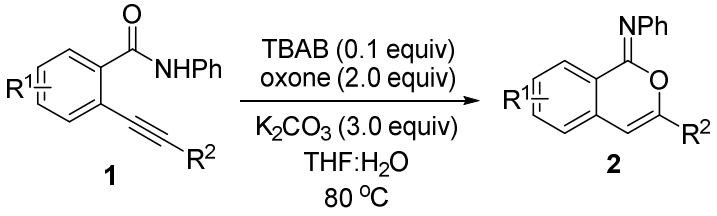
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

General experimental methods:

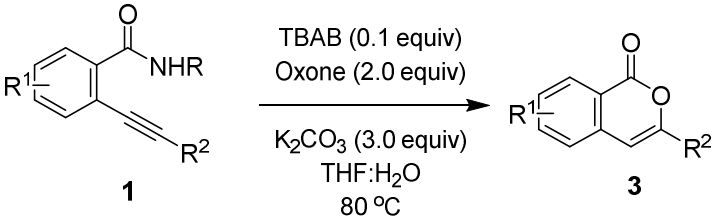
Unless otherwise stated, all commercial reagents and solvents were used without additional purification.All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å poresize, 32-63 μm, standard grade).Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultra violet light. Organic solutions were concentrated on rotary evaporators at ~20Torr (house vacuum) at 25-35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

General procedure for the synthesis of compound 2:



N-phenyl-2-alkynylbenzamide **1** (0.2 mmol), TBAB (0.1 equiv), oxone (2.0 equiv), K_2CO_3 (3.0 equiv) were added to a test tube, and then solvent THF:H_2O (v/v = 1:1, 2.0 mL) was added. The mixture was stirred at 80 ^oC overnight. After the disappearance of substrate as indicated by TLC, the last mixture was filtrated and the resulting filtrate was extracted by EA (3*2mL). The organic layers were combined and dried by Na_2SO_4. Then filtration again, evaporation of the solvent and purification by flash column chromatograph provided the desired products **2**.

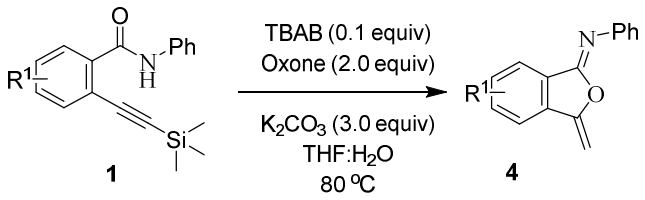
General procedure for the synthesis of compound 3:



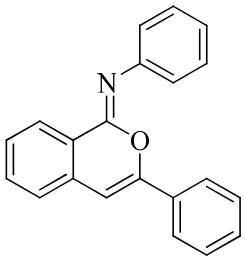
2-alkynylbenzamide **1** (0.2 mmol), TBAB (0.1 equiv), oxone (2.0 equiv), K_2CO_3 (3.0 equiv) were added to a test tube, and then solvent THF:H_2O (v/v = 1:1, 2.0 mL)

was added. The mixture was stirred at 80 °C overnight. After the disappearance of substrate as indicated by TLC, the last mixture was filtrated and the resulting filtrate was extracted by EA (3*2 mL). The organic layers were combined and dried by Na_2SO_4. Then filtration again,evaporation of the solvent and purification by flash column chromatograph provided the desired products **3**.

General procedure for the synthesis of compound 4:

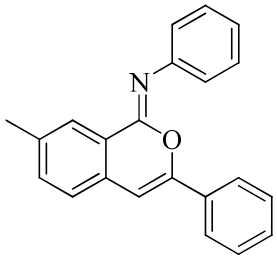


N-phenyl-2-alkynylbenzamide **1** (0.2 mmol), TBAB (0.1equiv), oxone (2.0 equiv), K_2CO_3 (3.0 equiv) were added to a test tube, and then solvent THF:H_2O (v/v = 1:1, 2.0 mL) was added. The mixture was stirred at 80 oC overnight. After the disappearance of substrate as indicated by TLC, the last mixture was filtrated and the resulting filtrate was extracted by EA (3*2 mL). The organic layers were combined and dried by Na_2SO_4. Then filtration again,evaporation of the solvent and purification by flash column chromatograph provided the desired products **4**.



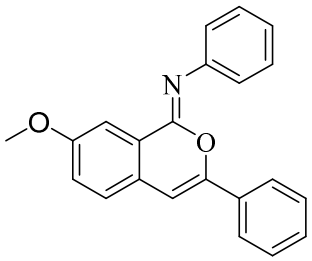
(Z)-*N*,3-diphenyl-1*H*-isochromen-1-imine (**2a**) (yellow solid, 41.6 mg, 70%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 7.9 Hz, 1H), 7.61 - 7.51 (m, 3H), 7.46 - 7.37 (m, 3H), 7.37 - 7.30 (m, 4H), 7.30 - 7.23 (m, 2H), 7.15 (t, J = 7.4 Hz, 1H), 6.72 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 149.8, 146.7, 133.9, 132.5, 132.3, 129.4, 128.7, 128.7, 128.2, 127.5, 125.6, 124.6, 123.6, 122.4, 100.9; HRMS (ESI) calcd for $C_{21}H_{16}NO^+$: 298.1226 (M^++H), found: 298.1225



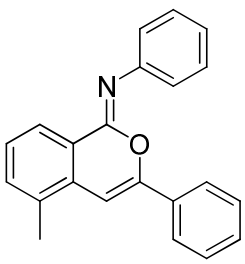
(*Z*)-7-methyl-*N*, 3-diphenyl-1*H*-isochromen-1-imine (**2b**) (yellow solid, 45.4 mg, 73%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.58 - 7.54 (m, 2H), 7.45 - 7.35 (m, 3H), 7.34 - 7.30 (m, 3H), 7.27 - 7.25 (m, 3H), 7.16 - 7.14 (m, 1H), 6.71 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 138.5, 133.7, 132.4, 131.4, 129.8, 129.3, 128.8, 128.6, 127.9, 127.4, 125.7, 124.5, 123.6, 123.3, 122.5, 100.9, 21.5; HRMS (ESI) calcd for $C_{22}H_{18}NO^+$: 312.1383 (M^++H), found: 312.1397

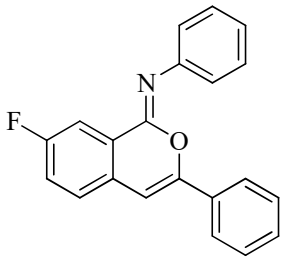


(Z)-7-methoxy-N,3-diphenyl-1H-isochromen-1-imine (**2c**) (yellow solid, 43.9 mg, 67 %)

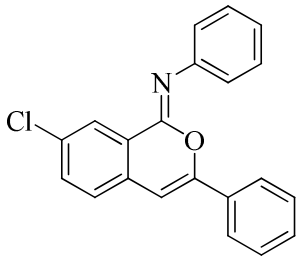
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.55 (d, J = 5.1 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.29 (dd, J = 17.0, 6.4 Hz, 6H), 7.14 (d, J = 7.6 Hz, 2H), 6.70 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 150.1, 147.2, 132.7, 129.3, 129.1, 128.9, 127.7, 127.5, 124.5, 123.9, 122.7, 122.1, 109.1, 100.9, 56.1; HRMS (ESI) calcd for $C_{22}H_{18}NO_2^+$: 328.1332 (M^++H), found: 328.1330



(*Z*)-5-methyl-*N*, 3-diphenyl-1*H*-isochromen-1-imine (**2d**) (red solid, 33.0 mg, 53%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 7.5 Hz, 1H), 7.61 - 7.59 (m, 2H), 7.39 (t, J = 7.3 Hz, 3H), 7.34 - 7.31 (m, 4H), 7.26 - 7.24 (m, 2H), 7.14 (t, J = 7.4 Hz, 1H), 6.87 (s, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 146.7, 142.7, 133.7, 132.9, 132.6, 129.4, 128.7, 128.7, 127.7, 125.4, 124.7, 123.6, 122.4, 97.6, 18.8; HRMS (ESI) calcd for $C_{22}H_{18}NO^+$: 312.1383 (M^++H), found: 312.1361

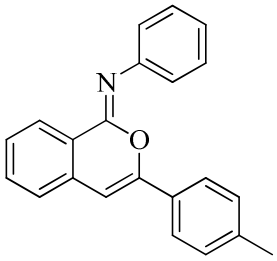


(Z)-7-fluoro-*N*, 3-diphenyl-1*H*-isochromen-1-imine (**2e**) (blue solid, 37.8 mg, 60%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 9.1 Hz, 1H), 7.62 - 7.53 (m, 2H), 7.43 - 7.39 (m, 2H), 7.34 - 7.31 (m, 4H), 7.27 (d, J = 8.7 Hz, 3H), 7.16 (t, J = 7.4 Hz, 1H), 6.71 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2(d, $^1J_{CF}$ = 247 Hz), 151.2, 132.1, 130.3, 129.5, 128.7 (d, $^3J_{CF}$ = 8 Hz), 127.6 (d, $^3J_{CF}$ = 8 Hz), 125.2, 124.5, 124.0, 123.7, 122.5, 120.5 (d, $^2J_{CF}$ = 24 Hz), 113.6 (d, $^2J_{CF}$ = 24 Hz), 100.1; HRMS (ESI) calcd for $C_{21}H_{15}FNO^+$: 316.1132 (M^++H), found: 316.1133



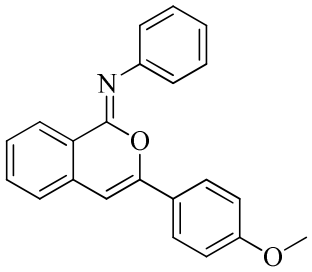
(Z)-7-chloro-*N*, 3-diphenyl-1*H*-isochromen-1-imine (**2f**) (blue solid, 41.1 mg, 62%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.58 - 7.56 (m, 2H), 7.50 - 7.48 (m, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.37 - 7.31 (m, 3H), 7.28 - 7.24 (m, 3H), 7.16 (t, J = 7.3 Hz, 1H), 6.69 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 133.8, 132.7, 132.4, 132.0,

129.7, 129.2, 128.8, 128.7, 127.2, 127.0, 125.0, 124.6, 124.0, 123.7, 122.4, 100.0; HRMS (ESI) calcd for $C_{21}H_{15}ClNO^+$: 332.0837 (M^++H), found: 332.08344



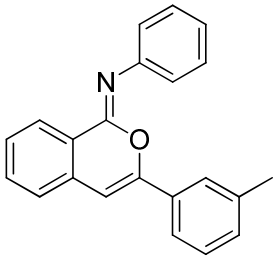
(Z)-*N*-phenyl-3-(*p*-tolyl)-1*H*-isochromen-1-imine (**2g**) (yellow solid, 46.1 mg, 74%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.9 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.47 (d, J = 8.3 Hz, 2H), 7.41 (t, J = 7.7 Hz, 3H), 7.34 - 7.24 (m, 3H), 7.15 (t, J = 7.9 Hz, 3H), 6.66 (s, 1H), 2.34 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 150.0, 146.8, 139.7, 134.2, 132.5, 129.5, 129.4, 128.7, 127.9, 127.5, 125.5, 124.6, 123.6, 123.4, 122.5, 100.1, 21.3; HRMS (ESI) calcd for $C_{22}H_{18}NO^+$: 312.1383 (M^++H), found: 312.1382



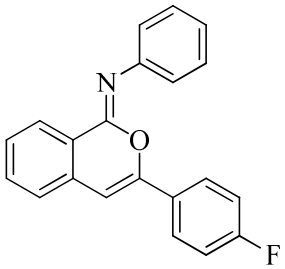
(Z)-*N*-phenyl-3-(4-methoxyphenyl)-*1H*-isochromen-1-imine (**2h**) (yellow solid, 42.5mg, 65%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 7.8 Hz, 1H), 7.55 - 7.49 (m, 3H), 7.42-7.38 (m, 3H), 7.30 - 7.25 (m, 3H), 7.15 (t, J = 7.3 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 6.59 (s, 1H), 3.80 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 151.6, 134.3, 132.5, 128.8, 127.7, 127.4, 126.1, 125.4, 124.9, 123.6, 123.1, 122.5, 114.1, 99.2, 55.3; HRMS (ESI) calcd for $C_{22}H_{18}NO_2^+$: 328.1332 (M^++H), found: 328.1331



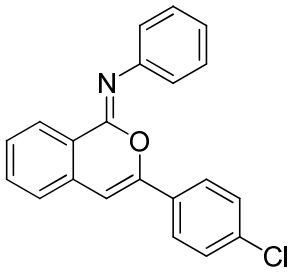
(Z)-*N*-phenyl-3-(*m*-tolyl)-*1H*-isochromen-1-imine (**2i**) (red solid, 45.4 mg, 73%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 7.9 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.46 - 7.38 (m, 5H), 7.31 (t, J = 9.0 Hz, 3H), 7.24 - 7.19 (m, 1H), 7.16 (t, J = 6.2 Hz, 2H), 6.70 (s, 1H), 2.32 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 150.0, 146.9, 138.3, 134.0, 132.4, 132.2, 130.2, 128.7, 128.5, 128.1, 127.4, 125.6, 125.4, 123.6, 122.6, 121.7, 100.6, 21.4; HRMS (ESI) calcd for $C_{22}H_{18}NO^+$: 312.1383 (M^++H), found: 312.1392



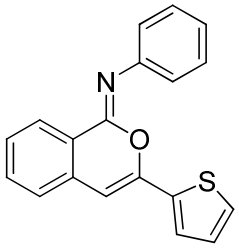
(Z)-*N*-phenyl-3-(4-fluorophenyl)-1*H*-isochromen-1-imine (**2j**) (blue solid, 38.4 mg, 61%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 6.7 Hz, 1H), 7.60 - 7.49 (m, 3H), 7.47 - 7.36 (m, 3H), 7.33 (d, J = 7.7 Hz, 1H), 7.25-7.23 (m, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.02 (t, J = 8.6 Hz, 2H), 6.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, $^1J_{CF}$ = 249 Hz), 150.8, 133.9, 132.7, 128.82, 128.3, 127.6, 126.6 (d, $^3J_{CF}$ = 9 Hz), 125.6, 123.8, 122.3, 115.8 (d, $^2J_{CF}$ = 22 Hz), 100.7; HRMS (ESI) calcd for $C_{21}H_{15}FNO^+$: 316.1132 (M^++H), found: 316.1136



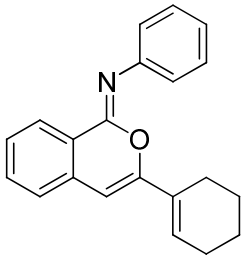
(Z)-*N*-phenyl-3-(4-chlorophenyl)-1*H*-isochromen-1-imine (**2k**) (yellow solid, 42.4 mg, 64%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 7.9 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.44 - 7.35 (m, 3H), 7.30 (t, J = 8.5 Hz, 3H), 7.24 (t, J = 7.3 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 6.67 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 149.5, 146.6, 135.3, 133.6, 132.5, 130.7, 128.9, 128.8, 128.4, 127.5, 125.8, 125.7, 123.7, 123.6, 122.3, 101.1; HRMS (ESI) calcd for $C_{21}H_{15}ClNO^+$: 332.0837 (M^++H), found: 332.08376



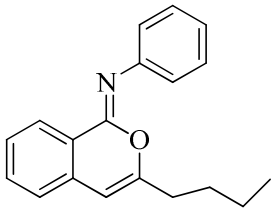
(Z)-*N*-phenyl-3-(thiophen-2-yl)-1*H*-isochromen-1-imine (**2l**) (yellow solid, 41.2 mg, 68%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 7.9 Hz, 1H), 7.55 - 7.51 (m, 1H), 7.43 - 7.35 (m, 4H), 7.33 - 7.28 (m, 2H), 7.26 - 7.23 (m, 3H), 7.14 (t, J = 7.4 Hz, 1H), 6.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 134.5, 134.0, 132.5, 128.7, 128.0, 127.5, 126.7, 125.5, 123.9, 123.7, 123.3, 123.0, 122.4, 100.5; HRMS (ESI) calcd for $C_{19}H_{14}NOS^+$: 304.0791 (M^++H), found: 304.0790



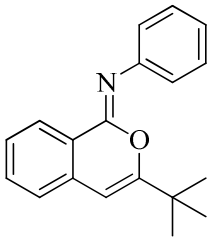
(Z)-*N*-phenyl-3-(cyclohex-1-en-1-yl)-1*H*-isochromen-1-imine (**2m**) (yellow oil, 36.2 mg, 60%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.5 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.39 - 7.32 (m, 3H), 7.27 - 7.18 (m, 3H), 7.09 (t, J = 7.4 Hz, 1H), 6.25 (s, 1H), 6.13 (s, 1H), 2.23 - 2.17 (m, 2H), 2.13 - 2.06 (m, 2H), 1.73 - 1.66 (m, 2H), 1.60 - 1.54 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 134.6, 134.3, 132.3, 128.6, 128.6, 128.5, 127.6, 127.4, 125.5, 123.5, 122.4, 99.5, 25.6, 23.9, 22.2, 21.8; HRMS (ESI) calcd for $C_{21}H_{20}NO^+$: 302.1539 (M^++H), found: 302.1537



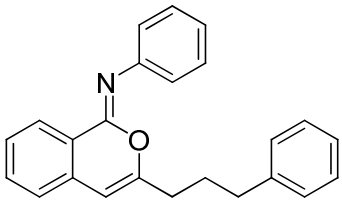
(Z)-*N*-phenyl-3-butyl-1*H*-isochromen-1-imine (**2n**) (yellow solid, 38.8 mg, 70%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.39 - 7.30 (m, 3H), 7.19 (t, J = 6.8 Hz, 3H), 7.10 (t, J = 7.2 Hz, 1H), 5.99 (s, 1H), 2.34 (t, J = 7.3 Hz, 2H), 1.57 - 1.49 (m, 2H), 1.36 - 1.30 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 134.1, 132.3, 128.6, 127.5, 127.4, 124.6, 123.4, 123.1, 122.8, 101.8, 32.7, 28.8, 21.9, 13.8; HRMS (ESI) calcd for $C_{19}H_{20}NO^+$: 278.1539 (M^++H), found: 278.1553



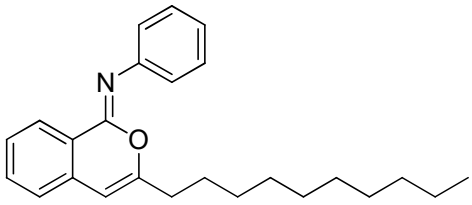
(Z)-*N*-phenyl-3-(*tert*-butyl)-1*H*-isochromen-1-imine (**2o**) (yellow solid, 47.1 mg, 85%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.9 Hz, 1H), 7.54 - 7.46 (m, 1H), 7.41 - 7.31 (m, 3H), 7.22 (d, J = 7.7 Hz, 1H), 7.18 - 7.12 (m, 2H), 7.09 (t, J = 7.3 Hz, 1H), 6.03 (s, 1H), 1.13 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$)δ 163.2, 150.7, 147.0, 134.2, 132.3, 128.5, 127.5, 127.2, 125.1, 123.3, 123.0, 122.5, 98.4, 35.6, 27.8; $C_{19}H_{20}NO^+$: 278.1539 (M^++H), found: 278.1525



(Z)-*N*-phenyl-3-(3-phenylpropyl)-1*H*-isochromen-1-imine (**2p**) (yellow solid, 46.8 mg, 69%)

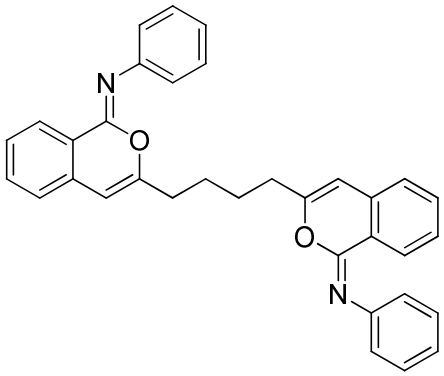
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.40 - 7.31 (m, 3H), 7.28 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 6.5 Hz, 4H), 7.15 - 7.06 (m, 3H), 5.99 (s, 1H), 2.62 (t, J = 7.6 Hz, 2H), 2.36 (t, J = 7.4 Hz, 2H), 1.93 - 1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 146.6, 141.5, 134.0, 132.3, 128.6, 128.4, 128.3, 127.6, 127.4, 125.9, 124.6, 123.4, 123.2, 122.7, 102.2, 34.8, 32.4, 28.2; HRMS (ESI) calcd for $C_{24}H_{22}NO^+$: 340.1696 (M^++H), found: 340.1690



(Z)-*N*-phenyl-3-decyl-1*H*-isochromen-1-imine (**2q**) (yellow oil, 51.3 mg, 71%)

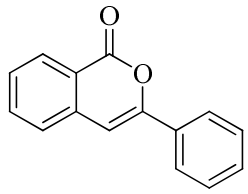
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.39 - 7.31 (m, 3H), 7.21 - 7.15 (m, 3H), 7.08 (t, J = 7.3 Hz, 1H), 5.98 (s, 1H), 2.32 (t, J = 7.4 Hz, 2H), 1.59 - 1.47 (m, 2H), 1.25 (s, 14H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 134.1, 132.3, 128.5, 127.4, 127.4, 124.6, 123.4, 122.8,

101.8, 33.0, 31.9, 29.7, 29.6, 29.4, 29.3, 28.8, 26.6, 22.7, 14.1; HRMS (ESI) calcd for $C_{25}H_{32}NO^+$: 362.2478 (M^++H), found: 362.2478



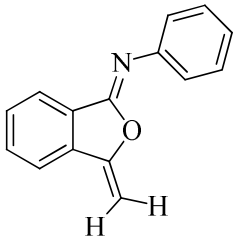
3, 3'-(butane-1,4-diyl)bis((Z)-*N*-phenyl-1*H*-isochromen-1-imine) (**2r**) (yellow solid, 61.5 mg, 62%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.25 (t, J = 7.7 Hz, 2H), 7.17 (d, J = 7.7 Hz, 1H), 7.12 (d, J = 7.5 Hz, 2H), 7.01 (t, J = 7.3 Hz, 1H), 5.95 (s, 1H), 2.30 (s, 2H), 1.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 151.2, 146.5, 133.9, 132.4, 128.5, 127.6, 127.4, 126.1, 124.6, 123.4, 122.6, 102.1, 32.7, 25.8; HRMS (ESI) calcd for $C_{34}H_{29}N_2O_2^+$: 497.2224 (M^++H), found: 497.2222



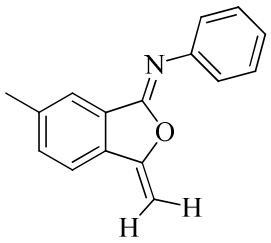
3-phenyl-1*H*-isochromen-1-one (**3a**) (white solid, 34.6 mg, 78%)[1-2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.2 Hz, 1H), 7.90 - 7.85 (m, 2H), 7.74 - 7.68 (m, 1H), 7.51 - 7.48 (m, 2H), 7.47-7.45 (m, 1H), 7.45 - 7.41 (m, 2H), 6.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 153.6, 137.5, 134.9, 131.9, 129.9, 129.6, 128.8, 128.2, 126.0, 125.2, 120.5, 101.8



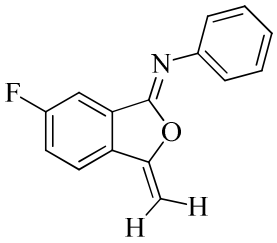
(Z)-*N*-phenyl-3-methyleneisobenzofuran-1-imine (**4a**) (blue solid, 38.1 mg, 86%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.90 (m, 1H), 7.79 - 7.73 (m, 1H), 7.67 - 7.61 (m, 1H), 7.59 - 7.48 (m, 3H), 7.44 - 7.34 (m, 3H), 5.24 - 7.21 (m, 1H), 4.82 - 4.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 143.1, 136.2, 134.5, 132.3, 129.8, 129.3, 128.9, 128.1, 128.0, 123.6, 120.0, 90.5; HRMS (ESI) calcd for $C_{15}H_{12}NO^+$: 222.0913 (M^++H), found: 222.0913



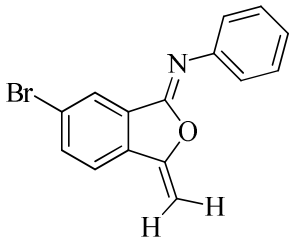
(Z)-*N*-phenyl-6-methyl-3-methyleneisobenzofuran-1-imine (**4b**) (blue solid, 39.5mg, 84%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.47 - 7.41 (m, 2H), 7.38 (t, J = 7.8 Hz, 2H), 5.16 (d, J = 1.9 Hz, 1H), 4.75 (d, J = 1.9 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 166.8, 143.1, 140.2, 134.6, 133.7, 133.3, 129.3, 128.1, 127.9, 126.5, 123.7, 119.9, 89.7, 21.6; HRMS (ESI) calcd for $C_{16}H_{14}NO^+$: 236.1070 (M^++H), found: 236.1076



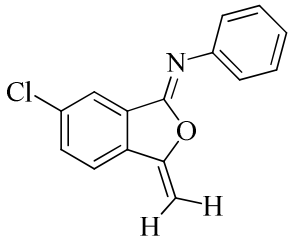
(Z)-*N*-phenyl-6-fluoro-3-methyleneisobenzofuran-1-imine (**4c**) (blue solid, 38.8 mg, 81%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H), 7.40 - 7.30 (m, 3H), 5.19 (d, J = 2.1 Hz, 1H), 4.80 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, $^{1}J_{CF}$ = 249 Hz), 161.4, 142.3, 134.3, 129.4, 129.2, 128.2, 128.0, 126.4, 122.0 (d, $^{3}J_{CF}$ = 8 Hz), 120.0 (d, $^{2}J_{CF}$ = 24 Hz), 110.3 (d, $^{2}J_{CF}$ = 23 Hz), 90.7; HRMS (ESI) calcd for $C_{15}H_{11}FNO^{+}$: 240.0819 (M^{+}+H), found: 240.0813



(Z)-*N*-phenyl-6-bromo-3-methyleneisobenzofuran-1-imine (**4d**) (blue solid, 49.7 mg, 83%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.77 - 7.71 (m, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.36 (d, J = 7.4 Hz, 2H), 5.24 (d, J = 2.2 Hz, 1H), 4.84 (d, J = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 165.2, 142.3, 135.3, 134.8, 134.2, 130.6, 129.4, 128.3, 128.0, 126.7, 123.8, 121.7, 91.5; HRMS (ESI) calcd for $C_{15}H_{11}BrNO^{+}$: 300.0019 (M^{+}+H), found: 300.0019



