

Antimicrobial activity of new benzazolyl *N*-sulfonyl amidines

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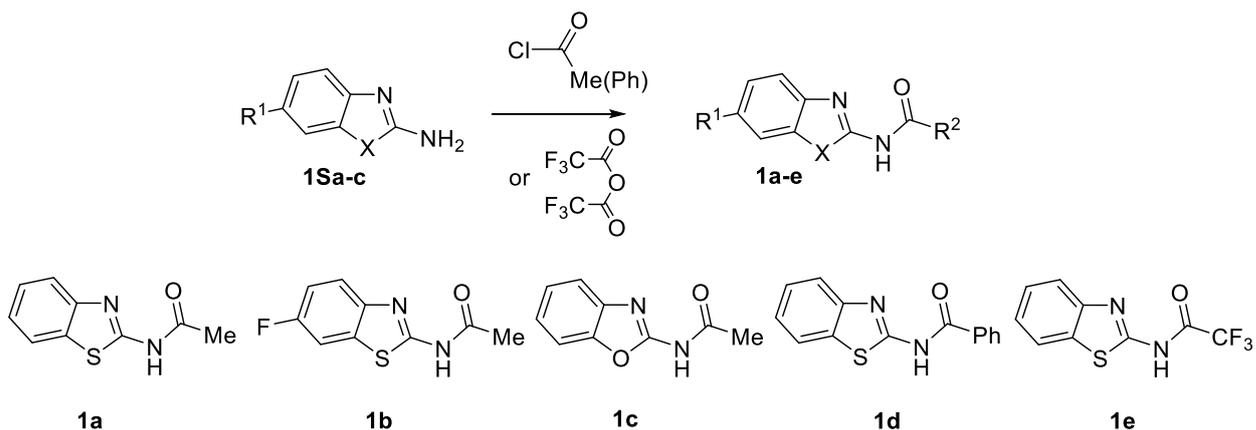
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General information

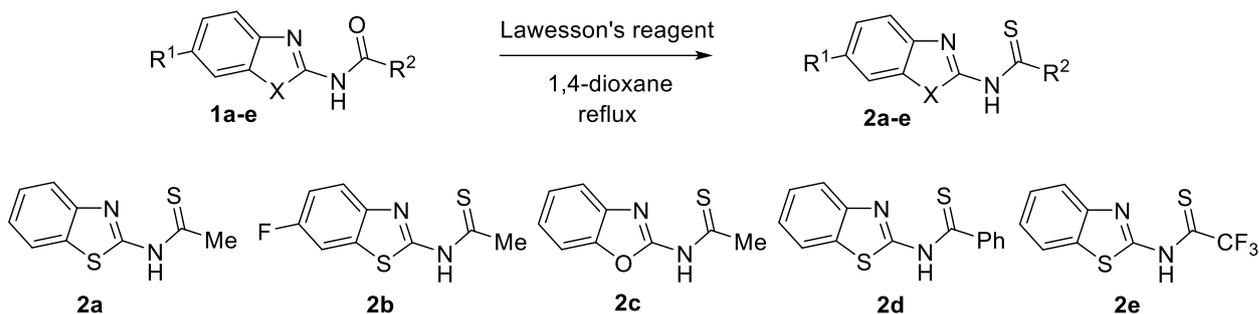
¹H and ¹³C NMR spectra were recorded at 400 or 600 and 100 or 150 MHz, respectively, with SiMe₄ as internal reference in DMSO-*d*₆, the chemical shifts (δ) were expressed in ppm, and *J* values were given in Hz. Mass spectra were recorded with Shimadzu GCMS-QP2010 Ultra instrument in electron ionization (EI) mode with direct sample introduction into the ion source. Electron energy – 70eV. The compounds were analyzed in positive ion detection mode. The IR spectra were recorded with a FT-IR ATR (attenuated total reflection, ZnSe) Bruker Alpha IR-Fur spectrometer in the 4000–400 cm⁻¹ region. Microanalyses were performed out using a CHNS/O analyser. The reactions were monitored by analytical TLC on aluminium foil plates with 0.2 mm silica gel with a fluorescent indicator visualized under UV light. All melting points were determined with a Stuart SMP3 apparatus and are uncorrected.

Preparation of amides



N-(Benzo[*d*]thiazol-2-yl)acetamide (**1a**) [S1], *N*-(6-fluorobenzo[*d*]thiazol-2-yl)acetamide (**1b**) [S2], *N*-(benzo[*d*]oxazol-2-yl)acetamide (**1c**) [S3], *N*-(benzo[*d*]thiazol-2-yl)benzamide (**1d**) [S4], *N*-(benzo[*d*]thiazol-2-yl)-2,2,2-trifluoroacetamide (**1e**) [S5] (Scheme 1) were synthesized from corresponding amines. Acetyl chloride, benzoyl chloride or trifluoroacetic anhydride were obtained as reported [S6].

Preparation of thioamides



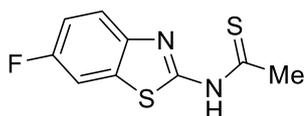
N-(Benzo[*d*]thiazol-2-yl)ethanethioamide (**2a**) [S7], *N*-(6-fluorobenzo[*d*]thiazol-2-yl)ethanethioamide (**2b**), *N*-(benzo[*d*]oxazol-2-yl)ethanethioamide (**2c**), *N*-(benzo[*d*]thiazol-2-yl)benzothioamide (**2d**) [S8] and *N*-(benzo[*d*]thiazol-2-yl)-2,2,2-trifluoroethanethioamide (**2e**) [S7] were synthesized from corresponding amide **1** by thionation with the Lawesson's reagent according to previously reported procedures [S6].

References

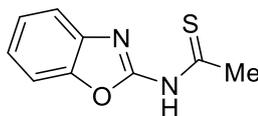
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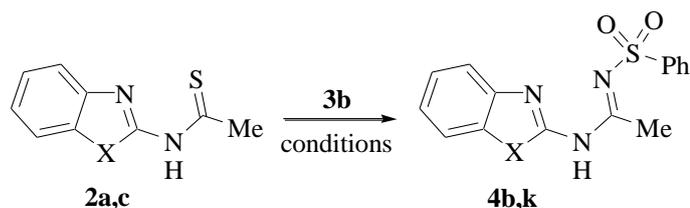
Analytical data for thioamides 2b,c



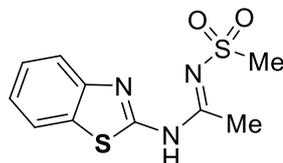
N-(6-Fluorobenzothiazol-2-yl)ethanethioamide (**2b**). Reaction time is 21 h. Light green crystals, 87% yield (984 mg), mp 205–207 °C. ¹H NMR (400 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 2.74 (3H, s, CH₃), 7.36 (1H, ddd, *J* = 9.0, 9.0, 2.3 Hz, H-Ar), 7.83 (1H, dd, *J* = 8.8, 4.8 Hz, H-Ar), 7.94 (1H, dd, *J* = 8.6, 2.4 Hz, H-Ar), 13.87 (1H, s, NH). ¹³C NMR (100 MHz, DMSO-*d*₆), δ, ppm: 34.2; 108.2 (d, *J* = 27.0 Hz); 114.8 (d, *J* = 24.0 Hz); 122.0 (d, *J* = 9.1 Hz); 131.6 (d, *J* = 10.7 Hz); 144.0; 157.8; 160.2; 200.3. MS (EI), *m/z* (%): 226 [M]⁺ (24), 168 (89), 59 [M–C₇H₄FN₂S]⁺ (100). IR (NPVO, ZnSe, ν/cm^{–1}): 1049, 1538, 3029. Found (%): C 47.77; H 3.12; N 12.38. Calcd for C₉H₇FN₂S₂ (%): C, 48.10; H, 2.90; N, 12.04.



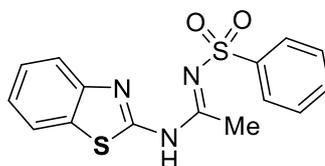
N-(Benzoxazol-2-yl)ethanethioamide (**2c**). Reaction time is 19 h. Brown crystals, 75% yield (720 mg), mp 160–165 °C. ¹H NMR (400 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 2.89 (3H, s, CH₃); 7.34–7.39 (2H, m, H-Ar); 7.66–7.69 (2H, m, H Ar); 13.10 (1H, br s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 35.0; 110.3; 118.8; 124.5; 124.8; 140.5; 147.5; 154.7; 207.6. MS (EI), *m/z* (%): 192 [M]⁺ (24), 134 [M–C₂H₃S]⁺ (100), 59 (66). IR (NPVO, ZnSe, ν/cm^{–1}): 1018, 1555, 3147. Found (%): C 56.23; H 4.19; N 14.57. Calcd for C₉H₈N₂OS (%): C, 56.16; H, 3.90; N, 14.35.

Table S1. Dependence of the yield of sulfonyl amidines **4b,k** on the reaction conditions^a

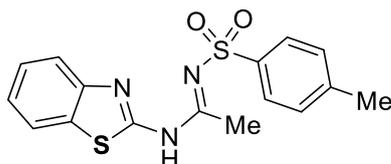
Entry	Solvent	thioamide/azide (equiv)	Yield 4b (from 2a and 3b)	Yield 4k (from 2c and 3b)
1	H ₂ O	1:2	40%	17%
2	EtOH	1:2	58%	50%
3	EtOH	1:5	20%	33%
4	neat	1:1.2	40%	33%
5	CF ₃ CH ₂ OH	1:2	0%	0%
6	<i>n</i> -BuOH	1:2	0%	2%
7	1,4-dioxane	1:2	4%	0%

^a**2a,c** (1.0 mmol), solvent (4 ml)**Analytical data for amidines 4a-t**

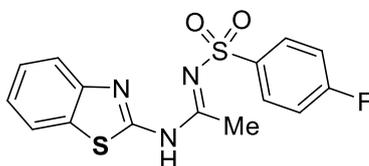
(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-*N'*-(methylsulfonyl)acetimidamide (**4a**). Reaction time is 21 h. Colorless crystals, 62% yield (167 mg), mp 181–185 °C (EtOH). ¹H NMR (400 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 2.56 (3H, s, CH₃), 3.20 (3H, s, CH₃), 7.33–7.35 (1H, t, H-Ar), 7.47–7.49 (1H, t, H-Ar), 7.79–7.80 (1H, d, H-Ar), 8.01–8.02 (1H, d, H-Ar), 12.56 (1H, s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ, ppm: 19.5 (C-CH₃), 42.8 (S-CH₃), 120.9 (C⁴), 121.7 (C⁷), 123.9 (C⁶), 126.3 (C⁵), 132.4 (C^{7a}), 148.2 (C^{3a}), 157.2 (C=S), 162.5 (C-CH₃). MS (EI), *m/z* (%): 269 [M]⁺ (45), 228 (28), 150 [M-C₃H₆NO₂S]⁺ (100), 149 (95), 105 (27), 79 (30), 56 (29), 42 (24). IR (NPVO, ZnSe, ν/cm⁻¹): 1130, 1529, 1630, 3179. Found (%): C, 44.33; H, 4.33; N, 15.94. Calcd for C₁₀H₁₁N₃O₂S₂ (%): C, 44.59; H, 4.12; N, 15.60.



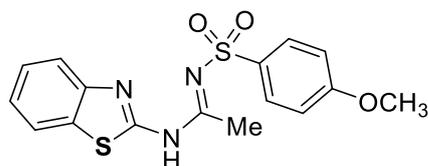
(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-*N'*-(phenylsulfonyl)acetimidamide (**4b**). Reaction time is 16 h. Colorless crystals, 53% yield (180 mg), mp 155–160 °C (EtOH). ¹H NMR (400 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 2.59 (3H, s, CH₃), 7.33 (1H, t, *J* = 8.0, H-Ar), 7.46 (1H, t, *J* = 8.0, H-Ar), 7.63–7.66 (2H, m, H-Ar), 7.69 (1H, d, *J* = 8.0, H-Ar), 7.78 (1H, d, *J* = 8.0, H-Ar), 7.95–7.98 (3H, m, H Ar), 12.70 (1H, s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ, ppm: 19.8 (CH₃), 121.0 (C⁴), 121.7 (C⁷), 124.1 (C⁶), 124.4 (C⁵), 126.3 (2C, C^{o-}), 129.2 (2C, C^{m-}), 132.5 (C^{7a}), 132.7 (C^{p-}), 142.0 (Cⁱ⁻), 148.2 (C^{3a}), 156.9 (C=S), 163.4 (C-CH₃). MS (EI), *m/z* (%): 331 [M]⁺ (14), 226 (38), 149 (54), 141 (44), 77 [M-C₉H₈N₃O₂S₂]⁺ (100). IR (NPVO, ZnSe, ν/cm⁻¹): 1149, 1590, 1612, 3244. Found (%): C, 54.73; H, 4.14; N, 12.39. Calcd for C₁₅H₁₃N₃O₂S₂ (%): C, 54.36; H, 3.95; N, 12.68;



(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-*N'*-tosylacetimidamide (**4c**). Reaction time is 19 h. Colorless crystals, 63% yield (220 mg), mp 201–205 °C (EtOH). ¹H NMR (600 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 2.40 (3H, s, Ar-CH₃), 2.57 (3H, s, CH₃), 7.32 (1H, t, *J* = 6.0, H-Ar), 7.43 (2H, d, *J* = 6.0, H-Ar), 7.46 (1H, d, *J* = 6.0, H-Ar), 7.78 (1H, d, *J* = 6.0, H-Ar), 7.84 (2H, d, *J* = 6.0, H-Ar), 7.96 (1H, d, *J* = 6.0, H-Ar), 12.68 (1H, s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ, ppm: 19.6 (CH₃), 21.0 (Ar-CH₃), 121.0 (C⁴), 121.7 (C⁷), 124.0 (C⁶), 126.4 (3C, C⁵, 2C^{o-}), 129.6 (2C, C^{m-}), 132.5 (C^{7a}), 139.2 (C^{p-}), 142.9 (Cⁱ⁻), 148.2 (C^{3a}), 156.9 (C-S), 163.0 (C-CH₃). MS (EI), *m/z* (%): 345 [M]⁺ (8), 240 (60), 149 (34), 91 [M-C₉H₈N₃O₂S₂]⁺ (100), 65 (24). IR (NPVO, ZnSe, ν/cm⁻¹): 1146, 1493, 1642, 3491. Found (%): C, 55.94; H, 4.42; N, 12.31. Calcd for C₁₆H₁₅N₃O₂S₂ (%): C, 55.63; H, 4.38; N, 12.16.

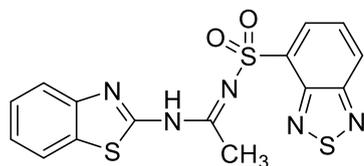


(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-*N'*-(4-fluorophenylsulfonyl)acetimidamide (**4d**). Reaction time is 19 h. Colorless crystals, yield 59% (210 mg), mp 190–194 °C (EtOH). ¹H NMR (400 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 2.60 (3H, s, CH₃), 7.33 (1H, t, *J* = 8.0, H-Ar), 7.44–7.50 (3H, m, H Ar), 7.79 (1H, d, *J* = 8.0, H-Ar), 7.97 (1H, d, *J* = 8.0, H-Ar), 8.01–8.05 (2H, m, H-Ar), 12.74 (1H, s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ, ppm (*J*, Γ_{II}): 19.8 (CH₃), 116.4 (2C, d, *J* = 22.5, C^{m-}), 121.0 (C⁴), 121.8 (C⁷), 124.1 (C⁶), 126.4 (C⁵), 129.4 (2C, d, *J* = 9.6, C^{o-}), 132.5 (C^{7a}), 138.5 (Cⁱ⁻), 148.2 (C^{3a}), 156.8 (C=S), 163.4 (C⁸), 165.0 (d, *J* = 250, C^{p-}). MS (EI), *m/z* (%): 349 [M]⁺ (18), 244 (51), 243 (32), 159 (48), 176 (75), 95 [M-C₉H₈N₃O₂S₂]⁺ (100). IR (NPVO, ZnSe, ν/cm⁻¹): 1011, 1147, 1590, 1622, 3486. Found (%): C, 51.44; H, 3.80; N, 12.32. Calcd for C₁₅H₁₂FN₃O₂S₂ (%): C, 51.56; H, 3.46; N, 12.03.

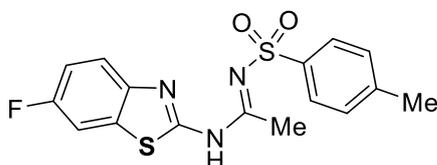


(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-*N'*-(4-methoxyphenylsulfonyl)acetimidamide (**4e**). Reaction time is 20 h. Colorless crystals, yield 62% (220 mg), mp 197–200 °C (EtOH). ¹H NMR (400

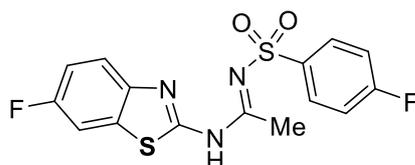
MHz, DMSO-*d*₆), δ , ppm (*J*, Hz): 2.57 (3H, s, CH₃), 3.86 (3H, s, CH₃), 7.15 (2H, d, *J* = 8.0, H-Ar), 7.32 (1H, t, *J* = 8, H-Ar), 7.46 (1H, t, *J* = 8.0, H-Ar), 7.78 (1H, d, *J* = 8.0, H-Ar), 7.89 (2H, d, *J* = 8.0, H-Ar), 7.97 (1H, d, *J* = 8.0, H-Ar), 12.62 (1H, s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ , ppm: 19.6 (CH₃), 55.7 (OCH₃), 114.3 (2C, C^{m-}), 121.0 (C⁴), 121.8 (C⁷), 124.0 (C⁶), 126.4 (C⁵), 128.6 (2C, C^{o-}), 132.5 (C^{7a}), 133.9 (Cⁱ⁻), 148.2 (C^{3a}), 156.9 (C=S), 165.3 (C^{p-}), 162.9 (C-CH₃). MS (EI), *m/z* (%): 361 [M]⁺ (4), 256 [M-C₇H₈O]⁺, 255 (25), 171 (62), 149 (30), 123 (35), 107 (71), 92 (33), 77 (61). IR (NPVO, ZnSe, ν /cm⁻¹): 1142, 1497, 2783, 2926. Found (%): C, 52.88; H, 4.47; N, 11.78. Calcd for C₁₆H₁₅N₃O₃S₂ (%): C, 53.17; H, 4.18; N, 11.63.



N'-(Benzo[*c*][1,2,5]thiadiazol-4-ylsulfonyl)-*N*-(benzo[*d*]thiazol-2-yl)acetimidamide (**4f**). Reaction time is 18 h. Colorless crystals, yield 88% (340 mg), mp 207–210 °C (EtOH). ¹H NMR (400 MHz, DMSO-*d*₆), δ , ppm (*J*, Hz): 2.76 (3H, s, CH₃), 7.25 (1H, t, *J* = 8.0, H-Ar), 7.41 (1H, t, *J* = 8.0, H-Ar), 7.74 (1H, d, *J* = 8.0, H-Ar), 7.79 (1H, d, *J* = 8.0, H-Ar), 7.92 (1H, t, *J* = 8.0, H-Ar), 8.38 (1H, d, *J* = 8.0, H-Ar), 8.42 (1H, d, *J* = 8.0, H-Ar), 12.77 (1H, br s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ , ppm: 20.1, 120.8, 121.6, 123.9, 126.2, 128.6, 128.8, 129.4, 132.5, 133.2, 148.0, 148.7, 155.0, 156.8, 164.2. MS (EI), *m/z* (%): 389 [M]⁺ (4), 285 (21), 284 [M-C₆H₅S]⁺ (100), 149 (49), 135 (70), 108 (29), 105 (25). IR (NPVO, ZnSe, ν /cm⁻¹): 1155, 1455, 1537, 3241. Found (%): C, 46.04; H, 3.20; N, 18.13. Calcd for C₁₅H₁₁N₅O₂S₃ (%): C, 46.26; H, 2.85; N, 17.98.



(*E*)-*N*-(6-Fluorobenzo[*d*]thiazol-2-yl)-*N'*-tosylacetimidamide (**4h**). Reaction time is 19 h. Colorless crystals, yield 49% (180 mg), mp 213–215 °C (EtOH). ¹H NMR (600 MHz, DMSO-*d*₆), δ , ppm (*J*, Hz): 2.40 (3H, s, CH₃), 2.56 (3H, s, CH₃), 7.31 (1H, ddd, *J* = 9.1, 9.1, 2.7, H-Ar), 7.44 (2H, d, *J* = 8.0, H-Ar), 7.79 (1H, dd, *J* = 8.0, *J* = 4.0, H-Ar), 7.80 (2H, dd, *J* = 8.8, 4.7, H-Ar), 7.90 (1H, dd, *J* = 8.7, *J* = 2.6, H-Ar), 12.69 (1H, s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ , ppm (*J*, Hz): 19.5 (CH₃), 21.0 (C-CH₃-Ar), 108.2 (d, *J* = 27.0, C⁷), 114.6 (d, *J* = 16.5, C⁵), 122.2 (d, *J* = 9.0, C⁴), 126.3 (2C, C^{o-}), 129.6 (2C, C^{m-}), 133.8 (d, *J* = 12.0, C^{7a}), 139.1 (Cⁱ⁻), 142.9 (C^{p-}), 144.9 (C^{3a}), 156.9 (C=S), 158.8 (d, *J* = 249.0, C⁶), 163.2 (C-CH₃). MS (EI), *m/z* (%): 363 [M]⁺ (6), 258 (40), 257 (20), 167 (24), 155 (39), 91 [M-C₉H₇FN₃O₂S₂]⁺ (100), 65 (22). IR (NPVO, ZnSe, ν /cm⁻¹): 1015, 1149, 1598, 1625, 3500. Found (%): C, 53.16; H, 3.72; N, 11.87. Calcd for C₁₆H₁₄FN₃O₂S (%): C, 52.88; H, 3.88; N, 11.56.

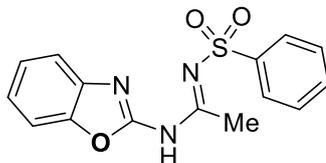


(*E*)-*N*-(6-Fluorobenzo[*d*]thiazol-2-yl)-*N'*-(4-fluorophenylsulfonyl)acetimidamide (**4i**). Reaction time is 19 h. Colorless crystals, yield 55% (150 mg), mp 132–135 °C (EtOH). ¹H NMR (600 MHz, DMSO-*d*₆), δ , ppm (*J*, Hz): 2.58 (3H, s, CH₃), 7.31 (1H, ddd, *J* = 9.0, 9.0, 2.0, H-Ar),

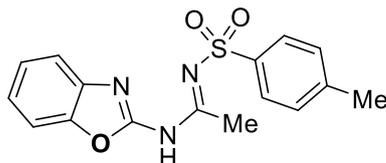
7.46–7.49 (2H, m, H-Ar), 7.81 (1H, dd, $J = 8.0, 4.0$, H-Ar), 7.90 (1H, dd, $J = 6.7, 2.3$, H-Ar), 8.01–8.03 (2H, m, H-Ar), 12.77 (1H, s, NH). ^{13}C NMR (150 MHz, DMSO- d_6), δ , ppm (J , Hz): 19.7 (CH₃), 108.2 (d, $J = 25.5$, C⁷), 114.7 (d, $J = 24.0$, C⁵), 116.4 (2C, d, $J = 22.8$, C^{m-}), 122.3 (C⁴), 129.4 (2C, d, $J = 9.7$, C^{o-}), 133.8 (d, $J = 11.0$, C^{7a}), 138.3 (d, $J = 2.9$, Cⁱ⁻), 144.9 (C^{3a}), 156.8 (C=S), 159.8 (d, $J = 166$, C⁶), 163.5 (C-CH₃), 165.2 (d, $J = 249.0$, C^{p-}). MS (EI), m/z (%): 367 [M]⁺ (15), 262 (37), 167 (52), 159 (54), 123 (22), 95 [M-C₉H₇FN₃O₂S₂]⁺ (100), 75 (18). IR (NPVO, ZnSe, ν/cm^{-1}): 1147, 1192, 1493, 1689, 3349. Found (%): C, 48.95; H, 3.22; N, 11.46. Calcd for C₁₅H₁₁F₂N₃O₂S₂ (%): C, 49.04; H, 3.02; N, 11.44.



(*E*)-*N*-(Benz[*d*]oxazol-2-yl)-*N'*-(methylsulfonyl)acetimidamide (**4j**). Reaction time is 10 h. Colorless crystals, yield 71% (180 mg), mp 148–150 °C (EtOH). ^1H NMR (400 MHz, DMSO- d_6), δ , ppm (J , Hz): 2.60 (3H, s, C-CH₃), 3.15 (3H, s, S-CH₃), 7.29–7.35 (2H, m, H-Ar), 7.60–7.63 (2H, m, H-Ar), 11.85 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO- d_6), δ , ppm: 19.7 (C-CH₃), 42.1 (S-CH₃), 109.9 (C⁷), 118.2 (C⁴), 123.8 (C⁶), 124.3 (C⁵), 140.6 (C^{3a}), 147.8 (C^{7a}), 154.7 (C²), 164.8 (C⁸). MS (EI), m/z (%): 253 [M]⁺ (27), 212 (26), 134 [M-C₃H₆NO₂S]⁺ (100), 133 (70), 105 (40), 79 (28), 56 (26), 42 (30). IR (NPVO, ZnSe, ν/cm^{-1}): 1132, 1565, 1648, 3100. Found (%): C, 47.55; H, 4.51; N, 16.58. Calcd for C₁₀H₁₁N₃O₃S (%): C, 47.42; H, 4.38; N, 16.59.

