Supporting Information

Oxazolines as Dual Function Traceless Chromophores and Chiral Auxiliaries: Enantioselective Photoassisted Synthesis of Polyheterocyclic Ketones.

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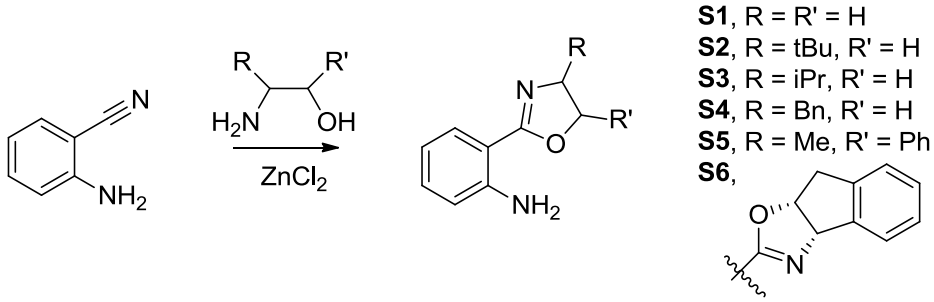
Common solvents were purchased from Fisher Scientific and used as is, except for THF, which was refluxed over and distilled from potassium benzophenone ketyl prior to use. Common reagents were purchased from Aldrich, TCI America or AK Scientific and used without additional purification, unless indicated otherwise. NMR spectra were recorded at 25°C on a Bruker Avance III 500 MHz in $CDCl_3$ with TMS as an internal standard (unless noted otherwise). High resolution mass spectra were obtained on the *MDS SCIEX/Applied Biosystems API QSTARTM Pulsar i Hybrid LC/MS/MS System* mass spectrometer at CU-Boulder by Weston Umstead and Dmitry Kuznetsov. Flash column chromatography was performed using Teledyne Ultra Pure Silica Gel (230 – 400 mesh) on a Teledyne Isco Combiflash Rf using Hexanes/EtOAc as eluent.

Synthesis of 2-(4-alkyl-4,5-dihydrooxazol-2-yl)anilines

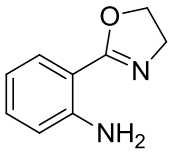


General procedure 1a: 3.0 g of 2-aminobenzonitrile (25mmol, 1eq) was suspended in 40mL xylenes along with 83 mmol (3.3eq) of 2-aminoalcohol and 3.46 g $ZnCl_2$ (26 mmol) as a catalyst. The mixture was refluxed under nitrogen atmosphere for 36 h. The solvent was removed and the crude product was dissolved in dichloromethane. After washing with water, the organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel using 95:5 (v.v) hexanes:EtOAc as eluent affording the corresponding oxazoline.

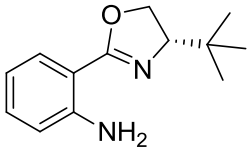
General procedure 1b[1]: Under nitrogen atmosphere, 2-aminobenzonitrile (25 mmol) and 2-aminoalcohol (75 mmol) were dissolved in anhydrous chlorobenzene (40 mL), $ZnCl_2$ (0.51 g, 3.75 mmol) was used as a catalyst. The mixture was refluxed for 36 h to give a red solution. The solvent was removed *in vacuo*, and the crude product was dissolved in dichloromethane. After washing with water, the organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The

residue was purified by column chromatography on silica gel using 95:5 (v.v) hexanes:EtOAc as eluent affording the corresponding oxazoline.

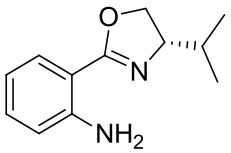
General procedure 1c[2]: To a solution of 2-aminobenzonitrile (25.4 mmol) in chlorobenzene (50 mL), $ZnCl_2$ (3.46 g, 25.4 mmol) and 2-aminoalcohol (25.6 mmol) were added. The mixture was heated to 130°C for 36 h. After cooling to room temperature, water (10 mL) was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL), the combined organic extracts were washed with water, brine, dried over $MgSO_4$. After filtration, the solution was concentrated *in vacuo*, and then purified by flash chromatography on silica gel using 95:5 (v.v) hexanes:EtOAc as eluent affording the corresponding oxazoline.



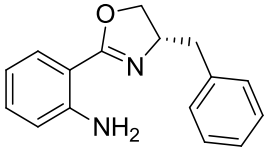
2-(4,5-dihydrooxazol-2-yl)aniline[1] (**S1**) General procedure **1a** was followed. From 2.95 g (25 mmol) of 2-aminobenzonitrile, 5.06 g (83 mmol) of 2-aminoethanol and 3.46 g (26 mmol) of $ZnCl_2$ 2.90 g (72%) of the title compound was obtained ^{1}H NMR (500 MHz, DMSO) δ = 7.54 (d, *J* = 7.9 Hz, 1H), 7.16 (m, 1H), 6.96 (s, 2H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.53 (m, 1H), 4.29 (t, *J* = 9.5 Hz, 2H), 4.02 (t, *J* = 9.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 148.5, 132.0, 129.6, 116.0, 115.7, 109.2, 65.8, 55.0.



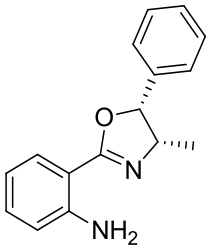
(*S*)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)aniline[3] **(S2)** General procedure 1c was followed. From 2.95 g (25 mmol) of 2-aminobenzonitrile, 2.92 g (25 mmol) of L-*tert*-leucinol and 3.46 g (26 mmol) of $ZnCl_2$ 2.20 g (40%) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.23 (td, *J* = 8.0, 7.3, 1.6 Hz, 1H), 6.73 (m, 1H), 6.68 (m, 1H), 6.19 (s, 2H), 4.27 (m, 1H), 4.13 (m, 2H), 0.97 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 163.5, 148.7, 131.9, 129.6, 115.9, 115.6, 109.2, 76.4, 66.9, 33.8, 25.9. HRMS (ESI) calcd for $C_{13}H_{19}N_2O^+$ (MH^+) 219.1492, found 219.1501



(*S*)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)aniline[1] **(S3)** General procedure **1b** was followed. From 2.95 g (25 mmol) of 2-aminobenzonitrile, 7.72 g (75 mmol) of L-valinol and 0.5 g (3.75 mmol) of $ZnCl_2$ 2.50 g (49%) of the title compound was obtained ^{1}H NMR (500 MHz, DMSO) δ = 7.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.17 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 6.99 (s, 2H), 6.76 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.52 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 4.32 (dd, *J* = 9.4, 8.2 Hz, 1H), 4.08 (ddd, *J* = 9.3, 7.8, 6.6 Hz, 1H), 4.01 (t, *J* = 8.0 Hz, 1H), 1.72 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 148.6, 131.9, 129.6, 116.0, 115.6, 109.2, 72.9, 68.7, 33.2, 19.0, 18.6. HRMS (ESI) calcd for $C_{12}H_{17}N_2O^+$ (MH^+) 205.1335, found 205.1338.

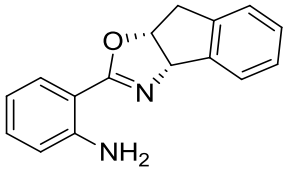


(*S*)-2-(4-benzyl-4,5-dihydrooxazol-2-yl)aniline[1] (**S4**) General procedure **1b** was followed. From 2.95 g (25 mmol) of 2-aminobenzonitrile, 11.3 g (75 mmol) of L-phenylalaninol and 0.51 g (3.75 mmol) of $ZnCl_2$ 3.10 g (49%) of the title compound was obtained ^{1}H NMR (500 MHz, DMSO) δ = 7.50 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.31 (m, 4H), 7.23 (m, 1H), 7.17 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 6.98 (s, 2H), 6.75 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.51 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 4.58 (dq, *J* = 9.2, 7.2 Hz, 1H), 4.31 (dd, *J* = 9.3, 8.3 Hz, 1H), 3.99 (m, 1H), 2.96 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.82 (dd, *J* = 13.5, 7.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 148.7, 138.4, 132.1, 129.6, 129.3, 128.5, 126.5, 116.0, 115.7, 109.0, 70.3, 68.1, 42.3. HRMS (ESI) calcd for $C_{16}H_{17}N_2O^+$ (MH^+) 253.1335, found 253.1337



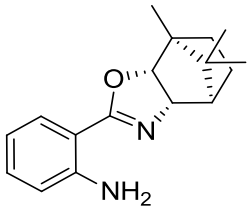
2-((*4S,5R*)-4-methyl-5-phenyl-4,5-dihydrooxazol-2-yl)aniline (S5) General procedure **1c** was followed. From 2.95g (25 mmol) of 2-aminobenzonitrile, 3.78 g (25 mmol) of *1R,2S*-norephedrine and 3.46 g (26mmol) of $ZnCl_2$ 2.4g (58%) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.39 (ddd, *J* = 7.5, 6.3, 1.3 Hz,

2H), 7.30 (m, 3H), 6.77 (dd, *J* = 8.2, 0.8 Hz, 1H), 6.73 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 6.16 (s, 2H), 5.69 (d, *J* = 9.7 Hz, 1H), 4.73 (dq, *J* = 9.7, 7.0 Hz, 1H), 0.90 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 148.7, 137.3, 132.1, 129.8, 128.2, 127.8, 126.2, 116.1, 115.7, 109.0, 82.2, 65.6, 18.1. calcd for $C_{16}H_{16}N_2OLi^+$ (MLi^+) 259.1417, found 259.1424



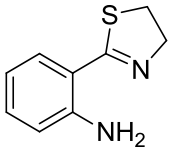
2-((3a*S*,8a*R*)-8,8a-dihydro-3aH-indeno[1,2-d]oxazol-2-yl)aniline[3] **(S6)**

General procedure **1c** was followed. From 2.95 g (25 mmol) of 2-aminobenzonitrile, 5.0 g (33.5 mmol) of (*1S,2R*)-1-amino-2-indanol and 3.46 g (26 mmol) of $ZnCl_2$ 3.20 g (51 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53 (m, 1H), 7.28 (m, 3H), 7.20 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 6.67 (m, 2H), 6.09 (s, 2H), 5.81 (d, *J* = 7.8 Hz, 1H), 5.40 (ddd, *J* = 7.9, 6.8, 1.6 Hz, 1H), 3.52 (dd, *J* = 17.8, 6.8 Hz, 1H), 3.39 (dd, *J* = 17.8, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 148.5, 142.4, 139.8, 132.0, 129.7, 128.4, 127.4, 125.5, 125.3, 116.0, 115.6, 109.1, 81.2, 77.0, 39.8. HRMS (ESI) calcd for $C_{16}H_{15}N_2O^+$ (MH^+) 251.1179, found 251.1190



2-((3a*S*,7a*R*)-7,8,8-trimethyl-3a,4,5,6,7,7a-hexahydro-4,7-methanobenzo[d]oxazol-2-yl)aniline[4] **(S7)** *Step 1. (3aS,4R,7S,7aR)-7,8,8-trimethyl-2-(2-nitrophenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanobenzo[d]oxazole* To a solution of (1S,2R,3S,4R)-3-amino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol[5] (2.40 g, 14.2 mmol) in 50 mL of CH_3CN was added 2-nitrobenzaldehyde (2.14 g, 14.2 mmol). After the mixture was stirred for 2 h at room temperature, NBS (2.51 g, 14.2 mmol) was added and the solution was stirred for 1.5 h. The solvents were removed under reduced pressure. The mixture was diluted in CH_2Cl_2 and washed with sat. aq. $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography with hexanes:EtOAc (85:15) to provide 1.71 g (44 %) of ^{1}H NMR (500 MHz,

$CDCl_3$) δ = 7.86 (dd, *J* = 7.5, 1.6, 1H), 7.79 (m, 1H), 7.62 (m, 2H), 4.47 (d, *J* = 8.6, 1H), 4.24 (d, *J* = 8.6, 1H), 2.20 (d, *J* = 4.5, 1H), 1.79 (tq, *J*=13.8, 4.4, 1H), 1.54 (m, 2H), 1.10 (m, 1H), 1.04 (d, *J* = 5.2, 3H), 0.99 (m, 3H), 0.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 149.5, 132.1, 131.3, 130.6, 123.6, 123.1, 92.5, 76.7, 48.8, 48.7, 47.1, 32.0, 26.0, 23.4, 18.9, 11.3. HRMS (ESI) calcd for $C_{17}H_{20}N_2O_3Li^+$ (MLi^+) 307.1641, found 307.1634 *Step 2. 2-((3aS,7aR)-7,8,8-trimethyl-3a,4,5,6,7,7a-hexahydro-4,7-methanobenzo[d]oxazol-2-yl)aniline* 1.71 g (5.7 mmol) of the imine was dissolved in 150mL of EtOH and treated with 1.5 eq of Na_2S. The mixture was brought to reflux at which it was maintained for 3h, then 0.5mL of TEA was added and the mixture was concentrated *in vacuo*. The residue was redissolved in DCM, washed with water and brine, dried over Na_2SO_4, then concentrated 1.4 g (91 %) of the product upon purification via flash chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.21 (m, 1H), 6.68 (m, 2H), 6.11 (s, 2H), 4.31 (d, *J* = 8.4 Hz, 1H), 4.26 (d, *J* = 8.4 Hz, 1H), 2.12 (d, *J* = 4.5 Hz, 1H), 1.80 (m, 1H), 1.55 (m, 1H), 1.12 (m, 5H), 0.89 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 148.6, 131.9, 129.8, 115.9, 115.6, 109.7, 89.4, 76.5, 49.2, 48.5, 46.9, 32.2, 26.0, 23.5, 18.7, 11.4. HRMS (ESI) calcd for $C_{17}H_{23}N_2O^+$ (MH^+) 271.1805, found 271.1822



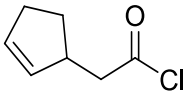
2-(4,5-dihydrooxazol-2-yl)aniline[6] **(S8)** *1. o-Chlorobenzoyl chloride* The *o*-nitrobenzoic acid (0.50 g, 2.99 mmol) was refluxed with $SOCl_2$ (3.0 mL) for 12 h, then the excess $SOCl_2$ was removed *in vacuo*. Benzene (5 mL) was added and removed again to dryness to remove the trace amount of $SOCl_2$ and afforded the acyl chloride. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.13 (m, 1H), 7.83 (m, 1H), 7.77 (m, 2H). *2. N-(2-hydroxyethyl)-2-nitrobenzamide* The acyl chloride in CH_2Cl_2 (15 mL) was added dropwise to a solution of amino alcohol (3.10 mmol) and Et_3N (2 mL, 14.5 mmol) in CH_2Cl_2 (15 mL) at 0°C and stirred at room temperature for 4-6 h. The reaction mixture was evaporated to remove the solvent *in vacuo* to yield crude hydroxyl amide. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.11 (d, *J*=8.1, 1H), 7.71 (t, *J*=7.5, 1H), 7.61 (m, 2H), 6.50 (s, 1H), 3.91 (m, 2H), 3.66 (m, 2H). *3. 2-(o-Nitrophenyl)-4,5-dihydrothiazoline*[7] Crude hydroxylamide was dissolved in toluene (20 mL), Et_3N (4 mL, 28.9 mmol) was added. Then, Lawesson's reagent (1.82 g, 4.5 mmol) was added under reflux in three portions within 1 h, and the suspension was refluxed for another 4-6 h. After cooling to room temperature, the solution was washed with H_2O,

dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give the crude product: 0.42 g (64% over three steps) of 2-(*o*-nitrophenyl)-4,5dihydrothiazoline. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (m, 1H), 7.66 (m, 2H), 7.60 (ddd, *J* = 8.0, 6.6, 2.4 Hz, 1H), 4.47 (t, *J* = 8.4 Hz, 2H), 3.55 (t, *J* = 8.4 Hz, 2H). *4. 2-(4,5-dihydrooxazol-2-yl)aniline* 0.8 g of the imine was dissolved in 10mL of EtOH and treated with 0.23 g of Na_2S. The mixture was brought to reflux at which it was maintained for 3h, then 0.5mL of TEA was added and the mixture was concentrated *in vacuo*. The residue was redissolved in DCM, washed with water and brine, dried over anhydrous Na_2SO_4, then concentrated and purified via flash chromatography to give 0.22 of amine (32%) ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.50 (d, *J*=8.0, 1H), 7.20 (m, 1H), 6.71 (m, 2H), 6.22 (s, 2H), 4.52 (t, *J* = 8.2, 2H), 3.30 (t, *J* = 8.2, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 147.6, 132.5, 131.5, 116.2, 116.0, 114.9, 65.3, 31.9.

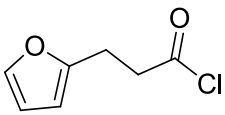
Coupling of amines with acids

General procedure 2 A carboxylic acid was dissolved in DCM, 10mL, 10 eq of $SOCl_2$ was added, the mixture was refluxed for 5h, then concentrated to give the corresponding acid chloride used in the following steps without purification

Synthesis of chloranhydrides

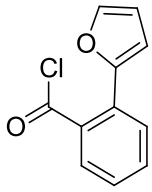


2-(Cyclopent-2-enyl)acetyl chloride (S9):[8] General procedure **2** was followed at a 15.85 mmol scale. Reaction was complete in 5 hours, providing 2.22 g of yellow-brown oil (97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (dq, *J* = 4.5, 2.2, 1H), 5.70 (dq, *J* = 5.7, 2.2, 1H), 3.31-3.15 (m, 1H), 3.01 (dd, *J* = 16.7, 6.7, 1H), 2.92 (dd, *J* = 16.7, 7.9, 1H), 2.53-2.32 (m, 2H), 2.23 (dtd, *J* = 13.7, 8.6, 5.2, 1H), 1.62-1.41 (m, 1H).

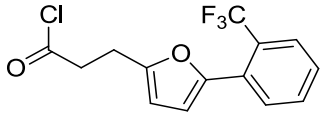


3-(2-Furyl)-propanoic acid chloride (S10): General procedure **2** was followed at a 4.6 mmol scale. CH_2Cl_2 was used as a solvent. Reaction mixture was refluxed for 3 hours and

concentrated, furnishing 0.65 g (89%) of yellow-brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (br s, 1H), 6.32 (br s, 1H), 6.10 (br s, 1H), 3.27 (t, *J* = 7.1, 2H), 3.06 (t, *J* = 7.1, 2H).

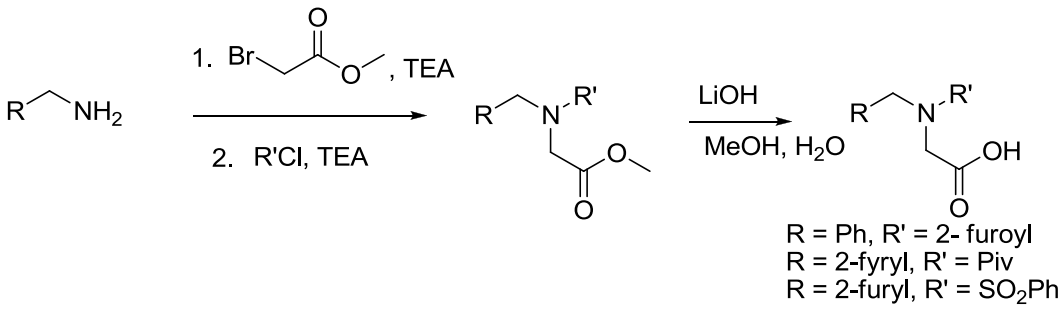


2-(furan-2-yl)benzoyl chloride (S11) General procedure **2** was followed at a 1.06 mmol scale. CH_2Cl_2 was used as a solvent. Reaction mixture was refluxed for 3 hours and concentrated, furnishing 0.21 g of brown oil (96%)^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.67 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.61 (td, *J* = 7.6, 1.3 Hz, 1H), 7.58 (d, *J* = 1.3 Hz, 1H), 7.45 (td, *J* = 7.7, 1.3 Hz, 1H), 6.71 (d, *J* = 3.2 Hz, 1H), 6.55 (dd, *J* = 3.4, 1.8 Hz, 1H).



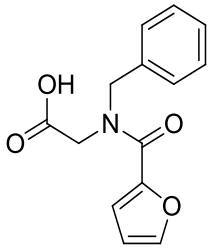
3-(5-(2-(trifluoromethyl)phenyl)furan-2-yl)propanoyl chloride (S12) General procedure **2** was followed at a 1.5 mmol scale. CH_2Cl_2 was used as a solvent. Reaction mixture was refluxed for 3 hours and concentrated, furnishing 0.43 g (95%) of brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 3.3 Hz, 1H), 6.23 (m, 1H), 3.34 (t, *J* = 7.3 Hz, 2H), 3.13 (t, *J* = 7.3 Hz, 2H).

Substituted glycines

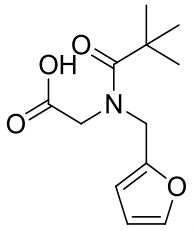


General procedure: Step 1: Alkyl amine, 1 eq, 10 mmol, was dissolved in 20mL of DCM, 1 eq of TEA was added, 1.01 g, 10 mmol, the mixture was treated with 1 eq of methyl bromoacetate 1.51 g (10 mmol) and left stirring overnight. Step 2: The mixture from the first step was treated with additional 1 eq of TEA, 1.01 g, 10mmol, and then sulfuryl or acyl chloride was added, 1eq,

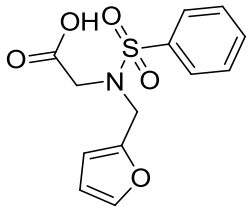
10mmol. The mixture was left stirring for 8h, then quenched with water, extracted with EtOAc, dried, concentrated and purified by chromatography. Step 3: Product of step 2 was dissolvwed in 50mL of MeOH, 5mL of H_2O was added followed by 0.24 g of LiOH. The mixture was stirred for 12 h, concentrated *in vacuo*, diluted with water, acidified and extracted with EtOAc. Combined organic layers were dried over Na_2SO_4 and concentrated to afford crude acid. If needed the crude acid can be purified by flash chromatography.



2-(N-benzylfuran-2-carboxamido)acetic acid From 0.97 g (10mmol) of 2-furylamine, 1.01 g of furoyl chloride following steps 1-3 of the general procedure, 0.54 g (21% over three steps) of the acid was obtained**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.40 (m, 5H), 7.17 (m, 1H), 6.52 (m, 2H), 4.93 (m, 2H), 4.24 (m, 2H).



2-(N-(furan-2-ylmethyl)pivalamido)acetic acid From 0.97 g (10mmol) of 2-furylamine, 1.20 g of pivaloyl chloride following steps 1-3 of the general procedure, 0.94 g (39% over three steps) of the acid was obtained**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42 (m, 1H), 6.38 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.31 (d, *J* = 3.2 Hz, 1H), 4.77 (s, 2H), 4.04 (s, 2H), 1.39 (s, 9H).



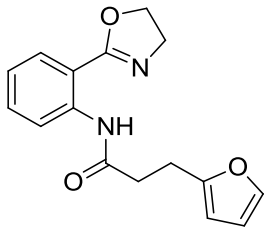
2-(N-(furan-2-ylmethyl)phenylsulfonamido)acetic acid From 0.97 g (10mmol) of 2-furylamine, 1.75 g of phenyl sulfuryl chloride following steps 1-3 of the general

procedure, 0.82 g (28% over three steps) of the acid was obtained**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (m, 2H), 7.61 (m, 1H), 7.53 (m, 2H), 7.32 (dd, *J* = 1.8, 0.7 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 4.58 (s, 2H), 4.04 (s, 2H).

Furanpropanoic acid-based photoprecursors

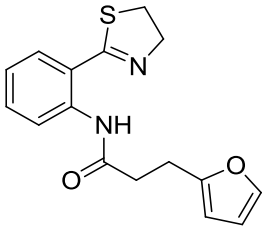
General procedure 3: A freshly prepared acid chloride (from 1.2 eq of the corresponding acid) was dissolved in DCM and added dropwise to a solution of an aniline (1 eq) and TEA (1.2 eq) in DCM, the mixture was allowed to stir for 12 h, then quenched with water, organic layer was separated, aqueous – extracted with DCM, combined organic fractions were dried over Na_2SO_4, then concentrated *in vacuo*. Crude product was purified by falsh chromatography using hexanes-ethyl acetate 100:0-60:40 gradient.

General procedure 4: 0.16 g of the amine was mixed with 0.38 g of HATU, 0.13 g of HOAt and 1 eq 1.0 mmol of the corresponding acid in DCM. The mixture was treated with 0.4 g of TEA and left stirring overnight, then concentrated and purified via flash chromatography.



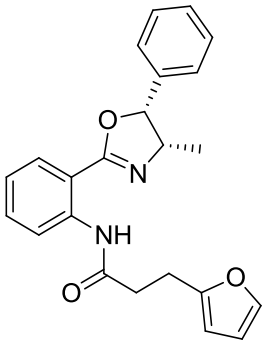
3-(furan-2-yl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)propanamide (1a)

General procedure **3** was followed. From 0.16 g (1.0 mmol) of 2-**(4,5-dihydrooxazol-2-yl)aniline S1** and chloranhydride prepared from 0.20 g (1.4 mmol) of 2-furanpropanoic acid 0.25 g (88 %) of the title compound was obtained ^{1}H NMR (500 MHz, DMSO) δ = 12.21 (s, 1H), 8.63 (m, 1H), 7.83 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.52 (m, 2H), 7.15 (m, 1H), 6.35 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.14 (m, 1H), 4.42 (t, *J* = 9.5 Hz, 2H), 4.13 (t, *J* = 9.6 Hz, 2H), 2.99 (t, *J* = 7.4 Hz 2H), 2.72 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 170.6, 164.0, 154.6, 141.9, 139.8, 132.9, 129.5, 122.8, 119.4, 113.1, 110.8, 105.8, 66.8, 54.8, 36.3, 23.6. HRMS (ESI) calcd for $C_{16}H_{17}N_2O_3^+$ (MH^+) 285.1234, found 285.1248

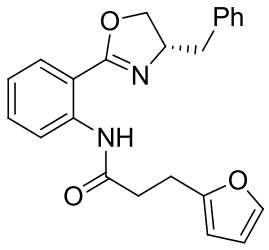


3-(furan-2-yl)-N-(2-(4,5-dihydrothiazol-2-yl)phenyl)propanamide (2)

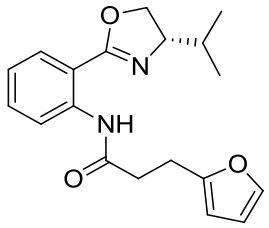
General procedure **3** was followed. From 0.18 g (1.0 mmol) of **2-(4,5-dihydrothiazol-2-yl)aniline S8** 0.22 g (73 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.39 (s, 1H), 8.78 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.46 (m, 1H), 7.34 (d, *J* = 1.1 Hz, 1H), 7.11 (td, *J* = 7.8, 1.2 Hz, 1H), 6.31 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.09 (m, 1H), 4.57 (t, *J* = 8.3 Hz, 2H), 3.37 (t, *J* = 8.3 Hz, 2H), 3.12 (m, 2H), 2.77 (dd, *J* = 8.6, 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 166.7, 154.5, 141.1, 138.8, 132.1, 132.0, 122.5, 120.0, 118.4, 110.3, 105.3, 65.0, 36.7, 31.9, 23.8. HRMS (ESI) calcd for $C_{16}H_{17}N_2O_2S^+$ (MH^+) 301.1005, found 301.1004



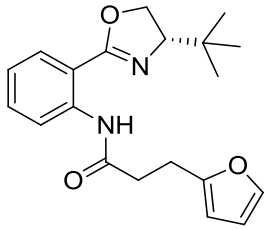
3-(furan-2-yl)-N-(2-((*4S,5R*)-4-methyl-5-phenyl-4,5-dihydrooxazol-2-yl)phenyl)propanamide (1e) General procedure **4** was followed. From 0.25 (1.0 mmol) of **2-((4*S*,5*R*)-4-methyl-5-phenyl-4,5-dihydrooxazol-2-yl)aniline** and 0.14 g of 2-furanpropanoic acid 0.17 g (45%) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.35 (s, 1H), 8.81 (dd, *J* = 8.5, 0.9 Hz, 1H), 8.01 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.53 (m, 1H), 7.39 (m, 3H), 7.33 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.28 (m, 2H), 7.14 (td, *J* = 7.9, 1.2 Hz, 1H), 6.29 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.10 (m, 1H), 5.75 (d, *J* = 9.8 Hz, 1H), 4.77 (dq, *J* = 9.8, 7.0 Hz, 1H), 3.14 (m, 2H), 2.81 (m, 2H), 0.93 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 163.1, 154.5, 141.1, 140.1, 136.5, 132.7, 129.3, 128.4, 128.1, 126.1, 122.3, 119.8, 112.9, 110.2, 105.3, 82.7, 65.4, 36.7, 23.8, 17.9. HRMS (ESI) calcd for $C_{23}H_{23}N_2O_3^+$ (MH^+) 375.1703, found 375.1708



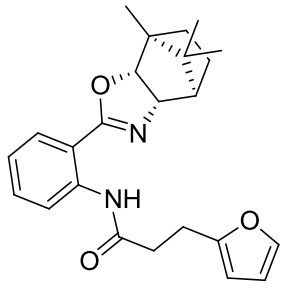
(*S*)-3-(furan-2-yl)-N-(2-(4-benzyl-4,5-dihydrooxazol-2-yl)phenyl)propanamide (1d) General procedure **3** was followed. From 0.50 g (2 mmol) of **(*S*)-2-(4-benzyl-4,5-dihydrooxazol-2-yl)aniline** 0.61 g (81 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.26 (s, 1H), 8.78 (m, 1H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.49 (m, 1H), 7.36 (m, 1H), 7.29 (m, 5H), 7.19 (m, 1H), 7.09 (m, 1H), 6.32 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.05 (m, 1H), 4.70 (m, 1H), 4.46 (dd, *J* = 9.3, 8.6 Hz, 1H), 4.12 (m, 1H), 3.00 (m, 4H), 2.59 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.9, 163.9, 154.6, 141.0, 140.1, 137.9, 132.7, 129.1, 129.0, 128.6, 126.6, 122.1, 119.7, 112.8, 110.2, 105.3, 70.9, 67.9, 42.2, 36.4, 23.6. HRMS (ESI) calcd for $C_{23}H_{23}N_2O_3^+$ (MH^+) 375.1703, found 375.1723



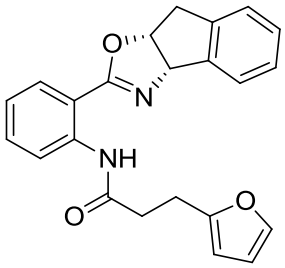
(*S*)-3-(furan-2-yl)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl)propanamide (1c) General procedure **3** was followed. From 0.41 g (2.0 mmol) of (**S**)-**2-(4-isopropyl-4,5-dihydrooxazol-2-yl)aniline** 0.49 g (75%) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.50 (s, 1H), 8.77 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.48 (m, 1H), 7.33 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.10 (td, *J* = 7.9, 1.2 Hz, 1H), 6.30 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.08 (m, 1H), 4.43 (dd, *J* = 9.5, 8.2 Hz, 1H), 4.18 (ddd, *J* = 9.4, 8.2, 6.9 Hz, 1H), 4.09 (t, *J* = 8.2 Hz, 1H), 3.13 (t, *J* = 7.6 Hz, 2H), 2.80 (m, 2H), 1.83 (m, *J* = 6.8 Hz, 1H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 163.5, 154.5, 141.1, 140.0, 132.5, 129.1, 122.2, 119.7, 113.0, 110.2, 105.2, 72.8, 69.4, 36.7, 33.2, 23.9, 18.9, 18.8. HRMS (ESI) calcd for $C_{19}H_{23}N_2O_3^+$ (MH^+) 327.1703, found 327.1699



(*S*)-3-(furan-2-yl)-N-(2-(4-tert-butyl-4,5-dihydrooxazol-2-yl)phenyl)propanamide (1b) General procedure **3** was followed. From 0.22 g (1.0 mmol) of **(S)-2-(4-tert-butyl-4,5-dihydrooxazol-2-yl)aniline** 0.12 g (35 %) of the title compound was obtained (^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.78 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.49 (ddd, *J* = 8.7, 7.5, 1.6 Hz, 1H), 7.10 (td, *J* = 7.9, 1.2 Hz, 1H), 6.29 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.08 (m, 1H), 4.34 (m, 1H), 4.19 (m, 2H), 3.13 (t, *J* = 7.6 Hz, 2H), 2.79 (m, 2H), 0.99 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 163.5, 154.5, 141.1, 140.1, 132.5, 129.1, 122.2, 119.6, 112.9, 110.2, 105.2, 76.2, 67.4, 36.7, 33.8, 25.9, 24.0. HRMS (ESI) calcd for $C_{20}H_{25}N_2O_3^+$ (MH^+) 341.1860, found 341.1862

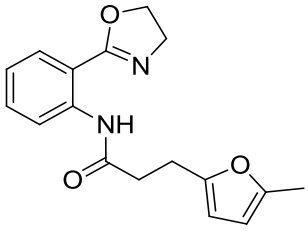


3-(furan-2-yl)-N-(2-((3aS,7aR)-7,8,8-trimethyl-3a,4,5,6,7,7a-hexahydro-4,7-methanobenzo[d]oxazol-2-yl)phenyl)propanamide (1g) General procedure **4** was followed. From 0.09 g (0.33 mmol) **2-((3a*S*,7a*R*)-7,8,8-trimethyl-3a,4,5,6,7,7a-hexahydro-4,7-methanobenzo[d]oxazol-2-yl)aniline (S7)**, 0.05 g (39%) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.47 (s, 1H), 8.75 (d, *J* = 7.8 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.47 (m, 1H), 7.35 (m, 1H), 7.09 (m, 1H), 6.31 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.11 (m, 1H), 4.38 (d, *J* = 8.4 Hz, 1H), 4.28 (d, *J* = 8.4 Hz, 1H), 3.14 (m, 2H), 2.82 (dd, *J* = 8.2, 6.8 Hz, 2H), 2.15 (d, *J* = 4.5 Hz, 1H), 1.82 (m, 1H), 1.58 (m, 1H), 1.13 (m, 4H), 0.90 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 165.4, 154.6, 141.1, 139.9, 132.5, 129.3, 122.2, 119.7, 113.5, 110.2, 105.3, 90.0, 76.1, 49.1, 48.6, 47.0, 36.6, 32.1, 25.9, 23.8, 23.5, 18.7, 11.4. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_3^+$ (MH^+) 393.2173, found 393.2171

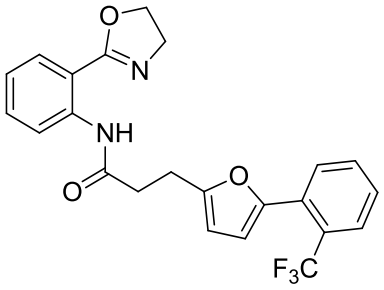


N-(2-((3a*S*,8a*R*)-8,8a-dihydro-3aH-indeno[1,2-d]oxazol-2-yl)phenyl)-3-(furan-2-yl)propanamide (1f) Following the general procedure **4** from 0.25 g (1.0 mmol) of **2-(8,8a-dihydro-3aH-indeno[1,2-d]oxazol-2-yl)aniline** 0.14 g (38 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.32 (s, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.52 (m, 1H), 7.45 (m, 1H), 7.36 (m, 1H), 7.31 (s, 2H), 7.06 (m, 1H), 6.32 (m, 1H), 6.12 (d, *J* = 2.9 Hz, 1H), 5.85 (d, *J* = 7.9 Hz, 1H), 5.47 (m, 1H), 3.56 (dd, *J* = 18.0, 6.8 Hz, 1H), 3.41 (d, *J* = 18.4 Hz, 1H), 3.15 (t, *J* = 7.8 Hz, 2H), 2.83 (td, *J* = 7.4, 1.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 164.0, 154.5, 141.7, 141.2, 139.8, 139.6, 132.6, 129.2, 128.8, 127.7, 125.5, 125.2, 122.2, 119.7, 113.1, 110.3, 105.3, 81.8, 76.6, 39.7, 36.8, 24.0. HRMS (ESI) calcd for $C_{23}H_{21}N_2O_3^+$ (MH^+) 373.1547, found 373.1548

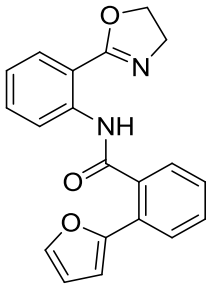
Variations in the unsaturated pendant and the linker



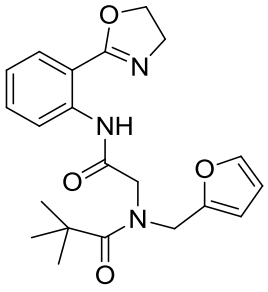
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-3-(5-methylfuran-2-yl)propanamide (5) Following general procedure **4**, from 0.16 g (1.0 mmol) **2-(4,5-dihydrooxazol-2-yl)aniline S1** and 0.32 g (2.07 mmol) of 5-methyl-2-furanpropanoic acid 0.14 g (47 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.27 (s, 1H), 8.78 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.48 (td, *J* = 8.7, 8.1, 1.6 Hz, 1H), 7.09 (td, *J* = 7.9, 1.2 Hz, 1H), 5.96 (d, *J* = 2.9 Hz, 1H), 5.87 (dd, *J* = 2.9, 1.0 Hz, 1H), 4.41 (m, 2H), 4.17 (m, 2H), 3.07 (m, 2H), 2.79 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 164.7, 152.8, 150.6, 139.9, 132.5, 129.1, 122.2, 119.7, 113.0, 105.9, 105.9, 66.2, 54.7, 36.8, 23.9, 13.5. HRMS (ESI) calcd for $C_{17}H_{19}N_2O_3^+$ (MH^+) 299.1390, found 299.1391



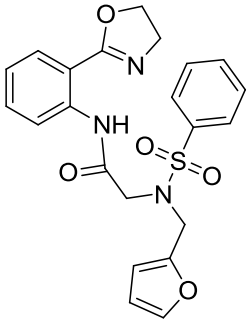
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-3-(5-(2-(trifluoromethyl)phenyl)furan-2-yl)propanamide (6) Following the general procedure **3** from 0.16 g (1.0 mmol) of **2-(4,5-dihydrooxazol-2-yl)aniline S1**, chloranhydride of the 5-[(2-trifluoromethyl)-phenyl)-2-furanpropanoic cid (from 0.50 g of the acid, 1.75 mmol), 0.23 g (54 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.36 (s, 1H), 8.79 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.74 (m, 2H), 7.50 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.10 (td, *J* = 7.9, 1.2 Hz, 1H), 6.64 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.3 Hz, 1H), 4.38 (m, 2H), 4.13 (t, *J* = 9.6 Hz, 2H), 3.20 (t, *J* = 7.6 Hz, 2H), 2.87 (dd, *J* = 8.4, 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 164.6, 155.4, 149.1, 139.8, 132.5, 131.6, 129.8 (q, *J* = 2.2 Hz, 1C), 129.4, 129.1, 127.2, 126.6 (q, *J* = 6.4 Hz, 1c),125.9 (q, *J* = 272.5 Hz, 1C), 125.9 (q, *J* = 31.4 Hz, 1C), 122.2, 119.7, 113.1, 110.9, 107.7, 66.2, 54.6, 36.6, 24.0. HRMS (ESI) calcd for $C_{23}H_{20}F_3N_2O_3^+$ (MH^+) 429.1421, found 429.1429



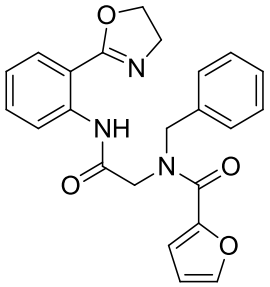
N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(furan-2-yl)benzamide Following the general procedure **3** from 0.16 g (1.0 mmol) of **2-(4,5-dihydrooxazol-2-yl)aniline) S1**, chloranhydride of 2-(2-furanyl)-benzoic acid (from 0.20 g of the acid, 1.06 mmol) 0.22 g (66 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.48 (s, 1H), 8.94 (d, *J* = 8.4, 1H), 7.87 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.76 (m, 1H), 7.65 (m, 1H), 7.53 (m, 2H), 7.43 (dd, *J* = 1.9, 0.6 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.15 (td, *J* = 7.8, 1.0 Hz, 1H), 6.65 (d, *J*=3.4 Hz, 1H), 6.41 (dd, *J*=3.4, 1.8 Hz, 1H), 4.31 (t, *J*=9.6, Hz 2H), 3.93 (t, *J*=9.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 164.2, 152.0, 142.5, 139.9, 135.1, 132.5, 129.9, 129.1, 128.3, 128.3, 127.6, 127.3, 122.6, 120.0, 113.6, 111.7, 108.5, 66.1, 54.6. HRMS (ESI) calcd for $C_{20}H_{17}N_2O_3^+$ (MH^+) 333.1234, found 333.1233



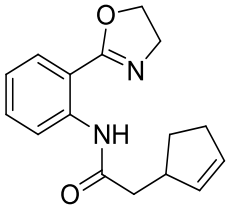
N-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)-2-oxoethyl)-N-(furan-2-ylmethyl)pivalamide Following general procedure **4**, from 0.16 g (1.0 mmol) of **2-(4,5-dihydrooxazol-2-yl)aniline S1** and 0.24 g (1.0 mmol) of the corresponding acid 0.23 g (60 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.84 (s, 1H), 8.79 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.50 (m, 1H), 7.37 (m, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.34 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.27 (d, *J* = 3.1 Hz, 1H), 4.74 (s, 2H), 4.41 (t, *J* = 9.6 Hz, 2H), 4.28 (s, 2H), 4.13 (t, *J* = 9.5 Hz, 2H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6, 168.3, 164.5, 150.6, 142.4, 139.2, 132.5, 129.1, 122.8, 119.7, 113.5, 110.3, 108.7, 66.4, 54.6, 52.4, 45.5, 39.1, 28.5. HRMS (ESI) calcd for $C_{21}H_{26}N_3O_4^+$ (MH^+) 384.1918, found 384.1935



N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-(N-(furan-2-ylmethyl)phenylsulfonamido)acetamide Following general procedure **4**, from 0.32 g (2.0 mmol) 2-(4,5-dihydrooxazol-2-yl)aniline **S1** and 0.60 g (2.0 mmol) of the corresponding acid 0.41 g (46 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 13.11 (s, 1H), 8.72 (d, *J* = 8.2 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.49 (m, 2H), 7.14 (m, 2H), 6.18 (m, 2H), 4.62 (s, 2H), 4.47 (m, 2H), 4.32 (t, *J* = 9.1 Hz, 2H), 3.99 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 164.1, 148.2, 143.0, 139.1, 132.8, 132.3, 129.0, 129.0, 127.4, 122.8, 119.6, 114.0, 110.6, 110.3, 66.5, 54.8, 51.5, 45.3. HRMS (ESI) calcd for $C_{22}H_{21}N_3O_5Li^+$ (MLi^+) 446.1357, found 446.1355



N-benzyl-N-(2-((2-(4,5-dihydrooxazol-2-yl)phenyl)amino)-2-oxoethyl)furan-2-carboxamide Following general procedure **4**, from 0.32 g (2.0 mmol) 2-(4,5-dihydrooxazol-2-yl)aniline **S1** and 0.51 g (2.0 mmol) of the corresponding acid 0.34 g (42 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ = 12.92 (m, 1H), 8.84 (m, 1H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.43 (m, 7H), 7.18 (m, 2H), 6.51 (m, 1H), 5.01 (m, 2H), 4.35 (m, 4H), 3.96 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 167.5, 164.6, 164.4, 160.5, 160.4, 147.6, 144.7, 144.4, 139.4, 139.3, 136.3, 132.6, 129.1, 128.9, 128.7, 127.8, 127.0, 122.9, 122.7, 119.7, 119.6, 117.8, 117.6, 113.7, 113.5, 111.7, 111.5, 66.5, 66.1, 54.4, 54.2, 52.9, 52.5, 51.1, 50.8. HRMS (ESI) calcd for $C_{23}H_{22}N_3O_4^+$ (MH^+) 404.1605, found 404.1609



2-(cyclopent-2-en-1-yl)-N-(2-(4,5-dihydrooxazol-2-yl)phenyl)acetamide Following the general procedure **3** from 0.16 g (2.0 mmol) **2-(4,5-dihydrooxazol-2-yl)aniline S1**, chloranhydride from 0.26 g (2.0 mmol) of the 2-cyclopenetene-1-acetic acid, 0.45 g (83 %) of the title compound was obtained ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.19 (s, 1H), 8.79 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.49 (m, 1H), 7.09 (m, 1H), 5.81 (dq, *J* = 6.1, 2.0 Hz, 1H), 5.78 (dq, *J* = 5.7, 1.9 Hz, 1H), 4.42 (m, 2H), 4.17 (m, 2H), 3.28 (dddt, *J* = 10.5, 6.2, 4.2, 2.2 Hz, 1H), 2.56 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.39 (m, 3H), 2.21 (m, 1H), 1.61 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 164.7, 140.0, 134.2, 132.5, 131.2, 129.1, 122.1, 119.7, 113.0, 66.1, 54.8, 44.8, 42.5, 31.9, 29.7. HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2^+$ (MH^+) 271.1441, found 271.1447

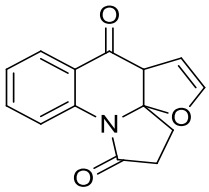
Irradiation of photoprecursors

General procedure 5: The photoprecursor was dissolved in anhydrous DCM, the solution was thoroughly degassed by bubbling nitrogen for 30 min, then irradiated with RPR-3000 until complete disappearance of the starting material as monitored by NMR. The solution was then concentrated, the residue was redissolved in methanol (50mL), and 1 eq of PPTS or 1 eq of Bu_4NHSO_4 was added, together with 5 mL of water. When hydrolysis was complete as determined by NMR, the solution was concentrated *in vacuo* and crude material was purified by flash chromatography (hexanes-ethyl acetate 90:10-40:60).