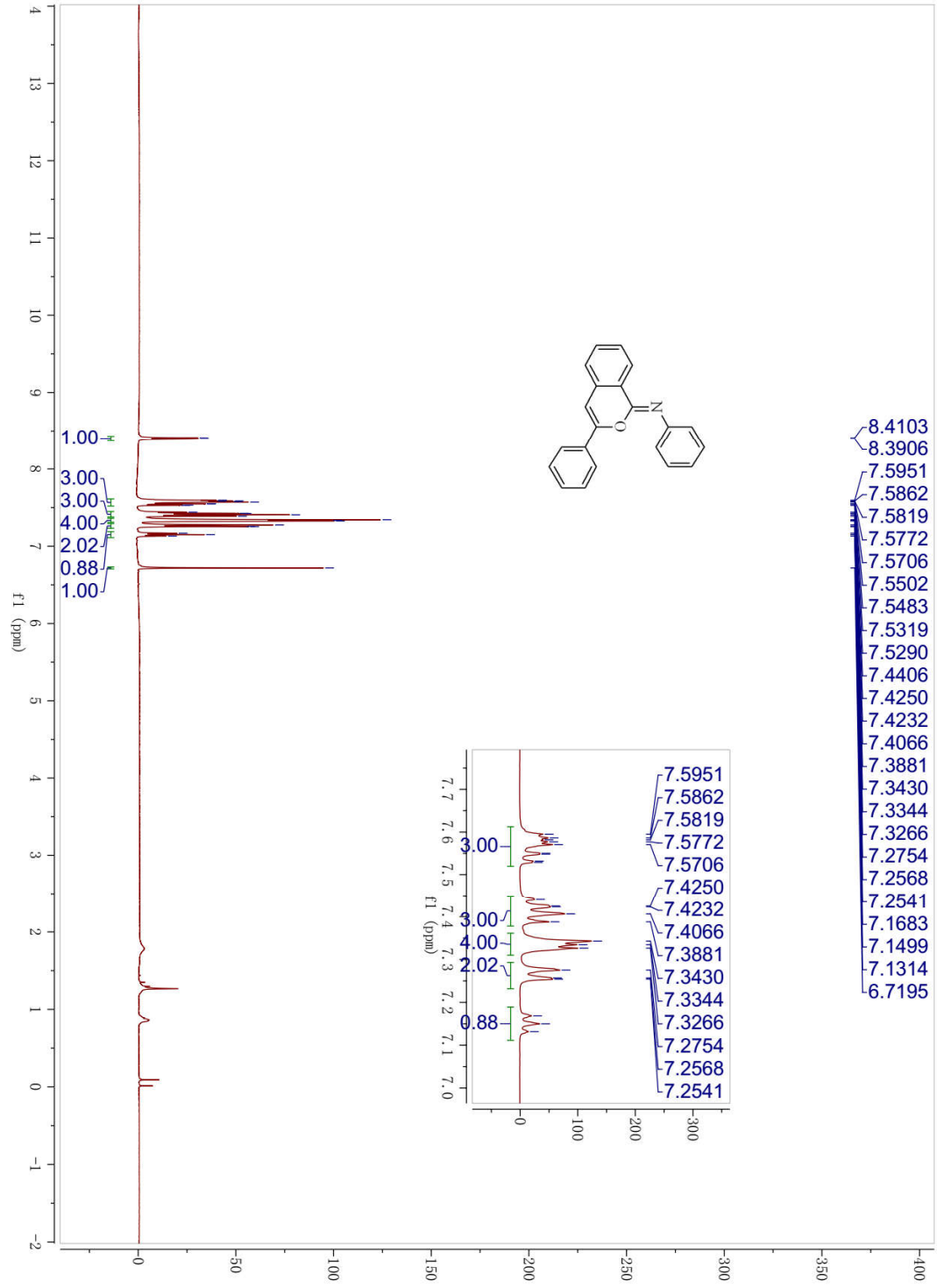
(Z)-*N*-phenyl-6-chloro-3-methyleneisobenzofuran-1-imine (**4e**) (blue solid, 41.8 mg, 82%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.63 - 7.57 (m, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H), 7.37 (d, J = 7.5 Hz, 2H), 5.23 (d, J = 1.9 Hz, 1H), 4.84 (d, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 142.3, 135.9, 134.4, 134.2, 132.5, 130.4, 129.4, 128.3, 128.0, 123.7, 121.4, 91.4; HRMS (ESI) calcd for $C_{15}H_{11}ClNO^{+}$: 256.0524 (M^{+}+H), found: 256.0530

References:

[1] Sudarshan, K.; Manna, M. K.; Aidhen, I. S. *Eur. J. Org. Chem.* **2015,** 1797-1803.

[2] Bian, M.;Yao, W.; Ding, H.; et al. *J. Org. Chem*. **2010**, 41, 269-272.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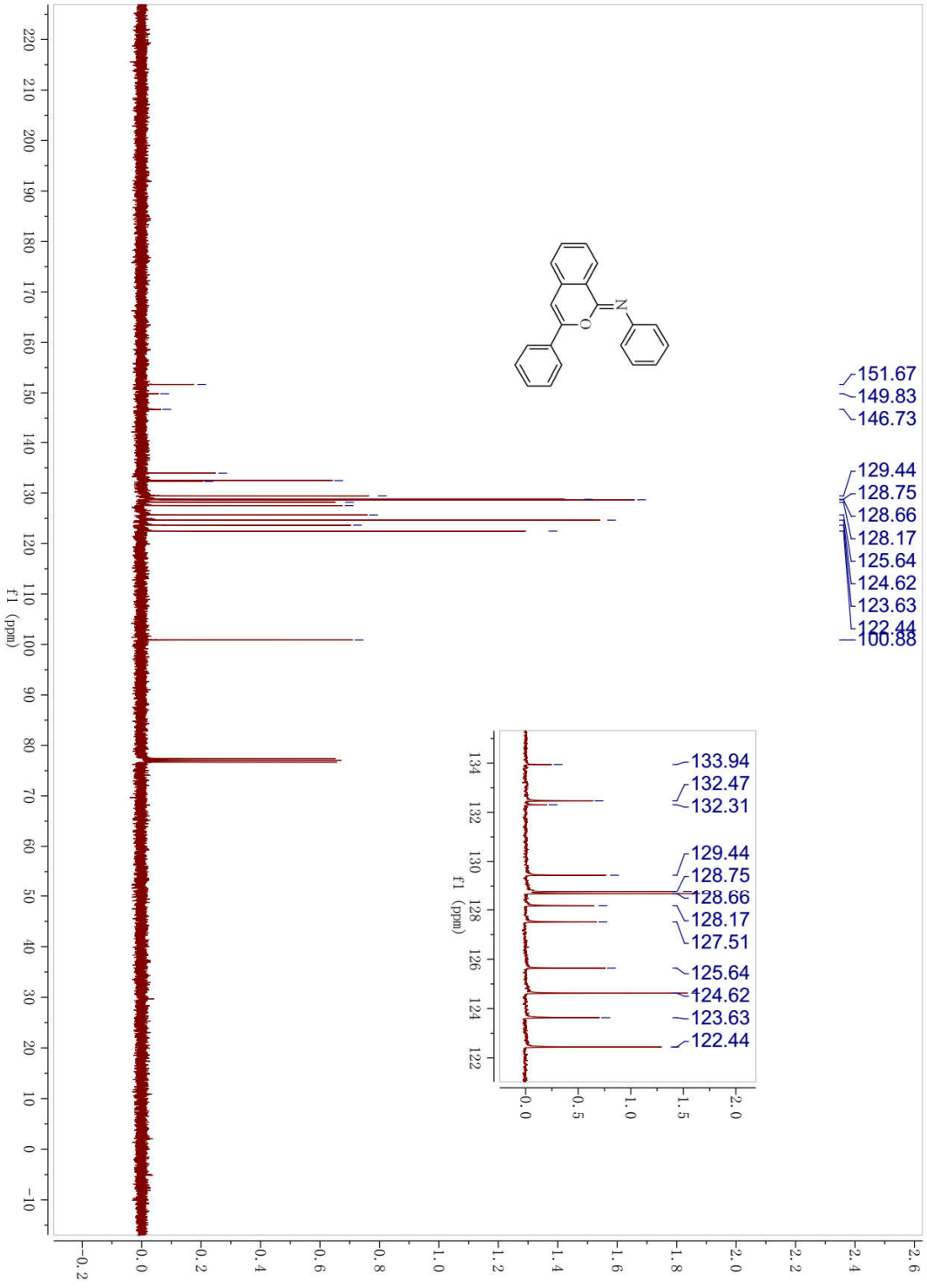
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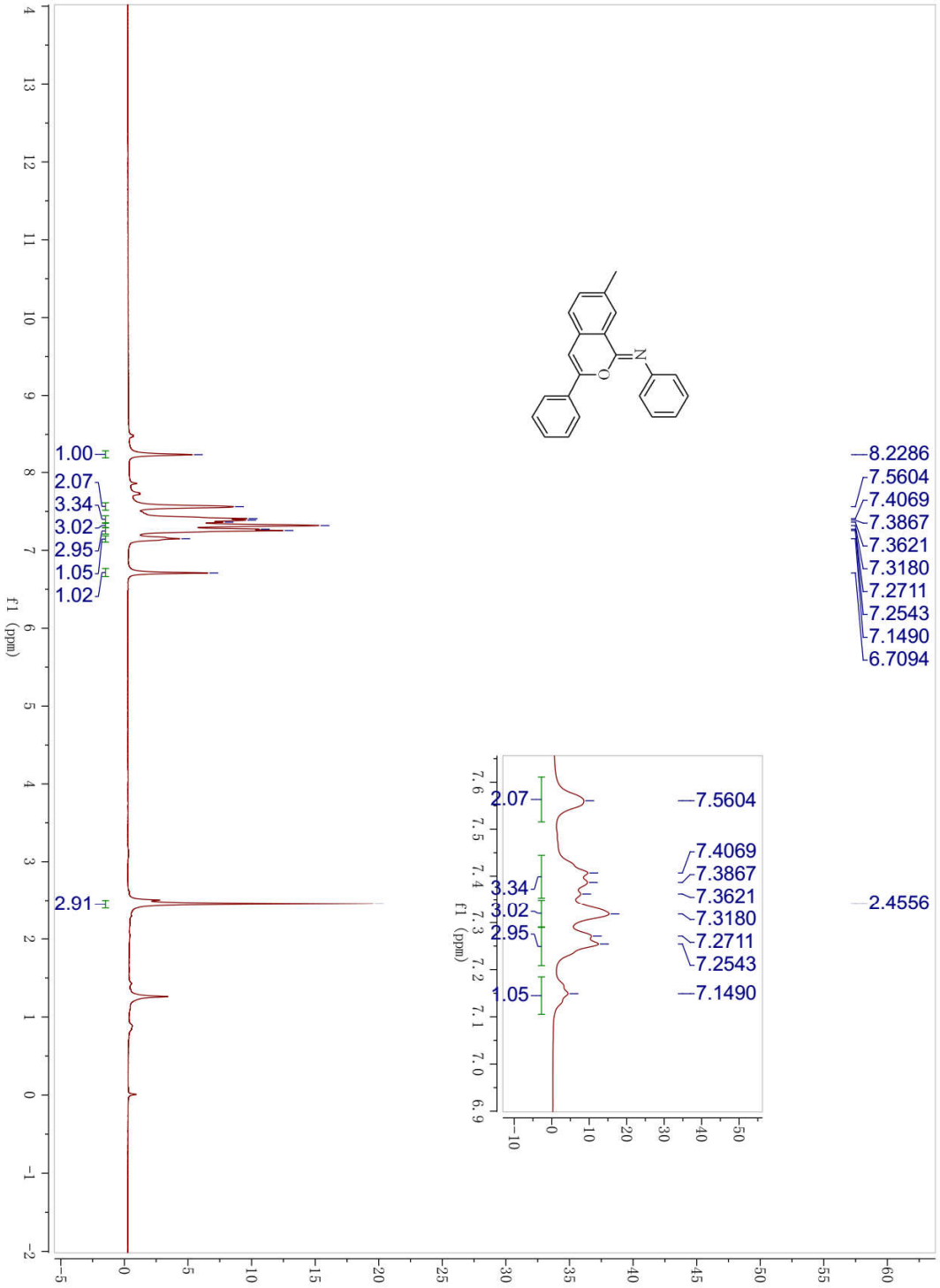
f1 (ppm)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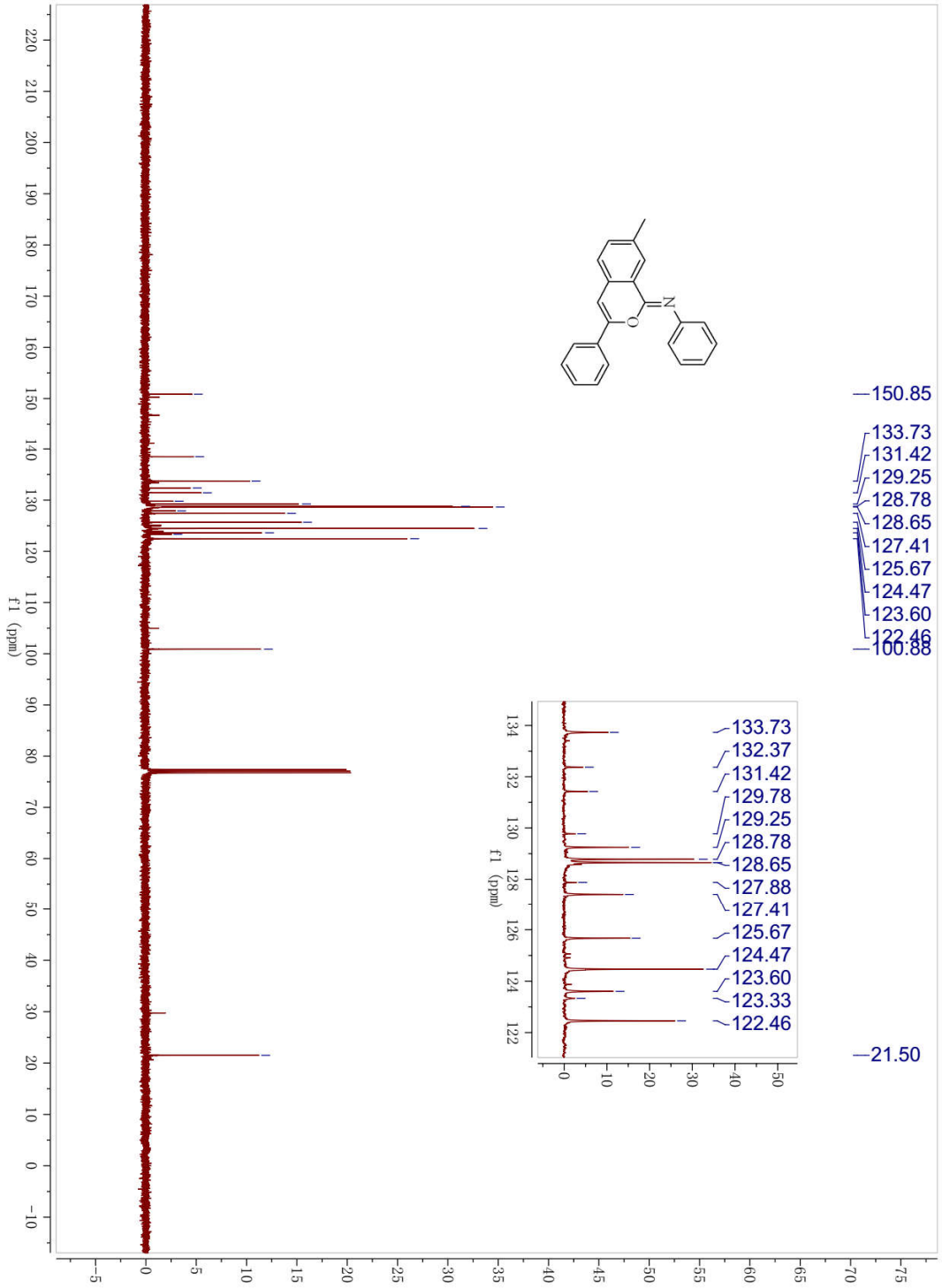
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f1 (ppm)

