Supplementary data

UV-assisted rearrangement of substituted 3-arylaminopyrazoles with allomaltol fragment into tricyclic cyclopenta[4,5]pyrrolo[2,3-*c*]pyrazole derivatives

Andrey N. Komogortsev, Constantine V. Milyutin, Boris V. Lichitsky and Vasily A. Migulin

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Science, Leninsky Pr., 47, Moscow 119991, Russian Federation

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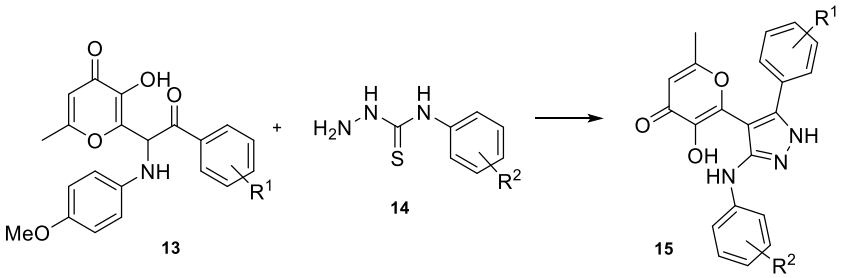
1. General information

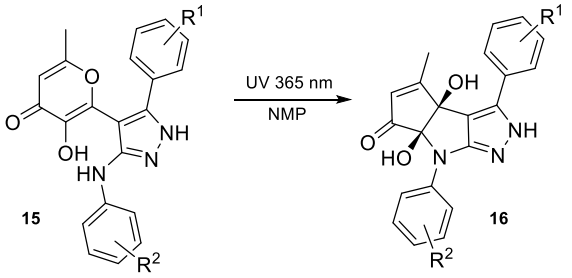
General information. Unless otherwise stated, all starting chemicals were commercially available and were used as received. The starting compounds **13** were prepared to a procedure described in the literature[1]. NMR spectra were recorded with Bruker AM 300 (300 MHz), Bruker Fourier 300 HD (300 MHz), Bruker Avance Neo 300 (300 MHz), Bruker DRX 500 (500 MHz) and Bruker AV 600 (600 MHz) in DMSO-d_6. Chemical shifts (ppm) are given relative to solvent signals (DMSO-d_6: 2.50 ppm (^{1}H NMR) and 39.52 ppm (^{13}C NMR). High-resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The melting points were determined on a Kofler hot stage. Magnetic stirrer IKA C-MAG HS 7 was used for the reactions that require heating. UV/Vis absorption spectra were recorded on a spectrometer Agilent Cary 60 UV-Vis. Fluorescence spectra were recorded on an Agilent Cary Eclipse Fluorescence Spectrometer. The experimental measurements were performed at ambient temperature in the presence of air in 1.0 cm quartz cuvettes in acetonitrile solution. The irradiation was carried out using a 6W Vilber Lourmat (France) UV-lamps model VL-6.LC (λ = 365 nm). Compounds **16** were isolated as a racemic mixture of isomers.

General experimental procedure for the synthesis of compounds 15.



The mixture of compound **13** (1 mmol) and 4-arylthiosemicarbazide **14** (1.1 mmol) in AcOH (5 ml) was refluxed for 1 h. The resulting solution was evaporated in vacuo and obtained residue was recrystallized from EtOH. The target product was filtered off and washed with EtOH (3 × 5 ml).

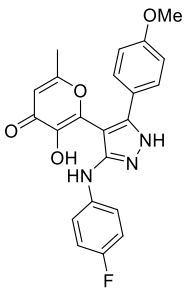
General photochemical procedure for the synthesis of products 16.



A solution of compound **15** (0.5 mmol) in *N*-methylpyrrolidone (10 ml) was irradiated in common glassware with a Vilber Lourmat VL-6.LM (365 nm, 6 W) for 72 h. After complete conversion the reaction mixture was poured into water (50 ml) and the resulting precipitate was filtered off and washed H_2O (3 x 10 ml). Obtained crude product was recrystallized from EtOH, filtered off and washed with EtOH (3 × 5 ml)

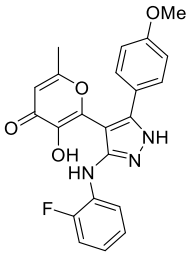
[1] Komogortsev A. N., Lichitsky B. V., Tretyakov A. D., Fakhrutdinov A. N., Dudinov A. A., Krayushkin M. M. *J. Heterocyclic Chem*. **2019**, *56*, 3081–3087.

2. Characterization data of compounds 15



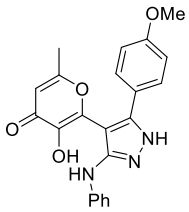
2-(3-((4-fluorophenyl)amino)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15a**).

White powder; yield 72% (0.29 g); m.p. 225-227°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.71 (s, 1H), 7.70 (s, 1H), 7.45 (s, 2H), 7.42 – 7.34 (m, 2H), 7.08 – 6.95 (m, 4H), 6.26 (s, 1H), 3.77 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.9, 165.1, 162.9, 159.6, 155.7 (d, J_{CF} = 234.4 Hz), 142.5, 141.7, 139.7, 128.2, 121.8 (d, J_{CF} = 4.0 Hz), 117.0 (d, J_{CF} = 7.4 Hz), 115.0 (d, J_{CF} = 22.0 Hz), 114.2, 111.1, 96.1, 55.3, 19.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{18}FN_3O_4$ $[M+H]^+$ 408.1354; Found: 408.1371.



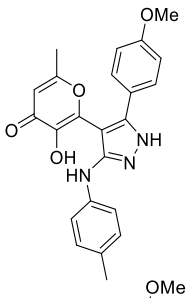
2-(3-((2-fluorophenyl)amino)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15b**).

Pale yellow powder; yield 70% (0.29 g); m.p. 227-229°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.97 (s, 1H), 8.00 (s, 1H), 7.52 – 7.46 (m, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.22 – 6.98 (m, 4H), 6.85 – 6.73 (m, 1H), 6.25 (s, 1H), 3.79 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 164.6, 159.7, 151.1 (d, J = 239.6 Hz), 142.2, 141.0, 131.1 (d, J = 10.1 Hz), 128.7, 124.6 (d, J = 3.4 Hz), 119.3 (d, J = 7.7 Hz), 116.9, 114.7 (d, J = 18.5 Hz), 114.1, 111.2, 97.6, 55.3, 19.1. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{18}FN_3O_4$ $[M+H]^+$ 408.1354; Found: 408.1350.



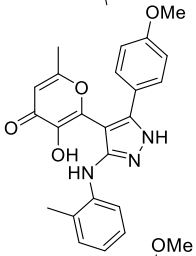
3-hydroxy-2-(5-(4-methoxyphenyl)-3-(phenylamino)-1H-pyrazol-4-yl)-6-methyl-4H-pyran-4-one (**15c**).

White powder; yield 63% (0.25 g); m.p. 222-224°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.75 (s, 1H), 7.66 (s, 1H), 7.48 – 7.35 (m, 4H), 7.24 – 7.13 (m, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.26 (s, 1H), 3.78 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.0, 165.1, 159.6, 143.2, 142.4, 141.9, 128.7, 128.3, 122.0, 118.9, 115.8, 114.2, 111.1, 96.6, 55.3, 19.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{19}N_3O_4$ $[M+H]^+$ 390.1448; Found: 390.1440.



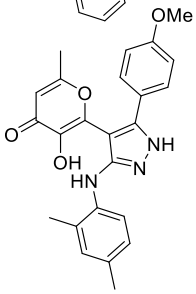
3-hydroxy-2-(5-(4-methoxyphenyl)-3-(p-tolylamino)-1H-pyrazol-4-yl)-6-methyl-4H-pyran-4-one (**15d**).

Grey powder; yield 75% (0.30 g); m.p. 239-241°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.69 (s, 1H), 9.08 (s, 1H), 7.54 (s, 1H), 7.43 – 7.27 (m, 4H), 7.04 – 6.95 (m, 4H), 6.26 (s, 1H), 3.78 (s, 3H), 2.20 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 173.9, 165.0, 159.5, 142.3, 141.9, 140.7, 129.1, 128.2, 127.3, 115.9, 114.1, 111.1, 96.1, 55.3, 20.3, 19.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{23}H_{21}N_3O_4$ $[M+H]^+$ 404.1605; Found: 404.1612.



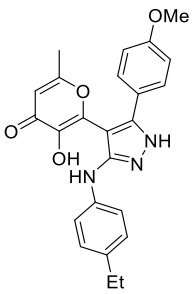
3-hydroxy-2-(5-(4-methoxyphenyl)-3-(o-tolylamino)-1H-pyrazol-4-yl)-6-methyl-4H-pyran-4-one (**15e**).

Pale yellow powder; yield 71% (0.29 g); m.p. 206-208°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.90 (s, 1H), 9.89 (s, 1H), 7.91 (s, 1H), 7.40 (d, J = 8.3 Hz, 2H), 7.13 – 6.98 (m, 5H), 6.72 (t, J = 7.4 Hz, 1H), 6.25 (s, 1H), 3.79 (s, 3H), 2.19 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.5, 164.5, 159.6, 149.9, 142.4, 141.1, 140.8, 130.0, 128.5, 126.4, 123.4, 121.5, 119.1, 115.0, 114.0, 111.0, 97.5, 55.3, 19.0, 17.6. HRMS (ESI-TOF) *m/z*: Calcld for $C_{23}H_{22}N_3O_4$ $[M+H]^+$ 404.1605; Found: 404.1605.



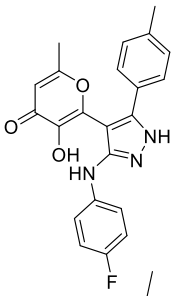
2-(3-((2,4-dimethylphenyl)amino)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15f**).

Grey powder; yield 79% (0.33 g); m.p. 186-188°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.85 (s, 1H), 9.86 (s, 1H), 7.79 (s, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 8.3 Hz, 2H), 6.95 – 6.85 (m, 3H), 6.25 (s, 1H), 3.78 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.4, 164.4, 159.5, 142.5, 140.8, 138.6, 130.7, 128.5, 127.9, 126.7, 123.8, 115.6, 114.0, 111.0, 97.0, 55.2, 20.2, 19.9, 17.5. HRMS (ESI-TOF) *m/z*: Calcld for $C_{24}H_{23}N_3O_4$ $[M+H]^+$ 418.1761; Found: 418.1750.



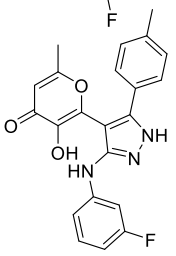
2-(3-((4-ethylphenyl)amino)-5-(4-methoxyphenyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15g**).

Grey powder; yield 74% (0.31 g); m.p. 192-194°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.74 (s, 1H), 7.55 (s, 1H), 7.43 – 7.29 (m, 4H), 7.07 – 6.95 (m, 4H), 6.25 (s, 1H), 3.77 (s, 3H), 2.07 (s, 3H), 1.13 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.9, 165.1, 159.6, 142.3, 142.0, 140.9, 134.2, 128.2, 127.9, 116.0, 114.2, 111.1, 96.2, 55.3, 27.5, 19.4, 16.1. HRMS (ESI-TOF) *m/z*: Calcld for $C_{24}H_{23}N_3O_4$ $[M+H]^+$ 418.1761; Found: 418.1763.



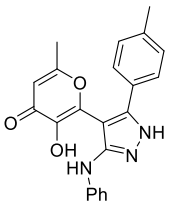
2-(3-((4-fluorophenyl)amino)-5-(p-tolyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15h**).

White powder; yield 67% (0.26 g); m.p. 300+ °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.74 (s, 1H), 9.05 (s, 1H), 7.75 (s, 1H), 7.52 – 7.42 (m, 2H), 7.35 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.09 – 6.98 (m, 2H), 6.27 (s, 1H), 2.32 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.9, 165.0, 155.7 (d, J_{CF} = 234.5 Hz), 142.6, 141.5, 139.6 (d, J_{CF} = 2.0 Hz), 138.2, 129.2, 126.6, 117.0 (d, J_{CF} = 7.3 Hz), 115.0 (d, J_{CF} = 21.8 Hz), 111.1, 96.3, 20.9, 19.3. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{19}FN_3O_3$ $[M+H]^+$ 392.1405; Found: 392.1411.



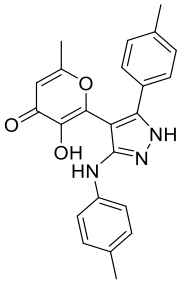
2-(3-((3-fluorophenyl)amino)-5-(p-tolyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15i**).

White powder; yield 59% (0.23 g); m.p. 268-270°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.84 (s, 1H), 9.01 (s, 1H), 8.02 (s, 1H), 7.50 – 7.41 (m, 1H), 7.36 (d, J = 7.9 Hz, 2H), 7.28 – 7.12 (m, 4H), 6.61 – 6.48 (m, 1H), 6.27 (s, 1H), 2.32 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.8, 165.1, 162.8 (d, J_{CF} = 239.1 Hz), 145.0 (d, J_{CF} = 11.5 Hz), 142.7, 141.2, 138.2, 129.9 (d, J_{CF} = 9.9 Hz), 129.3, 126.6, 111.8, 111.1, 104.8 (d, J_{CF} = 21.0 Hz), 102.1 (d, J_{CF} = 26.9 Hz), 96.8, 20.8, 19.3. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{19}FN_3O_3$ $[M+H]^+$ 392.1405; Found: 392.1407.



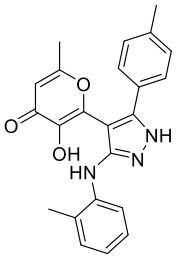
3-hydroxy-6-methyl-2-(3-(phenylamino)-5-(p-tolyl)-1H-pyrazol-4-yl)-4H-pyran-4-one (**15j**).

White powder; yield 55% (0.21 g); m.p. 206-208°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.79 (s, 1H), 9.09 (br. s, 1H), 7.68 (s, 1H), 7.51 – 7.31 (m, 4H), 7.28 – 7.13 (m, 4H), 6.81 – 6.70 (m, 1H), 6.25 (s, 1H), 2.32 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.8, 165.0, 149.6, 143.1, 142.3, 141.7, 138.1, 129.2, 128.6, 126.7, 118.8, 115.7, 111.1, 96.7, 20.9, 19.3. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{20}N_3O_3$ $[M+H]^+$ 374.1499; Found: 374.1503.



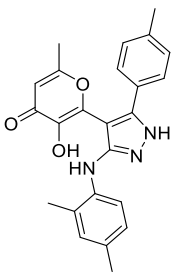
3-hydroxy-6-methyl-2-(5-(p-tolyl)-3-(p-tolylamino)-1H-pyrazol-4-yl)-4H-pyran-4-one (**15k**).

White powder; yield 74% (0.29 g); m.p. 207-209°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.73 (s, 1H), 8.99 (br. s, 1H), 7.55 (s, 1H), 7.34 (d, J = 7.8 Hz, 4H), 7.23 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.25 (s, 1H), 2.32 (s, 3H), 2.21 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 173.8, 165.0, 142.3, 141.8, 140.6, 138.1, 129.2, 129.1, 127.3, 126.6, 115.9, 111.0, 96.3, 83.5, 20.9, 20.3, 19.3. HRMS (ESI-TOF) *m/z*: Calcld for $C_{23}H_{22}N_3O_3$ $[M+H]^+$ 388.1656; Found: 388.1666.



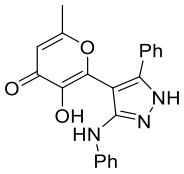
3-hydroxy-6-methyl-2-(5-(p-tolyl)-3-(o-tolylamino)-1H-pyrazol-4-yl)-4H-pyran-4-one (**15l**).

Yellow powder; yield 64% (0.25 g); m.p. 213-215°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.95 (s, 1H), 9.88 (s, 1H), 7.83 (s, 1H), 7.36 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 7.13 – 7.00 (m, 3H), 6.72 (t, J = 7.3 Hz, 1H), 6.24 (s, 1H), 2.34 (s, 3H), 2.19 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.5, 164.5, 142.3, 141.1, 140.9, 138.2, 130.1, 129.1, 127.0, 126.5, 123.5, 119.2, 115.0, 111.0, 97.8, 20.9, 18.9, 17.6. HRMS (ESI-TOF) *m/z*: Calcld for $C_{23}H_{22}N_3O_3$ $[M+H]^+$ 388.1656; Found: 388.1655.



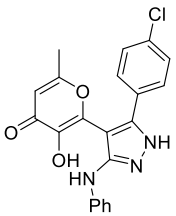
2-(3-((2,4-dimethylphenyl)amino)-5-(p-tolyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15m**).

White powder; yield 70% (0.28 g); m.p. 205-207°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.90 (s, 1H), 9.89 (s, 1H), 7.79 (s, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.95 – 6.85 (m, 3H), 6.24 (s, 1H), 2.33 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.5, 164.4, 142.4, 140.8, 138.6, 138.1, 130.7, 129.1, 127.0, 126.8, 115.6, 111.0, 97.3, 40.4, 40.1, 39.8, 39.5, 39.2, 39.0, 38.7, 20.9, 20.2, 19.0, 17.6. HRMS (ESI-TOF) *m/z*: Calcld for $C_{24}H_{24}N_3O_3$ $[M+H]^+$ 402.1812; Found: 402.1803.



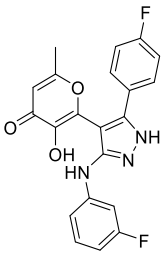
3-hydroxy-6-methyl-2-(5-phenyl-3-(phenylamino)-1H-pyrazol-4-yl)-4H-pyran-4-one (**15n**).

Grey powder; yield 60% (0.22 g); m.p. 219-221°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.83 (s, 1H), 9.15 (s, 1H), 7.72 (s, 1H), 7.48 – 7.38 (m, 7H), 7.25 – 7.14 (m, 2H), 6.82 – 6.71 (m, 1H), 6.26 (s, 1H), 2.04 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.0, 165.2, 143.2, 142.4, 141.8, 128.8, 126.9, 119.0, 115.8, 111.2, 97.1, 19.3. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{17}N_3O_3$ $[M+H]^+$ 360.1343; Found: 360.1347.



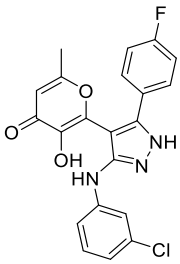
2-(5-(4-chlorophenyl)-3-(phenylamino)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15o**).

White powder; yield 59% (0.23 g); m.p. 208-210°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.94 (s, 1H), 9.09 (s, 1H), 7.75 (s, 1H), 7.62 – 7.32 (m, 6H), 7.24 – 7.13 (m, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.25 (s, 1H), 2.07 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.8, 165.0, 143.0, 142.3, 141.3, 133.2, 128.7, 128.6, 128.5, 118.9, 115.7, 111.1, 19.2. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{16}ClN_3O_3$ $[M+H]^+$ 394.0953; Found: 394.0969.



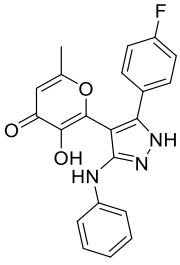
2-(5-(4-fluorophenyl)-3-((3-fluorophenyl)amino)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15p**).

White powder; yield 65% (0.26 g); m.p. 212-214°C.^{1}H NMR (300 MHz, DMSO-d_6) δ 8.07 (s, 1H), 7.55 – 7.46 (m, 2H), 7.46 – 7.36 (m, 1H), 7.34 – 7.24 (m, 2H), 7.23 – 7.08 (m, 2H), 6.55 (t, J = 8.4 Hz, 1H), 6.27 (s, 1H), 2.09 (s, 3H), 1.91 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.0, 165.3, 162.9 (d, J_{CF} = 238.9 Hz), 162.3 (d, J_{CF} = 246.3 Hz), 145.0 (d, J_{CF} = 11.7 Hz), 142.7, 141.1, 130.1 (d, J_{CF} = 9.6 Hz), 129.1 (d, J_{CF} = 8.5 Hz), 115.9 (d, J_{CF} = 21.7 Hz), 111.9, 111.2, 105.1 (d, J_{CF} = 21.4 Hz), 102.3 (d, J_{CF} = 26.5 Hz), 19.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{16}F_2N_3O_3$ $[M+H]^+$ 396.1154; Found: 396.1154.



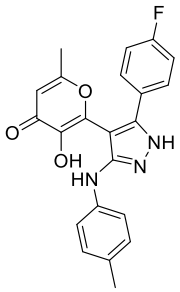
2-(3-((3-chlorophenyl)amino)-5-(4-fluorophenyl)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15q**).

White powder; yield 76% (0.31 g); m.p. 285-287°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.07 (s, 1H), 7.64 (s, 1H), 7.56 – 7.45 (m, 2H), 7.35 – 7.25 (m, 3H), 7.20 (t, J = 8.0 Hz, 1H), 6.78 (d, J = 7.7 Hz, 1H), 6.27 (s, 1H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.0, 165.3, 162.3 (d, J_{CF} = 246.4 Hz), 149.2, 144.6, 142.8, 141.0, 133.4, 130.3, 129.1 (d, J_{CF} = 8.4 Hz), 126.0, 118.4, 115.9 (d, J_{CF} = 21.8 Hz), 115.0, 114.4, 111.2, 97.3, 19.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{16}FClN_3O_3$ $[M+H]^+$ 412.0859; Found: 412.0857.



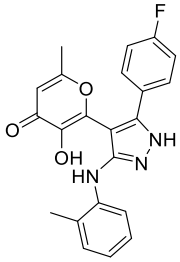
2-(5-(4-fluorophenyl)-3-(phenylamino)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15r**).

White powder; yield 61% (0.23 g); m.p. 282-284°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.81 (s, 1H), 9.15 (s, 1H), 7.74 (s, 1H), 7.56 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 7.35 – 7.24 (m, 2H), 7.24 – 7.12 (m, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.25 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 173.7, 164.9, 162.0 (d, J_{CF} = 245.9 Hz), 142.9, 142.2, 141.3, 128.9 (d, J_{CF} = 8.5 Hz), 128.5, 118.8, 115.6 (d, J_{CF} = 21.7 Hz), 115.5, 111.0, 19.1. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{17}FN_3O_3$ $[M+H]^+$ 378.1248; Found: 378.1237.



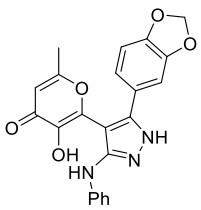
2-(5-(4-fluorophenyl)-3-(p-tolylamino)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15s**).

Pale yellow powder; yield 74% (0.29 g); m.p. 272-274°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.82 (s, 1H), 9.11 (s, 1H), 7.59 (s, 1H), 7.55 – 7.43 (m, 2H), 7.37 – 7.23 (m, 4H), 7.05 – 6.96 (m, 2H), 6.25 (s, 1H), 2.21 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.8, 164.9, 162.1 (d, J_{CF} = 246.0 Hz), 150.5, 142.1, 141.6, 140.6, 129.0, 129.0, 127.4, 125.9, 115.9, 115.6 (d, J_{CF} = 22.2 Hz), 111.0, 96.7, 20.2, 19.2. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{19}FN_3O_3$ $[M+H]^+$ 392.1405; Found: 392.1414.



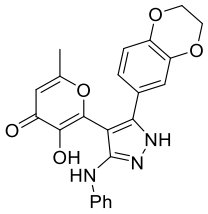
2-(5-(4-fluorophenyl)-3-(o-tolylamino)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15t**).

White powder; yield 67% (0.26 g); m.p. 198-200°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.78 – 7.70 (m, 1H), 7.55 – 7.44 (m, 2H), 7.36 – 7.24 (m, 2H), 7.13 – 7.02 (m, 3H), 6.79 – 6.68 (m, 1H), 6.24 (s, 1H), 2.19 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.7, 164.7, 162.3 (d, J_{CF} = 246.1 Hz), 149.1, 142.2, 141.1, 141.0, 130.3, 129.5 (d, J_{CF} = 8.5 Hz), 126.6, 126.5, 124.0, 119.6, 115.7 (d, J_{CF} = 21.7 Hz), 115.3, 111.2, 98.2, 19.0, 17.7. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{19}FN_3O_3$ $[M+H]^+$ 392.1405; Found: 392.1400.



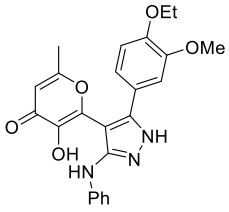
2-(5-(benzo[d][1,3]dioxol-5-yl)-3-(phenylamino)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15u**).

White powder; yield 66% (0.27 g); m.p. 252-254°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.75 (s, 1H), 7.69 (s, 1H), 7.43 (s, 2H), 7.23 – 7.12 (m, 2H), 7.03 – 6.89 (m, 3H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.26 (s, 1H), 6.06 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.9, 165.2, 147.6, 147.6, 143.2, 142.6, 141.6, 128.7, 121.0, 118.9, 115.7, 111.1, 108.7, 107.0, 101.5, 96.7, 19.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{18}N_3O_5$ $[M+H]^+$ 404.1241; Found: 404.1237.



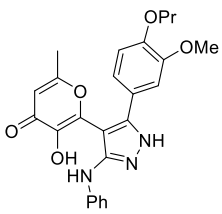
2-(5-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3-(phenylamino)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15v**).

White powder; yield 69% (0.29 g); m.p. 243-245°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.68 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.12 (m, 2H), 7.02 – 6.86 (m, 3H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.27 (s, 1H), 4.28 – 4.22 (m, 4H), 2.11 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.0, 165.2, 143.9, 143.4, 143.2, 142.7, 141.6, 128.7, 120.0, 118.9, 117.4, 115.8, 115.4, 111.2, 96.5, 64.3, 64.2, 19.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{23}H_{20}N_3O_5$ $[M+H]^+$ 418.1397; Found: 418.1400.



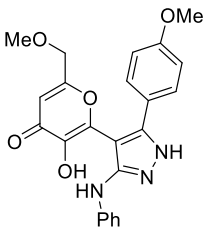
2-(5-(4-ethoxy-3-methoxyphenyl)-3-(phenylamino)-1H-pyrazol-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**15w**).

White powder; yield 54% (0.23 g); m.p. 247-249°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.70 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.12 (m, 2H), 7.06 (s, 1H), 7.02 – 6.96 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.27 (s, 1H), 4.02 (q, *J* = 6.9 Hz, 2H), 3.69 (s, 3H), 2.10 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.0, 165.2, 148.7, 148.4, 143.3, 142.9, 141.8, 128.7, 119.4, 118.9, 115.7, 112.8, 111.1, 110.4, 96.5, 63.8, 55.3, 19.4, 14.8. HRMS (ESI-TOF) *m/z*: Calcld for $C_{24}H_{24}N_3O_5$ $[M+H]^+$ 434.1710; Found: 434.1712.



3-hydroxy-2-(5-(3-methoxy-4-propoxyphenyl)-3-(phenylamino)-1H-pyrazol-4-yl)-6-methyl-4H-pyran-4-one (**15x**).

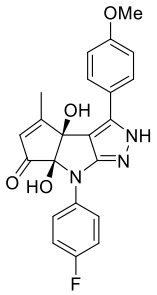
White powder; yield 56% (0.25 g); m.p. 222-224°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.76 (s, 1H), 7.70 (s, 1H), 7.45 – 7.39 (m, 2H), 7.24 – 7.13 (m, 2H), 7.06 (s, 1H), 7.03 – 6.97 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.27 (s, 1H), 3.93 (t, *J* = 6.6 Hz, 2H), 3.70 (s, 3H), 2.11 (s, 3H), 1.81 – 1.63 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.0, 165.2, 148.8, 148.6, 143.3, 142.9, 141.8, 128.7, 119.4, 118.8, 115.7, 112.9, 111.1, 110.5, 96.5, 69.7, 55.4, 22.1, 19.4, 10.5. HRMS (ESI-TOF) *m/z*: Calcld for $C_{25}H_{26}N_3O_5$ $[M+H]^+$ 448.1867; Found: 448.1865.



3-hydroxy-6-(methoxymethyl)-2-(5-(4-methoxyphenyl)-3-(phenylamino)-1H-pyrazol-4-yl)-4H-pyran-4-one (**15y**).

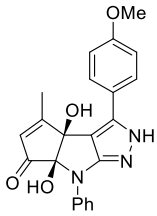
White powder; yield 53% (0.22 g); m.p. 207-209°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.68 (s, 1H), 7.44 – 7.36 (m, 4H), 7.24 – 7.13 (m, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.39 (s, 1H), 4.11 (s, 2H), 3.77 (s, 3H), 3.22 (s, 3H).^{13}C NMR (75 MHz, DMSO-d_6) δ 174.2, 164.2, 160.0, 143.5, 142.6, 129.1, 128.6, 126.7, 122.2, 119.3, 116.1, 114.6, 111.2, 96.6, 70.0, 58.6, 55.7.HRMS (ESI-TOF) *m/z*: Calcld for $C_{23}H_{22}N_3O_5$ $[M+H]^+$ 420.1554; Found: 420.1557.

2. Characterization data of compounds 16



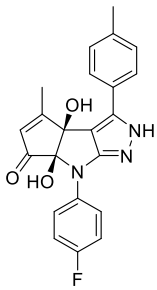
(3bS,6aR)-7-(4-fluorophenyl)-3b,6a-dihydroxy-3-(4-methoxyphenyl)-4-methyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16a**).

White powder; yield 66% (0.13 g); m.p. 219-221°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.33 (s, 1H), 8.20 – 8.09 (m, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.18 (s, 1H), 7.15 – 7.04 (m, 4H), 6.49 (s, 1H), 6.04 (s, 1H), 3.82 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.3, 173.2, 159.6, 156.7 (d, J_{CF} = 298.7 Hz), 157.4, 138.5, 136.6, 128.6, 128.3, 121.7, 119.2 (d, J_{CF}= 7.3 Hz), 114.3 (d, J_{CF} = 22.1 Hz), 114.2, 104.2, 99.0, 81.5, 55.3, 45.8, 15.5, 8.7. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{18}FN_3O_4$ $[M+H]^+$ 408.1354; Found: 408.1347.



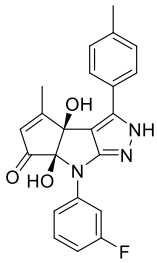
(3bS,6aR)-3b,6a-dihydroxy-3-(4-methoxyphenyl)-4-methyl-7-phenyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16b**).

White powder; yield 68% (0.13 g); m.p. 222-224°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.34 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.19 (m, 2H), 7.15 – 7.04 (m, 3H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.47 (s, 1H), 6.03 (s, 1H), 3.82 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.2, 172.8, 159.6, 158.0, 140.2, 138.4, 128.6, 128.3, 127.8, 121.7, 120.0, 117.7, 114.3, 104.4, 99.1, 81.4, 55.3, 15.5. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{19}N_3O_4$ $[M+H]^+$ 390.1448; Found: 390.1452.



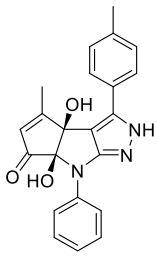
(3bS,6aR)-7-(4-fluorophenyl)-3b,6a-dihydroxy-4-methyl-3-(p-tolyl)-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16c**).

White powder; yield 69% (0.13 g); m.p. 211-213°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.41 (s, 1H), 8.19 – 8.09 (m, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.20 (s, 1H), 7.16 – 7.04 (m, 2H), 6.50 (s, 1H), 6.04 (s, 1H), 2.36 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 197.2, 173.1, 157.9, 156.5 (d, J_{CF} = 236.4 Hz), 138.6, 138.2, 136.5, 129.4, 128.3, 127.0, 126.4, 119.2 (d, J_{CF} = 7.2 Hz), 114.2 (d, J_{CF} = 21.9 Hz), 104.7, 99.0, 81.4, 20.9, 15.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{19}FN_3O_3$ $[M+H]^+$ 392.1405; Found: 392.1414.



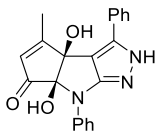
(3bS,6aR)-7-(3-fluorophenyl)-3b,6a-dihydroxy-4-methyl-3-(p-tolyl)-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16d**).

White powder; yield 74% (0.14 g); m.p. 232-234°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.54 (s, 1H), 8.03 (d, *J* = 10.4 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.22 (m, 4H), 6.68 (t, *J* = 8.2 Hz, 1H), 6.56 (s, 1H), 6.06 (s, 1H), 2.36 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.2, 173.4, 162.1 (d, J_{CF} = 238.2 Hz), 157.6, 141.7 (d, J_{CF} = 11.5 Hz), 138.6, 138.4, 129.5, 129.3 (d, J_{CF} = 9.7 Hz), 128.3, 127.1, 126.3, 113.5, 106.3 (d, J_{CF} = 21.3 Hz), 105.0, 104.4 (d, J_{CF} = 27.3 Hz), 99.2, 81.4, 21.0, 15.5. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{19}FN_3O_3$ $[M+H]^+$ 392.1405; Found: 392.1387.



(3bS,6aR)-3b,6a-dihydroxy-4-methyl-7-phenyl-3-(p-tolyl)-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16e**).

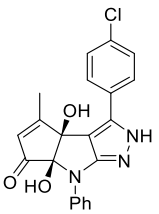
White powder; yield 71% (0.13 g); m.p. 227-229°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.50 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.28 – 7.19 (m, 2H), 7.13 (s, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.53 (s, 1H), 6.02 (s, 1H), 2.36 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.2, 172.8, 158.0, 140.2, 138.4, 138.2, 129.4, 128.3, 127.8, 127.1, 126.5, 120.0, 117.7, 104.9, 99.2, 81.5, 21.0, 15.5. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{20}N_3O_3$ $[M+H]^+$ 374.1499; Found: 374.1497.



(3bS,6aR)-3b,6a-dihydroxy-4-methyl-3,7-diphenyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16f**).

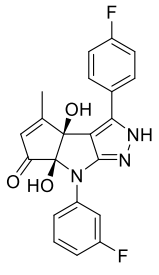
White powder; yield 75% (0.13 g); m.p. 201-203°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.50 (s, 1H), 8.16 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.47 (m, 2H), 7.46 – 7.36 (m, 1H), 7.31 – 7.20 (m, 2H), 7.17 (s, 1H), 6.94 – 6.83 (m, 1H), 6.51 (s, 1H), 6.04 (s, 1H), 1.87 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.4, 173.0, 140.2, 138.6, 129.3, 129.3,

129.1, 129.0, 128.9, 128.6, 128.0, 127.2, 120.3, 117.9, 99.3, 81.6, 15.5. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{17}N_3O_3$ $[M+H]^+$ 360.1343; Found: 360.1352.



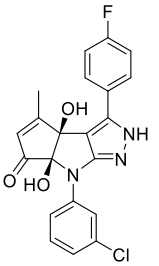
(3bS,6aR)-3-(4-chlorophenyl)-3b,6a-dihydroxy-4-methyl-7-phenyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16g**).

White powder; yield 77% (0.15 g); m.p. 223-225°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.57 (s, 1H), 8.14 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.19 (m, 3H), 6.94 – 6.83 (m, 1H), 6.58 (s, 1H), 6.06 (s, 1H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 197.2, 172.6, 158.1, 140.1, 137.3, 133.3, 129.0, 128.8, 128.6, 128.1, 127.9, 120.3, 117.9, 99.2, 81.5, 15.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{16}ClN_3O_3$ $[M+H]^+$ 394.0953; Found: 394.0960.



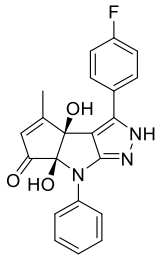
(3bS,6aR)-7-(3-fluorophenyl)-3-(4-fluorophenyl)-3b,6a-dihydroxy-4-methyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16h**).

White powder; yield 78% (0.15 g); m.p. 212-214°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.63 (s, 1H), 8.11 – 7.98 (m, 4H), 7.46 – 7.35 (m, 3H), 7.35 – 7.22 (m, 1H), 6.74 – 6.61 (m, 2H), 6.08 (s, 1H), 1.87 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 197.1, 173.1, 162.3 (d, J_{CF} = 246.5 Hz), 162.0 (d, J_{CF} = 238.3 Hz), 157.7, 141.6 (d, J_{CF} = 11.4 Hz), 137.6, 129.3 (d, J_{CF} = 8.3 Hz), 129.2 (d, J_{CF} = 9.4 Hz), 128.4, 125.7, 115.9 (d, J_{CF} = 21.9 Hz), 113.5, 106.3 (d, J_{CF} = 21.5 Hz), 105.3, 104.4 (d, J_{CF} = 27.3 Hz), 99.2, 81.3, 15.3. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{15}F_2N_3O_3$ $[M+H]^+$ 396.1154; Found: 396.1144.



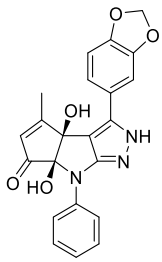
(3bS,6aR)-7-(3-chlorophenyl)-3-(4-fluorophenyl)-3b,6a-dihydroxy-4-methyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16i**).

White powder; yield 75% (0.15 g); m.p. 223-225°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.63 (s, 1H), 8.29 (s, 1H), 8.20 – 8.11 (m, 1H), 8.05 (s, 2H), 7.46 – 7.36 (m, 3H), 7.34 – 7.23 (m, 1H), 6.93 (s, 1H), 6.66 (s, 1H), 6.08 (s, 1H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 197.1, 173.2, 162.3 (d, J_{CF} = 246.6 Hz), 157.5, 141.3, 137.6, 132.4, 129.4, 129.3, 128.5, 125.7 (d, J_{CF} = 3.2 Hz), 119.6, 117.1, 116.0 (d, *J* = 8.5 Hz), 115.8, 105.4, 99.3, 81.3, 15.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{16}ClFN_3O_3$ $[M+H]^+$ 412.0859; Found: 412.0870.



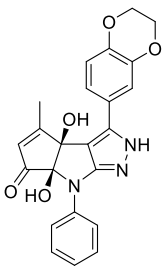
(3bS,6aR)-3-(4-fluorophenyl)-3b,6a-dihydroxy-4-methyl-7-phenyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16j**).

White powder; yield 72% (0.14 g); m.p. 219-221°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.50 (s, 1H), 8.15 (d, *J* = 8.2 Hz, 2H), 8.11 – 8.00 (m, 2H), 7.45 – 7.34 (m, 2H), 7.31 – 7.21 (m, 2H), 7.19 (s, 1H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.56 (s, 1H), 6.05 (s, 1H), 1.87 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.2, 172.6, 163.2, 161.2, 158.1, 140.1, 137.4, 129.3 (d, J_{CF} = 8.4 Hz), 128.9, 128.8, 128.5, 127.8, 125.8, 120.2, 117.8, 115.9 (d, J_{CF} = 21.7 Hz), 105.2, 99.2, 81.40, 15.3. HRMS (ESI-TOF) *m/z*: Calcld for $C_{21}H_{17}FN_3O_3$ $[M+H]^+$ 378.1248; Found: 378.1242.



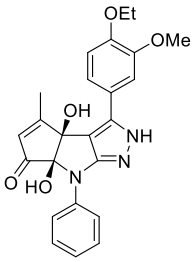
(3bS,6aR)-3-(benzo[d][1,3]dioxol-5-yl)-3b,6a-dihydroxy-4-methyl-7-phenyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16k**).

White powder; yield 65% (0.13 g); m.p. 220-222°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.34 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.50 (m, 2H), 7.30 – 7.19 (m, 2H), 7.16 (s, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.51 (s, 1H), 6.10 (s, 2H), 6.04 (s, 1H), 1.90 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 197.1, 172.7, 158.0, 147.6, 140.1, 138.3, 128.9, 128.4, 127.8, 123.2, 121.3, 120.1, 117.8, 108.7, 107.3, 104.6, 101.4, 99.1, 81.4, 15.4. HRMS (ESI-TOF) *m/z*: Calcld for $C_{22}H_{18}N_3O_5$ $[M+H]^+$ 404.1241; Found: 404.1232.



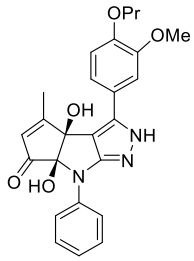
(3bS,6aR)-3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3b,6a-dihydroxy-4-methyl-7-phenyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16l**).

White powder; yield 66% (0.14 g); m.p. 238-240°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.33 (s, 1H), 8.14 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.47 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.13 (s, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.88 (t, *J* = 8.3 Hz, 1H), 6.46 (s, 1H), 6.03 (s, 1H), 4.36 – 4.25 (m, 4H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 197.2, 172.8, 158.0, 143.9, 143.5, 140.1, 138.1, 128.3, 127.8, 122.4, 120.4, 120.1, 117.8, 117.4, 115.8, 104.5, 99.1, 81.4, 64.3, 64.1, 15.5. HRMS (ESI-TOF) *m/z*: Calcld for $C_{23}H_{20}N_3O_5$ $[M+H]^+$ 418.1397; Found: 418.1419.



(3bS,6aR)-3-(4-ethoxy-3-methoxyphenyl)-3b,6a-dihydroxy-4-methyl-7-phenyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16m**).

Pale yellow powder; yield 61% (0.13 g); m.p. 218-220°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.41 (s, 1H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.74 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.19 (m, 2H), 7.14 – 7.03 (m, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.57 (s, 1H), 6.03 (s, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 1.92 (s, 3H), 1.35 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.2, 172.7, 157.9, 148.7, 148.3, 140.2, 138.6, 128.3, 127.8, 121.7, 120.0, 119.5, 117.7, 112.6, 111.3, 104.4, 99.1, 81.5, 63.7, 55.5, 15.6, 14.8. HRMS (ESI-TOF) *m/z*: Calcld for $C_{24}H_{24}N_3O_5$ $[M+H]^+$ 434.1710; Found: 434.1705.

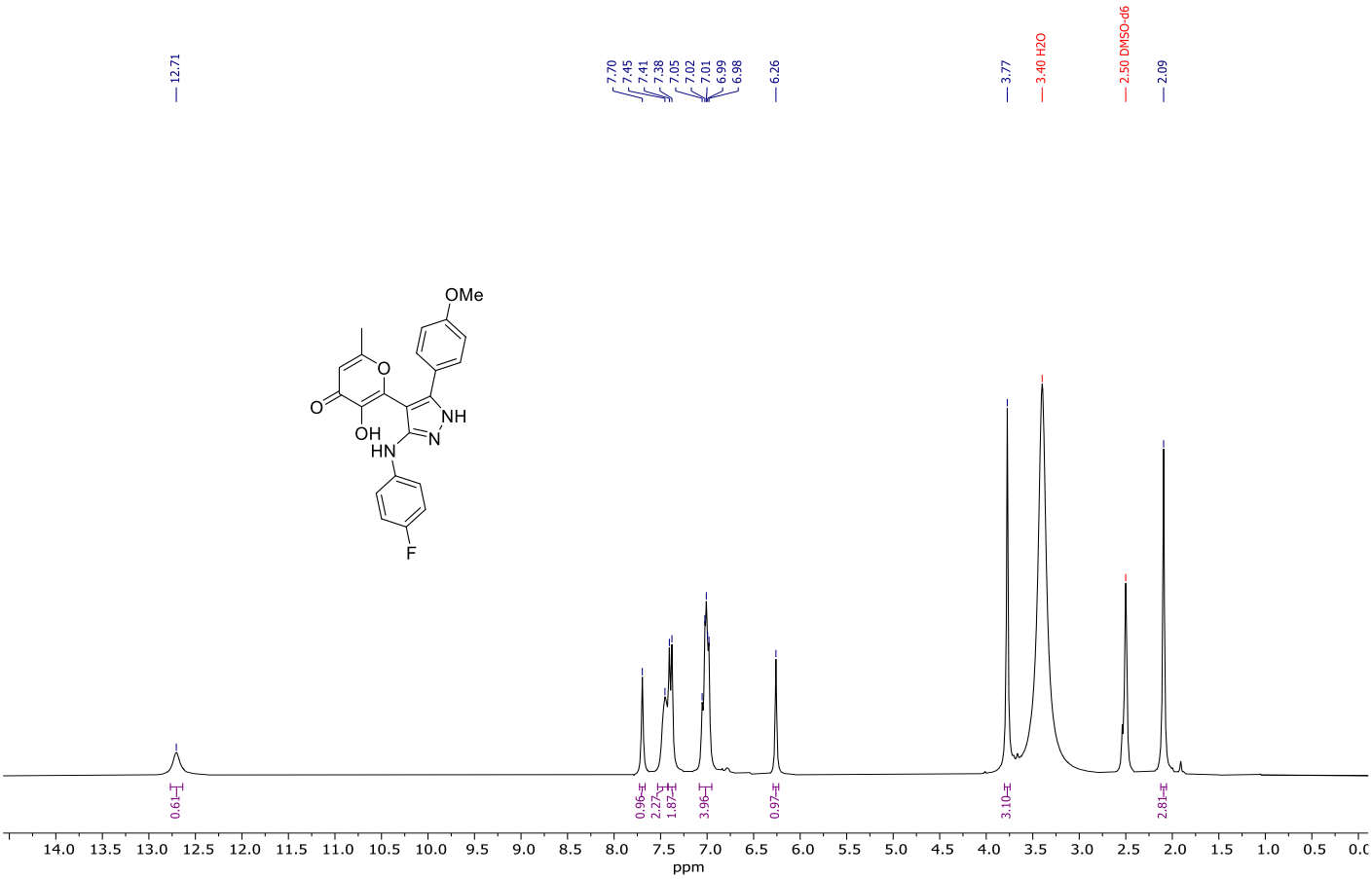


(3bS,6aR)-3b,6a-dihydroxy-3-(3-methoxy-4-propoxyphenyl)-4-methyl-7-phenyl-2,3b,6a,7-tetrahydro-6H-cyclopenta[4,5]pyrrolo[2,3-c]pyrazol-6-one (**16n**).

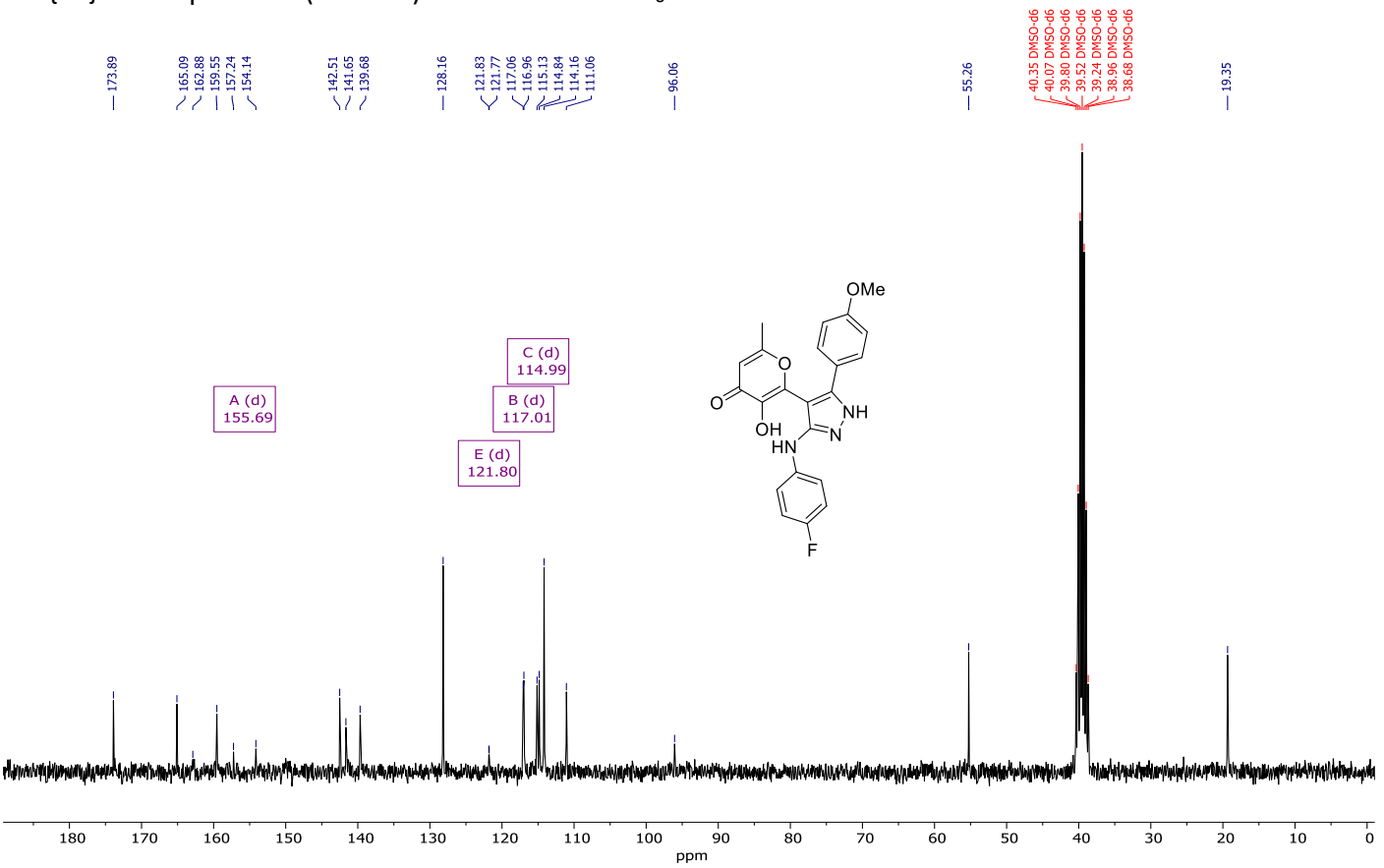
Pale yellow powder; yield 64% (0.14 g); m.p. 226-228C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.35 (s, 1H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.73 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.19 (m, 2H), 7.14 – 7.04 (m, 2H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.54 (s, 1H), 6.04 (s, 1H), 3.97 (t, *J* = 6.7 Hz, 2H), 3.84 (s, 3H), 1.92 (s, 3H), 1.76 (q, *J* = 7.0 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.2, 172.7, 158.0, 149.0, 148.8, 148.5, 140.2, 128.3, 127.8, 121.7, 119.4, 117.7, 112.7, 111.4, 104.4, 99.1, 81.5, 69.6, 55.5, 22.1, 15.6, 10.5. HRMS (ESI-TOF) *m/z*: Calcld for $C_{25}H_{26}N_3O_5$ $[M+H]^+$ 448.1867; Found: 448.1870.

