Supplementary data

Synthesis of allomaltol containing pyridazines and their photochemical transformation into substituted benzo[*h*]pyrano[2,3-*f*]cinnolin-8-ones

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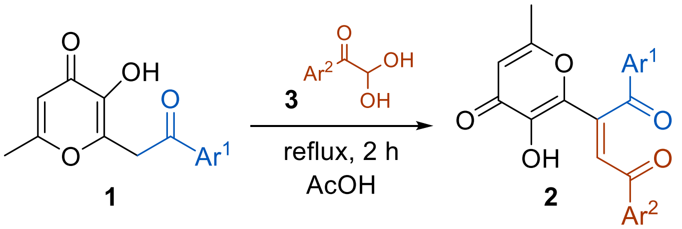
1. General information

General information. Unless otherwise stated, all starting chemicals were commercially available and were used as received. The starting compounds **1** 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 AV 400 (400 MHz), and Bruker DRX 500 (500 MHz) in DMSO-d_6. Chemical shifts (ppm) are given relative to solvents signals DMSO-d_6: 2.50 ppm, $CDCl_3$: 7.26 ppm (^{1}H NMR), 39.52 ppm and 77.16 ppm respectively (^{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).

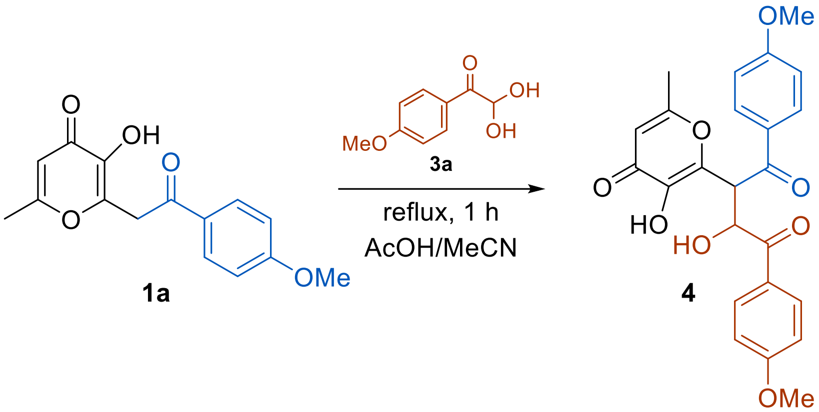
General procedure for the synthesis of compound 2.



1 2

A mixture of compound **1** (1 mmol), arylglyoxal **3** (1.2 mmol) in AcOH (5 ml) was refluxed for 2 h. Then the resulting solution was evaporated in vacuo, and the residue was recrystallized from EtOH (3 ml). The obtained product was filtered off and washed with EtOH (3 x 2 ml).

Experimental procedure for the synthesis of compound 4.

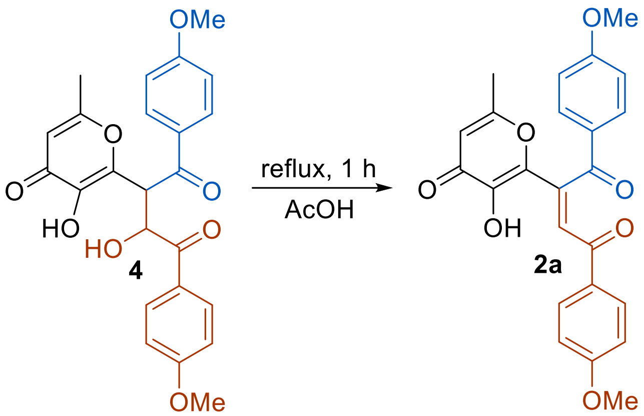


1a 4

A mixture of compound **1a** (1 mmol, 0.27 g), (4-methoxyphenyl)glyoxal **3a** (1.2 mmol, 0.22 g) and AcOH (1.1 mmol, 0.07 g) in MeCN (5 ml) was refluxed for 1 h. Then the resulting solution was evaporated in vacuo, and the residue was recrystallized from EtOH (3 ml). The obtained product was filtered off and washed with EtOH (3 x 2 ml).

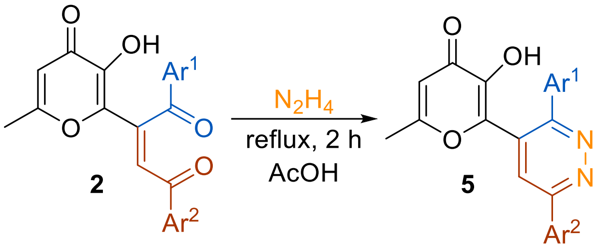
Experimental procedure for the synthesis of compound 2a from compound 4.

[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.



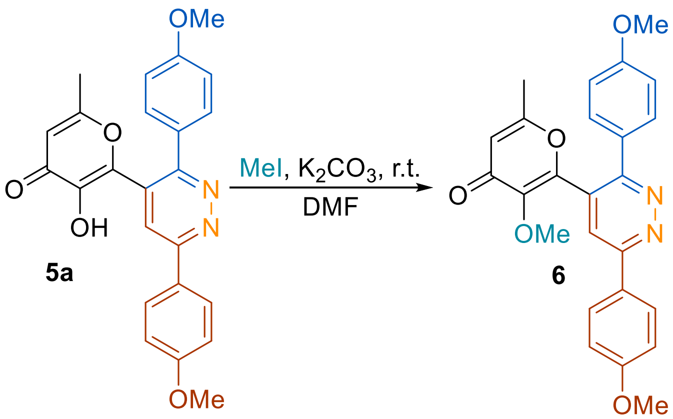
The solution of compound **4** (1 mmol, 0.44 g) in AcOH (5 ml) was refluxed for 1 h. The resulting solution was evaporated in vacuo and the residue was recrystallized from EtOH (2 ml). The resulting precipitate was filtered off and washed with EtOH (3 x 2 ml).

General procedure for the synthesis of compound 5.



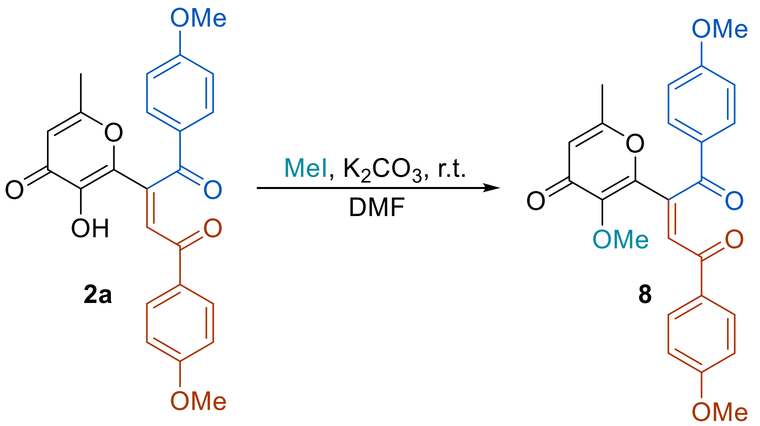
The mixture of compound **2** (0.5 mmol) and hydrazine hydrate (2 mmol, 0.1 g) in AcOH (5 ml) was refluxed for 2 h. The resulting solution was evaporated in vacuo and the residue was recrystallized from EtOH (2 ml). The resulting precipitate was filtered off and washed with EtOH (3 x 2 ml).

Experimental procedure for the synthesis of compound 6.



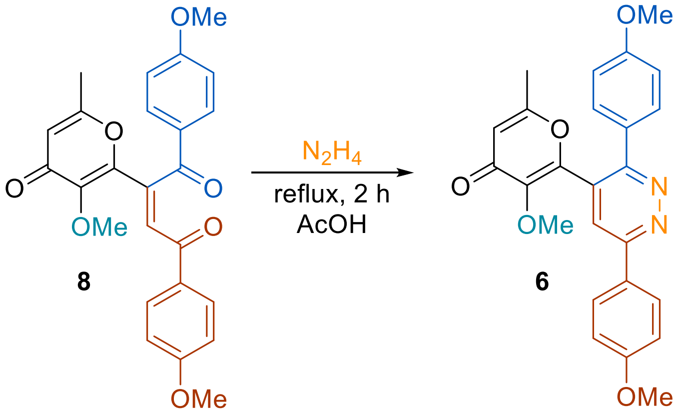
A mixture of compound **5a** (1 mmol, 0.42 g), K_2CO_3 (3 mmol, 0.41 g) and MeI (3 mmol, 0.43 g) in DMF (6 ml) was stirred for 10 h. The resulting solution was evaporated in vacuo and H_2O (20 ml) was added to obtained residue. The resulting precipitate was filtered off and washed with H_2O (3 x 5 ml).

Experimental procedure for the synthesis of compound 8.



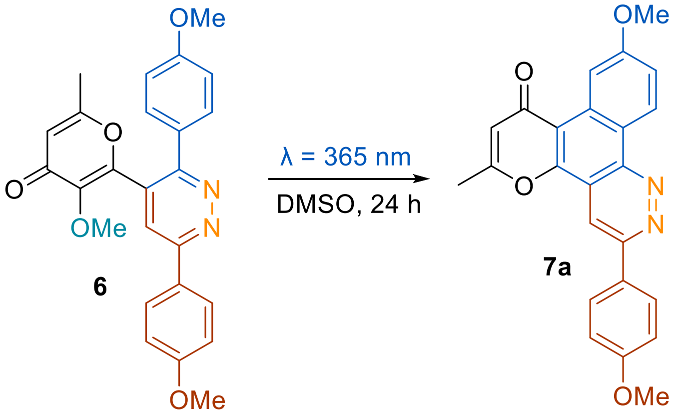
A mixture of compound **2a** (1 mmol, 0.42 g), K_2CO_3 (3 mmol, 0.41 g) and MeI (3 mmol, 0.43 g) in DMF (6 ml) was stirred for 10 h. The resulting solution was evaporated in vacuo and H_2O (20 ml) was added to obtained residue. The resulting precipitate was filtered off and washed with H_2O (3 x 5 ml).

Experimental procedure for the synthesis of compound 6 from compound 8.



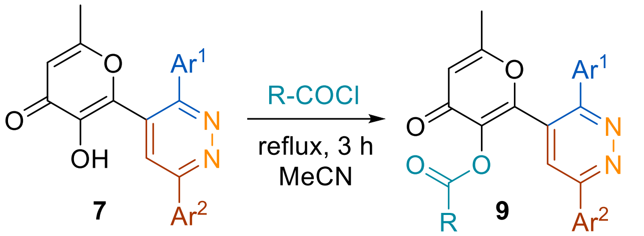
The mixture of compound **8** (0.5 mmol, 0.14 g) and hydrazine hydrate (2 mmol, 0.1 g) in AcOH (5 ml) was refluxed for 2 h. The resulting solution was evaporated in vacuo and the residue was recrystallized from EtOH (2 ml). The resulting precipitate was filtered off and washed with EtOH (3 x 2 ml).

Experimental procedure for the synthesis of compound 7a from compound 6.



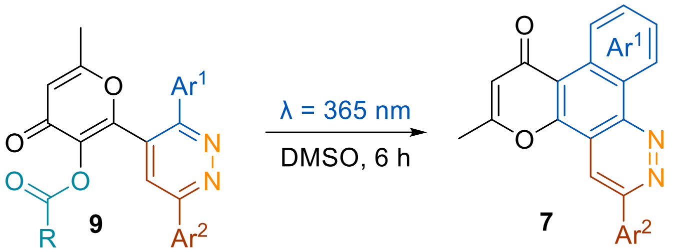
A solution of compound **6** (0.5 mmol, 0.22 g) in DMSO (10 ml) was irradiated in common glassware with a Vilber Lourmat VL-6.LM (365 nm, 6 W) for 24 h. The corresponding photoproduct was filtered off and washed with acetone (3 x 15 ml).

General procedure for the synthesis of compounds 9



The mixture of compound **7** (1 mmol) and corresponding acyl chloride (2 mmol) in MeCN (6 ml) was refluxed for 3 h. Then the resulting solution was evaporated in vacuo and the residue was triturated with Et_2O.

General procedure for the synthesis of photoproducts 7



A solution of compound **9** (0.5 mmol) in DMSO (10 ml) was irradiated in common glassware with a Vilber Lourmat VL-6.LM (365 nm, 6 W) for 6 h. The precipitated photoproduct was filtered off and washed with acetone (3 x 15 ml).

2. Characterization data of compounds 2

(Z)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-1,4-bis(4-methoxyphenyl)but-2-ene-1,4-dione (**2a**).
Yellow powder; yield 73% (0.31 g); m.p. 181-183°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.29 (s, 1H), 7.98 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 191.78, 186.59, 173.85, 165.80, 163.67, 162.94, 145.10, 144.73, 141.42, 131.02, 130.92, 130.21, 129.82, 129.64, 124.30, 114.29, 113.92, 110.97, 55.68, 55.50, 19.41. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{21}O_7$ [M+H]$^+$ 421.1282; Found: 421.1280.
(Z)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-1-(4-methoxyphenyl)-4-(p-tolyl)but-2-ene-1,4-dione (**2b**).
Yellow powder; yield 71% (0.29 g); m.p. 176-178°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.35 (s, 1H), 7.98 (s, 1H), 7.91 – 7.76 (m, 4H), 7.35 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.33 (s, 1H), 3.80 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 191.6, 187.8, 173.8, 165.8, 162.9, 145.2, 145.1, 144.3, 141.3, 134.4, 130.2, 129.5, 128.5, 124.2, 113.9, 110.9, 55.5, 21.2, 19.4. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{21}O_6$ [M+H]$^+$ 405.1333; Found: 405.1339.
(Z)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-1-(4-methoxyphenyl)-4-phenylbut-2-ene-1,4-dione (**2c**).
Yellow powder; yield 68% (0.27 g); m.p. 187-189°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.39 (s, 1H), 8.00 (s, 1H), 7.97 – 7.91 (m, 2H), 7.87 – 7.76 (m, 2H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.05 – 6.94 (m, 2H), 6.33 (s, 1H), 3.80 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 191.54, 188.36, 173.77, 165.79, 162.97, 145.27, 141.19, 136.83, 133.70, 130.20, 129.45, 128.97, 128.34, 123.99, 113.91, 110.92, 55.46, 19.35. HRMS (ESI-TOF) *m/z*: Calcd for $C_{22}H_{19}O_6$ [M+H]$^+$ 391.1176; Found: 391.1180.
(Z)-4-(4-bromophenyl)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-1-(4-methoxyphenyl)but-2-ene-1,4-dione (**2d**).
Yellow powder; yield 78% (0.37 g); m.p. 172-174°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.43 (s, 1H), 7.94 (s, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.83 – 7.73 (m, 4H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.34 (s, 1H), 3.80 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 165.1, 160.1, 156.5, 156.3, 143.4, 142.7, 135.4, 130.3, 129.6, 129.2, 128.1, 126.9, 124.8, 113.8, 111.6, 55.3, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{18}BrO_6$ [M+H]$^+$ 469.0281; Found: 469.0287.
(Z)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-4-(4-methoxyphenyl)-1-phenylbut-2-ene-1,4-dione (**2e**).
Yellow powder; yield 69% (0.27 g); m.p. 194-196°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.37 (s, 1H), 8.01 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.52 (m, 1H), 7.52 – 7.41 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.33 (s, 1H), 3.85 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 193.2, 186.5, 173.8, 165.8, 163.7, 161.3, 145.1, 144.8, 141.2, 136.4, 132.8, 131.0, 129.7, 128.6, 127.9, 124.3, 114.3, 111.0, 55.7, 19.4. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{19}O_6$ [M+H]$^+$ 391.1176; Found: 391.1173.
(Z)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-1-phenyl-4-(p-tolyl)but-2-ene-1,4-dione (**2f**).
Yellow powder; yield 64% (0.24 g); m.p. 185-187°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.37 (s, 1H), 8.01 (s, 1H), 7.89 – 7.81 (m, 4H), 7.63 – 7.52 (m, 1H), 7.52 – 7.41 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 6.33 (s, 1H), 2.38 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 193.2, 187.7, 173.9, 165.9, 145.2, 144.5, 141.1, 136.4, 134.3, 132.9, 129.6, 128.6, 128.6, 127.9, 124.1, 111.0, 21.3, 19.4. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{19}O_5$ [M+H]$^+$ 375.1227; Found: 375.1231.
(Z)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-1,4-diphenylbut-2-ene-1,4-dione (**2g**).
Pale brown powder; yield 63% (0.23 g); m.p. 201-203°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.46 (s, 1H), 8.02 (s, 1H), 8.00 – 7.92 (m, 2H), 7.90 – 7.81 (m, 2H), 7.73 – 7.63 (m, 1H), 7.62 – 7.54 (m, 3H), 7.54 – 7.43 (m, 2H), 6.34 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 193.1, 188.3, 173.8, 165.9, 145.5, 145.3, 141.0, 136.7, 136.3, 133.8, 133.0, 129.0, 128.6, 128.4, 127.9, 124.0, 111.0, 19.4. HRMS (ESI-TOF) *m/z*: Calcd for $C_{22}H_{17}O_5$ [M+H]$^+$ 361.1071; Found: 361.1084.
(Z)-1-(4-fluorophenyl)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-4-(4-methoxyphenyl)but-2-ene-1,4-dione (**2h**).
Yellow powder; yield 74% (0.30 g); m.p. 179-181°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.02 – 7.86 (m, 5H), 7.35 – 7.23 (m, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.33 (s, 1H), 3.85 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 191.9, 186.5, 173.8, 165.9, 164.7 (d, J_{CF} = 251.1 Hz), 163.8, 145.1, 144.4, 141.1, 133.4 (d, J_{CF} = 2.9 Hz), 131.0, 130.7 (d, J_{CF} = 9.4 Hz), 129.6, 124.2, 115.7 (d, J_{CF} = 22.1 Hz), 114.3, 111.0, 55.7, 19.4. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{18}FO_6$ [M+H]$^+$ 409.1082; Found: 409.1088.
(Z)-1-(4-fluorophenyl)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-4-(3-methoxyphenyl)but-2-ene-1,4-dione (**2i**).

Yellow powder; yield 62% (0.25 g); m.p. 166-168°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.98 (s, 1H), 7.97 – 7.88 (m, 2H), 7.60 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.38 (s, 1H), 7.36 – 7.21 (m, 3H), 6.34 (s, 1H), 3.80 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 191.8, 188.0, 173.8, 166.0, 164.8 (d, J_{CF} = 251.2 Hz), 159.6, 145.4, 145.3, 140.9, 138.1, 133.2 (d, J_{CF} = 2.6 Hz), 130.8 (d, J_{CF} = 9.4 Hz), 130.2, 123.9, 121.1, 120.0, 115.8 (d, J_{CF} = 22.2 Hz), 112.7, 111.0, 55.4, 19.4. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{18}FO_5$ [M+H]$^+$ 409.1082; Found: 409.1087.

(Z)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-1-(4-methoxyphenyl)-4-(thiophen-2-yl)but-2-ene-1,4-dione (**2j**).

Pale brown powder; yield 67% (0.27 g); m.p. 201-203°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.42 (s, 1H), 8.09 (s, 2H), 7.94 – 7.70 (m, 3H), 7.30 (s, 1H), 7.03 – 6.97 (m, 2H), 6.33 (s, 1H), 3.81 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.8, 165.9, 163.0, 145.5, 144.6, 140.9, 136.6, 134.0, 130.2, 129.5, 129.2, 122.9, 114.0, 111.0, 55.5, 19.4. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{17}O_6S$ [M+H]$^+$ 397.0740; Found: 397.0737.

(Z)-4-(4-bromophenyl)-1-(2,6-dimethoxyphenyl)-2-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)but-2-ene-1,4-dione (**2k**).

Yellow powder; yield 70% (0.35 g); m.p. 211-213°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.71 – 7.57 (m, 4H), 7.53 – 7.40 (m, 2H), 6.76 (d, J = 8.3 Hz, 2H), 6.15 (s, 1H), 3.71 – 3.65 (m, 6H), 1.71 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.5, 163.3, 158.7, 151.4, 145.6, 141.8, 140.8, 132.0, 131.6, 129.0, 125.5, 120.7, 117.3, 110.4, 108.7, 106.7, 104.0, 55.8, 18.3. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{20}BrO_7$ [M+H]$^+$ 499.0387; Found: 499.0381.

3. Characterization data of compounds 5

2-(3,6-bis(4-methoxyphenyl)pyridazin-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**5a**).
Grey powder; yield 84% (0.18 g); m.p. 220-222°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.57 (s, 1H), 8.41 (s, 1H), 8.19 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 165.1, 161.1, 160.0, 156.1, 155.7, 143.3, 142.9, 129.5, 129.2, 128.3, 128.0, 127.6, 124.0, 114.6, 113.8, 111.6, 55.4, 55.3, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{21}N_2O_5$ [M+H]$^+$ 417.1445; Found: 417.1458.
3-hydroxy-2-(3-(4-methoxyphenyl)-6-(p-tolyl)pyridazin-4-yl)-6-methyl-4H-pyran-4-one (**5b**).
Grey powder; yield 79% (0.16 g); m.p. 231-233°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.62 (s, 1H), 8.45 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.32 (s, 1H), 3.81 (s, 3H), 2.41 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 165.1, 160.1, 156.4, 156.1, 143.4, 142.8, 140.1, 132.6, 129.8, 129.6, 129.2, 128.1, 126.7, 124.5, 113.8, 111.6, 55.3, 20.9, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{21}N_2O_4$ [M+H]$^+$ 401.1496; Found: 401.1489.
3-hydroxy-2-(3-(4-methoxyphenyl)-6-phenylpyridazin-4-yl)-6-methyl-4H-pyran-4-one (**5c**).
White powder; yield 78% (0.15 g); m.p. 245-247°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.66 (s, 1H), 8.49 (s, 1H), 8.26 – 8.17 (m, 2H), 7.65 – 7.56 (m, 3H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.33 (s, 1H), 3.81 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 165.1, 160.1, 156.5, 156.3, 143.4, 142.7, 135.4, 130.3, 129.6, 129.2, 128.1, 126.9, 124.8, 113.8, 111.6, 55.3, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{19}N_2O_4$ [M+H]$^+$ 387.1339; Found: 387.1345.
2-(6-(4-bromophenyl)-3-(4-methoxyphenyl)pyridazin-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**5d**).
Pale brown powder; yield 87% (0.20 g); m.p. 225-227°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.66 (s, 1H), 8.53 (s, 1H), 8.18 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.33 (s, 1H), 3.81 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 165.1, 160.2, 156.5, 155.6, 143.5, 142.6, 134.6, 132.2, 129.7, 129.0, 128.9, 128.2, 124.8, 124.1, 113.9, 111.7, 55.3, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{18}BrN_2O_4$ [M+H]$^+$ 465.0444; Found: 465.0449.
3-hydroxy-2-(6-(4-methoxyphenyl)-3-phenylpyridazin-4-yl)-6-methyl-4H-pyran-4-one (**5e**).
White powder; yield 82% (0.16 g); m.p. 238-240°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.71 (s, 1H), 8.50 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.45 (m, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.31 (s, 1H), 3.88 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 165.0, 161.2, 156.6, 156.1, 143.8, 142.4, 137.2, 129.0, 128.5, 128.4, 128.3, 128.1, 127.6, 123.9, 114.7, 111.5, 55.4, 18.8. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{19}N_2O_4$ [M+H]$^+$ 387.1339; Found: 387.1333.
3-hydroxy-6-methyl-2-(3-phenyl-6-(p-tolyl)pyridazin-4-yl)-4H-pyran-4-one (**5f**).
Yellow powder; yield 76% (0.14 g); m.p. 236-238°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.71 (s, 1H), 8.51 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 2H), 7.58 – 7.38 (m, 7H), 6.29 (s, 1H), 2.42 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 165.0, 156.9, 156.5, 142.3, 140.3, 137.1, 132.5, 129.8, 129.0, 128.5, 128.32, 128.1, 126.8, 124.4, 111.5, 21.0, 18.8. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{19}N_2O_3$ [M+H]$^+$ 371.1390; Found: 371.1388.
2-(3,6-diphenylpyridazin-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**5g**).
White powder; yield 77% (0.13 g); m.p. 271-273°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.75 (s, 1H), 8.56 (s, 1H), 8.26 – 8.18 (m, 2H), 7.65 – 7.44 (m, 8H), 6.30 (s, 1H), 1.90 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.7, 165.0, 157.0, 156.7, 143.9, 142.2, 137.1, 135.4, 130.4, 129.2, 129.1, 128.9, 128.3, 128.2, 127.0, 124.7, 111.6, 18.8. HRMS (ESI-TOF) *m/z*: Calcd for $C_{22}H_{17}N_2O_3$ [M+H]$^+$ 357.1234; Found: 357.1241.
2-(3-(4-fluorophenyl)-6-(4-methoxyphenyl)pyridazin-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**5h**).
Grey powder; yield 81% (0.16 g); m.p. 251-253°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.48 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 2H), 7.66 – 7.55 (m, 2H), 7.37 – 7.26 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.32 (s, 1H), 3.87 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.7, 165.2, 162.7 (d, J_{CF} = 246.4 Hz), 161.3, 156.7, 155.3, 143.6, 142.4, 133.6 (d, J_{CF} = 3.3 Hz), 130.4 (d, J_{CF} = 8.5 Hz), 128.6, 128.5, 127.6, 124.0, 115.4 (d, J_{CF} = 21.7 Hz), 114.7, 111.7, 55.5, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{18}FN_2O_4$ [M+H]$^+$ 405.1245; Found: 405.1242.
2-(3-(4-fluorophenyl)-6-(3-methoxyphenyl)pyridazin-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**5i**).
White powder; yield 74% (0.15 g); m.p. 220-222°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.74 (s, 1H), 8.55 (s, 1H), 7.82 – 7.74 (m, 2H), 7.67 – 7.57 (m, 2H), 7.57 – 7.46 (m, 1H), 7.38 – 7.26 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 6.32 (s, 1H), 3.87 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 165.2, 162.7 (d, J_{CF} = 246.6 Hz), 159.9, 156.9, 156.0, 143.7, 142.2, 136.7, 133.5 (d, J_{CF} = 3.0 Hz), 130.6, 130.5, 130.4, 128.6, 125.0,

119.3, 116.3, 115.4 (d, J_{CF} = 21.8 Hz), 112.1, 111.7, 55.4, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{18}FN_2O_4$ $[M+H]^+$ 405.1245; Found: 405.1246.

3-hydroxy-2-(3-(4-methoxyphenyl)-6-(thiophen-2-yl)pyridazin-4-yl)-6-methyl-4H-pyran-4-one (**5j**). Yellow powder; yield 78% (0.15 g); m.p. 248-250°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.67 (s, 1H), 8.49 (s, 1H), 7.99 (s, 1H), 7.81 (d, *J* = 4.8 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.27 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.33 (s, 1H), 3.80 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.6, 168.0, 165.2, 160.1, 156.2, 152.8, 143.3, 142.6, 139.6, 130.3, 129.5, 129.0, 128.7, 128.2, 127.9, 123.4, 113.9, 111.7, 55.3, 20.4, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{17}N_2O_4S$ $[M+H]^+$ 393.0904; Found: 393.0911.

2-(6-(4-bromophenyl)-3-(2,6-dimethoxyphenyl)pyridazin-4-yl)-3-hydroxy-6-methyl-4H-pyran-4-one (**5k**). White powder; yield 80% (0.20 g); m.p. 252-254°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.28 (s, 1H), 7.71 – 7.57 (m, 4H), 7.52 – 7.40 (m, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.14 (s, 1H), 3.71 – 3.65 (m, 6H), 1.71 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.5, 163.3, 158.7, 151.4, 145.6, 141.8, 140.8, 132.0, 131.7, 129.0, 125.5, 120.7, 117.3, 110.4, 108.7, 106.7, 104.0, 55.8, 18.3. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{20}BrN_2O_5$ $[M+H]^+$ 495.0550; Found: 495.0558.

4. Characterization data of compounds 7

10-methoxy-3-(4-methoxyphenyl)-6-methyl-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7a**).
Yellow powder; yield 87% (0.18 g); m.p. 300+°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (d, J = 2.7 Hz, 1H), 9.45 (d, J = 9.0 Hz, 1H), 8.43 (s, 1H), 8.23 (d, J = 8.8 Hz, 2H), 7.39 (dd, J = 9.1, 2.7 Hz, 1H), 7.10 (d, J = 8.8 Hz, 2H), 6.39 (s, 1H), 4.02 (s, 3H), 3.92 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.2, 163.7, 161.8, 161.4, 155.2, 153.1, 147.1, 131.2, 128.9, 128.6, 125.4, 121.2, 118.4, 118.3, 115.3, 114.7, 113.7, 109.0, 55.7, 55.6, 19.9. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{19}N_2O_4$ $[M+H]^+$ 399.1339; Found: 399.1333.
10-methoxy-6-methyl-3-(p-tolyl)-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7b**).
Orange powder; yield 85% (0.16 g); m.p. 300+°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.50 (d, J = 2.6 Hz, 1H), 9.41 (d, J = 9.0 Hz, 1H), 8.40 (s, 1H), 8.14 (d, J = 7.9 Hz, 2H), 7.41 – 7.31 (m, 3H), 6.35 (s, 1H), 4.00 (s, 3H), 2.53 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.0, 164.8, 163.6, 162.1, 140.3, 133.9, 131.4, 130.1, 127.2, 125.6, 118.4, 115.3, 114.1, 109.4, 55.8, 21.5, 19.8. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{19}N_2O_3$ $[M+H]^+$ 383.1390; Found: 383.1391.
10-methoxy-6-methyl-3-phenyl-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7c**).
White powder; yield 82% (0.15 g); m.p. 300+°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (d, J = 2.7 Hz, 1H), 9.51 (d, J = 9.1 Hz, 1H), 8.56 (s, 1H), 8.37 – 8.28 (m, 2H), 7.70 – 7.53 (m, 3H), 7.43 (dd, J = 9.0, 2.7 Hz, 1H), 6.43 (s, 1H), 4.06 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 163.7, 161.9, 155.5, 153.0, 147.4, 136.4, 131.4, 130.1, 129.3, 127.3, 125.6, 121.1, 118.4, 118.2, 115.3, 114.6, 109.0, 55.7, 19.9. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{17}N_2O_3$ $[M+H]^+$ 369.1234; Found: 369.1241.
3-(4-bromophenyl)-10-methoxy-6-methyl-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7d**).
Yellow powder; yield 86% (0.19 g); m.p. 300+°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.57 (d, J = 2.6 Hz, 1H), 9.46 (d, J = 9.1 Hz, 1H), 8.50 (s, 1H), 8.16 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.40 (dd, J = 9.2, 2.6 Hz, 1H), 6.41 (s, 1H), 4.03 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.63, 128.84, 115.45, 109.45, 19.85. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{16}BrN_2O_3$ $[M+H]^+$ 447.0339; Found: 447.0342.
3-(4-methoxyphenyl)-6-methyl-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7e**).
Yellow powder; yield 84% (0.16 g); m.p. 300+°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.02 (d, J = 7.5 Hz, 1H), 9.63 (d, J = 7.4 Hz, 1H), 8.59 (s, 1H), 8.30 (d, J = 8.4 Hz, 2H), 7.89 – 7.81 (m, 1H), 7.13 (d, J = 8.4 Hz, 2H), 6.47 (s, 1H), 3.93 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 163.7, 161.6, 156.2, 152.7, 147.3, 130.9, 129.4, 128.8, 128.8, 128.7, 127.8, 127.5, 124.0, 119.8, 118.8, 115.5, 114.8, 113.8, 55.6, 20.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{17}N_2O_3$ $[M+H]^+$ 369.1234; Found: 369.1240.
6-methyl-3-(p-tolyl)-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7f**).
Yellow powder; yield 83% (0.15 g); m.p. 300+°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 – 9.91 (m, 1H), 9.61 – 9.52 (m, 1H), 8.51 (s, 0H), 8.23 – 8.14 (m, 2H), 7.88 – 7.74 (m, 2H), 7.39 (d, J = 7.8 Hz, 2H), 6.40 (s, 1H), 2.55 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.0, 163.7, 156.3, 152.5, 147.4, 140.6, 133.4, 130.9, 130.1, 129.4, 128.6, 127.7, 127.4, 127.2, 124.0, 119.7, 118.7, 115.4, 114.2, 21.6, 20.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{17}N_2O_2$ $[M+H]^+$ 353.1285; Found: 353.1287.
6-methyl-3-phenyl-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7g**).
Yellow powder; yield 78% (0.13 g); m.p. 300+°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.96 – 9.87 (m, 1H), 9.56 – 9.47 (m, 1H), 8.50 (s, 1H), 8.28 (d, J = 7.3 Hz, 2H), 7.85 – 7.71 (m, 2H), 7.66 – 7.49 (m, 3H), 6.36 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 163.7, 156.2, 152.3, 147.4, 136.2, 131.0, 130.3, 129.4, 128.6, 127.7, 127.4, 127.2, 124.0, 119.5, 118.6, 115.3, 114.5, 19.9. HRMS (ESI-TOF) *m/z*: Calcd for $C_{22}H_{15}N_2O_2$ $[M+H]^+$ 339.1128; Found: 339.1138.
10-fluoro-3-(4-methoxyphenyl)-6-methyl-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7h**).
Yellow powder; yield 86% (0.17 g); m.p. 300+°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 – 9.75 (m, 1H), 9.68 – 9.57 (m, 1H), 8.59 (s, 1H), 8.29 (d, J = 8.7 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.14 (d, J = 8.7 Hz, 2H), 6.48 (s, 1H), 3.94 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 151.8, 147.7, 146.9, 128.8, 126.4, 115.5, 114.9, 113.8, 113.5, 55.7, 20.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{16}FN_2O_3$ $[M+H]^+$ 387.1139; Found: 387.1141.
10-fluoro-3-(3-methoxyphenyl)-6-methyl-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7i**).
White powder; yield 80% (0.16 g); m.p. 300+°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 – 9.76 (m, 1H), 9.64 – 9.58 (m, 1H), 8.64 (s, 1H), 7.97 (s, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.14 – 7.09 (m, 1H), 6.47 (s, 1H), 3.97 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.7, 164.5 (d, J_{CF} = 249.1 Hz), 164.1, 164.03 160.6, 156.1, 153.3, 147.3, 137.5, 131.4 (d, J_{CF} = 11.7 Hz), 130.4, 130.4, 126.5 (d, J_{CF} = 9.4 Hz),

124.0, 119.6, 119.3, 117.3 (d, J_{CF} = 23.6 Hz), 116.4, 115.5, 115.1, 115.0, 113.7 (d, J_{CF} = 26.4 Hz), 112.7, 112.6, 55.7, 20.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{23}H_{16}FN_2O_3$ $[M+H]^+$ 387.1139; Found: 387.1133.

10-methoxy-6-methyl-3-(thiophen-2-yl)-8H-benzo[h]pyrano[2,3-f]cinnolin-8-one (**7j**).

Yellow powder; yield 82% (0.16 g); m.p. 300+°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.48 (d, *J* = 2.7 Hz, 1H), 9.35 (d, *J* = 9.1 Hz, 1H), 8.30 (s, 1H), 7.80 (d, *J* = 3.8 Hz, 1H), 7.54 (d, *J* = 5.0 Hz, 1H), 7.35 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.21 (t, *J* = 4.4 Hz, 1H), 6.36 (s, 1H), 4.00 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.0, 163.7, 161.9, 152.7, 151.4, 147.2, 141.0, 131.2, 129.2, 128.4, 126.1, 125.4, 121.1, 118.4, 118.3, 118.1, 115.3, 112.7, 109.0, 55.7, 19.9. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{15}N_2O_3S$ $[M+H]^+$ 375.0798; Found: 375.0801.

5. Characterization data of compounds 9

2-(3,6-bis(4-methoxyphenyl)pyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl hexanoate (**9a**).
Yellow powder; yield 74% (0.38 g); m.p. 219-221°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.41 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.44 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 2.35 (t, *J* = 7.1 Hz, 2H), 2.10 (s, 3H), 1.36 (p, *J* = 7.2 Hz, 2H), 1.09 – 0.89 (m, 4H), 0.64 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.7, 169.8, 166.5, 161.3, 160.4, 156.1, 155.3, 153.8, 137.6, 129.7, 128.3, 128.2, 127.2, 126.3, 123.9, 114.7, 114.1, 55.4, 55.3, 32.8, 30.2, 24.0, 21.6, 18.9, 13.6. HRMS (ESI-TOF) *m/z*: Calcd for $C_{30}H_{31}N_2O_6$ [M+H]$^+$ 515.2177; Found: 515.2184.
2-(3-(4-methoxyphenyl)-6-(p-tolyl)pyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl acetate (**9b**).
White powder; yield 80% (0.35 g); m.p. 241-243°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.43 (s, 1H), 8.14 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.44 (s, 1H), 3.82 (s, 3H), 2.41 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.6, 167.1, 166.7, 160.5, 156.6, 155.8, 153.6, 140.5, 137.7, 132.2, 129.9, 129.8, 128.3, 126.8, 126.5, 124.4, 114.2, 114.1, 55.3, 21.0, 19.9, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{26}H_{23}N_2O_5$ [M+H]$^+$ 443.1601; Found: 443.1595.
2-(3-(4-methoxyphenyl)-6-(p-tolyl)pyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl pivalate (**9b'**).
Grey powder; yield 86% (0.42 g); m.p. 200-202°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.53 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 2H), 7.71 – 7.62 (m, 2H), 7.58 – 7.48 (m, 3H), 7.42 (d, *J* = 7.9 Hz, 2H), 6.43 (s, 1H), 2.41 (s, 3H), 1.99 (s, 3H), 1.07 – 1.01 (m, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.5, 171.6, 166.3, 156.7, 156.1, 153.2, 140.7, 138.0, 135.9, 131.9, 129.9, 129.6, 128.6, 128.3, 126.7, 126.6, 124.2, 114.1, 38.3, 26.4, 20.9, 18.7. HRMS (ESI-TOF) *m/z*: Calcd for $C_{29}H_{29}N_2O_5$ [M+H]$^+$ 485.2071; Found: 485.2075.
2-(3-(4-methoxyphenyl)-6-phenylpyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl pivalate (**9c**).
White powder; yield 81% (0.38 g); m.p. 213-215°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.92 (s, 1H), 8.71 – 8.62 (m, 2H), 8.11 – 7.95 (m, 5H), 7.49 (d, *J* = 8.4 Hz, 2H), 6.86 (s, 1H), 4.23 (s, 3H), 2.50 (s, 3H), 1.46 – 1.40 (m, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.43, 171.62, 166.42, 160.55, 156.27, 155.91, 153.53, 137.76, 134.76, 130.60, 129.88, 129.26, 127.94, 126.67, 126.12, 124.62, 114.19, 114.14, 55.34, 38.25, 26.34, 18.89. HRMS (ESI-TOF) *m/z*: Calcd for $C_{28}H_{27}N_2O_5$ [M+H]$^+$ 471.1914; Found: 471.1911.
2-(6-(4-bromophenyl)-3-(4-methoxyphenyl)pyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl 2-methylbenzoate (**9d**).
White powder; yield 73% (0.43 g); m.p. 189-191°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.67 (s, 1H), 8.17 (d, *J* = 7.9 Hz, 2H), 7.79 (q, *J* = 7.3 Hz, 3H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.53 (s, 1H), 3.84 (s, 3H), 2.34 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.6, 166.8, 162.7, 160.7, 156.2, 155.6, 153.5, 140.6, 137.9, 134.0, 133.5, 132.2, 131.9, 130.9, 129.9, 128.8, 128.0, 126.5, 126.5, 126.2, 124.7, 124.4, 114.2, 55.4, 20.9, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{31}H_{24}BrN_2O_5$ [M+H]$^+$ 583.0863; Found: 583.0858.
2-(6-(4-methoxyphenyl)-3-phenylpyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl 2-(trifluoromethyl)benzoate (**9e**).
White powder; yield 69% (0.39 g); m.p. 170-172°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.54 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 2H), 7.96 – 7.88 (m, 1H), 7.88 – 7.79 (m, 3H), 7.66 – 7.58 (m, 2H), 7.54 – 7.47 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.53 (s, 1H), 3.85 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.3, 167.0, 162.3, 161.4, 156.7, 155.7, 154.0, 137.8, 136.0, 133.3, 133.0, 130.8, 129.6, 128.6, 128.4, 128.2, 127.7 (d, J_{CF} = 2.2 Hz), 127.3 (d, J_{CF} = 8.3 Hz), 127.1 (d, J_{CF} = 5.4 Hz), 127.1, 126.9, 126.5, 124.0, 122.9 (d, J_{CF} = 273.6 Hz), 114.7, 114.2, 55.4, 18.9. HRMS (ESI-TOF) *m/z*: Calcd for $C_{31}H_{22}F_3N_2O_5$ [M+H]$^+$ 559.1475; Found: 559.1469.
6-methyl-4-oxo-2-(3-phenyl-6-(p-tolyl)pyridazin-4-yl)-4H-pyran-3-yl benzoate (**9f**).
White powder; yield 73% (0.35 g); m.p. 213-215°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.66 (s, 1H), 8.12 (d, *J* = 7.9 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.75 – 7.63 (m, 3H), 7.59 – 7.48 (m, 5H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.50 (s, 1H), 2.39 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.5, 166.8, 162.4, 157.0, 156.2, 153.4, 140.7, 138.1, 136.1, 134.7, 131.9, 129.9, 129.9, 129.7, 129.0, 128.7, 128.4, 127.2, 126.9, 126.8, 124.2, 114.1, 20.9, 18.9. HRMS (ESI-TOF) *m/z*: Calcd for $C_{30}H_{23}N_2O_4$ [M+H]$^+$ 475.1652; Found: 475.1660.
6-methyl-4-oxo-2-(3-phenyl-6-(p-tolyl)pyridazin-4-yl)-4H-pyran-3-yl 2-methylbenzoate (**9f'**).
White powder; yield 76% (0.37 g); m.p. 174-176°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.63 (s, 1H), 8.12 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.57 – 7.47 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.50 (s, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.6, 166.7, 162.8, 156.9, 156.2, 153.4, 140.7, 140.6, 138.2, 136.0, 133.6, 131.9, 130.9, 129.9, 129.7, 128.6,

128.4, 126.9, 126.8, 126.5, 126.2, 124.2, 114.1, 21.0, 20.9, 18.8. HRMS (ESI-TOF) *m/z*: Calcd for $C_{31}H_{25}N_2O_4$ $[M+H]^+$ 489.1809; Found: 489.1814.

2-(3,6-diphenylpyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl pivalate (**9g**).

Grey powder; yield 81% (0.36 g); m.p. 193-195°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.58 (s, 1H), 8.33 – 8.24 (m, 2H), 7.73 – 7.62 (m, 2H), 7.61 (d, *J* = 6.6 Hz, 3H), 7.58 – 7.49 (m, 3H), 6.43 (s, 1H), 2.00 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.44, 171.55, 166.29, 156.80, 156.38, 153.13, 138.00, 135.84, 134.66, 130.72, 129.65, 129.27, 128.58, 128.31, 126.77, 126.64, 124.55, 114.11, 38.26, 26.34, 18.69. HRMS (ESI-TOF) *m/z*: Calcd for $C_{27}H_{25}$ N_2O_4 $[M+H]^+$ 441.1809; Found: 441.1808.

2-(3-(4-fluorophenyl)-6-(4-methoxyphenyl)pyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl benzoate (**9h**).

Yellow powder; yield 77% (0.39 g); m.p. 247-249°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.64 (s, 1H), 8.27 – 8.15 (m, 2H), 7.93 – 7.84 (m, 2H), 7.75 – 7.64 (m, 3H), 7.59 – 7.48 (m, 2H), 7.45 – 7.32 (m, 2H), 7.21 – 7.08 (m, 2H), 6.52 (s, 1H), 3.85 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.5, 166.8, 163.0 (d, J_{CF} = 247.4 Hz), 162.3, 161.5, 156.7, 154.8, 153.3, 138.0, 134.6, 132.5 (d, J_{CF} = 3.2 Hz), 130.6 (d, J_{CF} = 8.7 Hz), 129.9, 129.0, 128.4, 127.2, 126.9, 126.8, 123.8, 115.7 (d, J_{CF} = 21.9 Hz), 114.7, 114.2, 55.4, 18.9. HRMS (ESI-TOF) *m/z*: Calcd for $C_{30}H_{22}FN_2O_5$ $[M+H]^+$ 509.1507; Found: 509.1501.

2-(3-(4-fluorophenyl)-6-(4-methoxyphenyl)pyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl 4-(trifluoromethyl)benzoate (**9h'**).

White powder; yield 74% (0.43 g); m.p. 201-203°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.62 (s, 1H), 8.24 – 8.13 (m, 3H), 8.04 – 7.94 (m, 2H), 7.74 – 7.63 (m, 2H), 7.52 (d, *J* = 8.3 Hz, 3H), 7.43 – 7.31 (m, 2H), 7.18 – 7.07 (m, 2H), 6.52 (s, 1H), 3.85 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 171.4, 167.0, 163.1 (d, J_{CF} = 247.3 Hz), 161.5, 161.1, 155.8 (d, J_{CF} = 241.9 Hz), 153.4, 152.5, 137.9, 132.6 (d, J_{CF} = 3.1 Hz), 132.5, 130.7 (d, J_{CF} = 8.6 Hz), 128.5, 126.9 (d, J_{CF} = 20.1 Hz), 126.2, 123.9, 121.1, 115.8 (d, J_{CF} = 21.9 Hz), 114.7, 114.2, 55.4, 19.0. HRMS (ESI-TOF) *m/z*: Calcd for $C_{31}H_{21}F_4N_2O_5$ $[M+H]^+$ 577.1381; Found: 577.1378.

2-(3-(4-fluorophenyl)-6-(3-methoxyphenyl)pyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl propionate (**9i**).

White powder; yield 82% (0.38 g); m.p. 154-156°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.57 (s, 1H), 7.87 – 7.77 (m, 2H), 7.77 – 7.66 (m, 2H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.21 – 7.12 (m, 1H), 6.45 (s, 1H), 3.88 (s, 3H), 2.38 (q, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.5, 170.3, 166.6, 163.0 (d, J_{CF} = 247.4 Hz), 159.9, 157.0, 155.6, 152.9, 137.9, 136.2, 132.5 (d, J_{CF} = 3.2 Hz), 130.7, 130.5 (d, J_{CF} = 14.3 Hz), 127.0, 125.0, 119.3, 116.6, 115.8 (d, J_{CF} = 21.9 Hz), 114.1, 112.1, 55.4, 26.2, 18.9, 8.6. HRMS (ESI-TOF) *m/z*: Calcd for $C_{26}H_{22}FN_2O_5$ $[M+H]^+$ 461.1507; Found: 461.1498.

2-(3-(4-methoxyphenyl)-6-(thiophen-2-yl)pyridazin-4-yl)-6-methyl-4-oxo-4H-pyran-3-yl propionate (**9j**).

White powder; yield 79% (0.35 g); m.p. 207-209°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.50 (s, 1H), 8.03 (d, *J* = 3.7 Hz, 1H), 7.84 (d, *J* = 5.0 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.29 (t, *J* = 4.3 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.45 (s, 1H), 3.82 (s, 3H), 2.38 (q, *J* = 7.4 Hz, 2H), 2.12 (s, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.6, 170.4, 166.6, 160.5, 155.8, 153.3, 152.9, 139.3, 137.7, 130.6, 129.7, 128.8, 128.3, 128.2, 126.4, 123.2, 114.1, 55.3, 26.3, 18.9, 8.7. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{21}O_5S$ $[M+H]^+$ 449.1166; Found: 449.1171.

6. Characterization data of compounds 4, 6 and 8

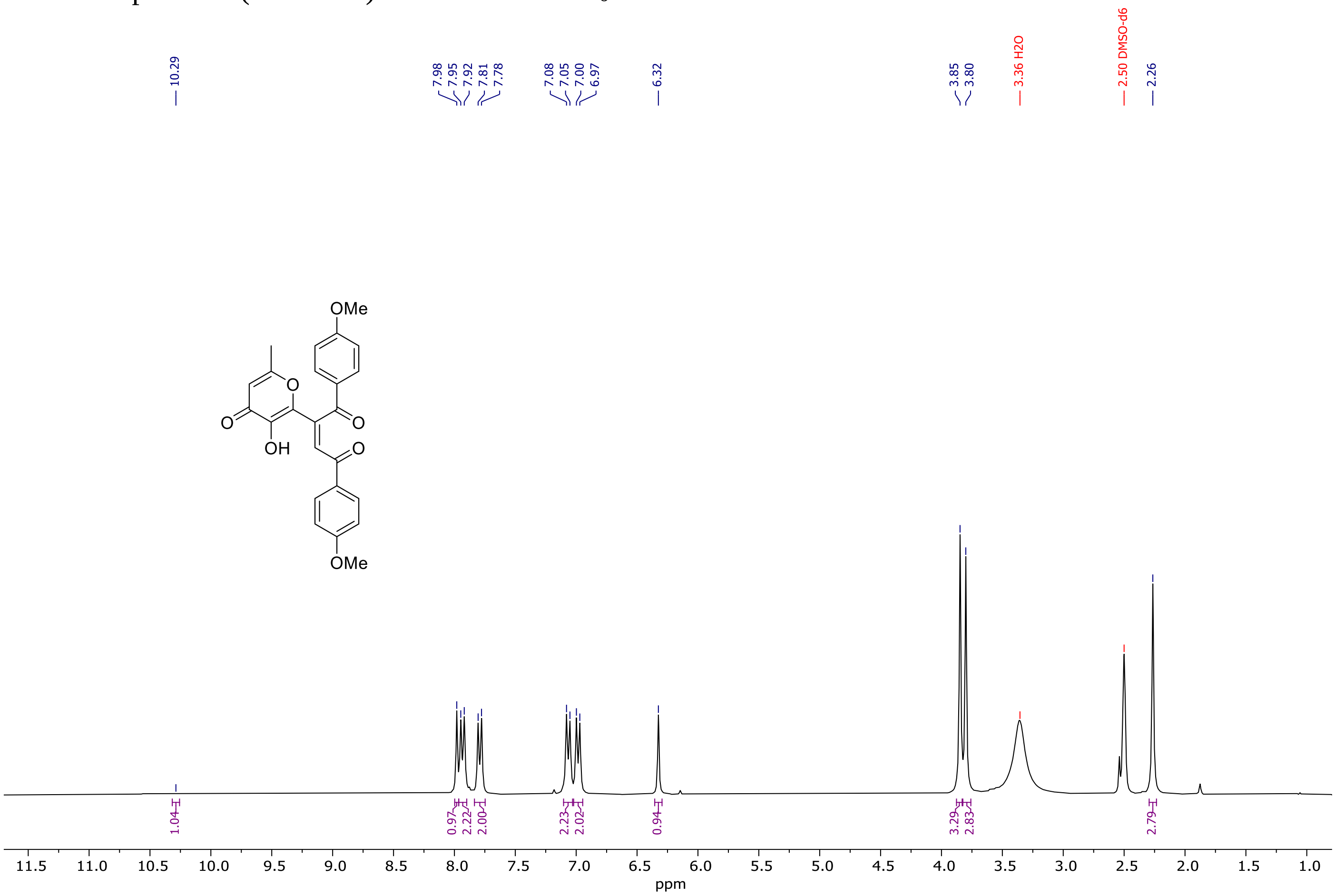
2-hydroxy-3-(3-hydroxy-6-methyl-4-oxo-4H-pyran-2-yl)-1,4-bis(4-methoxyphenyl)butane-1,4-dione (**4**). White powder; yield 46% (0.20 g); m.p. 169-171°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.40 (s, 1H), 8.07 – 7.93 (m, 4H), 7.13 – 6.99 (m, 4H), 6.23 (s, 1H), 6.20 (s, 1H), 5.69 (t, J = 9.2 Hz, 1H), 5.38 (d, J = 9.9 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 195.7, 193.9, 173.6, 165.0, 163.7, 163.4, 145.9, 143.3, 131.4, 130.4, 128.1, 127.9, 114.2, 114.1, 111.3, 69.7, 55.7, 48.8, 19.4. HRMS (ESI-TOF) *m/z*: Calcd for $C_{24}H_{23}O_7$ $[M+H]^+$ 439.1387; Found: 439.1397.

2-(3,6-bis(4-methoxyphenyl)pyridazin-4-yl)-3-methoxy-6-methyl-4H-pyran-4-one (**6**). Pale brown powder; yield 83% (0.36 g); m.p. 161-163°C. ^{1}H NMR (300 MHz, DMSO) δ 8.43 (s, 1H), 8.22 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 6.35 (s, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.42 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.6, 165.5, 161.2, 160.4, 156.3, 155.8, 152.2, 143.9, 129.8, 128.6, 128.4, 128.0, 127.4, 124.1, 114.7, 114.6, 114.0, 58.9, 55.4, 55.3, 18.9. HRMS (ESI-TOF) *m/z*: Calcd for $C_{25}H_{23}N_2O_5$ $[M+H]^+$ 431.1601; Found: 431.1590.

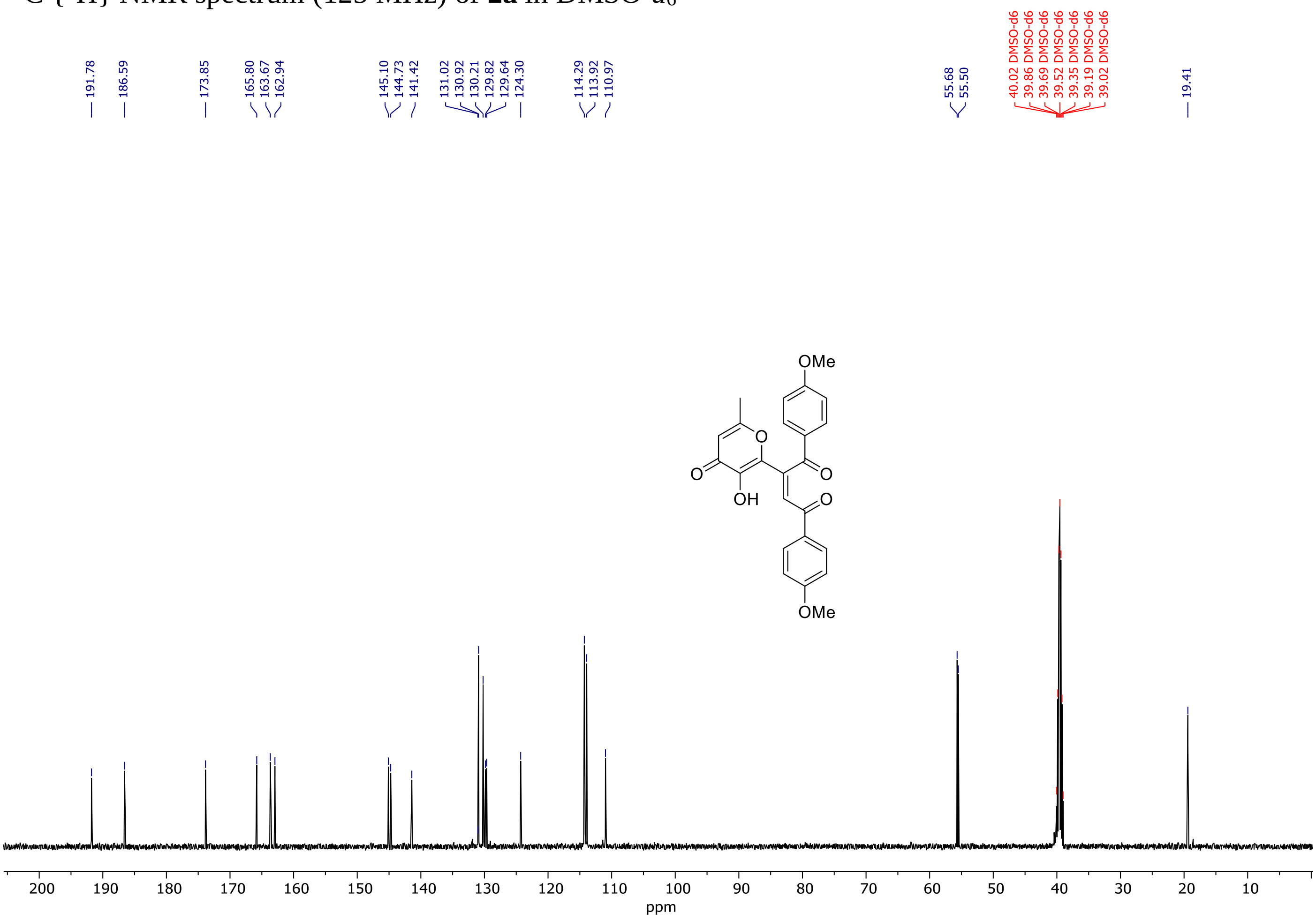
(Z)-2-(3-methoxy-6-methyl-4-oxo-4H-pyran-2-yl)-1,4-bis(4-methoxyphenyl)but-2-ene-1,4-dione (**8**). Yellow powder; yield 92% (0.40 g); m.p. 174-176°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.01 – 7.98 (m, 1H), 7.96 (s, 2H), 7.85 – 7.74 (m, 2H), 7.12 – 7.02 (m, 2H), 7.07 – 6.92 (m, 2H), 6.36 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.30 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 190.55, 186.66, 175.03, 165.86, 163.82, 162.86, 150.49, 145.13, 142.65, 131.17, 129.99, 129.53, 129.34, 127.13, 114.26, 113.87, 58.69, 55.69, 55.46, 19.15. HRMS (ESI-TOF) *m/z*: Calcd for $C_{25}H_{23}O_7$ $[M+H]^+$ 435.1438; Found: 435.1444.

