CBr_4 Promoted Intramolecular Aerobic Oxidative Dehydrogenative Arylation of Aldehydes: Applied in the Synthesis of Xanthones and Fluorenones

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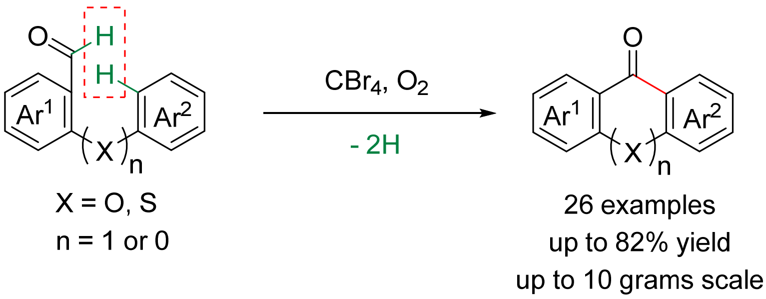


Supporting Information

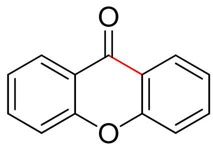
Table of Contents

Experimental Section

General procedure for the preparation of xanthones and fluorenones.

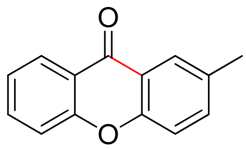
A mixture of **1** (1.0 mmol) and CBr_4 (1.2 mmol) was stirred at 140°C under oxygen atmosphere (O_2 balloon). The reactions were completed as monitored by TLC. Products **2** were isolated by silica gel column chromatography using petroleum ether/acetone (v/v 100:1 to 50:1).

Characterization of the products



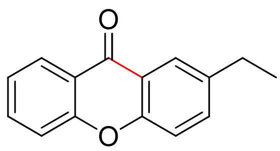
9H-xanthen-9-one (2a) [3]

The desired pure product was obtained in 60% yield (118 mg) as a white solid, mp 177-178°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.76 – 7.68 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.33 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 156.1, 134.8, 126.7, 123.9, 121.8, 117.9.



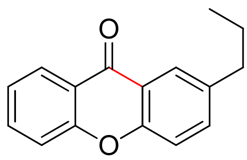
2-methyl-9H-xanthen-9-one (2b) [3]

The desired pure product was obtained in 65% yield (137 mg) as a white solid, mp 124-125°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.9 Hz, 1H), 8.11 (s, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.36 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.1, 156.1, 154.3, 136.0, 134.5, 133.6, 126.6, 125.9, 123.6, 121.7, 121.4, 117.9, 117.7, 20.8.



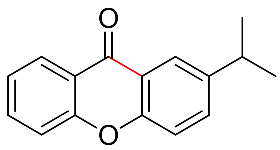
2-ethyl-9H-xanthen-9-one (2c)[4]

The desired pure product was obtained in 43% yield (97 mg) as a white solid, mp 71-72°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.9 Hz, 1H), 8.15 (s, 1H), 7.73 – 7.67 (m, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.41 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.36 (m, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.34 – 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 156.2, 154.5, 140.0, 135.0, 134.6, 126.7, 124.8, 123.7, 121.8, 121.5, 117.9, 117.8, 28.3, 15.5.



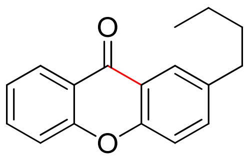
2-propyl-9H-xanthen-9-one (2d)

The desired pure product was obtained in 48% yield (115 mg) as a white solid, mp 74-75°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.9 Hz, 1H), 8.12 (s, 1H), 7.70 (m, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.75 – 1.66 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 156.2, 154.6, 138.5, 135.5, 134.6, 126.7, 125.5, 123.7, 121.8, 121.5, 117.9, 117.7, 37.3, 24.4, 13.7. HRMS (ESI) exact mass calcd for $C_{16}H_{15}O_2$ [M+H] m/z 239.1072, found 239.1068.



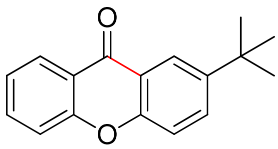
2-isopropyl-9H-xanthen-9-one (2e)

The desired pure product was obtained in 42% yield (101 mg) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.19 (d, *J* = 2.1 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.62 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 3.10 – 3.02 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 156.2, 154.6, 144.7, 134.6, 133.7, 126.7, 123.7, 123.4, 121.8, 121.5, 117.9, 117.8, 33.7, 24.0. HRMS (ESI) exact mass calcd for $C_{16}H_{15}O_2$ [M+H] m/z 239.1072, found 239.1077.



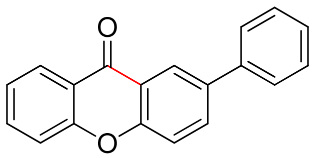
2-butyl-9H-xanthen-9-one (2f)

The desired pure product was obtained in 53% yield (134 mg) as a white solid, mp 60-62°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.13 (d, *J* = 1.7 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.54 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 2.73 (t, *J* = 7.8 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.41 – 1.33 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 156.2, 154.5, 138.7, 135.5, 134.6, 126.7, 125.4, 123.7, 121.8, 121.5, 117.9, 117.7, 34.9, 33.5, 22.2, 13.9. HRMS (ESI) exact mass calcd for $C_{17}H_{17}O_2$ [M+H] m/z 253.1229, found 253.1233.



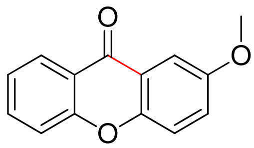
2-(tert-butyl)-9H-xanthen-9-one (2g) [3]

The desired pure product was obtained in 73% yield (184 mg) as a white solid, mp 114-115°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.32 (d, *J* = 2.5 Hz, 1H), 7.78 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.70 (m, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.38 – 7.34 (m, 1H), 1.40 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 156.1, 154.3, 147.0, 134.6, 132.7, 126.7, 123.7, 122.4, 121.8, 121.1, 117.9, 117.6, 34.7, 31.3.



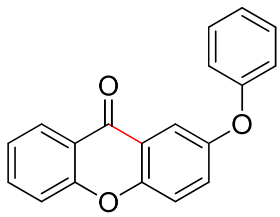
2-phenyl-9H-xanthen-9-one (2h) [3]

The desired pure product was obtained in 80% yield (219 mg) as a white solid, mp 158-160°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.37 (d, *J* = 7.9 Hz, 1H), 7.99 – 7.94 (m, 1H), 7.73 (m, 1H), 7.68 (d, J = 7.9 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.53 – 7.45 (m, 3H), 7.41 – 7.37 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 156.1, 155.5, 139.4, 137.0, 134.8, 133.6, 129.0, 127.7, 127.1, 126.8, 124.5, 124.0, 121.9, 121.8, 118.5, 118.0.



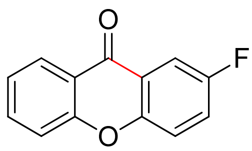
2-methoxy-9H-xanthen-9-one (2i) [3]

The desired pure product was obtained in 38% yield (86 mg) as a white solid, mp 132-133°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (dd, J = 8.0, 1.5 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.49 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 9.1 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.33 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.1, 156.1, 156.0, 151.0, 134.6, 126.7, 124.9, 123.7, 122.1, 121.2, 119.4, 117.9, 105.8, 55.9.



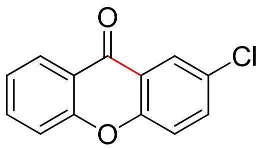
2-phenoxy-9H-xanthen-9-one (2j) [3]

The desired pure product was obtained in 35% yield (101 mg) as a white solid, mp 75-76°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 2.4 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.51 (t, J = 8.2 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.38 (m, 3H), 7.15 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 8.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 156.9, 156.1, 153.6, 152.1, 134.8, 132.9, 130.0, 126.8, 126.7, 123.9, 123.8, 122.5, 121.2, 120.6, 119.7, 119.0, 117.9, 114.1.



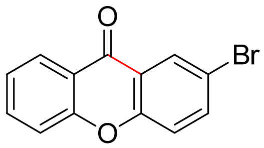
2-fluoro-9H-xanthen-9-one (2k) [1]

The desired pure product was obtained in 62% yield (133 mg) as a white solid, mp 136-138°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.95 (dd, *J* = 8.2, 3.1 Hz, 1H), 7.73 (m, 1H), 7.51 – 7.46 (m, 2H), 7.44 (m, 1H), 7.40 – 7.36 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 176.5, 159.5, 157.9, 156.1, 152.3, 152.3, 135.1, 126.7, 124.1, 123.0, 122.8, 121.0, 120.0, 119.9, 118.0, 111.5, 111.3.



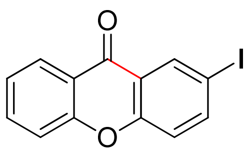
2-chloro-9H-xanthen-9-one (2l) [1]

The desired pure product was obtained in 67% yield (155 mg) as a white solid, mp 175-176°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.27 (d, *J* = 2.6 Hz, 1H), 7.73 (m, 1H), 7.64 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.49 – 7.46 (d, *J* = 8.4, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.41 – 7.36 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 156.0, 154.4, 135.1, 134.9, 129.7, 126.8, 126.0, 124.2, 122.7, 121.4, 119.7, 118.0.



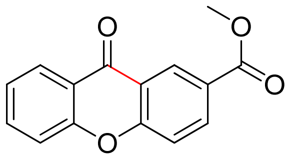
2-bromo-9H-xanthen-9-one (2m) [2]

The desired pure product was obtained in 52% yield (143 mg) as a white solid, mp 154-155°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.3 Hz, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.73 (m, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 156.0, 154.9, 137.6, 135.2, 129.2, 126.8, 124.3, 123.1, 121.5, 120.0, 118.0, 117.0.



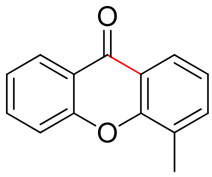
2-iodo-9H-xanthen-9-one (2n)[5]

The desired pure product was obtained in 50% yield (162 mg) as a white solid, mp 140-142℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, J = 2.2 Hz, 1H), 8.30 (dd, J = 7.9, 1.5 Hz, 1H), 7.95 (dd, J = 8.8, 2.2 Hz, 1H), 7.73 (m, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.25 (d, J = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 156.0, 155.6, 143.2, 135.5, 135.1, 126.8, 124.2, 123.5, 121.6, 120.1, 118.0, 87.2.



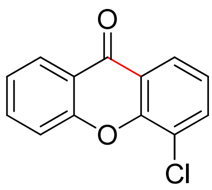
Methyl 9-oxo-9H-xanthene-2-carboxylate (2o) [1]

The desired pure product was obtained in 39% yield (100 mg) as a white solid, mp 229-230℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (d, J = 1.9 Hz, 1H), 8.37 – 8.29 (m, 2H), 7.76 – 7.71 (m, 1H), 7.51 (m, 2H), 7.40 (t, J = 7.5 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 165.8, 158.7, 155.9, 135.3, 135.2, 129.3, 126.8, 126.0, 124.5, 121.8, 121.4, 118.4, 118.0, 52.4.



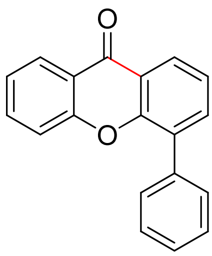
4-methyl-9H-xanthen-9-one (2p) [3]

The desired pure product was obtained in 50% yield (105 mg) as a white solid, mp 122-123℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, J = 7.9 Hz, 1H), 8.19 (d, J = 7.9 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.58 – 7.51 (m, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.27 (m, 1H), 2.56 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 156.0, 154.5, 135.7, 134.6, 127.2, 126.7, 124.3, 123.8, 123.4, 121.7, 121.6, 118.0, 15.8.



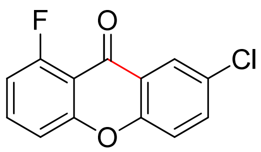
4-chloro-9H-xanthen-9-one (2q)[3]

The desired pure product was obtained in 35% yield (81 mg) as a white solid, mp 133-134°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.24 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 155.8, 151.8, 135.2, 134.9, 126.7, 125.3, 124.5, 123.8, 123.2, 122.8, 121.4, 118.2.



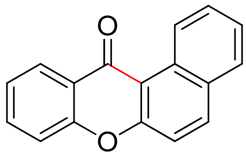
4-phenyl-9H-xanthen-9-one (2r)[3]

The desired pure product was obtained in 82% yield (223 mg) as a white solid, mp 137-138°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (m, 2H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.68 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 156.0, 153.0, 136.4, 135.8, 134.7, 131.5, 129.7, 128.4, 127.9, 126.7, 126.1, 124.0, 123.8, 122.3, 121.5, 118.1.



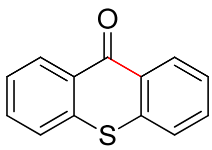
7-chloro-1-fluoro-9H-xanthen-9-one (2s)

The desired pure product was obtained in 62% yield (154 mg) as a white solid, mp 172-174°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.69 – 7.62 (m, 2H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.06 – 7.01 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 162.4, 160.6, 156.9, 153.7, 135.1, 135.1, 135.0, 130.1, 126.0, 123.1, 119.4, 113.9, 113.9, 112.1, 112.0, 111.3, 111.1. HRMS (ESI) exact mass calcd for $C_{13}H_7ClFO_2$ [M+H] m/z 249.0119, found 249.0128.



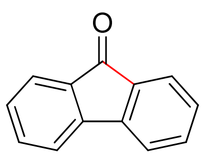
12H-benzo[a]xanthen-12-one (2t) [3]

The desired pure product was obtained in 70% yield (173 mg) as a white solid, mp 145-146°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.09 (d, *J* = 8.6 Hz, 1H), 8.44 (d, *J* = 7.9 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.54 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 157.5, 154.6, 136.6, 133.8, 131.1, 130.1, 129.5, 128.3, 126.9, 126.6, 126.1, 124.2, 123.5, 118.0, 117.5, 114.5.



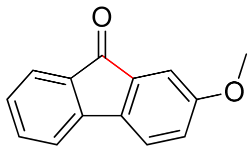
9H-thioxanthen-9-one (2u)[5]

The desired pure product was obtained in 52% yield (110 mg) as a white solid, mp 181-182°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 8.1, 0.7 Hz, 2H), 7.60 (d, *J* = 6.9 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.9, 137.3, 132.2, 129.8, 129.2, 126.3, 126.0.



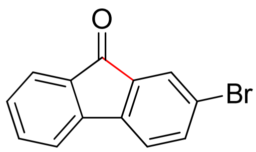
9H-fluoren-9-one (2v) [2]

The desired pure product was obtained in 78% yield (141 mg) as a yellow solid, mp 79-80°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.3 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.8, 144.3, 134.6, 134.0, 129.0, 124.2, 120.3.



2-methoxy-9H-fluoren-9-one (2w) [2]

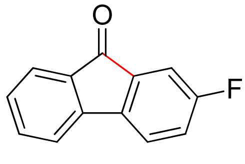
The desired pure product was obtained in 56% yield (118 mg) as a yellow solid, mp 121-123°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.17 (m, 2H), 6.97 (dd, *J* = 8.1, 2.4 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.8, 160.8, 144.9, 137.0, 135.9, 134.8, 134.3, 127.9, 124.3, 121.3, 120.3, 119.5, 109.4, 55.7.



2-bromo-9H-fluoren-9-one (2x) [2]

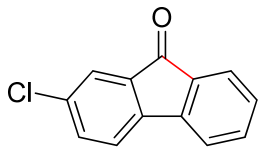
The desired pure product was obtained in 51% yield (132 mg) as a yellow solid, mp 132-133°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.31 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 143.7, 143.0, 137.1, 135.8, 135.0, 133.7, 129.4, 127.5, 124.6, 122.9, 121.7,

120.4.



2-fluoro-9H-fluoren-9-one (2y) [2]

The desired pure product was obtained in 42% yield (83 mg) as a yellow solid, mp 115-116°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.46 (s, 2H), 7.44 (d, *J* = 4.3 Hz, 1H), 7.31 (dd, *J* = 7.3, 2.4 Hz, 1H), 7.14 (td, *J* = 8.6, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 164.3, 162.7, 143.9, 140.1, 140.1, 136.3, 136.3, 135.0, 134.3, 134.3, 128.7, 124.6, 121.6, 121.5, 120.9, 120.7, 120.1, 120.1, 112.0, 111.8.



2-chloro-9H-fluoren-9-one (2z) [2]

The desired pure product was obtained in 48% yield (103 mg) as a yellow solid, mp 125-126°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.3 Hz, 1H), 7.60 (s, 1H), 7.50 (m, 2H), 7.44 (s, 2H), 7.33 – 7.28 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 143.6, 142.5, 135.6, 135.1, 135.0, 134.1, 133.9, 129.3, 121.3, 120.4.

References:

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4. Mao, M.; Wu, Q.-Q.; Ren, M.-G.; Song, Q.-H. *Org. Biomol. Chem.* **2011**, *9*, 3165.

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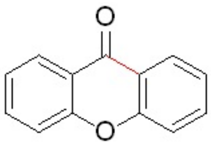

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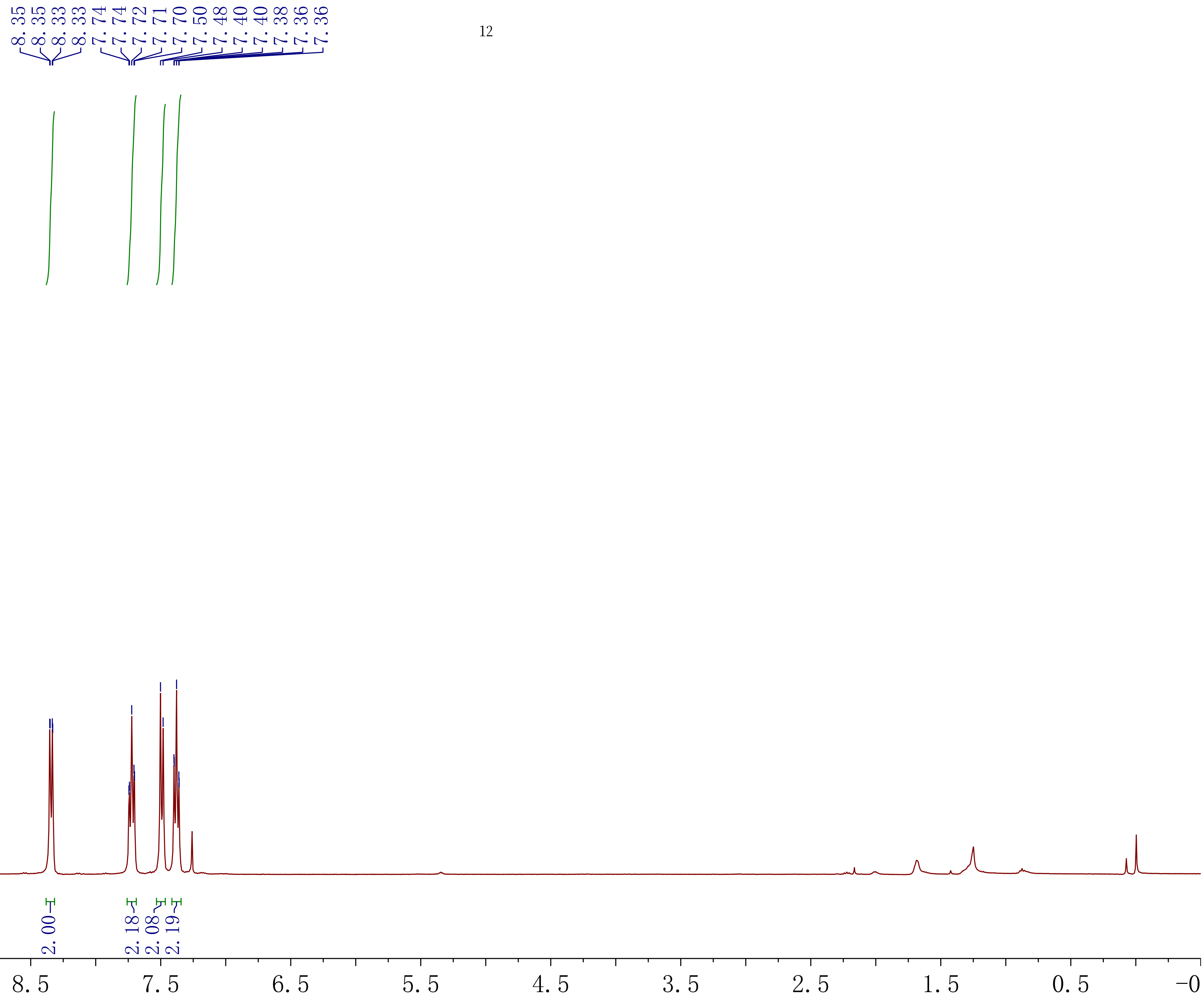
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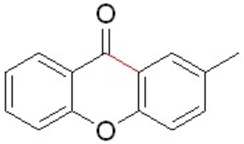