6. NMR ^{1}H and ^{13}C spectra for compounds 15

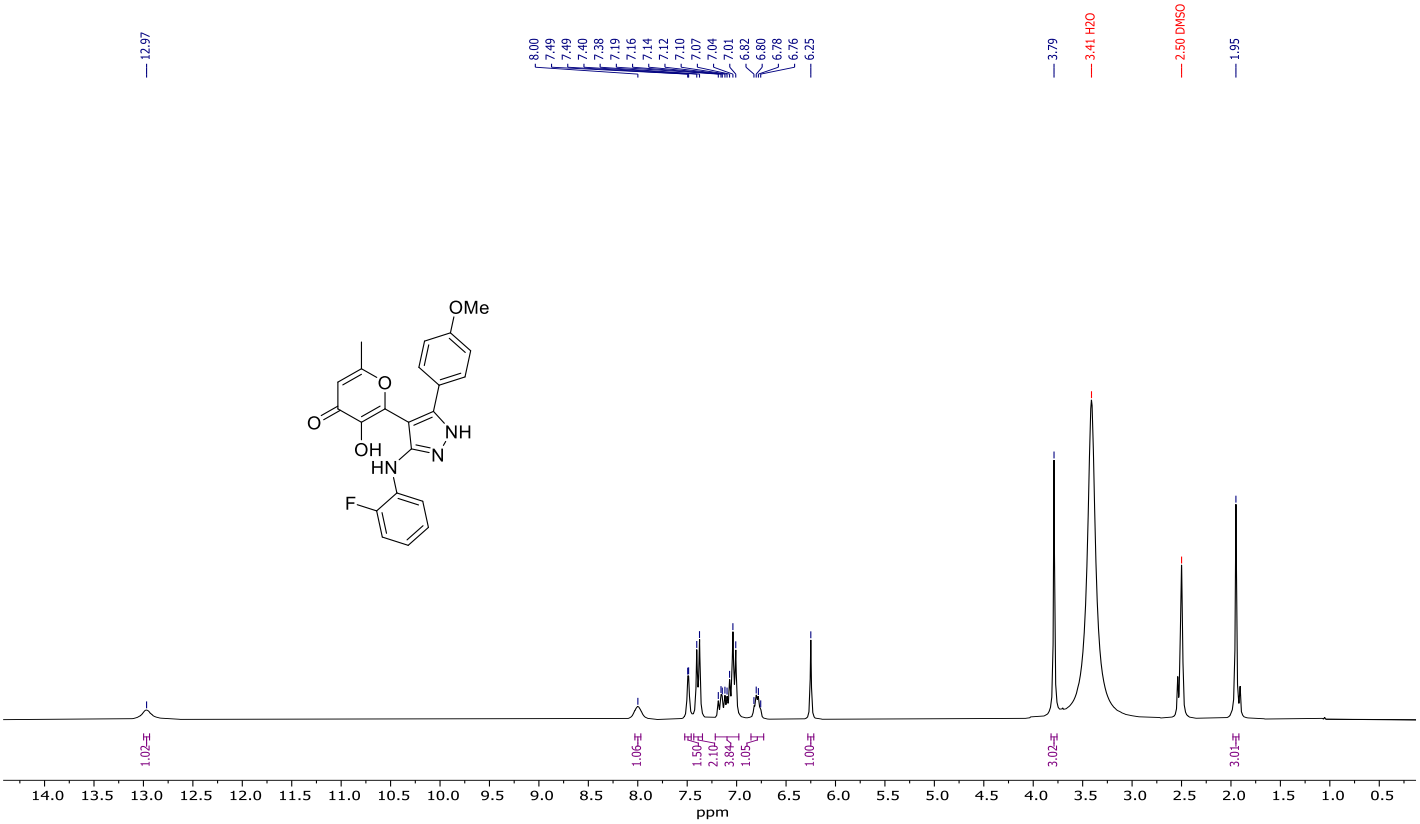
^{1}H NMR spectrum (300 MHz) of **15a** in DMSO-d_6



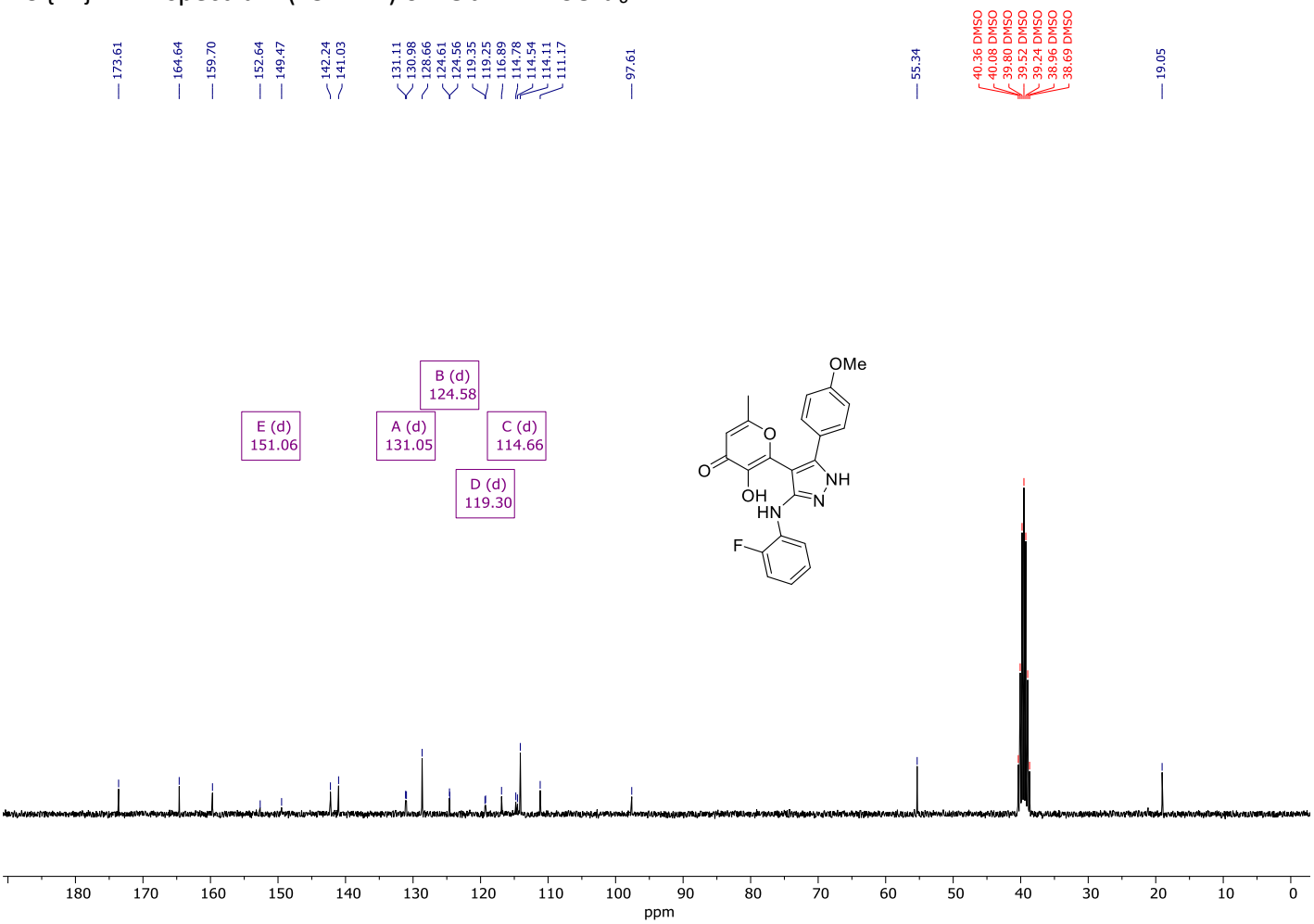
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15a** in DMSO-d_6



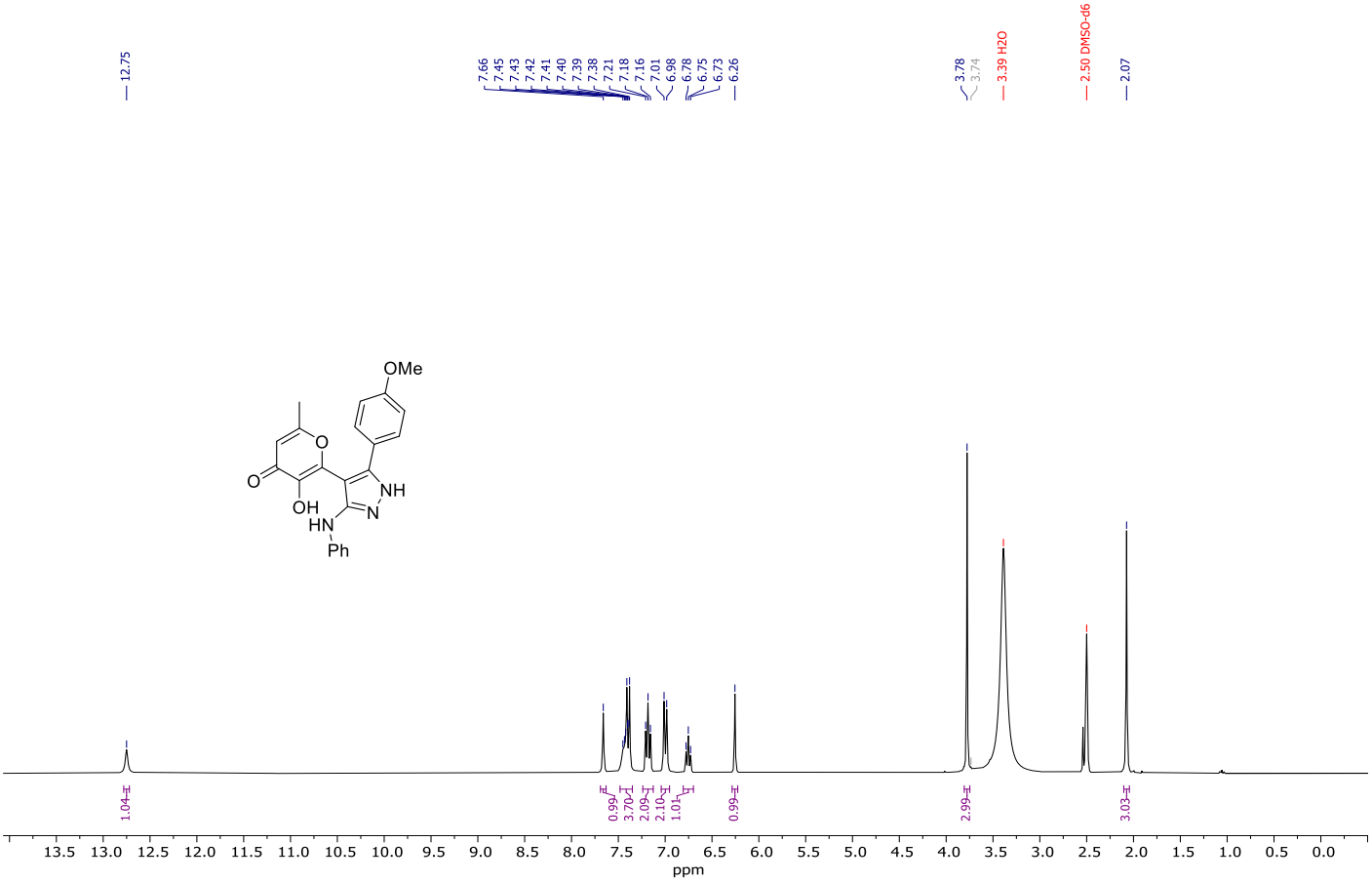
^{1}H NMR spectrum (300 MHz) of **15b** in DMSO-d_6



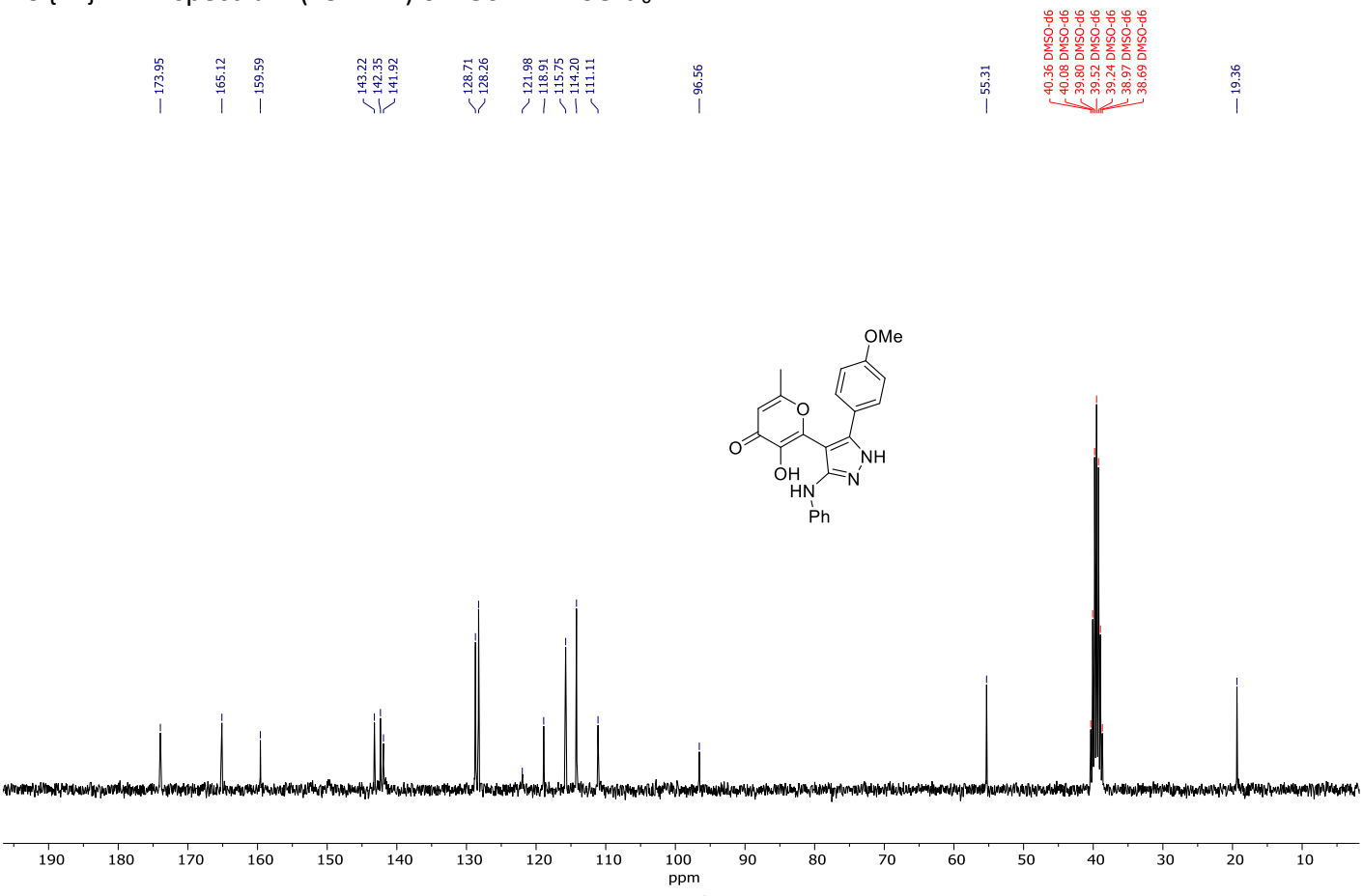
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15b** in DMSO-d_6



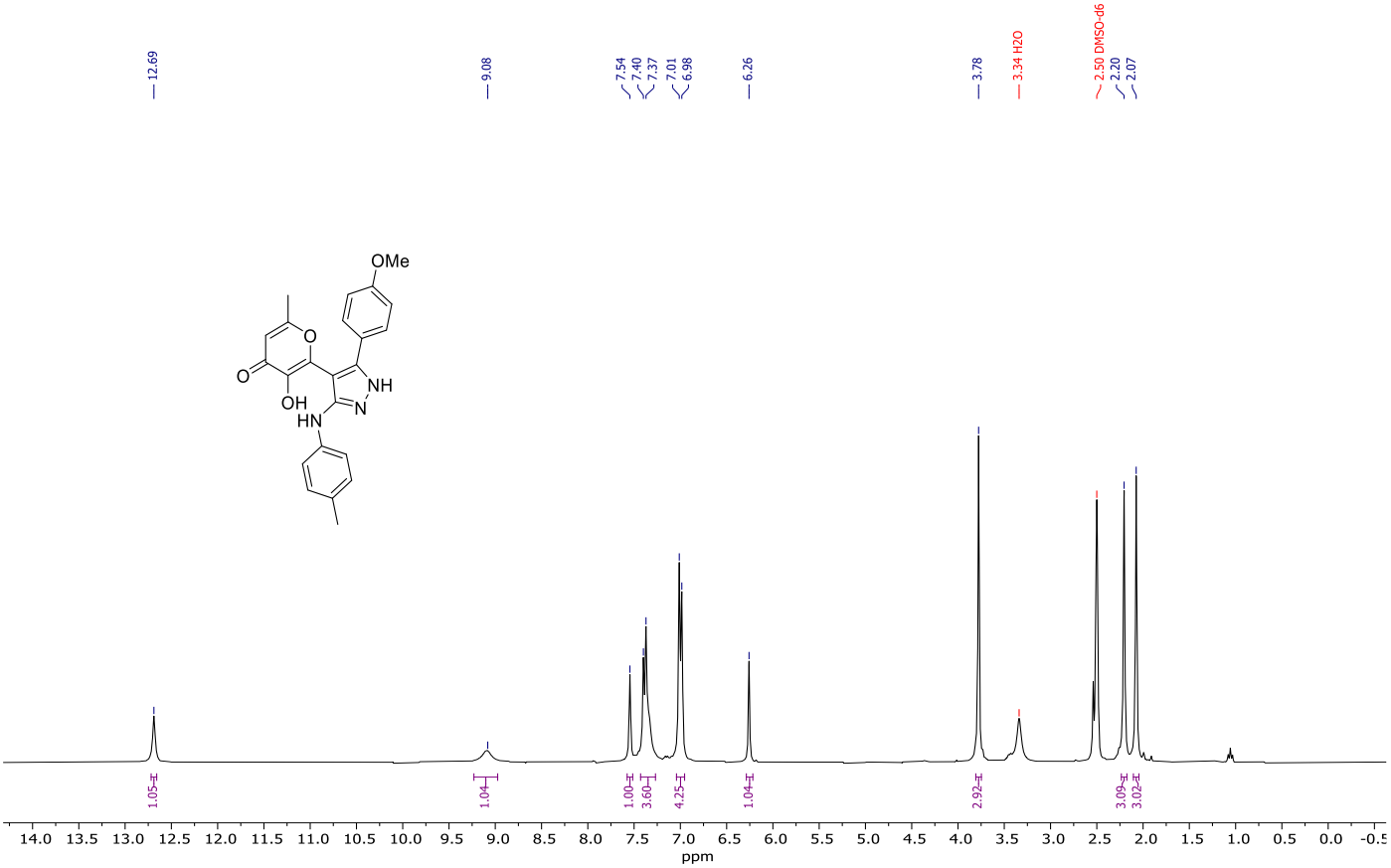
^{1}H NMR spectrum (300 MHz) of **15c** in DMSO-d_6



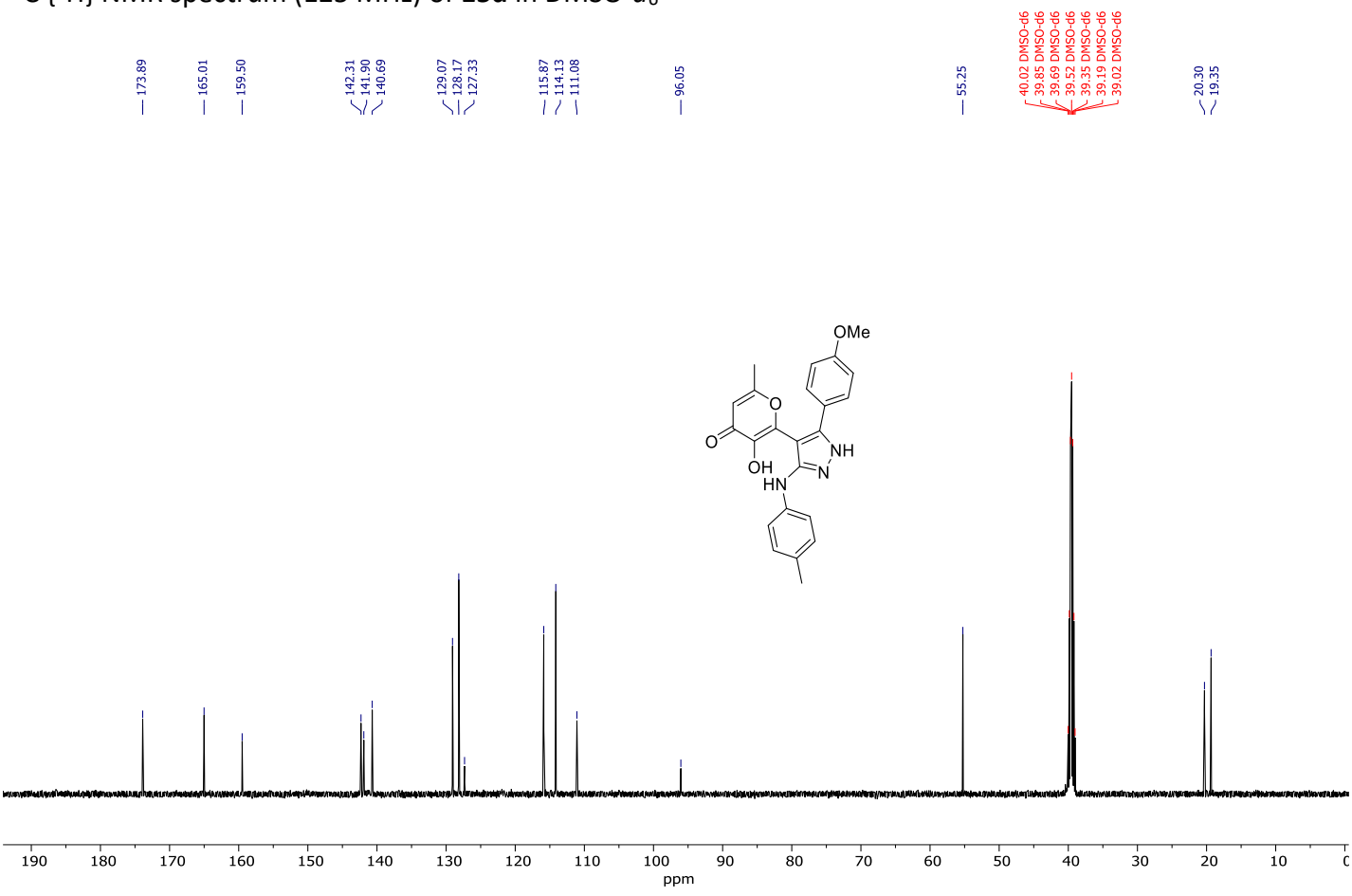
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15c** in DMSO-d_6



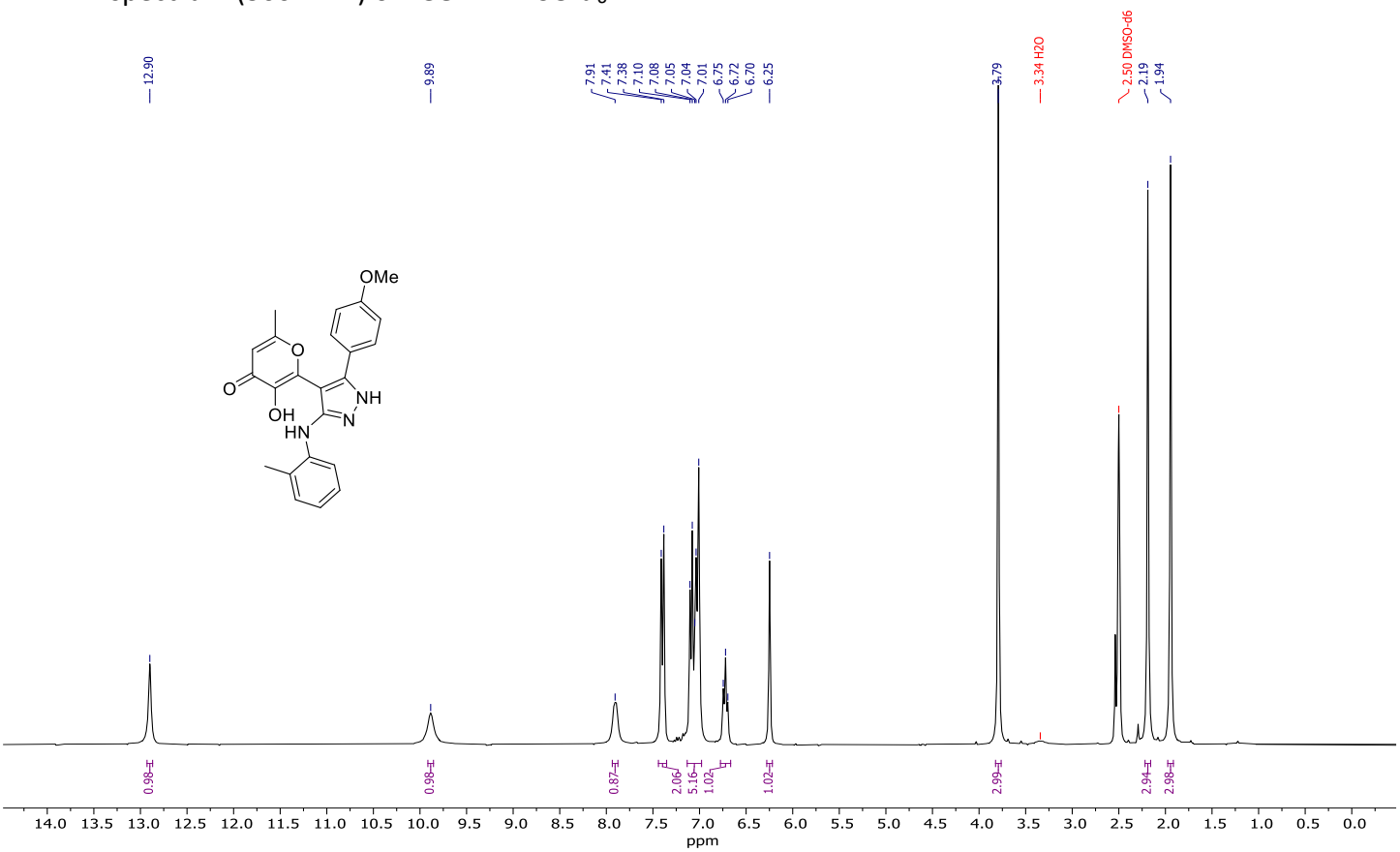
^{1}H NMR spectrum (300 MHz) of **15d** in DMSO-d_6



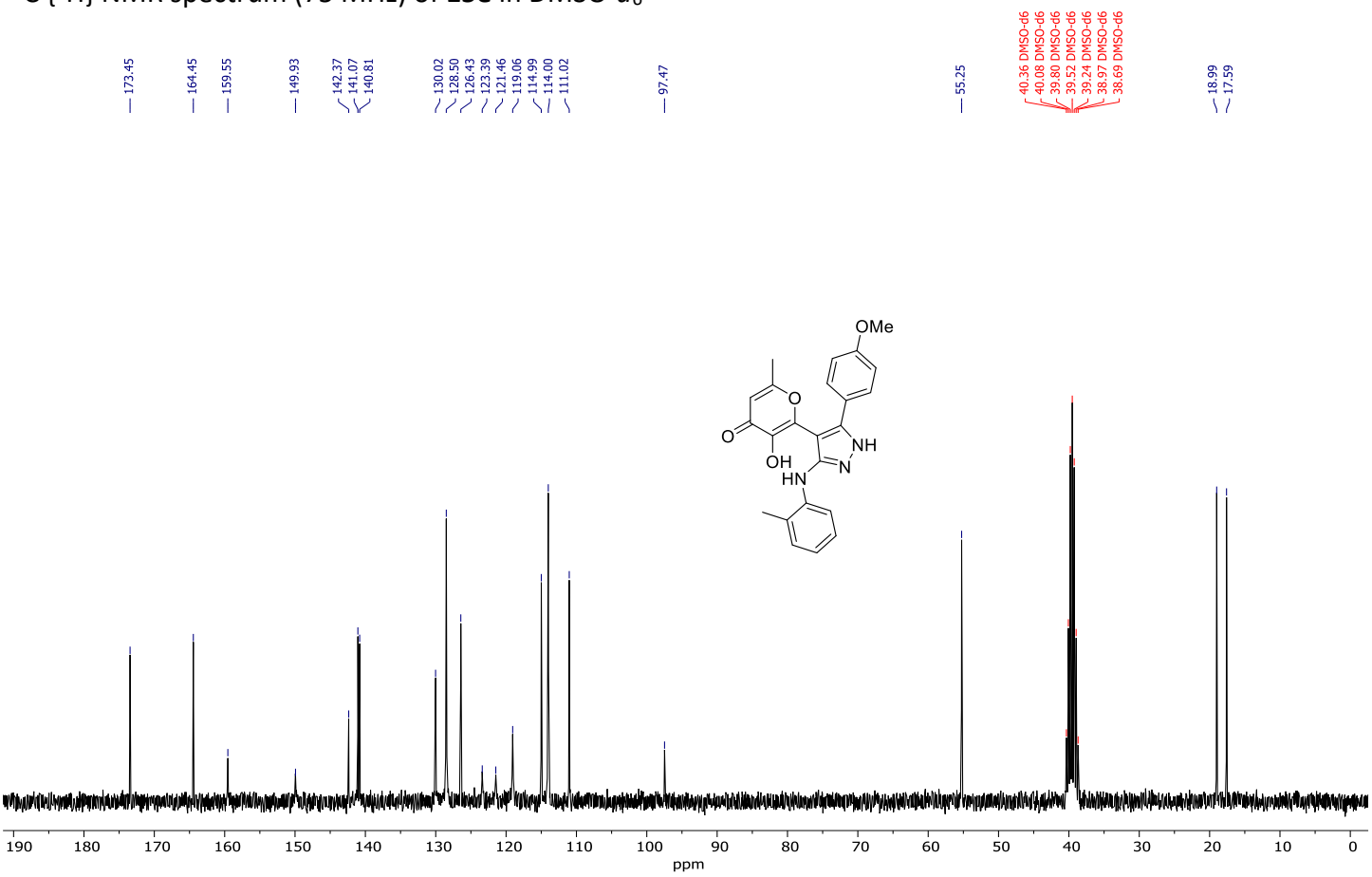
^{13}C {^{1}H} NMR spectrum (125 MHz) of **15d** in DMSO-d_6



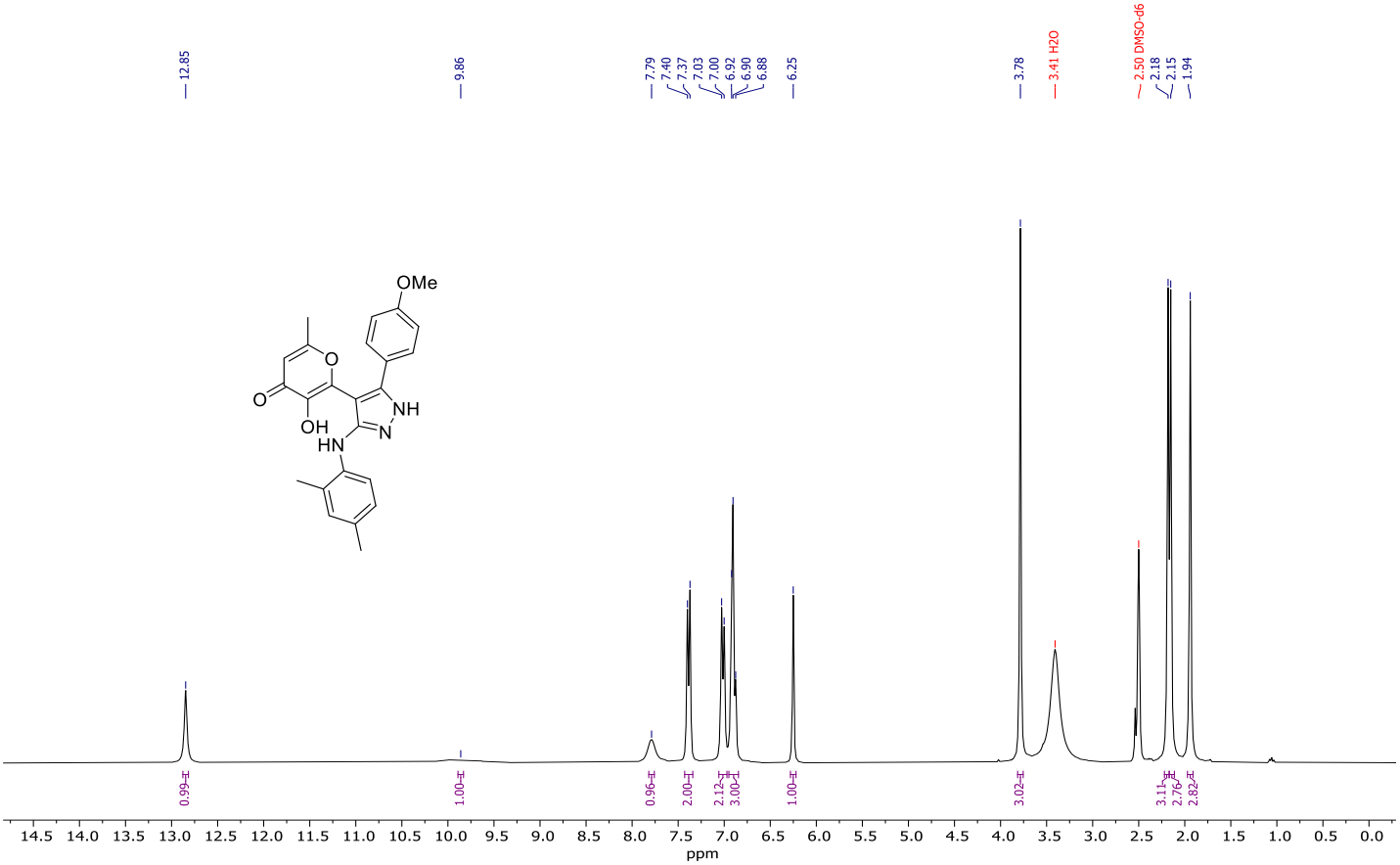
^{1}H NMR spectrum (300 MHz) of **15e** in DMSO-d_6



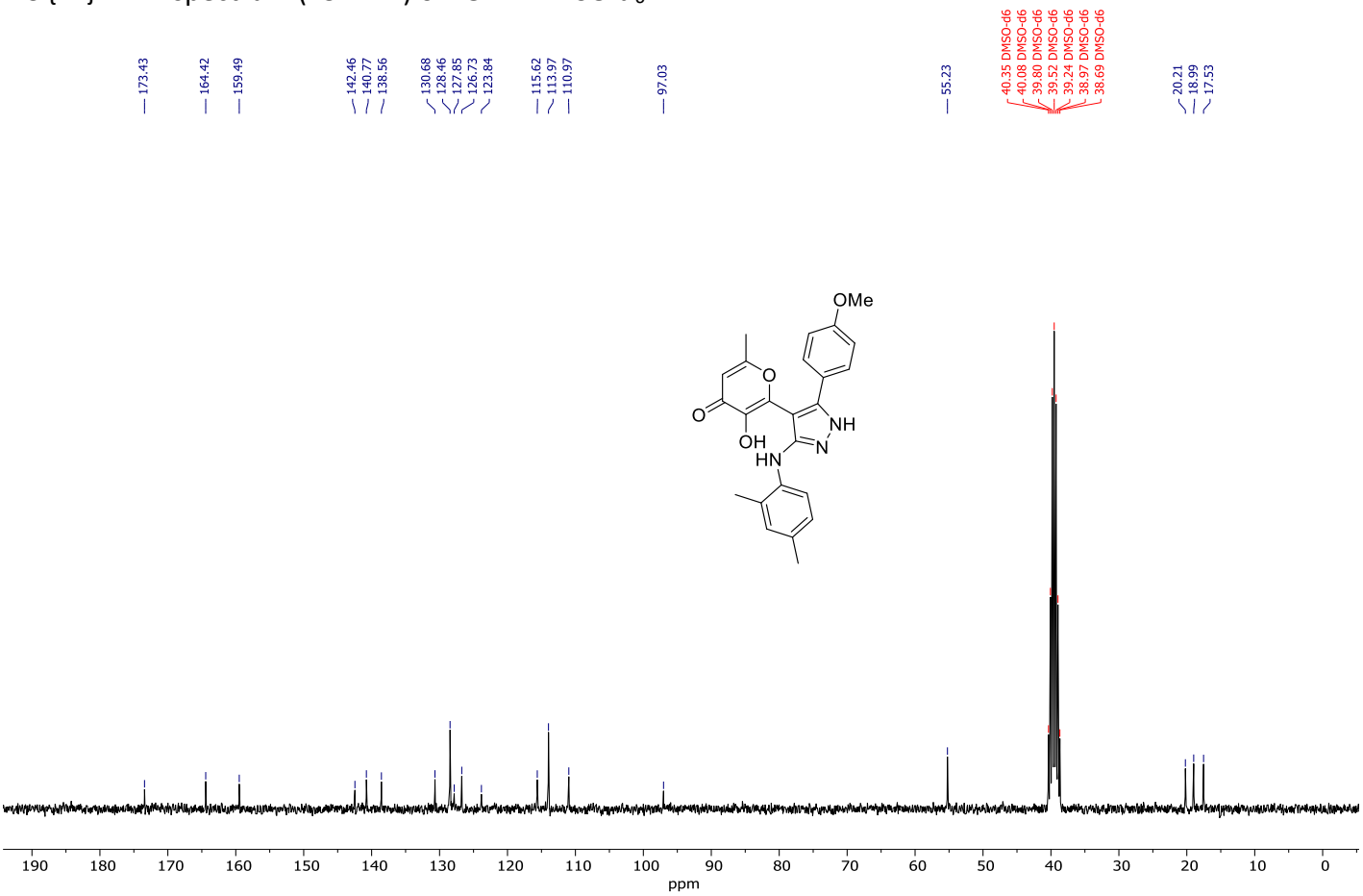
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15e** in DMSO-d_6



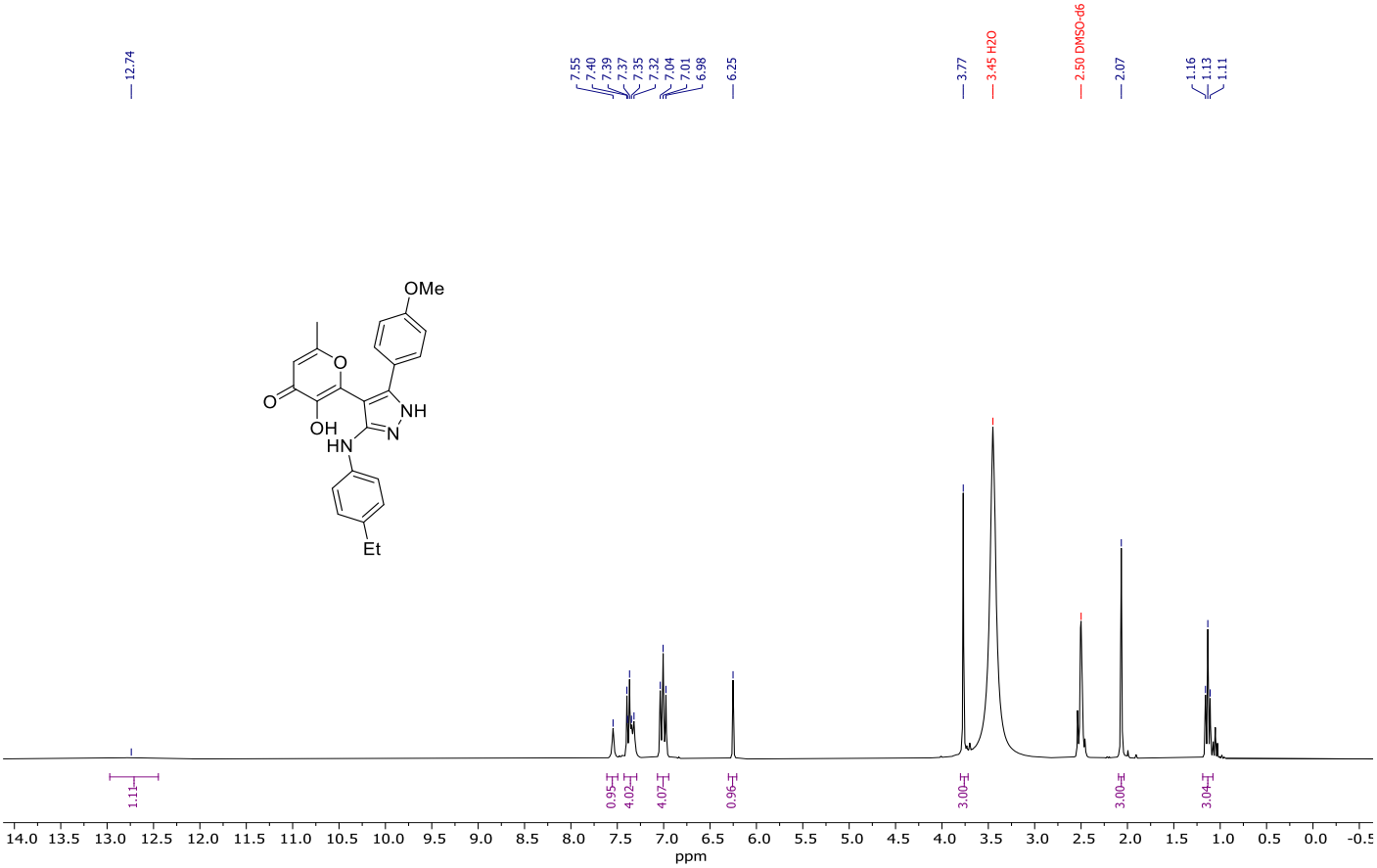
^{1}H NMR spectrum (300 MHz) of **15f** in DMSO-d_6



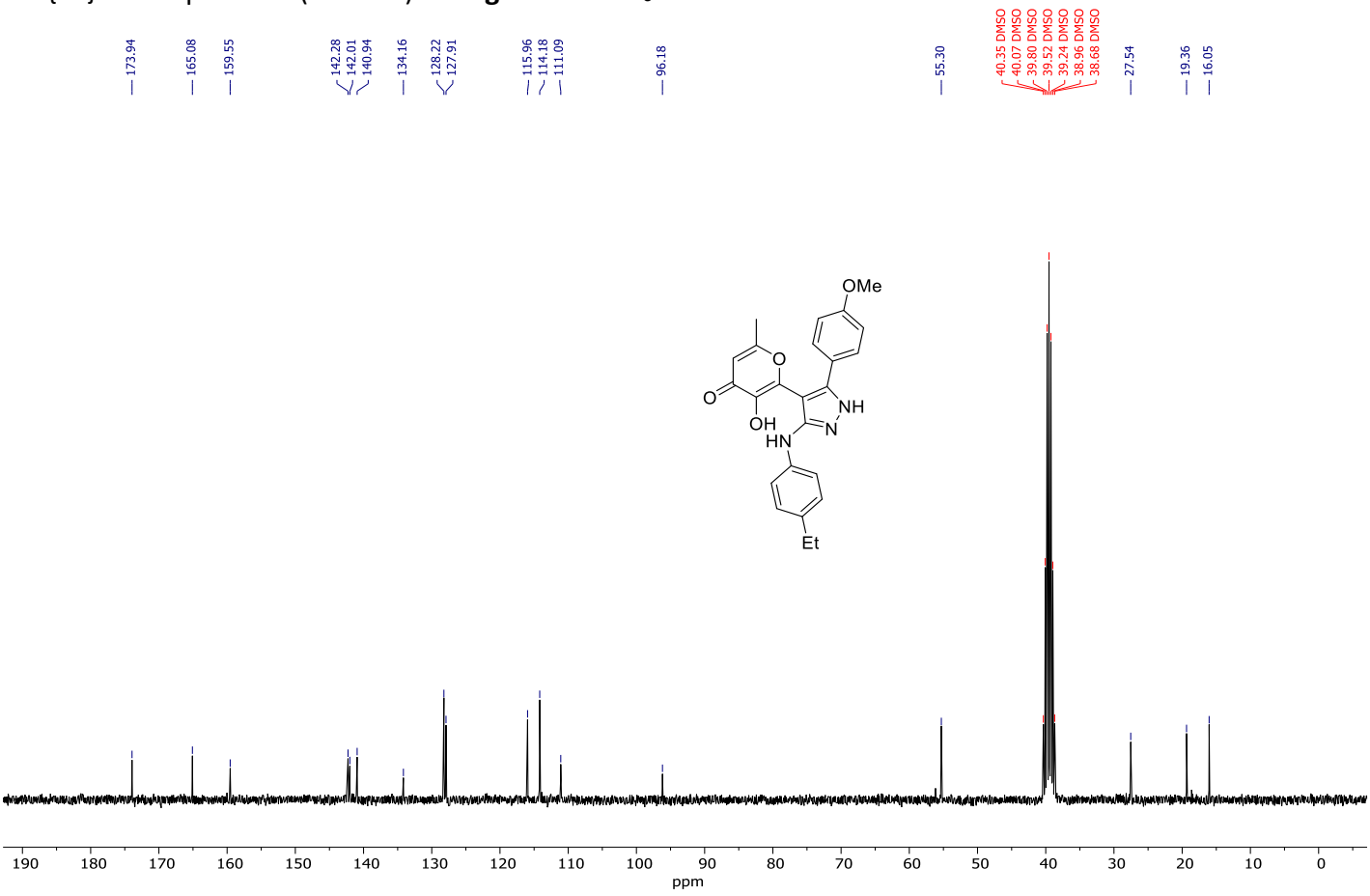
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15f** in DMSO-d_6



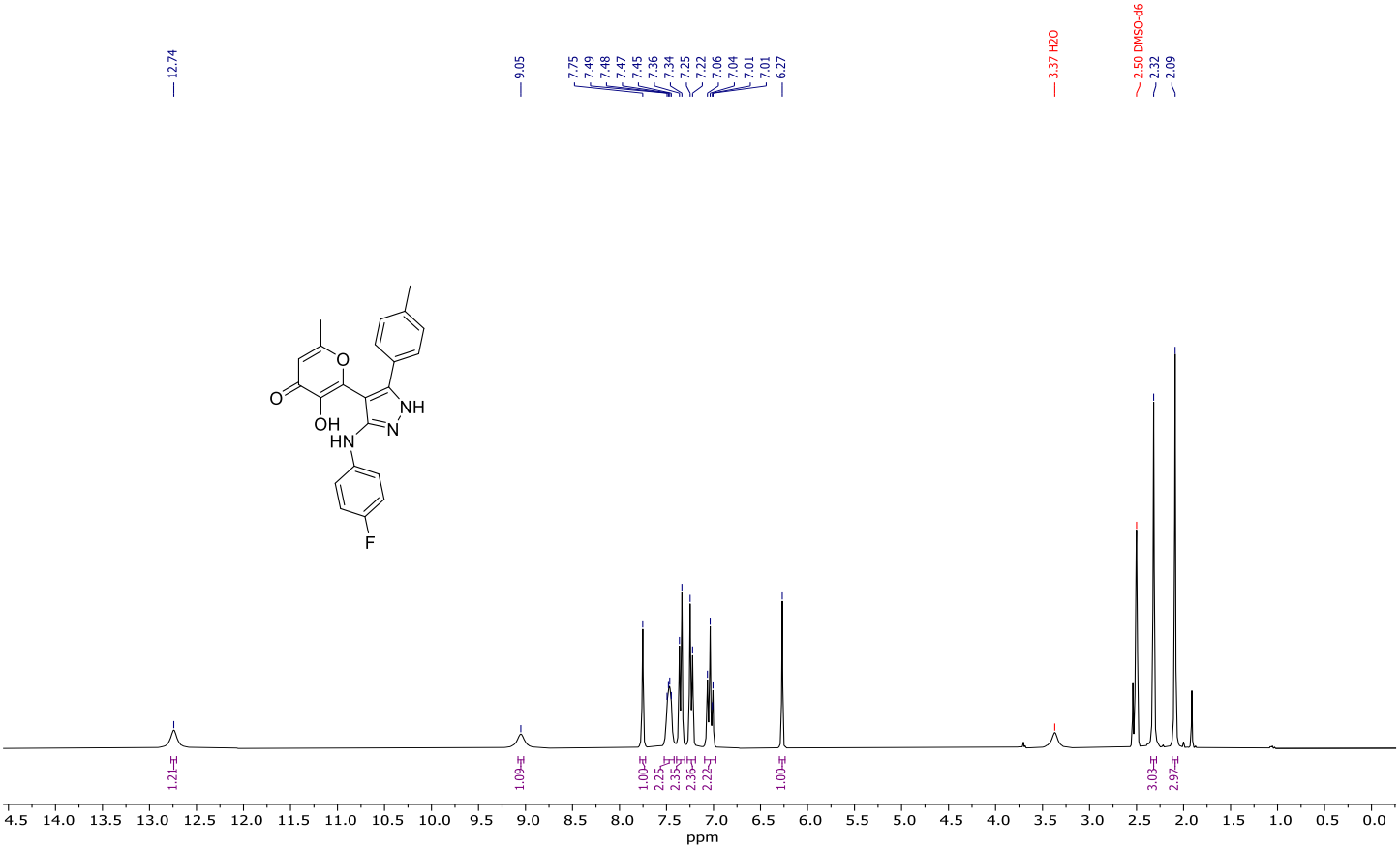
^{1}H NMR spectrum (300 MHz) of **15g** in DMSO-d_6



