Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Concise construction of 12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-ones via an unusual TBHP/Na_2CO_3 promoted cascade oxidative cyclization and interrupted Dimroth rearrangement

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1. General

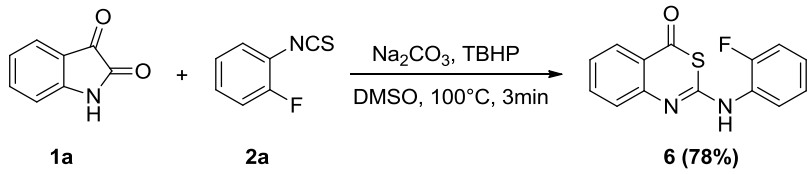
All chemicals were used as received without further purification unless stated otherwise. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300, 400 or 600 MHz spectrometer. Chemical shifts of ^1H NMR are reported in ppm, relative to the internal standard of tetramethylsilane (TMS, δ = 0.00 ppm). Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.0 ppm, DMSO-d_6: δ = 39.52 ppm). HRMS were obtained on an Apex-Ultra MS equipped with an electrospray source. Melting points were determined using XT-4 apparatus and not corrected. Compound **4a** was synthesized according to a known process.[1]

2. Experimental procedures.

2.1. General procedure for preparation of 3a–3u (3a as an example).

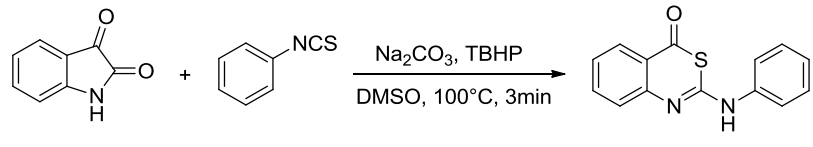
General procedure: To a sealed tube charged with isatin **1a** (74mg, 0.5 mmol), 1-fluoro-2-isothiocyanatobenzene **2a** (77mg, 0.5mmol), sodium carbonate (159 mg, 1.5 mmol) in DMSO (3mL) was added TBHP (*tert*-butyl hydroperoxide, 5.5M in decane, 110mg, 0.75mmol) at room temperature. The resulting mixture was stirred at 100 ℃ in a sealed vessel under air, after disappearance of the reactant (monitored by TLC), the mixture was quenched with water (50mL), extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) to yield the desired product **3aa** as white solid (82% yield).

2.2. Experimental procedure for preparation of 6, 7, 8.



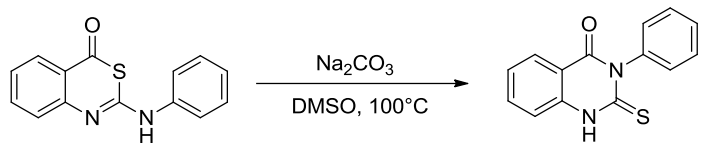
1a 2a 6 (78%)

2-((2-fluorophenyl)amino)-4*H*-benzo[*d*][1,3]thiazin-4-one(5): To a sealed tube charged with isatin **1a** (74 mg, 0.5 mmol), 1-fluoro-2-isothiocyanatobenzene **2a** (77 mg, 0.5 mmol), sodium carbonate (159 mg, 1.5 mmol) in DMSO (3 mL) was added TBHP (5.5 M in decane, 110 mg, 0.75 mmol) at room temperature. The resulting mixture was stirred at 100 ℃ in a sealed vessel under air for 3 min, then quenched with water (50 mL), extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to yield the target molecule **5** as yellow solid (78% yield).



1a 7 (75%)

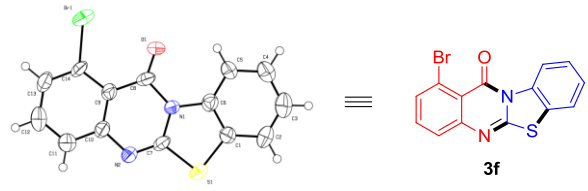
2-(phenylamino)-4*H*-benzo[*d*][1,3]thiazin-4-one(7): Following the procedure for **5**, isatin **1a** (74 mg, 0.5 mmol), 2-isothiocyanatobenzene (77 mg, 0.5 mmol), sodium carbonate (159 mg, 1.5 mmol), TBHP (5.5 M in decane, 110 mg, 0.75 mmol) in DMSO (3 mL) yielded **7** as yellow solid (75% yield).



7 **8 (75%)**

3-phenyl-2-thioxo-2,3-dihydroquinazolin-4(1*H*)-one(8): To a sealed tube charged with **6** (127 mg, 0.5 mmol) and sodium carbonate (159 mg, 1.5 mmol) was added DMSO (3 mL) at room temperature. The resulting mixture was stirred at 100 ℃ in a sealed vessel under air, after disappearance of the reactant (monitored by TLC), the mixture was quenched with water (50 mL), extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was recrystallized from ethanol to yield the target molecule **8** as white solid (75% yield).

3. Crystallographic data and molecular structure of 3f



3f

CCDC 1511240 (**3f**) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif/

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Bond precision:  C-C = 0.0099 A          Wavelength=0.71073

Cell:            a=7.508(5)     b=11.017(7)          c=14.78(1)
                 alpha=90       beta=90.564(12)      gamma=90
Temperature:     273 K

                 Calculated                Reported
Volume           1222.5(14)                1222.3(14)
Space group      P 21/n                    P2(1)/n
Hall group       -P 2yn                    ?
Moiety formula   C14 H7 Br N2 O S          ?
Sum formula      C14 H7 Br N2 O S          C14 H7 Br N2 O S
Mr               331.18                    331.19
Dx,g cm-3        1.799                     1.800
Z                4                         4
Mu (mm-1)        3.524                     3.524
F000             656.0                     656.0
F000'            655.58
h,k,lmax         8,13,17                   8,13,17
Nref             2144                      2068
Tmin,Tmax        0.465,0.530               0.511,0.570
Tmin'            0.456

Correction method= # Reported T Limits: Tmin=0.511 Tmax=0.570
AbsCorr = MULTI-SCAN

Data completeness= 0.965          Theta(max)= 25.000

R(reflections)= 0.0612( 1201)     wR2(reflections)= 0.1547( 2068)

S = 0.910                 Npar= 172
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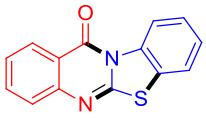
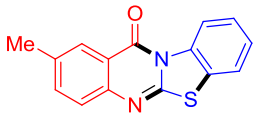
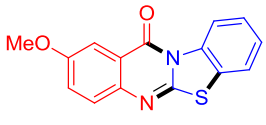
4. Spectral data of compound 3a–3u, 6, 7, 8.



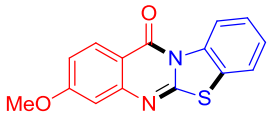
12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3a)[2]: white solid; yield: 82% (X = F, 104 mg), 66% (X = Cl, 84 mg), 77% (X = Br, 97 mg), 75% (X = I, 95 mg); m.p. 193–195 ℃; IR (KBr): 1689, 1591, 1554, 1468, 1305 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ =160.6, 156.9, 147.0, 136.0, 134.8, 127.1, 126.7, 126.6, 125.8, 125.8, 123.6, 121.7, 119.2, 118.5. MS (EI): m/z = 253.05 $[M]^+$.



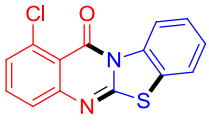
2-methyl-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3b): white solid; yield: 83% (110 mg); m.p. 209–210 ℃; IR (KBr): 1731, 1619, 1542, 1485, 1303 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.92 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H), 7.55–7.46 (m, 3H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 2.45 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.5, 155.8, 145.0, 136.2, 135.9, 135.8, 126.5, 126.4, 126.2, 125.5, 123.6, 121.6, 119.1, 118.1, 21.2. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_{10}N_2NaOS$: 289.0406; found: 289.0404.



2-methoxy-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3c): white solid; yield: 88% (X = F, 124 mg), 80%(X = Br, 113 mg); m.p. 189–190 ℃; IR (KBr): 1716, 1614, 1579, 1487, 1363, 1272, 1030 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.95 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.58–7.50 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.34–7.30 (m, 1H), 3.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.4, 157.5, 154.2, 141.8, 135.9, 127.3, 126.5, 126.5, 125.2, 123.8, 121.6, 119.1, 119.1, 106.0, 55.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{11}N_2O_2S$: 283.0536; found: 283.0540.

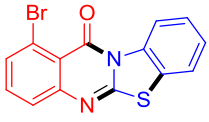


3-methoxy-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3d): white solid, m.p. 223–225 ℃; IR (KBr): 1679, 1610, 1589, 1511, 1486, 1360, 1302, 1282, 1162 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.89 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.41–7.29 (m, 2H), 6.97–6.88 (m, 2H), 3.91–3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 159.8, 157.4, 149.1, 135.9, 128.3, 126.5, 126.2, 123.3, 121.4, 118.9, 115.8, 111.8, 106.2, 55.6. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{11}N_2O_2S$: 283.0536; found: 283.0539.

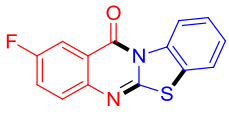


1-chloro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3e): white solid; yield: 75% (107 mg); m.p. 221–222 ℃; IR (KBr): 1683, 1588, 1538, 1455, 1304 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.99 (d, *J* = 8.4Hz, 1H), 7.60 (t, *J* = 8.4Hz, 2H), 7.53 (d, *J* = 7.8Hz, 1H), 7.48–7.40 (m, 3H). ^{13}C NMR (150

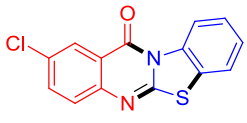
MHz, $CDCl_3$): δ = 158.6, 157.6, 149.4, 135.9, 134.7, 134.0, 128.6, 126.9, 126.8, 125.2, 123.6, 121.8, 119.4, 115.5. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7ClN_2NaOS$: 308.9860; found: 308.9854.



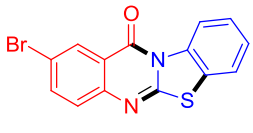
1-bromo-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3f): white solid, yield: 63%; m.p. 218–220 ℃; IR (KBr): 1686, 1573, 1533, 1449, 1300 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 9.01 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 8.4 Hz, 2H), 7.54–7.41(m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 157.4, 149.4, 136.0, 134.3, 132.5, 126.9, 126.9, 126.0, 123.7, 121.9, 121.8, 119.5, 116.5. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7BrN_2NaOS$: 352.9355; found: 352.9351.



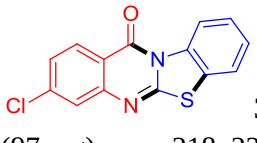
2-fluoro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3g): white solid, yield: 78% (105 mg); m.p. 230–232 ℃; IR (KBr): 1688, 1591, 1559, 1481, 1202 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.2 Hz, 1H), 7.68–7.63 (m, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.52–7.45 (m, 2H), 7.45–7.40 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.8, 159.9, 159.2, 156.2, 143.8, 135.7, 128.2, 128.1, 126.9, 126.8, 123.7, 123.6, 123.4, 121.8, 119.6, 119.2, 111.8, 111.7. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7FN_2NaOS$: 293.0155; found: 293.0160.



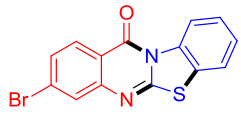
2-chloro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3h)[3]: yellow solid; yield: 71% (X = F, 94 mg); 65% (X = Br, 86 mg); m.p. 223–224 ℃; IR (KBr): 1688, 1567, 1466, 1330, 1267 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.91 (d, *J* = 8.0 Hz, 1H), 8.33–8.21 (m, 1H), 7.67–7.62 (m, 1H), 7.58–7.51 (m, 2H), 7.46–7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 157.2, 145.7, 135.8, 135.2, 131.4, 127.5, 127.0, 126.9, 126.4, 123.7, 121.8, 119.5, 119.3. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7ClN_2NaOS$: 308.9860; found: 308.9864.



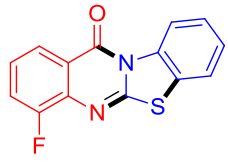
2-bromo-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3i): yellow solid; yield: 58% (96 mg); m.p. 225–226 ℃; IR (KBr): 1686, 1588, 1545, 1450, 1302 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.92 (d, *J* = 8.0 Hz, 1H), 8.51–8.42 (m, 1H), 7.85–7.75 (m, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.53–7.31 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 157.4, 146.0, 138.0, 135.9, 129.6, 127.7, 127.0, 127.0, 123.7, 121.9, 119.9, 119.3, 119.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7BrN_2NaOS$: 352.9355; found: 352.9345.



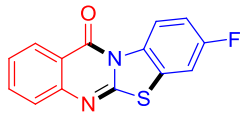
3-chloro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3j)[3]: white solid; yield: 68% (97 mg); m.p. 218–220 ℃; IR (KBr): 1691, 1572, 1546, 1463, 1300, 1239 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.66–7.57 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 158.4, 148.0, 141.1, 135.8, 128.5, 126.9, 126.9, 126.4, 125.4, 123.6, 121.8, 119.2, 116.9. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7ClN_2NaOS$: 308.9860; found: 308.9862.



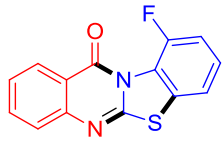
3-bromo-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3k): yellow solid; yield: 55% (91 mg); m.p. 239–240 ℃; IR (KBr): 1689, 1587, 1463, 1330, 1239 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.93 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.81–7.72 (m, 1H), 7.63–7.55 (m, 1H), 7.50–7.53 (m, 1H), 7.49–7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 158.3, 148.0, 135.9, 129.7, 129.2, 128.6, 128.5, 127.0, 126.9, 123.6, 121.8, 119.3, 117.3. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7BrN_2NaOS$: 352.9355; found: 352.9348.



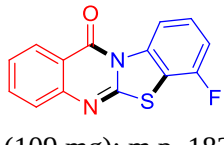
4-fluoro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3l): yellow solid, yield: 33% (45 mg) m.p. 215–216 ℃; IR (KBr): 1695, 1615, 1590, 1448, 1255, 1195 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.92 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.51–7.31 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7, 159.7, 157.9, 157.5, 154.1, 136.8, 136.7, 135.7, 126.9, 126.9, 125.6, 125.5, 123.8, 122.6, 122.5, 121.8, 120.4, 120.1, 119.9, 119.3. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7FN_2NaOS$: 293.0155; found: 293.0150.



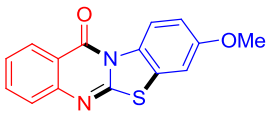
8-fluoro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3m)[3]: white solid; yield: 72% (194 mg). m.p. 225–226 ℃; IR (KBr): 1688, 1585, 1550, 1469, 1294, 1185 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.98–8.94 (m, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.34–7.26 (m, 1H), 7.20–7.09 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.9, 160.5, 159.4, 156.5, 147.1, 135.0, 132.4, 127.1, 126.1, 126.0, 125.5, 125.4, 120.6, 120.5, 118.5, 114.2, 114.0, 109.2, 109.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7FN_2NaOS$: 293.0155; found: 293.0155.



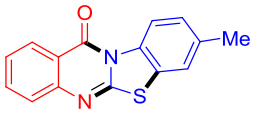
10-fluoro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3n): white solid, yield: 75% (101.25 mg); m.p. 163–165 ℃; IR (KBr): 1718, 1583, 1555, 1464, 1281, 1252, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.0 Hz, 1H), 7.74–7.66 (m, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.43–7.29 (m, 3H), 7.23–7.12 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5, 156.2, 152.0, 149.4, 146.8, 134.8, 128.1, 128.0, 127.4, 126.8, 126.8, 125.9, 125.4, 122.6, 122.4, 118.8, 118.8, 117.6, 117.6, 116.0, 115.8. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_7FN_2NaOS$: 293.0155; found: 293.0152.



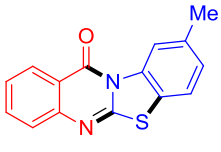
7-fluoro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3o): white solid, yield: 81% (109 mg); m.p. 182–183 ℃; IR (KBr): 1699, 1599, 1466, 1250, 1206, 1117 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.45–7.31 (m, 2H), 7.10 (t, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 157.5, 156.4, 155.0, 146.9, 137.8, 137.8, 135.1, 128.3, 128.2, 127.1, 126.1, 126.0, 118.4, 115.0, 114.9, 113.2, 113.0, 111.4, 111.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_7FN_2NaOS$: 293.0155; found: 293.0150.



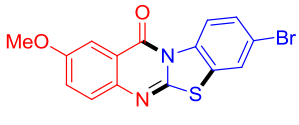
8-methoxy-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3p)[3]: white solid; yield: 61% (86 mg); m.p. 208–210 ℃; IR (KBr): 1678, 1583, 1553, 1479, 1261, 1179 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, *J* = 8.8 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.08 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4, 158.3, 147.2, 134.6, 129.8, 127.0, 125.9, 125.8, 125.1, 120.1, 118.6, 112.9, 106.7, 55.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{11}N_2O_2S$: 283.0536; found: 283.0530.



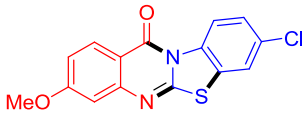
8-methyl-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3q)[3]: white solid; yield: 75% (100 mg); m.p. 238–240 ℃; IR (KBr): 1647, 1581, 1450, 1287, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 8.8 Hz, 1H), 8.36–8.30 (m, 1H), 7.75–7.67 (m, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.32 (s, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 157.0, 147.1, 137.0, 134.7, 133.8, 127.6, 127.0, 125.8, 125.7, 123.6, 121.9, 118.8, 118.5, 21.3. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_{10}N_2NaOS$: 289.0406; found: 289.0400.



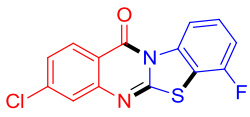
9-methyl-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3r): white solid, yield: 68% (90 mg); m.p. 213–214 ℃; IR (KBr): 1688, 1579, 1550, 1463, 1306 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.46–7.33 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 157.4, 147.1, 137.1, 136.0, 134.7, 127.6, 127.0, 125.8, 125.6, 121.2, 120.2, 119.6, 118.5, 21.7. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_{10}N_2NaOS$: 289.0406; found: 289.0403.



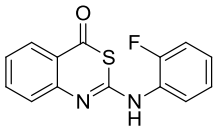
8-bromo-2-methoxy-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3s): white solid; yield: 80% (144 mg) ;m.p. 232–234 ℃; IR (KBr): 1674, 1616, 1585, 1552, 1485, 1457, 1361, 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.83 (d, *J* = 8.8 Hz, 1H), 7.73–7.65 (m, 2H), 7.57–7.53 (m, 2H), 7.37–7.34 (m, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 157.8, 153.5, 141.8, 134.9, 129.8, 127.6, 125.9, 125.5, 124.4, 120.3, 119.8, 119.1, 106.1, 55.84. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{10}BrN_2O_2S$: 360.9641; found: 360.9646.



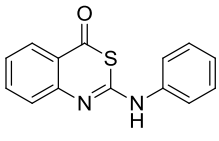
8-chloro-3-methoxy-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3t): light yellow solid; yield: 71% (112 mg); m.p. 229–231 ℃; IR (KBr): 1685, 1586, 1551, 1483, 1443, 1357, 1246, 1213 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 9.00 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.05–6.93 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 160.1, 157.6, 149.3, 136.9, 133.0, 128.8, 126.8, 122.4, 121.9, 119.5, 116.4, 111.9, 106.7, 55.8. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{10}ClN_2O_2S$: 317.0146; found:317.0150.



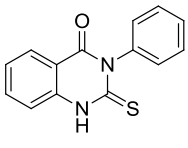
3-chloro-7-fluoro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3u):white solid, yield: 66% (100 mg); m.p. 201–202 ℃; IR (KBr): 1692, 1578, 1545, 1459, 1421, 1269, 1241, 1199, 1111 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.67–7.53 (m, 1H), 7.47–7.37 (m, 2H), 7.17 (t, *J* = 8.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 157.9, 157.5, 155.1, 147.9, 141.4, 137.7, 137.6, 128.6, 128.5, 128.5, 126.8, 125.6, 116.9, 115.1, 115.0, 113.4, 113.2, 111.4, 111.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_7ClFN_2OS$: 304.9946; found: 304.9951.



2-((2-fluorophenyl)amino)-4*H*-benzo[*d*][1,3]thiazin-4-one(6): yellow solid; yield: 78% (106 mg); m.p. 149–150 ℃; IR (KBr): 3330, 1647, 1600, 1546, 1460, 1332, 1148 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.36 (t, *J* = 8.0Hz ,1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.69–7.59 (m, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.20–7.04 (m, 3H), 5.27 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.0, 154.5, 152.1, 152.0, 149.1, 136.0, 128.5, 126.8, 126.7, 125.3, 125.2, 125.0, 124.9, 124.6, 124.5, 123.2, 118.0, 115.3, 115.1, 105.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{10}FN_2OS$: 273.0492; found: 273.0508.

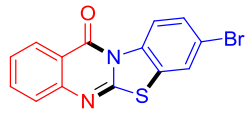


2-(phenylamino)-4*H*-benzo[*d*][1,3]thiazin-4-one(7): yellow solid; yield: 75% (95 mg). m.p. 147–148 ℃; IR (KBr): 3334, 1643, 1599, 1542, 1455 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 10.21 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.88–7.77 (m, 2H), 7.75–7.71 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.1, 151.2, 149.3, 139.2, 135.9, 128.5, 128.1, 124.3, 124.1, 123.2, 120.1, 117.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{11}N_2OS$: 255.0587; found: 255.0587.

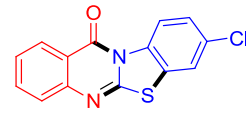


3-phenyl-2-thioxo-2,3-dihydroquinazolin-4(1*H*)-one(8)[5]: white solid. yield: 75% (95 mg); m.p. > 300 ℃; IR (KBr): 3450, 1662, 1626, 1528, 1196 cm^{-1}; ^1H NMR(600MHz, DMSO-d_6): δ = 13.06 (s, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.82–7.73 (m, 1H), 7.55–7.44 (m, 3H), 7.44–7.39 (m, 1H), 7.38–7.24 (m, 3H). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 176.1, 159.8, 139.6, 139.3, 135.6, 129.0, 128.9, 128.1, 127.4, 124.3, 116.2, 115.7. MS (EI): m/z = 253.03 $[M]^+$.

Note: Target products such as **8-bromo-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3v)**, **8-chloro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(3w), etc.** could be obtained by this method in high yields, but we cannot obtain their ^{13}C NMR spectra due to their poor solubility in most solvents.