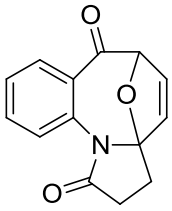
Model studies:

Following general procedure **5** and using *n*-Bu_4NHSO_4 for the hydrolysis from 0.110 g (0.39 mmol) of photoprecursor **1a** 12 mg (13%) of the compound **3** and 57 mg (61 %) of the compound **4** was obtained upon the purification with flash chromatography

Following general procedure **5** and using *n*-Bu_4NHSO_4 for the hydrolysis from 0.100 g (0.33 mmol) of photoprecursor **2** 27 mg (34 %) of the compound **4** was obtained after purification with flash chromatography

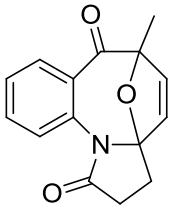


2,3-dihydro-1H-furo[2,3-b]pyrrolo[1,2-a]quinoline-1,7(6aH)-dione (3) ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.38 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.67 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.29 (m, 1H), 6.46 (m, 1H), 5.11 (t, *J* = 3.0 Hz, 1H), 3.88 (dd, *J* = 3.1, 2.3 Hz, 1H), 2.94 (m, 1H), 2.62 (m, 2H), 2.25 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.1, 173.7, 147.3, 138.4. 135.4, 128.1, 125.2, 123.6, 121.2, 101.8, 100.2, 58.4, 34.6, 29.4. HRMS (ESI) calcd for $C_{14}H_{12}NO_3^+$ (MH^+) 242.0812, found 242.0806

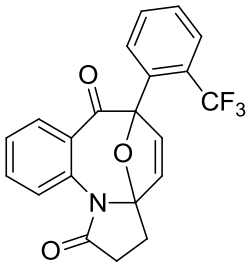


2,3-dihydro-1H-3a,6-epoxybenzo[g]pyrrolo[1,2-a]azocine-1,7(6H)-dione (4) ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.57 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.50 (ddd, *J* = 8.2, 7.2, 1.7 Hz, 1H), 7.23 (ddd, *J* = 8.0, 7.2, 1.3 Hz, 1H), 6.33 (dd, *J* = 5.8, 2.0 Hz, 1H), 5.83 (dd, *J* = 5.7, 1.3 Hz, 1H), 5.08 (dd, *J* = 2.0, 1.3 Hz, 1H), 2.84 (dt, *J* = 17.4, 9.7 Hz, 1H), 2.66 (ddd, *J* = 17.4, 10.0, 2.0 Hz, 1H), 2.56 (m, 1H), 2.43 (ddd, *J* = 14.0, 9.7, 2.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 173.2, 133.8, 133.6, 133.1, 131.5, 130.6, 127.9, 127.0, 126.1, 105.0, 87.4, 30.0, 29.0. HRMS (ESI) calcd for $C_{14}H_{12}NO_3^+$ (MH^+) 242.0812, found 256.0815

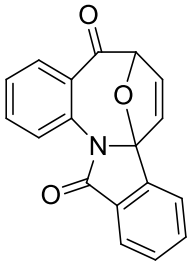
Irradiation of photoprecursors 5-10:



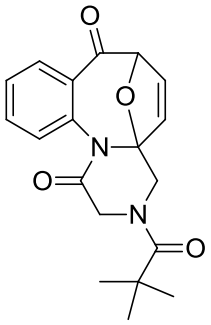
6-methyl-2,3-dihydro-1H-3a,6-epoxybenzo[g]pyrrolo[1,2-a]azocine-1,7(6H)-dione (11) Following general procedure **5** using *n*-Bu_4NHSO_4 for the hydrolysis from 170 mg mmol of photoprecursor **5** 74 mg (51 %) of the title compound was obtained after purification via flash chromatography ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.57 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.31 (m, 1H), 6.22 (d, *J* = 5.6 Hz, 1H), 5.82 (d, *J* = 5.6 Hz, 1H), 2.92 (dt, *J* = 17.3, 9.7 Hz, 1H), 2.73 (ddd, *J* = 17.3, 10.0, 2.0 Hz, 1H), 2.63 (dt, *J* = 14.0, 9.8 Hz, 1H), 2.52 (ddd, *J* = 14.0, 9.7, 2.0 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 173.0, 138.5, 133.0, 132.7, 131.9, 130.1, 129.1, 126.5, 126.0, 105.5, 90.1, 30.0, 29.7, 18.6. HRMS (ESI) calcd for $C_{15}H_{14}NO_3^+$ (MH^+) 256.0968, found 256.0962



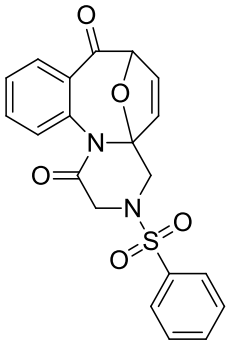
6-(2-(trifluoromethyl)phenyl)-2,3-dihydro-1H-3a,6-epoxybenzo[g]pyrrolo[1,2-a]azocine-1,7(6H)-dione (12) Following general procedure **5** 110 mg mmol of photoprecursor **6** using *n*-Bu_4NHSO_4 for the hydrolysis from 41 mg (42 %) of the title compound was obtained after purification via flash chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.64 (m, 2H), 7.58 (m, 2H), 7.35 (ddd, *J* = 7.8, 7.3, 1.3 Hz, 1H), 6.70 (dq, *J* = 5.6, 1.8 Hz, 1H), 5.95 (d, *J* = 5.8 Hz, 1H), 3.04 (m, 1H), 2.80 (ddd, *J* = 16.8, 9.3, 2.6 Hz, 1H), 2.73 (m, 1H), 2.68 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.7, 172.8, 137.8, 132.2, 132.0, 131.6, 131.3, 130.6, 130.6, 128.7, 127.8, 127.8, 127.4, 126.6, 126.1, 105.0, 93.2, 30.0, 29.6. HRMS (ESI) calcd for $C_{21}H_{14}F_3NO_3Li^+$ (MLi^+) 392.1082, found 392.1076 Oam44512



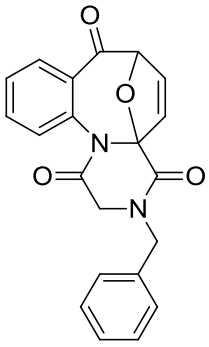
5H-6,8a-epoxybenzo[7,8]azocino[2,1-a]isoindole-5,13(6H)-dione Following general procedure **5** from 160 mg (0.48 mmol) of the photoprecursor **7** using *n*-Bu_4NHSO_4 for the hydrolysis 63 mg (45%) of the title compound was obtained after purification with flash chromatography ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.30 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.01 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.76 (td, *J* = 7.5, 1.1 Hz, 1H), 7.70 (td, *J* = 7.5, 1.1 Hz, 1H), 7.66 (ddd, *J* = 8.5, 7.2, 1.8 Hz, 1H), 7.63 (dt, *J* = 7.3, 0.8 Hz, 1H), 7.33 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 6.64 (dd, *J* = 5.8, 2.0 Hz, 1H), 6.00 (dd, *J* = 5.8, 1.3 Hz, 1H), 5.44 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 165.3, 141.7, 134.3, 134.1, 133.6, 133.5, 131.9, 131.5, 131.1, 129.1, 126.3, 125.2, 124.9, 124.3, 123.4, 103.0, 88.2. HRMS (ESI) calcd for $C_{18}H_{11}NO_3Li^+$ (MLi^+) 296.0893, found 296.0901



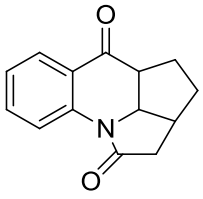
3-pivaloyl-3,4-dihydro-4a,7-epoxybenzo[g]pyrazino[1,2-a]azocine-1,8(2H,7H)-dione (14) Following general procedure **5** from 140 mg (0.37 mmol) of photoprecursor **8** using 1 eq of *n*-Bu_4NHSO_4 for the hydrolysis 42 mg (34%) of the title compound was obtained after purification via flash chromatography ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.74 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.52 (td, *J* = 7.9, 1.7 Hz, 1H), 7.38 (td, *J* = 7.7, 1.1 Hz, 1H), 7.33 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.38 (dd, *J* = 5.9, 1.9 Hz, 1H), 6.01 (dd, *J* = 5.9, 1.0 Hz, 1H), 5.17 (dd, *J* = 1.8, 1.1 Hz, 1H), 4.85 (dd, *J* = 18.2, 1.4 Hz, 1H), 4.65 (dd, *J* = 14.0, 1.5 Hz, 1H), 4.36 (d, *J* = 18.2 Hz, 1H), 4.07 (d, *J* = 14.0 Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 176.7, 166.2, 135.0, 133.9, 132.1, 131.1, 130.1, 129.8, 129.7, 127.7, 98.8, 87.5, 50.6, 49.8, 38.9, 28.2. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_4^+$ (MH^+) 341.1496, found 341.1497



3-(phenylsulfonyl)-3,4-dihydro-4a,7-epoxybenzo[g]pyrazino[1,2-a]azocine-1,8(2H,7H)-dione (**15**) Following general procedure **5** from 350 mg (0.79 mmol) of photoprecursor **9** using 1eq of *n*-Bu_4NHSO_4 for the hydrolysis 150 mg (48%) of the title compound was obtained after purification via flash chromatography ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (m, 2H), 7.72 (m, 2H), 7.64 (t, *J* =7.6 Hz, 2H), 7.49 (td, *J*=8.0, 1.7 Hz, 1H), 7.36 (td, *J* = 7.7, 1.2 Hz, 1H), 7.24 (dd, *J*=8.1, 1.0 Hz, 1H), 6.39 (dd, *J*=5.8, 1.9 Hz, 1H), 5.98 (dd, *J*=5.8, 1.1 Hz, 1H), 5.18 (m, 1H), 4.16 (dd, *J*=16.7, 1.4 Hz, 1H), 3.98 (dd, *J*=12.9, 1.4 Hz, 1H), 3.91 (dd, *J*=16.7, 0.9, 1H), 3.69 (d, *J*=12.9, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.9, 165.0, 135.5, 135.1, 133.7, 132.1, 131.2, 129.8, 129.7, 129.5, 129.5, 127.9, 127.7, 98.8, 87.6, 51.2, 49.8. HRMS (ESI) calcd for $C_{20}H_{17}N_2O_5S^+$ (MH^+) 397.0853, found 397.0855

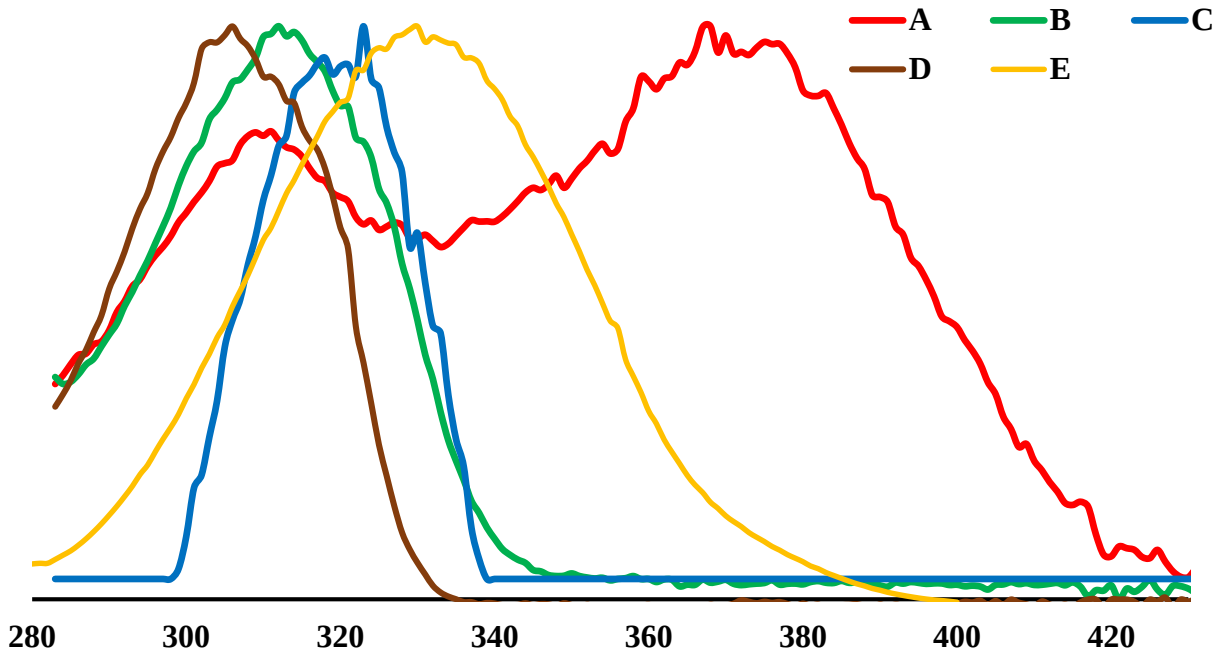


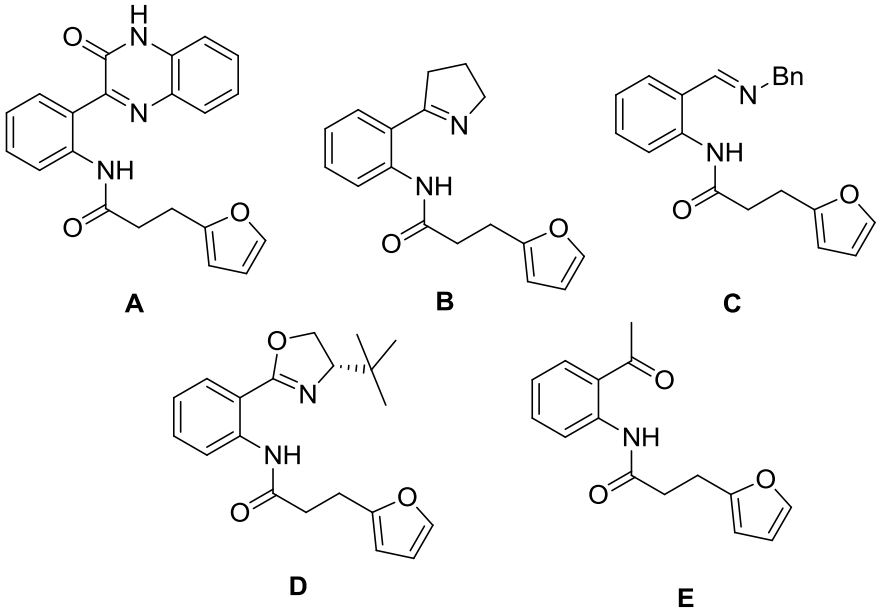
3-benzyl-2,3-dihydro-4a,7-epoxybenzo[g]pyrazino[1,2-a]azocine-1,4,8(7H)-trione (16) Following general procedure **5** from 210 mg (0.52 mmol) of photoprecursor **10** using 1 eq of *n*-Bu_4NHSO_4 for the hydrolysis 89 mg (47 %) of the title compound was obtained after purification via flash chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.75 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.55 (td, *J* = 7.7, 1.6 Hz, 1H), 7.41 (m, 5H), 7.26 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.47 (dd, *J* = 5.9, 1.9 Hz, 1H), 6.23 (dd, *J* = 5.9, 0.9 Hz, 1H), 5.31 (dd, *J* = 1.8, 0.9 Hz, 1H), 4.90 (d, *J* = 14.5 Hz, 1H), 4.62 (d, *J* = 14.5 Hz, 1H), 4.28 (d, *J* = 18.3 Hz, 1H), 4.10 (d, *J* = 18.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 166.1, 162.0, 134.6, 134.4, 133.6, 132.4, 131.5, 130.3, 130.1, 129.8, 129.4, 129.2, 128.5, 128.5, 98.6, 88.8, 50.0, 49.6. HRMS (ESI) calcd for $C_{21}H_{17}N_2O_4^+$ (MH^+) 361.1182, found 361.1178



9,10-Benzo-1-azatricyclo[5.3.1.0^{4,11}]undec-9-ene-2,8-dione (18): Following general procedure **5** from 220 mg (0.81 mmol) of photoprecursor **17** upon hydrolysis with 1 eq of TsOH 82 mg (44%) of the title compound was obtained after purification via flash chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.63 (ddd, *J* = 8.6, 7.4, 1.7 Hz, 1H), 7.25 (m, 1H), 4.76 (t, *J* = 5.3 Hz, 1H), 3.03 (dd, *J* = 17.5, 8.9 Hz, 1H), 2.93 (m, 2H), 2.45 (d, *J* = 17.5 Hz, 1H), 2.20 (m, 2H), 1.97 (m, 1H), 1.76 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.4, 173.2, 139.5, 135.2, 127.7, 124.7, 122.3, 121.1, 66.8, 53.0, 40.0, 35.0, 33.7, 27.5. HRMS (ESI) calcd for $C_{14}H_{13}NNaO_2^+$ (MNa^+) 250.0839, found 250.0830.

UV-vis absorption Spectra of Selected Azaxylylene Photoprecursors





Compounds **A-C** and **E** were described in previous publications[9]

Description of a typical low temperature experiment:

40 mg of a photoprecursor was dissolved in 0.6 mL of the deuterated solvent**,** the solution was thoroughly degassed by bubbling nitrogen for 5-7 min, cooled to the desired temperature in acetone-dry ice bath or (methanol-water-dry ice baths depending on the temperature) and irradiated with Hanovia medium pressure lamp until complete disappearance of the starting material as monitored by NMR. The solution was then concentrated, the residue was redissolved in CD_3OD (1 mL), and 1 eq of Bu_4NHSO_4 was added, together with 2 drops of water. When hydrolysis was complete as determined by NMR, the solution was concentrated *in vacuo* and crude material was purified by flash chromatography (hexanes-ethyl acetate 90:10-40:60). HPLC with Chiracel AD column was used to determine the *ee* values of the product (eluent hexanes-ethanol 70:30)

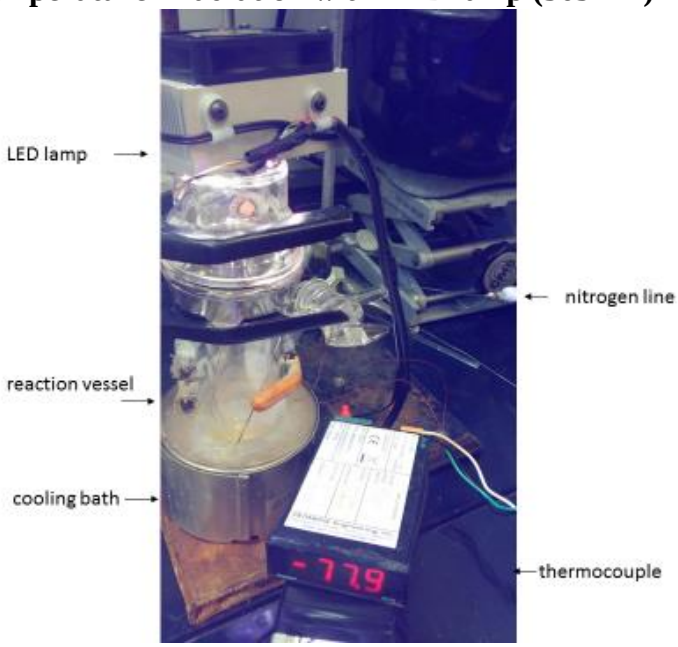
Description of a large-scale low temperature experiment with a sensitizer:

Experiment 1: 100 mg of the photoprecursor **1b** (0.29 mmol) was dissolved in 80 mL of DCM, dimethoxybenzophenone was added as a sensitizer, the mixture was thoroughly degassed by bubbling nitrogen for 20 min, cooled to -78^{o}C and irradiated with LED-365 lamp until complete disappearance of the starting material as monitored by NMR. The solution was then concentrated, the residue was redissolved in MeOH (10 mL), and 1 eq of TsOH was added, together with 0.2 mL of water. When hydrolysis was complete as determined by NMR, the solution was concentrated *in vacuo* and crude material was purified by flash chromatography (hexanes-ethyl acetate 90:10-40:60), yielding 38 mg (53%) of compound **4**. HPLC with Chiracel AD column was used to determine the *ee* values of the product (eluent hexanes-ethanol 70:30) to be 91%.

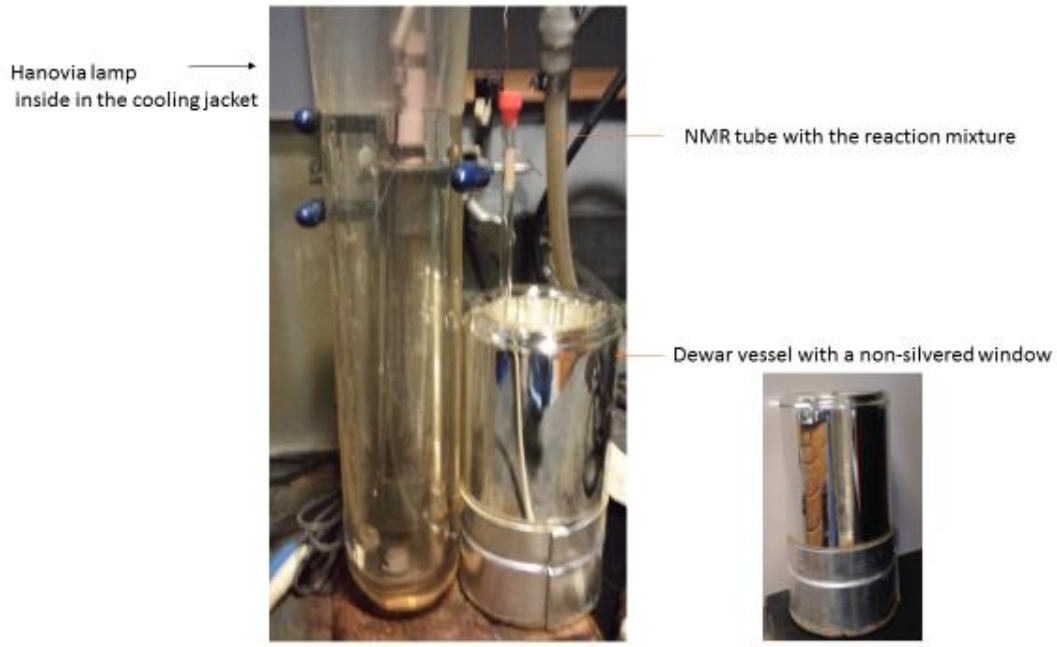
Experiment 2: 85 mg of the photoprecursor **1b** (0.25 mmol) was dissolved in 80 mL of DCM, dimethoxybenzophenone was added as a sensitizer, the mixture was thoroughly degassed by bubbling nitrogen for 20 min, cooled to -78^{o}C and irradiated with LED-365 lamp until complete disappearance of the starting material as monitored by NMR. The solution was then concentrated, the residue was redissolved in MeOH (10 mL), and 1 eq of TsOH was added, together with 0.2 mL of water. When hydrolysis was complete as determined by NMR, the solution was

concentrated *in vacuo* and crude material was purified by flash chromatography (hexanes-ethyl acetate 90:10-40:60), yielding 29 mg (48%) of compound **4**. HPLC with Chiracel AD column was used to determine the *ee* values of the product (eluent hexanes-ethanol 70:30) to be 90%.

Set-up for low temperature irradiation with LED lamp (365 nm)

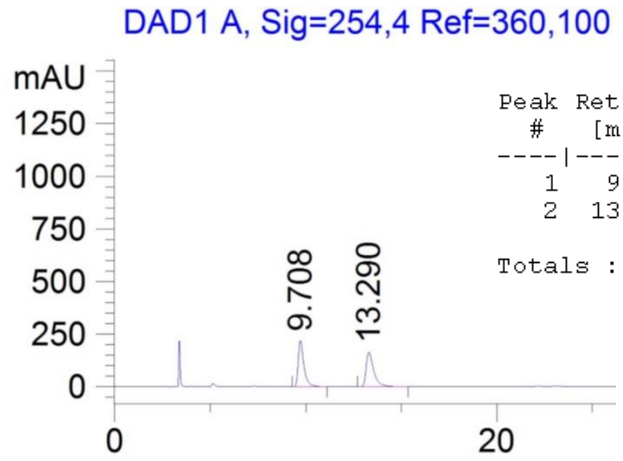


Set-up for low temperature irradiation with Hanovia lamp (temperature is controlled with thermocouple not shown)



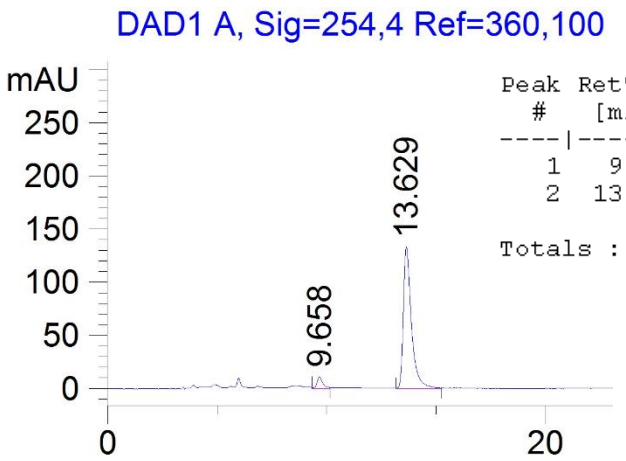
Selected HPLC traces:

Compound 4 (racemic):



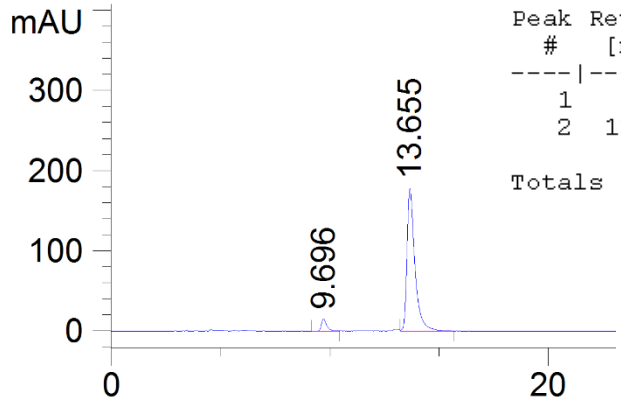
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	9.708	BB	0.3070	4798.76855	50.0884
2	13.290	BB	0.4092	4781.83643	49.9116
Totals :				9580.60498	

Large-scale experiment 1 (p. S24):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	9.655	BB	0.2392	171.83804	4.7917
2	13.629	BB	0.3732	3414.35571	95.2083
Totals :				3586.19376	

Large-scale experiment 2 (p. S24):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	9.697	BB	0.2438	251.78940	5.2660
2	13.655	VB	0.3718	4529.58301	94.7340
Totals :				4781.37241	

