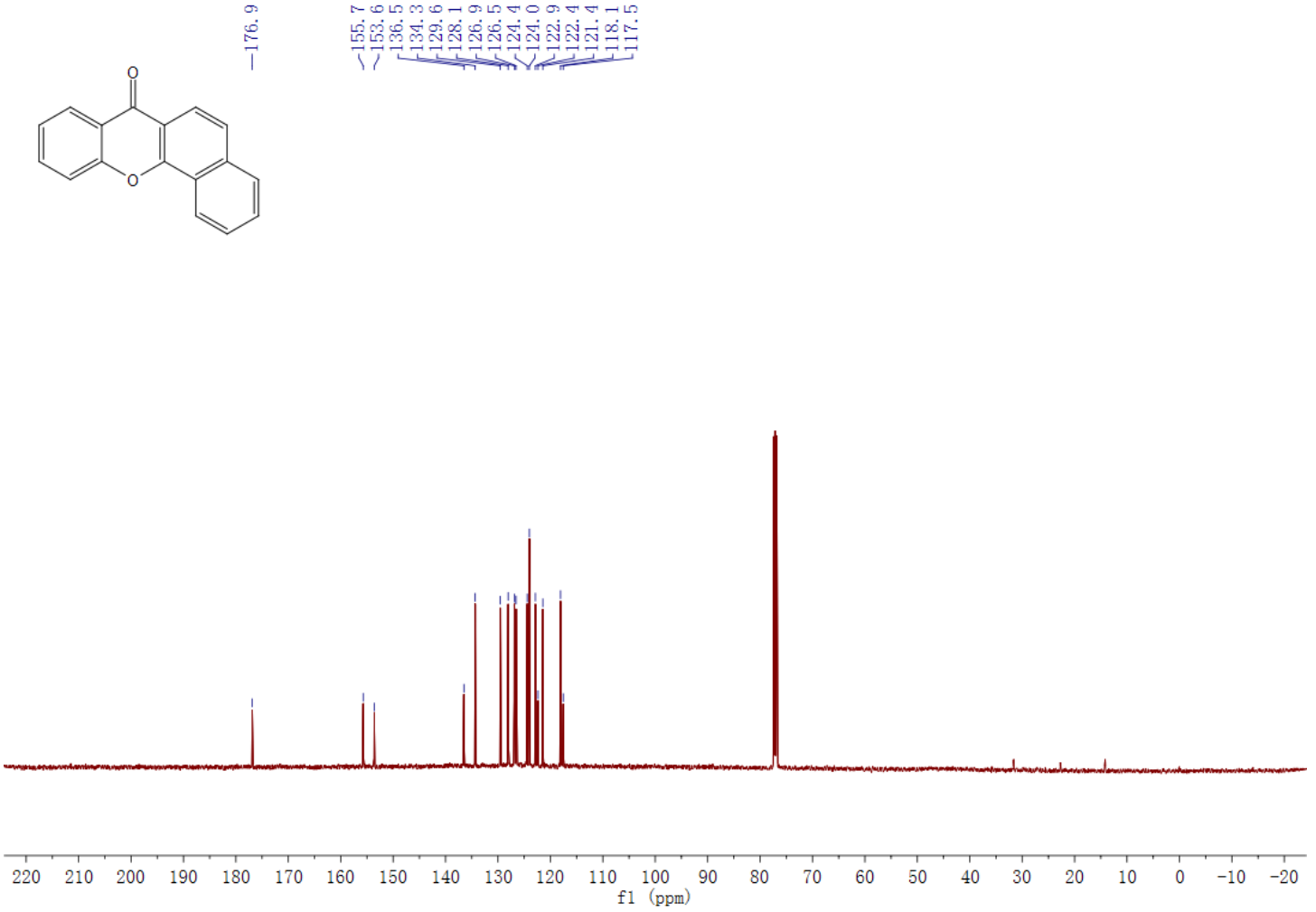
^{13}C NMR Spectra of 4a



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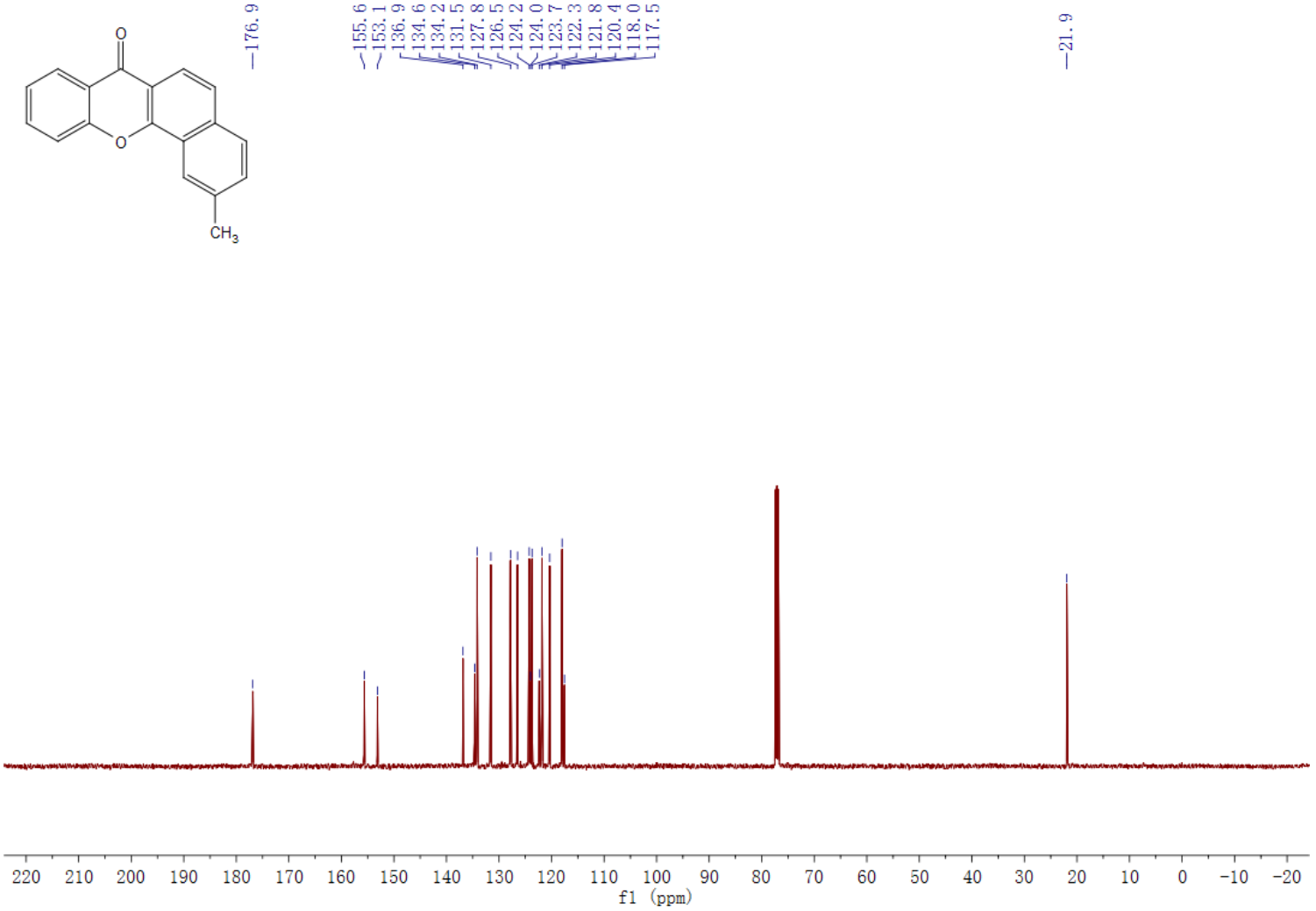
^{13}C NMR Spectra of 4b