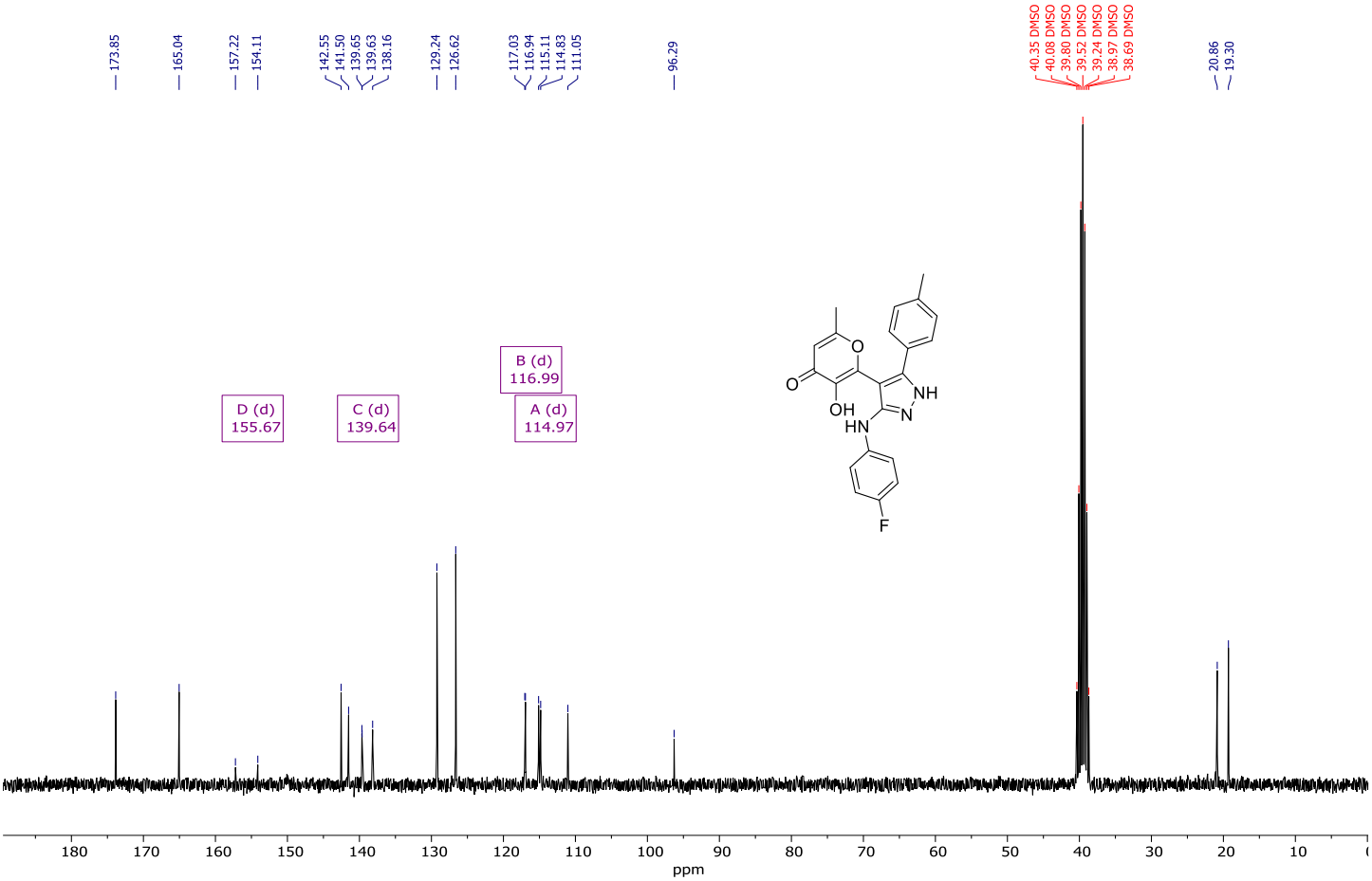
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15g** in DMSO-d_6



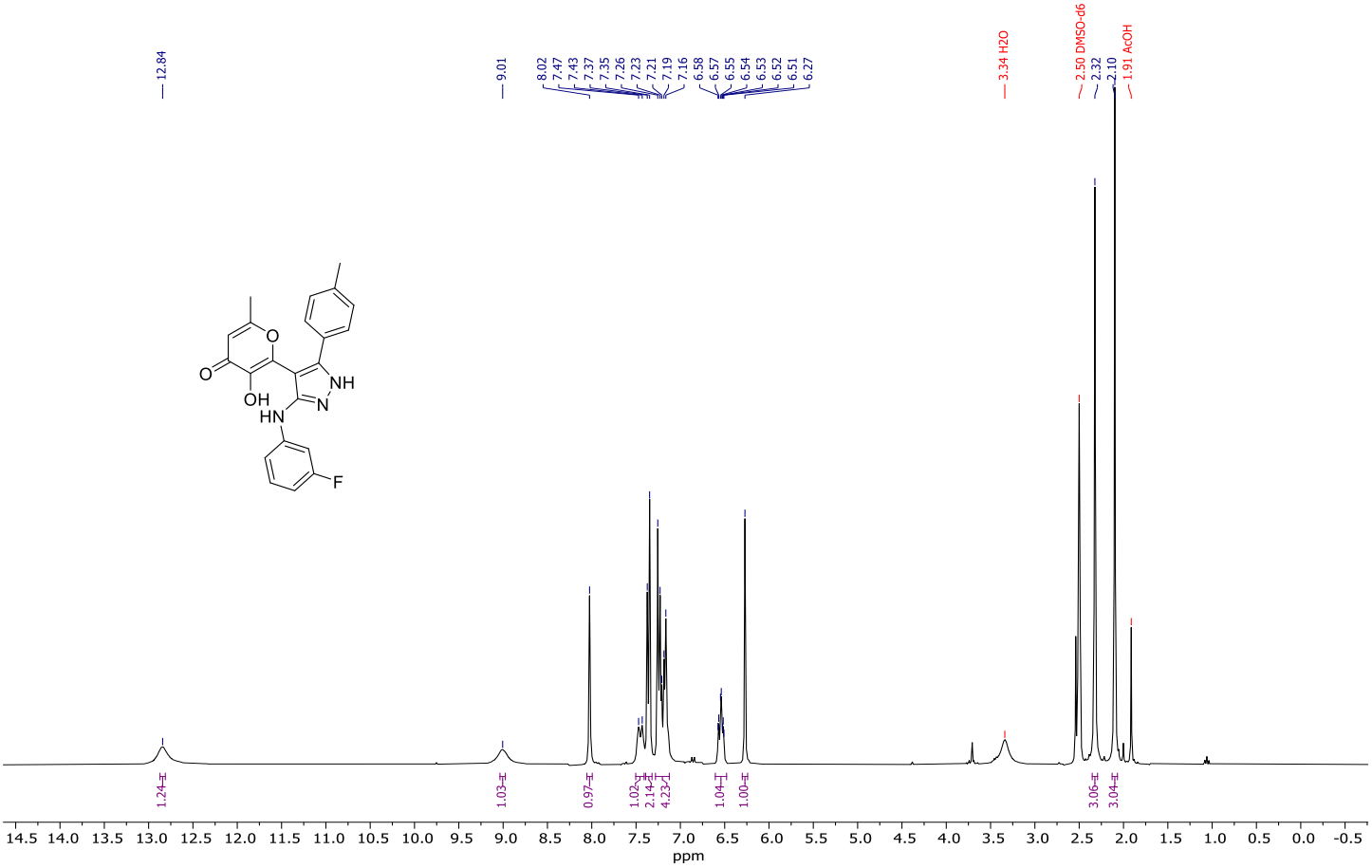
^{1}H NMR spectrum (300 MHz) of **15h** in DMSO-d_6



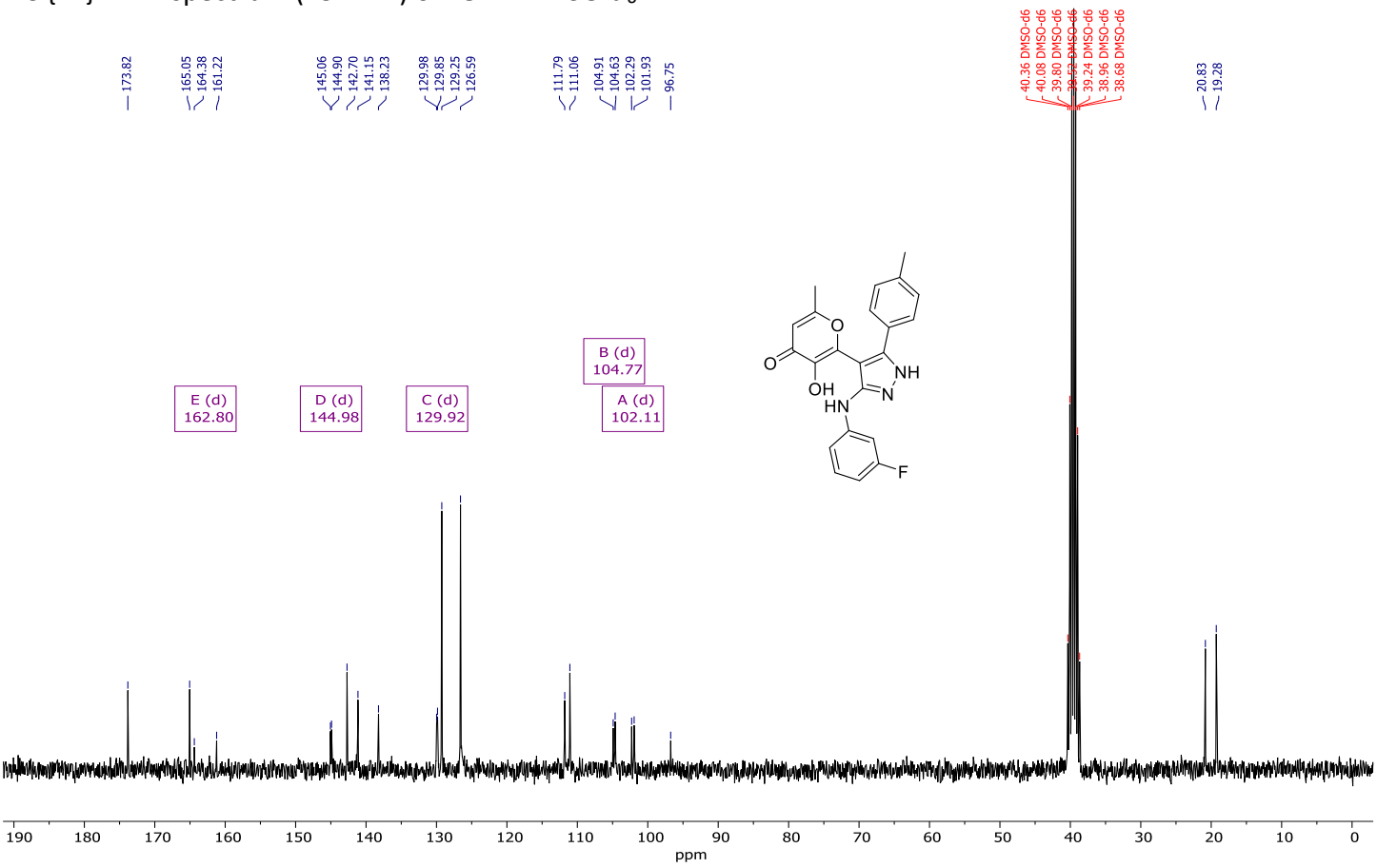
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15h** in DMSO-d_6



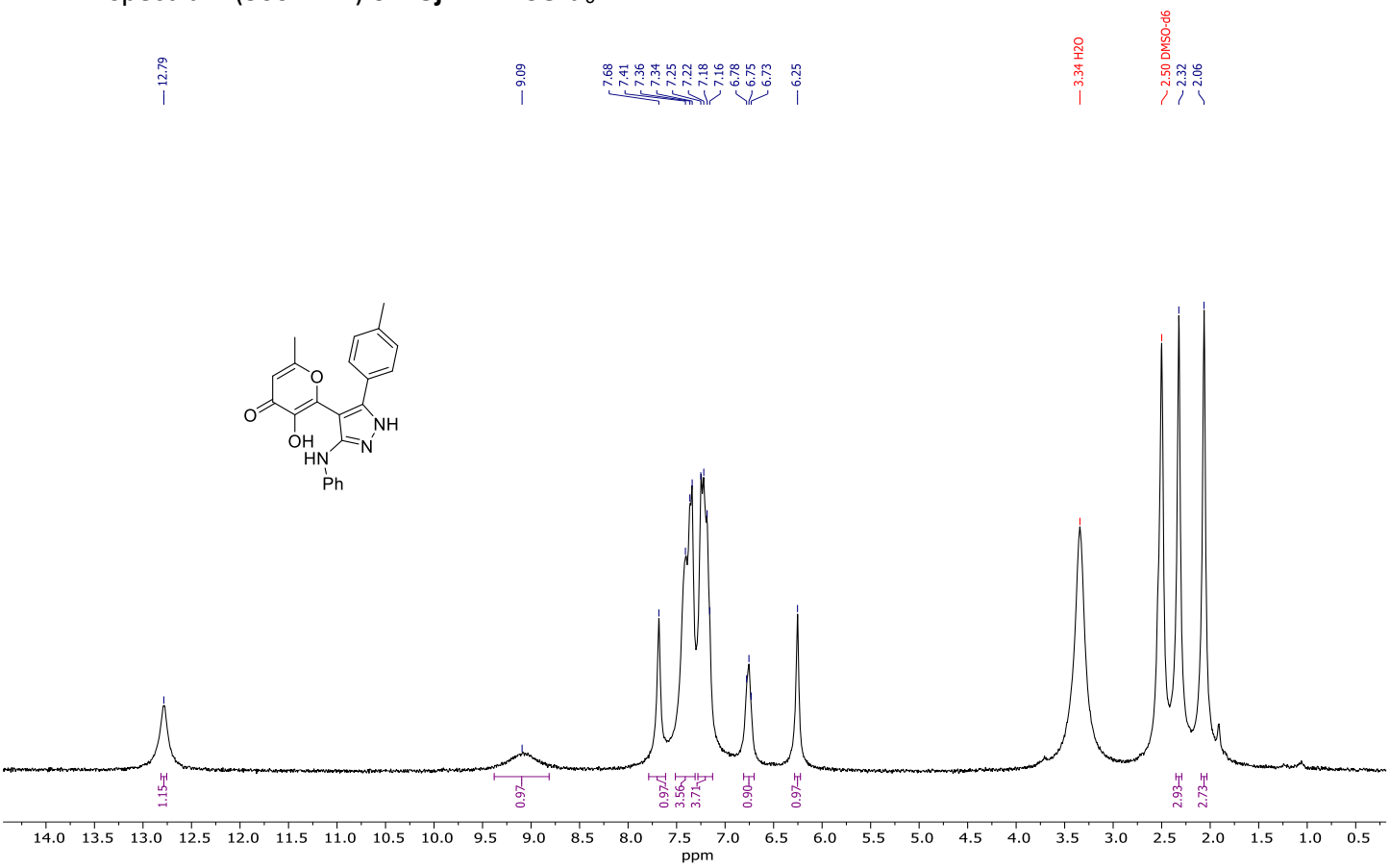
^{1}H NMR spectrum (300 MHz) of **15i** in DMSO-d_6



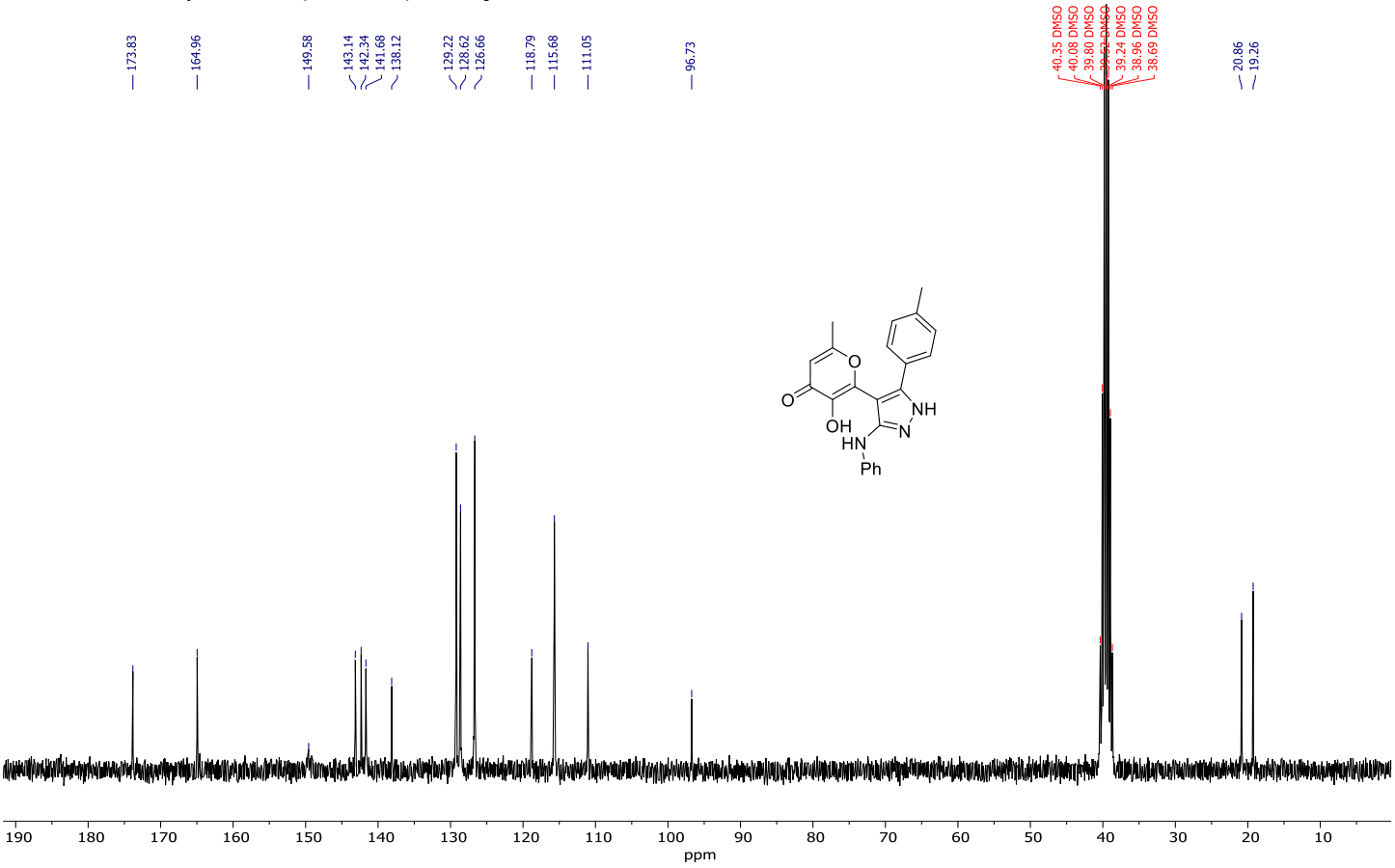
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15i** in DMSO-d_6



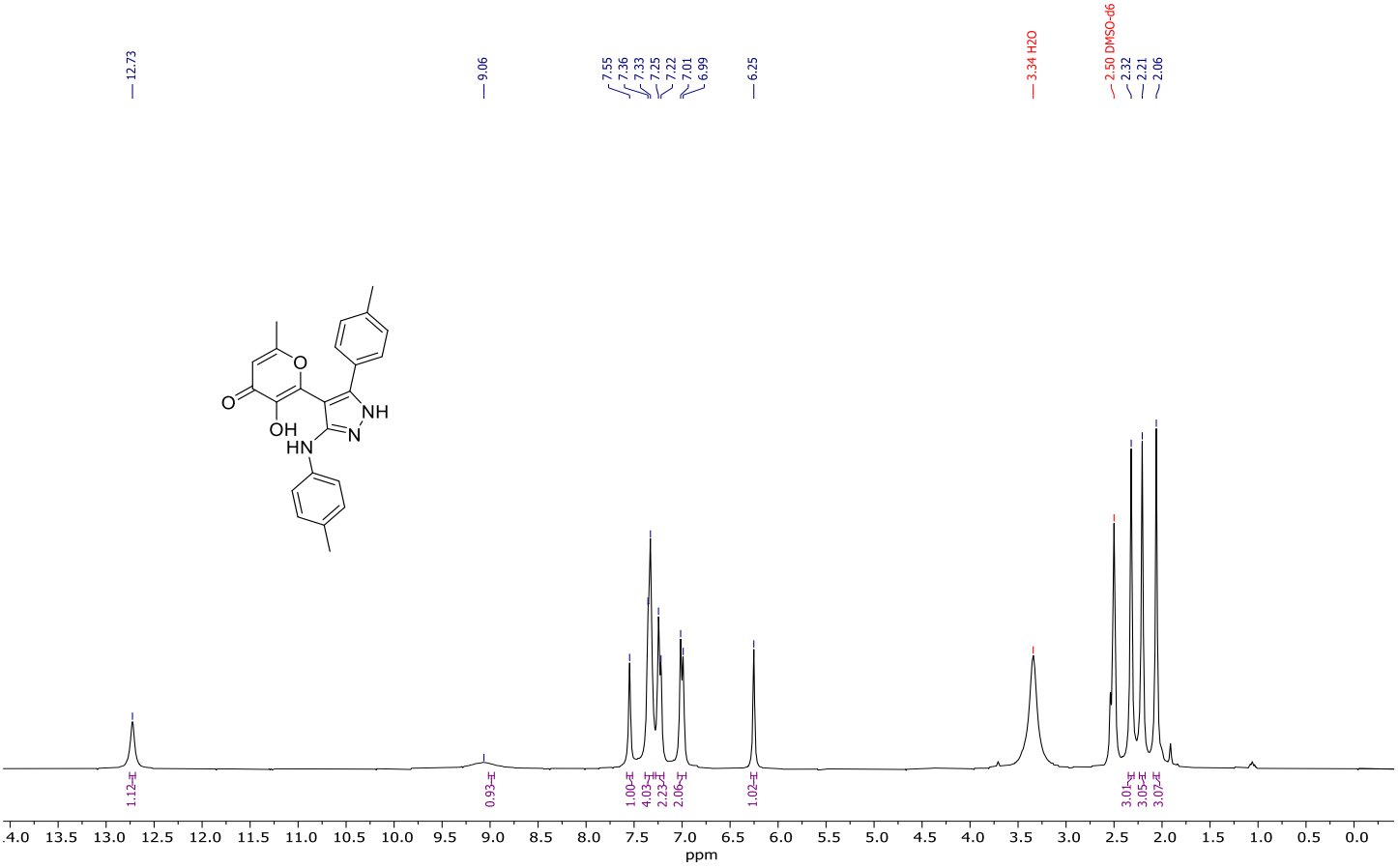
^{1}H NMR spectrum (300 MHz) of **15j** in DMSO-d_6



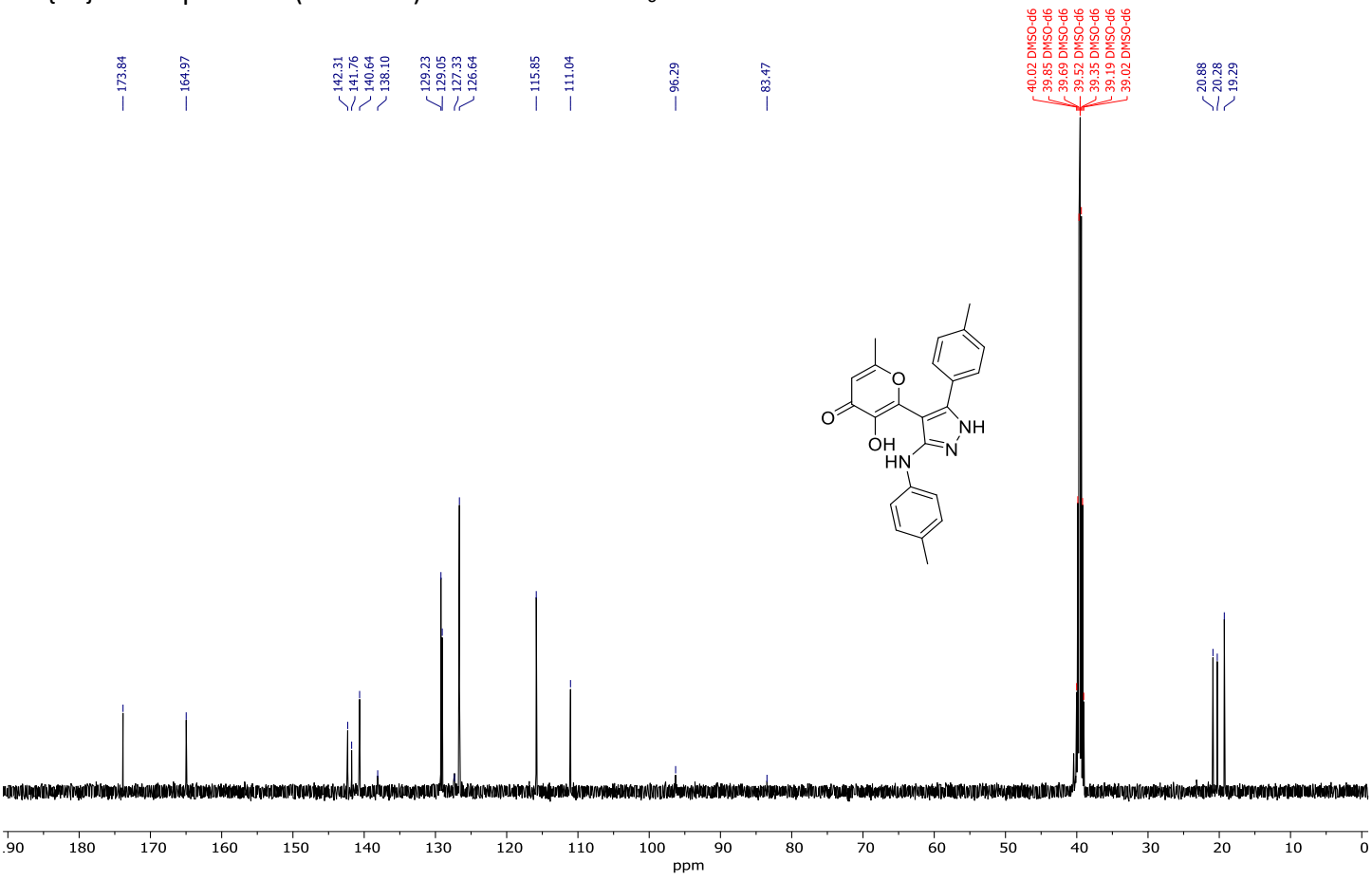
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15j** in DMSO-d_6



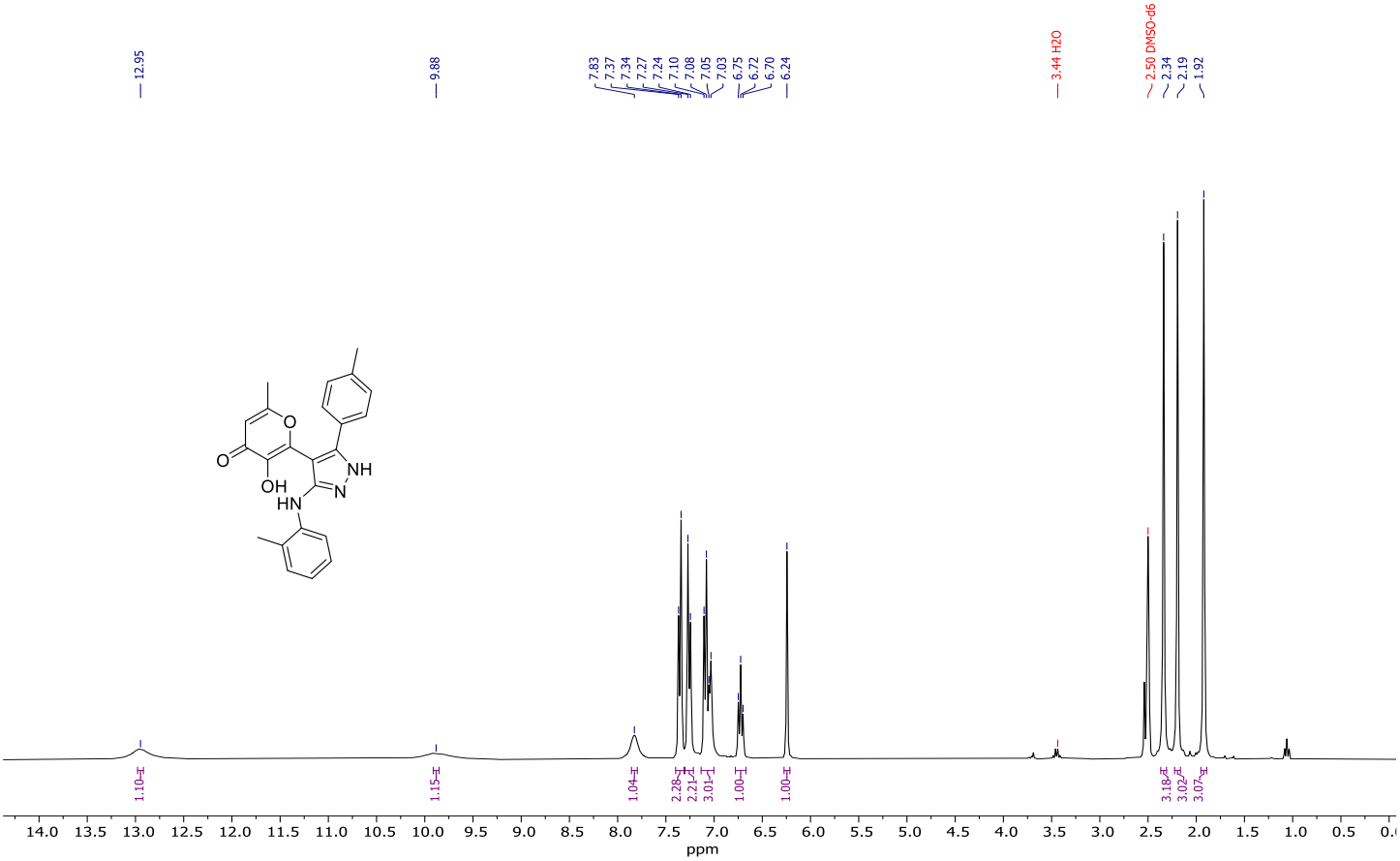
^{1}H NMR spectrum (300 MHz) of **15k** in DMSO-d_6



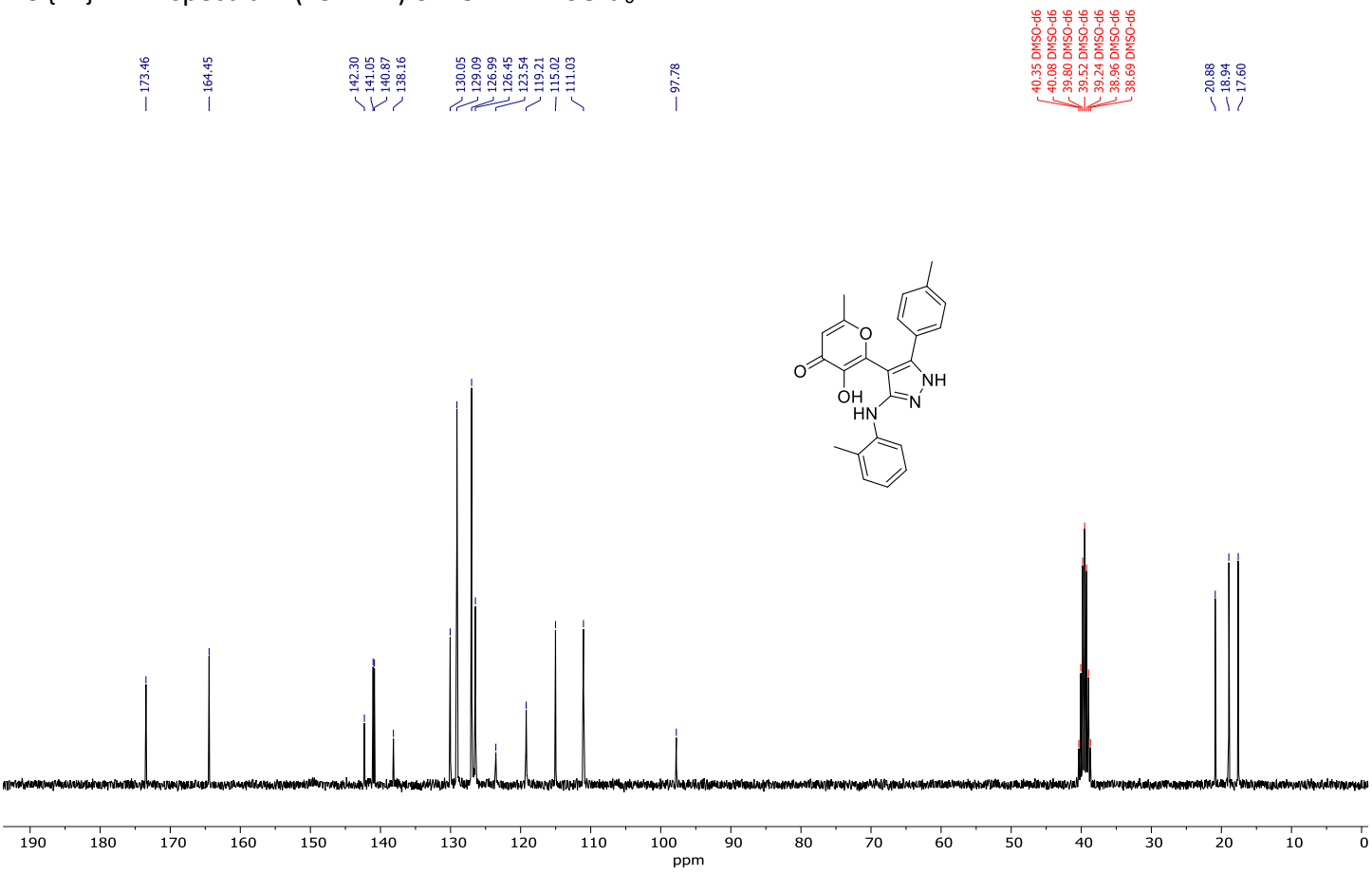
^{13}C {^{1}H} NMR spectrum (125 MHz) of **15k** in DMSO-d_6



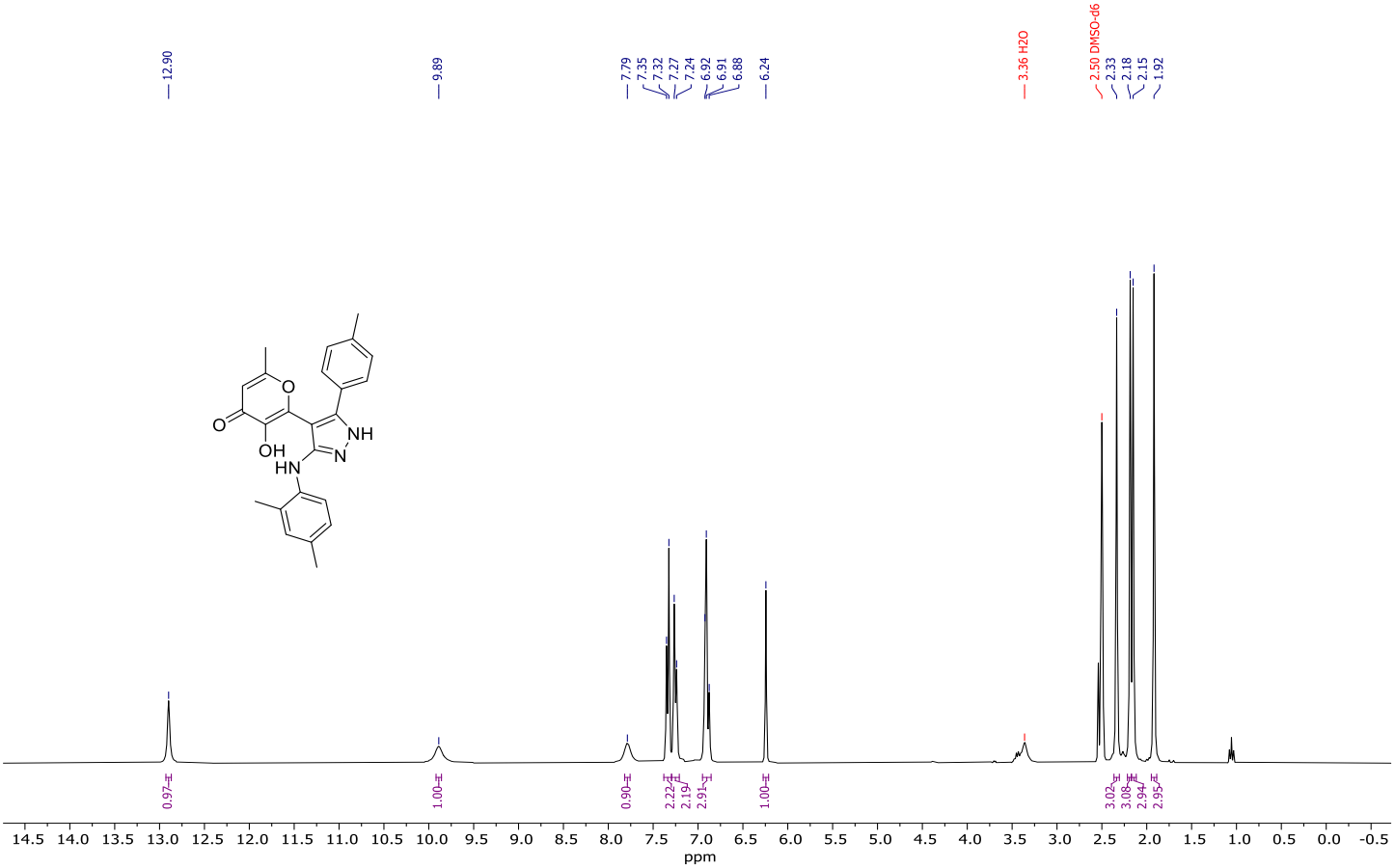
^{1}H NMR spectrum (300 MHz) of **15l** in DMSO-d_6



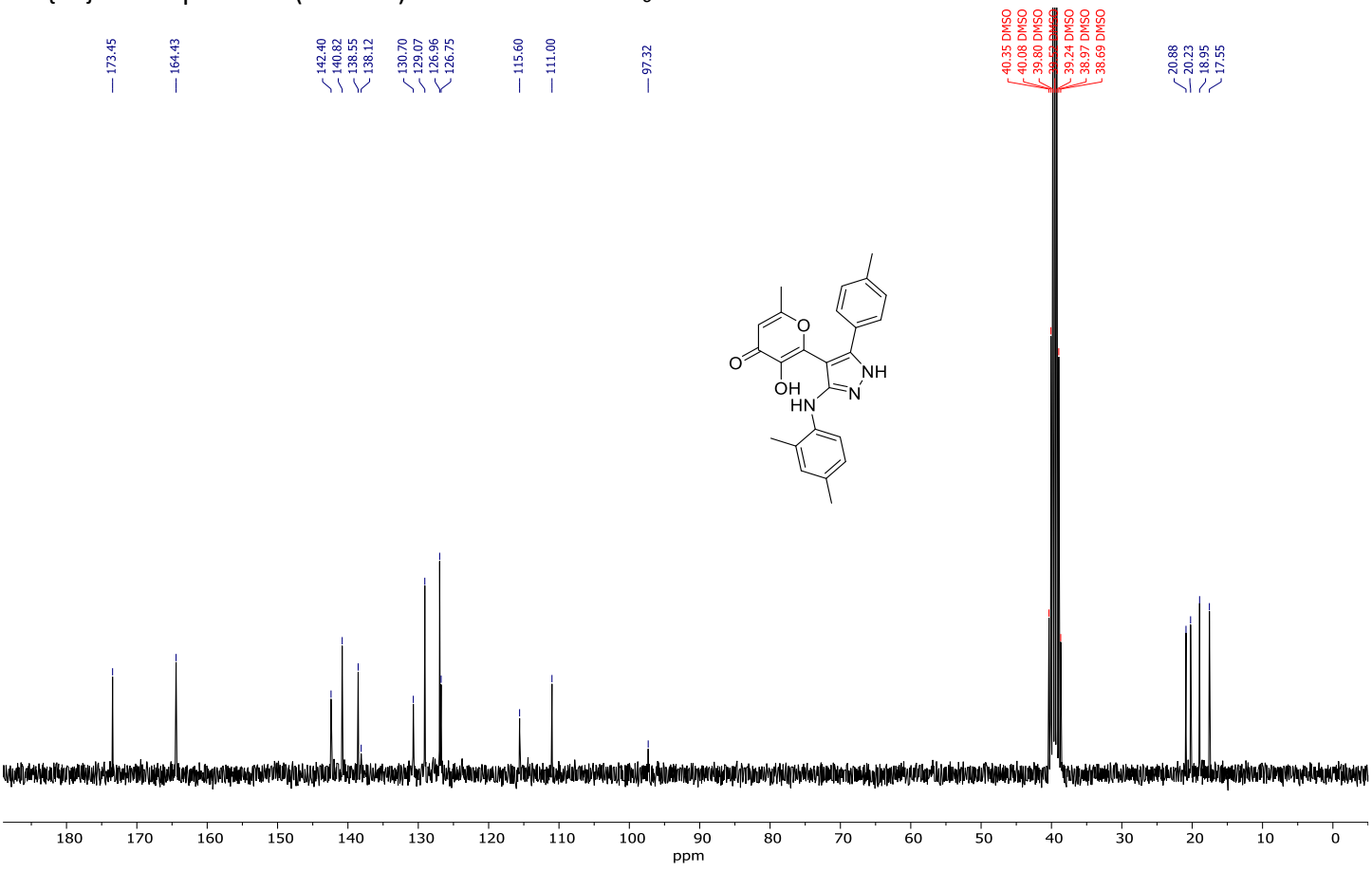
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15l** in DMSO-d_6



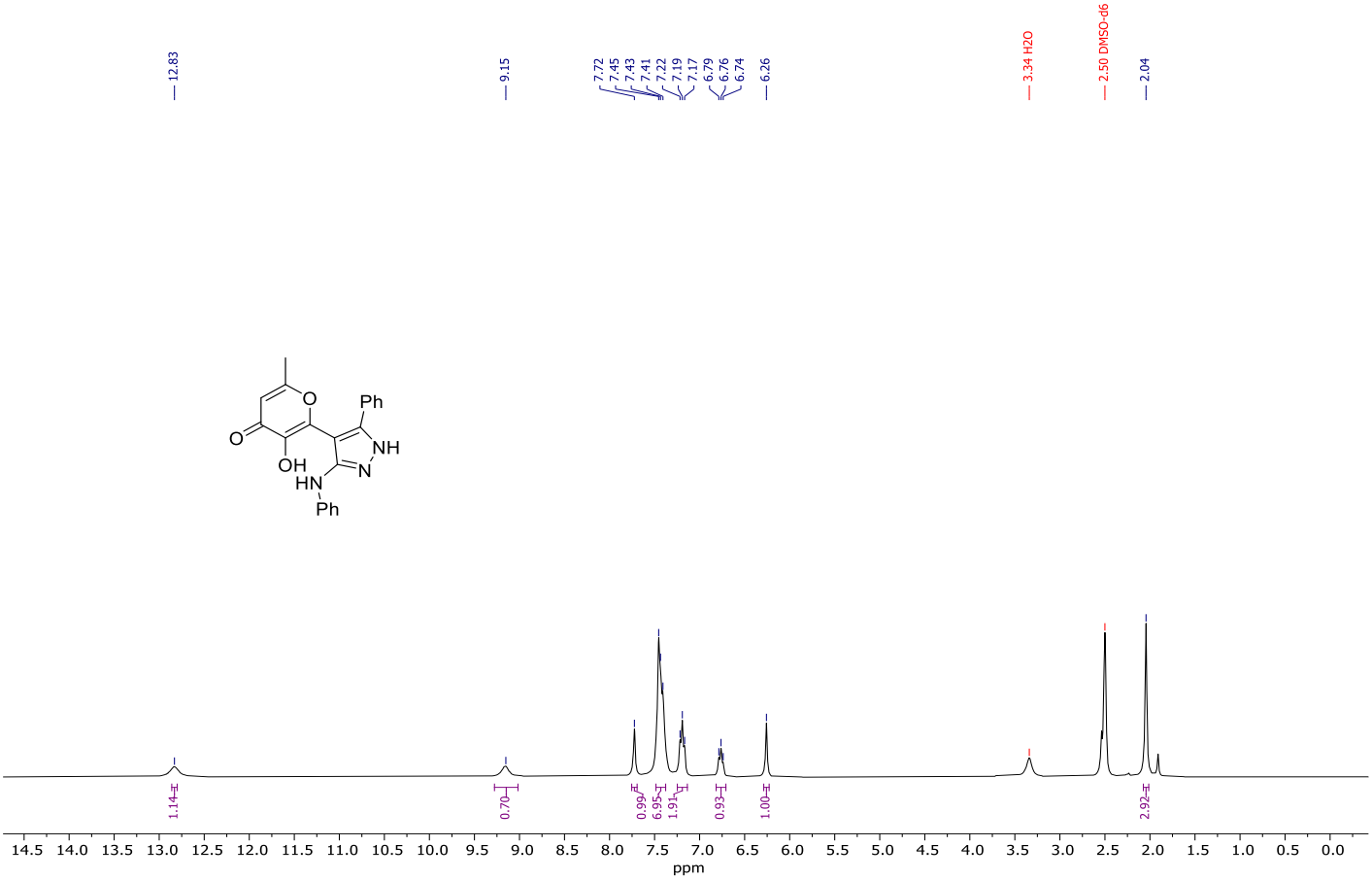
^{1}H NMR spectrum (300 MHz) of **15m** in DMSO-d_6



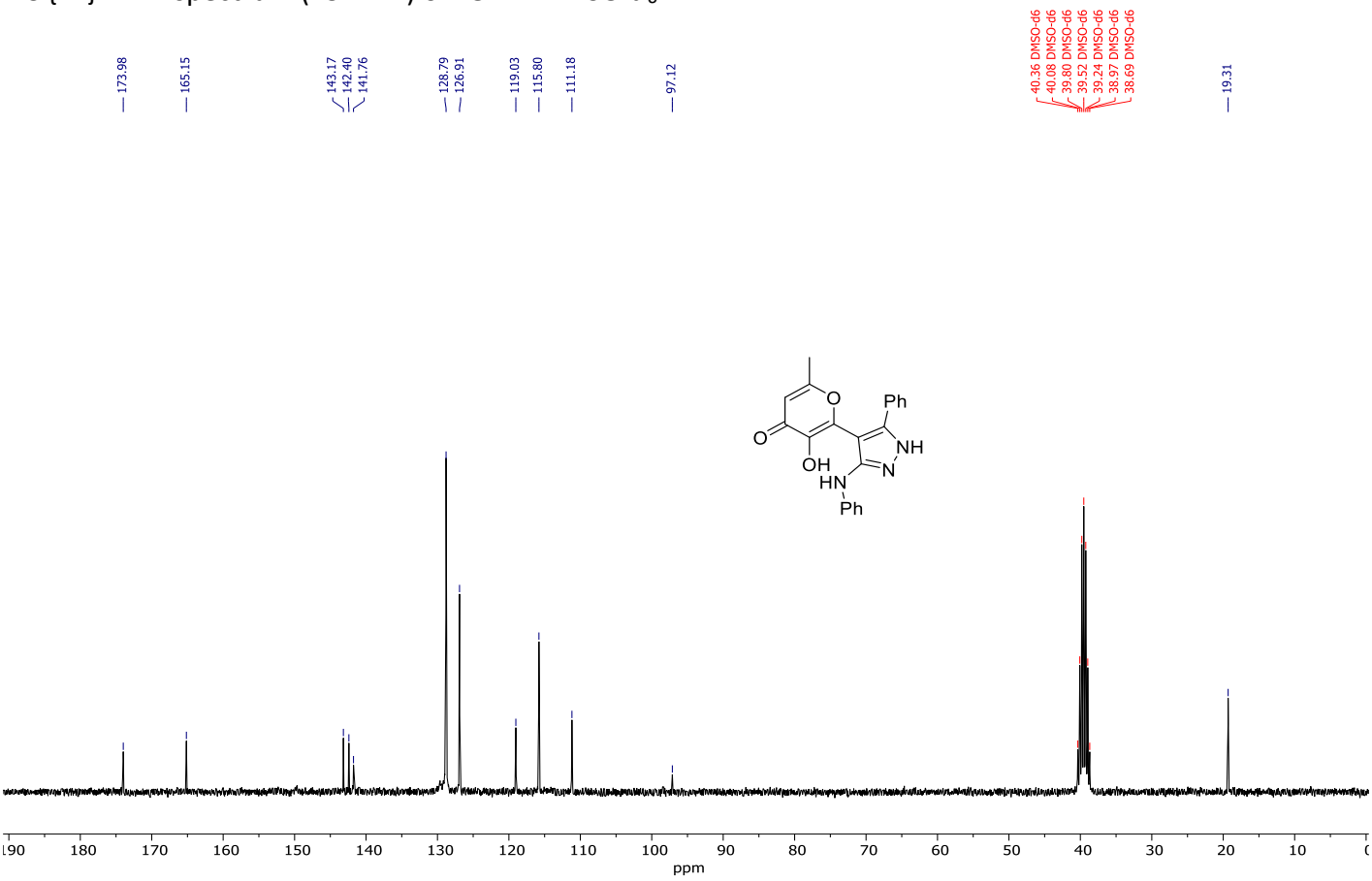
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15m** in DMSO-d_6