References

[1] Procedure adapted from Zhang, Z.; Lippert, K. M.; Hausmann, H.; Kotke, M.; Schreiner, P. R. *J. Org. Chem.* **2011**, *76*, 9764
[2]Procedure adapted from Yu, J.; RajanBabu, T. V.; Parquette, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 7845.
[3] Wolińska, E. *Tetrahedron: Asymmetry*, **2014**, *25*, 1478
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[5] Boobalan, R.; Chen, C.; Lee, G.-H. *Org. Biomol. Chem.*, **2012**, *10*, 1638. Detailed procedure is described for the synthesis starting from *R*-camphorquinone: White, J.D.; Wardrop, D.J.; Sundermann, K.F. *Org. Synth.* **2002**, *79*, 125 White, J.D.; Wardrop, D.J.; Sundermann, K.F. *Org. Synth.* **2002**, *79*, 130. Bosiak, M.J.; Krzemiński, M.P.; Jaisamkar, P.; Zaidlewicz, M. *Tetrahedron: Asymmetry*, **2008**, *19*, 956.
[6] Li, X.; Zhou, B.; Zhang, J.; She, M.; An,S.; Ge,H.; Li,C.; Yin, B.; Li, J.; Shi, Z. Solvent-Free Tandem Synthesis of 2-Thiazolines and 2-Oxazolines *Eur. J. Org. Chem.* **2012**, 1626
[7] Procedure adapted from Zhao, Q.; Li, J.; Yan, X.; Yuan, H.; Qin, Z.; Fu, B. *J. Heterocyclic Chem.*, **2011,** *48*, 729.
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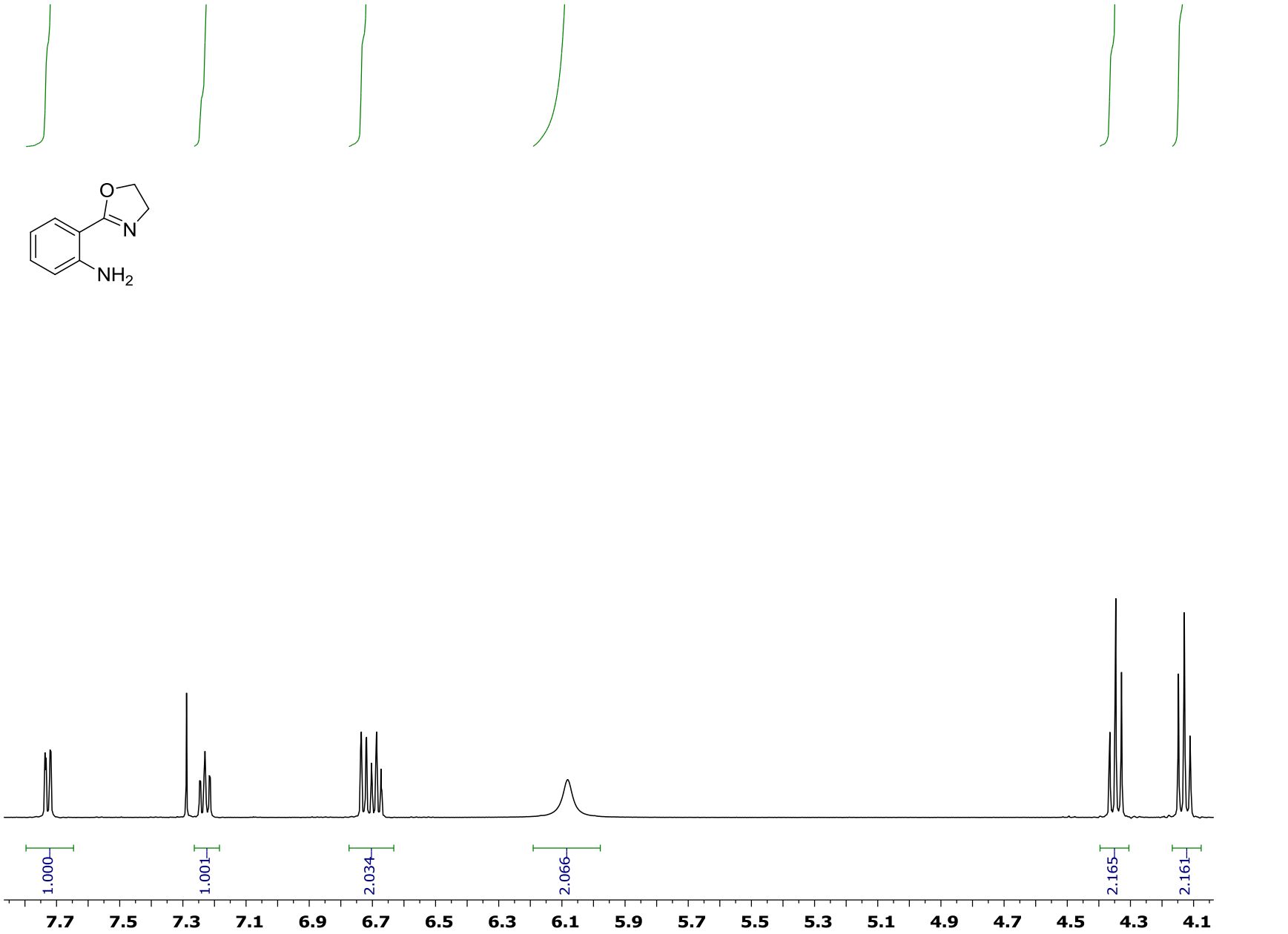
[9] (a) Mukhina, O. A.; Kumar, N. N. B.; Arisco, T. M.; Valiulin, R. A.; Metzel, G. A.; Kutateladze, A. G. *Angew. Chem., Int. Ed.* **2011**, *50*, 9423. (b) Mukhina, O.A.; Kuznetsov, D.M.; Cowger, T.M.; Kutateladze, A.G. *Angew. Chem. Int. Ed.*, **2015**, *39*, 11516.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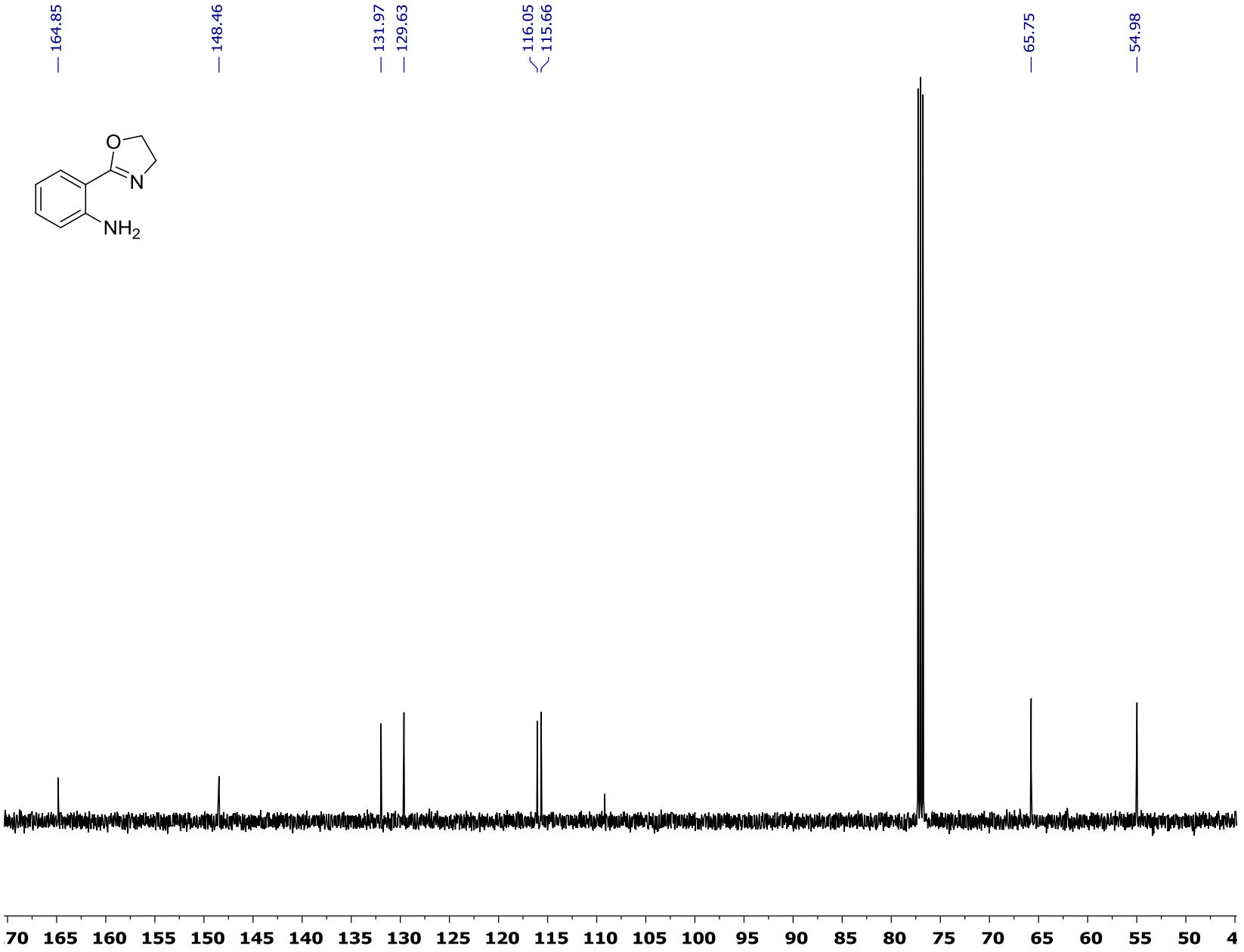
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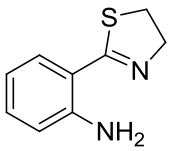
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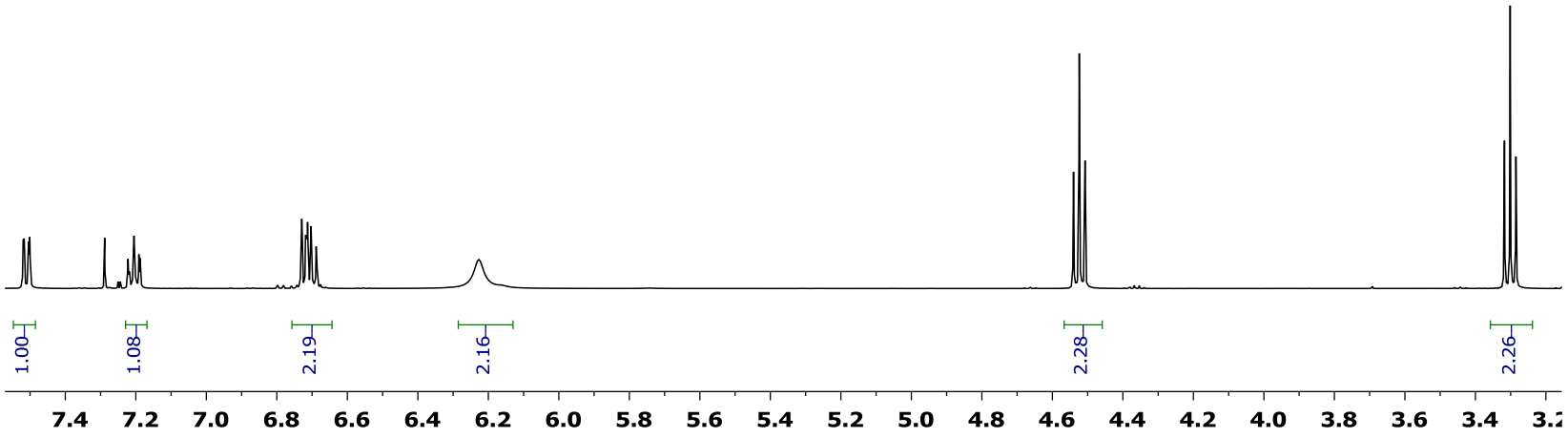
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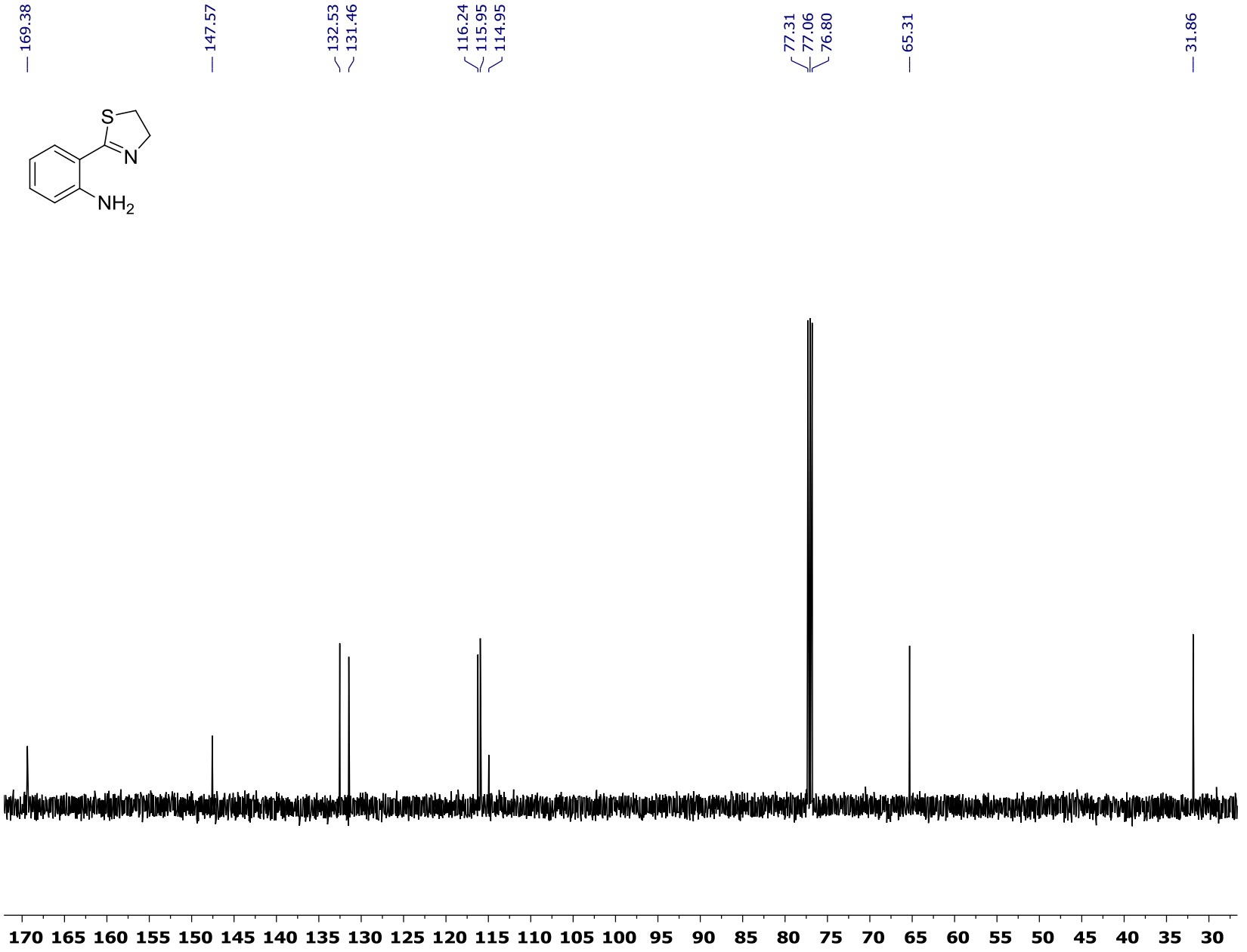
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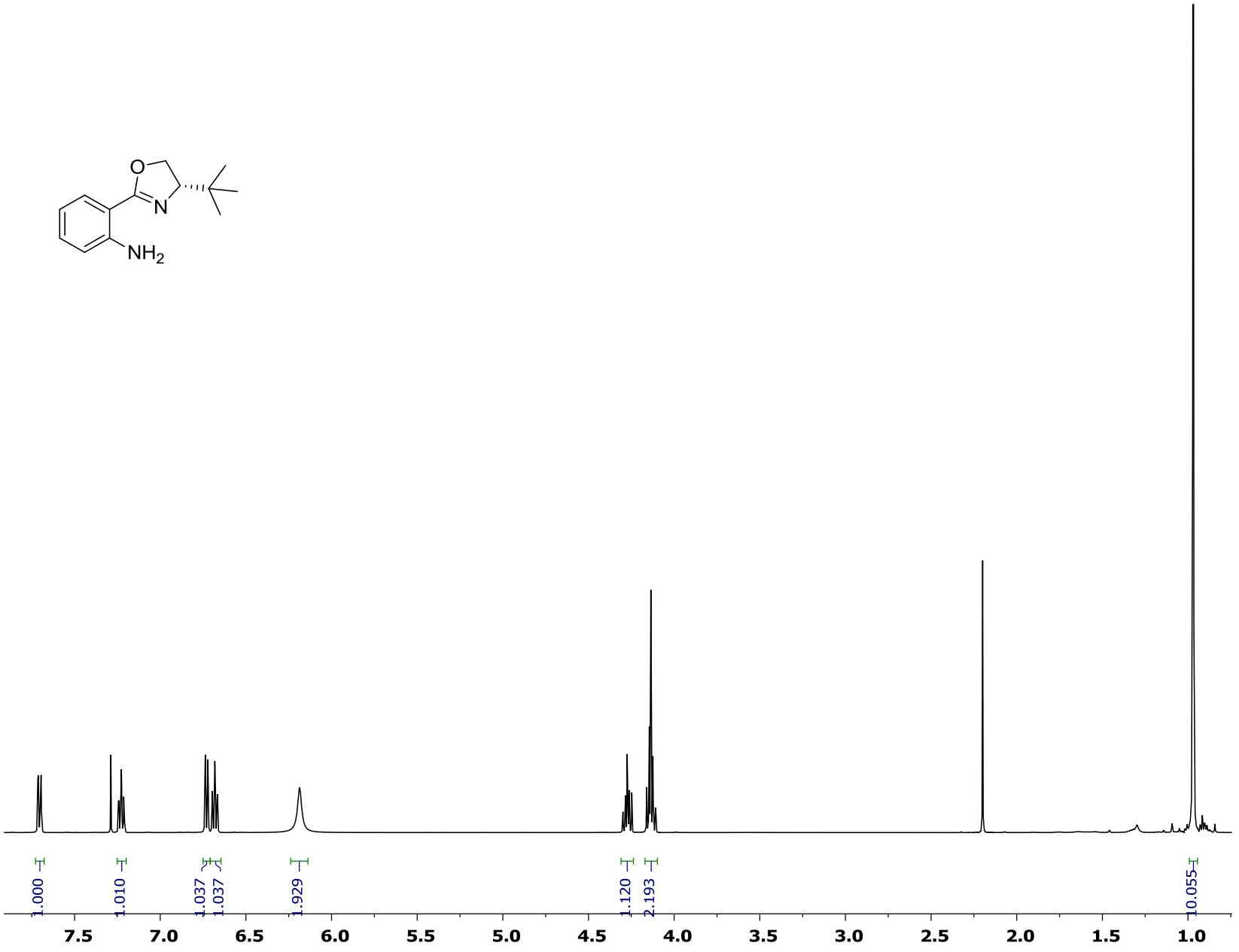
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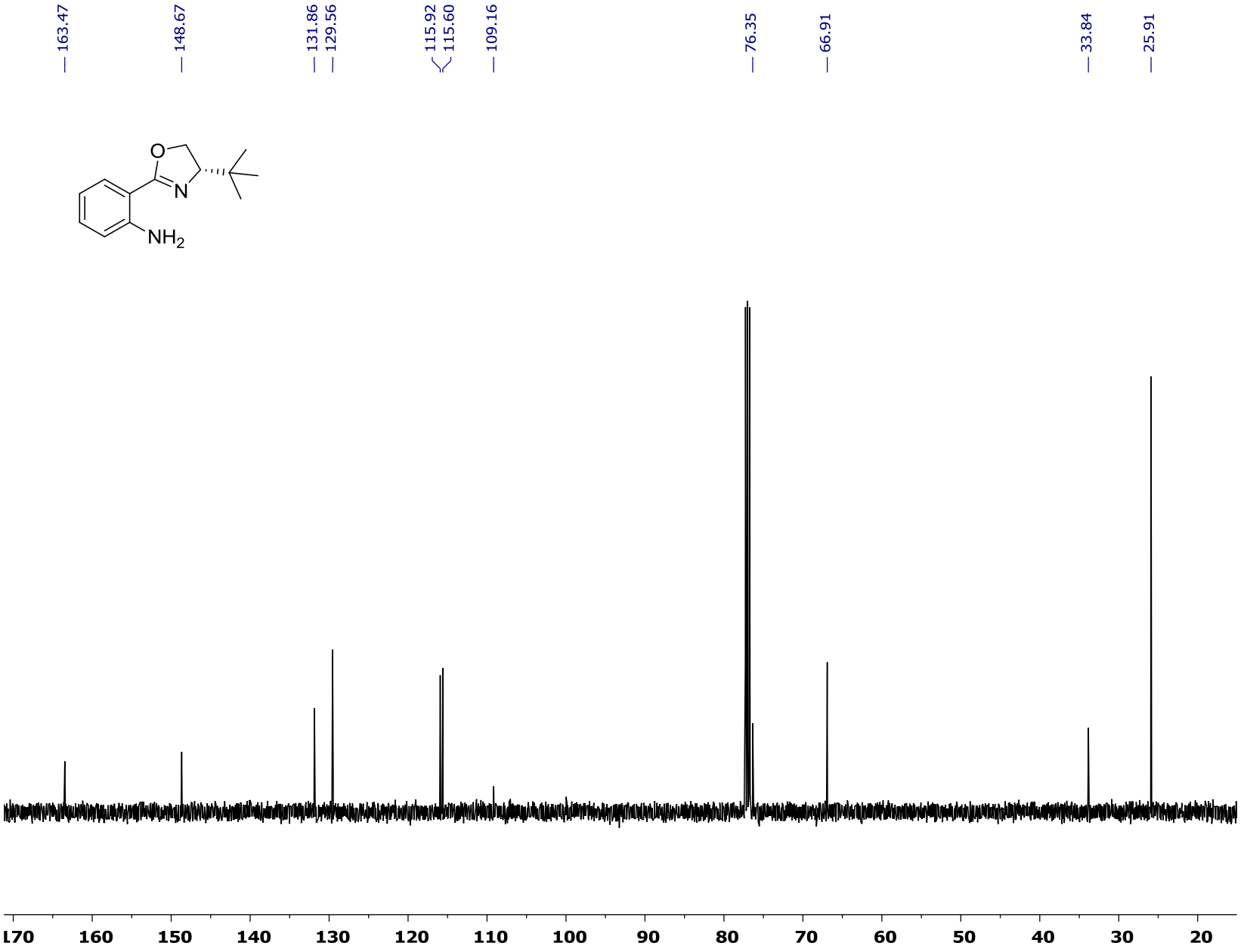
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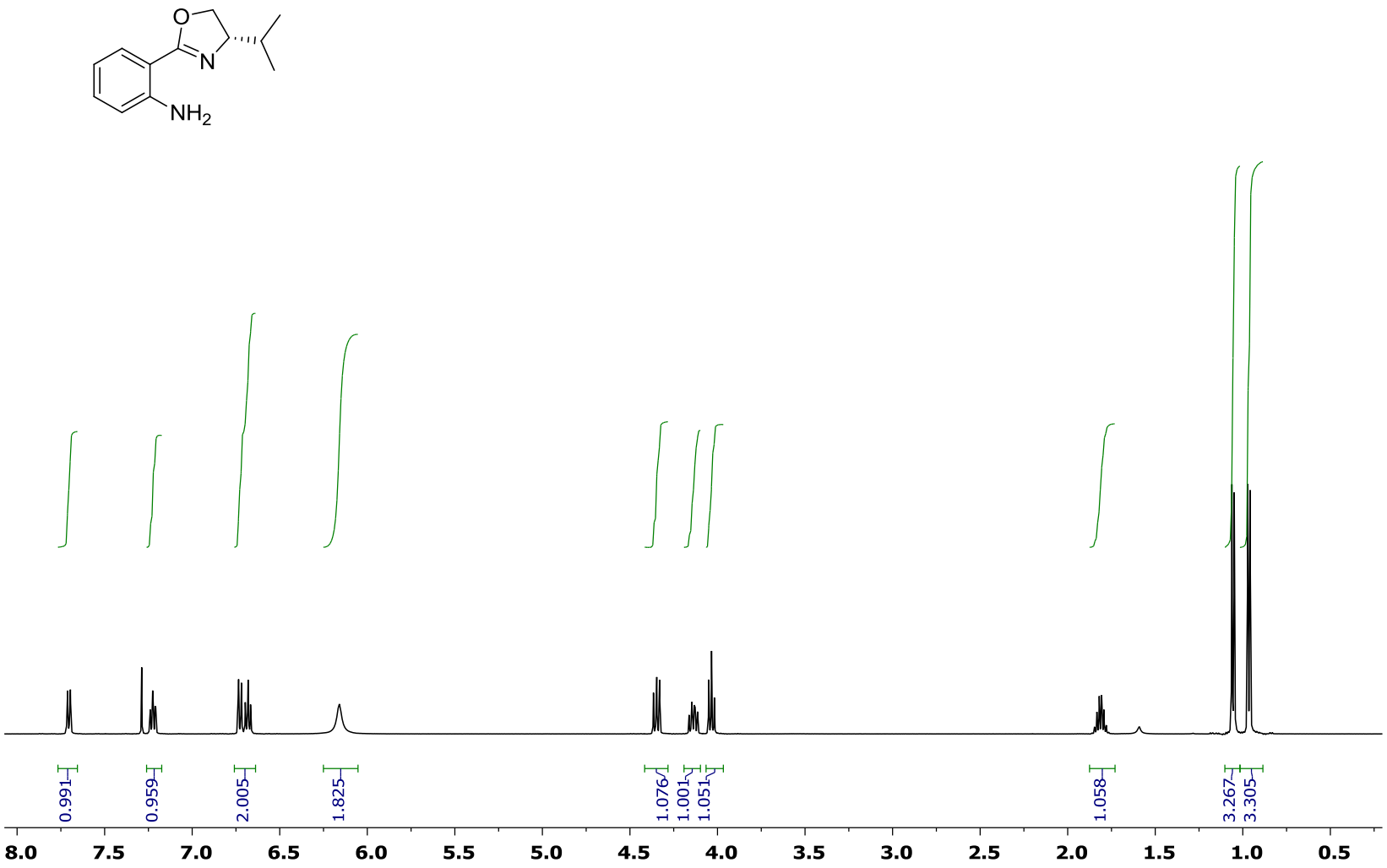
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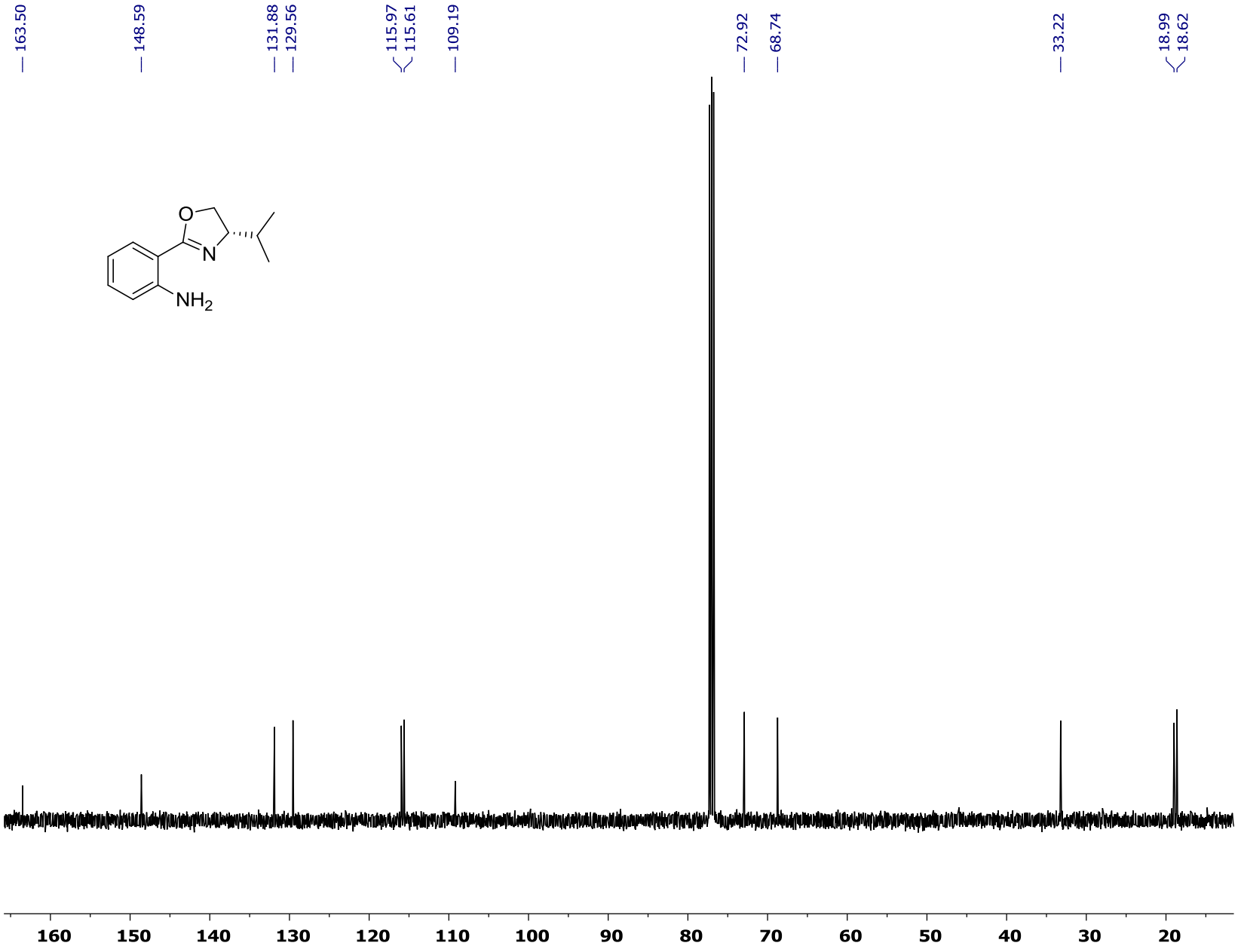
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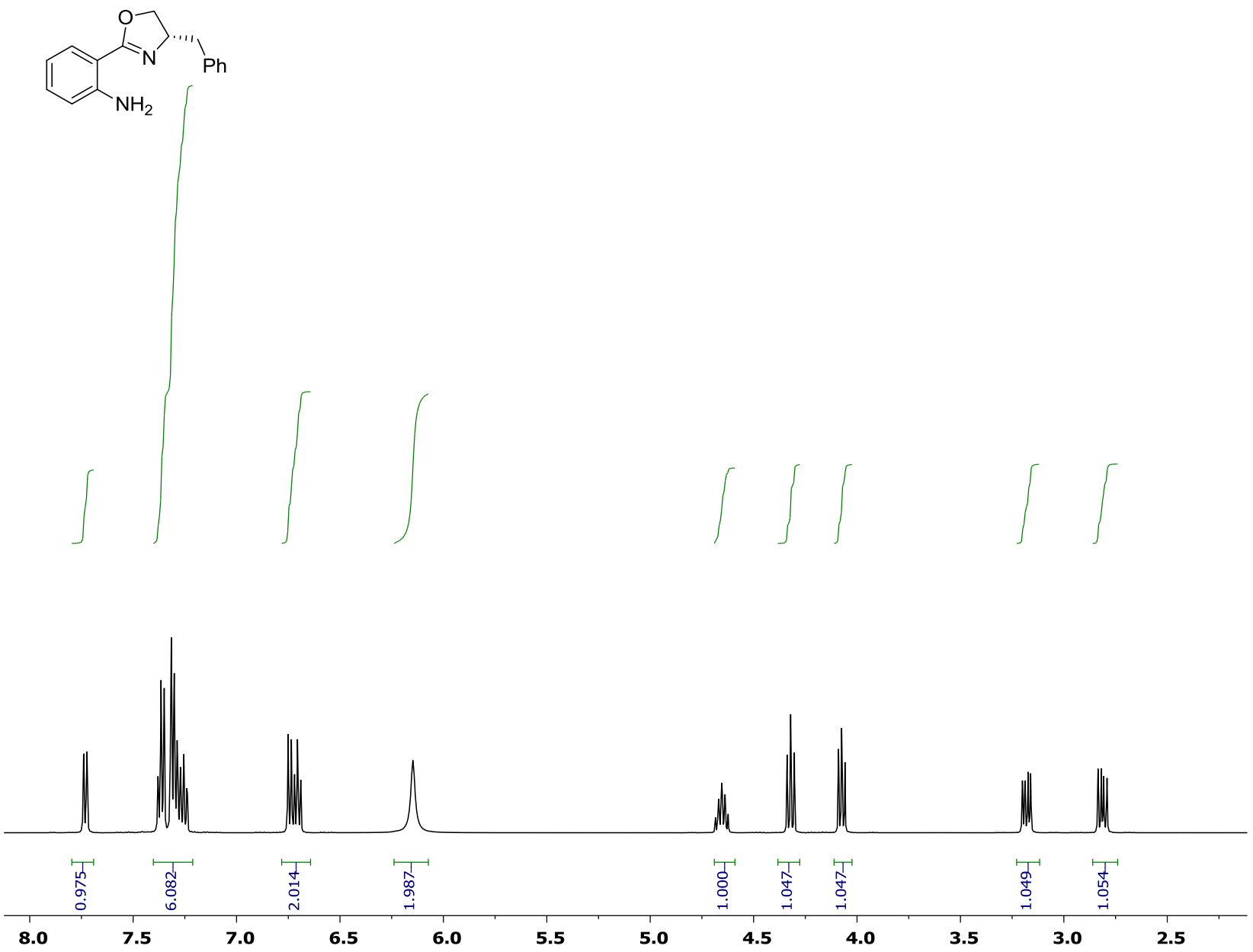
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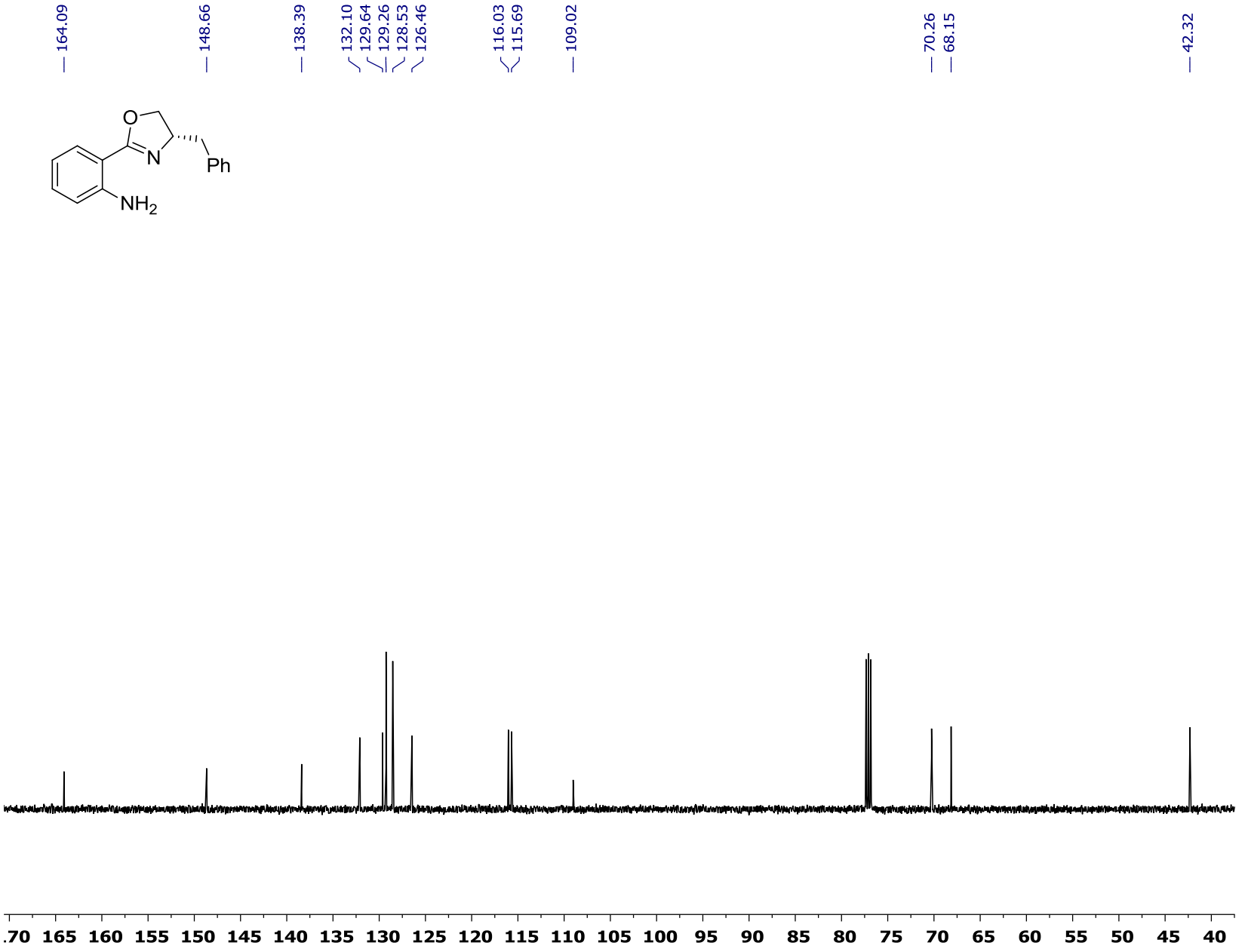
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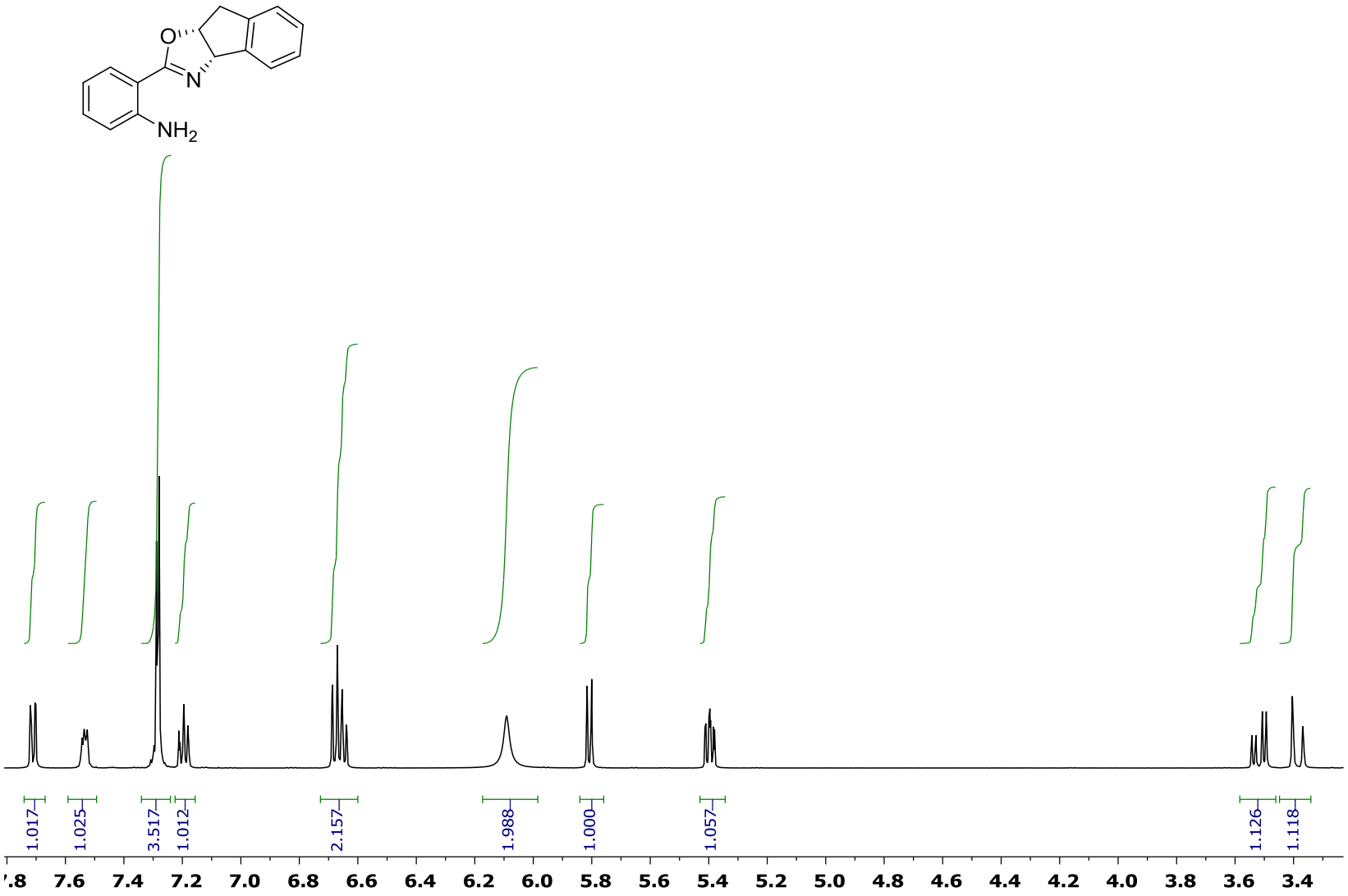
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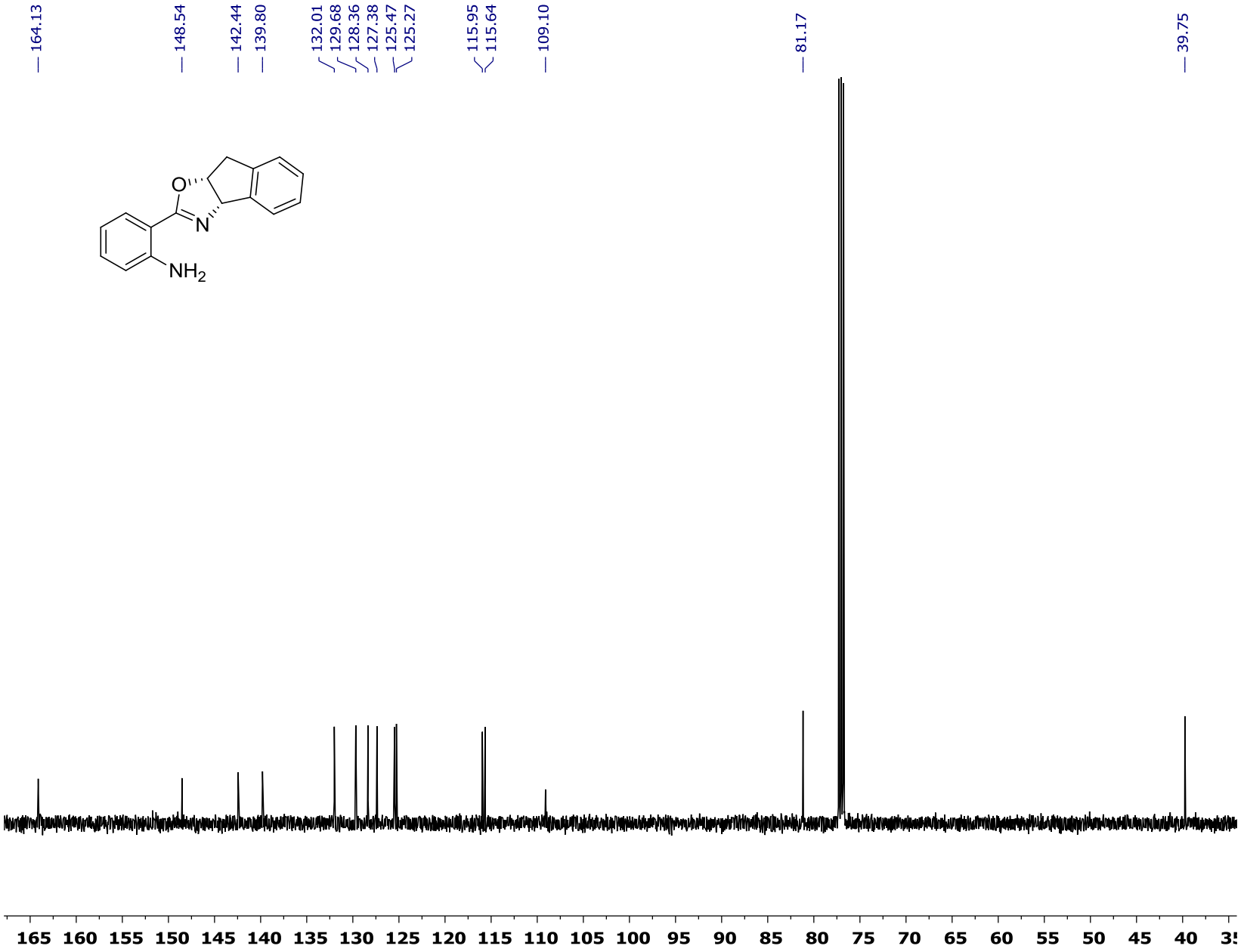
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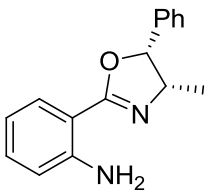
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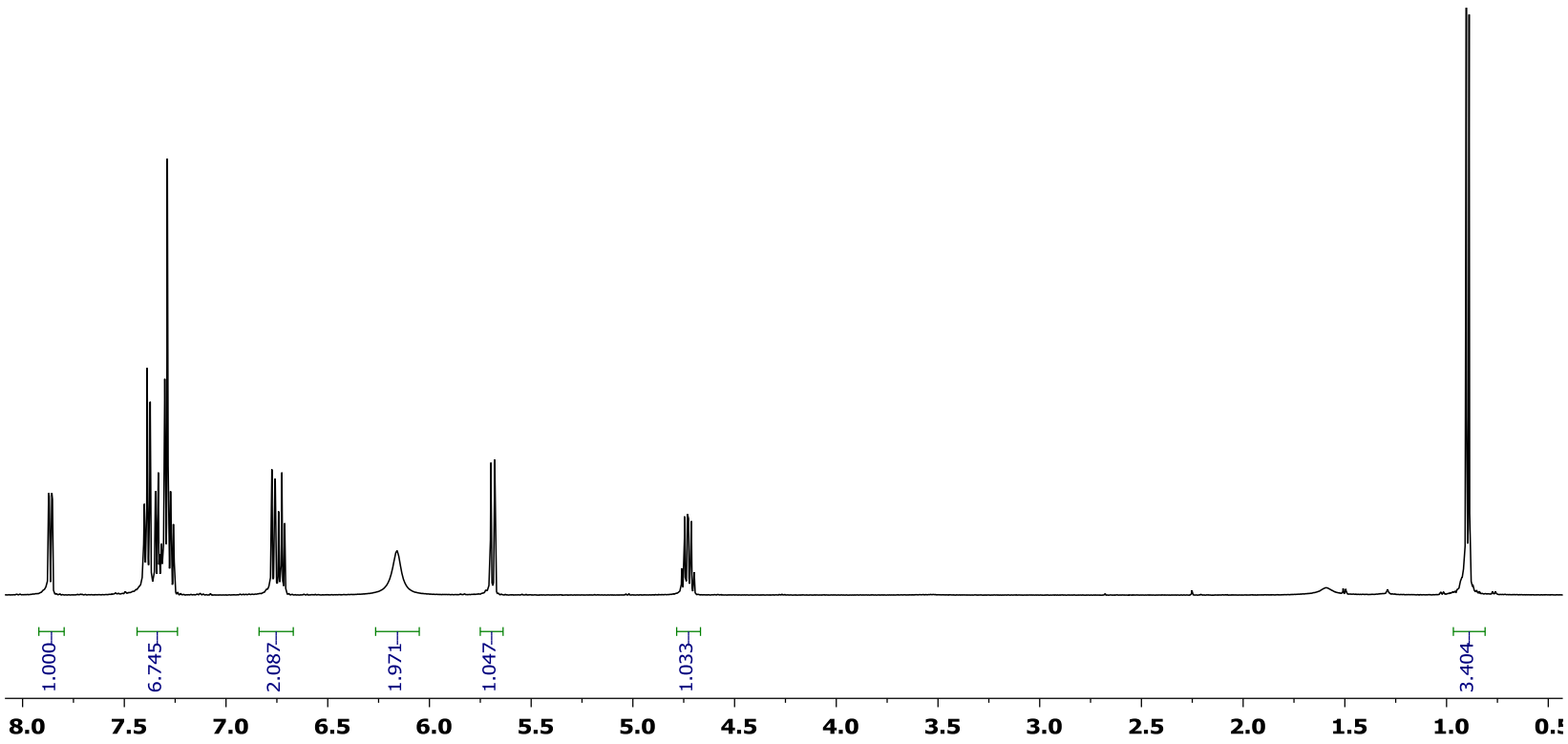
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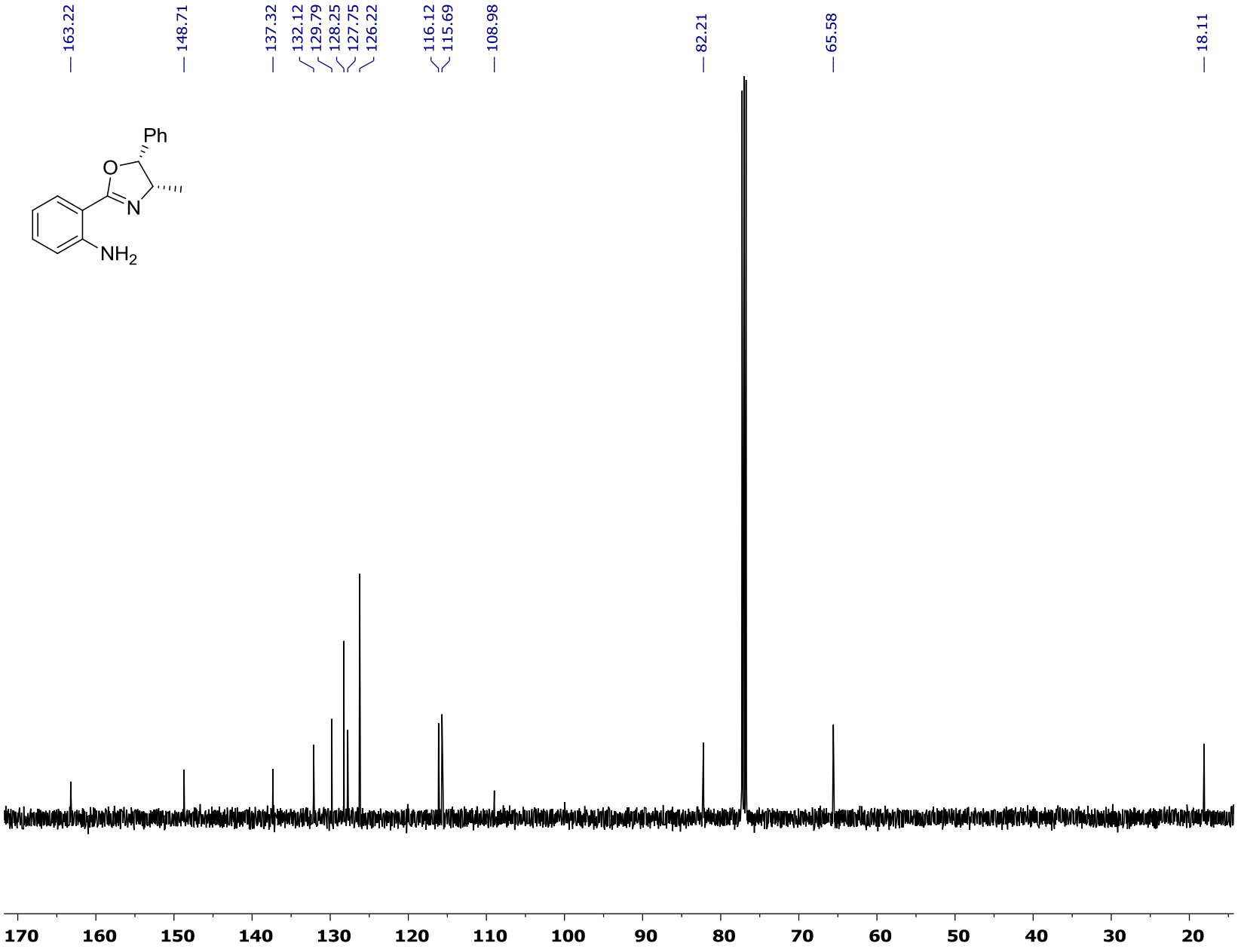
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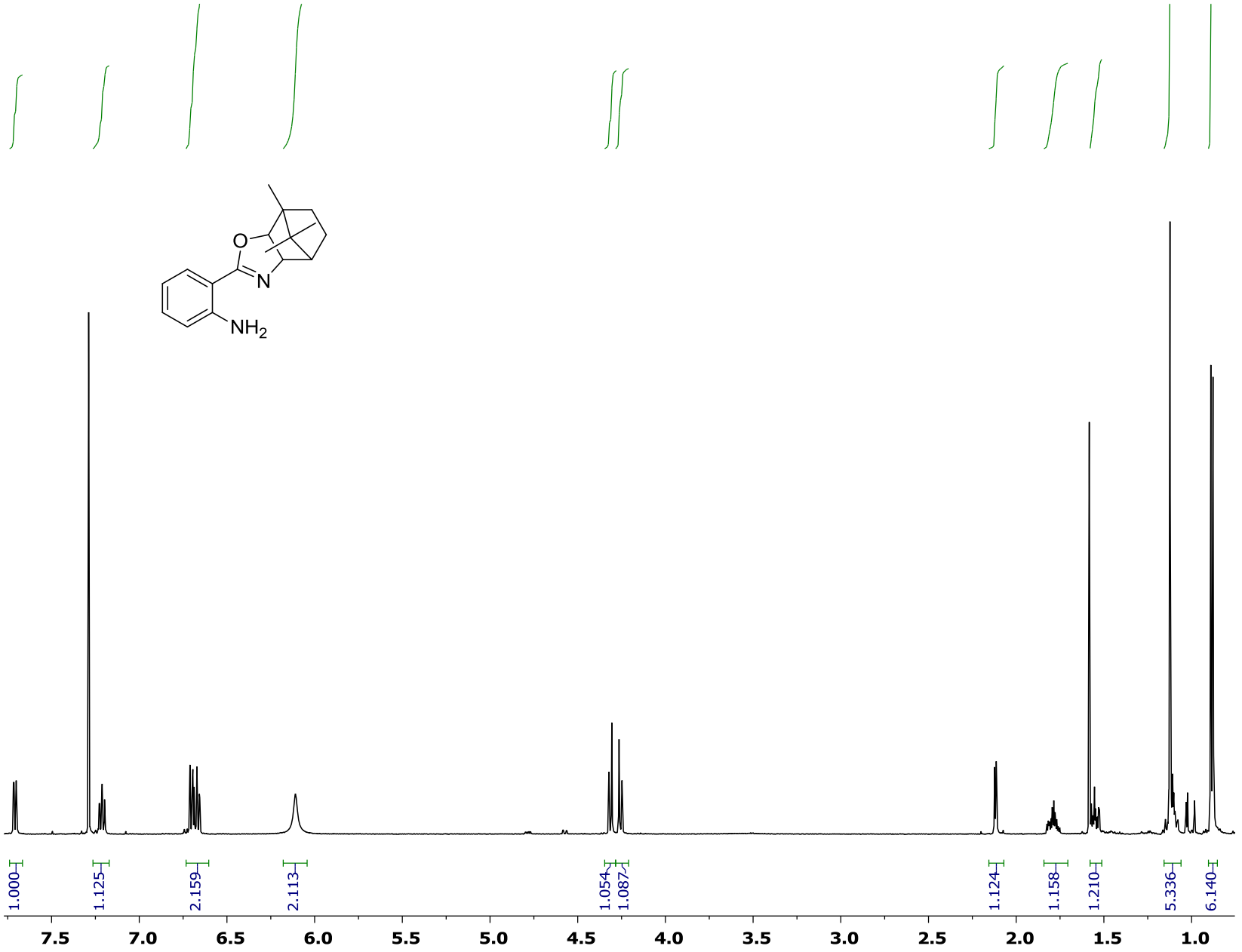
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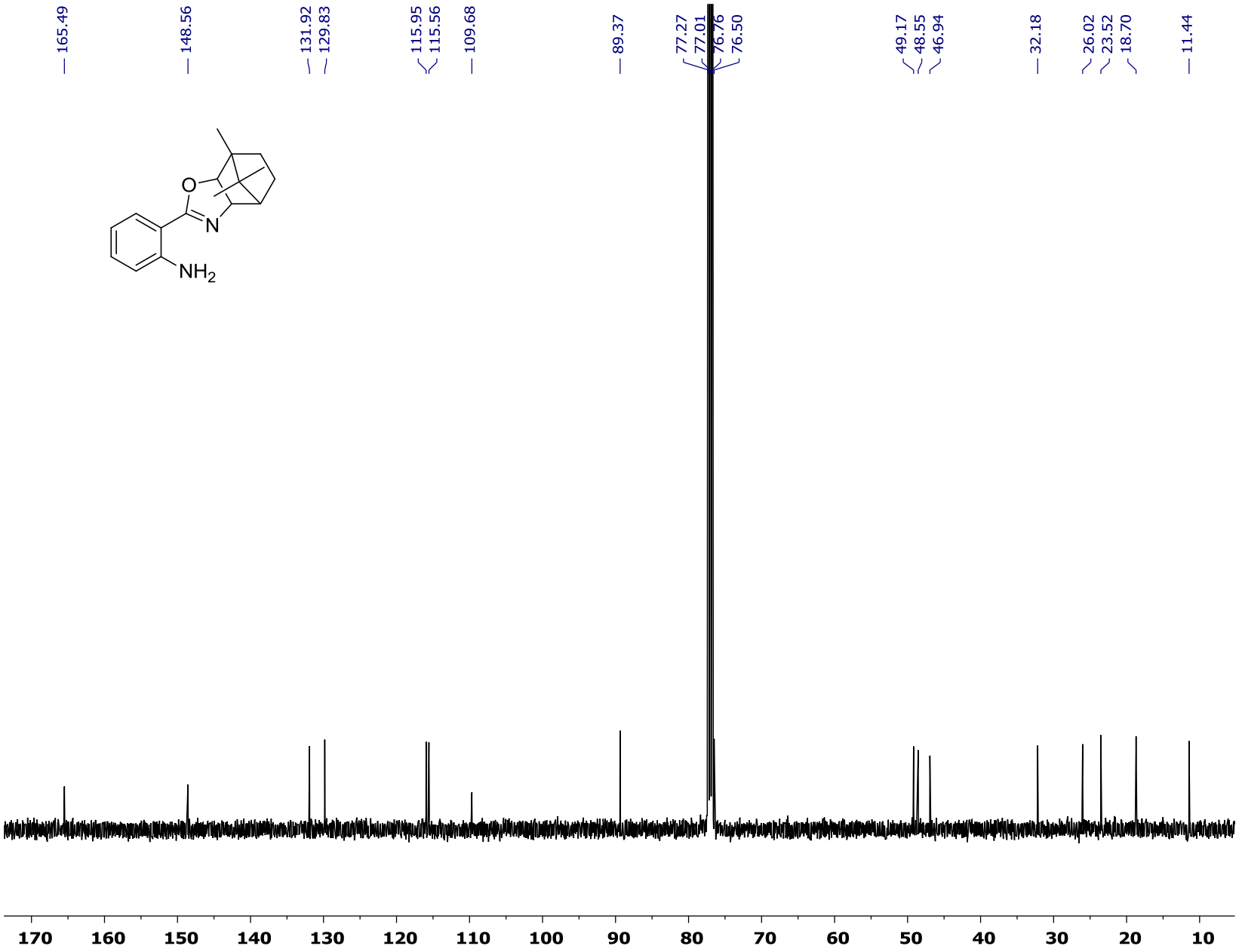
