



Supporting Information

for

***N*-Boc- α -diazo glutarimide as efficient reagent for assembling *N*-heterocycle-glutarimide diads via Rh(II)-catalyzed N–H insertion reaction**

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General experimental information, X-ray crystallographic data, synthetic procedures, analytical data and NMR spectra for the reported compounds

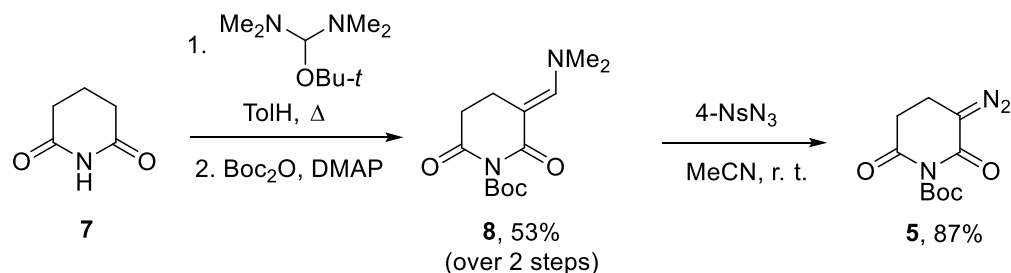
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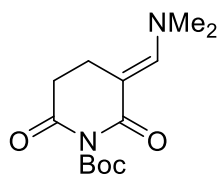
1. Experimental procedures and characterization data

General considerations. All reagents were used as purchased from commercial suppliers without further purification. Dichloromethane (DCM) was freshly distilled over P₂O₅. NMR spectra were recorded using Bruker Avance III spectrometer in CDCl₃ or DMSO-*d*₆ (¹H: 400.13 MHz; ¹³C: 100.61 MHz; ¹⁹F 376.50 MHz); chemical shifts are reported as parts per million (δ, ppm); the residual solvent peaks were used as internal standard: 7.26 or 2.5 for ¹H and 77.16 or 39.7 ppm for ¹³C in CDCl₃ or DMSO-*d*₆, respectively; multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet/doublets of doublets; coupling constants, *J*, are reported in Hz. Mass spectra were recorded using a Bruker microTOF spectrometer (ionization by electrospray, positive ions detection). Melting points were determined in open capillary tubes on a Stuart SMP50 Automatic Melting Point Apparatus. Analytical thin-layer chromatography was carried out on UV-254 silica gel plates using appropriate eluents. Compounds were visualized with short-wavelength UV light. Column chromatography was performed using silica gel Merk grade 60 (0.040–0.063 mm) 230–400 mesh.

Synthesis of diazo reagent 5



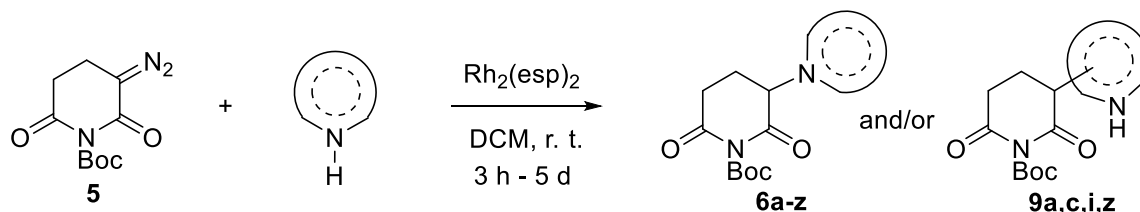
***tert*-Butyl (*E*)-3-((dimethylamino)methylene)-2,6-dioxopiperidine-1-carboxylate (8).** Glutarimide 7 (4.52 g, 0.04 mol) was placed in a 100 mL round bottom flask, followed by 30 mL of anhydrous toluene and Bredereck's reagent (9.07 mL, 0.044 mol). The resulting mixture was stirred at 75 °C for 5 h. After cooling to room temperature, the precipitate was filtered off, washed with 2 × 5 mL of toluene and 2 × 10 mL of petroleum ether and dried in air to obtain 3.59 g of light-yellow crystals which were used in the next step.



α-Dimethylaminomethylene glutarimide (3.57 g, 0.021 mol), Boc₂O (5.0 g, 0.023 mol) and DMAP (0.122 g, 1.0 mmol) were mixed with 40 mL of anhydrous DCM in a 100 mL round bottom flask. The reaction mixture was stirred overnight at room temperature. The product was isolated by column chromatography (80 g silica, eluted with DCM). Yield: 5.63 g (53%). Light-yellow solid; m.p. 139.1–140.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (s, 1 H), 3.11 (s, 6 H), 2.84–2.81 (m, 2 H), 2.59–2.55 (m, 2 H), 1.57 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 170.3, 167.1, 150.8, 150.3, 90.6, 84.9, 43.5, 32.2, 27.5, 19.4 ppm. HRMS (ESI), *m/z* calcd for C₁₃H₂₀N₂NaO₄ [M+Na]⁺ 291.1315 found 291.1302.

tert-Butyl 3-diazo-2,6-dioxopiperidine-1-carboxylate (5). Boc-protected dimethylaminomethylene glutarimide (**8**) (1.072 g, 4 mmol) was dissolved in 8 mL of anhydrous acetonitrile. *p*-Nosylazide (0.958 g, 4.2 mmol) was added, and the mixture was stirred overnight at room temperature. Volatiles were evaporated, and the residue was purified by column chromatography (40 g silica, eluted with 10–50% acetone in *n*-hexane). Yield: 0.83 g (87%). Light-yellow or greenish yellow solid; m.p. 92.7–93.1 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 2.92–2.88 (m, 2 H), 2.78–2.74 (m, 2 H), 1.48 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 169.5, 164.5, 149.0, 85.9, 55.8, 30.8, 27.5, 15.5 ppm. HRMS (ESI), *m/z* calcd for C₁₀H₁₃N₃NaO₄ [M+Na]⁺ 262.0798 found 262.0801.

General procedure GP1 for the preparation of compounds 6a–z, 9a,c,i,z.

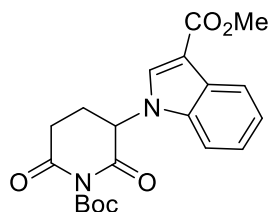


To a solution/suspension of the corresponding NH-substrate (0.33 mmol, 1 equiv) in DCM (1 mL) was added the catalyst solution (2.5 mM Rh₂(esp)₂ in DCM, 100 μL, 0.06 mol %). To the vigorously stirred mixture the solution of diazo reagent **5** (96 mg, 0.4 mmol, 1.2 equiv) in DCM (1 mL) was added during 1–2 minutes. The reaction mixture was stirred at ambient temperature until full consumption of starting material (controlled by TLC). If starting materials were present after 16 h additional portion of the catalyst solution was added and stirring was continued for another day. Upon full conversion of diazo reagent, the reaction mixture was directly subjected to column chromatography on silica gel (*n*-hexane–acetone) to afford pure product.

tert-Butyl 3-(1*H*-indol-1-yl)-2,6-dioxopiperidine-1-carboxylate (6a). Prepared according to GP1 using indole as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 51 mg (47%). White solid; m.p. 145.7–148.5 °C (decomp.). ¹H NMR (400 MHz, CDCl₃) δ 7.69–7.66 (m, 1 H), 7.27–7.26 (m, 2 H), 7.19–7.15 (m, 1 H), 7.09 (d, *J* = 3.3 Hz, 1 H), 6.64 (d, *J* = 3.3 Hz, 1 H), 5.18 (dd, *J* = 12.7, 5.0 Hz, 1 H), 3.05–2.99 (m, 1 H), 2.95–2.86 (m, 1 H), 2.71–2.60 (m, 1 H), 2.43–2.36 (m, 1 H), 1.59 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.6, 167.1, 147.9, 136.2, 128.7, 125.4, 122.4, 121.5, 120.3, 109.1, 103.7, 87.2, 55.9, 31.6, 27.4, 24.4 ppm. HRMS (ESI), *m/z* calcd for C₁₈H₂₀N₂NaO₄ [M+Na]⁺ 351.1315 found 351.1306.

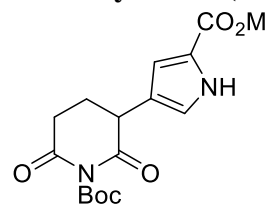
tert-Butyl 3-(1*H*-indol-3-yl)-2,6-dioxopiperidine-1-carboxylate (9a). Yield: 24 mg (22%). Pale yellow amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 8.39 (br. s, 1 H), 7.55 (d, *J* = 7.9 Hz, 1 H), 7.38 (d, *J* = 8.1 Hz, 1 H), 7.25–7.21 (m, 1 H), 7.17–7.13 (m, 1 H), 7.01–7.00 (m, 1 H), 4.20–4.17 (m, 1 H), 2.74–2.70 (m, 2 H), 2.39–2.28 (m, 2 H), 1.62 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 171.4, 170.4, 149.3, 136.4, 126.1, 122.6, 122.4, 119.9, 118.6, 111.7, 111.1, 86.5, 39.9, 30.6, 27.5, 24.2 ppm. HRMS (ESI), *m/z* calcd for C₁₈H₂₀N₂NaO₄ [M+Na]⁺ 351.1315 found 351.1305.

Methyl 1-(1-(*tert*-butoxycarbonyl)-2,6-dioxopiperidin-3-yl)-1*H*-indole-3-carboxylate (6b). Prepared



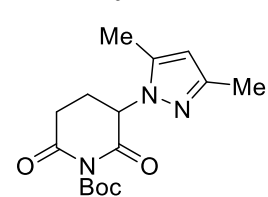
according to GP1 using methyl indole-3-carboxylate as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 102 mg (80%). White solid; m.p. 147.9–149.2 °C (decomp.). ¹H NMR (400 MHz, CDCl₃) δ 8.26–8.22 (m, 1 H), 7.85 (s, 1 H), 7.34–7.29 (m, 3 H), 5.22 (dd, *J* = 13.0, 5.0 Hz, 1 H), 3.93 (s, 3 H), 3.10–3.03 (m, 1 H), 2.98–2.89 (m, 1 H), 2.74–2.63 (m, 1 H), 2.48–2.41 (m, 1 H), 1.59 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.2, 166.3, 165.1, 147.7, 136.7, 132.0, 126.5, 123.6, 122.6, 122.2, 109.6, 109.4, 87.5, 56.2, 51.2, 31.5, 27.4, 24.3 ppm. HRMS (ESI), *m/z* calcd for C₂₀H₂₂N₂NaO₆ [M+Na]⁺ 409.1370 found 409.1370.

***tert*-Butyl 3-(5-(methoxycarbonyl)-1*H*-pyrrol-3-yl)-2,6-dioxopiperidine-1-carboxylate (9c).**



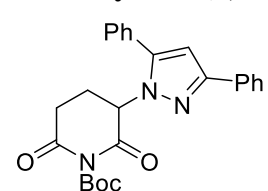
Prepared according to GP1 using methyl pyrrole-2-carboxylate as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 22 mg (20%). White amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 9.92 (br. s, 1 H), 6.89–6.87 (m, 1 H), 6.14–6.12 (m, 1 H), 3.94–3.90 (m, 1 H), 3.85 (s, 3 H), 2.89 (dt, *J* = 17.6, 5.1 Hz, 1 H), 2.79–2.71 (m, 1 H), 2.48–2.30 (m, 2 H), 1.58 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.9, 169.4, 161.4, 148.5, 130.8, 123.2, 115.5, 108.6, 86.9, 51.5, 40.4, 31.0, 27.4, 22.4 ppm. HRMS (ESI), *m/z* calcd for C₁₆H₂₀N₂NaO₆ [M+Na]⁺ 359.1213 found 359.1210.

***tert*-Butyl 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2,6-dioxopiperidine-1-carboxylate (6d).** Prepared



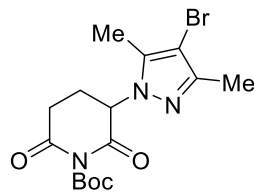
according to GP1 using 3,5-dimethylpyrazole as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 90 mg (89%). White solid; m.p. 162.3–163.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.90 (s, 1 H), 4.85 (dd, *J* = 11.4, 5.1 Hz, 1 H), 3.10 (dt, *J* = 17.1, 4.0 Hz, 1 H), 2.98–2.88 (m, 1 H), 2.84–2.76 (m, 1 H), 2.41–2.34 (m, 1 H), 2.28 (s, 3 H), 2.22 (s, 3 H), 1.56 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.9, 166.8, 149.0, 148.0, 140.8, 106.1, 86.9, 56.9, 31.1, 27.4, 23.3, 13.6, 11.0 ppm. HRMS (ESI), *m/z* calcd for C₁₅H₂₂N₃O₄ [M+H]⁺ 308.1605 found 308.1617.

***tert*-Butyl 3-(3,5-diphenyl-1*H*-pyrazol-1-yl)-2,6-dioxopiperidine-1-carboxylate (6e).** Prepared



according to GP1 using 3,5-diphenylpyrazole as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 112 mg (74%). White solid; m.p. 129.3–131.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87–7.85 (m, 2 H), 7.54–7.50 (m, 5 H), 7.45–7.41 (m, 2 H), 7.37–7.32 (m, 1 H), 6.68 (s, 1 H), 5.07 (dd, *J* = 10.4, 4.9 Hz, 1 H), 3.13 (dt, *J* = 17.5, 4.6 Hz, 1 H), 3.03–2.93 (m, 1 H), 2.77–2.69 (m, 1 H), 2.39–2.32 (m, 1 H), 1.60 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.1, 166.9, 151.9, 148.1, 146.8, 132.9, 129.9, 129.3, 129.14, 129.09, 128.6, 128.1, 125.9, 103.9, 86.9, 57.4, 30.7, 27.5, 24.0 ppm. HRMS (ESI), *m/z* calcd for C₂₅H₂₅N₃NaO₄ [M+Na]⁺ 454.1737 found 454.1745.

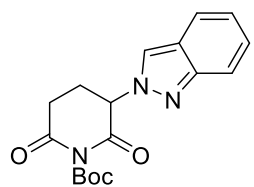
tert-Butyl 3-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)-2,6-dioxopiperidine-1-carboxylate (6f).



Prepared according to GP1 using 4-bromo-3,5-dimethylpyrazole as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 120 mg (94%). White solid; m.p. 237.1–239.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 4.93 (dd, *J* = 11.2, 5.0 Hz, 1 H), 3.13–3.07 (m, 1 H), 2.96–2.77 (m, 2 H), 2.40–2.34 (m, 1 H), 2.29 (s, 3 H), 2.23 (s, 3 H), 1.57 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.7, 166.3, 147.8, 147.6, 139.1, 95.6, 87.1, 57.9, 30.9, 27.4, 23.0, 12.4, 10.5 ppm. HRMS (ESI), *m/z* calcd for C₁₅H₂₁N₃O₄Br [M+H]⁺ 386.0710/388.689 found 386.0711/388.0692.

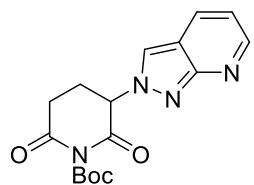
The of compound **6f** synthesis was run according to GP1 on a gram scale (3.3 mmol); yield 1.19 g (93%).

tert-Butyl 3-(2H-indazol-2-yl)-2,6-dioxopiperidine-1-carboxylate (6g).



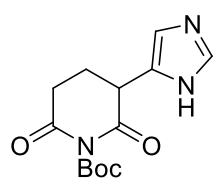
using indazole as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 100 mg (92%). White solid; m.p. 143.2–144.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (s, 1 H), 7.72–7.69 (m, 2 H), 7.34–7.31 (m, 1 H), 7.14–7.11 (m, 1 H), 5.33 (dd, *J* = 10.7, 4.5 Hz, 1 H), 3.13 (dt, *J* = 17.2, 4.5 Hz, 1 H), 3.03–2.94 (m, 1 H), 2.90–2.82 (m, 1 H), 2.58–2.52 (m, 1 H), 1.57 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.6, 166.0, 147.8, 126.8, 124.3, 122.4, 121.8, 120.4, 117.7, 87.2, 61.8, 30.7, 27.4, 24.2 ppm. HRMS (ESI), *m/z* calcd for C₁₇H₂₀N₃O₄ [M+H]⁺ 330.1449 found 330.1453.

tert-Butyl 2,6-dioxo-3-(2H-pyrazolo[3,4-*b*]pyridin-2-yl)piperidine-1-carboxylate (6h).



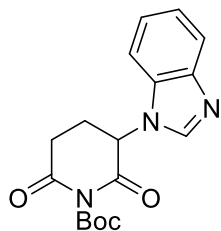
according to GP1 using pyrazolo[3,4-*b*]pyridine as NH-substrate; reaction time – 3 days, after 16 h additional portion of catalyst was added; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 36 mg (33%). Pale grey amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 8.73 (s, 1 H), 8.17 (s, 1 H), 8.11–8.01 (m, 1H), 7.09 (dd, *J* = 8.4, 4.1 Hz, 1 H), 5.50 (dd, *J* = 10.7, 5.0 Hz, 1 H), 3.25–3.13 (m, 1 H), 3.11–3.00 (m, 1 H), 2.98–2.86 (m, 1 H), 2.69–2.54 (m, 1 H), 1.55 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.7, 165.9, 158.1, 152.2, 147.8, 130.4, 124.9, 118.4, 114.1, 87.3, 62.2, 30.6, 27.4, 23.9 ppm. HRMS (ESI), *m/z* calcd for C₁₆H₁₉N₄O₄ [M+H]⁺ 331.1401 found 331.1399.

tert-Butyl 3-(1H-imidazol-5-yl)-2,6-dioxopiperidine-1-carboxylate (9i).

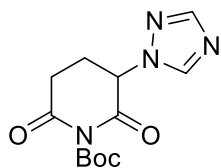


using imidazole as NH-substrate; reaction time – 3 days, after 16 h additional portion of catalyst was added; eluent – *n*-hexane–acetone (15% to 80% of acetone). Yield: 26 mg (28%). Pale grey amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 1 H), 8.13 (s, 1 H), 6.98 (s, 1 H), 4.91 (s, 1 H), 3.11–3.03 (m, 1 H), 2.75 (dt, *J* = 18.1, 5.2 Hz, 1 H), 2.47–2.39 (m, 1 H), 2.36–2.26 (m, 1 H), 1.53 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 171.8, 166.9, 150.3, 134.7, 127.9, 127.2, 83.6, 36.5, 30.7, 27.9, 24.3 ppm. HRMS (ESI), *m/z* calcd for C₁₃H₁₈N₃O₄ [M+H]⁺ 280.1292 found 280.1283.

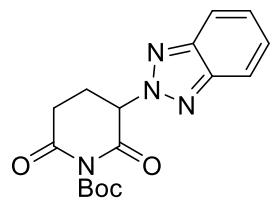
tert-Butyl 3-(1H-benzo[d]imidazol-1-yl)-2,6-dioxopiperidine-1-carboxylate (6j). Prepared according to GP1 using benzimidazole as NH-substrate; reaction time – 2 days, after 16 h additional portion of catalyst was added; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 43 mg (39%). Grey amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (s, 1 H), 7.91–7.77 (m, 1 H), 7.40–7.29 (m, 3 H), 5.29 (dd, *J* = 13.2, 4.9 Hz, 1 H), 3.05 (ddd, *J* = 17.8, 4.8, 2.6 Hz, 1 H), 2.94 (ddd, *J* = 17.9, 12.9, 5.0 Hz, 1 H), 2.74 (qd, *J* = 13.0, 4.8 Hz, 1 H), 2.49–2.38 (m, 1 H), 1.58 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.2, 166.0, 147.6, 143.3, 141.8, 123.8, 123.0, 120.7, 109.9, 87.6, 55.5, 31.4, 27.4, 24.2 ppm. HRMS (ESI), *m/z* calcd for C₁₇H₂₀N₃O₄ [M+H]⁺ 330.1448 found 330.1447.



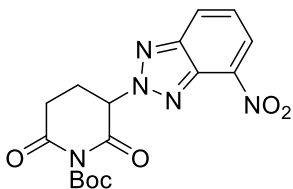
tert-Butyl 2,6-dioxo-3-(1H-1,2,4-triazol-1-yl)piperidine-1-carboxylate (6l). Prepared according to GP1 using 1,2,4-triazole as NH-substrate; reaction time – 4 days, after 16 h and 40 h 2 additional portions of catalyst were sequentially added; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 74 mg (80%). White solid; m.p. 128.4–132.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (br. s, 1 H), 8.03 (br. s, 1 H), 5.24–5.22 (m, 1 H), 3.12–3.03 (m, 1 H), 2.91–2.76 (m, 2 H), 2.53–2.49 (m, 1 H), 1.57 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.2, 165.5, 152.2, 147.6, 140.8, 87.5, 58.4, 30.6, 27.4, 23.6 ppm. HRMS (ESI), *m/z* calcd for C₁₂H₁₇N₄O₄ [M+H]⁺ 281.1245 found 281.1247.



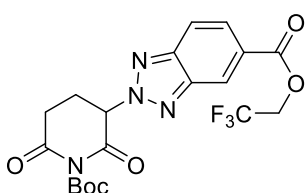
tert-Butyl 3-(2H-benzotriazol-2-yl)-2,6-dioxopiperidine-1-carboxylate (6m). Prepared according to GP1 using benzotriazole as NH-substrate; reaction time – 5 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 103 mg (89%). White amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 7.92–7.88 (m, 2 H), 7.46–7.42 (m, 2 H), 5.83 (dd, *J* = 10.5, 5.0 Hz, 1 H), 3.15–3.02 (m, 2 H), 2.95–2.86 (m, 1 H), 2.67–2.59 (m, 1 H), 1.58 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.3, 164.9, 147.5, 144.7, 127.2, 118.3, 87.3, 64.7, 30.3, 27.4, 23.9 ppm. HRMS (ESI), *m/z* calcd for C₁₆H₁₉N₄O₄ [M+H]⁺ 331.1401 found 331.1392.



tert-Butyl 3-(4-nitro-2H-benzotriazol-2-yl)-2,6-dioxopiperidine-1-carboxylate (6n). Prepared according to GP1 using 1H-4-nitrobenzotriazole as NH-substrate; reaction time – 5 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 62 mg (50%). Grey amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 8.47–8.45 (m, 1 H), 8.33–8.31 (m, 1 H), 7.63–7.59 (m, 1 H), 6.02 (dd, *J* = 11.5, 5.0 Hz, 1 H), 3.25–3.12 (m, 2 H), 3.02–2.93 (m, 1 H), 2.74–2.67 (m, 1 H), 1.57 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 167.9, 164.4, 147.3, 146.7, 138.2, 137.4, 126.5, 125.8, 125.4, 87.6, 65.6, 30.4, 27.4, 23.9 ppm. HRMS (ESI), *m/z* calcd for C₁₆H₁₇N₅NaO₆ [M+Na]⁺ 398.1071 found 398.1073.