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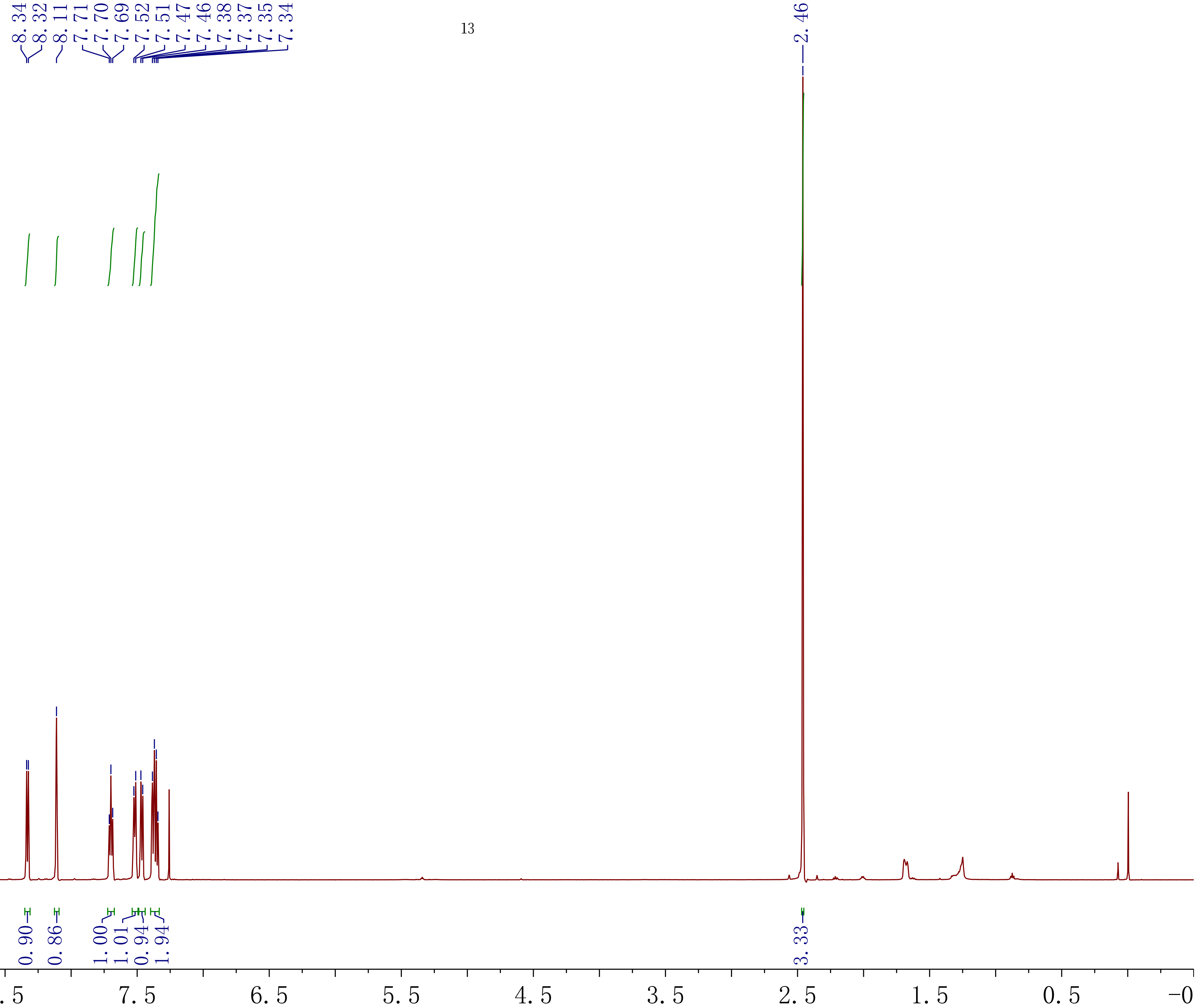
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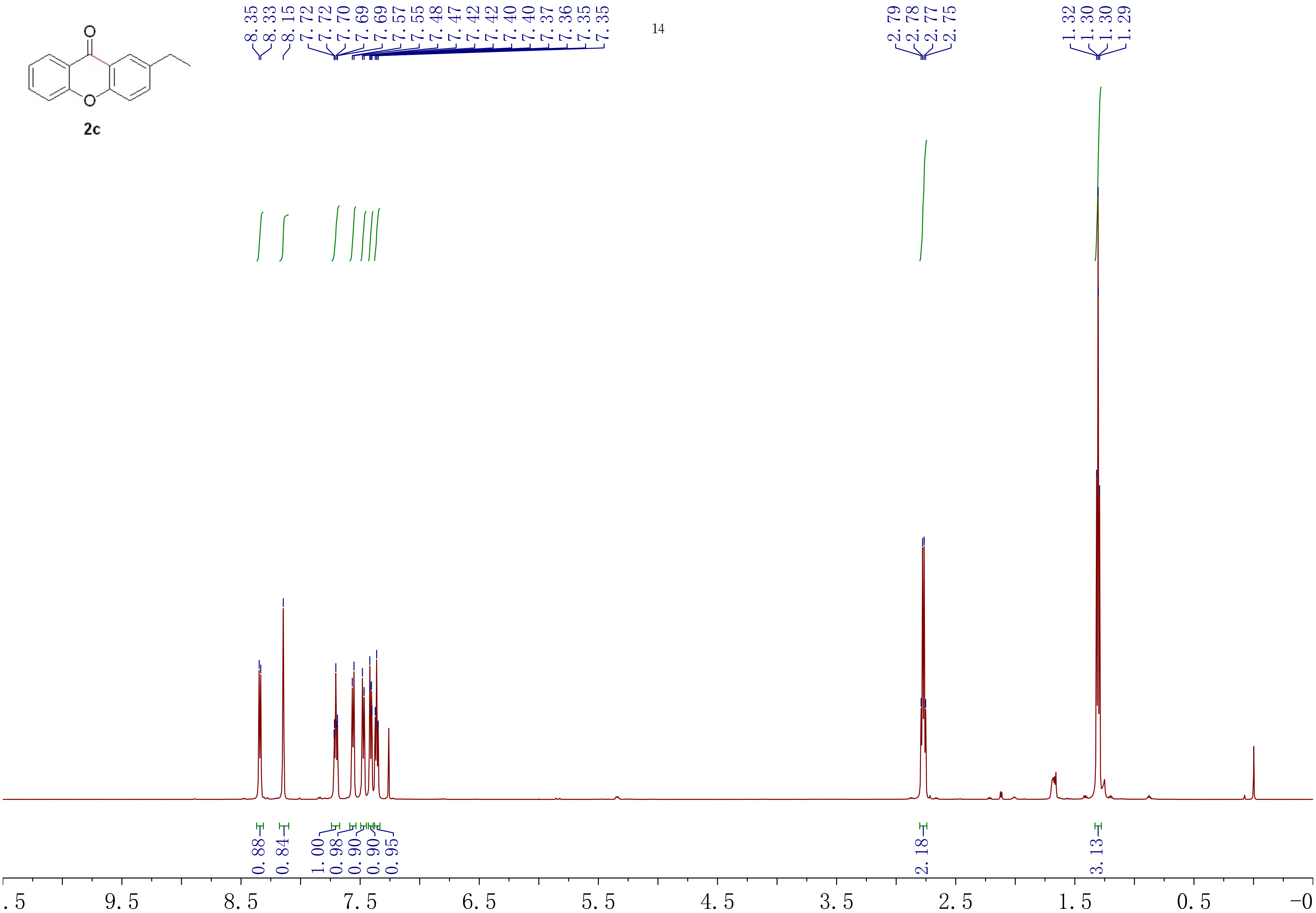
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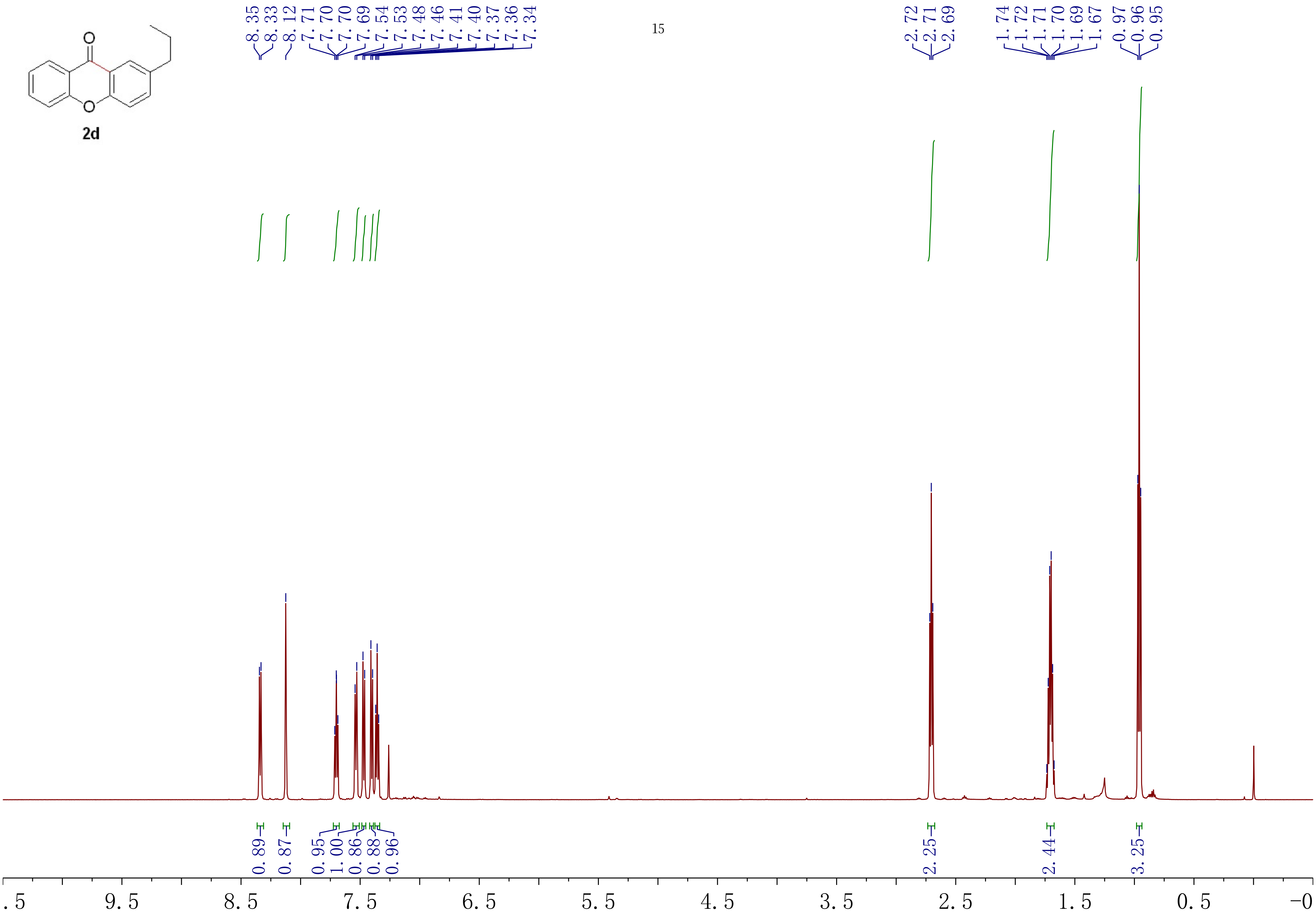
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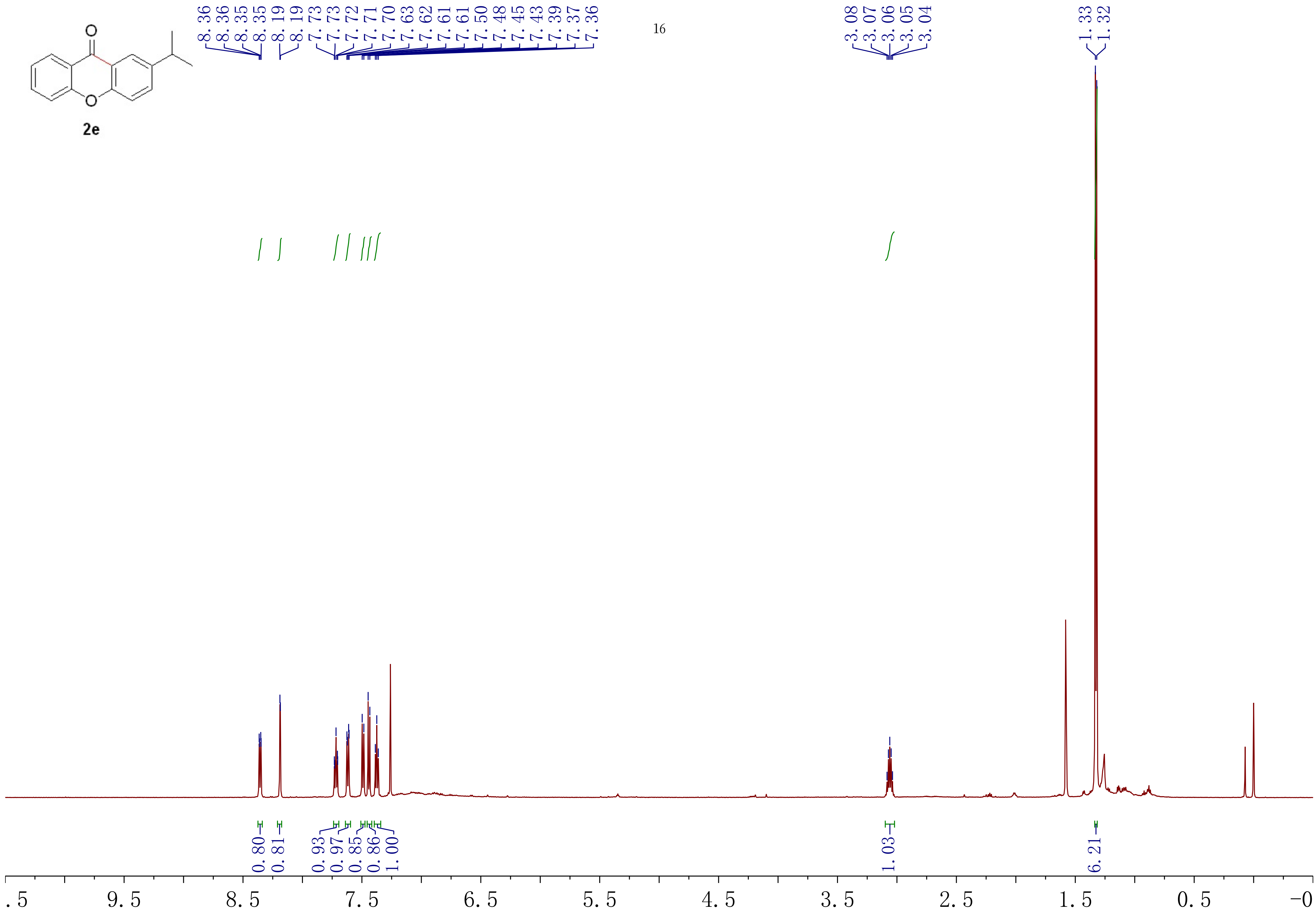
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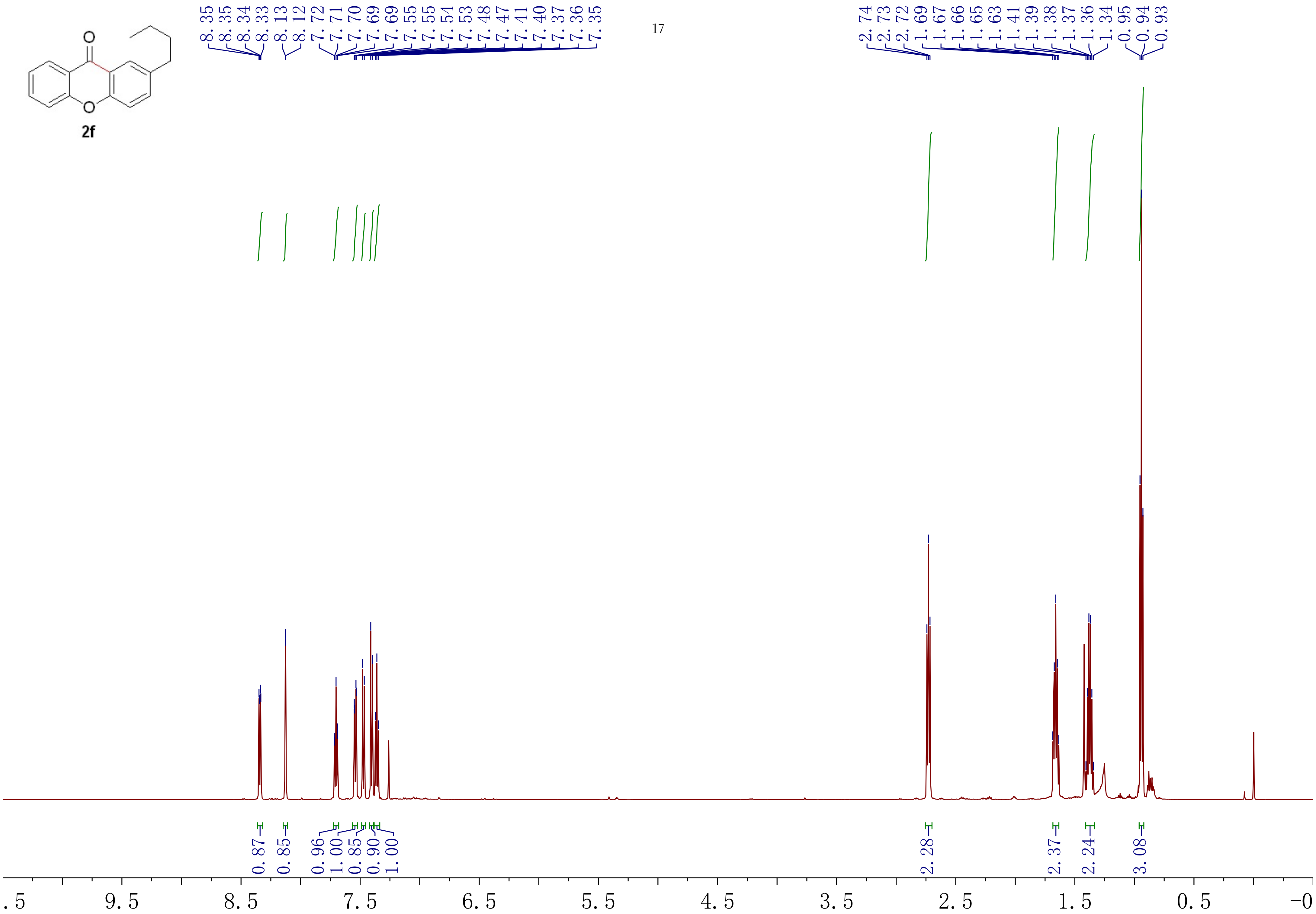
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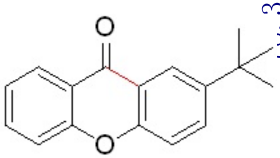

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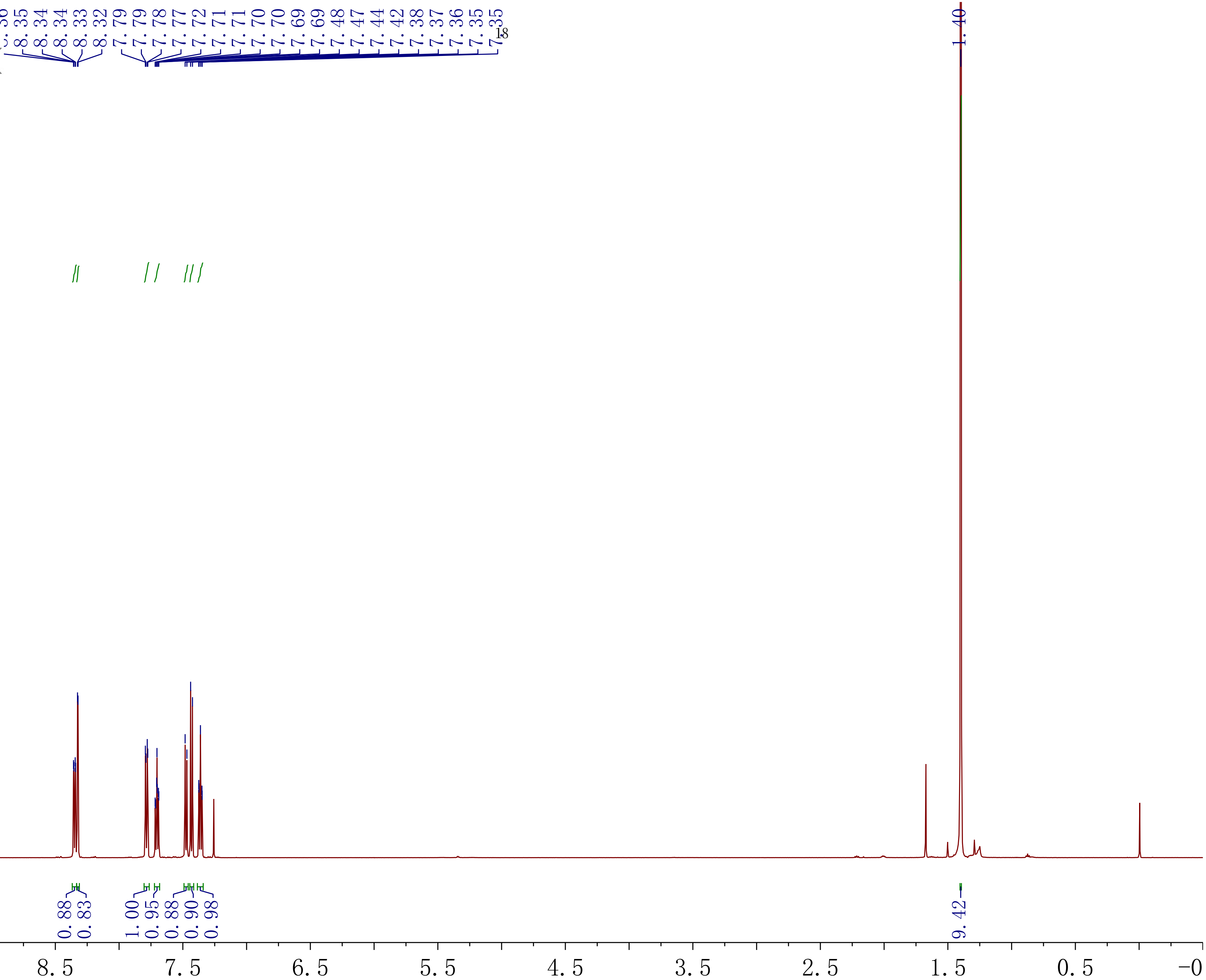
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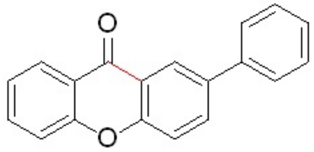

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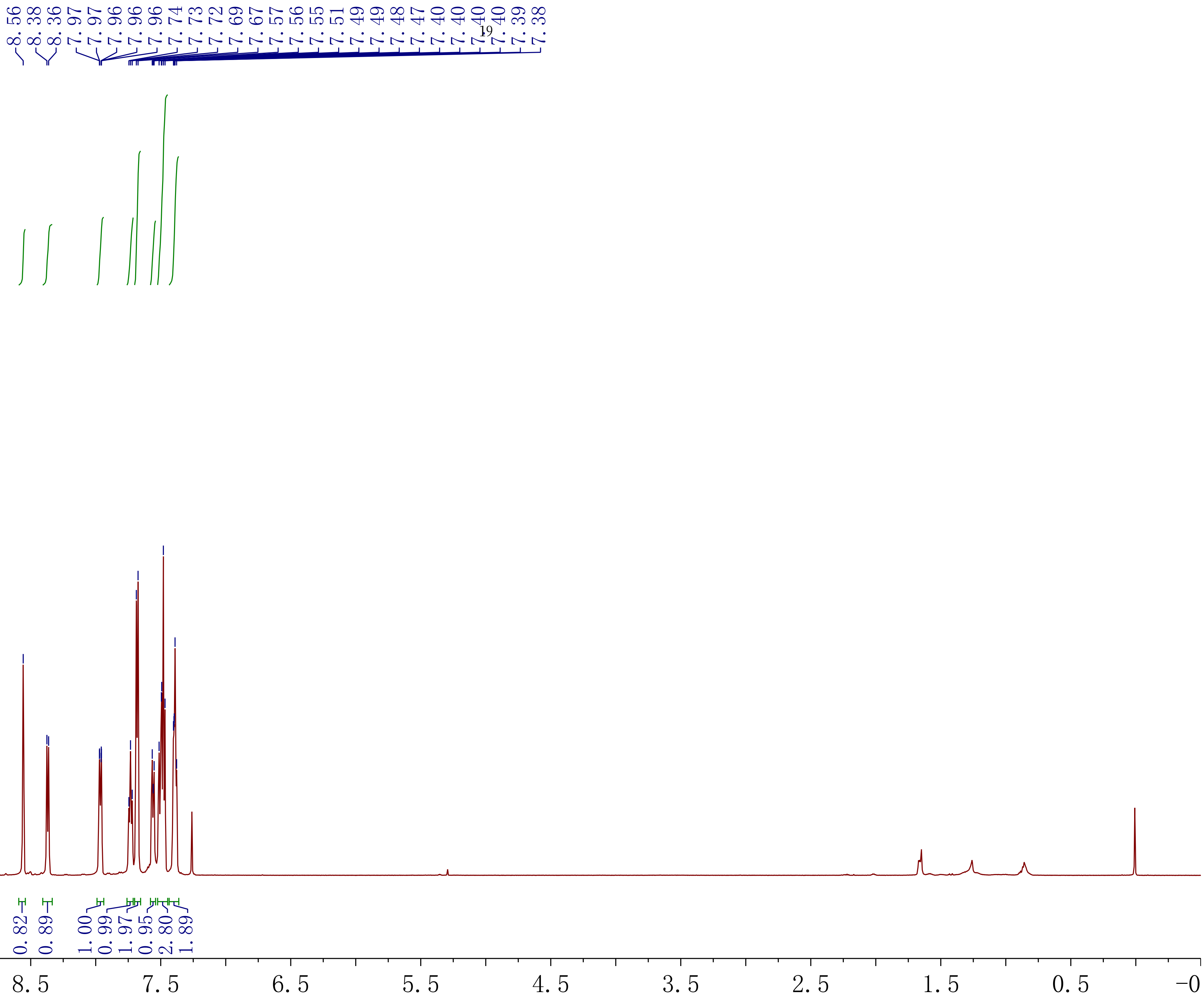
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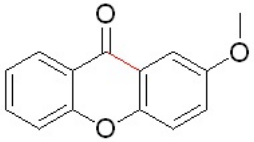

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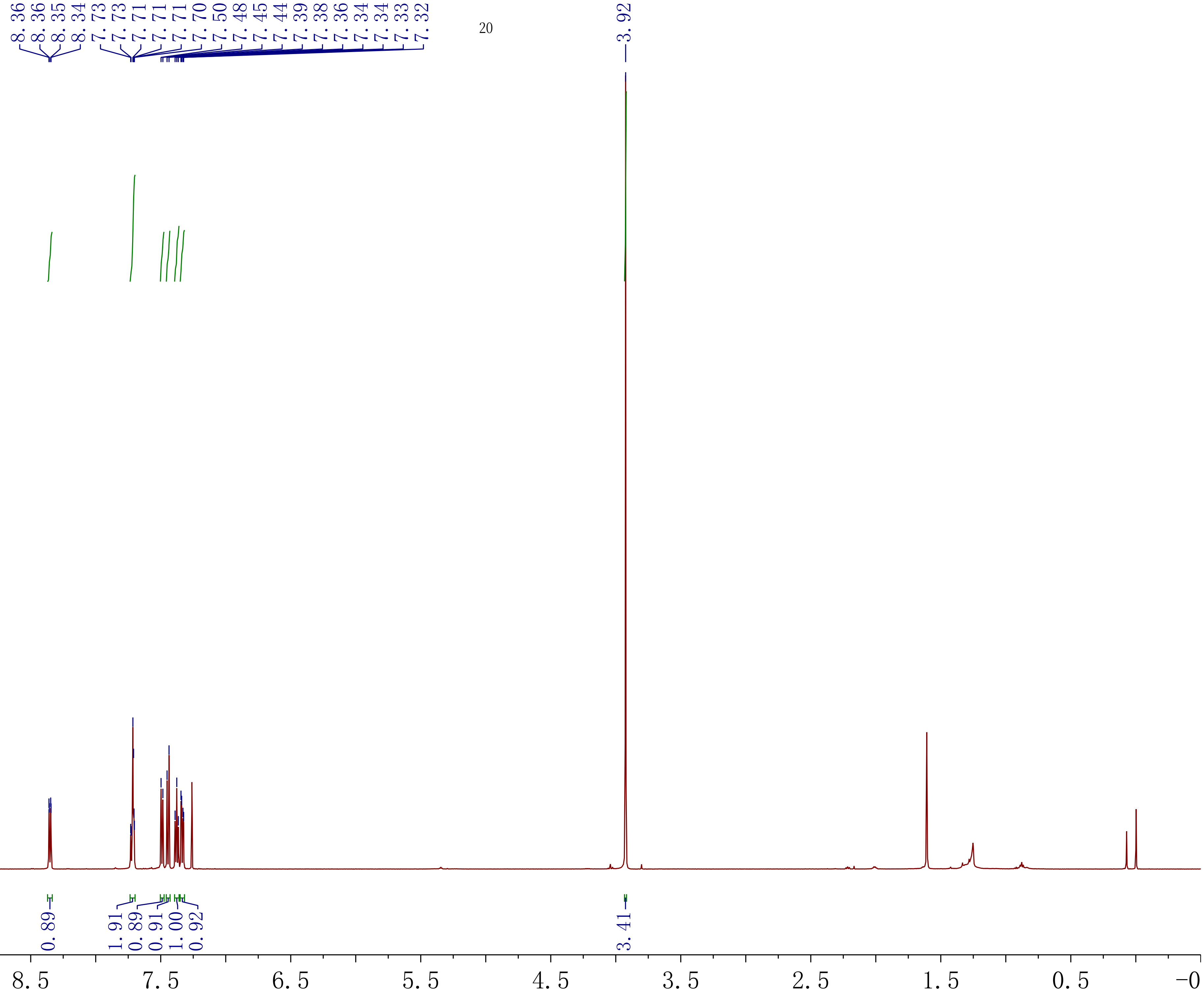
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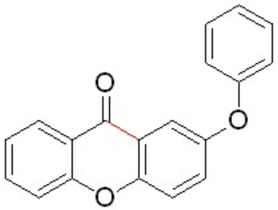

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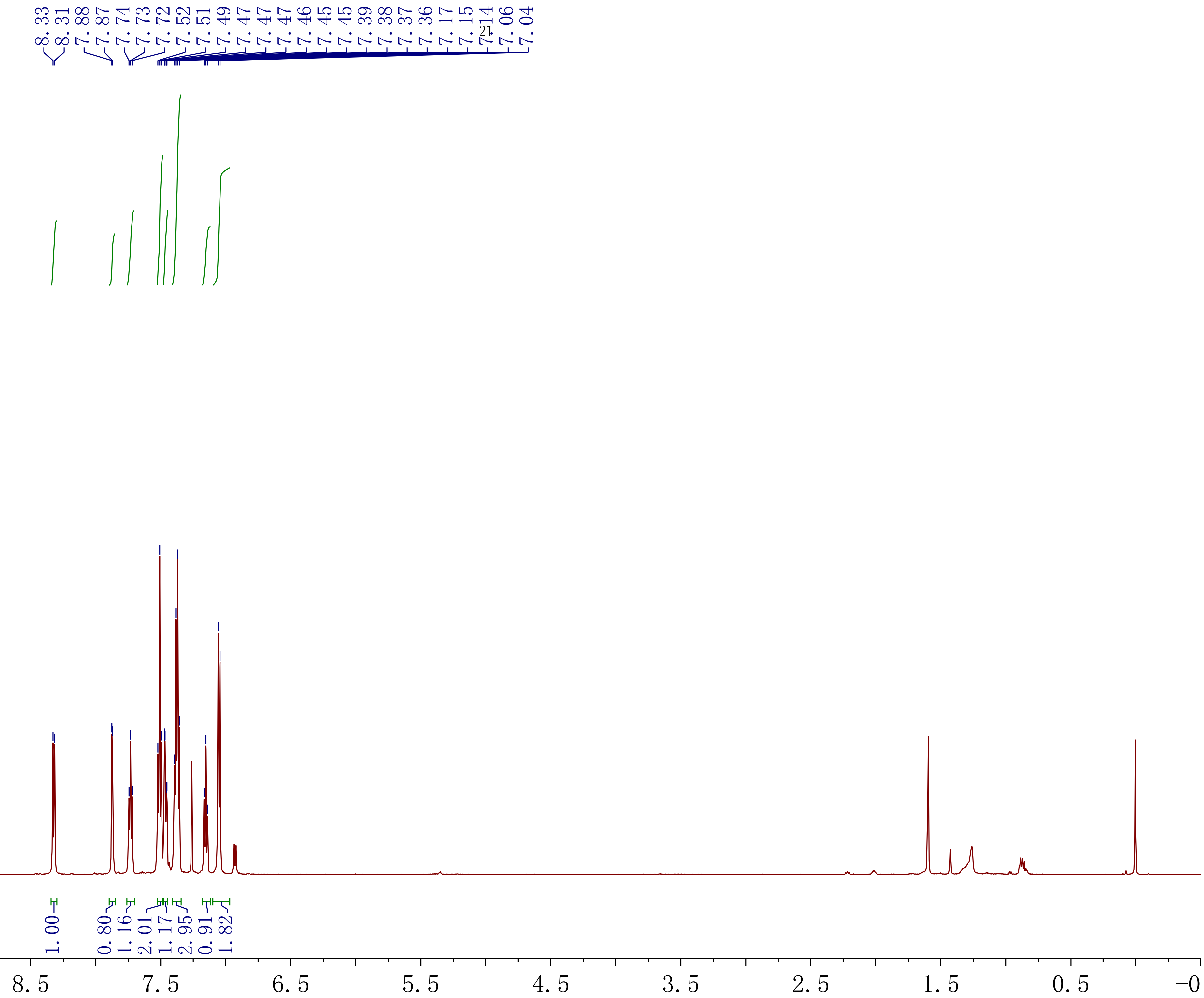
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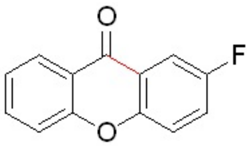