8-bromo-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(**3v**)

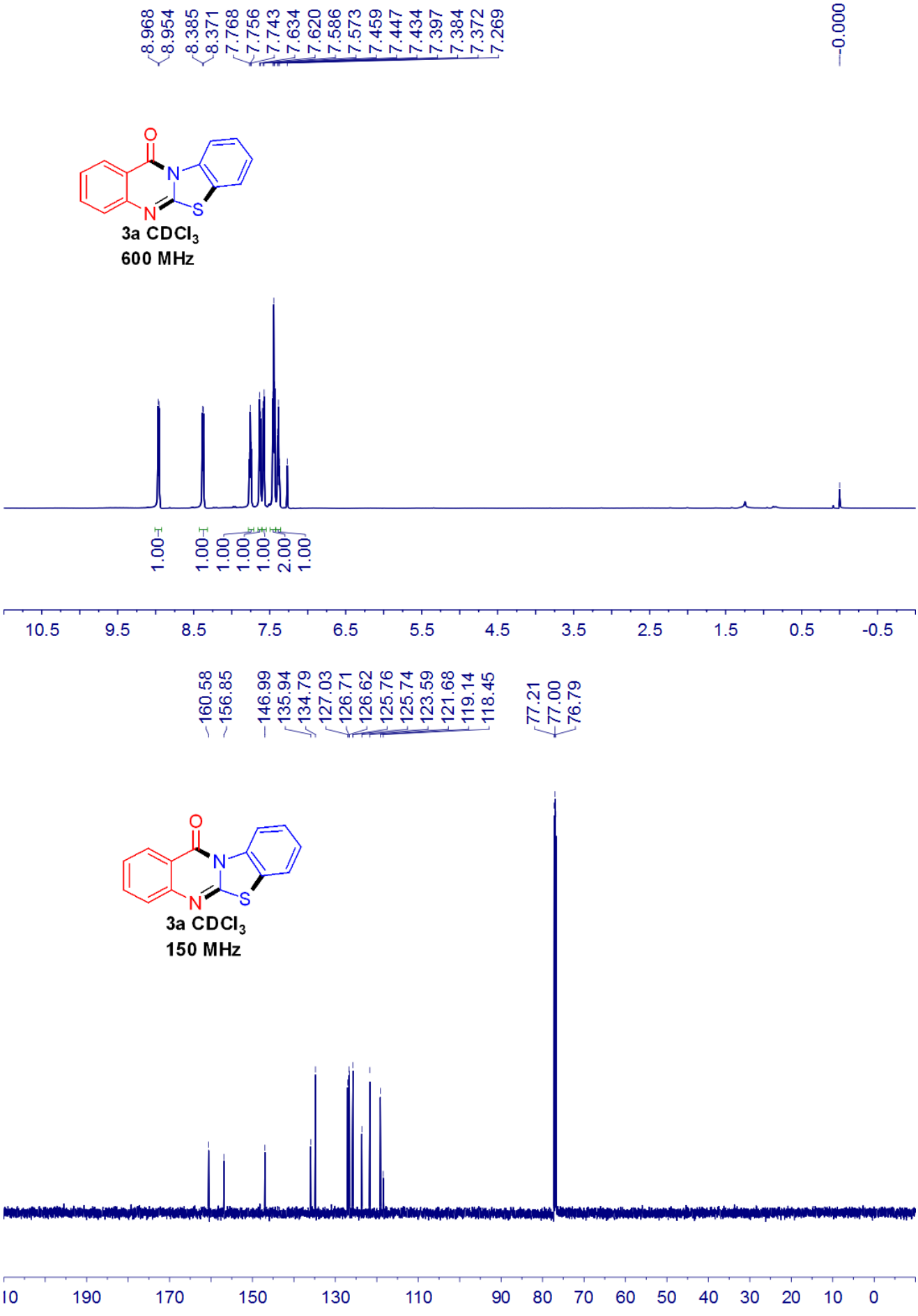


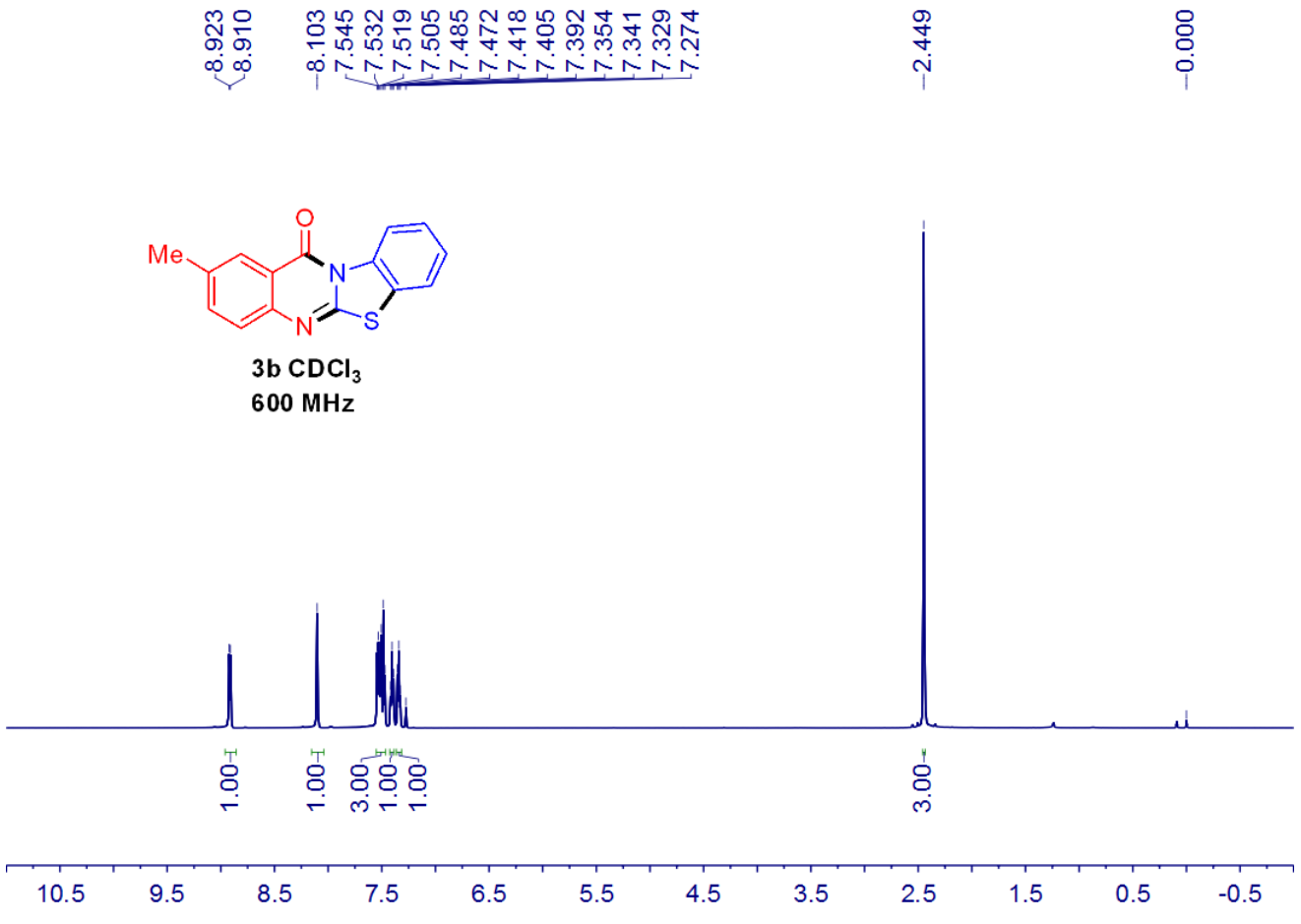
8-chloro-12*H*-benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one(**3w**)

5. Reference

1. H. J. Zhang, P. Jin, S. B. Wang, F. N. Li, L. P. Guan, Z. S. Quan, *Arch. Pharm. Chem. Life Sci.*, 2015, **348**, 564.
2. M. Liu, M. Shu, C. Yao, G. Yin, D. Wang, J. Huang, *Org. Lett.*, 2016, **18**, 824.
3. R. F. Pellon, M. L. Docampo, M. L. Fascio, *Synth. Commun.* 2007, **37**, 1853.
4. J. A. Bleda, P. M. Fresneda, R. Orenes, P. Molina, *Eur. J. Org. Chem.* 2009, 2490.
5. M. R. Mahmoud, W. S. I. Abou-Elmagd, S. S. Abdelwahab, E. S. A. Soliman, *Synth. Commun.* 2013, **43**, 1484.