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O
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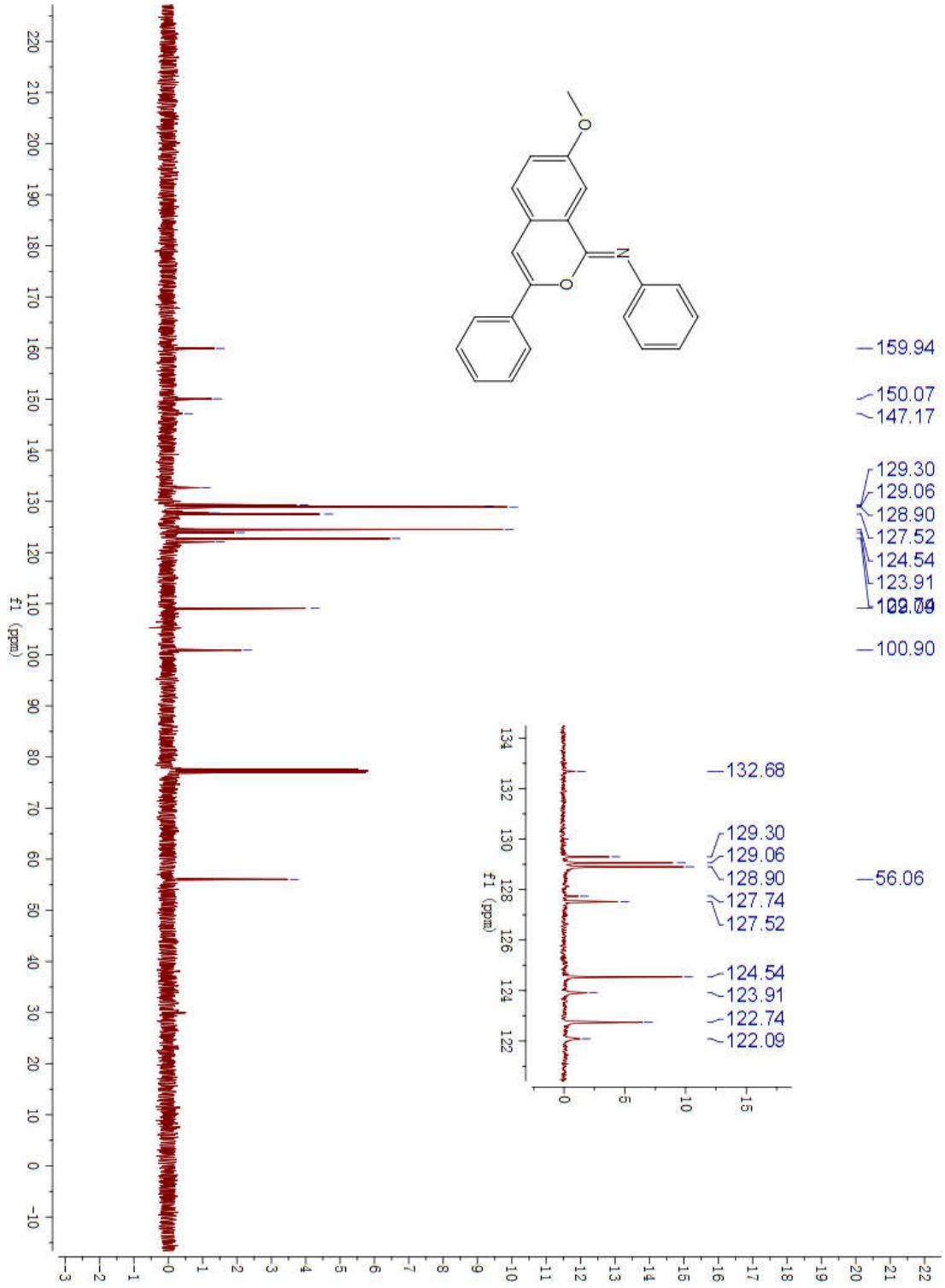
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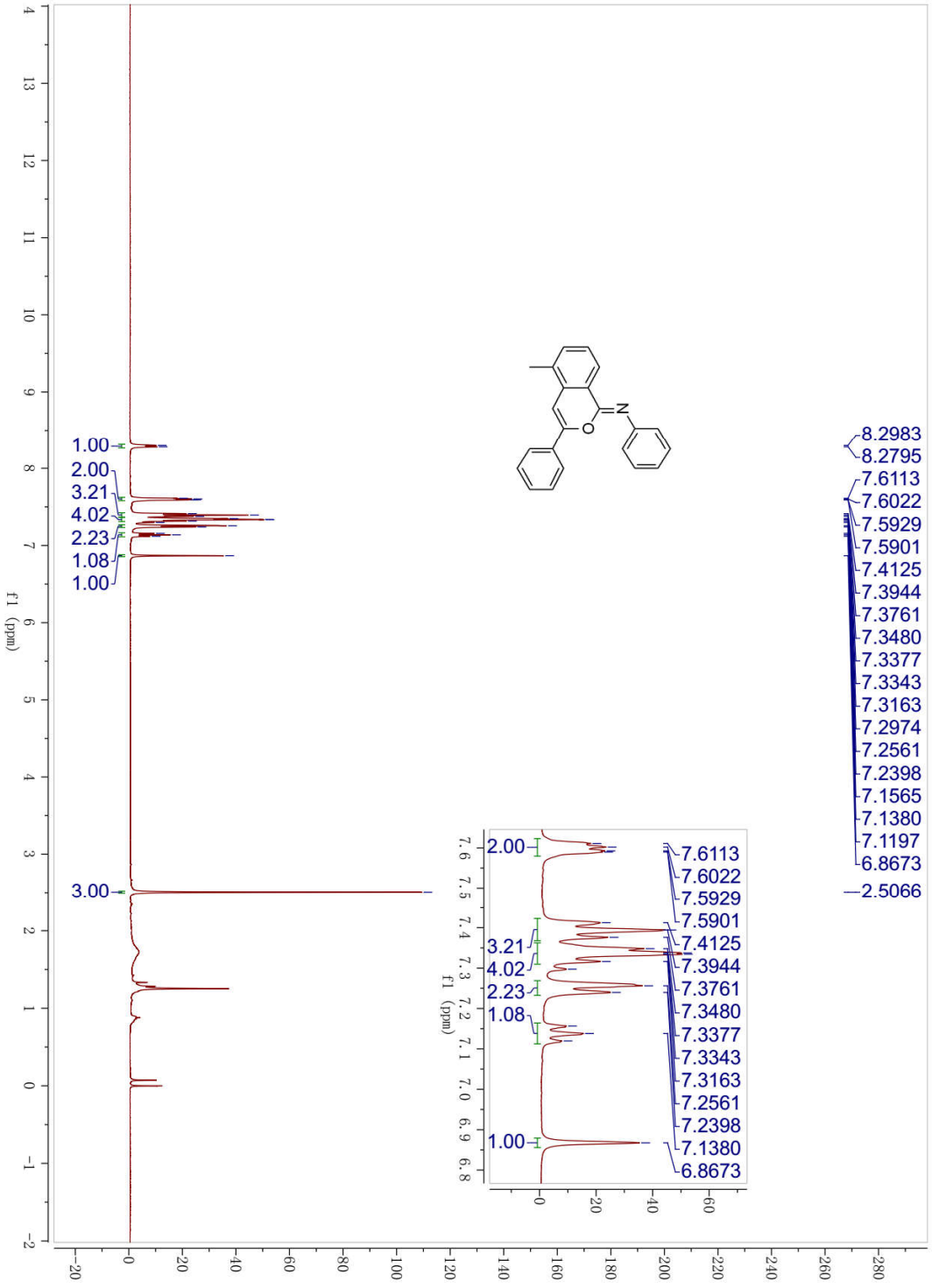
f1 (ppm)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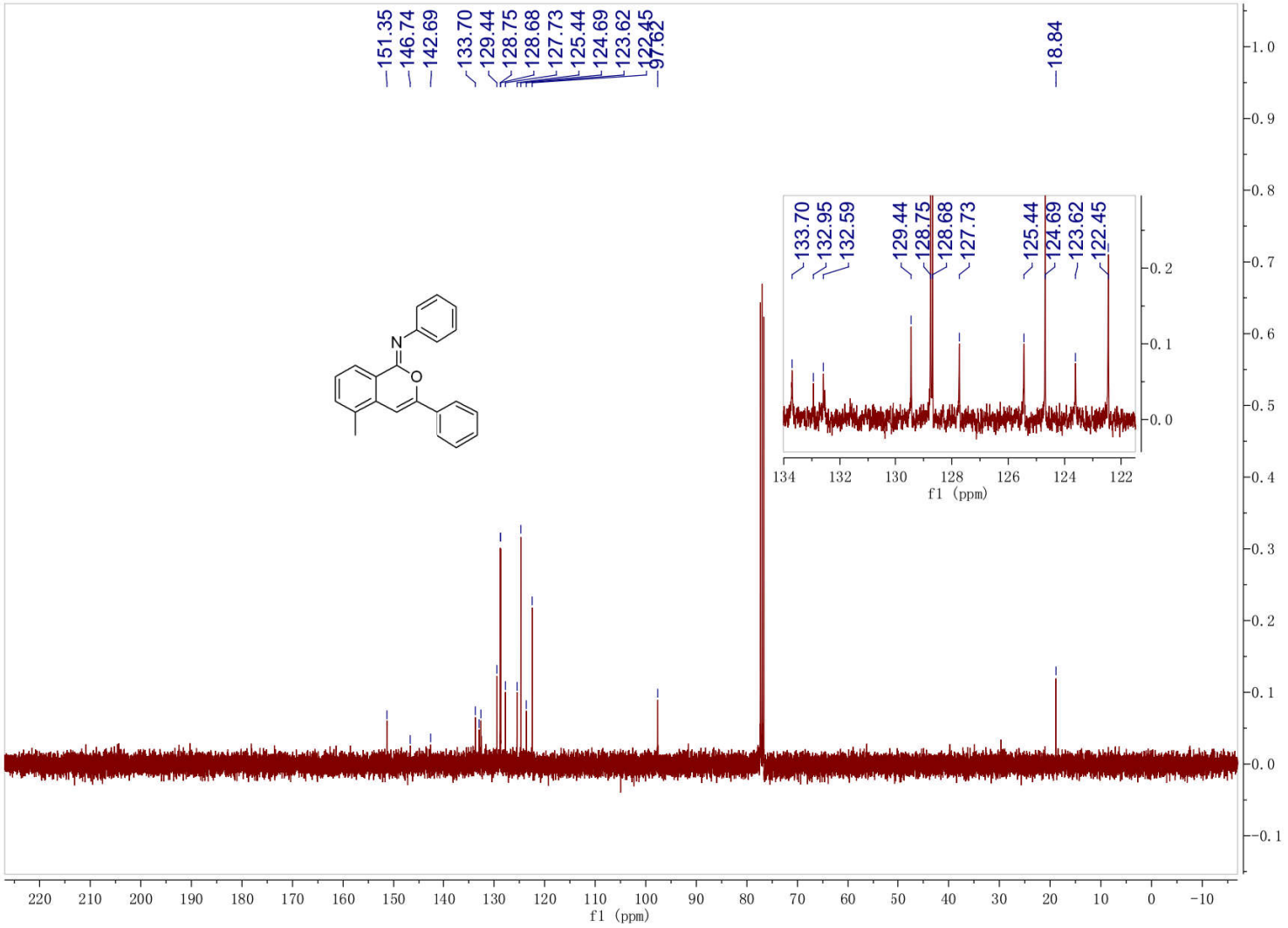
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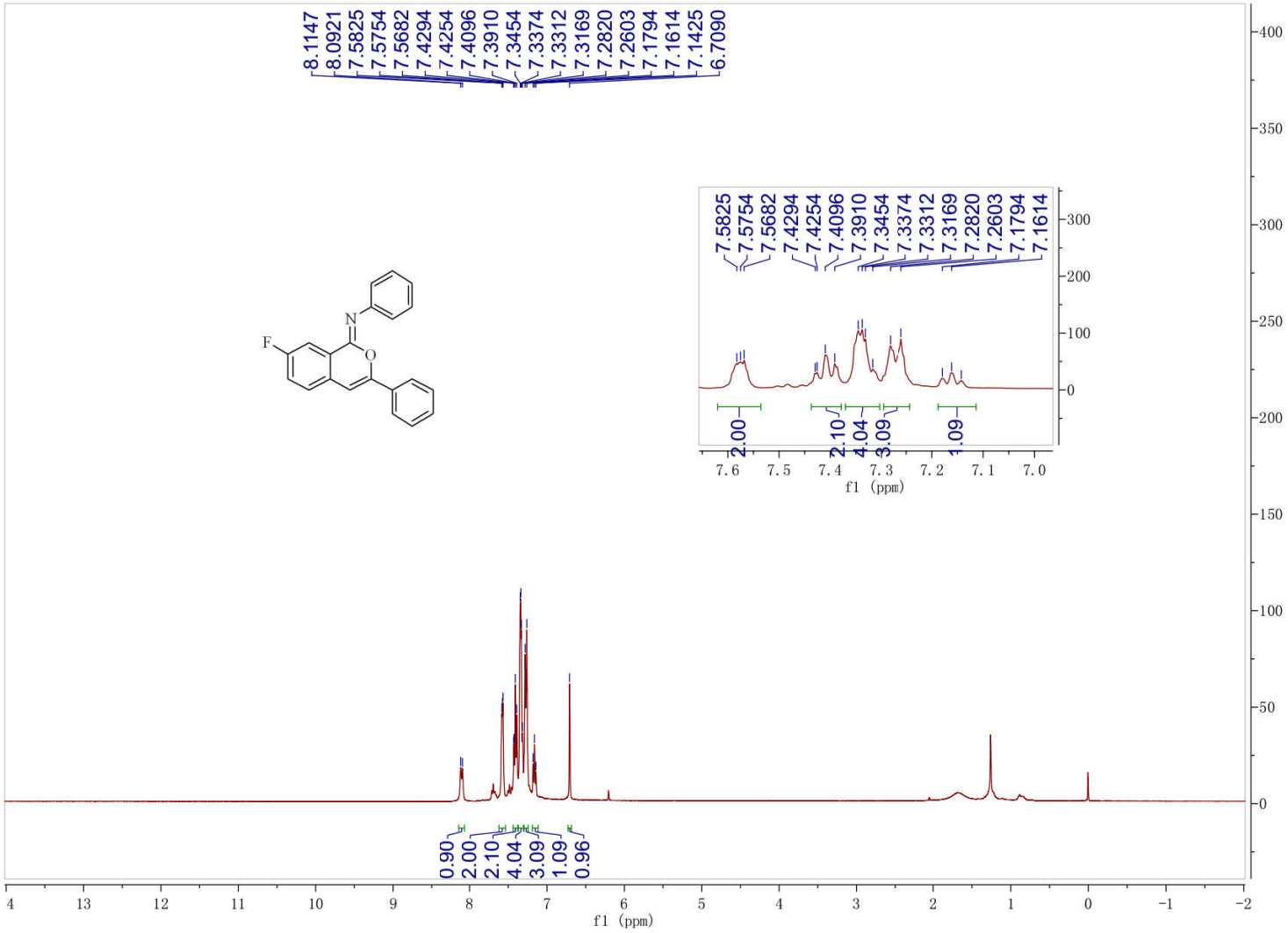
f1 (ppm)
f1 (ppm)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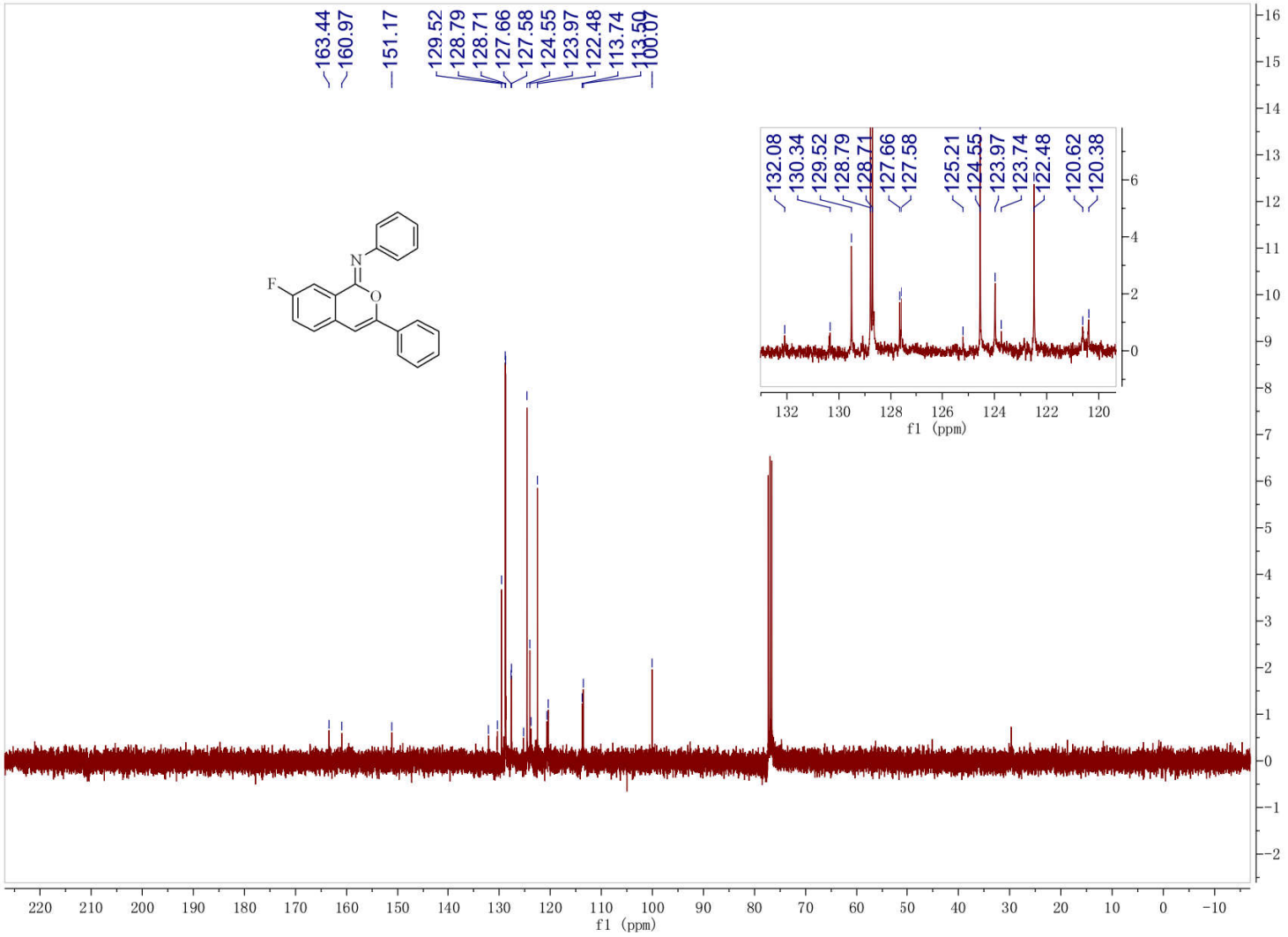
f1 (ppm)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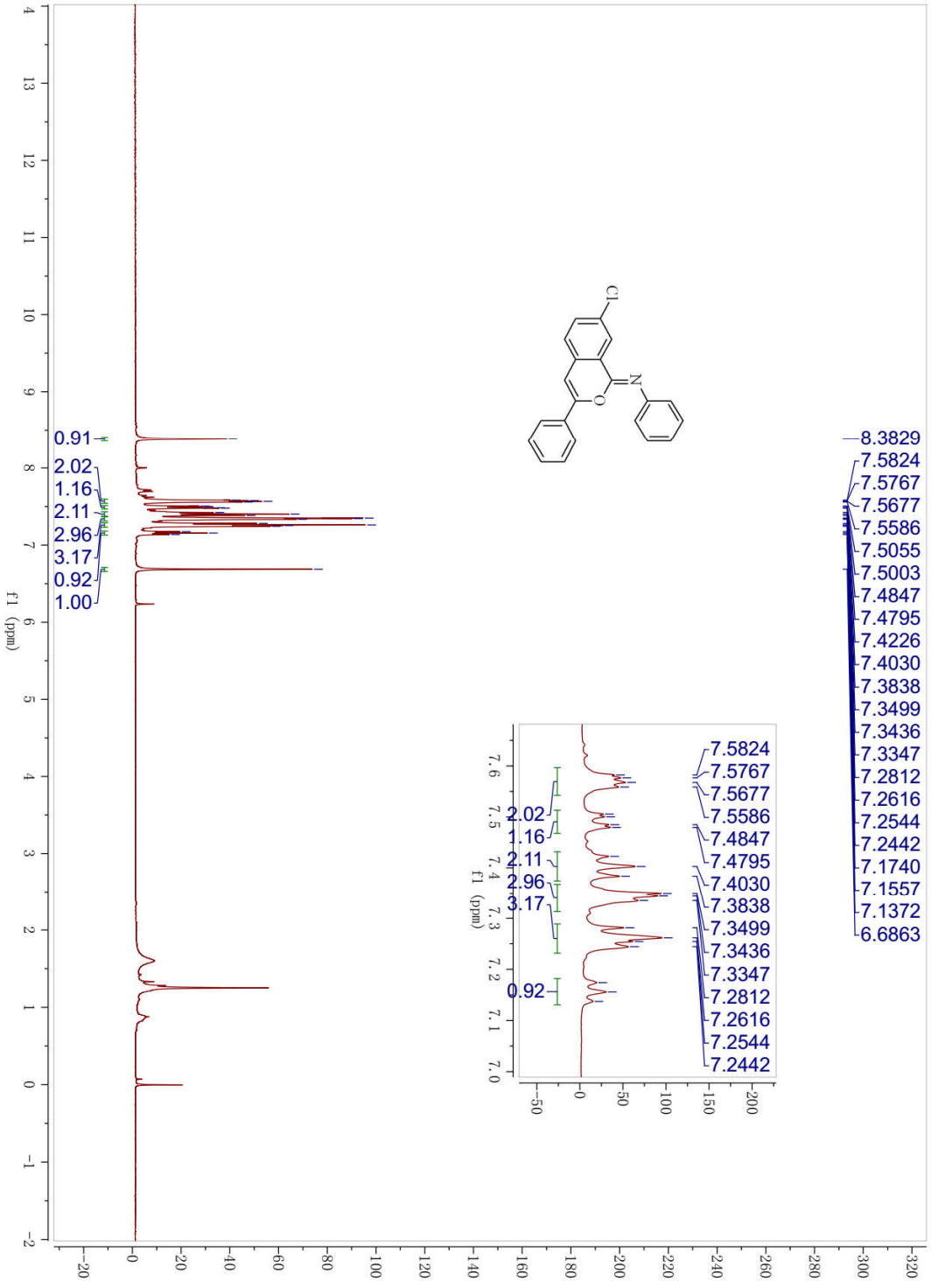
f1 (ppm)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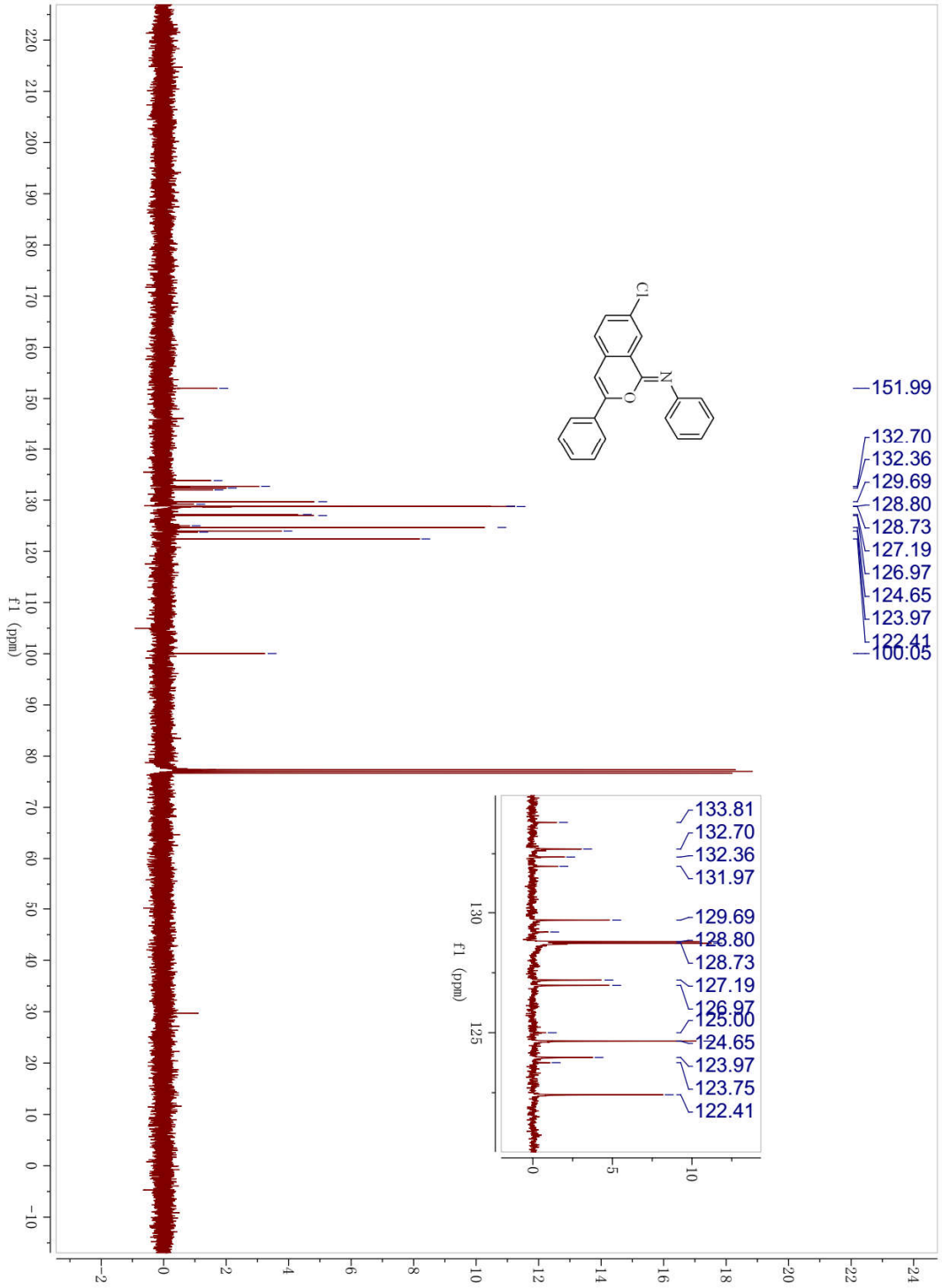
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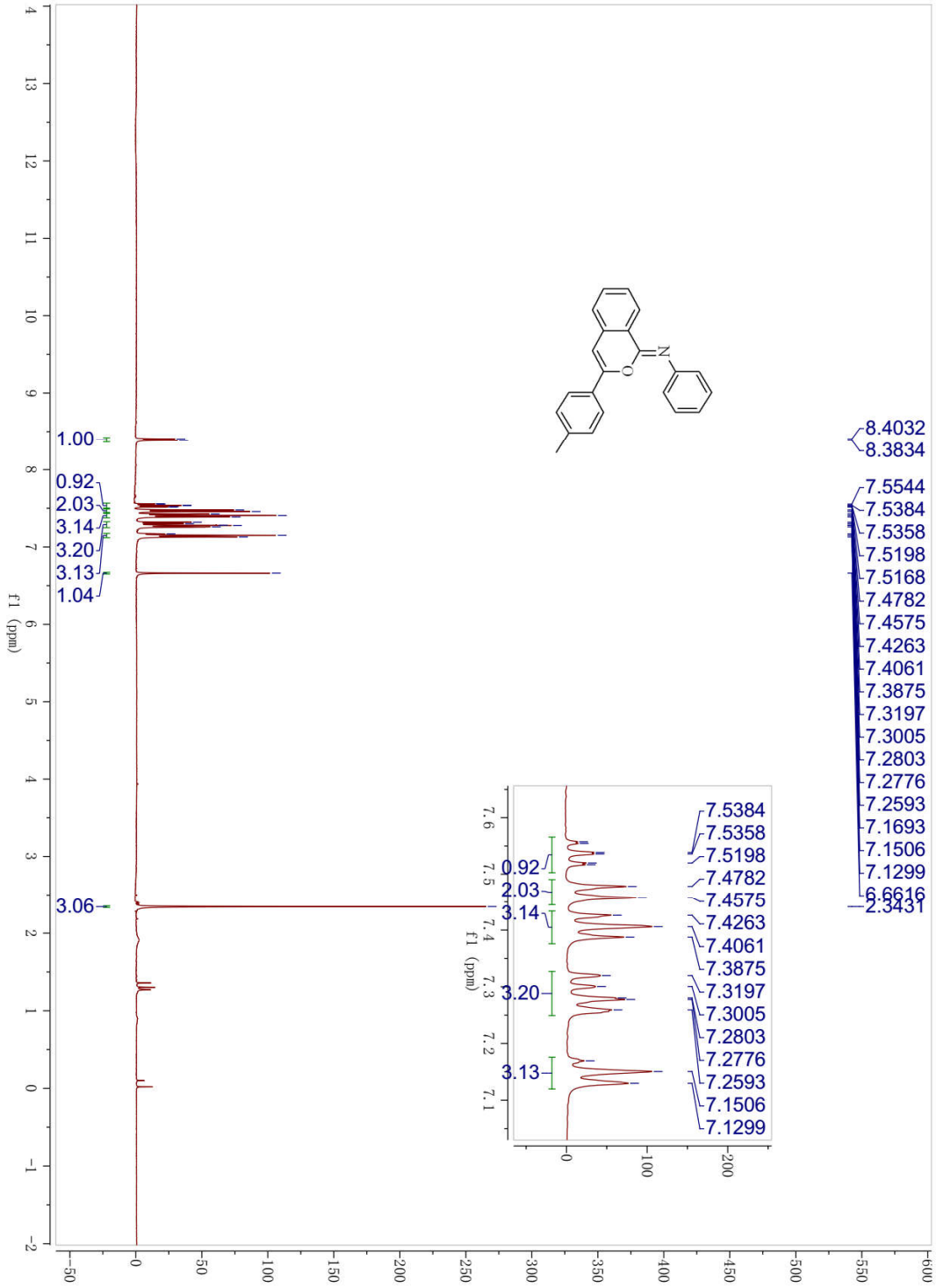
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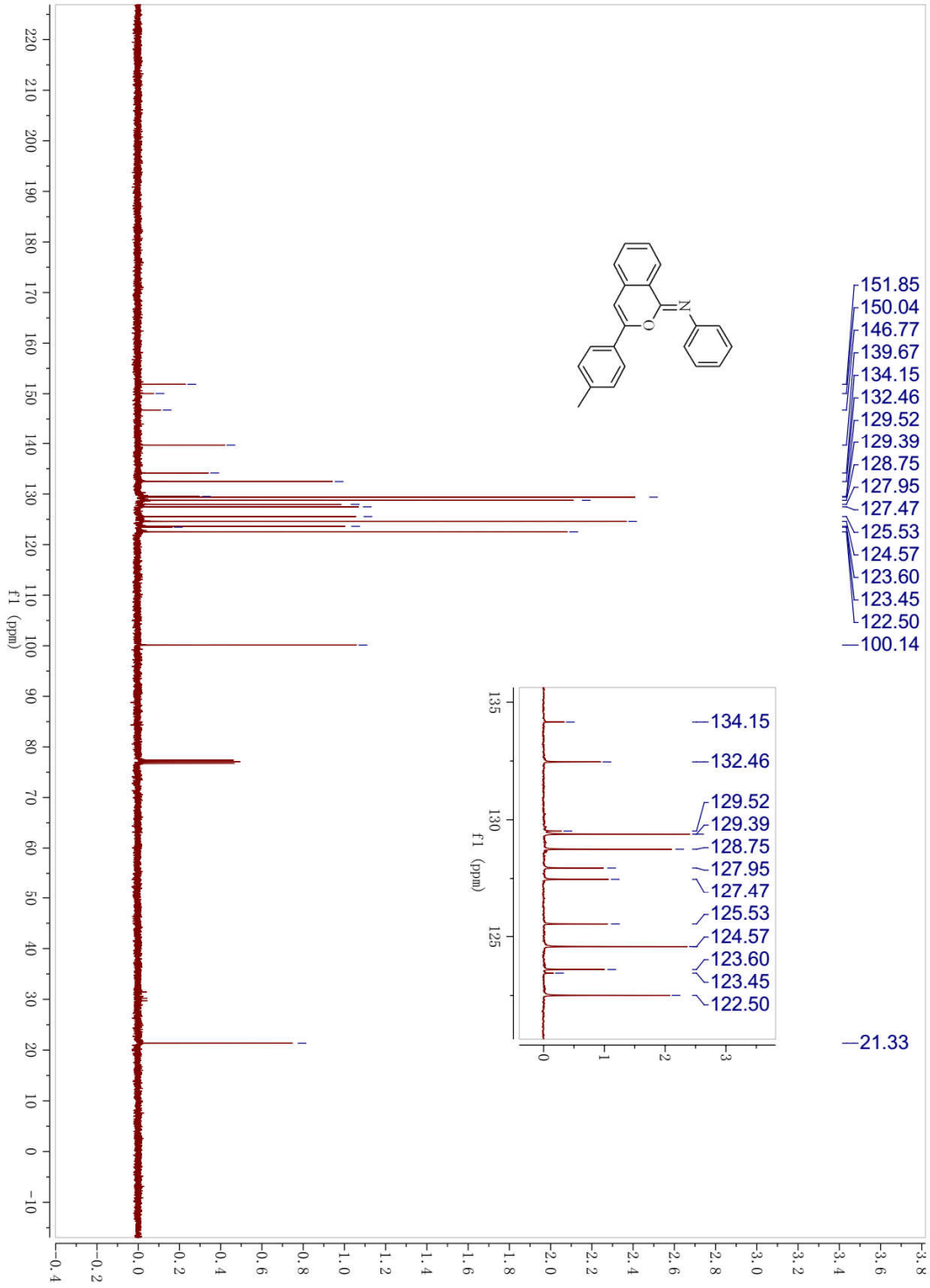