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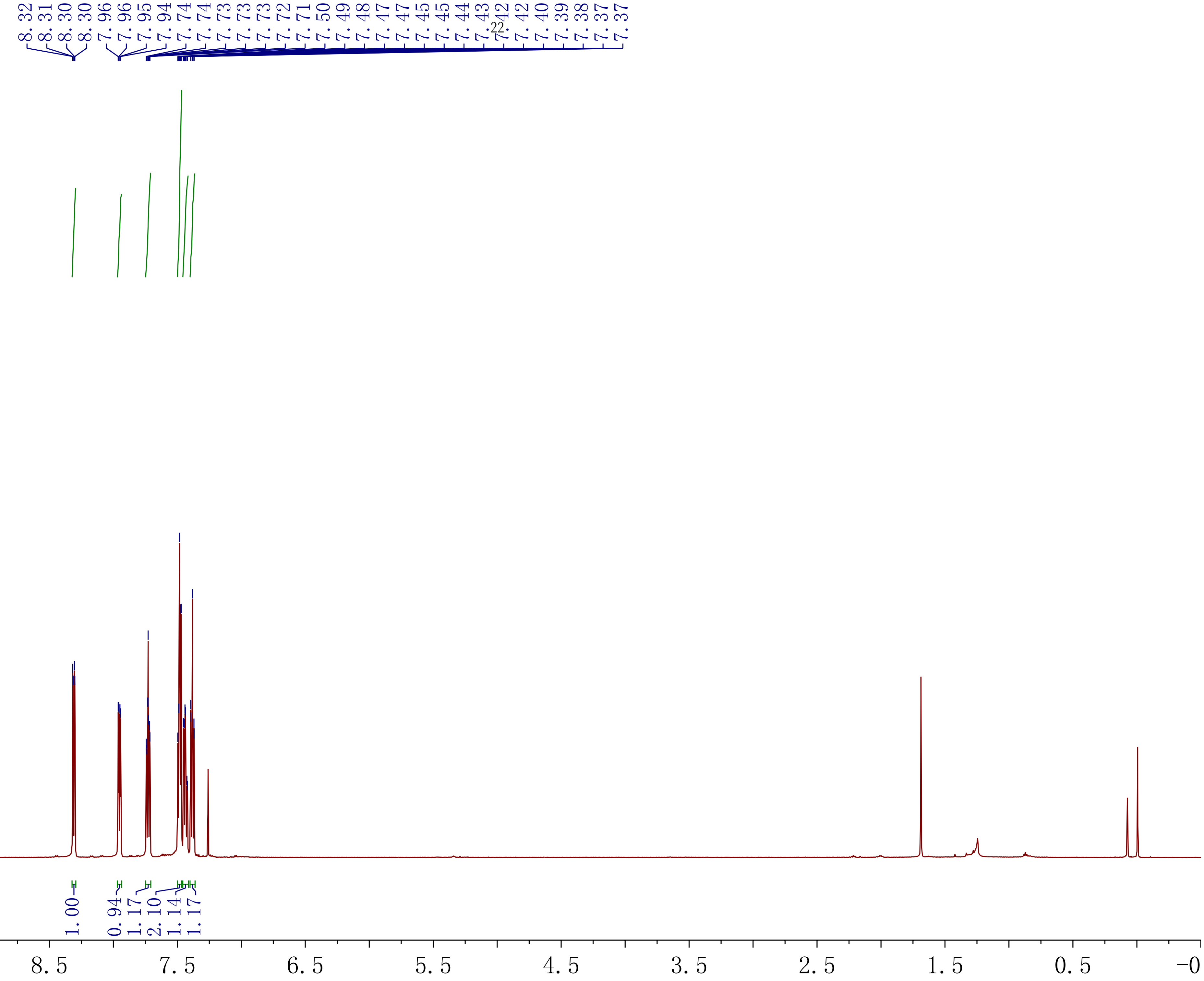
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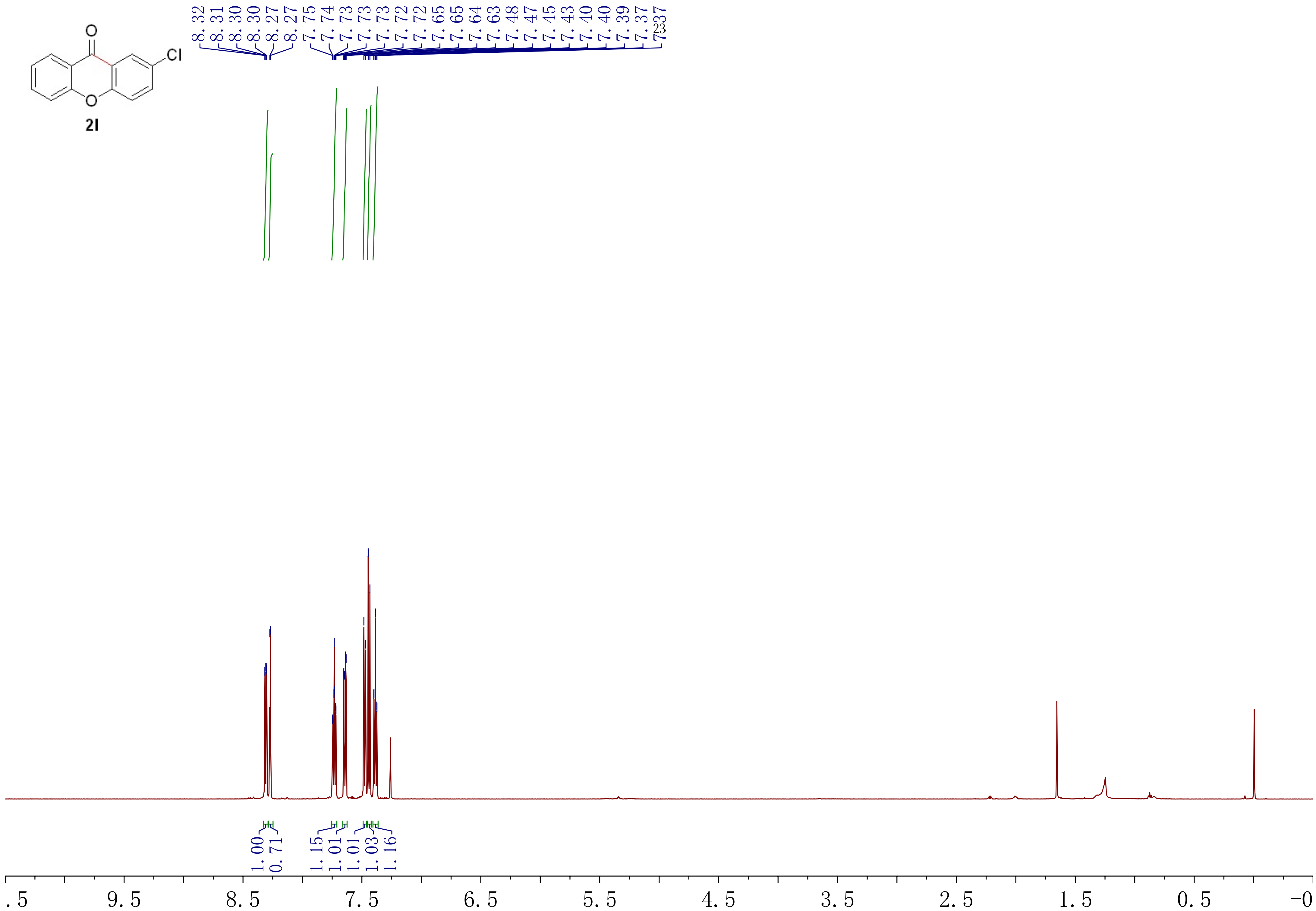
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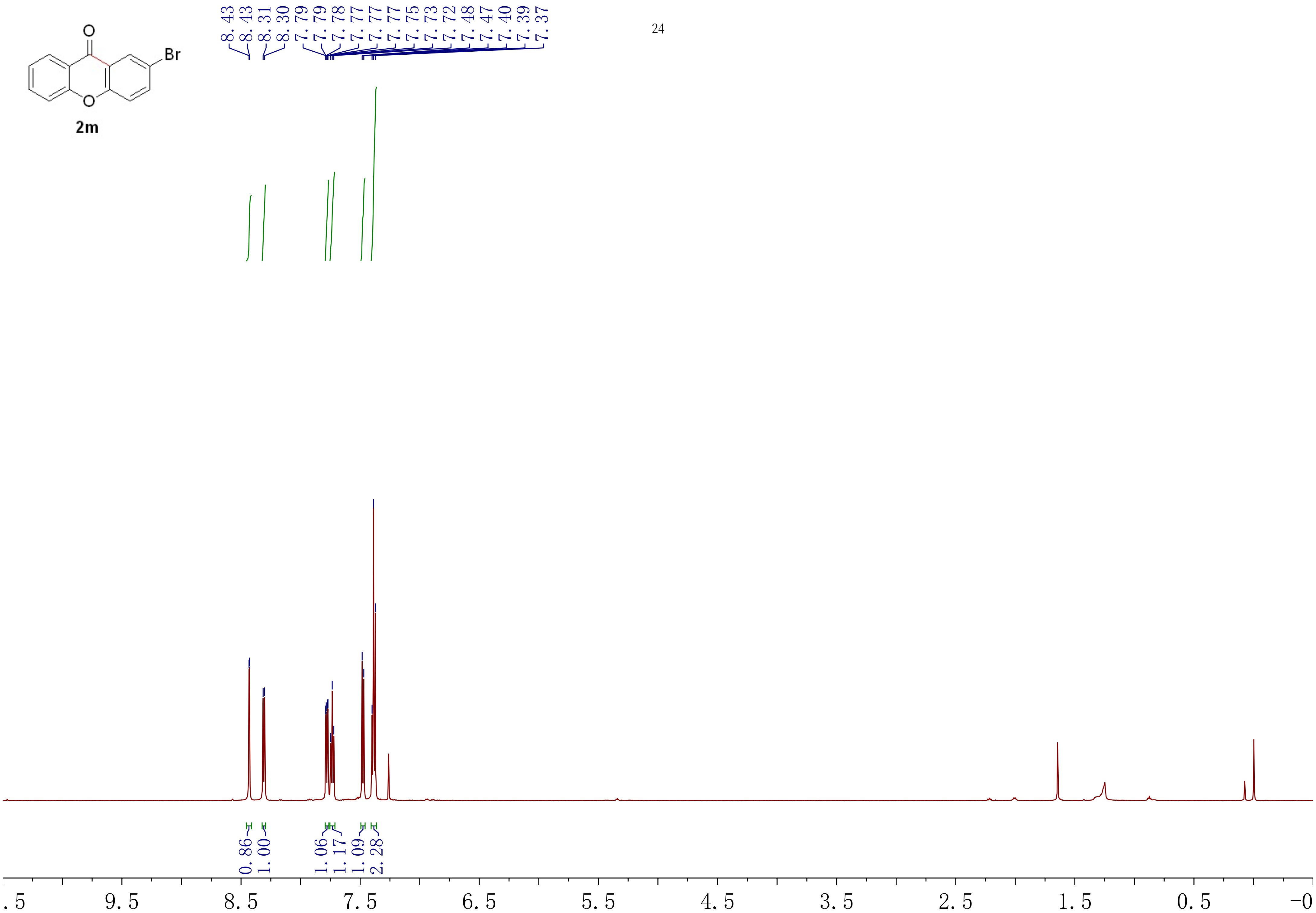
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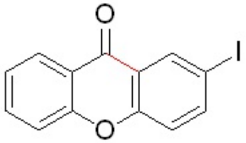

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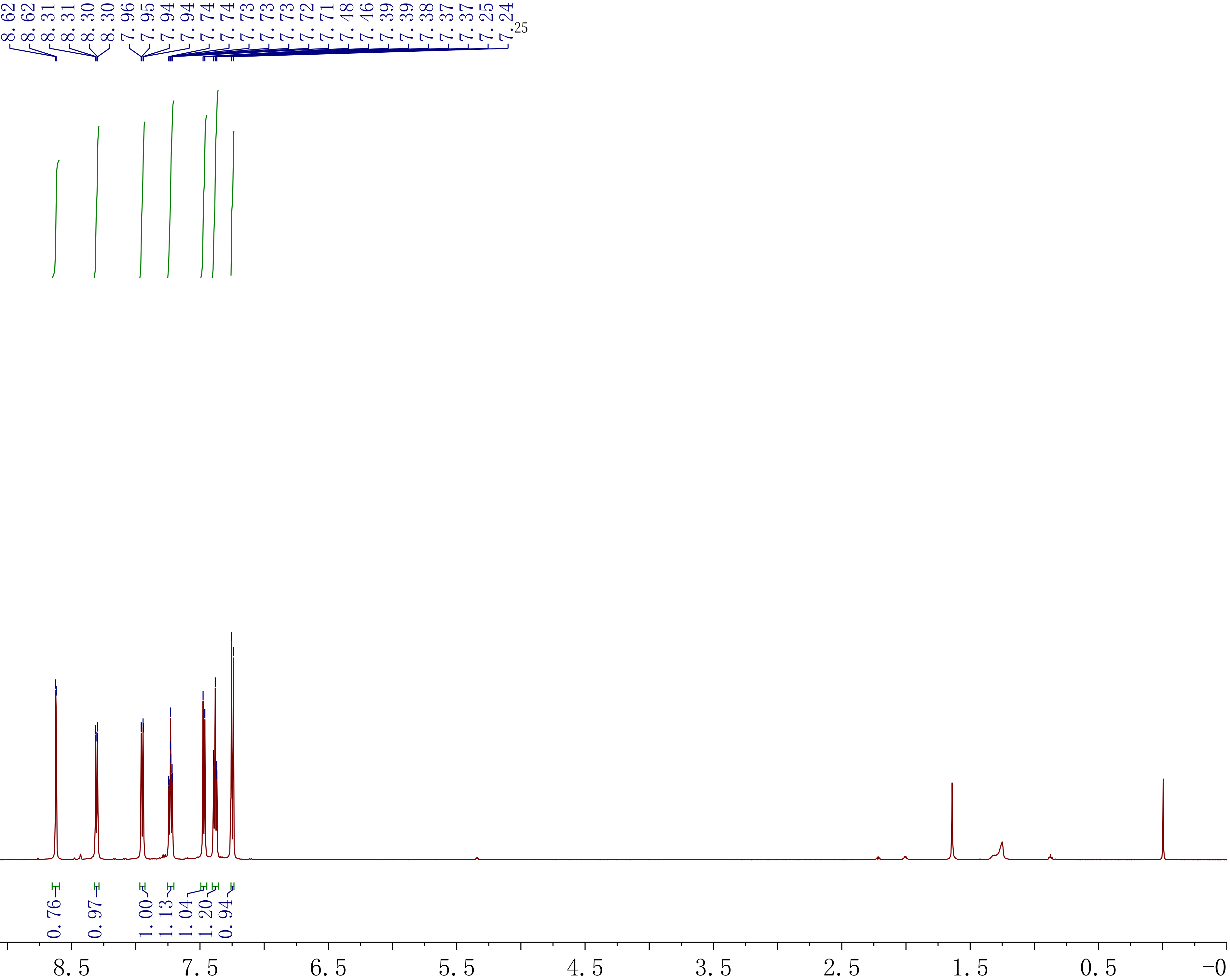

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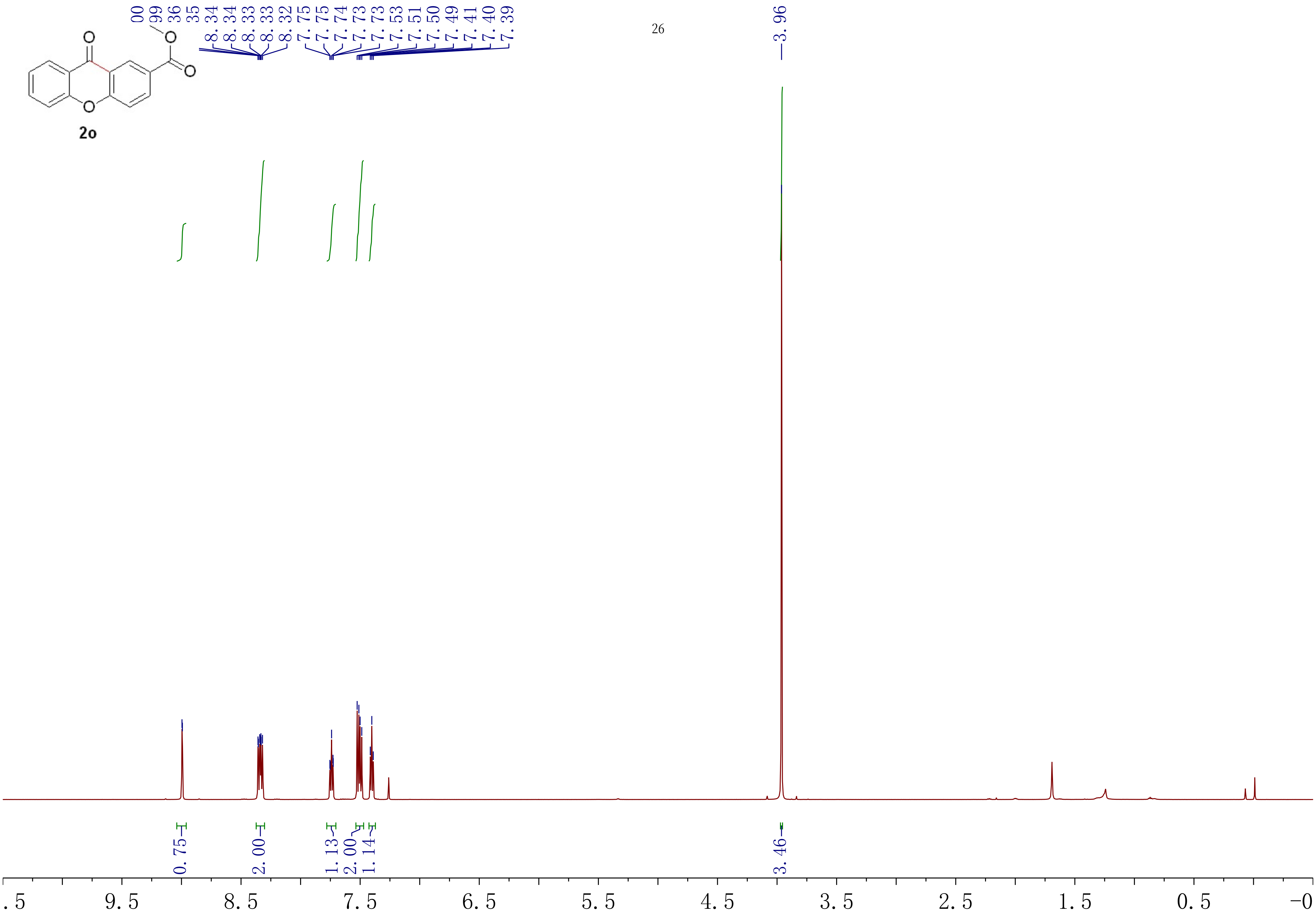

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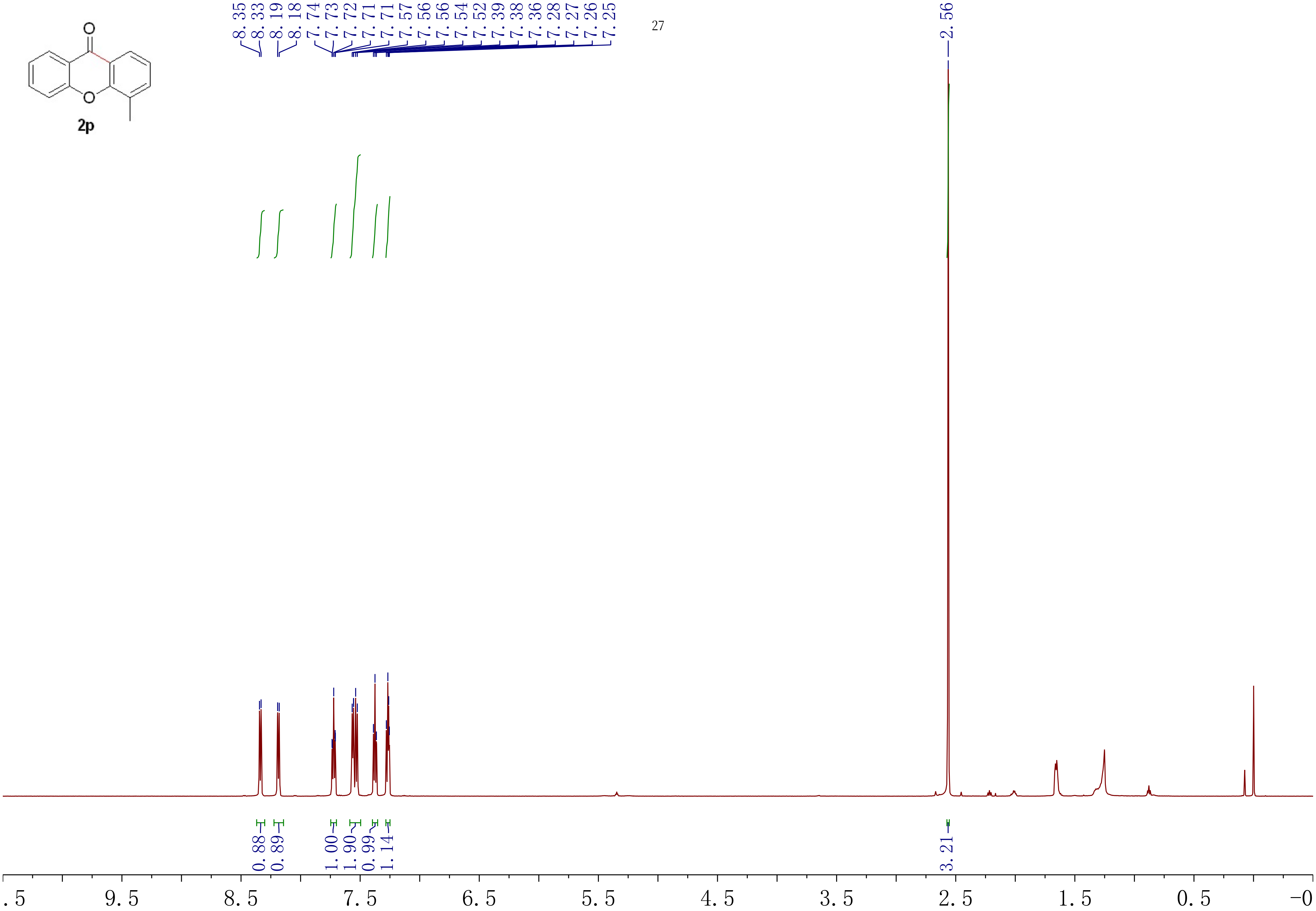
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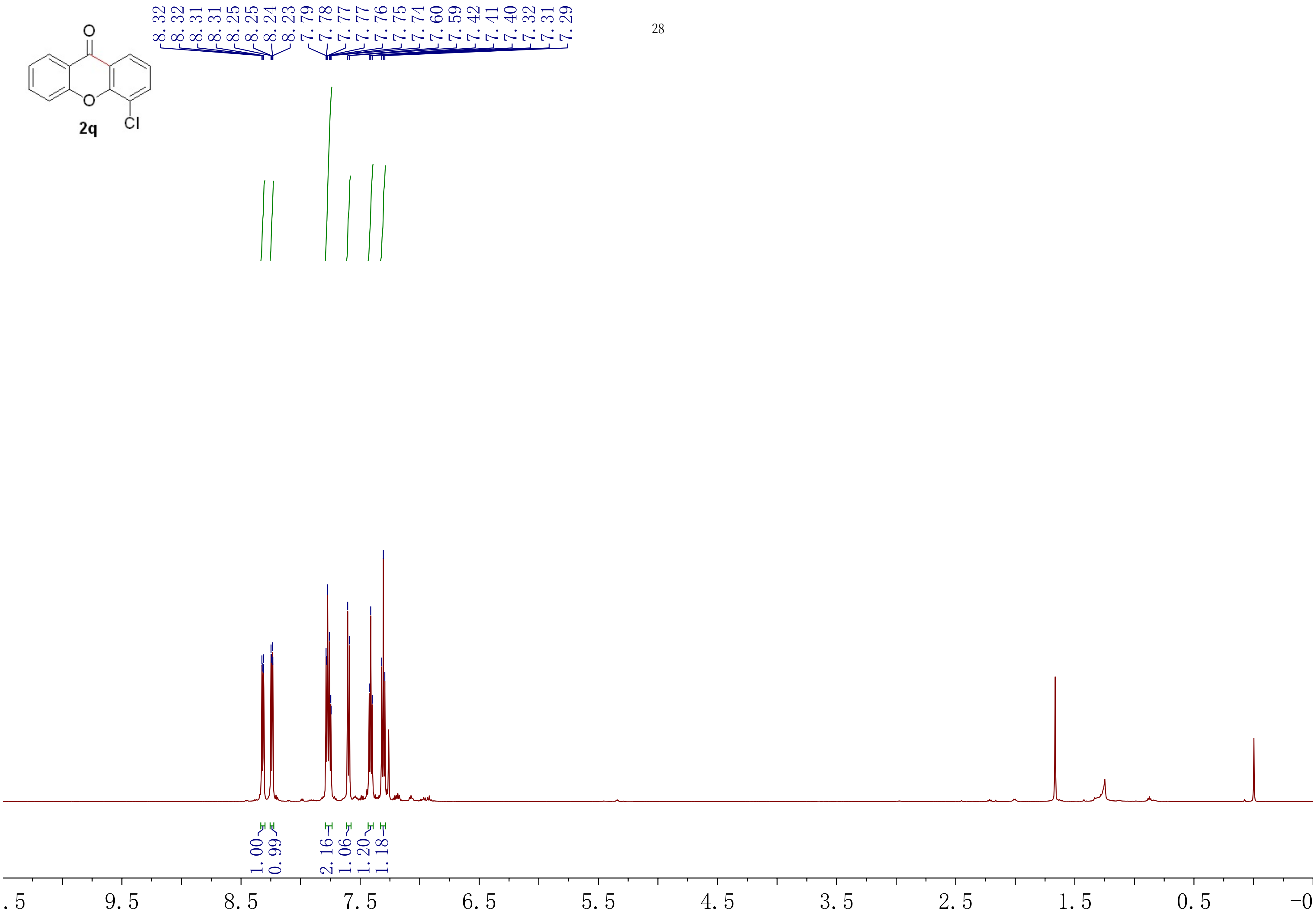
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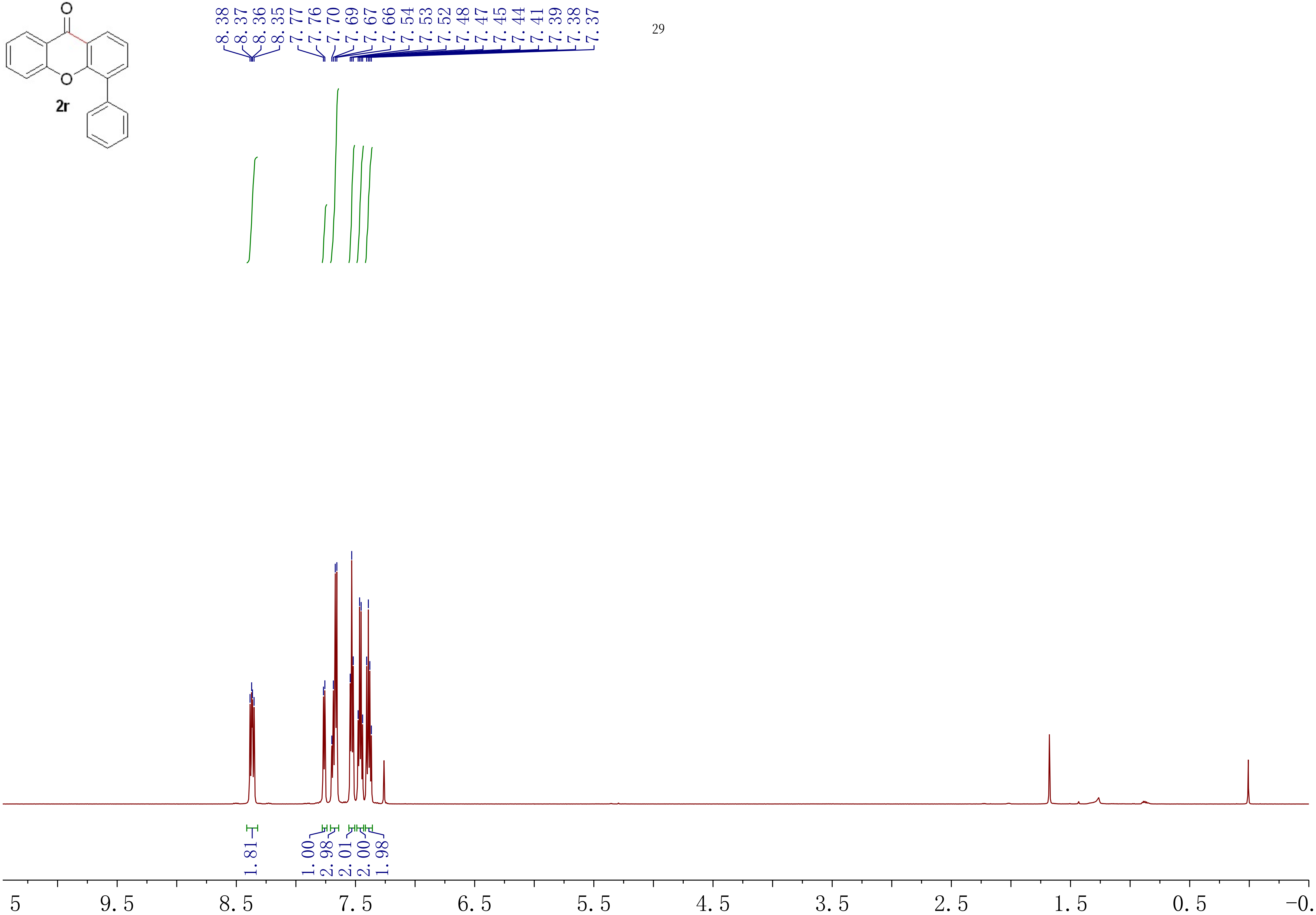
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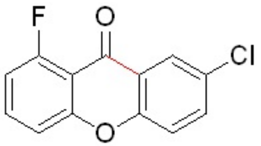
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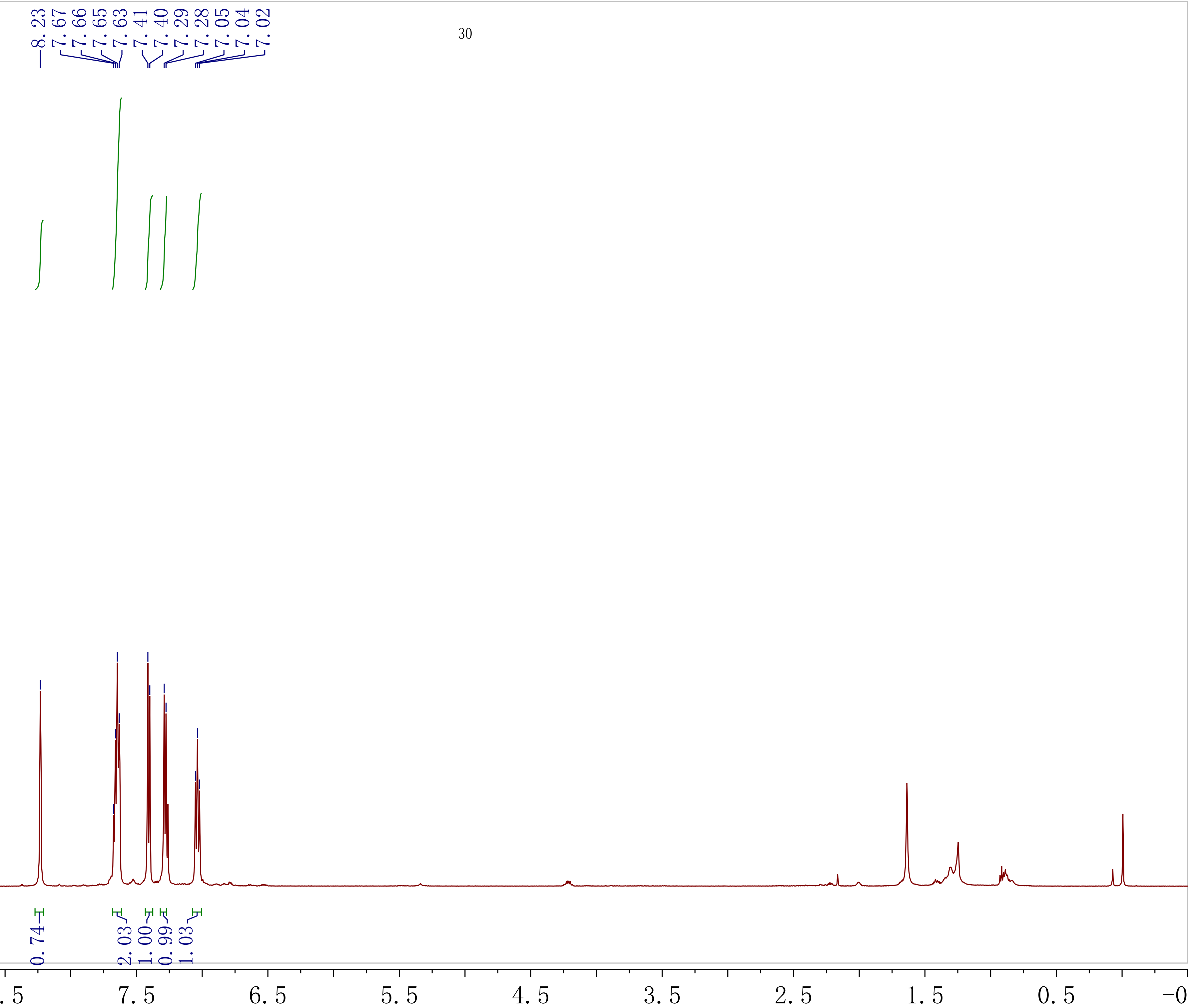
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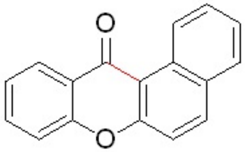

