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Supporting information

Double 1, 4-additions of (Thio)salicylamide/Thiosalicylic acid with Propiolate Derivatives: A Direct, General Synthesis of Diverse Heterocyclic Scaffolds

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Experimental details, characterization data of all products, copies of NMR spectra and crystal data.

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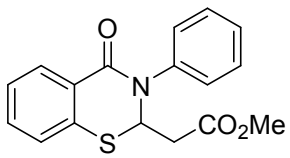
General Information:

All reactions were carried out in a dry solvent under argon atmosphere unless otherwise noted. NMR spectra were recorded on Bruker 400 MHz (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometers. Proton chemical shifts are reported relative to a residual solvent peak ($CDCl_3$ at 7.26 ppm,). Carbon chemical shifts are reported relative to a residual solvent peak ($CDCl_3$ at 77.3 ppm,). The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were measured on a Brucker Daltonics Apex Ⅱ 47e Specification (for HRMS). Substrates were purchased from commercial sources and used as received. No compounds have been published previously.

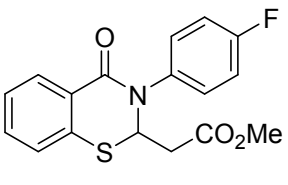
General Procedure for the Synthesis of Methyl 2-(4-oxo-3-phenyl-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate (3a):

A mixture of 2-mercapto-N-phenylbenzamide (22.9mg, 0.1mmol) with methyl propiolate (10.8mg, 0.12mmol), Potassium Phosphate (21.2mg, 0.1mmol) and (1.0 mL) toluene was stirred at 110 °C in the schlenk tube for 20 h under argon atmosphere. The mixture was then cooled to room temperature, diluted with water, extracted with ethyl acetate, dried over sodium sulfate and concentrated. The crude products were purified by column chromatography on silica gel to give the corresponding products.

Methyl 2-(4-oxo-3-phenyl-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate (3a) : Yellow solid (21.32mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.1, 1.3 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.40 – 7.31 (m, 5H), 5.34 (dd, J = 9.6, 5.0 Hz, 1H), 3.63 (s, 3H), 3.22 – 3.02 (m, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 169.72, 162.75, 142.18, 133.92, 132.78, 131.12, 129.76, 128.87, 128.48, 128.00, 127.13, 126.77, 60.16, 52.29, 40.16. HRMS (ESI^+) Calcd for $C_{17}H_{15}NO_3S$ $[M + H]^+$ 314.0845, found 314.0841.

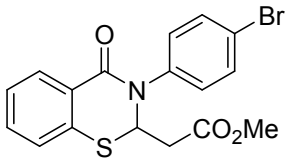


Methyl 2-(3-(4-fluorophenyl)-4-oxo-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-



yl)acetate(3b): White solid (27.17 mg, 82% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.37 – 7.31 (m, 4H), 7.16 – 7.11 (m, 2H), 5.29 (dd, *J* = 9.3, 5.2 Hz, 1H), 3.63 (s, 3H), 3.17 – 3.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.66, 162.89, 161.90 (d, *J* = 247.8 Hz), 138.09 (d, *J* = 3.2 Hz), 133.93, 132.90, 131.14, 129.06 (d, *J* = 8.6 Hz), 128.68, 128.51, 126.86, 116.66 (d, *J* = 22.8 Hz), 60.26, 52.35, 40.16. HRMS (ESI^+) Calcd for $C_{17}H_{14}FNO_3S$ $[M + H]^+$ 332.0751, found 332.0749.

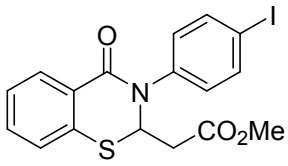
Methyl 2-(3-(4-bromophenyl)-4-oxo-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3c): Brown solid (33.74 mg, 86 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 5.34 – 5.28 (m, 1H), 3.63 (s, 3H), 3.17 – 3.02 (m, 2H).



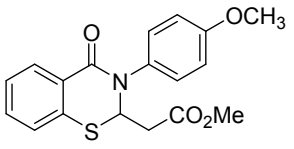
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.56, 162.62, 141.09, 135.78, 133.86, 132.83, 131.13, 128.74, 128.51, 127.87, 126.85, 121.56, 60.05, 52.35, 40.21. HRMS (ESI^+) Calcd for $C_{17}H_{14}BrNO_3S$ $[M + H]^+$ 391.9951, found 391.9948.

Methyl 2-(3-(4-iodophenyl)-4-oxo-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3d)

Brown solid (35.14 mg, 80 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, 1H), 7.77 (d, 2H), 7.48 – 7.43 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 5.33 – 5.30 (m, 1H), 3.63 (s, 3H), 3.16 – 3.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.59, 162.60, 141.85, 138.86, 133.88, 132.98, 131.18, 128.96, 128.62, 128.54, 126.88, 92.93, 60.04, 52.38, 40.25. HRMS (ESI^+) Calcd for $C_{17}H_{14}INO_3S$ $[M + H]^+$ 439.9812, found 439.9811.

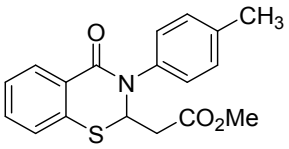


Methyl 2-(3-(4-methoxyphenyl)-4-oxo-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3e): White solid (22.32 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 1H), 7.39 – 7.33 (m, 1H), 7.25 – 7.17 (m, 4H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.19 (dd, *J* =



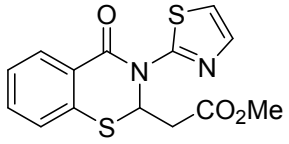
9.4, 5.1 Hz, 1H), 3.75 (s, 3H), 3.55 (s, 3H), 3.08 – 2.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.80, 163.01, 159.15, 134.95, 133.92, 132.70, 131.10, 128.92, 128.43, 126.75, 125.75, 115.02, 60.32, 55.78, 52.32, 40.01. HRMS (ESI+) Calcd for C18H17NO4S [M + H]+ 344.0951, found 344.0948.

Methyl 2-(4-oxo-3-(p-tolyl)-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3f):



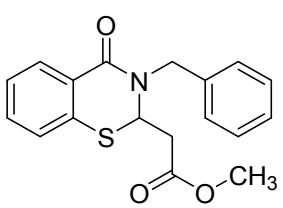
White solid (25.54 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 1H), 7.40 – 7.34 (m, 1H), 7.28 – 7.23 (m, 2H), 7.19 (s, 4H), 5.24 (dd, *J* = 9.6, 5.0 Hz, 1H), 3.57 (s, 3H), 3.11 – 2.98 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.78, 162.82, 139.58, 137.97, 133.90, 132.70, 131.09, 130.39, 128.93, 128.45, 126.94, 126.73, 60.19, 52.30, 40.06, 21.36. HRMS (ESI^+) Calcd for $C_{18}H_{17}NO_3S$ $[M + H]^+$ 328.1002, found 328.1000.

Methyl 2-(4-oxo-3-(thiazol-2-yl)-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3g):



White solid (25.95 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 3.5 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.39 – 7.34 (m, 2H), 7.10 (d, *J* = 3.5 Hz, 1H), 6.97 (dd, *J* = 9.6, 5.1 Hz, 1H), 3.67 (s, 3H), 3.09 – 2.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.82, 161.70, 158.34, 137.83, 134.14, 134.02, 131.52, 129.12, 128.05, 127.34, 116.62, 55.45, 52.66, 39.49. HRMS (ESI^+) Calcd for $C_{14}H_{12}N_2O_3S_2$ $[M + H]^+$ 321.0362, found 321.0360.

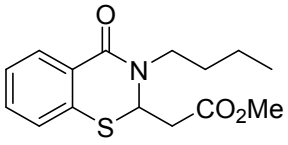
Methyl 2-(3-benzyl-4-oxo-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3h):



White solid (29.14 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.25 (m, 8H), 5.36 (d, *J* = 15.0 Hz, 1H), 4.94 (dd, *J* = 9.4, 5.1 Hz, 1H), 4.40 (d, *J* = 15.0 Hz, 1H), 3.65 (s, 3H), 2.95 (dd, *J* = 16.2, 9.4 Hz, 1H), 2.77 (dd, *J* = 16.3, 5.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.91, 162.92, 136.48, 133.52, 132.36, 130.64, 128.87, 128.36, 128.22, 128.17, 127.94, 126.39, 55.93, 52.11, 50.95, 39.88. HRMS (ESI^+) Calcd for $C_{18}H_{17}NO_3S$ $[M + H]^+$ 328.1002, found

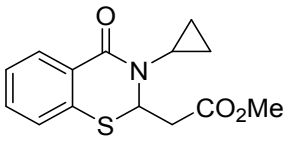
328.1000.

Methyl 2-(3-butyl-4-oxo-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3i):



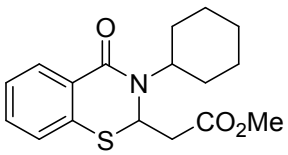
White solid (25.23 mg, 86 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.34 – 7.27 (m, 2H), 4.96 (dd, *J* = 9.4, 5.1 Hz, 1H), 4.23 – 4.15 (m, 1H), 3.72 (s, 3H), 3.14 – 3.06 (m, 1H), 3.04 – 2.87 (m, 2H), 1.75 – 1.67 (m, 2H), 1.49 – 1.40 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.26, 162.89, 133.52, 132.32, 130.60, 128.94, 128.31, 126.57, 56.75, 52.38, 48.40, 40.31, 30.77, 20.36, 14.08. HRMS (ESI$^+$) Calcd for $C_{15}H_{19}NO_3S$ $[M + H]^+$ 294.1158, found 294.1155.

Methyl 2-(3-cyclopropyl-4-oxo-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3j):



White solid (20.52 mg, 74 % yield); ^{1}H NMR (400 MHz, CDCl3) δ 8.18 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.39 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 – 7.21 (m, 2H), 5.09 (dd, *J* = 8.1, 6.5 Hz, 1H), 3.71 (s, 3H), 3.01 – 2.95 (m, 2H), 2.88 – 2.81 (m, 1H), 1.18 – 1.11 (m, 1H), 0.92 – 0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.17, 164.48, 133.50, 132.60, 130.61, 128.24, 128.15, 126.36, 58.11, 52.32, 39.94, 31.37, 10.32, 7.01. HRMS (ESI$^+$) Calcd for $C_{14}H_{15}NO_3S$ $[M + H]^+$ 278.0845, found 278.0841.

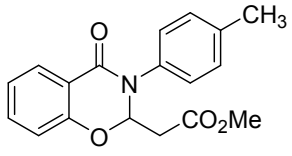
Methyl 2-(3-cyclohexyl-4-oxo-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3k):



White solid (23.64 mg, 74 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.30 – 7.23 (m, 2H), 5.11 (dd, *J* = 11.2, 3.0 Hz, 1H), 4.73 – 4.64 (m, 1H), 3.70 (s, 3H), 3.08 (dd, *J* = 16.5, 11.2 Hz, 1H), 2.70 (dd, *J* = 16.4, 3.0 Hz, 1H), 1.86 (br, 4H), 1.73 – 1.60 (m, 2H), 1.50 – 1.41 (m, 3H), 1.22 – 1.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.98, 162.54, 133.40, 132.03, 130.63, 129.41,

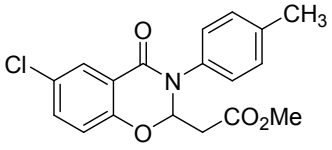
128.28, 126.33, 54.78, 52.12, 51.99, 41.54, 32.98, 31.38, 30.38, 25.85, 25.40. HRMS (ESI^+) Calcd for $C_{17}H_{21}NO_3S$ $[M + H]^+$ 320.1315, found 320.1313.

Methyl 2-(4-oxo-3-(p-tolyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-2-yl)acetate(3l):



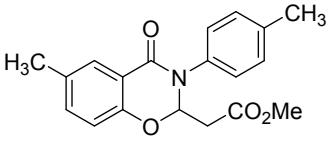
White solid (27.06 mg, 87 % yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.28 – 7.21 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.12 (dd, *J* = 8.8, 3.9 Hz, 1H), 3.62 (s, 3H), 3.05 (dd, *J* = 15.5, 8.8 Hz, 1H), 2.79 (dd, J = 15.5, 3.9 Hz, 1H), 2.38 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 169.11, 160.61, 155.06, 137.69, 135.11, 134.55, 130.36, 128.72, 127.47, 122.53, 117.78, 116.89, 86.99, 52.18, 37.95, 20.83. HRMS (ESI^+) Calcd for $C_{18}H_{17}NO_4$ $[M + H]^+$ 312.1230, found 312.1227.

Methyl 2-(6-chloro-4-oxo-3-(p-tolyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-2-yl)acetate(3m):



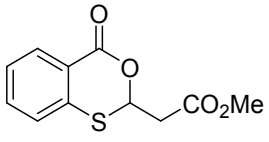
White solid (31.47 mg, 91 % yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.5 Hz, 1H), 7.45 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.23 (dd, *J* = 20.9, 7.5 Hz, 4H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.11 (dd, *J* = 8.8, 3.8 Hz, 1H), 3.63 (s, 3H), 3.02 (dd, *J* = 15.6, 8.8 Hz, 1H), 2.79 (dd, *J* = 15.6, 3.9 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.75, 159.90, 153.79, 138.47, 135.03, 134.79, 130.21, 128.36, 128.19, 127.02, 119.27, 118.33, 87.20, 51.98, 38.27, 20.87. HRMS (ESI^+) Calcd for $C_{18}H_{16}ClNO_4$ $[M + H]^+$ 346.0841, found 346.0839.

Methyl 2-(6-methyl-4-oxo-3-(p-tolyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-2-yl)acetate(3n):

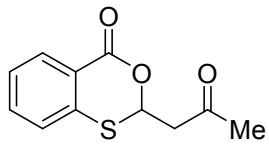


White solid (24.73 mg, 76 % yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.1 Hz, 1H), 7.32 – 7.20 (m, 5H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.09 (dd, *J* = 8.8, 3.9 Hz, 1H), 3.62 (s, 3H), 3.04 (dd, *J* = 15.5, 8.8 Hz, 1H), 2.77 (dd, *J* = 15.5, 3.9 Hz, 1H), 2.36 (d, *J* = 8.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.97, 160.92, 153.12, 137.91, 135.57, 135.51, 132.49, 130.22, 128.46, 127.44, 117.82, 116.86, 87.11, 52.04, 38.16, 21.14, 20.63. HRMS (ESI^+) Calcd for $C_{19}H_{19}NO_4$ $[M + H]^+$ 326.1387, found 326.1383.

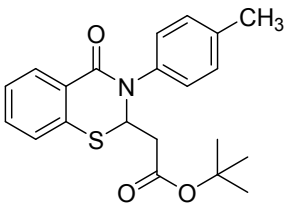
Methyl 2-(4-oxo-4H-benzo[d][1,3]oxathiin-2-yl)acetate(3o): White solid (21.50 mg, 90 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.58 – 7.47 (m, 1H), 7.42 – 7.29 (m, 2H), 6.02 (dd, *J* = 7.2, 5.7 Hz, 1H), 3.77 (s, 3H), 3.21 (dd, *J* = 16.4, 7.3 Hz, 1H), 2.98 (dd, *J* = 16.4, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.41, 162.29, 136.53, 132.76, 131.72, 126.70, 125.97, 123.03, 77.27, 51.43, 38.28.HRMS (ESI+) Calcd for C11H11O4S [M + H]+ 239.0373, found 239.0373.



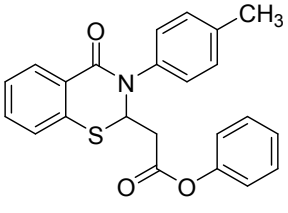
2-(2-oxopropyl)-4H-benzo[d][1,3]oxathiin-4-one(3o'): White solid (27.40 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.2 Hz, 1H), 7.55 – 7.43 (m, 1H), 7.38 – 7.29 (m, 2H), 6.06 (dd, *J* = 6.9, 5.1 Hz, 1H), 3.35 (dd, *J* = 17.3, 7.0 Hz, 1H), 3.01 (dd, *J* = 17.3, 5.0 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.10, 163.51, 137.81, 133.70, 132.72, 127.67, 126.93, 124.07, 77.69, 47.24, 30.78. HRMS (ESI^+) Calcd for $C_{11}H_{11}O_3S^+$ $[M + H]^+$ 223.0423, found 223.0426.



Tert-butyl 2-(4-oxo-3-(p-tolyl)-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3p): White solid (27.40 mg, 88 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.36 (td, *J* = 7.9, 1.4 Hz, 1H), 7.25 – 7.15 (m, 6H), 5.17 (t, *J* = 7.4 Hz, 1H), 2.94 (s, 1H), 2.92 (s, 1H), 2.31 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.47, 162.95, 139.63, 137.85, 134.21, 132.61, 131.04, 130.35, 129.03, 128.37, 126.97, 126.59, 82.06, 60.41, 41.28, 28.23, 21.36. HRMS (ESI^+) Calcd for $C_{21}H_{23}NO_3S$ $[M + H]^+$ 370.1471, found 370.1468.

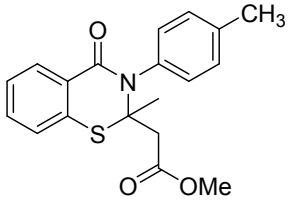


Phenyl 2-(4-oxo-3-(p-tolyl)-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3q): White solid (20.30 mg, 82 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.49 – 7.45 (m, 1H),

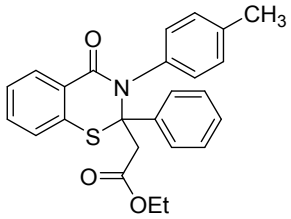


7.39 – 7.33 (m, 4H), 7.33 – 7.27 (m, 4H), 7.25 – 7.21 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 2H), 5.41 (dd, *J* = 9.5, 5.4 Hz, 1H), 3.42 – 3.29 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.75, 162.84, 150.43, 139.50, 138.14, 133.71, 132.86, 131.20, 130.51, 129.71, 128.95, 128.52, 127.05, 126.90, 126.42, 121.55, 60.22, 40.36, 21.38. HRMS (ESI^+) Calcd for $C_{23}H_{19}NO_3S$ $[M + H]^+$ 390.1158, found 390.1155.

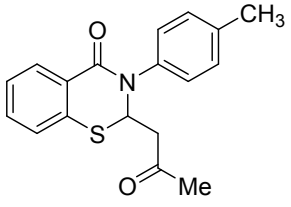
2-methyl-2-(2-oxopropyl)-3-(p-tolyl)-2H-benzo[e][1,3]thiazin-4(3H)-one(3r): White solid (26.21 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, 1H), 7.46 – 7.42 (m, 1H), 7.30 (m, 2H), 7.25 – 7.22 (m, 2H), 7.11 (m, 2H), 3.58 (s, 3H), 3.16 (d, *J* = 13.9 Hz, 1H), 2.98 (d, *J* = 13.9 Hz, 1H), 2.39 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.03, 164.49, 138.37, 135.85, 134.19, 132.45, 130.86, 130.18, 130.00, 129.94, 129.12, 128.36, 127.16, 126.33, 65.26, 51.84, 46.00, 27.11, 21.19. HRMS (ESI^+) Calcd for $C_{19}H_{19}NO_3S$ $[M + H]^+$ 342.1158, found 342.1154.



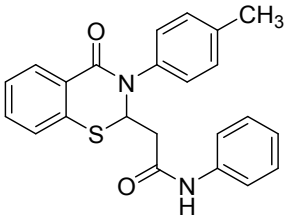
Ethyl 2-(4-oxo-2-phenyl-3-(p-tolyl)-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(3s): White solid (31.94 mg, 82 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.24 – 7.09 (m, 10H), 3.83 – 3.72 (m, 2H), 3.18 (q, *J* = 15.5 Hz, 2H), 2.35 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.90, 166.08, 142.13, 138.32, 136.31, 134.87, 132.32, 130.68, 129.91, 129.53, 128.39, 128.15, 127.77, 127.20, 126.39, 123.92, 73.04, 61.12, 45.97, 21.40, 13.94. HRMS (ESI^+) Calcd for $C_{25}H_{23}NO_3S$ $[M + H]^+$ 418.1471, found 418.1469.



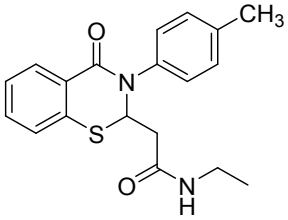
2-(2-oxopropyl)-3-(p-tolyl)-2H-benzo[e][1,3]thiazin-4(3H)-one(3t): White solid (24.09 mg,62 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 1H), 7.44 (m, 1H), 7.35 – 7.29 (m, 2H), 7.23 (s, 4H), 5.35 (dd, *J* = 10.2, 3.5 Hz, 1H), 3.41 – 3.33 (m, 1H), 3.06 (dd, *J* = 17.4, 3.5 Hz, 1H), 2.37 (s, 3H), 2.05 (s, 3H). ^{13}C NMR



(100 MHz, $CDCl_3$) δ204.04, 162.78, 139.21, 137.67, 134.20, 132.36, 130.88, 130.12, 128.83, 128.12, 126.67, 126.37, 58.78, 47.77, 30.71, 21.12. HRMS (ESI^+) Calcd for $C_{18}H_{17}NO_2S$ $[M + H]^+$ 312.1053, found 312.1050.

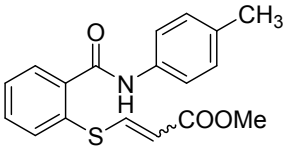
2-(4-oxo-3-(p-tolyl)-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)-N-phenylacetamide(3u); Yellow solid (20.50mg, 63 % yield); 

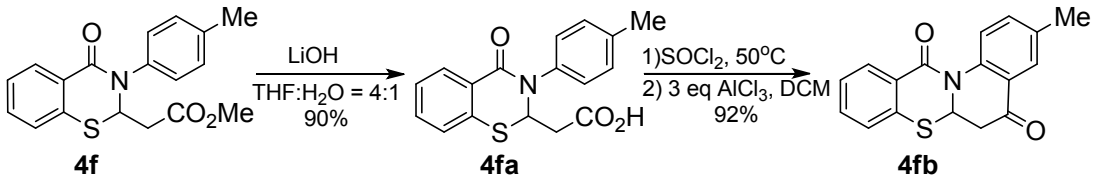
^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.7 Hz, 1H), 7.47 – 7.36 (m, 4H), 7.34 – 7.27 (m, 4H), 7.20 (d, J = 4.4 Hz, 3H), 7.12 – 7.07 (m, 1H), δ 5.44 (dd, J = 9.5, 4.8 Hz, 1H), 3.11 – 2.98 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.26, 162.85, 139.10, 137.79, 137.41, 134.32, 132.54, 130.83, 130.17, 128.96, 128.69, 128.21, 126.52, 126.43, 124.62, 119.92, 60.26, 42.46, 21.11. HRMS (ESI^+) Calcd for $C_{23}H_{20}N_2O_2S$ $[M + H]^+$ 389.1318, found 389.1315.

N-ethyl-2-(4-oxo-3-(p-tolyl)-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetamide(3v): White solid (25.47 mg, 61 % yield); 

^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 7.8, 1.0 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.25 – 7.12 (m, 6H), 5.39 (br, 1H), δ 5.32 (dd, J = 10.0, 4.5 Hz, 1H), 3.17 – 3.11 (m, 2H), 2.86 (dd, J = 14.6, 4.5 Hz, 1H), 2.77 – 2.71 (m, 1H), 2.30 (s, 3H), 1.00 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.00, 162.94, 139.41, 137.81, 134.59, 132.59, 131.03, 130.29, 129.09, 128.31, 126.77, 126.52, 60.64, 41.93, 34.73, 21.34, 14.88. HRMS (ESI^+) Calcd for $C_{19}H_{20}N_2O_2S$ $[M + H]^+$ 341.1318, found 341.1315.

Methyl 3-((2-(p-tolylcarbamoyl)phenyl)thio)acrylate(4a): White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.73 (s, 1H), 7.57 (s, 1H), 7.44 (d, J = 8.1 Hz, 4H), 7.12 (d, J = 9.7 Hz, 3H), 5.88 (d, J = 10.0 Hz, 1H), 3.72 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.69, 165.49, 148.68, 138.89, 135.07, 134.48, 133.80, 133.10, 131.01, 129.69, 129.50, 129.16, 120.33, 114.28, 51.49, 20.93. HRMS (ESI^+) Calcd for $C_{18}H_{17}NO_3S$ $[M + H]^+$ 328.1002, found 328.1000.

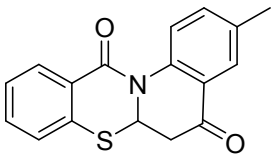




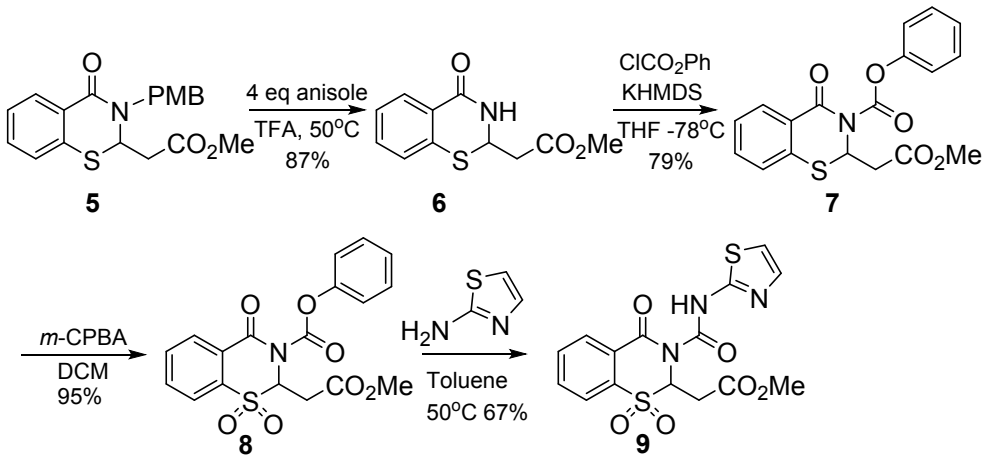
178 mg (0.544 mmol) of **4f** dissolved in THF/H_2O (4:1, 3.63mL) and 39.07mg (1.632mmol) of LiOH was added and the mixture was stirred under Ar atmosphere at ambient temperature for 2 h. Upon completion of the reaction detected by TLC, the mixture was cooled to 0 °C, then quenched with an aqueous solution of 1N HCl to destroy any excess base and the PH was adjusted to 3. After removing THF under reduced pressure in vacuo, extracted with EtOAc (3×5mL) in a separating funnel and concentrated the combined organic layers, then purification by the column chromatography gave 153.43 mg (90% yield) of **4fa** as a white solide.