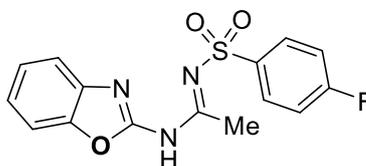


(*E*)-*N*-(Benz[*d*]oxazol-2-yl)-*N'*-(phenylsulfonyl)acetimidamide (**4k**). Reaction time is 9 h. Colorless crystals, yield 50% (78 mg), mp 170–172 °C (EtOH). ^1H NMR (600 MHz, DMSO- d_6), δ , ppm (J , Hz): 2.69 (3H, s, CH₃), 7.32 (2H, t, $J = 6.0$, H-Ar), 7.61–7.64 (3H, m, H-Ar), 7.66 (2H, d, $J = 6.0$, H-Ar), 7.99 (2H, d, $J = 6.0$, H-Ar), 12.15 (1H, br s, NH). ^{13}C NMR (150 MHz, DMSO- d_6 + Sc₂CO₃), δ , ppm: 20.6 (C⁹), 109.9 (C⁷), 118.3 (C⁴), 123.8 (C⁶), 124.4 (C⁵), 126.2 (2C, C¹¹, C¹⁵), 128.9 (C¹²), 129.0 (C¹⁴), 132.3 (C¹³), 140.8 (C^{3a}), 142.4 (C¹⁰), 147.8 (C^{7a}), 156.2 (C²), 165.8 (C⁸). MS (EI), m/z (%): 315 [M]⁺ (13), 210 (23), 141 (47), 133 (61), 105 (29), 78 (21), 77 [M-C₉H₈N₃O₃S]⁺ (100), 51 (24). IR (NPVO, ZnSe, ν/cm^{-1}): 1152, 1591, 1649, 3104. Found (%): C, 56.87; H, 4.26; N, 13.28. Calcd for C₁₅H₁₃N₃O₃S (%): C, 57.13; H, 4.16; N, 13.33.

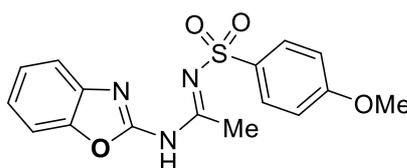


(*E*)-*N*-(Benz[*d*]oxazol-2-yl)-*N'*-tosylacetimidamide (**4l**). Reaction time is 19 h. Colorless crystals, yield 40% (220 mg), mp 198–200 °C (EtOH). ^1H NMR (400 MHz, DMSO- d_6), δ , ppm (J , Hz): 2.39 (3H, s, Ar-CH₃), 2.66 (3H, s, CH₃), 7.27–7.35 (2H, m, H-Ar), 7.42 (2H, d, $J = 8.0$, H-Ar), 7.61 (2H, d, $J = 4.0$, H-Ar), 7.86 (2H, d, $J = 8.0$, H-Ar), 12.07 (1H, s, NH). ^{13}C NMR (100 MHz, DMSO- d_6), δ , ppm: 20.5 (CH₃), 21.4 (Ar-CH₃), 110.6 (C⁷), 119.1 (C⁴), 124.6 (C⁶),

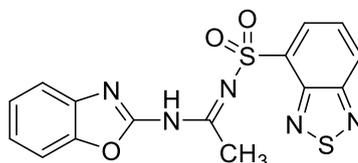
125.1 (C⁵), 126.7 (2C, C^o), 129.9 (2C, C^m), 140.0 (C¹⁰), 141.0 (C^{3a}), 143.2 (C^p), 148.2 (C^{7a}), 154.7 (C–O), 166.1 (C–CH₃). MS (EI), *m/z* (%): 329 [M]⁺ (13), 224 (44), 155 (55), 133 (47), 105 (24), 91 [M–C₉H₈N₃O₃S]⁺ (100), 65 (21). IR (NPVO, ZnSe, *v*/cm⁻¹): 1151, 1437, 1637, 3093. Found (%): C, 58.59; H, 4.65; N, 12.55. Calcd for C₁₆H₁₅N₃O₃S (%): C, 58.35; H, 4.59; N, 12.76.



(*E*)-*N*-(Benz[*d*]oxazol-2-yl)-*N'*-(4-fluorophenylsulfonyl)acetimidamide (**4m**). Reaction time is 14 h. Colorless crystals, yield 61% (203 mg), mp 181–185 °C (EtOH). ¹H NMR (600 MHz, DMSO-*d*₆), δ , ppm (*J*, Hz): 2.67 (3H, s, CH₃); 7.32 (2H, t, *J* = 6.0, H-Ar), 7.47 (2H, t, *J* = 6.0, H-Ar), 7.63 (2H, s, H-Ar), 8.03–8.12 (2H, m, H-Ar), 12.20 (1H, br s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ , ppm (*J*, Hz): 20.3 (CH₃), 110.2 (C⁷), 116.2 (d, *J* = 22.5, 2C, C^m), 118.6 (C⁴), 124.2 (C⁵), 124.7 (C⁶), 129.3 (br s, 2C, C^o), 138.8 (br s, Cⁱ), 140.5 (C^{3a}), 147.7 (C^{7a}), 154.2 (C–O), 163.3 (d, *J* = 249.0, C^p), 165.0 (C–CH₃). MS (EI), *m/z* (%): 333 [M]⁺ (20), 292 (20), 228 (41), 159 (68), 133 [M–C₈H₇FN₂O₂S]⁺ (100), 105 (40), 95 (92), 75 (16). IR (NPVO, ZnSe, *v*/cm⁻¹): 1006, 1153, 1575, 1638, 3094. Found (%): C, 54.37; H, 3.86; N, 12.66. Calcd for C₁₅H₁₂FN₃O₃S (%): C, 54.05; H, 3.63; N, 12.61.

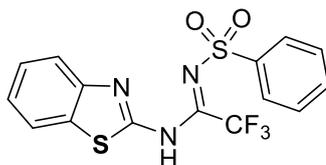


(*E*)-*N*-(Benz[*d*]oxazol-2-yl)-*N'*-(4-methoxyphenylsulfonyl)acetimidamide (**4n**). Reaction time is 16 h. Colorless crystals, yield 59% (200 mg), mp 177–180 °C (EtOH). ¹H NMR (600 MHz, DMSO-*d*₆), δ , ppm (*J*, Hz): 2.65 (3H, s, CH₃), 3.85 (3H, s, OCH₃), 7.13 (2H, d, *J* = 12.0, H-Ar), 7.28–7.33 (2H, m, H-Ar), 7.58–7.65 (2H, m, H-Ar), 7.91 (2H, d, *J* = 12.0, H-Ar), 12.03 (1H, br s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆ + Sc₂CO₃), δ , ppm: 20.3 (CH₃), 55.6 (OCH₃), 110.0 (C⁴), 114.1 (2C, C^o), 118.4 (C⁷), 123.8 (C⁶), 124.5 (C⁵), 128.9 (2C, C^m), 133.9 (Cⁱ), 141.0 (C^{7a}), 148.0 (C^{3a}), 156.8 (C–S), 162.2 (C^p), 165.3 (C–CH₃). MS (EI), *m/z* (%): 345 [M]⁺ (7), 240 (79), 171 [M–C₉H₈N₃O]⁺ (100), 133 (36), 123 (32), 107 (69), 105 (40), 77 (60), 64 (20), 42 (28). IR (NPVO, ZnSe, *v*/cm⁻¹): 1152, 1590, 1639, 2874, 3119. Found (%): C, 55.57; H, 4.40; N, 11.94. Calcd for C₁₆H₁₅N₃O₄S (%): C, 55.64; H, 4.38; N, 12.17.



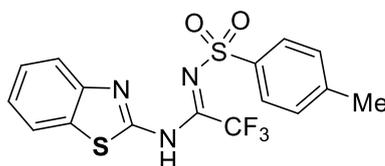
N'-(Benzo[*c*][1,2,5]thiadiazol-4-ylsulfonyl)-*N*-(benz[*d*]oxazol-2-yl)acetimidamide (**4o**). Reaction time is 13 h. Colorless crystals, yield 63% (235 mg), mp 186–190 °C (EtOH). ¹H NMR (600 MHz, DMSO-*d*₆), δ , ppm (*J*, Hz): 2.82 (3H, s, CH₃), 7.30 (2H, br s, H-Ar), 7.51 (1H, s, H-Ar), 7.61 (1H, s, H-Ar), 7.92 (1H, br s, H-Ar), 8.41 (1H, s, H-Ar), 8.51 (1H, s, H-Ar), 12.24 (1H, br s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ , ppm: 20.6 (C⁹), 110.2 (C⁷), 118.7 (C⁴), 124.3 (C⁶), 124.7 (C⁵), 126.2 (C¹³), 128.8 (C¹²), 129.7 (C¹¹), 133.3 (C¹⁰), 140.5 (C^{3a}), 147.7 (C^{7a}), 148.7 (C¹⁵), 154.0 (2C, C², C⁸), 155.1 (C¹⁴). MS (EI), *m/z* (%): 373 [M]⁺ (6), 268 (90), 199 (36),

135 [M-C₉H₈N₃O₃S]⁺ (100), 133 (69), 105 (64), 78 (25), 42 (25). IR (NPVO, ZnSe, ν/cm⁻¹): 1156, 1522, 2840. Found (%): C, 48.36; H, 3.20; N, 18.68. Calcd for C₁₅H₁₁N₅O₃S (%): C, 48.25; H, 2.97; N, 18.76.

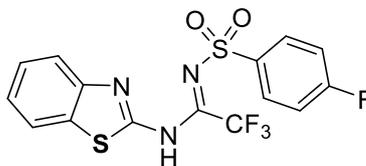


(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-2,2,2-trifluoro-*N'*-(phenylsulfonyl)acetimidamide (**4p**).

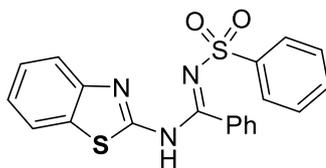
Reaction time is 12 h. Colorless crystals, yield 65% (250 mg), mp 237–239 °C (EtOH). ¹H NMR (600 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 7.42 (1H, t, *J* = 8.0, H-Ar), 7.57–7.71 (5H, m, H-Ar), 7.91 (1H, d, *J* = 8.0, H-Ar), 7.97–7.98 (2H, m, H-Ar). ¹³C NMR (150 MHz, DMSO-*d*₆), δ, ppm: 79.1 (C-CF₃), 114.9 (C⁵), 116.6 (C⁵), 118.5 (C⁶), 123.2 (C⁷), 125.2 (C⁴), 126.3 (2C, C^{12,14}), 128.3 (C^{3a}), 129.1 (2C, C^{11,16}), 132.4 (C¹⁴), 135.9 (C^{7a}), 143.0 (C¹⁰), 150.8 (qv, *J* = 36.0, C-CF₃), 166.5 (C-NH). MS (EI), *m/z* (%): 385 [M]⁺ (14), 226 (39), 149 (26), 141 (26), 77 [M-C₉H₅F₃N₃O₂S₂]⁺ (100). IR (NPVO, ZnSe, ν/cm⁻¹): 1134, 1449, 1553, 3184. Found (%): C, 47.06; H, 2.72; N, 10.97. Calcd for C₁₅H₁₀F₃N₃O₂S₂ (%): C, 46.75; H, 2.62; N, 10.90.



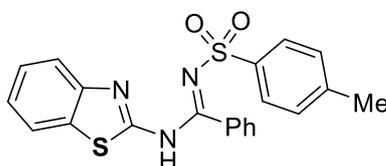
(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-2,2,2-trifluoro-*N'*-(4-methylphenylsulfonyl)acetimidamide (**4q**). Reaction time is 20 h. Colorless crystals, yield 55% (219 mg), mp 238–240 °C (EtOH). ¹H NMR (400 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 2.43 (3H, s, CH₃), 7.43–7.45 (3H, m, H-Ar), 7.57–7.63 (2H, m, H-Ar), 7.86 (2H, d, *J* = 12.0, H-Ar), 7.94 (2H, d, *J* = 8.0, H-Ar). ¹³C NMR (150 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 21.1 (CH₃), 117.5 (qv, *J* = 270.0, C-CF₃), 123.4, 125.2, 126.4, 126.9 (2C), 128.3, 129.5 (2C), 135.6, 140.6, 141.3, 142.7, 150.7 (qv, *J* = 36.0, C-CF₃), 167.5 (C-NH). MS (EI), *m/z* (%): 399 [M]⁺ (5), 240 (42), 155 (20), 91 [M-C₉H₅F₃N₃O₂S₂]⁺ (100), 65 (19). IR (NPVO, ZnSe, ν/cm⁻¹): 1134, 1481, 1545, 3051. Found (%): C, 49.7; H, 2.98; N, 11.05. Calcd for C₁₆H₁₂F₃N₃O₂S₂ (%): C, 48.12; H, 3.03; N, 10.52.



(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-2,2,2-trifluoro-*N'*-(4-fluorophenylsulfonyl)acetimidamide (**4r**). Reaction time is 17 h. Colorless crystals, yield 55% (222 mg), mp 205–207 °C (EtOH). ¹H NMR (400 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 7.43–7.49 (3H, m, H-Ar), 7.57–7.64 (2H, mm, H-Ar), 7.96 (H, d, *J* = 12.0, H-Ar), 8.02–8.05 (2H, m, H-Ar). ¹³C NMR (150 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 115.0 (C⁵), 116.1 (d, *J* = 22.5, C^{m-}), 117.5 (qv, *J* = 282.0, C-CF₃), 123.3 (C⁴), 125.2 (C⁷), 128.3 (C⁶), 128.4 (C^{3a}), 129.3 (d, *J* = 282.0 C^{o-}), 136.0 (C^{7a}), 139.5 (d, *J* = 3.0, C^{p-}), 150.7 (qv, *J* = 36, C-CF₃), 164.0 (d, *J* = 249.0, Cⁱ⁻), 167.6 (C-NH). MS (EI), *m/z* (%): 403 [M]⁺ (14), 244 (52), 159 (35), 149 (33), 105 (18), 95 [M-C₉H₅F₃N₃O₃S₂]⁺ (100), 75 (17). IR (NPVO, ZnSe, ν/cm⁻¹): 1140, 1458, 1547, 3080. Found (%): C, 45.07; H, 2.68; N, 11.05. Calcd for C₁₅H₅F₄N₃O₃S₂ (%): C, 44.66; H, 2.25; N, 10.42.



(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-*N'*-(phenylsulfonyl)benzimidamide (**4s**). Reaction time is 9 h. Light brown crystals, yield 60% (235 mg), mp 154–157 °C (EtOH). ¹H NMR (600 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 7.34 (1H, t, *J* = 7.6, H-Ar), 7.46–7.51 (3H, m, H-Ar), 7.56–7.60 (3H, m, H-Ar), 7.65 (3H, t, *J* = 7.7, H-Ar), 7.77 (1H, d, *J* = 7.7, H-Ar), 7.80 (1H, d, *J* = 7.7, H-Ar), 7.90 (1H, d, *J* = 8.0, H-Ar) 12.95 (1H, s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆ + Sc₂CO₃), δ, ppm (*J*, Hz): 120.8, 121.7, 124.2, 126.4, 126.5, 127.8, 128.6, 128.9, 130., 131.4, 132.1, 132.4, 142.3, 157.5 (C-S), 162.0 (C-Ph). MS (EI), *m/z* (%): 393 [M]⁺ (9), 226 (30), 225 (20), 149 (36), 141 (53), 77 [M-C₉H₈N₃O₂S₂]⁺ (100). IR (NPVO, ZnSe, ν/cm⁻¹): 1149, 1590, 1612, 3244. Found (%): C, 54.36; H, 3.95; N, 12.68. Calcd for C₂₀H₁₅N₃O₂S₂ (%): C, 61.05; H, 3.84; N, 10.68.



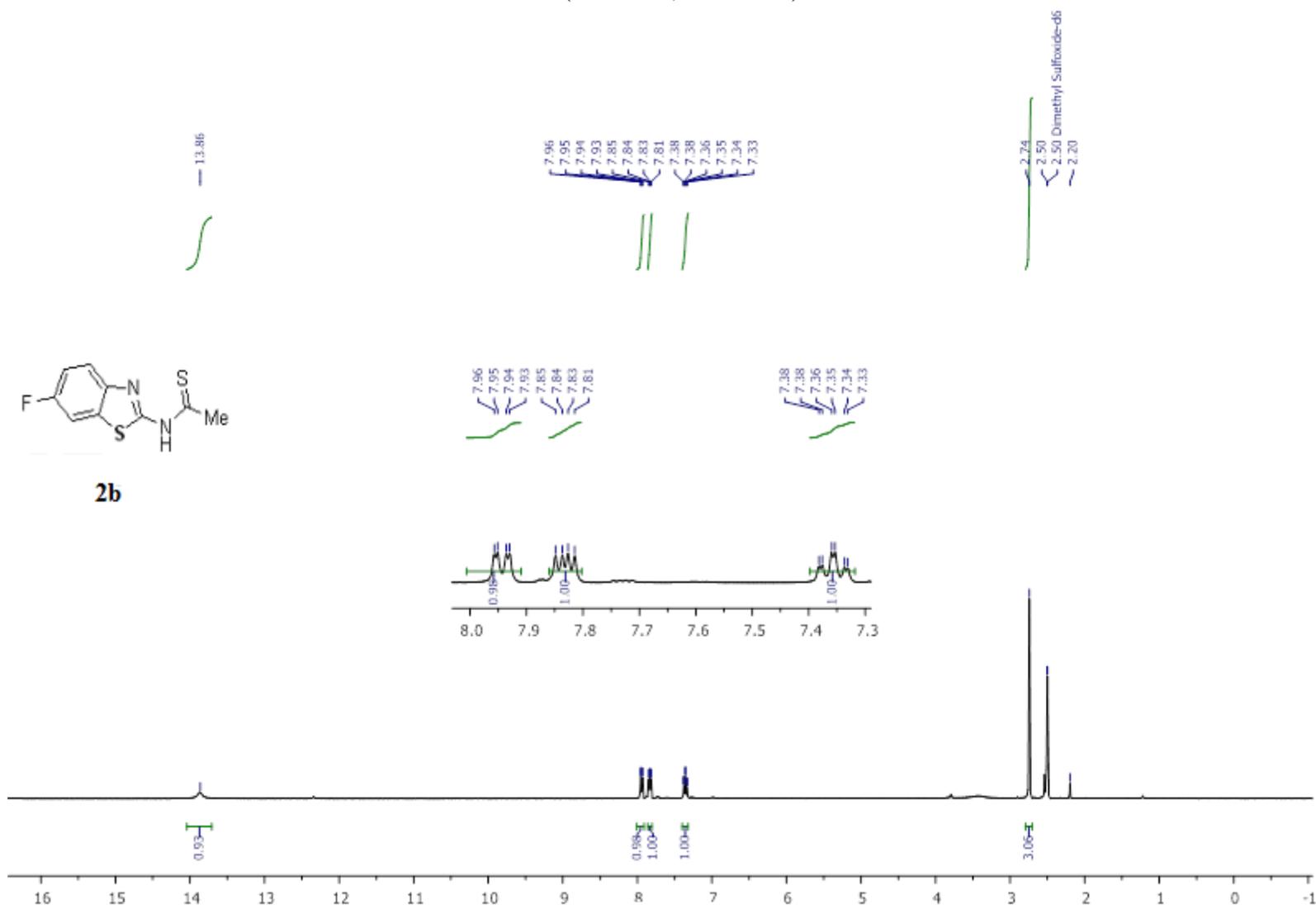
(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-*N'*-tosylbenzimidamide (**4t**). Reaction time is 9 h. Light brown crystals, yield 68% (276 mg), mp 205–207 °C (EtOH). ¹H NMR (600 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 2.39 (3H, s, CH₃), 7.33–7.37 (3H, m, H-Ar), 7.46–7.51 (3H, m, H-Ar), 7.59 (1H, t, *J* = 8.0, H-Ar), 7.63 (2H, d, *J* = 8.0, Hz, H-Ar), 7.68 (2H, d, *J* = 8.0 Hz, H Ar), 7.77 (1H, d, *J* = 8.0 Hz, H-Ar), 7.92 (1H, d, *J* = 8.0 Hz, H-Ar), 12.93 (1H, br s, NH). ¹³C NMR (150 MHz, DMSO-*d*₆), δ, ppm: 21.1 (CH₃), 120.7 (C⁴), 121.8 (C⁷), 124.2 (C⁶), 126.5 (2C, C^{o'}), 126.6 (3C, C^{7a} + C^{m-}), 127.9 (2C, C^{o-}), 128.6 (C⁵), 129.4 (2C, C^{m'}), 131.4 (C^p), 132.2 (Cⁱ), 139.6 (C^{i'}), 142.6 (C^p), 147.9 (C^{3a}), 157.3 (C²), 162.0 (C⁸). MS (EI), *m/z* (%): 407 [M]⁺ (5), 240 (62), 239 (26), 155 (42), 149 (27), 91 (100), 65 (20). IR (NPVO, ZnSe, ν/cm⁻¹): 1149, 1590, 1612, 3244. Found (%): C, 62.15; H, 4.01; N, 10.38. Calcd for C₂₁H₁₇N₃O₂S₂ (%): C, 61.90; H, 4.21; N, 10.31.

Description of work which are financed by foundations

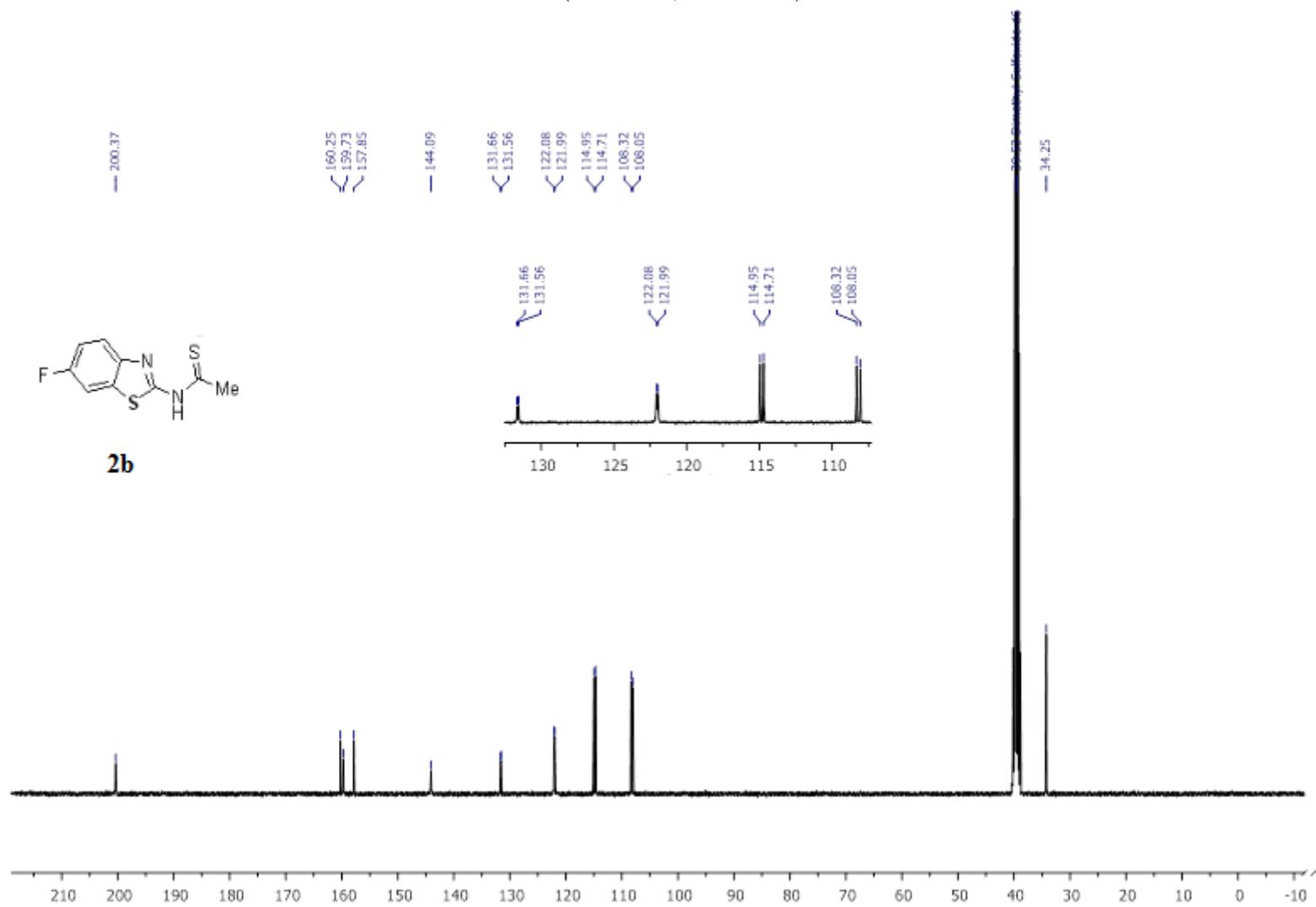
Starting compounds (benzo[*d*]thiazol-2-amine, benzo[*d*]oxazol-2-amine, 6-fluorobenzo[*d*]thiazol-2-amine) were synthesized by Chinese colleagues. This part of the work was supported by the National Natural Science Foundation of China (no. 31872007) and the Tianjin Development Program for Innovation and Entrepreneurship (no. 2018-18).

Synthesis of acetamides **1a-c**, benzamide **1d**, trifluoroacetamide **1e**, thioamides **2a-e**, sulfonyl amidines **4a-t** was supported by the Russian Science Foundation (grant no. 18-13-00161, prolongation).