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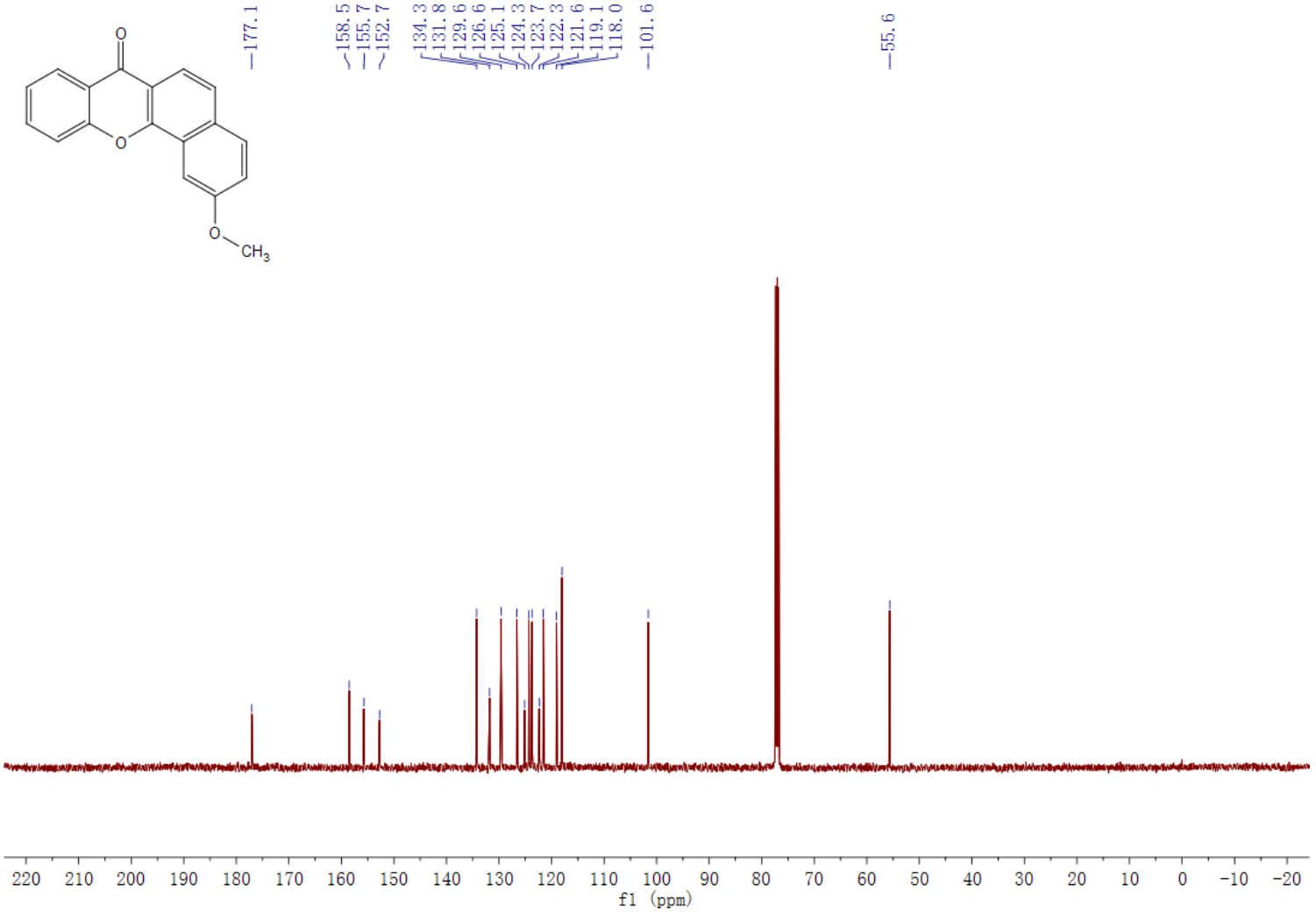
^{13}C NMR Spectra of 4c



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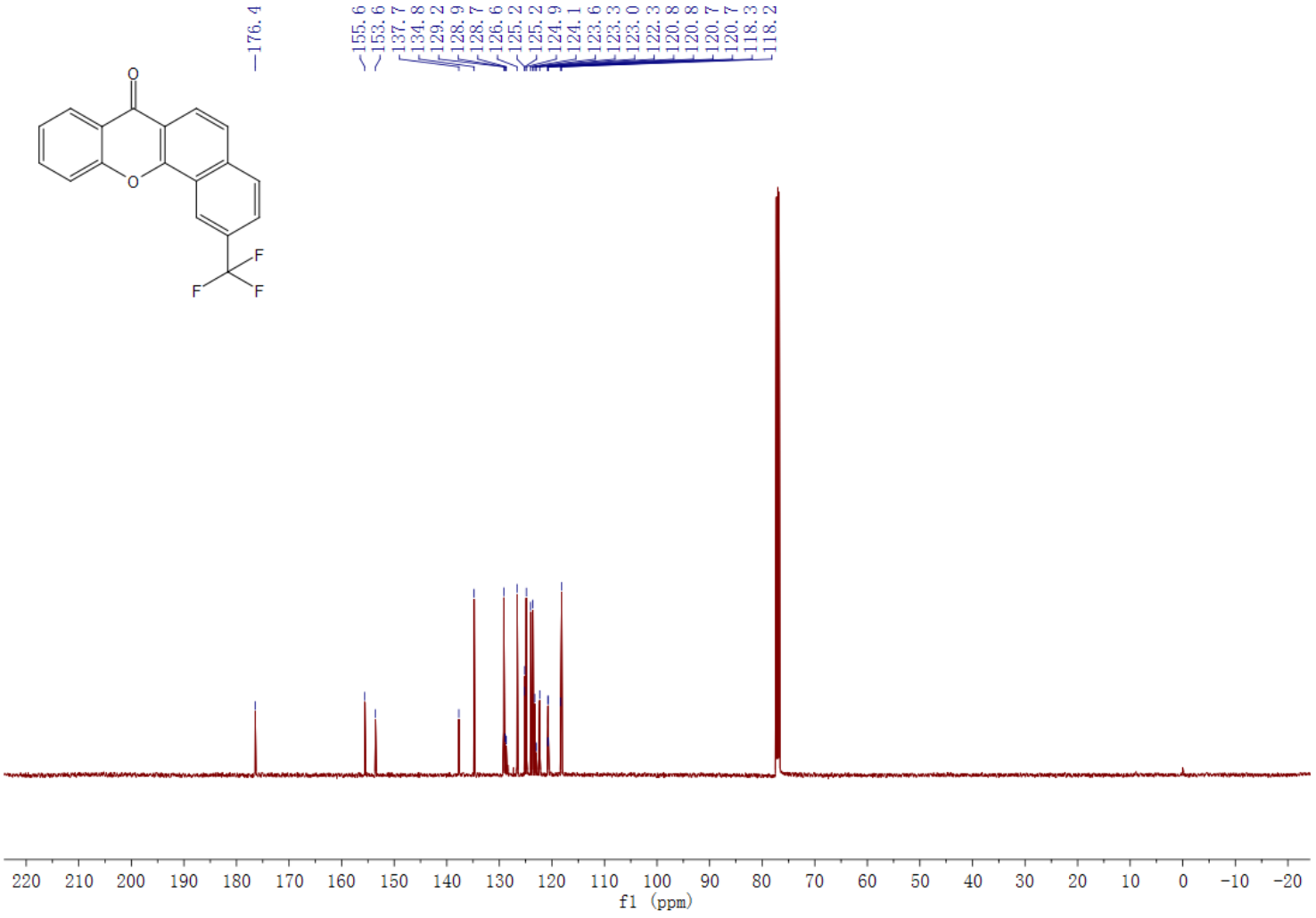
^{13}C NMR Spectra of 4d



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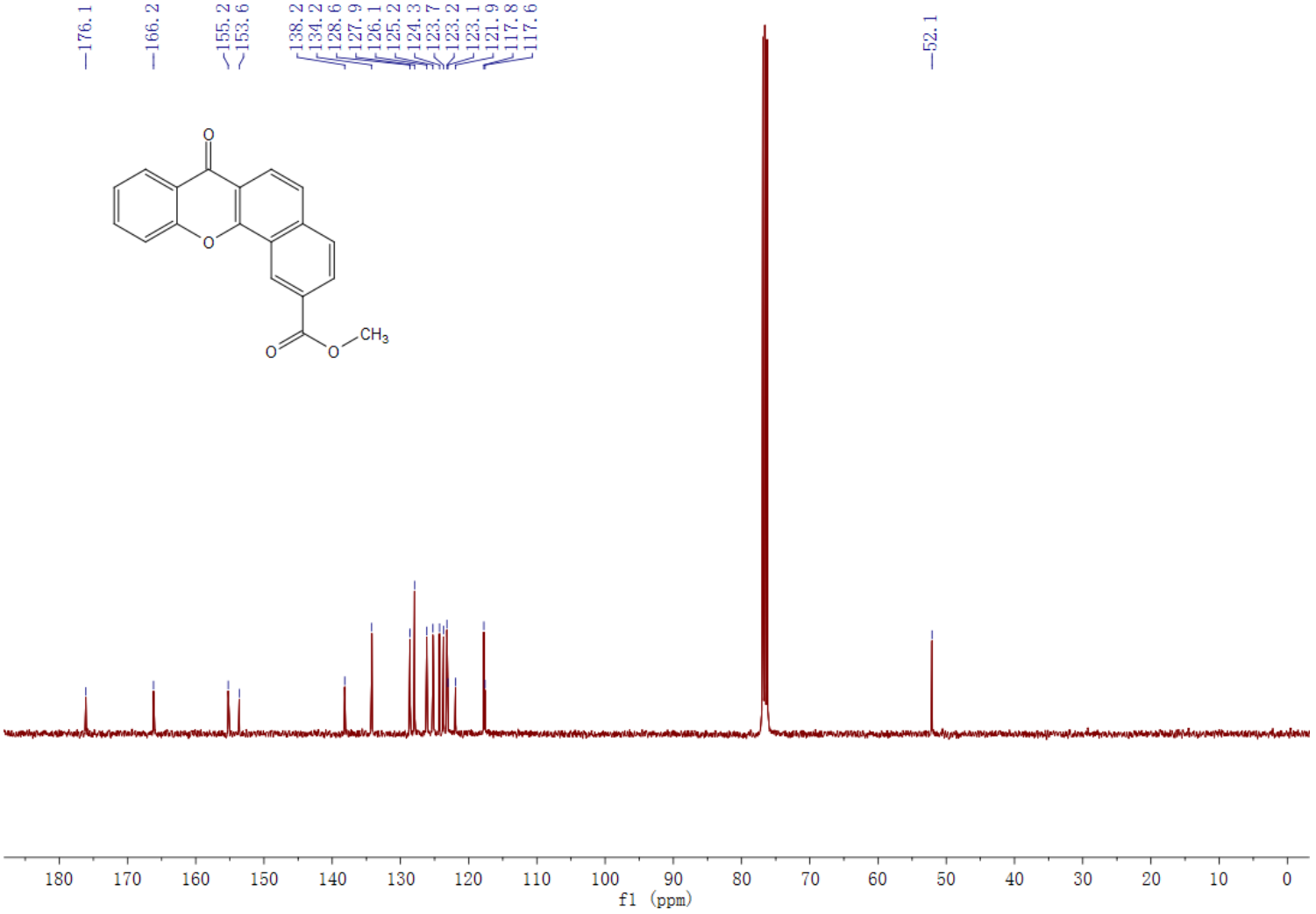
^{13}C NMR Spectra of 4e



