Supporting Information

Direct oxidation of bromo-derived Fischer-Borsche oxo-ring using molecular iodine with combined experimental and computational study

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General Information

The NMR experiments were performed with 300 MHz, 400 MHz and 500 MHz spectrometer, and chemical shifts are expressed in ppm (δ) with TMS as an internal reference. *J* values are given in hertz. The ^{1}H and ^{13}C NMR spectra are referenced to the residual solvent signals (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C in $CDCl_3$, 2.50 ppm for ^{1}H and 39.9 ppm for ^{13}C in DMSO-d_6). TOF and quadruple mass analyzer types were used for the HRMS measurements. Column chromatography was performed on silica gel (100−200 mesh) in glass columns to purify the compounds and visualized with UV light (254 nm), PMA and DNP stain. Commercially available reagents and solvents were used without further purification and were purchased.

(a) General method for the preparation of substituted 1-oxo-2-Bromo-tetrahydrocarbazoles (2):

In a 100 mL round bottom flask, copper (II) bromide, $CuBr_2$ (2.17 mmol) was dissolved in ethylacetate (20 mL) and chloroform (20 mL). To this reaction mixture, 1-oxotetrahydrocarbazole (1.08 mmol) was added and stirred at 120 ºC for 6 h. The process of the reaction was monitored by TLC. After completion of the reaction, filter the reaction mixture in hot condition. The mother liquor diluted with ethylacetate, washed with H_2O, dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (ethylacetate:hexame: : 2:8).

1-oxo-2-bromo-tetrahydrocarbazole (2a): Yield: 194 mg (68 %); mp 139-142 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.78 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.29 (m, 2H), 7.10 (t, *J* = t 8.5 Hz, 1H), 4.94 (t, *J* = 13.2 Hz, 1H), 3.06 – 2.91 (m, 2H), 2.63 – 2.49 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): 189.3, 127.0, 126.9, 124.4, 124.2, 120.7, 120.1, 119.9, 112.6, 67.8, 47.5, 21.3; HRMS (ESI-qTOF) Calcd for $C_{12}H_{10}BrNO$ $[M+H]^+$, 263.9946, Found 263.0037.

1-oxo-2-bromo- 6-cyano-tetrahydrocarbazole (2b): Yield: 194 mg (70 %); mp 167-169 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.38 (s, 1H), 8.29 (s, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 4.94 (t, J = 13.2 Hz, 1H), 3.06 – 2.91 (m, 2H), 2.63 – 2.49 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): 183.6, 139.9, 130.0, 129.2, 128.0, 126.0, 124.5, 120.5, 114.0, 112.6, 67.8, 47.5, 21.3; HRMS (ESI) m/z = $[M + H]^+$ Calcd for $C_{13}H_9BrN_2O$ 288.9898, Found 288.9789.

1-oxo-2-bromo-tetrahydrocarbazole-6-methylcarboxylate (2c): Yield: 173 mg (65 %); mp 140-142 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.03 (s, 1H), 8.32 (s, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 4.34 (d, J = 7.5 Hz, 1H), 3.83 (s, 3H), 3.49-2.91 (m, 2H), 2.47-2.06 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): 187.6, 166.0, 147.9, 133.8, 129.7, 123.7, 122.1, 121.8, 113.6, 111.0, 53.9, 51.5, 34.2, 21.2; HRMS (ESI-qTOF) Calcd for $C_{14}H_{12}BrNO_3$ $[M+H]^+$, 322.0073, Found 322.0103.

1-oxo-2-bromo-6-chloro-tetrahydrocarbazole (2d): Yield: 184 mg (67 %); mp 182-185 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.76 (s, 1H), 7.67 (s, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 8.2 Hz, 1H), 4.84 (t, J = 13.1 Hz, 1H), 2.97-2.89 (m, 2H), 2.62 – 2.45 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): 190.1, 136.3, 132.0, 126.5, 126.1, 124.0, 120.1, 114.3, 112.6, 67.8, 47.5, 21.3; HRMS (ESI-qTOF) Calcd for $C_{12}H_9BrClNO$ $[M+H]^+$, 297.9556, Found 297.8769.

1-oxo-2-bromo-3-methyl-tetrahydrocarbazole (2e): Yield: 188 mg (67%); mp 131-134 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.32 (s, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.37 (t, J = 6.6 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 4.83 (d, J = 6.3 Hz, 1H), 3.20-2.46 (m, 3H), 1.15 (d, J = 4.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.9, 137.7, 130.4, 127.3, 125.4, 124.6, 120.1, 118.9, 112.1, 45.8, 32.1, 28.8, 29.6; HRMS (ESI-qTOF) Calcd for $C_{13}H_{12}BrNO$ $[M + H]^+$ 278.0102, Found 278.1058.

1-oxo-2-bromo-3,6-dimethyl-tetrahydrocarbazole (2f): Yield: 188 mg (68 %); decomposed > 173 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.41 (s, 1H), 7.36 (s, 1H), 7.26 (d, J = 8.1 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 4.81 (d, J = 1.8 Hz, 1H), 3.15 (s, 3H), 3.02-2.95 (m, 1H), 2.57 (d, J = 13.5 Hz, 2H), 1.08 (d, J = 5.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): 190.0, 136.6, 131.0, 128.3, 128.0, 126.9, 125.3, 120.3, 112.7, 58.8, 32.5, 29.1, 21.2, 21.0; HRMS (ESI-qTOF) Calcd for $C_{14}H_{14}BrNO[M+H]^+$ 292.0259, Found 292.0319.

1-oxo-2-bromo-3-methyl-6-cyano-tetrahydrocarbazole (2g): Yield: 193 mg (71 %); mp 197-199 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.38 (s, 1H), 8.29 (s, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 4.83 (d, J = 6.3 Hz, 1H), 3.20-2.46 (m, 3H), 1.15 (d, J = 4.2 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): 183.6, 139.9, 130.0, 129.2, 128.0, 126.0, 124.5, 120.5, 114.0, 102.2, 60.1, 36.1, 26.1, 19.1; HRMS (ESI-qTOF) Calcd for $C_{14}H_{11}BrN_2O$ [M + H]$^+$ 303.0055, Found 303.0199.

1-oxo-2-bromo-3-methyl-tetrahydrocarbazole-6-methylcarboxylate (2h): Yield: 189 mg (72 %); mp 286-288 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.41 (s, 1H), 8.41 (s, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 4.52 (d, J = 6.5 Hz, 1H), 3.93 (s, 3H), 3.43-2.42 (m, 3H); 1.31 (d, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 183.6, 167.0, 141.1, 129.2, 127.2, 124.8, 124.1, 121.9, 115.4, 112.5, 58.9, 51.5, 36.8, 25.8, 19.0: HRMS (ESI-qTOF) Calcd for $C_{15}H_{14}BrNO_3$[M + H]$^+$ 336.0157, Found 336.1218.

1-oxo-2-bromo-6-chloro-3-methyl- tetrahydrocarbazole (2i): Yield: 183 mg (68 %); mp 167-170 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.76 (s, 1H), 7.67 (s, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 4.84 (s, 1H), 2.97 (d, J = 15.5 Hz, 1H), 2.48-2.35 (m, 2H), 1.09 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): 190.1, 136.3, 132.0, 126.5, 126.1, 126.0, 124.0, 120.1, 114.3,

59.3, 32.2, 28.7, 20.9; HRMS (ESI-qTOF) Calcd for $C_{13}H_{11}BrClNO$ [M+H]+, 311.9713, Found 311.9002.

1-oxo-2,6-dibromo-3-methyl-tetradrocarbazole (2j): Yield: 175 mg (68 %); mp 186-188 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.59 (s, 1H), 7.66 (s, 1H), 7.03-6.92 (m, 2H), 4.87 (bs, 1H), 3.11-2.81 (m, 1H), 2.48-2.33 (m, 2H), 0.56 (d, J = 3.3 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): 190.3, 139.2, 132.6, 127.8, 127.4, 124.8, 120.0, 113.9, 101.7, 59.1, 32.1, 28.6, 20.9; HRMS (ESI) m/z =$[M+H]^+$ Calcd for $C_{13}H_{11}Br_2NO$ 357.9187, Found 357.8265.

1-oxo-2-bromo-3-methyl-6,8-dichloro-tetrahydrocarbazole (2k): Yield: 197 mg (76 %); mp 169-172 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.4 (s, 1H), 7.79 (s, 1H), 7.50 (s, 1H), 4.74 (bs, 1H), 3.03 – 2.94 (m, 2H), 2.49 – 2.39 (m, 1H) 1.17 (d, J = 3.3 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): 188.7, 139.5, 135.2, 133.1, 131.9, 130.9, 129.8, 124.8, 123.4, 65.4, 41.2, 30.6, 23.9; HRMS (ESI-qTOF) Calcd for $C_{13}H_{10}BrCl_2NO$ $[M + H]^+$ 345. 9323, Found 345.9405.

N-Propyl-1-oxo-2-bromo-3-methyl-tetrahydrocarbazole (2l): Yield:184 mg (69%) ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.19 (d, J = 2.8 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.72-7.65 (m, 1H), 7.58 (d, J = 8.8 Hz, 1H), 4.83 – 4.53 (m, 3H), 3.20 – 2.46 (m, 3H), 1.78 – 1.61 (m, 5H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 183.19, 180.81, 147.47, 137.53, 133.28, 129.43, 124.60, 117.51, 115.41, 46.3, 45.8, 32.1, 29.6, 28.8, 23.3, 15.6; HRMS (ESI-qTOF) Calcd for $C_{16}H_{18}BrNO$ $[M+H]^+$, 320.0572: found 320.1142.

N-Propyl-1-oxo-2-bromo-tetrahydrocarbazole (2m): Yield: 179 mg (66 %); mp 123-125 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.69 (d, J = 8.0 Hz, 1H), 7.43 – 7.29 (m, 2H), 7.10 (t, J = 8.5 Hz, 1H), 4.94 (m, 3H), 3.06 – 2.91 (m, 2H), 2.63 – 2.49 (m, 4H), 0.85 (t, J = 6.8 Hz, 3H);^{13}C NMR (75 MHz, DMSO-d_6): 189.3, 127.0, 126.9, 124.4, 124.2, 120.7, 120.1, 119.9, 112.6, 67.8,

46.3, 45.8, 32.1, 29.6, 23.3; HRMS (ESI-qTOF) Calcd for $C_{15}H_{16}BrNO$ $[M+H]^+$, 306.0415, Found 306.1105.

***N*-Benzyl-1-oxo-2-bromo-tetrahydrocarbazole (2n):** 168 mg (65%) ; mp 137-140 ºC; ^1H NMR (400 MHz, DMSO- d_6): δ 8.07 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.44-7.33 (m, 2H), 7.27-7.20 (m, 3H), 7.16 (d, J = 7.2 Hz, 2H), 5.86 (s, 2H), 4.94 (t, J = 13.2 Hz, 1H), 3.06 – 2.91 (m, 2H), 2.63 – 2.49 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 181.20, 173.14, 140.98, 140.22, 139.47, 139.27, 137.16, 136.71, 129.18, 129.09, 128.07, 127.93, 125.51, 48.15, 67.8, 47.5, 21.3; HRMS (ESI-qTOF) Calcd for $C_{19}H_{16}BrNO$ $[M+H]^+$, 354.0415: found 354.1015.

***N*-Methyl-1-oxo-2-bromo-tetrahydrocarbazole (2o):** Yield: 168 mg (60%); mp 111-115 ºC; ^1H NMR (300 MHz, DMSO-d_6): δ 7.69 (d, J = 8.0 Hz, 1H), 7.43 -7.29 (m, 2H), 7.10 (t, J = 8.5 Hz, 1H), 4.94 (t, J = 13.2 Hz, 1H), 3.06 - 2.91 (m, 2H), 2.63 - 2.49 (m, 2H); 1.82 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): 189.3, 127.0, 126.9, 124.4, 124.2, 120.7, 120.1, 119.9, 112.6, 67.8, 47.5, 25.6, 21.3; HRMS (ESI-qTOF) Calcd for $C_{13}H_{12}BrNO$ $[M+H]^+$, 278.0102, Found 278.1061.

(b) Representative procedure for the synthesis of Carbazolo-1,4-quinone by molecular iodine (3):

A mixture of molecular iodine (0.757 mmol) and substituted 2-bromo-1-oxo-tetrahydrocabazole **2** (0.757 mmol) in DMSO (5 mL) was stirred at 100 °C for appropriate time. The progress of reaction was monitored by thin layer chromatography. The reaction mixture was poured in ice cold saturated solution of sodium thiosulphate and kept at 0 °C for overnight. The solid product was separated out. The crude product was purified by column chromatography using *n*-hexane /ethyl acetate as eluent to afford carbazolo-1,4-quinone **(3).**

Carbazolo-1,4-quinone (3a)[1]: 86 mg (58%) as a red solid; mp: 138-140 °C; ^{1}H NMR (400 MHz, DMSO- d_6): δ 12.01 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.33 (t, J = 7.4 Hz, 1H), 6.26 (s, 2H); ^{13}C NMR (101 MHz, DMSO- d_6): δ 187.6, 180.8, 152.7, 139.4, 132.9, 127.4, 126.0, 124.8, 123.0, 122.6, 116.9, 112.7; HRMS (ESI-qTOF) Calcd for $C_{12}H_7NO_2$ $[M+H]^+$, 198.0477: found 198.1544.

6-cyno-carbazolo-1,4-quinone (3b): 100 mg (65%) as a red solid; mp: 197-199 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.13 (s, 1H), 8.26 (s, 1H), 7.59 (d, J = 8.6 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 6.45 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 191.3, 183.4, 139.6, 136.0, 133.3, 129.2, 128.4, 128.0, 125.5, 120.5, 114.5, 109.0, 102.3; HRMS (ESI-qTOF) Calcd for $C_{13}H_6N_2O_2$ $[M+H]^+$, 223.0429: found 223.0505.

6-Methylcarboxylate-carbazolo-1,4-quinone (3c): 107 mg (68%) as an orange solid; mp: 185-187 °C; mp: decomposed >245 °C; ^{1}H NMR (300 MHz, DMSO- d_6): δ 12.03 (s, 1H), 8.33 (s, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.7 Hz, 1H), 6.95 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 192.3, 183.0, 167.1, 141.2, 139.0, 138.9, 132.2, 129.5, 126.8, 125.1, 124.40, 121.7, 113.3, 52.3; HRMS (ESI-qTOF) Calcd for $C_{14}H_9NO_4$ $[M+H]^+$, 256.0532: found 256.0608.

6-Chloro-carbazolo-1,4-quinone (3d)[1a]: 94 mg (61%) as a red solid; mp: decomposed >245 °C; ^{1}H NMR (500 MHz, DMSO- d_6): δ 11.99 (s, 1H), 8.32 (s, 1H), 7.84 (d, J = 6.5 Hz, 1H), 7.43 (d, J = 9.0 Hz, 1H), 6.79 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 185.6, 180.2, 139.2, 137.3, 129.6, 127.2, 126.7, 125.0, 121.8, 121.0, 116.1, 115.0; HRMS (ESI-qTOF) Calcd for $C_{12}H_6ClNO_2$ $[M+H]^+$, 232.0087: found 232.0162.

Murrayaquinone (3e)[1, 2]: 138 mg (91%) as a red solid; mp: 236-239 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.80 (s, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.39-7.27 (m, 2H), 6.57 (s, 1H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 183.2, 180.2, 148.4, 136.8,

136.6, 134.6, 132.2, 130.2, 126.1, 116.5, 116.1, 114.6, 16.0; HRMS (ESI-qTOF) Calcd for $C_{13}H_9NO_2$ $[M+H]^+$, 212.0633: found 212.0711.

3,6-Dimethyl-carbazolo-1,4-quinone (3f)[1a, 2]: 120 mg (78%) as a red solid; mp: 228-230 ºC; ^{1}H NMR (300 MHz, DMSO- d_6): δ 12.54 (s, 1H), 7.67 (s, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.10 (d, J = 8.7 Hz, 1H), 6.53 (s, 1H), 1.84 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 180.1, 167.5, 149.9, 140.9, 139.2, 135.9, 133.6, 131.9, 128.9, 124.1, 121.1, 116.2, 21.5, 19.1; HRMS (ESI-qTOF) Calcd for $C_{14}H_{11}NO_2$ $[M+H]^+$, 226.0790: found 226.0864.

3-Methyl-6-cyno-carbazolo-1,4-quinone (3g): 137 mg (88%) as an orange solid; mp: 181-184 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.70 (s, 1H), 8.41(s, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 9.0 Hz, 1H), 6.40 (s, 1H), 2.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.0, 180.1, 148.6, 139.2, 137.7, 131.8, 128.2, 127.9, 123.5, 119.6, 116.2, 114.9, 106.6, 16.0; HRMS (ESI-qTOF) Calcd for $C_{14}H_8N_2O_2$ $[M+H]^+$, 237.0586: found 237.0664.

3-Methylcarboxylate-3-methyl-carbazolo-1,4-quinone (3h): 137 mg (86%) as an orange solid; mp: decomposed >229 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.02 (s, 1H), 8.55 (s, 1H), 7.84 (d, J = 10.2 Hz, 1H), 7.50 (d, J = 8.7 Hz, 1H), 6.56 (s, 1H), 3.79 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 183.2, 180.2, 166.6, 148.3, 140.0, 137.8, 132.0, 126.8, 125.1, 124.1, 123.3, 116.3, 114.3, 52.4, 15.8; HRMS (ESI-qTOF) Calcd for $C_{15}H_{11}NO_4$ $[M+H]^+$, 270.0688: found 270.0756.

6-Chloro-3-methyl-carbazolo-1,4-quinone (3i) [1a, 2]: 142 mg (91%) as a red solid; mp: decomposed >253 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.95 (s, 1H), 7.91 (s, 1H), 7.50 (d, J = 8.7 Hz, 1H), 7.35 (d, J = 8.7 Hz, 1H), 6.58 (s, 1H), 2.02 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 185.0, 174.1, 139.2, 135.8, 132.6, 127.8, 127.8, 127.4, 124.8, 120.0, 117.0, 113.9, 20.9; HRMS (ESI-qTOF) Calcd for $C_{13}H_8ClNO_2$ $[M+H]^+$, 246.0244: found 246.0320.

6-Bromo-3-methyl-carbazolo-1,4-quinone (3j) [1a]: 146 mg (90%) as a red solid; mp: 253-255 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.83 (s, 1H), 8.06 (s, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.32 (d, J = 7.8 Hz, 1H), 6.61 (s, 1H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 184.4, 174.2, 140.2, 136.3, 132.3, 130.3, 128.6, 126.2, 124.7, 123.9, 121.0, 112.7, 18.6; HRMS (ESI-qTOF) Calcd for $C_{13}H_8BrNO_2$ $[M+H]^+$, 289.9738: found 289.9817.

6,8-Dichlro-3-methyl-carbazolo-1,4-quinone (3k): 143 mg (89%) as a red solid; mp 240-244 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.49 (s, 1H), 7.96 (s, 1H), 7.60 (s, 1H), 6.69 (s, 1H), 2.07 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 185.1, 179.9, 148.2, 143.8, 138.2, 134.8, 132.6, 130.7, 128.7, 126.0, 120.5, 119.9, 18.9; HRMS (ESI-qTOF) Calcd for $C_{13}H_7Cl_2NO_2$ $[M+H]^+$, 279.9854: found 279.9930.

9-Propyl-3-methyl-carbazolo-1,4-quinone (3l): 109 mg (69%) as a red solid; mp: 156-160°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.19 (d, J = 2.8 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.72-7.65 (m, 1H), 7.58 (d, J = 8.8 Hz, 1H), 6.62 (d, J = 1.6 Hz, 1H), 4.53 (t, J_1 = 6.8 Hz, J_2 = 7.2 Hz, 2H), 2.05 (d, J = 1.6 Hz, 3H), 1.78-1.71 (m, 2H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 183.1, 180.8, 147.4, 137.5, 134.5, 133.2, 129.4, 124.6, 124.1, 117.5, 115.4, 115.1, 46.3, 23.3, 15.6, 11.3; ^{13}C NMR (DEPT) (101 MHz, DMSO- d_6): δ 134.5, 133.2, 129.4, 124.1, 115.1, 46.3, 23.3, 15.6, 11.3; HRMS (ESI-qTOF) Calcd for $C_{16}H_{15}NO_2$ $[M+H]^+$, 254.1103: found 254.1172.

9-Propyl-carbazolo-1,4-quinone (3m): 89 mg (57%) as a red solid; mp: decomposed >235 ºC; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.09 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.45 (t, J_1 = 7.2 Hz, J_2 = 8.4 Hz, 1H), 7.33 (t, J_1 = 7.2 Hz, J_2 = 7.6 Hz, 1H), 6.25 (s, 2H), 4.52 (t, J_1 = 7.2 Hz, J_2 = 7.2 Hz, 2H), 1.79-1.70 (m, 2H), 0.87 (t, J_1 = 7.6 Hz, J_2 = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 180.8, 177.1, 152.7, 139.4, 132.9, 127.4, 126.0, 124.8, 123.0, 122.6, 116.9, 112.7,

46.3, 23.4, 11.4.; ^{13}C NMR (DEPT) (101 MHz, DMSO- d_6): δ 127.4, 126.0, 124.8, 123.0, 122.6, 112.7, 46.3, 23.4, 11.4: HRMS (ESI-qTOF) Calcd for $C_{15}H_{13}NO_2$ $[M+H]^+$, 240.0946: found 240.1022.

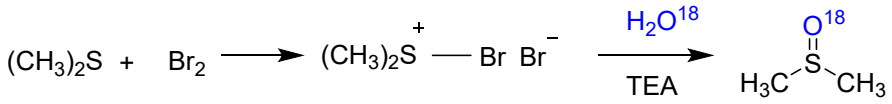
9-Benzyl-carbazolo-1,4-quinone (3n)[3]: 102 mg (61%) as a red solid; decomposed >247 ºC ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.07 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.68, 7.44-7.33 (m, 3H), 7.27-7.20 (m, 4H), 7.16 (d, J = 7.2 Hz, 2H), 5.86 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 181.2, 173.1, 140.9, 140.2, 139.4, 139.2, 137.1, 136.7, 129.1, 129.0, 128.0, 127.9, 127.2, 125.5, 122.6, 120.7, 119.1, 113.1, 48.1; ^{13}C NMR (DEPT) (101 MHz, DMSO-d_6): δ 139.4, 139.2, 129.1, 129.0, 128.0, 127.9, 127.2, 125.5, 122.6, 120.7, 113.1, 48.1; HRMS (ESI-qTOF) Calcd for $C_{19}H_{13}NO_2$ $[M+H]^+$, 288.0946: found 288.1023.

9-Methyl-carbazolo-1,4-quinone (3o)[3]: 92 mg (61%) as a red solid; mp: 121-125°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 7.5 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.50 – 7.42 (m, 1H), 6.30 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.5, 181.3, 145.0, 136.0, 132.7, 130.9, 128.4, 127.9, 127.0, 125.6, 124.9, 117.0, 21.9; HRMS (ESI-qTOF) Calcd for $C_{13}H_9NO_2$ $[M+H]^+$, 212.0633: found 212.0710.

(b) Isotope Labeling Experiment:

Method for preparation of ^{18}O labeled DMSO

The [^{18}O]-DMSO was prepared according to the literature[4]

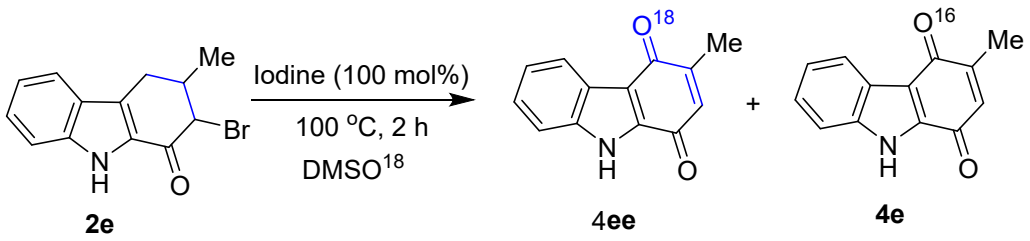


Step I: Bromine (1.8 mL, 33 mmoles) was added dropwise over 40 min to a vigorously stirred, ice-cooled solution of dimethyl sulfide (2.43 mL, 33 mmoles) in carbon tetrachloride (30 mL).

The resulting yellowish precipitate were removed by filtration and washed with cold chloroform to remove unreacted bromine. After removing the solvent on rotator evaporator under reduced pressure at room temperature, 71% (5.2 g) of yellow solid product was obtained. (***Avoid*** *heating dimethylsulfur dibromide, it may cause brominating side products of dimethyl sulfide*).

Step II : Solid dimethylsulfur dibromide (5.0 g, 22.5 mmoles) was added portion wise over 15 min to a vigorously stirred solution of triethylamine (6.3 ml, 45 mmoles, freshly distilled from sodium hydroxide) and ^{18}O-labeled water (97 atom % ^{18}O) (0.20 ml, 11 mmoles) in 15 ml of tetrahydrofuran (freshly distilled from sodium metal). The temperature of the reaction was maintained below 50°C by occasional cooling in ice. The precipitate of triethylamine hydrobromide was removed by centrifugation and washed twice with ether. The combined yellow supernatant and washings were dried on high vacuum pressure pump at room temperature (15 mm) to remove the solvent and the tan residue was distilled in a short path distillation to get 850 mg (97%) of ^{18}O-labeled DMSO.

Step II



0^{18}-incorparated murrayaquinone (41%)

Without further purification the distilled ^{18}O-labeled DMSO was applied on the oxidation of substrate **2e** under the standard conditions. After 2 h, reaction mixture was poured in cold sodium thiosulphate and purified by column chromatography. The isolated product was subjected to the ESI-MS analysis, a significant amount (42%) of ^{18}O incorporated oxidized product (M+H, m/z = 212) along with the unlabeled product (M+H,m/z = 214) was observed.

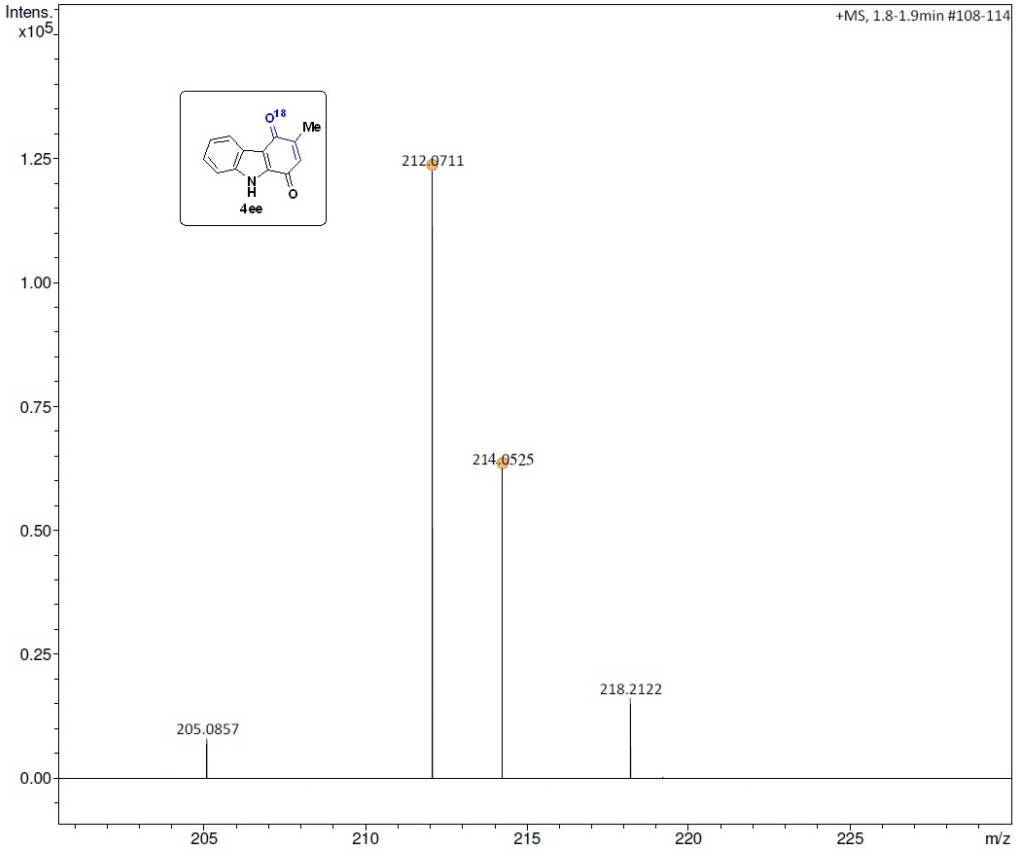
Savitribai Phule Pune University - Central Instrumentation Facility

Analysis Info

Analysis Name	D:\Data\2016\JUNE\SPPU\CHEMISTRY\PD LOKHANDE\MAHAVIR\MS -21_BC1_01_2814.d	Acquisition Date	6/7/2016 7:10:08 PM
Method	dlc-ms350mz_10min_90b.m	Operator	CIF
Sample Name	MS -21	Instrument	impact HD 1819696.00184
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
212.0711	1	C13H10NO2	212.0706	-2.5	4.8	1	100.00	9.5	even	ok	M+H
214.0524	1	C13H10NO2	214.0525	0.4	73.9	1	100.00	9.5	even	ok	M+H

Computational Details

All the DFT calculations were carried out using the Turbomole 6.0 suite of programs.[5] Geometry optimizations were performed using dispersion corrected Perdew, Burke, and Erzenhof density functional (PBE).[6] The TZVP basis set was employed for the calculations.[7] The resolution of identity (ri), along with the multipole accelerated resolution of identity (marij) approximations

were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations. Solvent effects were incorporated with the COSMO model,[8] with ε = 46.7 for DMSO. The contributions of internal energy and entropy were obtained from frequency calculations done on the DFT structures at 298.15 K. Therefore, the energies reported in the figures are the ΔG values. It was ensured that the obtained transition state structures possessed only one imaginary frequency corresponding to the correct normal mode.