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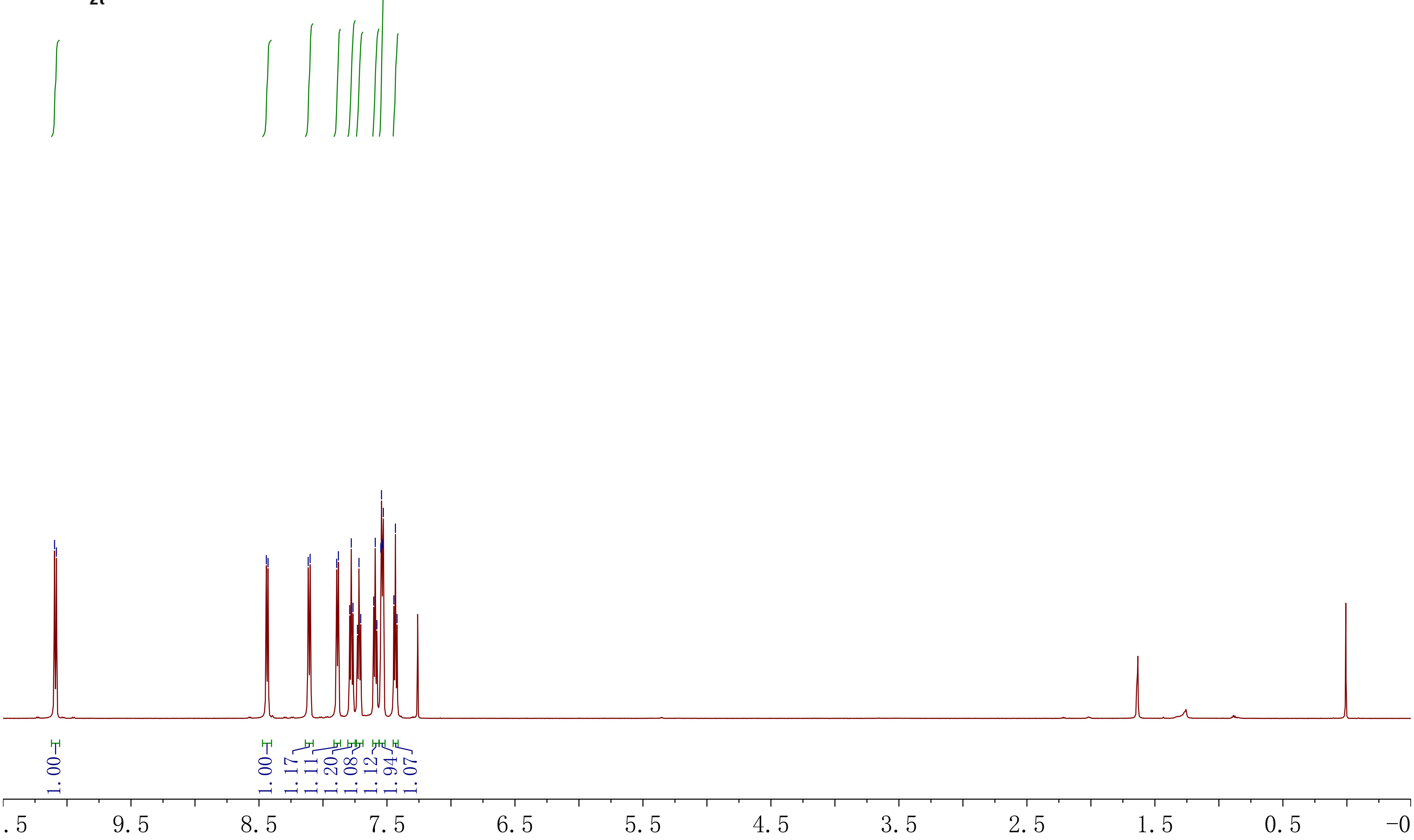
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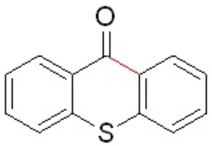
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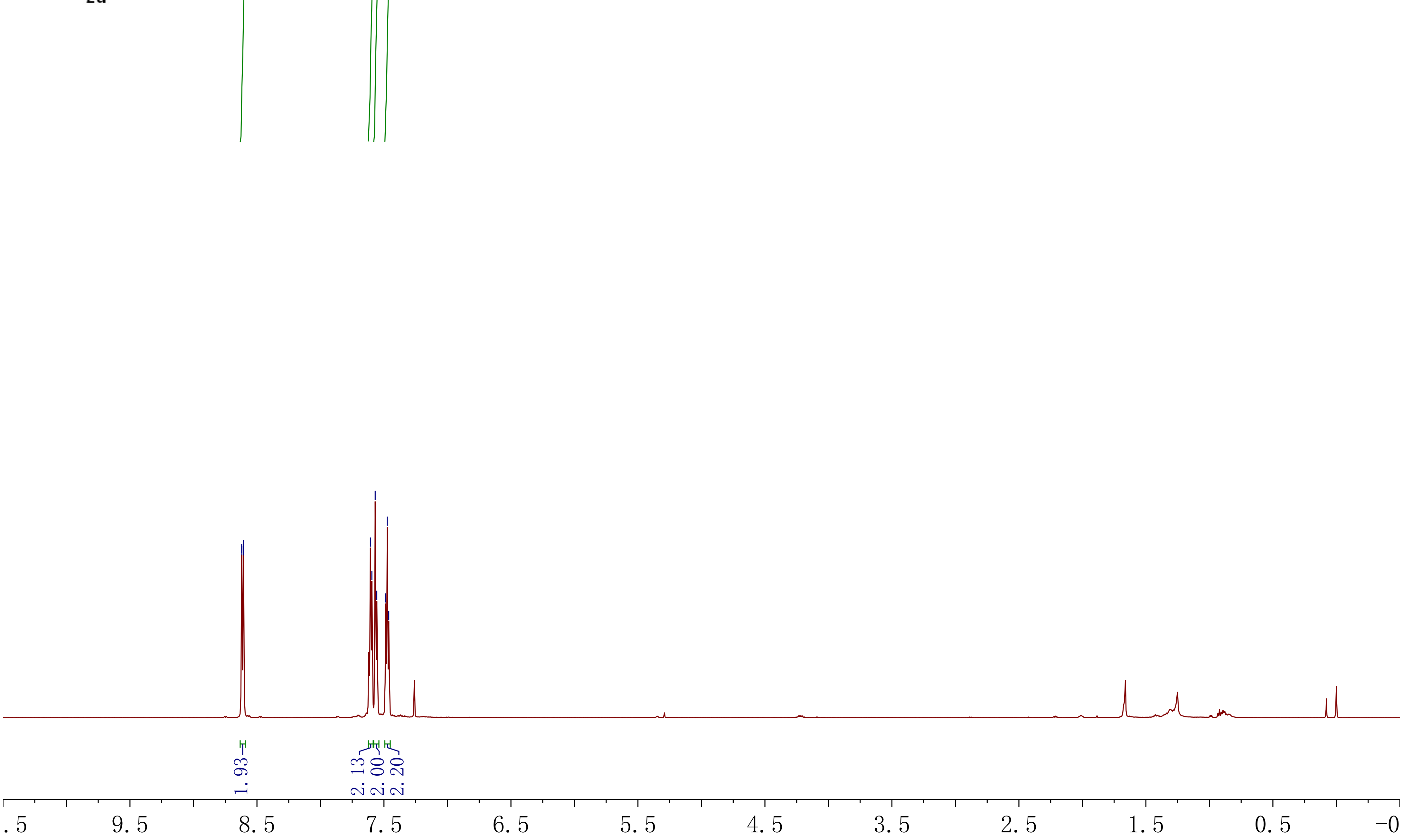
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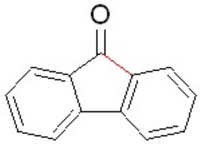

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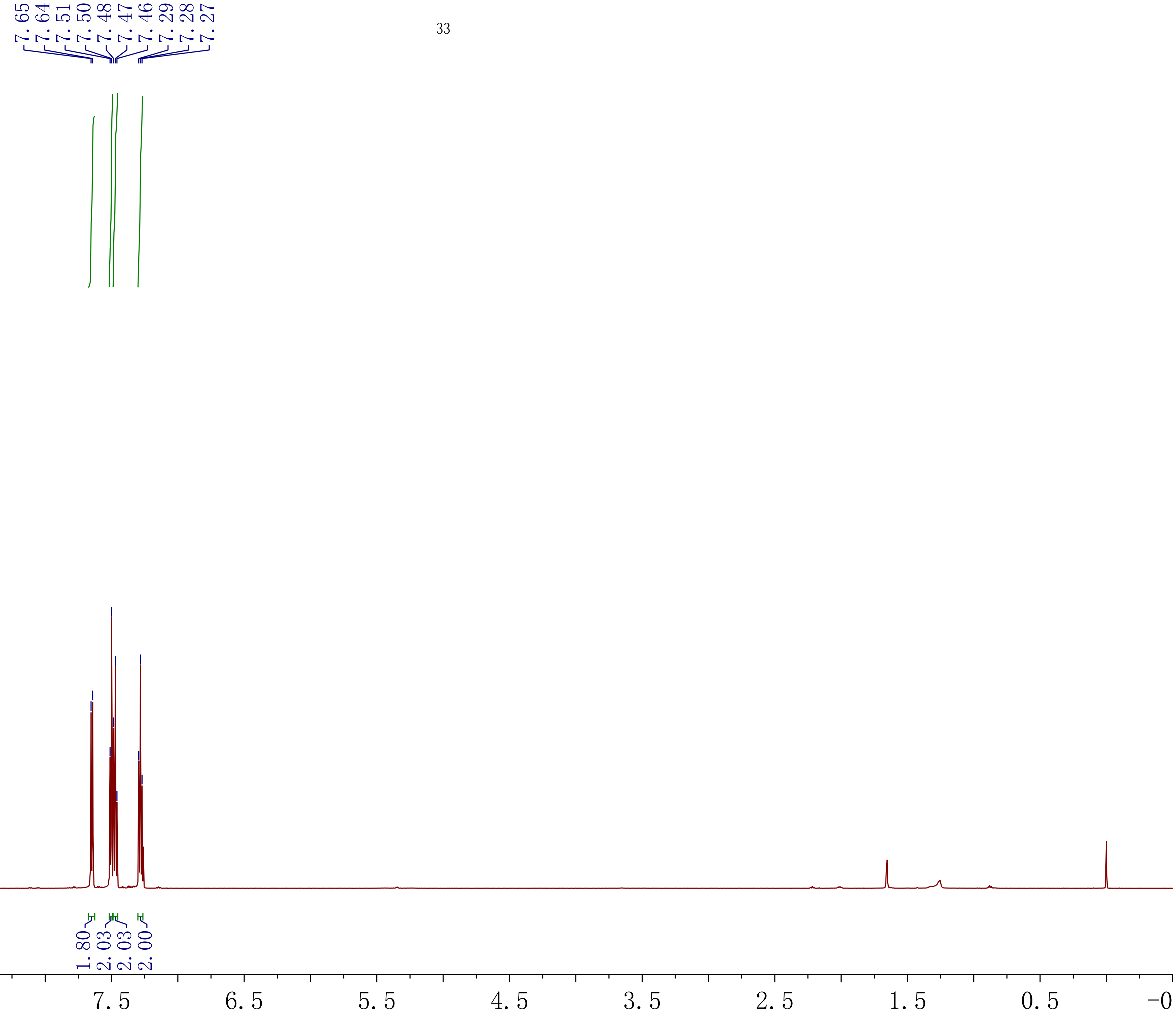
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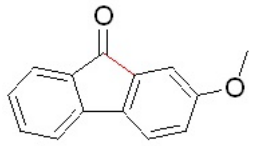

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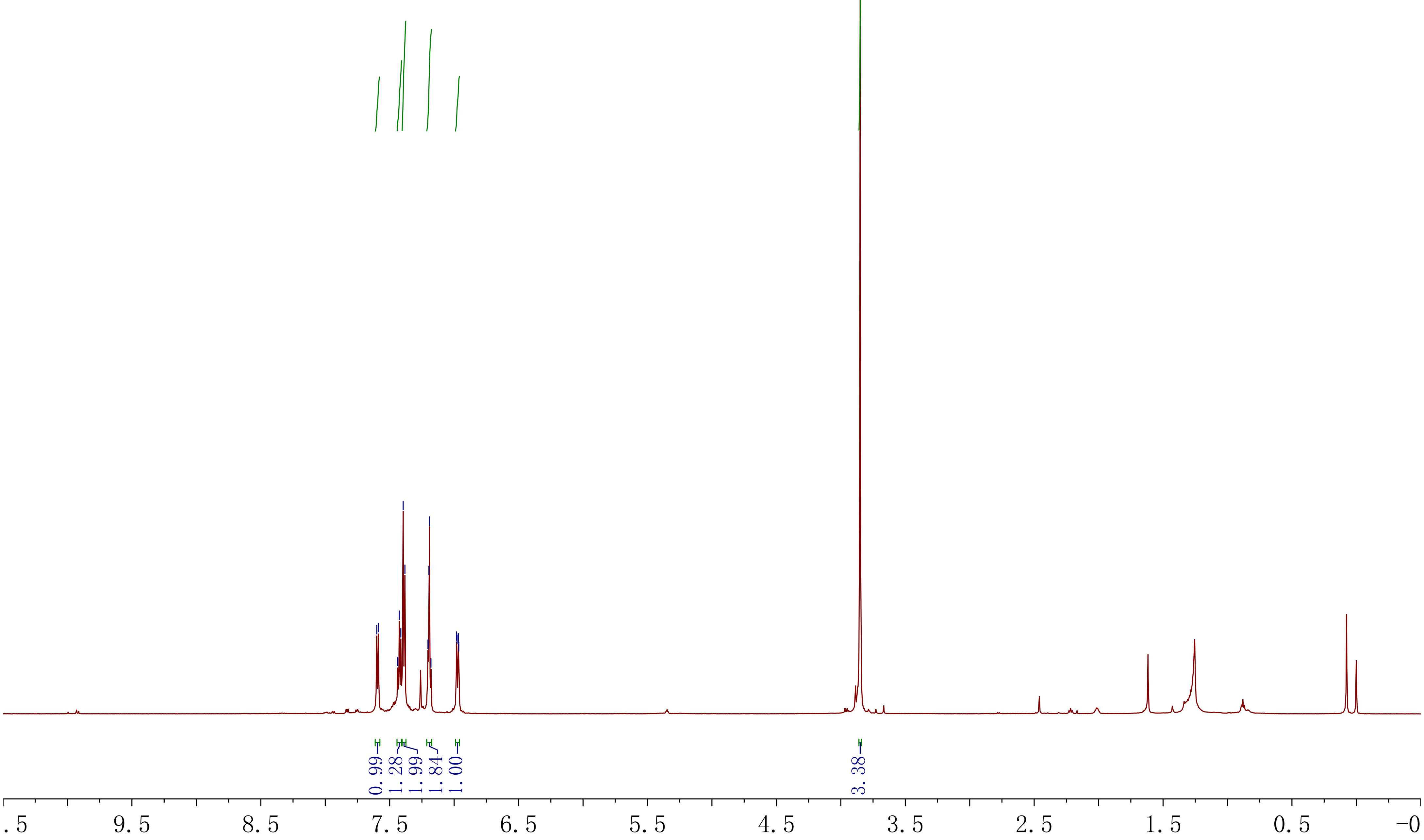
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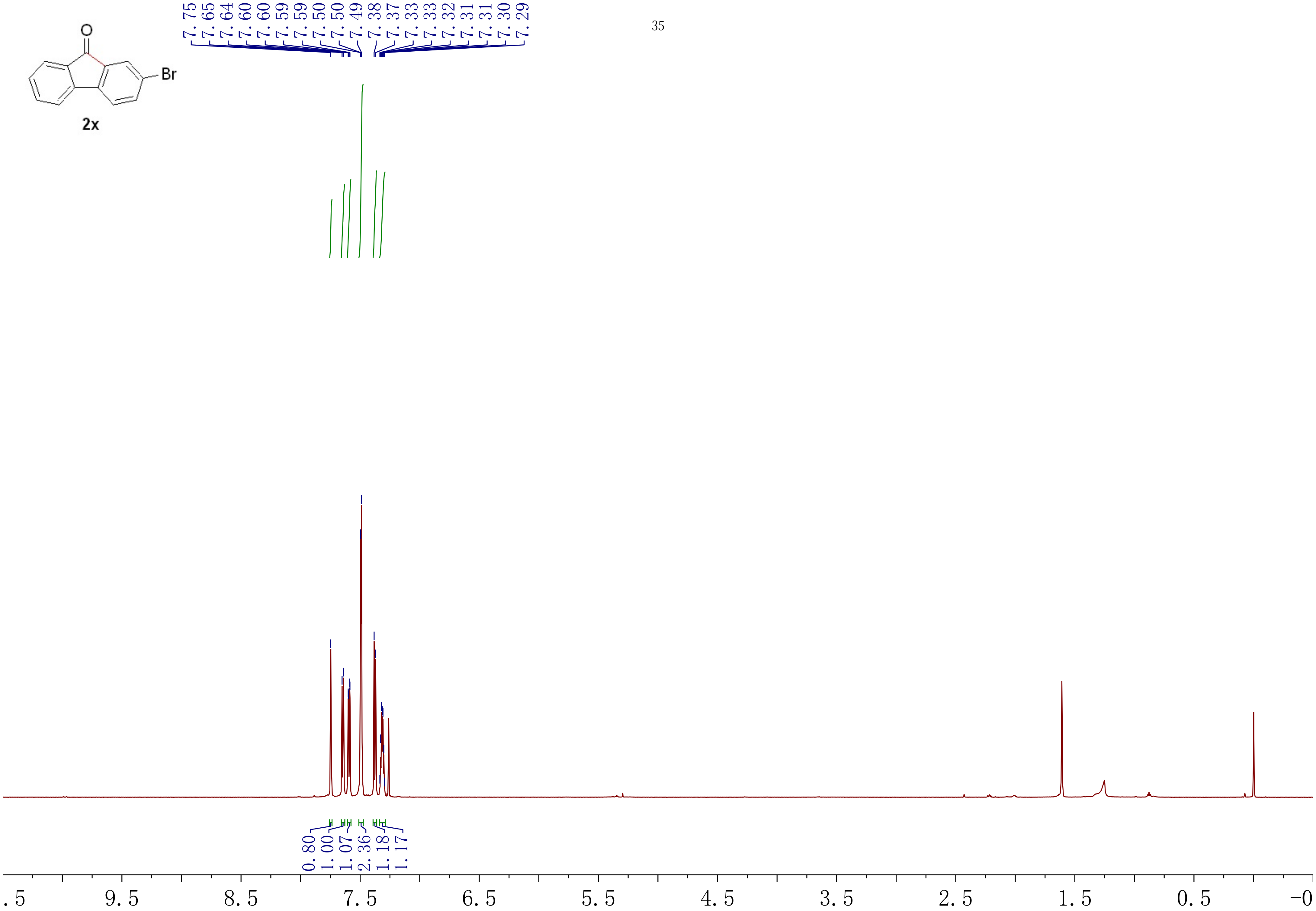

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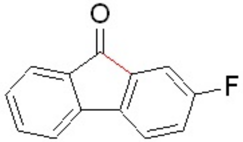

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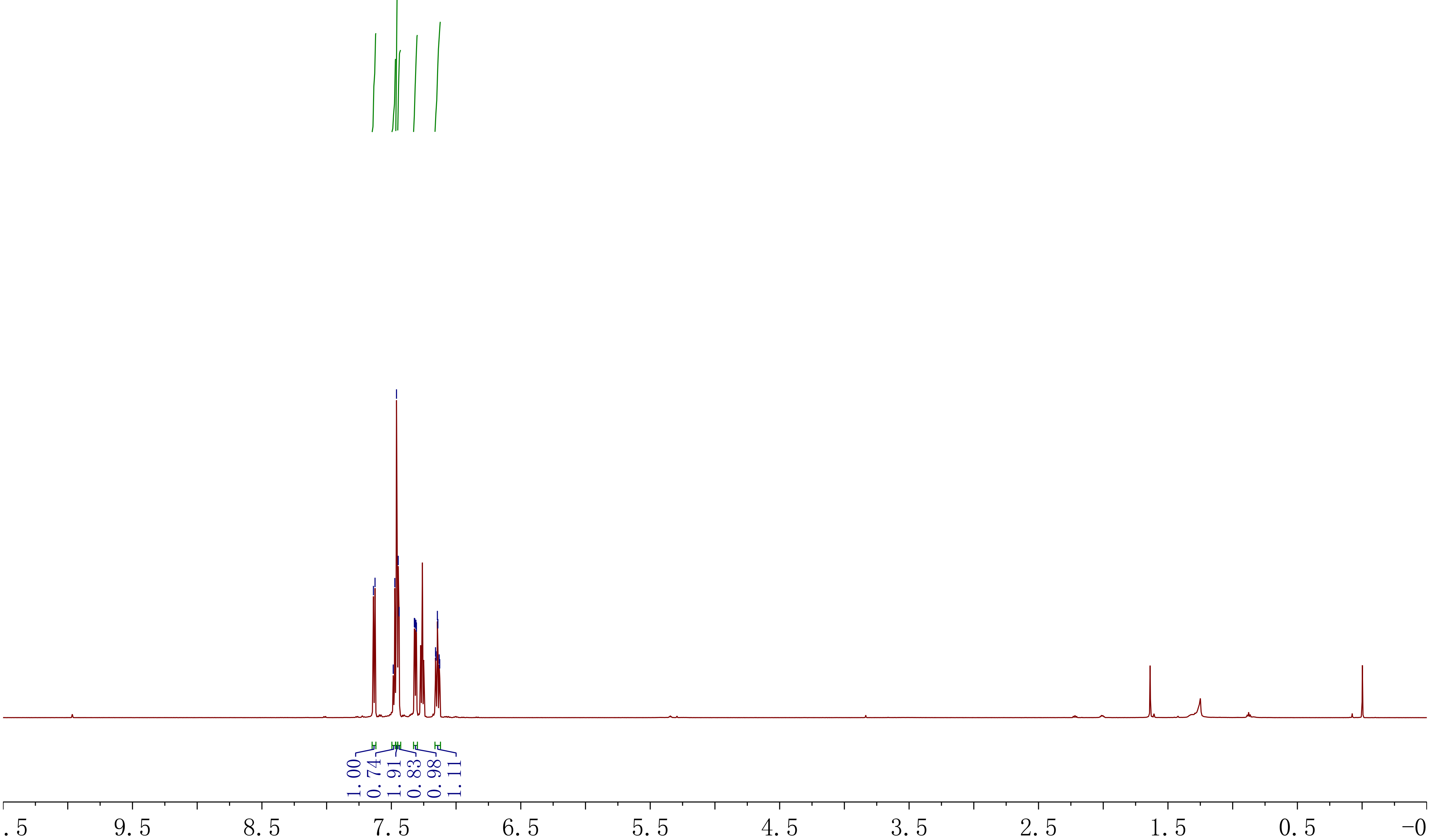
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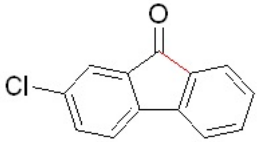

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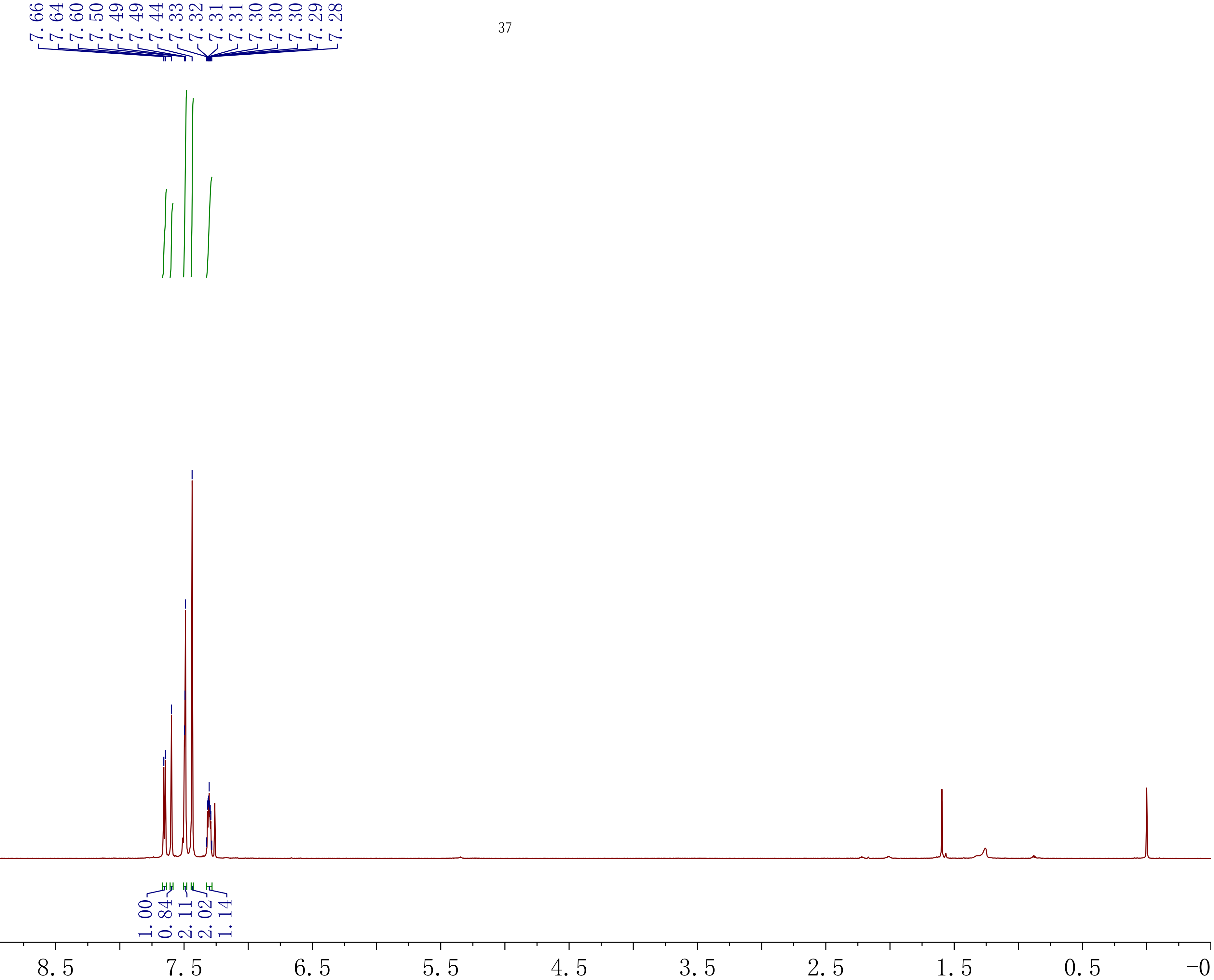
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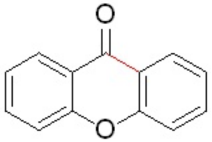