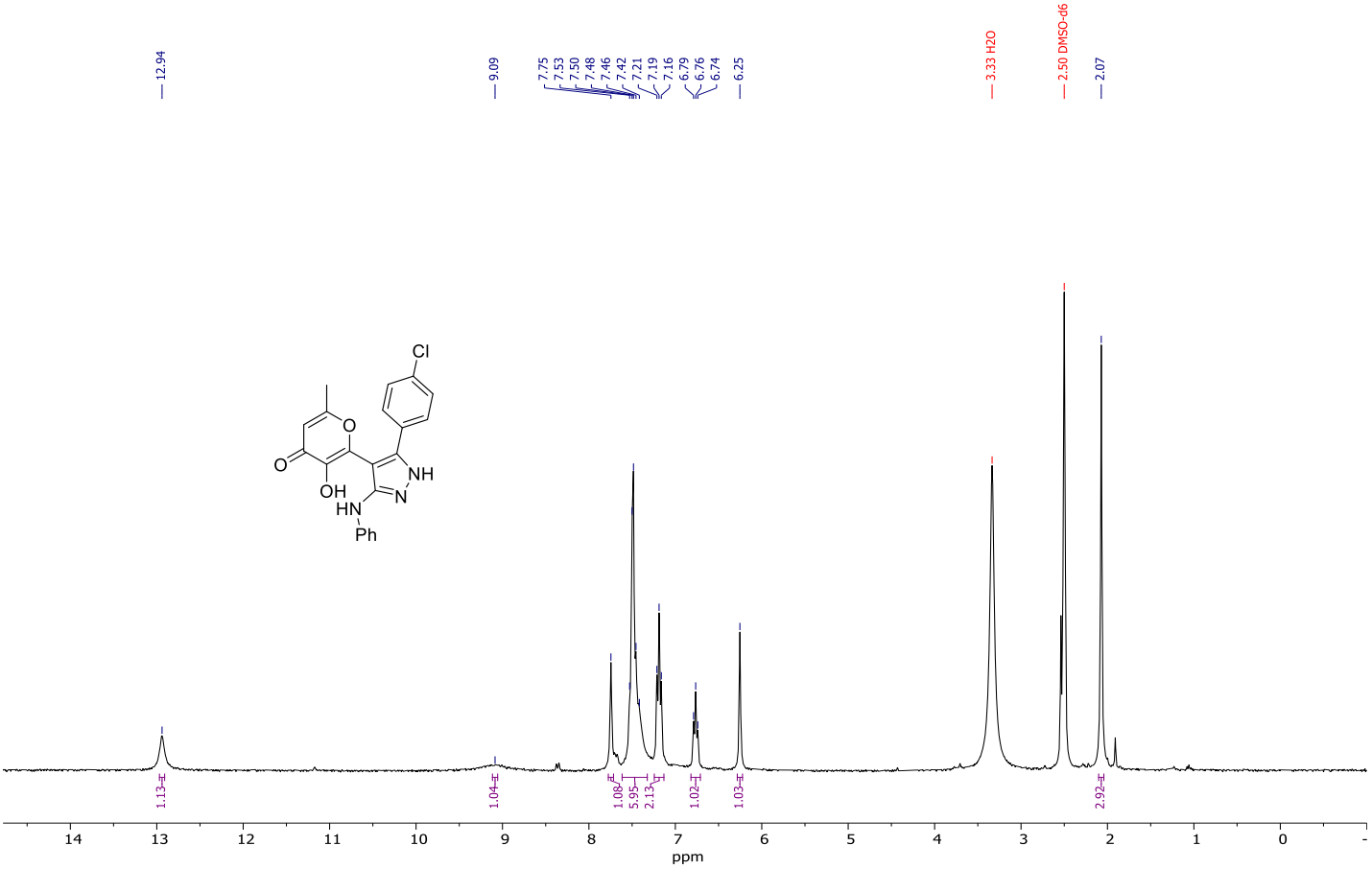
^{1}H NMR spectrum (300 MHz) of **15n** in DMSO-d_6



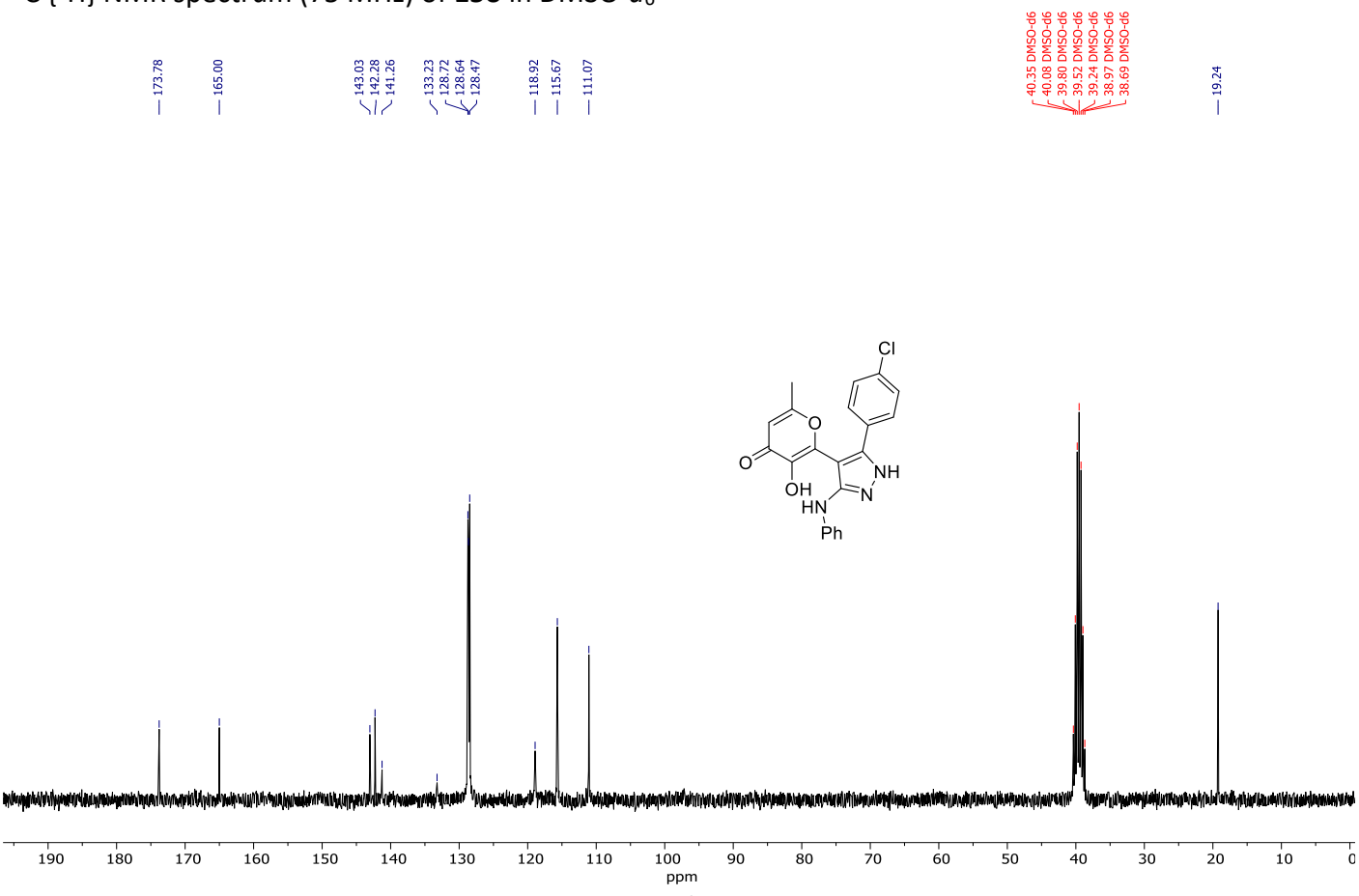
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15n** in DMSO-d_6



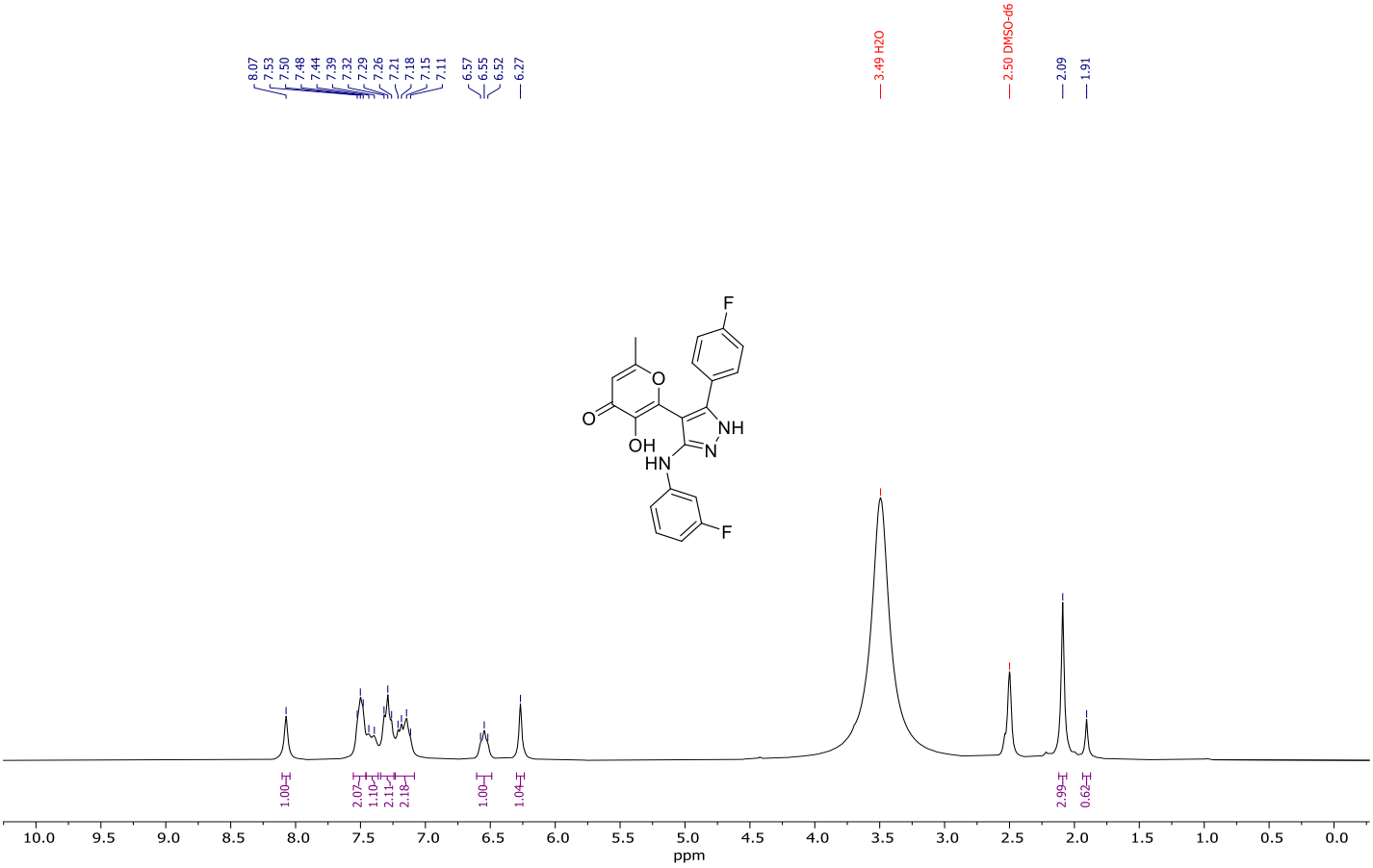
^{1}H NMR spectrum (300 MHz) of **15o** in DMSO-d_6



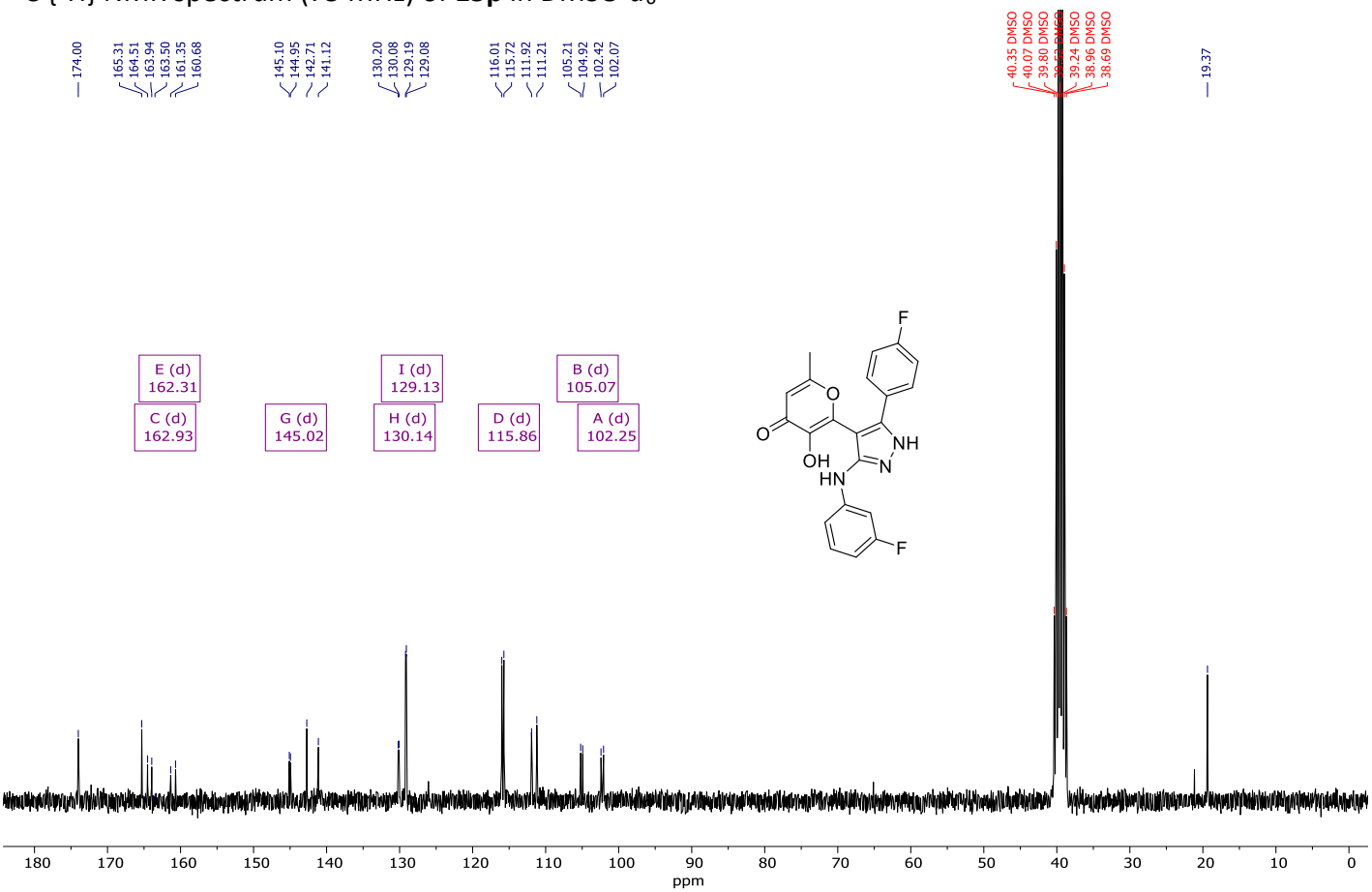
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15o** in DMSO-d_6



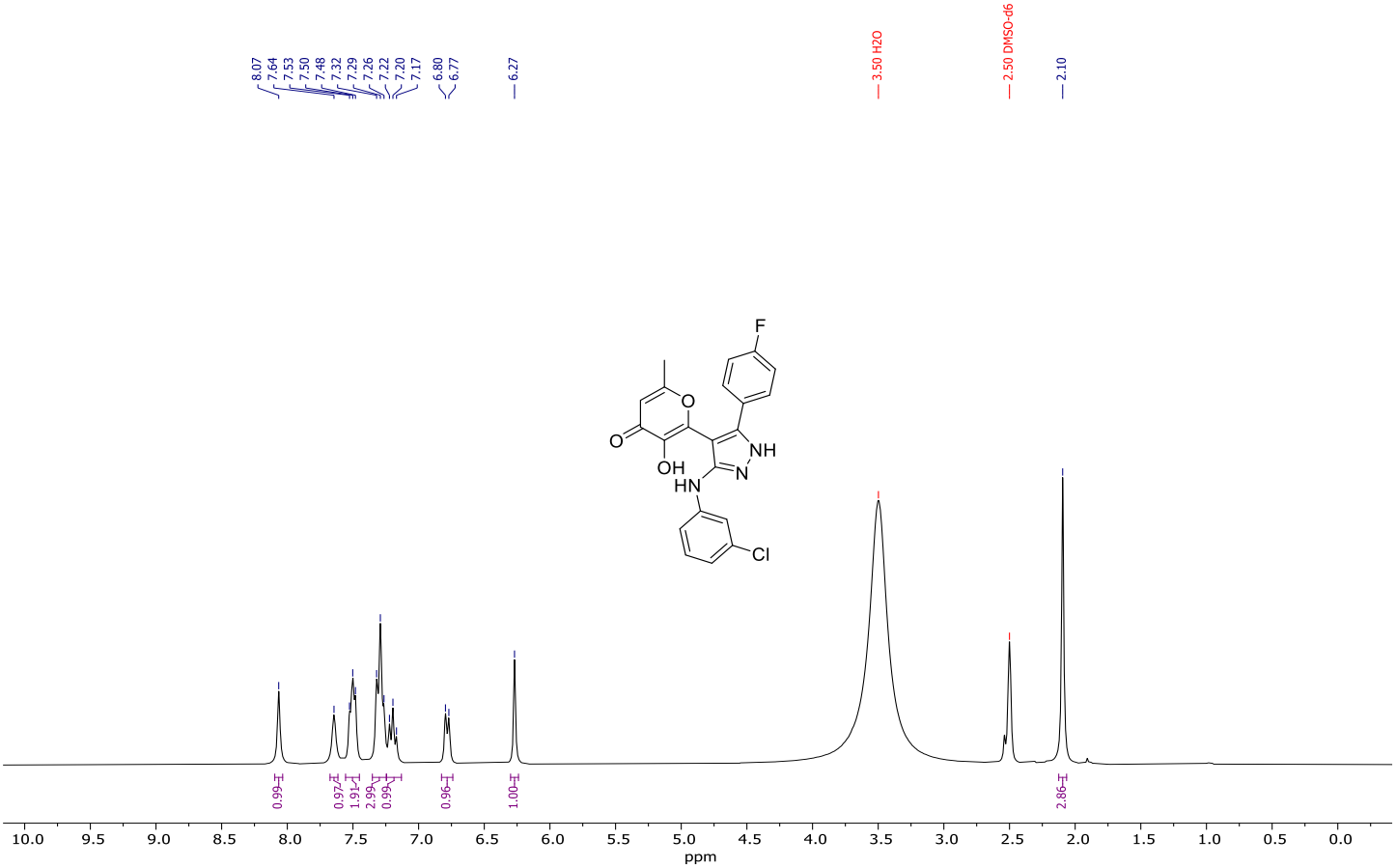
^{1}H NMR spectrum (300 MHz) of **15p** in DMSO-d_6



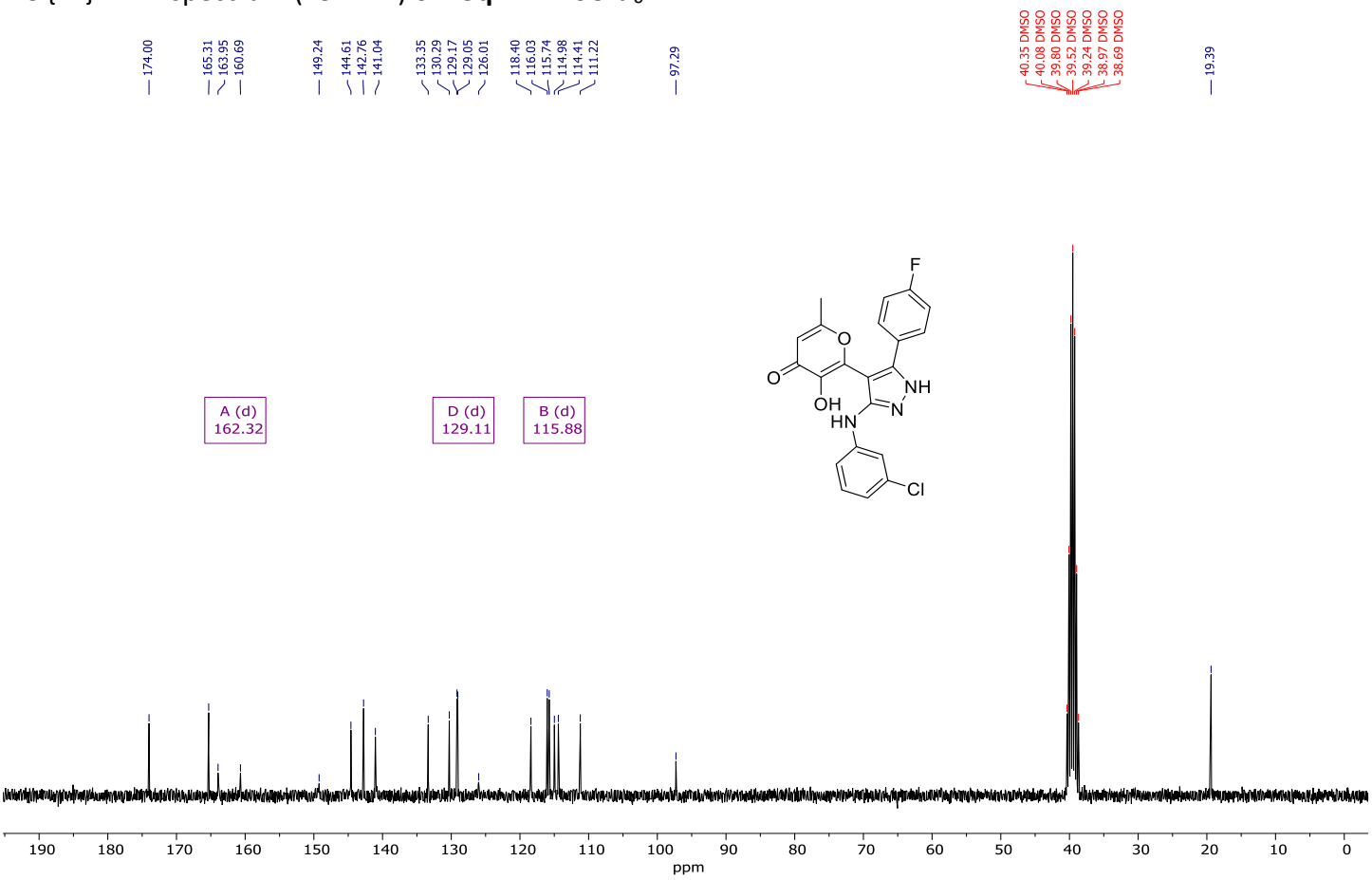
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15p** in DMSO-d_6



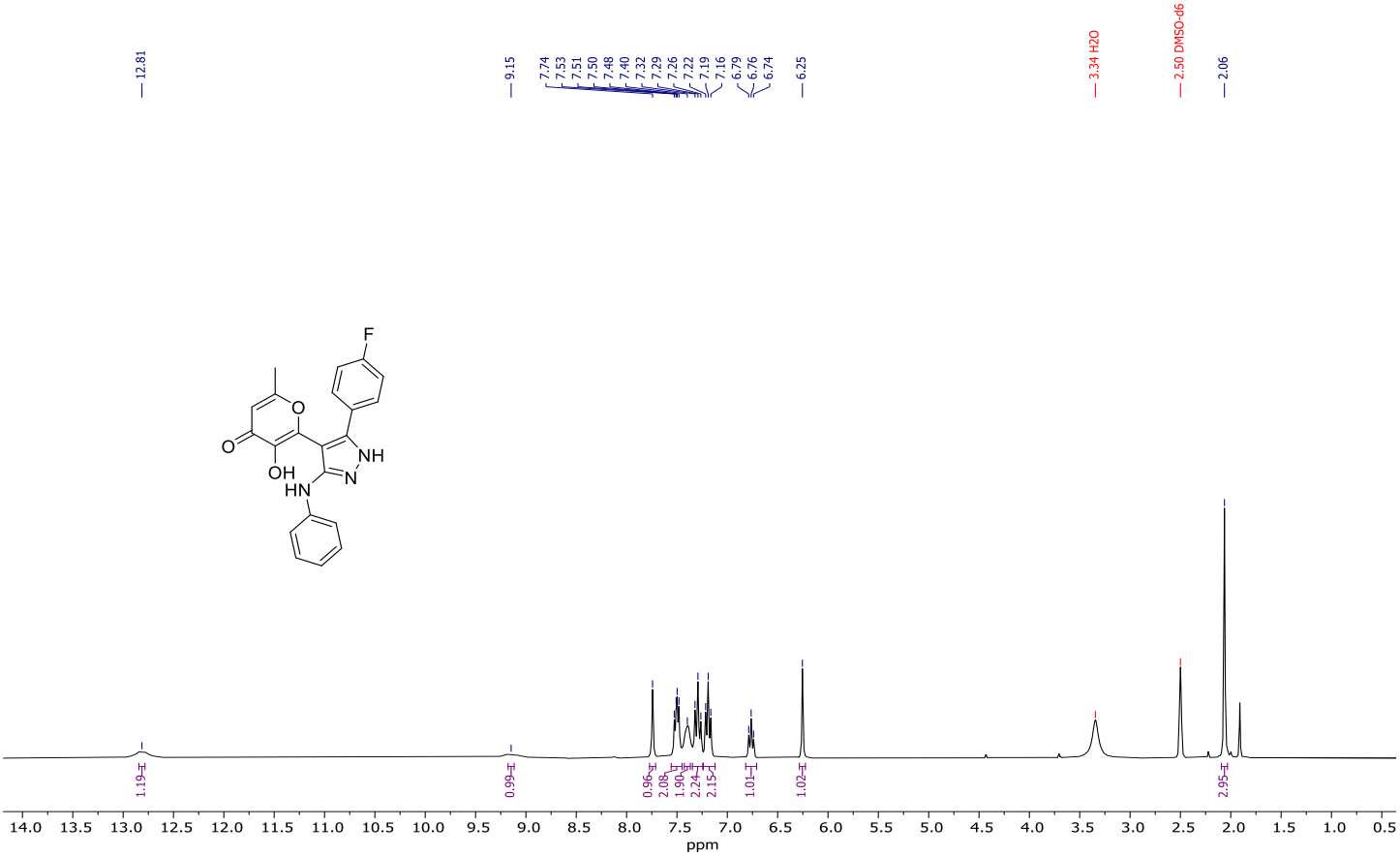
^{1}H NMR spectrum (300 MHz) of **15q** in DMSO-d_6



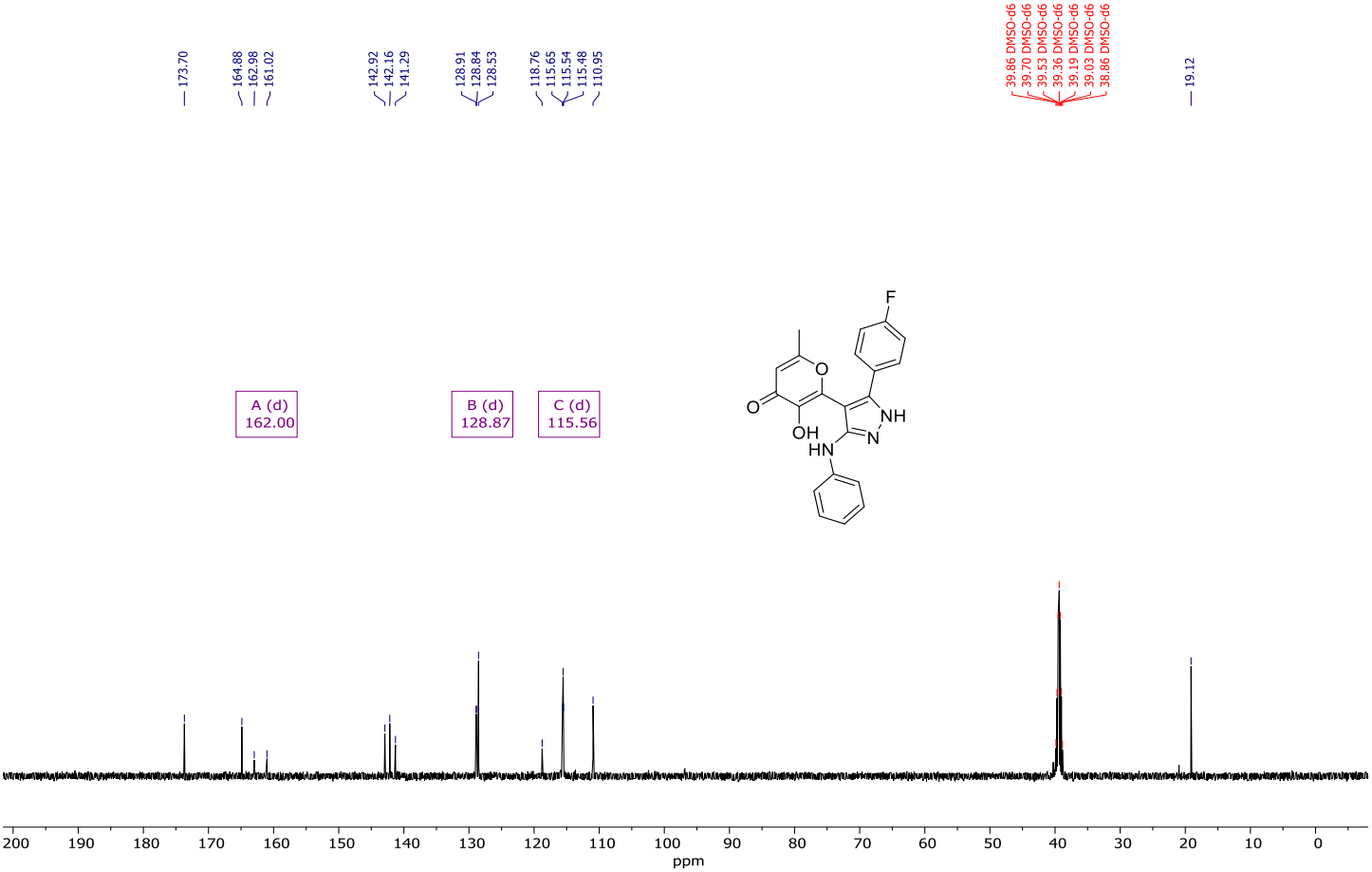
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15q** in DMSO-d_6



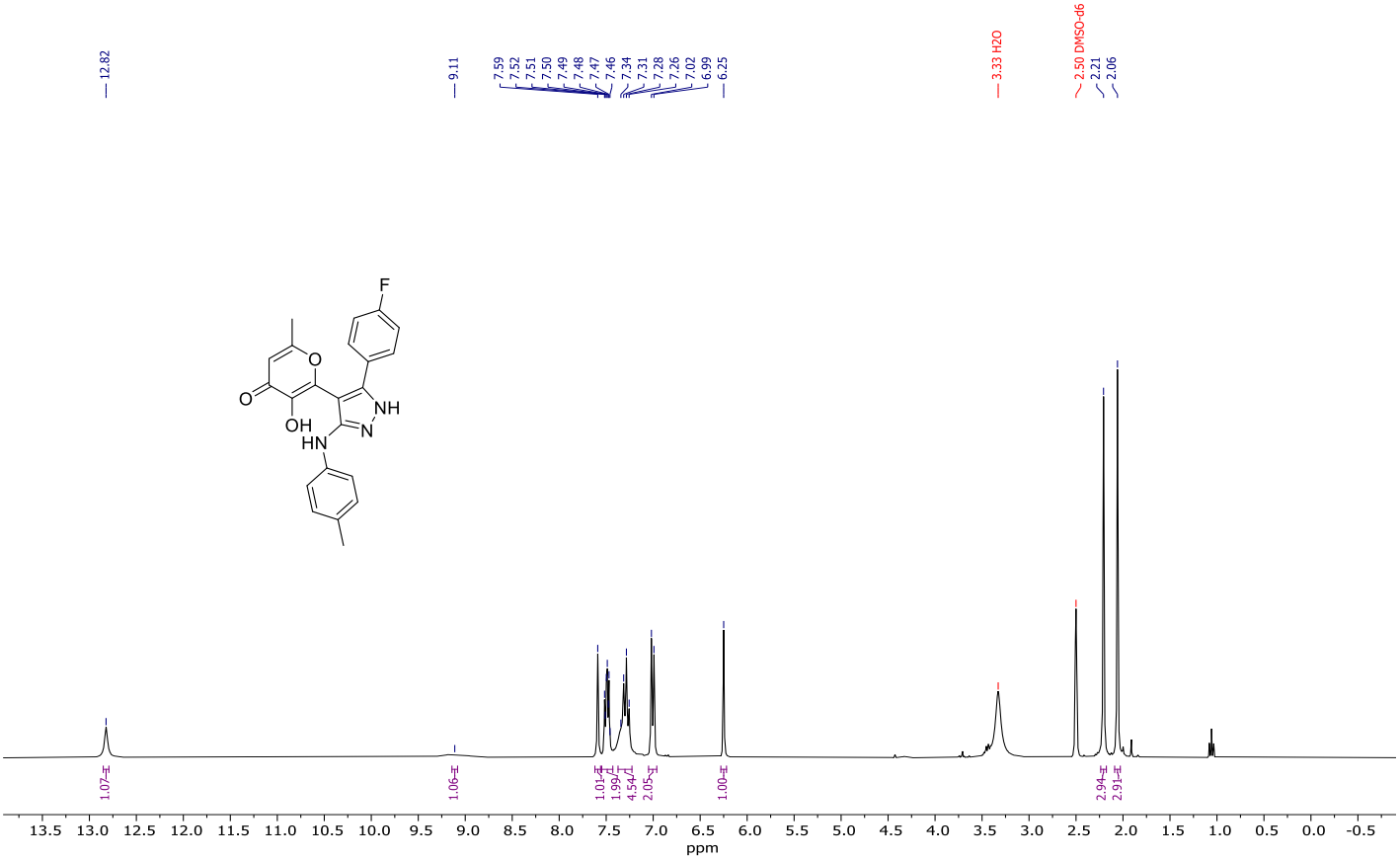
^{1}H NMR spectrum (300 MHz) of **15r** in DMSO-d_6



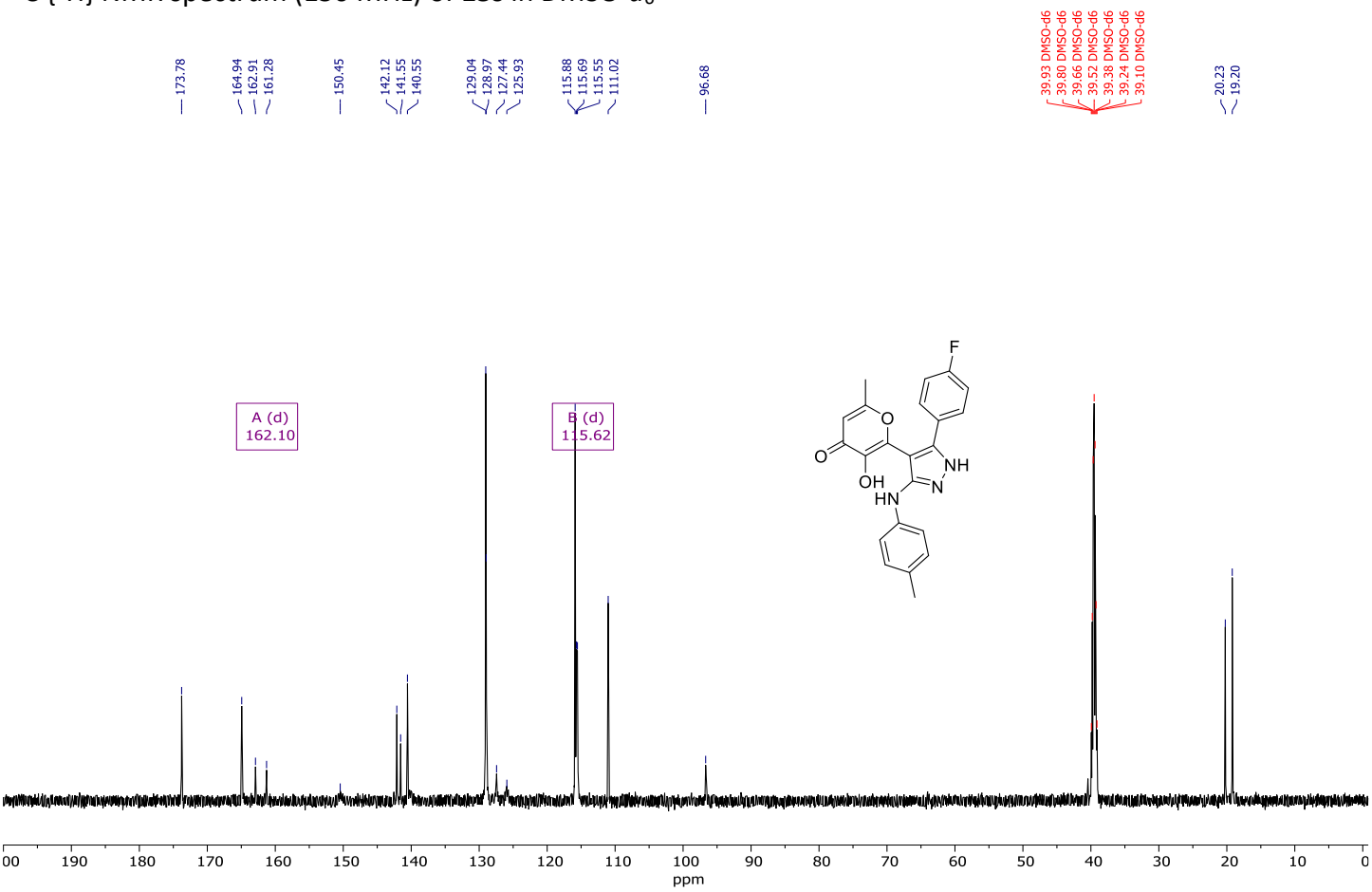
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15r** in DMSO-d_6



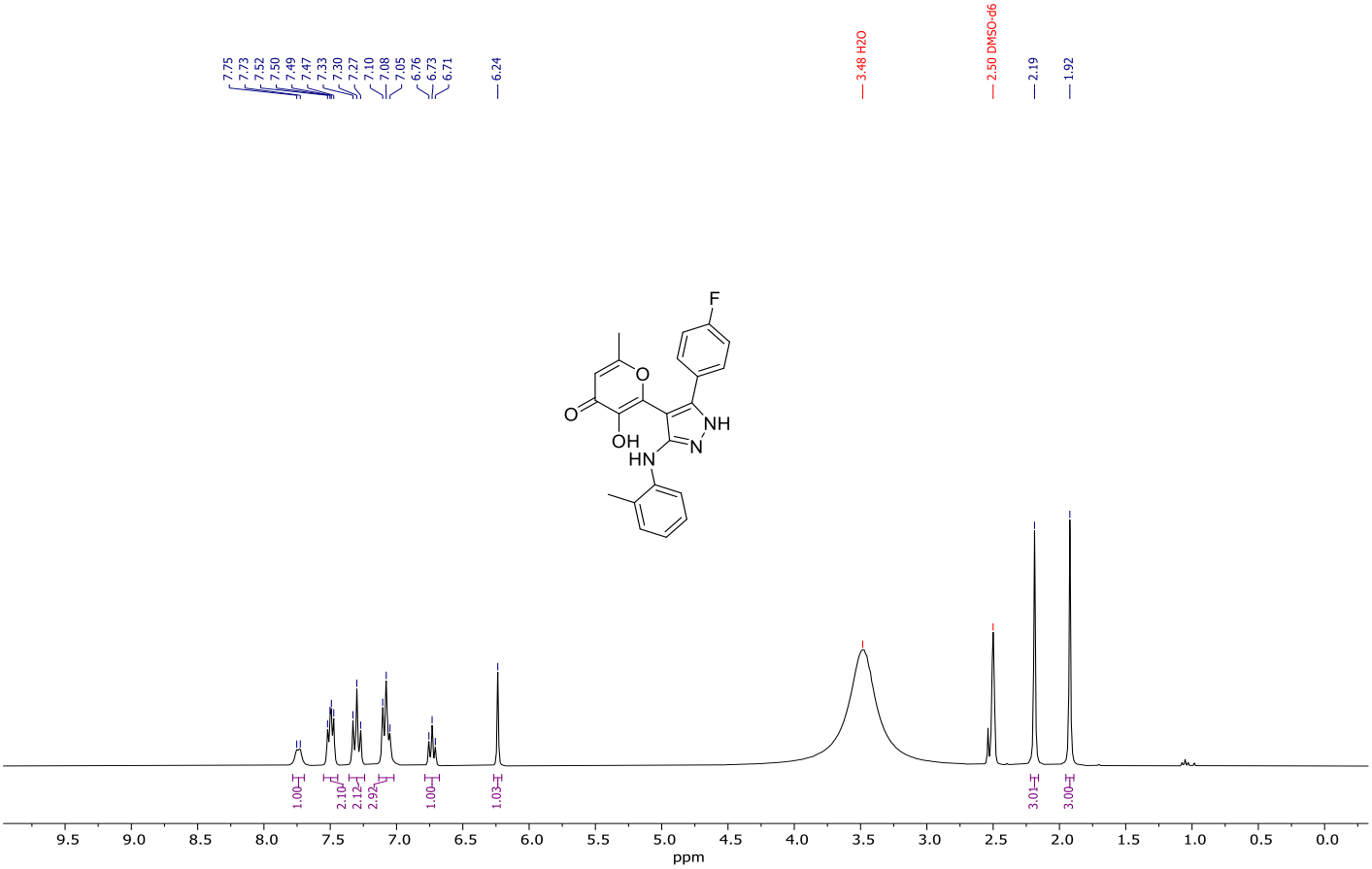
^{1}H NMR spectrum (300 MHz) of **15s** in DMSO-d_6



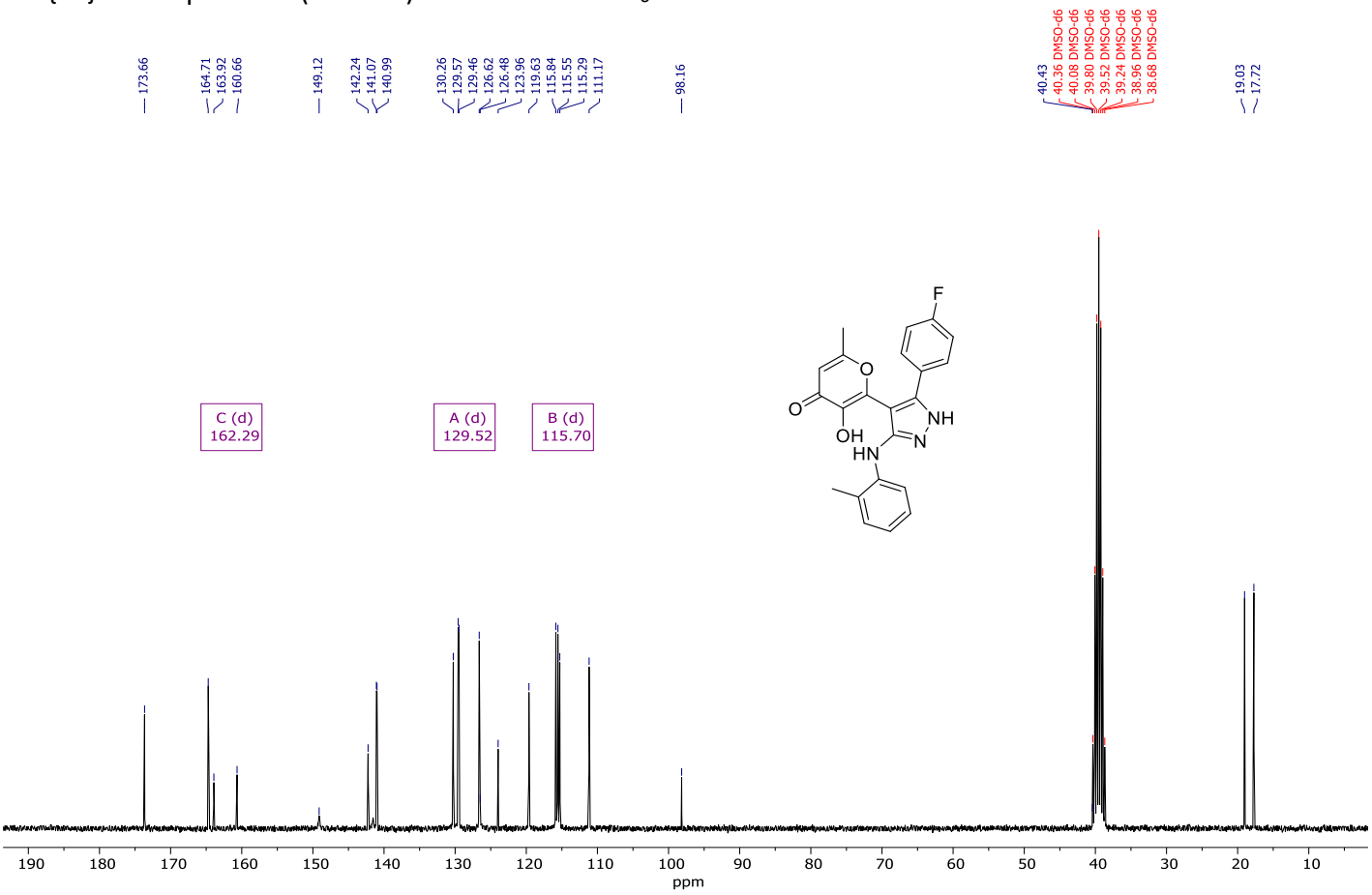
^{13}C {^{1}H} NMR spectrum (150 MHz) of **15s** in DMSO-d_6



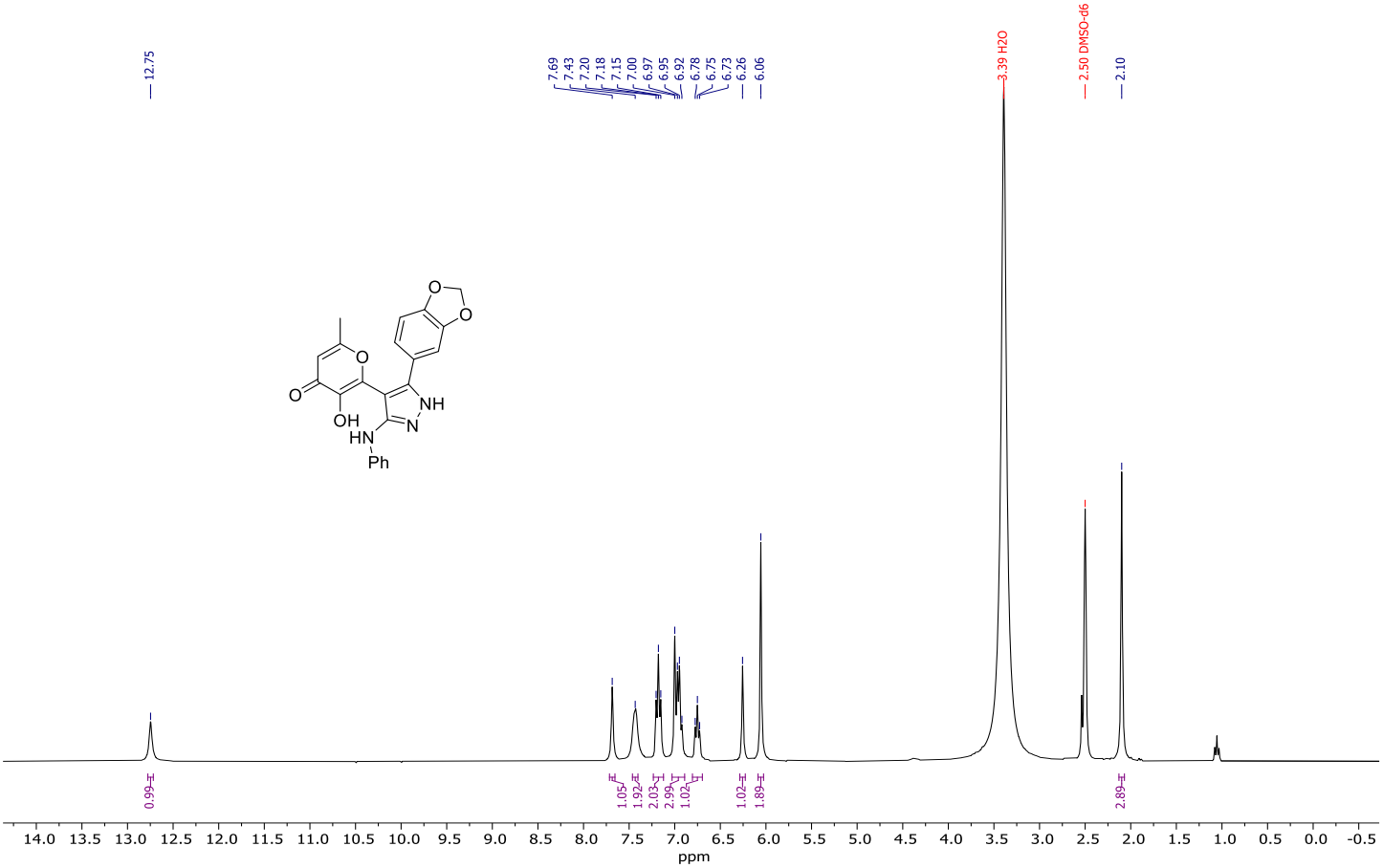
^{1}H NMR spectrum (300 MHz) of **15t** in DMSO-d_6