7. NMR ^{1}H and ^{13}C spectra for compounds 2

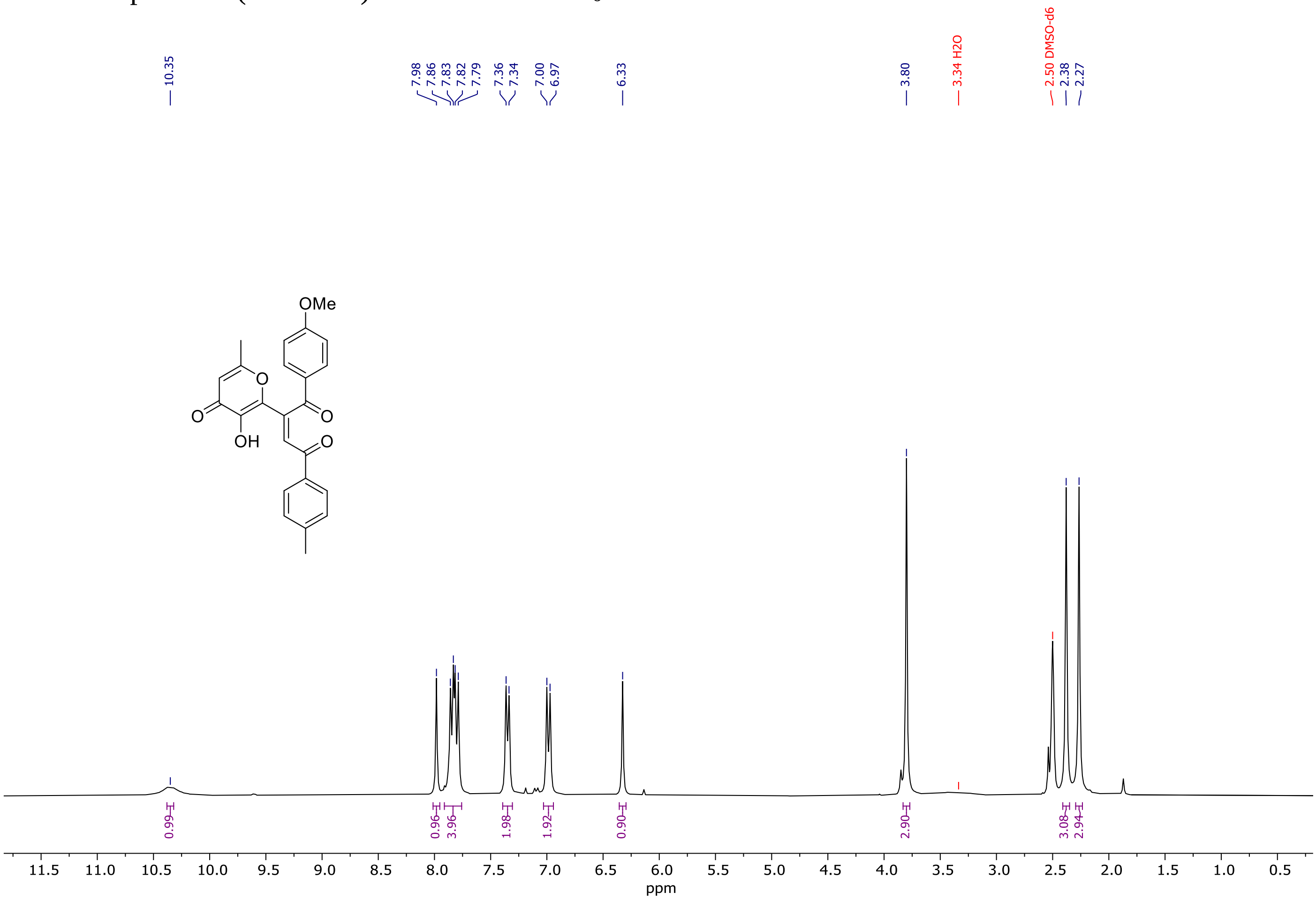
^{1}H NMR spectrum (300 MHz) of **2a** in DMSO-d_6



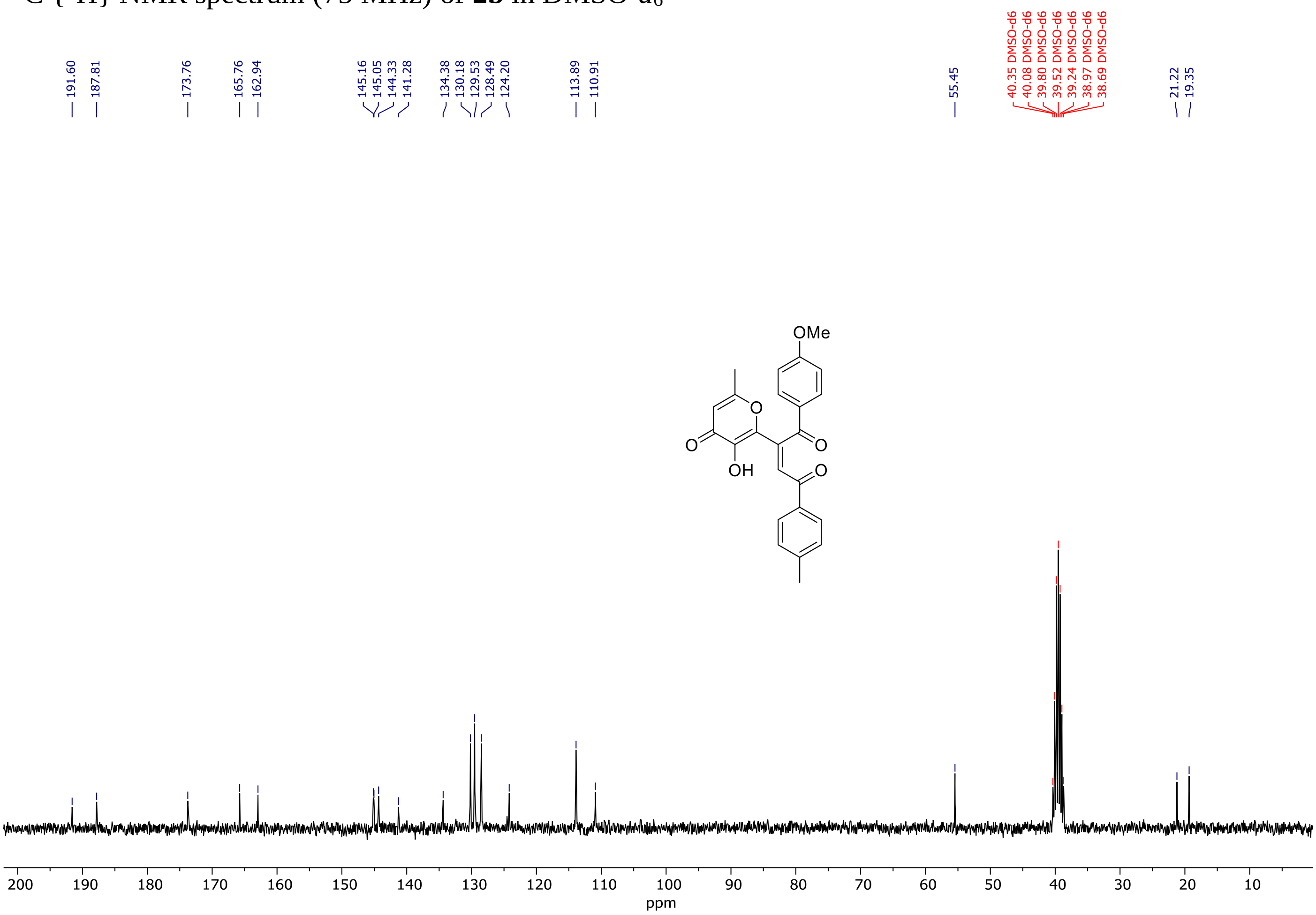
^{13}C {^{1}H} NMR spectrum (125 MHz) of **2a** in DMSO-d_6



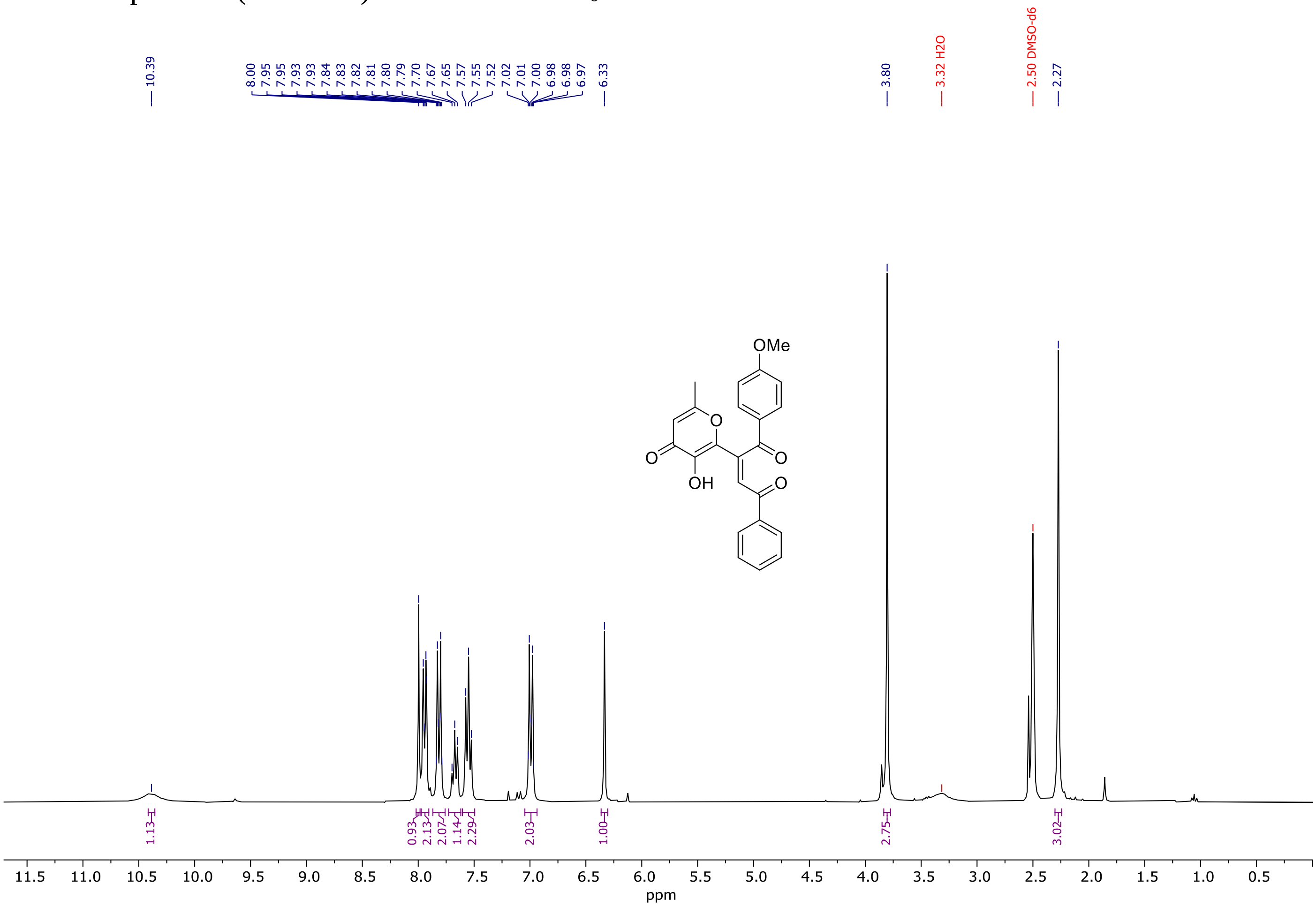
^{1}H NMR spectrum (300 MHz) of **2b** in DMSO-d_6



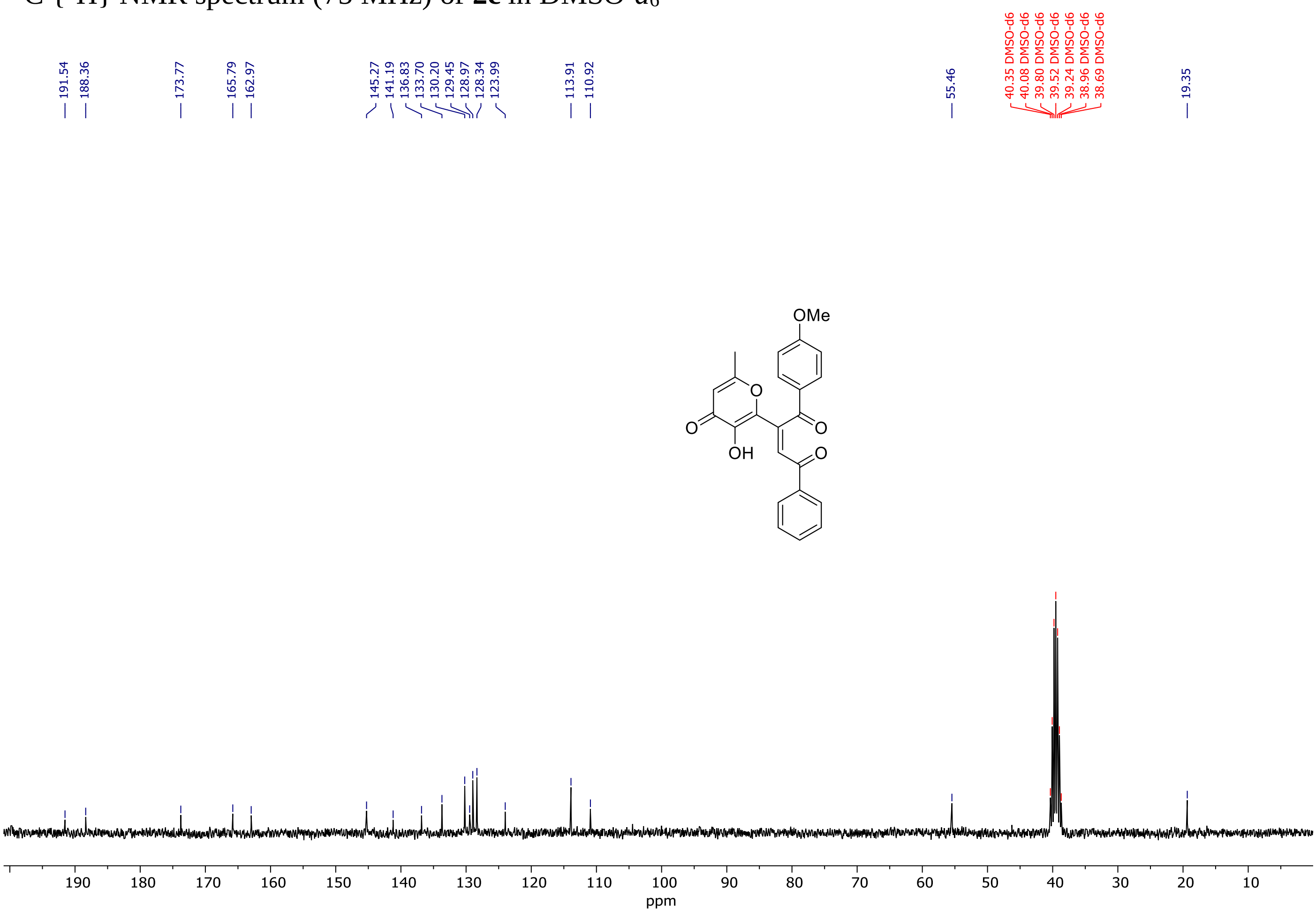
^{13}C {^{1}H} NMR spectrum (75 MHz) of **2b** in DMSO-d_6



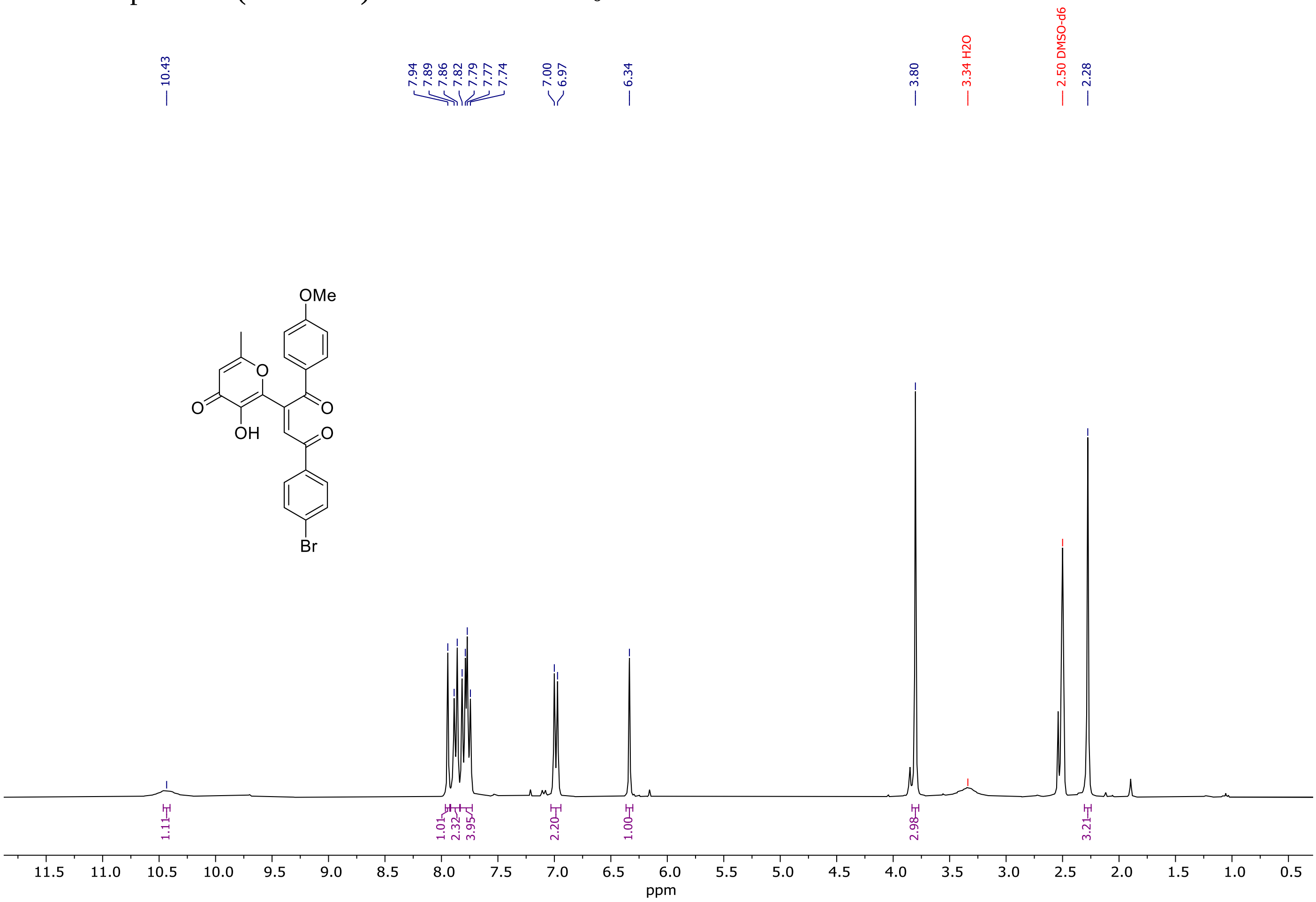
[1]H NMR spectrum (300 MHz) of **2c** in DMSO-d_6



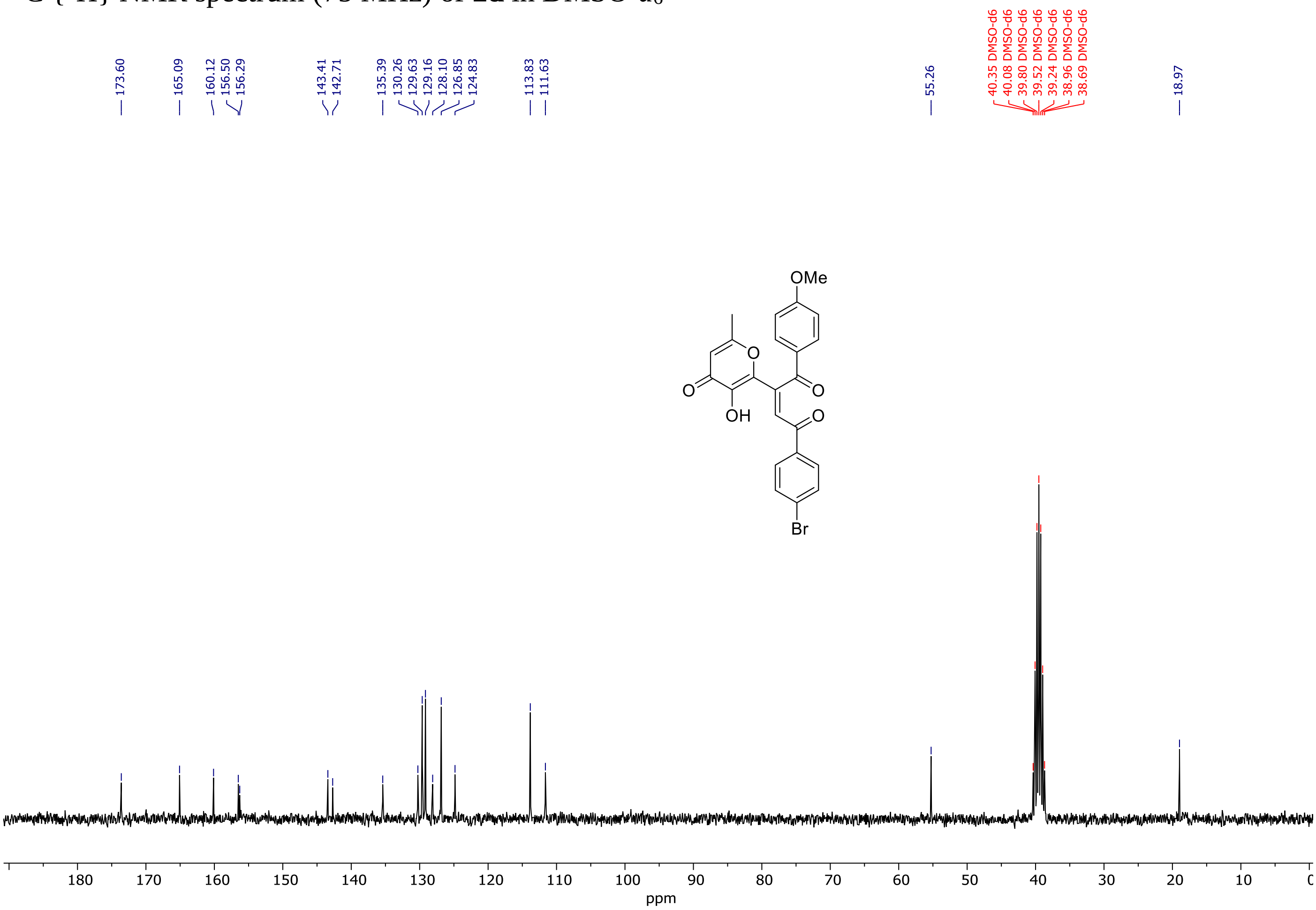
[13]C {[1]H} NMR spectrum (75 MHz) of **2c** in DMSO-d_6



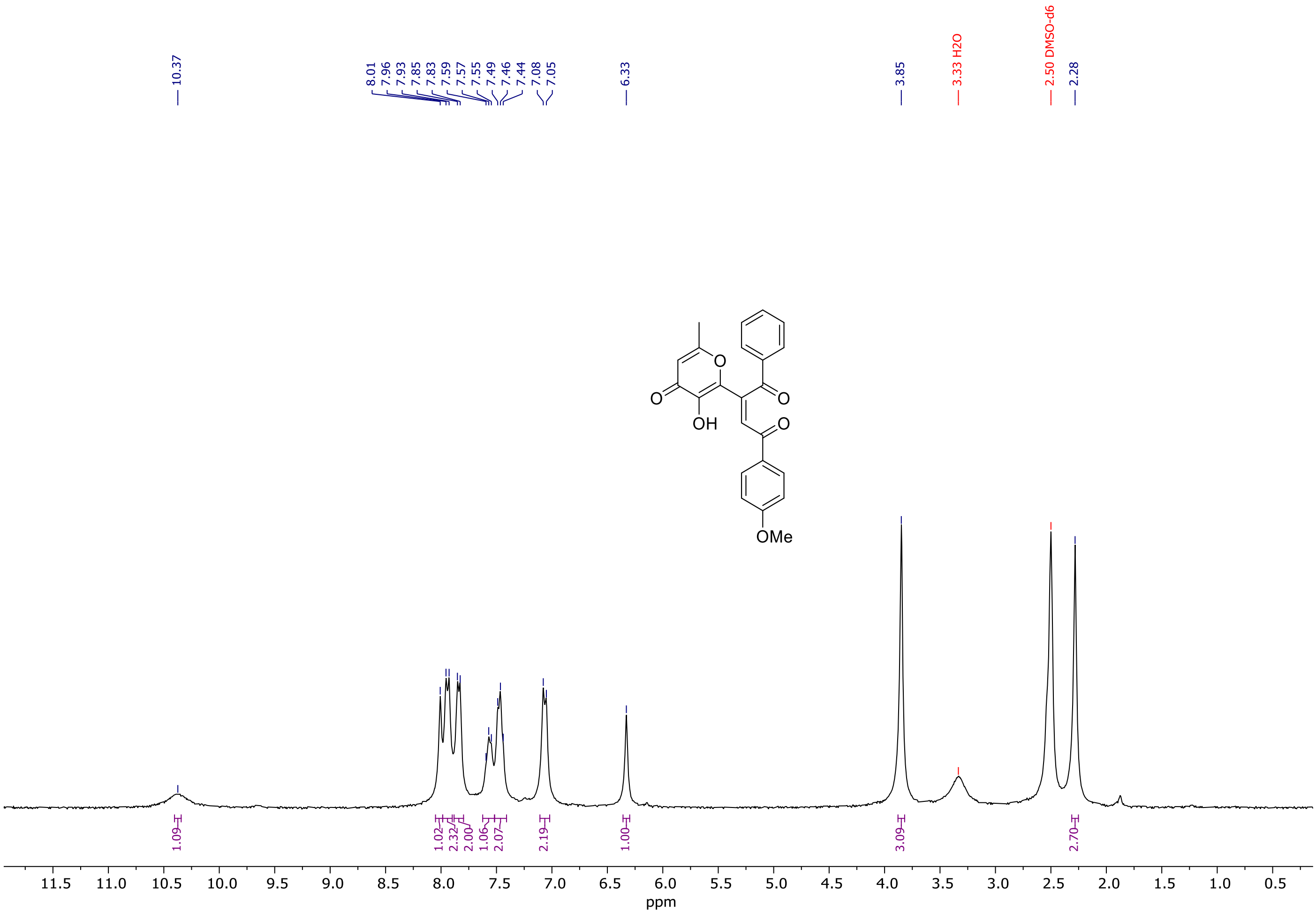
^{1}H NMR spectrum (300 MHz) of **2d** in DMSO-d_6



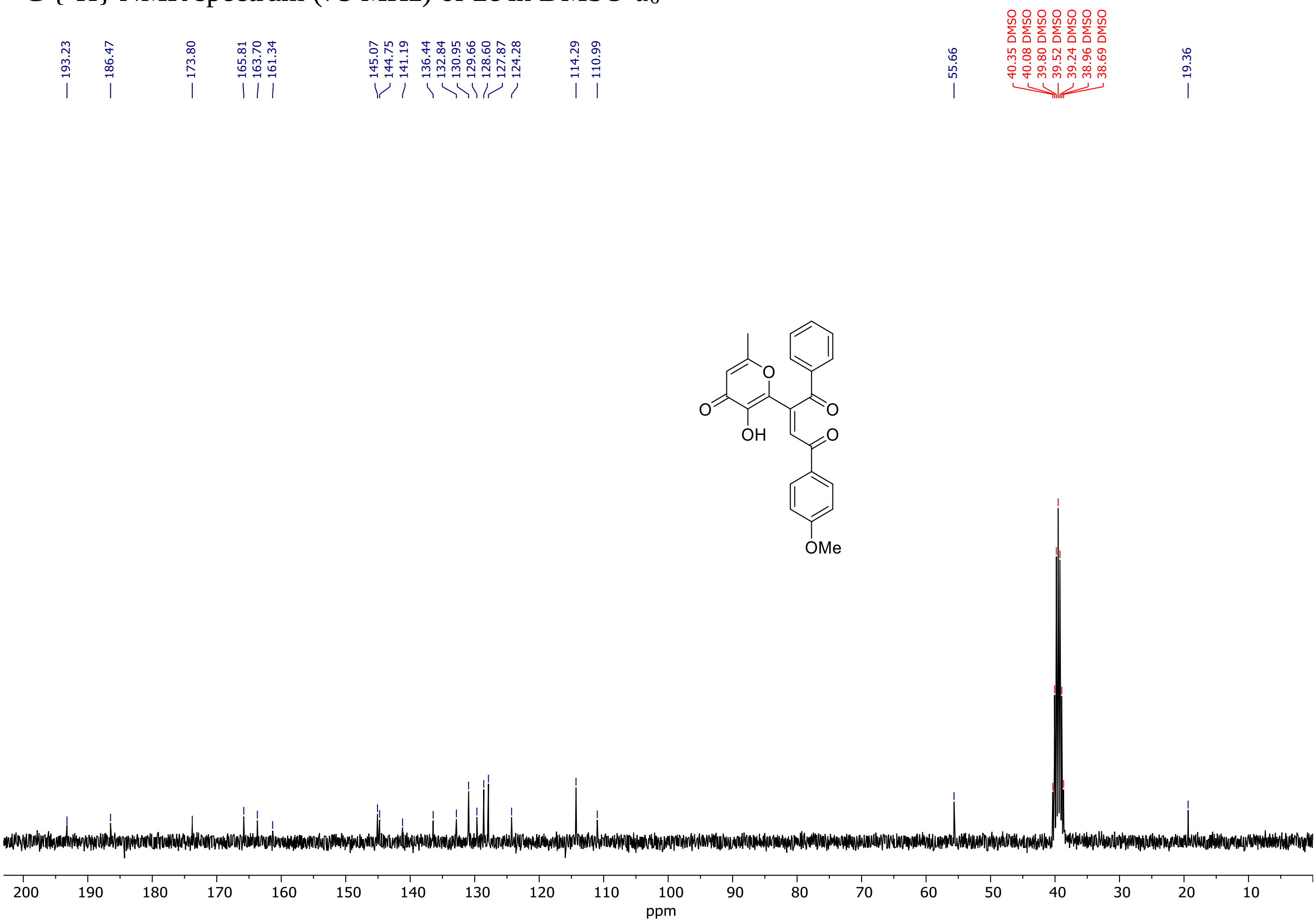
^{13}C {^{1}H} NMR spectrum (75 MHz) of **2d** in DMSO-d_6



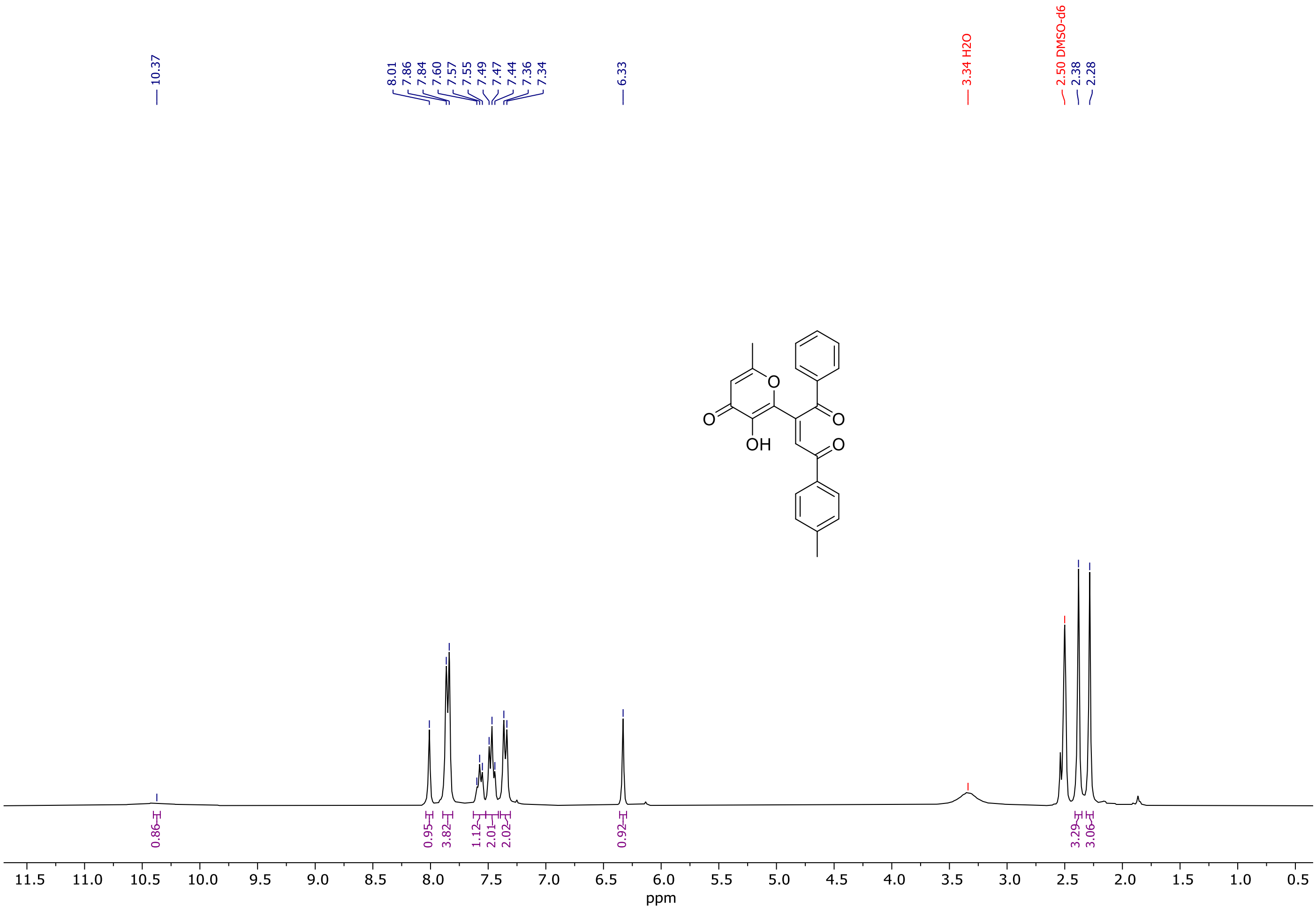
^{1}H NMR spectrum (300 MHz) of **2e** in DMSO-d_6



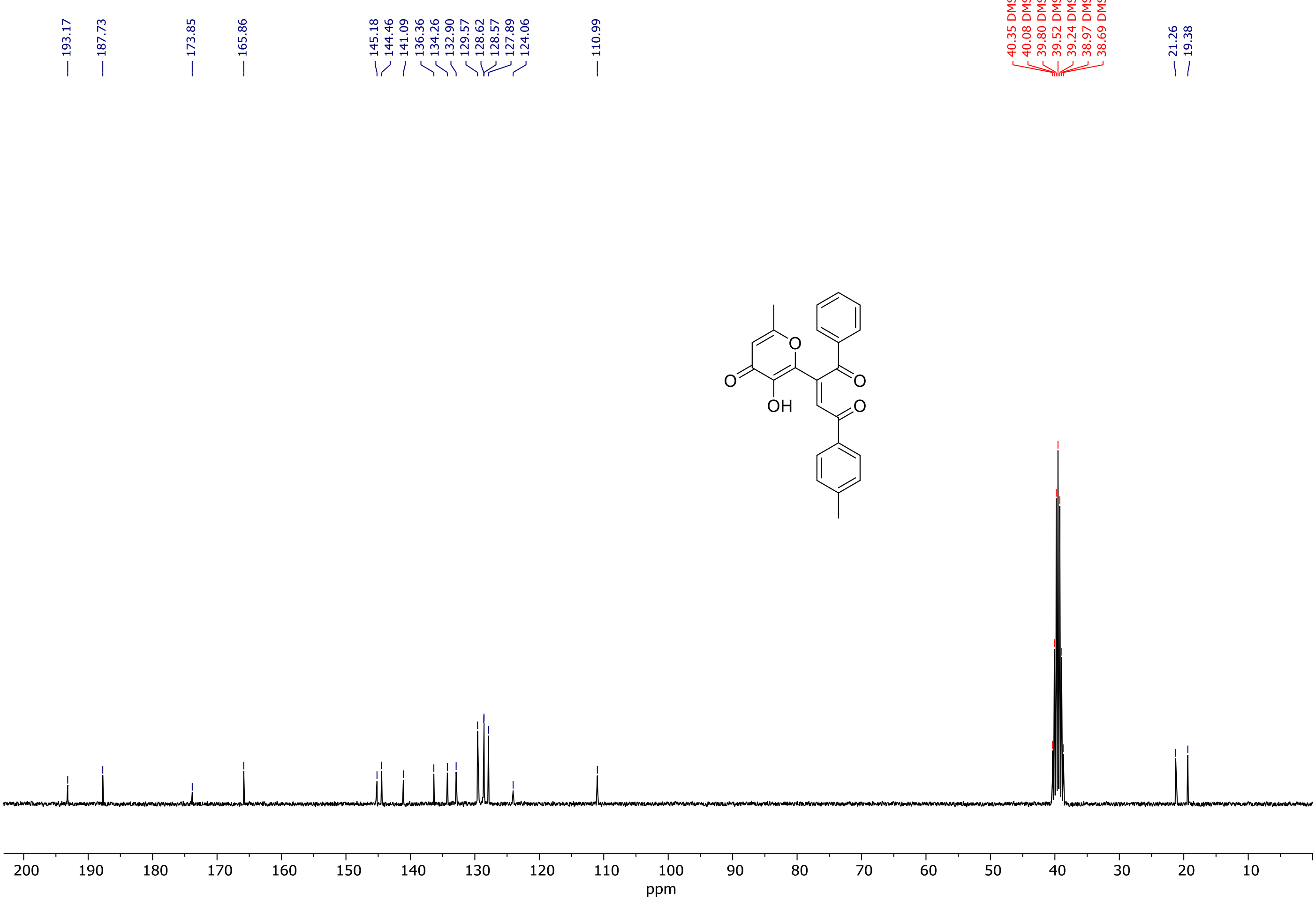
^{13}C {^{1}H} NMR spectrum (75 MHz) of **2e** in DMSO-d_6



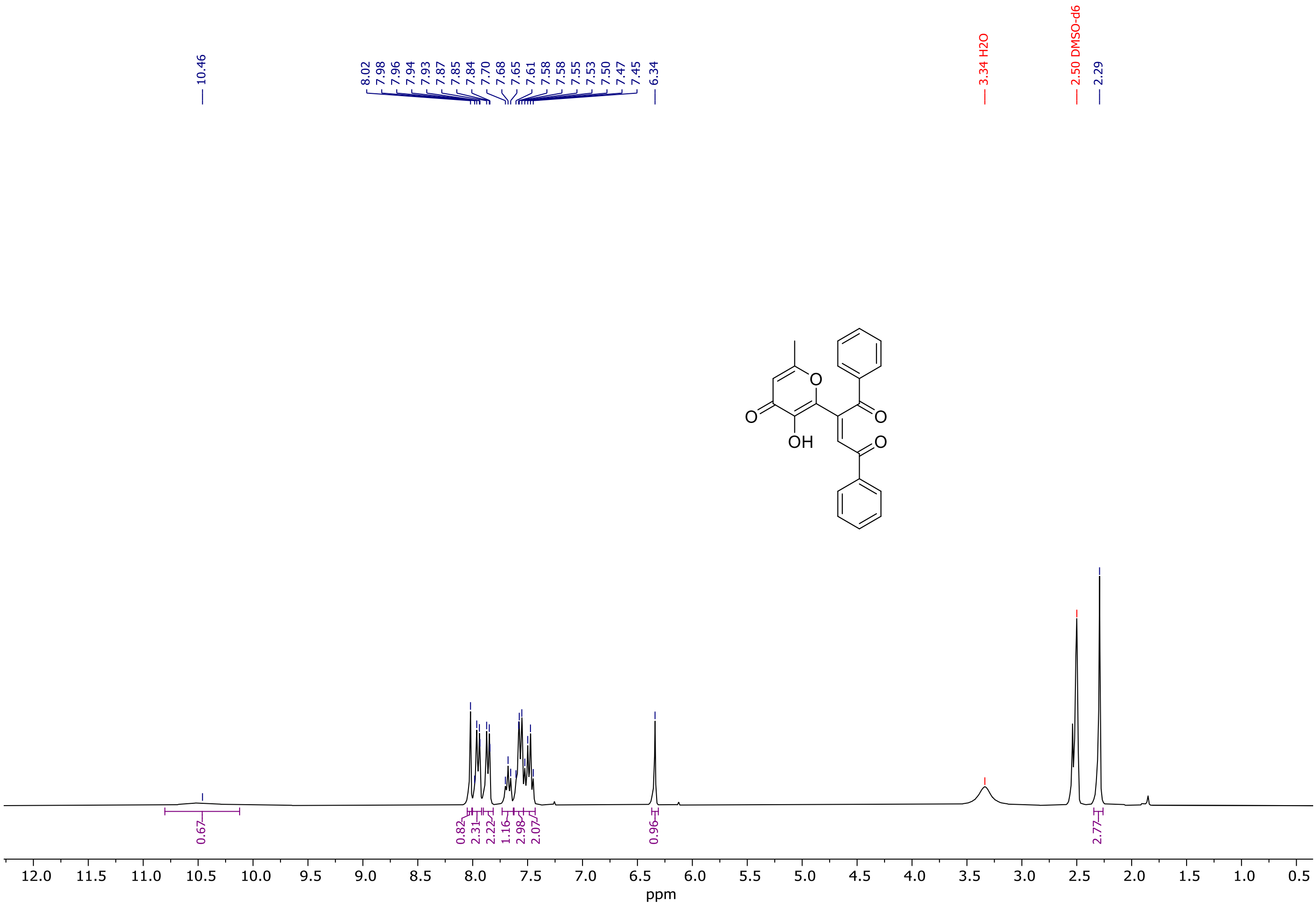
^{1}H NMR spectrum (300 MHz) of **2f** in DMSO-d_6



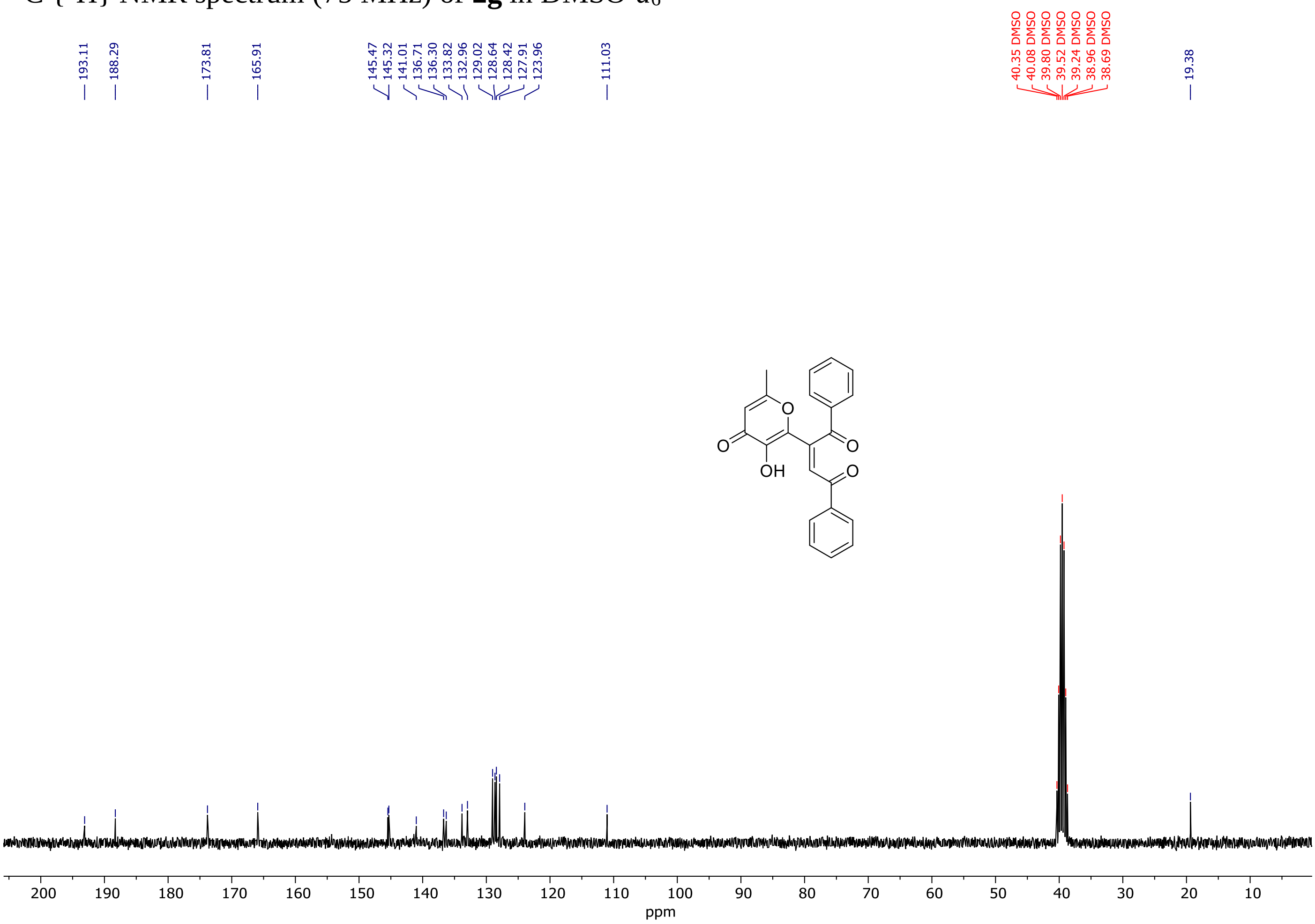
^{13}C {^{1}H} NMR spectrum (75 MHz) of **2f** in DMSO-d_6



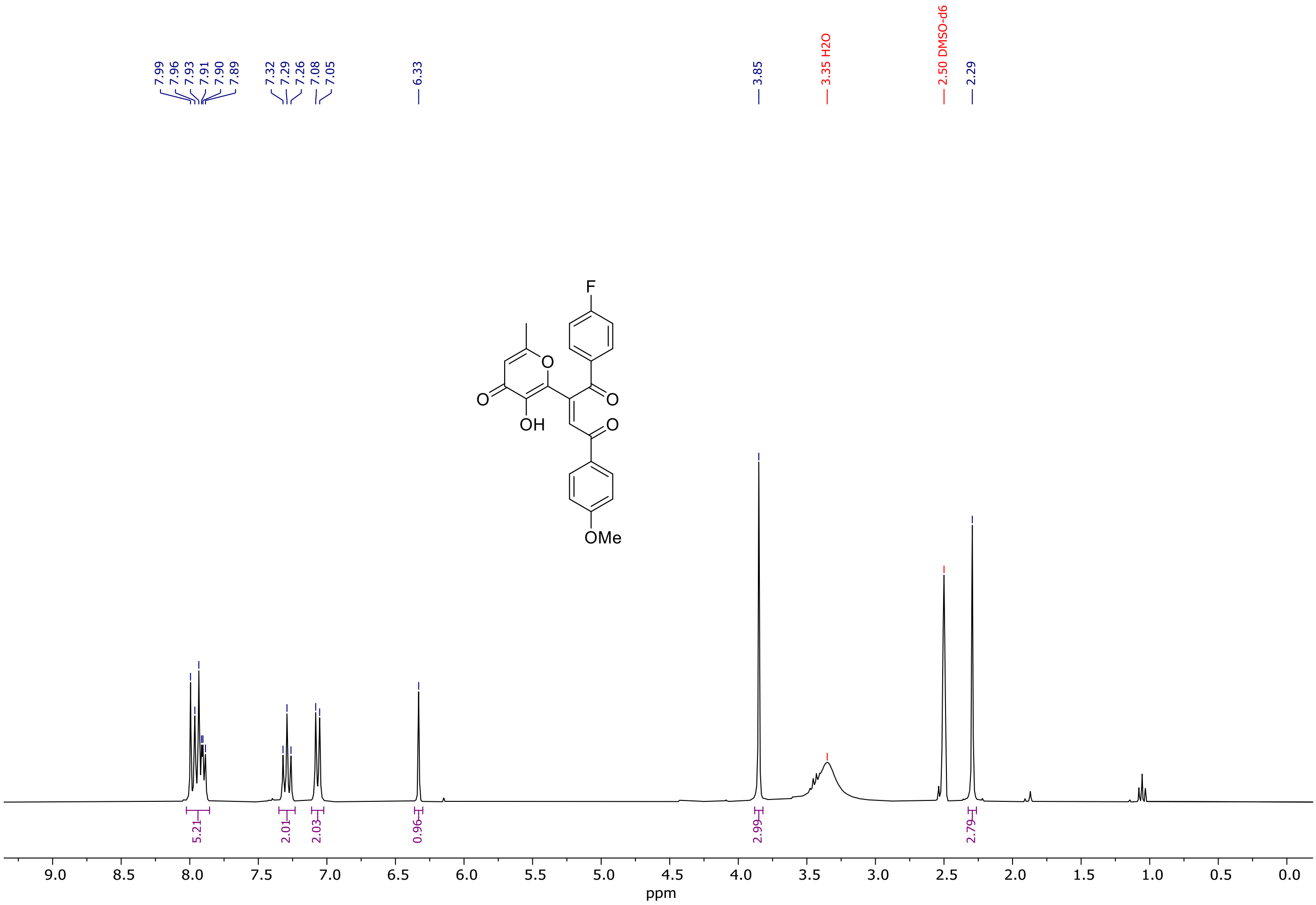
^{1}H NMR spectrum (300 MHz) of **2g** in DMSO-d_6



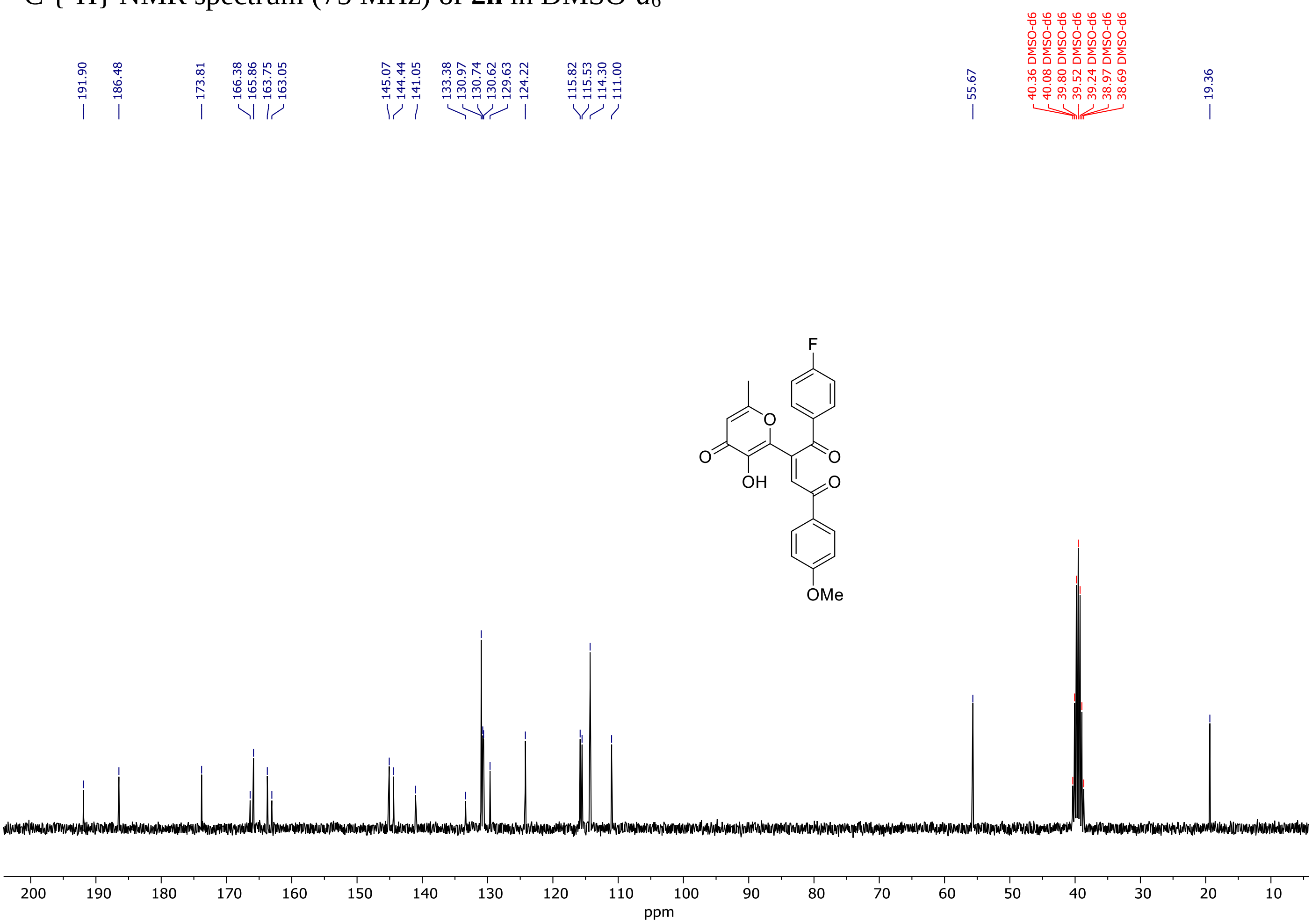
^{13}C {^{1}H} NMR spectrum (75 MHz) of **2g** in DMSO-d_6



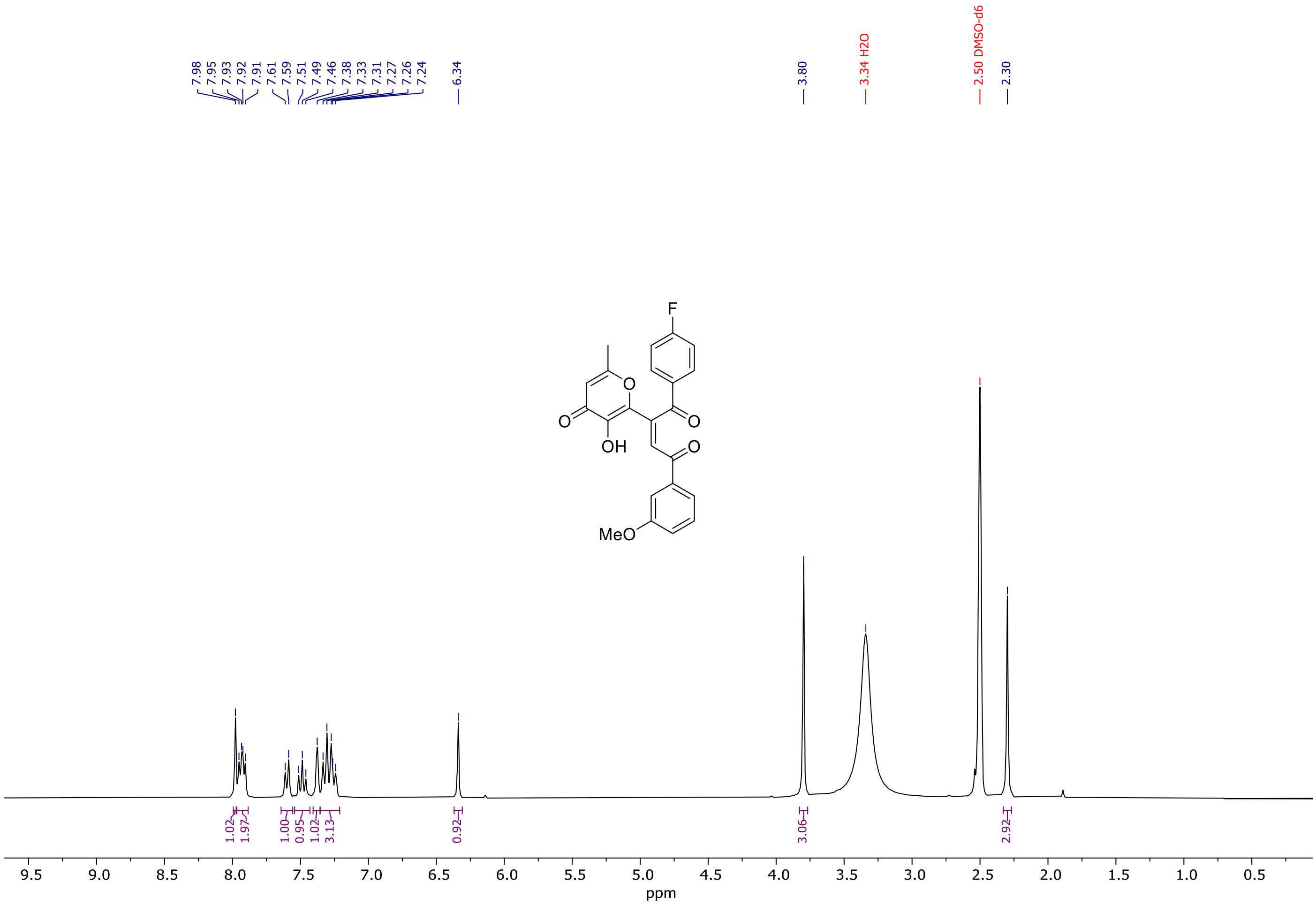
^{1}H NMR spectrum (300 MHz) of **2h** in DMSO-d_6



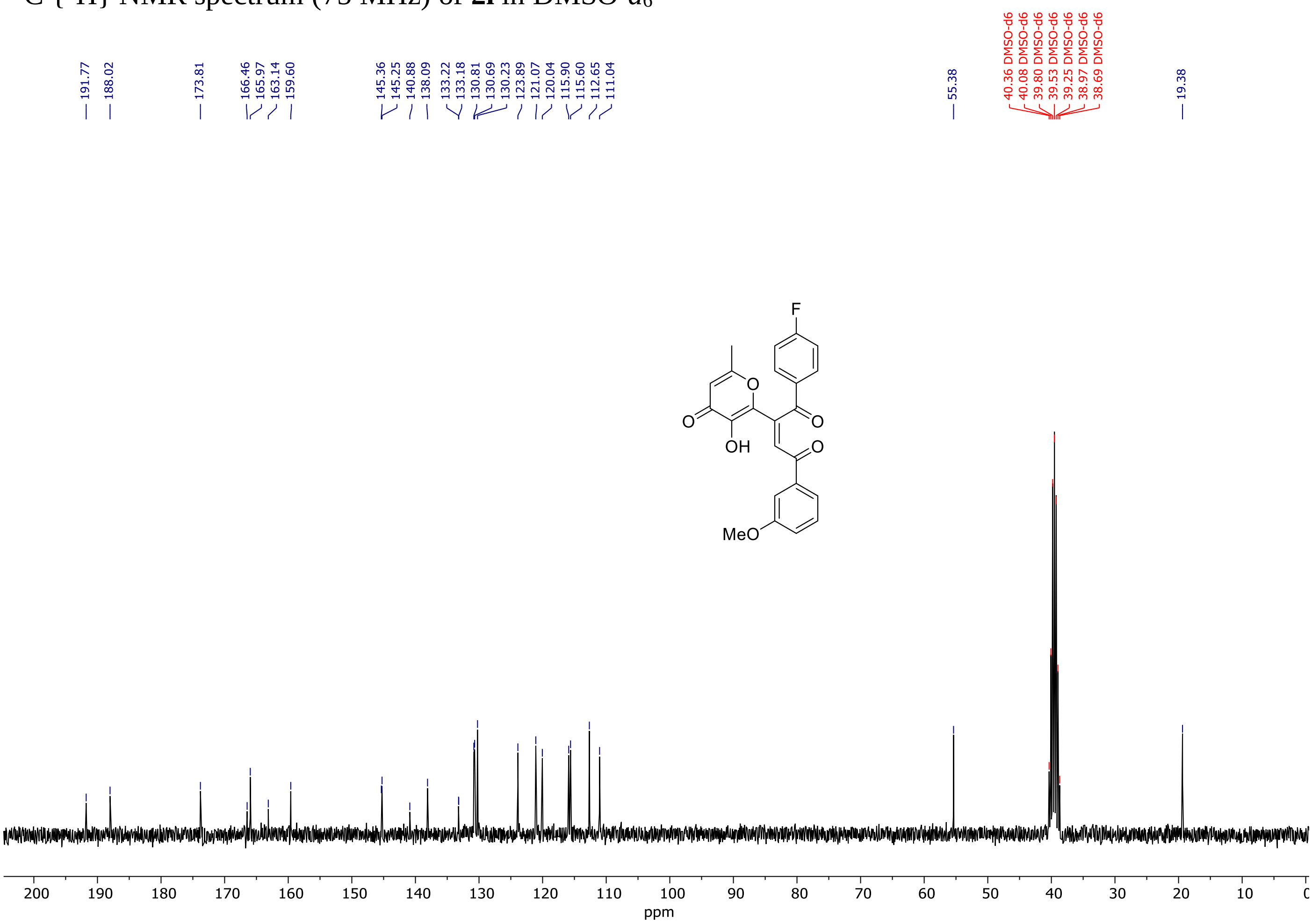
^{13}C {^{1}H} NMR spectrum (75 MHz) of **2h** in DMSO-d_6