The conversion of **2e** to **4e** has been investigated with density functional theory (DFT). The role molecular iodine could be justified in the conversion of **2e** to **4e** in two important steps; (a) for the elimination of HBr and, (b) I_2/DMSO-mediated oxidation. In order to explore these two steps, four different conformations of **2e** were considered as shown in Figure 1. The lowest energy conformation **2ea** has been considered as a starting reactant.

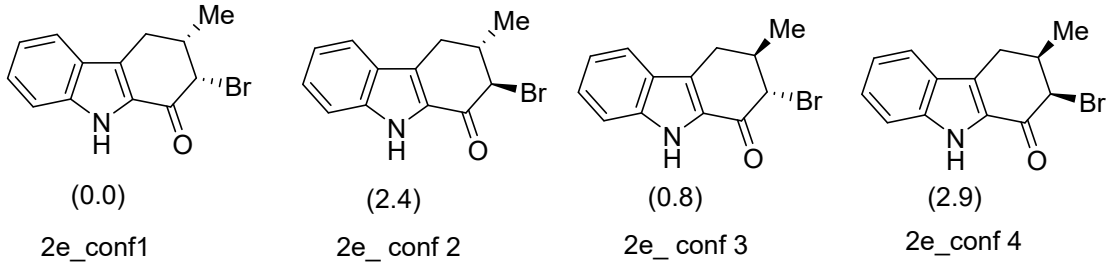


Figure 1. Different possible conformations for **2e** and the values in the bracket represent the energies in kcal/mol.

The free energy profile diagram shows that the interaction of molecular iodine with **2e** forms **2e_I_2**, a complex that is slightly endergonic, by 0.2 kcal/mol. This is because of the interaction of iodine with the *pi*-cloud of the aromatic ring in **2a_I_2**. The dissociation of bromine allows the change in conformation of **2e_I_2** to **2e_I_2** *via* **TS1** with a barrier of 31.6 kcal/mol. The subsequent HBr elimination is a feasible process *via* **TS2** with a barrier of 23.1 kcal/mol and leads to the

formation of **c_I$_2$**, which is 4.5 kcal/mol exergonic with respect to **2e**. Thereafter, C(sp^3)-H oxidation of **c_I$_2$** can occur *via* **TS3** with a barrier of 32.4 kcal/mol, as shown in Figure 2. This is the slowest step of the reaction and generates the cation-anion adduct **(d)**. The formation of **4e** from **d** is a feasible process with a barrier of only 9.4 kcal/mol *via* **TS4**. The final product is stable and exergonic by 21.4 kcal/mol with respect to **2e**.

The DFT investigations suggested that the conversion of **2e** to **4e** occurs in two steps: HBr elimination followed by activation of C(sp^3)-H bond by molecular iodine in DMSO. The oxidation step is the rate limiting step with a barrier of 32.4 kcal/mol.

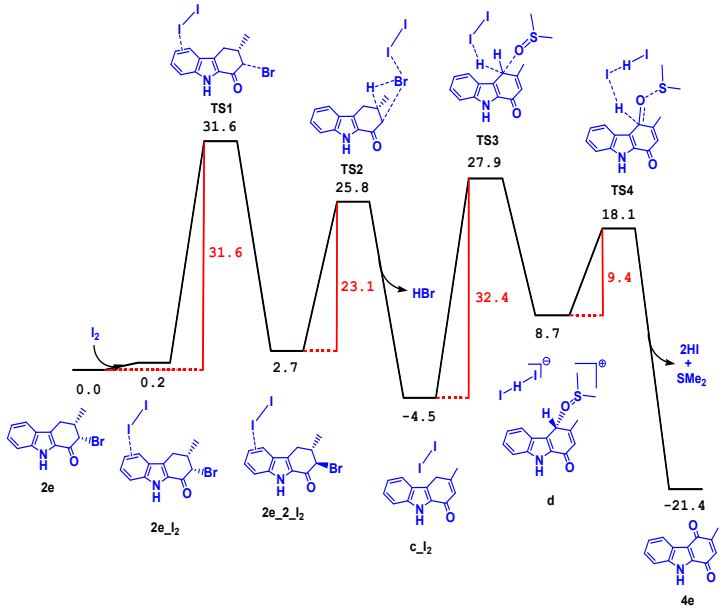


Figure 2. The free energy profile diagram for the conversion of **2a** to **4**; energy values are in kcal/mol.

References:

1. (a) Chakraborty, S.; Chattopadhyay, G.; Saha, C. *J. Heterocyclic Chem.* 2011, **48**, 331. (b) Fujii, M.; Nishiyama, T.; Choshi, T.; Satsuki, N.; Fujiwaki, T.; Abe, T.; Ishikura M.; Hibino, S. *Tetrahedron* 2014, **70**,1805. (c) Paul, H. B.; Christina, L. L. C.; Maurice, L. G.; Geoffrey, D. S.; Paul W. *Bioorg. Med. Chem. Lett.* 2007, **17**, 82.

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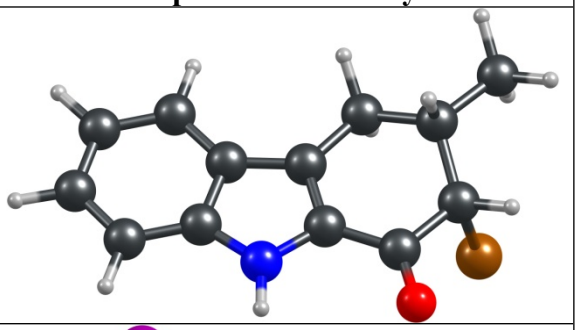
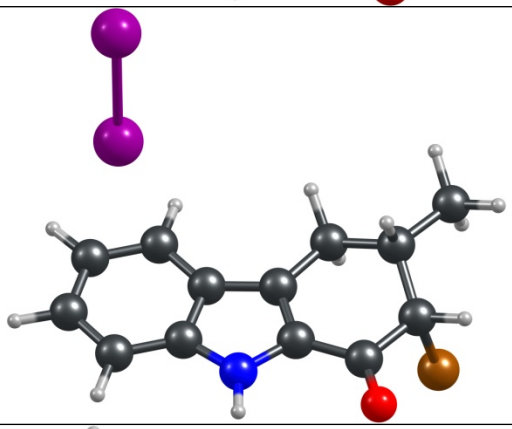
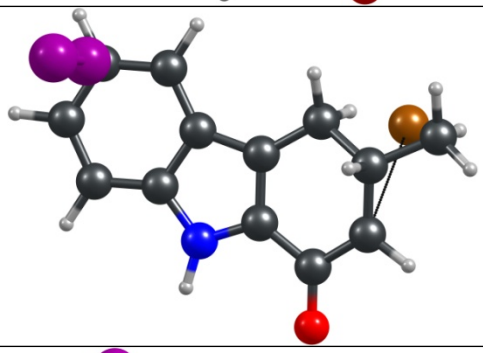
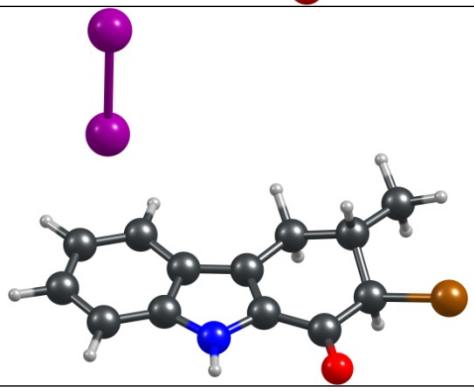
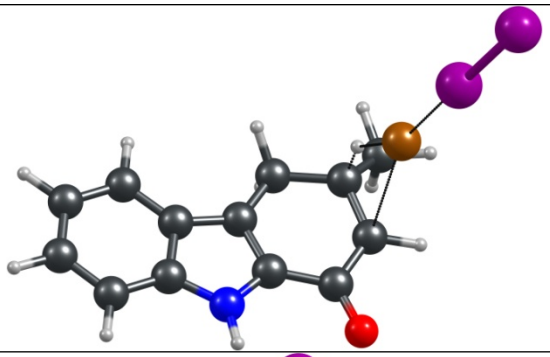
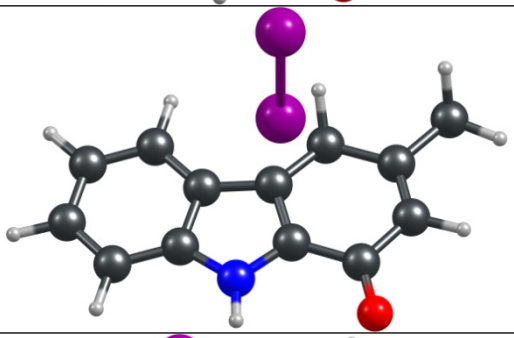
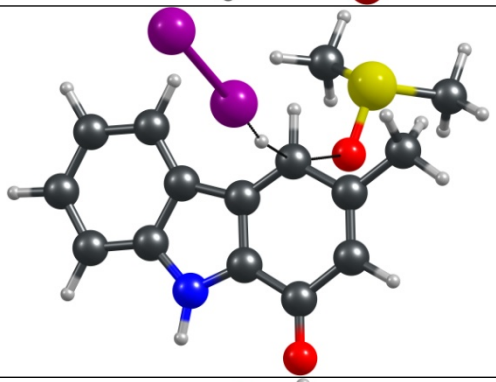
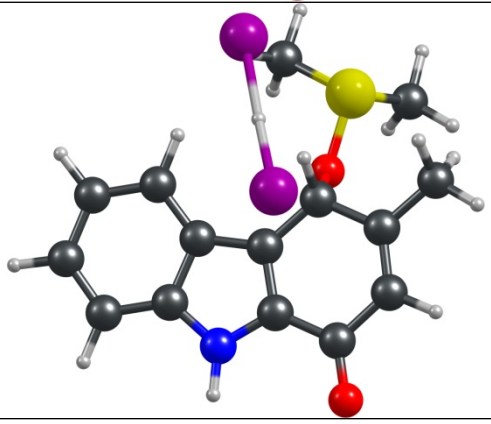
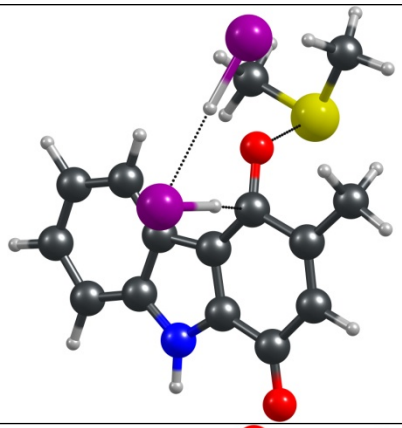
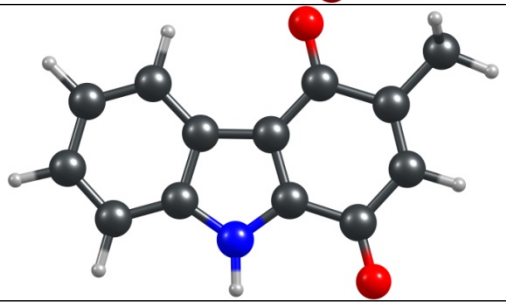
Table S1. Optimized geometries for different intermediate and transition states investigated in the present study.

Intermediate/ TSs	Optimize Geometry
2a	
2a_I_2	
TS1	
2b_I_2	

TS2	
C_I_2	
TS3	
d	

TS4	
3e	

Cartesian Coordinates:

2a

C	-1.125	6.290	-2.459
C	-0.685	5.335	-1.530
C	0.659	5.334	-1.023
C	1.566	6.323	-1.463
C	1.127	7.266	-2.384
C	-0.203	7.247	-2.875
C	0.759	4.241	-0.114
C	-0.493	3.621	-0.101
N	-1.357	4.290	-0.950
C	1.896	3.754	0.718
C	1.387	2.907	1.898
C	0.345	1.879	1.461
C	-0.833	2.461	0.679
O	-1.964	1.955	0.728
H	0.809	3.582	2.560
Br	1.139	0.476	0.233
H	-2.149	6.282	-2.838
H	-0.512	8.004	-3.599
H	1.813	8.037	-2.741
H	2.591	6.340	-1.088
H	2.576	3.133	0.105
H	2.494	4.596	1.099
C	2.528	2.299	2.708
H	-2.325	4.026	-1.114
H	-0.028	1.289	2.306
H	2.141	1.721	3.562
H	3.133	1.628	2.080
H	3.181	3.096	3.093

2b

C	-1.008	2.369	0.566
C	-0.674	3.568	-0.160
C	0.570	4.195	-0.155
C	1.705	3.666	0.649
C	1.207	2.815	1.842
C	0.191	1.779	1.334
N	-1.540	4.245	-1.001
C	-0.876	5.314	-1.547
C	0.466	5.312	-1.034
C	1.365	6.320	-1.446
C	0.919	7.287	-2.338
C	-0.410	7.270	-2.832
C	-1.324	6.294	-2.446
H	0.680	3.487	2.540

Br	-0.497	0.633	2.817
O	-2.126	1.841	0.520
H	0.694	1.061	0.665
H	-2.346	6.288	-2.828
H	-0.724	8.045	-3.534
H	1.599	8.074	-2.670
H	2.390	6.335	-1.069
H	2.360	3.039	0.017
H	2.334	4.484	1.035
C	2.406	2.178	2.546
H	-2.508	3.983	-1.165
H	2.106	1.653	3.463
H	2.904	1.458	1.877
H	3.134	2.959	2.814

2c

C	-1.101	6.259	-2.489
C	-0.657	5.291	-1.522
C	0.619	5.252	-0.956
C	1.674	6.252	-1.294
C	1.390	6.911	-2.660
C	-0.069	7.347	-2.792
N	-1.419	4.240	-1.039
C	-0.660	3.519	-0.152
C	0.636	4.132	-0.076
C	1.617	3.575	0.772
C	1.293	2.447	1.514
C	0.005	1.857	1.425
C	-0.984	2.378	0.597
C	1.714	5.957	-3.825
Br	-0.491	8.854	-1.514
O	-2.212	6.240	-3.042
H	-1.972	1.918	0.533
H	-0.213	0.970	2.023
H	2.035	2.003	2.180
H	2.608	4.028	0.845
H	1.704	7.034	-0.514
H	2.669	5.782	-1.309
H	2.021	7.807	-2.761
H	-2.383	4.056	-1.302
H	1.487	6.429	-4.793
H	2.784	5.702	-3.803
H	1.134	5.025	-3.747
H	-0.278	7.783	-3.776

2d

C	-0.977	2.382	0.587

C	-0.656	3.522	-0.165
C	0.635	4.146	-0.083
C	1.617	3.594	0.768
C	1.297	2.464	1.510
C	0.012	1.868	1.420
C	0.612	5.263	-0.966
C	-0.655	5.284	-1.546
N	-1.414	4.233	-1.060
C	1.651	6.280	-1.307
C	1.385	6.883	-2.711
C	-0.077	7.362	-2.747
C	-1.110	6.243	-2.526
O	-2.218	6.190	-3.070
C	1.723	5.882	-3.819
H	-0.232	8.105	-1.949
H	-1.963	1.918	0.521
H	-0.204	0.983	2.021
H	2.041	2.023	2.176
H	2.606	4.052	0.841
H	1.642	7.091	-0.557
H	2.659	5.838	-1.286
H	2.022	7.772	-2.821
H	-2.372	4.035	-1.337
H	1.533	6.315	-4.812
H	2.786	5.607	-3.756
H	1.124	4.963	-3.720
Br	-0.484	8.381	-4.405

2a_I_2

C	-0.861	2.571	0.777
C	-0.478	3.684	-0.058
C	0.812	4.210	-0.153
C	1.952	3.668	0.637
C	1.442	2.901	1.871
C	0.312	1.933	1.520
N	-1.338	4.402	-0.870
C	-0.631	5.386	-1.501
C	0.734	5.291	-1.074
C	1.676	6.217	-1.570
C	1.237	7.199	-2.479
C	-0.120	7.260	-2.894
C	-1.064	6.362	-2.418
C	2.577	2.241	2.649
Br	0.943	0.445	0.302
O	-2.020	2.155	0.896
H	0.946	3.637	2.532

H	-2.105	6.409	-2.740
H	-0.419	8.029	-3.607
H	1.963	7.881	-2.924
H	2.734	6.129	-1.318
H	2.551	2.980	0.013
H	2.629	4.476	0.955
H	-2.332	4.208	-0.973
H	-0.057	1.400	2.403
H	2.192	1.724	3.541
H	3.103	1.508	2.020
H	3.302	3.003	2.973
I	1.442	8.629	0.112
I	1.404	10.461	2.274

TS1

C	-0.911	2.511	0.900
C	-0.579	3.674	0.106
C	0.720	4.241	0.004
C	1.872	3.583	0.592
C	1.517	2.667	1.768
C	0.205	2.039	1.690
N	-1.463	4.432	-0.590
C	-0.800	5.512	-1.150
C	0.580	5.412	-0.796
C	1.480	6.406	-1.226
C	0.975	7.477	-1.981
C	-0.400	7.545	-2.322
C	-1.305	6.567	-1.914
C	2.654	1.738	2.200
O	-2.052	1.986	0.927
I	1.077	8.829	0.694
I	1.034	10.384	3.013
Br	2.376	1.037	-1.415
H	1.351	3.381	2.620
H	-2.362	6.624	-2.176
H	-0.755	8.386	-2.918
H	1.659	8.231	-2.372
H	2.544	6.338	-0.997
H	2.234	2.810	-0.195
H	2.721	4.247	0.799
H	-2.463	4.243	-0.647
H	0.000	1.194	2.356
H	2.365	1.147	3.080
H	2.888	1.057	1.367
H	3.546	2.331	2.443

2b_I_2

C	-1.348	6.240	-2.436

C	-0.884	5.247	-1.553
C	0.444	5.266	-1.012
C	1.315	6.319	-1.363
C	0.844	7.316	-2.239
C	-0.474	7.265	-2.767
C	0.565	4.130	-0.164
C	-0.659	3.468	-0.218
N	-1.525	4.147	-1.058
C	1.690	3.623	0.666
C	1.180	2.734	1.827
C	0.213	1.675	1.268
C	-0.980	2.243	0.477
O	-2.082	1.694	0.392
C	2.375	2.125	2.560
Br	-0.478	0.476	2.701
H	0.608	3.377	2.517
H	0.760	0.992	0.597
H	-2.359	6.202	-2.844
H	-0.798	8.050	-3.451
H	1.525	8.099	-2.576
H	2.351	6.327	-1.021
H	2.383	3.028	0.042
H	2.279	4.453	1.085
H	-2.479	3.859	-1.258
H	2.060	1.570	3.454
H	2.920	1.436	1.894
H	3.064	2.924	2.869
I	0.666	8.588	0.426
I	0.250	10.247	2.685

TS2

C	-1.387	2.896	0.996
C	-0.948	3.917	0.160
C	0.431	4.075	-0.189
C	1.391	3.175	0.323
C	0.955	2.154	1.159
C	-0.412	2.019	1.489
C	0.515	5.210	-1.036
C	-0.814	5.694	-1.189
N	-1.667	4.925	-0.471
C	1.675	5.873	-1.657
C	1.296	6.870	-2.761
C	-0.066	7.367	-2.760
C	-1.190	6.810	-2.023
O	-2.352	7.267	-2.111
C	2.366	7.935	-3.045
H	1.238	6.249	-3.715

H	-0.298	8.220	-3.406
H	-2.440	2.782	1.260
H	-0.720	1.206	2.149
H	1.674	1.443	1.569
H	2.446	3.282	0.067
H	2.212	6.451	-0.880
H	2.407	5.138	-2.026
H	-2.676	5.059	-0.437
H	2.104	8.518	-3.939
H	2.455	8.616	-2.187
H	3.335	7.444	-3.212
Br	-0.243	5.467	-5.428
I	-1.020	4.388	-7.954
I	-1.844	3.301	-10.525

C_I_2

C	-0.811	-0.613	5.000
C	-0.165	-0.311	3.719
C	1.219	-0.459	3.484
C	2.092	-1.120	4.495
C	1.425	-1.342	5.826
C	0.100	-1.109	6.029
N	-0.798	0.034	2.566
C	0.132	0.130	1.545
C	1.414	-0.203	2.081
C	2.537	-0.216	1.236
C	2.360	0.117	-0.104
C	1.087	0.465	-0.611
C	-0.045	0.478	0.202
C	2.313	-1.841	6.920
O	-2.036	-0.466	5.168
H	-1.028	0.742	-0.190
H	0.987	0.728	-1.665
H	3.218	0.115	-0.778
H	3.525	-0.472	1.625
H	2.402	-2.111	4.109
H	3.039	-0.573	4.646
H	-0.343	-1.305	7.009
H	-1.789	0.259	2.502
H	3.069	-1.075	7.166
H	1.744	-2.082	7.828
H	2.870	-2.734	6.590
I	1.368	2.247	4.486
I	1.988	4.882	5.381

TS3

C	-2.790	-0.779	0.743
C	-4.141	-0.211	0.626

C	-4.876	-0.194	-0.579
C	-4.289	-0.701	-1.741
C	-2.944	-1.295	-1.686
C	-2.248	-1.312	-0.511
N	-4.880	0.340	1.609
C	-6.112	0.747	1.107
C	-6.147	0.425	-0.281
C	-7.286	0.736	-1.029
C	-8.356	1.358	-0.377
C	-8.301	1.669	0.997
C	-7.176	1.367	1.766
C	-2.385	-1.844	-2.959
O	-2.173	-0.797	1.822
I	-3.304	2.231	-3.373
I	-2.660	5.072	-5.192
H	-7.127	1.606	2.830
H	-9.155	2.156	1.469
H	-9.255	1.610	-0.943
H	-7.343	0.504	-2.094
H	-4.845	-0.750	-2.676
H	-3.663	0.860	-2.410
H	-4.572	0.433	2.578
H	-1.251	-1.753	-0.463
H	-2.354	-1.061	-3.735
H	-1.373	-2.244	-2.814
H	-3.036	-2.646	-3.344
O	-5.257	-2.959	-1.572
S	-5.873	-3.499	-2.910
C	-5.474	-5.282	-2.958
C	-7.671	-3.634	-2.608
H	-5.978	-5.718	-3.832
H	-4.385	-5.362	-3.065
H	-5.819	-5.741	-2.023
H	-8.132	-4.108	-3.486
H	-7.826	-4.229	-1.699
H	-8.049	-2.611	-2.486

d

C	-6.920	1.463	1.896
C	-5.878	0.800	1.231
C	-6.010	0.336	-0.119
C	-7.219	0.557	-0.809
C	-8.250	1.217	-0.150
C	-8.103	1.660	1.188
C	-4.763	-0.273	-0.453
C	-3.941	-0.161	0.660
N	-4.611	0.483	1.668

C	-4.290	-0.918	-1.693
C	-2.831	-1.326	-1.679
C	-2.068	-1.178	-0.572
C	-2.557	-0.606	0.696
O	-1.835	-0.498	1.704
C	-2.282	-1.879	-2.956
O	-5.147	-2.166	-1.833
S	-5.509	-2.656	-3.391
C	-7.315	-2.569	-3.370
C	-5.275	-4.437	-3.184
I	-6.018	0.886	-4.718
I	-3.055	2.461	-2.710
H	-6.805	1.811	2.924
H	-8.935	2.174	1.672
H	-9.191	1.403	-0.670
H	-7.328	0.246	-1.849
H	-4.496	-0.292	-2.578
H	-4.210	0.711	2.575
H	-1.015	-1.470	-0.589
H	-2.524	-1.215	-3.802
H	-1.193	-2.005	-2.896
H	-2.711	-2.870	-3.188
H	-5.678	-4.908	-4.091
H	-4.196	-4.619	-3.106
H	-5.814	-4.764	-2.286
H	-7.658	-3.101	-4.269
H	-7.681	-3.047	-2.453
H	-7.581	-1.507	-3.435
H	-4.437	1.765	-3.650

TS4

C	0.796	-2.237	-0.348
C	0.207	-1.422	0.704
C	-0.451	-0.213	0.479
C	-0.507	0.363	-0.864
C	0.001	-0.514	-1.974
C	0.640	-1.685	-1.701
N	0.194	-1.711	2.044
C	-0.450	-0.695	2.719
C	-0.859	0.286	1.757
C	-1.503	1.457	2.199
C	-1.743	1.611	3.562
C	-1.352	0.618	4.493
C	-0.699	-0.544	4.089
O	-1.436	1.266	-1.159
C	-0.184	0.000	-3.363
O	1.377	-3.318	-0.117

S	-3.457	0.593	-1.469
C	-3.648	1.739	-2.860
C	-4.125	1.601	-0.123
I	2.167	2.338	-0.718
H	-0.388	-1.303	4.809
H	-1.560	0.771	5.554
H	-2.240	2.512	3.925
H	-1.794	2.227	1.485
H	0.533	1.200	-0.800
H	0.595	-2.550	2.457
H	1.040	-2.295	-2.515
H	-1.255	0.039	-3.620
H	0.183	1.037	-3.443
H	0.332	-0.634	-4.094
H	-4.698	2.058	-2.913
H	-2.977	2.593	-2.695
H	-3.368	1.201	-3.774
H	-5.200	1.751	-0.294
H	-3.959	1.054	0.812
H	-3.594	2.563	-0.110
H	0.753	3.518	-2.173
I	-0.296	4.321	-3.253

4

C	-0.159	0.324	0.052
C	-0.025	-0.024	1.466
C	1.197	-0.125	2.130
C	2.444	0.103	1.425
C	2.333	0.454	-0.046
C	1.120	0.552	-0.649
N	-1.044	-0.293	2.333
C	-0.519	-0.575	3.579
C	0.907	-0.476	3.490
C	1.687	-0.717	4.637
C	1.035	-1.047	5.822
C	-0.376	-1.145	5.887
C	-1.175	-0.911	4.771
C	3.617	0.678	-0.773
O	-1.259	0.420	-0.514
H	-2.262	-0.986	4.817
H	-0.848	-1.411	6.835
H	1.620	-1.238	6.723
H	2.774	-0.644	4.587
H	1.042	0.809	-1.708
H	-2.032	-0.285	2.085
H	4.236	-0.233	-0.741
H	3.437	0.957	-1.820

