

Efficient construction of C–N and C–S bonds in 2-iminothiazoles via cascade reaction of enamines with potassium thiocyanate †

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Supporting Information

Table of Contents

General Information	3
Spectroscopic Data of 2-iminothiazoles 4	4
Spectroscopic Data of 5v	15
Figure 1. ¹ H NMR (400 MHz, CDCl ₃) spectra of compound 4a	16
Figure 2. ¹³ C NMR (100 MHz, CDCl ₃) spectra of compound 4a	17
Figure 3. ¹ H NMR (400 MHz, CDCl ₃) spectra of compound 4b	18
Figure 4. ¹³ C NMR (100 MHz, CDCl ₃) spectra of compound 4b	19
Figure 5. ¹ H NMR (400 MHz, CDCl ₃) spectra of compound 4c	20
Figure 6. ¹³ C NMR (100 MHz, CDCl ₃) spectra of compound 4c	21
Figure 7. ¹ H NMR (400 MHz, CDCl ₃) spectra of compound 4d	22
Figure 8. ¹³ C NMR (100 MHz, CDCl ₃) spectra of compound 4d	23
Figure 9. ¹ H NMR (400 MHz, CDCl ₃) spectra of compound 4e	24
Figure 10. ¹³ C NMR (100 MHz, CDCl ₃) spectra of compound 4e	25
Figure 11. ¹ H NMR (400 MHz, CDCl ₃) spectra of compound 4f	26
Figure 12. ¹³ C NMR (100 MHz, CDCl ₃) spectra of compound 4f	27
Figure 13. ¹ H NMR (400 MHz, CDCl ₃) spectra of compound 4g	28
Figure 14. ¹³ C NMR (100 MHz, CDCl ₃) spectra of compound 4g	29
Figure 15. ¹ H NMR (400 MHz, CDCl ₃) spectra of compound 4h	30
Figure 16. ¹³ C NMR (100 MHz, CDCl ₃) spectra of compound 4h	31
Figure 17. ¹ H NMR (400 MHz, CDCl ₃) spectra of compound 4i	32
Figure 18. ¹³ C NMR (100 MHz, CDCl ₃) spectra of compound 4i	33

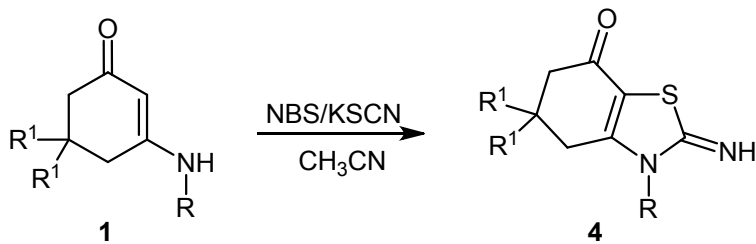
Figure 19.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4j	34
Figure 20.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4j	35
Figure 21.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4k	36
Figure 22.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4k	37
Figure 23.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4l	38
Figure 24.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4l	39
Figure 25.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4m	40
Figure 26.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4m	41
Figure 27.	^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of compound 4n	42
Figure 28.	^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) spectra of compound 4n	43
Figure 29.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4o	44
Figure 30.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4o	45
Figure 31.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4p	46
Figure 32.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4p	47
Figure 33.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4q	48
Figure 34.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4q	49
Figure 35.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4r	50
Figure 36.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4r	51
Figure 37.	^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of compound 4s	52
Figure 38.	^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) spectra of compound 4s	53
Figure 39.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4t	54
Figure 40.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4t	55
Figure 41.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4u	56
Figure 42.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4u	57
Figure 43.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4v	58
Figure 44.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4v	59
Figure 45.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4w	60
Figure 46.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4w	61
Figure 47.	^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of compound 4x	62
Figure 48.	^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) spectra of compound 4x	63
Figure 49.	^1H NMR (400 MHz, CDCl_3) spectra of compound 4y	64
Figure 50.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4y	65
Figure 51.	^1H NMR (400 MHz, CDCl_3) spectra of compound 5v	66
Figure 52.	^{13}C NMR (100 MHz, CDCl_3) spectra of compound 5v	67

General Information

All compounds were fully characterized by spectroscopic data. NMR spectra were recorded on a Bruker DRX500 (^1H : 500 MHz, ^{13}C : 125 MHz), Bruker AVIII-400 (^1H : 400 MHz, ^{13}C : 100 MHz) or Bruker AVIII-300 (^1H : 300 MHz, ^{13}C : 75 MHz). Chemical shifts (δ) are expressed in units of ppm, and J values are given in Hz. DMSO- d_6 or CDCl_3 were used as solvents. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. The melting points are uncorrected and were determined on a XT-4A melting point apparatus. HRMs were performed on an Agilent LC/MSD TOF instrument and a Monoisotopic Mass instrument. All chemicals and solvents were used as received without further purification unless otherwise stated.

All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh).

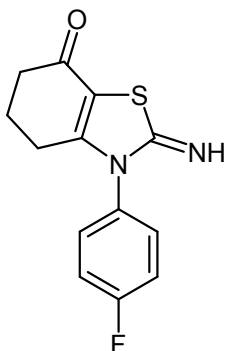
General Procedure for the Preparation of 2-iminothiazoles 4



A mixture of enaminones **1** (1.0 mmol), NBS **2** (2.0mmol) and CH_3CN (15 mL) was stirred at room temperature for 0.5 hours. Upon completion, monitored by TLC, KSCN **3** (1.0 mmol) was then added. After the desired product formation indicated by TLC, the reaction mixture was quenched with saturated NH_4Cl solution (2 mL) and extracted with ethyl acetate (20 mL). The organic phase were dried over Na_2SO_4 , and concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 1:1) giving a yellow solid **4**.

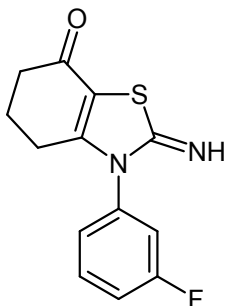
Spectroscopic Data of 2-iminothiazoles 4

3-(4-fluorophenyl)-2-imino-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4a)



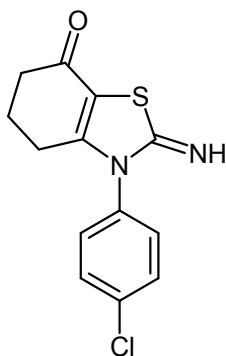
Yellow solid; Mp 122–123 °C; IR (KBr): 3283, 1640, 1509, 1358, 1219, 1191, 828 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.30–7.34 (m, 2H, ArH), 7.21–7.25 (m, 2H, ArH), 2.50–2.55 (m, 2H, CH₂), 2.33–2.37 (m, 2H, CH₂), 2.07–2.13 (m, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 189.0, 164.5, 162.8 (d, ¹J_{C-F} = 249.0 Hz), 153.8, 131.0, 130.4 (d, ³J_{C-F} = 9.0 Hz), 130.3 (d, ³J_{C-F} = 9.0 Hz), 117.3 (d, ²J_{C-F} = 23.0 Hz), 117.1 (d, ²J_{C-F} = 23.0 Hz), 111.5, 36.9, 24.9, 21.9; HRMS (ESI-TOF): *m/z* calcd for C₁₃H₁₂FN₂OS [(M+H)⁺], 263.0649; found, 263.0667.

3-(3-fluorophenyl)-2-imino-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4b)



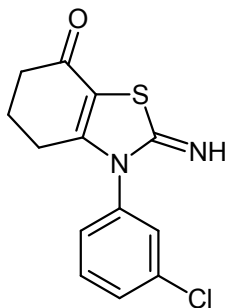
Yellow solid; Mp 102–104 °C; IR (KBr): 3281, 1654, 1489, 1402, 1308, 1171, 925 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.51–7.55 (m, 1H, ArH), 7.19–7.24 (m, 1H, ArH), 7.08–7.15 (m, 2H, ArH), 2.52–2.55 (m, 2H, CH₂), 2.37–2.40 (m, 2H, CH₂), 2.08–2.12 (m, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 189.1, 163.1 (d, ¹J_{C-F} = 249.0 Hz), 164.1, 153.5, 136.3, 131.3 (d, ³J_{C-F} = 9.0 Hz), 124.3, 116.9 (d, ²J_{C-F} = 19.0 Hz), 116.1 (d, ²J_{C-F} = 23.0 Hz), 111.7, 36.9, 24.9, 21.9; HRMS (ESI-TOF): *m/z* calcd for C₁₃H₁₂FN₂OS [(M+H)⁺], 263.0649; found, 263.0650.

3-(4-chlorophenyl)-2-imino-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4c)



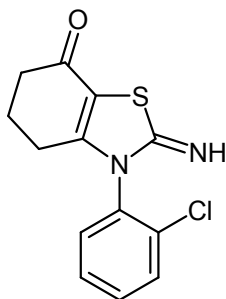
Yellow solid; Mp 130–132 °C; IR (KBr): 3291, 1640, 1494, 1357, 1191, 1090, 813 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.51–7.54 (m, 2H, ArH), 7.27–7.30 (m, 2H, ArH), 2.52–2.55 (m, 2H, CH₂), 2.34–2.38 (m, 2H, CH₂), 2.11–2.14 (m, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 189.0, 164.2, 153.4, 135.7, 133.5, 130.4, 129.8, 111.7, 36.9, 24.9, 21.9; HRMS (ESI-TOF): *m/z* calcd for C₁₃H₁₂ClN₂OS [(M+H)⁺], 279.0353; found, 279.0352.

3-(3-chlorophenyl)-2-imino-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4d)



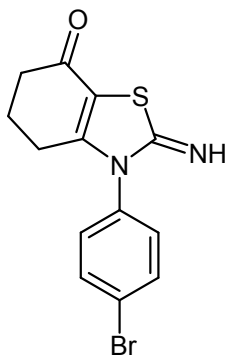
Yellow solid; Mp 108–109 °C; IR (KBr): 3329, 1639, 1574, 1406, 1358, 1046, 797 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.47–7.50 (m, 2H, ArH), 7.35 (s, 1H, ArH), 7.23–7.26 (m, 1H, ArH), 2.52–2.56 (m, 2H, CH₂), 2.36–2.39 (m, 2H, CH₂), 2.09–2.13 (m, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 189.0, 164.1, 153.3, 136.2, 135.6, 131.0, 130.0, 128.8, 126.8, 111.8, 36.9, 24.9, 22.0; HRMS (ESI-TOF): *m/z* calcd for C₁₃H₁₂ClN₂OS [(M+H)⁺], 279.0353; found, 279.0353.

3-(2-chlorophenyl)-2-imino-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4e)



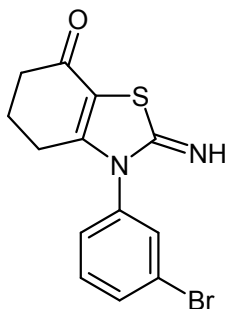
Yellow solid; Mp 116–118 °C; IR (KBr): 3216, 1657, 1597, 1522, 1402, 1076, 760 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.61 (d, J = 8.0 Hz, 1H, ArH), 7.45–7.49 (m, 2H, ArH), 7.42 (d, J = 8.0 Hz, 1H, ArH), 2.53–2.56 (m, 2H, CH_2), 2.29–2.32 (m, 2H, CH_2), 2.09–2.13 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 189.1, 163.5, 153.7, 133.3, 132.8, 131.4, 131.0, 130.8, 128.6, 111.8, 36.9, 24.3, 21.9; HRMS (ESI-TOF): m/z calcd for $\text{C}_{13}\text{H}_{12}\text{ClN}_2\text{OS}$ [(M+H) $^+$], 279.0353; found, 279.0352.

3-(4-bromophenyl)-2-imino-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4f)



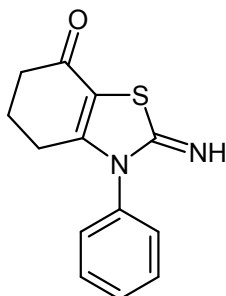
Yellow solid; Mp 129–131 °C; IR (KBr): 3283, 1644, 1489, 1409, 1189, 1070, 837 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.67 (d, J = 8.0 Hz, 2H, ArH), 7.22 (t, J = 4.0 Hz, 2H, ArH), 2.52–2.55 (m, 2H, CH_2), 2.35–2.38 (m, 2H, CH_2), 2.09–2.12 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 189.0, 164.2, 153.3, 134.1, 133.3, 130.1, 123.8, 111.7, 36.9, 24.9, 21.9; HRMS (ESI-TOF): m/z calcd for $\text{C}_{13}\text{H}_{12}\text{BrN}_2\text{OS}$ [(M+H) $^+$], 322.9848; found, 322.9848.

3-(3-bromophenyl)-2-imino-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4g)



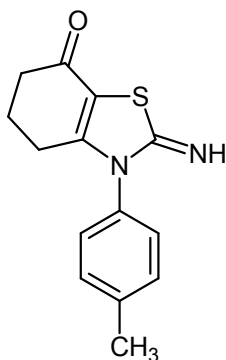
Yellow solid; Mp 182–184 °C; IR (KBr): 3293, 1634, 1579, 1401, 1361, 1192, 801 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.62–7.65 (m, 1H, ArH), 7.50 (s, 1H, ArH), 7.41–7.45 (m, 1H, ArH), 7.27–7.30 (m, 1H, ArH), 2.52–2.56 (m, 2H, CH_2), 2.35–2.38 (m, 2H, CH_2), 2.08–2.12 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 189.0, 164.1, 153.3, 136.3, 132.9, 131.6, 131.3, 127.2, 123.4, 111.8, 36.9, 25.0, 22.0; HRMS (ESI-TOF): m/z calcd for $\text{C}_{13}\text{H}_{12}\text{BrN}_2\text{OS}$ [(M+H) $^+$], 322.9848; found, 322.9846.

2-imino-3-phenyl-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4h)



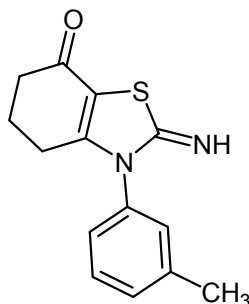
Yellow solid; Mp 129–130 °C; IR (KBr): 3322, 1641, 1609, 1417, 1359, 1058, 744 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.50–7.58 (m, 3H, ArH), 7.32 (d, J = 8.0 Hz, 2H, ArH), 2.52–2.55 (m, 2H, CH_2), 2.34–2.37 (m, 2H, CH_2), 2.08–2.11 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 189.1, 164.7, 154.0, 134.9, 130.2, 129.8, 128.3, 111.3, 36.9, 25.0, 22.0; HRMS (ESI-TOF): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{N}_2\text{OS}$ [(M+H) $^+$], 245.0743; found, 245.0742.

2-imino-3-(p-tolyl)-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4i)



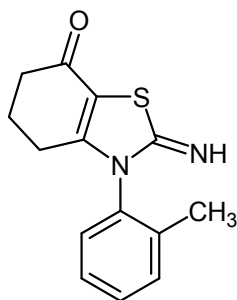
White solid; Mp 148–149 °C; IR (KBr): 3285, 1620, 1568, 1416, 1358, 1068, 814 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.34 (d, J = 8.0 Hz, 2H, ArH), 7.19 (d, J = 8.0 Hz, 2H, ArH), 2.50–2.53 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.34–2.37 (m, 2H, CH_2), 2.07–2.10 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 189.1, 164.8, 154.3, 140.0, 132.2, 130.8, 128.0, 111.1, 36.9, 24.9, 21.9, 21.3; HRMS (ESI-TOF): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{OS}$ [(M+H) $^+$], 259.0900; found, 259.0899.

2-imino-3-(*m*-tolyl)-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4j)



Light yellow solid; Mp 154–156 °C; IR (KBr): 3196, 1596, 1408, 1361, 1312, 1195, 1009 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.43 (t, J = 8.0 Hz, 1H, ArH), 7.30 (d, J = 8.0 Hz, 1H, ArH), 7.09–7.13 (m, 2H, ArH), 2.51–2.54 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.34–2.37 (m, 2H, CH_2), 2.07–2.11 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 189.1, 164.8, 154.2, 140.4, 134.8, 130.6, 130.0, 128.8, 125.3, 111.1, 36.9, 25.0, 22.0, 21.4; HRMS (ESI-TOF): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{OS}$ [(M+H) $^+$], 259.0900; found, 259.0900.

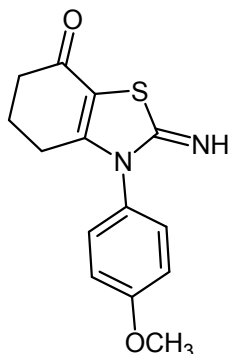
2-imino-3-(*o*-tolyl)-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4k)



Yellow oily liquid; IR (KBr): 3245, 1647, 1594, 1404, 1354, 1196, 1003 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.34–7.42 (m, 3H, ArH), 7.21 (d, J = 8.0 Hz, 1H, ArH), 2.52–2.56 (m, 2H, CH_2), 2.22 (m, 3H, CH_3), 2.17–2.21 (m, 1H, CH_2), 2.04–2.11 (m, 3H, CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.8, 164.1, 154.0, 136.7, 133.8, 131.8, 130.3, 128.7, 127.8, 111.5, 36.9, 24.5, 22.0, 17.4; HRMS (ESI-TOF): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{OS}$

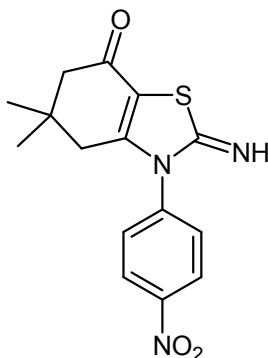
[(M+H)⁺], 259.0900; found, 259.0900.

2-imino-3-(4-methoxyphenyl)-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4l)



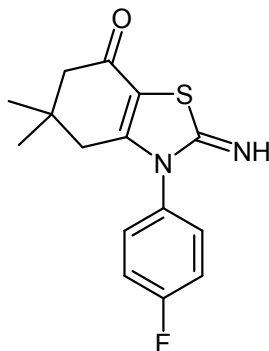
Yellow solid; Mp 146–148 °C; IR (KBr): 3257, 1639, 1512, 1361, 1246, 1075, 1008 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.70 (br, 1H, C=NH), 7.31 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.06 (d, *J* = 8.8 Hz, 2H, Ar*H*), 3.80 (s, 3H, OCH₃), 2.39 (t, *J* = 6.0 Hz, 2H, CH₂), 2.31 (t, *J* = 6.0 Hz, 2H, CH₂), 1.93–1.99 (m, 2H, CH₂); ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 188.9, 161.3, 159.8, 156.1, 130.3, 128.4, 115.1, 109.2, 55.9, 36.9, 24.9, 21.9; HRMS (ESI-TOF): *m/z* calcd for C₁₄H₁₅N₂O₂S [(M+H)⁺], 275.0849; found, 275.0842.

2-imino-5,5-dimethyl-3-(4-nitrophenyl)-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4m)



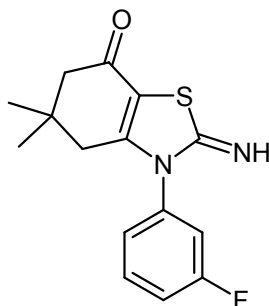
Yellow solid; Mp 142–143 °C; IR (KBr): 3289, 1638, 1520, 1404, 1342, 1042, 738 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.41 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.55 (t, *J* = 4.0 Hz, 2H, Ar*H*), 2.43 (s, 2H, CH₂), 2.26 (s, 2H, CH₂), 1.12 (s, 6H, 2 × CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 188.5, 163.6, 150.7, 147.9, 140.8, 129.7, 111.4, 50.9, 38.8, 34.7, 28.4; HRMS (ESI-TOF): *m/z* calcd for C₁₅H₁₆N₃O₃S [(M+H)⁺], 318.0907; found, 318.0908.

3-(4-fluorophenyl)-2-imino-5,5-dimethyl-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4n)



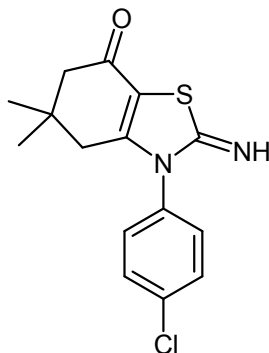
Yellow solid; Mp 148–149 °C; IR (KBr): 3218, 1648, 1510, 1351, 1226, 1157, 1048 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.29–7.33 (m, 2H, ArH), 7.23–7.27 (m, 2H, ArH), 2.41 (s, 2H, CH_2), 2.21 (s, 2H, CH_2), 1.10 (s, 6H, $2 \times \text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.6, 164.7, 162.8 (d, $^1J_{\text{C-F}} = 249.0$ Hz), 130.9 (d, $^3J_{\text{C-F}} = 3.0$ Hz), 130.4, 130.3, 117.4 (d, $^2J_{\text{C-F}} = 22.0$ Hz), 117.2 (d, $^2J_{\text{C-F}} = 22.0$ Hz), 110.1, 50.9, 38.6, 34.4, 28.4; HRMS (ESI-TOF): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{FN}_2\text{OS}$ [(M+H) $^+$], 291.0962; found, 291.0962.

3-(3-fluorophenyl)-2-imino-5,5-dimethyl-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4o)



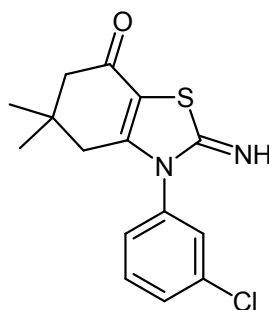
Yellow solid; Mp 180–182 °C; IR (KBr): 3296, 1612, 1492, 1361, 1225, 1045, 740 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.56 (t, $J = 8.0$ Hz, 1H, ArH), 7.22 (t, $J = 8.0$ Hz, 2H, ArH), 7.12 (AB, $J = 8.0$ Hz, 1H, ArH), 7.07 (AB, $J = 8.0$ Hz, 1H, ArH), 2.41 (s, 2H, CH_2), 2.23 (s, 2H, CH_2), 1.11 (s, 6H, $2 \times \text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.6, 164.3, 163.0 (d, $^1J_{\text{C-F}} = 236.0$ Hz), 151.8, 136.3, 131.3 (d, $^3J_{\text{C-F}} = 9.0$ Hz), 124.3, 117.9 (d, $^2J_{\text{C-F}} = 19.0$ Hz), 116.2 (d, $^2J_{\text{C-F}} = 23.0$ Hz), 110.3, 50.9, 38.6, 34.5, 28.4; HRMS (ESI-TOF): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{FN}_2\text{OS}$ [(M+H) $^+$], 291.0962; found, 291.0962.

3-(4-chlorophenyl)-2-imino-5,5-dimethyl-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4p)



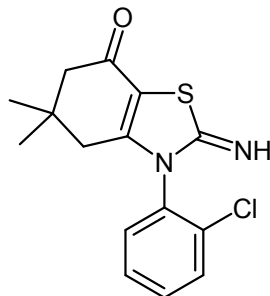
Yellow solid; Mp 129–130 °C; IR (KBr): 3283, 1646, 1491, 1351, 1322, 1089, 1018 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.53 (d, J = 8.0 Hz, 2H, ArH), 7.26 (d, J = 8.4 Hz, 2H, ArH), 2.41 (s, 2H, CH_2), 2.21 (s, 2H, CH_2), 1.10 (s, 6H, 2 \times CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.6, 164.5, 151.9, 135.7, 133.5, 130.4, 129.8, 110.3, 50.9, 38.7, 34.5, 28.4; HRMS (ESI-TOF): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{ClN}_2\text{OS}$ [(M+H) $^+$], 307.0666; found, 307.0665.

3-(3-chlorophenyl)-2-imino-5,5-dimethyl-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4q)



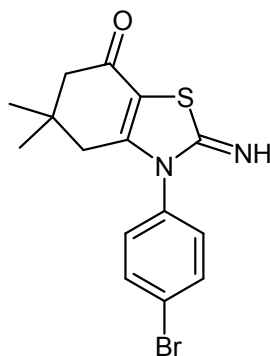
Yellow solid; Mp 98–99 °C; IR (KBr): 3252, 1649, 1480, 1411, 1361, 1044, 864 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.47–7.51 (m, 2H, ArH), 7.34 (s, 1H, ArH), 7.21–7.24 (m, 1H, ArH), 2.39 (s, 2H, CH_2), 2.23 (s, 2H, CH_2), 1.10 (s, 6H, 2 \times CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.5, 164.1, 151.8, 135.5, 135.4, 131.1, 129.9, 128.8, 126.8, 110.3, 50.9, 38.6, 34.5, 28.4; HRMS (ESI-TOF): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{ClN}_2\text{OS}$ [(M+H) $^+$], 307.0666; found, 307.0665.

3-(2-chlorophenyl)-2-imino-5,5-dimethyl-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4r)



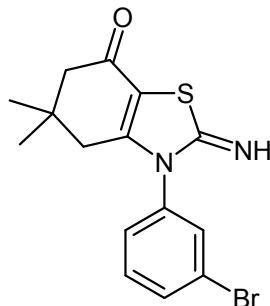
Yellow brown solid; Mp 138–140 °C; IR (KBr): 3311, 1643, 1590, 1410, 1351, 1039, 749 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.60–7.63 (m, 1H, ArH), 7.46–7.50 (m, 2H, ArH), 7.38–7.41 (m, 1H, ArH), 2.37–2.42 (m, 2H, CH_2), 2.06–2.11 (m, 2H, CH_2), 1.11 (s, 3H, CH_3), 1.08 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.6, 163.5, 152.3, 133.2, 132.8, 131.5, 131.0, 130.9, 128.6, 110.3, 51.0, 38.0, 34.4, 28.9, 27.9; HRMS (ESI-TOF): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{ClN}_2\text{OS}$ [(M+H) $^+$], 307.0666; found, 307.0667.

3-(4-bromophenyl)-2-imino-5,5-dimethyl-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4s)



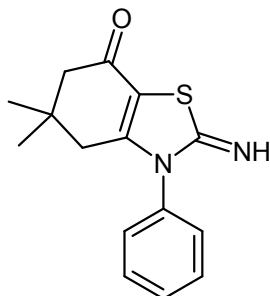
Yellow solid; Mp 115–117 °C; IR (KBr): 3208, 1649, 1602, 1512, 1255, 1048, 848 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.77 (d, J = 8.4 Hz, 2H, ArH), 7.41 (d, J = 8.4 Hz, 2H, ArH), 2.34 (s, 2H, CH_2), 2.28 (s, 2H, CH_2), 1.11 (s, 6H, $2 \times \text{CH}_3$); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 188.8, 162.5, 153.4, 134.7, 133.2, 133.0, 131.3, 123.1, 109.6, 50.8, 39.4, 34.6, 28.2; HRMS (ESI-TOF): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{BrN}_2\text{OS}$ [(M+H) $^+$], 351.0161; found, 351.0161.

3-(3-bromophenyl)-2-imino-5,5-dimethyl-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4t)



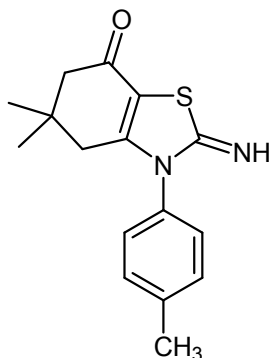
Yellow solid; Mp 103–104 °C; IR (KBr): 3259, 1614, 1572, 1479, 1361, 1043, 689 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.63–7.66 (m, 1H, ArH), 7.42–7.48 (m, 2H, ArH), 7.25–7.28 (m, 1H, ArH), 2.41 (s, 2H, CH_2), 2.21 (s, 2H, CH_2), 1.11 (s, 6H, 2 \times CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.6, 164.4, 151.7, 136.3, 132.9, 131.6, 131.3, 127.3, 123.4, 110.5, 50.9, 38.7, 34.5, 28.4; HRMS (ESI-TOF): m/z calcd for $\text{C}_{15}\text{H}_{16}\text{BrN}_2\text{OS}$ [(M+H) $^+$], 351.0161; found, 351.0159.

2-imino-5,5-dimethyl-3-phenyl-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4u)



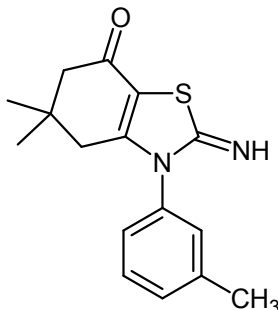
Light yellow solid; Mp 142–144 °C; IR (KBr): 3281, 1646, 1573, 1359, 1320, 1044, 740 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.53–7.57 (m, 2H, ArH), 7.48–7.50 (m, 1H, ArH), 7.31 (d, J = 8.0 Hz, 2H, ArH), 2.38 (s, 2H, CH_2), 2.23 (s, 2H, CH_2), 1.11 (s, 6H, 2 \times CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.4, 164.3, 152.5, 134.8, 130.1, 129.5, 128.4, 109.6, 50.8, 38.5, 34.3, 28.3; HRMS (ESI-TOF): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{OS}$ [(M+H) $^+$], 273.1056; found, 273.1056.