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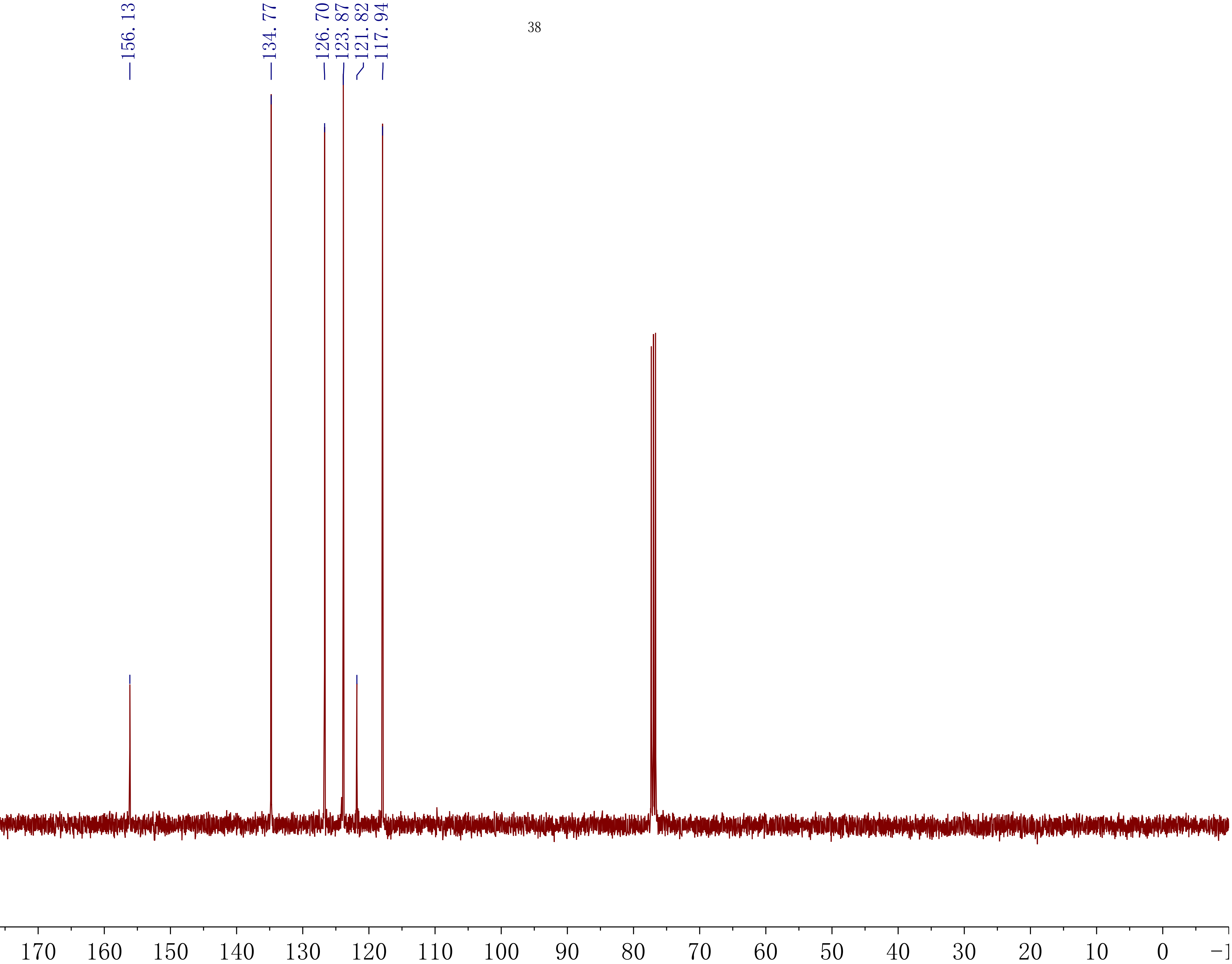
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121. 82
117. 94
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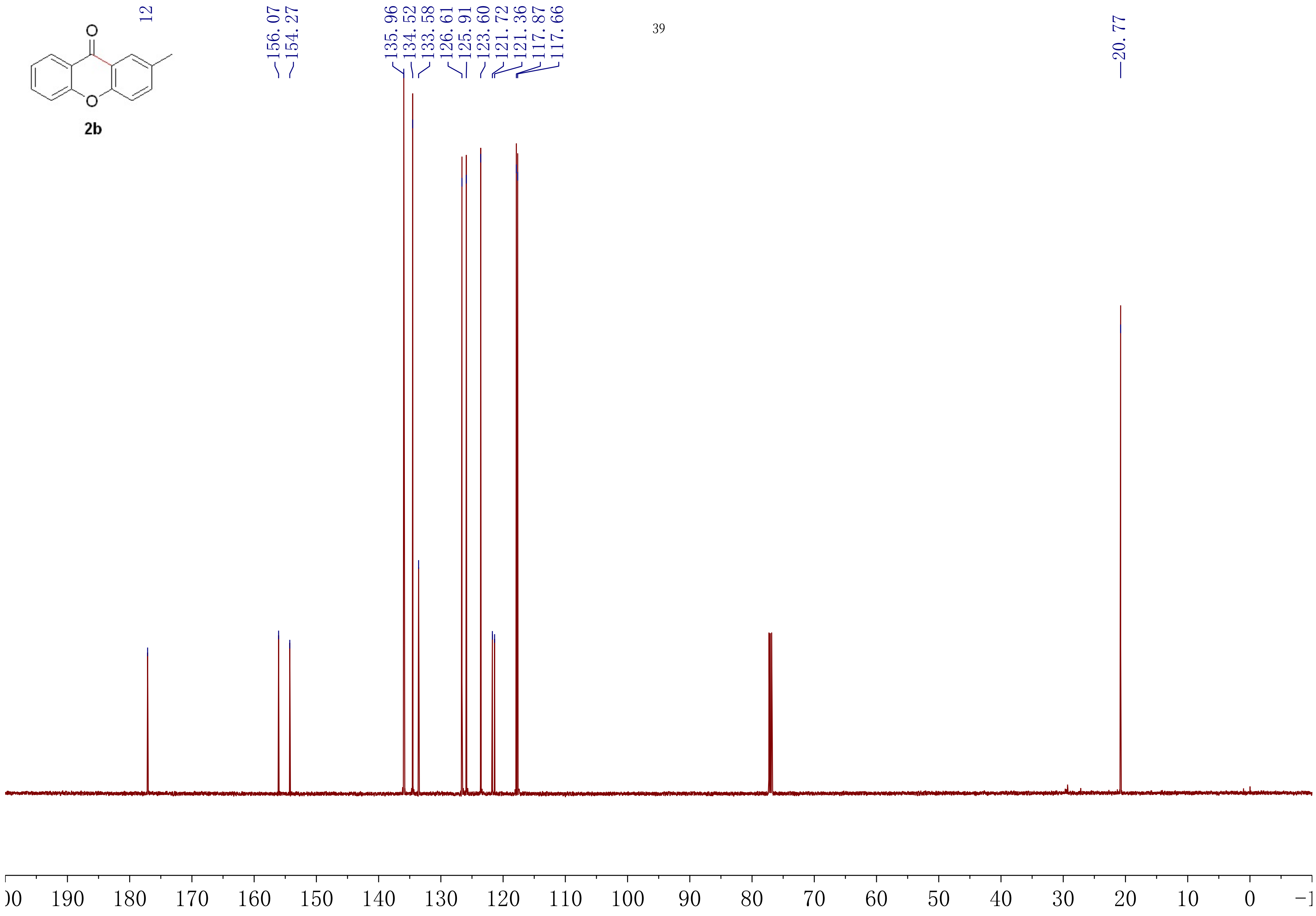
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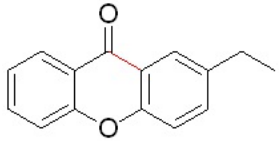

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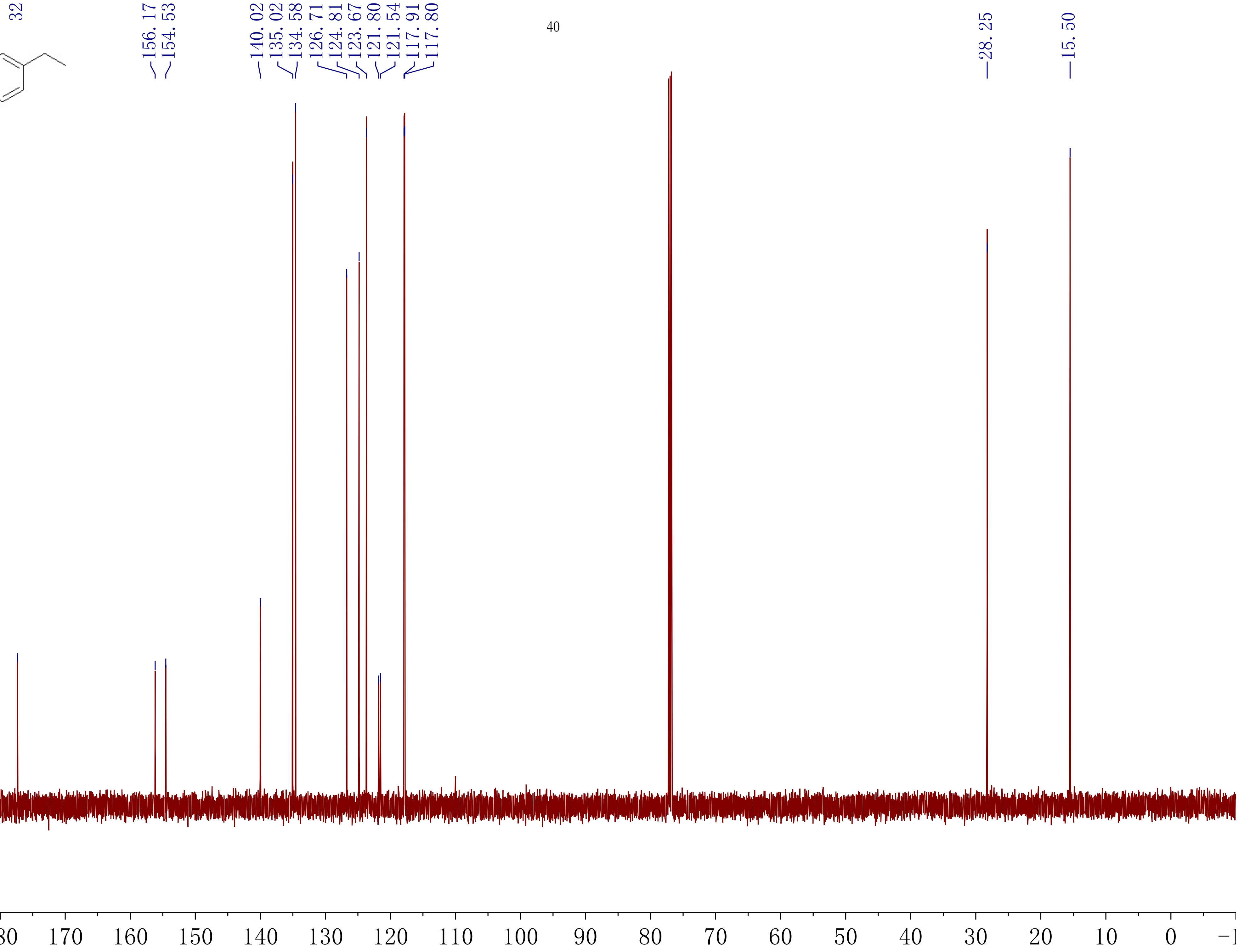
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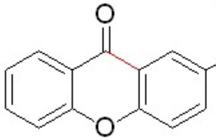

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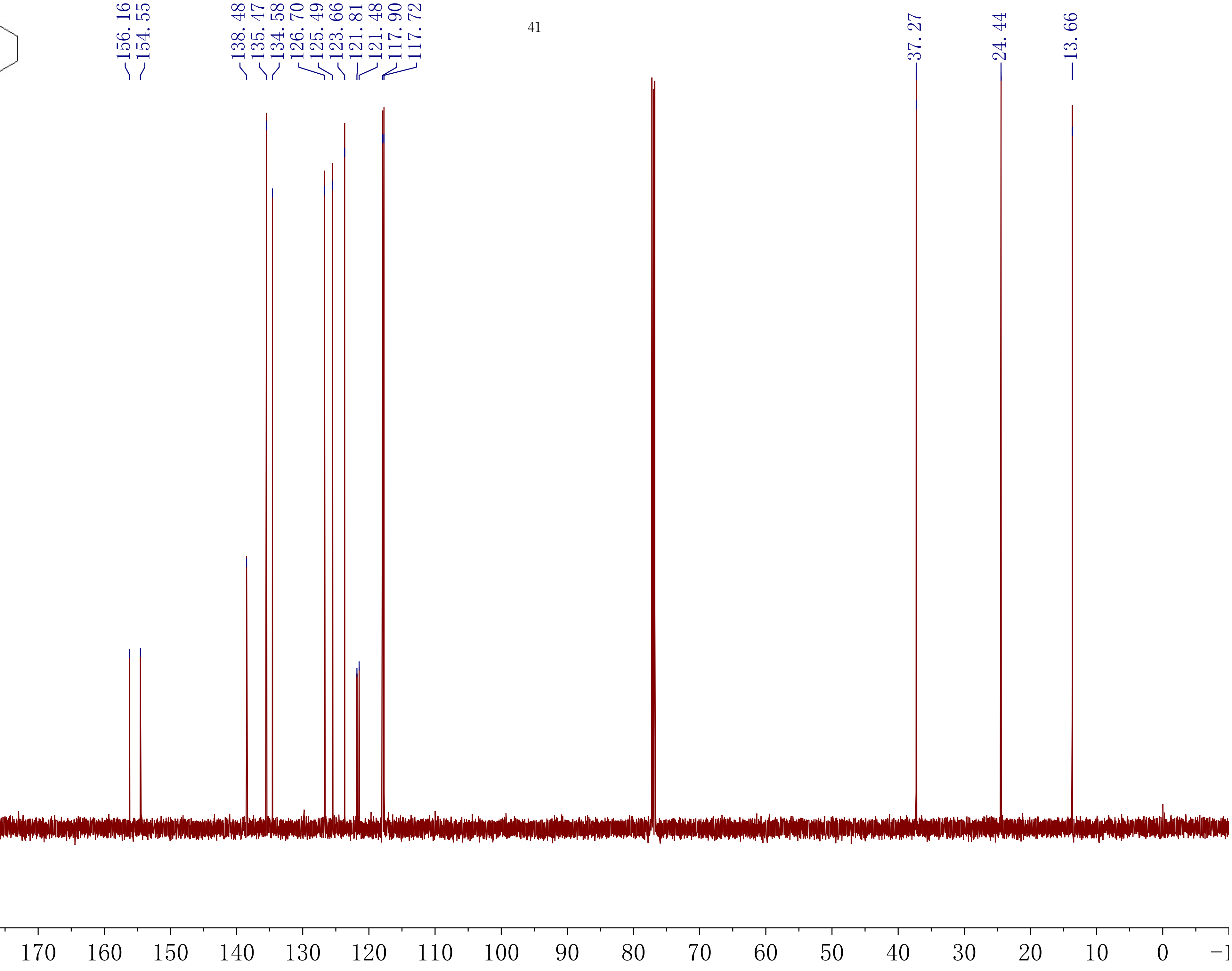
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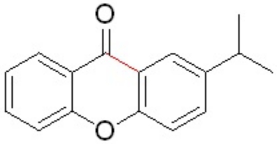

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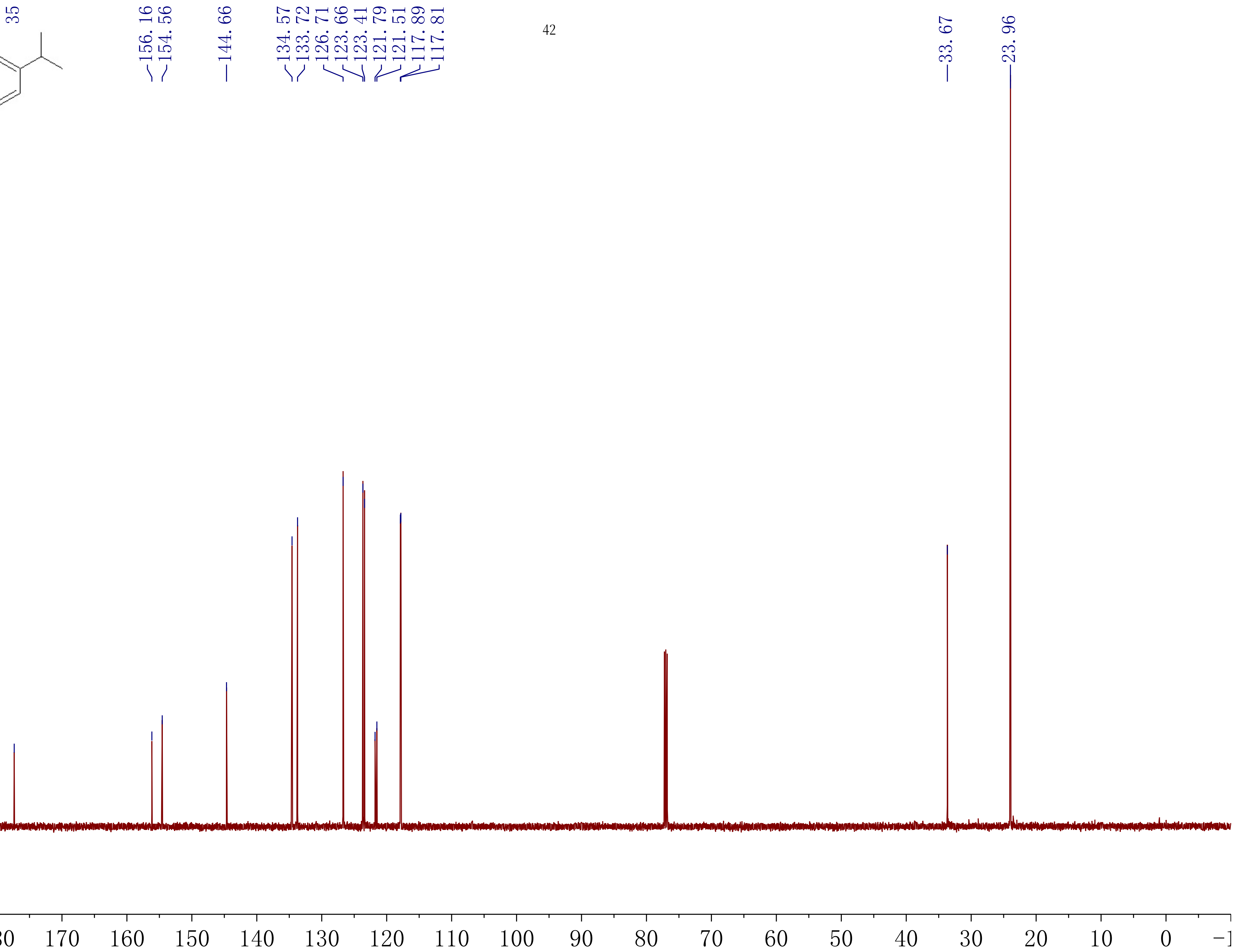

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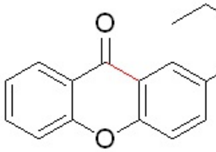

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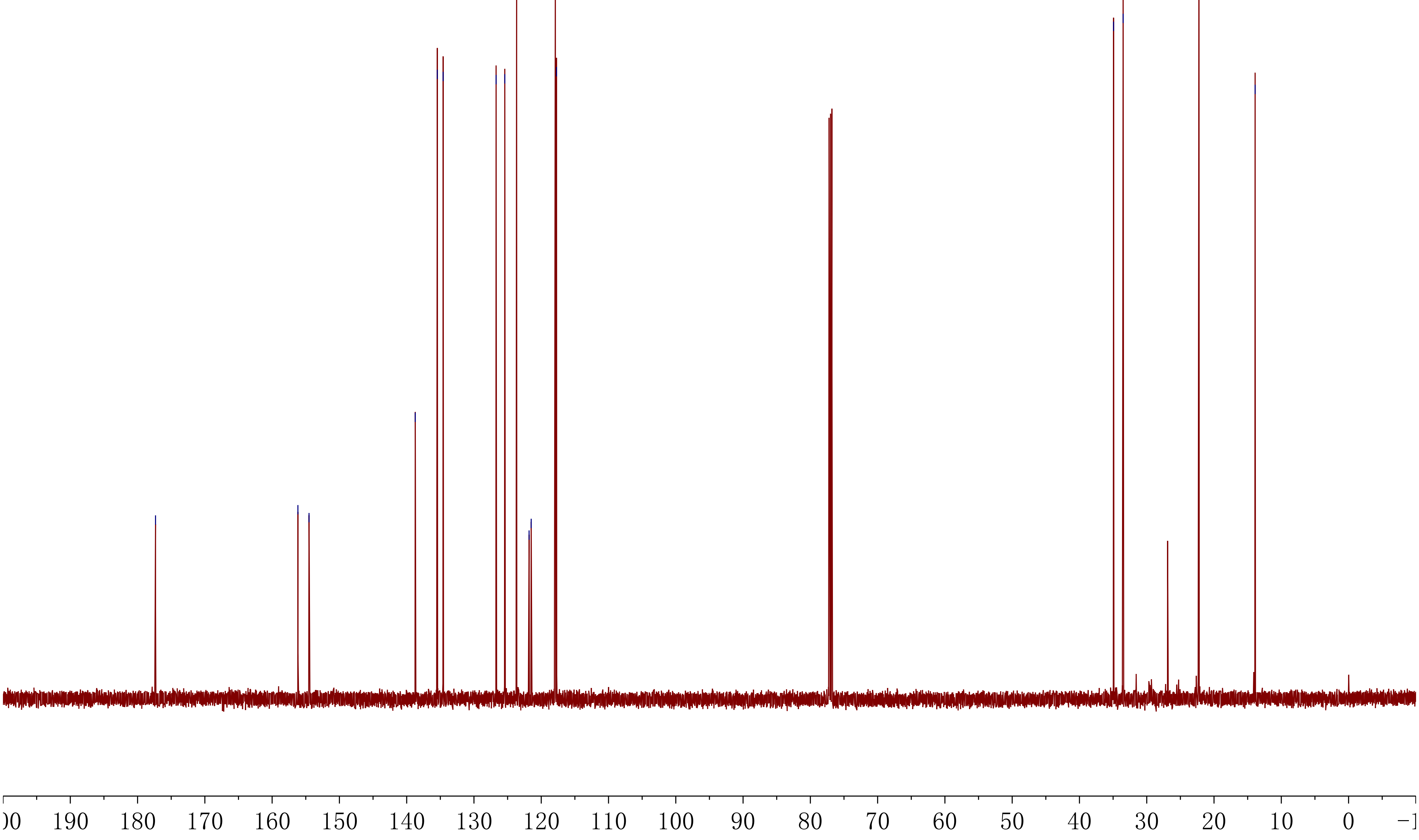
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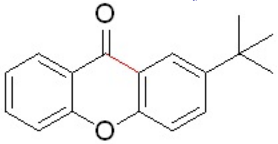

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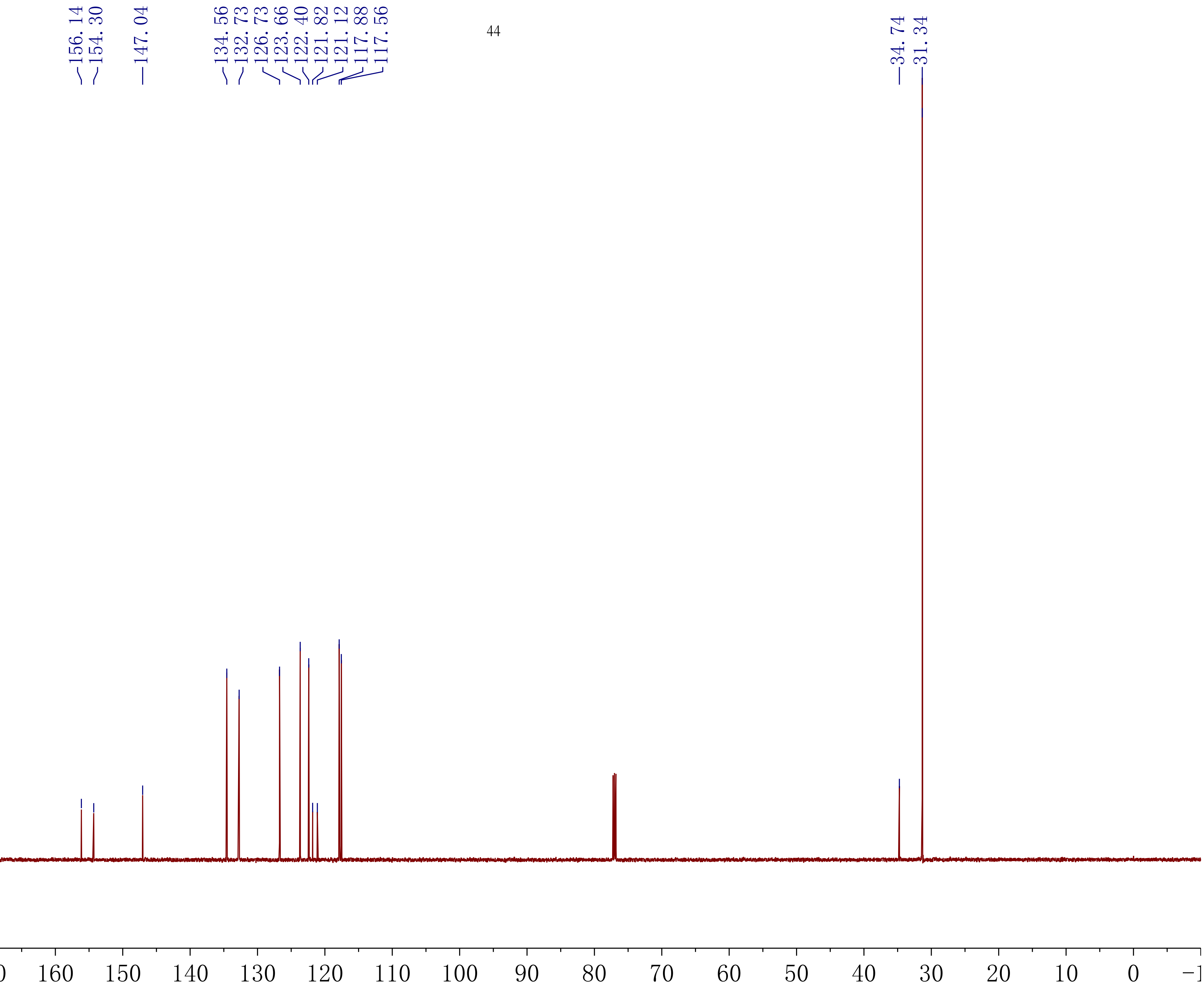