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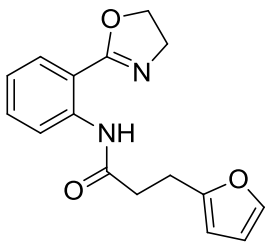
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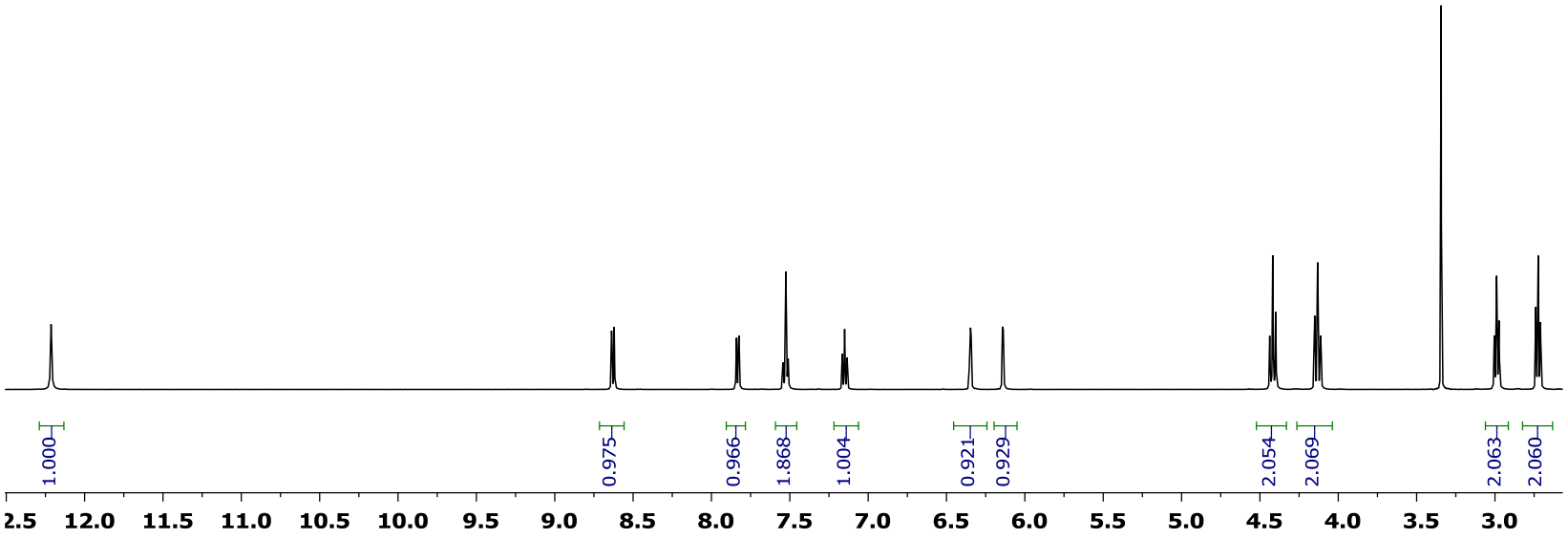
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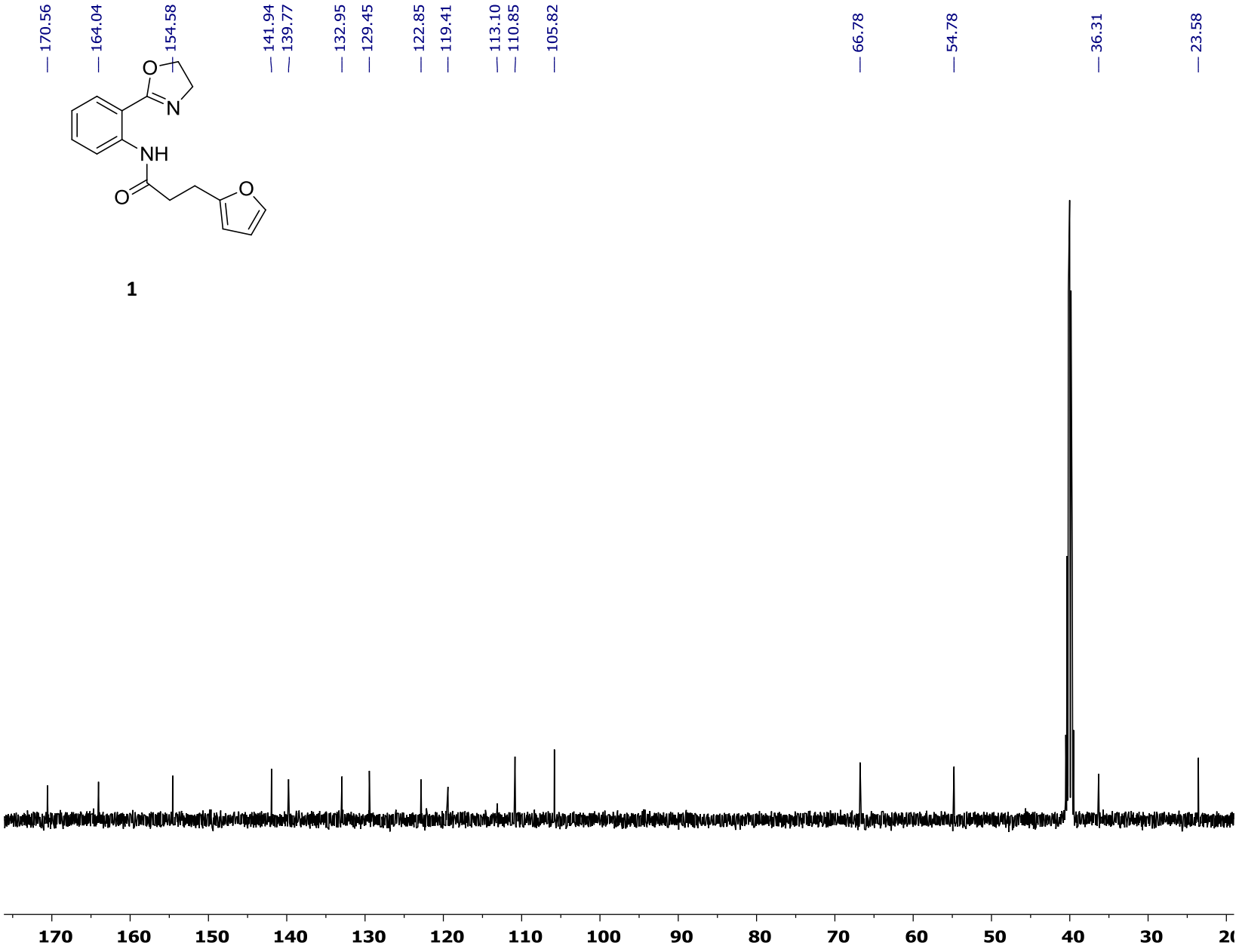
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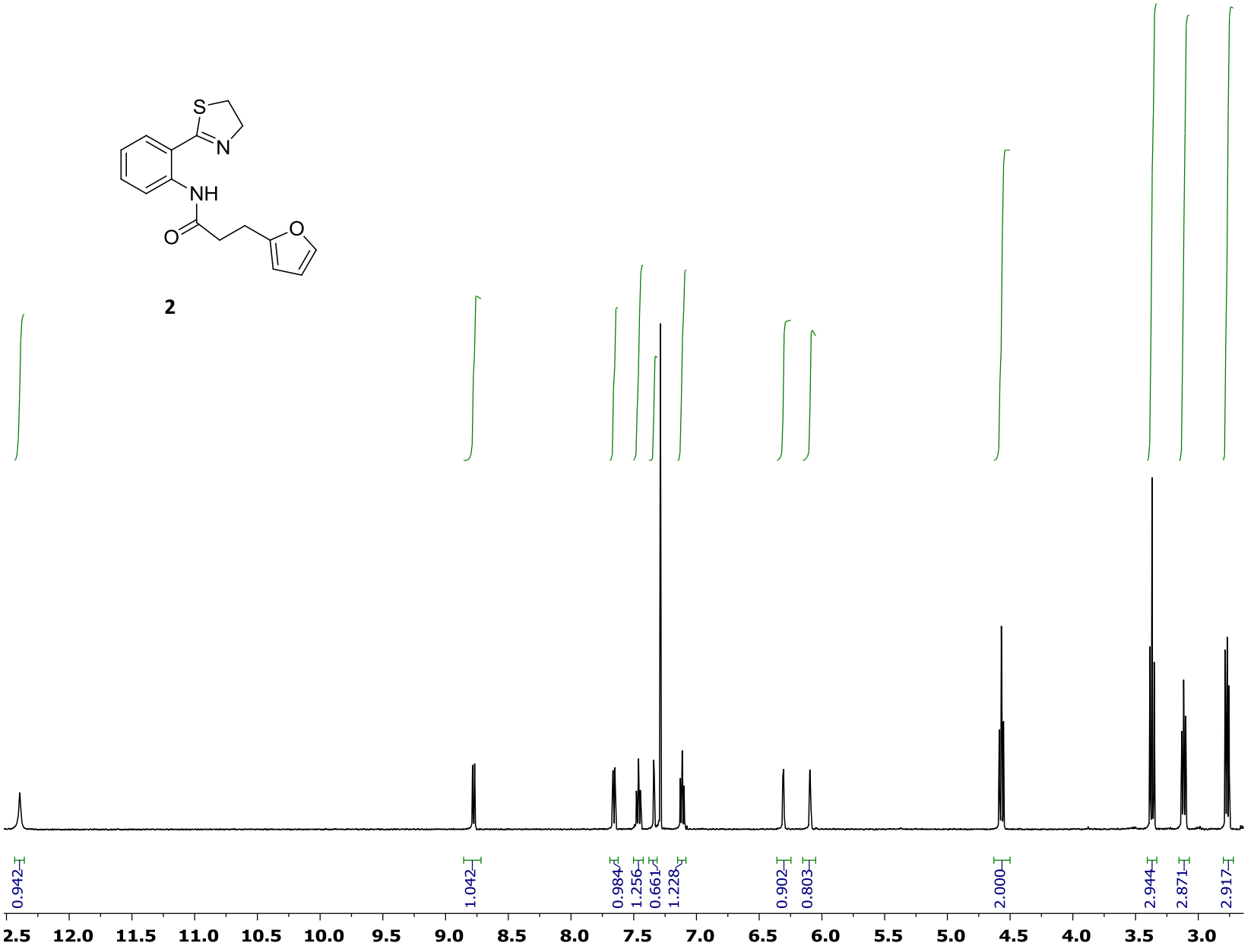
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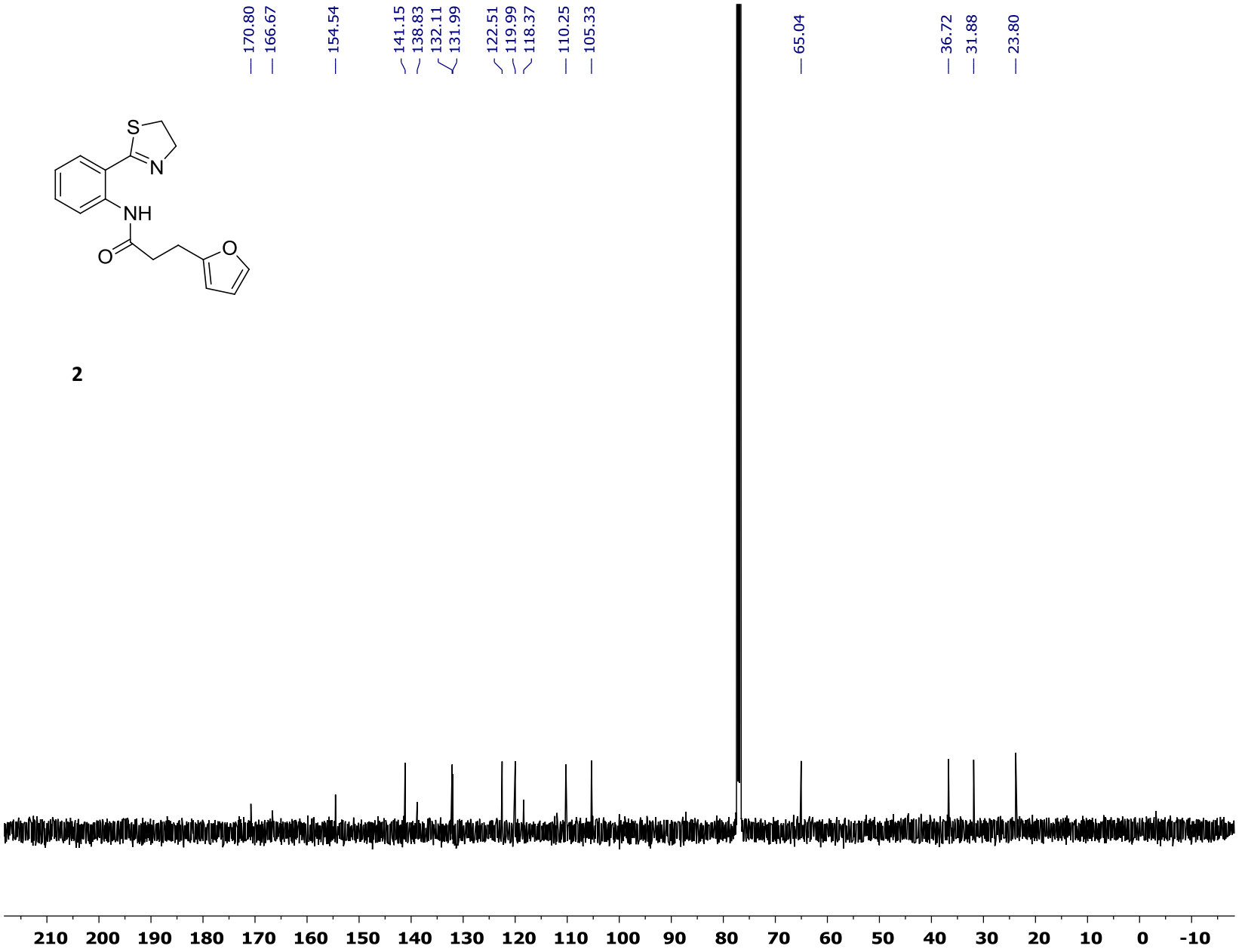
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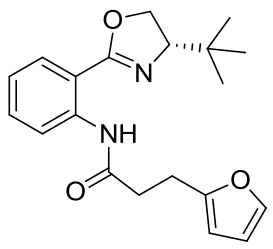
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9.223
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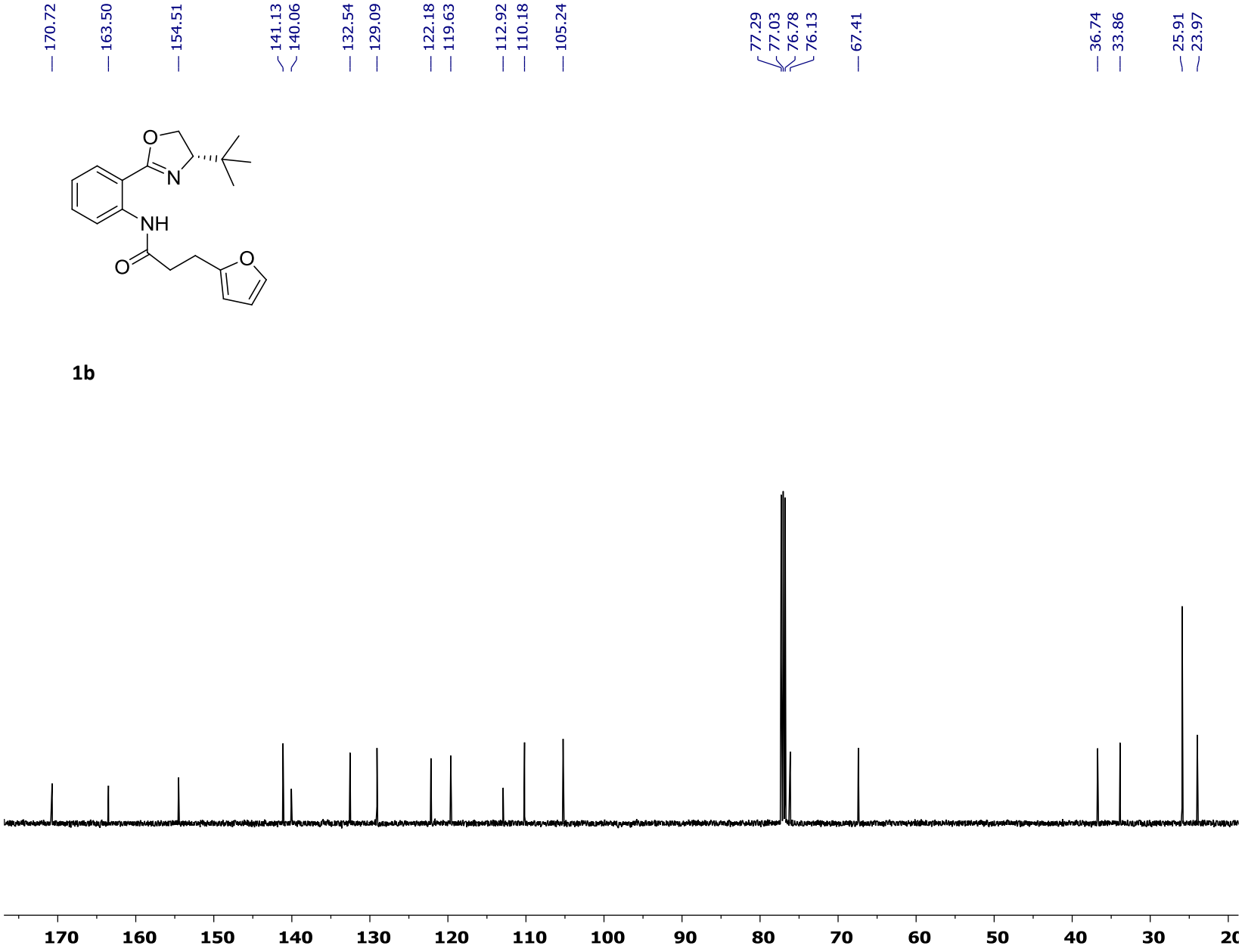
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76.13
67.41
36.74
33.86
25.91
23.97
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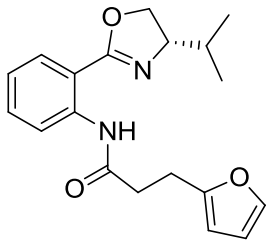
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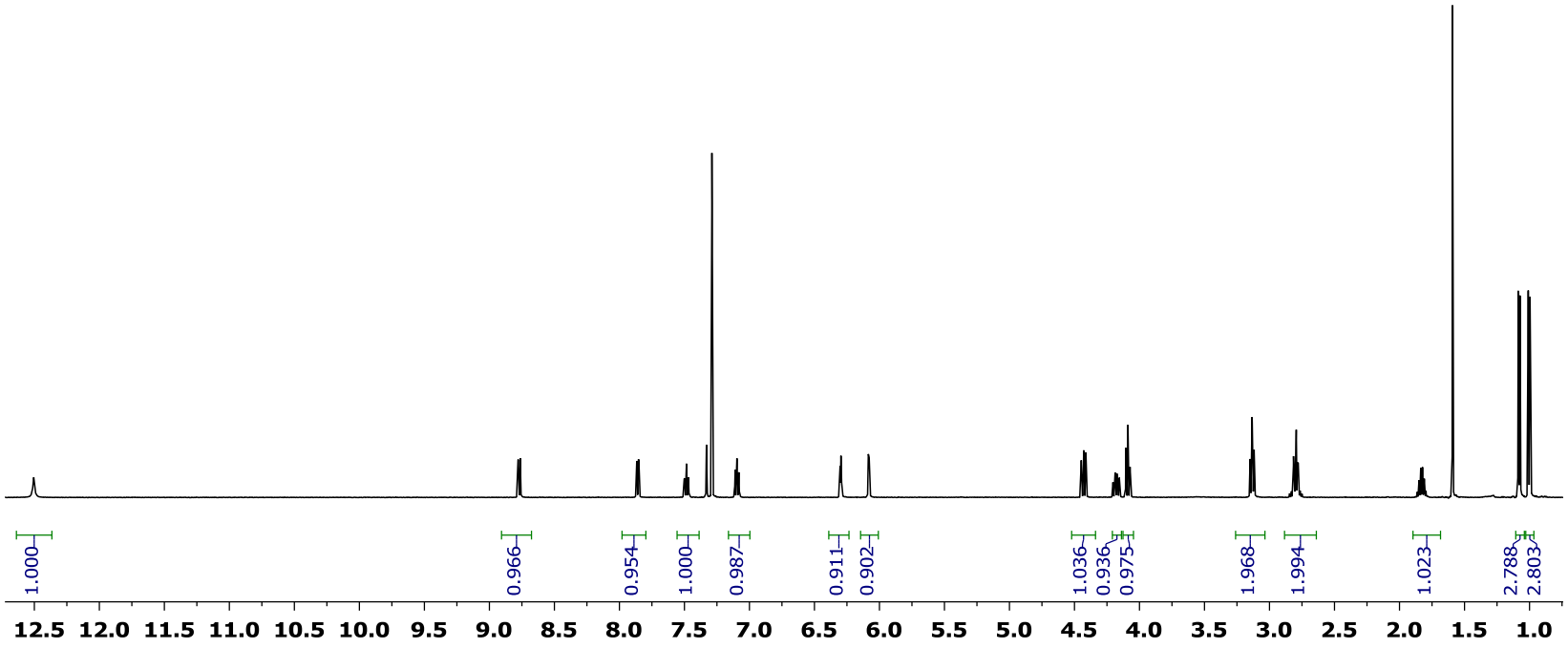
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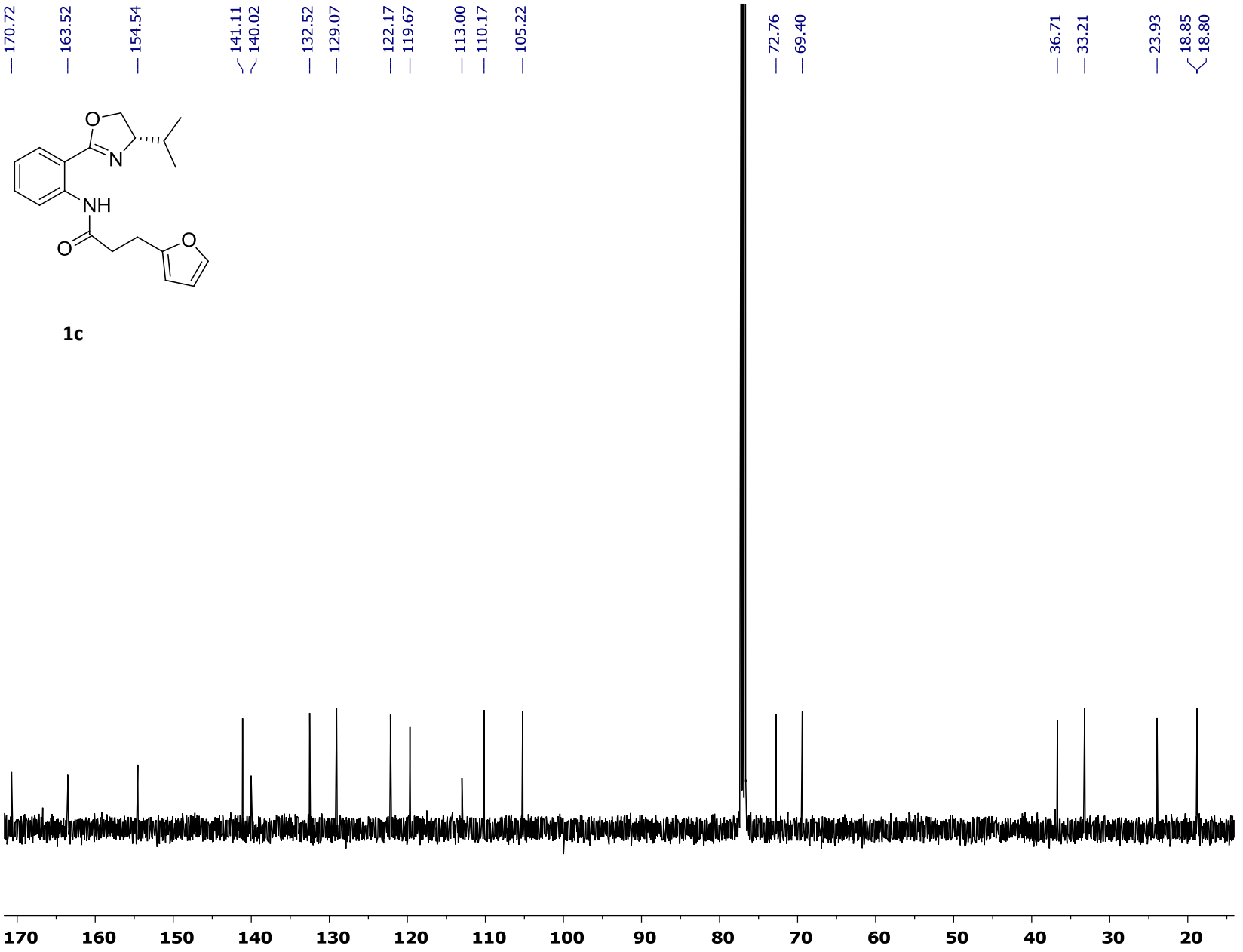
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N
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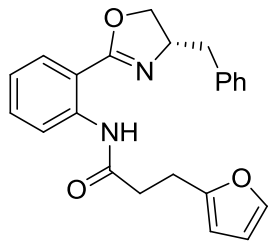
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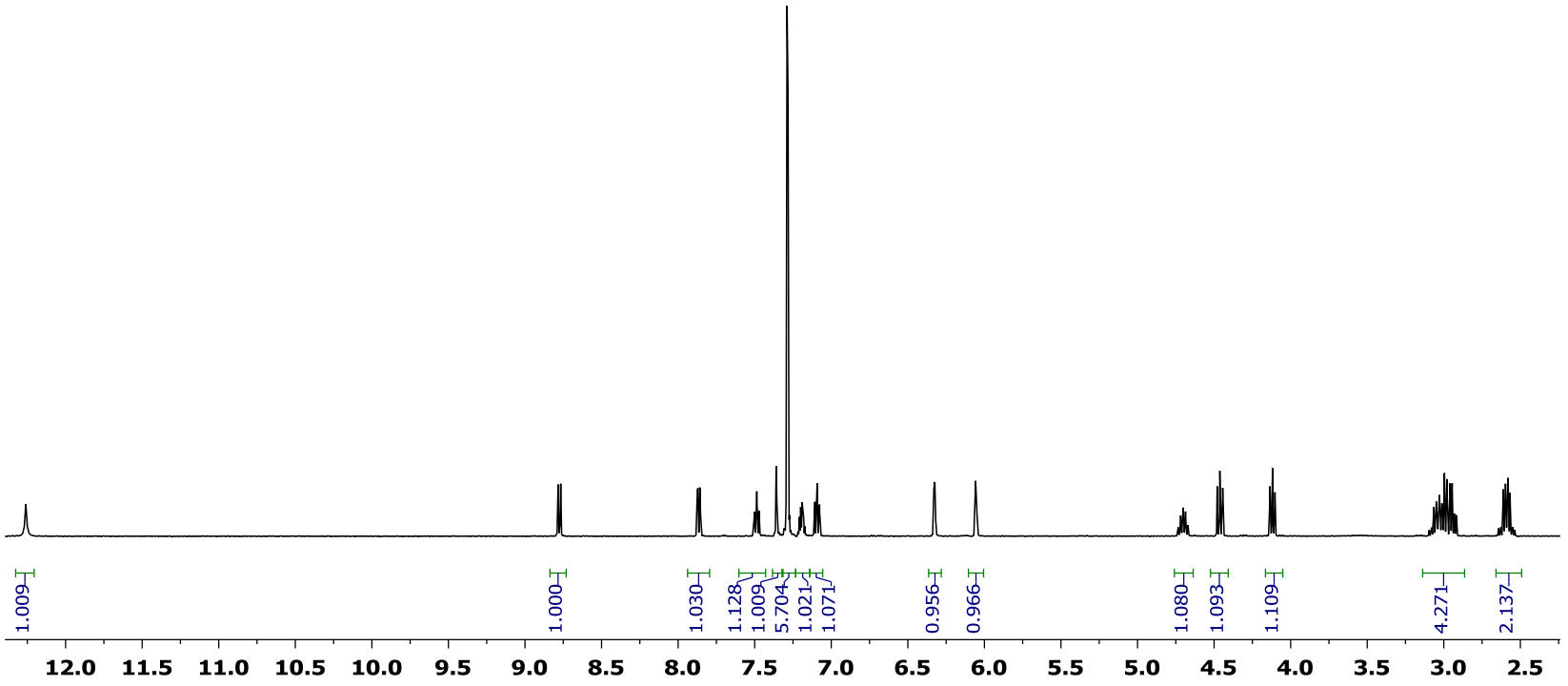
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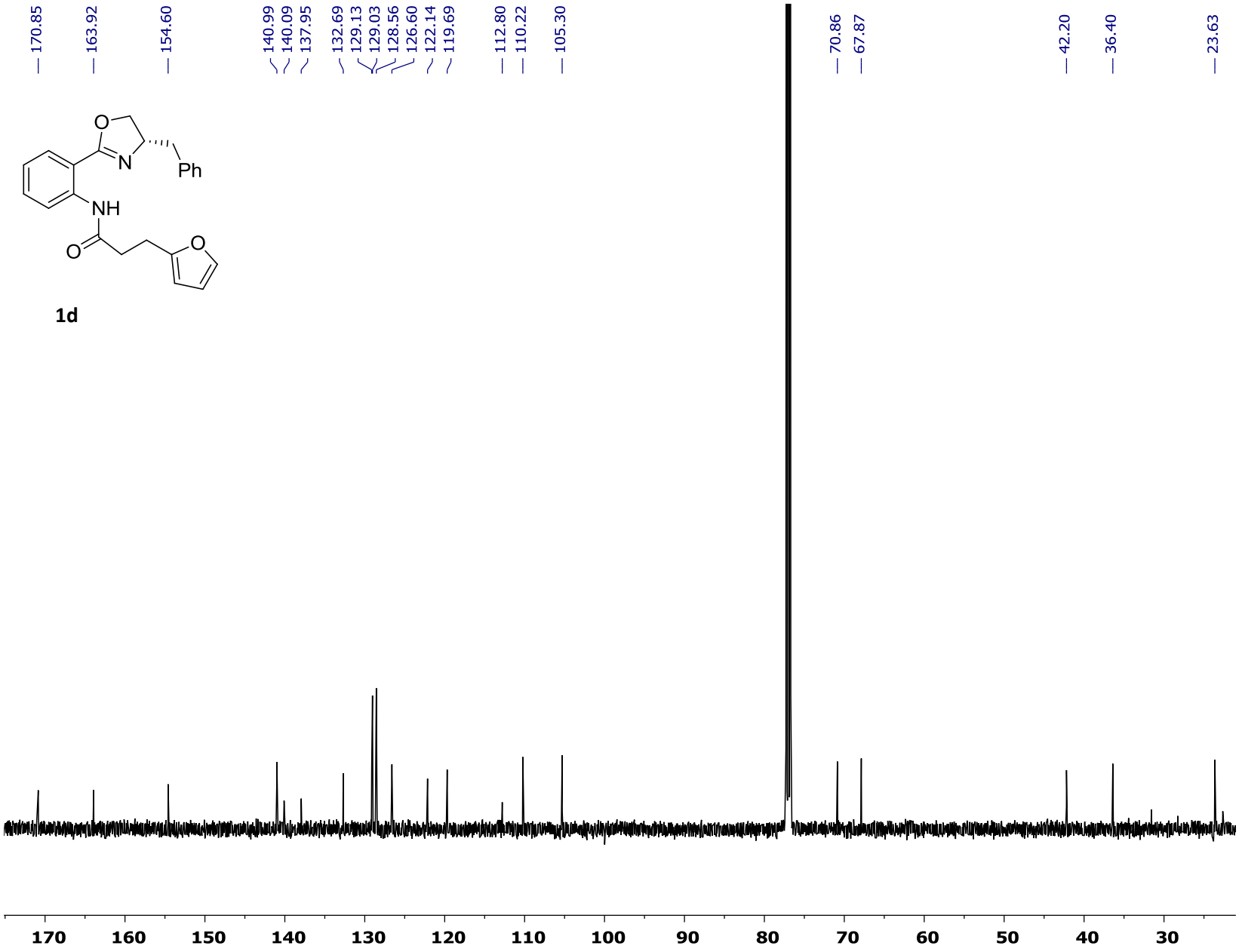
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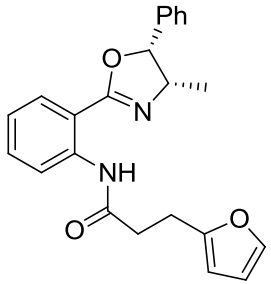
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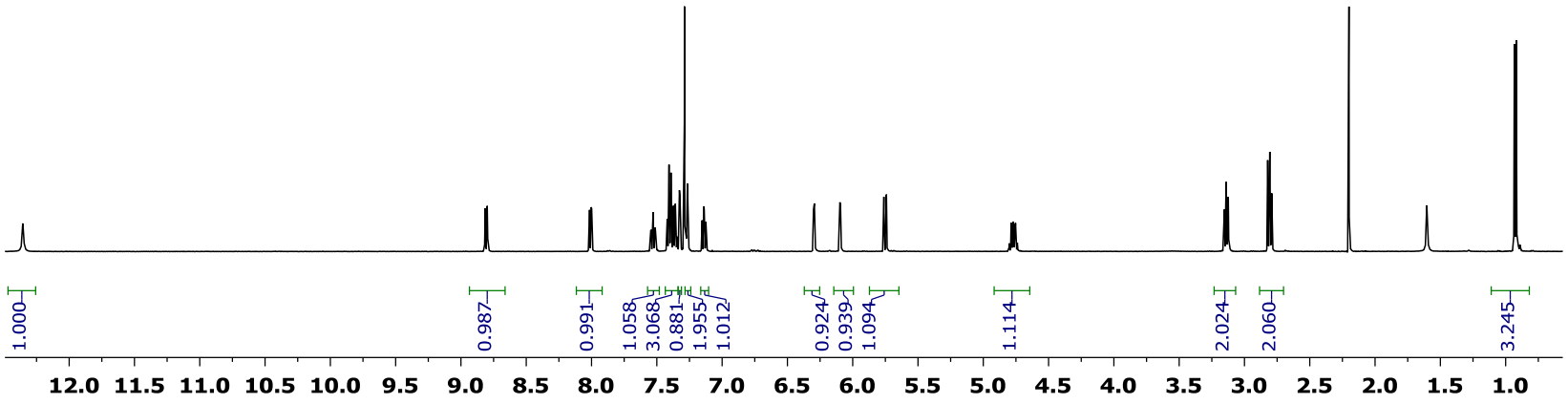
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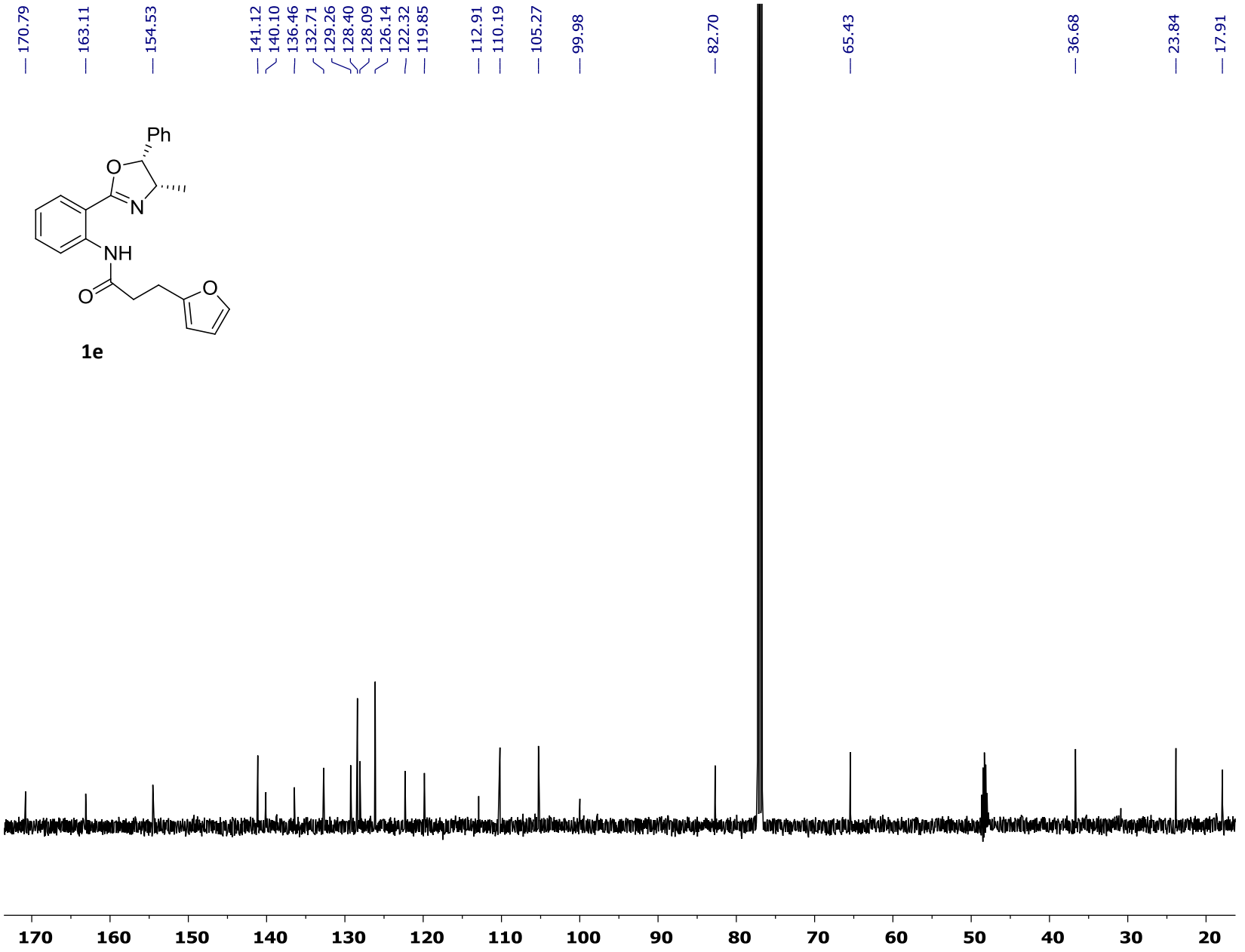
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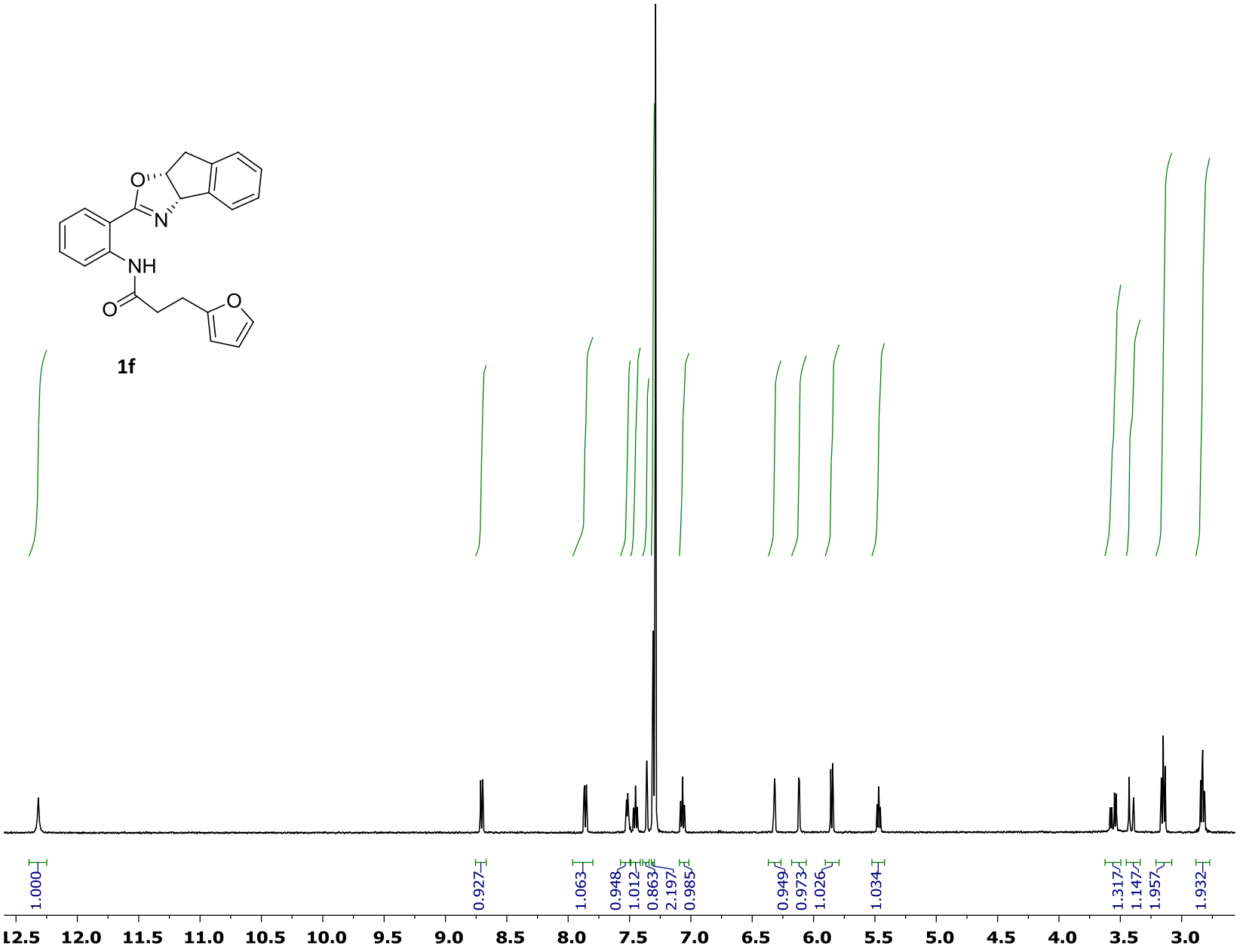
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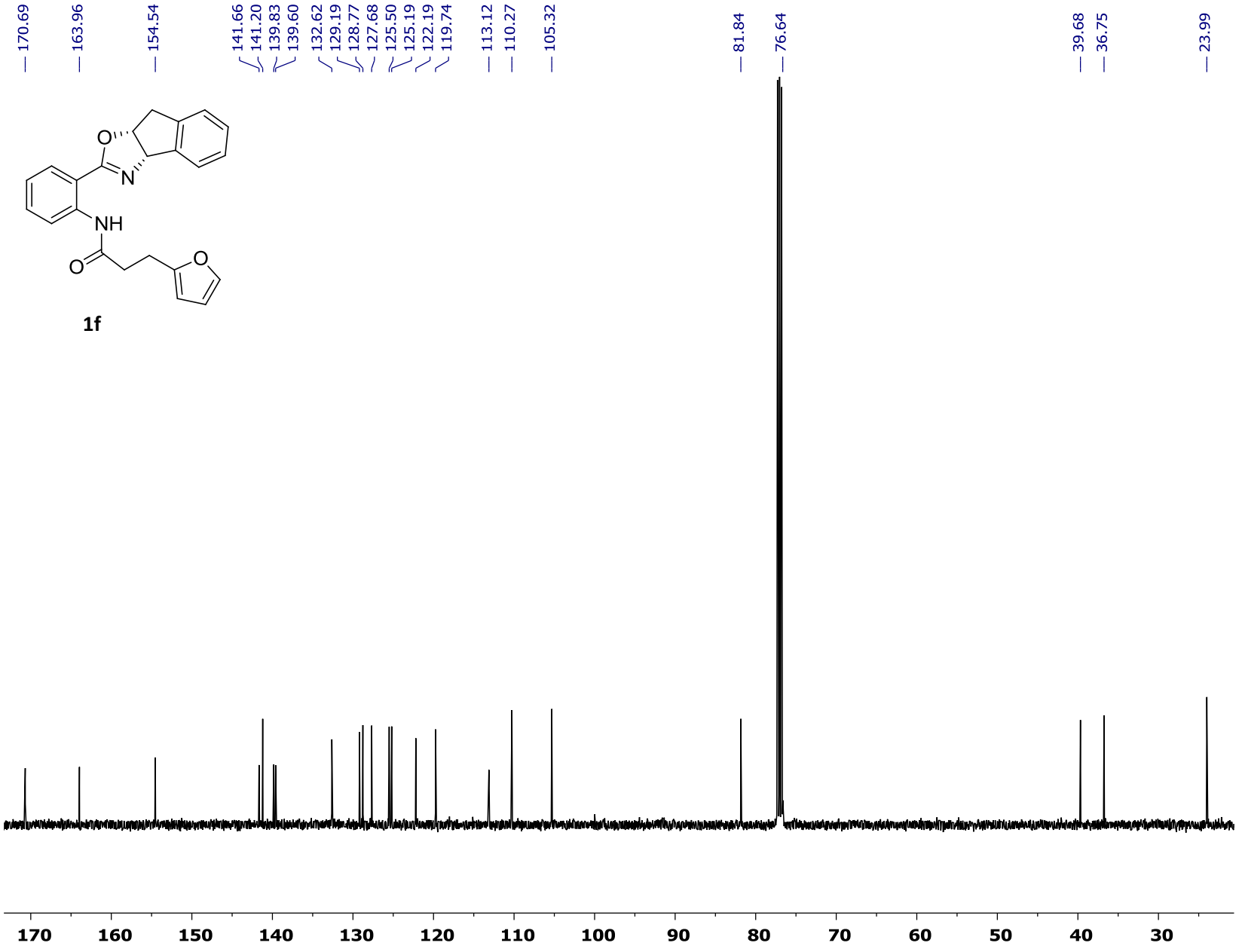
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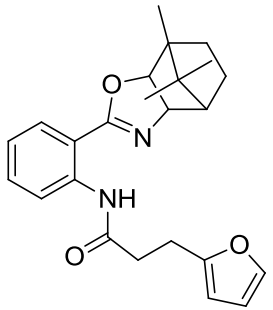
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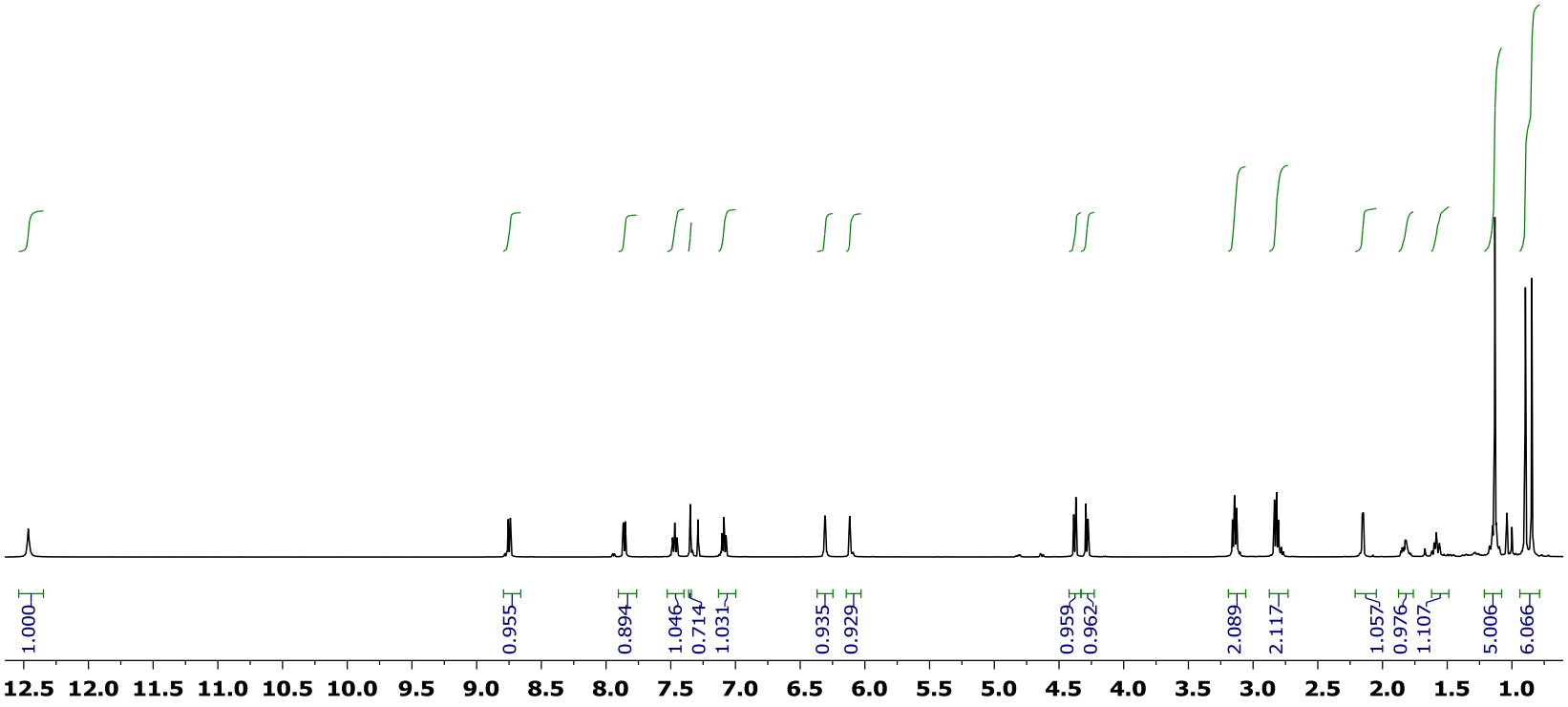
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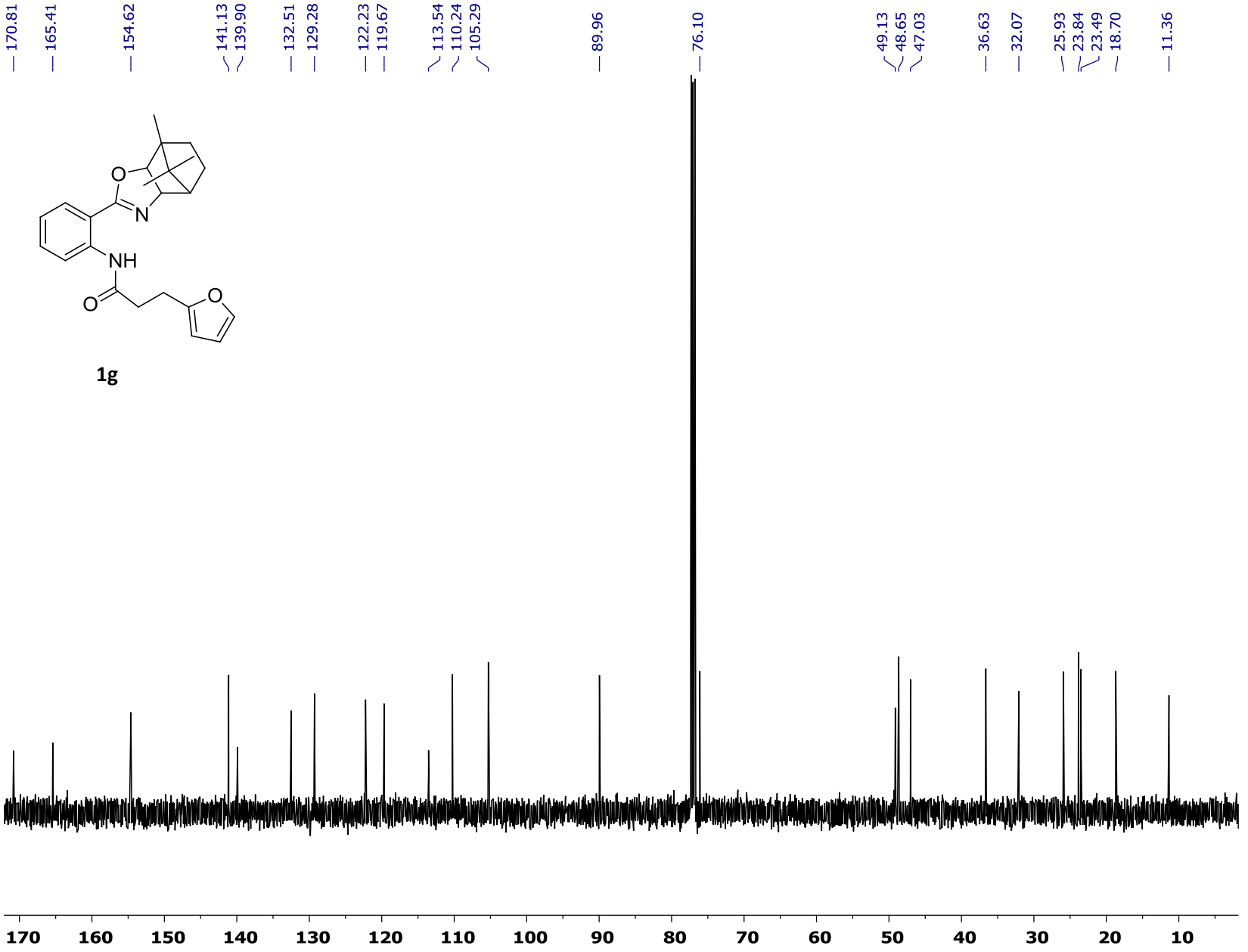
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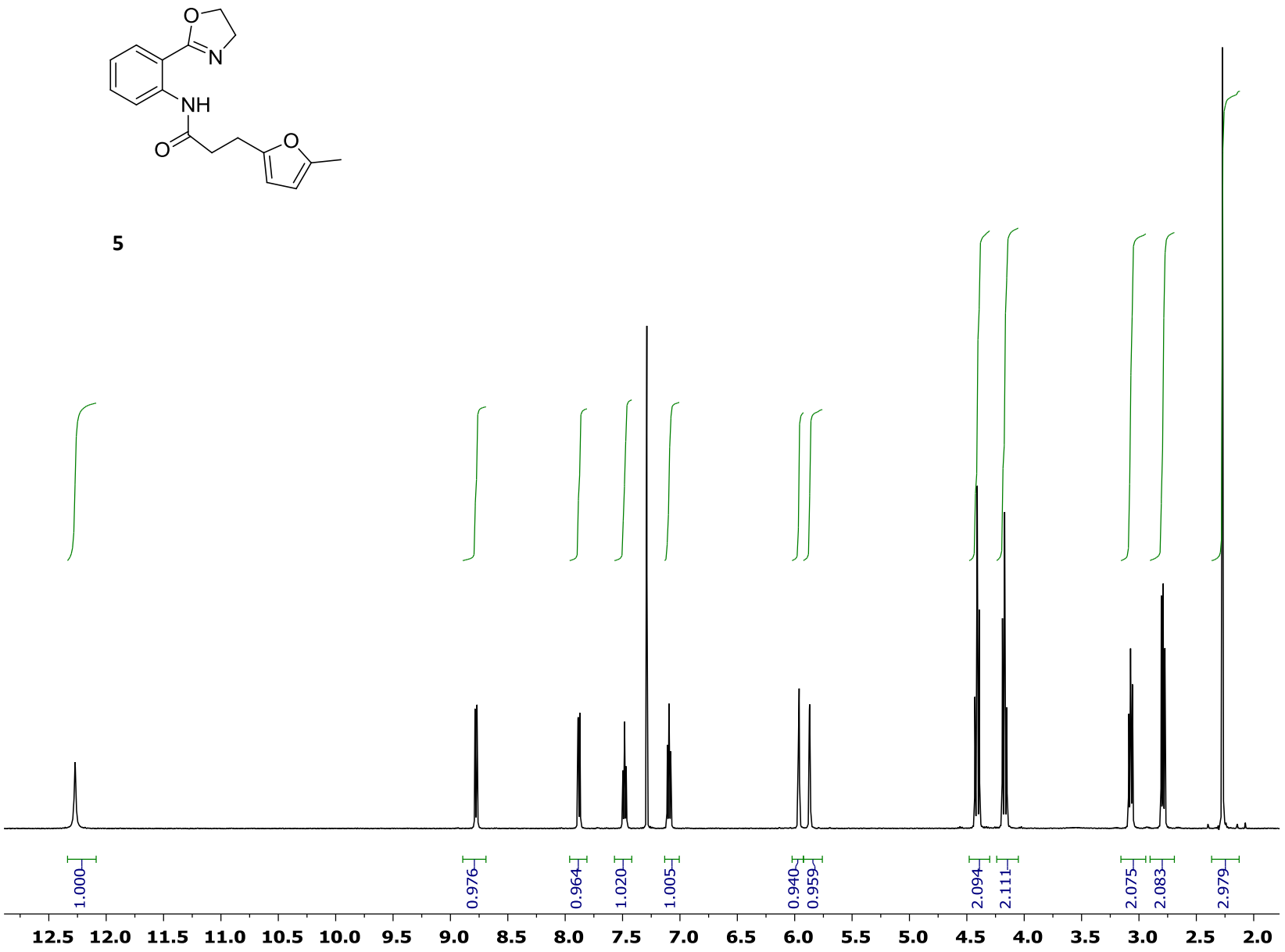
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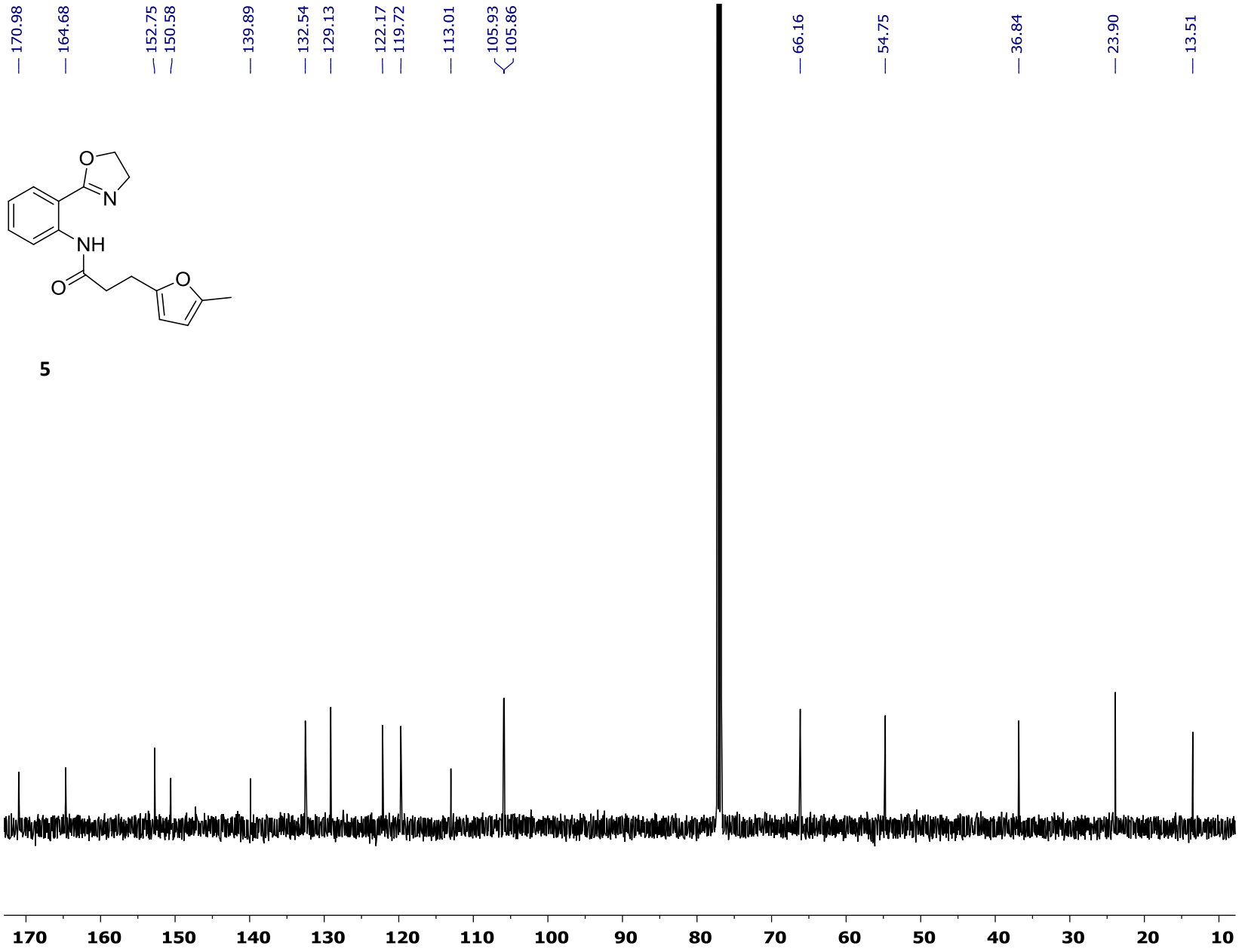
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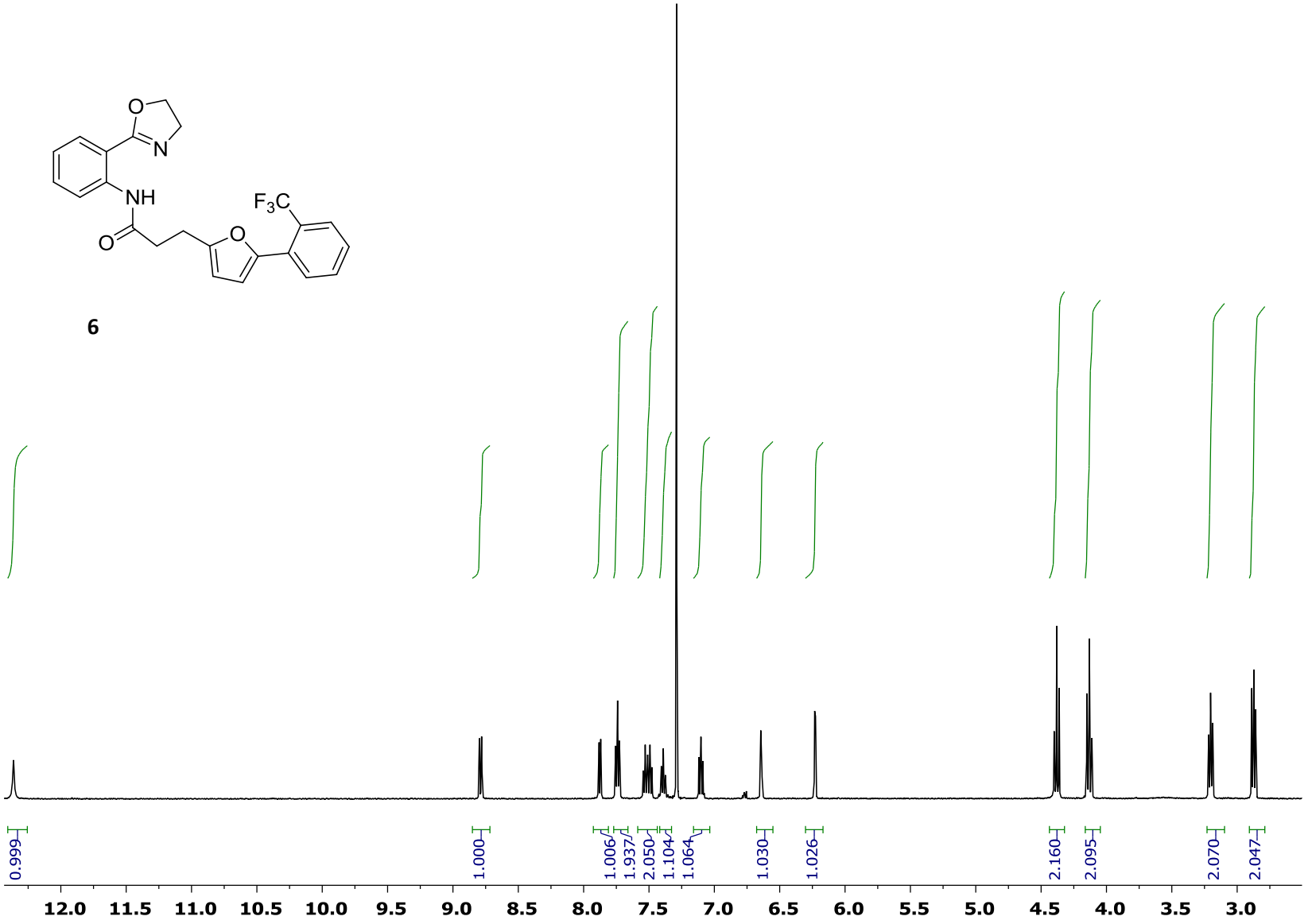
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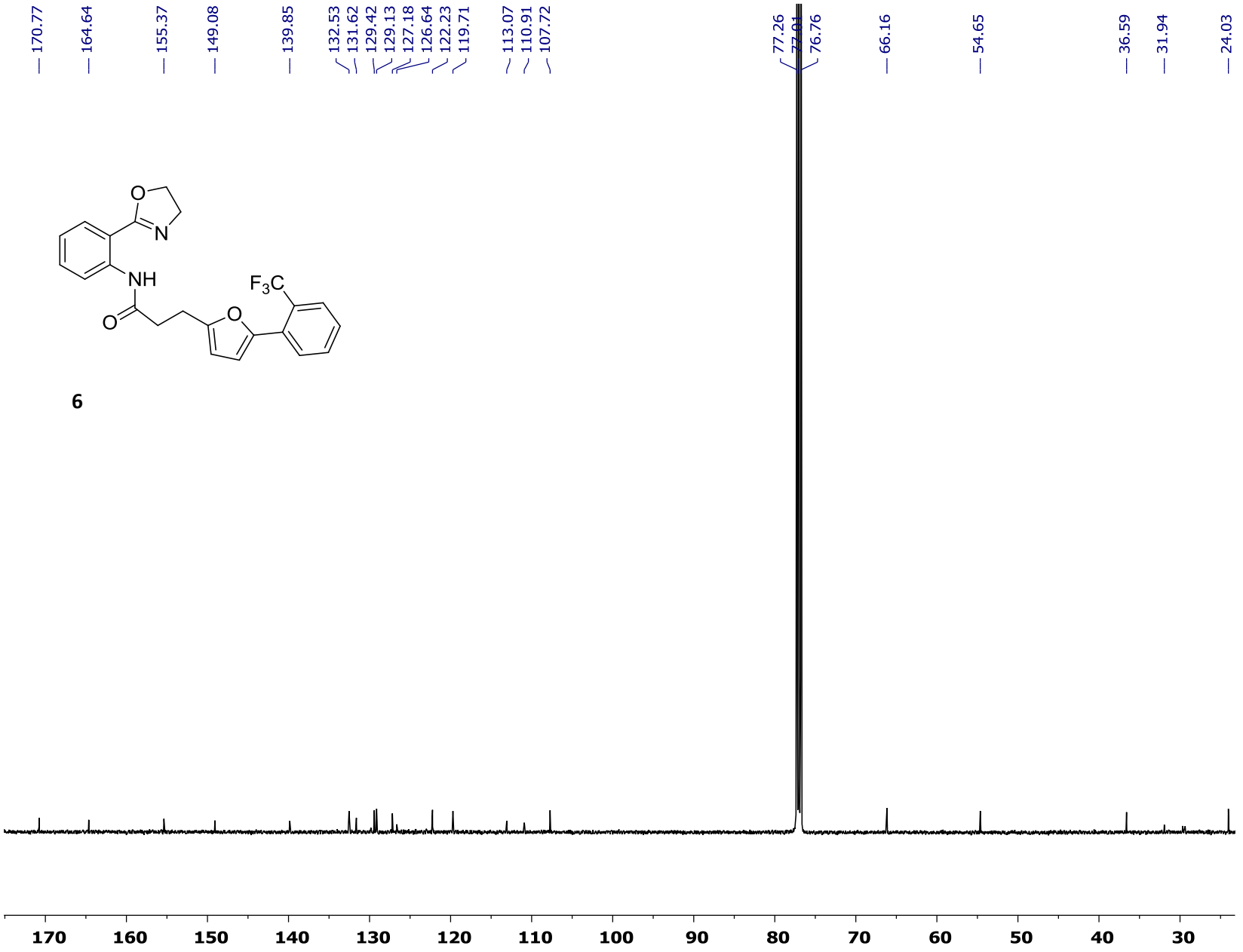
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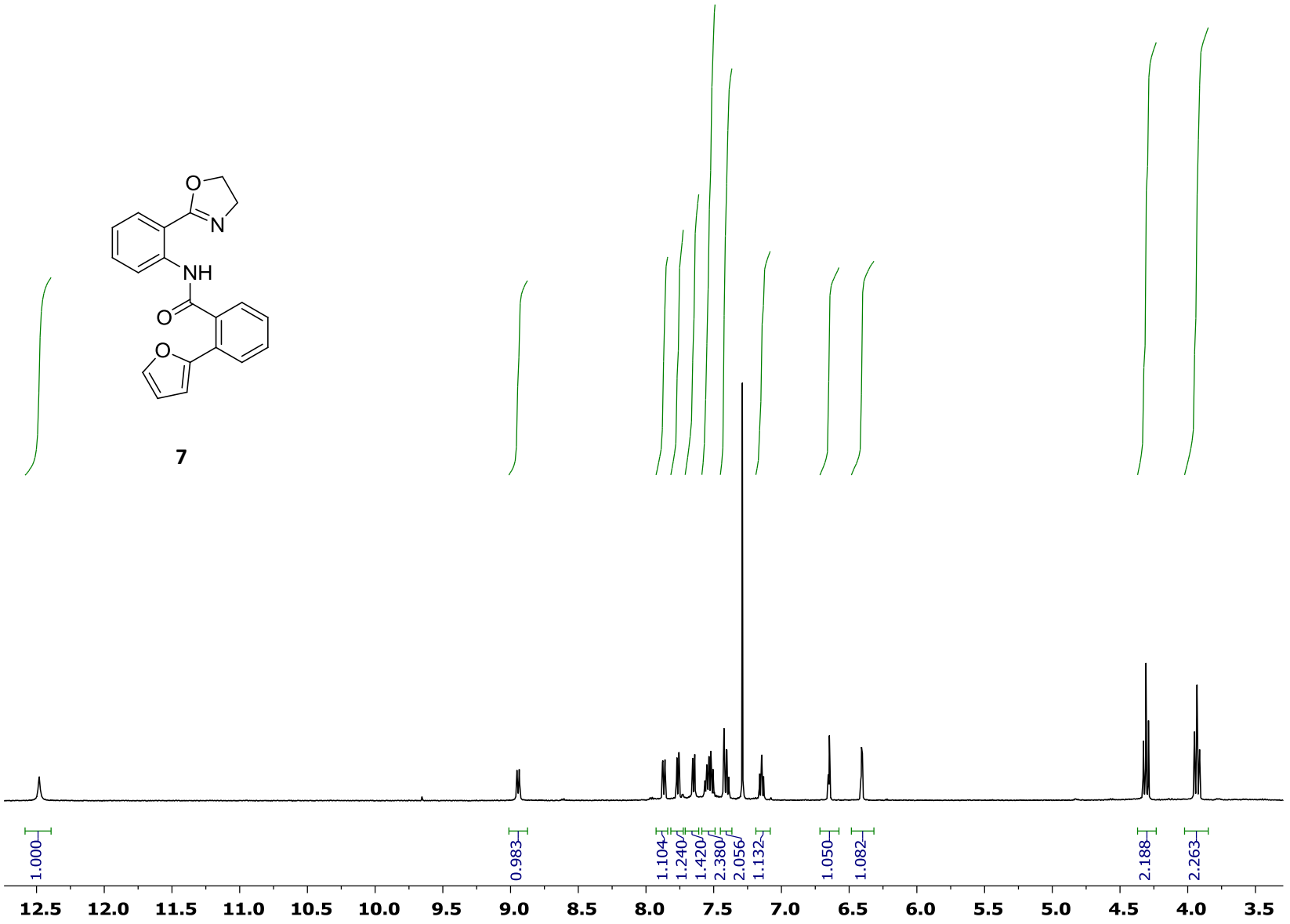
6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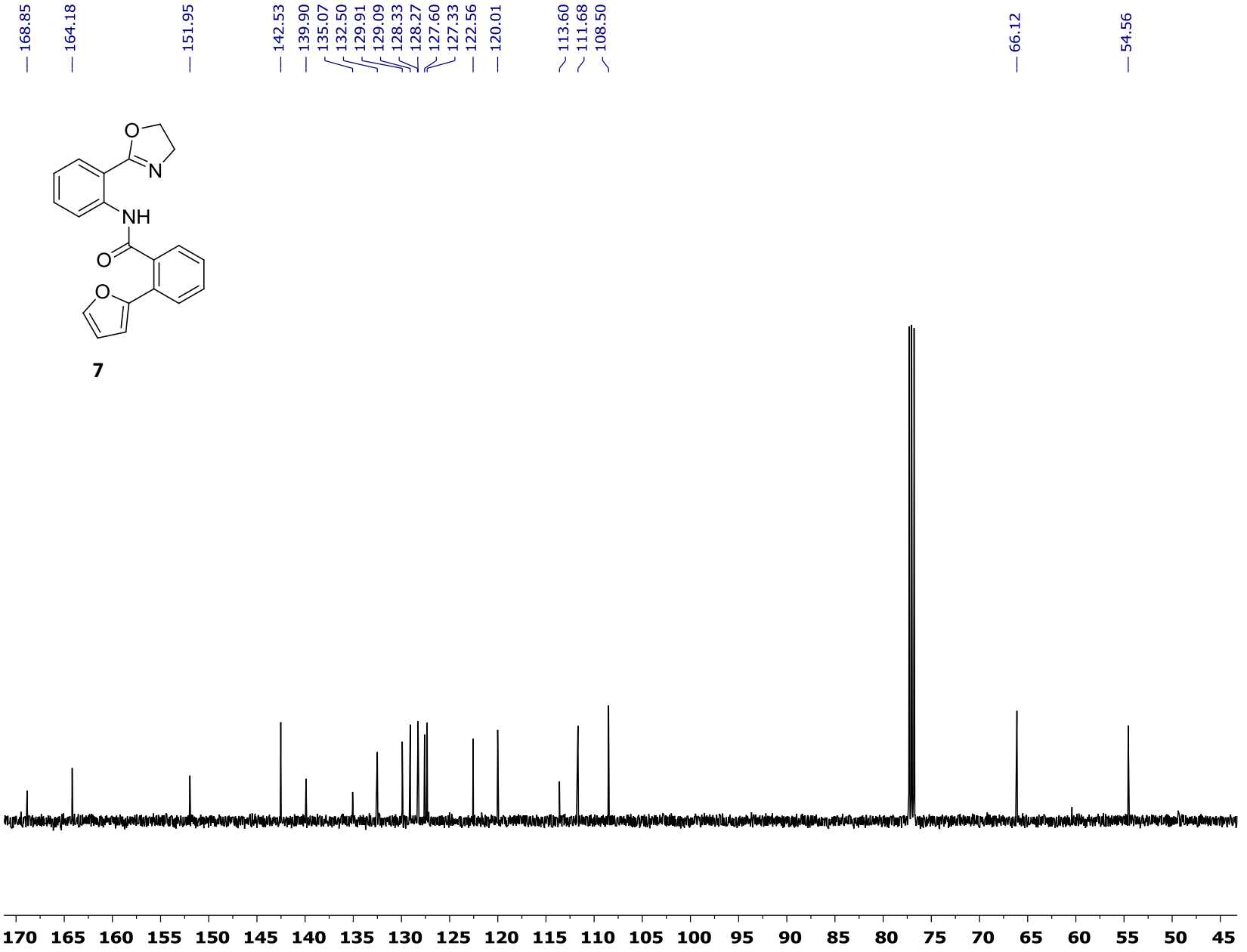
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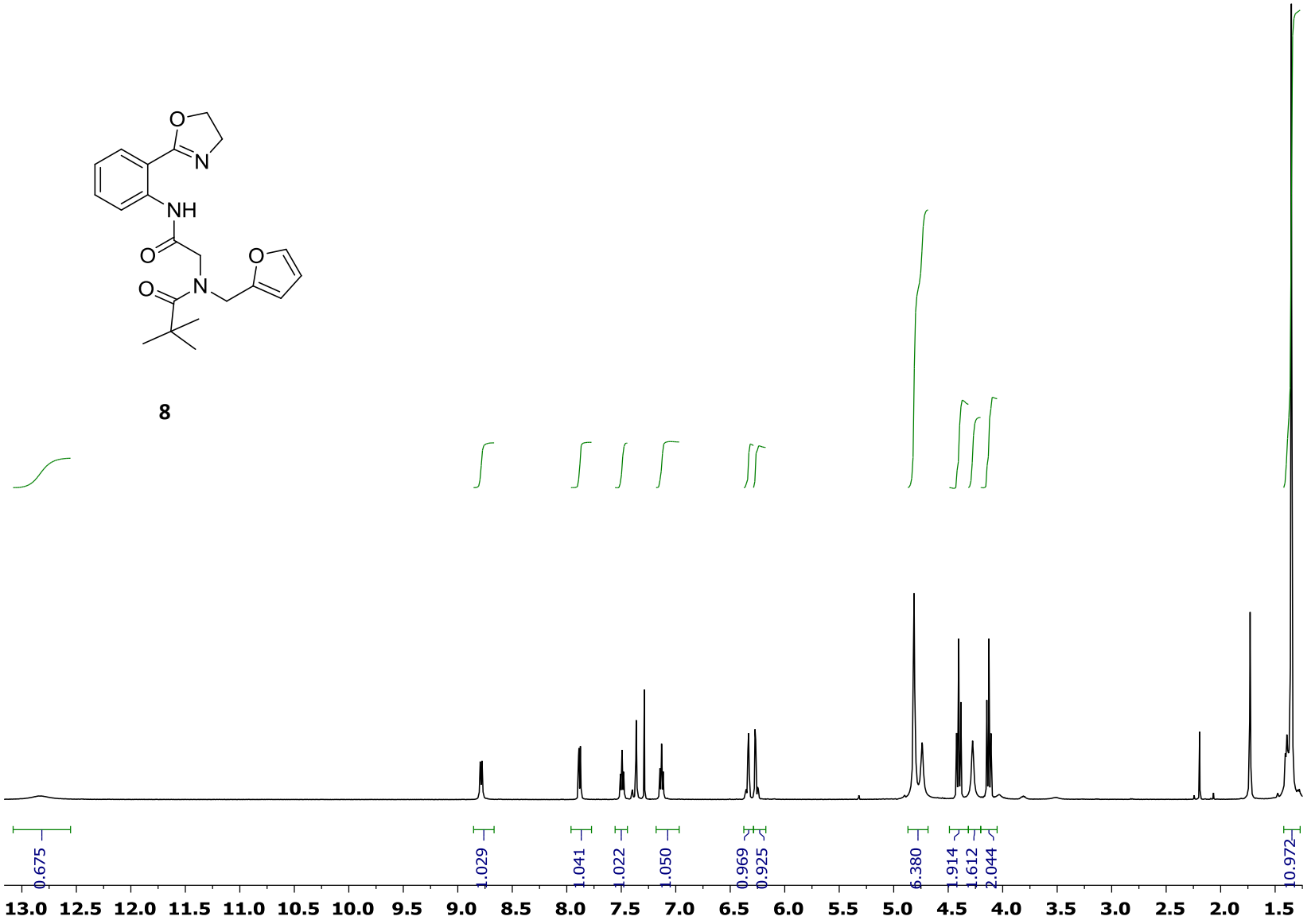
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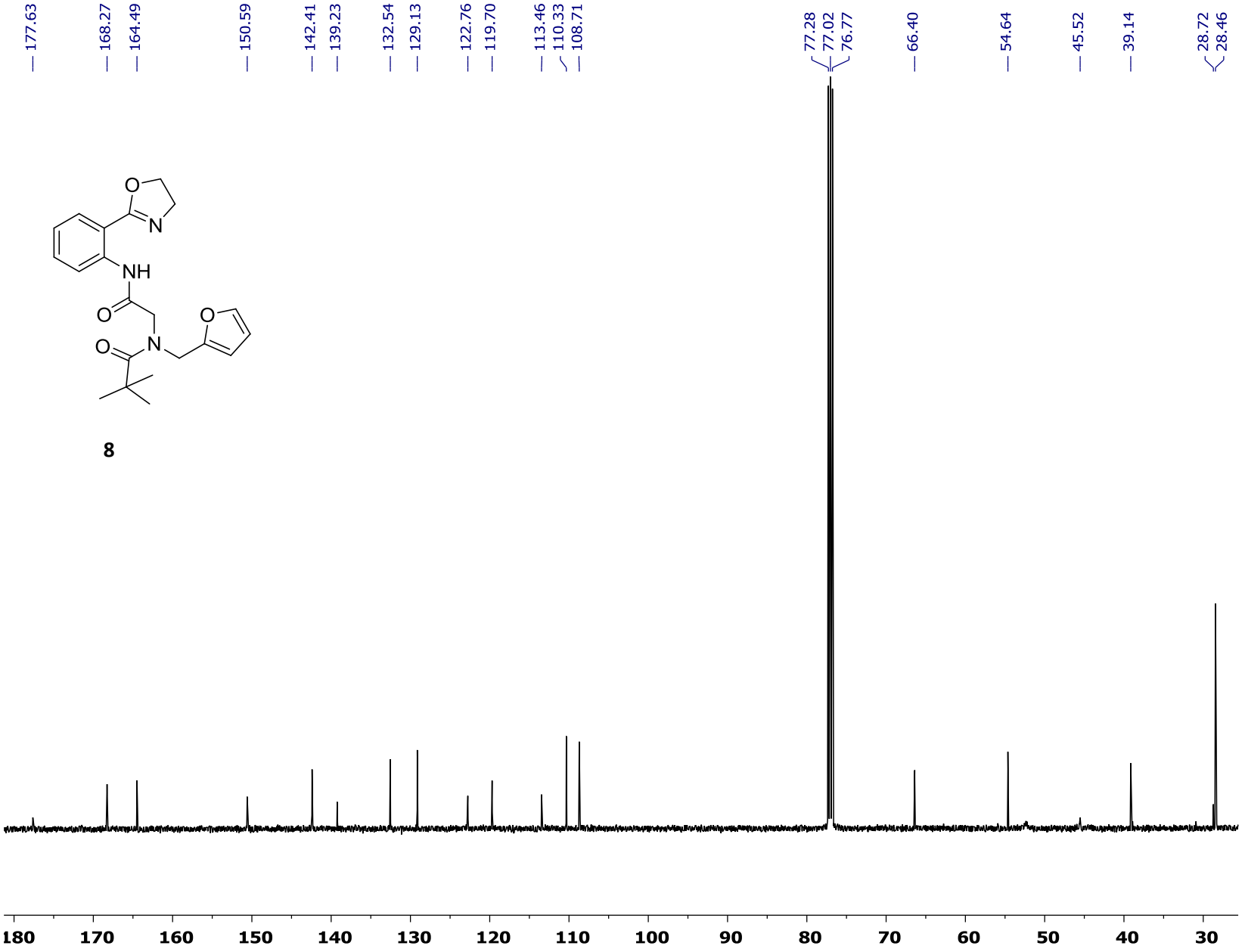
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28.72
28.46
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NH
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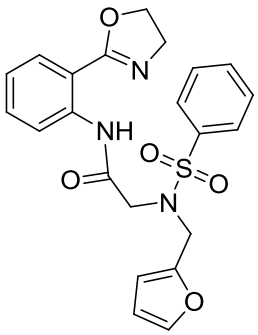