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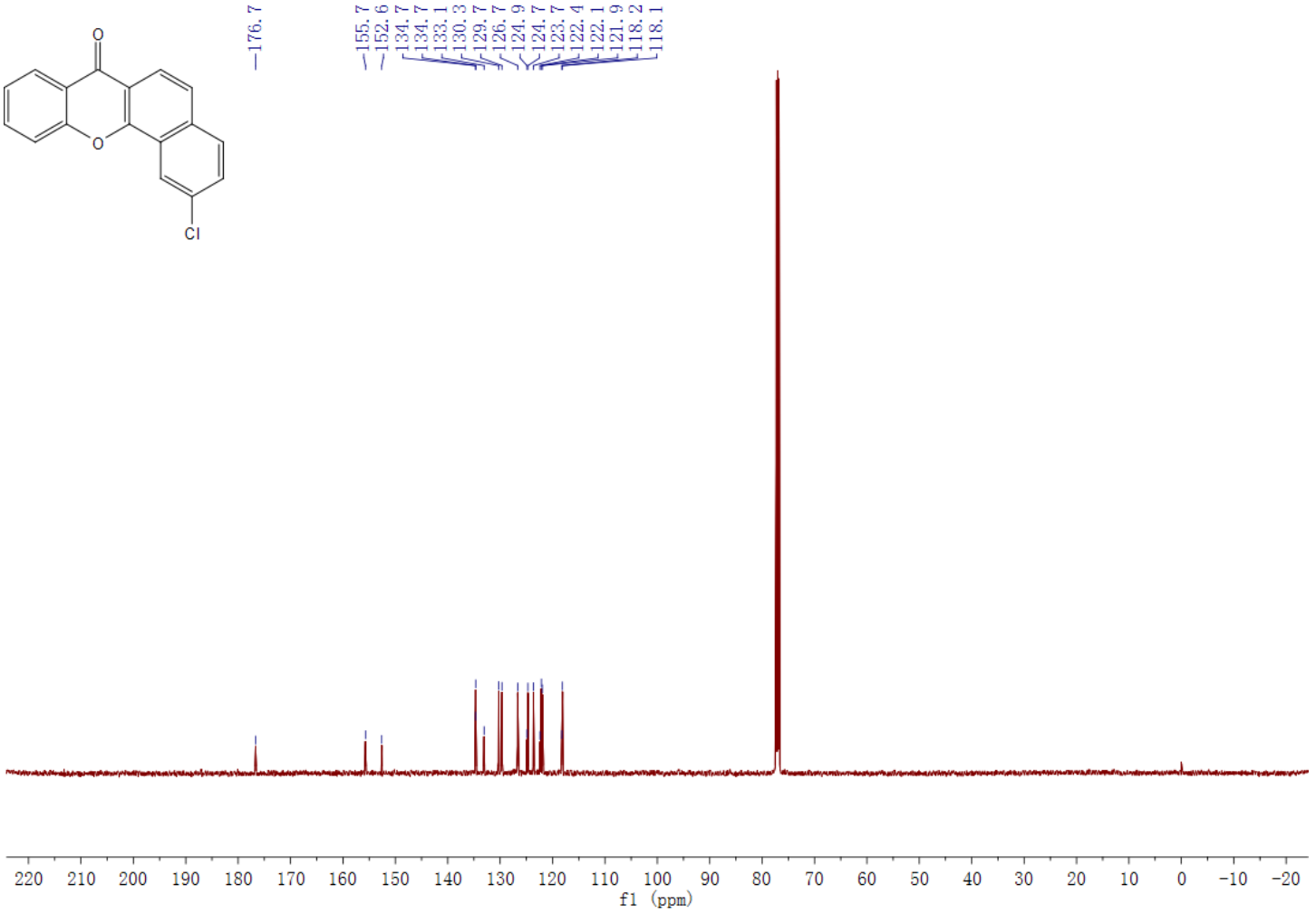
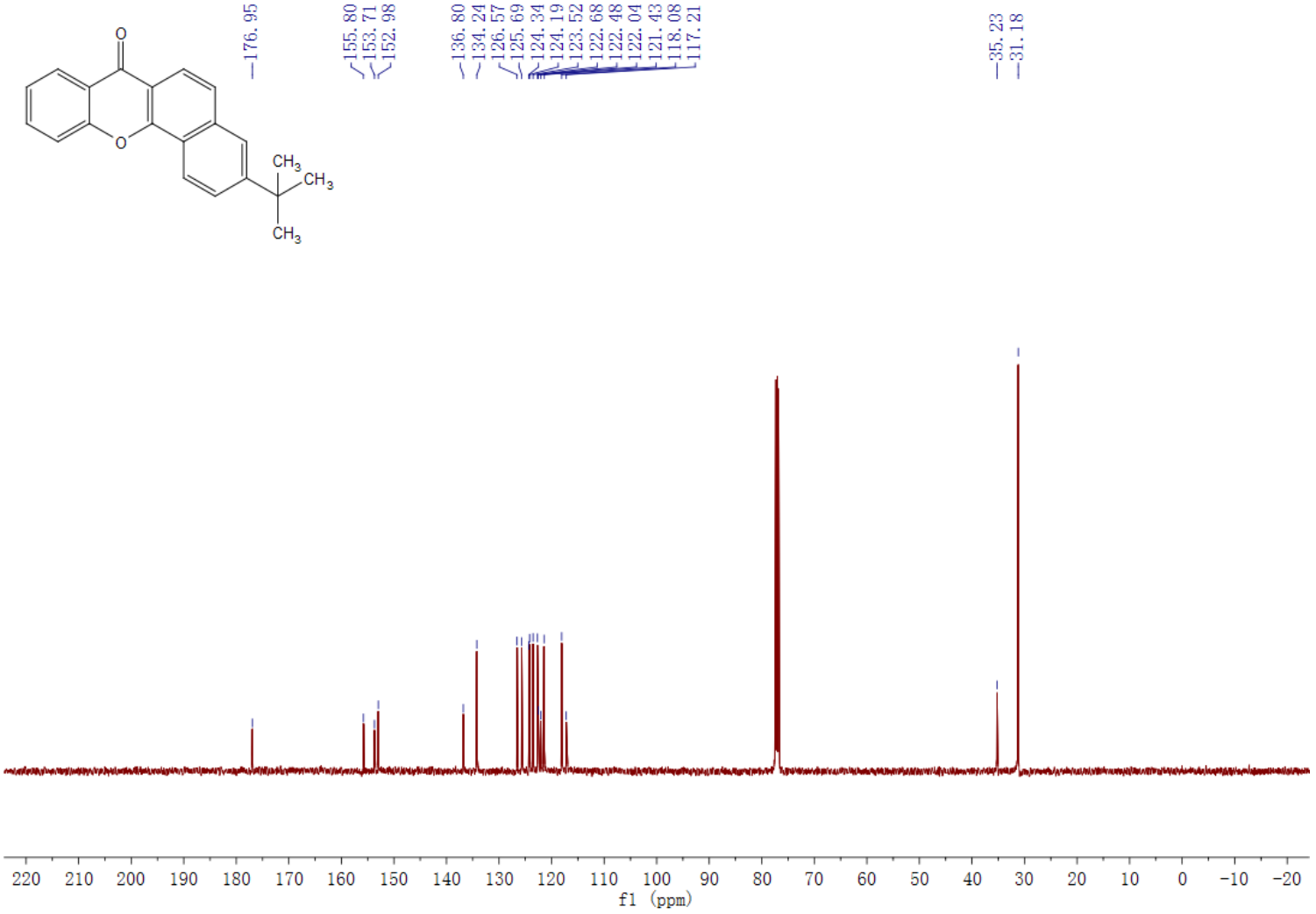
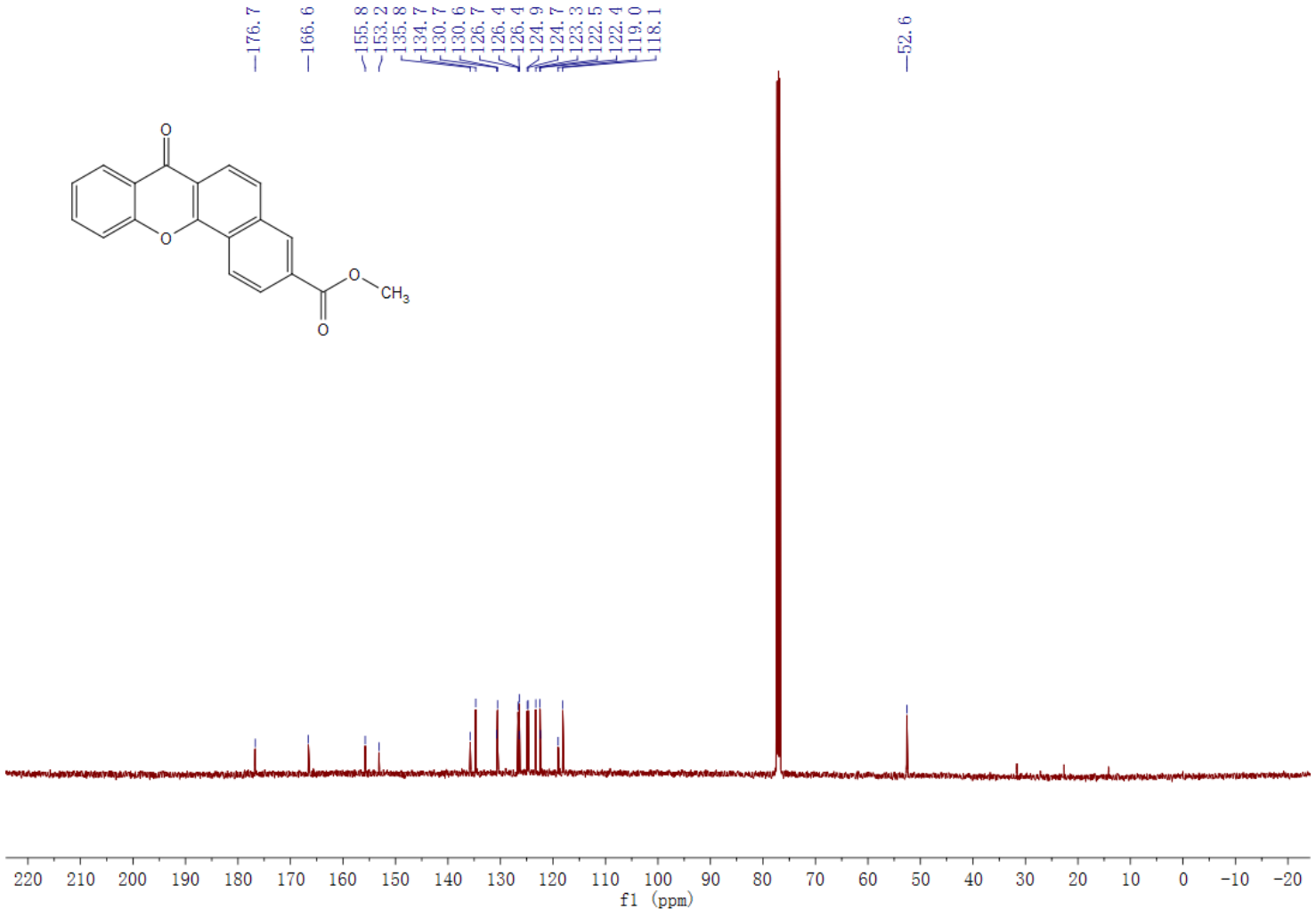
^{13}C NMR Spectra of 4f