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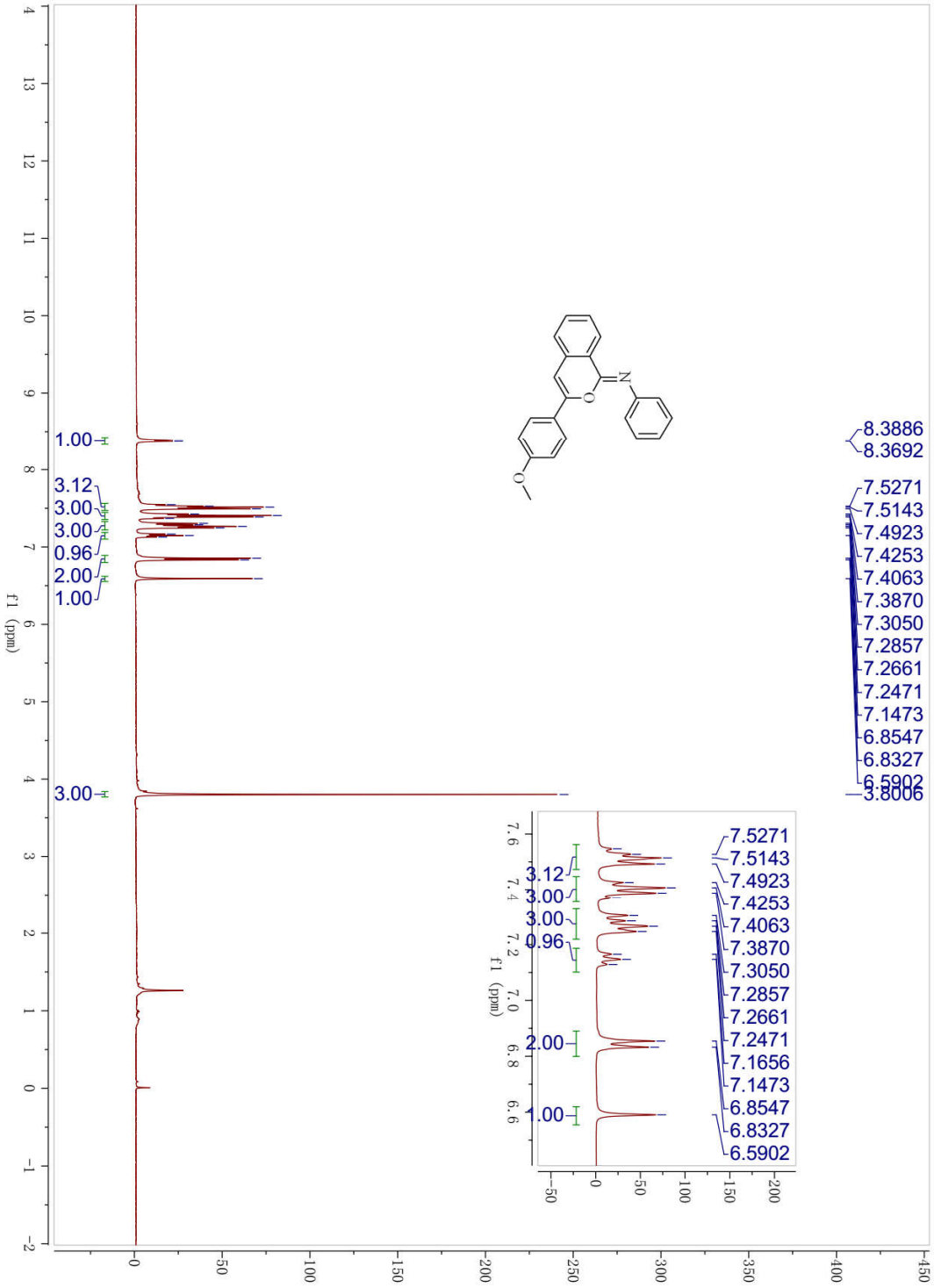
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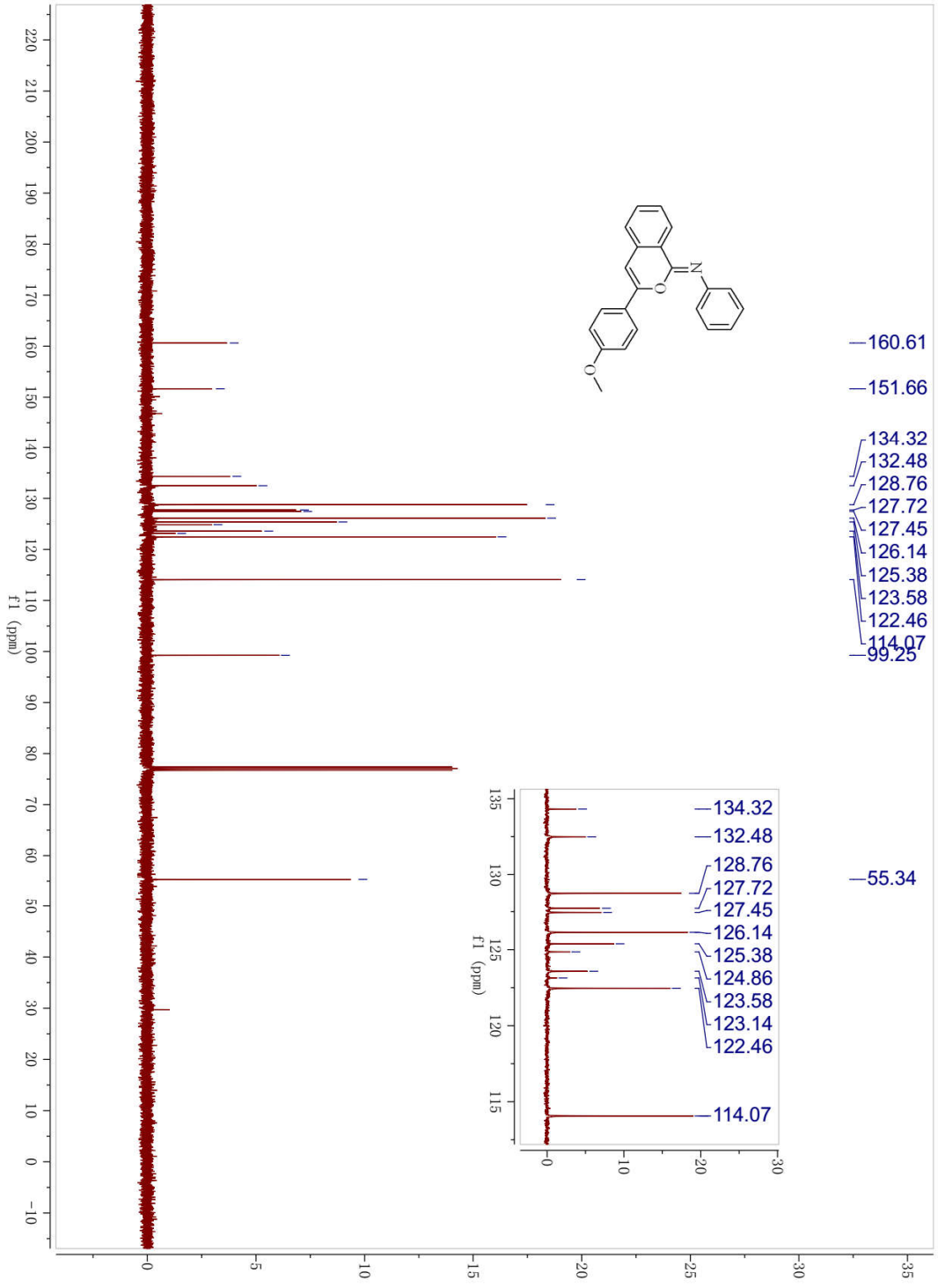
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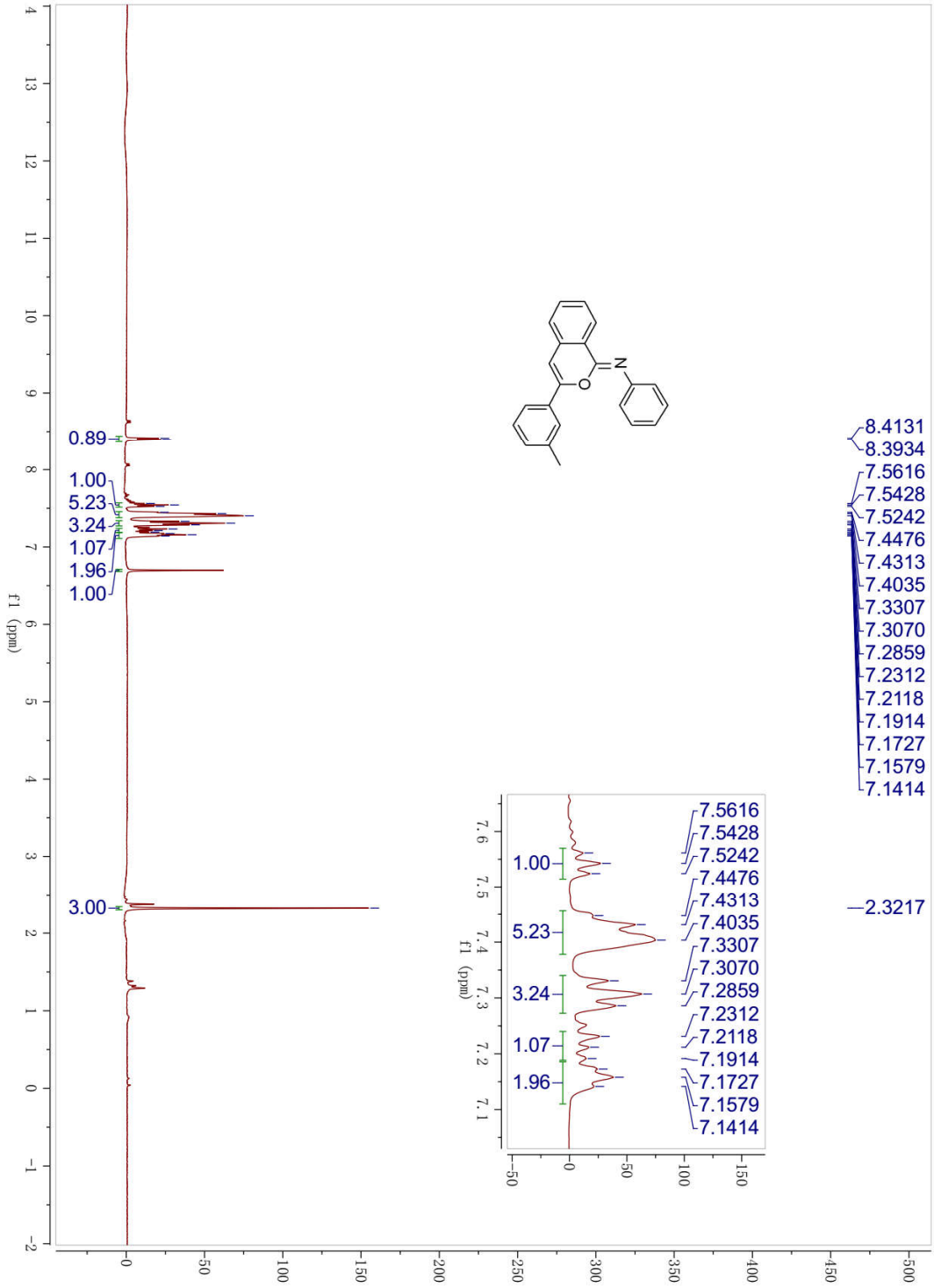
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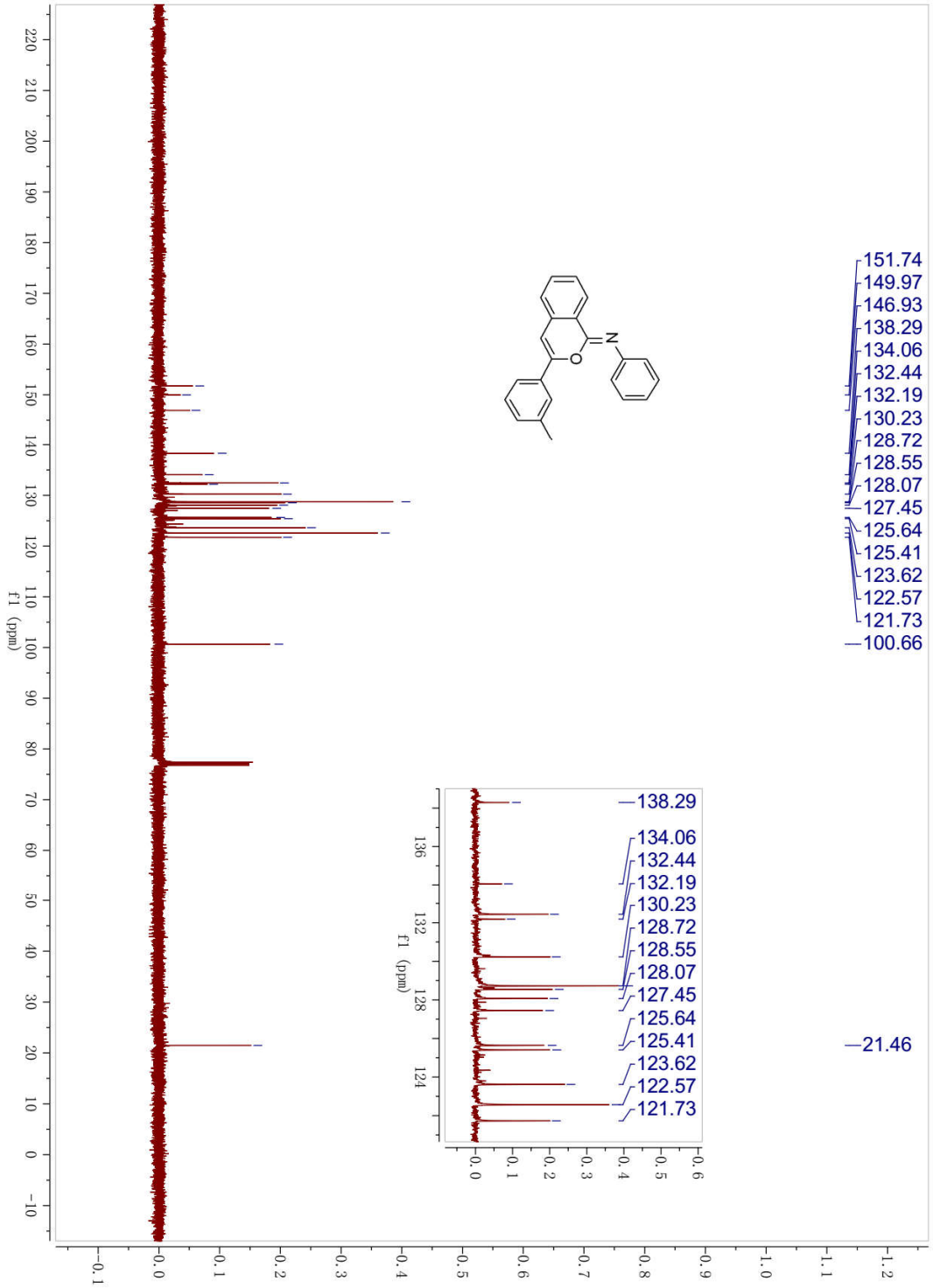
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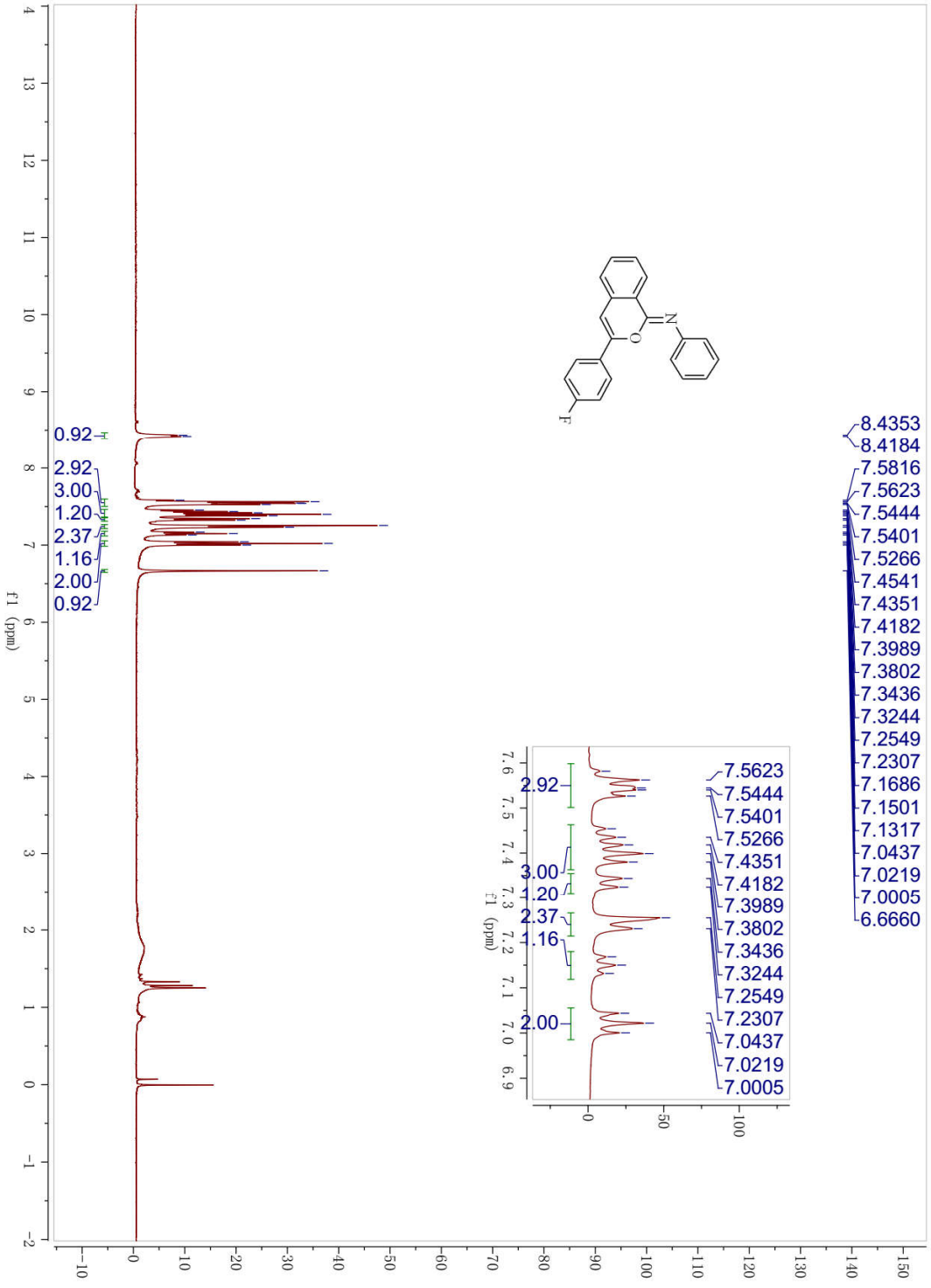
127.45
125.64
125.41
123.62
122.57
121.73
100.66
21.46
f1 (ppm)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2.37
1.16
2.00
0.92
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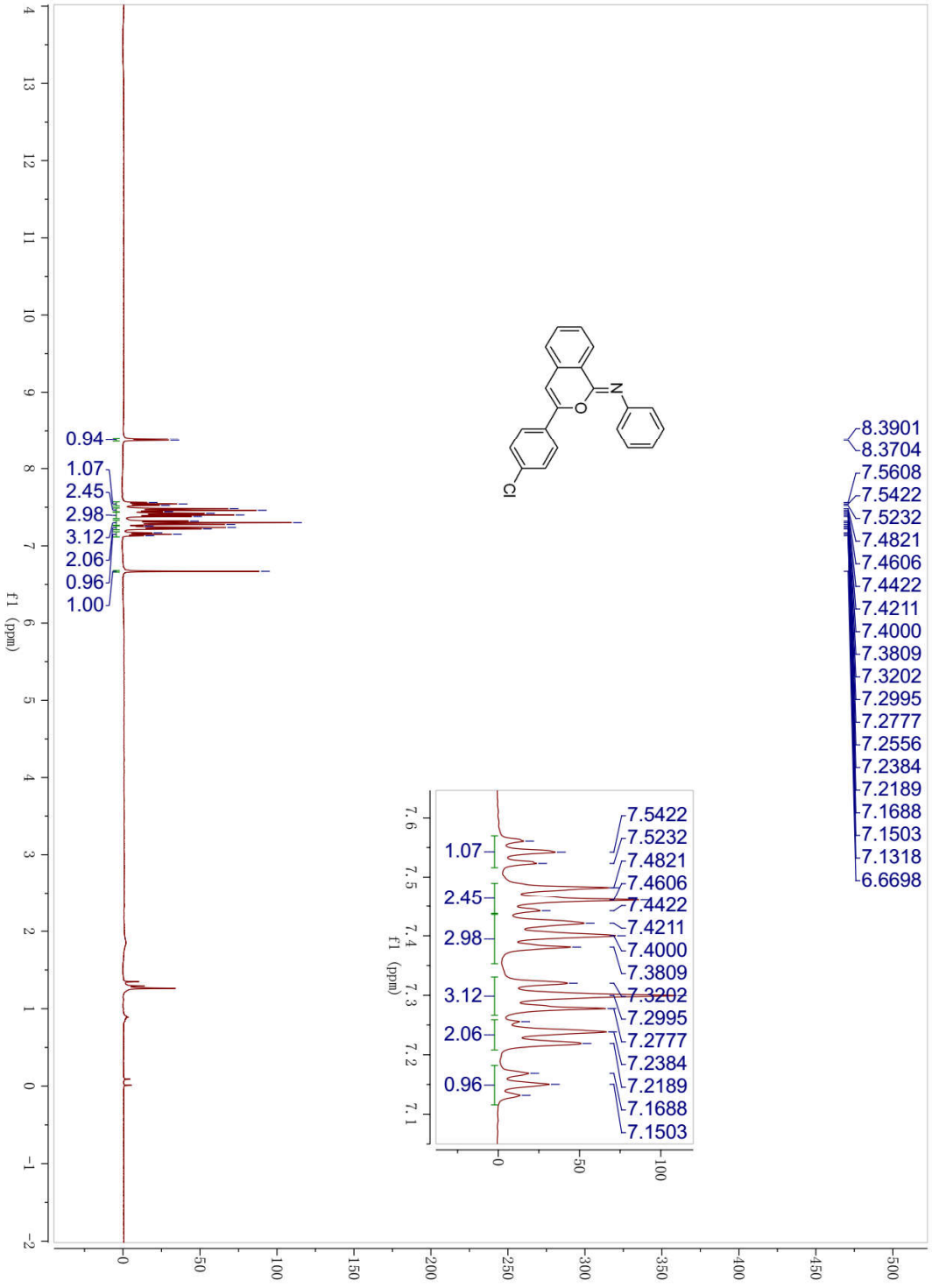
8.4184
7.5816
7.5623
7.5444
7.5401
7.5266
7.4541
7.4351
7.4182
7.3989
7.3802
7.3436
7.3244
7.2549
7.2307
7.1686
7.1501
7.1317
7.0437
7.0219
7.0005
6.6660
f1 (ppm)
O
N
F