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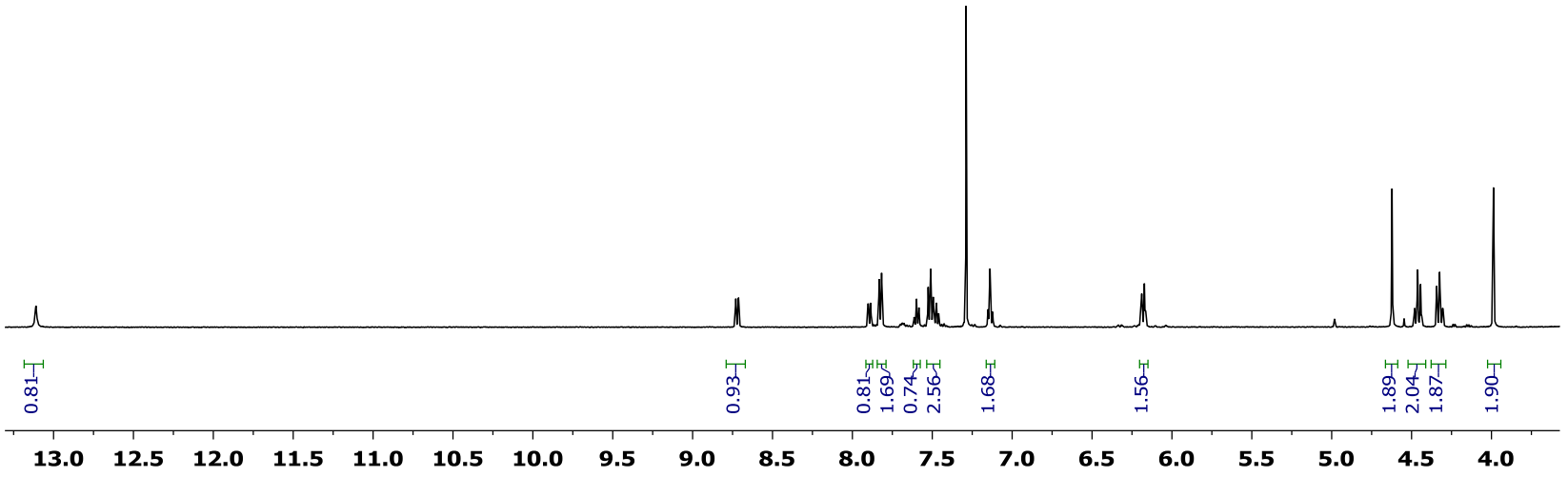
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11.0
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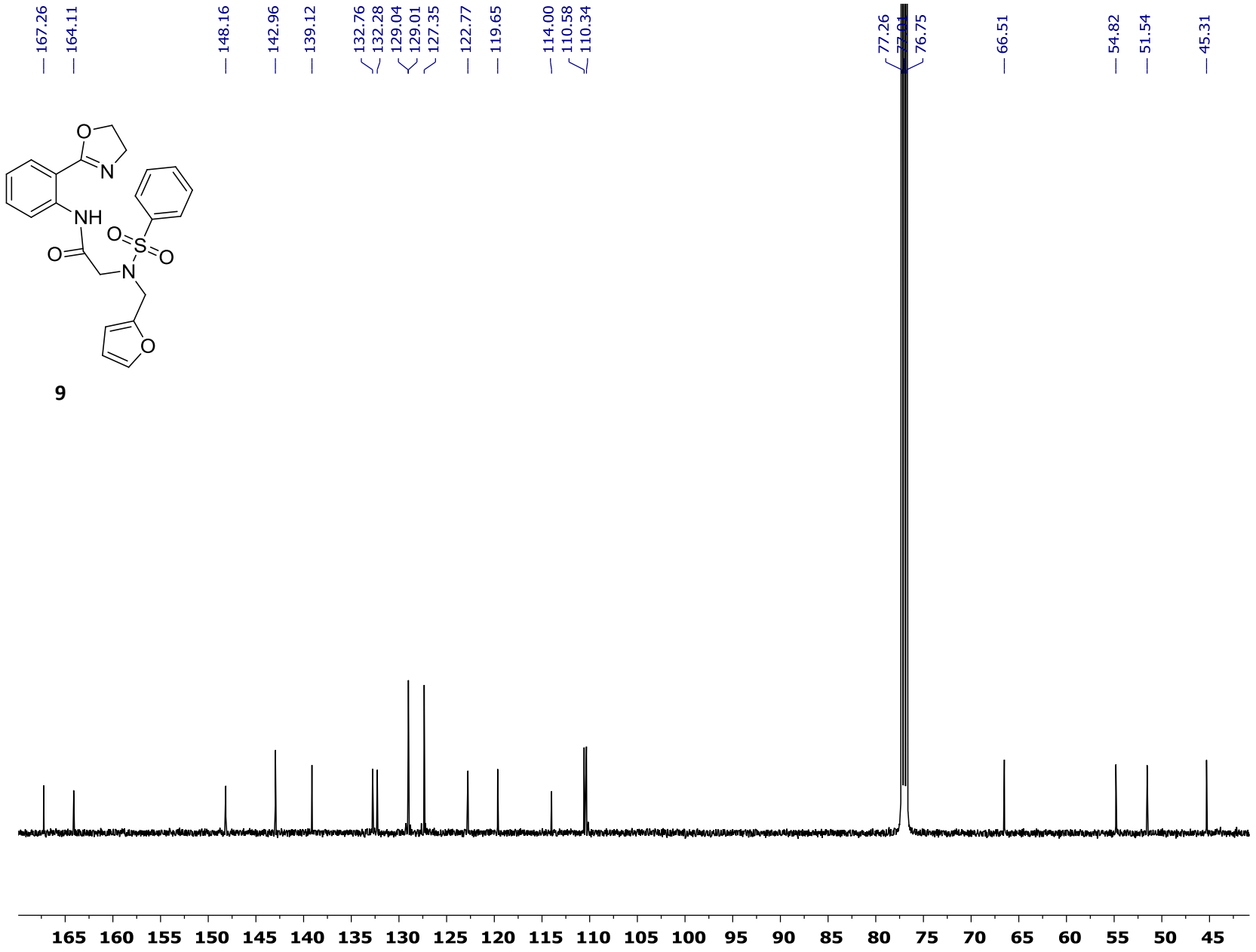
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76.75
66.51
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51.54
45.31
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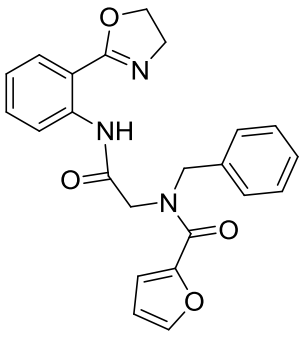
9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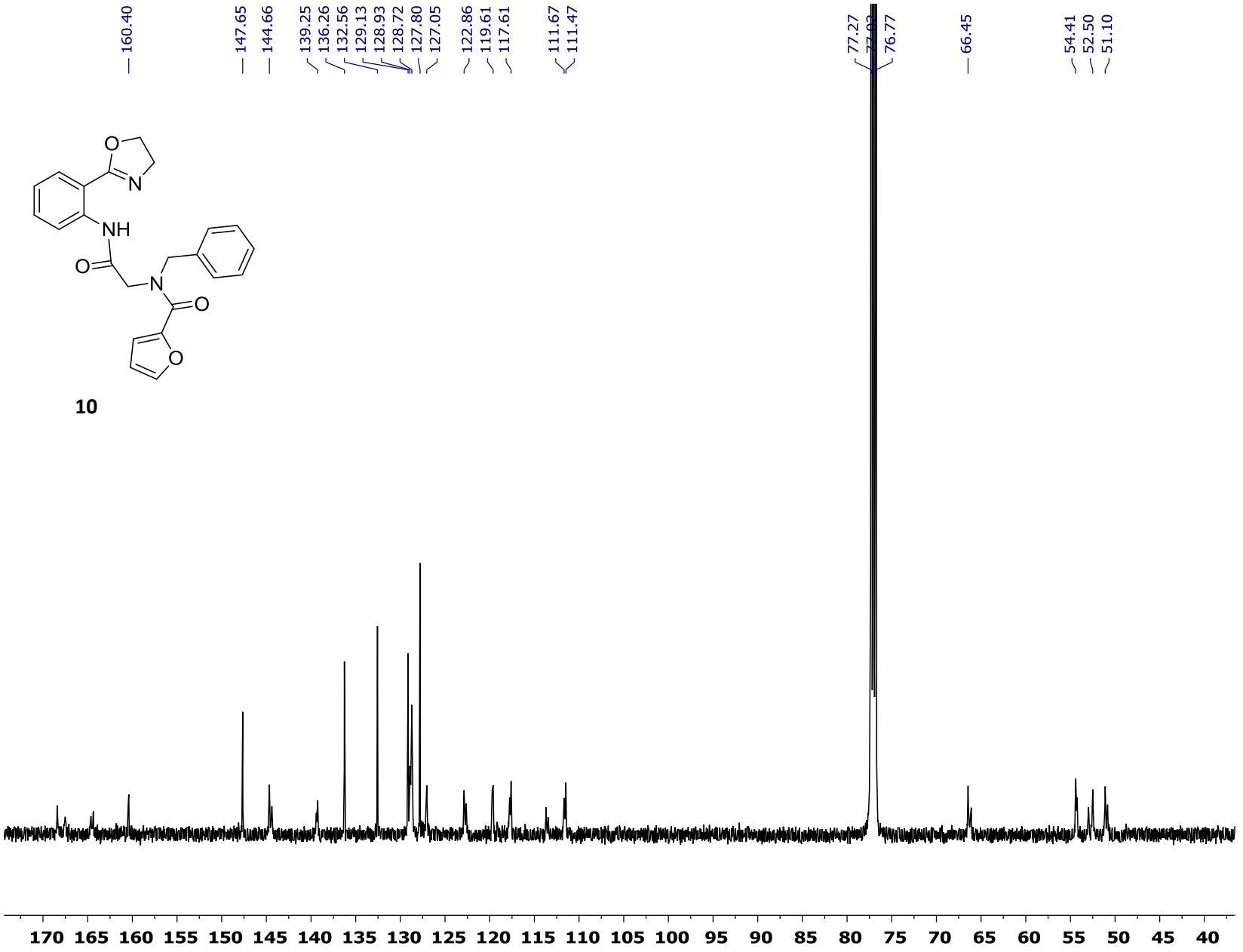
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77.27
77.02
76.77
66.45
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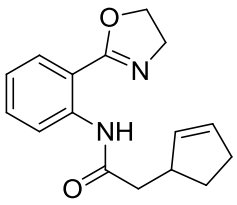
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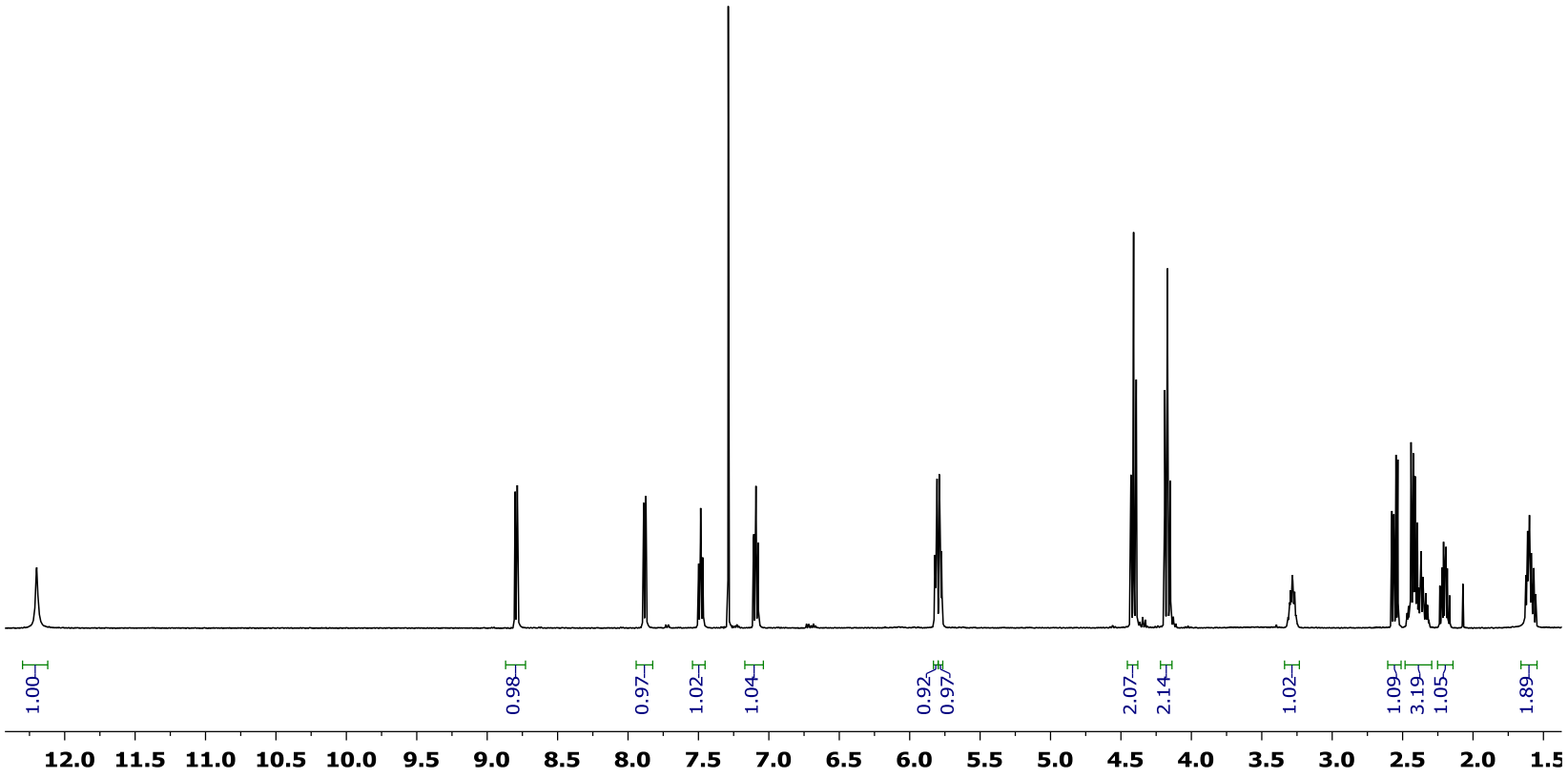
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3.19
1.05
1.89
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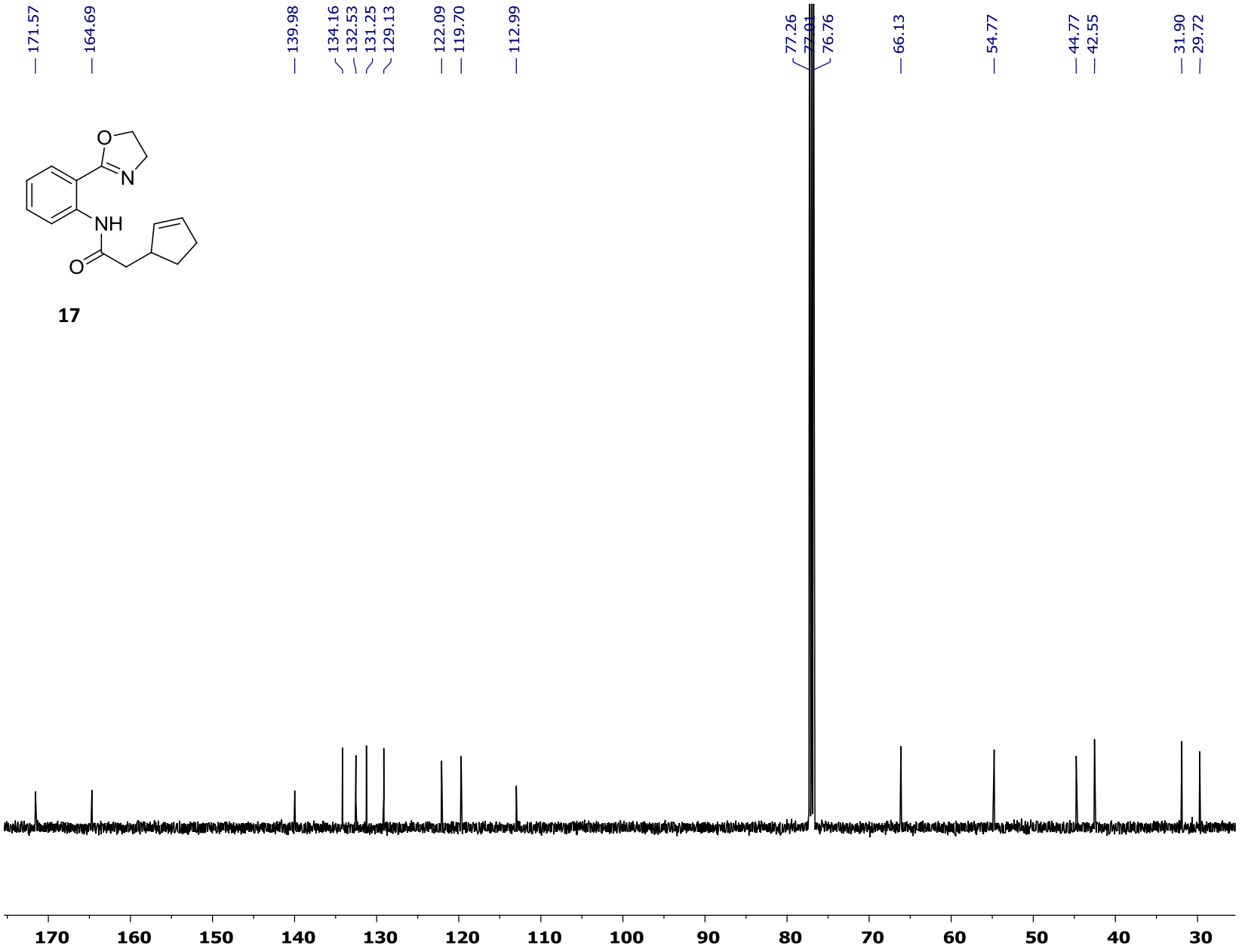
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77.01
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44.77
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29.72
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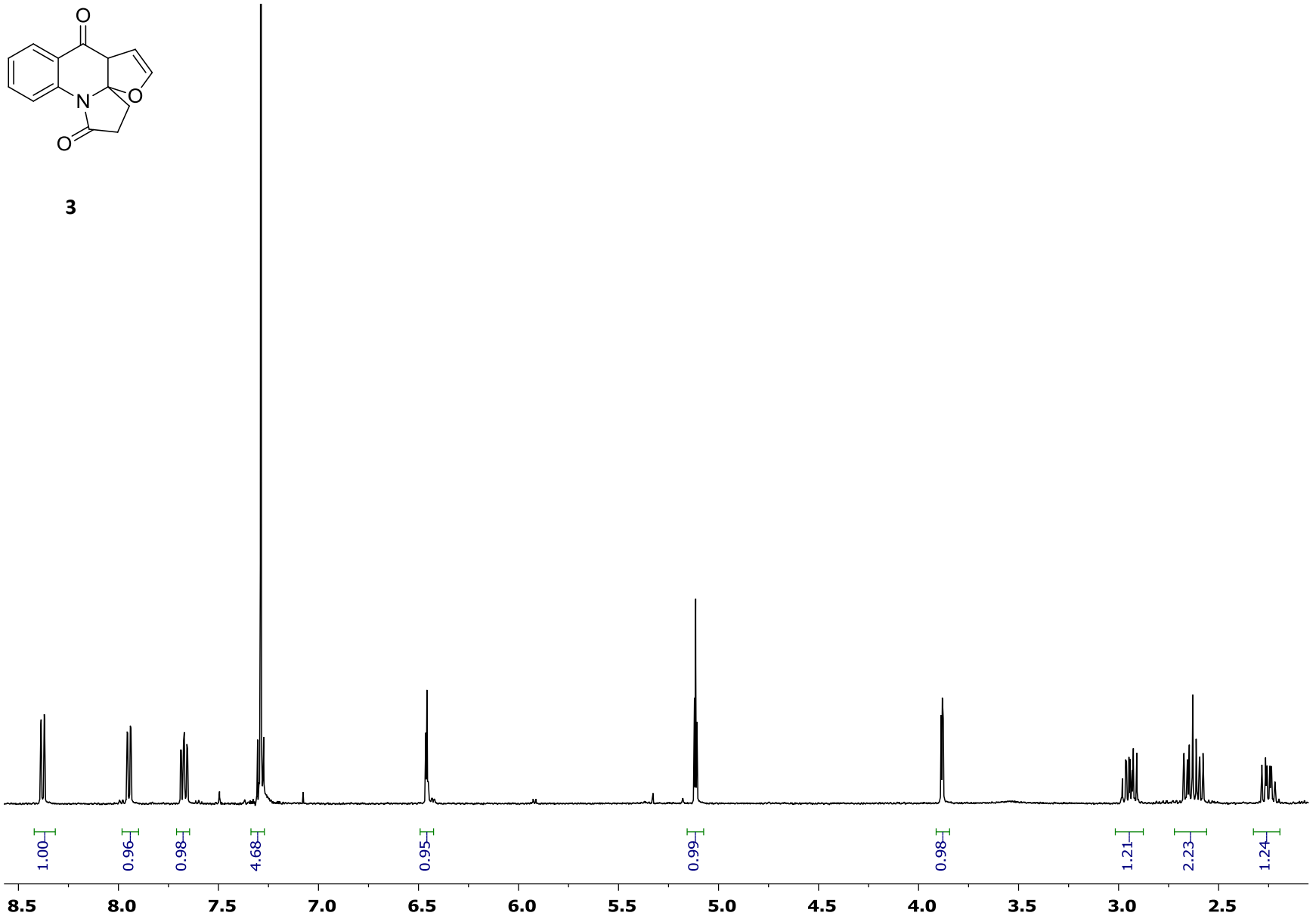
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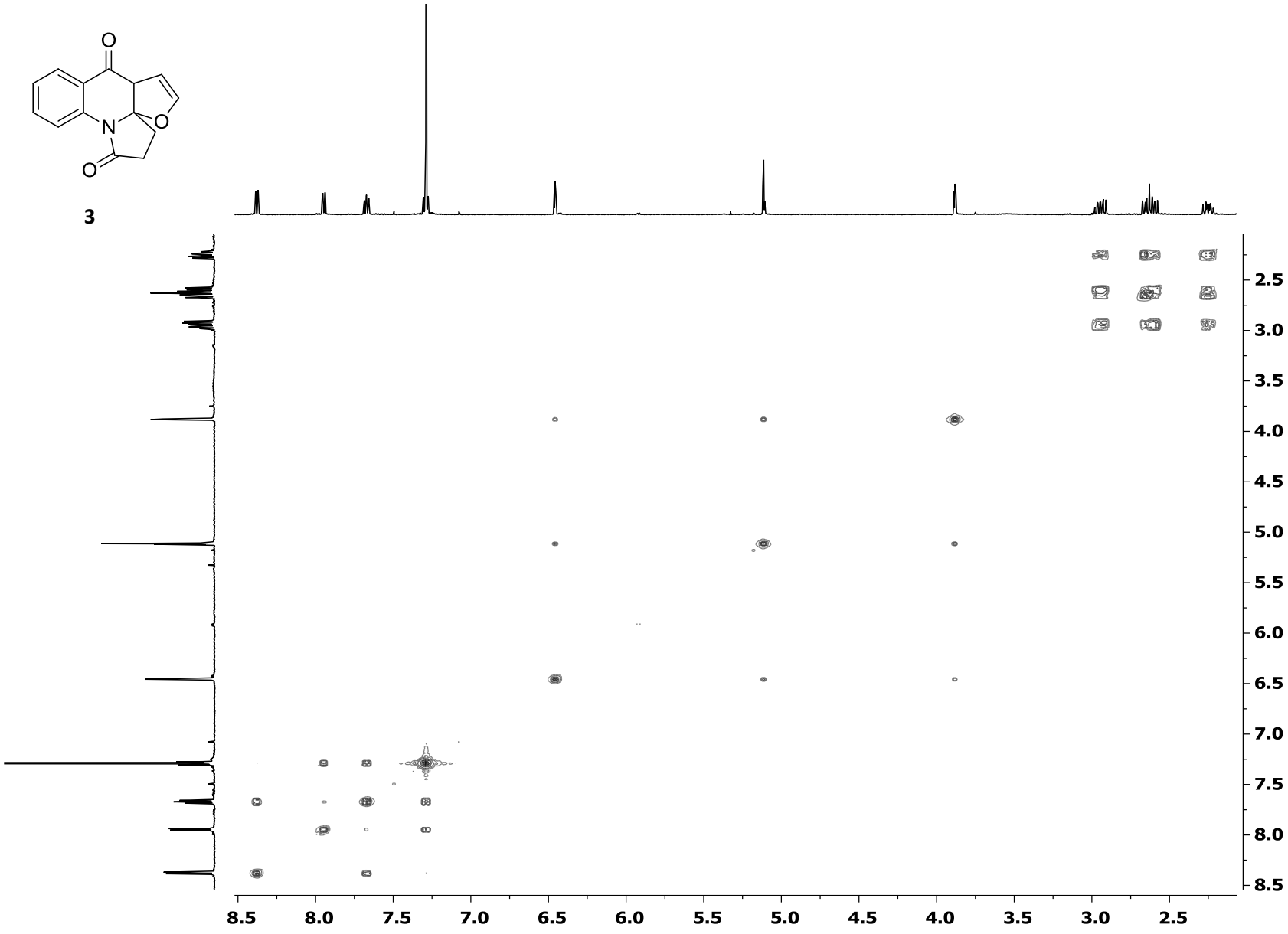
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8.5
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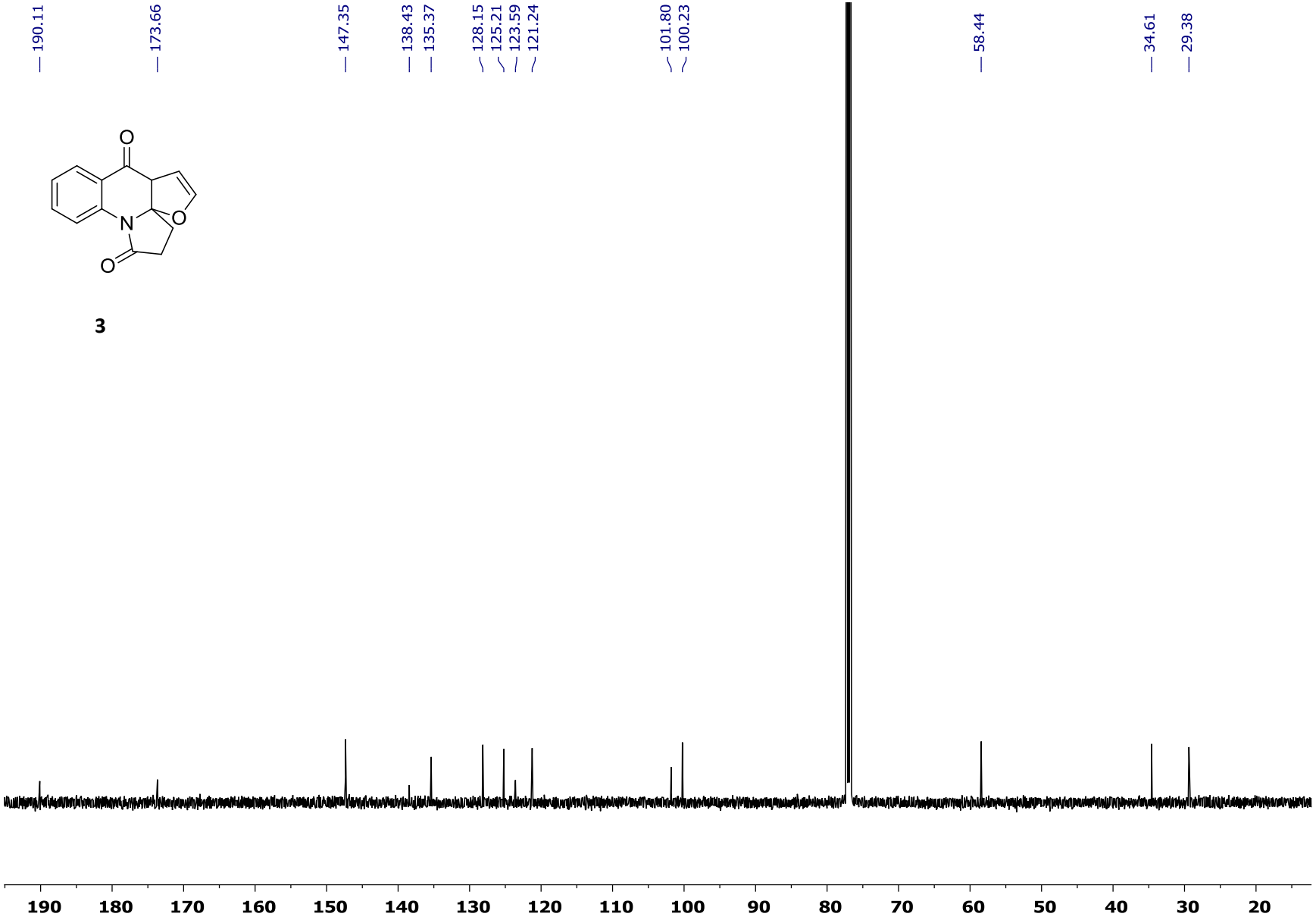
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N
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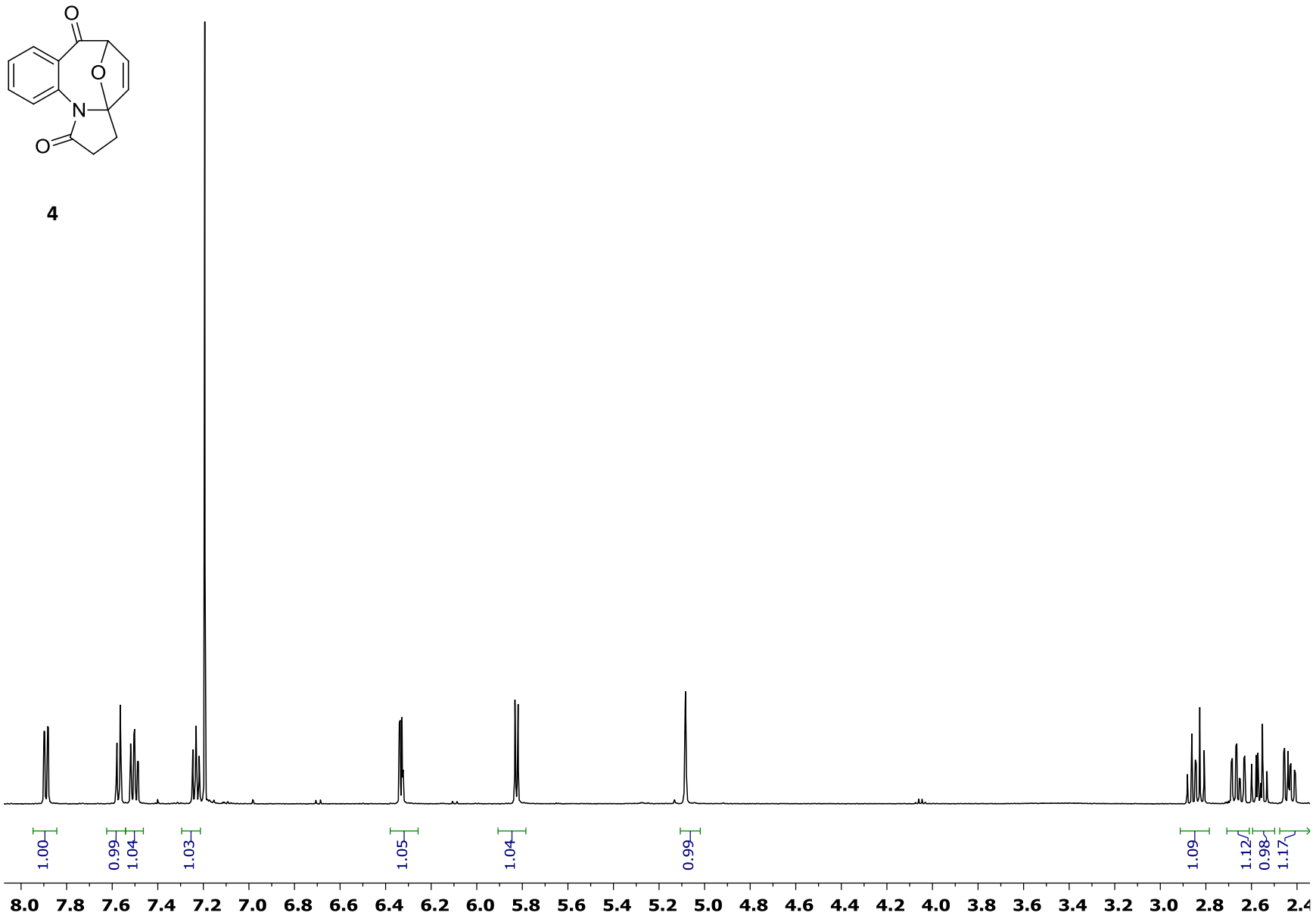
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0.99
1.09
1.12
0.98
1.17
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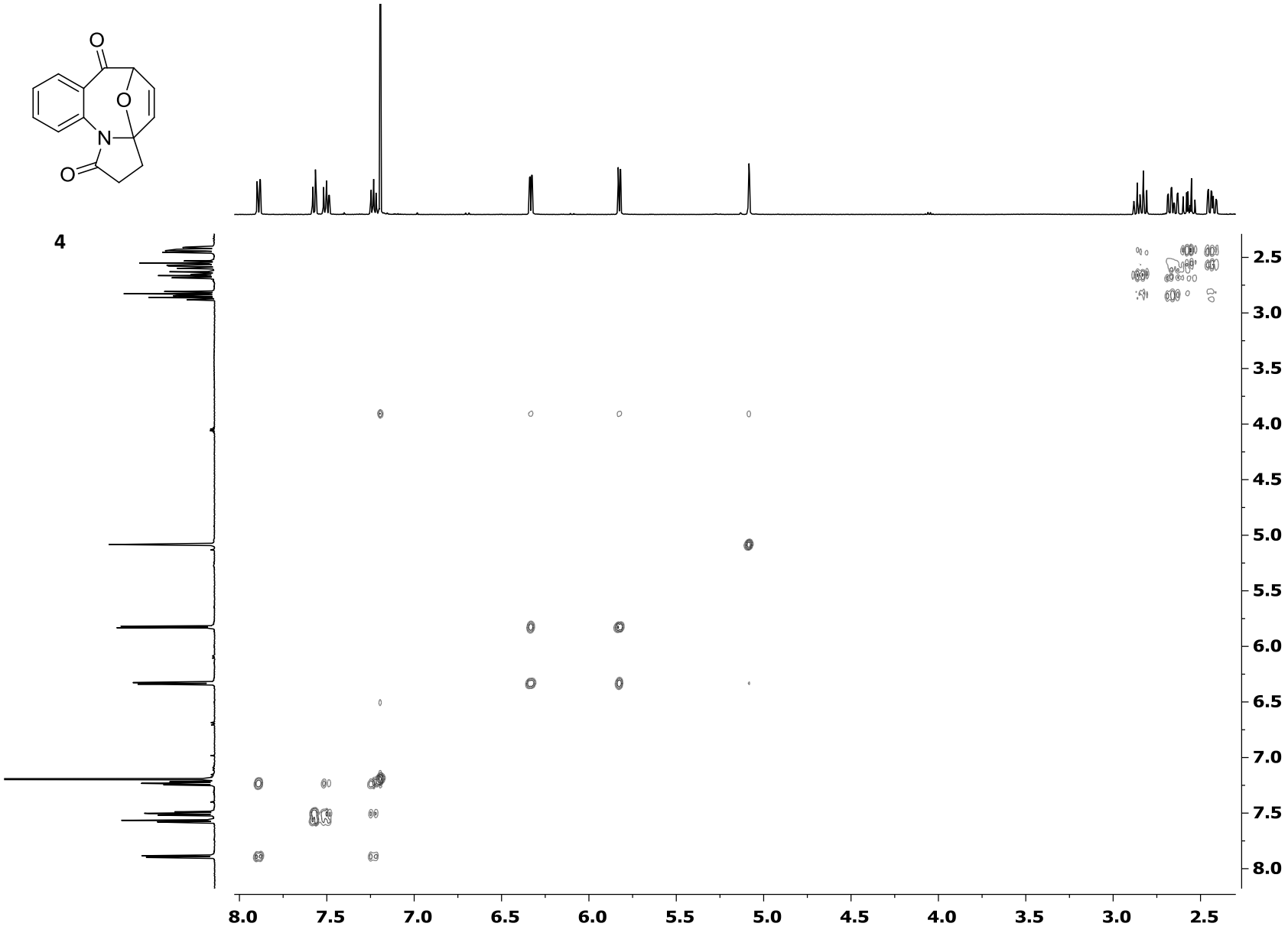
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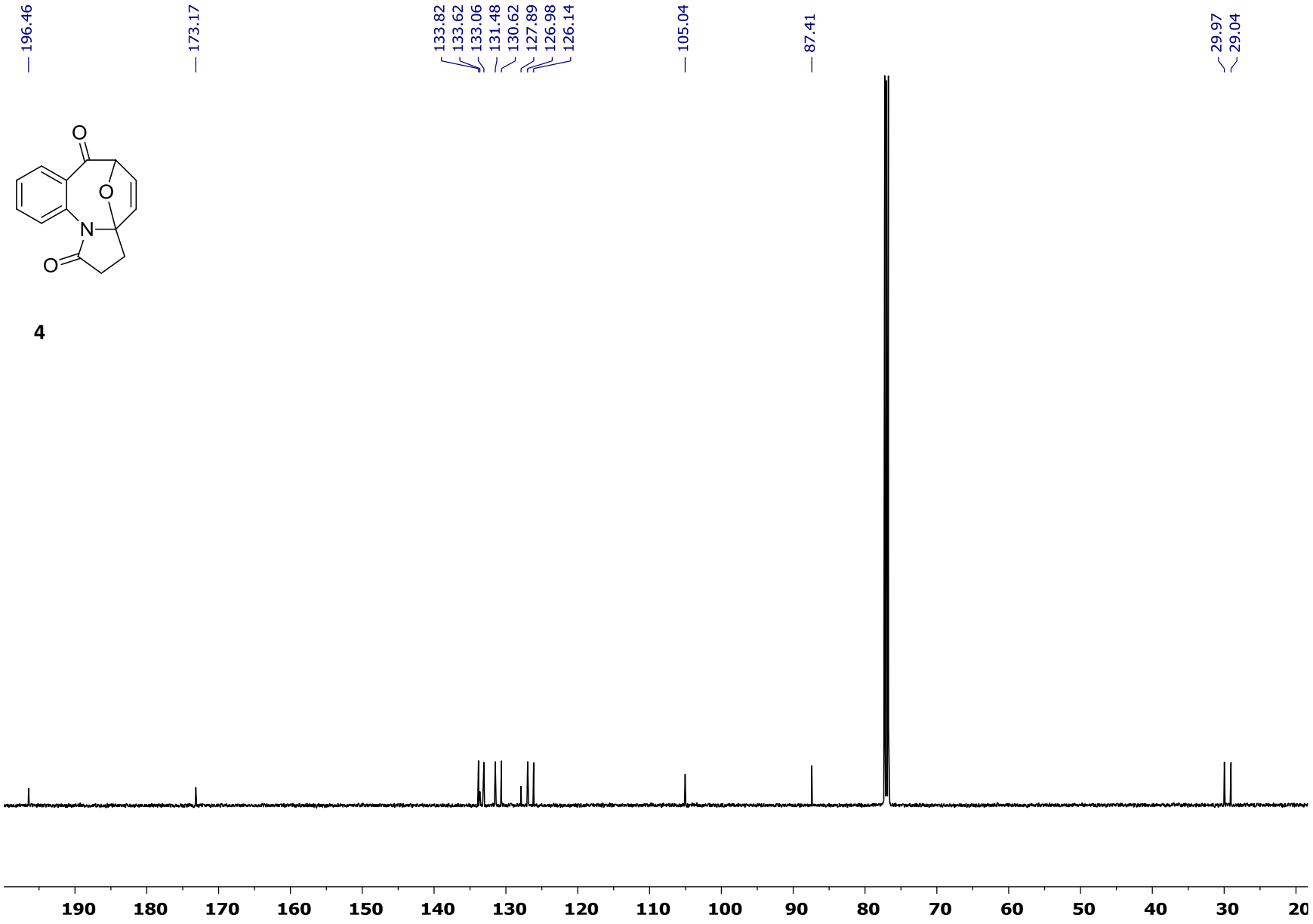
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O
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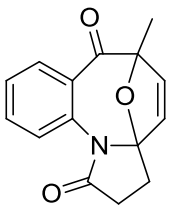
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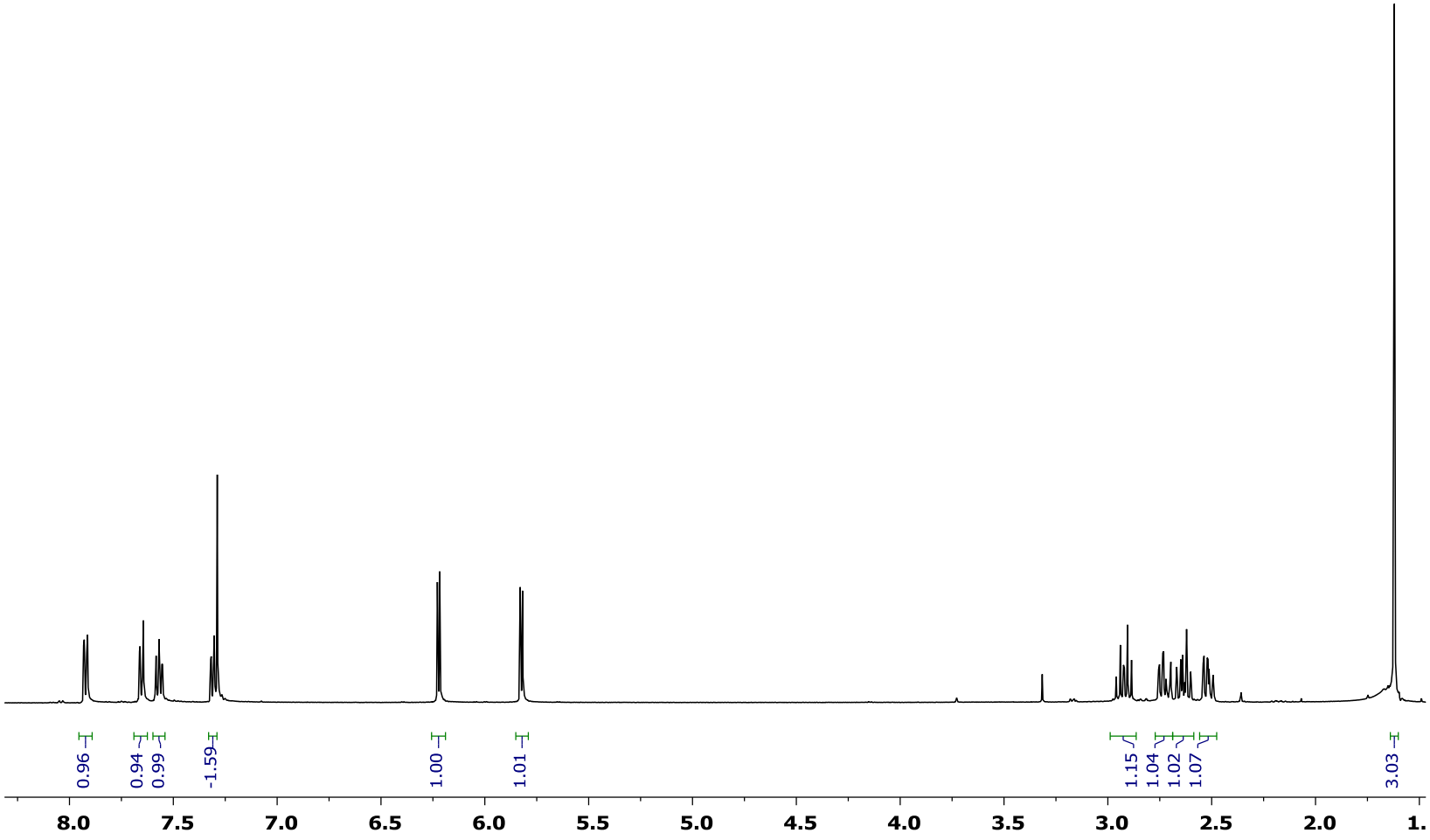
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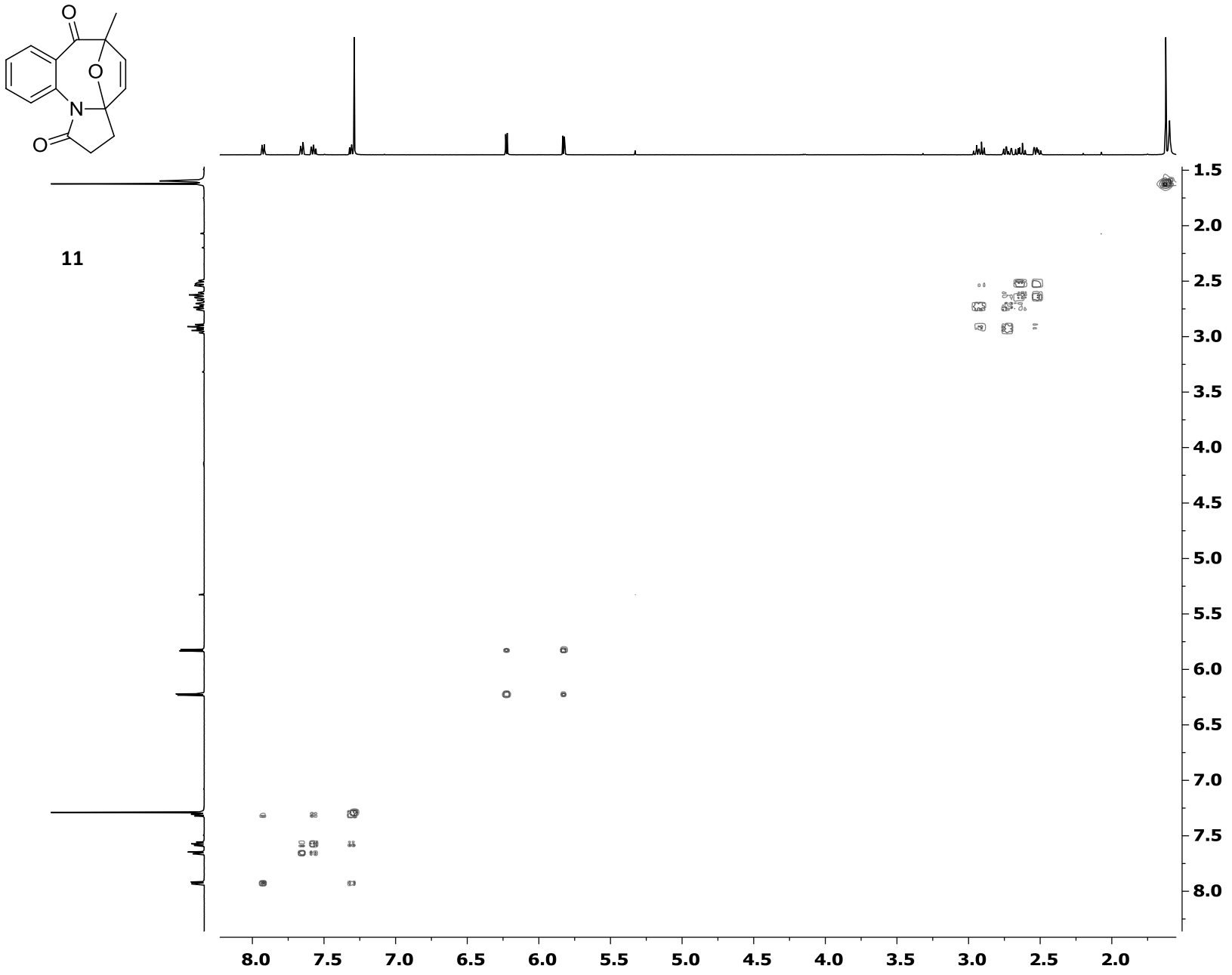
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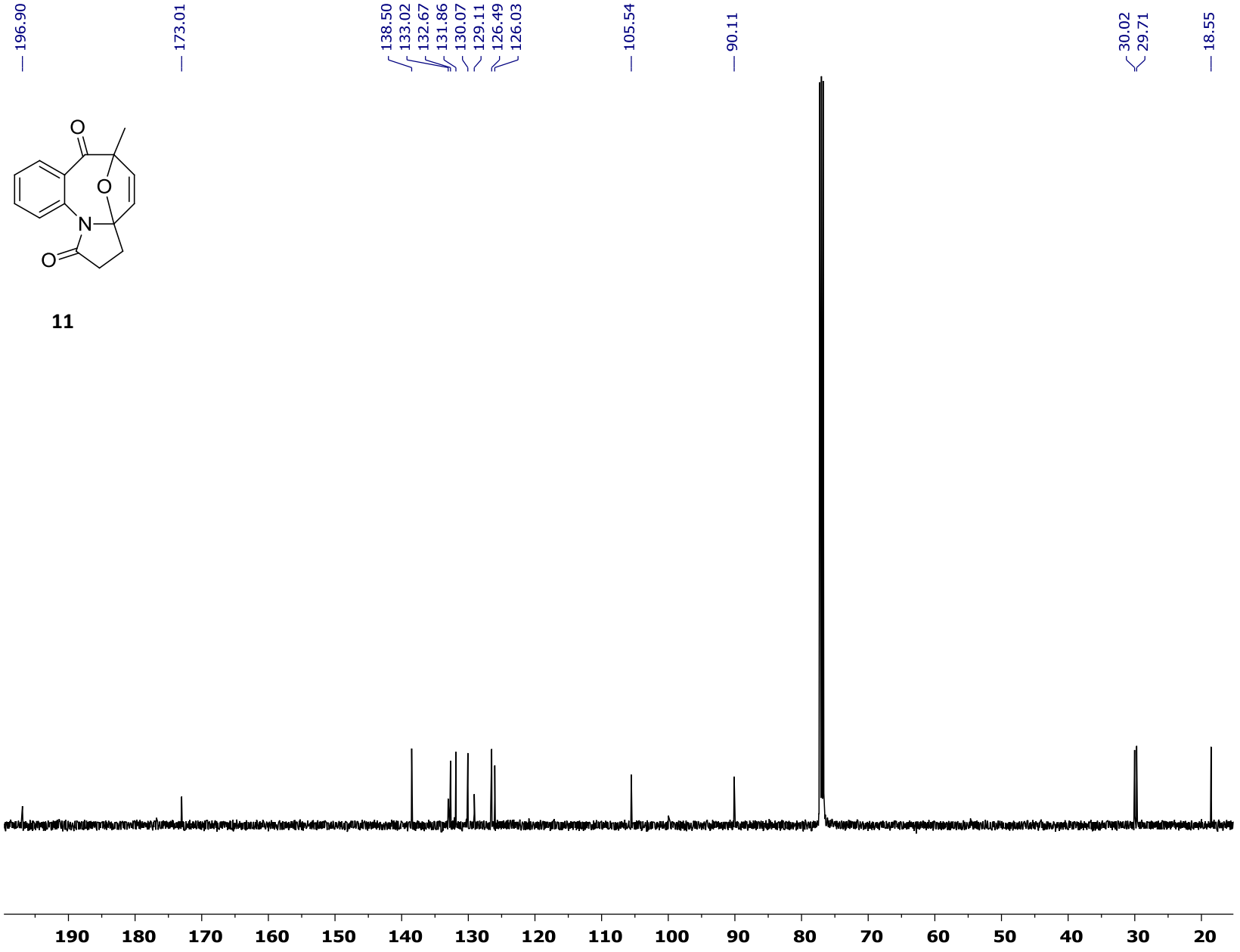
2.0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90.11
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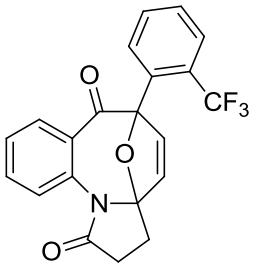
20