100 mg (0.319 mmol) of **4fa** was dissolved in 2.13 mL(0.15 mmol/mL) of $SOCl_2$, after being stirred under Ar atmosphere at 50 °C for 2 h, removal of $SOCl_2$ under reduced pressure in vacuo gave the acyl chloride as a yellow liquid without further purified. The resulting acyl chloride was dissolved in dry DCM at 0 °C, then added 127.61 mg (0.957 mmol) of $AlCl_3$. Upon completion of the reaction detected by TLC, quenched the reaction mixture with cooled 5M HCl and extracted with DCM (3×5mL) , removal of solvent under reduced pressure in vacuo gave the residue, then purification by column chromatography provided 86.68 mg (92% yield) of **4fb** as a yellow solid.

3-methyl-6,6a-dihydrobenzo[5,6][1,3]thiazino[3,2-a]quinoline-5,12-dione(4fb):



Yellow solid (86.68 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.3 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.76 (s, 1H), 7.49 – 7.40 (m, 2H), 7.34 – 7.25 (m, 2H), 5.42 (dd, J = 11.7, 4.0 Hz, 1H), 3.41 – 3.29 (m, 1H), 3.00 (dd, J = 16.9, 4.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.77, 163.13, 141.06, 135.78, 135.35, 134.40, 133.04, 131.32, 127.84, 127.49, 127.31, 126.52, 126.20, 125.11, 58.51, 45.40, 20.81. HRMS (ESI^+) Calcd for $C_{17}H_{13}NO_2S$ $[M + H]^+$ 296.0740, found 296.0736.



1g (2.798 mmol) of **5** dissolved in 13.99 mL of TFA and 1.21 g (11.192 mmol) of anisole was added. After being stirred under Ar atmosphere at 50 °C for 12 h, removed TFA under reduced pressure in high vacuum and the residue was passed through silica to provide 577.59 mg (87% yield) of **6** as a white solid.

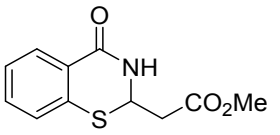
300 mg (1.264 mmol) of **6** in 8.43 mL of dry THF（12.64 mL）was cooled to -78 °C under Ar atmosphere and KHMDS was added dropwise by syringe, after being stirred for 20min, $ClCO_2Ph$ was added slowly to the above solution via syringe, then the reaction mixture was allowed to warm to ambient temperature and stirred for 30min. After completion of the reaction detected by TLC, quenched with sat. aq. NH_4Cl, and the mixture was placed under reduced pressure in high vacuum to remove any residue THF. The solution was taken into a separating funnel and extracted with DCM (3×5mL), then the combined organic layers were placed under reduced pressure in vacuo to remove DCM and purified by silica-gel chromatography to afford 356.87 mg (79% yield) of 7 as a white solid.

A solution of 200 mg (0.560 mmol) of **7** in 5.6 mL of DCM was added 290.64 mg (1.680 mmol) of *m*-CPBA under Ar atmosphere at 0°C slowly, the reaction was allowed to warm to ambient temperature. After being stirred for 15 min at r.t, filtered with petroleum ether to get rid of insolubility impurities, the residue was purified by column chromatography and provided 207.15 mg (95% yield) of **8** as a white solid.

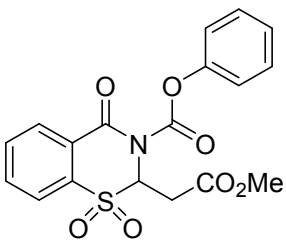
100mg (0.25 mmol) of **8** dissolved in 1mL of toluene and 25.7mg (0.25mmol) of 2-aminothiazol was added. After being stirred under Ar atmosphere at 50 °C for 1 h,

removed toluene under reduced pressure in high vacuum and the residue was passed through silica to provide 68.1mg (67% yield) of **9** as a white solid

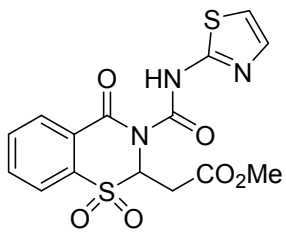
Methyl 2-(4-oxo-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(6): White solid (577.58 mg, 87 % yield) ^{1}H NMR (400 MHz, $CDCl_3$). δ 8.12 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.56 – 7.37 (m, 2H), 7.33 – 7.23 (m, 2H), 5.28 – 5.04 (m, 1H), 3.72 (s, 3H), 3.05 (dd, *J* = 16.5, 8.5 Hz, 1H), 2.90 (dd, *J* = 16.5, 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.84, 164.68, 134.98, 132.67, 130.20, 127.76, 126.35, 100.00, 52.30, 51.49, 40.72. HRMS (ESI^+) Calcd for $C_{11}H_{11}NO_3S$ $[M + H]^+$ 238.0532, found 238.0530.



Phenyl 2-(2-methoxy-2-oxoethyl)-4-oxo-2H-benzo[e][1,3]thiazine-3(4H)-carboxylate 1,1-dioxide(8)： White solid (207.15 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.7 Hz, 1H), 7.92 – 7.75 (m, 3H), 7.47 – 7.37 (m, 2H), 7.34 – 7.26 (m, 3H), 6.38 (t, *J* = 7.1 Hz, 1H), 3.71 (s, 3H), 2.68 (dd, *J* = 16.5, 7.1 Hz, 1H), 2.52 (dd, *J* = 16.5, 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.98, 159.71, 152.87, 150.69, 136.81, 134.82, 134.22, 132.26, 131.19, 129.55, 127.17, 126.49, 121.28, 68.71, 52.77, 35.86. HRMS (ESI^+) Calcd for $C_{18}H_{15}NO_7S$ $[M + H]^+$ 390.0642, found 390.0639



Methyl 2-(1,1-dioxido-4-oxo-3-(thiazol-2-ylcarbamoyl)-3,4-dihydro-2H-benzo[e][1,3]thiazin-2-yl)acetate(9)： White solid (207.15 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 1H), 7.99 – 7.56 (m, 5H), 6.57 (s, 1H), 5.06 – 4.97 (m, 1H), 3.77 (s, 3H), 3.15 (dd, *J* = 16.2, 3.4 Hz, 1H), 2.86 – 2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.00, 163.06, 141.92, 133.93, 132.09, 130.08, 126.45, 126.06, 125.76, 124.29, 116.34, 100.00, 68.62, 52.79, 34.21. HRMS (ESI^+) Calcd for $C_{15}H_{13}N_3O_6S_2$ $[M + H]^+$ 396.0319, found 396.0315.



X-ray Structure Report for 3a

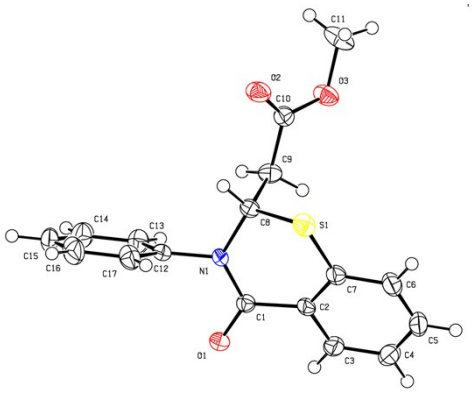


Figure S1. Single crystal X-ray structure of **3a.**

Experimental:

Single crystals of $C_{17}H_{15}NO_3S$ were obtained by recrystallization from mixed solvents of dichloromethane and hexane. A suitable crystal was selected and carried out on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

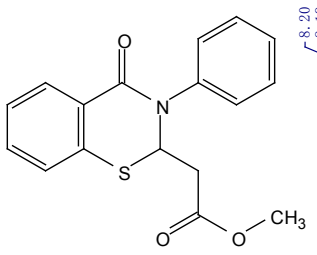
1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{17}H_{15}NO_3S$ (M =313.36 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 15.0717(8) Å, b = 10.5131(5) Å, c = 9.6899(5) Å, β = 99.871(5)°, V = 1512.63(14) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 0.226 mm^{-1}, $Dcalc$ = 1.376 g/cm^3, 5315 reflections measured (6.718° ≤ 2Θ ≤ 52.044°), 2966 unique (R_{int} = 0.0328, R_{sigma} = 0.0610) which were used in all calculations. The final R_1 was 0.0476 (I > 2σ(I)) and wR_2 was 0.1097 (all data)

Table 1 Crystal data and structure refinement for3a.

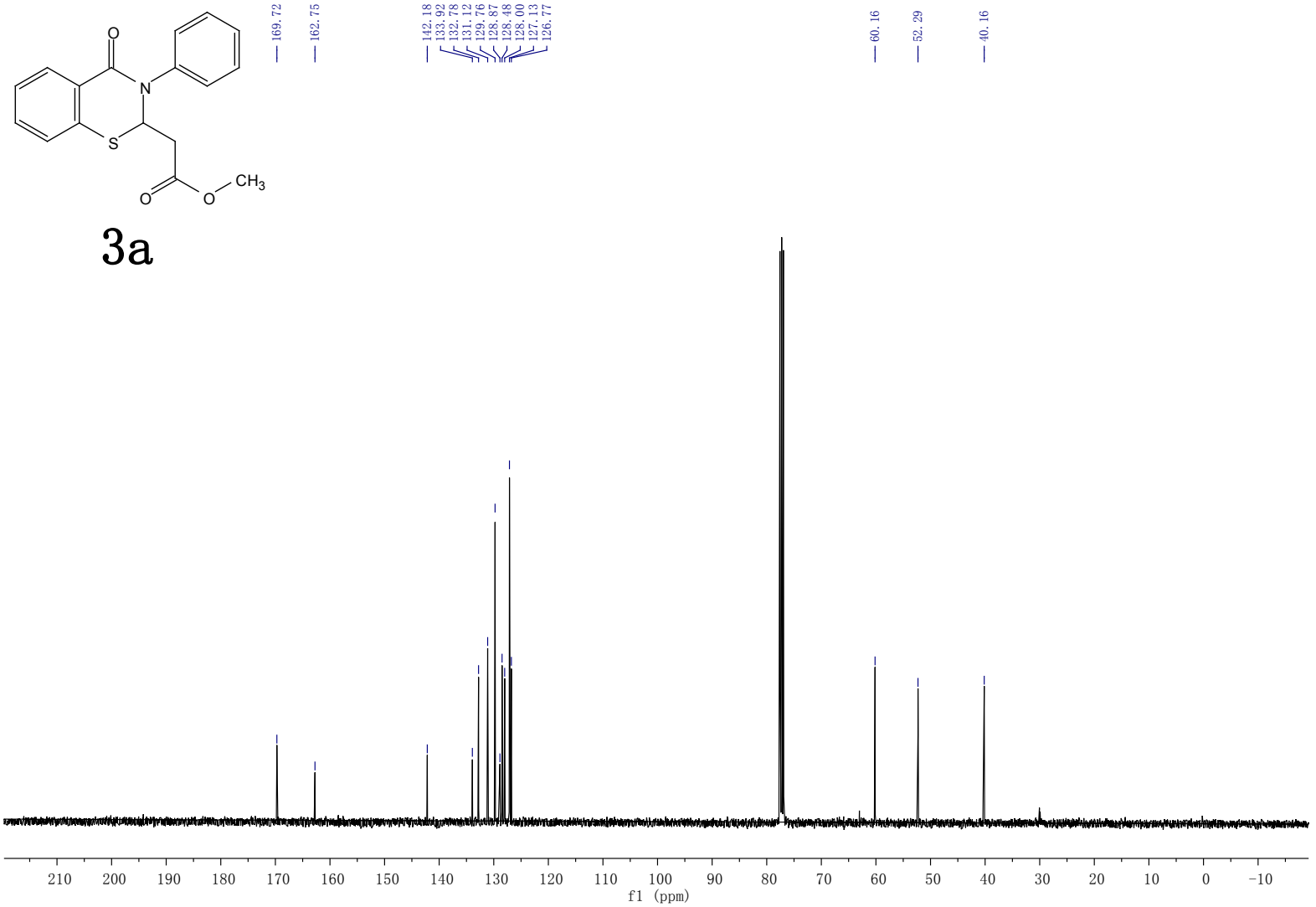
Identification code	3a
Empirical formula	$C_{17}H_{15}NO_3S$
Formula weight	313.36
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$

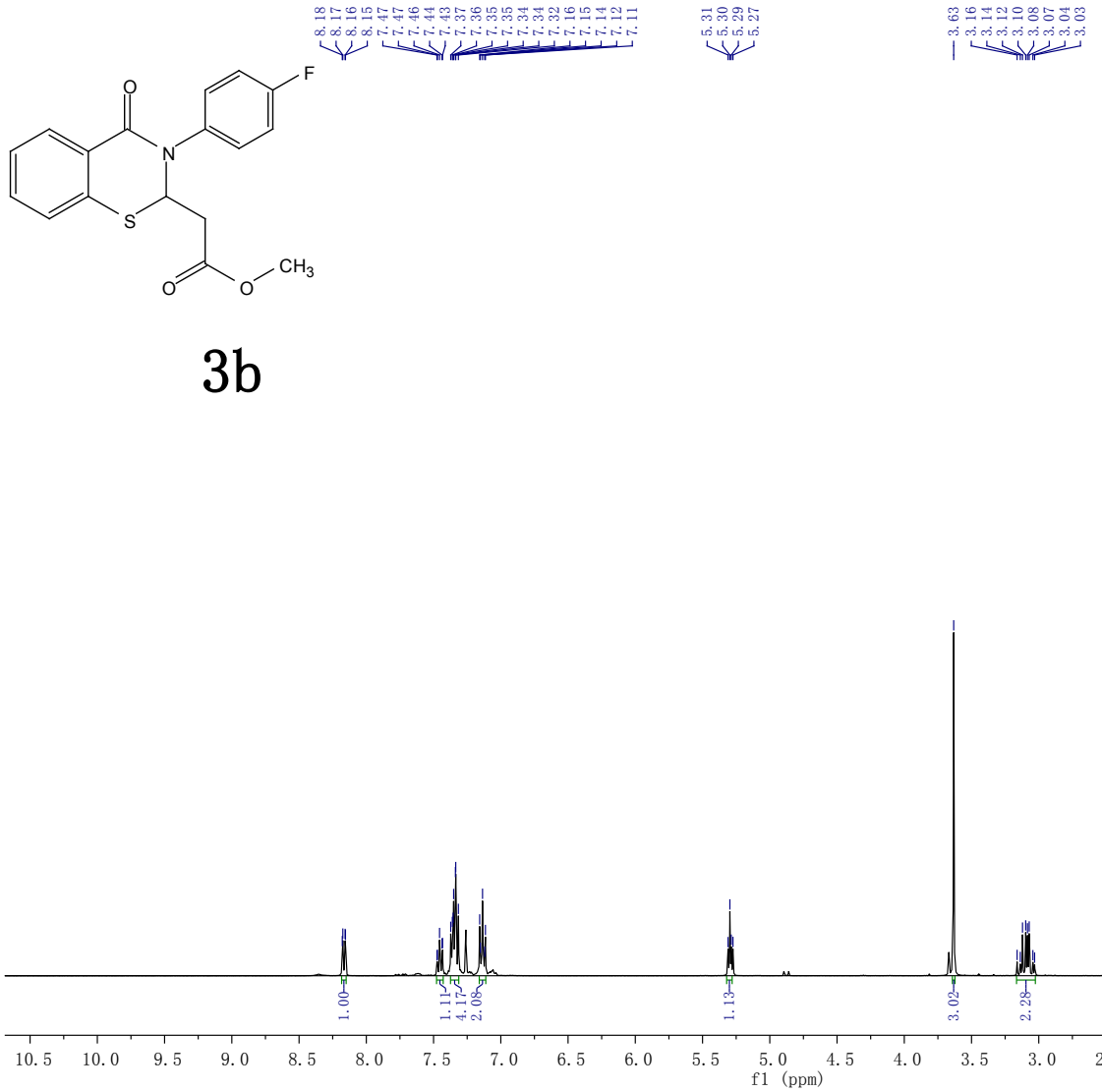
a/Å	15.0717(8)
b/Å	10.5131(5)
c/Å	9.6899(5)
α/°	90
β/°	99.871(5)
γ/°	90
Volume/Å^3	1512.63(14)
Z	4
ρ_{calc}g/cm^3	1.376
μ/mm^{-1}	0.226
F(000)	656.0
Crystal size/mm^3	0.22 × 0.21 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.718 to 52.044
Index ranges	-18 ≤ h ≤ 7, -12 ≤ k ≤ 8, -11 ≤ l ≤ 11
Reflections collected	5315
Independent reflections	2966 [R_{int} = 0.0328, R_{sigma} = 0.0610]
Data/restraints/parameters	2966/0/200
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0476, wR_2 = 0.0947
Final R indexes [all data]	R_1 = 0.0696, wR_2 = 0.1097
Largest diff. peak/hole / e Å^{-3}	0.25/-0.30


O
N
S
O
O
CH3

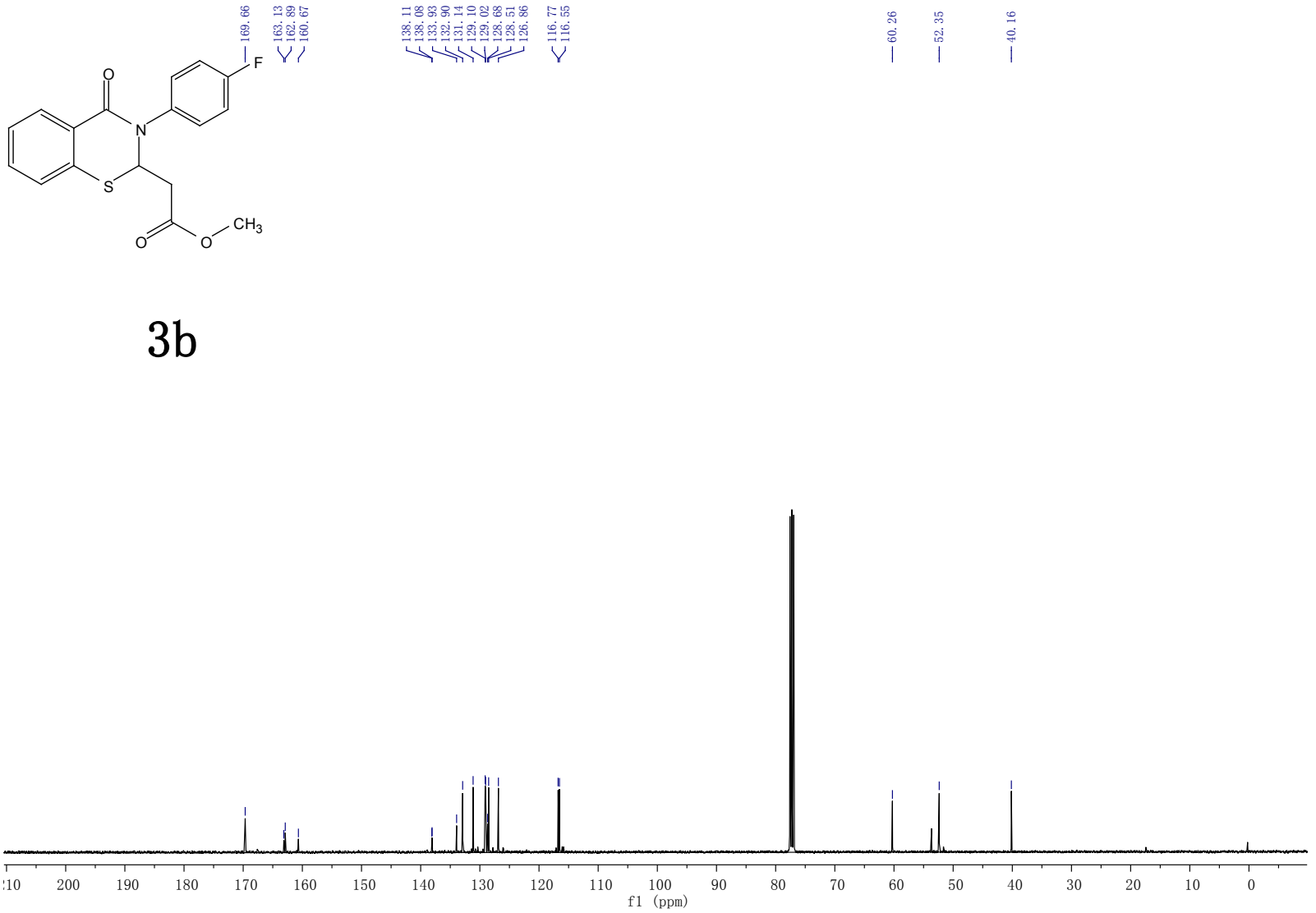
3a

8.20
8.19
8.18
8.17
7.47
7.47
7.46
7.45
7.45
7.43
7.43
7.43
7.39
7.37
7.37
7.35
7.33
7.33
7.31
5.36
5.35
5.34
5.33
3.63
3.18
3.16
3.14
3.12
3.11
3.10
3.07
3.06
0.95
3.03
5.00
1.00
3.01
2.10
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
-0.5
f1 (ppm)

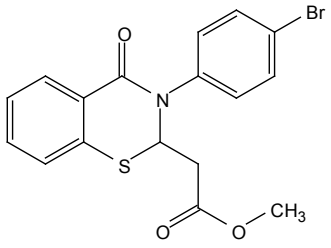

169.72
162.75
142.18
133.92
132.78
131.12
129.76
128.87
128.48
128.00
127.13
126.77
60.16
52.29
40.16
O
N
S
O
O
CH3
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.18
8.17
8.16
8.15
7.47
7.47
7.46
7.44
7.43
7.37
7.36
7.35
7.35
7.34
7.34
7.32
7.16
7.15
7.14
7.12
7.11
5.31
5.30
5.29
5.27
3.63
3.16
3.14
3.12
3.10
3.08
3.07
3.04
3.03
O
F
N
S
O
O
CH3
1.00
1.11
4.17
2.08
1.13
3.02
2.28
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 -0.5
f1 (ppm)

3b

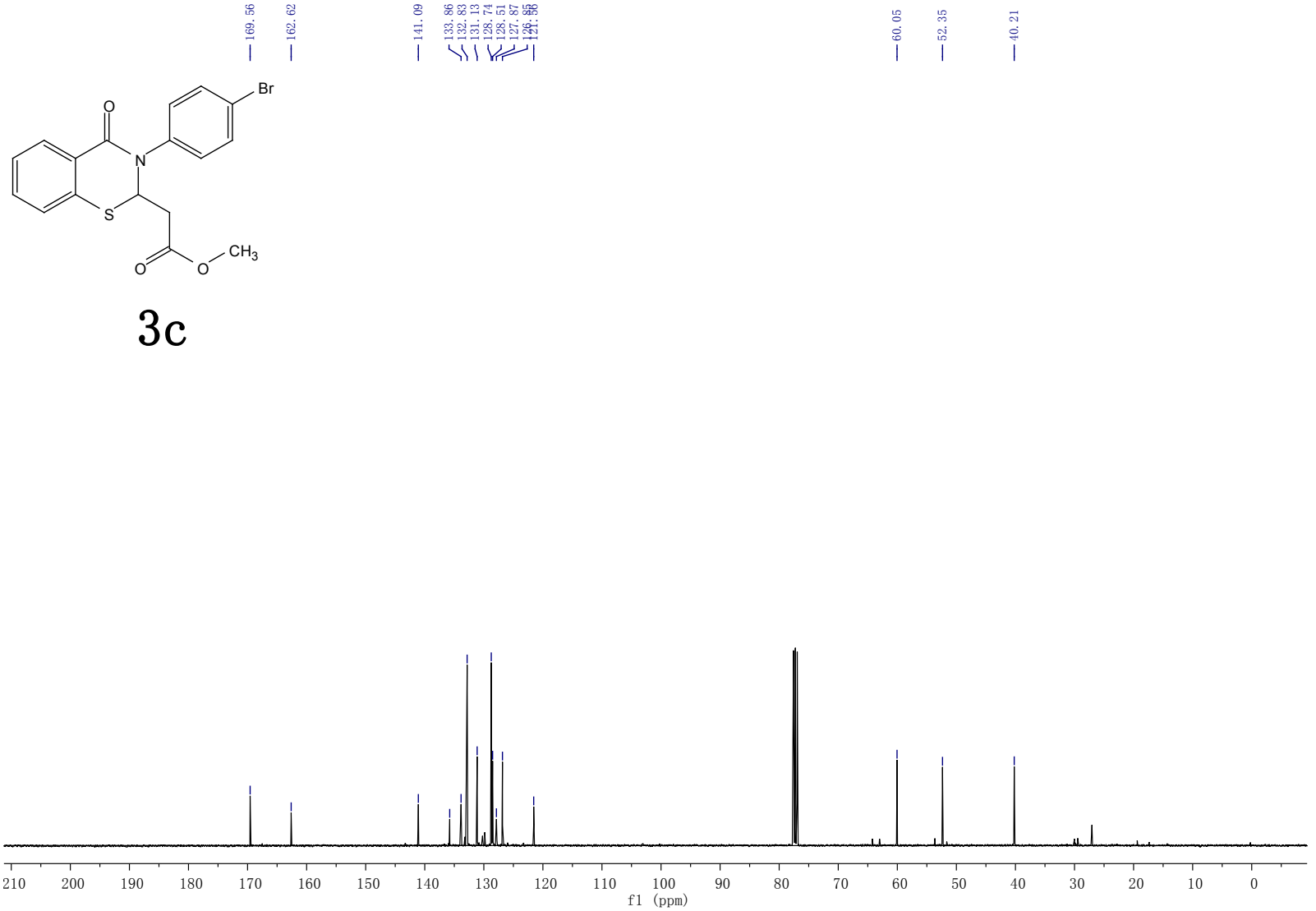

169.66
163.13
162.89
160.67
138.11
138.08
133.93
132.90
131.14
129.10
129.02
128.68
128.51
126.86
116.77
116.55
60.26
52.35
40.16
F
O
N
S
O
O
CH3
f1 (ppm)