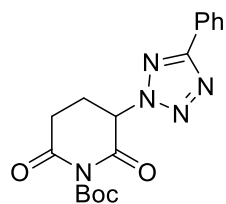


2,2,2-Trifluoroethyl 2-(1-(tert-butoxycarbonyl)-2,6-dioxopiperidin-3-yl)-2H-benzotriazole-5-carboxylate (6o). Prepared according to GP1 using 1H-4-nitrobenzotriazole as NH-substrate; reaction time – 5 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 84 mg (56%). White amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 8.77 (dd, *J* = 1.5, 0.9 Hz, 1 H), 8.09 (dd, *J* = 9.0, 1.5 Hz, 1 H), 7.98 (dd, *J* = 9.0, 0.9 Hz, 1 H), 5.88 (dd, *J* = 10.8, 4.9 Hz, 1 H), 4.78 (q, *J* = 8.4 Hz,

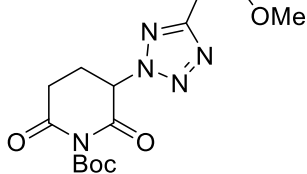


2 H), 3.17–3.06 (m, 2 H), 2.97–2.87 (m, 1 H), 2.70–2.63 (m, 1 H), 1.58 (s, 9 H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 168.0, 164.5, 164.4, 147.3, 146.7, 143.9, 127.3, 126.9, 123.1, 123.0 (q, $J = 275.6$ Hz), 118.9, 87.5, 61.1 (q, $J = 36.5$ Hz), 30.3, 27.4, 23.9 ppm. ^{19}F NMR (376.5 MHz, CDCl_3) δ –73.61 ppm. HRMS (ESI), m/z calcd for $\text{C}_{19}\text{H}_{19}\text{N}_4\text{NaO}_6\text{F}_3$ $[\text{M}+\text{Na}]^+$ 479.1149 found 479.1150.

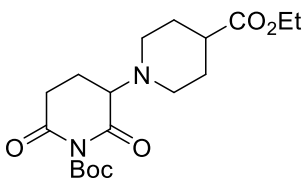
***tert*-Butyl 2,6-dioxo-3-(5-phenyl-2*H*-tetrazol-2-yl)piperidine-1-carboxylate (6p).** Prepared according to GP1 using 5-phenyltetrazole as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 60 mg (51%). White solid; m.p. 149.4–150.4 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.19–8.16 (m, 2 H), 7.53–7.49 (m, 3 H), 5.89–5.85 (m, 1 H), 3.16–3.06 (m, 1 H), 3.04–2.90 (m, 2 H), 2.65–2.59 (m, 1 H), 1.58 (s, 9 H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 167.9, 165.7, 163.9, 147.3, 130.7, 128.9, 127.1, 126.8, 87.6, 61.8, 30.4, 27.4, 23.4 ppm. HRMS (ESI), m/z calcd for $\text{C}_{17}\text{H}_{19}\text{N}_5\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 380.1329 found 380.1329.



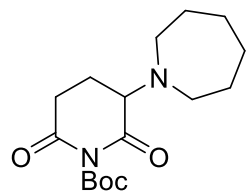
***tert*-Butyl 3-(5-(2-methoxyethyl)-2*H*-tetrazol-2-yl)-2,6-dioxopiperidine-1-carboxylate (6q).** Prepared according to GP1 using 5-(2-methoxyethyl)tetrazole as NH-substrate; reaction time – 2 days, after 16 h additional portion of catalyst was added; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 65 mg (58%). Colorless viscous oil. ^1H NMR (400 MHz, CDCl_3) δ 5.79–5.75 (m, 1 H), 3.83 (t, $J = 6.7$ Hz, 2 H), 3.39 (s, 3 H), 3.22 (t, $J = 6.7$ Hz, 2 H), 3.11–3.06 (m, 1 H), 2.99–2.86 (m, 2 H), 2.62–2.54 (m, 1 H), 1.58 (s, 9 H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 167.8, 164.9, 163.9, 147.2, 87.6, 69.8, 61.6, 58.8, 30.4, 27.4, 26.4, 23.3 ppm. HRMS (ESI), m/z calcd for $\text{C}_{14}\text{H}_{22}\text{N}_5\text{O}_5$ $[\text{M}+\text{H}]^+$ 340.1616 found 340.1609.



***tert*-Butyl 3-(4-ethoxycarbonylpiperidin-1-yl)-2,6-dioxopiperidine-1-carboxylate (6r).** Prepared according to GP1 using ethyl isonipecotatate as NH-substrate; reaction time – 5 days, after 16 h and 40 h 2 additional portions of catalyst were sequentially added; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 22 mg (18%). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.15 (q, $J = 7.2$ Hz, 2 H), 3.37 (dd, $J = 10.4, 4.3$ Hz, 1 H), 2.94–2.82 (m, 3 H), 2.79–2.73 (m, 1 H), 2.66–2.53 (m, 2 H), 2.37–2.29 (m, 1 H), 2.21–2.01 (m, 2 H), 1.96–1.92 (m, 2 H), 1.81–1.71 (m, 2 H), 1.57 (s, 9 H), 1.26 (t, $J = 7.2$ Hz, 3 H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 174.8, 169.9, 169.6, 148.7, 86.4, 64.4, 60.4, 50.5, 47.8, 40.9, 30.8, 28.7, 28.4, 27.5, 21.0, 14.2 ppm. HRMS (ESI), m/z calcd for $\text{C}_{18}\text{H}_{29}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$ 369.2019 found 369.2011.



***tert*-Butyl 3-(azepan-1-yl)-2,6-dioxopiperidine-1-carboxylate (6s).** Prepared according to GP1 using hexamethyleneimine as NH-substrate; reaction time – 5 days, after 16 h and 40 h 2 additional portions of catalyst were sequentially added; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 13 mg (13%). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 3.55–3.51 (m, 1 H), 2.98–2.93 (m, 2 H), 2.87–2.78 (m, 3 H), 2.68–2.59 (m, 1 H), 2.14–2.08 (m, 2 H), 1.74–1.59 (m, 8 H), 1.58 (s, 9 H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 171.1, 169.9, 148.9, 86.3, 65.9, 52.5, 31.6, 29.7, 27.5, 27.0, 22.9 ppm. HRMS (ESI), m/z calcd for $\text{C}_{16}\text{H}_{27}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 311.1966 found 311.1967.



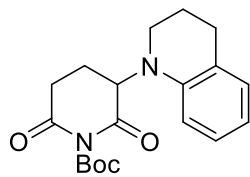
tert-Butyl 3-(indolin-1-yl)-2,6-dioxopiperidine-1-carboxylate (6t). Prepared according to GP1 using indoline as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 101 mg (87%). White solid; m.p. 151.9–153.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.13–7.11 (m, 1 H), 7.10–7.05 (m, 1 H), 6.75–6.71 (m, 1 H), 6.46 (d, *J* = 7.8 Hz, 1 H), 4.38 (dd, *J* = 12.6, 5.1 Hz, 1 H), 3.56–3.45 (m, 2 H), 3.16–3.01 (m, 2 H), 2.99–2.93 (m, 1 H), 2.84–2.75 (m, 1 H), 2.36–2.18 (m, 2 H), 1.57 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.2, 168.1, 149.9, 148.3, 129.5, 127.3, 124.9, 118.8, 107.1, 86.7, 56.6, 48.8, 31.9, 28.4, 27.5, 21.5 ppm. HRMS (ESI), *m/z* calcd for C₁₈H₂₃N₂O₄ [M+H]⁺ 331.1653 found 331.1651.

tert-Butyl 3-(5-acetylindolin-1-yl)-2,6-dioxopiperidine-1-carboxylate (6u). Prepared according to GP1 using 5-acetylindoline as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 116 mg (94%). White solid; m.p. 168.2–171.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.76–7.73 (m, 2 H), 6.40 (d, *J* = 8.2 Hz, 1 H), 4.46 (dd, *J* = 13.0, 5.0 Hz, 1 H), 3.67–3.52 (m, 2 H), 3.20–3.04 (m, 2 H), 3.02–2.95 (m, 1 H), 2.89–2.79 (m, 1 H), 2.50 (s, 3 H), 2.40–2.29 (m, 1 H), 2.28–2.18 (m, 1 H), 1.56 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 196.4, 168.9, 167.6, 154.9, 148.1, 130.3, 129.3, 128.3, 125.2, 105.1, 86.9, 55.9, 48.6, 31.8, 27.5, 27.4, 26.2, 22.0 ppm. HRMS (ESI), *m/z* calcd for C₂₀H₂₅N₂O₅ [M+H]⁺ 373.1758 found 373.1757.

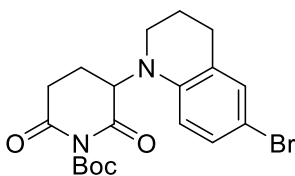
tert-Butyl 3-(5-(*N,N*-dimethylsulfamoyl)indolin-1-yl)-2,6-dioxopiperidine-1-carboxylate (6v). Prepared according to GP1 using *N,N*-dimethylindoline-5-sulfonamide as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 133 mg (92%). White solid; m.p. 157.1–158.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.48–7.45 (m, 1 H), 7.42 (m, 1 H), 6.43 (d, *J* = 8.3 Hz, 1 H), 4.46 (dd, *J* = 12.9, 4.9 Hz, 1 H), 3.68–3.62 (m, 1 H), 3.60–3.54 (m, 1 H), 3.20–3.05 (m, 2 H), 3.01–2.95 (m, 1 H), 2.91–2.82 (m, 1 H), 2.67 (s, 6 H), 2.38–2.21 (m, 2 H), 1.56 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.9, 167.7, 154.4, 148.1, 129.8, 129.1, 124.4, 123.6, 105.4, 86.9, 55.7, 48.5, 38.0, 31.8, 27.6, 27.4, 22.0 ppm. HRMS (ESI), *m/z* calcd for C₂₀H₂₈N₃O₆S [M+H]⁺ 438.1694 found 438.1699.

tert-Butyl 3-(6-nitroindolin-1-yl)-2,6-dioxopiperidine-1-carboxylate (6w). Prepared according to GP1 using 6-nitroindoline as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 110 mg (89%). Yellow solid; m.p. >250 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (dd, *J* = 8.0, 1.8 Hz, 1 H), 7.21 (d, *J* = 1.8 Hz, 1 H), 7.18–7.15 (m, 1 H), 4.50–4.46 (m, 1 H), 4.48 (dd, *J* = 12.8, 4.9 Hz, 1 H), 3.69–3.63 (m, 1 H), 3.60–3.53 (m, 1 H), 3.25–3.07 (m, 2 H), 3.03–2.98 (m, 1 H), 2.93–2.84 (m, 1 H), 2.40–2.24 (m, 2 H), 1.56 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.8, 167.7, 151.9, 148.5, 148.0, 137.0, 124.5, 114.5, 100.8, 87.0, 56.0, 48.7, 31.9, 28.3, 27.4, 22.2 ppm. HRMS (ESI), *m/z* calcd for C₁₈H₂₂N₃O₆ [M+H]⁺ 376.1503 found 376.1499.

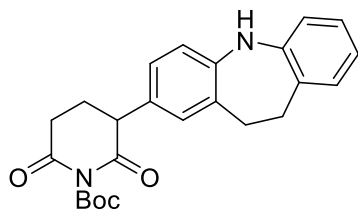
tert-Butyl 3-(tetrahydroquinolin-1-yl)-2,6-dioxopiperidine-1-carboxylate (6x). Prepared according to GP1 using 1,2,3,4-tetrahydroquinoline as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 73 mg (64%). White solid; m.p. 141.6–142.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.08–7.04 (m, 1 H), 7.03–7.00 (m, 1 H), 6.70–6.66 (m, 1 H), 6.56 (d, *J* = 8.2 Hz, 1 H), 4.61 (dd, *J* = 12.7, 4.9 Hz, 1 H), 3.24 (t, *J* = 5.8 Hz, 2 H), 2.95 (ddd, *J* = 17.7, 4.5, 2.7 Hz, 1 H), 2.87–2.73 (m, 3 H), 2.42 (qd, *J* = 13.2, 4.5 Hz, 1 H), 2.18–2.11 (m, 1 H), 2.09–1.93 (m, 2 H), 1.59 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.3, 168.9, 148.4, 144.2, 129.6, 127.0, 124.2, 117.4, 110.9, 86.6, 58.9, 45.4, 32.1, 28.0, 27.5, 22.4, 21.5 ppm. HRMS (ESI), *m/z* calcd for C₁₉H₂₅N₂O₄ [M+H]⁺ 345.1809 found 345.1801.



tert-Butyl 3-(6-bromotetrahydroquinolin-1-yl)-2,6-dioxopiperidine-1-carboxylate (6y). Prepared according to GP1 using 6-bromo-1,2,3,4-tetrahydroquinoline as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 118 mg (84%). White solid; m.p. 173.8–174.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.14–7.12 (m, 2 H), 6.44 (d, *J* = 8.4 Hz, 1 H), 4.54 (dd, *J* = 12.8, 4.8 Hz, 1 H), 3.27–3.17 (m, 2 H), 2.96 (ddd, *J* = 17.7, 4.5, 2.5 Hz, 1 H), 2.85–2.68 (m, 3 H), 2.42 (qd, *J* = 13.2, 4.5 Hz, 1 H), 2.17–2.11 (m, 1 H), 2.06–1.92 (m, 2 H), 1.58 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 169.0, 168.6, 148.3, 143.4, 131.9, 129.6, 126.4, 112.7, 109.3, 86.8, 59.0, 45.3, 32.1, 27.8, 27.5, 22.1, 21.6 ppm. HRMS (ESI), *m/z* calcd for C₁₉H₂₄BrN₂O₄ [M+H]⁺ 423.0914/425.0893 found 423.0913/423.0895.

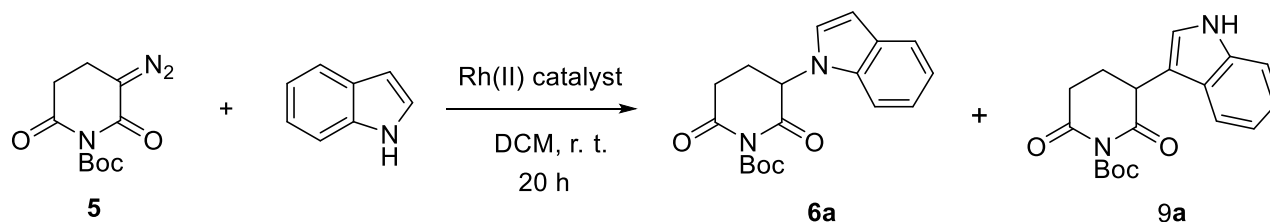


tert-Butyl 3-(10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-2-yl)-2,6-dioxopiperidine-1-carboxylate (9z). Prepared according to GP1 using 10,11-dihydro-5*H*-dibenzo[*b,f*]azepine as NH-substrate; reaction time – 16 h; eluent – *n*-hexane–acetone (10% to 40% of acetone). Yield: 62 mg (46%). White amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 7.12–7.05 (m, 2 H), 6.93–6.89 (m, 2 H), 6.83–6.73 (m, 3 H), 3.76–3.72 (m, 1 H), 3.10–3.05 (m, 4 H), 2.79 (dt, *J* = 17.7, 5.4 Hz, 1 H), 2.73–2.64 (m, 1 H), 2.28–2.21 (m, 2 H), 1.61 (s, 9 H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 171.5, 170.1, 149.1, 142.2, 142.0, 130.6, 130.4, 128.8, 128.7, 127.1, 126.9, 126.4, 119.8, 118.5, 118.1, 86.4, 47.0, 35.1, 34.7, 31.0, 27.5, 25.3 ppm. HRMS (ESI), *m/z* calcd for C₂₄H₂₇N₂O₄ [M+H]⁺ 407.1966 found 407.1957.



Additional experiments on catalysts screening

General procedure for testing of Rh(II) catalysts in the reaction of **5** with indole.

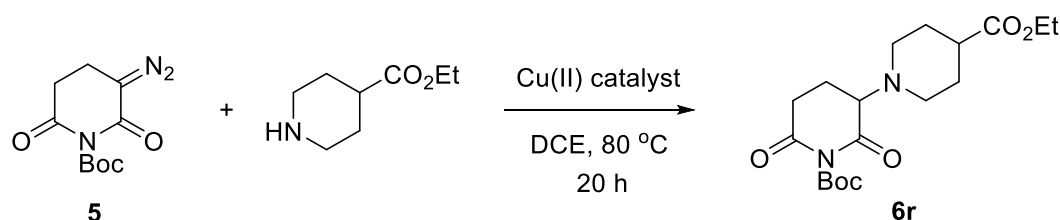


To a solution of indole (19 mg, 0.165 mmol, 1 equiv.) in DCM (0.5 mL) was added the Rh(II) catalyst ($\text{Rh}_2(\text{TFA})_4$ or $\text{Rh}_2(\text{OAc})_4$, 1 mol %). To the vigorously stirred mixture the solution of diazo reagent **5** (48 mg, 0.2 mmol, 1.2 equiv.) in DCM (0.5 mL) was added during 1-2 minutes. The reaction mixture was stirred at ambient temperature until full consumption of starting material (20 h, controlled by TLC). To the reaction mixture was added 2,4-dinitrotoluene (27 mg, 0.15 mmol) as the internal NMR standard, the solvent was evaporated and the residue was redissolved in CDCl_3 (1 mL) followed by registration of ^1H NMR spectrum.

Table S1. Results of testing $\text{Rh}_2(\text{TFA})_4$ and $\text{Rh}_2(\text{OAc})_4$ catalysts for the reaction **5→**6a/9a**.**

Entry	Rh(II) catalyst	NMR yield of 6a	NMR yield of 6a	Ratio 6a/9a
1	$\text{Rh}_2(\text{TFA})_4$	11%	21%	34:66
2	$\text{Rh}_2(\text{OAc})_4$	40%	22%	64:36

General procedure for testing of Cu(II) catalysts in the reaction of **5** with ethyl isonipecotate.

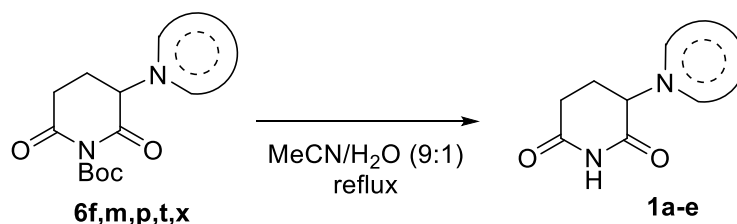


To a solution of ethyl isonipecotate (26 mg, 0.165 mmol, 1 equiv.) in DCE (0.5 mL) were added the Cu(II) catalyst ($\text{Cu}(\text{OTf})_2$, 5 mol% or $\text{Cu}(\text{acac})_2$, 10 mol %) and the solution of diazo reagent **5** (48 mg, 0.2 mmol, 1.2 equiv.) in DCE (0.5 mL). The mixture was vigorously stirred in a closed vessel at 80 °C until full consumption of starting material (20 h, controlled by TLC). Upon cooling to ambient temperature to the reaction mixture was added 2,4-dinitrotoluene (27 mg, 0.15 mmol) as the internal NMR standard, the solvent was evaporated and the residue was redissolved in CDCl_3 (1 mL) followed by registration of ^1H NMR spectrum.

Table S2. Results of testing Cu(OTf)₂ and Cu(acac)₂ catalysts for the reaction 5→6r.

Entry	Cu(II) catalyst	NMR yield of 6r
1	Cu(OTf) ₂ (5 mol%)	0%
2	Cu(acac) ₂ (10 mol %)	25%

General procedure GP1 for the preparation of compounds 1a-e by Boc-group removal



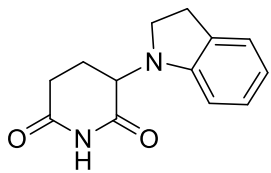
To a solution of the corresponding *N*-Boc-protected substrate **6** (0.10 mmol) in a mixture of MeCN and H₂O (9:1, 700 μ L) was heated at reflux for 8 hours. Then, the solvents were removed under reduced pressure and the resulting substance was dried in high vacuum at ambient temperature.

3-(2*H*-Benzo[*d*][1,2,3]triazol-2-yl)piperidine-2,6-dione (1a). Prepared according to GP2 using compound **6m**. Yield: 23 mg (99%). White solid; m.p. > 250 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.29 (s, 1H), 8.01–7.91 (m, 2H), 7.52–7.43 (m, 2H), 6.23–6.11 (m, 1H), 3.05 – 2.53 (m, 4H) ppm. NMR data are in accordance with previously reported.[1] HRMS (ESI), *m/z* calcd for C₁₁H₁₁N₄O₂ [M+H]⁺ 231.0877 found 231.0890.

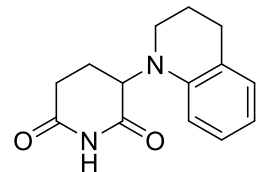
3-(4-Bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)piperidine-2,6-dione (1b). Prepared according to GP2 using compound **6f**. Yield: 28 mg (97%). White solid; m.p. 241.7–243.5 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.04 (br. s, 1H), 5.34 (dd, *J* = 12.1, 5.1 Hz, 1H), 2.85–2.72 (m, 1H), 2.70–2.54 (m, 2H), 2.21 (s, 3H), 2.19–2.15 (m, 1H), 2.10 (s, 3H) ppm. ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 173.1, 170.6, 145.6, 139.4, 93.6, 58.0, 31.1, 23.8, 12.6, 10.4 ppm. HRMS (ESI), *m/z* calcd for C₁₀H₁₃BrN₃O₂ [M+H]⁺ 286.0186 found 286.0188.

3-(5-Phenyl-2*H*-tetrazol-2-yl)piperidine-2,6-dione (1c). Prepared according to GP2 using compound **6p**. Yield: 24 mg (95%). White solid; m.p. 197.4–199.1 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.38 (br. s, 1H), 8.14–8.03 (m, 2H), 7.65–7.50 (m, 3H), 6.34 (dd, *J* = 12.2, 5.0 Hz, 1H), 2.99–.70 (m, 3H), 2.60–2.48 (m, 1H) ppm. ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 172.6, 168.8, 164.6, 131.2, 129.8 (2C), 127.1, 126.8 (2C), 62.5, 30.8, 24.1 ppm. HRMS (ESI), *m/z* calcd for C₁₂H₁₂N₅O₂ [M+H]⁺ 258.0986 found 258.0983.

3-(Indolin-1-yl)piperidine-2,6-dione (1d). Prepared according to GP2 compound **6t**. Yield: 21 mg (93%). White solid; m.p. 146.6–148.4 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ 9.55 (br. s, 1H), 7.09–6.80 (m, 2H), 6.80–6.36 (m, 2H), 4.65 (dd, *J* = 13.0, 5.0 Hz, 1H), 3.64–3.37 (m, 2H), 3.11–2.70 (m, 4H), 2.35 (qd, *J* = 13.1, 4.5 Hz, 1H), 2.23–2.09 (m, 1H) ppm. ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 173.5, 172.0, 151.9, 129.1, 127.3, 124.6, 117.3, 107.0, 55.3, 48.1, 32.0, 28.2, 22.2 ppm. HRMS (ESI), *m/z* calcd for C₁₃H₁₅N₂O₂ [M+H]⁺ 231.1128 found 231.1125.

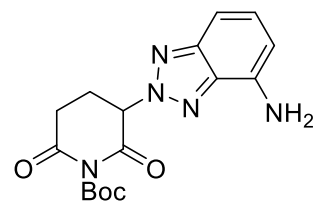


3-(3,4-Dihydroquinolin-1(2H)-yl)piperidine-2,6-dione (1e). Prepared according to GP2 using compound **6x**. Yield: 22 mg (90%). White solid; m.p. 155.4–157.0 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.79 (br. s, 1H), 6.99–6.87 (m, 2H), 6.68 (d, *J* = 8.3 Hz, 1H), 6.51 (t, *J* = 7.2 Hz, 1H), 4.86 (dd, *J* = 12.7, 4.9 Hz, 1H), 3.15 (dt, *J* = 11.5, 5.3 Hz, 1H), 3.06 (dt, *J* = 11.5, 5.3 Hz, 1H), 2.86 (ddd, *J* = 17.2, 13.6, 5.3 Hz, 1H), 2.75–2.61 (m, 2H), 2.61–2.53 (m, 1H), 2.39–2.21 (m, 1H), 1.93–1.76 (m, 3H) ppm. ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 173.5, 172.7, 145.5, 129.4, 127.0, 122.9, 116.2, 111.4, 57.7, 44.7, 32.0, 28.1, 22.2, 22.0 ppm. HRMS (ESI), *m/z* calcd for C₁₄H₁₇N₂O₂ [M+H]⁺ 245.1285 found 245.1289.