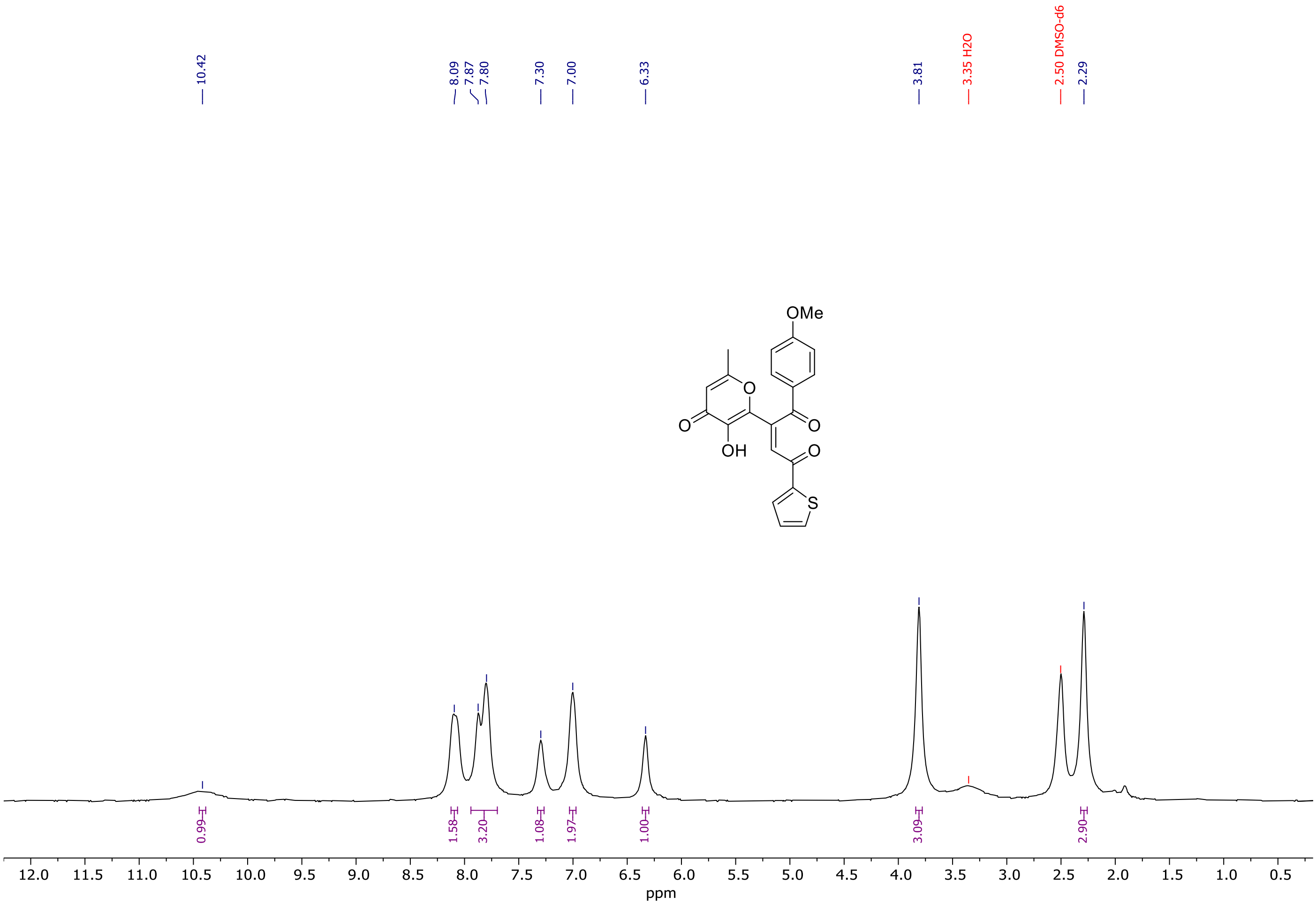
^{1}H NMR spectrum (300 MHz) of **2i** in DMSO-d_6



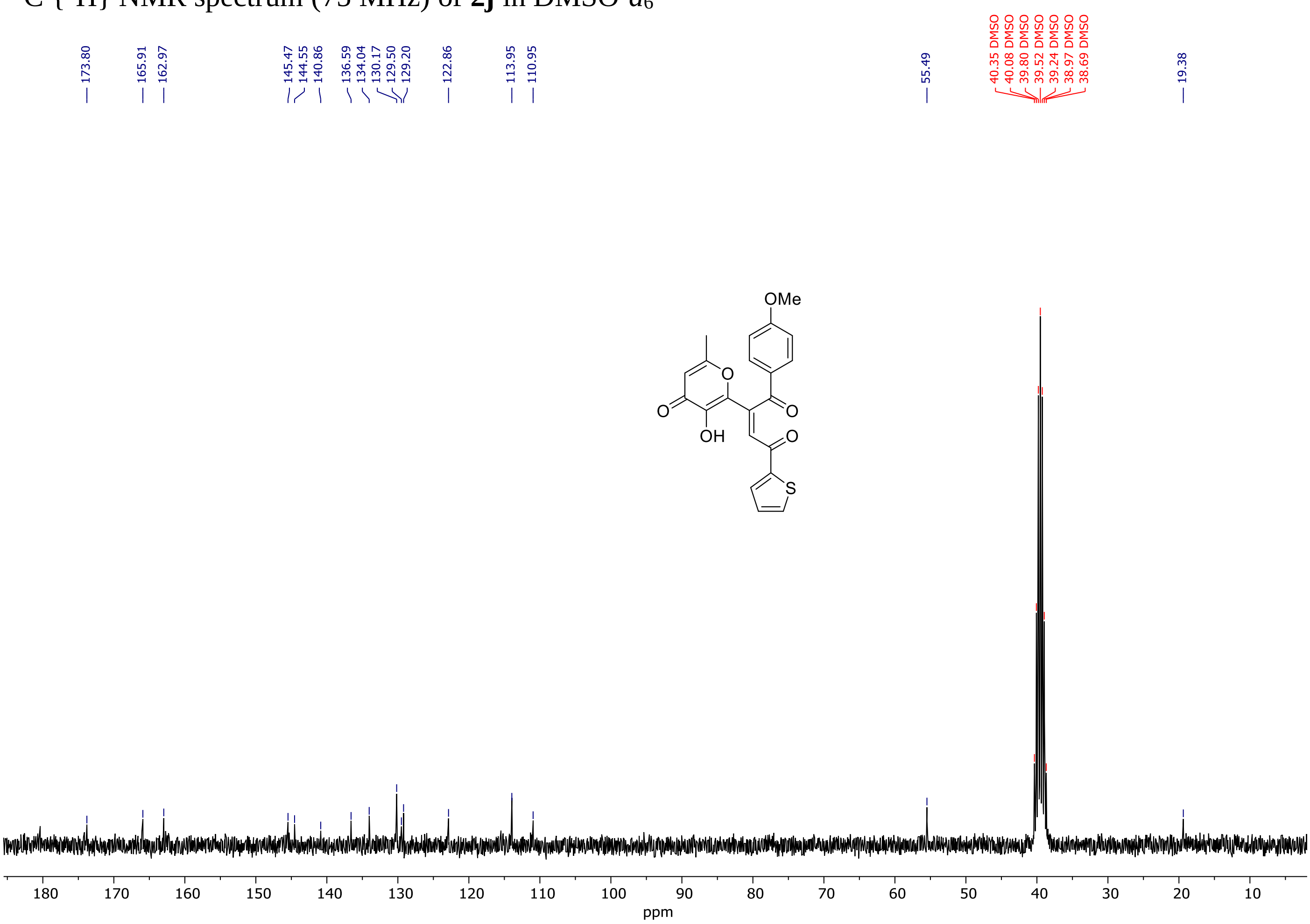
^{13}C {^{1}H} NMR spectrum (75 MHz) of **2i** in DMSO-d_6



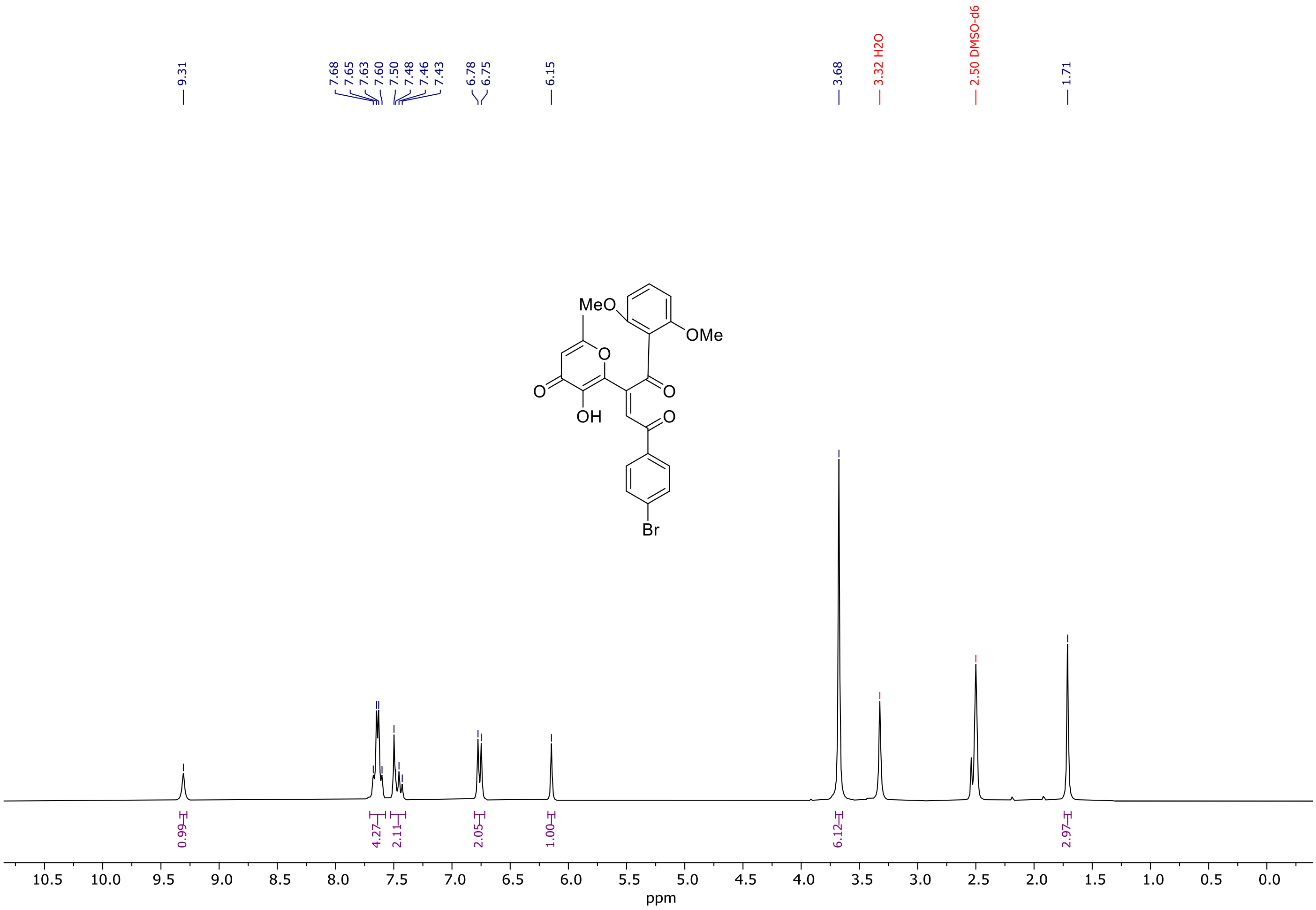
^{1}H NMR spectrum (300 MHz) of **2j** in DMSO-d_6



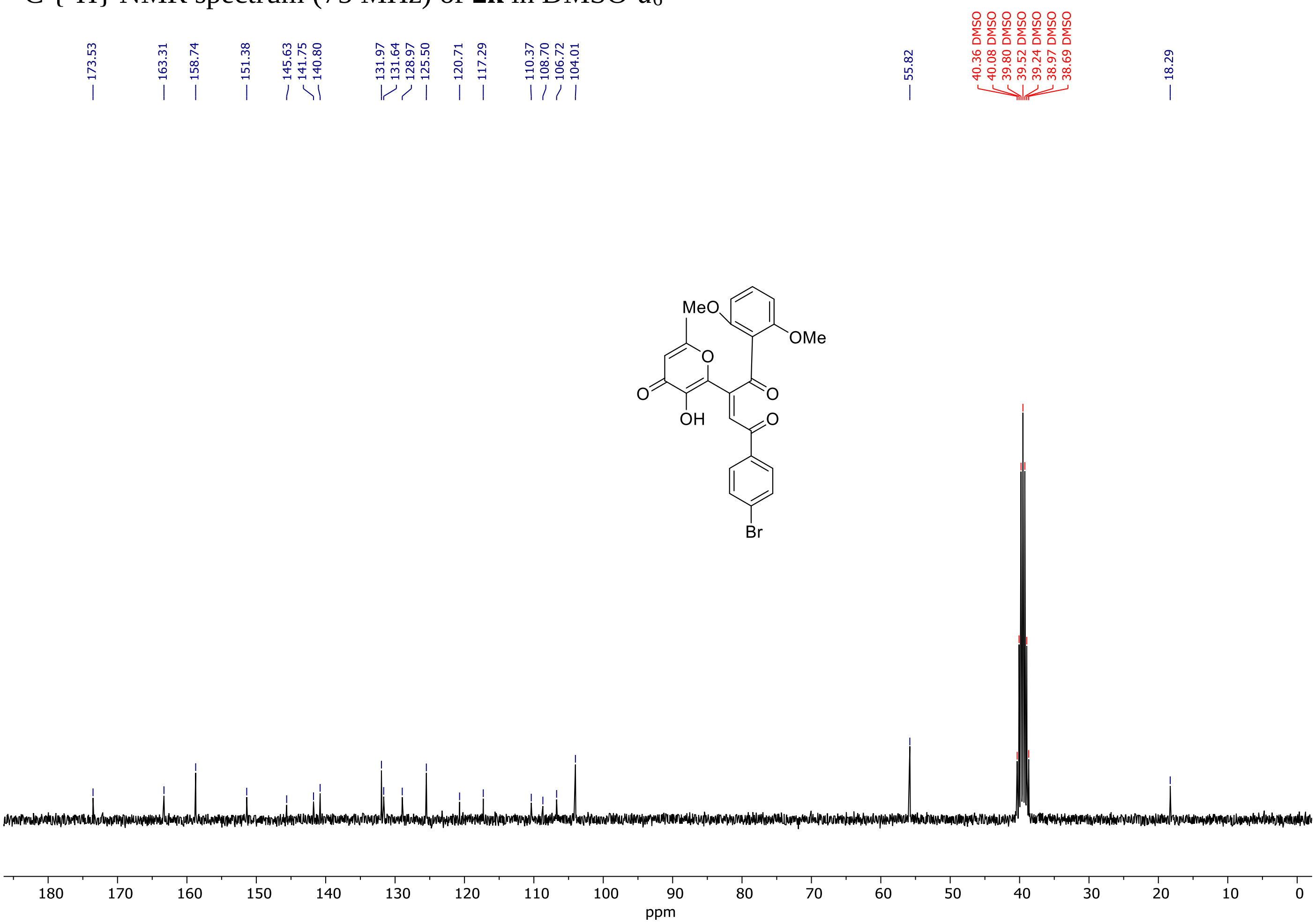
^{13}C {^{1}H} NMR spectrum (75 MHz) of **2j** in DMSO-d_6



^{1}H NMR spectrum (300 MHz) of **2k** in DMSO-d_6

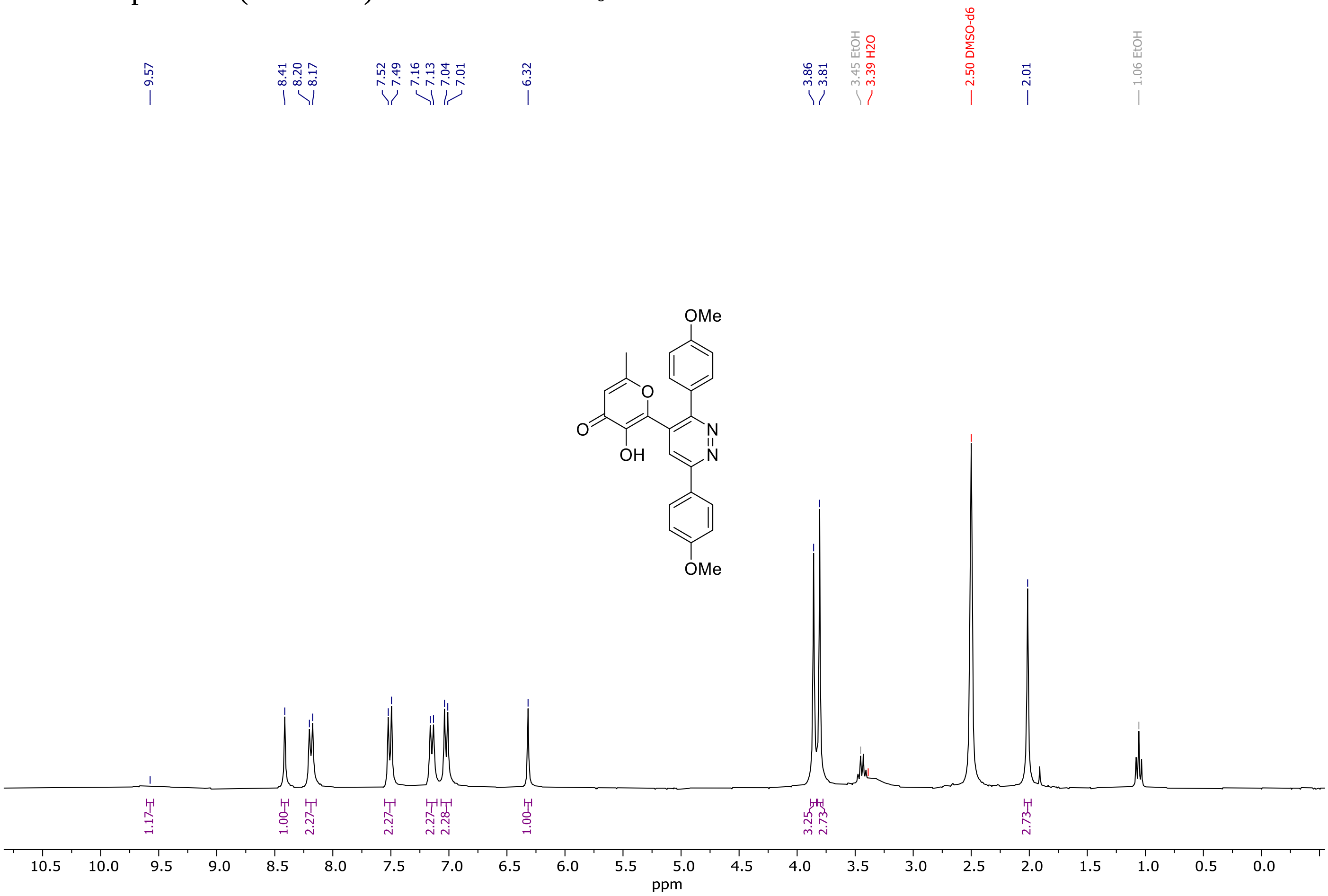


^{13}C {^{1}H} NMR spectrum (75 MHz) of **2k** in DMSO-d_6

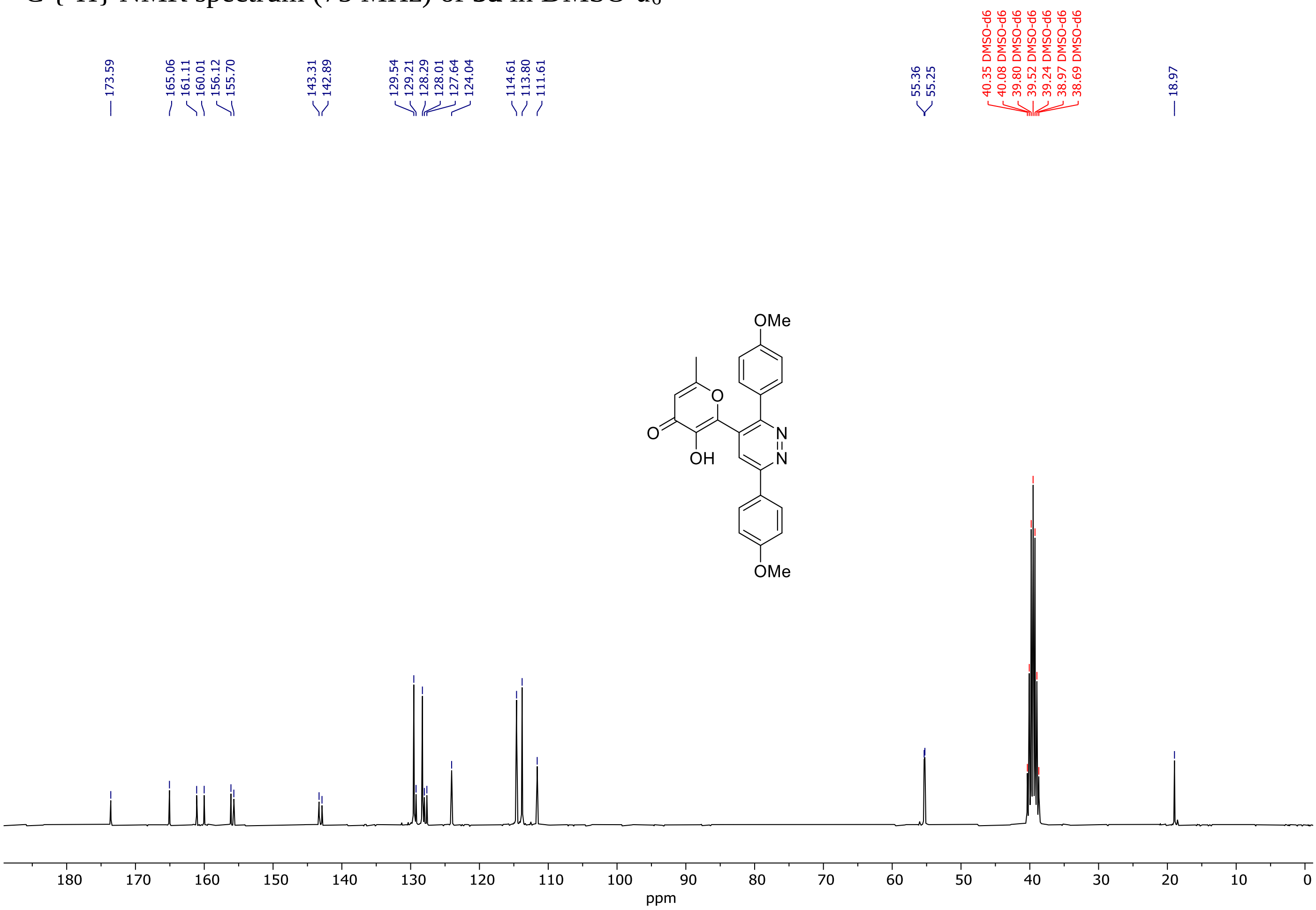


8. NMR ^{1}H and ^{13}C spectra for compounds 5

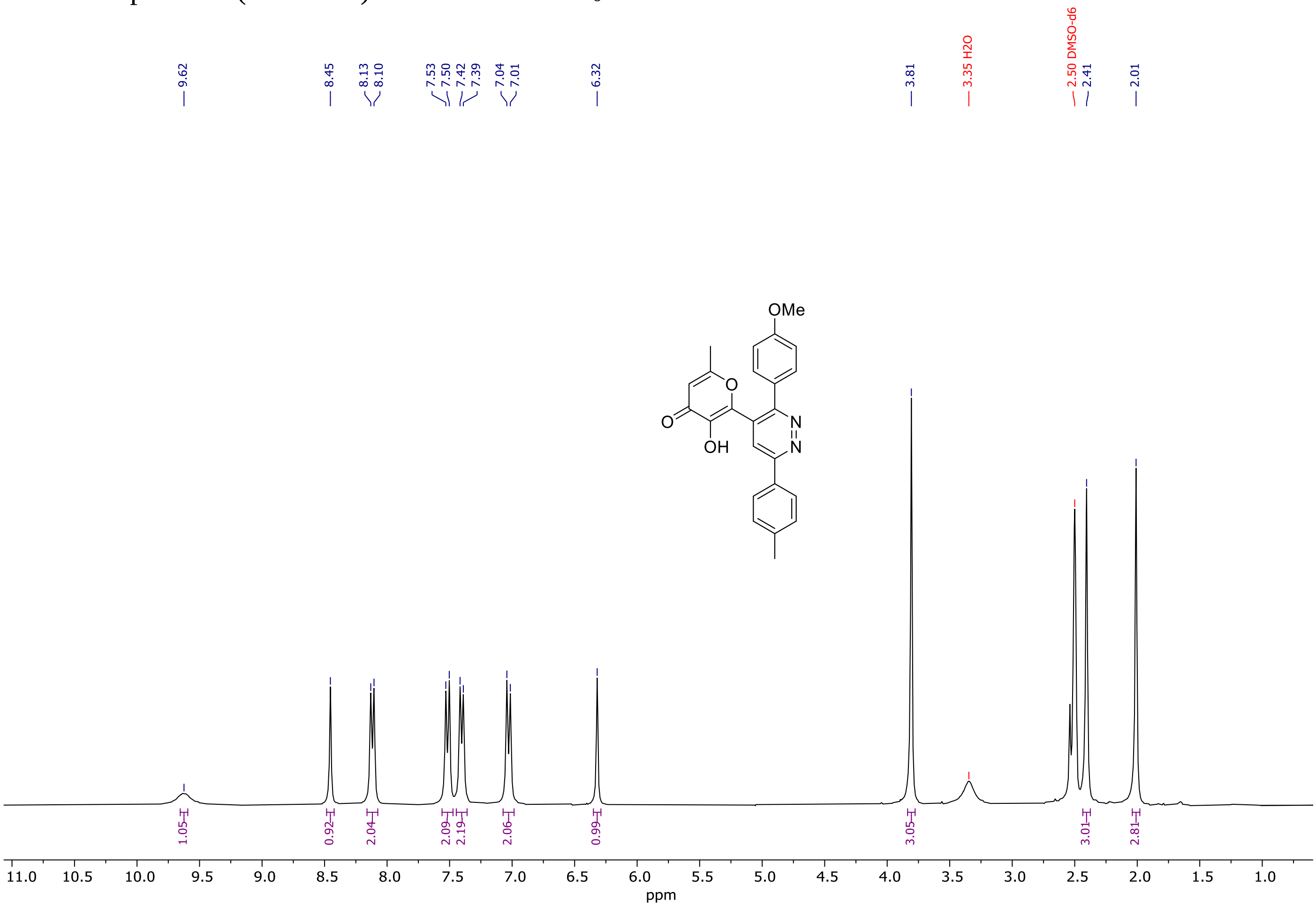
^{1}H NMR spectrum (300 MHz) of **5a** in DMSO-d_6



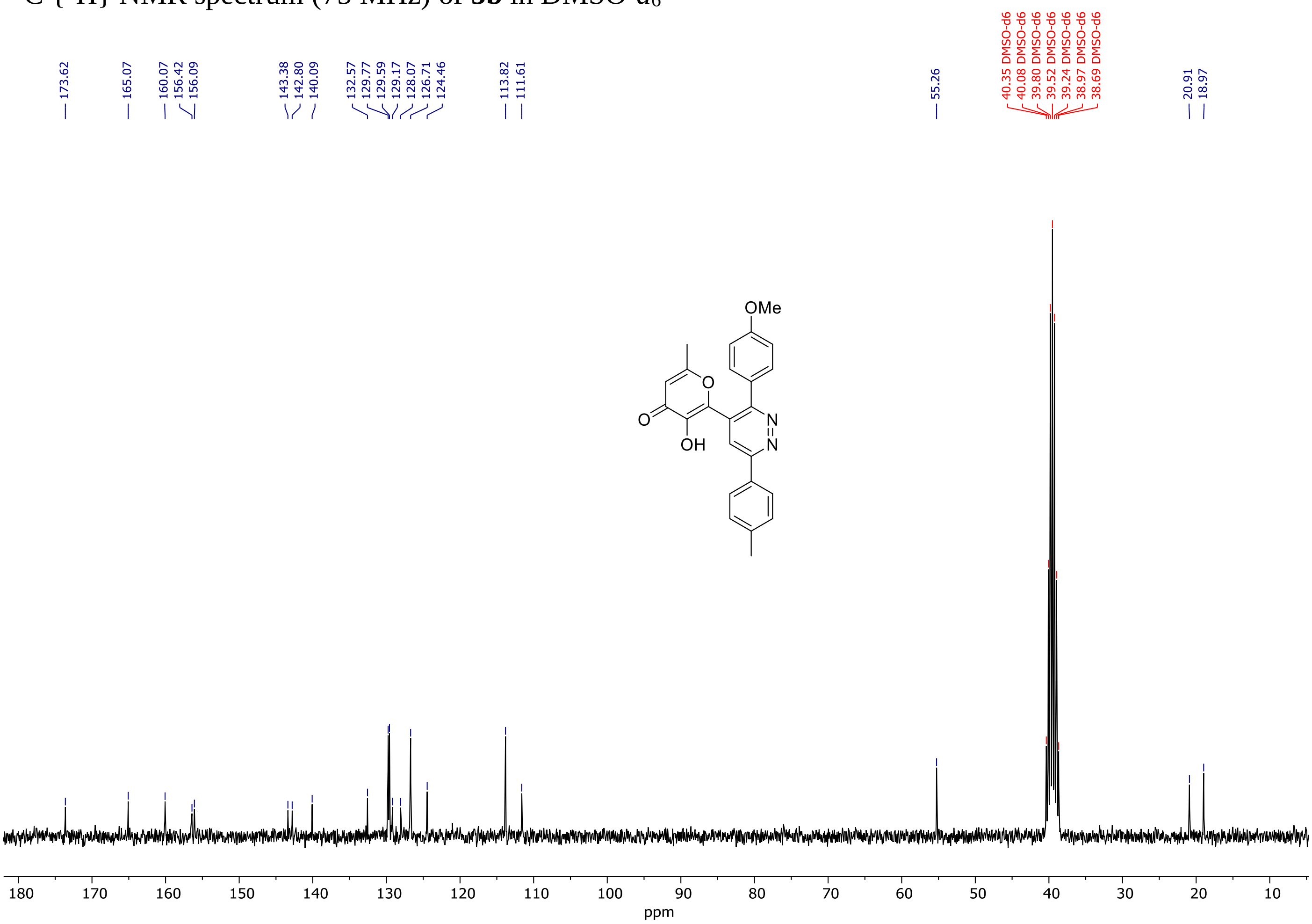
^{13}C {^{1}H} NMR spectrum (75 MHz) of **5a** in DMSO-d_6



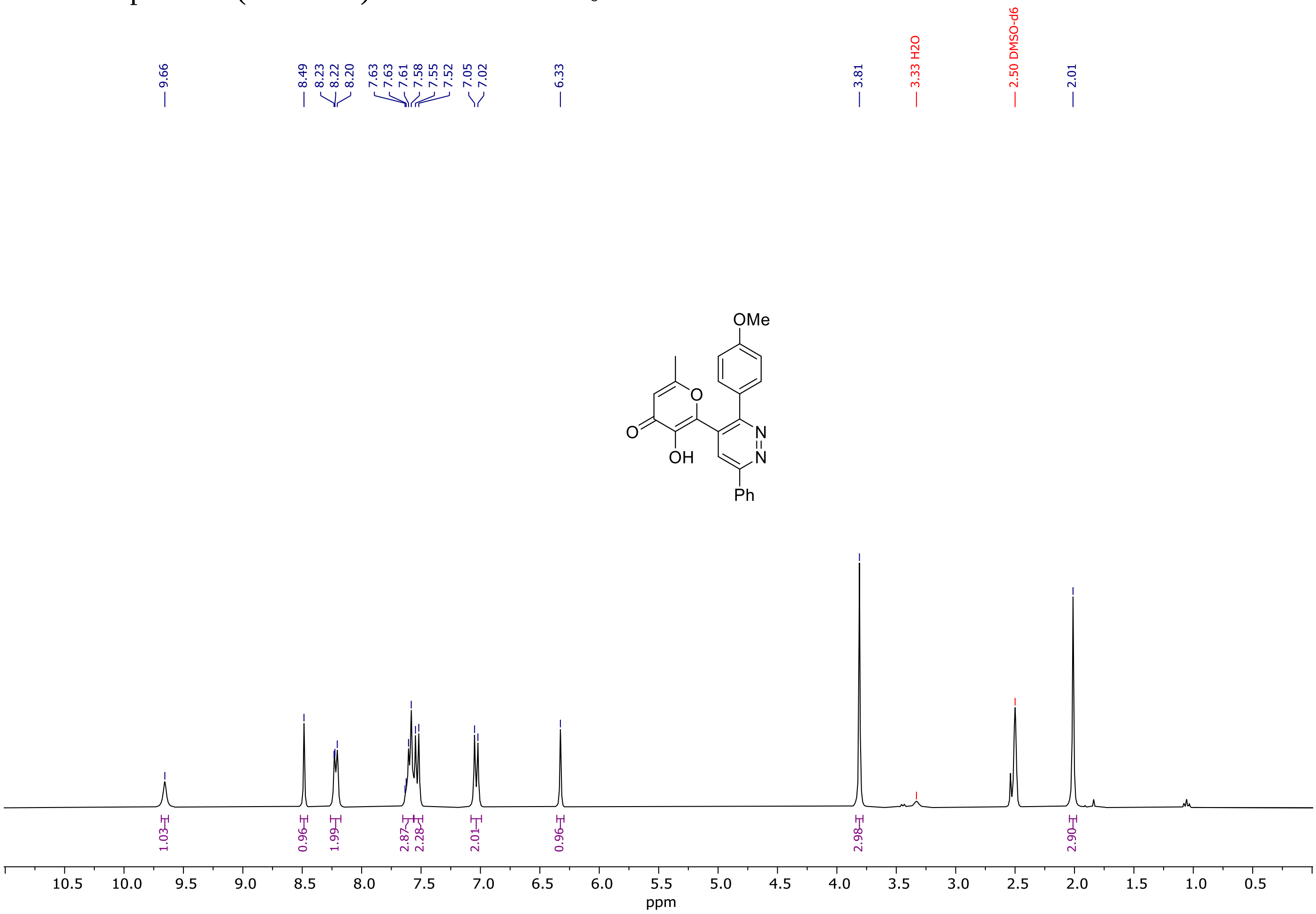
^{1}H NMR spectrum (300 MHz) of **5b** in DMSO-d_6



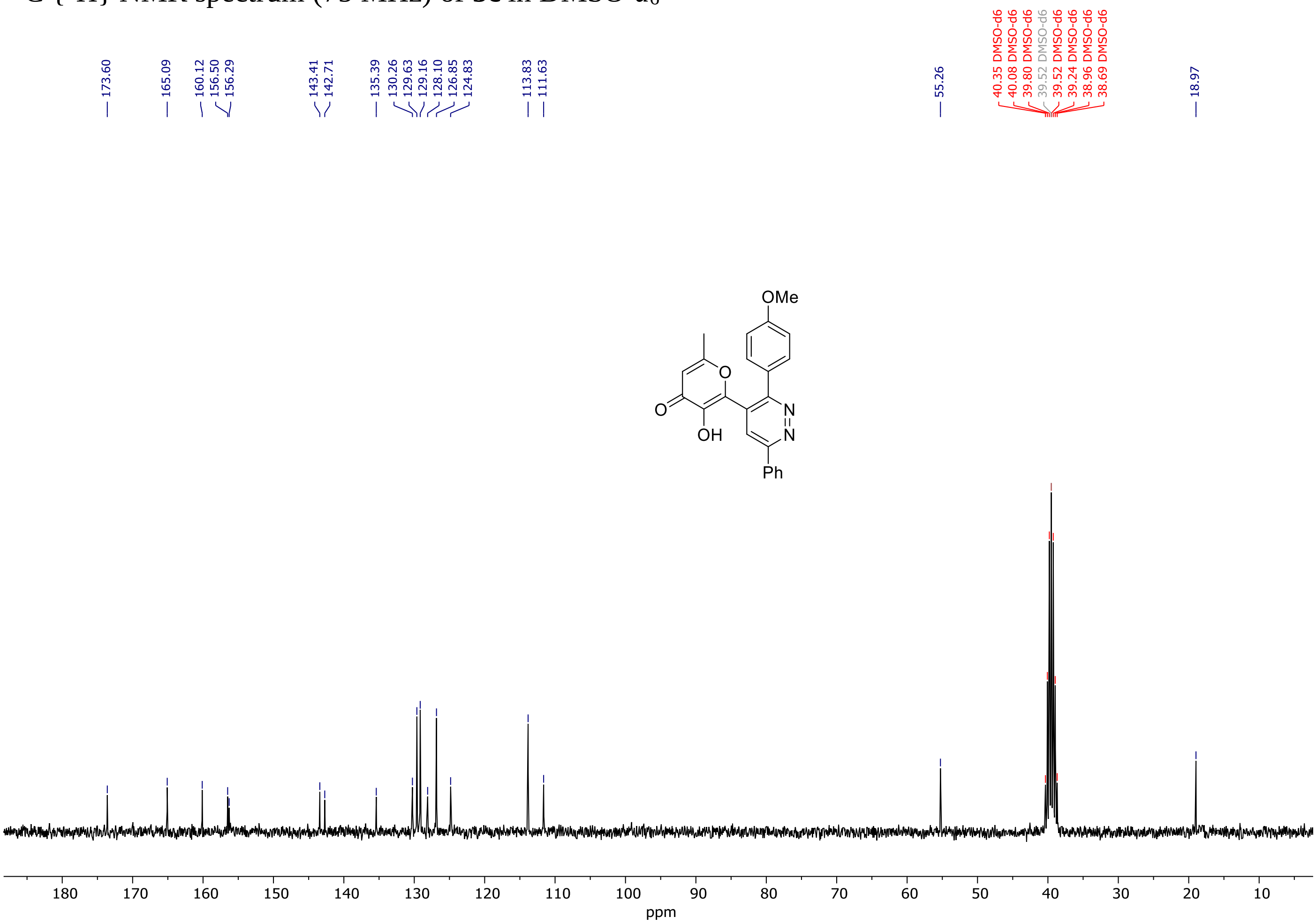
^{13}C {^{1}H} NMR spectrum (75 MHz) of **5b** in DMSO-d_6



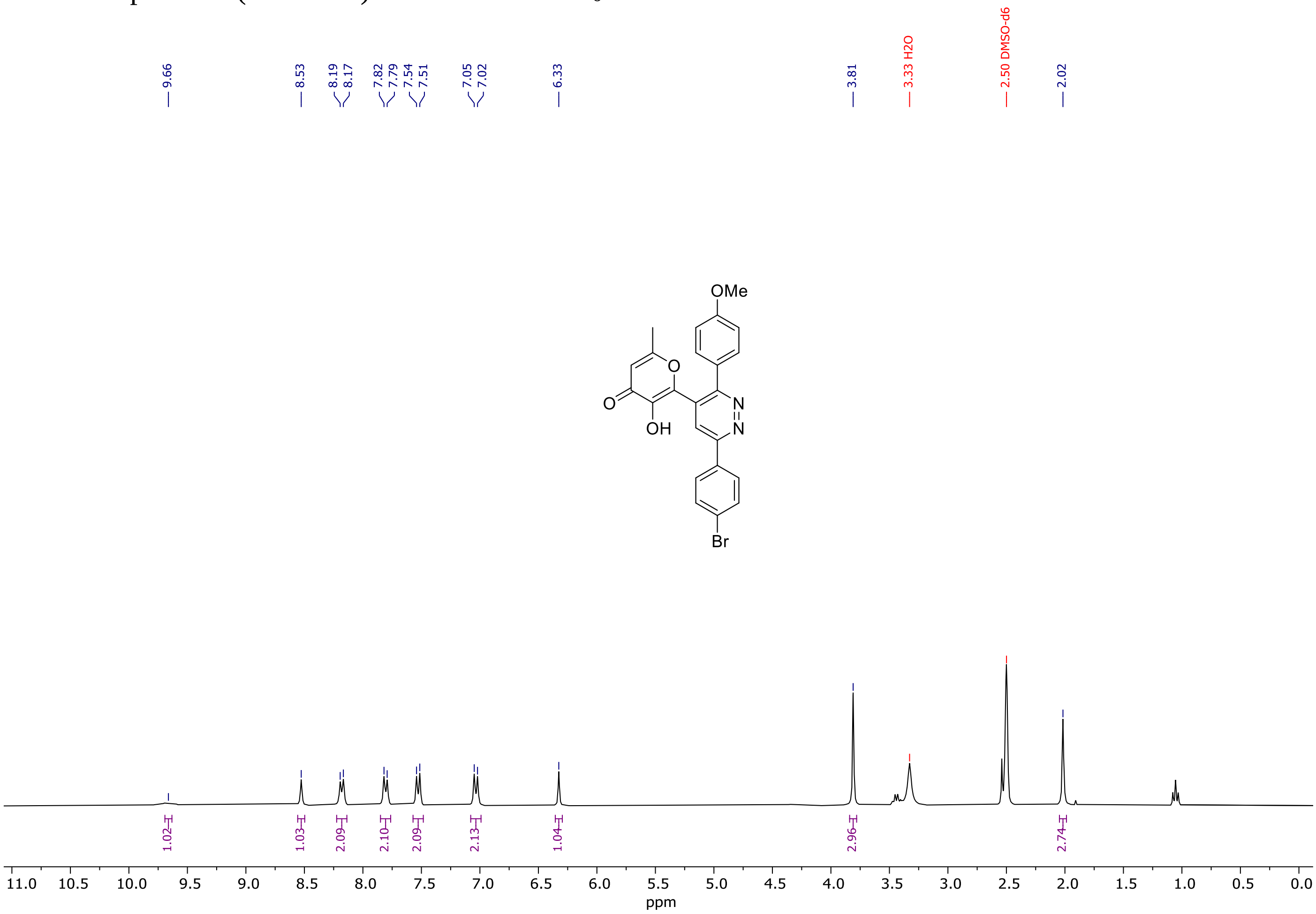
^{1}H NMR spectrum (300 MHz) of **5c** in DMSO-d_6



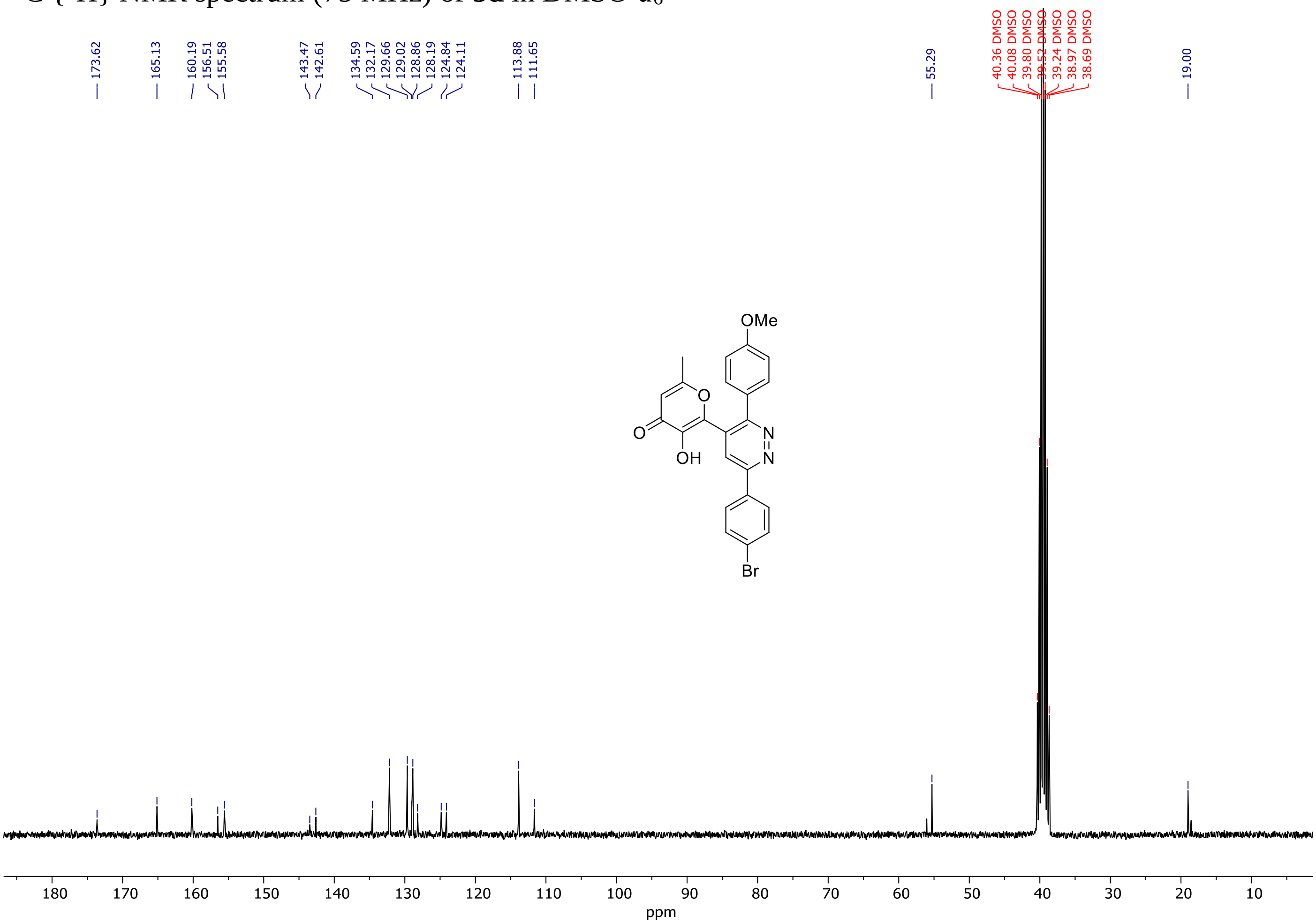
^{13}C {^{1}H} NMR spectrum (75 MHz) of **5c** in DMSO-d_6



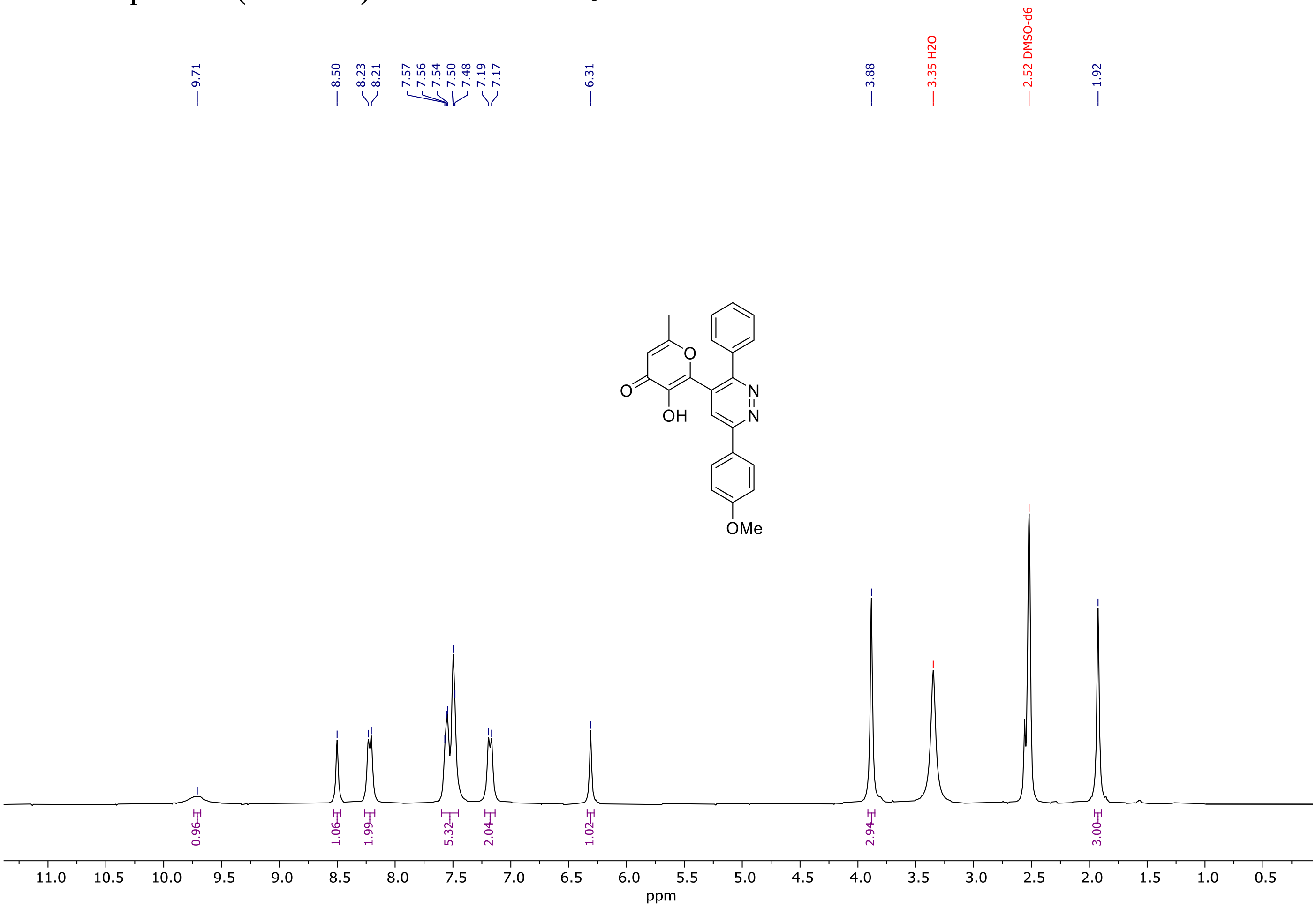
^{1}H NMR spectrum (300 MHz) of **5d** in DMSO-d_6



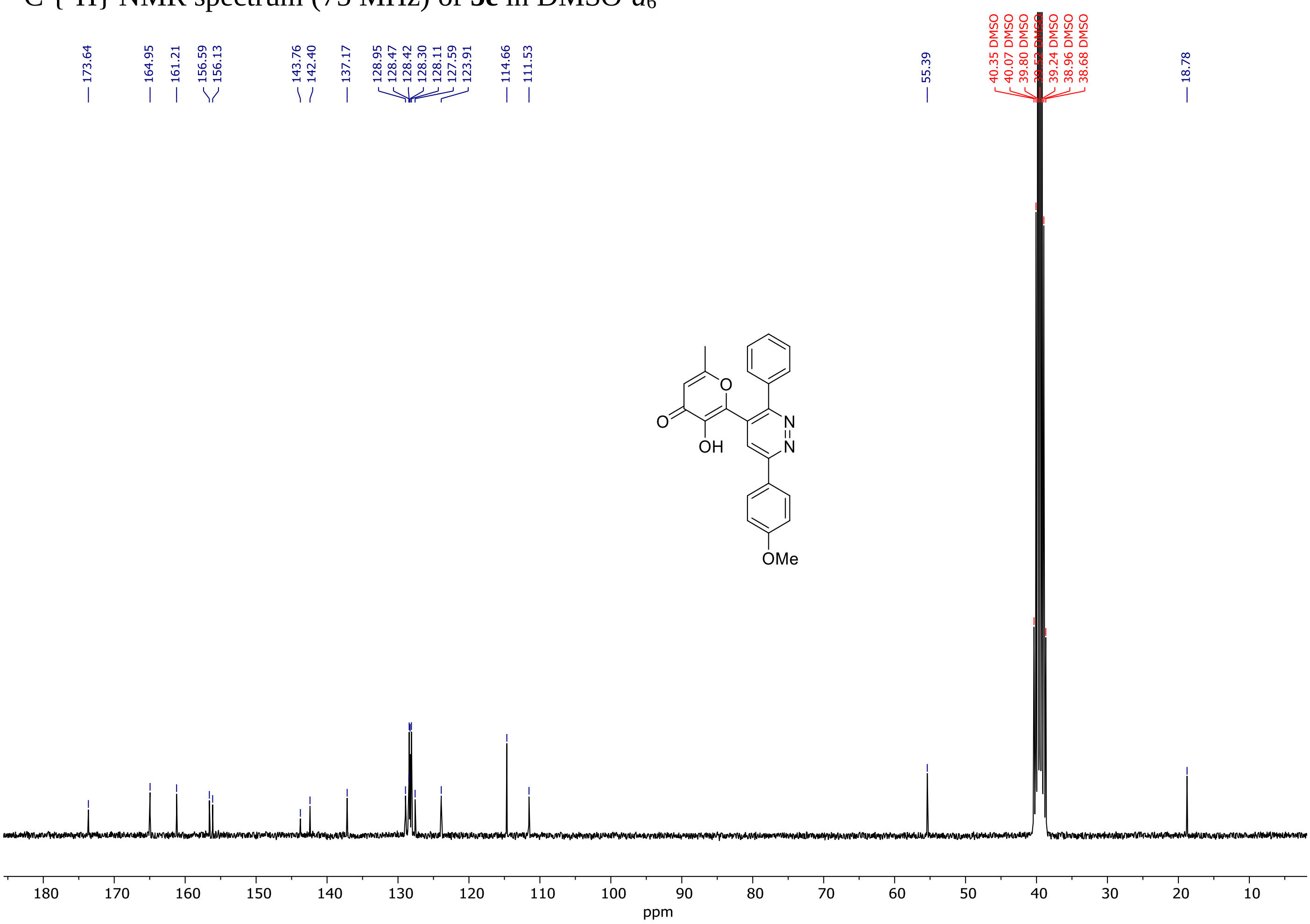
^{13}C {^{1}H} NMR spectrum (75 MHz) of **5d** in DMSO-d_6



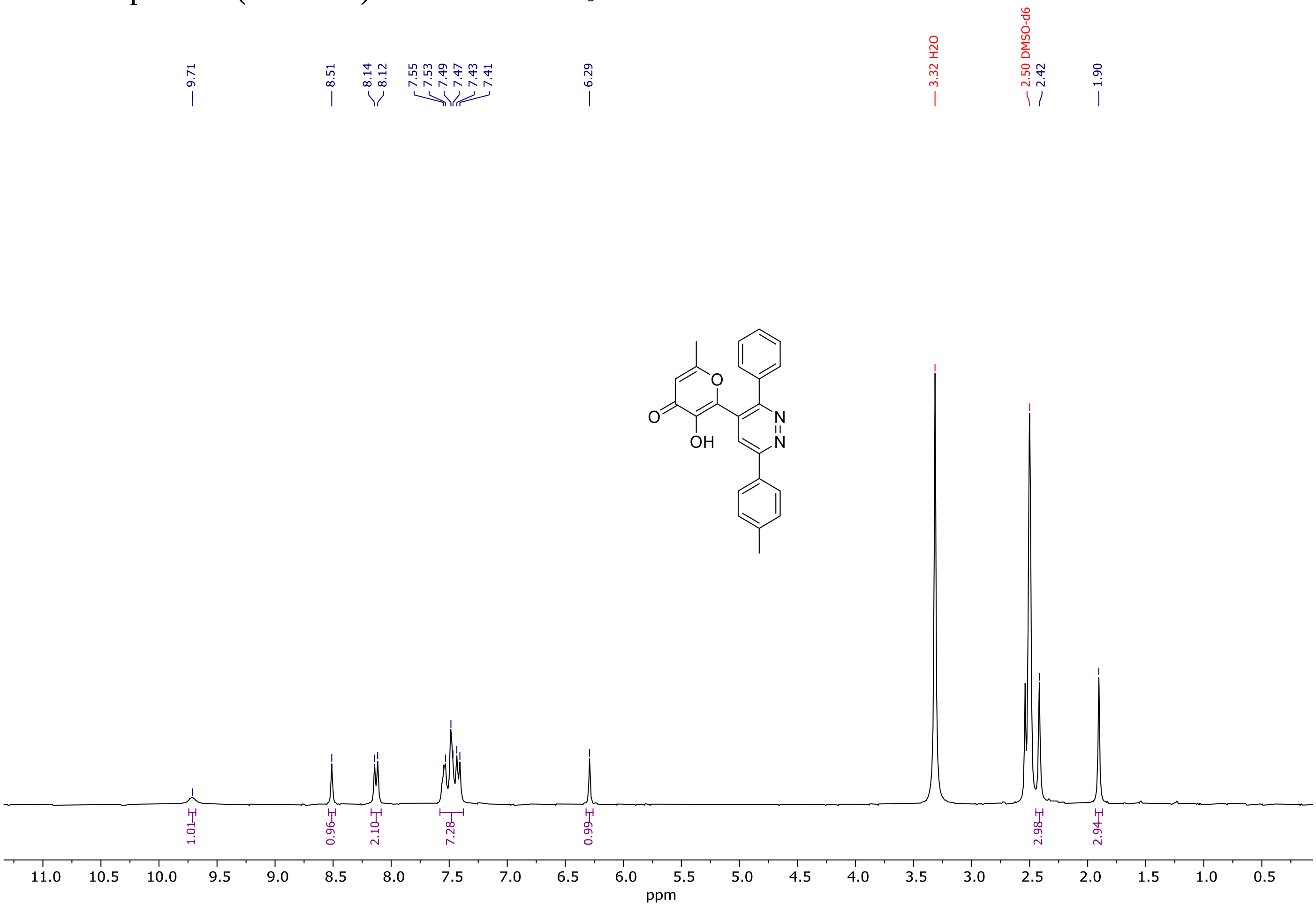
^{1}H NMR spectrum (300 MHz) of **5e** in DMSO-d_6