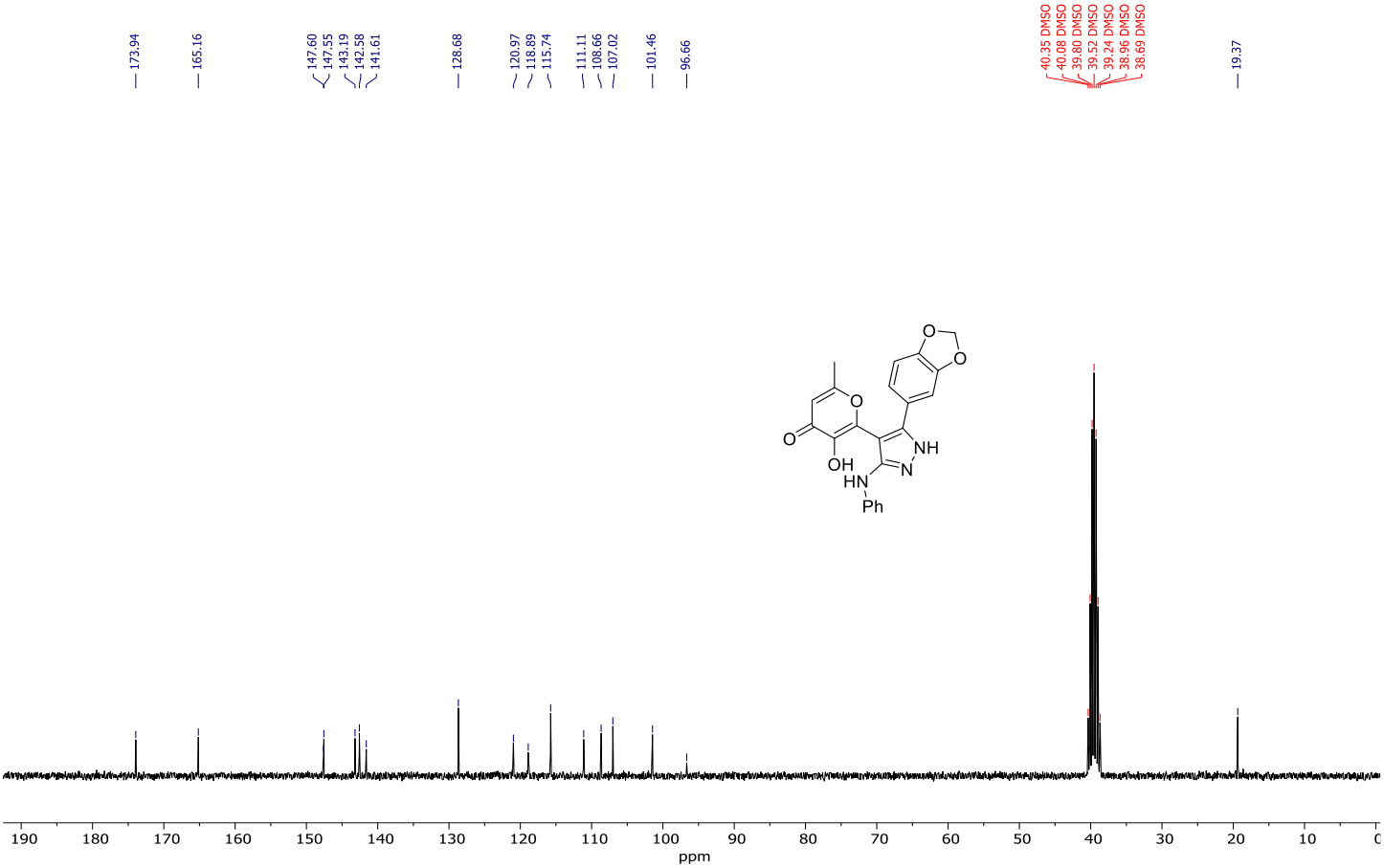
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15t** in DMSO-d_6



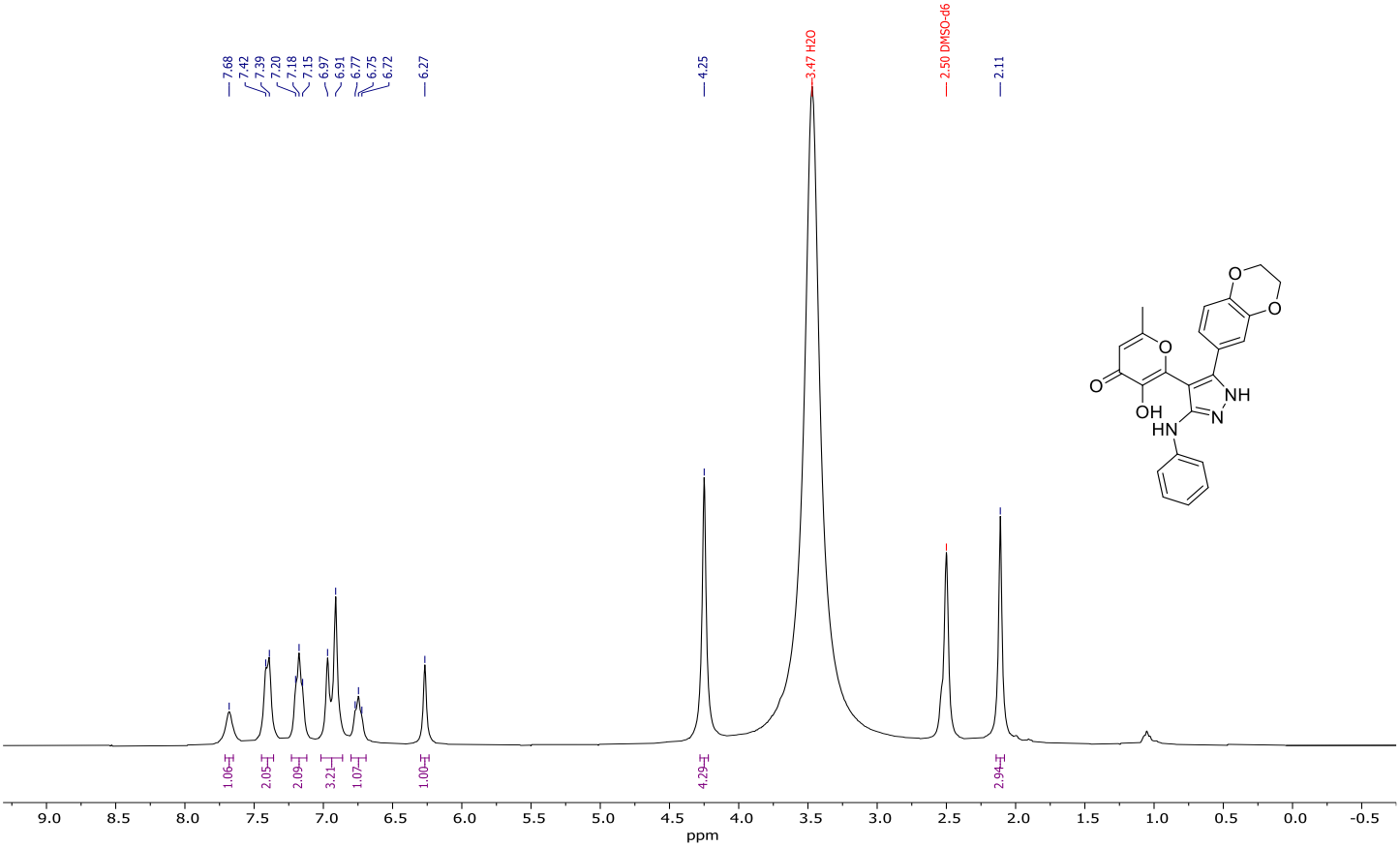
^{1}H NMR spectrum (300 MHz) of **15u** in DMSO-d_6



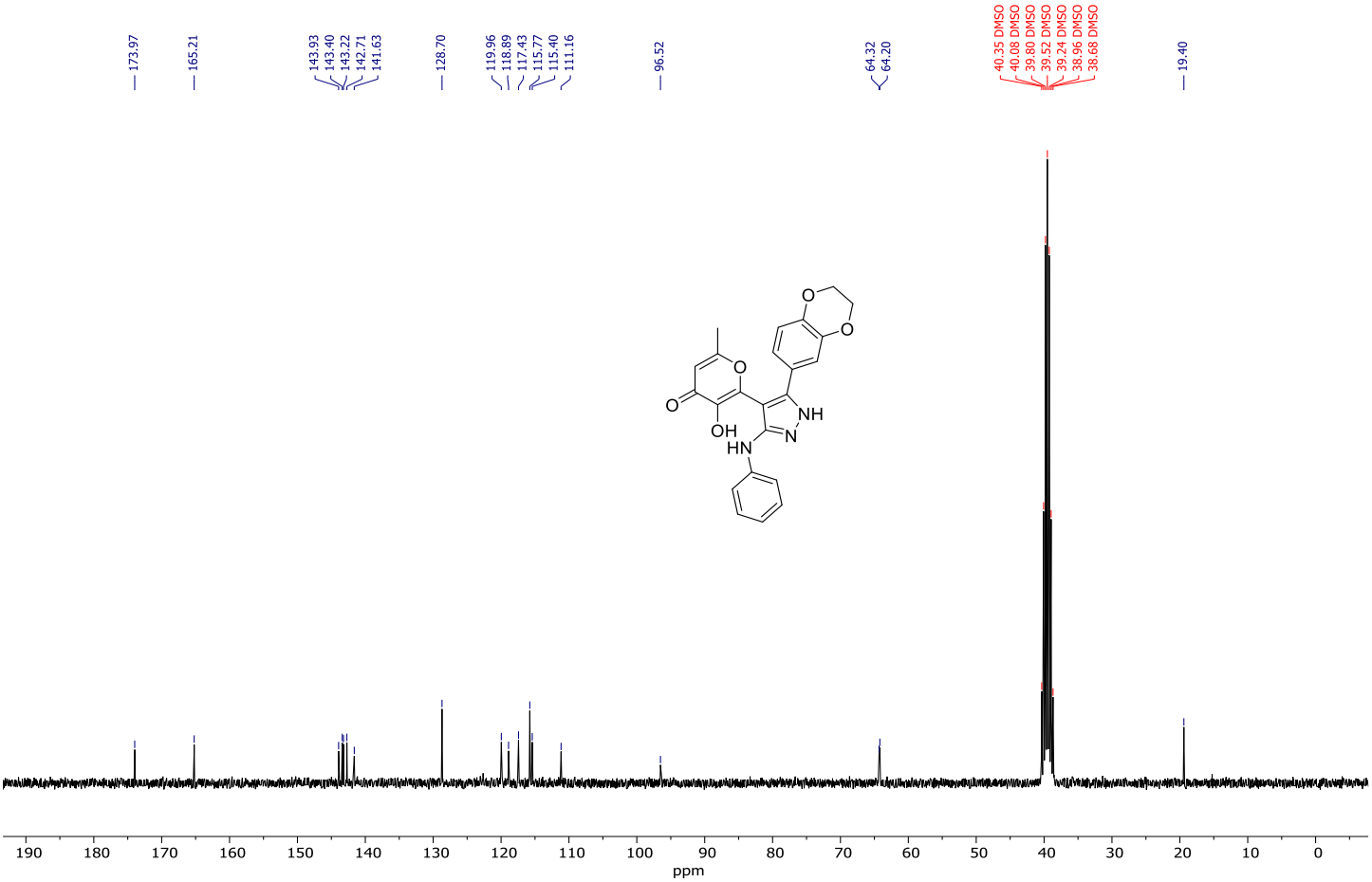
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15u** in DMSO-d_6



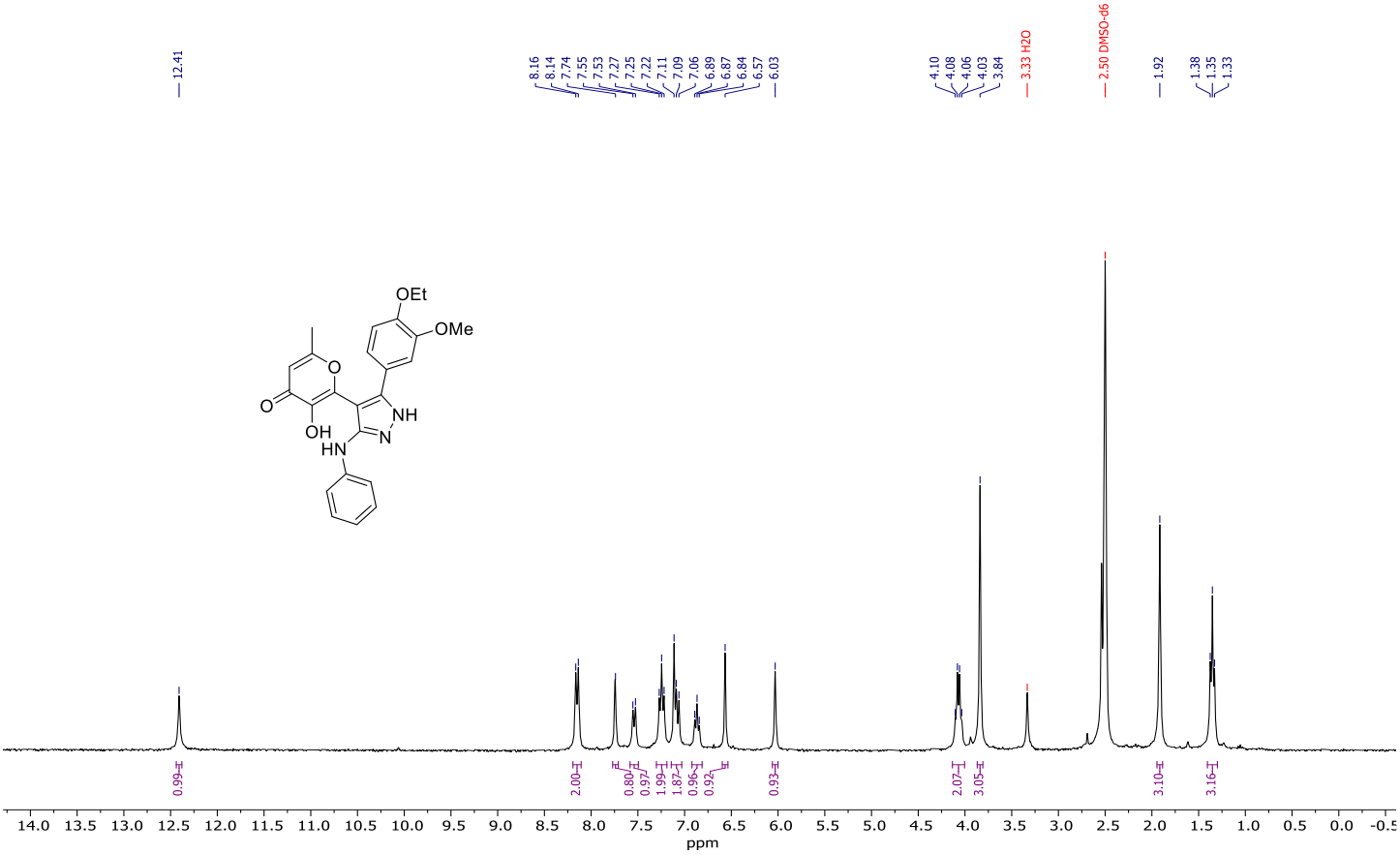
^{1}H NMR spectrum (300 MHz) of **15v** in DMSO-d_6



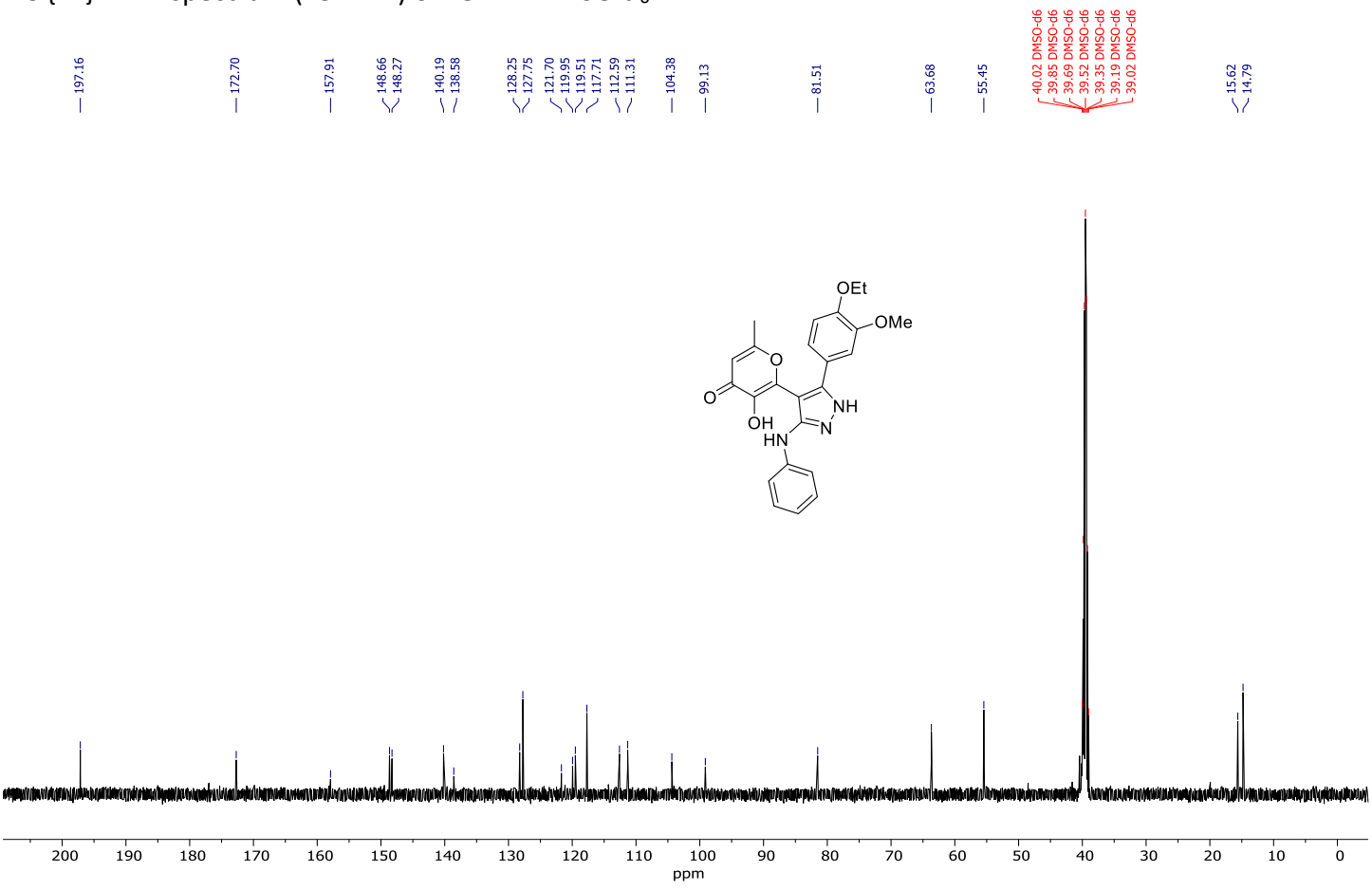
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15v** in DMSO-d_6



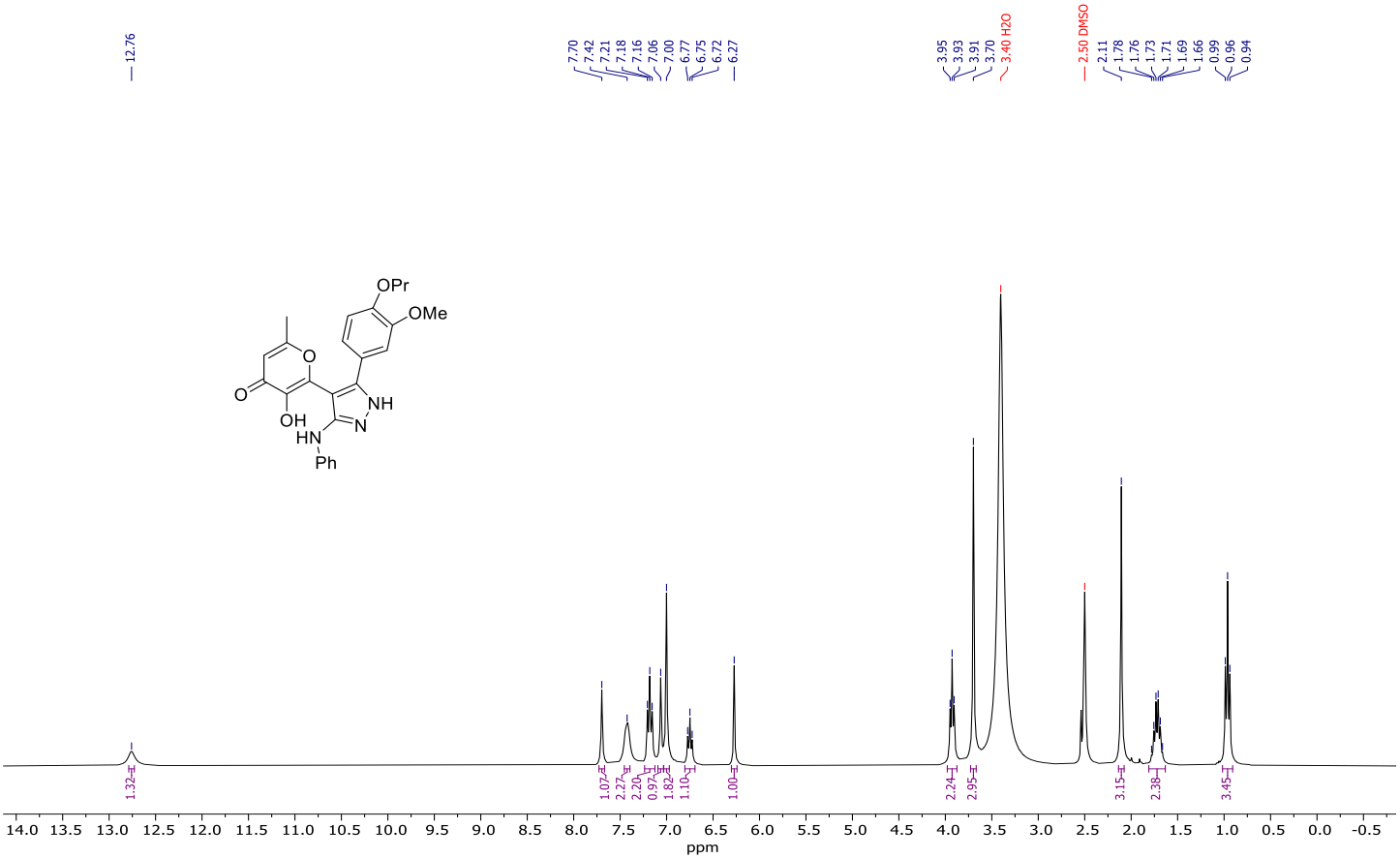
^{1}H NMR spectrum (300 MHz) of **15w** in DMSO-d_6



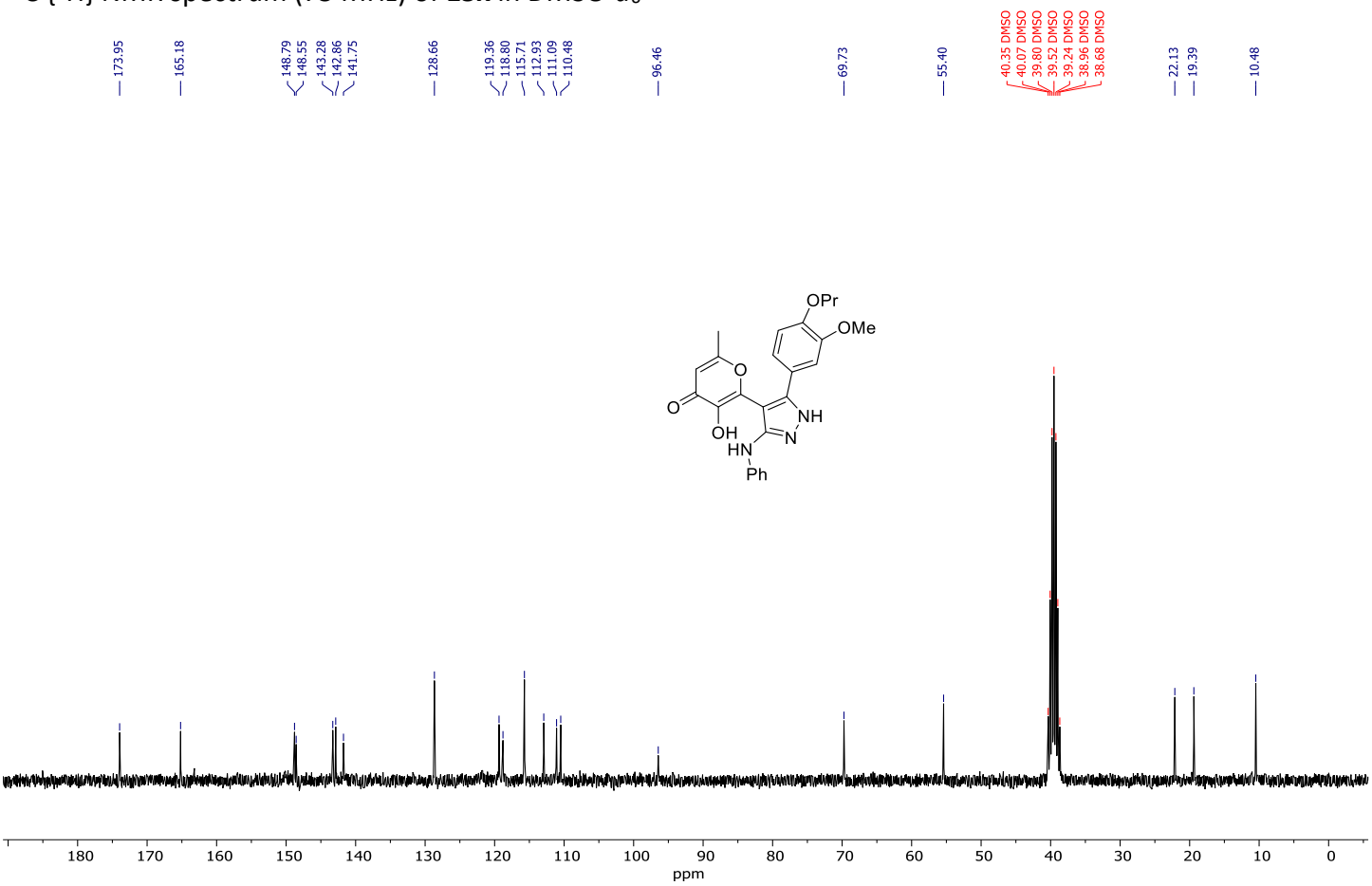
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15w** in DMSO-d_6



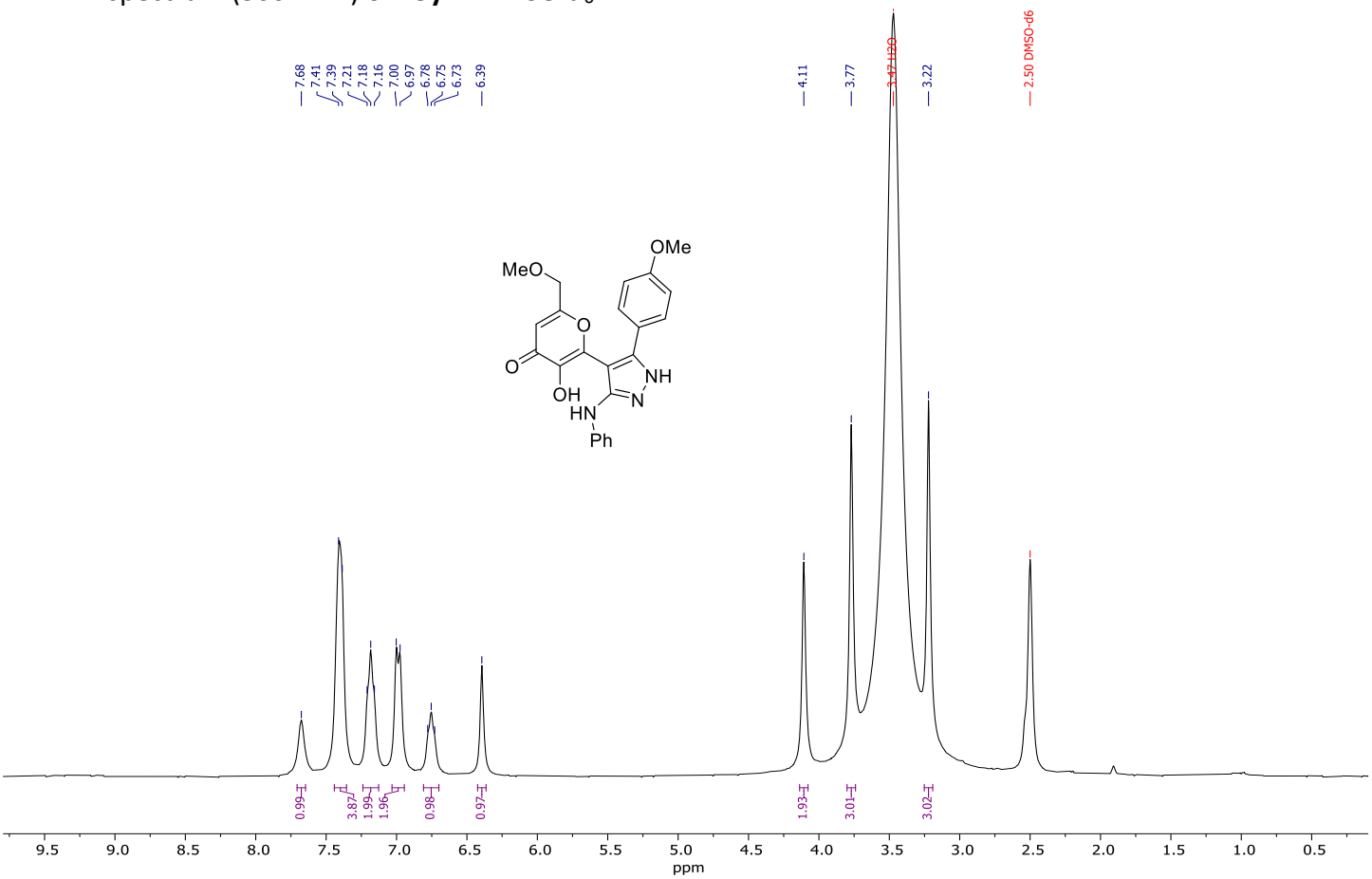
^{1}H NMR spectrum (300 MHz) of **15x** in DMSO-d_6



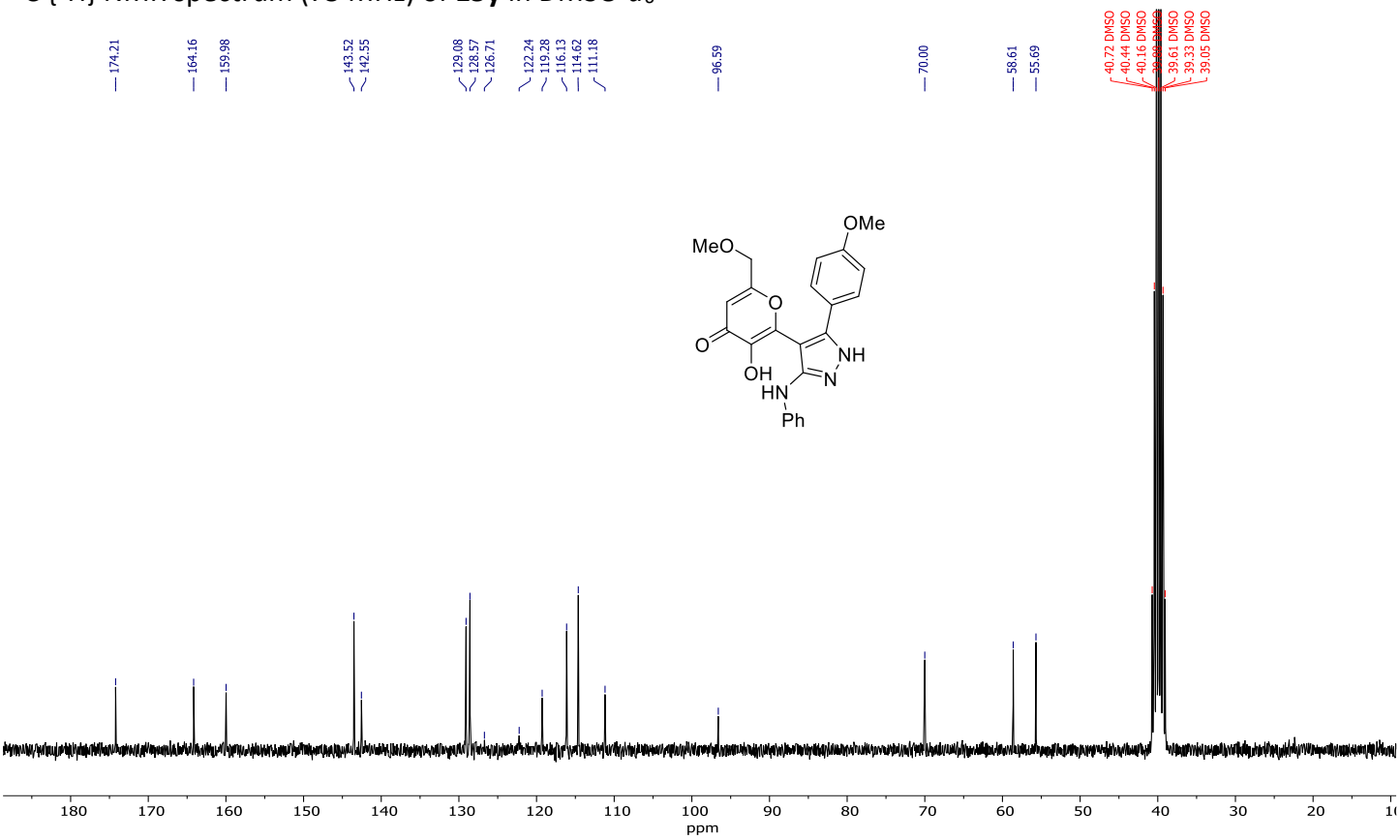
^{13}C {^{1}H} NMR spectrum (75 MHz) of **15x** in DMSO-d_6



^{1}H NMR spectrum (300 MHz) of **15y** in DMSO-d_6

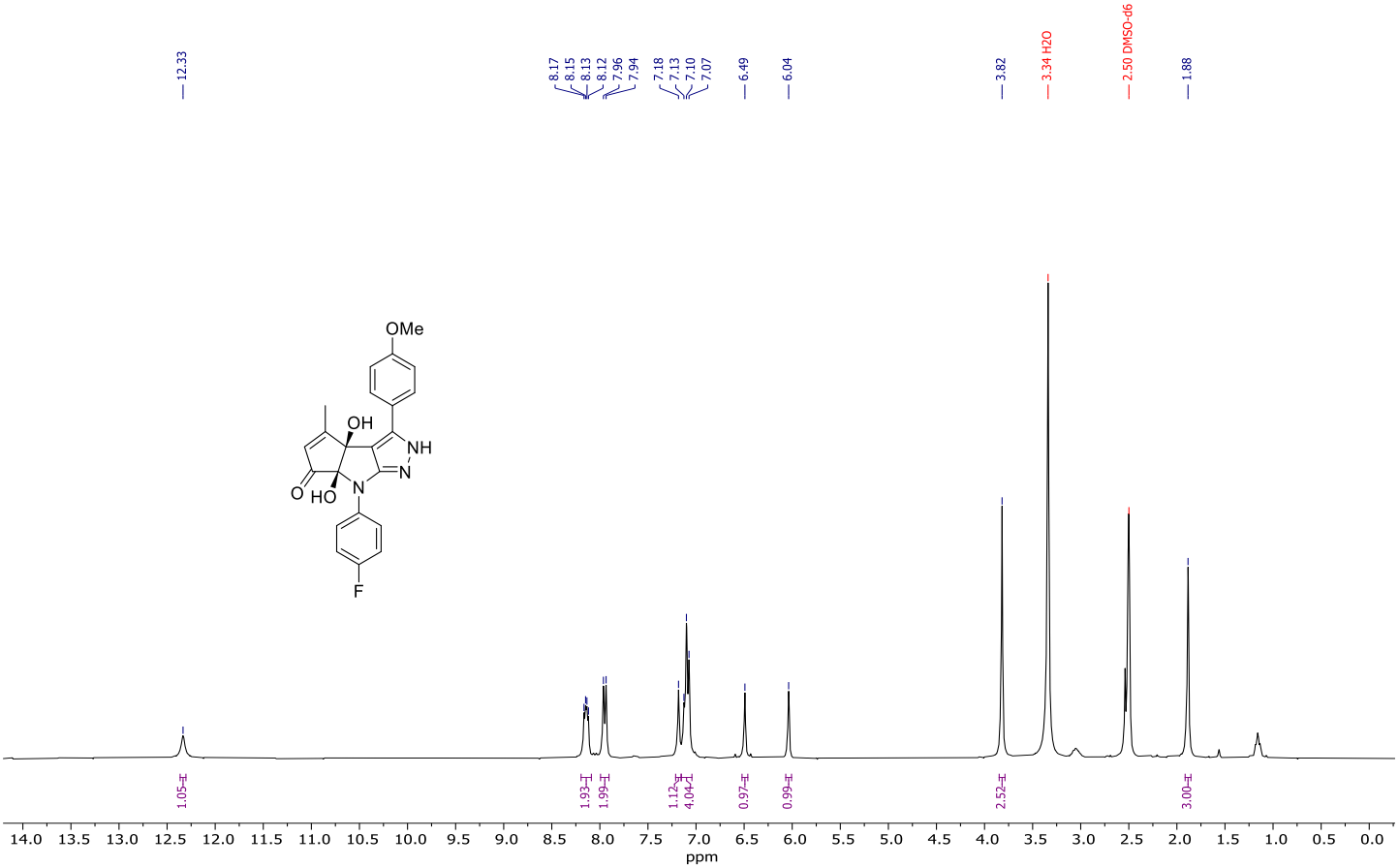


^{13}C {^{1}H} NMR spectrum (75 MHz) of **15y** in DMSO-d_6

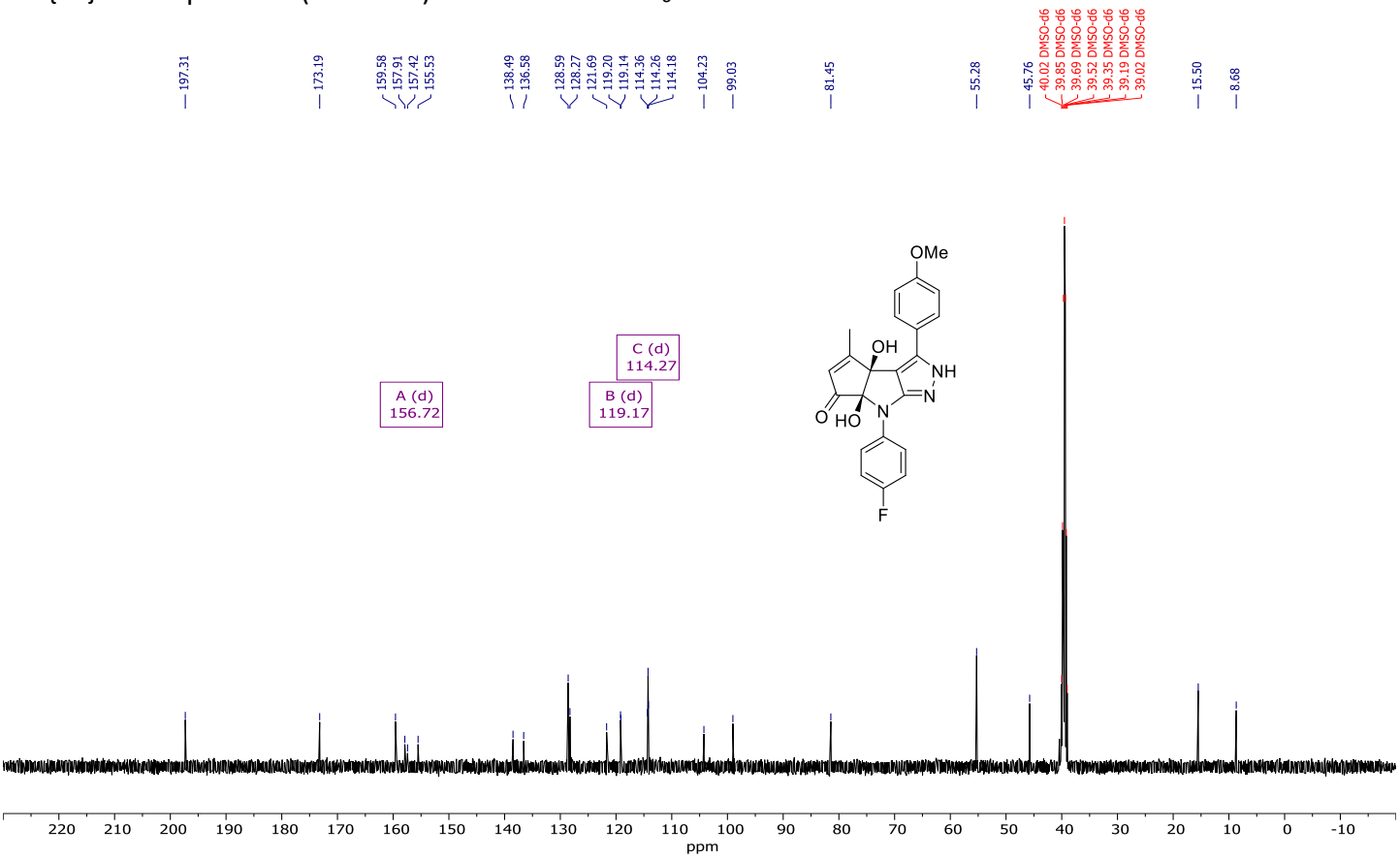


6. NMR ^{1}H and ^{13}C spectra for compounds 16

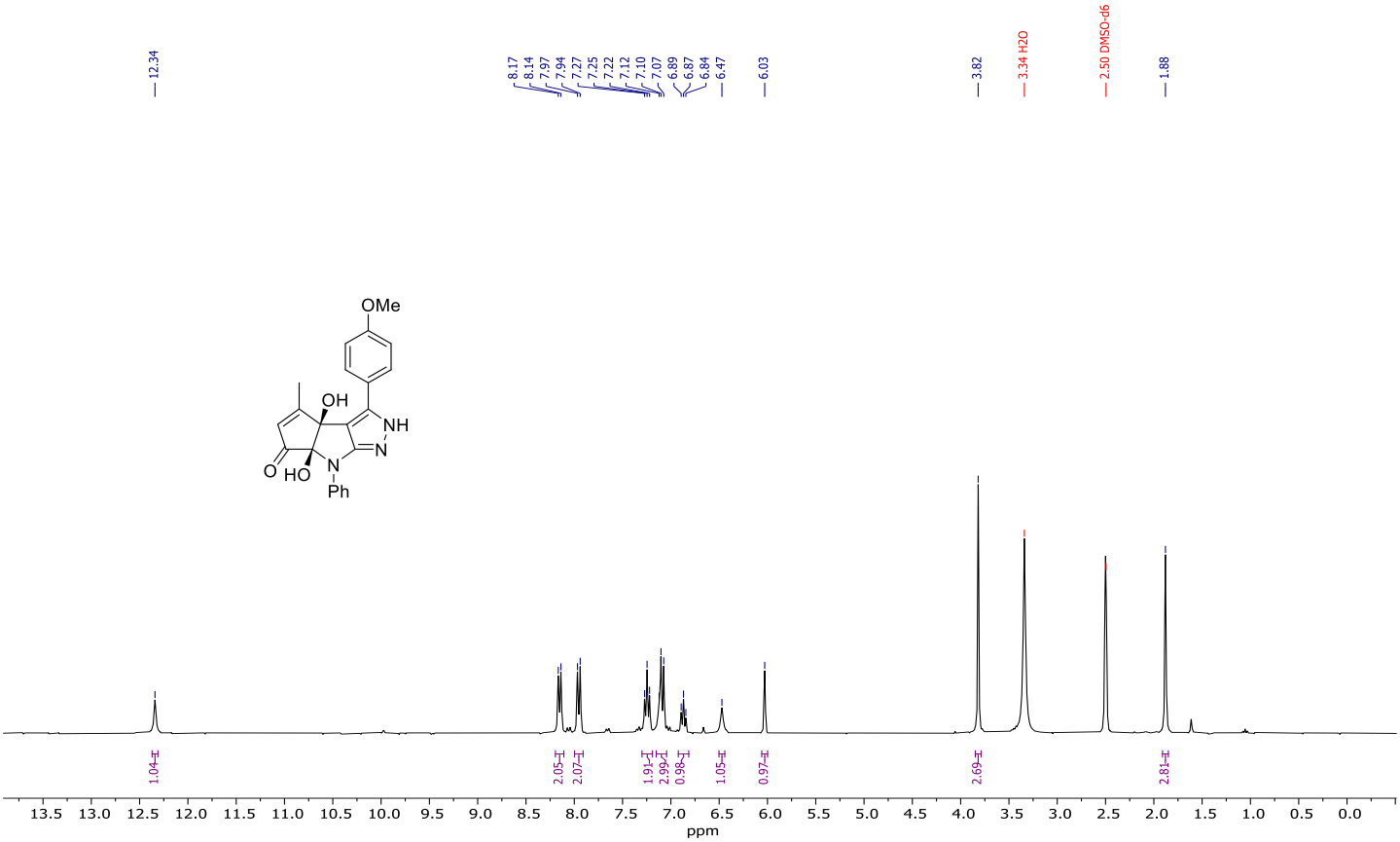
^{1}H NMR spectrum (300 MHz) of **16a** in DMSO-d_6



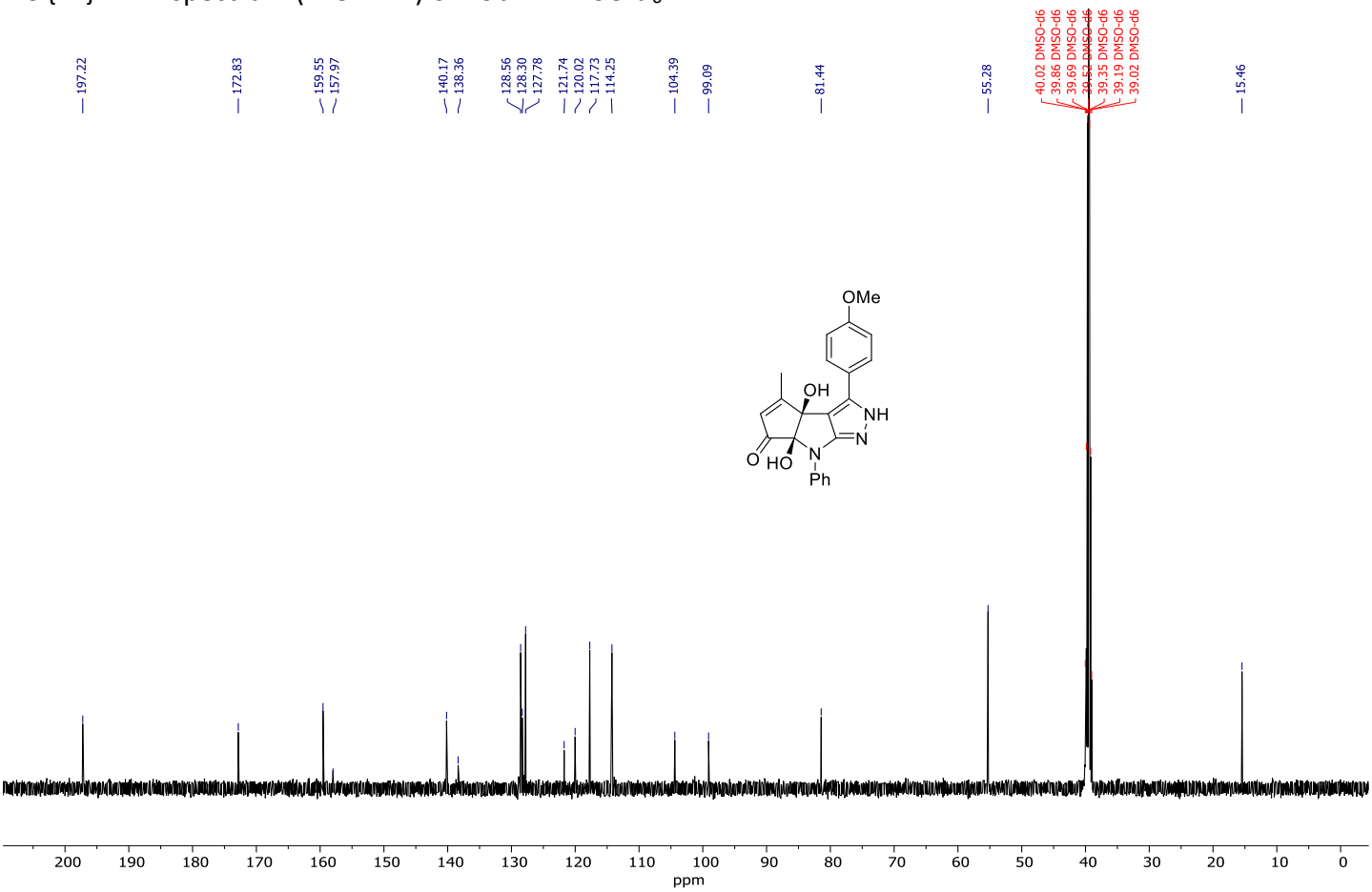
^{13}C {^{1}H} NMR spectrum (125 MHz) of **16a** in DMSO-d_6