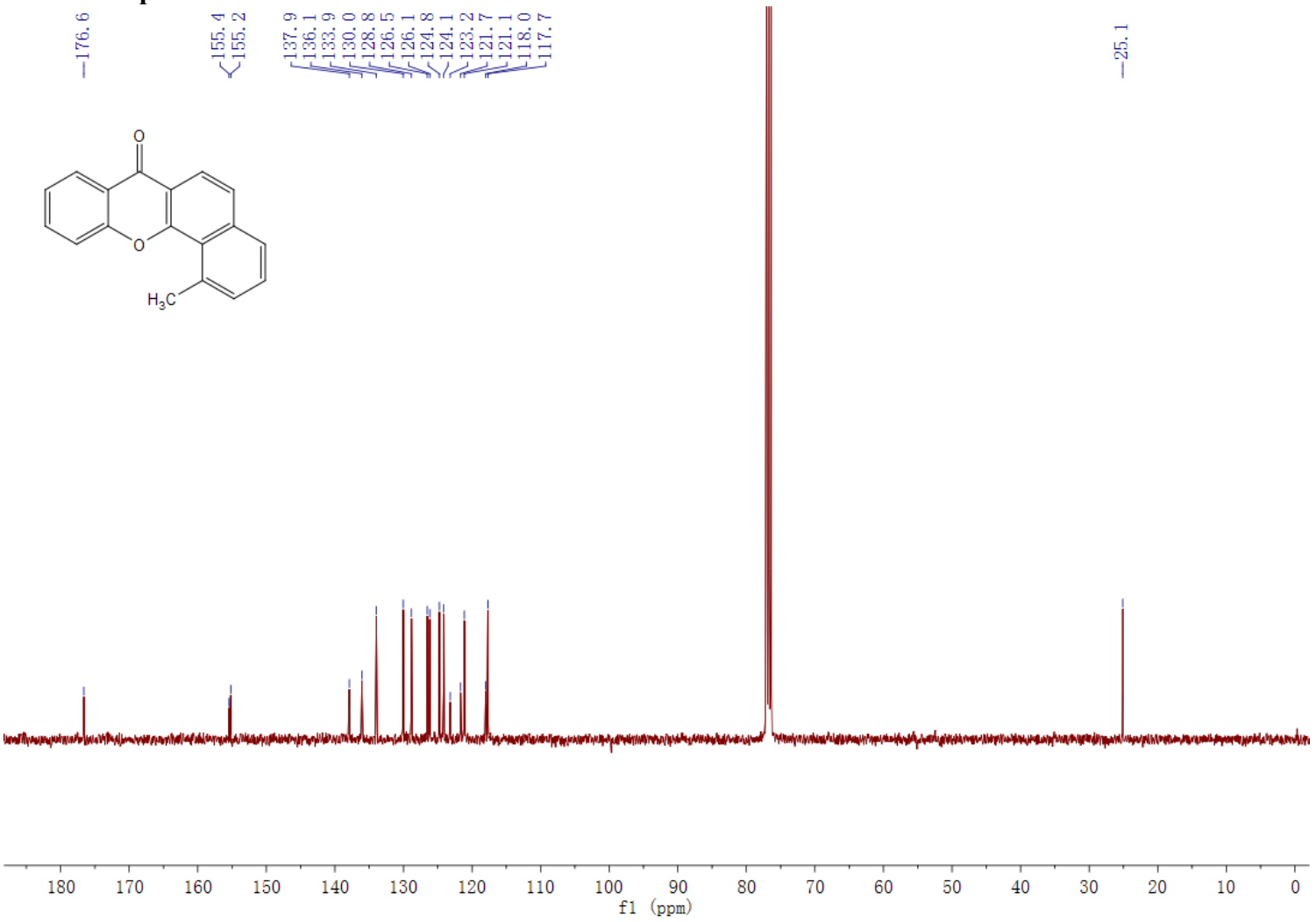
^{13}C NMR Spectra of 4g



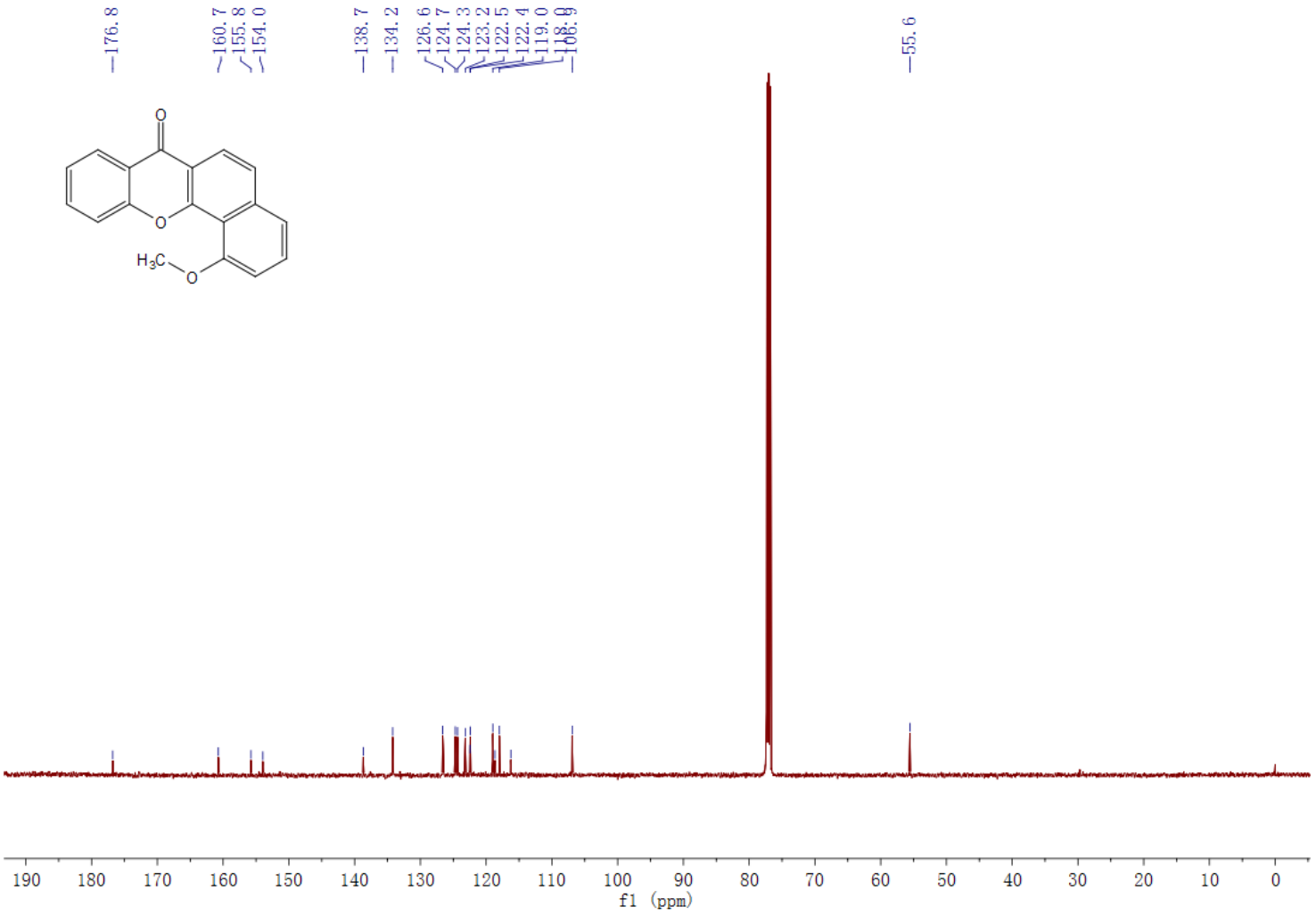
^{13}C NMR Spectra of 4h



^{13}C NMR Spectra of 4i



^{13}C NMR Spectra of 4j



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