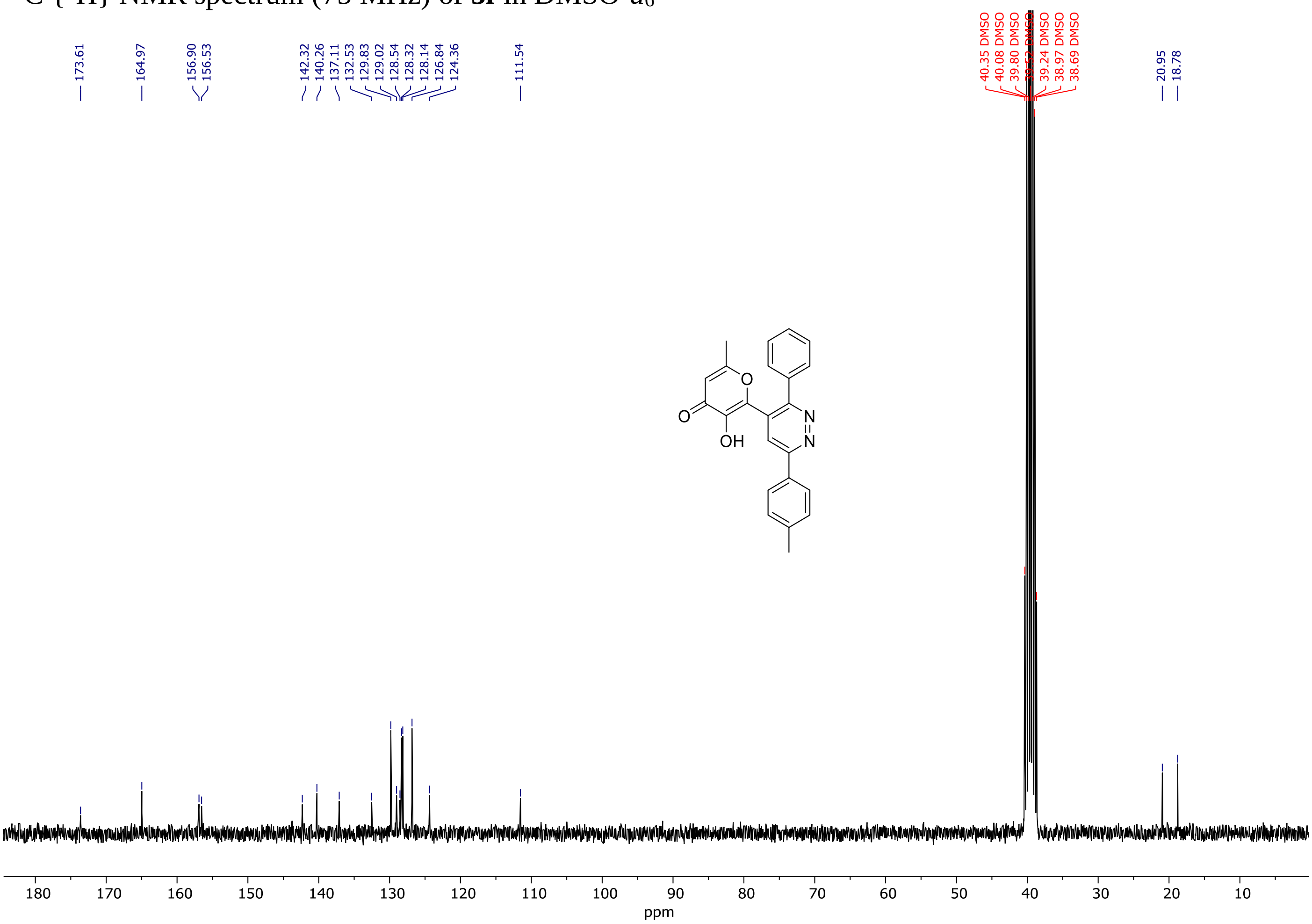
^{13}C {^{1}H} NMR spectrum (75 MHz) of **5e** in DMSO-d_6



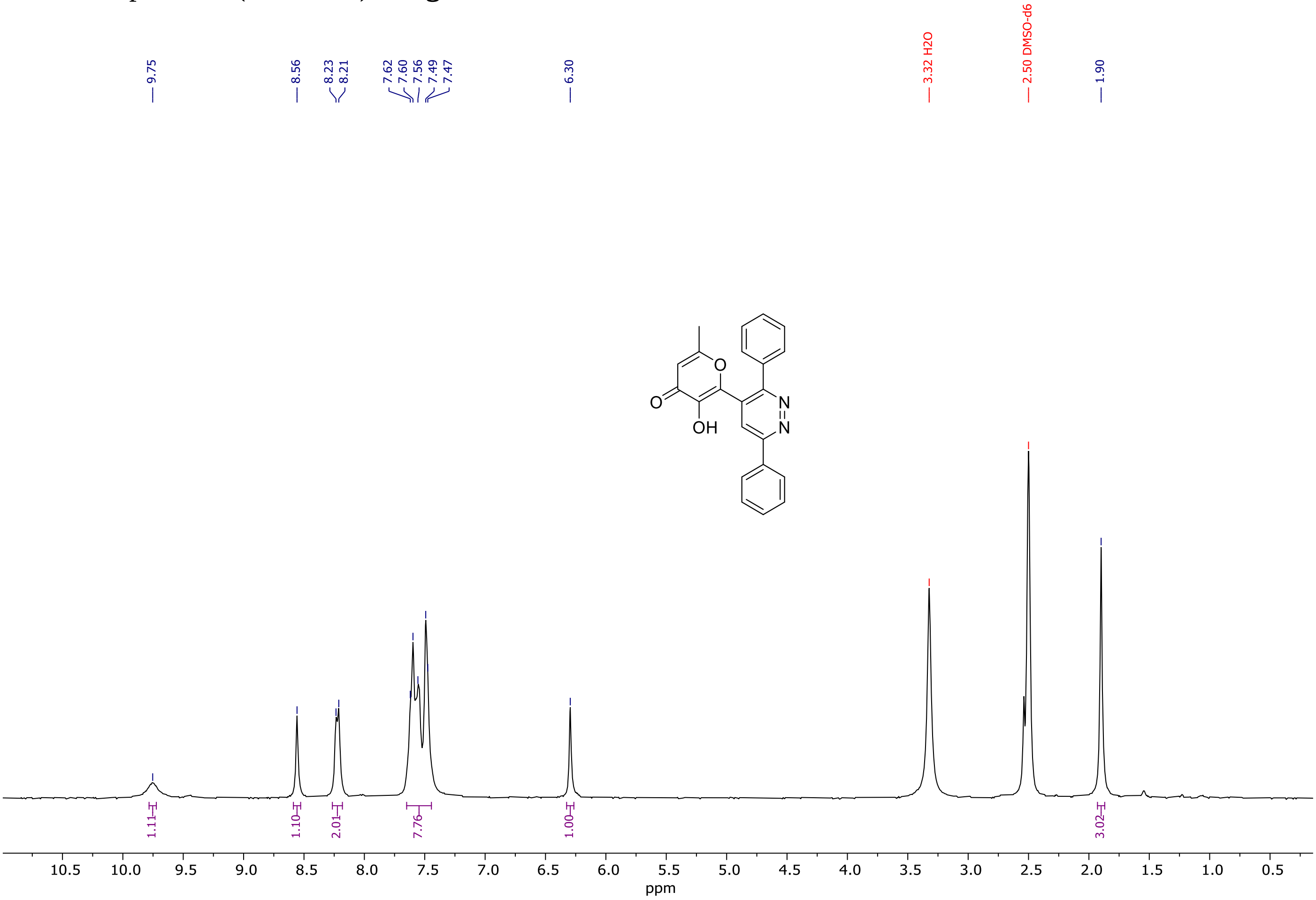
[1]H NMR spectrum (300 MHz) of **5f** in DMSO-d_6



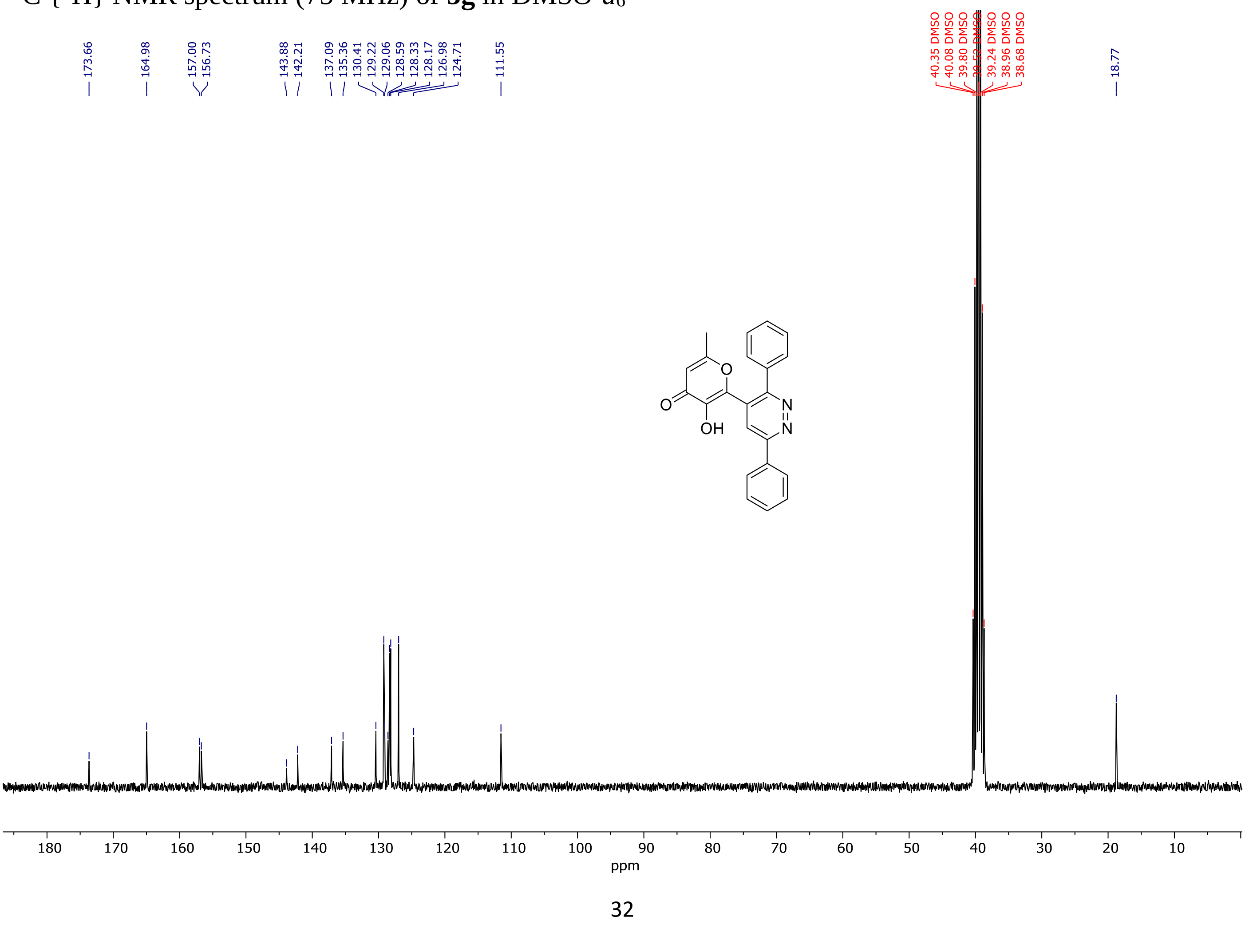
[13]C {[1]H} NMR spectrum (75 MHz) of **5f** in DMSO-d_6



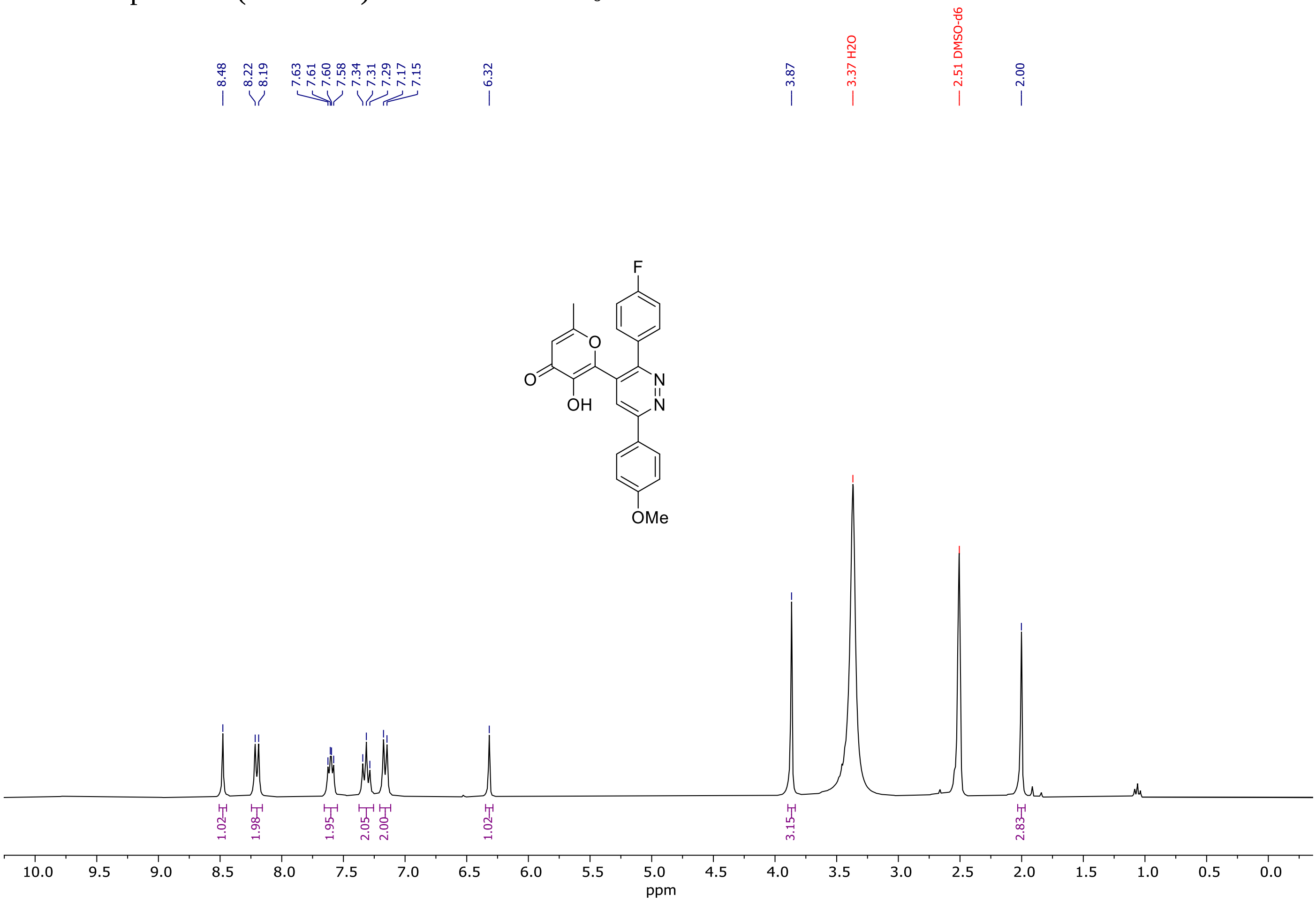
^{1}H NMR spectrum (300 MHz) of **5g** in DMSO-d_6



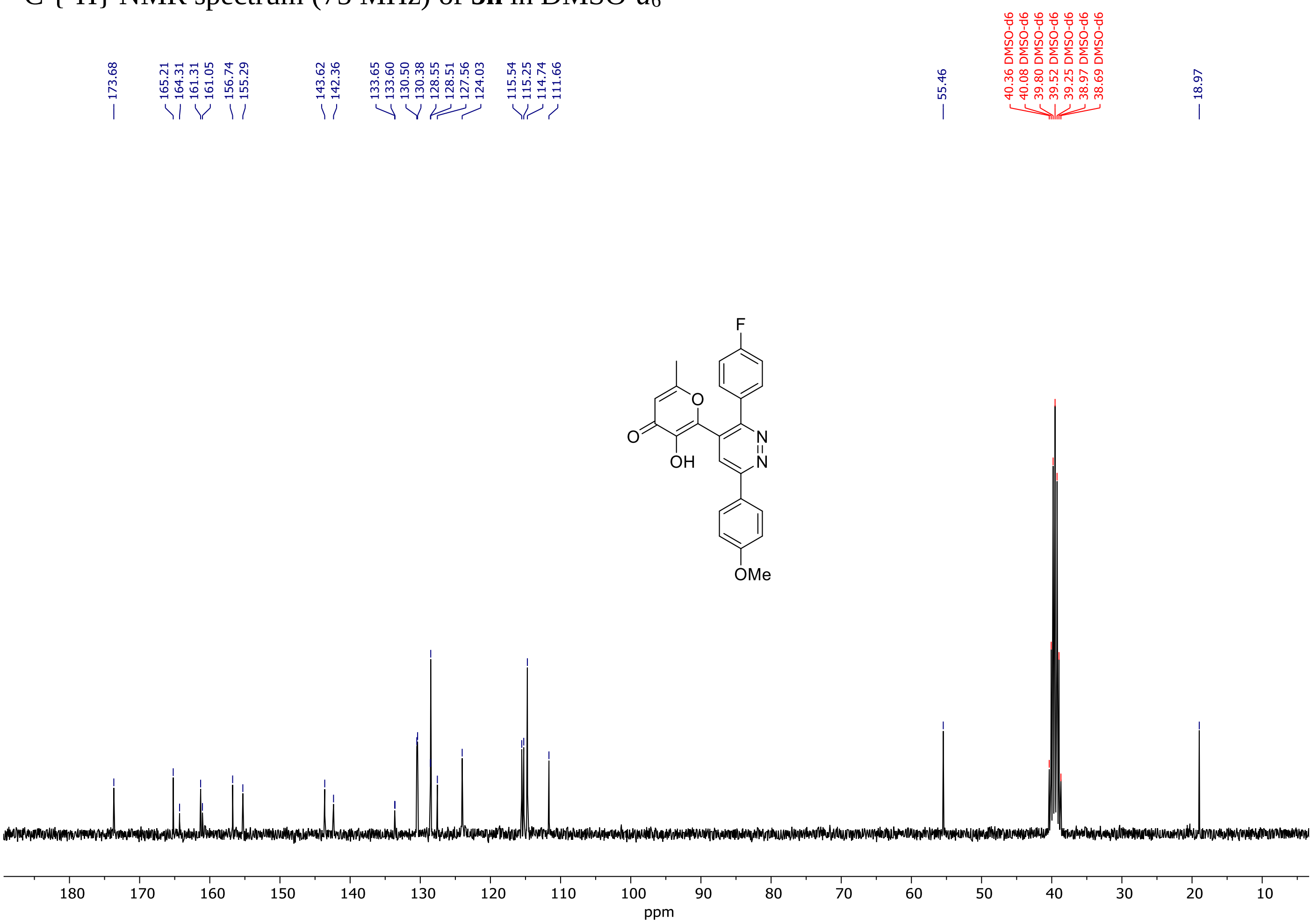
^{13}C {^{1}H} NMR spectrum (75 MHz) of **5g** in DMSO-d_6



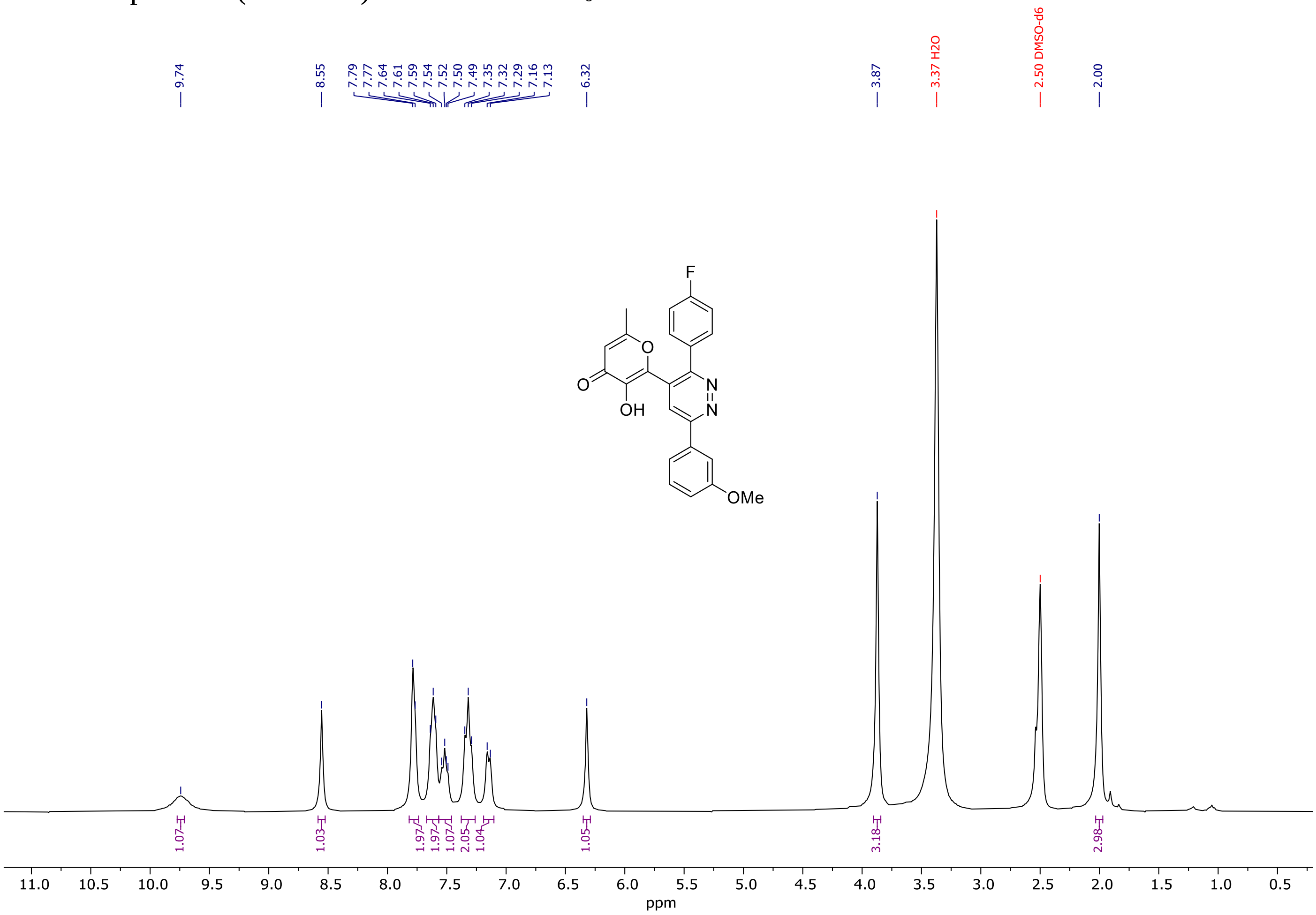
[1]H NMR spectrum (300 MHz) of **5h** in DMSO-d_6



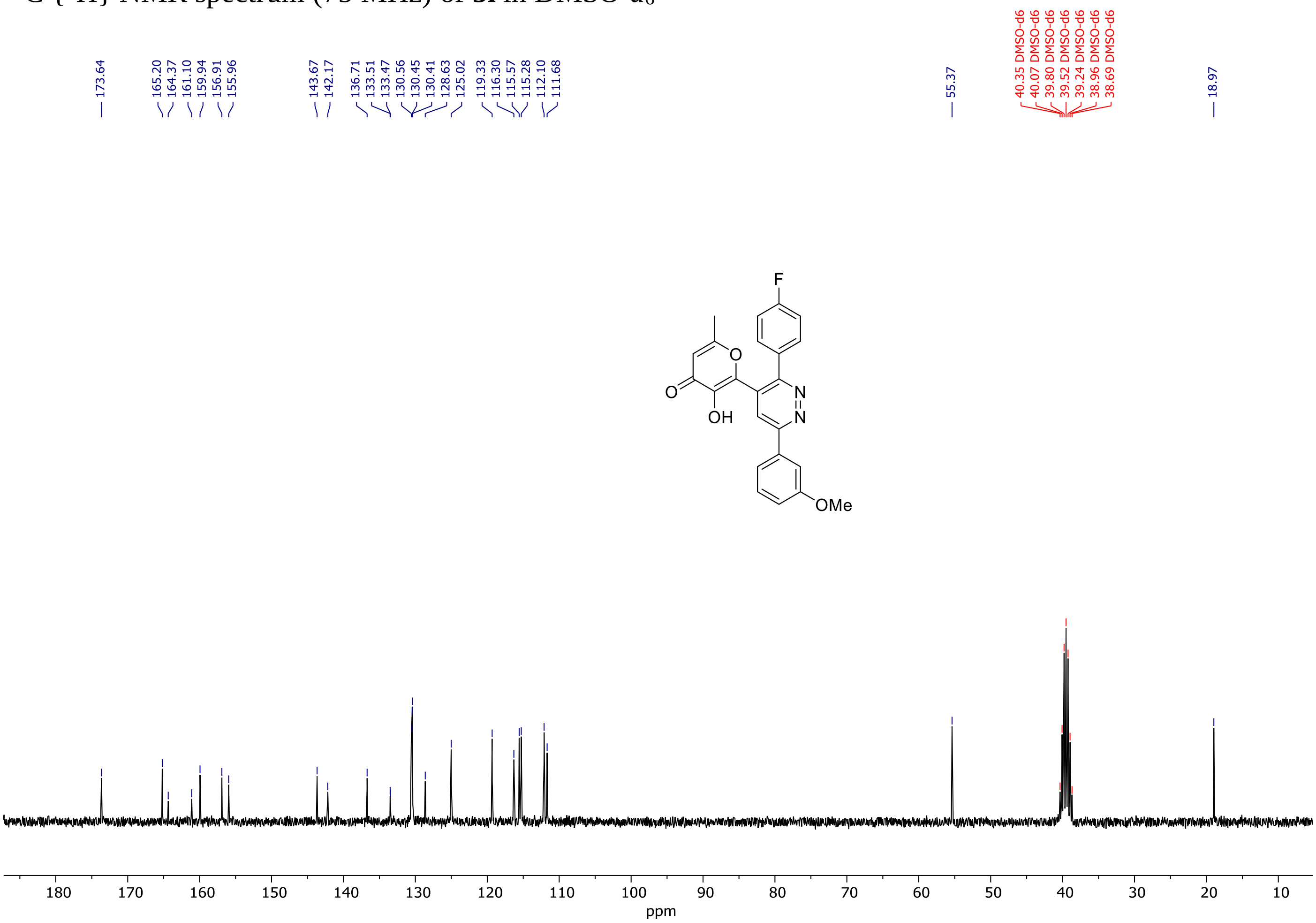
[13]C {[1]H} NMR spectrum (75 MHz) of **5h** in DMSO-d_6



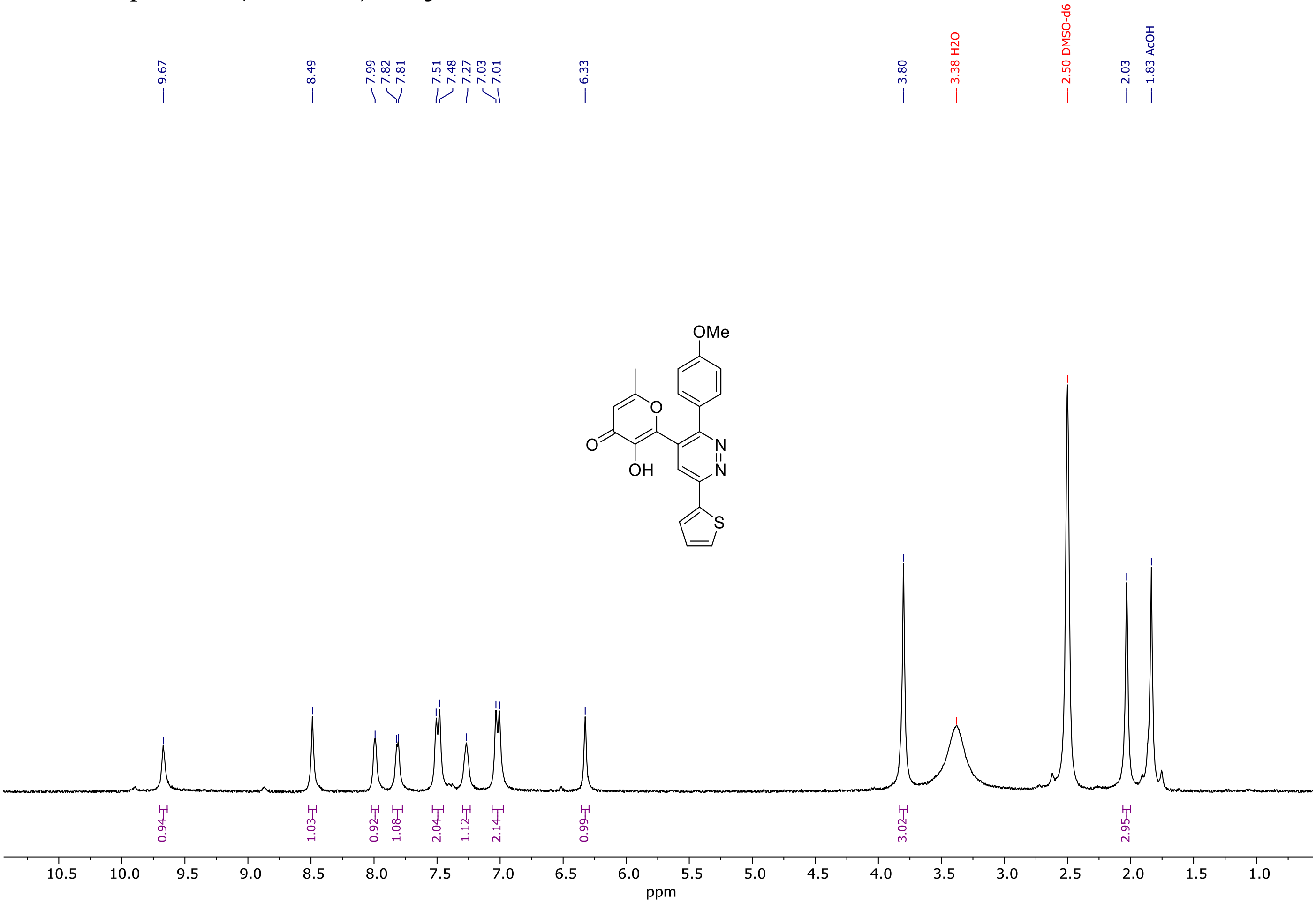
^{1}H NMR spectrum (300 MHz) of **5i** in DMSO-d_6



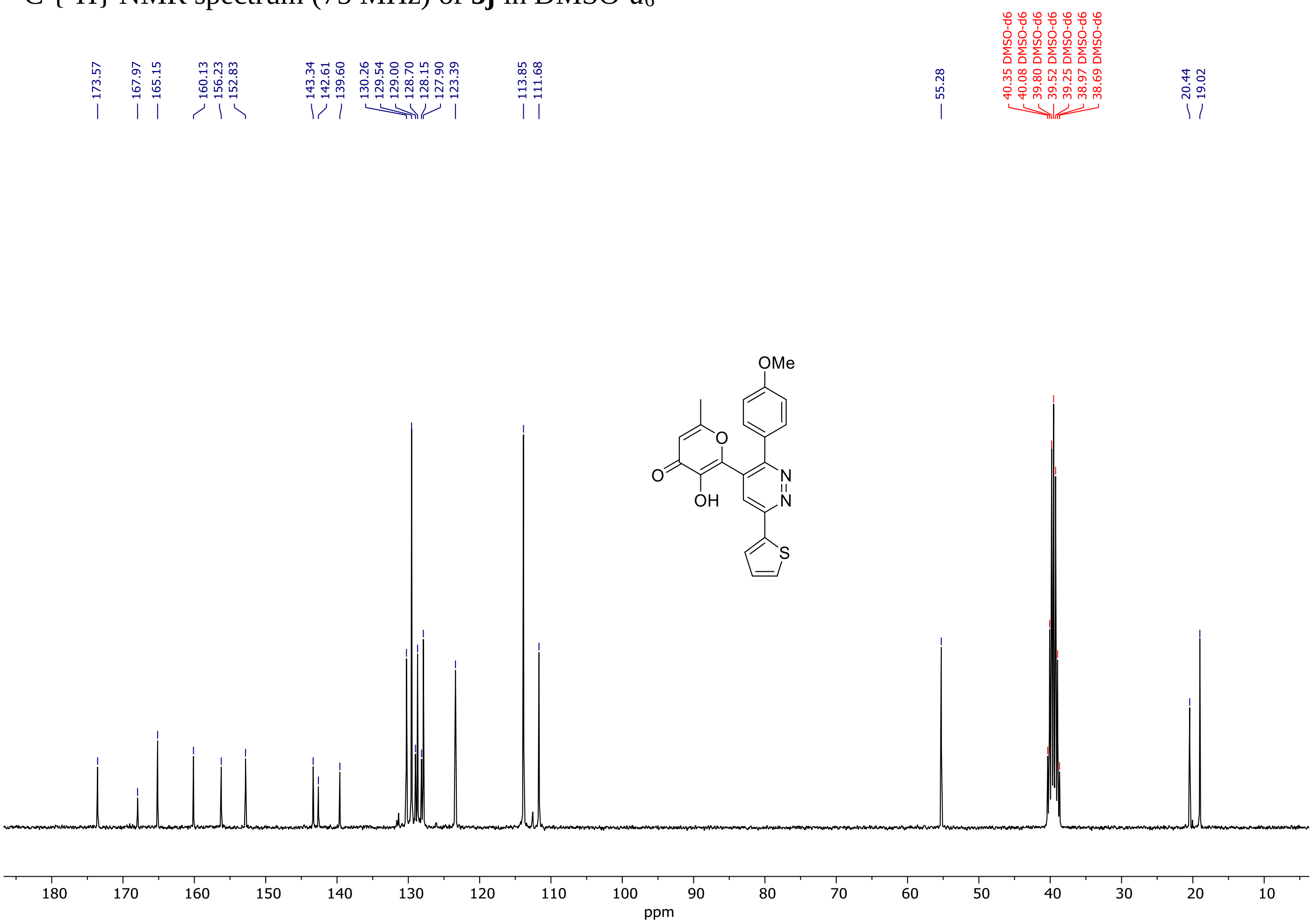
^{13}C {^{1}H} NMR spectrum (75 MHz) of **5i** in DMSO-d_6



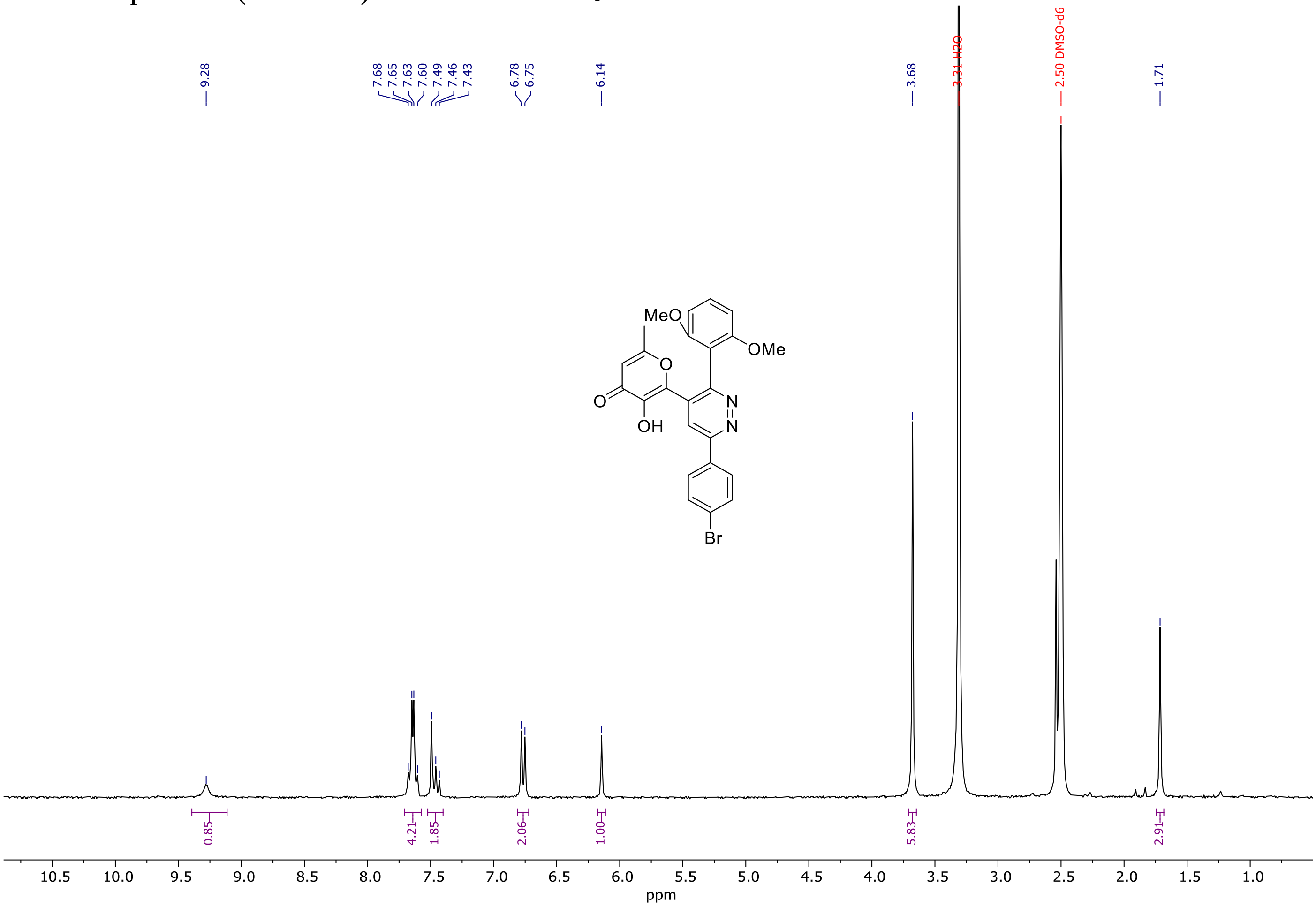
[1]H NMR spectrum (300 MHz) of **5j** in DMSO-d_6



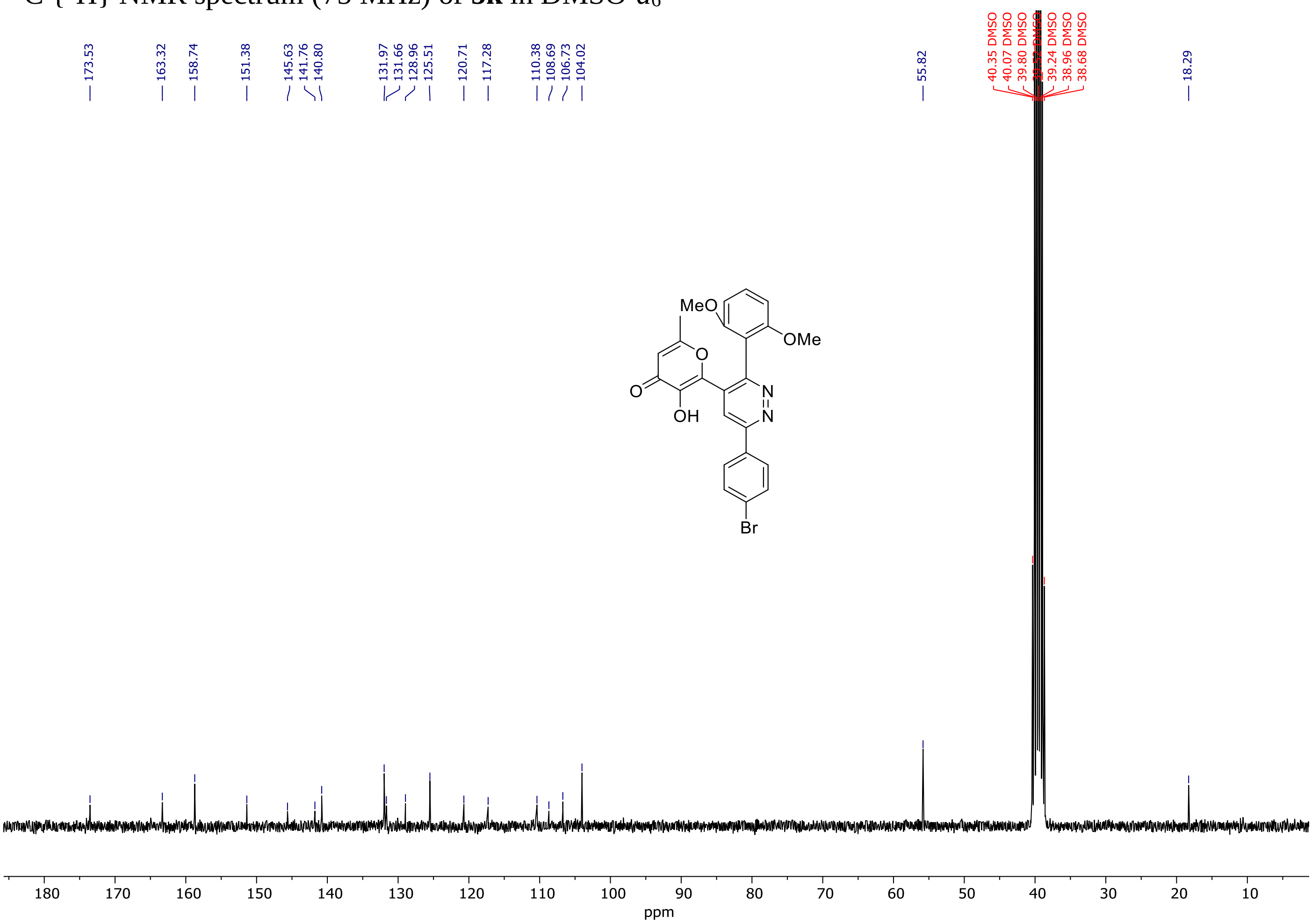
[13]C {[1]H} NMR spectrum (75 MHz) of **5j** in DMSO-d_6



[1]H NMR spectrum (300 MHz) of **5k** in DMSO-d_6

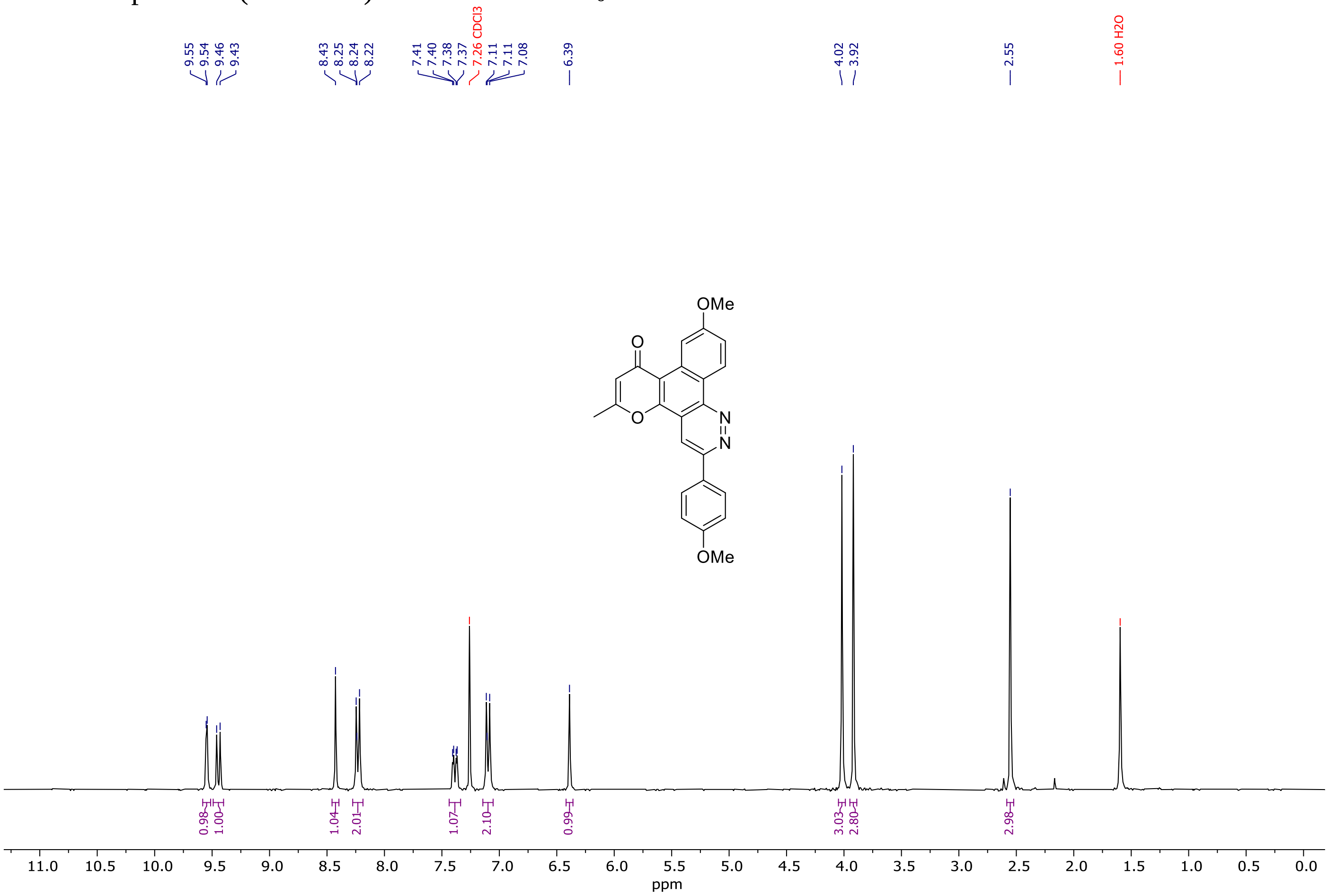


[13]C {[1]H} NMR spectrum (75 MHz) of **5k** in DMSO-d_6

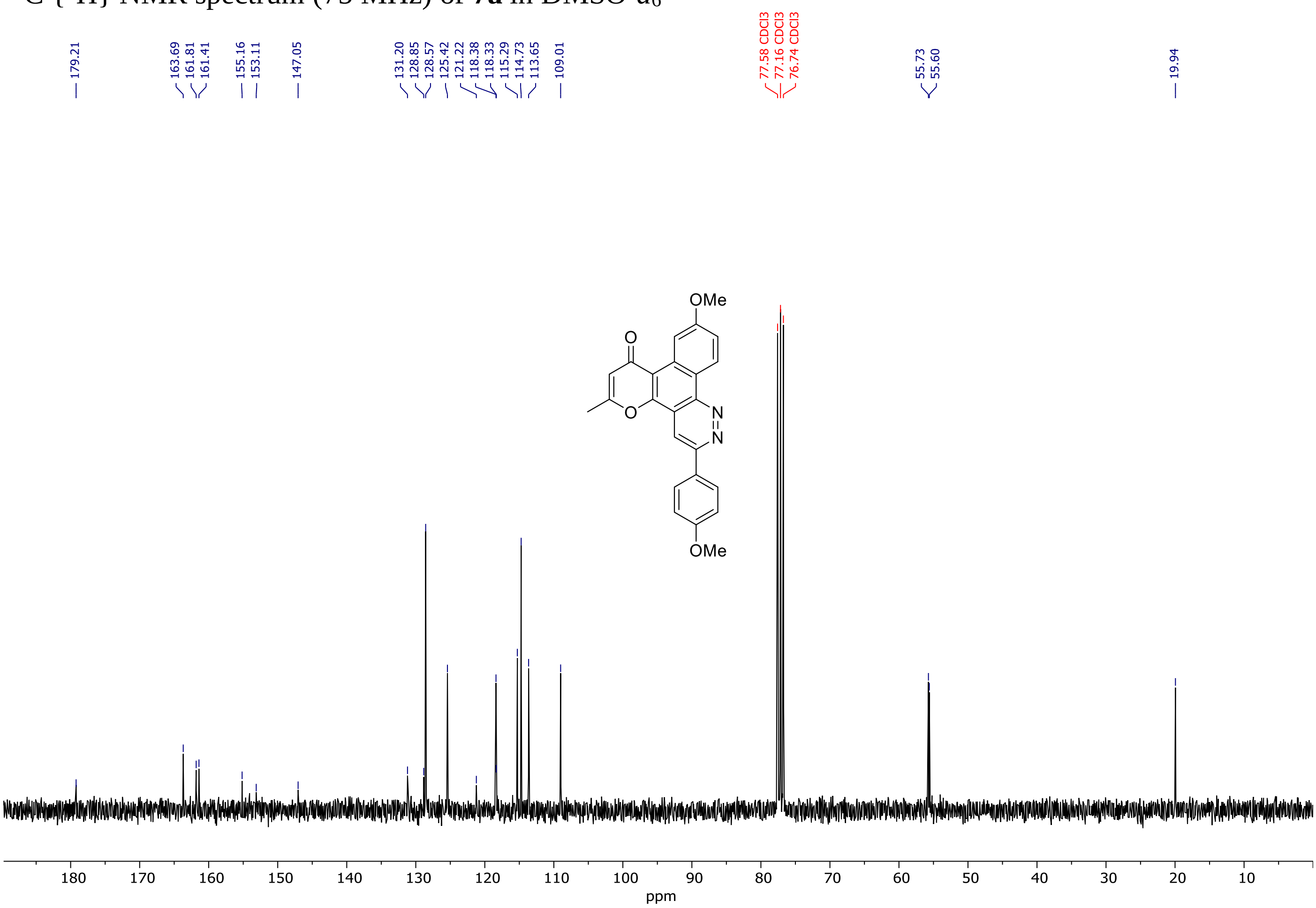


9. NMR ^{1}H and ^{13}C spectra for compounds 7

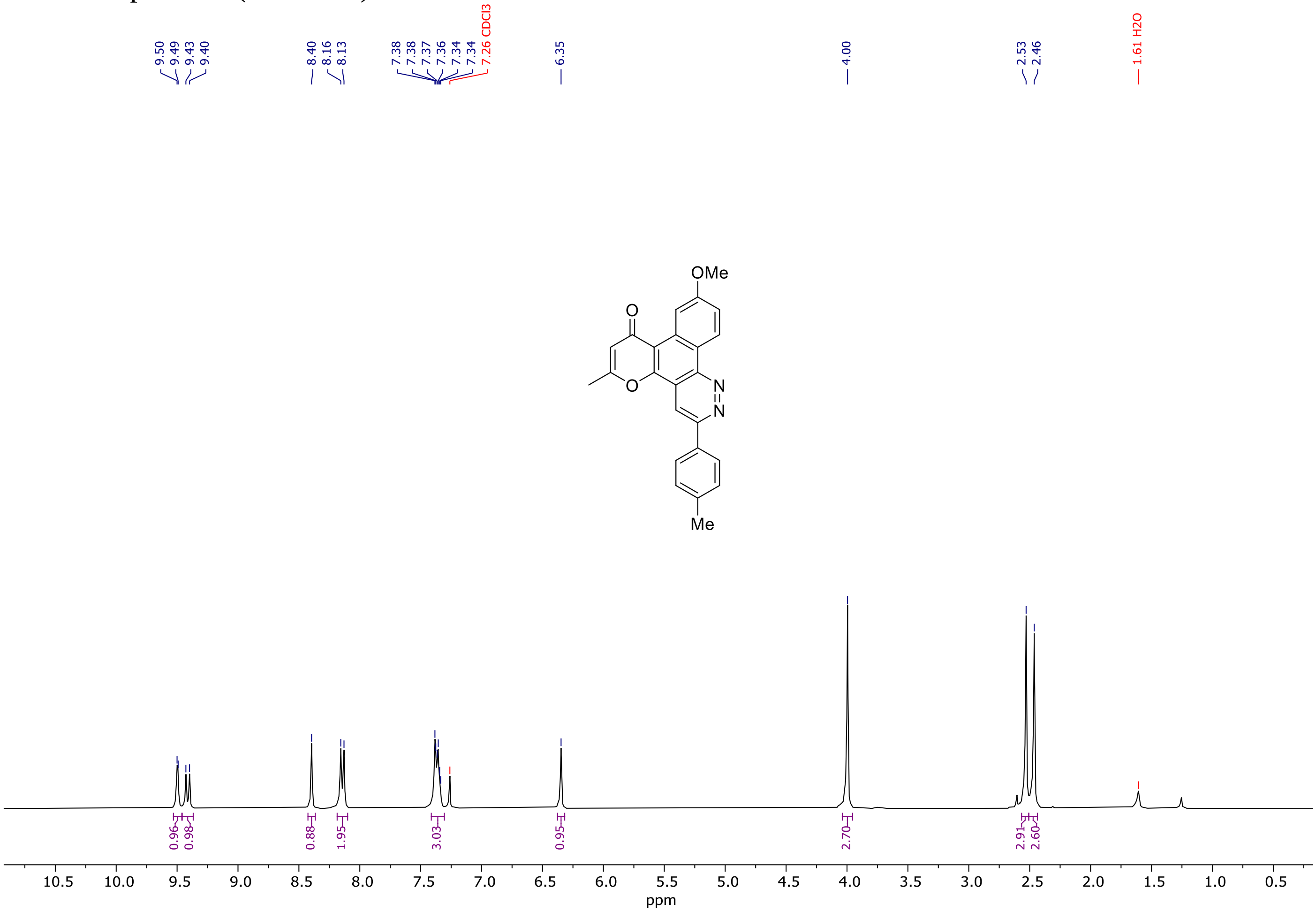
^{1}H NMR spectrum (300 MHz) of **7a** in DMSO-d_6



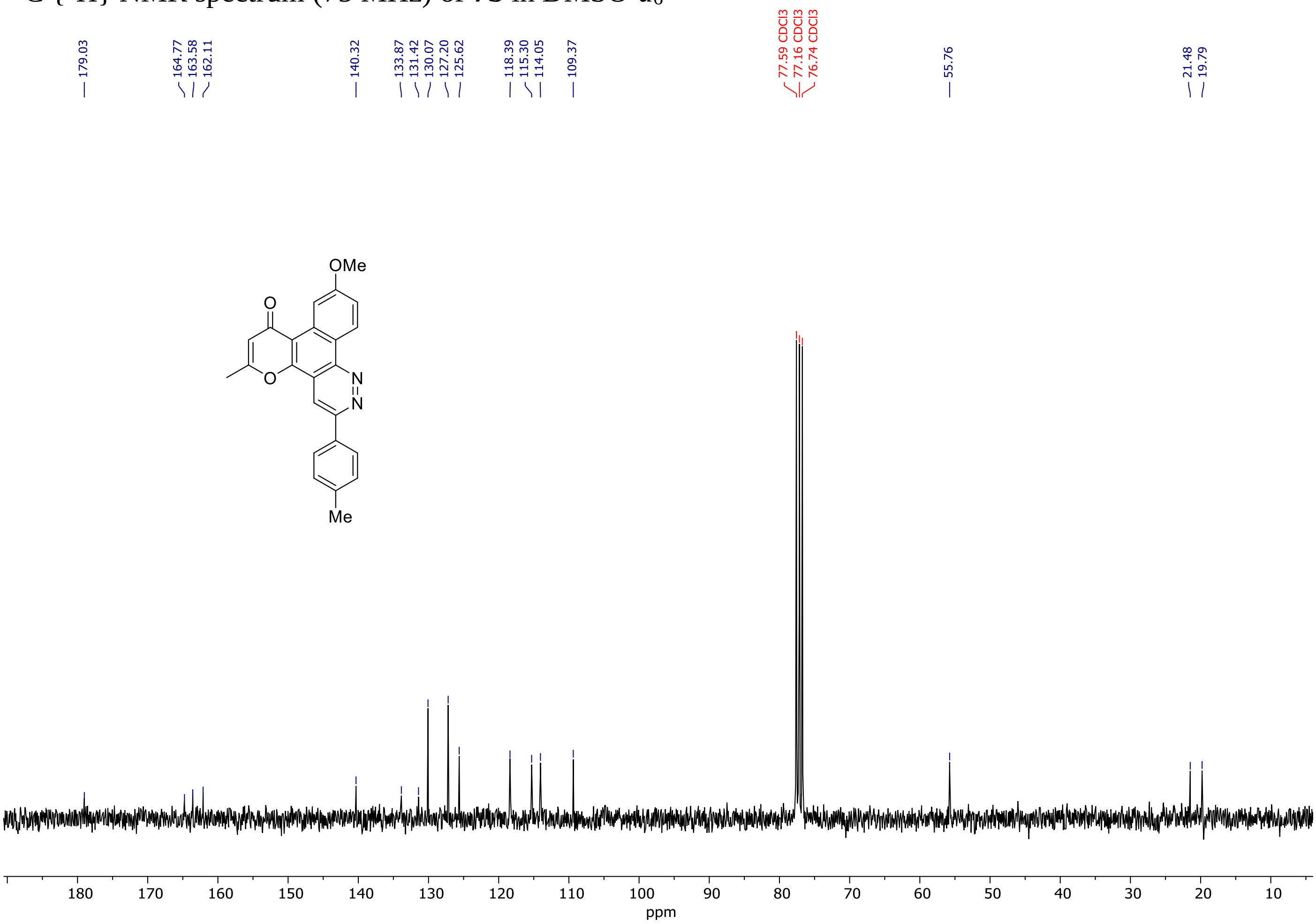
^{13}C {^{1}H} NMR spectrum (75 MHz) of **7a** in DMSO-d_6



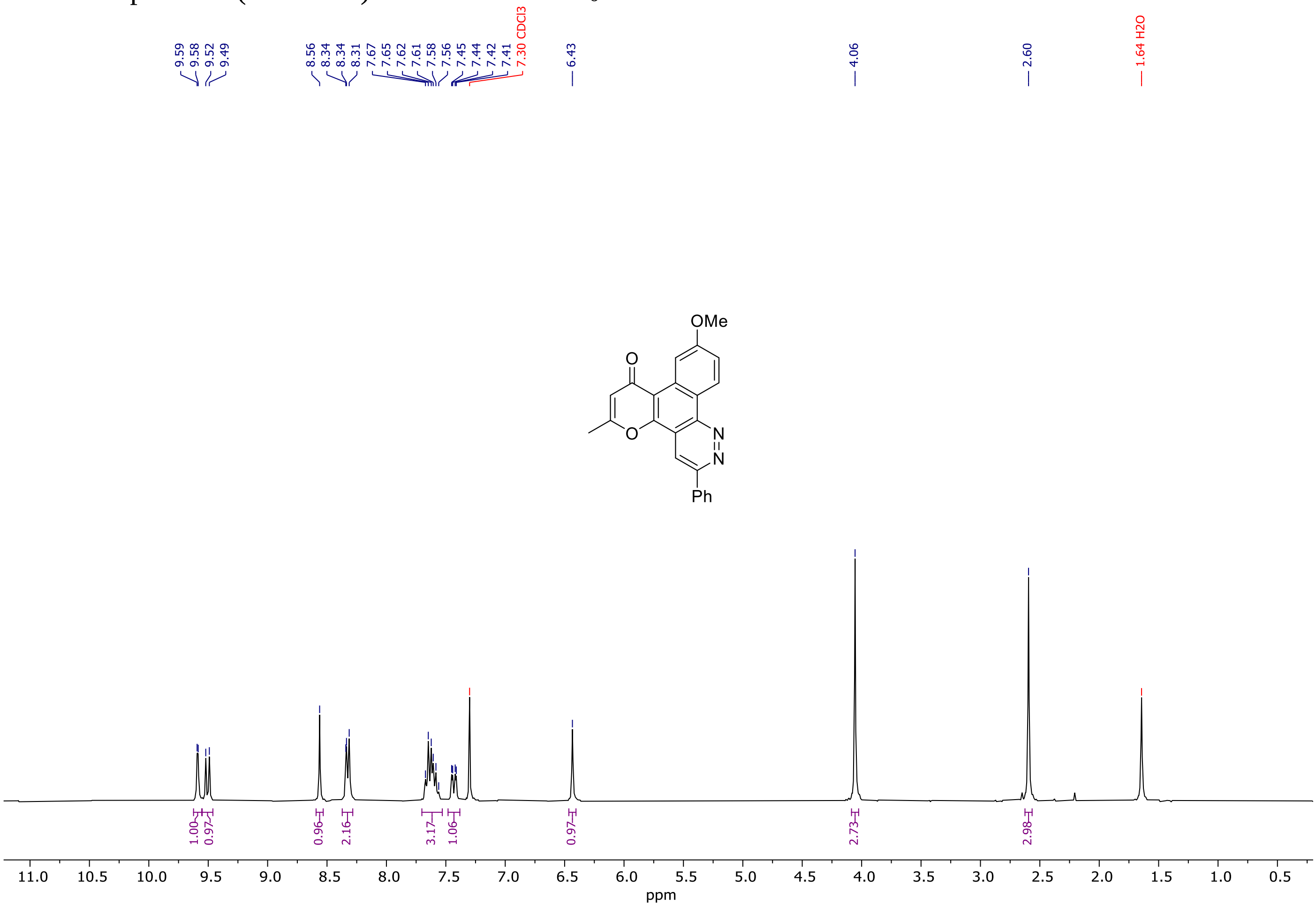
[1]H NMR spectrum (300 MHz) of **7b** in DMSO-d_6