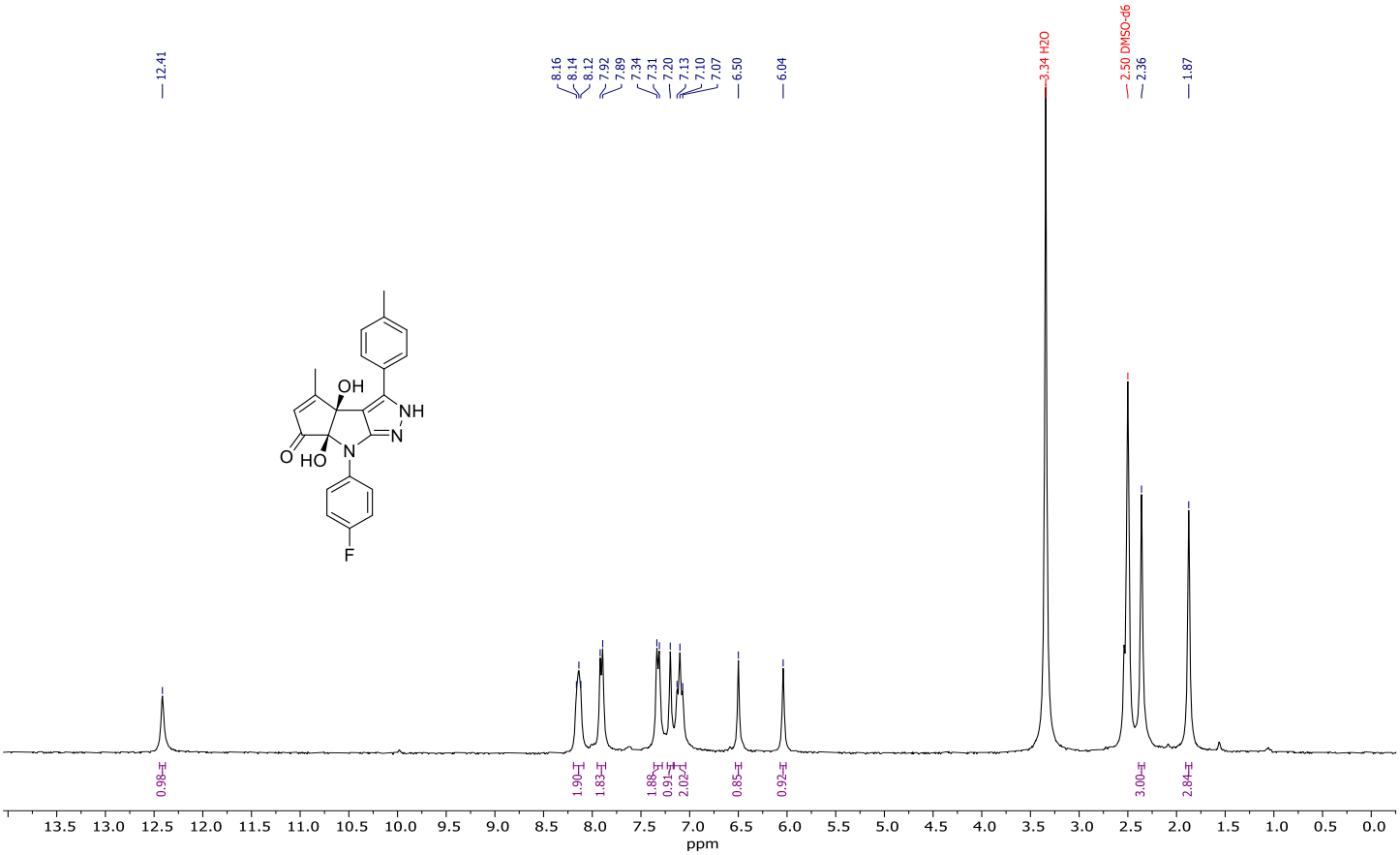
^{1}H NMR spectrum (300 MHz) of **16b** in DMSO-d_6



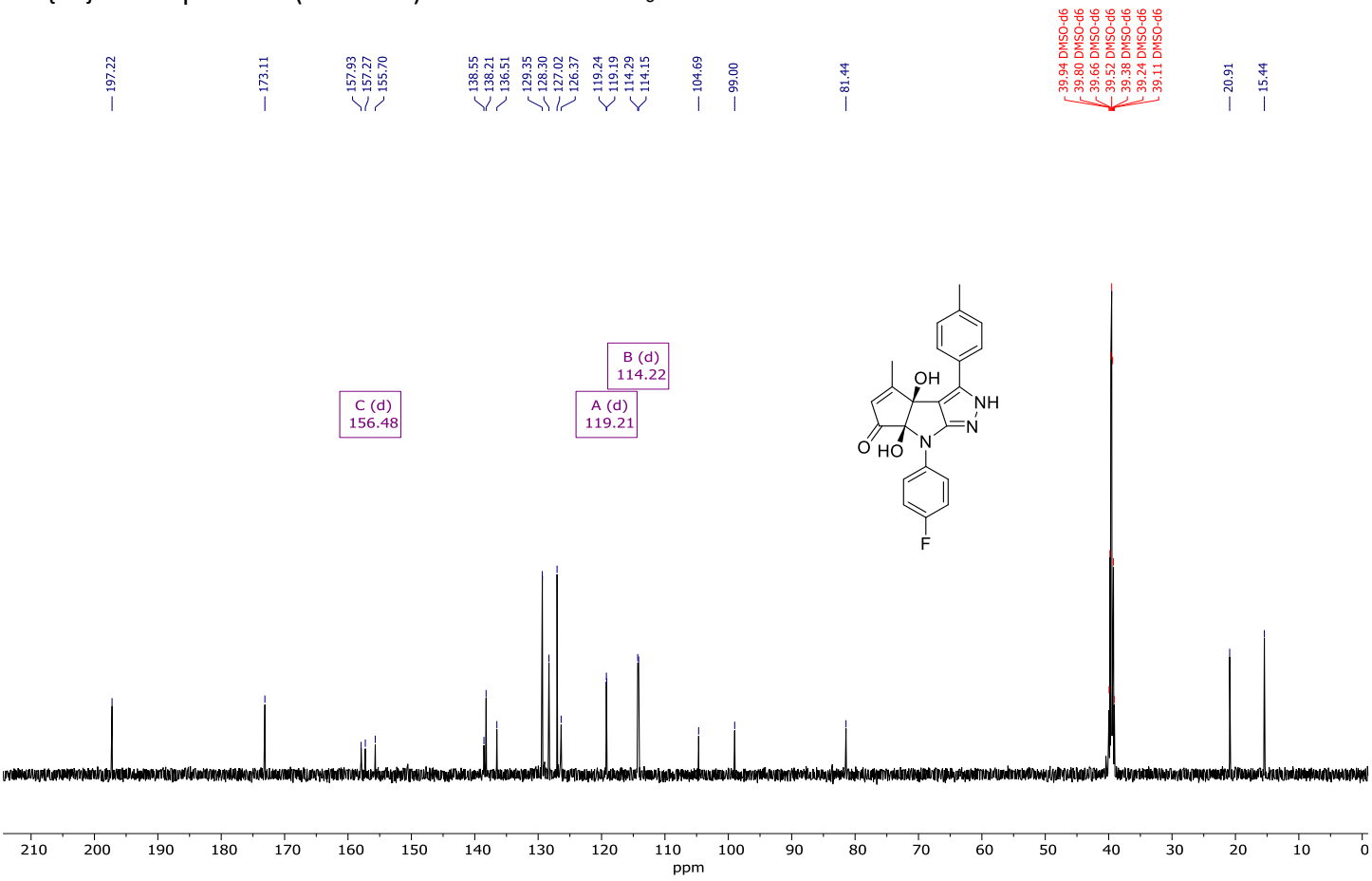
^{13}C {^{1}H} NMR spectrum (125 MHz) of **16b** in DMSO-d_6



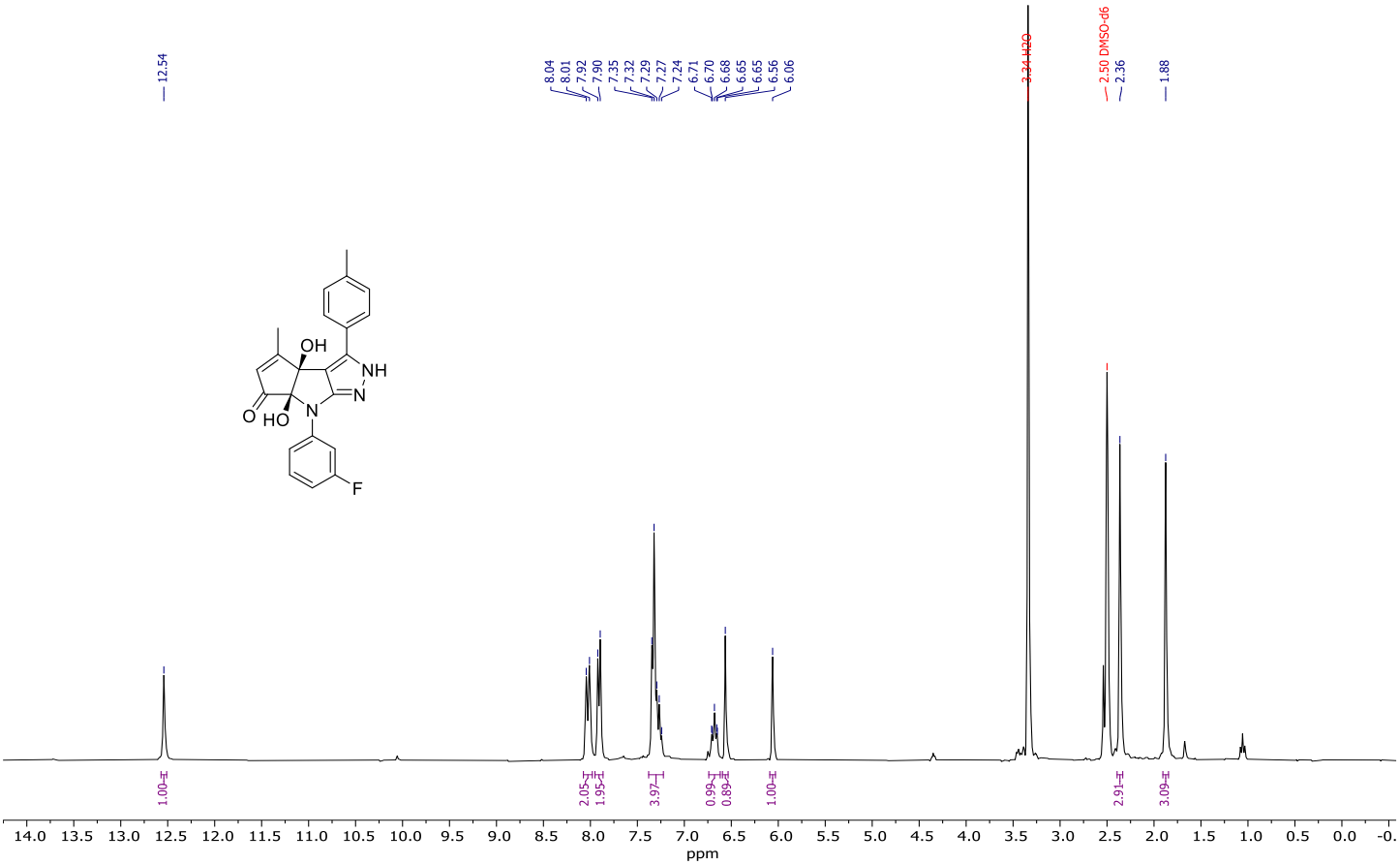
^{1}H NMR spectrum (300 MHz) of **16c** in DMSO-d_6



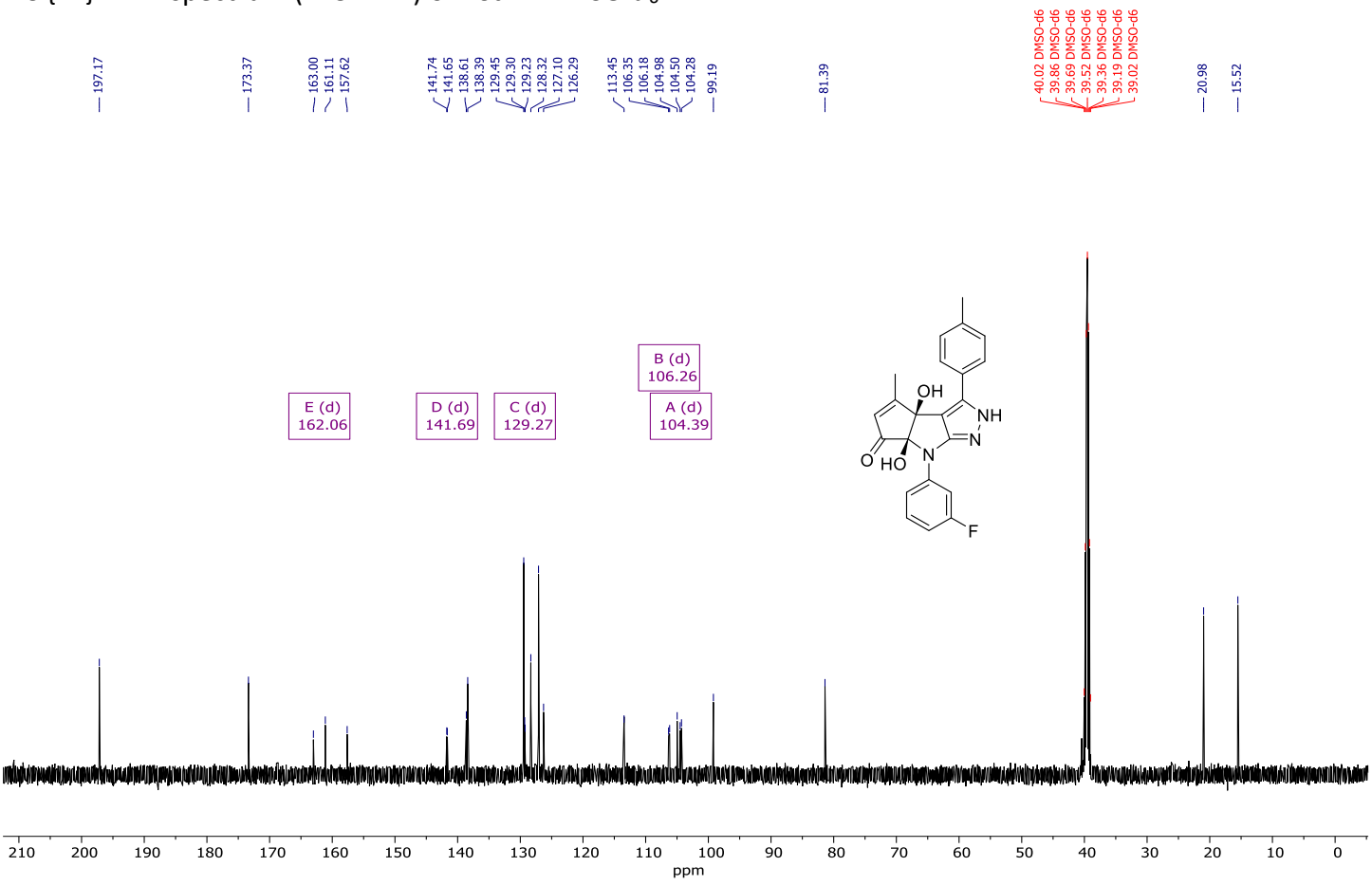
^{13}C {^{1}H} NMR spectrum (150 MHz) of **16c** in DMSO-d_6



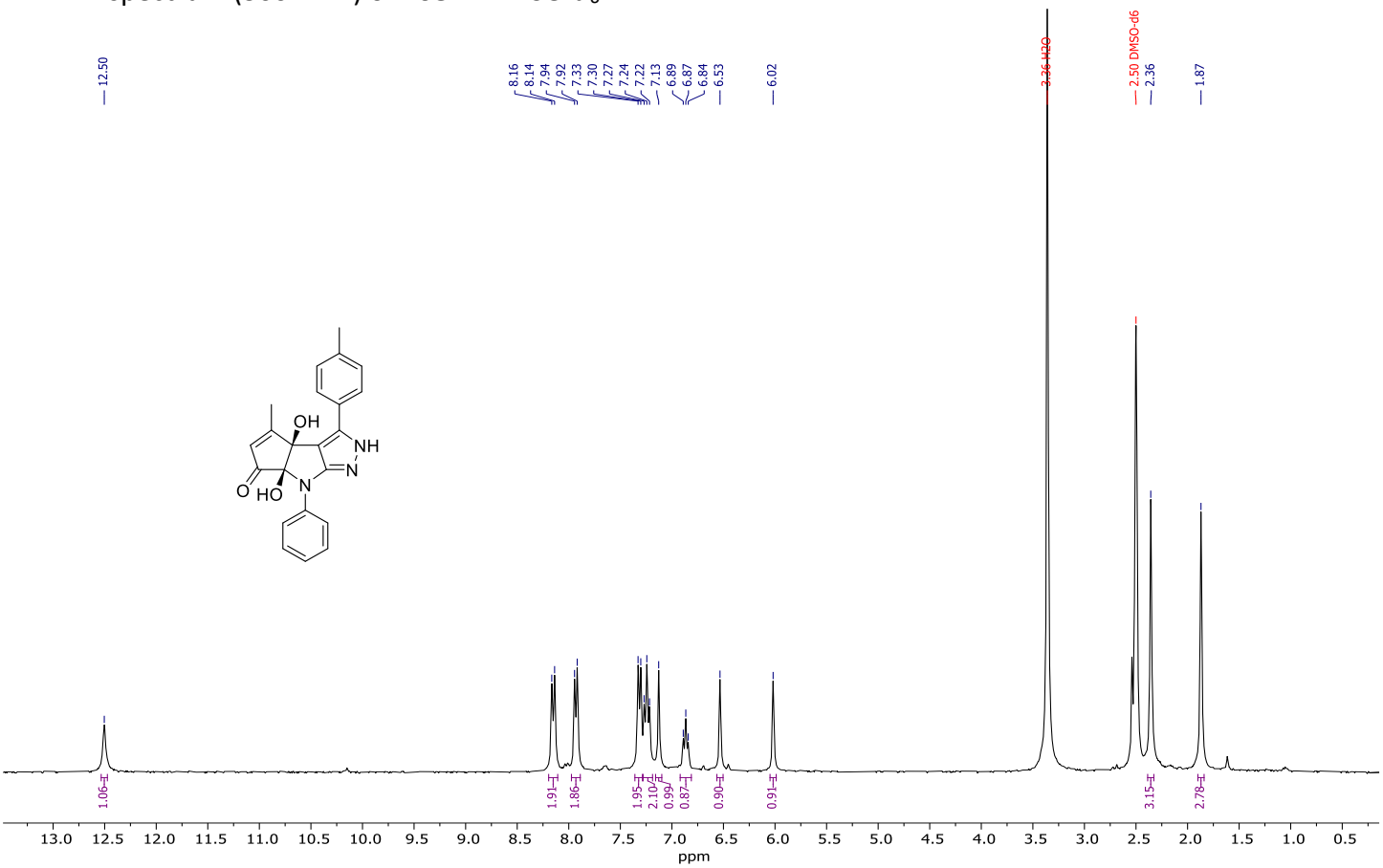
^{1}H NMR spectrum (300 MHz) of **16d** in DMSO-d_6



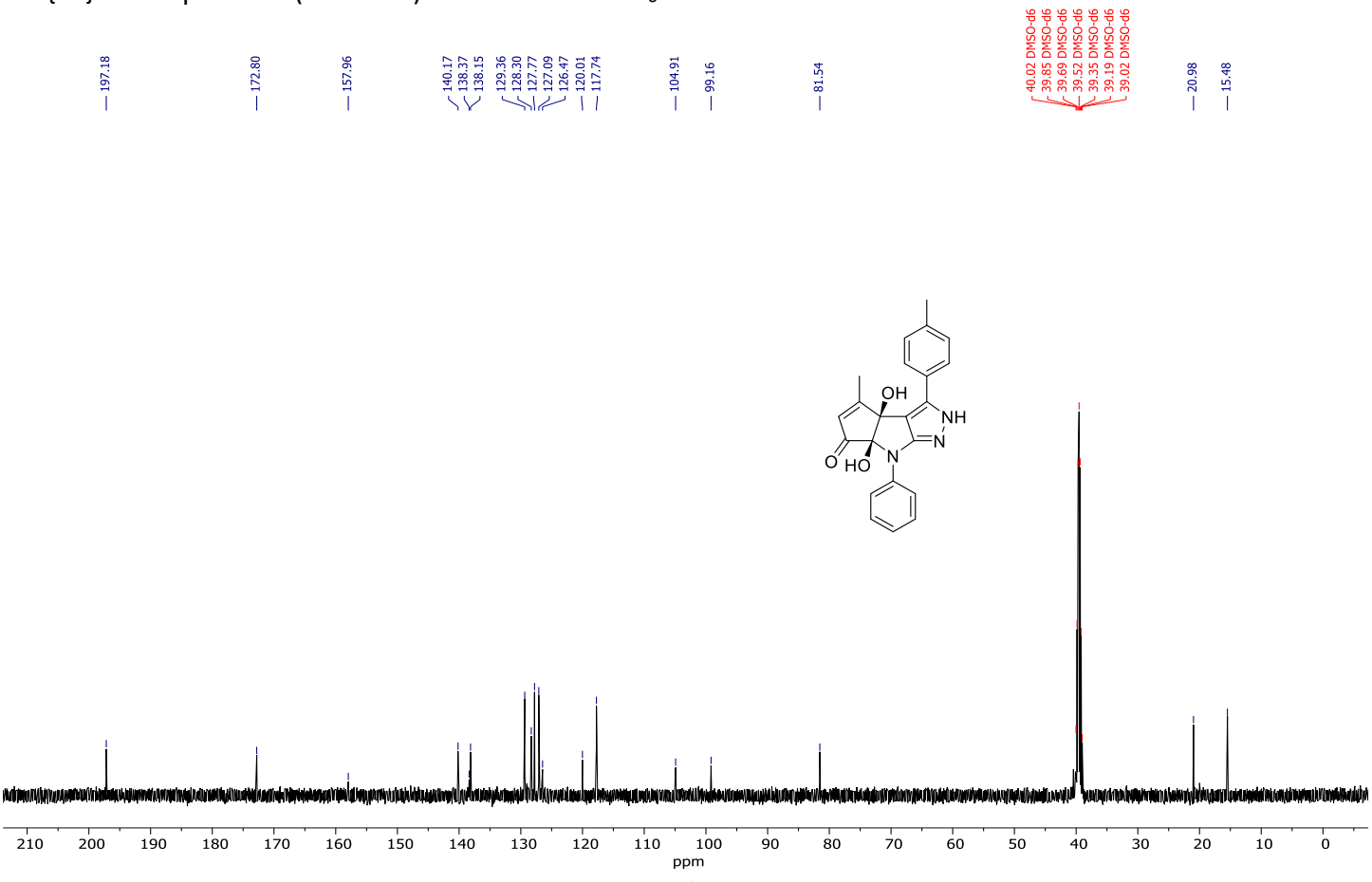
^{13}C {^{1}H} NMR spectrum (125 MHz) of **16d** in DMSO-d_6



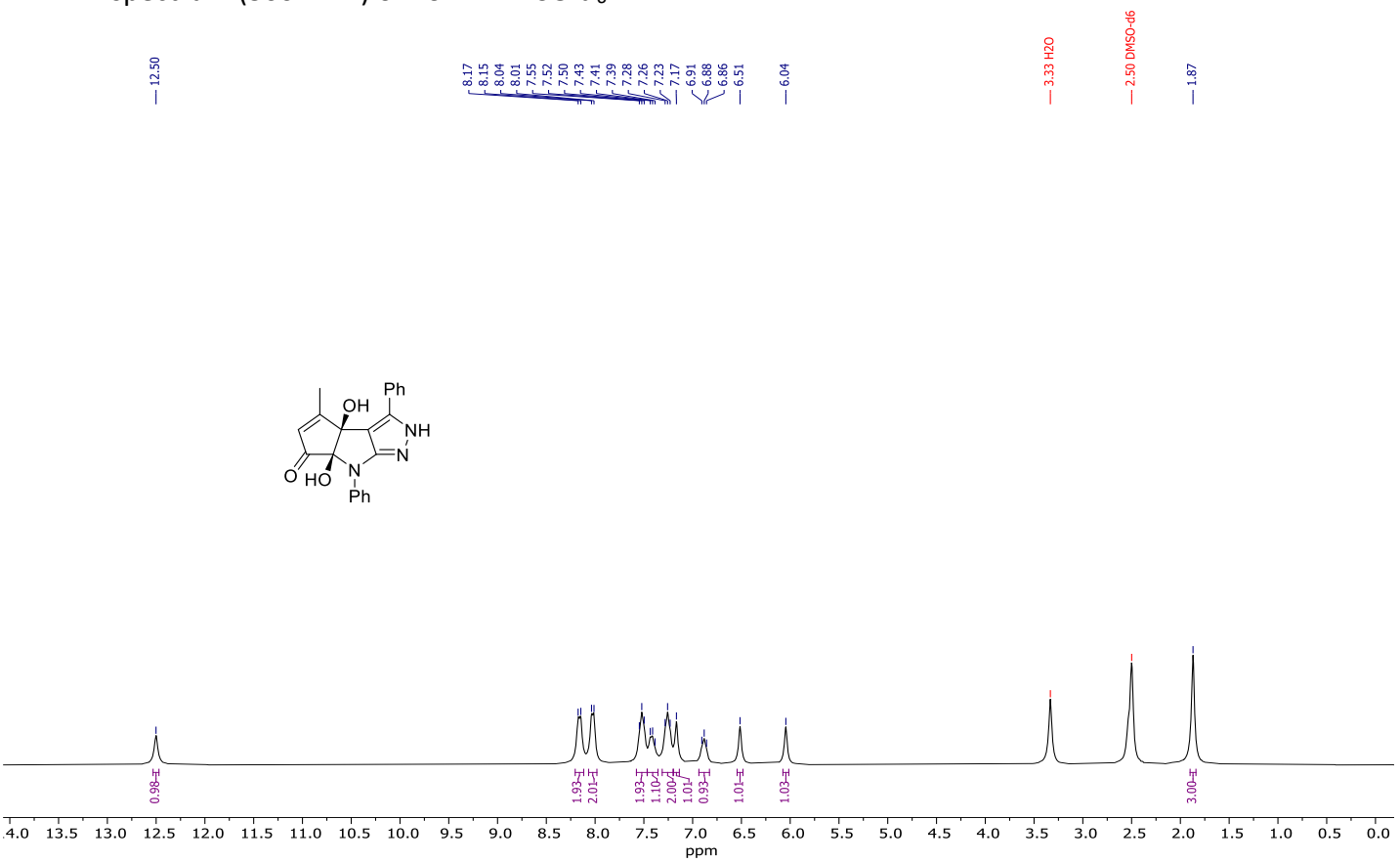
^{1}H NMR spectrum (300 MHz) of **16e** in DMSO-d_6



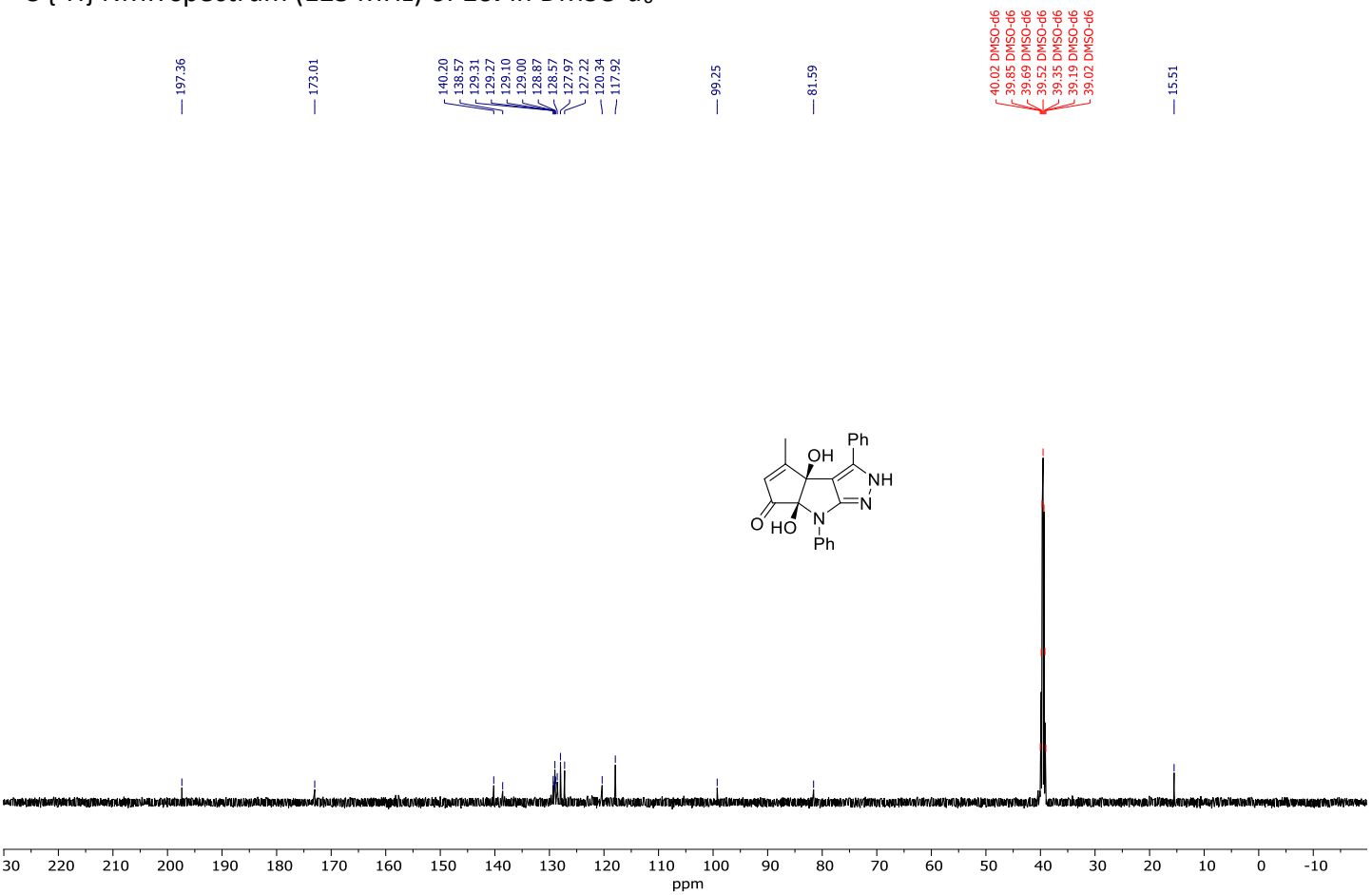
^{13}C {^{1}H} NMR spectrum (125 MHz) of **16e** in DMSO-d_6



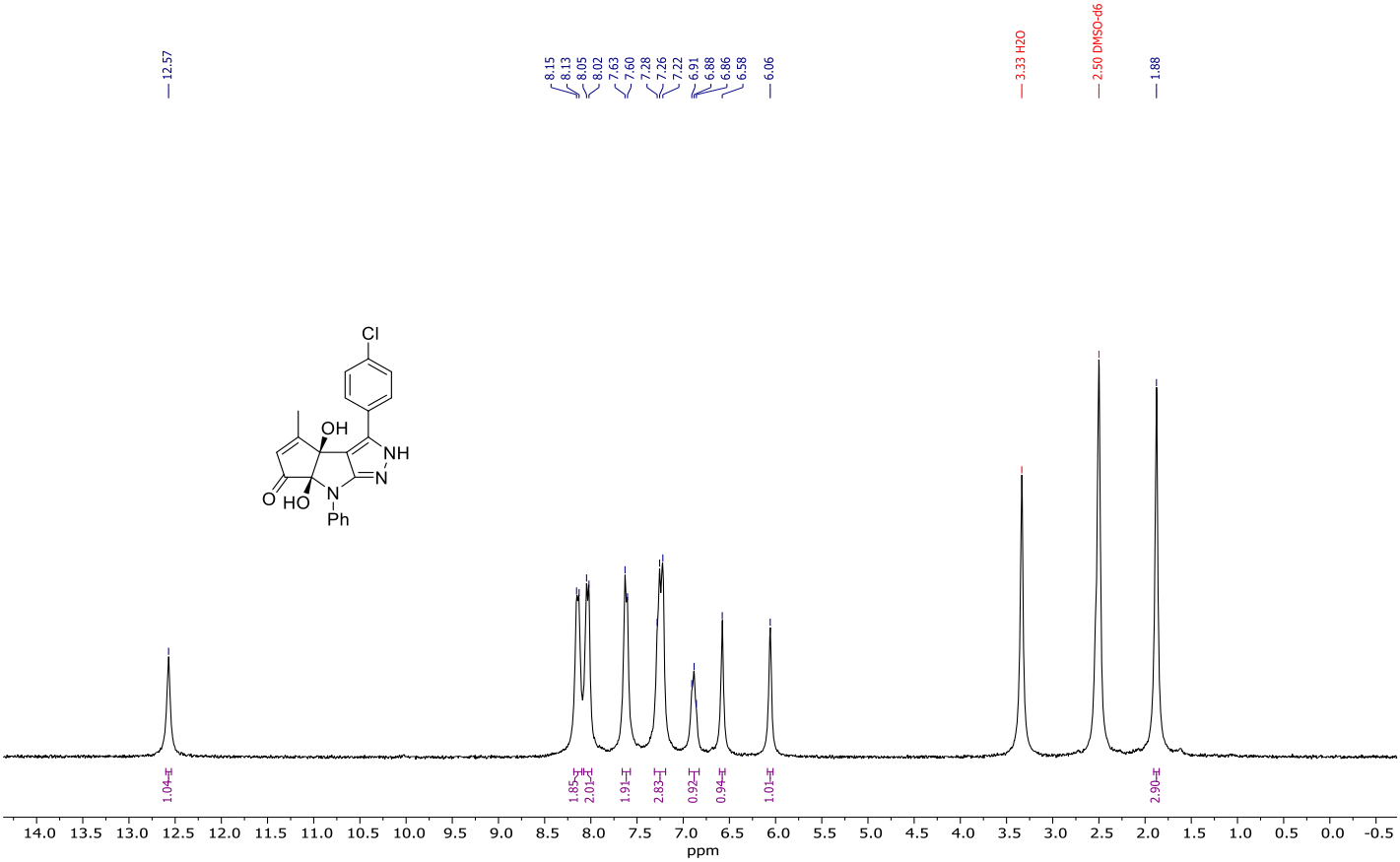
^{1}H NMR spectrum (300 MHz) of **16f** in DMSO-d_6



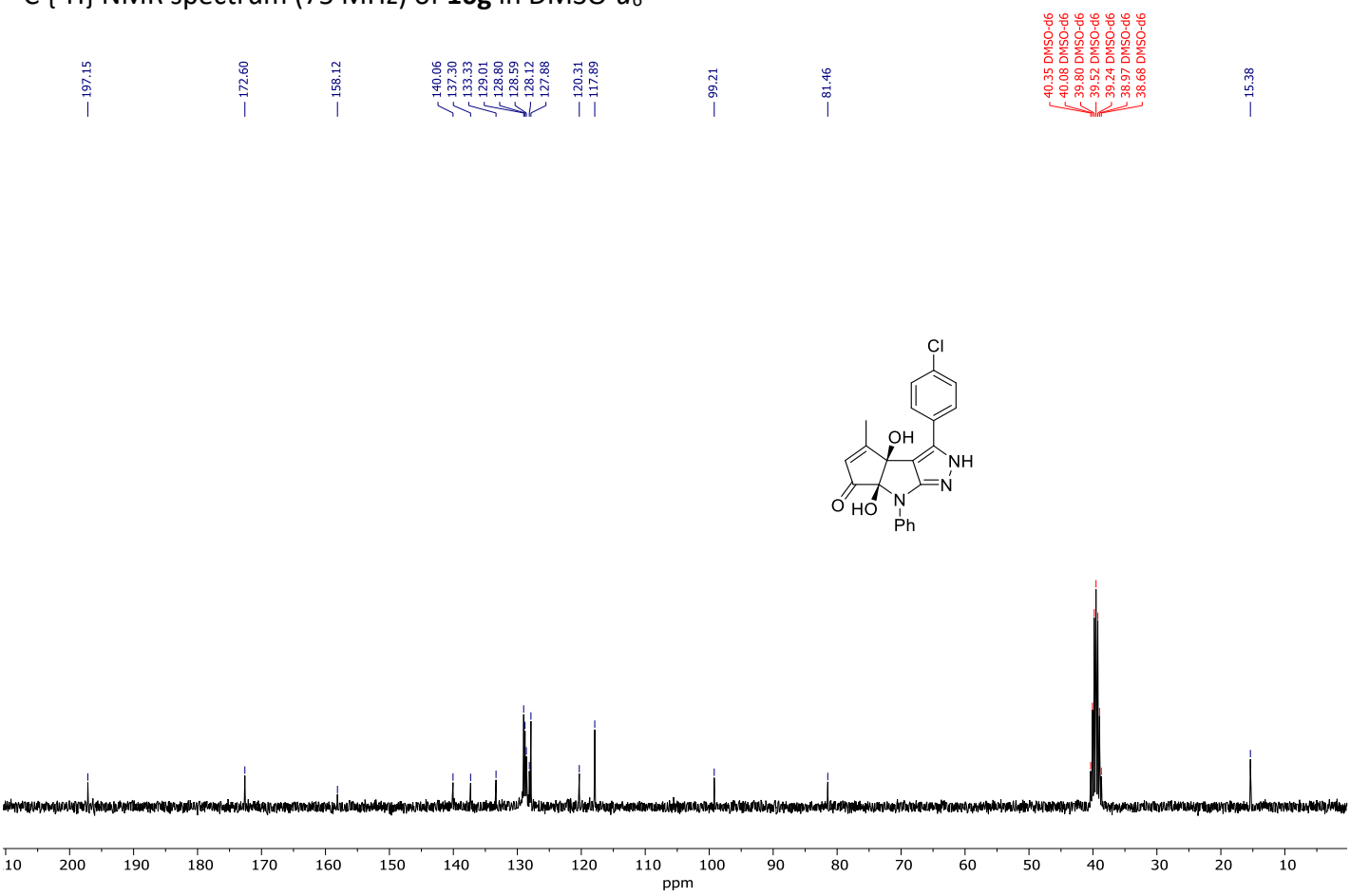
^{13}C {^{1}H} NMR spectrum (125 MHz) of **16f** in DMSO-d_6



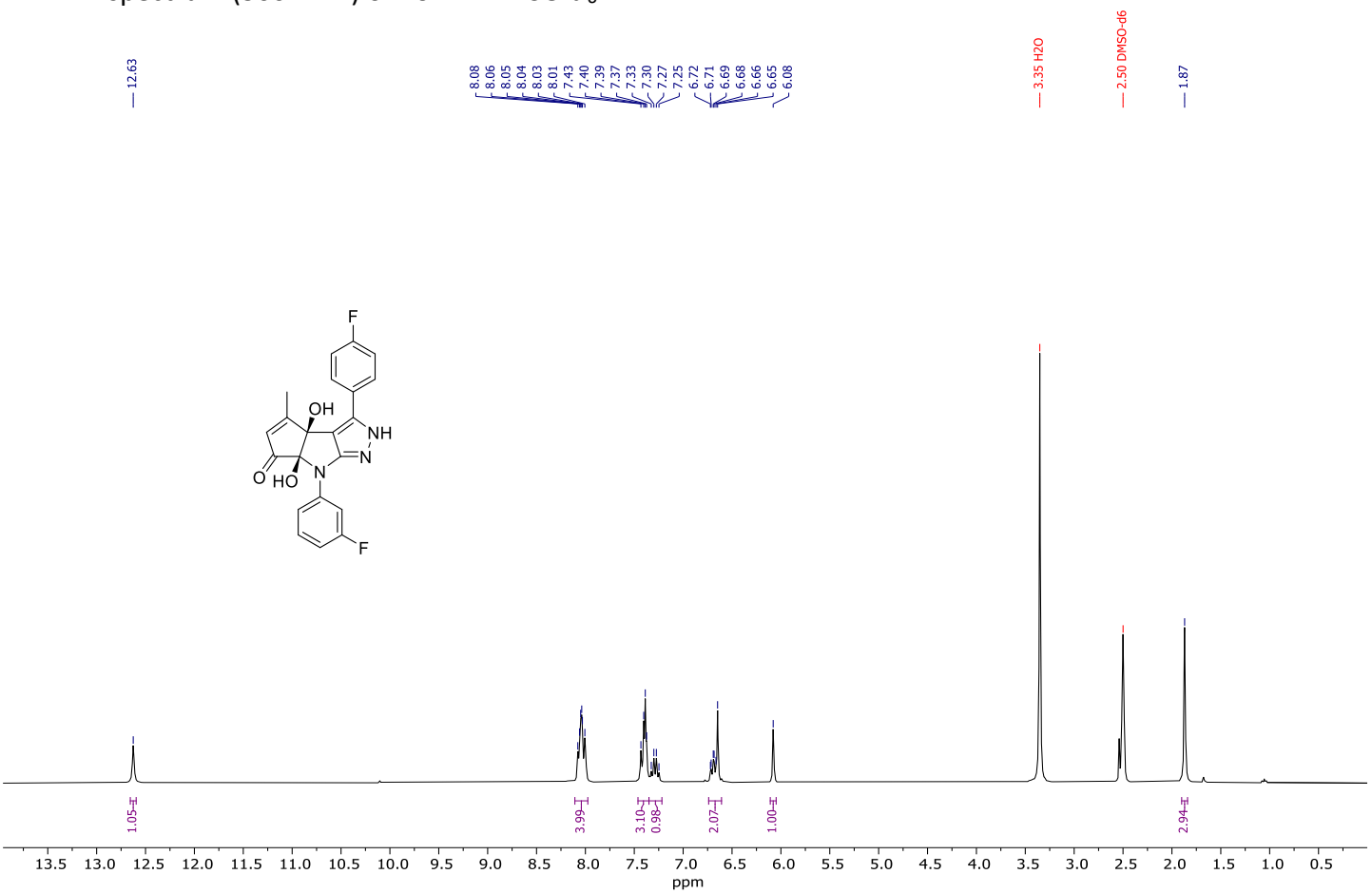
^{1}H NMR spectrum (300 MHz) of **16g** in DMSO-d_6



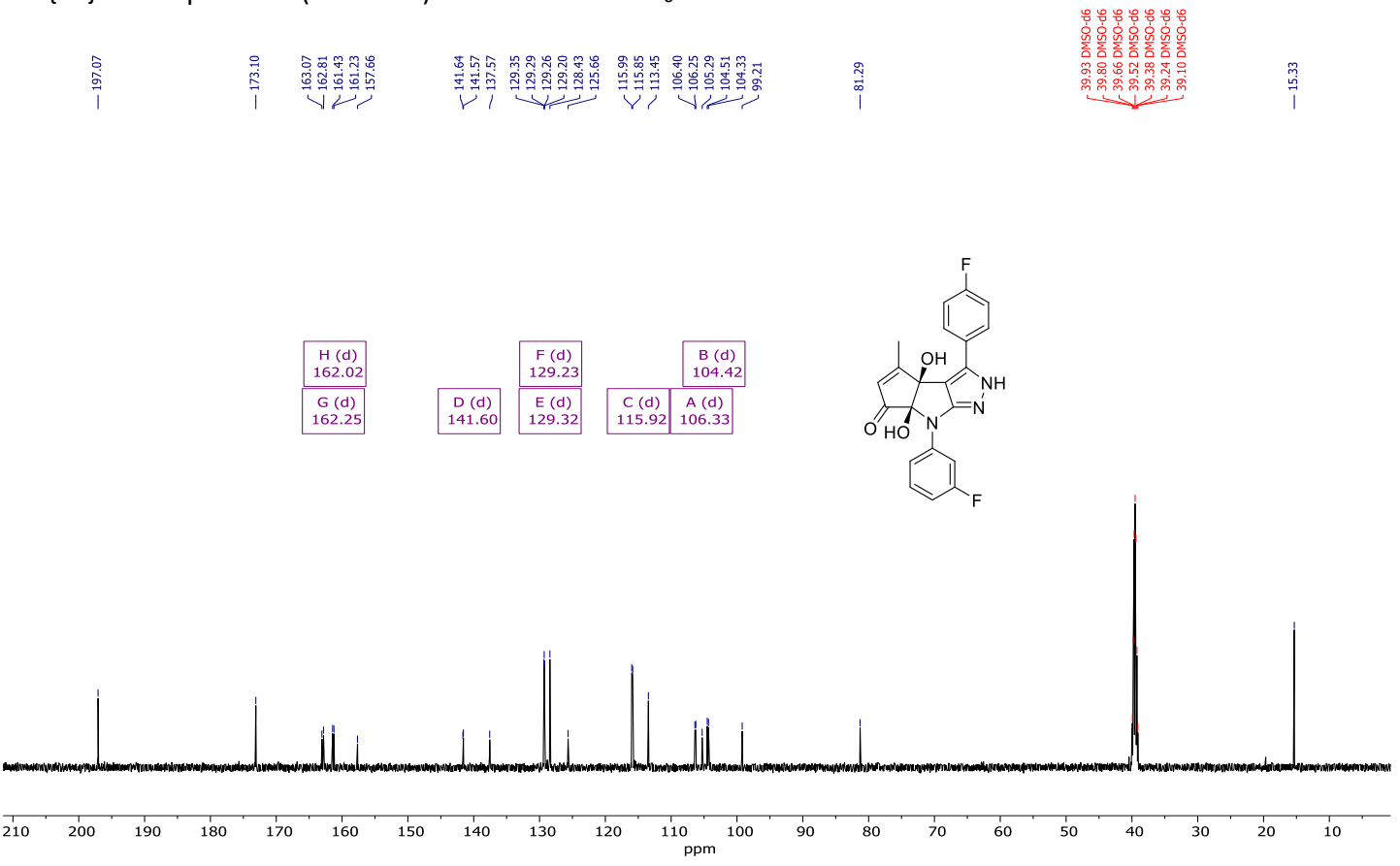
^{13}C {^{1}H} NMR spectrum (75 MHz) of **16g** in DMSO-d_6



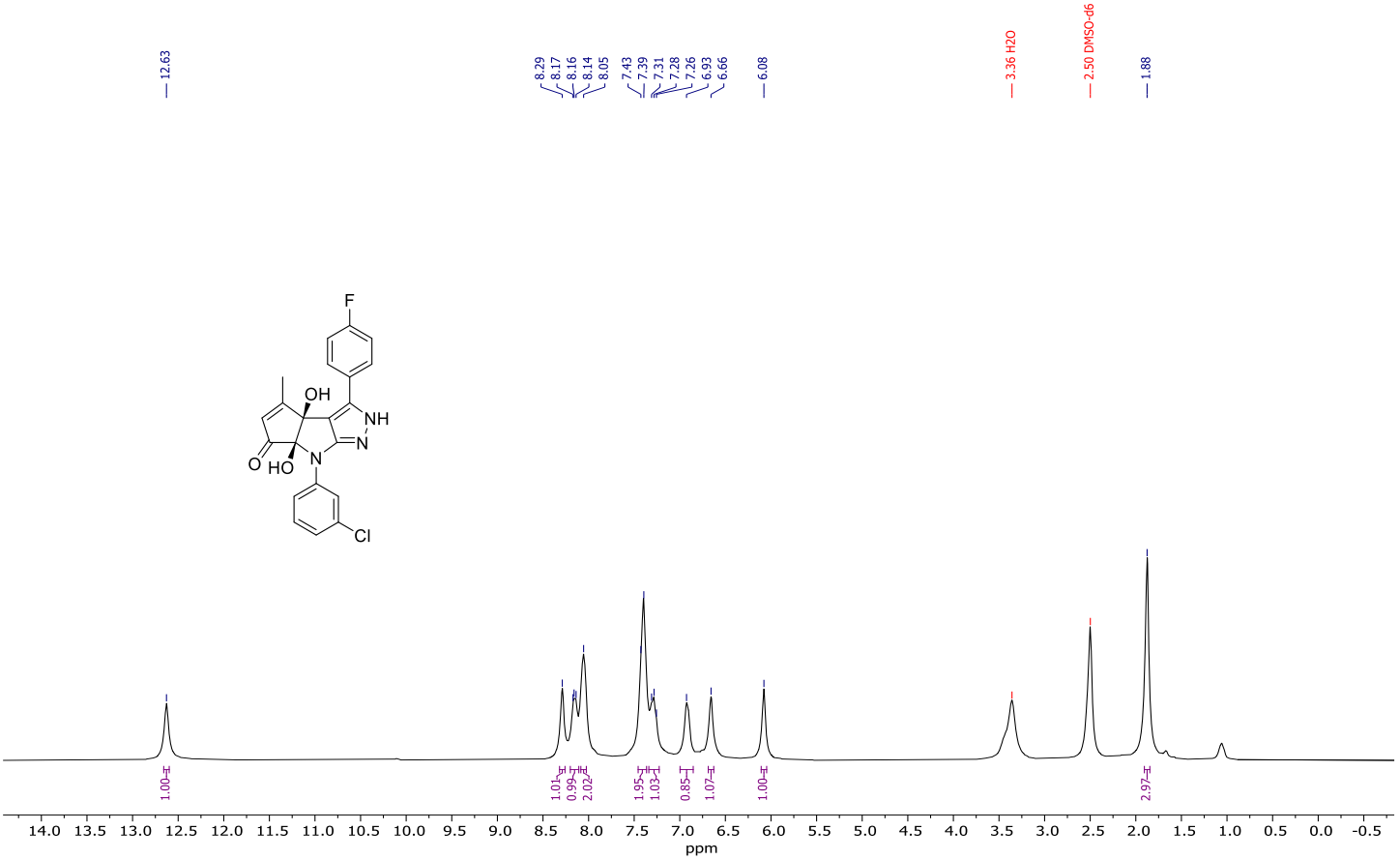
^{1}H NMR spectrum (300 MHz) of **16h** in DMSO-d_6