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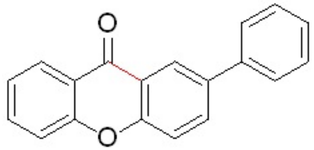

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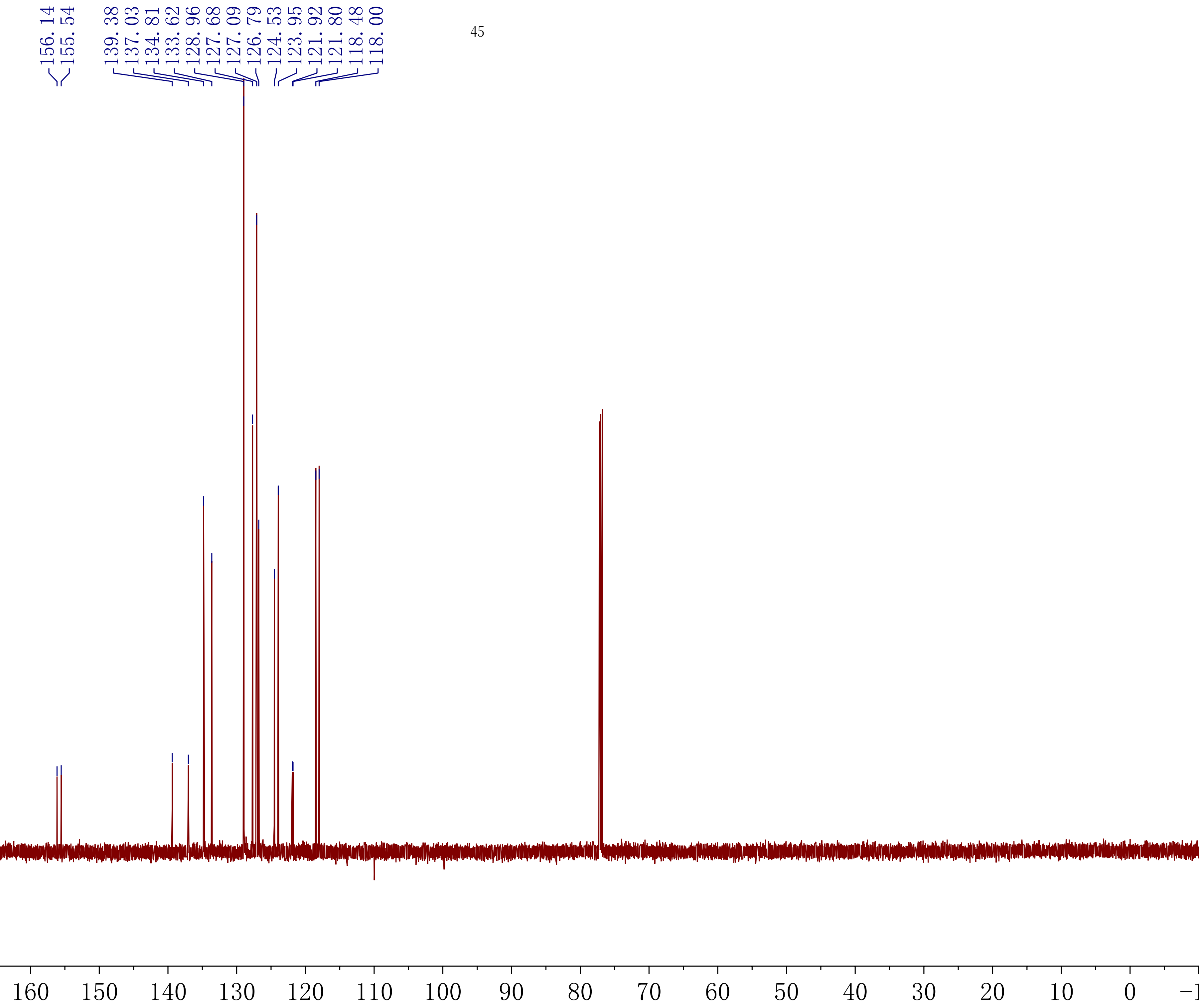
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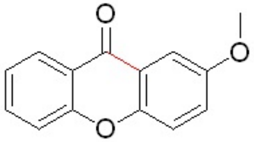

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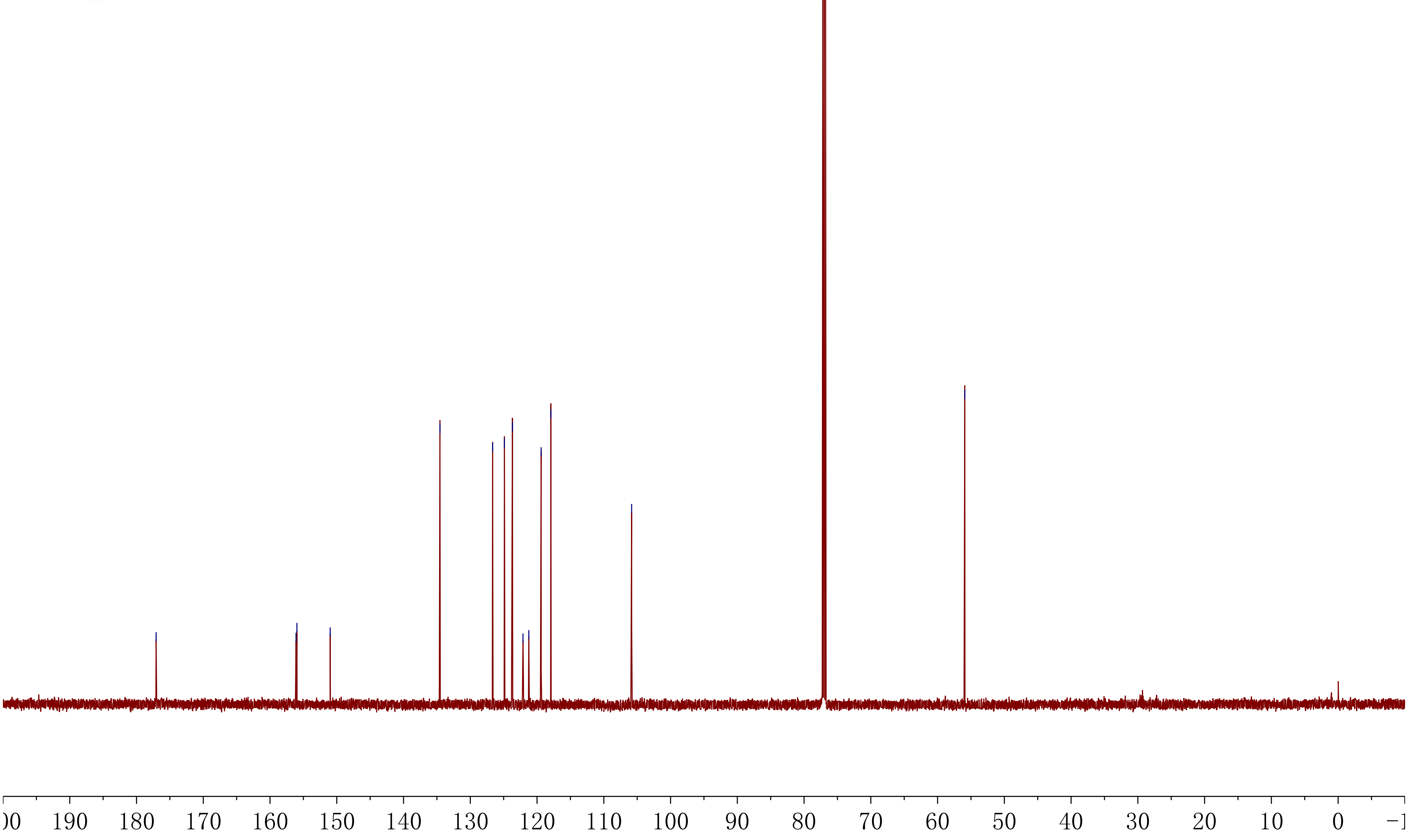
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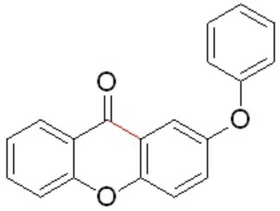
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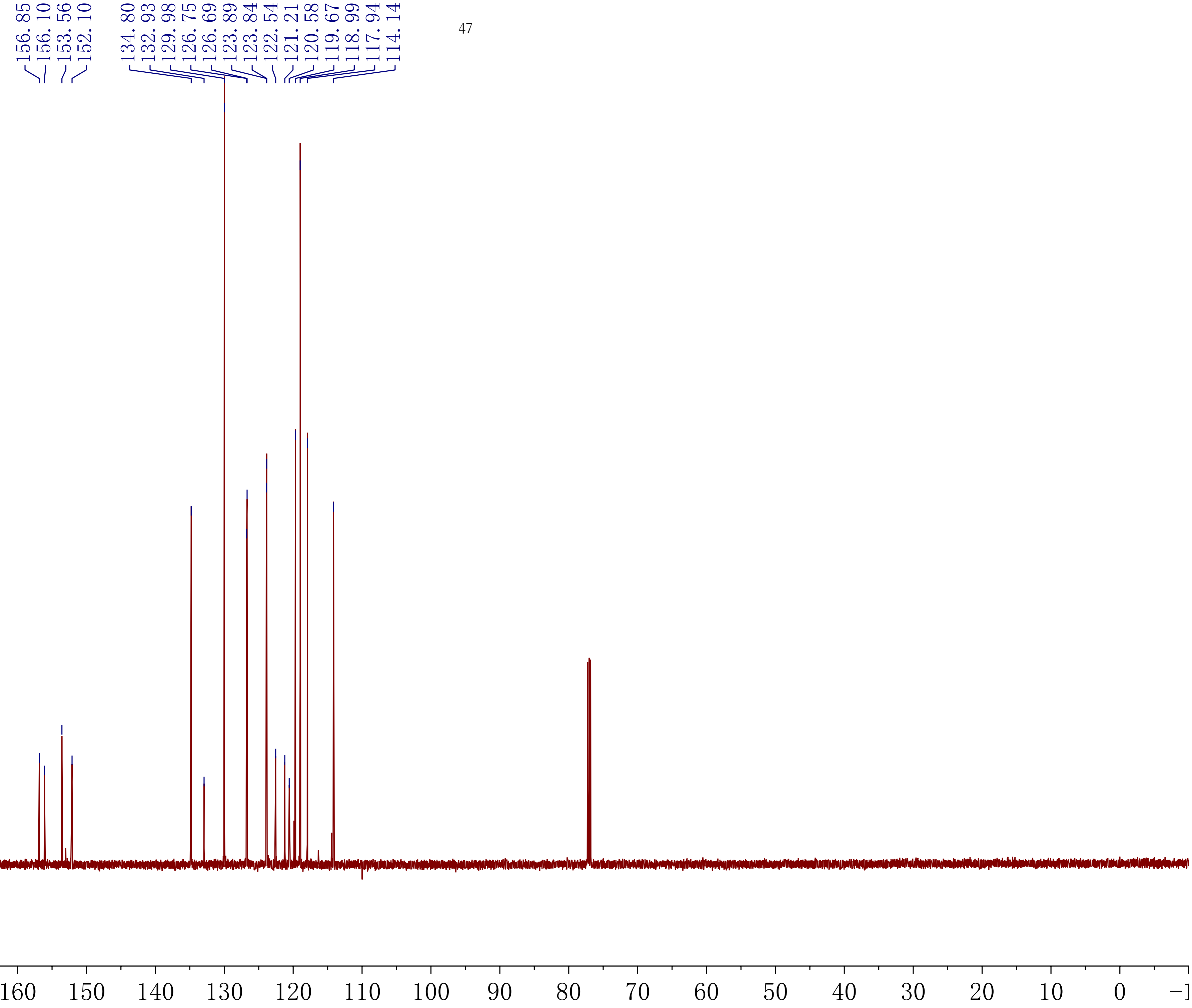
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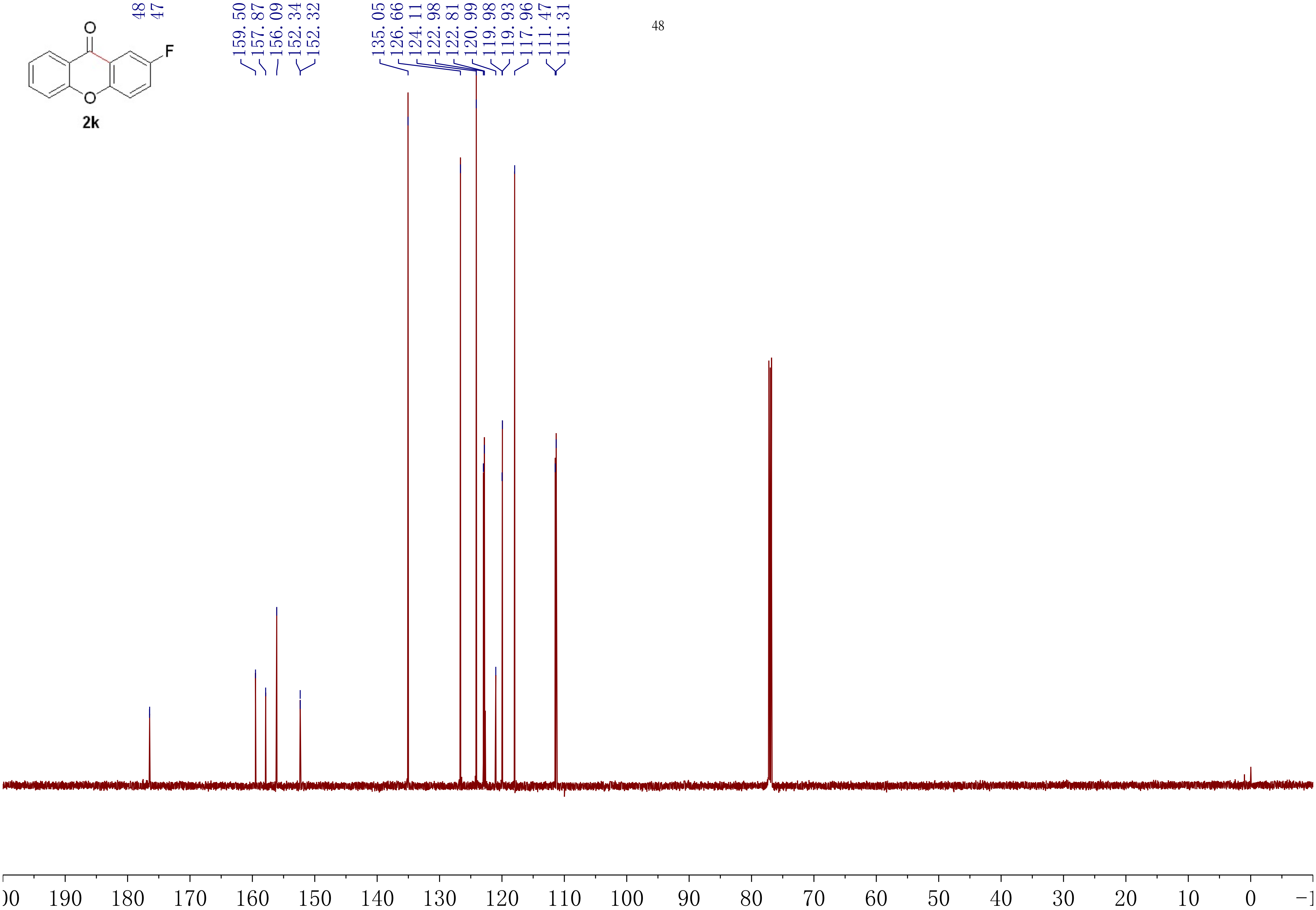
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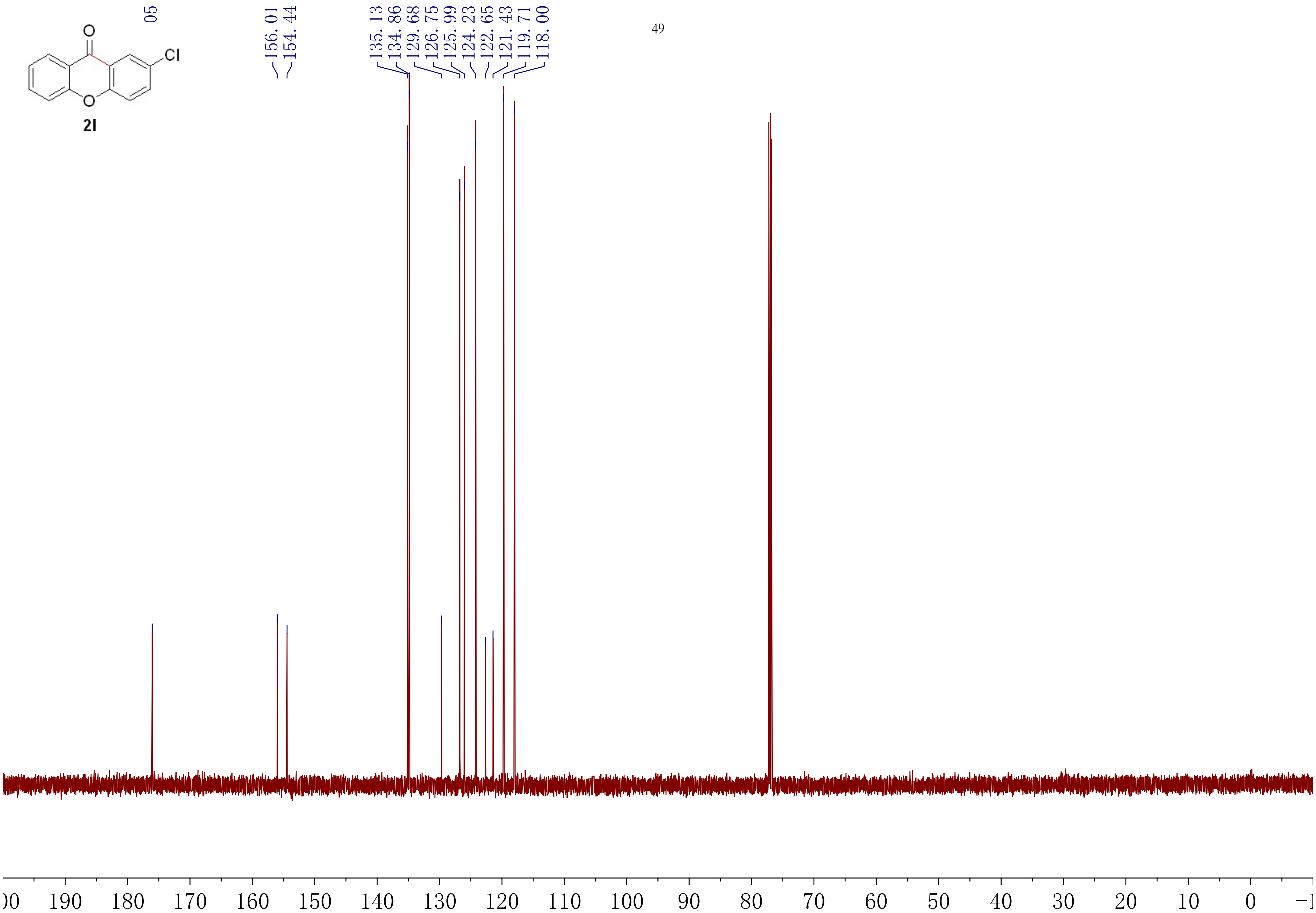

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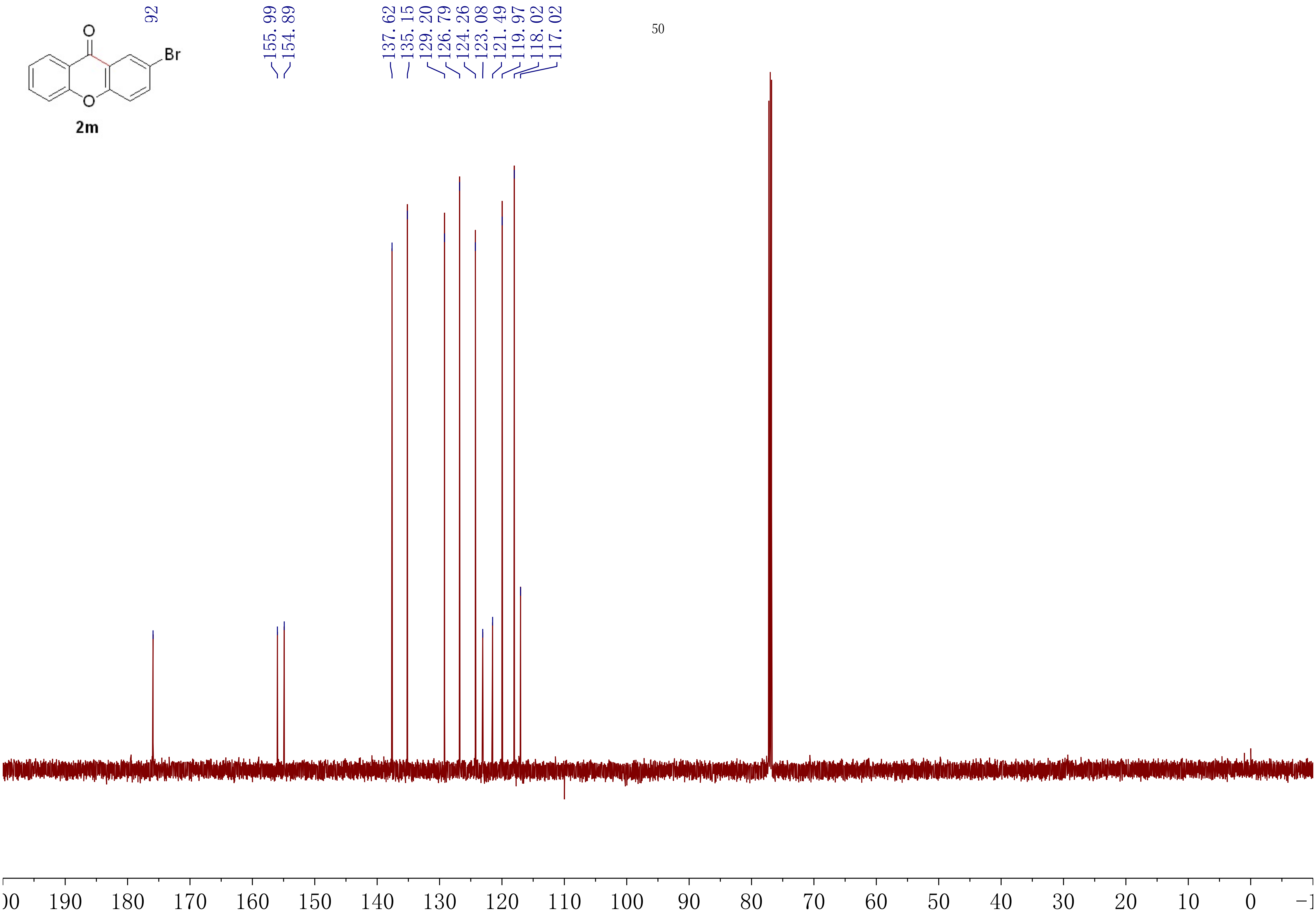

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O
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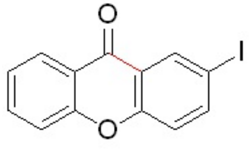

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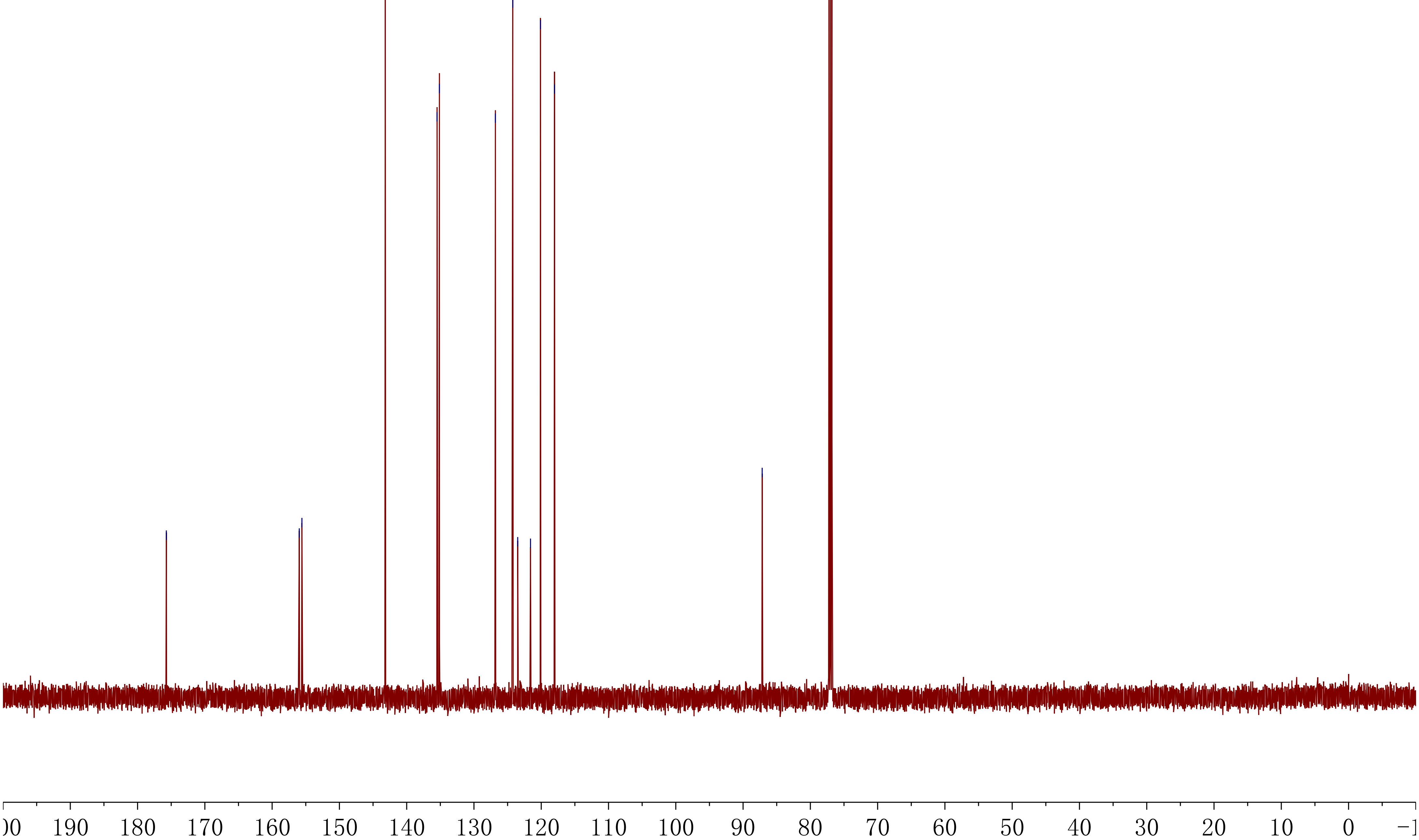
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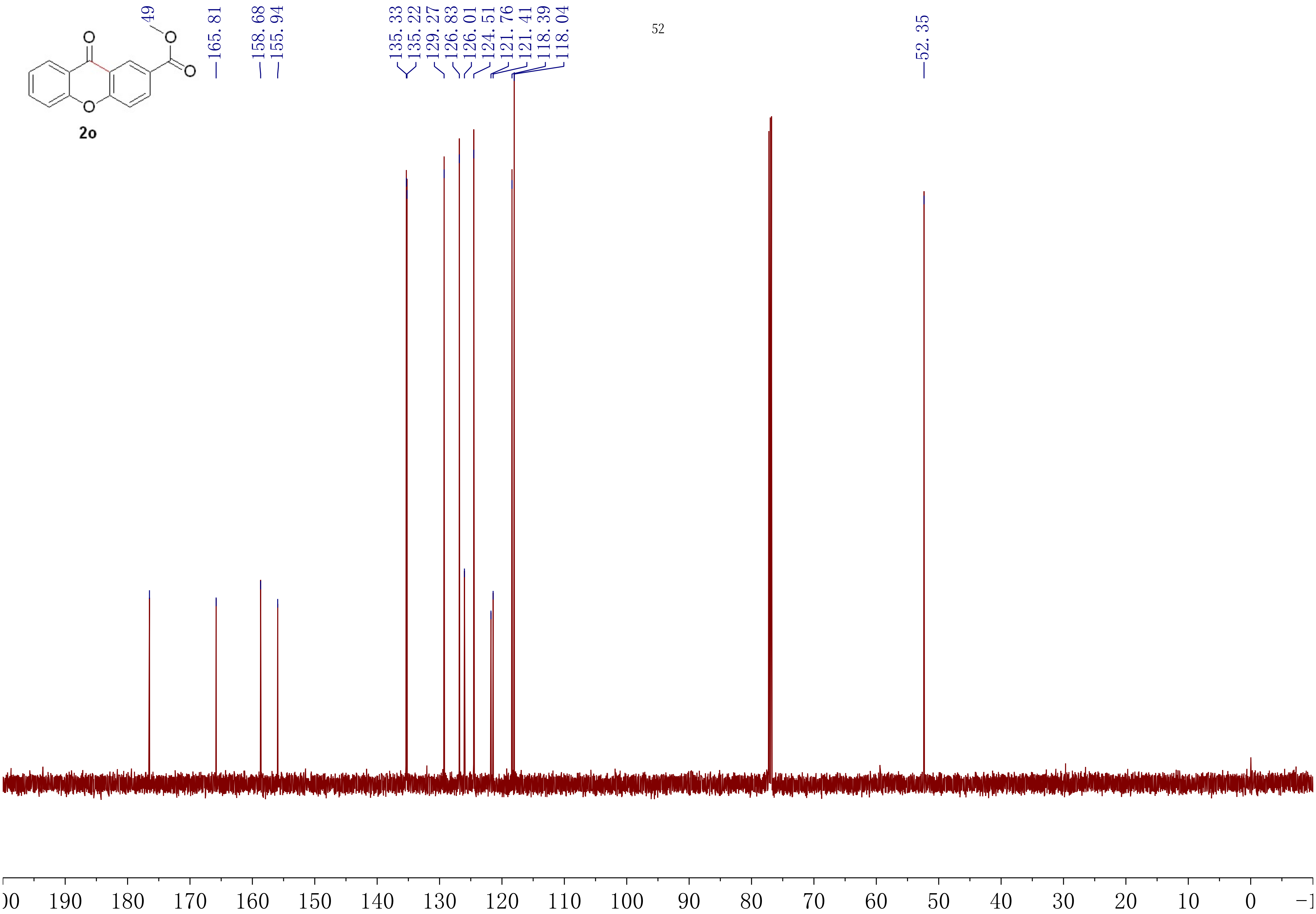