3b

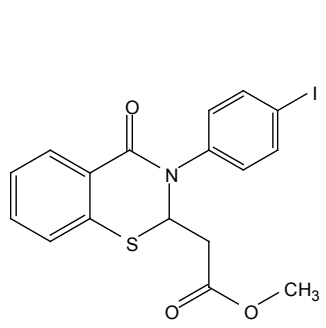

Br
O
N
S
O
O
CH3

3c

8.18
8.16
7.58
7.56
7.47
7.45
7.43
7.35
7.33
7.31
7.28
7.26
5.33
5.32
5.31
5.29
3.63
3.16
3.14
3.12
3.10
3.08
3.06
3.04
3.02
0.99
2.03
1.10
2.20
2.02
1.00
3.00
2.07
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 -0.
f1 (ppm)

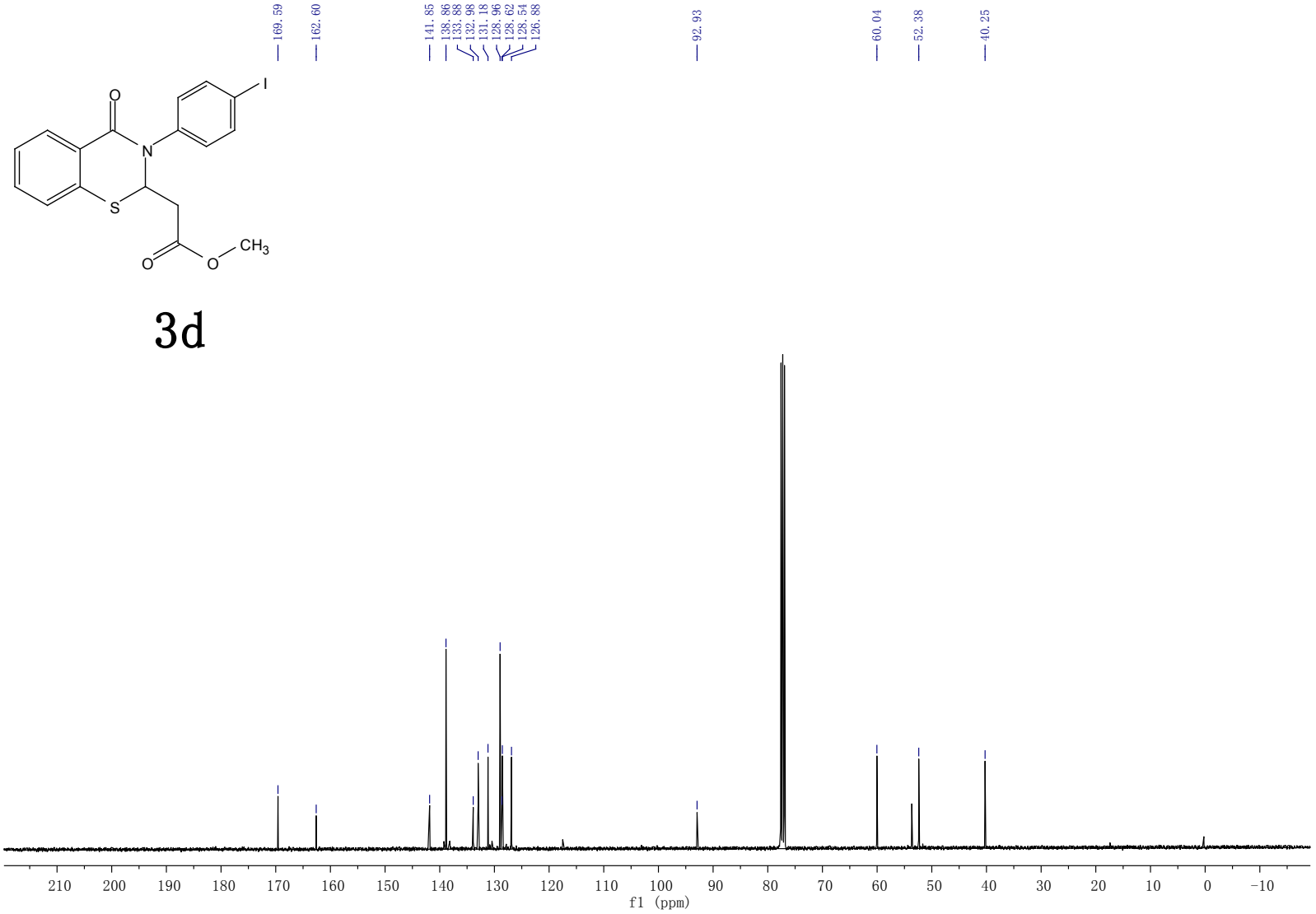

169.56
162.62
141.09
133.86
132.83
131.13
128.74
128.51
127.87
60.05
52.35
40.21
Br
O
N
S
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3c

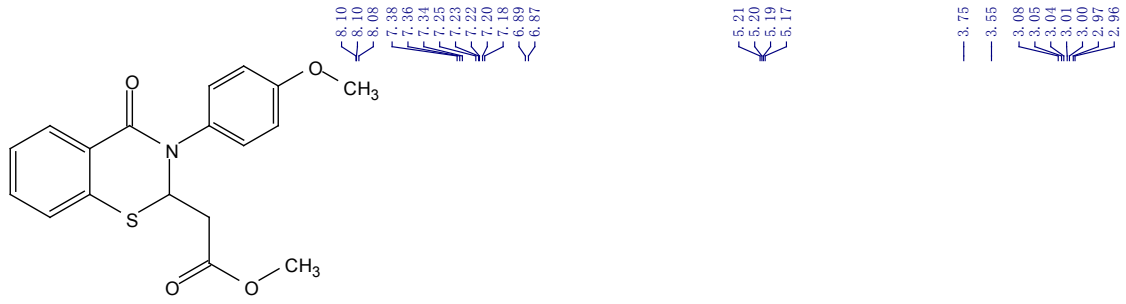

O
N
S
I
O
O
CH3

3d

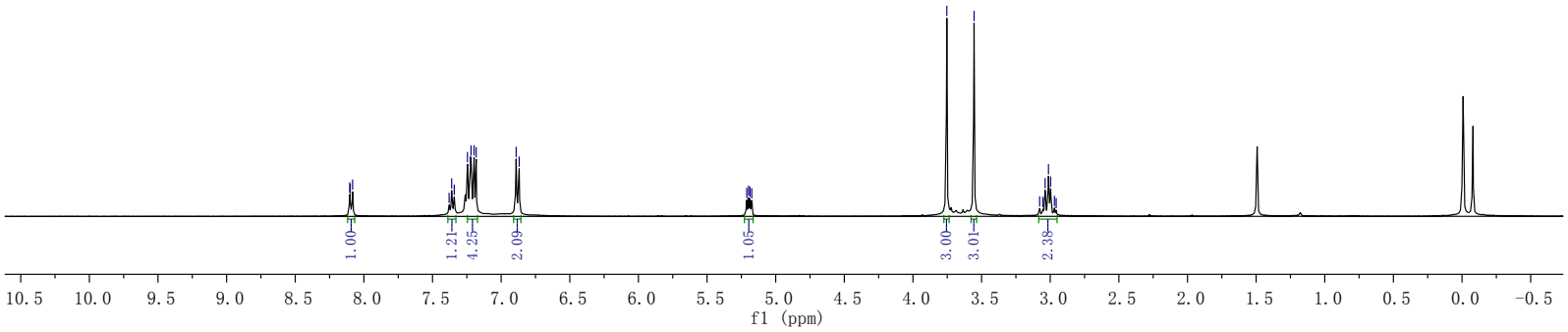
8.18
8.18
8.16
7.78
7.76
7.47
7.46
7.44
7.43
7.35
7.33
7.31
7.15
7.13
5.33
5.32
5.30
5.29
3.63
3.16
3.13
3.12
3.09
3.07
3.06
3.03
3.02
1.00
2.01
1.10
2.09
2.02
1.11
3.00
2.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

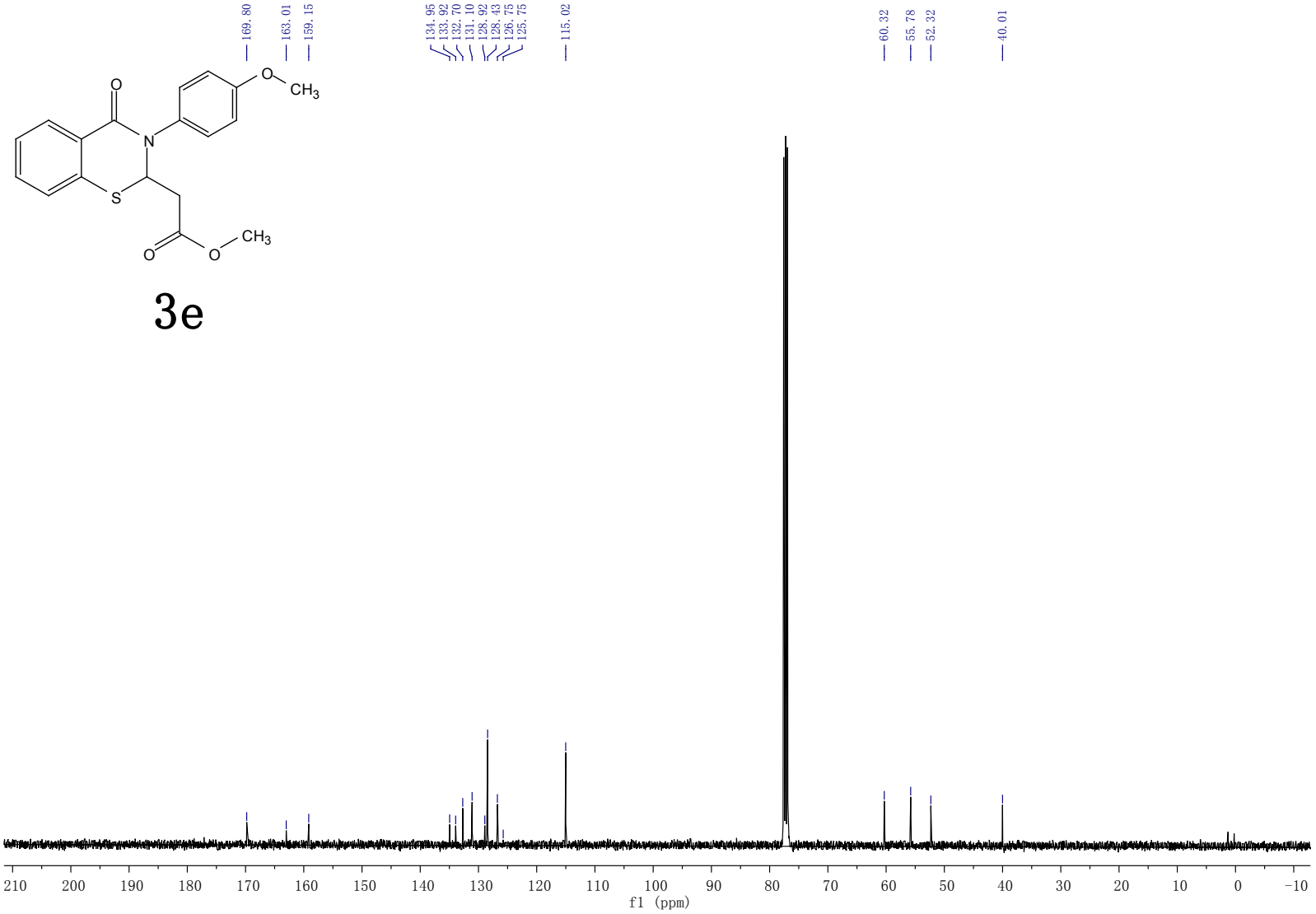

169.59
162.60
141.85
138.86
133.88
132.98
131.18
128.96
128.62
128.54
126.88
92.93
60.04
52.38
40.25
O
N
S
I
O
O
CH3
f1 (ppm)

3d

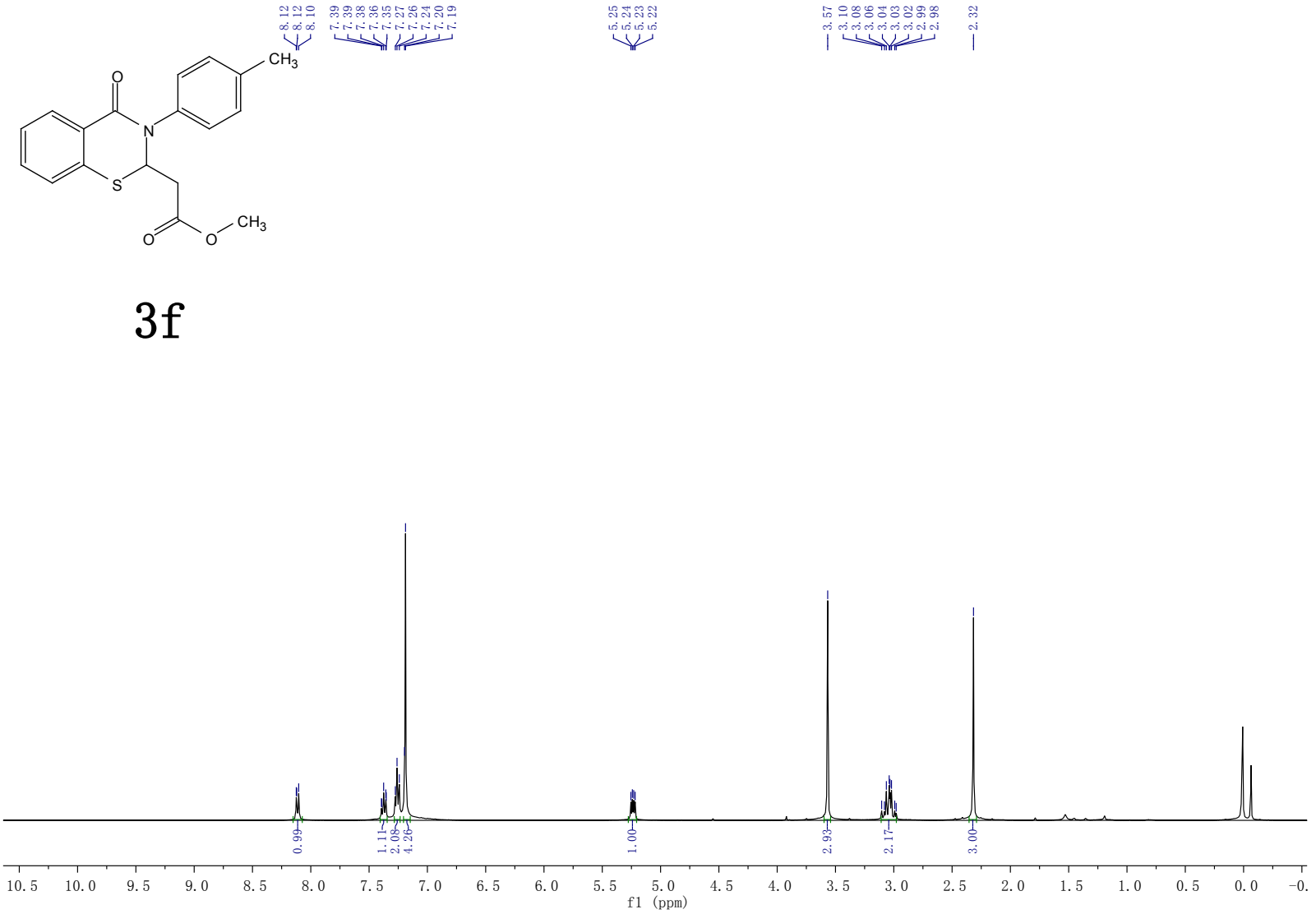

8.10
8.10
8.08
7.38
7.36
7.34
7.25
7.23
7.22
7.20
7.18
6.89
6.87
5.21
5.20
5.19
5.17
3.75
3.55
3.08
3.05
3.04
3.01
3.00
2.97
2.96
O
N
S
O
CH3
O
O
CH3

3e

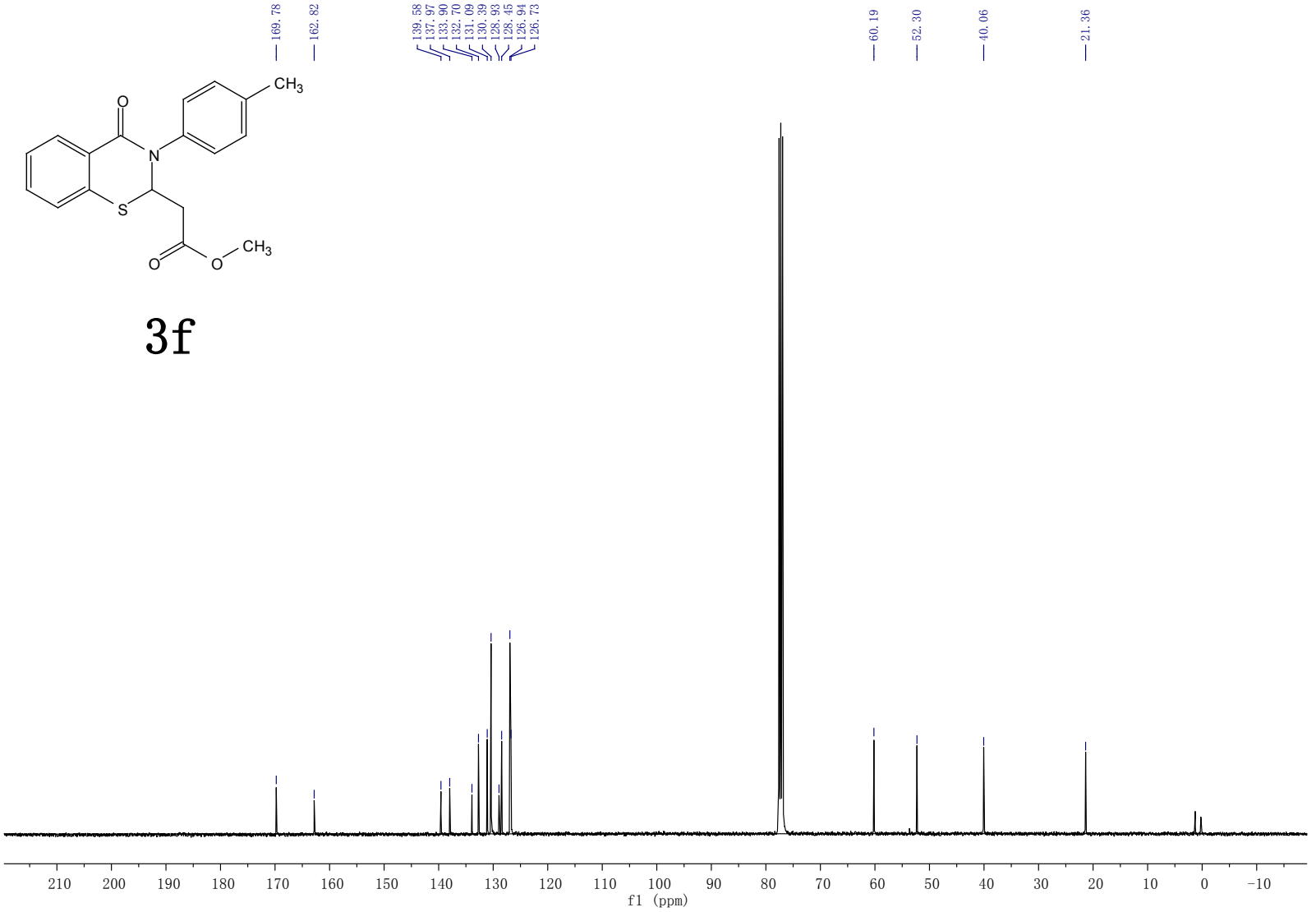

1.00
1.21
4.25
2.09
1.05
3.00
3.01
2.38
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

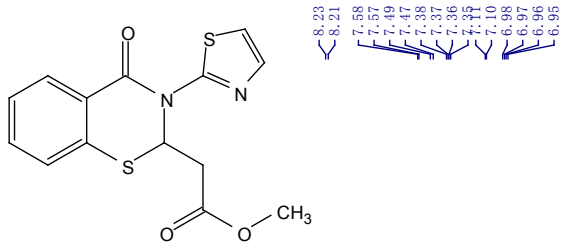

169.80
163.01
159.15
134.95
133.92
132.70
131.10
128.92
128.43
126.75
125.75
115.02
60.32
55.78
52.32
40.01
O
N
S
O
CH3
O
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3e


8.12
8.12
8.10
7.39
7.39
7.38
7.36
7.35
7.27
7.26
7.24
7.20
7.19
5.25
5.24
5.23
5.22
3.57
3.10
3.08
3.06
3.04
3.03
3.02
2.99
2.98
2.32
O
N
S
CH3
O
O
CH3
0.99
1.11
2.08
4.26
1.00
2.93
2.17
3.00
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 -0.
f1 (ppm)

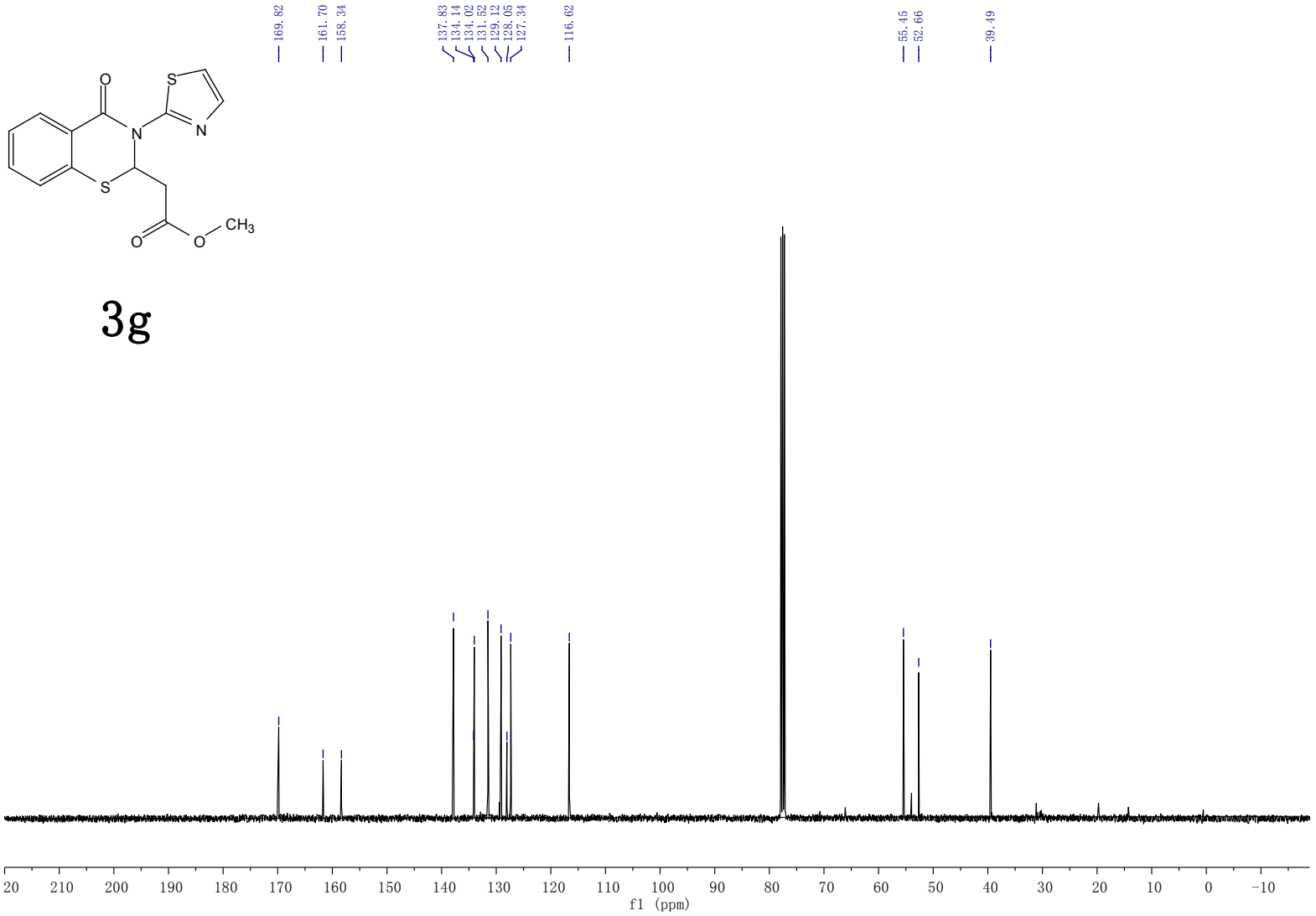
3f

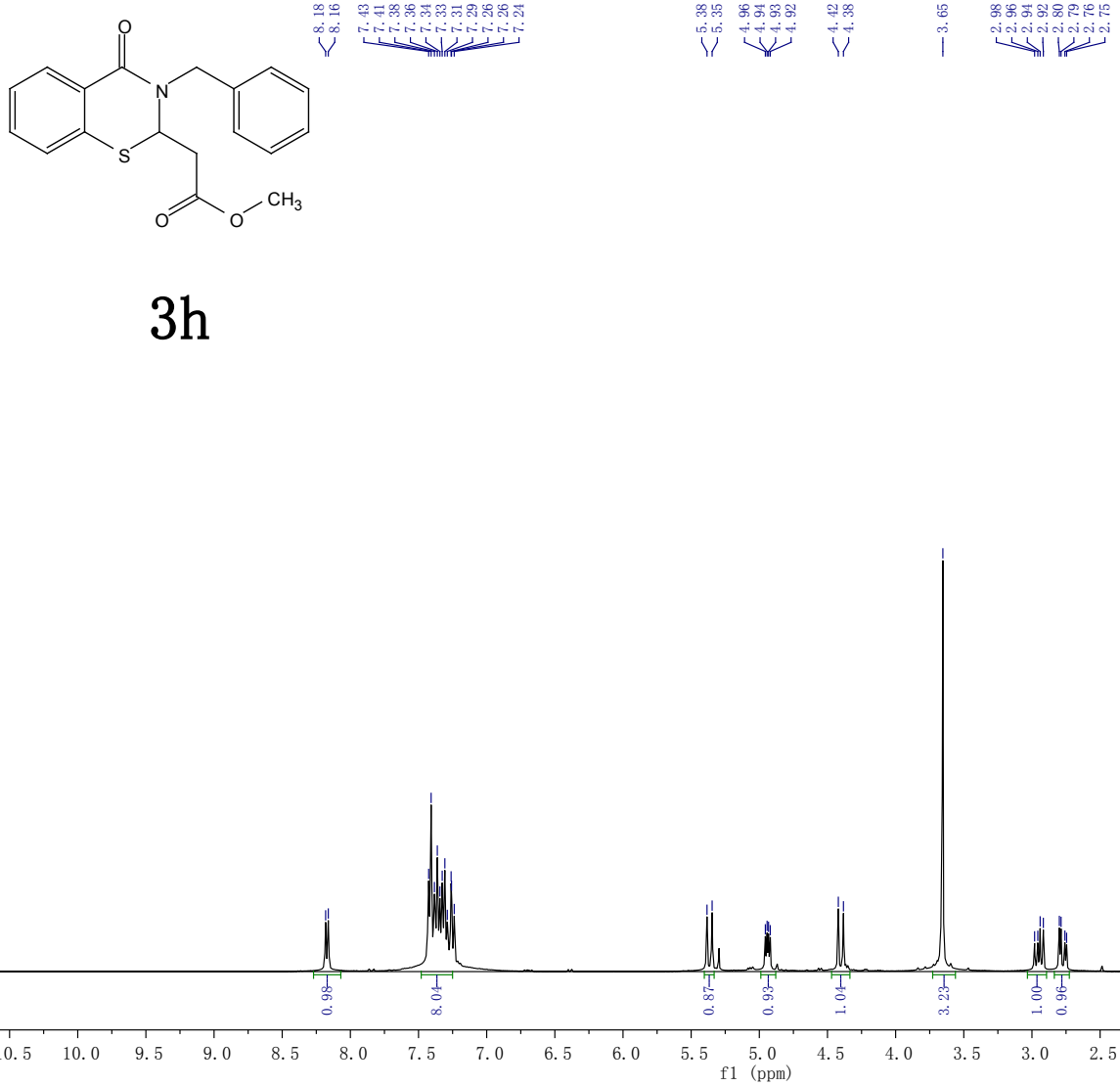

169.78
162.82
139.58
137.97
133.90
132.70
131.09
130.39
128.93
128.45
126.94
126.73
60.19
52.30
40.06
21.36
O
N
S
O
O
CH3
CH3
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
S
N
N
S
O
O
CH3

