SUPPORTING INFORMATION

Photoassisted Access to Enantiopure Conformationally Locked Ribofuranosylamines Spiro-Linked to Oxazolidino- Diketopiperazines.

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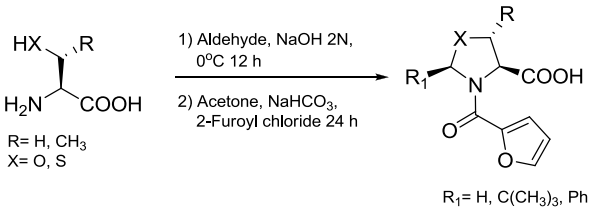
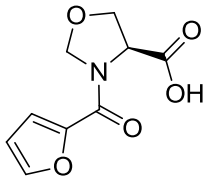
1. Synthetic procedures

Common solvents were purchased from Pharmco and used as is. Common reagents were purchased from Aldrich or TCI America 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). X-Ray structures were obtained with a Bruker APEX II instrument. High resolution mass spectra were obtained on the *MDS SCIEX/Applied Biosystems API QSTARTM Pulsar i Hybrid LC/MS/MS System* mass spectrometer by Dr. Shuji Kato from the University of Colorado at Boulder. Flash column chromatography was performed using Teledyne UltraPure Silica Gel (230 – 400 mesh) on a Teledyne Isco Combiflash *Rf*.

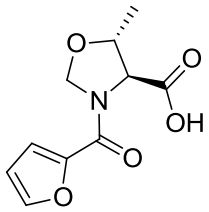
General scheme for synthesis of proline derivatives



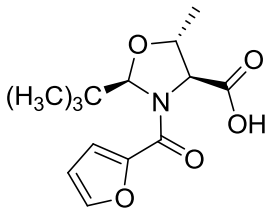
General procedure A: Amino acid (4 mmol, 1eq) was added to 2N NaOH (1.9 mL) at 0°C, followed by addition of the corresponding aldehyde (1.5 eq). After completion of addition the reaction mixture was stirred at ambient temperature overnight. Then $NaHCO_3$ (1 eq) and acetone (1.9 mL) were added at 0°C followed by addition of 2-furoyl chloride (1.5 eq). After stirring at ambient temperature for 24 h, the reaction mixture was acidified with 3N HCI and concentrated *in vacuo* to afford the crude product, which was purified by flash chromatography.

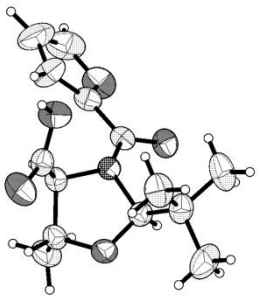


***S*-N-(2-Furoyl)-2-oxaazolidine-4-carboxylic acid (1a)**: The general procedure **A** was followed on a 3.80 mmol scale of serine. Purification by flash chromatography afforded 0.50 g (68%). ^{1}H NMR (500 MHz, MeOD) δ 7.87 – 7.54 (m, 1H), 7.34 – 7.12 (m, 1H), 6.74 – 6.57 (s, 1H), 5.54 – 5.34 (m, 1H), 5.33 – 5.10 (m, 2H), 4.45 – 4.09 (m, 2H). HRMS (ESI) calcd for $C_9H_{10}NO_5^+$ (MH^+) 212.0554, found 212.0546

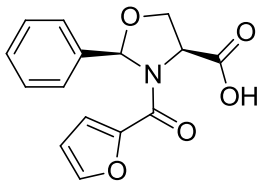


(4*S*,5*R*)-3-(Furan-2-carbonyl)-5-methyloxazolidine-4-carboxylic acid (1b): The general procedure **A** was followed on a 3.35 mmol scale of L-threonine. Purification by flash chromatography afforded 0.55 g (73%). ^{1}H NMR (500 MHz, MeOD) δ 7.86 – 7.57 (m, 1H), 7.27 – 7.12 (m, 1H), 6.68 – 6.53 (m, 1H), 5.70 – 5.41 (m, 1H), 5.40 – 5.01 (m, 1H), 4.66-4.93 (m, 1H), 4.45 – 4.16 (m, 1H), 1.62 – 1.47 (m, 3H). HRMS (ESI) calcd for $C_{10}H_{12}NO_5^+$ (MH^+) 226.0710, found 226.0710