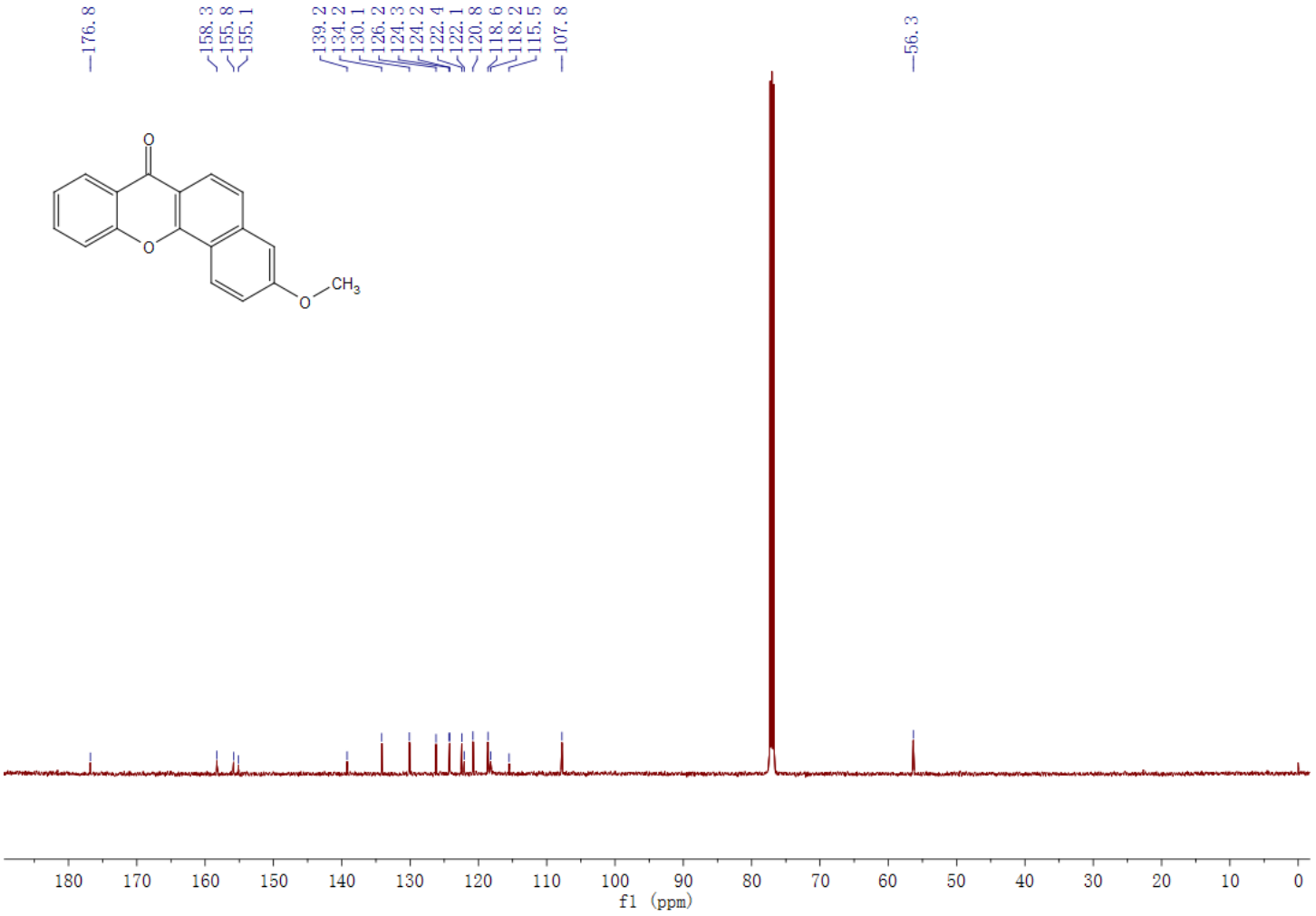
^{13}C NMR Spectra of 4j′



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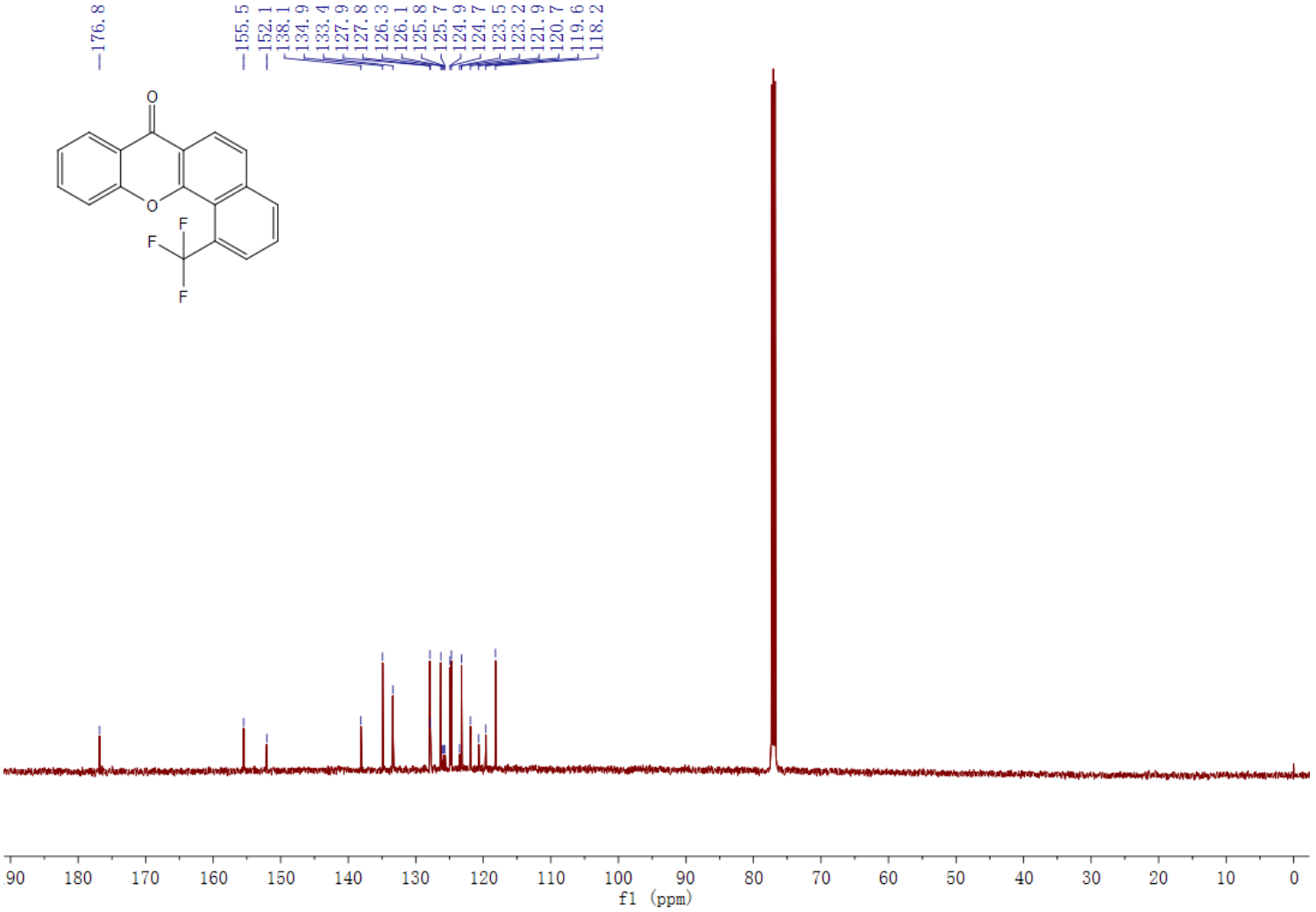
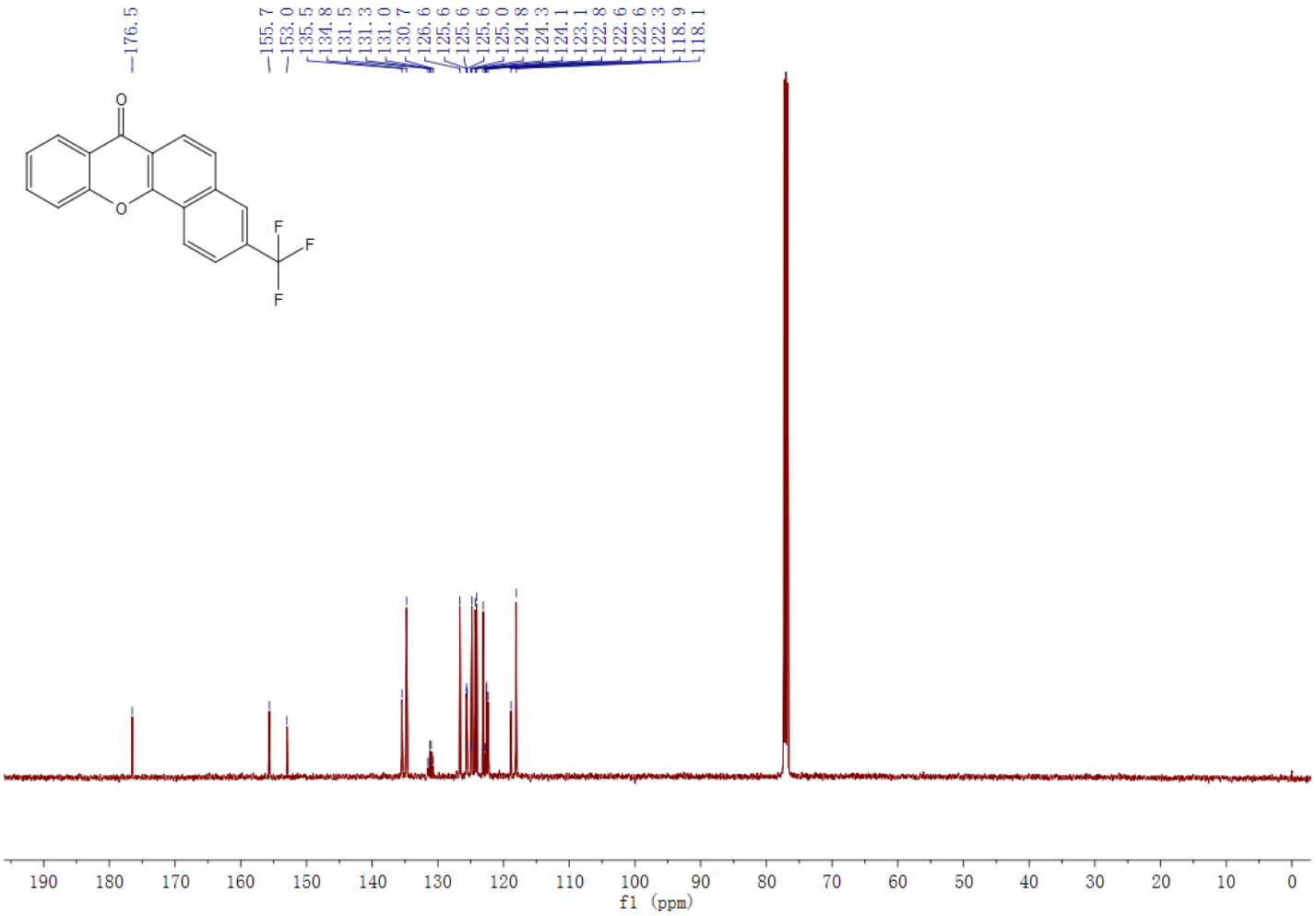
^{13}C NMR Spectra of 4k