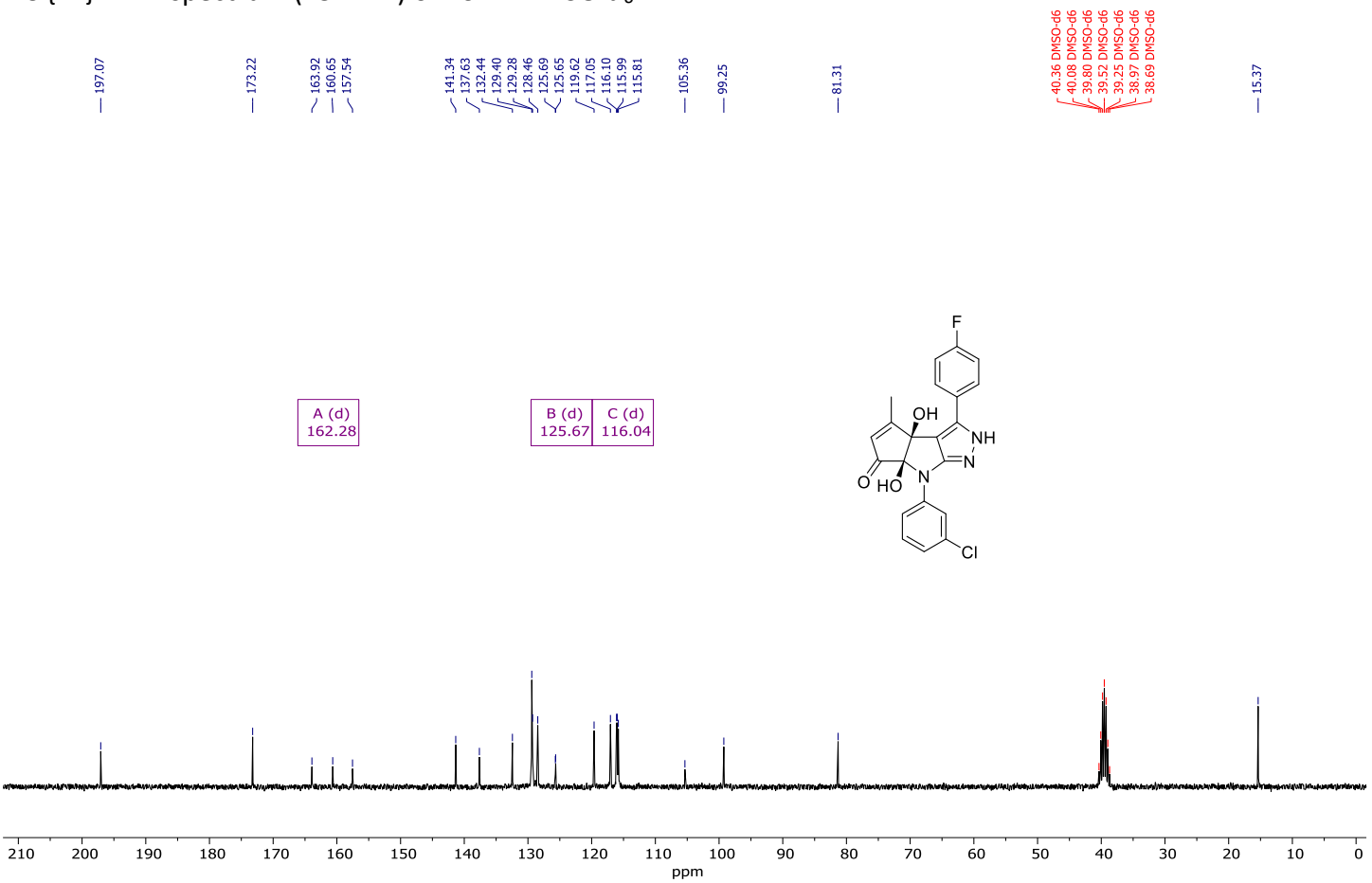
^{13}C {^{1}H} NMR spectrum (150 MHz) of **16h** in DMSO-d_6



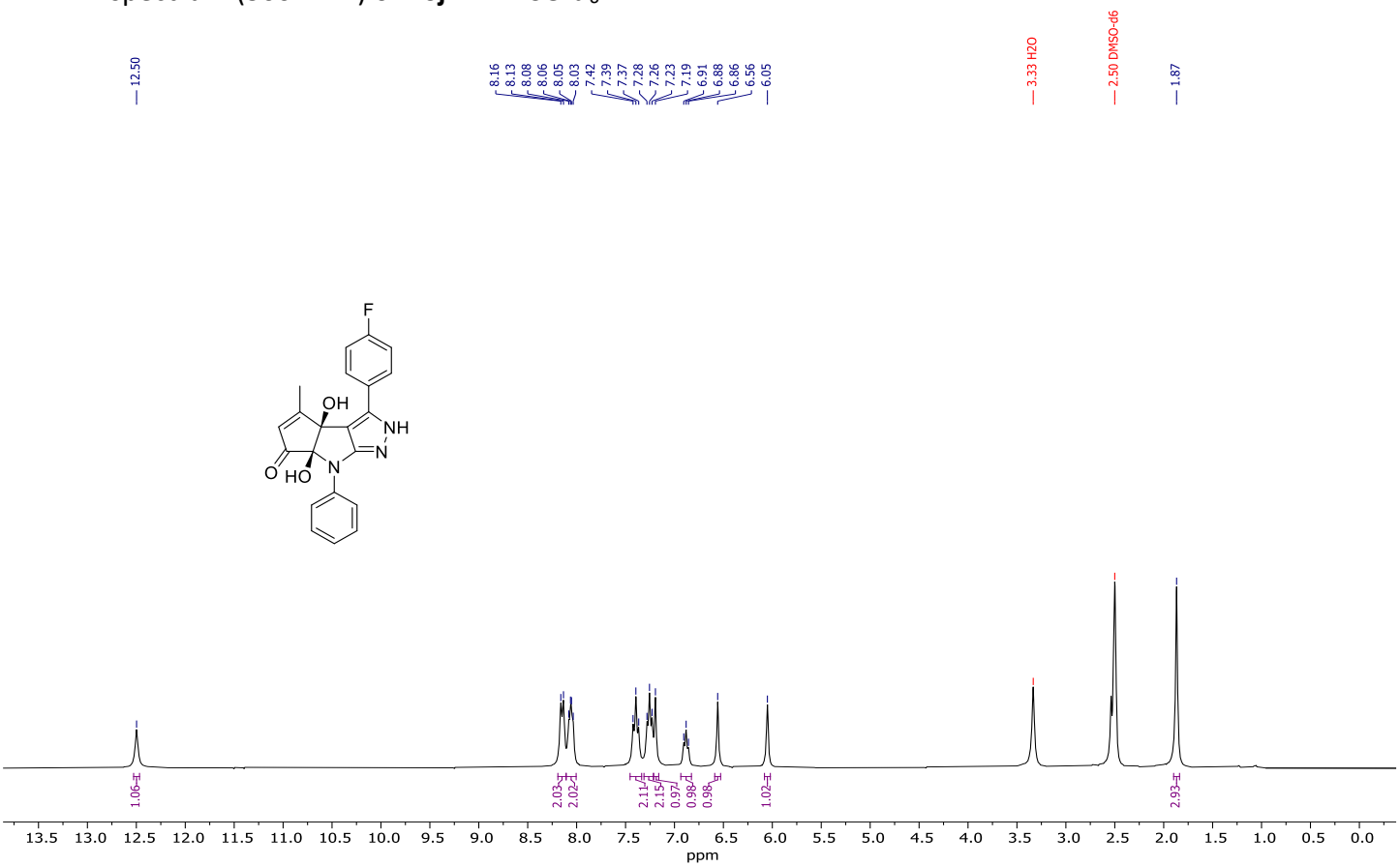
^{1}H NMR spectrum (300 MHz) of **16i** in DMSO-d_6



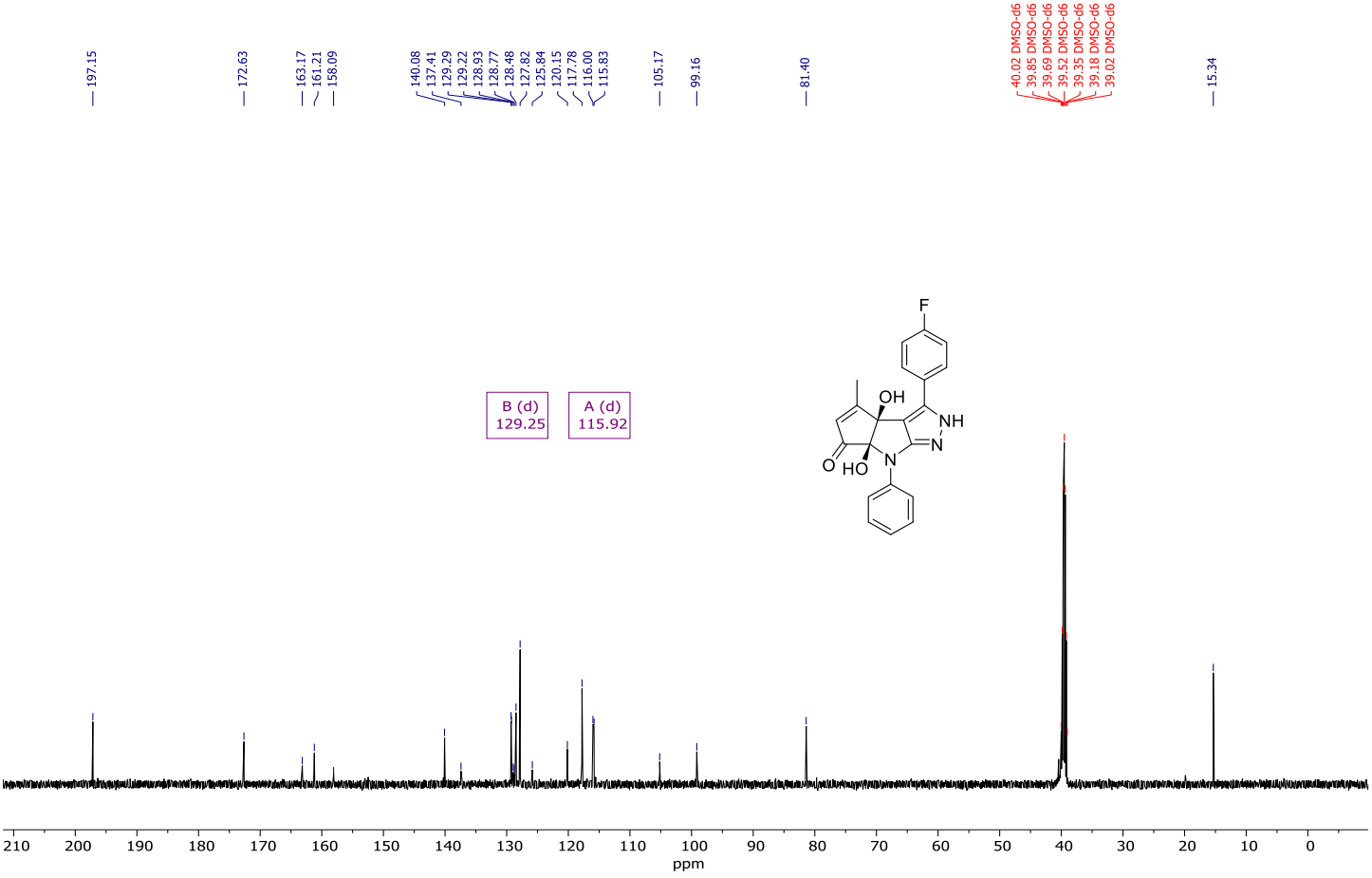
^{13}C {^{1}H} NMR spectrum (75 MHz) of **16i** in DMSO-d_6



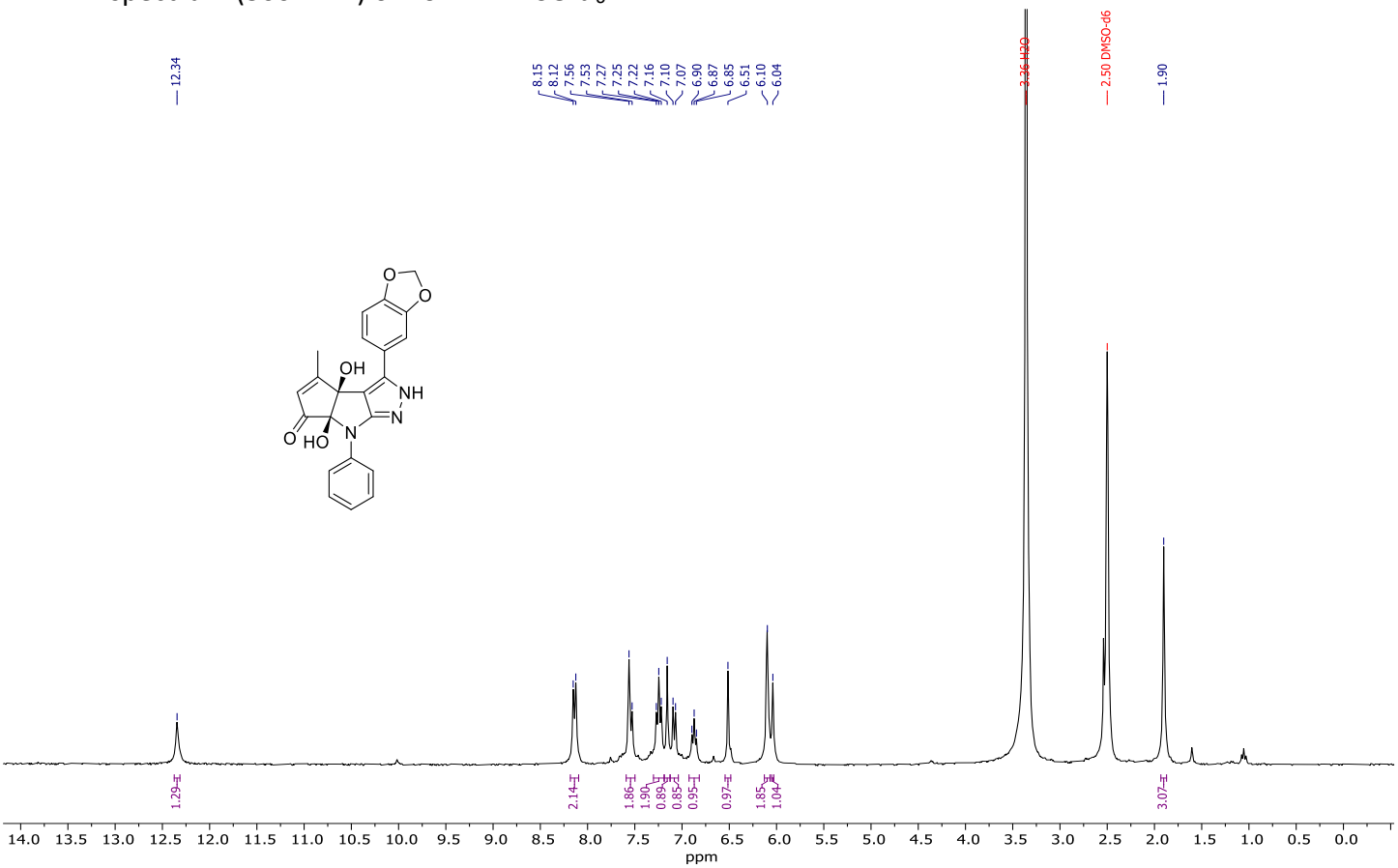
^{1}H NMR spectrum (300 MHz) of **16j** in DMSO-d_6



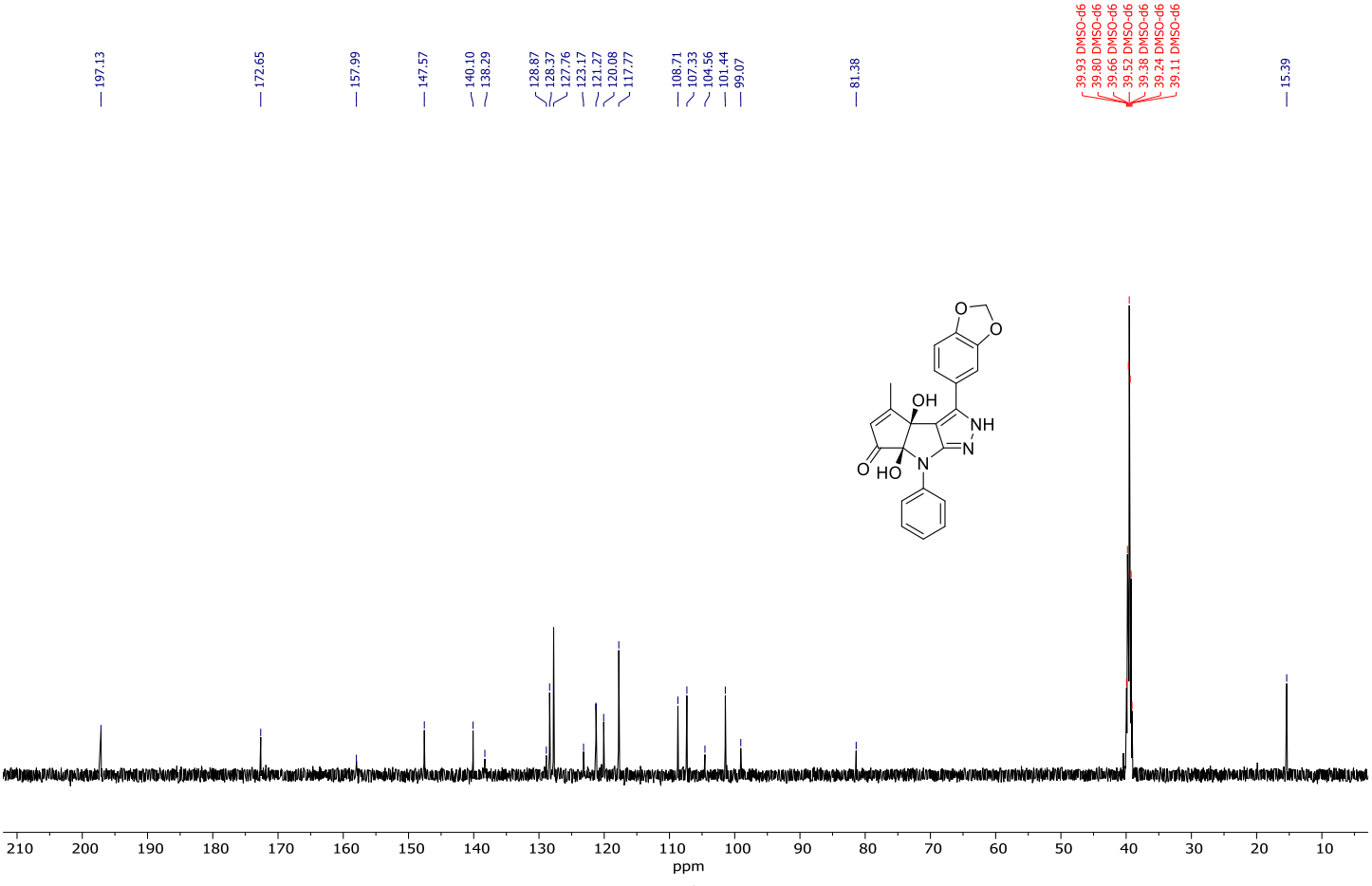
^{13}C {^{1}H} NMR spectrum (125 MHz) of **16j** in DMSO-d_6



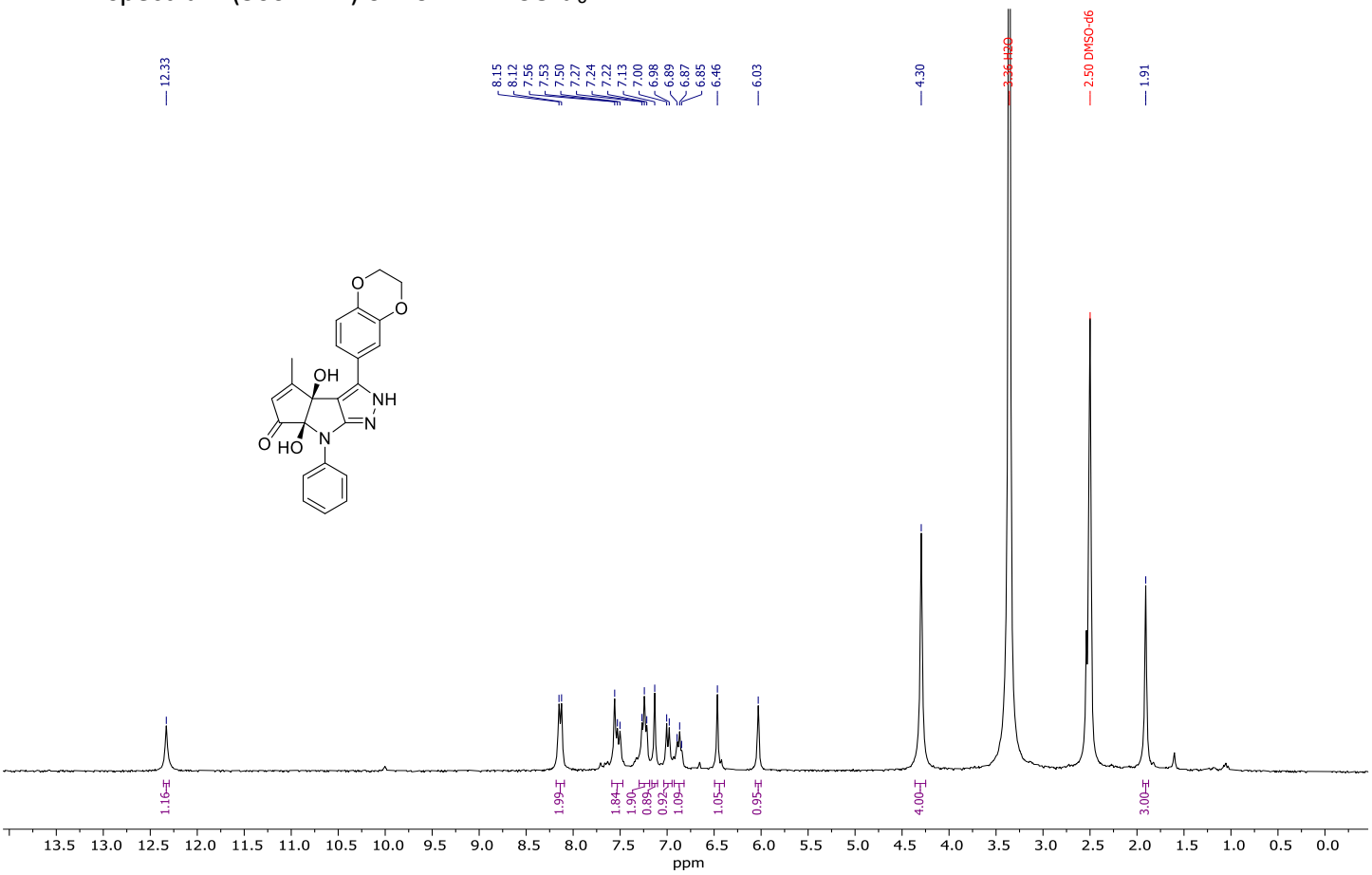
^{1}H NMR spectrum (300 MHz) of **16k** in DMSO-d_6



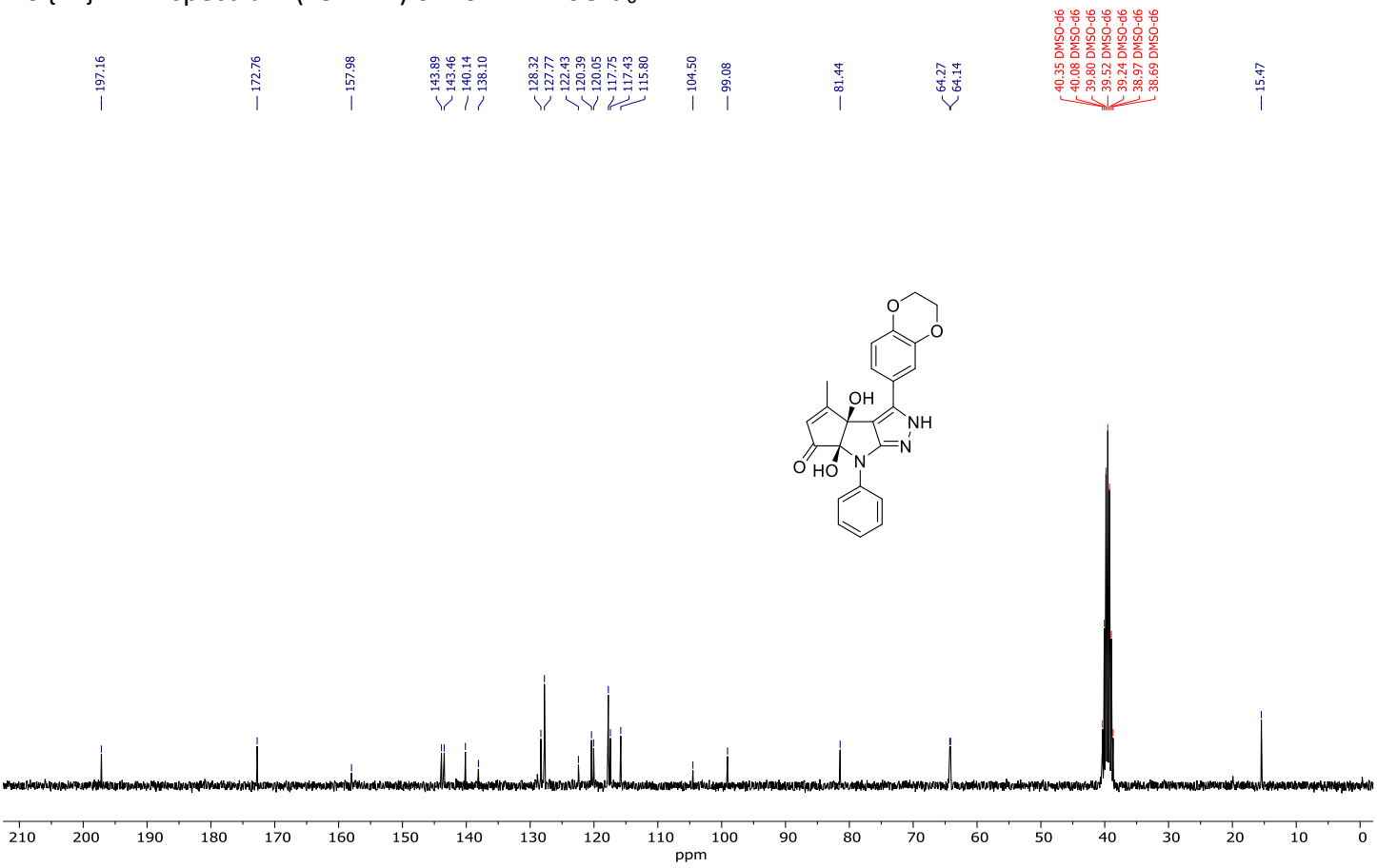
^{13}C {^{1}H} NMR spectrum (150 MHz) of **16k** in DMSO-d_6



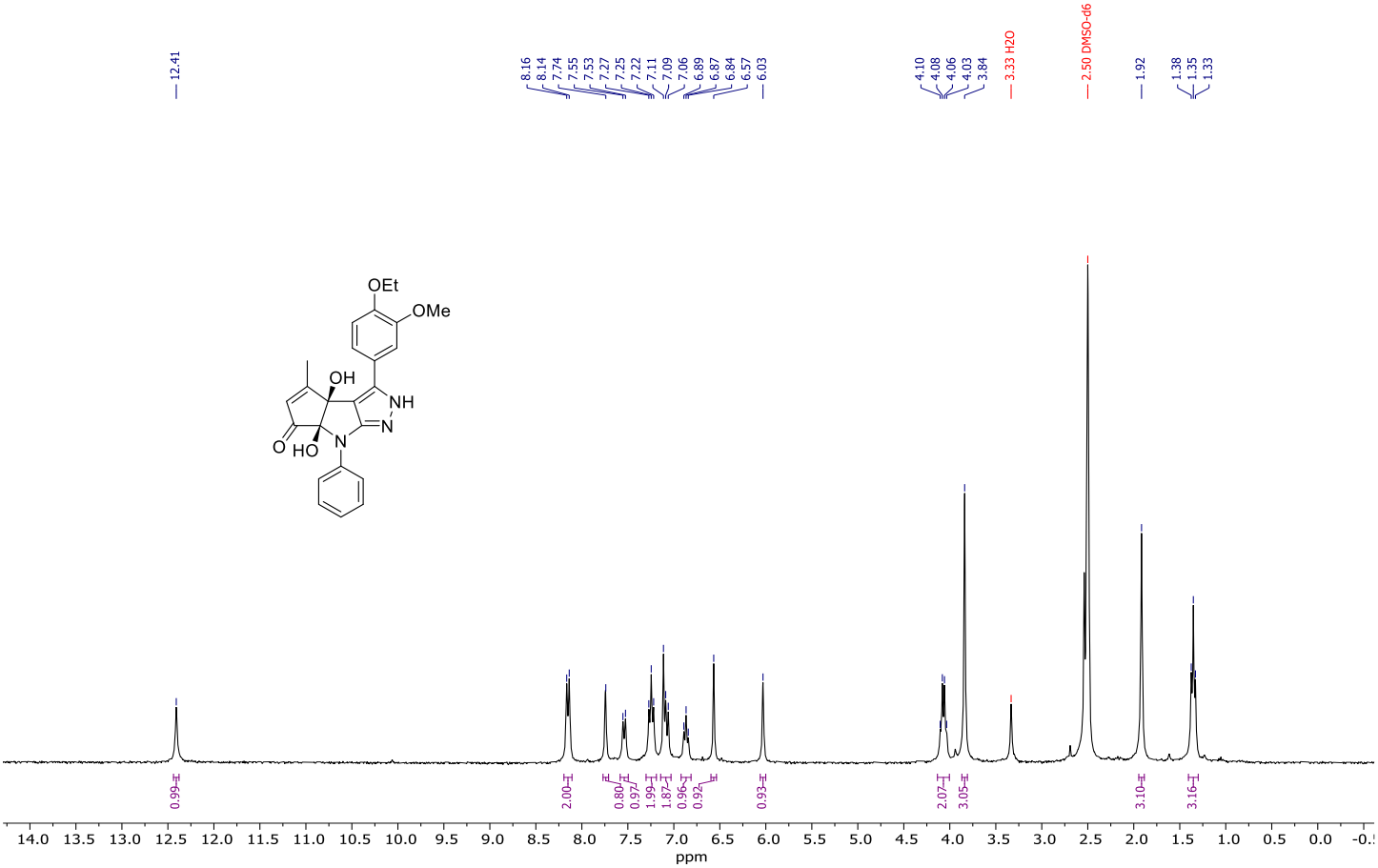
^{1}H NMR spectrum (300 MHz) of **16l** in DMSO-d_6



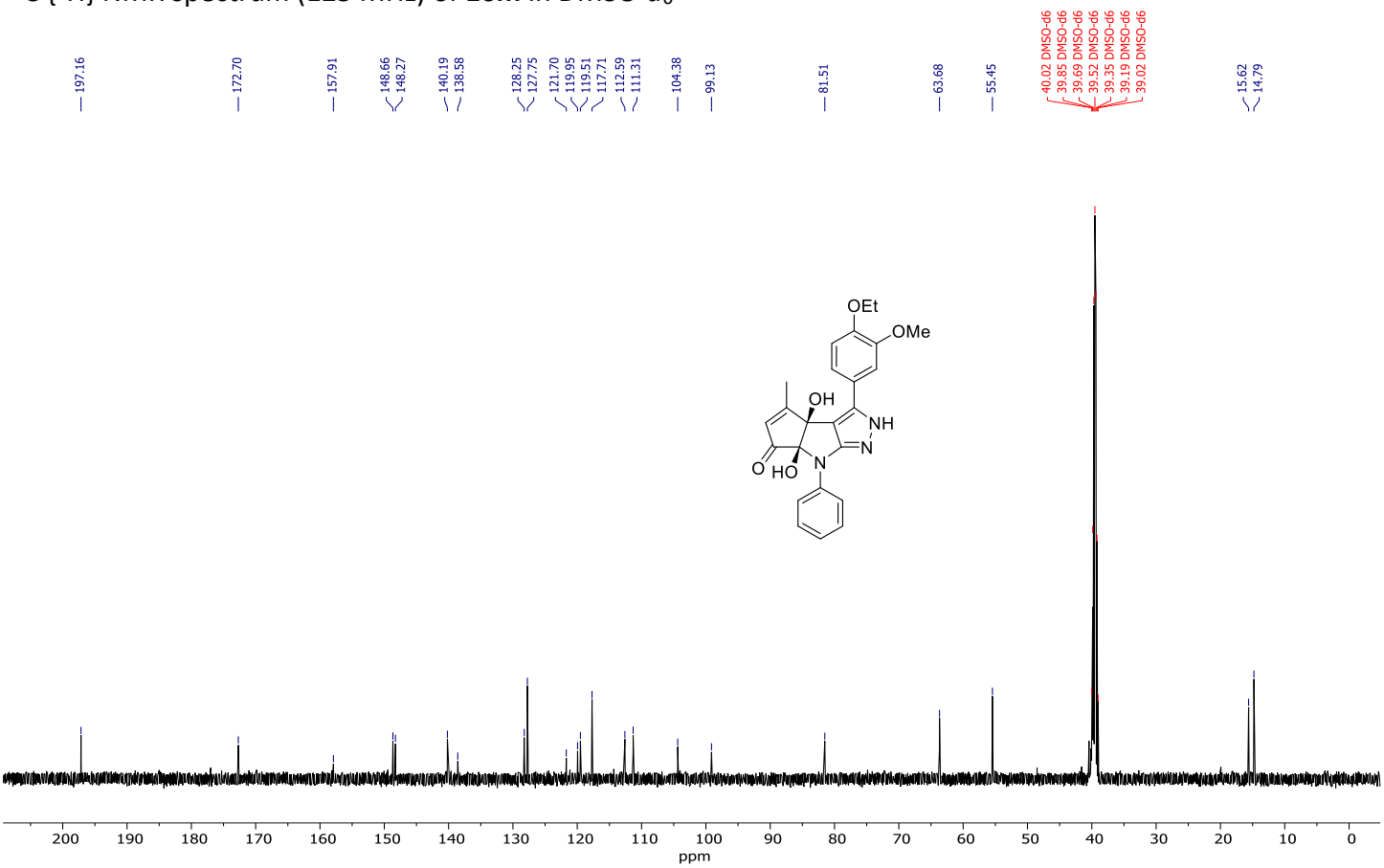
^{13}C {^{1}H} NMR spectrum (75 MHz) of **16l** in DMSO-d_6



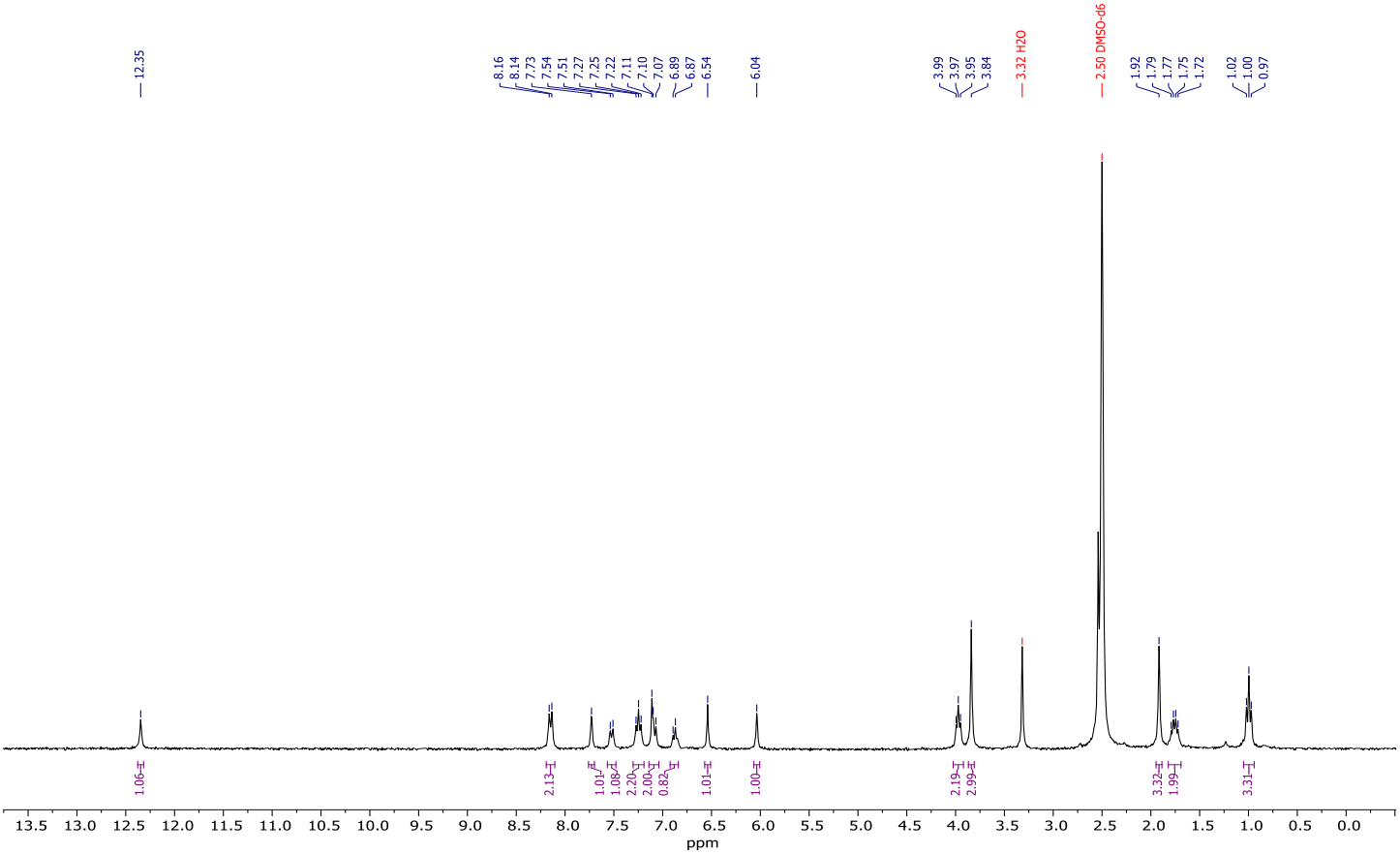
^{1}H NMR spectrum (300 MHz) of **16m** in DMSO-d_6



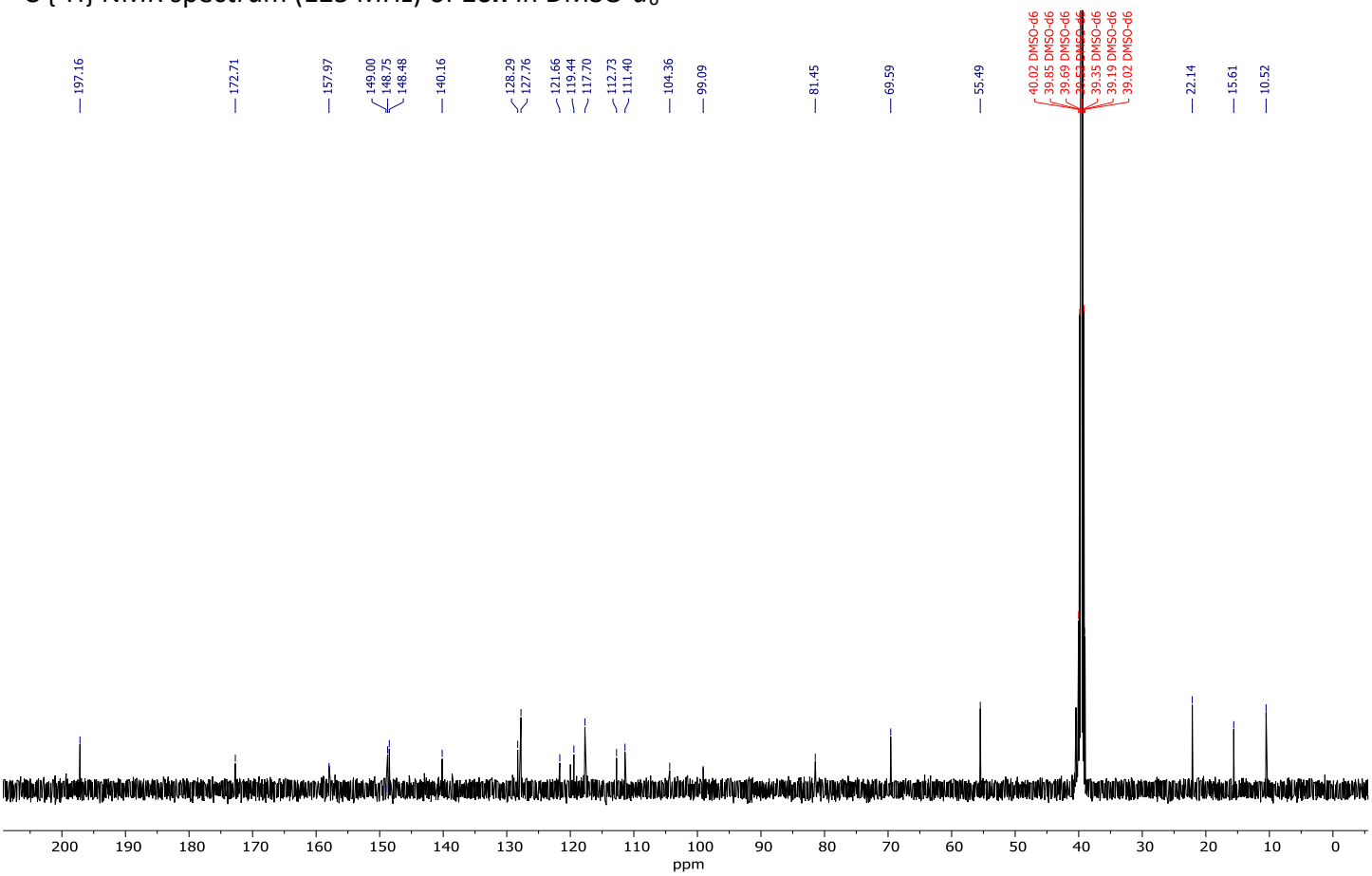
^{13}C {^{1}H} NMR spectrum (125 MHz) of **16m** in DMSO-d_6



^{1}H NMR spectrum (300 MHz) of **16n** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (125 MHz) of **16n** in DMSO-d_6



X-ray crystallographic data and refinement details.

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using graphite monochromatized Cu K_α-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program[1]. The structure was solved by direct methods using SHELXT[2] and refined on F^2 using SHELXL-2018[3] in the OLEX2 program.[4] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. The locations of hydrogen atoms H2, H6 and H9 for compound **15a** were found from the electron density-difference map; these hydrogen atoms were refined with individual isotropic displacement parameters. The locations of hydrogen atoms of amino and hydroxy groups for compound **16j** were found from the electron density-difference map; these hydrogen atoms were refined with individual isotropic displacement parameters. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite[5] was used for molecular graphics. A rotating group model was applied for methyl groups.
Compound **15a** is crystallized with dimethylformamide molecule in the ratio 1:1. The studied crystal of compound **16j** was a twin with the ratio for two major components being of 0.6839(8): 0.3161(8).

1. CrysAlisPro. Version 1.171.41.106a. *Rigaku Oxford Diffraction*, **2021**.
2. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, A71(1), 3-8. http://doi.org/10.1107/S2053273314026370
3. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71(1), 3-8. http://doi.org/10.1107/S2053229614024218
4. Dolomanov O.V.; Bourhis L.J.; Gildea R.J.; Howard J.A.K.; Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, 42(2), 339-341. http://doi.org/10.1107/S0021889808042726
5. Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.; Wood, P. A. Mercury 4.0: from visualization to analysis, design and prediction. *J. Appl. Cryst.* **2020**, 53, 226-235. https://doi.org/10.1107/S1600576719014092

Crystallographic data for compound **15a**.

Table 1. Crystal data and structure refinement for **15a**.

Identification code	2448542
Empirical formula	$C_{24}H_{24}FN_3O_5S$
Formula weight	485.52
Temperature	99.98(10) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a = 10.4253(3) Å	α= 95.717(2)°.
b = 10.7006(3) Å	β= 91.608(2)°.
c = 11.1367(3) Å	γ = 110.539(3)°.
Volume	1154.97(6) Å3
Z	2
Density (calculated)	1.396 g/cm^3
Absorption coefficient	1.676 mm^{-1}
F(000)	508
Crystal size	0.63 x 0.26 x 0.05 mm^3
Theta range for data collection	3.998 to 80.018°.
Index ranges	-13<=h<=13, -13<=k<=13, -12<=l<=14
Reflections collected	25240
Independent reflections	4966 [R(int) = 0.0308]
Observed reflections	4711
Completeness to theta = 67.684°	99.8 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.349
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4966 / 0 / 323
Goodness-of-fit on F^2	1.101
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0964
R indices (all data)	R1 = 0.0373, wR2 = 0.0975
Largest diff. peak and hole	0.331 and -0.411 e.Å^{-3}

Table 2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for **15a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)	
S(27)	2932(1)	8130(1)	7533(1)	21(1)	
O(27)	4054(1)	7639(1)	7090(1)	27(1)	
C(28)	2747(2)	9174(2)	6434(1)	28(1)	
C(29)	3741(2)	9401(2)	8751(1)	28(1)	
F(17)	10815(1)		317(1)	8389(1)	43(1)
O(7)	3828(1)	2549(1)	9131(1)	20(1)	
O(9)	4152(1)	5262(1)	7358(1)	26(1)	
O(10)	3214(1)	6115(1)	9460(1)	25(1)	
O(26)	-120(1)	3859(1)	3882(1)	32(1)	
N(1)	6158(1)	2140(1)	6041(1)	23(1)	
N(2)	5184(1)	2342(1)	5324(1)	23(1)	
N(6)	6612(1)	2342(1)	8170(1)	23(1)	
C(3)	4287(1)	2745(1)	5950(1)	21(1)	
C(4)	4666(1)	2805(1)	7171(1)	20(1)	
C(5)	5842(1)	2413(1)	7164(1)	20(1)	
C(8)	4079(1)	3327(1)	8193(1)	18(1)	
C(9)	3840(1)	4503(1)	8272(1)	20(1)	
C(10)	3341(1)	4987(1)	9362(1)	20(1)	
C(11)	3086(1)	4112(1)	10289(1)		21(1)
C(12)	3340(1)	2951(1)	10157(1)		20(1)
C(13)	3135(2)	1985(1)	11066(1)		26(1)
C(14)	7682(1)	1833(1)	8162(1)	21(1)	
C(15)	7804(2)	897(1)	7239(1)	24(1)	
C(16)	8865(2)	395(2)	7314(1)	28(1)	
C(17)	9772(2)	815(2)	8316(2)	30(1)	
C(18)	9675(2)	1717(2)	9246(2)	32(1)	
C(19)	8630(2)	2234(2)	9170(1)	27(1)	
C(20)	3145(1)	3007(1)	5361(1)	21(1)	
C(21)	1821(2)	2503(1)	5770(1)	24(1)	
C(22)	755(2)	2789(2)	5250(1)	27(1)	
C(23)	990(2)	3607(1)	4312(1)	24(1)	
C(24)	2299(2)	4105(1)	3891(1)	24(1)	
C(25)	3360(2)	3795(1)	4410(1)	23(1)	
C(26)	104(2)	4757(2)	2978(2)	37(1)	

Table 3. Bond lengths [Å] and angles [°] for **15a**.