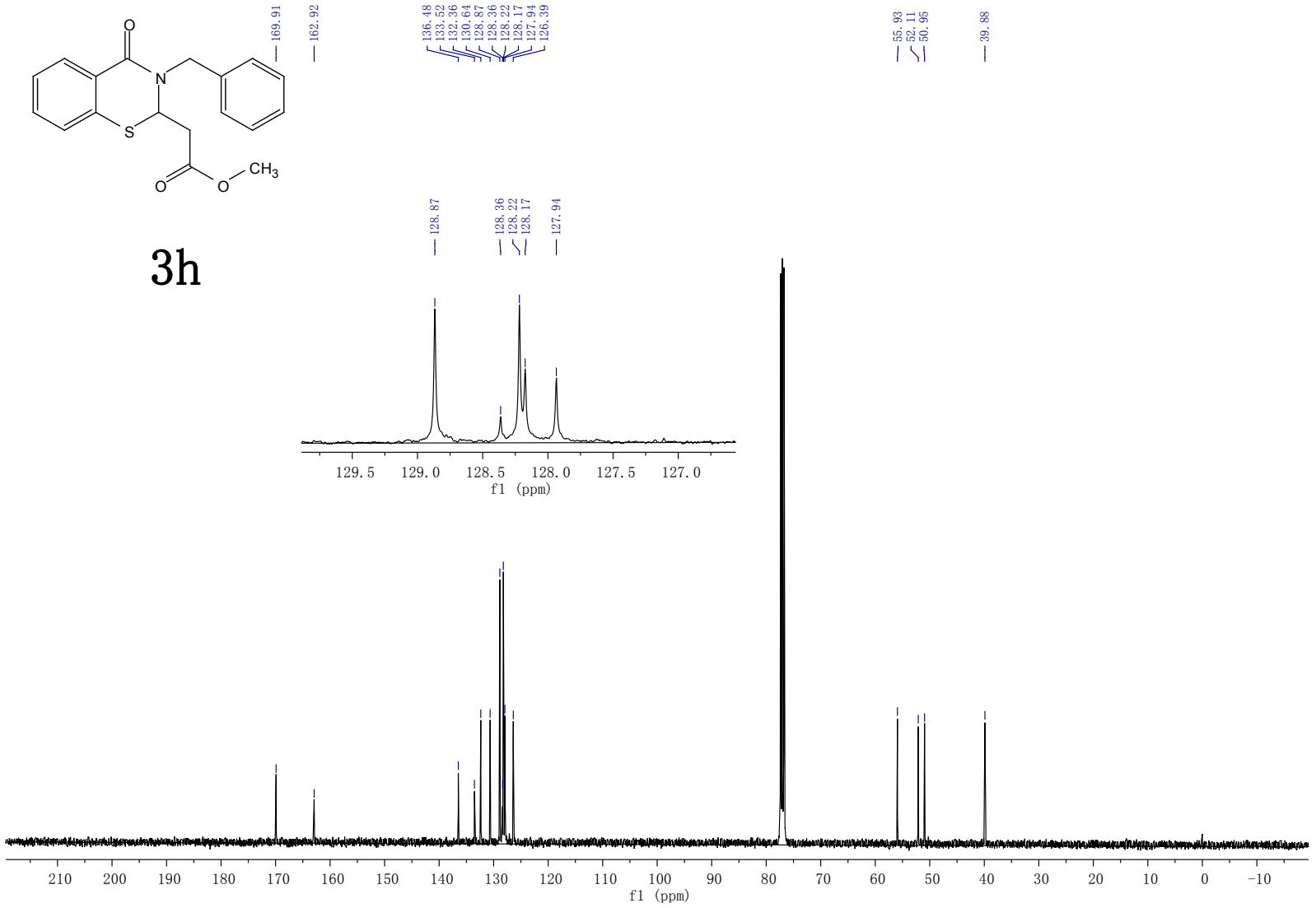
3g

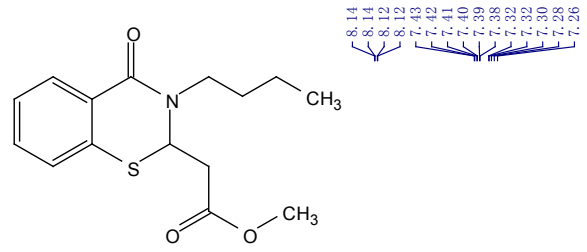
8.23
8.21
7.58
7.57
7.49
7.47
7.38
7.37
7.36
7.35
7.11
7.10
6.98
6.97
6.96
6.95
3.67
3.08
3.06
3.04
3.02
3.01
2.98
2.97
1.00
1.00
1.05
2.07
1.00
1.00
3.00
2.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.82
161.70
158.34
137.83
134.14
134.02
131.52
129.12
128.05
127.34
116.62
55.45
52.66
39.49
O
S
N
N
S
O
O
CH3
3g
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.18
8.16
7.43
7.41
7.38
7.36
7.34
7.33
7.31
7.29
7.26
7.26
7.24
5.38
5.35
4.96
4.94
4.93
4.92
4.42
4.38
3.65
2.98
2.96
2.94
2.92
2.80
2.79
2.76
2.75
O
N
S
O
O
CH3
0.98
8.04
0.87
0.93
1.04
3.23
1.00
0.96
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
-0.5
f1 (ppm)

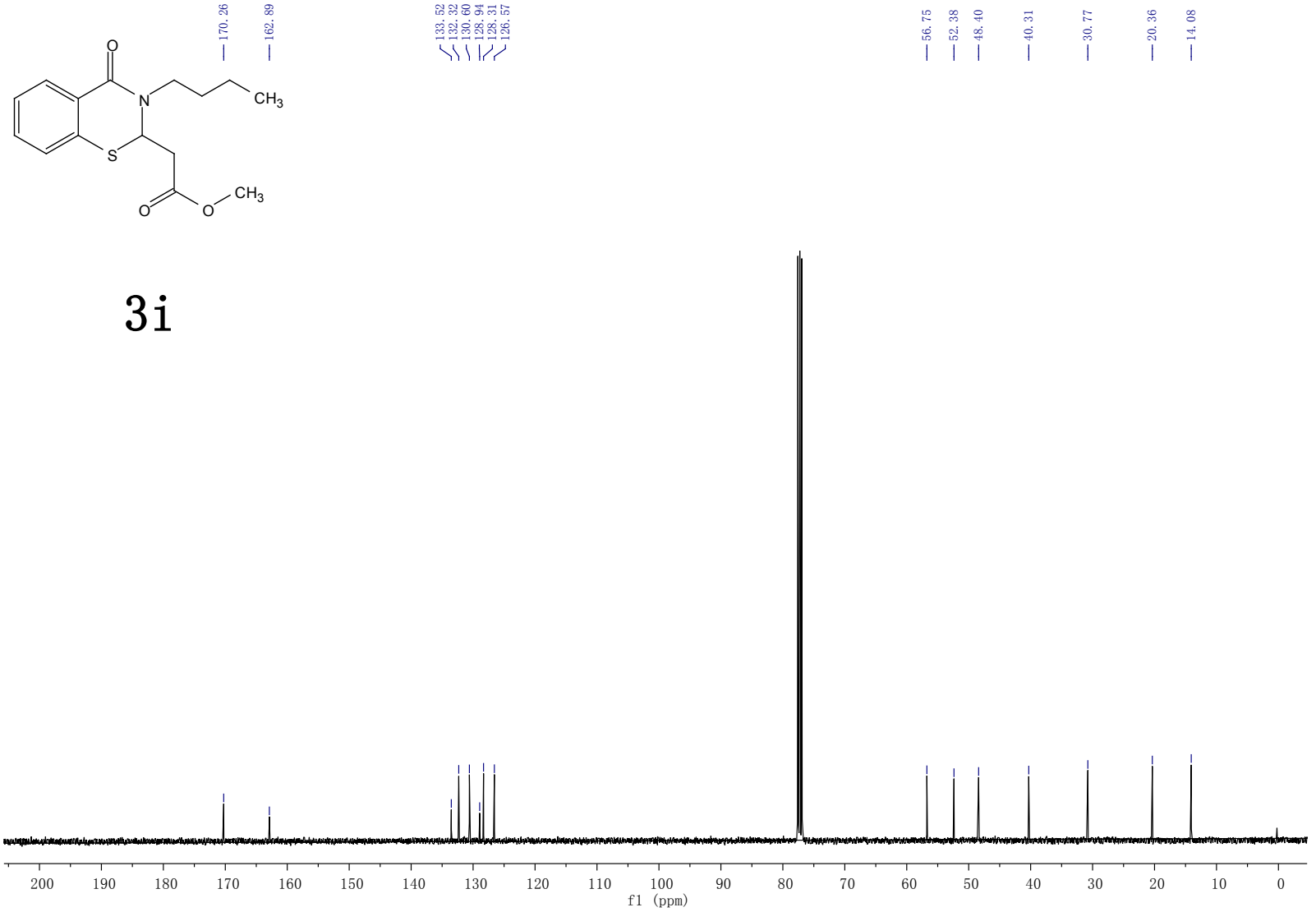
3h

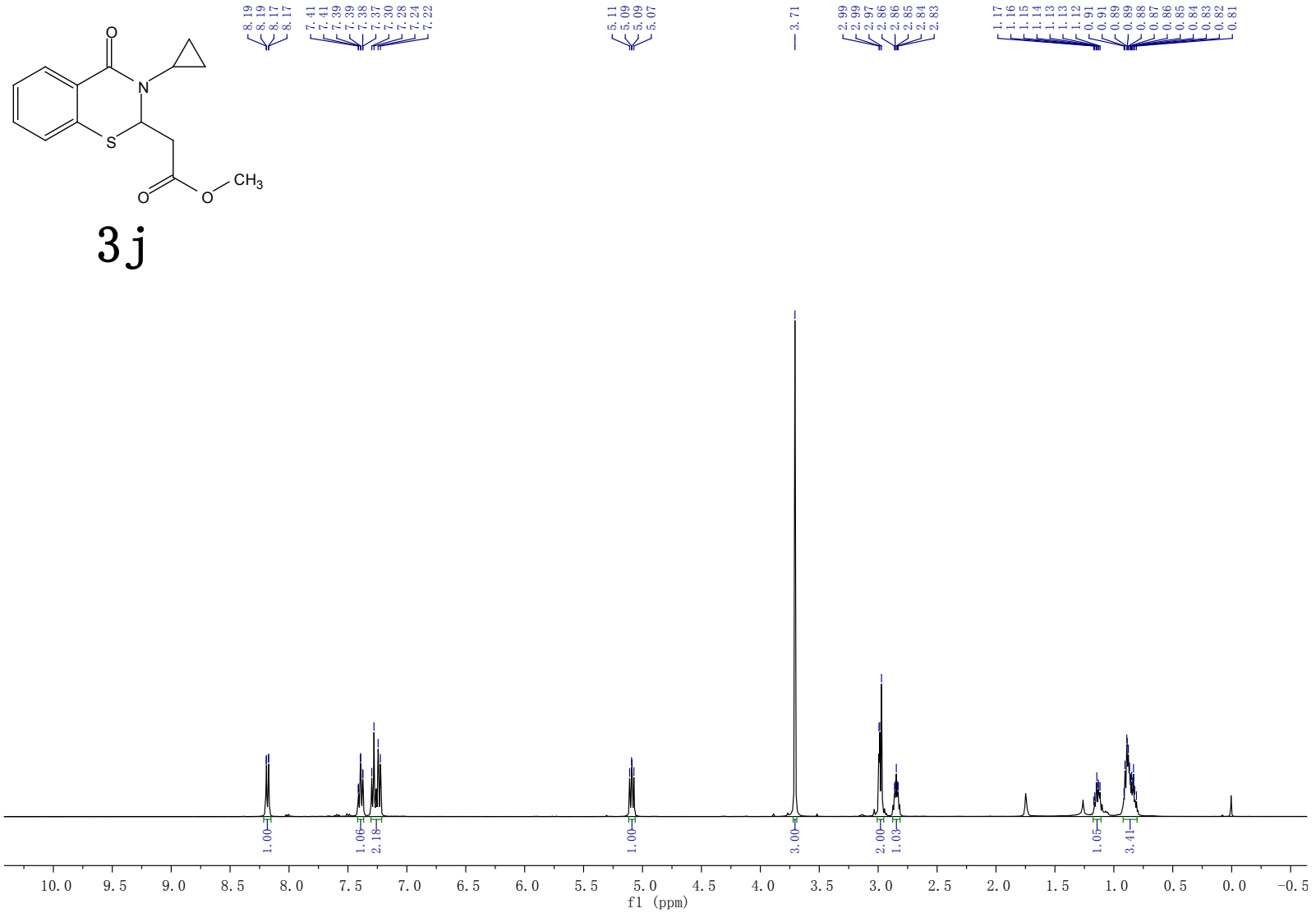

3h
O
N
S
O
O
CH3
169.91
162.92
136.48
133.52
132.36
130.64
128.87
128.36
128.22
128.17
127.94
126.39
55.93
52.11
50.95
39.88
128.87
128.36
128.22
128.17
127.94
129.5
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
N
CH3
S
O
O
CH3

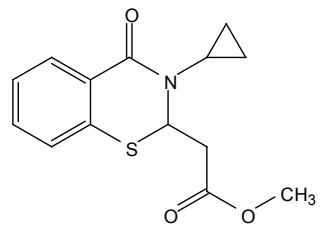
3i

8.14
8.14
8.12
8.12
7.43
7.42
7.41
7.40
7.39
7.38
7.32
7.30
7.28
7.26
4.98
4.96
4.95
4.94
4.23
4.21
4.19
4.18
4.16
3.72
3.12
3.10
3.08
3.04
3.02
3.00
2.98
2.93
2.92
2.89
2.88
1.75
1.73
1.71
1.69
1.67
1.47
1.45
1.44
1.42
0.98
0.97
1.00
1.06
2.15
1.00
1.05
3.00
1.12
2.48
2.09
2.33
3.01
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
f1 (ppm)


170.26
162.89
133.52
132.32
130.60
128.94
128.31
126.57
56.75
52.38
48.40
40.31
30.77
20.36
14.08
O
N
S
CH3
O
O
CH3
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

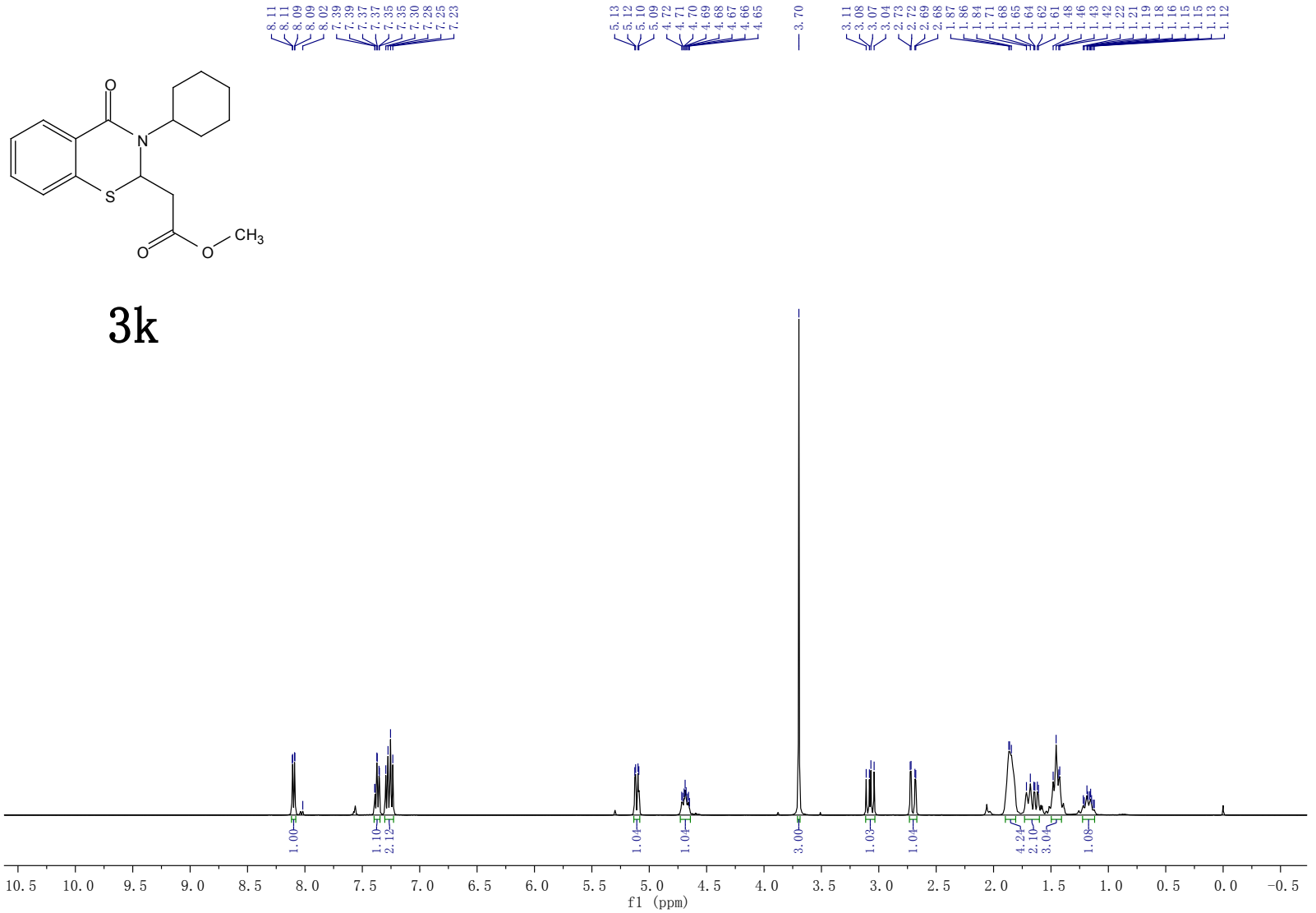

8.19
8.19
8.17
8.17
7.41
7.41
7.39
7.39
7.38
7.37
7.30
7.28
7.24
7.22
5.11
5.09
5.09
5.07
3.71
2.99
2.99
2.97
2.86
2.86
2.85
2.84
2.83
1.17
1.16
1.15
1.14
1.13
1.13
1.12
0.91
0.91
0.89
0.89
0.88
0.87
0.86
0.85
0.84
0.83
0.82
0.81
O
N
S
O
O
CH3
1.00
1.06
2.18
1.00
3.00
2.00
1.03
1.05
3.41
10.0
9.5
9.0
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
-0.5
f1 (ppm)

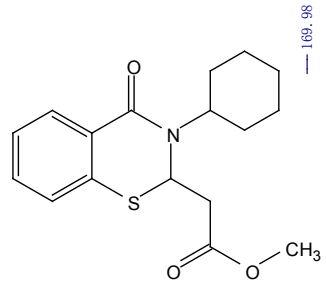
3j


O
N
S
O
O
CH3

3j

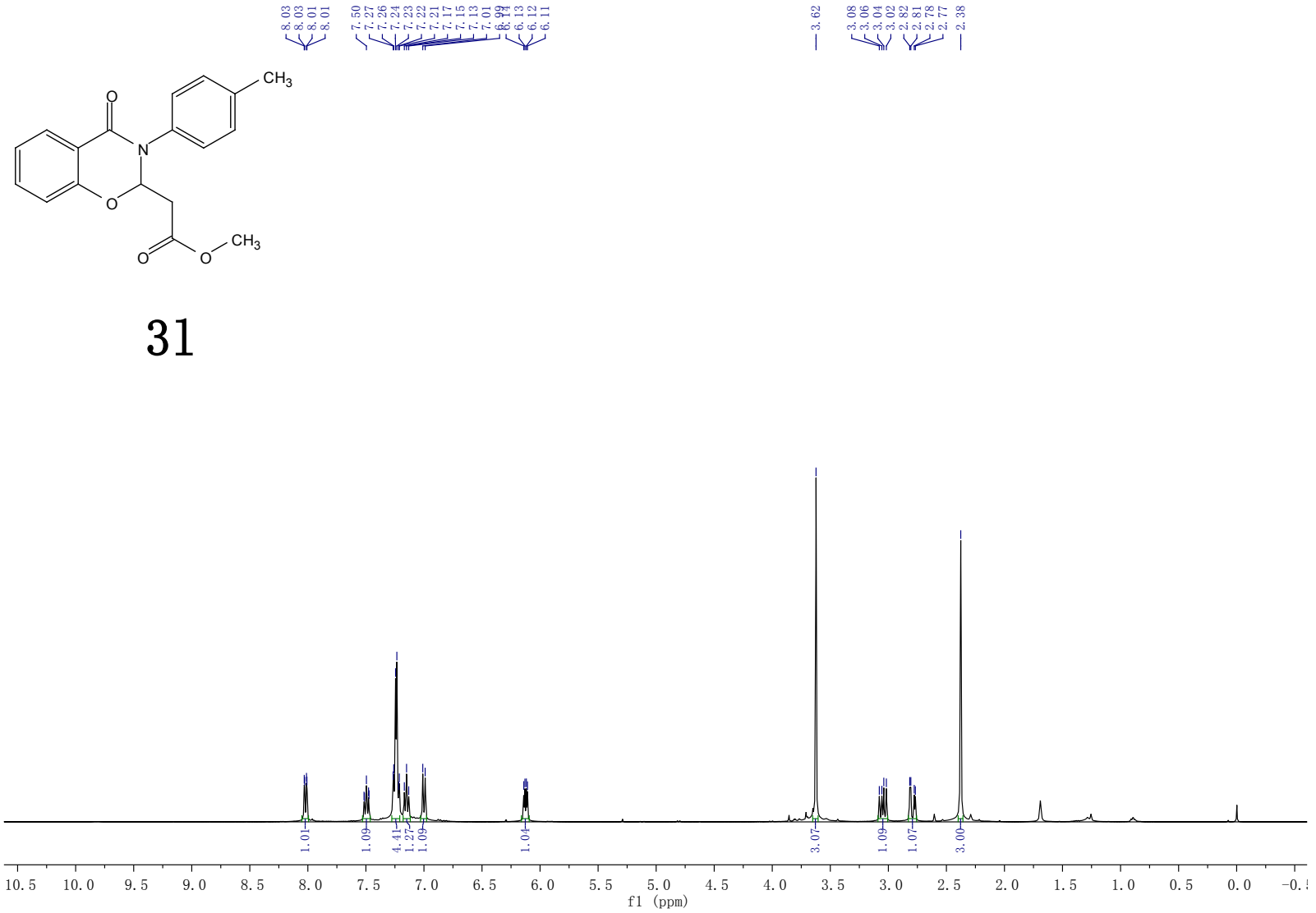
170.17
164.48
133.50
132.60
130.61
128.24
128.15
126.36
58.11
52.32
39.94
31.37
10.32
7.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.11
8.11
8.09
8.09
8.02
7.39
7.39
7.37
7.37
7.35
7.30
7.28
7.25
7.23
5.13
5.12
5.10
5.09
4.72
4.71
4.70
4.69
4.68
4.67
4.66
4.65
3.70
3.11
3.08
3.07
3.04
2.73
2.72
2.69
2.68
1.87
1.86
1.84
1.71
1.68
1.65
1.64
1.62
1.61
1.48
1.46
1.43
1.42
1.22
1.21
1.19
1.18
1.16
1.15
1.13
1.12
O
N
S
O
O
CH3
3k
1.00
1.10
2.12
1.04
1.04
3.00
1.03
1.04
4.24
2.10
3.04
1.08
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 -0.5
f1 (ppm)