^{13}C NMR Spectra of 4k′



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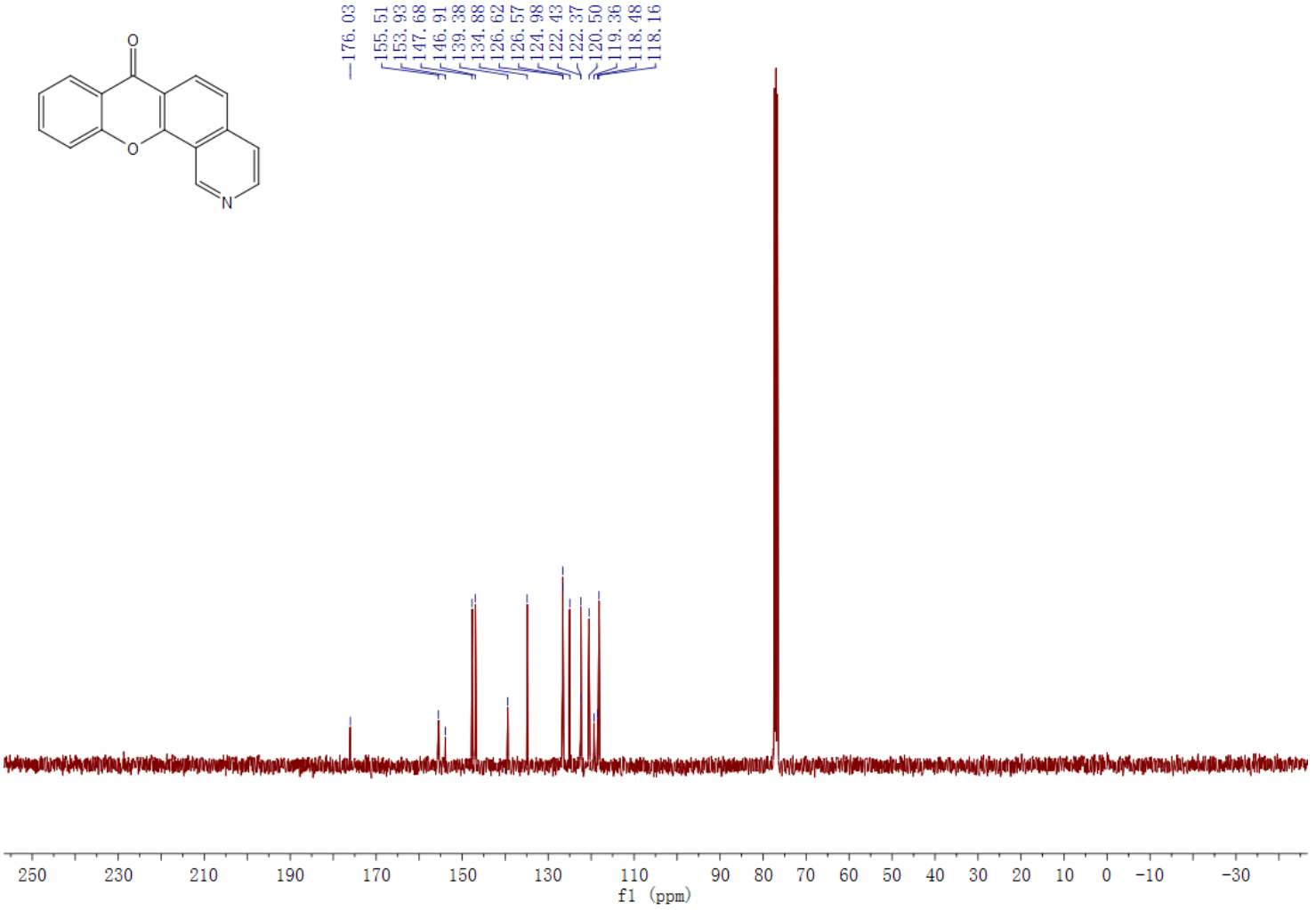
^{13}C NMR Spectra of 4l



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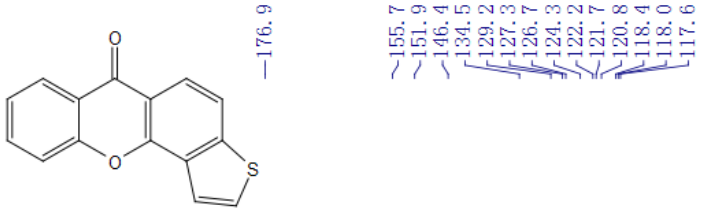
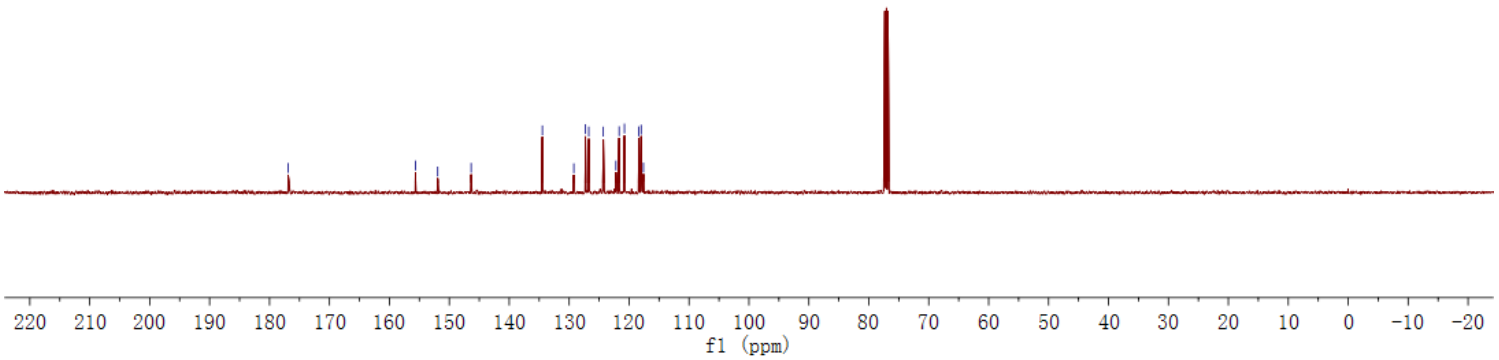
^{13}C NMR Spectra of 4m