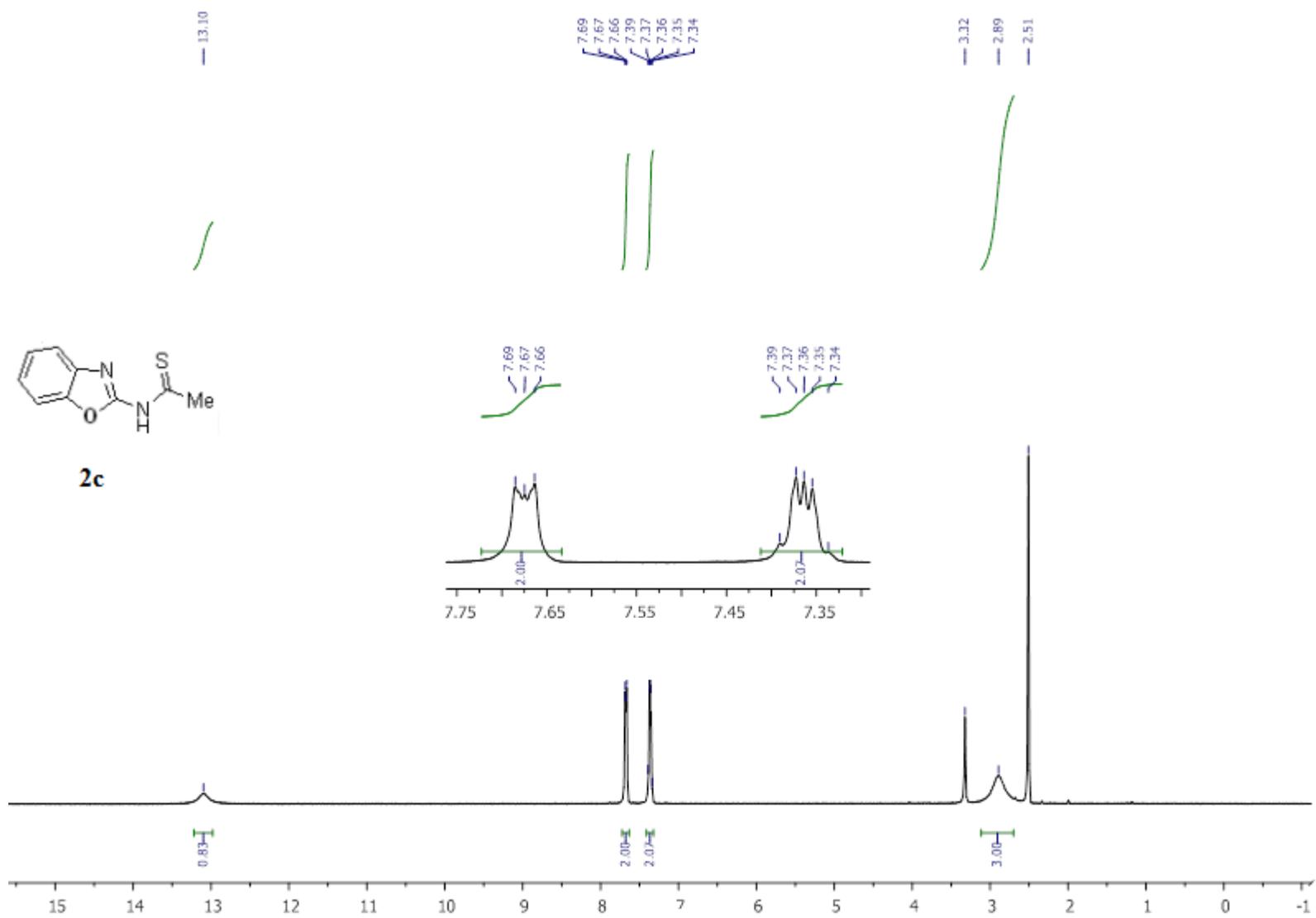
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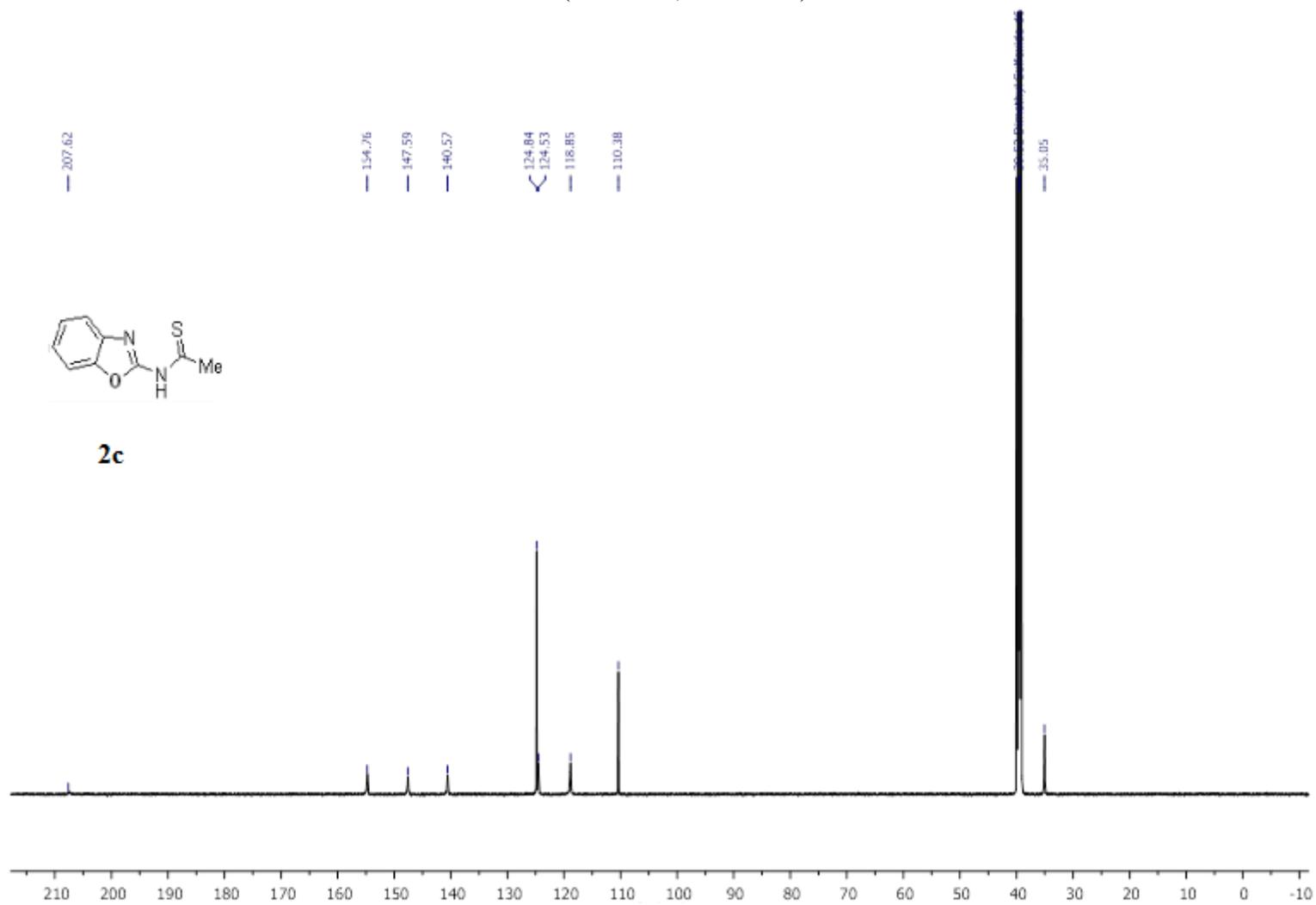
^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) of **2b**



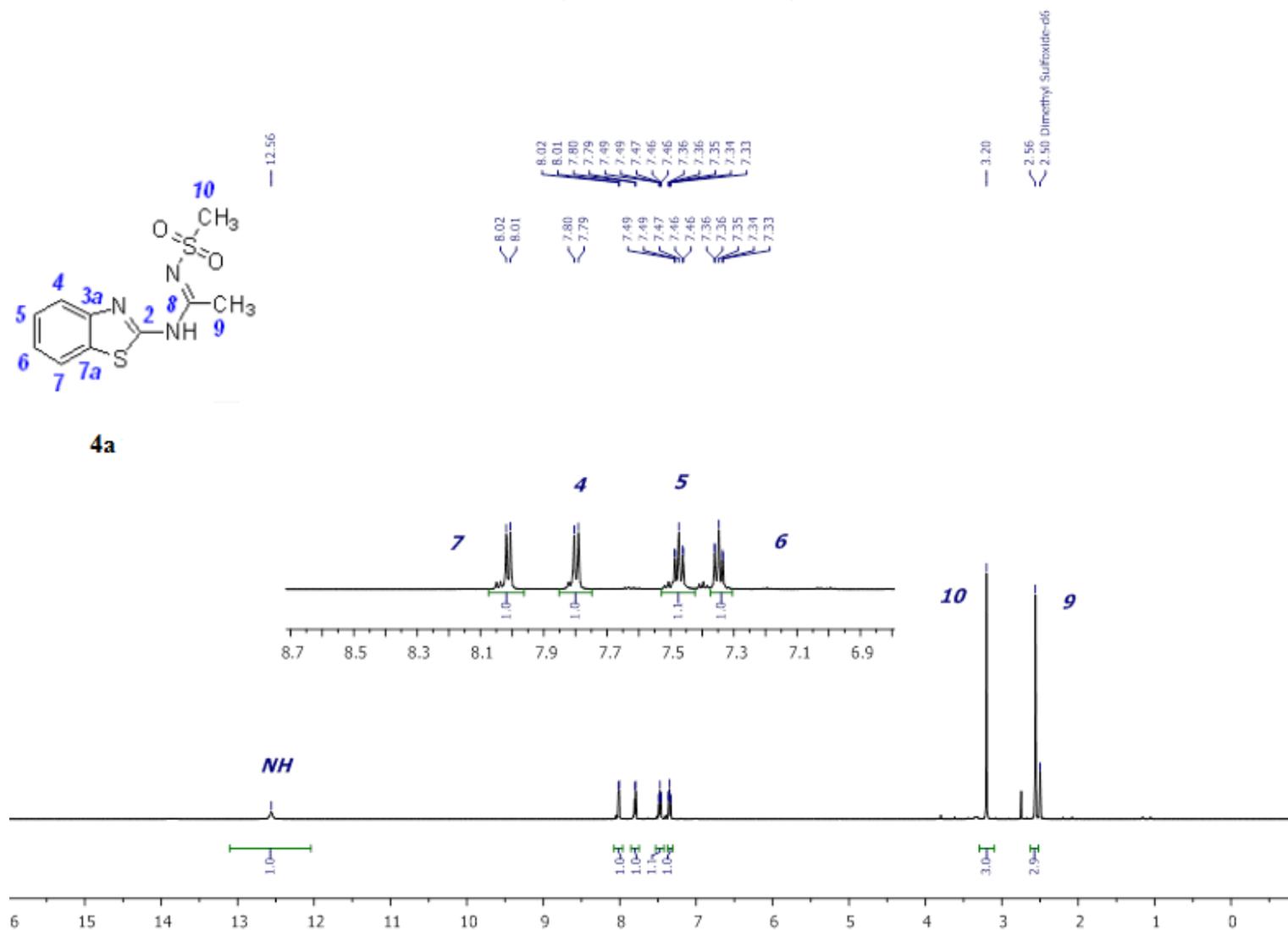
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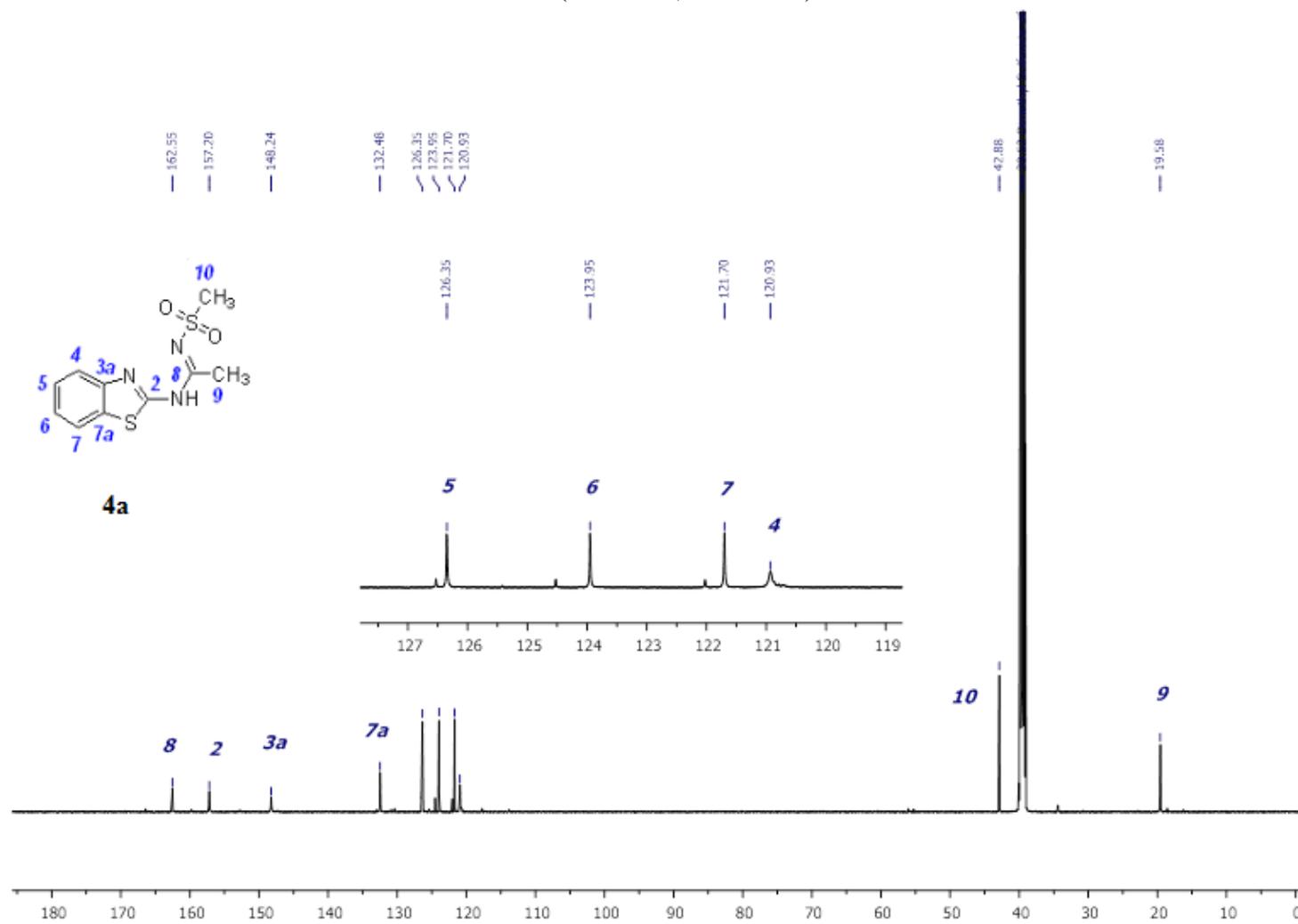
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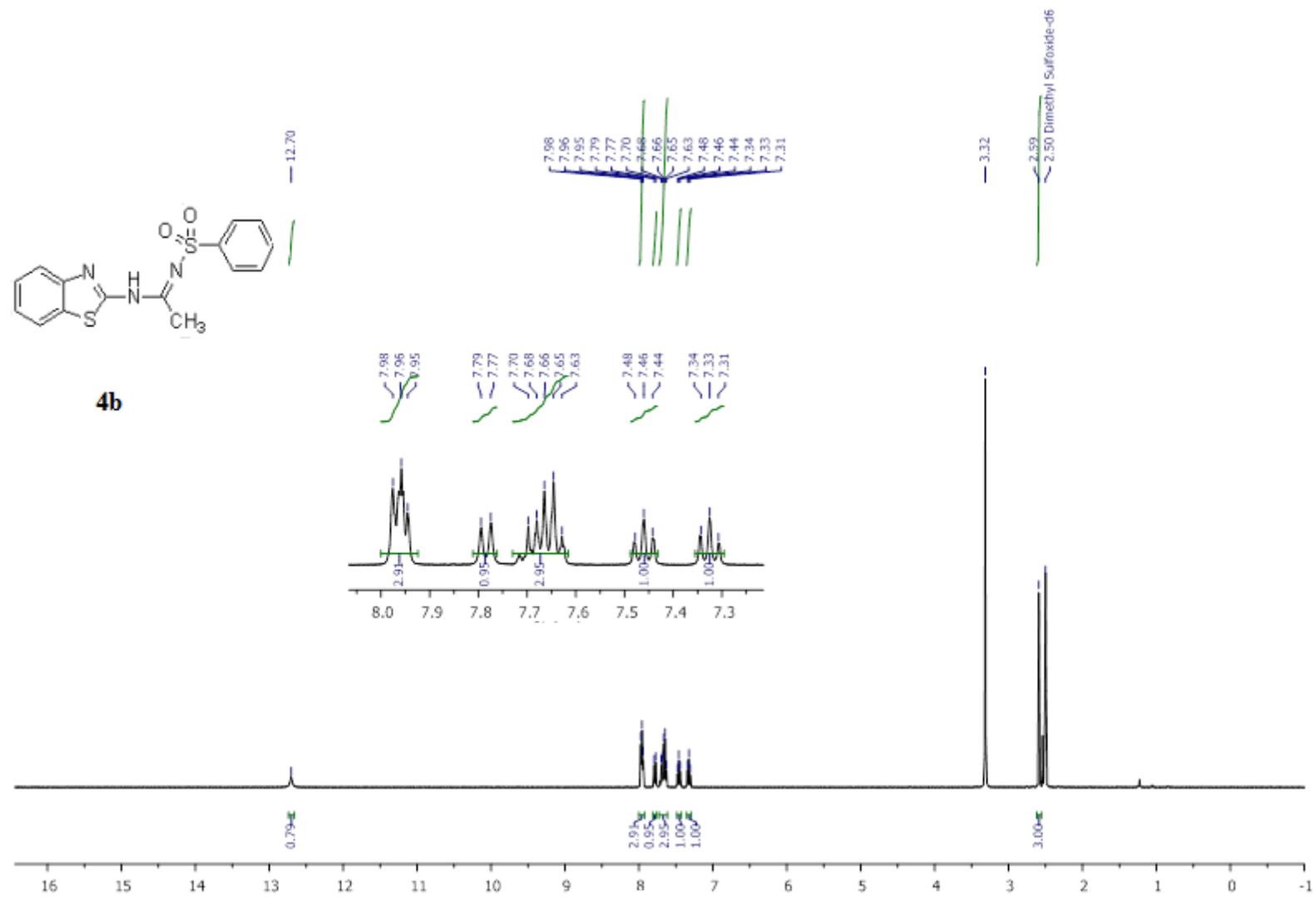
¹H NMR (600 MHz, DMSO-d₆) of **4a**



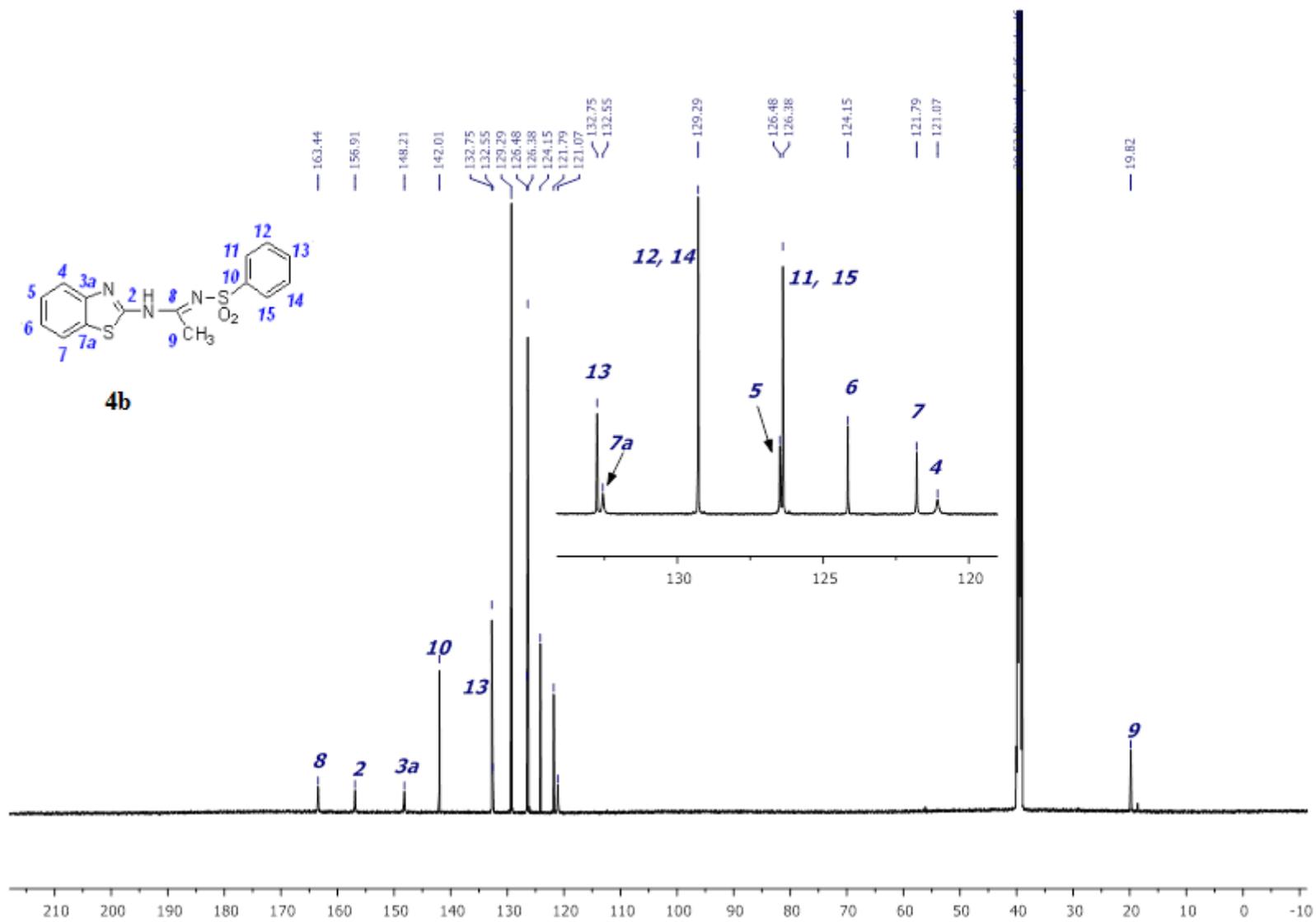
^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) of **4a**