6. Appendix: spectral copies of ^{1}H NMR, and ^{13}C NMR

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7.505
7.485
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7.354
7.341
7.329
7.274
2.449
0.000
Me
O
N
S
N
3b CDCl3
600 MHz
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1.00
3.00
1.00
1.00
3.00
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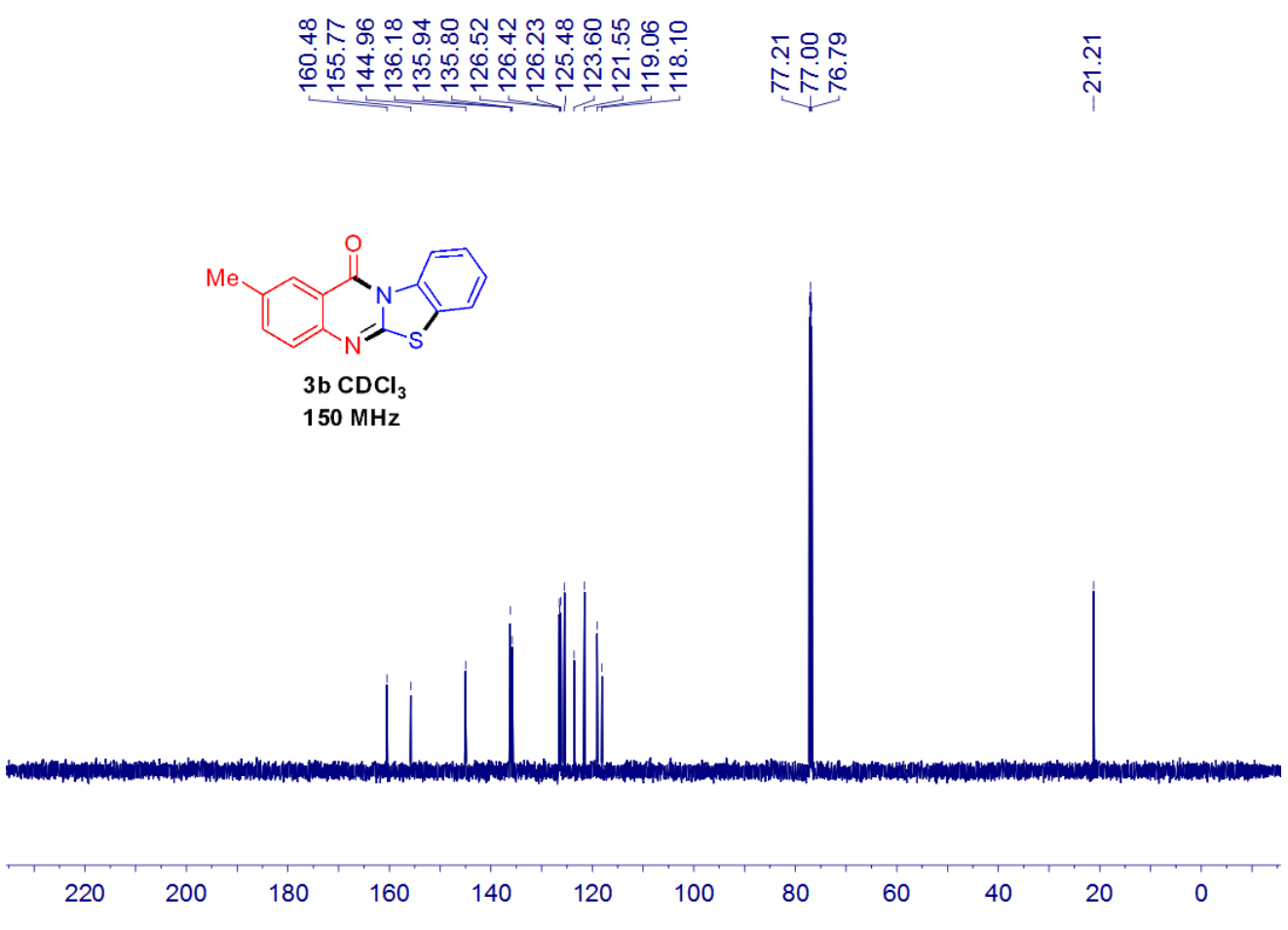
-0.5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119.06
118.10
77.21
77.00
76.79
21.21
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140
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40
20
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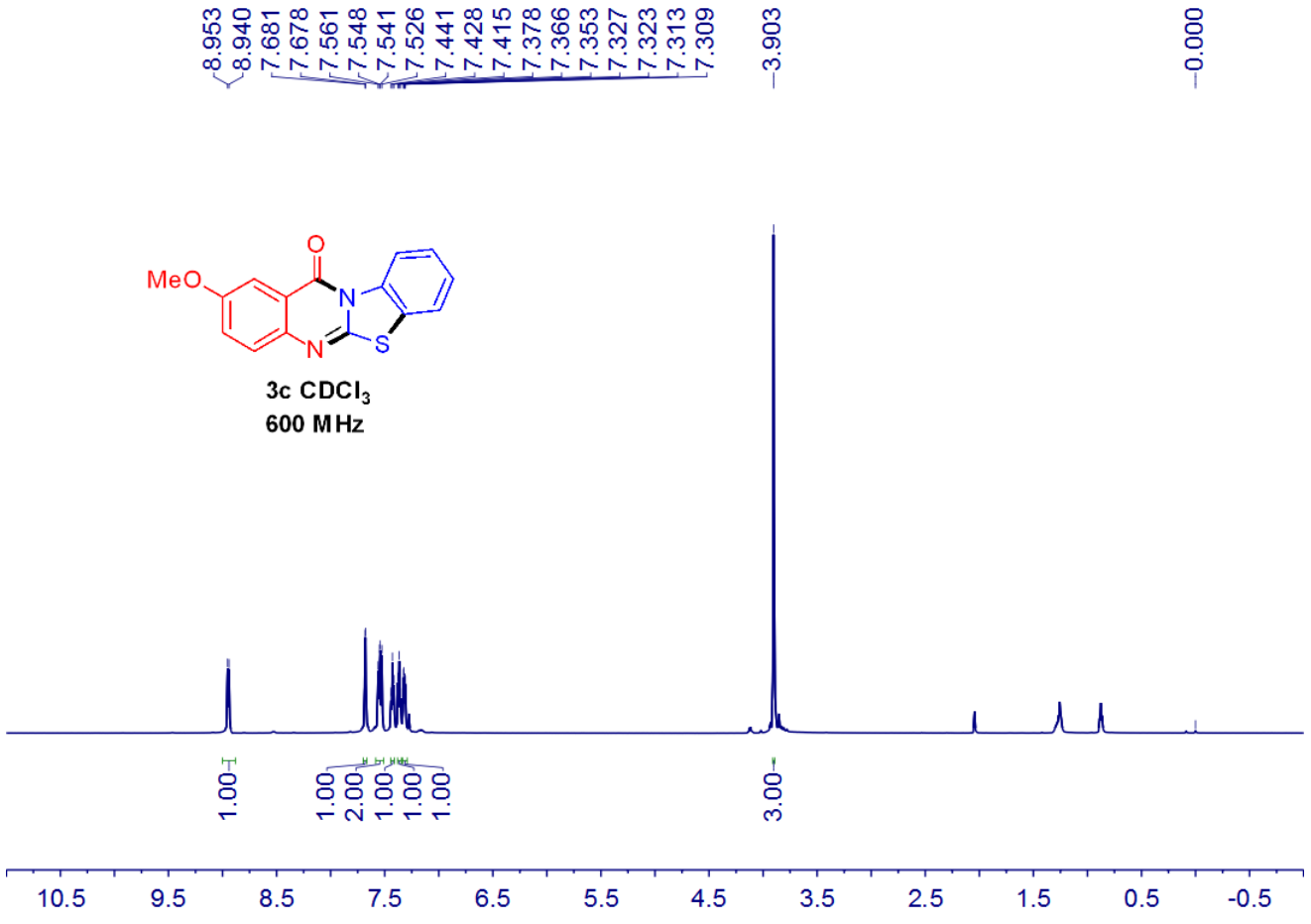
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7.353
7.327
7.323
7.313
7.309
3.903
0.000
MeO
O
N
S
N
3c CDCl3
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1.00
2.00
1.00
1.00
3.00
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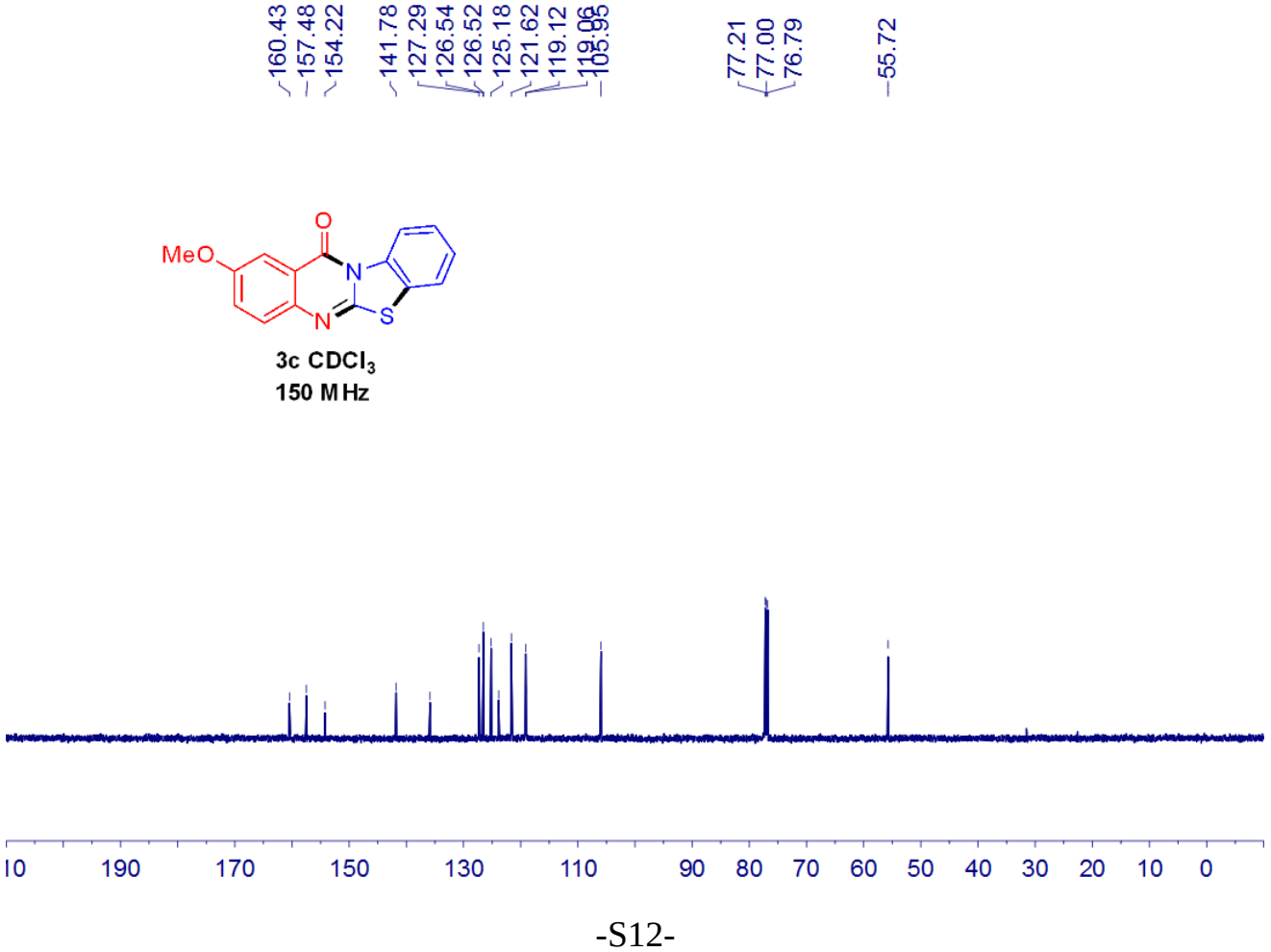
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55.72
MeO
O
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S
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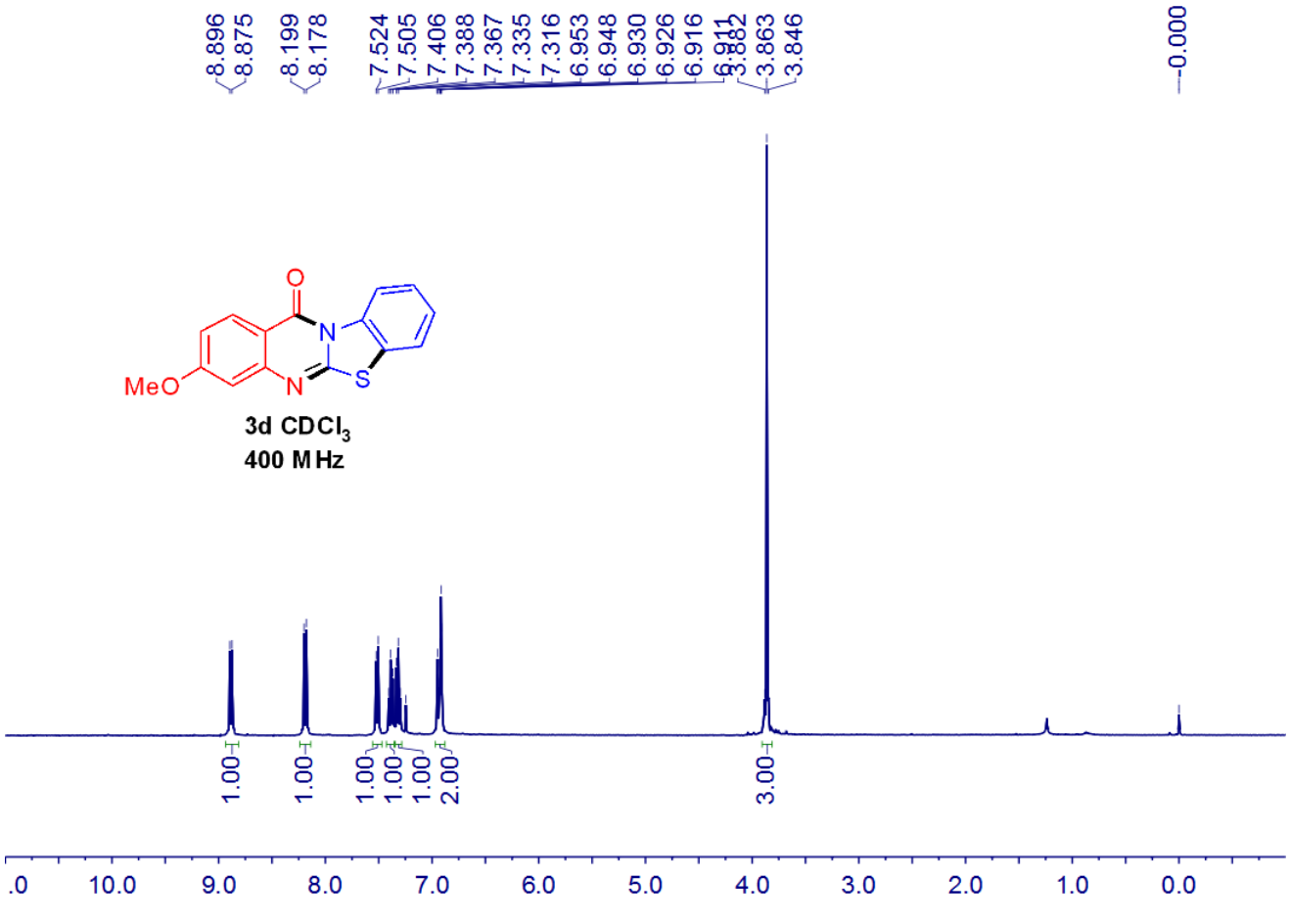
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MeO
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1.00
1.00
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2.00
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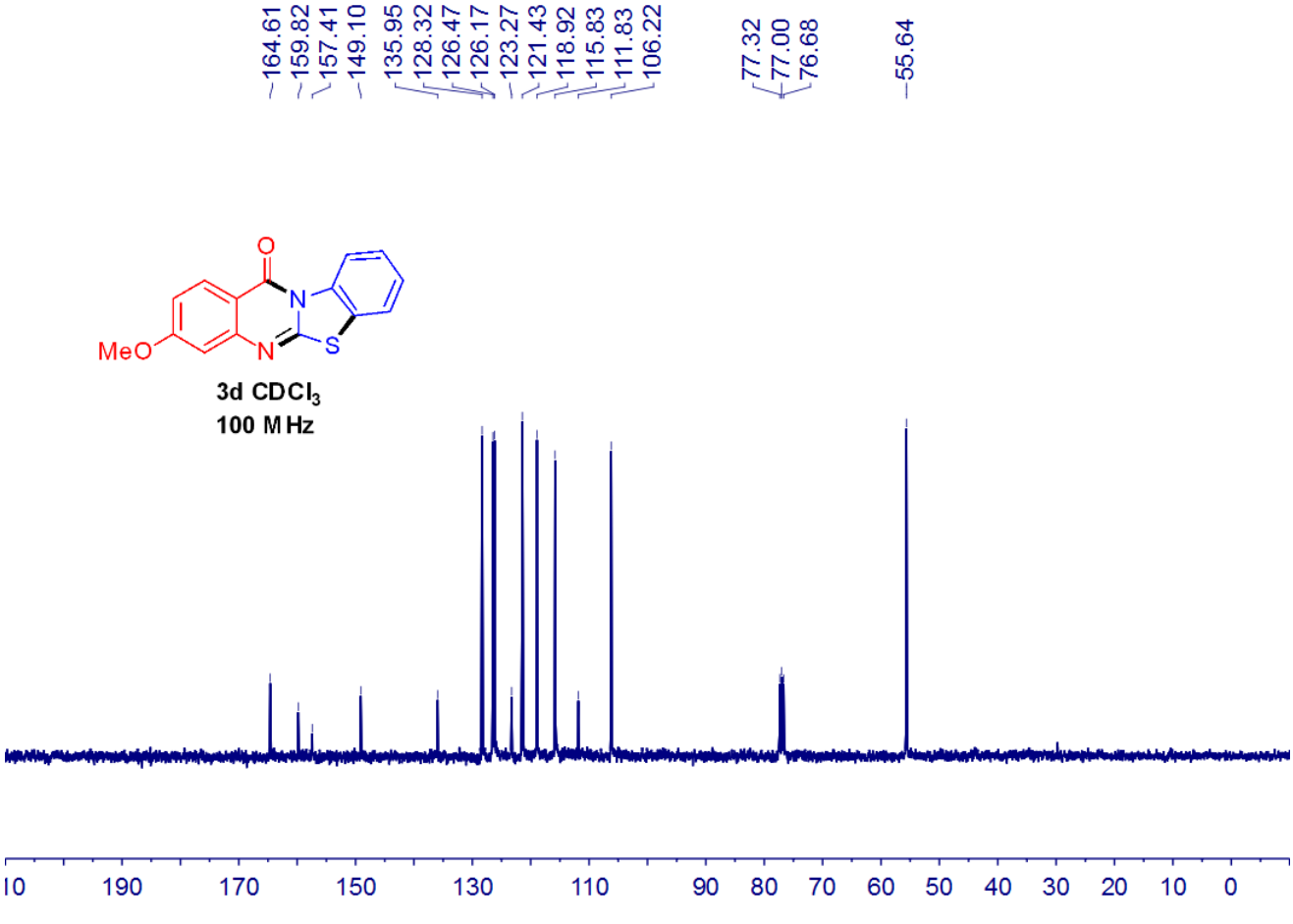
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121.43
118.92
115.83
111.83
106.22
77.32
77.00
76.68
55.64
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100 MHz
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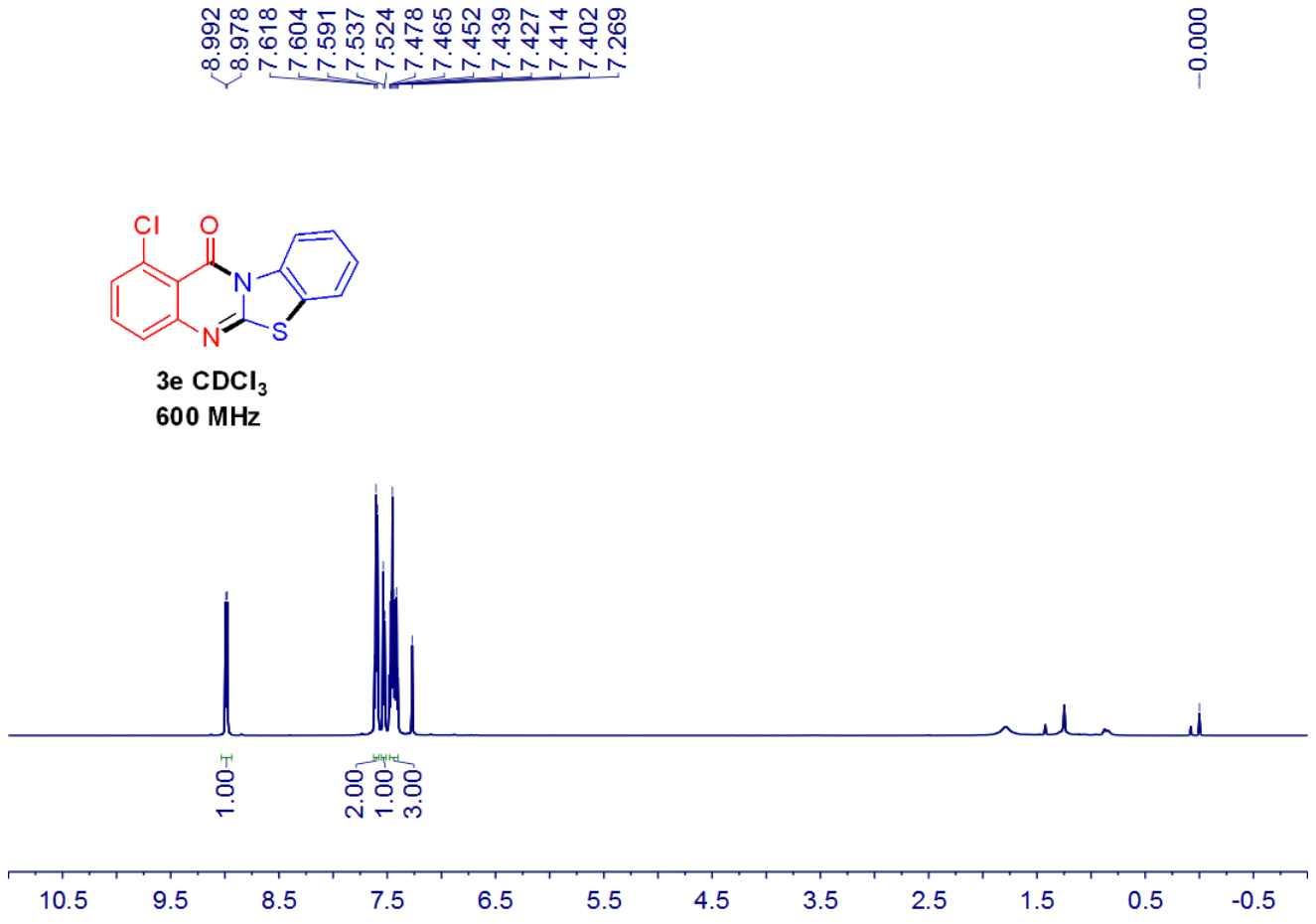
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7.478
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7.452
7.439
7.427
7.414
7.402
7.269
0.000
Cl
O
N
S
N
3e CDCl3
600 MHz
1.00
2.00
1.00
3.00
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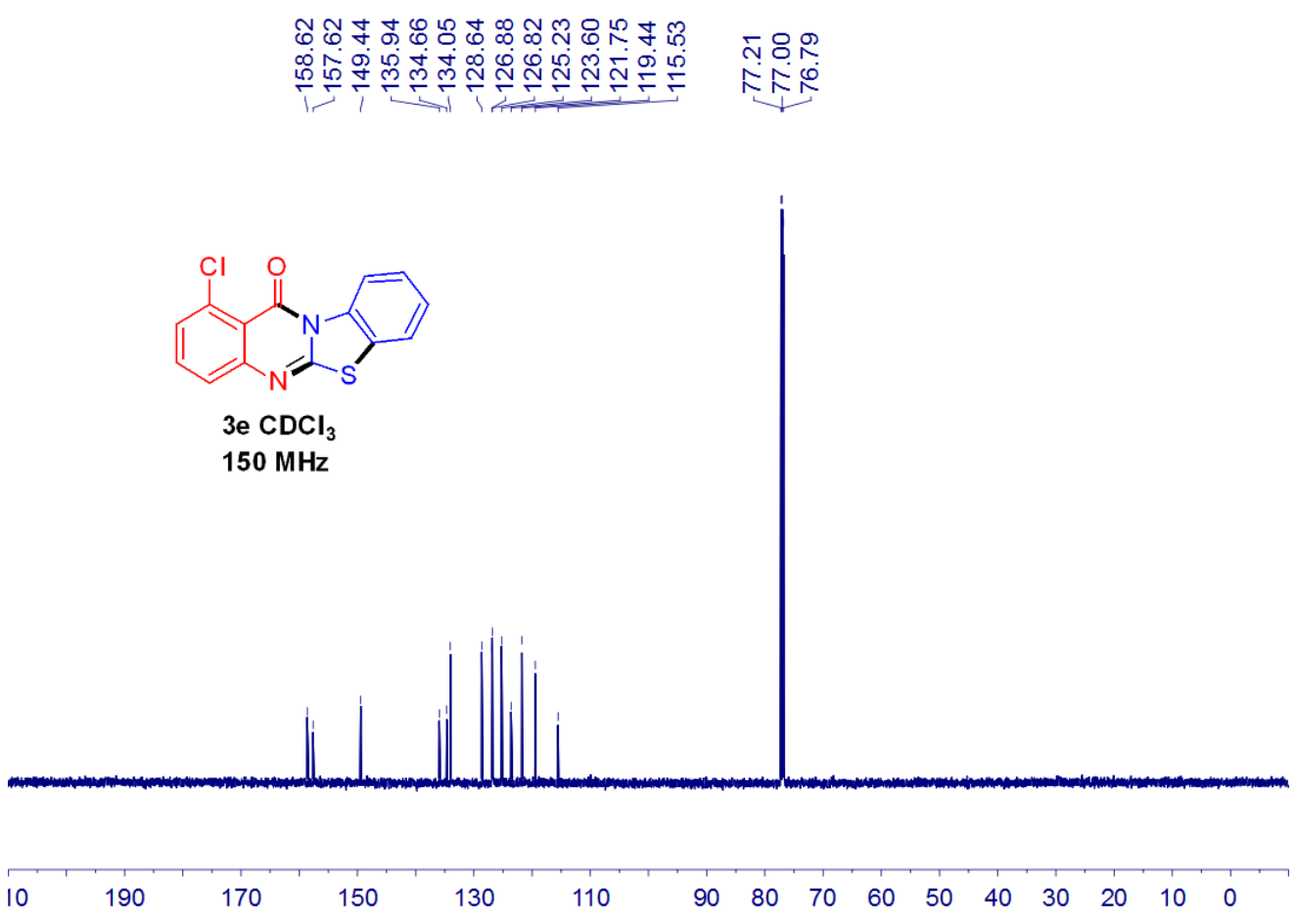
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119.44
115.53
77.21
77.00
76.79
Cl
O
N
S
N
3e CDCl3
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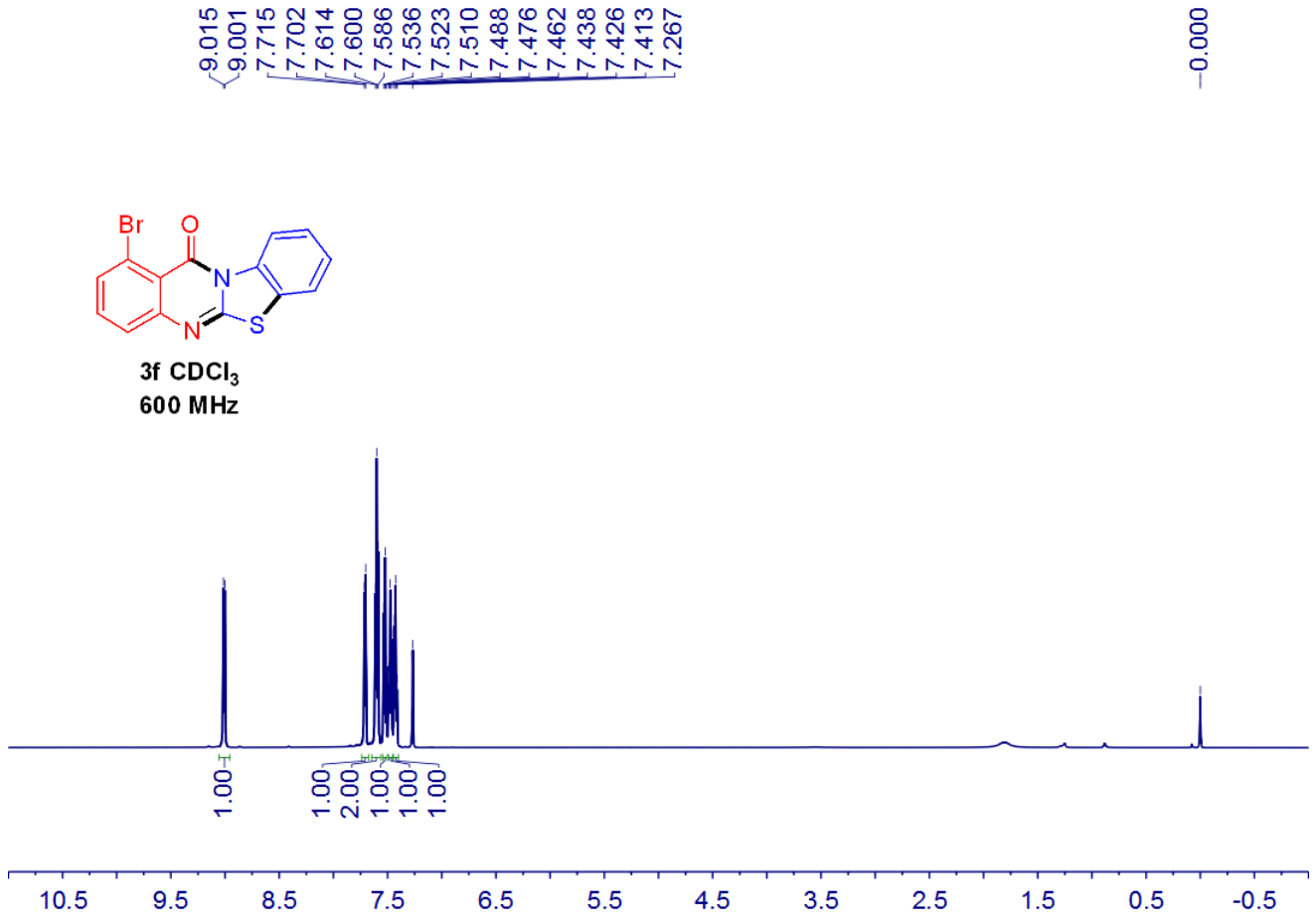
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7.586
7.536
7.523
7.510
7.488
7.476
7.462
7.438
7.426
7.413
7.267
0.000
Br
O
N
S
N
3f CDCl3
600 MHz
1.00
1.00
2.00
1.00
1.00
1.00
10.5
9.5
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7.5
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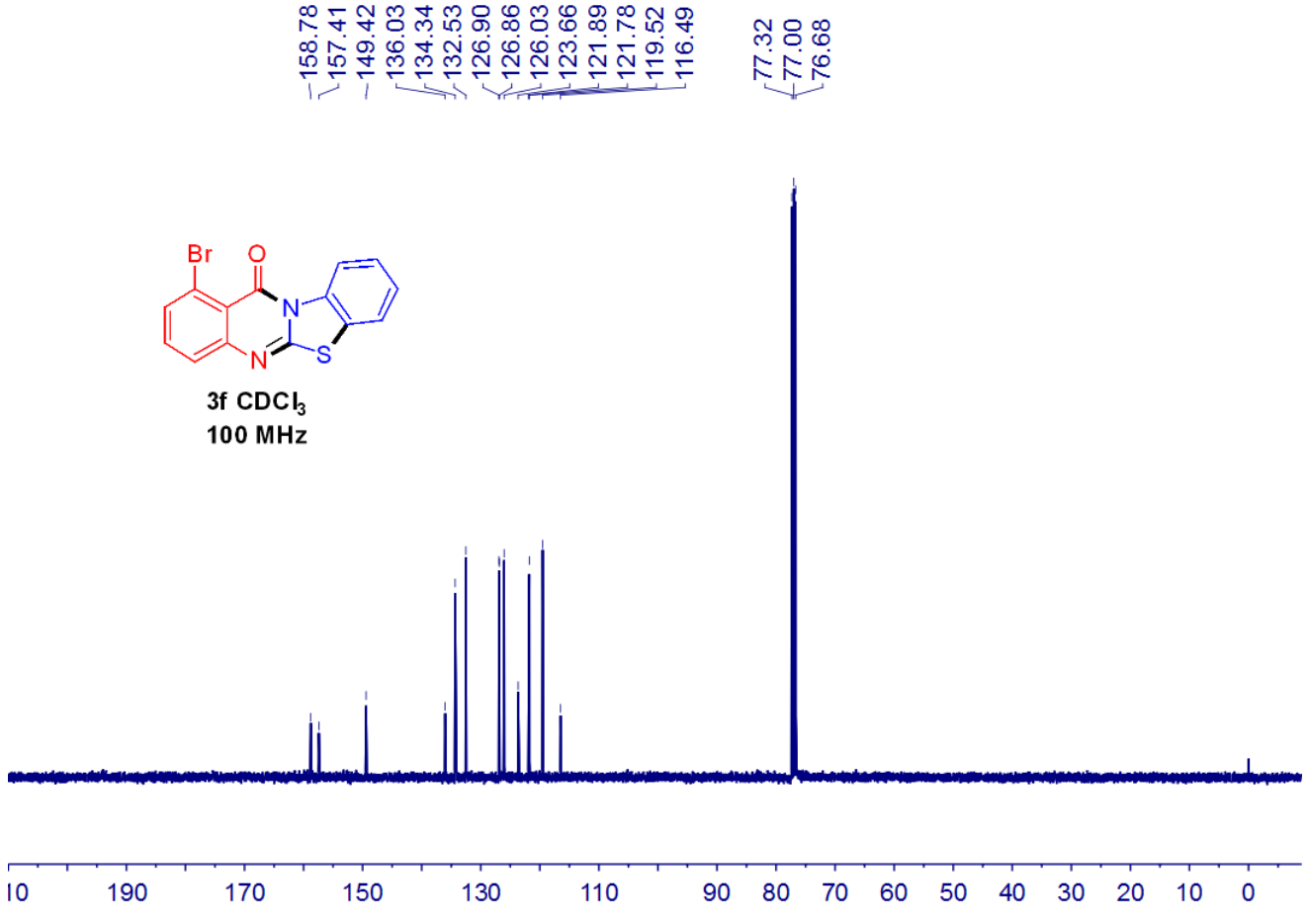
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126.86
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121.78
119.52
116.49
77.32
77.00
76.68
Br
O
N
S
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3f CDCl3
100 MHz
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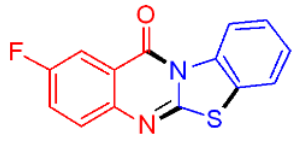
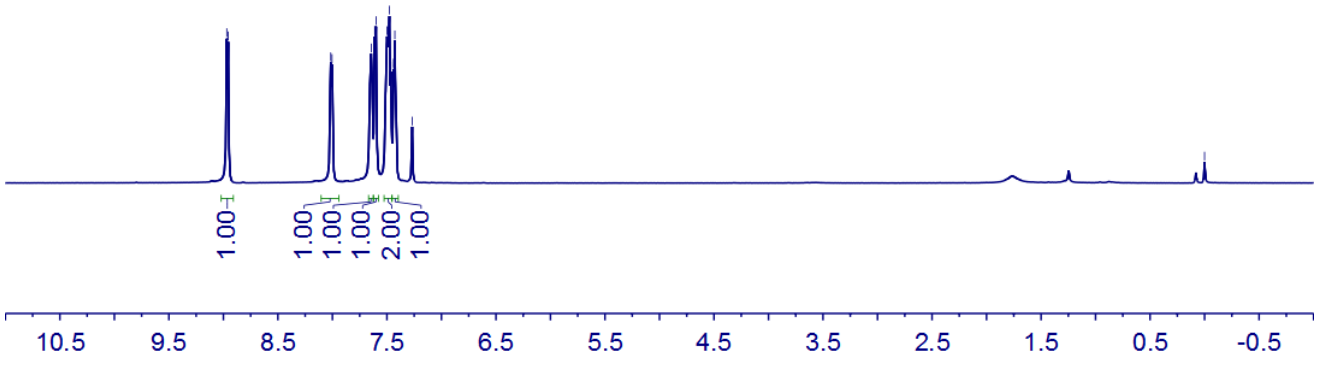
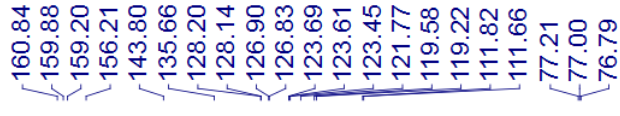
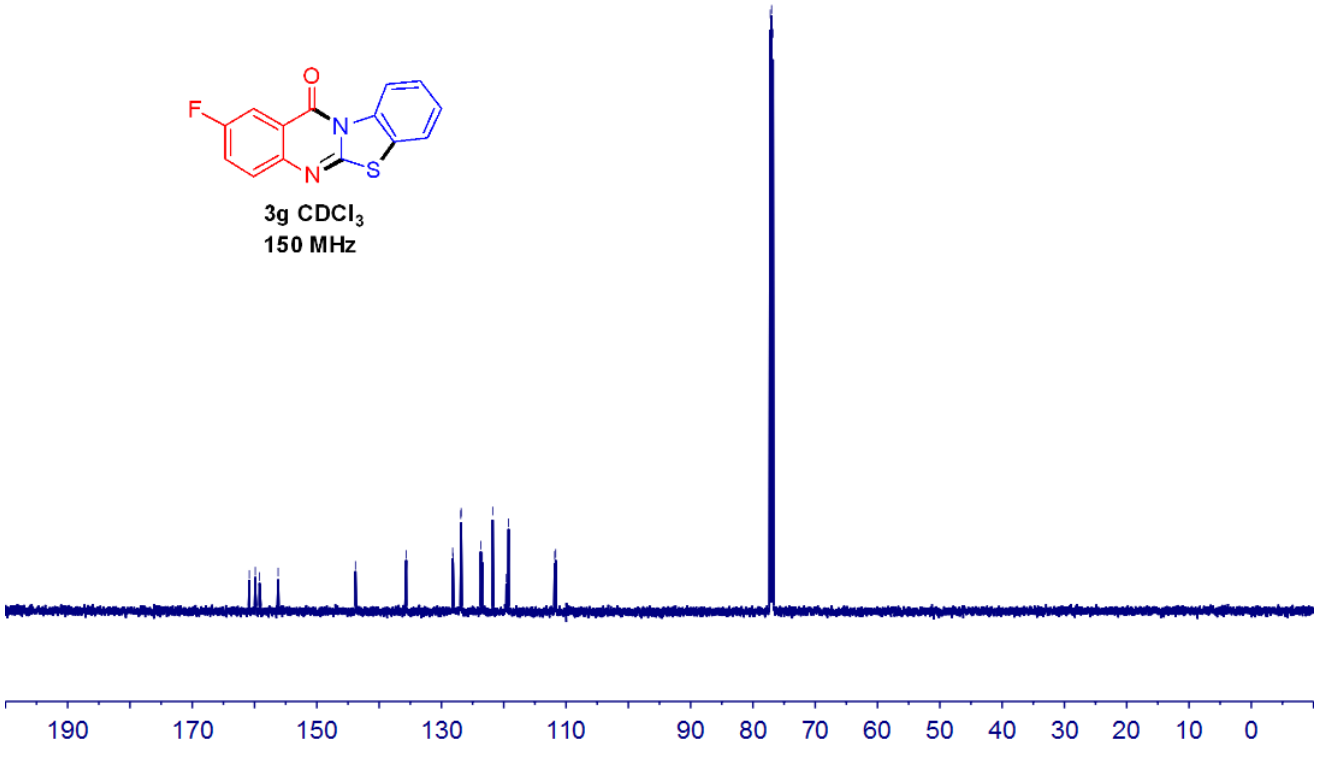