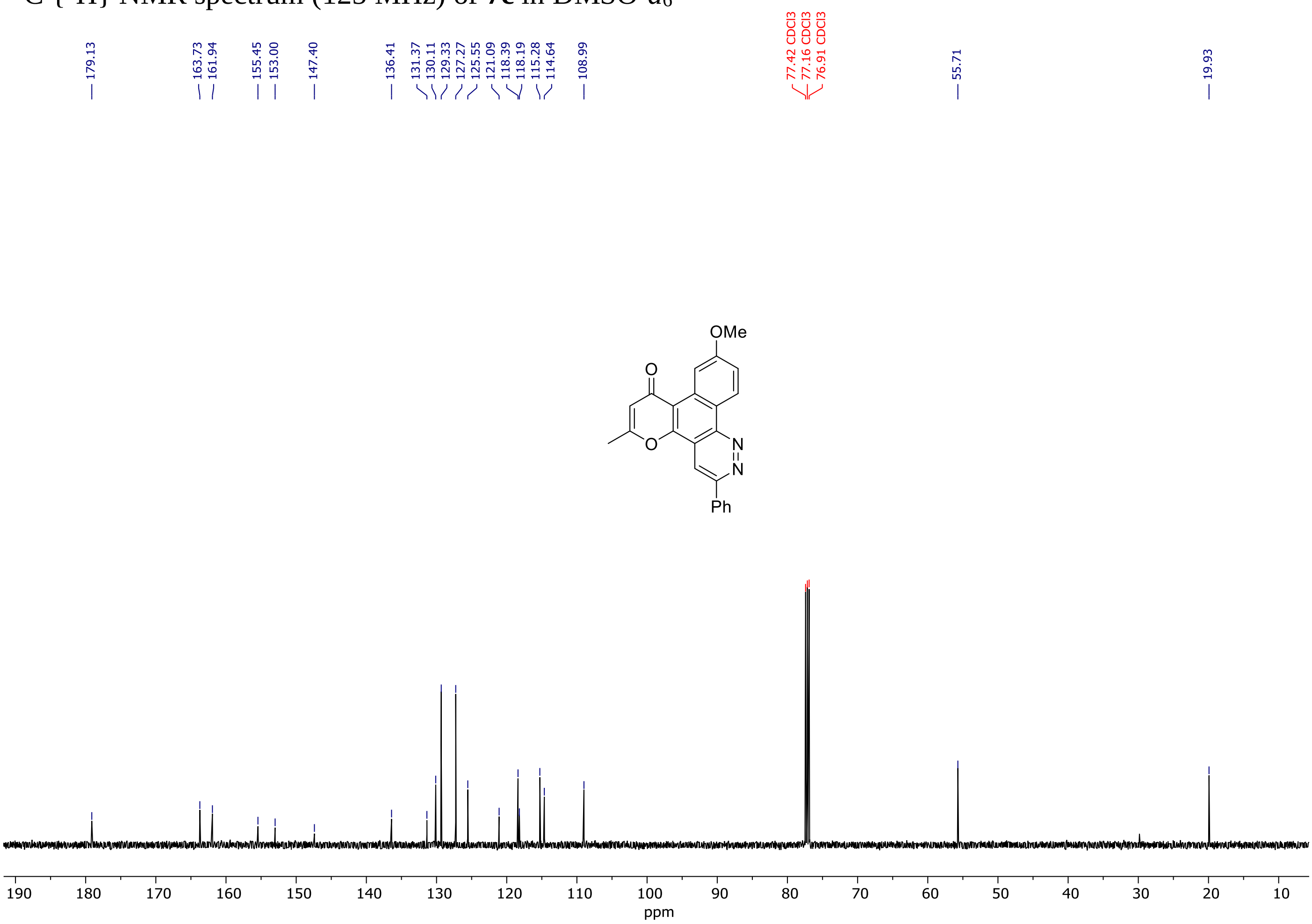
[13]C {[1]H} NMR spectrum (75 MHz) of **7b** in DMSO-d_6



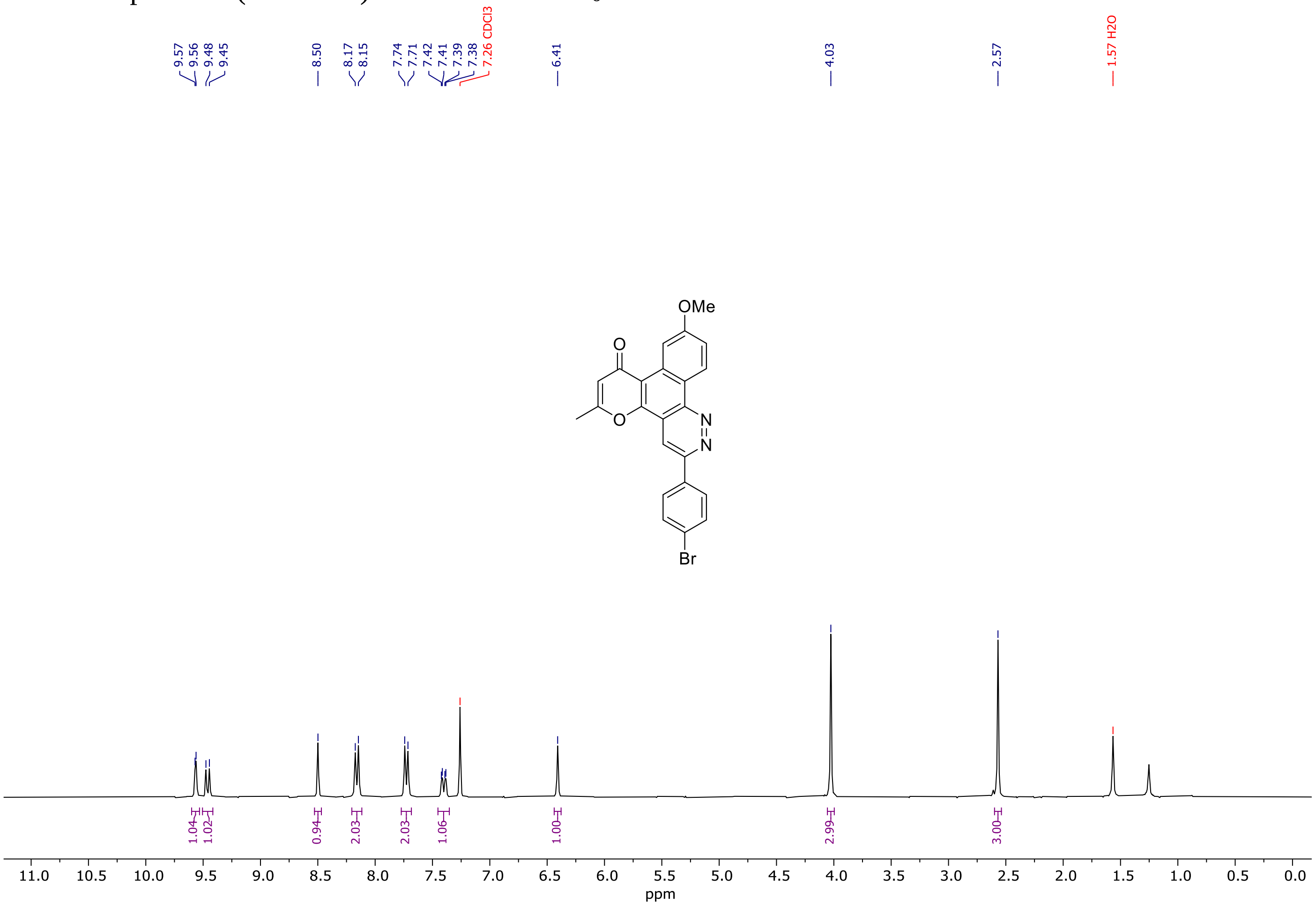
^{1}H NMR spectrum (300 MHz) of **7c** in DMSO-d_6



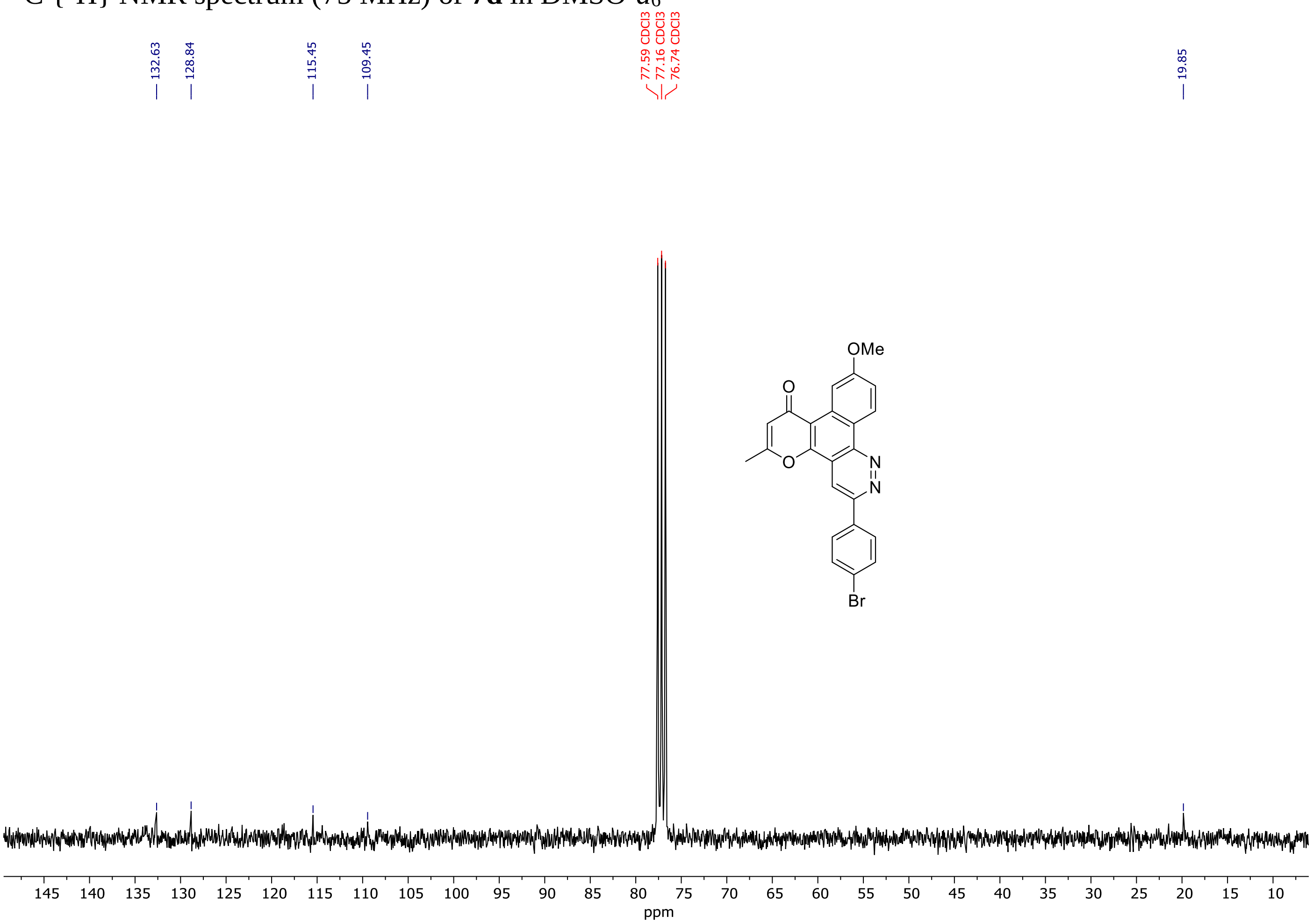
^{13}C {^{1}H} NMR spectrum (125 MHz) of **7c** in DMSO-d_6



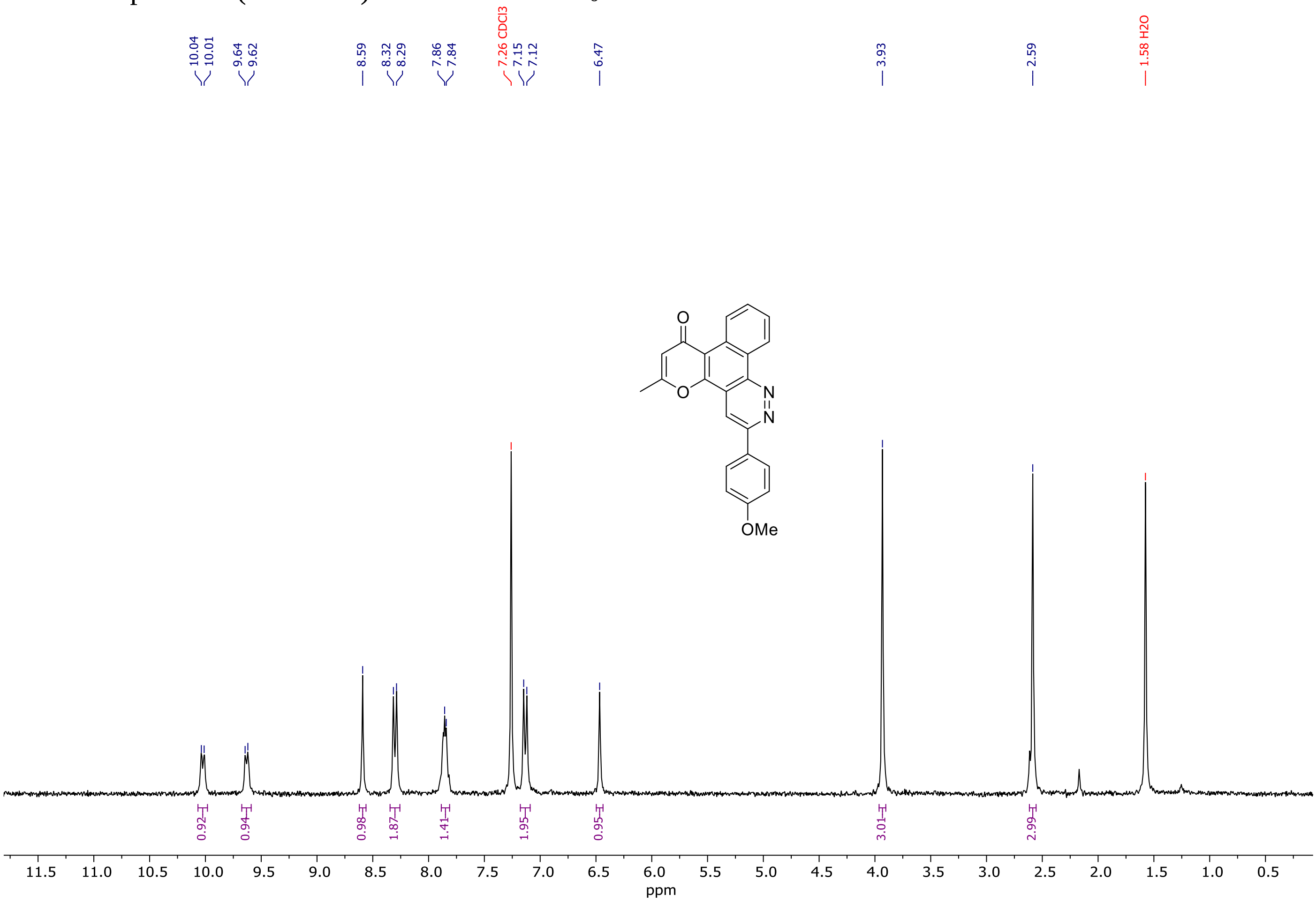
[1]H NMR spectrum (300 MHz) of **7d** in DMSO-d_6



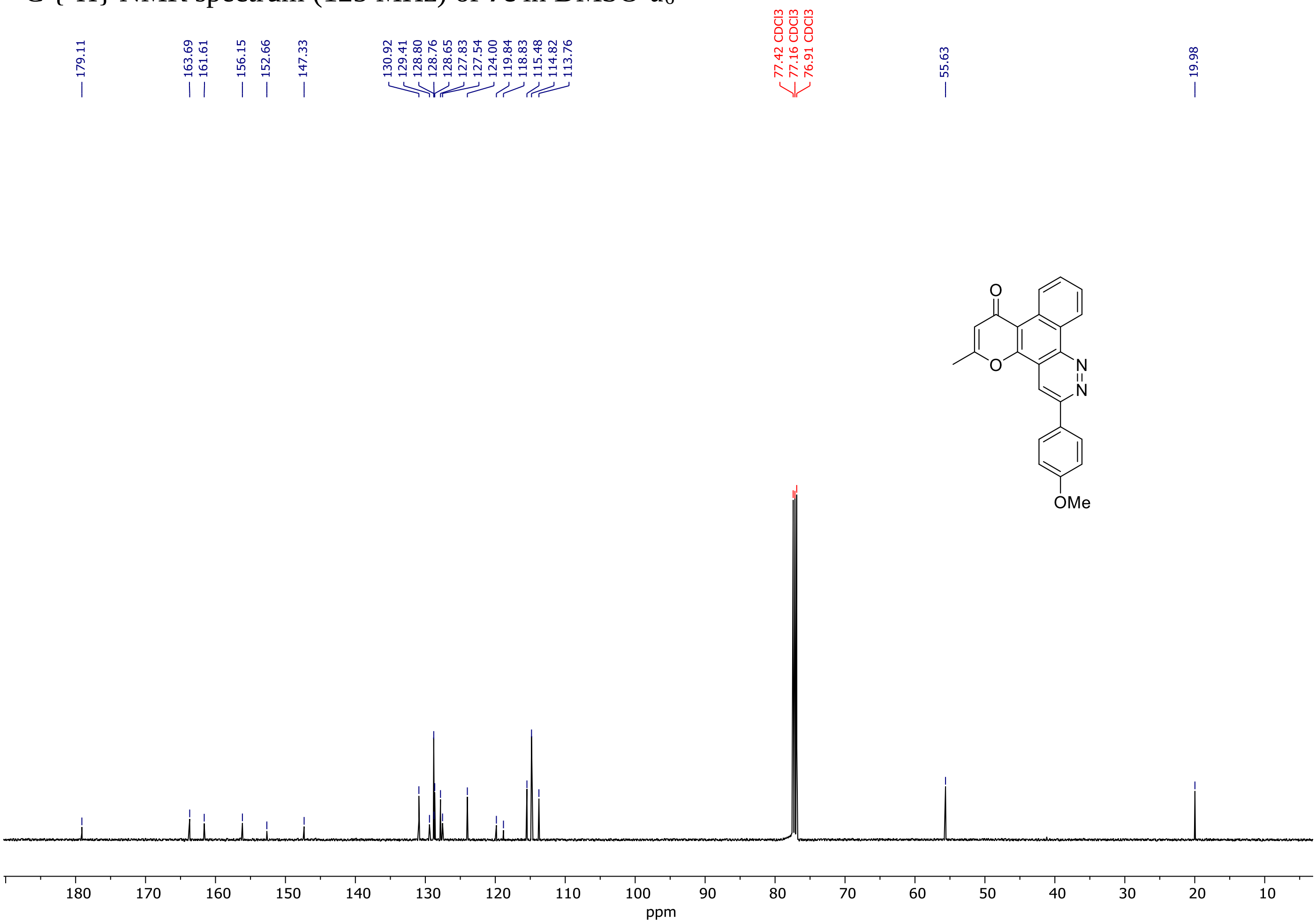
[13]C {[1]H} NMR spectrum (75 MHz) of **7d** in DMSO-d_6



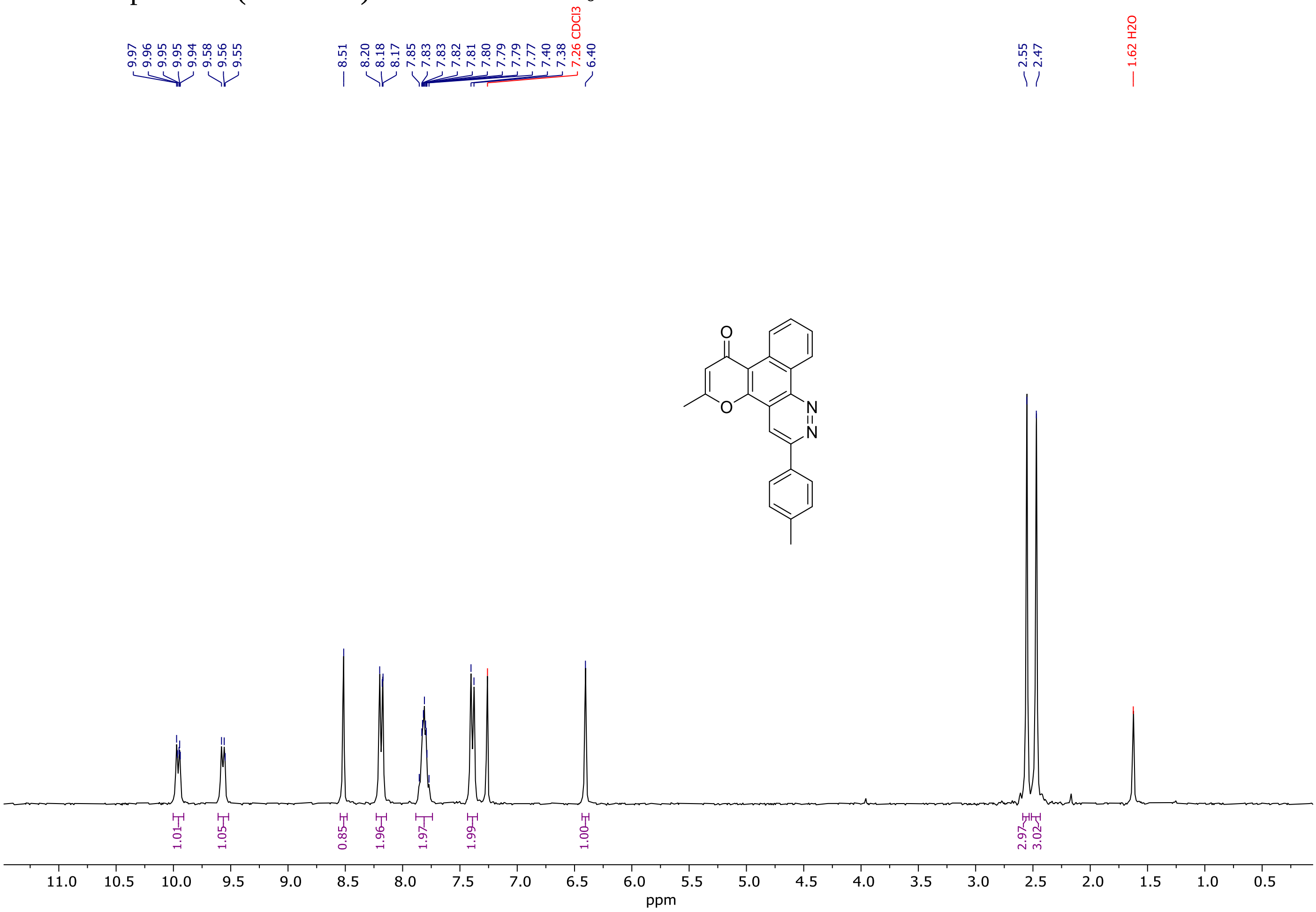
^{1}H NMR spectrum (300 MHz) of **7e** in DMSO-d_6



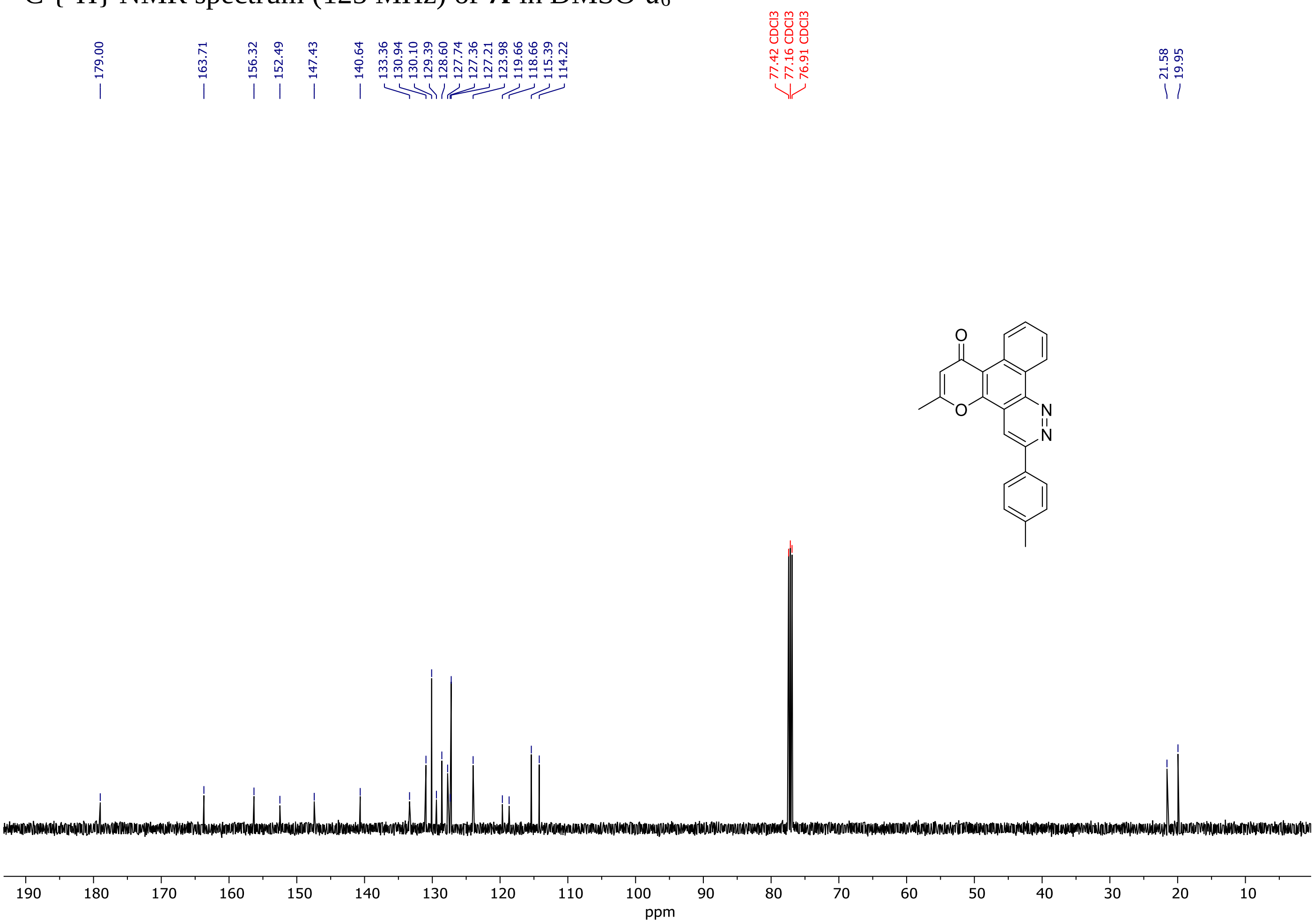
^{13}C {^{1}H} NMR spectrum (125 MHz) of **7e** in DMSO-d_6



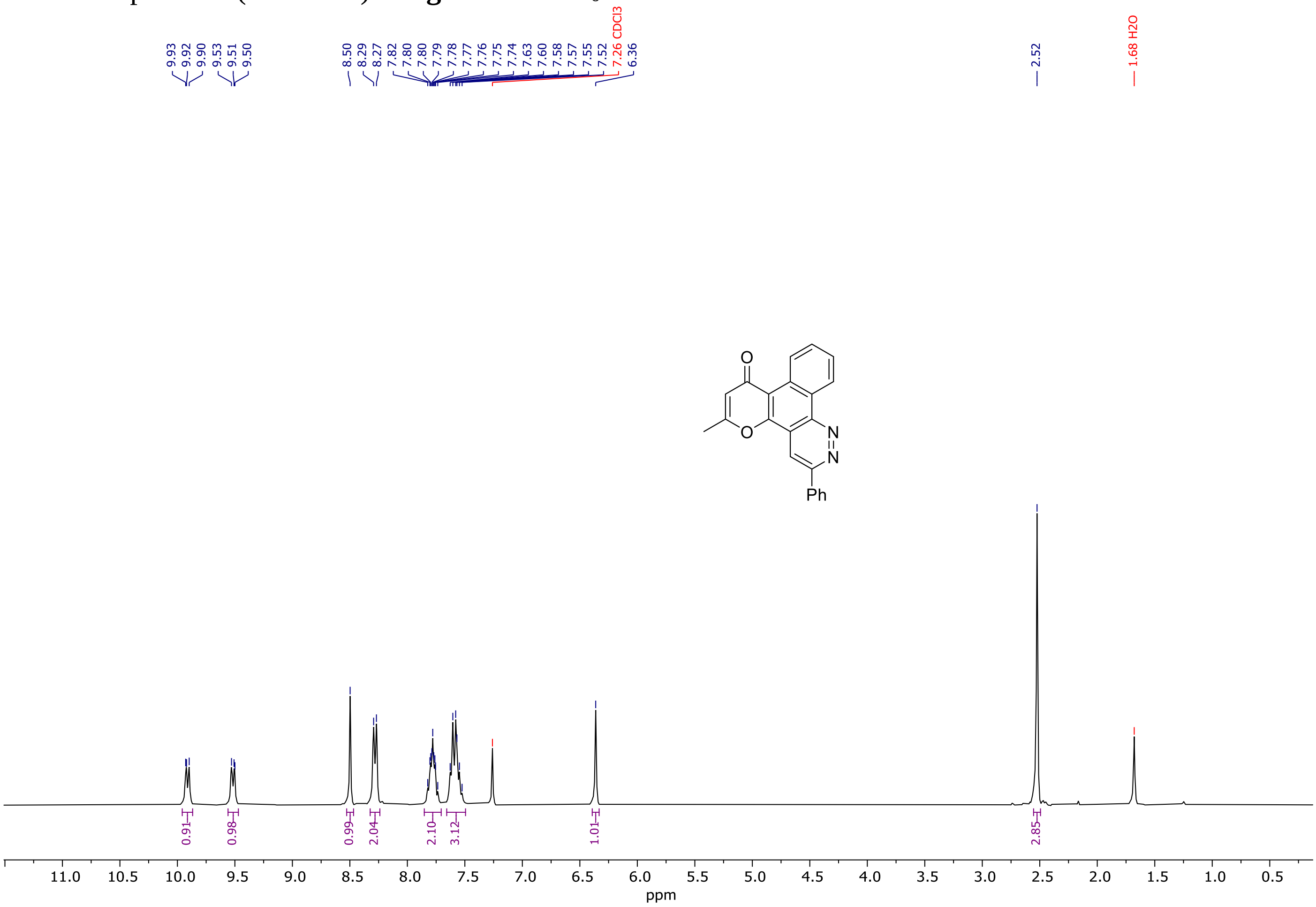
^{1}H NMR spectrum (300 MHz) of **7f** in DMSO-d_6



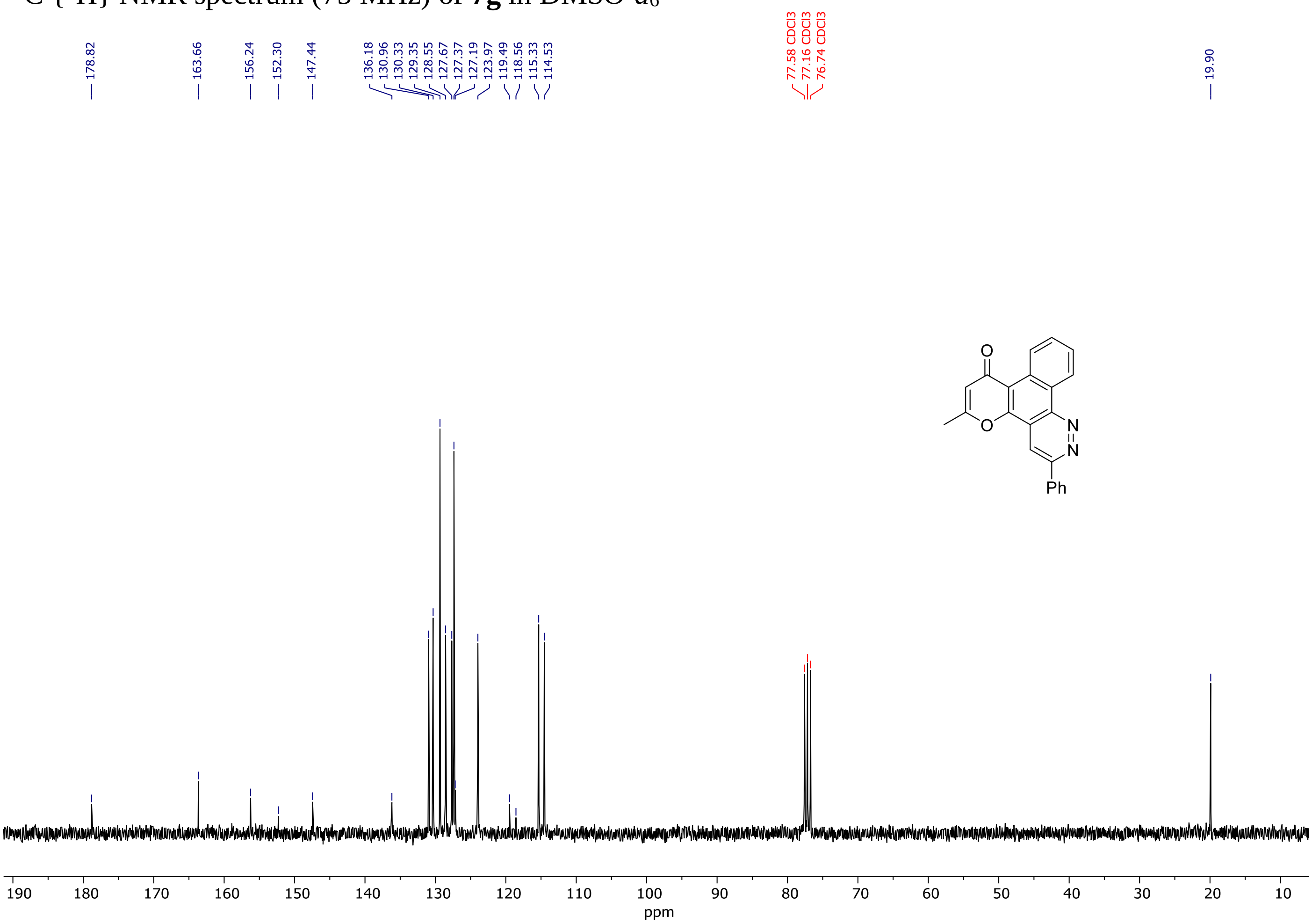
^{13}C {^{1}H} NMR spectrum (125 MHz) of **7f** in DMSO-d_6



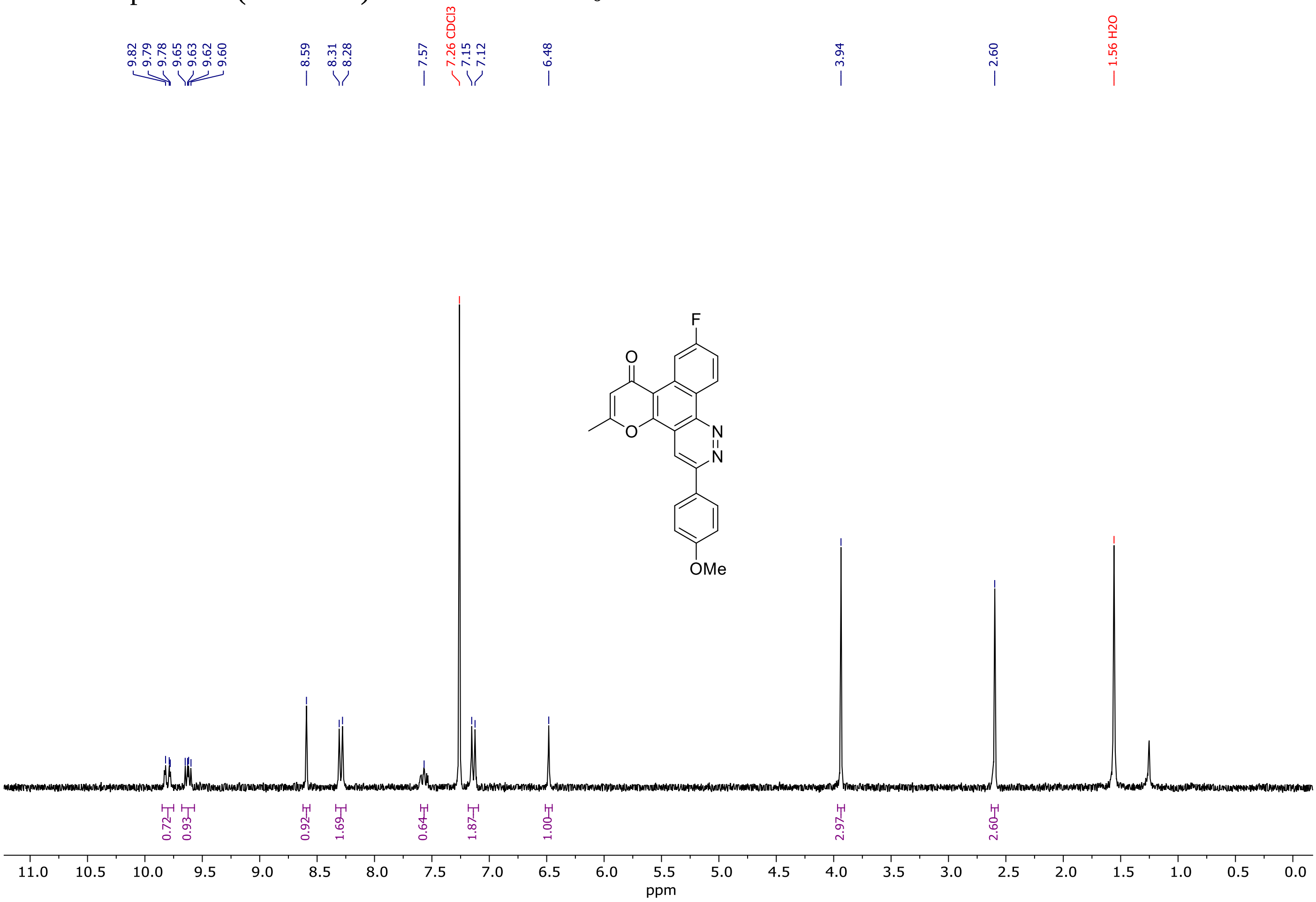
^{1}H NMR spectrum (300 MHz) of **7g** in DMSO-d_6



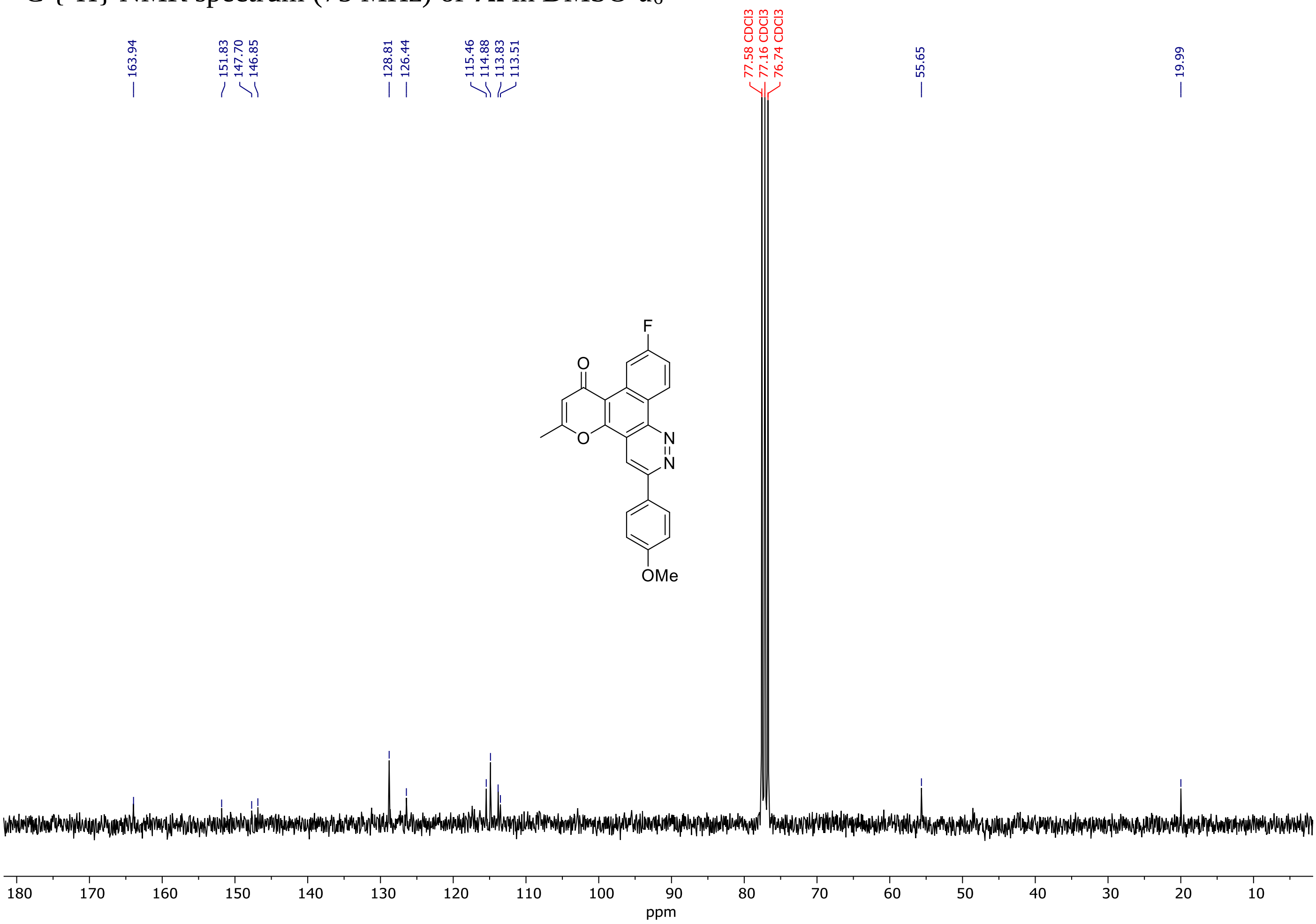
^{13}C {^{1}H} NMR spectrum (75 MHz) of **7g** in DMSO-d_6



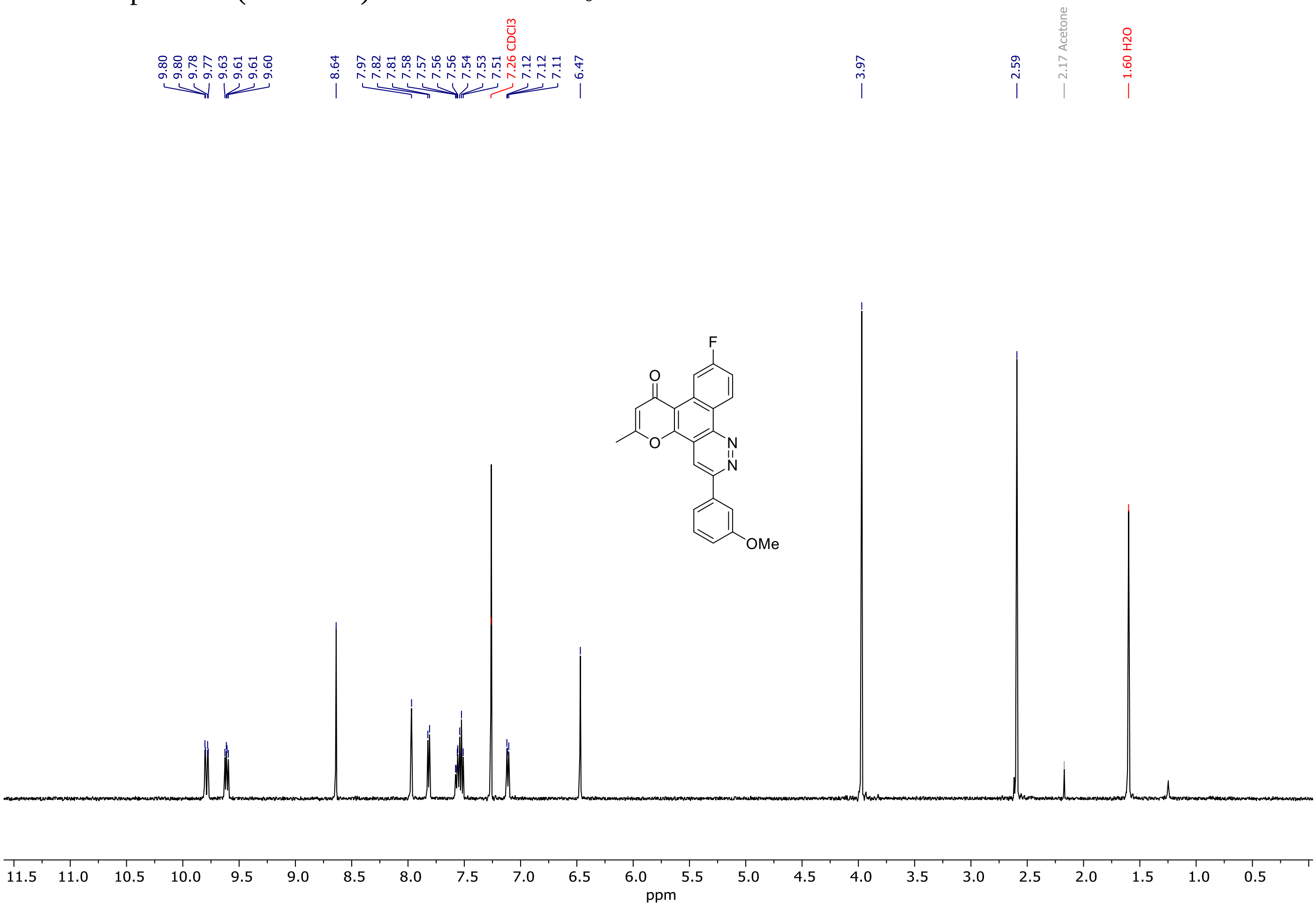
[1]H NMR spectrum (300 MHz) of **7h** in DMSO-d_6



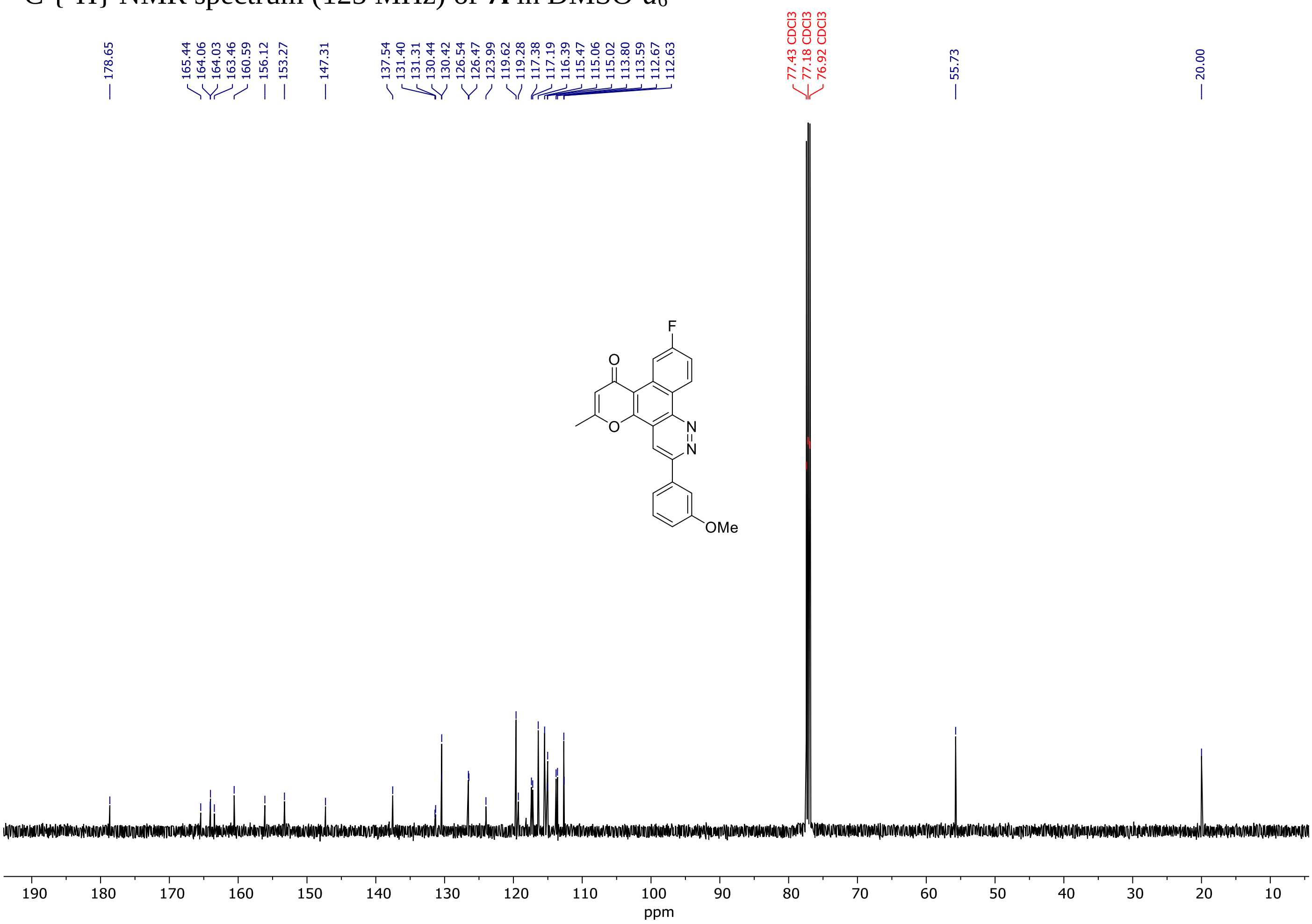
[13]C {[1]H} NMR spectrum (75 MHz) of **7h** in DMSO-d_6



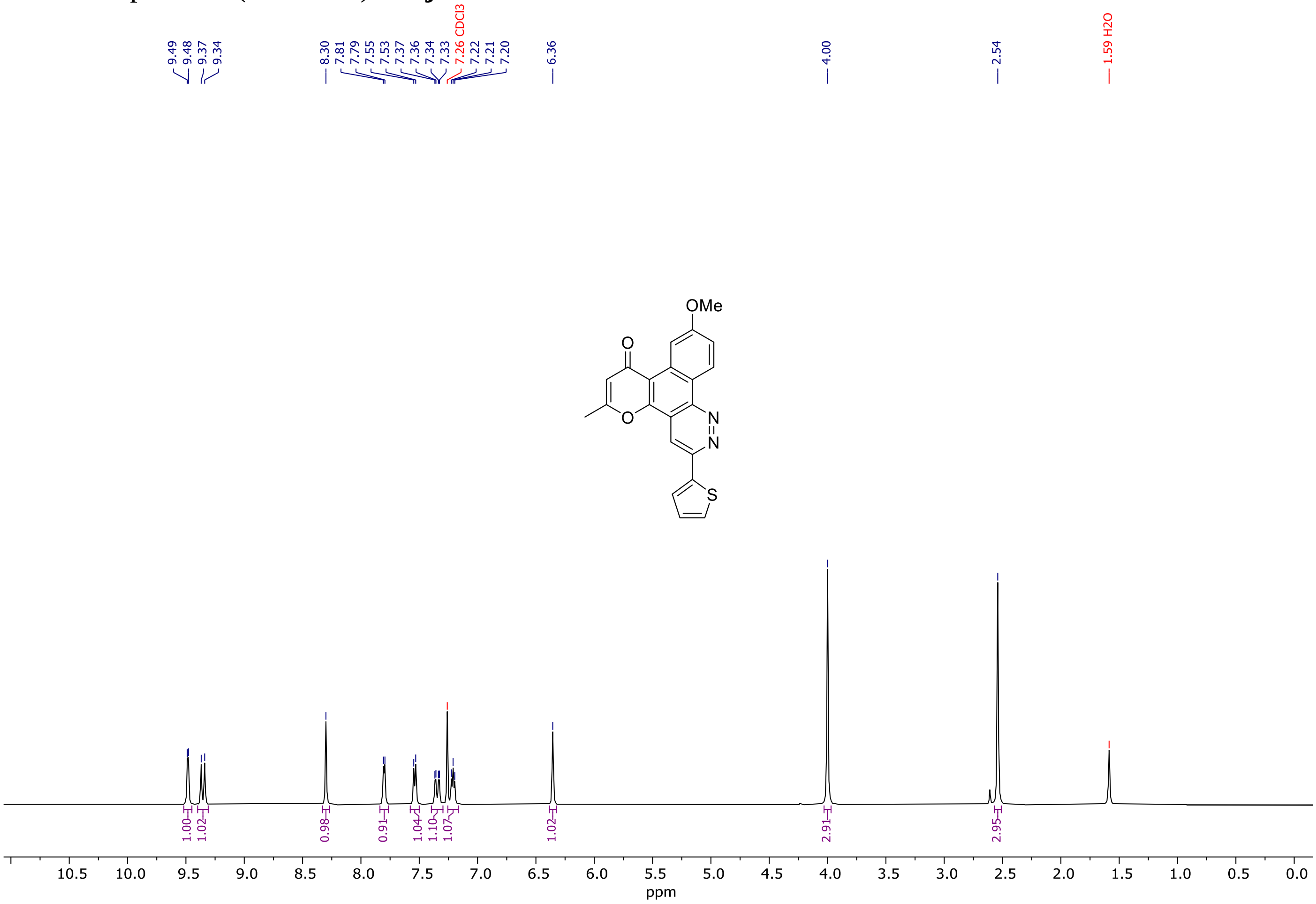
^{1}H NMR spectrum (300 MHz) of **7i** in DMSO-d_6



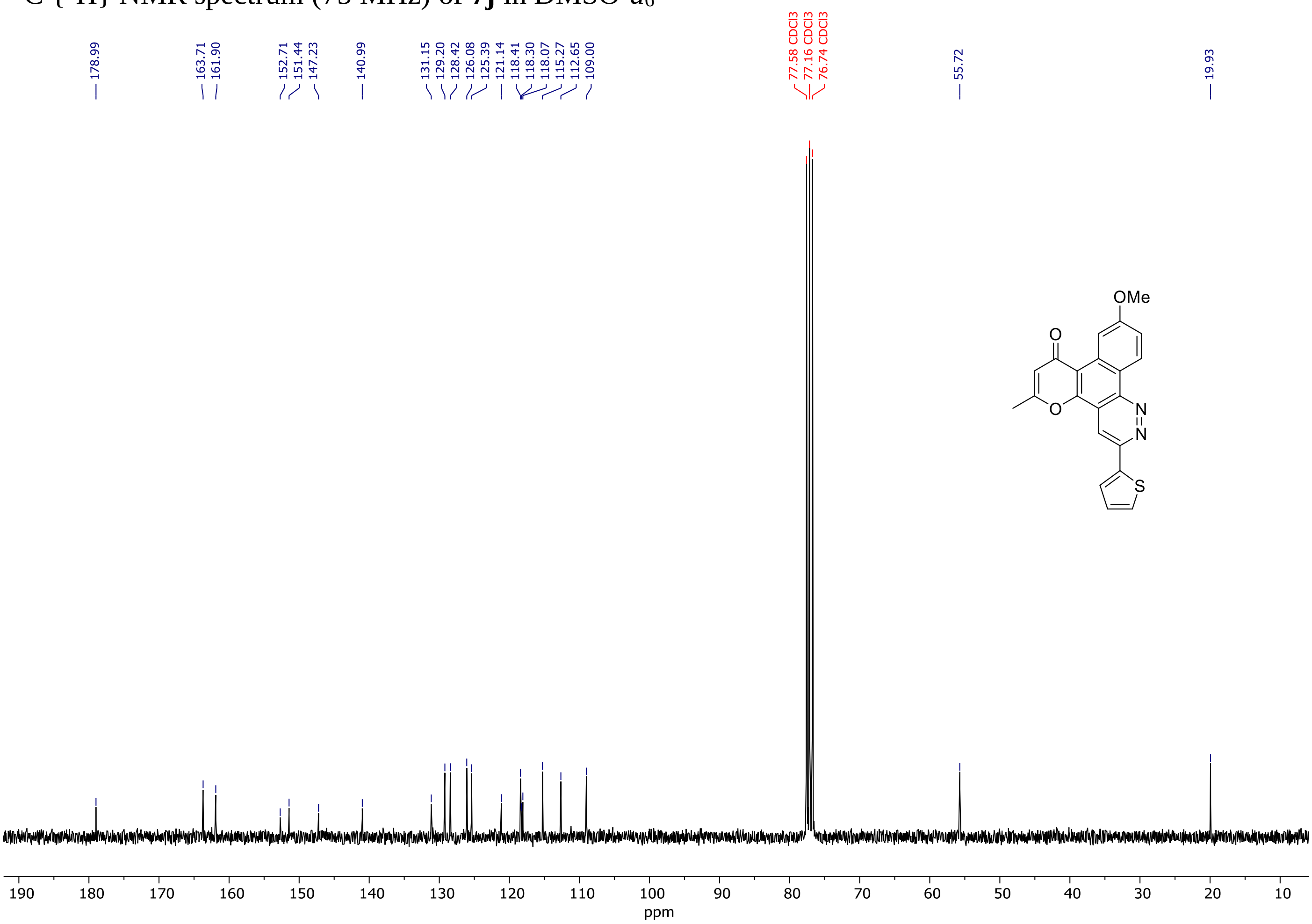
^{13}C {^{1}H} NMR spectrum (125 MHz) of **7i** in DMSO-d_6