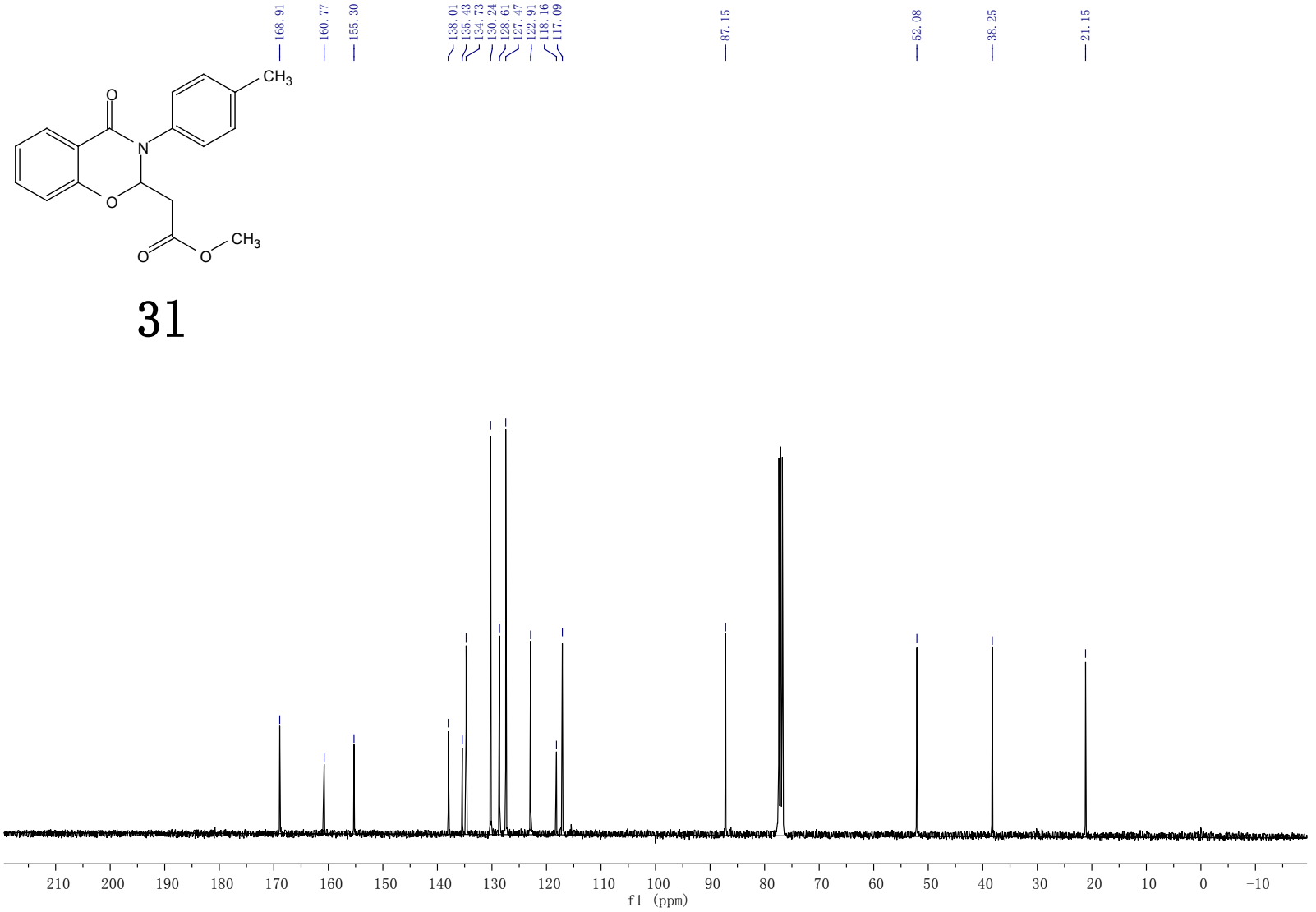

O
N
S
O
O
CH3

3k

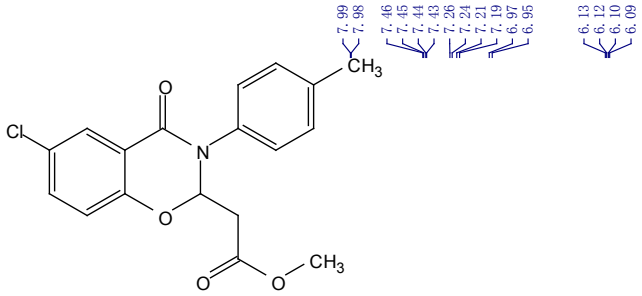
169.98
162.54
133.40
132.03
130.63
129.41
128.28
126.33
54.78
52.12
51.99
41.54
32.98
31.38
30.38
25.85
25.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.03
8.03
8.01
8.01
7.50
7.27
7.26
7.24
7.23
7.22
7.21
7.17
7.15
7.13
7.01
6.99
6.14
6.13
6.12
6.11
3.62
3.08
3.06
3.04
3.02
2.82
2.81
2.78
2.77
2.38
CH3
O
N
O
O
O
CH3
1.01
1.09
4.41
1.27
1.09
1.04
3.07
1.09
1.07
3.00
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
f1 (ppm)

31

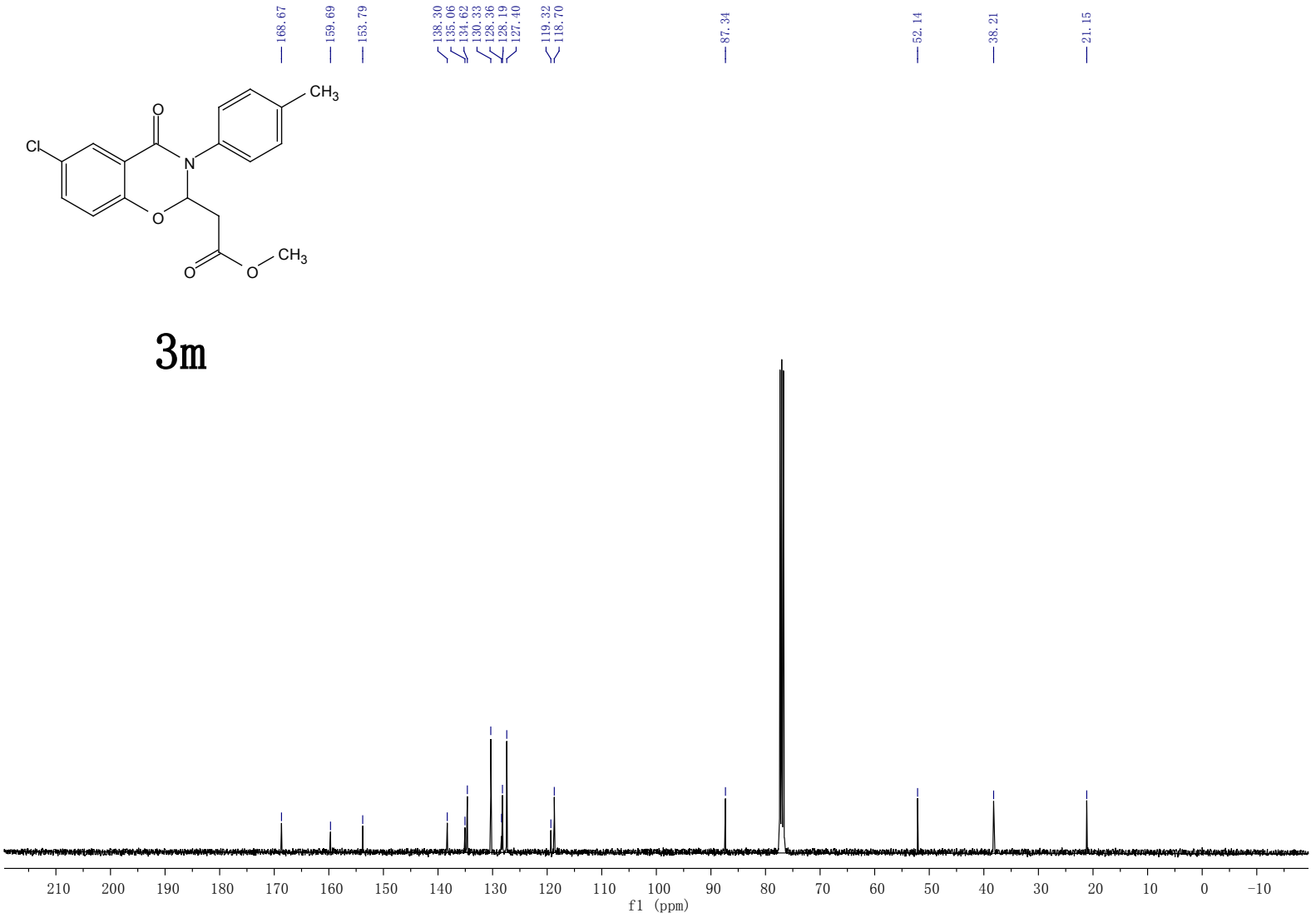

168.91
160.77
155.30
138.01
135.43
134.73
130.24
128.61
127.47
122.91
118.16
117.09
87.15
52.08
38.25
21.15
CH3
O
N
O
O
O
CH3
f1 (ppm)

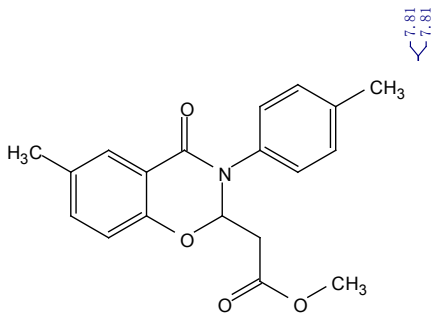
31


Cl
O
N
O
CH3
O
O
CH3

3m

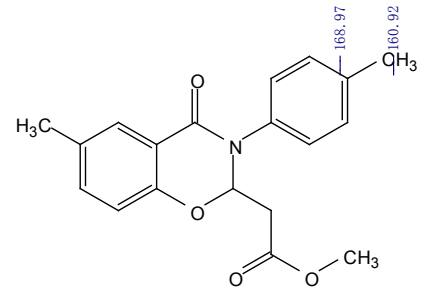
7.99
7.98
7.46
7.45
7.44
7.43
7.26
7.24
7.21
7.19
6.97
6.95
6.13
6.12
6.10
6.09
3.63
3.05
3.03
3.01
2.99
2.81
2.80
2.77
2.76
2.38
0.84
1.04
4.43
1.05
0.99
3.00
1.06
1.03
3.20
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


168.67
159.69
153.79
138.30
135.06
134.62
130.33
128.36
128.19
127.40
119.32
118.70
87.34
52.14
38.21
21.15
Cl
O
N
O
CH3
O
O
CH3
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

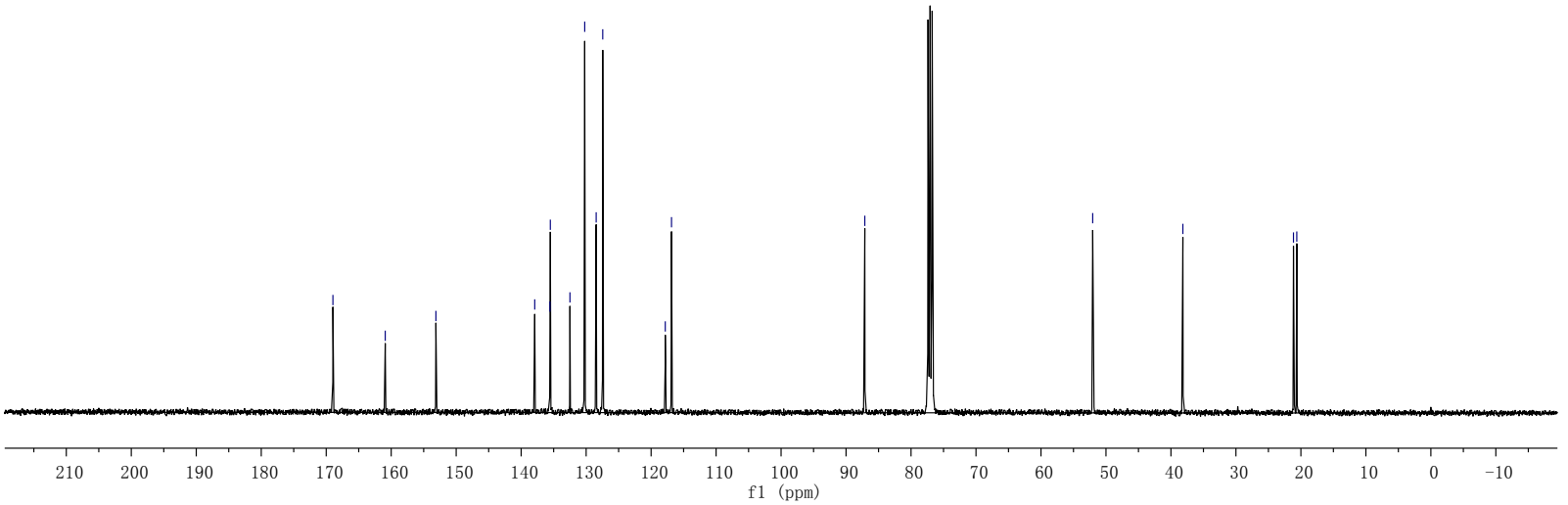

O
CH3
H3C
N
O
O
O
CH3

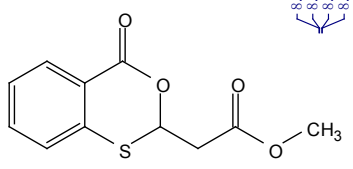
3n

7.81
7.81
7.31
7.28
7.26
7.24
7.23
7.21
6.90
6.88
6.10
6.10
6.08
6.07
3.62
3.07
3.05
3.03
3.01
2.80
2.79
2.76
2.75
2.37
2.35
1.00
5.39
1.08
1.04
3.08
1.01
1.02
6.05
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
f1 (ppm)


O
H3C
N
O
O
O
CH3
168.97
160.92
153.12
137.91
135.57
135.51
132.49
130.22
128.46
127.44
117.82
116.86
87.11
52.04
38.16
21.14
20.63

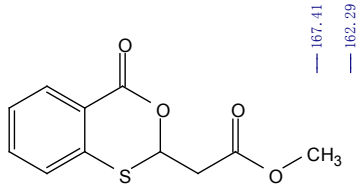
3n


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
O
S
O
CH3

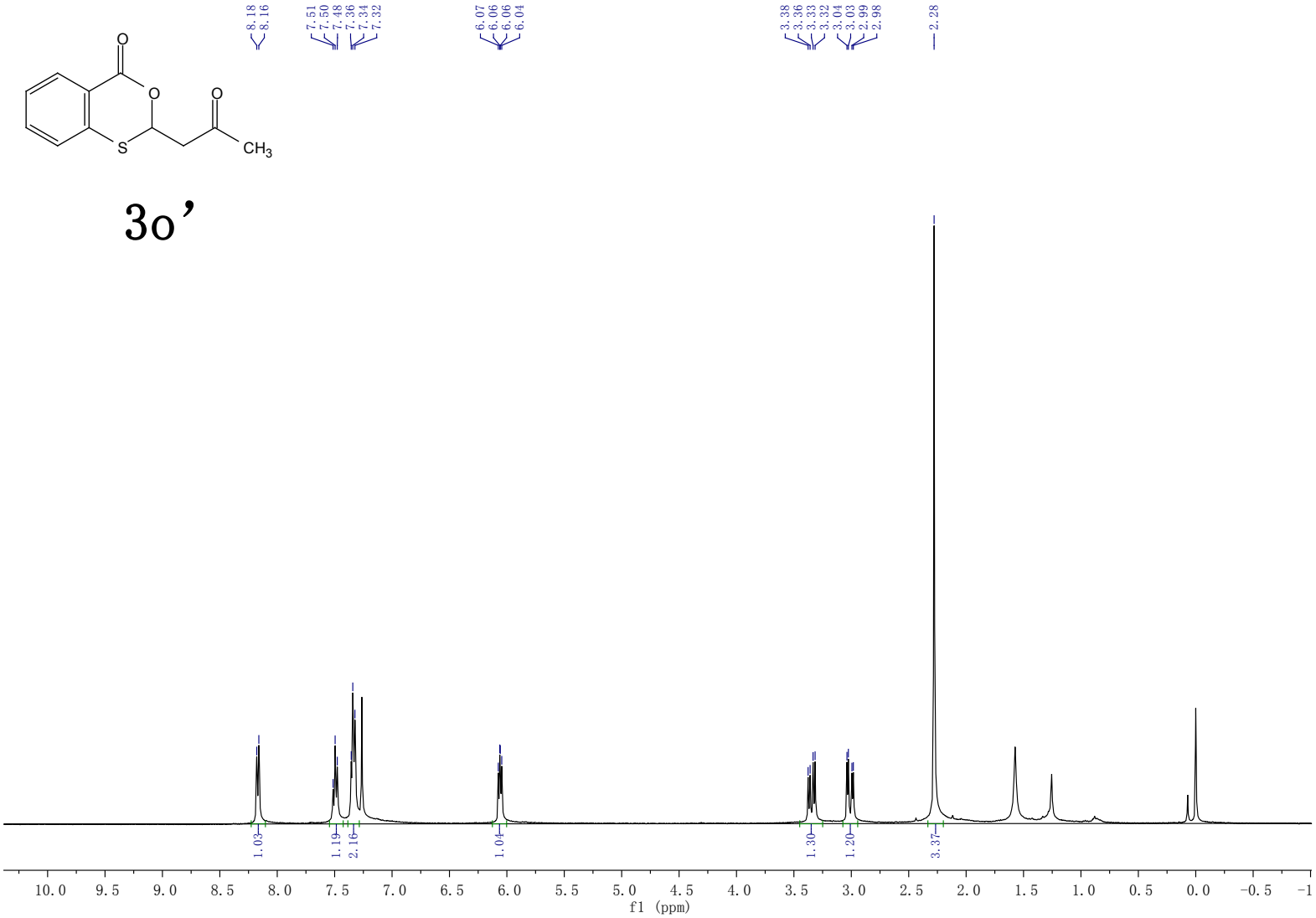
3o

8.19
8.19
8.17
8.17
7.53
7.52
7.51
7.49
7.48
7.36
7.36
7.35
7.35
7.34
7.33
6.03
6.02
6.01
6.00
3.77
3.24
3.22
3.20
3.18
3.01
3.00
2.97
2.96
1.02
1.03
2.03
0.99
2.94
1.11
1.12
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 -0.5
f1 (ppm)

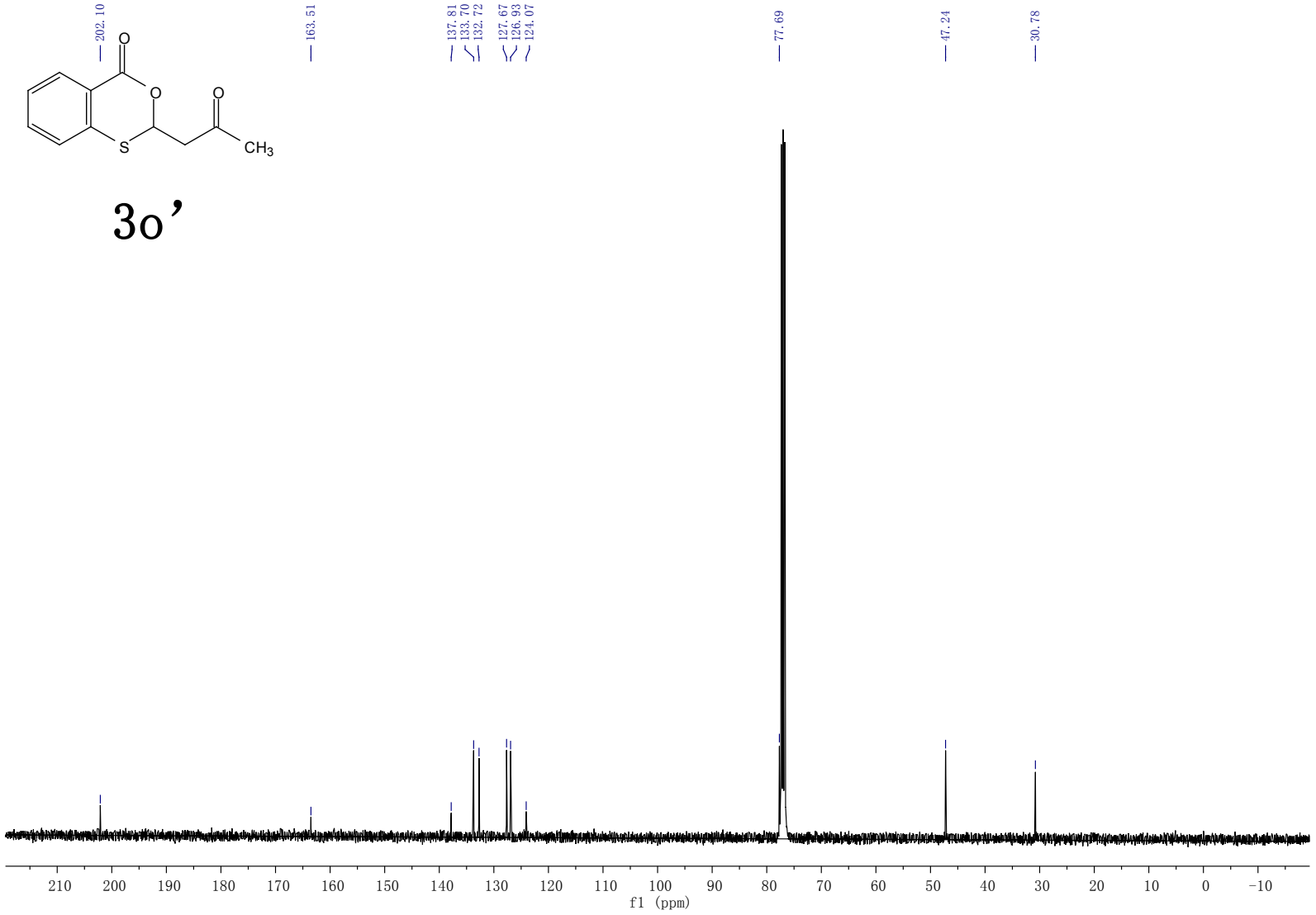

O
O
O
S
O
CH3

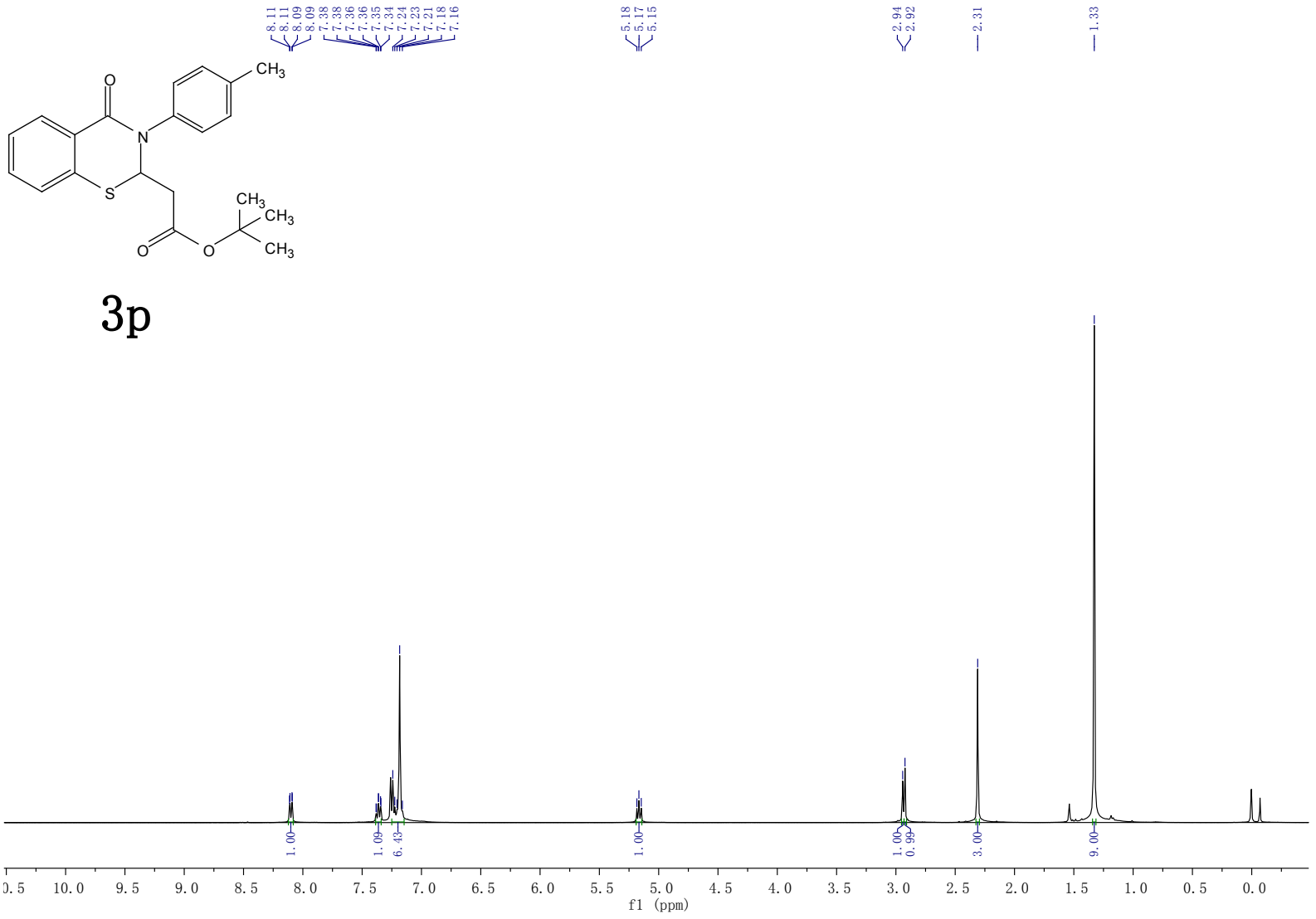
3o

167.41
162.29
136.53
132.76
131.72
126.70
125.97
123.03
77.27
51.43
38.28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