Preparation of compound 10

***tert*-Butyl 3-(4-amino-2H-benzo[*d*][1,2,3]triazol-2-yl)-2,6-dioxopiperidine-1-carboxylate (10).** In a 5 mL Schlenk flask, compound **6n** (30 mg, 0.1 mmol), 10% Pt/C catalyst (3 mg) and 600 μL EtOAc were added. The mixture was stirred at room temperature for 12 h under H₂ atmosphere. After the reaction was completed, the solution was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure to obtain 27 mg (94%) of the titled compound as grey oil. ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.16 (m, 2H), 6.50 (dd, *J* = 5.5, 2.5 Hz, 1H), 5.79 (dd, *J* = 10.8, 5.1 Hz, 1H), 4.38–3.69 (m, 3H), 3.13–2.94 (m, 2H), 2.94–2.79 (m, 1H), 2.61–2.47 (m, 1H), 1.57 (s, 9H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 168.5, 165.1, 147.6, 145.6, 137.7, 137.3, 128.6, 106.7, 106.3, 87.3, 64.4, 30.3, 27.41, 23.8 ppm. HRMS (ESI), *m/z* calcd for C₁₆H₂₀N₅O₄ [M+H]⁺ 346.1510 found 346.1513.



Crystallographic data for compounds **6n**

X-ray Single Crystal analysis was performed on SuperNova, Single source at offset/far, HyPix3000 diffractometer. Crystal growth was performed by slow evaporation of solution in *n*-hexane/acetone mixture (1:1) at 5 °C. The crystal was kept at 100 K during data collection. Using Olex2 [2], the structure was solved with the SHELXD [3] structure solution program using Dual Space and refined with the SHELXL[4] refinement package using Least Squares minimization. CCDC 2298240 (**6n**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/>.

Table S1. Crystal data and ORTEP representation for 6n (2298240)	
Empirical Formula	C ₁₆ H ₁₇ N ₅ O ₆
Formula weight	500.46
Temperature, K	99.99(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	5.5905(2)
b/Å	27.5779(9)
c/Å	11.1992(4)
α/°	90
β/°	93.357(3)
γ/°	90
Volume/Å ³	1723.67(10)
Z	3
ρ _{calc} /cm ³	1.446
μ/mm ⁻¹	0.960
F(000)	784
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.41 to 138.636
Index ranges	-6 ≤ h ≤ 6, -33 ≤ k ≤ 33, -11 ≤ l ≤ 13
Reflections collected	15668
Independent reflections	3211 [R _{int} = 0.0448, R _{sigma} = 0.0369]
Data/restraints/parameters	3211/0/298
Goodness-of-fit on F ²	1.063
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0975, wR ₂ = 0.2355
Final R indexes [all data]	R ₁ = 0.1097, wR ₂ = 0.2426
Largest diff. peak/hole / e Å ⁻³	0.37/−0.38

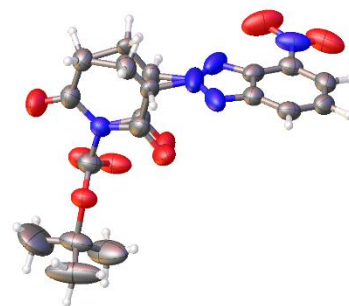


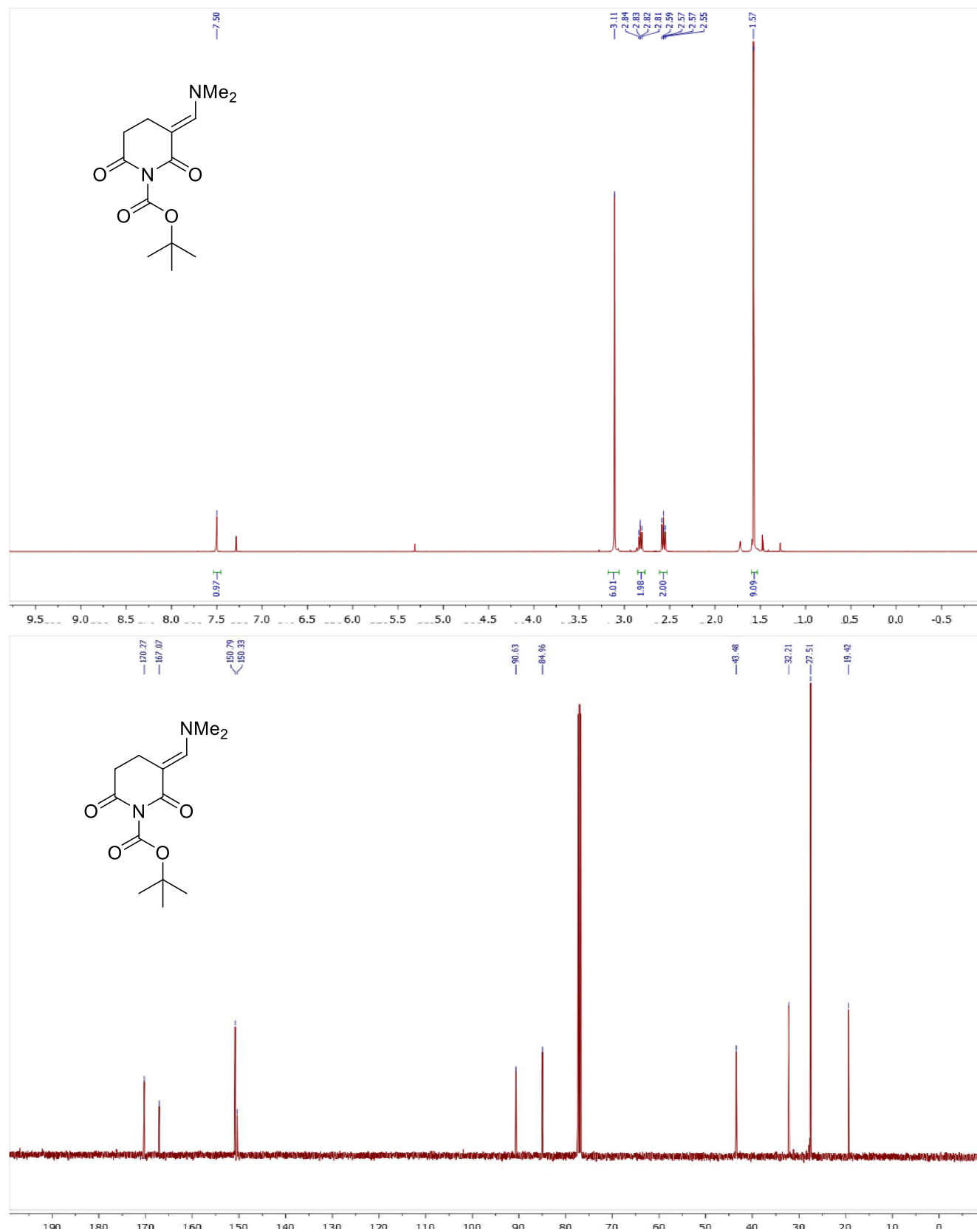
Figure S1. ORTEP representation of compound **6n** (thermal ellipsoids are shown at 50% probability)

References

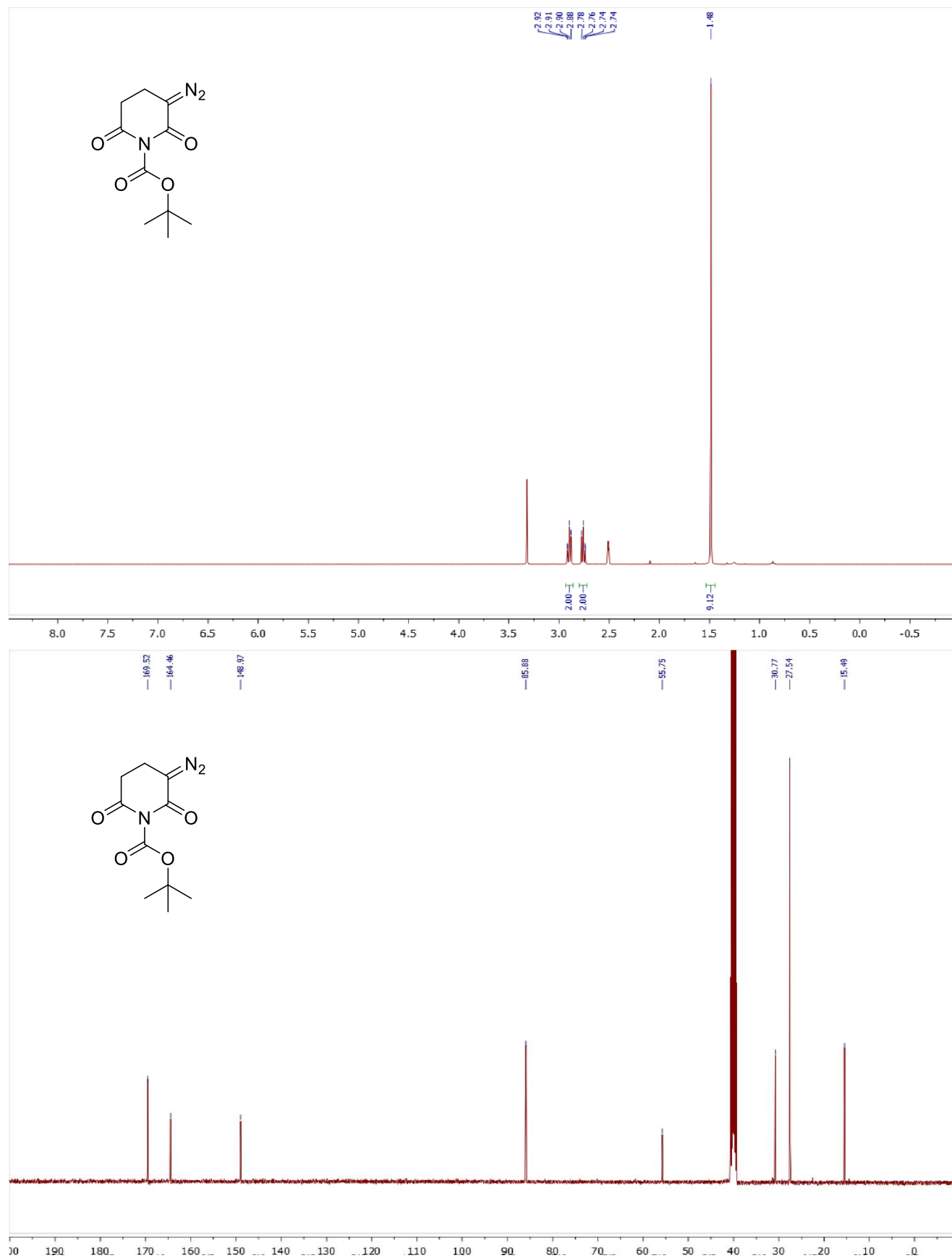
1. Krasavin, M.; Bubyrev, A.; Kazantsev, A.; Heim, C.; Maiwald, S.; Zhukovsky, D.; Dar'in, D.; Hartmann, M. D.; Bunev, A. *J. Enz. Inh.Med. Chem.* **2022**, *37*(1), 527–530.
2. Dolomanov, O. V; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
3. Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
4. Sheldrick, G. M. *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.

1. Copies of ^1H , ^{13}C NMR, ^{19}F and NOESY NMR spectra

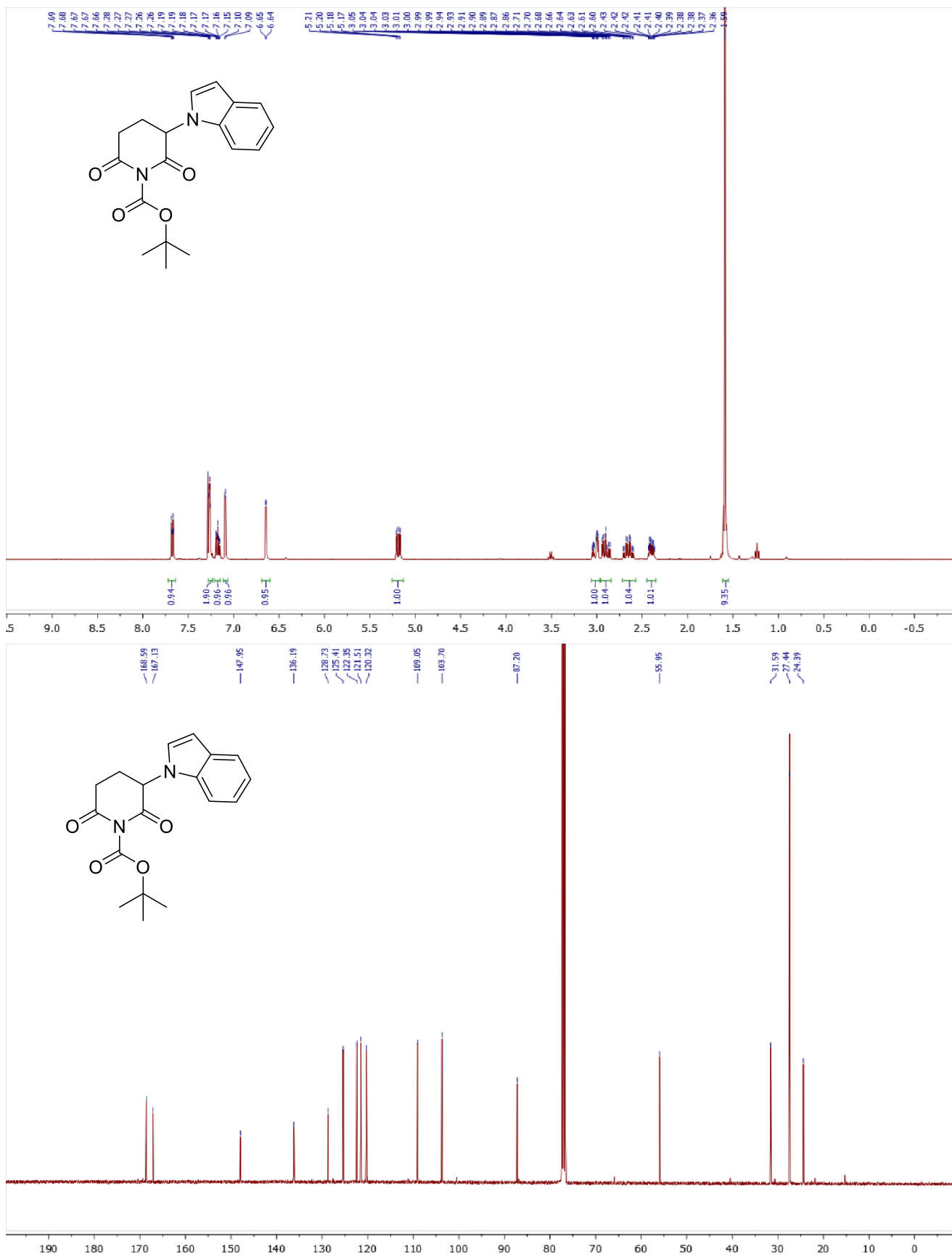
Copies of ^1H (400.13 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (100.61 MHz, CDCl_3) spectra of **8**



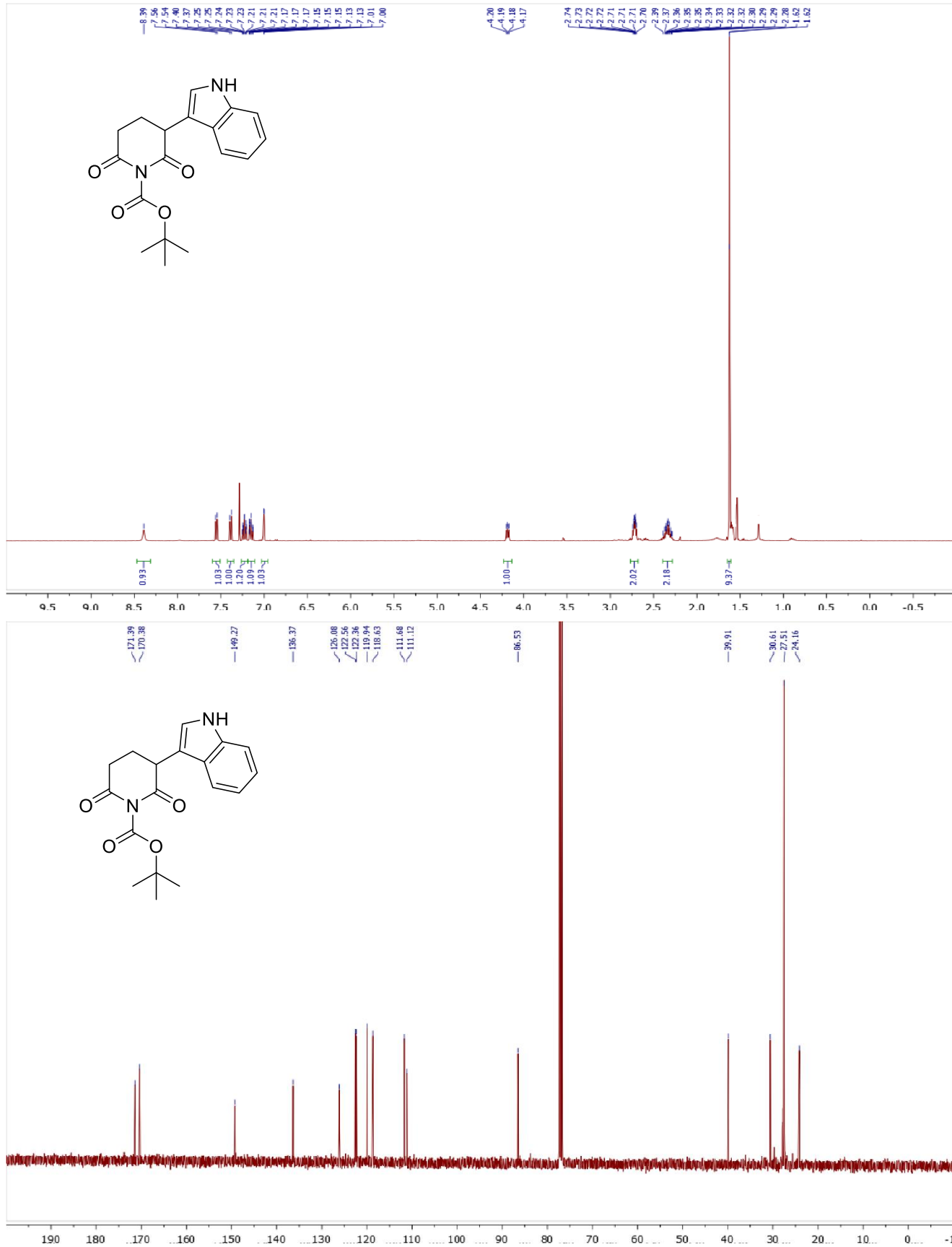
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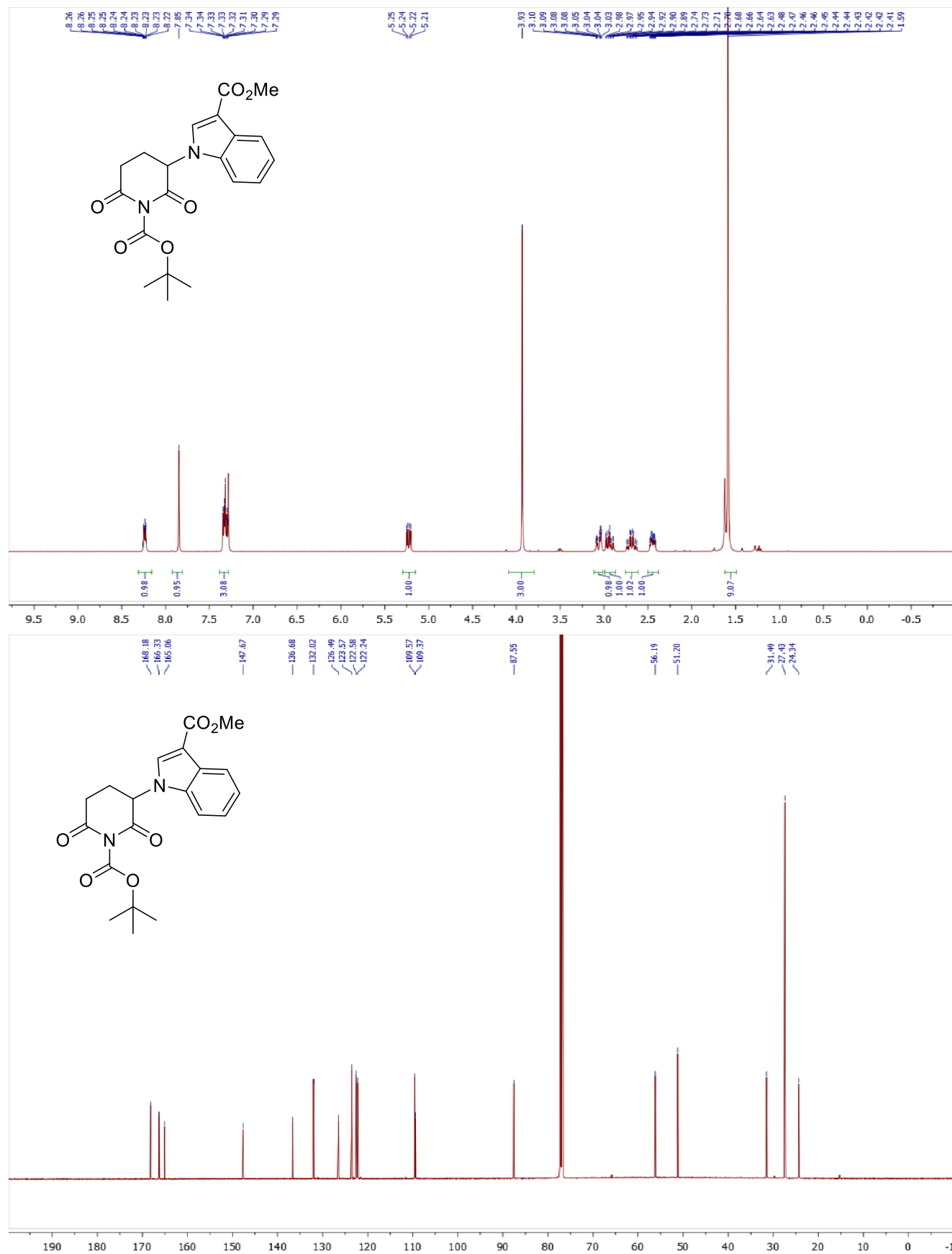
Copies of ^1H (400.13 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (100.61 MHz, CDCl_3) spectra of **6a**