164.64
162.15
150.79
128.82
128.32
127.60
126.62
126.53
125.64
123.83
122.36
115.91
115.69
100.71
133.88
132.70
128.82
128.32
127.60
126.62
126.53
125.64
123.83
122.36
115.91
115.69
f1 (ppm)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2.45
2.98
3.12
2.06
0.96
1.00
f1 (ppm)
8.3901
8.3704
7.5608
7.5422
7.5232
7.4821
7.4606
7.4422
7.4211
7.4000
7.3809
7.3202
7.2995
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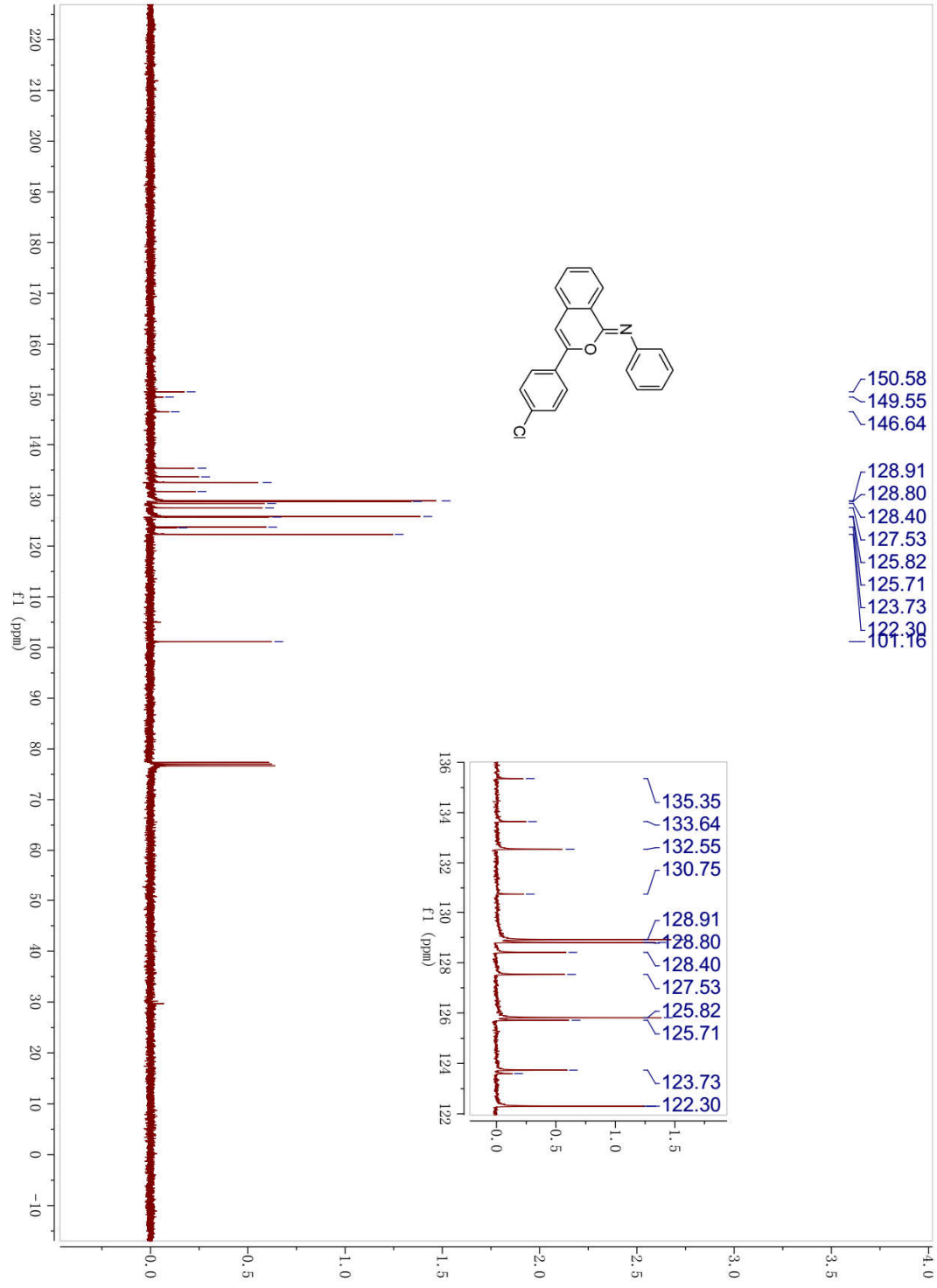
7.2556
7.2384
7.2189
7.1688
7.1503
7.1318
6.6698
Cl
N
O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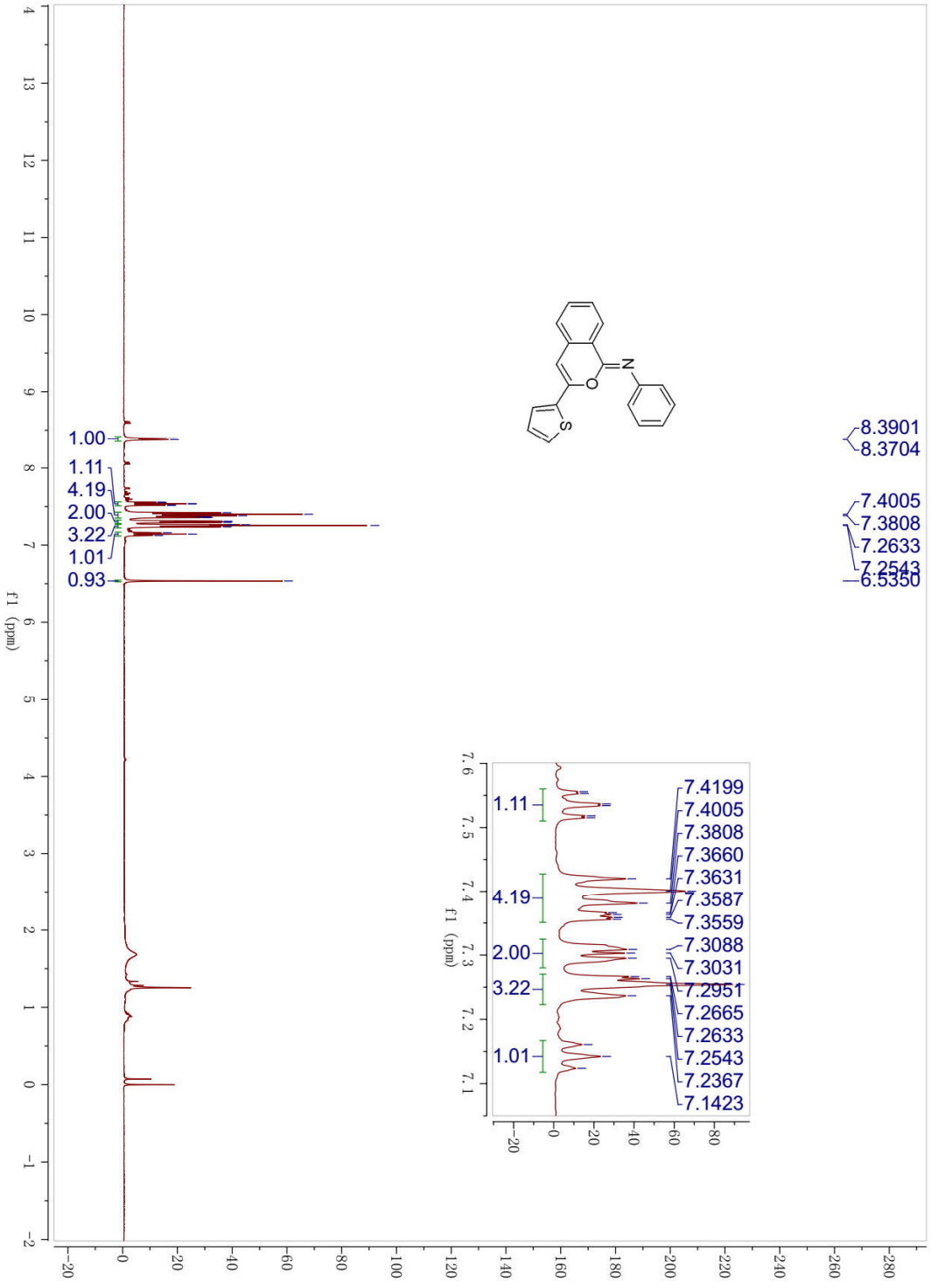
146.64
128.91
128.80
128.40
127.53
125.82
125.71
123.73
122.30
101.16
135.35
133.64
132.55
130.75
128.91
128.80
128.40
127.53
125.82
125.71
123.73
122.30
f1 (ppm)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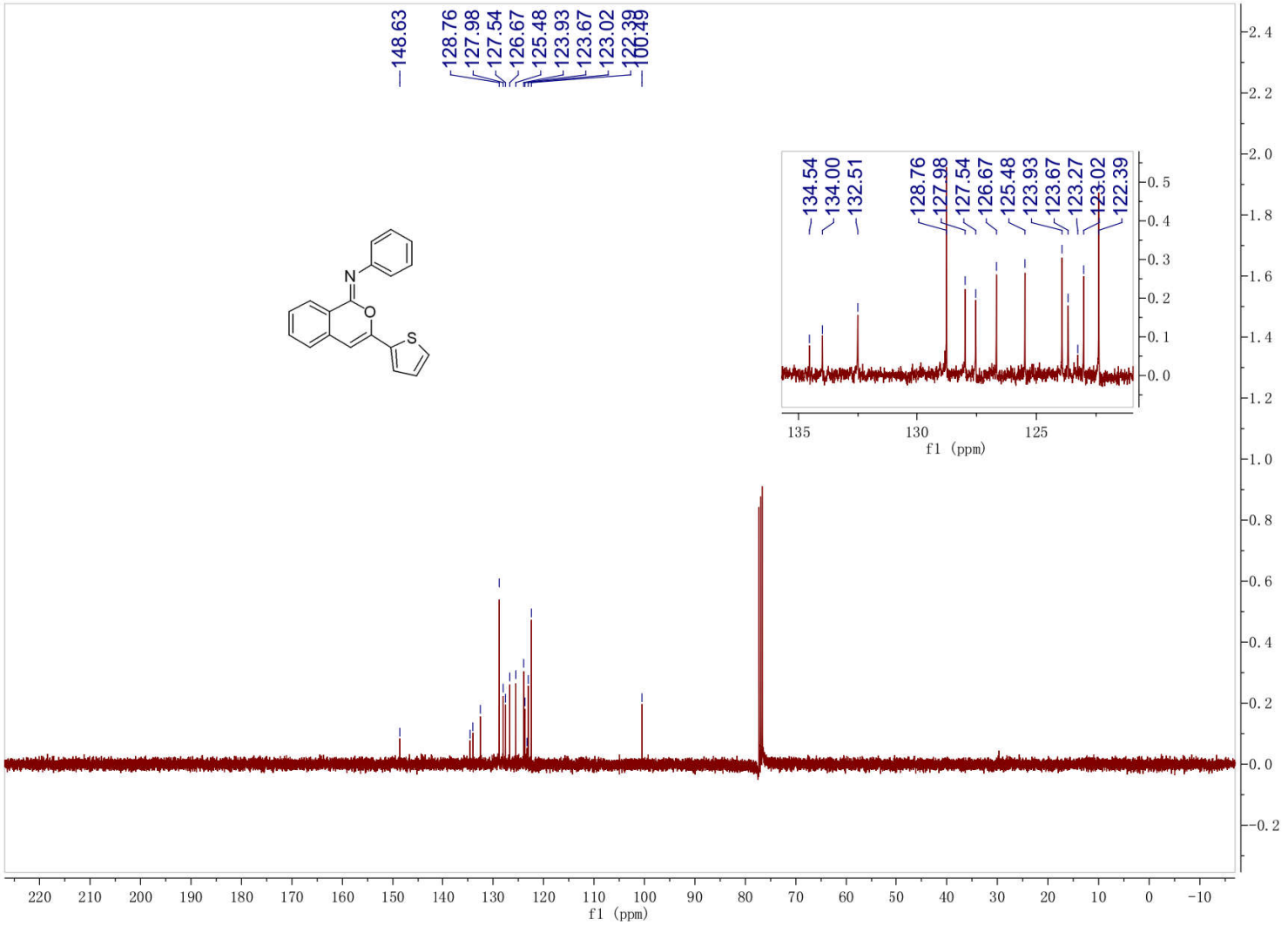
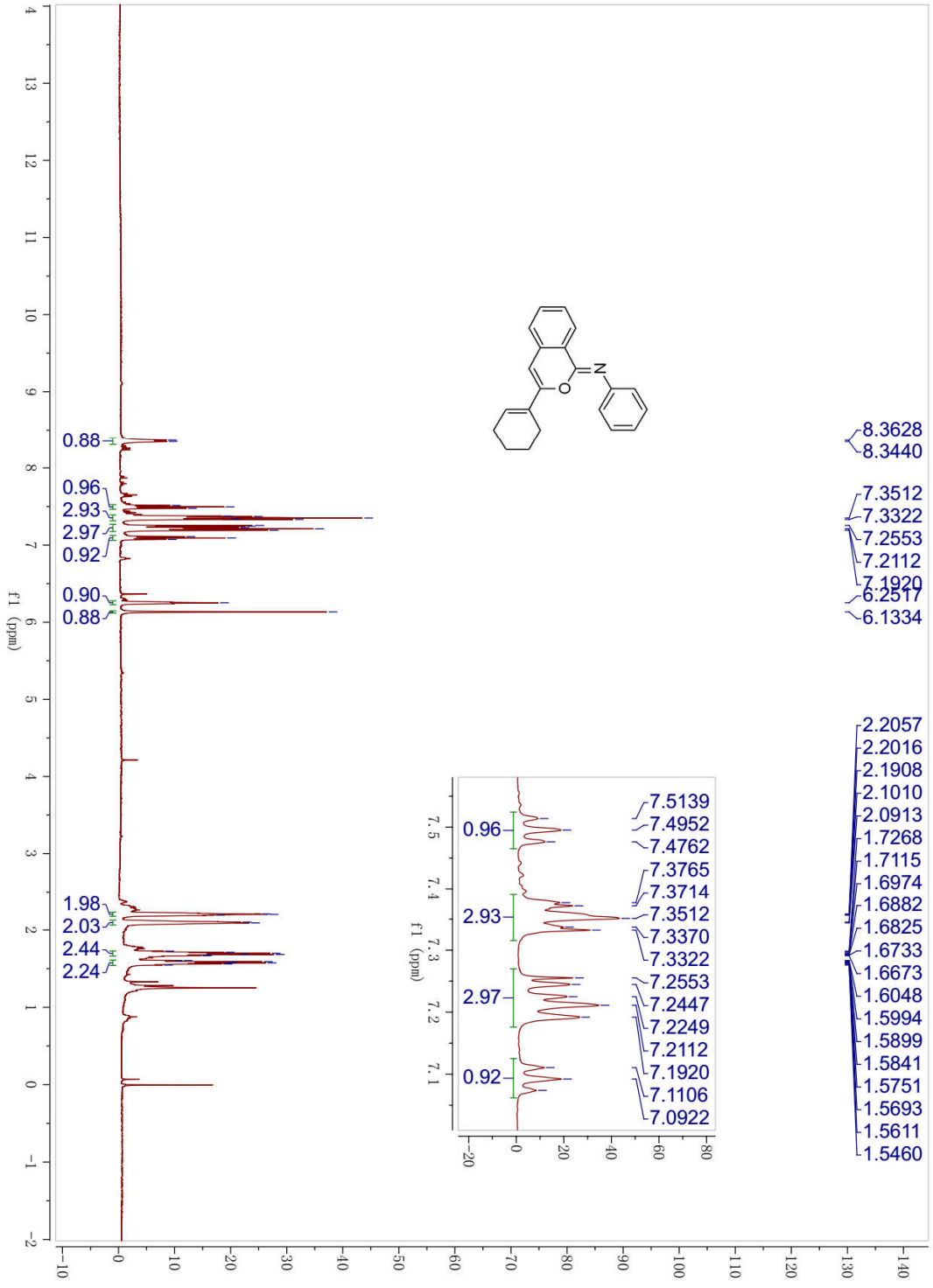
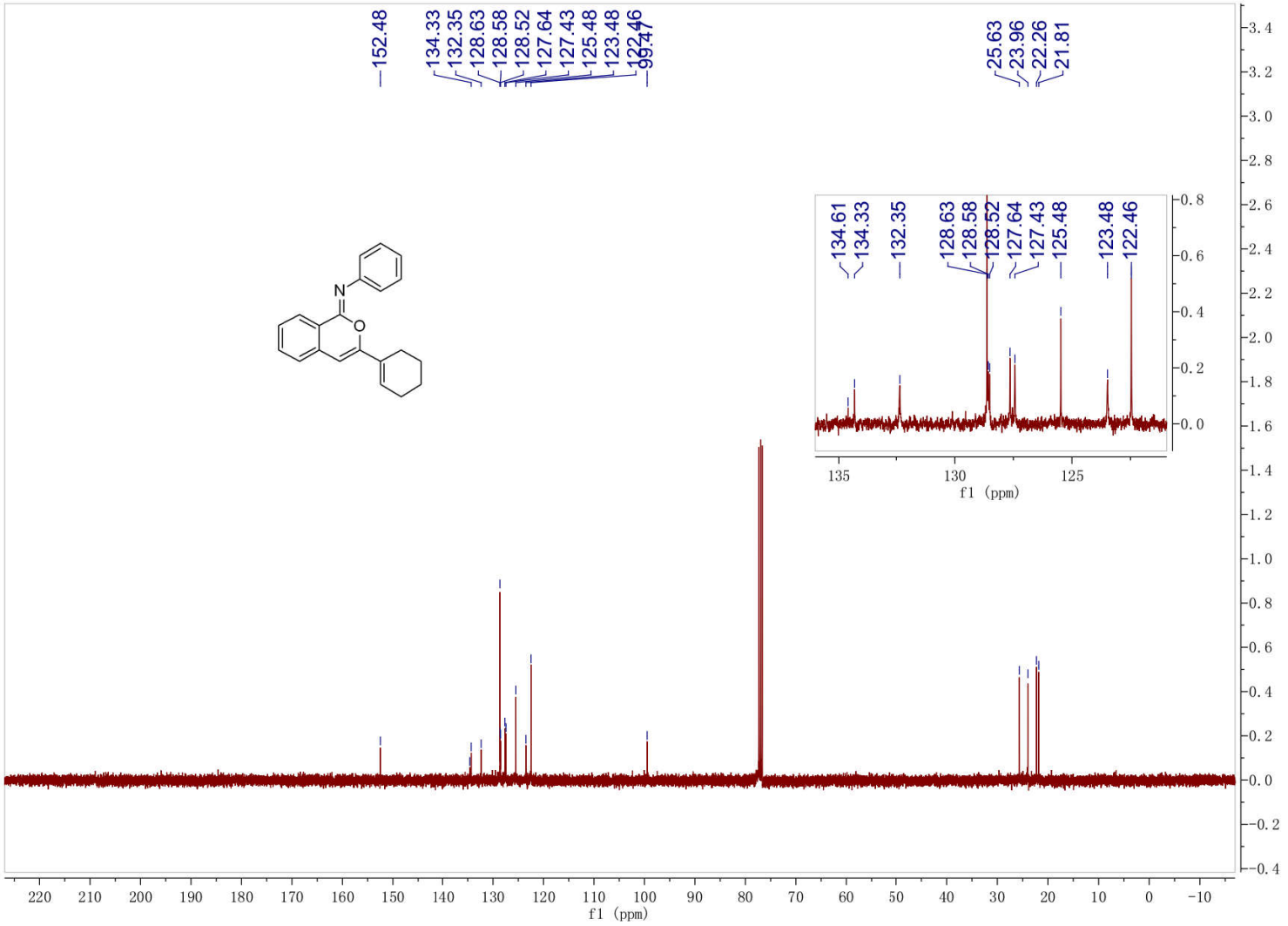
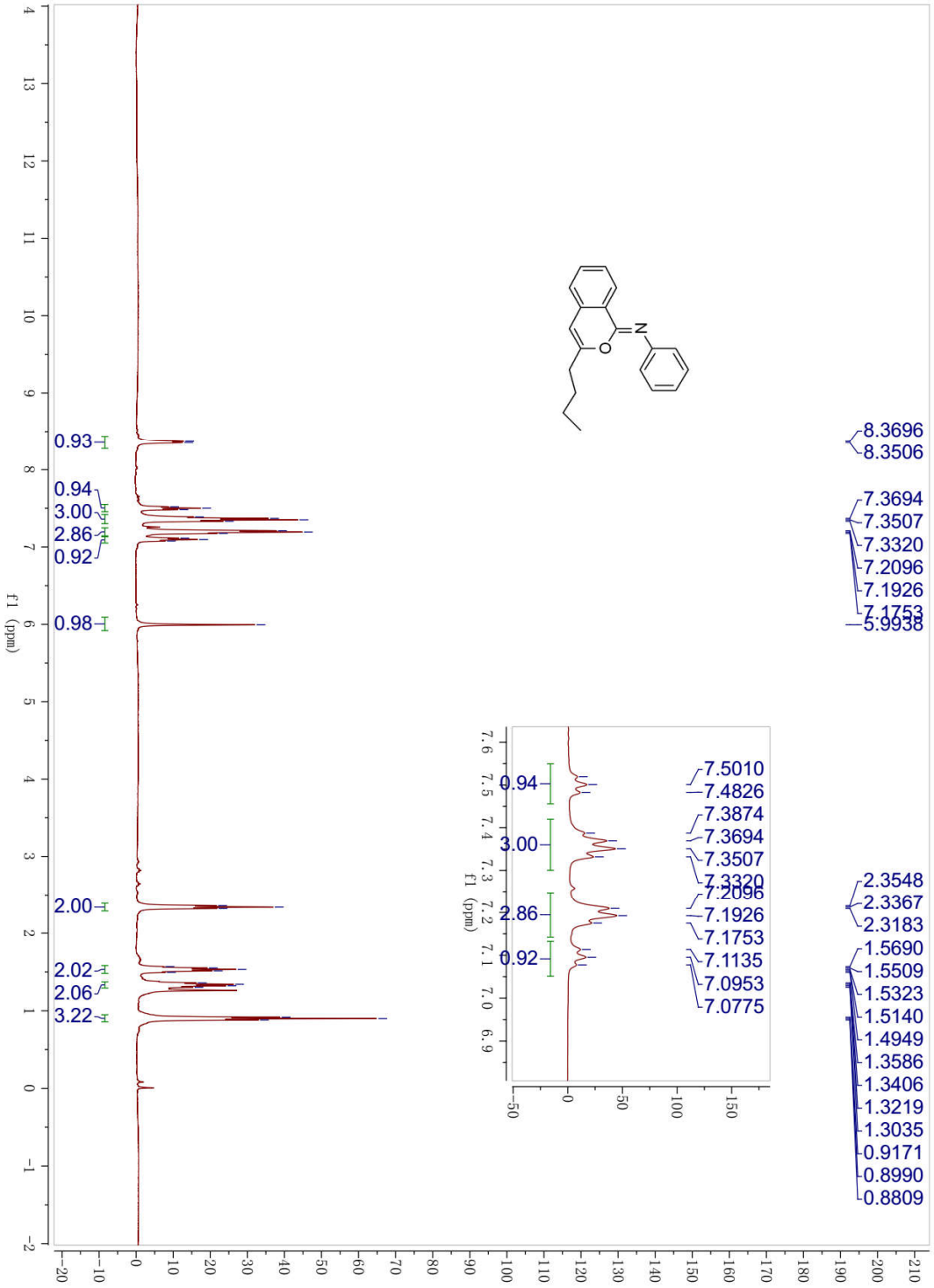
4.19
2.00
3.22
1.01
0.93
8.3901
8.3704
7.4005
7.3808
7.2633
7.2543
6.5350
f1 (ppm)
1.11
4.19
2.00
3.22
1.01
7.4199
7.4005
7.3808
7.3660
7.3631
7.3587
7.3559
7.3088
7.3031
7.2951
7.2665
7.2633
7.2543
7.2367
7.1423
f1 (ppm)