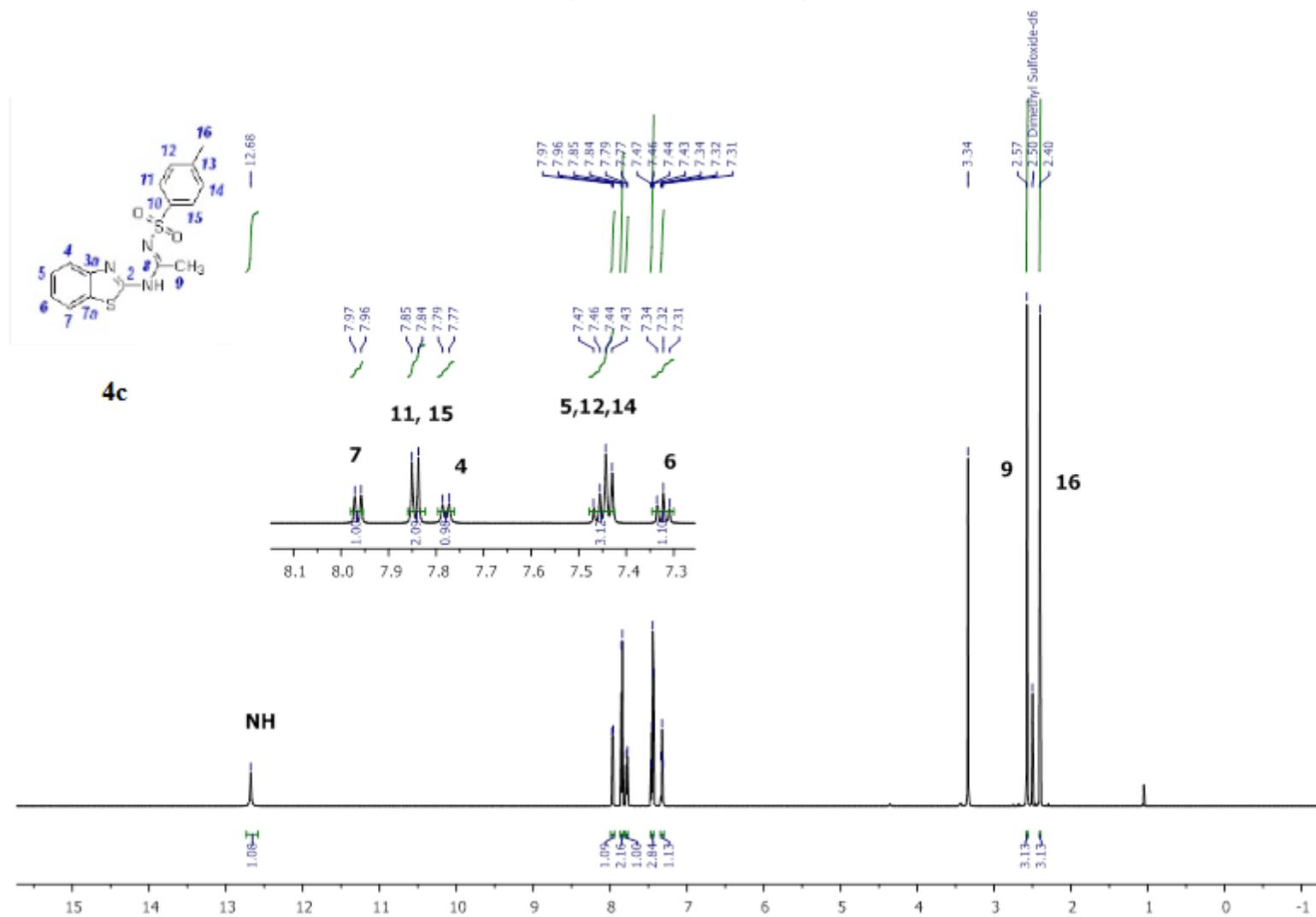
¹H NMR (400 MHz, DMSO-d₆) of **4b**



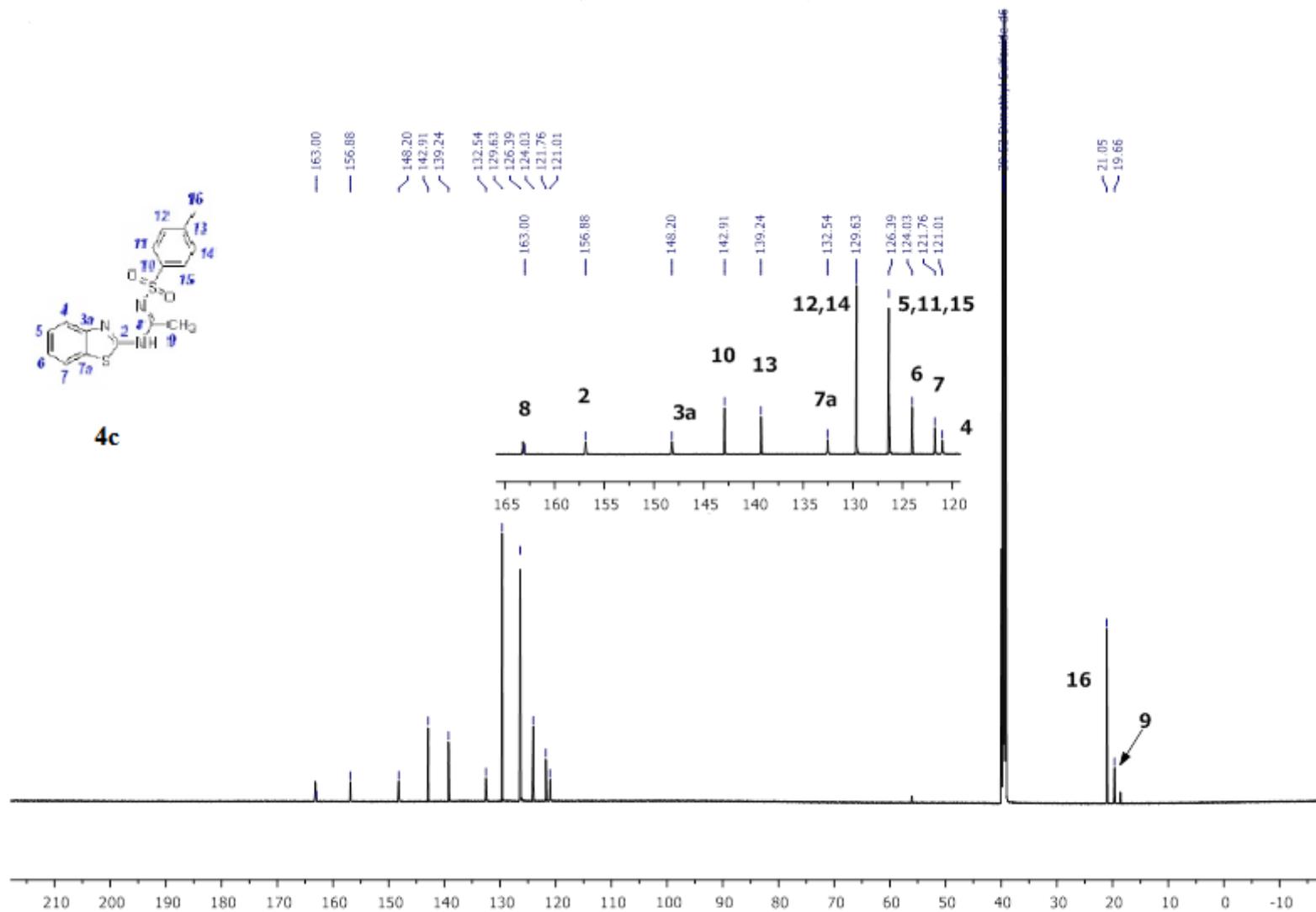
^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) of **4b**



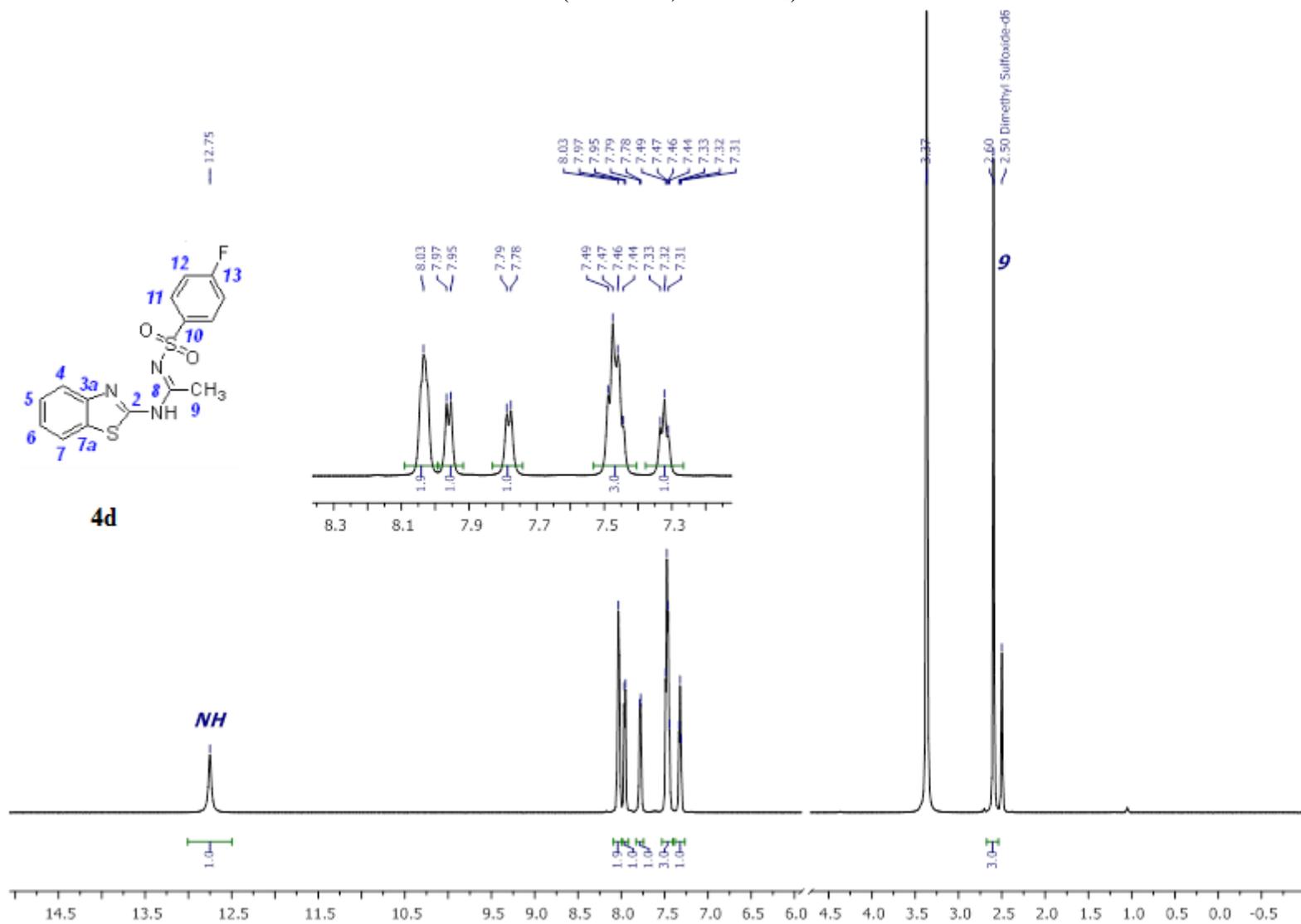
¹H NMR (600 MHz, DMSO-d₆) of **4c**



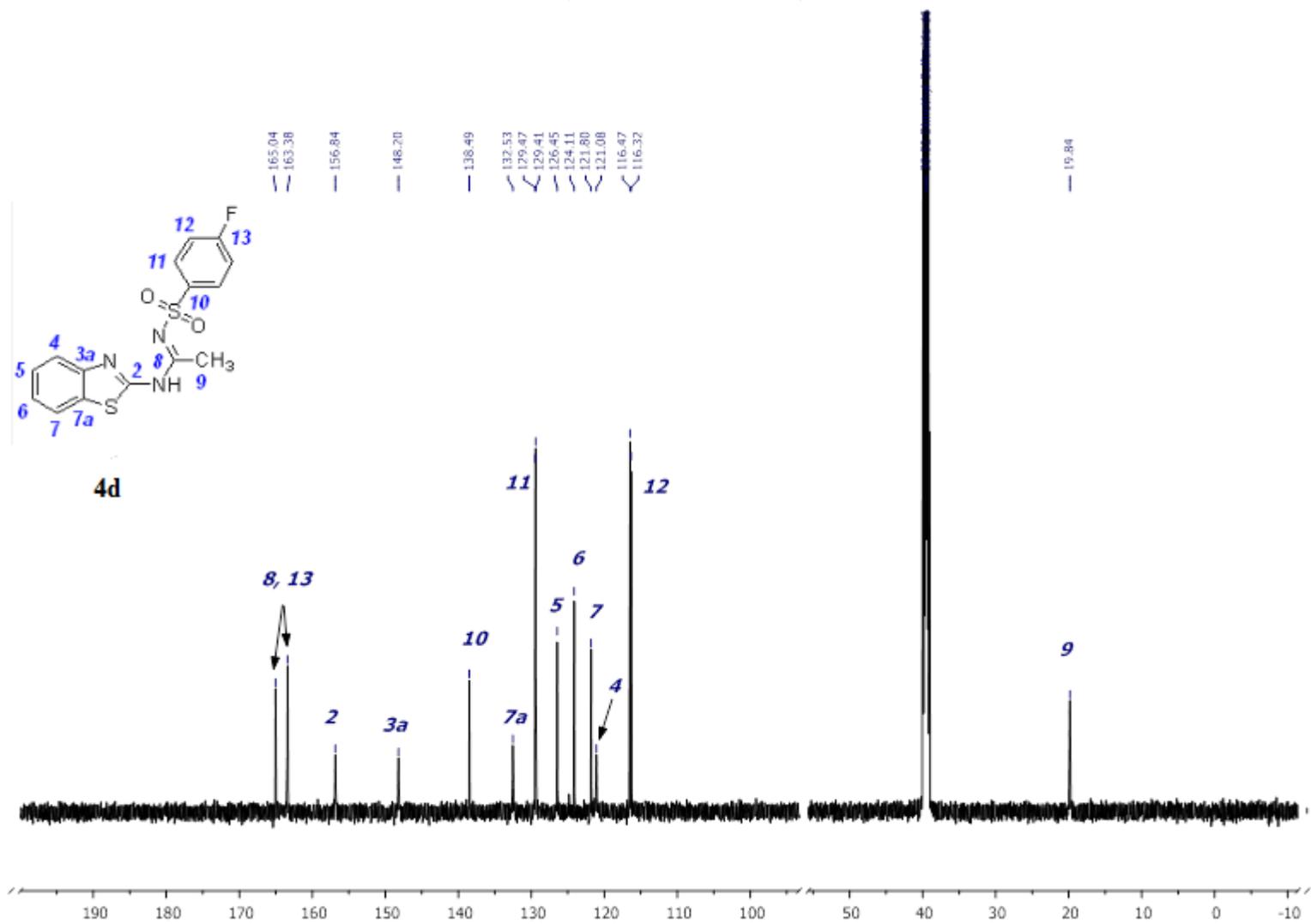
^{13}C NMR (150 MHz, DMSO- d_6) of **4c**



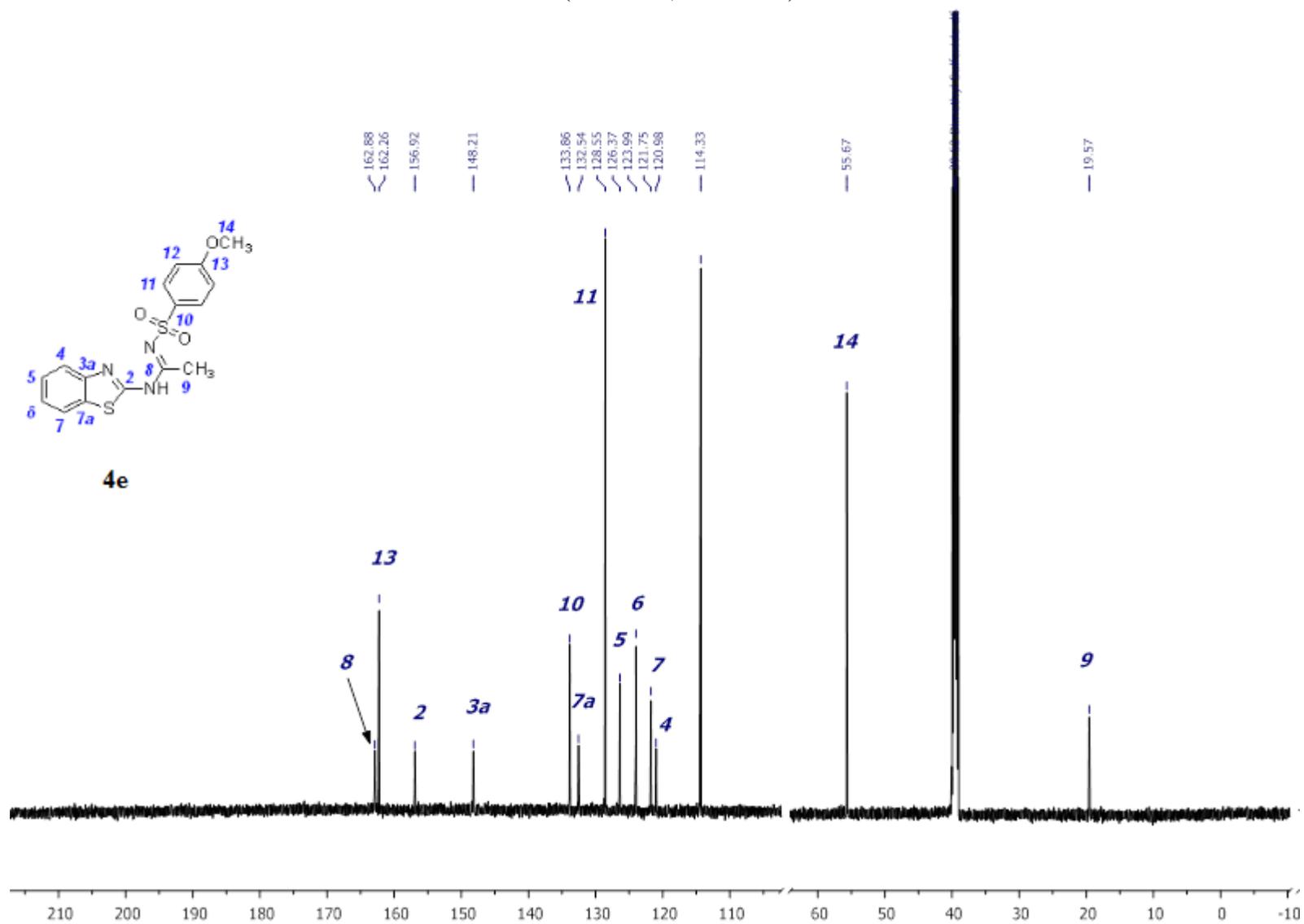
^1H NMR (600 MHz, $\text{DMSO-}d_6$) of **4d**



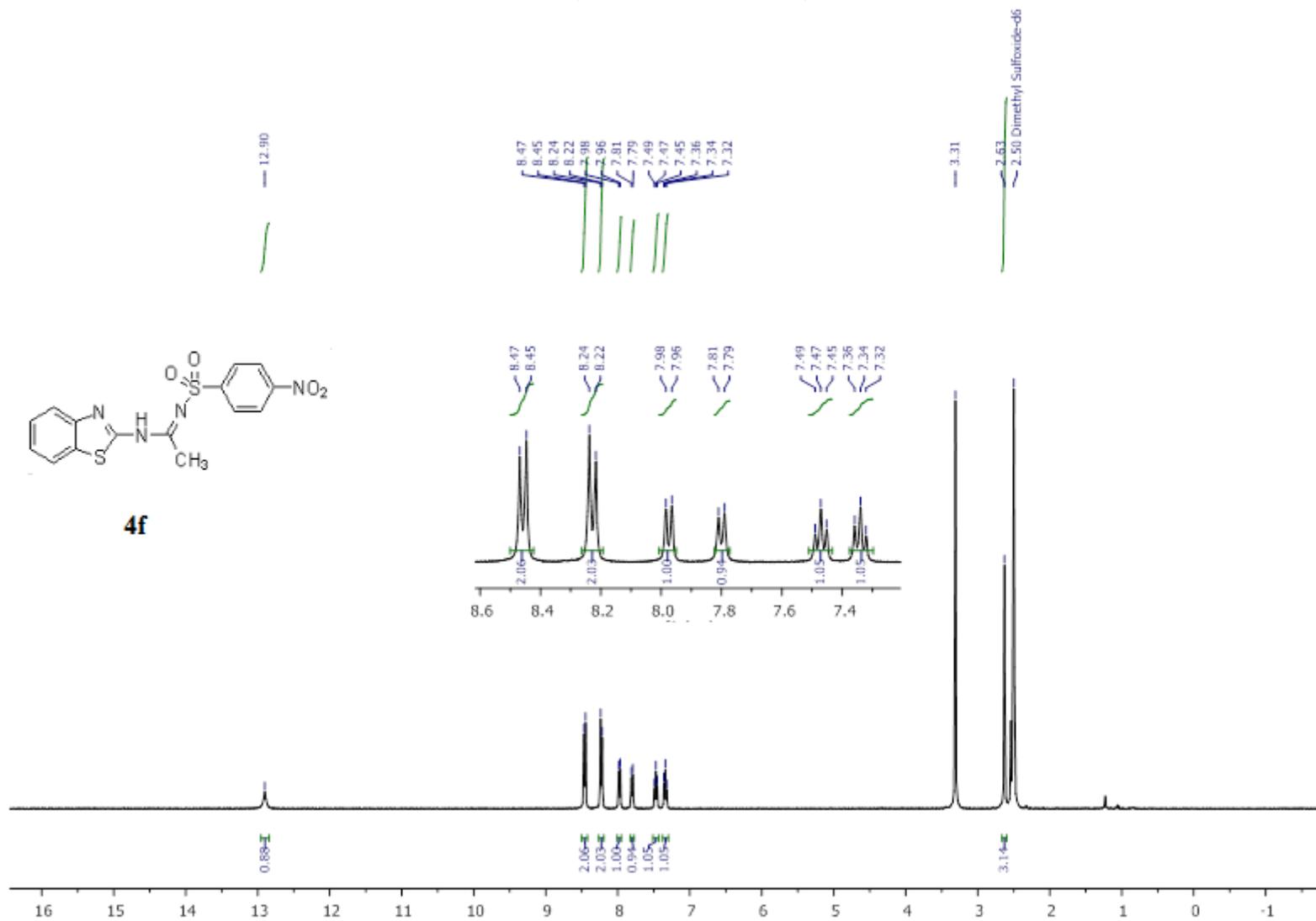
^{13}C NMR (600 MHz, $\text{DMSO-}d_6$) of **4d**



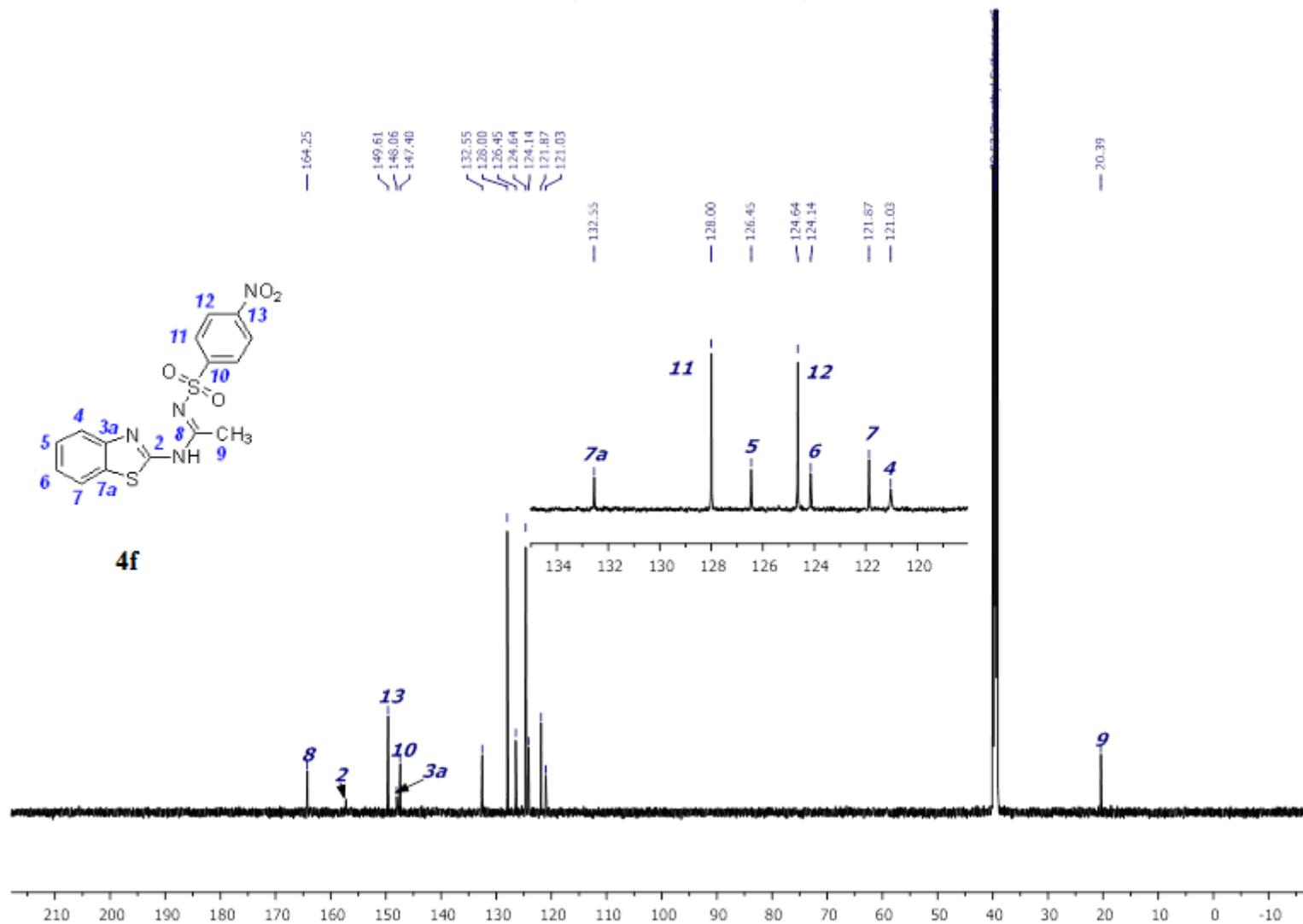
^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) of **4e**