2-imino-5,5-dimethyl-3-(*p*-tolyl)-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4v)



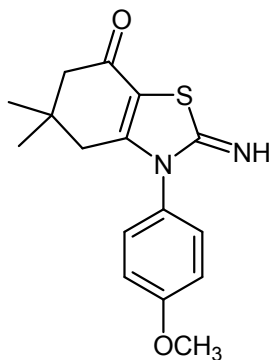
Yellow solid; Mp 147–149 °C; IR (KBr): 3298, 1648, 1511, 1410, 1349, 1047, 740 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.28 (d, J = 8.0 Hz, 2H, ArH), 7.09 (d, J = 8.0 Hz, 2H, ArH), 2.35 (s, 3H, CH_3), 2.32 (s, 2H, CH_2), 2.14 (s, 2H, CH_2), 1.01 (s, 6H, $2 \times \text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.7, 165.1, 152.6, 140.0, 132.2, 130.9, 128.1, 109.7, 51.0, 38.7, 34.4, 28.4, 21.3; HRMS (ESI-TOF): m/z calcd for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{OS}$ [(M+H) $^+$], 287.1213; found, 287.1213.

2-imino-5,5-dimethyl-3-(*m*-tolyl)-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4w)



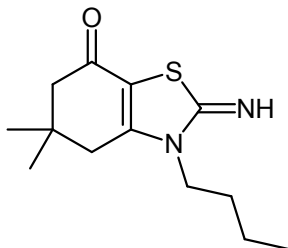
Yellow solid; Mp 99–100 °C; IR (KBr): 3120, 1640, 1614, 1399, 1248, 1150, 1046 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.42 (t, J = 8.0 Hz, 1H, ArH), 7.30 (t, J = 8.0 Hz, 1H, ArH), 7.06–7.10 (m, 2H, ArH), 2.43 (s, 3H, CH_3), 2.40 (s, 2H, CH_2), 2.20 (s, 2H, CH_2), 1.19 (s, 6H, $2 \times \text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.6, 165.1, 152.5, 140.5, 134.9, 130.6, 130.0, 128.8, 125.3, 109.9, 51.0, 38.7, 34.5, 28.4, 21.4; HRMS (ESI-TOF): m/z calcd for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{OS}$ [(M+H) $^+$], 287.1213; found, 287.1212.

2-imino-3-(4-methoxyphenyl)-5,5-dimethyl-2,3,5,6-tetrahydrobenzo[*d*]thiazol-7(4*H*)-one (4x)



Yellow solid; Mp 98–100 °C; IR (KBr): 3219, 1637, 1511, 1351, 1248, 1169, 1026 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ = 7.29–7.33 (m, 2H, ArH), 7.08–7.12 (m, 2H, ArH), 3.84 (s, 3H, OCH_3), 2.34 (s, 2H, CH_2), 2.26 (s, 2H, CH_2), 1.02 (s, 6H, $2 \times \text{CH}_3$); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ = 187.4, 160.7, 158.9, 153.2, 129.4, 127.4, 114.3, 107.0, 55.0, 49.9, 37.5, 33.4, 27.3; HRMS (ESI-TOF): m/z calcd for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$ [(M+H) $^+$], 303.1162; found, 303.1177.

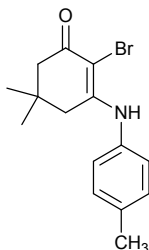
3-butyl-2-imino-5,5-dimethyl-2,3,5,6-tetrahydrobenzo[d]thiazol-7(4H)-one (4y)



Oily liquid; IR (KBr): 2959, 1644, 1591, 1351, 1032, 924, 577 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 3.76 (t, J = 8.0 Hz, 2H, CH_2), 2.51 (s, 2H, CH_2), 2.38 (s, 2H, CH_2), 1.64–1.68 (m, 2H, CH_2), 1.35–1.41 (m, 2H, CH_2), 1.15 (s, 6H, $2 \times \text{CH}_3$), 0.96 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 188.0, 163.7, 152.8, 108.9, 50.7, 43.8, 37.9, 34.4, 30.3, 28.6, 20.1, 13.8; HRMS (ESI-TOF): m/z calcd for $\text{C}_{13}\text{H}_{21}\text{N}_2\text{OS}$ [(M+H) $^+$], 253.1369; found, 253.1361.

Spectroscopic Data of α -bromo enaminone 5

2-bromo-5,5-dimethyl-3-(*p*-tolylamino)cyclohex-2-enone (5)



White solid; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ = 7.28 (s, 1H, CH), 7.20–7.23 (m, 2H, ArH), 7.02–7.04 (m, 2H, ArH), 2.42 (s, 2H, CH_2), 2.38 (s, 5H, CH_2+CH_3), 2.26 (s, 2H, CH_2), 1.03 (s, 6H, $2 \times \text{CH}_3$); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ = 188.0, 157.8, 137.1, 134.7, 130.1, 125.9, 96.3, 50.8, 41.1, 32.7, 28.0, 21.0; HRMS (ESI-TOF): m/z calcd for $\text{C}_{16}\text{H}_{18}\text{BrNNaO}$ [(M+H) $^+$], 330.0464; found, 330.0479.