H 4.207 1.465 -0.278
O 3.558 0.022 1.965
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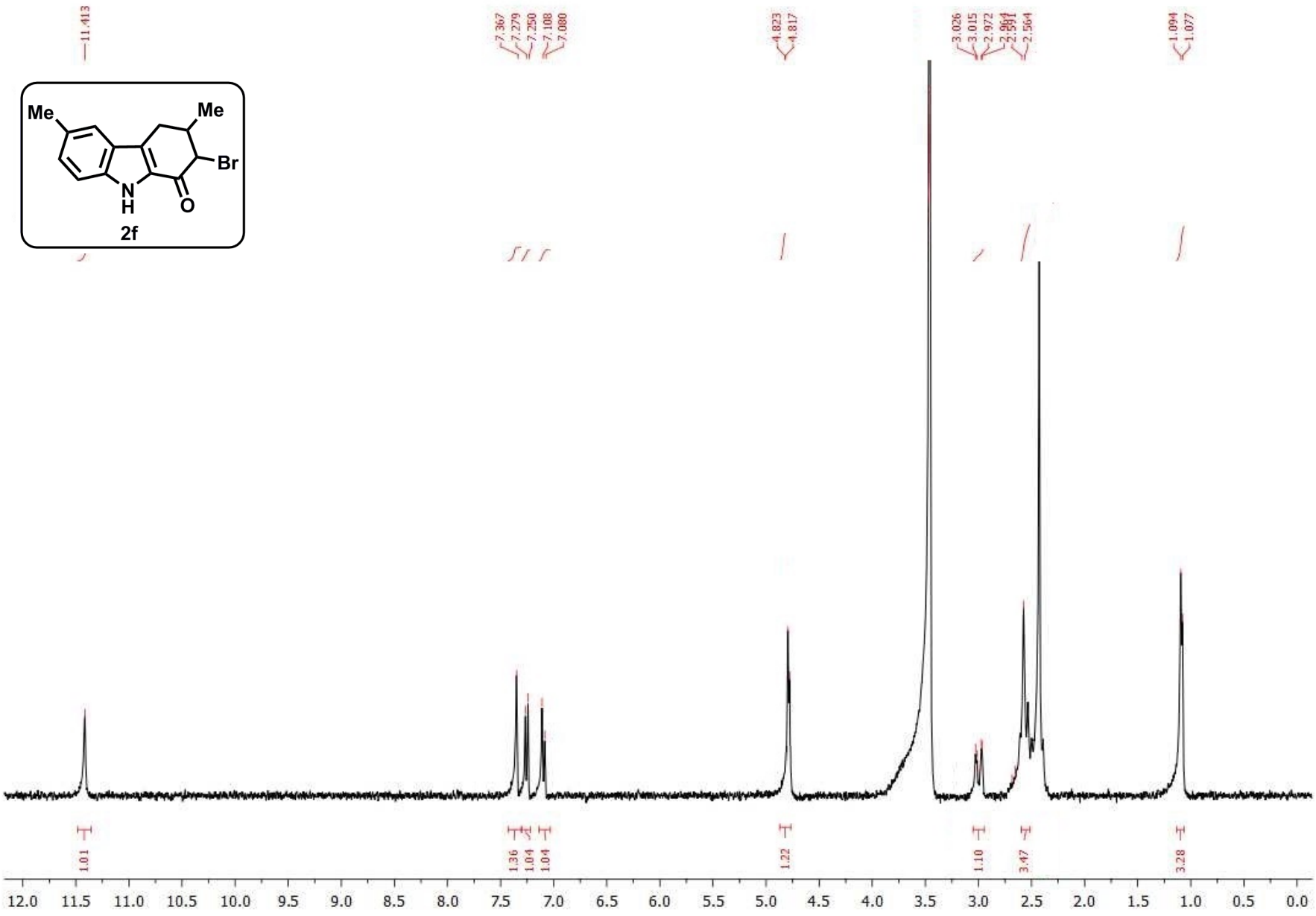
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Me
Br
N
H
O
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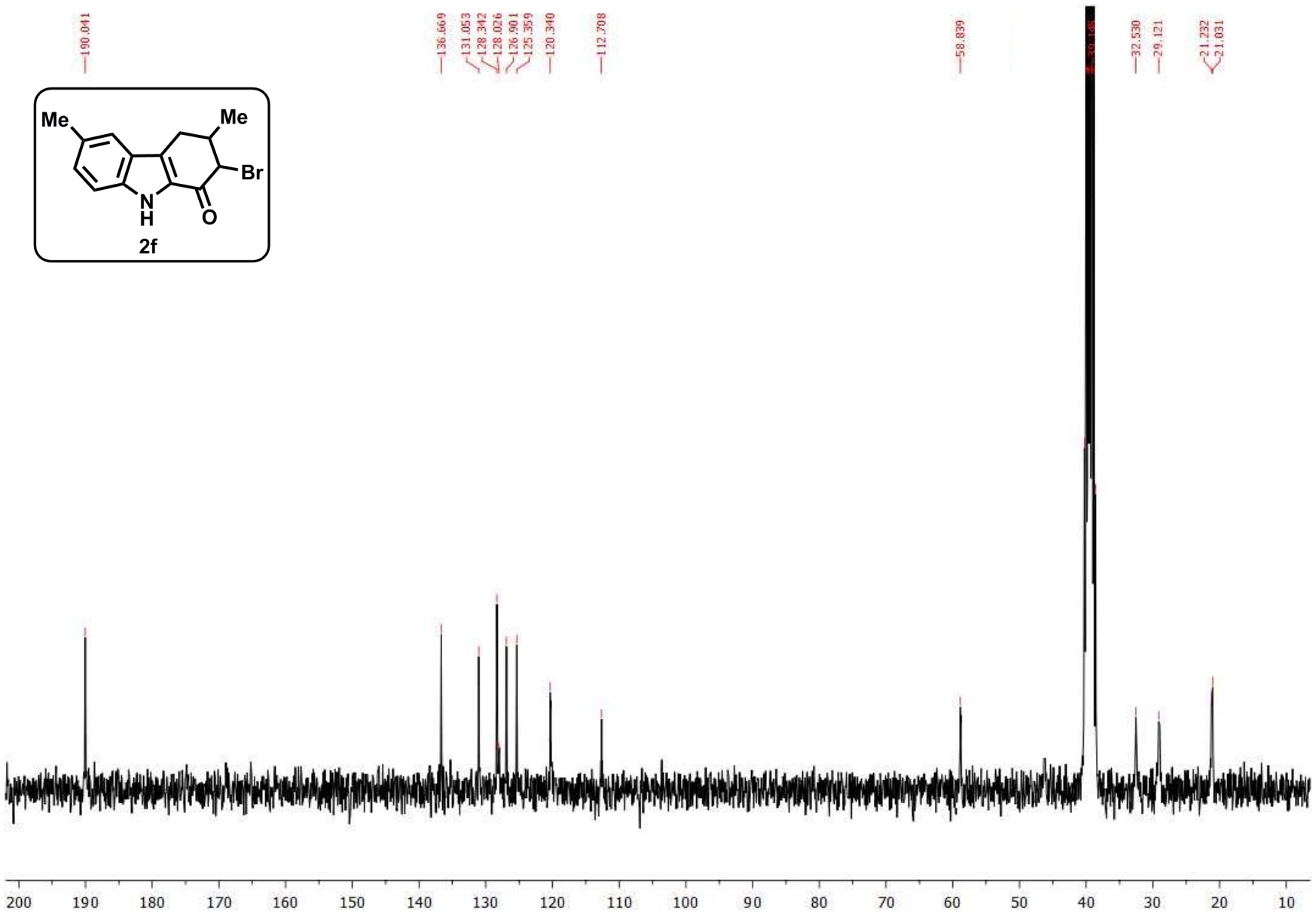
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Me
Me
Br
N
H
O
2f
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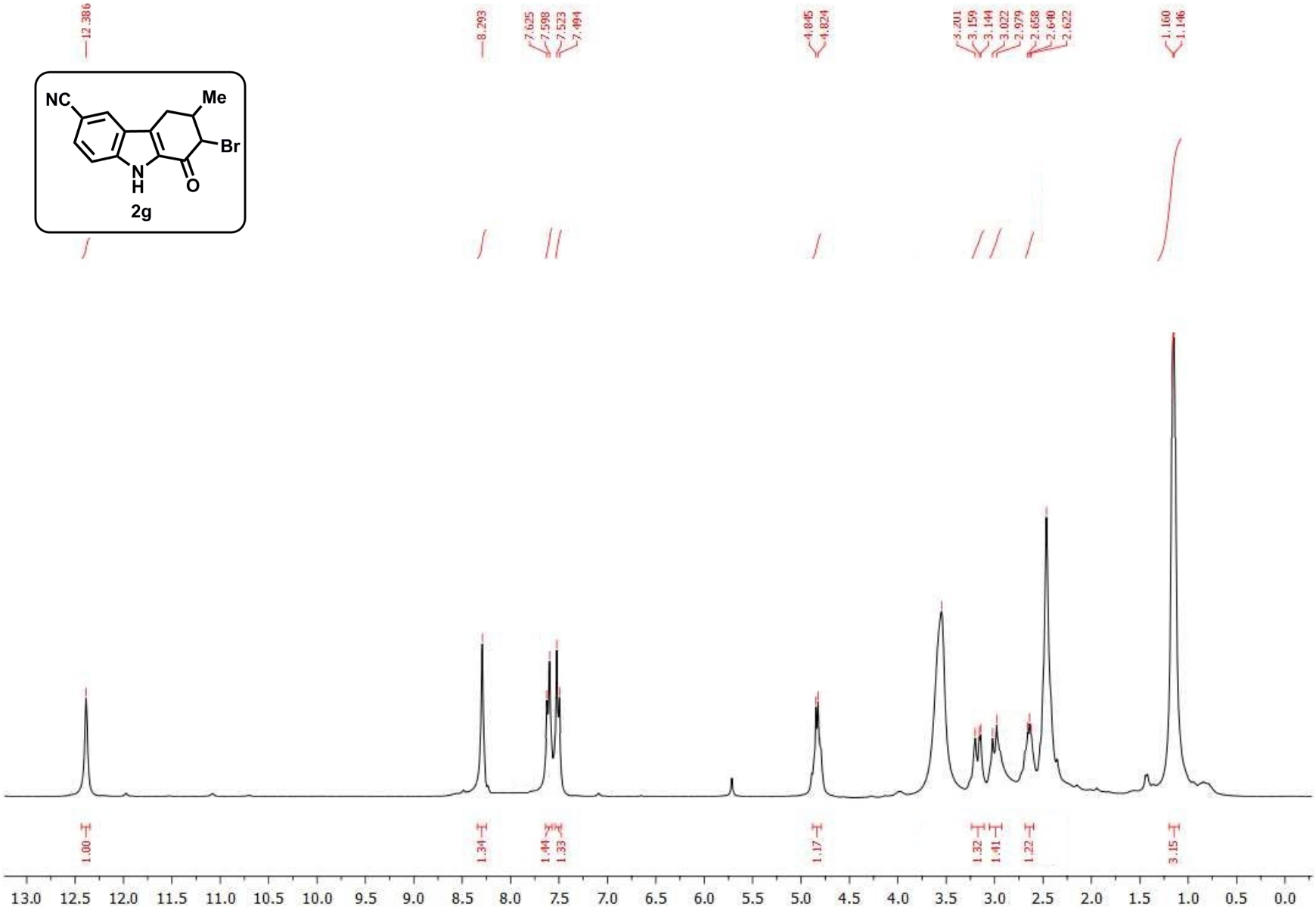
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Br
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H
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2g
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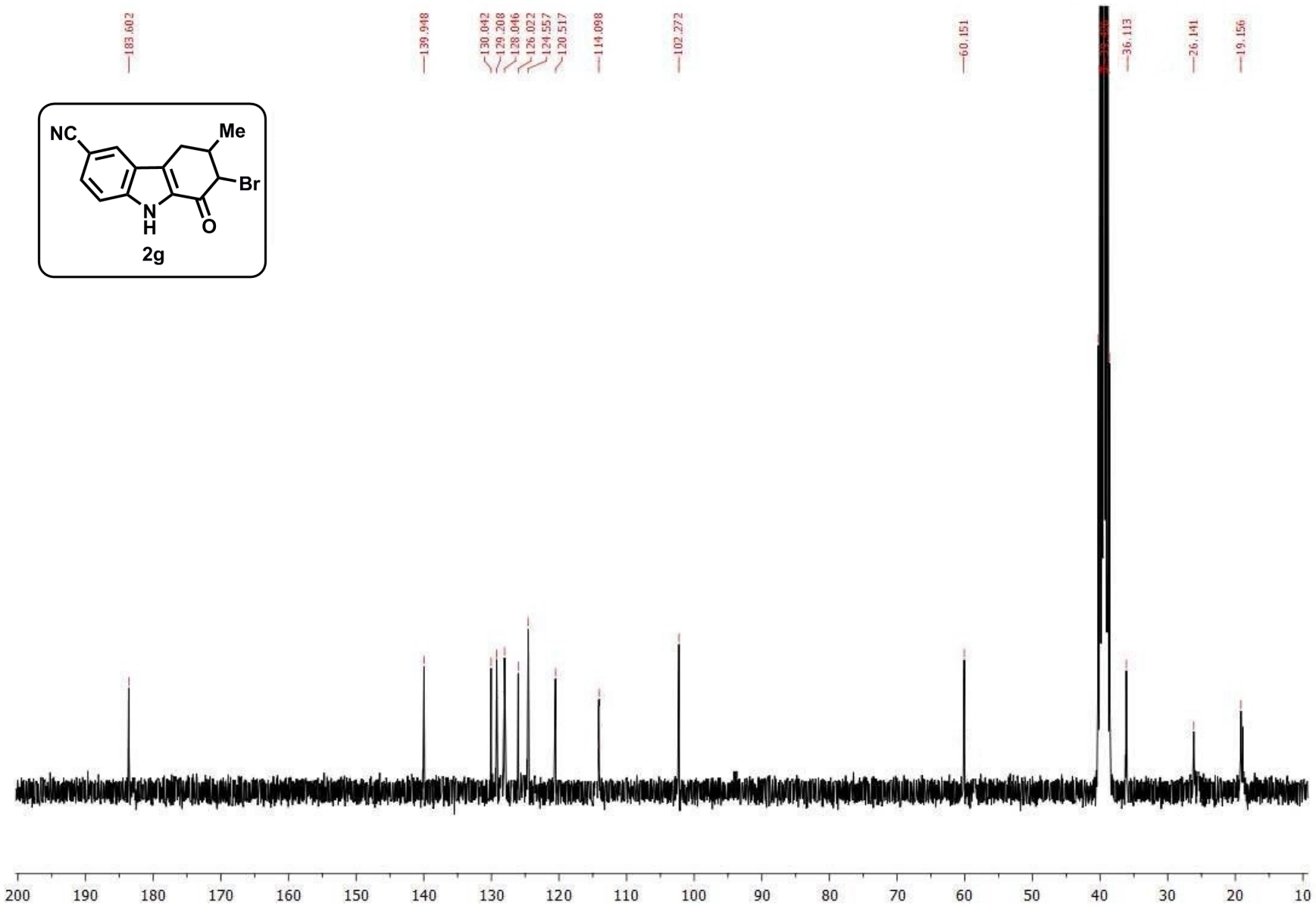
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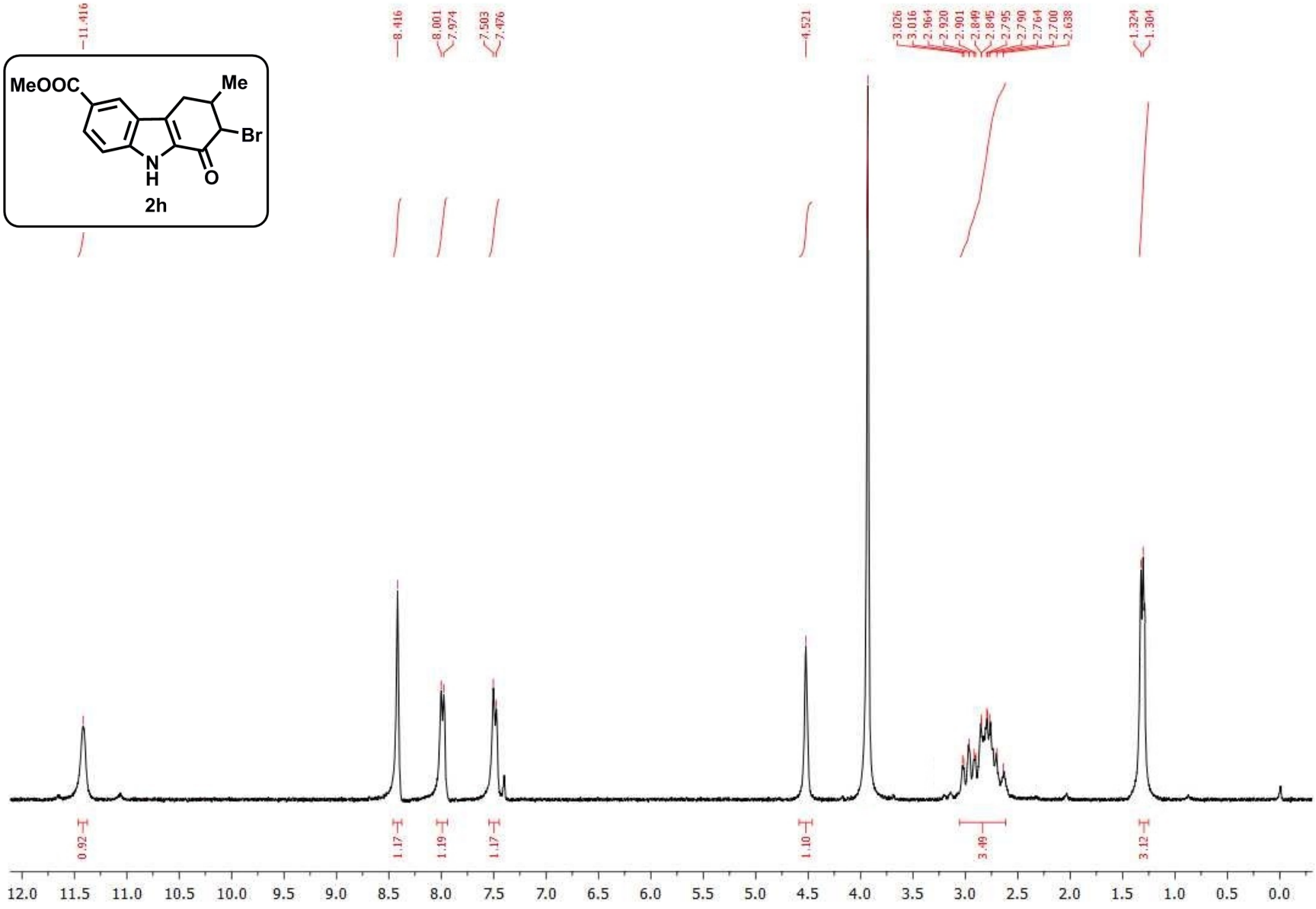
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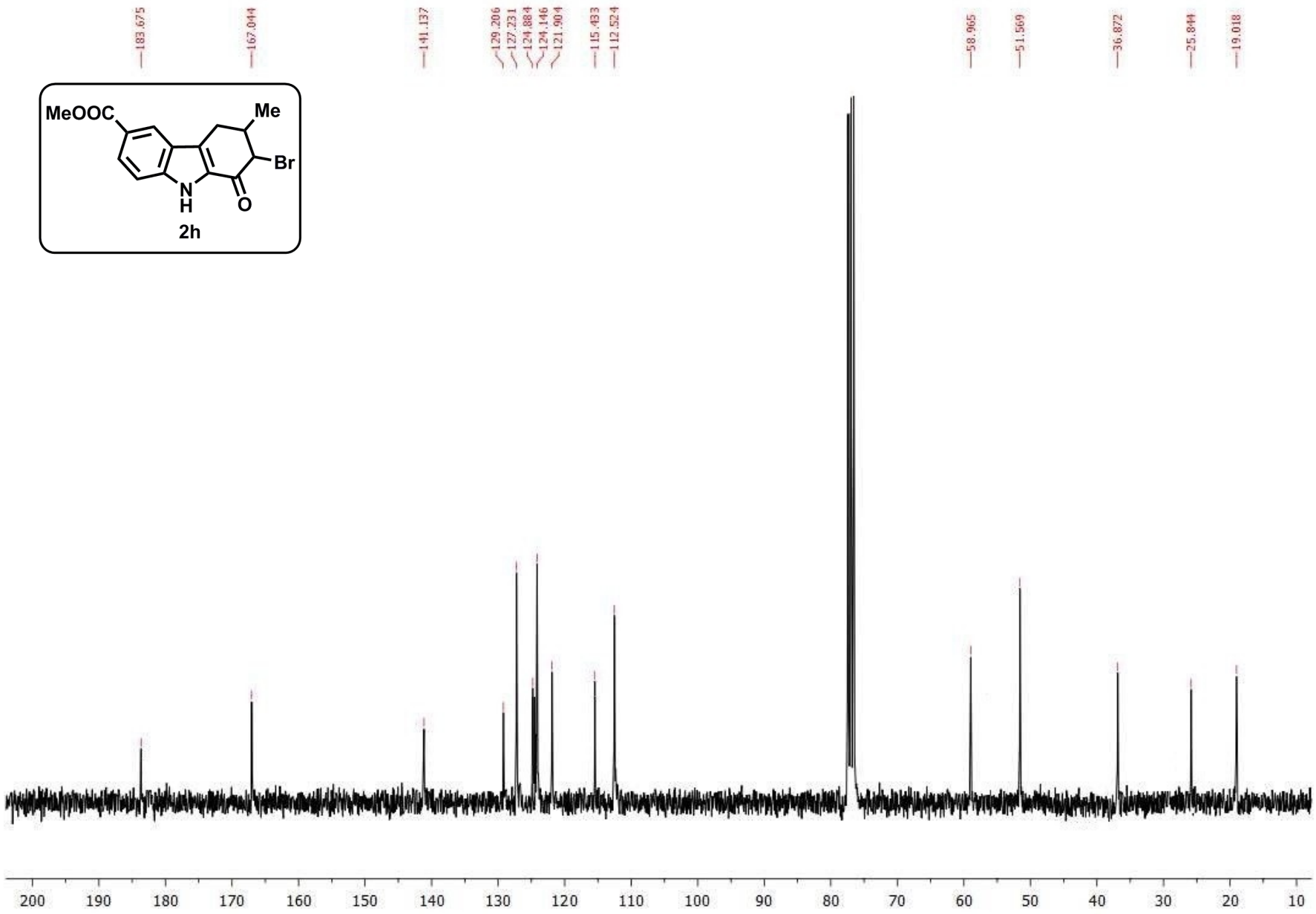
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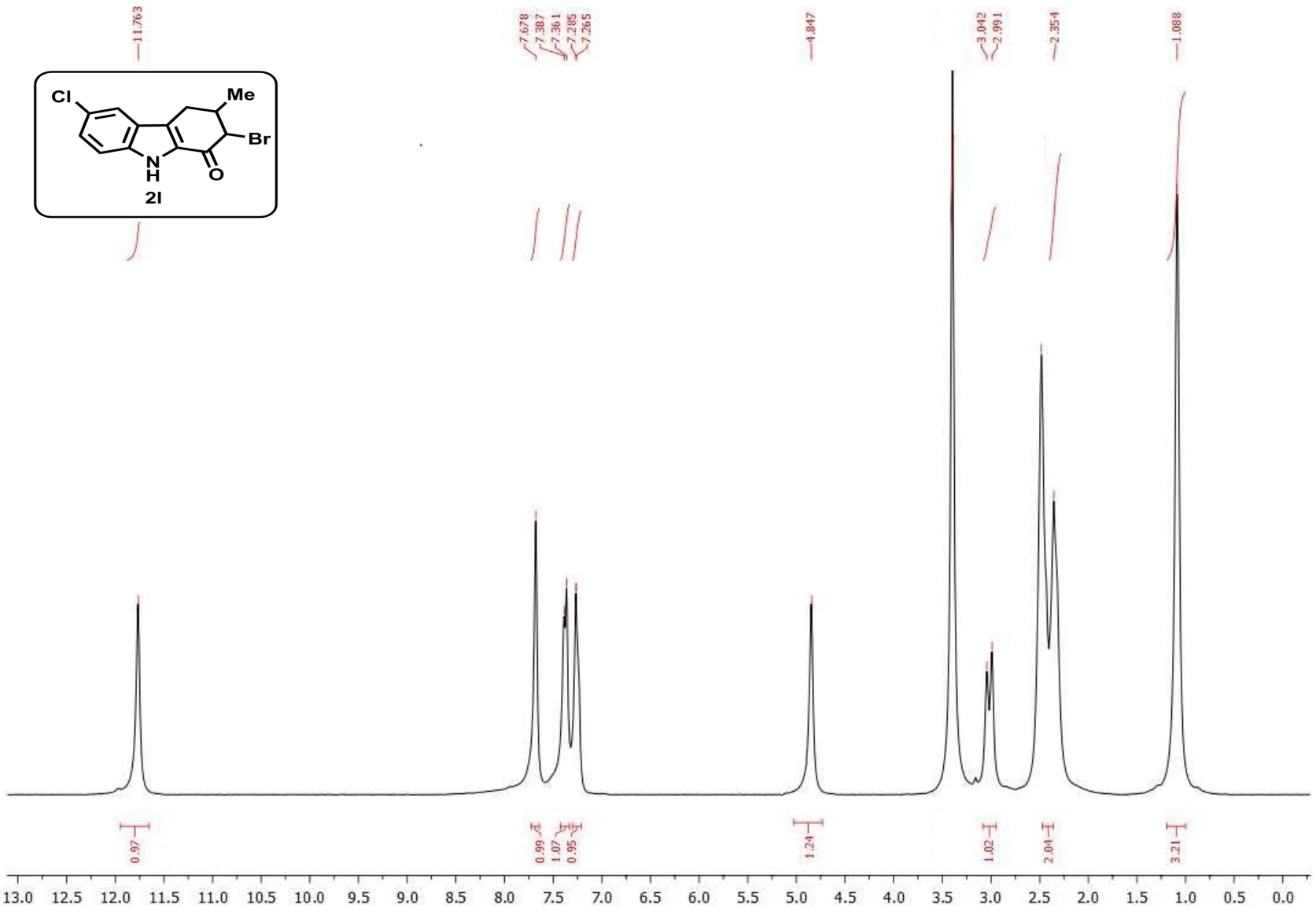
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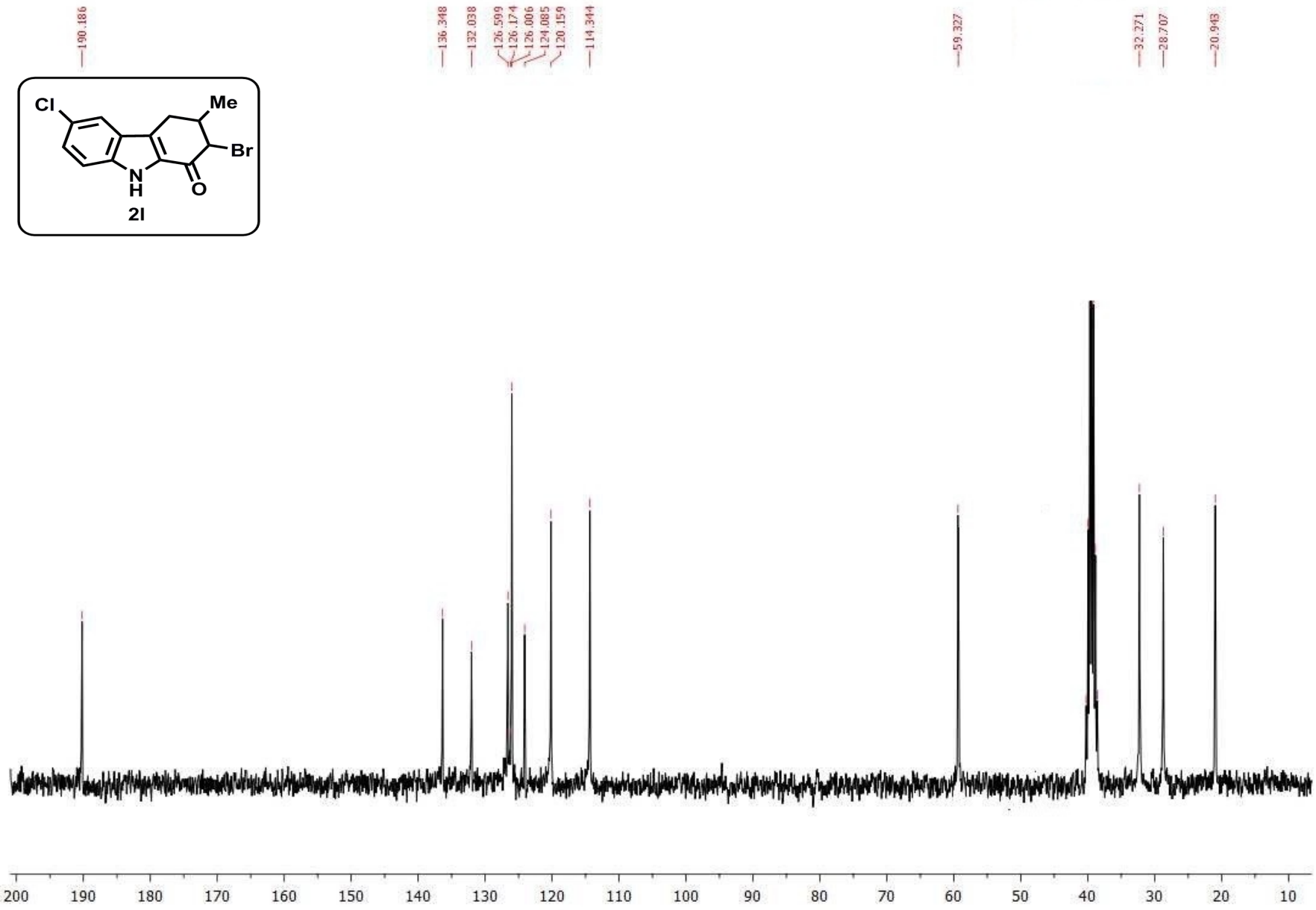
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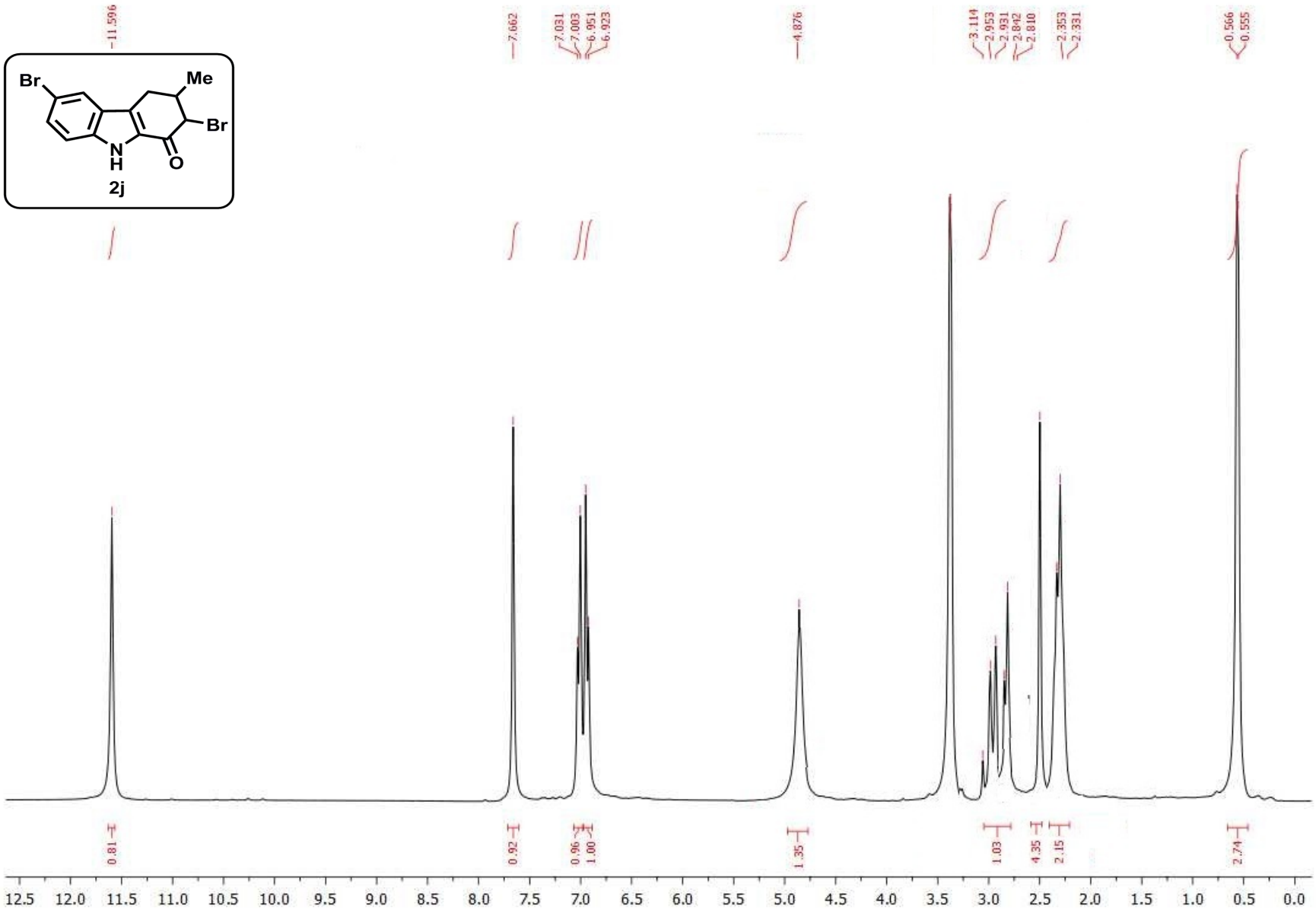
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2.74
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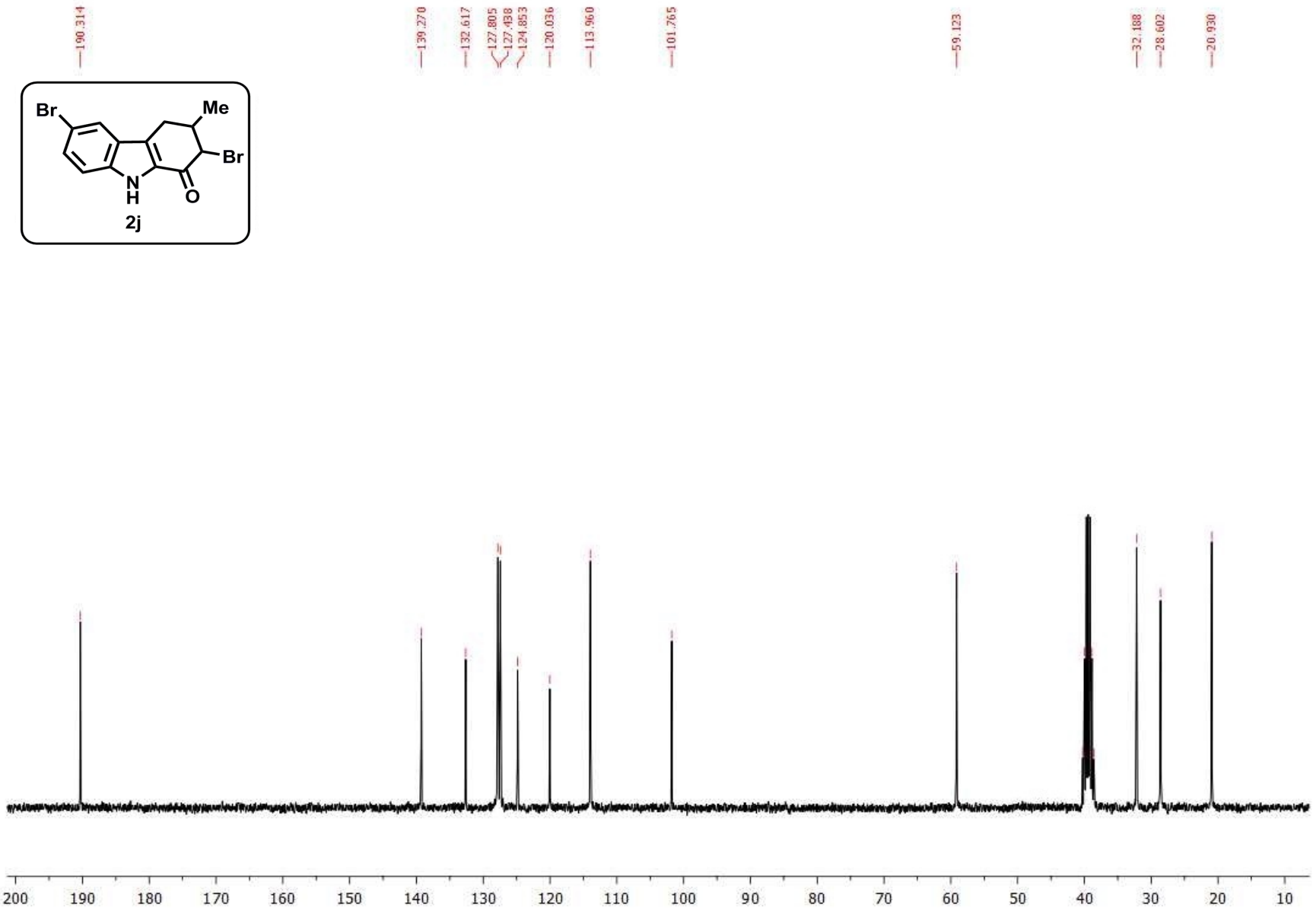
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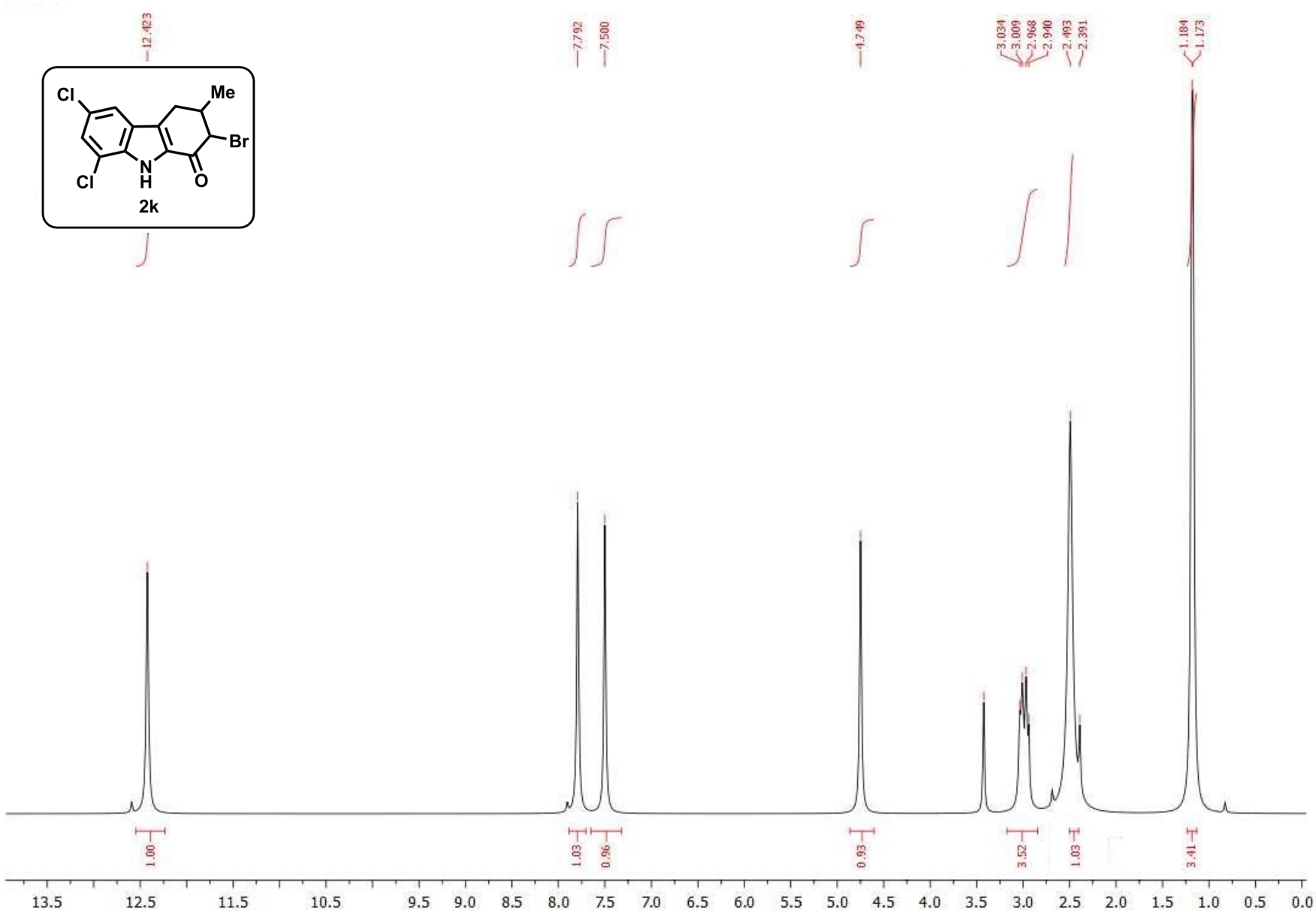
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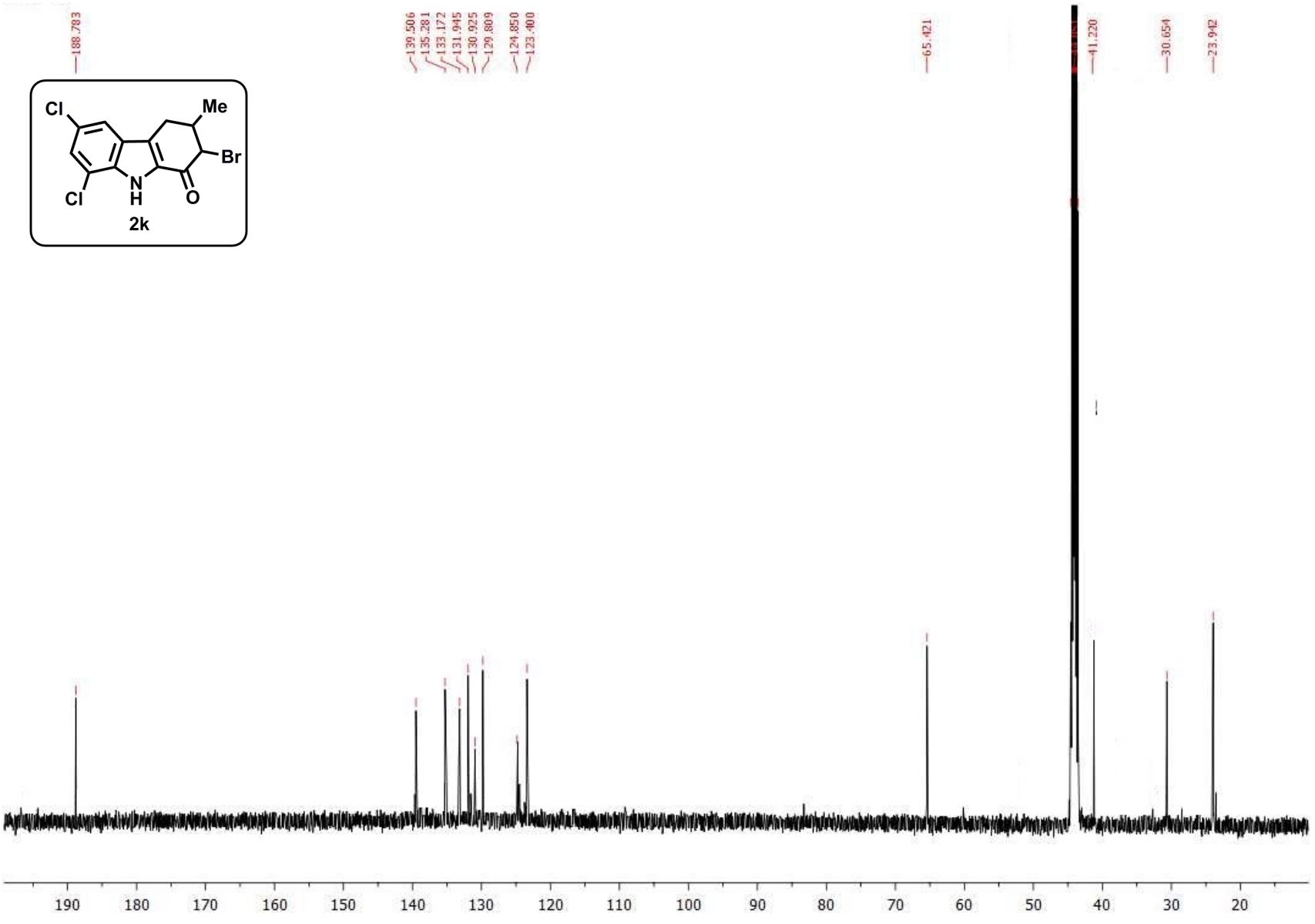
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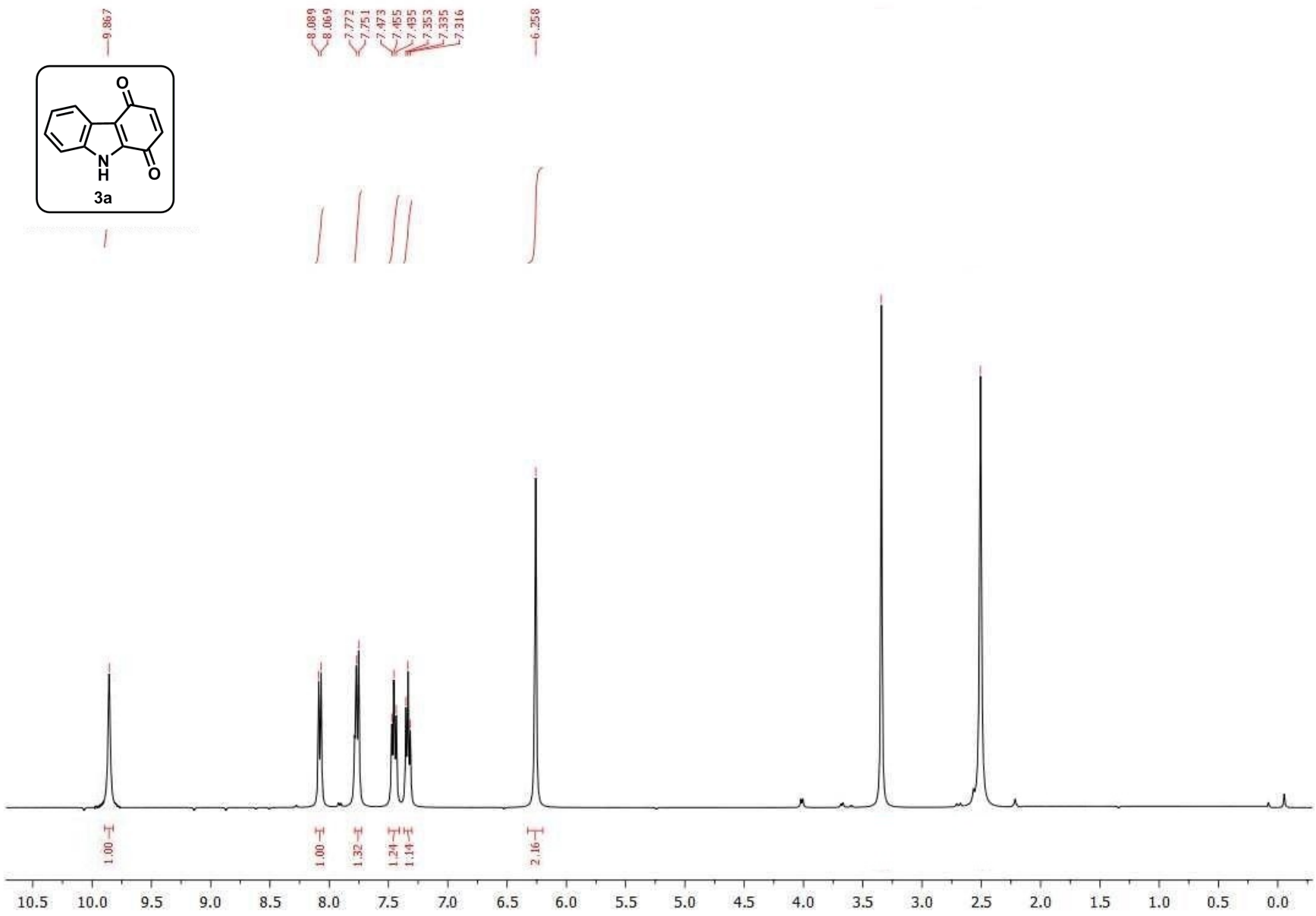
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7.772
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7.473
7.455
7.435
7.353
7.335
7.316
6.258
O
N
H
O
3a
1.00
1.00
1.32
1.24
1.14
2.16
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.5
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2.0
1.5
1.0
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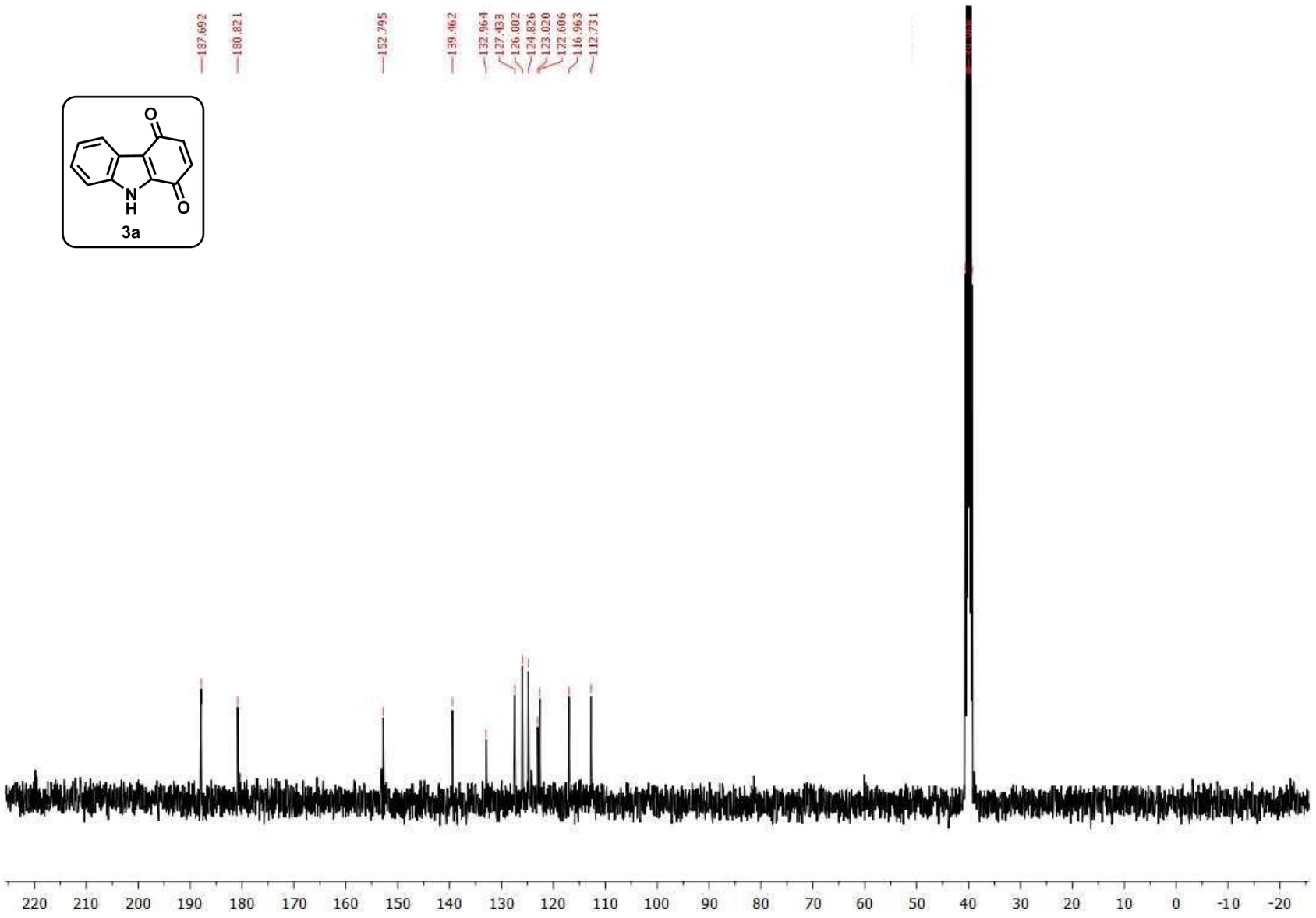
0.0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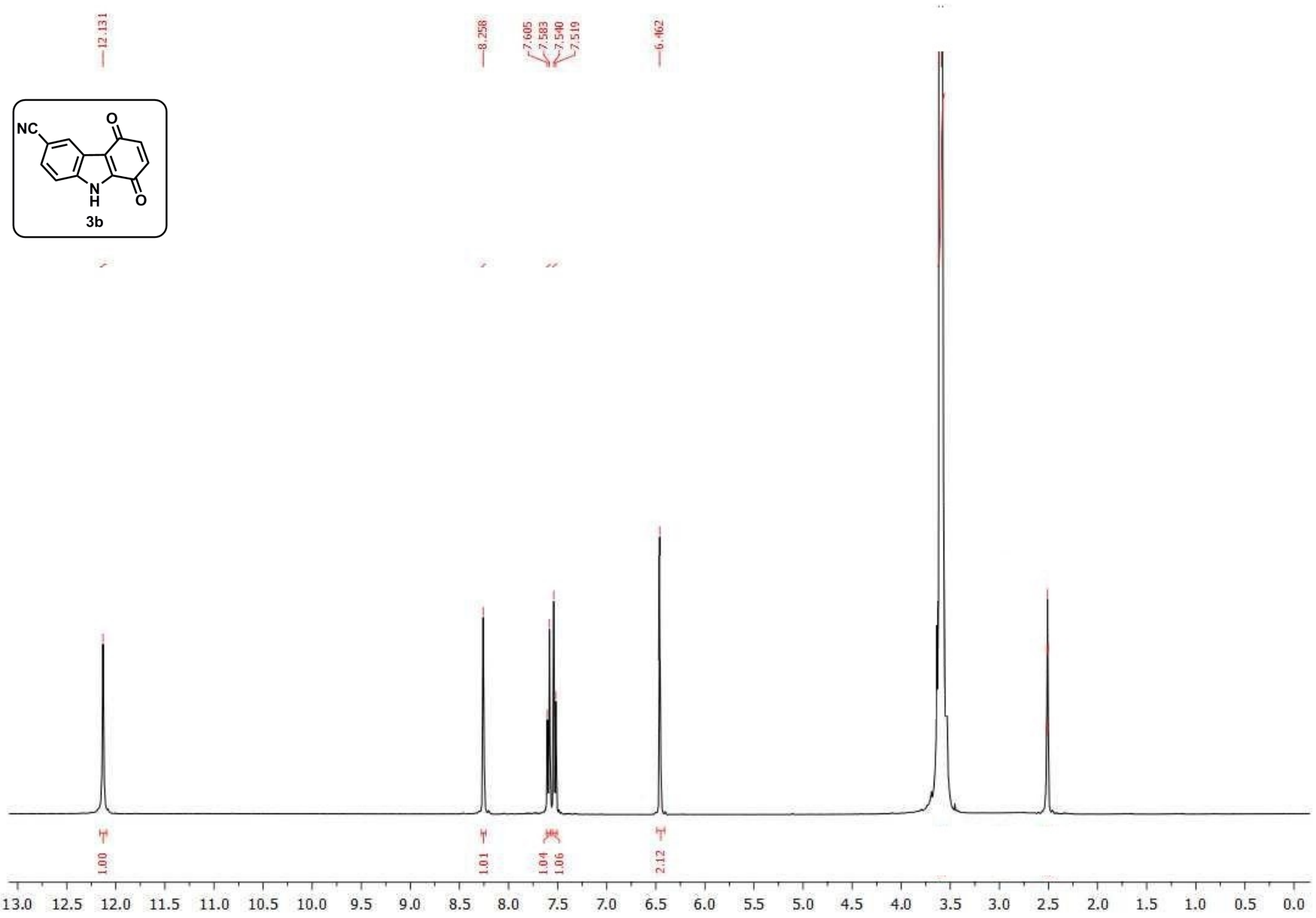
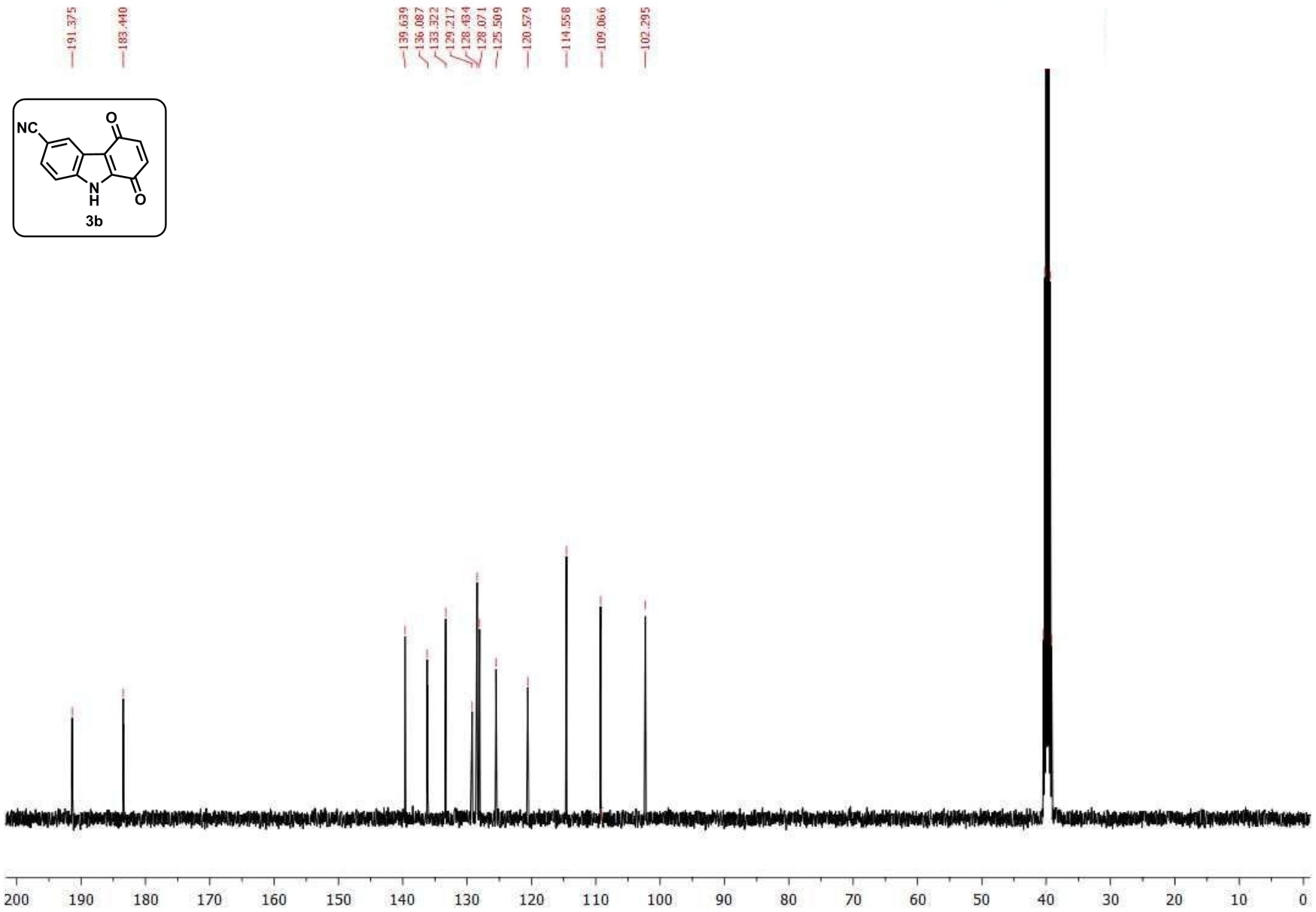
152.795
139.462
132.964
127.433
126.002
124.826
123.020
122.606
116.963
112.731
O
N
H
O
3a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20