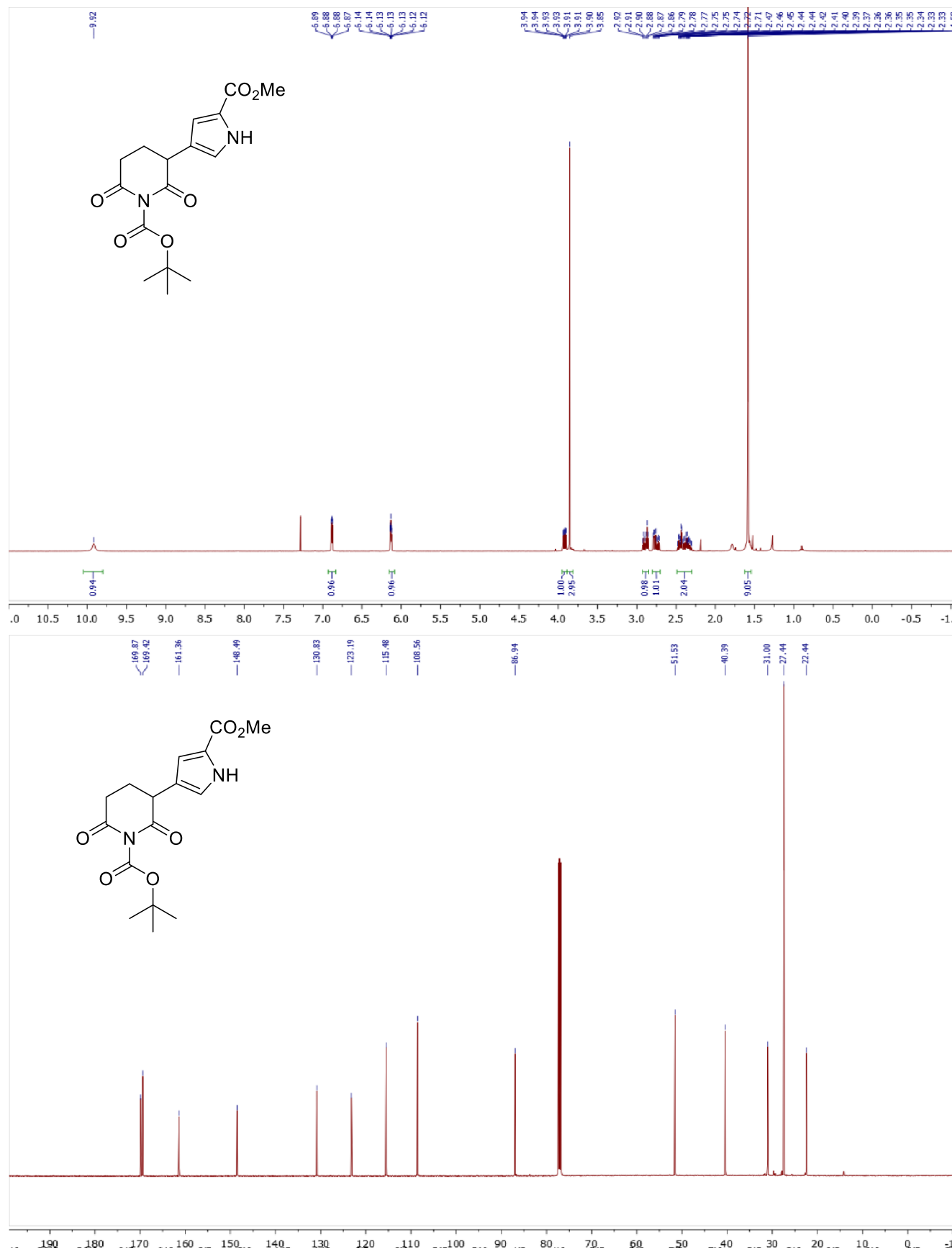
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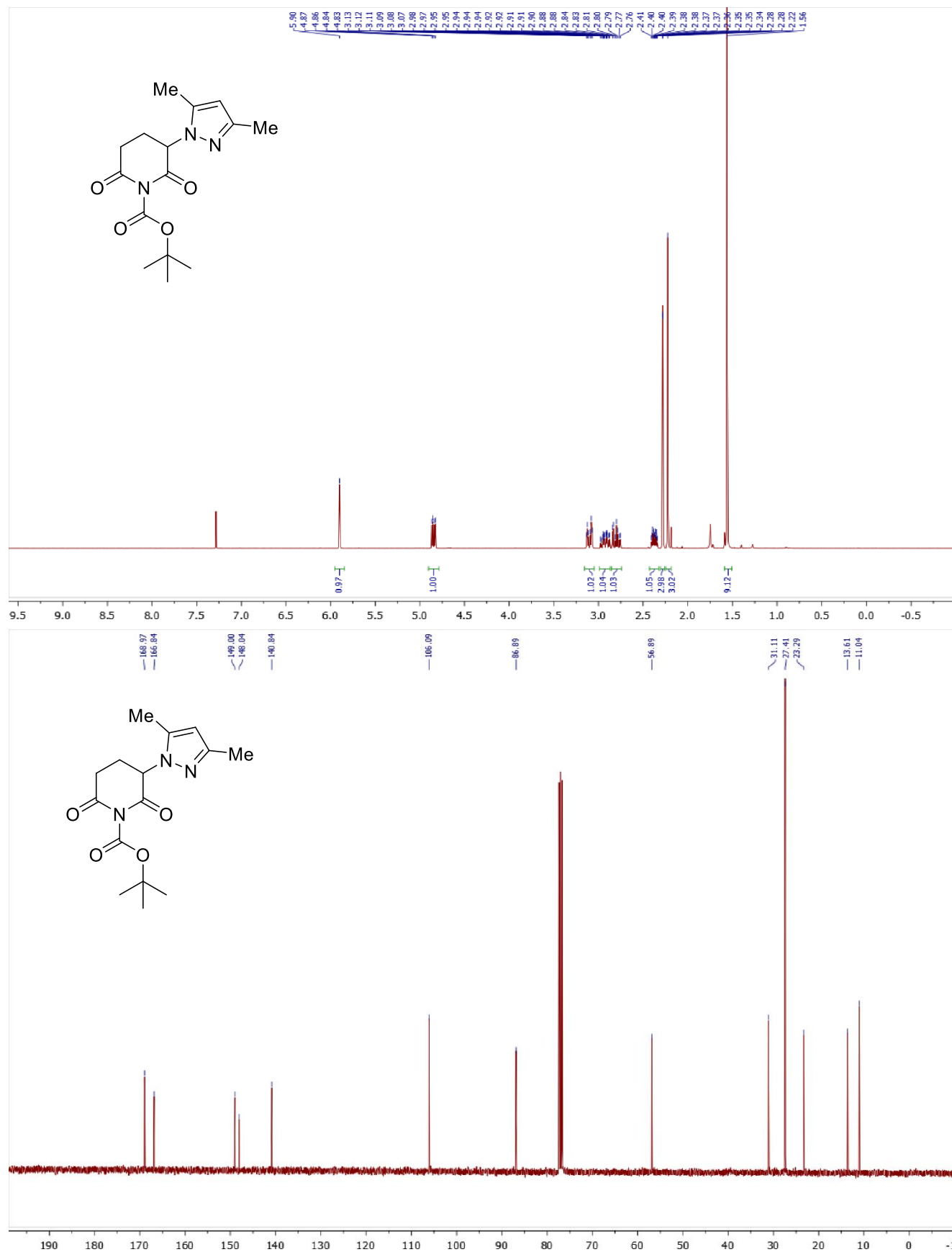
Copies of ^1H (400.13 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (100.61 MHz, CDCl_3) spectra of **6b**



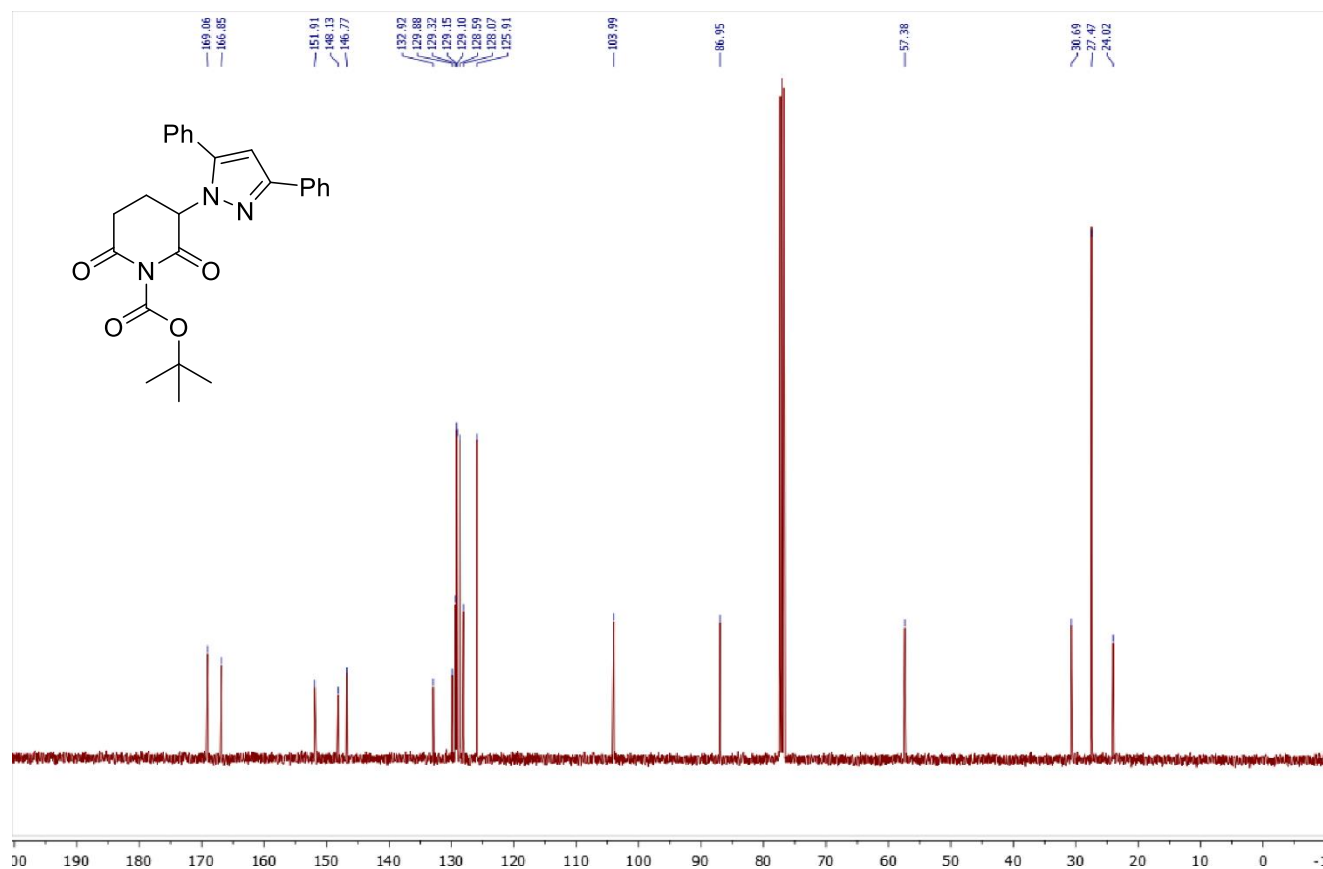
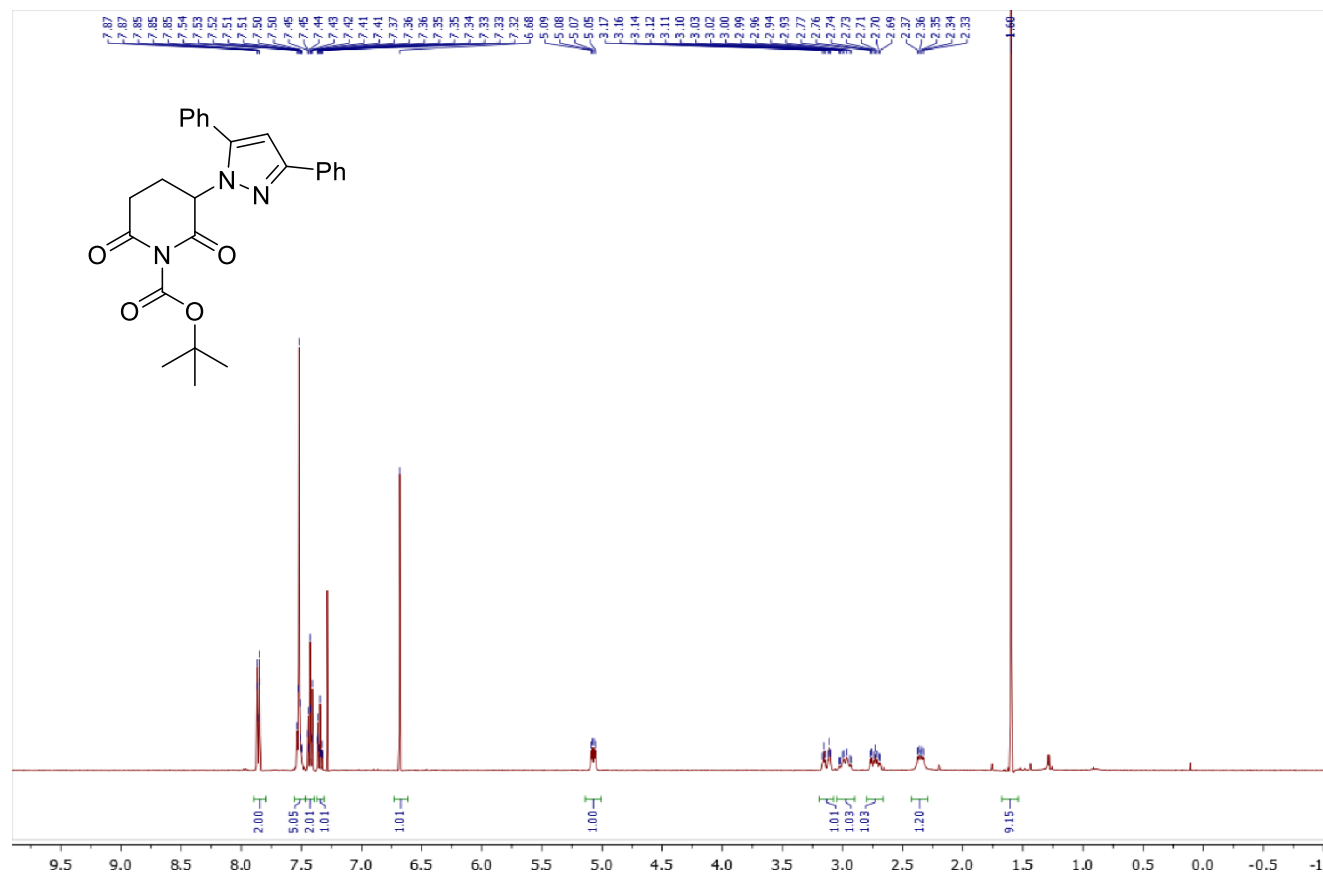
Copies of ^1H (400.13 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (100.61 MHz, CDCl_3) spectra of **9c**