148.63
128.76
127.98
127.54
126.67
125.48
123.93
123.67
123.02
122.39
100.49
134.54
134.00
132.51
128.76
127.98
127.54
126.67
125.48
123.93
123.67
123.27
123.02
122.39
N
O
S
f1 (ppm)
f1 (ppm)


0.88
0.96
2.93
2.97
0.92
0.90
0.88
1.98
2.03
2.44
2.24
f1 (ppm)
8.3628
8.3440
7.3512
7.3322
7.2553
7.2112
7.1920
6.2517
6.1334
2.2057
2.2016
2.1908
2.1010
2.0913
1.7268
1.7115
1.6974
1.6882
1.6825
1.6733
1.6673
1.6048
1.5994
1.5899
1.5841
1.5751
1.5693
1.5611
1.5460
0.96
2.93
2.97
0.92
7.5139
7.4952
7.4762
7.3765
7.3714
7.3512
7.3370
7.3322
7.2553
7.2447
7.2249
7.2112
7.1920
7.1106
7.0922
O
N


152.48
134.33
132.35
128.63
128.58
128.52
127.64
127.43
125.48
123.48
122.46
99.47
25.63
23.96
22.26
21.81
N
O
134.61
134.33
132.35
128.63
128.58
128.52
127.64
127.43
125.48
123.48
122.46
135
130
125
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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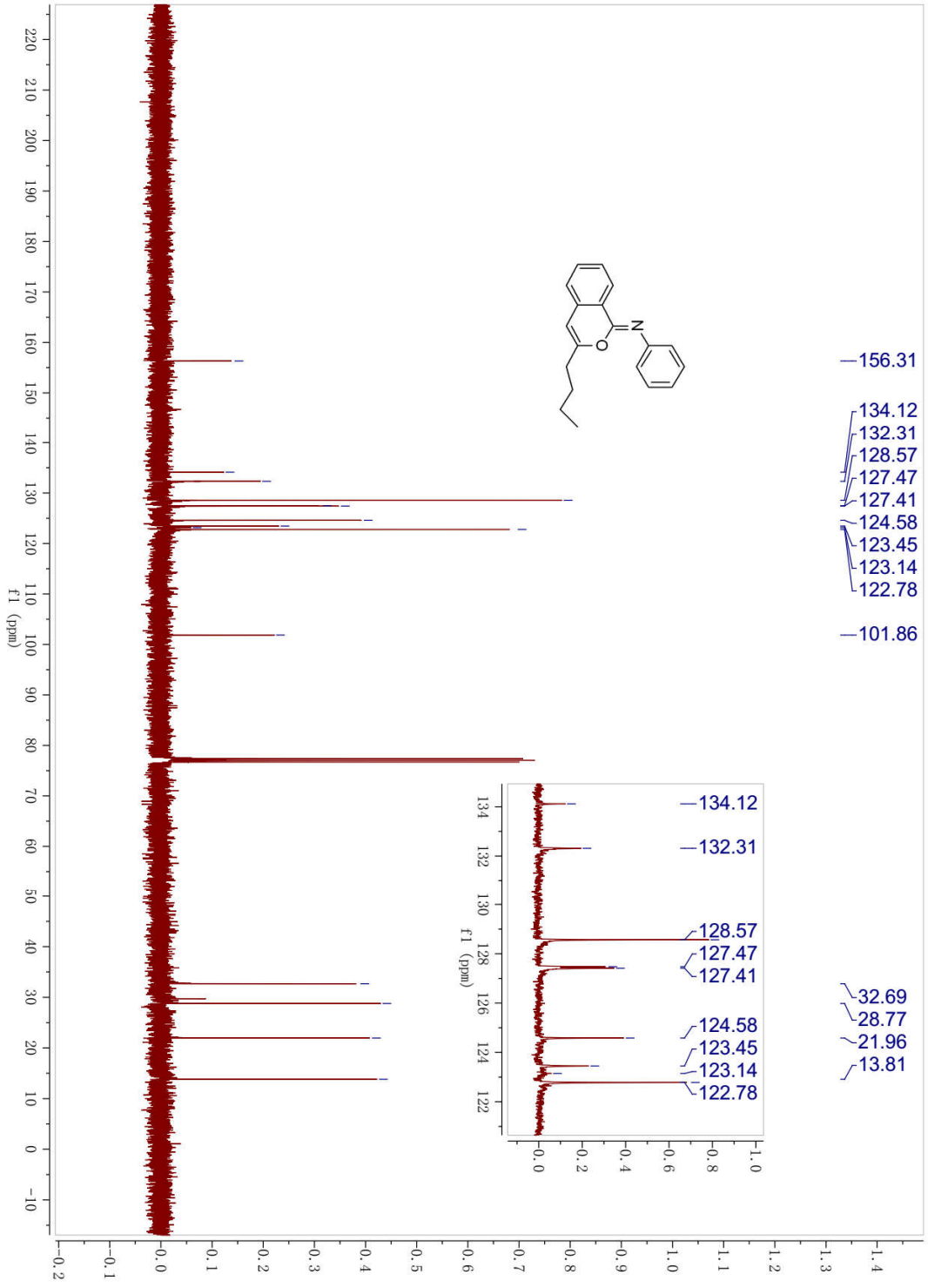
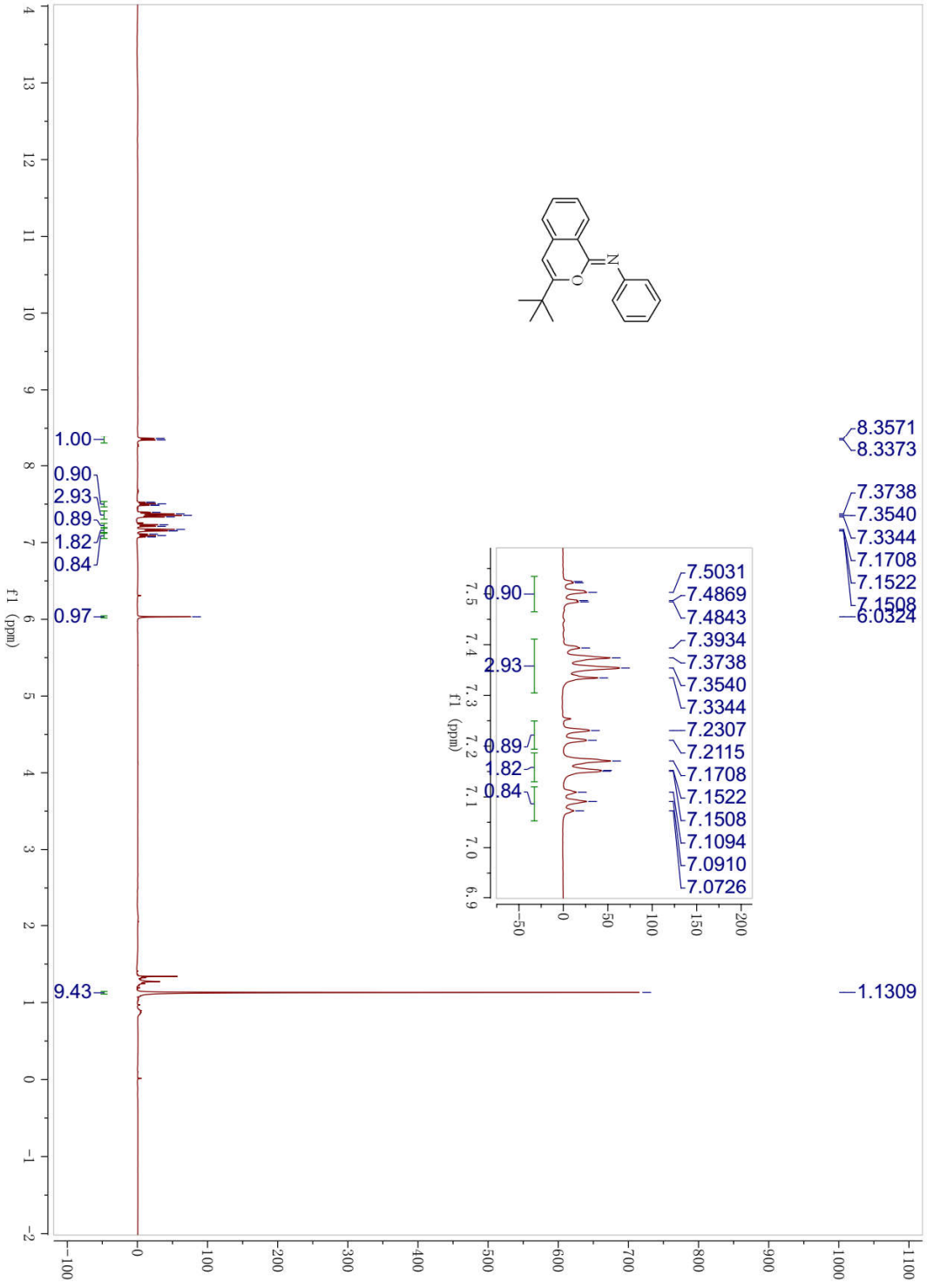
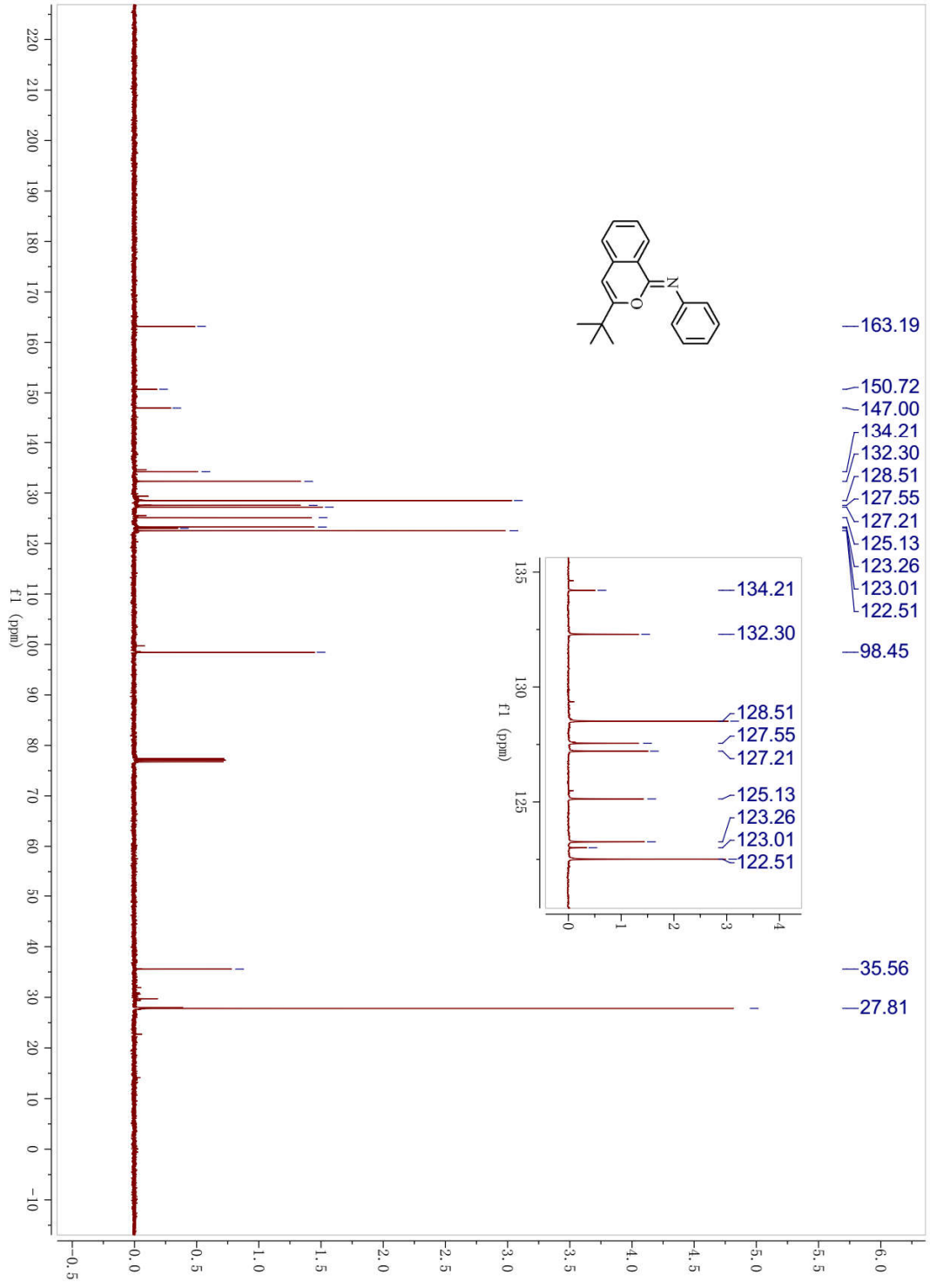
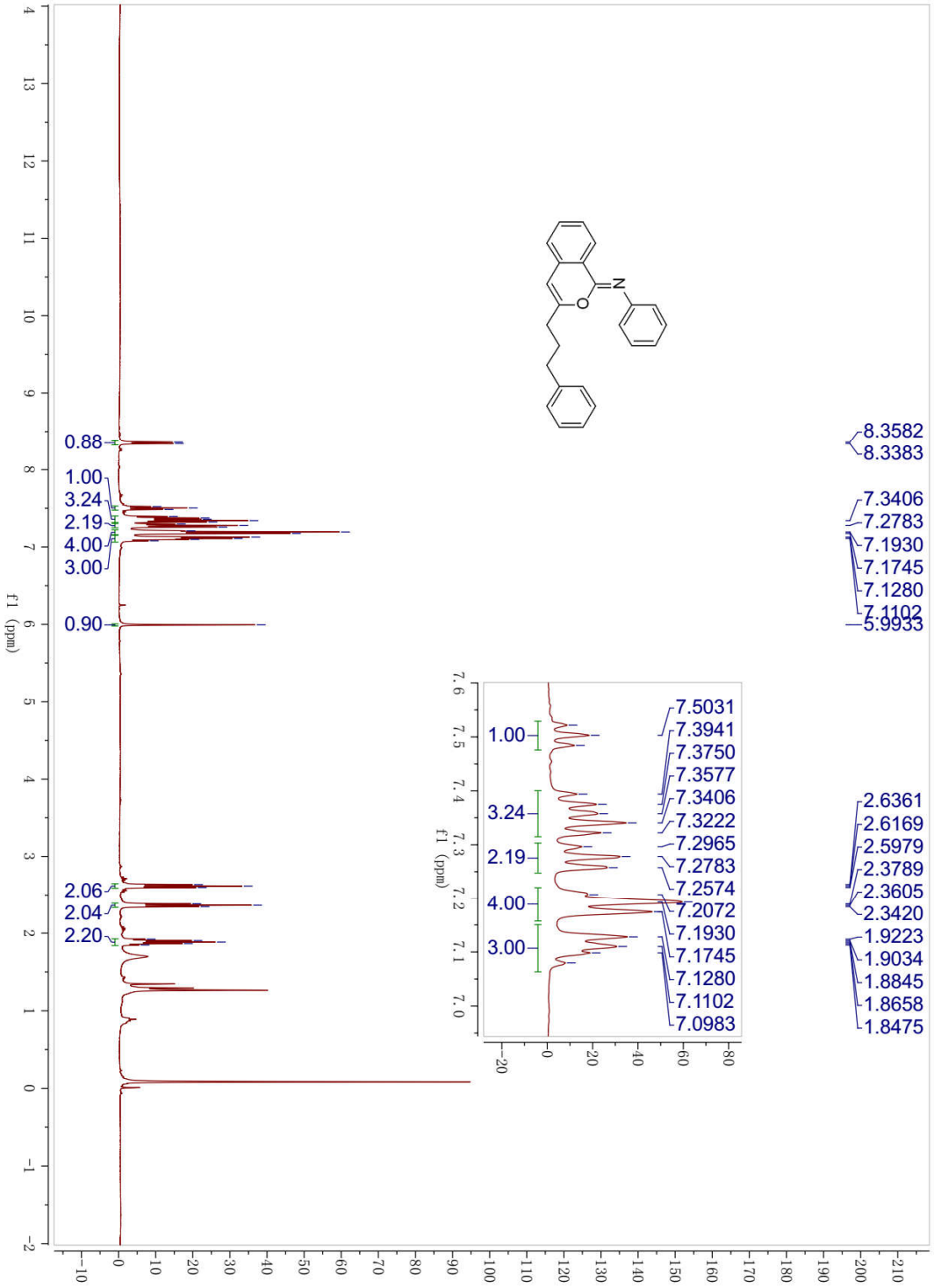
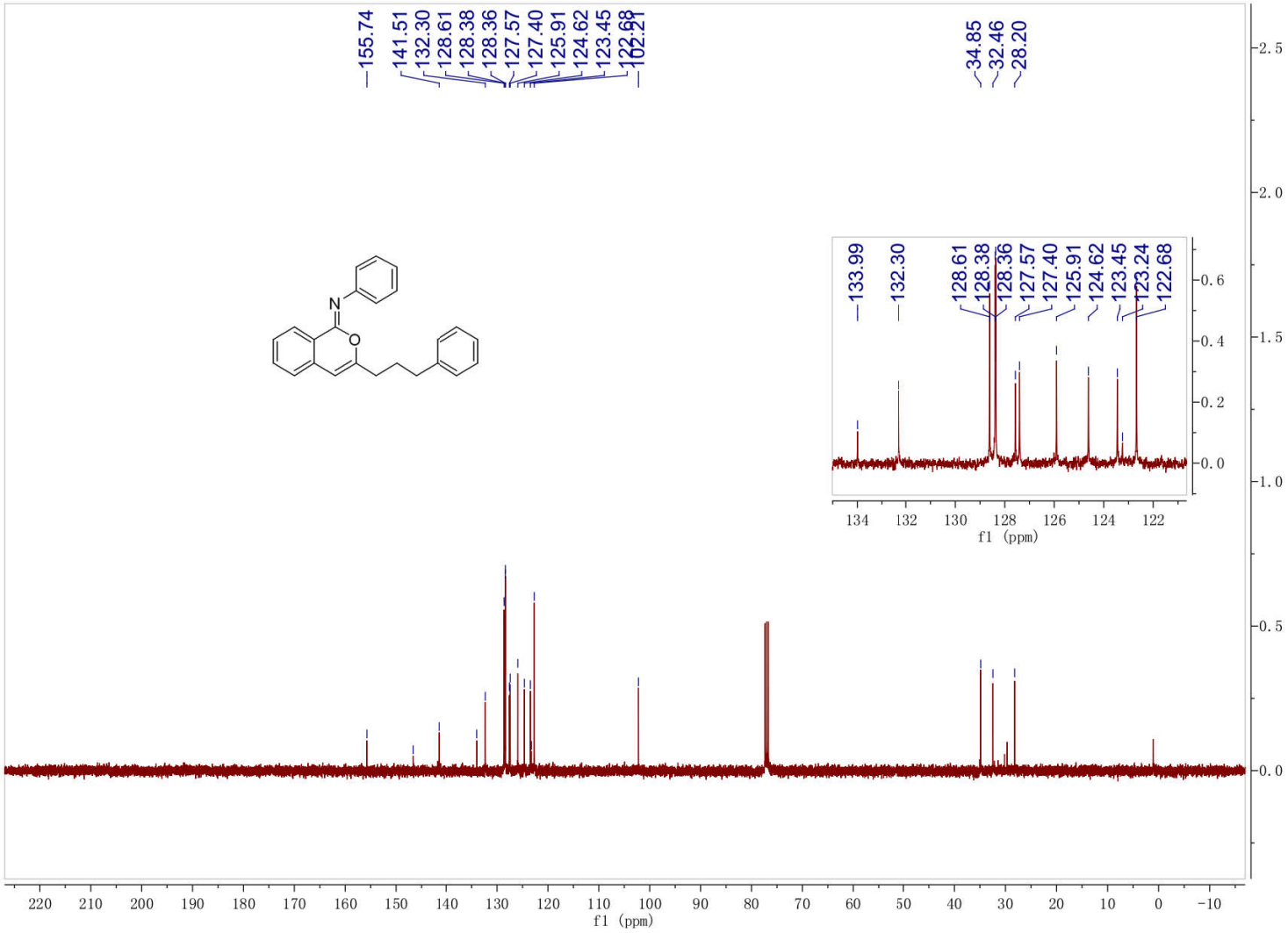
0.94
3.00
2.86
0.92
0.98
2.00
2.02
2.06
3.22
8.3696
8.3506
7.3694
7.3507
7.3320
7.2096
7.1926
7.1753
5.9938
2.3548
2.3367
2.3183
1.5690
1.5509
1.5323
1.5140
1.4949
1.3586
1.3406
1.3219
1.3035
0.9171
0.8990
0.8809
f1 (ppm)
0.94
3.00
2.86
0.92
7.5010
7.4826
7.3874
7.3694
7.3507
7.3320
7.2096
7.1926
7.1753
7.1135
7.0953
7.0775
f1 (ppm)

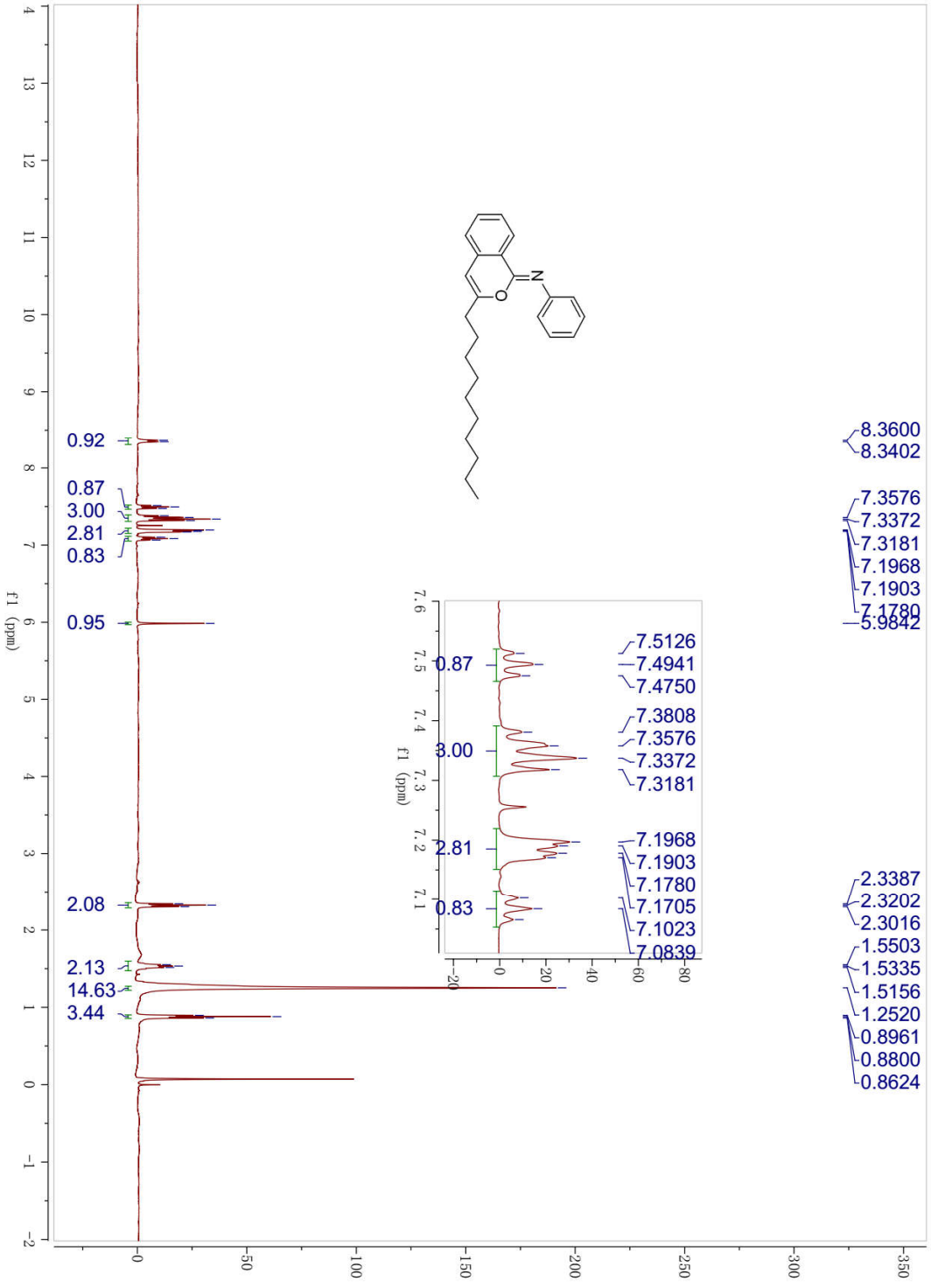

156.31
134.12
132.31
128.57
127.47
127.41
124.58
123.45
123.14
122.78
101.86
32.69
28.77
21.96
13.81
f1 (ppm)

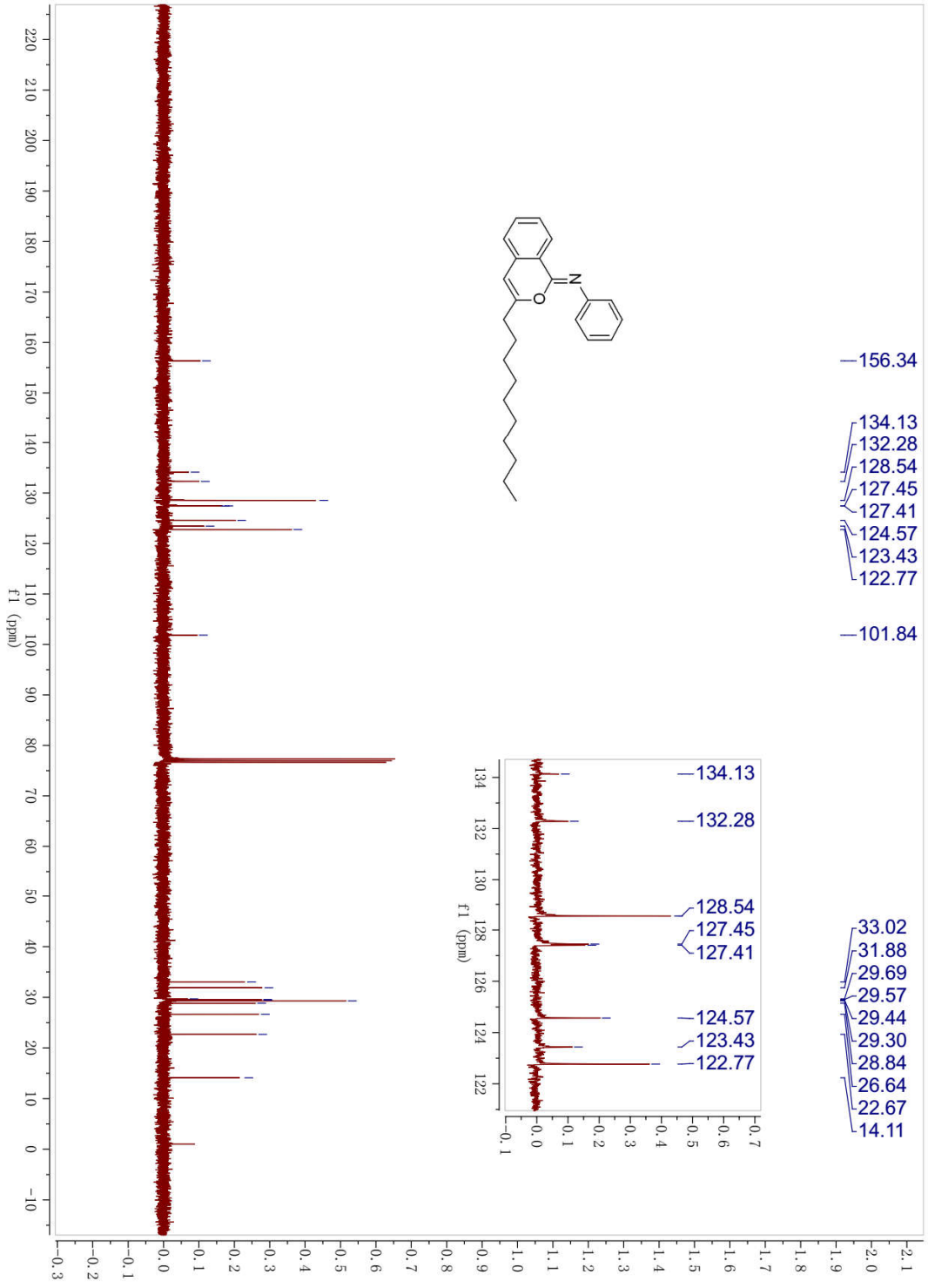

1.00
0.90
2.93
0.89
1.82
0.84
0.97
9.43
8.3571
8.3373
7.3738
7.3540
7.3344
7.1708
7.1522
7.1508
6.0324
1.1309
f1 (ppm)
7.5031
7.4869
7.4843
7.3934
7.3738
7.3540
7.3344
7.2307
7.2115
7.1708
7.1522
7.1508
7.1094
7.0910
7.0726

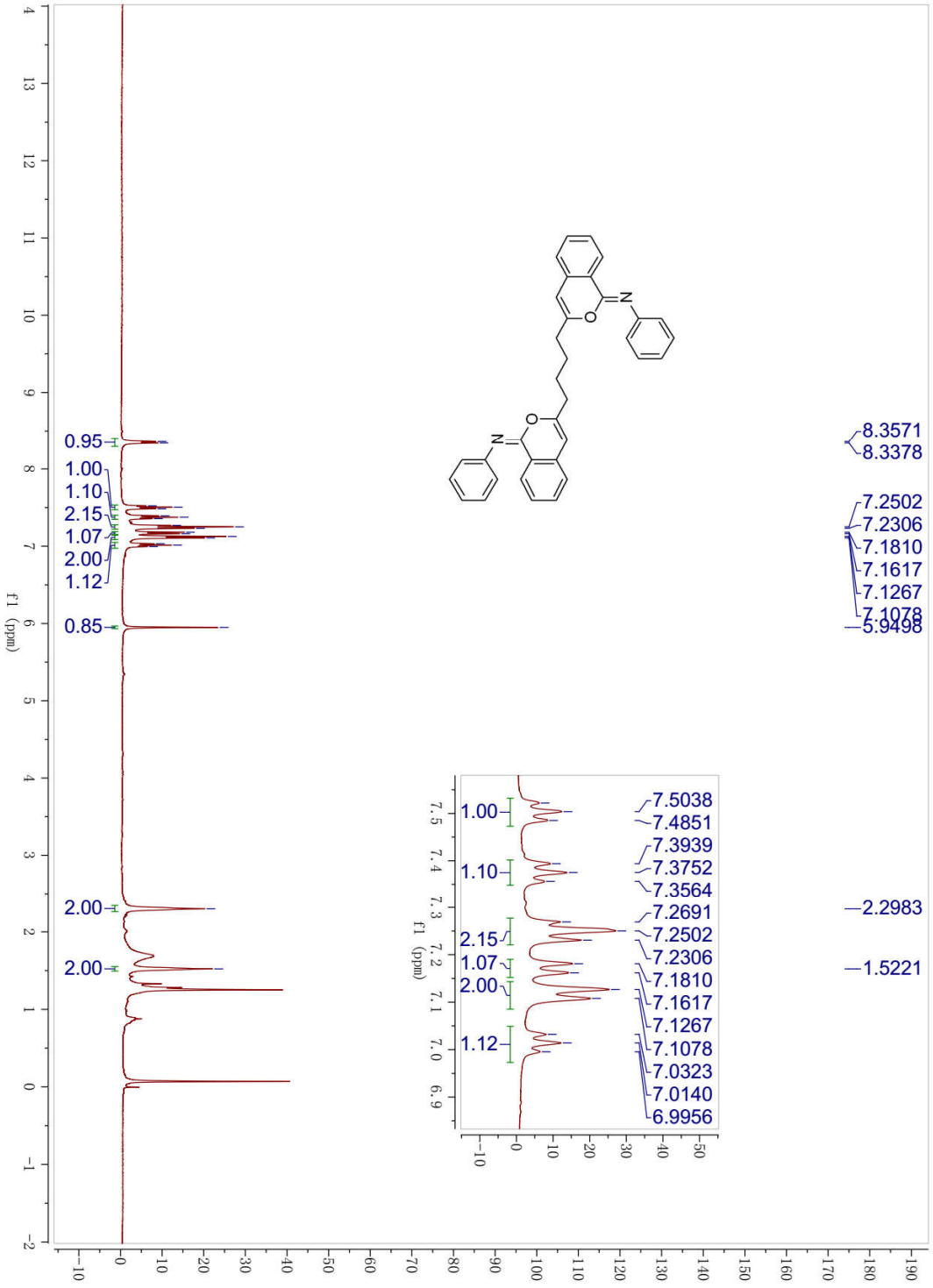

163.19
150.72
147.00
134.21
132.30
128.51
127.55
127.21
125.13
123.26
123.01
122.51
98.45
35.56
27.81
f1 (ppm)


0.88
1.00
3.24
2.19
4.00
3.00
0.90
2.06
2.04
2.20
8.3582
8.3383
7.3406
7.2783
7.1930
7.1745
7.1280
7.1102
5.9933
2.6361
2.6169
2.5979
2.3789
2.3605
2.3420
1.9223
1.9034
1.8845
1.8658
1.8475
f1 (ppm)
7.5031
7.3941
7.3750
7.3577
7.3406
7.3222
7.2965
7.2783
7.2574
7.2072
7.1930
7.1745
7.1280
7.1102
7.0983


155.74
141.51
132.30
128.61
128.38
128.36
127.57
127.40
125.91
124.62
123.45
122.68
102.21
34.85
32.46
28.20
N
O
133.99
132.30
128.61
128.38
128.36
127.57
127.40
125.91
124.62
123.45
123.24
122.68
f1 (ppm)
f1 (ppm)


0.92
0.87
3.00
2.81
0.83
0.95
2.08
2.13
14.63
3.44
8.3600
8.3402
7.3576
7.3372
7.3181
7.1968
7.1903
7.1780
5.9842
2.3387
2.3202
2.3016
1.5503
1.5335
1.5156
1.2520
0.8961
0.8800
0.8624
f1 (ppm)
0.87
3.00
2.81
0.83
7.5126
7.4941
7.4750
7.3808
7.3576
7.3372
7.3181
7.1968
7.1903
7.1780
7.1705
7.1023
7.0839
f1 (ppm)


