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# Synthetic protocol for the preparation of new ([2,2′:6′,2′′-terpyridin]-4′-yl)naphthalene derivatives

**Eugenii N. Shepelenko, Vitaly A. Podshibyakin, Oleg P. Demidov, Konstantin E. Shepelenko and Victor M. Chernyshev**

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## General information

$^{1}H$ and $^{13}C$ NMR spectra were recorded at 20 °C on a Bruker Avance Neo 300 (300 and 75 MHz, respectively) using DMSO-$d_6$ as solvent. Chemical shifts of nuclei $^{1}H$ (δ , ppm) and $^{13}C$ were measured relatively to the residual signals of the deuteron solvents (δ = 2.50 ppm for protons and 39.52 ppm for carbon nuclei). Mass spectrum of compounds **2a,b** and **3a,b** were recorded on a Bruker maXis Q-TOF instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. The measurements were performed in a positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: –500 V) with a scan range of *m/z* 50 – 1500. External calibration of the mass spectrometer was achieved using a low-concentration tuning mix solution (Agilent Technologies). Direct syringe injection was applied for the analysed solutions at a flow rate 3 μL $min^{-1}$. Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L $min^{-1}$). The dry temperature was established at 250 °C. Melting points were determined on a Fisher-Johns Melting Point Apparatus.

## Experimental

**General procedures for the synthesis of compounds 2a,b.**

a) In a 50 mL round bottom flask 2.56 mmol of either 4'-(4-methoxynaphthalen-1-yl)-2,2':6',2"-terpyridine or 4'-(6-methoxynaphthalen-2-yl)-2,2':6',2"-terpyridine was fused with 26 mmol pyridine hydrochloride, gradually increasing the temperature from 140 °C to 210 °C for 6 hours. The reaction mass was cooled and dissolved with 5% solution of $Na_2CO_3$. The precipitate was filtered off, washed with water and recrystallized from $CH_3CN$ – $C_2H_5OH$ in ratio of 1:1.

b) In 50 mL round bottom flask 2.56 mmol of either 4'-(4-methoxynaphthalen-1-yl)-2,2':6',2"-terpyridine or 4'-(6-methoxynaphthalen-2-yl)-2,2':6',2"-terpyridine was dissolved in 20 mL of $CH_2Cl_2$. The reaction mixture was cooled with an ice bath and 5 mmol of $BBr_3$ was added. After stirring for 30 min, the temperature was brought to ambient, and the solvent was removed under reduced pressure. The resulting precipitate was recrystallized from $CH_3CN$ – $C_2H_5OH$ in ratio of 1:1.

c) In 50 mL round bottom flask 2.56 mmol of either 4'-(4-methoxynaphthalen-1-yl)-2,2':6',2"-terpyridine or 4'-(6-methoxynaphthalen-2-yl)-2,2':6',2"-terpyridine, 20 mL of AcOH and 3 mL 48% HBr were refluxed for 4 h. The mixture was then poured into water and the pH was adjusted to neutral using $Na_2CO_3$. The precipitate was filtered off, washed with water and recrystallized from $CH_3CN$ – $C_2H_5OH$ in ratio of 1:1.

**4-([2,2':6',2''-Terpyridin]-4'-yl)naphthalen-1-ol (2a).** Colorless crystals, m.p. 253-255 °C. Method *a* yield 0.70 g (73%). Method *b* yield 0.80 g (83%). Method *c* yield 0.89 g (93%). $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ: 7.05 (d, 1H, HAr, J = 7.8 Hz), 7.55 (m, 5H, HAr), 7.92 (m, 1H, HAr), 8.06 (m, 2H, HAr), 8.30 (m, 1H, HAr), 8.54 (s, 2H, HAr), 8.73 (m, 4H, HAr), 10.56 (s, 1H, OH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 108.41, 121.42, 122.09, 123.24, 124.73, 124.97, 125.26, 125.45, 127.72, 128.06, 128.58, 131.75, 137.96, 149.87, 150.86, 154.58, 155.52, 155.60. ESI-MS(TOF) *m/z:* $[M+H]^+$ Calcd for $[C_{25}H_{18}N_3O]^+$ *m/z:* 376.1444, found 376.1447.

**6-([2,2':6',2''-Terpyridin]-4'-yl)naphthalen-2-ol (2b).** Colorless crystals, m.p. 235-237 °C. Method *a* yield 0.66 g (69%). Method *b* yield 0.69 g (72%). Method *c* yield 0.75 g (78%). $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ: 7.20 (m, 2H, HAr), 7.54 (m, 2H, HAr), 7.92 (m, 2H, HAr), 8.05 (m, 3H, HAr), 8.42 (s, 1H, HAr), 8.69 (m, 2H, HAr), 8.79 (m, 2H, HAr), 8.83 (s, 2H, HAr), 9.99 (s, 1H, OH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 109.03, 118.22, 119.92, 121.43, 124.98, 126.66, 127.74, 128.36, 130.98, 131.89, 135.54, 137.93, 149.81, 150.05, 155.56, 156.13, 156.93. ESI-MS(TOF) *m/z:* $[M+H]^+$ Calcd for $[C_{25}H_{18}N_3O]^+$ *m/z:* 376.1444, found 376.1451.

**General procedures for the synthesis of compounds 3a-b.**

In 100 mL round bottom flask 3.32 mmol of **2a** or **2b** and 33.5 mmol of ethyl *N*-phenylformimidate PhN=CHOEt were gradually heated from 140 °C to 180 °C over 6 hours. The mixture was then cooled, and 50 mL of $C_2H_5OH$ was added. The resulting precipitate was filtered off, washed with $C_2H_5OH$ and recrystallized from $C_2H_5OH$ – DMF in ratio of 1:1.

**4-([2,2':6',2''-Terpyridin]-4'-yl)-2-(phenyliminomethyl)naphthalen-1-ol (3a).** Yield 2.4 g (94%), orange solid, m.p. 170-171 °C.

$^{1}$H NMR (300 MHz, DMSO-$d_6$) δ: 7.28 (tr, 1H, HAr, J = 7.2 Hz), 7.57 (m, 9H, HAr), 7.82 (m, 1H, HAr), 8.05 (m, 2H, HAr), 8.49 (m, 1H, HAr), 8.59 (s, 2H, HAr), 8.72 (m, 4H, HAr), 9.11 (s, 1H, NH), 14.80 (s, 1H, OH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 110.19, 119.45, 121.40, 121.51, 124.58, 125.00, 126.23, 126.33, 126.88, 130.06, 130.37, 131.18, 131.84, 137.96, 140.66, 149.84, 150.27, 155.48, 155.74, 156.74, 176.54. ESI-MS(TOF) *m/z:* $[M+H]^+$ Calcd for $[C_{32}H_{23}N_4O]^+$ *m/z:* 479.1866, found 479.1870.

**6-([2,2':6',2''-Terpyridin]-4'-yl)-1-(phenyliminomethyl)naphthalen-2-ol (3b).** Yield 2.35 g (92%), orange solid, m.p. 172-173 °C. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ: 7.02 (d, 1H, HAr, J = 9 Hz), 7.32 (tr, 1H, HAr, J = 7.2 Hz), 7.52 (m, 4H, HAr), 7.66 (m, 2H, HAr), 8.03 (m, 4H, HAr), 8.12 (m, 1H, HAr), 8.36 (m, 1H, HAr), 8.67 (m, 2H, HAr), 8.79 (m, 4H, HAr), 9.64 (s, 1H, NH), 12.04 (s, 1H, OH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 108.62, 118.17, 120.78,

121.50, 124.18, 125.01, 126.67, 127.07, 127.33, 130.15, 132.52, 134.49, 138.01, 138.28, 143.33, 149.46, 149.72, 155.23, 155.44, 156.03, 173.53. ESI-MS(TOF) *m/z:* $[M+H]^+$ Calcd for $[C_{32}H_{23}N_4O]^+$ *m/z:* 479.1866, found 479.1872.

**General procedures for the synthesis of compounds 4a-b.**

1) In a 100 mL round bottom flask 3.32 mmol of either **3a** or **3b** and 62.5 mmol of NaOH in 50 mL of water were refluxed for 2 hours. The reaction mixture was then cooled and neutralized with AcOH. The resulting precipitate was filtered off, washed with $C_2H_5OH$ and recrystallized from acetone.

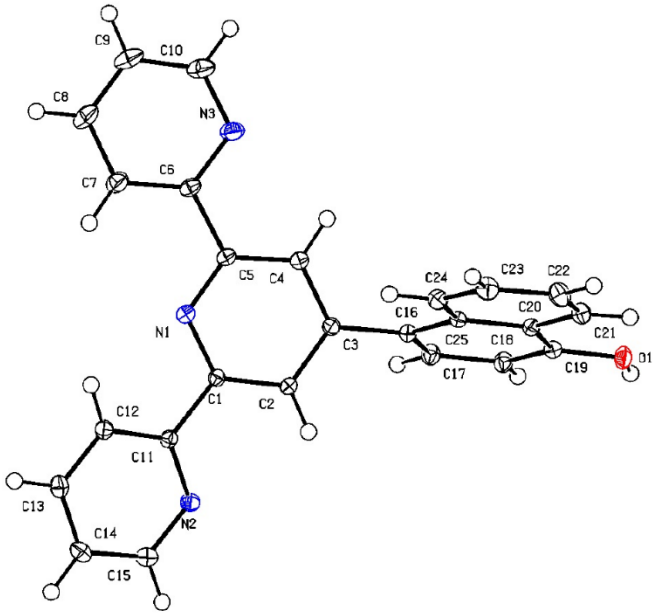
2) In a 100 mL round bottom flask 3.32 mmol of either **2a** or **2b** was dissolved in 10 mL of TFA under argon atmosphere, and 6.64 mmol hexamethylenetetramine was added in portions. The solution was stirred at 70 °C for 72 h and then at 100 °C for another 4 h. Subsequently, HCl (10% aq., 4 mL) was added, and the reaction mixture was kept at 100 °C for 1 h. The suspension was cooled to room temperature and left overnight. The mixture was extracted with $CH_2Cl_2$ (3×20 mL), the organic layer was separated, dried over anhydrous $Na_2SO_4$, the solvent was removed on rotary evaporator, and the residue was recrystallized from acetone.

**4-([2,2':6',2''-Terpyridin]-4'-yl)-1-hydroxy-2-naphthaldehyde (4a).** Pale yellow solid, m.p. 140-142 °C. Method 1 yield 0.48 g (35.6%). Method 2 yield 0.55 g (41%). $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 7.52 (m, 2H, HAr), 7.75 (m, 2H, HAr), 7.93 (m, 2H, HAr), 8.06 (m, 2H, HAr), 8.53 (m, 3H, HAr), 8.72 (m, 4H, HAr), 10.29 (s, 1H, CHO), 12.71 (s, 1H, OH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 108.22, 115.61, 119.97, 121.46, 121.92, 124.82, 125.08, 127.09, 127.73, 128.89, 131.72, 134.63, 138.01, 140.16, 149.65, 149.88, 155.34, 155.81, 196.09. ESI-MS(TOF) *m/z:* $[M+H]^+$ Calcd for $[C_{26}H_{18}N_3O_2]^+$ *m/z:* 404.1394, found 404.1388

**6-([2,2':6',2''-Terpyridin]-4'-yl)-2-hydroxy-1-naphthaldehyde (4b).** Pale yellow solid, m.p. 141-143 °C. Method 1 yield 0.39 g (28.8%). Method 2 yield 0.18 g (13%). $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 7.32 (d, 1H, HAr, J = 9 Hz), 7.54 (m, 2H, HAr), 8.05 (m, 2H, HAr), 8.15 (m, 1H, HAr), 8.37 (d, 1H, HAr, J = 9 Hz),8.51 (m, 1H, HAr), 8.68 (m, 2H, HAr), 8.78 (m, 2H, HAr), 8.82 (s, 2H, HAr), 9.12 (d, 1H, HAr), 10.83 (s, 1H, OH), 12.04 (s, 1H, OH). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 113.02, 118.31, 120.01, 121.47, 124.16, 125.02, 127.60, 128.00, 128.42, 132.52, 133.34, 137.95, 139.50, 149.31, 149.80, 155.45, 156.18, 165.07, 192.91. ESI-MS(TOF) *m/z:* $[M+H]^+$ Calcd for $[C_{26}H_{18}N_3O_2]^+$ *m/z:* 404.1394, found 404.1400

## X-Ray diffracton study

**Table S1** Crystal data and structure refinement for **2a**




| | |
|---|---|
| CCDC Number | 2371441 |
| Empirical formula | $C_{25}H_{17}N_3O$ |
| Formula weight | 375.41 |
| Temperature/K | 100.00(10) |
| Crystal system | orthorhombic |
| Space group | $Pna2_1$ |
| a/Å | 8.7581(3) |
| b/Å | 16.1319(4) |
| c/Å | 12.8091(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1809.73(10) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.378 |
| μ/mm$^{-1}$ | 0.086 |
| F(000) | 784.0 |
| Crystal size/mm$^3$ | 0.396 × 0.221 × 0.198 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.05 to 67.918 |
| Index ranges | $-13 \le h \le 12$, $-24 \le k \le 24$, $-19 \le l \le 19$ |
| Reflections collected | 24971 |
| Independent reflections | 6431 [$R_{int}$ = 0.0432, $R_{sigma}$ = 0.0395] |
| Data/restraints/parameters | 6431/1/263 |
| Goodness-of-fit on $F^2$ | 1.072 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0462, $wR_2$ = 0.1165 |
| Final R indexes [all data] | $R_1$ = 0.0521, $wR_2$ = 0.1217 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.42/-0.23 |
| Flack parameter | 0.1(6) |

**Table S2** Bond Lengths for **2a**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O1 | C19 | 1.356(2) | C25 | C24 | 1.423(3) |
| N2 | C11 | 1.352(2) | C14 | C13 | 1.389(3) |
| N2 | C15 | 1.339(3) | C1 | C2 | 1.398(2) |
| N1 | C5 | 1.337(2) | C19 | C18 | 1.377(3) |
| N1 | C1 | 1.349(2) | C3 | C16 | 1.484(2) |
| N3 | C6 | 1.342(3) | C3 | C4 | 1.397(2) |
| N3 | C10 | 1.341(2) | C3 | C2 | 1.394(3) |
| C11 | C1 | 1.483(3) | C16 | C17 | 1.377(2) |
| C11 | C12 | 1.400(2) | C12 | C13 | 1.382(3) |
| C5 | C6 | 1.490(2) | C23 | C24 | 1.372(3) |
| C5 | C4 | 1.399(2) | C23 | C22 | 1.417(3) |
| C20 | C25 | 1.428(2) | C17 | C18 | 1.418(3) |
| C20 | C19 | 1.432(2) | C22 | C21 | 1.376(3) |
| C20 | C21 | 1.416(3) | C7 | C8 | 1.394(3) |
| C15 | C14 | 1.393(3) | C9 | C10 | 1.386(3) |
| C6 | C7 | 1.398(3) | C9 | C8 | 1.386(3) |
| C25 | C16 | 1.427(2) | | | |

**Table S3** Bond Angles for **2a**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C15 | N2 | C11 | 117.41(15) | O1 | C19 | C20 | 116.19(16) |
| C5 | N1 | C1 | 117.96(15) | O1 | C19 | C18 | 123.84(16) |
| C10 | N3 | C6 | 117.43(18) | C18 | C19 | C20 | 119.97(16) |
| N2 | C11 | C1 | 118.37(14) | C4 | C3 | C16 | 121.18(16) |
| N2 | C11 | C12 | 122.27(17) | C2 | C3 | C16 | 120.57(15) |
| C12 | C11 | C1 | 119.35(15) | C2 | C3 | C4 | 118.22(16) |
| N1 | C5 | C6 | 116.97(15) | C25 | C16 | C3 | 121.08(15) |
| N1 | C5 | C4 | 123.11(15) | C17 | C16 | C25 | 119.35(16) |

**Table S3** Bond Angles for **2a**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C4 | C5 | C6 | 119.82(16) | C17 | C16 | C3 | 119.56(16) |
| C25 | C20 | C19 | 119.30(16) | C13 | C12 | C11 | 119.24(16) |
| C21 | C20 | C25 | 119.67(16) | C3 | C4 | C5 | 118.84(17) |
| C21 | C20 | C19 | 121.03(16) | C24 | C23 | C22 | 120.37(18) |
| N2 | C15 | C14 | 123.88(17) | C23 | C24 | C25 | 121.10(17) |
| N3 | C6 | C5 | 115.72(16) | C3 | C2 | C1 | 119.06(15) |
| N3 | C6 | C7 | 122.89(16) | C12 | C13 | C14 | 118.97(17) |
| C7 | C6 | C5 | 121.26(17) | C16 | C17 | C18 | 121.60(17) |
| C16 | C25 | C20 | 119.56(16) | C19 | C18 | C17 | 120.21(17) |
| C24 | C25 | C20 | 118.15(17) | C21 | C22 | C23 | 120.10(18) |
| C24 | C25 | C16 | 122.26(16) | C8 | C7 | C6 | 118.65(19) |
| C13 | C14 | C15 | 118.17(18) | C22 | C21 | C20 | 120.57(17) |
| N1 | C1 | C11 | 115.29(14) | C10 | C9 | C8 | 118.74(18) |
| N1 | C1 | C2 | 122.71(16) | N3 | C10 | C9 | 123.7(2) |
| C2 | C1 | C11 | 122.00(14) | C9 | C8 | C7 | 118.6(2) |

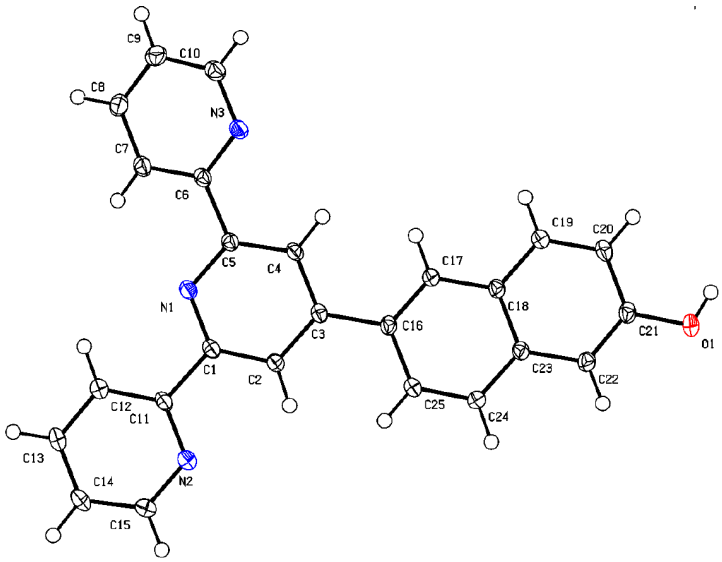
**Table S4** Torsion Angles for **2a**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C19 | C18 | C17 | 178.08(18) | C1 | C11 | C12 | C13 | 179.23(17) |
| N2 | C11 | C1 | N1 | 160.68(16) | C19 | C20 | C25 | C16 | -0.6(2) |
| N2 | C11 | C1 | C2 | -20.0(3) | C19 | C20 | C25 | C24 | 177.55(16) |
| N2 | C11 | C12 | C13 | -1.5(3) | C19 | C20 | C21 | C22 | -177.44(18) |
| N2 | C15 | C14 | C13 | -1.8(3) | C3 | C16 | C17 | C18 | -179.47(17) |
| N1 | C5 | C6 | N3 | -176.42(17) | C16 | C25 | C24 | C23 | 178.12(18) |
| N1 | C5 | C6 | C7 | -0.4(3) | C16 | C3 | C4 | C5 | 176.07(16) |
| N1 | C5 | C4 | C3 | 3.8(3) | C16 | C3 | C2 | C1 | -178.95(17) |
| N1 | C1 | C2 | C3 | 2.3(3) | C16 | C17 | C18 | C19 | 1.1(3) |
| N3 | C6 | C7 | C8 | 2.1(3) | C12 | C11 | C1 | N1 | -20.1(2) |
| C11 | N2 | C15 | C14 | 2.3(3) | C12 | C11 | C1 | C2 | 159.22(18) |

**Table S4** Torsion Angles for **2a**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C11 | C1 | C2 | C3 | -176.88(17) | C4 | C5 | C6 | N3 | 0.1(3) |
| C11 | C12 | C13 | C14 | 1.9(3) | C4 | C5 | C6 | C7 | 176.19(19) |
| C5 | N1 | C1 | C11 | 178.69(15) | C4 | C3 | C16 | C25 | 73.4(2) |
| C5 | N1 | C1 | C2 | -0.6(3) | C4 | C3 | C16 | C17 | -108.0(2) |
| C5 | C6 | C7 | C8 | -173.64(18) | C4 | C3 | C2 | C1 | -1.0(3) |
| C20 | C25 | C16 | C3 | 179.16(16) | C23 | C22 | C21 | C20 | -0.2(3) |
| C20 | C25 | C16 | C17 | 0.5(3) | C24 | C25 | C16 | C3 | 1.1(3) |
| C20 | C25 | C24 | C23 | 0.1(3) | C24 | C25 | C16 | C17 | -177.53(17) |
| C20 | C19 | C18 | C17 | -1.2(3) | C24 | C23 | C22 | C21 | -1.6(3) |
| C15 | N2 | C11 | C1 | 178.70(16) | C2 | C3 | C16 | C25 | -108.8(2) |
| C15 | N2 | C11 | C12 | -0.5(3) | C2 | C3 | C16 | C17 | 69.9(2) |
| C15 | C14 | C13 | C12 | -0.4(3) | C2 | C3 | C4 | C5 | -1.9(3) |
| C6 | N3 | C10 | C9 | 0.6(3) | C22 | C23 | C24 | C25 | 1.7(3) |
| C6 | C5 | C4 | C3 | -172.56(17) | C21 | C20 | C25 | C16 | -179.99(17) |
| C6 | C7 | C8 | C9 | -0.1(3) | C21 | C20 | C25 | C24 | -1.9(3) |
| C25 | C20 | C19 | O1 | -178.42(16) | C21 | C20 | C19 | O1 | 1.0(3) |
| C25 | C20 | C19 | C18 | 0.9(3) | C21 | C20 | C19 | C18 | -179.66(17) |
| C25 | C20 | C21 | C22 | 2.0(3) | C10 | N3 | C6 | C5 | 173.65(18) |
| C25 | C16 | C17 | C18 | -0.8(3) | C10 | N3 | C6 | C7 | -2.3(3) |
| C1 | N1 | C5 | C6 | 173.91(16) | C10 | C9 | C8 | C7 | -1.5(3) |
| C1 | N1 | C5 | C4 | -2.5(3) | C8 | C9 | C10 | N3 | 1.4(3) |

**Table S5** Crystal data and structure refinement for **2b**




| | |
|---|---|
| CCDC Number | 2371447 |
| Empirical formula | $C_{25}H_{17}N_3O$ |
| Formula weight | 375.41 |
| Temperature/K | 100.01(11) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 4.8933(2) |
| b/Å | 15.7625(9) |
| c/Å | 23.8086(10) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1836.37(15) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.358 |
| μ/mm$^{-1}$ | 0.085 |
| F(000) | 784.0 |
| Crystal size/mm$^3$ | 0.477 × 0.137 × 0.071 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.168 to 68.094 |
| Index ranges | $-7 \le h \le 7$, $-22 \le k \le 24$, $-35 \le l \le 35$ |
| Reflections collected | 27165 |
| Independent reflections | 7055 [$R_{int}$ = 0.0584, $R_{sigma}$ = 0.0658] |
| Data/restraints/parameters | 7055/0/266 |
| Goodness-of-fit on F$^2$ | 1.038 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0597, $wR_2$ = 0.1287 |
| Final R indexes [all data] | $R_1$ = 0.0811, $wR_2$ = 0.1401 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.37/-0.26 |
| Flack parameter | 0.2(8) |

**Table S6** Bond Lengths for **2b**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O1 | C21 | 1.364(3) | C6 | C7 | 1.393(3) |
| N3 | C6 | 1.356(3) | C11 | C12 | 1.394(3) |
| N3 | C10 | 1.337(3) | C18 | C19 | 1.422(3) |
| N1 | C5 | 1.350(3) | C18 | C17 | 1.415(3) |
| N1 | C1 | 1.338(3) | C16 | C25 | 1.422(3) |
| N2 | C11 | 1.339(3) | C16 | C17 | 1.381(3) |
| N2 | C15 | 1.337(3) | C16 | C3 | 1.484(3) |
| C23 | C18 | 1.418(3) | C4 | C3 | 1.398(3) |
| C23 | C22 | 1.415(3) | C19 | C20 | 1.371(3) |
| C23 | C24 | 1.424(3) | C25 | C24 | 1.374(3) |
| C5 | C6 | 1.480(3) | C7 | C8 | 1.385(3) |
| C5 | C4 | 1.391(3) | C10 | C9 | 1.385(3) |
| C2 | C1 | 1.396(3) | C9 | C8 | 1.389(3) |
| C2 | C3 | 1.399(3) | C12 | C13 | 1.387(3) |
| C1 | C11 | 1.497(3) | C13 | C14 | 1.375(4) |
| C21 | C22 | 1.371(3) | C14 | C15 | 1.382(3) |
| C21 | C20 | 1.414(3) | | | |

**Table S7** Bond Angles for **2b**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C10 | N3 | C6 | 117.96(19) | C17 | C18 | C23 | 119.95(19) |
| C1 | N1 | C5 | 117.22(18) | C17 | C18 | C19 | 121.6(2) |
| C15 | N2 | C11 | 117.5(2) | C25 | C16 | C3 | 121.12(18) |
| C18 | C23 | C24 | 117.82(19) | C17 | C16 | C25 | 117.98(19) |
| C22 | C23 | C18 | 119.59(19) | C17 | C16 | C3 | 120.83(19) |
| C22 | C23 | C24 | 122.6(2) | C5 | C4 | C3 | 120.19(18) |
| N1 | C5 | C6 | 115.56(18) | C21 | C22 | C23 | 120.5(2) |
| N1 | C5 | C4 | 122.83(19) | C20 | C19 | C18 | 121.1(2) |
| C4 | C5 | C6 | 121.60(18) | C24 | C25 | C16 | 121.5(2) |

**Table S7** Bond Angles for **2b**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C1 | C2 | C3 | 119.6(2) | C16 | C17 | C18 | 121.8(2) |
| N1 | C1 | C2 | 123.44(18) | C19 | C20 | C21 | 120.0(2) |
| N1 | C1 | C11 | 116.43(18) | C25 | C24 | C23 | 121.0(2) |
| C2 | C1 | C11 | 120.12(19) | C8 | C7 | C6 | 119.7(2) |
| O1 | C21 | C22 | 118.3(2) | N3 | C10 | C9 | 124.2(2) |
| O1 | C21 | C20 | 121.2(2) | C2 | C3 | C16 | 121.55(19) |
| C22 | C21 | C20 | 120.44(19) | C4 | C3 | C2 | 116.60(19) |
| N3 | C6 | C5 | 117.71(19) | C4 | C3 | C16 | 121.79(18) |
| N3 | C6 | C7 | 121.3(2) | C10 | C9 | C8 | 117.6(2) |
| C7 | C6 | C5 | 121.00(19) | C7 | C8 | C9 | 119.2(2) |
| N2 | C11 | C1 | 116.46(19) | C13 | C12 | C11 | 118.7(2) |
| N2 | C11 | C12 | 122.4(2) | C14 | C13 | C12 | 119.3(2) |
| C12 | C11 | C1 | 121.1(2) | C13 | C14 | C15 | 118.1(2) |
| C23 | C18 | C19 | 118.42(19) | N2 | C15 | C14 | 124.0(2) |

**Table S8** Torsion Angles for **2b**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C21 | C22 | C23 | 179.0(2) | C18 | C19 | C20 | C21 | 0.2(3) |
| O1 | C21 | C20 | C19 | -179.4(2) | C16 | C25 | C24 | C23 | 1.0(3) |
| N3 | C6 | C7 | C8 | 0.8(3) | C4 | C5 | C6 | N3 | -17.9(3) |
| N3 | C10 | C9 | C8 | 0.4(4) | C4 | C5 | C6 | C7 | 160.7(2) |
| N1 | C5 | C6 | N3 | 162.8(2) | C22 | C23 | C18 | C19 | 0.6(3) |
| N1 | C5 | C6 | C7 | -18.5(3) | C22 | C23 | C18 | C17 | -179.5(2) |
| N1 | C5 | C4 | C3 | 1.1(3) | C22 | C23 | C24 | C25 | 178.9(2) |
| N1 | C1 | C11 | N2 | 176.7(2) | C22 | C21 | C20 | C19 | 1.1(3) |
| N1 | C1 | C11 | C12 | -4.0(3) | C19 | C18 | C17 | C16 | 180.0(2) |
| N2 | C11 | C12 | C13 | 1.0(4) | C25 | C16 | C17 | C18 | 1.1(3) |
| C23 | C18 | C19 | C20 | -1.1(3) | C25 | C16 | C3 | C2 | -14.9(3) |
| C23 | C18 | C17 | C16 | 0.2(3) | C25 | C16 | C3 | C4 | 167.9(2) |

**Table S8** Torsion Angles for **2b**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C5 | N1 | C1 | C2 | -1.6(3) | C17 | C18 | C19 | C20 | 179.1(2) |
| C5 | N1 | C1 | C11 | 177.16(19) | C17 | C16 | C25 | C24 | -1.6(3) |
| C5 | C6 | C7 | C8 | -177.8(2) | C17 | C16 | C3 | C2 | 162.1(2) |
| C5 | C4 | C3 | C2 | -3.0(3) | C17 | C16 | C3 | C4 | -15.1(3) |
| C5 | C4 | C3 | C16 | 174.3(2) | C20 | C21 | C22 | C23 | -1.5(3) |
| C2 | C1 | C11 | N2 | -4.5(3) | C24 | C23 | C18 | C19 | 179.3(2) |
| C2 | C1 | C11 | C12 | 174.8(2) | C24 | C23 | C18 | C17 | -0.8(3) |
| C1 | N1 | C5 | C6 | -179.47(19) | C24 | C23 | C22 | C21 | -178.0(2) |
| C1 | N1 | C5 | C4 | 1.3(3) | C10 | N3 | C6 | C5 | 177.32(18) |
| C1 | C2 | C3 | C16 | -174.6(2) | C10 | N3 | C6 | C7 | -1.3(3) |
| C1 | C2 | C3 | C4 | 2.7(3) | C10 | C9 | C8 | C7 | -1.0(3) |
| C1 | C11 | C12 | C13 | -178.3(2) | C3 | C2 | C1 | N1 | -0.4(3) |
| C6 | N3 | C10 | C9 | 0.7(3) | C3 | C2 | C1 | C11 | -179.1(2) |
| C6 | C5 | C4 | C3 | -178.2(2) | C3 | C16 | C25 | C24 | 175.4(2) |
| C6 | C7 | C8 | C9 | 0.4(3) | C3 | C16 | C17 | C18 | -176.0(2) |
| C11 | N2 | C15 | C14 | 0.2(5) | C12 | C13 | C14 | C15 | -1.5(4) |
| C11 | C12 | C13 | C14 | 0.5(4) | C13 | C14 | C15 | N2 | 1.2(5) |
| C18 | C23 | C22 | C21 | 0.7(3) | C15 | N2 | C11 | C1 | 178.0(3) |
| C18 | C23 | C24 | C25 | 0.3(3) | C15 | N2 | C11 | C12 | -1.3(4) |

# NMR-spectra of compounds 2-4

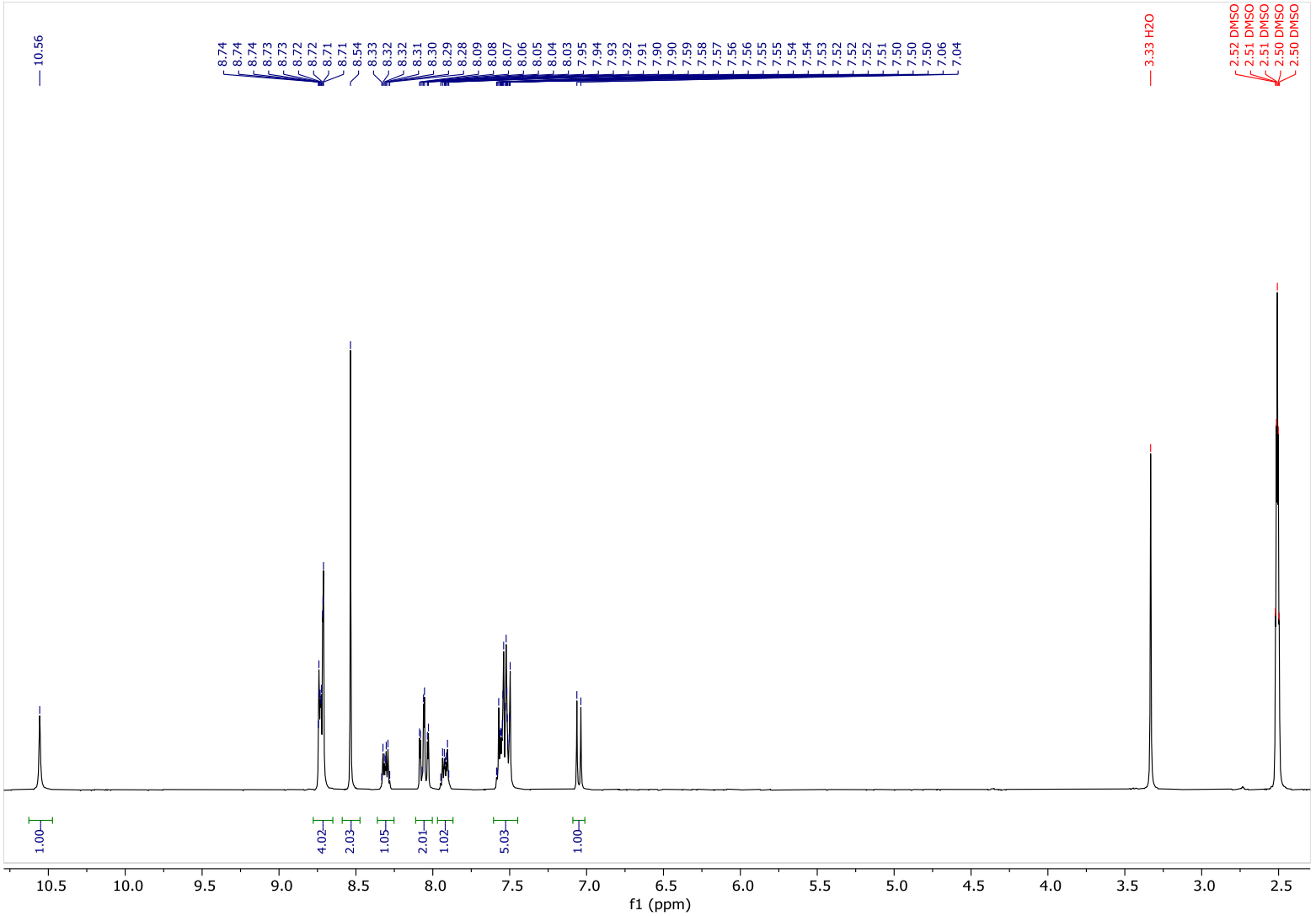



Figure S1 $^{1}$H NMR spectrum of compound **2a** recorded at 300 MHz in DMSO-$d_6$.

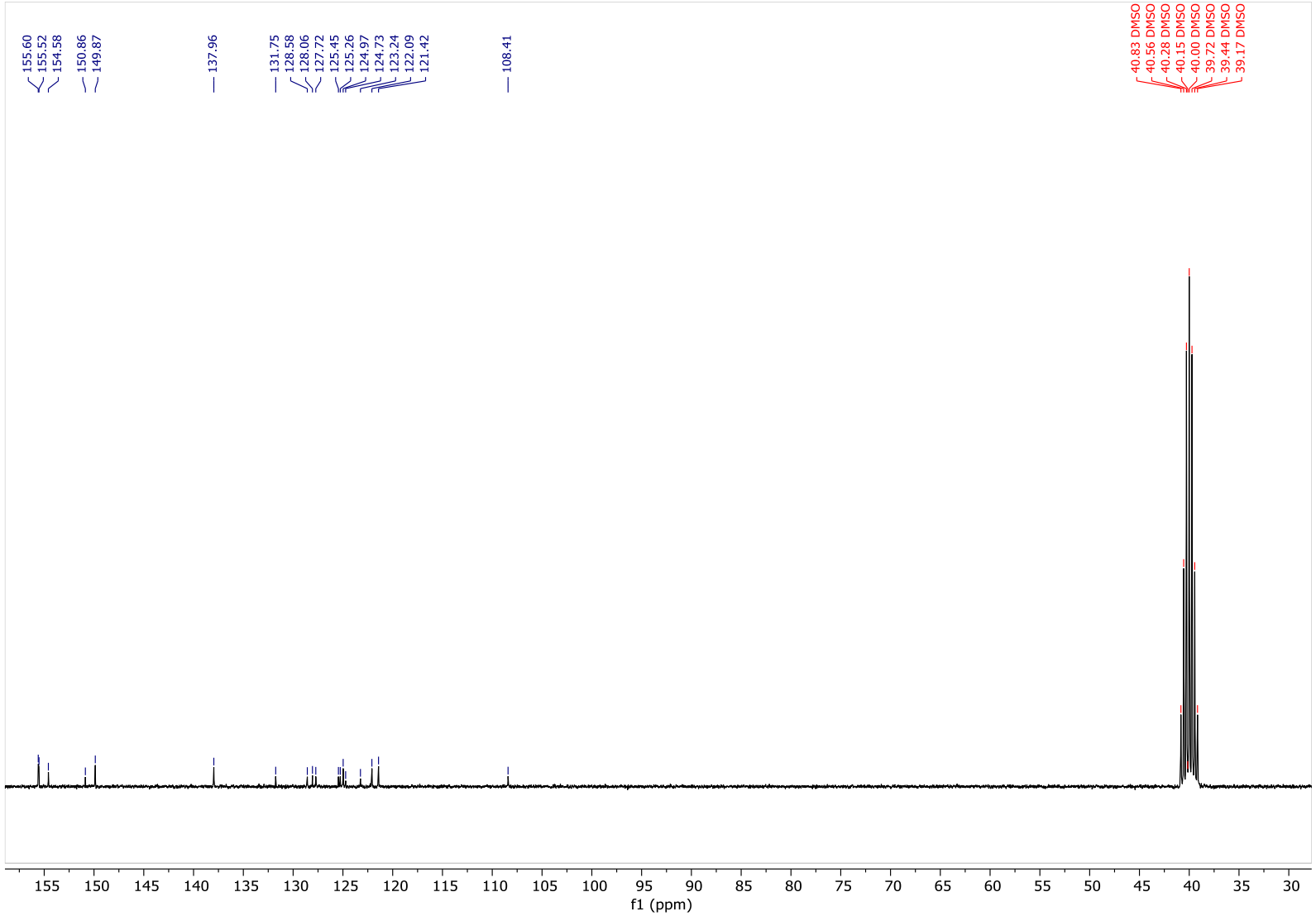



Figure S2 $^{13}C$ NMR spectrum of compound **2a** recorded at 75 MHz in DMSO-$d_6$.

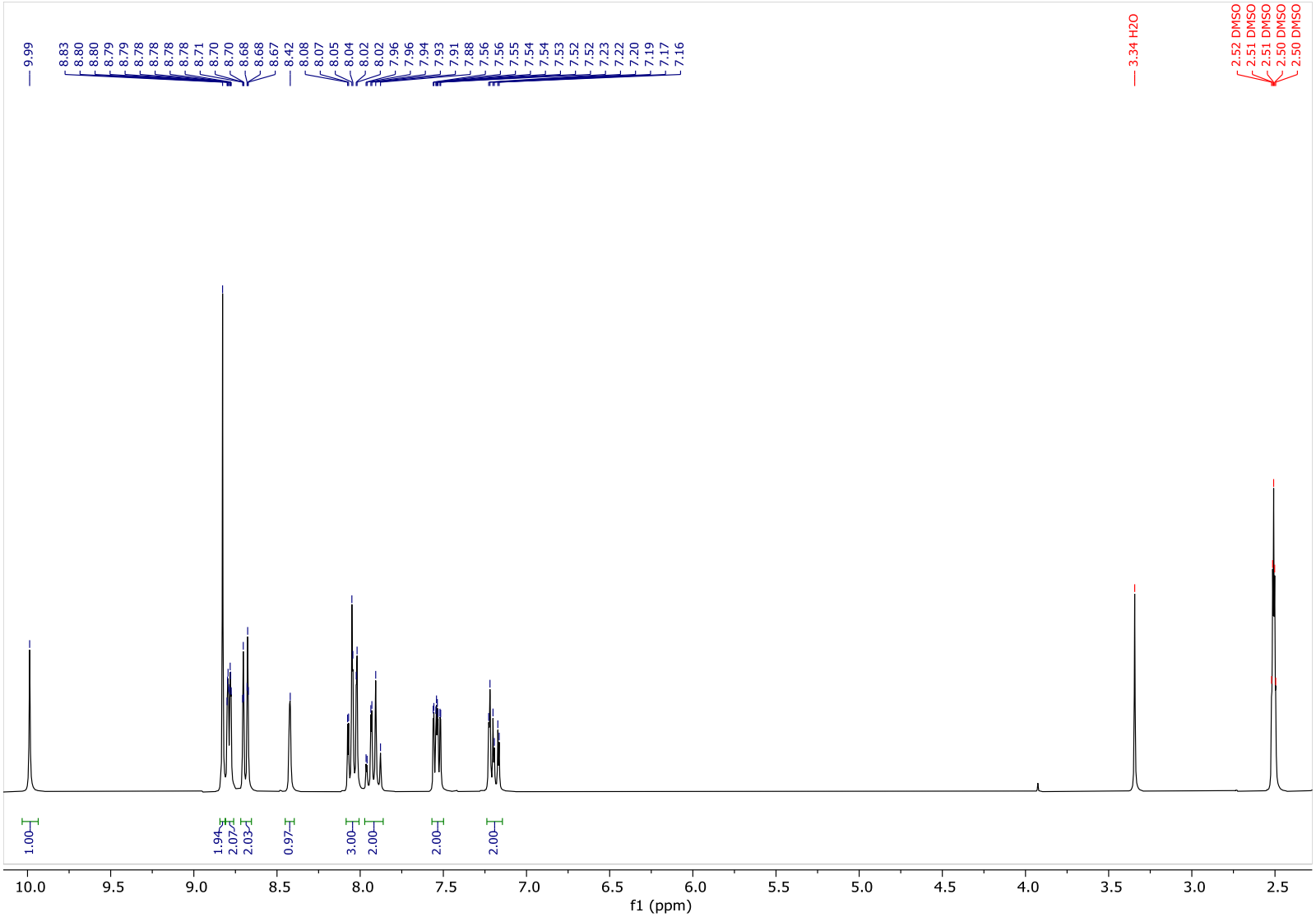



Figure S3 $^{1}$H NMR spectrum of compound **2b** recorded at 300 MHz in DMSO-$d_6$.

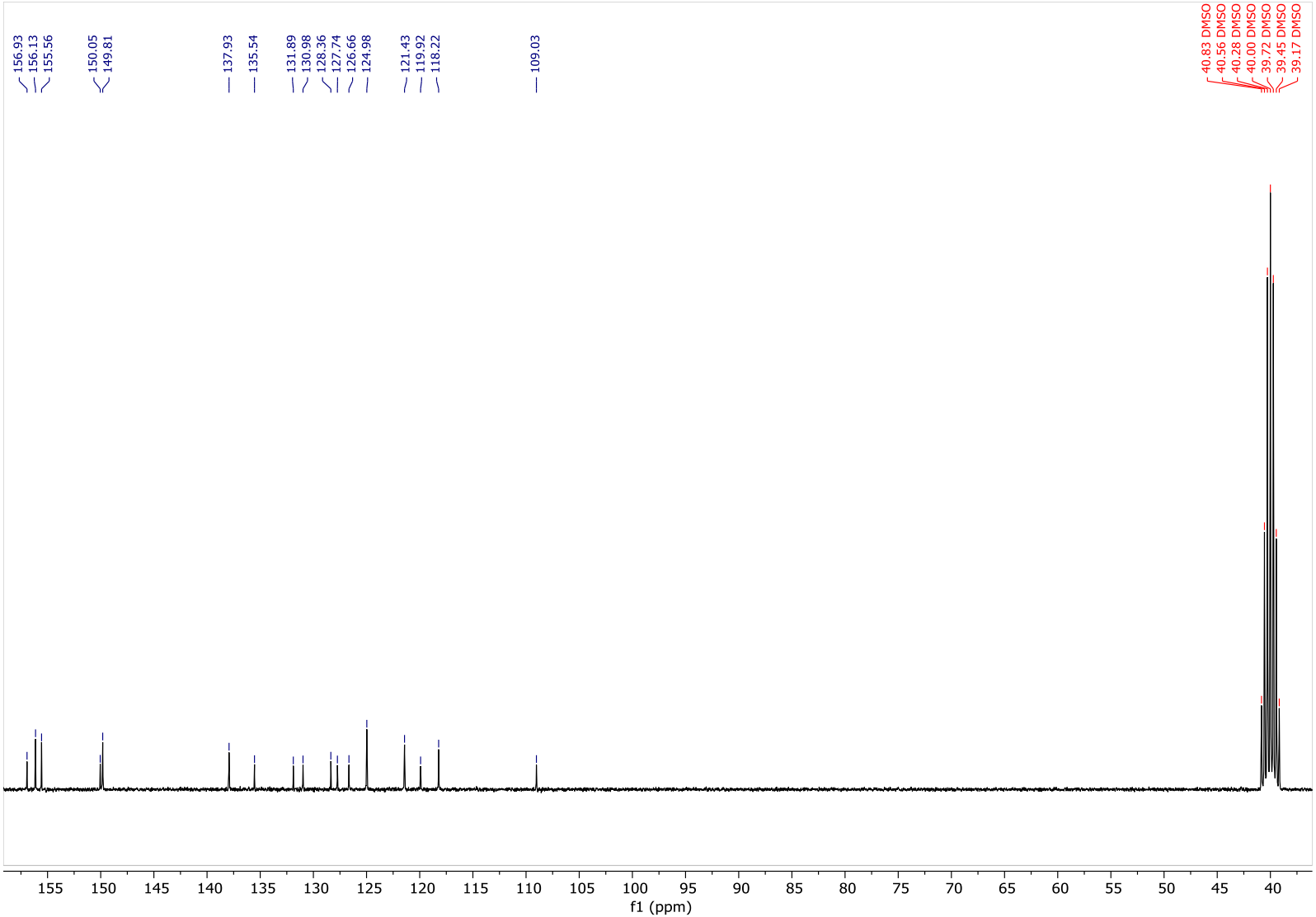



Figure S4 $^{13}C$ NMR spectrum of compound **2b** recorded at 75 MHz in DMSO-$d_6$.

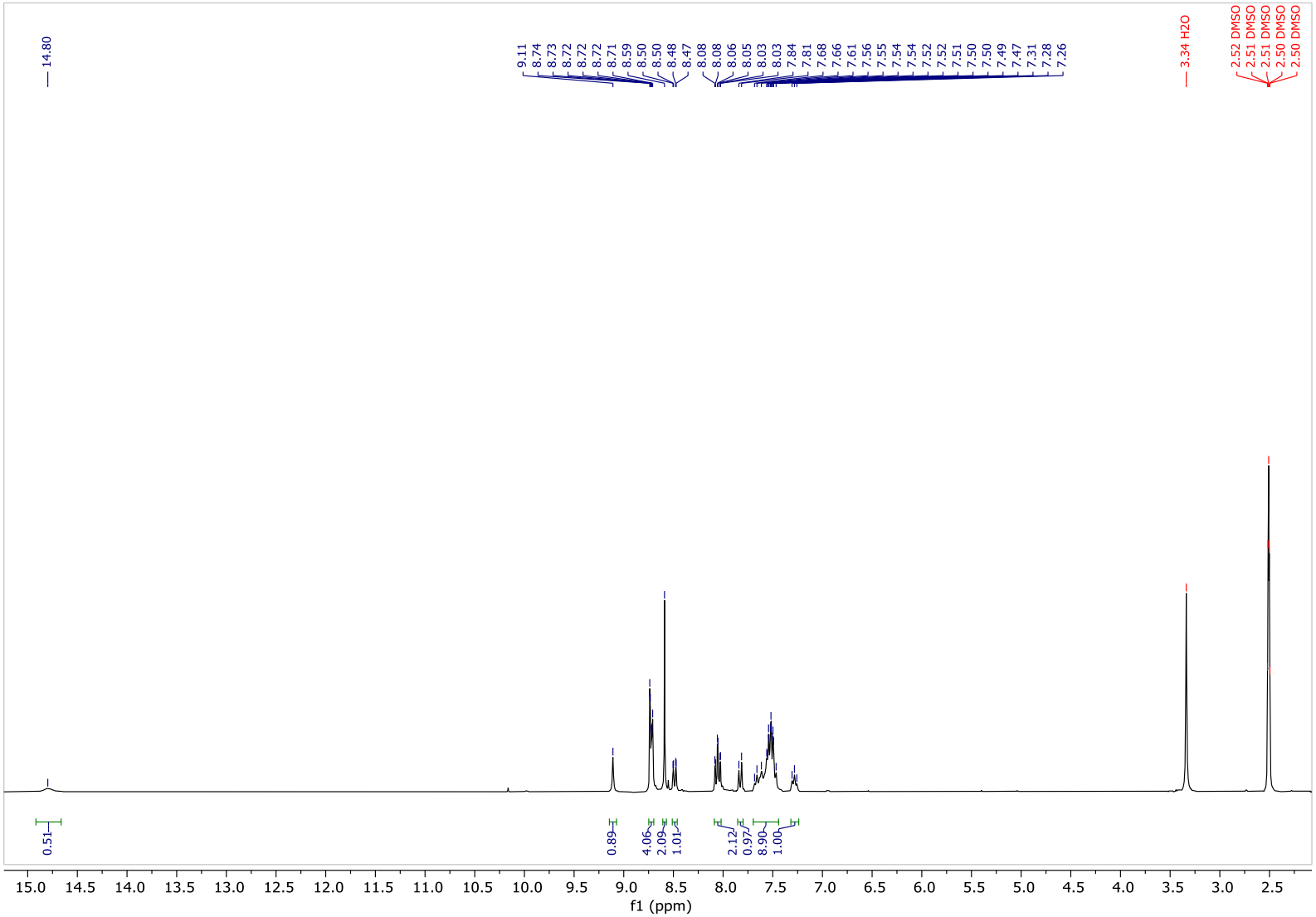



Figure S5 $^{1}$H NMR spectrum of compound **3a** recorded at 300 MHz in DMSO-$d_6$.

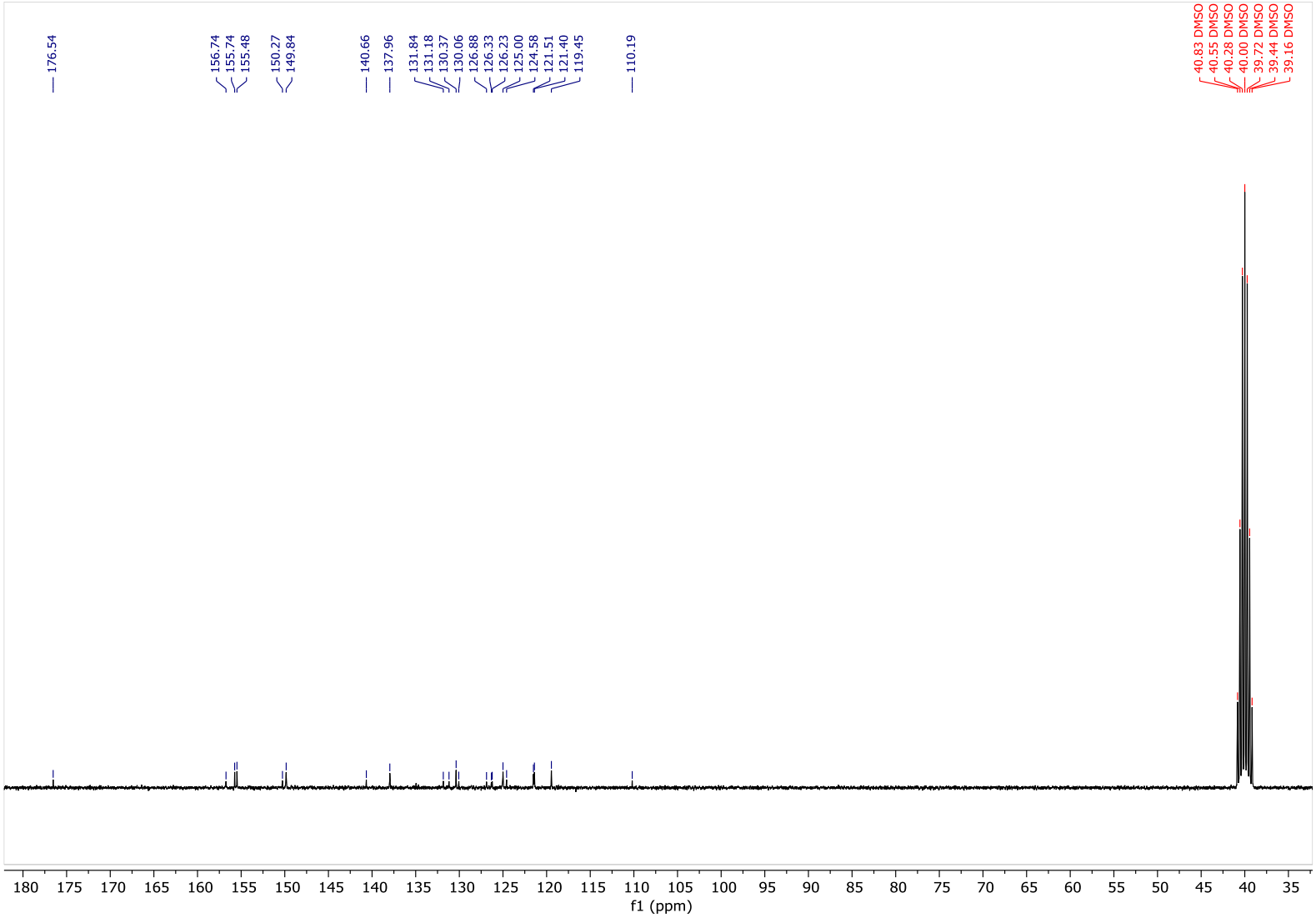



Figure S6 $^{13}C$ NMR spectrum of compound **3a** recorded at 75 MHz in DMSO-$d_6$.

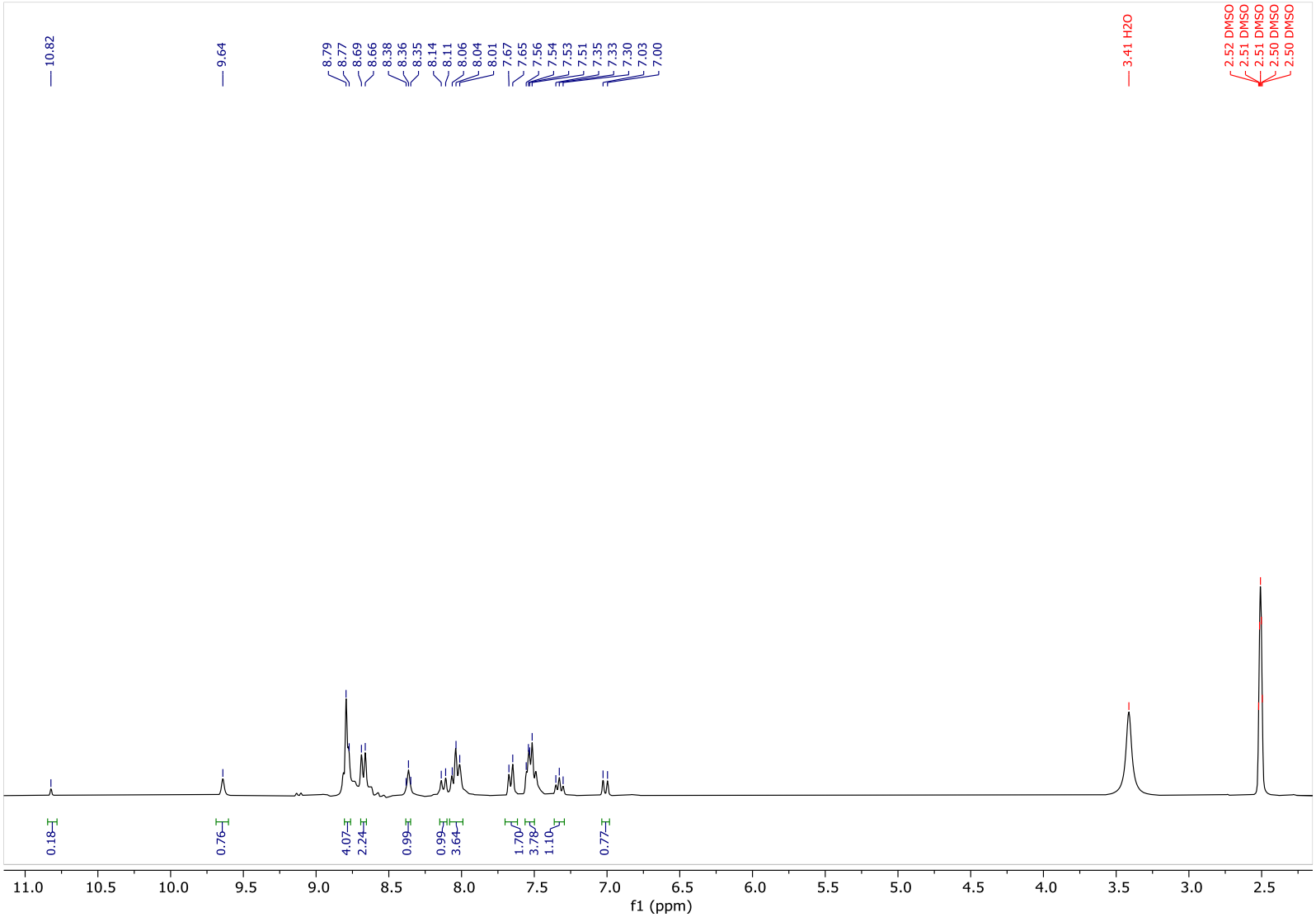



Figure S7 $^{1}$H NMR spectrum of compound **3b** recorded at 300 MHz in DMSO-$d_6$.

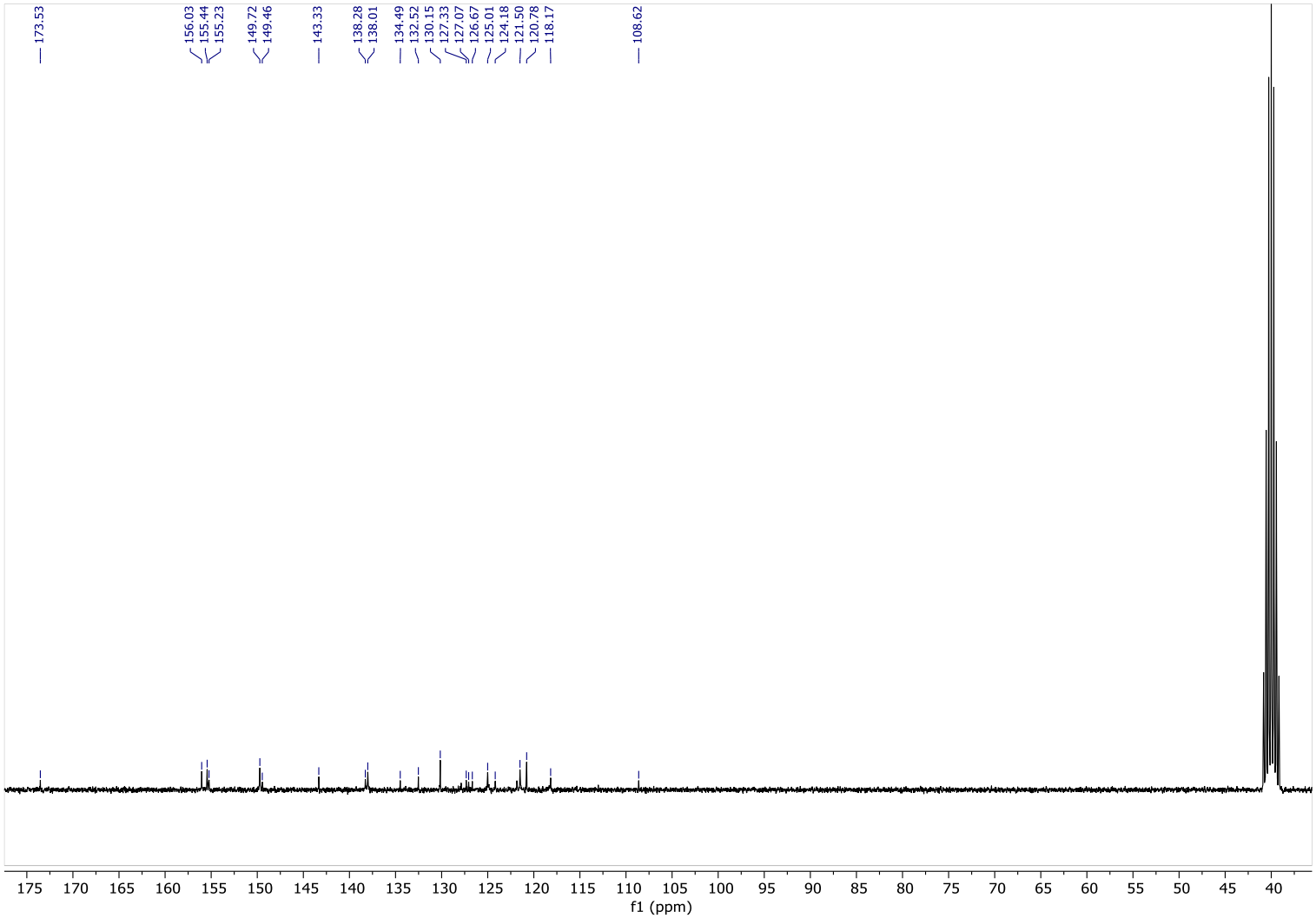



Figure S8 $^{13}C$ NMR spectrum of compound **3b** recorded at 75 MHz in DMSO-$d_6$.

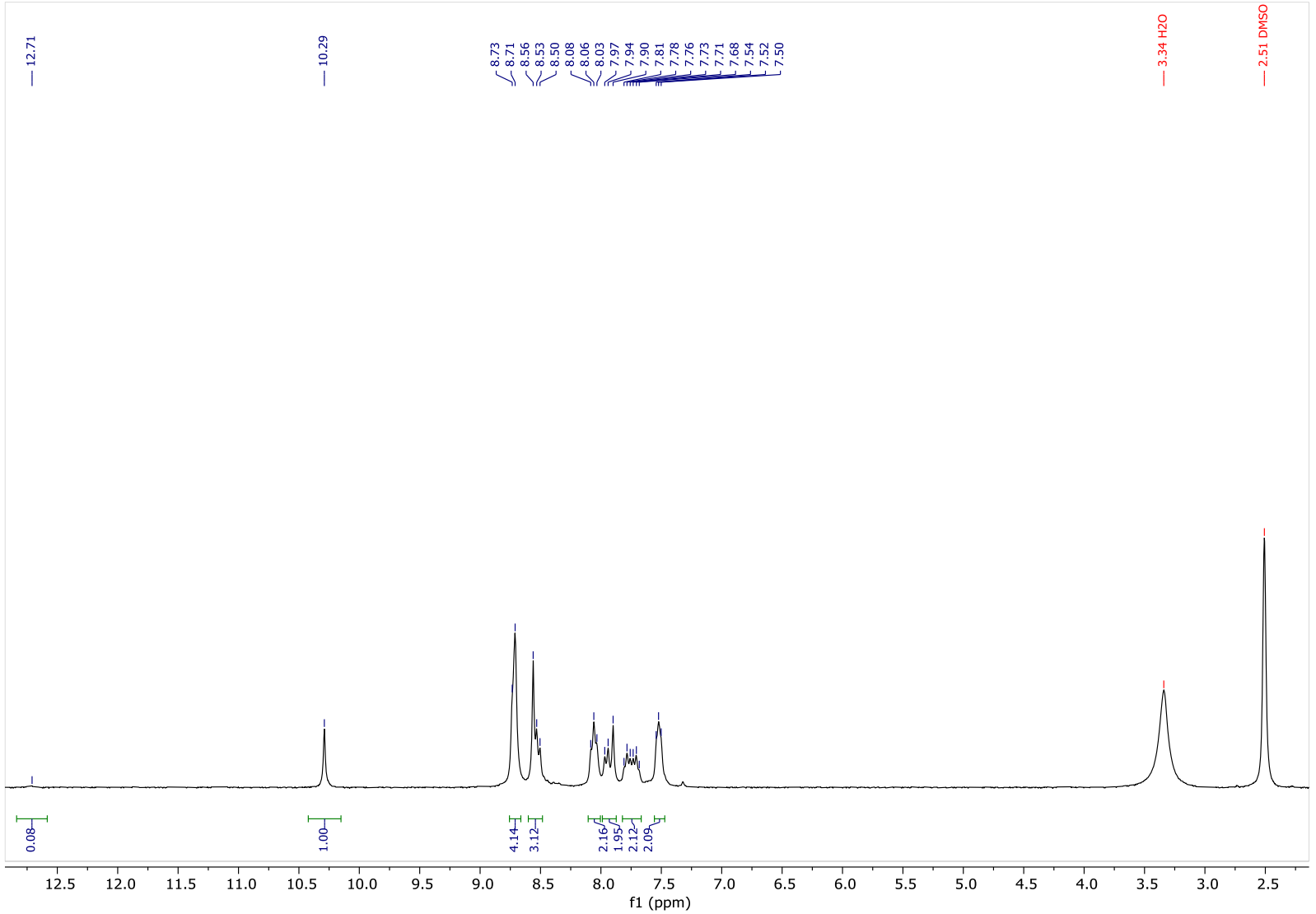



Figure S9 $^{1}$H NMR spectrum of compound **4a** recorded at 300 MHz in DMSO-$d_6$.

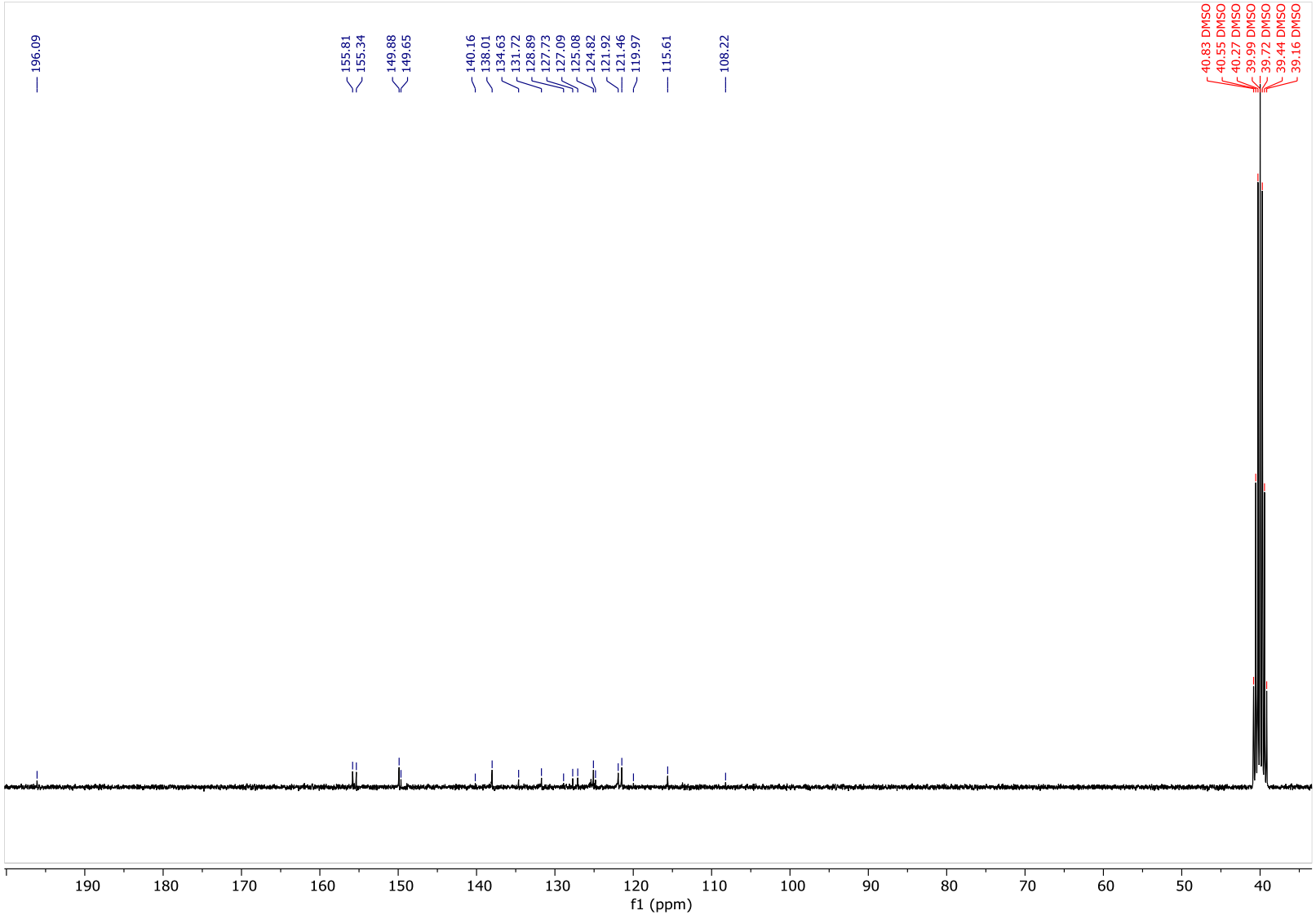



Figure S10 $^{13}C$ NMR spectrum of compound **4a** recorded at 75 MHz in DMSO-$d_6$.

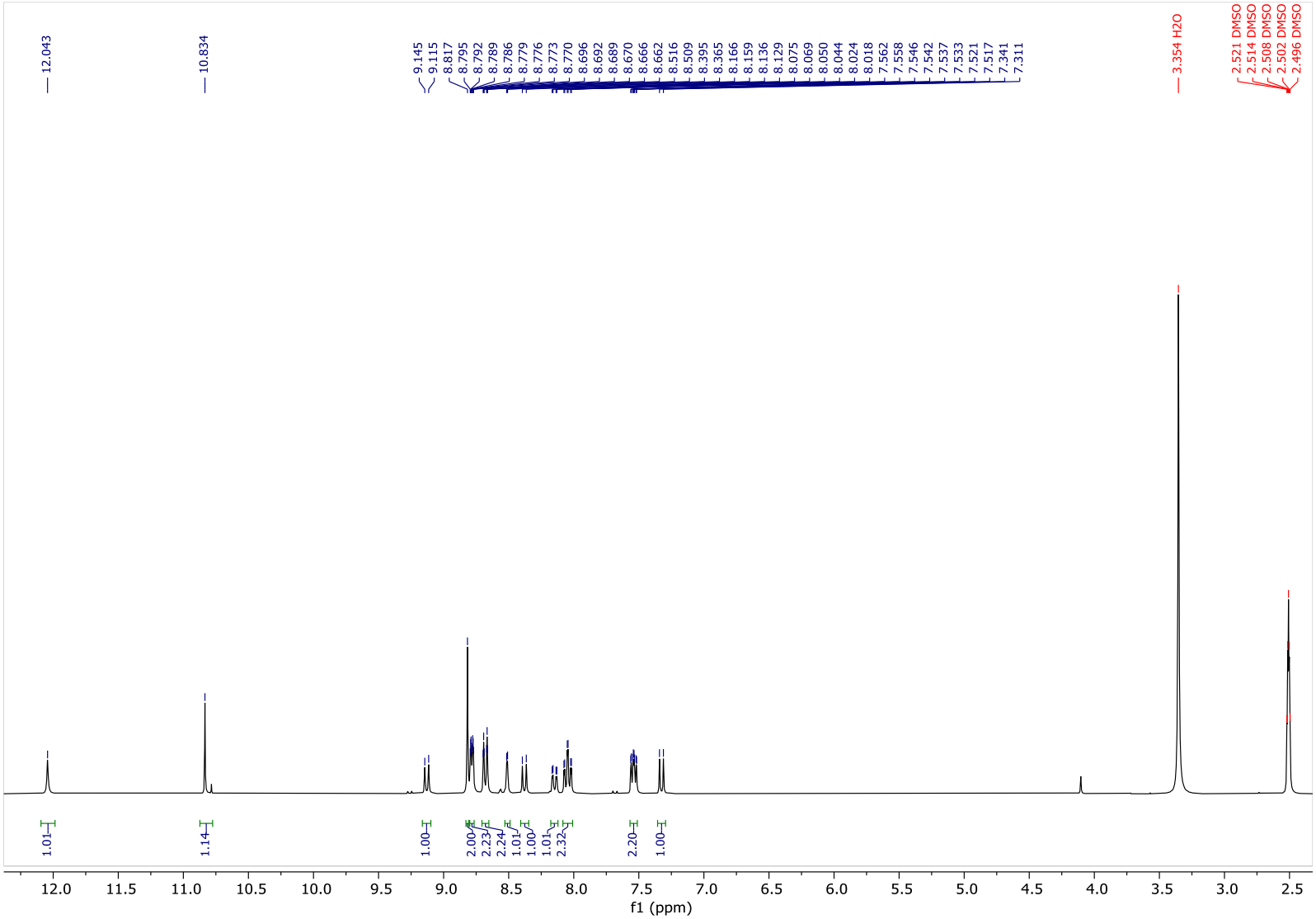



Figure S11 $^{1}$H NMR spectrum of compound **4b** recorded at 300 MHz in DMSO-$d_6$.

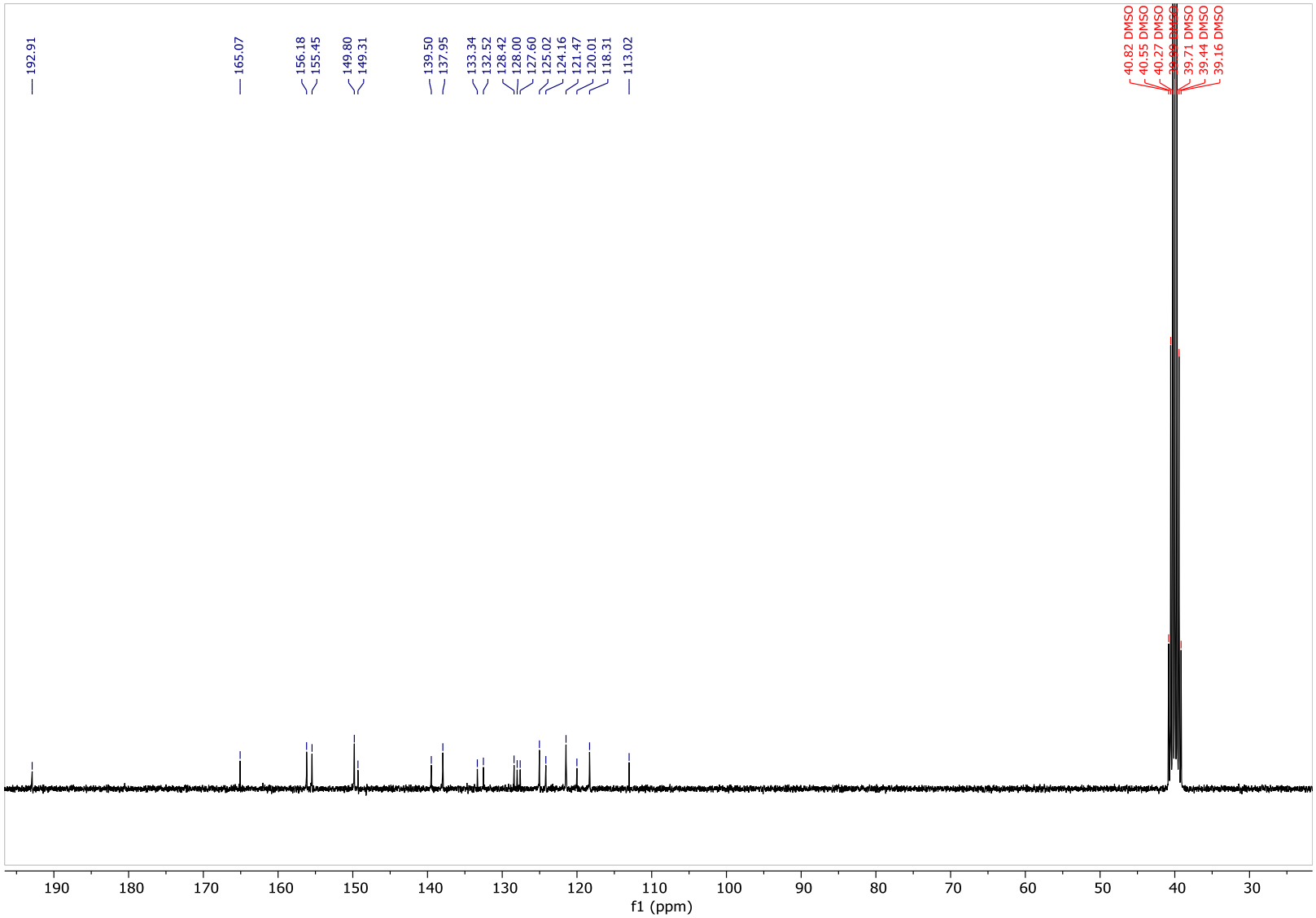



Figure S12 $^{13}C$ NMR spectrum of compound **4b** recorded at 75 MHz in DMSO-$d_6$.