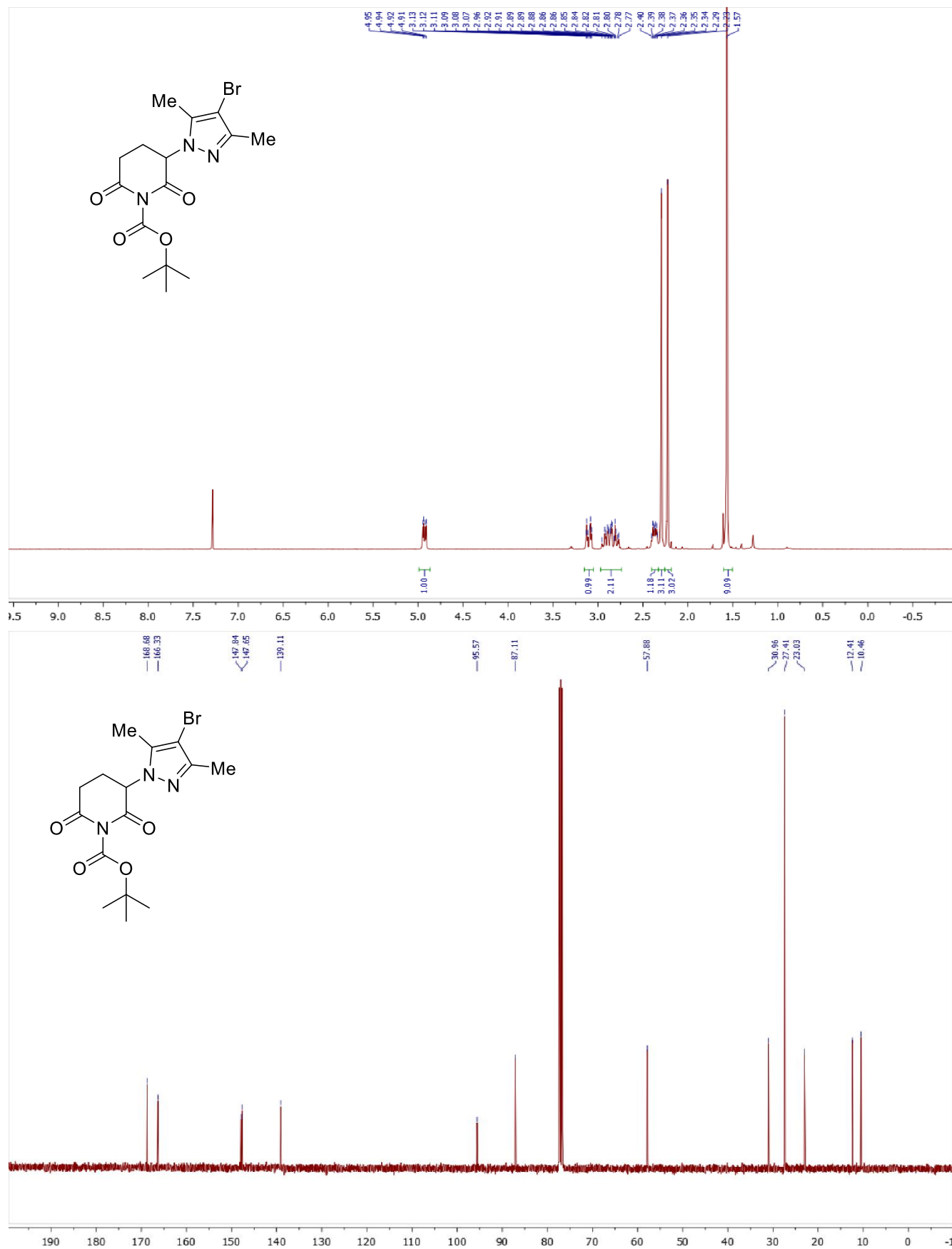
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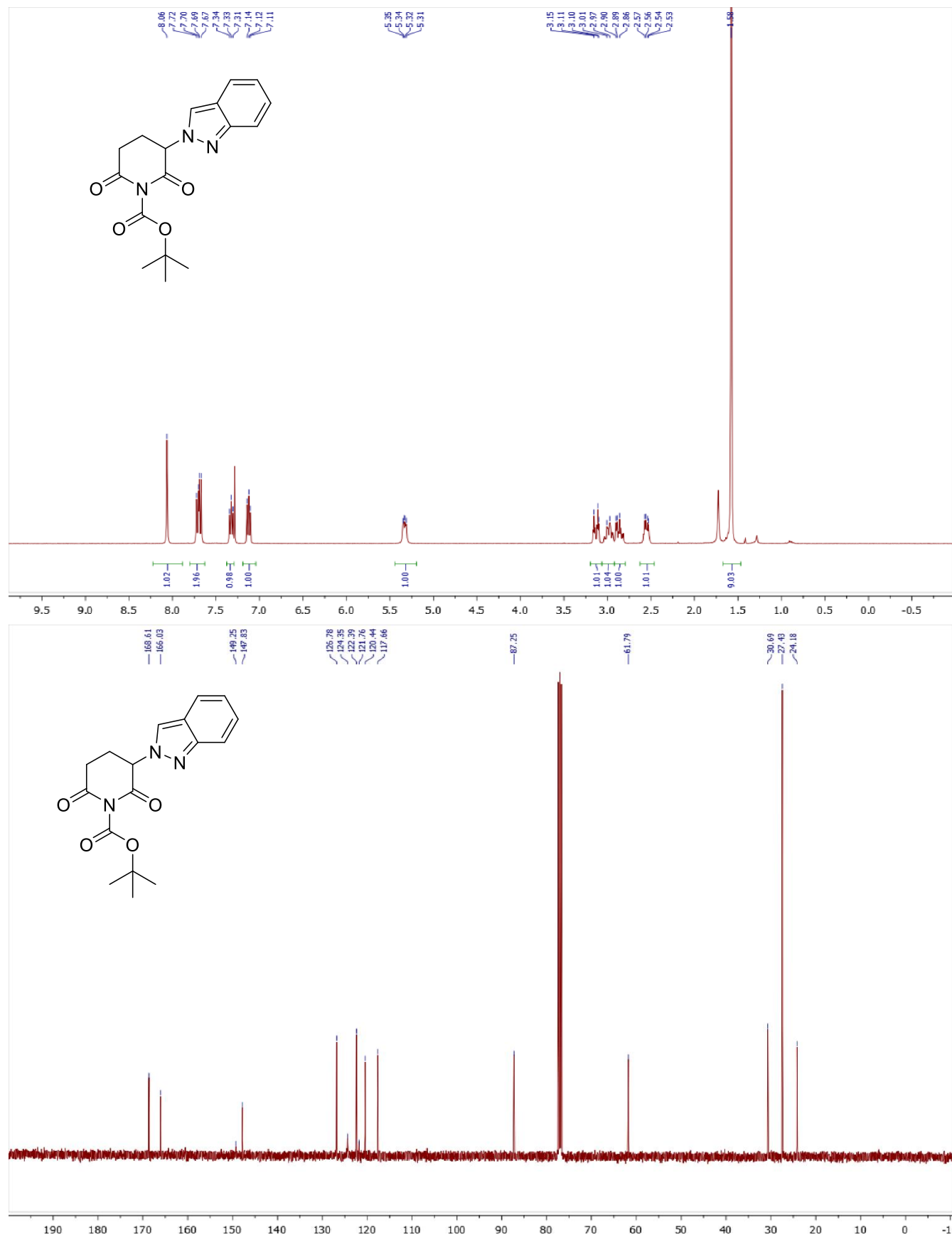
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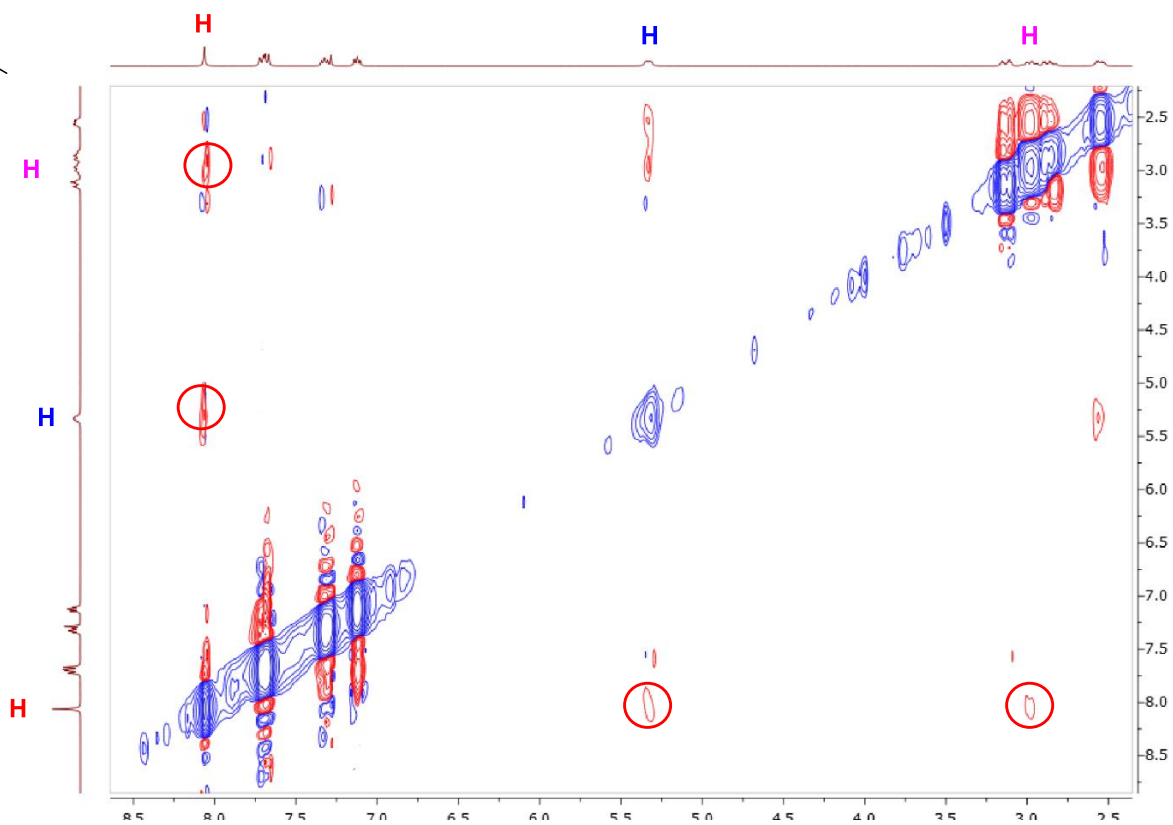
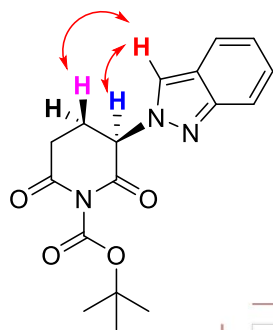
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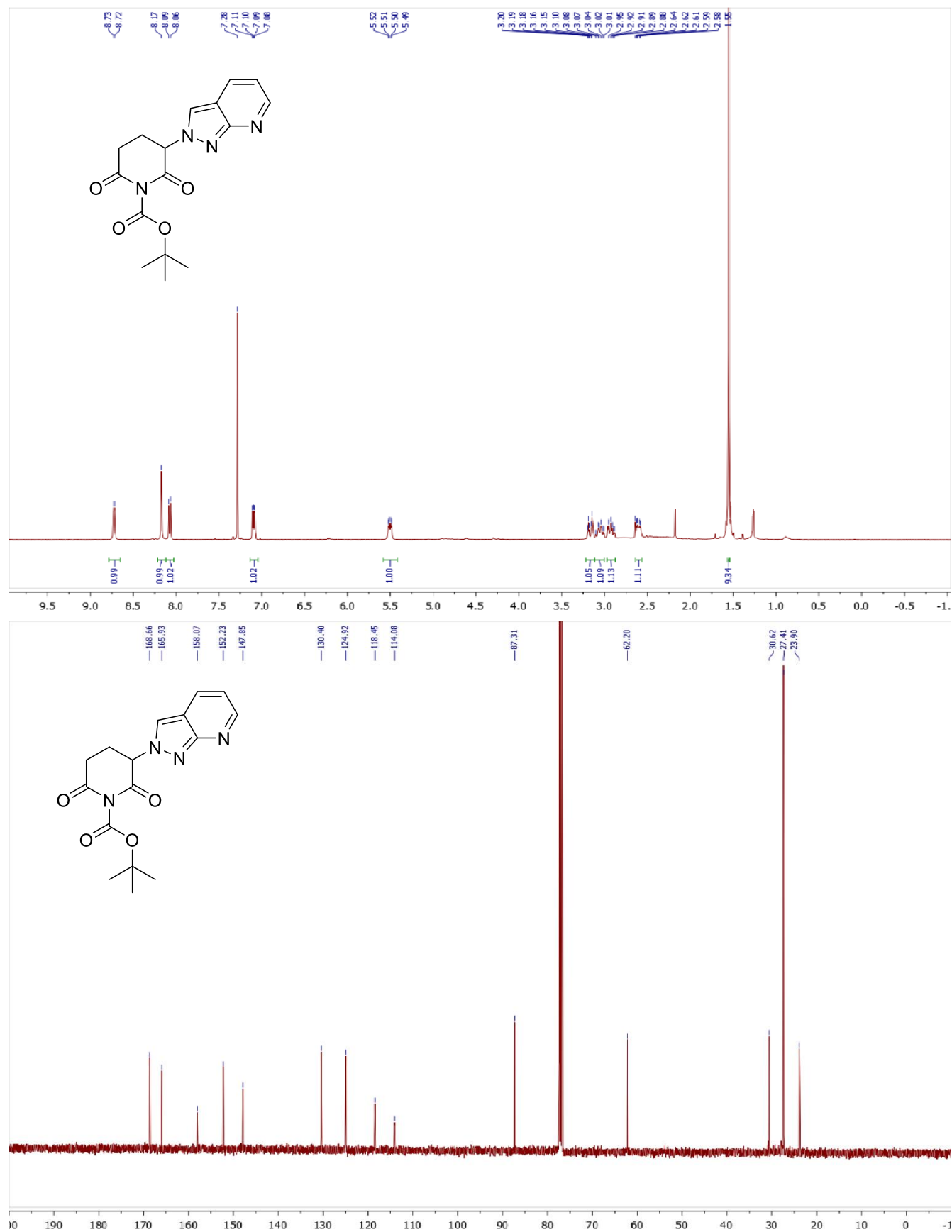
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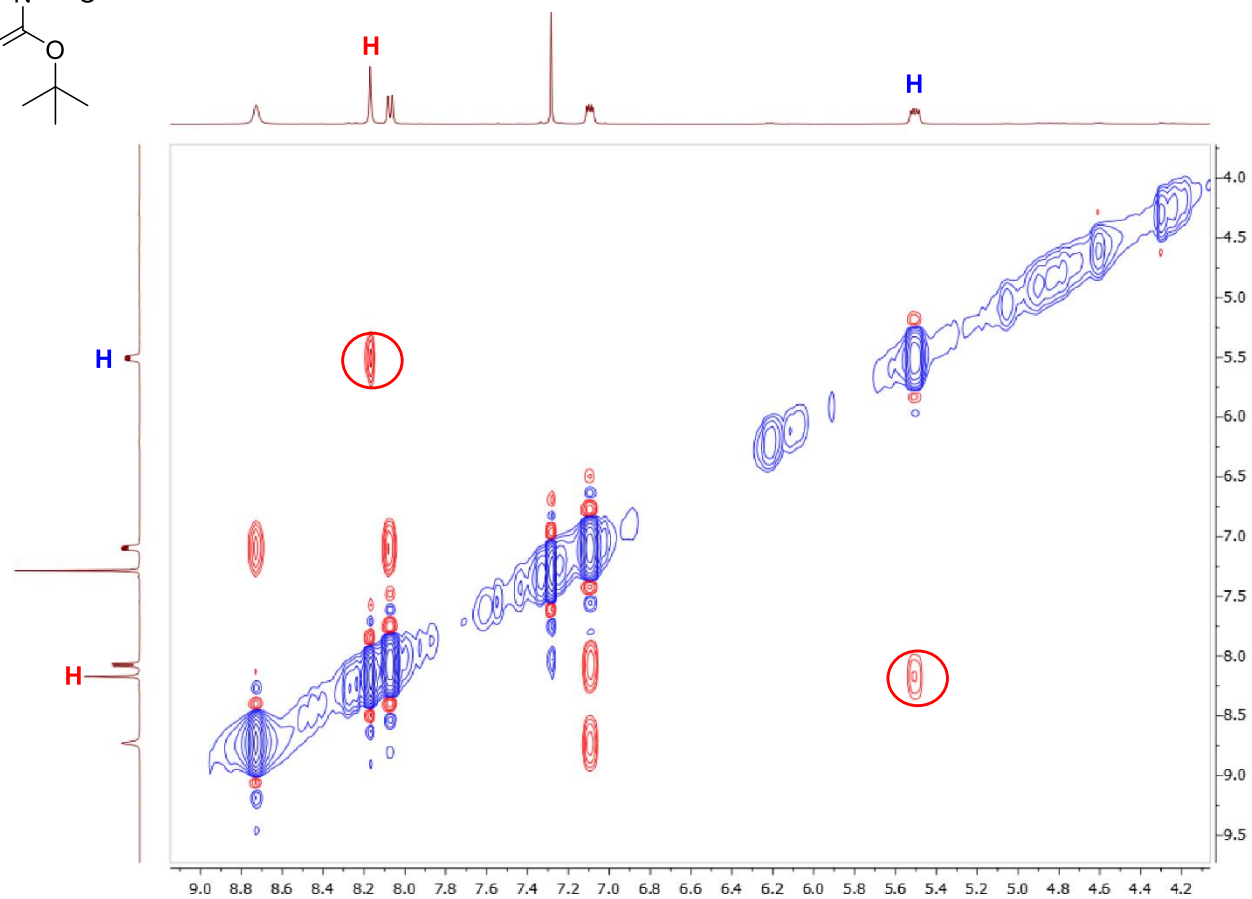
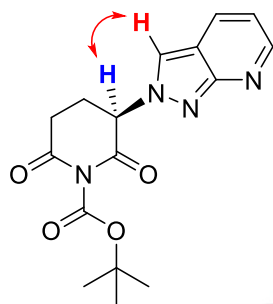
Copy of NOESY spectrum of **6g**



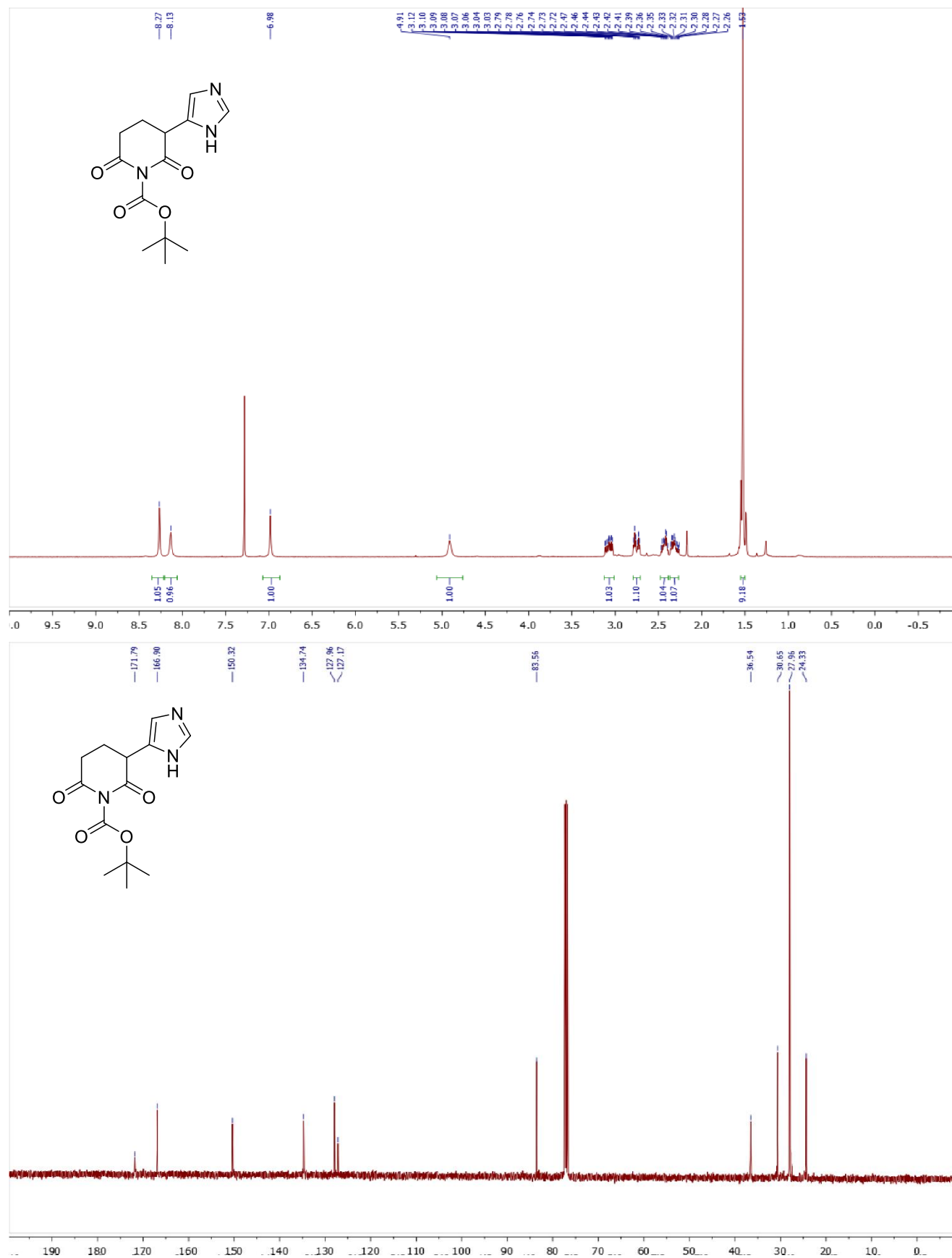
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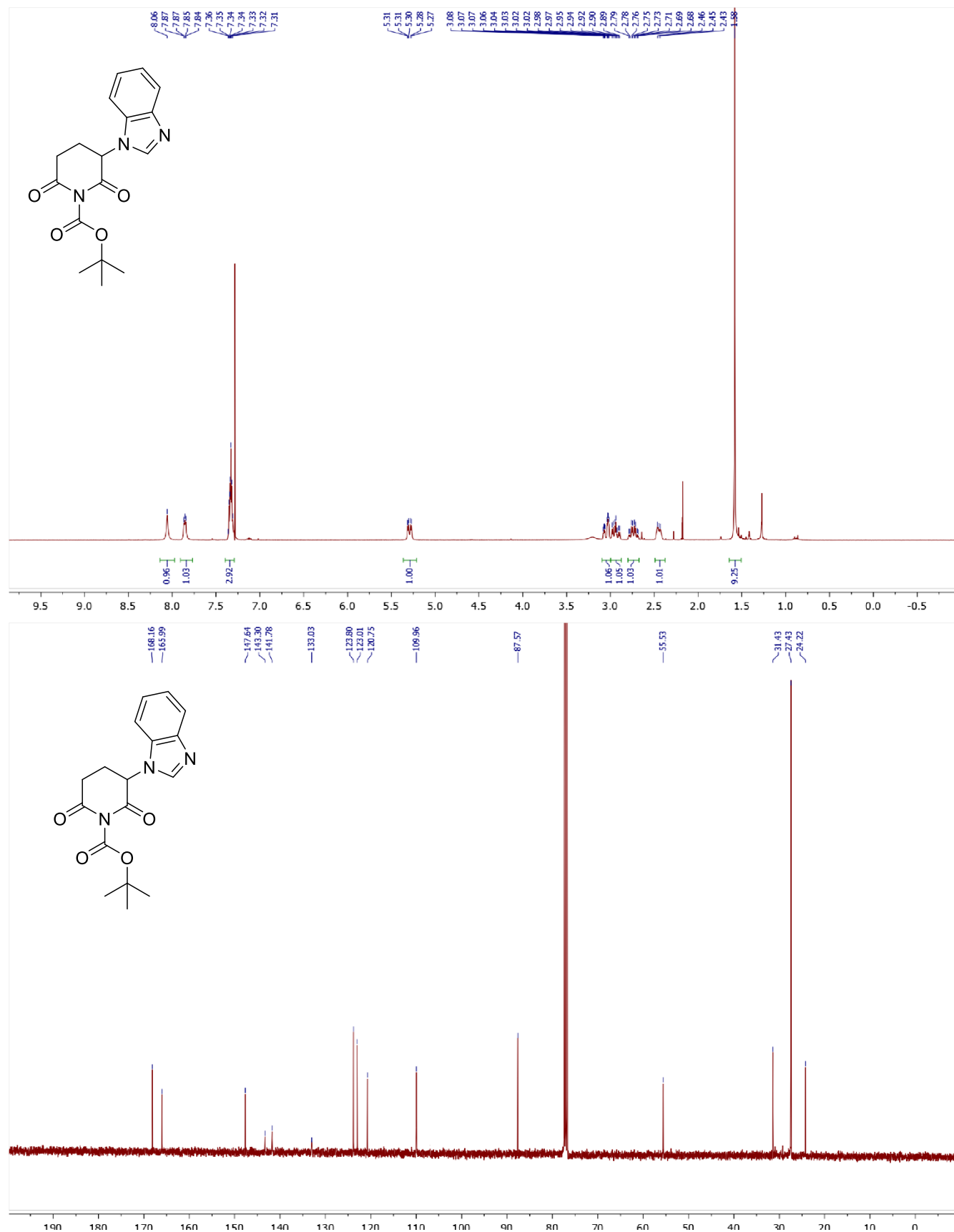
Copy of NOESY spectrum of **6h**