11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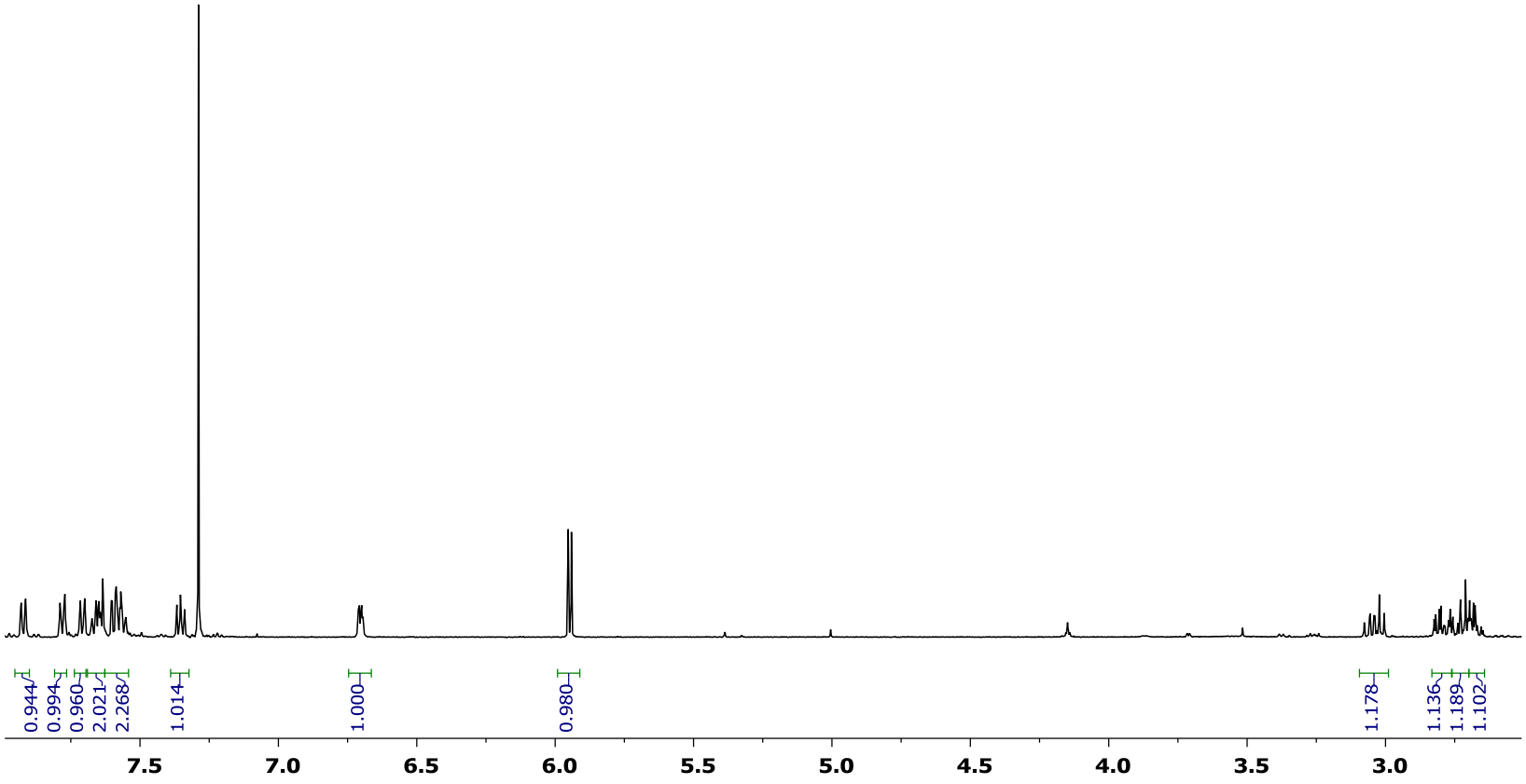
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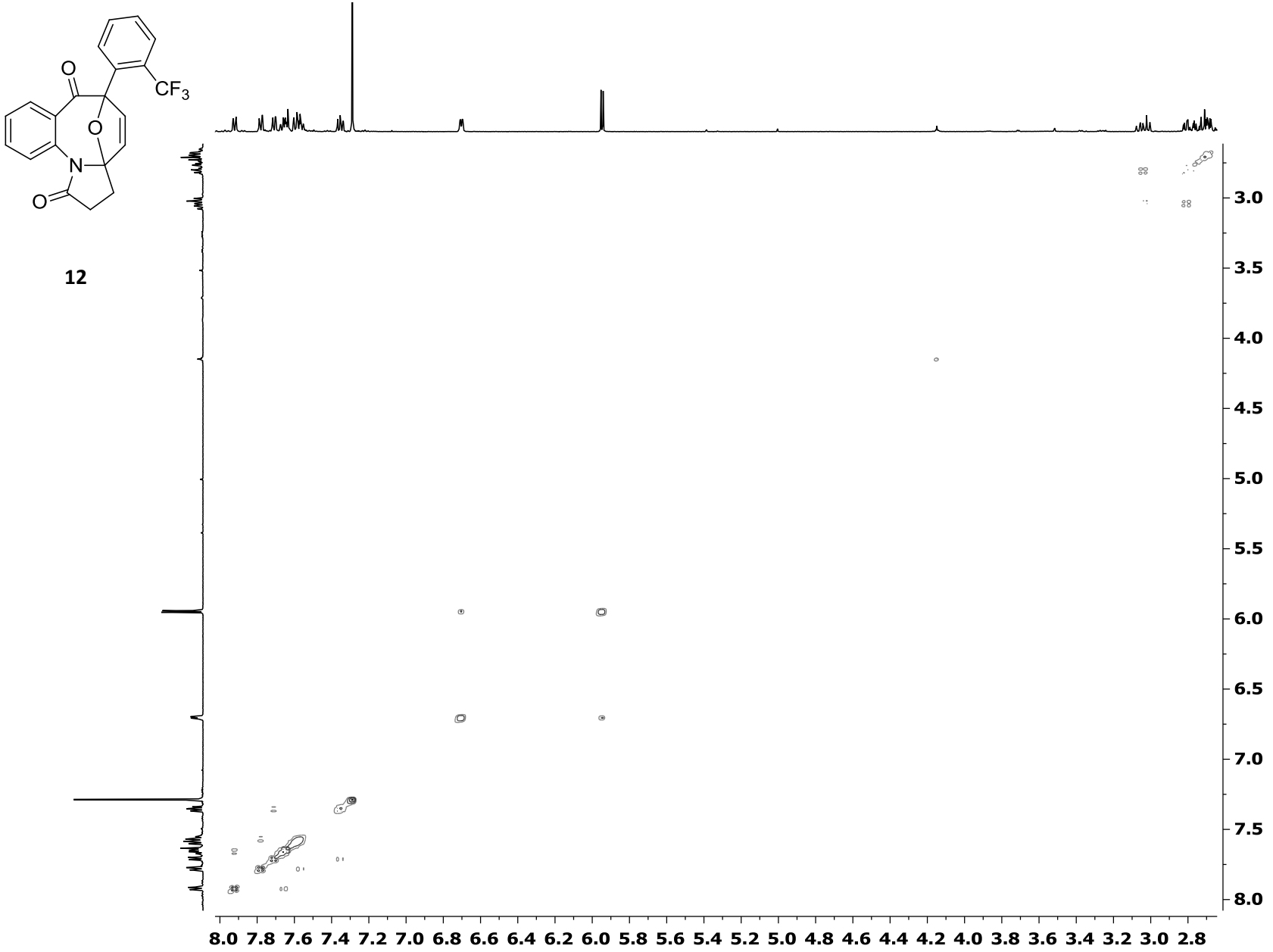
3.0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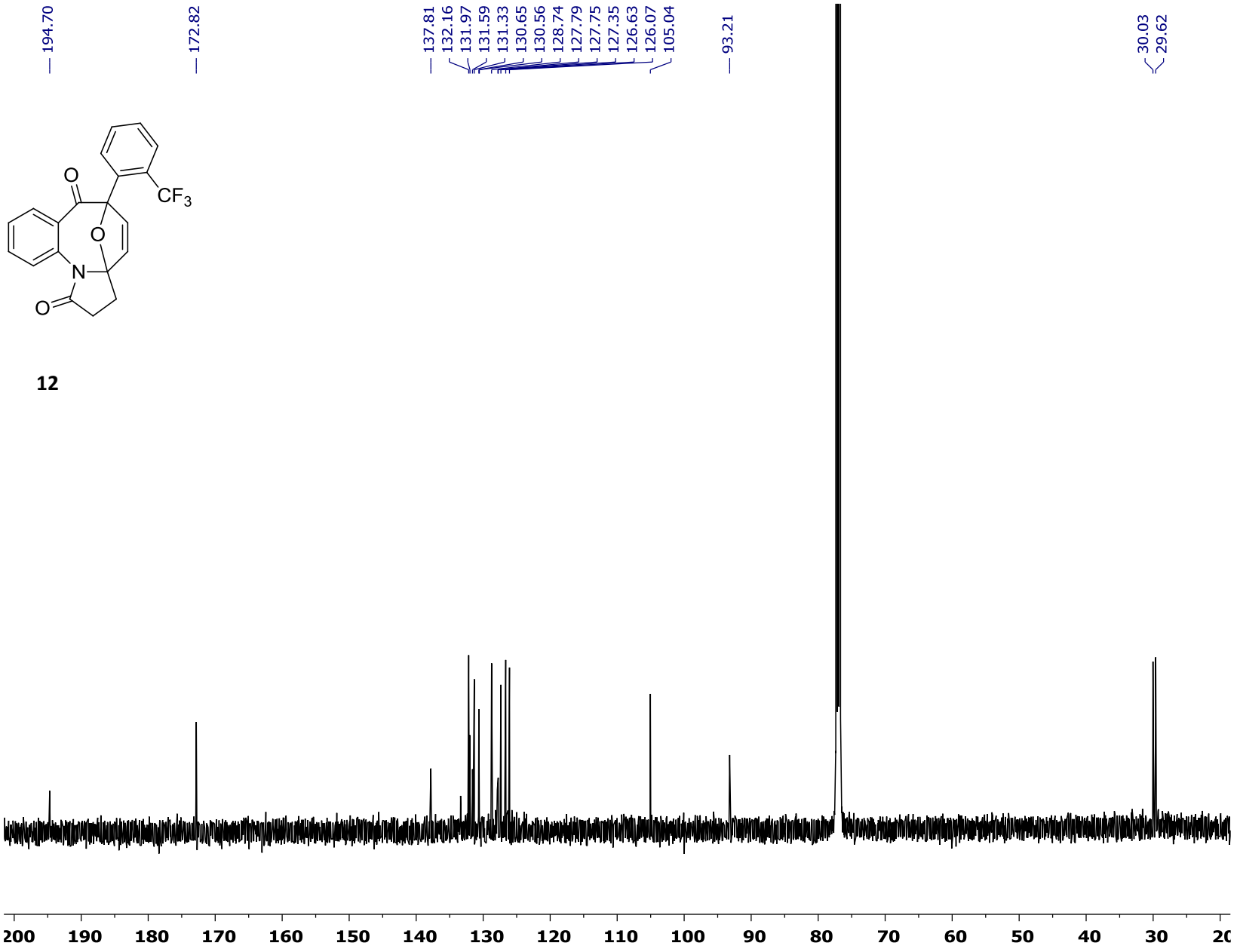
6.0
6.5
7.0
7.5
8.0
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8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127.35
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30.03
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CF3
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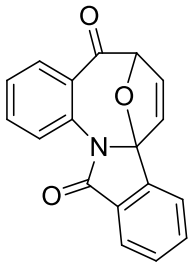
12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13