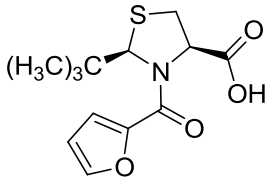




(2*R*,4*S*,5*R*)-2-*tert*-Butyl-3-(furan-2-carbonyl)-5-methyloxazolidine-4-carboxylic acid (1c): The general procedure **A** was followed on a 3.35 mmol scale of L-threonine. Purification by flash chromatography afforded 0.78 g (83%). ^{1}H NMR (500 MHz, MeOD) δ 7.68 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.26 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.59 (d, *J* = 3.5, 1.7 Hz, 1H), 5.66 (s, br, 1H), 4.74-4.69 (m, 1H), 4.61 (d, *J* = 5.0 Hz, 1H), 1.35 (d, *J* = 6.2 Hz, 3H), 1.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.5, 161.1, 147.4, 145.1, 119.5, 112.3, 97.1, 77.4, 66.8, 38.2, 26.1, 20.5. HRMS (ESI) calcd for $C_{14}H_{20}NO_5^+$ (MH^+) 282.1337, found 282.1334

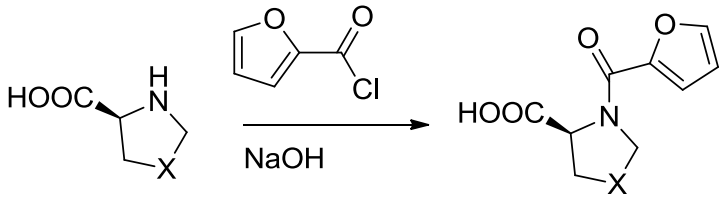


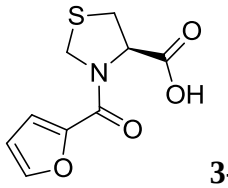
(2*R*,4*S*)-3-(Furan-2-carbonyl)-5-phenyloxazolidine-4-carboxylic acid (1d): The general procedure **A** was followed at (3.80 mmol) scale of acid. Purification by flash chromatography afforded 0.43 g (40%). ^{1}H NMR (500 MHz, MeOD) δ 7.83 – 7.47 (d, *J* = 5.8 Hz, 4H), 7.44 – 7.23 (m, 3H), 7.26 – 6.95 (s, 1H), 6.74 – 6.08 (m, 2H), 5.34 – 4.81 (m, 1H), 4.59 – 4.22 (m, 1H).



(2*R*,4*S*)-2-*tert*-Butyl-3-(furan-2-carbonyl)thiazolidine-4-carboxylic acid (1e): The general procedure **A** was followed on a 3.30 mmol scale of cysteine. Purification by flash chromatography afforded 0.55 g (74%). ^{1}H NMR (500 MHz, MeOD) δ 7.69 (s, br, 1H), 7.23 (d, *J* = 3.4 Hz, 1H), 6.60 (d, *J* = 3.4, 1.8 Hz, 1H), 5.84 (s, br, 1H), 5.29 (s, br, 1H), 3.53 (dd, *J* = 11.6, 9.3 Hz 1H), 3.37 (m, 1H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, MeOD) δ = 174.0, 161.8, 149.0, 146.6, 119.9, 113.0, 74.7, 66.3, 40.0, 35.6, 27.4 HRMS (ESI) calcd for $C_{13}H_{18}NO_4S^+$ (MH^+) 284.0951, found 284.0941.

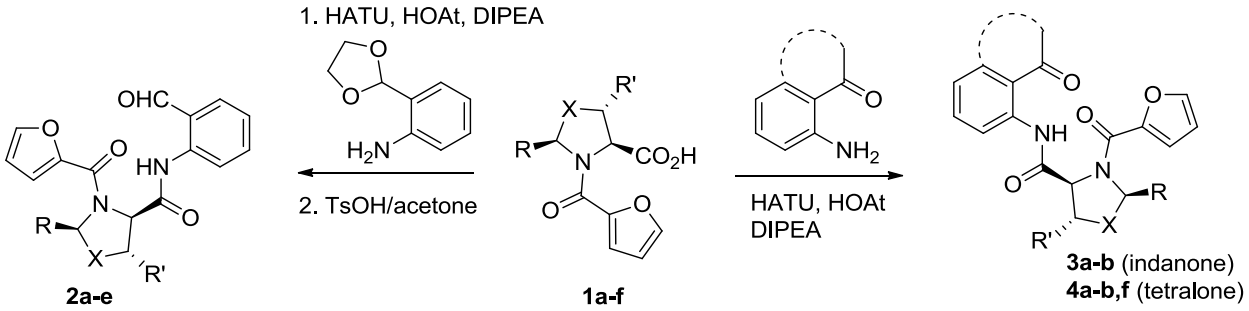
Synthesis of unsubstitued thiazolidine derivatives from commercially available thiaprolin