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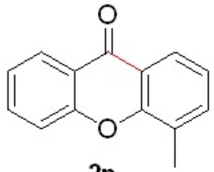

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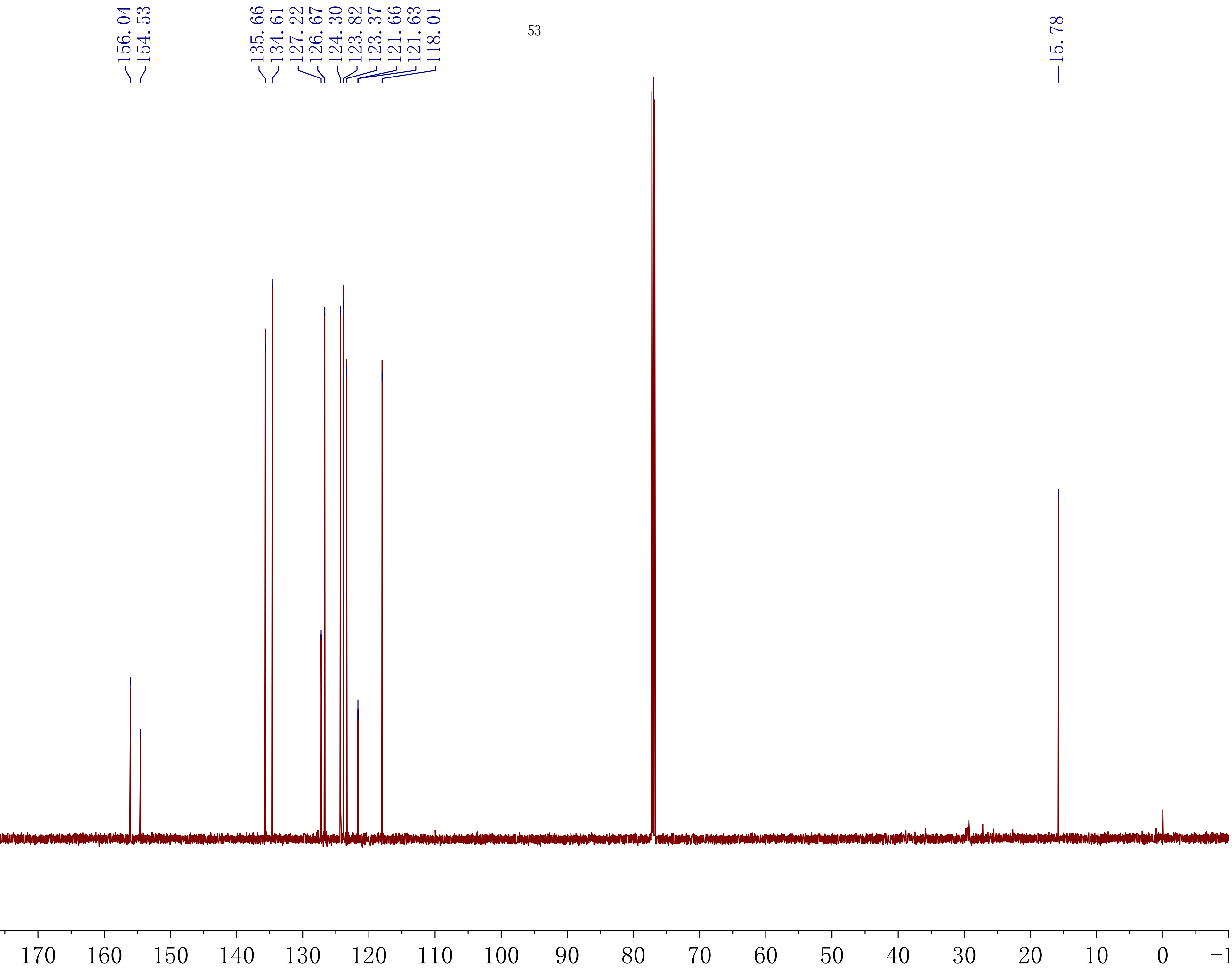
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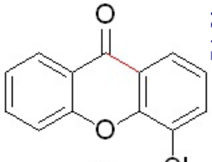
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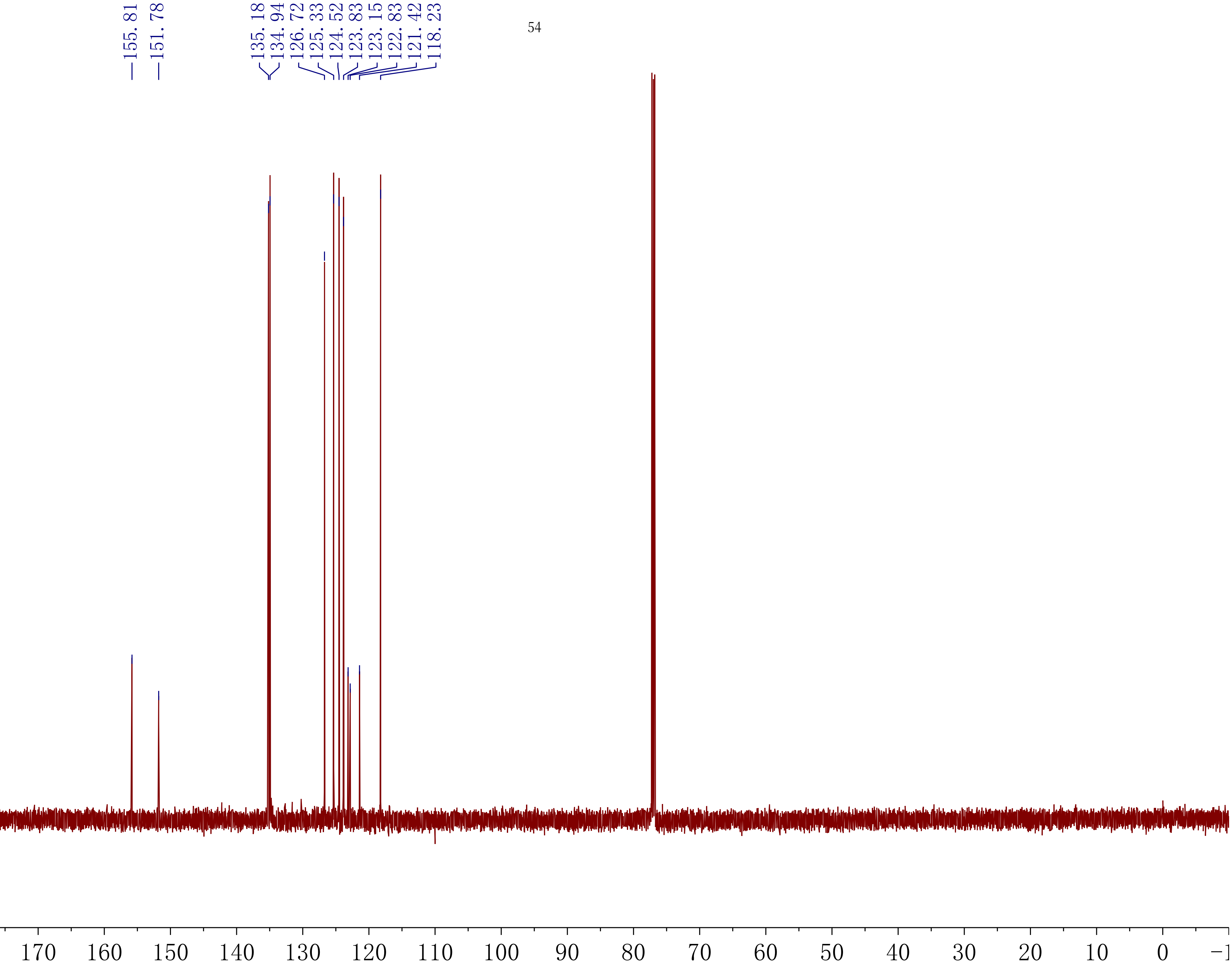
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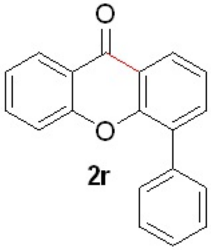
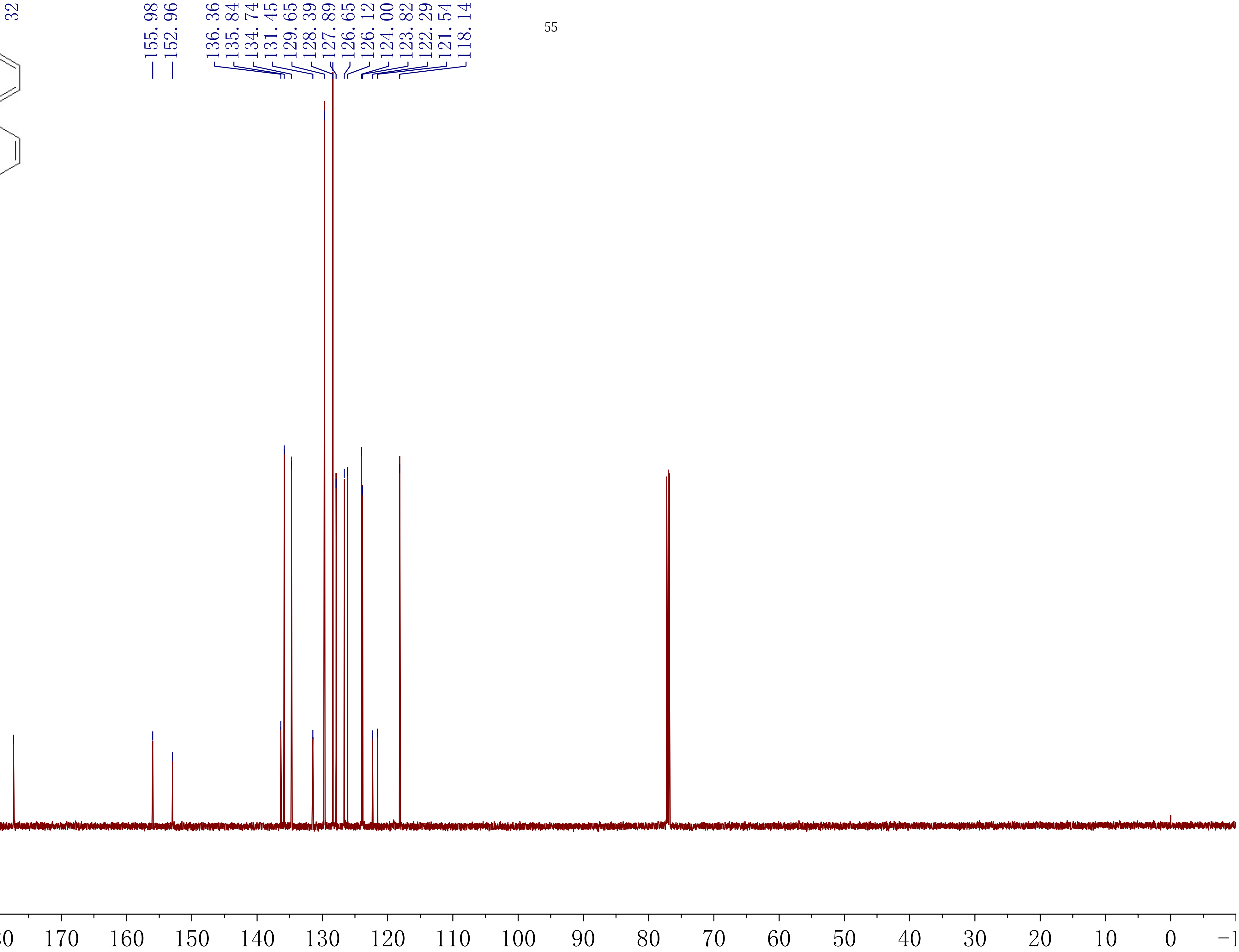


2r


32
155.98
152.96
136.36
135.84
134.74
131.45
129.65
128.39
127.89
126.65
126.12
124.00
123.82
122.29
121.54
118.14
190
180
170
160
150
140
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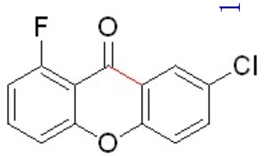
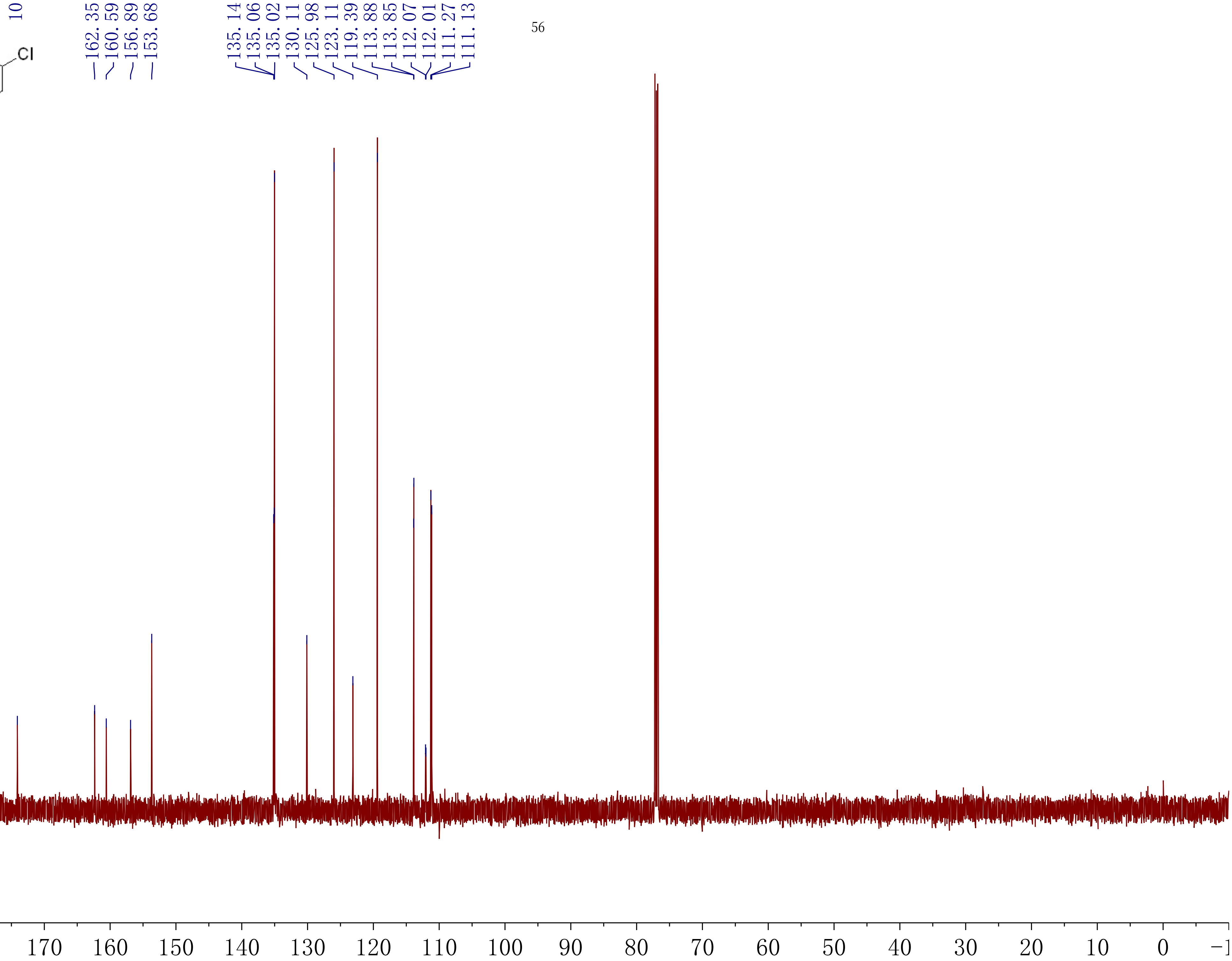
120
110
100
90
80
70
60
50
40
30
20
10
0


F
O
Cl
O

2s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162.35
160.59
156.89
153.68
135.14
135.06
135.02
130.11
125.98
123.11
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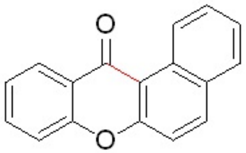
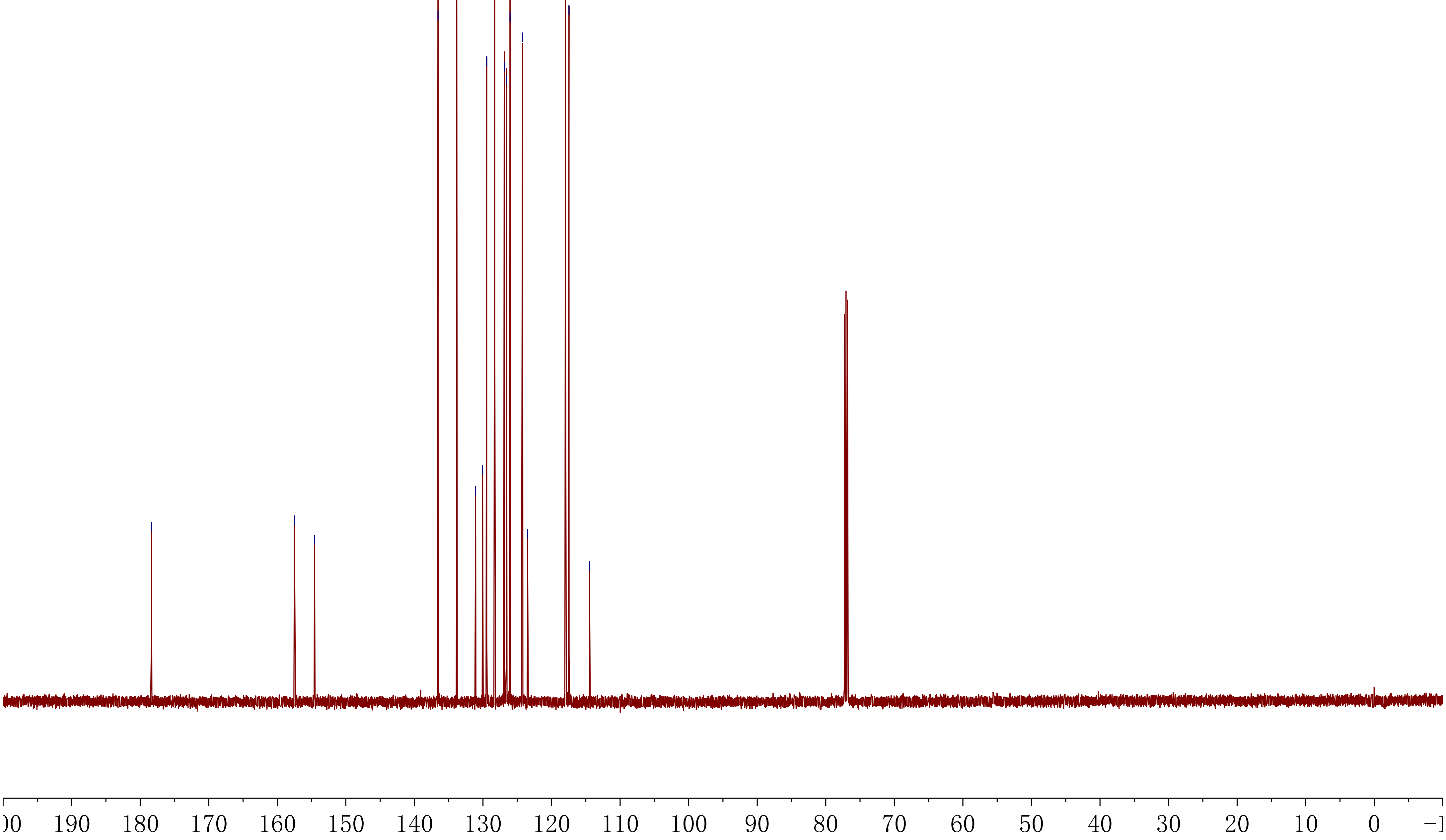
113.88
113.85
112.07
112.01
111.27
111.13
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1


O
O

2t


157.50
154.57
136.55
133.83
131.07
130.05
129.46
128.29
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126.59
126.05
124.23
123.50
117.96
117.46
114.46
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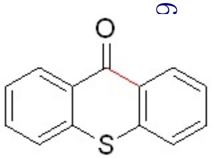
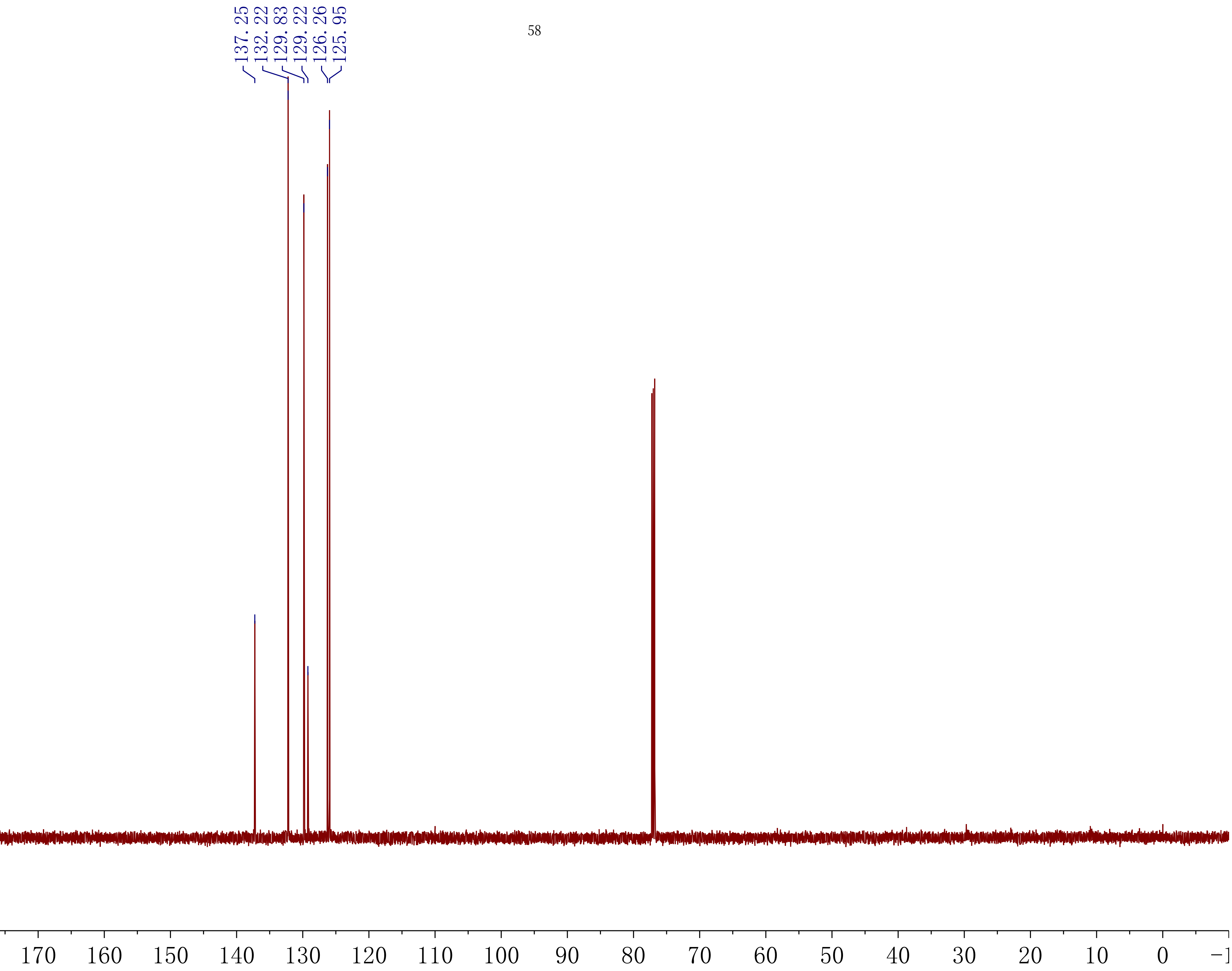
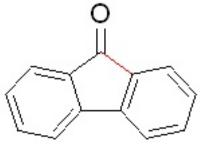
30
20
10
0



2u


90
137.25
132.22
129.83
129.22
126.26
125.95
)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1