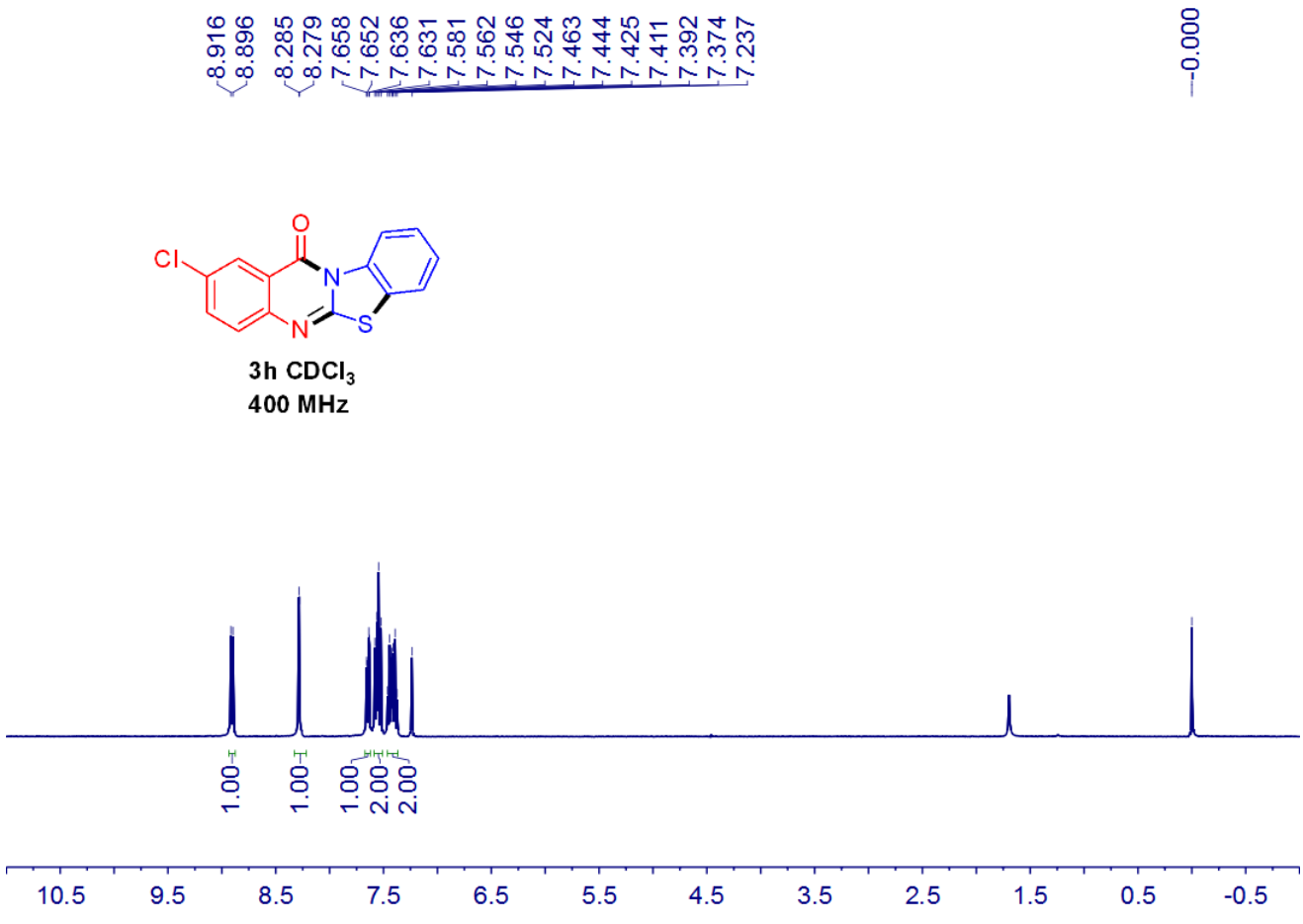
3g $CDCl_3$
600 MHz





3g $CDCl_3$
150 MHz

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7.636
7.631
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7.562
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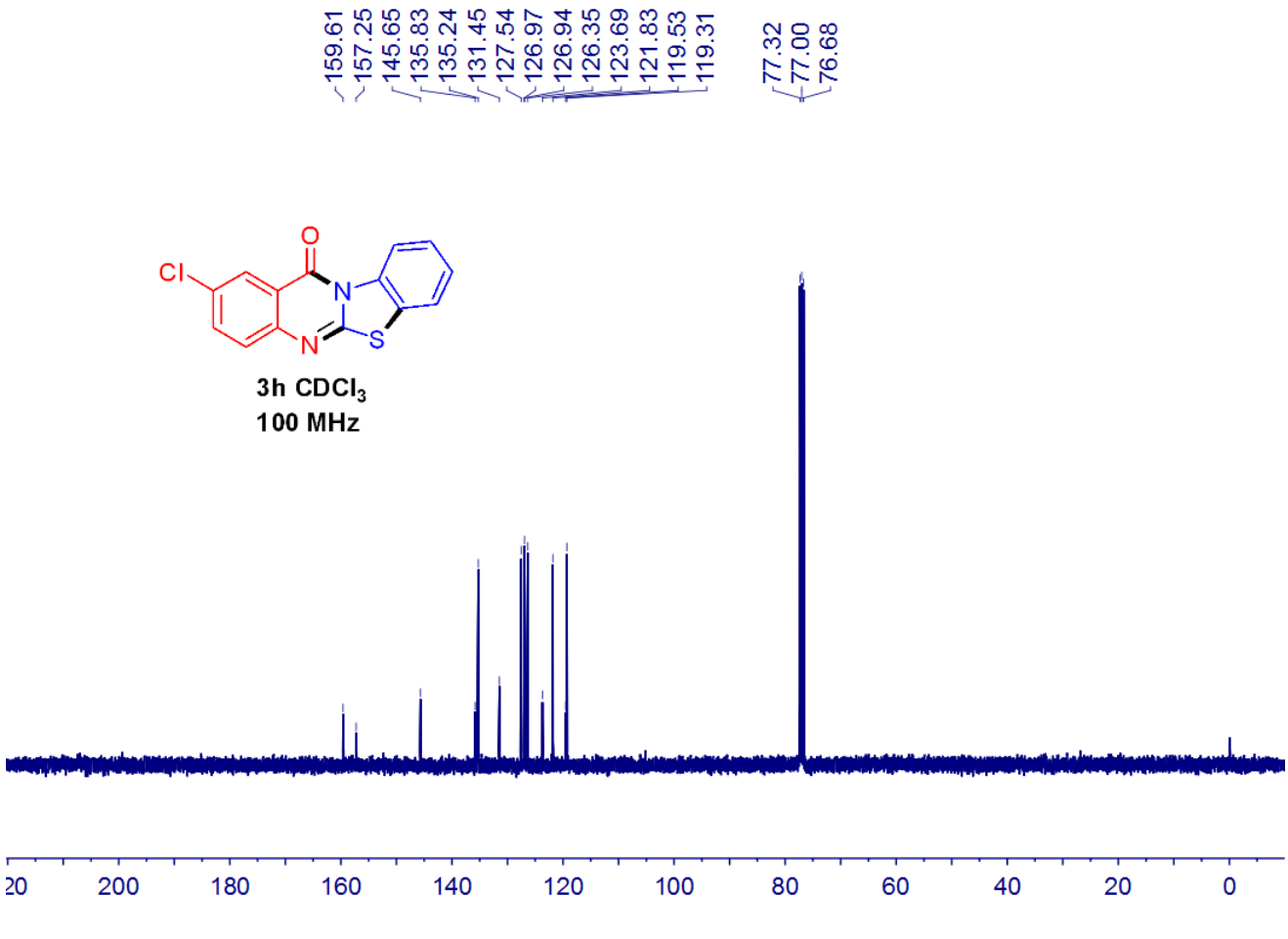
7.524
7.463
7.444
7.425
7.411
7.392
7.374
7.237
-0.000
Cl
O
N
S
N
3h CDCl3
400 MHz
1.00
1.00
1.00
2.00
2.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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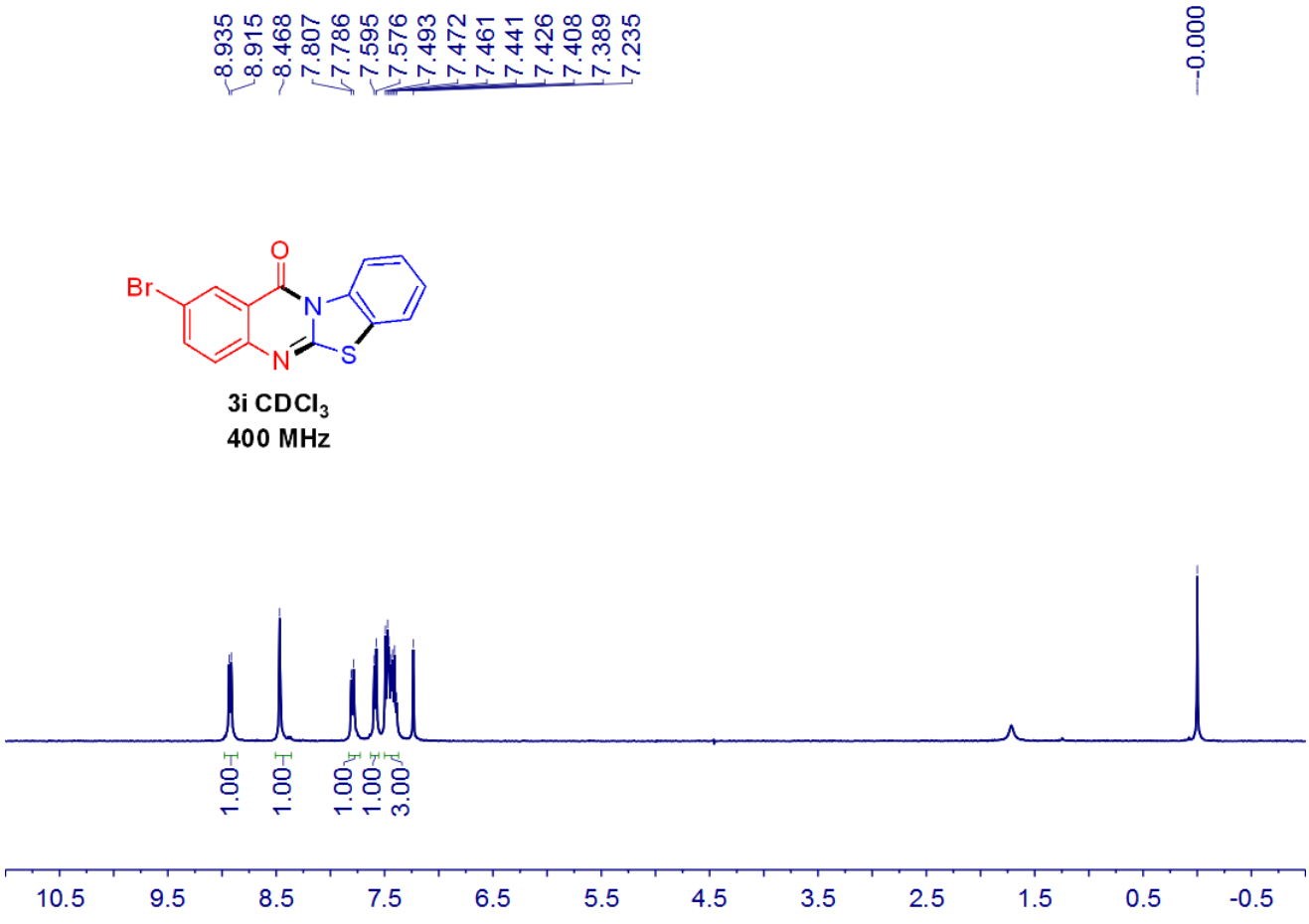
157.25
145.65
135.83
135.24
131.45
127.54
126.97
126.94
126.35
123.69
121.83
119.53
119.31
77.32
77.00
76.68
Cl
O
N
S
N
3h CDCl3
100 MHz
200
180
160
140
120
100
80
60
40
20
0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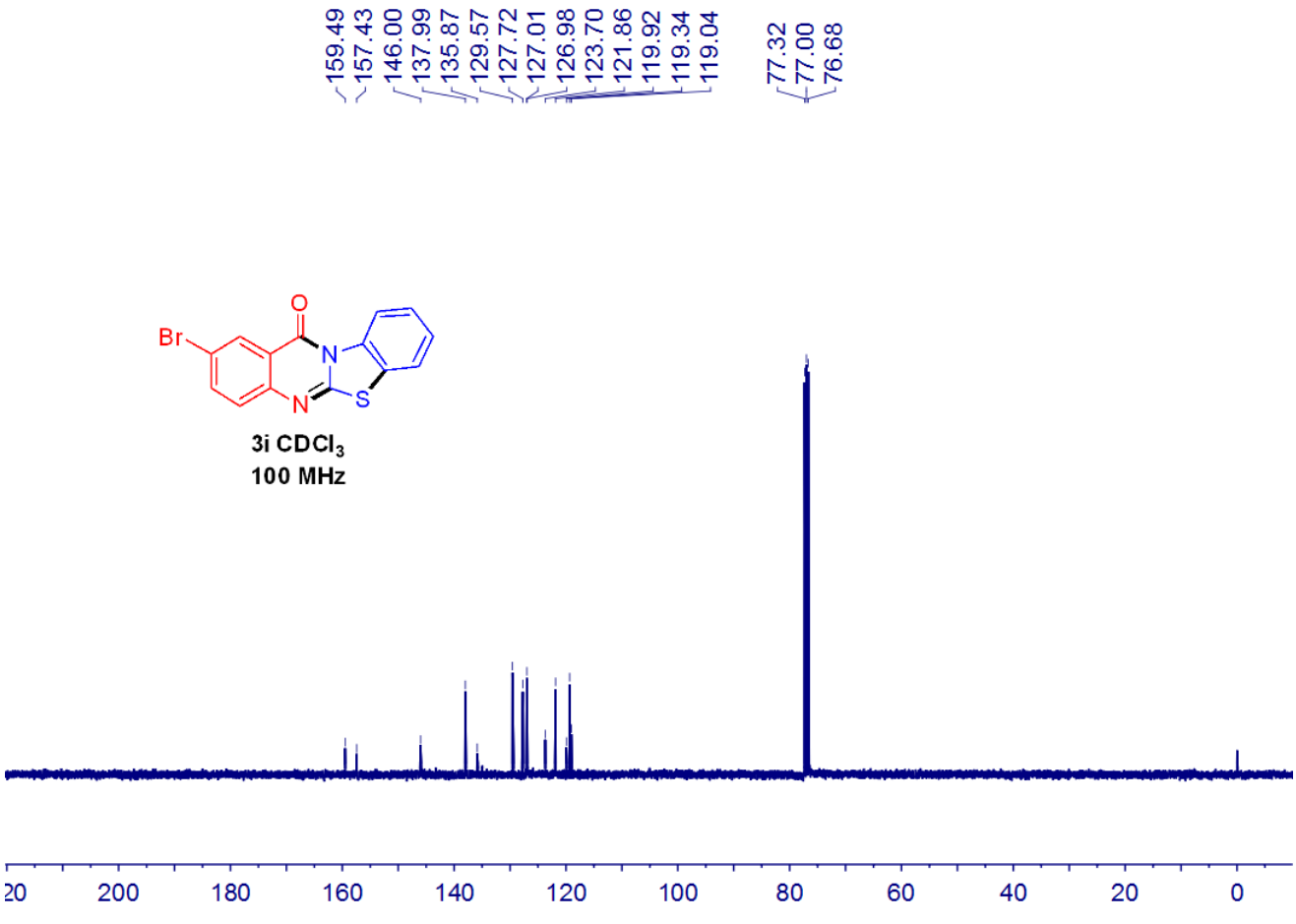
8.915
8.468
7.807
7.786
7.595
7.576
7.493
7.472
7.461
7.441
7.426
7.408
7.389
7.235
0.000
Br
O
N
N
S
3i CDCl3
400 MHz
1.00
1.00
1.00
1.00
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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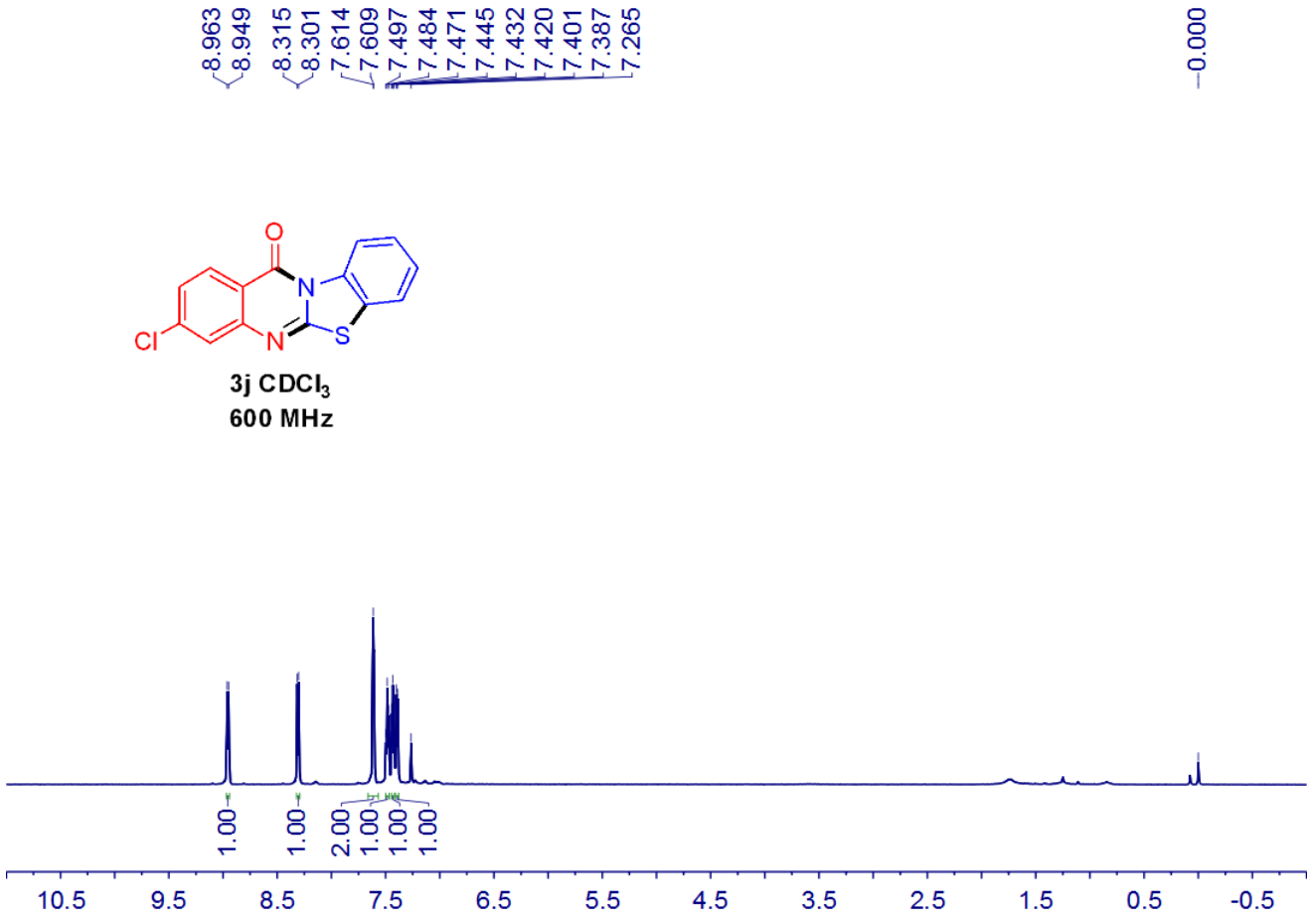
137.99
135.87
129.57
127.72
127.01
126.98
123.70
121.86
119.92
119.34
119.04
77.32
77.00
76.68
Br
O
N
N
S
3i CDCl3
100 MHz
200
180
160
140
120
100
80
60
40
20
0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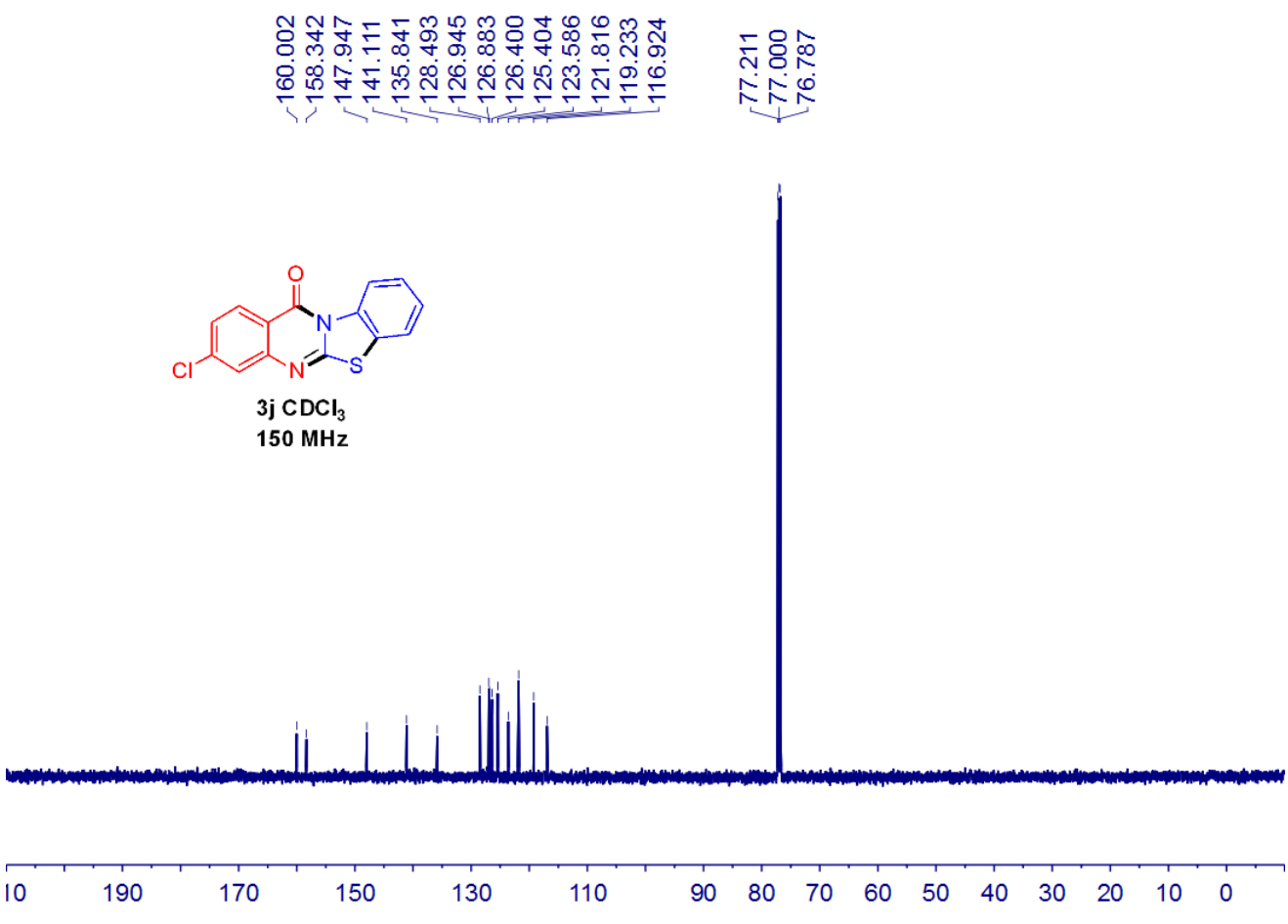
8.949
8.315
8.301
7.614
7.609
7.497
7.484
7.471
7.445
7.432
7.420
7.401
7.387
7.265
0.000
Cl
N
S
O
3j CDCl3
600 MHz
1.00
1.00
2.00
1.00
1.00
1.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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126.883
126.400
125.404
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119.233
116.924
77.211
77.000
76.787
Cl
N
S
O
3j CDCl3
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150
130
110
90
80
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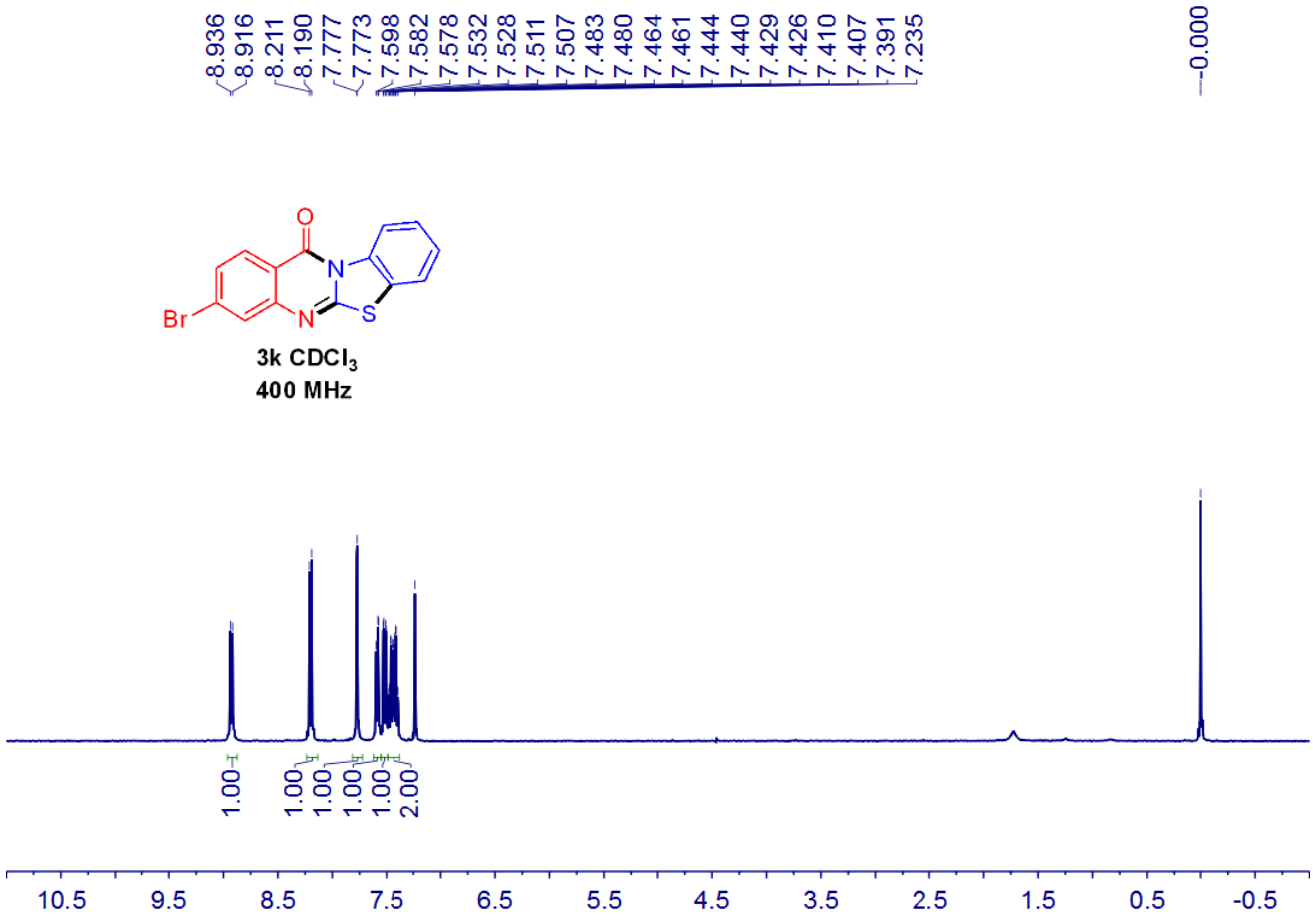
10
0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8.190
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7.773
7.598
7.582
7.578
7.532
7.528
7.511
7.507
7.483
7.480
7.464
7.461
7.444
7.440
7.429
7.426
7.410
7.407
7.391
7.235
0.000
Br
O
N
S
3k CDCl3
400 MHz
1.00
1.00
1.00
1.00
1.00
2.00
10.5
9.5
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7.5
6.5
5.5
4.5
3.5
2.5
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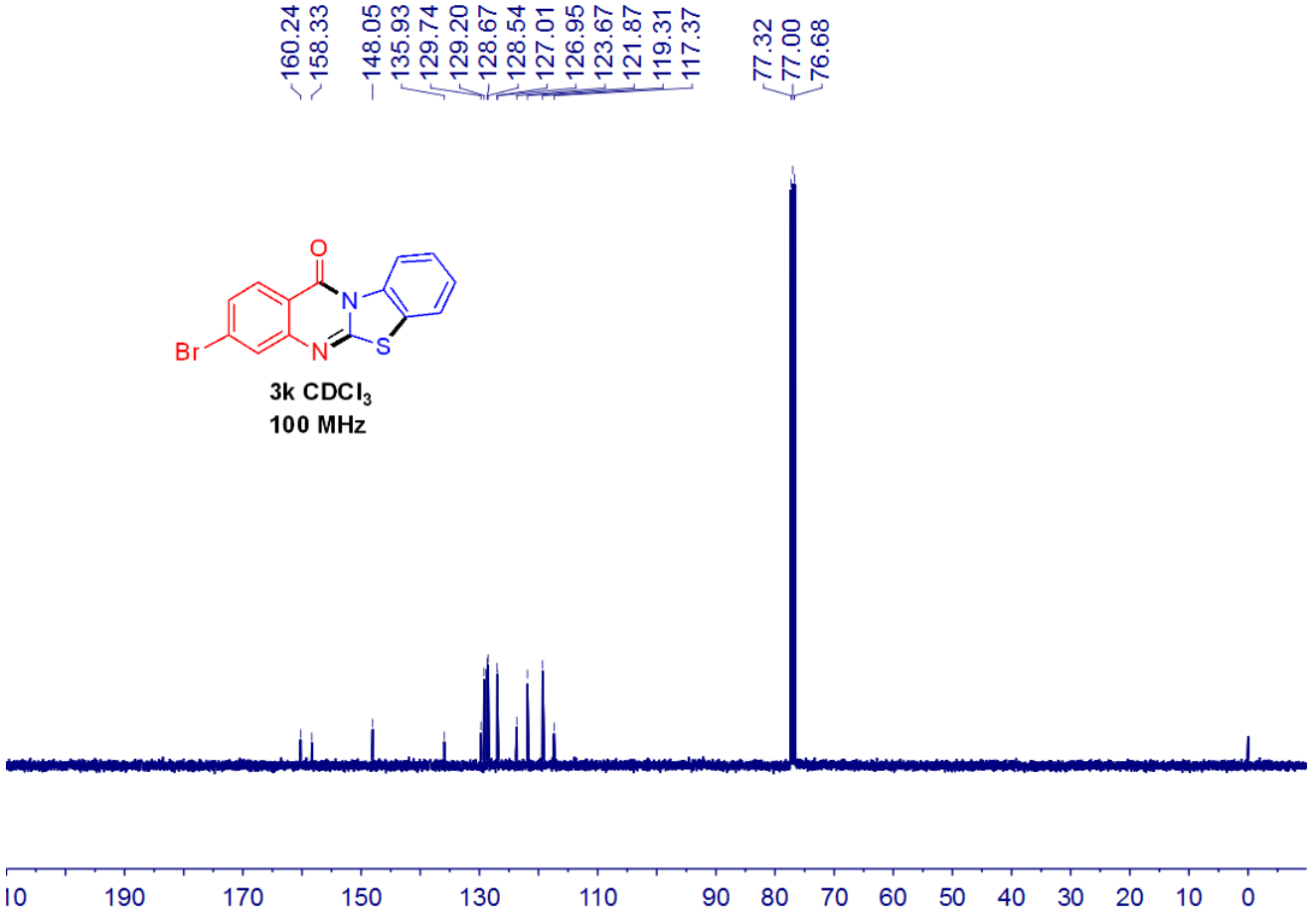
-0.5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129.20
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128.54
127.01
126.95
123.67
121.87
119.31
117.37
77.32
77.00
76.68
Br
O
N
S
3k CDCl3
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150
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110
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70
60
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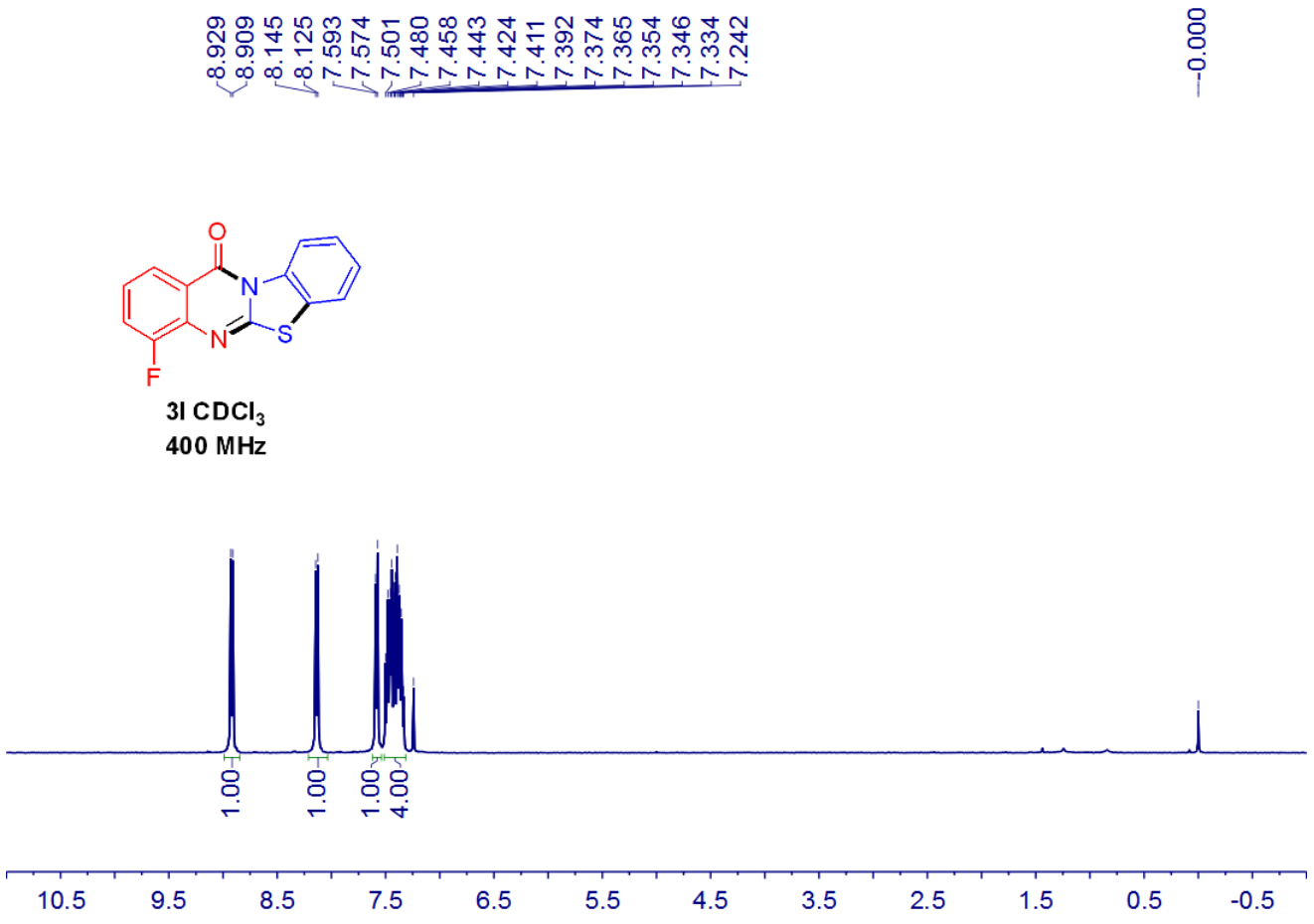
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7.501
7.480
7.458
7.443
7.424
7.411
7.392
7.374
7.365
7.354
7.346
7.334
7.242
0.000
O
N
N
S
F
3l CDCl3
400 MHz
1.00
1.00
1.00
4.00
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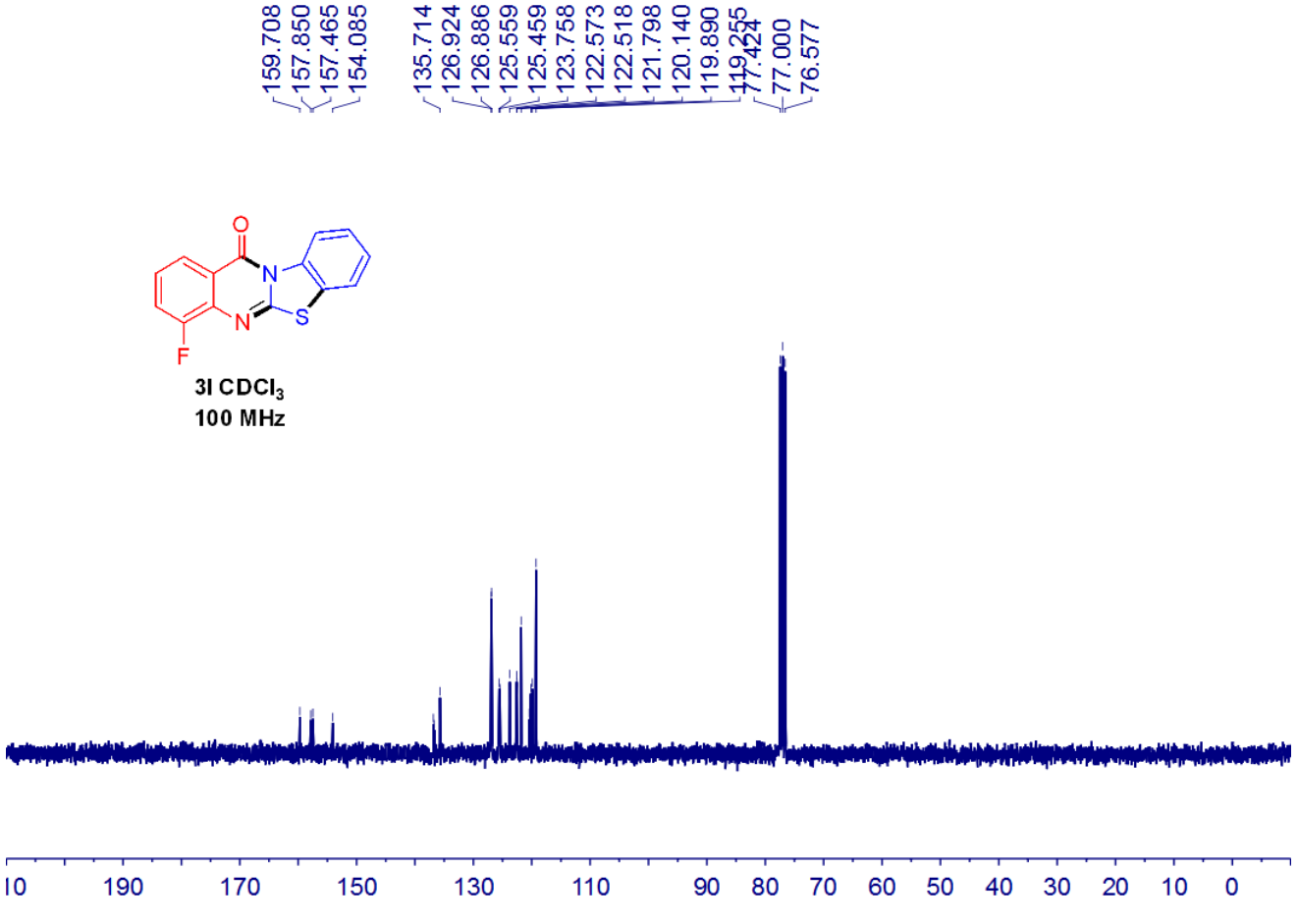
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125.559
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123.758
122.573
122.518
121.798
120.140
119.890
119.255
77.424
77.000
76.577
O
N
N
S
F
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130
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10
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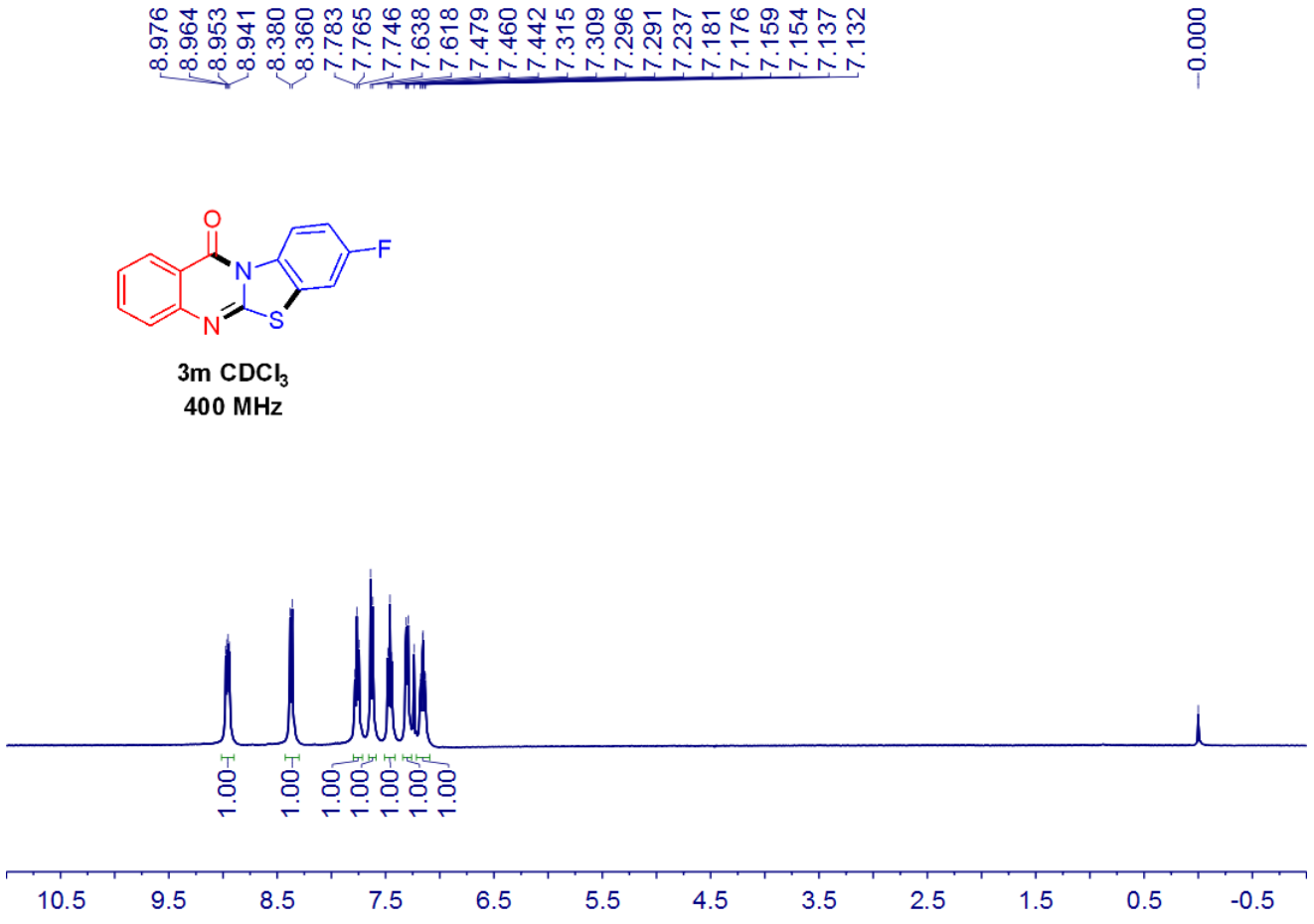
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7.638
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7.479
7.460
7.442
7.315
7.309