12.131
8.258
7.605
7.583
7.540
7.519
6.462
NC
O
N
H
O
3b
1.00
1.01
1.04
1.06
2.12
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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139.639
136.087
133.322
129.217
128.434
128.071
125.509
120.579
114.558
109.066
102.295
NC
O
N
H
O
3b
200
190
180
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150
140
130
120
110
100
90
80
70
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50
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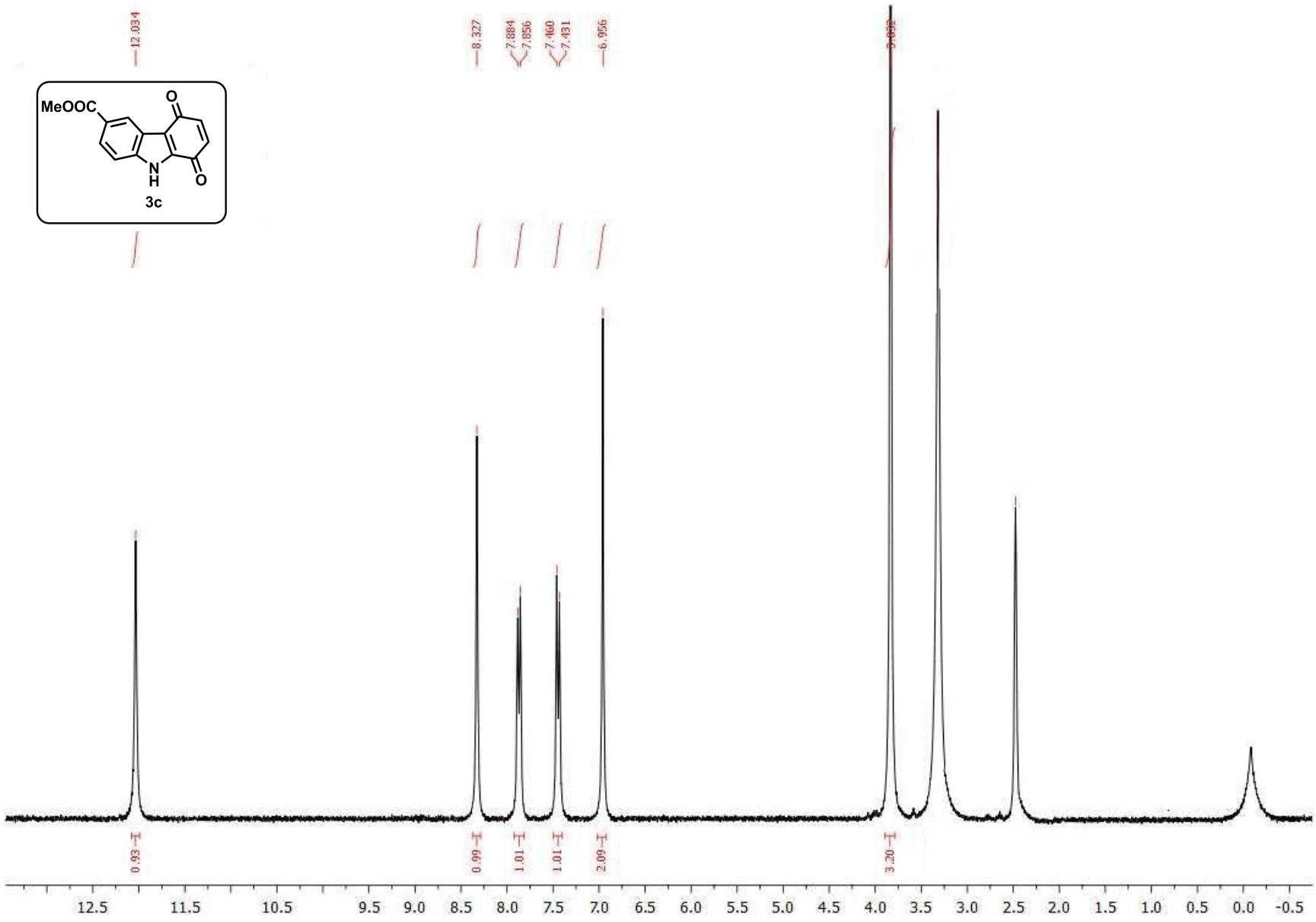
30
20
10
0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7.460
7.431
6.956
3.632
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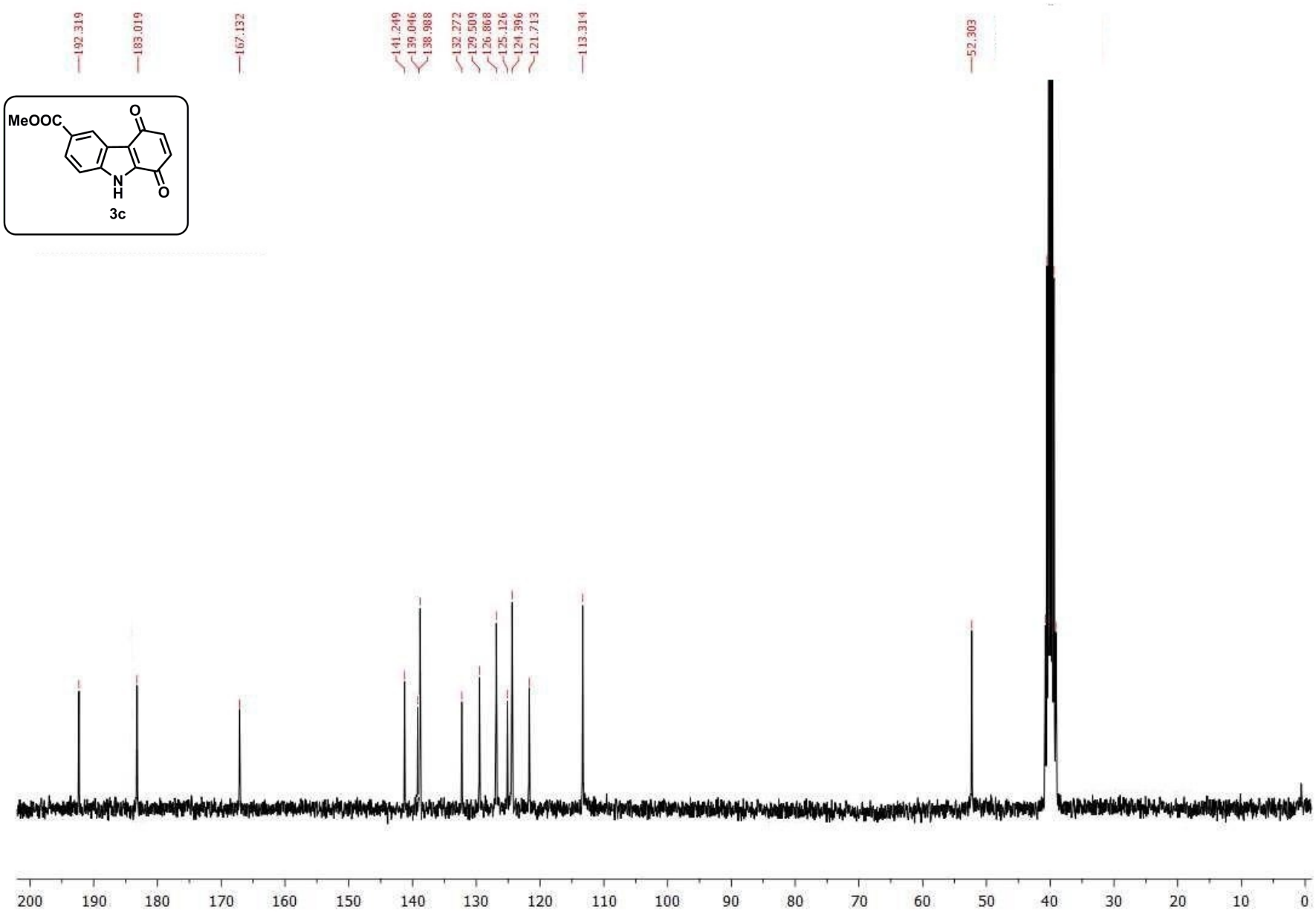
N
H
O
3c
0.93
0.99
1.01
1.01
2.09
3.20
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