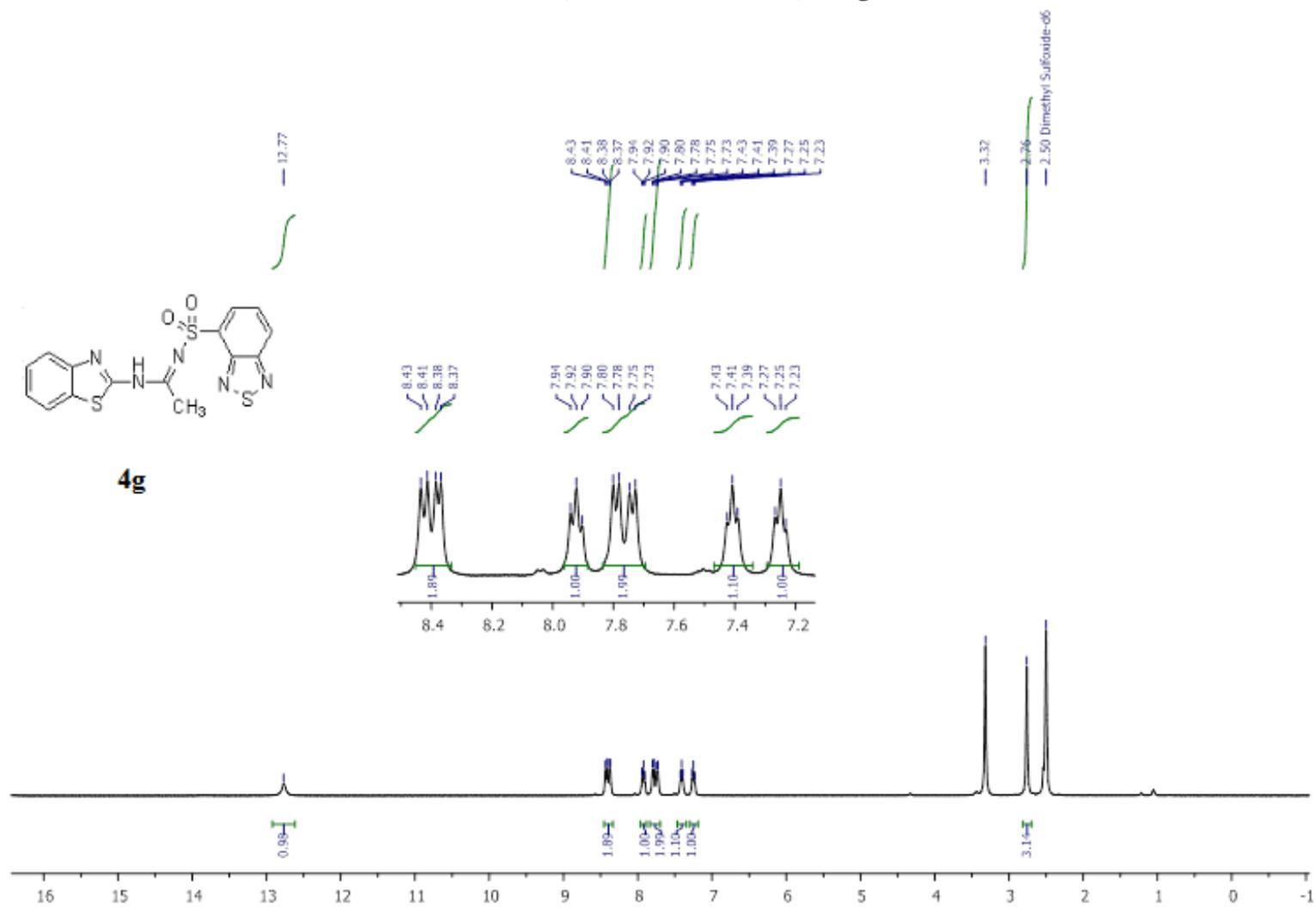
^1H NMR (400 MHz, $\text{DMSO-}d_6$) of **4f**



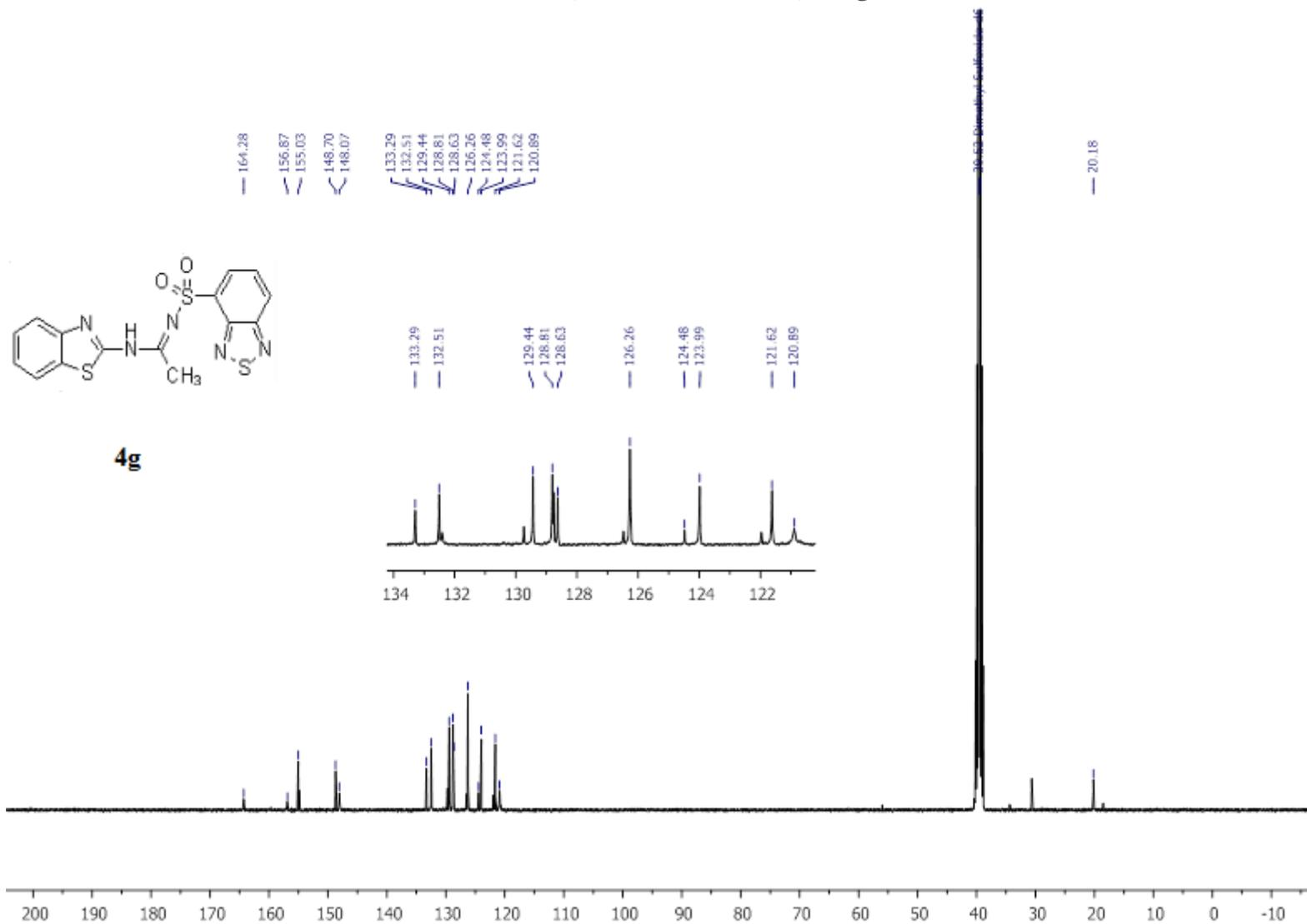
^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) of **4f**



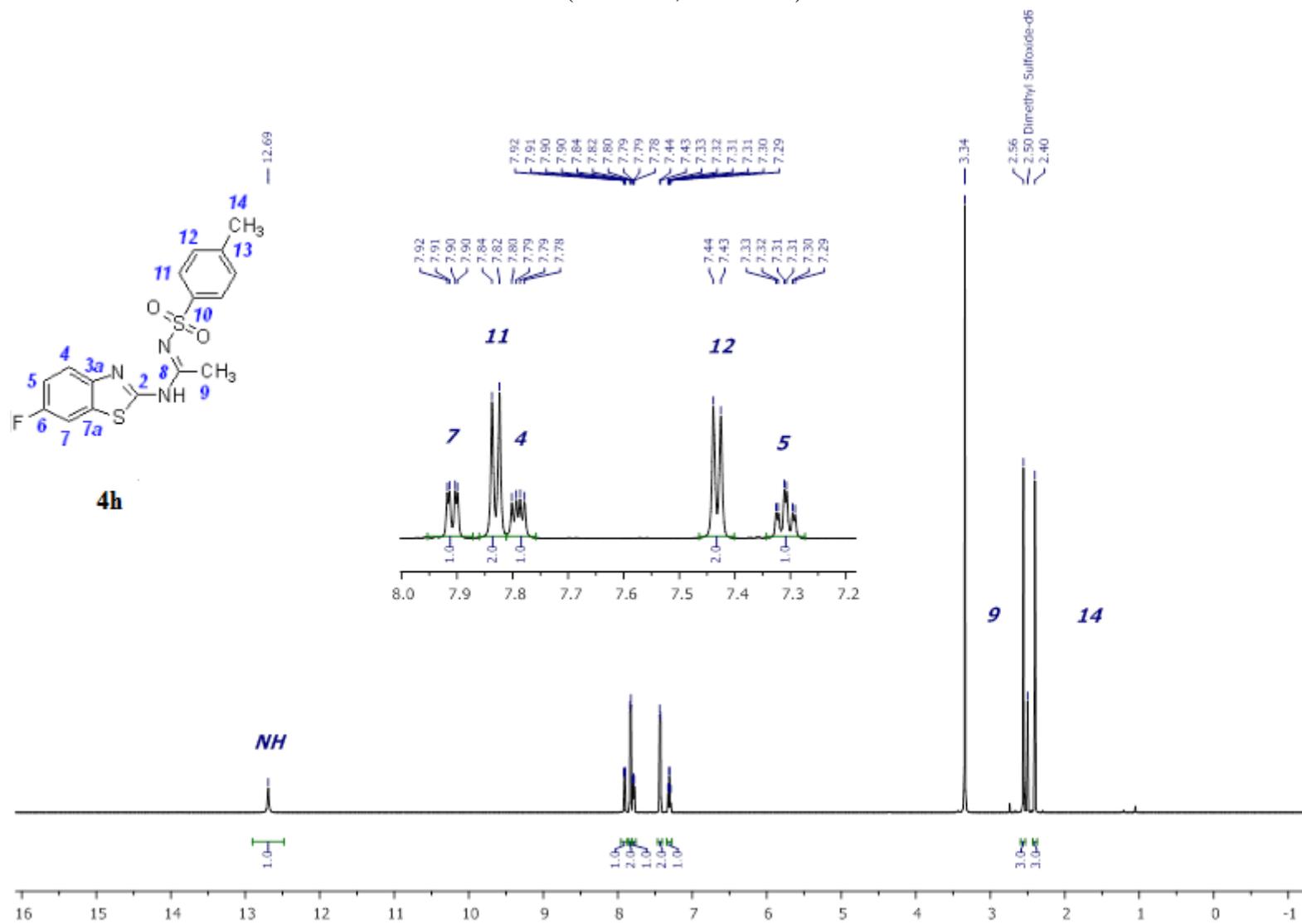
¹H NMR (400 MHz, DMSO-d₆) of **4g**



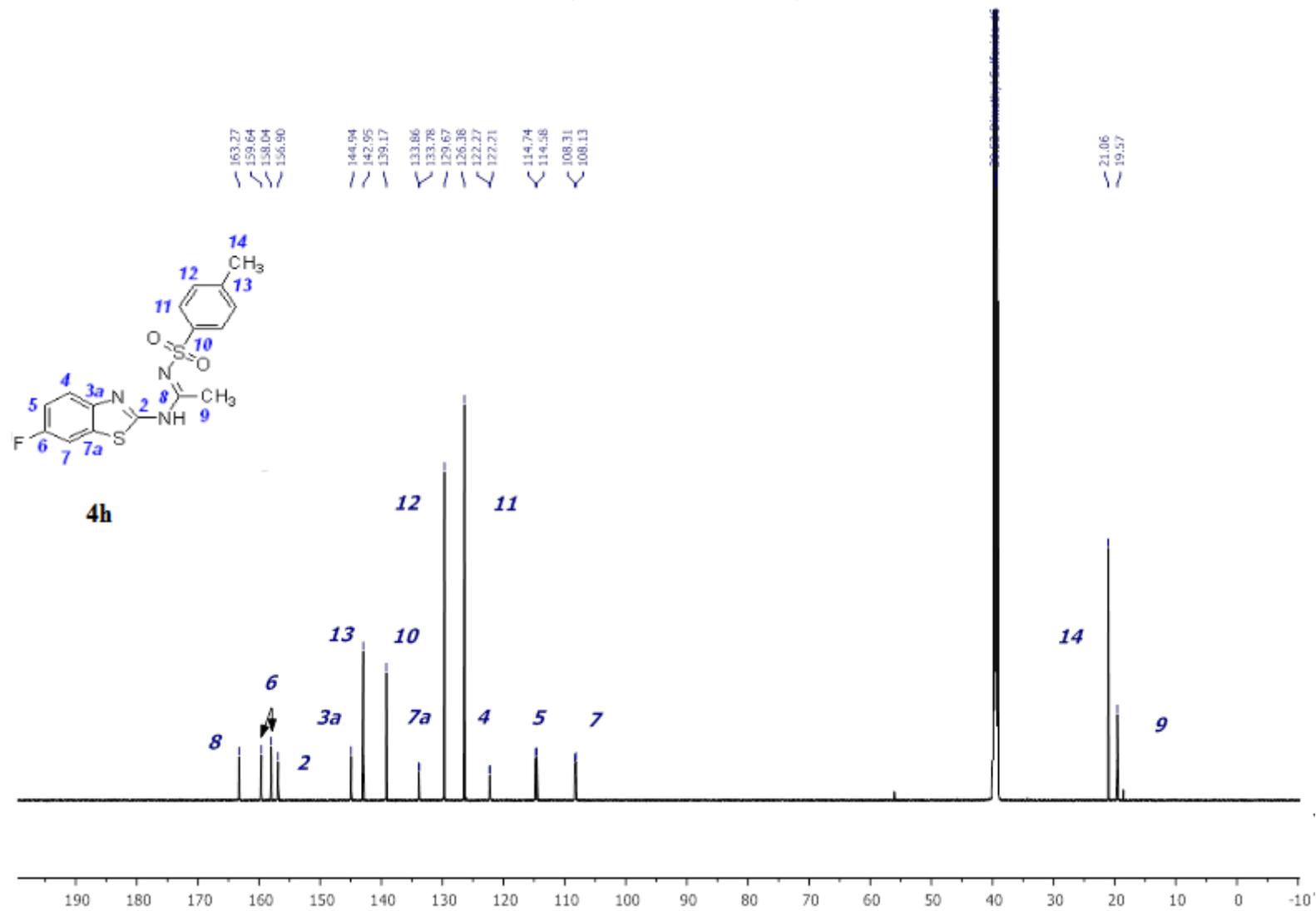
¹³C NMR (100 MHz, DMSO-*d*₆) of **4g**



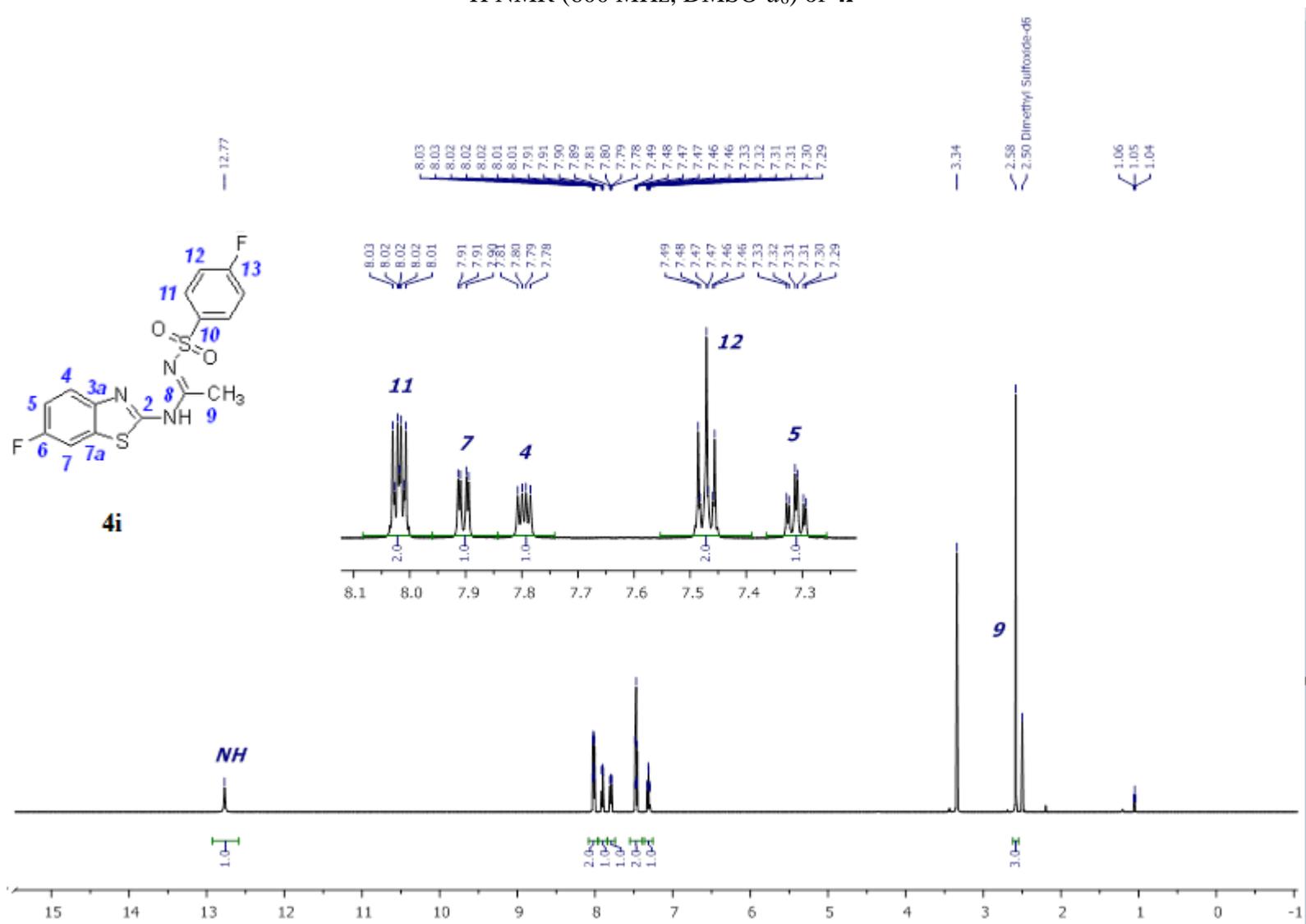
^1H NMR (600 MHz, $\text{DMSO-}d_6$) of **4h**