3-(Furan-2-carbonyl)thiazolidine-4-carboxylic acid[1] **(1f):** 3.05g (23.0mmol, 1.1 equivalents) of thiazolidine-4-carboxylic acid in 10mL of water was made alkaline with 5mL of a 20% NaOH solution. Then 3g (23 mmol) of 2-furoyl chloride in 10mL of acetone was added dropwise to the solution. During the addition the reaction mixture was kept under alkaline conditions by additions of the 20% NaOH solution. After 1 hour the solution was acidified with dilute hydrochloric acid. The reaction mixture was cooled, the precipitate formed filtered yielding 4.80g (92%) of the product. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (s, 1H), 7.26 (s, 1H), 6.55 (s, 1H), 5.42-4.65 (m, 3H), 3.46-3.29 (m, 2H).

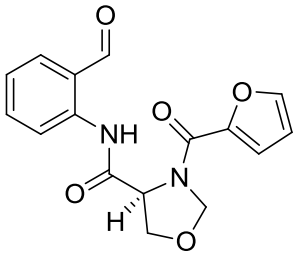
General scheme for synthesis of photoprecursors 2-4



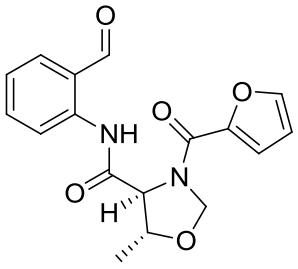
General procedure B: 2-(1,3-dioxolan-2-yl)aniline (0.37 g, 2.27 mmol, 1.2 eq) was dissolved in CH_2Cl_2 (15 mL), DIPEA (0.75 mL, 4.36 mmol), HATU (0.86 g 2.27 mmol, 1.2 eq), HOAt (0.31 g, 2.27 mmol, 1.2 eq) and carboxylic acid (1 eq, 1.89 mmol) were added at 20°C. After the completion of addition the reaction was allowed to stir at ambient temperature for 48 h. The

[1] Ladurée, D.; Lancelot, J.-C.; Robba, M.; Chenu, E.; Mathé, G.; *J. Med. Chem.* **1989**, *32*, 456-461.

mixture was diluted with CH_2Cl_2 and successively washed with $NaHCO_3$ and brine. The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was deprotected in 20 mL of acetone with PTS (0.072 g, 0.38 mmol, 20mol%) stirring overnight at ambient temperature. The compounds were purified by flash chromatography.

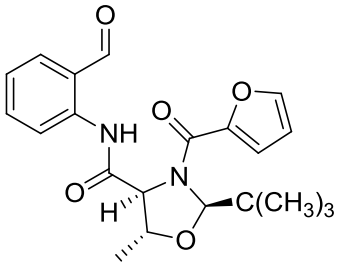


(4*S*)-N-(2-Formylphenyl)-3-(furan-2-carbonyl)oxazolidine-4-carboxamide (2a): General procedure **B** was followed on a 1.89 scale of the carboxylic acid **1a.** Purification by flash chromatography afforded 0.43 g (72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.81 (s, 1H), 9.84 (s, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 7.69-7.50 (m, 3H), 7.31-7.21 (m, 2H), 6.55 (s, 1H), 5.72 (s, 1H), 5.42 (m, 1H), 5.03 (dd, *J* = 6.8, 2.6 Hz, 1H), 4.41 (s, 1H), 4.25 (dd, *J* = 9.1, 6.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.3, 169.5, 157.5, 147.3, 145.3, 139.9, 136.0, 135.8, 123.5, 122.2, 119.8, 117.8, 112.0, 80.9, 70.6, 60.4 HRMS (ESI) calcd for $C_{16}H_{14}N_2NaO_5^+$ (MNa^+) 337.0795, found 337.0792