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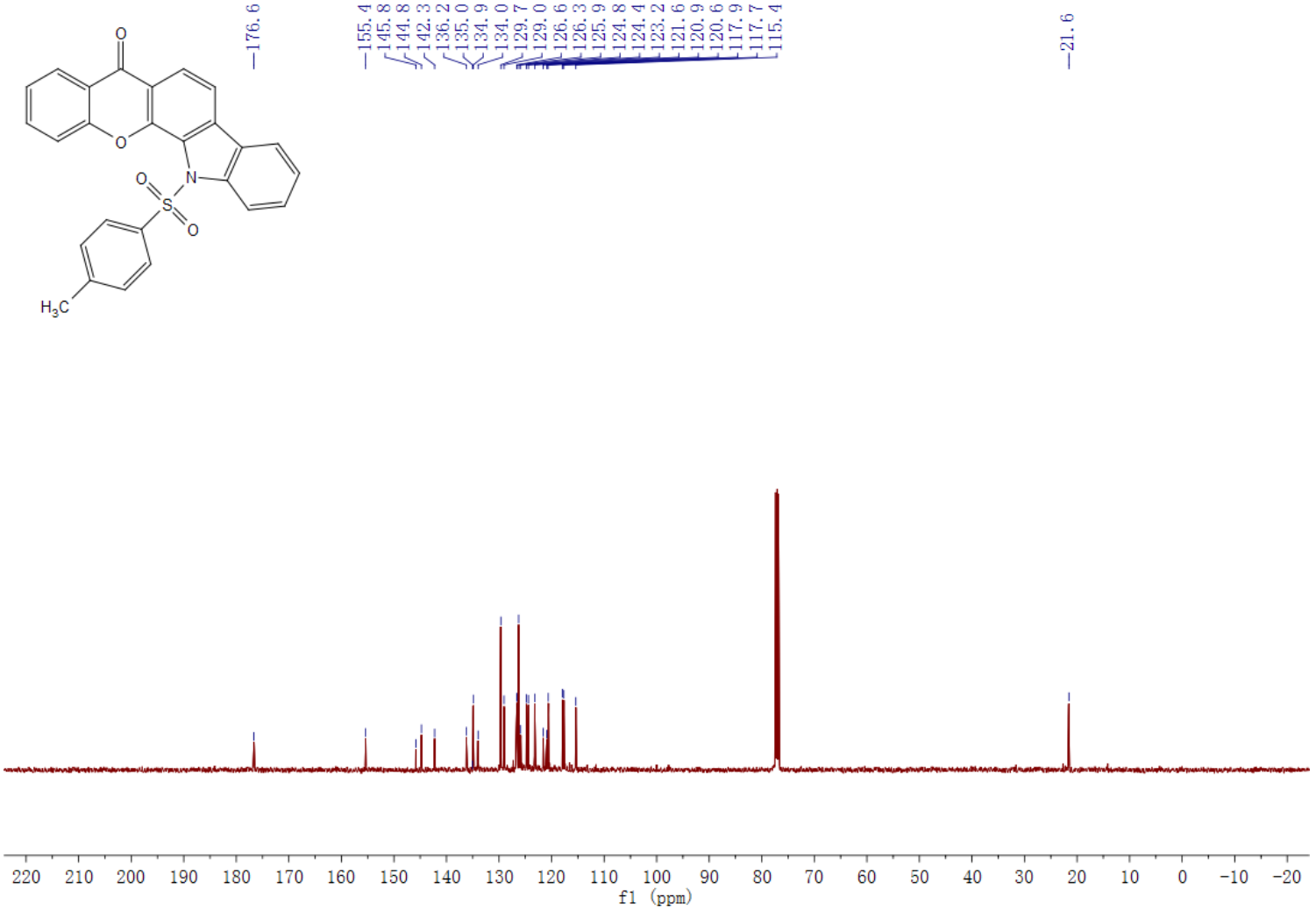
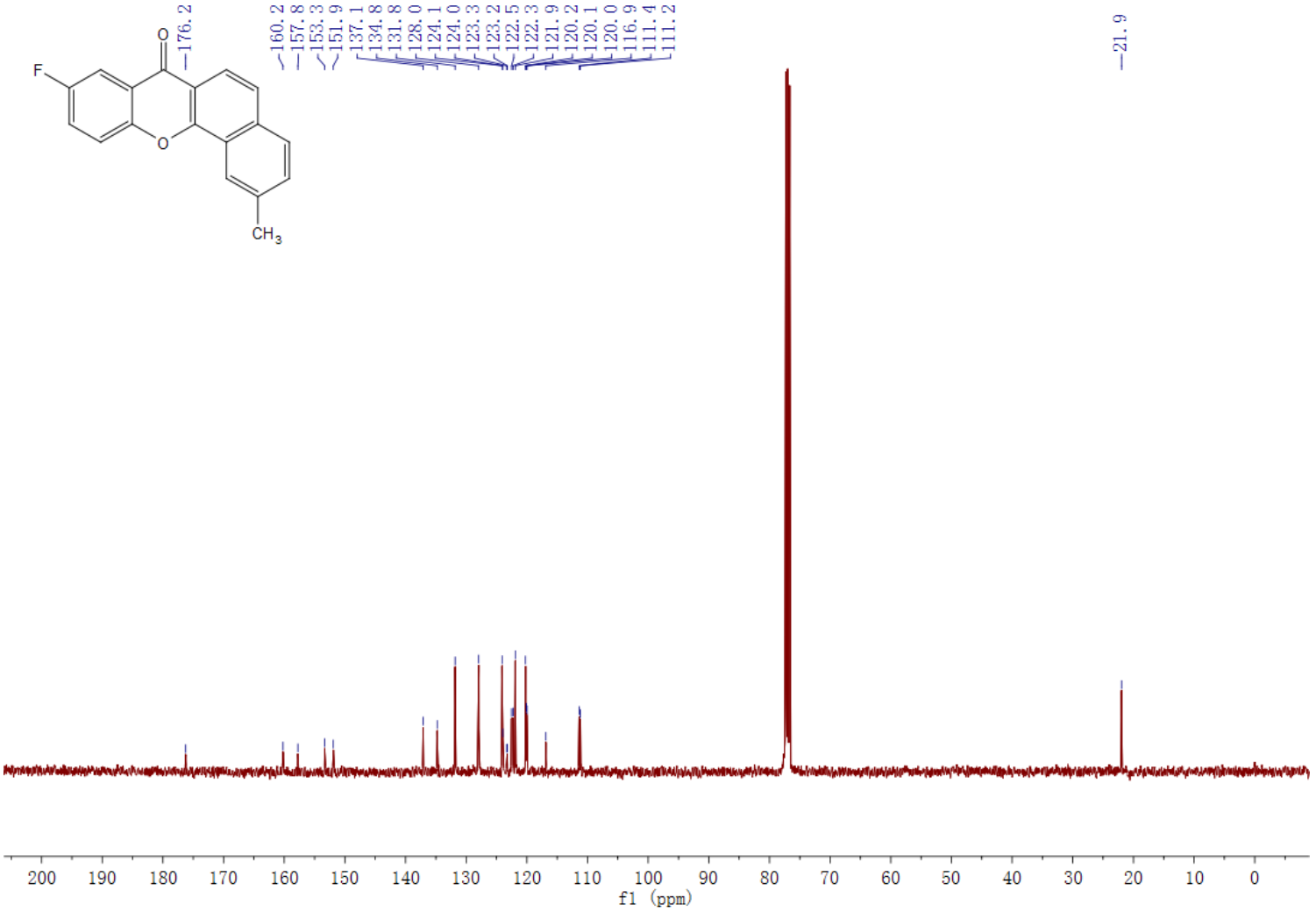
^{13}C NMR Spectra of 4n



^{13}C NMR Spectra of 4o



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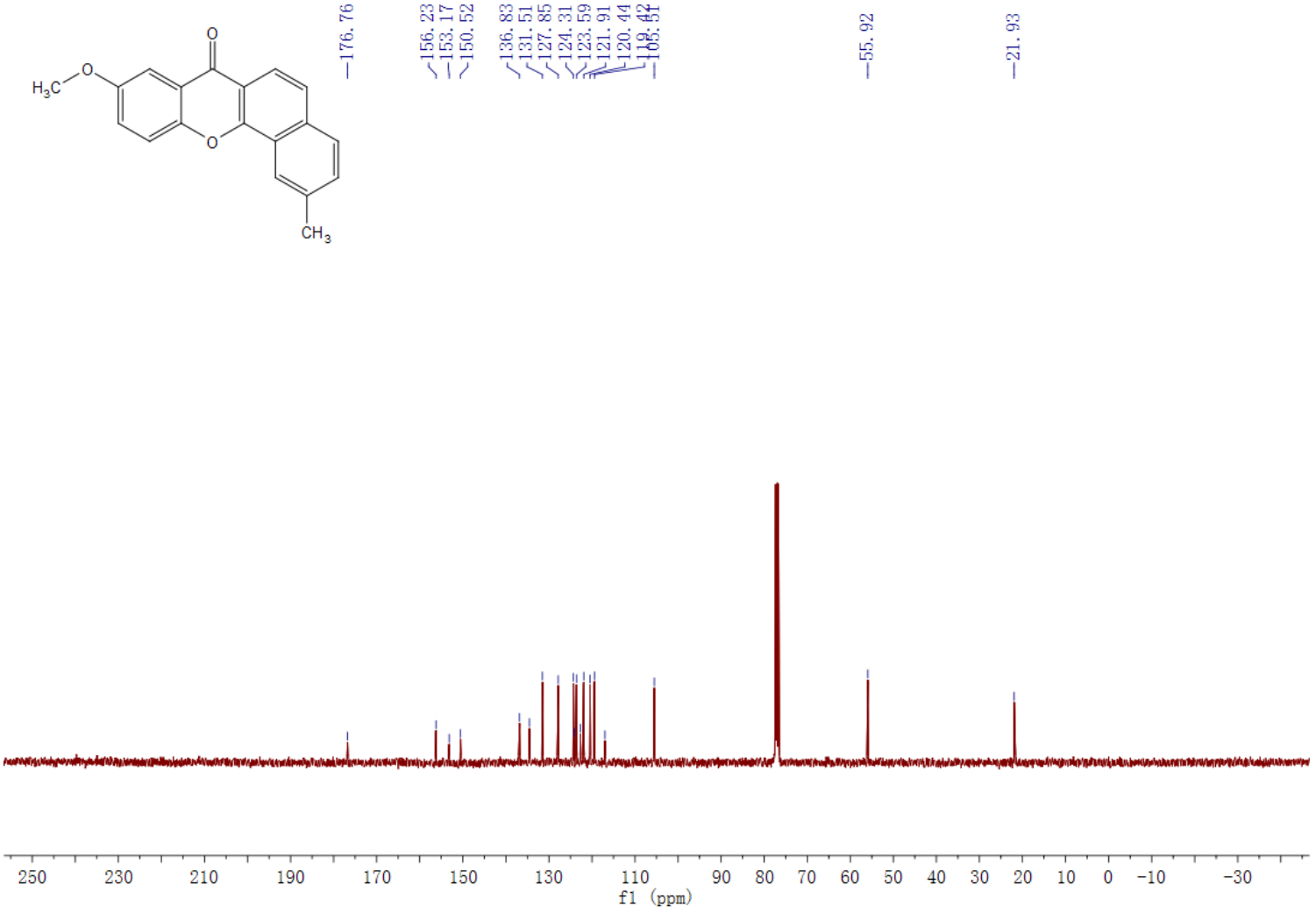
^{13}C NMR Spectra of 4p