156.34
134.13
132.28
128.54
127.45
127.41
124.57
123.43
122.77
101.84
33.02
31.88
29.69
29.57
29.44
29.30
28.84
26.64
22.67
14.11
f1 (ppm)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1.10
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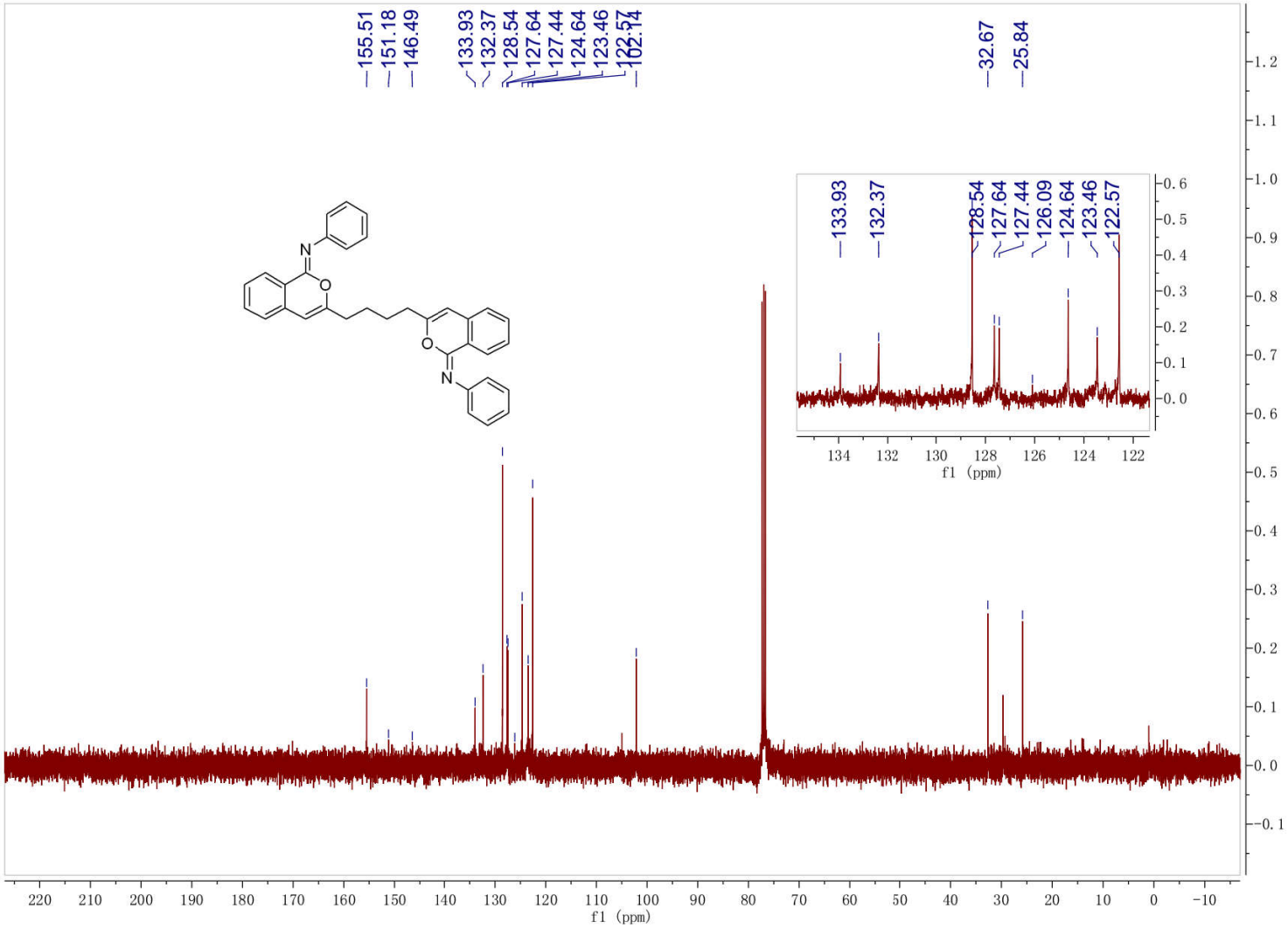
1.12
0.85
2.00
2.00
8.3571
8.3378
7.2502
7.2306
7.1810
7.1617
7.1267
7.1078
5.9498
2.2983
1.5221
1.00
1.10
2.15
1.07
2.00
1.12
7.5038
7.4851
7.3939
7.3752
7.3564
7.2691
7.2502
7.2306
7.1810
7.1617
7.1267
7.1078
7.0323
7.0140
6.9956
f1 (ppm)


155.51
151.18
146.49
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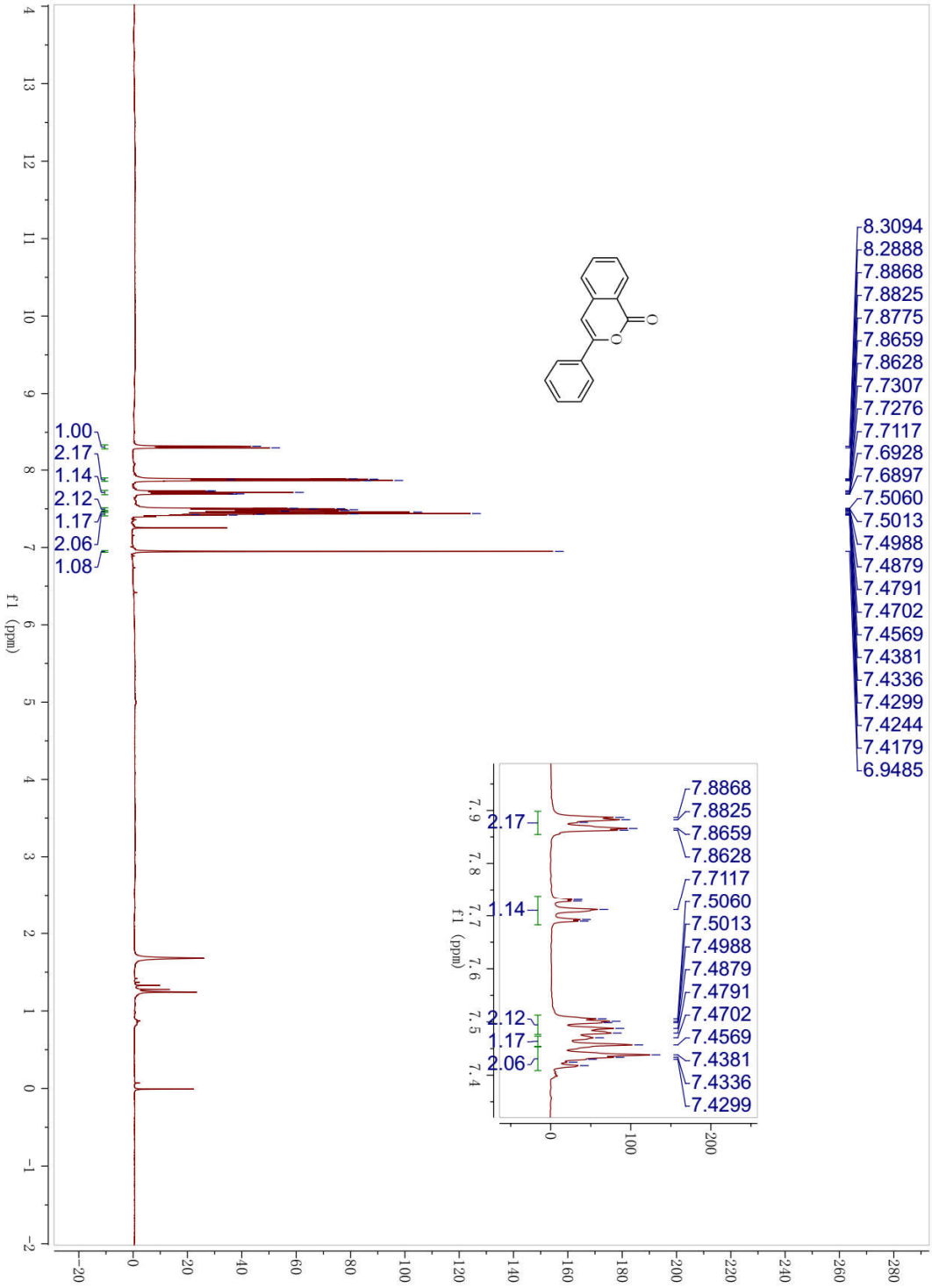
132.37
128.54
127.64
127.44
124.64
123.46
122.57
102.14
32.67
25.84
N
O
O
N
133.93
132.37
128.54
127.64
127.44
126.09
124.64
123.46
122.57
f1 (ppm)
f1 (ppm)

.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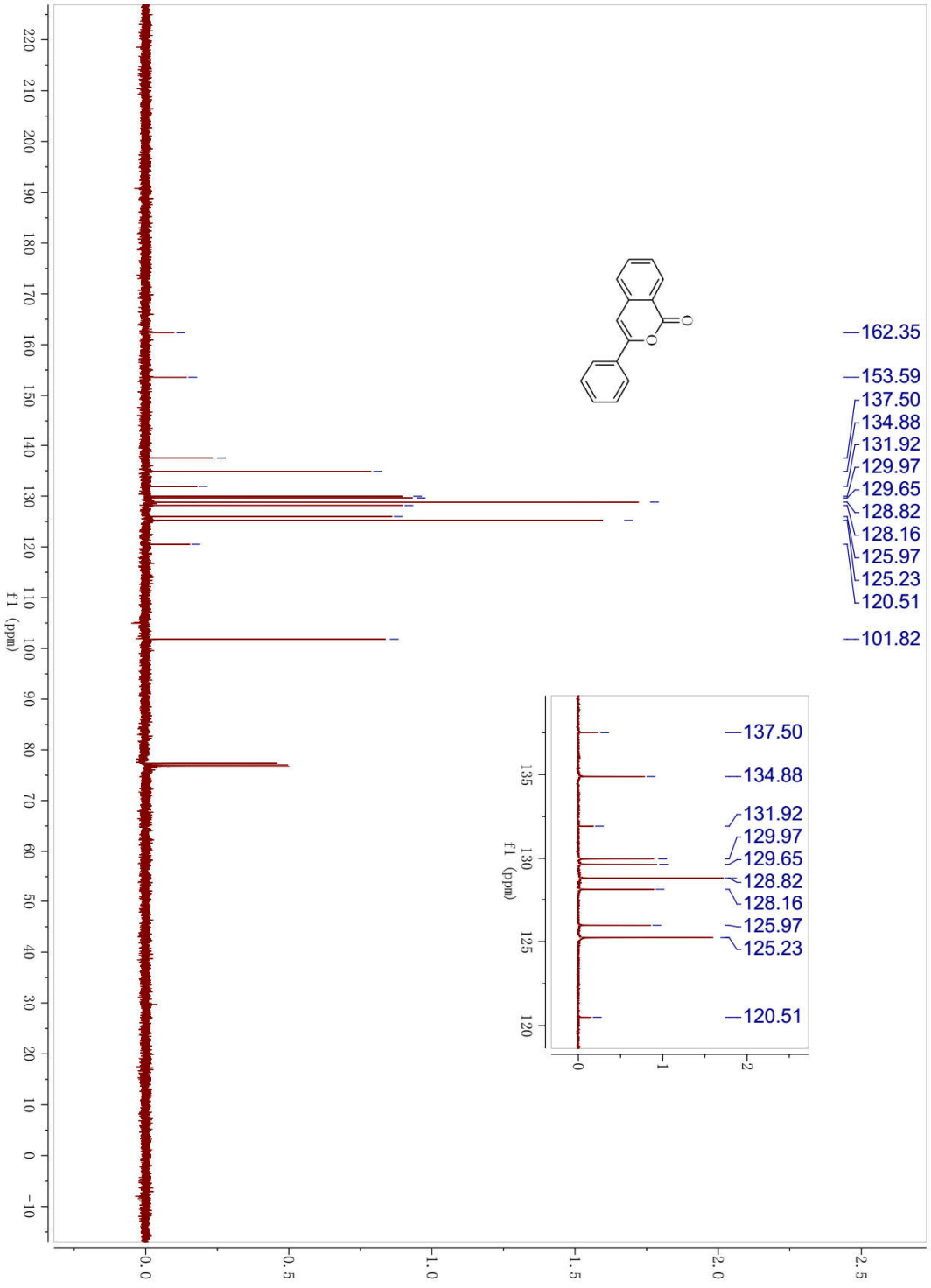
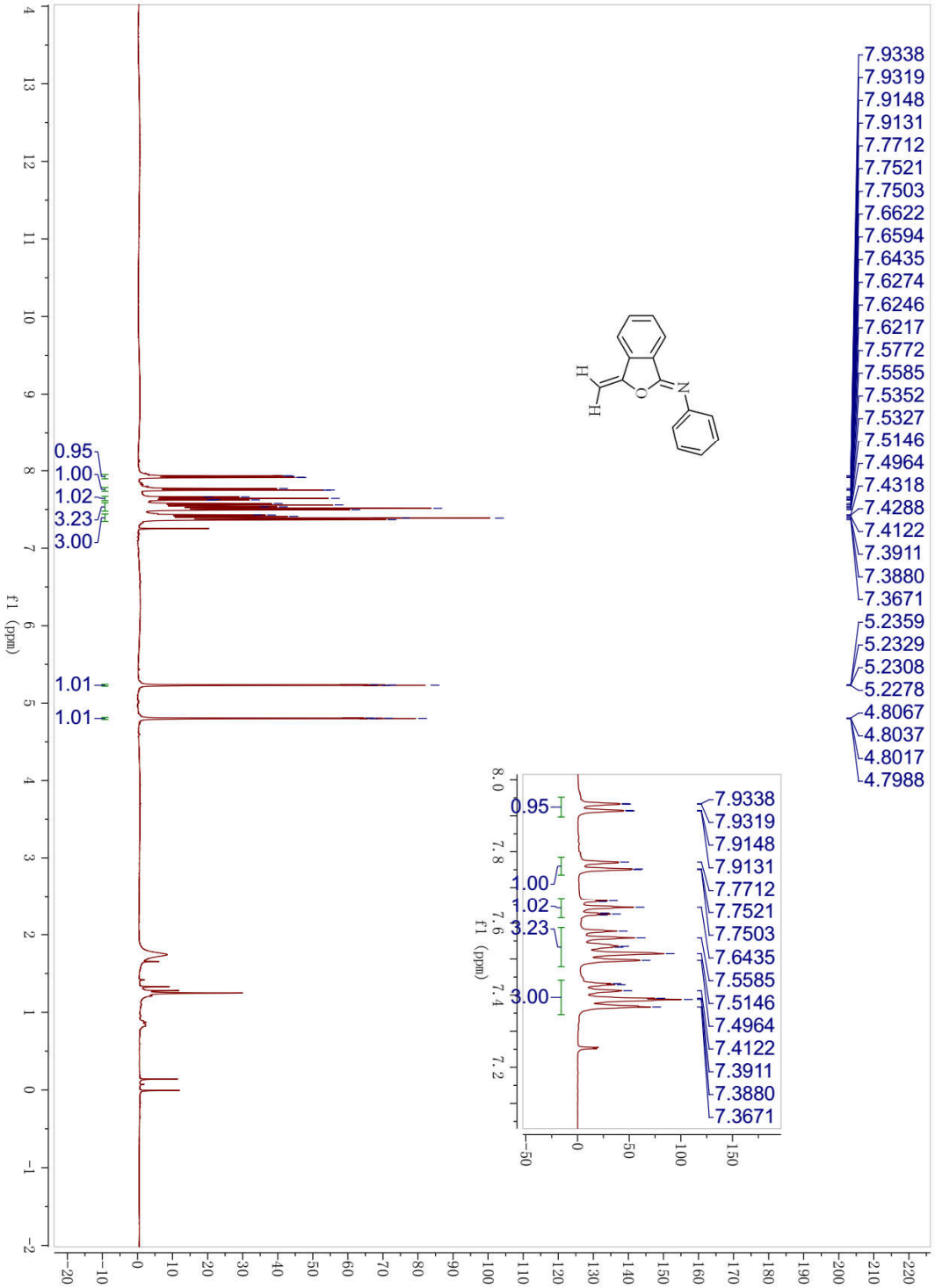
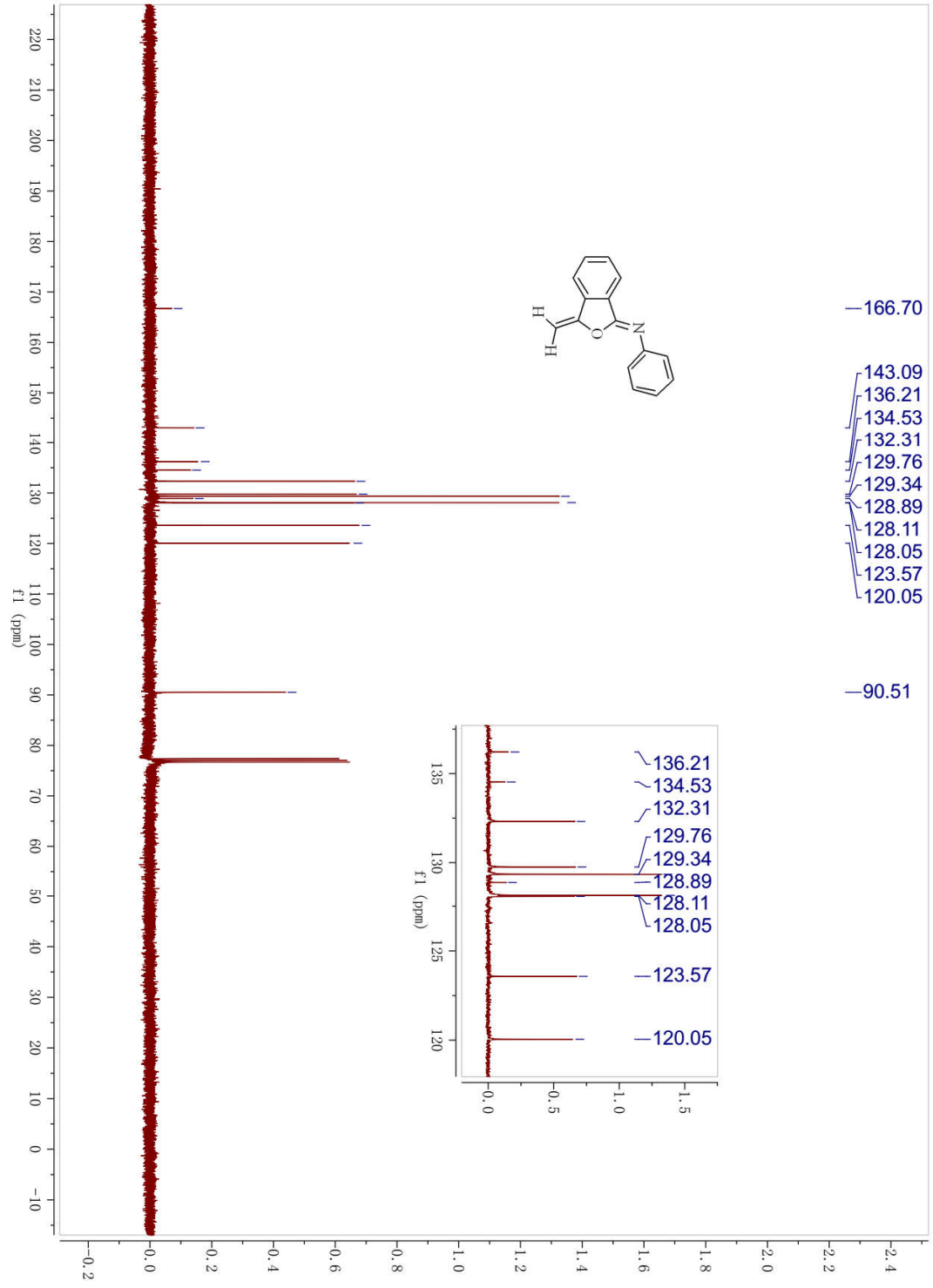
7.8868
7.8825
7.8775
7.8659
7.8628
7.7307
7.7276
7.7117
7.6928
7.6897
7.5060
7.5013
7.4988
7.4879
7.4791
7.4702
7.4569
7.4381
7.4336
7.4299
7.4244
7.4179
6.9485
1.00
2.17
1.14
2.12
1.17
2.06
1.08
f1 (ppm)
O
O
2.17
1.14
2.12
1.17
2.06
7.8868
7.8825
7.8659
7.8628
7.7117
7.5060
7.5013
7.4988
7.4879
7.4791
7.4702
7.4569
7.4381
7.4336
7.4299


162.35
153.59
137.50
134.88
131.92
129.97
129.65
128.82
128.16
125.97
125.23
120.51
101.82
f1 (ppm)


7.9338
7.9319
7.9148
7.9131
7.7712
7.7521
7.7503
7.6622
7.6594
7.6435
7.6274
7.6246
7.6217
7.5772
7.5585
7.5352
7.5327
7.5146
7.4964
7.4318
7.4288
7.4122
7.3911
7.3880
7.3671
5.2359
5.2329
5.2308
5.2278
4.8067
4.8037
4.8017
4.7988
0.95
1.00
1.02
3.23
3.00
1.01
1.01
f1 (ppm)
H
H
O
N


166.70
143.09
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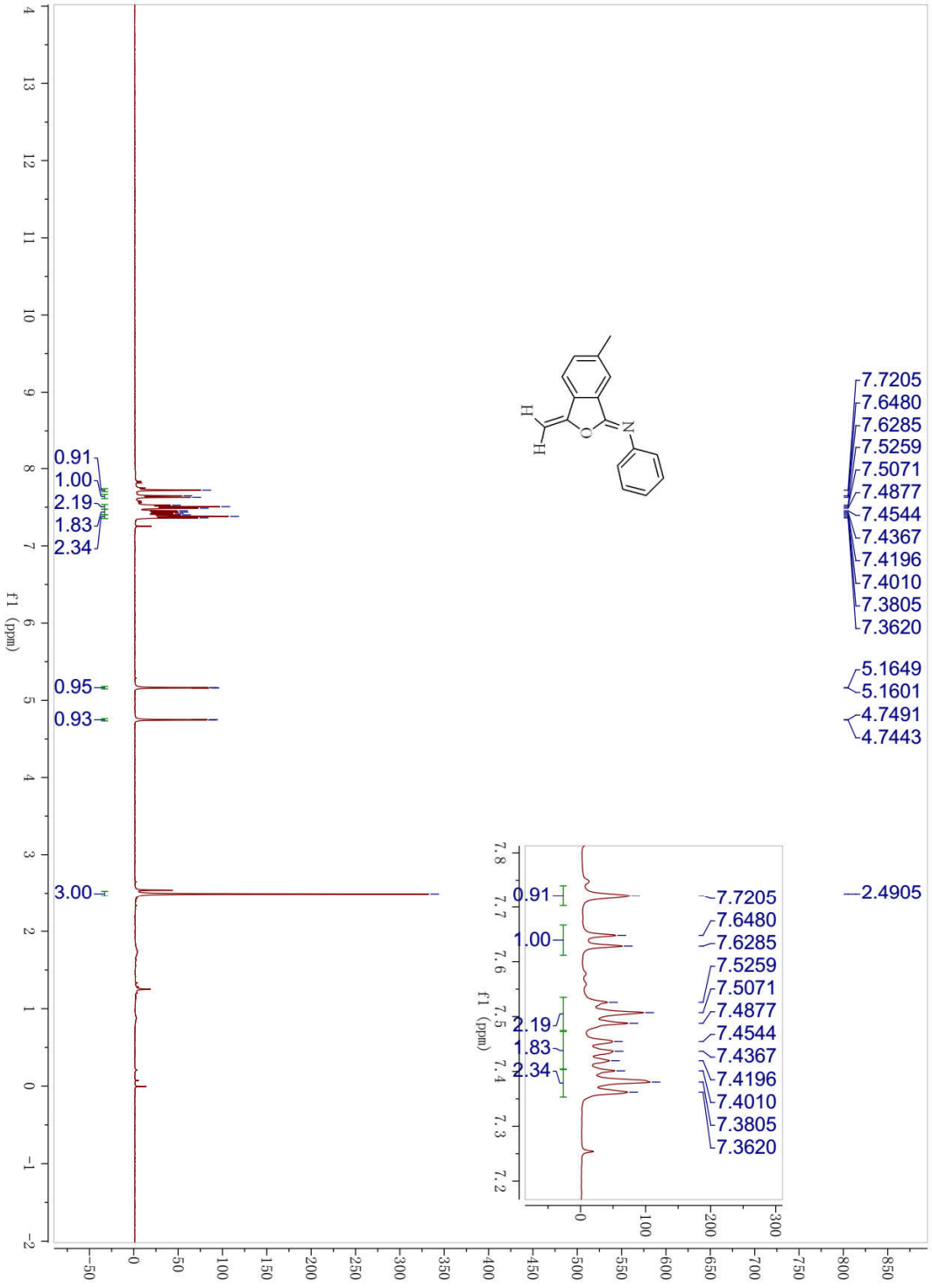
134.53
132.31
129.76
129.34
128.89
128.11
128.05
123.57
120.05
90.51
f1 (ppm)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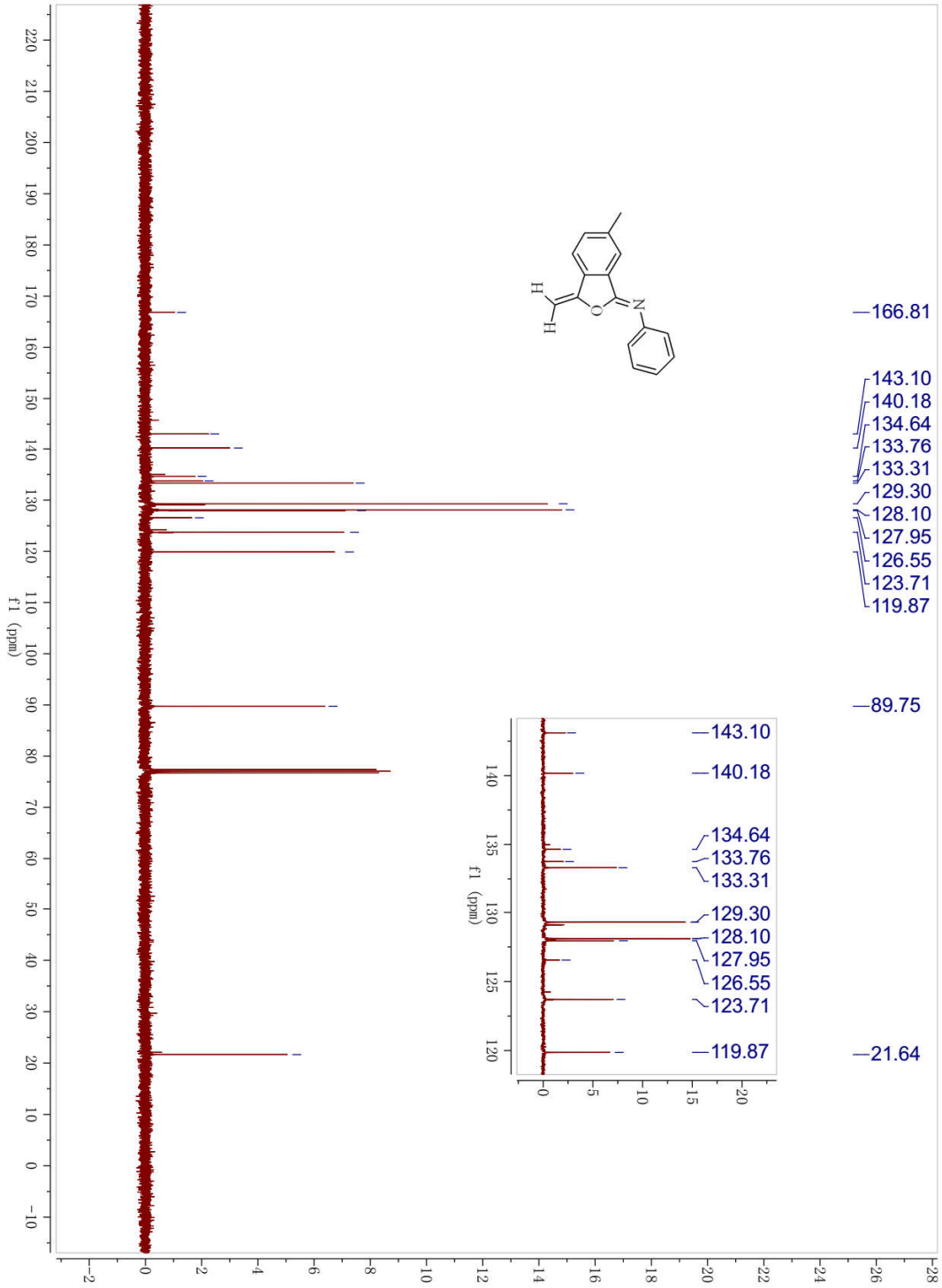
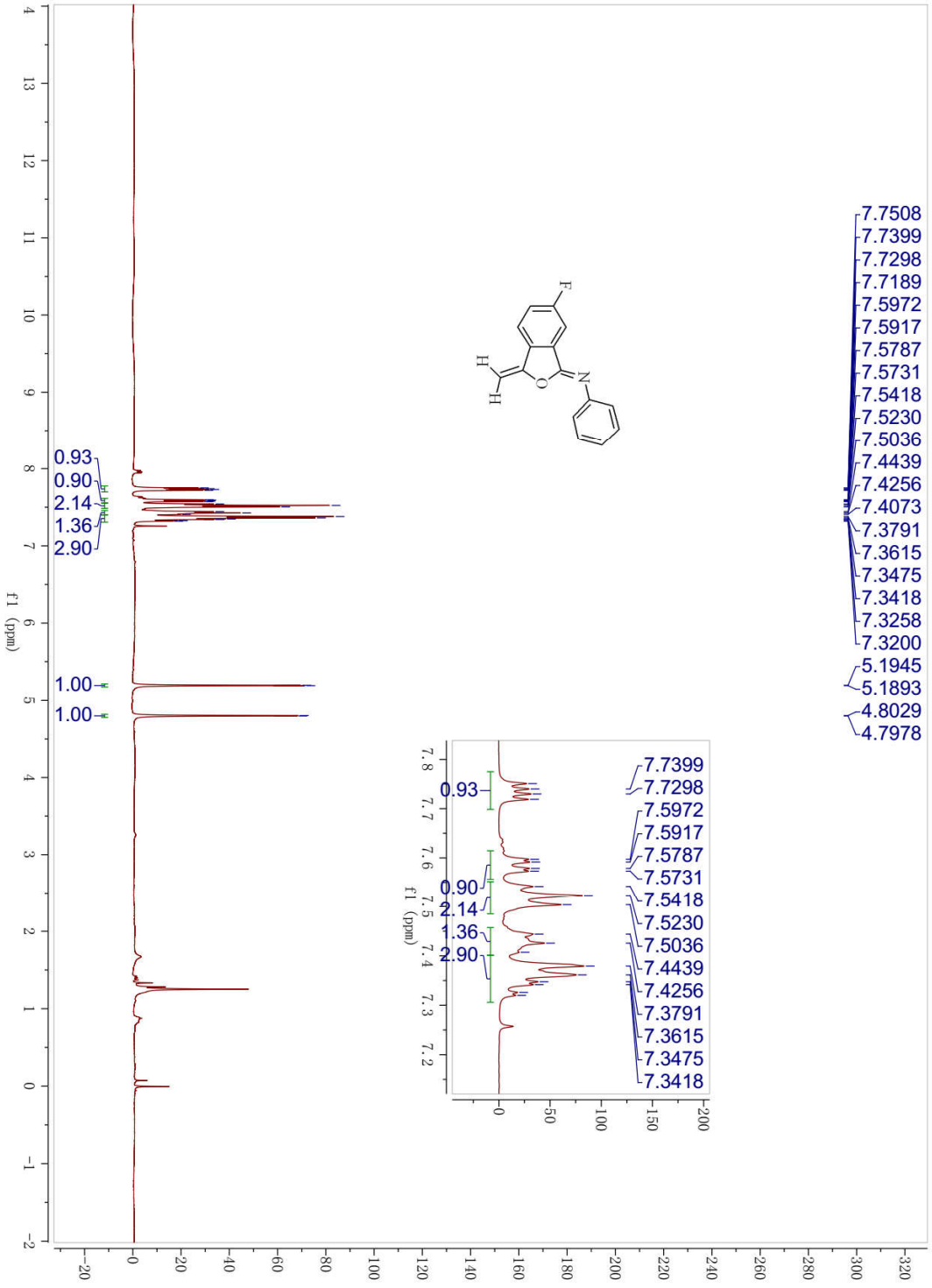
1.00
2.19
1.83
2.34
0.95
0.93
3.00
7.7205
7.6480
7.6285
7.5259
7.5071
7.4877
7.4544
7.4367
7.4196
7.4010
7.3805
7.3620
5.1649
5.1601
4.7491
4.7443
2.4905
f1 (ppm)