S(27)-O(27)	1.5166(10)
S(27)-C(28)	1.7865(15)
S(27)-C(29)	1.7788(15)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
F(17)-C(17)	1.3718(16)
O(7)-C(8)	1.3738(15)
O(7)-C(12)	1.3561(15)
O(9)-H(9)	0.85(3)
O(9)-C(9)	1.3416(16)
O(10)-C(10)	1.2543(16)
O(26)-C(23)	1.3617(17)
O(26)-C(26)	1.4283(19)
N(1)-N(2)	1.3630(16)
N(1)-C(5)	1.3321(17)
N(2)-H(2)	0.88(2)
N(2)-C(3)	1.3441(17)
N(6)-H(6)	0.85(2)
N(6)-C(5)	1.3836(17)
N(6)-C(14)	1.4029(17)
C(3)-C(4)	1.3939(18)
C(3)-C(20)	1.4677(18)
C(4)-C(5)	1.4279(18)
C(4)-C(8)	1.4607(17)
C(8)-C(9)	1.3616(18)
C(9)-C(10)	1.4528(17)
C(10)-C(11)	1.4309(18)
C(11)-H(11)	0.9500
C(11)-C(12)	1.3537(19)
C(12)-C(13)	1.4839(18)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.4026(19)
C(14)-C(19)	1.401(2)
C(15)-H(15)	0.9500
C(15)-C(16)	1.3929(19)
C(16)-H(16)	0.9500
C(16)-C(17)	1.373(2)
C(17)-C(18)	1.374(2)
C(18)-H(18)	0.9500
C(18)-C(19)	1.389(2)
C(19)-H(19)	0.9500
C(20)-C(21)	1.402(2)
C(20)-C(25)	1.3931(19)
C(21)-H(21)	0.9500

C(21)-C(22) 1.379(2)
C(22)-H(22) 0.9500
C(22)-C(23) 1.401(2)
C(23)-C(24) 1.393(2)
C(24)-H(24) 0.9500
C(24)-C(25) 1.389(2)
C(25)-H(25) 0.9500
C(26)-H(26A) 0.9800
C(26)-H(26B) 0.9800
C(26)-H(26C) 0.9800
O(27)-S(27)-C(28) 104.44(6)
O(27)-S(27)-C(29) 104.89(7)
C(29)-S(27)-C(28) 98.87(7)
S(27)-C(28)-H(28A) 109.5
S(27)-C(28)-H(28B) 109.5
S(27)-C(28)-H(28C) 109.5
H(28A)-C(28)-H(28B) 109.5
H(28A)-C(28)-H(28C) 109.5
H(28B)-C(28)-H(28C) 109.5
S(27)-C(29)-H(29A) 109.5
S(27)-C(29)-H(29B) 109.5
S(27)-C(29)-H(29C) 109.5
H(29A)-C(29)-H(29B) 109.5
H(29A)-C(29)-H(29C) 109.5
H(29B)-C(29)-H(29C) 109.5
C(12)-O(7)-C(8) 120.11(10)
C(9)-O(9)-H(9) 112.9(16)
C(23)-O(26)-C(26) 116.99(12)
C(5)-N(1)-N(2) 104.29(11)
N(1)-N(2)-H(2) 117.4(13)
C(3)-N(2)-N(1) 113.40(11)
C(3)-N(2)-H(2) 128.9(13)
C(5)-N(6)-H(6) 116.9(13)
C(5)-N(6)-C(14) 125.85(12)
C(14)-N(6)-H(6) 115.2(13)
N(2)-C(3)-C(4) 106.51(12)
N(2)-C(3)-C(20) 122.68(12)
C(4)-C(3)-C(20) 130.79(12)
C(3)-C(4)-C(5) 104.19(11)
C(3)-C(4)-C(8) 126.30(12)
C(5)-C(4)-C(8) 129.05(12)
N(1)-C(5)-N(6) 122.19(12)
N(1)-C(5)-C(4) 111.60(12)
N(6)-C(5)-C(4) 126.20(12)
O(7)-C(8)-C(4) 114.09(11)
C(9)-C(8)-O(7) 120.97(11)
C(9)-C(8)-C(4) 124.88(12)
O(9)-C(9)-C(8) 119.20(12)
O(9)-C(9)-C(10) 119.75(11)
C(8)-C(9)-C(10) 120.92(12)
O(10)-C(10)-C(9) 120.49(12)
O(10)-C(10)-C(11) 124.74(12)

C(11)-C(10)-C(9)	114.71(11)
C(10)-C(11)-H(11)	119.2
C(12)-C(11)-C(10)	121.68(12)
C(12)-C(11)-H(11)	119.2
O(7)-C(12)-C(13)	112.36(11)
C(11)-C(12)-O(7)	121.57(12)
C(11)-C(12)-C(13)	126.07(12)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-N(6)	123.57(13)
C(19)-C(14)-N(6)	117.44(12)
C(19)-C(14)-C(15)	118.90(13)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-C(14)	120.45(14)
C(16)-C(15)-H(15)	119.8
C(15)-C(16)-H(16)	120.6
C(17)-C(16)-C(15)	118.79(14)
C(17)-C(16)-H(16)	120.6
F(17)-C(17)-C(16)	118.65(14)
F(17)-C(17)-C(18)	118.93(14)
C(16)-C(17)-C(18)	122.42(14)
C(17)-C(18)-H(18)	120.5
C(17)-C(18)-C(19)	119.09(14)
C(19)-C(18)-H(18)	120.5
C(14)-C(19)-H(19)	119.8
C(18)-C(19)-C(14)	120.35(14)
C(18)-C(19)-H(19)	119.8
C(21)-C(20)-C(3)	120.58(12)
C(25)-C(20)-C(3)	120.78(12)
C(25)-C(20)-C(21)	118.61(13)
C(20)-C(21)-H(21)	119.6
C(22)-C(21)-C(20)	120.77(13)
C(22)-C(21)-H(21)	119.6
C(21)-C(22)-H(22)	119.9
C(21)-C(22)-C(23)	120.13(13)
C(23)-C(22)-H(22)	119.9
O(26)-C(23)-C(22)	115.60(13)
O(26)-C(23)-C(24)	124.77(13)
C(24)-C(23)-C(22)	119.63(13)
C(23)-C(24)-H(24)	120.1
C(25)-C(24)-C(23)	119.75(13)
C(25)-C(24)-H(24)	120.1
C(20)-C(25)-H(25)	119.5
C(24)-C(25)-C(20)	121.09(13)
C(24)-C(25)-H(25)	119.5
O(26)-C(26)-H(26A)	109.5
O(26)-C(26)-H(26B)	109.5
O(26)-C(26)-H(26C)	109.5

H(26A)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2x10^3$) for **15a**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2hka^*b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(27)	26(1)	20(1)	17(1)	1(1)	2(1)	8(1)
O(27)	45(1)	28(1)	18(1)	6(1)	8(1)	24(1)
C(28)	36(1)	31(1)	24(1)	4(1)	1(1)	20(1)
C(29)	40(1)	25(1)	20(1)	-2(1)	1(1)	13(1)
F(17)	36(1)	60(1)	48(1)	10(1)	7(1)	34(1)
O(7)	27(1)	19(1)	15(1)	3(1)	4(1)	10(1)
O(9)	45(1)	21(1)	19(1)	6(1)	10(1)	18(1)
O(10)	37(1)	23(1)	20(1)	1(1)	4(1)	17(1)
O(26)	30(1)	34(1)	34(1)	9(1)	-4(1)	13(1)
N(1)	31(1)	27(1)	18(1)	4(1)	3(1)	16(1)
N(2)	33(1)	27(1)	14(1)	3(1)	4(1)	17(1)
N(6)	29(1)	27(1)	17(1)	0(1)	3(1)	16(1)
C(3)	28(1)	18(1)	16(1)	2(1)	4(1)	10(1)
C(4)	26(1)	17(1)	17(1)	2(1)	3(1)	9(1)
C(5)	26(1)	19(1)	18(1)	3(1)	4(1)	10(1)
C(8)	22(1)	19(1)	14(1)	2(1)	2(1)	7(1)
C(9)	24(1)	20(1)	16(1)	3(1)	3(1)	9(1)
C(10)	24(1)	21(1)	16(1)	0(1)	0(1)	10(1)
C(11)	25(1)	22(1)	15(1)	0(1)	3(1)	9(1)
C(12)	22(1)	22(1)	14(1)	2(1)	2(1)	7(1)
C(13)	36(1)	25(1)	18(1)	5(1)	5(1)	12(1)
C(14)	24(1)	23(1)	21(1)	7(1)	6(1)	11(1)
C(15)	31(1)	27(1)	19(1)	6(1)	5(1)	15(1)
C(16)	36(1)	31(1)	25(1)	10(1)	13(1)	20(1)
C(17)	25(1)	36(1)	35(1)	12(1)	9(1)	18(1)
C(18)	24(1)	37(1)	34(1)	4(1)	-1(1)	11(1)
C(19)	26(1)	27(1)	26(1)	1(1)	2(1)	10(1)
C(20)	28(1)	20(1)	15(1)	-1(1)	1(1)	10(1)
C(21)	29(1)	24(1)	20(1)	5(1)	3(1)	8(1)
C(22)	26(1)	29(1)	26(1)	5(1)	3(1)	9(1)
C(23)	28(1)	23(1)	22(1)	0(1)	-2(1)	10(1)
C(24)	32(1)	24(1)	18(1)	4(1)	1(1)	10(1)
C(25)	28(1)	24(1)	17(1)	2(1)	4(1)	11(1)
C(26)	40(1)	34(1)	41(1)	13(1)	-4(1)	17(1)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for **15a**.

	x	y	z	U(eq)		
H(28A)	3633	9887	6370	43		
H(28B)	2070	9576	6683	43		
H(28C)	2436	8631	5648	43		
H(29A)	3964	8989	9436	42		
H(29B)	3119	9872	8995	42		
H(29C)	4587	10042	8491	42		
H(9)	3990(20)		5990(30)		7490(20)	54(7)
H(2)	5270(20)		2270(20)		4535(19)	34(5)
H(6)	6588(19)		2830(20)		8818(19)	30(5)
H(11)	2729	4352	11016	25		
H(13A)	2501	1099	10713	39		
H(13B)	2749	2297	11777	39		
H(13C)	4018	1920	11307	39		
H(15)	7158	604	6558	29		
H(16)	8959	-227	6684	34		
H(18)	10314	1982	9931	38		
H(19)	8557	2864	9804	32		
H(21)	1656	1957	6413	29		
H(22)	-140	2432	5529	32		
H(24)	2465	4655	3252	29		
H(25)	4247	4125	4112	27		
H(26A)	384	4361	2246	55		
H(26B)	829	5613	3280	55		
H(26C)	-746	4914	2788	55		

Table 6. Torsion angles [°] for **15a**.

F(17)-C(17)-C(18)-C(19)	179.33(14)
O(7)-C(8)-C(9)-O(9)	177.18(11)
O(7)-C(8)-C(9)-C(10)	1.4(2)
O(9)-C(9)-C(10)-O(10)	-0.7(2)
O(9)-C(9)-C(10)-C(11)	-177.99(12)
O(10)-C(10)-C(11)-C(12)	-175.02(13)
O(26)-C(23)-C(24)-C(25)	179.15(13)
N(1)-N(2)-C(3)-C(4)	-0.78(16)
N(1)-N(2)-C(3)-C(20)	-179.29(12)
N(2)-N(1)-C(5)-N(6)	-179.12(12)
N(2)-N(1)-C(5)-C(4)	-0.48(15)
N(2)-C(3)-C(4)-C(5)	0.42(14)
N(2)-C(3)-C(4)-C(8)	173.18(12)
N(2)-C(3)-C(20)-C(21)	133.86(14)
N(2)-C(3)-C(20)-C(25)	-48.09(19)
N(6)-C(14)-C(15)-C(16)	-177.48(13)
N(6)-C(14)-C(19)-C(18)	176.90(13)
C(3)-C(4)-C(5)-N(1)	0.05(15)
C(3)-C(4)-C(5)-N(6)	178.61(13)
C(3)-C(4)-C(8)-O(7)	136.77(13)
C(3)-C(4)-C(8)-C(9)	-46.0(2)
C(3)-C(20)-C(21)-C(22)	177.49(13)
C(3)-C(20)-C(25)-C(24)	-176.59(12)
C(4)-C(3)-C(20)-C(21)	-44.2(2)
C(4)-C(3)-C(20)-C(25)	133.80(15)
C(4)-C(8)-C(9)-O(9)	0.1(2)
C(4)-C(8)-C(9)-C(10)	-175.67(12)
C(5)-N(1)-N(2)-C(3)	0.79(15)
C(5)-N(6)-C(14)-C(15)	-24.4(2)
C(5)-N(6)-C(14)-C(19)	159.17(13)
C(5)-C(4)-C(8)-O(7)	-52.29(18)
C(5)-C(4)-C(8)-C(9)	124.97(16)
C(8)-O(7)-C(12)-C(11)	0.08(19)
C(8)-O(7)-C(12)-C(13)	-179.96(11)
C(8)-C(4)-C(5)-N(1)	-172.43(13)
C(8)-C(4)-C(5)-N(6)	6.1(2)
C(8)-C(9)-C(10)-O(10)	175.01(13)
C(8)-C(9)-C(10)-C(11)	-2.24(19)
C(9)-C(10)-C(11)-C(12)	2.09(19)
C(10)-C(11)-C(12)-O(7)	-1.1(2)
C(10)-C(11)-C(12)-C(13)	178.96(13)
C(12)-O(7)-C(8)-C(4)	177.12(11)
C(12)-O(7)-C(8)-C(9)	-0.26(18)
C(14)-N(6)-C(5)-N(1)	-8.2(2)
C(14)-N(6)-C(5)-C(4)	173.34(13)
C(14)-C(15)-C(16)-C(17)	1.1(2)
C(15)-C(14)-C(19)-C(18)	0.3(2)
C(15)-C(16)-C(17)-F(17)	179.88(13)
C(15)-C(16)-C(17)-C(18)	-0.2(2)
C(16)-C(17)-C(18)-C(19)	-0.6(2)

C(17)-C(18)-C(19)-C(14)	0.5(2)
C(19)-C(14)-C(15)-C(16)	-1.1(2)
C(20)-C(3)-C(4)-C(5)	178.76(13)
C(20)-C(3)-C(4)-C(8)	-8.5(2)
C(20)-C(21)-C(22)-C(23)	-0.8(2)
C(21)-C(20)-C(25)-C(24)	1.5(2)
C(21)-C(22)-C(23)-O(26)	-178.31(13)
C(21)-C(22)-C(23)-C(24)	1.3(2)
C(22)-C(23)-C(24)-C(25)	-0.4(2)
C(23)-C(24)-C(25)-C(20)	-1.0(2)
C(25)-C(20)-C(21)-C(22)	-0.6(2)
C(26)-O(26)-C(23)-C(22)	176.15(14)
C(26)-O(26)-C(23)-C(24)	-3.4(2)

Table 7. Hydrogen bonds for **15a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(28)-H(28B)...F(17)#1	0.98	2.55	3.4255(18)	148.3
O(9)-H(9)...O(27)	0.85(3)	1.85(3)	2.6265(14)	152(2)
N(2)-H(2)...O(27)#2	0.88(2)	1.96(2)	2.8246(15)	165.3(19)
N(6)-H(6)...O(10)#3	0.85(2)	2.09(2)	2.9364(15)	169.6(18)
C(13)-H(13C)...O(27)#3	0.98	2.53	3.4117(18)	149.2
C(15)-H(15)...N(1)	0.95	2.34	2.8844(18)	115.8
C(19)-H(19)...O(10)#3	0.95	2.57	3.3401(17)	138.5

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y+1,z #2 -x+1,-y+1,-z+1 #3 -x+1,-y+1,-z+2

Crystallographic data for compound **16j**.

Table 8. Crystal data and structure refinement for **16j**.

Identification code	2448540
Empirical formula	$C_{21}H_{16}FN_3O_3$
Formula weight	377.37
Temperature	99.97(15) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a = 9.28605(11) Å	α= 63.9662(18)°.
b = 14.2749(3) Å	β= 89.9415(12)°.
c = 14.7953(3) Å	γ = 81.1842(13)°.
Volume	1736.55(6) $Å^3$
Z	4
Density (calculated)	1.443 g/cm^3
Absorption coefficient	0.882 mm^{-1}
F(000)	784
Crystal size	0.53 x 0.21 x 0.03 mm^3
Theta range for data collection	3.334 to 80.035°.
Index ranges	-11<=h<=10, -18<=k<=18, -18<=l<=18
Reflections collected	13773
Independent reflections	13773 [R(int) = 0.0680]
Observed reflections	12677
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	0.973 and 0.772
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13773 / 0 / 532
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1304
R indices (all data)	R1 = 0.0487, wR2 = 0.1333
Largest diff. peak and hole	0.334 and -0.301 $e.Å^{-3}$

Table 9. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for **16j**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)	
F(1A)	3936(1)	-620(1)	9087(1)	38(1)	
O(5A)	925(1)	3928(1)	9493(1)	20(1)	
O(8A)	2869(1)	6257(1)	10308(1)		34(1)
O(9A)	659(1)	6054(1)	9016(1)	21(1)	
N(1A)	4368(1)	5277(1)	7293(1)	18(1)	
N(2A)	4586(1)	4239(1)	7450(1)	18(1)	
N(10A)	2915(1)	6036(1)	8298(1)	19(1)	
C(3A)	3876(1)	3606(1)	8223(1)	18(1)	
C(4A)	3149(1)	4266(1)	8604(1)	18(1)	
C(5A)	2276(1)	4302(1)	9436(1)	18(1)	
C(6A)	3131(1)	3728(1)	10463(1)		23(1)
C(7A)	3440(1)	4392(1)	10826(1)		25(1)
C(8A)	2841(1)	5487(1)	10163(1)		23(1)
C(9A)	2095(1)	5526(1)	9200(1)	18(1)	
C(11A)	3482(1)	5264(1)	8004(1)	17(1)	
C(12A)	3912(1)	2493(1)	8459(1)	19(1)	
C(13A)	5060(2)	1933(1)	8185(1)	24(1)	
C(14A)	5078(2)	884(1)	8392(1)	27(1)	
C(15A)	3935(2)	401(1)	8878(1)	27(1)	
C(16A)	2784(2)	925(1)	9160(1)	29(1)	
C(17A)	2773(2)	1976(1)	8945(1)	25(1)	
C(18A)	3567(2)	2559(1)	10939(1)		33(1)
C(19A)	2552(1)	7129(1)	7613(1)	21(1)	
C(20A)	2333(2)	7442(1)	6581(1)	23(1)	
C(21A)	1960(2)	8514(1)	5914(1)	29(1)	
C(22A)	1792(2)	9276(1)	6268(1)	32(1)	
C(23A)	2016(2)	8961(1)	7297(1)	31(1)	
C(24A)	2400(2)	7894(1)	7972(1)	26(1)	
F(1B)	5996(1)	10605(1)	6283(1)		38(1)
O(5B)	5328(1)	6231(1)	5433(1)	19(1)	
O(8B)	8355(1)	4045(1)	4487(1)	31(1)	
O(9B)	6154(1)	4115(1)	5900(1)	19(1)	
N(1B)	9468(1)	4890(1)	7606(1)	18(1)	
N(2B)	9158(1)	5906(1)	7507(1)	19(1)	
N(10B)	8427(1)	4175(1)	6543(1)	19(1)	
C(3B)	8115(1)	6531(1)	6758(1)	18(1)	
C(4B)	7720(1)	5902(1)	6335(1)	17(1)	
C(5B)	6859(1)	5890(1)	5489(1)	17(1)	
C(6B)	7410(1)	6516(1)	4462(1)	21(1)	
C(7B)	8043(1)	5894(1)	4057(1)	23(1)	
C(8B)	7983(1)	4781(1)	4685(1)	21(1)	
C(9B)	7306(1)	4681(1)	5677(1)	18(1)	
C(11B)	8581(1)	4915(1)	6886(1)	17(1)	
C(12B)	7577(2)	7618(1)	6591(1)	20(1)	
C(13B)	8480(2)	8182(1)	6839(1)	27(1)	
C(14B)	7950(2)	9188(1)	6736(2)	33(1)	
C(15B)	6515(2)	9618(1)	6390(1)	28(1)	

C(16B)	5588(2)	9088(1)	6139(1)	26(1)
C(17B)	6124(2)	8086(1)	6233(1)	23(1)
C(18B)	7234(2)	7688(1)	4024(1)	28(1)
C(19B)	8675(1)	3070(1)	7186(1)	22(1)
C(20B)	8592(2)	2693(1)	8225(1)	26(1)
C(21B)	8832(2)	1606(1)	8850(2)	35(1)
C(22B)	9161(2)	898(1)	8440(2)	41(1)
C(23B)	9245(2)	1280(1)	7407(2)	40(1)
C(24B)	9002(2)	2359(1)	6773(1)	32(1)

Table 10. Bond lengths [Å] and angles [°] for **16j**.

F(1A)-C(15A)	1.3517(17)
O(5A)-H(5A)	0.93(4)
O(5A)-C(5A)	1.4250(15)
O(8A)-C(8A)	1.212(2)
O(9A)-H(9A)	0.91(3)
O(9A)-C(9A)	1.3898(15)
N(1A)-N(2A)	1.3774(16)
N(1A)-C(11A)	1.3300(17)
N(2A)-H(2A)	0.86(2)
N(2A)-C(3A)	1.3531(17)
N(10A)-C(9A)	1.4845(17)
N(10A)-C(11A)	1.3870(17)
N(10A)-C(19A)	1.4244(19)
C(3A)-C(4A)	1.3900(18)
C(3A)-C(12A)	1.4642(19)
C(4A)-C(5A)	1.4875(17)
C(4A)-C(11A)	1.3923(19)
C(5A)-C(6A)	1.5238(18)
C(5A)-C(9A)	1.6062(19)
C(6A)-C(7A)	1.341(2)
C(6A)-C(18A)	1.486(2)
C(7A)-H(7A)	0.9500
C(7A)-C(8A)	1.451(2)
C(8A)-C(9A)	1.5604(18)
C(12A)-C(13A)	1.4006(18)
C(12A)-C(17A)	1.3975(19)
C(13A)-H(13A)	0.9500
C(13A)-C(14A)	1.388(2)
C(14A)-H(14A)	0.9500
C(14A)-C(15A)	1.381(2)
C(15A)-C(16A)	1.379(2)
C(16A)-H(16A)	0.9500
C(16A)-C(17A)	1.389(2)
C(17A)-H(17A)	0.9500
C(18A)-H(18A)	0.9800
C(18A)-H(18B)	0.9800
C(18A)-H(18C)	0.9800
C(19A)-C(20A)	1.396(2)
C(19A)-C(24A)	1.3980(19)
C(20A)-H(20A)	0.9500
C(20A)-C(21A)	1.395(2)
C(21A)-H(21A)	0.9500
C(21A)-C(22A)	1.389(2)
C(22A)-H(22A)	0.9500
C(22A)-C(23A)	1.390(3)
C(23A)-H(23A)	0.9500
C(23A)-C(24A)	1.393(2)
C(24A)-H(24A)	0.9500
F(1B)-C(15B)	1.3559(17)
O(5B)-H(5B)	0.94(3)

O(5B)-C(5B)	1.4202(15)
O(8B)-C(8B)	1.2107(19)
O(9B)-H(9B)	0.90(3)
O(9B)-C(9B)	1.3912(15)
N(1B)-N(2B)	1.3747(16)
N(1B)-C(11B)	1.3319(17)
N(2B)-H(2B)	0.95(3)
N(2B)-C(3B)	1.3528(18)
N(10B)-C(9B)	1.4855(16)
N(10B)-C(11B)	1.3821(17)
N(10B)-C(19B)	1.4215(18)
C(3B)-C(4B)	1.3894(18)
C(3B)-C(12B)	1.4641(19)
C(4B)-C(5B)	1.4933(18)
C(4B)-C(11B)	1.3916(18)
C(5B)-C(6B)	1.5222(18)
C(5B)-C(9B)	1.6091(19)
C(6B)-C(7B)	1.342(2)
C(6B)-C(18B)	1.486(2)
C(7B)-H(7B)	0.9500
C(7B)-C(8B)	1.457(2)
C(8B)-C(9B)	1.5529(18)
C(12B)-C(13B)	1.3978(19)
C(12B)-C(17B)	1.4004(19)
C(13B)-H(13B)	0.9500
C(13B)-C(14B)	1.385(2)
C(14B)-H(14B)	0.9500
C(14B)-C(15B)	1.375(2)
C(15B)-C(16B)	1.378(2)
C(16B)-H(16B)	0.9500
C(16B)-C(17B)	1.386(2)
C(17B)-H(17B)	0.9500
C(18B)-H(18D)	0.9800
C(18B)-H(18E)	0.9800
C(18B)-H(18F)	0.9800
C(19B)-C(20B)	1.395(2)
C(19B)-C(24B)	1.394(2)
C(20B)-H(20B)	0.9500
C(20B)-C(21B)	1.394(2)
C(21B)-H(21B)	0.9500
C(21B)-C(22B)	1.387(3)
C(22B)-H(22B)	0.9500
C(22B)-C(23B)	1.386(3)
C(23B)-H(23B)	0.9500
C(23B)-C(24B)	1.389(3)
C(24B)-H(24B)	0.9500

C(5A)-O(5A)-H(5A)	112(2)
C(9A)-O(9A)-H(9A)	115(2)
C(11A)-N(1A)-N(2A)	102.40(11)
N(1A)-N(2A)-H(2A)	117.2(15)
C(3A)-N(2A)-N(1A)	113.98(11)

C(3A)-N(2A)-H(2A)	128.0(15)
C(11A)-N(10A)-C(9A)	107.38(11)
C(11A)-N(10A)-C(19A)	123.21(11)
C(19A)-N(10A)-C(9A)	122.51(11)
N(2A)-C(3A)-C(4A)	104.95(12)
N(2A)-C(3A)-C(12A)	121.40(12)
C(4A)-C(3A)-C(12A)	133.54(12)
C(3A)-C(4A)-C(5A)	144.70(13)
C(3A)-C(4A)-C(11A)	105.44(11)
C(11A)-C(4A)-C(5A)	109.58(11)
O(5A)-C(5A)-C(4A)	114.01(11)
O(5A)-C(5A)-C(6A)	109.52(11)
O(5A)-C(5A)-C(9A)	113.88(10)
C(4A)-C(5A)-C(6A)	112.95(10)
C(4A)-C(5A)-C(9A)	102.43(10)
C(6A)-C(5A)-C(9A)	103.46(11)
C(7A)-C(6A)-C(5A)	112.69(13)
C(7A)-C(6A)-C(18A)	127.10(14)
C(18A)-C(6A)-C(5A)	120.18(13)
C(6A)-C(7A)-H(7A)	123.8
C(6A)-C(7A)-C(8A)	112.45(13)
C(8A)-C(7A)-H(7A)	123.8
O(8A)-C(8A)-C(7A)	127.84(14)
O(8A)-C(8A)-C(9A)	124.16(14)
C(7A)-C(8A)-C(9A)	107.99(12)
O(9A)-C(9A)-N(10A)	109.62(11)
O(9A)-C(9A)-C(5A)	114.79(10)
O(9A)-C(9A)-C(8A)	111.20(11)
N(10A)-C(9A)-C(5A)	106.05(10)
N(10A)-C(9A)-C(8A)	111.67(10)
C(8A)-C(9A)-C(5A)	103.31(11)
N(1A)-C(11A)-N(10A)	132.10(13)
N(1A)-C(11A)-C(4A)	113.21(12)
N(10A)-C(11A)-C(4A)	114.51(12)
C(13A)-C(12A)-C(3A)	121.15(12)
C(17A)-C(12A)-C(3A)	120.13(12)
C(17A)-C(12A)-C(13A)	118.70(13)
C(12A)-C(13A)-H(13A)	119.5
C(14A)-C(13A)-C(12A)	121.05(13)
C(14A)-C(13A)-H(13A)	119.5
C(13A)-C(14A)-H(14A)	120.8
C(15A)-C(14A)-C(13A)	118.39(13)
C(15A)-C(14A)-H(14A)	120.8
F(1A)-C(15A)-C(14A)	119.18(14)
F(1A)-C(15A)-C(16A)	118.48(14)
C(16A)-C(15A)-C(14A)	122.34(14)
C(15A)-C(16A)-H(16A)	120.6
C(15A)-C(16A)-C(17A)	118.81(14)
C(17A)-C(16A)-H(16A)	120.6
C(12A)-C(17A)-H(17A)	119.6
C(16A)-C(17A)-C(12A)	120.70(13)
C(16A)-C(17A)-H(17A)	119.6

C(6A)-C(18A)-H(18A)	109.5
C(6A)-C(18A)-H(18B)	109.5
C(6A)-C(18A)-H(18C)	109.5
H(18A)-C(18A)-H(18B)	109.5
H(18A)-C(18A)-H(18C)	109.5
H(18B)-C(18A)-H(18C)	109.5
C(20A)-C(19A)-N(10A)	120.10(12)
C(20A)-C(19A)-C(24A)	119.67(14)
C(24A)-C(19A)-N(10A)	120.23(13)
C(19A)-C(20A)-H(20A)	120.0
C(21A)-C(20A)-C(19A)	119.90(14)
C(21A)-C(20A)-H(20A)	120.0
C(20A)-C(21A)-H(21A)	119.7
C(22A)-C(21A)-C(20A)	120.60(16)
C(22A)-C(21A)-H(21A)	119.7
C(21A)-C(22A)-H(22A)	120.4
C(21A)-C(22A)-C(23A)	119.28(15)
C(23A)-C(22A)-H(22A)	120.4
C(22A)-C(23A)-H(23A)	119.6
C(22A)-C(23A)-C(24A)	120.81(15)
C(24A)-C(23A)-H(23A)	119.6
C(19A)-C(24A)-H(24A)	120.1
C(23A)-C(24A)-C(19A)	119.73(15)
C(23A)-C(24A)-H(24A)	120.1
C(5B)-O(5B)-H(5B)	111.0(16)
C(9B)-O(9B)-H(9B)	113.8(16)
C(11B)-N(1B)-N(2B)	103.22(11)
N(1B)-N(2B)-H(2B)	116.7(16)
C(3B)-N(2B)-N(1B)	112.80(11)
C(3B)-N(2B)-H(2B)	129.8(16)
C(11B)-N(10B)-C(9B)	107.72(11)
C(11B)-N(10B)-C(19B)	122.60(12)
C(19B)-N(10B)-C(9B)	122.44(11)
N(2B)-C(3B)-C(4B)	106.10(12)
N(2B)-C(3B)-C(12B)	120.17(12)
C(4B)-C(3B)-C(12B)	133.59(12)
C(3B)-C(4B)-C(5B)	145.16(13)
C(3B)-C(4B)-C(11B)	104.84(12)
C(11B)-C(4B)-C(5B)	109.67(12)
O(5B)-C(5B)-C(4B)	115.45(11)
O(5B)-C(5B)-C(6B)	108.27(11)
O(5B)-C(5B)-C(9B)	113.92(10)
C(4B)-C(5B)-C(6B)	112.95(11)
C(4B)-C(5B)-C(9B)	102.15(10)
C(6B)-C(5B)-C(9B)	103.46(10)
C(7B)-C(6B)-C(5B)	112.62(13)
C(7B)-C(6B)-C(18B)	127.29(13)
C(18B)-C(6B)-C(5B)	120.08(12)
C(6B)-C(7B)-H(7B)	123.8
C(6B)-C(7B)-C(8B)	112.32(13)
C(8B)-C(7B)-H(7B)	123.8
O(8B)-C(8B)-C(7B)	127.71(14)

O(8B)-C(8B)-C(9B)	124.33(13)
C(7B)-C(8B)-C(9B)	107.94(12)
O(9B)-C(9B)-N(10B)	109.14(11)
O(9B)-C(9B)-C(5B)	114.36(10)
O(9B)-C(9B)-C(8B)	112.62(11)
N(10B)-C(9B)-C(5B)	105.87(10)
N(10B)-C(9B)-C(8B)	111.17(10)
C(8B)-C(9B)-C(5B)	103.42(10)
N(1B)-C(11B)-N(10B)	132.36(12)
N(1B)-C(11B)-C(4B)	113.04(12)
N(10B)-C(11B)-C(4B)	114.43(12)
C(13B)-C(12B)-C(3B)	120.50(12)
C(13B)-C(12B)-C(17B)	119.03(13)
C(17B)-C(12B)-C(3B)	120.37(12)
C(12B)-C(13B)-H(13B)	119.7
C(14B)-C(13B)-C(12B)	120.68(13)
C(14B)-C(13B)-H(13B)	119.7
C(13B)-C(14B)-H(14B)	120.7
C(15B)-C(14B)-C(13B)	118.68(14)
C(15B)-C(14B)-H(14B)	120.7
F(1B)-C(15B)-C(14B)	118.78(14)
F(1B)-C(15B)-C(16B)	118.75(14)
C(14B)-C(15B)-C(16B)	122.47(14)
C(15B)-C(16B)-H(16B)	120.6
C(15B)-C(16B)-C(17B)	118.79(13)
C(17B)-C(16B)-H(16B)	120.6
C(12B)-C(17B)-H(17B)	119.8
C(16B)-C(17B)-C(12B)	120.35(13)
C(16B)-C(17B)-H(17B)	119.8
C(6B)-C(18B)-H(18D)	109.5
C(6B)-C(18B)-H(18E)	109.5
C(6B)-C(18B)-H(18F)	109.5
H(18D)-C(18B)-H(18E)	109.5
H(18D)-C(18B)-H(18F)	109.5
H(18E)-C(18B)-H(18F)	109.5
C(20B)-C(19B)-N(10B)	120.43(13)
C(24B)-C(19B)-N(10B)	119.64(14)
C(24B)-C(19B)-C(20B)	119.93(14)
C(19B)-C(20B)-H(20B)	120.0
C(21B)-C(20B)-C(19B)	120.00(16)
C(21B)-C(20B)-H(20B)	120.0
C(20B)-C(21B)-H(21B)	119.9
C(22B)-C(21B)-C(20B)	120.17(18)
C(22B)-C(21B)-H(21B)	119.9
C(21B)-C(22B)-H(22B)	120.3
C(23B)-C(22B)-C(21B)	119.45(16)
C(23B)-C(22B)-H(22B)	120.3
C(22B)-C(23B)-H(23B)	119.4
C(22B)-C(23B)-C(24B)	121.21(17)
C(24B)-C(23B)-H(23B)	119.4
C(19B)-C(24B)-H(24B)	120.4
C(23B)-C(24B)-C(19B)	119.24(18)

C(23B)-C(24B)-H(24B) 120.4

Table 11. Anisotropic displacement parameters ($Å^2x10^3$) for **16j**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2hka^* b^* U^{12}]$

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	
F(1A)	41(1)	25(1)	49(1)	-17(1)	0(1)	-5(1)
O(5A)	12(1)	32(1)	17(1)	-11(1)	2(1)	-6(1)
O(8A)	36(1)	46(1)	32(1)	-28(1)	-1(1)	-6(1)
O(9A)	12(1)	34(1)	22(1)	-18(1)	2(1)	-1(1)
N(1A)	14(1)	26(1)	20(1)	-14(1)	4(1)	-5(1)
N(2A)	15(1)	26(1)	19(1)	-13(1)	5(1)	-4(1)
N(10A)	14(1)	27(1)	20(1)	-14(1)	5(1)	-4(1)
C(3A)	12(1)	27(1)	17(1)	-12(1)	2(1)	-3(1)
C(4A)	11(1)	27(1)	17(1)	-12(1)	2(1)	-3(1)
C(5A)	9(1)	30(1)	16(1)	-12(1)	2(1)	-3(1)
C(6A)	13(1)	38(1)	17(1)	-12(1)	2(1)	-1(1)
C(7A)	13(1)	44(1)	20(1)	-17(1)	0(1)	-4(1)
C(8A)	14(1)	42(1)	22(1)	-21(1)	4(1)	-7(1)
C(9A)	12(1)	31(1)	18(1)	-15(1)	3(1)	-4(1)
C(11A)	10(1)	26(1)	18(1)	-13(1)	1(1)	-3(1)
C(12A)	15(1)	26(1)	18(1)	-11(1)	0(1)	-2(1)
C(13A)	18(1)	31(1)	26(1)	-16(1)	4(1)	-4(1)
C(14A)	23(1)	31(1)	30(1)	-18(1)	1(1)	1(1)
C(15A)	28(1)	24(1)	29(1)	-12(1)	-4(1)	-3(1)
C(16A)	23(1)	29(1)	34(1)	-11(1)	4(1)	-7(1)
C(17A)	19(1)	28(1)	27(1)	-11(1)	4(1)	-3(1)
C(18A)	36(1)	36(1)	20(1)	-9(1)	-4(1)	4(1)
C(19A)	12(1)	28(1)	27(1)	-16(1)	4(1)	-6(1)
C(20A)	19(1)	27(1)	27(1)	-15(1)	4(1)	-5(1)
C(21A)	25(1)	31(1)	29(1)	-12(1)	4(1)	-5(1)
C(22A)	23(1)	28(1)	43(1)	-14(1)	5(1)	-5(1)
C(23A)	23(1)	32(1)	48(1)	-26(1)	6(1)	-6(1)
C(24A)	20(1)	34(1)	33(1)	-22(1)	4(1)	-6(1)
F(1B)	38(1)	27(1)	52(1)	-22(1)	1(1)	2(1)
O(5B)	12(1)	28(1)	18(1)	-12(1)	2(1)	-3(1)
O(8B)	34(1)	41(1)	34(1)	-27(1)	13(1)	-12(1)
O(9B)	14(1)	31(1)	19(1)	-16(1)	4(1)	-9(1)
N(1B)	16(1)	23(1)	19(1)	-12(1)	0(1)	-3(1)
N(2B)	16(1)	23(1)	22(1)	-13(1)	0(1)	-4(1)
N(10B)	14(1)	24(1)	22(1)	-14(1)	-1(1)	-3(1)
C(3B)	12(1)	26(1)	20(1)	-13(1)	2(1)	-6(1)
C(4B)	12(1)	24(1)	17(1)	-10(1)	2(1)	-4(1)
C(5B)	12(1)	25(1)	16(1)	-10(1)	1(1)	-4(1)
C(6B)	13(1)	31(1)	17(1)	-10(1)	0(1)	-5(1)
C(7B)	14(1)	37(1)	19(1)	-14(1)	4(1)	-7(1)
C(8B)	12(1)	37(1)	22(1)	-19(1)	4(1)	-7(1)
C(9B)	11(1)	27(1)	19(1)	-14(1)	2(1)	-5(1)
C(11B)	12(1)	23(1)	18(1)	-11(1)	2(1)	-4(1)
C(12B)	17(1)	25(1)	21(1)	-12(1)	3(1)	-5(1)
C(13B)	16(1)	29(1)	40(1)	-19(1)	-1(1)	-3(1)
C(14B)	27(1)	30(1)	49(1)	-24(1)	-1(1)	-7(1)
C(15B)	29(1)	23(1)	32(1)	-14(1)	5(1)	-1(1)

C(16B)	19(1)	30(1)	26(1)	-11(1)	1(1)	0(1)
C(17B)	19(1)	28(1)	23(1)	-12(1)	0(1)	-5(1)
C(18B)	27(1)	30(1)	23(1)	-8(1)	5(1)	-5(1)
C(19B)	13(1)	23(1)	31(1)	-14(1)	-2(1)	-2(1)
C(20B)	22(1)	26(1)	31(1)	-11(1)	-1(1)	-5(1)
C(21B)	30(1)	29(1)	38(1)	-6(1)	-6(1)	-8(1)
C(22B)	31(1)	23(1)	60(1)	-11(1)	-12(1)	-4(1)
C(23B)	32(1)	30(1)	66(1)	-29(1)	-7(1)	-2(1)
C(24B)	27(1)	32(1)	43(1)	-24(1)	-3(1)	-2(1)

Table 12. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å2x10^3) for **16j**.

	x	y	z	U(eq)		
H(5A)	460(40)	4160(30)	8860(30)	82(10)		
H(9A)	220(40)	6020(20)	9580(20)	71(9)		
H(2A)	5030(30)	4096(18)	7007(18)	37(6)		
H(7A)	3991	4170	11447	30		
H(13A)	5839	2277	7852	28		
H(14A)	5859	507	8205	33		
H(16A)	2014	572	9496	35		
H(17A)	1983	2347	9130	30		
H(18A)	2694	2229	11018	49		
H(18B)	4076	2320	11602	49		
H(18C)	4220	2356	10510	49		
H(20A)	2439	6926	6333	28		
H(21A)	1819	8724	5211	35		
H(22A)	1526	10004	5812	38		
H(23A)	1907	9479	7542	38		
H(24A)	2558	7688	8672	31		
H(5B)	4990(30)	6020(20)	6080(20)	47(6)		
H(9B)	5810(30)	4021(19)	5380(20)	43(6)		
H(2B)	9590(30)	6030(20)	8010(20)	49(7)		
H(7B)	8481	6150	3432	27		
H(13B)	9468	7872	7081	32		
H(14B)	8566	9572	6902	39		
H(16B)	4599	9404	5905	31		
H(17B)	5503	7714	6054	27		
H(18D)	6194	7987	3957	42		
H(18E)	7626	7964	3359	42		
H(18F)	7764	7885	4469	42		
H(20B)	8371	3176	8508	32		
H(21B)	8771	1351	9557	42		
H(22B)	9327	158	8865	49		
H(23B)	9473	794	7128	49		
H(24B)	9058	2610	6066	38		

Table 13. Torsion angles [°] for **16j**.

F(1A)-C(15A)-C(16A)-C(17A)	-179.75(14)
O(5A)-C(5A)-C(6A)-C(7A)	-121.62(13)
O(5A)-C(5A)-C(6A)-C(18A)	60.18(16)
O(5A)-C(5A)-C(9A)-O(9A)	-4.39(16)
O(5A)-C(5A)-C(9A)-N(10A)	-125.57(11)
O(5A)-C(5A)-C(9A)-C(8A)	116.85(11)
O(8A)-C(8A)-C(9A)-O(9A)	-52.33(18)
O(8A)-C(8A)-C(9A)-N(10A)	70.46(17)
O(8A)-C(8A)-C(9A)-C(5A)	-175.97(13)
N(1A)-N(2A)-C(3A)-C(4A)	-0.34(14)
N(1A)-N(2A)-C(3A)-C(12A)	176.31(11)
N(2A)-N(1A)-C(11A)-N(10A)	175.54(13)
N(2A)-N(1A)-C(11A)-C(4A)	0.73(14)
N(2A)-C(3A)-C(4A)-C(5A)	-171.92(17)
N(2A)-C(3A)-C(4A)-C(11A)	0.74(14)
N(2A)-C(3A)-C(12A)-C(13A)	24.4(2)
N(2A)-C(3A)-C(12A)-C(17A)	-154.05(13)
N(10A)-C(19A)-C(20A)-C(21A)	179.22(12)
N(10A)-C(19A)-C(24A)-C(23A)	-178.78(12)
C(3A)-C(4A)-C(5A)-O(5A)	-62.1(2)
C(3A)-C(4A)-C(5A)-C(6A)	63.8(2)
C(3A)-C(4A)-C(5A)-C(9A)	174.41(17)
C(3A)-C(4A)-C(11A)-N(1A)	-0.96(15)
C(3A)-C(4A)-C(11A)-N(10A)	-176.73(11)
C(3A)-C(12A)-C(13A)-C(14A)	-178.76(13)
C(3A)-C(12A)-C(17A)-C(16A)	179.08(14)
C(4A)-C(3A)-C(12A)-C(13A)	-160.05(14)
C(4A)-C(3A)-C(12A)-C(17A)	21.5(2)
C(4A)-C(5A)-C(6A)-C(7A)	110.14(14)
C(4A)-C(5A)-C(6A)-C(18A)	-68.06(17)
C(4A)-C(5A)-C(9A)-O(9A)	119.21(11)
C(4A)-C(5A)-C(9A)-N(10A)	-1.97(12)
C(4A)-C(5A)-C(9A)-C(8A)	-119.55(10)
C(5A)-C(4A)-C(11A)-N(1A)	174.55(11)
C(5A)-C(4A)-C(11A)-N(10A)	-1.22(15)
C(5A)-C(6A)-C(7A)-C(8A)	1.94(16)
C(6A)-C(5A)-C(9A)-O(9A)	-123.18(12)
C(6A)-C(5A)-C(9A)-N(10A)	115.63(11)
C(6A)-C(5A)-C(9A)-C(8A)	-1.94(12)
C(6A)-C(7A)-C(8A)-O(8A)	175.75(14)
C(6A)-C(7A)-C(8A)-C(9A)	-3.24(16)
C(7A)-C(8A)-C(9A)-O(9A)	126.70(12)
C(7A)-C(8A)-C(9A)-N(10A)	-110.50(13)
C(7A)-C(8A)-C(9A)-C(5A)	3.06(13)
C(9A)-N(10A)-C(11A)-N(1A)	-174.93(13)
C(9A)-N(10A)-C(11A)-C(4A)	-0.17(15)
C(9A)-N(10A)-C(19A)-C(20A)	-127.89(13)
C(9A)-N(10A)-C(19A)-C(24A)	51.60(17)
C(9A)-C(5A)-C(6A)-C(7A)	0.15(14)
C(9A)-C(5A)-C(6A)-C(18A)	-178.05(12)

C(11A)-N(1A)-N(2A)-C(3A) -0.22(14)
C(11A)-N(10A)-C(9A)-O(9A) -123.09(11)
C(11A)-N(10A)-C(9A)-C(5A) 1.37(13)
C(11A)-N(10A)-C(9A)-C(8A) 113.22(12)
C(11A)-N(10A)-C(19A)-C(20A) 19.32(18)
C(11A)-N(10A)-C(19A)-C(24A) -161.18(12)
C(11A)-C(4A)-C(5A)-O(5A) 125.42(12)
C(11A)-C(4A)-C(5A)-C(6A) -108.71(13)
C(11A)-C(4A)-C(5A)-C(9A) 1.92(13)
C(12A)-C(3A)-C(4A)-C(5A) 12.0(3)
C(12A)-C(3A)-C(4A)-C(11A) -175.32(13)
C(12A)-C(13A)-C(14A)-C(15A) 0.0(2)
C(13A)-C(12A)-C(17A)-C(16A) 0.6(2)
C(13A)-C(14A)-C(15A)-F(1A) -179.94(14)
C(13A)-C(14A)-C(15A)-C(16A) 0.0(2)
C(14A)-C(15A)-C(16A)-C(17A) 0.3(2)
C(15A)-C(16A)-C(17A)-C(12A) -0.6(2)
C(17A)-C(12A)-C(13A)-C(14A) -0.3(2)
C(18A)-C(6A)-C(7A)-C(8A) 179.99(13)
C(19A)-N(10A)-C(9A)-O(9A) 28.57(16)
C(19A)-N(10A)-C(9A)-C(5A) 153.03(11)
C(19A)-N(10A)-C(9A)-C(8A) -95.12(14)
C(19A)-N(10A)-C(11A)-N(1A) 33.7(2)
C(19A)-N(10A)-C(11A)-C(4A) -151.58(12)
C(19A)-C(20A)-C(21A)-C(22A) -0.5(2)
C(20A)-C(19A)-C(24A)-C(23A) 0.7(2)
C(20A)-C(21A)-C(22A)-C(23A) 0.7(2)
C(21A)-C(22A)-C(23A)-C(24A) -0.3(2)
C(22A)-C(23A)-C(24A)-C(19A) -0.4(2)
C(24A)-C(19A)-C(20A)-C(21A) -0.3(2)
F(1B)-C(15B)-C(16B)-C(17B) 179.06(14)
O(5B)-C(5B)-C(6B)-C(7B)-120.48(12)
O(5B)-C(5B)-C(6B)-C(18B) 60.34(15)
O(5B)-C(5B)-C(9B)-O(9B) -8.87(16)
O(5B)-C(5B)-C(9B)-N(10B) -129.06(11)
O(5B)-C(5B)-C(9B)-C(8B)113.95(11)
O(8B)-C(8B)-C(9B)-O(9B) -49.81(18)
O(8B)-C(8B)-C(9B)-N(10B) 73.02(17)
O(8B)-C(8B)-C(9B)-C(5B)-173.78(13)
N(1B)-N(2B)-C(3B)-C(4B) -0.39(15)
N(1B)-N(2B)-C(3B)-C(12B) 175.83(11)
N(2B)-N(1B)-C(11B)-N(10B) 174.84(14)
N(2B)-N(1B)-C(11B)-C(4B) 0.02(14)
N(2B)-C(3B)-C(4B)-C(5B)-171.73(17)
N(2B)-C(3B)-C(4B)-C(11B) 0.36(14)
N(2B)-C(3B)-C(12B)-C(13B) 28.8(2)
N(2B)-C(3B)-C(12B)-C(17B) -147.63(13)
N(10B)-C(19B)-C(20B)-C(21B) 179.81(13)
N(10B)-C(19B)-C(24B)-C(23B) 179.90(13)
C(3B)-C(4B)-C(5B)-O(5B)-61.1(2)
C(3B)-C(4B)-C(5B)-C(6B) 64.3(2)
C(3B)-C(4B)-C(5B)-C(9B) 174.77(18)

C(3B)-C(4B)-C(11B)-N(1B)	-0.24(15)
C(3B)-C(4B)-C(11B)-N(10B)	-176.04(11)
C(3B)-C(12B)-C(13B)-C(14B)	-176.28(15)
C(3B)-C(12B)-C(17B)-C(16B)	175.68(13)
C(4B)-C(3B)-C(12B)-C(13B)	-156.25(15)
C(4B)-C(3B)-C(12B)-C(17B)	27.3(2)
C(4B)-C(5B)-C(6B)-C(7B)	110.38(13)
C(4B)-C(5B)-C(6B)-C(18B)	-68.81(16)
C(4B)-C(5B)-C(9B)-O(9B)	116.32(11)
C(4B)-C(5B)-C(9B)-N(10B)	-3.87(12)
C(4B)-C(5B)-C(9B)-C(8B)	-120.86(10)
C(5B)-C(4B)-C(11B)-N(1B)	174.97(11)
C(5B)-C(4B)-C(11B)-N(10B)	-0.83(16)
C(5B)-C(6B)-C(7B)-C(8B)	2.56(16)
C(6B)-C(5B)-C(9B)-O(9B)	-126.18(11)
C(6B)-C(5B)-C(9B)-N(10B)	113.63(11)
C(6B)-C(5B)-C(9B)-C(8B)	-3.36(12)
C(6B)-C(7B)-C(8B)-O(8B)	173.75(14)
C(6B)-C(7B)-C(8B)-C(9B)	-4.84(15)
C(7B)-C(8B)-C(9B)-O(9B)	128.84(12)
C(7B)-C(8B)-C(9B)-N(10B)	-108.33(12)
C(7B)-C(8B)-C(9B)-C(5B)	4.87(13)
C(9B)-N(10B)-C(11B)-N(1B)	-176.65(13)
C(9B)-N(10B)-C(11B)-C(4B)	-1.89(15)
C(9B)-N(10B)-C(19B)-C(20B)	-124.35(14)
C(9B)-N(10B)-C(19B)-C(24B)	55.63(18)
C(9B)-C(5B)-C(6B)-C(7B)	0.72(14)
C(9B)-C(5B)-C(6B)-C(18B)	-178.46(11)
C(11B)-N(1B)-N(2B)-C(3B)	0.23(14)
C(11B)-N(10B)-C(9B)-O(9B)	-119.97(11)
C(11B)-N(10B)-C(9B)-C(5B)	3.57(13)
C(11B)-N(10B)-C(9B)-C(8B)	115.21(12)
C(11B)-N(10B)-C(19B)-C(20B)	22.22(18)
C(11B)-N(10B)-C(19B)-C(24B)	-157.81(13)
C(11B)-C(4B)-C(5B)-O(5B)	127.07(12)
C(11B)-C(4B)-C(5B)-C(6B)	-107.58(13)
C(11B)-C(4B)-C(5B)-C(9B)	2.89(13)
C(12B)-C(3B)-C(4B)-C(5B)	12.8(3)
C(12B)-C(3B)-C(4B)-C(11B)	-175.12(14)
C(12B)-C(13B)-C(14B)-C(15B)	0.3(3)
C(13B)-C(12B)-C(17B)-C(16B)	-0.8(2)
C(13B)-C(14B)-C(15B)-F(1B)	-179.65(15)
C(13B)-C(14B)-C(15B)-C(16B)	-0.2(3)
C(14B)-C(15B)-C(16B)-C(17B)	-0.4(3)
C(15B)-C(16B)-C(17B)-C(12B)	0.9(2)
C(17B)-C(12B)-C(13B)-C(14B)	0.2(2)
C(18B)-C(6B)-C(7B)-C(8B)	-178.33(13)
C(19B)-N(10B)-C(9B)-O(9B)	30.87(16)
C(19B)-N(10B)-C(9B)-C(5B)	154.41(11)
C(19B)-N(10B)-C(9B)-C(8B)	-93.95(14)
C(19B)-N(10B)-C(11B)-N(1B)	32.6(2)
C(19B)-N(10B)-C(11B)-C(4B)	-152.67(12)

C(19B)-C(20B)-C(21B)-C(22B)	0.3(2)
C(20B)-C(19B)-C(24B)-C(23B)	-0.1(2)
C(20B)-C(21B)-C(22B)-C(23B)	-0.1(3)
C(21B)-C(22B)-C(23B)-C(24B)	-0.2(3)
C(22B)-C(23B)-C(24B)-C(19B)	0.3(3)
C(24B)-C(19B)-C(20B)-C(21B)	-0.2(2)

Table 14. Hydrogen bonds for **16j** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5A)-H(5A)...N(1B)#1	0.93(4)	1.84(4)	2.7541(15)	168(3)
O(5A)-H(5A)...N(2B)#1	0.93(4)	2.52(4)	3.2569(16)	136(3)
O(9A)-H(9A)...O(5A)#2	0.91(3)	1.76(3)	2.6574(14)	169(3)
N(2A)-H(2A)...O(9B)	0.86(2)	1.93(2)	2.7724(15)	166(2)
O(5B)-H(5B)...N(1A)	0.94(3)	1.79(3)	2.7016(15)	163(2)
O(9B)-H(9B)...O(5B)#3	0.90(3)	1.79(3)	2.6644(14)	163(2)
N(2B)-H(2B)...O(9A)#4	0.95(3)	1.80(3)	2.7369(15)	169(2)

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z #2 -x,-y+1,-z+2 #3 -x+1,-y+1,-z+1
#4 x+1,y,z