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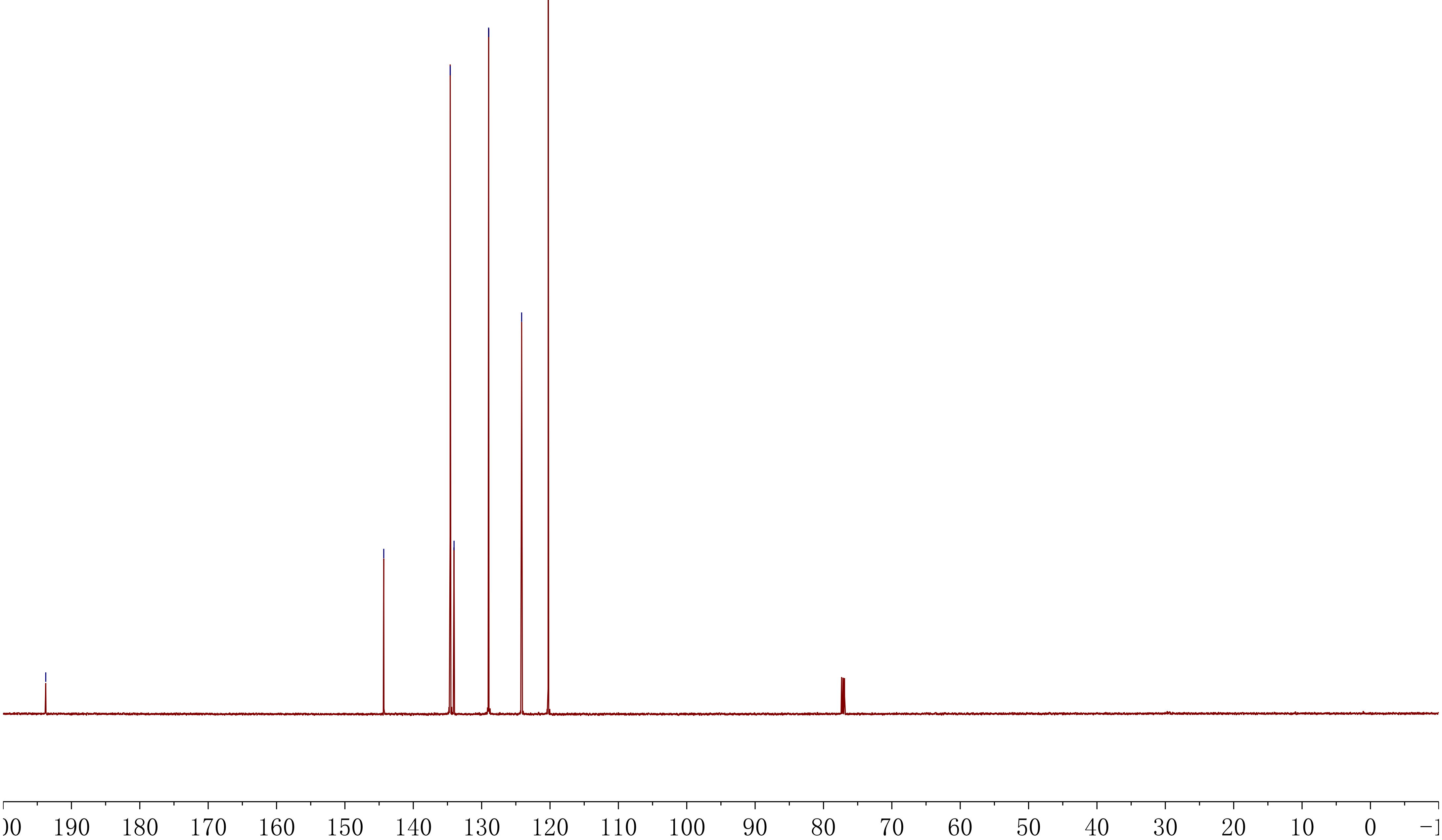
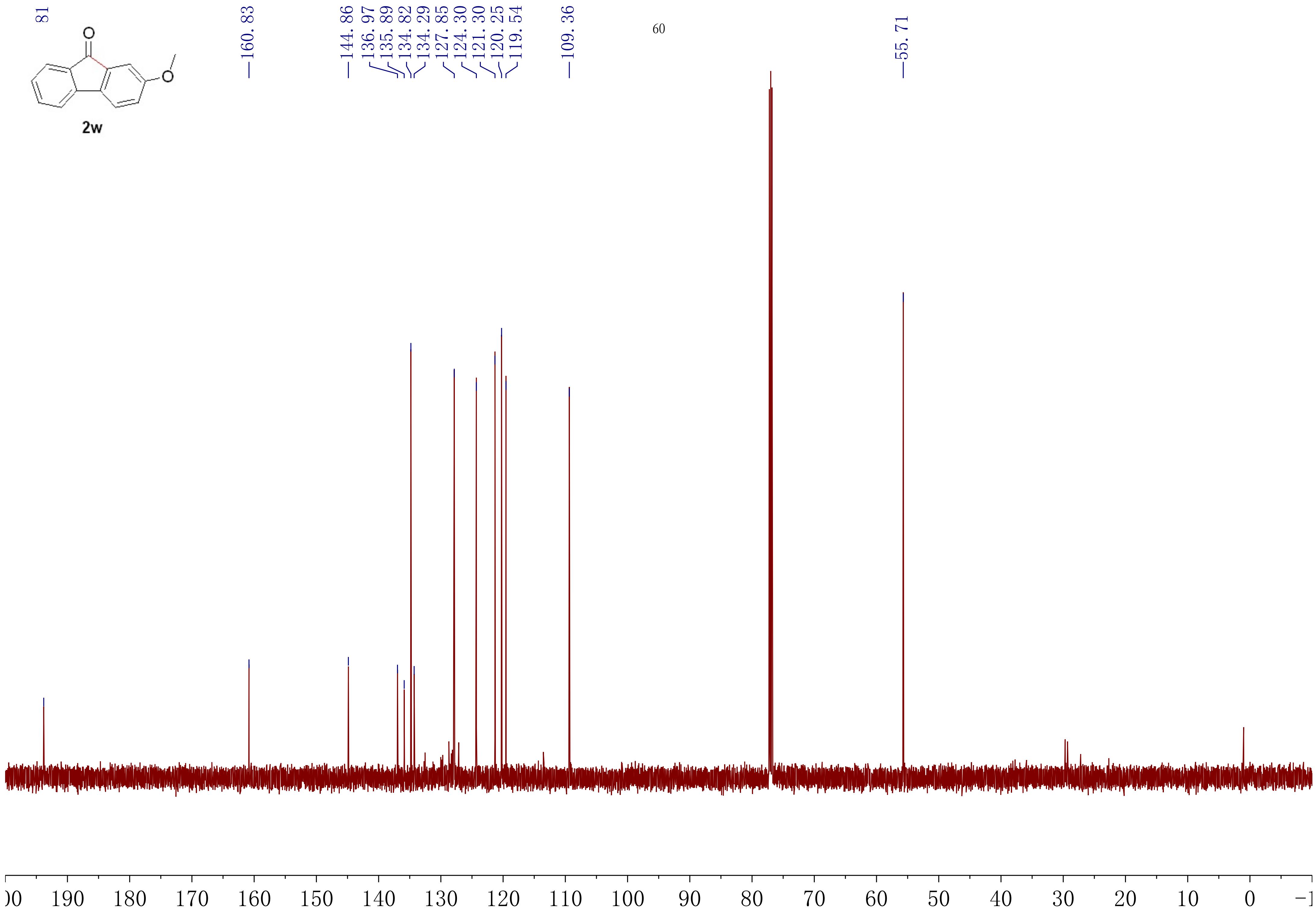


76
144.32
134.60
134.04
128.98
124.15
120.26
)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1


81
160.83
144.86
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134.82
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127.85
124.30
121.30
120.25
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109.36
55.71
2w
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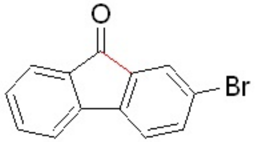

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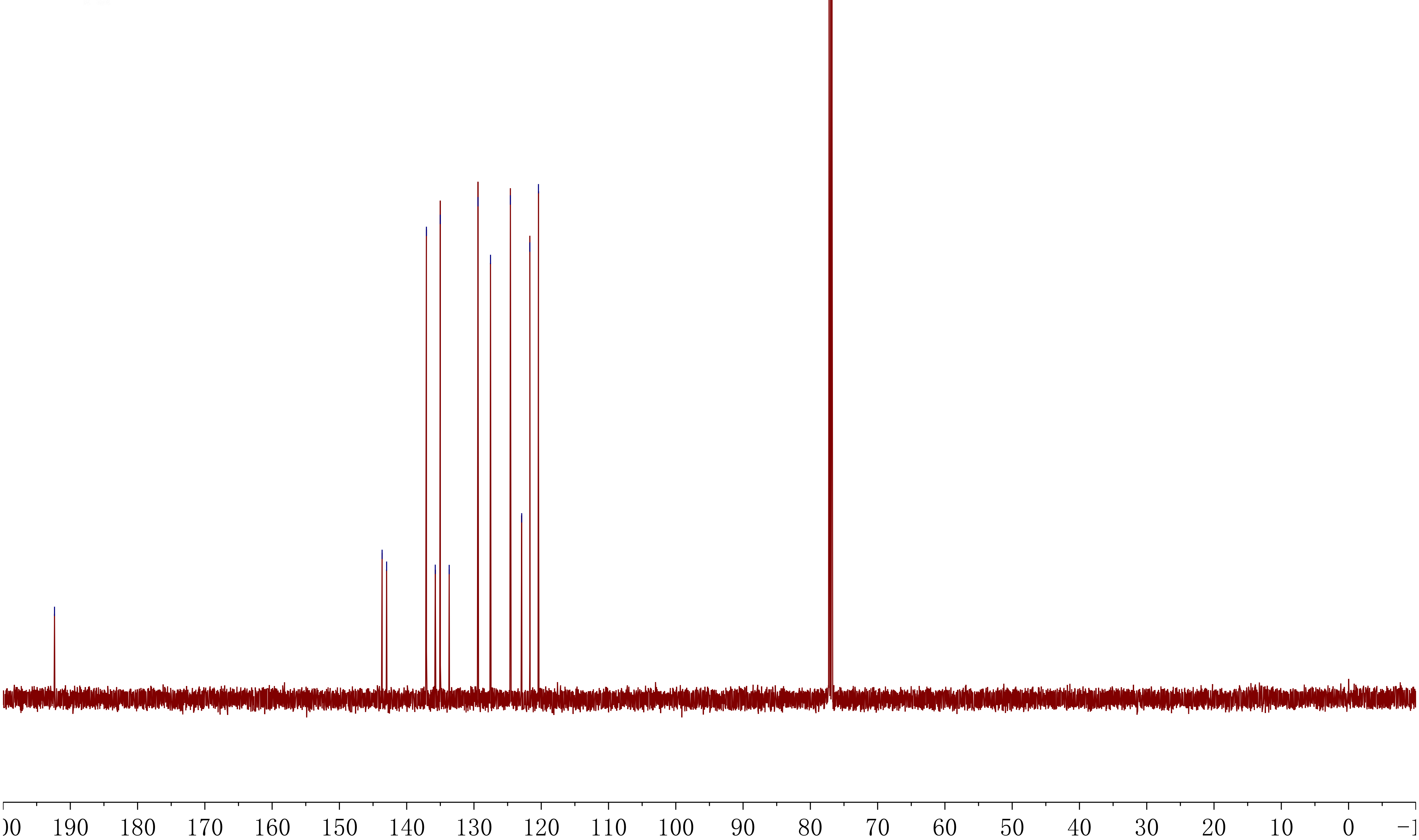
35
143.65
142.98
137.07
135.75
135.01
133.68
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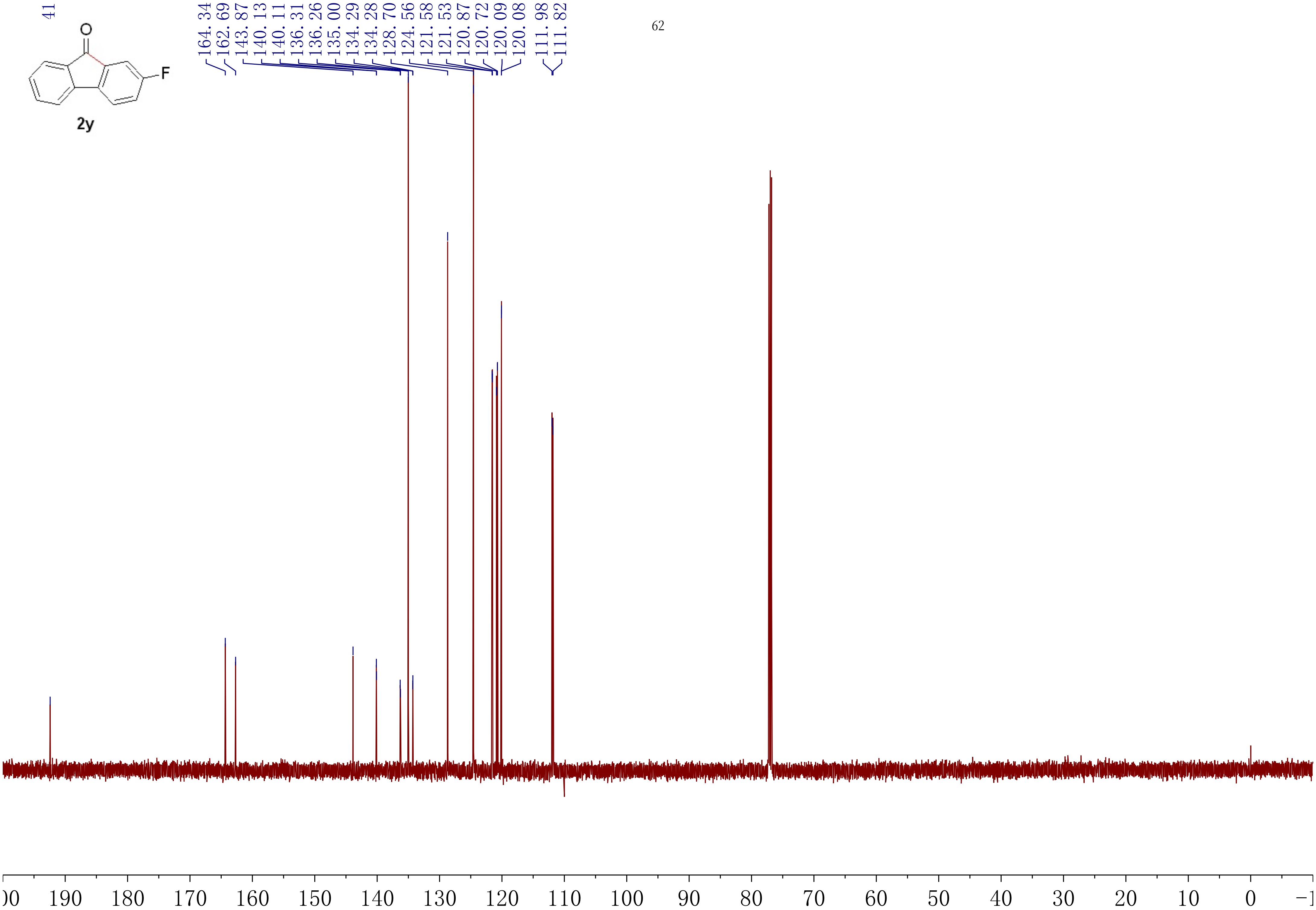
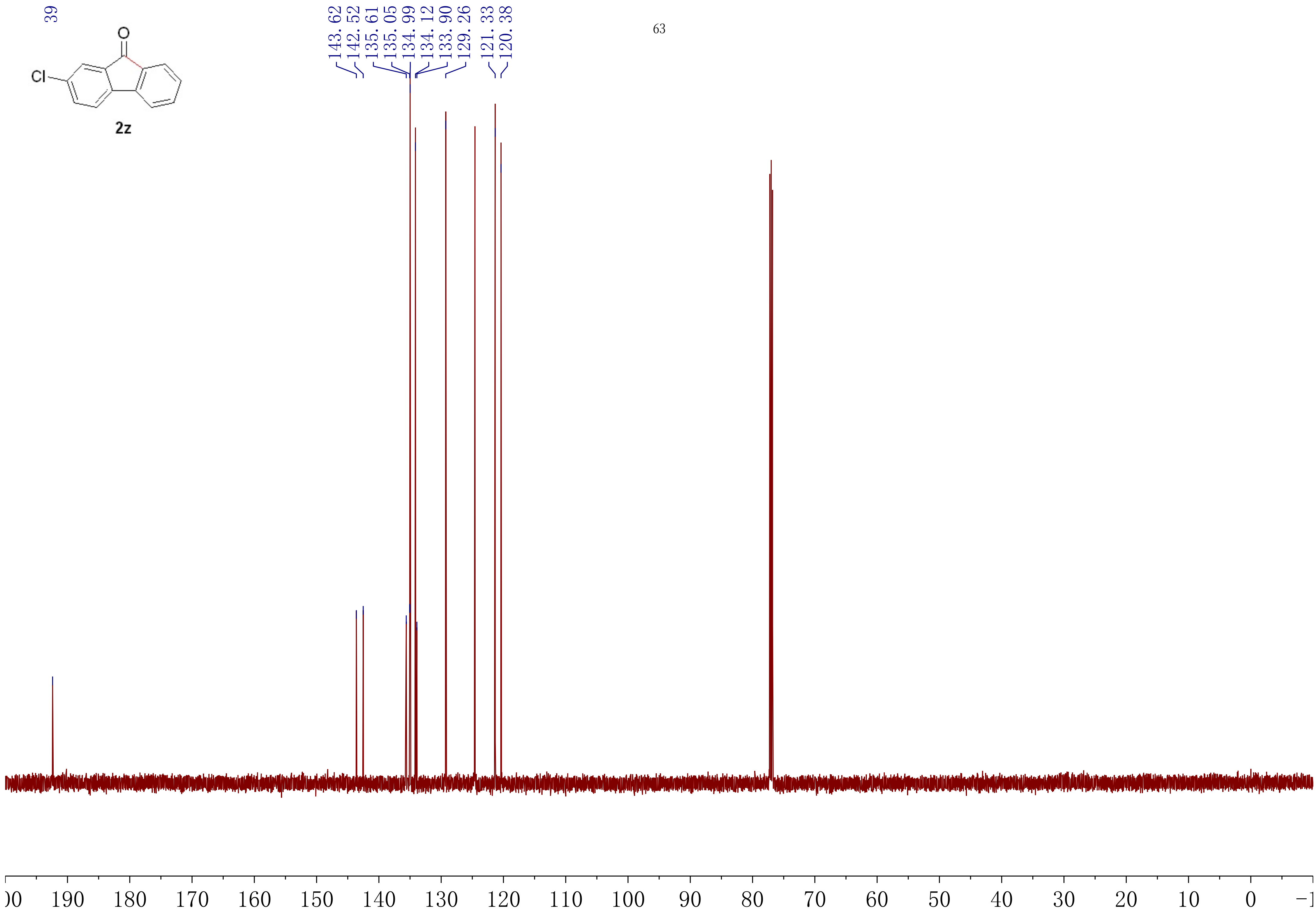
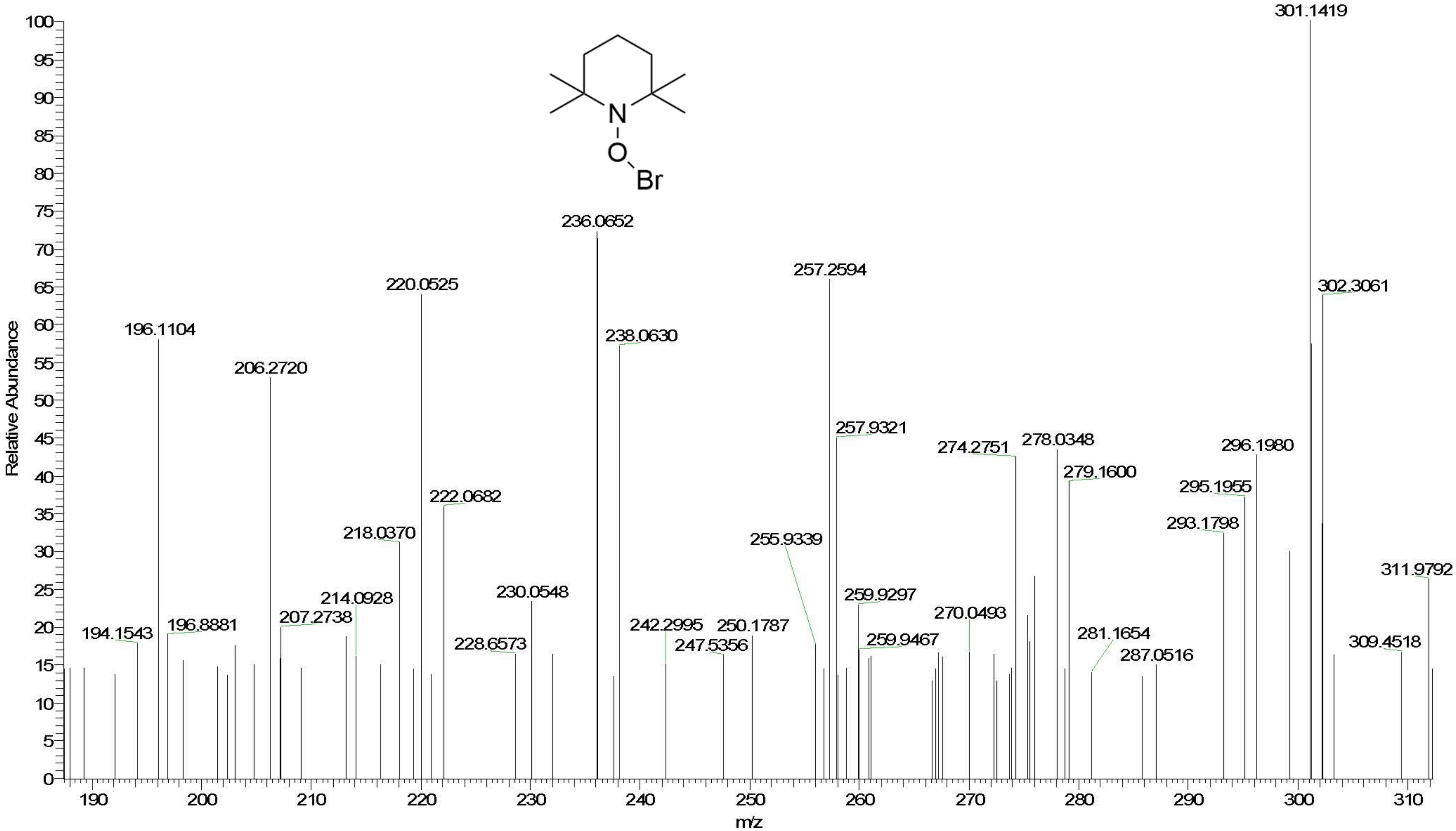
124.59
122.90
121.69
120.41
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

2y


O
F
41
164.34
162.69
143.87
140.13
140.11
136.31
136.26
135.00
134.29
134.28
128.70
124.56
121.58
121.53
120.87
120.72
120.09
120.08
111.98
111.82
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1


39
143.62
142.52
135.61
135.05
134.99
134.12
133.90
129.26
121.33
120.38
O
Cl
2z
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


N
O
Br
Relative Abundance
m/z
301.1419
236.0652
257.2594
220.0525
302.3061
196.1104
238.0630
206.2720
257.9321
274.2751
278.0348
296.1980
279.1600
295.1955
222.0682
293.1798
218.0370
255.9339
311.9792
214.0928
230.0548
259.9297
270.0493
194.1543
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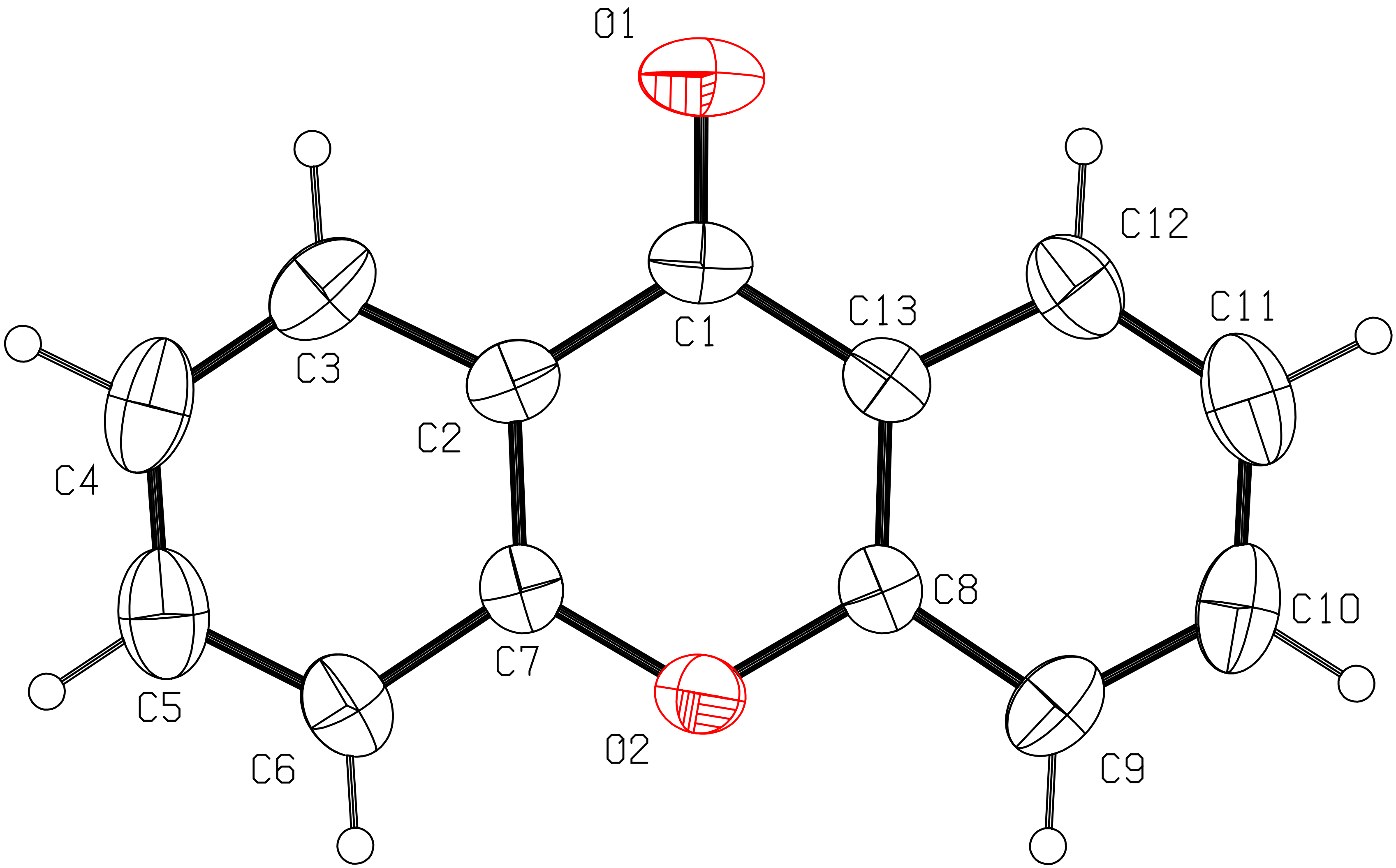
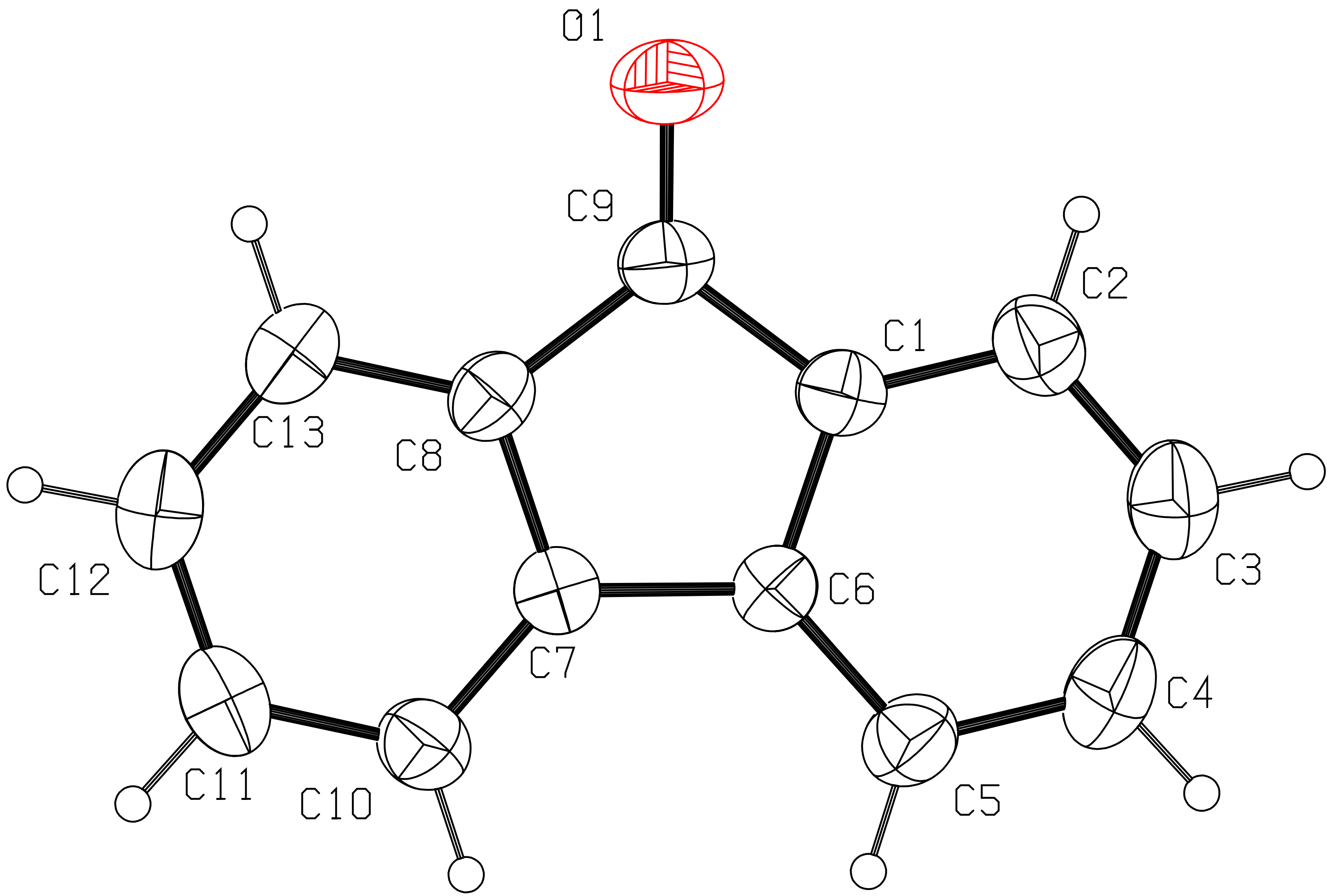
207.2738
242.2995
250.1787
281.1654
228.6573
247.5356
259.9467
309.4518
287.0516


O1
C12
C3
C1
C13
C11
C2
C4
C8
C10
C7
C5
C6
O2
C9


O1
C9
C2
C1
C13
C8
C12
C3
C6
C7
C4
C11
C10
C5