Supporting Information

Tandem radical cyclization to construct poly-brominated 2-oxindoles

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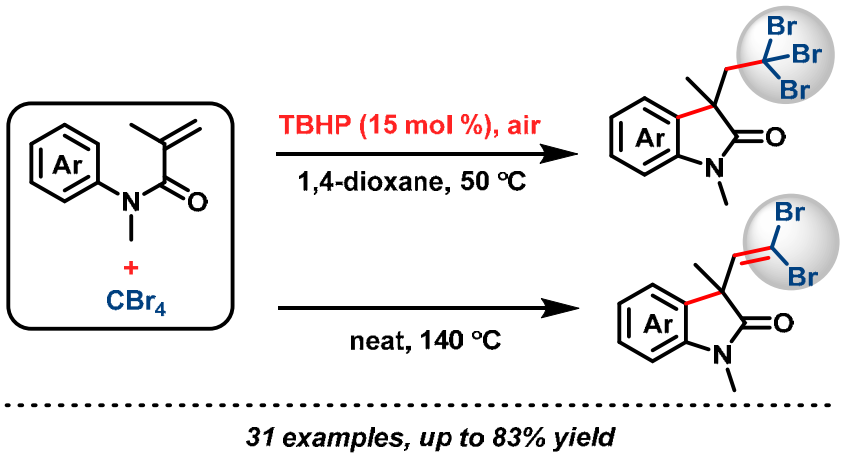

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General information. The starting materials and reagents, purchased from commercial suppliers, were used without further purification. Literature procedures were used for the preparation of *N*-arylacrylamides (*Tetrahedron,* **2015**, *56,* 2512). Solvents were purified by standard methods. Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Flash chromatography was carried out using silica gel 200−300. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were measured with TMS as internal standard when $CDCl_3$ was used as solvent. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. High resolution mass spectra (HR-MS) were recorded under electrospray ionization (ESI) conditions.

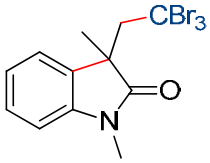
General procedure for the synthesis of tribromomethylated 2-oxindoles (2).

To a stirred solution of *N*-arylacrylamide (**1**, 1 mmol) and CBr_4 (1.1 equiv.) in dioxane (10 mL), TBHP (15 mol %) were added. The reactions were performed at 50 ^{o}C under air atmosphere (open flask) and completed within 18-48 hours as monitored by TLC. The products (**2)** were isolated by flash column chromatographic separation (EA/PE = 1:10).

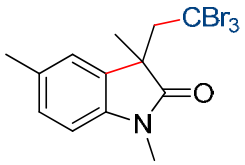
General procedure for the synthesis of dibromoalkenes (3).

A mixture of **1** (1 mmol) and CBr_4 (1 equiv.) was stirred at 140 ^{o}C. The reactions were completed in 8 hours as monitored by TLC. The products (**3)** were isolated by flash column chromatographic separation (EA/PE = 1:9).

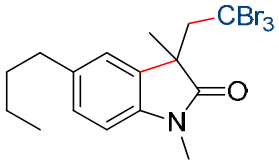
Characterization of the products



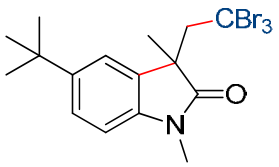
1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2a) The desired pure product was obtained in 81% yield (342.5 mg) as a white solid, mp 148-150 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.12 (d, *J* = 15.6 Hz, 1H), 3.72 (d, *J* = 15.6 Hz, 1H), 3.23 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 143.5, 128.7, 128.7, 128.6, 126.6, 121.8, 108.4, 63.7, 50.1, 32.9, 32.9, 32.8, 27.1, 26.7, 26.7. HRMS (ESI) exact mass calcd for $C_{12}H_{13}Br_3NO$ [M+H] m/z 423.8547, found 423.8545.



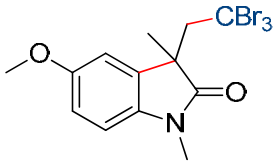
1,3,5-trimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2b) The desired pure product was obtained in 80% yield (353.8 mg) as a white solid, mp 167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 3.2 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 4.11 (d, *J* = 15.5 Hz, 1H), 3.70 (d, *J* = 15.5 Hz, 1H), 3.22 (s, 3H), 2.34 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 141.2, 131.3, 128.8, 128.7, 127.3, 108.1, 63.6, 50.1, 33.0, 27.1, 26.7, 21.2. HRMS (ESI) exact mass calcd for $C_{13}H_{15}Br_3NO$ [M+H] m/z 437.8704, found 437.8700.



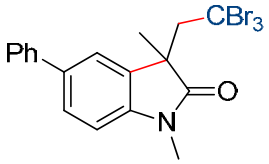
5-butyl-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2c) The desired pure product was obtained in 79% yield (377.6 mg) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 4.11 (d, *J* = 15.5 Hz, 1H), 3.70 (d, *J* = 15.5 Hz, 1H), 3.22 (s, 3H), 2.67 – 2.52 (m, 2H), 1.62 – 1.47 (m, 2H), 1.38 (s, 3H), 1.32 (dd, *J* = 14.7, 7.3 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 141.3, 136.5, 128.6, 128.3, 126.7, 108.0, 63.6, 50.1, 35.3, 34.0, 33.0, 27.1, 26.7, 22.2, 13.9. HRMS (ESI) exact mass calcd for $C_{16}H_{21}Br_3NO$ [M+H] m/z 479.9173, found 479.9168.



5-(tert-butyl)-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2d) The desired pure product was obtained in 80% yield (382.4 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.8 Hz, 1H), 7.34 – 7.29 (m, 1H), 6.79 (t, *J* = 8.1 Hz, 1H), 4.11 (dd, *J* = 15.6, 8.3 Hz, 1H), 3.71 (dd, *J* = 12 Hz， 1H), 3.22 – 3.19 (m, 3H), 1.38 (d, *J* = 8.2 Hz, 3H), 1.30 – 1.27 (m, 9H). ^{13}C NMR (151 MHz, cdcl$_3$) δ 178.6, 144.8, 141.1, 128.1, 124.9, 124.2, 107.7, 63.6, 50.3, 34.6, 33.0, 31.5, 27.1, 26.7. HRMS (ESI) exact mass calcd for $C_{16}H_{21}Br_3NO$ [M+H] m/z 479.9173, found 479.9176.

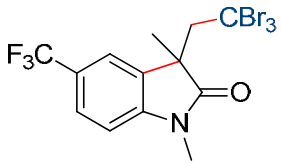


5-methoxy-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2e) The desired pure product was obtained in 77% yield (348.0 mg) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 2.5 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 4.13 (d, *J* = 15.6 Hz, 1H), 3.80 (s, 3H), 3.70 (d, *J* = 15.5 Hz, 1H), 3.22 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 155.4, 137.2, 130.0, 114.2, 112.9, 108.6, 63.6, 55.9, 50.5, 32.8, 27.2, 26.8. HRMS (ESI) exact mass calcd for $C_{13}H_{15}Br_3NO_2$ [M+H] m/z 453.8653, found 453.8655.

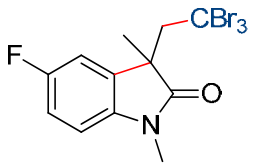


1,3-dimethyl-5-phenyl-3-(2,2,2-tribromoethyl)indolin-2-one (2f) The desired pure product was obtained in 75% yield (373.5 mg) as a white solid, mp 142-144 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.3 Hz, 1H), 7.54 (dd, *J* = 11.6, 4.6 Hz, 3H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 4.16 (d, *J* = 15.6 Hz, 1H), 3.78 (d, *J* = 15.6 Hz, 1H), 3.27 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 143.5, 128.7, 128.7, 128.6, 126.6, 121.8,

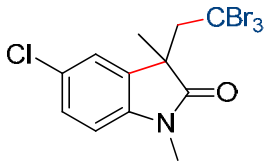
108.4, 63.7, 50.1, 32.9, 32.9, 32.8, 27.1, 26.7, 26.7. HRMS (ESI) exact mass calcd for $C_{18}H_{17}Br_3NO$ [M+H] m/z 499.8860, found 499.8868.



1,3-dimethyl-3-(2,2,2-tribromoethyl)-5-(trifluoromethyl)indolin-2-one (2g) The desired pure product was obtained in 74% yield (362.6 mg) as a white solid, mp 181-183 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.62 – 7.57 (m, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 4.15 (d, *J* = 15.6 Hz, 1H), 3.75 (d, *J* = 15.6 Hz, 1H), 3.27 (d, *J* = 4.8 Hz, 3H), 1.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 143.5, 128.7, 128.7, 128.6, 126.6, 121.8, 108.4, 63.7, 50.1, 32.9, 32.9, 32.8, 27.1, 26.7, 26.7. HRMS (ESI) exact mass calcd for $C_{13}H_{12}$ Br_3F_3NO [M+H] m/z 491.8421, found 491.8416.

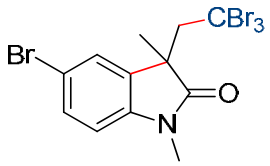


5-fluoro-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2h) The desired pure product was obtained in 79% yield (347.6 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.1, 2.5 Hz, 1H), 7.02 (td, *J* = 8.9, 2.5 Hz, 1H), 6.79 (dd, *J* = 8.5, 4.1 Hz, 1H), 4.13 (d, *J* = 15.6 Hz, 1H), 3.70 (d, *J* = 15.6 Hz, 1H), 3.22 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 159.5, 157.9, 139.5, 139.5, 130.4, 130.4, 115.0, 114.9, 114.7, 114.5, 108.8, 108.8, 63.5, 50.5, 50.5, 32.4, 27.0, 26.8. HRMS (ESI) exact mass calcd for $C_{12}H_{12}$ Br_3FNO [M+H] m/z 441.8453, found 441.8456.

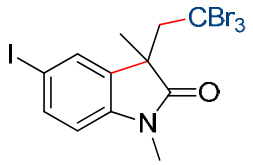


5-chloro-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2i) The desired pure product was obtained in 80% yield (364.8 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* =

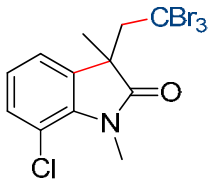
2.0 Hz, 1H), 7.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 4.12 (d, *J* = 15.6 Hz, 1H), 3.70 (d, *J* = 15.6 Hz, 1H), 3.22 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9, 142.1, 130.4, 128.5, 127.3, 127.0, 109.3, 77.2, 77.0, 76.8, 63.5, 50.2, 32.4, 27.0, 26.8. HRMS (ESI) exact mass calcd for $C_{12}H_{12}$ Br_3ClNO [M+H] m/z 457.8158, found 457.8162.



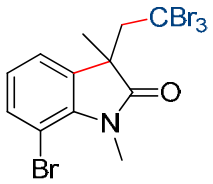
5-bromo-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2j) The desired pure product was obtained in 83% yield (415.0 mg) as a white solid, mp 155-156 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.8 Hz, 1H), 7.44 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 4.11 (d,*J* = 6 Hz，1H), 3.69 (d, *J* = 15.6 Hz, 1H), 3.21 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 138.9, 129.0, 125.1, 120.0, 58.1, 52.7, 49.4, 44.7, 33.5, 33.3, 20.0. HRMS (ESI) exact mass calcd for $C_{12}H_{12}Br_4NO$ [M+H] m/z 501.7652, found 501.7647.



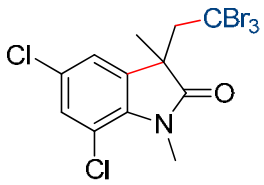
5-iodo-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2k) The desired pure product was obtained in 76% yield (416.5 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 1.4 Hz, 1H), 7.62 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.09 (d, *J* = 15.6 Hz, 1H), 3.68 (d, *J* = 12 Hz, 1H), 3.20 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 143.3, 137.3, 135.3, 131.2, 110.4, 84.2, 63.5, 50.0, 32.4, 27.0, 26.7. HRMS (ESI) exact mass calcd for $C_{12}H_{12}$ Br_3INO [M+H] m/z 549.7514, found 549.7509.



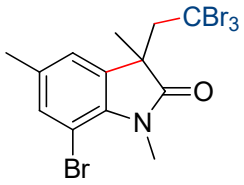
7-chloro-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2l) The desired pure product was obtained in 80% yield (364.8 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.23 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 4.11 (d, *J* = 15.6 Hz, 1H), 3.69 (d, *J* = 15.6 Hz, 1H), 3.61 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.6, 139.5, 131.5, 130.9, 125.0, 122.6, 115.8, 63.7, 49.8, 32.2, 30.2, 27.3. HRMS (ESI) exact mass calcd for $C_{12}H_{12}Br_3ClNO$ [M+H] m/z 457.8158, found 457.8161.



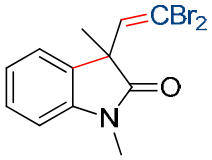
7-bromo-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2m) The desired pure product was obtained in 78% yield (390.0 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.36 (dd, *J* = 7.4, 1.0 Hz, 1H), 6.89 (dd, *J* = 8.0, 7.5 Hz, 1H), 4.11 (d, *J* = 15.6 Hz, 1H), 3.69 (d, *J* = 15.6 Hz, 1H), 3.62 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.7, 141.0, 134.3, 131.9, 125.5, 123.0, 102.7, 63.7, 49.7, 32.2, 30.4, 27.4. HRMS (ESI) exact mass calcd for $C_{12}H_{12}Br_4NO$ [M+H] m/z 501.7652, found 501.7647.



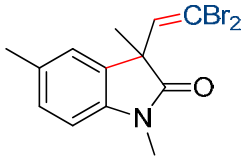
5,7-dichloro-1,3-dimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2n) The desired pure product was obtained in 82% yield (401.8 mg) as a white solid, mp 92-94 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 2.0 Hz, 1H), 7.26 (d, *J* = 1.2 Hz, 1H), 4.10 (d, *J* = 15.6 Hz, 1H), 3.72 – 3.64 (m, 1H), 3.58 (s, 3H), 1.37 (s,3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1, 138.4, 132.8, 130.3, 127.4, 125.5, 116.2, 63.6, 50.0, 31.8, 30.1, 27.2. HRMS (ESI) exact mass calcd for $C_{12}H_{11}Br_3Cl_2NO$ [M+H] m/z 491.7768, found 491.7770.



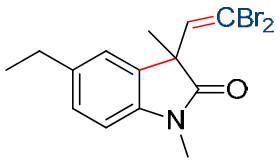
7-bromo-1,3,5-trimethyl-3-(2,2,2-tribromoethyl)indolin-2-one (2o) The desired pure product was obtained in 79% yield (406.1 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 0.6 Hz, 1H), 7.16 (s, 1H), 4.08 (d, *J* = 15.5 Hz, 1H), 3.66 (d, *J* = 15.5 Hz, 1H), 3.58 (s, 3H), 2.28 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.6, 138.6, 134.2, 132.8, 131.7, 126.4, 102.2, 63.7, 49.8, 32.3, 30.3, 27.4, 20.5. HRMS (ESI) exact mass calcd for $C_{13}H_{14}Br_4NO$ [M+H] m/z 515.7809, found 515.7808.



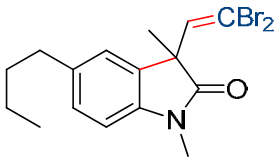
3-(2,2-dibromovinyl)-1,3-dimethylindolin-2-one (3a) The desired pure product was obtained in 82% yield (280.4 mg) as a yellow liquid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 1H), 7.18 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.85 – 6.82 (m, 2H), 3.24 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 143.5, 138.9, 132.4, 128.3, 123.0, 122.9, 108.1, 92.4, 51.5, 26.5, 26.3. HRMS (ESI) exact mass calcd for $C_{12}H_{12}Br_2NO$ [M+H] m/z 343.9286, found 343.9282.



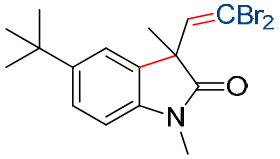
3-(2,2-dibromovinyl)-1,3,5-trimethylindolin-2-one (3b) The desired pure product was obtained in 74% yield (263.4 mg) as a yellow liquid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.00 – 6.97 (m, 1H), 6.80 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.21 (s, 3H), 2.35 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 141.1, 139.0, 132.5, 132.4, 128.5, 123.8, 107.8, 92.2, 51.5, 26.5, 26.4, 21.2. HRMS (ESI) exact mass calcd for $C_{13}H_{14}Br_2NO$ [M+H] m/z 357.9442, found 357.9437.



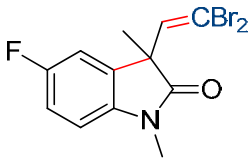
3-(2,2-dibromovinyl)-5-ethyl-1,3-dimethylindolin-2-one (3c) The desired pure product was obtained in 72% yield (266.4 mg) as a yellow liquid**.** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 – 7.10 (m, 1H), 7.00 (d, *J* = 1.2 Hz, 1H), 6.80 (s, 1H), 6.74 (d, *J* = 6.0 Hz, 1H), 3.21 (s, 3H), 2.70 – 2.60 (q, *J* = 6.0 Hz, 2H), 1.54 (s, 3H), 1.24 (t, *J* = 7.6 Hz,3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 141.3, 139.2, 139.0, 132.4, 127.4, 122.7, 107.9, 92.2, 51.6, 28.6, 26.5, 26.4, 15.9. HRMS (ESI) exact mass calcd for $C_{14}H_{16}Br_2NO$ [M+H] m/z 371.9599, found 371.9602.



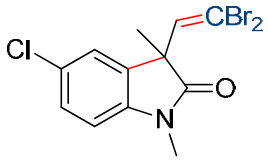
5-butyl-3-(2,2-dibromovinyl)-1,3-dimethylindolin-2-one (3d) The desired pure product was obtained in 80% yield (318.4 mg) as a yellow liquid**.** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 6.0, 6.0 Hz, 1H), 6.98 (s, 1H), 6.80 (s, 1H), 6.73 (d, *J* = 6.0 Hz, 1H), 3.21 (s, 3H), 2.62 – 2.58 (m, 2H), 1.58 (dt, *J* = 18.0, 18.0, Hz, 2H), 1.54 (s, 3H), 1.35 (dq, *J* = 12.0, 12.0 Hz, 2H), 0.93 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 141.3, 139.0, 137.8, 132.3, 127.9, 123.2, 107.8, 92.2, 51.6, 35.4, 33.9, 26.5, 26.4, 22.3, 13.9. HRMS (ESI) exact mass calcd for $C_{16}H_{20}Br_2NO$ [M+H] m/z 399.9912, found 399.9920.



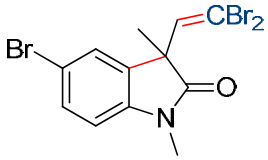
5-(tert-butyl)-3-(2,2-dibromovinyl)-1,3-dimethylindolin-2-one (3e) The desired pure product was obtained in 78% yield (310.4 mg) as a yellow liquid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.2, 1.2 Hz, 1H), 7.20 (d, *J* = 1.8 Hz, 1H), 6.82 (d, *J* = 0.8 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 3.22 (s, 3H), 1.56 (s, 3H), 1.33 (t, *J* = 0.8 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.9, 146.3, 141.0, 139.0, 132.0, 124.9, 120.2, 107.5, 92.1, 51.7, 34.6, 31.6, 26.5, 26.4. HRMS (ESI) exact mass calcd for $C_{16}H_{20}Br_2NO$ [M+H] m/z 399.9912, found 399.9917.



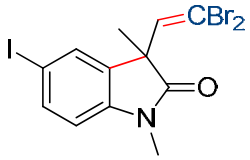
3-(2,2-dibromovinyl)-5-fluoro-1,3-dimethylindolin-2-one (3f) The desired pure product was obtained in 78% yield (280.8 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 – 6.97 (m, 1H), 6.95 – 6.90 (m, 1H), 6.78 (d, *J* = 6.0 Hz, 1H), 6.75 (m, 1H), 3.22 (d, *J* = 3.9 Hz, 3H), 1.54 (d, *J* = 3.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 160.2, 158.6, 139.5, 138.3, 133.8, 133.7, 115.0, 114.8, 114.7, 114.6, 114.5, 114.5, 111.3, 111.2, 108.8, 108.8, 108.6, 108.6, 93.0, 63.5, 51.8, 27.0, 26.8, 26.6, 26.3. HRMS (ESI) exact mass calcd for $C_{12}H_{11}Br_2FNO$ [M+H] m/z 361.9191, found 361.9194.



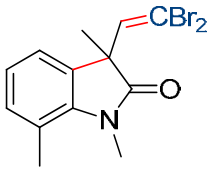
5-chloro-3-(2,2-dibromovinyl)-1,3-dimethylindolin-2-one (3g) The desired pure product was obtained in 79% yield (297.1 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 6.77 (s, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 3.21 (d, *J* = 4.8 Hz, 3H), 1.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 142.1, 138.2, 133.8, 128.3, 128.3, 123.5, 109.0, 93.2, 51.5, 26.6, 26.3. HRMS (ESI) exact mass calcd for $C_{12}H_{11}Br_2ClNO$ [M+H] m/z 377.8896, found 377.8895.



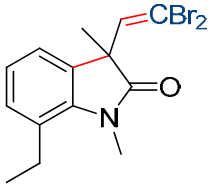
5-bromo-3-(2,2-dibromovinyl)-1,3-dimethylindolin-2-one (3h) The desired pure product was obtained in 77% yield (323.4 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 1H), 7.27 (d, *J* = 1.9 Hz, 1H), 6.77 (s, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 3.21 (d, *J* = 4.8 Hz, 3H), 1.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 142.6, 138.1, 134.2, 131.2, 126.3, 115.5, 109.6, 93.2, 51.5, 26.6, 26.3. HRMS (ESI) exact mass calcd for $C_{12}H_{11}Br_3NO$ [M+H] m/z 421.8391, found 421.8386.



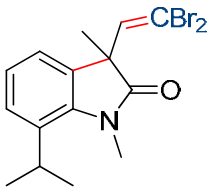
3-(2,2-dibromovinyl)-5-iodo-1,3-dimethylindolin-2-one (3i) The desired pure product was obtained in 80% yield (374.4 mg) as a yellow liquid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.29 (d, *J* = 1.9 Hz, 1H), 6.78 (d, *J* = 0.8 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 3.22 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 142.6, 138.1, 134.2, 131.2, 126.3, 115.5, 109.6, 93.2, 51.5, 26.6, 26.3. HRMS (ESI) exact mass calcd for $C_{12}H_{11}Br_2INO$ [M+H] m/z 469.8252, found 469.8245.



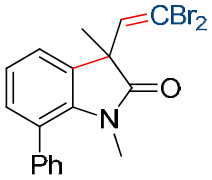
3-(2,2-dibromovinyl)-1,3,7-trimethylindolin-2-one (3j) The desired pure product was obtained in 77% yield (274.1 mg) as a yellow liquid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.93 (m, 3H), 6.80 (s, 1H), 3.51 (s, 3H), 2.57 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 141.2, 139.2, 133.1, 132.0, 122.8, 121.0, 119.7, 92.3, 51.0, 29.9, 26.8, 19.0. HRMS (ESI) exact mass calcd for $C_{13}H_{14}Br_2NO$ [M+H] m/z 357.9442, found 357.9440.



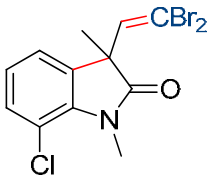
3-(2,2-dibromovinyl)-7-ethyl-1,3-dimethylindolin-2-one (3k) The desired pure product was obtained in 73% yield (270.1 mg) as a yellow liquid**.** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 – 7.06 (m, 1H), 7.02 – 6.97 (m, 2H), 6.80 (s, 1H), 3.50 (s, 3H), 2.90 (q, *J* = 7.5 Hz, 2H), 1.53 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 140.5, 139.3, 133.2, 130.4, 126.6, 123.0, 121.0, 92.2, 50.8, 29.6, 26.8, 24.9, 16.9. HRMS (ESI) exact mass calcd for $C_{14}H_{16}Br_2NO$ [M+H] m/z 371.9599, found 371.9596.



3-(2,2-dibromovinyl)-7-isopropyl-1,3-dimethylindolin-2-one (3l) The desired pure product was obtained in 76% yield (291.8 mg) as a yellow liquid**.** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.9 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.1 Hz, 1H), 6.81 (s, 1H), 3.64 – 3.56 (m, 1H), 3.53 (s, 3H), 1.53 (s, 3H), 1.30 (dd, *J* = 17.2, 6.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 139.3, 126.3, 126.0, 123.8, 123.2, 122.1, 120.8, 92.0, 50.7, 30.3, 27.1, 26.8, 24.6, 24.0. HRMS (ESI) exact mass calcd for $C_{15}H_{18}Br_2NO$ [M+H] m/z 385.9755, found 385.9757.

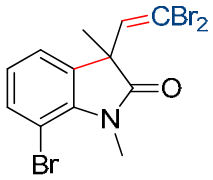


3-(2,2-dibromovinyl)-1,3-dimethyl-7-phenylindolin-2-one (3m) The desired pure product was obtained in 70% yield (292.6 mg) as a yellow liquid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 7.18 – 7.08 (m, 3H), 6.85 (s, 1H), 2.75 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 140.5, 139.1, 138.7, 133.3, 131.2, 130.4, 129.1, 128.8, 127.8, 127.7, 125.6, 122.2, 122.1, 92.3, 50.9, 30.5, 26.7. HRMS (ESI) exact mass calcd for $C_{18}H_{16}Br_2NO$ [M+H] m/z 419.9599, found 419.9603.

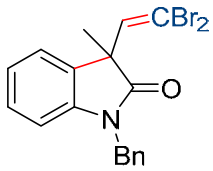


7-chloro-3-(2,2-dibromovinyl)-1,3-dimethylindolin-2-one (3n) The desired pure product was obtained in 79% yield (297.0 mg) as a yellow liquid**.** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.03 (dd, *J* = 7.3, 1.0 Hz, 1H), 6.97 (t, 1H), 6.78 (s, 1H), 3.59 (d, *J* = 6.6 Hz, 3H), 1.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 143.5, 138.9, 132.4, 128.3, 123.0, 122.9, 108.1,

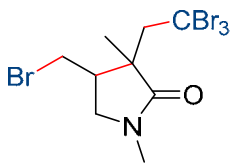
92.4, 51.5, 26.5, 26.3. HRMS (ESI) exact mass calcd for $C_{12}H_{11}Br_2ClNO$ [M+H] m/z 377.8896, found 377.8900.



7-bromo-3-(2,2-dibromovinyl)-1,3-dimethylindolin-2-one (3o) The desired pure product was obtained in 77% yield (311.1 mg) as a yellow liquid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.08 (dd, *J* = 7.3, 1.1 Hz, 1H), 6.93 (dd, *J* = 8.1, 7.4 Hz, 1H), 6.79 (s, 1H), 3.62 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.1, 140.8, 138.5, 135.4, 133.9, 124.1, 122.1, 102.4, 93.2, 51.2, 30.1, 26.8. HRMS (ESI) exact mass calcd for $C_{12}H_{11}Br_3NO$ [M+H] m/z 421.8391, found 421.8393.

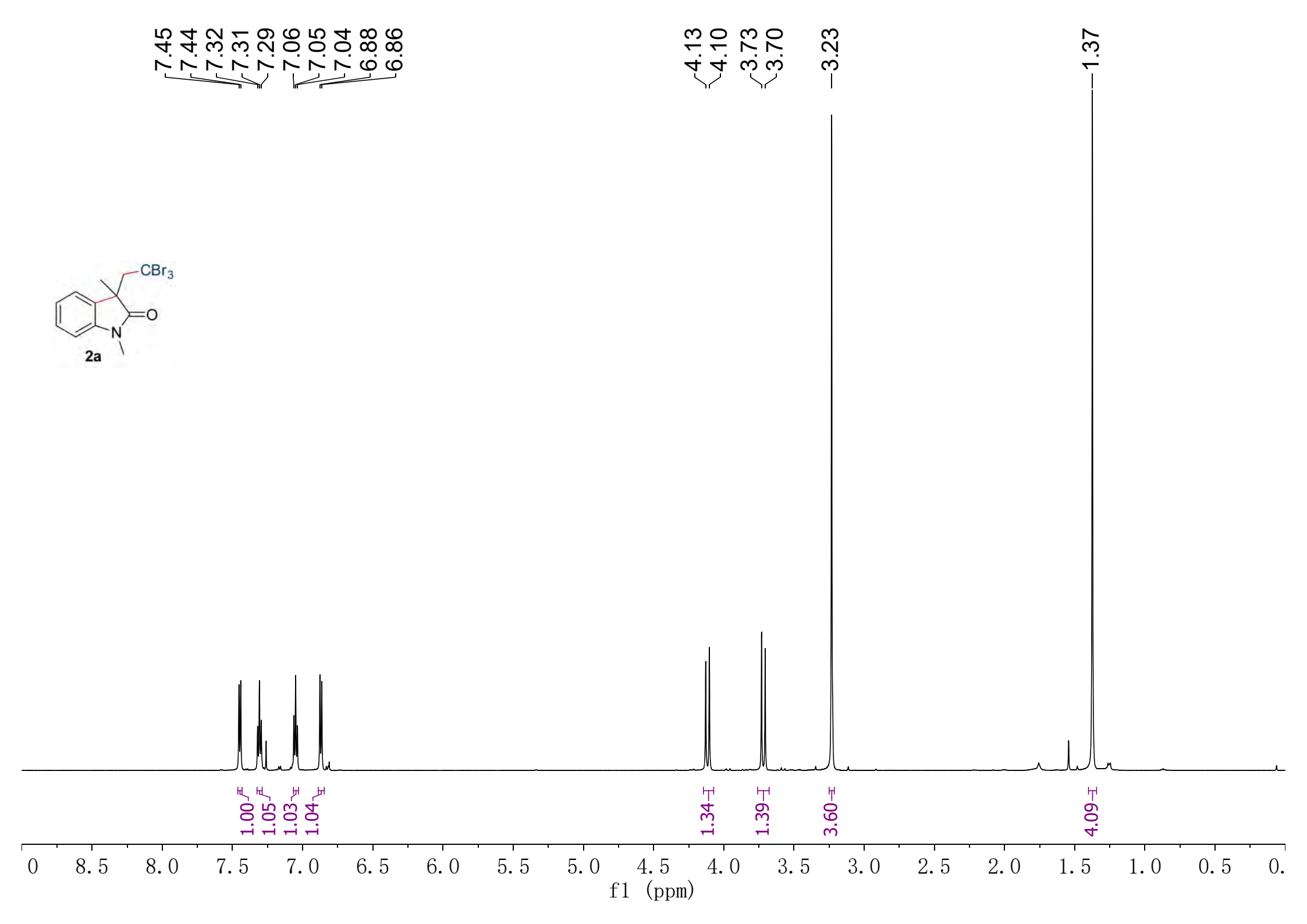


1-benzyl-3-(2,2-dibromovinyl)-3-methylindolin-2-one (3p) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.23 (m, 4H), 7.21 – 7.15 (m, 1H), 7.04 (dd, *J* = 11.0, 4.1 Hz, 1H), 6.85 (s, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.02 (t, *J* = 15.3 Hz, 1H), 4.78 (t, 1H), 1.60 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.8, 142.7, 138.6, 137.9, 135.7, 132.4, 131.1, 128.8, 128.7, 128.2, 127.9, 127.7, 127.7, 127.7, 126.3, 123.1, 122.9, 110.6, 109.2, 92.8, 51.5, 44.2, 26.9, 26.9. HRMS (ESI) exact mass calcd for $C_{18}H_{16}Br_2NO$ [M+H] m/z 419.9599, found 419.9596.