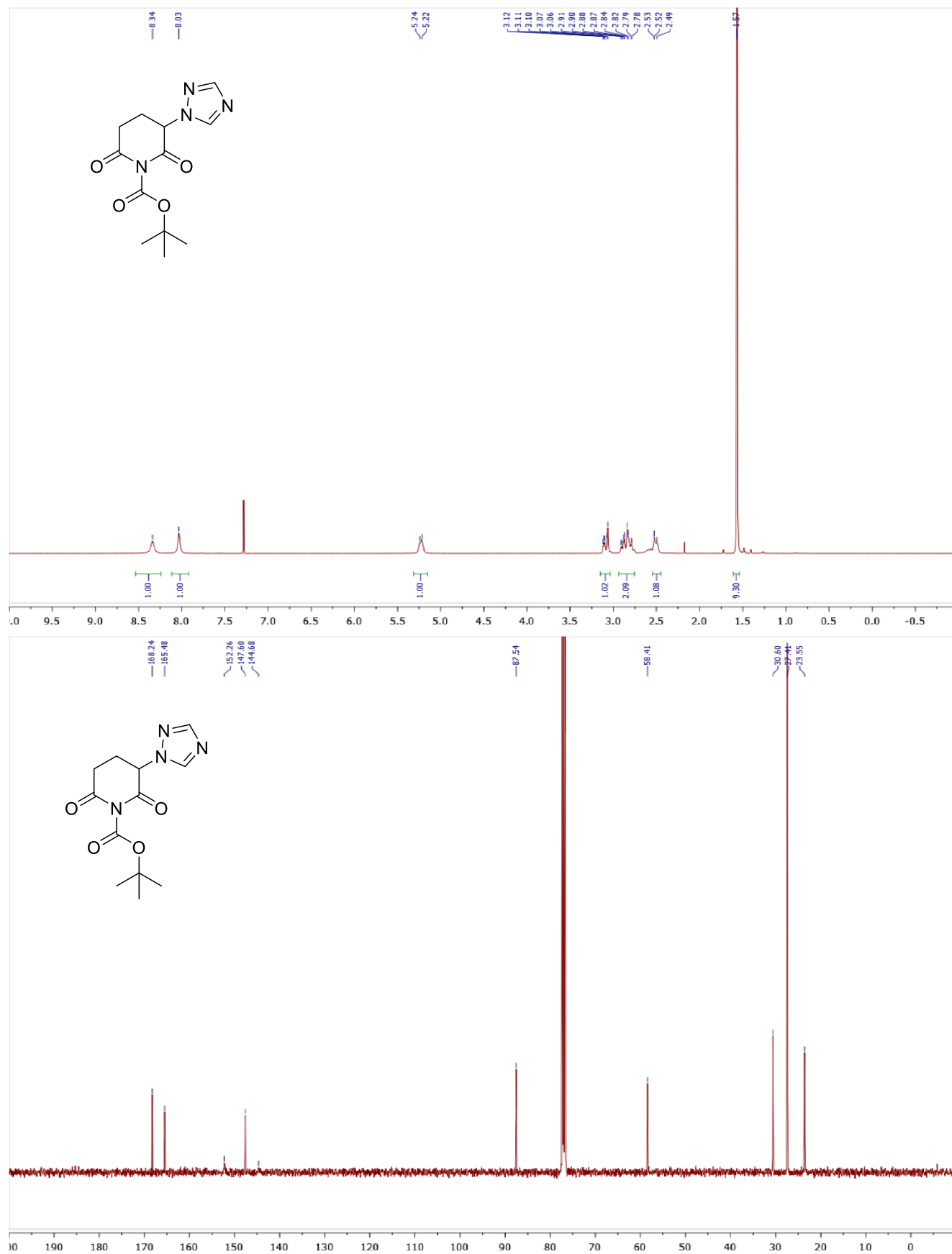
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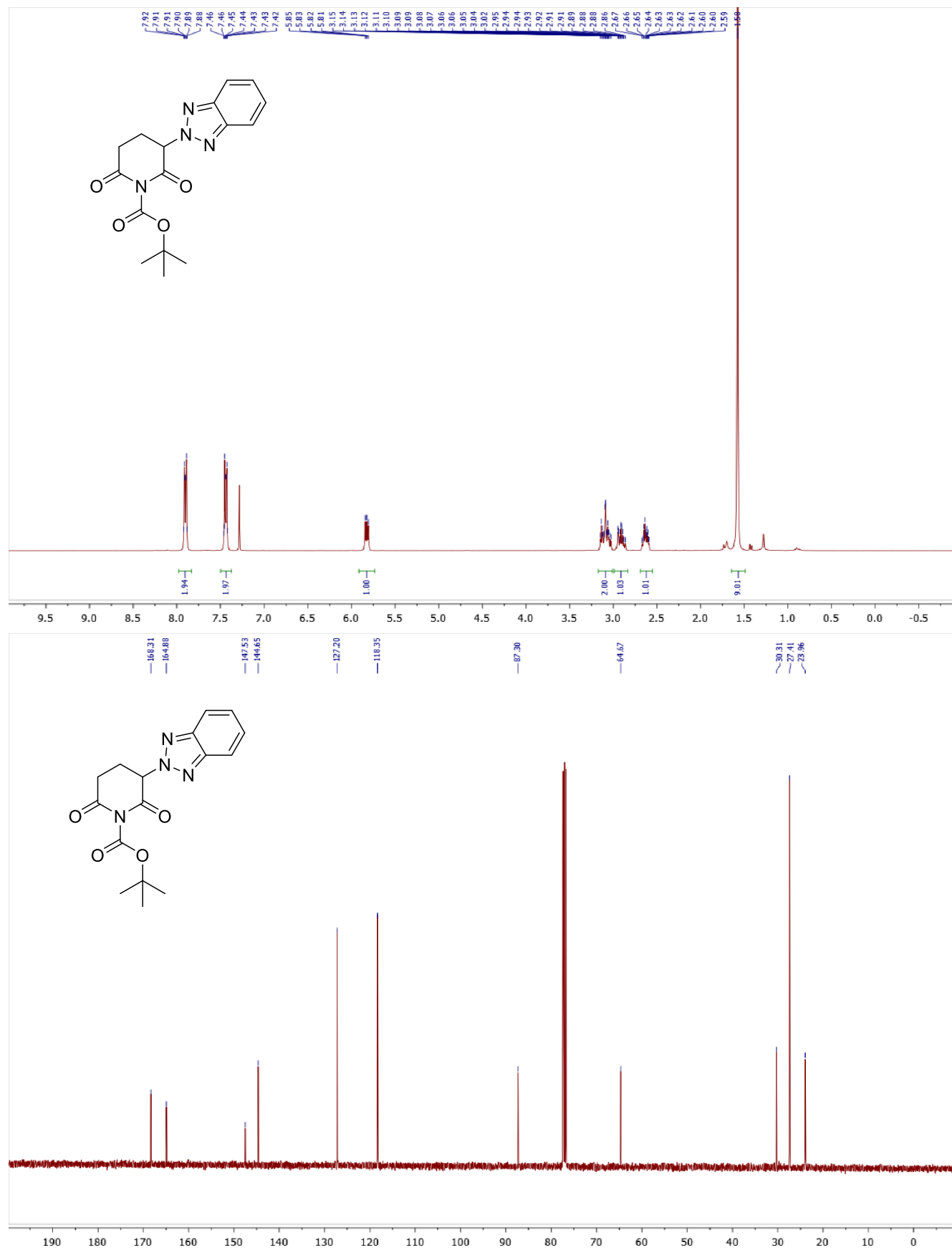
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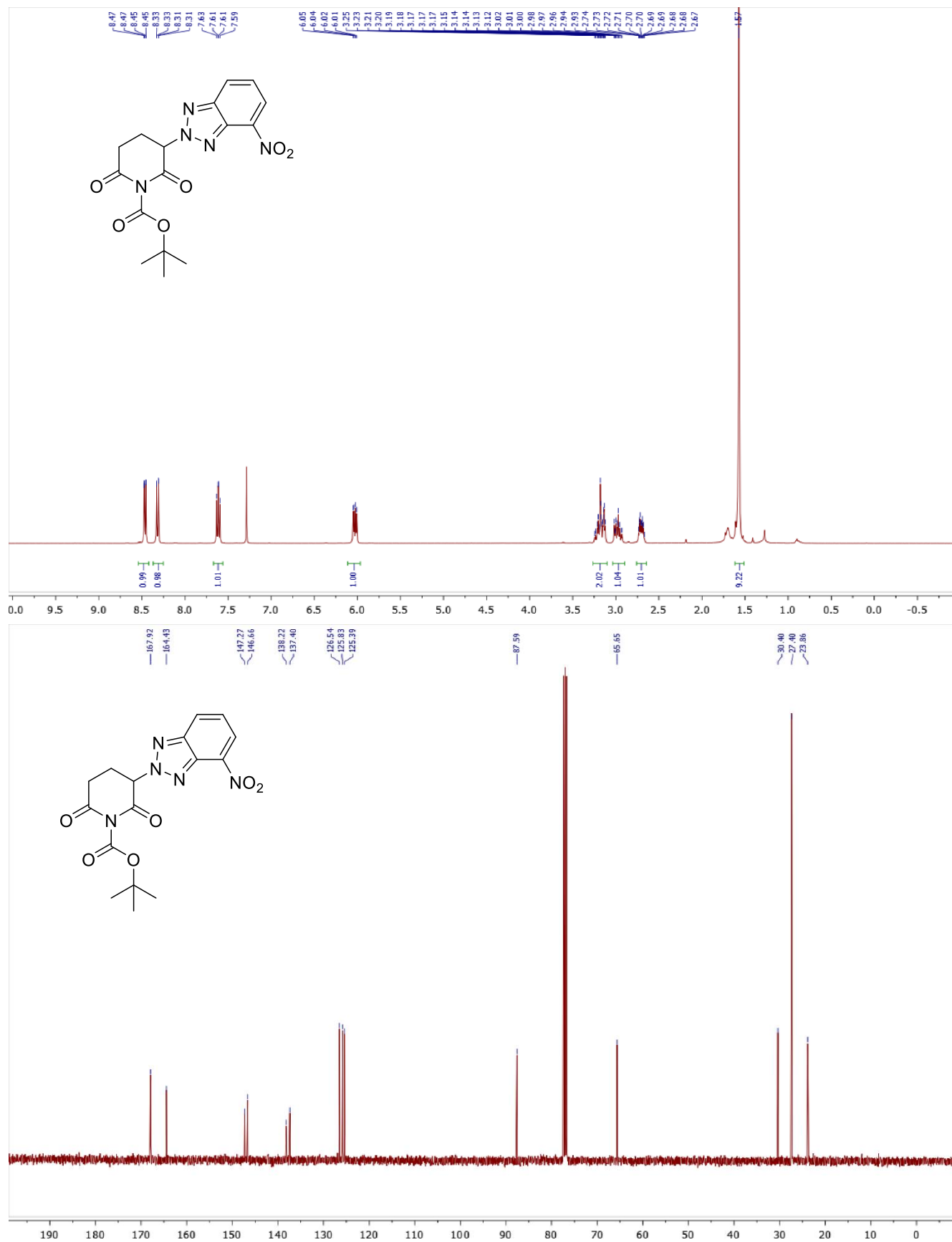
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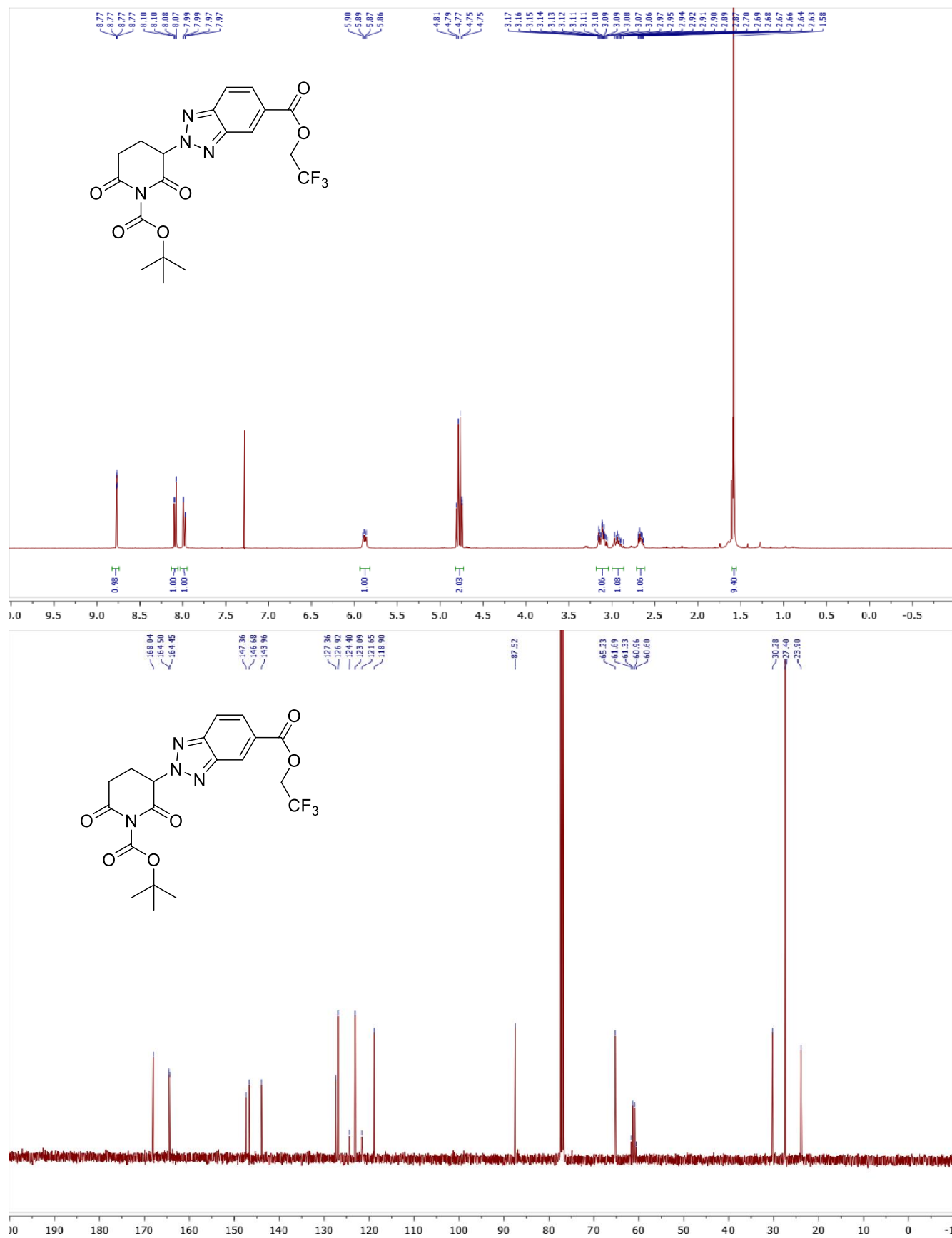
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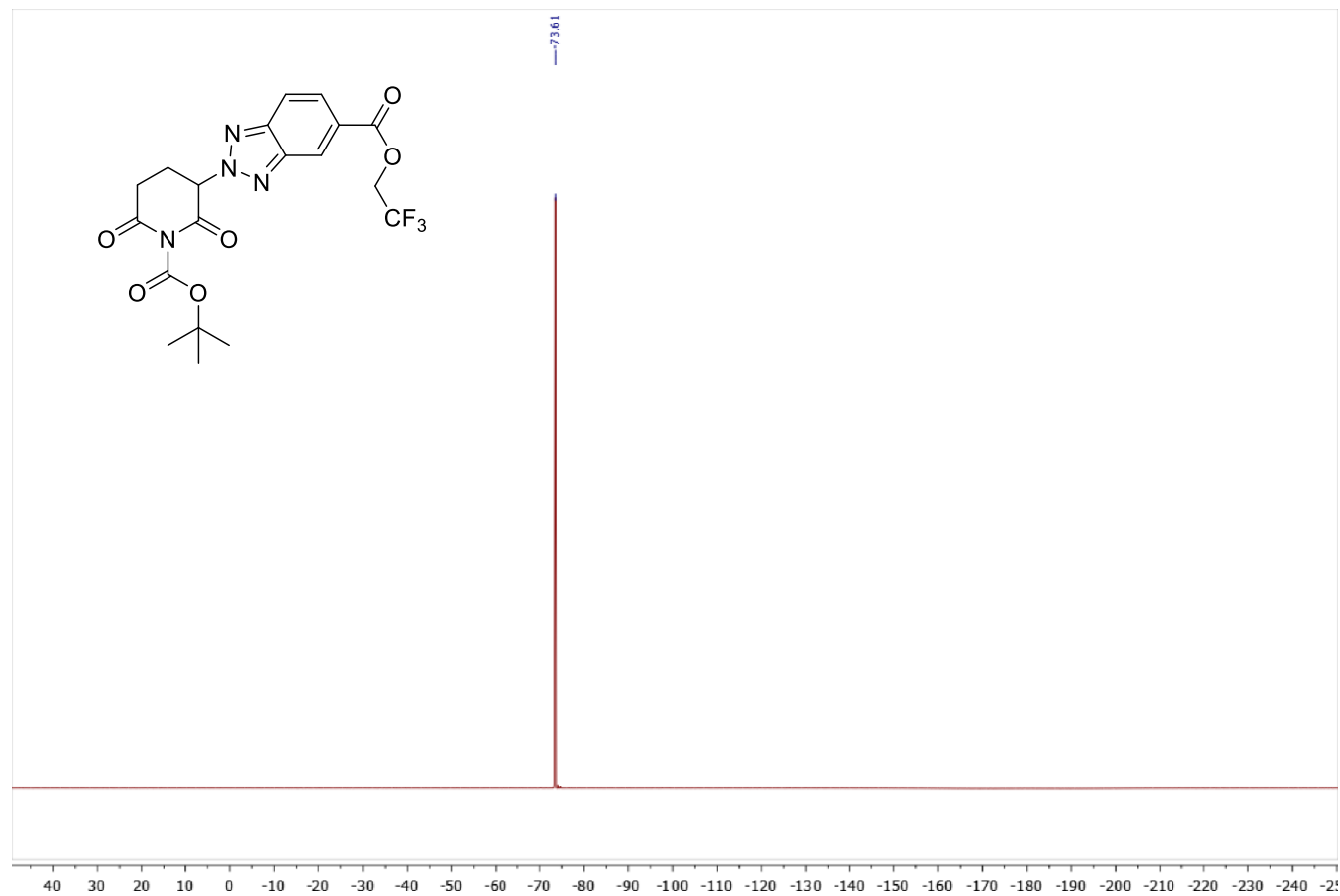
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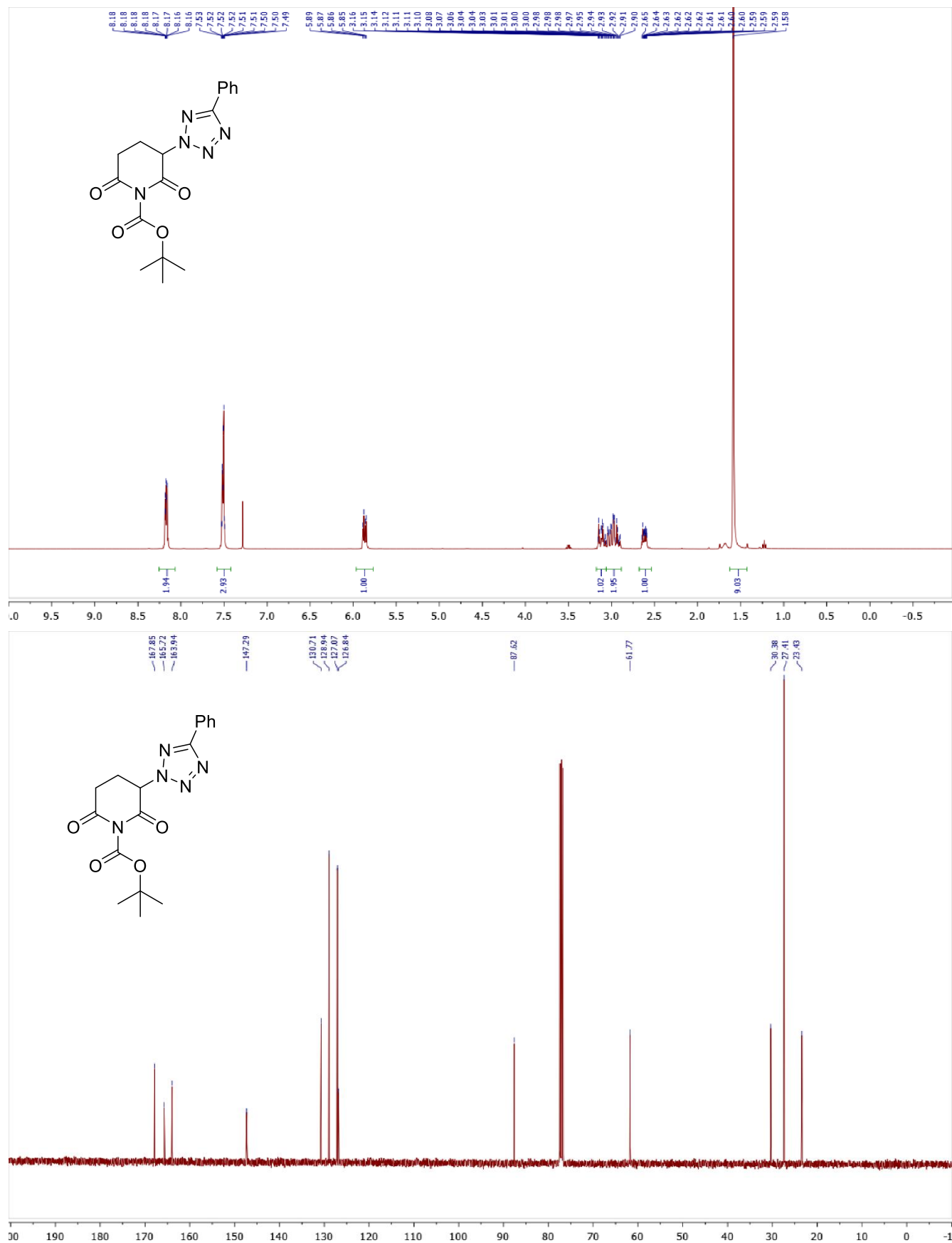
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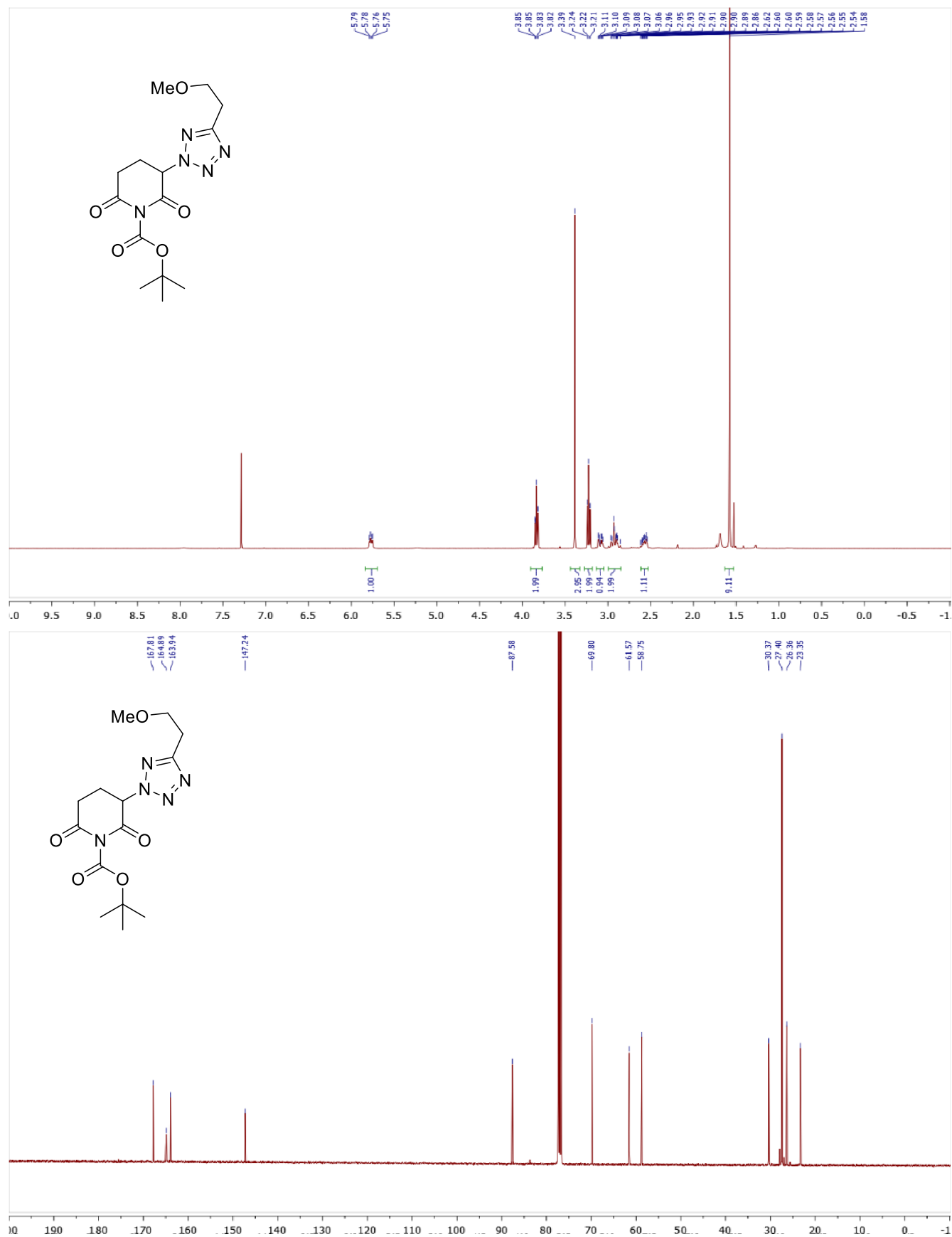
Copy of $^{19}\text{F}\{^1\text{H}\}$ (376.50 MHz, CDCl_3) spectrum of **6o**