7.296
7.291
7.237
7.181
7.176
7.159
7.154
7.137
7.132
0.000
O
N
S
N
F
3m CDCl3
400 MHz
1.00
1.00
1.00
1.00
1.00
1.00
1.00
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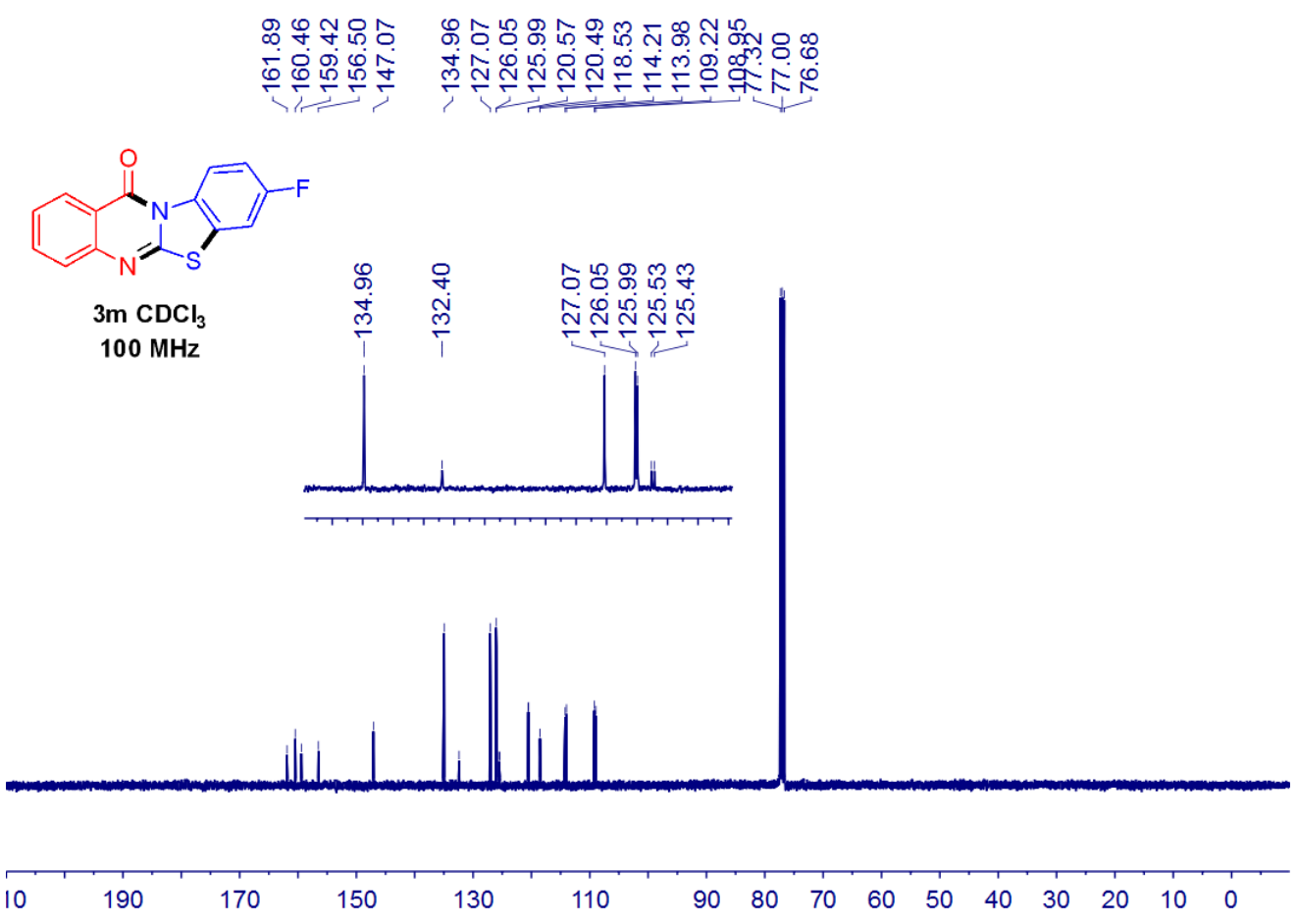
-0.5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120.49
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114.21
113.98
109.22
108.95
77.32
77.00
76.68
O
N
S
N
F
3m CDCl3
100 MHz
134.96
132.40
127.07
126.05
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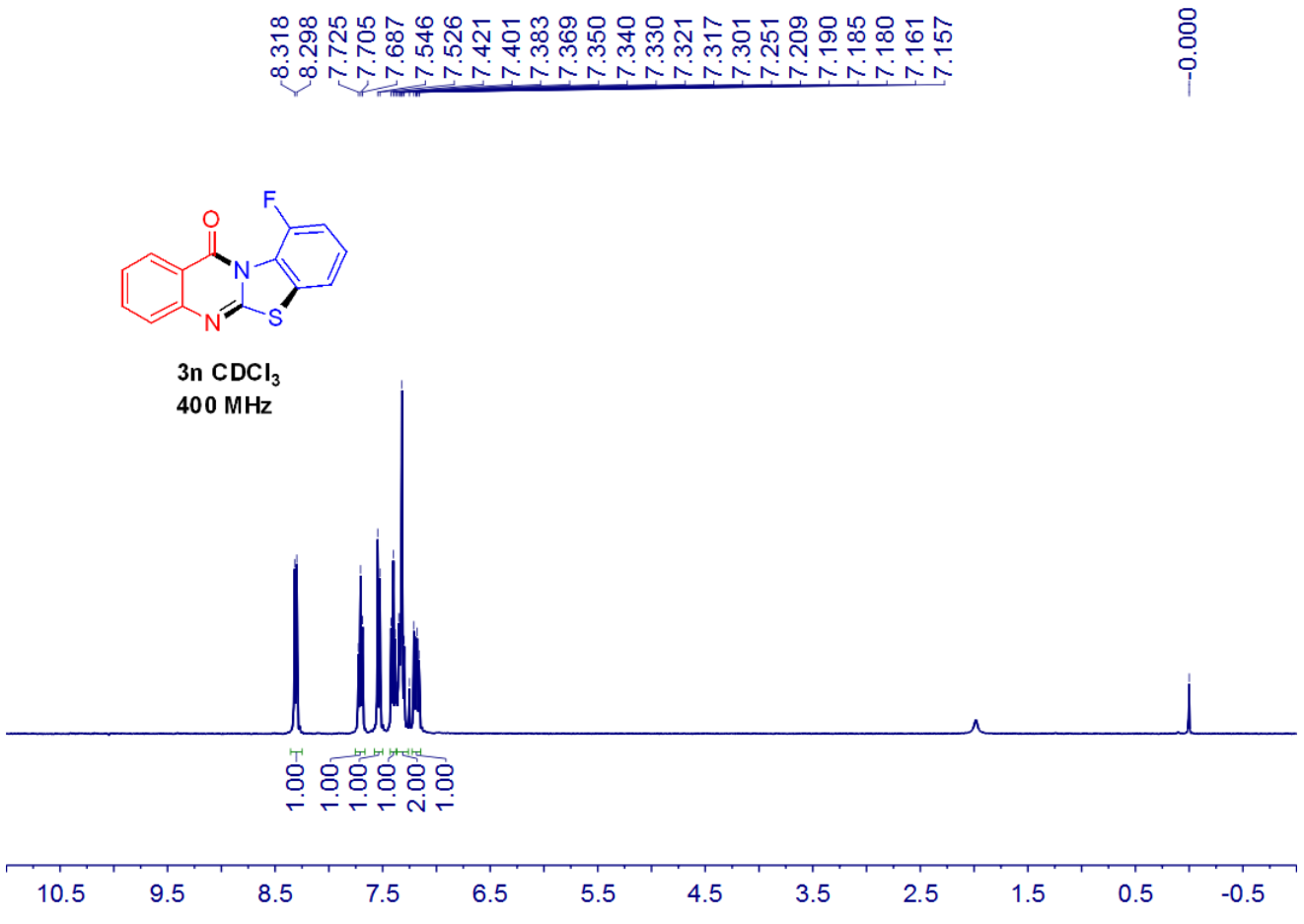
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7.546
7.526
7.421
7.401
7.383
7.369
7.350
7.340
7.330
7.321
7.317
7.301
7.251
7.209
7.190
7.185
7.180
7.161
7.157
0.000
F
O
N
N
S
3n CDCl3
400 MHz
1.00
1.00
1.00
1.00
2.00
1.00
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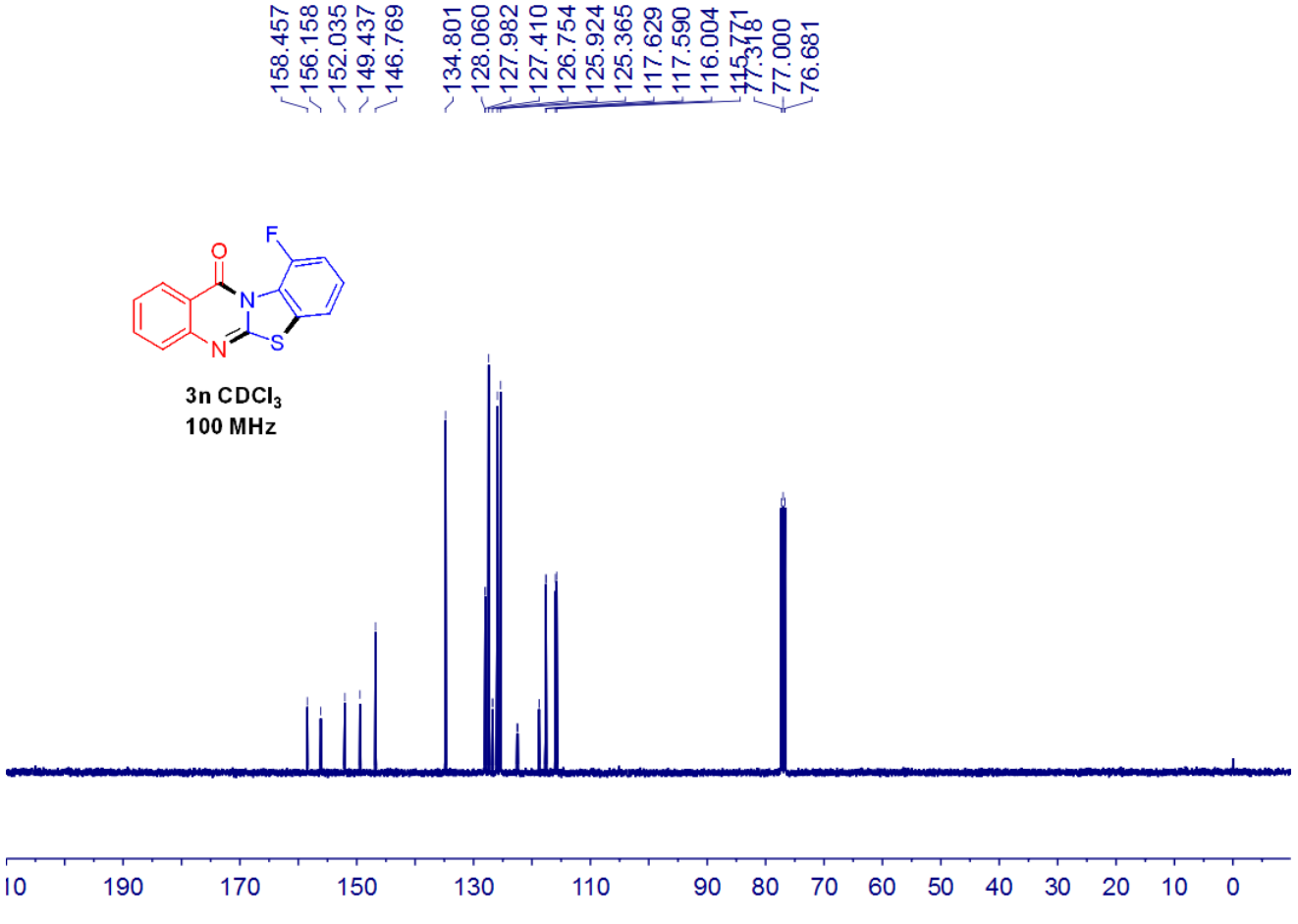
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128.060
127.982
127.410
126.754
125.924
125.365
117.629
117.590
116.004
115.771
77.318
77.000
76.681
F
O
N
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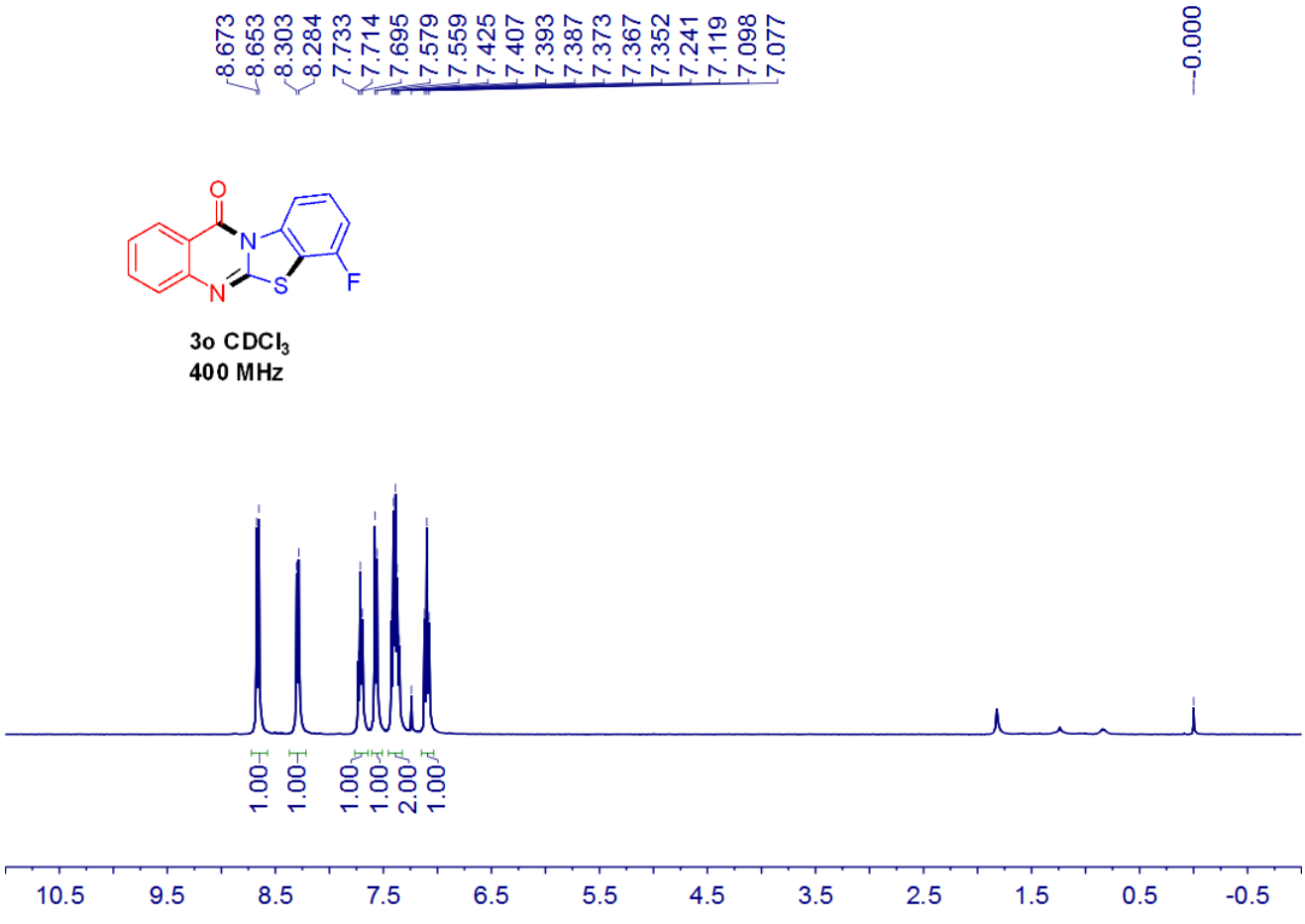
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7.579
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7.425
7.407
7.393
7.387
7.373
7.367
7.352
7.241
7.119
7.098
7.077
0.000
O
N
S
N
F
3o CDCl3
400 MHz
1.00
1.00
1.00
1.00
2.00
1.00
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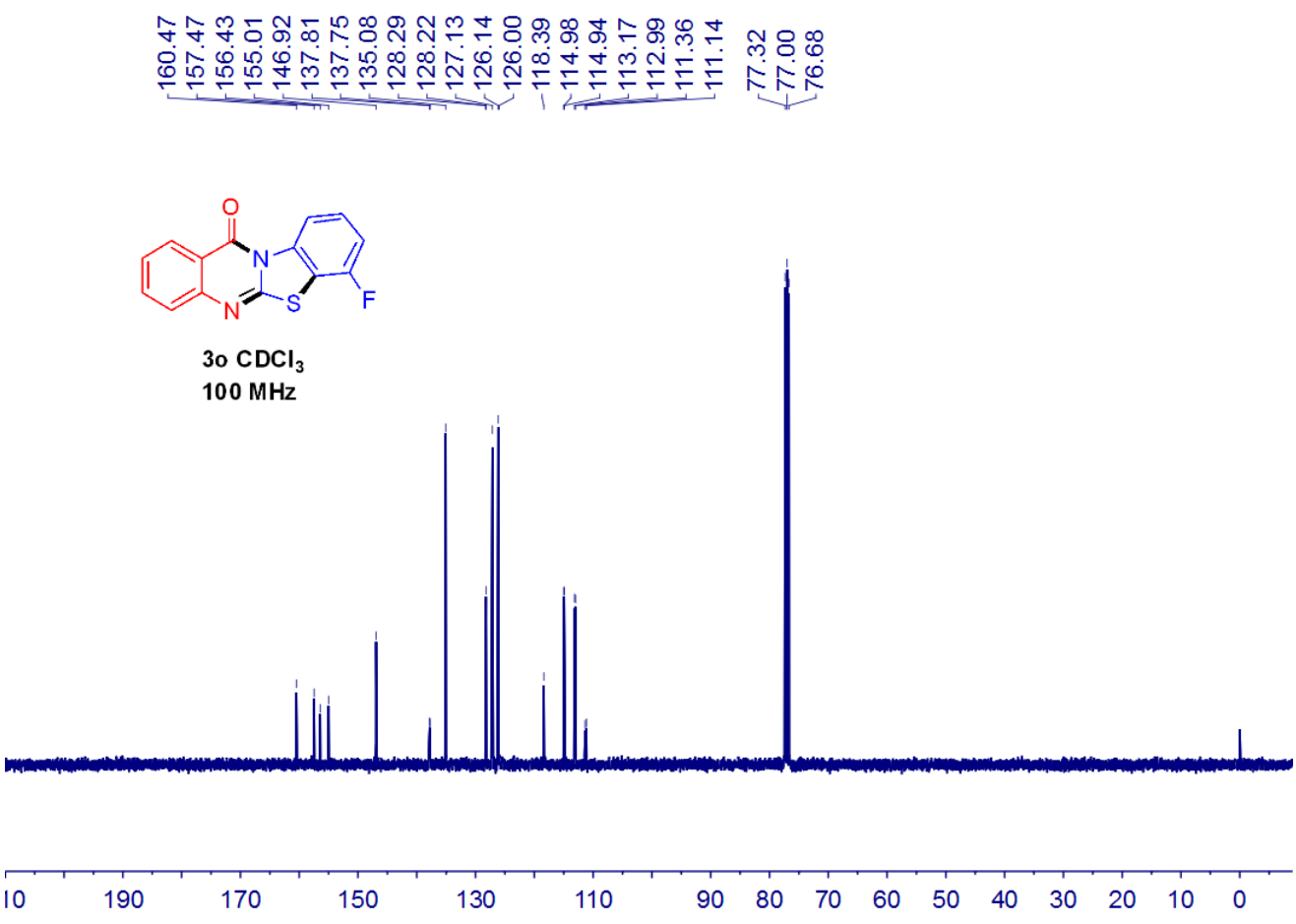
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135.08
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128.22
127.13
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126.00
118.39
114.98
114.94
113.17
112.99
111.36
111.14
77.32
77.00
76.68
O
N
S
N
F
3o CDCl3
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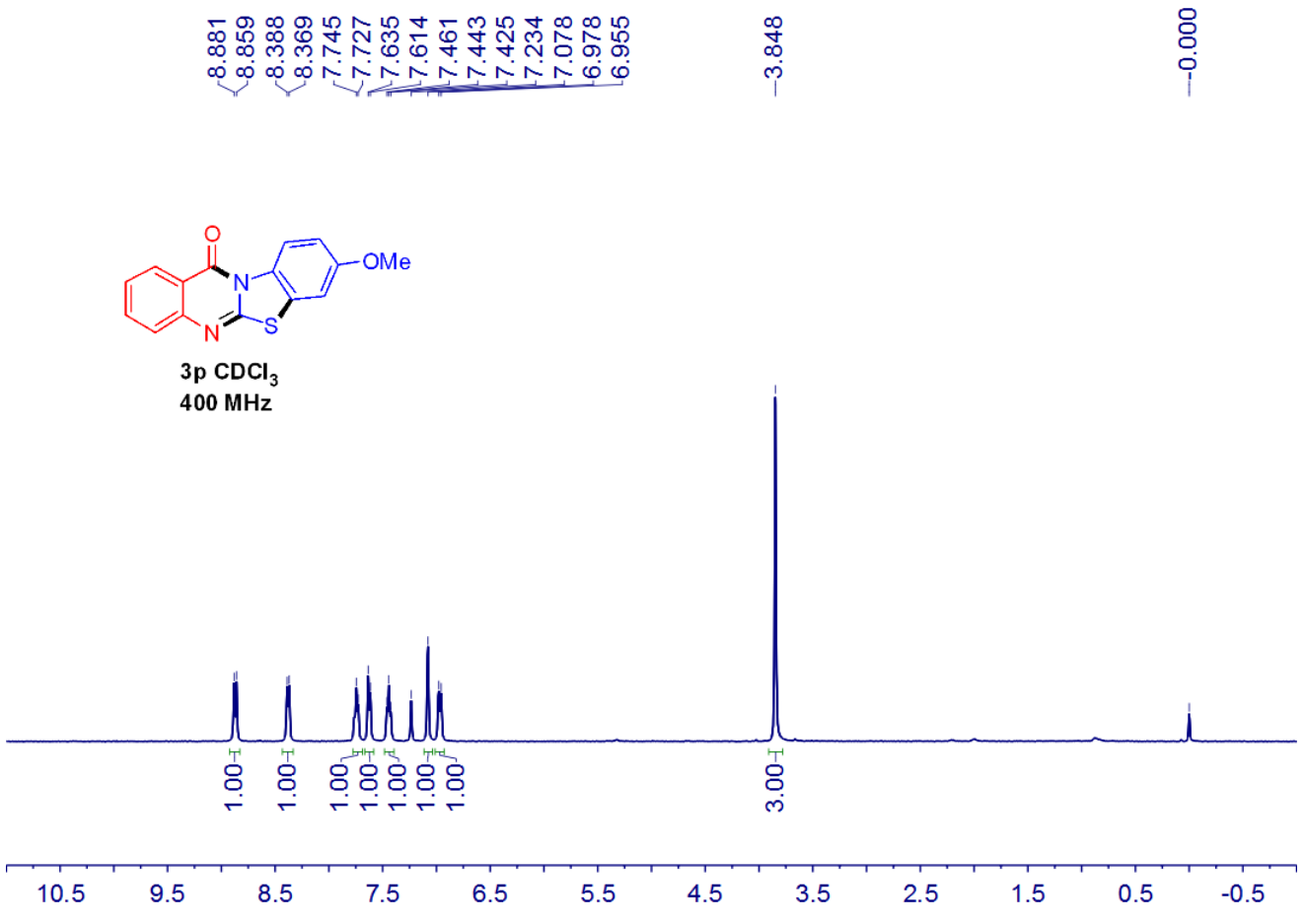
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7.727
7.635
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7.461
7.443
7.425
7.234
7.078
6.978
6.955
3.848
0.000
OMe
3p CDCl3
400 MHz
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
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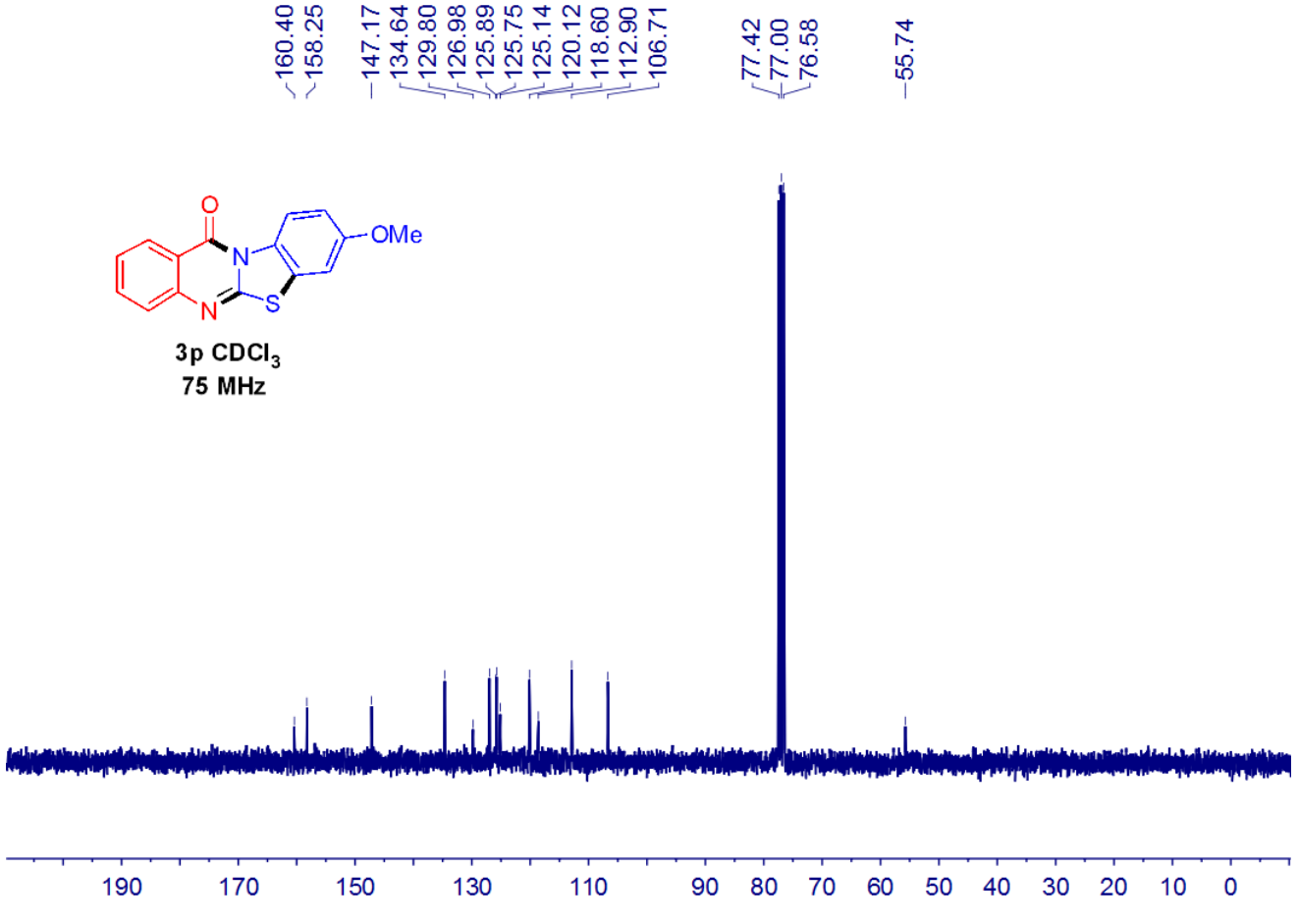
-0.5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120.12
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112.90
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77.00
76.58
55.74
OMe
3p CDCl3
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70
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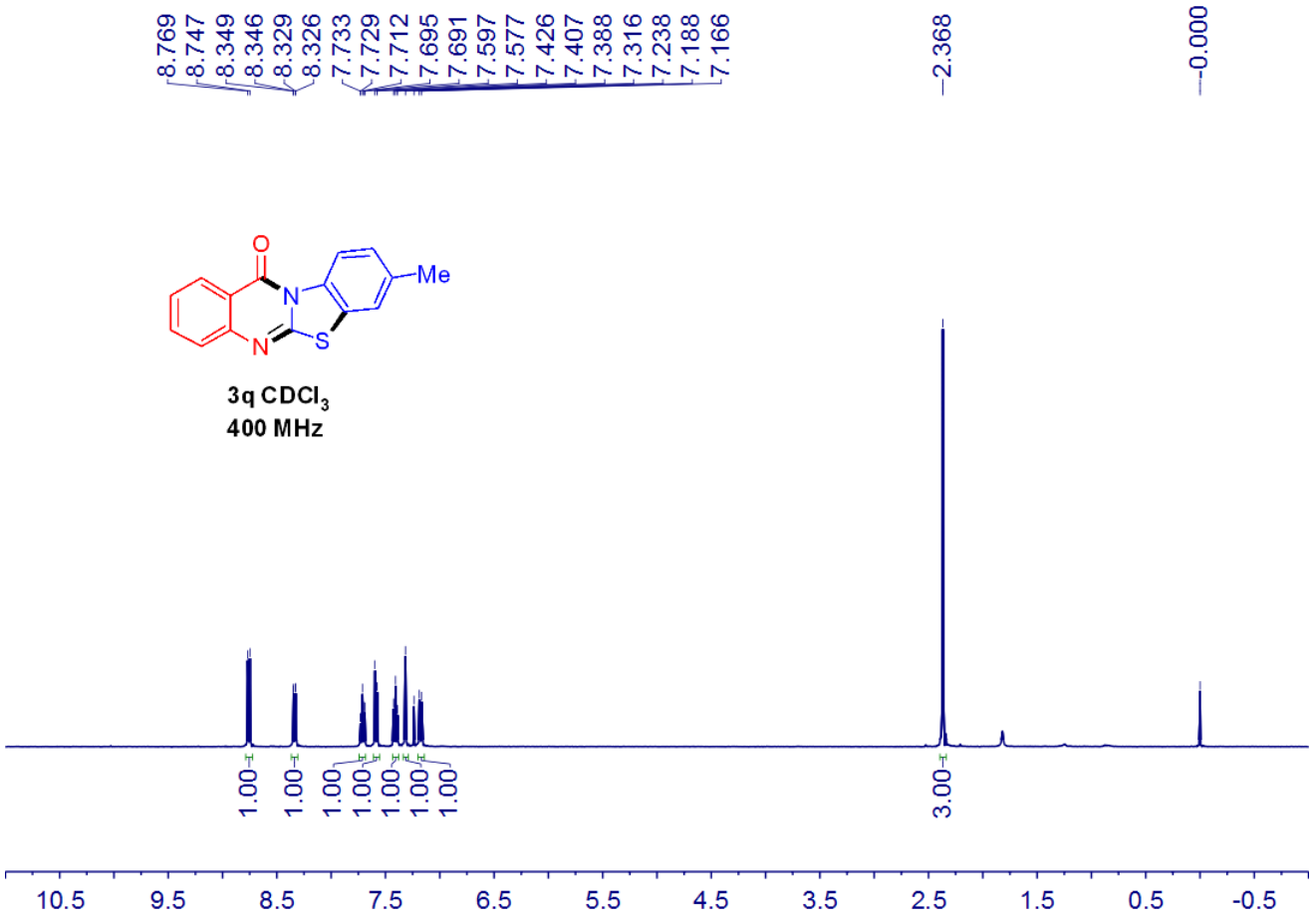
10
0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7.695
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7.597
7.577
7.426
7.407
7.388
7.316
7.238
7.188
7.166
2.368
0.000
O
N
S
N
Me
3q CDCl3
400 MHz
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
10.5
9.5
8.5
7.5
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5.5
4.5
3.5
2.5
1.5
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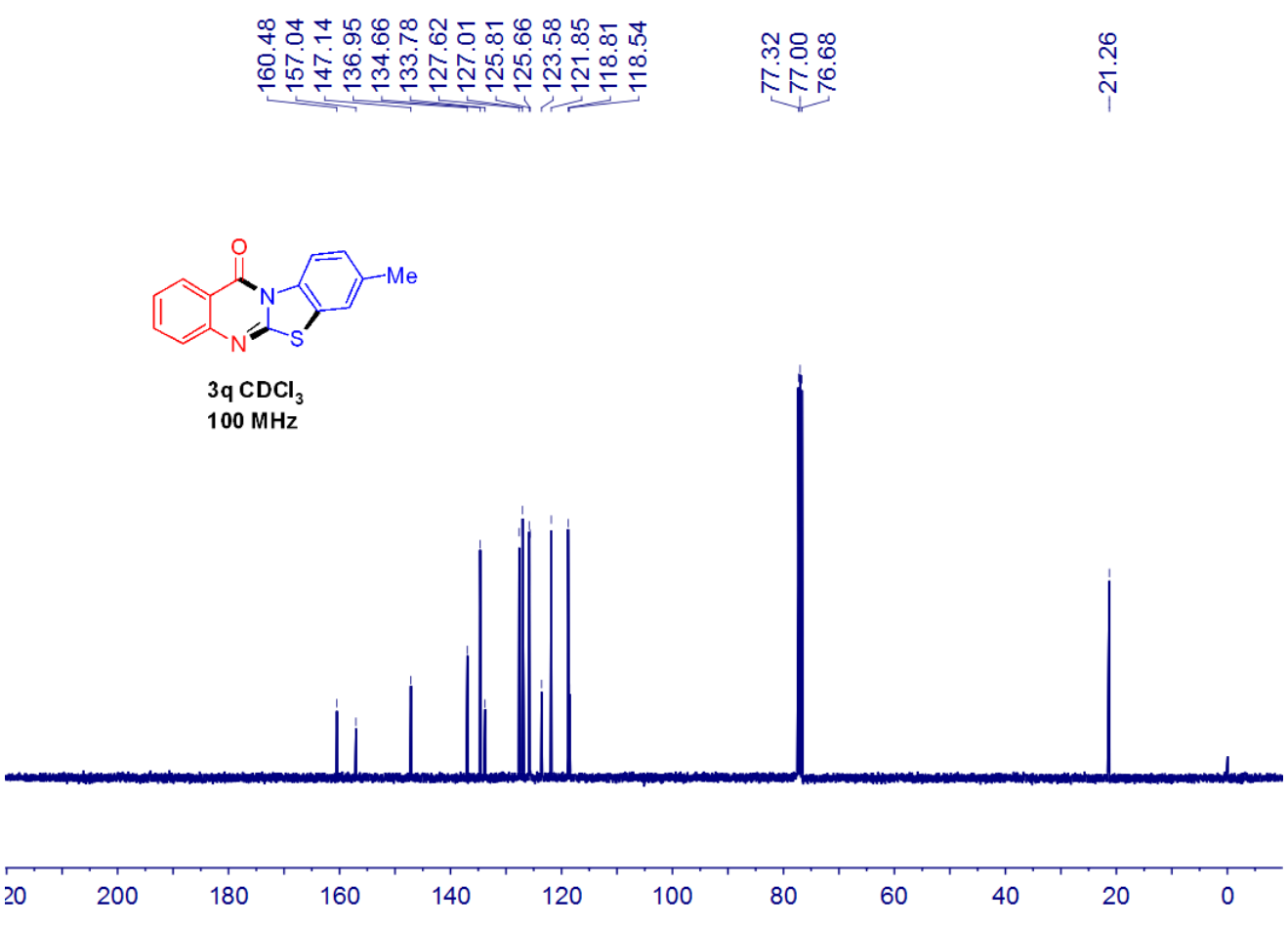
-0.5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157.04
147.14
136.95
134.66
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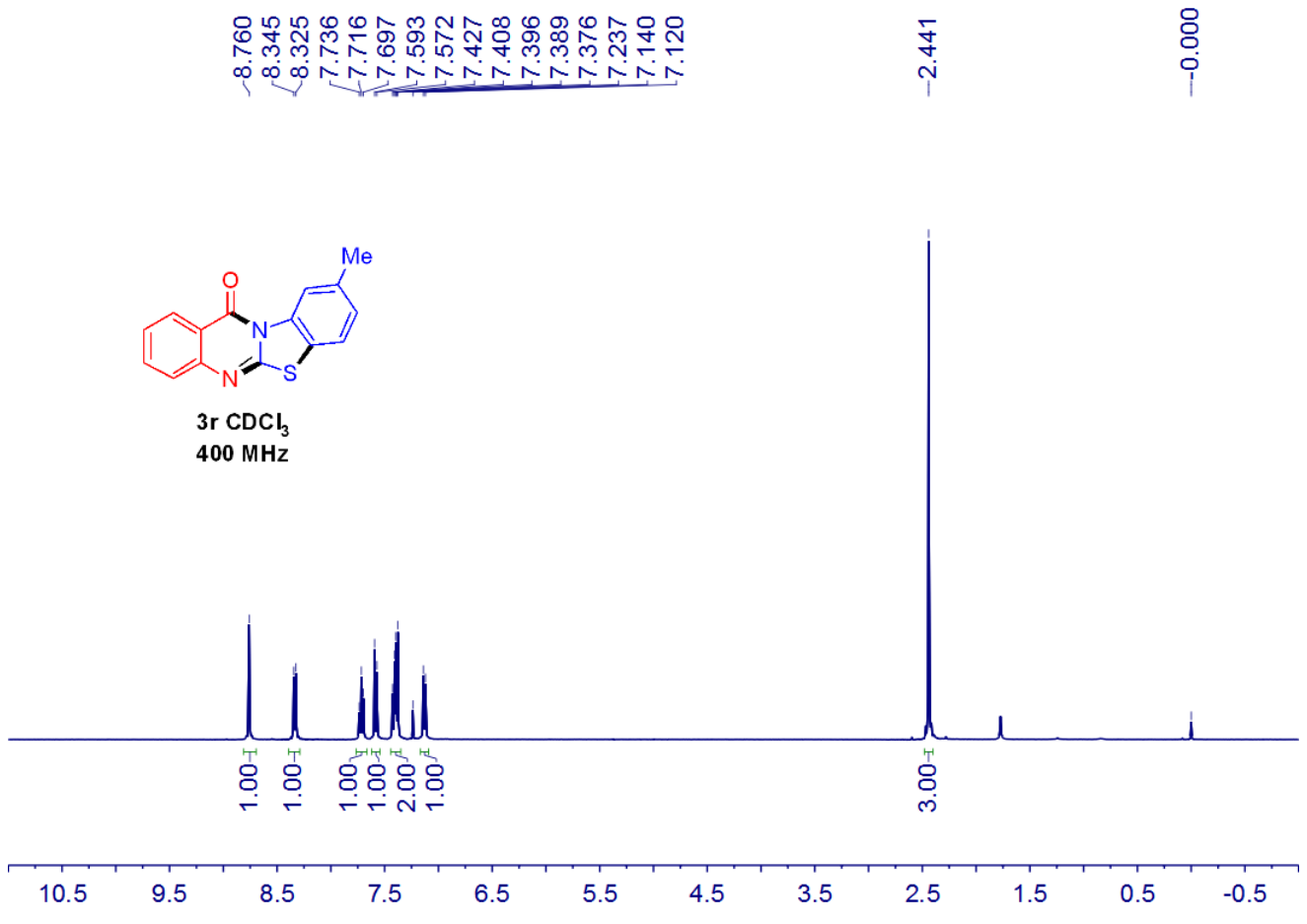
127.62
127.01
125.81
125.66
123.58
121.85
118.81
118.54
77.32
77.00
76.68
21.26
O
N
S
N
Me
3q CDCl3
100 MHz
200
180
160
140
120
100
80
60
40
20
0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8.345
8.325
7.736
7.716
7.697
7.593
7.572
7.427
7.408
7.396
7.389
7.376
7.237
7.140
7.120
2.441
0.000
Me
O
N
S
N
3r CDCl3
400 MHz
1.00
1.00
1.00
1.00
2.00
1.00
3.00
10.5
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8.5
7.5
6.5
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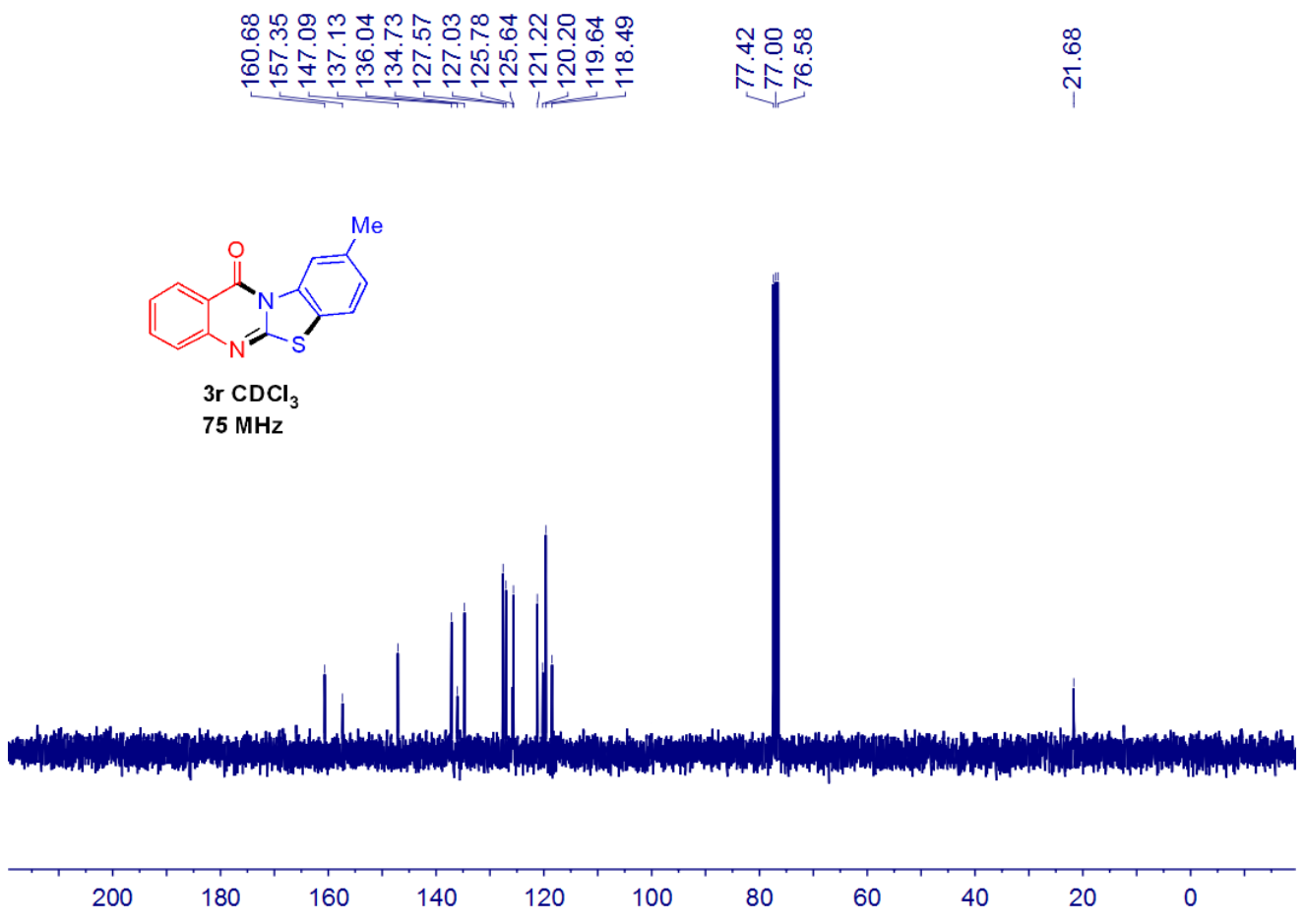
3.5
2.5
1.5
0.5
-0.5