4-(bromomethyl)-3-methyl-1-phenyl-3-(2,2,2-tribromoethyl)pyrrolidin-2-one (5) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 4.10 (dd, *J* = 10.4, 6.2 Hz, 1H), 4.01 (d, *J* = 16.5 Hz, 1H), 3.95 (dd, *J* = 10.2, 2.5 Hz, 1H), 3.90 (d, *J* =

10.5 Hz, 1H), 3.59 (d, *J* = 16.5 Hz, 1H), 3.40 (t, *J* = 10.2 Hz, 1H), 3.04 – 2.95 (m, 1H), 1.69 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.8, 138.9, 129.0, 125.1, 120.0, 58.1, 52.7, 49.4, 44.7, 33.5, 33.3, 20.0. HRMS (ESI) exact mass calcd for $C_9H_{14}Br_4NO$ [M+H] m/z 467.7809, found 467.7815.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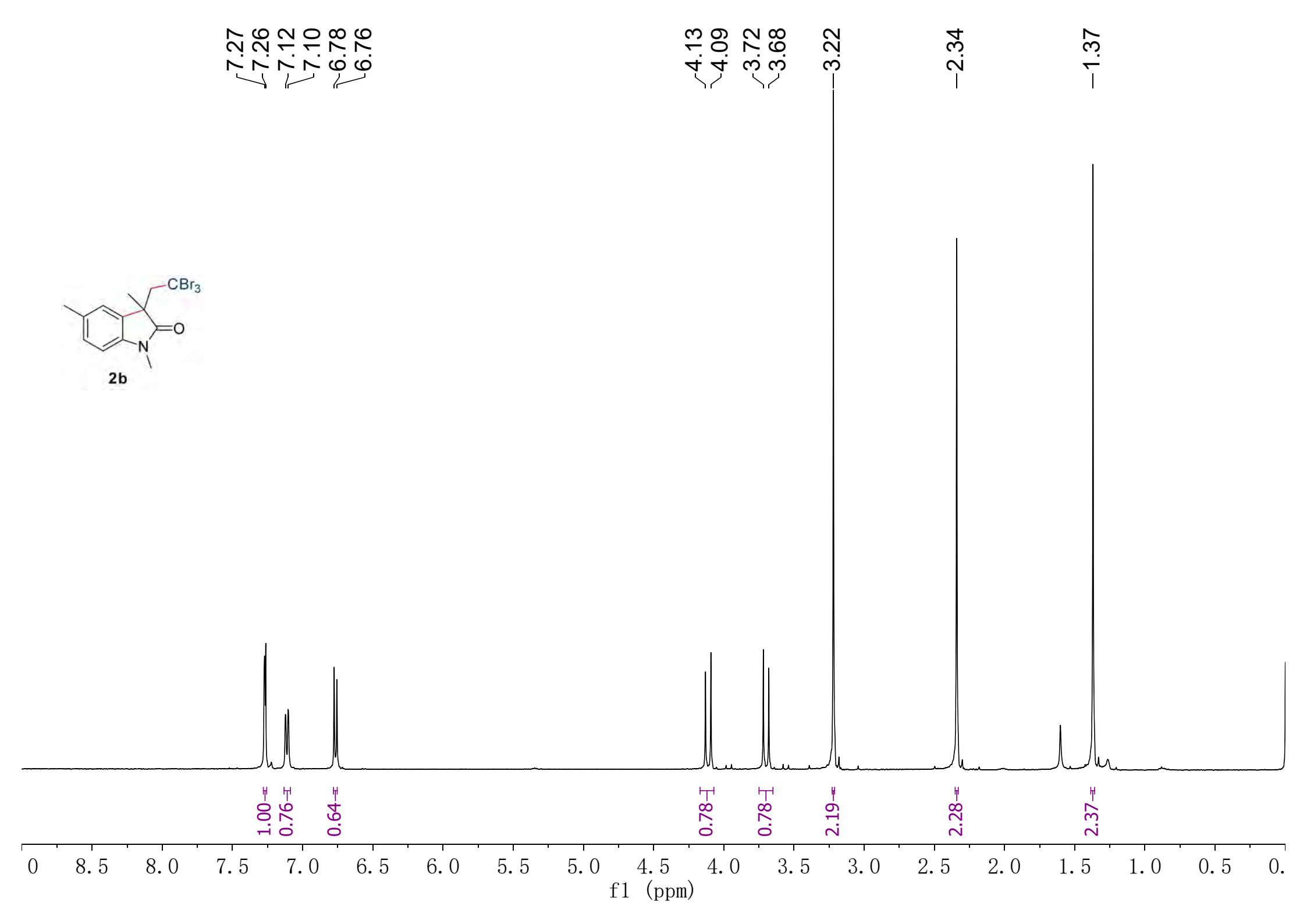
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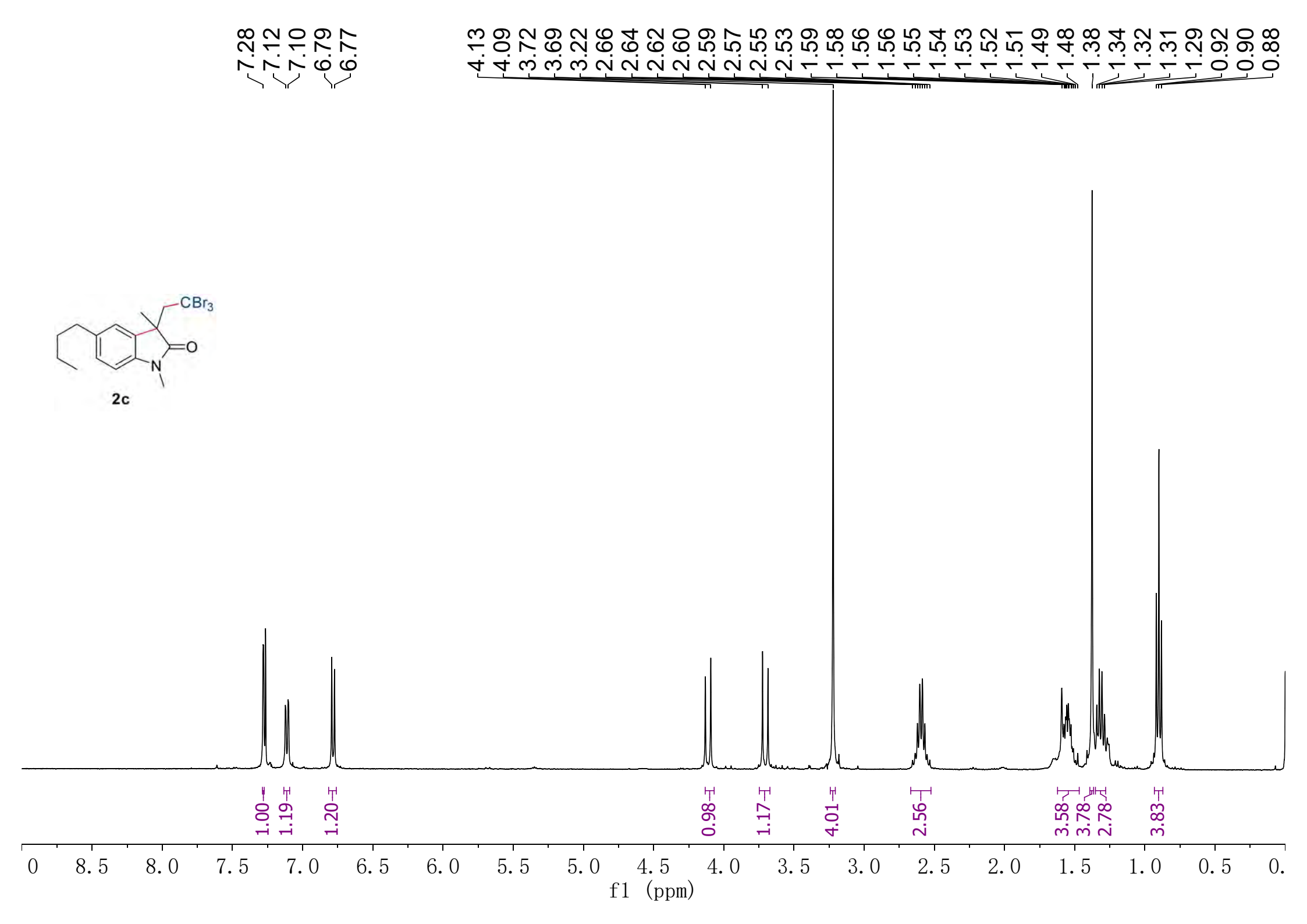
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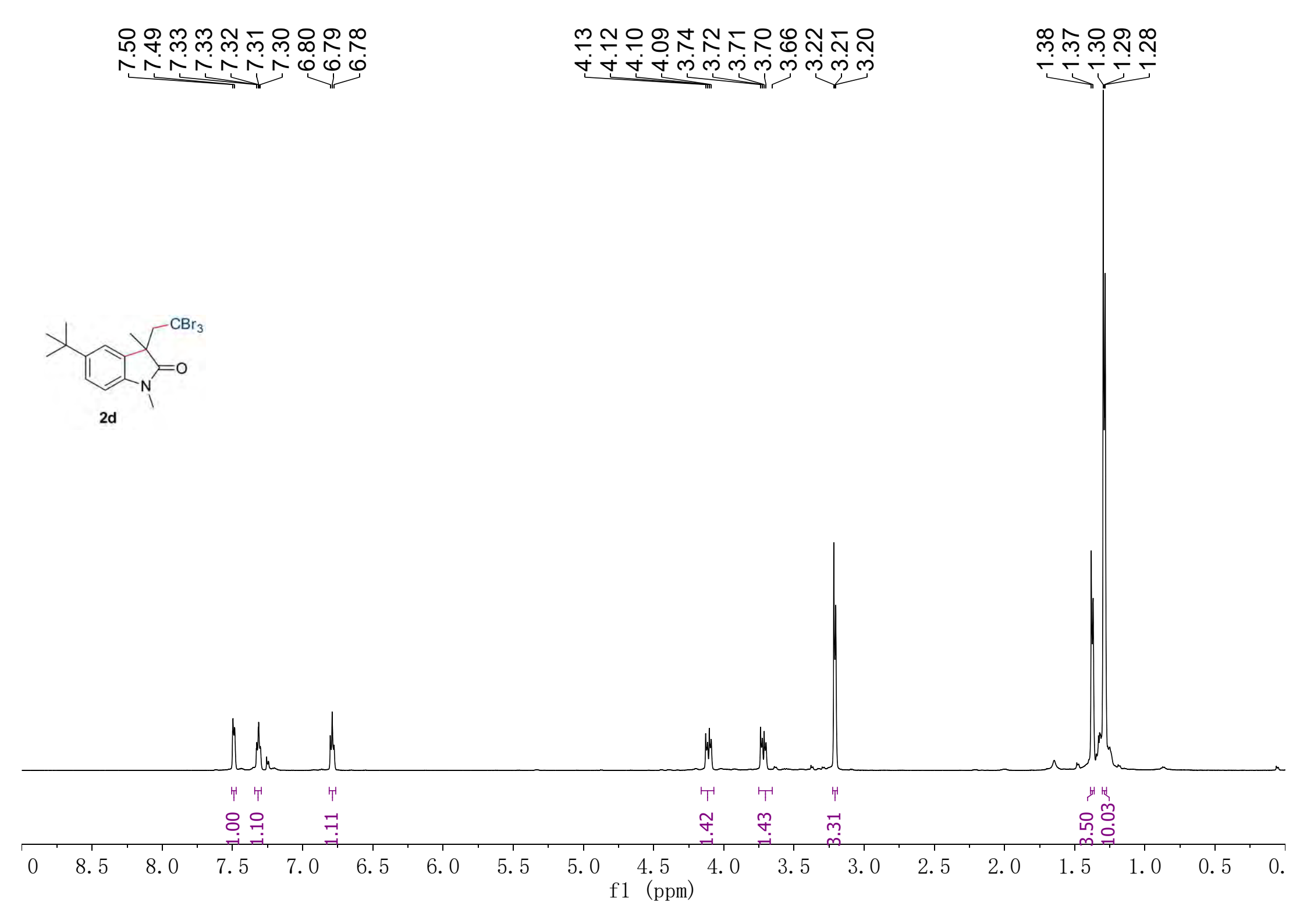
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3.72
3.71
3.70
3.66
3.22
3.21
3.20
1.38
1.37
1.30
1.29
1.28
CBr3
O
N
2d
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1.10
1.11
1.42
1.43
3.31
3.50
10.03
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7.0
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6.0
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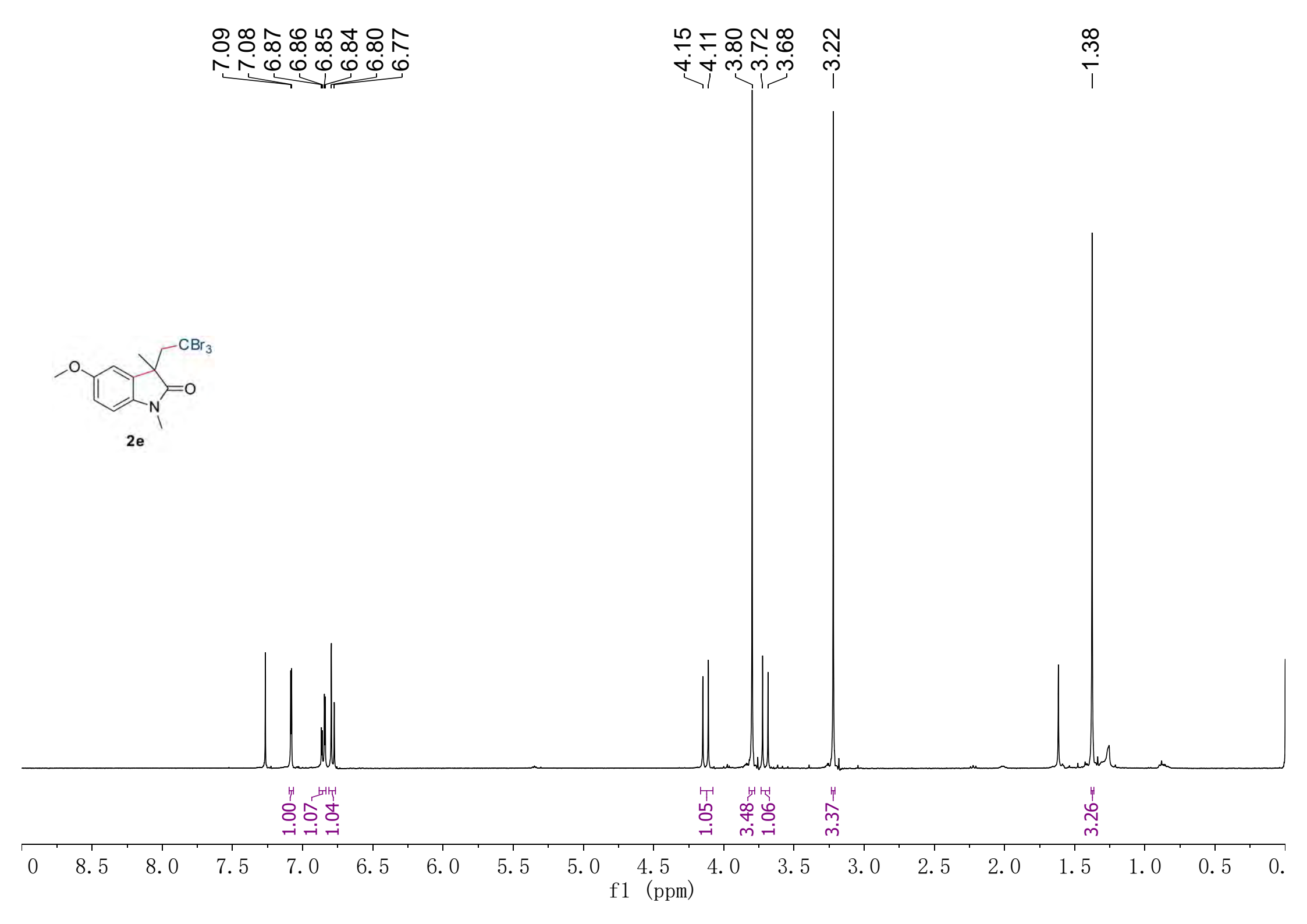
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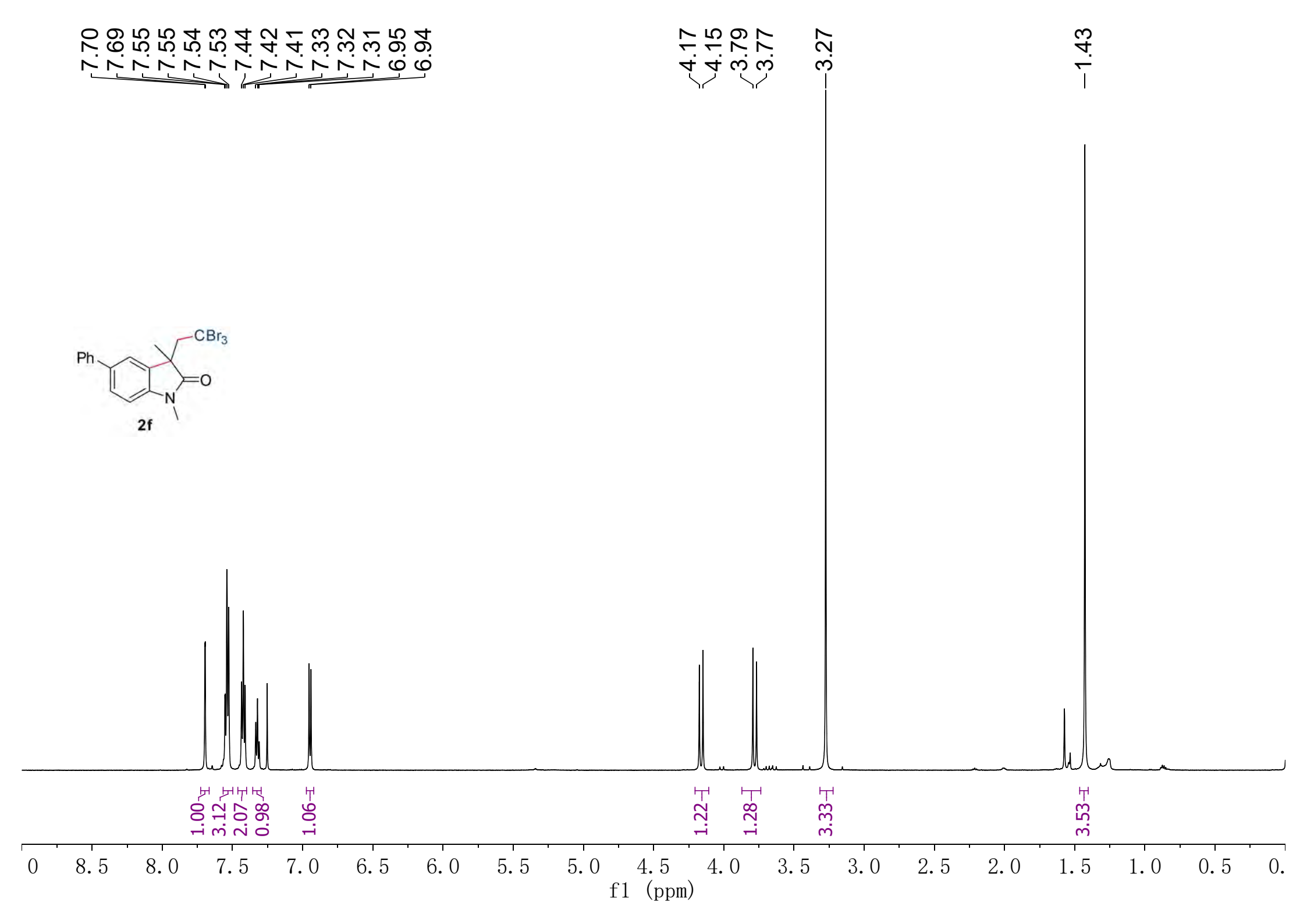
f1 (ppm)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4.15
3.79
3.77
3.27
1.43
CBr3
Ph
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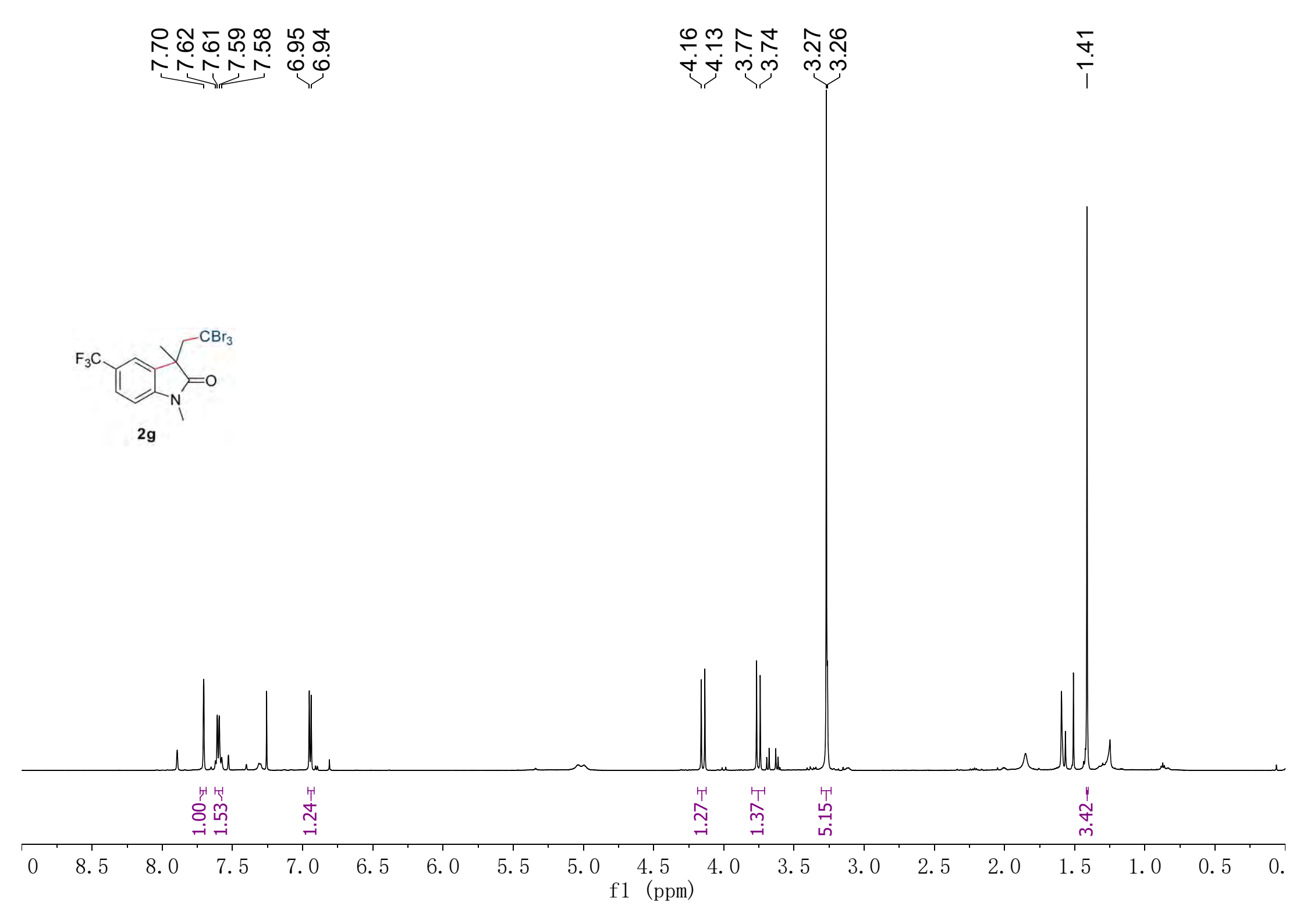
f1 (ppm)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3.26
1.41
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N
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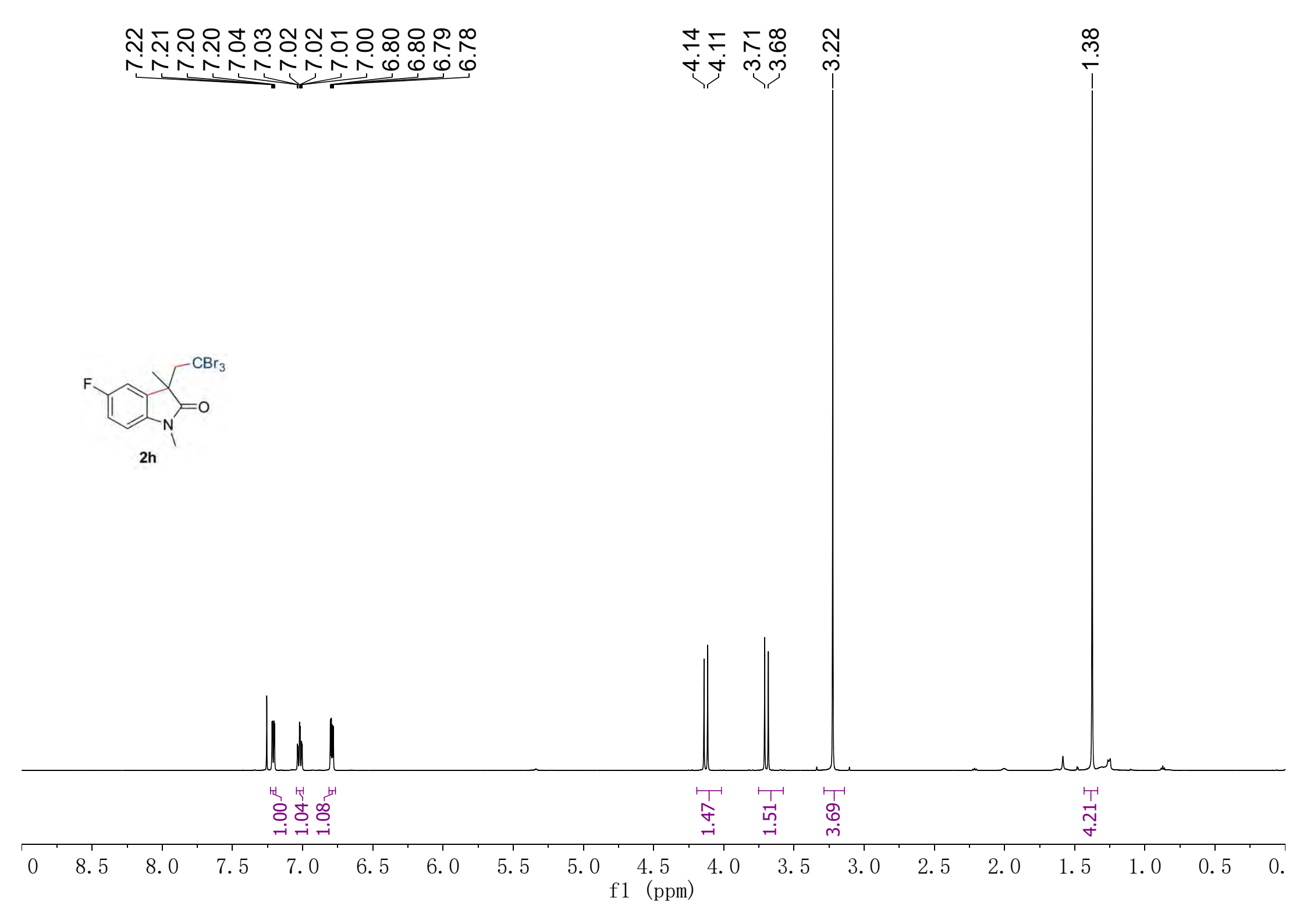
3.42
f1 (ppm)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7.00
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6.80
6.79
6.78
4.14
4.11
3.71
3.68
3.22
1.38
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N
2h
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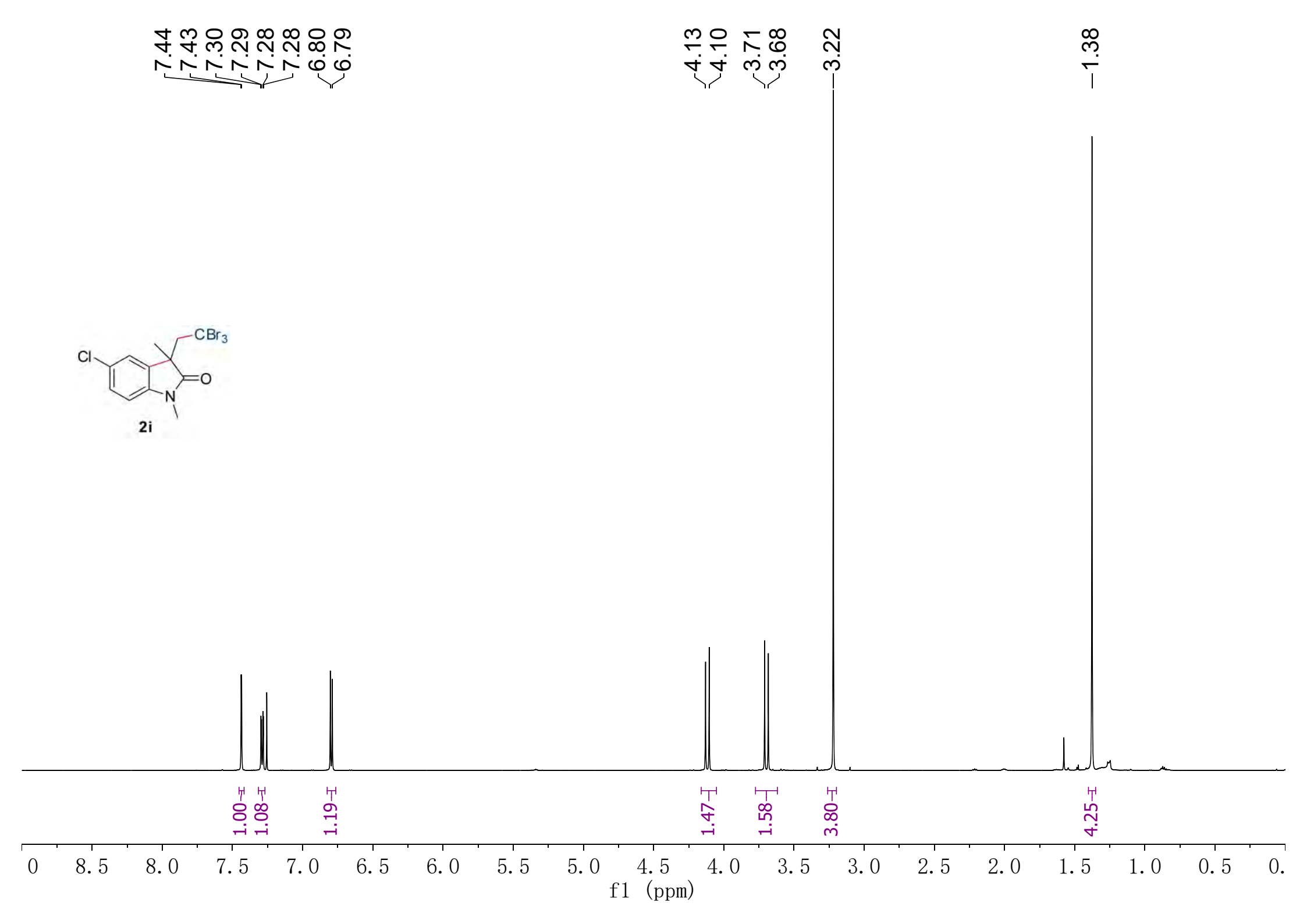
4.21
f1 (ppm)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1.38
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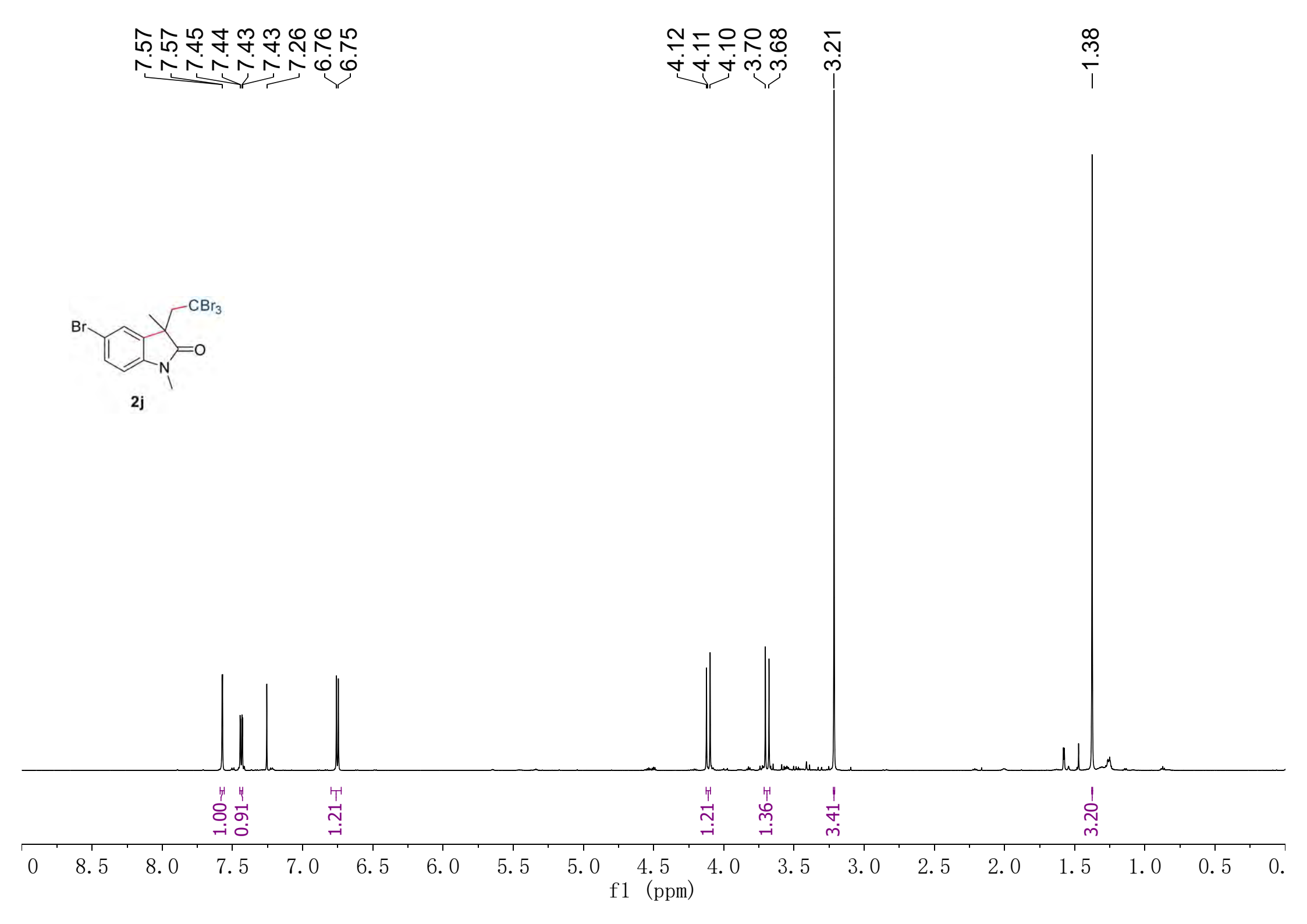
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3.21
1.38
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CBr3
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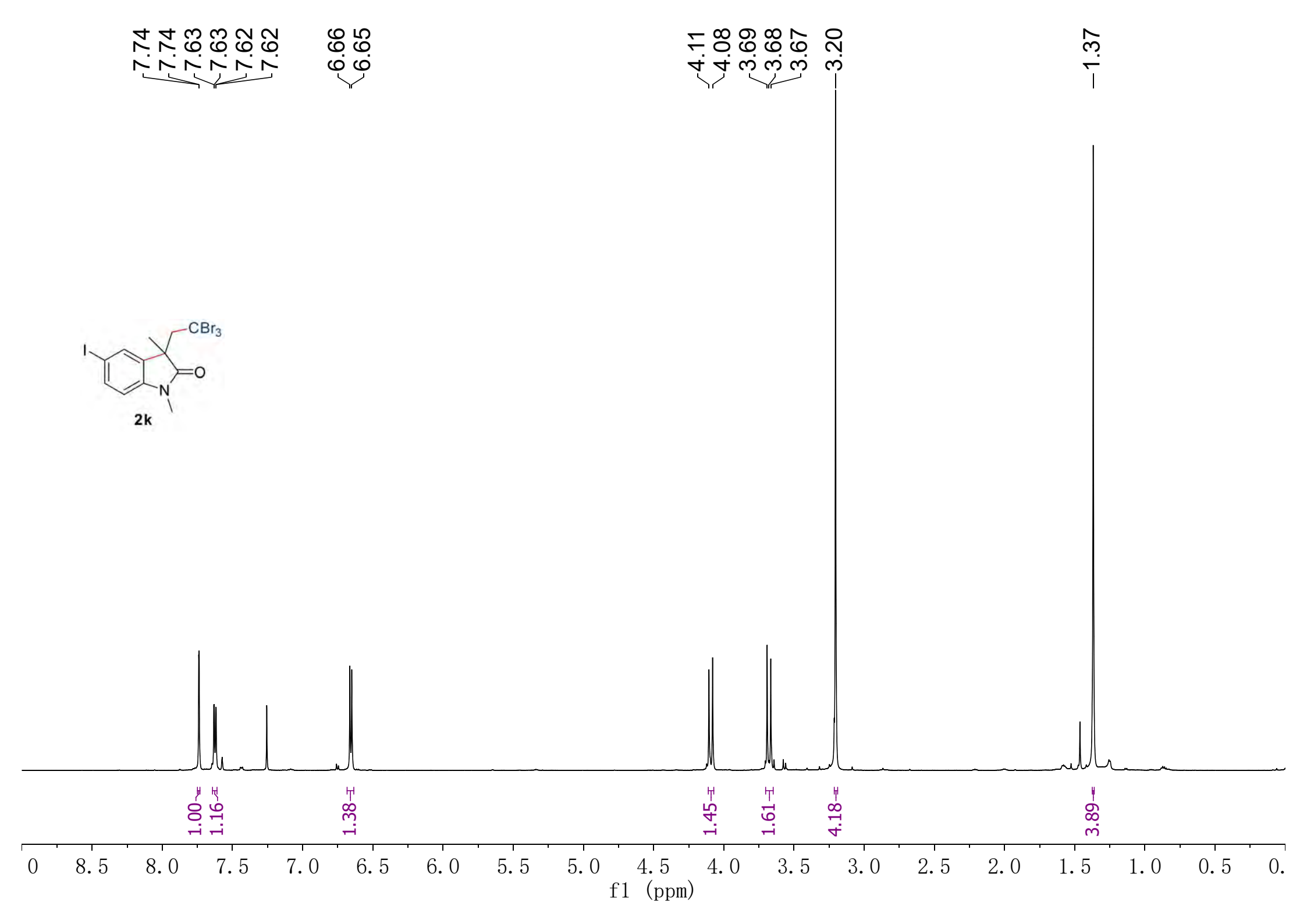
3.20
f1 (ppm)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1.37
CBr3
I
O
N
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1.61
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6.0
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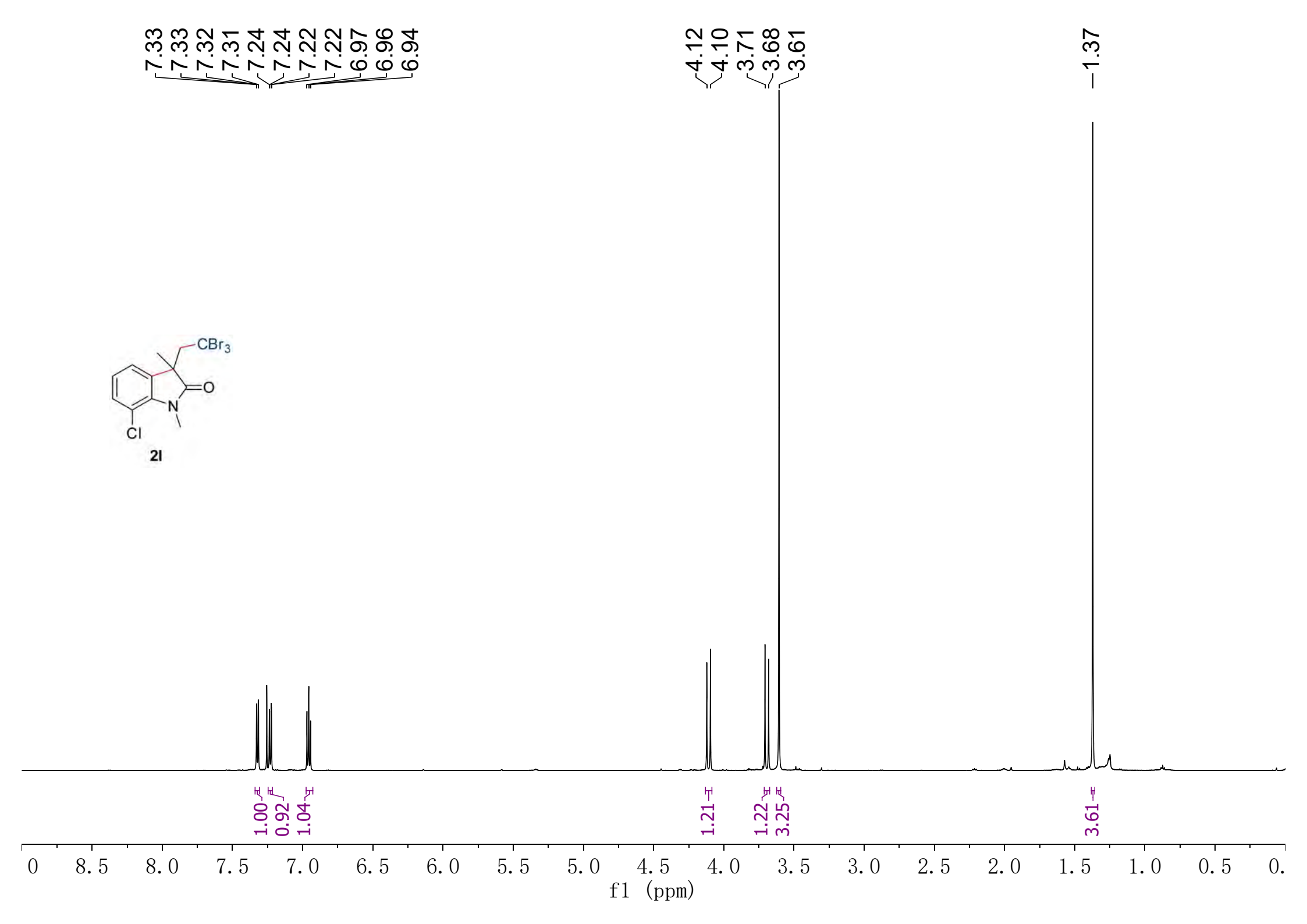
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7.24
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7.22
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6.96
6.94
4.12
4.10
3.71
3.68
3.61
1.37
CBr3
O
N
Cl
2l
1.00
0.92
1.04
1.21
1.22
3.25
3.61
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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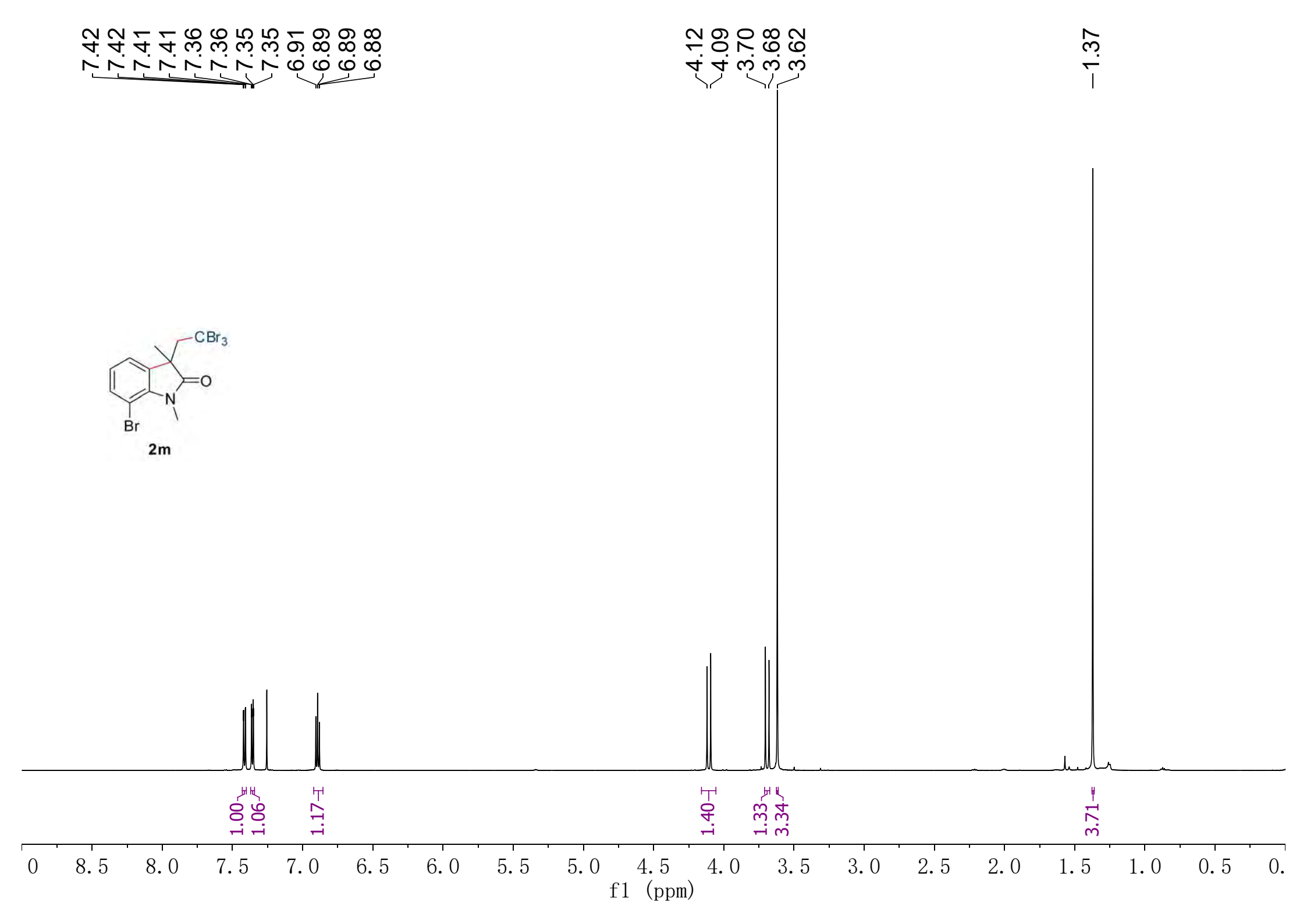