¹H NMR and ¹³C NMR Spectra for 2-iminothiazoles 4

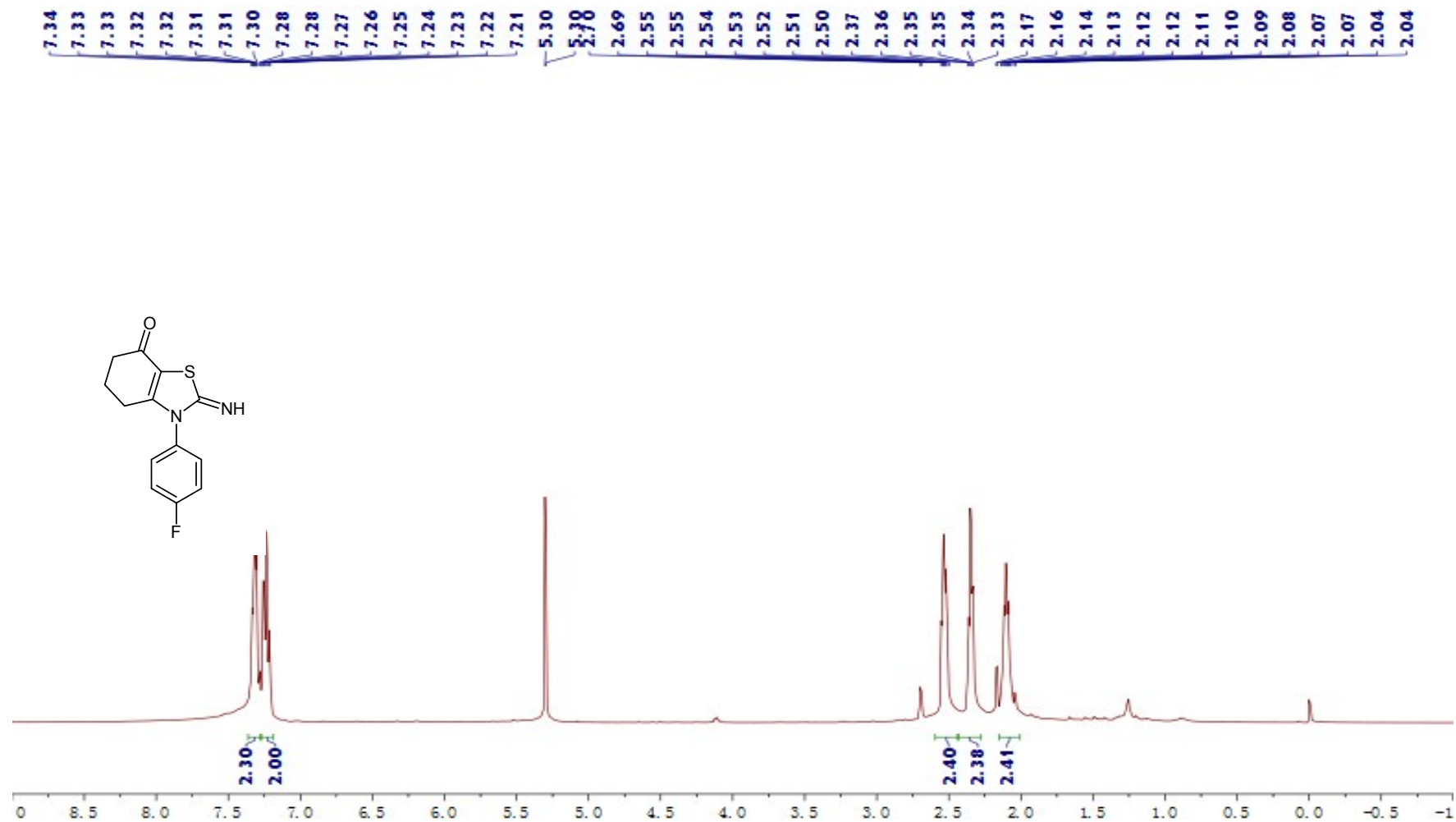


Figure 1. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4a

N-23.12.fid

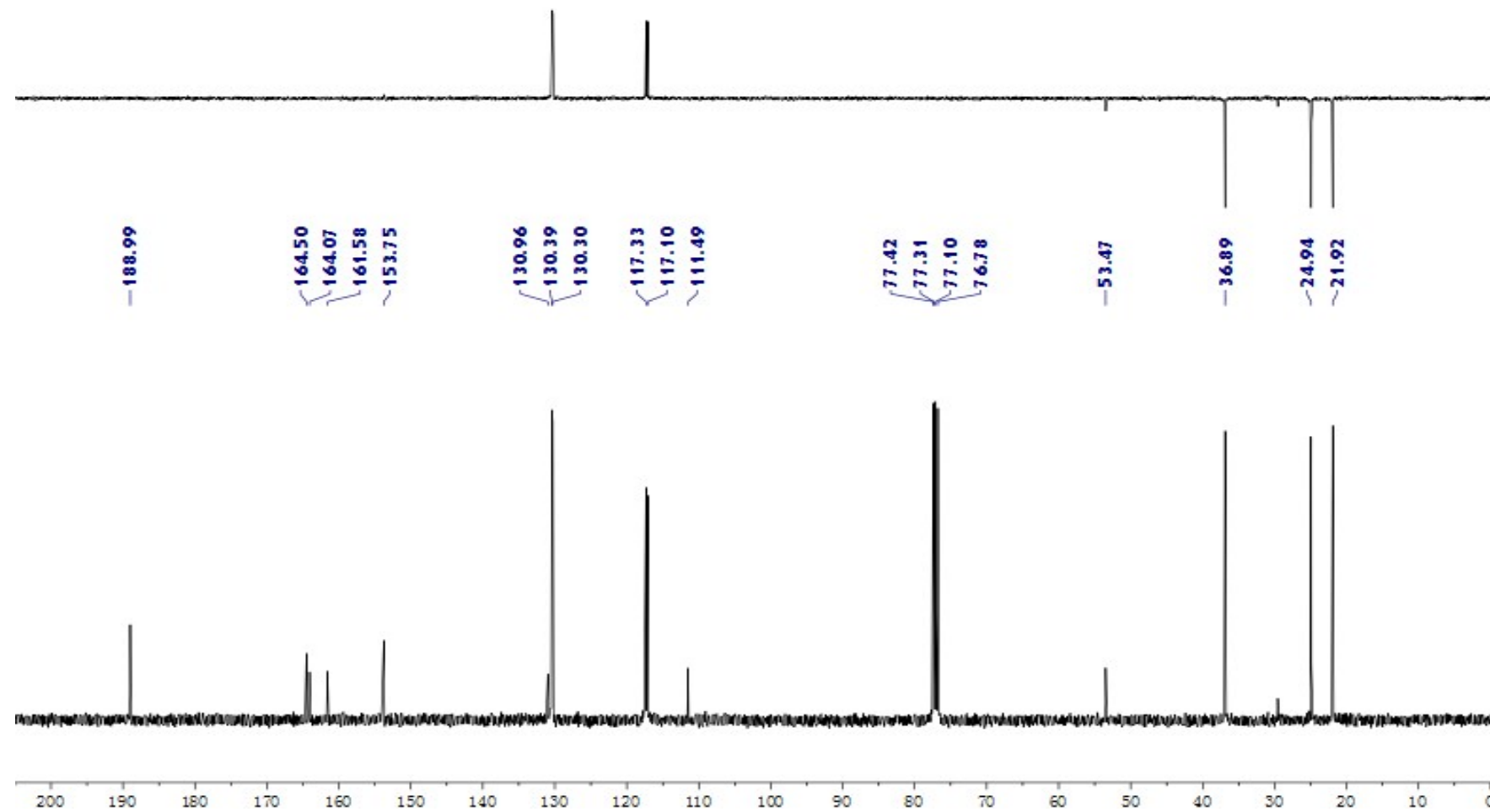


Figure 2. ^{13}C NMR (400 MHz, CDCl_3) spectra of compound 4a

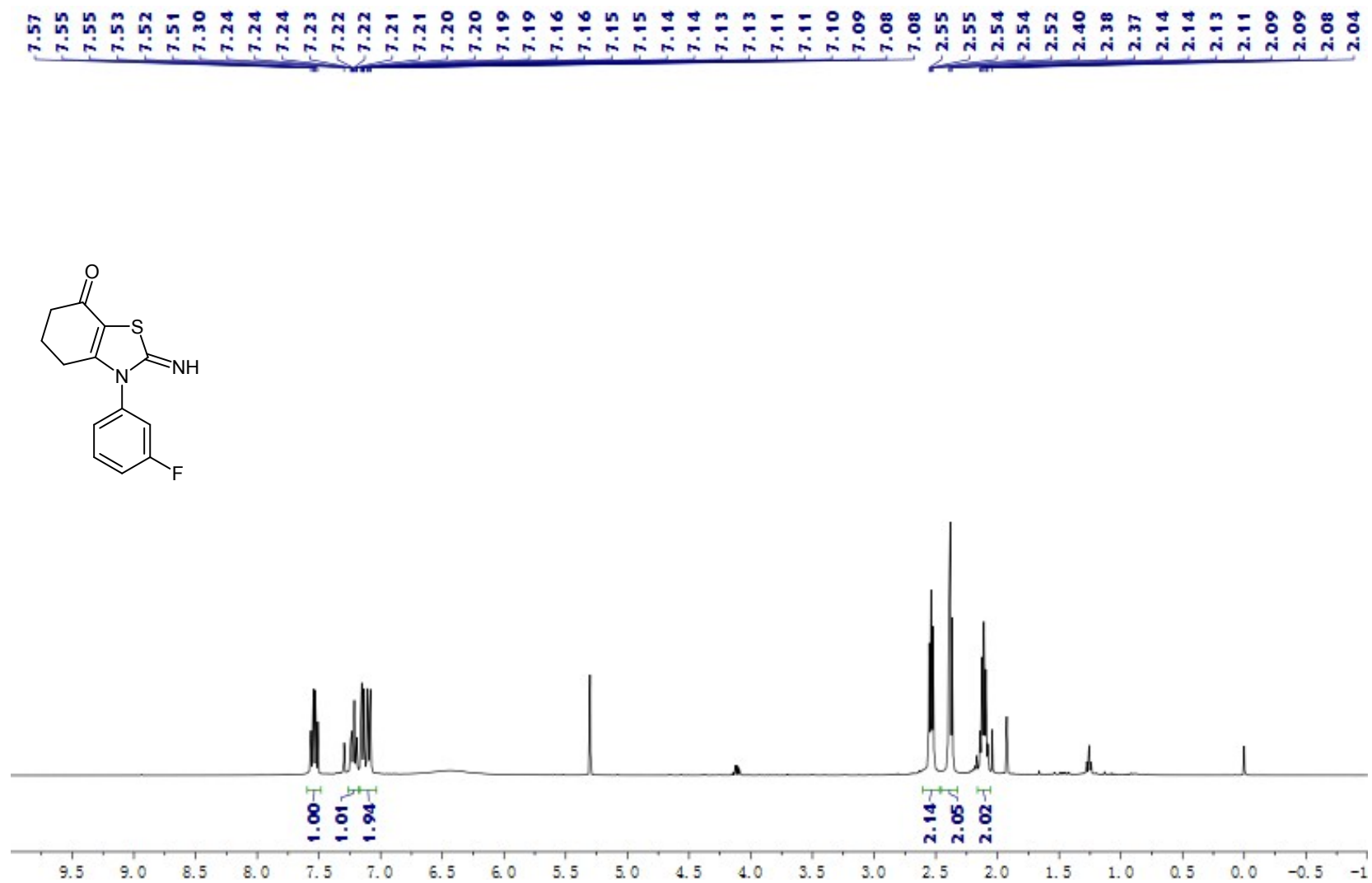


Figure 3. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4b

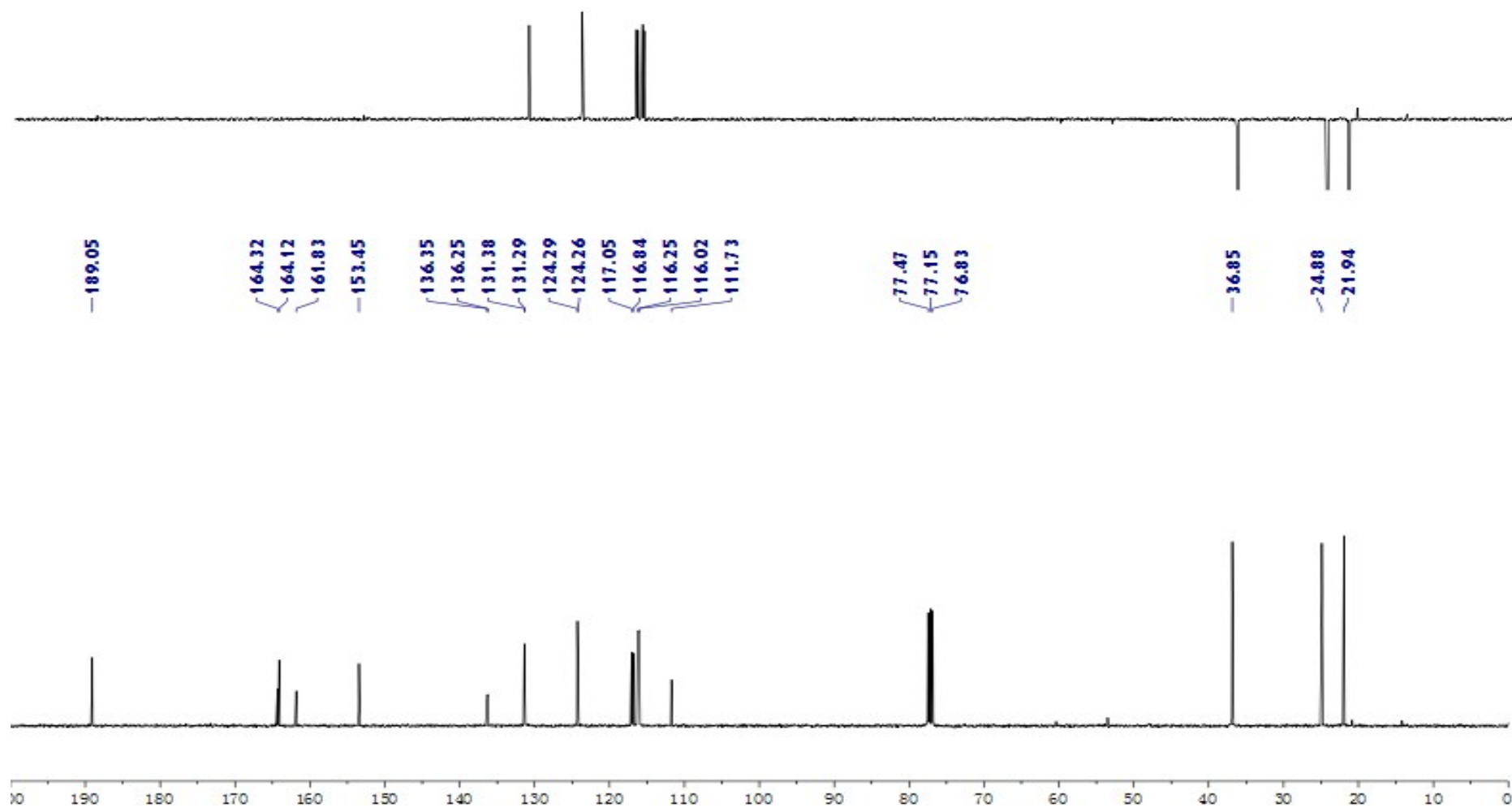


Figure 4. ¹³C NMR (100 MHz, CDCl₃) spectra of compound 4b

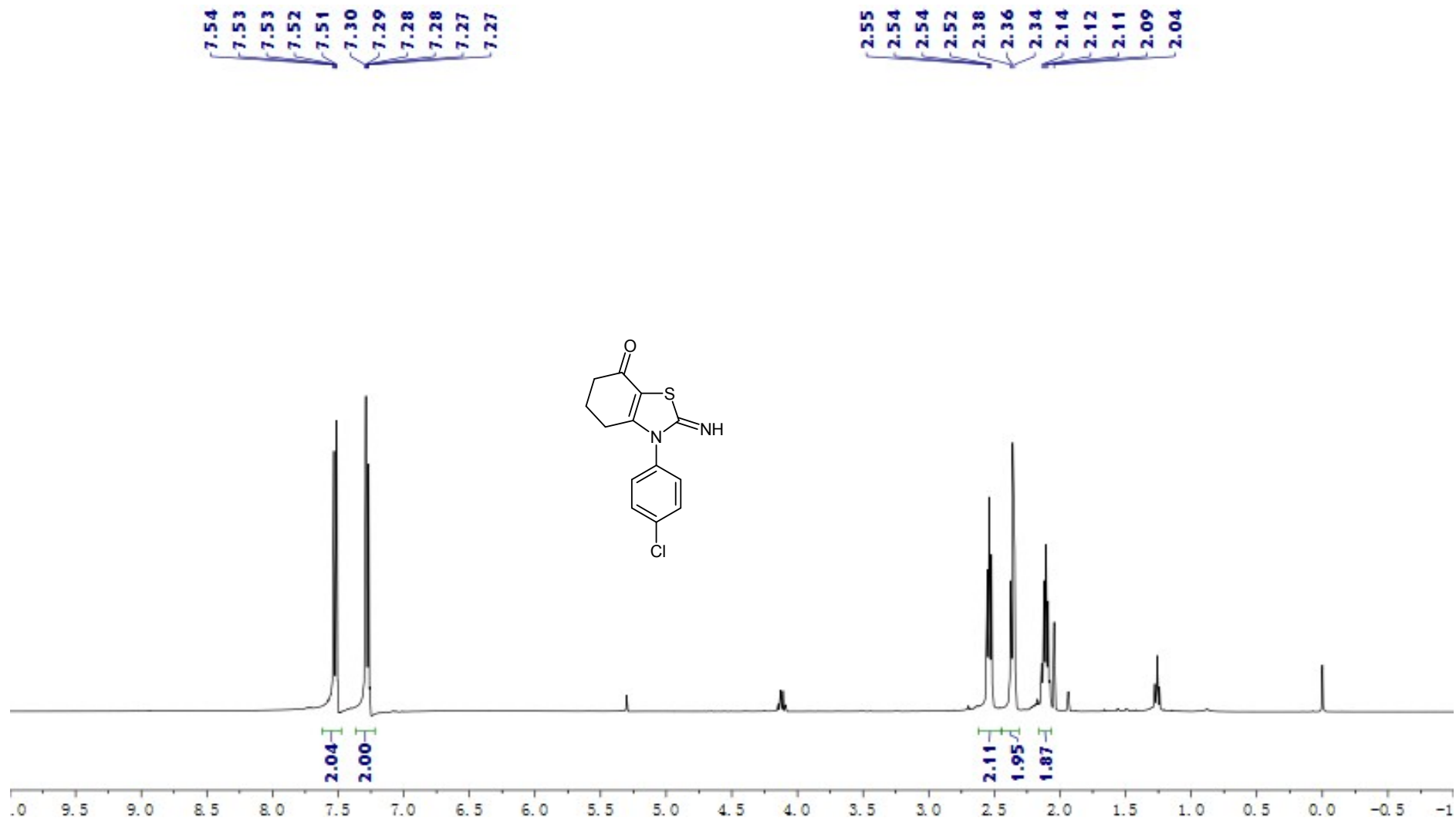


Figure 5. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4c

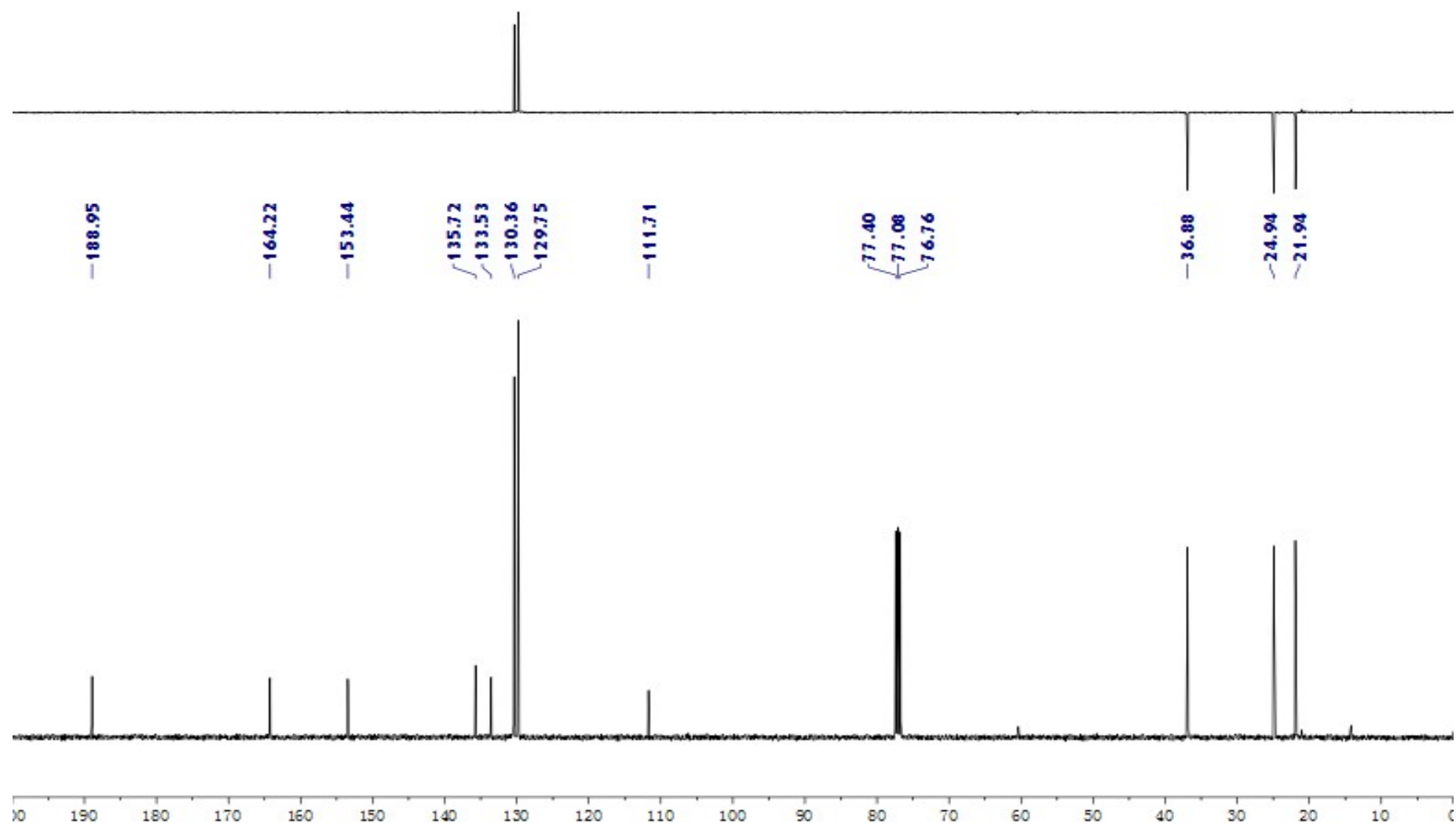


Figure 6. ¹³C NMR (100 MHz, CDCl₃) spectra of compound 4c

N-20.10.fid

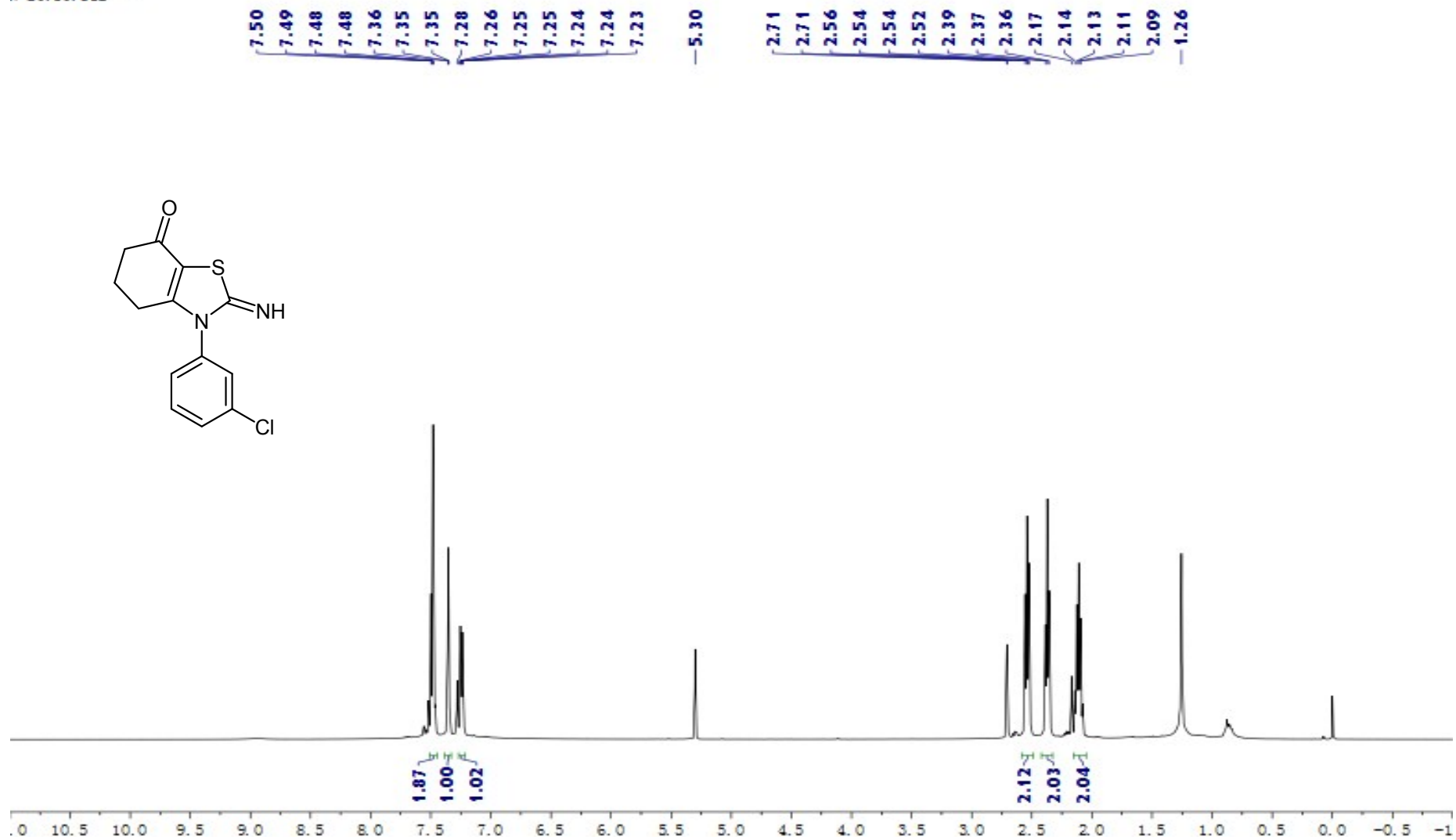


Figure 7. ^1H NMR (400 MHz, CDCl_3) spectra of compound **4d**

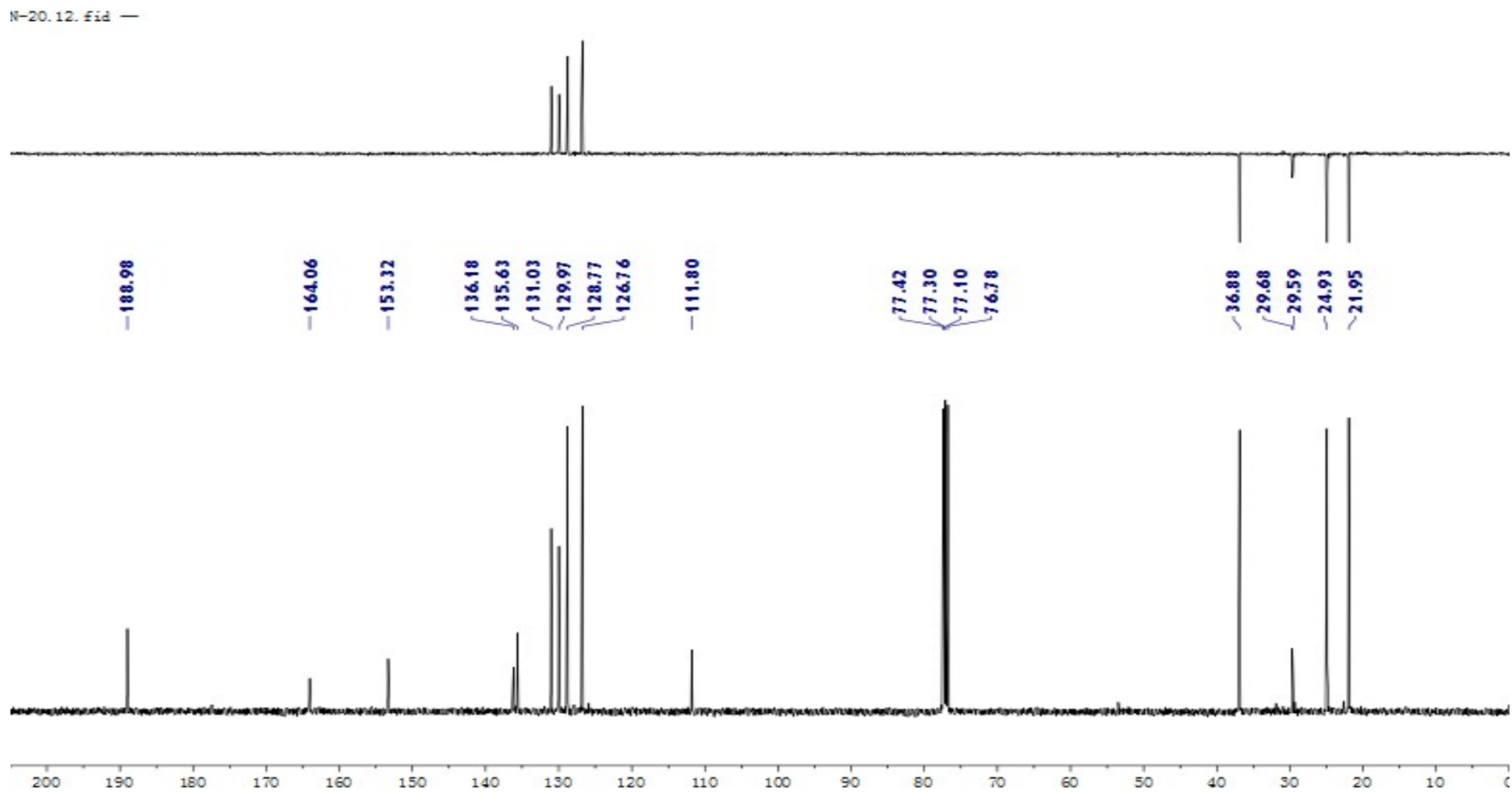


Figure 8. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4d

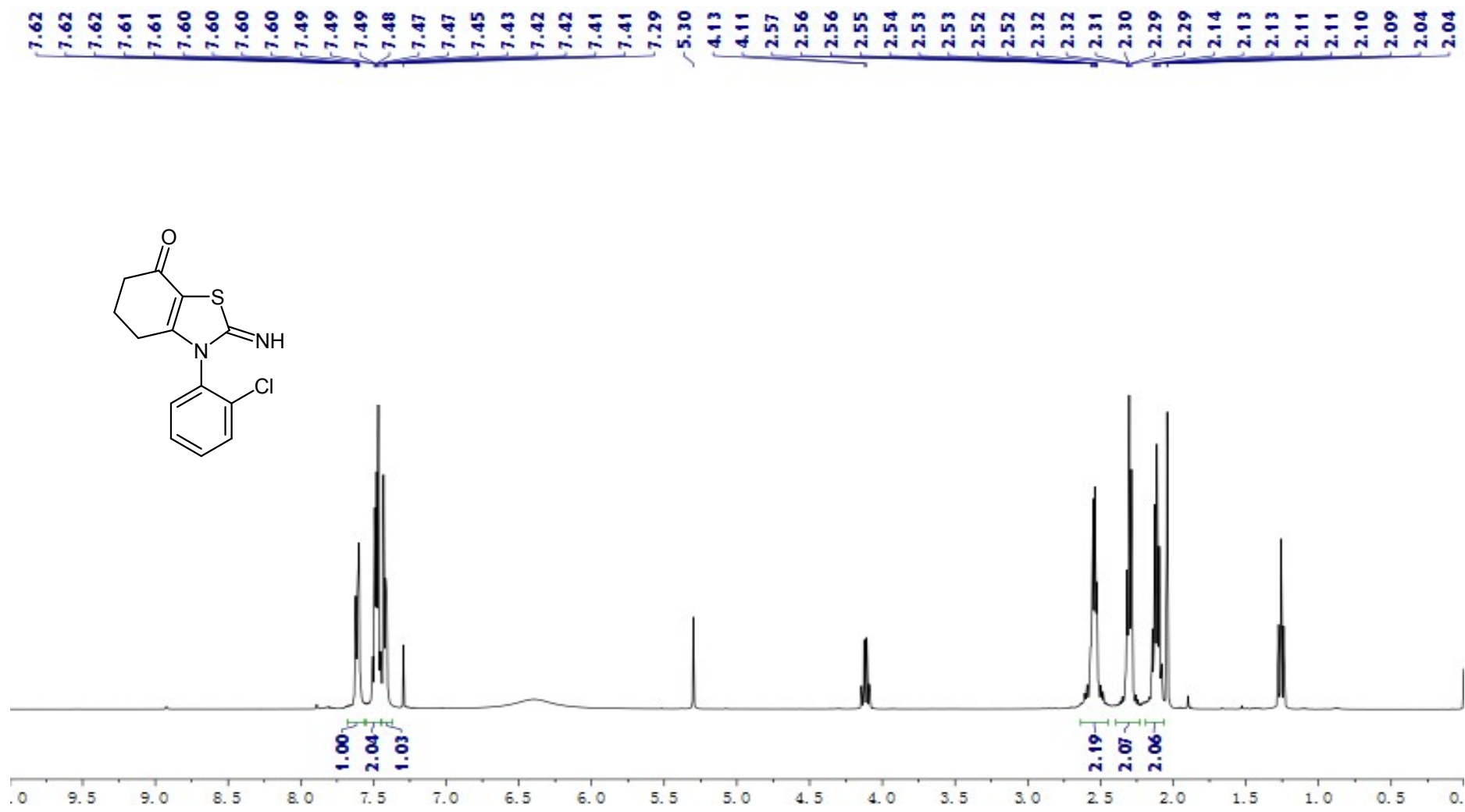


Figure 9. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4e