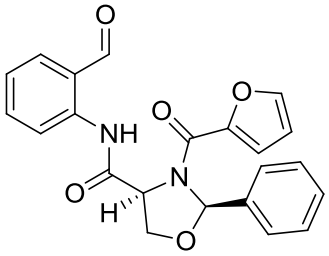


(4*S*,5*R*)-N-(2-Formylphenyl)-3-(furan-2-carbonyl)-5-methyloxazolidine-4-carboxamide (2b): General procedure **B** was followed on a 1.77 scale of the carboxylic acid **1b**. Purification by flash chromatography afforded 0.40 g (68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.77 (s, 1H), 9.82 (s, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 7.71-7.50 (m, 3H), 7.28-7.19 (m, 2H), 6.54 (s, br, 1H), 5.67 (m, 1H), 5.47 (s, 1H), 4.58-4.30 (s, br, 2 H), 1.55 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.4, 168.6, 157.8, 147.2, 145.3, 139.9, 135.8, 135.8, 123.5, 122.1, 119.8, 117.6,

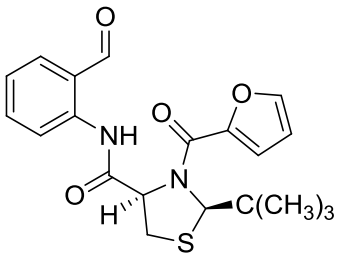
111.9, 79.8, 77.4, 66.3, 18.5. HRMS (ESI) calcd for $C_{17}H_{17}N_2O_5^+$ (MH^+) 329.1132, found 329.1127



(2*R*,4*S*,5*R*)-2-*tert*-Butyl-N-(2-formylphenyl)-3-(furan-2-carbonyl)-5-methyloxazolidine-4-carboxamide (2c): General procedure **B** was followed on a 1.42 scale of the carboxylic acid **1c**. Purification by flash chromatography afforded 0.39 g (72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.02 (s, 1H), 9.82 (s, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 7.70-7.62 (m, 2H), 7.38-7.32 (m, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 6.49 (dd, *J* =3.5, 1.7 Hz, 1H), 5.83 (s, 1H), 4.96 (m, 1H), 4.69 (d, *J* = 3.7 Hz, 1H), 1.40 (d, *J* = 6.1 Hz, 3H), 1.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 194.6, 169.9, 162.1, 147.8, 144.7, 139.8, 136.0, 135.9, 123.5, 122.2, 120.0, 119.1, 112.0, 96.8, 76.6, 68.9, 37.3, 26.0, 20.1. HRMS (ESI) calcd for $C_{21}H_{25}N_2O_5^+$ (MH^+) 385.1759, found 385.1756



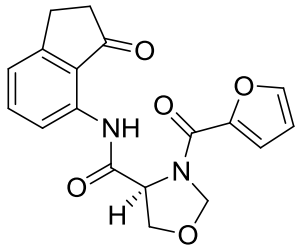
(2*R*,4*S*,*5R*)-N-(2-Formylphenyl)-3-(furan-2-carbonyl)-2-phenyloxazolidine-4-carboxamide (2d): General procedure **B** was followed on a 2.43 scale of the carboxylic acid **1d**. Purification by flash chromatography afforded 0.37 g (39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.76 (s, 1H), 9.64 (s, 1H), 8.72 (d, *J* = 8.6 Hz, 1H), 7.68-7.63 (m, 2H), 7.62-7.57 (m, 2H), 7.36 (s, br, 1H), 7.26-7.21 (m, 5H), 6.71 (s, br, 1H), 6.44 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.20 (dd, *J* = 7.1, 4.0 Hz, 1H), 4.59 (b, s, 1H), 4.34 (t, *J* = 3.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 194.4, 169.7, 159.6, 147.5, 145.3, 139.8, 137.5, 136.0, 135.9, 128.9, 128.3, 127.6, 123.8, 122.4, 120.0, 118.6, 112.2, 91.89, 69.63, 61.75. HRMS (ESI) calcd for $C_{22}H_{19}N_2O_5^+$ (MH^+) 391.1289, found 391.1287.



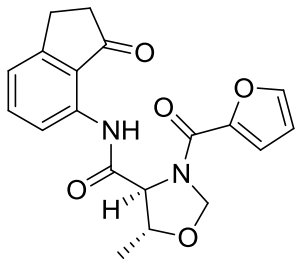
(2*R*,4*S*)-2-*tert*-Butyl-N-(2-formylphenyl)-3-(furan-2-carbonyl)thiazolidine-4-carboxamide(2e): General procedure **B** was followed on a 1.41 scale of the carboxylic acid **1e**. Purification by flash chromatography afforded 0.41 g (75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.66 (s, 1H), 9.84 (s, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 7.66 (dd, *J* =7.7, 1.6 Hz, 1H), 7.61 (m, 1H), 7.39 (s, br, 1H), 7.31 (dd, *J* =3.6, 0.7 Hz, 1H), 7.24 (td, *J* =7.7, 0.7 Hz, 1H), 6.48 (m, 1H), 6.04 (s, br, 1H), 5.42 (t, *J* = 8.03 Hz, 1H), 3.61 (dd, *J* = 11.7, 7.1 Hz, 1H), 3.38 (dd, *J* = 8.4, 11.7 Hz, 1H), 1.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.1, 170.1, 161.2, 148.1, 144.4, 140.2, 136.3, 136.1, 123.7, 122.3, 120.4, 119.8, 112.2, 73.9, 67.8, 39.2, 33.6, 27.1. HRMS (ESI) calcd for $C_{20}H_{23}N_2O_4S^+$ (MH^+) 387.1371, found 387.1373.