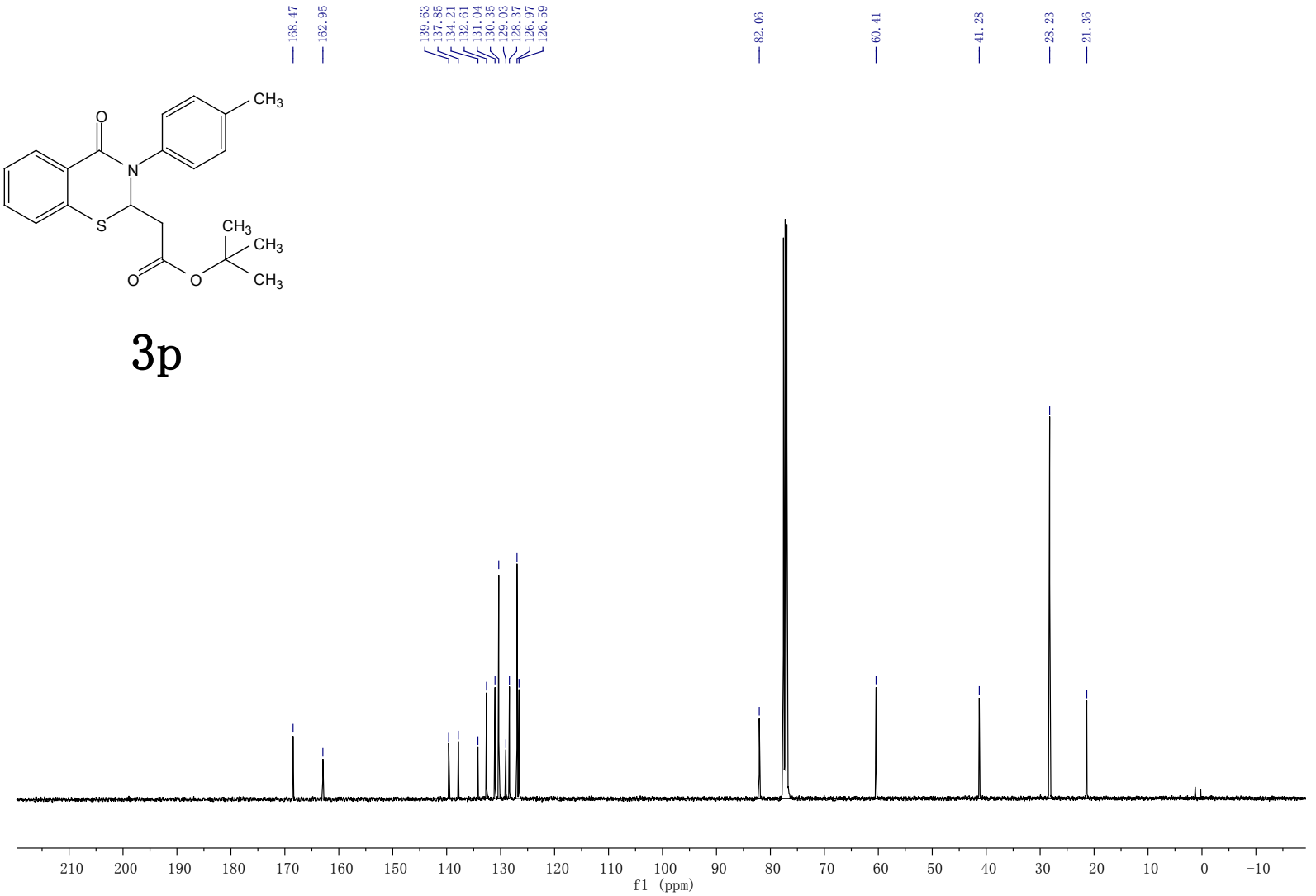

8.18
8.16
7.51
7.50
7.48
7.36
7.34
7.32
6.07
6.06
6.06
6.04
3.38
3.36
3.33
3.32
3.04
3.03
2.99
2.98
2.28
O
O
O
S
CH3
1.03
1.19
2.16
1.04
1.30
1.20
3.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

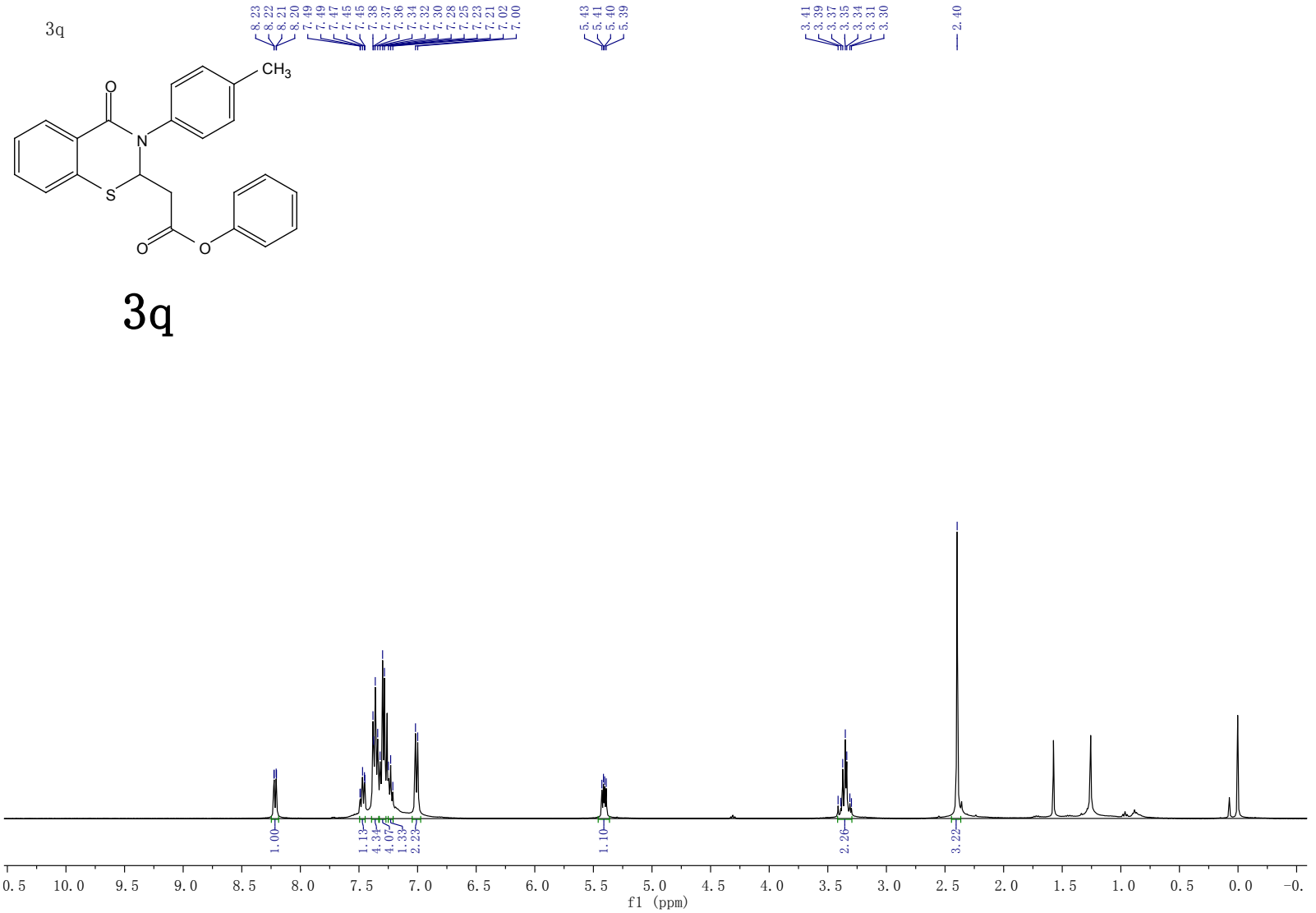
3o’


202.10
163.51
137.81
133.70
132.72
127.67
126.93
124.07
77.69
47.24
30.78
O
O
O
S
CH3
3o’
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

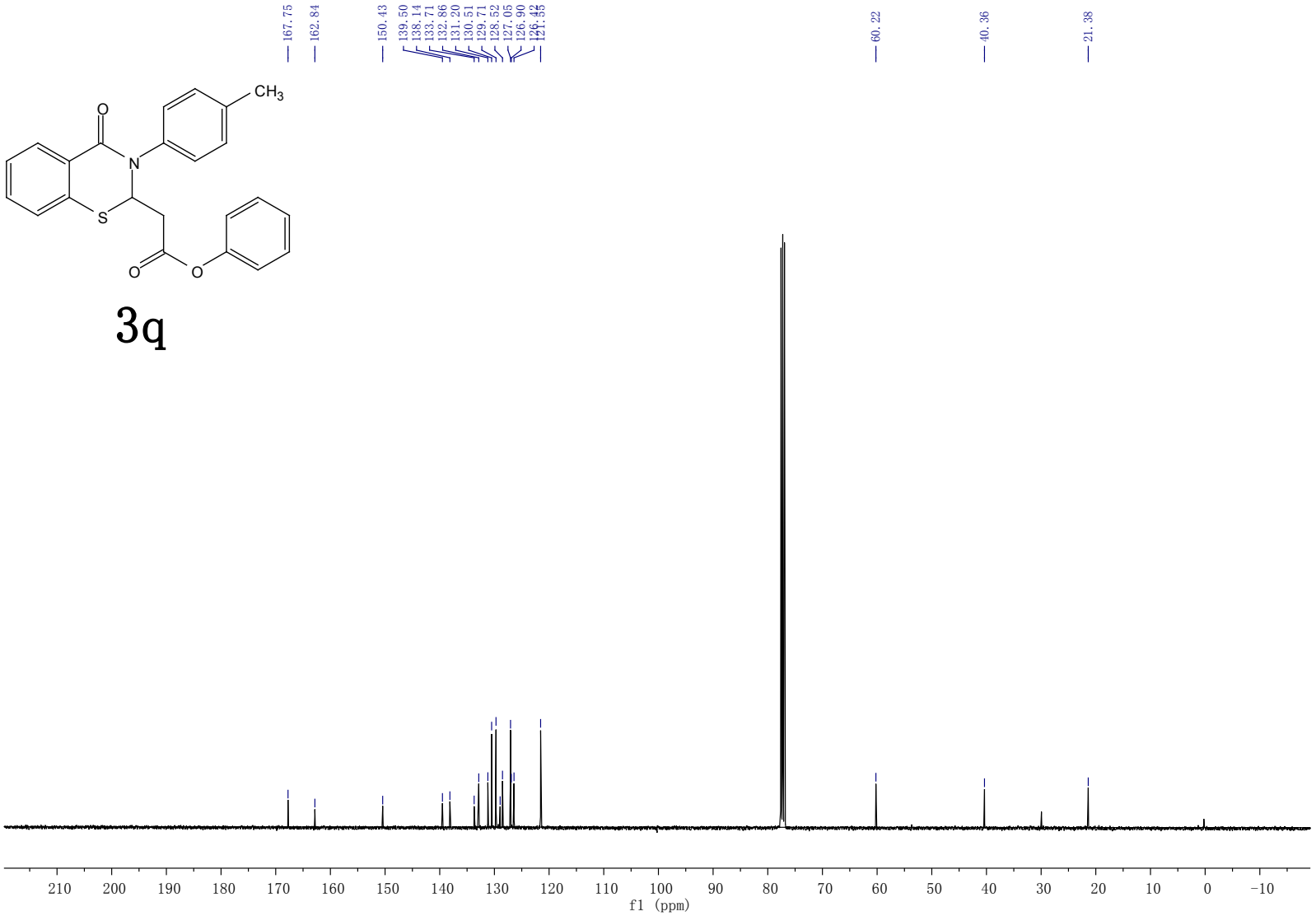

8.11
8.11
8.09
8.09
7.38
7.38
7.36
7.36
7.35
7.34
7.24
7.23
7.21
7.18
7.16
5.18
5.17
5.15
2.94
2.92
2.31
1.33
O
N
S
CH3
CH3
CH3
CH3
O
O
1.00
1.09
6.43
1.00
1.00
0.99
3.00
9.00
f1 (ppm)

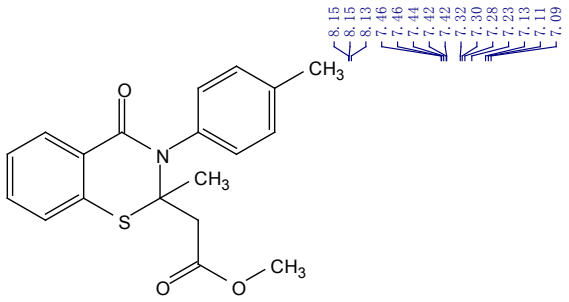
3p


168.47
162.95
139.63
137.85
134.21
132.61
131.04
130.35
129.03
128.37
126.97
126.59
82.06
60.41
41.28
28.23
21.36
O
N
S
CH3
O
O
CH3
CH3
CH3
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3q
8.23
8.22
8.21
8.20
7.49
7.49
7.47
7.47
7.45
7.38
7.37
7.36
7.34
7.32
7.30
7.28
7.25
7.23
7.21
7.02
7.00
5.43
5.41
5.40
5.39
3.41
3.39
3.37
3.35
3.34
3.31
3.30
2.40
CH3
O
N
S
O
O
1.00
1.13
4.34
4.07
1.33
2.23
1.10
2.26
3.22
f1 (ppm)

3q

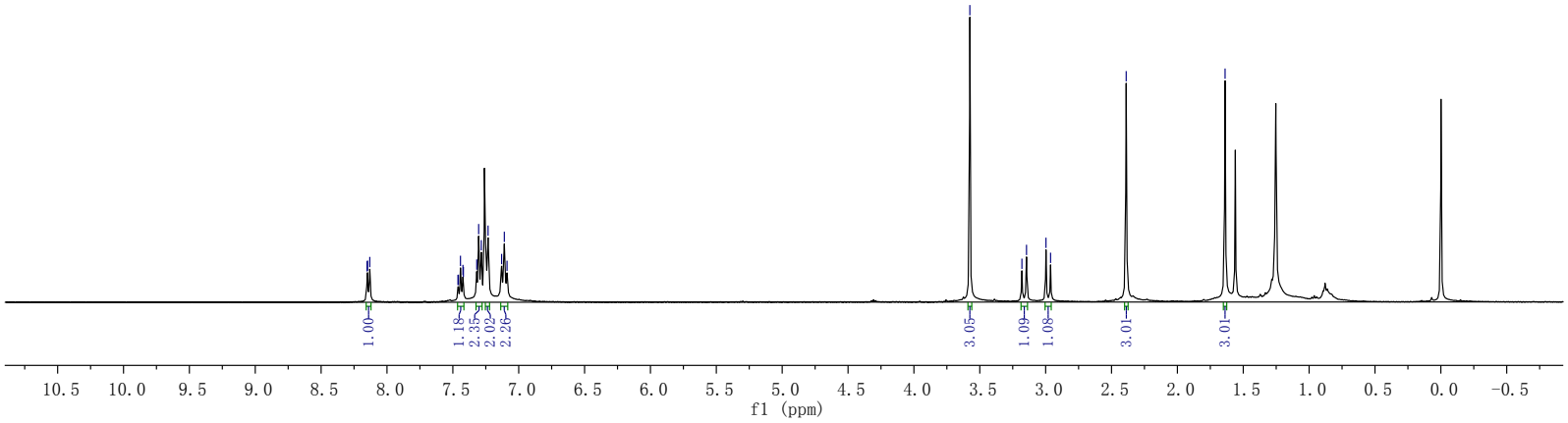

167.75
162.84
150.43
139.50
138.14
133.71
132.86
131.20
130.51
129.71
128.52
127.05
126.90
126.42
121.55
60.22
40.36
21.38
CH3
O
N
S
O
O
3q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

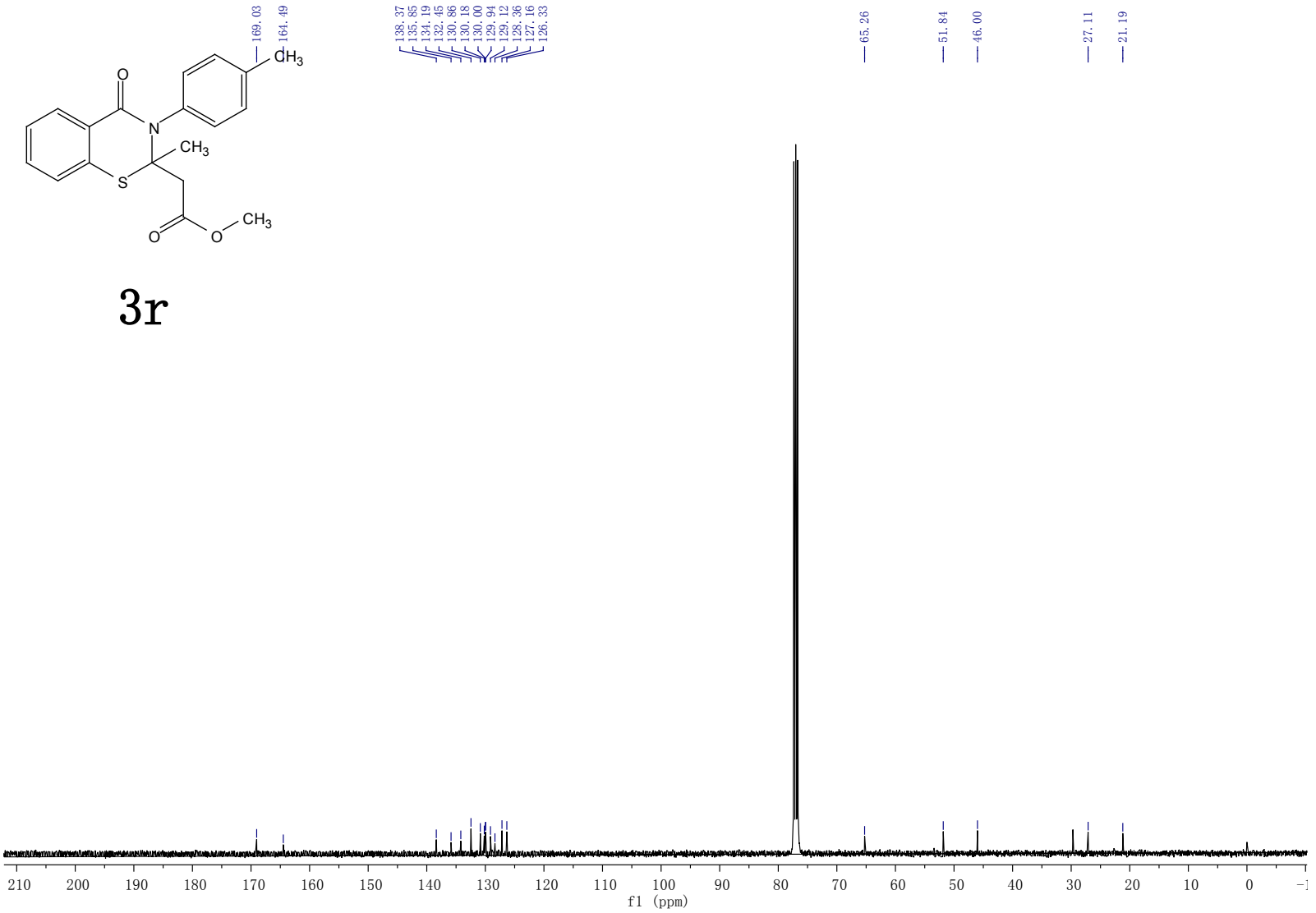


8.15
8.15
8.13
7.46
7.46
7.44
7.42
7.32
7.30
7.28
7.23
7.13
7.11
7.09

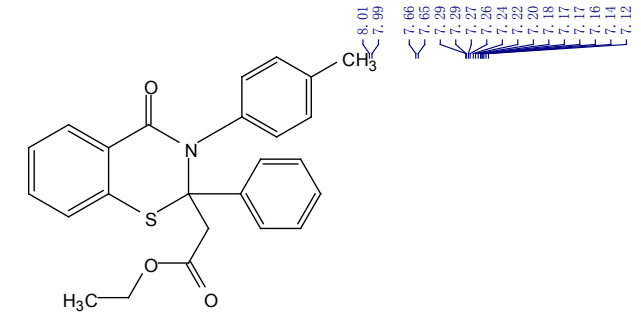
3.58
3.18
3.15
3.00
2.96
2.39
1.64

3r



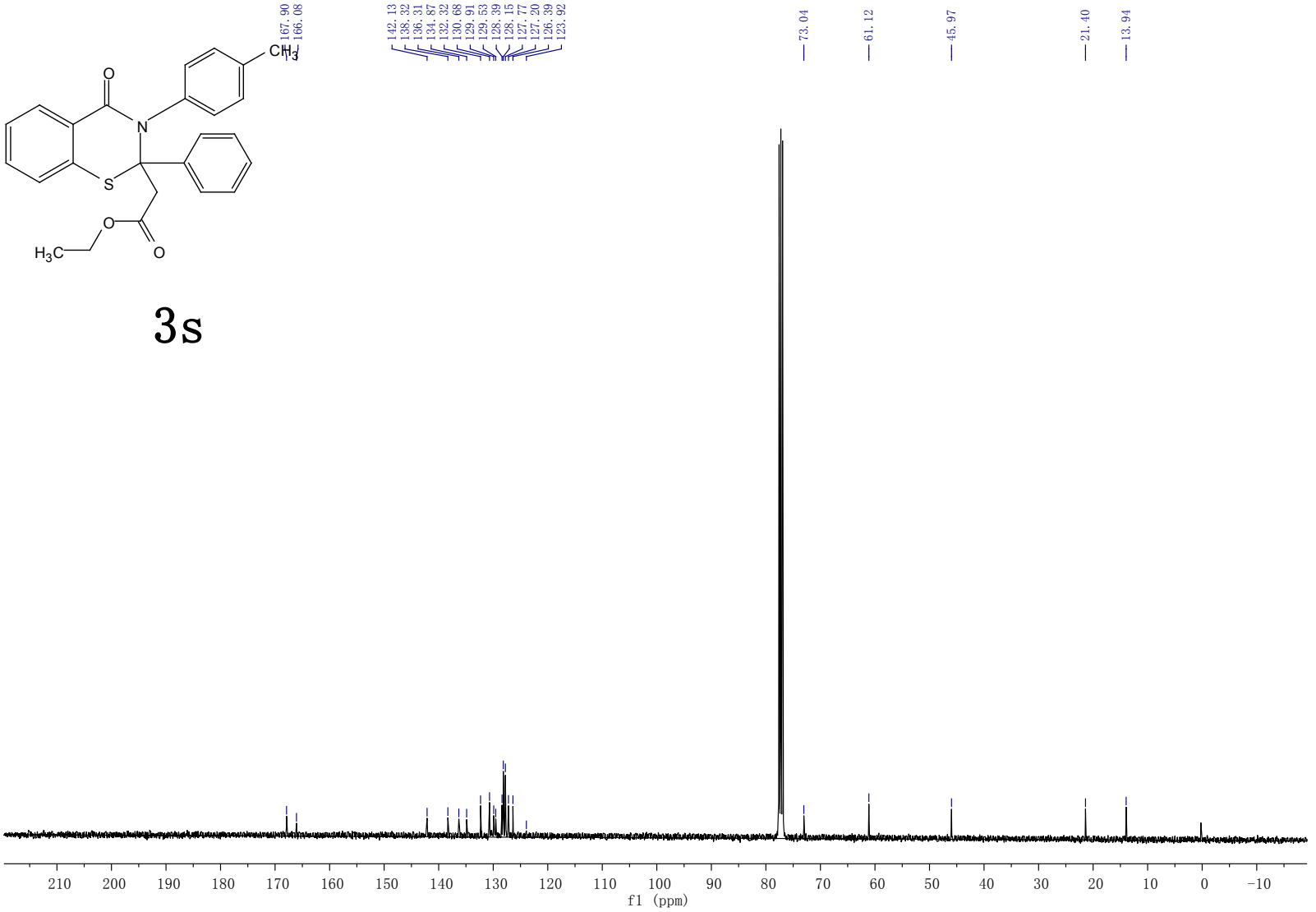

169.03
164.49
138.37
135.65
134.19
132.45
130.86
130.18
130.00
129.94
129.12
128.36
127.16
126.33
65.26
51.84
46.00
27.11
21.19
O
N
CH3
S
O
O
CH3
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3r