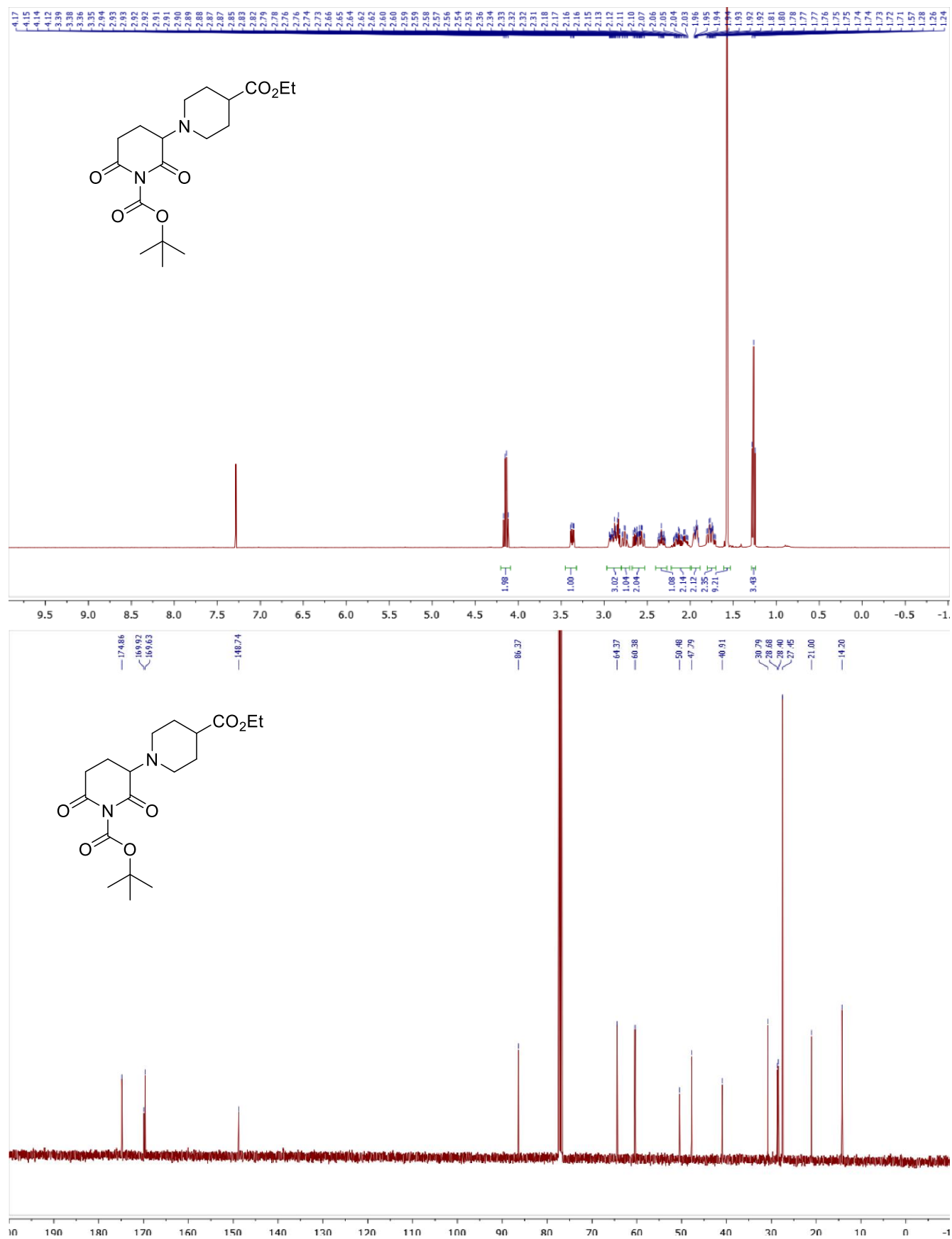
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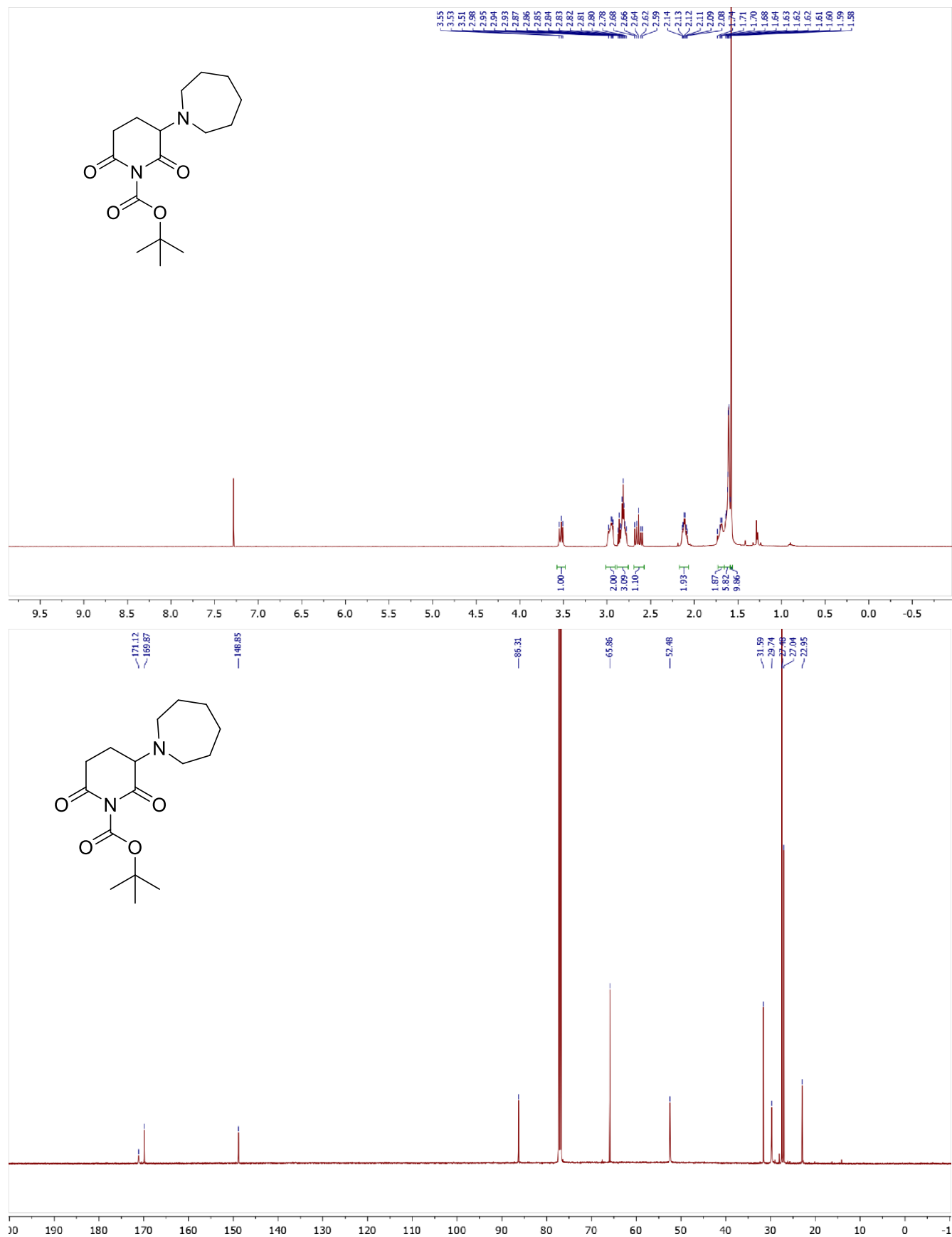
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Copies of ^1H (400.13 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (100.61 MHz, CDCl_3) spectra of **6r**



Copies of ^1H (400.13 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (100.61 MHz, CDCl_3) spectra of **6s**



¹H NMR Spectrum (Top):

Chemical structure: CC(C)(C)OC(=O)N1C(=O)CC(N1C2=CC=CC=C2)C(=O)OC(C)(C)C

Peak list (ppm): 7.13, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 6.75, 6.74, 6.73, 6.72, 6.71, 6.47, 6.45, 4.40, 4.39, 4.37, 4.36, 3.56, 3.54, 3.54, 3.54, 3.52, 3.52, 3.50, 3.49, 3.47, 3.45, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 2.99, 2.98, 2.97, 2.95, 2.94, 2.93, 2.84, 2.83, 2.81, 2.80, 2.78, 2.76, 2.75, 2.73, 2.72, 2.70, 2.69, 2.68, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20.

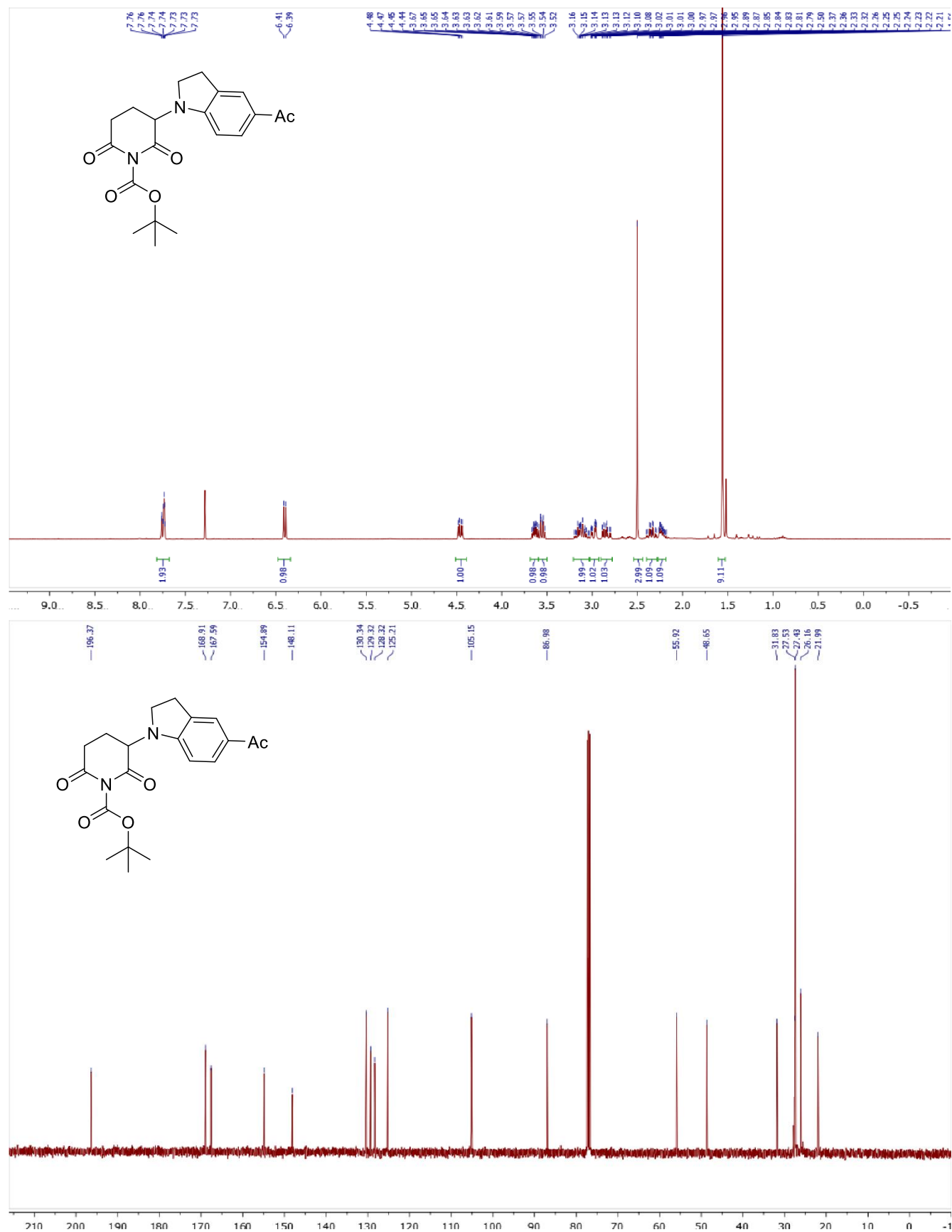
Integration values: 0.99, 0.99, 0.97, 0.98, 1.00, 1.99, 2.01, 1.02, 1.07, 2.24, 9.03.

¹³C NMR Spectrum (Bottom):

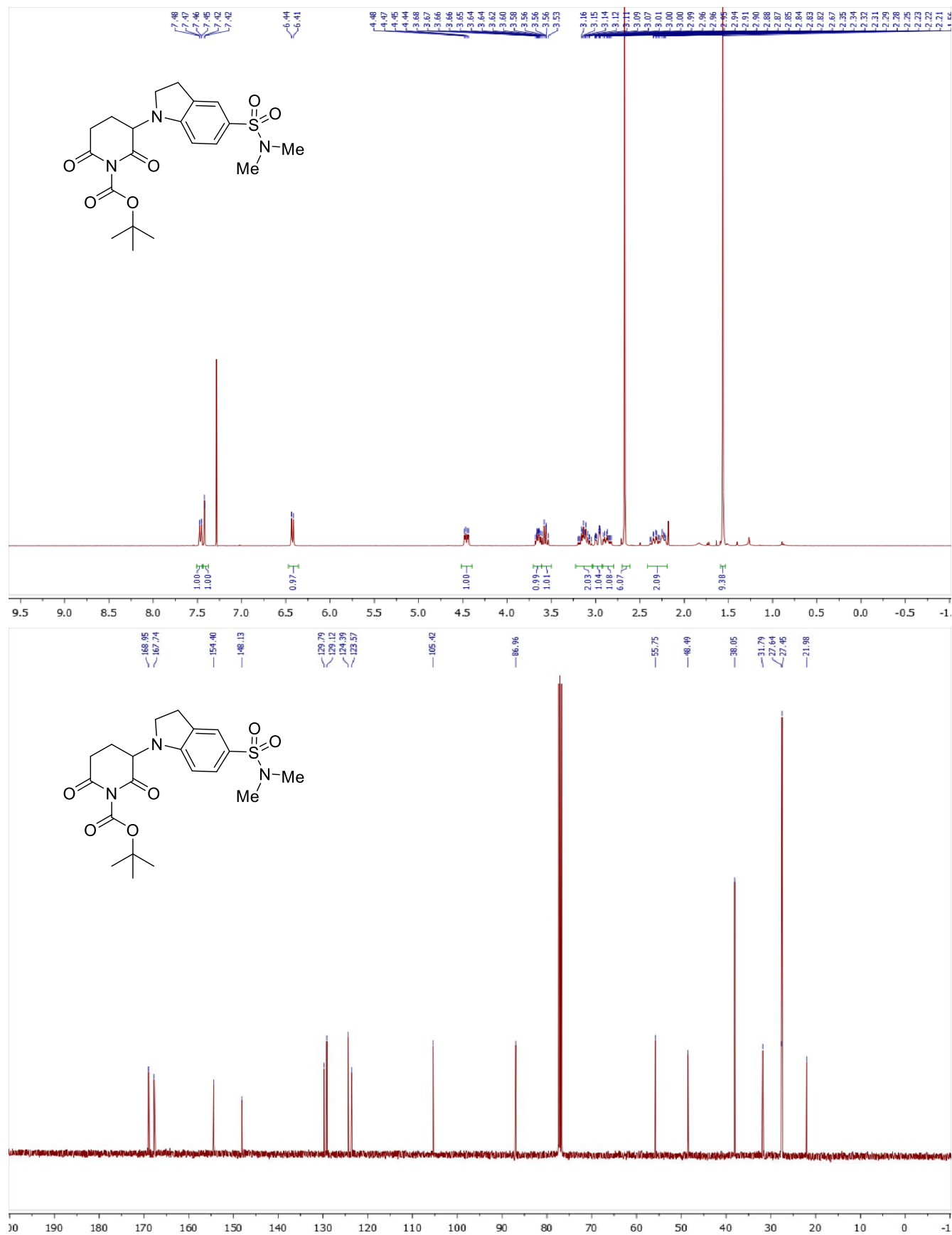
Chemical structure: CC(C)(C)OC(=O)N1C(=O)CC(N1C2=CC=CC=C2)C(=O)OC(C)(C)C

Peak list (ppm): 169.25, 168.13, 150.00, 148.35, 129.49, 127.31, 124.92, 118.84, 107.07, 86.70, 56.64, 48.78, 31.91, 28.43, 27.46, 21.53.