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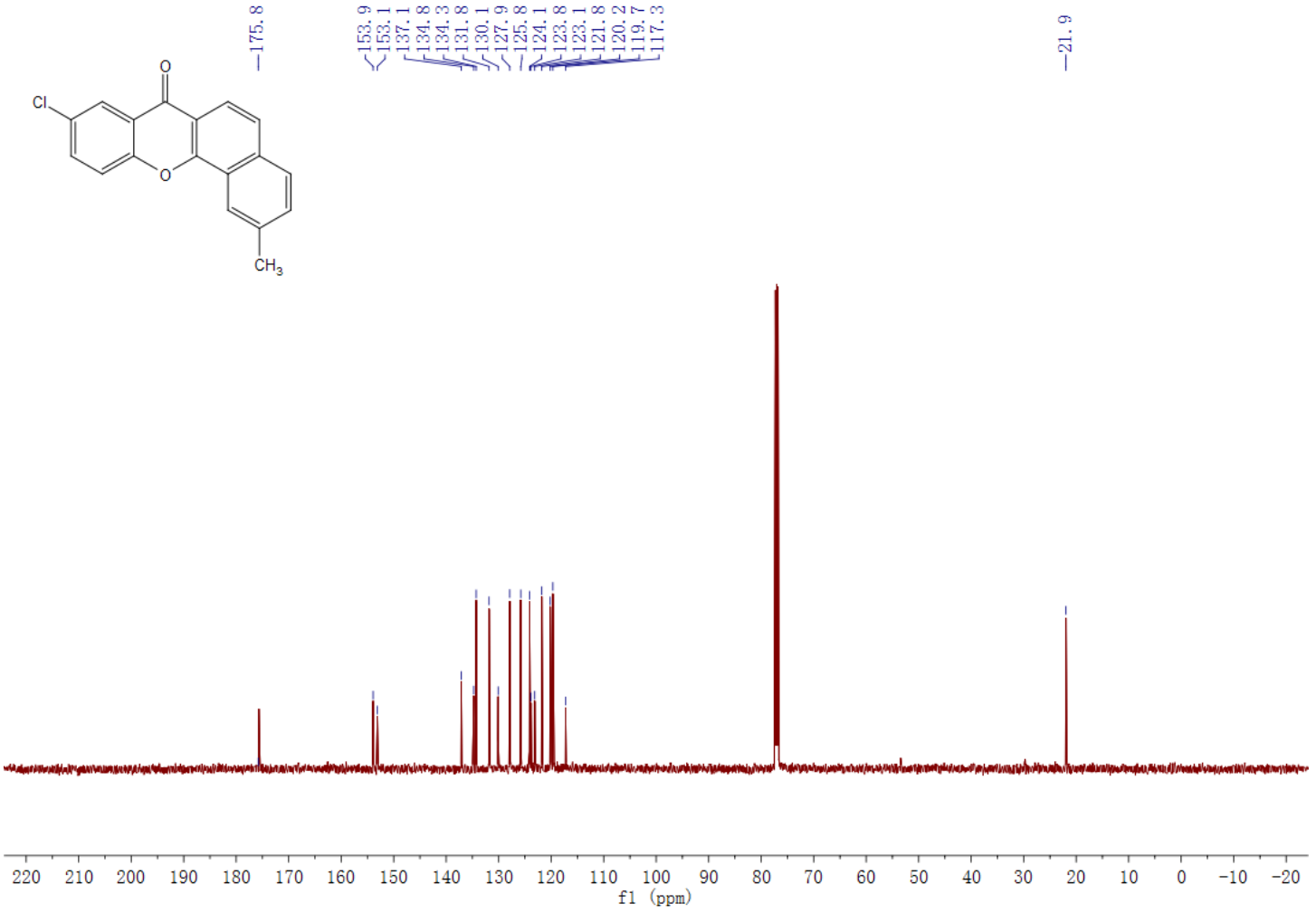
^{13}C NMR Spectra of 4q



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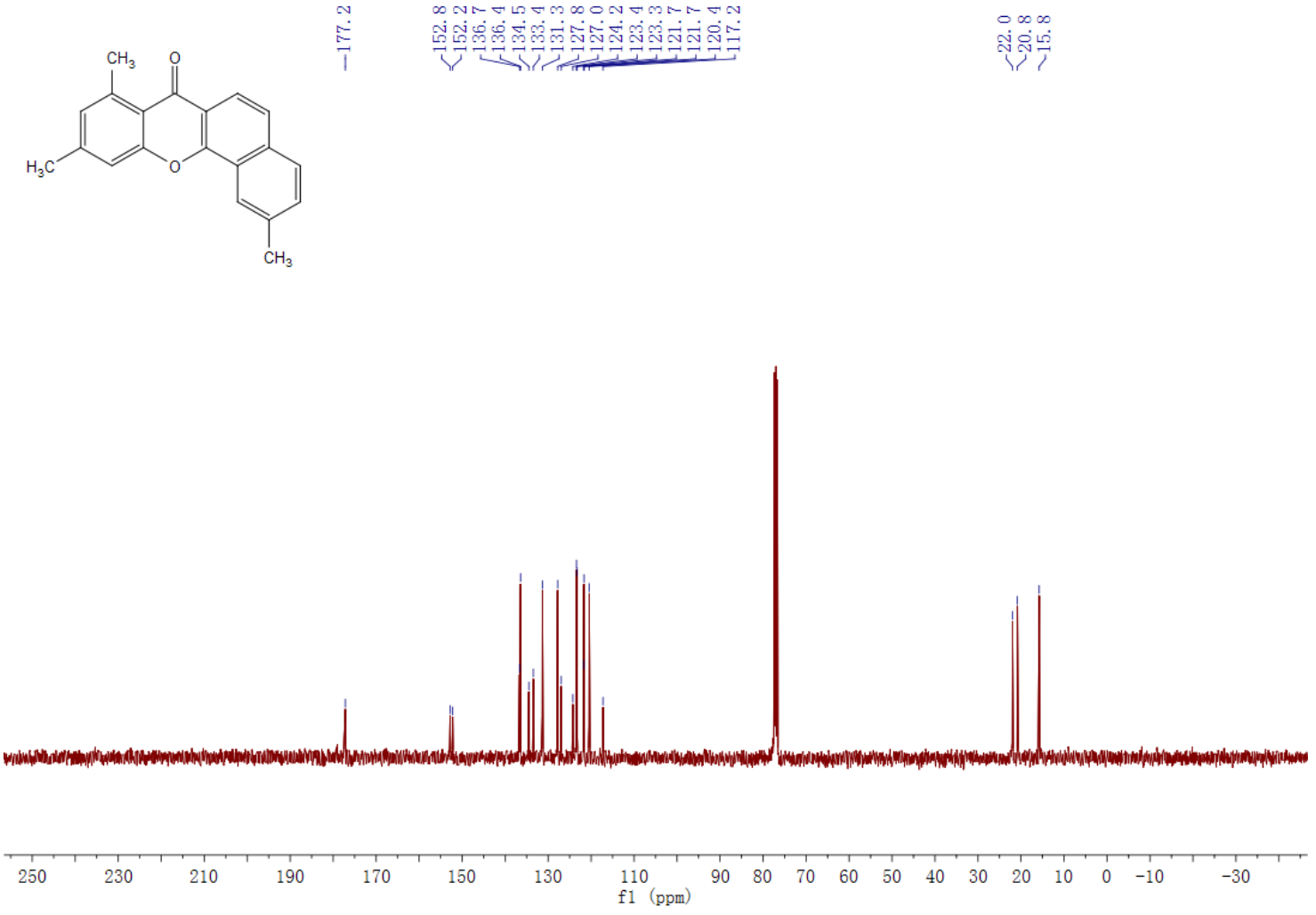
^{13}C NMR Spectra of 4r



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^{13}C NMR Spectra of 4s