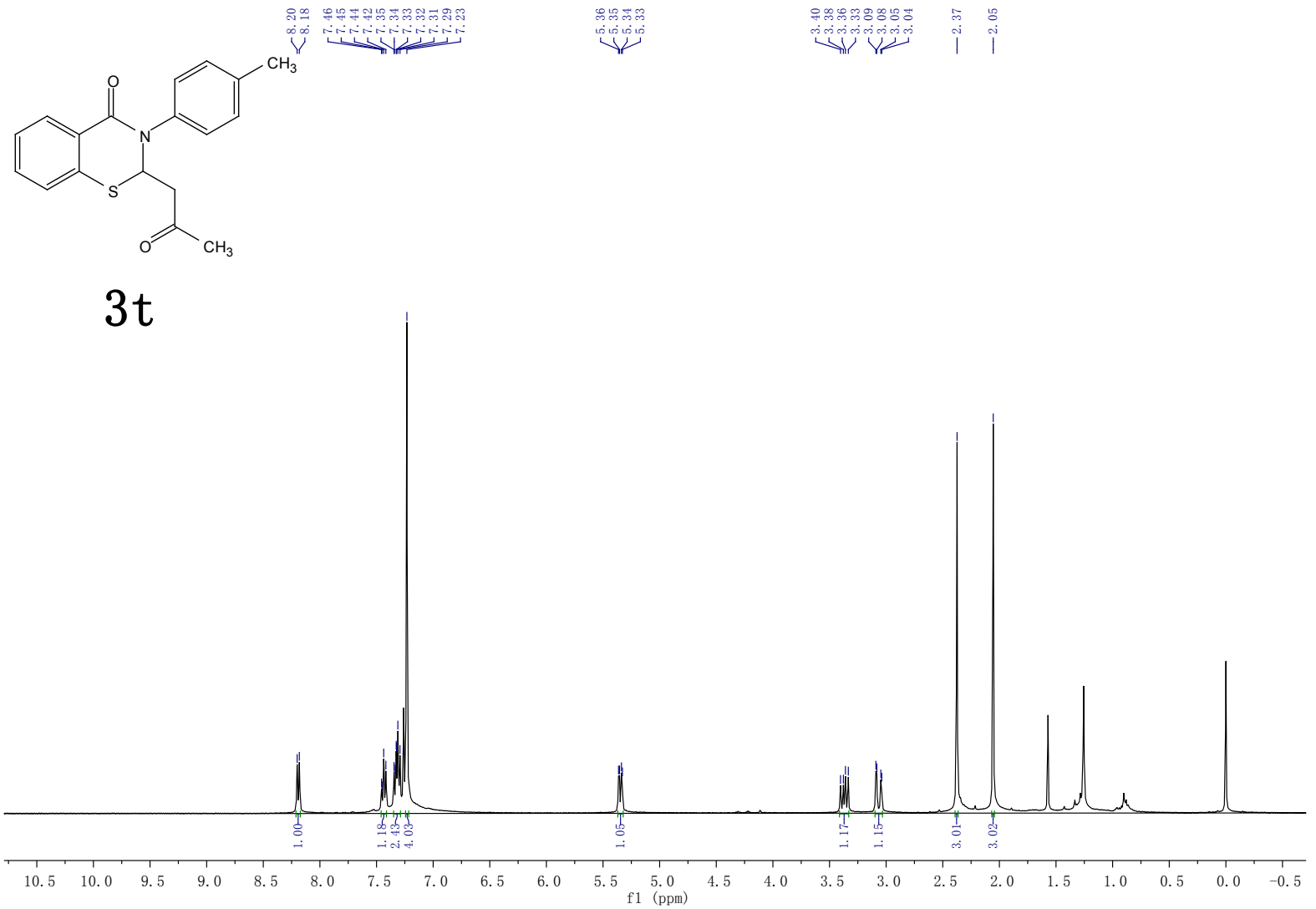

O
N
S
O
O
H_3C
CH_3

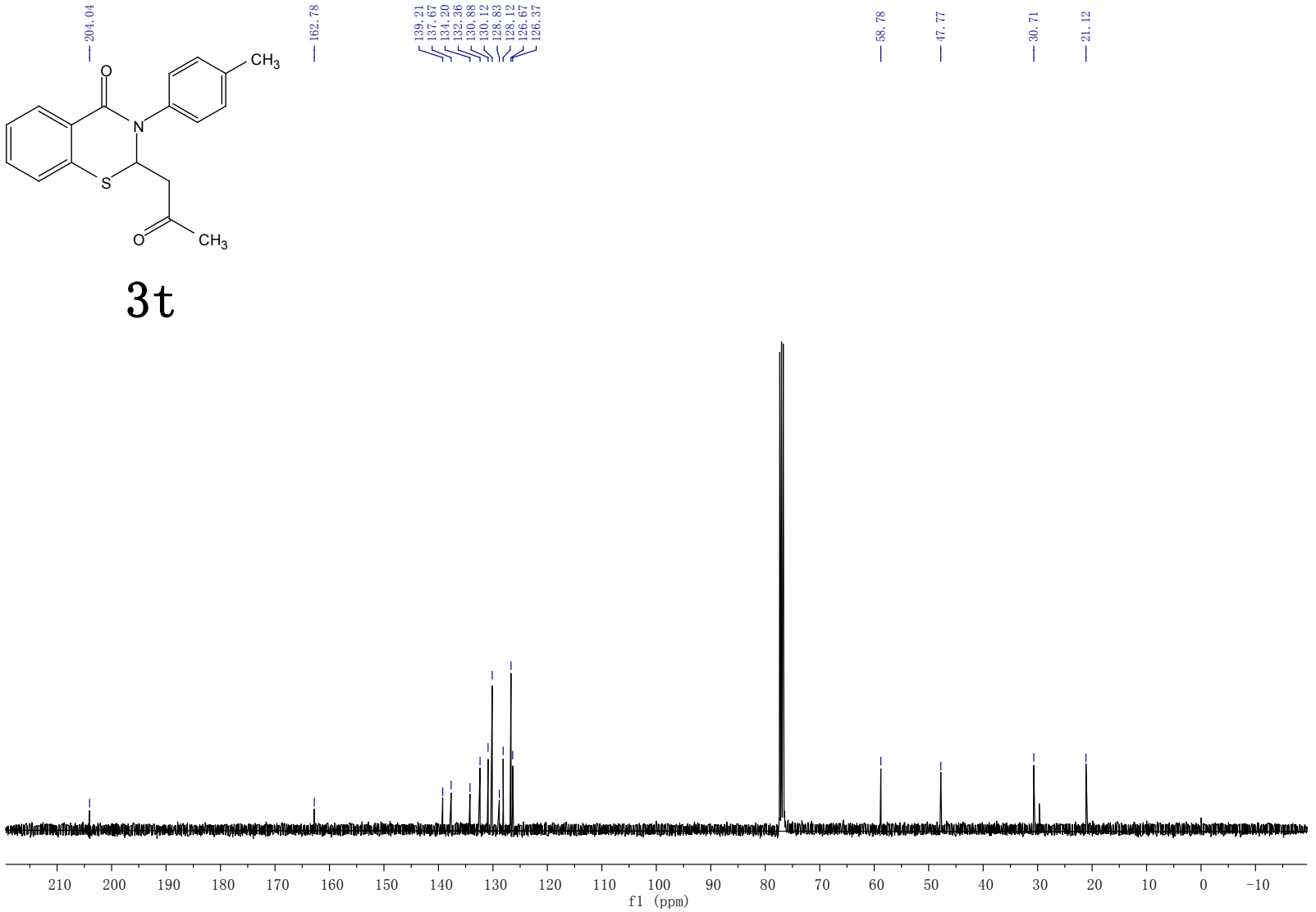
3s

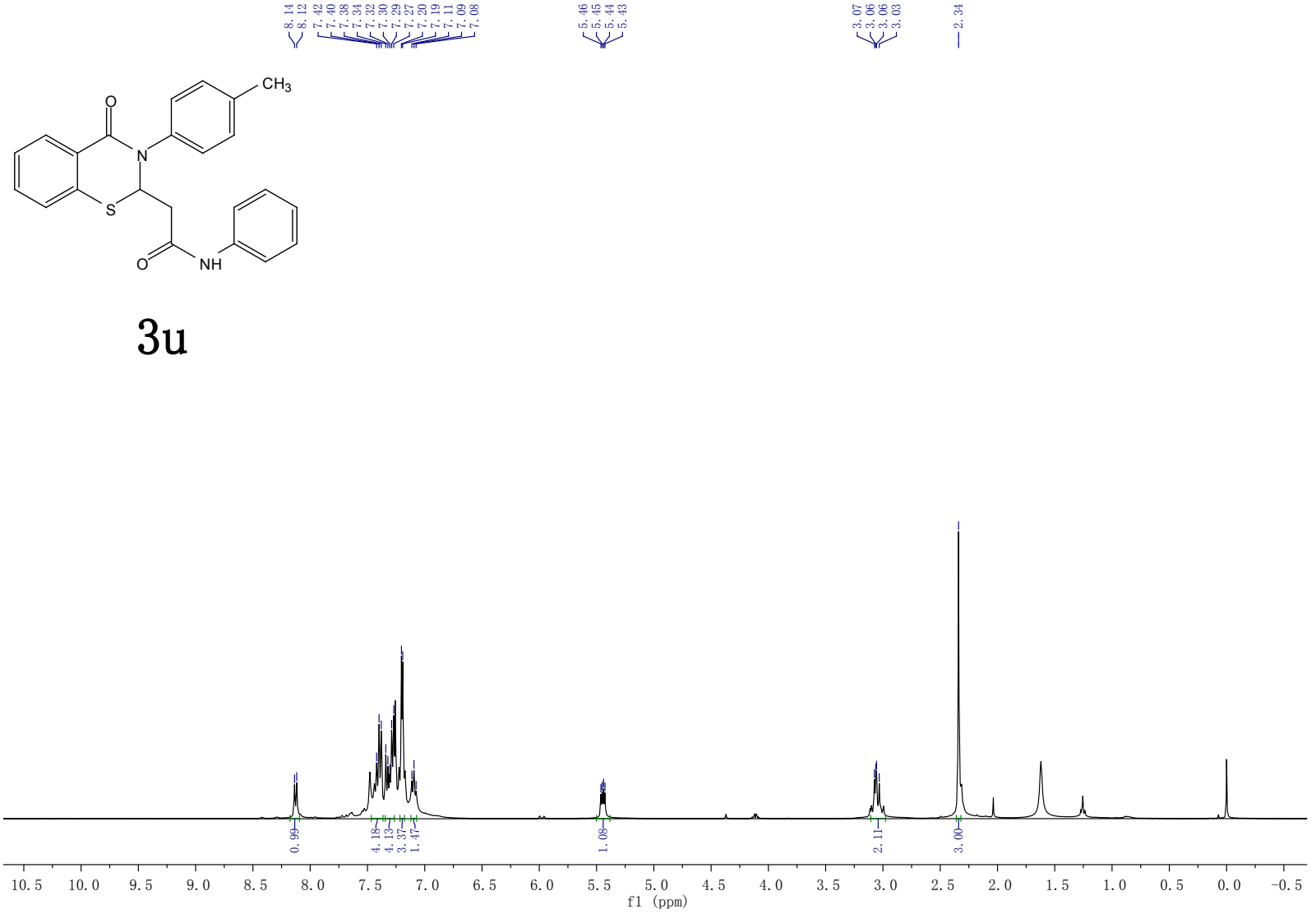
8.01
7.99
7.66
7.65
7.29
7.29
7.27
7.26
7.24
7.22
7.20
7.18
7.17
7.17
7.16
7.14
7.12
3.81
3.80
3.79
3.79
3.77
3.75
3.75
3.22
3.19
3.17
3.13
2.35
1.00
0.99
0.97
0.99
2.14
10.31
2.08
2.15
3.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.90
166.08
142.13
138.32
136.31
134.87
132.32
130.68
129.91
129.53
128.39
128.15
127.77
127.20
126.39
123.92
73.04
61.12
45.97
21.40
13.94
CH3
O
N
S
O
O
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

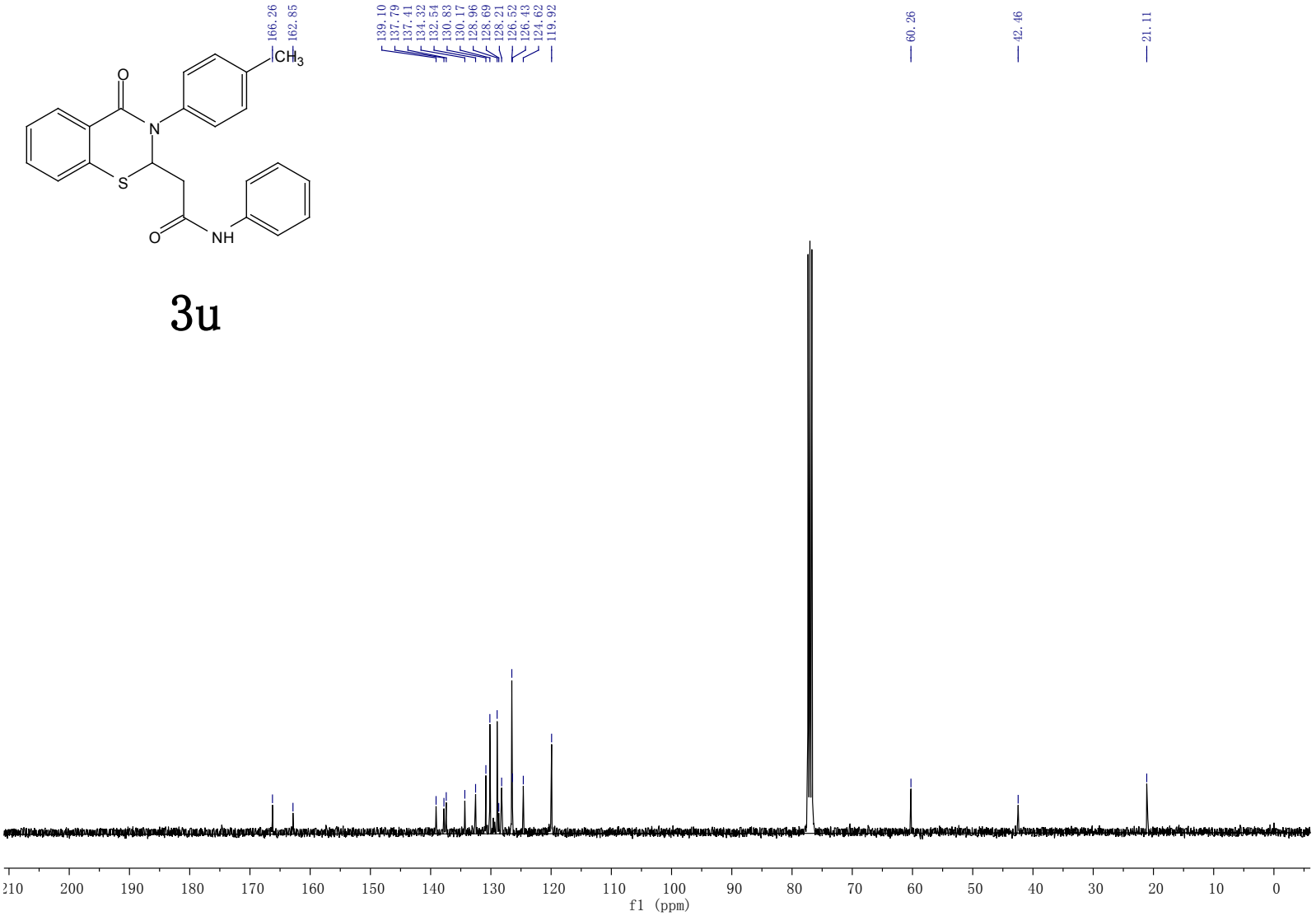
3s


8.20
8.18
7.46
7.45
7.44
7.42
7.35
7.34
7.33
7.32
7.31
7.29
7.23
5.36
5.35
5.34
5.33
3.40
3.38
3.36
3.33
3.09
3.08
3.05
3.04
2.37
2.05
CH3
O
N
S
O
CH3
3t
1.00
1.18
2.43
4.03
1.05
1.17
1.15
3.01
3.02
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 -0.5
f1 (ppm)

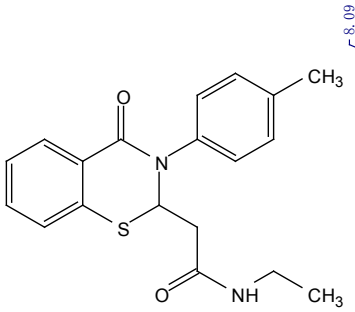

204.04
162.78
139.21
137.67
134.20
132.36
130.88
130.12
128.83
128.12
126.67
126.37
58.78
47.77
30.71
21.12
O
N
S
O
CH3
CH3
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.14
8.12
7.42
7.40
7.38
7.34
7.32
7.30
7.29
7.27
7.20
7.19
7.11
7.09
7.08
5.46
5.45
5.44
5.43
3.07
3.06
3.06
3.03
2.34
CH3
O
N
S
O
NH
0.99
4.18
4.13
3.37
1.47
1.08
2.11
3.00
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
-0.5
f1 (ppm)

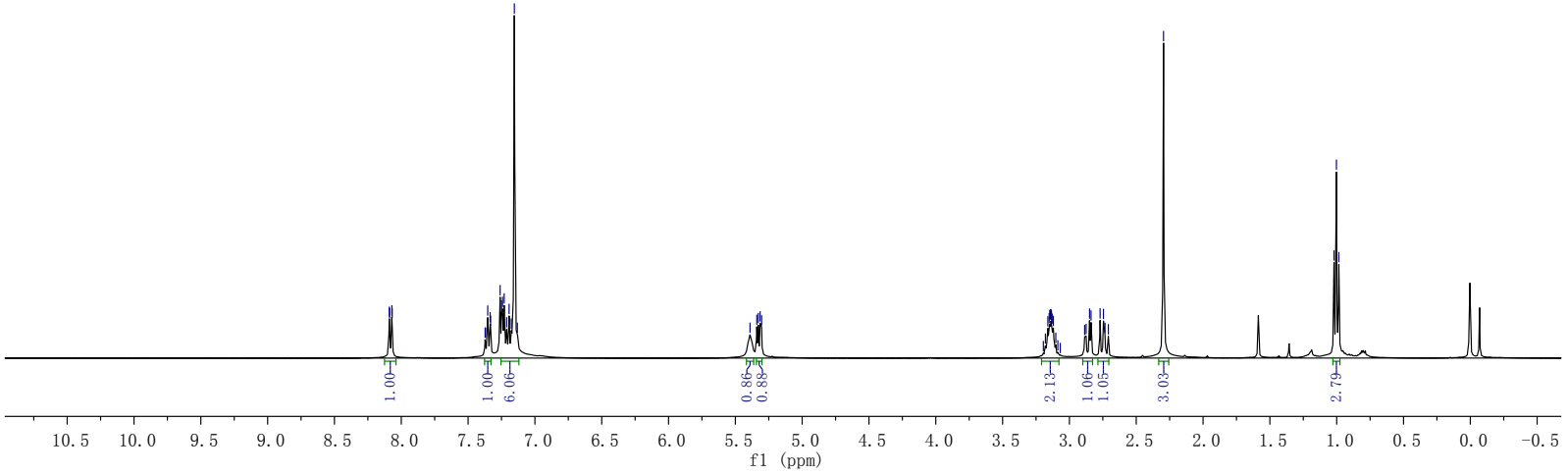
3u

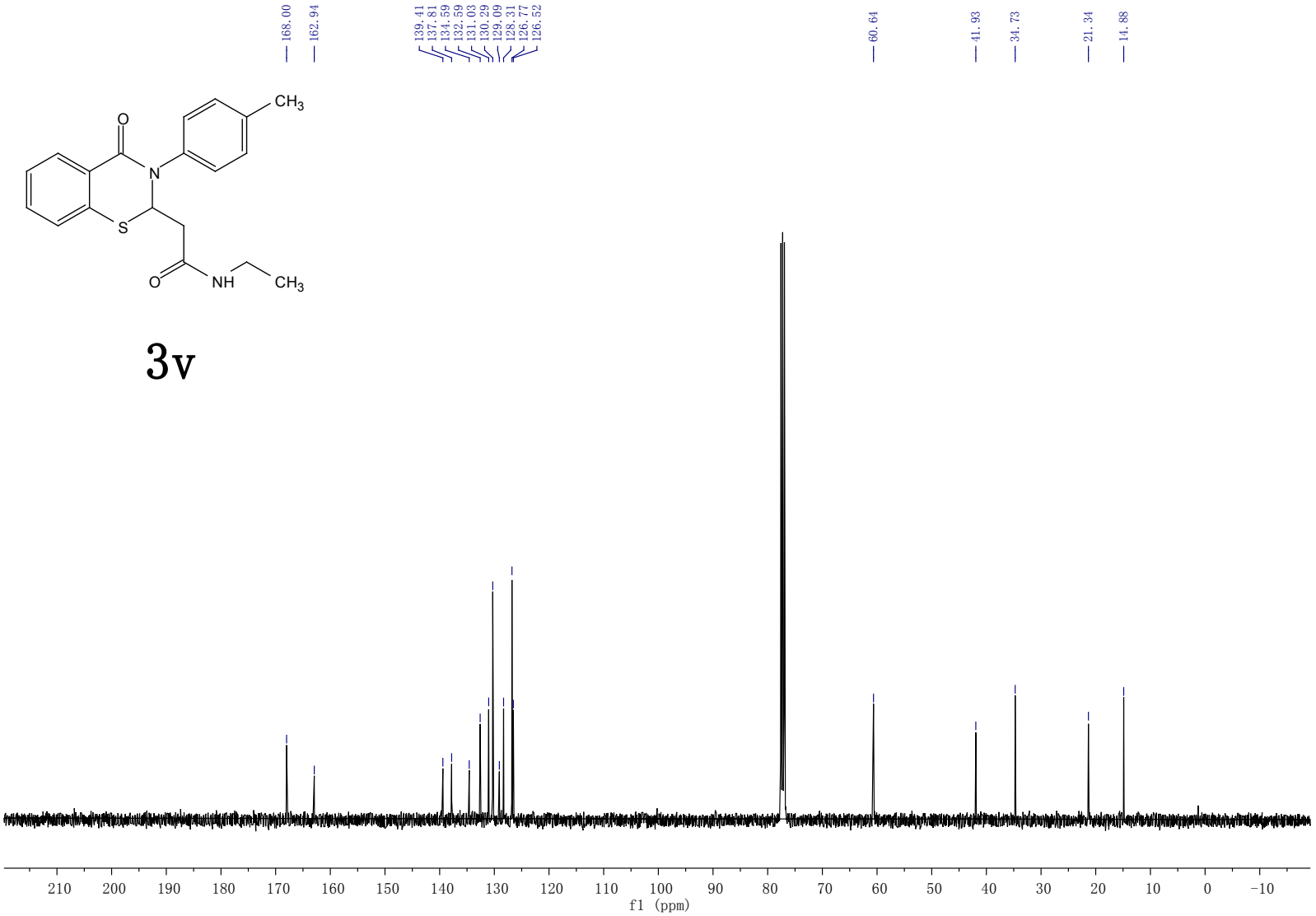

166.26
162.85
139.10
137.79
137.41
134.32
132.54
130.83
130.17
128.96
128.69
128.21
126.52
126.43
124.62
119.92
60.26
42.46
21.11
CH3
O
N
S
O
NH
f1 (ppm)

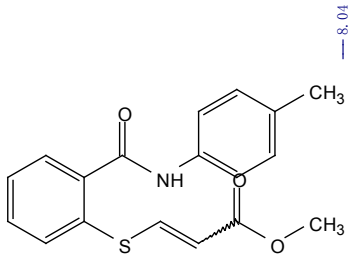
3u


O
N
S
CH3
O
NH
CH3

3v

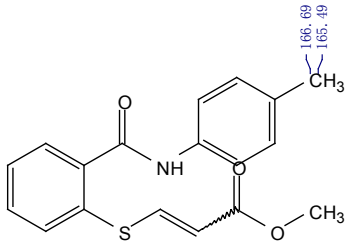

8.09
8.09
8.07
8.07
7.37
7.37
7.35
7.33
7.33
7.26
7.25
7.24
7.23
7.21
7.19
7.18
7.15
7.13
5.39
5.34
5.33
5.31
5.30
3.20
3.18
3.16
3.15
3.15
3.14
3.14
3.13
3.13
3.12
3.10
3.09
3.07
2.89
2.87
2.85
2.84
2.77
2.75
2.73
2.71
2.30
1.02
1.00
0.98
1.00
1.00
6.06
0.86
0.88
2.13
1.06
1.05
3.03
2.79
10.5 10.0 9.5 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 -0.5
f1 (ppm)


168.00
162.94
139.41
137.81
134.59
132.59
131.03
130.29
129.09
128.31
126.77
126.52
60.64
41.93
34.73
21.34
14.88
O
N
S
O
NH
CH3
CH3
3v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
NH
O
CH3
S
O
CH3