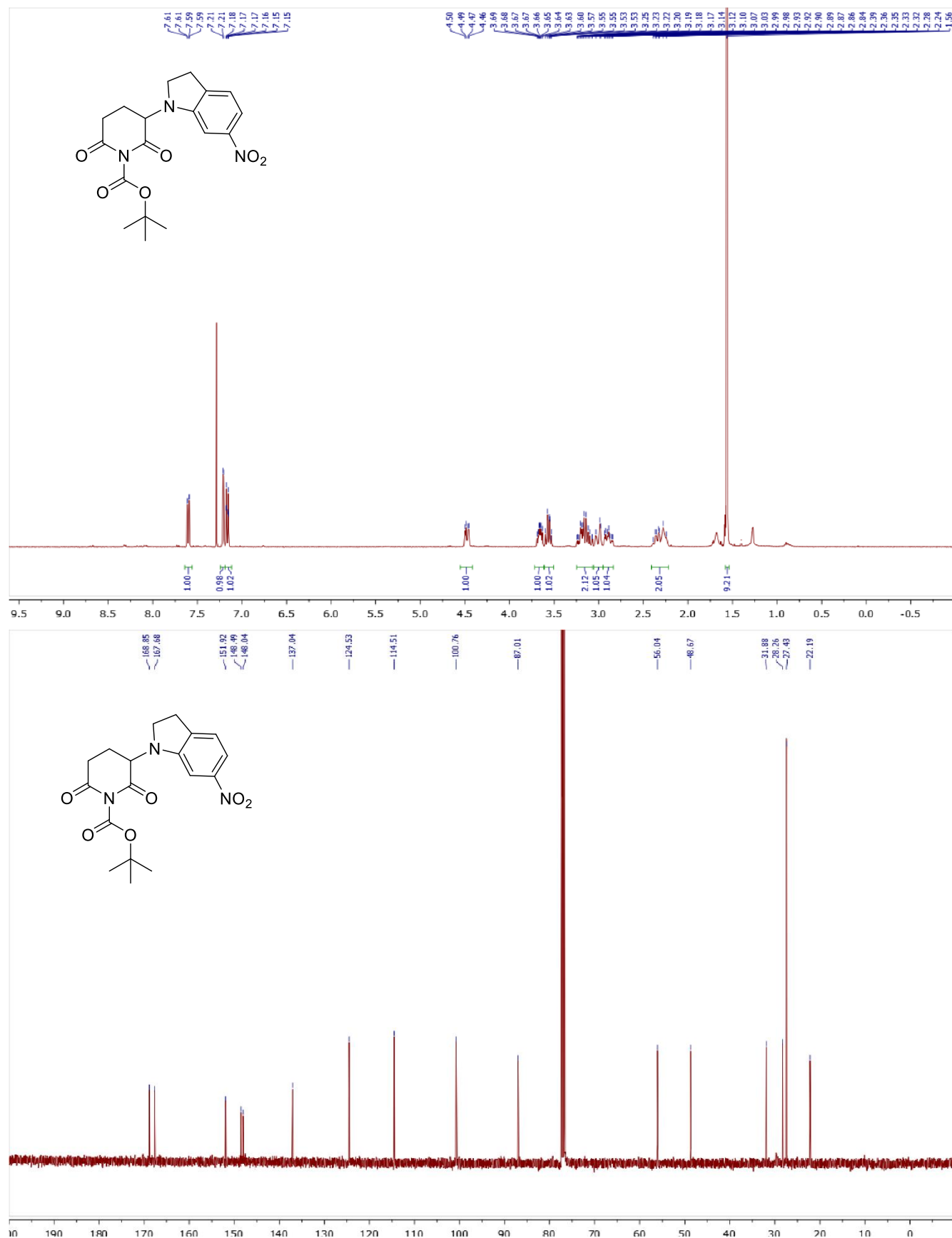
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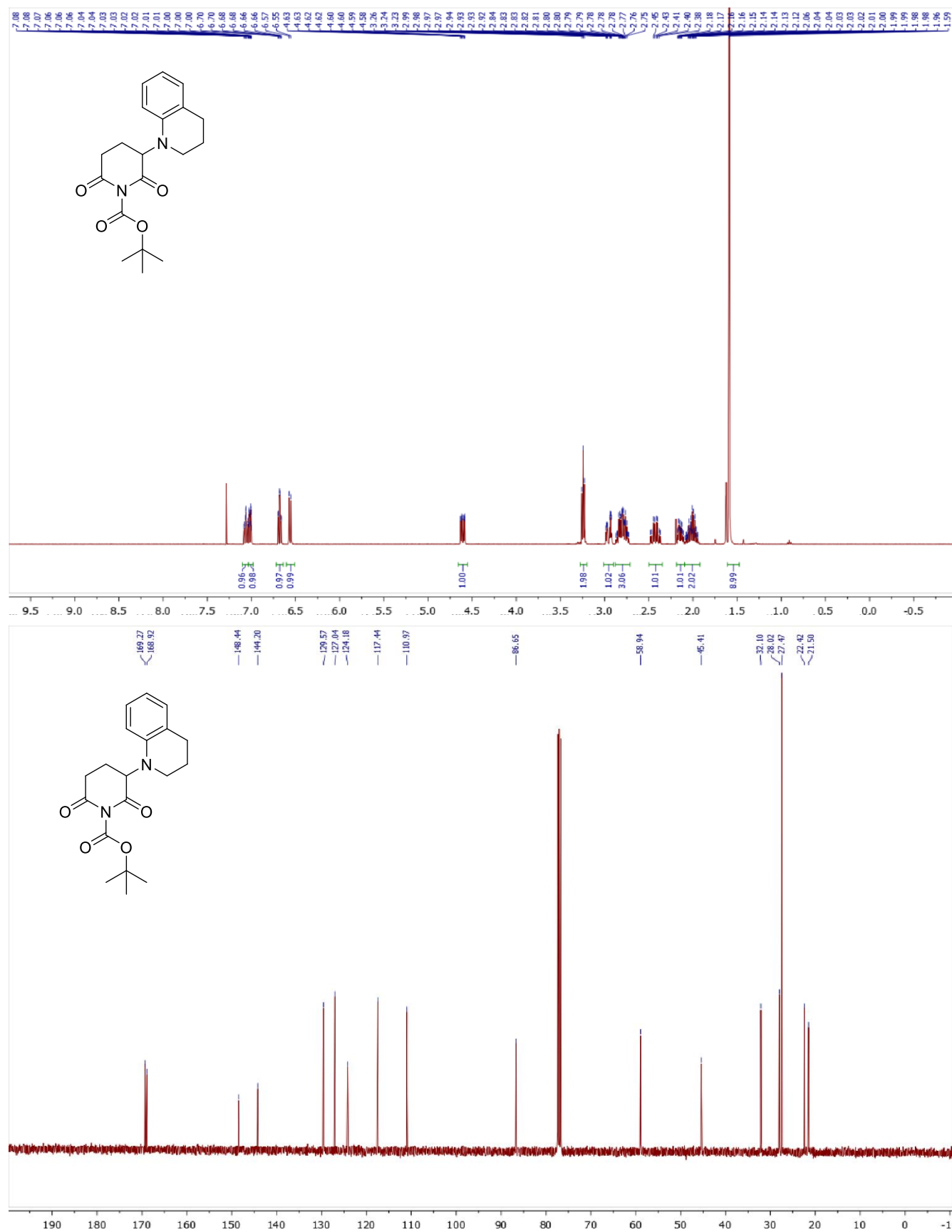
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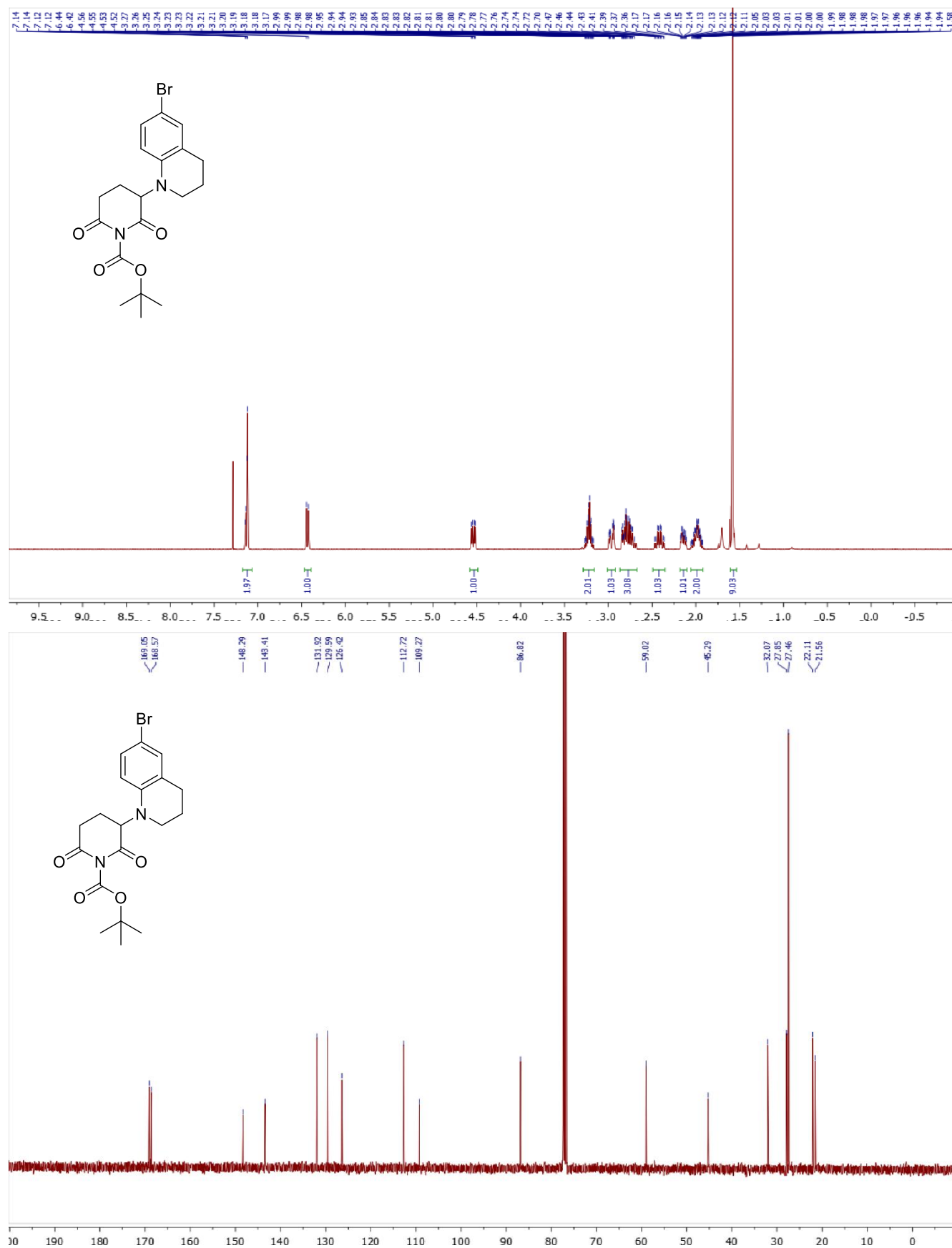
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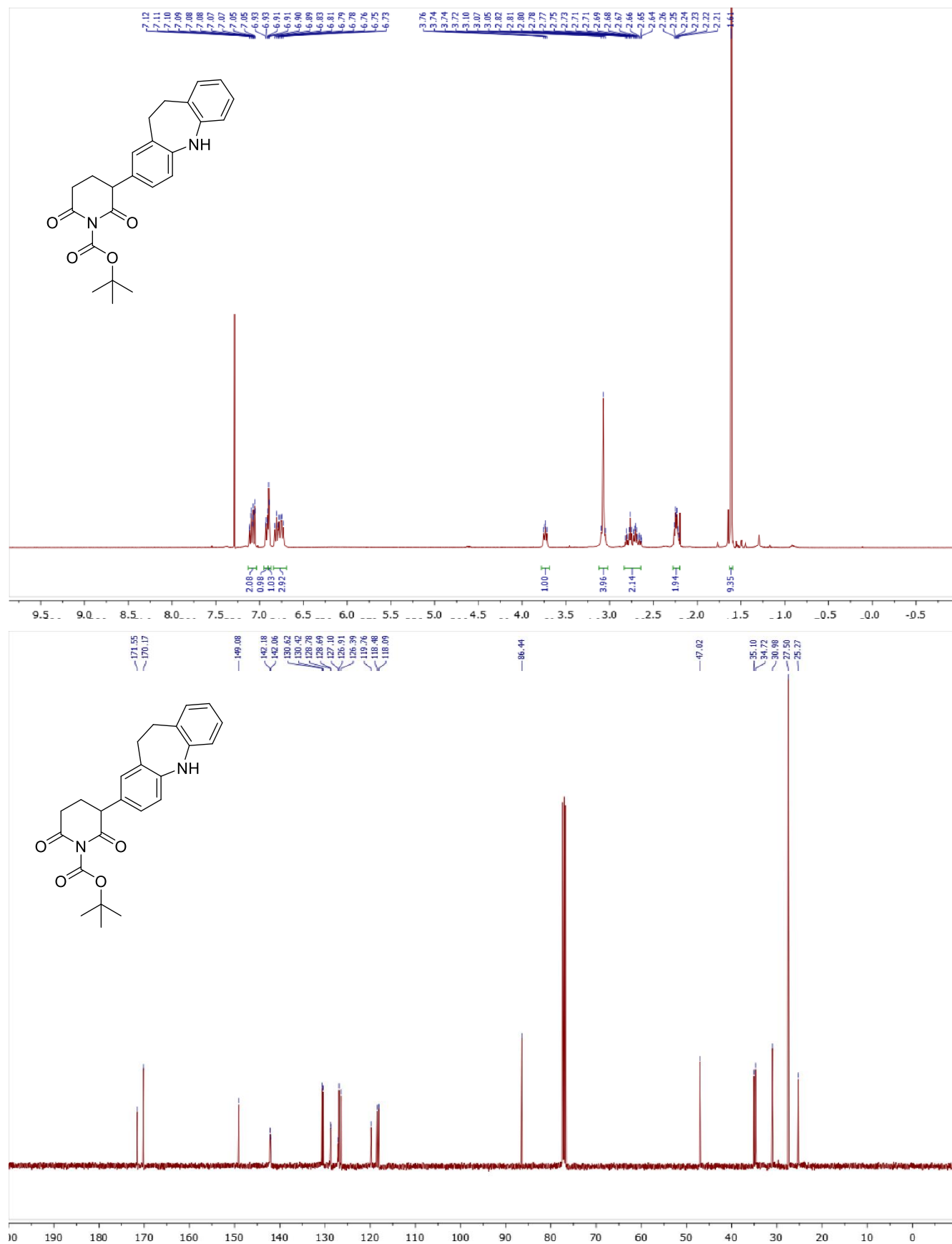
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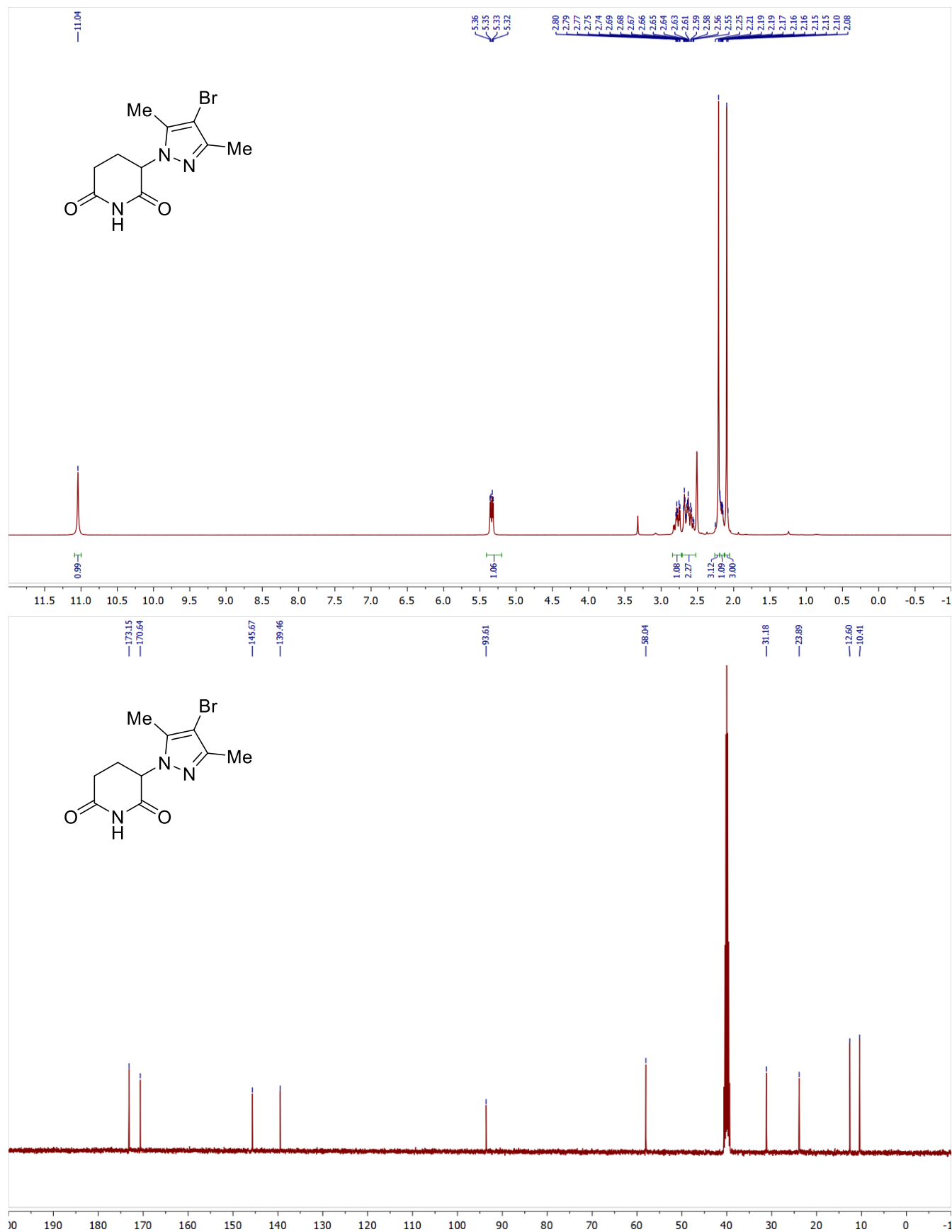
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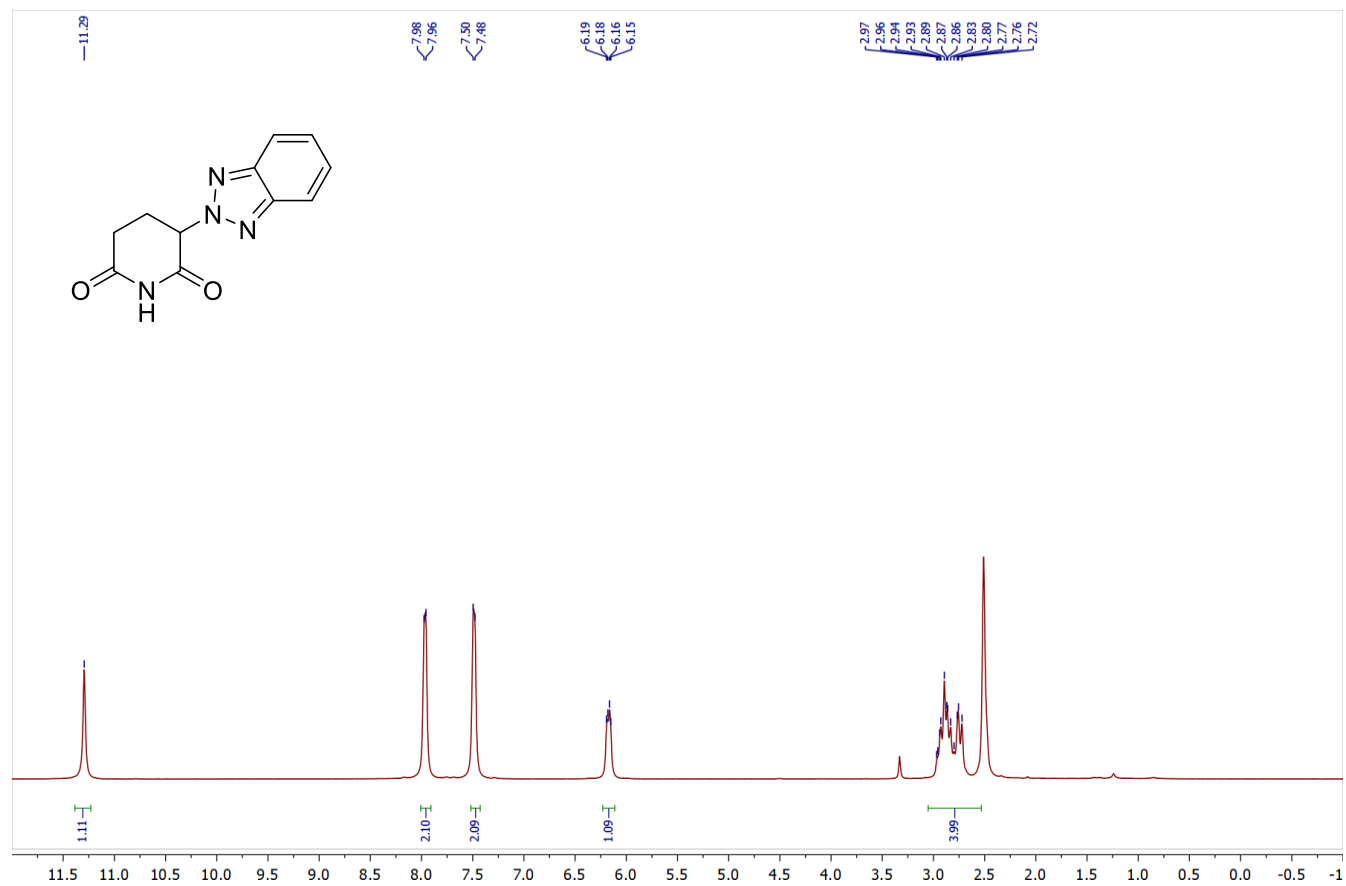
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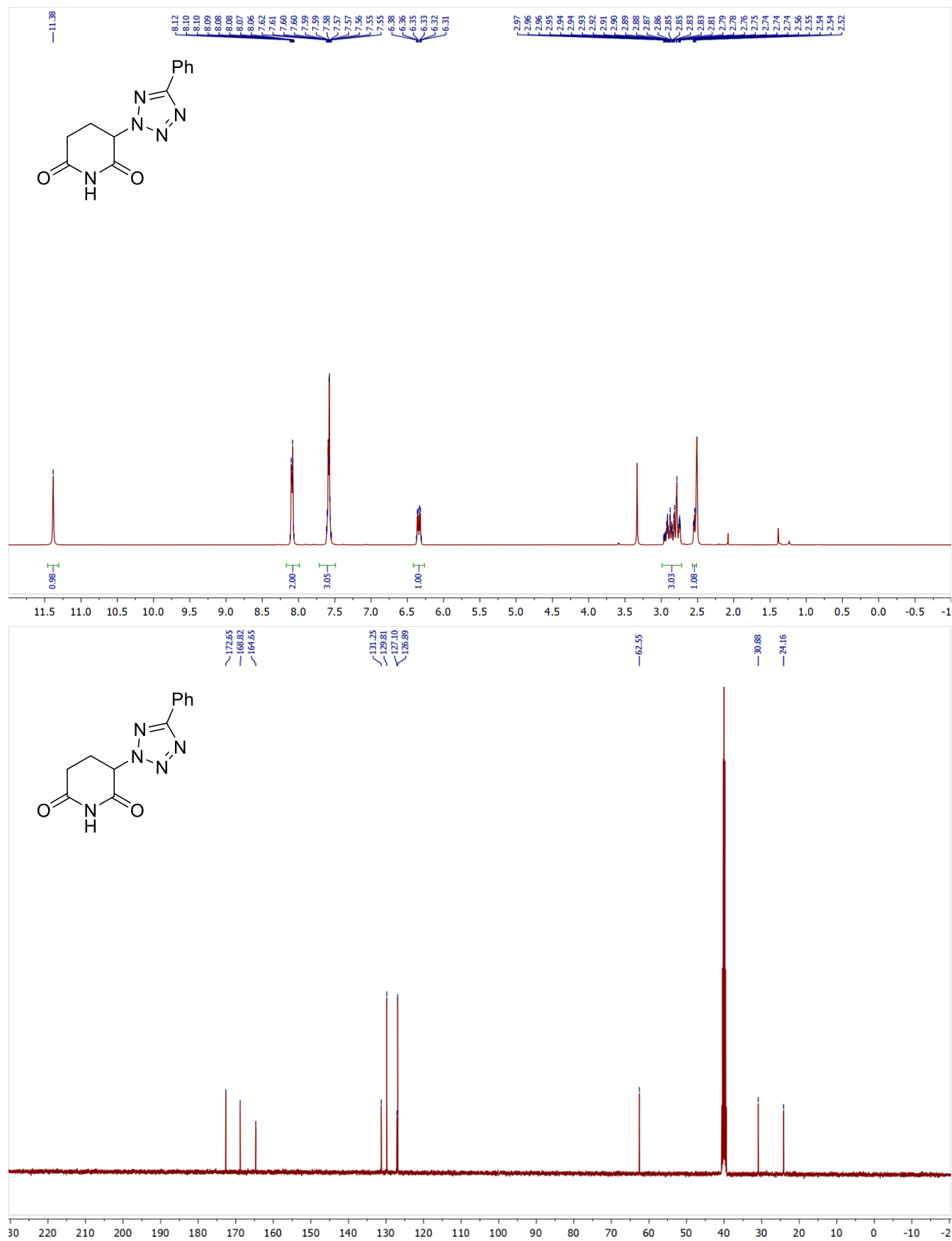
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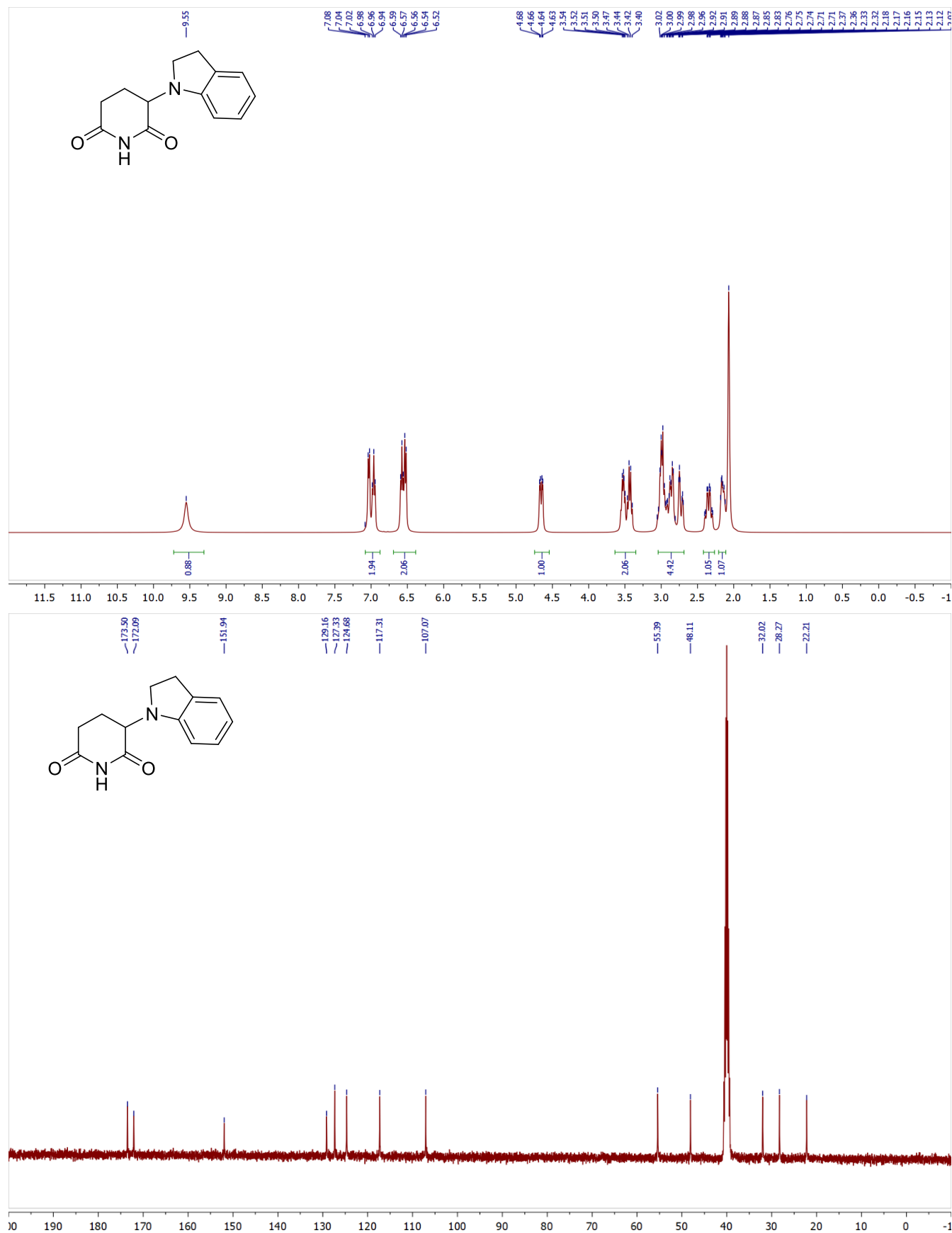
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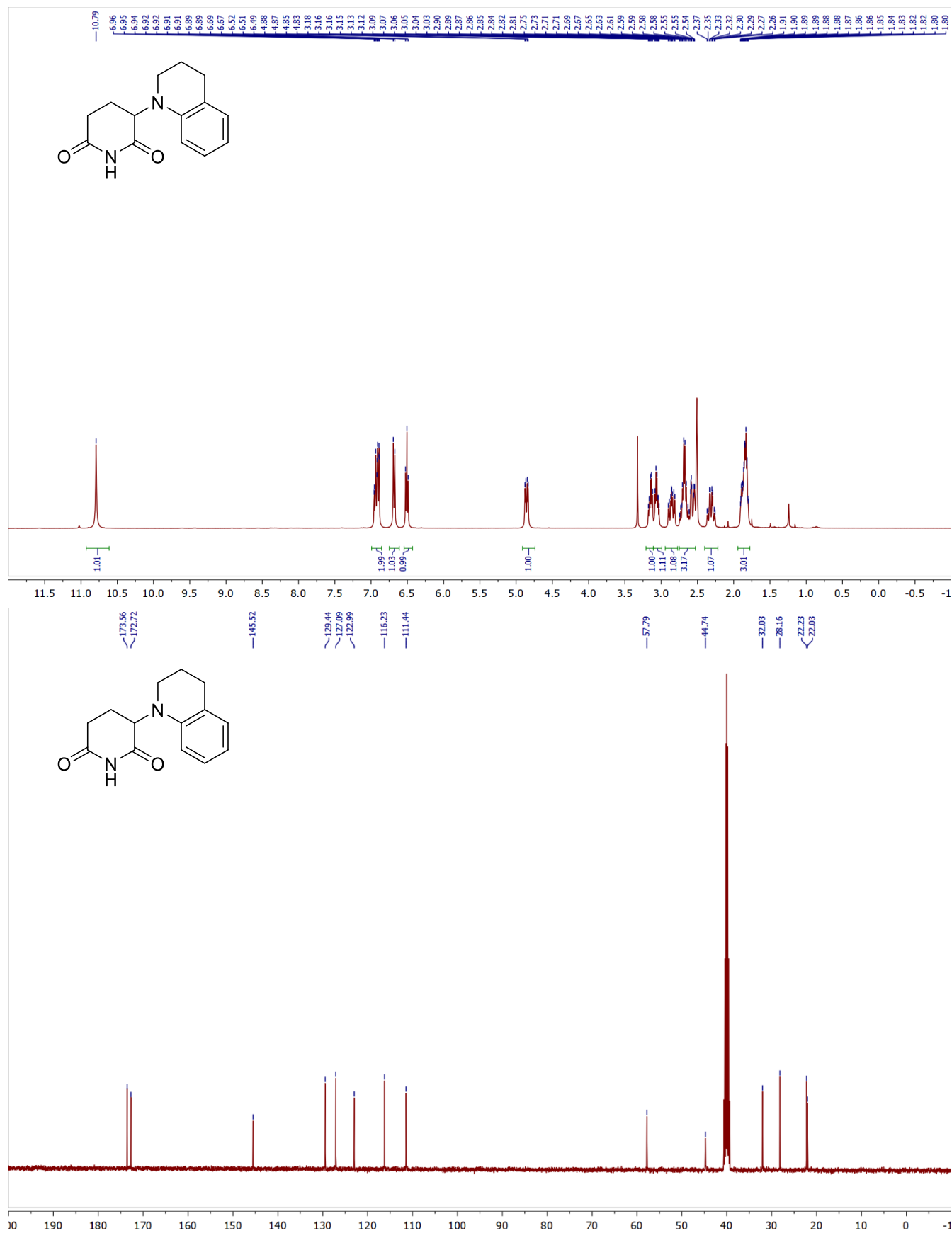
Copies of ^1H (400.13 MHz, $\text{DMSO}-d_6$) and $^{13}\text{C}\{^1\text{H}\}$ (101.61 MHz, $\text{DMSO}-d_6$) spectra of **1c**



Copies of ^1H (400.13 MHz, Acetone- d_6) and $^{13}\text{C}\{^1\text{H}\}$ (101.61 MHz, DMSO- d_6) spectra of **1d**



Copies of ^1H (400.13 MHz, $\text{DMSO-}d_6$) and $^{13}\text{C}\{^1\text{H}\}$ (101.61 MHz, $\text{DMSO-}d_6$) spectra of **1e**



Copies of ^1H (400.13 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (101.61 MHz, CDCl_3) spectra of **10**