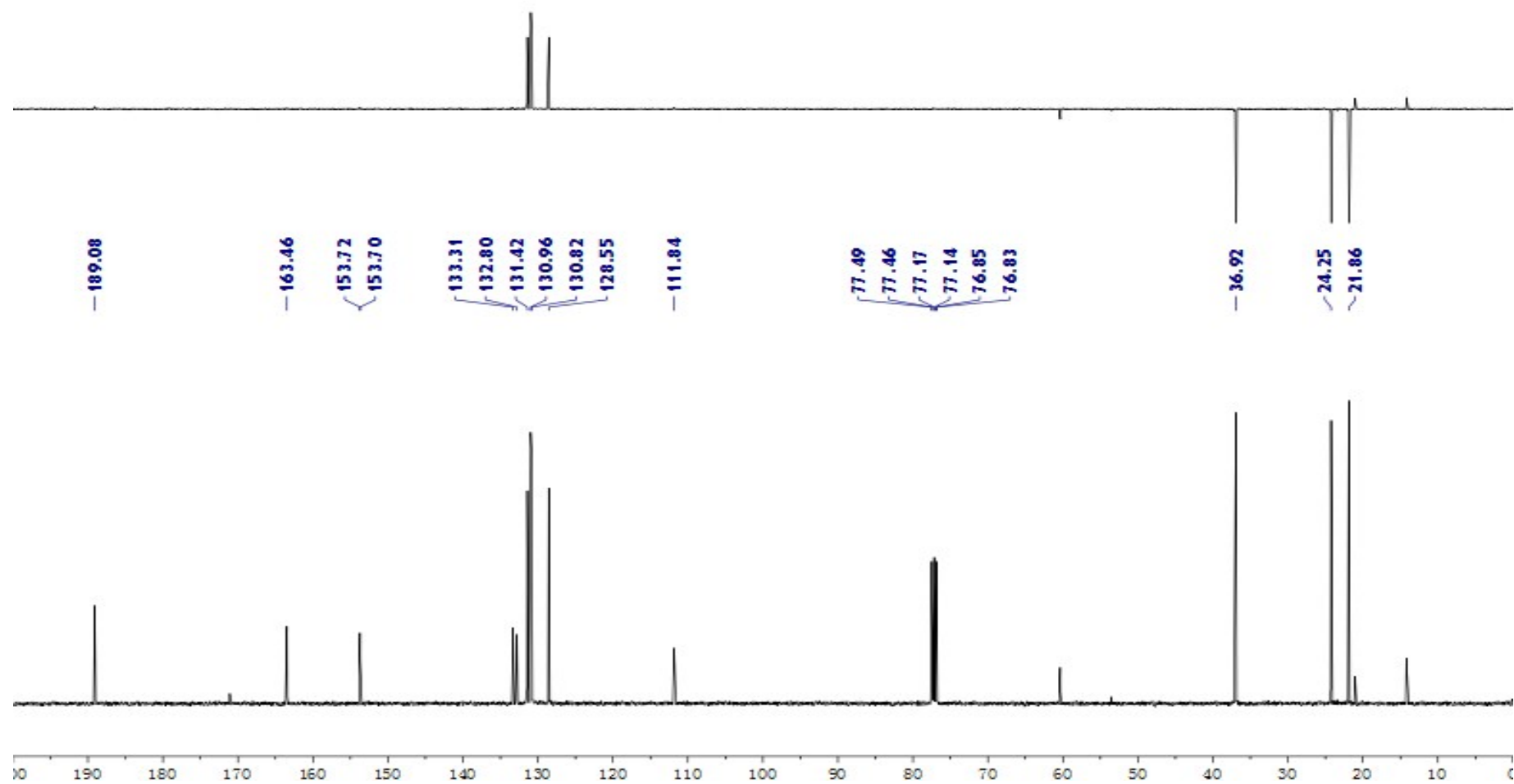


Figure 10. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **4e**

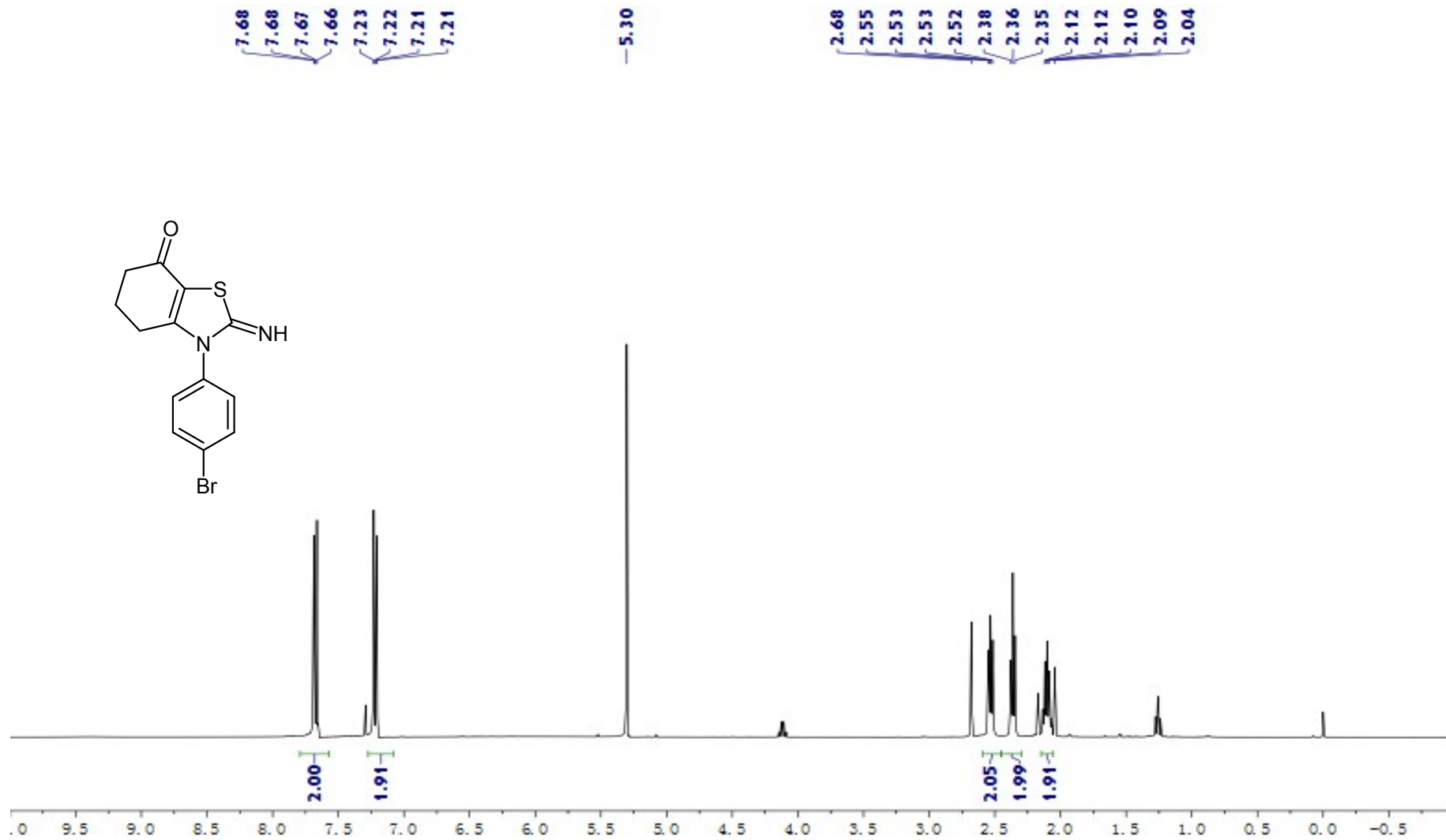


Figure 11. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4f

N-26.12.fid

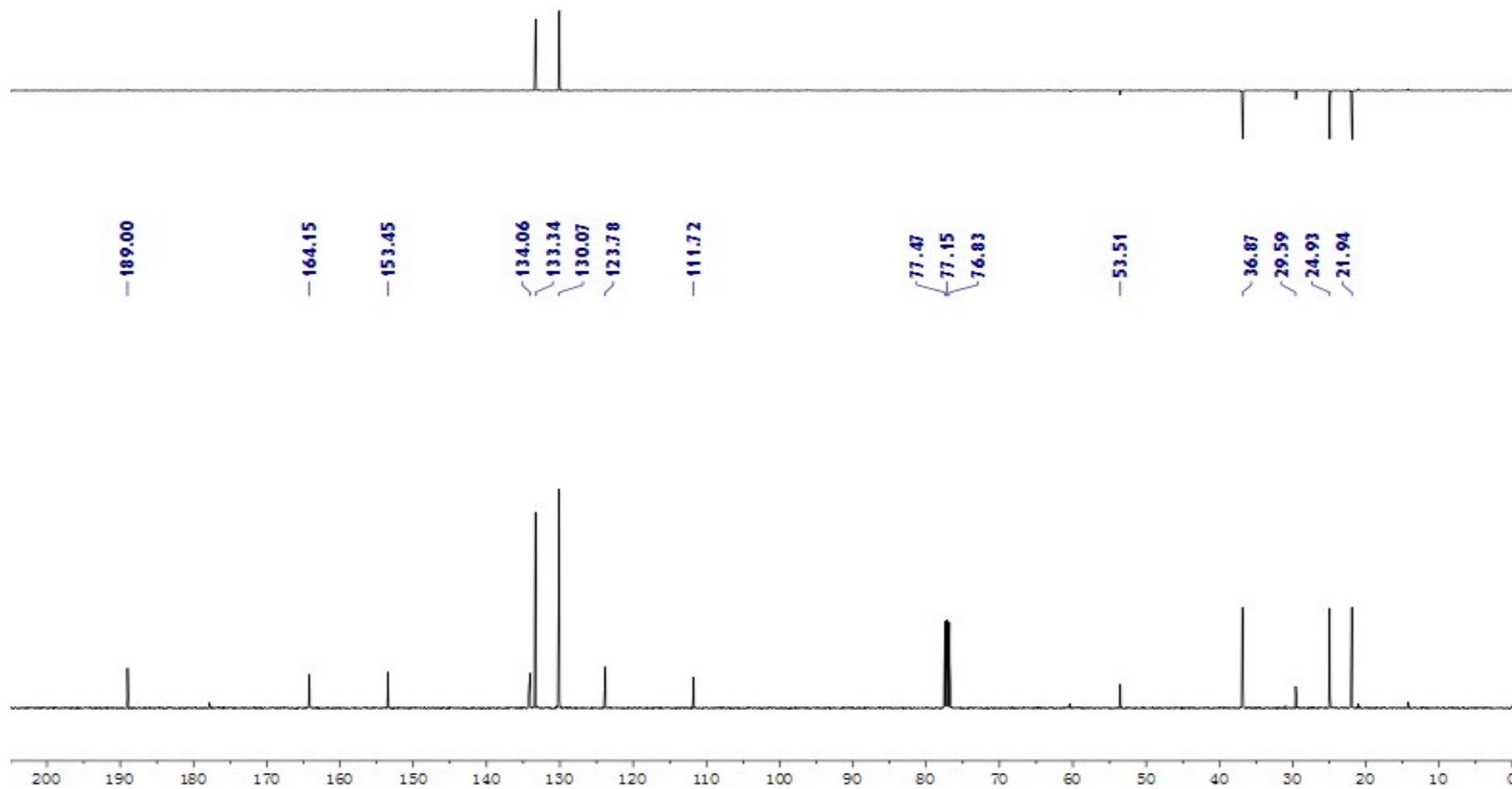


Figure 12. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4f

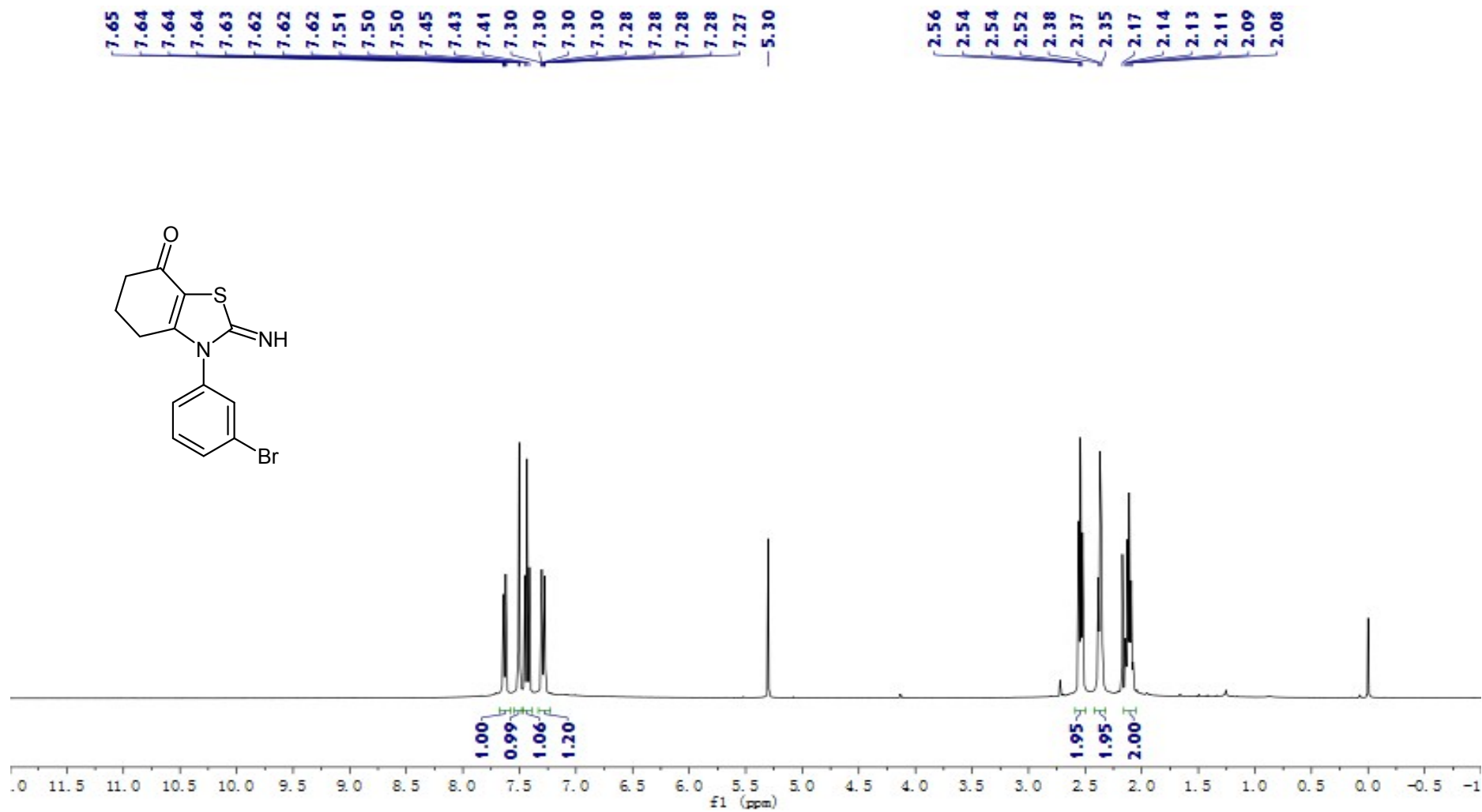


Figure 13. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4g

N-19.12.fid

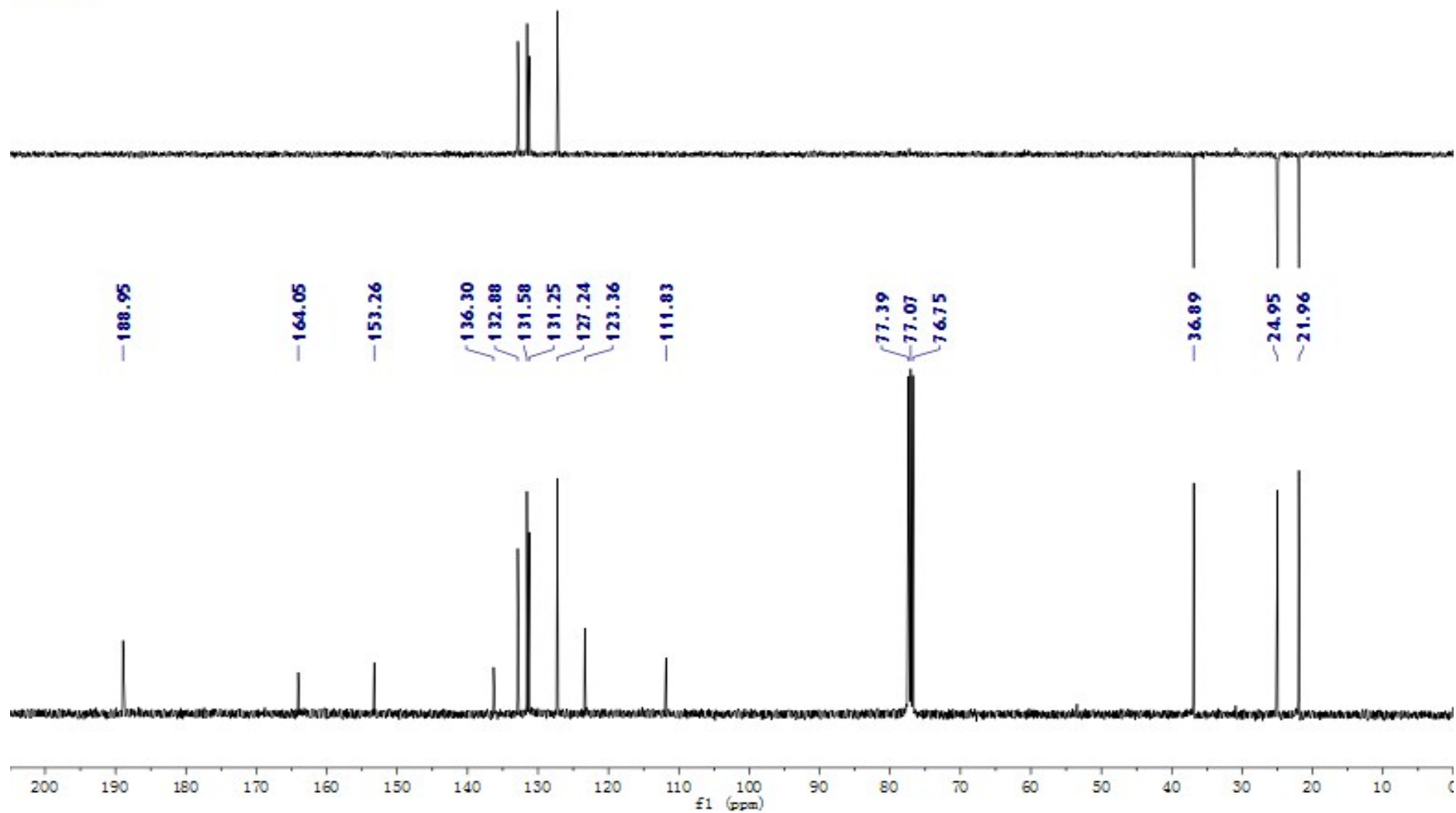


Figure 14. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **4g**

22014000178.16.fid
N-13 CDCl3

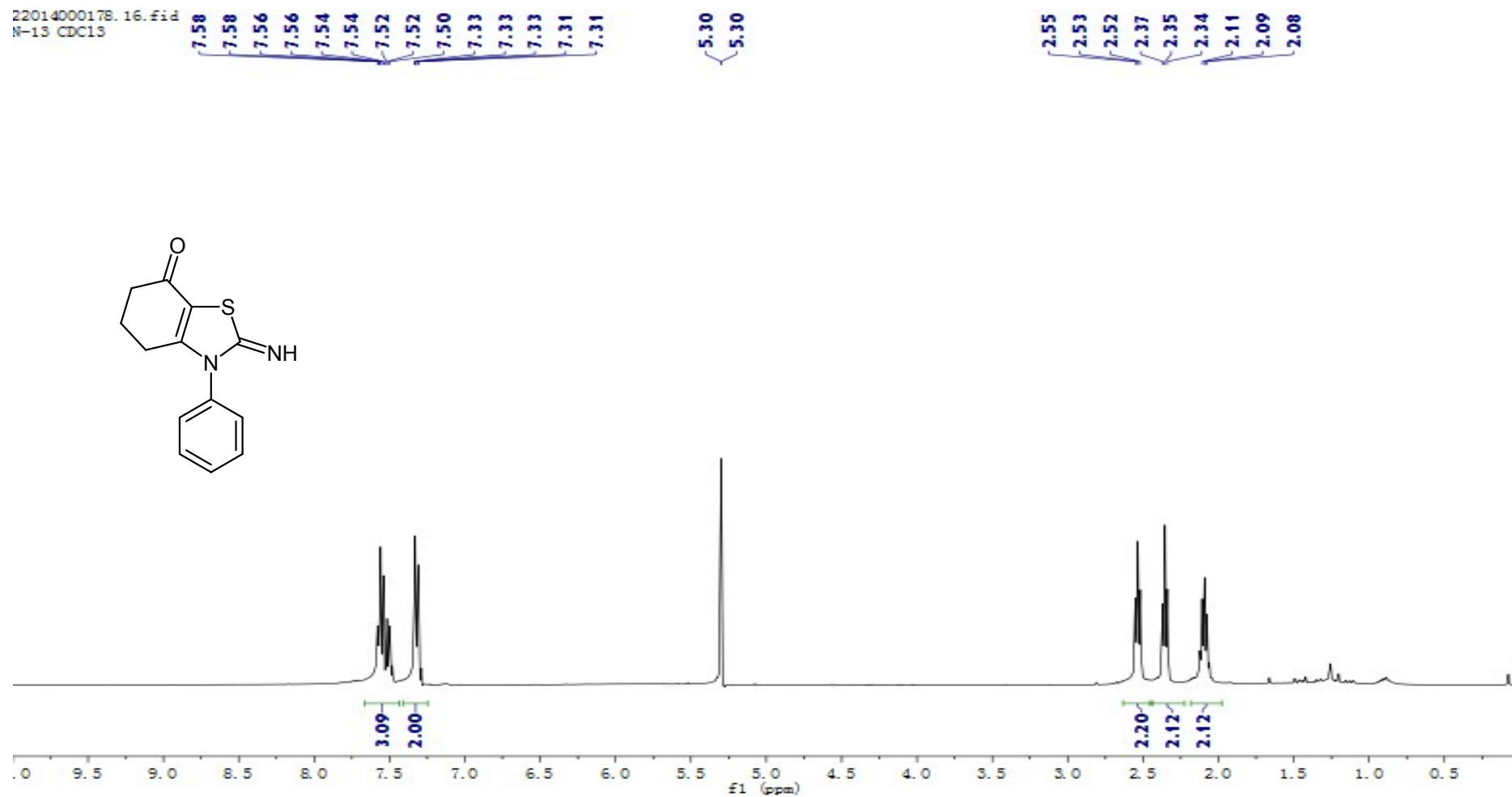


Figure 15. ^1H NMR (400 MHz, CDCl_3) spectra of compound 4h

22014000178.18.fid
N-13 CDCl3

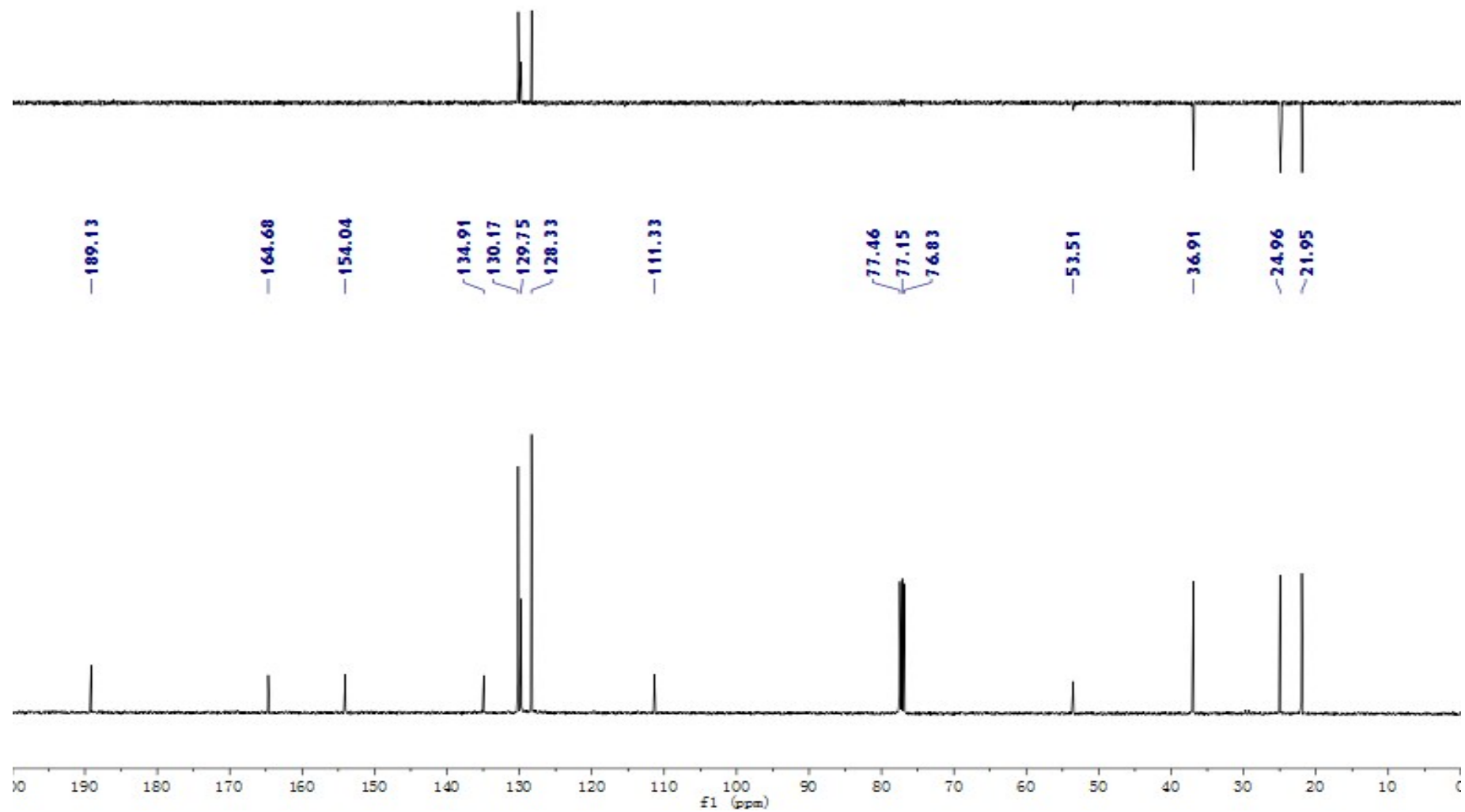


Figure 16. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **4h**

N-18.10.fid

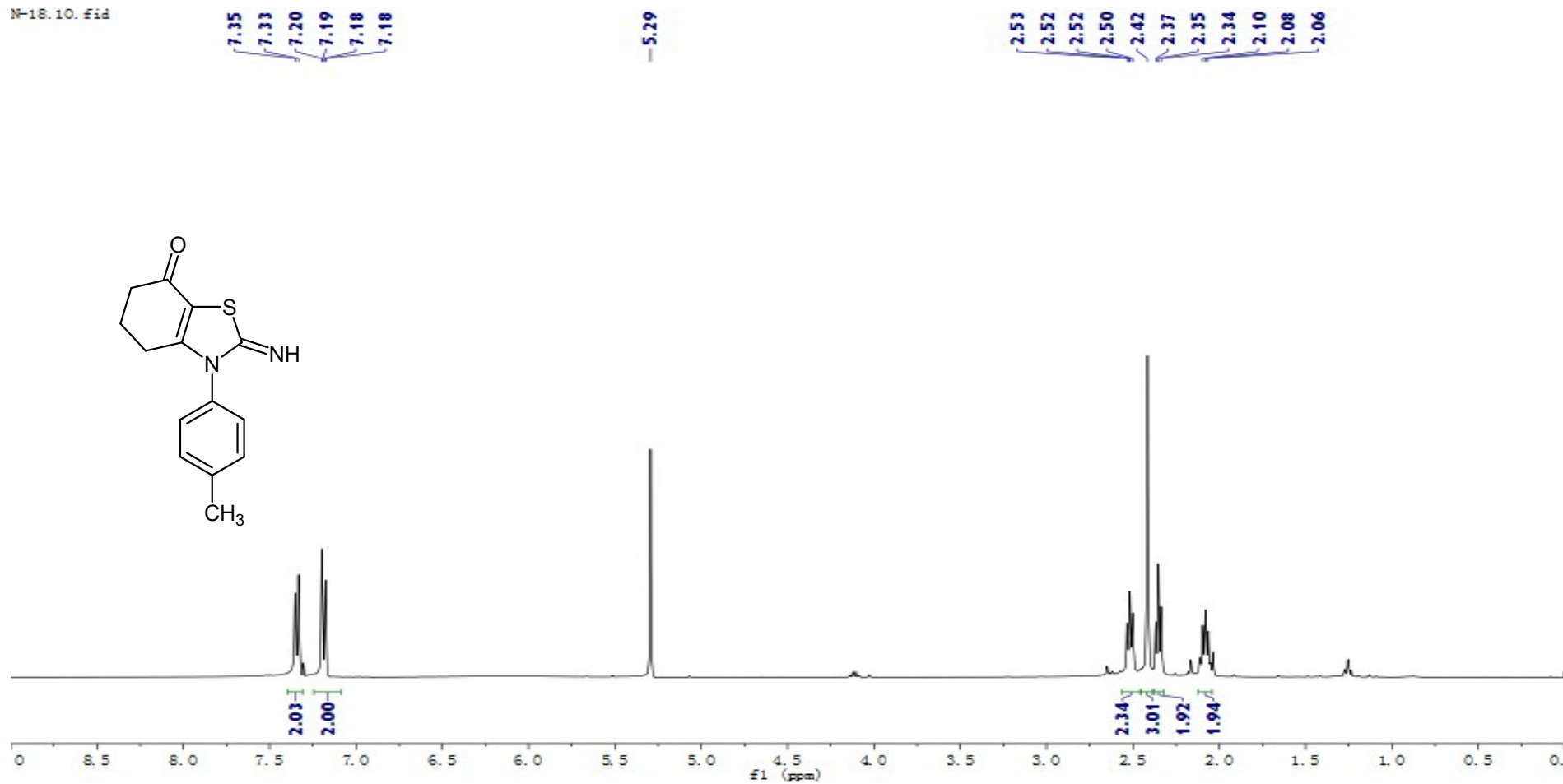


Figure 14. ^1H NMR (400 MHz, CDCl_3) spectra of compound 4i

N-18.12.fid

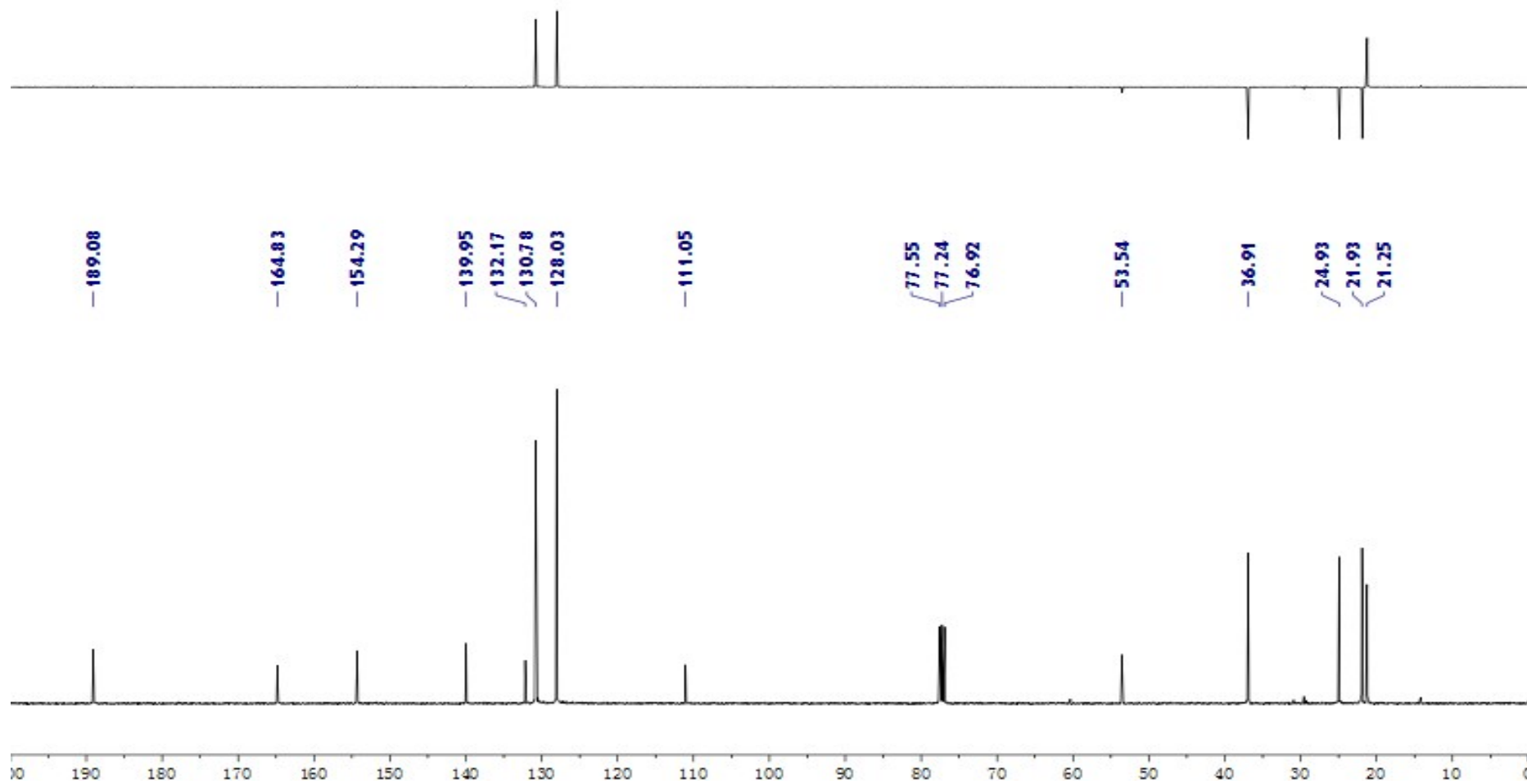