General procedure C: 7-Aminoindan-1-one or 8-amino-1-tetralone[2] 2 (2.27 mmol, 1.2 eq) was dissolved in CH_2Cl_2 (15 mL), DIPEA (0.75 mL, 4.36 mmol), HATU (0.86 g 2.27 mmol, 1.2 eq), HOAt (0.31 g, 2.27 mmol, 1.2 eq) and carboxylic acid (1 eq, 1.89 mmol) were added at 20°C. After the completion of addition the reaction was allowed to stir at ambient temperature for 48 h. The mixture was diluted with CH_2Cl_2 and successively washed with $NaHCO_3$ and brine. The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was deprotected in 20 mL of acetone with PTS (0.072 g, 0.38 mmol, 20mol%) stirring overnight at ambient temperature. The compounds were purified by flash chromatography.

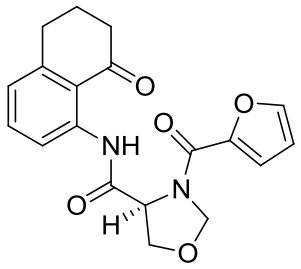
[2] Nguyen, P.; Corpuz, E.; Heidelbaugh, T.M.; Chowm K.; Garst, M. E. *J. Org. Chem.* **2003**, *68*, 10195-10198.



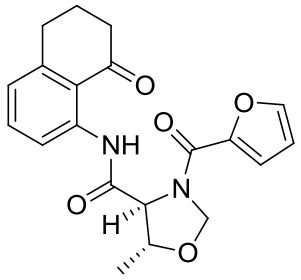
4*S*-3-(Furan-2-carbonyl)-N-(3-oxo-2,3-dihydro-1H-inden-4-yl)oxazolidine-4-carboxamide (3a): General procedure **C** was followed on a 1.89 mmol scale of the carboxylic acid **1a**. Purification by flash chromatography afforded 0.40 g (62%) of the title compound. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.13 (s, 1H), 8.36 (d, *J* = 8.2 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2 H), 7.27 (d, *J* = 3.5 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.51 (s, br, 1H), 5.68 (s, br, 1H), 5.39 (m, 1H), 5.00 (dd, *J* = 6.7, 2.7 Hz, 1H), 4.38 (s, br, 1H), 4.21 (dd, *J* = 9.1, 6.9 Hz, 1H), 3.05 (m, 2H), 2.64 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 209.0, 169.5, 157.6, 155.8, 147.4, 145.5, 137.9, 136.8, 123.7, 121.4, 118.1, 116.9, 112.2, 81.0, 71.1, 60.5, 36.4, 25.6. HRMS (ESI) calcd for $C_{18}H_{16}N_2O_5^+$ (MH^+) 341.1132, found 341.1133.



(4*S*,5*R*)-3-(Furan-2-carbonyl)-5-methyl-N-(3-oxo-2,3-dihydro-1H-inden-4-yl)oxazolidine-4-carboxamide (3b): General procedure **C** was followed on a 1.77 mmol scale of the carboxylic acid **1b**. Purification by flash chromatography afforded 0.41 g (65%) of the title compound. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.08 (s, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.23 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.51 (s, br, 1H), 5.65 (d, *J* = 5.1 Hz, 1H), 5.45 (s, 1H), 4.49 (s, br, 1H), 4.40 (s, br, 1H), 3.06 (m, 2H), 2.66 (m, 2H), 1.52 (d, *J* = 6.1, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 209.1, 168.5, 158.0, 155.8, 147.4, 145.4, 137.9, 136.9, 123.6, 121.3, 117.9, 116.9, 112.1, 80.0, 78.2, 66.3, 36.4, 25.5, 18.7. HRMS (ESI) calcd for $C_{19}H_{19}N_2O_5^+$ (MH^+) 355.1289, found 355.1282.