^{1}H NMR spectrum (300 MHz) of **7j** in DMSO-d_6

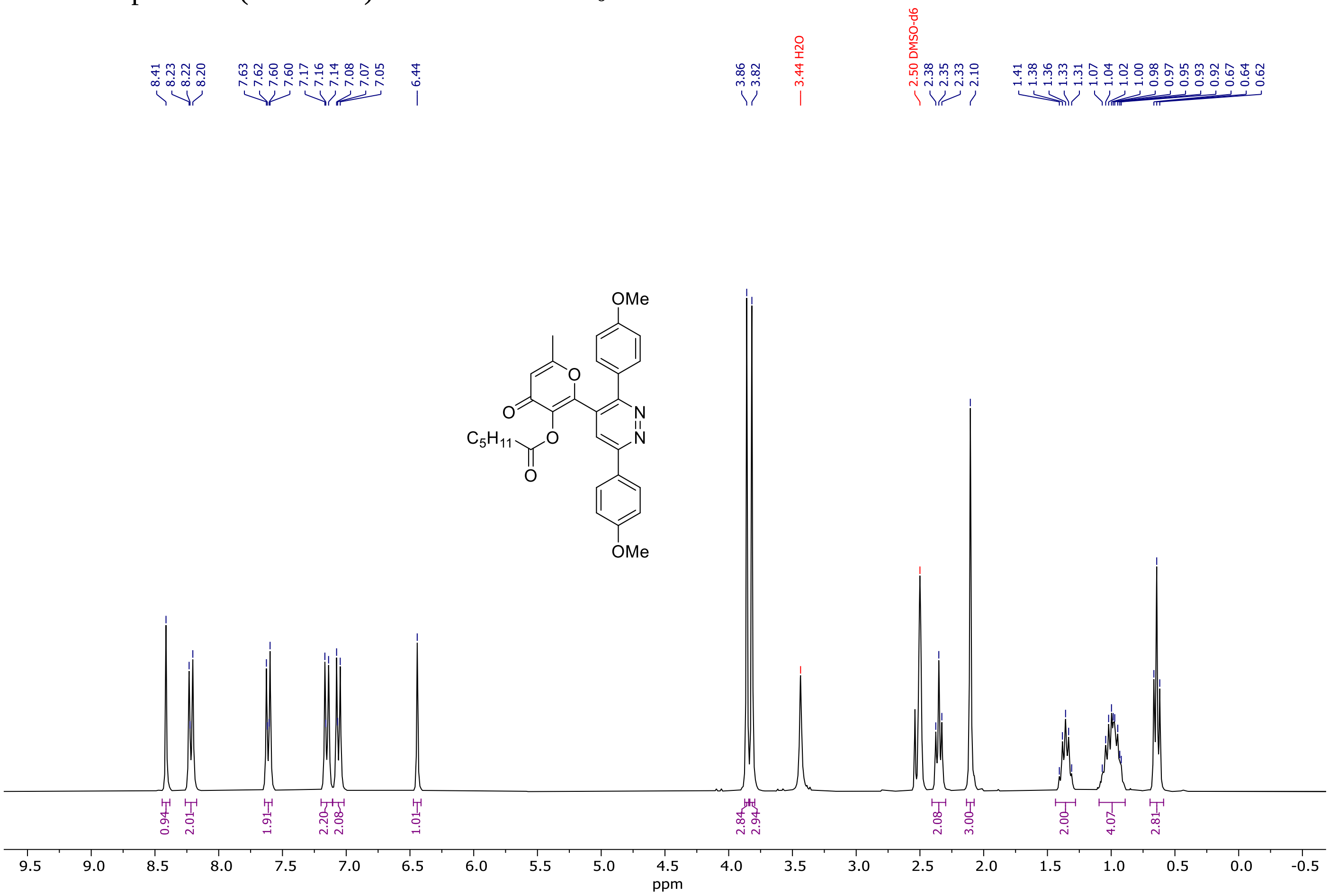


^{13}C {^{1}H} NMR spectrum (75 MHz) of **7j** in DMSO-d_6

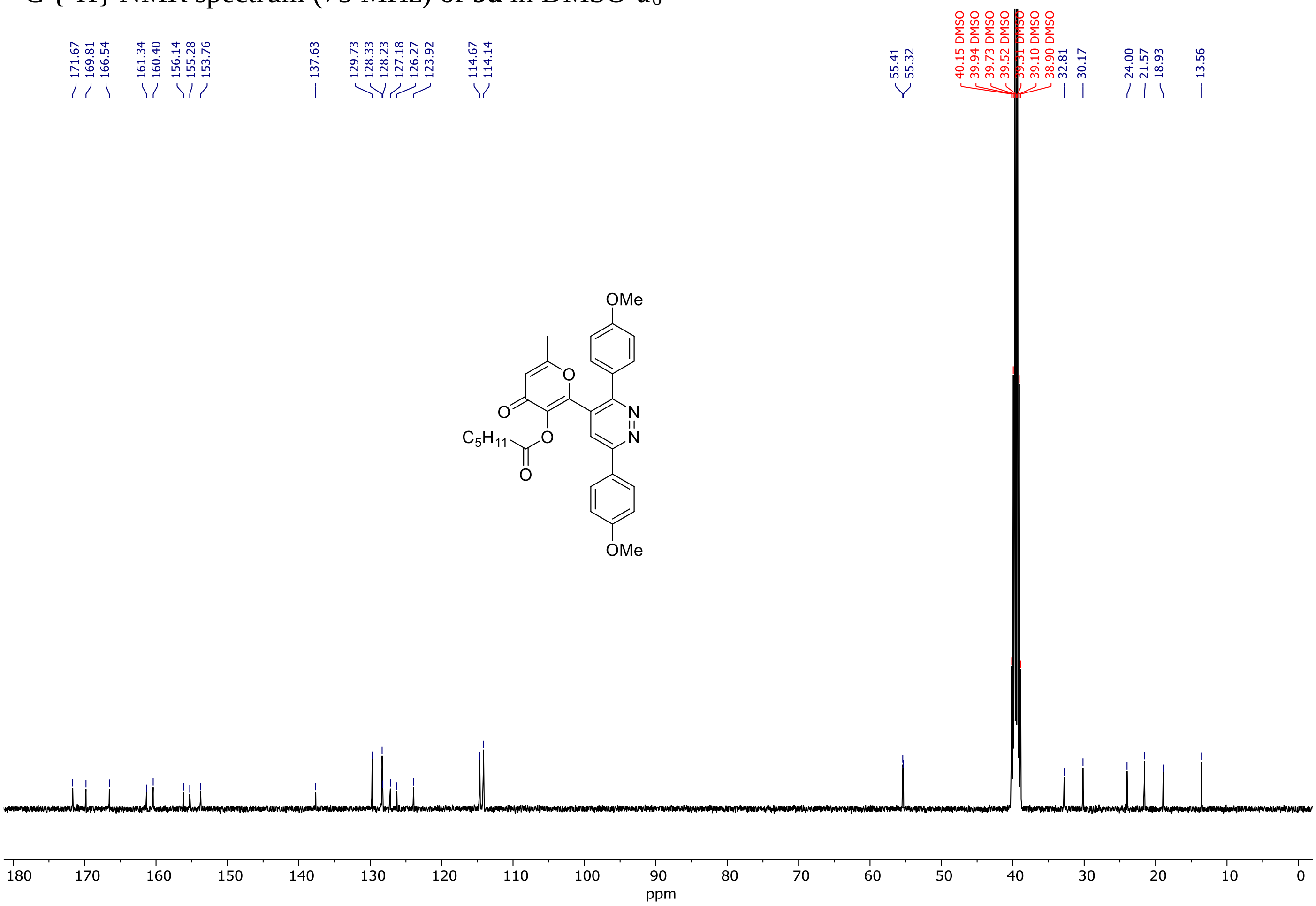


10. NMR ^{1}H and ^{13}C spectra for compounds 9

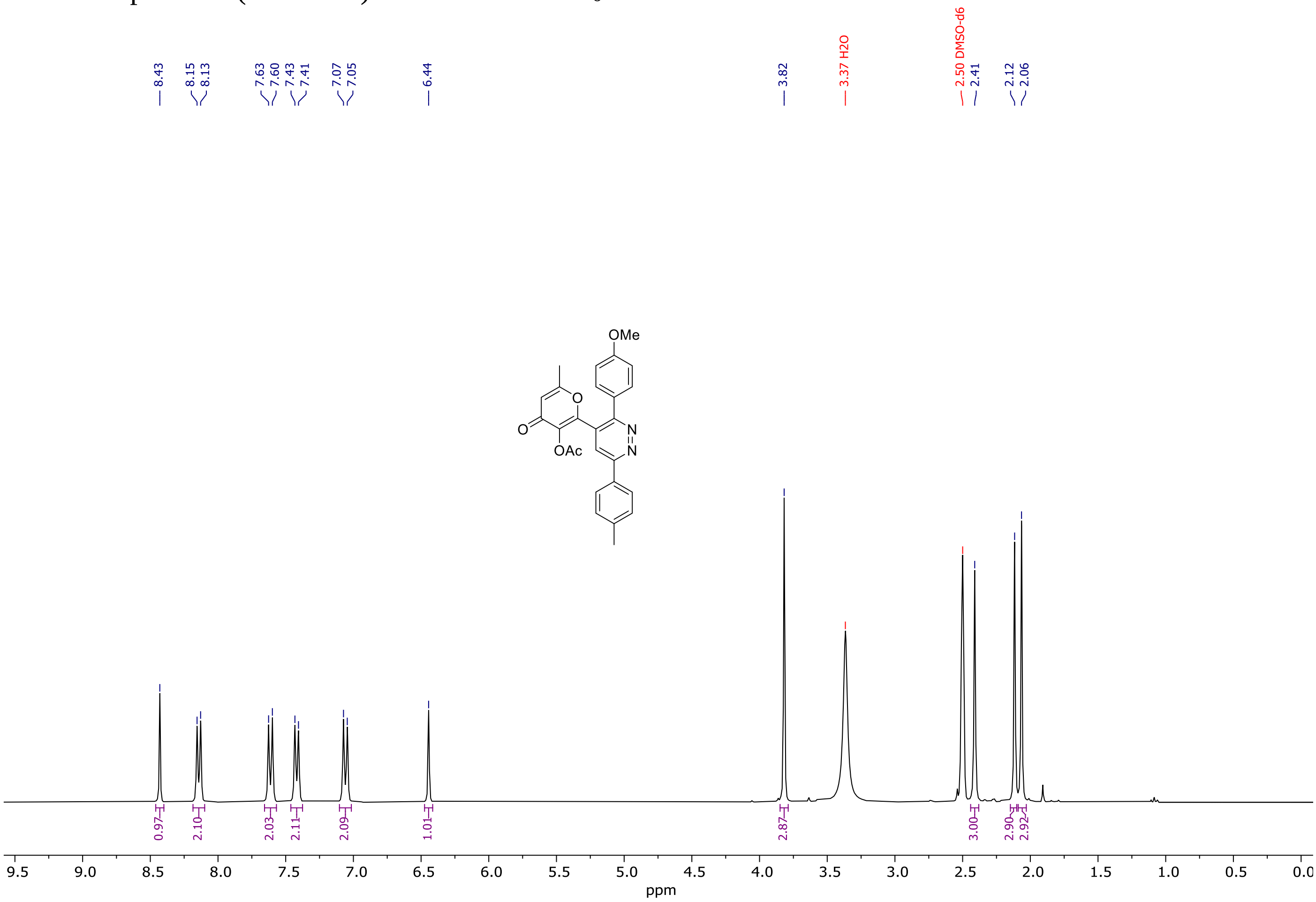
^{1}H NMR spectrum (300 MHz) of **9a** in DMSO-d_6



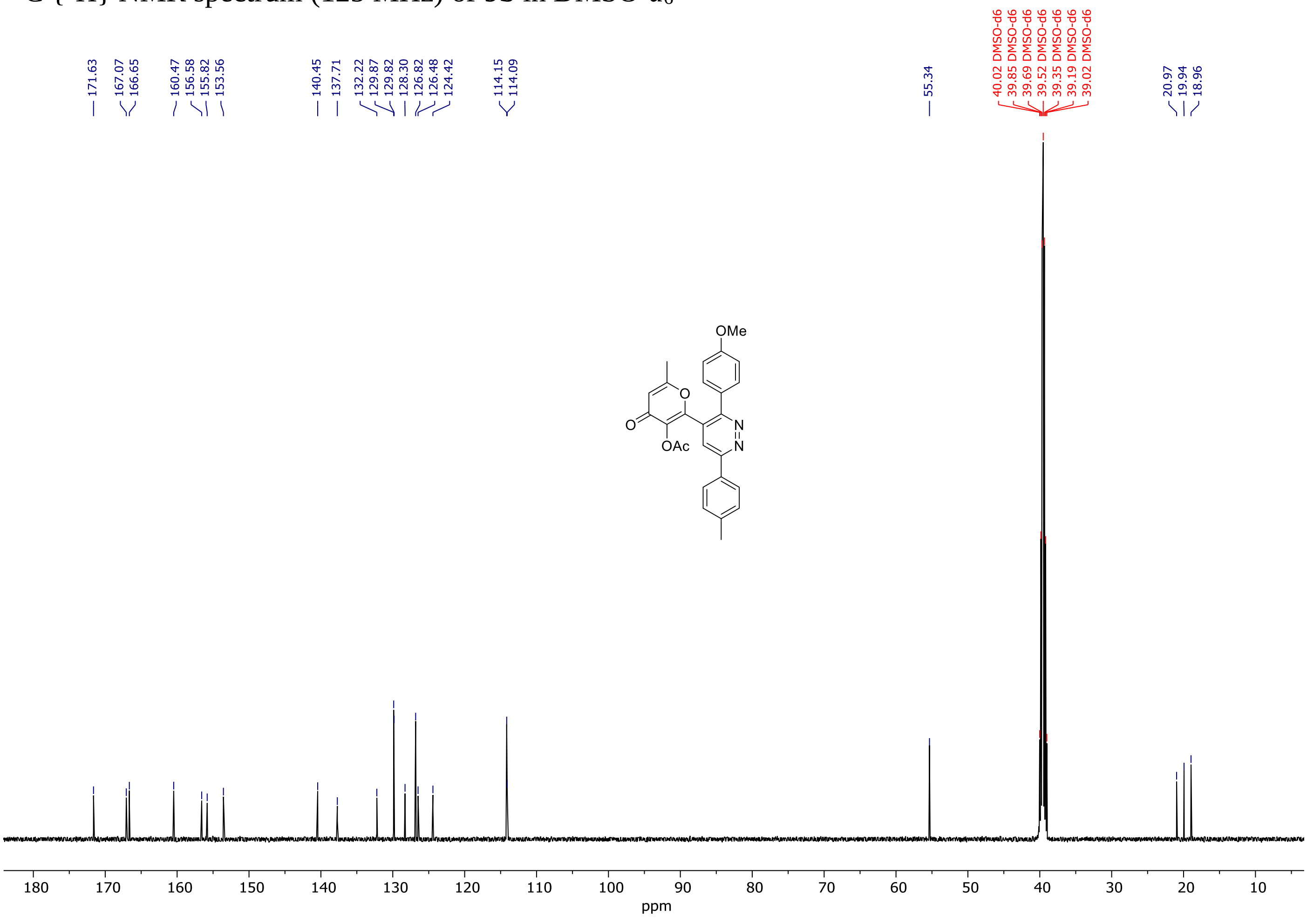
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9a** in DMSO-d_6



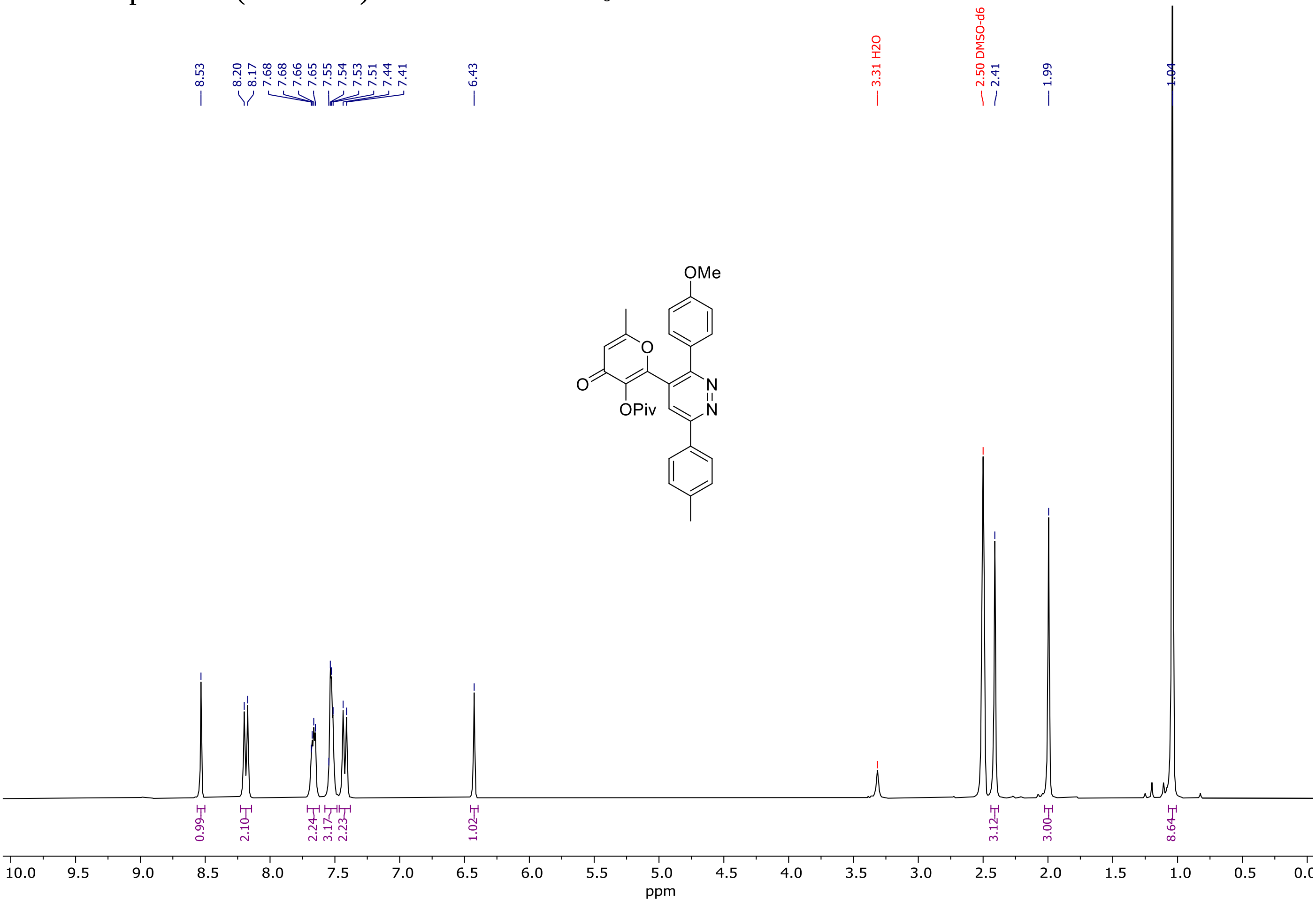
^{1}H NMR spectrum (300 MHz) of **9b** in DMSO-d_6



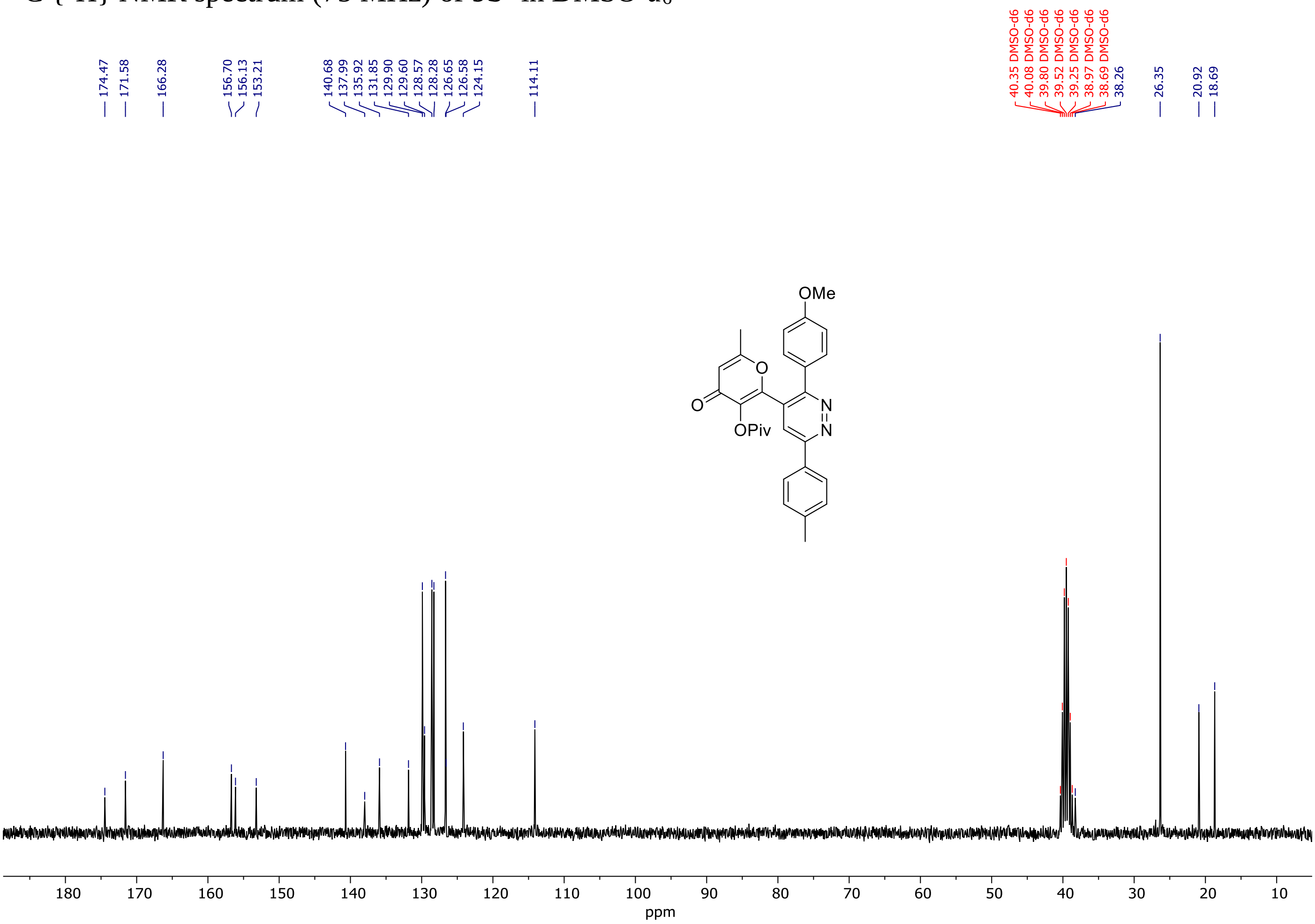
^{13}C {^{1}H} NMR spectrum (125 MHz) of **9b** in DMSO-d_6



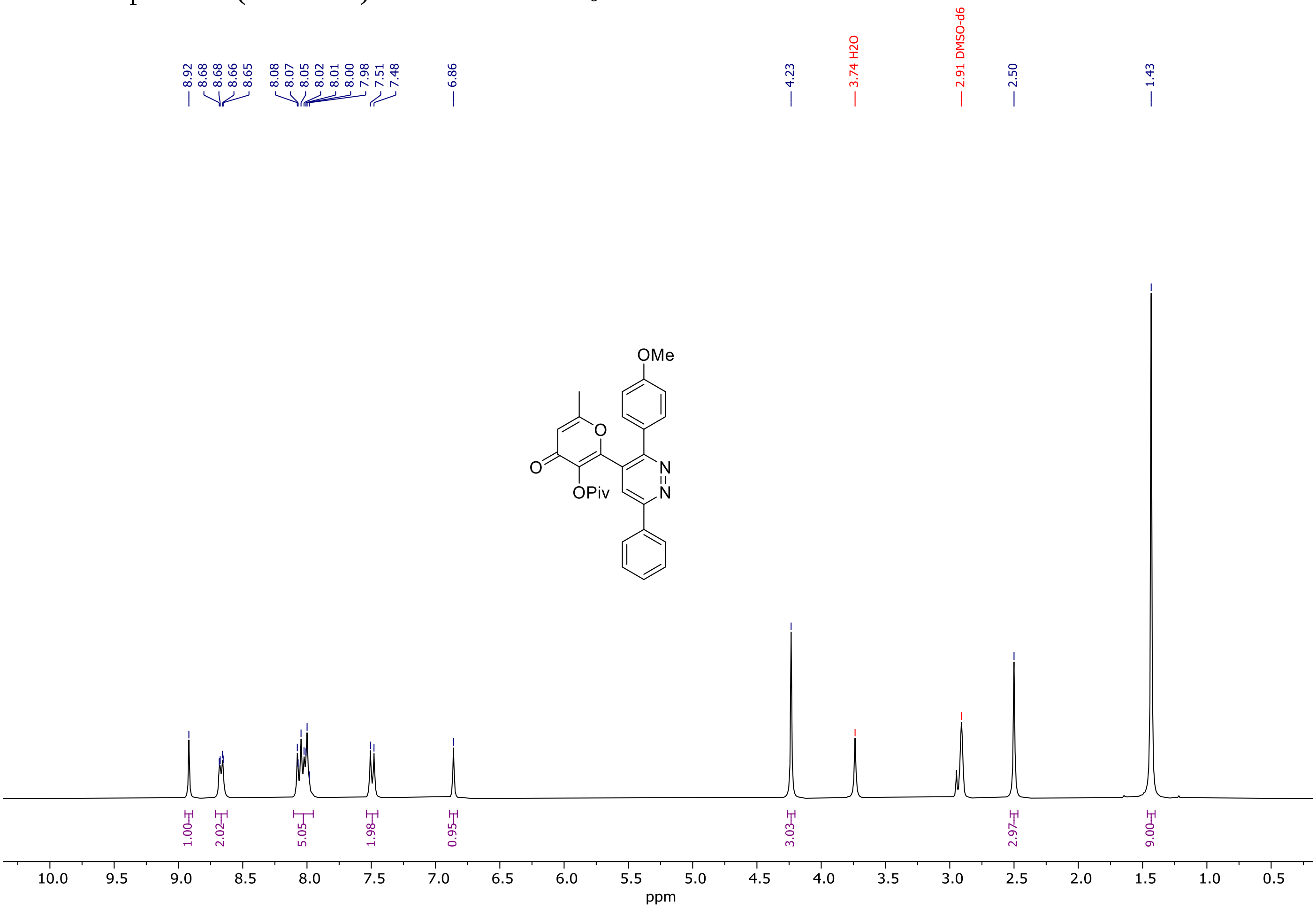
^{1}H NMR spectrum (300 MHz) of **9b'** in DMSO-d_6



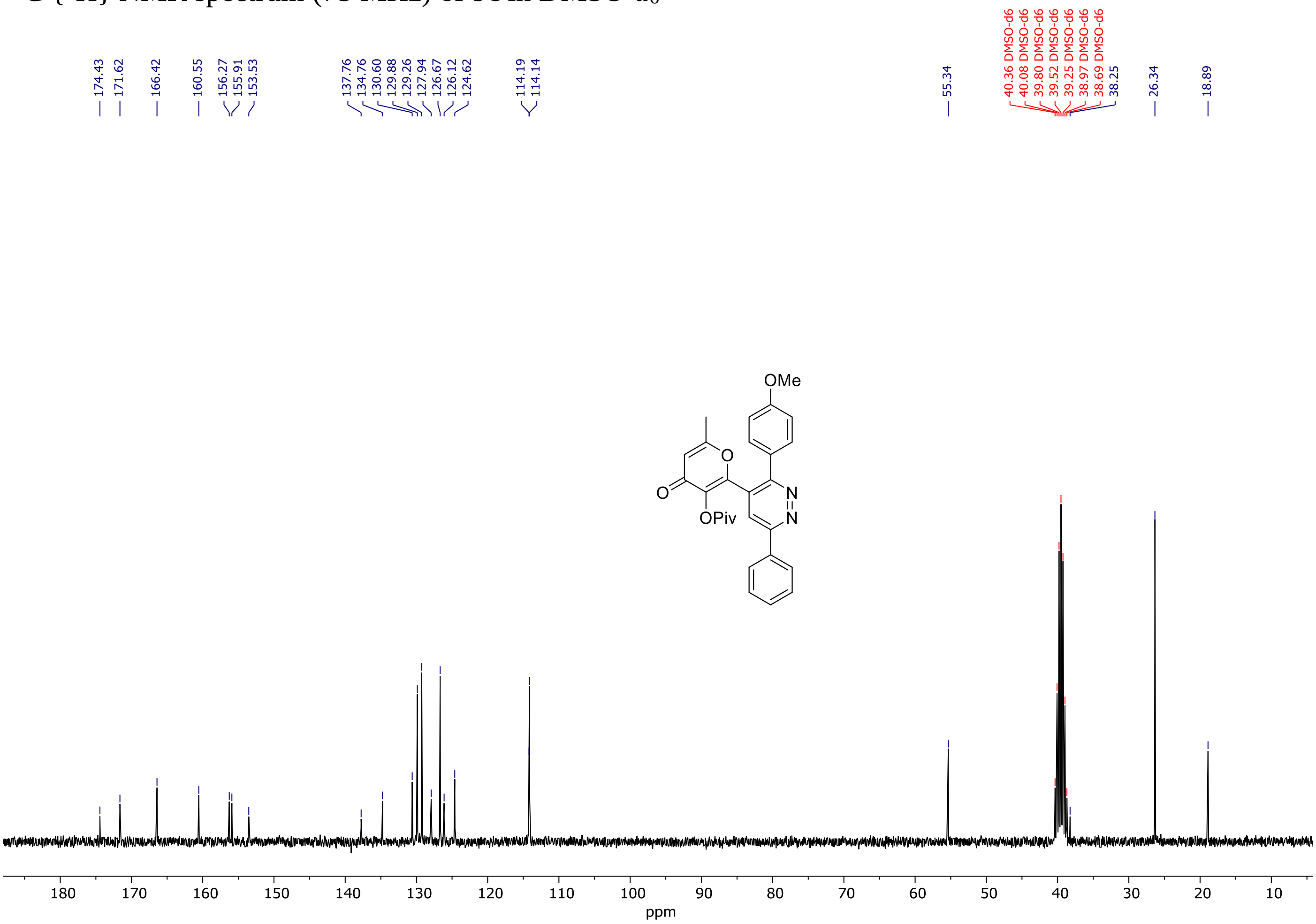
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9b'** in DMSO-d_6



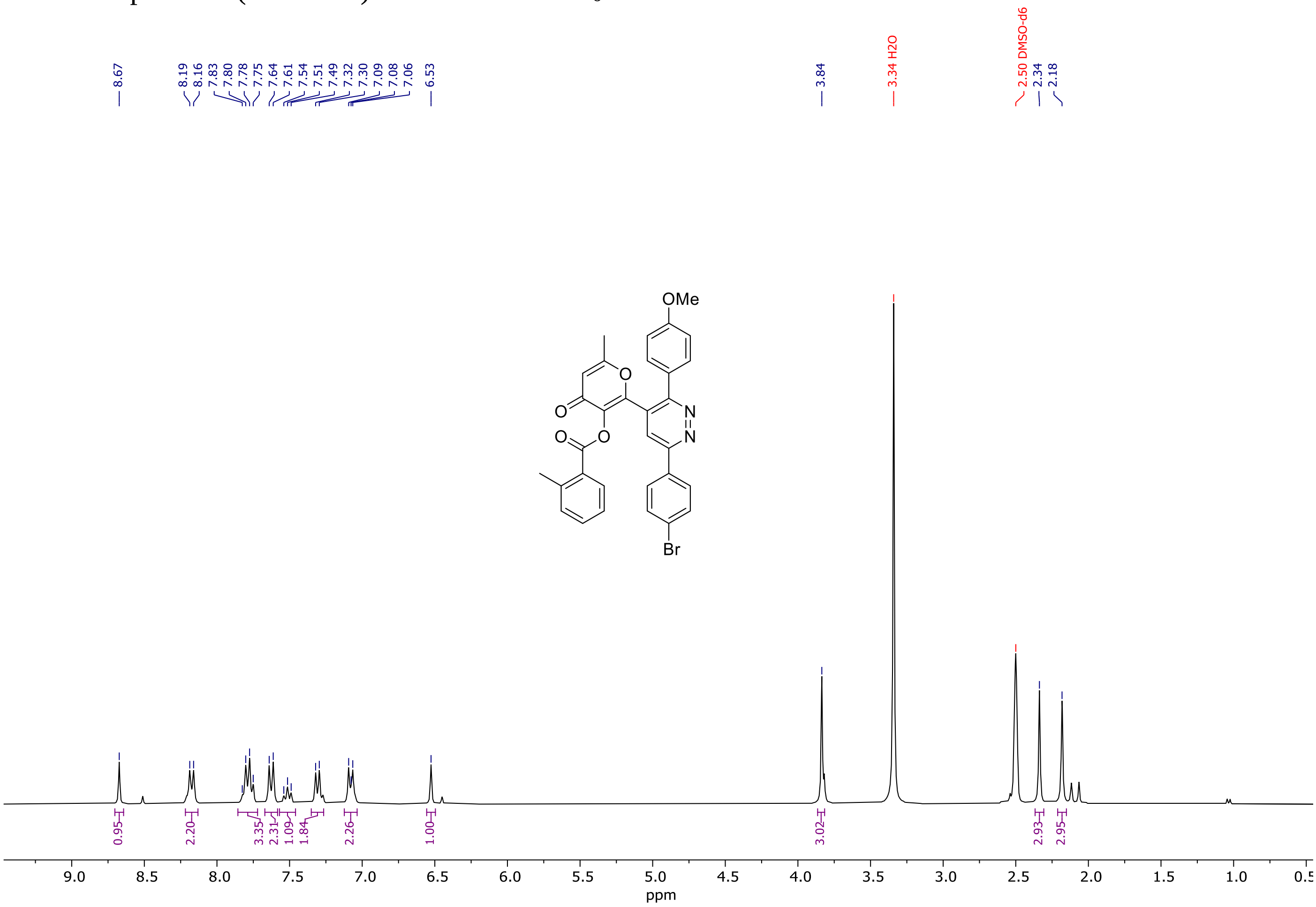
[1]H NMR spectrum (300 MHz) of **9c** in DMSO-d_6



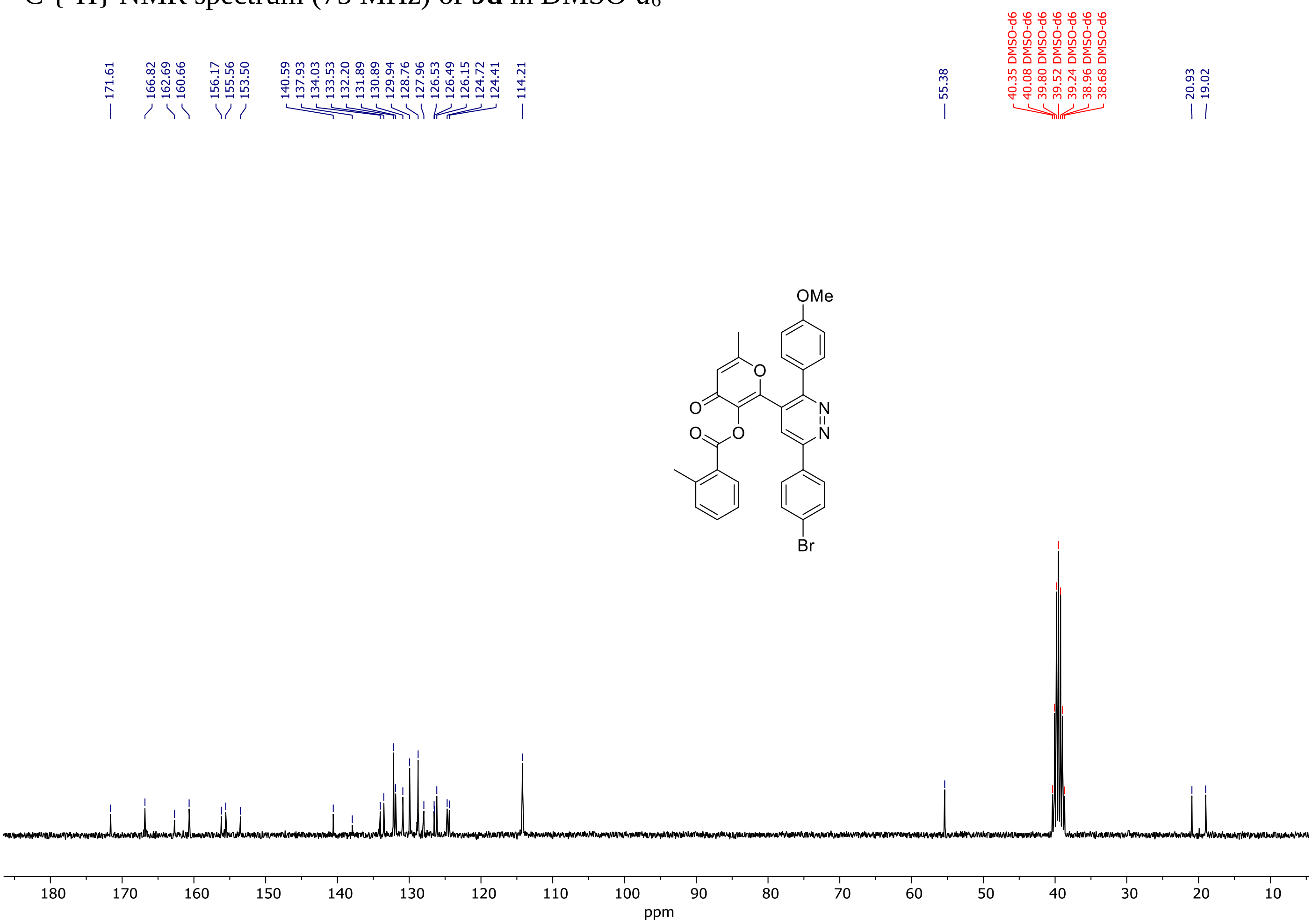
[13]C {[1]H} NMR spectrum (75 MHz) of **9c** in DMSO-d_6



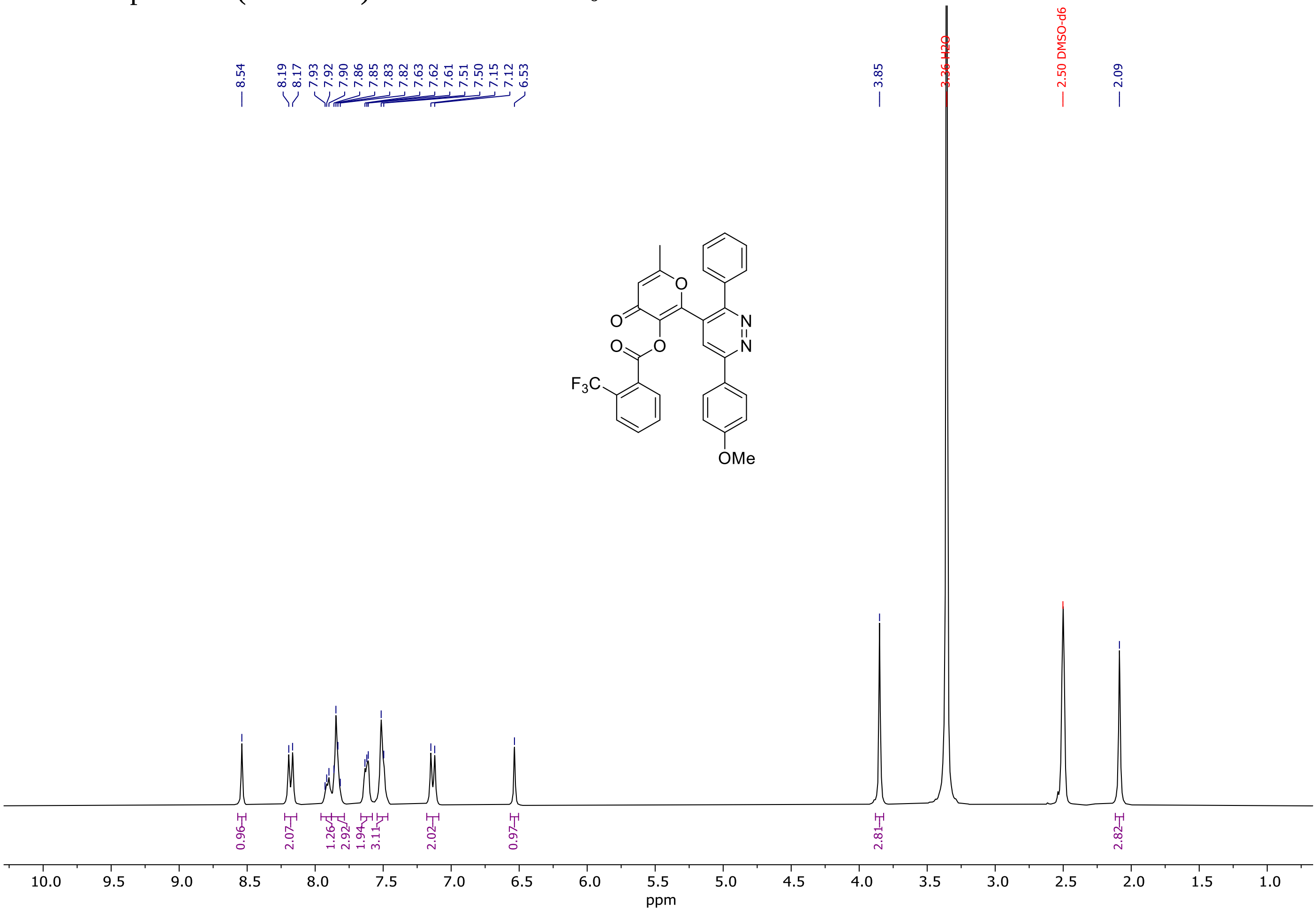
^{1}H NMR spectrum (300 MHz) of **9d** in DMSO-d_6



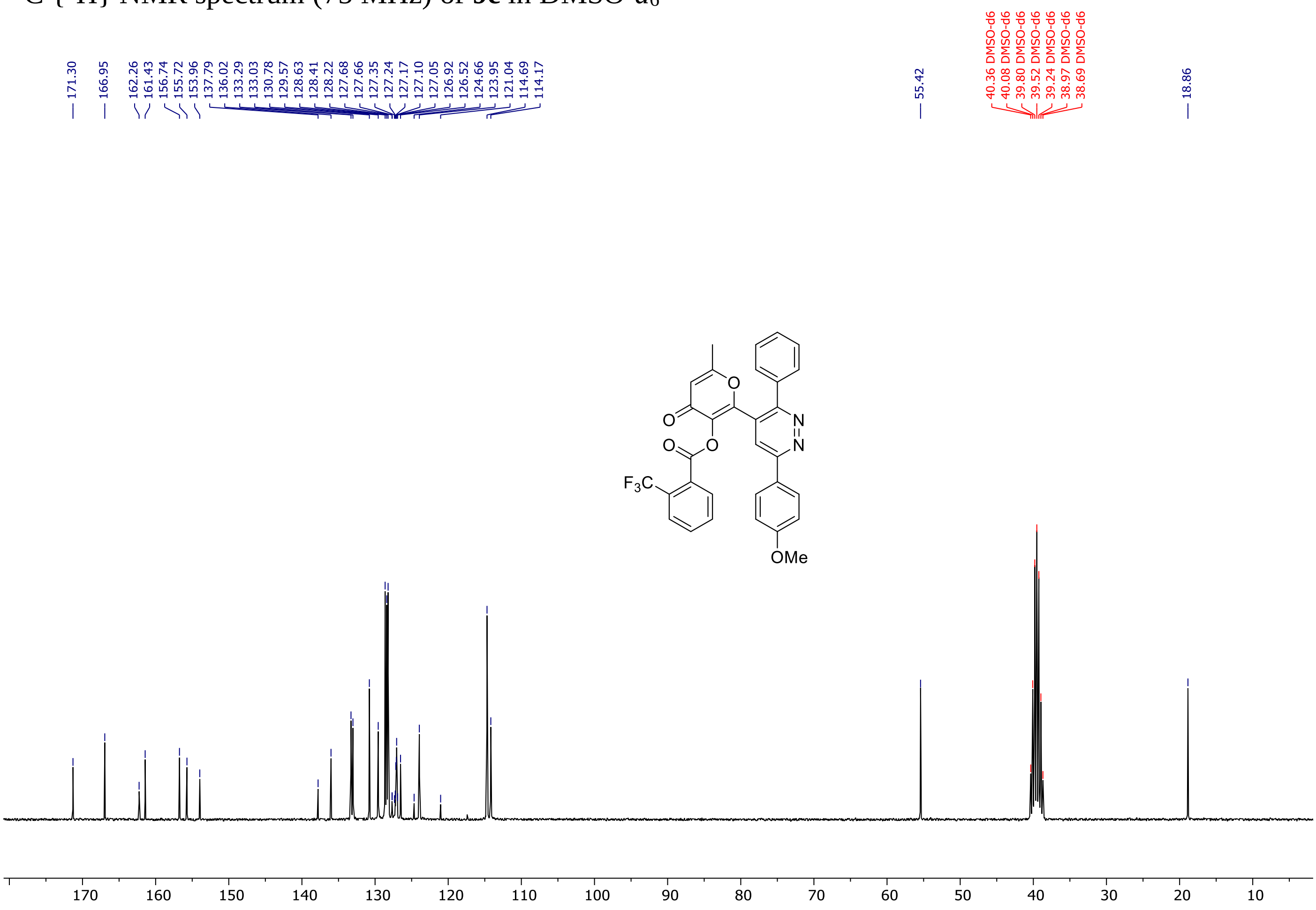
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9d** in DMSO-d_6



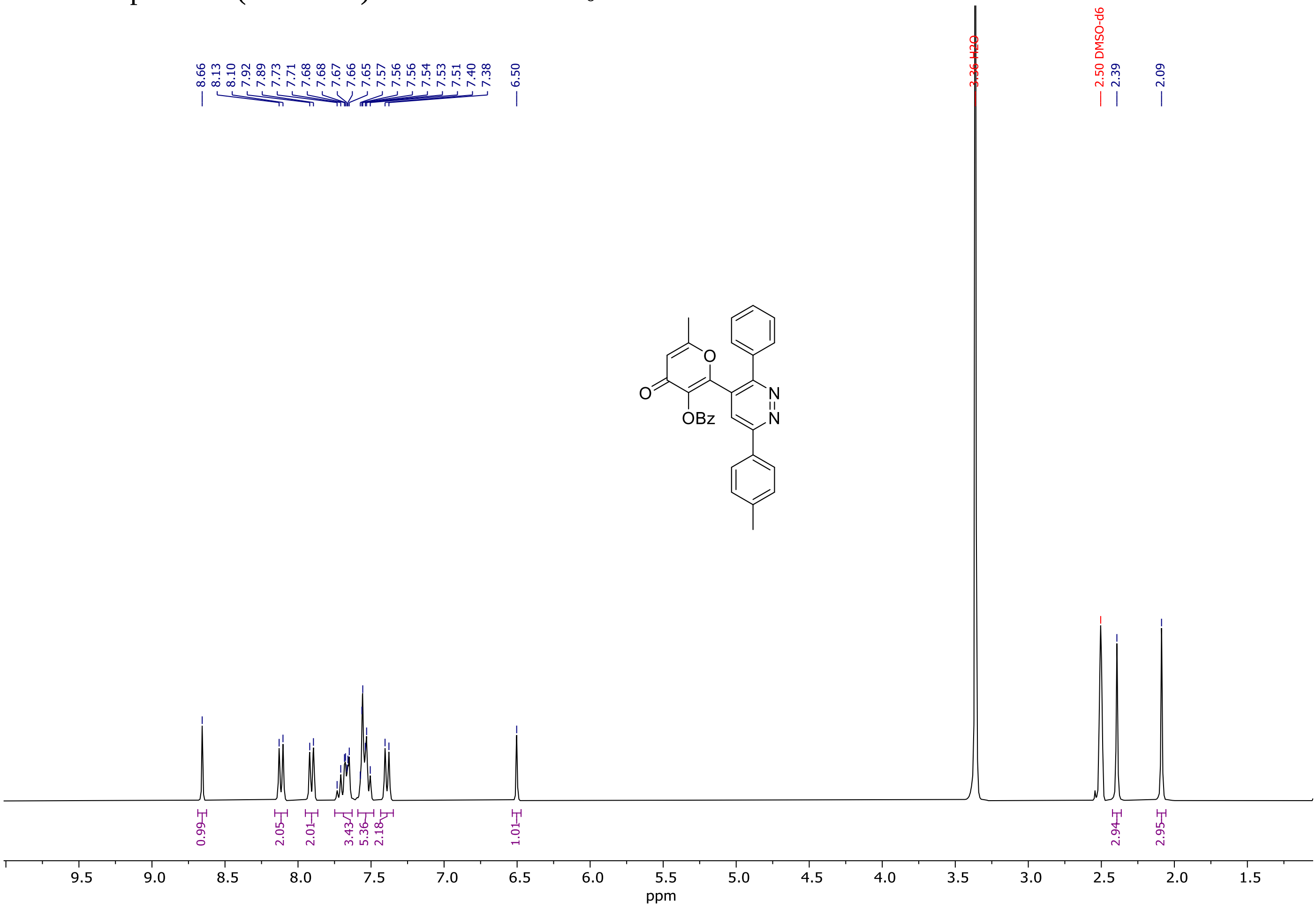
^{1}H NMR spectrum (300 MHz) of **9e** in DMSO-d_6



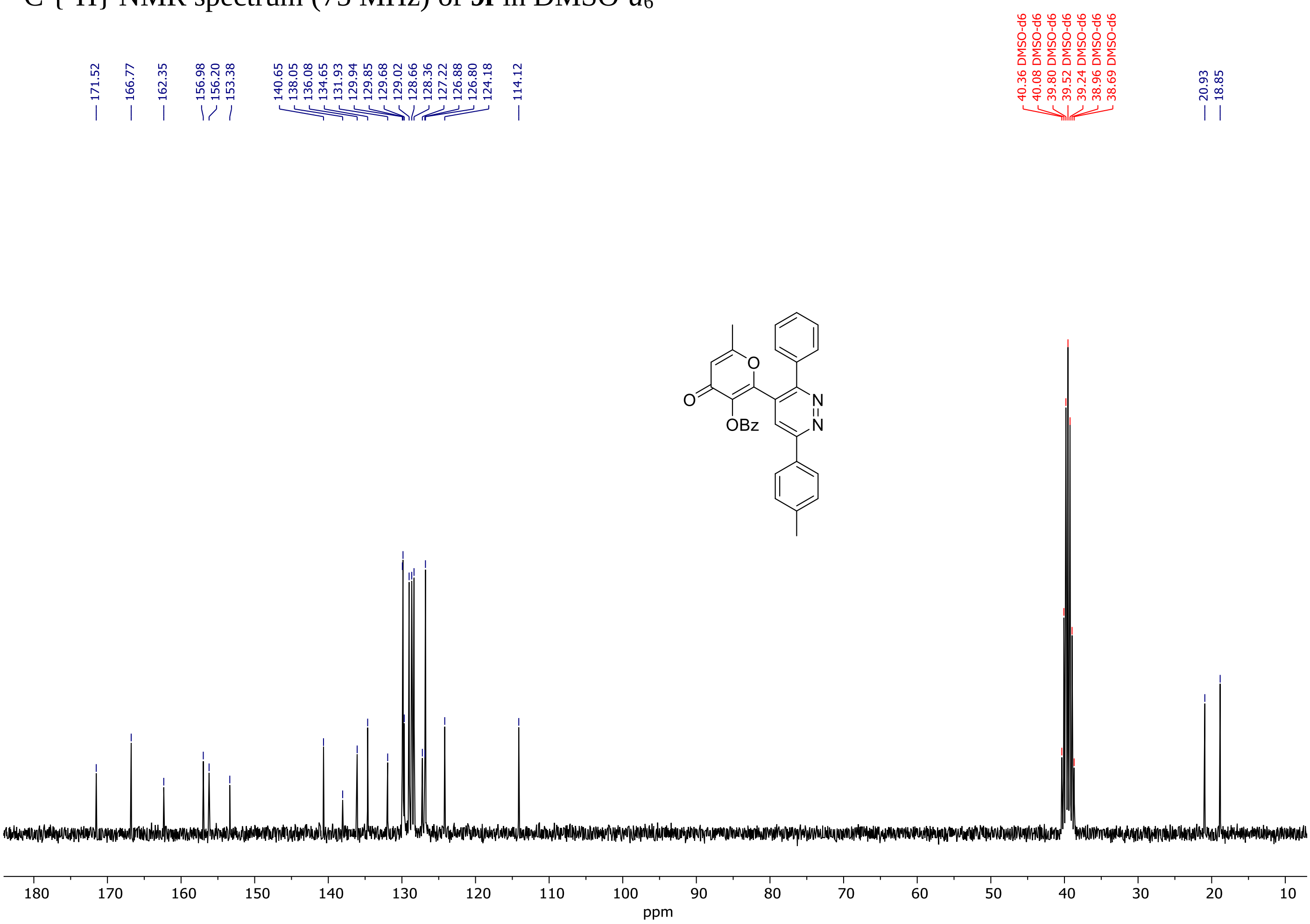
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9e** in DMSO-d_6



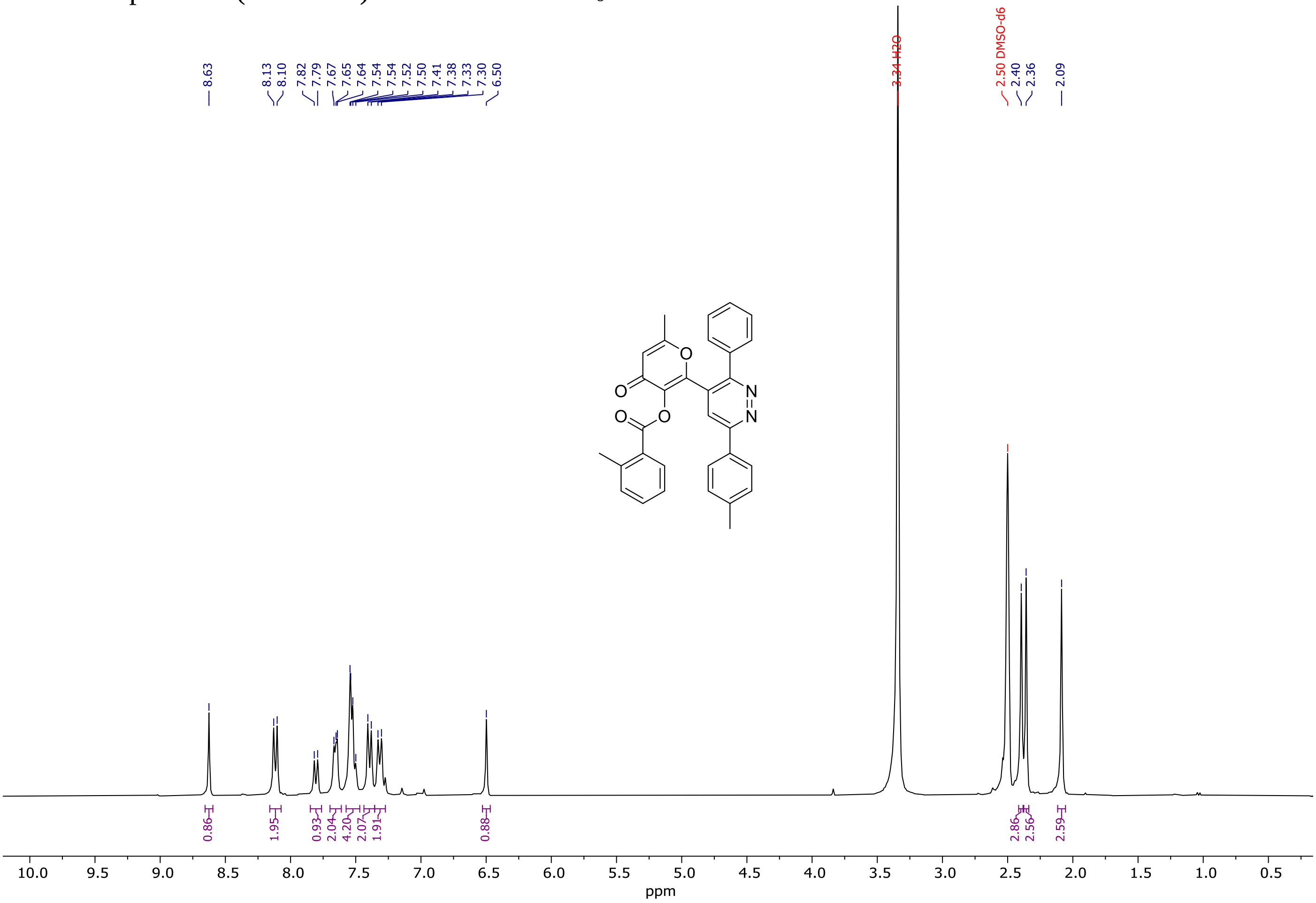
^{1}H NMR spectrum (300 MHz) of **9f** in DMSO-d_6