192.319
183.019
167.132
141.249
139.046
138.988
132.272
129.509
126.868
125.126
124.396
121.713
113.314
52.303
MeOOC
O
N
H
O
3c
200
190
180
170
160
150
140
130
120
110
100
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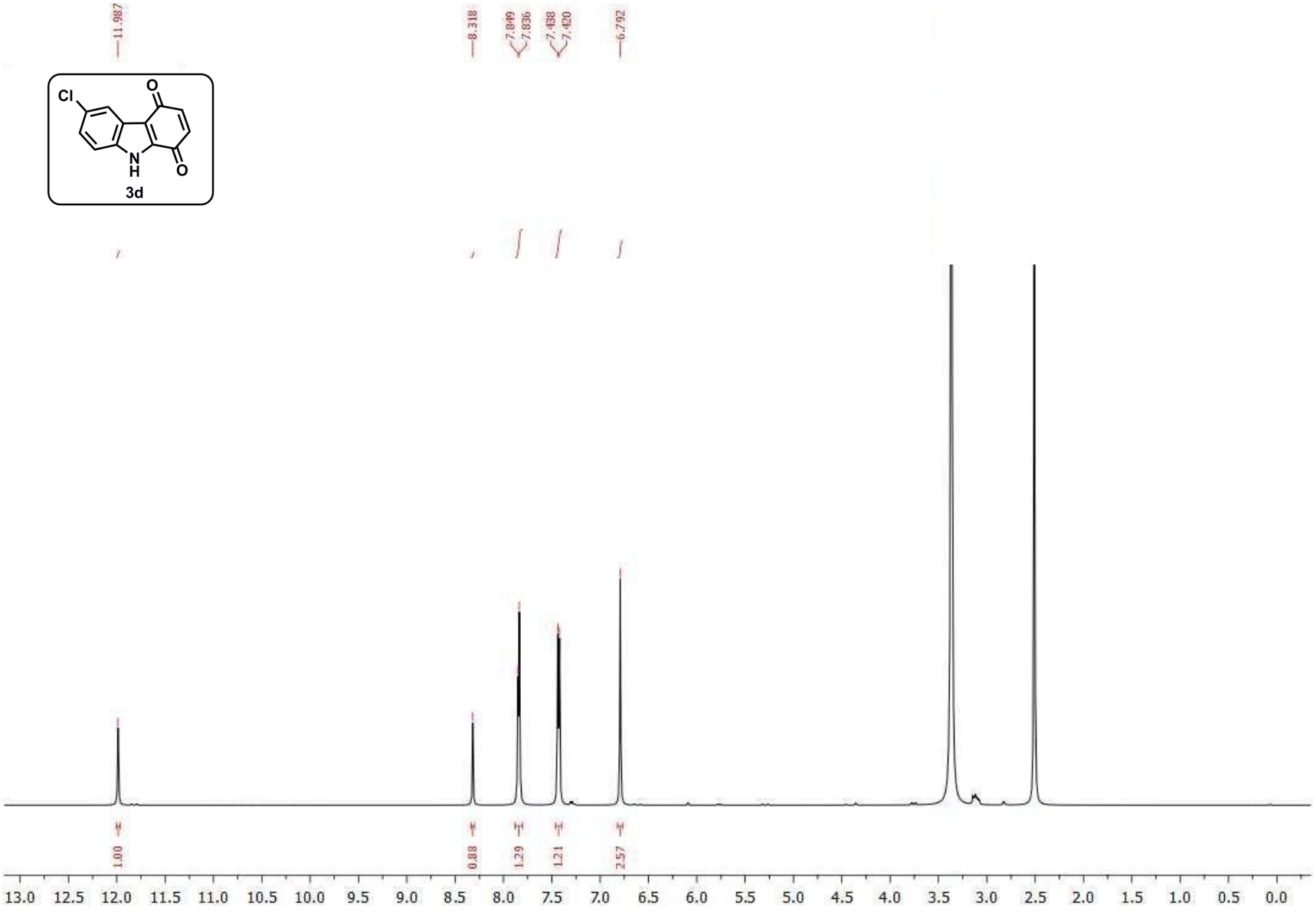
70
60
50
40
30
20
10
0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H
O
3d
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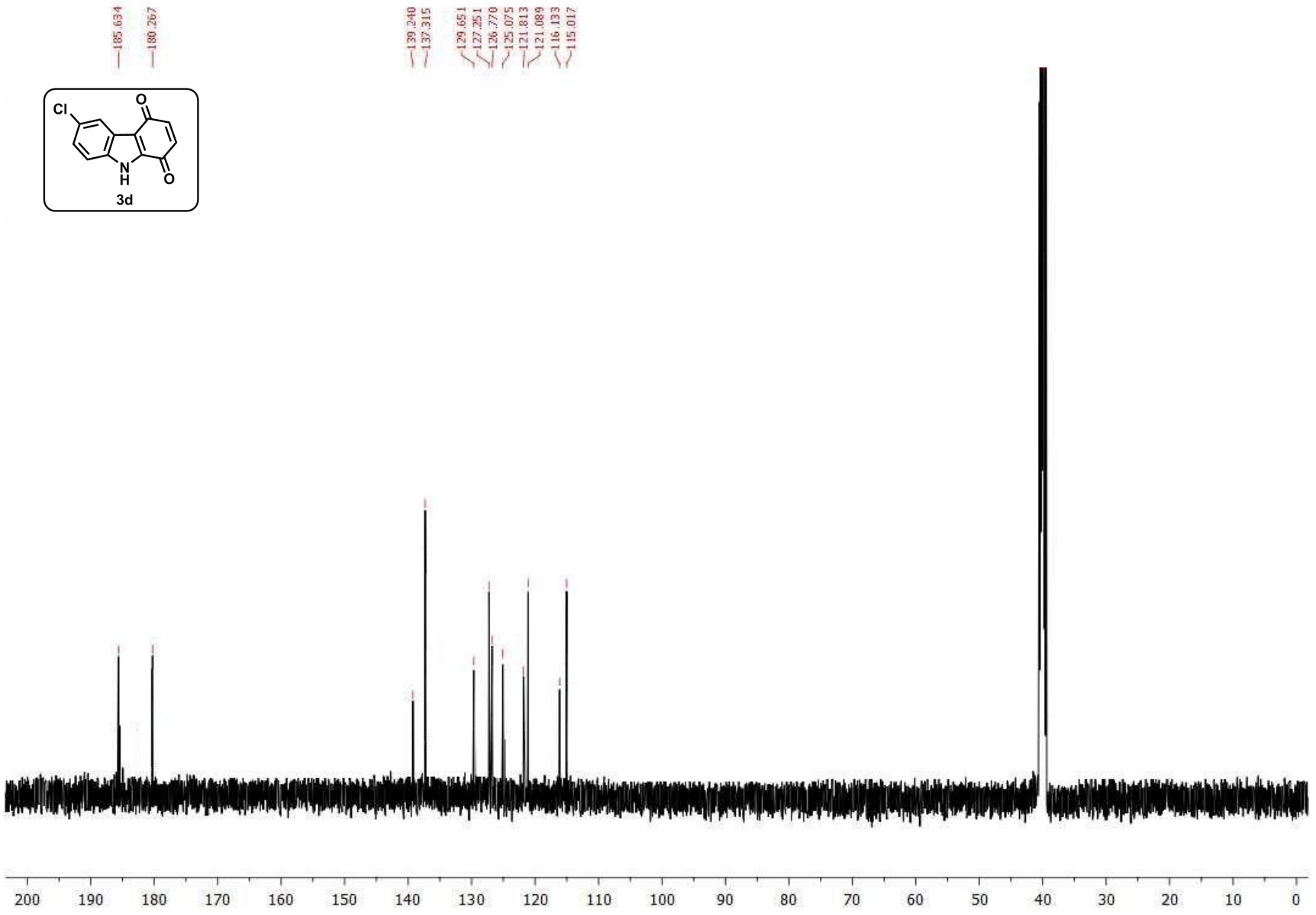
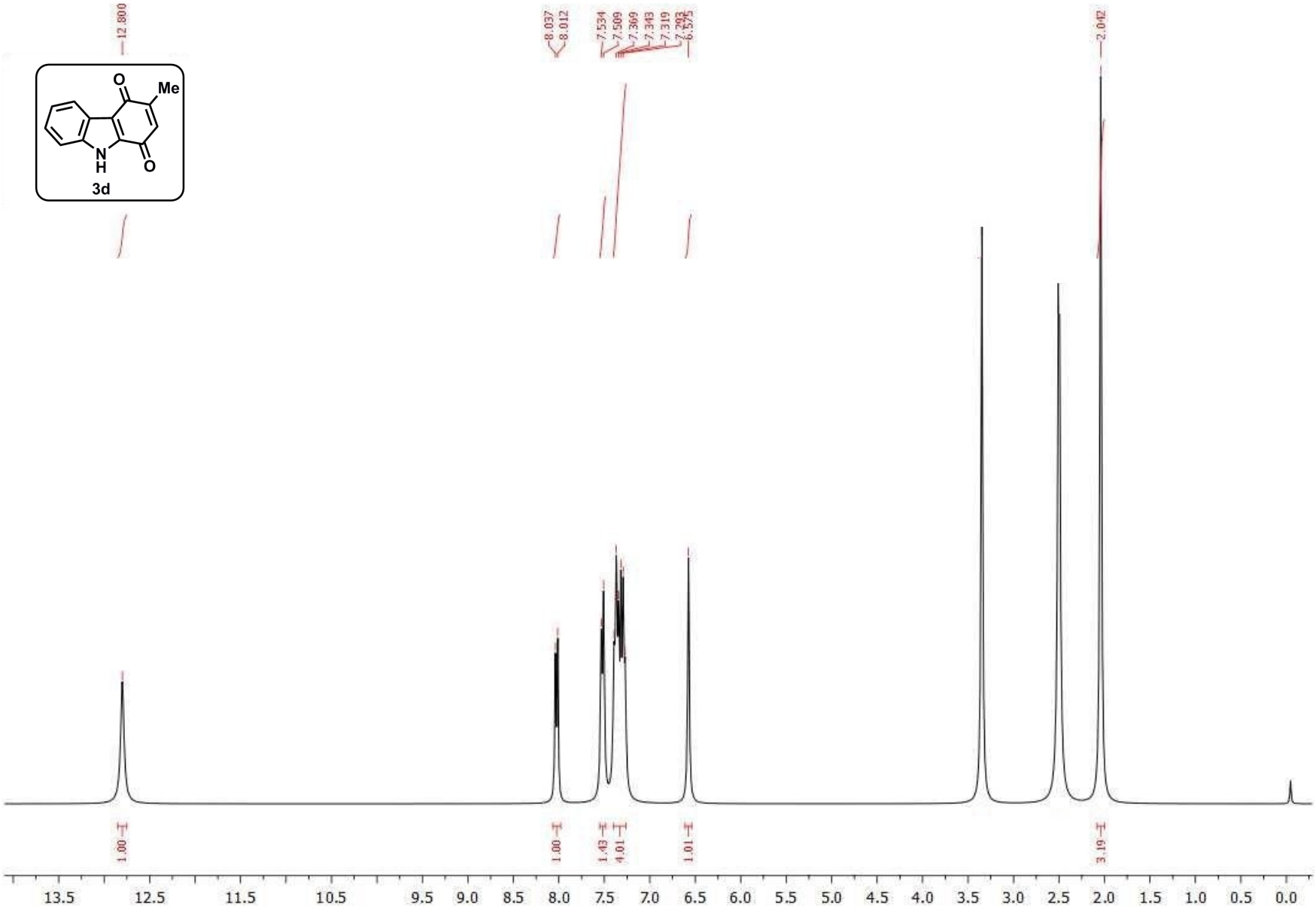
0.88
1.29
1.21
2.57
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


185.634
180.267
139.240
137.315
129.651
127.251
126.770
125.075
121.813
121.089
116.133
115.017
Cl
O
N
H
O
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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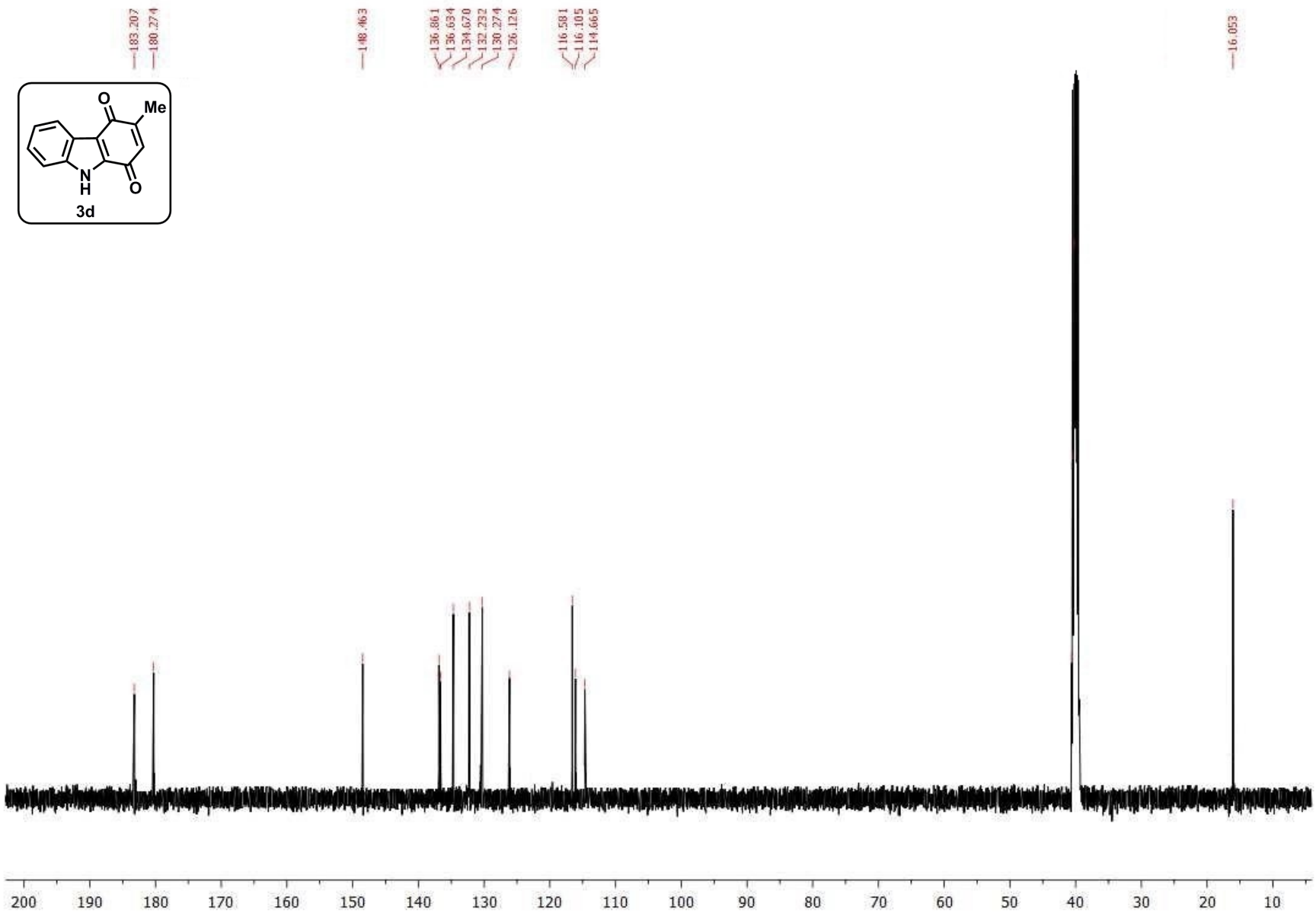
8.012
7.534
7.509
7.369
7.343
7.319
7.293
6.575
2.042
O
Me
N
H
O
3d
1.00
1.00
1.43
4.01
1.01
3.19
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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136.634
134.670
132.232
130.274
126.126
116.581
116.105
114.665
16.053
O
Me
N
H
O
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

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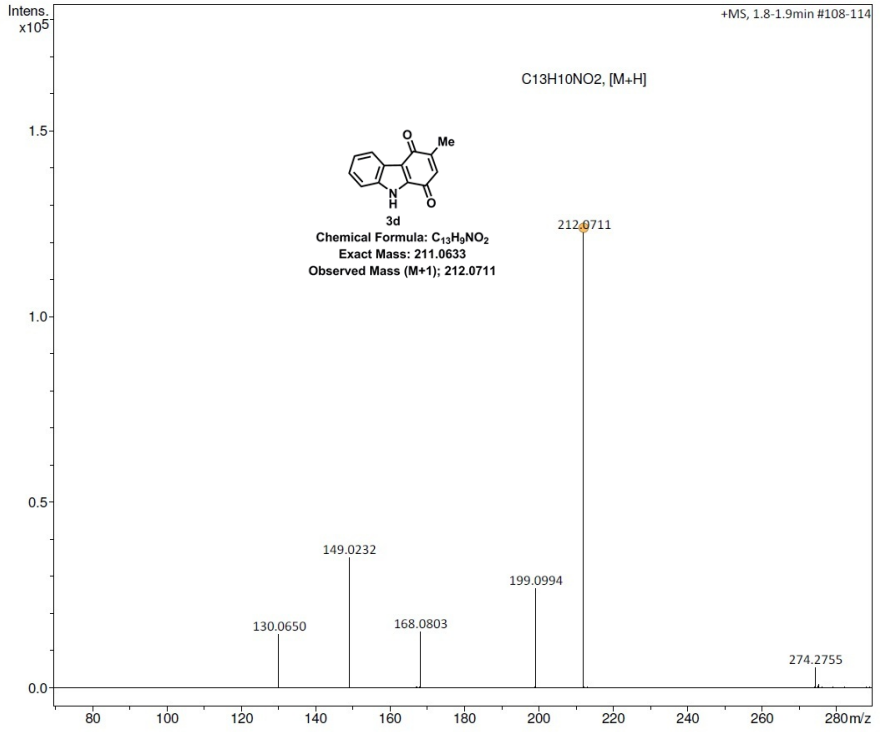
Analysis Info