166.81
143.10
140.18
134.64
133.76
133.31
129.30
128.10
127.95
126.55
123.71
119.87
89.75
21.64
f1 (ppm)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7.7399
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7.7189
7.5972
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7.5787
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7.5418
7.5230
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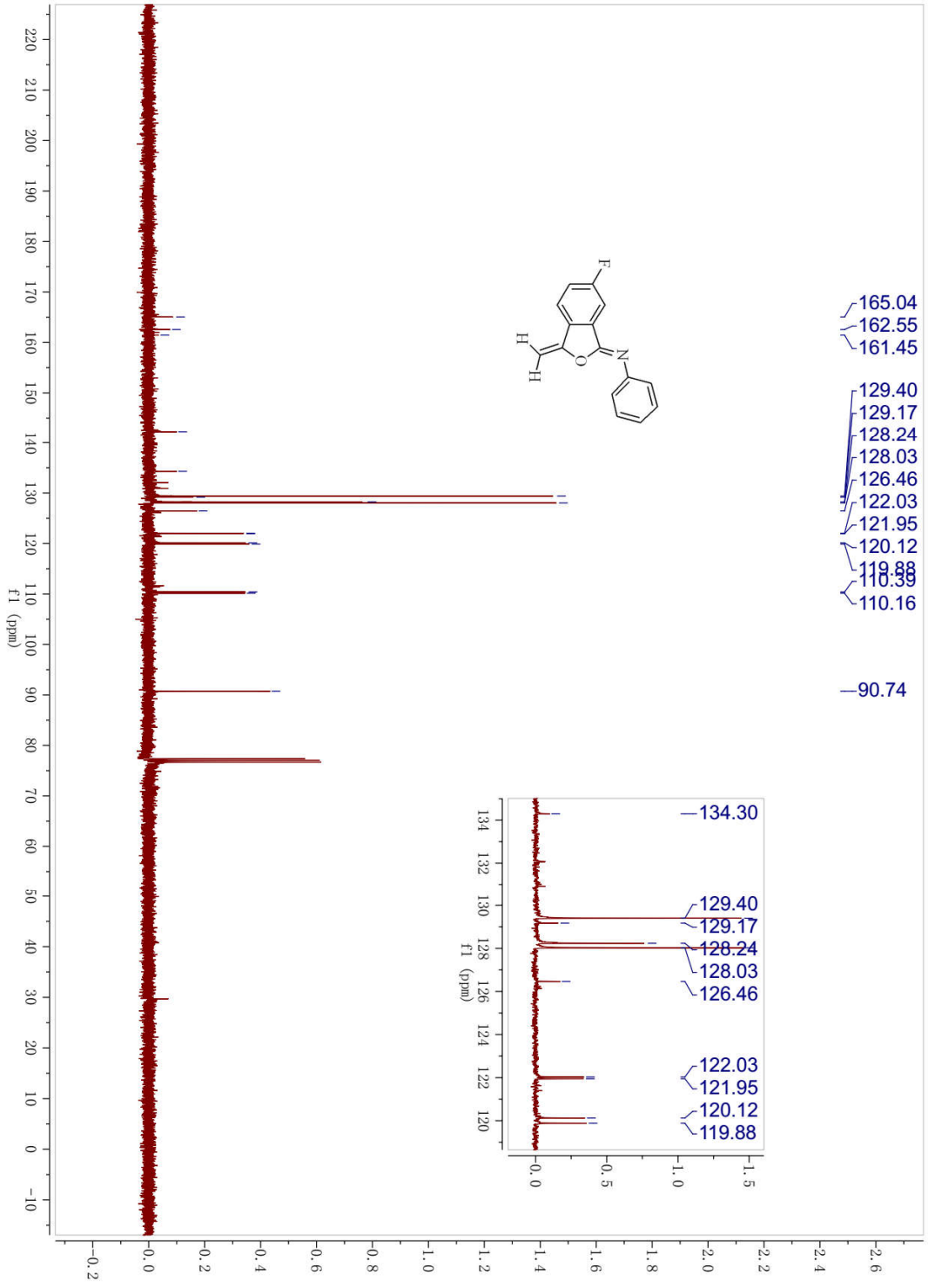
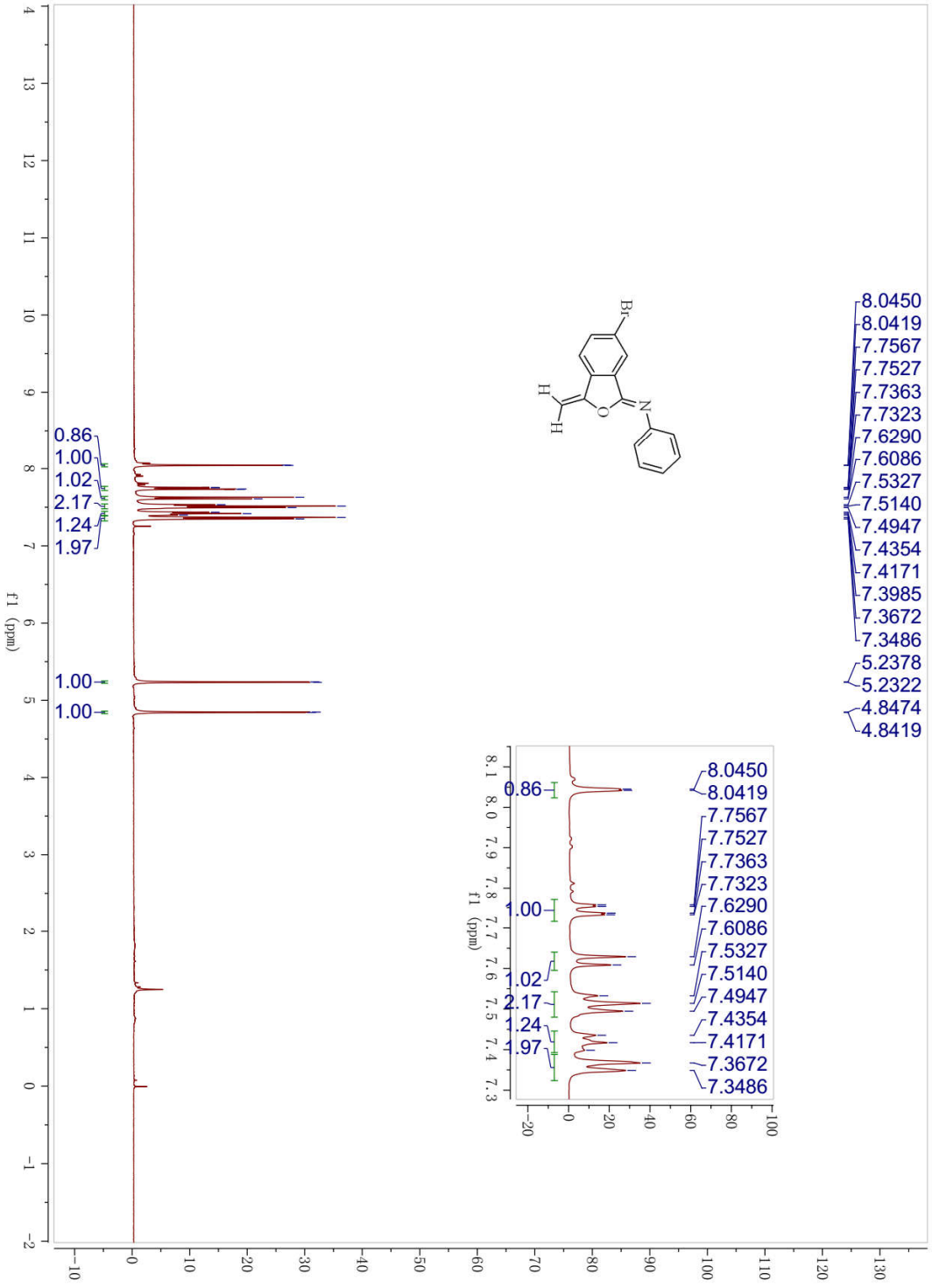
7.4439
7.4256
7.4073
7.3791
7.3615
7.3475
7.3418
7.3258
7.3200
5.1945
5.1893
4.8029
4.7978
0.93
0.90
2.14
1.36
2.90
1.00
1.00
F
H
H
O
N
f1 (ppm)


165.04
162.55
161.45
129.40
129.17
128.24
128.03
126.46
122.03
121.95
120.12
119.88
110.39
110.16
90.74
134.30
129.40
129.17
128.24
128.03
126.46
122.03
121.95
120.12
119.88
f1 (ppm)


f1 (ppm)
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1.24
1.97
1.00
1.00
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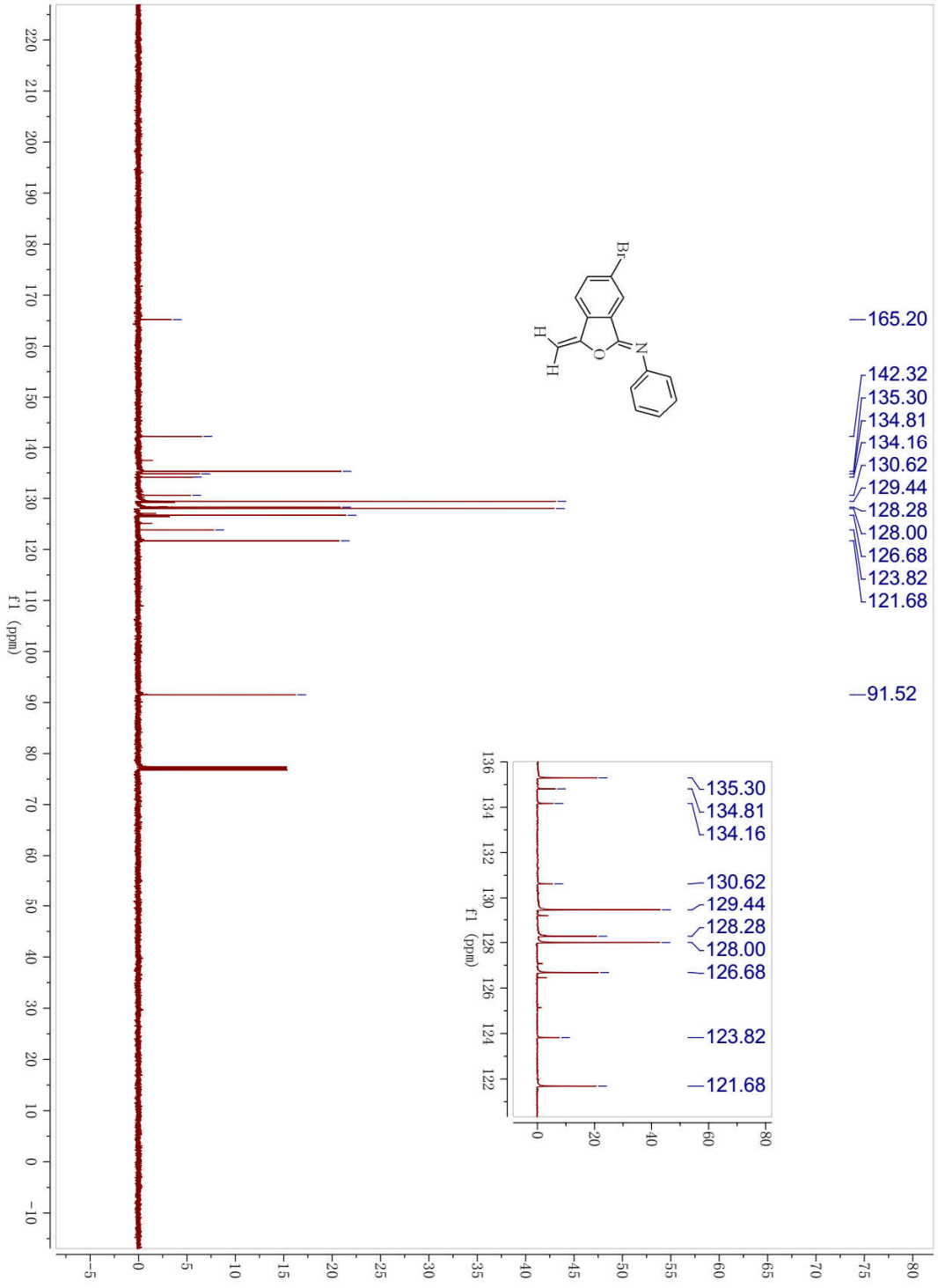
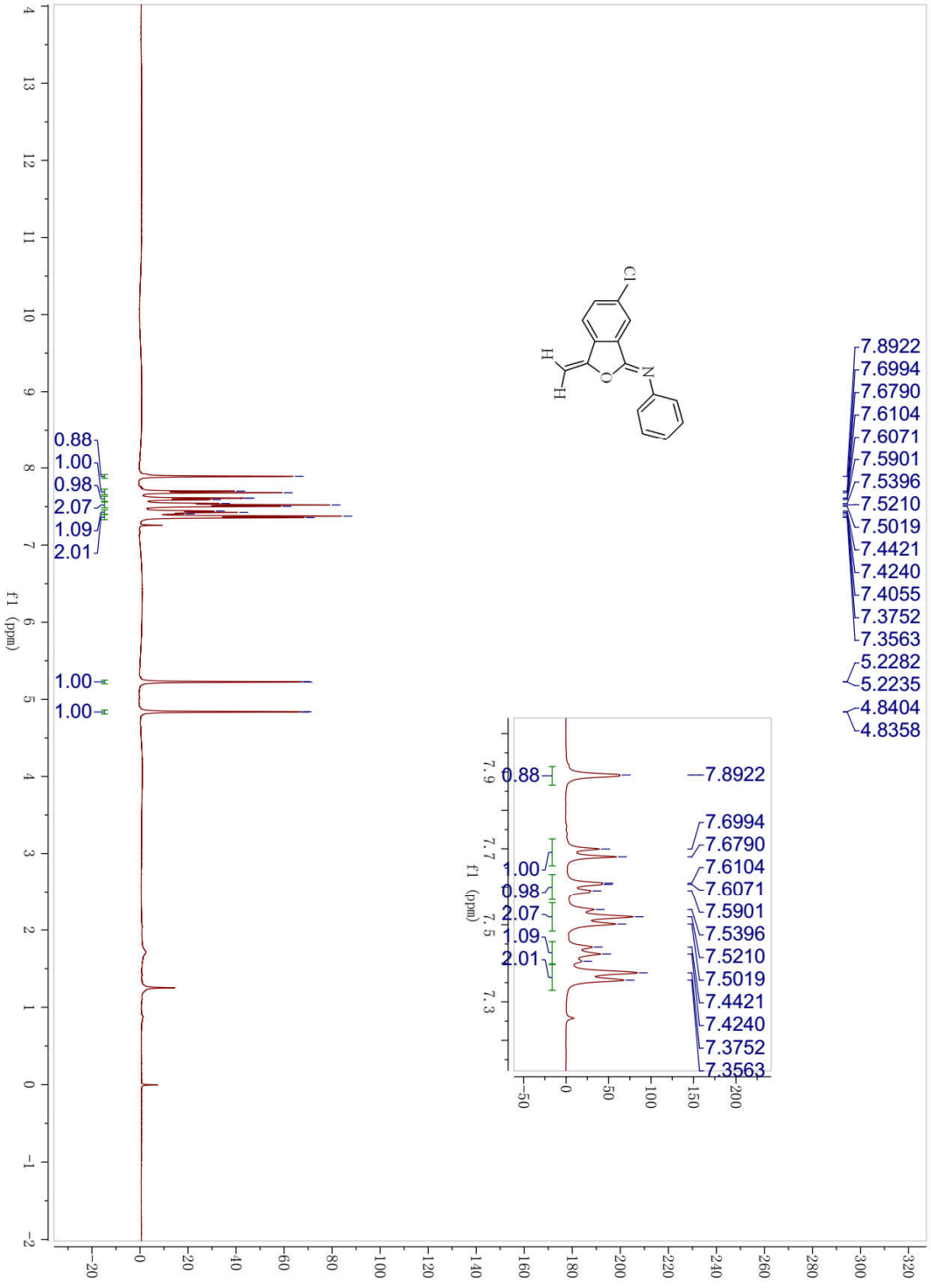
8.0419
7.7567
7.7527
7.7363
7.7323
7.6290
7.6086
7.5327
7.5140
7.4947
7.4354
7.4171
7.3985
7.3672
7.3486
5.2378
5.2322
4.8474
4.8419
Br
H
H
O
N
f1 (ppm)


Br
H
H
O
N
165.20
142.32
135.30
134.81
134.16
130.62
129.44
128.28
128.00
126.68
123.82
121.68
91.52
f1 (ppm)


Cl
H
H
O
N
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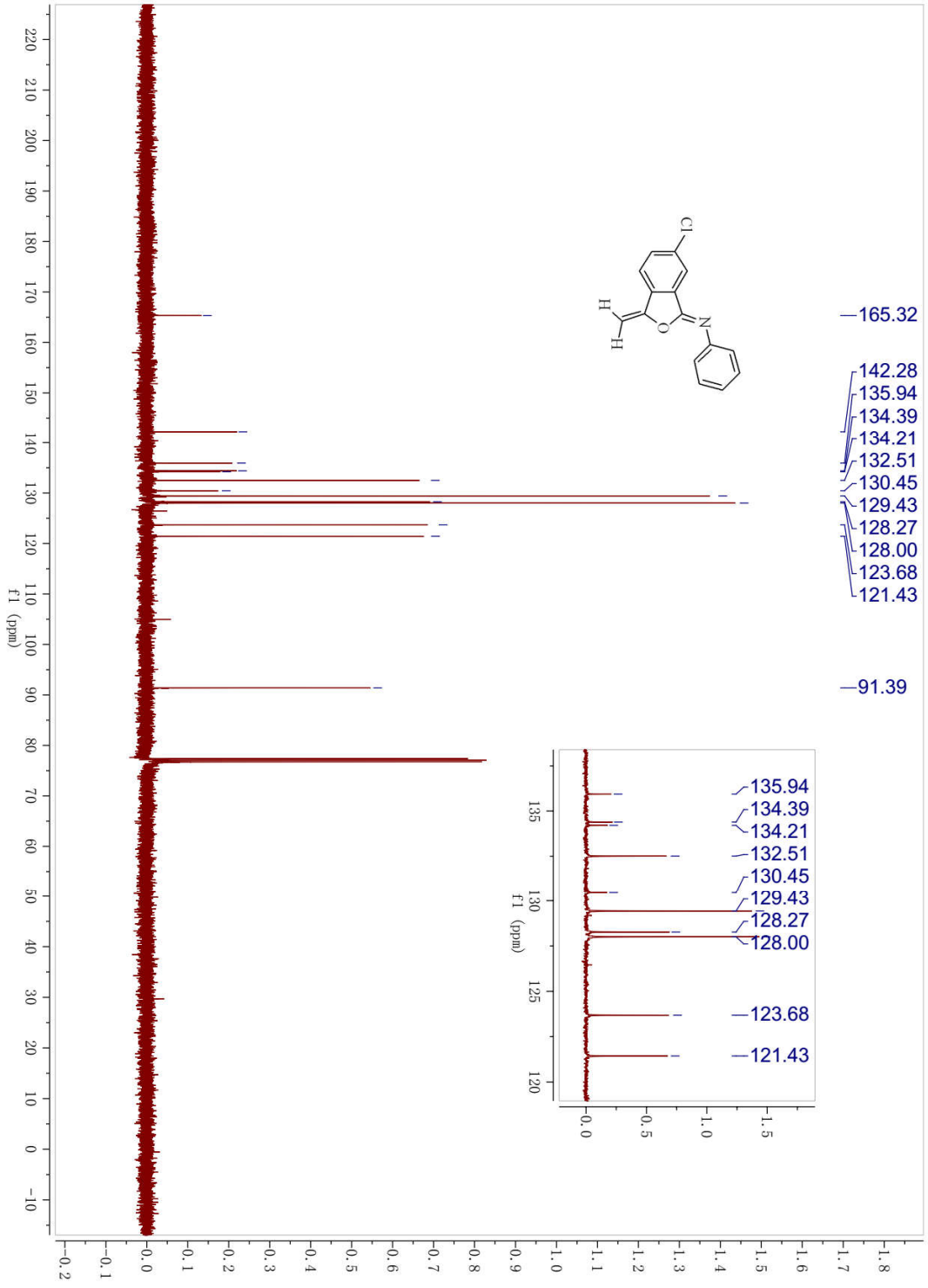
7.6994
7.6790
7.6104
7.6071
7.5901
7.5396
7.5210
7.5019
7.4421
7.4240
7.4055
7.3752
7.3563
5.2282
5.2235
4.8404
4.8358
0.88
1.00
0.98
2.07
1.09
2.01
1.00
1.00
f1 (ppm)


Cl
H
H
O
N
165.32
142.28
135.94
134.39
134.21
132.51
130.45
129.43
128.27
128.00
123.68
121.43
91.39
f1 (ppm)