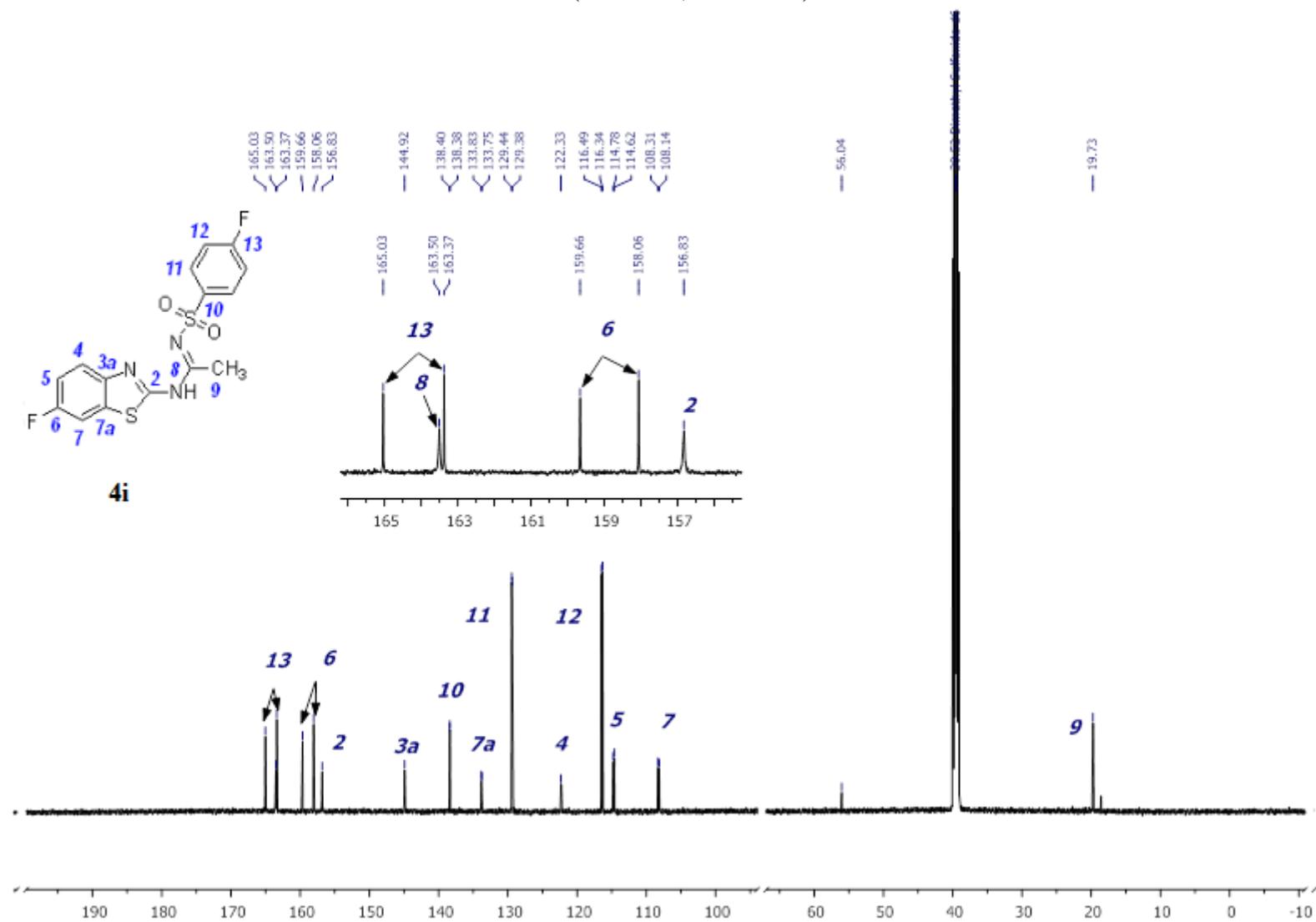
¹³C NMR (150 MHz, DMSO-*d*₆) of **4h**



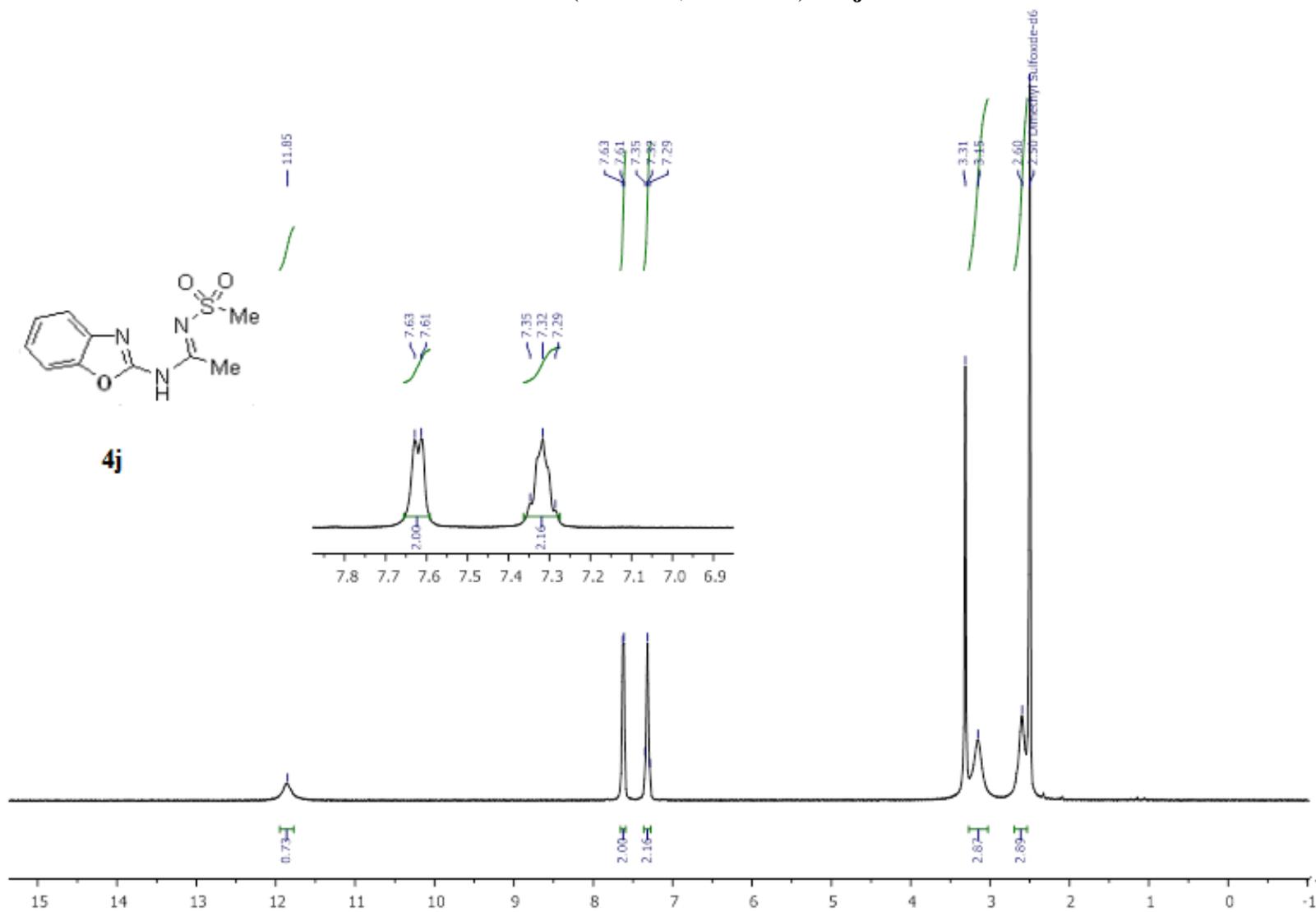
^1H NMR (600 MHz, DMSO- d_6) of **4i**



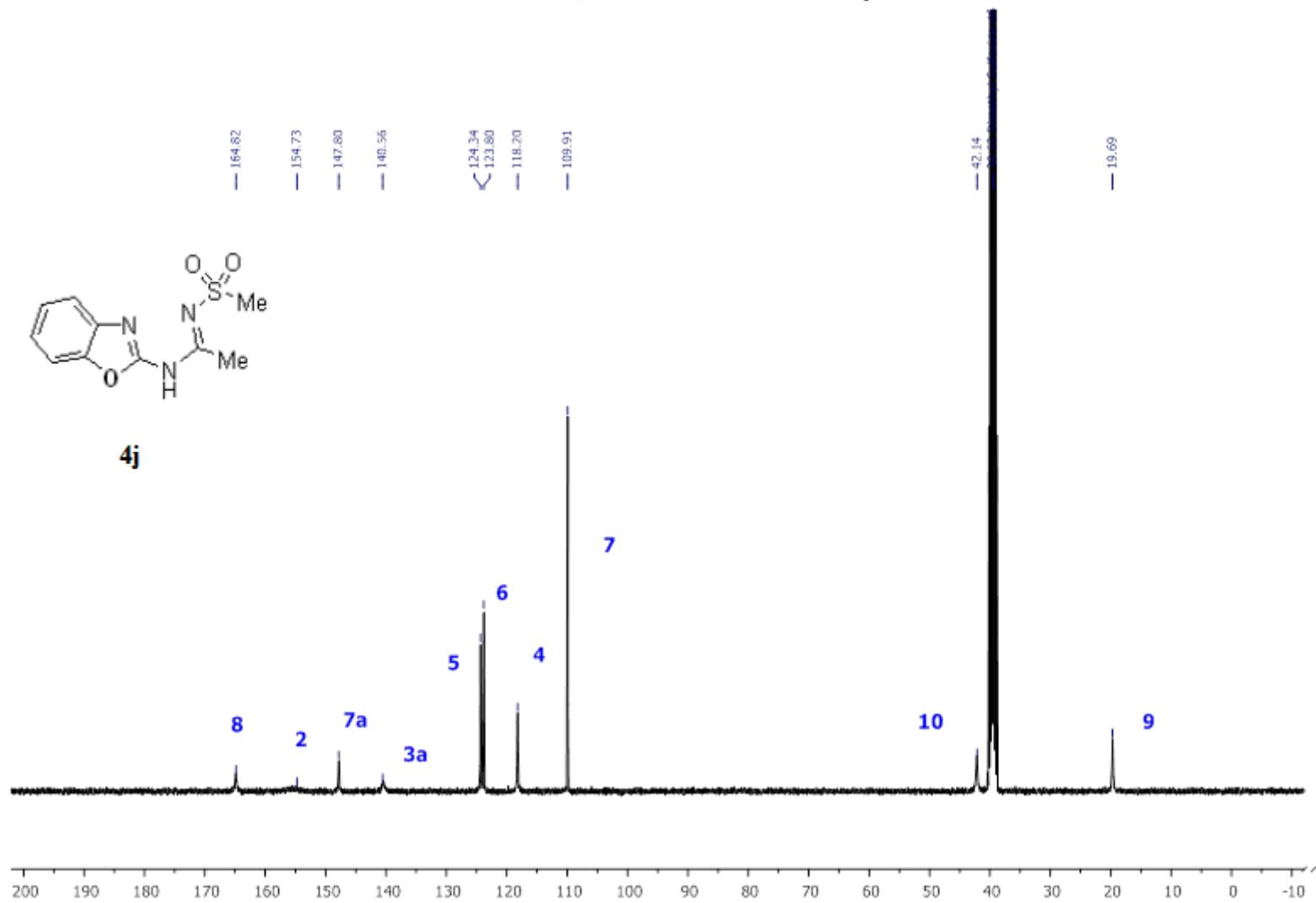
¹³C NMR (150 MHz, DMSO-*d*₆) of **4i**



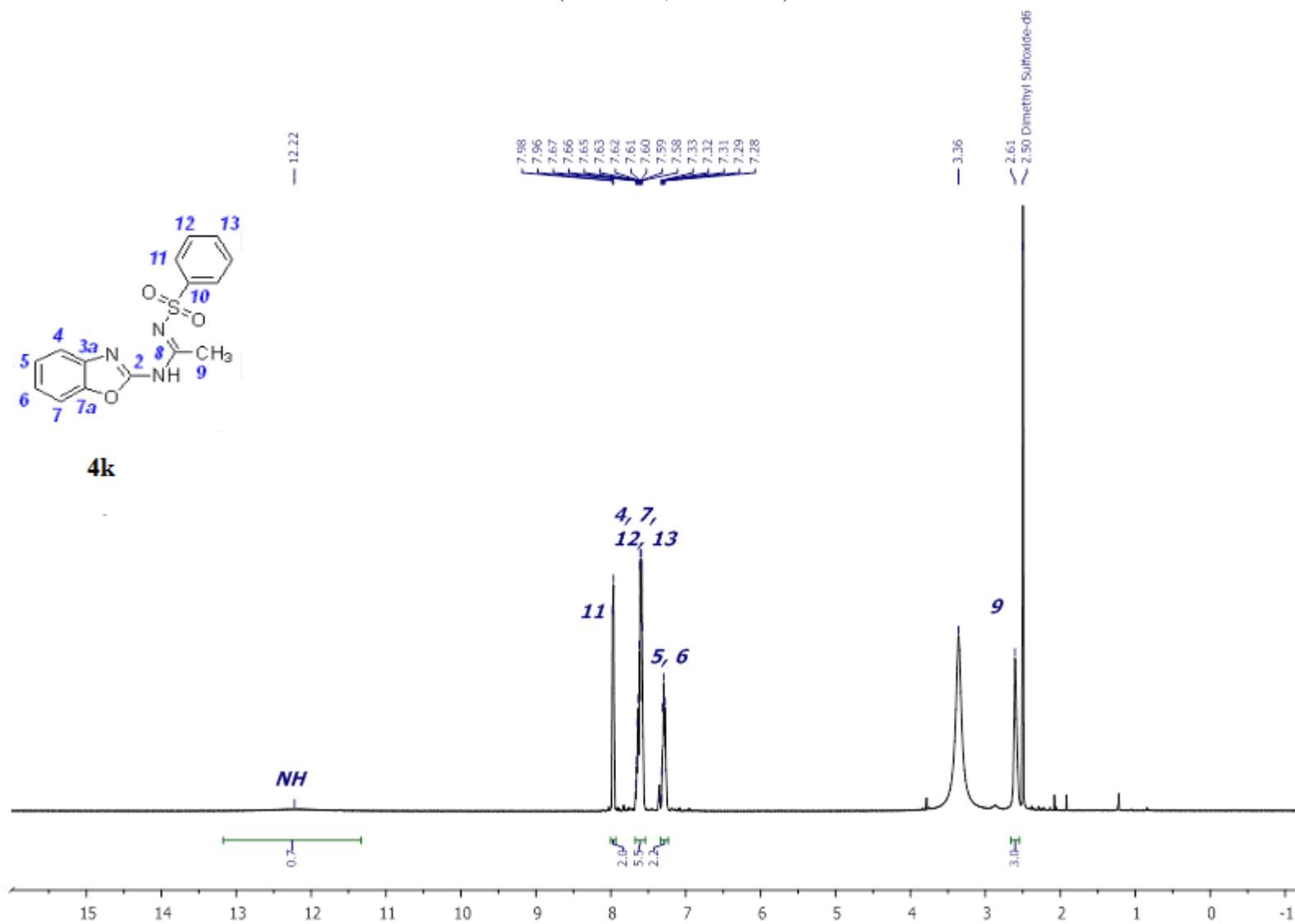
¹H NMR (400 MHz, DMSO-*d*₆) of **4j**



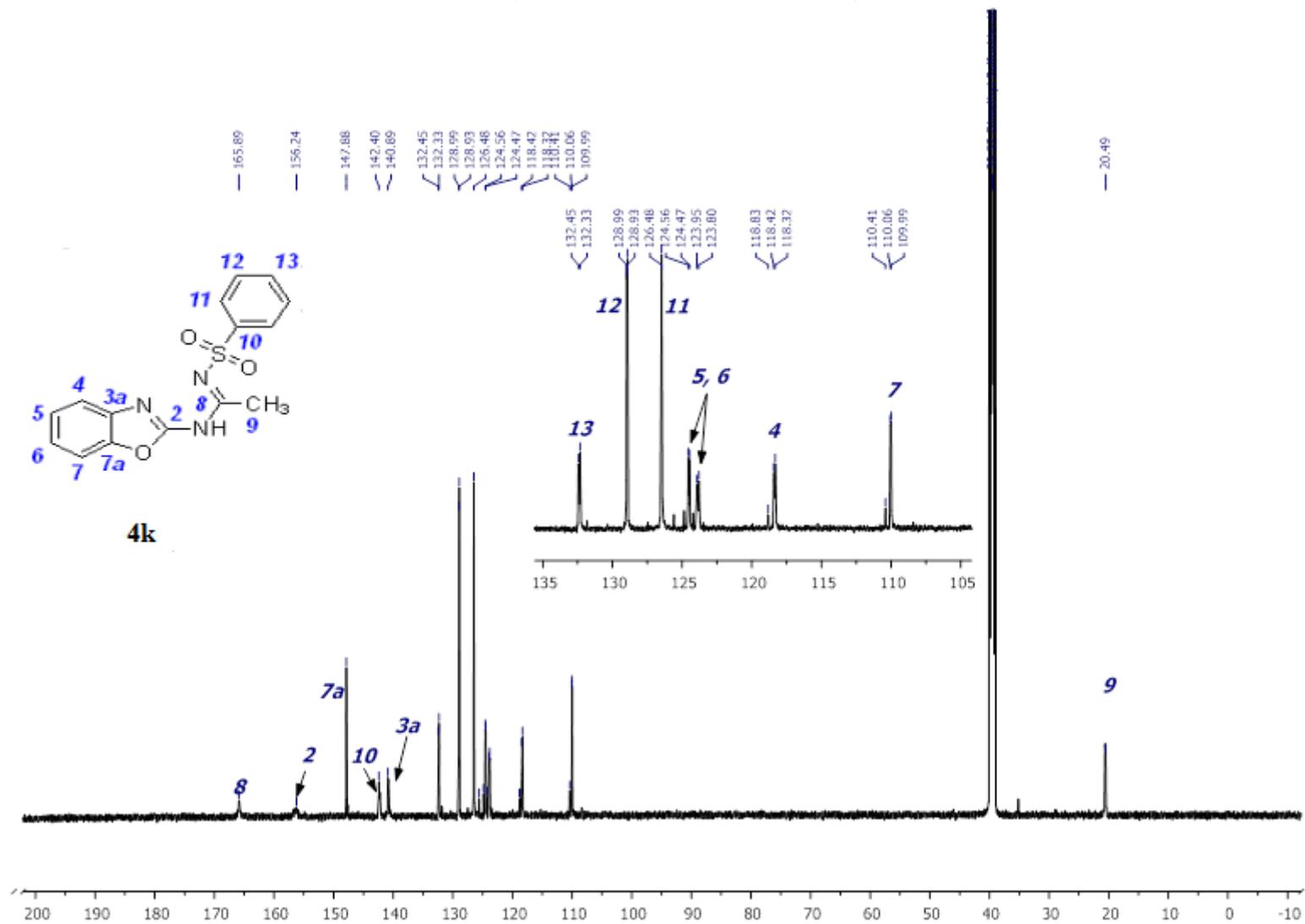
^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) of **4j**



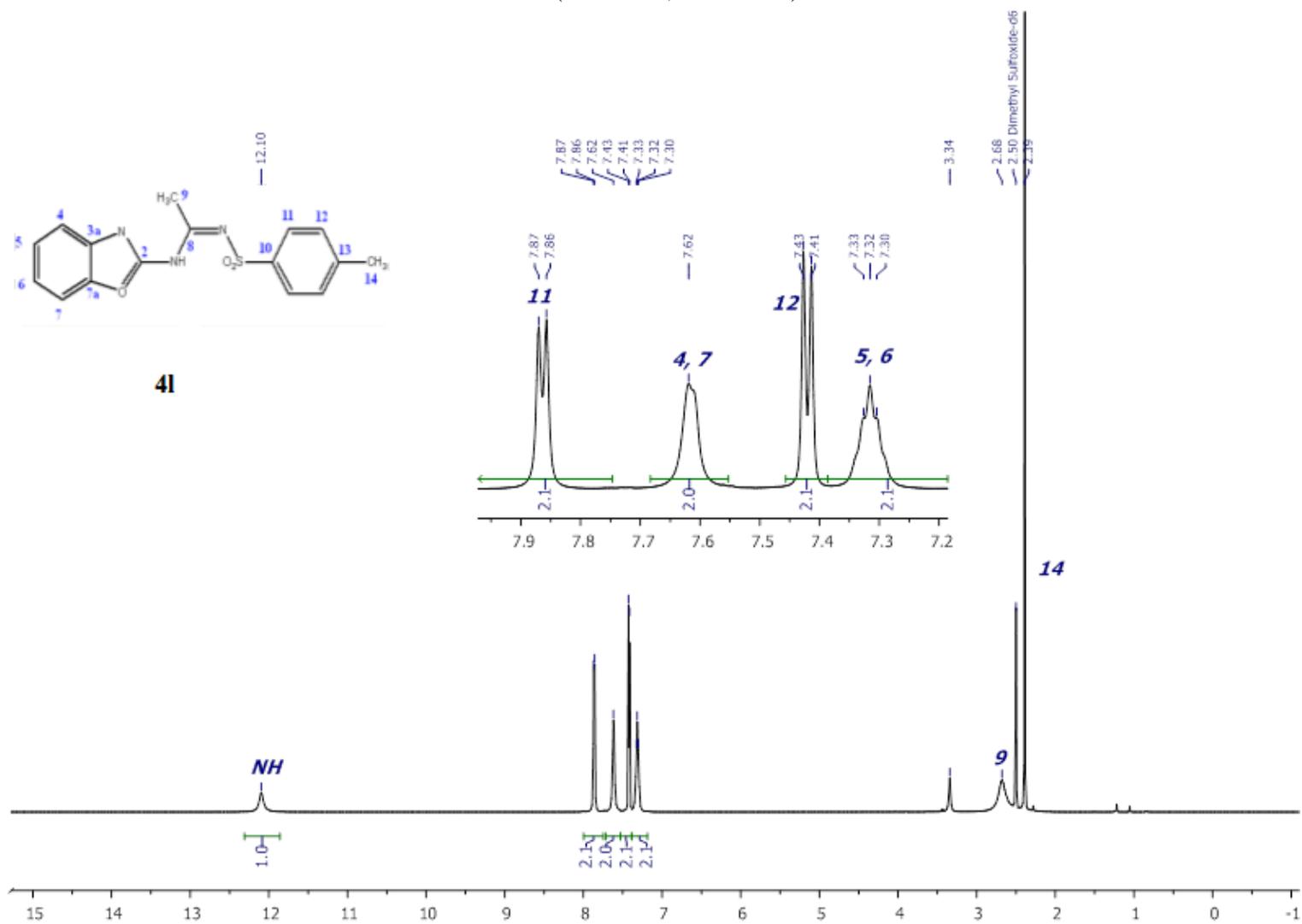
¹H NMR (600 MHz, DMSO-d₆) of **4k**



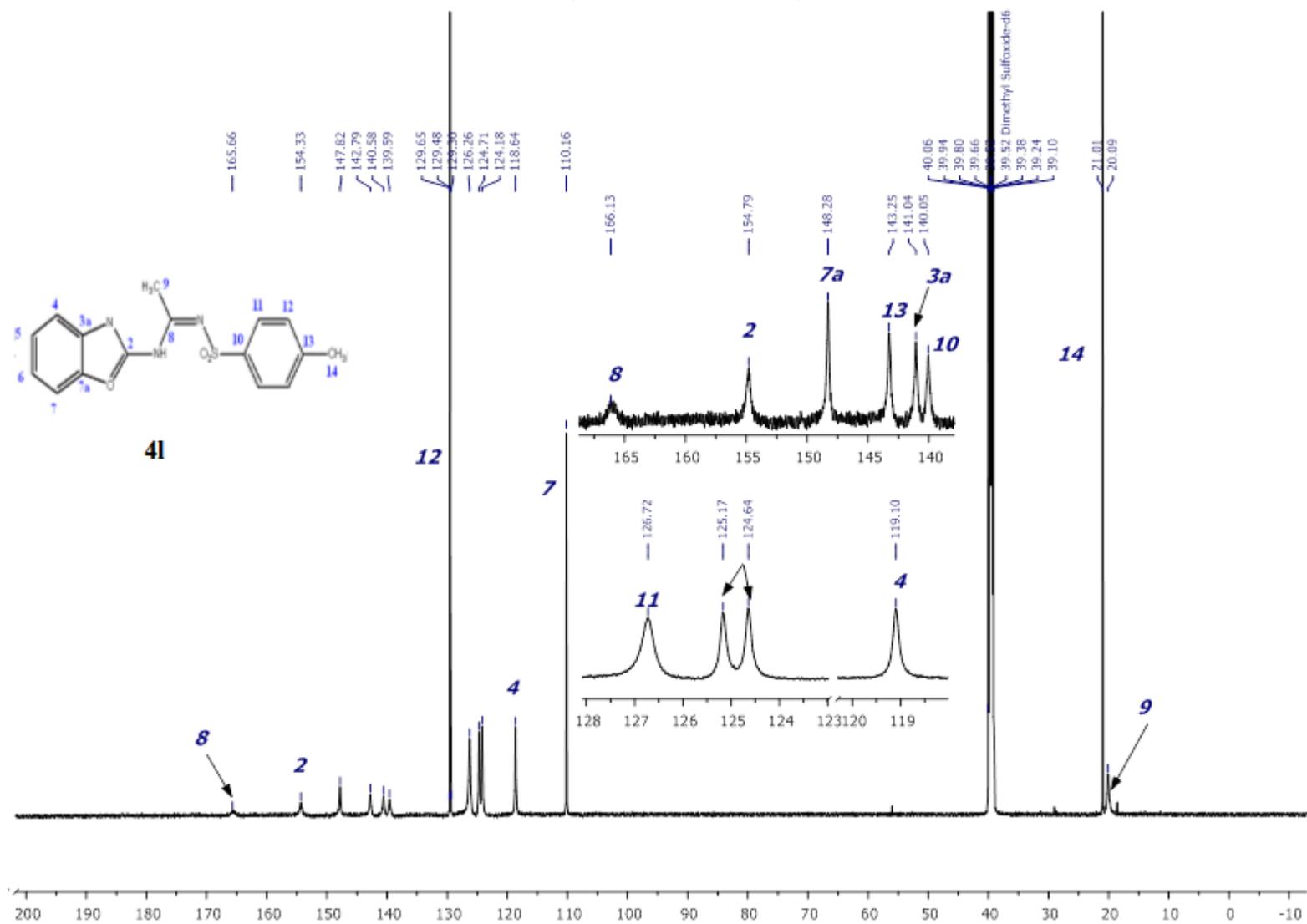
^{13}C NMR (600 MHz, $\text{DMSO-}d_6 + \text{Cs}_2\text{CO}_3$) of **4k**



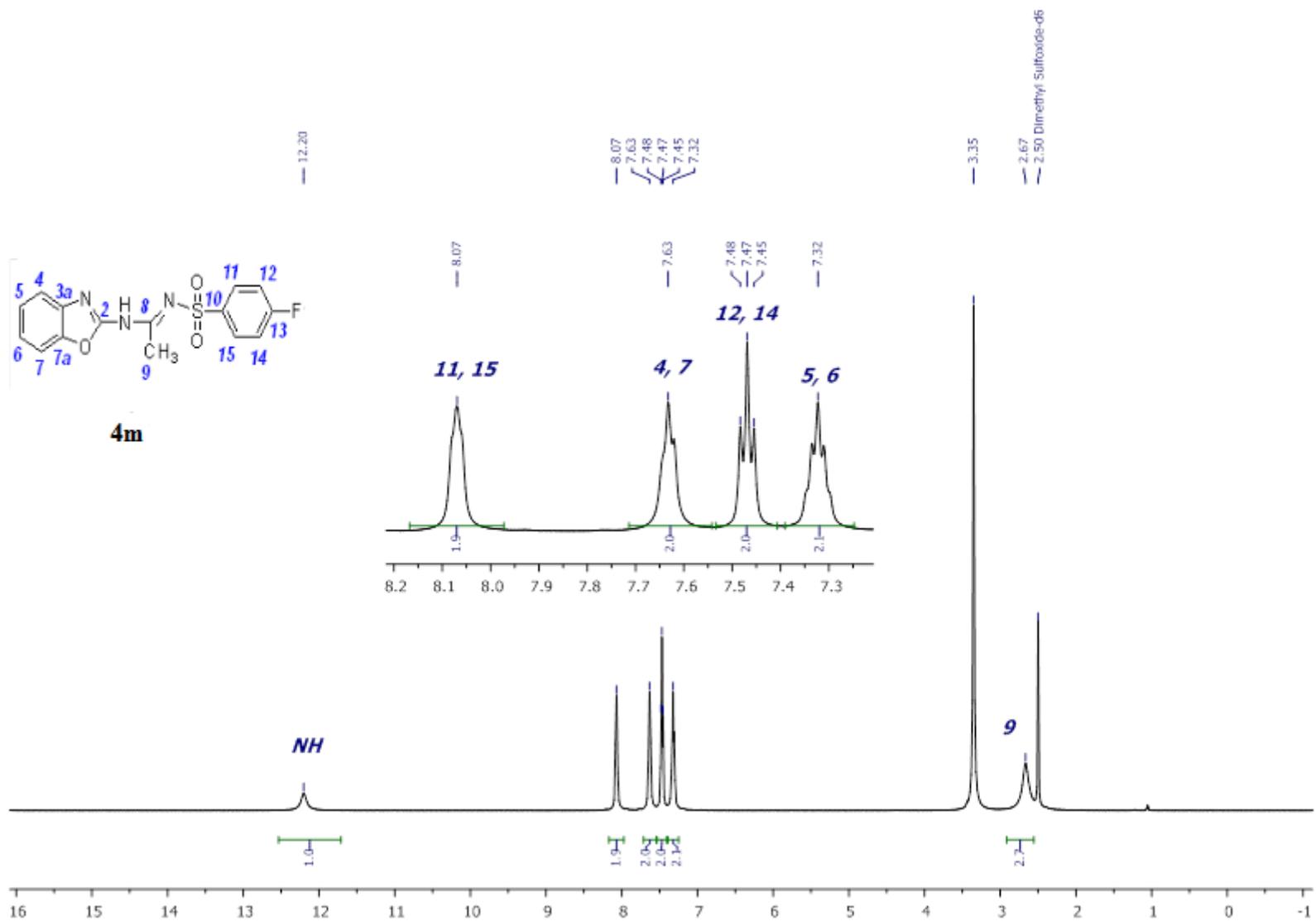
^1H NMR (600 MHz, $\text{DMSO-}d_6$) of **41**