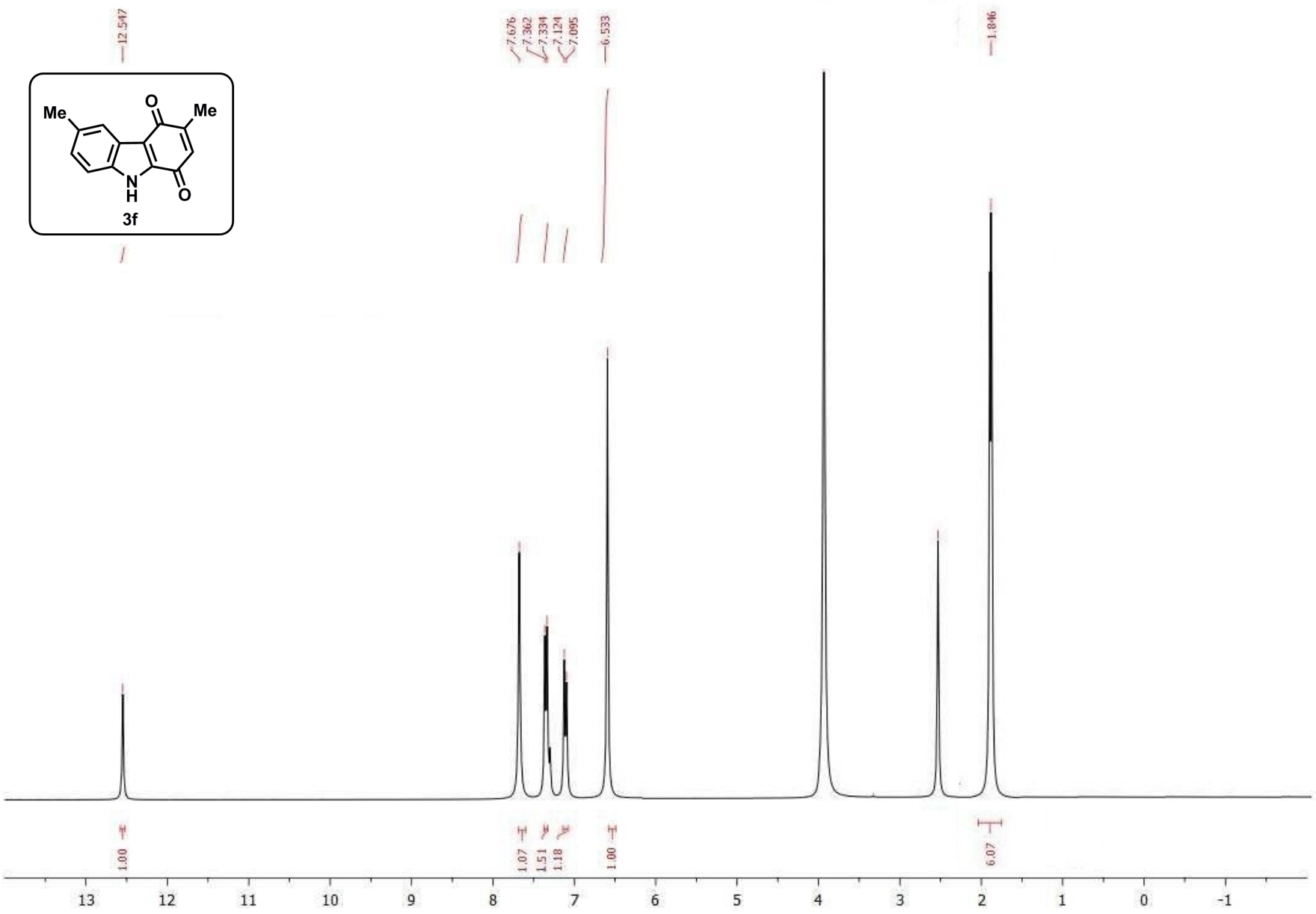
Analysis Name	D:\Data\2016\JUNE\SPPU\CHEMISTRY\PD LOKHANDE\MAHAVIR\MS -21_BC1_01_2814.d	Acquisition Date	6/7/2016 7:10:08 PM
Method	dlc-ms350mz_10min_90b.m	Operator	CIF
Sample Name	MS -21	Instrument	impact HD 1819696.00184
Comment			

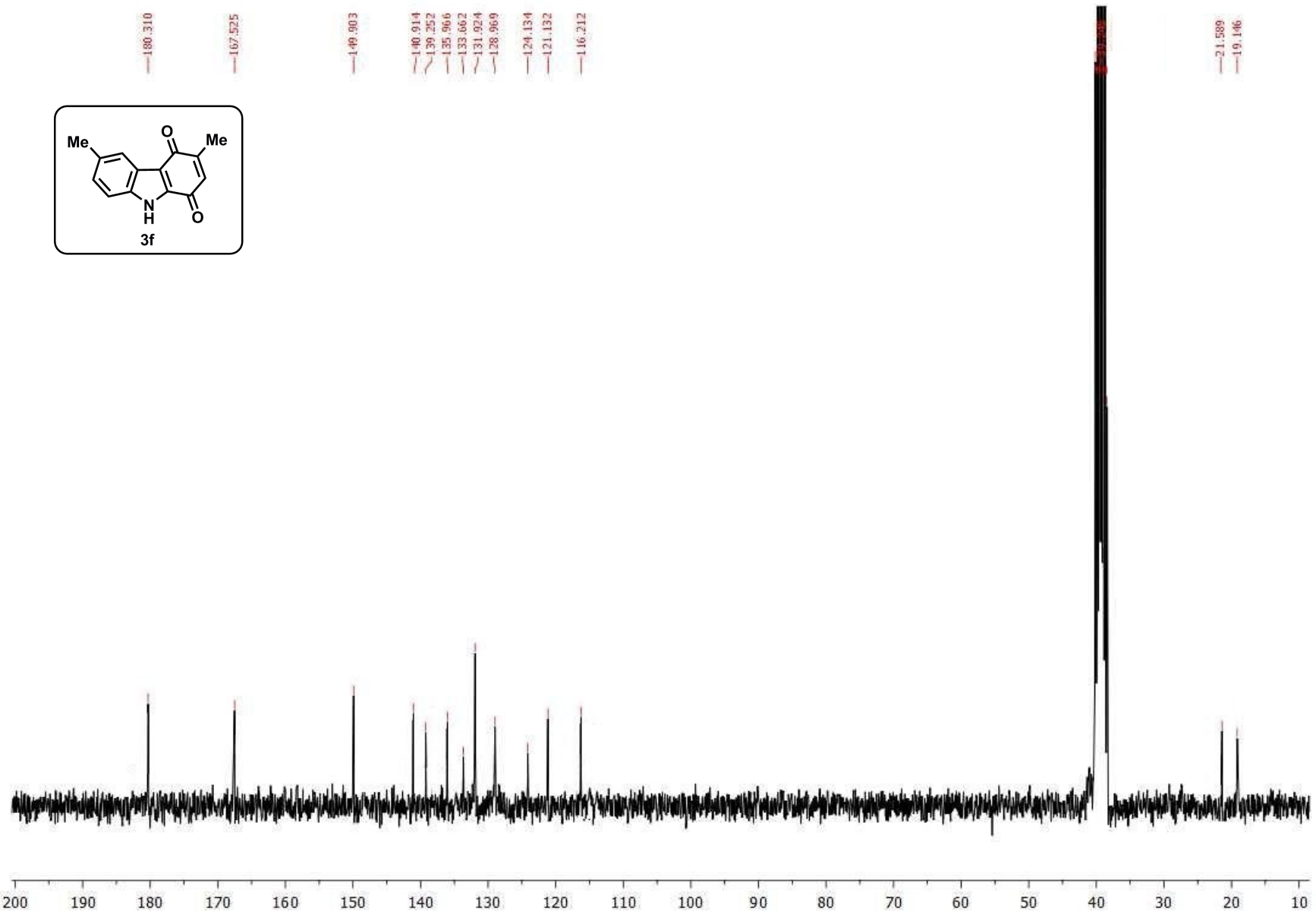
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
212.0711	1	C13H10NO2	212.0706	-2.5	4.8	1	100.00	9.5	even	ok	M+H


12.547
7.676
7.362
7.334
7.124
7.095
6.533
1.846
Me
Me
O
O
N
H
3f
1.00
1.07
1.51
1.18
1.00
6.07
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1


180.310
167.525
149.903
140.914
139.252
135.966
133.662
131.924
128.969
124.134
121.132
116.212
21.589
19.146
Me
Me
O
O
N
H
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

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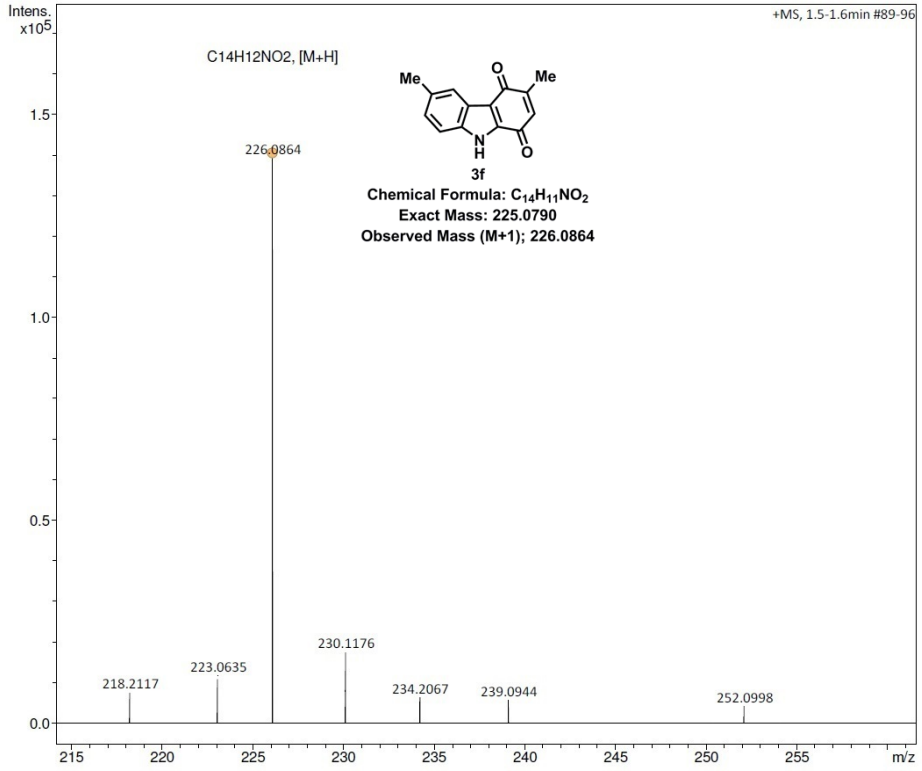
Analysis Info

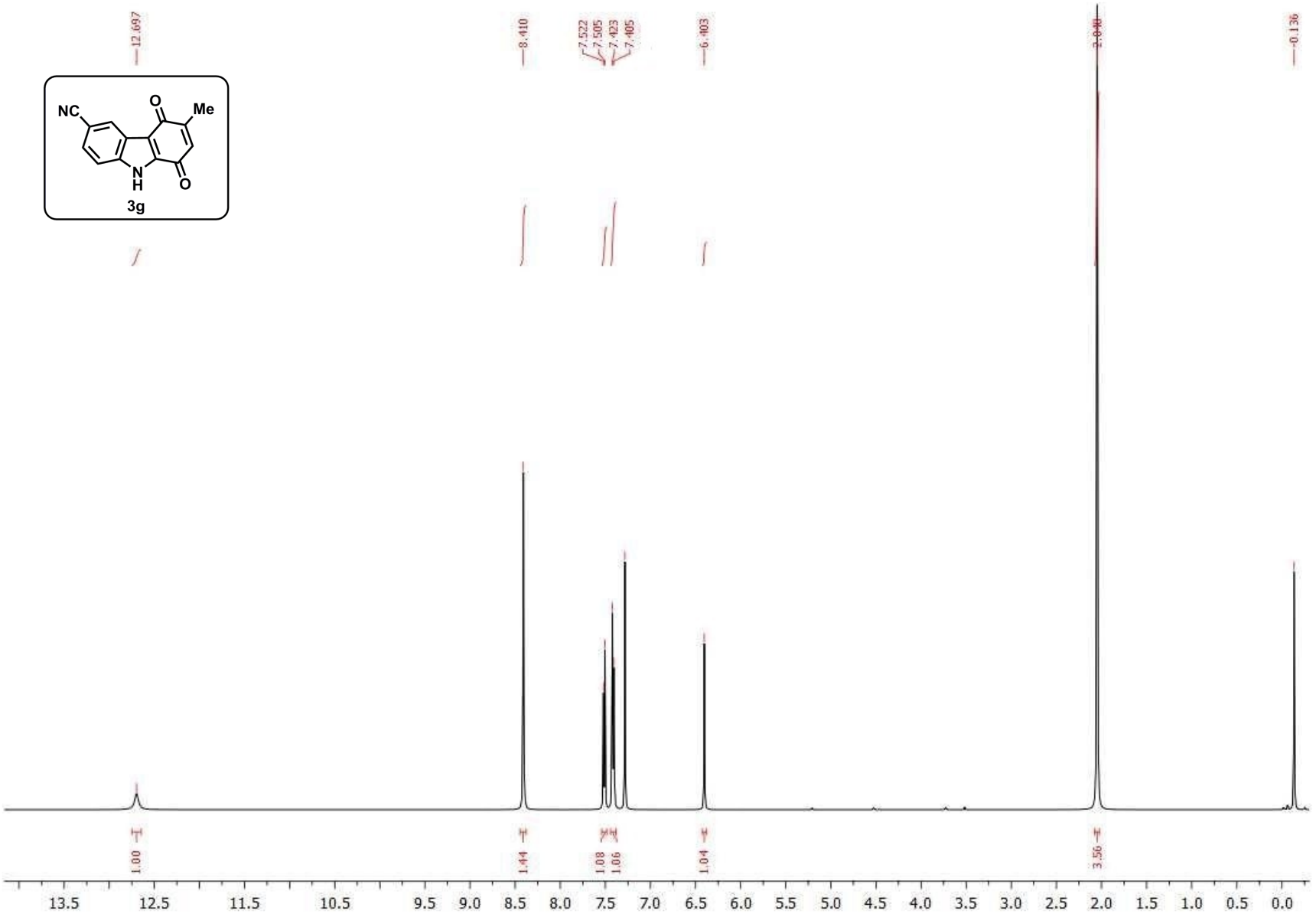
Analysis Name	D:\Data\2016\JUNE\SPPU\CHEMISTRY\PD LOKHANDE\MAHAVIR\MS -24_BC4_01_2817.d	Acquisition Date	6/7/2016 7:42:18 PM
Method	dlc-ms350mz_10min_90b.m	Operator	CIF
Sample Name	MS -24	Instrument	impact HD 1819696.00184
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
226.0864	1	C14H12NO2	226.0863	-0.5	15.4	1	100.00	9.5	even	ok	M+H


12.697
8.410
7.522
7.505
7.423
7.405
6.403
3.040
-0.136
NC
O
Me
N
H
O
3g
1.00
1.44
1.08
1.06
1.04
3.56
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
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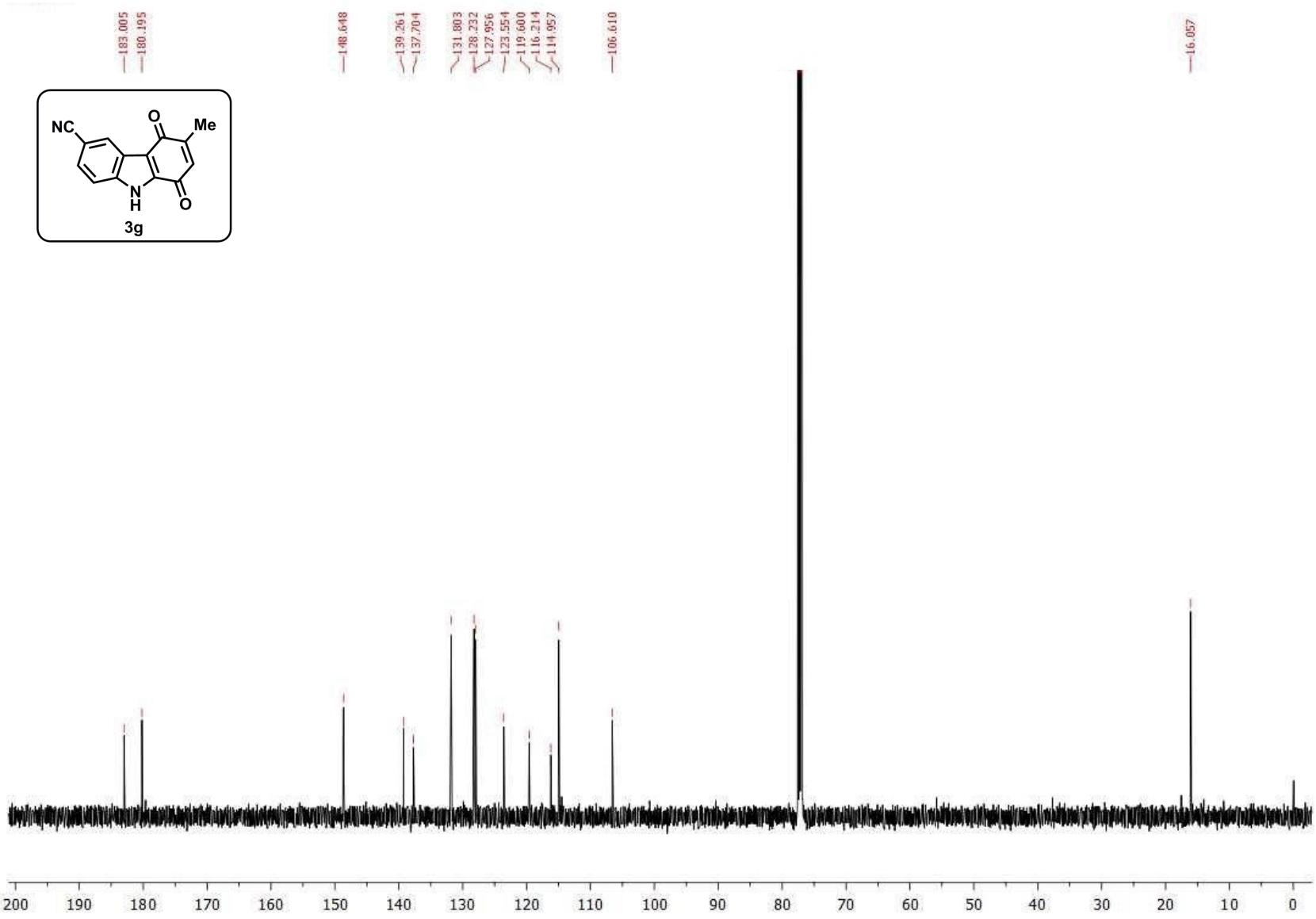
0.0


183.005
180.195
148.648
139.261
137.704
131.803
128.232
127.956
123.554
119.600
116.214
114.957
106.610
16.057
NC
O
Me
N
H
O
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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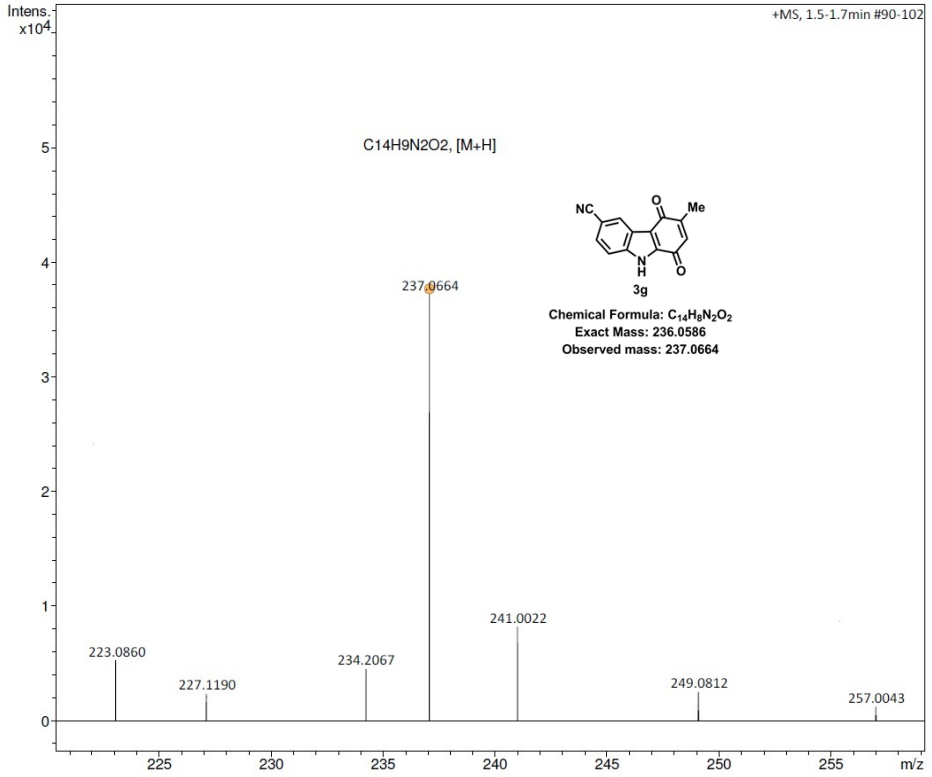
Analysis Info

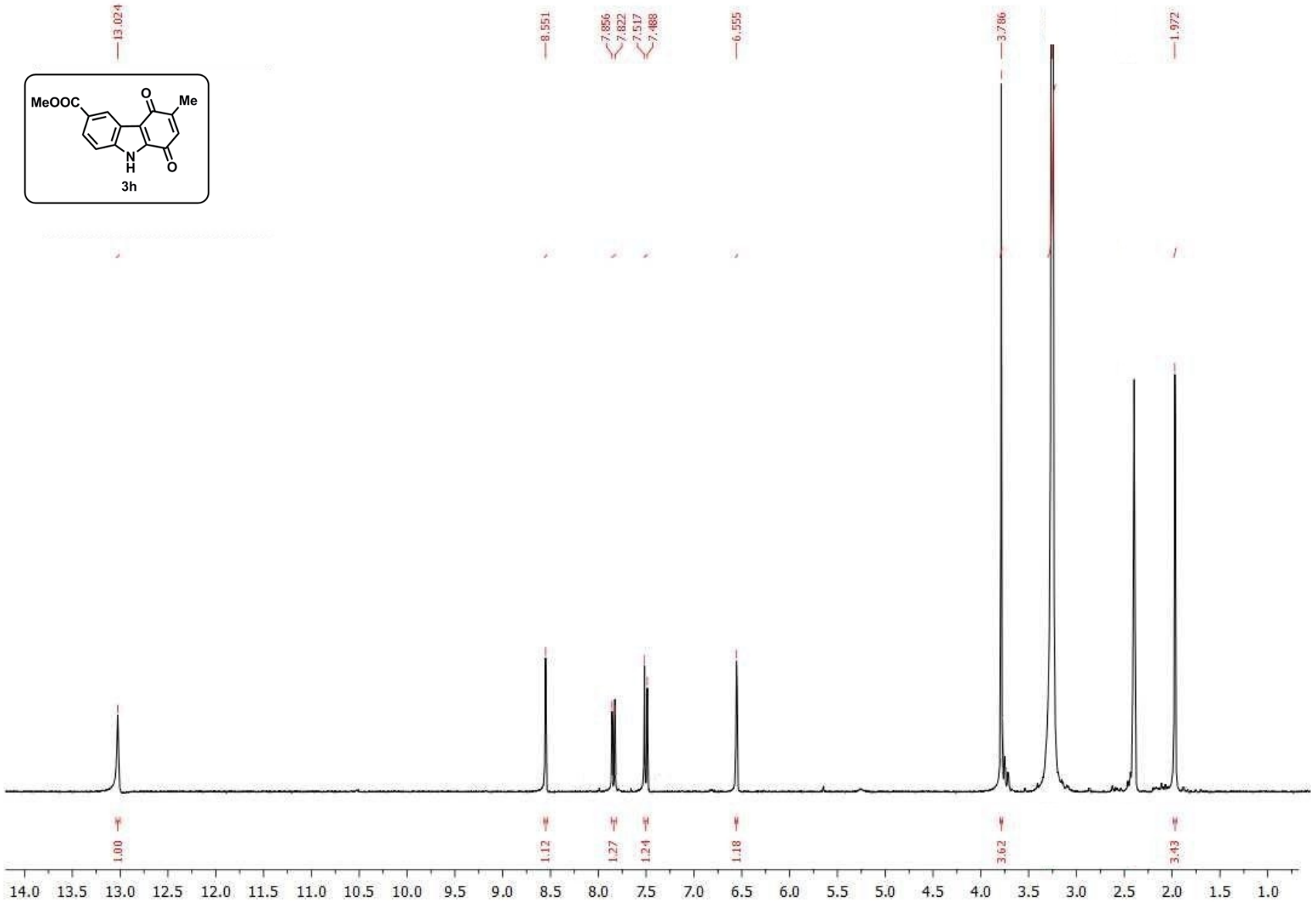
Analysis Name	D:\Data\2016\JUNE\SPPU\CHEMISTRY\PD LOKHANDE\MAHAVIR\MS -22_BC2_01_2804.d	Acquisition Date	6/6/2016 8:39:13 PM
Method	dlc-ms350mz_10min_90b.m	Operator	CIF
Sample Name	MS -22	Instrument	impact HD 1819696.00184
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
237.0664	1	C14H9N2O2	237.0659	-2.4	27.3	1	100.00	11.5	even	ok	M+H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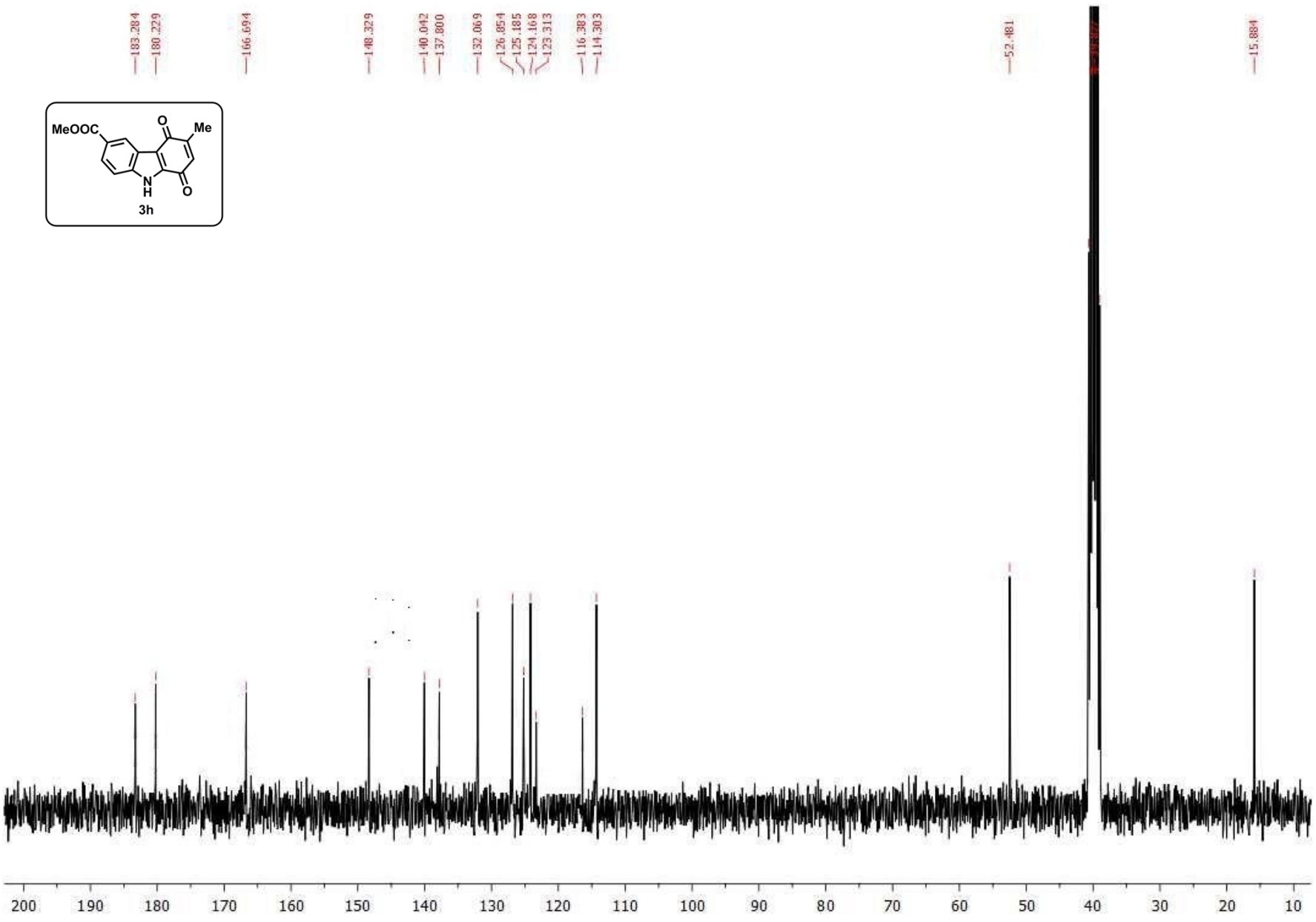
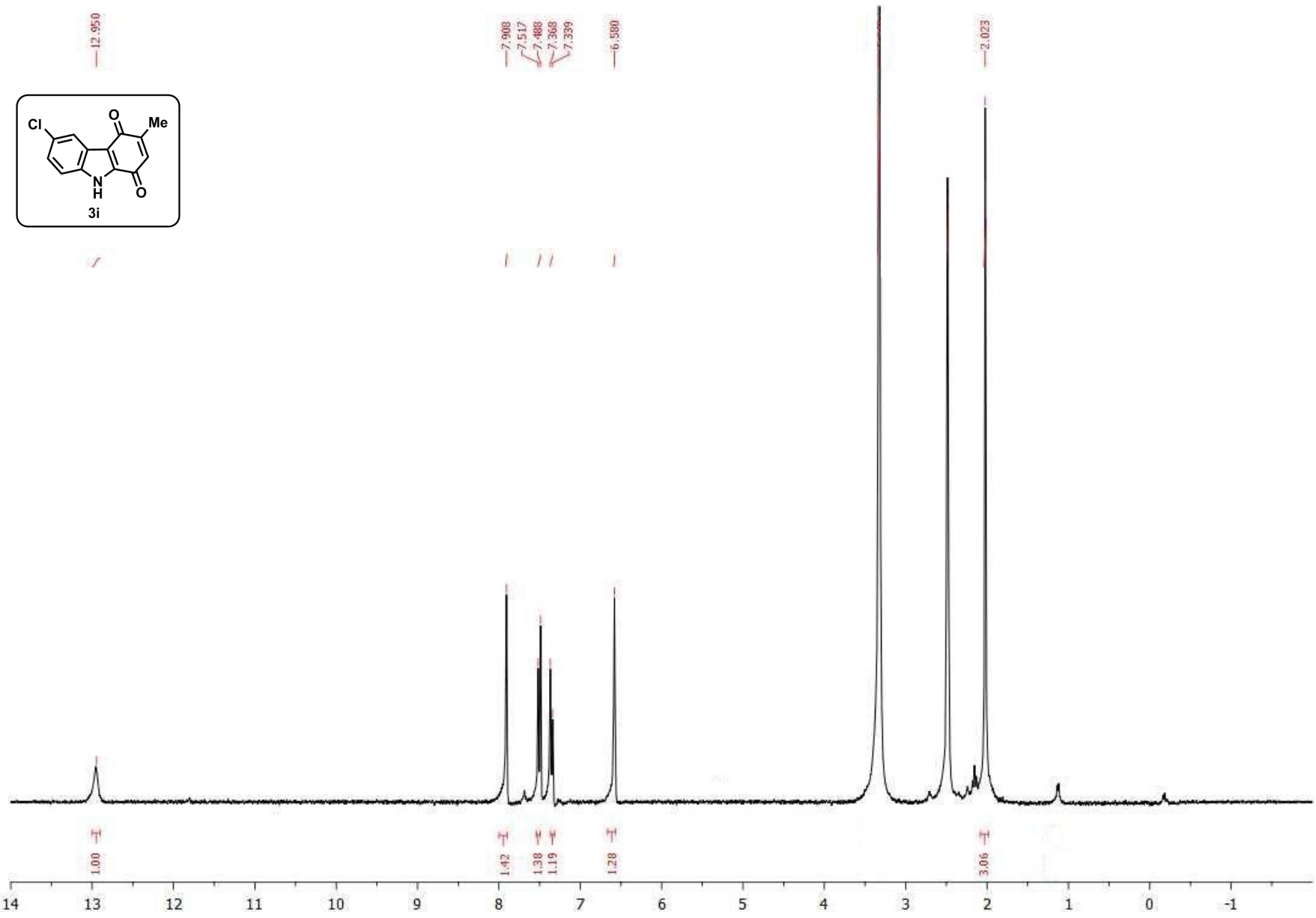
7.822
7.517
7.488
6.555
3.786
1.972
MeOOC
Me
O
N
H
O
3h
1.00
1.12
1.27
1.24
1.18
3.62
3.43
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0