160.68
157.35
147.09
137.13
136.04
134.73
127.57
127.03
125.78
125.64
121.22
120.20
119.64
118.49
77.42
77.00
76.58
21.68
Me
O
N
S
N
3r CDCl3
75 MHz
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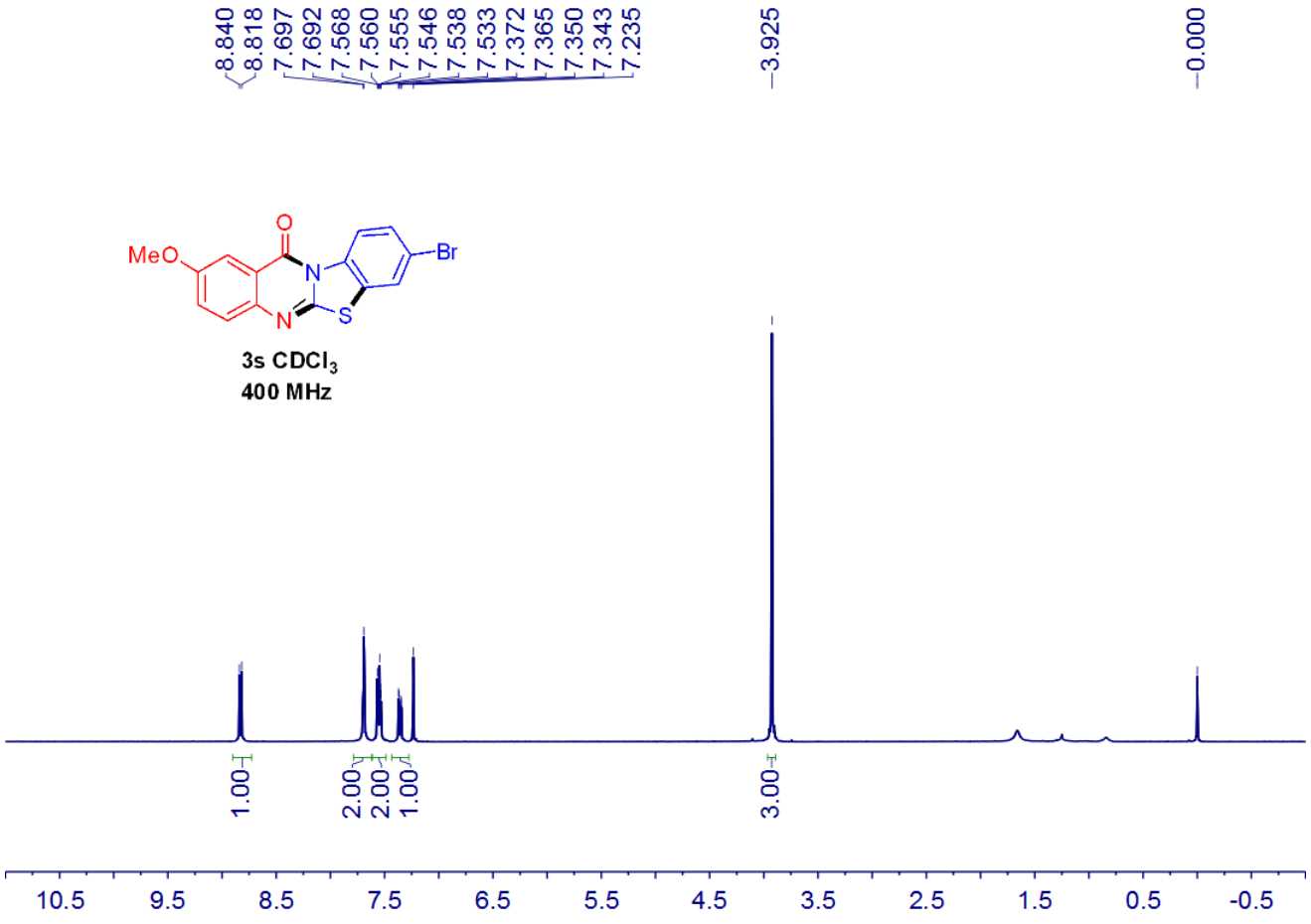
180
160
140
120
100
80
60
40
20
0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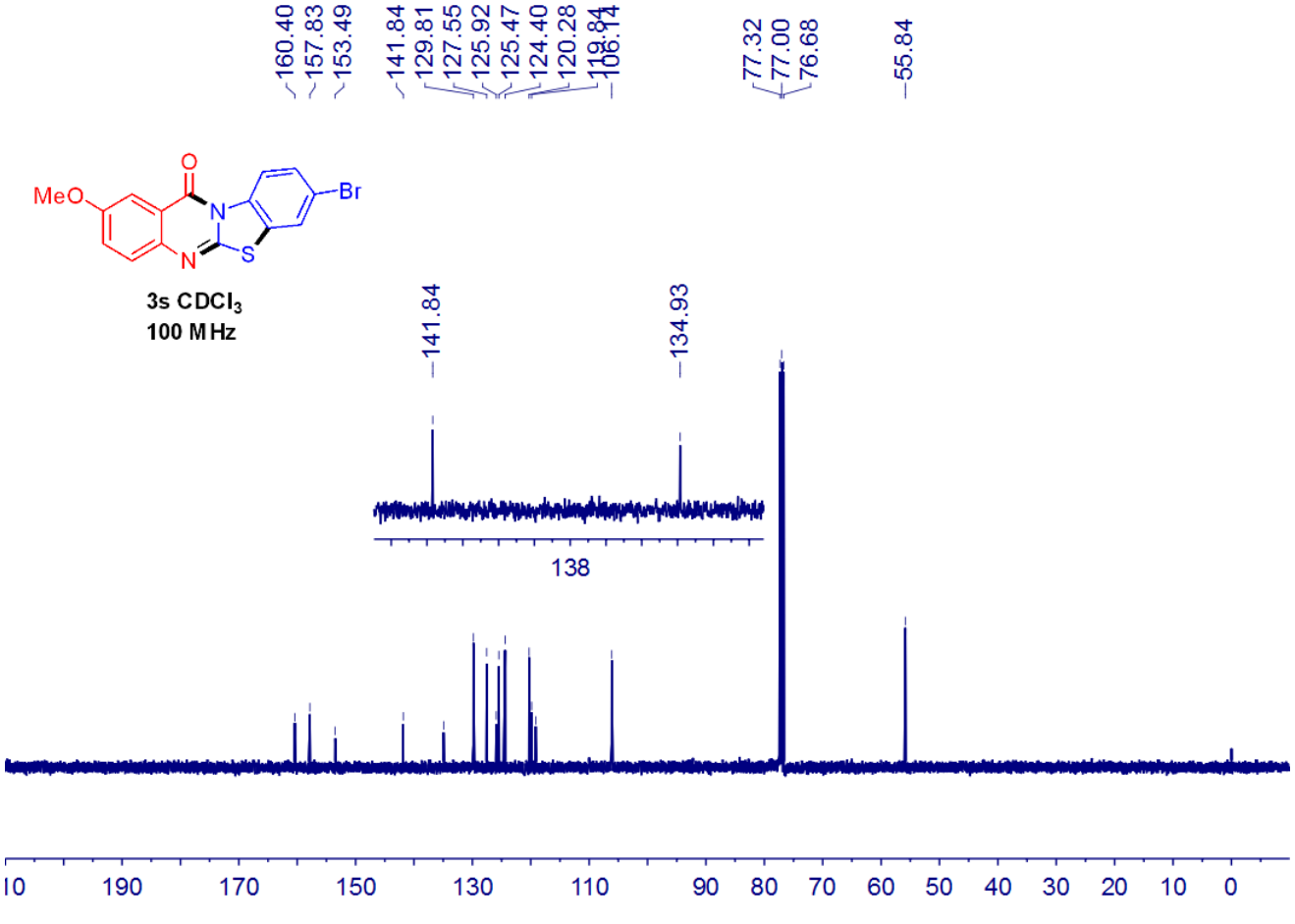
8.818
7.697
7.692
7.568
7.560
7.555
7.546
7.538
7.533
7.372
7.365
7.350
7.343
7.235
3.925
0.000
MeO
O
N
Br
N
S
3s CDCl3
400 MHz
1.00
2.00
2.00
1.00
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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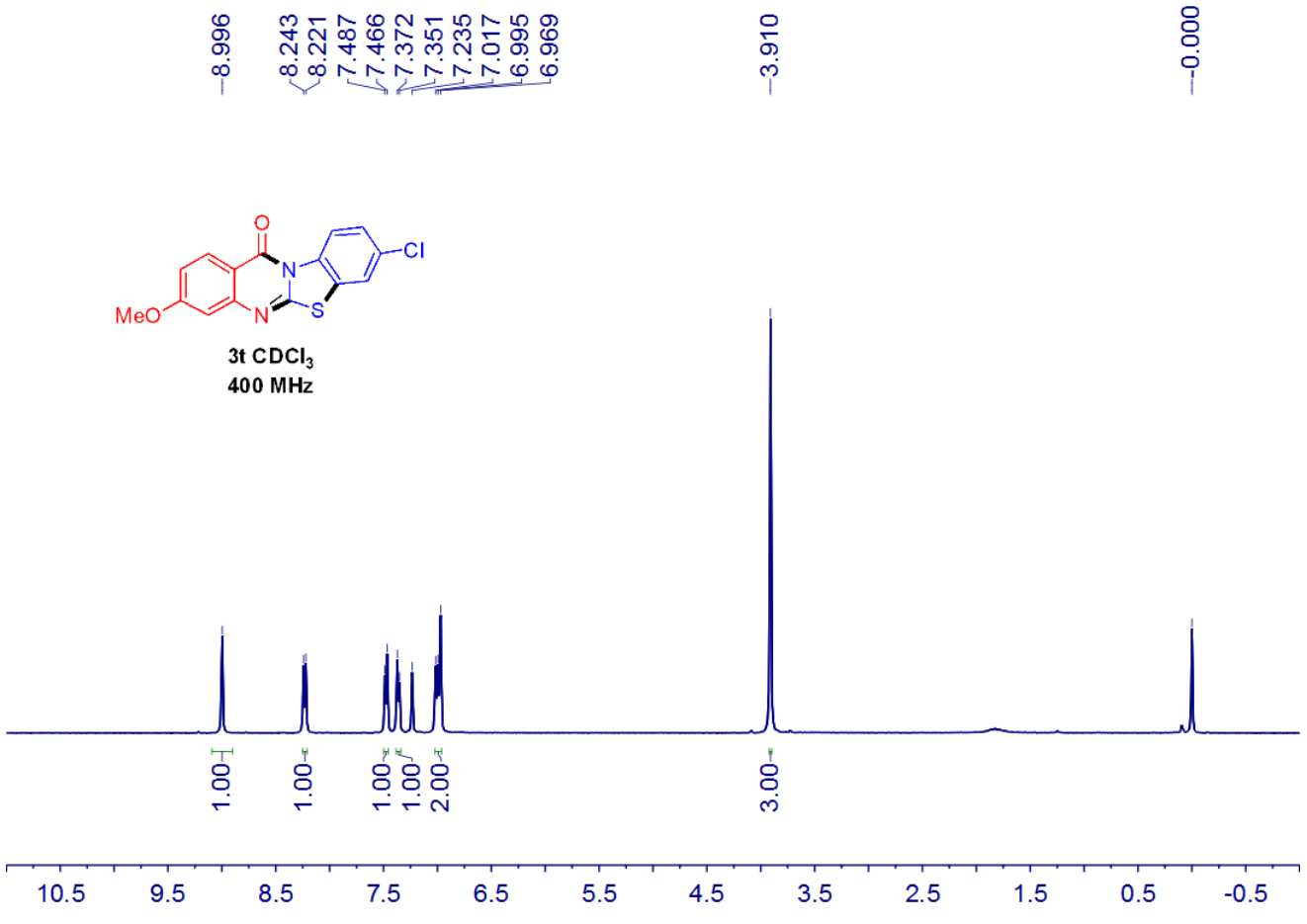
157.83
153.49
141.84
129.81
127.55
125.92
125.47
124.40
120.28
77.32
77.00
76.68
55.84
MeO
O
N
Br
N
S
3s CDCl3
100 MHz
141.84
134.93
138
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