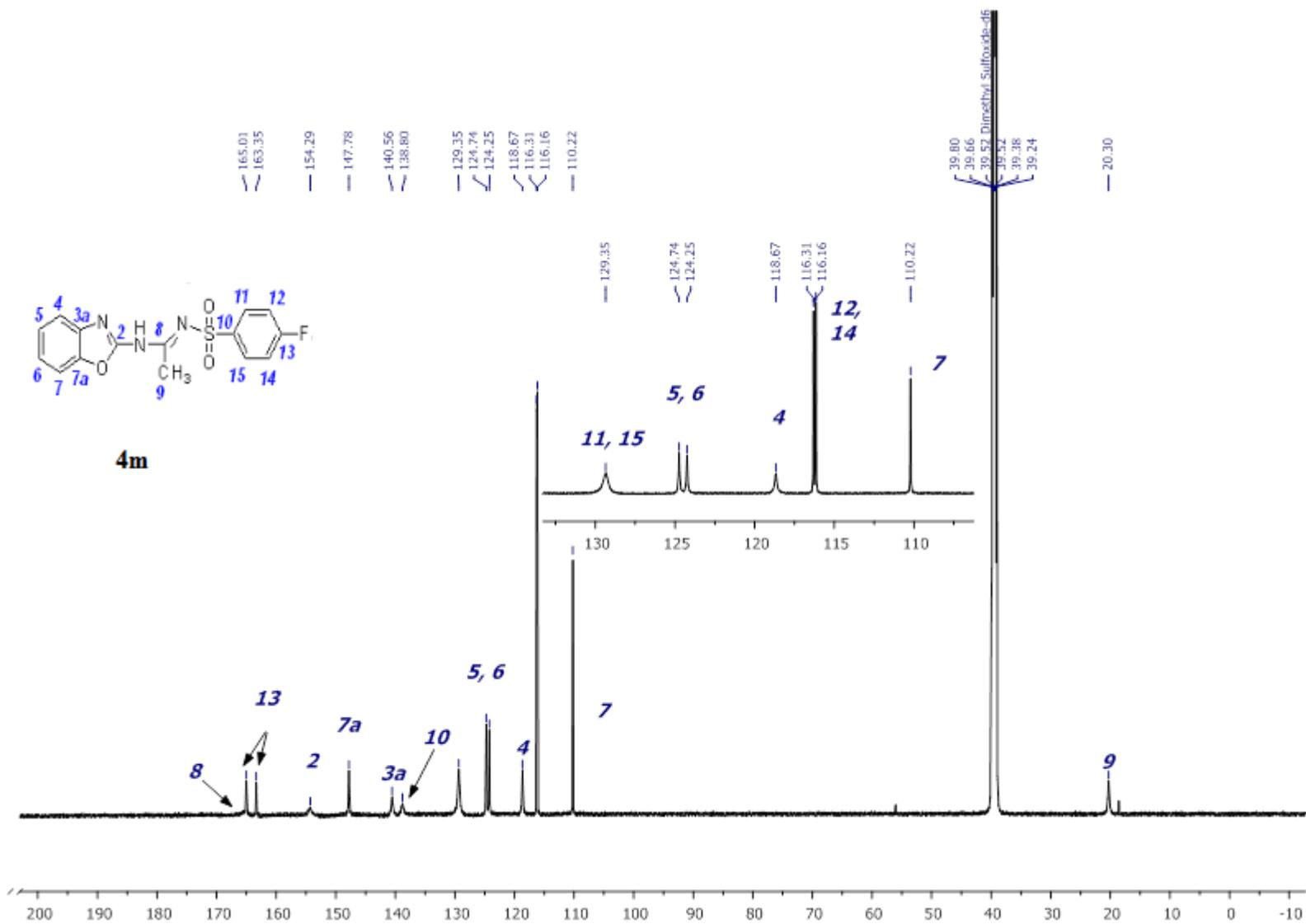
¹³C NMR (150 MHz, DMSO-*d*₆) of **41**



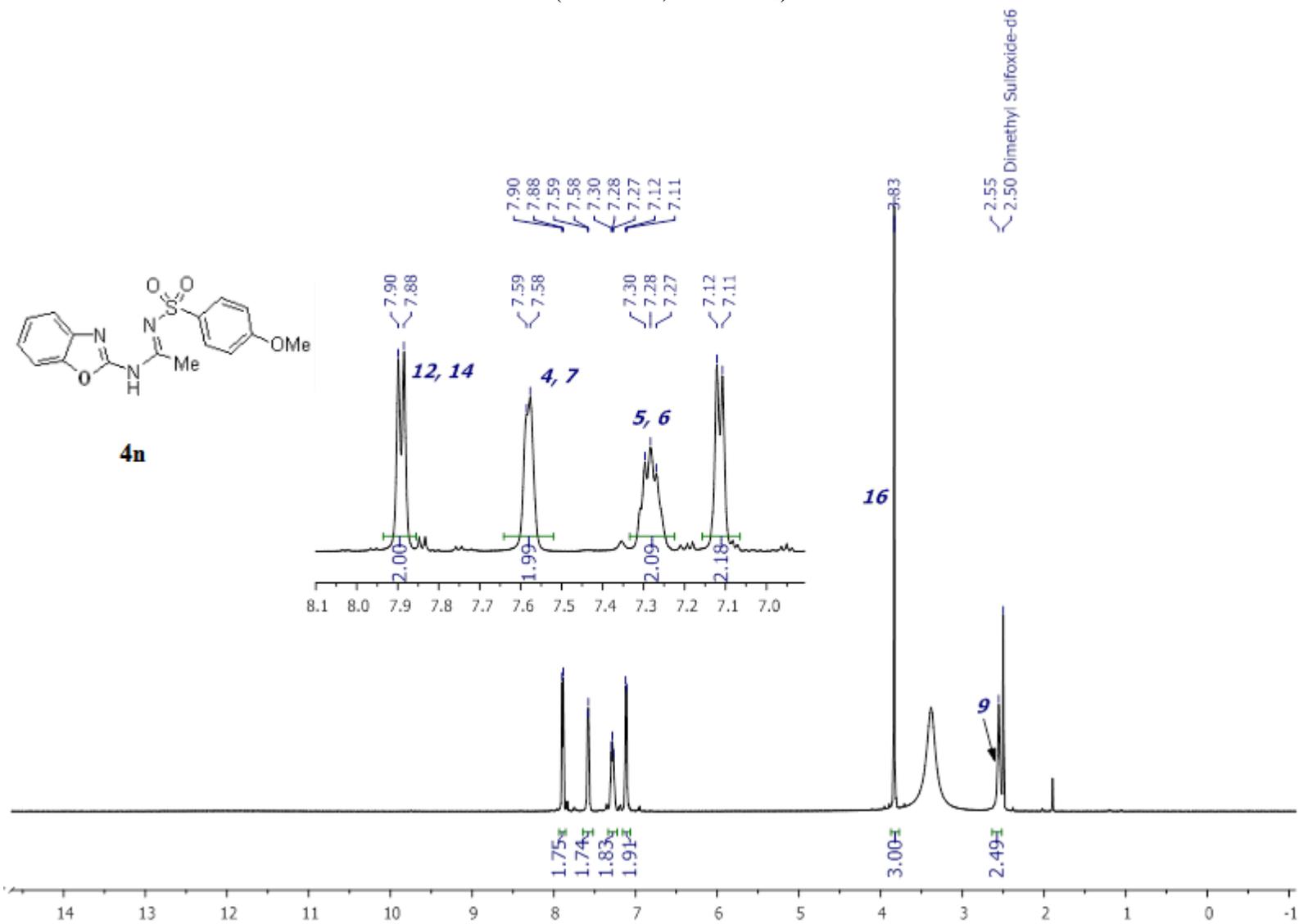
¹H NMR (600 MHz, DMSO-d₆) of **4m**



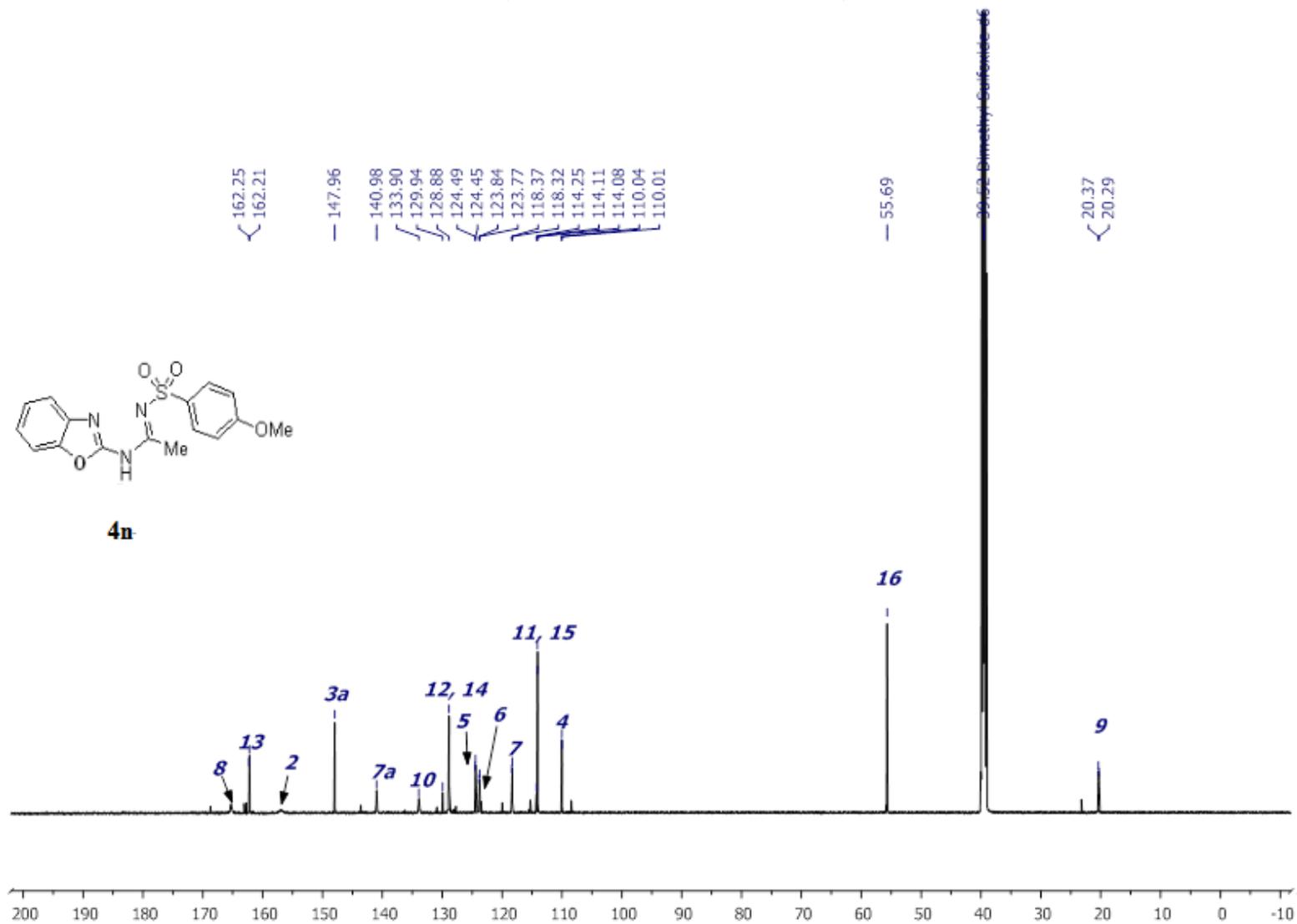
^{13}C NMR (150 MHz, DMSO- d_6) of **4m**



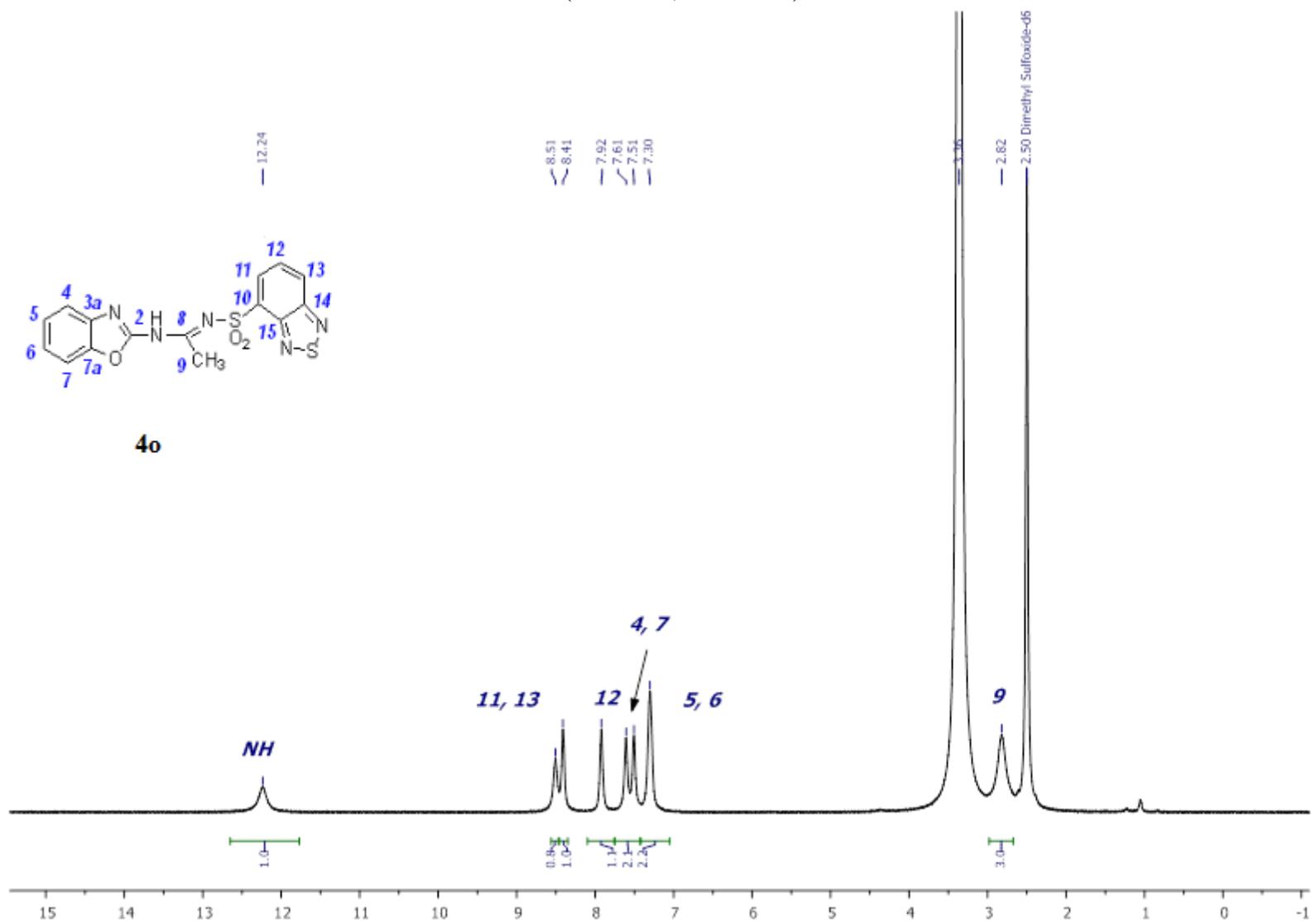
^1H NMR (600 MHz, DMSO- d_6) of **4n**



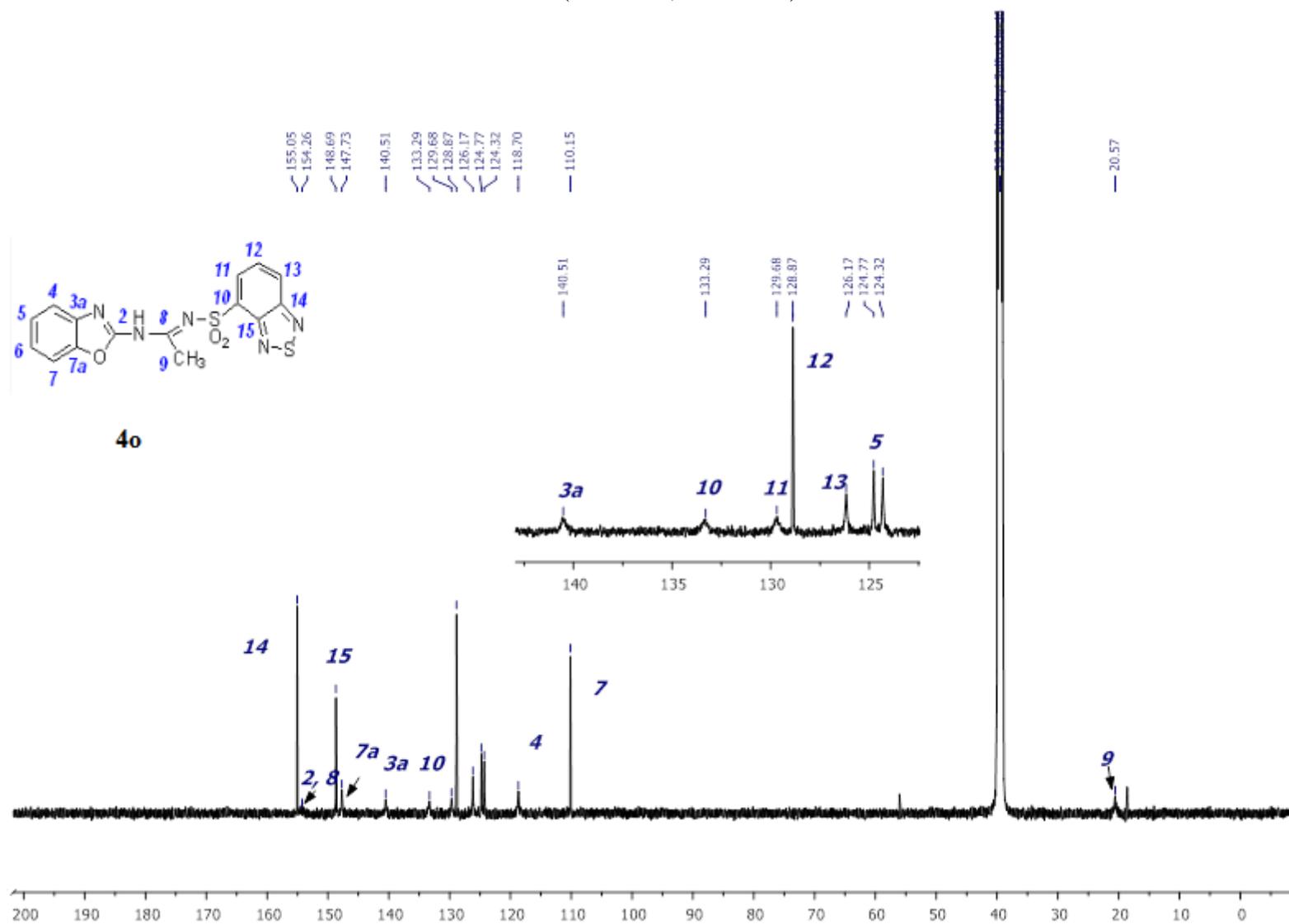
^{13}C NMR (150 MHz, $\text{DMSO-}d_6 + \text{Cs}_2\text{CO}_3$) of **4n**



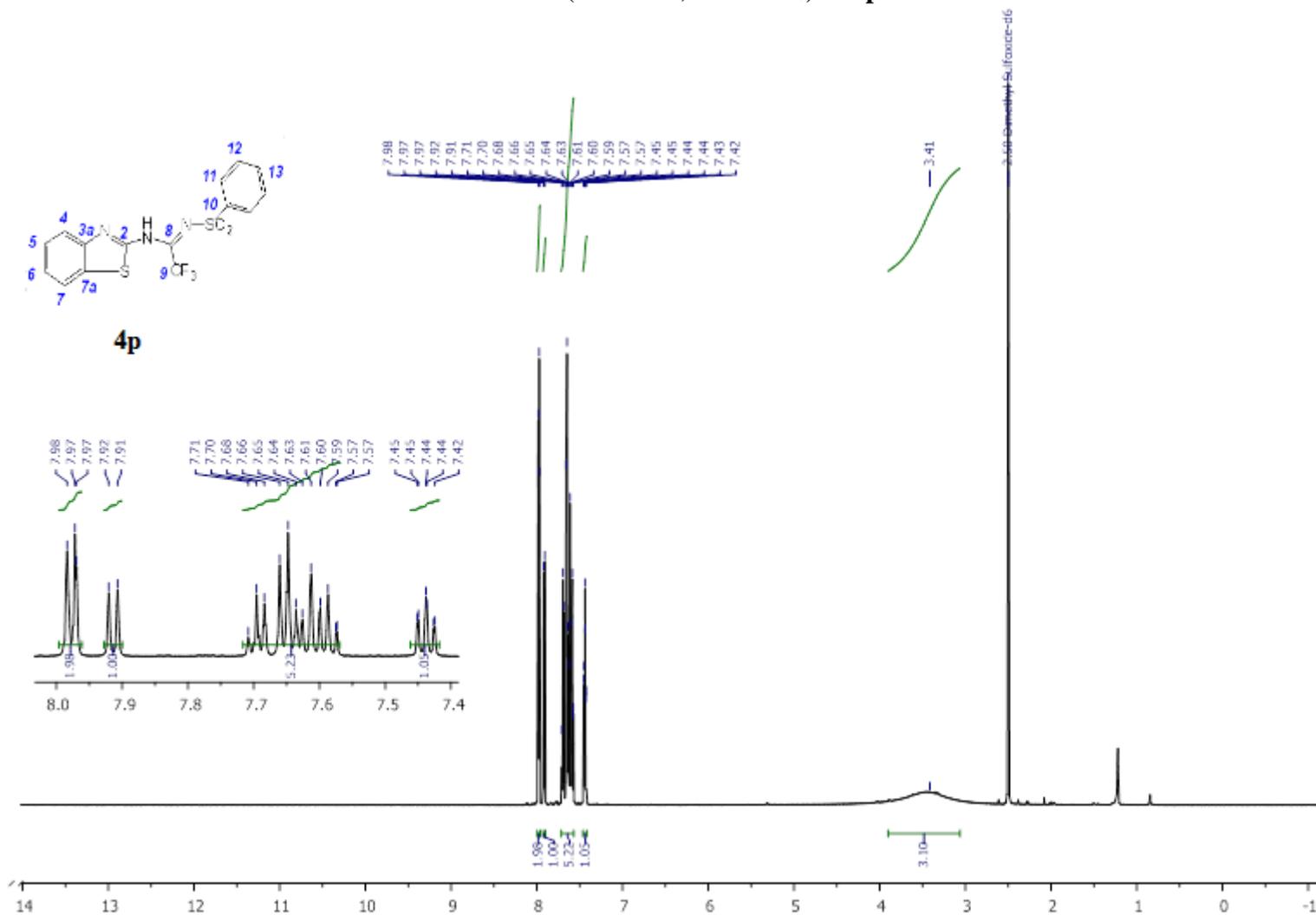
^1H NMR (600 MHz, $\text{DMSO-}d_6$) of **4o**



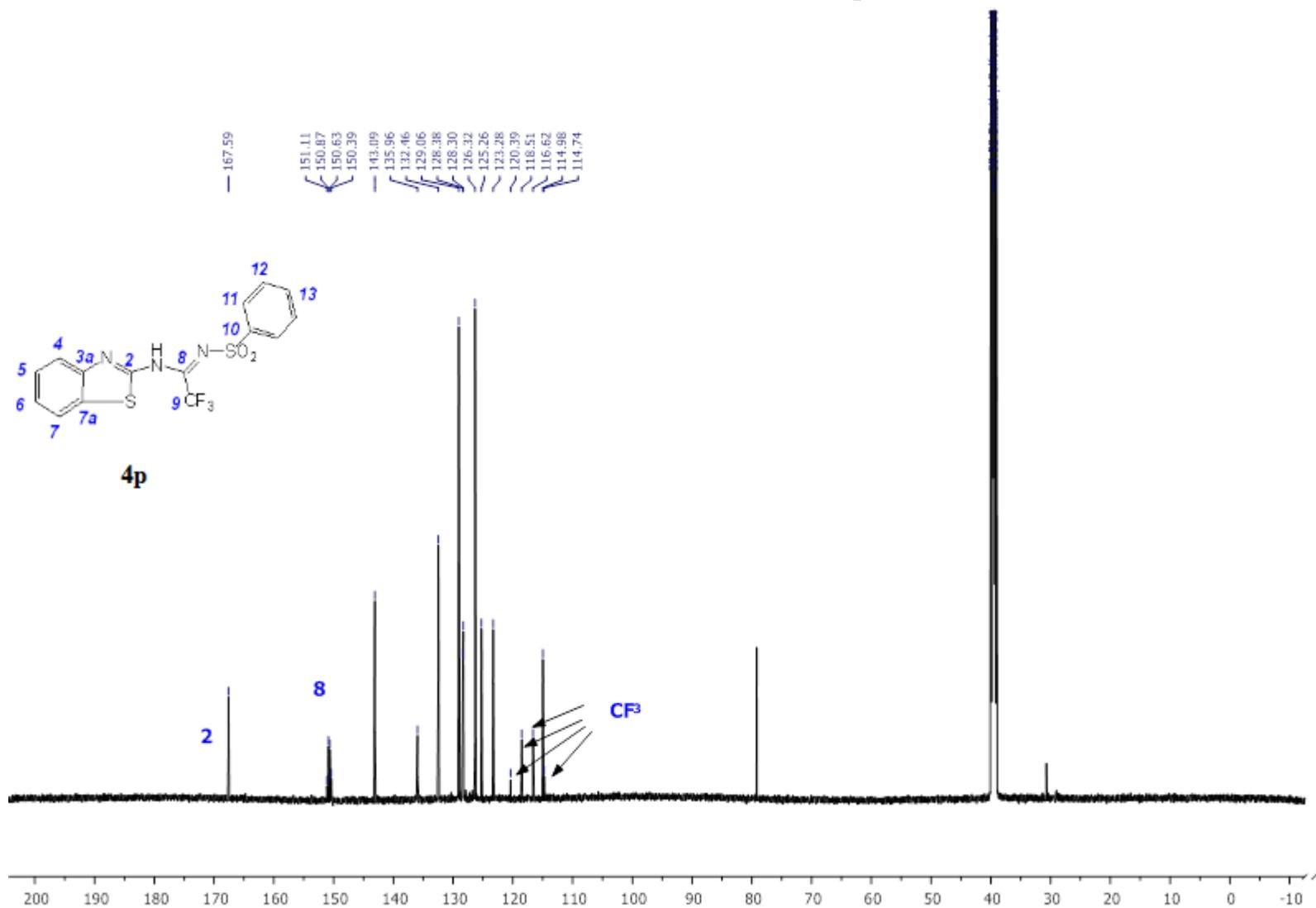
^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) of **4o**