183.284
180.229
166.694
148.329
140.042
137.800
132.069
126.854
125.185
124.168
123.313
116.383
114.303
52.481
15.884
MeOOC
Me
O
O
N
H
3h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.517
7.488
7.368
7.339
6.580
2.023
Cl
O
Me
N
H
O
3i
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1.42
1.38
1.19
1.28
3.06
14
13
12
11
10
9
8
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6
5
4
3
2
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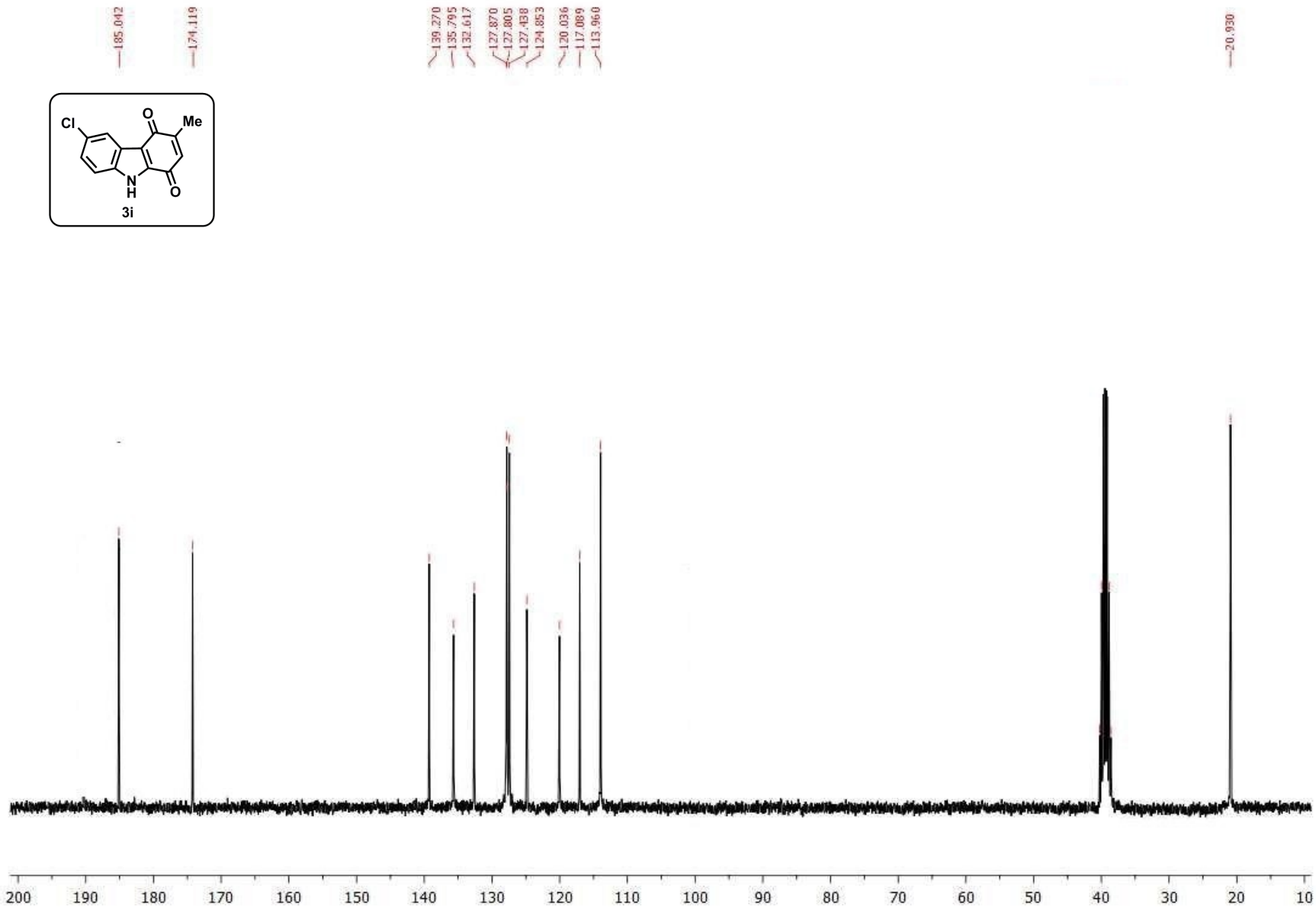
0
-1


185.042
174.119
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135.795
132.617
127.870
127.805
127.438
124.853
120.036
117.089
113.960
20.930
Cl
O
Me
N
H
O
3i
200
190
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160
150
140
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120
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100
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80
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20
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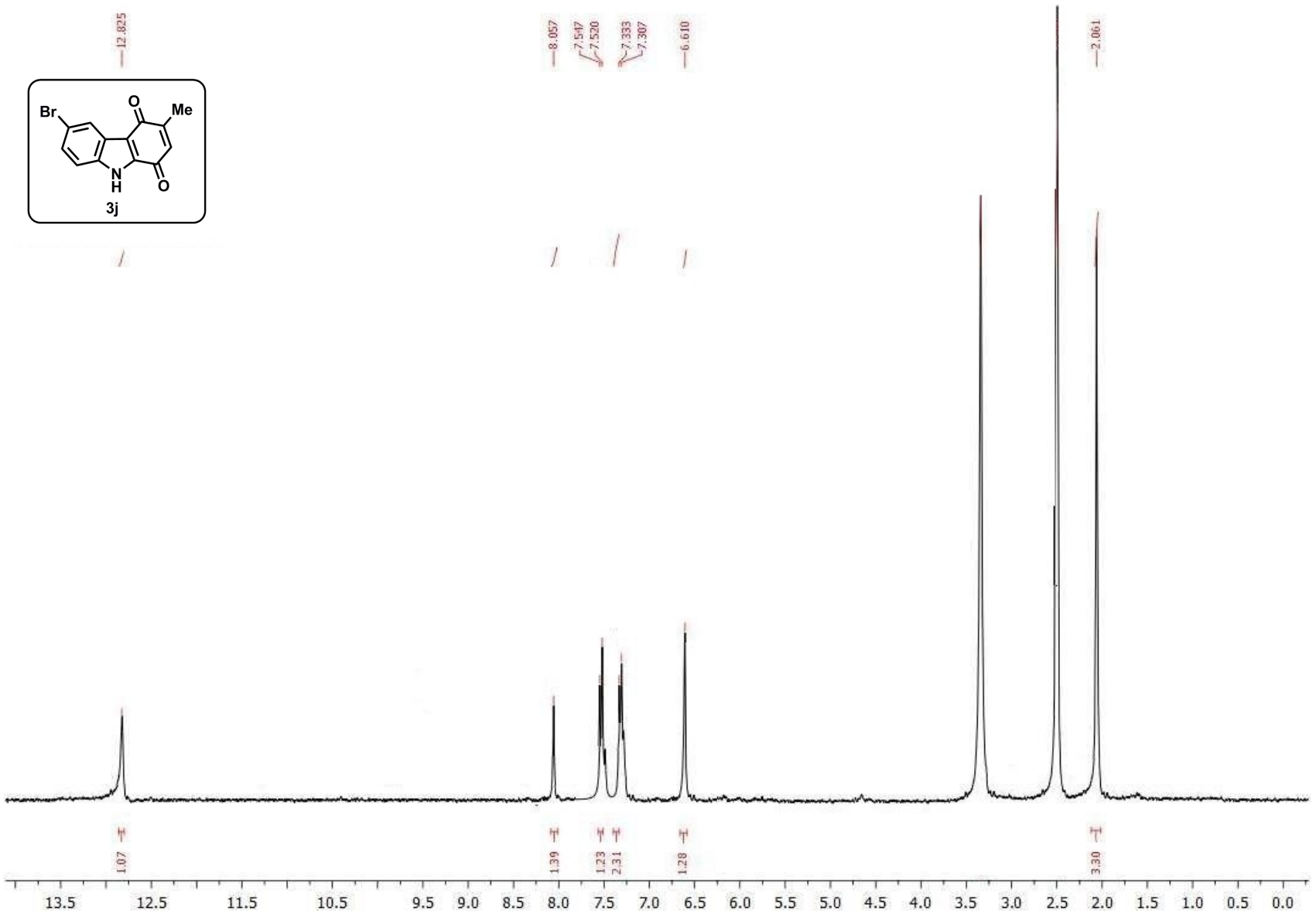
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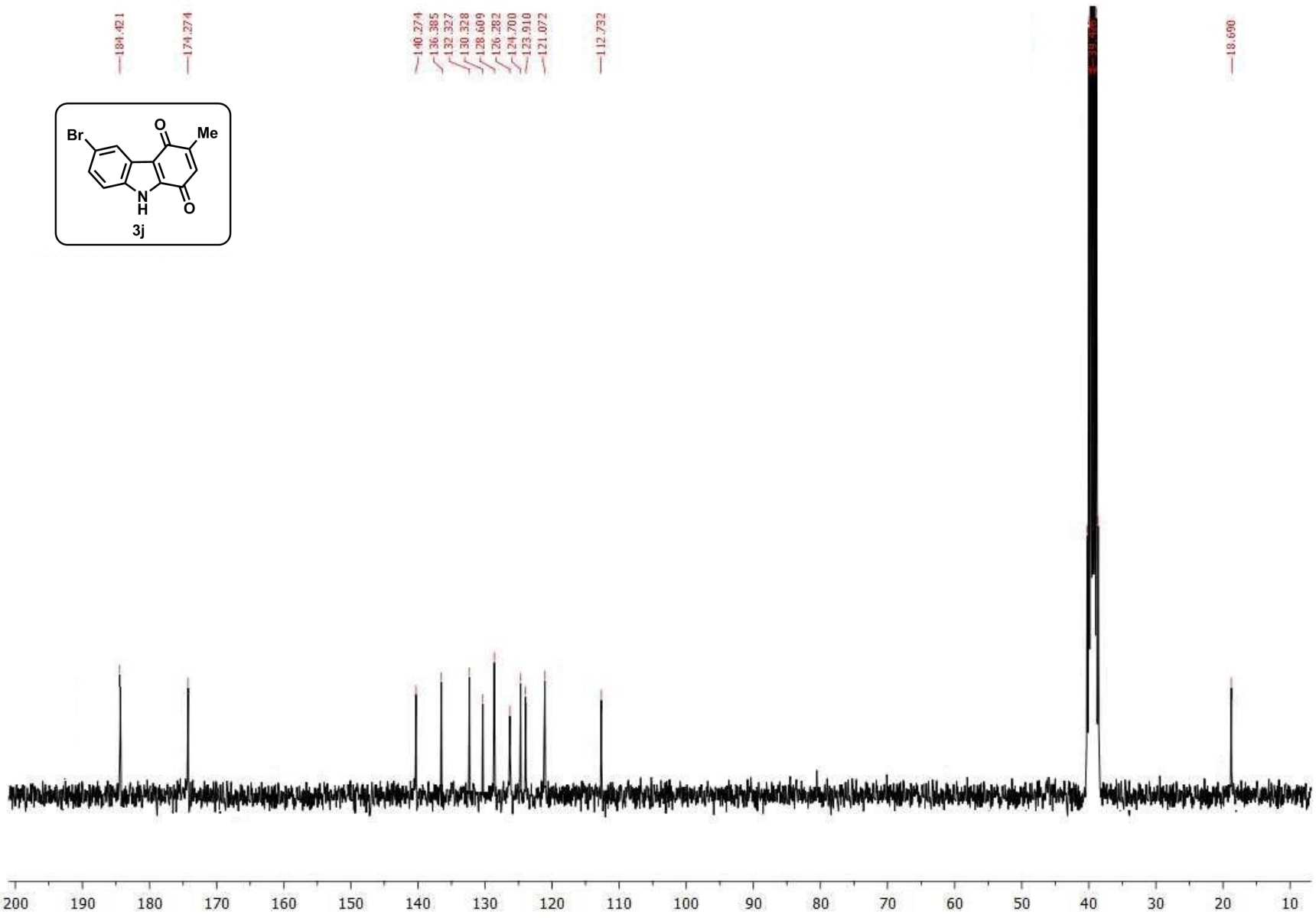
7.333
7.307
6.610
2.061
Br
O
Me
N
H
O
3j
1.07
1.39
1.23
2.31
1.28
3.30
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


184.421
174.274
140.274
136.385
132.327
130.328
128.609
126.282
124.700
123.910
121.072
112.732
18.690
Br
O
Me
N
H
O
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

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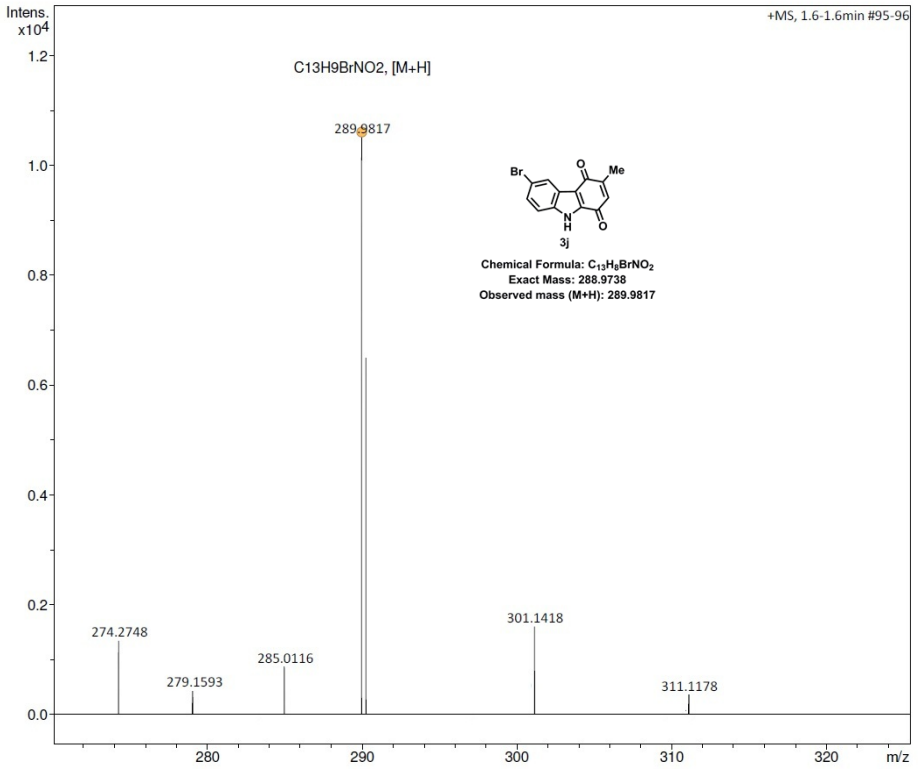
Analysis Info

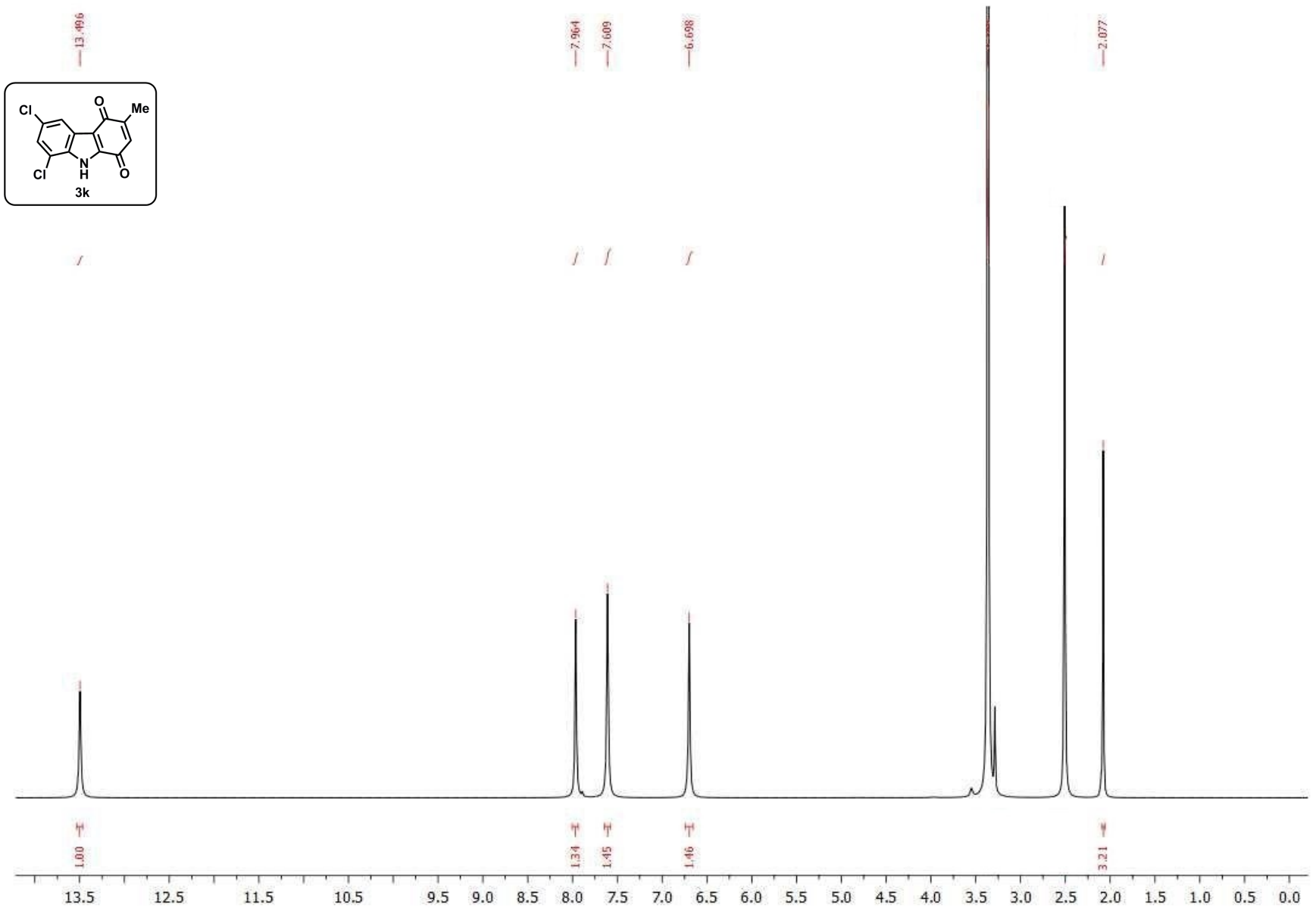
Analysis Name	D:\Data\2016\JUNE\SPPU\CHEMISTRY\PD LOKHANDE\MAHAVIR\MS -23_BC3_01_2816.d	Acquisition Date	6/7/2016 7:31:35 PM
Method	dlc-ms350mz_10min_90b.m	Operator	CIF
Sample Name	MS -23	Instrument	impact HD 1819696.00184
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
289.9817	1	C13H9BrNO2	289.9811	-2.1	44.0	1	100.00	9.5	even	ok	M+H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7.964
7.609
6.698
2.077
Cl
O
Me
Cl
N
H
O
3k
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1.34
1.45
1.46
3.21
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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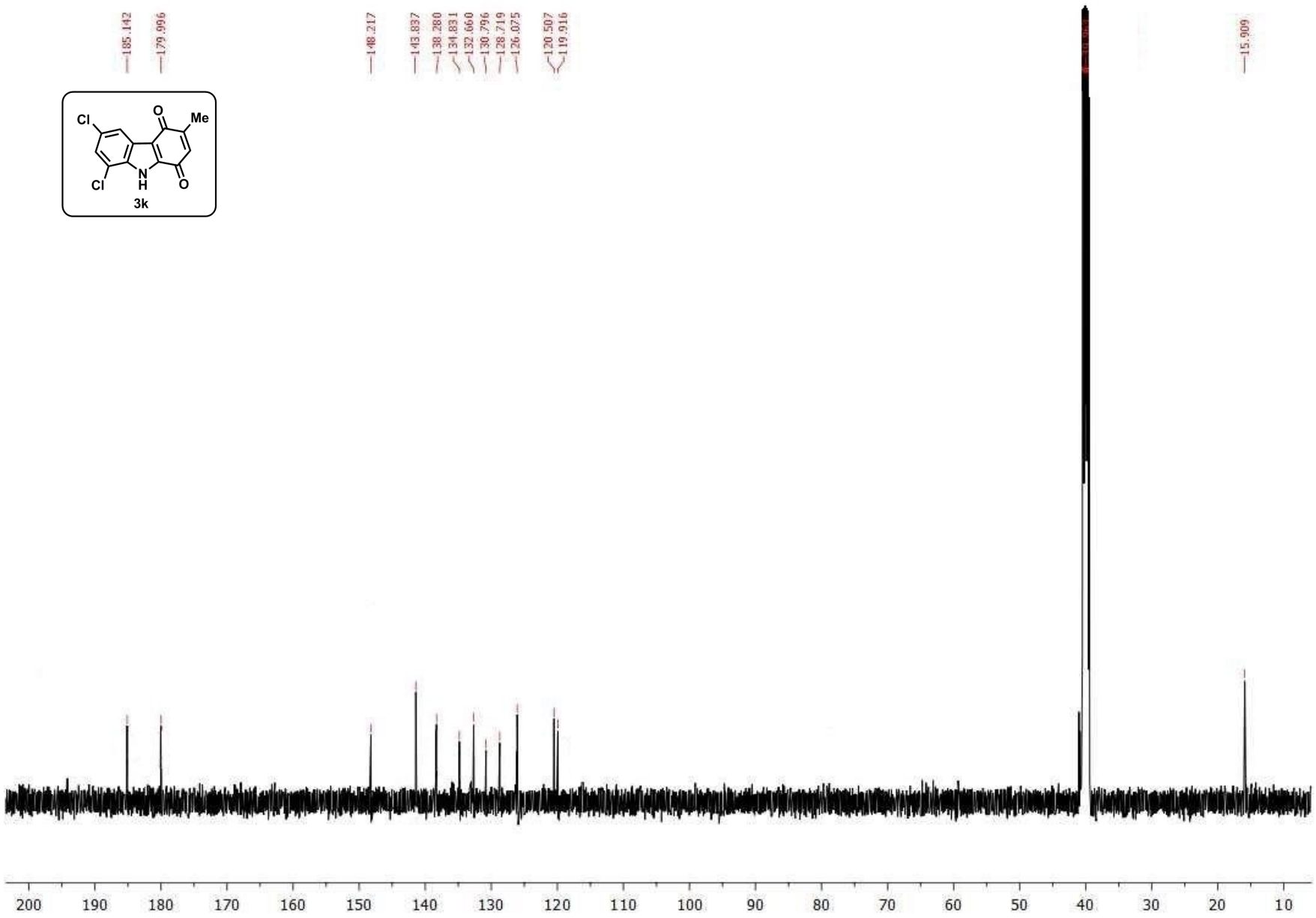
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119.916
15.909
Cl
O
Me
Cl
N
H
O
3k
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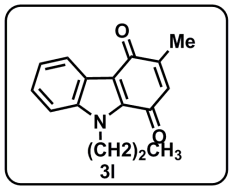
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(CH2)2CH3
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7.595
7.590
7.573
7.568
6.627
6.623
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4.537
4.519
2.053
2.049
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1.766
1.748
1.730
1.712
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0.850
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1.00
1.08
1.87
1.26
2.31
3.07
2.03
3.25
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9.0
8.5
8.0
7.5
7.0
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6.0
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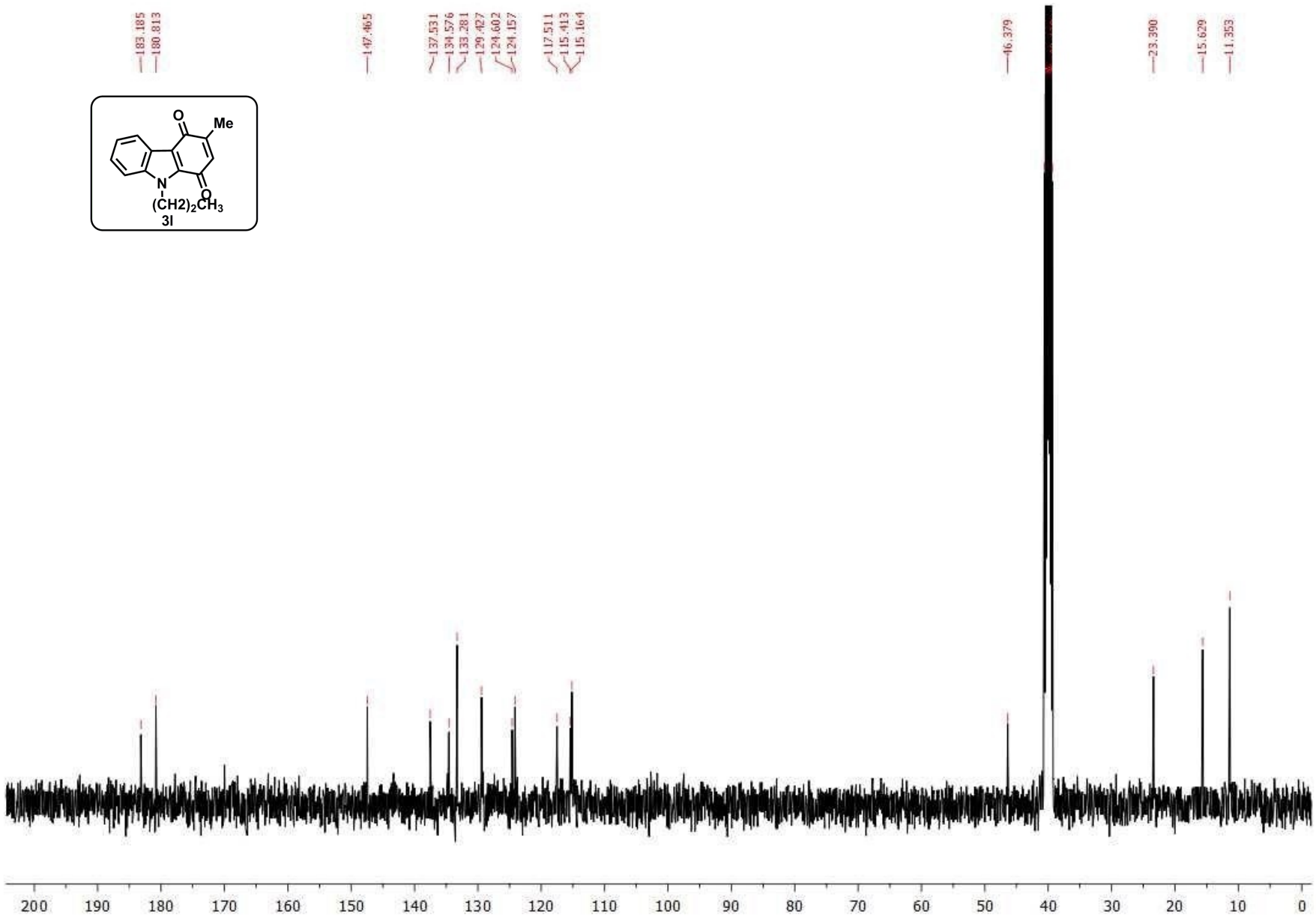
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124.602
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117.511
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46.379
23.390
15.629
11.353
O
Me
N
O
(CH2)2CH3
3l
200
190
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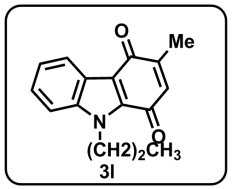
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Me
N
O
(CH2)2CH3
3l