8.996
8.243
8.221
7.487
7.466
7.372
7.351
7.235
7.017
6.995
6.969
3.910
0.000
O
N
Cl
MeO
N
S
3t CDCl3
400 MHz
1.00
1.00
1.00
1.00
2.00
3.00
10.5
9.5
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7.5
6.5
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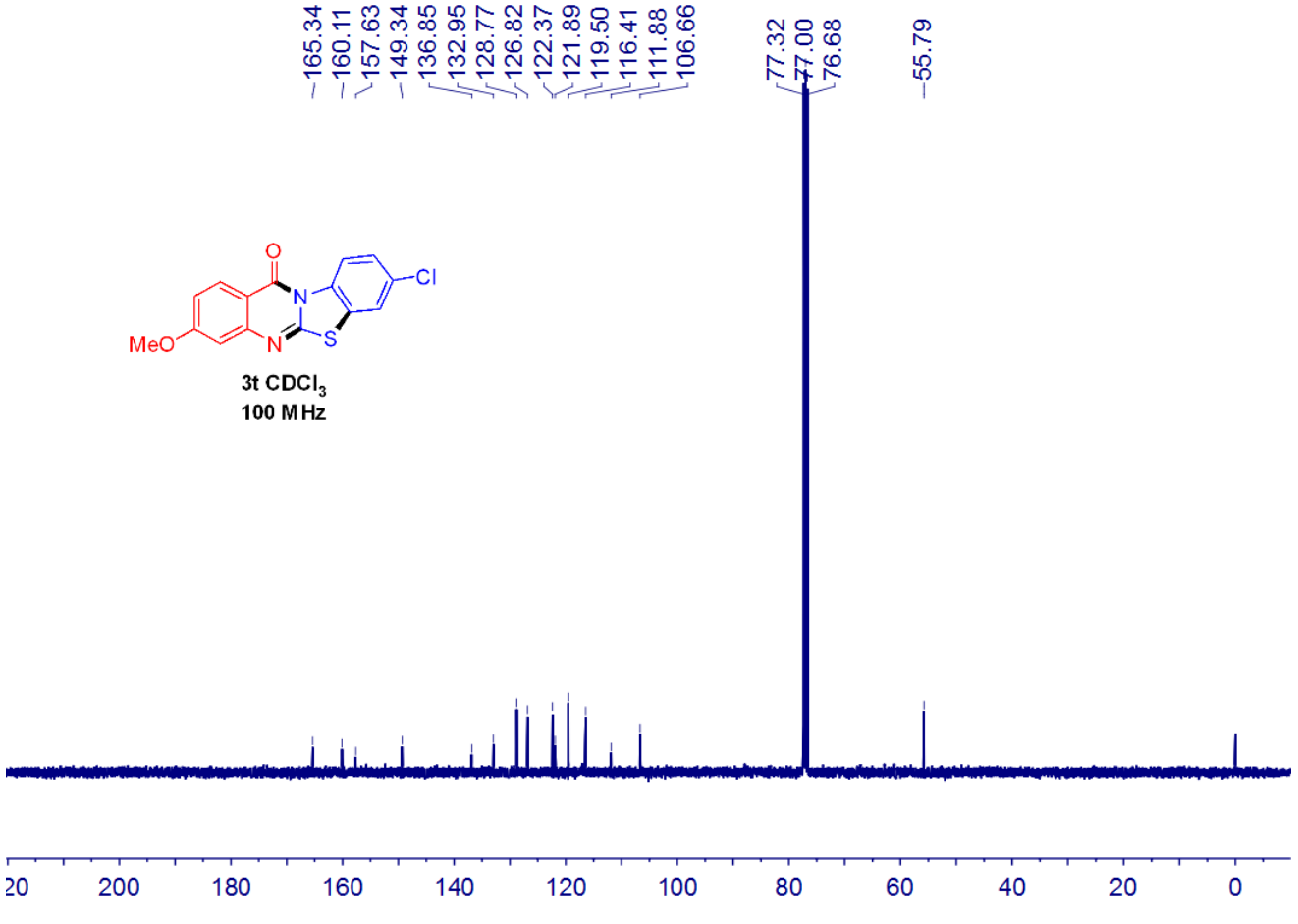
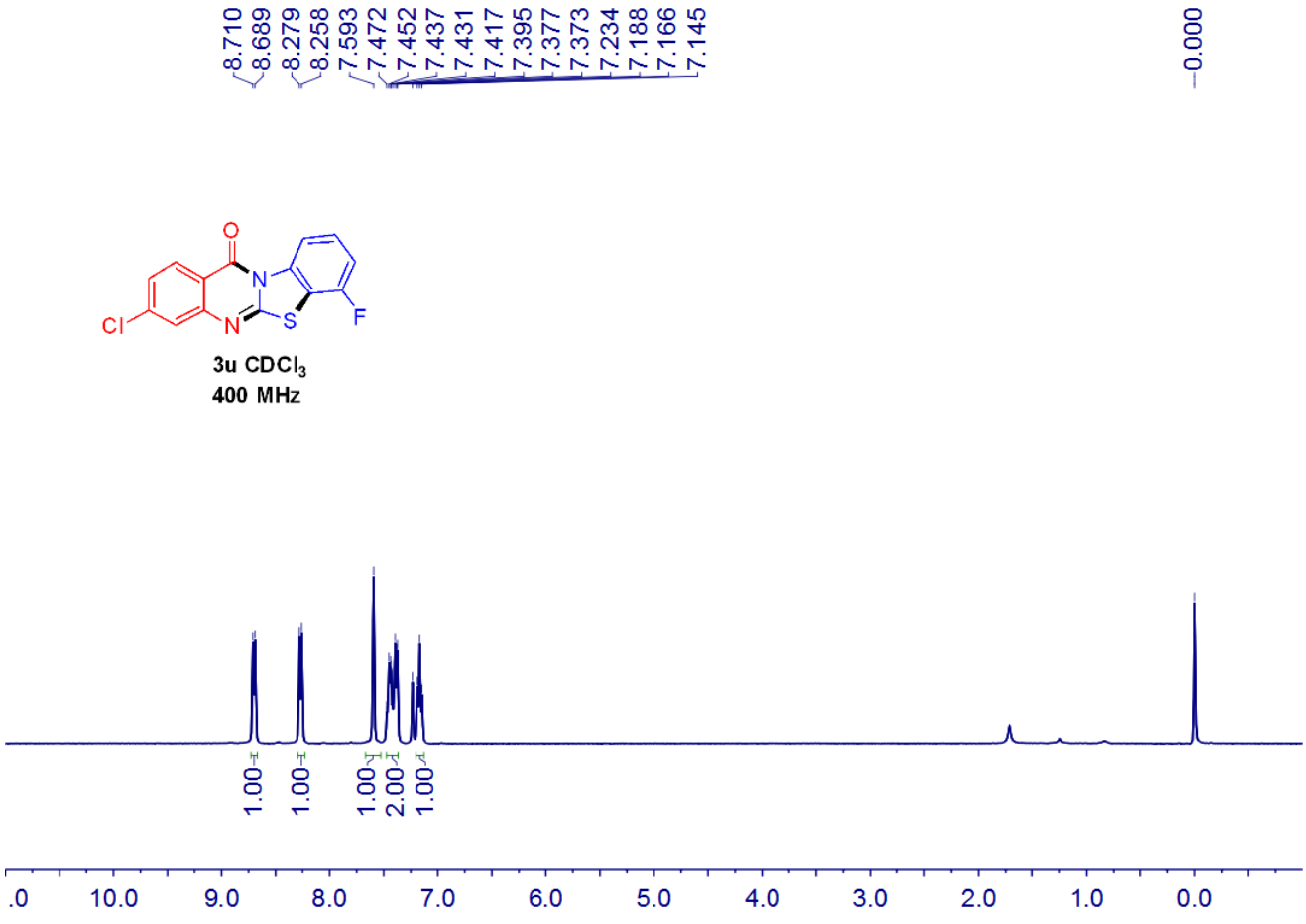
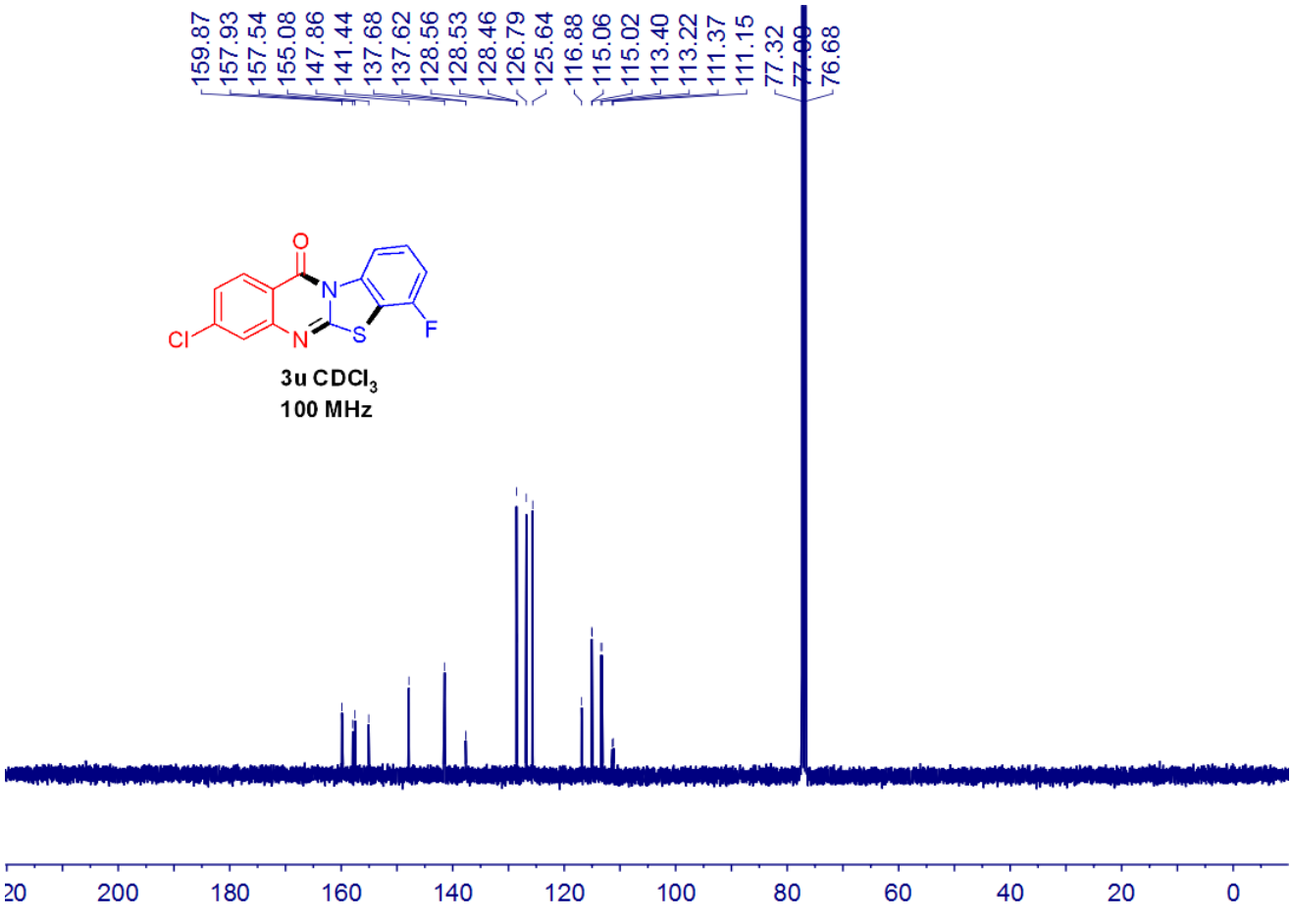
4.5
3.5
2.5
1.5
0.5
-0.5