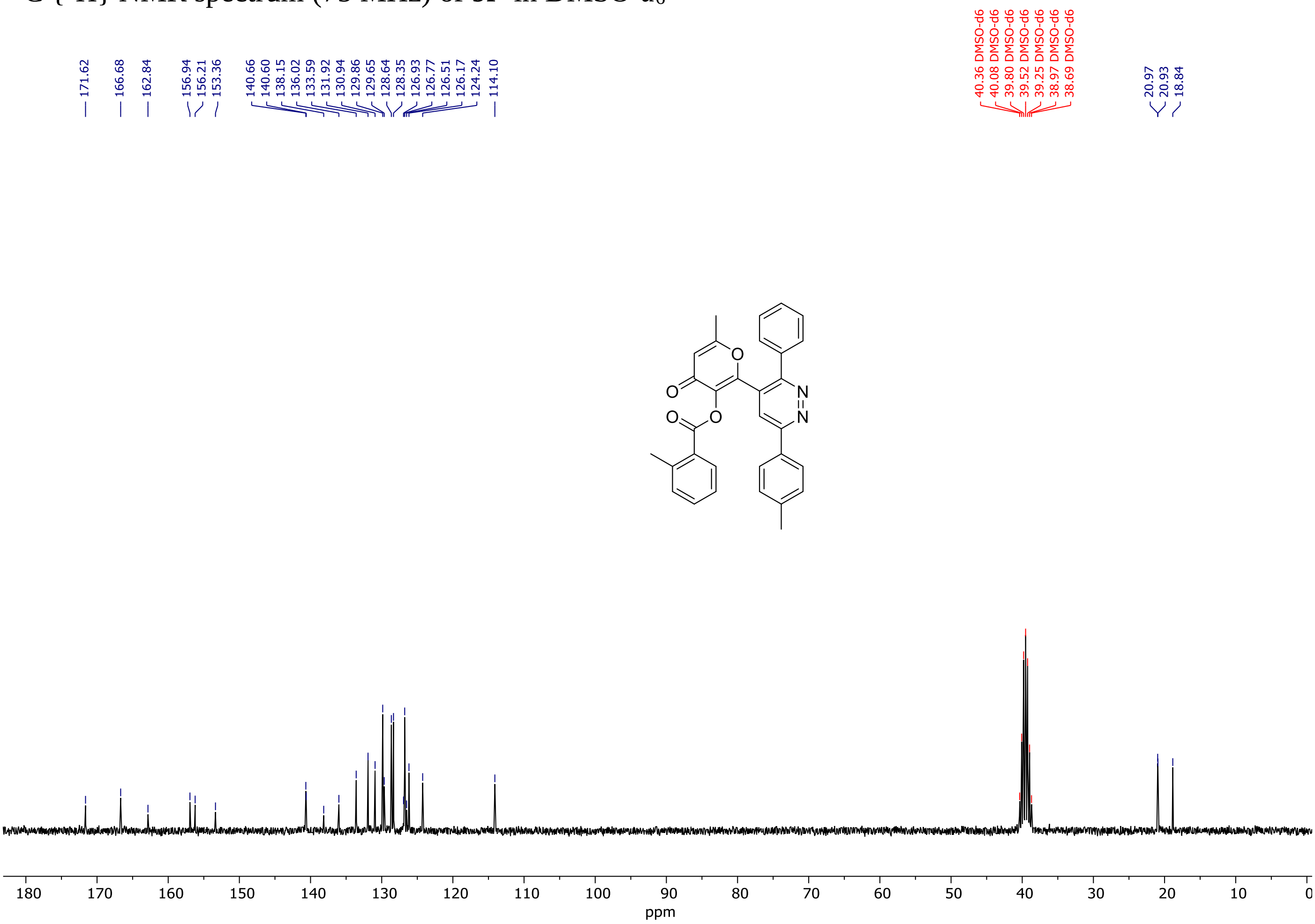
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9f** in DMSO-d_6



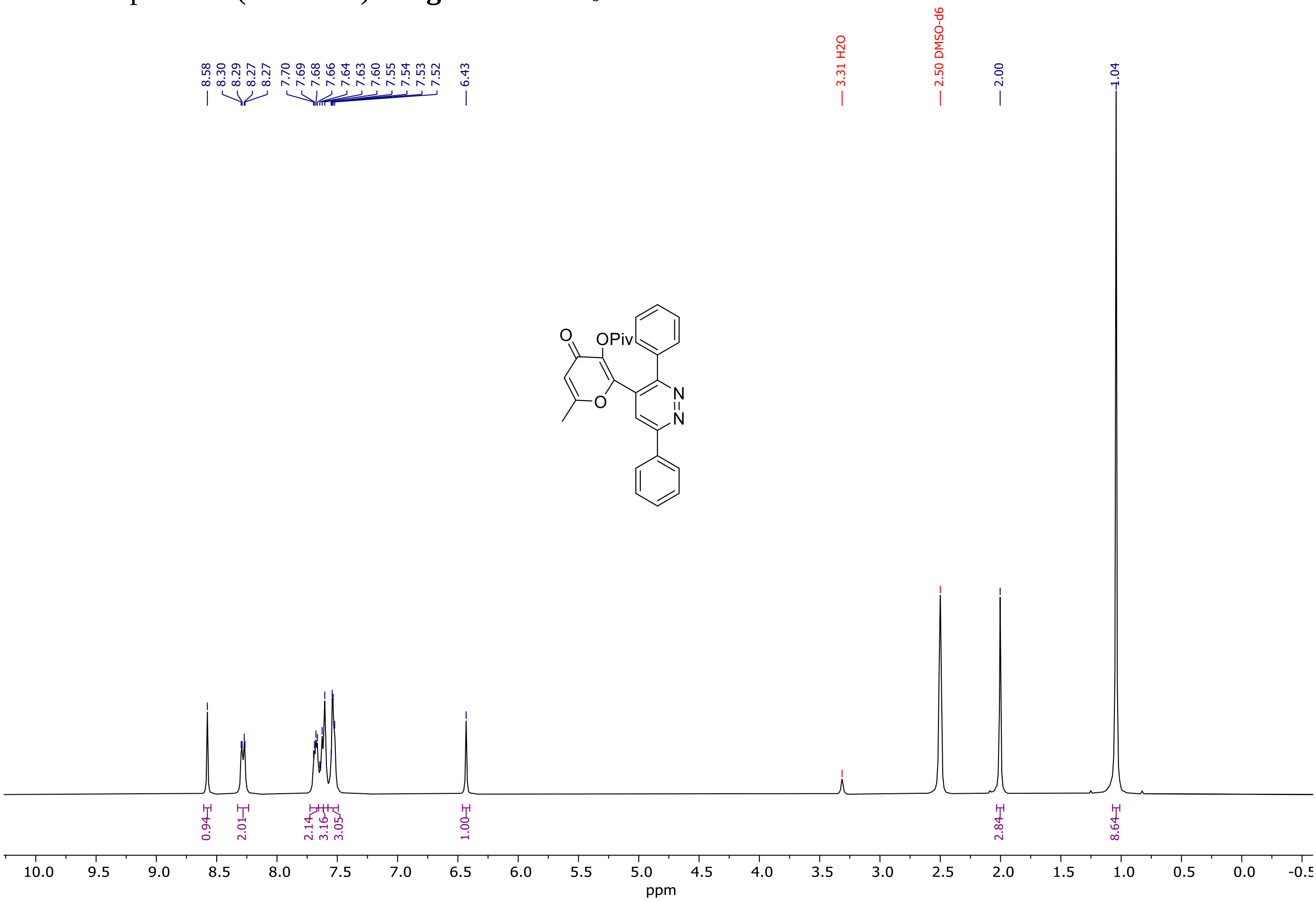
[1]H NMR spectrum (300 MHz) of **9f'** in DMSO-d_6



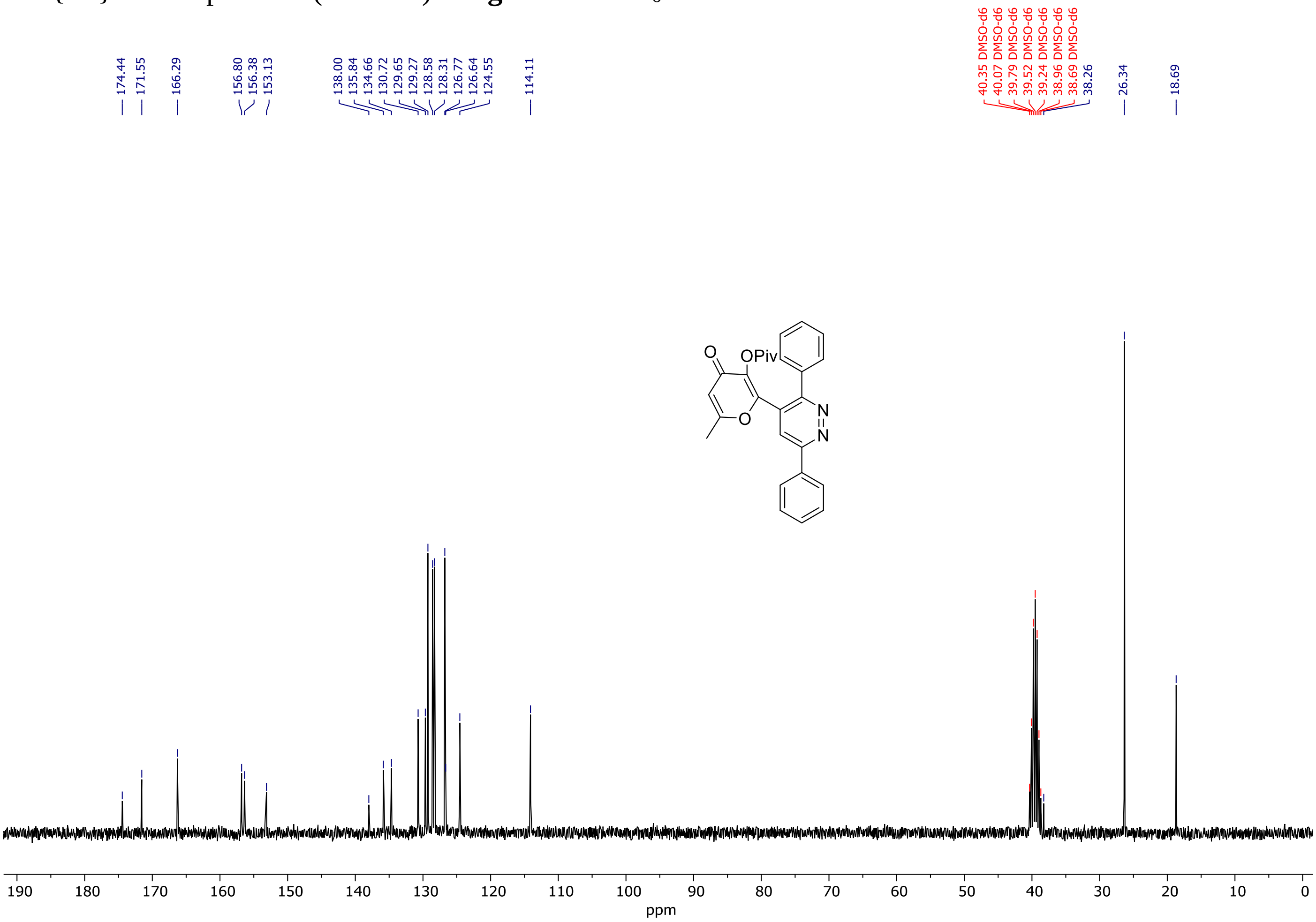
[13]C {[1]H} NMR spectrum (75 MHz) of **9f'** in DMSO-d_6



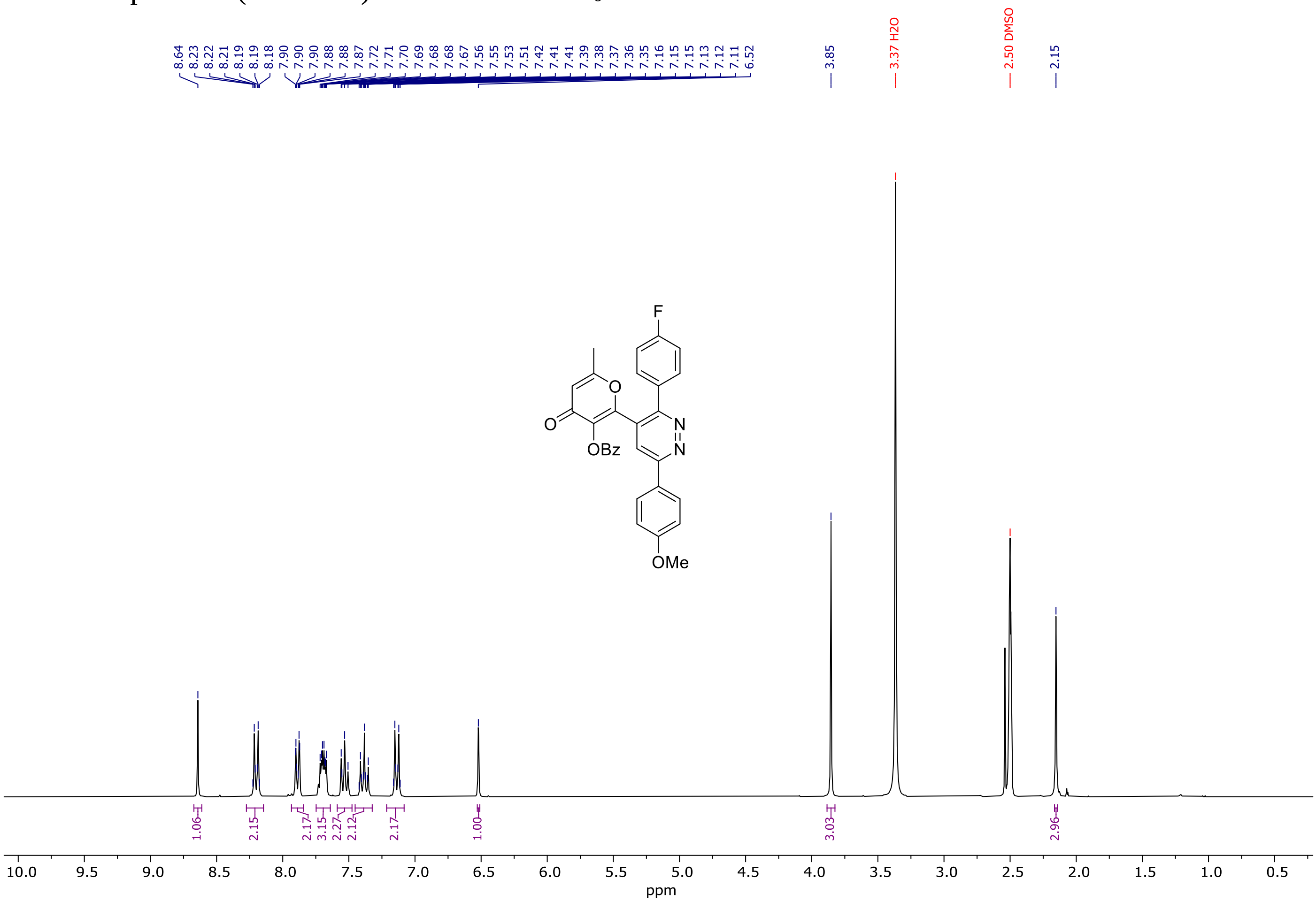
^{1}H NMR spectrum (300 MHz) of **9g** in DMSO-d_6



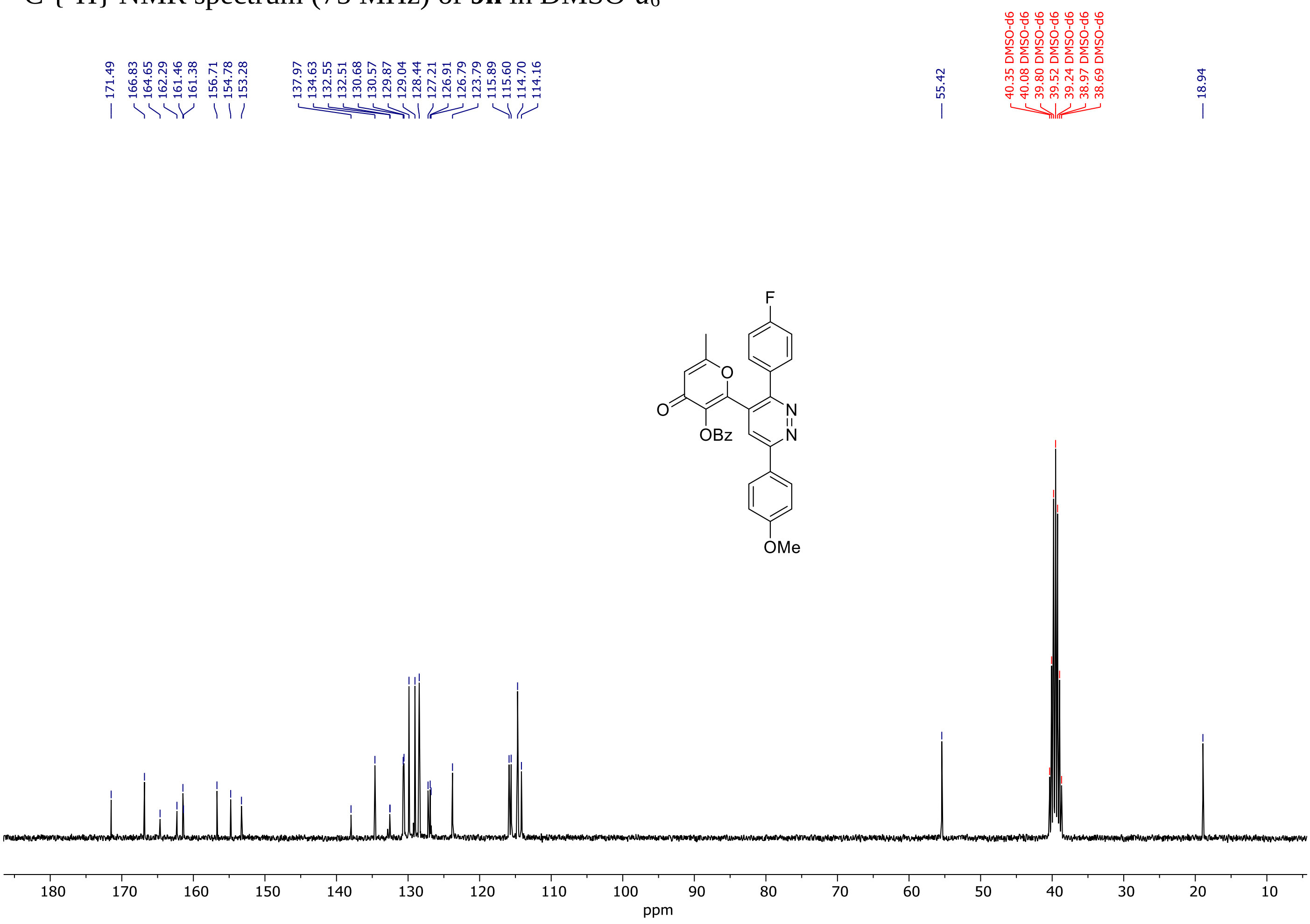
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9g** in DMSO-d_6



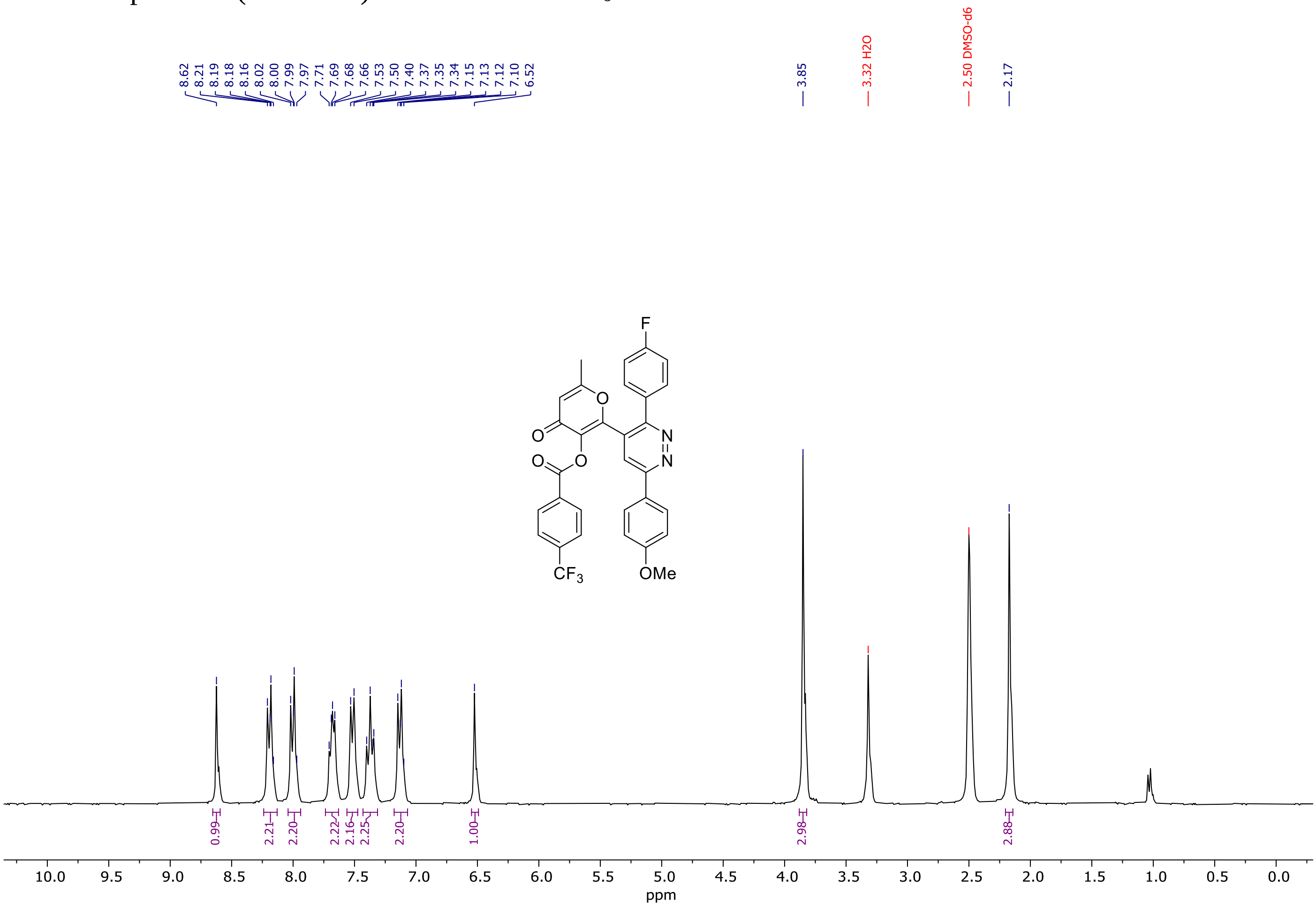
[1]H NMR spectrum (300 MHz) of **9h** in DMSO-d_6



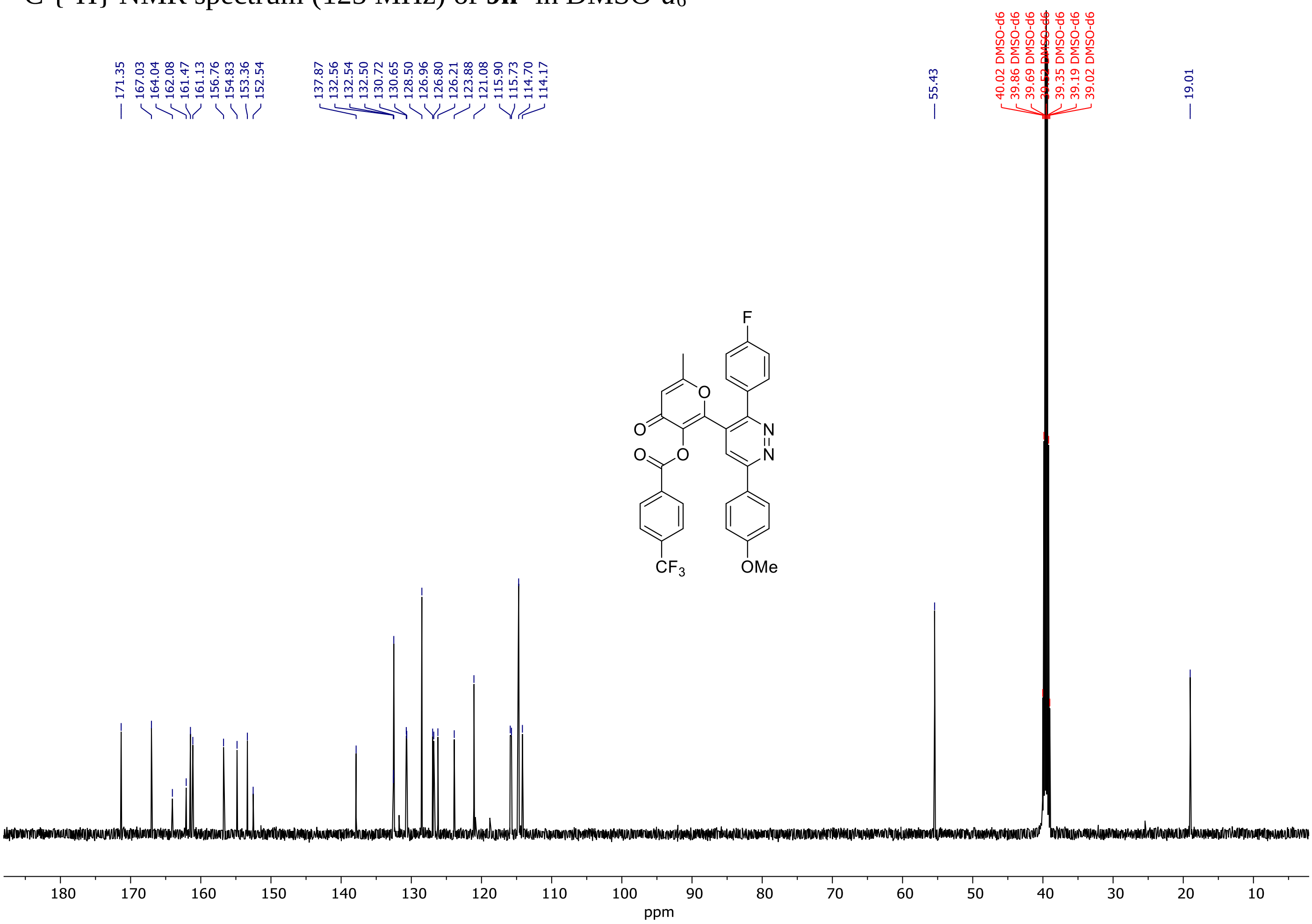
[13]C {[1]H} NMR spectrum (75 MHz) of **9h** in DMSO-d_6



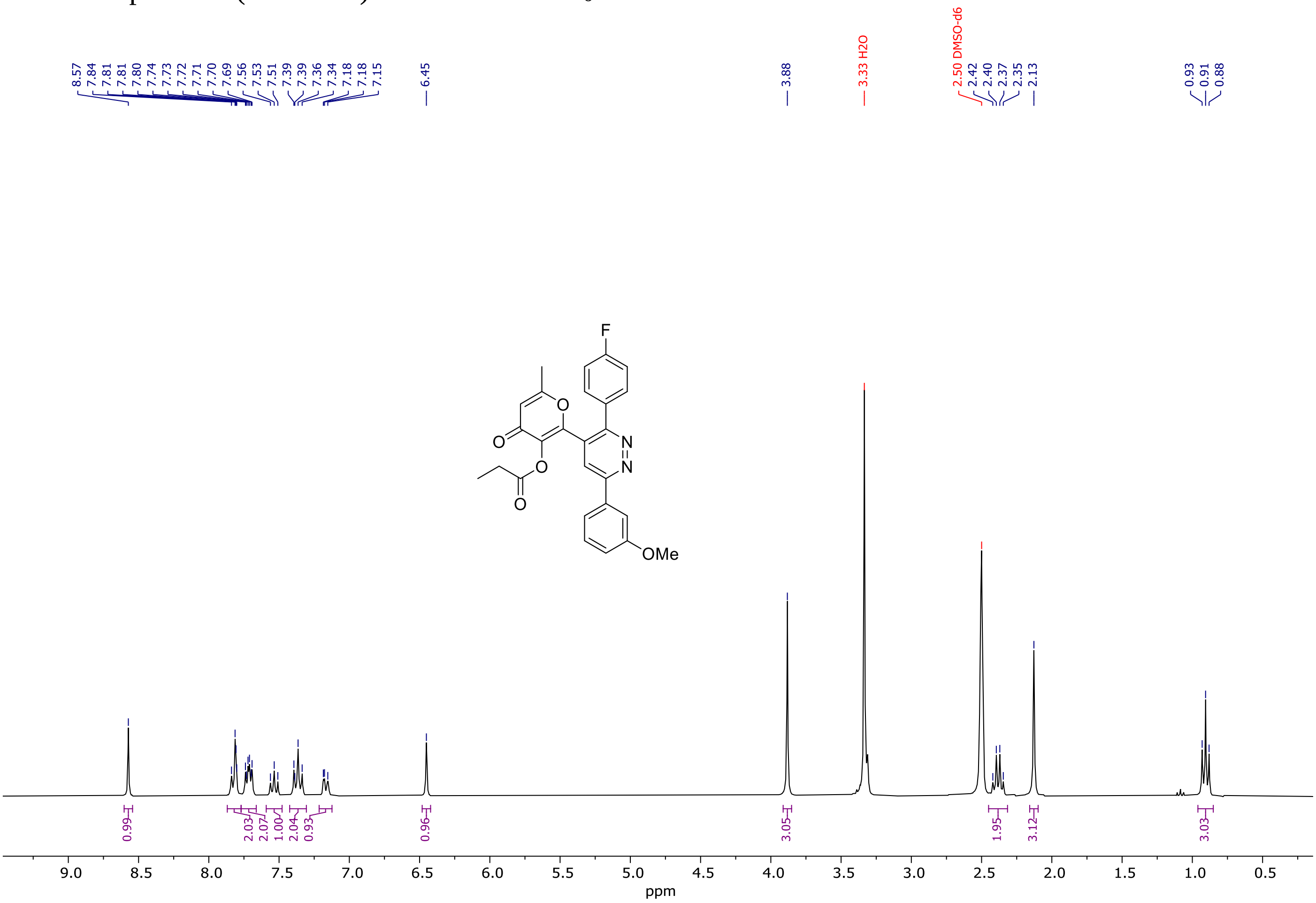
^{1}H NMR spectrum (300 MHz) of **9h’** in DMSO-d_6



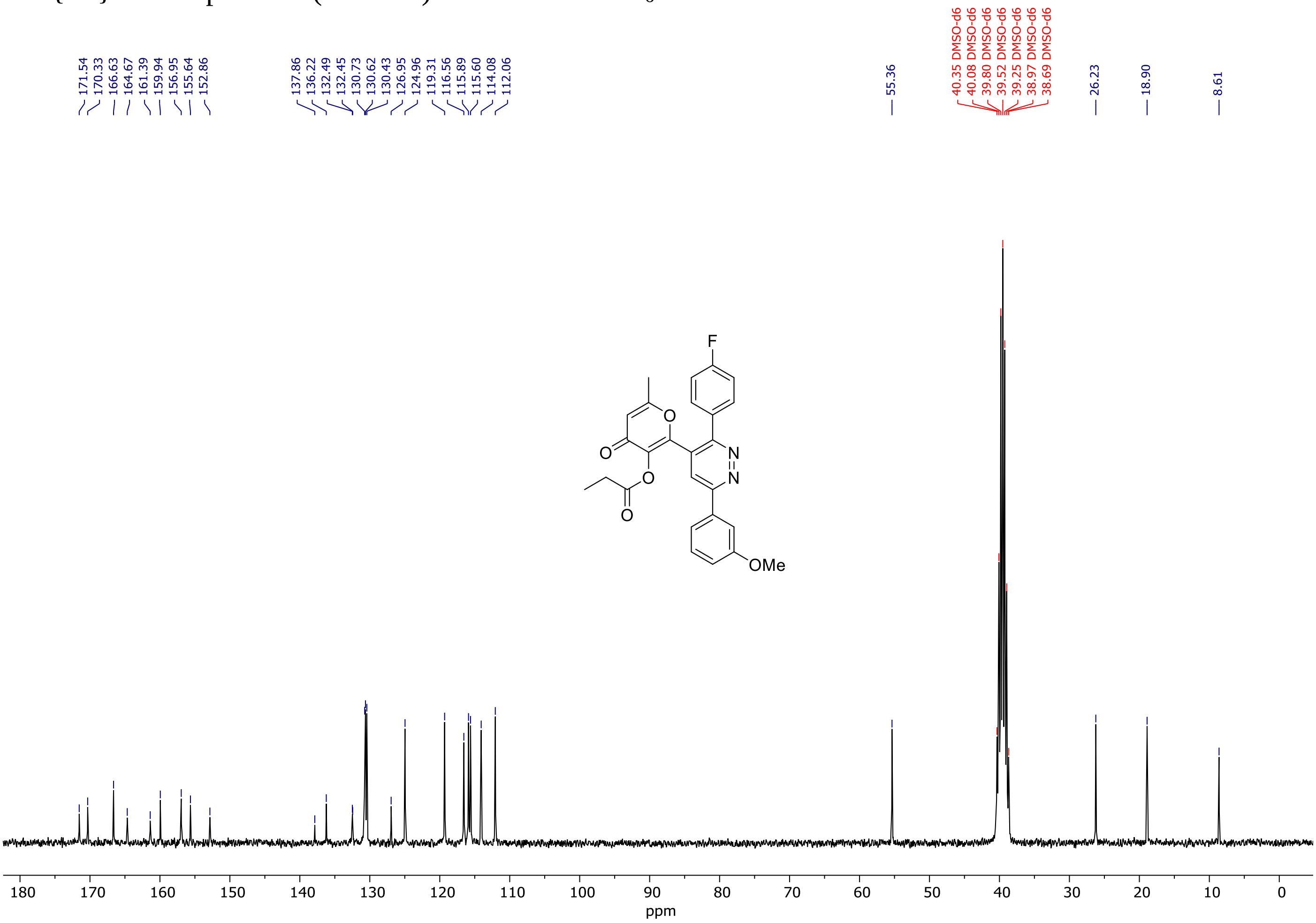
^{13}C {^{1}H} NMR spectrum (125 MHz) of **9h’** in DMSO-d_6



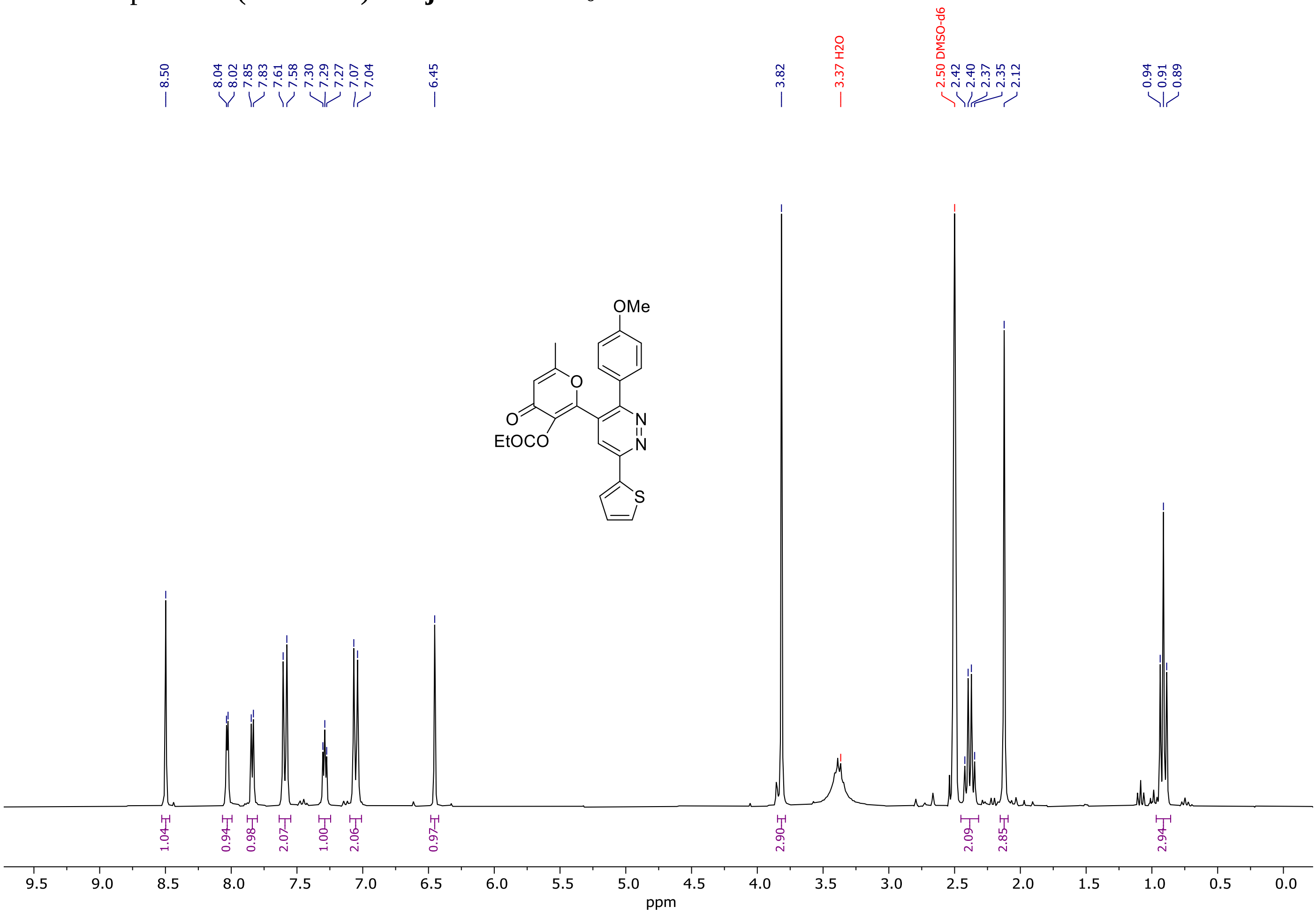
^{1}H NMR spectrum (300 MHz) of **9i** in DMSO-d_6



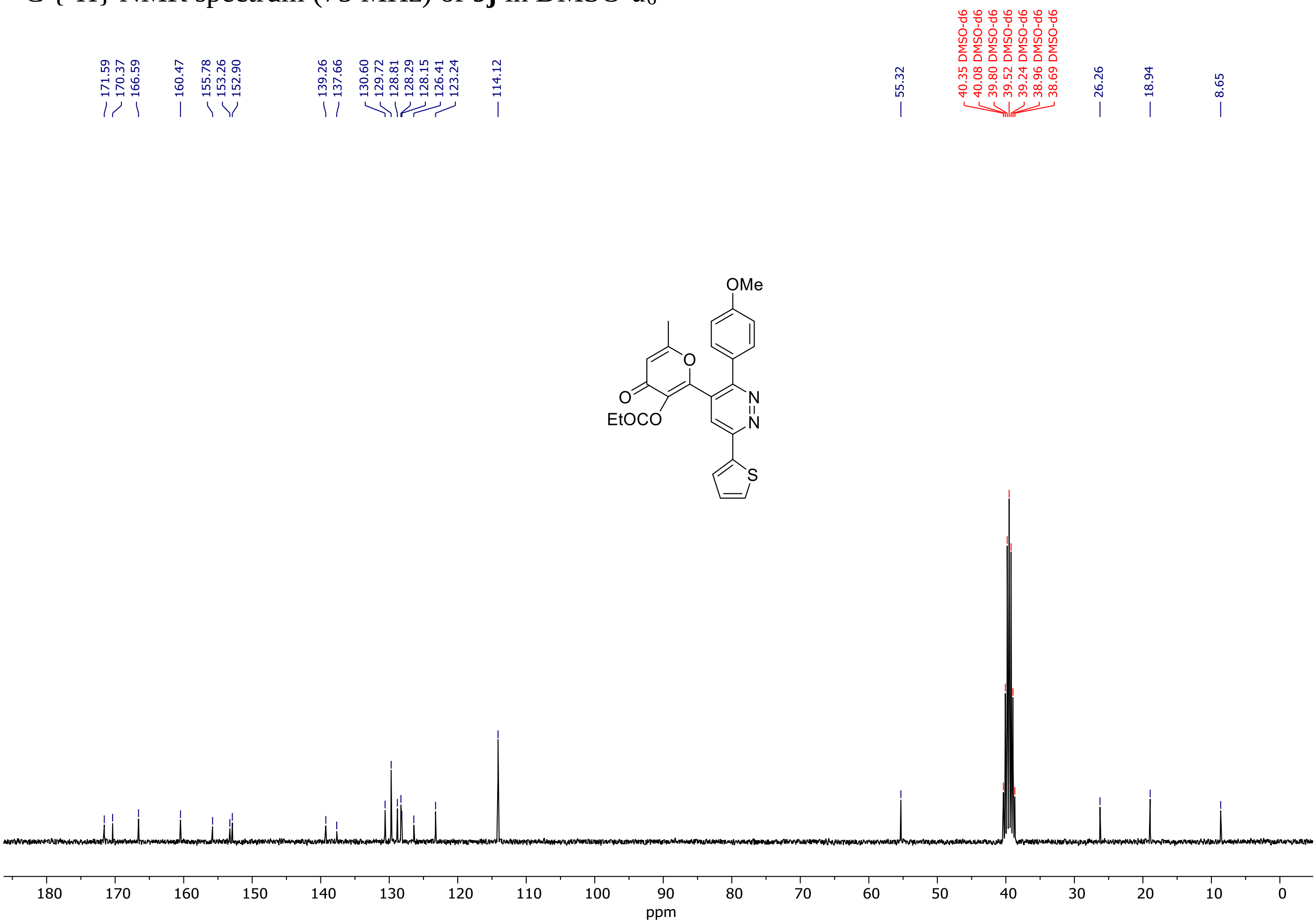
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9i** in DMSO-d_6



^{1}H NMR spectrum (300 MHz) of **9j** in DMSO-d_6

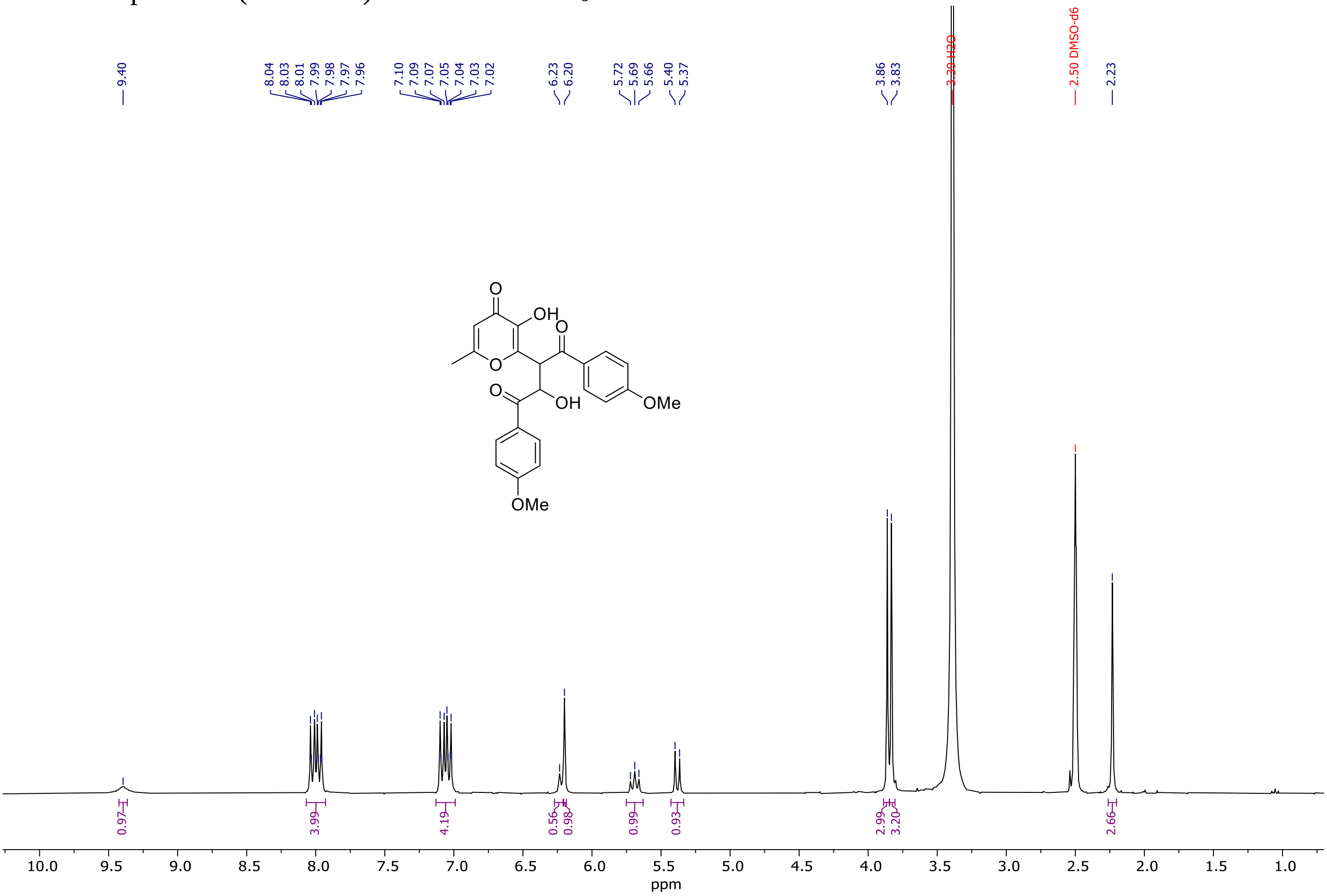


^{13}C {^{1}H} NMR spectrum (75 MHz) of **9j** in DMSO-d_6

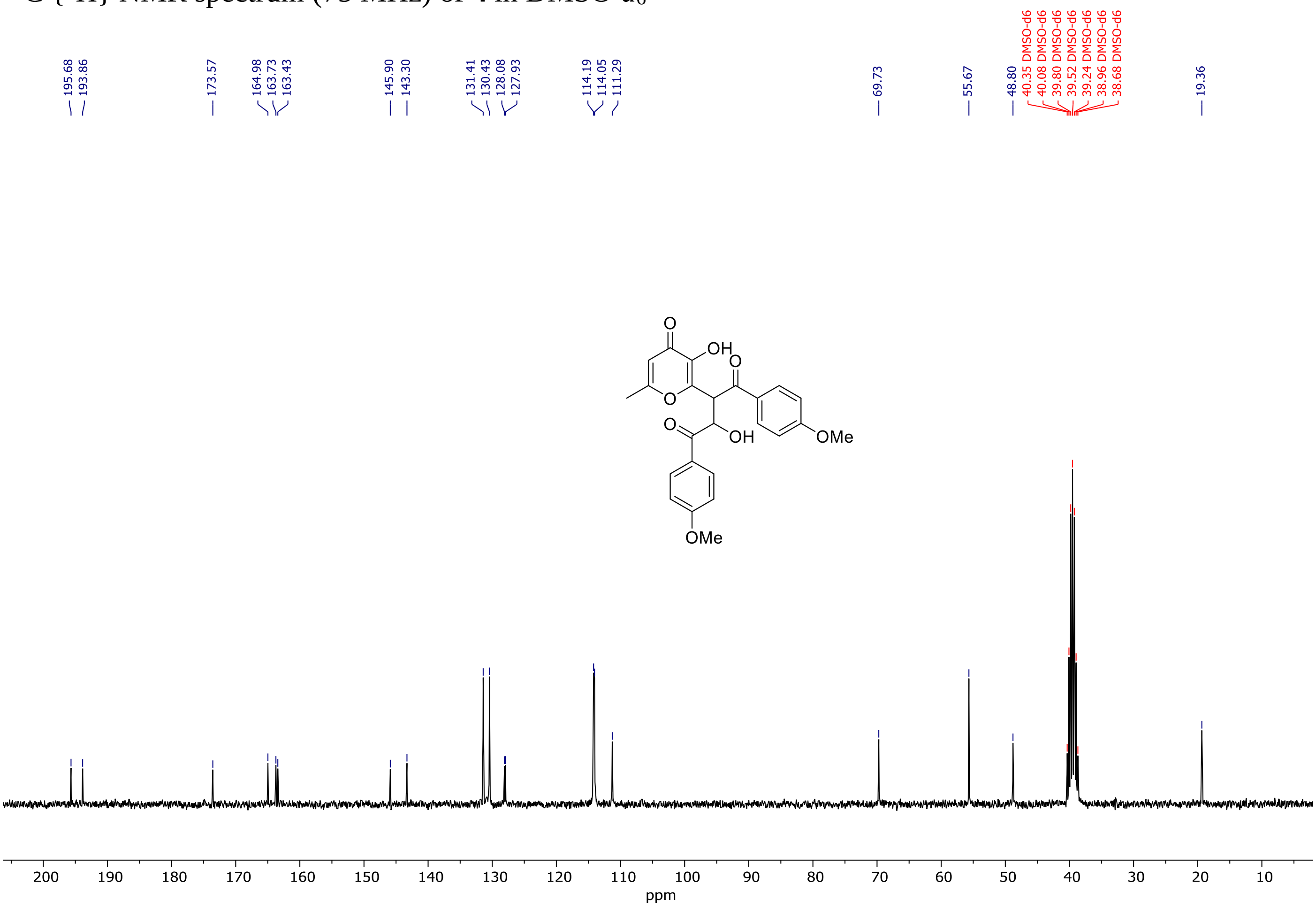


11. NMR ^{1}H and ^{13}C spectra for compounds 4, 6 and 8

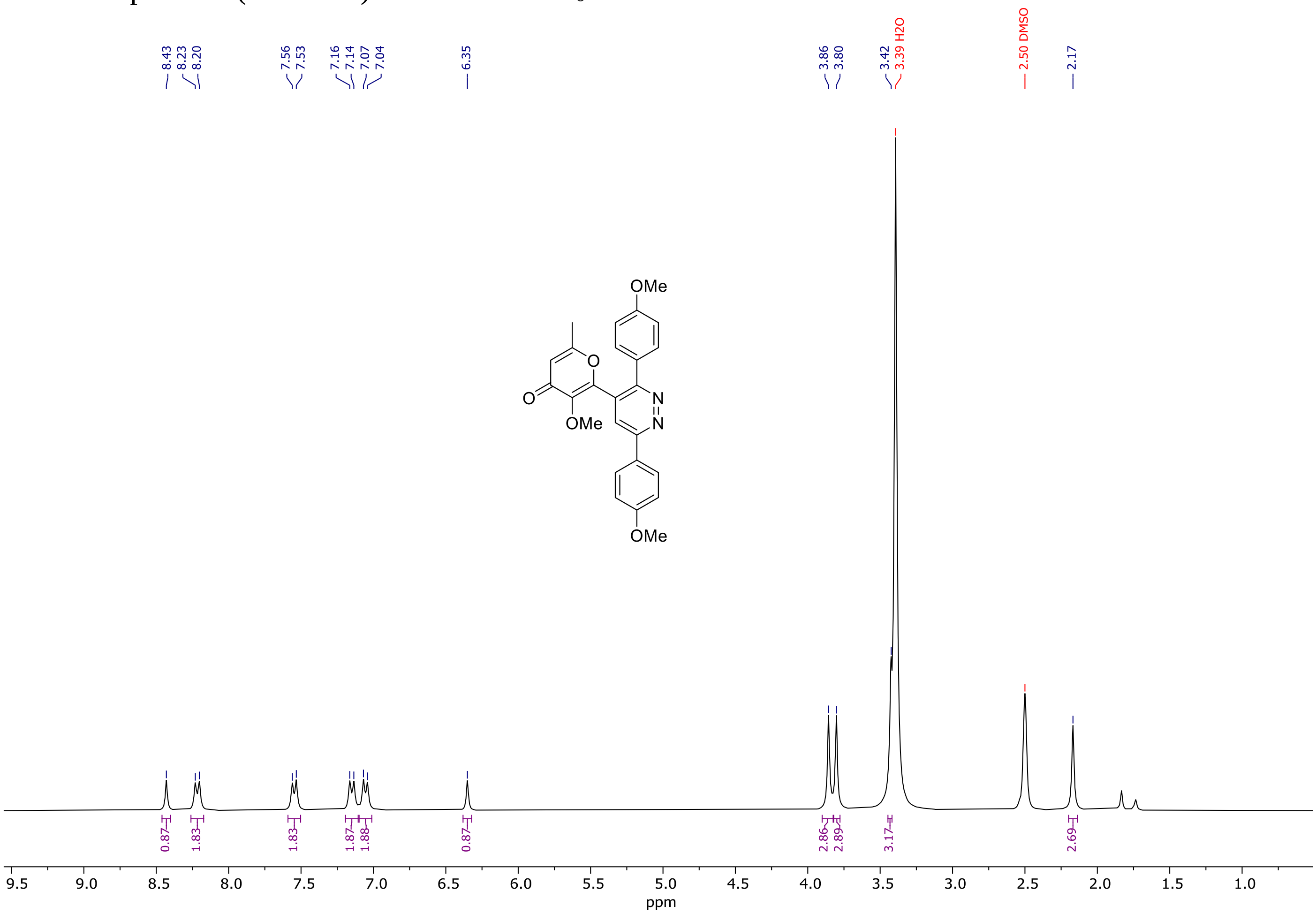
^{1}H NMR spectrum (300 MHz) of **4** in DMSO-d_6



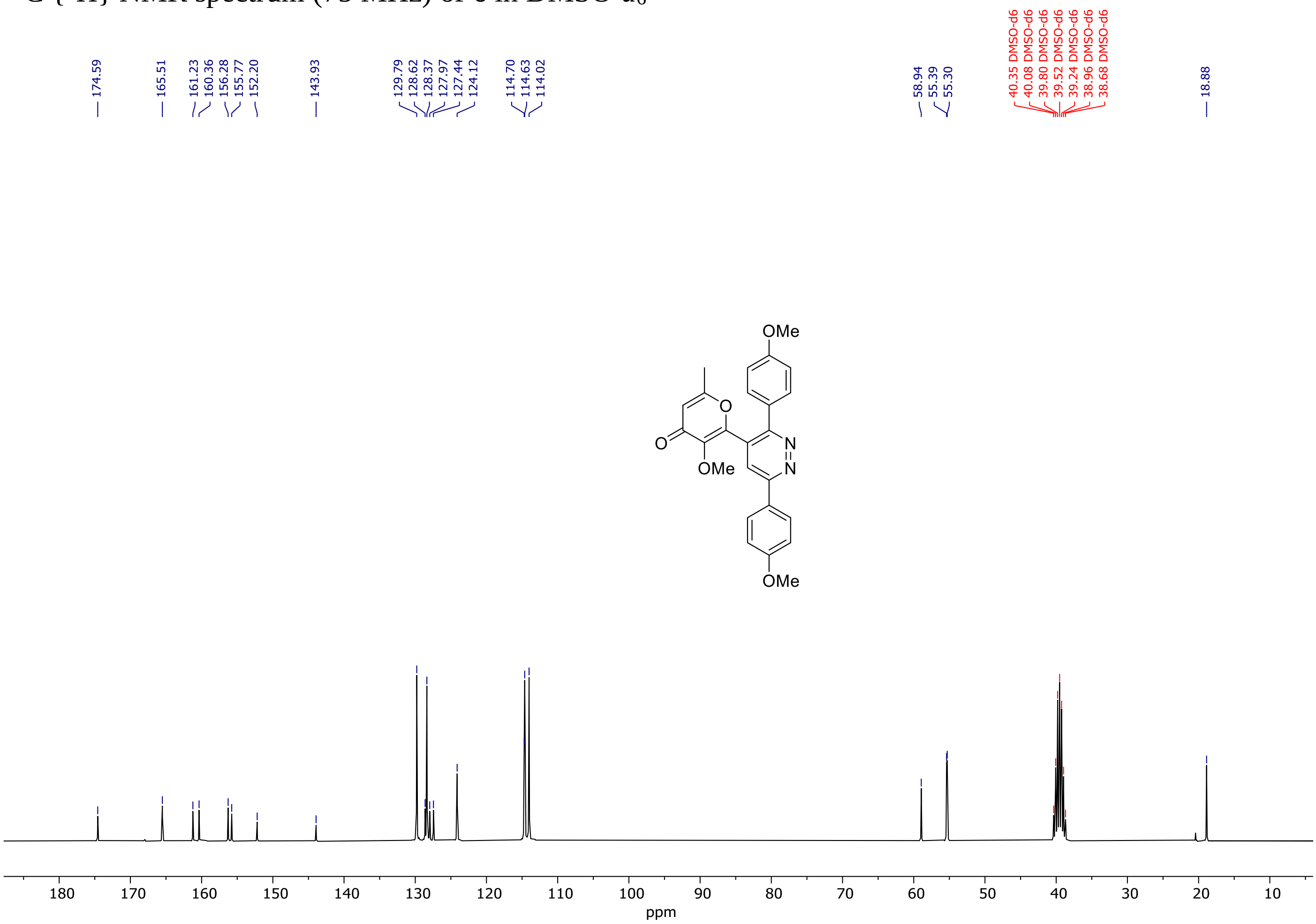
^{13}C {^{1}H} NMR spectrum (75 MHz) of **4** in DMSO-d_6



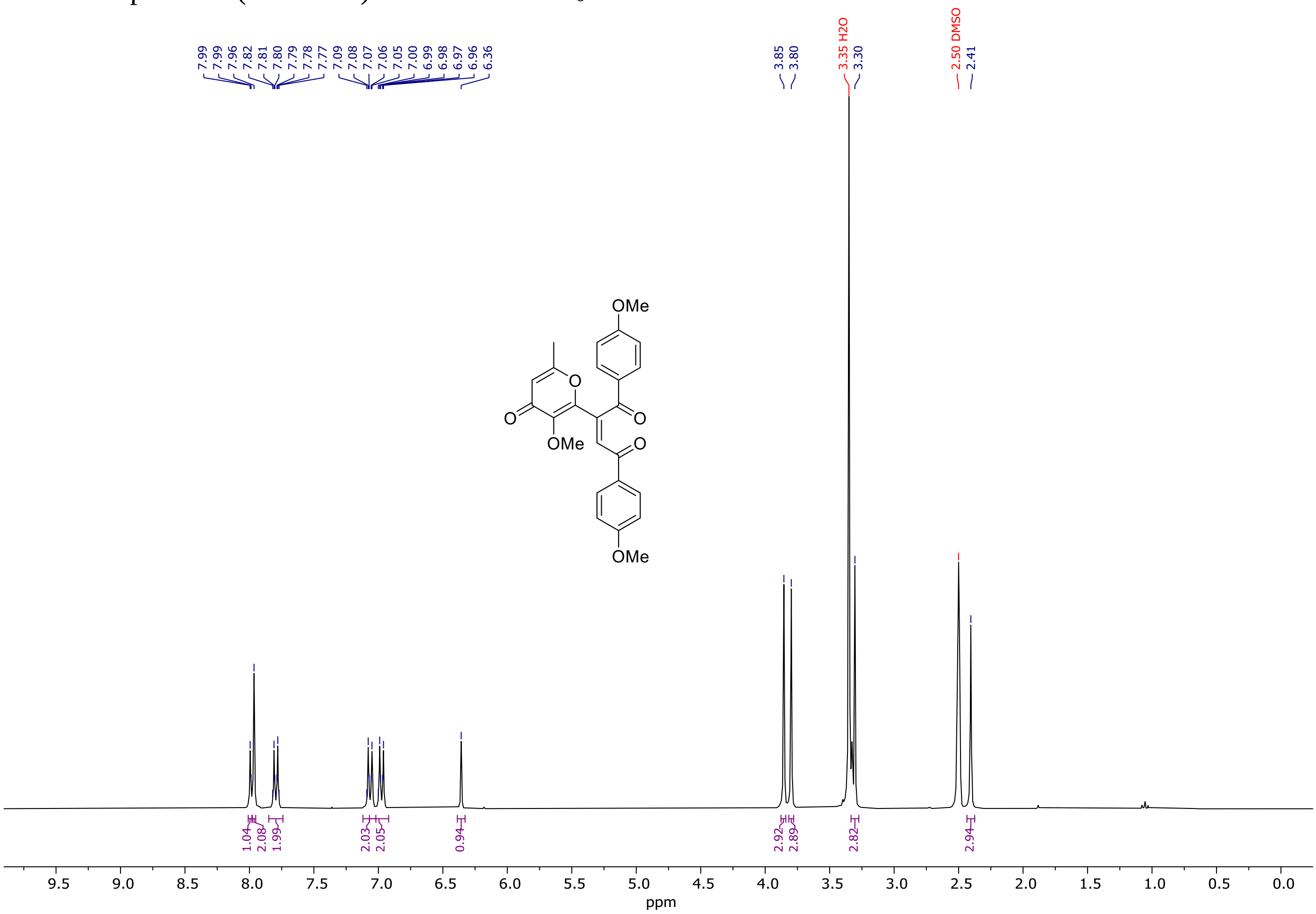
^{1}H NMR spectrum (300 MHz) of **6** in DMSO-d_6



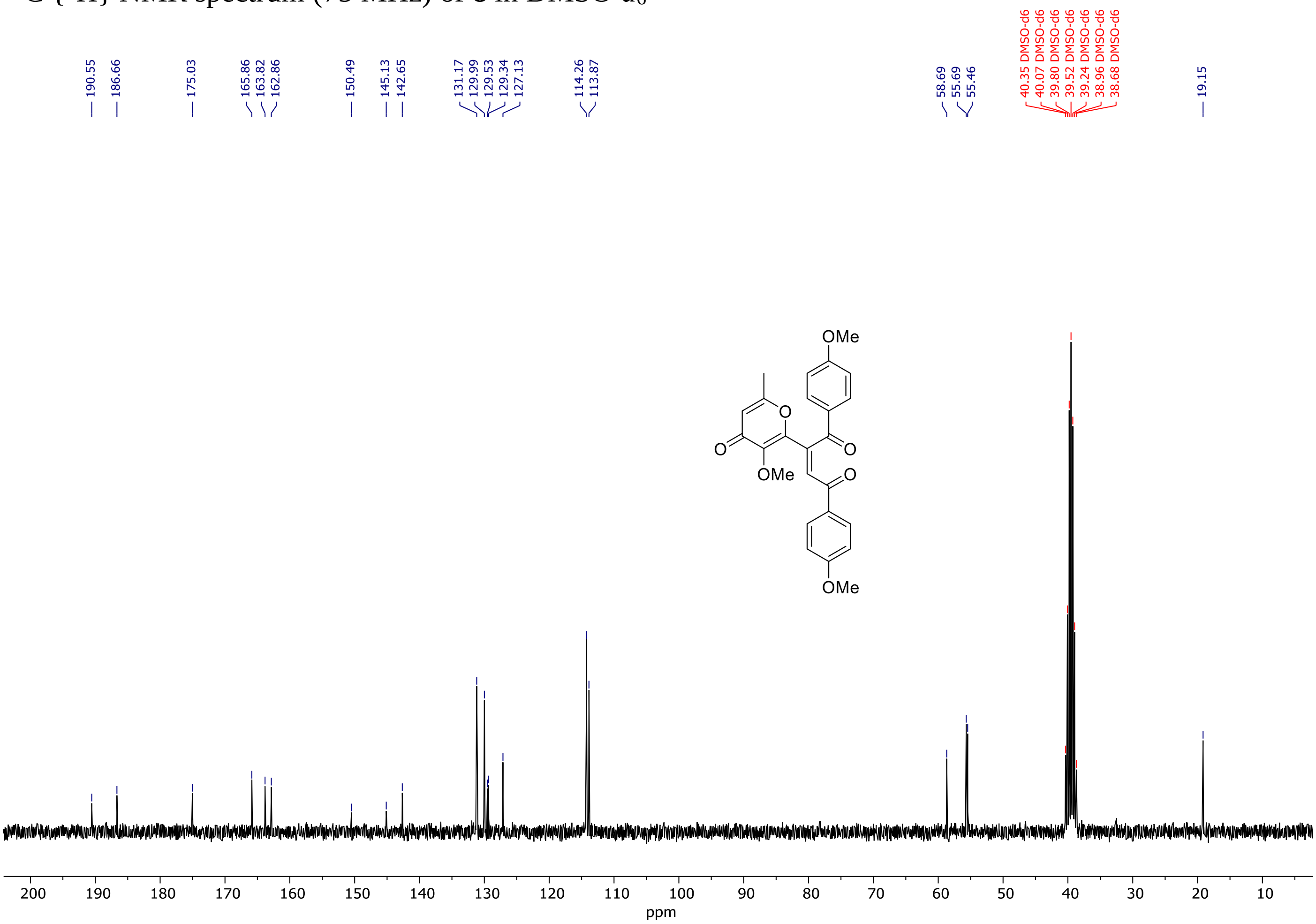
^{13}C {^{1}H} NMR spectrum (75 MHz) of **6** in DMSO-d_6



^{1}H NMR spectrum (300 MHz) of **8** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (75 MHz) of **8** in DMSO-d_6



12. Computational details

Initial geometries of all compounds were obtained with a conformational search procedure using CREST 3.0.1 program package at GFN2-xTB level of theory[2]. The obtained geometries of lowest energy conformers were optimized at PBE0/def2-TZVP/CPCM(DMSO) level of theory in Orca 6.1.1 program package[3]. Analytical frequencies were calculated at 298.15 K to confirm the absence of imaginary frequencies for all molecules and intermediates in ground singlet state. Geometries of first singlet excited states were found with TD-DFT at PBE0/def2-TZVP/CPCM(DMSO) level of theory. The number of roots was set to 20 in all calculations. Analytical frequencies were calculated at 298.15 K for all molecules in excited state. TD-DFT calculations were used to analyze the molecular orbital contributions to the vertical electronic excitations. NTO analysis shows that the photoactivity of model derivative 5 is mainly associated with a HOMO–LUMO transition.