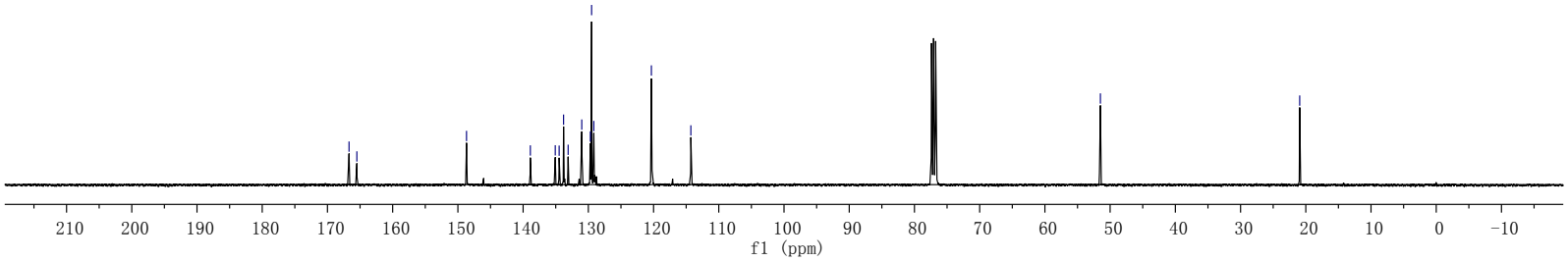
4a

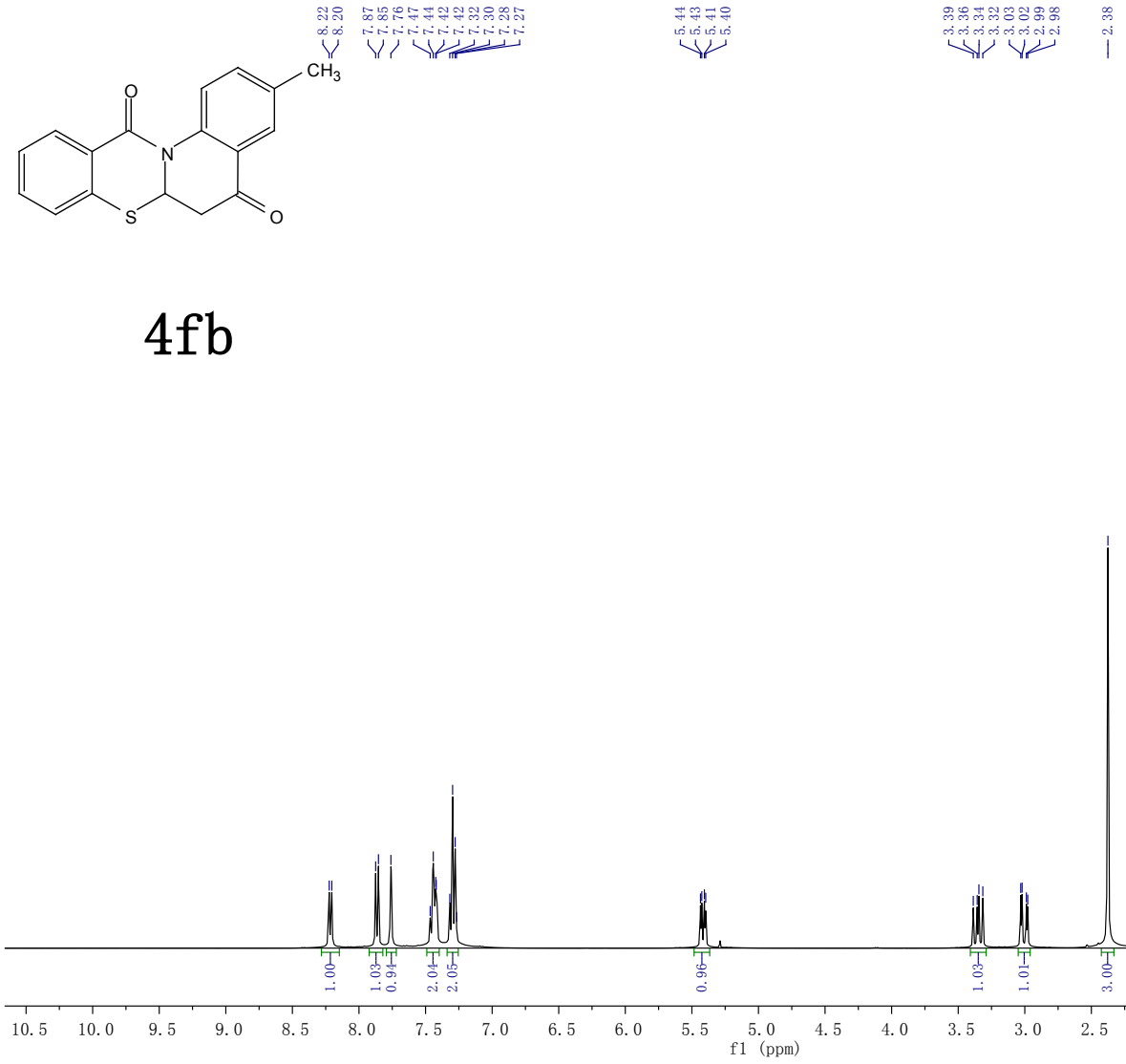
8.04
7.73
7.57
7.45
7.43
7.14
7.11
5.89
5.86
3.72
2.32
1.00
1.23
1.26
4.24
3.10
1.00
3.07
3.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


O
NH
O
CH3
S
O
CH3

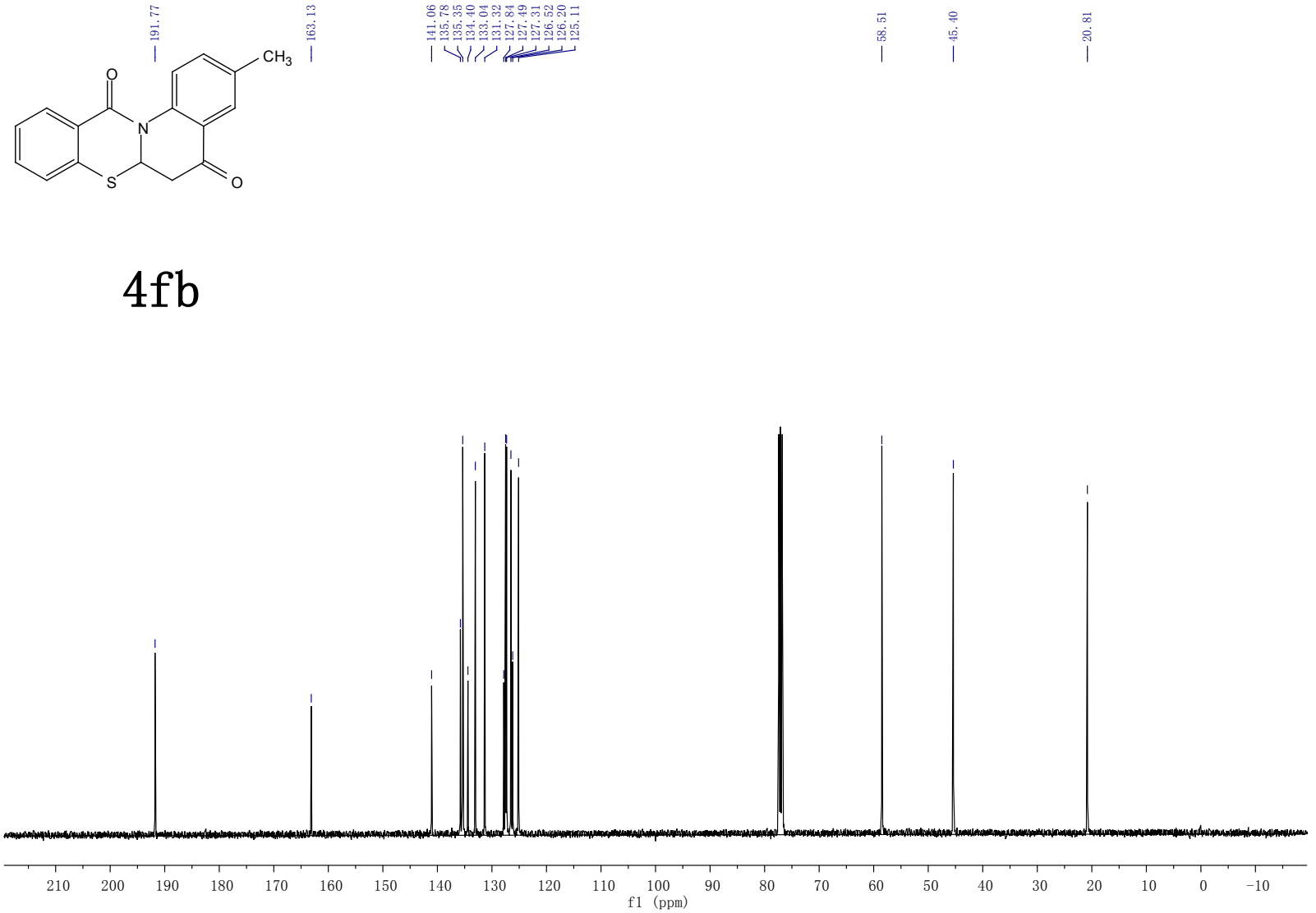
4a

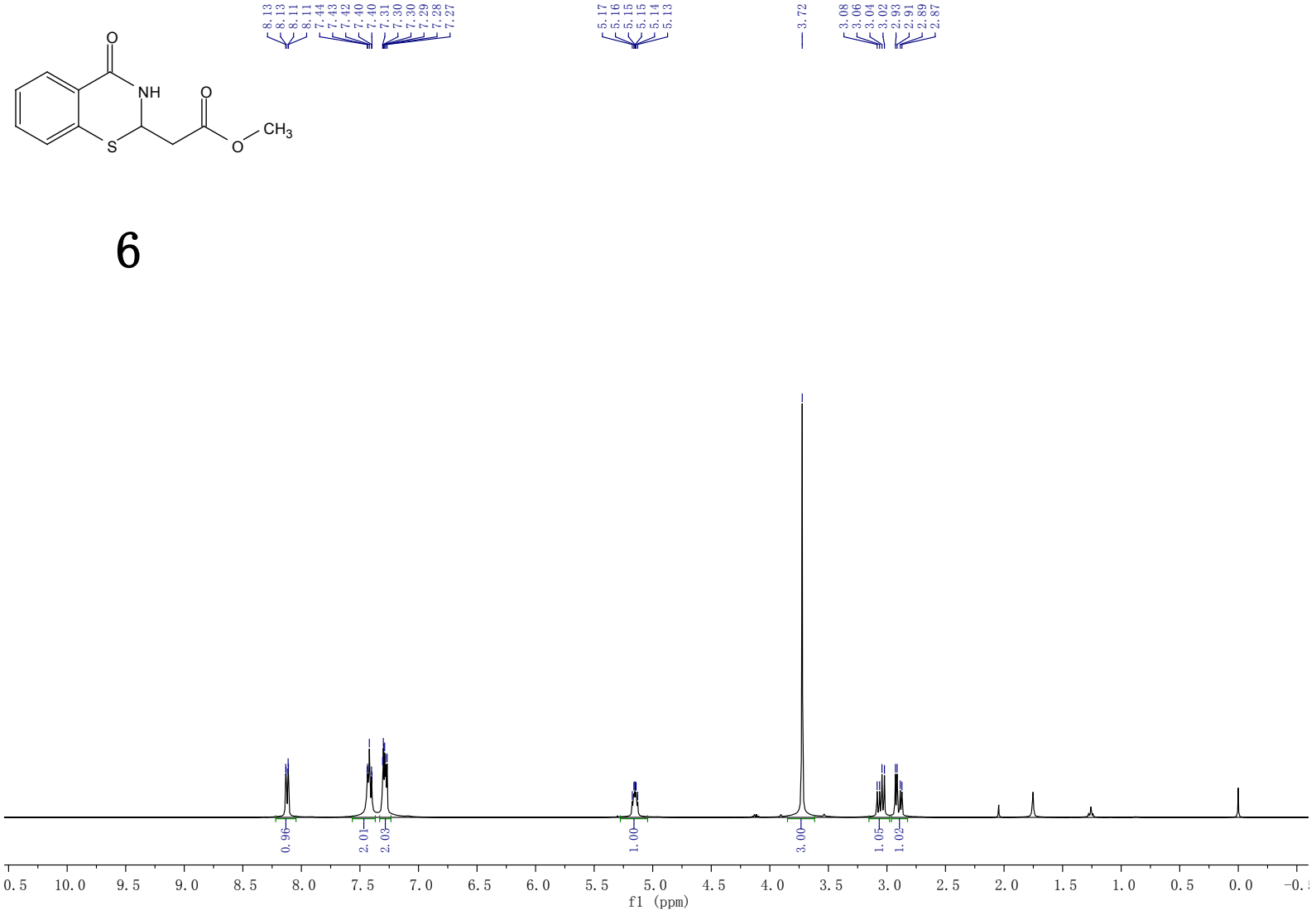

166.69
165.49
148.68
138.89
135.07
134.48
133.80
133.10
131.01
129.69
129.50
129.16
120.33
114.28
51.49
20.93


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

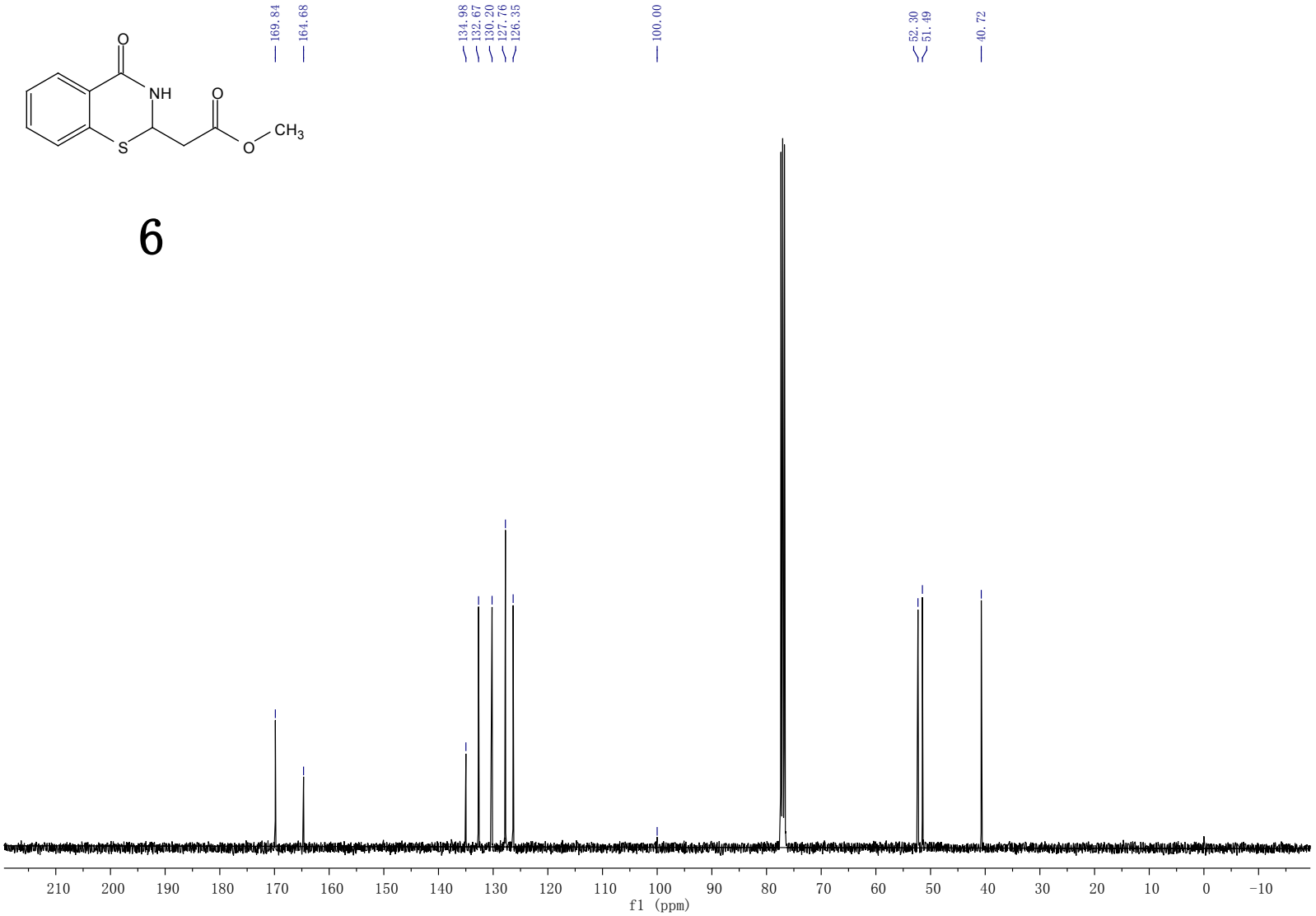

8.22
8.20
7.87
7.85
7.76
7.47
7.44
7.42
7.42
7.32
7.30
7.28
7.27
5.44
5.43
5.41
5.40
3.39
3.36
3.34
3.32
3.03
3.02
2.99
2.98
2.38
CH3
O
N
S
O
1.00
1.03
0.94
2.04
2.05
0.96
1.03
1.01
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

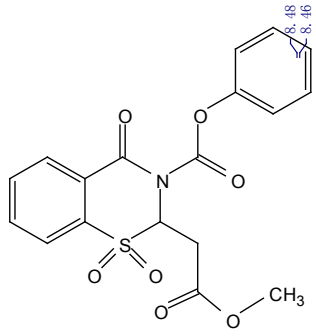
4fb


191.77
163.13
141.06
135.78
135.35
134.40
133.04
131.32
127.84
127.49
127.31
126.52
126.20
125.11
58.51
45.40
20.81
CH3
O
N
S
O
4fb
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.13
8.13
8.11
8.11
7.44
7.43
7.42
7.40
7.40
7.31
7.30
7.30
7.29
7.28
7.27
5.17
5.16
5.15
5.15
5.14
5.13
3.72
3.08
3.06
3.04
3.02
2.93
2.91
2.89
2.87
O
NH
O
CH3
S
O
0.96
2.01
2.03
1.00
3.00
1.05
1.02
f1 (ppm)

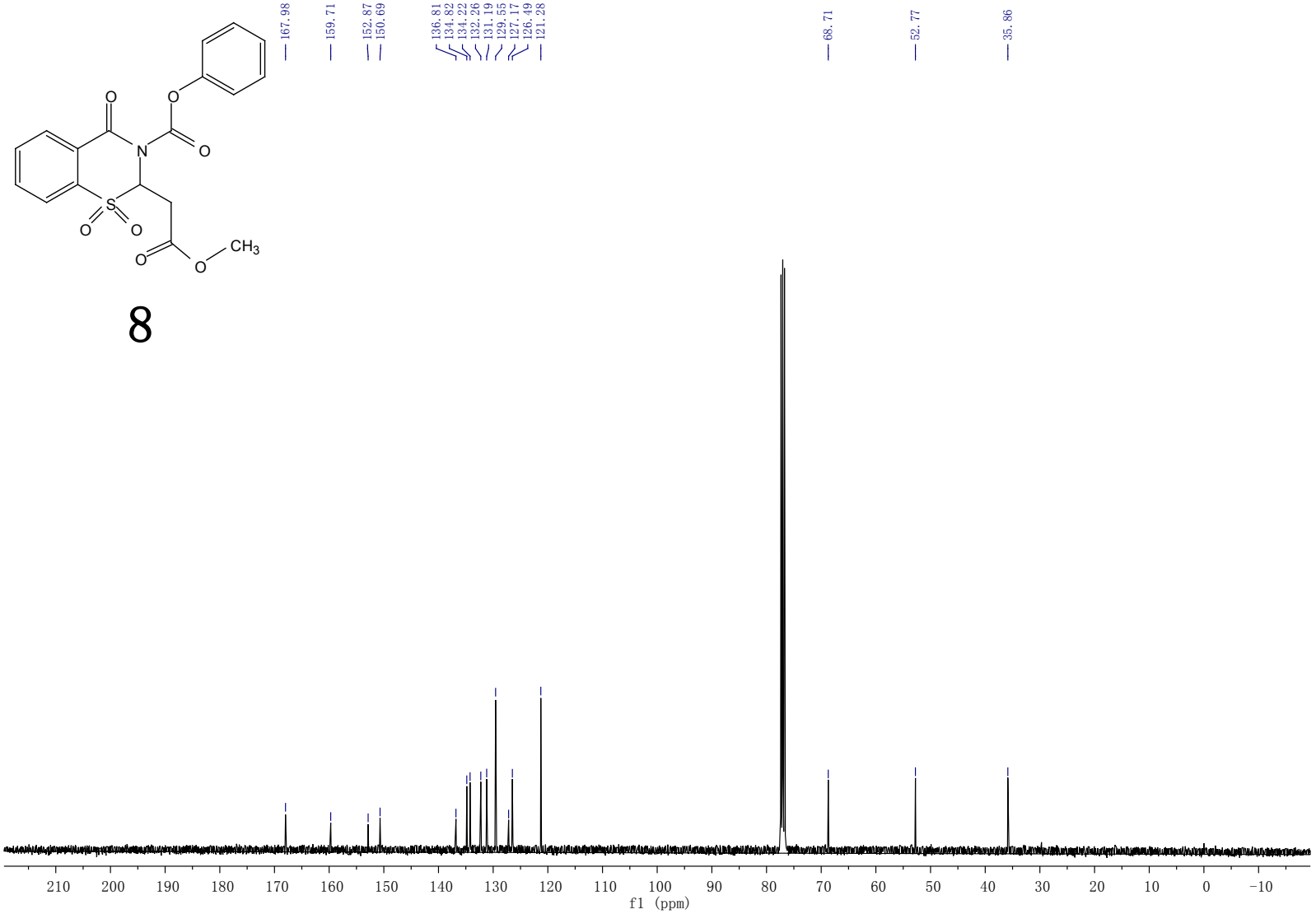
6


169.84
164.68
134.98
132.67
130.20
127.76
126.35
100.00
52.30
51.49
40.72
O
NH
O
S
O
CH3
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

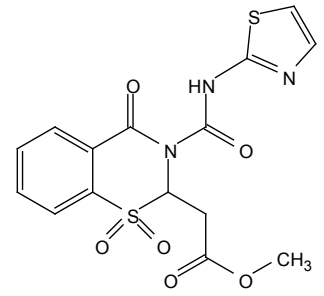

O
O
N
O
O
S
O
O
O
O
CH3

8

8.48
8.46
7.86
7.84
7.84
7.82
7.81
7.79
7.44
7.42
7.40
7.30
7.28
7.26
6.39
6.38
6.36
3.71
2.71
2.69
2.67
2.65
2.55
2.54
2.51
2.49
0.98
3.11
2.13
3.02
1.01
3.15
1.08
1.08
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
f1 (ppm)

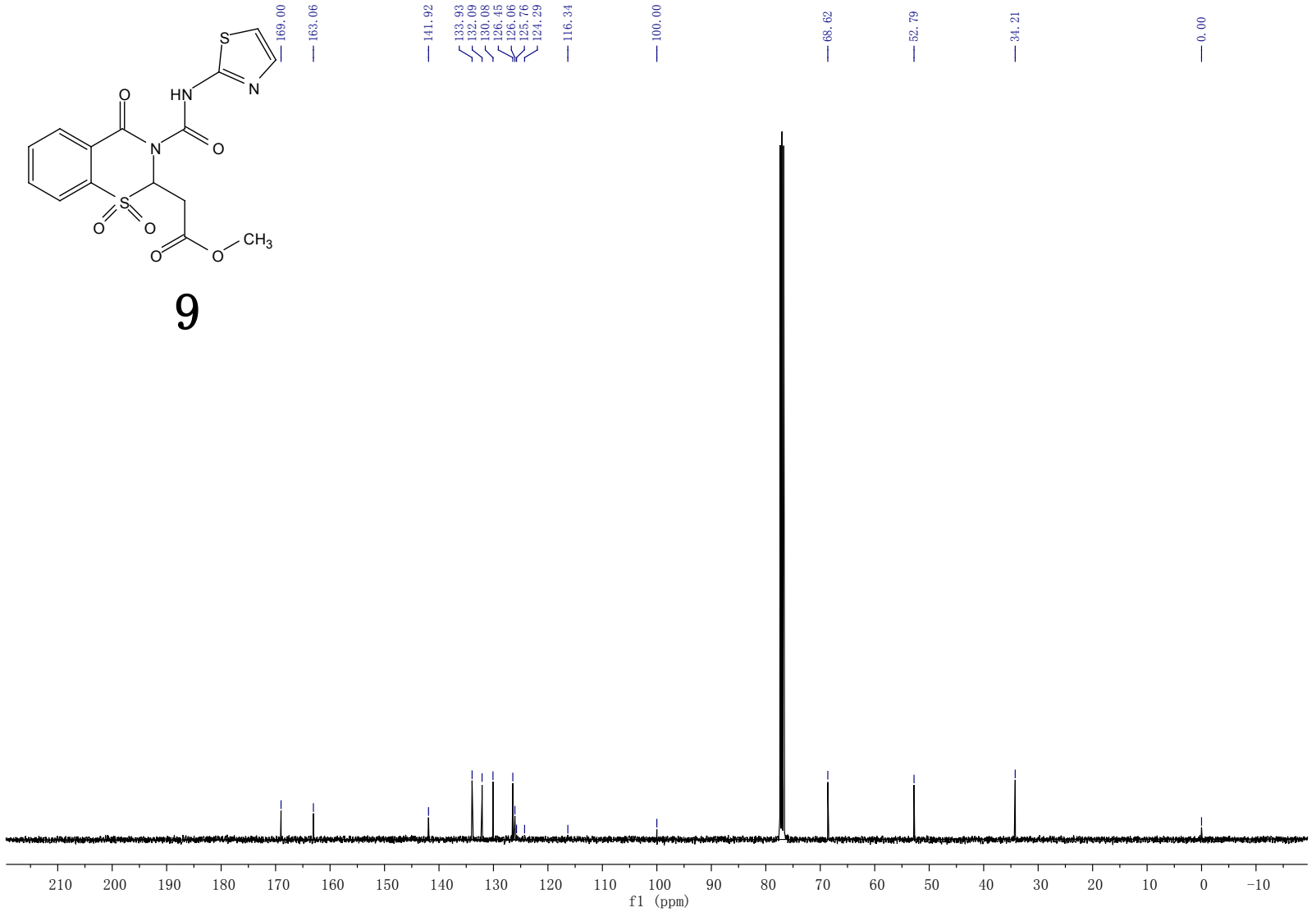

167.98
159.71
152.87
150.69
136.81
134.82
134.22
132.26
131.19
129.55
127.17
126.49
121.28
68.71
52.77
35.86
O
O
N
O
O
S
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

8


S
HN
N
O
N
O
S
O
O
O
O
CH3

9

8.16
8.14
7.85
7.83
7.79
7.78
7.76
7.70
7.69
7.67
6.57
5.03
5.02
5.01
5.01
5.00
4.99
3.18
3.17
3.14
3.13
2.84
2.81
2.80
2.77
1.18
4.80
1.00
1.19
3.20
1.12
1.22
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 -0.5
f1 (ppm)


169.00
163.06
141.92
133.93
132.09
130.08
126.45
126.06
125.76
124.29
116.34
100.00
68.62
52.79
34.21
0.00
S
HN
N
O
O
N
O
S
O
O
O
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

9