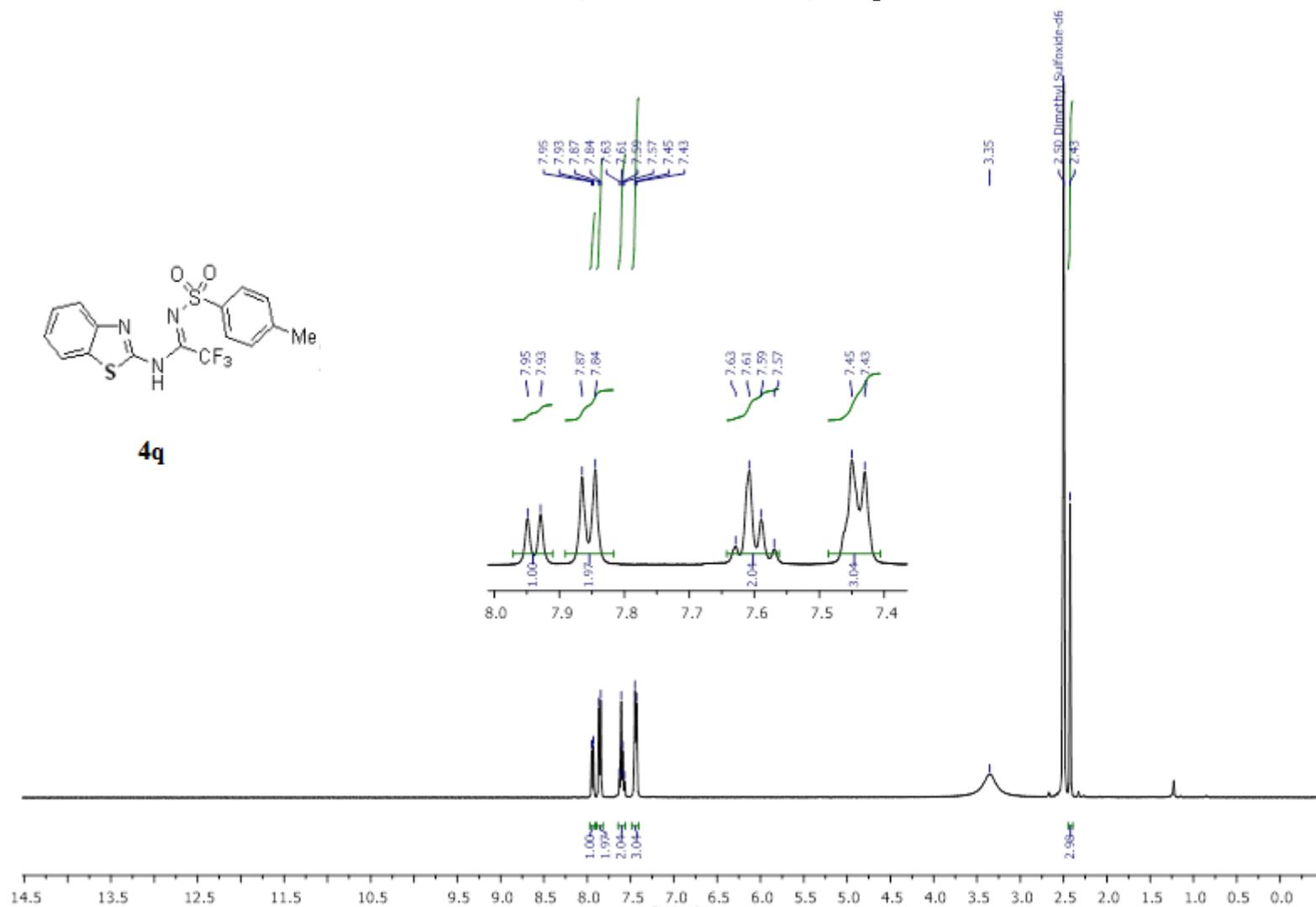
¹H NMR (600 MHz, DMSO-d₆) of **4p**



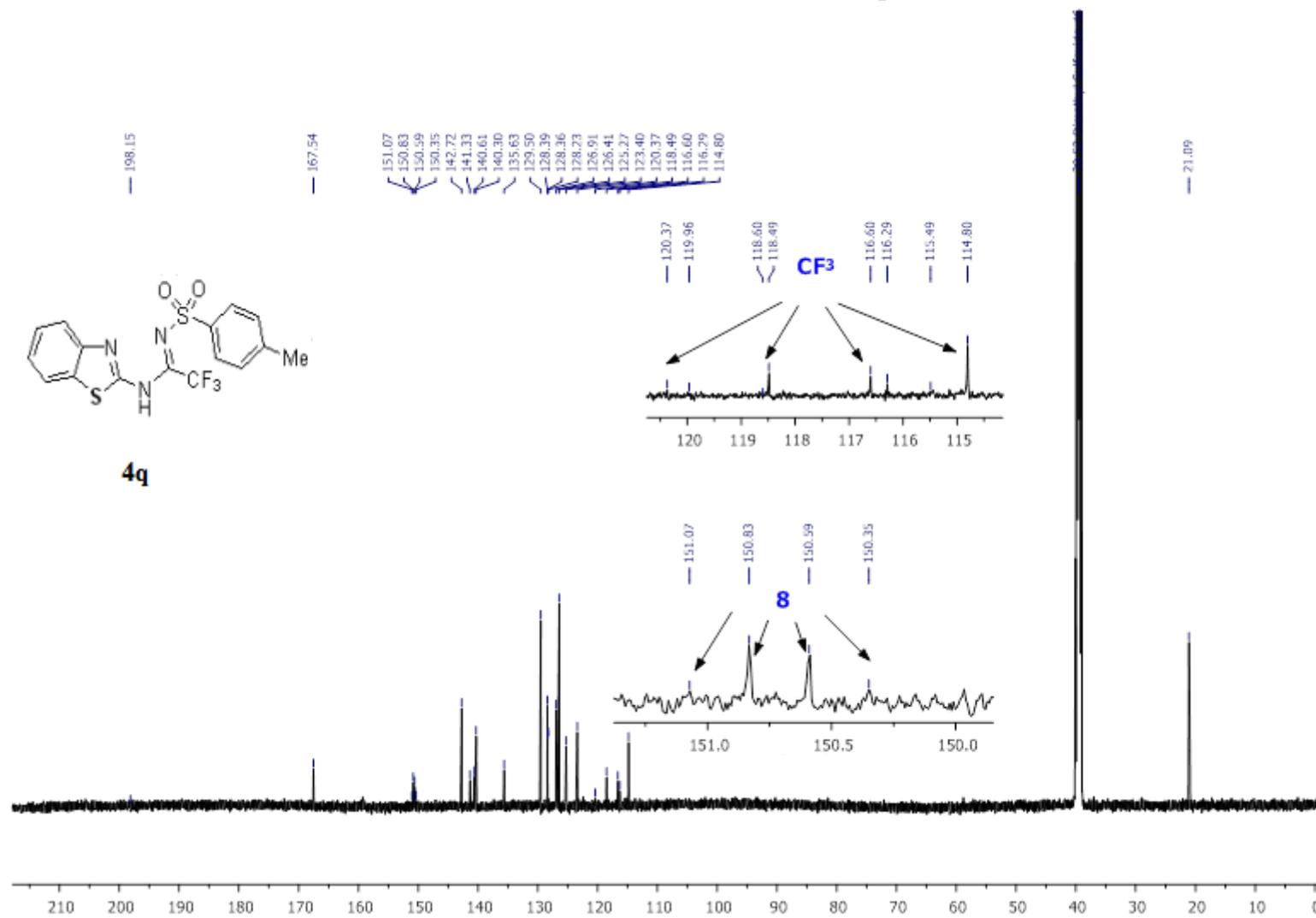
^{13}C NMR (150 HMz, DMSO- d_6) of **4p**



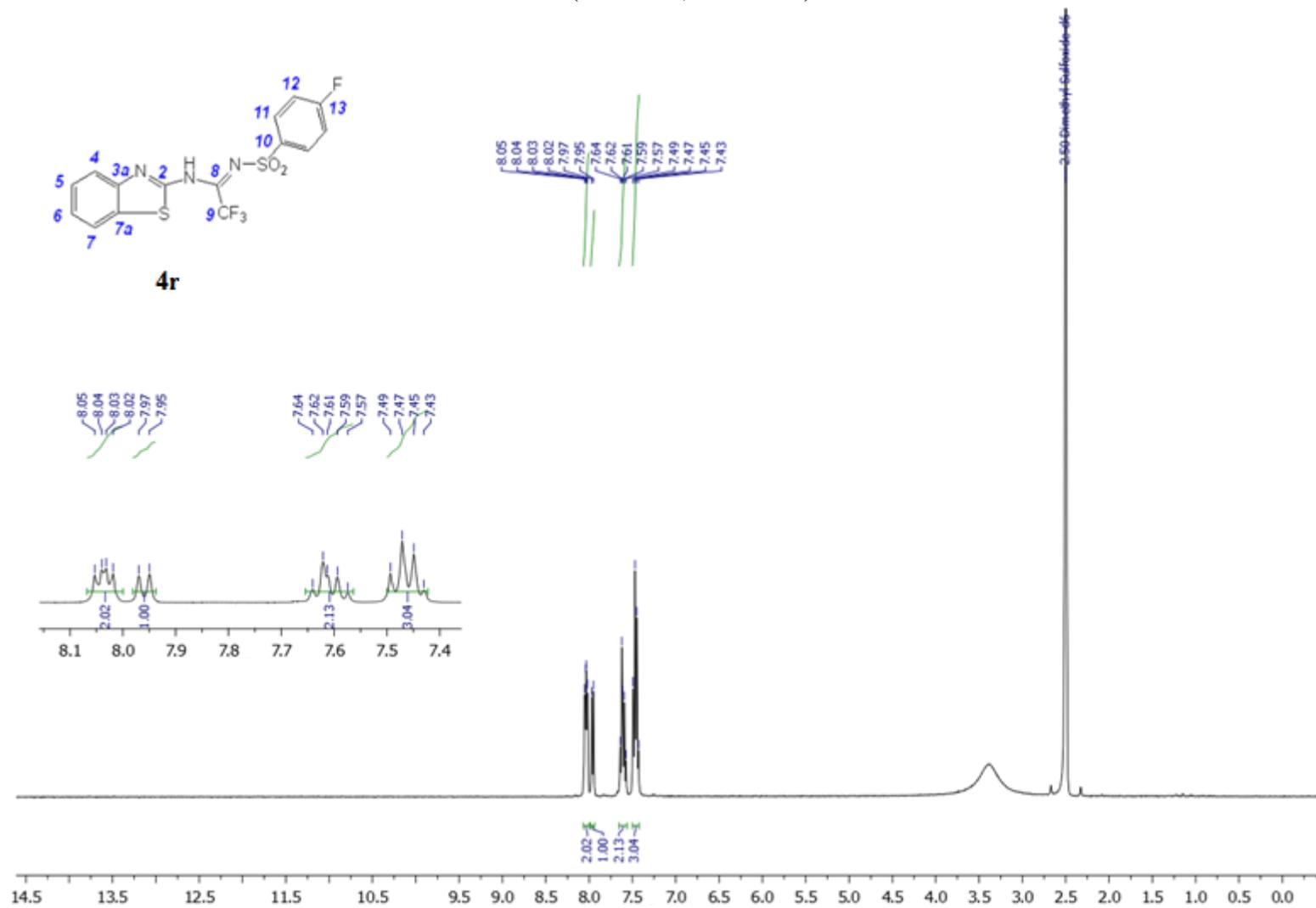
^1H NMR (400 MHz, $\text{DMSO-}d_6$) of **4q**



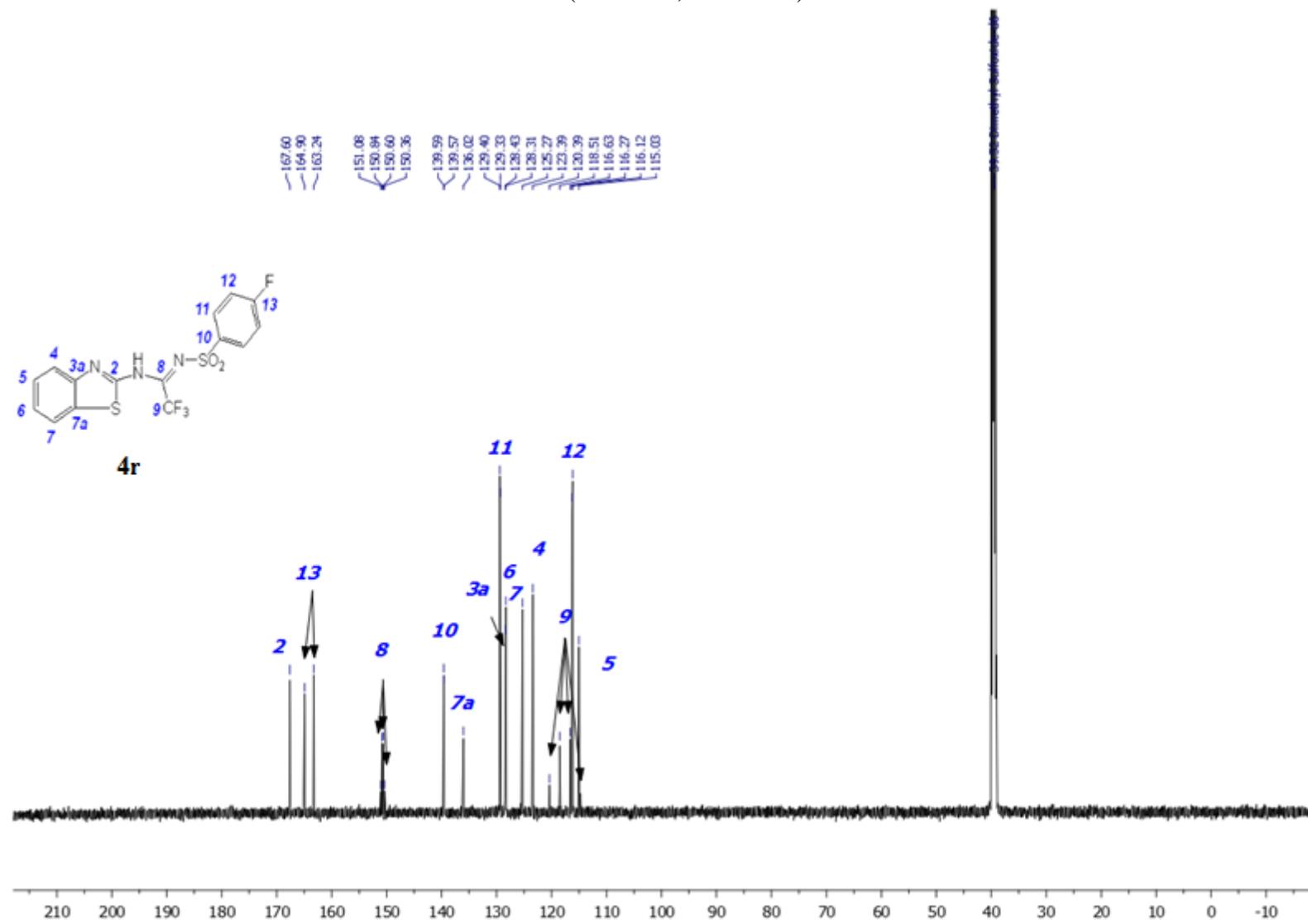
^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) of **4q**



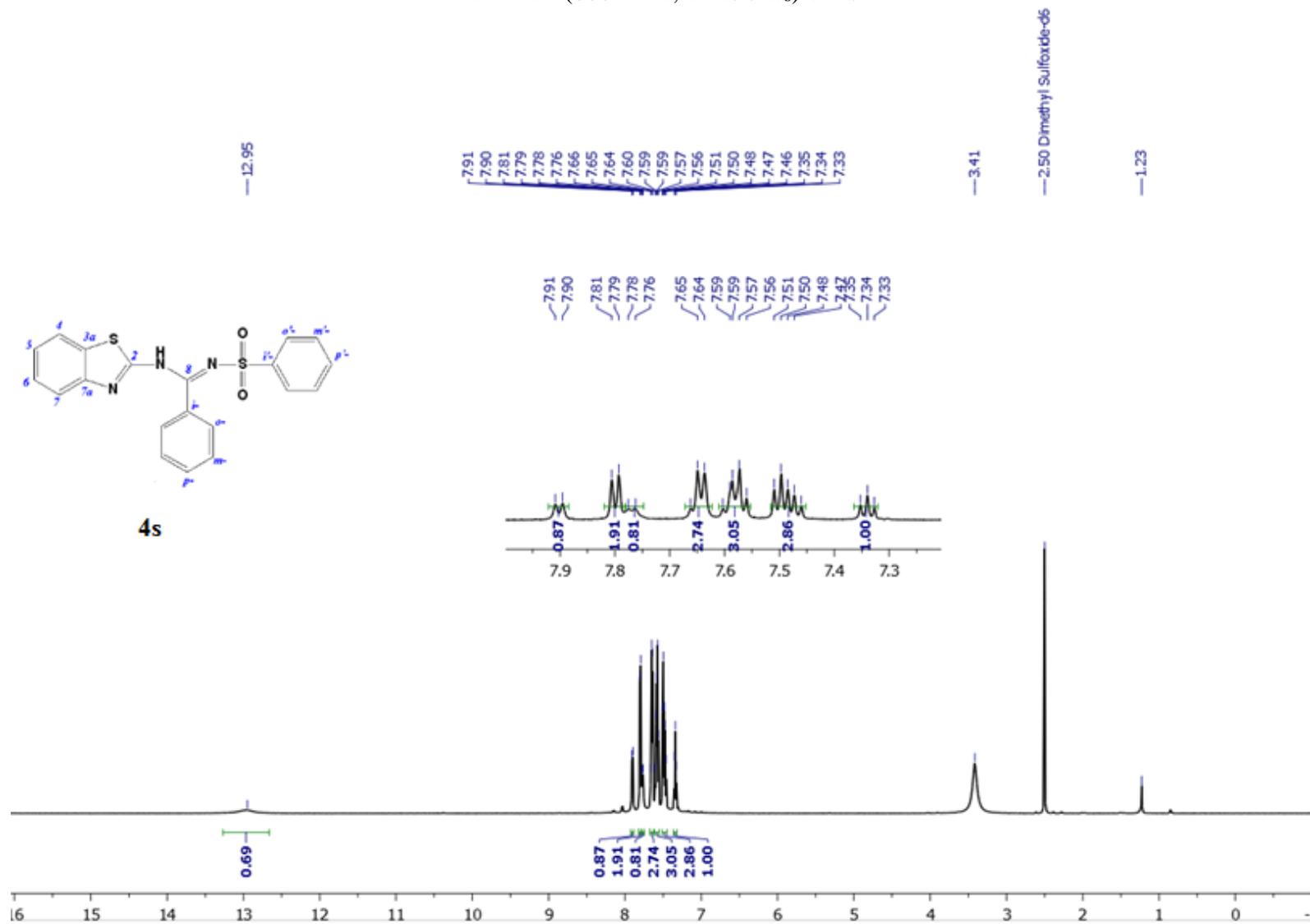
^1H NMR (400 MHz, DMSO- d_6) of **4r**



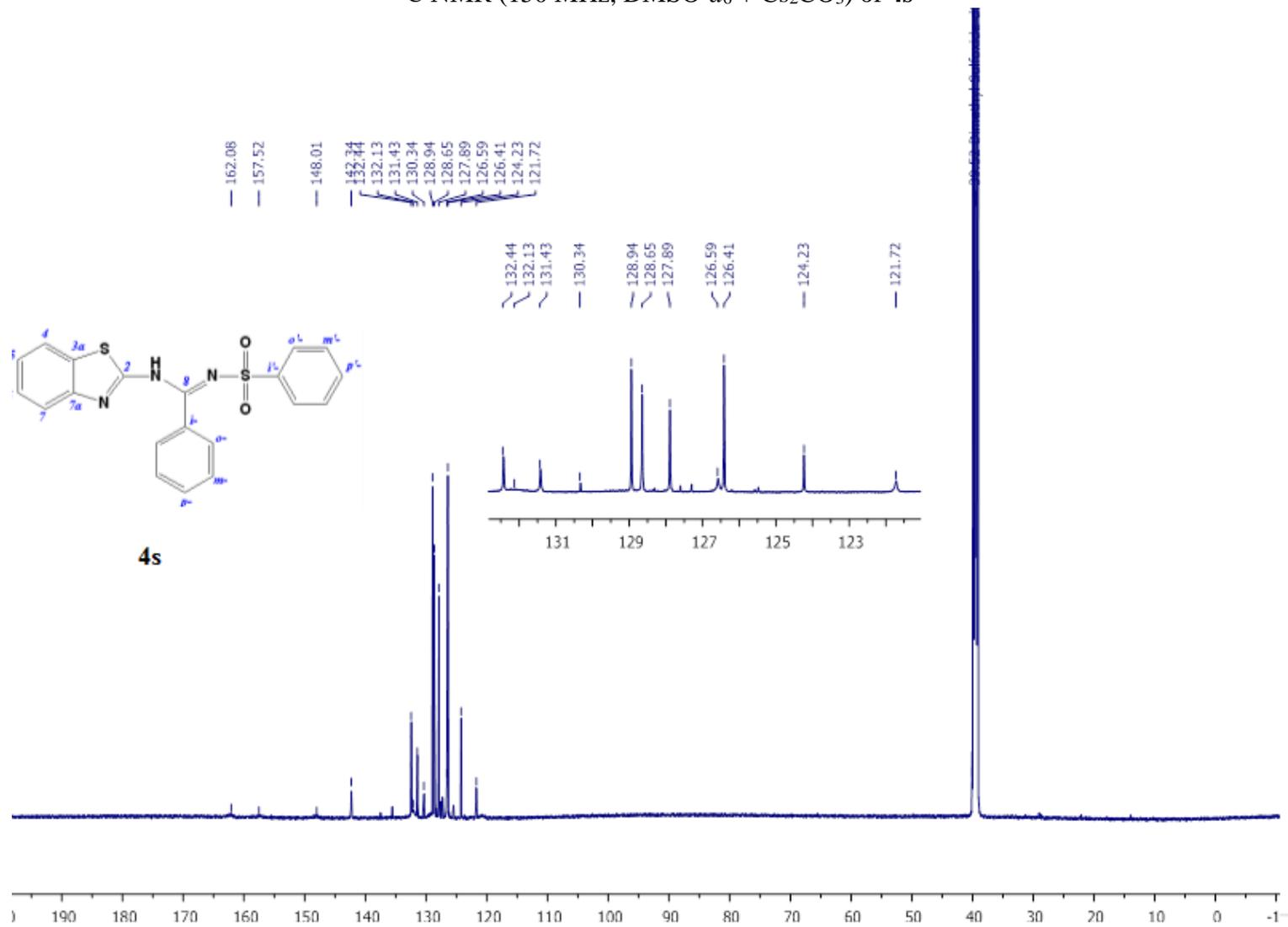
^{13}C NMR (600 MHz, $\text{DMSO-}d_6$) of **4r**



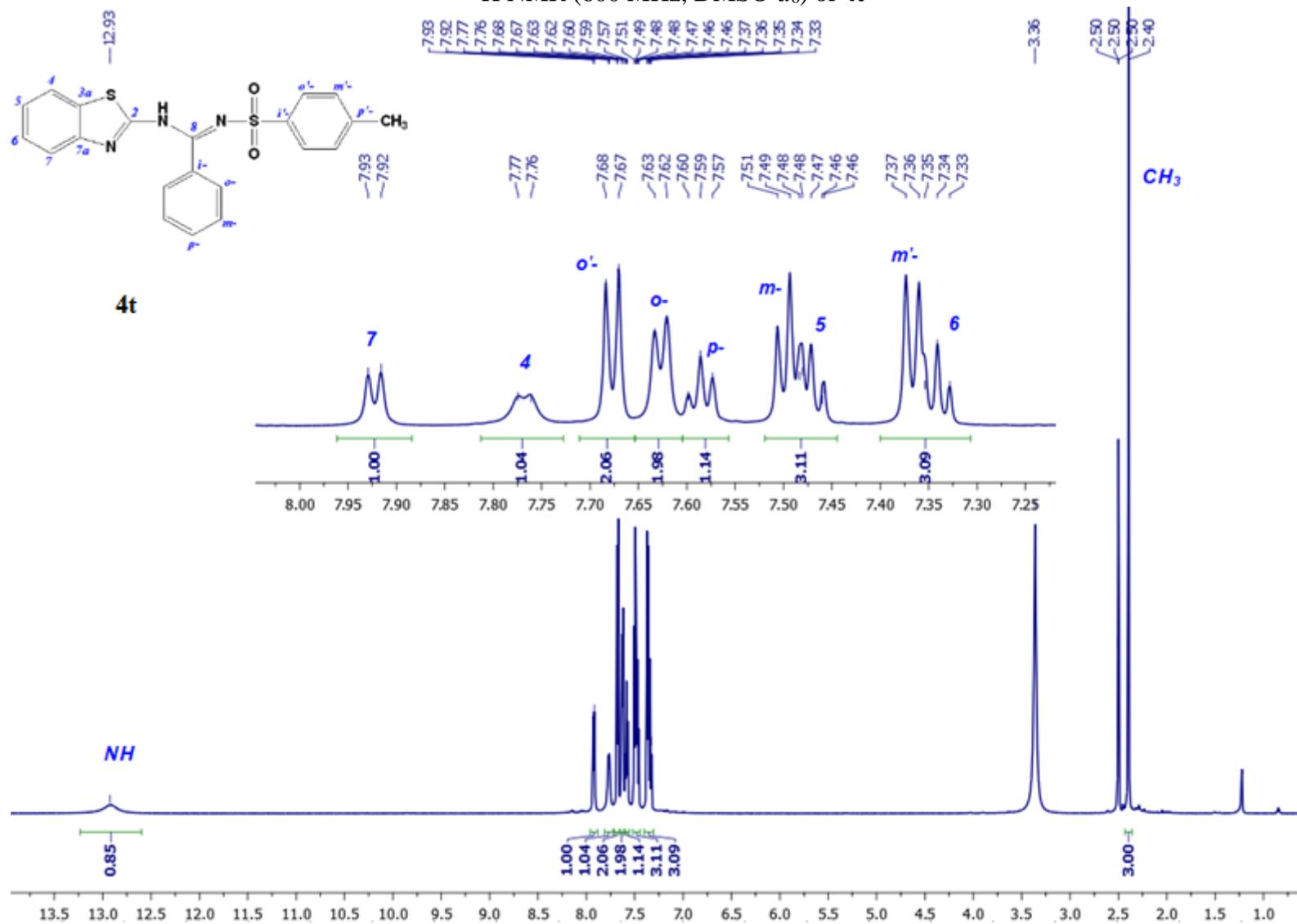
^1H NMR (600 MHz, $\text{DMSO-}d_6$) of **4s**



^{13}C NMR (150 MHz, $\text{DMSO-}d_6 + \text{Cs}_2\text{CO}_3$) of **4s**



¹H NMR (600 MHz, DMSO-d₆) of 4t



^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) of **4t**