Figure 18. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4i

22014000178.10.fid
N-7 CDCl3

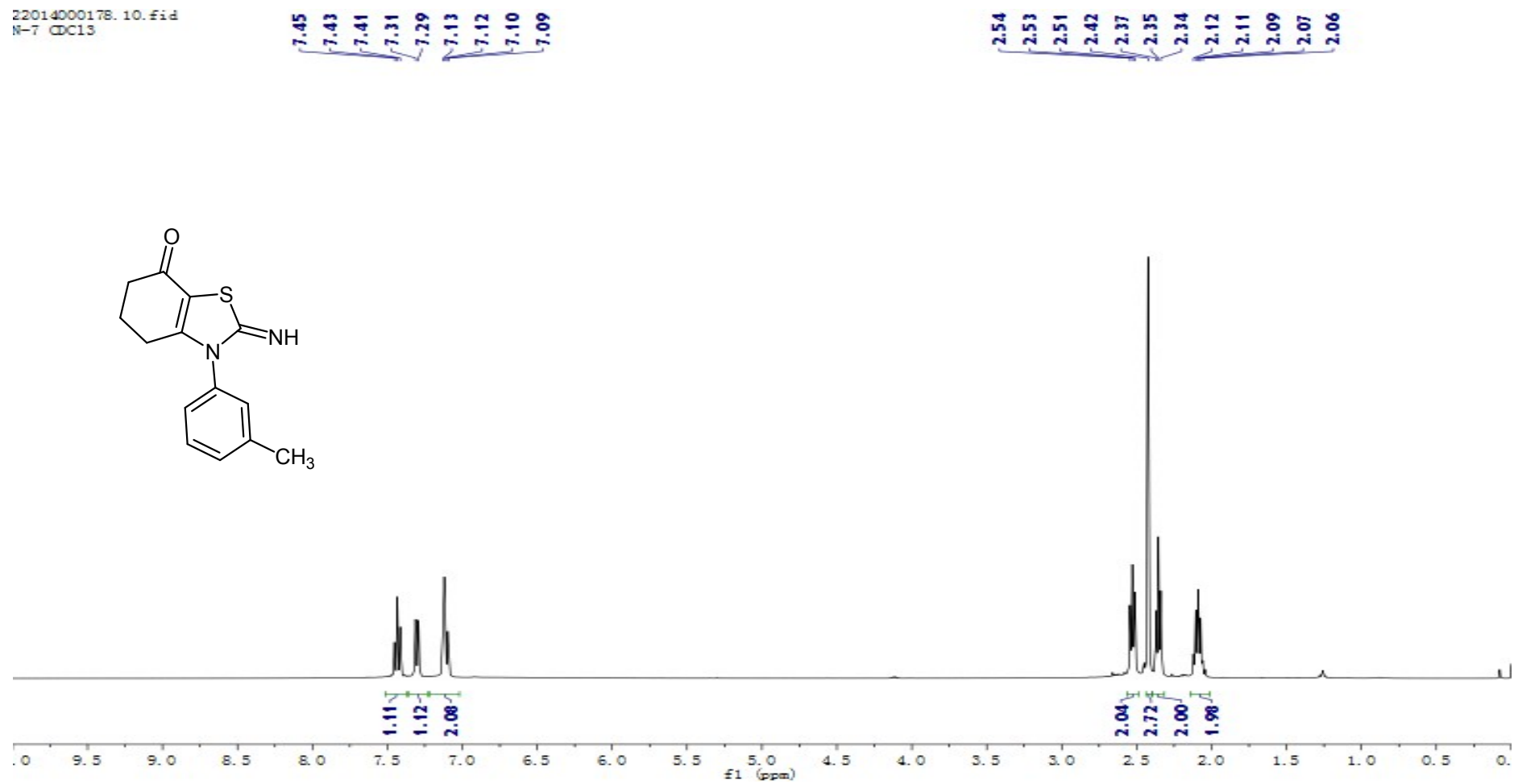


Figure 19. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4j

22014000178.12.fid
N-7 CDCl₃

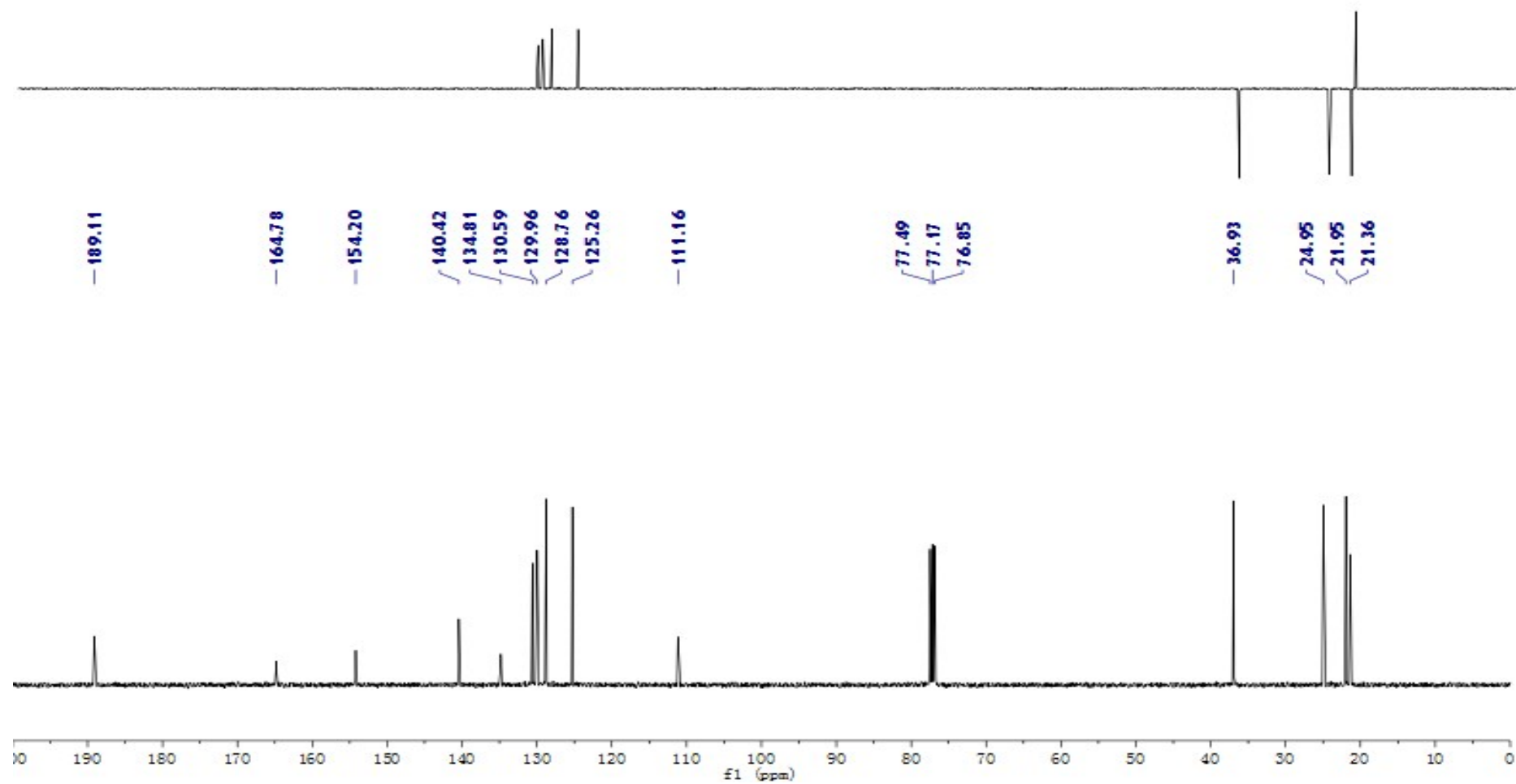


Figure 20. ¹³C NMR (100 MHz, CDCl₃) spectra of compound 4j

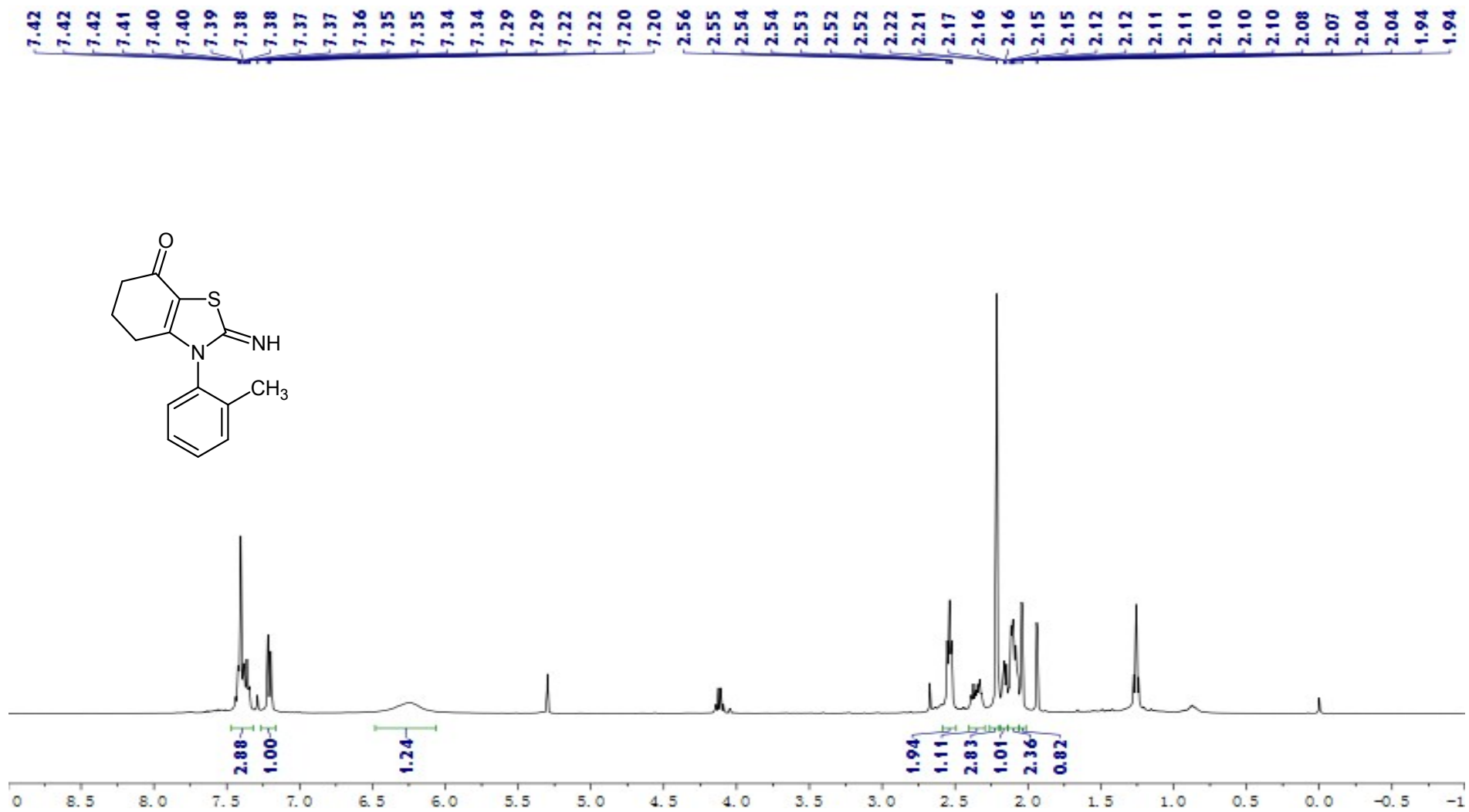


Figure 21. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4k

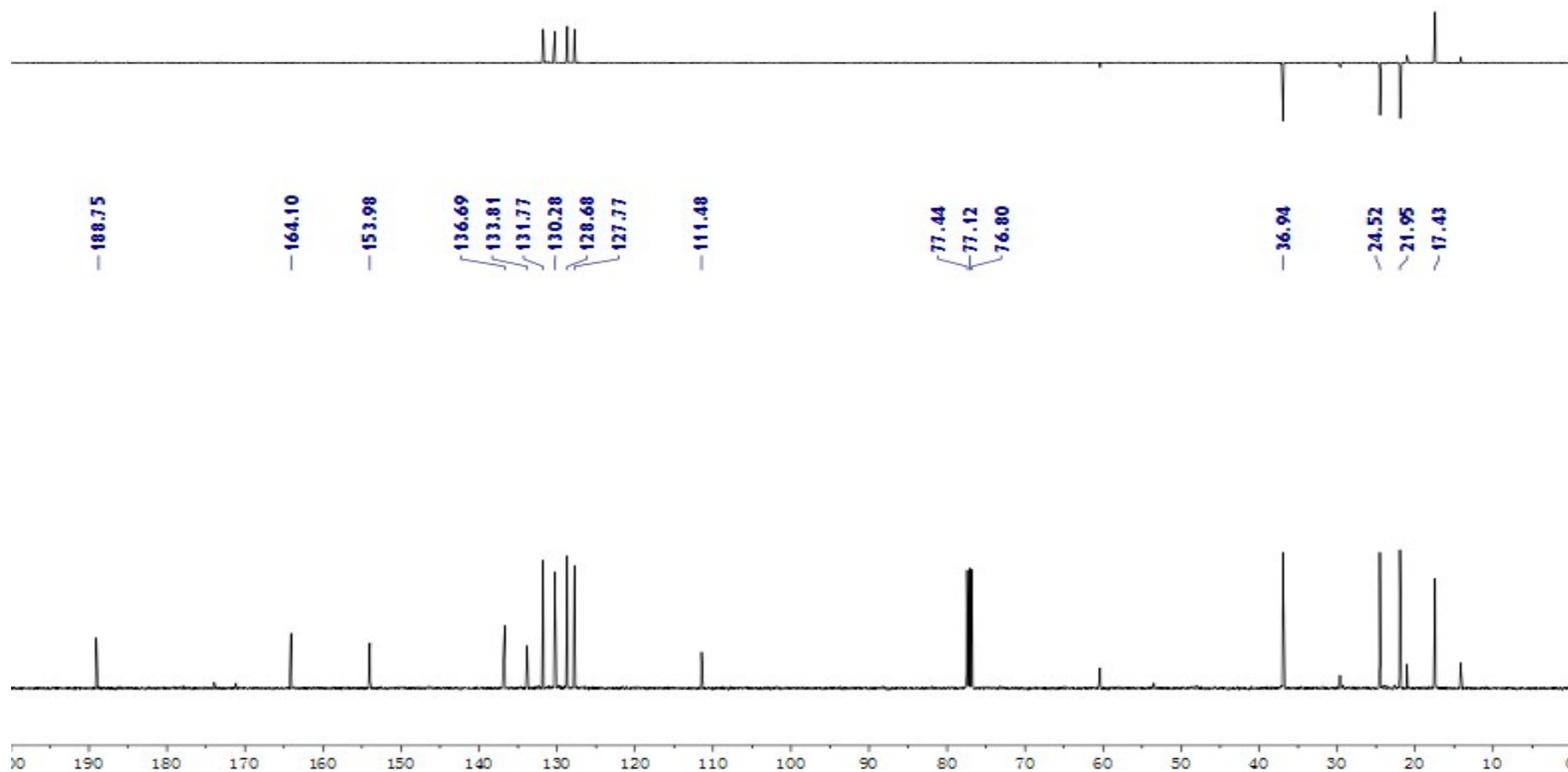


Figure 22. ¹³C NMR (100 MHz, CDCl₃) spectra of compound **4k**

20160620 N1-1 DMSO

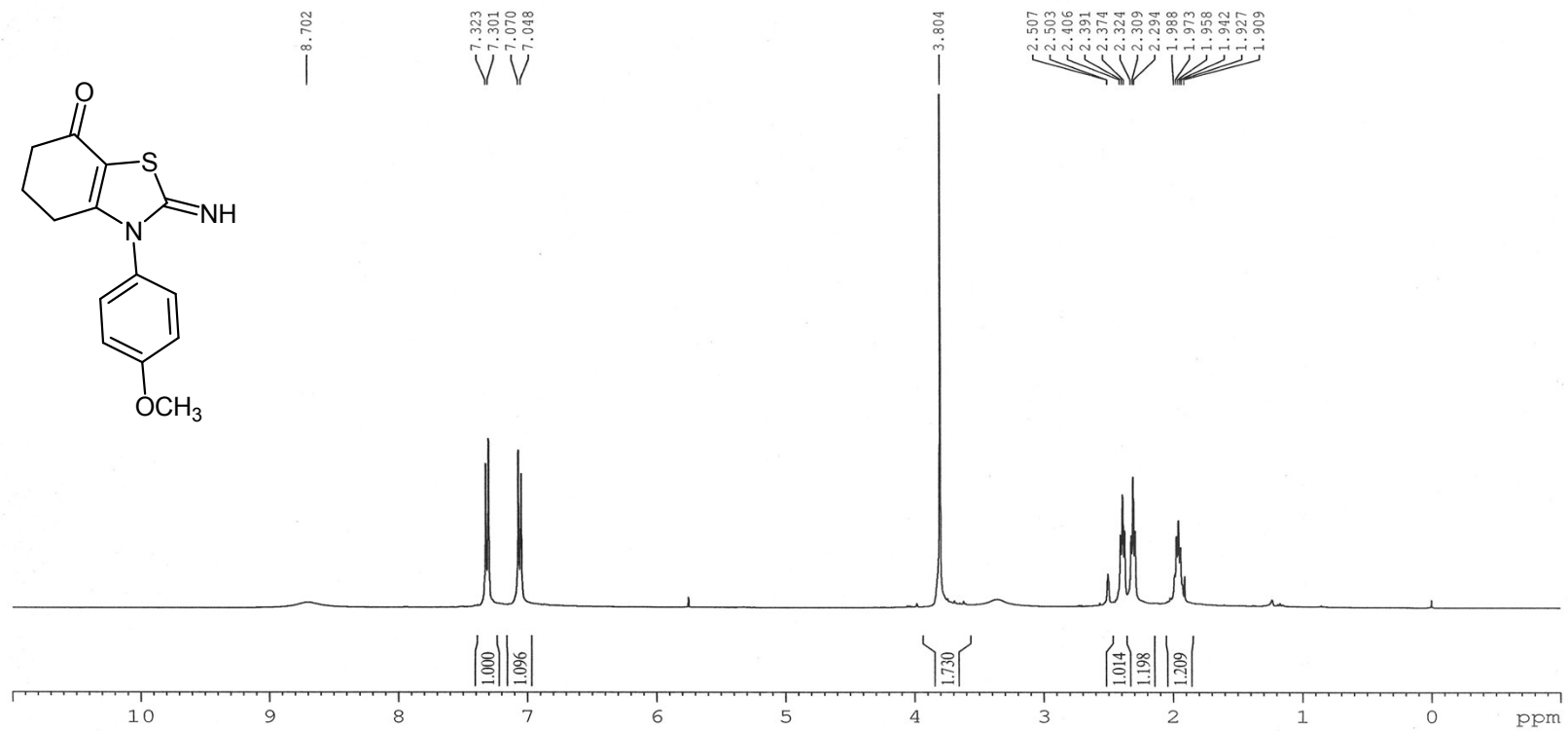


Figure 23. ¹H NMR (400 MHz, DMSO-*d*₆) spectra of compound **4I**

20160620 N1-1 DMSO

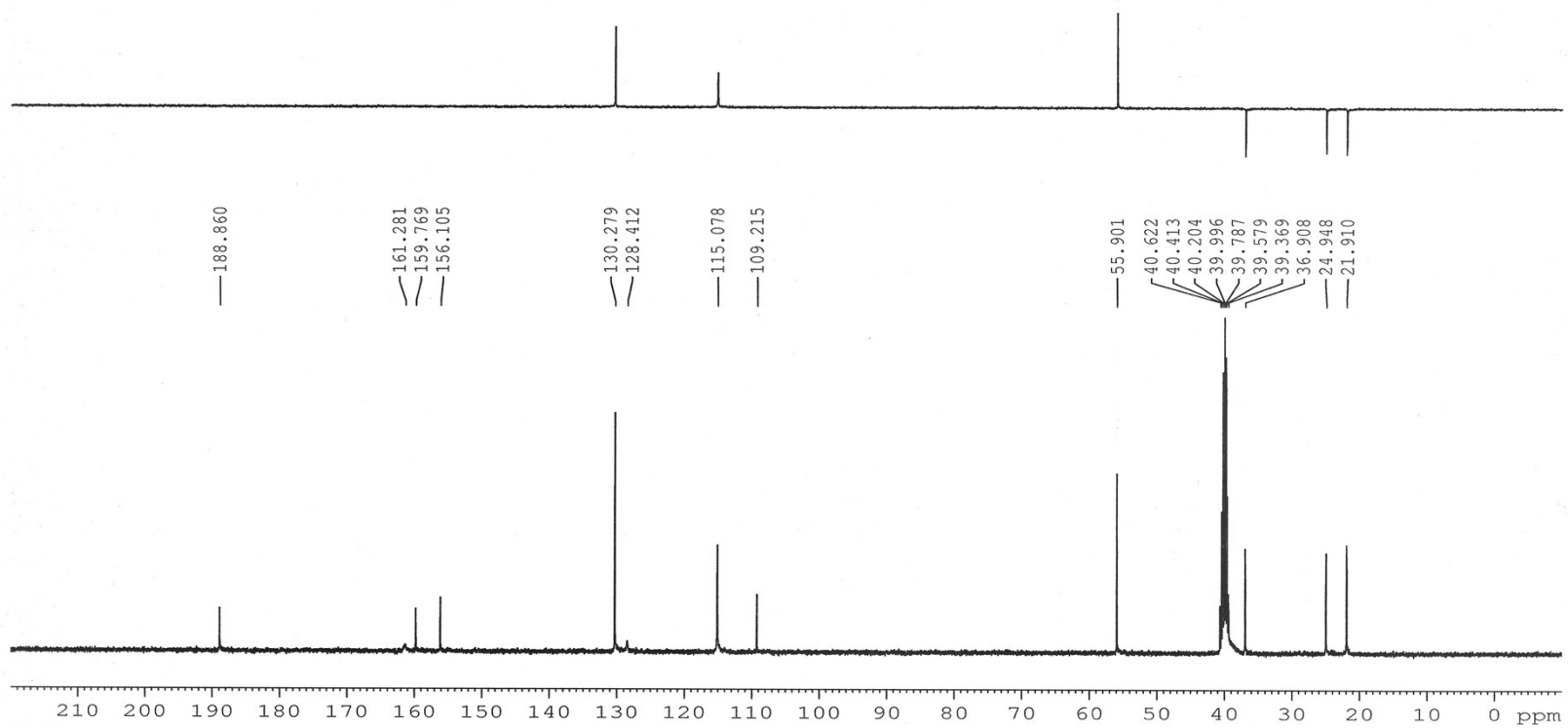


Figure 24. ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) spectra of compound 41

N-24.12.fid

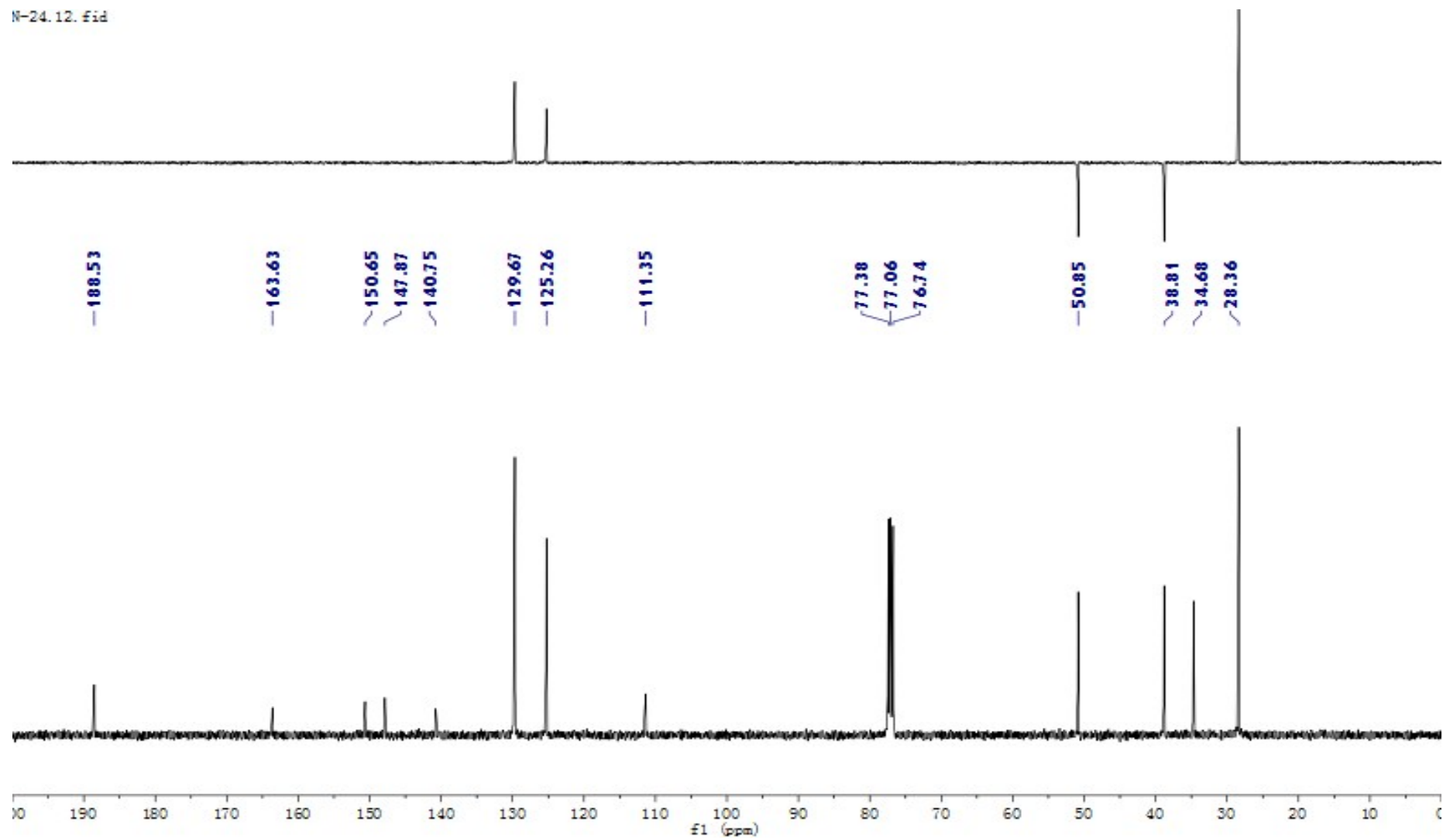


Figure 26. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound 4m

22014000178_4
N-4 CDCl3

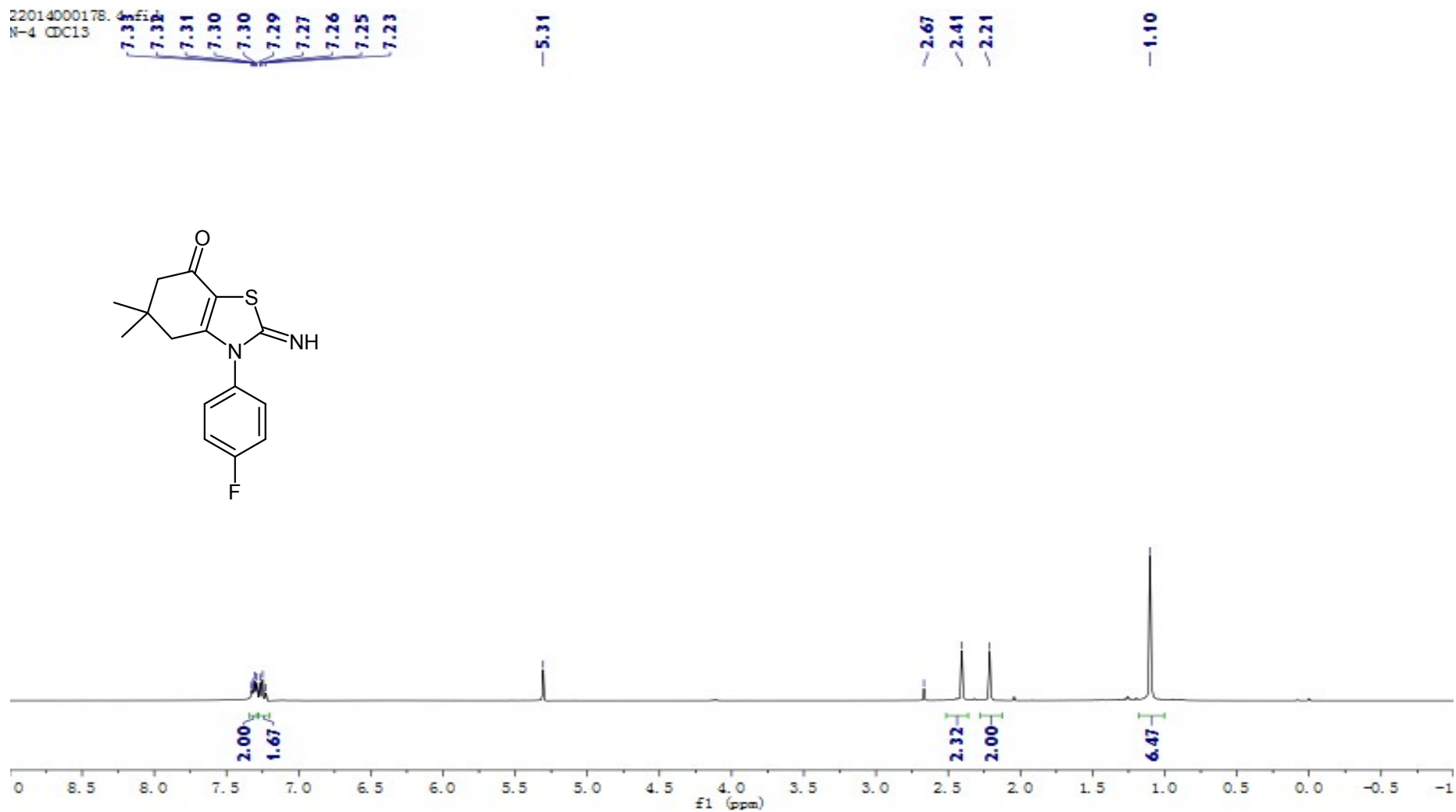
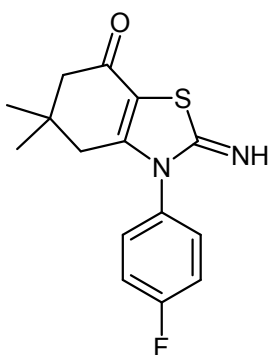


Figure 27. ^1H NMR (400 MHz, CDCl_3) spectra of compound **4n**

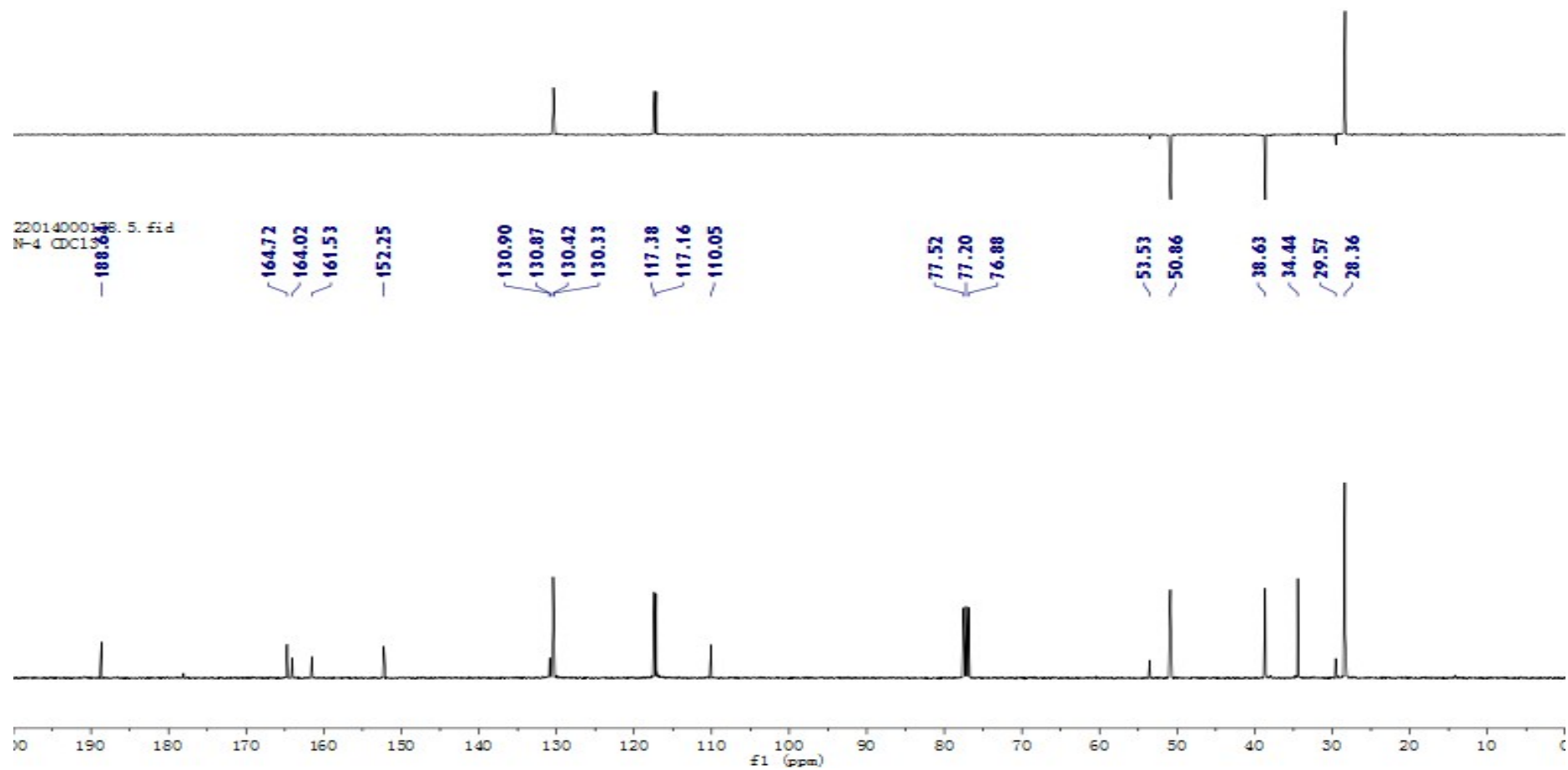


Figure 28. ¹³C NMR (100 MHz, CDCl₃) spectra of compound **4n**

N-10-1.10.fid

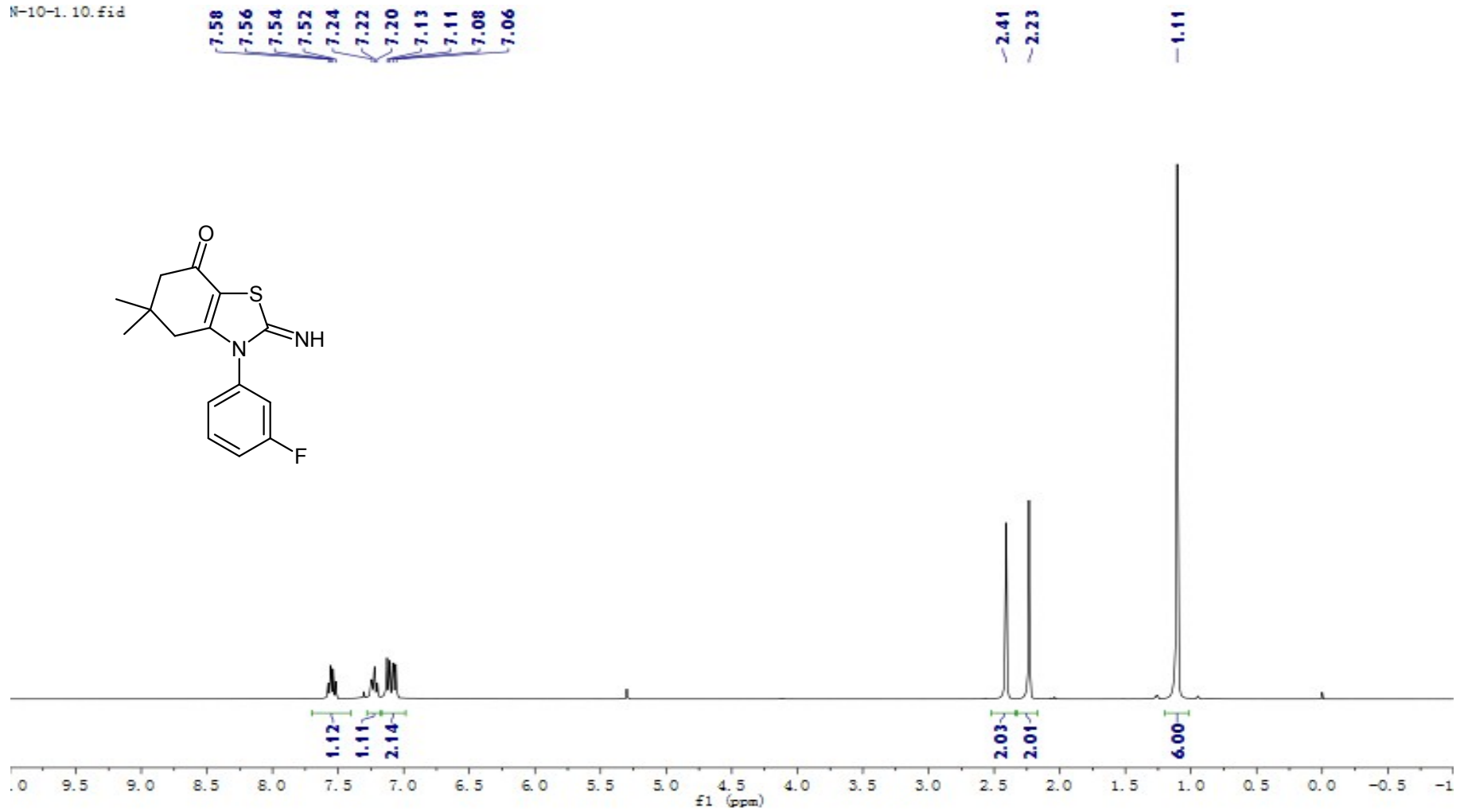


Figure 29. ^1H NMR (400 MHz, CDCl_3) spectra of compound 4o

N-10-1.12.fid

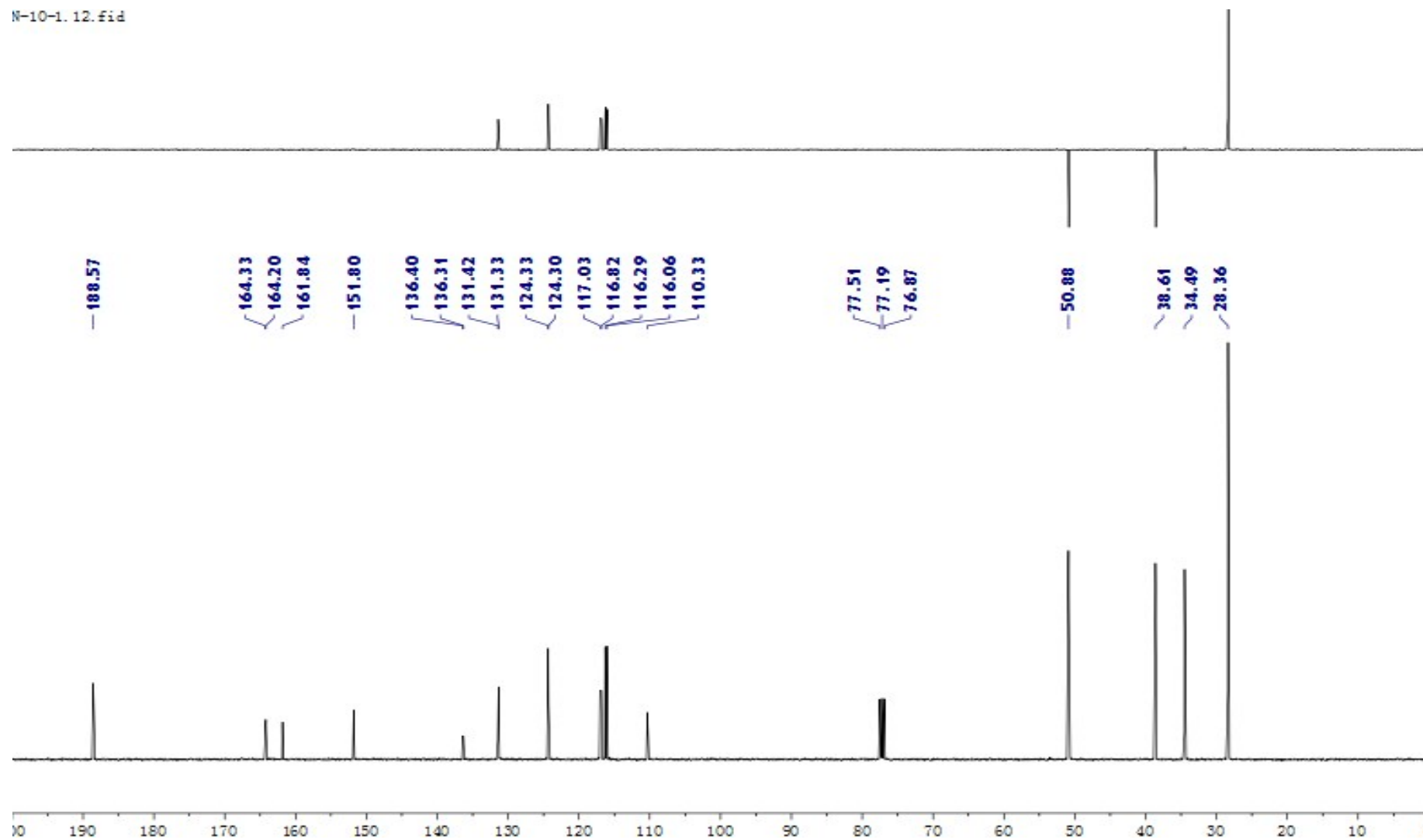


Figure 30. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **40**

22014000178. 7. fid
N-5 CDCl3

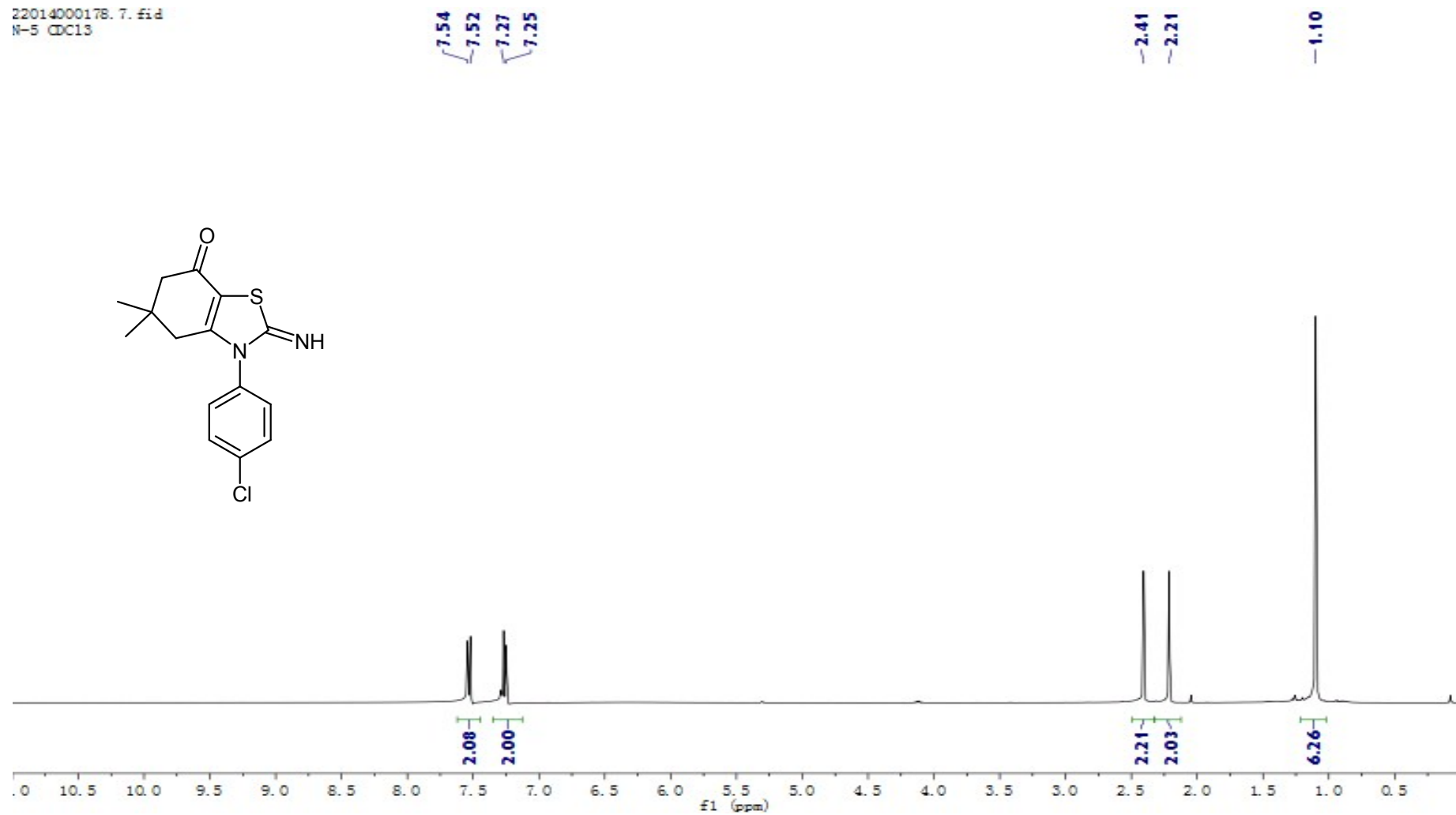


Figure 31. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4p

22014000178. 9. fid
N-5 CDCl3

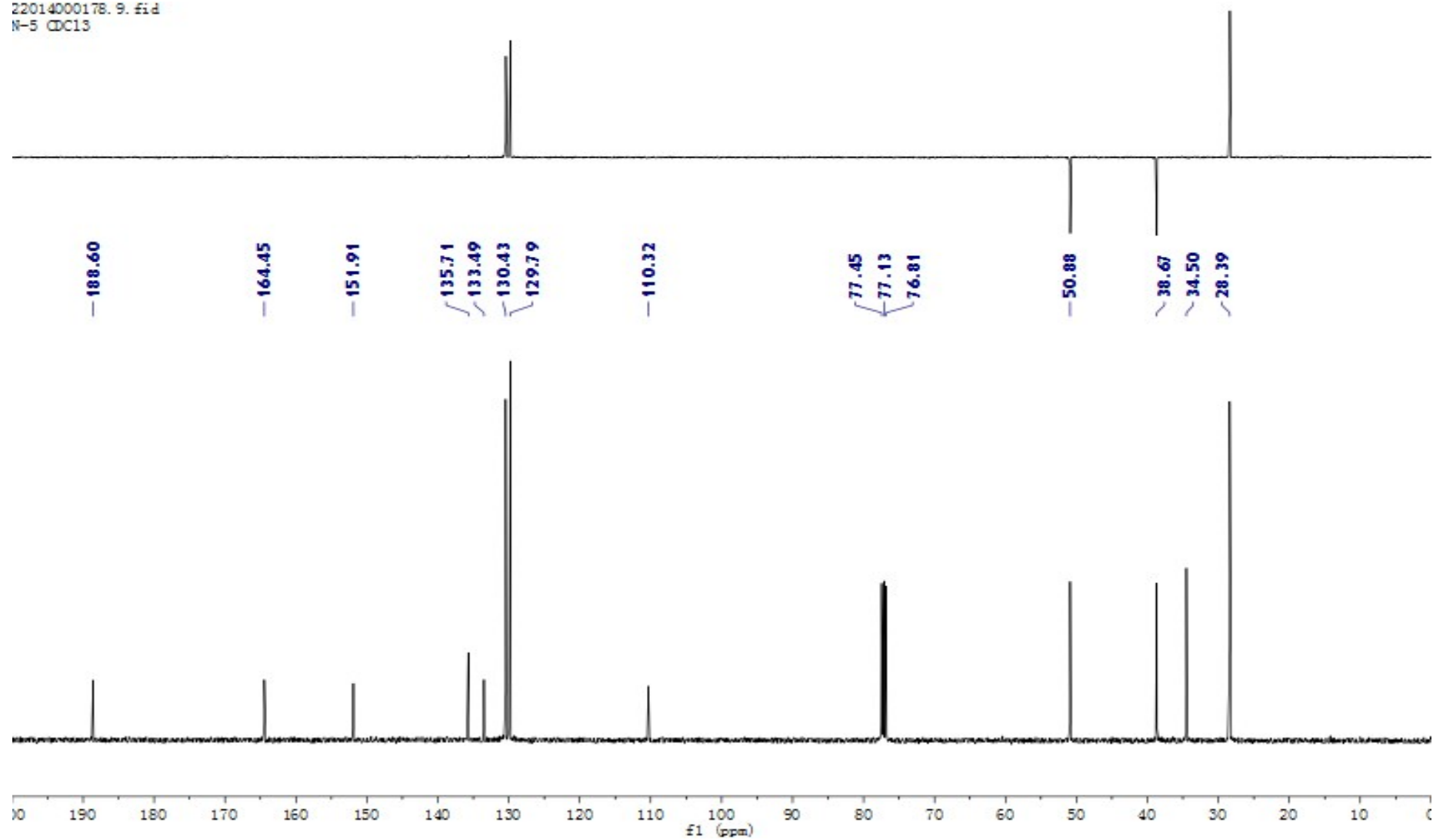


Figure 32. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **4p**

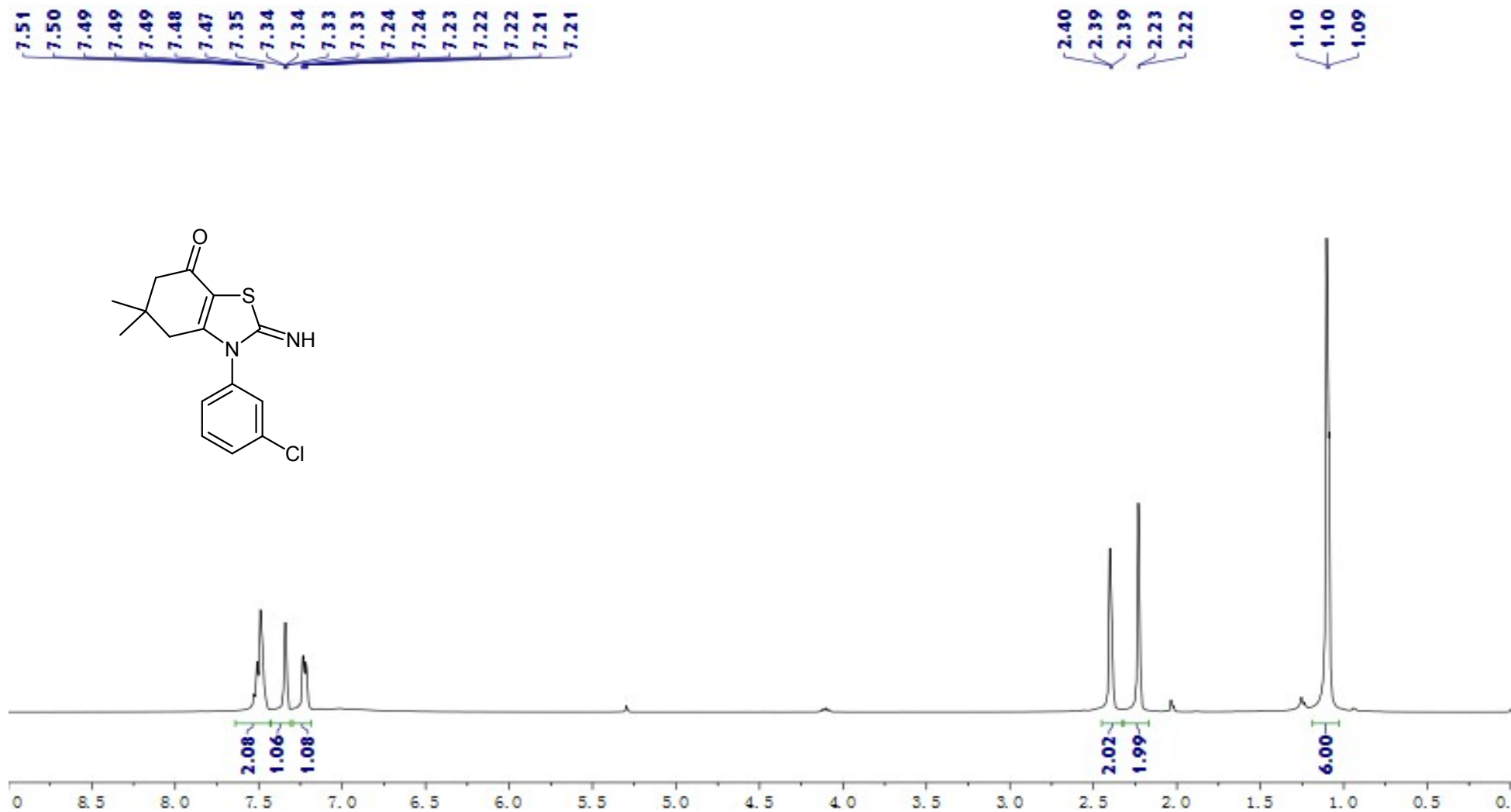


Figure 33. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4q

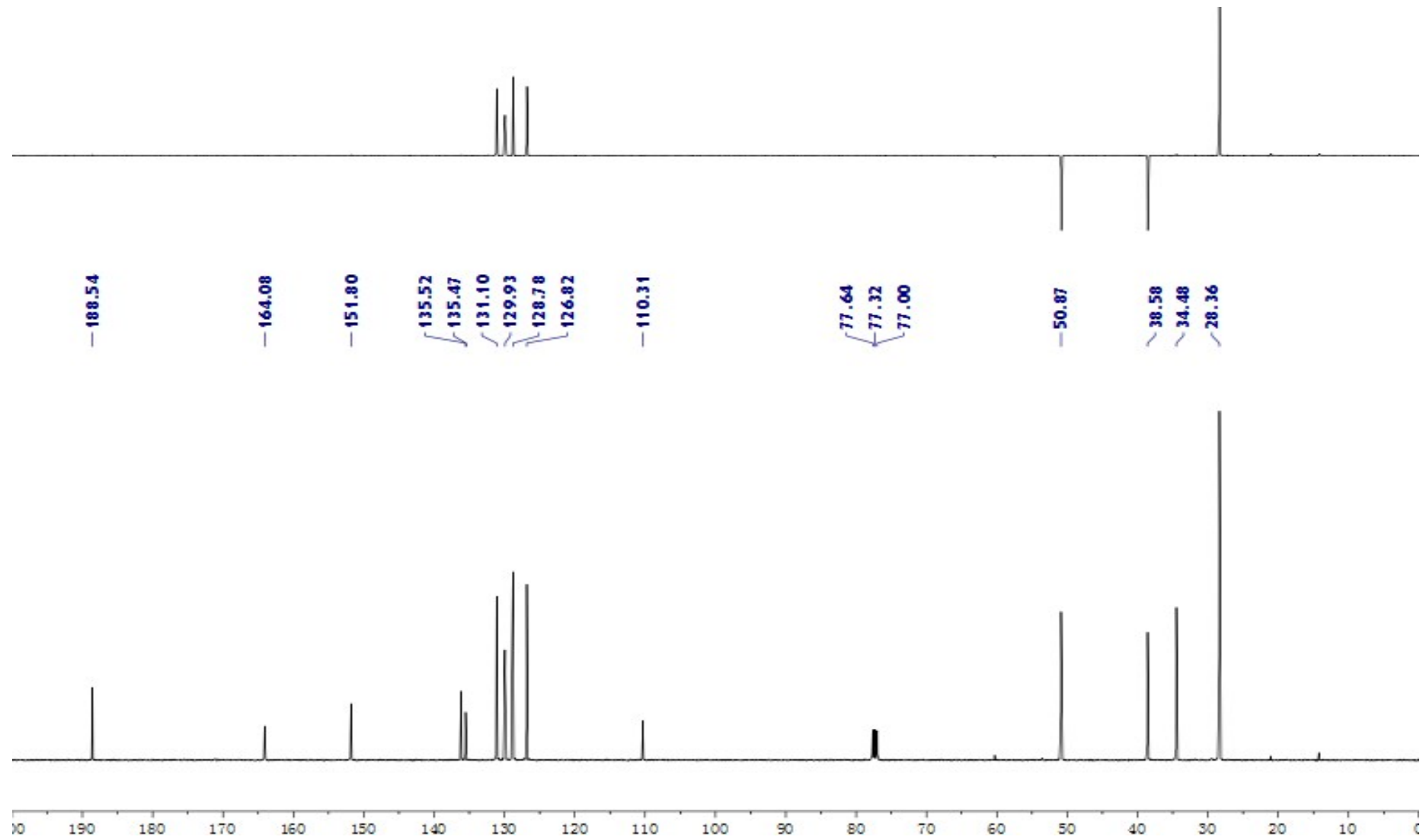


Figure 34. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **4q**

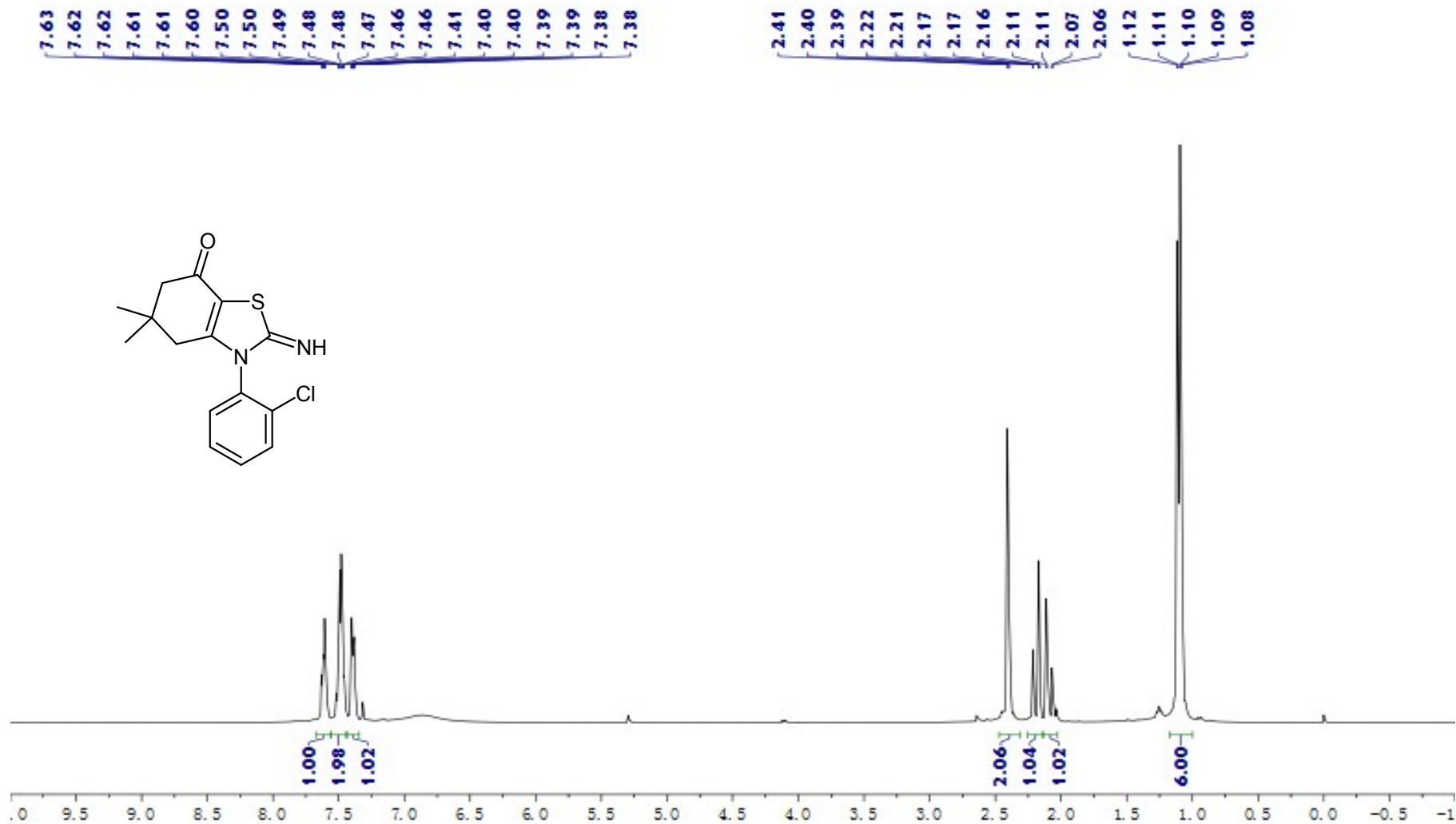


Figure 35. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4r

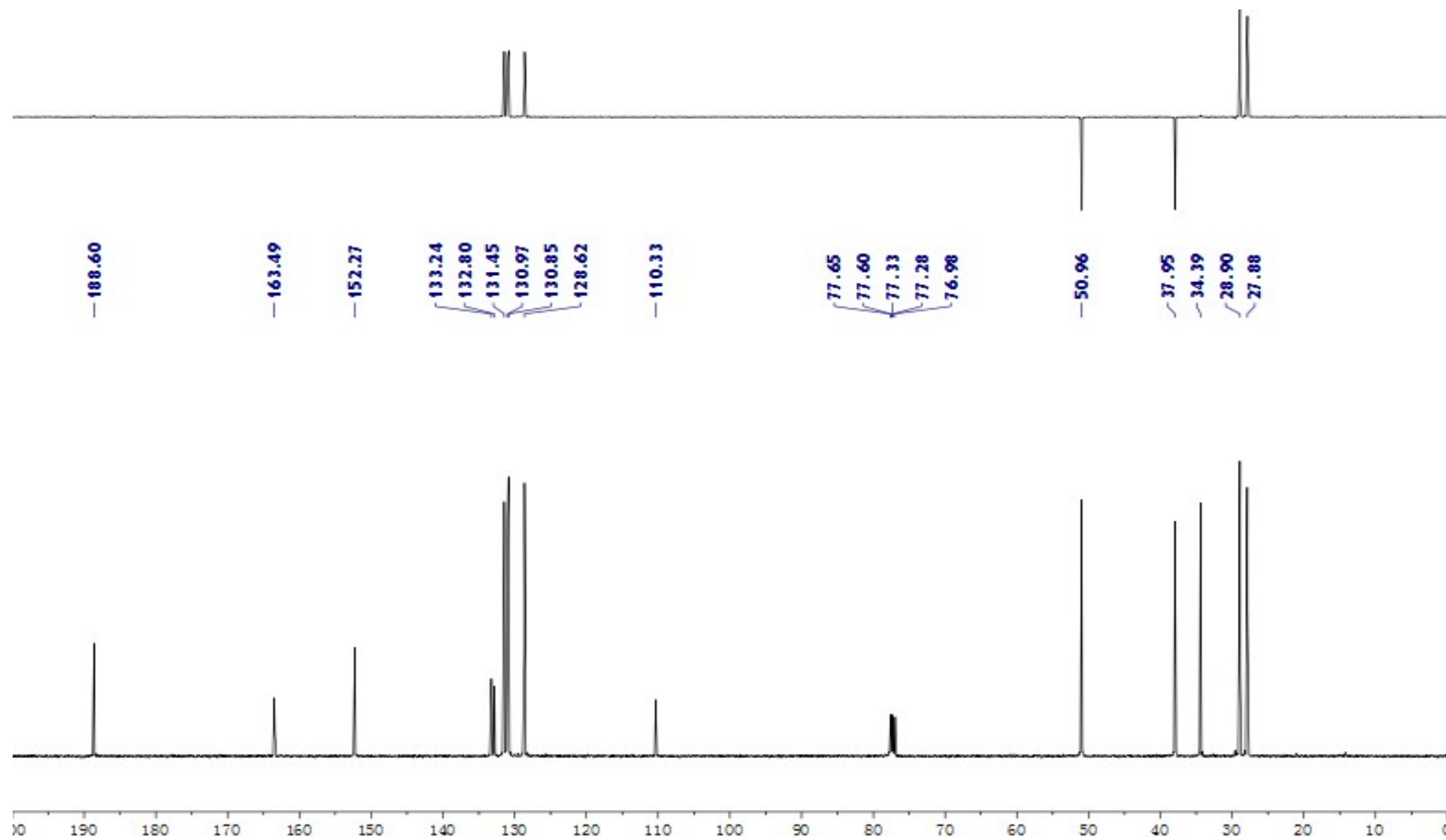


Figure 36. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **4r**

20160812 N-2 DMSO

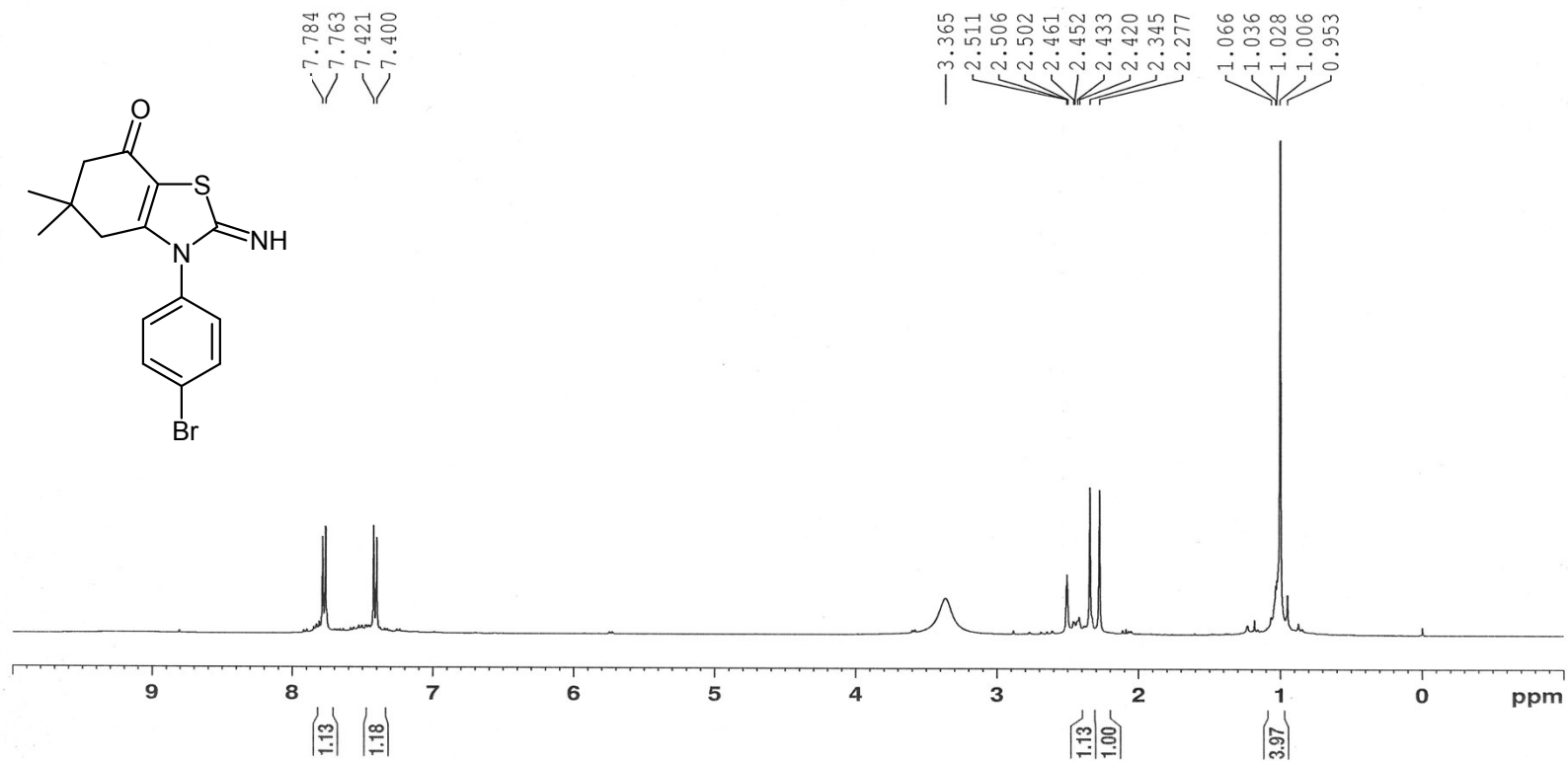


Figure 37. ¹H NMR (400 MHz, DMSO-*d*₆) spectra of compound 4s

20160812 N-2 DMSO

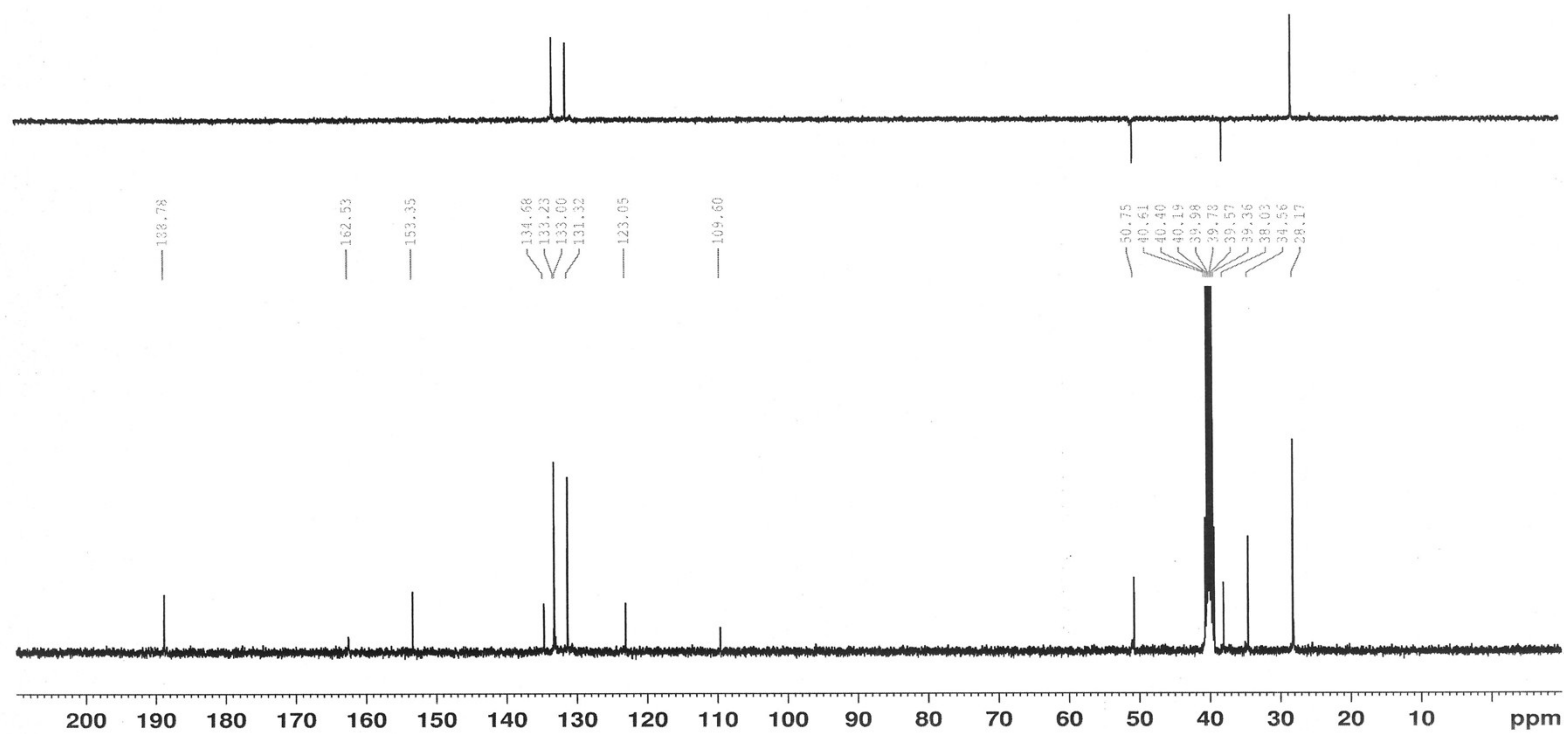


Figure 38. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) spectra of compound 4s