[2] S. Grimme. J. Chem. Theory Comput. 2019 15 (5), 2847-2862; Pracht P, Bohle F, Grimme S. *Phys. Chem. Chem. Phys.* **2020**, 22, 7169–7192.

[3] Neese, F. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 73-78; Neese F, Wennmohs F, Becker U, Riplinger C. *J. Chem. Phys.* **2020**, 152, 224108.

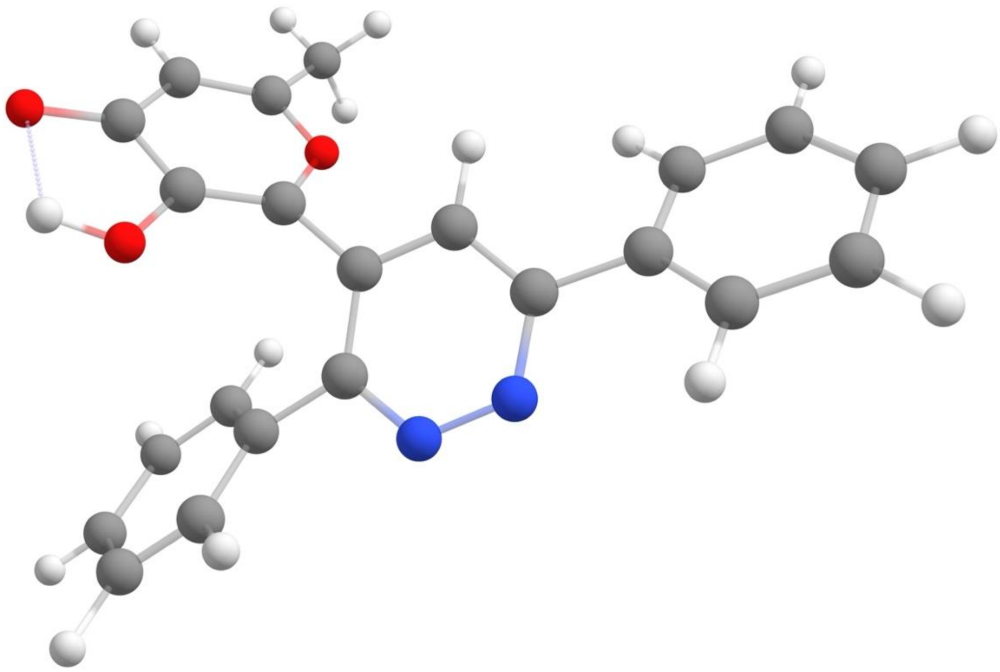


Figure S1. Model of structure **5** in S_0 geometry

Atomic coordinates

C	-0.875523	-5.395009	-4.667153
C	-0.526697	-4.120386	-4.964102
O	0.212027	-3.381341	-4.128617
C	0.655660	-3.878173	-2.945875
C	0.327109	-5.133702	-2.567681
C	-0.471724	-5.988476	-3.434756
C	-0.888145	-3.386927	-6.198588
C	1.390213	-2.886082	-2.152738
C	0.833407	-1.639701	-1.959126
C	1.476826	-0.735737	-1.115366
N	2.599108	-1.075931	-0.479863
N	3.163266	-2.238207	-0.698594
C	2.627333	-3.135034	-1.526910
C	3.441066	-4.345918	-1.750521
C	0.938173	0.611113	-0.848330
O	-0.738556	-7.132700	-3.039840
O	0.681073	-5.665847	-1.395686
C	4.069291	-4.972875	-0.675102
C	4.864344	-6.089149	-0.881117
C	5.052241	-6.584502	-2.165384
C	4.443163	-5.955235	-3.242992
C	3.640282	-4.843226	-3.037866
C	0.163564	1.270983	-1.803025
C	-0.336762	2.538923	-1.548976
C	-0.074768	3.162281	-0.336397
C	0.694858	2.511725	0.620188
C	1.200587	1.247165	0.366339
H	-1.473662	-5.961059	-5.369230
H	-1.496202	-4.014913	-6.846734
H	-1.445389	-2.480529	-5.948466
H	0.014790	-3.083849	-6.734781
H	-0.118758	-1.392002	-2.411409
H	0.302555	-6.567677	-1.418590
H	3.920889	-4.585290	0.325896
H	5.338374	-6.575288	-0.035828
H	5.676411	-7.456244	-2.326711
H	4.598627	-6.326511	-4.249649
H	3.186530	-4.346505	-3.888193
H	-0.034933	0.803988	-2.761104
H	-0.929415	3.043123	-2.303825
H	-0.468559	4.152576	-0.137096
H	0.898968	2.990694	1.571216
H	1.796088	0.737456	1.113662

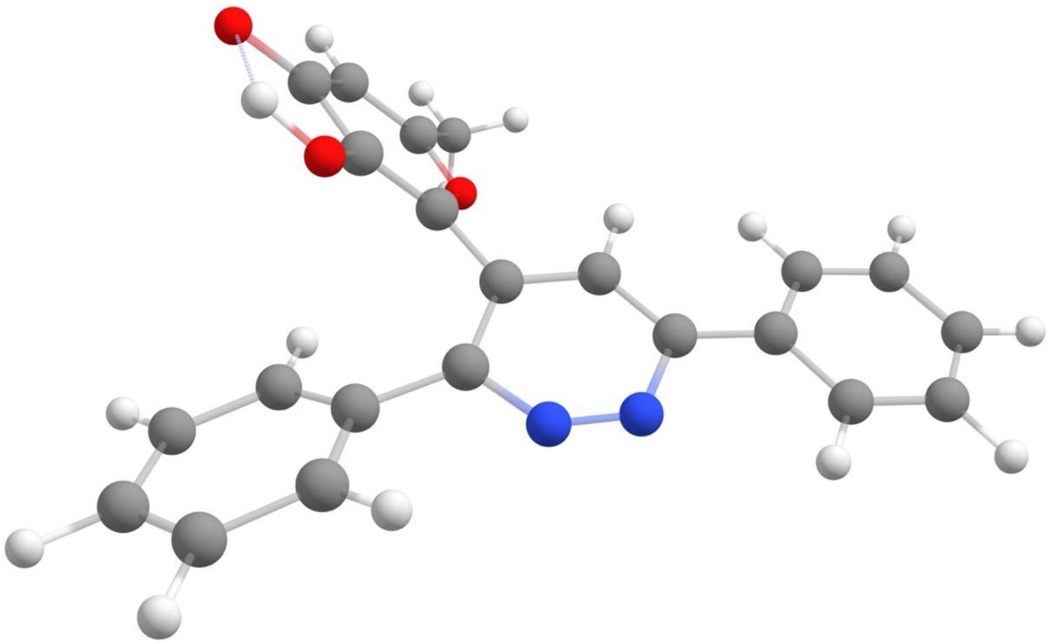


Figure S2. Model of structure **5** in S_1 geometry

Atomic coordinates

C	-0.903030	-5.295469	-4.924508
C	-0.593892	-3.994096	-5.126730
O	0.155468	-3.304147	-4.257142
C	0.632234	-3.872218	-3.112884
C	0.322979	-5.165960	-2.830005
C	-0.465936	-5.967834	-3.742066
C	-1.010261	-3.173517	-6.287579
C	1.347080	-2.940435	-2.261969
C	0.810749	-1.684557	-2.060826
C	1.335810	-0.747640	-1.166466
N	2.462249	-1.228599	-0.513916
N	2.918526	-2.326142	-0.694516
C	2.567895	-3.296242	-1.526409
C	3.443894	-4.447568	-1.633346
C	0.869021	0.576680	-0.862356
O	-0.725147	-7.141881	-3.424112
O	0.671646	-5.763853	-1.684312
C	4.261013	-4.794558	-0.545804
C	5.144632	-5.853728	-0.631813
C	5.242392	-6.595727	-1.805338
C	4.447437	-6.253931	-2.891692
C	3.558265	-5.194077	-2.812534
C	-0.202994	1.163416	-1.557089
C	-0.626731	2.442136	-1.248292
C	-0.000275	3.178039	-0.245568
C	1.061320	2.609296	0.447888
C	1.490710	1.328073	0.149648
H	-1.506561	-5.820844	-5.653101
H	-1.605664	-3.769172	-6.976878
H	-1.600320	-2.316787	-5.951657
H	-0.132689	-2.786366	-6.811625
H	-0.095090	-1.422450	-2.596223
H	0.308068	-6.668074	-1.771159
H	4.187251	-4.227058	0.376043
H	5.759795	-6.106636	0.224749
H	5.934014	-7.427561	-1.871799
H	4.523912	-6.813760	-3.817387
H	2.964290	-4.935742	-3.680111
H	-0.705492	0.620421	-2.348961
H	-1.455490	2.873204	-1.799234
H	-0.336654	4.180847	-0.009673
H	1.558983	3.167880	1.233160
H	2.314327	0.892637	0.704669

The lowest excited state (S1) is dominated by a HOMO→LUMO transition (96.7%), while higher excited states correspond to transitions involving deeper occupied orbitals (HOMO−1 and HOMO−2) to the LUMO. TD-DFT calculations show that the S_1 state is dominated by a HOMO→LUMO excitation (≈97%). The corresponding NTO pair therefore closely resembles the frontier molecular orbitals and reveals that the excited-state electron density remains largely localized on the pyranone fragment.

Table S1. Calculated vertical excitations by TD-DFT method for model compound **5**

State	Energy (eV)	λ (nm)	Dominant transitions (weight)
S_1	2.114	586.6	92→93 (0.967) (HOMO-LUMO)
S_2	2.917	425.0	92→94 (0.809); 92→95 (0.134)
S_3	3.398	364.9	91→93 (0.955)
S_4	3.621	342.4	90→93 (0.944)
S_5	3.930	315.5	92→95 (0.668); 92→94 (0.164); 92→96 (0.119)
S_6	4.074	304.3	91→94 (0.927)
S_7	4.270	290.3	89→93 (0.926)
S_8	4.322	286.8	85→93 (0.519); 85→94 (0.181)
S_9	4.363	284.2	88→93 (0.659); 92→96 (0.158)
S_{10}	4.373	283.5	92→96 (0.636); 88→93 (0.185)

NTO for state 1

```
E=   0.130161 au      3.542 eV    28566.9 cm**-1
   92a ->  93a  : n=  0.99332924
   91a ->  94a  : n=  0.00366948
```

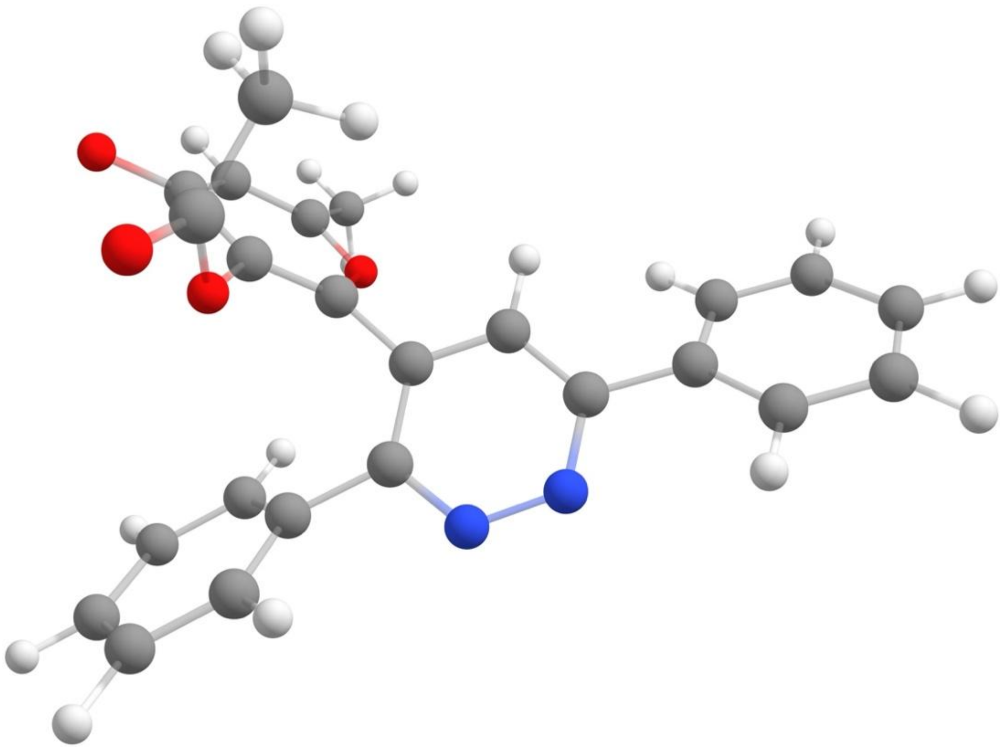


Figure 3. Model of structure **9** in S_0 geometry

Atomic coordinates

C	-0.572708	-5.494257	-5.064350
C	-0.195136	-4.225933	-5.319678
O	0.456405	-3.487849	-4.396752
C	0.754491	-4.001578	-3.190769
C	0.384277	-5.254489	-2.851701
C	-0.314466	-6.120323	-3.794229
C	-0.415971	-3.477211	-6.576085
C	1.429826	-3.031160	-2.310753
C	0.795364	-1.840732	-2.037100
C	1.385357	-0.958985	-1.130865
N	2.526841	-1.276041	-0.519214
N	3.156491	-2.388203	-0.807299
C	2.673065	-3.259010	-1.693582
C	3.535288	-4.421819	-1.976194
C	0.770614	0.333309	-0.776579
O	-0.647858	-7.266983	-3.496478
O	0.760720	-5.768874	-1.643236
C	4.185412	-5.075258	-0.929362
C	5.016408	-6.153899	-1.185741
C	5.218004	-6.584813	-2.491149
C	4.586636	-5.929182	-3.539494
C	3.747982	-4.854440	-3.284634
C	-0.049163	1.005114	-1.684170
C	-0.620909	2.222546	-1.347593
C	-0.386095	2.782123	-0.098896
C	0.428287	2.119133	0.810984
C	1.005439	0.905463	0.475037
H	-1.088183	-6.058866	-5.830532
H	-0.941208	-4.098453	-7.298619
H	-1.004481	-2.577692	-6.377822
H	0.541211	-3.161501	-6.998821
H	-0.169143	-1.621170	-2.478041
C	-0.156068	-6.027613	-0.660482
H	4.024499	-4.738931	0.088044
H	5.507304	-6.661870	-0.363325
H	5.870189	-7.427453	-2.691335
H	4.752484	-6.249638	-4.561727
H	3.281727	-4.333687	-4.113773
H	-0.227521	0.589553	-2.669550
H	-1.248164	2.737610	-2.066227
H	-0.835816	3.732746	0.164775

H	0.611700	2.548311	1.789560
H	1.635857	0.385730	1.185862
O	0.230685	-6.647890	0.288920
H	-1.483772	-4.399607	-1.031126
C	-1.528243	-5.473386	-0.837041
H	-2.019031	-5.949123	-1.688304
H	-2.101444	-5.664452	0.066443

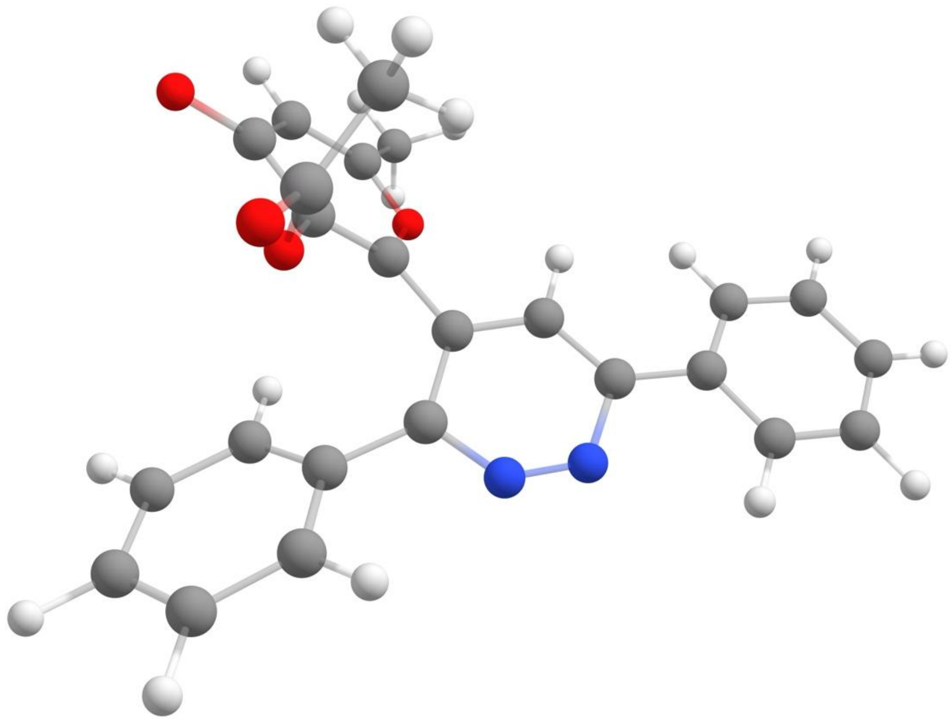


Figure 4. Model of structure **9** in S_1 geometry

Atomic coordinates

C	-0.856889	-5.238233	-4.950348
C	-0.592875	-3.931742	-5.135971
O	0.145982	-3.227374	-4.254760
C	0.639868	-3.803939	-3.129260
C	0.341244	-5.108483	-2.854852
C	-0.417221	-5.934275	-3.764488
C	-1.034616	-3.100649	-6.278917
C	1.368040	-2.878403	-2.295440
C	0.848586	-1.596724	-2.121756
C	1.366112	-0.670513	-1.232580
N	2.499762	-1.131926	-0.572147
N	2.932644	-2.247896	-0.730359
C	2.567642	-3.226916	-1.530963
C	3.432475	-4.396392	-1.611797
C	0.894435	0.661888	-0.935868
O	-0.694172	-7.113413	-3.512850
O	0.793137	-5.673211	-1.688689
C	4.174530	-4.784744	-0.489809
C	5.043975	-5.858221	-0.557450
C	5.195589	-6.564425	-1.746223
C	4.472821	-6.177911	-2.867213
C	3.598436	-5.104372	-2.805562
C	-0.163089	1.247187	-1.647892
C	-0.591435	2.525714	-1.343092
C	0.019811	3.255047	-0.327139
C	1.068633	2.685959	0.382946
C	1.501963	1.404755	0.085963
H	-1.441766	-5.774168	-5.686575
H	-1.612913	-3.699425	-6.979880
H	-1.649311	-2.269223	-5.923959
H	-0.169310	-2.676221	-6.794395
H	-0.039570	-1.323343	-2.679974
C	-0.052589	-5.902850	-0.646186
H	4.053693	-4.243083	0.442407
H	5.604118	-6.149660	0.324006
H	5.874867	-7.407502	-1.797898
H	4.594232	-6.712663	-3.802617
H	3.057056	-4.807260	-3.695307
H	-0.650614	0.705286	-2.449629
H	-1.409714	2.960616	-1.906052
H	-0.319839	4.257404	-0.093495
H	1.552802	3.242385	1.177771

H	2.316353	0.964872	0.650799
O	0.387676	-6.516425	0.287422
H	-1.410881	-4.286791	-0.983402
C	-1.434935	-5.350130	-0.737854
H	-1.988034	-5.863805	-1.527031
H	-1.935719	-5.503078	0.214709

Table 2. Calculated vertical excitations by TD-DFT method for model compound **9**

State	Energy (eV)	λ (nm)	Dominant transitions (weight)
S_1	2.089	593.6	103→104 (0.967) (HOMO-LUMO)
S_2	2.971	417.3	103→105 (0.865); 103→106 (0.076)
S_3	3.342	371.0	102→104 (0.969)
S_4	3.912	316.9	97→104 (0.438); 98→104 (0.311)
S_5	3.939	314.8	101→104 (0.901)
S_6	4.012	309.0	103→106 (0.559); 103→107 (0.211)
S_7	4.120	300.9	100→104 (0.462); 102→105 (0.423)
S_8	4.134	299.9	100→104 (0.472); 102→105 (0.430)
S_9	4.240	292.4	99→104 (0.867)
S_{10}	4.286	289.3	98→104 (0.568); 97→104 (0.343)

13. 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. Locations of hydrogen atom was found from the electron density-difference map; this hydrogen atom was 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.

Acknowledgment

Crystal structure determination was performed in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

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), 229-341. http://doi.org/10.1107/S0021889808042726

Crystallographic data for compound **2c**

Table 1. Crystal data and structure refinement for **2c**.

Identification code	2525369	
Empirical formula	$C_{23}H_{18}O_6$	
Formula weight	390.37	
Temperature	99.97(15) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.0262(2) Å	α= 66.963(2)°.
	b = 10.3038(3) Å	β= 80.090(2)°.
	c = 12.5236(3) Å	γ= 89.957(2)°.
Volume	936.35(4) $Å^3$	
Z	2	
Density (calculated)	1.385 mg/m^3	
Absorption coefficient	0.834 mm^{-1}	
F(000)	408	
Crystal size	0.37 x 0.27 x 0.15 mm^3	
Theta range for data collection	3.904 to 79.703°.	
Index ranges	-10<=h<=9, -13<=k<=13, -15<=l<=15	
Reflections collected	24394	
Independent reflections	4028 [R(int) = 0.0523]	
Completeness to theta = 67.684°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.319	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	4028 / 0 / 268	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1466	
R indices (all data)	R1 = 0.0530, wR2 = 0.1495	
Largest diff. peak and hole	0.324 and -0.453 e.$Å^{-3}$	

Table 2. Atomic coordinates (x10[4]) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8538(1)	7311(1)	4282(1)	28(1)
O(2)	9984(1)	10469(1)	1062(1)	32(1)
O(3)	9617(1)	7766(1)	1235(1)	31(1)
O(4)	10835(1)	4829(1)	2461(1)	31(1)
O(5)	4885(1)	2895(1)	561(1)	30(1)
O(6)	8153(1)	2445(1)	4466(1)	32(1)
C(1)	8676(2)	8665(1)	4188(1)	28(1)
C(2)	9207(2)	9749(1)	3138(1)	29(1)
C(3)	9560(2)	9524(1)	2064(1)	27(1)
C(4)	9352(2)	8047(1)	2206(1)	27(1)
C(5)	8877(2)	6995(1)	3302(1)	26(1)
C(6)	8632(2)	5476(1)	3610(1)	26(1)
C(7)	9305(2)	4915(1)	2671(1)	26(1)
C(8)	8097(2)	4491(1)	2085(1)	26(1)
C(9)	6364(2)	4636(1)	2320(1)	28(1)
C(10)	5232(2)	4128(1)	1829(1)	28(1)
C(11)	5859(2)	3465(1)	1076(1)	26(1)
C(12)	7597(2)	3346(1)	803(1)	28(1)
C(13)	8698(2)	3844(1)	1307(1)	27(1)
C(14)	3085(2)	2853(2)	889(1)	33(1)
C(15)	7942(2)	4601(1)	4726(1)	29(1)
C(16)	7616(2)	3058(1)	5107(1)	28(1)
C(17)	6549(2)	2266(1)	6294(1)	28(1)
C(18)	5601(2)	1032(1)	6470(1)	30(1)
C(19)	4616(2)	243(2)	7559(1)	34(1)
C(20)	4572(2)	662(2)	8491(1)	36(1)
C(21)	5512(2)	1877(2)	8330(1)	35(1)
C(22)	6488(2)	2686(1)	7235(1)	30(1)
C(23)	8144(2)	8732(1)	5360(1)	32(1)

Table 3. Bond lengths [Å] and angles [°] for **2c**.

O(1)-C(1)	1.3560(15)
O(1)-C(5)	1.3729(15)
O(2)-C(3)	1.2393(17)
O(3)-H(3)	0.88(3)
O(3)-C(4)	1.3391(16)
O(4)-C(7)	1.2211(16)
O(5)-C(11)	1.3572(16)
O(5)-C(14)	1.4285(16)
O(6)-C(16)	1.2265(17)
C(1)-C(2)	1.349(2)
C(1)-C(23)	1.4843(18)
C(2)-H(2)	0.9500
C(2)-C(3)	1.4335(18)
C(3)-C(4)	1.4680(17)
C(4)-C(5)	1.3634(19)
C(5)-C(6)	1.4621(17)
C(6)-C(7)	1.5246(17)
C(6)-C(15)	1.3493(19)
C(7)-C(8)	1.4719(18)
C(8)-C(9)	1.3921(18)
C(8)-C(13)	1.4035(17)
C(9)-H(9)	0.9500
C(9)-C(10)	1.3870(19)
C(10)-H(10)	0.9500
C(10)-C(11)	1.3969(18)
C(11)-C(12)	1.3948(19)
C(12)-H(12)	0.9500
C(12)-C(13)	1.3747(19)
C(13)-H(13)	0.9500
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15)	0.9500
C(15)-C(16)	1.4795(18)
C(16)-C(17)	1.4905(19)
C(17)-C(18)	1.4029(18)
C(17)-C(22)	1.3998(19)
C(18)-H(18)	0.9500
C(18)-C(19)	1.381(2)
C(19)-H(19)	0.9500
C(19)-C(20)	1.389(2)
C(20)-H(20)	0.9500
C(20)-C(21)	1.388(2)
C(21)-H(21)	0.9500
C(21)-C(22)	1.387(2)
C(22)-H(22)	0.9500
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(1)-O(1)-C(5)	121.19(11)
C(4)-O(3)-H(3)	113.8(16)

C(11)-O(5)-C(14)	118.06(11)
O(1)-C(1)-C(23)	110.71(11)
C(2)-C(1)-O(1)	121.56(12)
C(2)-C(1)-C(23)	127.72(12)
C(1)-C(2)-H(2)	119.4
C(1)-C(2)-C(3)	121.12(12)
C(3)-C(2)-H(2)	119.4
O(2)-C(3)-C(2)	125.05(12)
O(2)-C(3)-C(4)	119.64(12)
C(2)-C(3)-C(4)	115.30(12)
O(3)-C(4)-C(3)	118.39(12)
O(3)-C(4)-C(5)	121.19(11)
C(5)-C(4)-C(3)	120.41(12)
O(1)-C(5)-C(6)	111.73(11)
C(4)-C(5)-O(1)	120.32(11)
C(4)-C(5)-C(6)	127.94(12)
C(5)-C(6)-C(7)	118.16(11)
C(15)-C(6)-C(5)	119.98(12)
C(15)-C(6)-C(7)	121.67(11)
O(4)-C(7)-C(6)	117.21(11)
O(4)-C(7)-C(8)	123.79(12)
C(8)-C(7)-C(6)	119.00(11)
C(9)-C(8)-C(7)	122.48(12)
C(9)-C(8)-C(13)	118.55(12)
C(13)-C(8)-C(7)	118.88(12)
C(8)-C(9)-H(9)	119.2
C(10)-C(9)-C(8)	121.50(12)
C(10)-C(9)-H(9)	119.2
C(9)-C(10)-H(10)	120.6
C(9)-C(10)-C(11)	118.80(12)
C(11)-C(10)-H(10)	120.6
O(5)-C(11)-C(10)	124.61(12)
O(5)-C(11)-C(12)	114.94(11)
C(12)-C(11)-C(10)	120.45(12)
C(11)-C(12)-H(12)	120.1
C(13)-C(12)-C(11)	119.89(12)
C(13)-C(12)-H(12)	120.1
C(8)-C(13)-H(13)	119.6
C(12)-C(13)-C(8)	120.76(12)
C(12)-C(13)-H(13)	119.6
O(5)-C(14)-H(14A)	109.5
O(5)-C(14)-H(14B)	109.5
O(5)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(6)-C(15)-H(15)	118.3
C(6)-C(15)-C(16)	123.47(12)
C(16)-C(15)-H(15)	118.3
O(6)-C(16)-C(15)	121.98(13)
O(6)-C(16)-C(17)	120.56(12)
C(15)-C(16)-C(17)	117.43(11)
C(18)-C(17)-C(16)	117.98(12)
C(22)-C(17)-C(16)	122.83(12)

C(22)-C(17)-C(18)	119.17(13)
C(17)-C(18)-H(18)	119.8
C(19)-C(18)-C(17)	120.40(13)
C(19)-C(18)-H(18)	119.8
C(18)-C(19)-H(19)	120.0
C(18)-C(19)-C(20)	120.06(13)
C(20)-C(19)-H(19)	120.0
C(19)-C(20)-H(20)	119.9
C(21)-C(20)-C(19)	120.10(14)
C(21)-C(20)-H(20)	119.9
C(20)-C(21)-H(21)	119.9
C(22)-C(21)-C(20)	120.27(14)
C(22)-C(21)-H(21)	119.9
C(17)-C(22)-H(22)	120.0
C(21)-C(22)-C(17)	120.00(13)
C(21)-C(22)-H(22)	120.0
C(1)-C(23)-H(23A)	109.5
C(1)-C(23)-H(23B)	109.5
C(1)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for **2c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*2U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	38(1)	21(1)	26(1)	-12(1)	-6(1)	2(1)
O(2)	42(1)	24(1)	28(1)	-9(1)	-6(1)	-2(1)
O(3)	43(1)	25(1)	26(1)	-12(1)	-4(1)	1(1)
O(4)	29(1)	30(1)	36(1)	-16(1)	-7(1)	3(1)
O(5)	29(1)	32(1)	34(1)	-17(1)	-8(1)	2(1)
O(6)	43(1)	25(1)	31(1)	-13(1)	-5(1)	4(1)
C(1)	32(1)	23(1)	32(1)	-14(1)	-9(1)	4(1)
C(2)	35(1)	22(1)	32(1)	-14(1)	-9(1)	3(1)
C(3)	29(1)	25(1)	29(1)	-11(1)	-7(1)	2(1)
C(4)	30(1)	25(1)	28(1)	-12(1)	-6(1)	2(1)
C(5)	31(1)	24(1)	27(1)	-13(1)	-6(1)	3(1)
C(6)	29(1)	24(1)	29(1)	-13(1)	-8(1)	3(1)
C(7)	31(1)	20(1)	27(1)	-9(1)	-4(1)	2(1)
C(8)	30(1)	21(1)	26(1)	-9(1)	-4(1)	3(1)
C(9)	31(1)	25(1)	28(1)	-13(1)	-4(1)	4(1)
C(10)	27(1)	27(1)	30(1)	-12(1)	-4(1)	4(1)
C(11)	30(1)	23(1)	26(1)	-9(1)	-7(1)	2(1)
C(12)	31(1)	28(1)	28(1)	-14(1)	-4(1)	4(1)
C(13)	28(1)	26(1)	28(1)	-12(1)	-3(1)	3(1)
C(14)	28(1)	34(1)	38(1)	-14(1)	-8(1)	0(1)
C(15)	35(1)	25(1)	29(1)	-13(1)	-7(1)	2(1)
C(16)	34(1)	24(1)	28(1)	-11(1)	-9(1)	4(1)
C(17)	31(1)	24(1)	29(1)	-11(1)	-9(1)	5(1)
C(18)	35(1)	24(1)	34(1)	-11(1)	-11(1)	4(1)
C(19)	33(1)	26(1)	39(1)	-9(1)	-10(1)	2(1)
C(20)	36(1)	34(1)	32(1)	-6(1)	-4(1)	4(1)
C(21)	43(1)	35(1)	28(1)	-12(1)	-8(1)	6(1)
C(22)	34(1)	27(1)	32(1)	-13(1)	-9(1)	5(1)
C(23)	41(1)	27(1)	31(1)	-16(1)	-6(1)	4(1)

Table 5. Hydrogen coordinates (x10^{4}) and isotropic displacement parameters (Å^{2}x10^{3}) for **2c**.

	x	y	z	U(eq)		
H(3)	9800(30)		8530(30)		570(20)	61(7)
H(2)	9351	10678	3109	34		
H(9)	5947	5094	2830	33		
H(10)	4051	4229	2002	33		
H(12)	8019	2923	269	34		
H(13)	9879	3750	1128	33		
H(14A)		2543	2408	461	50	
H(14B)		2734	3818	690	50	
H(14C)		2743	2305	1741	50	
H(15)	7650	4996	5297	35		
H(18)	5636	738	5837	36		
H(19)	3969	-586	7671	40		
H(20)	3897	116	9241	44		
H(21)	5487	2155	8971	42		
H(22)	7115	3525	7125	36		
H(23A)		8326	9707	5283	47	
H(23B)		8815	8115	5915	47	
H(23C)		6939	8418	5654	47	

Table 6. Torsion angles [°] for **2c**.

O(1)-C(1)-C(2)-C(3)	3.5(2)
O(1)-C(5)-C(6)-C(7)	-167.32(11)
O(1)-C(5)-C(6)-C(15)	7.77(18)
O(2)-C(3)-C(4)-O(3)	-0.56(19)
O(2)-C(3)-C(4)-C(5)	-179.65(13)
O(3)-C(4)-C(5)-O(1)	-177.08(11)
O(3)-C(4)-C(5)-C(6)	1.8(2)
O(4)-C(7)-C(8)-C(9)	-178.28(12)
O(4)-C(7)-C(8)-C(13)	5.32(19)
O(5)-C(11)-C(12)-C(13)	-177.79(11)
O(6)-C(16)-C(17)-C(18)	-26.28(19)
O(6)-C(16)-C(17)-C(22)	152.23(13)
C(1)-O(1)-C(5)-C(4)	-0.45(19)
C(1)-O(1)-C(5)-C(6)	-179.50(11)
C(1)-C(2)-C(3)-O(2)	176.88(13)
C(1)-C(2)-C(3)-C(4)	-1.87(19)
C(2)-C(3)-C(4)-O(3)	178.25(11)
C(2)-C(3)-C(4)-C(5)	-0.83(19)
C(3)-C(4)-C(5)-O(1)	2.0(2)
C(3)-C(4)-C(5)-C(6)	-179.14(12)
C(4)-C(5)-C(6)-C(7)	13.7(2)
C(4)-C(5)-C(6)-C(15)	-171.19(14)
C(5)-O(1)-C(1)-C(2)	-2.34(19)
C(5)-O(1)-C(1)-C(23)	176.60(11)
C(5)-C(6)-C(7)-O(4)	75.40(16)
C(5)-C(6)-C(7)-C(8)	-105.50(14)
C(5)-C(6)-C(15)-C(16)	178.65(12)
C(6)-C(7)-C(8)-C(9)	2.68(18)
C(6)-C(7)-C(8)-C(13)	-173.71(11)
C(6)-C(15)-C(16)-O(6)	9.6(2)
C(6)-C(15)-C(16)-C(17)	-168.32(13)
C(7)-C(6)-C(15)-C(16)	-6.4(2)
C(7)-C(8)-C(9)-C(10)	-174.83(12)
C(7)-C(8)-C(13)-C(12)	175.62(12)
C(8)-C(9)-C(10)-C(11)	-0.4(2)
C(9)-C(8)-C(13)-C(12)	-0.92(19)
C(9)-C(10)-C(11)-O(5)	178.42(12)
C(9)-C(10)-C(11)-C(12)	-1.4(2)
C(10)-C(11)-C(12)-C(13)	2.1(2)
C(11)-C(12)-C(13)-C(8)	-0.9(2)
C(13)-C(8)-C(9)-C(10)	1.6(2)
C(14)-O(5)-C(11)-C(10)	-5.87(19)
C(14)-O(5)-C(11)-C(12)	174.01(11)
C(15)-C(6)-C(7)-O(4)	-99.60(15)
C(15)-C(6)-C(7)-C(8)	79.50(16)
C(15)-C(16)-C(17)-C(18)	151.65(13)
C(15)-C(16)-C(17)-C(22)	-29.84(19)
C(16)-C(17)-C(18)-C(19)	178.73(12)
C(16)-C(17)-C(22)-C(21)	-177.85(13)
C(17)-C(18)-C(19)-C(20)	-0.6(2)
C(18)-C(17)-C(22)-C(21)	0.6(2)
C(18)-C(19)-C(20)-C(21)	0.2(2)

C(19)-C(20)-C(21)-C(22)	0.6(2)
C(20)-C(21)-C(22)-C(17)	-1.0(2)
C(22)-C(17)-C(18)-C(19)	0.2(2)
C(23)-C(1)-C(2)-C(3)	-175.26(13)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **2c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(2)#1	0.88(3)	1.87(3)	2.6976(14)	155(2)

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

Table 8. Crystal data and structure refinement for **7c**.

Identification code	2525368	
Empirical formula	$C_{24}H_{17}Cl_3N_2O_3$	
Formula weight	487.74	
Temperature	99.96(16) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.17070(10) Å	α= 90°.
	b = 30.9855(4) Å	β= 109.806(2)°.
	c = 7.13450(10) Å	γ = 90°.
Volume	2115.39(5) $Å^3$	
Z	4	
Density (calculated)	1.531 Mg/m^3	
Absorption coefficient	4.188 mm^{-1}	
F(000)	1000	
Crystal size	0.32 x 0.16 x 0.12 mm^3	
Theta range for data collection	2.852 to 79.612°.	
Index ranges	-12<=h<=12, -38<=k<=39, -6<=l<=8	
Reflections collected	16251	
Independent reflections	4376 [R(int) = 0.0324]	
Completeness to theta = 67.684°	98.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.401	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4376 / 0 / 291	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0836	
R indices (all data)	R1 = 0.0342, wR2 = 0.0852	
Largest diff. peak and hole	0.342 and -0.527 e.$Å^{-3}$	

Table 9. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **7c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	3959(1)	5453(1)	10600(1)	31(1)
Cl(2)	1557(1)	5642(1)	7072(1)	32(1)
Cl(3)	4347(1)	5796(1)	7071(1)	39(1)
O(1)	4288(1)	7862(1)	2492(1)	18(1)
O(2)	3149(1)	6617(1)	1040(2)	23(1)
O(3)	6350(1)	5638(1)	4860(2)	28(1)
N(1)	9298(1)	7942(1)	6476(2)	24(1)
N(2)	8991(1)	7526(1)	6259(2)	23(1)
C(1)	8301(1)	8245(1)	5722(2)	20(1)
C(2)	6925(1)	8136(1)	4643(2)	20(1)
C(3)	6593(1)	7700(1)	4403(2)	18(1)
C(4)	5220(1)	7539(1)	3266(2)	17(1)
C(5)	2950(1)	7761(1)	1327(2)	18(1)
C(6)	2558(1)	7350(1)	864(2)	19(1)
C(7)	3505(1)	6991(1)	1588(2)	18(1)
C(8)	4912(1)	7108(1)	2979(2)	17(1)
C(9)	5995(1)	6794(1)	4001(2)	18(1)
C(10)	5714(2)	6350(1)	3977(2)	21(1)
C(11)	6756(2)	6061(1)	4993(2)	23(1)
C(12)	8108(2)	6205(1)	6047(2)	24(1)
C(13)	8396(2)	6639(1)	6087(2)	24(1)
C(14)	7365(1)	6940(1)	5099(2)	20(1)
C(15)	7663(1)	7398(1)	5255(2)	19(1)
C(16)	8769(2)	8701(1)	6077(2)	21(1)
C(17)	7832(2)	9026(1)	6102(2)	23(1)
C(18)	8264(2)	9453(1)	6415(2)	26(1)
C(19)	9647(2)	9559(1)	6709(2)	28(1)
C(20)	10593(2)	9236(1)	6686(2)	29(1)
C(21)	10162(2)	8808(1)	6371(2)	25(1)
C(22)	2079(2)	8155(1)	717(2)	23(1)
C(23)	7369(2)	5324(1)	5891(2)	32(1)
C(24)	3263(2)	5799(1)	8543(2)	26(1)

Table 10. Bond lengths [Å] and angles [°] for **7c**.

Cl(1)-C(24)	1.7594(16)
Cl(2)-C(24)	1.7648(16)
Cl(3)-C(24)	1.7618(16)
O(1)-C(4)	1.3620(17)
O(1)-C(5)	1.3689(16)
O(2)-C(7)	1.2378(18)
O(3)-C(11)	1.3666(19)
O(3)-C(23)	1.4322(19)
N(1)-N(2)	1.3231(19)
N(1)-C(1)	1.353(2)
N(2)-C(15)	1.3564(18)
C(1)-C(2)	1.3921(19)
C(1)-C(16)	1.483(2)
C(2)-H(2)	0.9500
C(2)-C(3)	1.389(2)
C(3)-C(4)	1.4452(19)
C(3)-C(15)	1.407(2)
C(4)-C(8)	1.371(2)
C(5)-C(6)	1.341(2)
C(5)-C(22)	1.483(2)
C(6)-H(6)	0.9500
C(6)-C(7)	1.448(2)
C(7)-C(8)	1.4836(18)
C(8)-C(9)	1.4646(19)
C(9)-C(10)	1.403(2)
C(9)-C(14)	1.4213(19)
C(10)-H(10)	0.9500
C(10)-C(11)	1.389(2)
C(11)-C(12)	1.398(2)
C(12)-H(12)	0.9500
C(12)-C(13)	1.375(2)
C(13)-H(13)	0.9500
C(13)-C(14)	1.403(2)
C(14)-C(15)	1.446(2)
C(16)-C(17)	1.392(2)
C(16)-C(21)	1.400(2)
C(17)-H(17)	0.9500
C(17)-C(18)	1.387(2)
C(18)-H(18)	0.9500
C(18)-C(19)	1.389(2)
C(19)-H(19)	0.9500
C(19)-C(20)	1.390(3)
C(20)-H(20)	0.9500
C(20)-C(21)	1.392(2)
C(21)-H(21)	0.9500
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24)	1.0000

C(4)-O(1)-C(5)	119.34(11)
C(11)-O(3)-C(23)	117.90(13)
N(2)-N(1)-C(1)	120.99(12)
N(1)-N(2)-C(15)	120.03(13)
N(1)-C(1)-C(2)	121.86(14)
N(1)-C(1)-C(16)	116.05(12)
C(2)-C(1)-C(16)	122.08(13)
C(1)-C(2)-H(2)	121.2
C(3)-C(2)-C(1)	117.56(13)
C(3)-C(2)-H(2)	121.2
C(2)-C(3)-C(4)	123.59(13)
C(2)-C(3)-C(15)	118.24(13)
C(15)-C(3)-C(4)	118.13(13)
O(1)-C(4)-C(3)	112.39(12)
O(1)-C(4)-C(8)	124.33(12)
C(8)-C(4)-C(3)	123.28(13)
O(1)-C(5)-C(22)	111.23(12)
C(6)-C(5)-O(1)	121.20(13)
C(6)-C(5)-C(22)	127.57(13)
C(5)-C(6)-H(6)	118.8
C(5)-C(6)-C(7)	122.40(13)
C(7)-C(6)-H(6)	118.8
O(2)-C(7)-C(6)	121.32(12)
O(2)-C(7)-C(8)	123.50(13)
C(6)-C(7)-C(8)	115.17(12)
C(4)-C(8)-C(7)	117.20(12)
C(4)-C(8)-C(9)	118.46(12)
C(9)-C(8)-C(7)	124.31(12)
C(10)-C(9)-C(8)	121.90(13)
C(10)-C(9)-C(14)	118.49(13)
C(14)-C(9)-C(8)	119.59(13)
C(9)-C(10)-H(10)	119.7
C(11)-C(10)-C(9)	120.64(14)
C(11)-C(10)-H(10)	119.7
O(3)-C(11)-C(10)	115.02(14)
O(3)-C(11)-C(12)	124.15(13)
C(10)-C(11)-C(12)	120.83(14)
C(11)-C(12)-H(12)	120.5
C(13)-C(12)-C(11)	119.10(14)
C(13)-C(12)-H(12)	120.5
C(12)-C(13)-H(13)	119.2
C(12)-C(13)-C(14)	121.55(14)
C(14)-C(13)-H(13)	119.2
C(9)-C(14)-C(15)	119.76(13)
C(13)-C(14)-C(9)	119.38(14)
C(13)-C(14)-C(15)	120.80(13)
N(2)-C(15)-C(3)	121.29(14)
N(2)-C(15)-C(14)	118.26(13)
C(3)-C(15)-C(14)	120.45(12)
C(17)-C(16)-C(1)	120.69(13)
C(17)-C(16)-C(21)	119.23(14)
C(21)-C(16)-C(1)	120.08(14)
C(16)-C(17)-H(17)	119.6

C(18)-C(17)-C(16)	120.81(14)
C(18)-C(17)-H(17)	119.6
C(17)-C(18)-H(18)	120.1
C(17)-C(18)-C(19)	119.84(16)
C(19)-C(18)-H(18)	120.1
C(18)-C(19)-H(19)	120.0
C(18)-C(19)-C(20)	119.92(15)
C(20)-C(19)-H(19)	120.0
C(19)-C(20)-H(20)	119.8
C(19)-C(20)-C(21)	120.33(14)
C(21)-C(20)-H(20)	119.8
C(16)-C(21)-H(21)	120.1
C(20)-C(21)-C(16)	119.87(15)
C(20)-C(21)-H(21)	120.1
C(5)-C(22)-H(22A)	109.5
C(5)-C(22)-H(22B)	109.5
C(5)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(3)-C(23)-H(23A)	109.5
O(3)-C(23)-H(23B)	109.5
O(3)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Cl(1)-C(24)-Cl(2)	111.44(9)
Cl(1)-C(24)-Cl(3)	109.80(8)
Cl(1)-C(24)-H(24)	108.7
Cl(2)-C(24)-H(24)	108.7
Cl(3)-C(24)-Cl(2)	109.44(8)
Cl(3)-C(24)-H(24)	108.7

Symmetry transformations used to generate equivalent atoms:

Table 11. Anisotropic displacement parameters ($Å^2x10^3$) for **7c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	29(1)	32(1)	28(1)	2(1)	4(1)	6(1)
Cl(2)	20(1)	42(1)	31(1)	1(1)	4(1)	2(1)
Cl(3)	27(1)	55(1)	38(1)	2(1)	14(1)	-6(1)
O(1)	12(1)	21(1)	17(1)	0(1)	1(1)	0(1)
O(2)	19(1)	21(1)	26(1)	-2(1)	3(1)	-1(1)
O(3)	30(1)	23(1)	26(1)	3(1)	5(1)	8(1)
N(1)	16(1)	31(1)	21(1)	-2(1)	3(1)	-2(1)
N(2)	15(1)	32(1)	20(1)	-2(1)	3(1)	0(1)
C(1)	15(1)	31(1)	15(1)	-1(1)	5(1)	-2(1)
C(2)	16(1)	28(1)	15(1)	0(1)	5(1)	0(1)
C(3)	14(1)	28(1)	13(1)	0(1)	5(1)	-1(1)
C(4)	13(1)	24(1)	14(1)	1(1)	5(1)	1(1)
C(5)	13(1)	27(1)	14(1)	-1(1)	2(1)	0(1)
C(6)	14(1)	25(1)	17(1)	-1(1)	3(1)	-1(1)
C(7)	15(1)	23(1)	16(1)	-1(1)	6(1)	-1(1)
C(8)	14(1)	24(1)	14(1)	0(1)	5(1)	2(1)
C(9)	16(1)	26(1)	14(1)	0(1)	6(1)	3(1)
C(10)	19(1)	26(1)	18(1)	1(1)	5(1)	4(1)
C(11)	25(1)	26(1)	18(1)	0(1)	9(1)	6(1)
C(12)	22(1)	32(1)	18(1)	2(1)	5(1)	12(1)
C(13)	17(1)	36(1)	17(1)	-1(1)	4(1)	6(1)
C(14)	16(1)	29(1)	15(1)	-1(1)	6(1)	3(1)
C(15)	14(1)	30(1)	14(1)	-1(1)	5(1)	1(1)
C(16)	16(1)	32(1)	13(1)	0(1)	3(1)	-4(1)
C(17)	19(1)	32(1)	17(1)	0(1)	4(1)	-4(1)
C(18)	27(1)	31(1)	20(1)	0(1)	6(1)	-2(1)
C(19)	31(1)	31(1)	21(1)	-1(1)	6(1)	-10(1)
C(20)	21(1)	41(1)	23(1)	0(1)	4(1)	-10(1)
C(21)	17(1)	37(1)	19(1)	-1(1)	4(1)	-4(1)
C(22)	16(1)	23(1)	25(1)	-1(1)	0(1)	1(1)
C(23)	39(1)	28(1)	25(1)	4(1)	6(1)	14(1)
C(24)	25(1)	24(1)	27(1)	-2(1)	6(1)	2(1)

Table 12. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x10^3) for **7c**.

	x	y	z	U(eq)	
H(2)	6238	8351	4090	24	
H(6)	1626	7293	31	23	
H(10)	4803	6247	3258	26	
H(12)	8818	6005	6727	29	
H(13)	9314	6737	6801	29	
H(17)	6886	8955	5903	28	
H(18)	7615	9673	6428	32	
H(19)	9946	9850	6926	34	
H(20)	11538	9309	6886	35	
H(21)	10811	8589	6355	30	
H(22A)		1171	8077	-261	35
H(22B)		2551	8362	123	35
H(22C)		1938	8285	1887	35
H(23A)		6941	5036	5679	48
H(23B)		7713	5390	7319	48
H(23C)		8151	5330	5381	48
H(24)	3228	6098	9042	31	

Table 13. Torsion angles [°] for **7c**.

O(1)-C(4)-C(8)-C(7)	5.64(19)
O(1)-C(4)-C(8)-C(9)	-176.32(11)
O(1)-C(5)-C(6)-C(7)	1.2(2)
O(2)-C(7)-C(8)-C(4)	172.10(13)
O(2)-C(7)-C(8)-C(9)	-5.8(2)
O(3)-C(11)-C(12)-C(13)	-179.67(13)
N(1)-N(2)-C(15)-C(3)	0.9(2)
N(1)-N(2)-C(15)-C(14)	-178.35(12)
N(1)-C(1)-C(2)-C(3)	1.6(2)
N(1)-C(1)-C(16)-C(17)	-154.62(13)
N(1)-C(1)-C(16)-C(21)	26.02(18)
N(2)-N(1)-C(1)-C(2)	-1.8(2)
N(2)-N(1)-C(1)-C(16)	179.43(12)
C(1)-N(1)-N(2)-C(15)	0.5(2)
C(1)-C(2)-C(3)-C(4)	-177.89(12)
C(1)-C(2)-C(3)-C(15)	-0.24(19)
C(1)-C(16)-C(17)-C(18)	-179.39(13)
C(1)-C(16)-C(21)-C(20)	179.44(13)
C(2)-C(1)-C(16)-C(17)	26.7(2)
C(2)-C(1)-C(16)-C(21)	-152.71(13)
C(2)-C(3)-C(4)-O(1)	-1.19(18)
C(2)-C(3)-C(4)-C(8)	177.70(13)
C(2)-C(3)-C(15)-N(2)	-0.99(19)
C(2)-C(3)-C(15)-C(14)	178.20(12)
C(3)-C(4)-C(8)-C(7)	-173.11(12)
C(3)-C(4)-C(8)-C(9)	4.93(19)
C(4)-O(1)-C(5)-C(6)	-2.86(18)
C(4)-O(1)-C(5)-C(22)	177.02(11)
C(4)-C(3)-C(15)-N(2)	176.79(12)
C(4)-C(3)-C(15)-C(14)	-4.01(18)
C(4)-C(8)-C(9)-C(10)	172.31(12)
C(4)-C(8)-C(9)-C(14)	-5.98(19)
C(5)-O(1)-C(4)-C(3)	178.10(11)
C(5)-O(1)-C(4)-C(8)	-0.77(19)
C(5)-C(6)-C(7)-O(2)	-175.23(13)
C(5)-C(6)-C(7)-C(8)	3.66(19)
C(6)-C(7)-C(8)-C(4)	-6.75(17)
C(6)-C(7)-C(8)-C(9)	175.34(12)
C(7)-C(8)-C(9)-C(10)	-9.8(2)
C(7)-C(8)-C(9)-C(14)	171.90(12)
C(8)-C(9)-C(10)-C(11)	-178.71(13)
C(8)-C(9)-C(14)-C(13)	179.53(12)
C(8)-C(9)-C(14)-C(15)	2.19(19)
C(9)-C(10)-C(11)-O(3)	179.79(12)
C(9)-C(10)-C(11)-C(12)	-0.6(2)
C(9)-C(14)-C(15)-N(2)	-177.93(12)
C(9)-C(14)-C(15)-C(3)	2.85(19)
C(10)-C(9)-C(14)-C(13)	1.18(19)
C(10)-C(9)-C(14)-C(15)	-176.15(12)
C(10)-C(11)-C(12)-C(13)	0.7(2)
C(11)-C(12)-C(13)-C(14)	0.1(2)
C(12)-C(13)-C(14)-C(9)	-1.1(2)

C(12)-C(13)-C(14)-C(15)	176.25(13)
C(13)-C(14)-C(15)-N(2)	4.77(19)
C(13)-C(14)-C(15)-C(3)	-174.45(12)
C(14)-C(9)-C(10)-C(11)	-0.4(2)
C(15)-C(3)-C(4)-O(1)	-178.85(11)
C(15)-C(3)-C(4)-C(8)	0.04(19)
C(16)-C(1)-C(2)-C(3)	-179.71(12)
C(16)-C(17)-C(18)-C(19)	-0.1(2)
C(17)-C(16)-C(21)-C(20)	0.1(2)
C(17)-C(18)-C(19)-C(20)	0.1(2)
C(18)-C(19)-C(20)-C(21)	-0.1(2)
C(19)-C(20)-C(21)-C(16)	0.0(2)
C(21)-C(16)-C(17)-C(18)	0.0(2)
C(22)-C(5)-C(6)-C(7)	-178.70(13)
C(23)-O(3)-C(11)-C(10)	-179.35(13)
C(23)-O(3)-C(11)-C(12)	1.0(2)

Symmetry transformations used to generate equivalent atoms: