



Supporting Information

for

A facile approach to spiro[dihydrofuran-2,3'-oxindoles] via formal [4 + 1] annulation reaction of fused 1*H*-pyrrole-2,3-diones with diazooxindoles

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Experimental part, compound characterization, and copies of NMR spectra

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General information

¹H and ¹³C NMR spectra were acquired on a Bruker Avance-III spectrometer (400 and 100 MHz, respectively) in DMSO-*d*₆ using the residual solvent signals (in ¹H NMR 2.50 ppm for DMSO-*d*₆; in ¹³C NMR 39.51 ppm for DMSO-*d*₆) as internal standards. Melting points were measured on a Khimlabpribor PTP apparatus or a Mettler Toledo MP70 apparatus. The reaction conditions were optimized using UPLC–UV–MS [Waters ACQUITY UPLC I-Class system; Acquity UPLC BEH C18 column, grain size of 1.7 μm; acetonitrile/water as eluents; flow rate of 0.6 mL/min; ACQUITY UPLC PDA eλ Detector (wavelength range of 230–780 nm); Xevo TQD mass detector; electrospray ionization; positive and negative ion detection; ion source temperature of 150 °C; capillary voltage of 3500–4000 V; cone voltage of 20–70 V; vaporizer temperature of 200 °C]. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F₂₅₄ plates using EtOAc/toluene 1:3 (v/v), acetic acid/EtOAc/toluene 1:8:24 (v/v) acetic acid, toluene, EtOAc as eluents, and the spots were visualized with UV light (254 and 365 nm) or by treating the plate with iodine vapor. HRMS were recorded on Bruker MicroTOF (ESI+), acetonitrile and methanol were used as solvents. The single crystal X-ray analyses of compounds **3aa**, **3ab**, and **3ha** were performed on an Xcalibur Ruby diffractometer (Agilent Technologies). The empirical absorption correction was introduced by multi-scan method using SCALE3 ABSPACK algorithm.¹ Using OLEX2², the structures were solved with the SUPERFLIP³ program or with the olex2.solve⁴ program and refined by the full-matrix least-squares minimization in the anisotropic approximation for all non-hydrogen atoms with the SHELXL⁵ program. Hydrogen atoms bound to carbon were positioned geometrically and refined using a riding model. The hydrogen atoms of NH groups were refined freely with isotropic displacement parameters.

Starting FPDs **1a–k** were obtained according to reported procedures⁶ from oxalyl chloride (purchased from commercial vendors) and heterocyclic enamines (obtained according to reported procedures⁶ from commercially available reagents).

Diazooxindoles **2a–d** and 3-bromooxindole (**4**) were obtained according to reported procedures⁷ from commercially available reagents.

Toluene, and 1,4-dioxane were distilled over Na before use. Ethyl acetate, chloroform, and acetone were distilled over P₂O₅ before the use. Acetonitrile, DMSO, DMF were dried over molecular sieves 4 Å before use. All other solvents and reagents were purchased from commercial vendors and were used as received.

Procedures involving FPDs **1a–k** were carried out in oven-dried glassware.

General procedure to compounds 3aa–ka

A suspension of the corresponding FPD **1** (500 μ mol) and diazooxindole **2** (500 μ mol) in 3 mL of acetonitrile was vigorously stirred at room temperature for 24 hours or at 83 °C for 3–5 hours (for FPDs **1h–j**) (until the disappearance of the dark violet color of FPD **1**). Then, the resulting yellow or pale-yellow precipitate was filtered off and washed with acetonitrile (2 $\times$ 1 mL) to afford the desired compounds **3**. Product **3ja** was additionally recrystallized from 1,4-dioxane.

Control experiment:

A suspension of the FPD **1i** (500 μ mol) and 3-bromoxindole (**4**, 500 μ mol) in 3 mL of acetonitrile was stirred at room temperature for 2 minutes and then 1.1 equiv of TEA was added in one portion. The mixture was stirred for 5 minutes (until the disappearance of the dark violet color of FPD **1i**). Then, the resulting yellow precipitate was filtered off and washed with acetonitrile (2 $\times$ 1 mL) to afford the desired compound **3ia**.

((5R*,5aR*)-3-Phenyl-6H-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3aa)

Yield: 165 mg (73%); yellow solid; mp 246–247°C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.83 (s, 1H), 8.24 (d, *J* = 7.3 Hz, 2H), 7.86 (t, *J* = 7.5 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 2H), 7.30 (qd, *J* = 5.3, 4.8, 2.2 Hz, 3H), 7.06 (ddd, *J* = 8.6, 6.1, 2.7 Hz, 1H), 7.00 – 6.90 (m, 3H), 6.65 (d, *J* = 7.8 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.28, 169.07, 167.07, 160.47, 158.64, 143.17, 141.48, 135.55, 132.61, 129.99 (2C), 129.34 (2C), 127.89, 125.69, 124.60, 124.11, 122.77, 121.81, 121.44, 121.28, 116.67, 110.77, 105.02, 91.14, 70.63.

MS (ESI⁺): *m/z* calcd for C₂₆H₁₄N₂O₆+MeOH+Na⁺: 505.1006 [M+ MeOH+Na⁺]; found: 505.1011.

((5R*,5aR*)-5'-Bromo-3-phenyl-6H-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ab)

Yield: 159 mg (60%); yellow solid; mp 225–226 °C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.00 (s, 1H), 8.23 (d, *J* = 7.5 Hz, 2H), 7.85 (t, *J* = 7.4 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.36 (d, *J* = 1.5 Hz, 1H), 7.29 (d, *J* = 5.4 Hz, 2H), 7.12 – 7.06 (m, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.14, 169.01, 166.82, 160.44, 158.35, 143.16, 140.82, 135.44, 135.27, 130.09 (2C), 129.25 (2C), 127.92, 127.27, 125.73, 124.75, 123.40, 121.88, 121.44, 116.72, 114.04, 112.63, 104.46, 90.51, 71.18.

MS (ESI⁺): *m/z* calcd for C₂₆H₁₃BrN₂O₆+MeOH+Na⁺: 583.0111 [M+ MeOH+Na⁺]; found: 583.0117.

(5R*,5aR*)-5'-Methoxy-3-phenyl-6H-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ac)

Yield: 146 mg (61%); yellow solid; mp 255–256°C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.67 (s, 1H), 8.23 (d, *J* = 7.5 Hz, 2H), 7.86 (t, *J* = 7.4 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.10 – 7.05 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.90 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.58 (d, *J* = 8.6 Hz, 1H), 6.51 (d, *J* = 2.3 Hz, 1H), 3.60 (s, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.28, 168.96, 167.20, 160.49, 158.59, 155.09, 143.15, 135.54, 134.73, 130.06 (2C), 129.32 (2C), 127.85, 125.71, 124.64, 122.26, 121.77, 121.45, 117.35, 116.66, 111.50, 110.93, 104.85, 91.27, 70.68, 55.79.

MS (ESI⁺): *m/z* calcd for C₂₇H₁₆N₂O₇+Na⁺: 503.0850 [M+Na⁺]; found: 503.0860.

(5R*,5aR*)-1'-Benzyl-3-phenyl-6H-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ad)

Yield: 157 mg (58%); yellow solid; mp 240–241°C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.28 – 8.22 (m, 2H), 7.89 – 7.82 (m, 1H), 7.72 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.23 (m, 5H), 7.18 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.05 (dtd, *J* = 21.0, 7.6, 1.1 Hz, 3H), 6.97 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 4.80 (d, *J* = 15.9 Hz, 1H), 4.64 (d, *J* = 15.9 Hz, 1H), minor product: 5.00 (d, *J* = 15.8 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.13, 167.70, 166.87, 160.77, 158.40, 142.95, 142.02, 135.62, 134.60, 132.70, 130.01 (2C), 129.36 (2C), 128.67 (2C), 127.93, 127.41, 126.75 (2C), 125.64, 124.69, 124.06, 123.70, 121.98, 121.23, 120.79, 116.81, 110.52, 105.33, 90.51, 70.59, 43.39.

MS (ESI⁺): *m/z* calcd for C₃₃H₂₀N₂O₆+Na⁺: 563.1213 [M+Na⁺]; found: 563.1215.

(5R*,5aR*)-3-(4-Chlorophenyl)-6H-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ba)

Yield: 172 mg (71%); yellow solid; mp 225–226 °C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.83 (s, 1H), 8.23 (d, *J* = 8.6 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.28 (q, *J* = 6.0, 5.1 Hz, 3H), 7.04 (ddd, *J* = 18.3, 10.1, 4.8 Hz, 2H), 6.97 – 6.89 (m, 2H), 6.64 (d, *J* = 7.8 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.38, 168.98, 165.68, 160.31, 158.53, 143.17, 141.46, 140.43, 132.66, 131.49 (2C), 129.65 (2C), 127.95, 124.64, 124.50, 124.24, 122.78, 121.84, 121.40, 121.21, 116.69, 110.75, 105.40, 91.34, 70.65.

MS (ESI⁺): *m/z* calcd for C₂₆H₁₃ClN₂O₆+MeOH+Na⁺: 539.0616 [M+ MeOH+Na⁺]; found: 539.0638.

(5*R,5*aR**)-3-(4-Bromophenyl)-6*H*-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ca)**

Yield: 159 mg (62%); yellow solid; mp 230–231 °C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.83 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.29 (q, *J* = 7.3, 5.2 Hz, 3H), 7.04 (ddd, *J* = 18.9, 10.4, 4.8 Hz, 2H), 6.98 – 6.88 (m, 2H), 6.64 (d, *J* = 7.8 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.38, 168.97, 165.81, 160.29, 158.49, 143.16, 141.45, 132.65, 132.60 (2C), 131.44 (2C), 129.77, 127.94, 124.80, 124.63, 124.24, 122.77, 121.83, 121.39, 121.20, 116.69, 110.74, 105.46, 91.33, 70.65.

MS (ESI⁺): *m/z* calcd for C₂₆H₁₃BrN₂O₆+MeOH+Na⁺: 583.0111 [M+Na⁺]; found: 583.0126.

(5*R,5*aR**)-3-(4-Methylphenyl)-6*H*-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3da)**

Yield: 170 mg (73%); yellow solid; mp 247–248 °C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.82 (s, 1H), 8.14 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.05 (ddd, *J* = 8.6, 6.1, 2.6 Hz, 1H), 7.00 – 6.88 (m, 3H), 6.65 (d, *J* = 7.8 Hz, 1H), 2.48 (s, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.15, 169.11, 167.41, 160.65, 158.76, 147.02, 143.17, 141.50, 132.59, 130.10 (2C), 129.98 (2C), 127.86, 124.59, 123.95, 123.08, 122.76, 121.77, 121.48, 121.31, 116.67, 110.80, 104.33, 91.02, 70.58, 21.56.

MS (ESI⁺): *m/z* calcd for C₂₇H₁₆N₂O₆+MeOH+Na⁺: 519.1162 [M+Na⁺]; found: 519.1173.

(5*R,5*aR**)-3-(4-Methoxyphenyl)-6*H*-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ea)**

Yield: 187 mg (78%); yellow solid; mp 247–248 °C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.81 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.22 (m, 5H), 7.05 (td, *J* = 7.0, 6.1, 2.6 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 3.94 (s, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 172.91, 169.17, 167.50, 165.47, 160.97, 158.95, 143.15, 141.51, 132.76 (2C), 132.53, 127.76, 124.56, 123.84, 122.73, 121.71, 121.55, 121.34, 118.13, 116.64, 115.10 (2C), 110.79, 103.00, 90.79, 70.56, 55.97.

MS (ESI⁺): *m/z* calcd for C₂₇H₁₆N₂O₇+Na⁺: 503.0850 [M+Na⁺]; found: 503.0850.

(5*R,5*aR**)-3-(4-Nitrophenyl)-6*H*-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3fa)**

Yield: 119 mg (48%); yellow solid; mp 234–236 °C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.87 (s, 1H), 8.56 – 8.38 (m, 4H), 7.31 (q, *J* = 7.8 Hz, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.10 – 7.02 (m, 1H), 7.00 – 6.89 (m, 2H), 6.64 (d, *J* = 7.8 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.60, 168.90, 163.84, 159.91, 158.26, 150.75, 143.19, 141.45, 132.77, 130.97 (2C), 130.79, 128.09, 124.72, 124.56, 124.30 (2C), 122.80, 121.94, 121.30, 121.16, 116.75, 110.75, 107.52, 91.72, 70.77.

MS (ESI⁺): *m/z* calcd for C₂₆H₁₃N₃O₈+MeOH+Na⁺: 550,0857 [M+ MeOH+Na⁺]; found: 550.0875.

(5*R,5*aR**)-10-Chloro-3-phenyl-6*H*-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ga)**

Yield: 208 mg (86%); yellow solid; mp 259–260°C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.89 (s, 1H), 8.24 (d, *J* = 7.6 Hz, 2H), 7.86 (t, *J* = 7.4 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 12.6 Hz, 3H), 7.04 – 6.95 (m, 2H), 6.88 (s, 1H), 6.70 (d, *J* = 7.8 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 172.79, 169.12, 167.57, 160.35, 158.06, 142.10, 141.42, 135.69, 132.67, 130.10 (2C), 129.36 (2C), 128.13, 127.74, 125.59, 124.33, 122.92, 122.45, 121.20, 121.07, 118.51, 110.83, 104.46, 91.20, 70.54.

MS (ESI⁺): *m/z* calcd for C₂₆H₁₃ClN₂O₆+MeOH+Na⁺: 539,0616 [M+ MeOH+Na⁺]; found: 539.0623.

(5*R,5*aR**)-3-(4-Chlorophenyl)spiro[furo[3',4':2,3]pyrrolo[1,2-*a*]quinoxaline-5,3'-indoline]-1,2,2',6(7*H*)-tetraone ACN solvate 1:1 (3ha)**

Yield: 184 mg (70%); yellow solid; mp 252–253°C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.06 (s, 1H), 10.65 (s, 1H), 8.24 (d, *J* = 8.7 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.21 (m, 1H), 7.19 – 7.14 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.98 – 6.90 (m, 2H), 6.86 – 6.81 (m, 1H), 6.77 (d, *J* = 6.8 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), minor product: 10.98 (s, 1H), 10.76 (s, 1H), 7.92 – 7.86 (m, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.81, 169.21, 165.37, 160.83, 160.66, 141.43, 140.15, 132.22, 131.42 (2C), 130.40, 129.55 (2C), 127.41, 124.80, 123.79, 122.40, 122.20, 122.13, 121.62, 121.39, 115.66, 110.50, 106.10, 92.13, 71.19.

MS (ESI⁺): *m/z* calcd for C₂₆H₁₄ClN₃O₅+MeOH+Na⁺: 538,0776 [M+MeOH+Na⁺]; found: 538.0764.

(5*R,5*aR**)-3,7-Diphenyl-6*H*-spiro[benzo[*b*]furo[3',4':2,3]pyrrolo[1,2-*d*][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ia)**

Yield: 223 mg (85%); yellow solid; mp 254–255°C (decomp.).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.82 (s, 1H), 8.26 – 8.22 (m, 2H), 7.84 (tt, *J* = 7.0, 1.2 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.39 (br s,

2H) 7.31 – 7.26 (m, 1H), 7.12 – 7.07 (m, 1H), 7.02 – 6.95 (m, 2H), 6.89 (td, $J = 7.7, 1.2$ Hz, 1H), 6.84 (dd, $J = 7.9, 1.5$ Hz, 1H), 6.62 (d, $J = 7.8$ Hz, 1H), 6.35 (dd, $J = 8.3, 0.9$ Hz, 1H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 173.87, 169.50, 166.83, 160.51, 160.32, 141.45, 137.08, 135.35, 133.24, 132.31, 129.95 (2C), 129.56 (2C), 129.30 (2C), 128.74 (2C), 128.57, 127.17, 125.95, 123.77, 122.88, 122.63, 122.52, 122.17, 121.88, 116.72, 110.62, 105.87, 91.73, 71.06.

MS (ESI⁺): m/z calcd for $\text{C}_{32}\text{H}_{19}\text{N}_3\text{O}_5 + \text{Na}^+$: 548.1217 [$\text{M} + \text{Na}^+$]; found: 548.1208.

Control experiment:

Yield: 142 mg (54%); yellow solid; mp 254–255°C (decomp.).

^1H NMR (400 MHz, DMSO- d_6) δ 10.81 (s, 1H), 8.27 – 8.22 (m, 2H), 7.84 (tt, $J = 7.0, 1.2$ Hz, 1H), 7.72 (t, $J = 7.7$ Hz, 2H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.52 – 7.47 (m, 1H), 7.39 (br s, 2H), 7.31 – 7.26 (m, 1H), 7.12 – 7.07 (m, 1H), 7.02 – 6.95 (m, 2H), 6.89 (dd, $J = 15.3, 1.2$ Hz, 1H), 6.83 (dd, $J = 7.9, 1.5$ Hz, 1H), 6.62 (d, $J = 7.8$ Hz, 1H), 6.34 (dd, $J = 8.3, 0.9$ Hz, 1H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 173.85, 169.47, 166.80, 160.48, 160.29, 141.43, 137.06, 135.32, 133.23, 132.29, 129.93 (2C), 129.54 (2C), 129.28 (2C), 128.73 (2C), 128.54, 127.14, 125.94, 123.76, 122.86, 122.60, 122.51, 122.16, 121.85, 116.69, 110.59, 105.85, 91.71, 71.04.

(5S*,5aS*)-7-Benzyl-3-(4-chlorophenyl)spiro[furo[3',4':2,3]pyrrolo[1,2-*a*]quinoxaline-5,3'-indoline]-1,2,2',6(7H)-tetraone 1:1 dioxane solvate (3ja)

Yield: 210 mg (63%); yellow solid; mp 258–260 °C (decomp.).

^1H NMR (400 MHz, DMSO- d_6) δ 10.68 (s, 1H), 8.26 (d, $J = 8.6$ Hz, 2H), 7.81 (d, $J = 8.6$ Hz, 2H), 7.38 (d, $J = 7.4$ Hz, 2H), 7.27 (td, $J = 7.3, 3.1$ Hz, 3H), 7.22 (d, $J = 7.2$ Hz, 1H), 7.14 (d, $J = 7.0$ Hz, 2H), 6.96 (dt, $J = 14.8, 7.1$ Hz, 2H), 6.88 – 6.83 (m, 1H), 6.80 (d, $J = 7.4$ Hz, 1H), 6.60 (d, $J = 7.8$ Hz, 1H), 5.40 (d, $J = 16.5$ Hz, 1H), 4.93 (d, $J = 16.4$ Hz, 1H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 173.83, 169.20, 165.44, 161.39, 160.28, 141.49, 140.20, 136.04, 132.31, 131.45 (2C), 130.85, 129.59 (2C), 128.19 (2C), 127.33, 127.21 (2C), 126.97, 124.78, 123.76, 122.74, 122.70, 122.53, 122.03, 121.80, 116.15, 110.57, 106.58, 91.80, 71.10, 45.63.

MS (ESI⁺): m/z calcd for $\text{C}_{33}\text{H}_{20}\text{ClN}_3\text{O}_5 + \text{Na}^+$: 596.0983 [$\text{M} + \text{Na}^+$]; found: 596.0986.

(10R*,10aR*)-8-Phenyl-3,4-dihydro-1H-spiro[furo[3',4':2,3]pyrrolo[2,1-*c*][1,4]oxazine-10,3'-indoline]-1,2',6,7-tetraone (3ka)

Yield: 113 mg (56%); yellow solid; mp 217–218°C (decomp.).

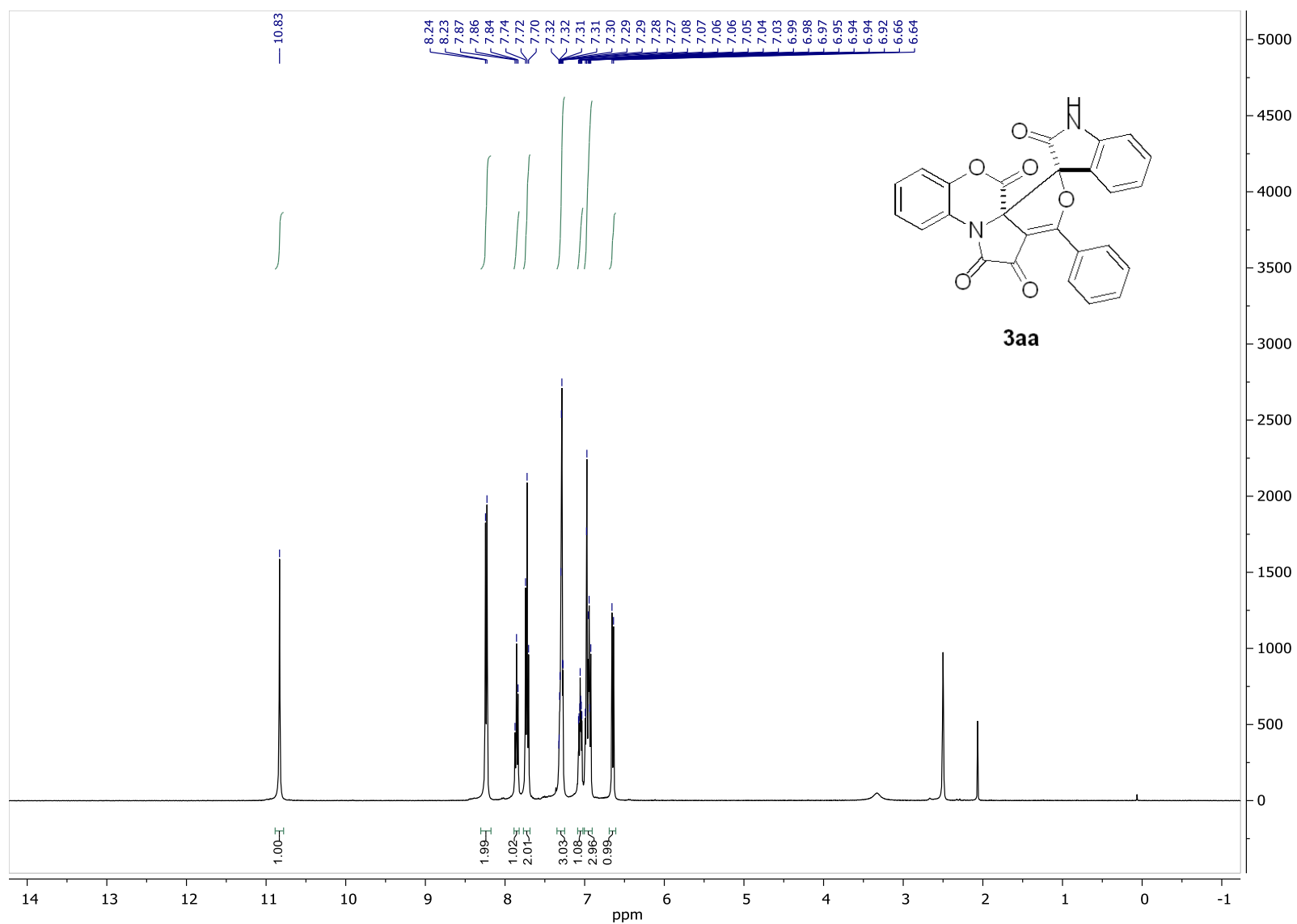
^1H NMR (400 MHz, DMSO- d_6) δ 11.35 (s, 1H), 8.19 (d, $J = 8.4$ Hz, 2H), 7.82 (t, $J = 7.5$ Hz, 1H), 7.68 (t, $J = 7.8$ Hz, 2H), 7.48 – 7.42 (m, 1H), 7.09 – 6.94 (m, 3H), 4.61 (ddd, $J = 12.9, 5.8, 2.0$ Hz, 1H), 3.99 (td, $J = 12.7, 12.3, 4.3$ Hz, 1H), 3.74 (ddd, $J = 13.2, 11.7, 6.0$ Hz, 1H), 2.94 (ddd, $J = 13.4, 4.1, 2.0$ Hz, 1H).

^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 173.55, 169.72, 165.82, 164.54, 164.05, 141.81, 135.45, 132.93, 129.86 (2C), 129.29 (2C), 125.64, 125.01, 123.39, 121.98, 111.66, 108.44, 90.39, 72.14, 63.54 (2C).

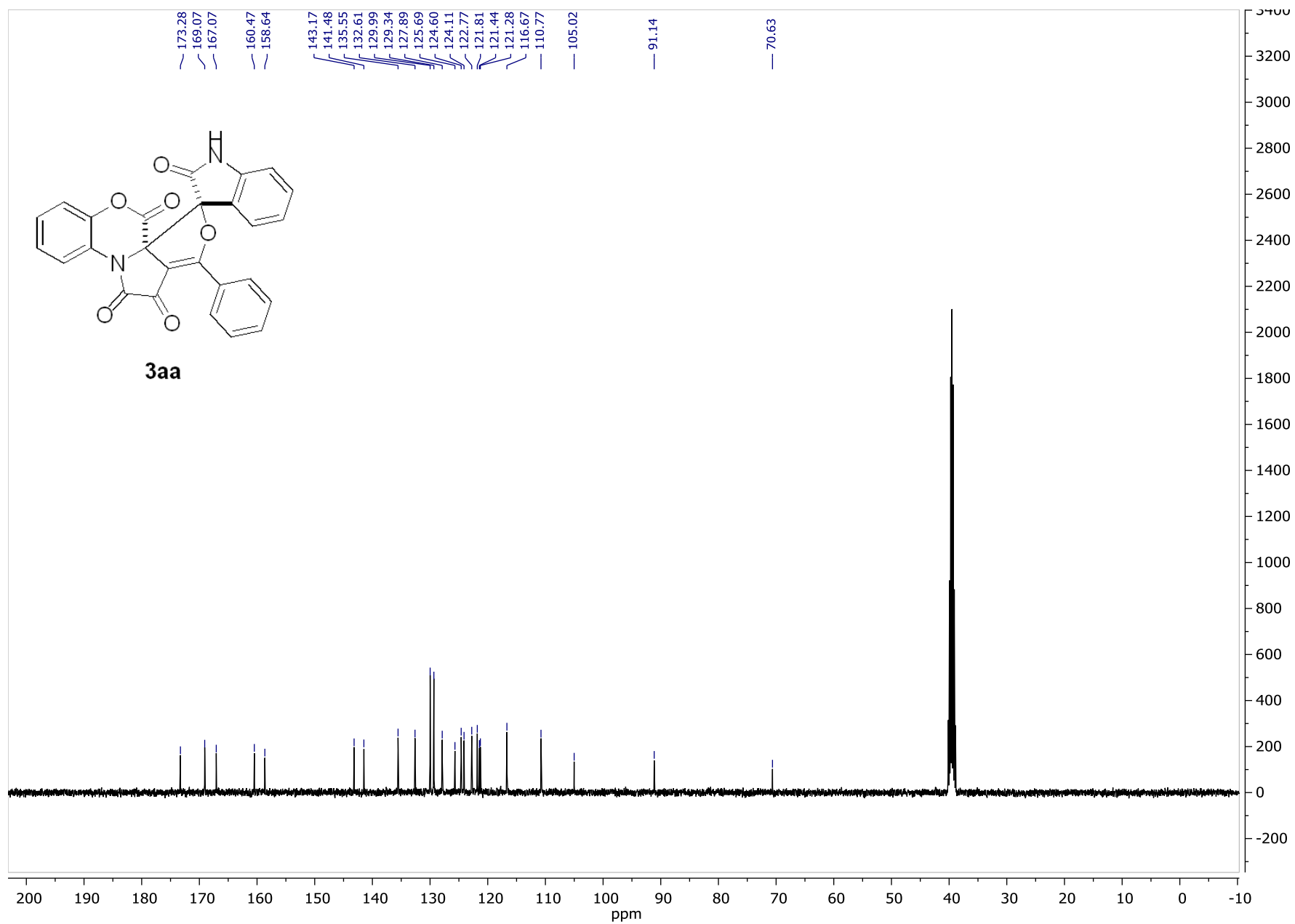
MS (ESI⁺): m/z calcd for $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_6 + \text{Na}^+$: 425,0744 [$\text{M} + \text{Na}^+$]; found: 425.0747.

NMR charts of compounds 3aa–ka

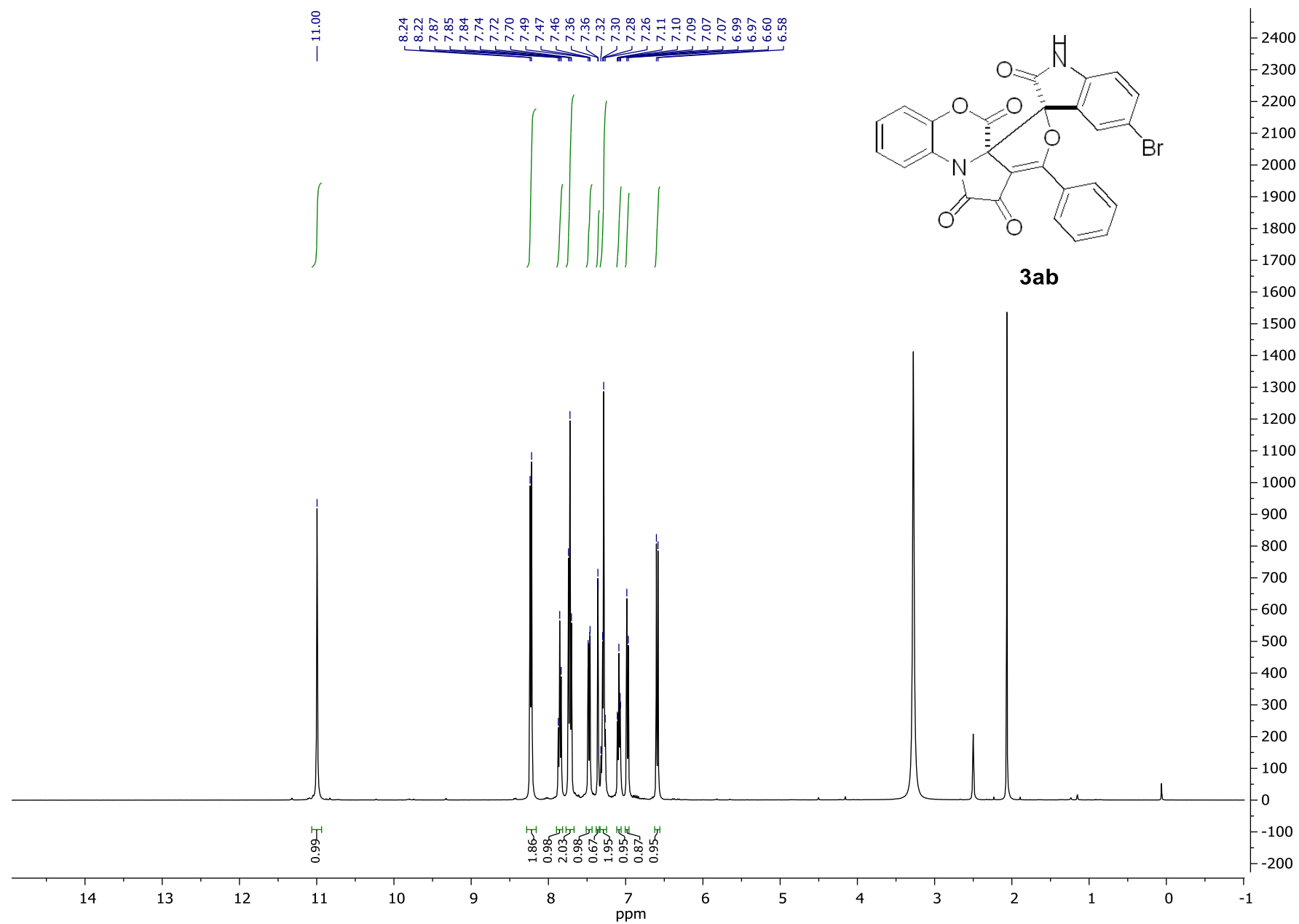
3aa ^1H (400 MHz, DMSO- d_6)



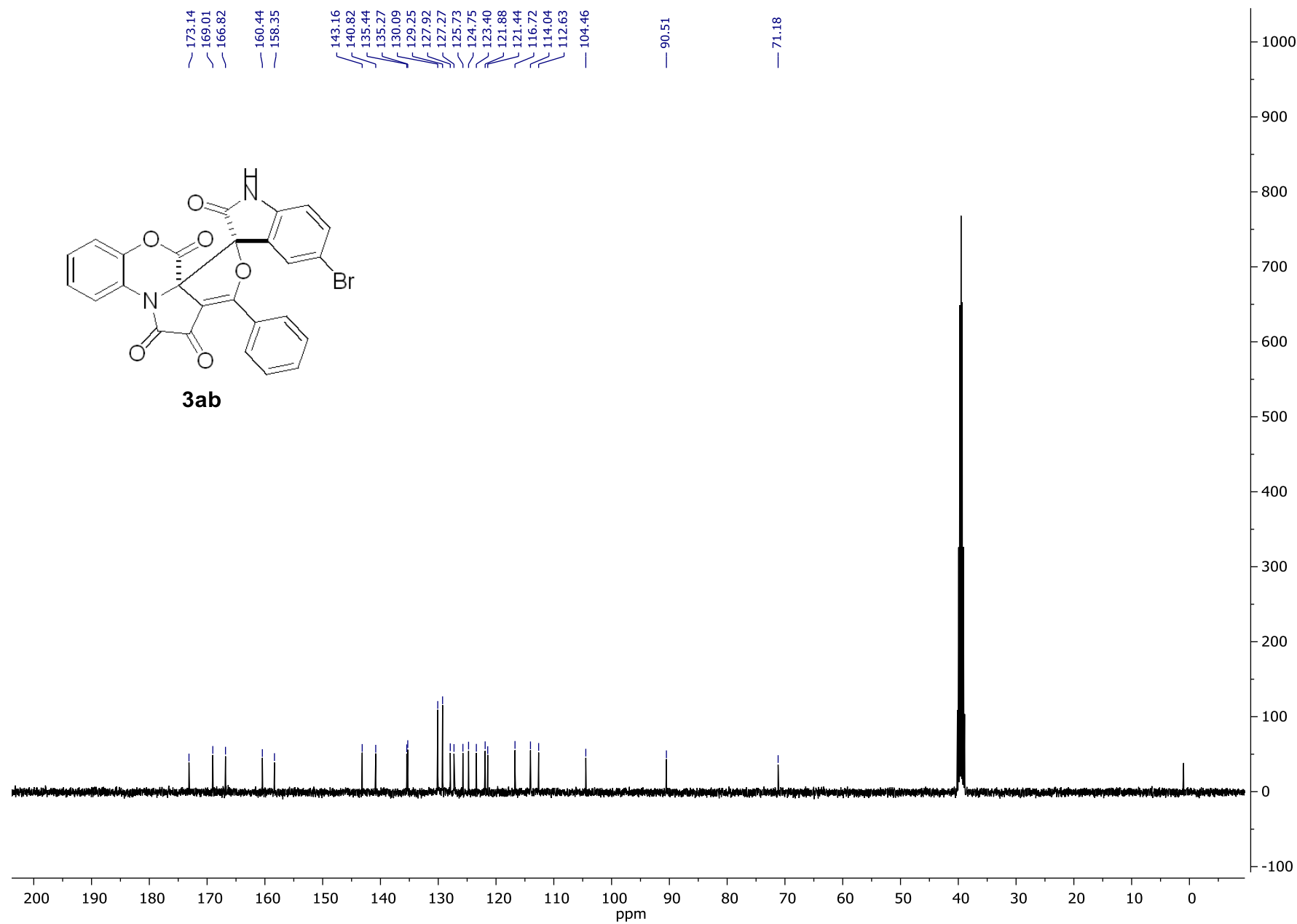
3aa ^{13}C (101 MHz, DMSO- d_6)



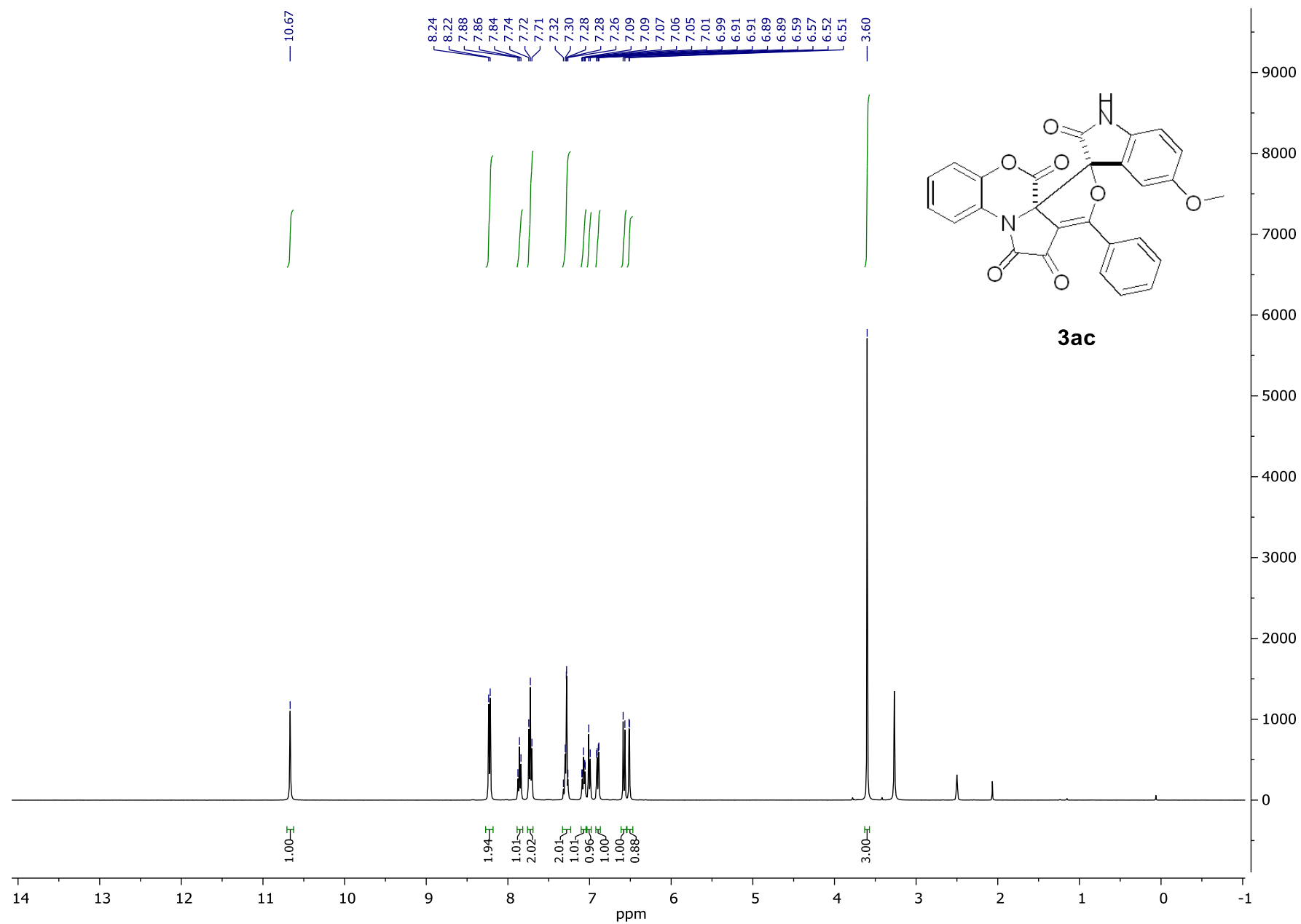
3ab ^1H (400 MHz, DMSO- d_6)



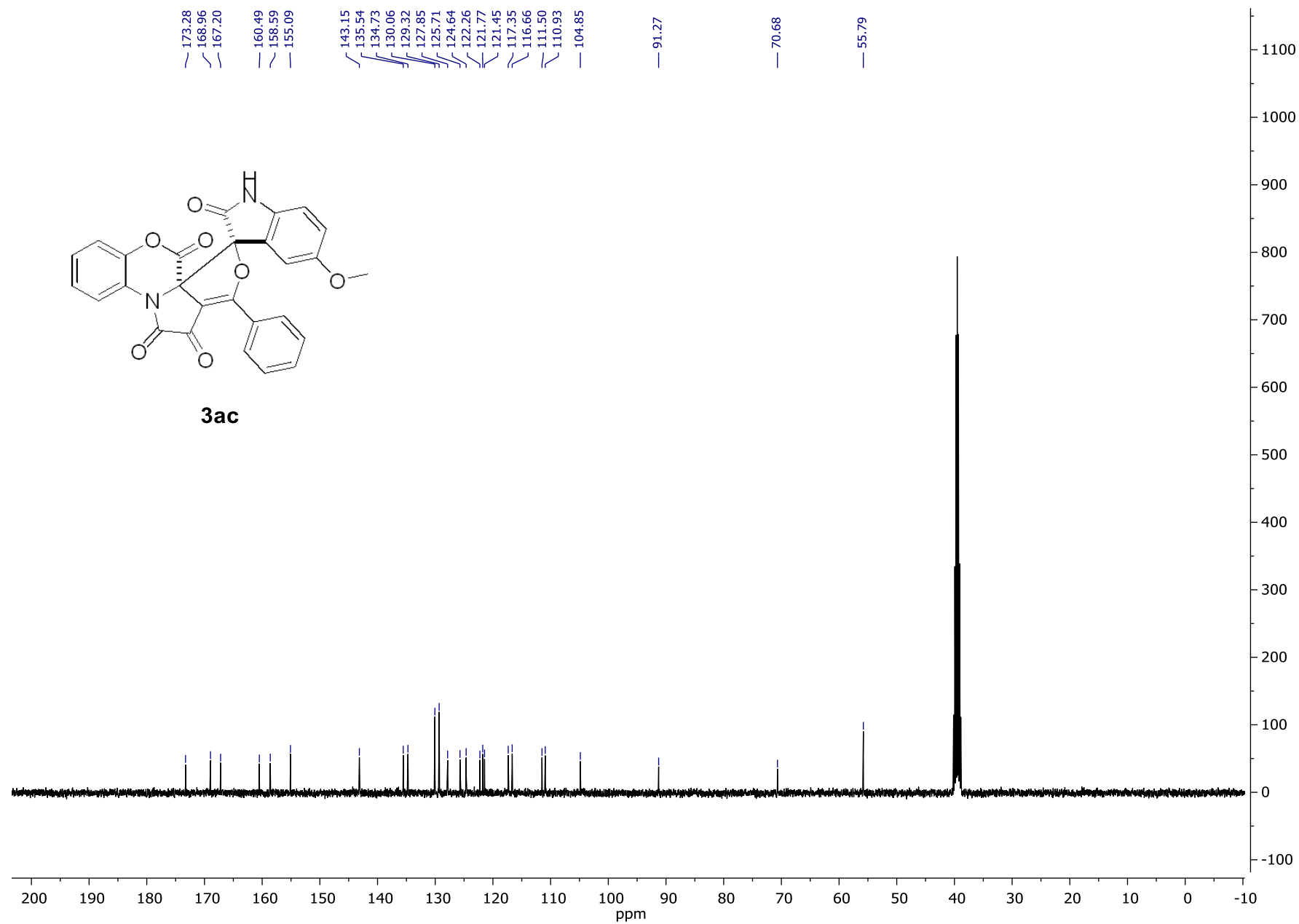
3ab ^{13}C (101 MHz, DMSO- d_6)



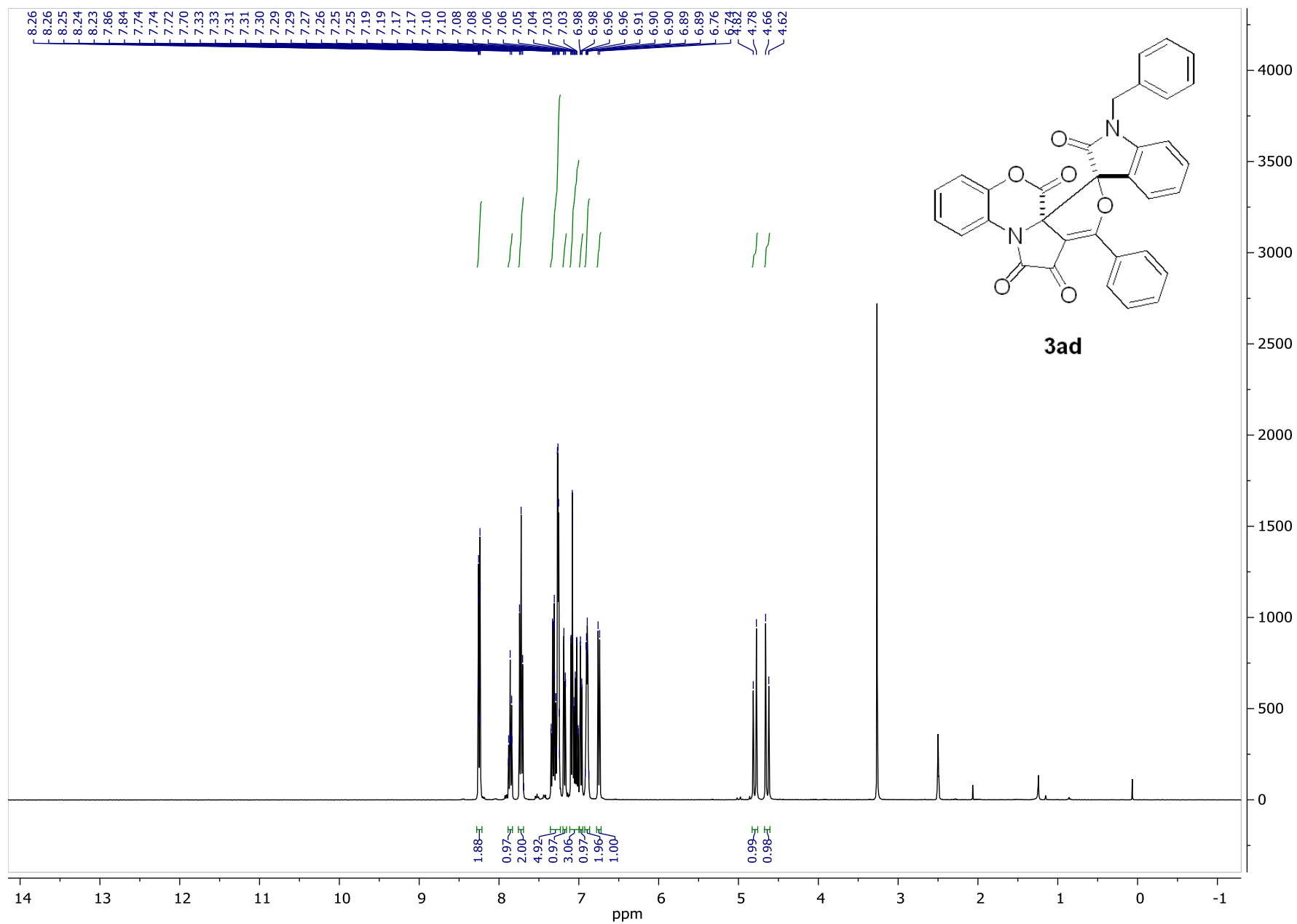
3ac ^1H (400 MHz, DMSO- d_6)



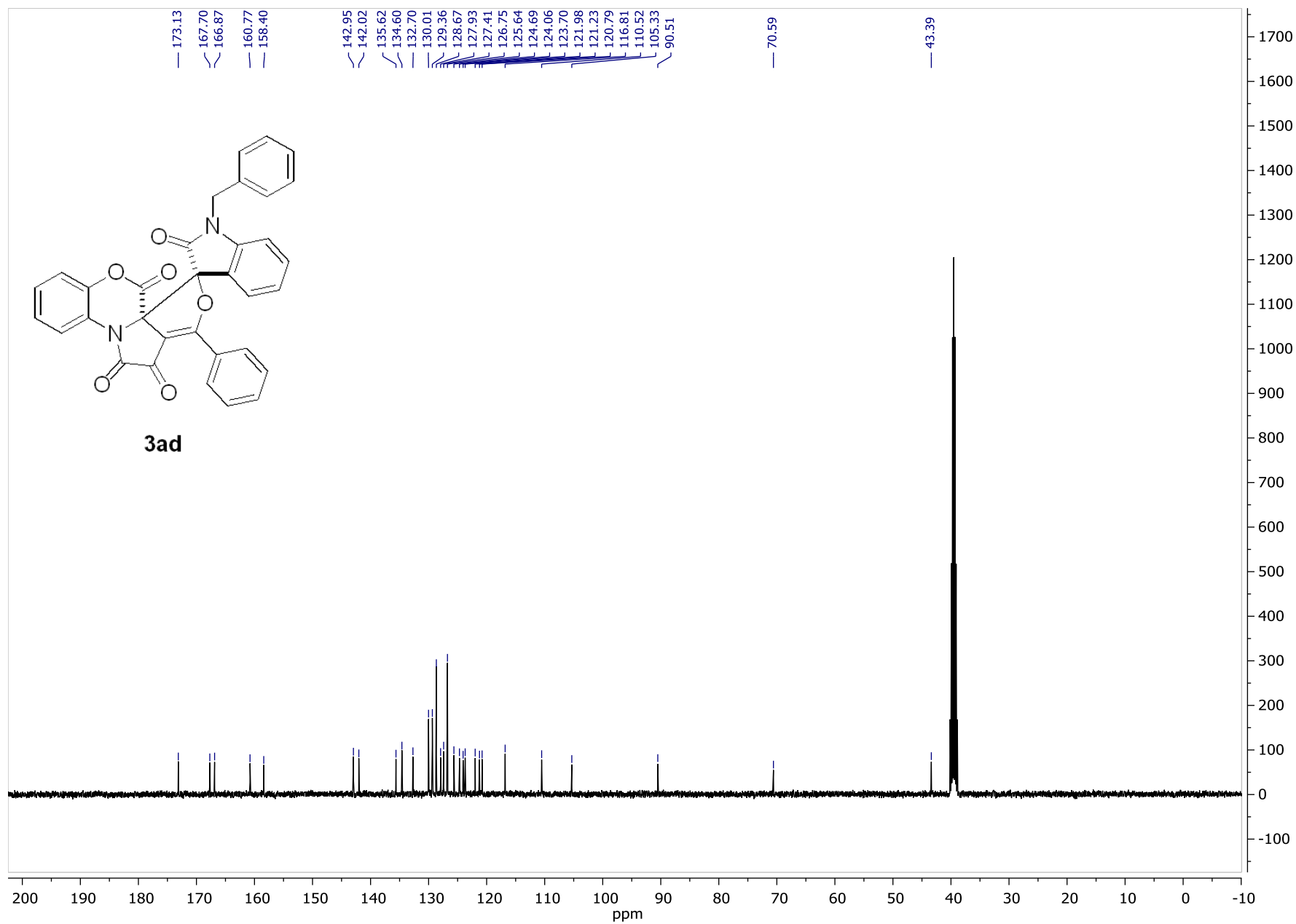
3ac ^{13}C (101 MHz, DMSO- d_6)



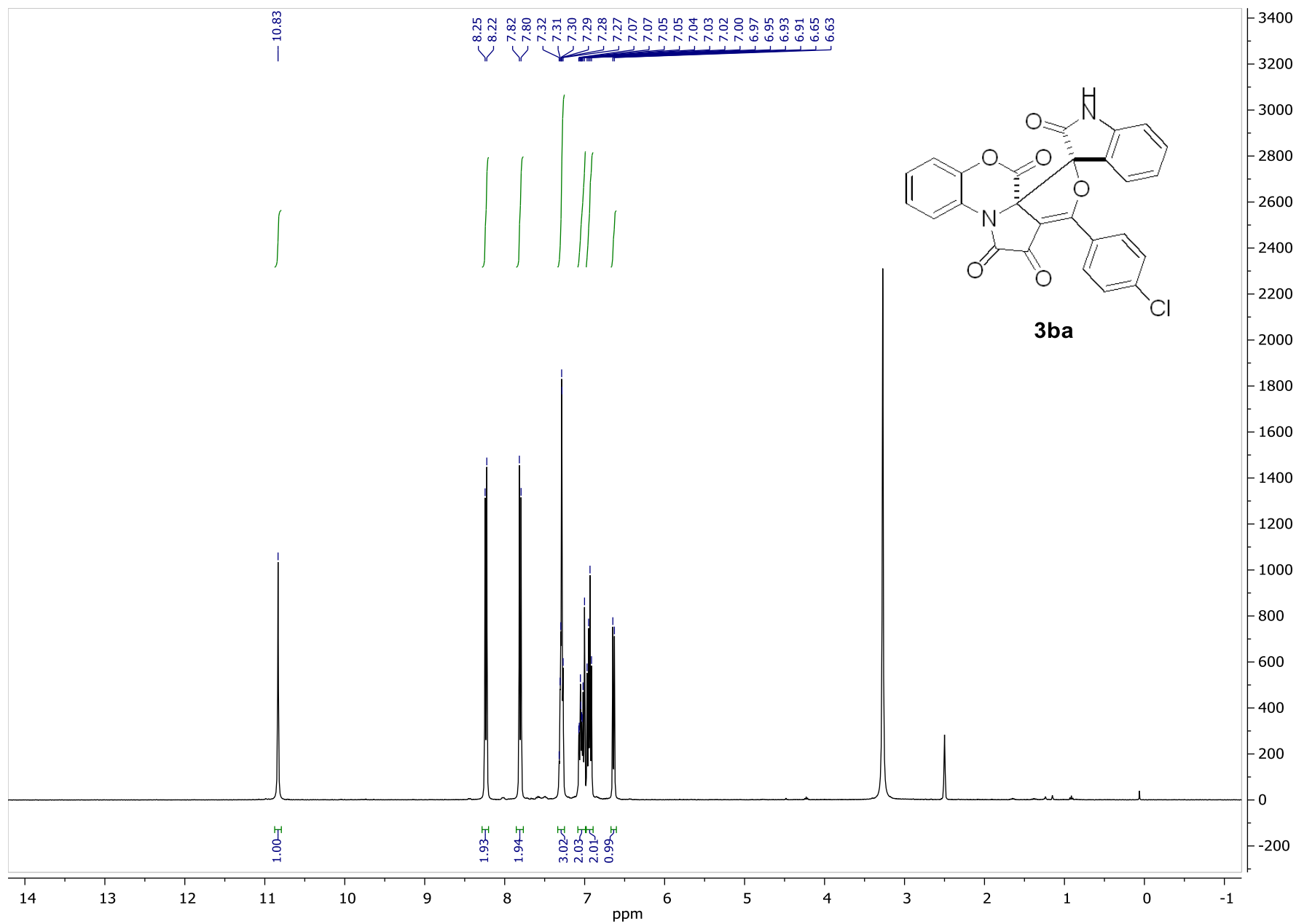
3ad ^1H (400 MHz, DMSO- d_6)



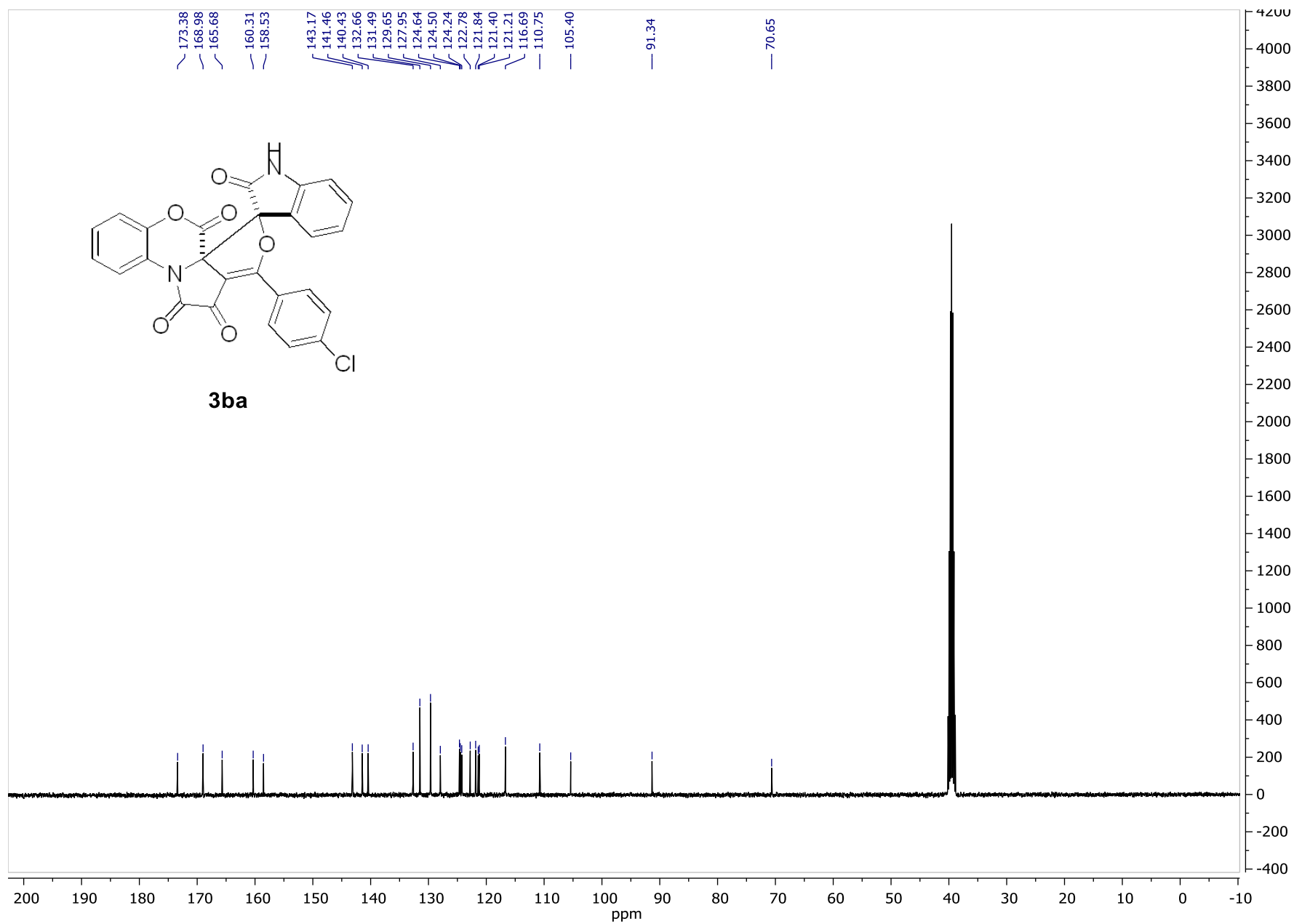
3ad ^{13}C (101 MHz, DMSO- d_6)



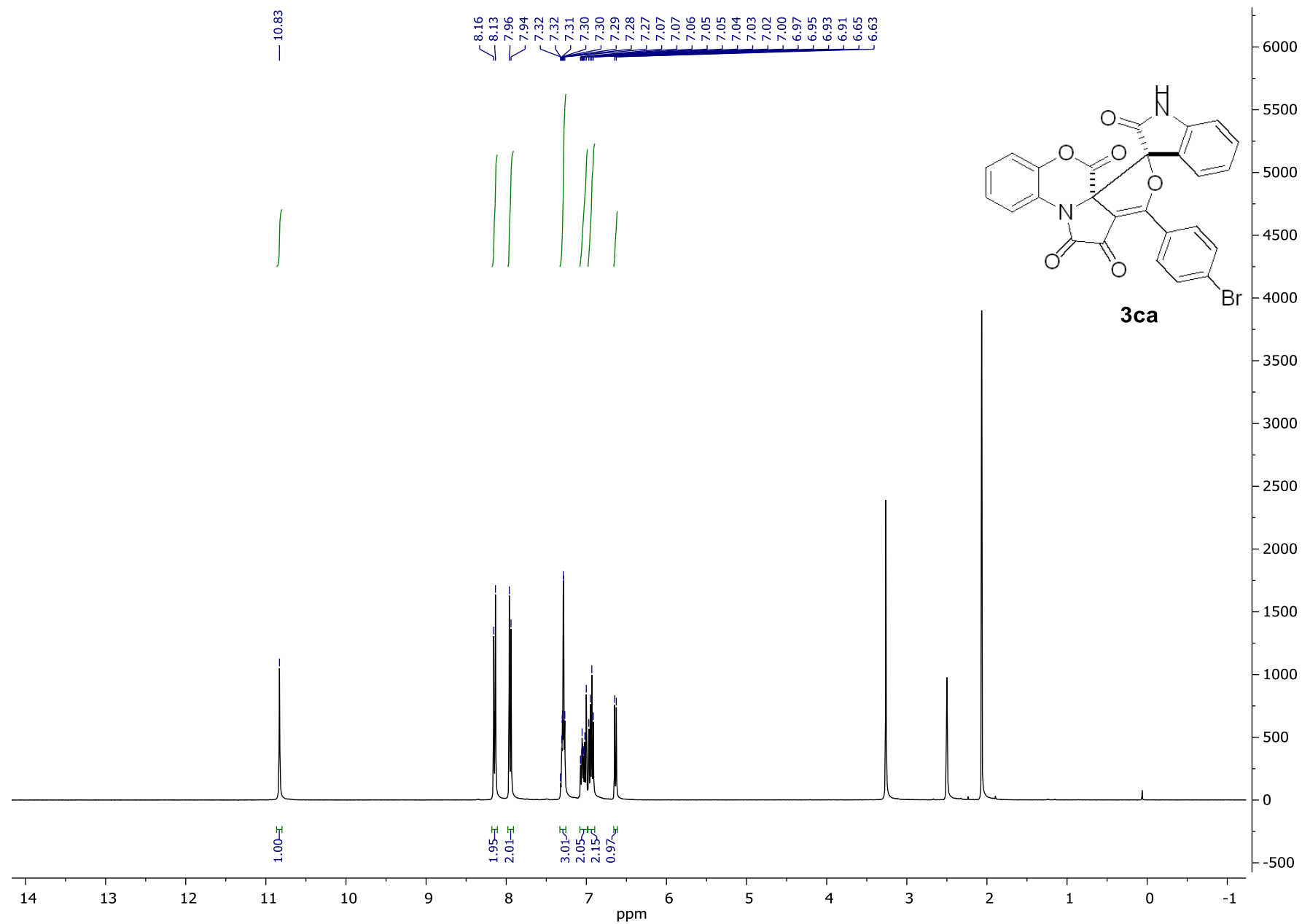
3ba ^1H (400 MHz, $\text{DMSO-}d_6$)



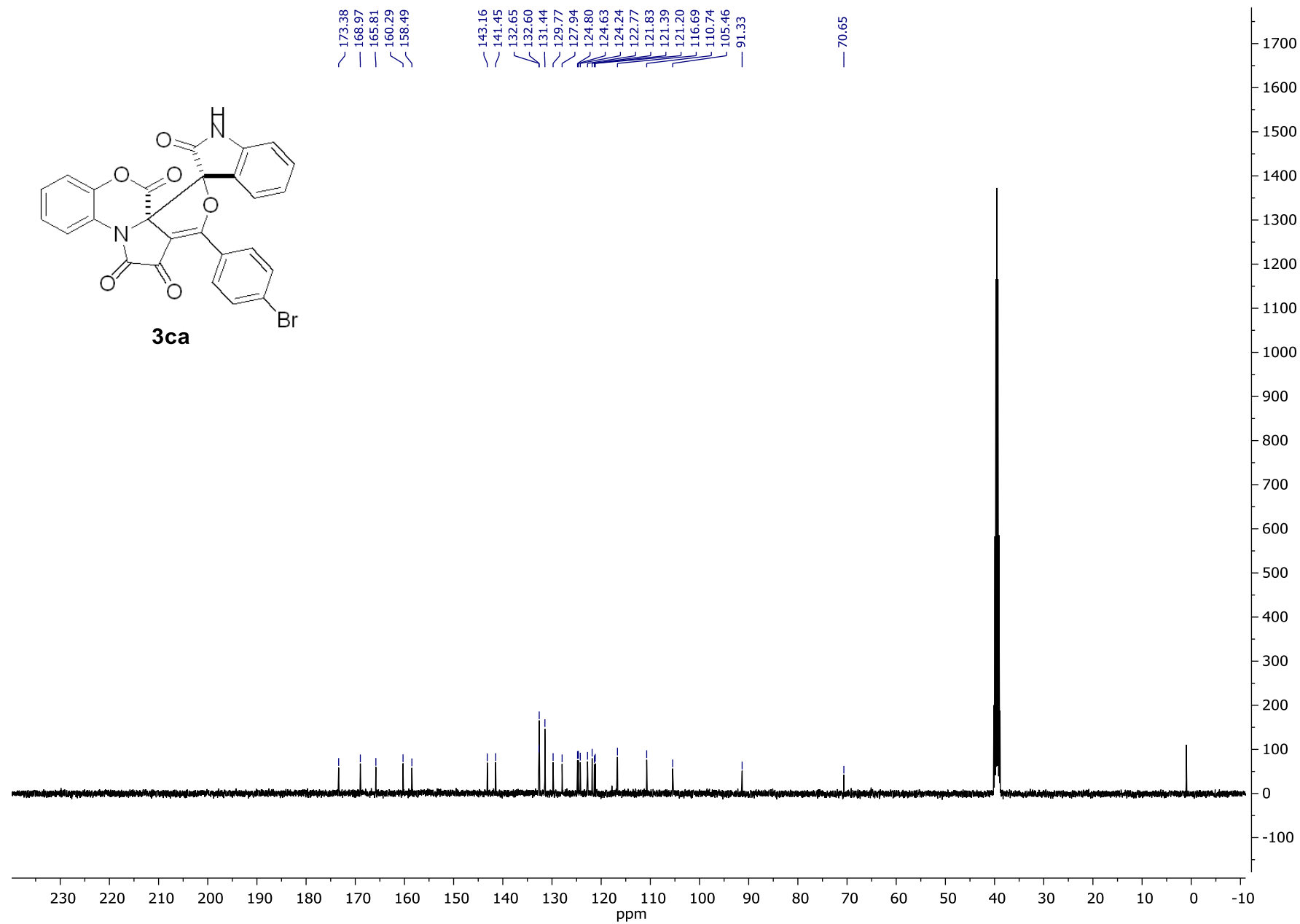
3ba ^{13}C (101 MHz, $\text{DMSO}-d_6$)



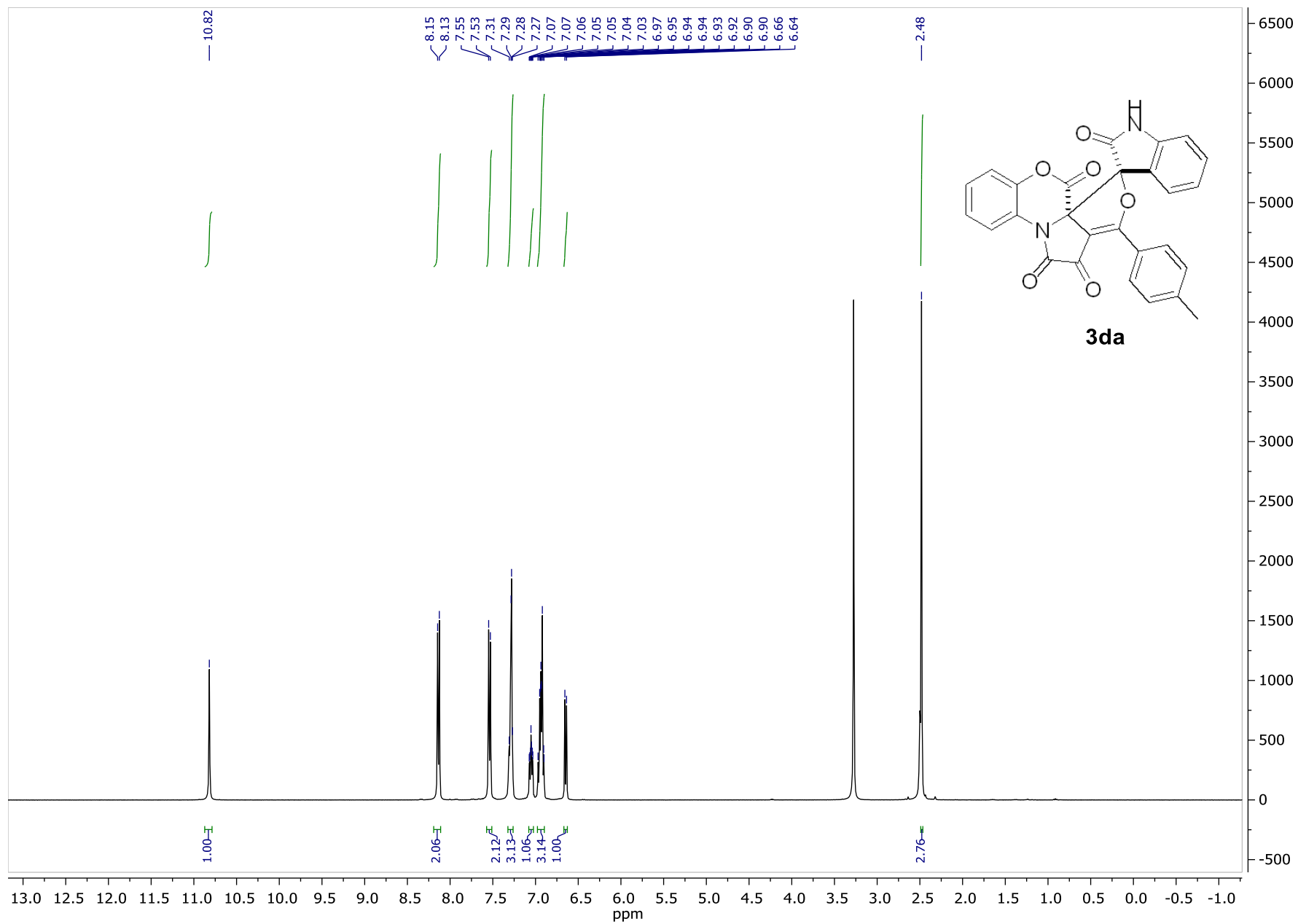
3ca ^1H (400 MHz, DMSO- d_6)



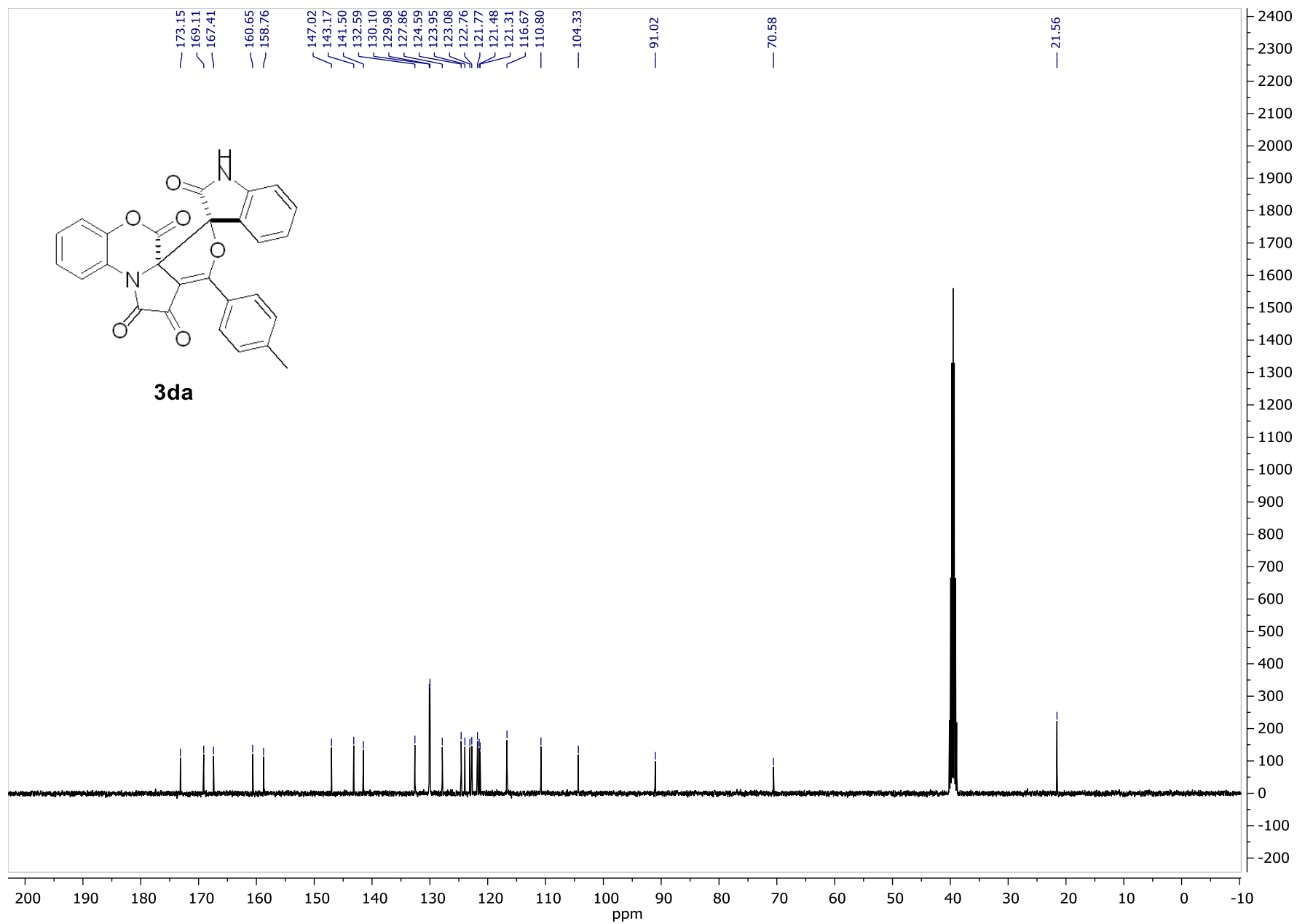
3ca ^{13}C (101 MHz, DMSO- d_6)



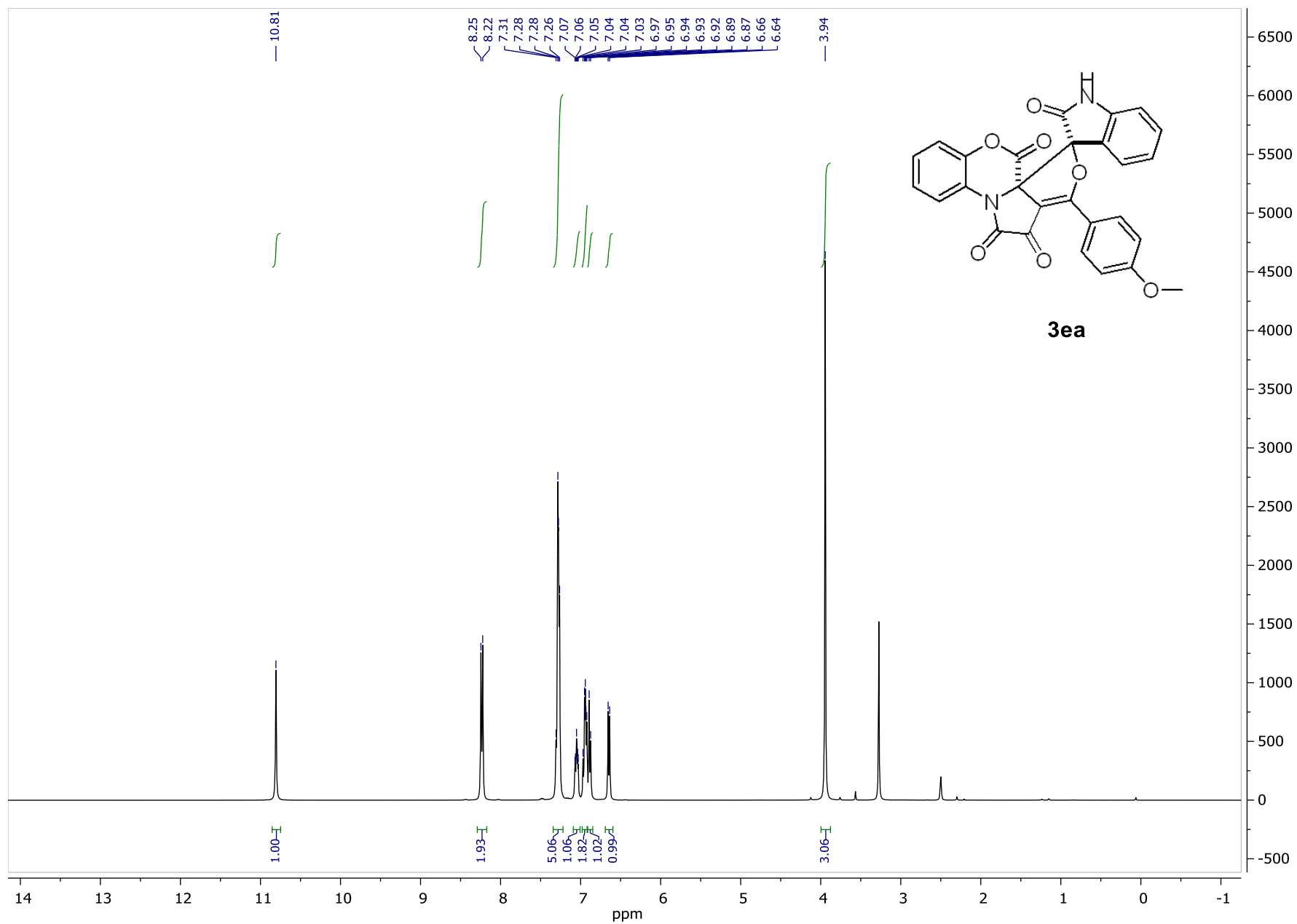
3da ^1H (400 MHz, DMSO- d_6)



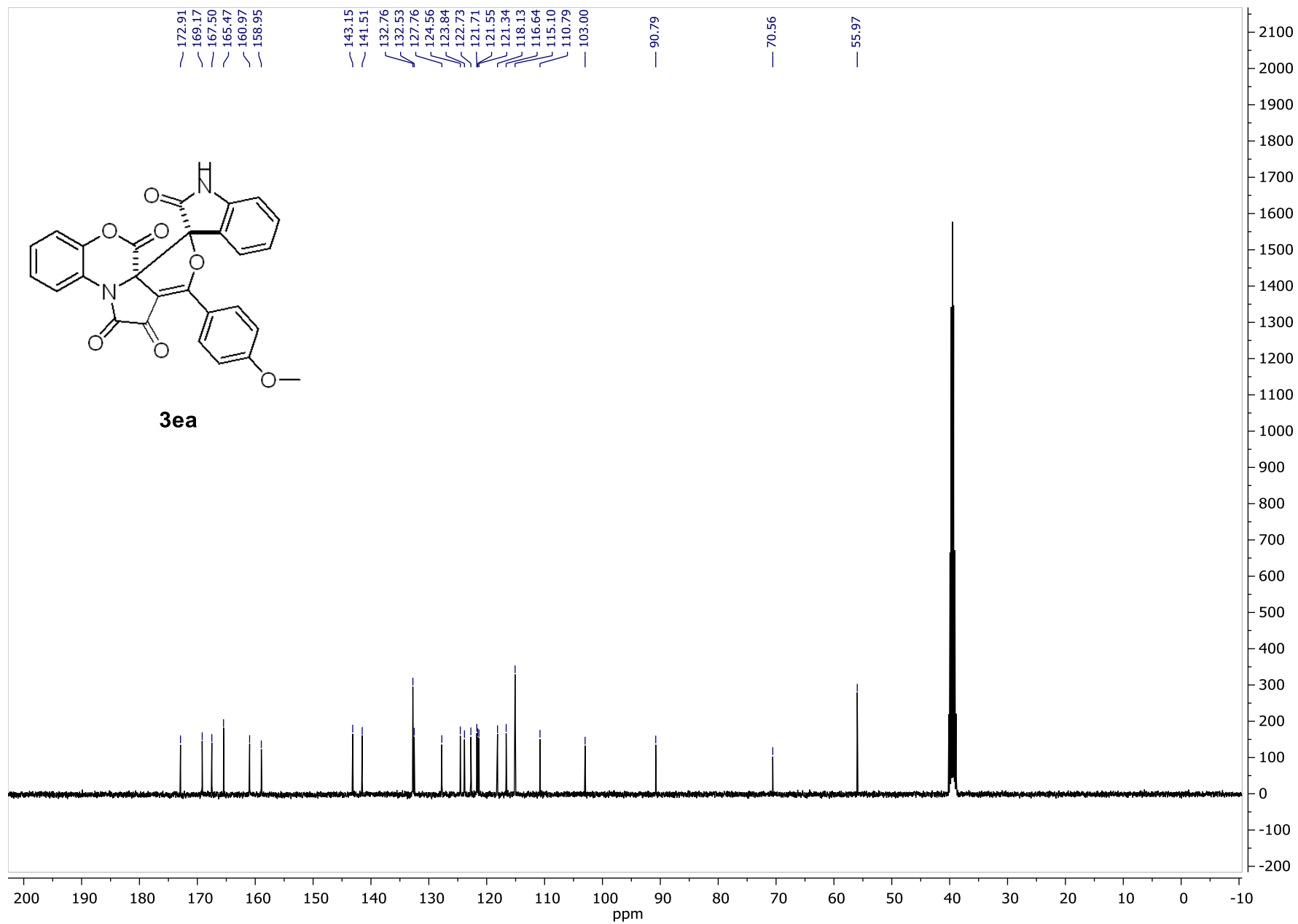
3da ^{13}C (101 MHz, $\text{DMSO}-d_6$)



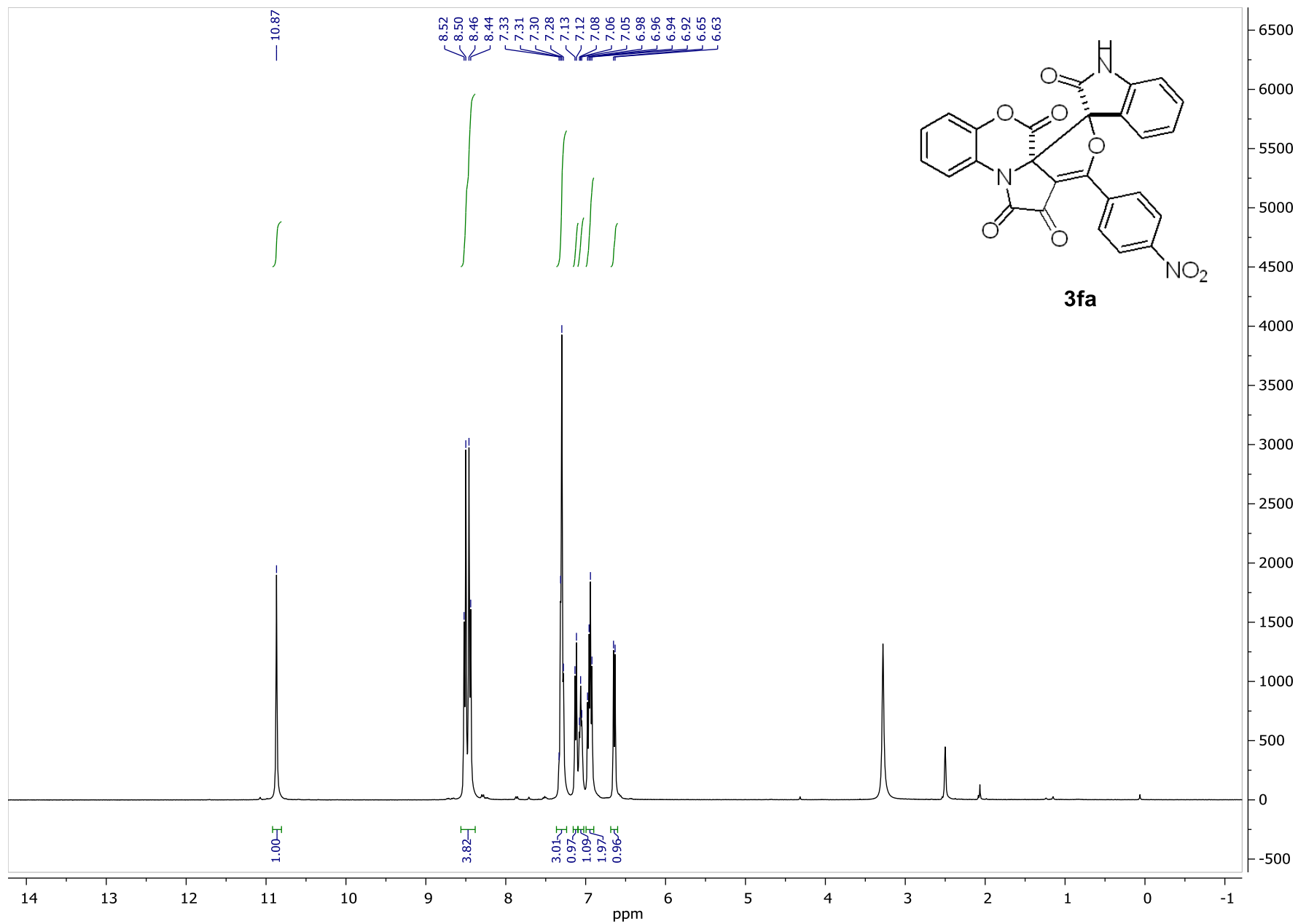
3ea ^1H (400 MHz, DMSO- d_6)



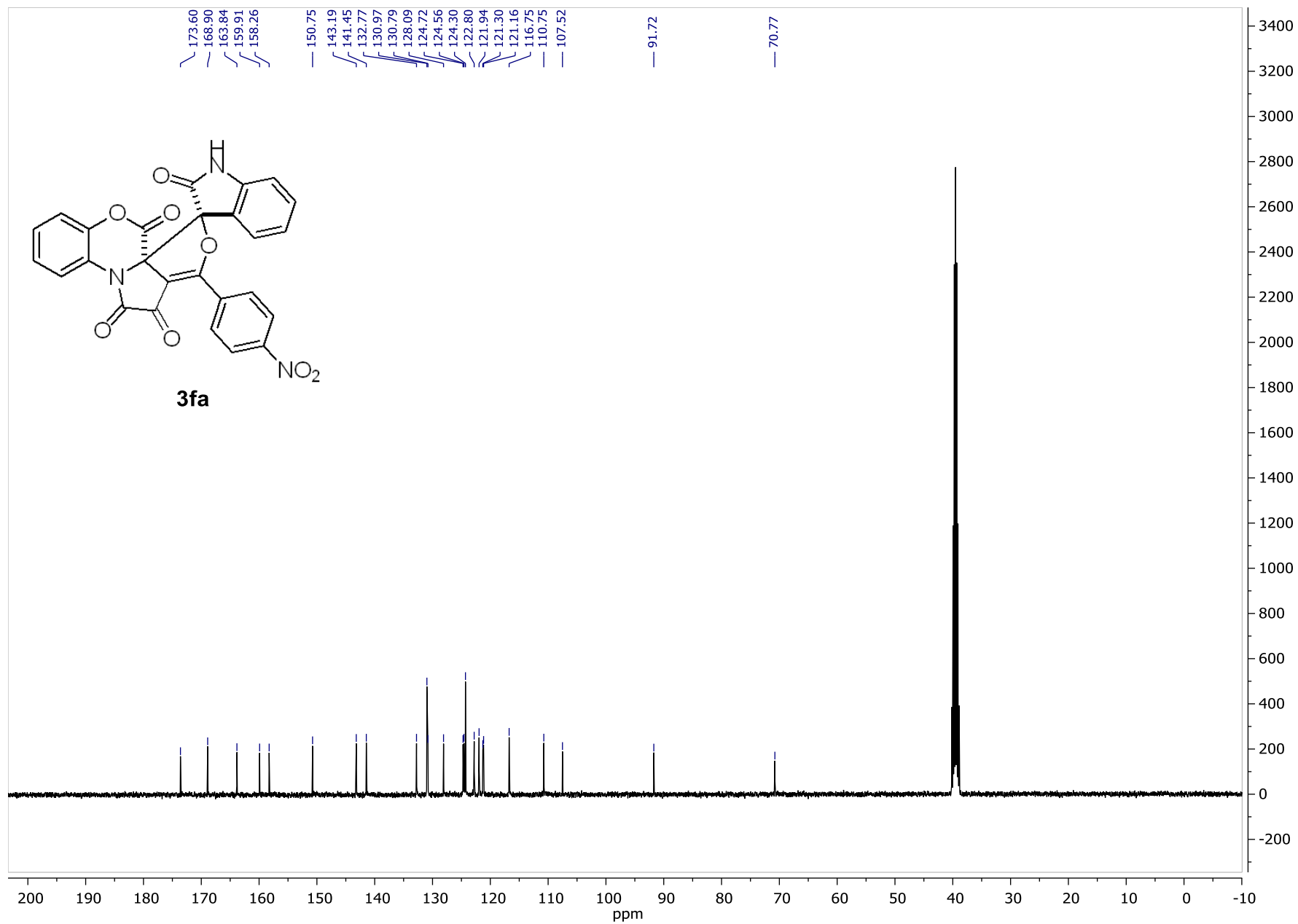
3ea ^{13}C (101 MHz, DMSO- d_6)



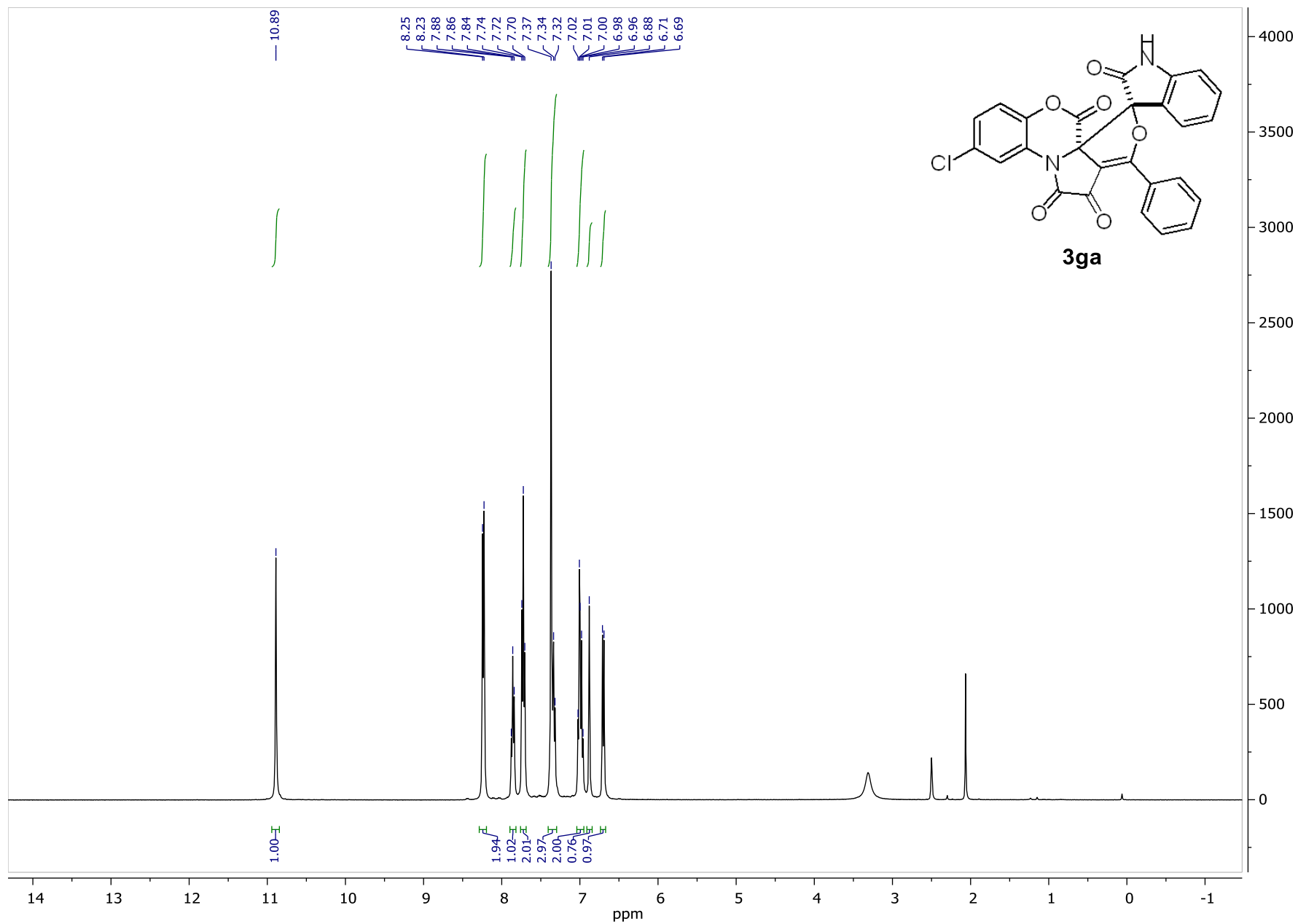
3fa ¹H (400 MHz, DMSO-*d*₆)



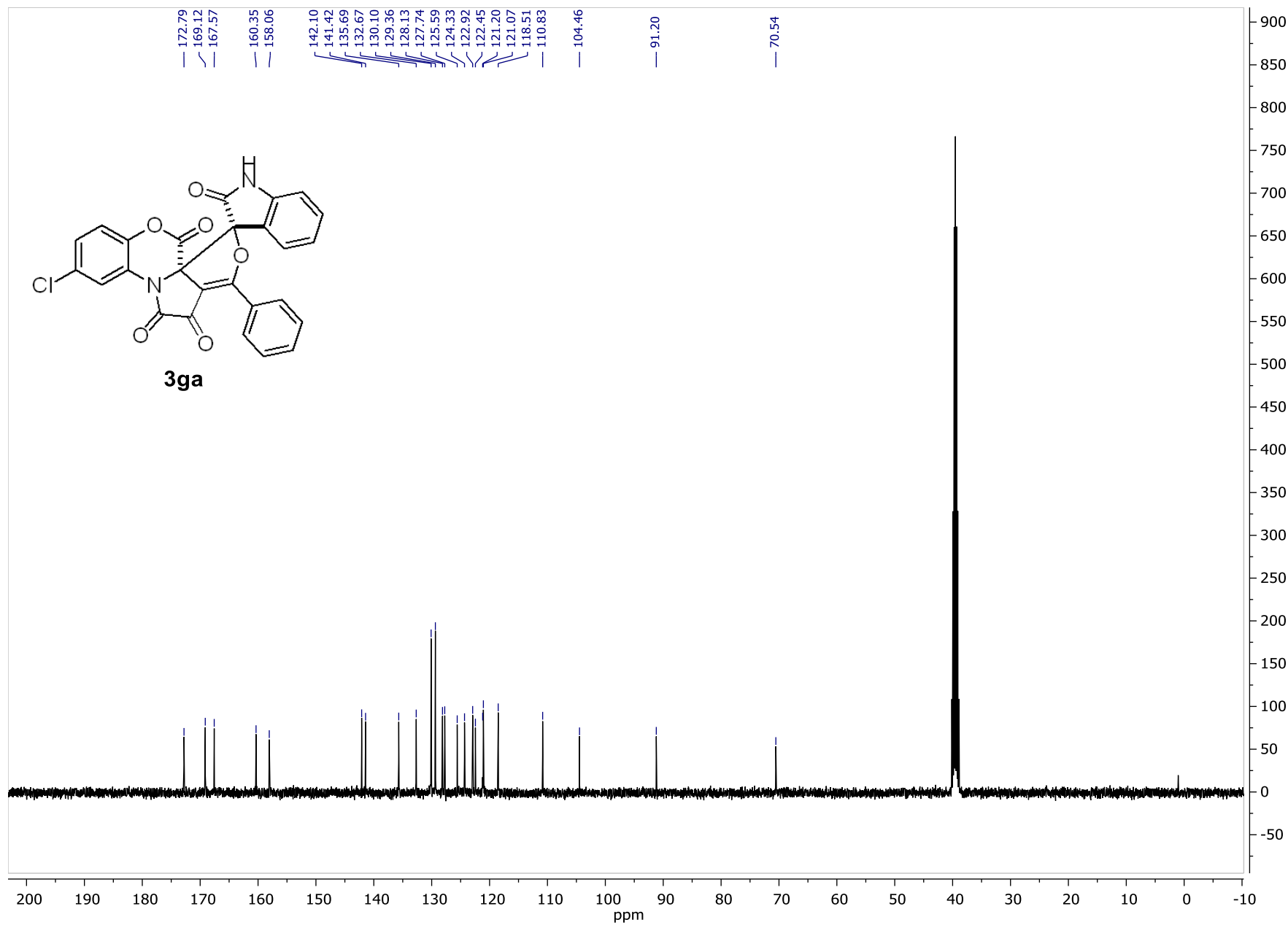
3fa ^{13}C (101 MHz, $\text{DMSO}-d_6$)



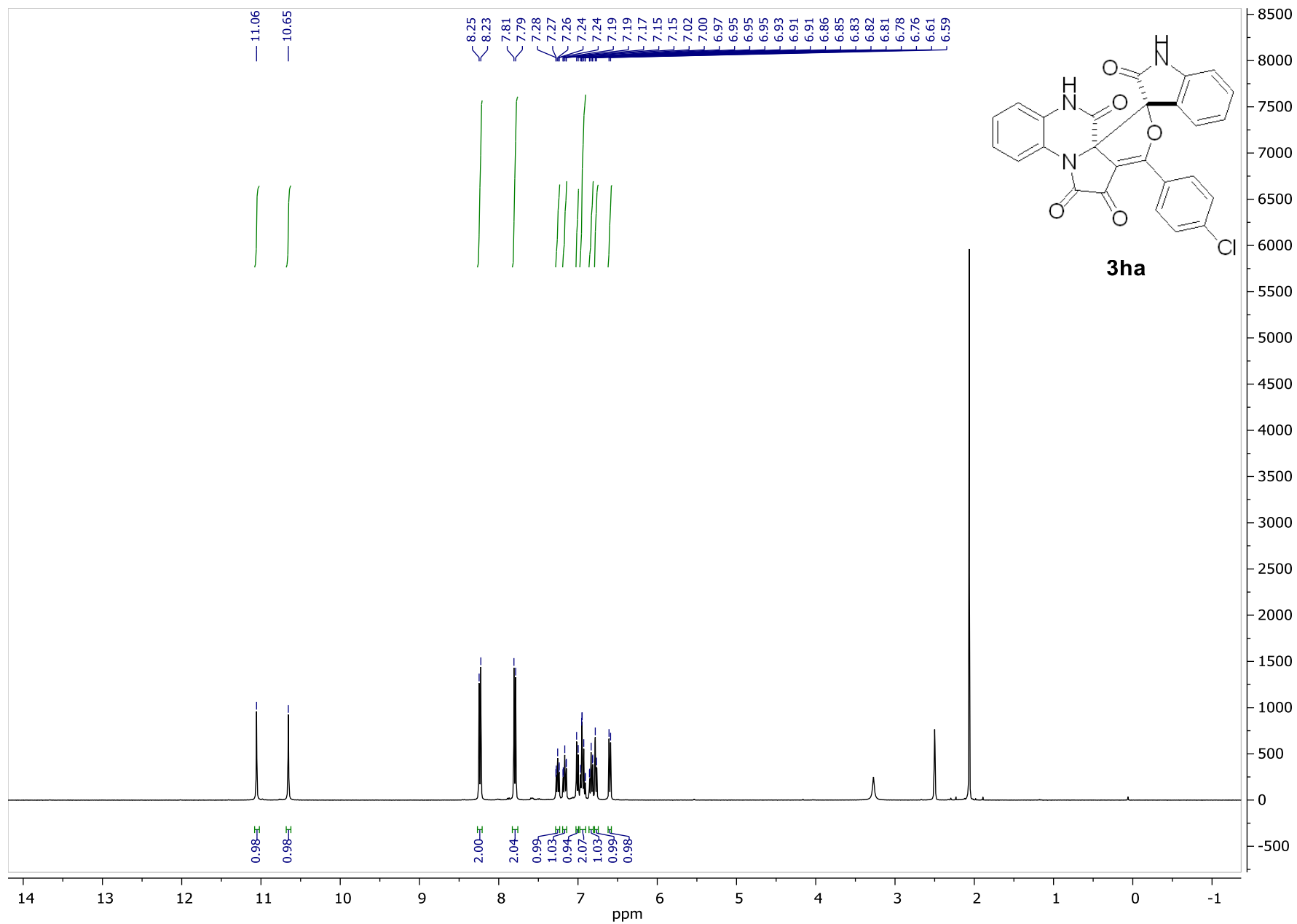
3ga ^1H (400 MHz, DMSO- d_6)



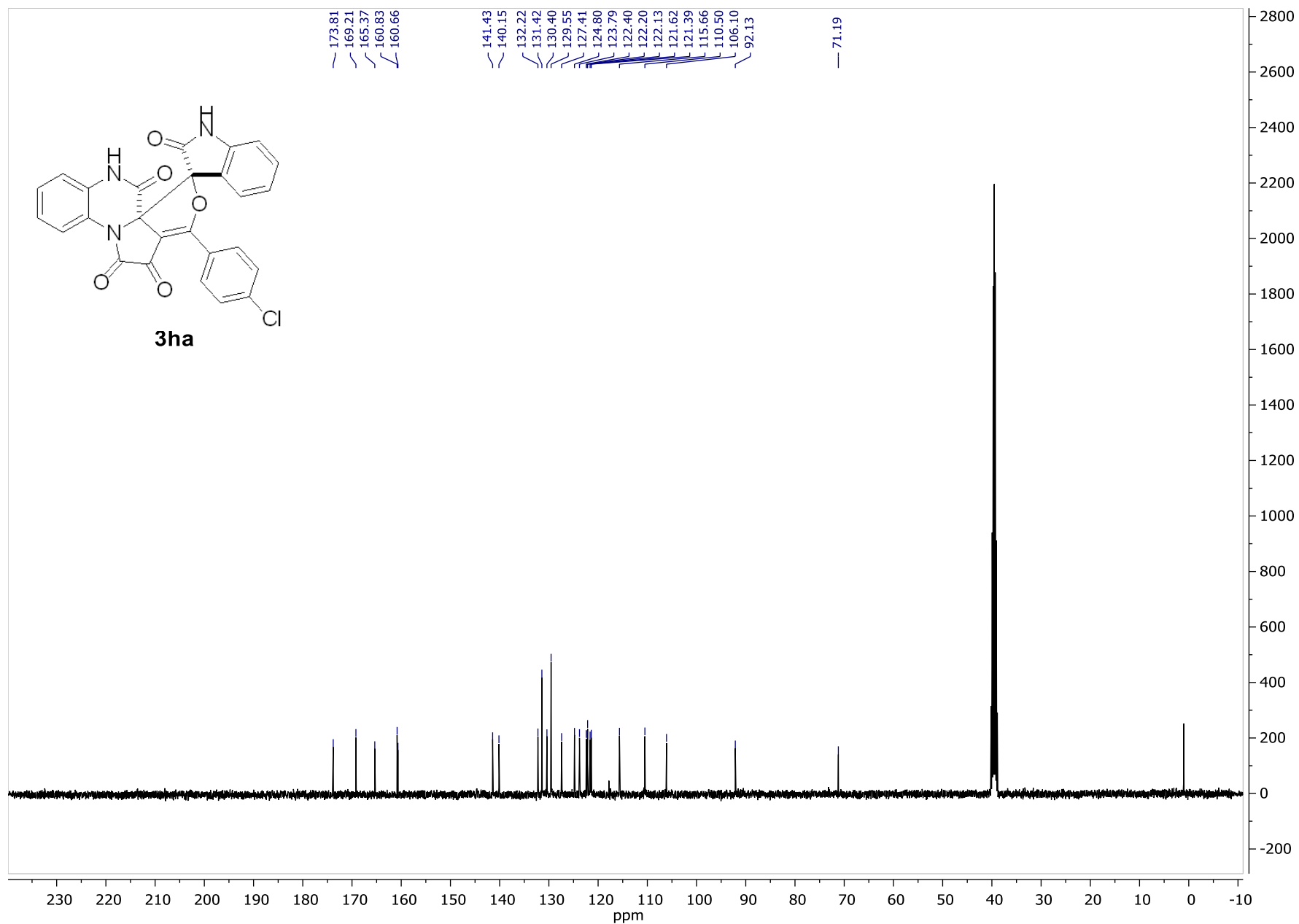
3ga ^{13}C (101 MHz, DMSO- d_6)



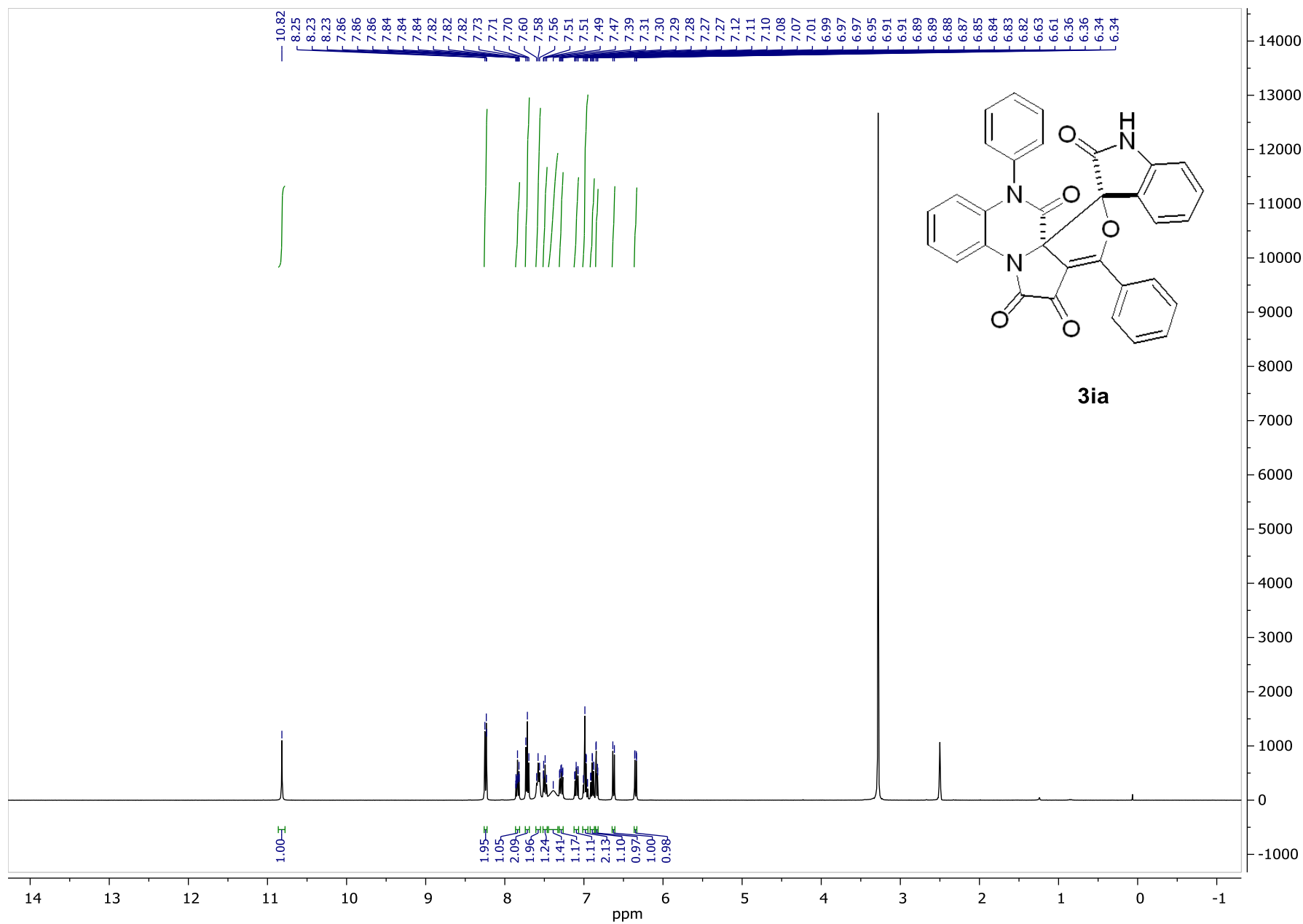
3ha ^1H (400 MHz, $\text{DMSO-}d_6$) ACN solvate 1:1



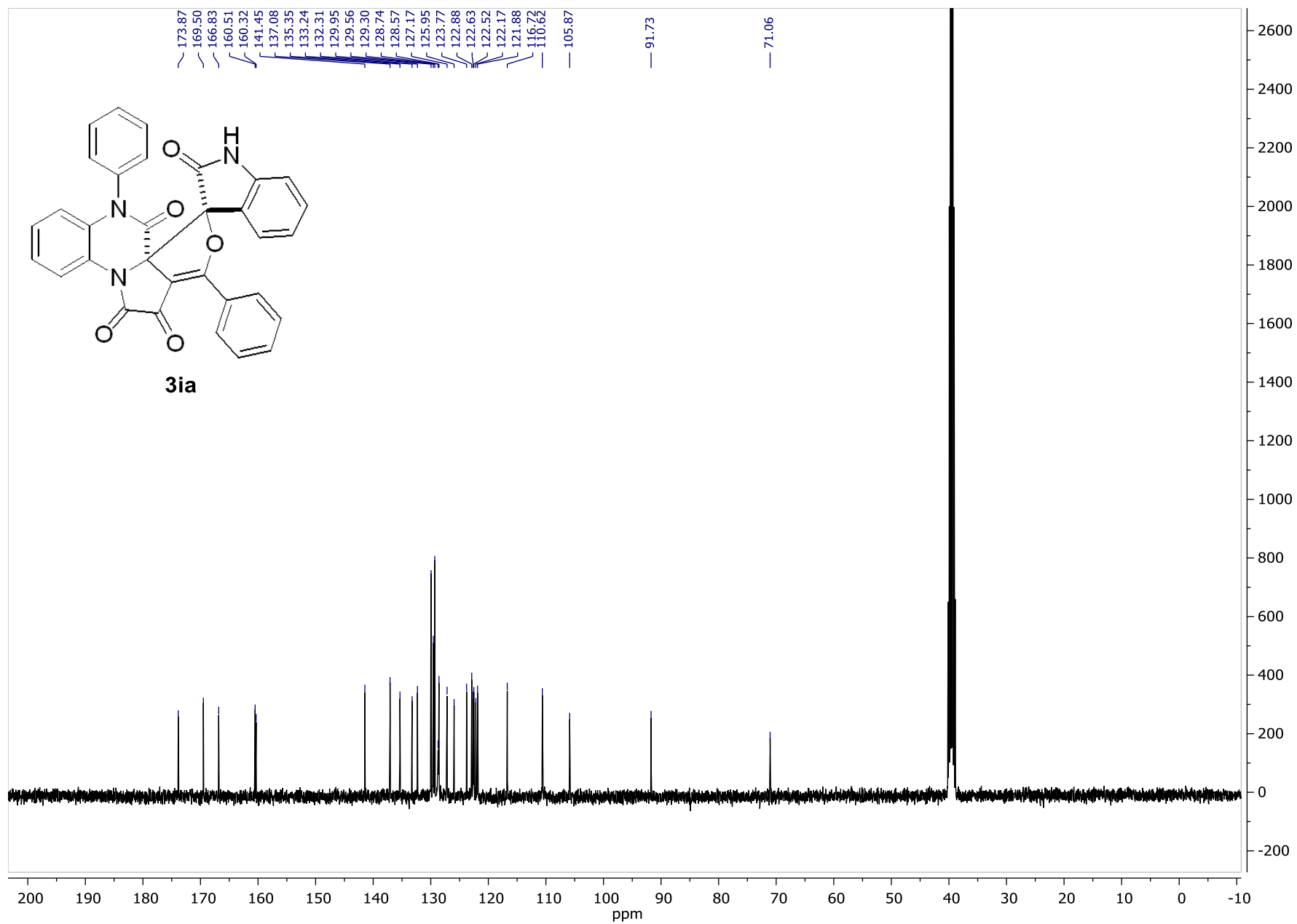
3ha ^{13}C (101 MHz, $\text{DMSO-}d_6$) ACN solvate 1:1



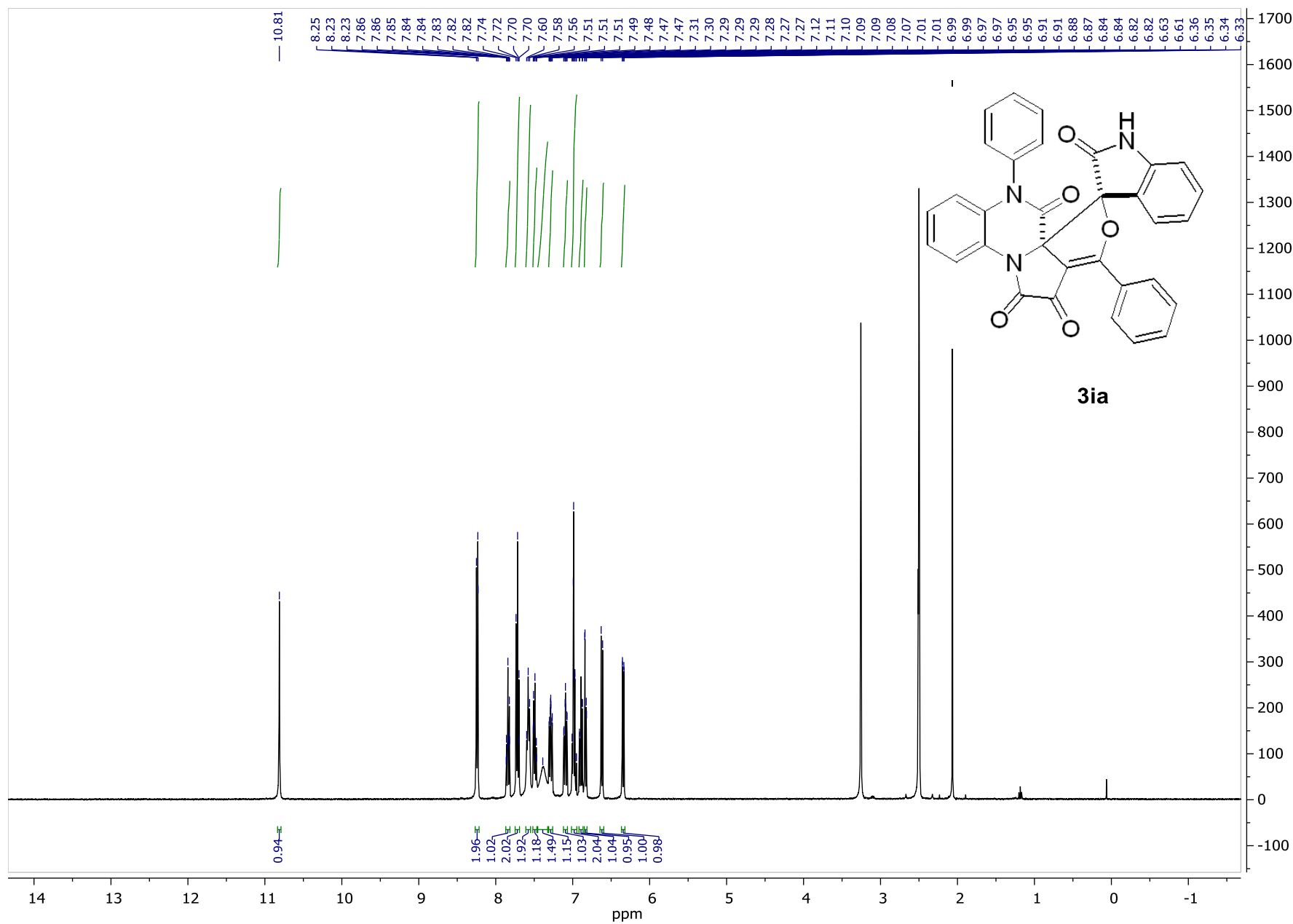
3ia ¹H (400 MHz, DMSO-*d*₆)



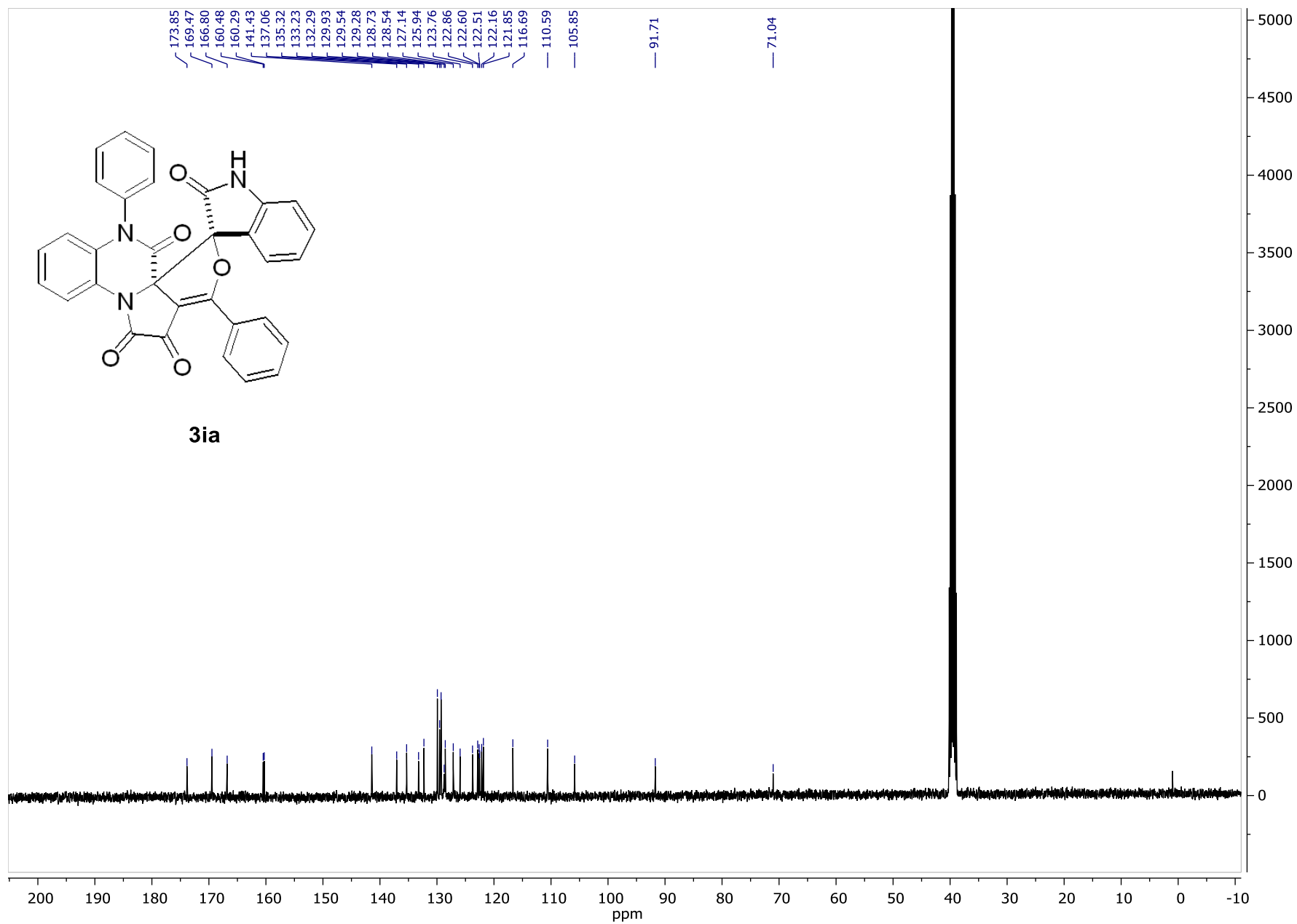
3ia ^{13}C (101 MHz, DMSO- d_6)



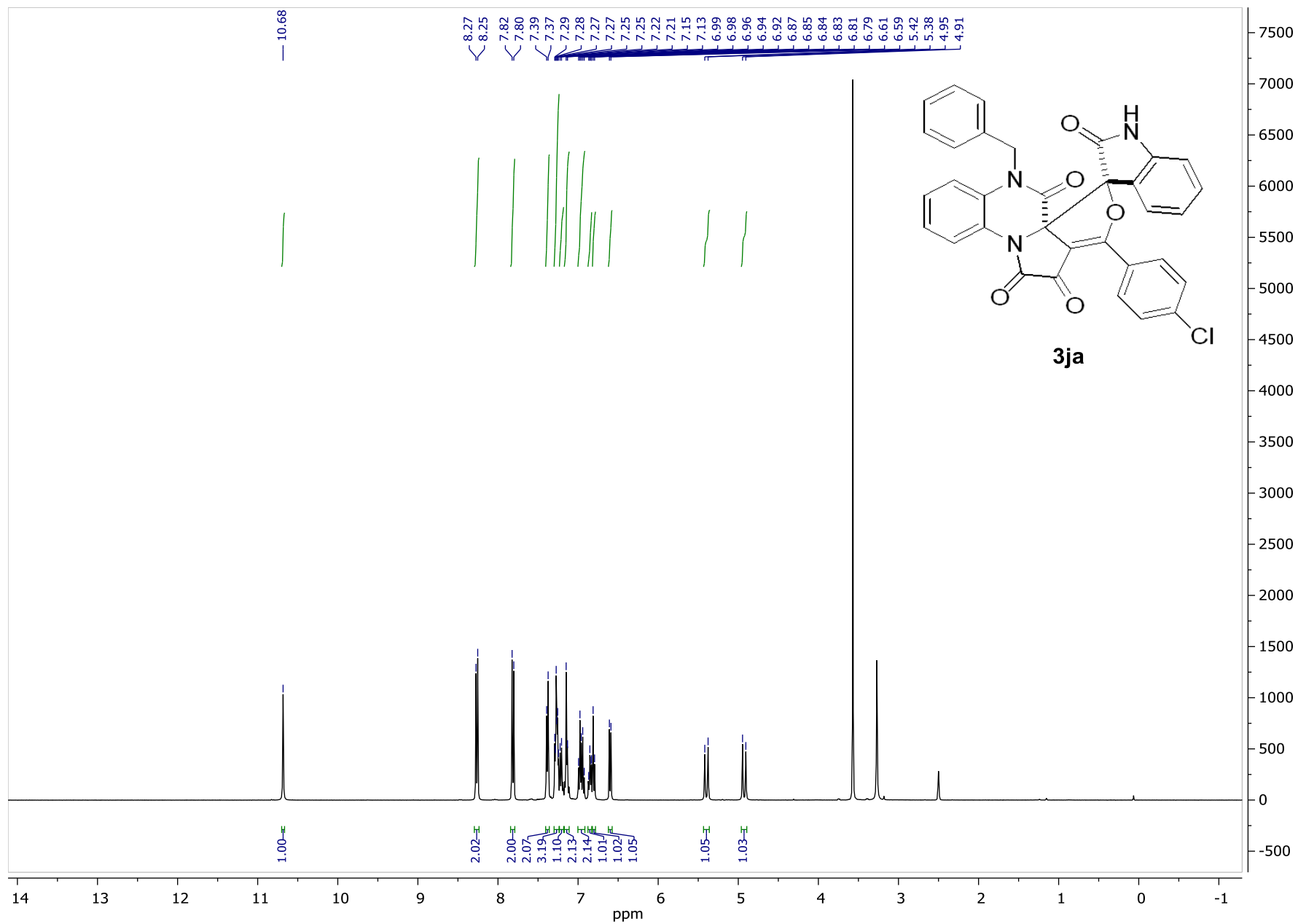
3ia (control experiment) ¹H (400 MHz, DMSO-*d*₆)



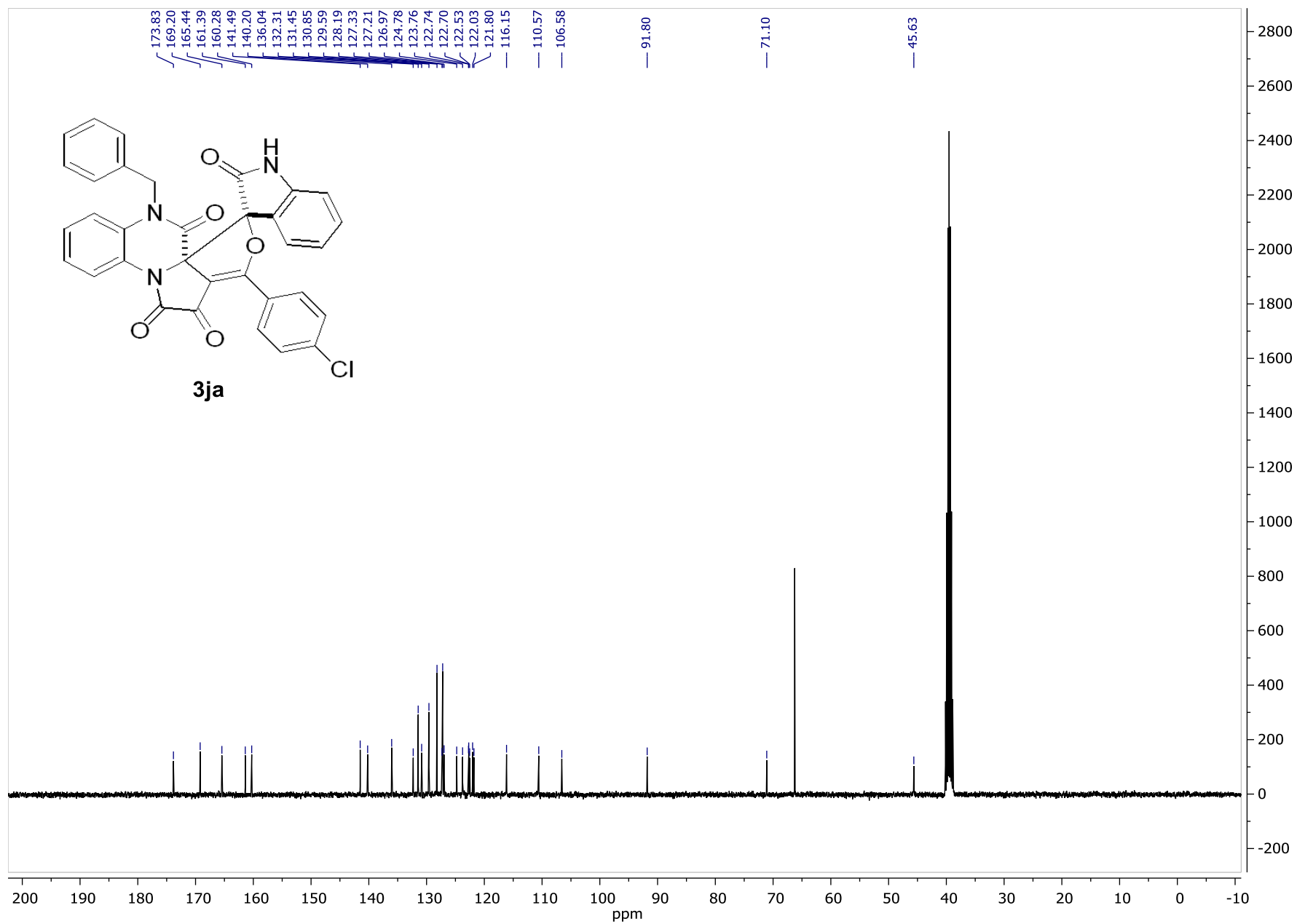
3ia (control experiment) ^{13}C (101 MHz, DMSO- d_6)



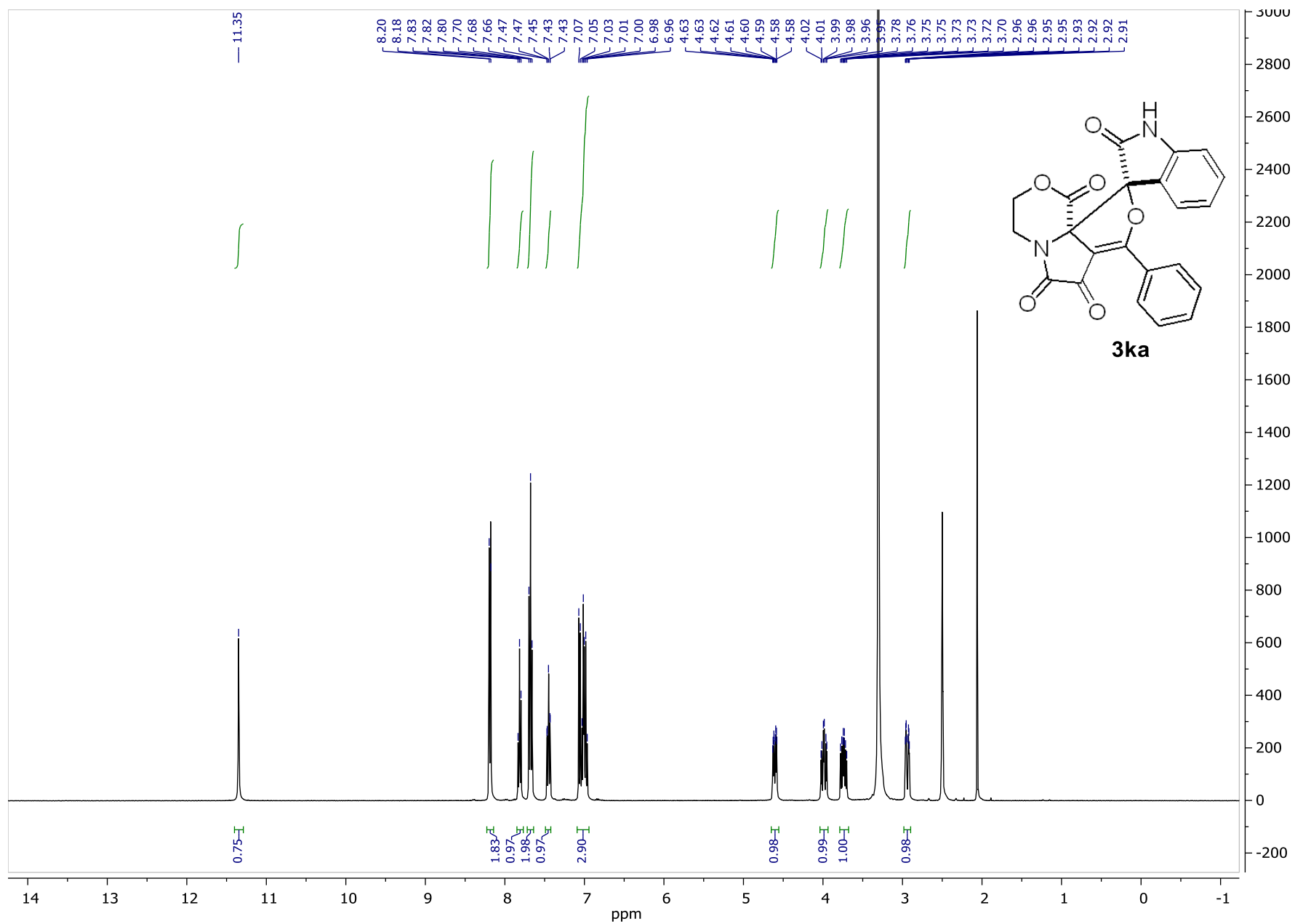
3ja ^1H (400 MHz, $\text{DMSO}-d_6$) 1,4-dioxane solvate 1:1



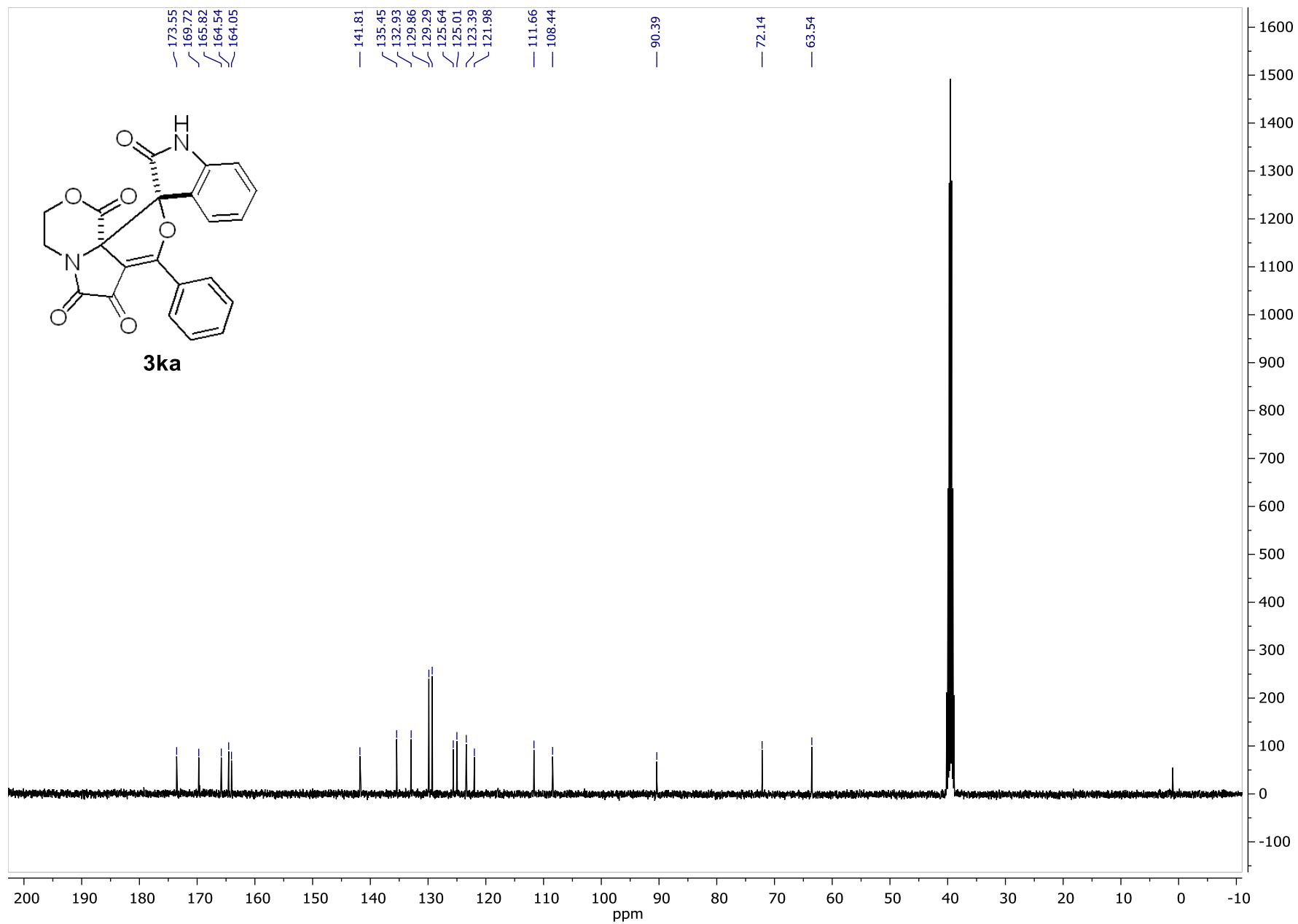
3ja ^{13}C (101 MHz, DMSO- d_6) 1,4-dioxane solvate 1:1



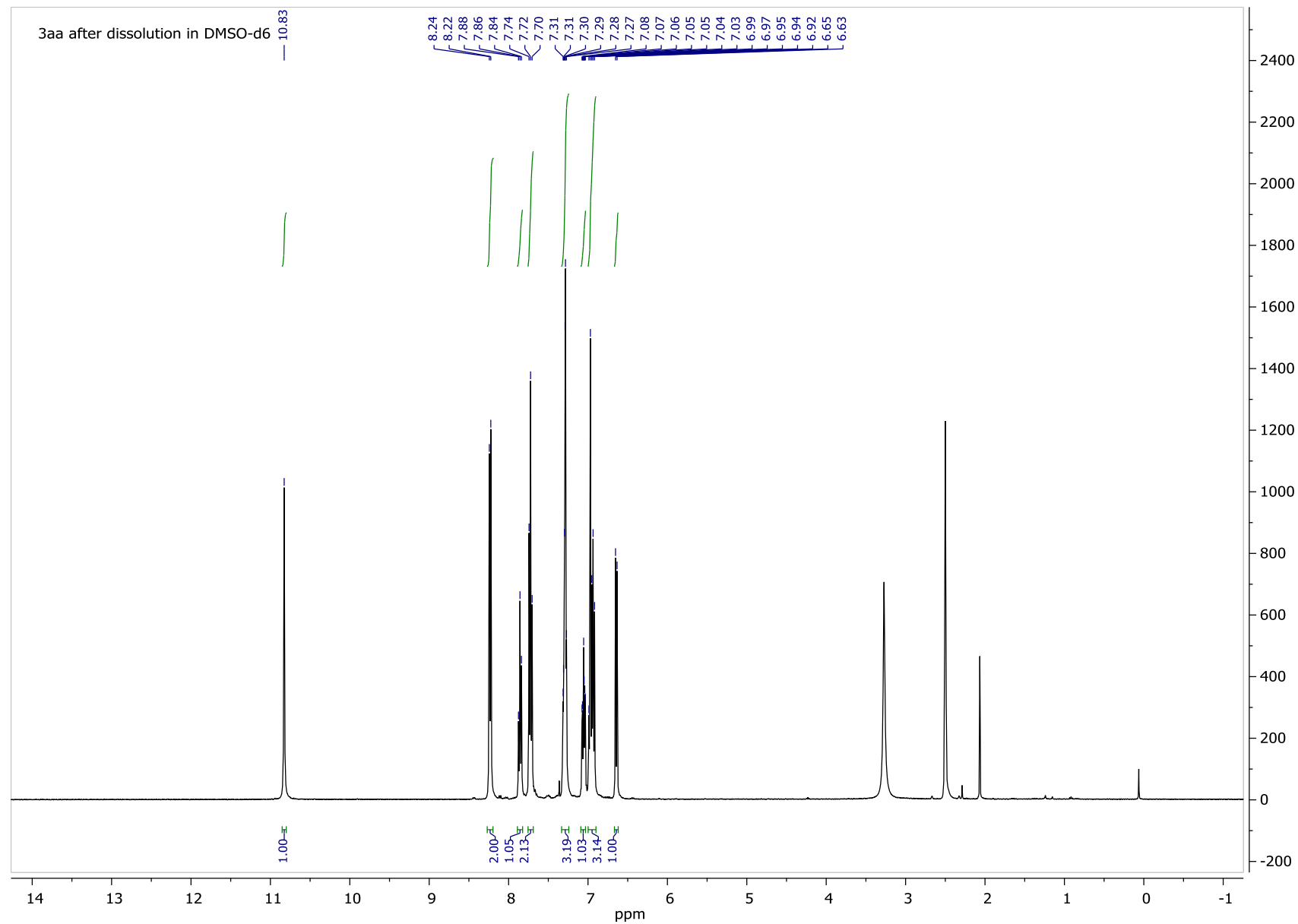
3ka ¹H (400 MHz, DMSO-d₆)

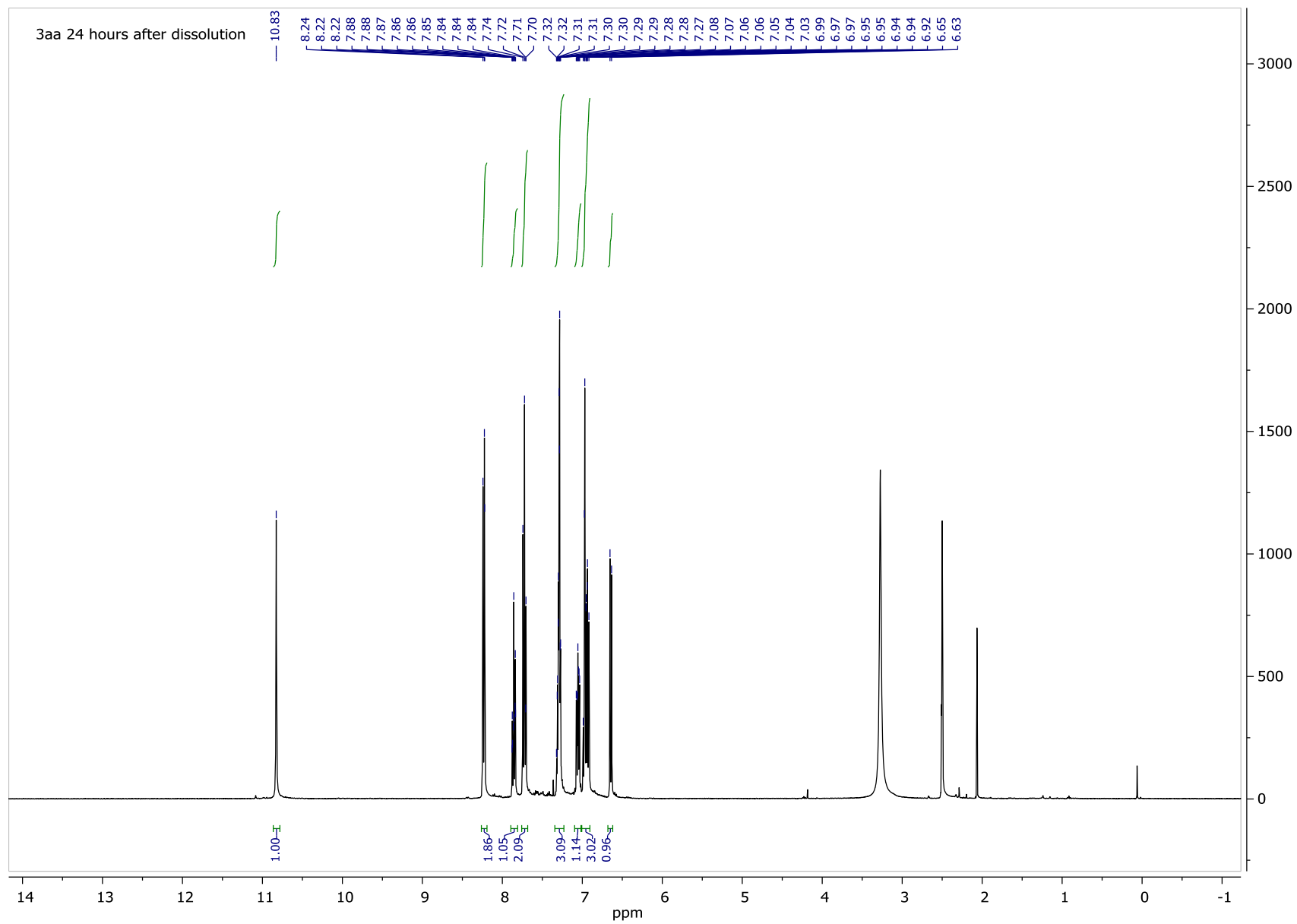


3ka ^{13}C (101 MHz, $\text{DMSO}-d_6$)



NMR charts of compound 3aa after dissolution and 24 h later





X-Ray crystal data of CCDC 2201614 (3aa)

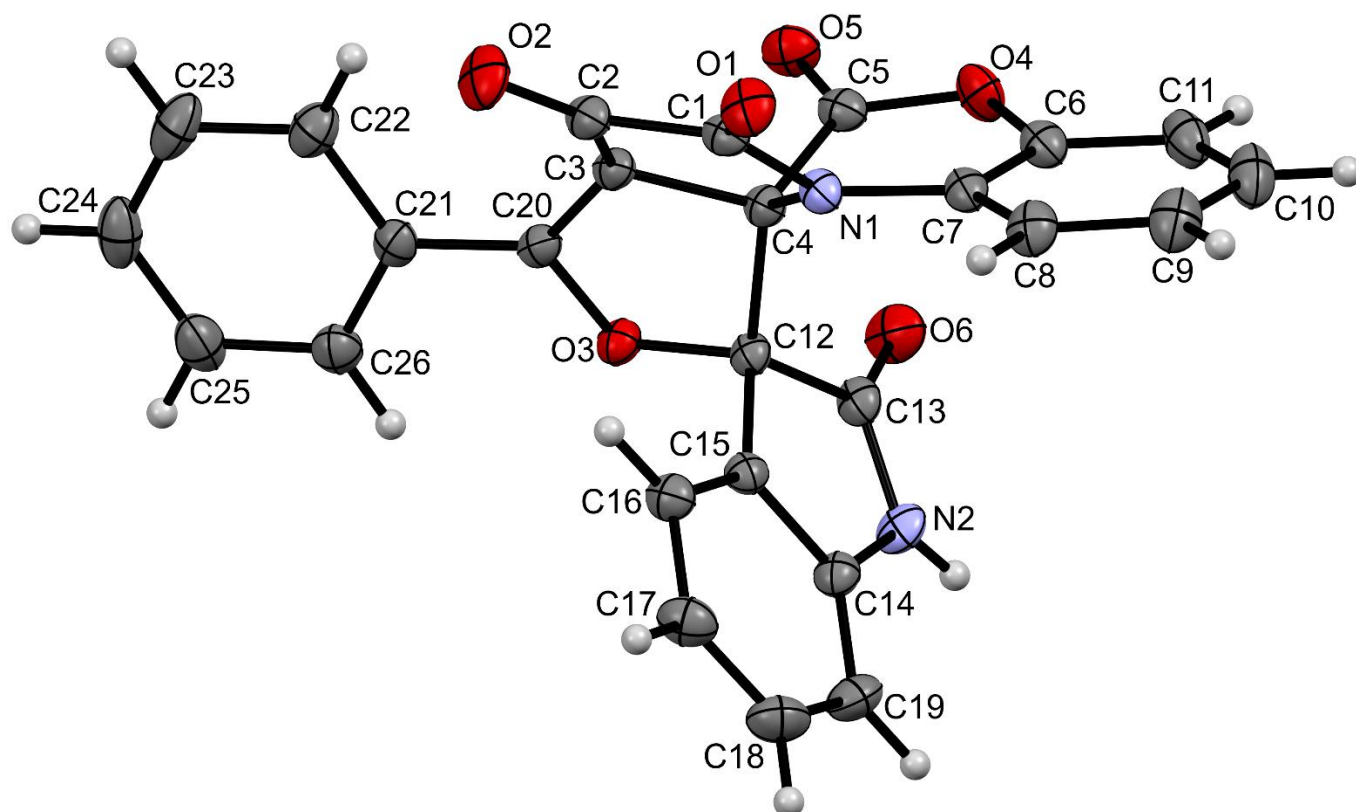


Figure S1. Molecular structure of compound **3aa** showing 30% probability amplitude displacement ellipsoids (CCDC 2201614).

Table S1. Crystal data and structure refinement for compound **3aa**.

Empirical formula	C ₂₆ H ₁₄ N ₂ O ₆
Formula weight	450.39
Temperature, K	295.15
Crystal system	triclinic
Space group	P-1
a, Å	9.1925(12)
b, Å	9.5653(12)
c, Å	12.2709(16)
α , °	79.986(11)
β , °	82.628(10)
γ , °	67.316(12)
Volume, Å ³	978.1(2)
Z	2
Density (calculated), g/cm ³	1.529
Absorption coefficient, mm ⁻¹	0.111
F(000)	464.0

Crystal size, mm ³	0.56 × 0.44 × 0.19
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection, °	6.066 to 58.674
Index ranges	-12 ≤ h ≤ 12, -8 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	7645
Independent reflections	4485 [R _{int} = 0.0275, R _{sigma} = 0.0396]
Data/restraints/parameters	4485/0/311
Goodness-of-fit on F ²	1.040
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0457, wR ₂ = 0.1113
Final R indexes [all data]	R ₁ = 0.0573, wR ₂ = 0.1219
Largest diff. peak/hole, eÅ ⁻³	0.26/-0.23

X-Ray crystal data of CCDC 2201616 (3ab)

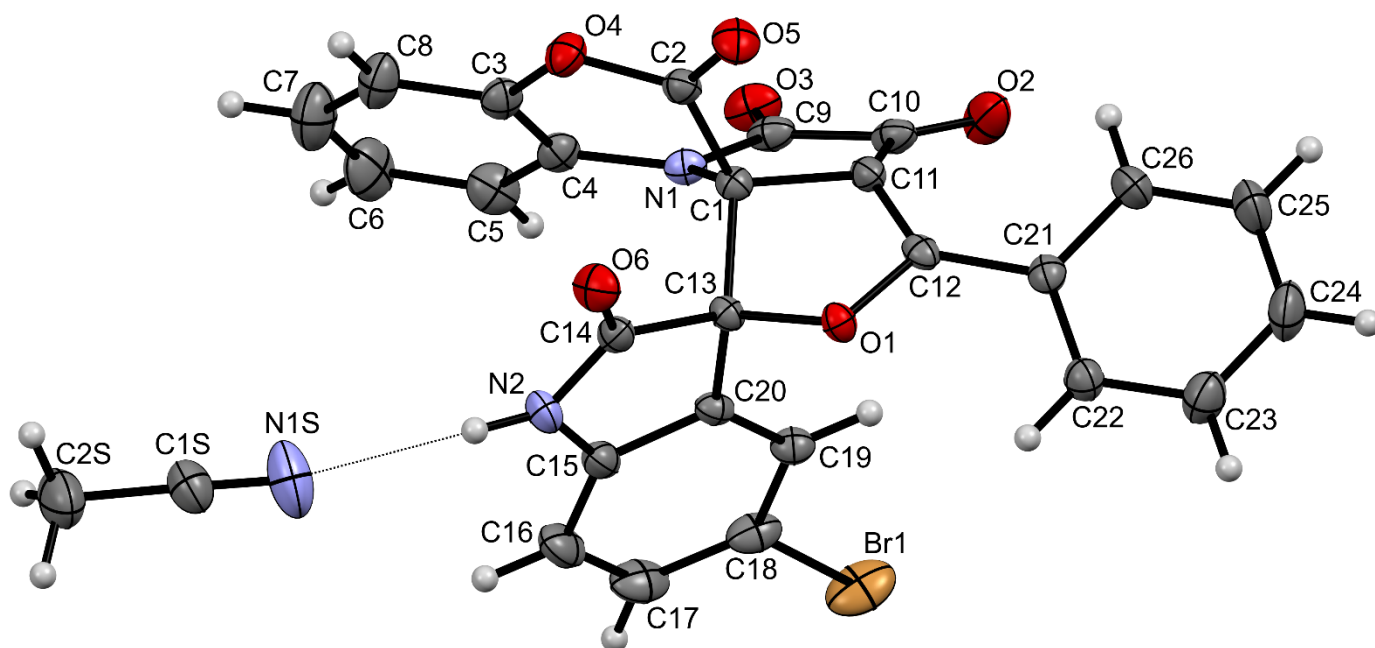


Figure S2. Molecular structure of compound **3ab** showing 30% probability amplitude displacement ellipsoids (CCDC 2201616).

Table S2. Crystal data and structure refinement for compound **3ab**.

Empirical formula	C ₂₈ H ₁₆ BrN ₃ O ₆
Formula weight	570.35
Temperature, K	295.15
Crystal system	triclinic
Space group	P-1
a, Å	8.9672(17)
b, Å	11.983(3)
c, Å	13.017(2)
α, °	107.746(17)
β, °	93.660(15)
γ, °	109.614(18)
Volume, Å ³	1233.2(4)
Z	2
Density (calculated), g/cm ³	1.536
Absorption coefficient, mm ⁻¹	1.717
F(000)	576.0
Crystal size, mm ³	0.55 × 0.5 × 0.4
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection, °	5.754 to 58.83
Index ranges	-11 ≤ h ≤ 9, -15 ≤ k ≤ 16, -17 ≤ l ≤ 16

Reflections collected	10367
Independent reflections	5707 [$R_{\text{int}} = 0.0369$, $R_{\text{sigma}} = 0.0656$]
Data/restraints/parameters	5707/1/348
Goodness-of-fit on F^2	1.021
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0576$, $wR_2 = 0.1315$
Final R indexes [all data]	$R_1 = 0.0935$, $wR_2 = 0.1578$
Largest diff. peak/hole, $\text{e}\text{\AA}^{-3}$	0.91/-1.23

X-Ray crystal data of CCDC 2201615 (3ha)

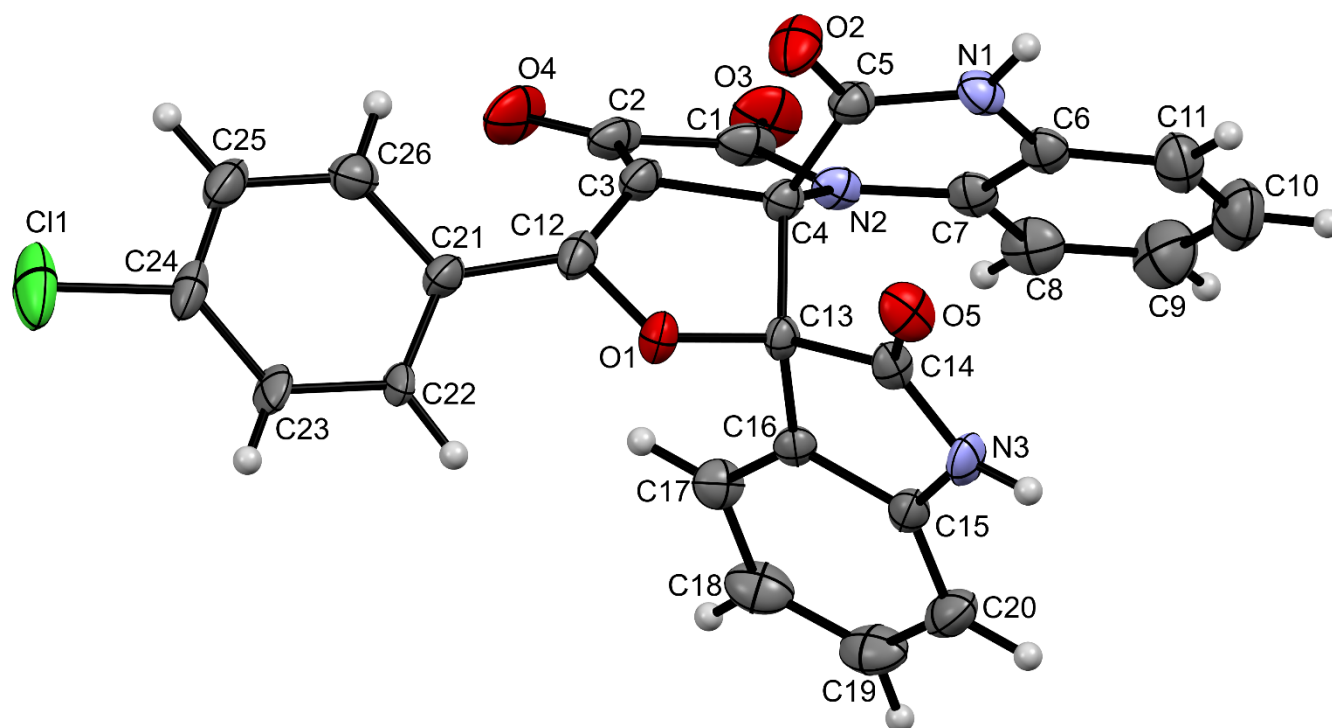


Figure S3. Molecular structure of compound **3ha** showing 30% probability amplitude displacement ellipsoids (CCDC 2201615).

Table S3. Crystal data and structure refinement for compound **3ha**.

Empirical formula	C ₂₆ H ₁₄ ClN ₃ O ₅
Formula weight	483.85
Temperature, K	295.15
Crystal system	monoclinic
Space group	C2/c
a, Å	22.204(3)
b, Å	11.7801(15)
c, Å	17.325(2)
α , °	90
β , °	90.997(12)
γ , °	90
Volume, Å ³	4531.0(11)
Z	8
Density (calculated), g/cm ³	1.419
Absorption coefficient, mm ⁻¹	0.213
F(000)	1984.0
Crystal size, mm ³	0.5 × 0.3 × 0.2
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection, °	6.016 to 58.588

Index ranges	$-20 \leq h \leq 28, -10 \leq k \leq 16, -21 \leq l \leq 22$
Reflections collected	11513
Independent reflections	5313 [$R_{\text{int}} = 0.0414, R_{\text{sigma}} = 0.0537$]
Data/restraints/parameters	5313/84/384
Goodness-of-fit on F^2	1.032
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0509, wR_2 = 0.1263$
Final R indexes [all data]	$R_1 = 0.0812, wR_2 = 0.1488$
Largest diff. peak/hole, $\text{e}\text{\AA}^{-3}$	0.21/-0.26

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