f1 (ppm)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6.89
6.89
6.88
4.12
4.09
3.70
3.68
3.62
1.37
CBr3
O
N
Br
2m
1.00
1.06
1.17
1.40
1.33
3.34
3.71
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8.5
8.0
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7.0
6.5
6.0
5.5
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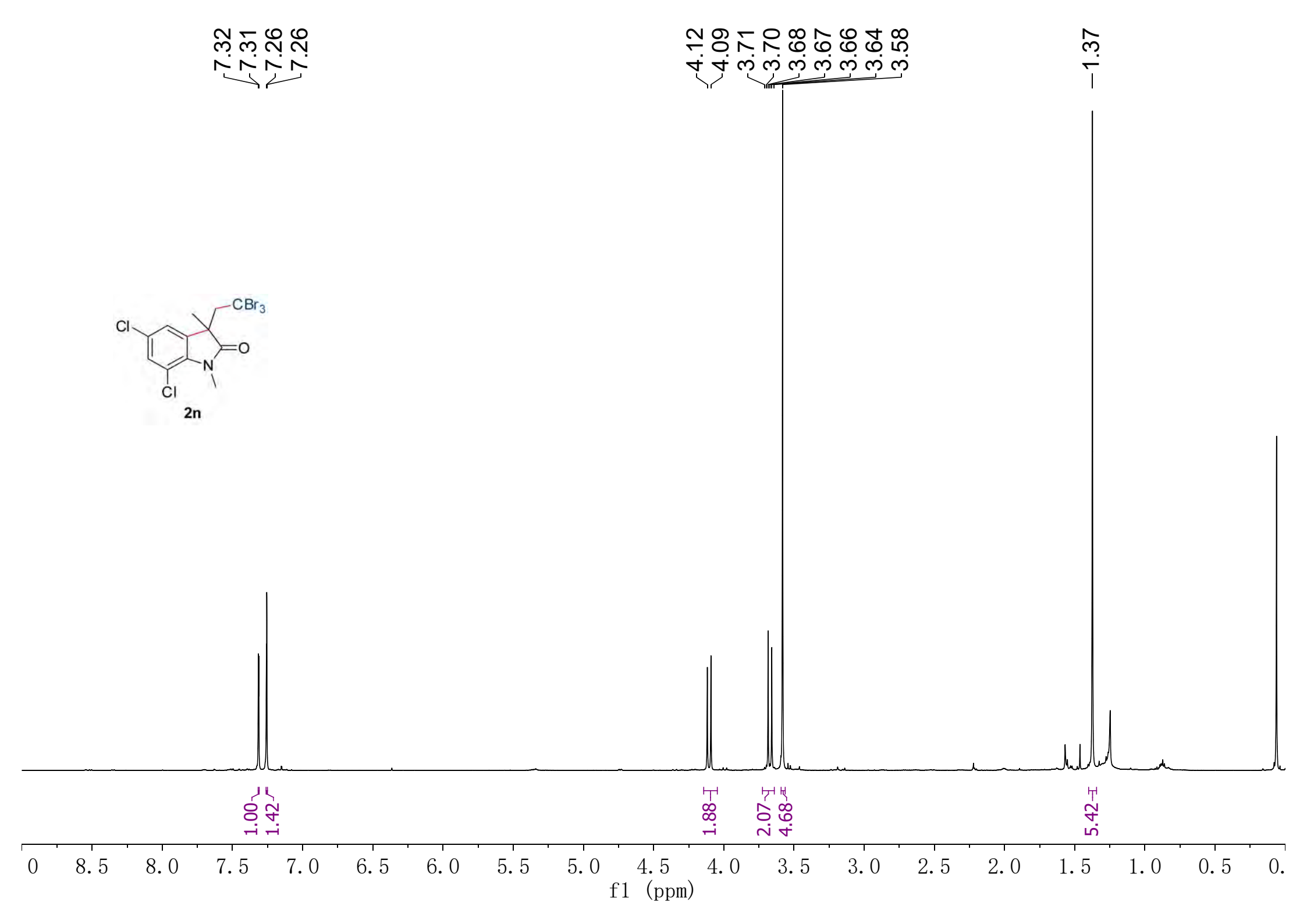
f1 (ppm)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3.58
1.37
CBr3
Cl
O
N
Cl
2n
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1.88
2.07
4.68
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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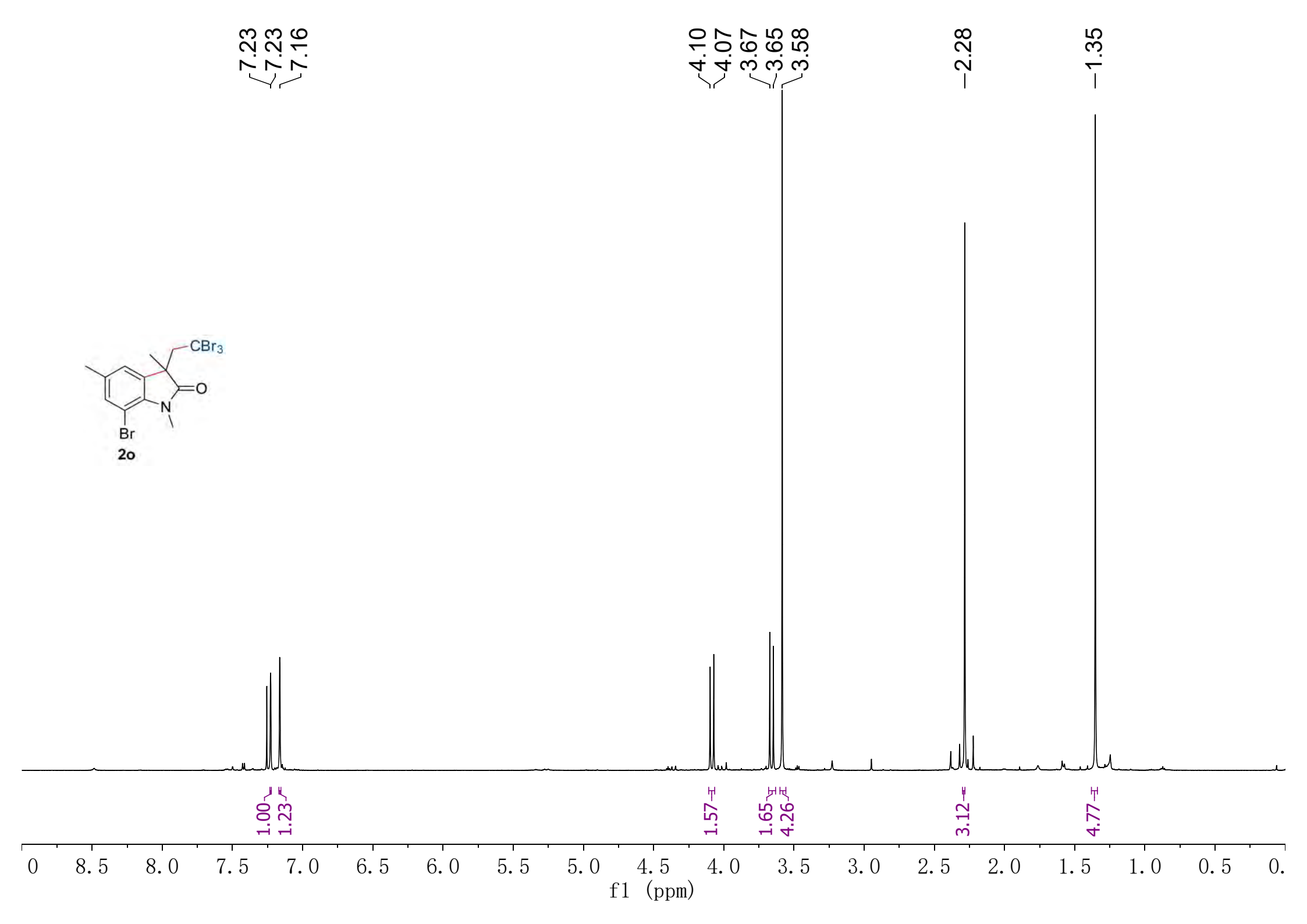
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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Br
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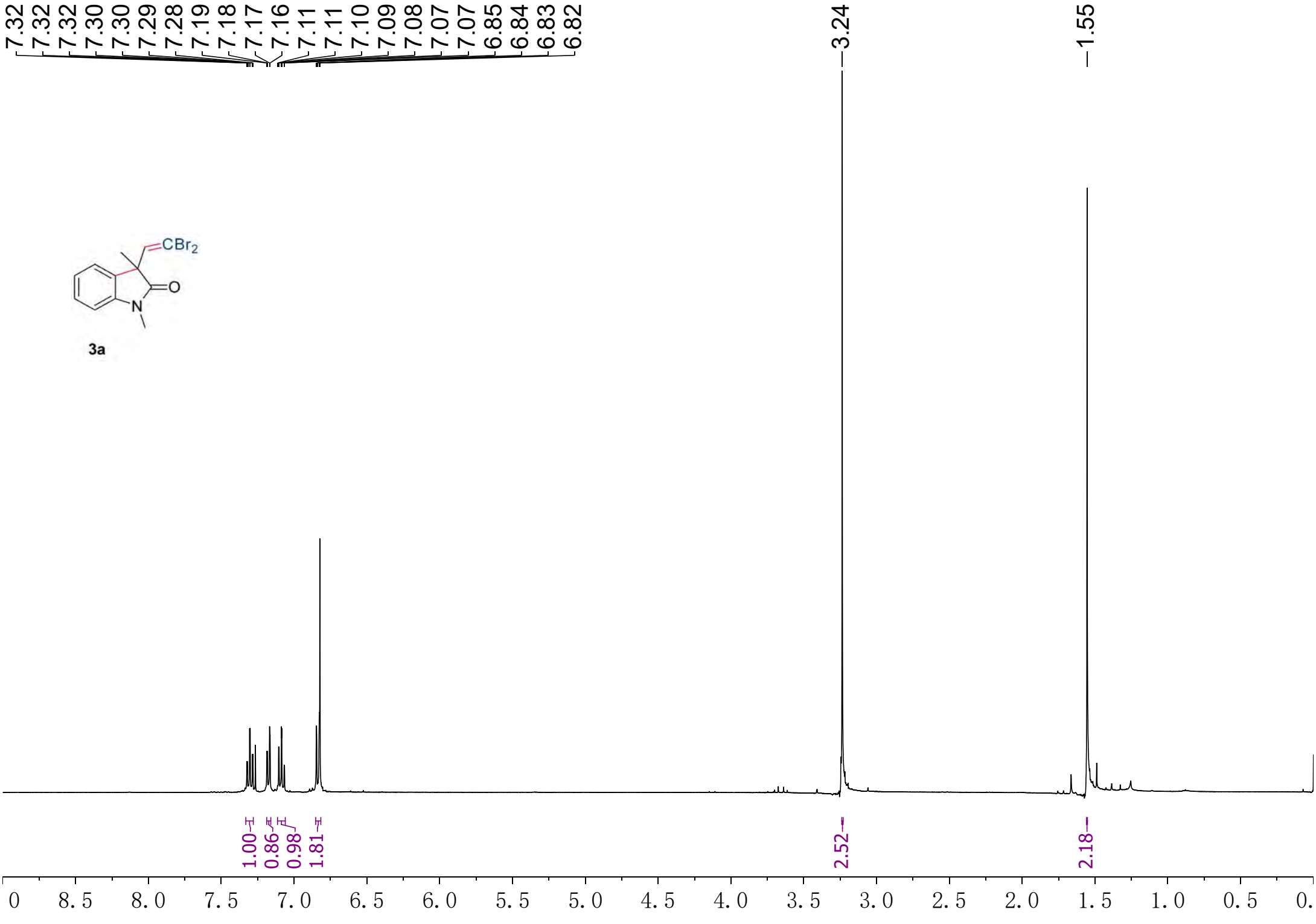
4.77
f1 (ppm)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7.11
7.10
7.09
7.08
7.07
7.07
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6.84
6.83
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O
N
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6.0
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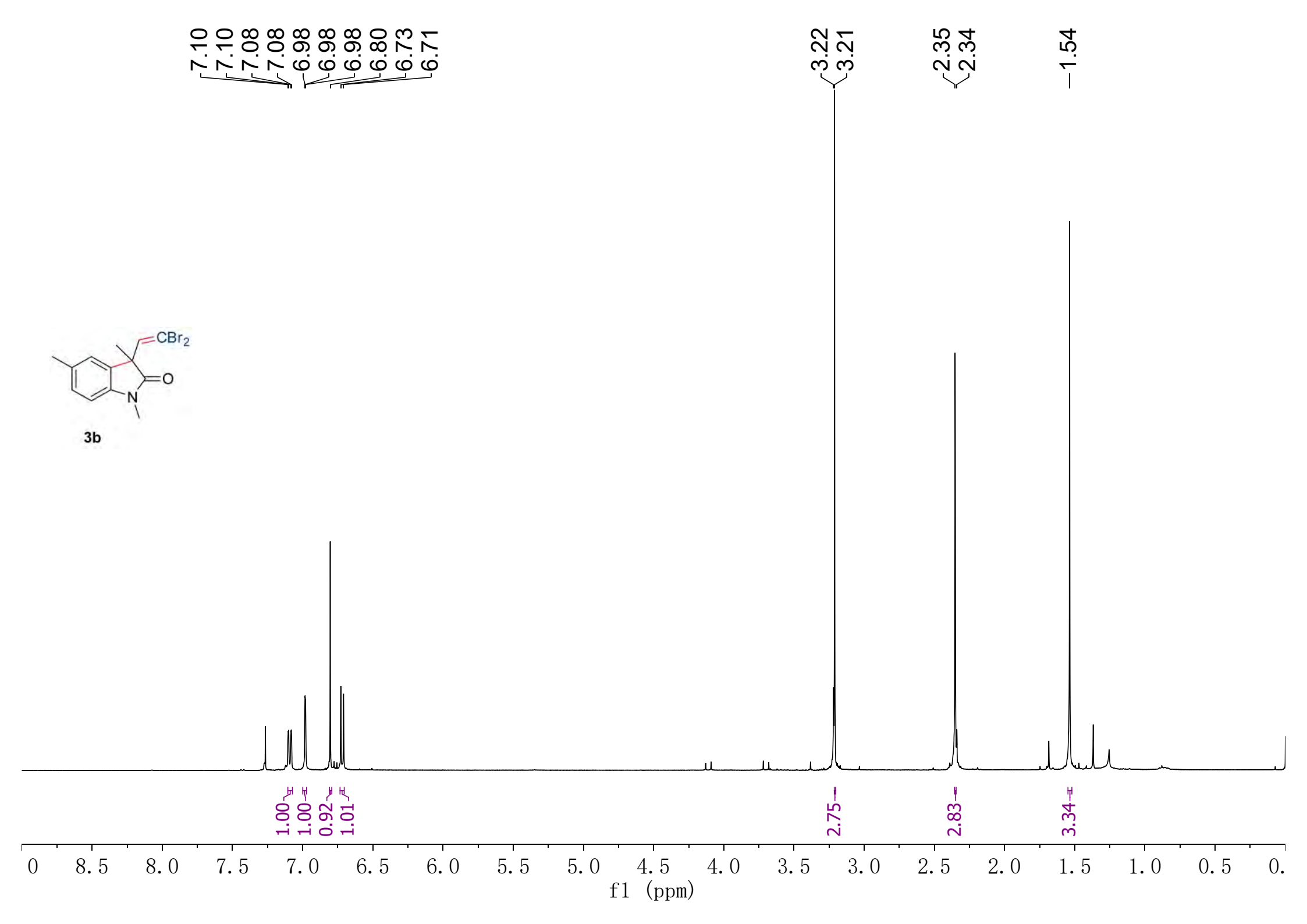
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6.71
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2.34
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N
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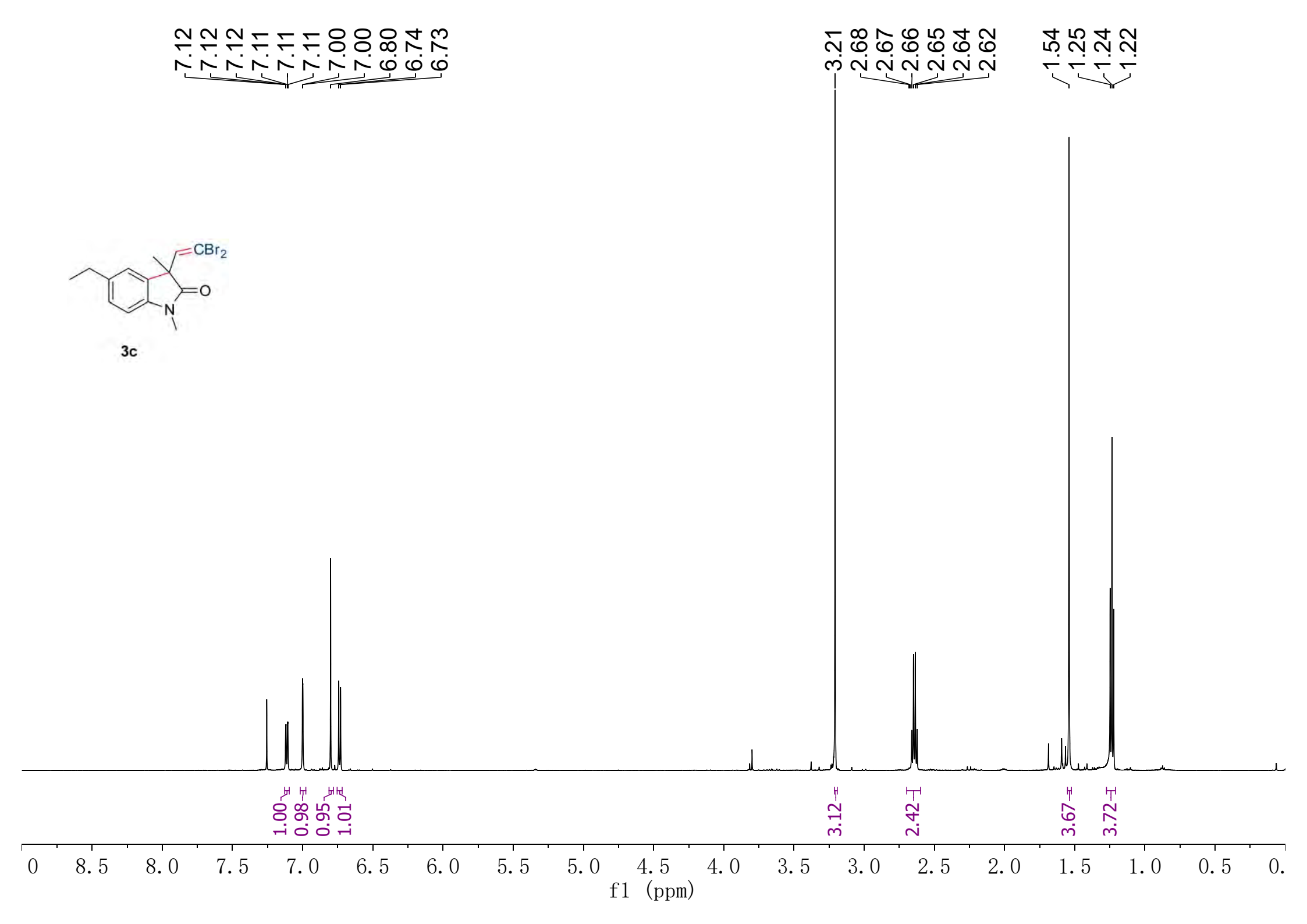
2.75
2.83
3.34
f1 (ppm)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2.66
2.65
2.64
2.62
1.54
1.25
1.24
1.22
CBr2
O
N
3c
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0.98
0.95
1.01
3.12
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3.67
3.72
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8.5
8.0
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7.0
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6.0
5.5
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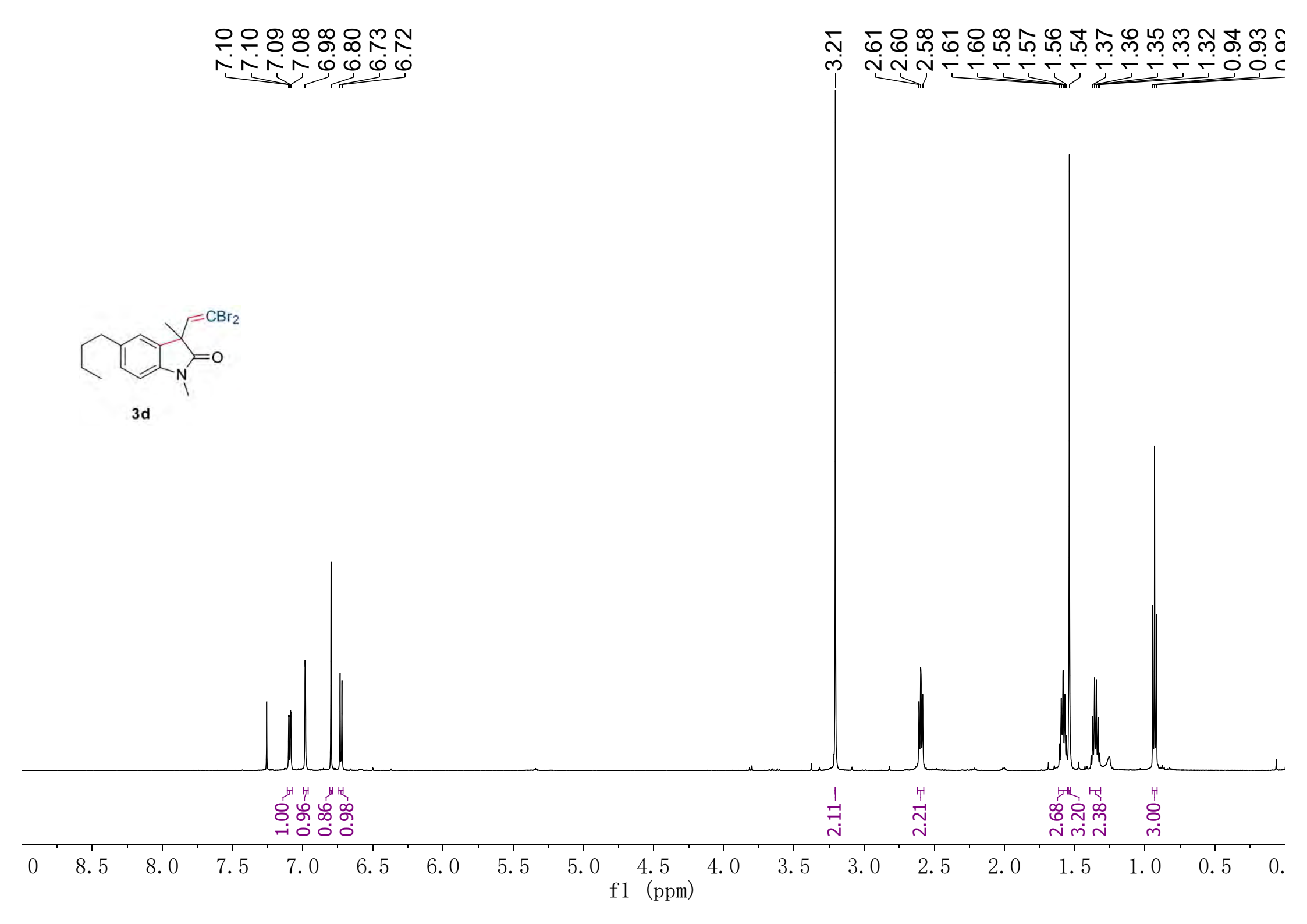
f1 (ppm)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7.08
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2.58
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1.60
1.58
1.57
1.56
1.54
1.37
1.36
1.35
1.33
1.32
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0.93
CBr2
O
N
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3.00
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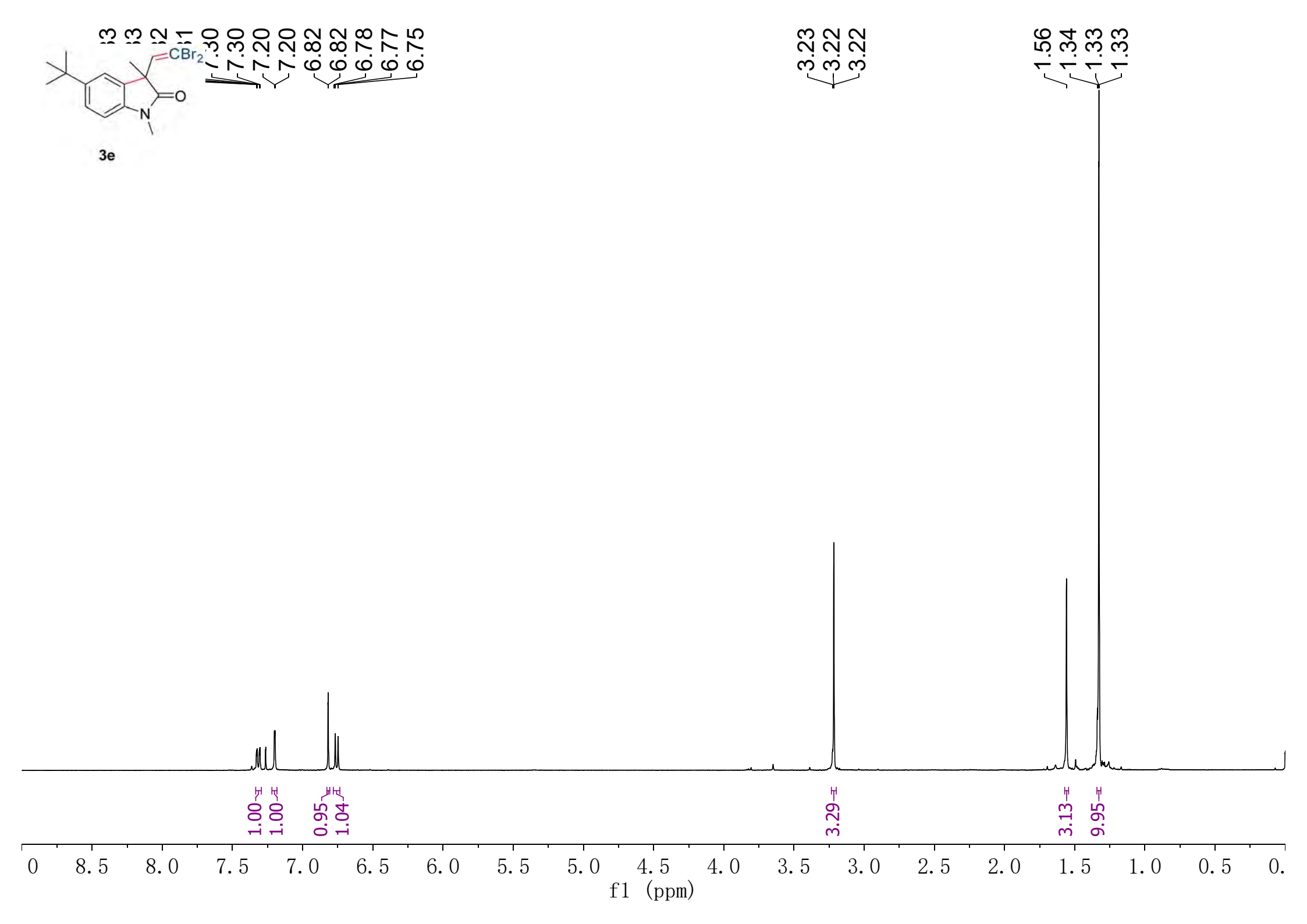
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1.33
1.33
CBr2
O
N
3e
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1.00
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1.04
3.29
3.13
9.95
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8.5
8.0
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7.0
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6.0
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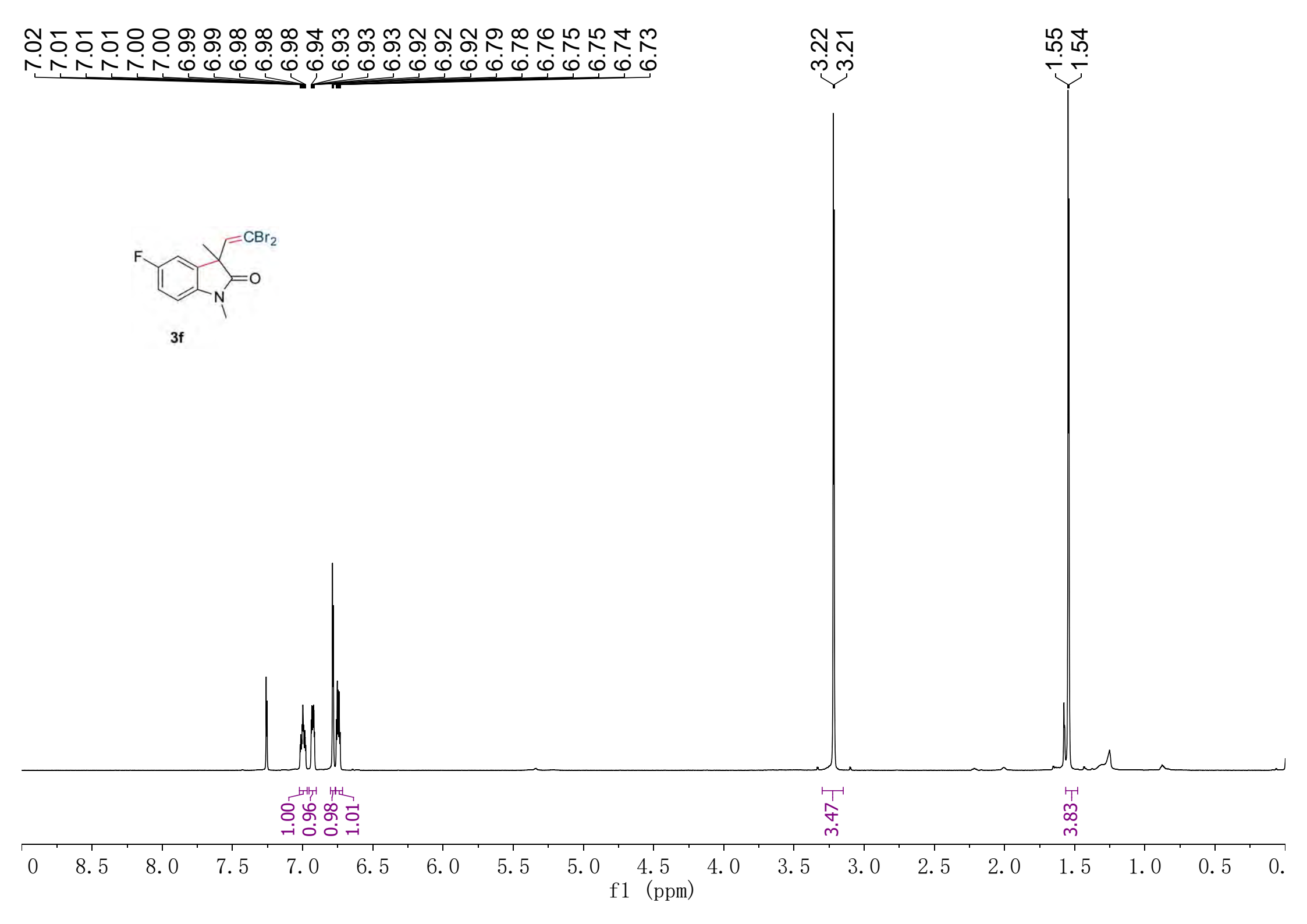
f1 (ppm)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6.93
6.93
6.93
6.92
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6.75
6.74
6.73
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3.21
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CBr2
O
N
3f
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0.98
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6.0
5.5
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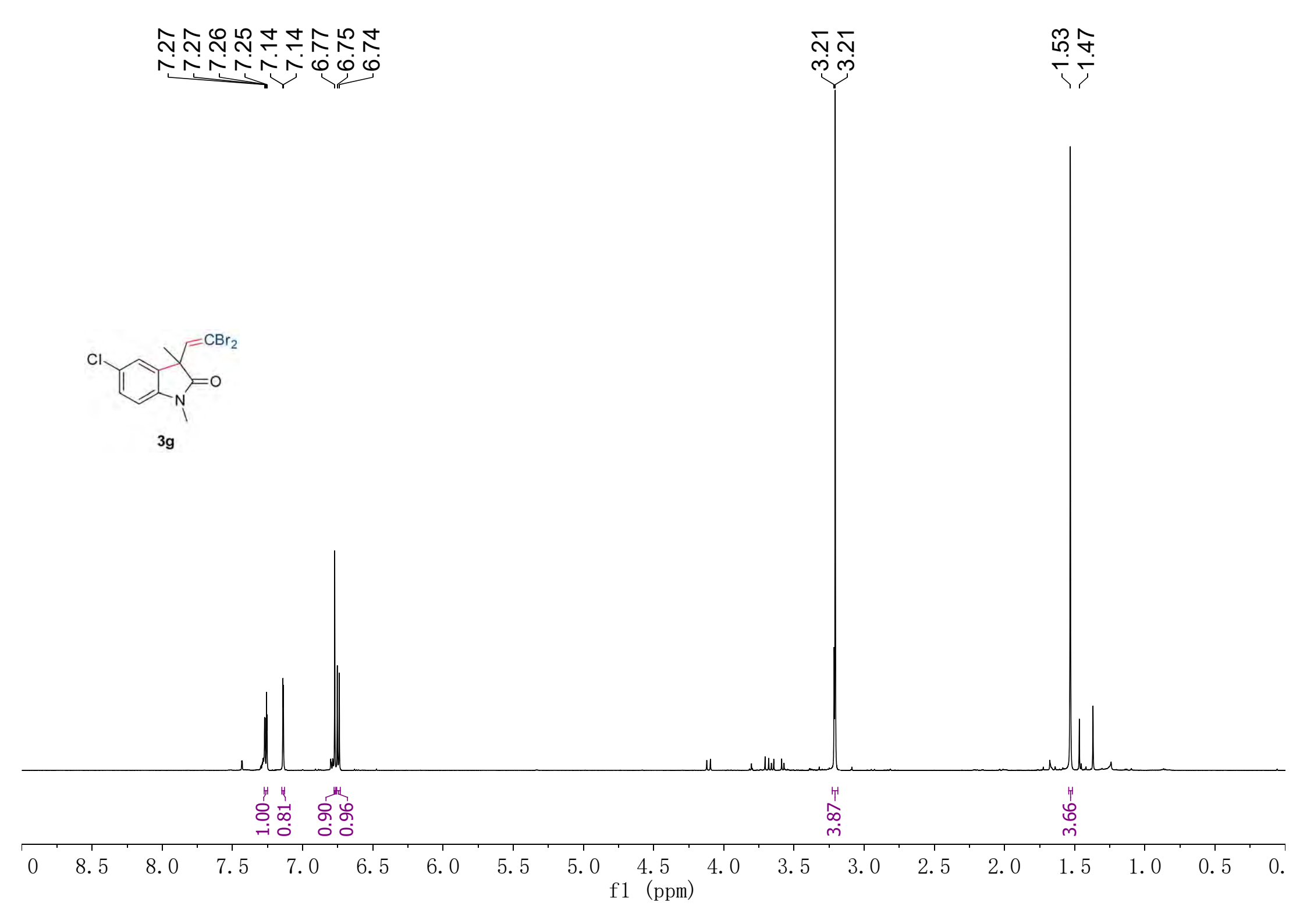
f1 (ppm)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Cl
CBr2
O
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2.0
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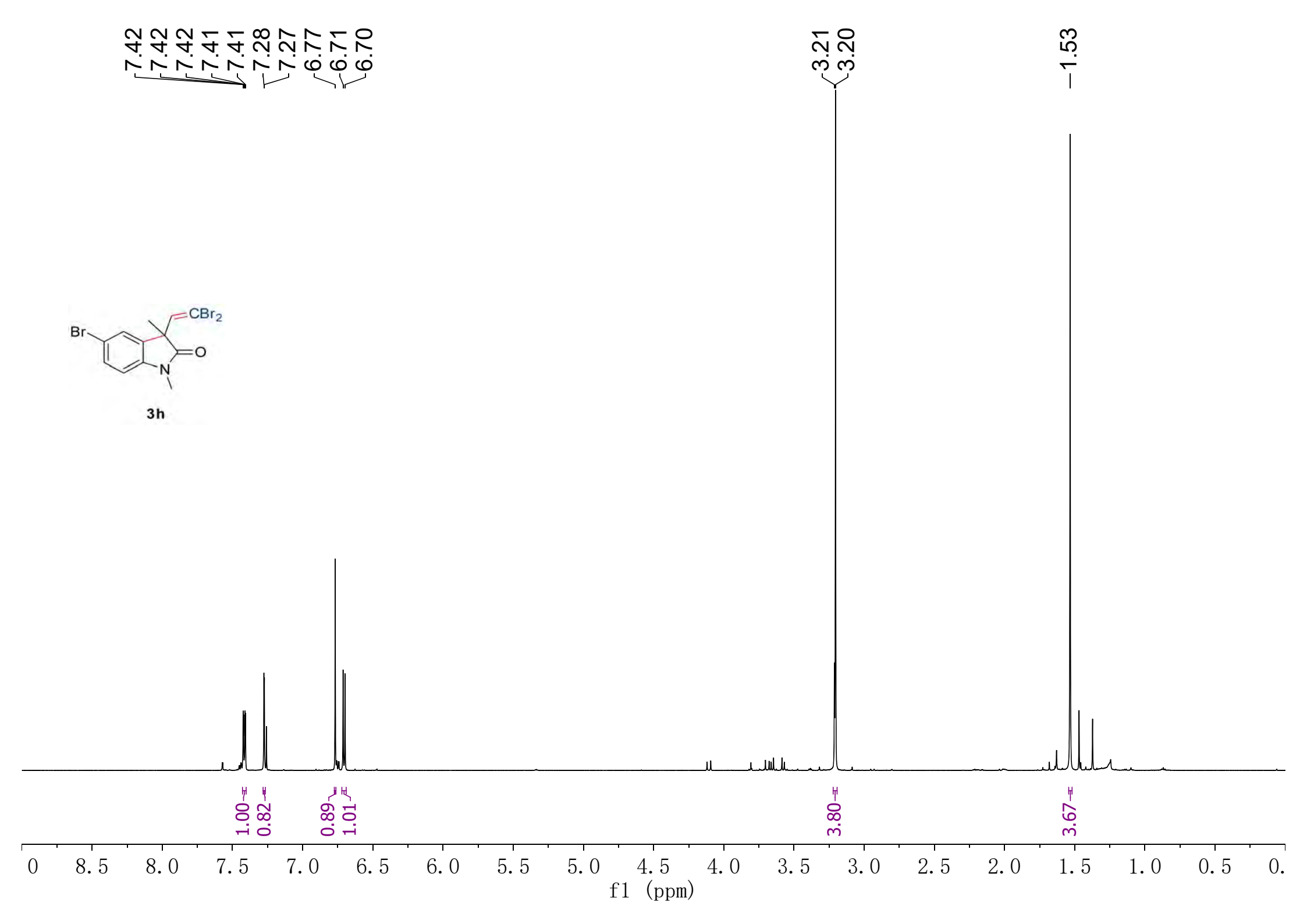
f1 (ppm)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CBr2
O
N
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8.0
7.5
7.0
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5.5
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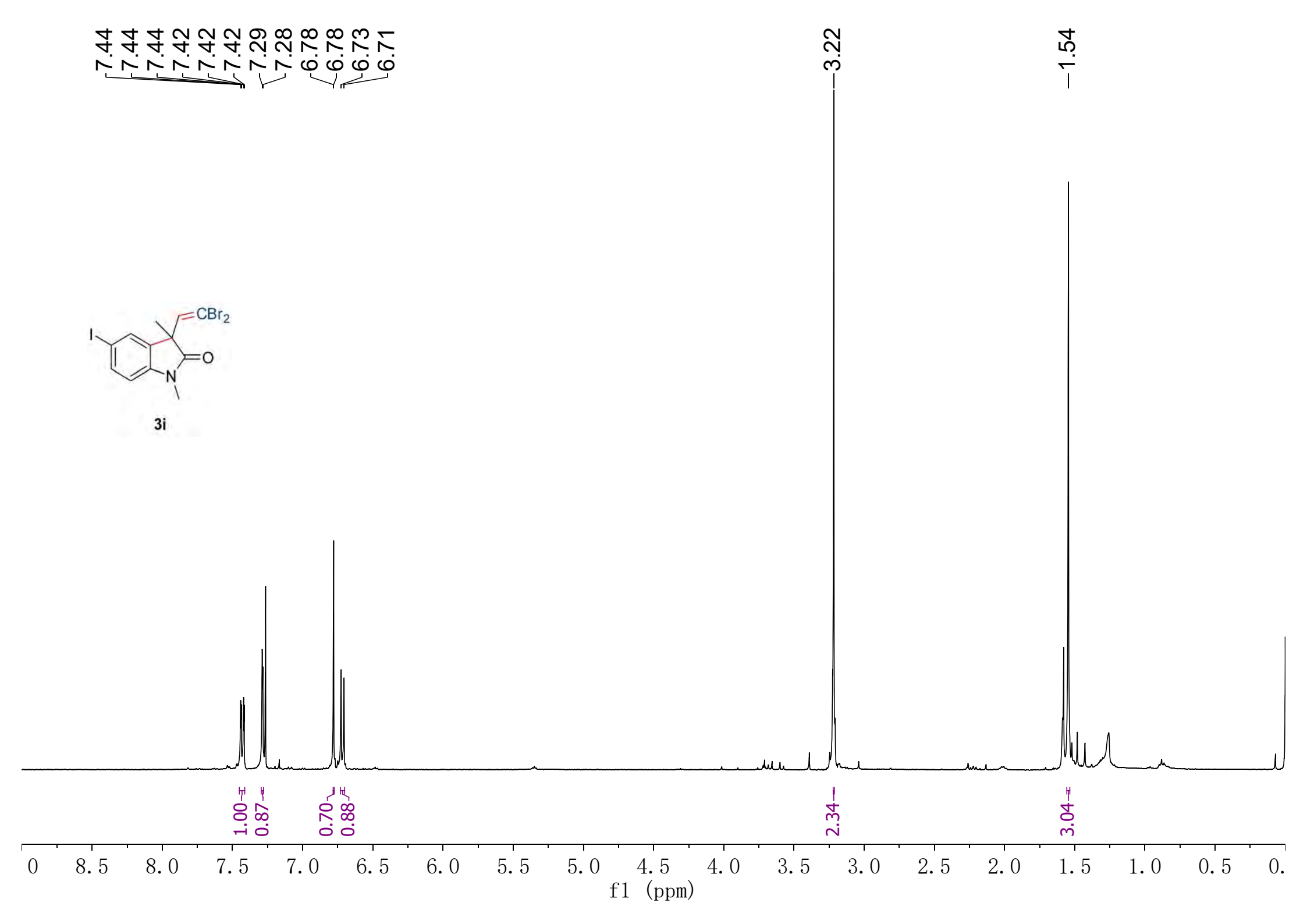
f1 (ppm)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I
O
N
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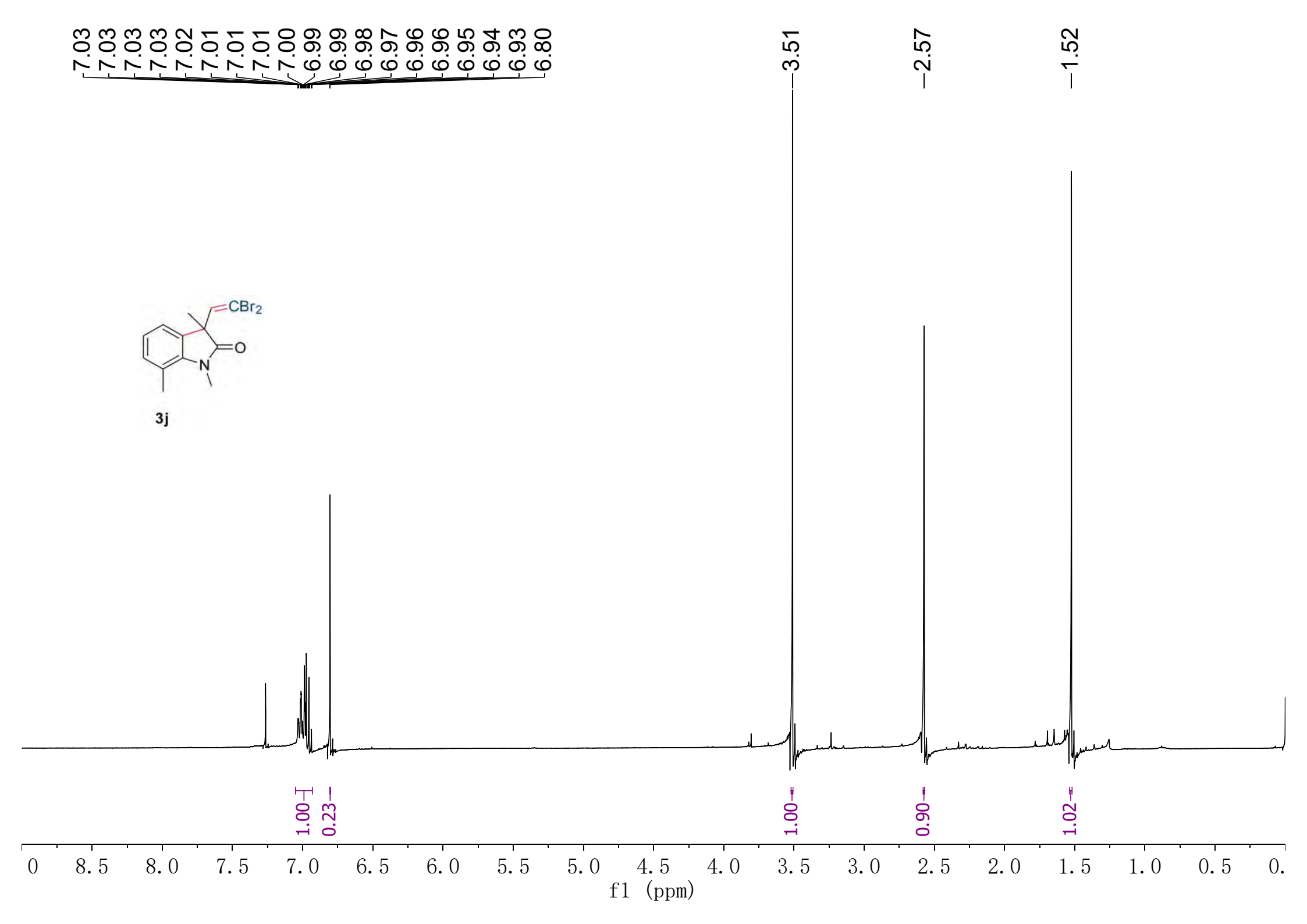
3.04
f1 (ppm)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6.99
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6.96
6.96
6.95
6.94
6.93
6.80
3.51
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CBr2
O
N
3j
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1.00
0.90
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5.5
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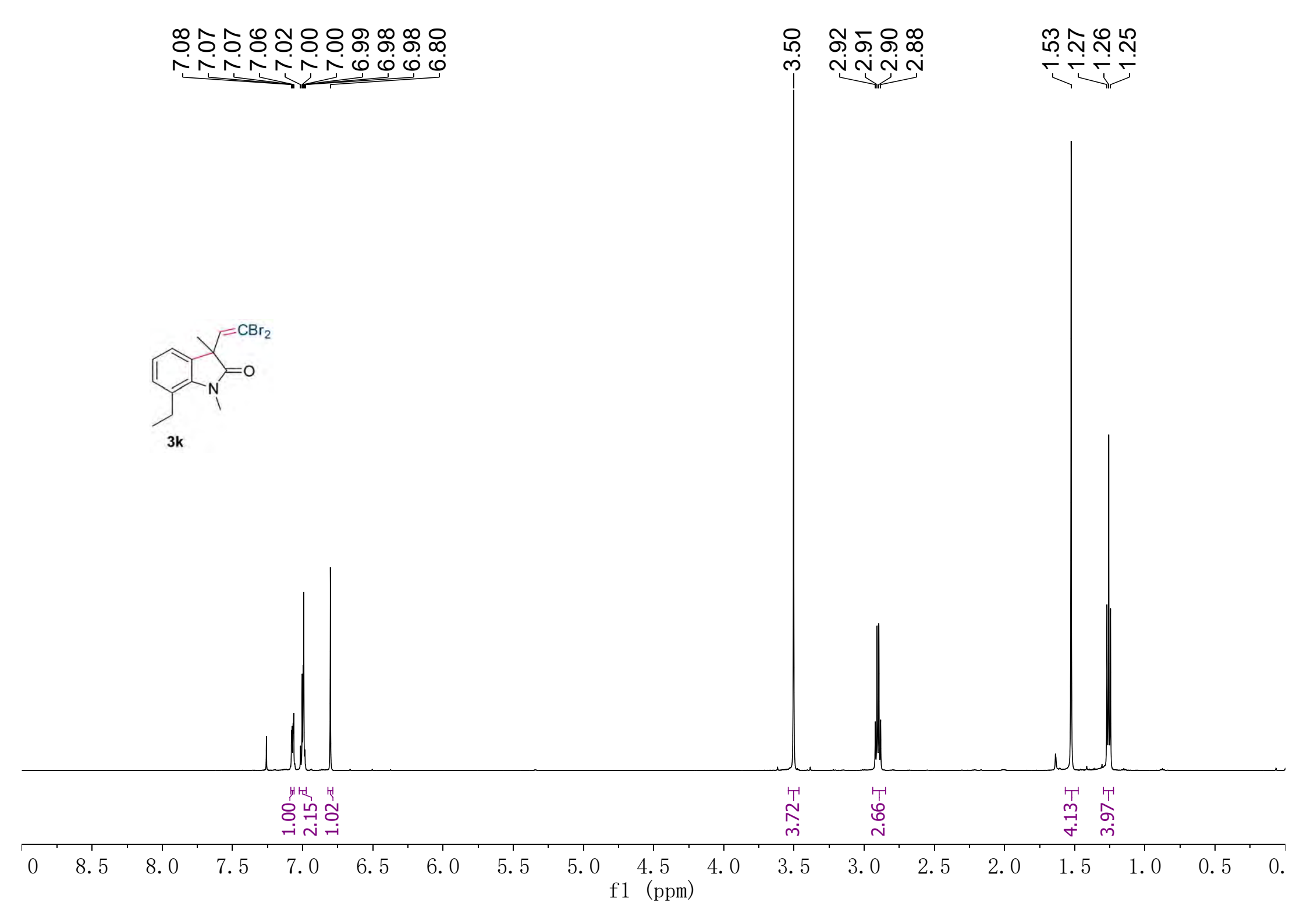
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2.92
2.91
2.90
2.88
1.53
1.27
1.26
1.25
CBr2
O
N
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2.0
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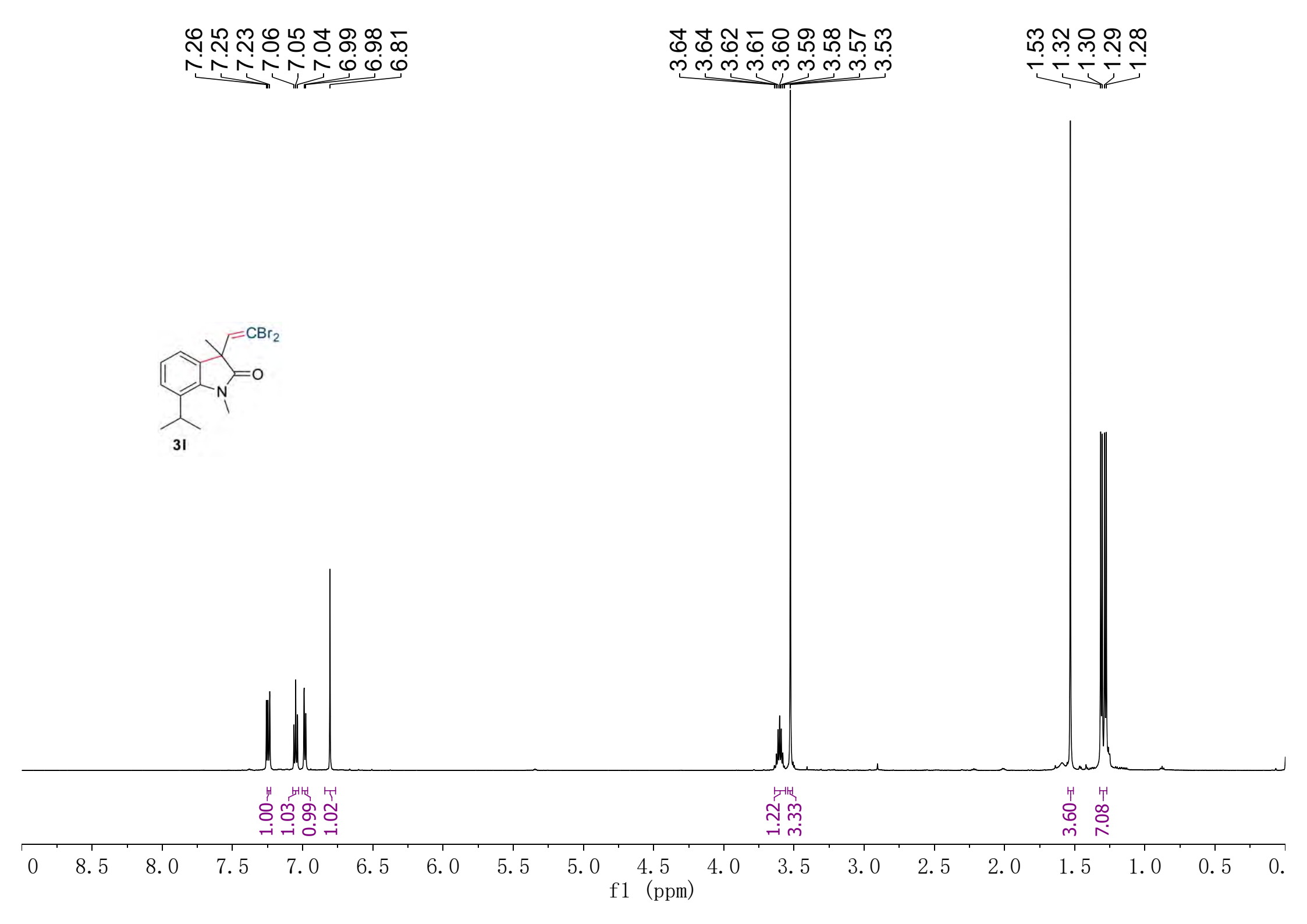
f1 (ppm)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3.57
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1.53
1.32
1.30
1.29
1.28
CBr2
O
N
3l
1.00
1.03
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1.02
1.22
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3.60
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8.0
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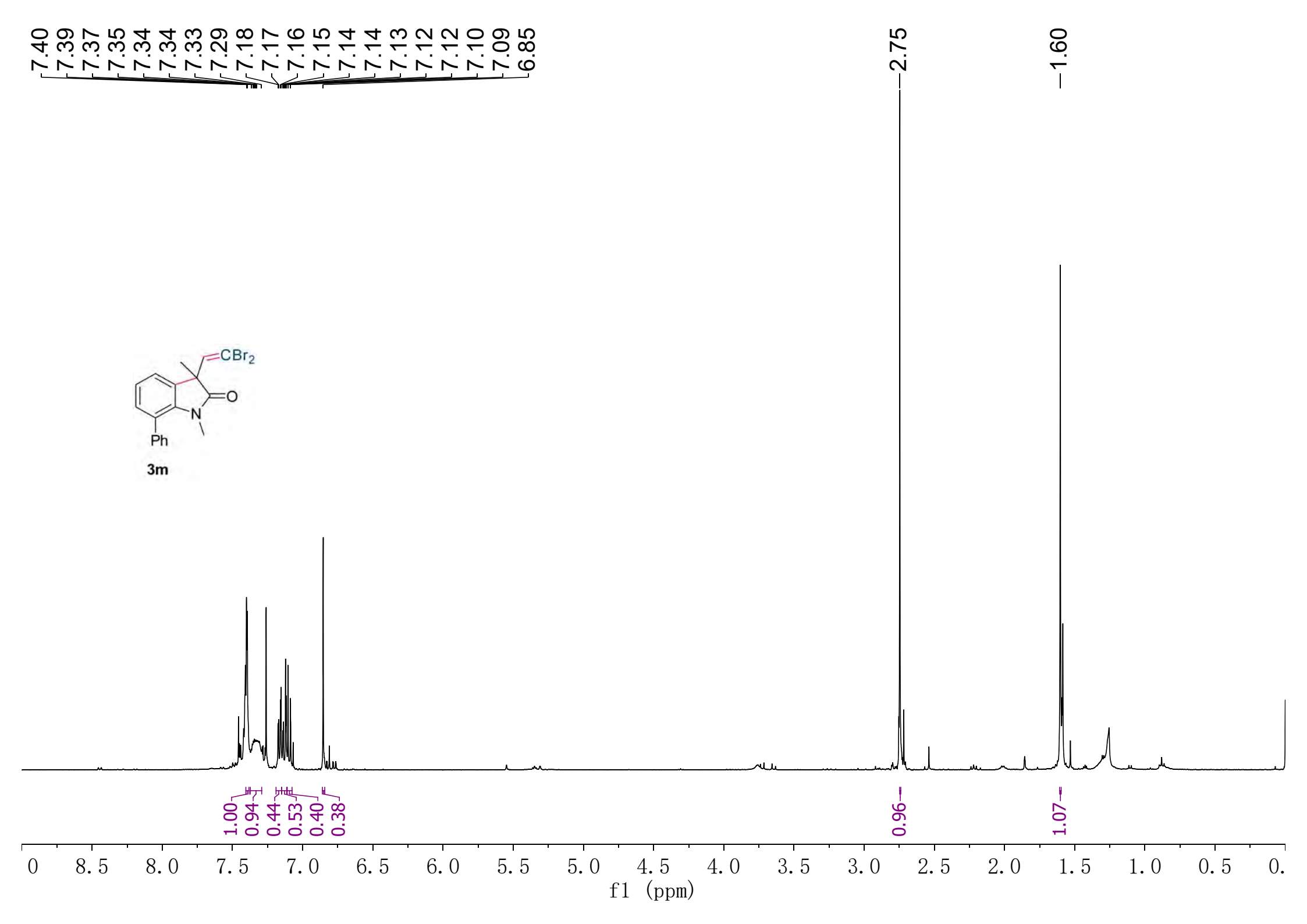
f1 (ppm)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7.10
7.09
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CBr2
O
N
Ph
3m
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0.53
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0.96
1.07
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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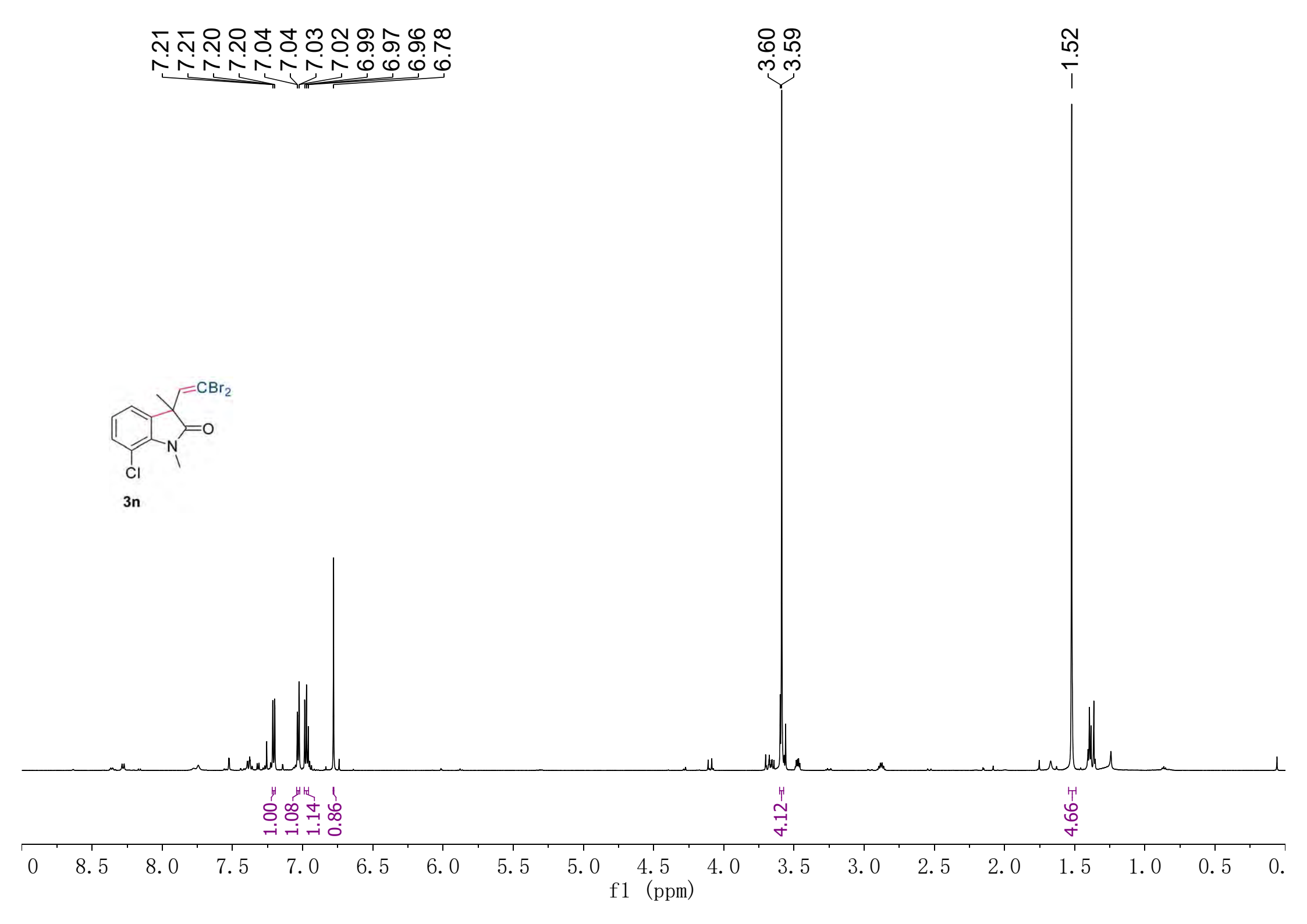
f1 (ppm)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7.04
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7.02
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6.97
6.96
6.78
3.60
3.59
1.52
CBr2
O
N
Cl
3n
1.00
1.08
1.14
0.86
4.12
4.66
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
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1.0
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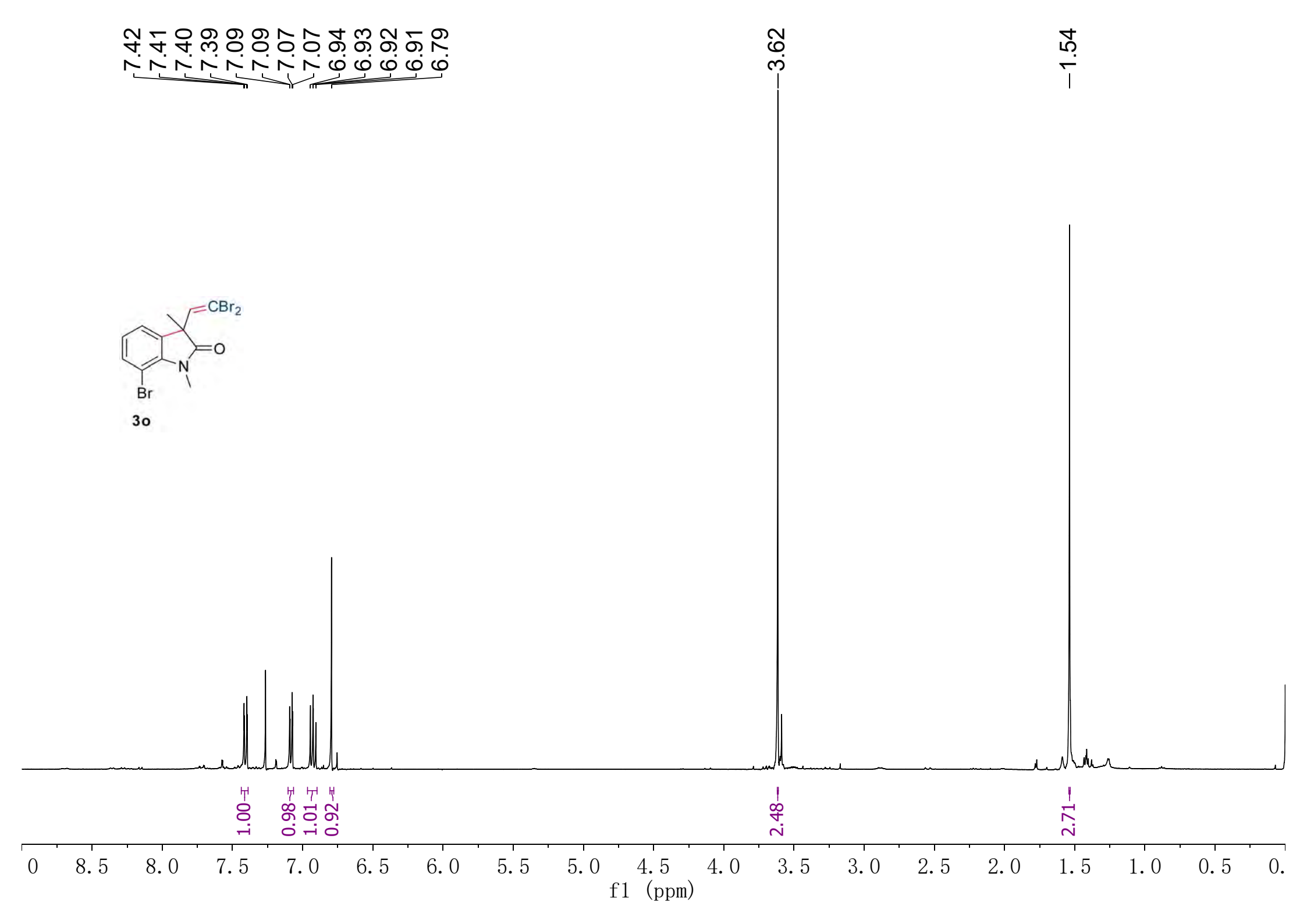
f1 (ppm)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6.92
6.91
6.79
3.62
1.54
CBr2
O
N
Br
3o
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0.98
1.01
0.92
2.48
2.71
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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1.5
1.0
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0.
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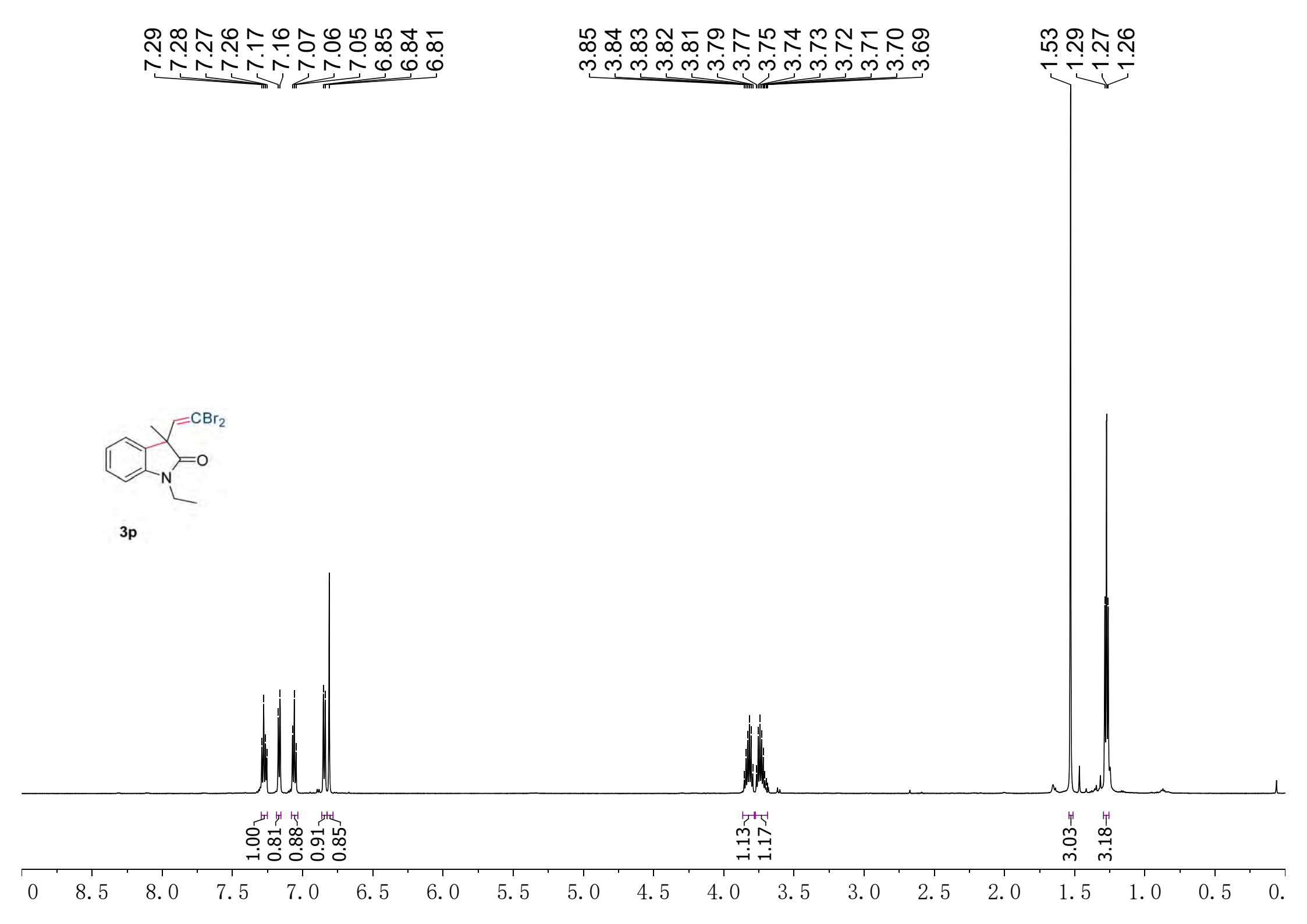
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6.84
6.81
3.85
3.84
3.83
3.82
3.81
3.79
3.77
3.75
3.74
3.73
3.72
3.71
3.70
3.69
1.53
1.29
1.27
1.26
CBr2
O
N
3p
1.00
0.81
0.88
0.91
0.85
1.13
1.17
3.03
3.18
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8.0
7.5
7.0
6.5
6.0
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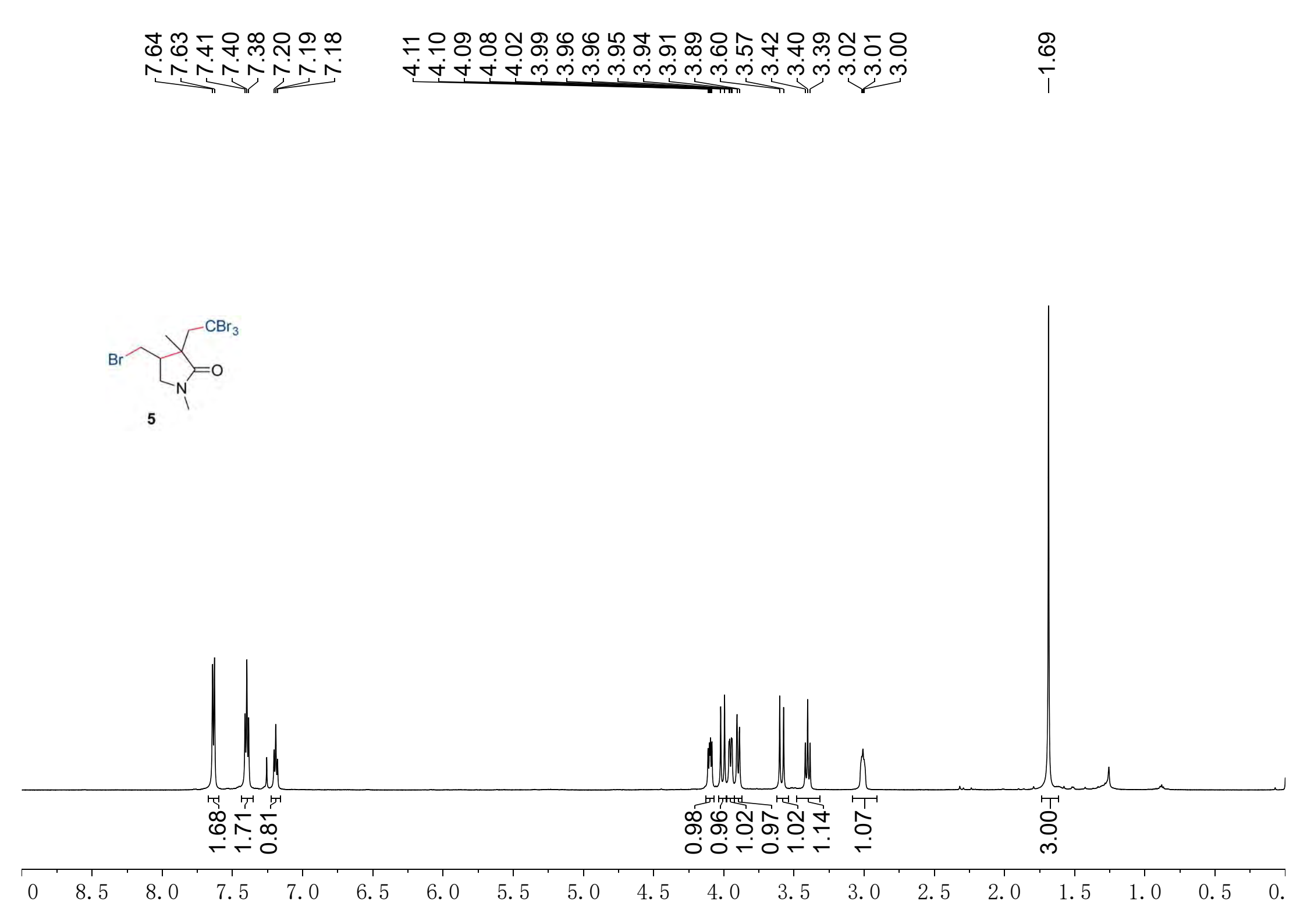
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4.09
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4.02
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3.96
3.96
3.95
3.94
3.91
3.89
3.60
3.57
3.42
3.40
3.39
3.02
3.01
3.00
1.69
Br
CBr3
O
N
5
1.68
1.71
0.81
0.98
0.96
1.02
0.97
1.02
1.14
1.07
3.00
0
8.5
8.0
7.5
7.0
6.5
6.0
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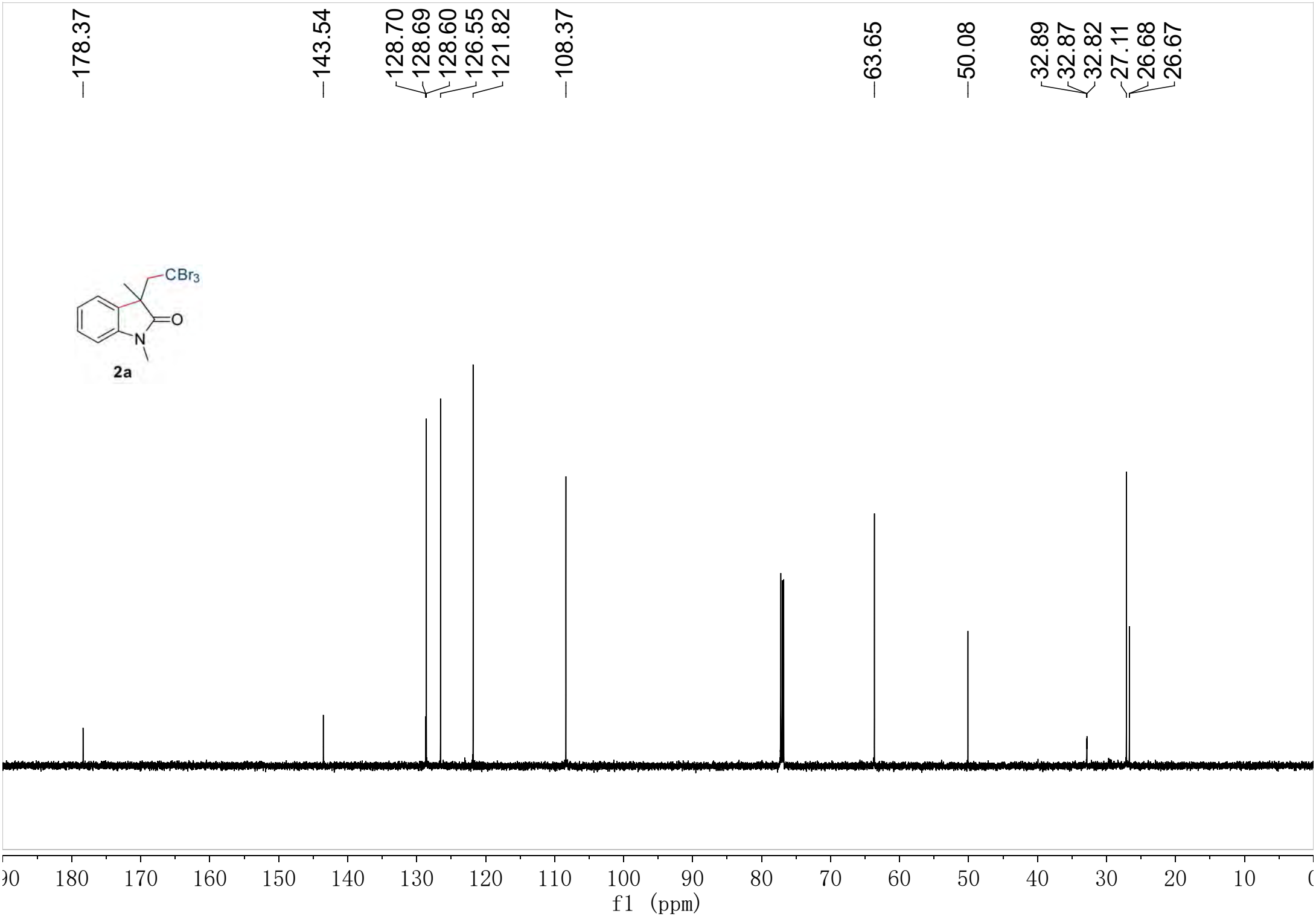
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128.60
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121.82
108.37
63.65
50.08
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32.87
32.82
27.11
26.68
26.67
CBr3
O
N
2a
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140
130
120
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100
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80
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60
50
40
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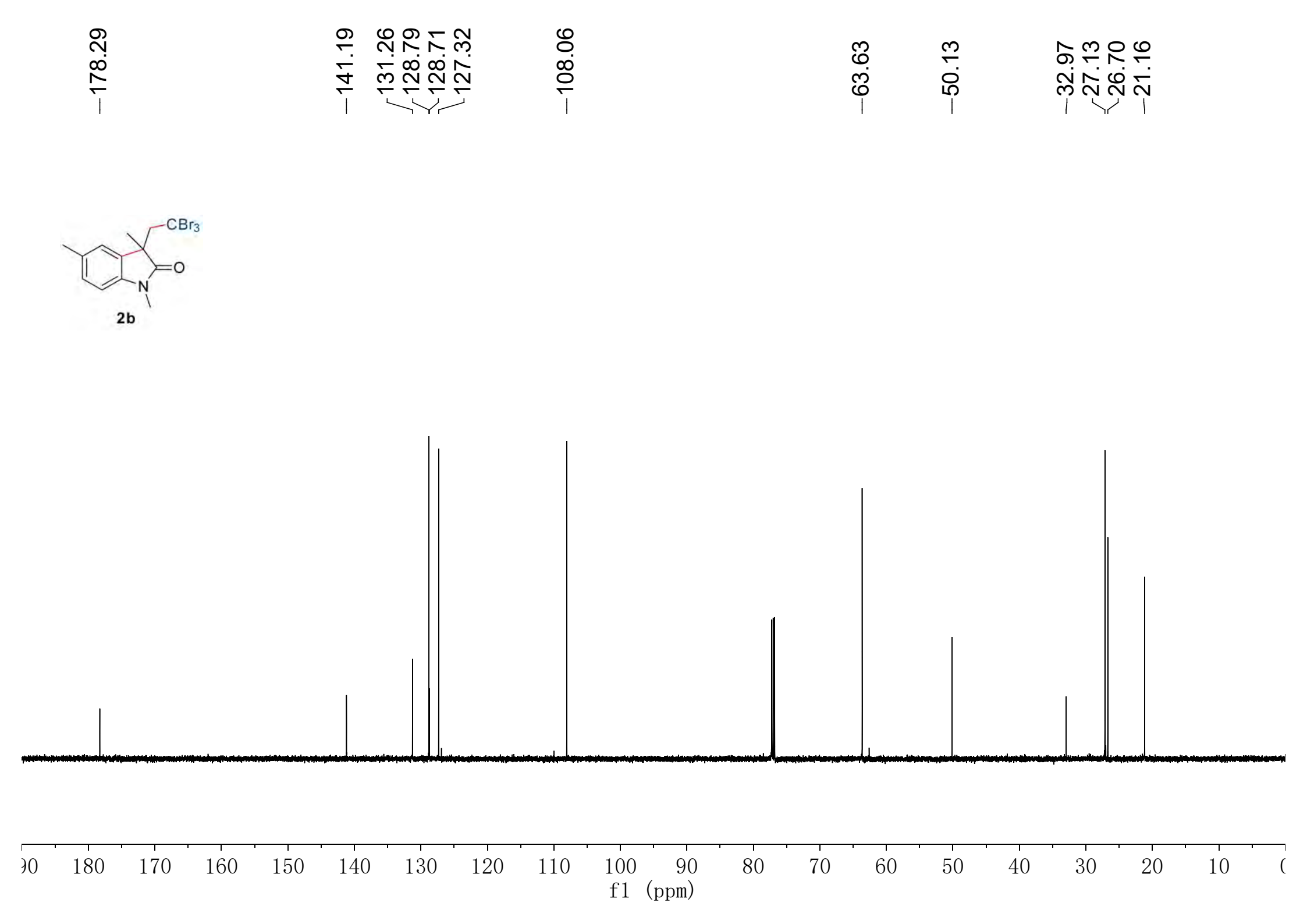
20
10
f1 (ppm)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127.32
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63.63
50.13
32.97
27.13
26.70
21.16
CBr3
O
N
2b
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140
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120
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100
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80
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60
50
40
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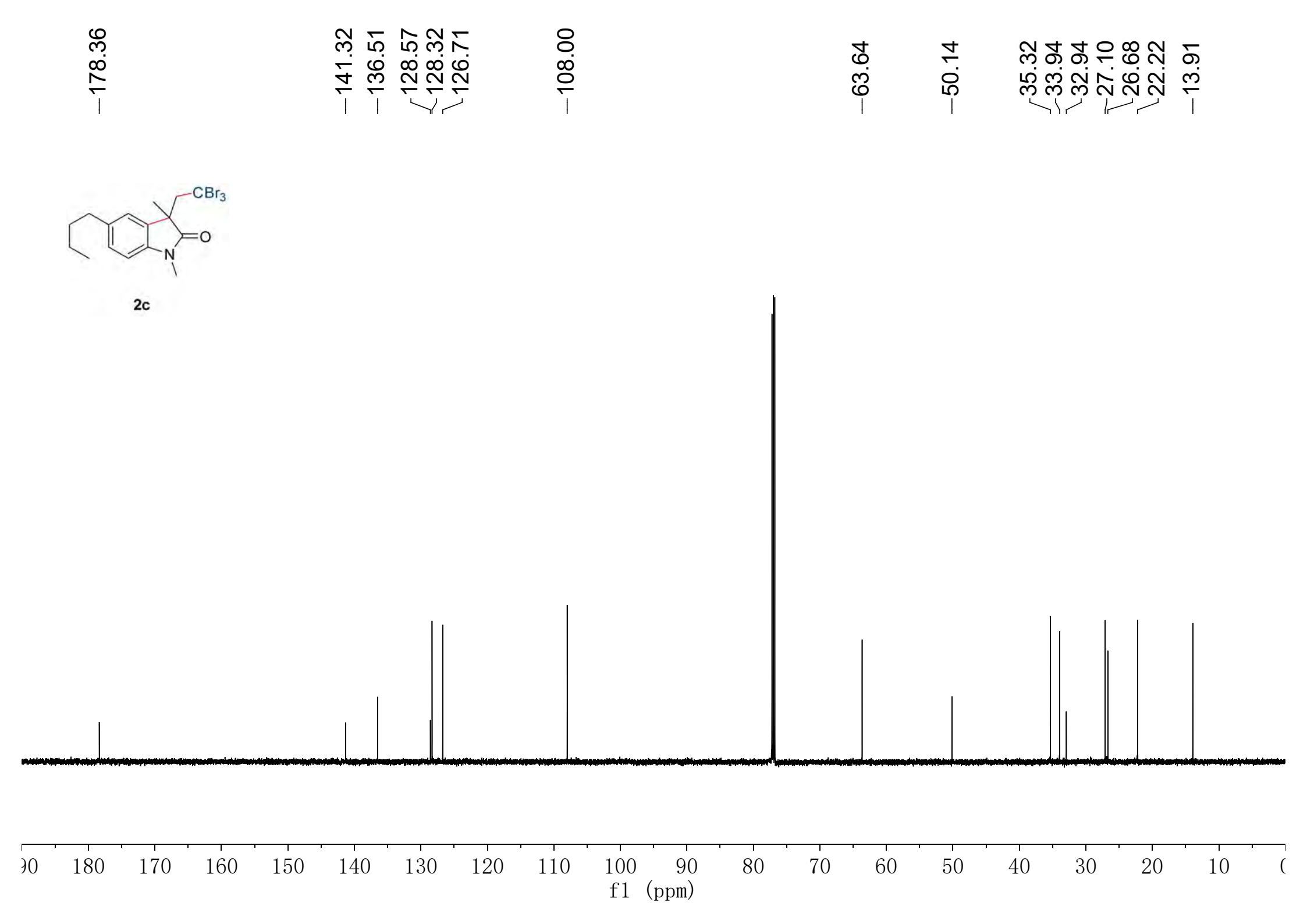
20
10
f1 (ppm)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136.51
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128.32
126.71
108.00
63.64
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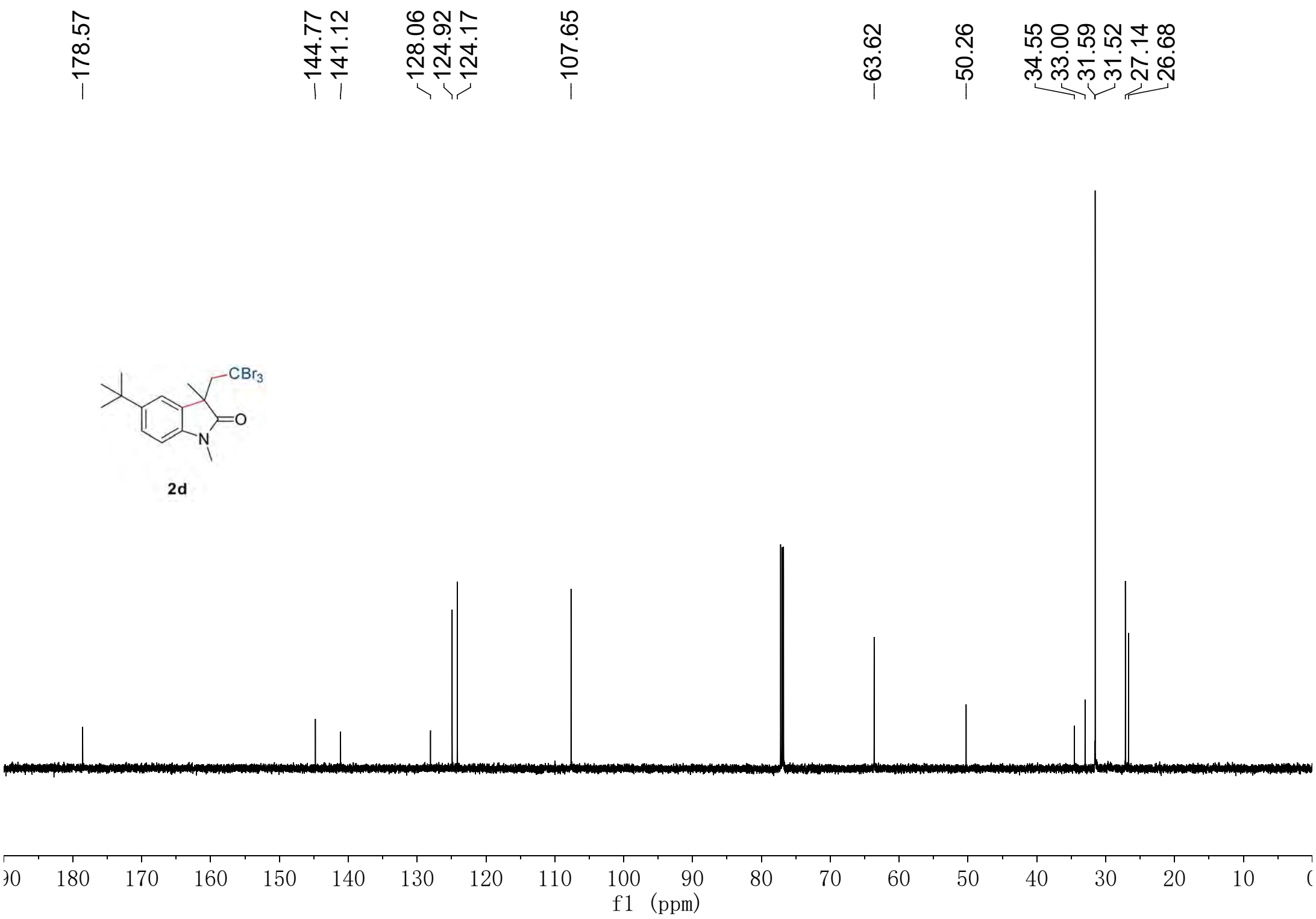
32.94
27.10
26.68
22.22
13.91
CBr3
O
N
2c
f1 (ppm)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124.92
124.17
107.65
63.62
50.26
34.55
33.00
31.59
31.52
27.14
26.68
CBr3
O
N
2d
180
170
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130
120
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100
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80
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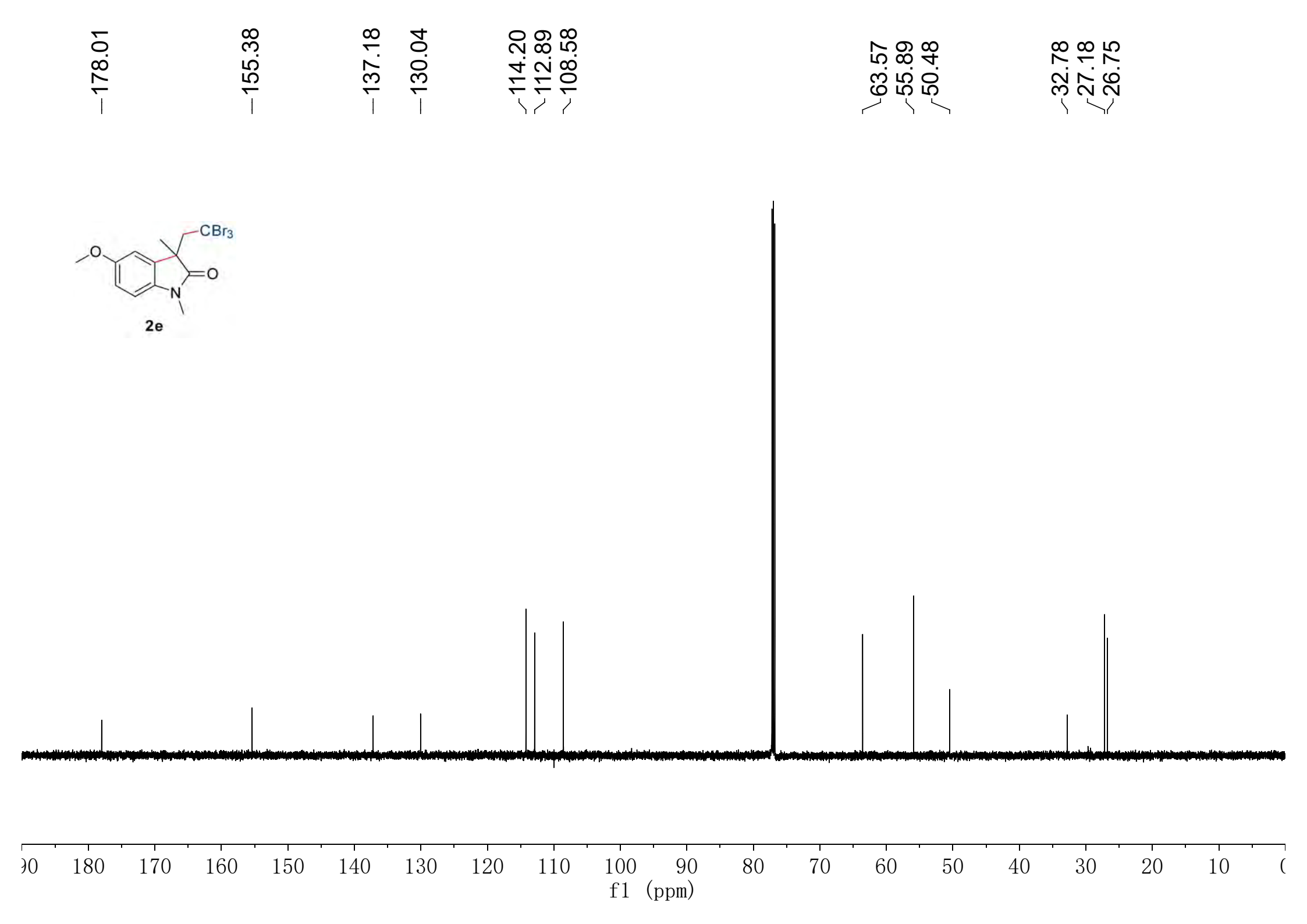
50
40
30
20
10
f1 (ppm)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114.20
112.89
108.58
63.57
55.89
50.48
32.78
27.18
26.75
CBr3
O
O
N
2e
180
170
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140
130
120
110
100
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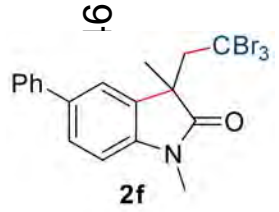
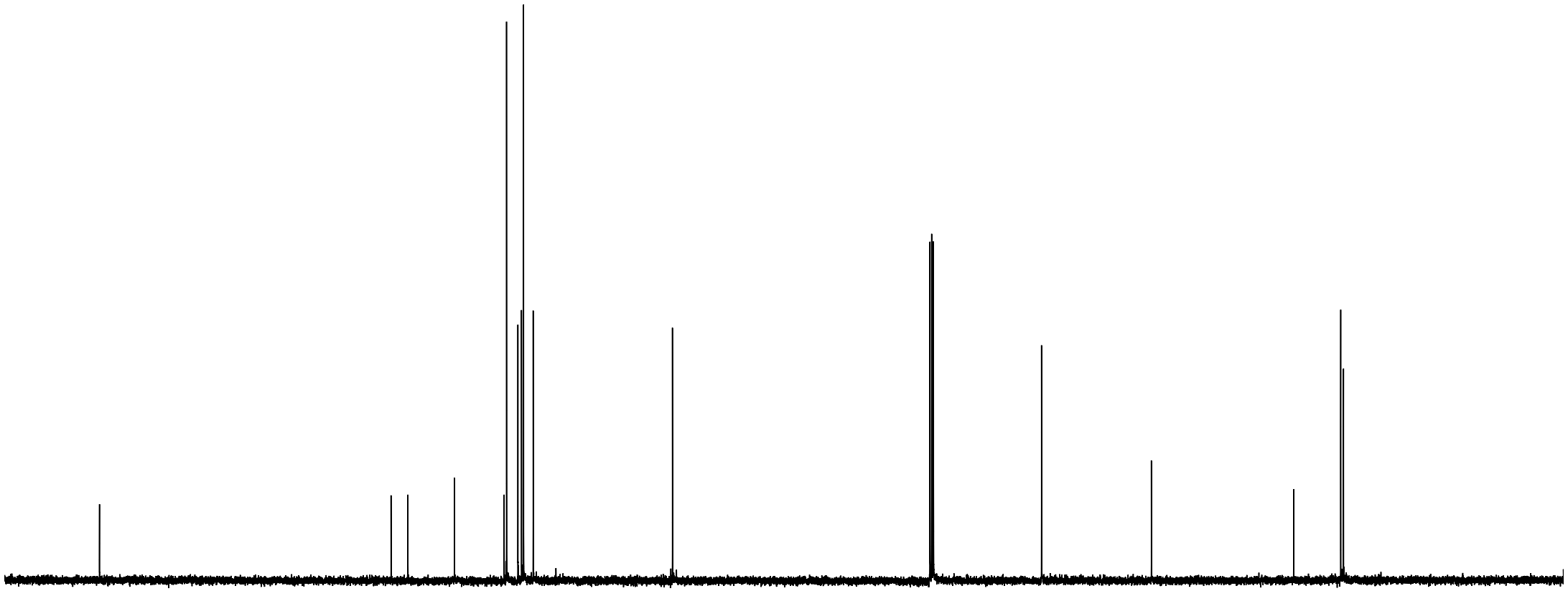
80
70
60
50
40
30
20
10
f1 (ppm)

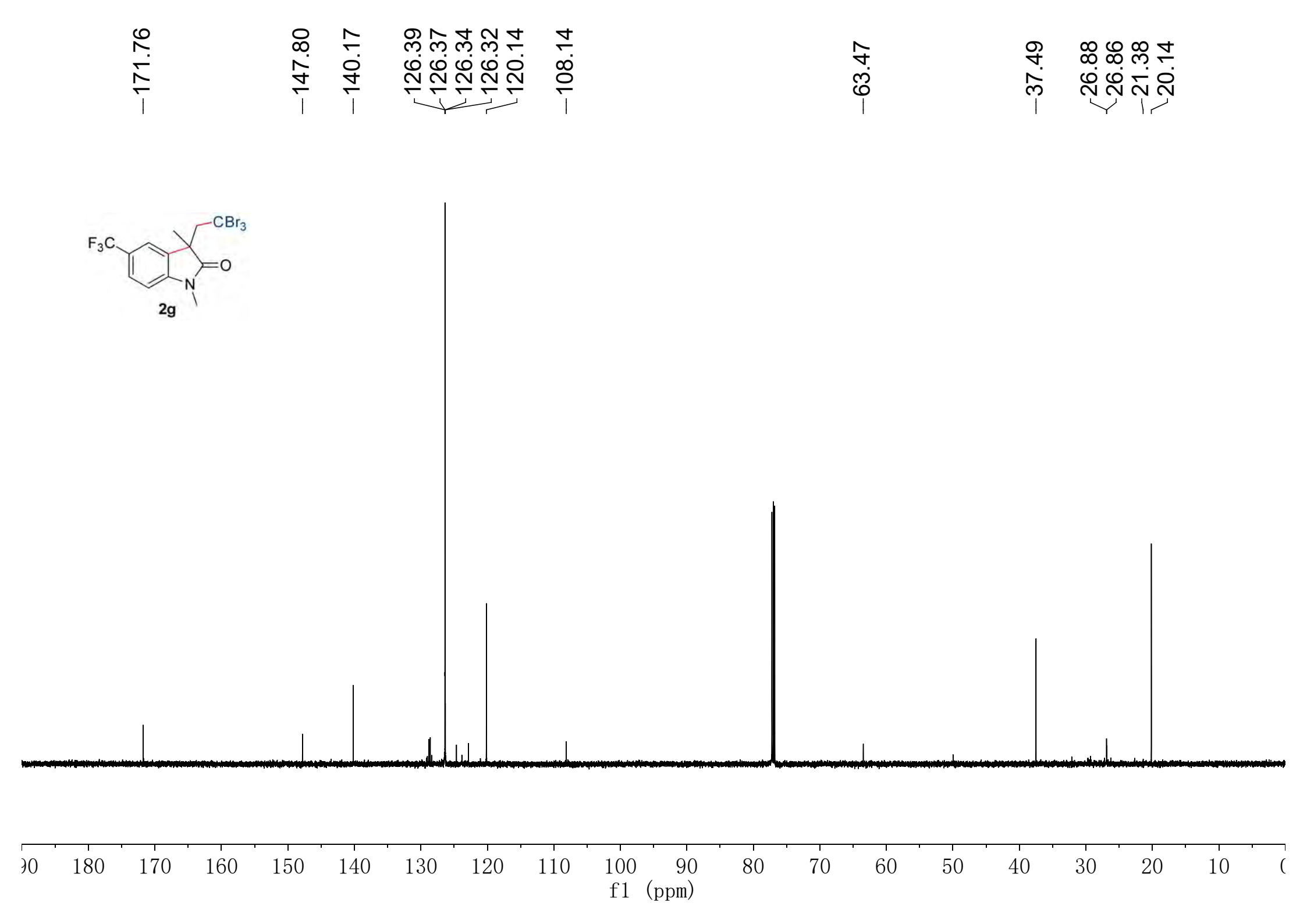


142.91
140.87
135.19
129.14
128.83
127.45
127.02
126.77
125.59
108.61
63.62
50.23
32.89
27.16
26.82



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)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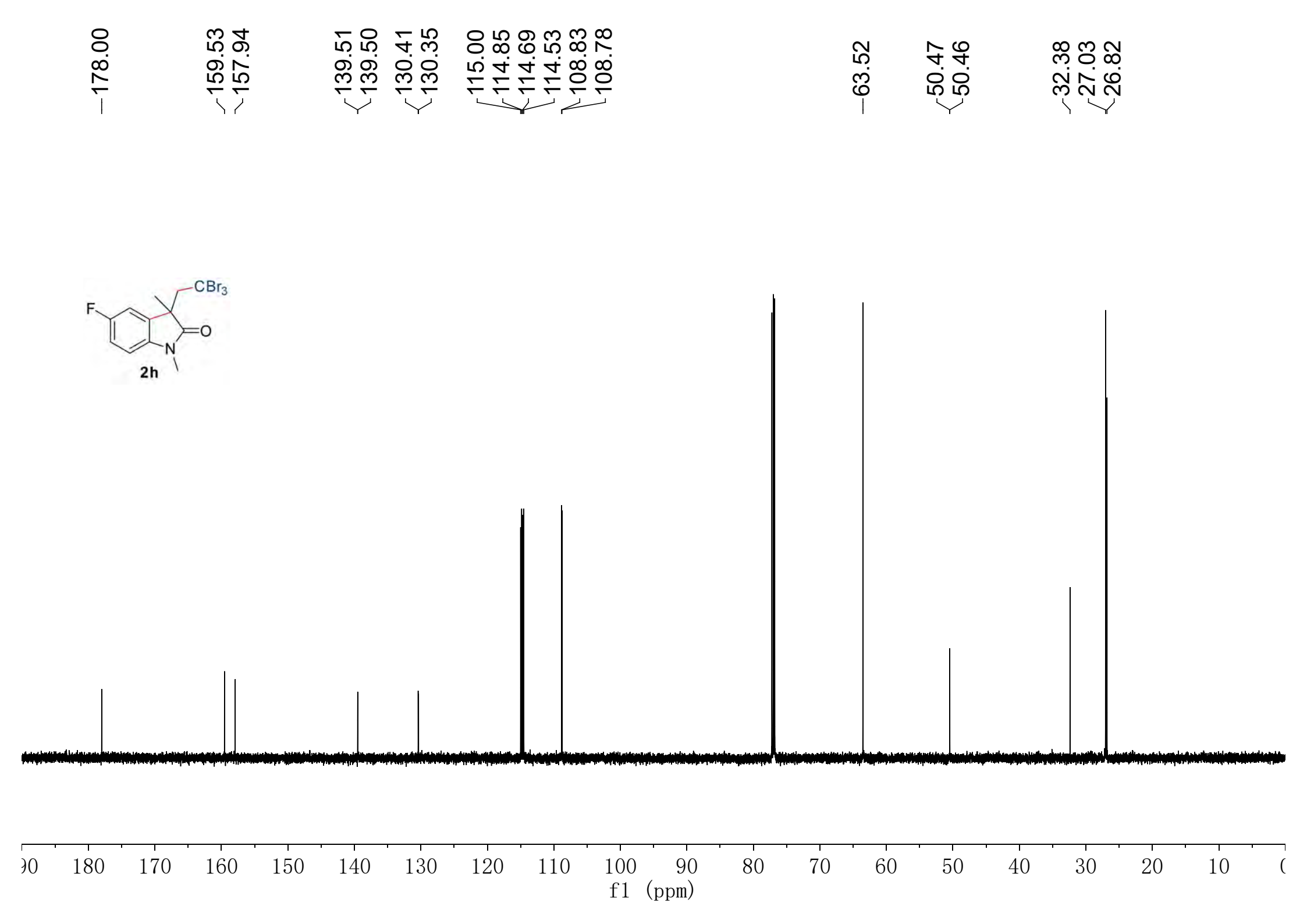
147.80
140.17
126.39
126.37
126.34
126.32
120.14
108.14
63.47
37.49
26.88
26.86
21.38
20.14
CBr3
F3C
O
N
2g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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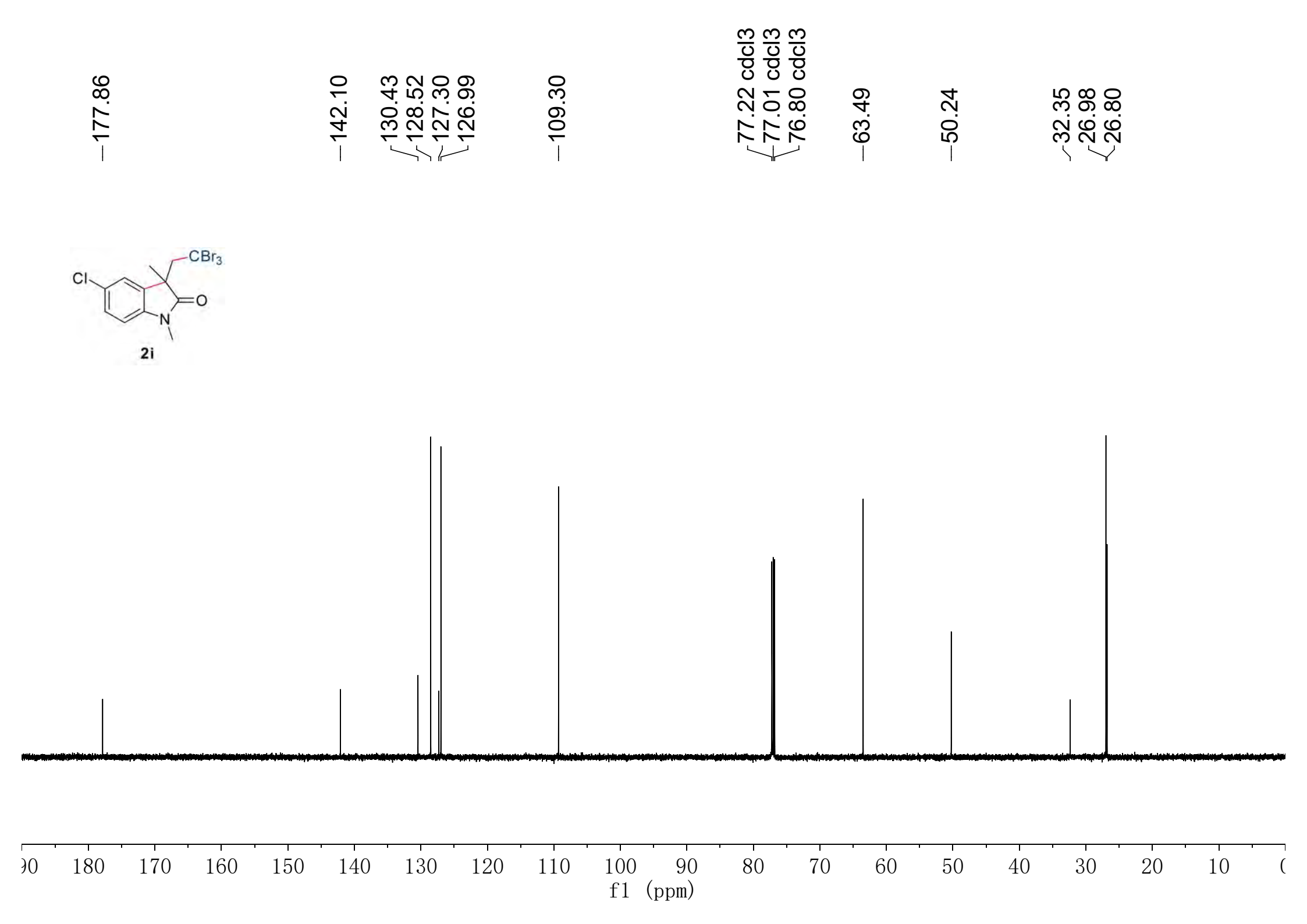
130.41
130.35
115.00
114.85
114.69
114.53
108.83
108.78
63.52
50.47
50.46
32.38
27.03
26.82
CBr3
F
O
N
2h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


177.86
142.10
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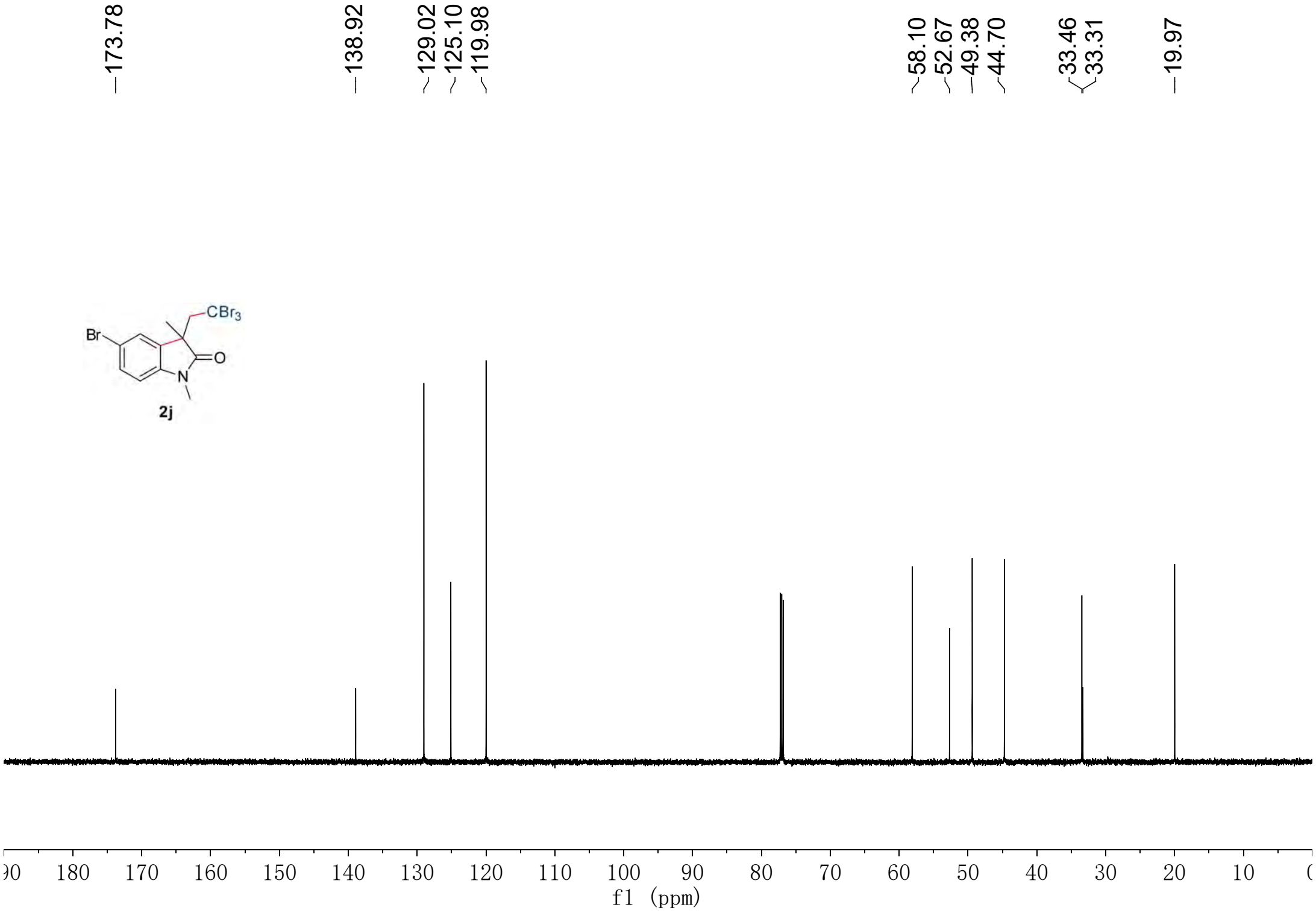
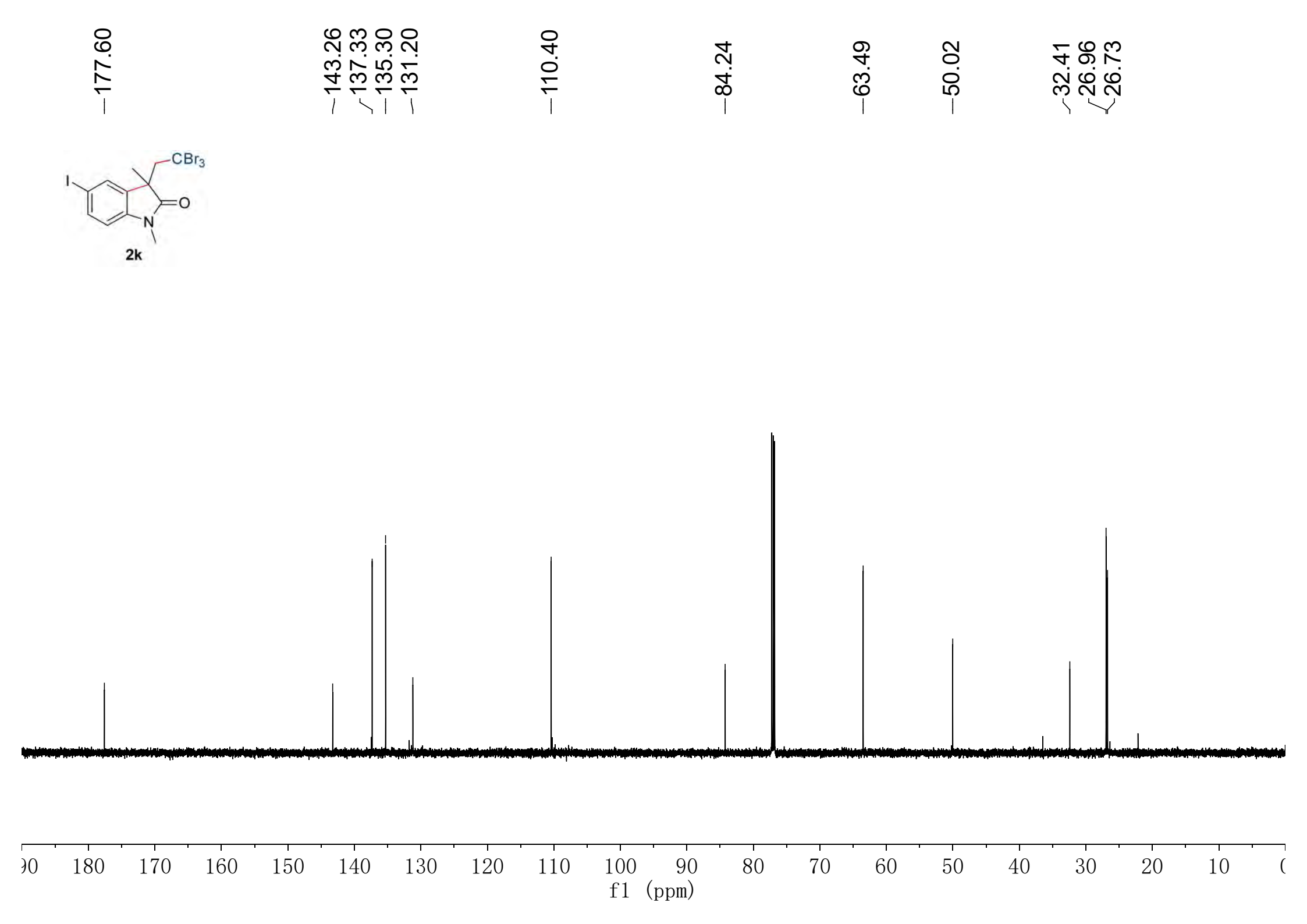
127.30
126.99
109.30
77.22 cdcl3
77.01 cdcl3
76.80 cdcl3
63.49
50.24
32.35
26.98
26.80
CBr3
Cl
O
N
2i
f1 (ppm)


173.78
138.92
129.02
125.10
119.98
58.10
52.67
49.38
44.70
33.46
33.31
19.97
Br
CBr3
O
N
2j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


177.60
143.26
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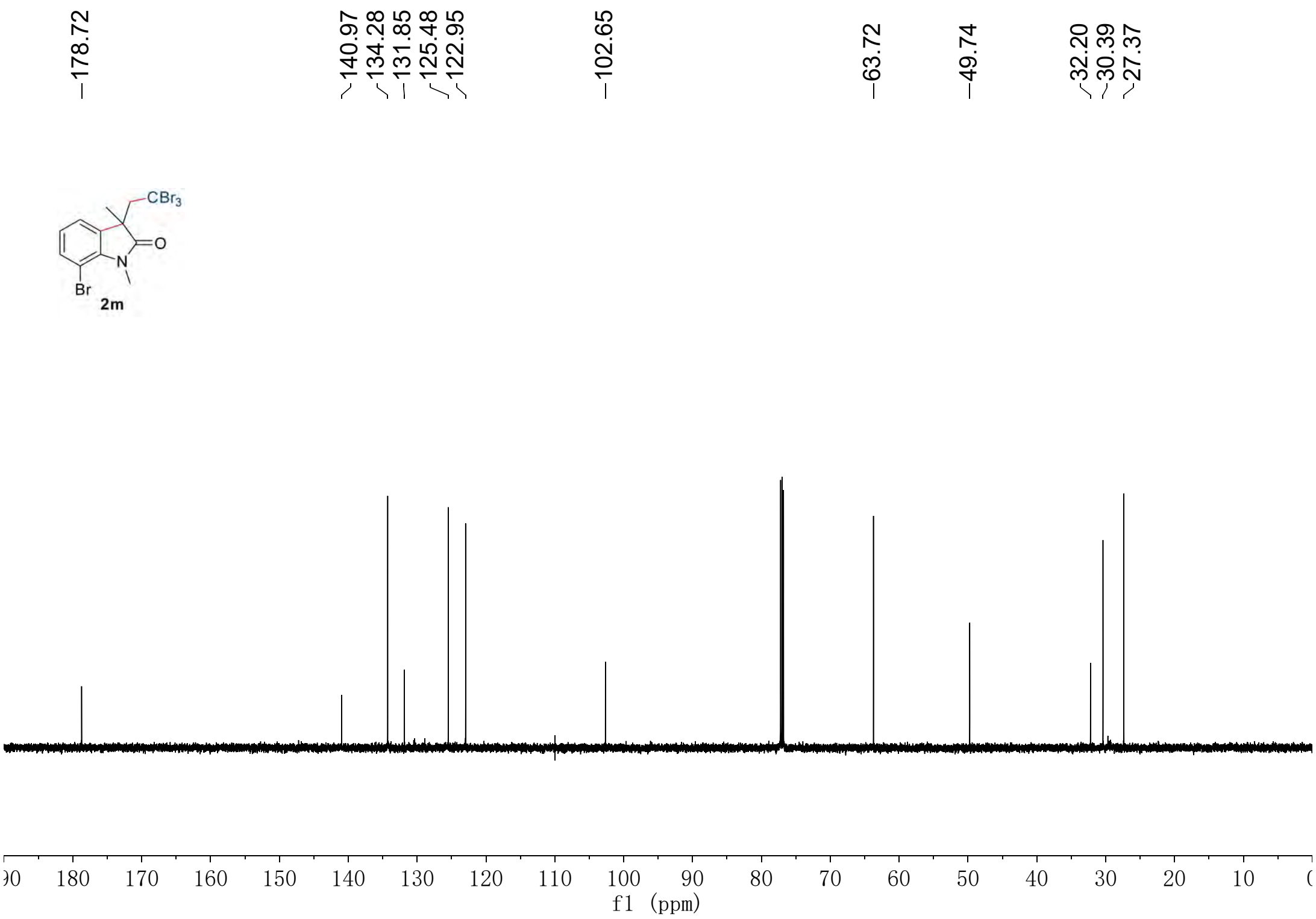
135.30
131.20
110.40
84.24
63.49
50.02
32.41
26.96
26.73
CBr3
I
O
N
2k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2l

139.54
131.54
130.91
124.96
122.55
115.81
63.72
49.79
32.24
30.15
27.34

f1 (ppm)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140.97
134.28
131.85
125.48
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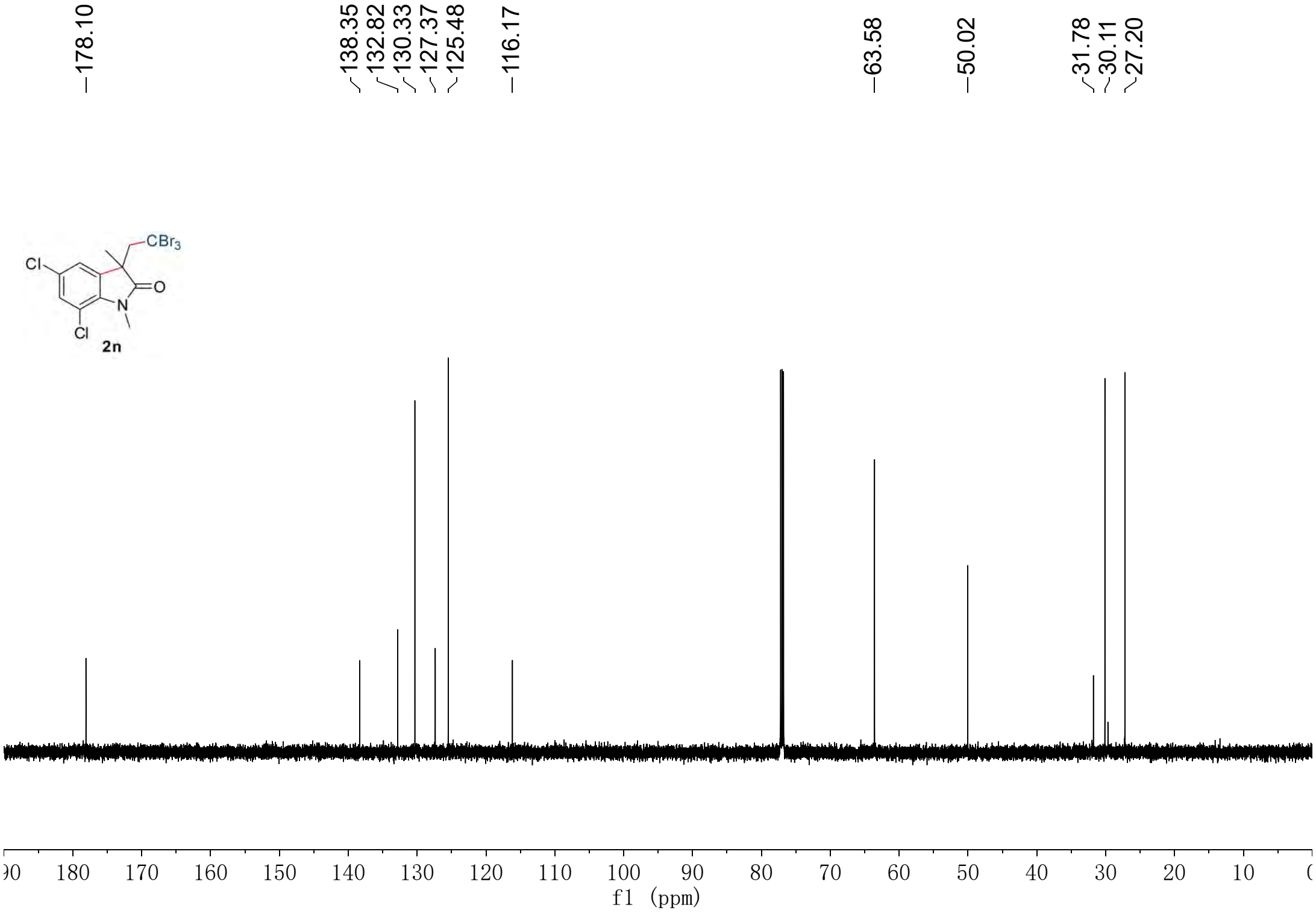
102.65
63.72
49.74
32.20
30.39
27.37
CBr3
O
N
Br
2m
f1 (ppm)


178.10
138.35
132.82
130.33
127.37
125.48
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63.58
50.02
31.78
30.11
27.20
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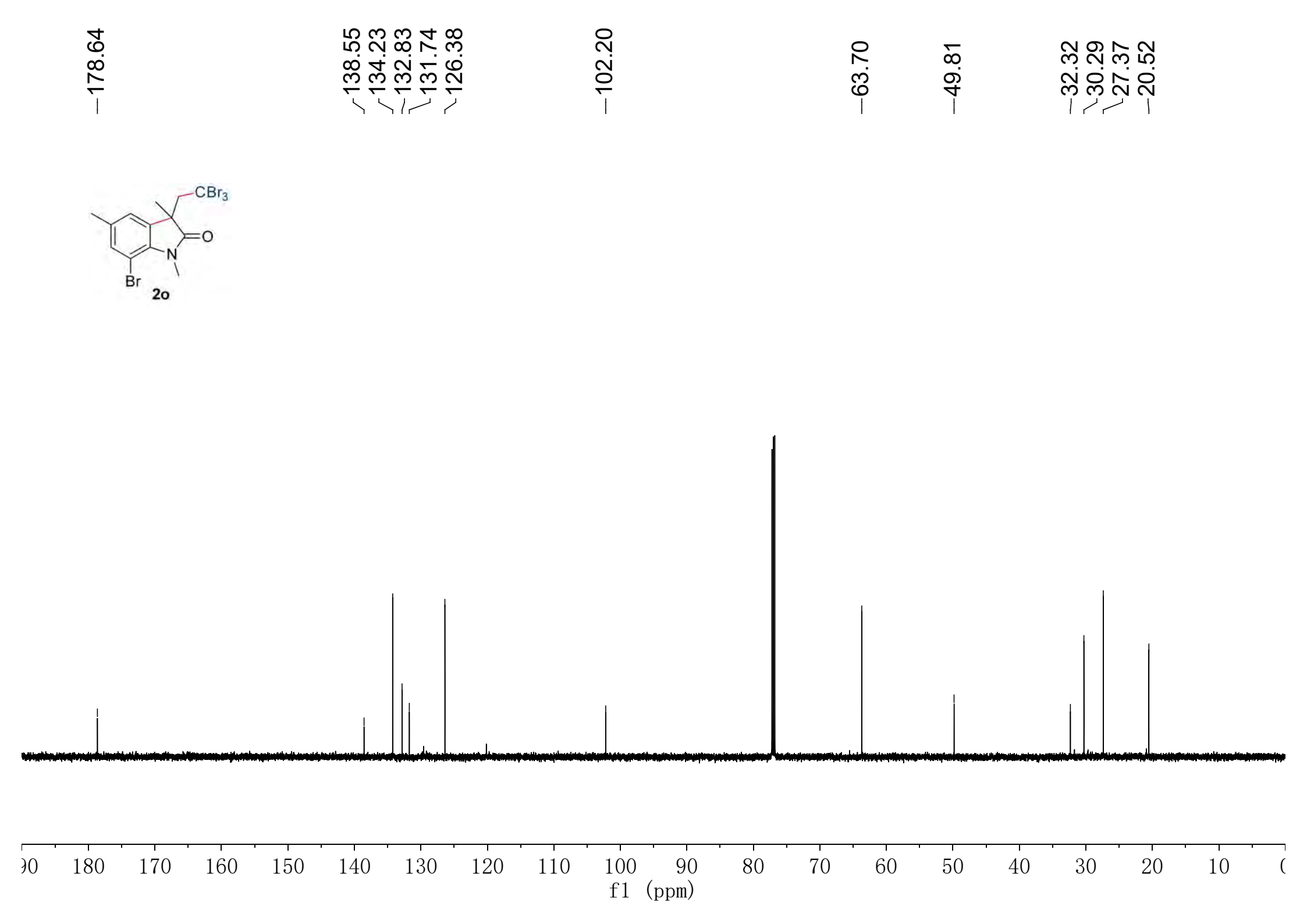
Cl
O
N
Cl
2n
f1 (ppm)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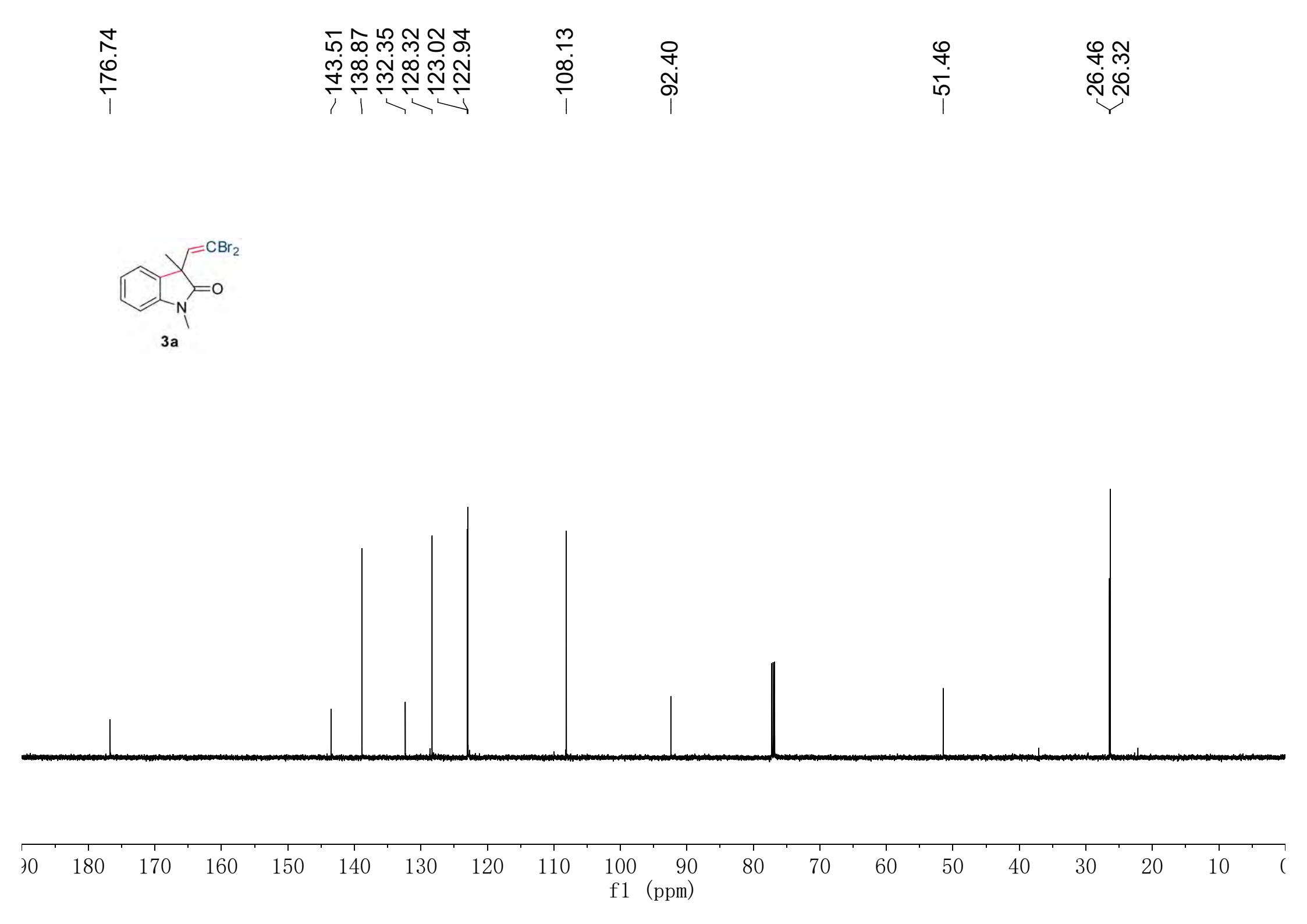
32.32
30.29
27.37
20.52
CBr3
O
N
Br
2o
f1 (ppm)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132.35
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123.02
122.94
108.13
92.40
51.46
26.46
26.32
CBr2
O
N
3a
180
170
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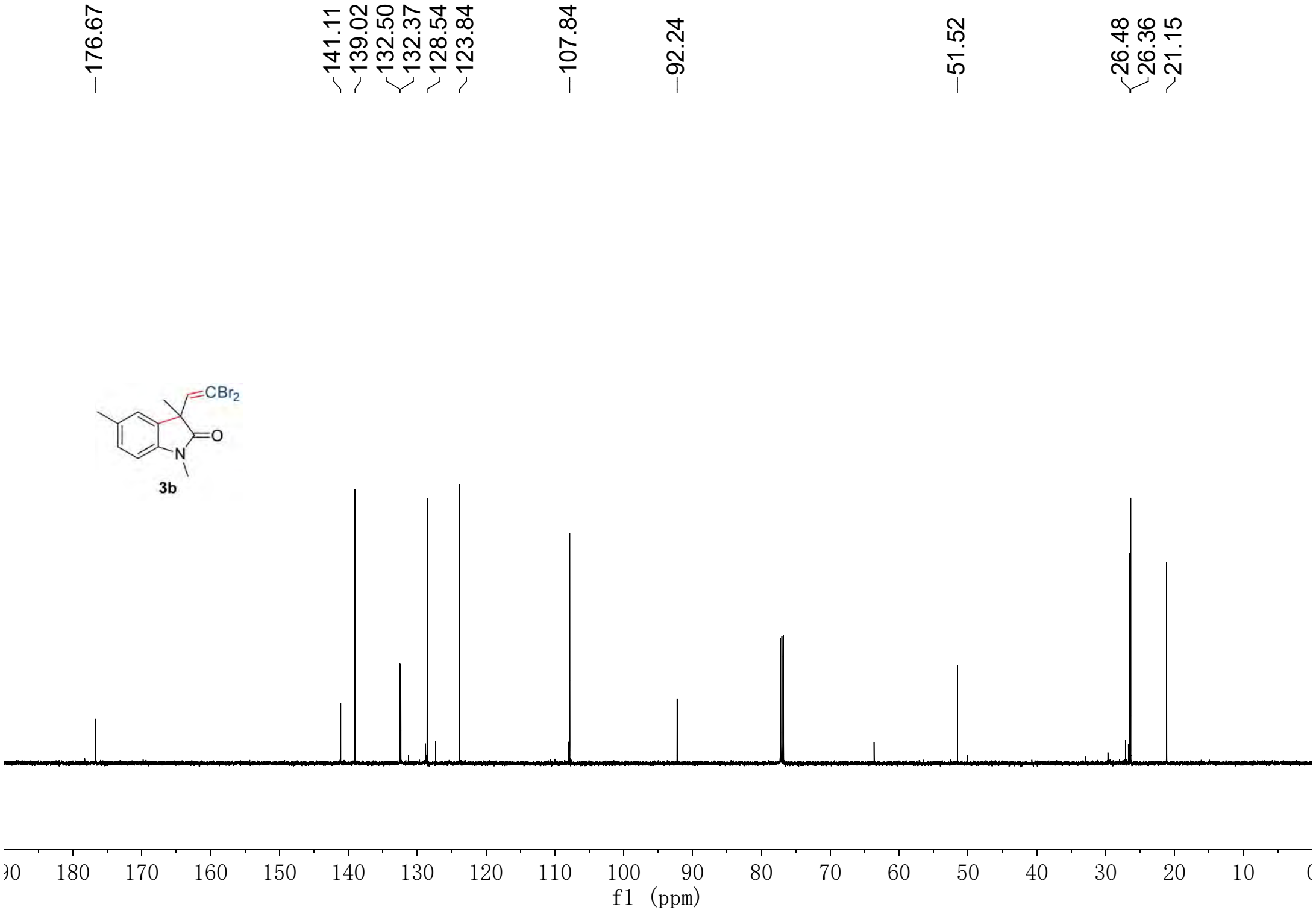
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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132.50
132.37
128.54
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107.84
92.24
51.52
26.48
26.36
21.15
CBr2
O
N
3b
180
170
160
150
140
130
120
110
100
90
80
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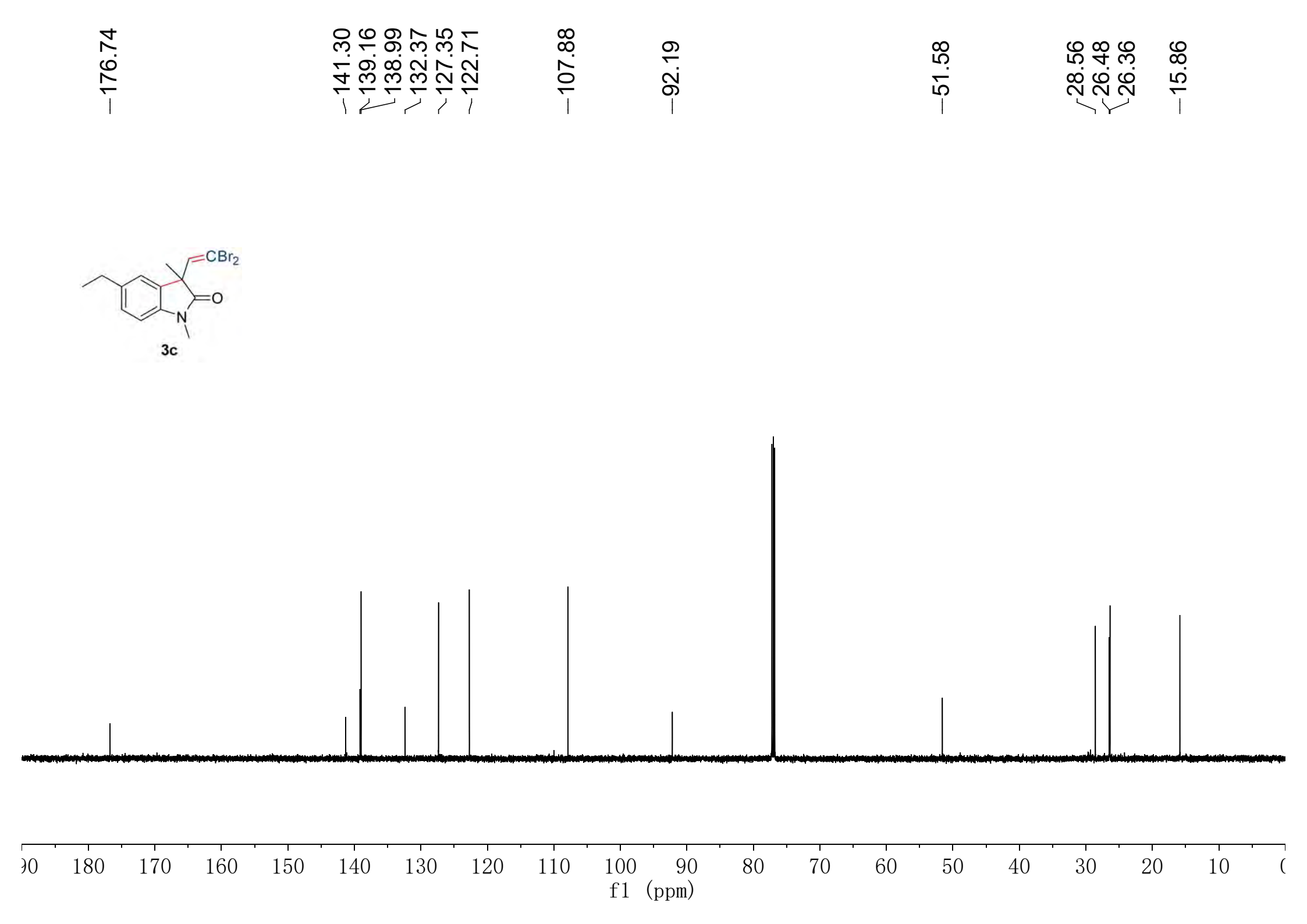
60
50
40
30
20
10
f1 (ppm)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51.58
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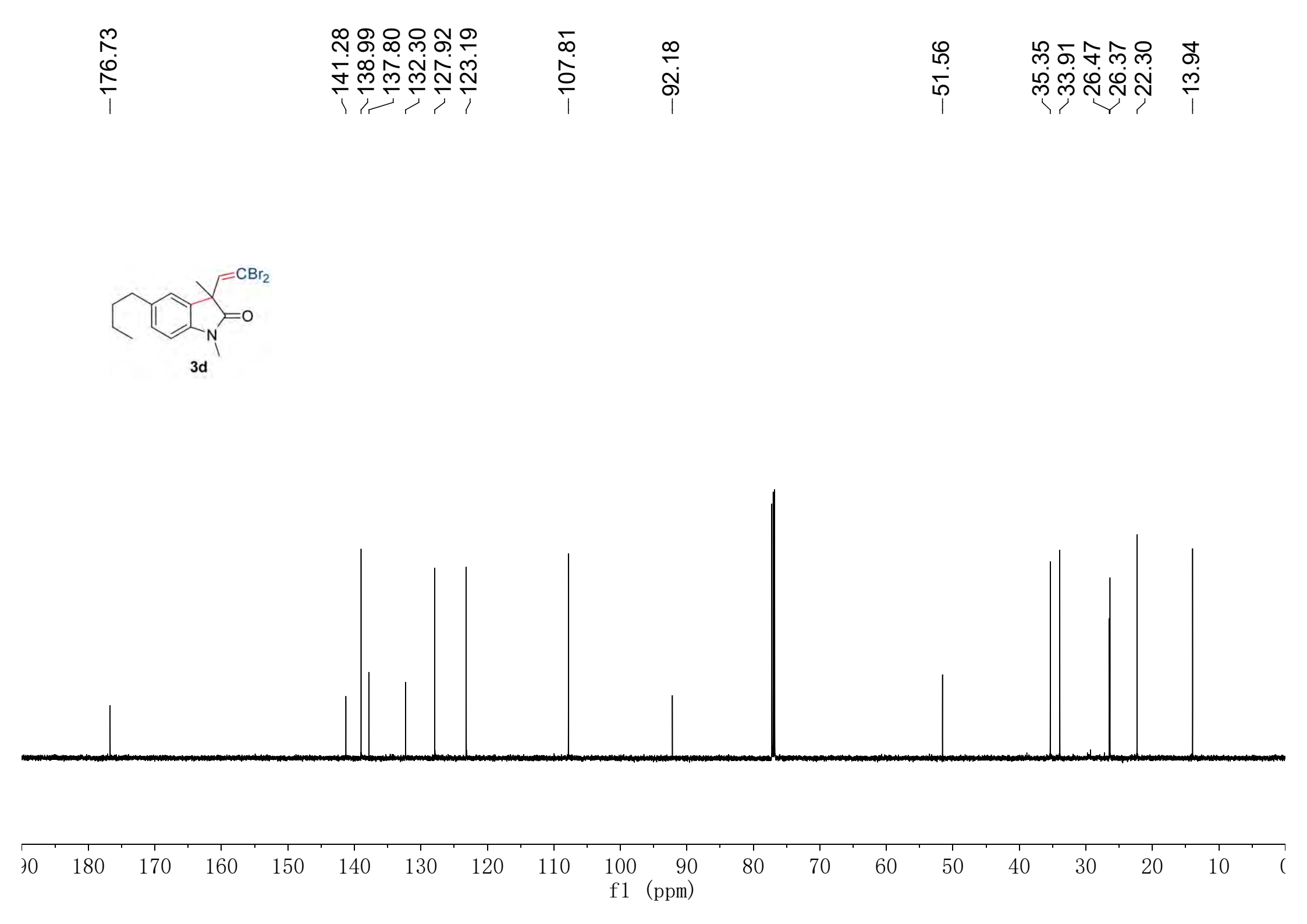
26.48
26.36
15.86
CBr2
O
N
3c
f1 (ppm)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123.19
107.81
92.18
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35.35
33.91
26.47
26.37
22.30
13.94
CBr2
O
N
3d
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120
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100
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80
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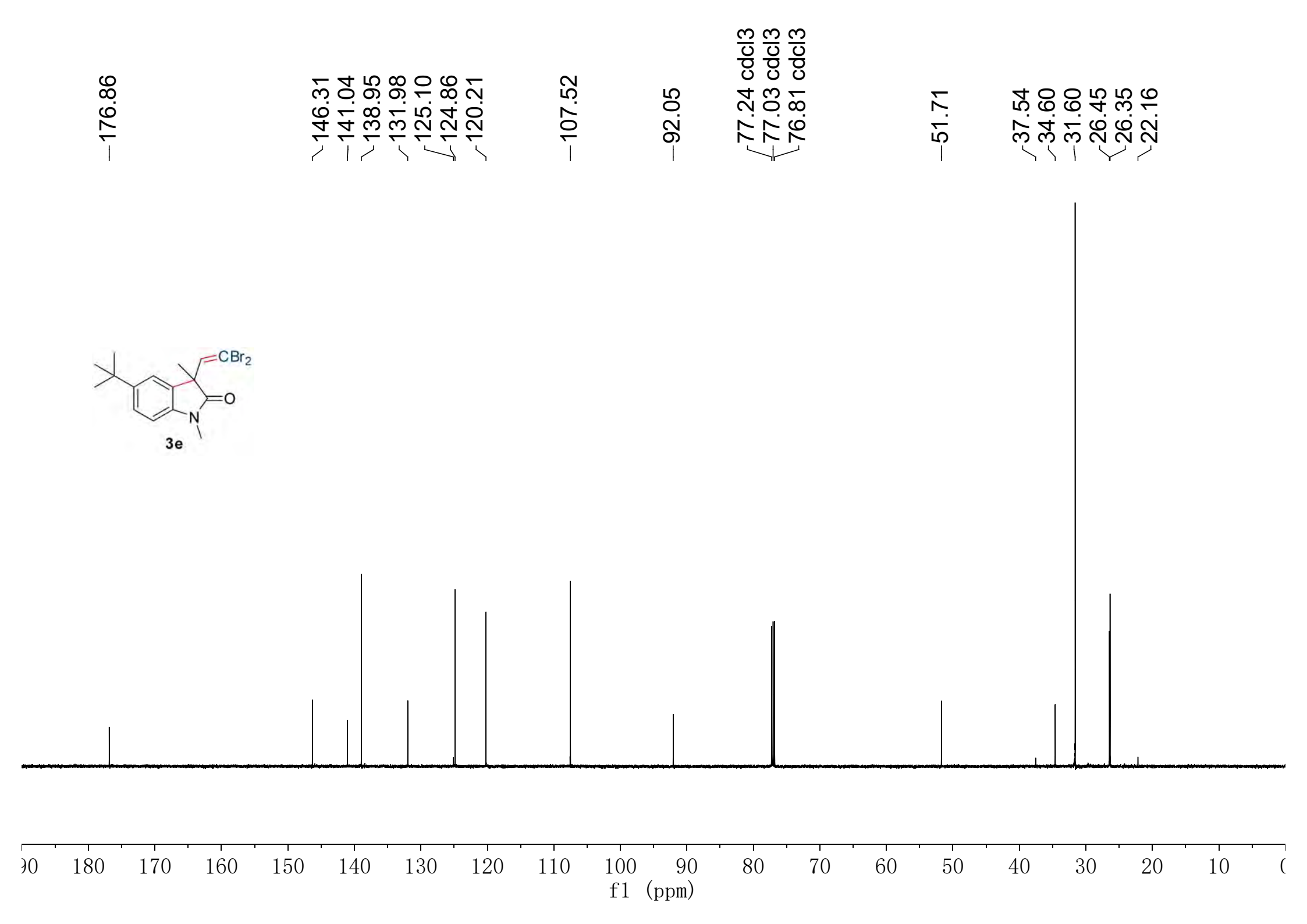
60
50
40
30
20
10
f1 (ppm)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124.86
120.21
107.52
92.05
77.24 cdcl3
77.03 cdcl3
76.81 cdcl3
51.71
37.54
34.60
31.60
26.45
26.35
22.16
CBr2
O
N
3e
180
170
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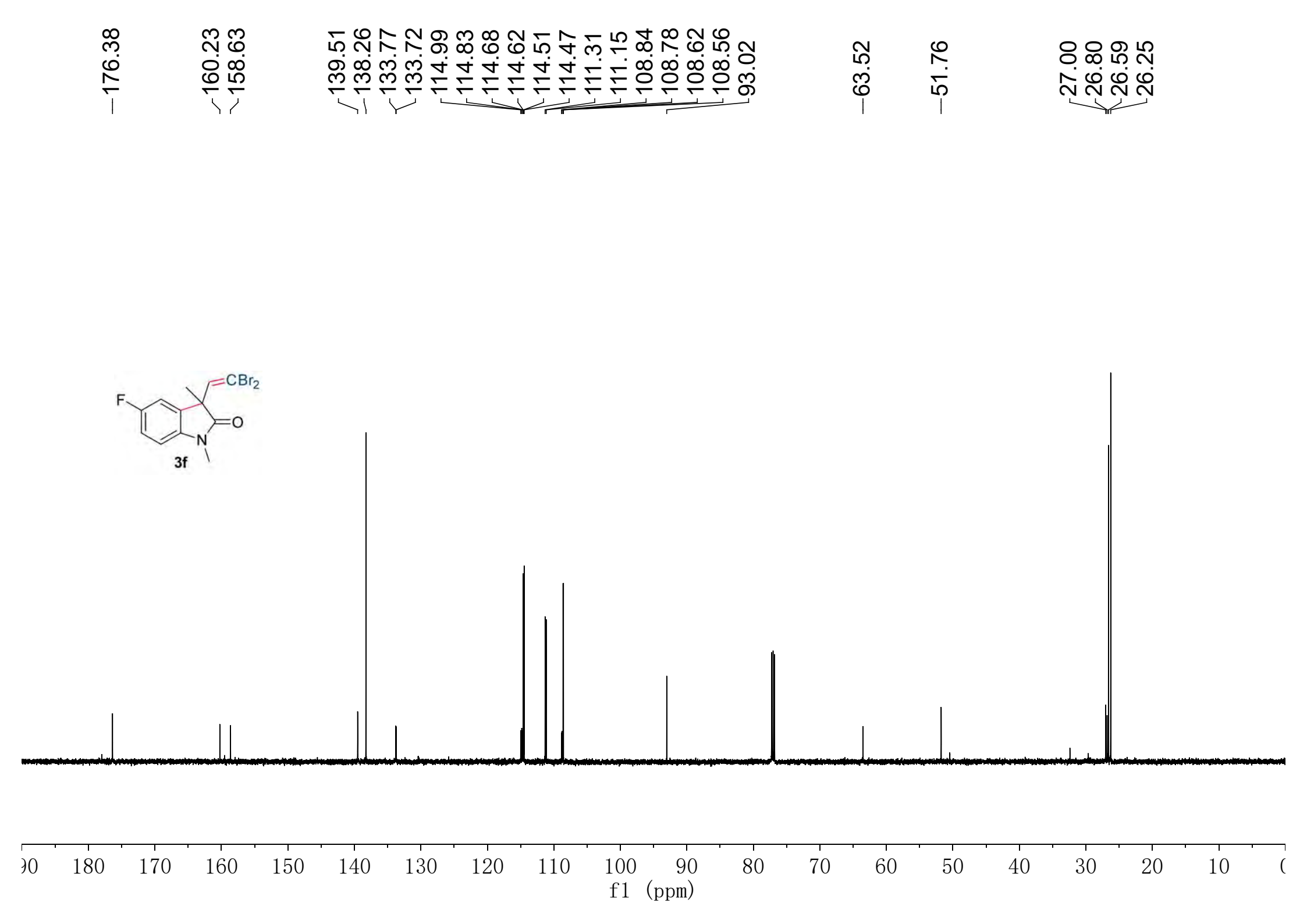
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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114.47
111.31
111.15
108.84
108.78
108.62
108.56
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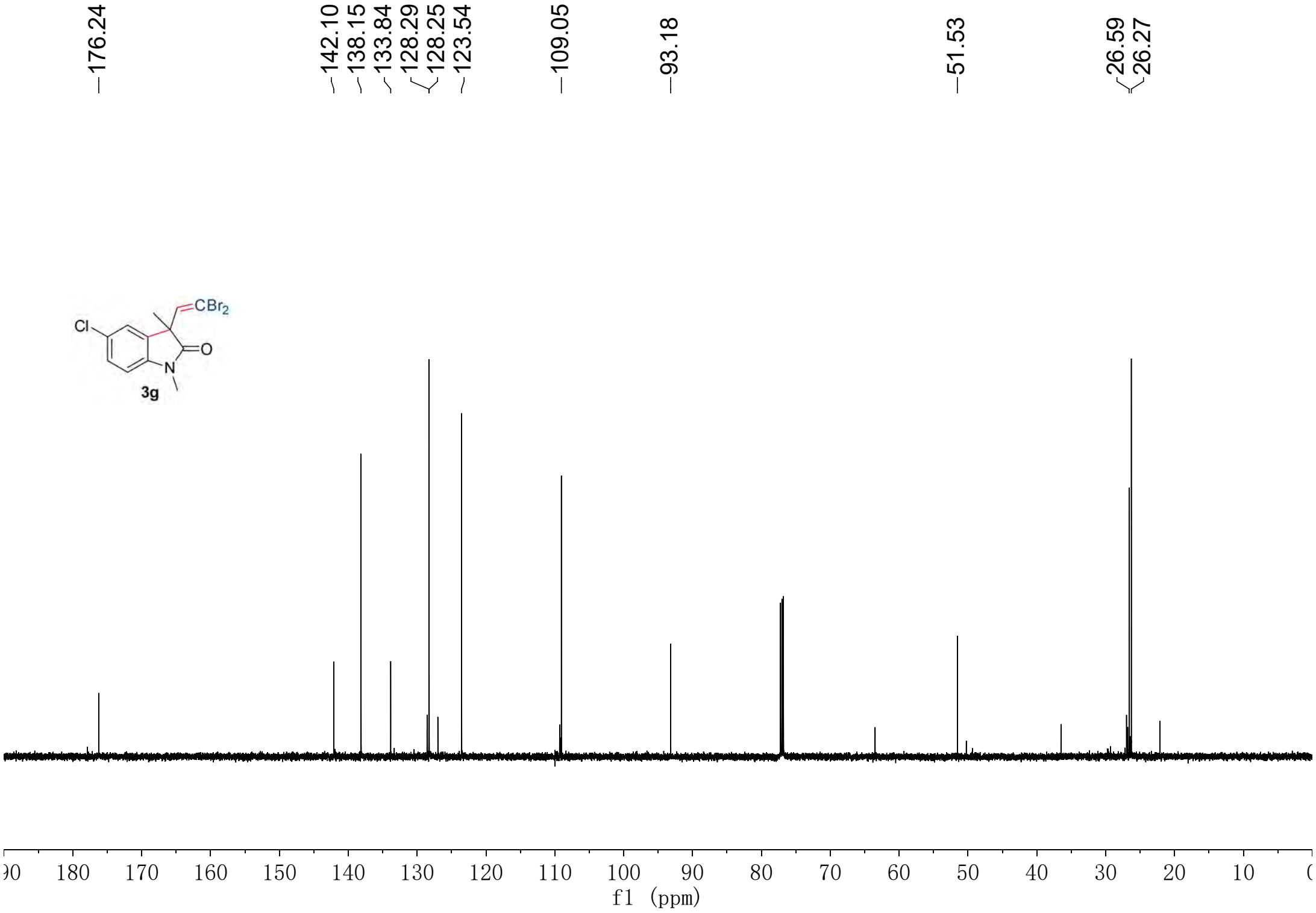
26.59
26.25
F
CBr2
O
N
3f
f1 (ppm)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109.05
93.18
51.53
26.59
26.27
Cl
CBr2
O
N
3g
180
170
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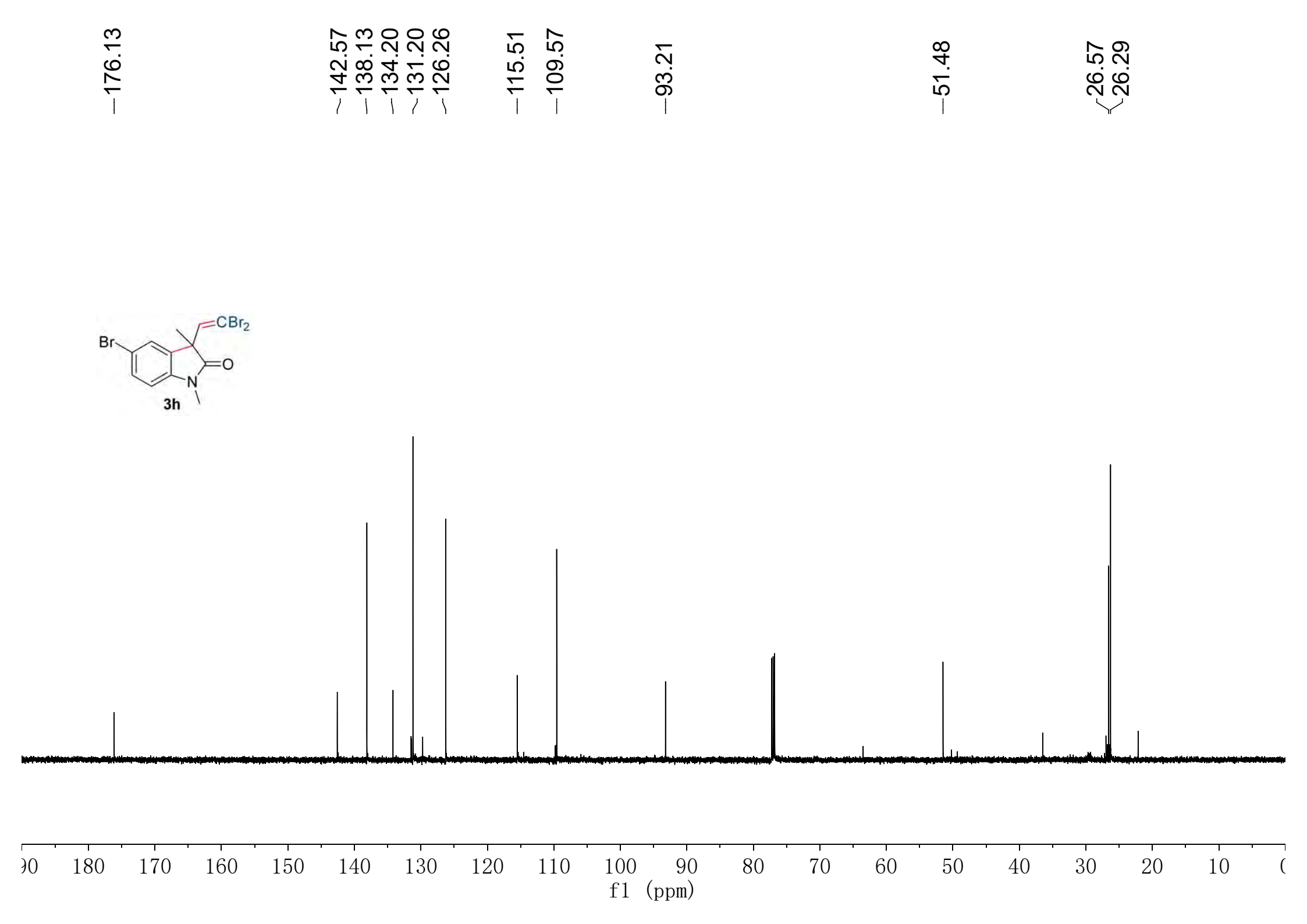
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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Br
CBr2
O
N
3h
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140
130
120
110
100
90
80
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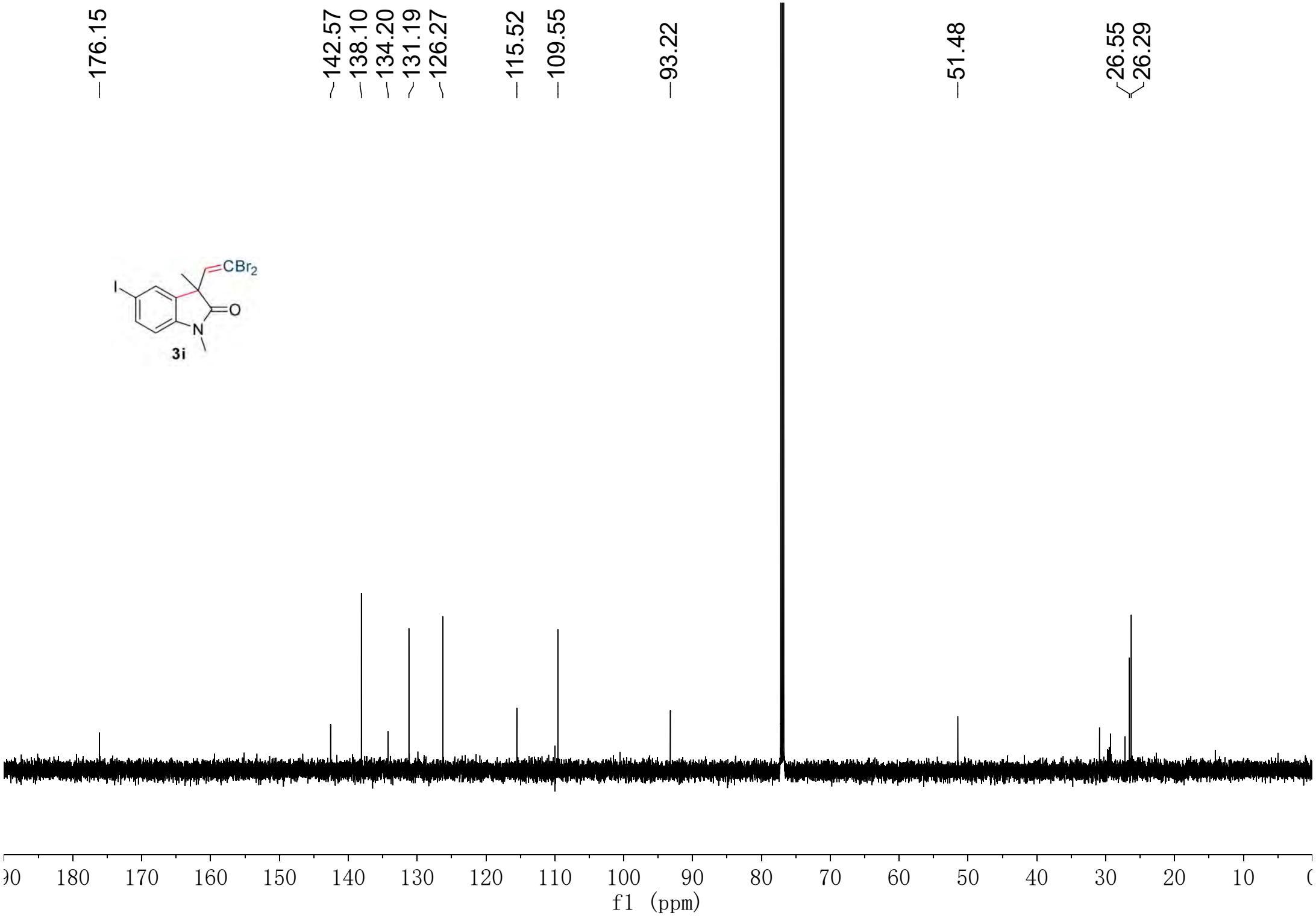
60
50
40
30
20
10
f1 (ppm)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131.19
126.27
115.52
109.55
93.22
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26.55
26.29
CBr2
I
O
N
3i
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130
120
110
100
90
80
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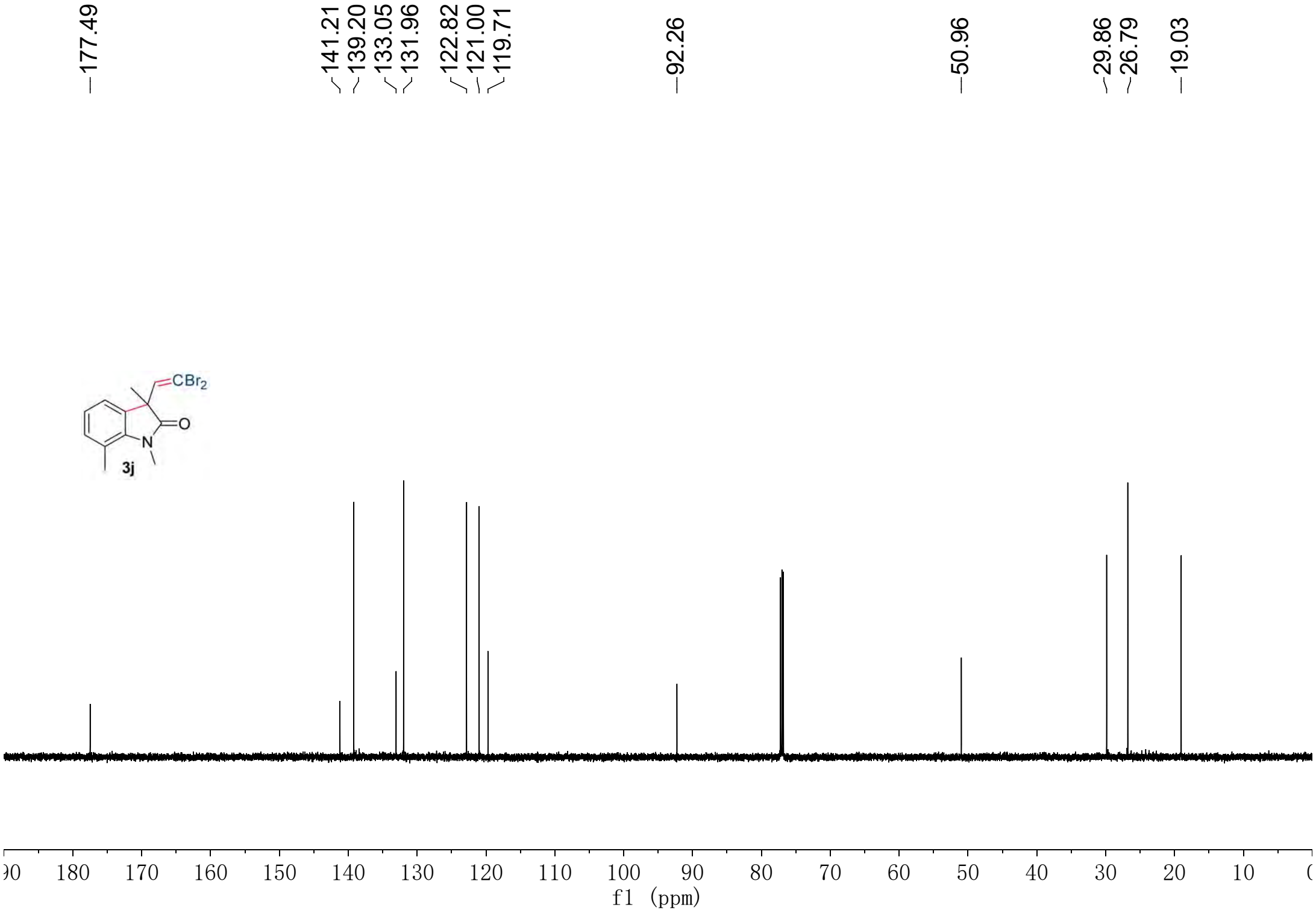
60
50
40
30
20
10
f1 (ppm)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122.82
121.00
119.71
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29.86
26.79
19.03
CBr2
O
N
3j
180
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120
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100
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80
70
60
50
40
30
20
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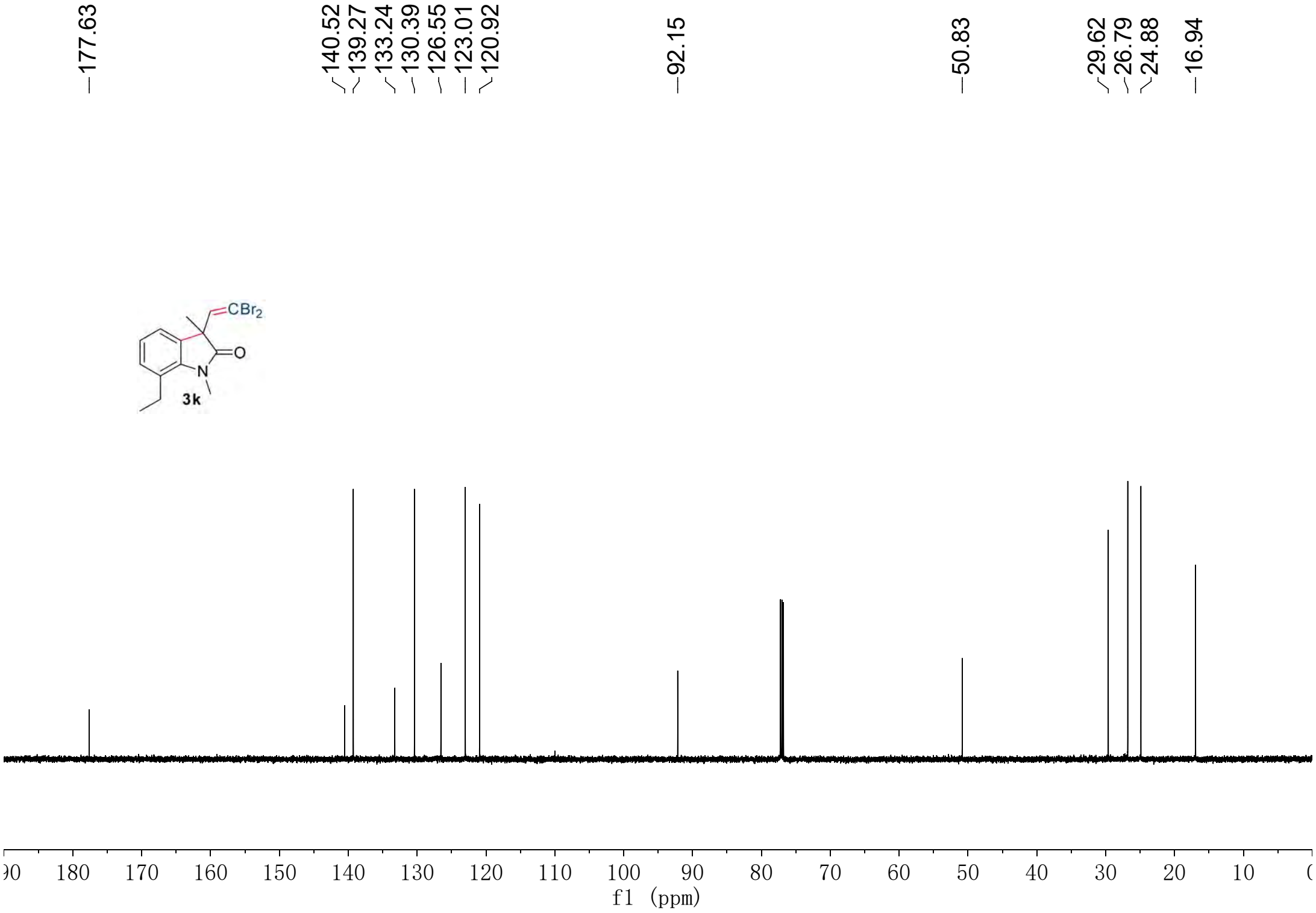
f1 (ppm)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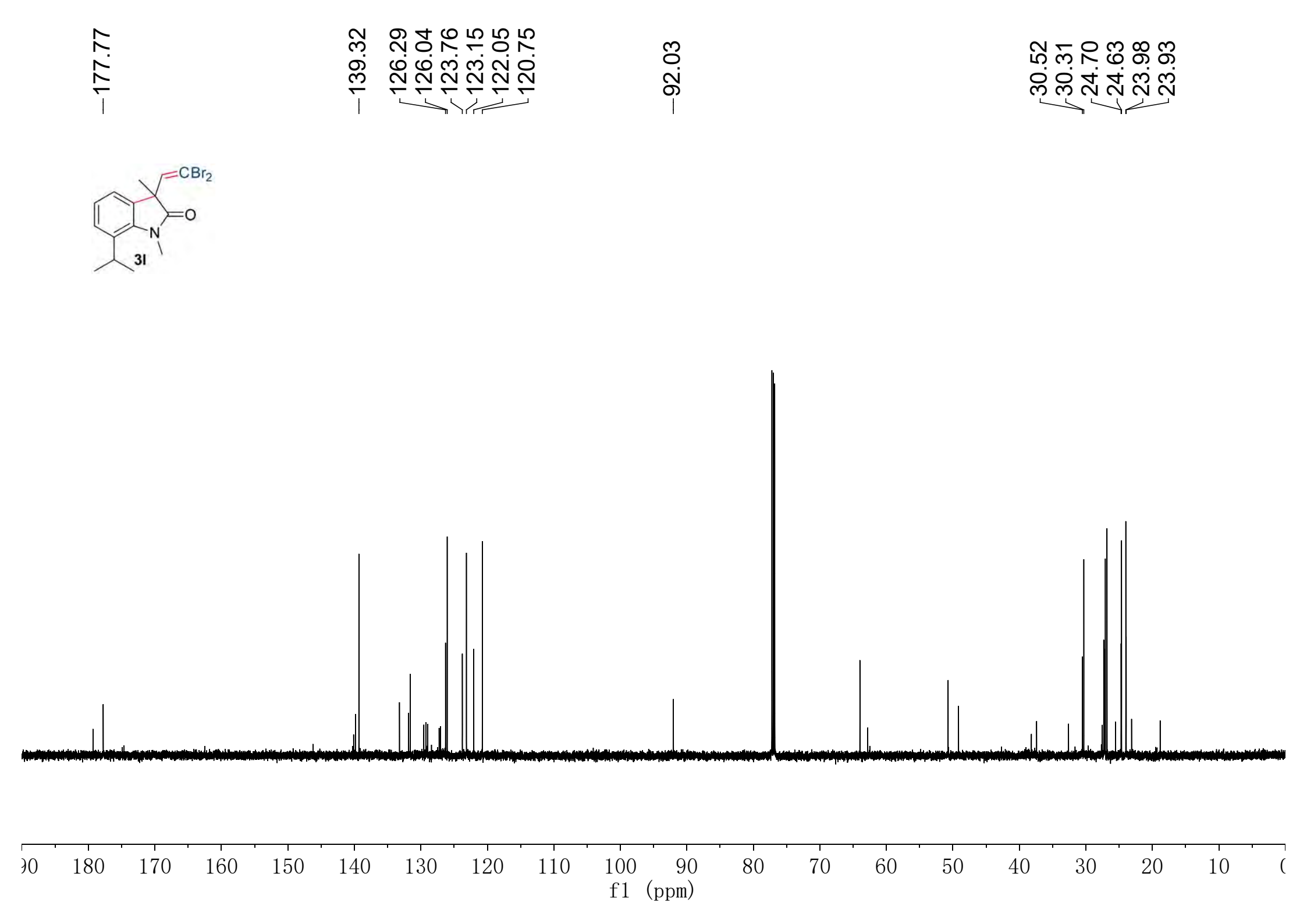
139.27
133.24
130.39
126.55
123.01
120.92
92.15
50.83
29.62
26.79
24.88
16.94
CBr2
O
N
3k
f1 (ppm)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126.29
126.04
123.76
123.15
122.05
120.75
92.03
30.52
30.31
24.70
24.63
23.98
23.93
CBr2
O
N
3l
180
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150
140
130
120
110
100
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80
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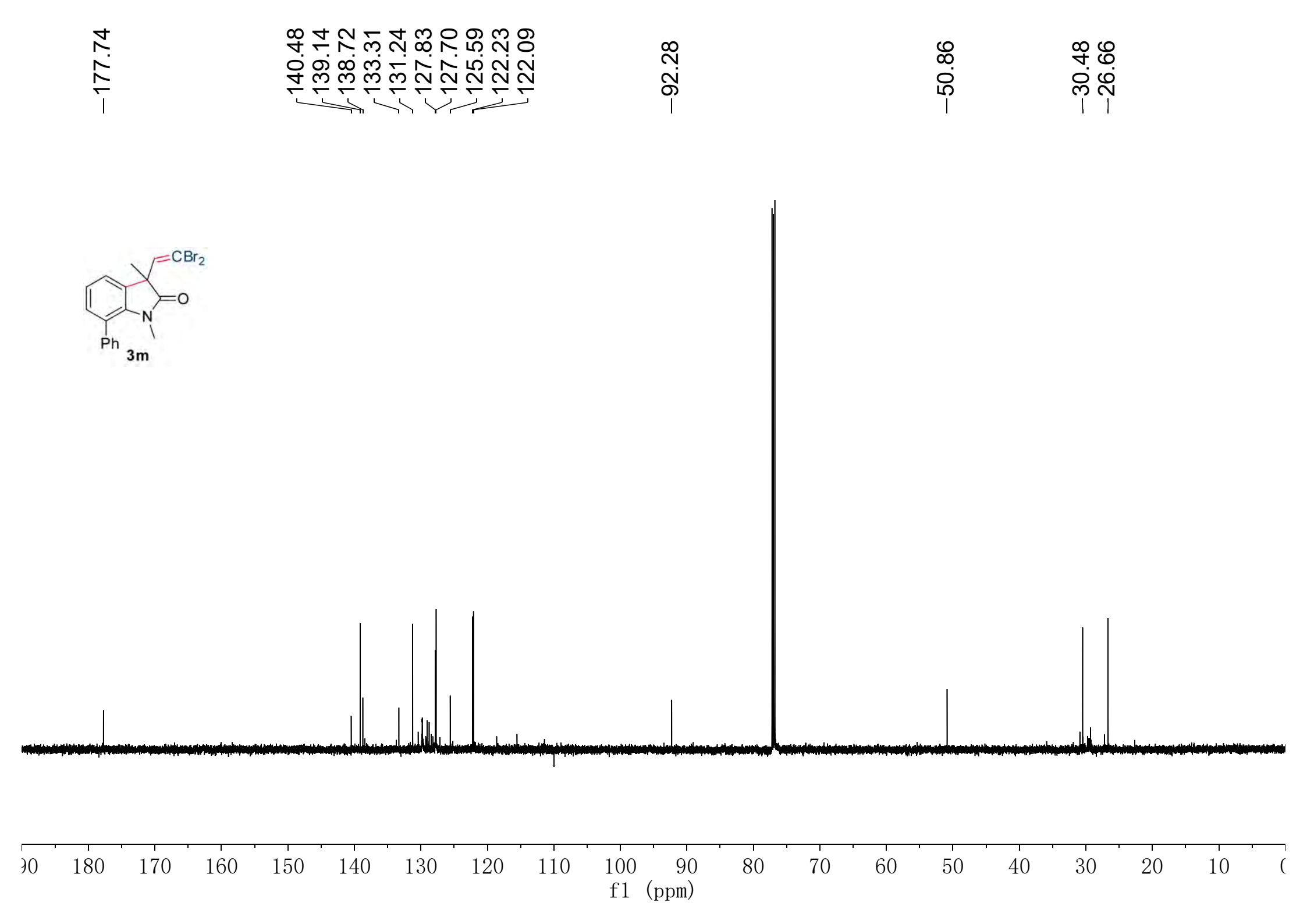
60
50
40
30
20
10
f1 (ppm)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139.14
138.72
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131.24
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122.23
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92.28
50.86
30.48
26.66
CBr2
O
N
Ph
3m
180
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140
130
120
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100
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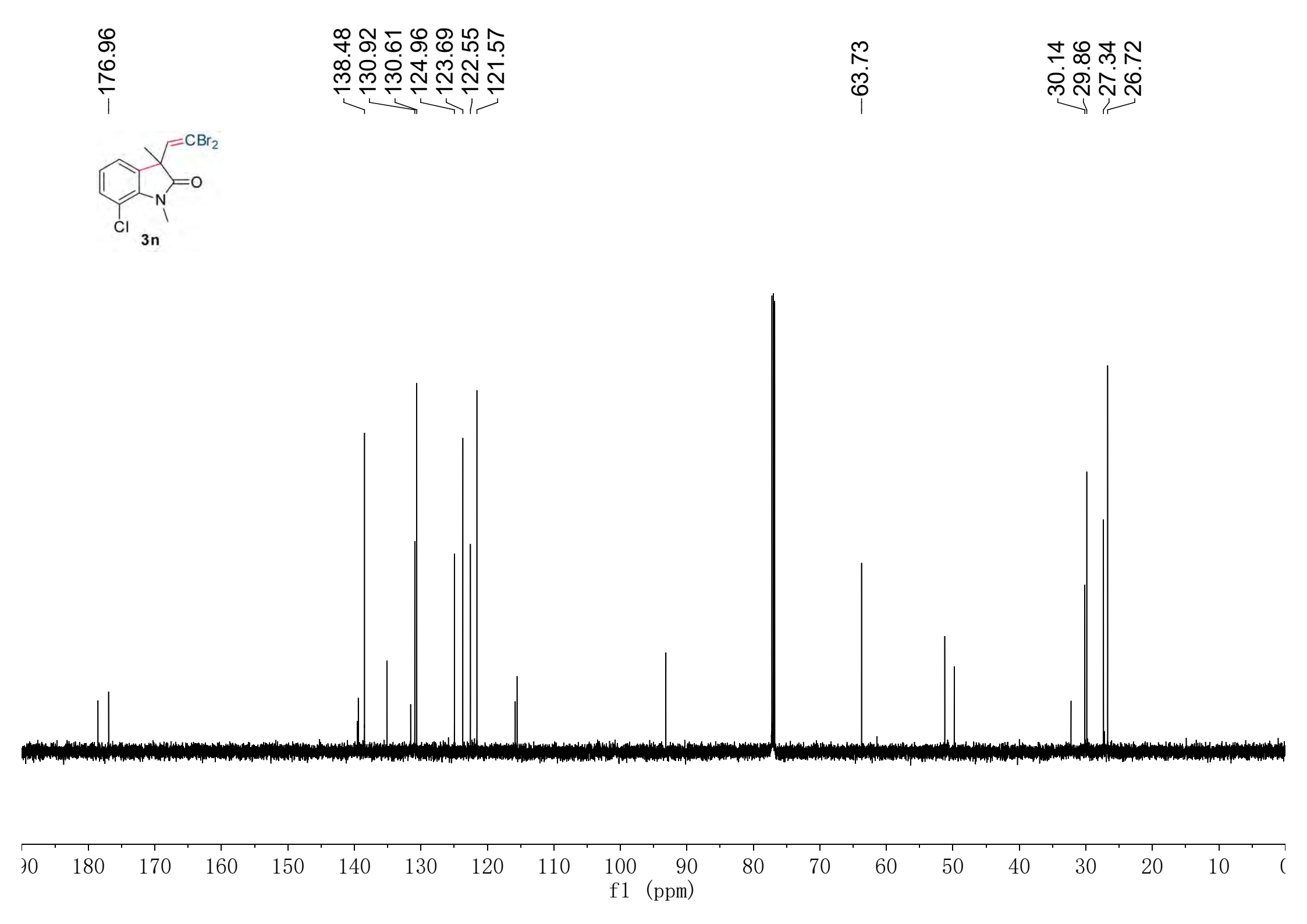
80
70
60
50
40
30
20
10
f1 (ppm)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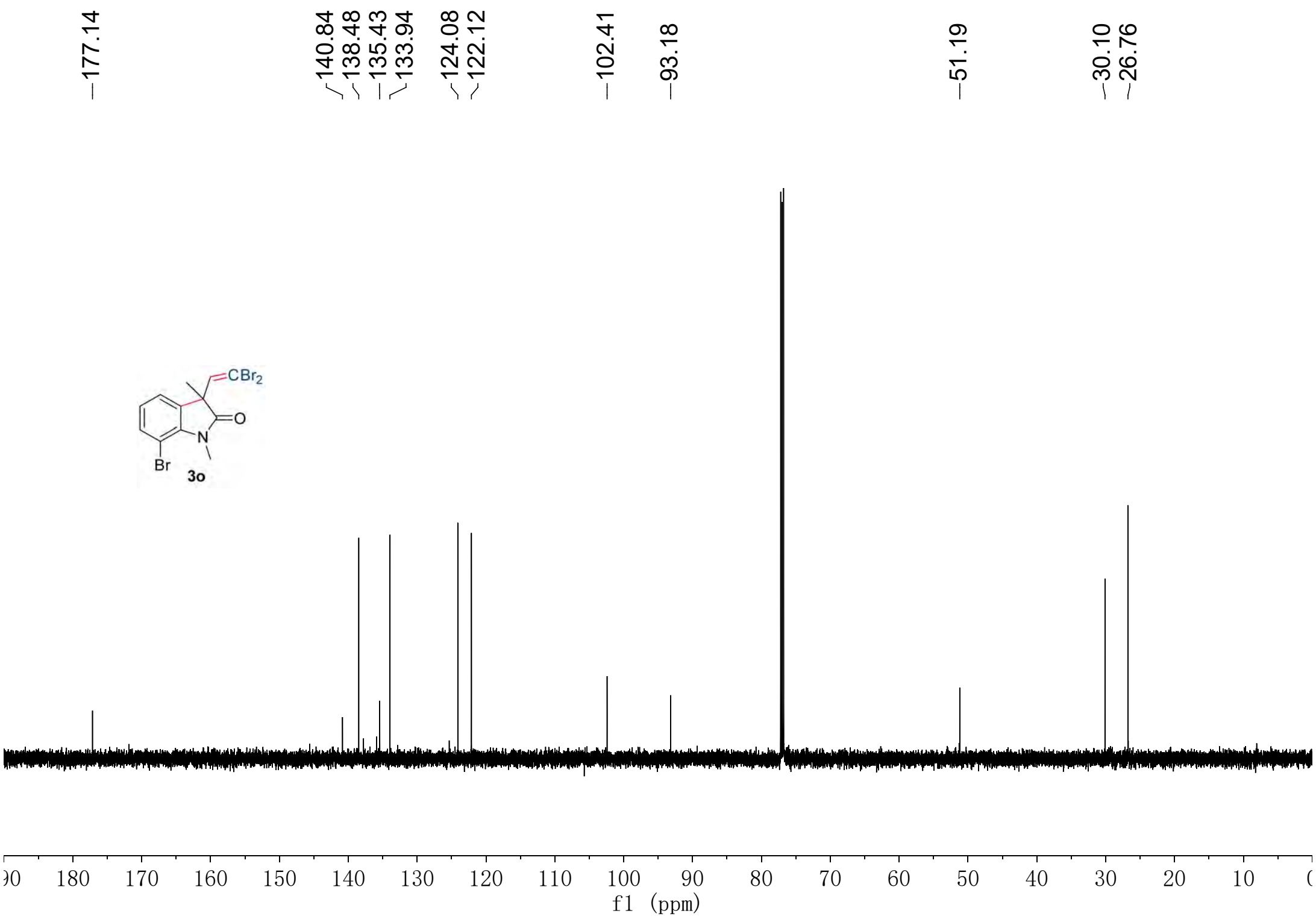
138.48
130.92
130.61
124.96
123.69
122.55
121.57
63.73
30.14
29.86
27.34
26.72
CBr2
O
N
Cl
3n
f1 (ppm)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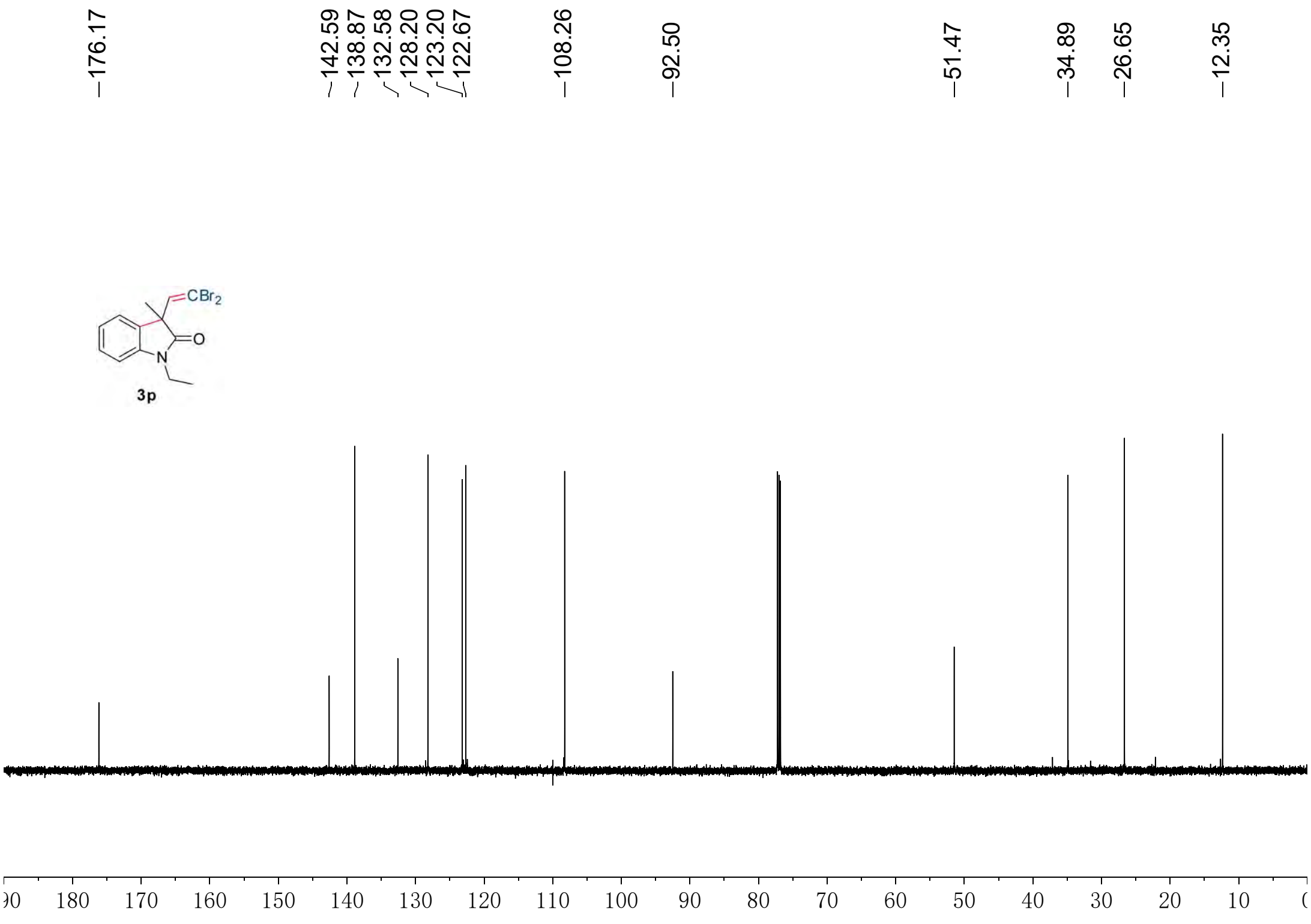
26.76
CBr2
O
N
Br
3o
f1 (ppm)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132.58
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123.20
122.67
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34.89
26.65
12.35
CBr2
O
N
3p
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160
150
140
130
120
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100
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80
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60
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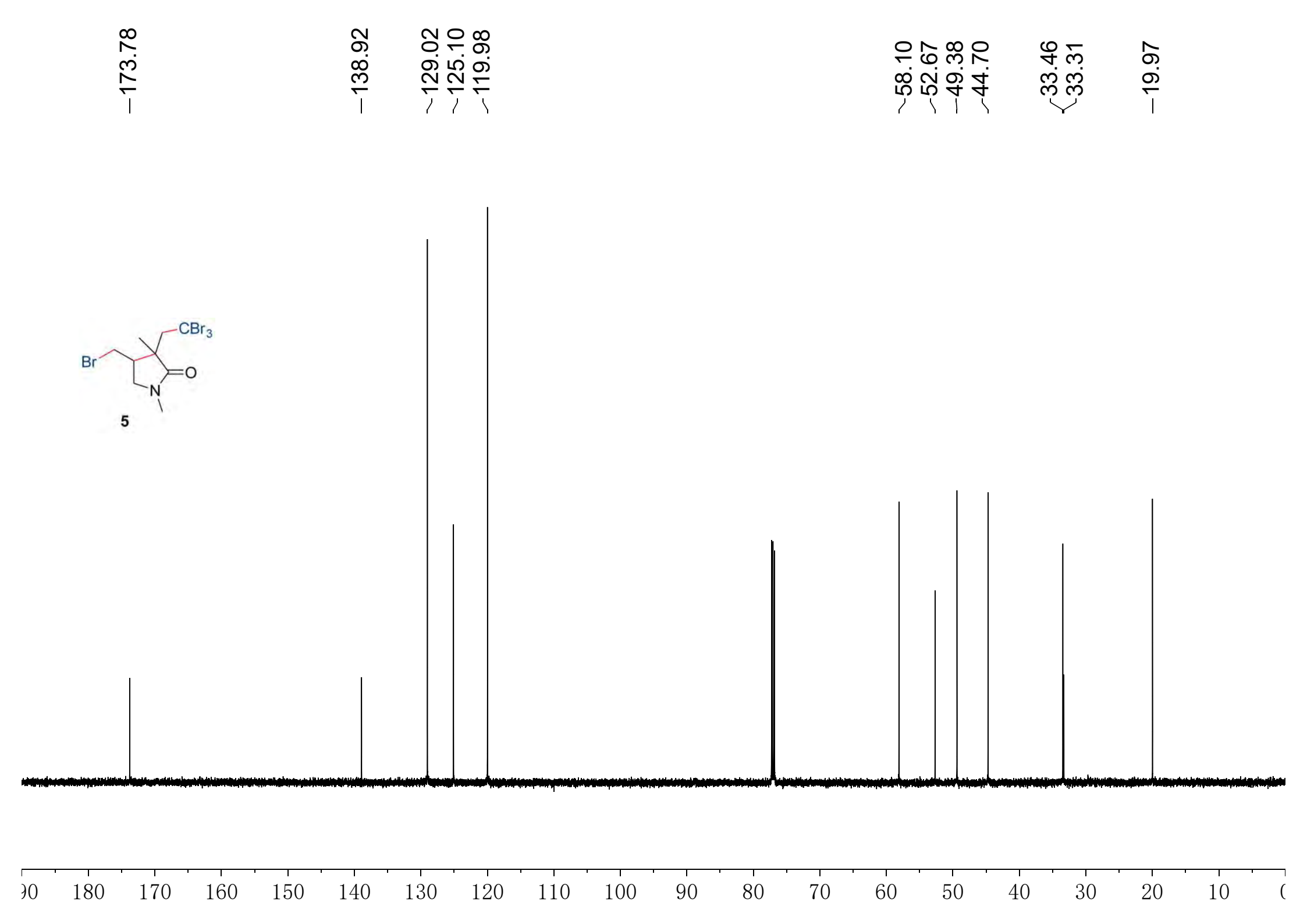
40
30
20
10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129.02
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58.10
52.67
49.38
44.70
33.46
33.31
19.97
CBr3
Br
O
N
5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10