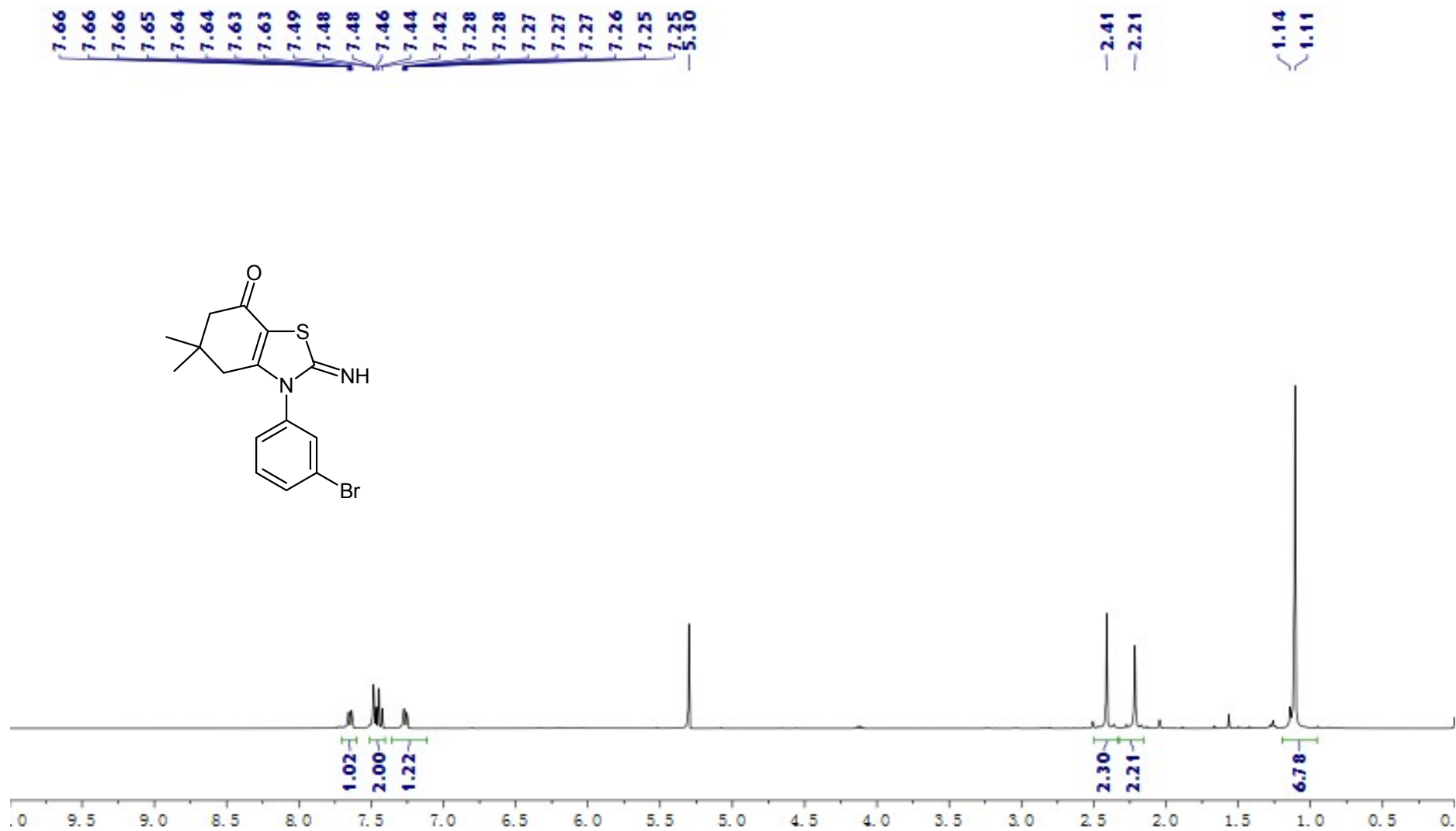


Figure 39. ^1H NMR (400 MHz, CDCl_3) spectra of compound 4t

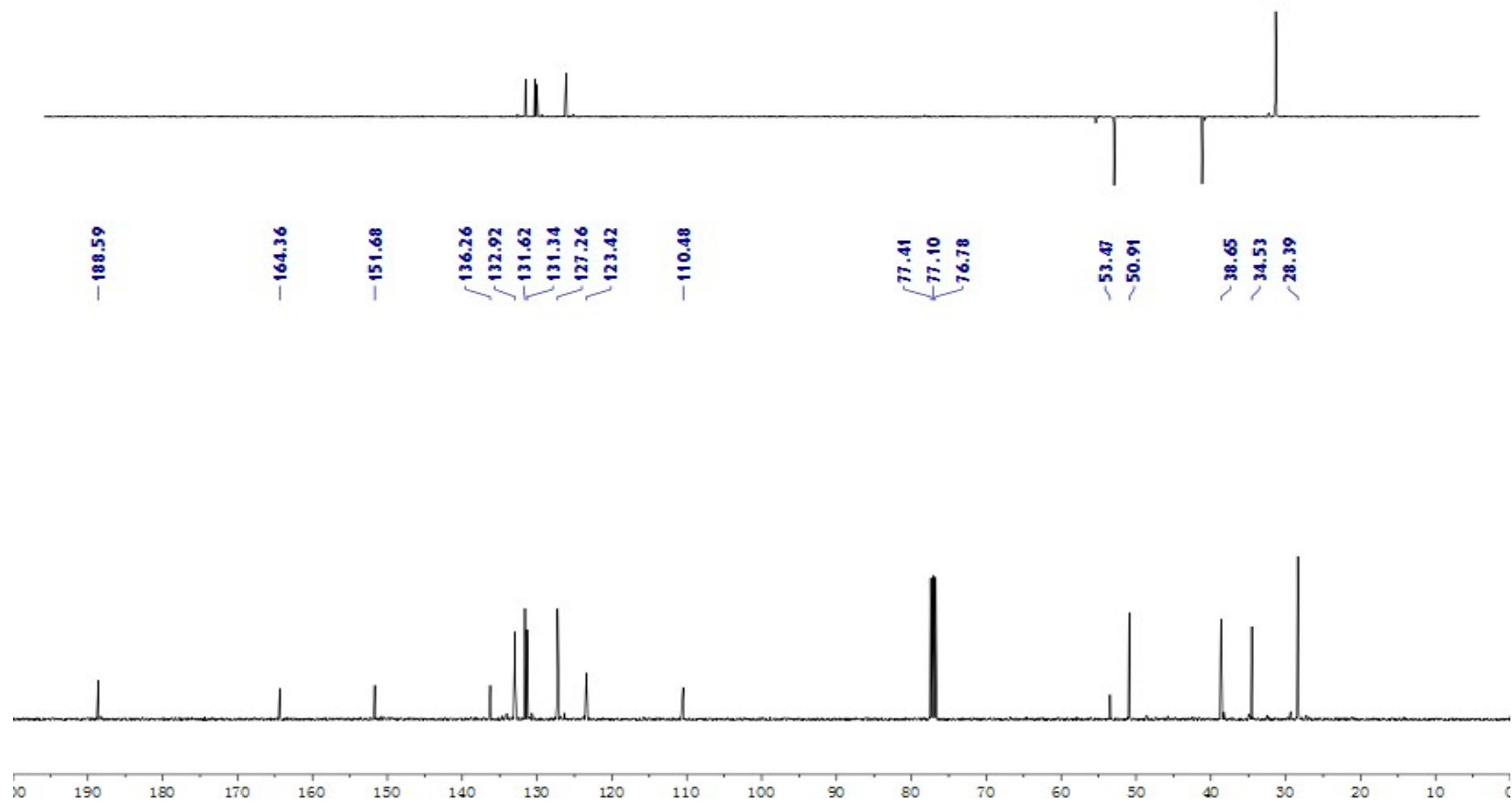


Figure 40. ^{13}C NMR (100 MHz, CDCl₃) spectra of compound **4t**

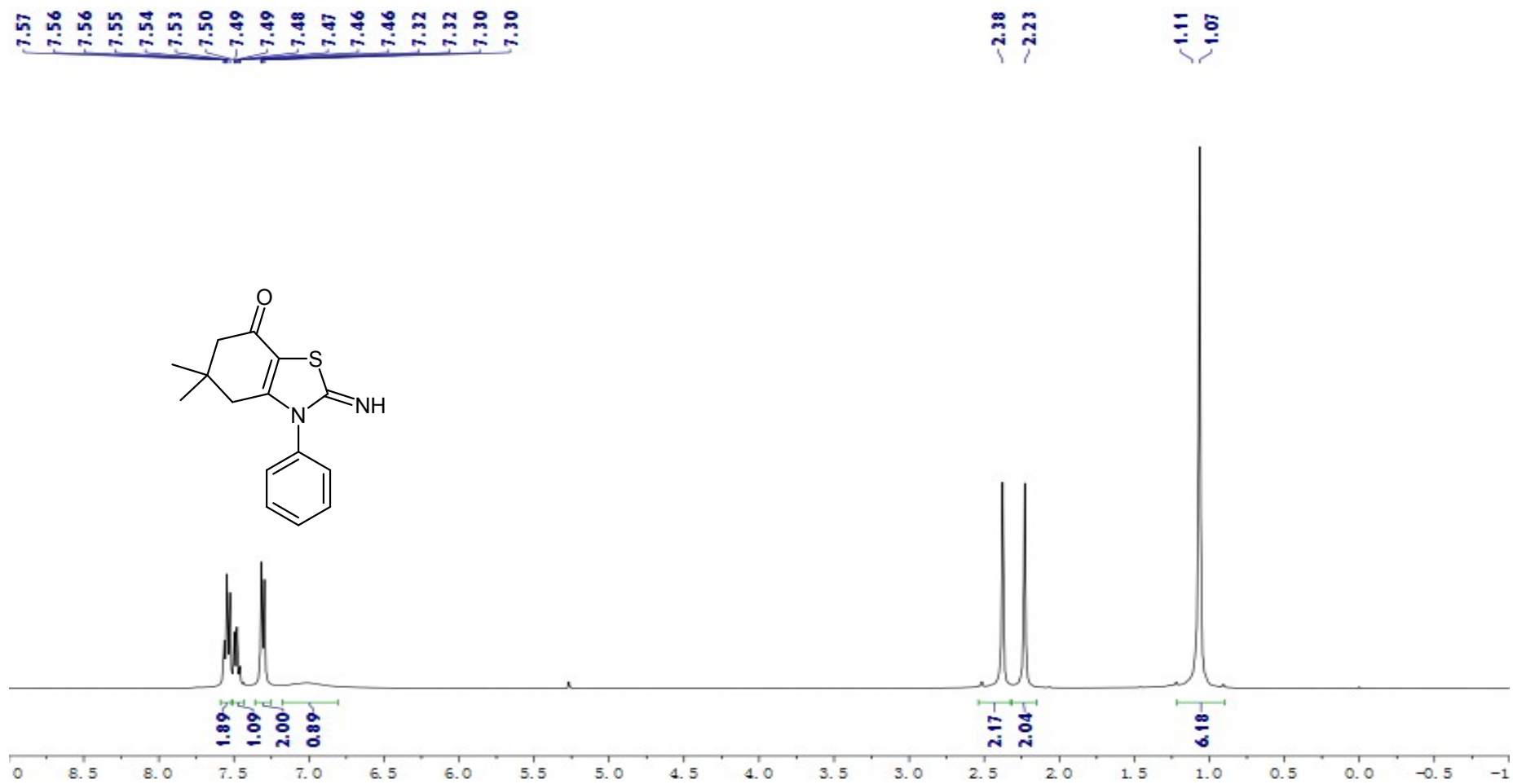


Figure 41. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4u

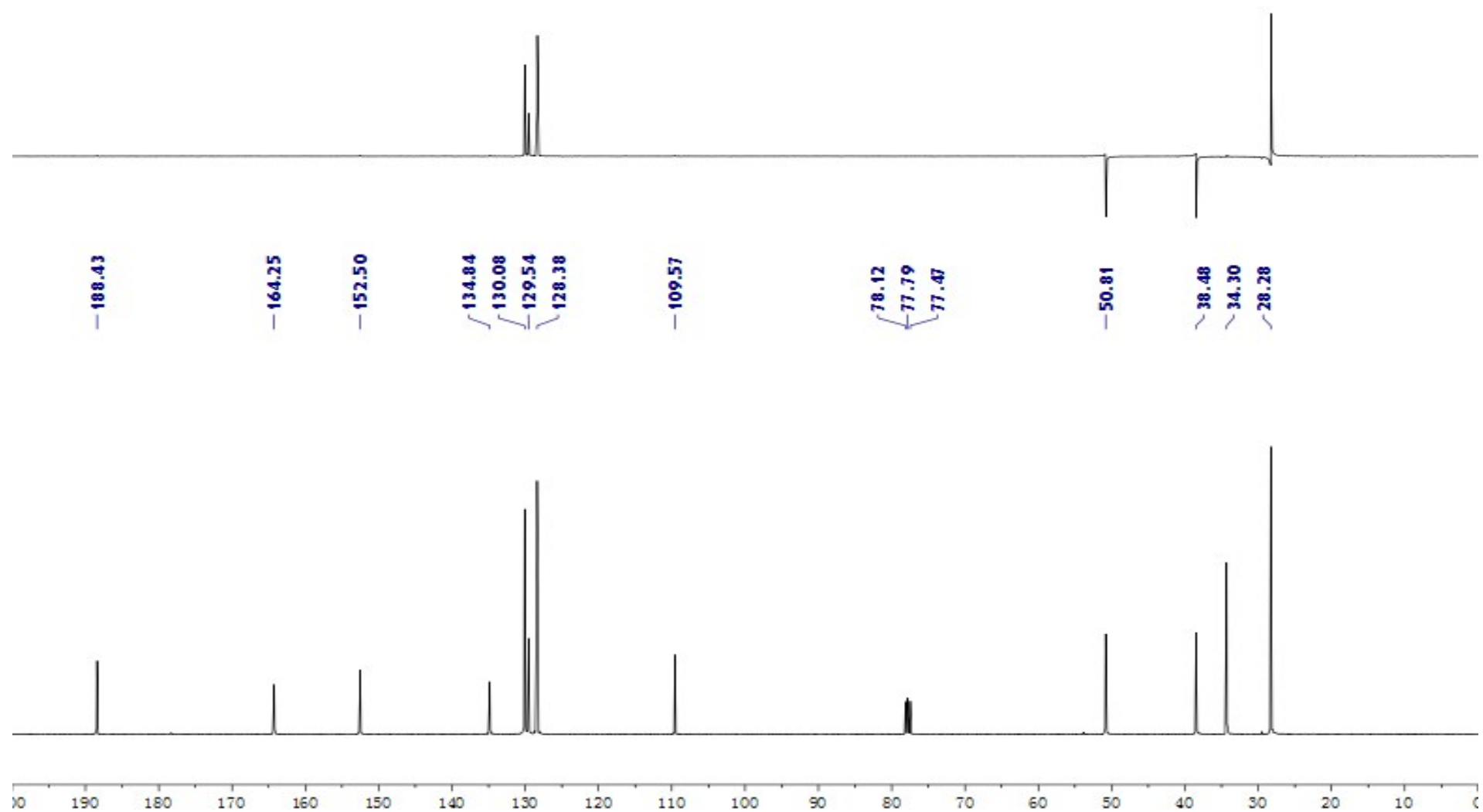


Figure 42. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **4u**

22014000178. 1. fid
N-8 CDCl3

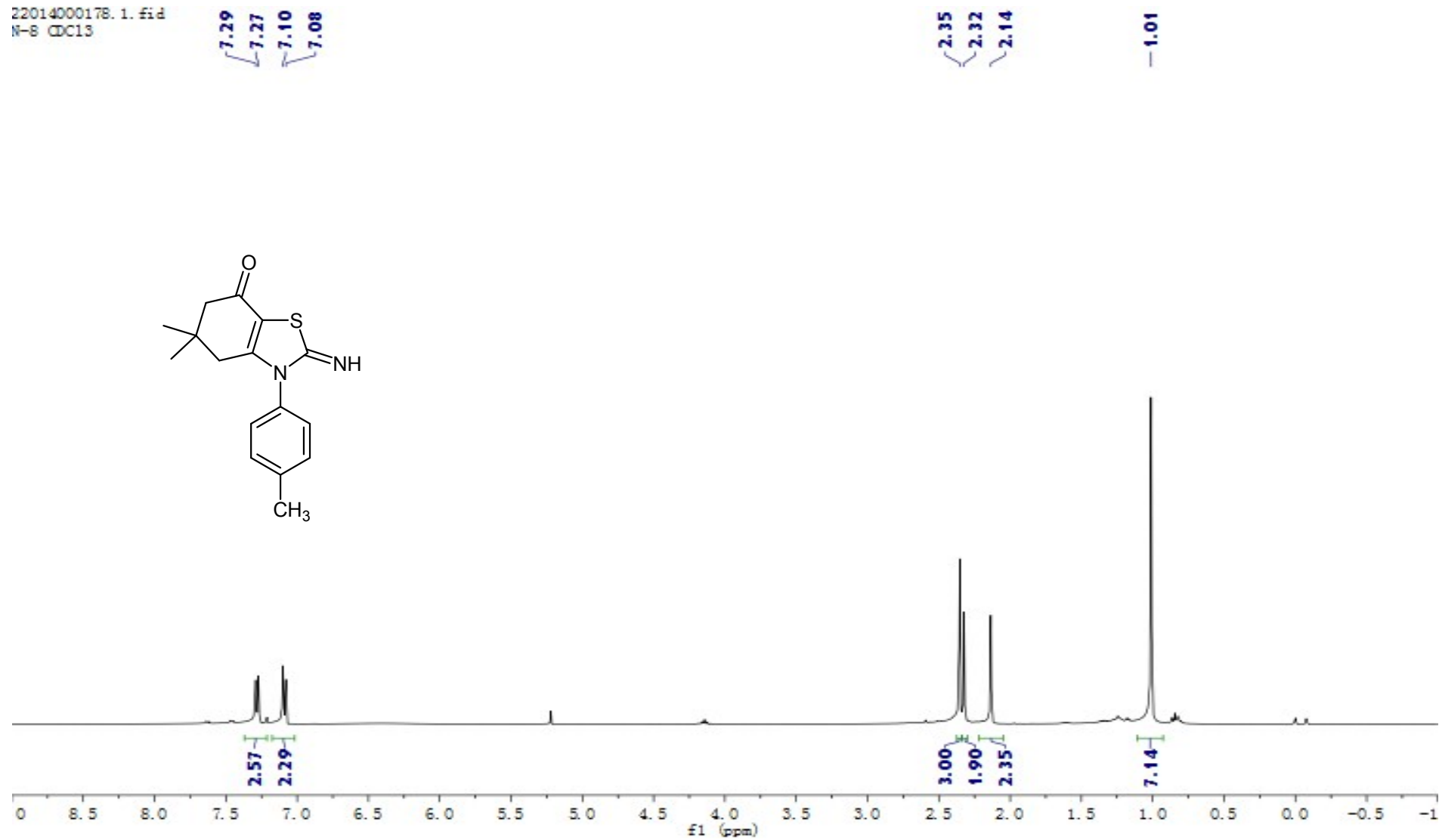


Figure 43. ^1H NMR (400 MHz, CDCl_3) spectra of compound 4v

22014000178. 3. fid
N-8 CDCl3

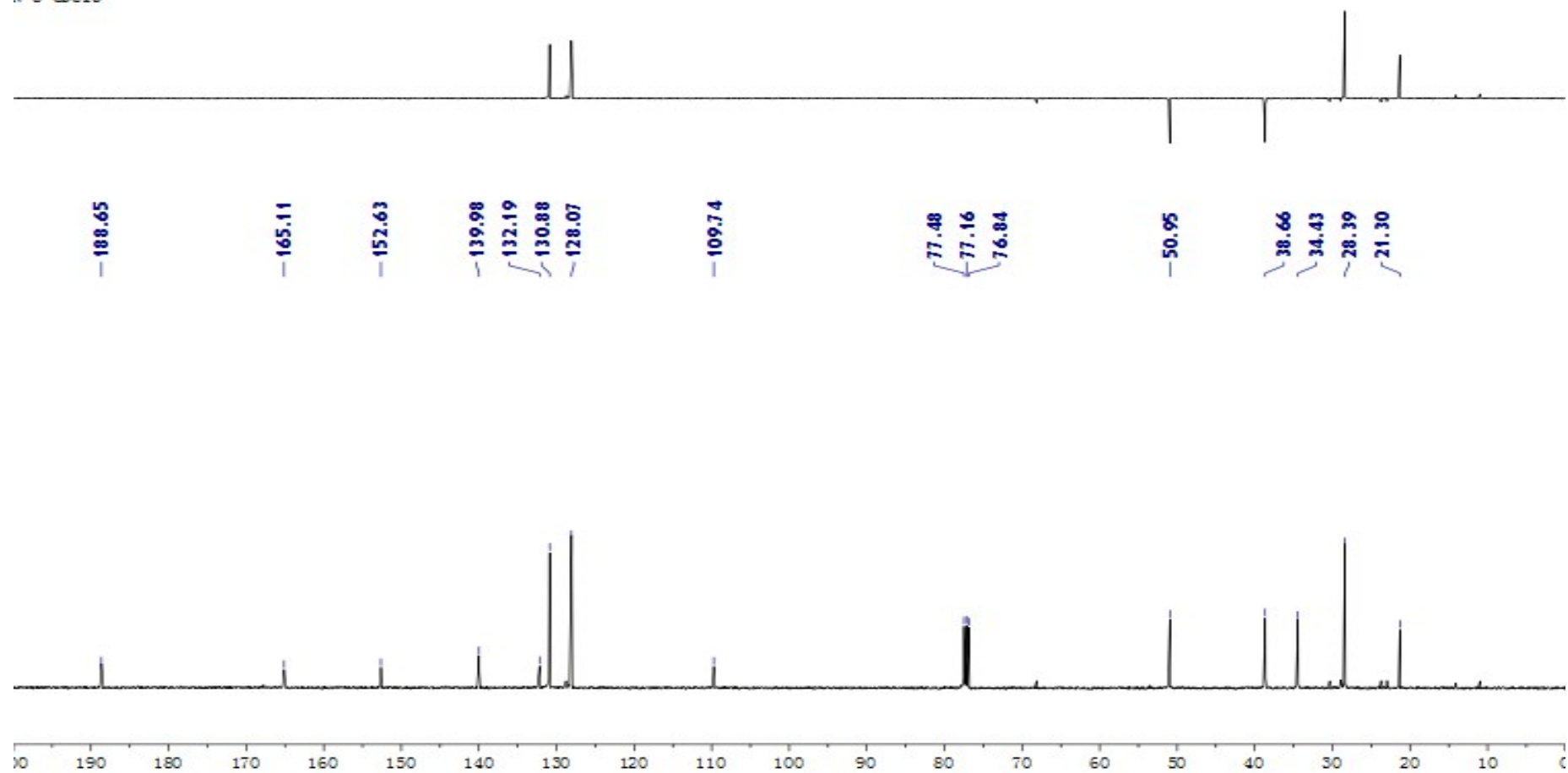


Figure 44. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **4v**

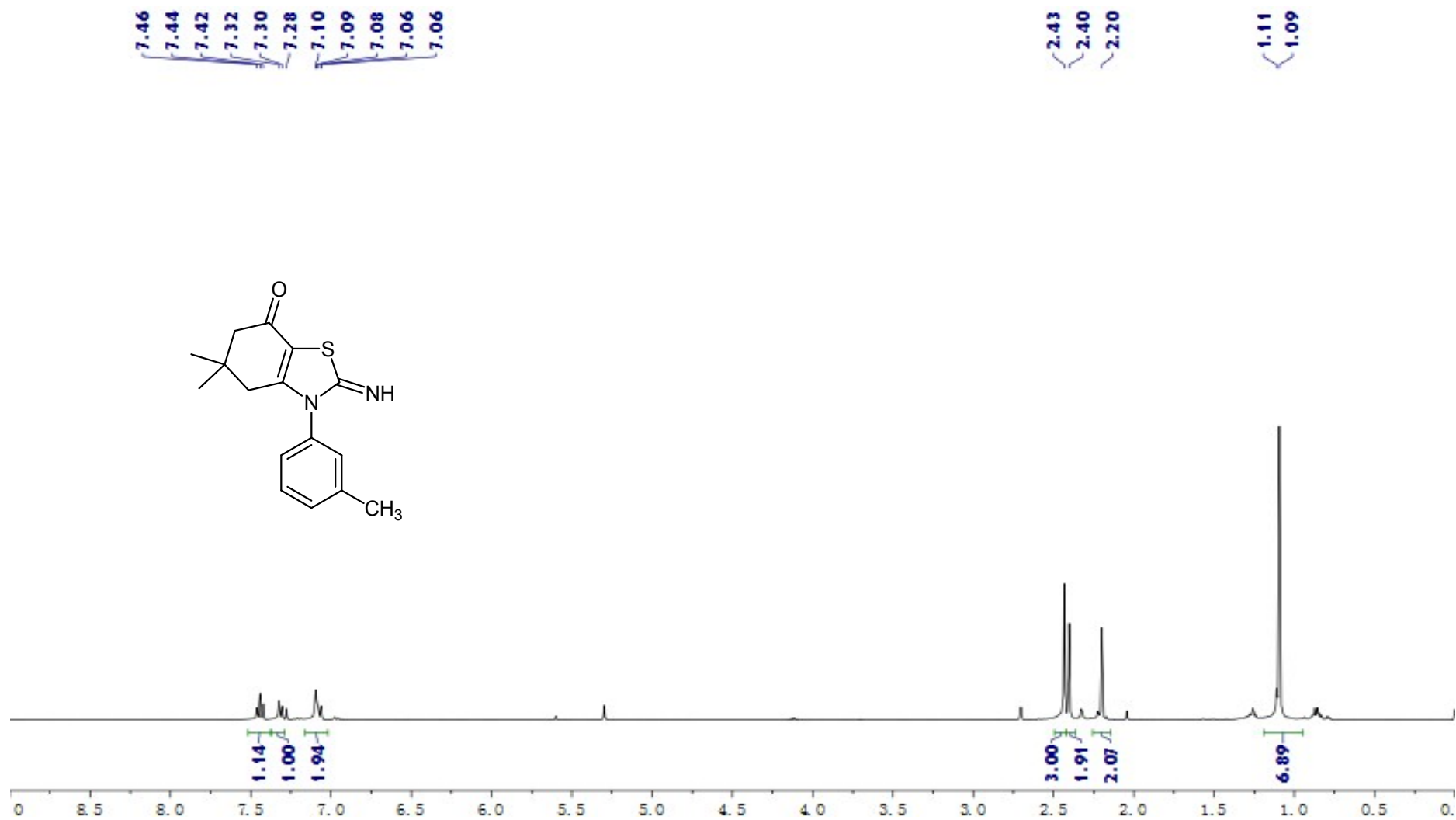


Figure 45. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4w

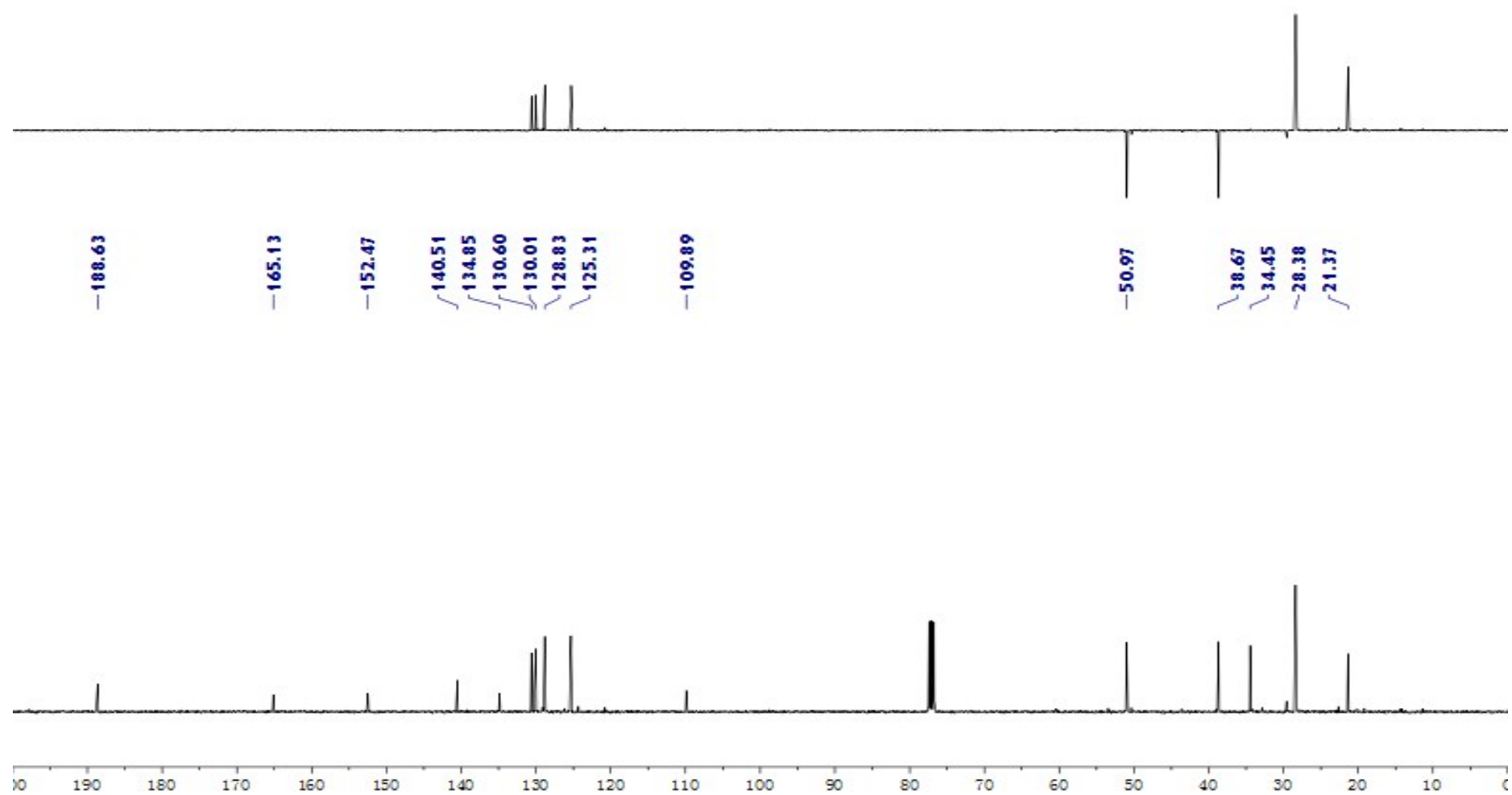


Figure 46. ¹³C NMR (100 MHz, CDCl₃) spectra of compound 4w

7-3

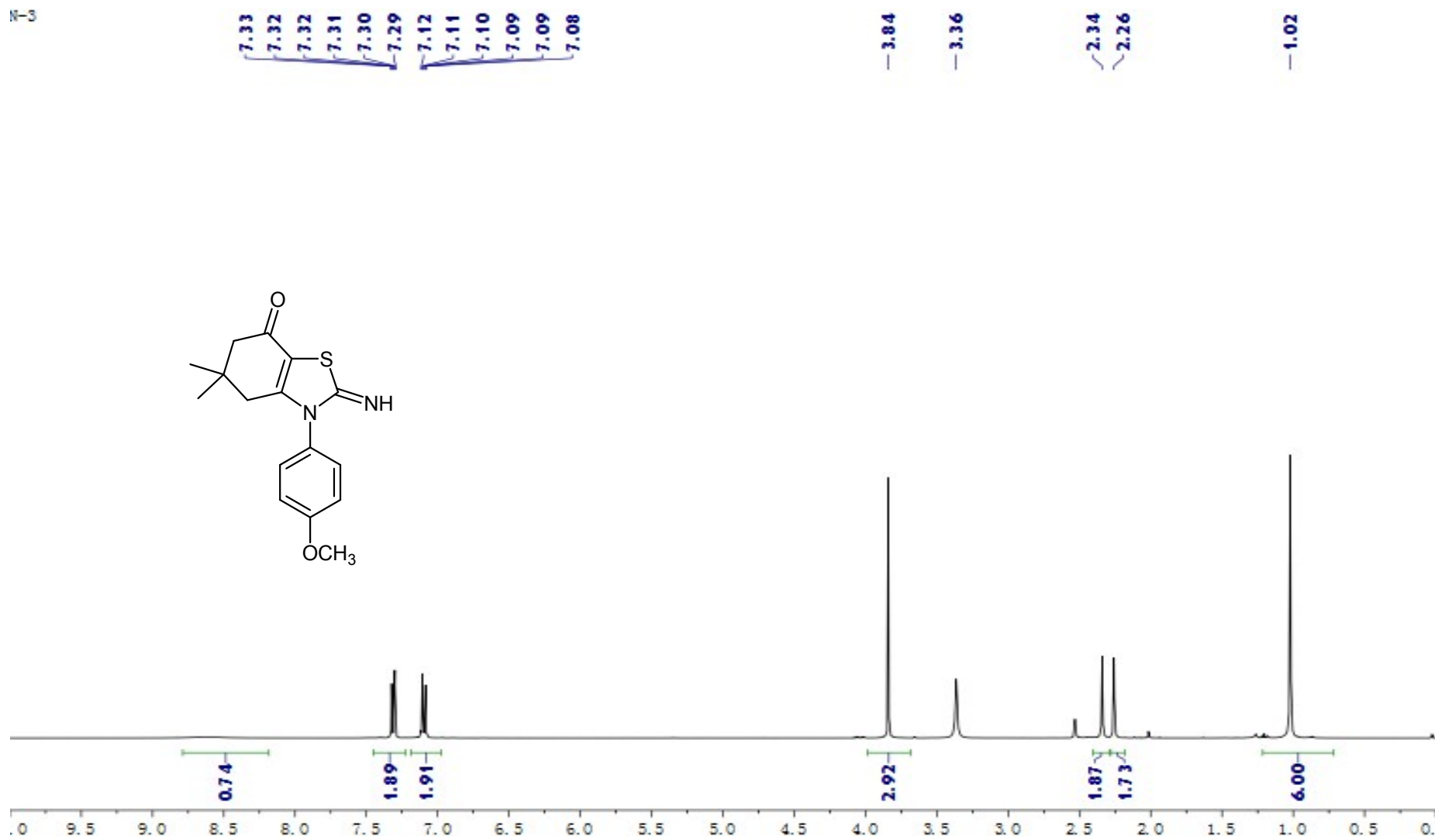


Figure 47. ¹H NMR (400 MHz, DMSO-*d*₆) spectra of compound 4x

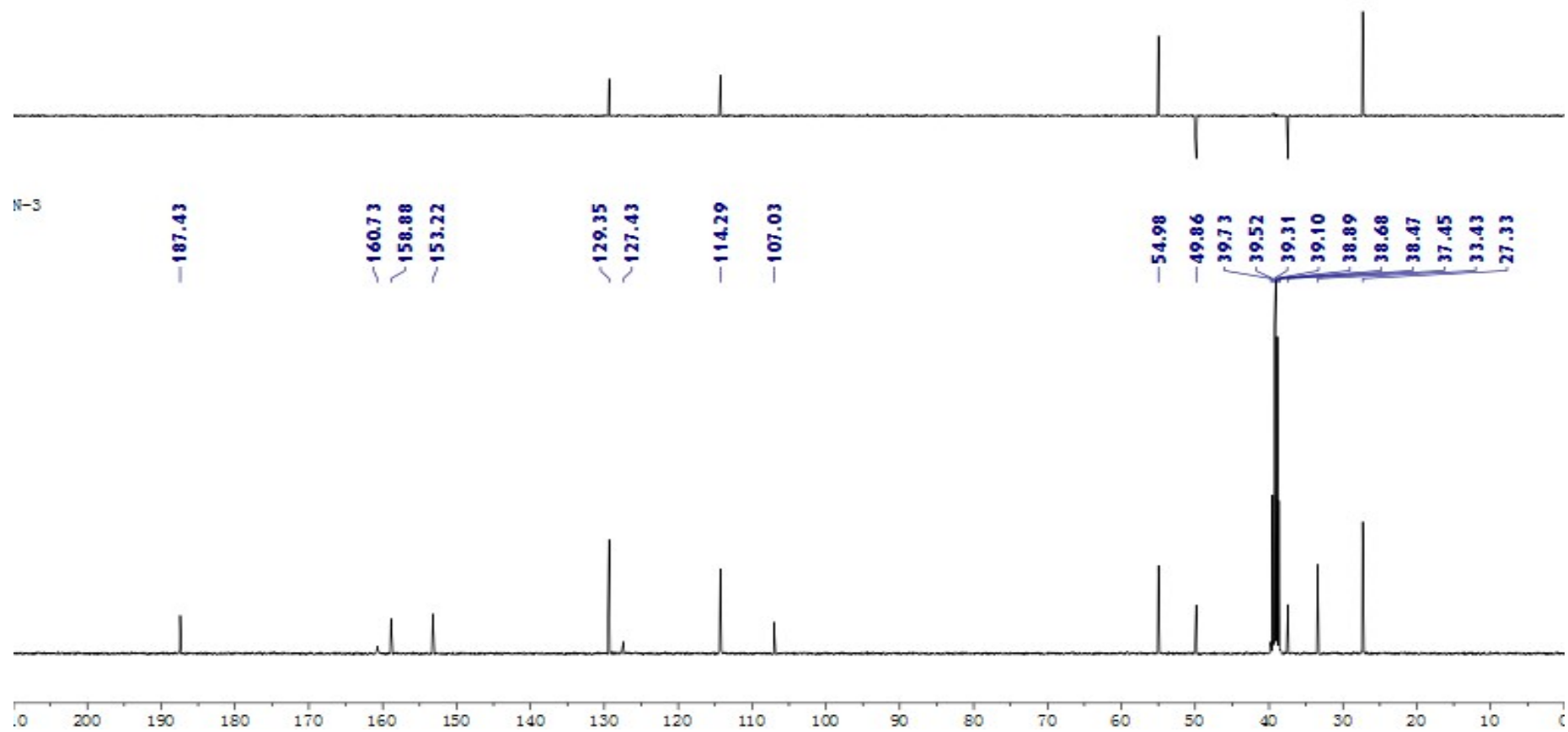


Figure 48. ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) spectra of compound **4x**

-7.29

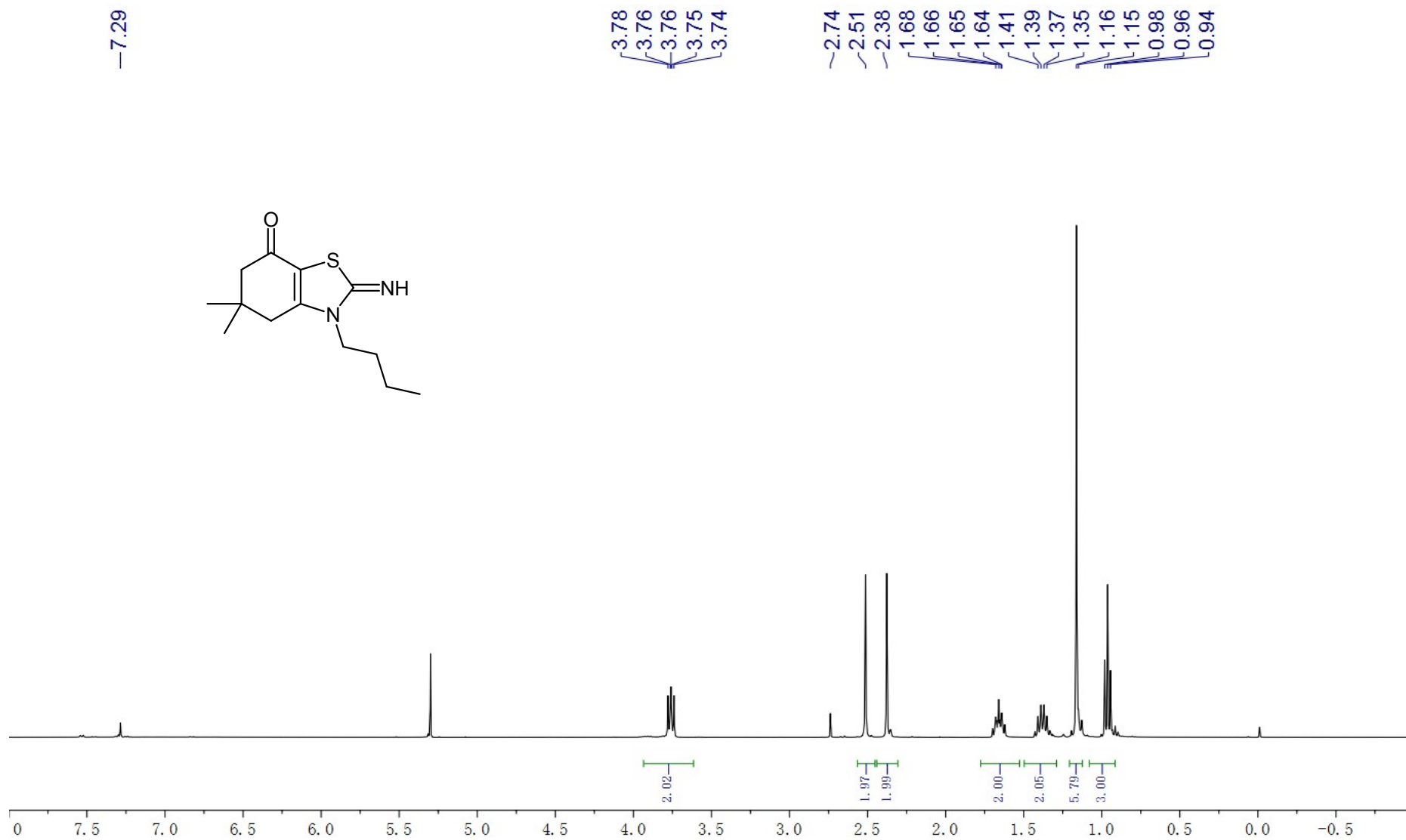


Figure 49. ¹H NMR (400 MHz, CDCl₃) spectra of compound 4y

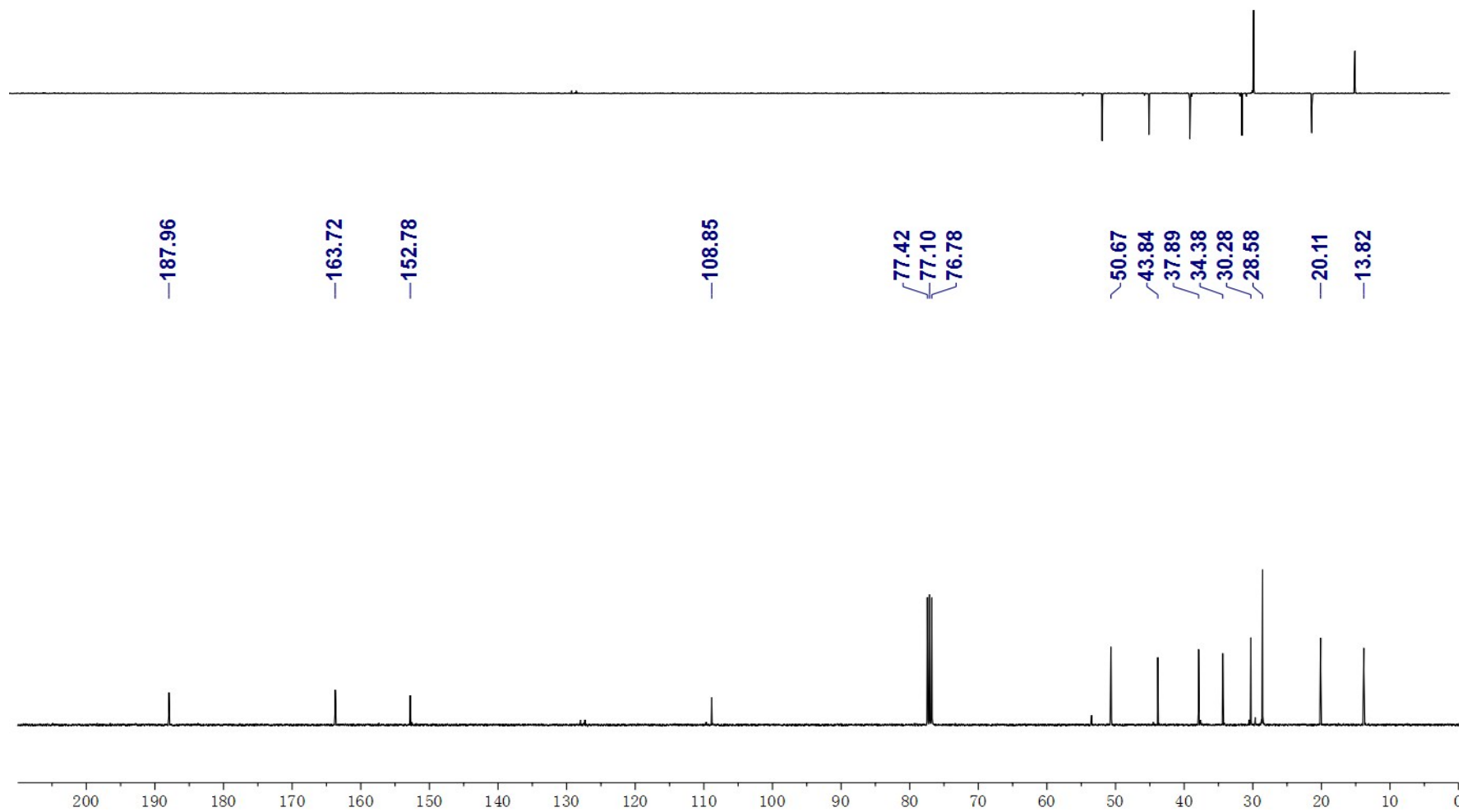


Figure 50. ¹³C NMR (100 MHz, CDCl₃) spectra of compound 4y

^1H NMR and ^{13}C NMR Spectra for α -bromo enaminone 5

N-28.10.fid

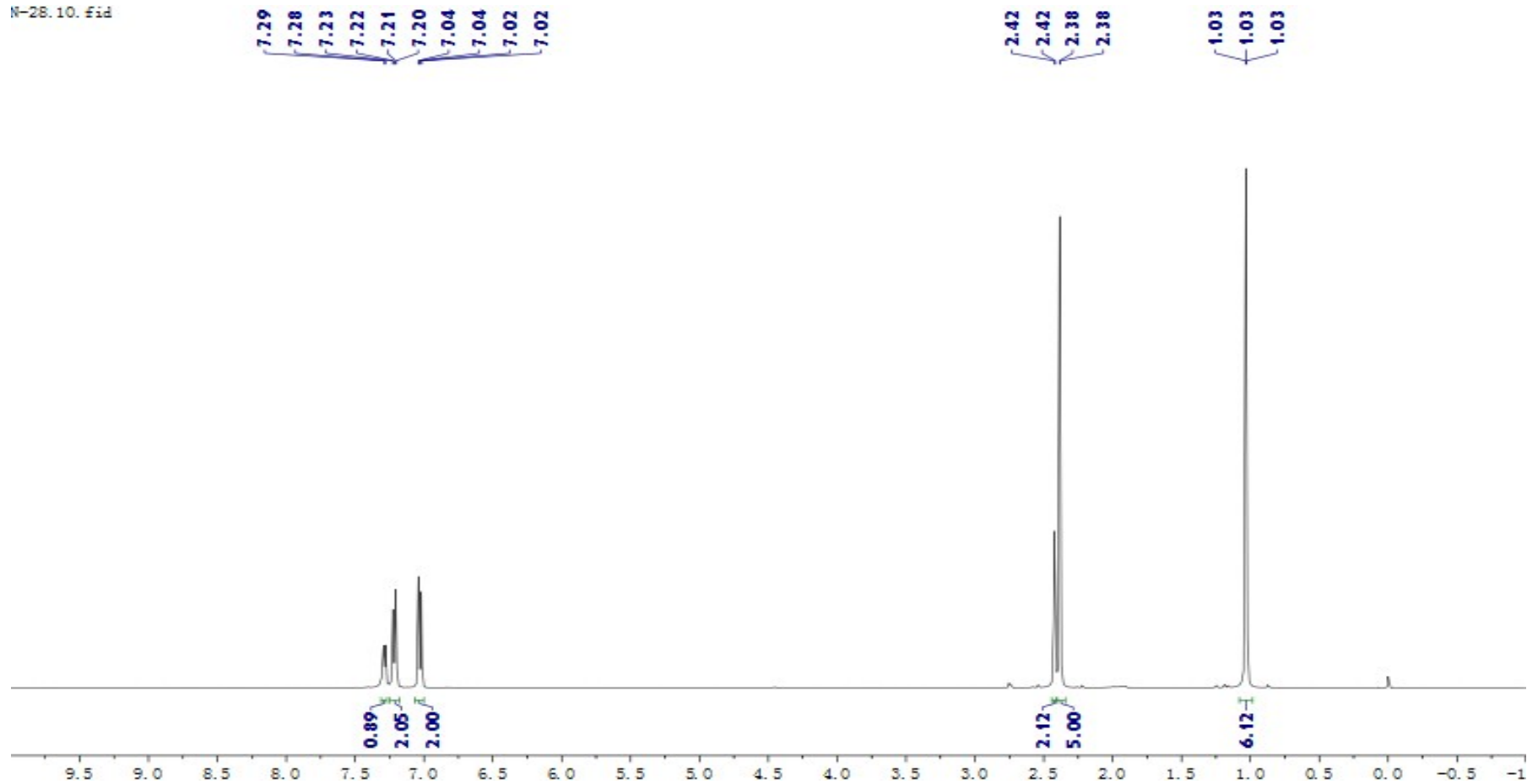


Figure 51. ^1H NMR (400 MHz, CDCl_3) spectra of compound 5v

N-28.12.fid

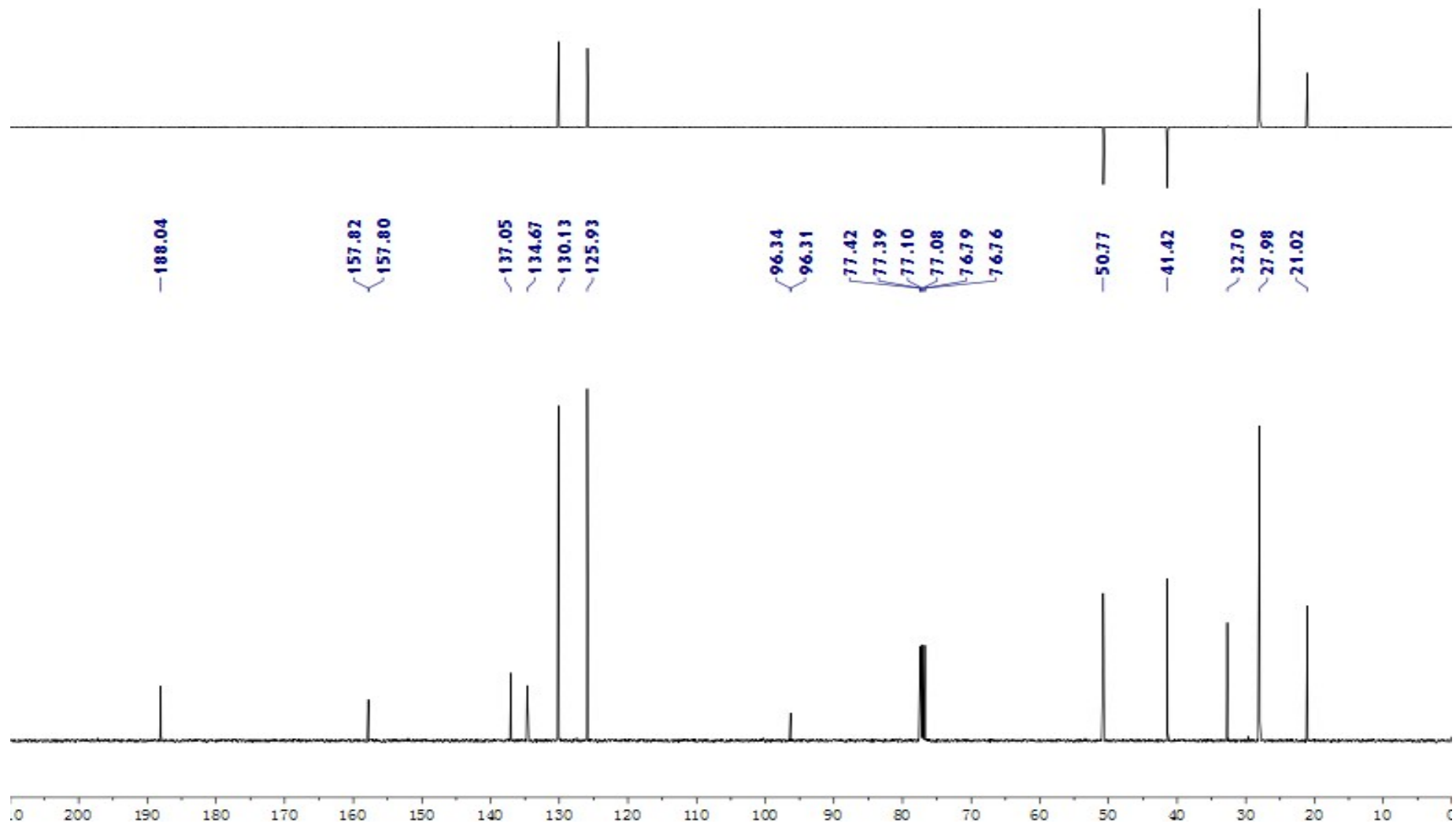


Figure 52. ^{13}C NMR (100 MHz, CDCl_3) spectra of compound **5v**