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133.281
129.427
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115.164
46.379
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11.353
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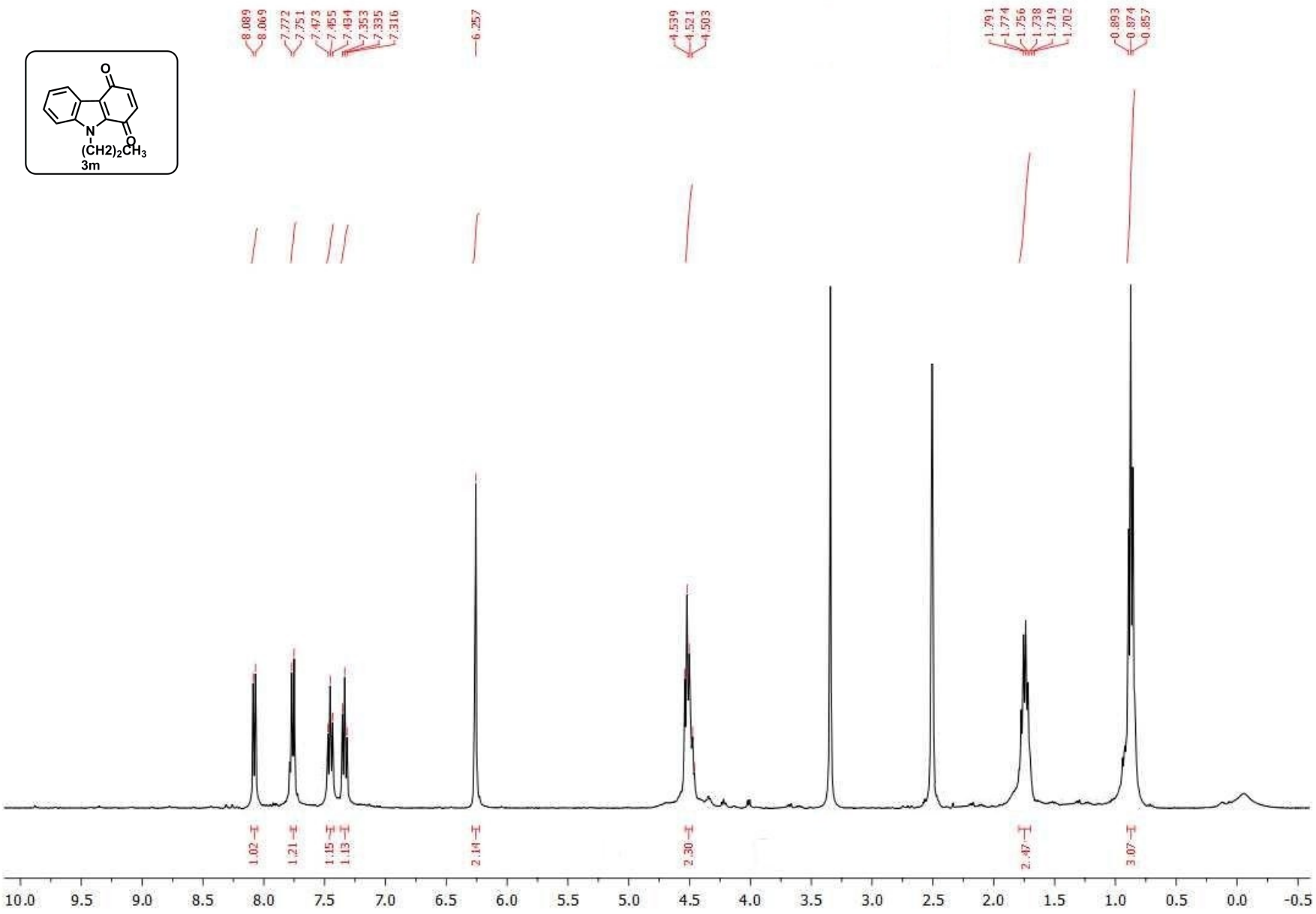
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4.503
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1.774
1.756
1.738
1.719
1.702
0.893
0.874
0.857
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N
O
(CH2)2CH3
3m
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1.21
1.15
1.13
2.14
2.30
2.47
3.07
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8.0
7.5
7.0
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6.0
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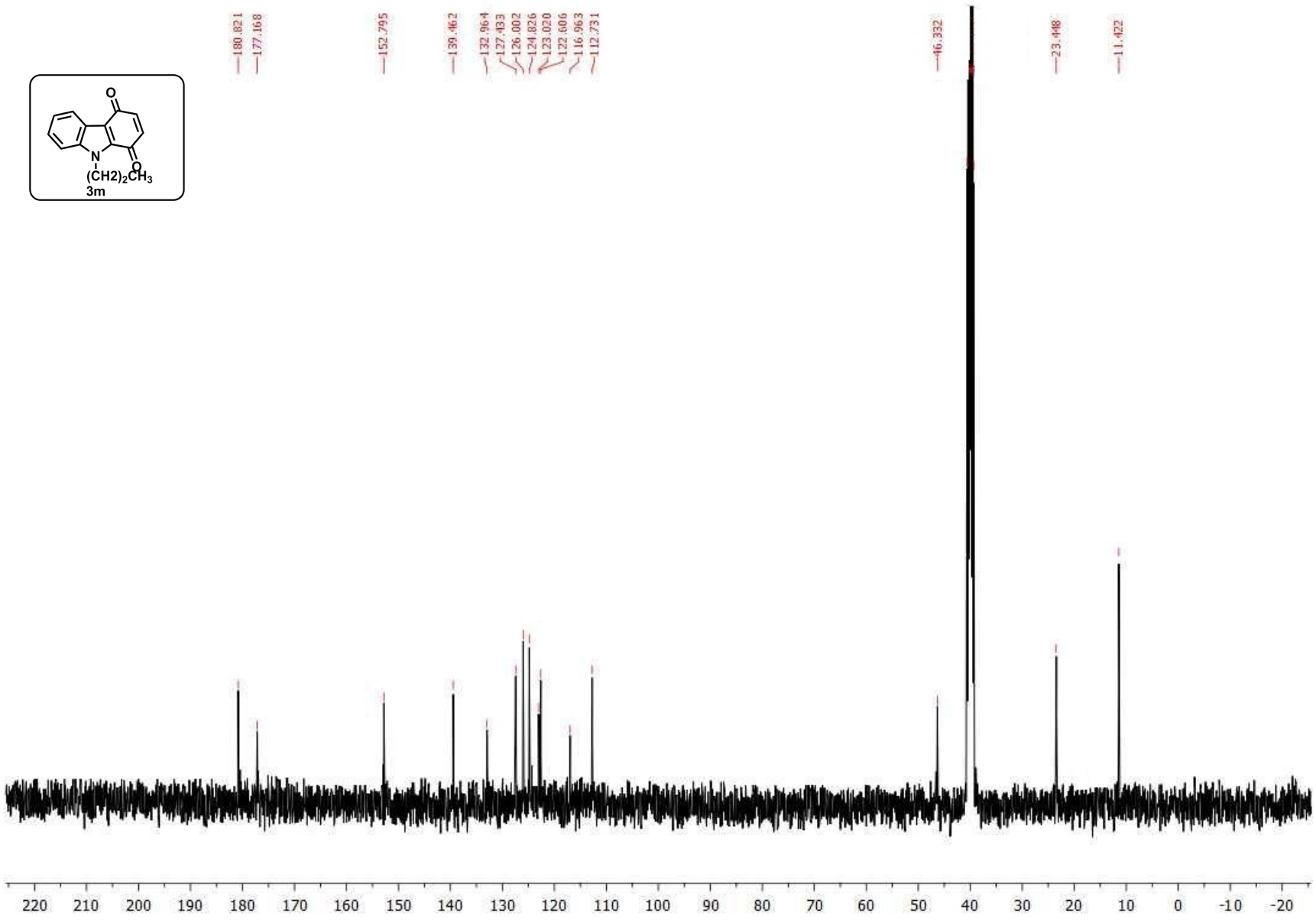
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123.020
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112.731
46.332
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O
(CH2)2CH3
3m
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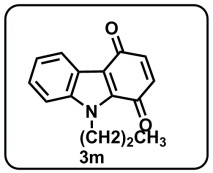
O
N
(CH2)2CH3
O
3m

127.433
126.002
124.826
123.020
122.606
112.731
46.332
23.448
11.422
200
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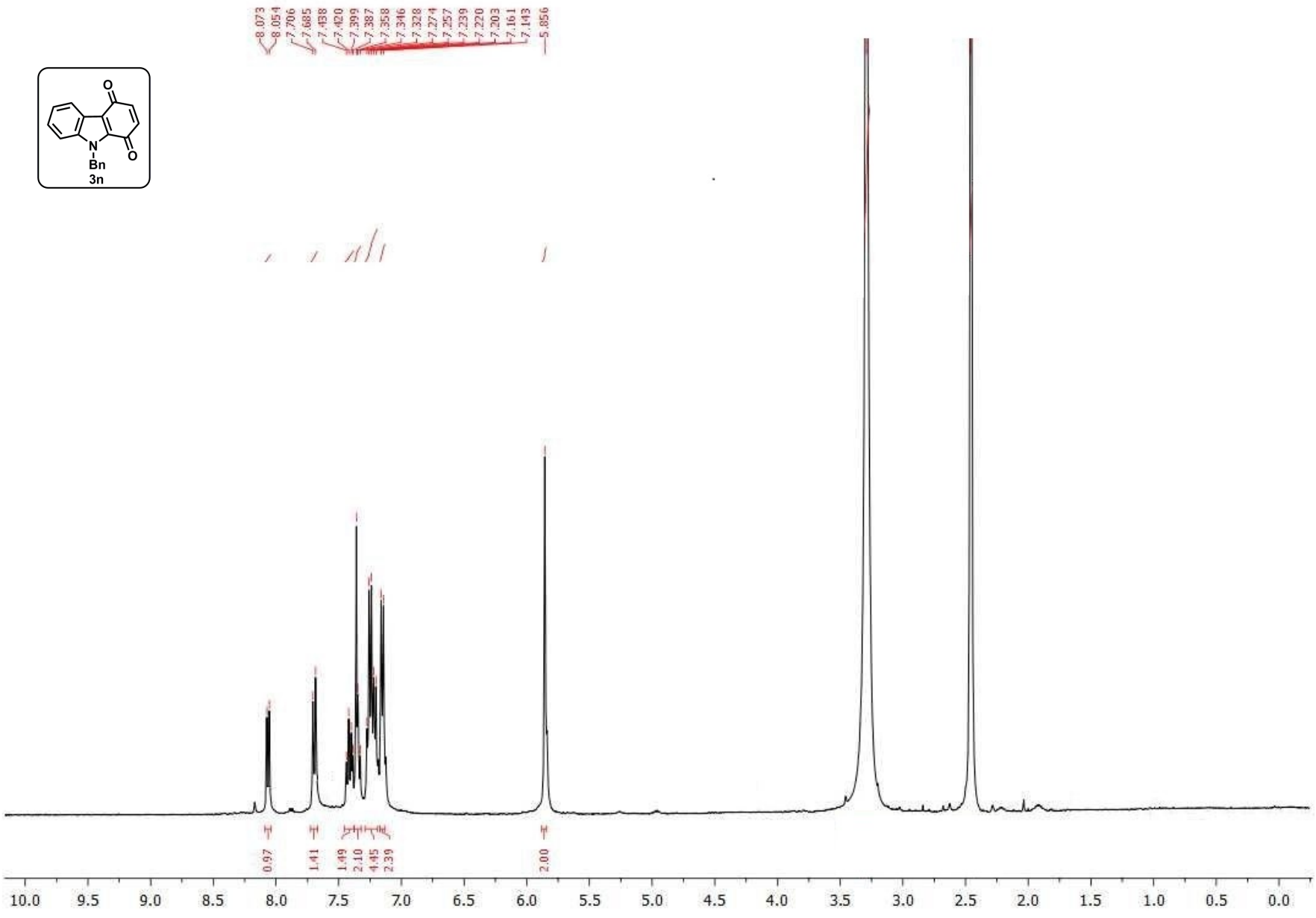
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7.257
7.239
7.220
7.203
7.161
7.143
5.856
O
N
Bn
O
3n
0.97
1.41
1.49
2.10
4.45
2.39
2.00
10.0
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9.0
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8.0
7.5
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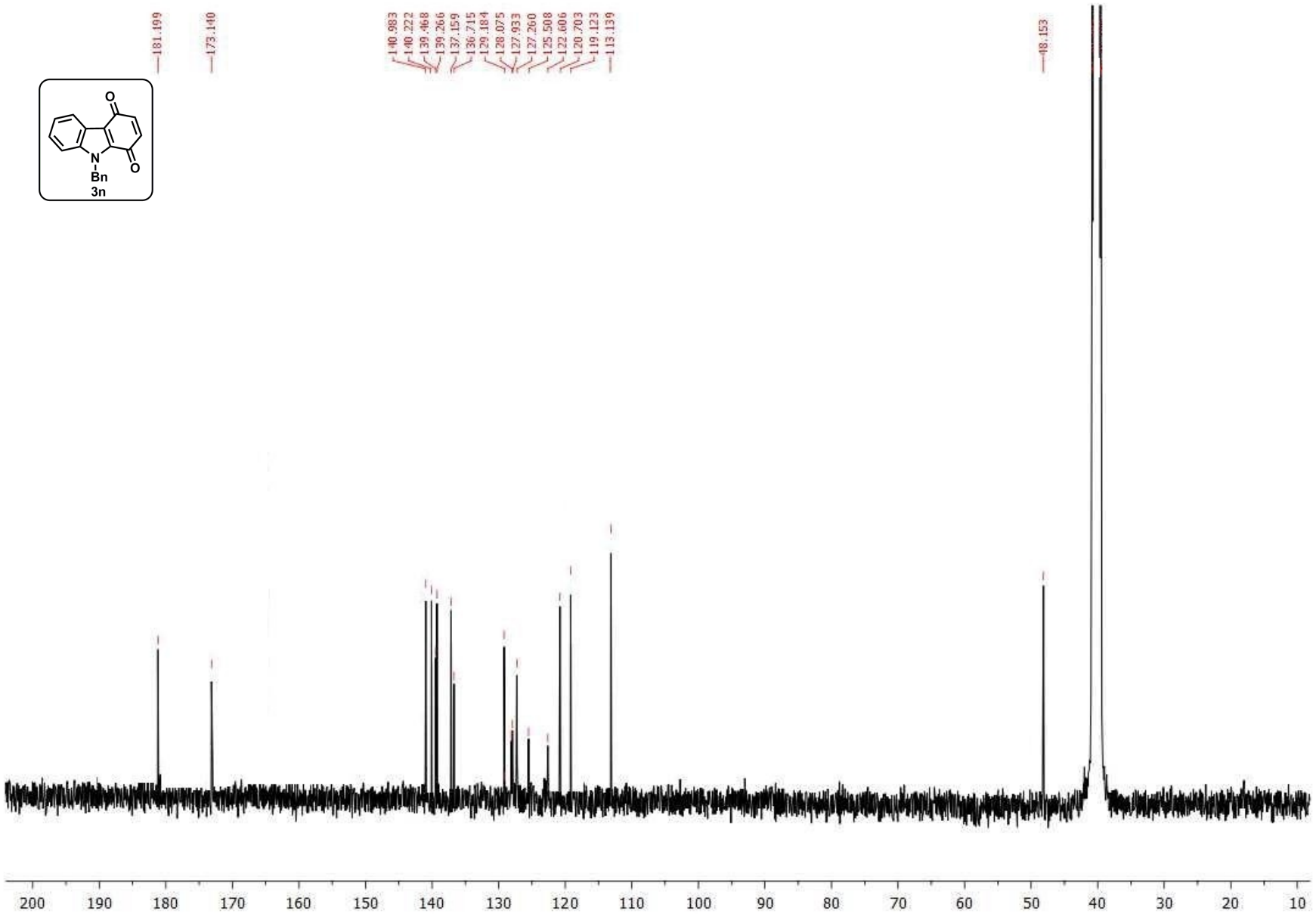
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136.715
129.184
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127.933
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125.508
122.606
120.703
119.123
113.139
48.153
O
O
N
Bn
3n
200
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180
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160
150
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120
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80
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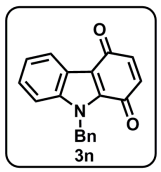
O
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Bn
O

3n

139.468
139.266
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125.508
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113.139
48.153
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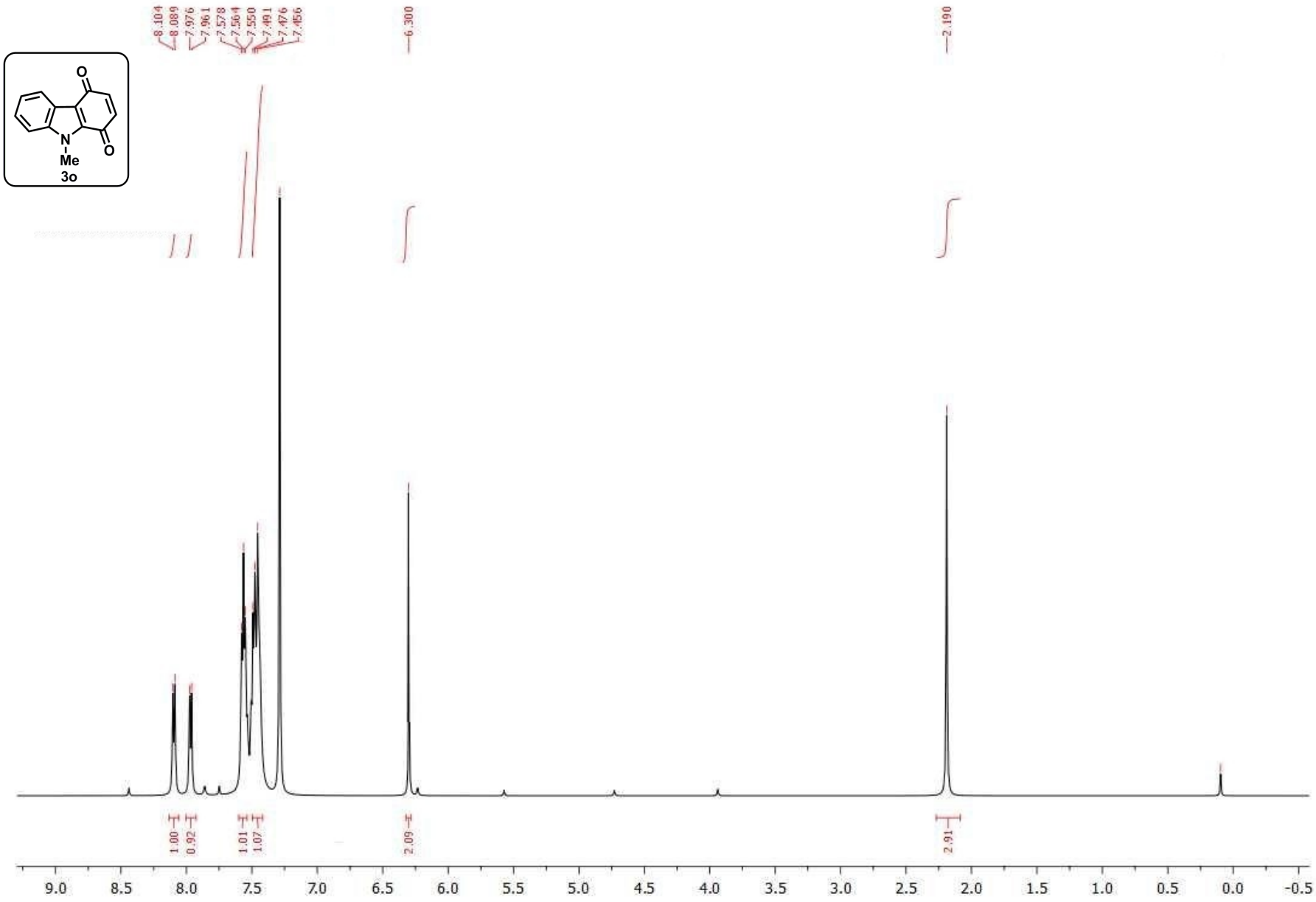
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7.491
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7.456
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O
O
N
Me
3o
1.00
0.92
1.01
1.07
2.09
2.91
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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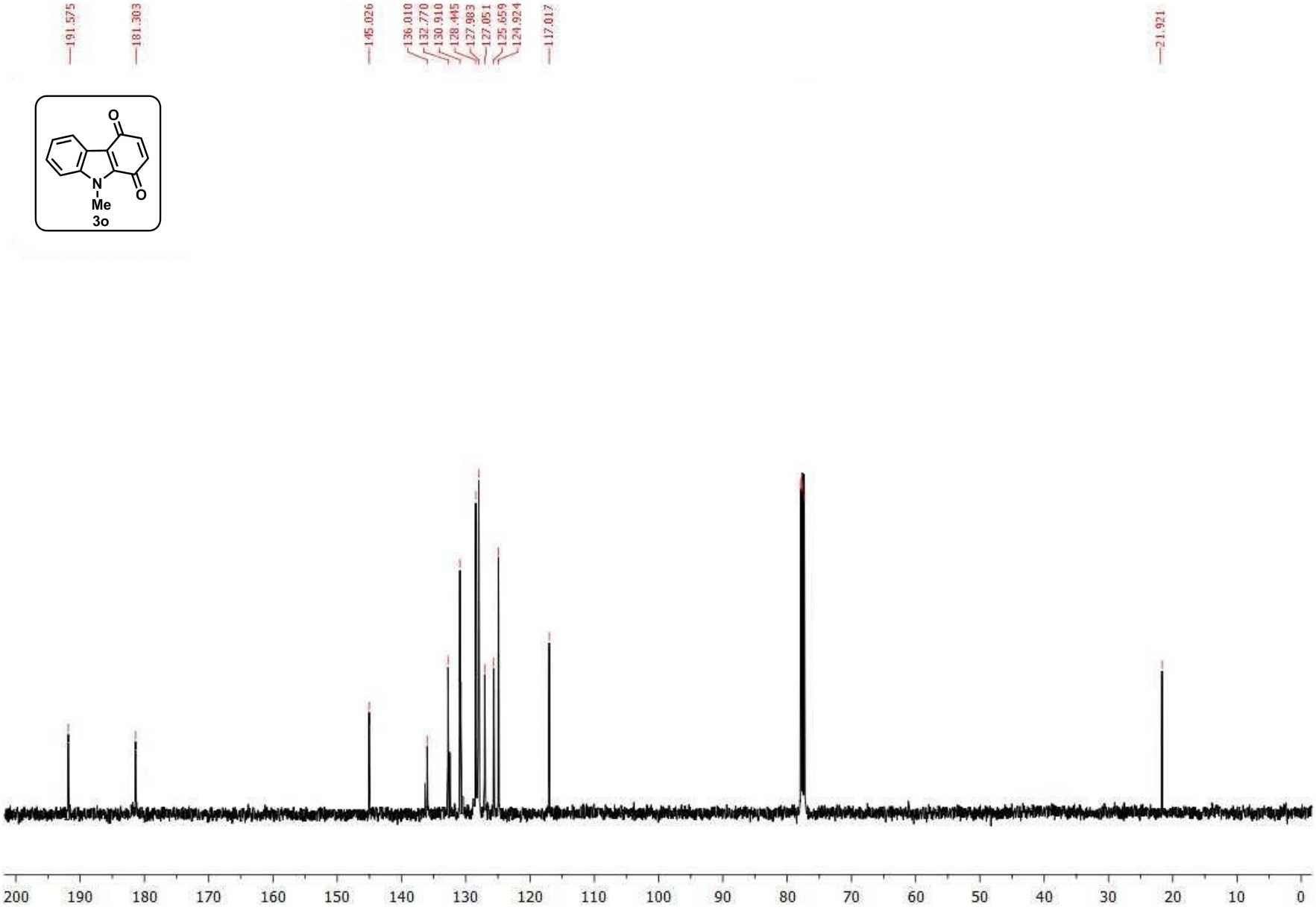
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127.051
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21.921
O
N
Me
O
3o
200
190
180
170
160
150
140
130
120
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100
90
80
70
60
50
40
30
20
10
0