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1.03
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1.07
1.02
1.00
0.95
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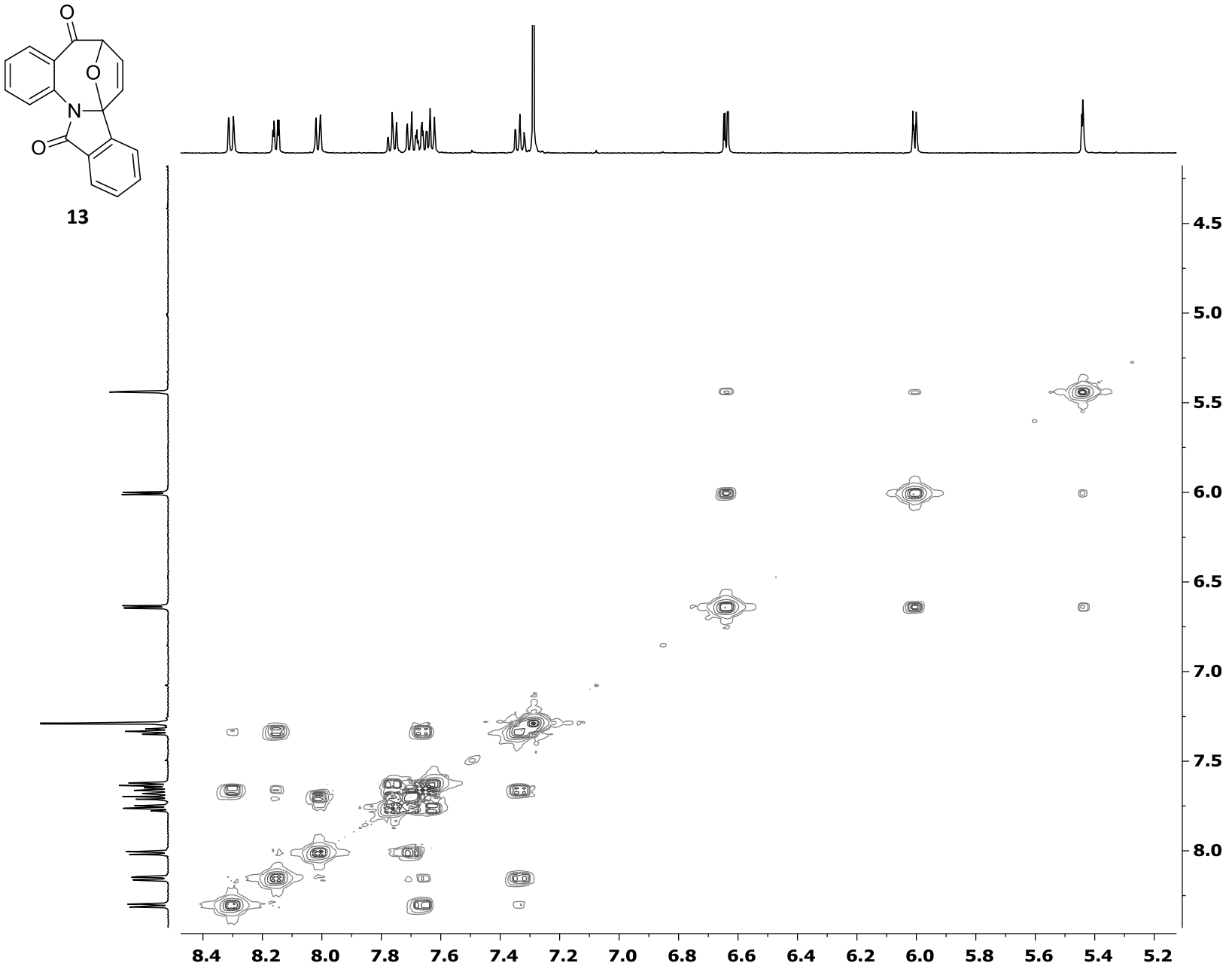
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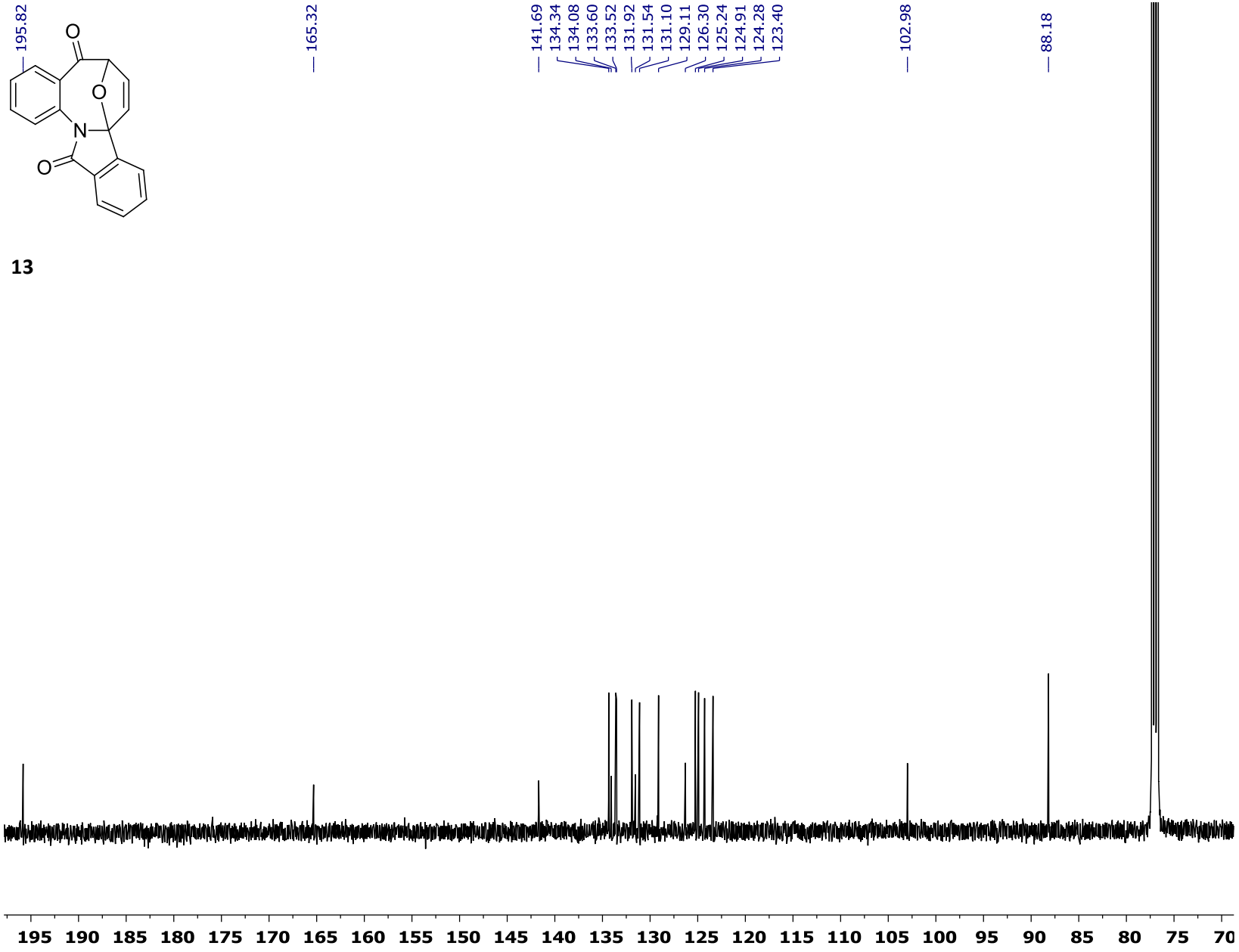
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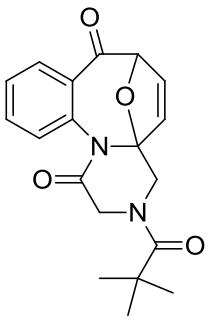
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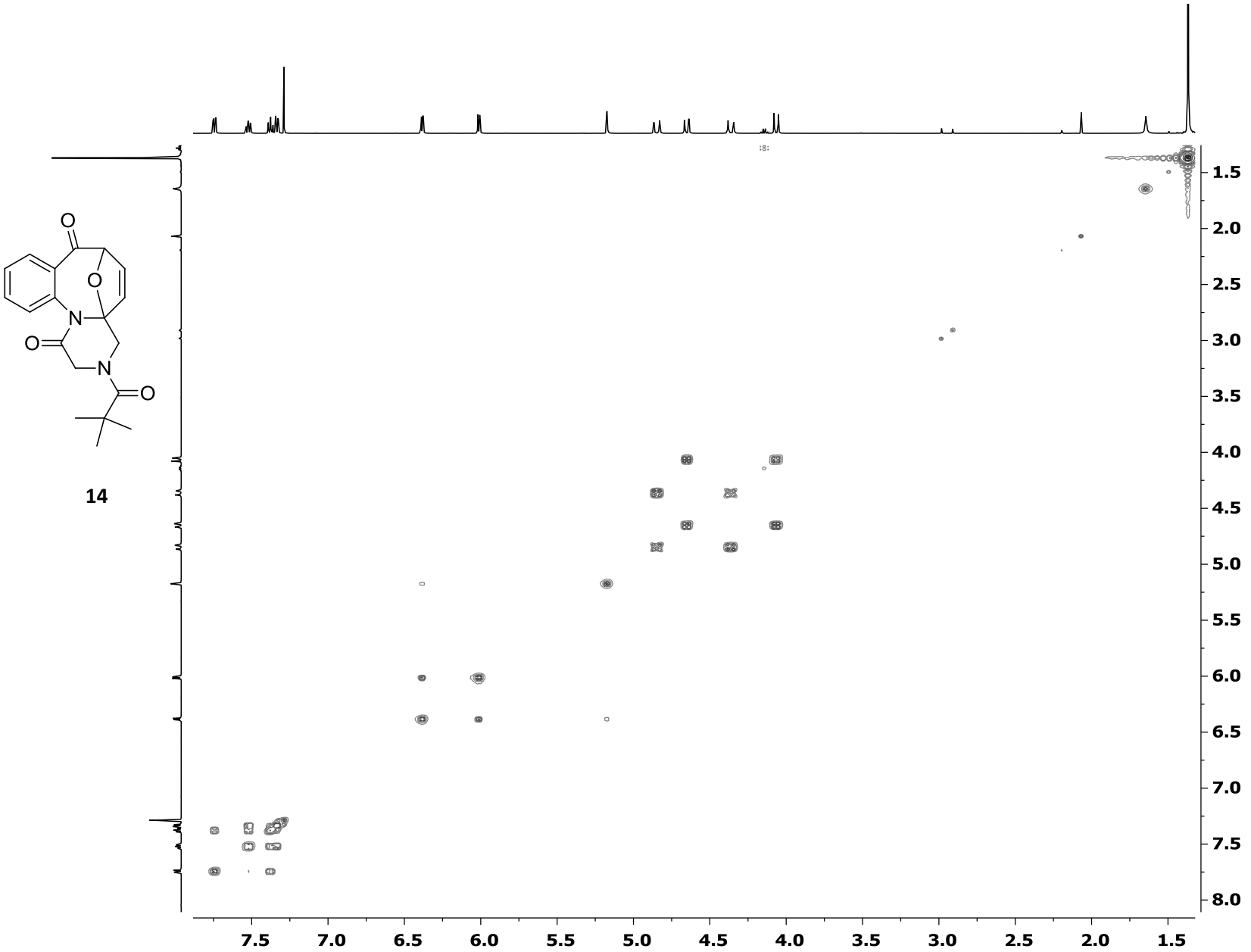
1.07
9.62
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4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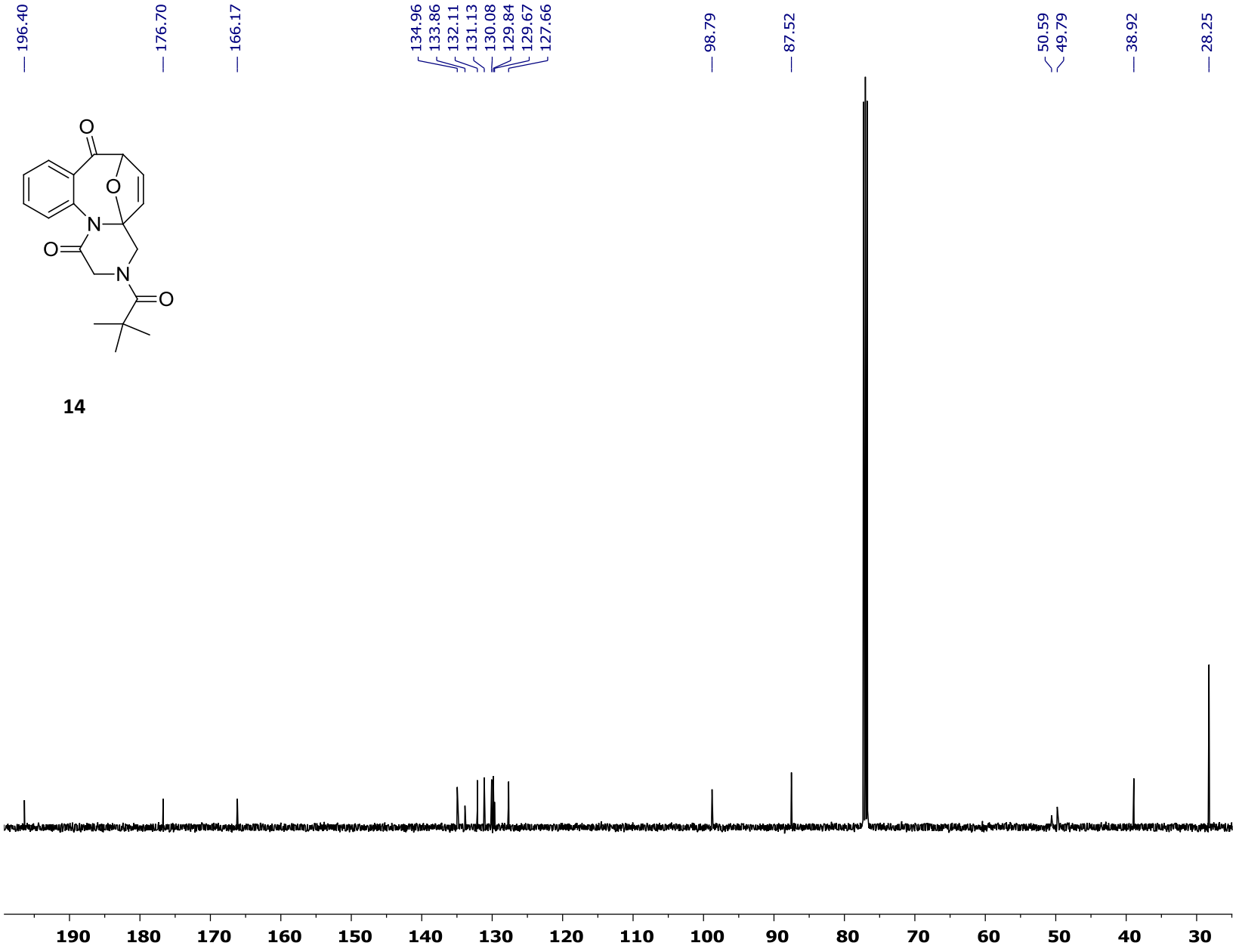
1.5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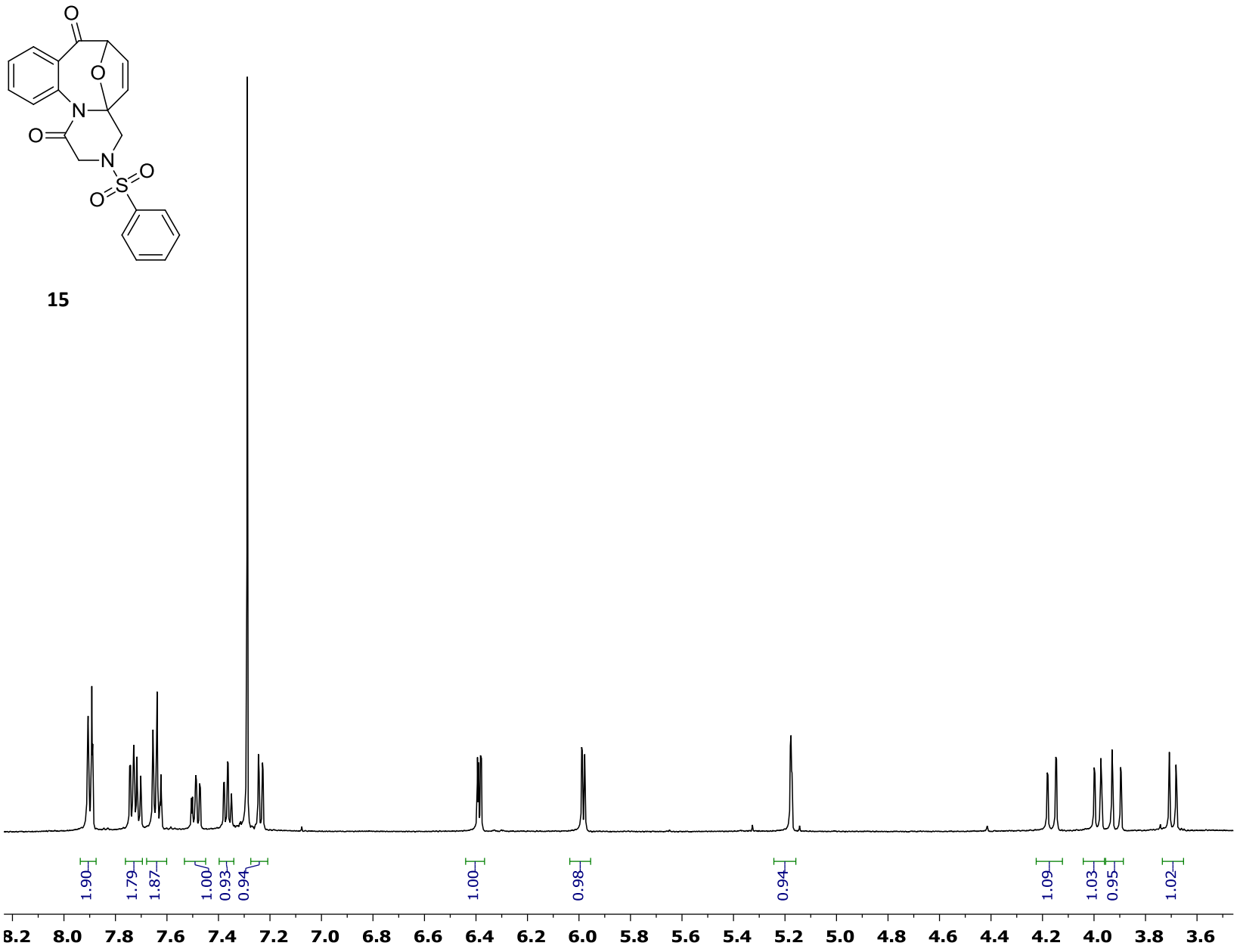
30