165.34
160.11
157.63
149.34
136.85
132.95
128.77
126.82
122.37
121.89
119.50
116.41
111.88
106.66
77.32
77.00
76.68
55.79
O
N
Cl
MeO
N
S
3t CDCl3
100 MHz
220
200
180
160
140
120
100
80
60
40
20
0


8.710
8.689
8.279
8.258
7.593
7.472
7.452
7.437
7.431
7.417
7.395
7.377
7.373
7.234
7.188
7.166
7.145
0.000
3u CDCl3
400 MHz
1.00
1.00
1.00
2.00
1.00
.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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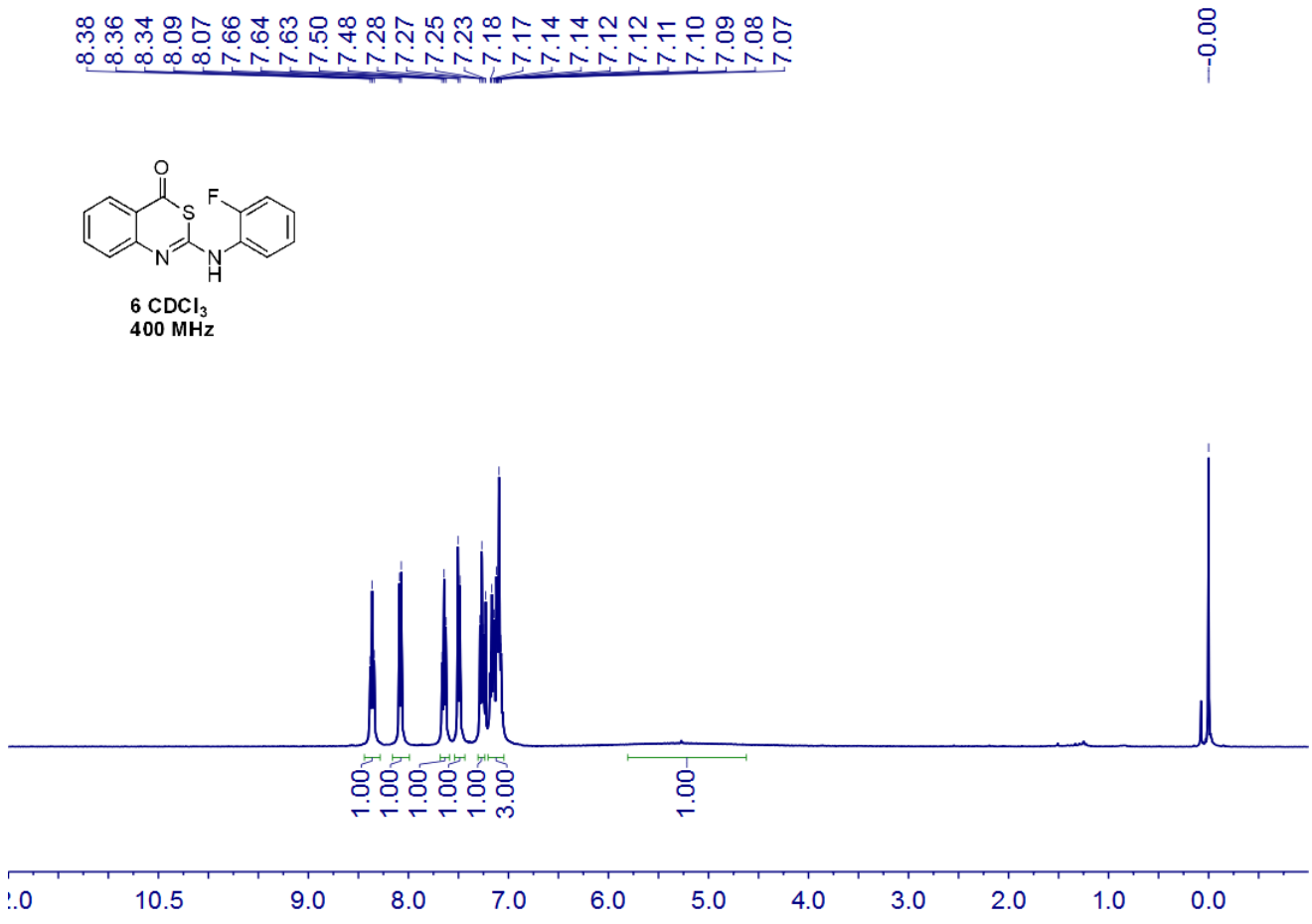
157.54
155.08
147.86
141.44
137.68
137.62
128.56
128.53
128.46
126.79
125.64
116.88
115.06
115.02
113.40
113.22
111.37
111.15
77.32
77.00
76.68
3u CDCl3
100 MHz
20
200
180
160
140
120
100
80
60
40
20
0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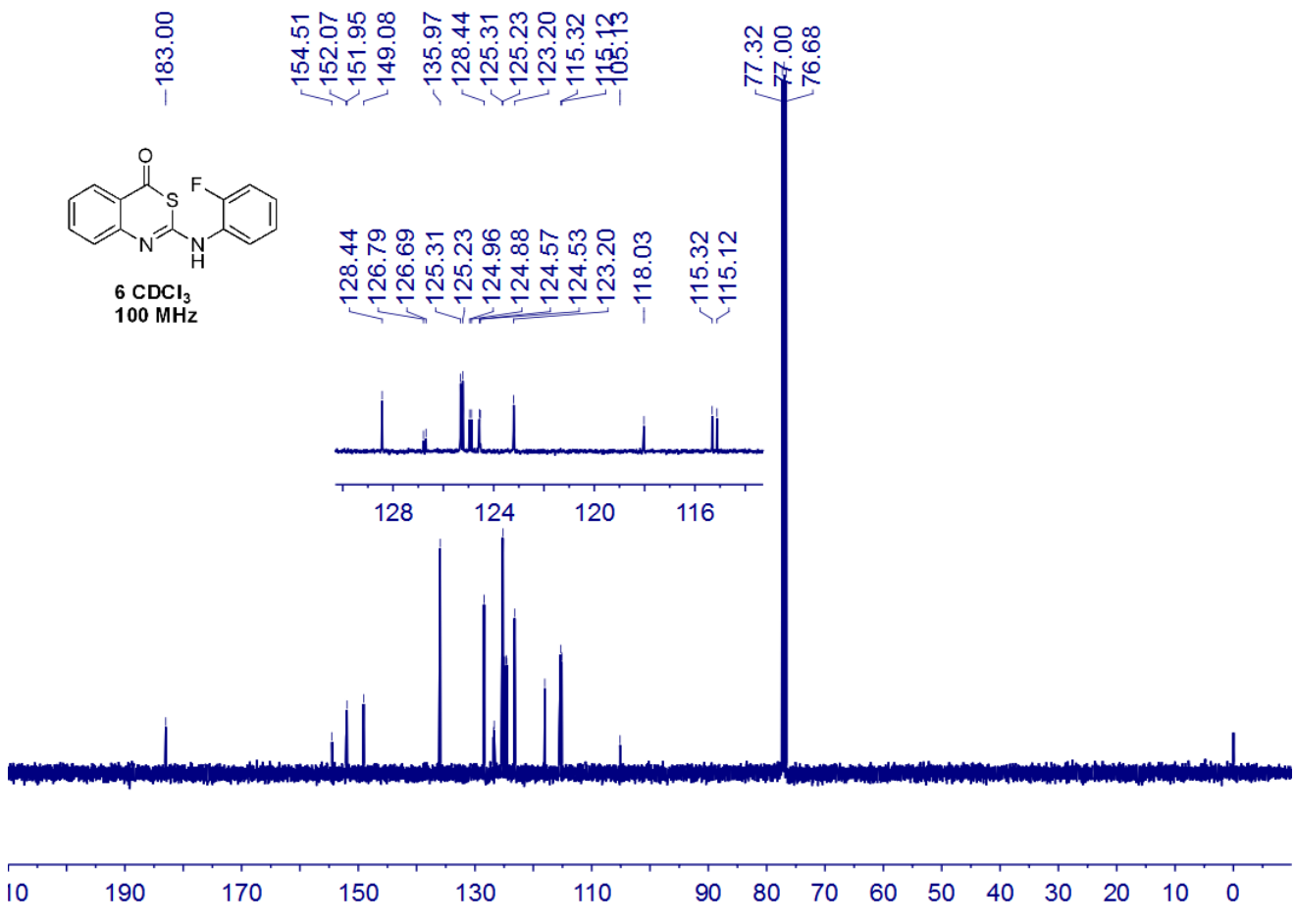
8.36
8.34
8.09
8.07
7.66
7.64
7.63
7.50
7.48
7.28
7.27
7.25
7.23
7.18
7.17
7.14
7.14
7.12
7.12
7.11
7.10
7.09
7.08
7.07
0.00
6 CDCl3
400 MHz
1.00
1.00
1.00
1.00
1.00
3.00
1.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


183.00
154.51
152.07
151.95
149.08
135.97
128.44
125.31
125.23
123.20
115.32
115.12
105.13
77.32
77.00
76.68
6 CDCl3
100 MHz
128.44
126.79
126.69
125.31
125.23
124.96
124.88
124.57
124.53
123.20
118.03
115.32
115.12
128
124
120
116
190
170
150
130
110
90
80
70
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50
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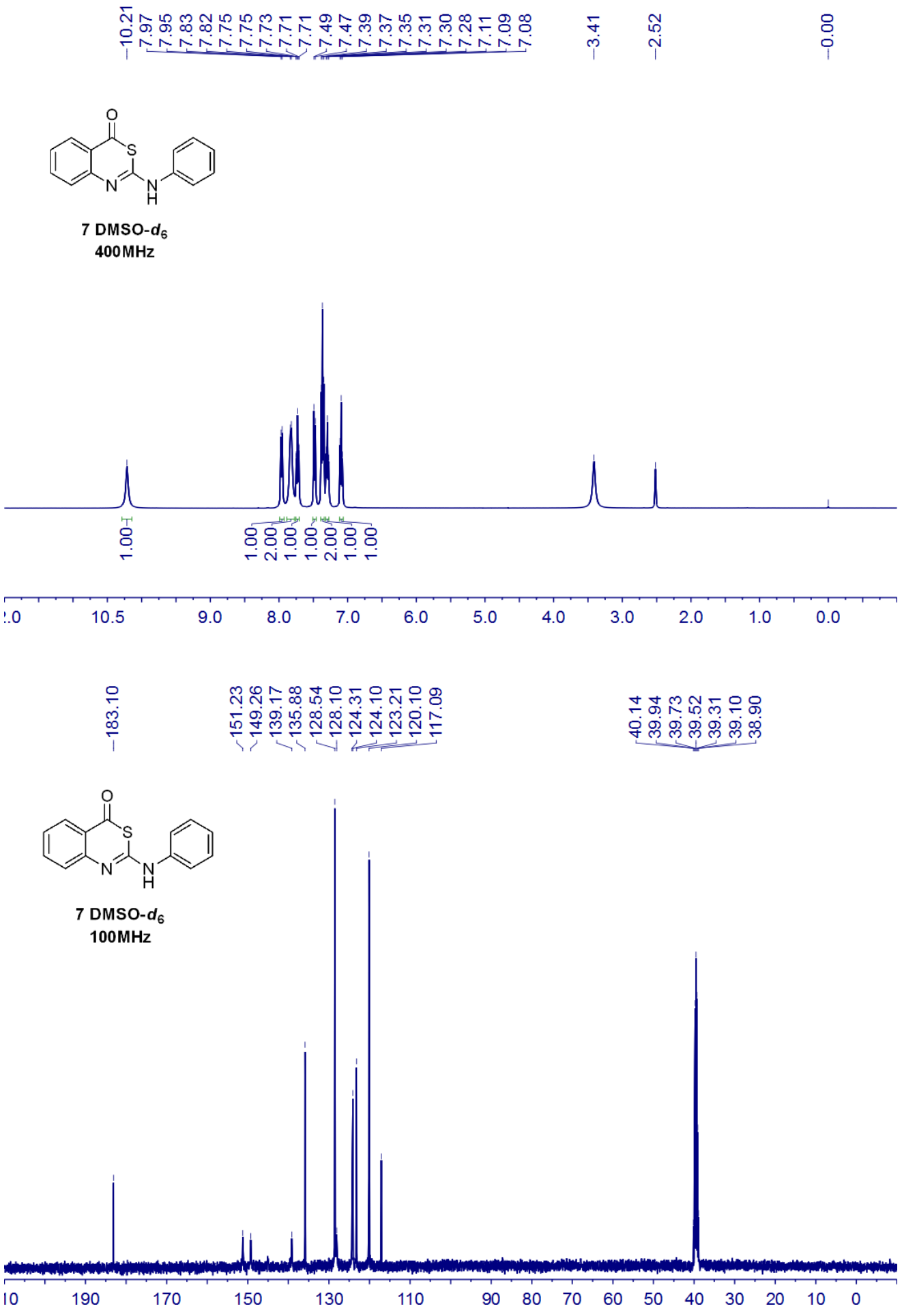
30
20
10
0


10.21
7.97
7.95
7.83
7.82
7.75
7.75
7.73
7.71
7.71
7.49
7.47
7.39
7.37
7.35
7.31
7.30
7.28
7.11
7.09
7.08
3.41
2.52
0.00
7 DMSO-d6
400MHz
1.00
1.00
2.00
1.00
1.00
2.00
1.00
1.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
183.10
151.23
149.26
139.17
135.88
128.54
128.10
124.31
124.10
123.21
120.10
117.09
40.14
39.94
39.73
39.52
39.31
39.10
38.90
7 DMSO-d6
100MHz
190
170
150
130
110
90
80
70
60
50
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30
20
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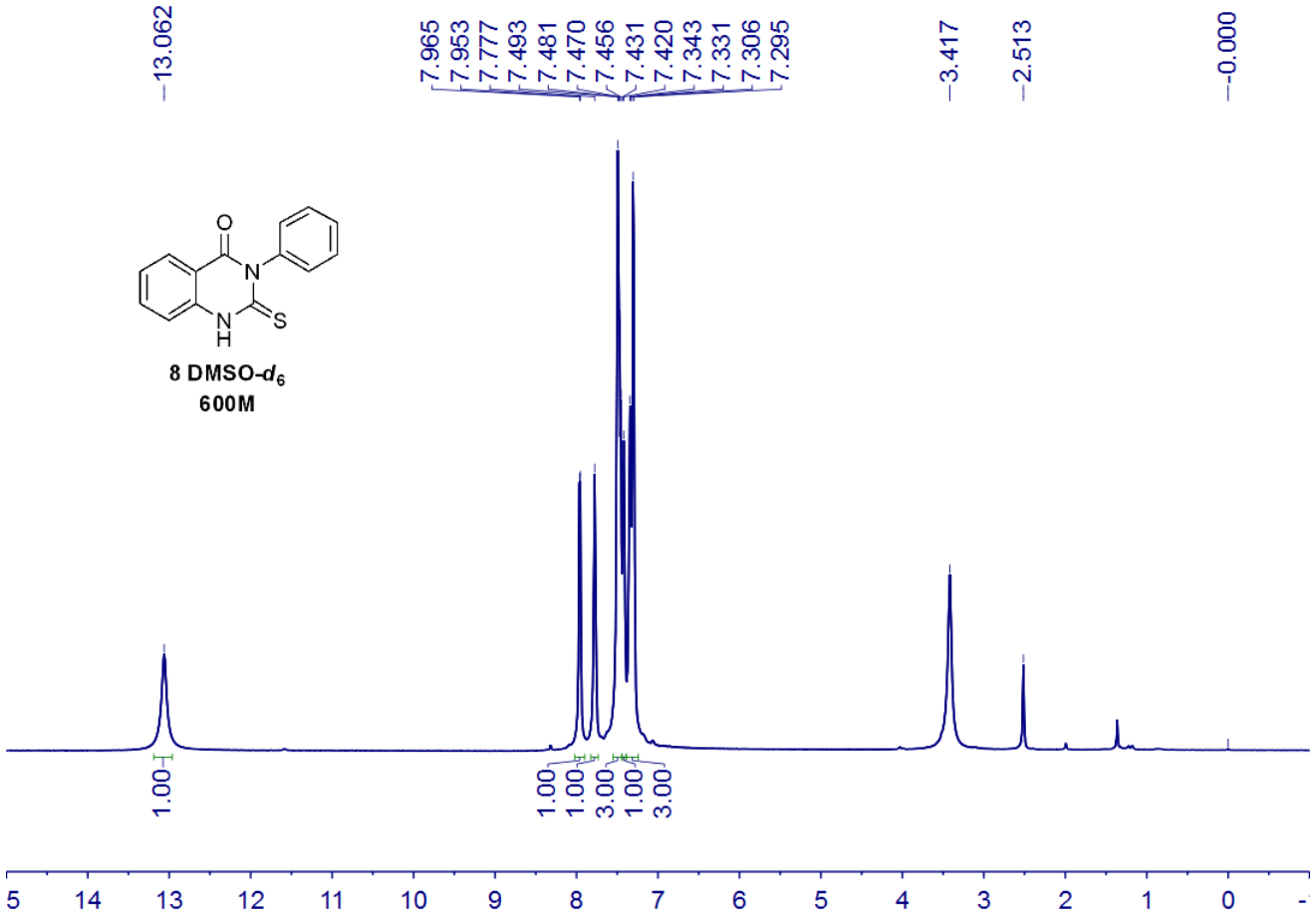
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7.777
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7.470
7.456
7.431
7.420
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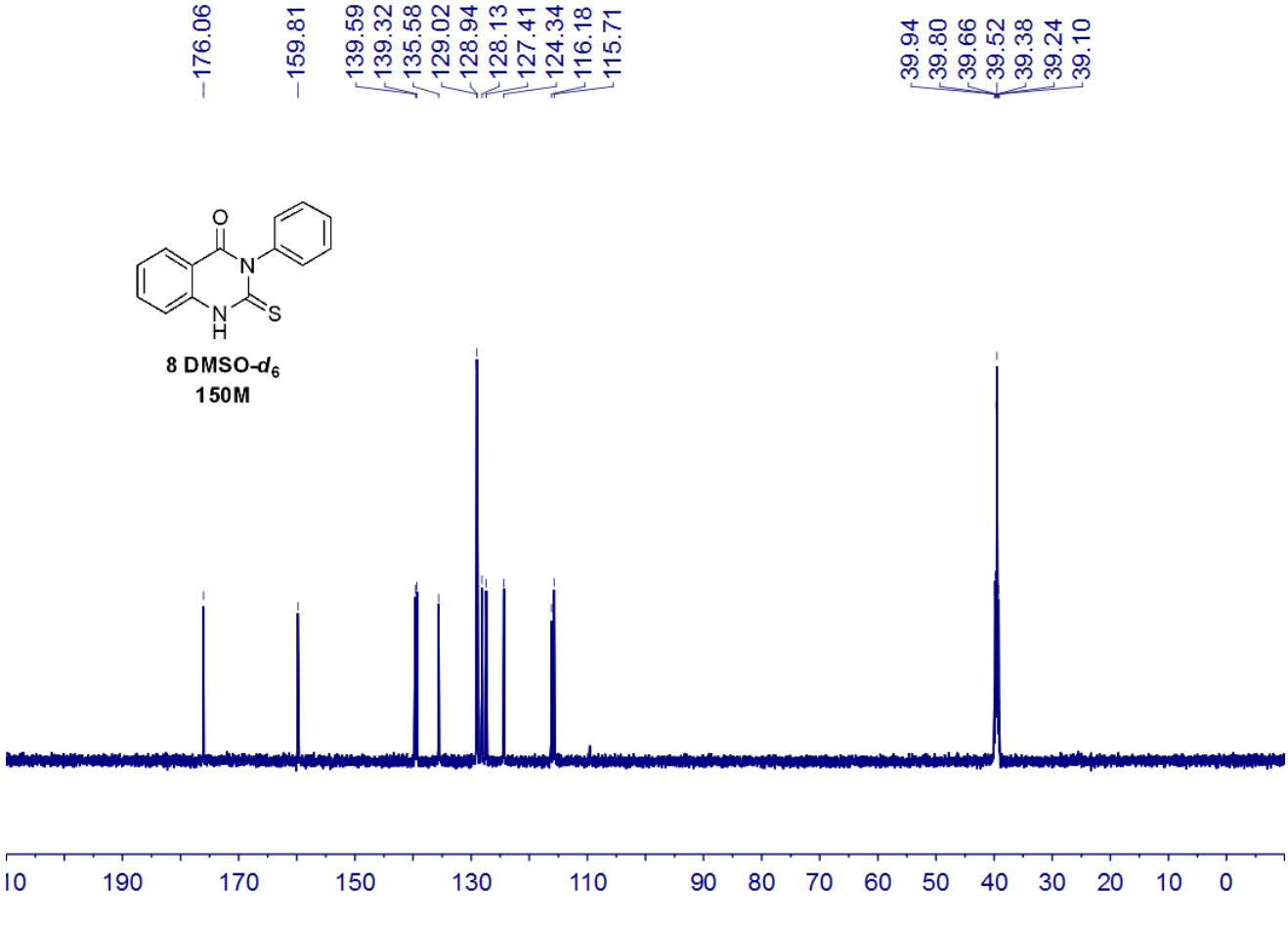
7.331
7.306
7.295
3.417
2.513
0.000
8 DMSO-d_6
600M
1.00
1.00
1.00
3.00
1.00
3.00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159.81
139.59
139.32
135.58
129.02
128.94
128.13
127.41
124.34
116.18
115.71
39.94
39.80
39.66
39.52
39.38
39.24
39.10
8 DMSO-d_6
150M