14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0.95
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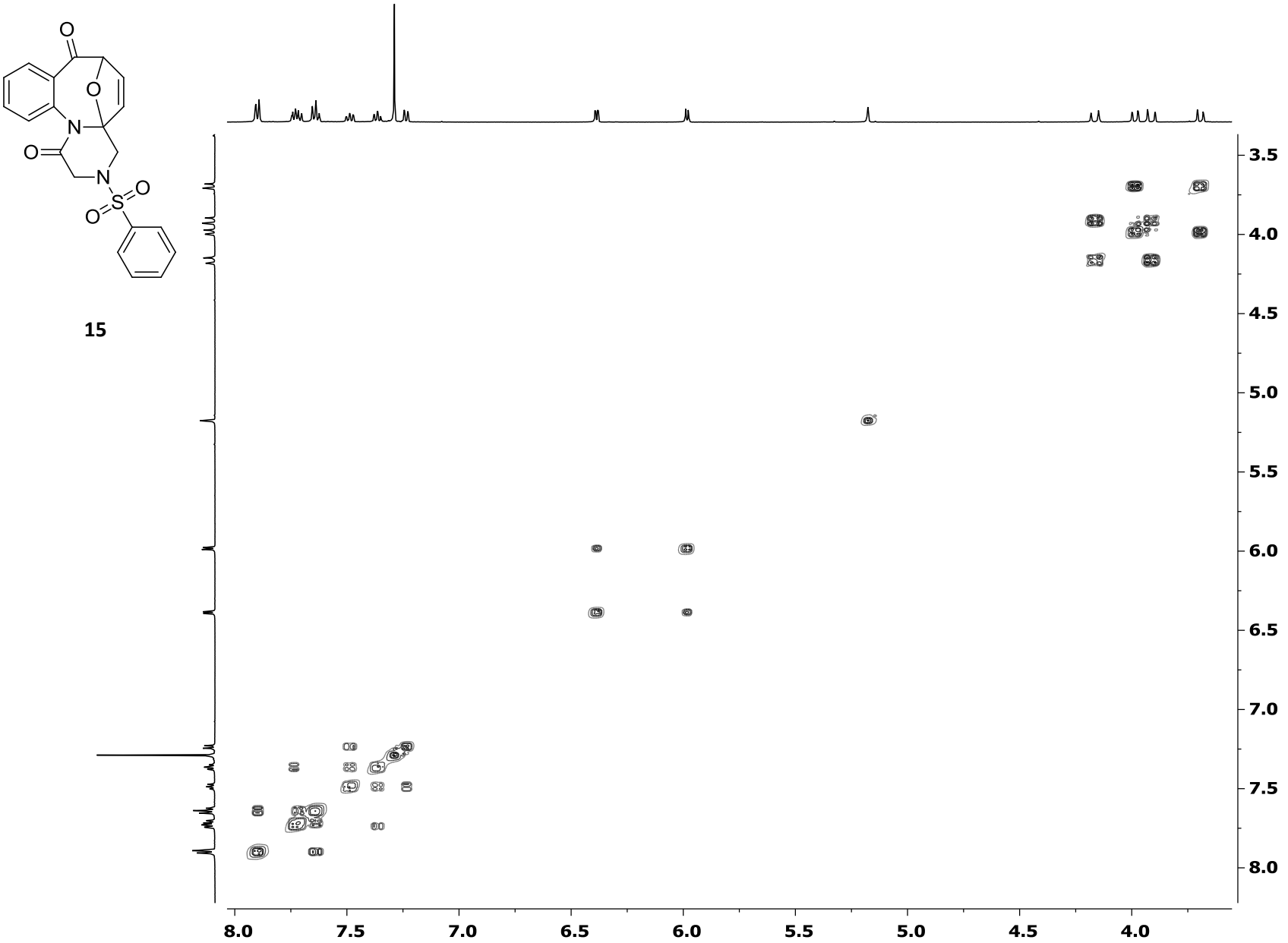
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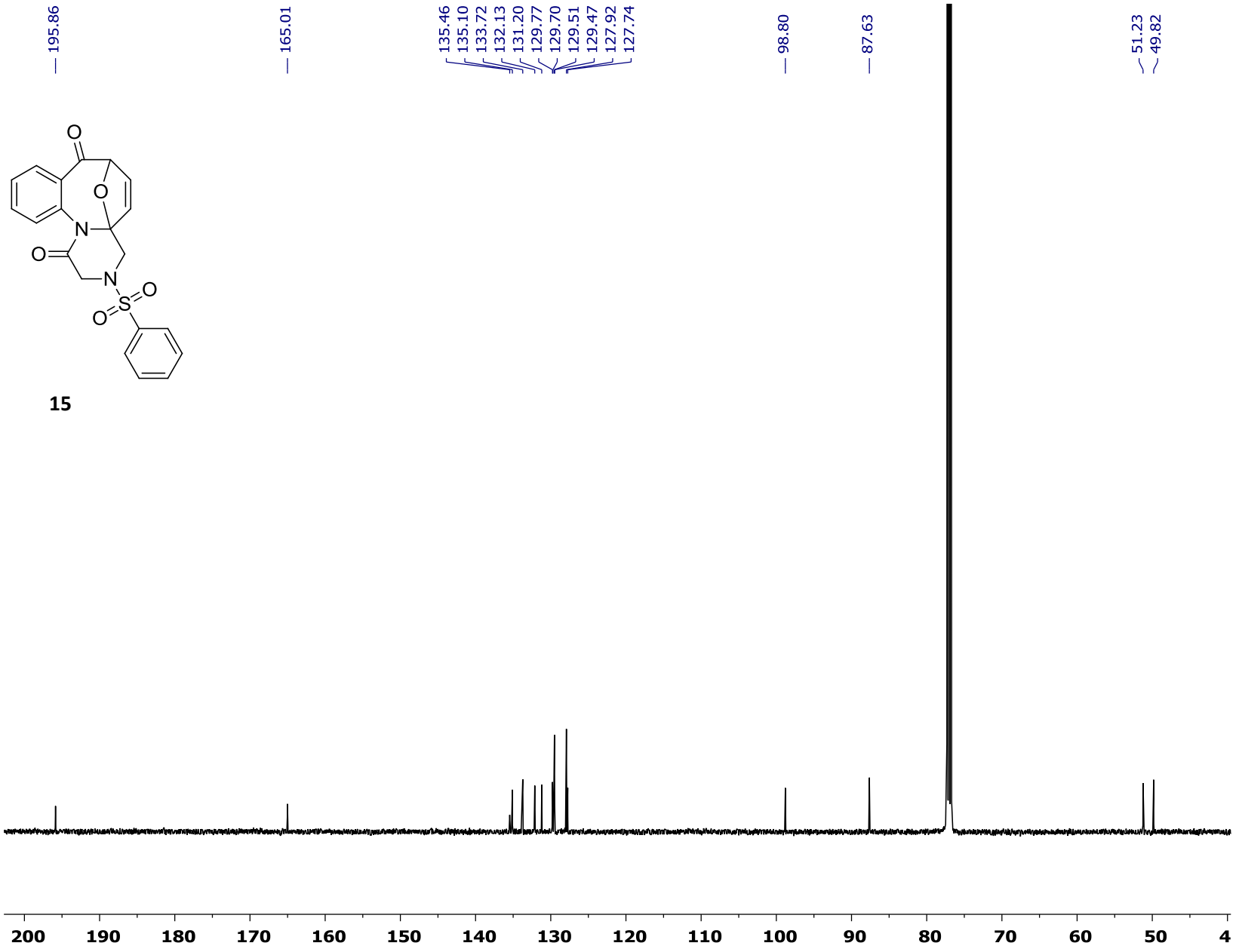
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51.23
49.82
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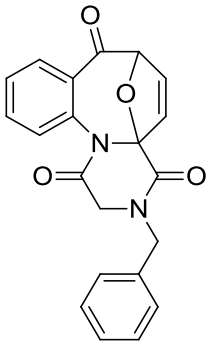

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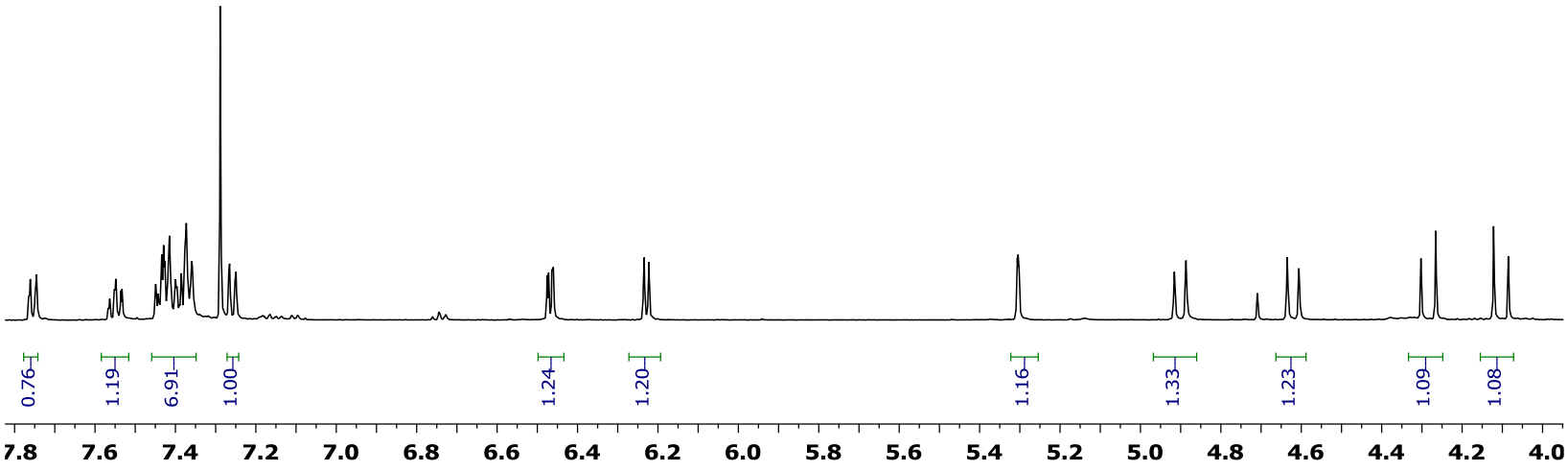
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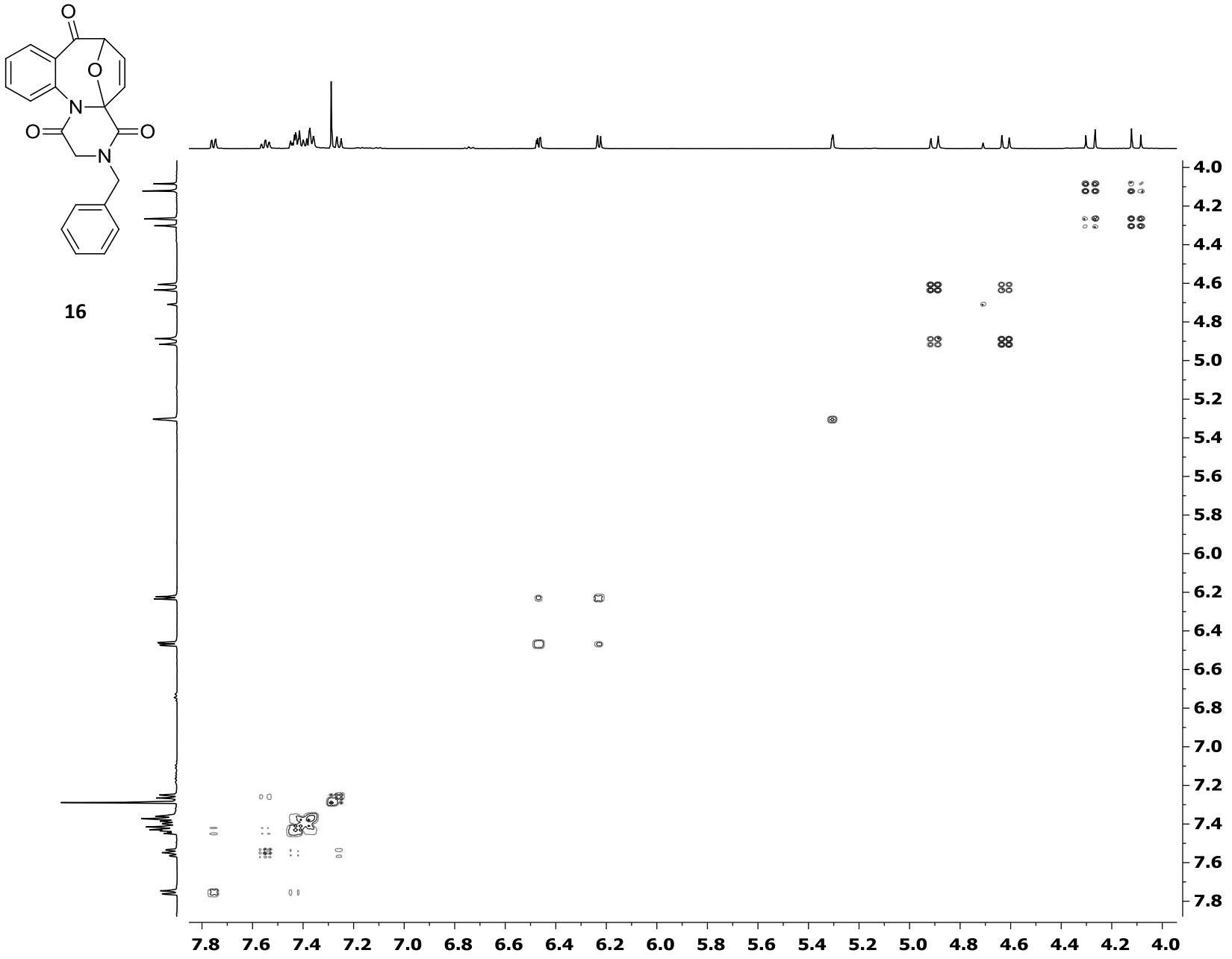
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7.6
7.8
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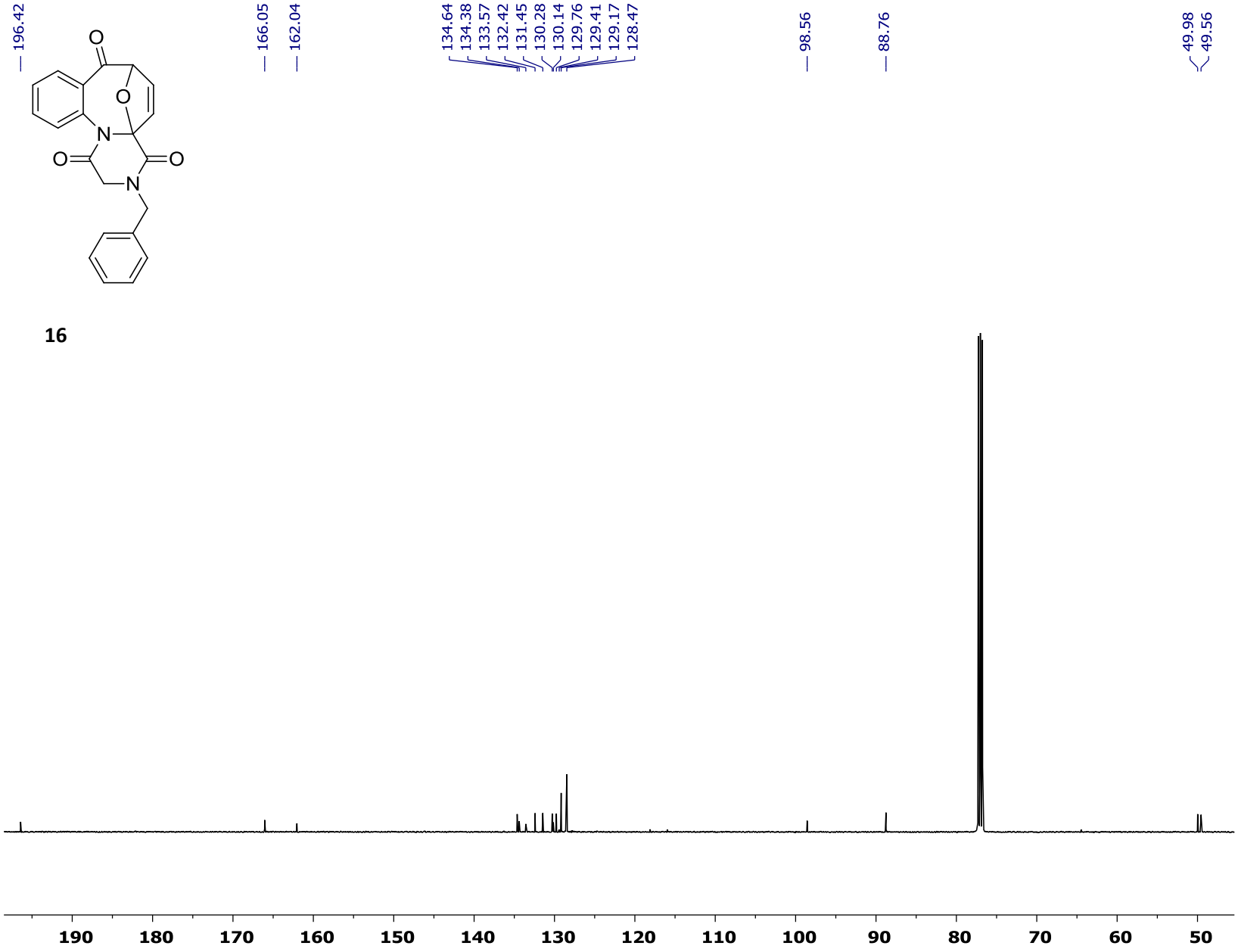
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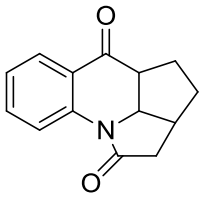
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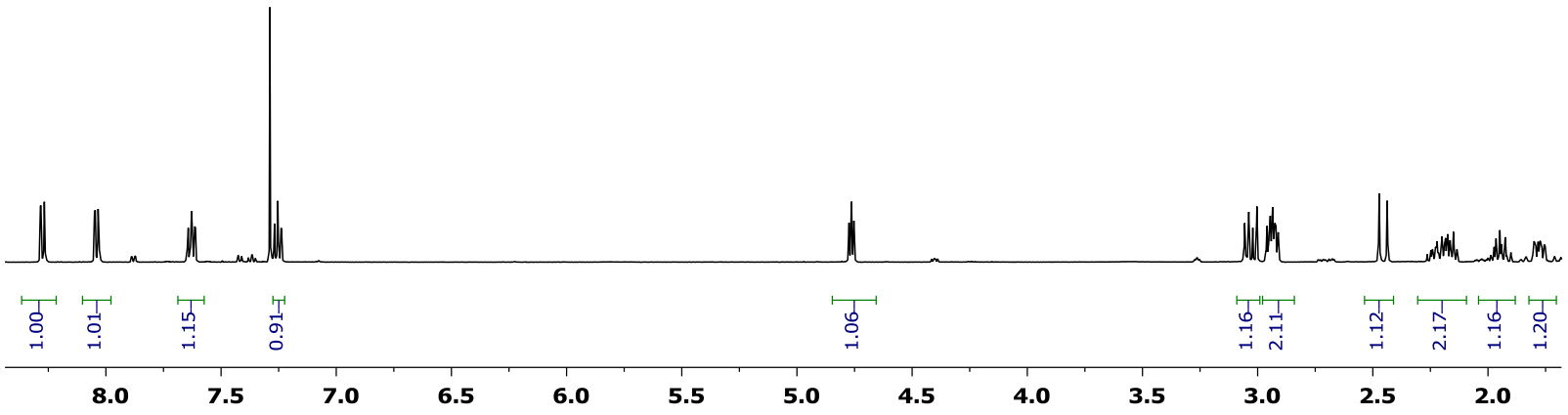
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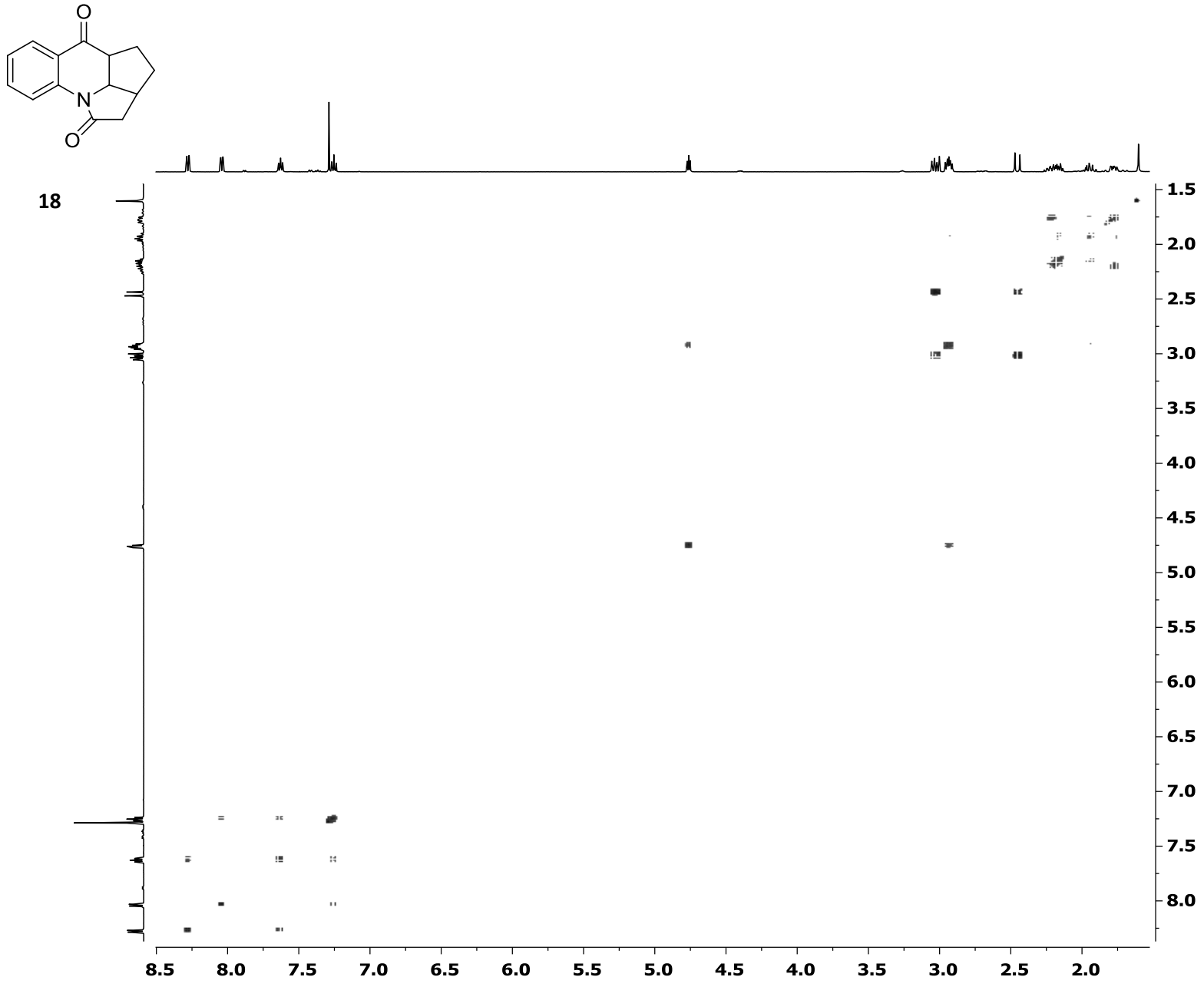
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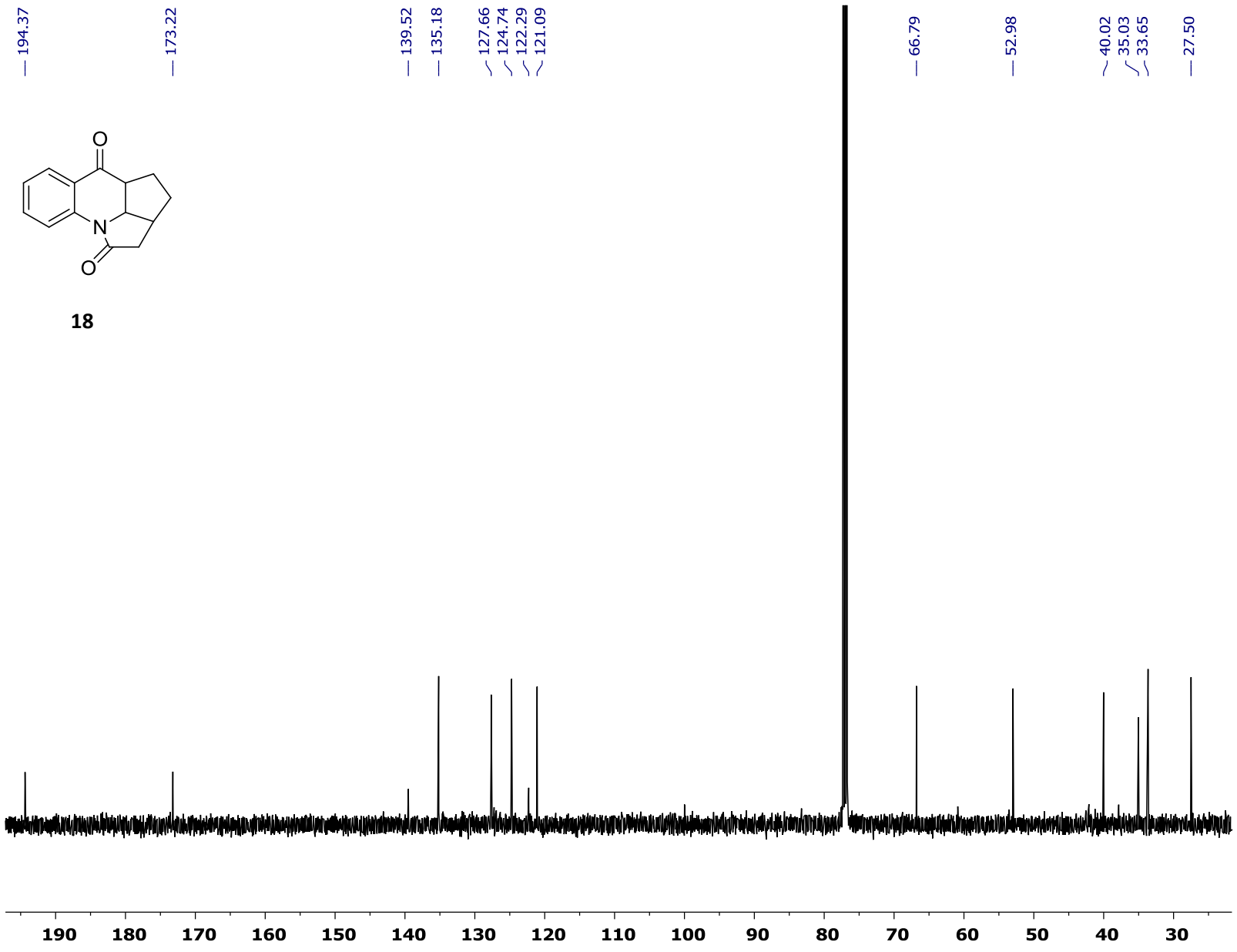
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27.50
O
N
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180
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100
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50
40
30