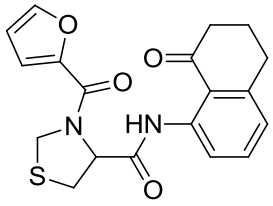


4*S*-3-(Furan-2-carbonyl)-N-(8-oxo-5,6,7,8-tetrahydronaphthalen-1-yl)oxazolidine-4-carboxamide (4a): General procedure **C** was followed on a 1.89 mmol scale of the carboxylic acid **1a**. Purification by flash chromatography afforded 0.16g (42%) of the title compound. Purification by flash chromatography afforded 0.4 g (59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.75 (s, 1H), 8.56 (d, *J* = 8.3 Hz, 1H), 7.47 (s, br 1 H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.20 (m, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.45 (s, br, 1H), 5.65 (s, br, 1H), 5.35 (s, br 1H), 4.94 (dd, *J* = 6.8, 2.6 Hz, 1H), 4.33 (s, br, 1H), 4.18 (dd, *J* = 9.0, 6.8 Hz, 1H), 2.87 (m, 2H), 2.55 (m, 2H), 1.97 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 203.1, 169.5, 157.4, 147.4, 146.0, 145.2, 141.0, 134.9, 123.7, 118.9, 118.1, 117.7, 111.9, 80.9, 70.2, 60.5, 40.5, 30.8, 22.6. HRMS (ESI) calcd for $C_{19}H_{19}N_2O_5$ (MH^+) 355.1289, found 355.1284.



(4*S*,5*R*)-3-(Furan-2-carbonyl)-5-methyl-N-(8-oxo-5,6,7,8-tetrahydronaphthalen-1-yl)oxazolidine-4-carboxamide (4b) General procedure **C** was followed on a 1.77 mmol scale of the carboxylic acid **1b**. Purification by flash chromatography afforded 0.44 g (67%) of the title compound. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.70 (s, 1H), 8.53 (d, *J* = 8.3 Hz, 1H), 7.49 (s, br 1 H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.16 (m, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.45 (s, br, 1H), 5.60 (d, *J* = 7.5 Hz, 1H), 5.40 (s, br, 1H), 4.58-4.15 (s, br, 2H), 2.87 (m, 2H), 2.56 (m, 2H), 1.97 (m, 2H), 1.47 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 203.3, 168.5, 157.7, 147.5, 146.2,

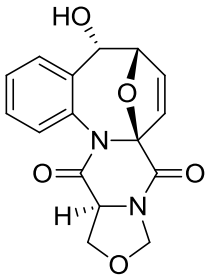
145.3, 141.2, 135.1, 123.8, 118.9, 118.4, 117.7, 112.0, 80.0, 78.2, 66.8, 40.7, 31.0, 22.7, 18.8. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_5^+$ (MH^+) 369.1446, found 369.1443.

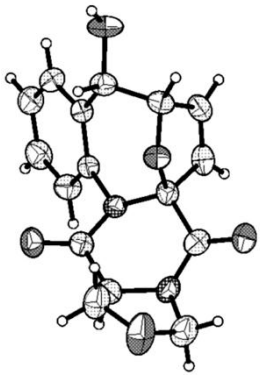


3-(Furan-2-carbonyl)-N-(8-oxo-5,6,7,8-tetrahydronaphthalen-1-yl)thiazolidine-4-carboxamide (4f): General procedure **C** was followed on a 1.03 mmol scale of the carboxylic acid **1f**. Purification by flash chromatography afforded 0.16g (42%) of the title compound. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.74 (s, 1H), 8.57 (m, 1H), 7.47 (br s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.45 (br s, 1H), 5.37 (dd, *J* = 6.8, 2.8 Hz, 1H), 5.10 (m, 2H), 3.42 (d, *J* = 11.4 Hz, 1H), 3.29 (dd, *J* = 11.8, 6.8 Hz, 1H), 2.87 (m, 2H), 2.55 (m, 2H), 1.98 (m, 2H), 1.53 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.1, 157.7, 146.4, 145.0, 144.0, 140.0, 134.0, 122.7, 117.9, 117.2, 110.8, 64.3, 49.5, 39.6, 29.9, 21.6.

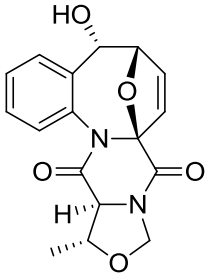
Products of photoinduced cyclizations

General procedure D: Photoprecursor **2a-e**, **3a-b** or **4a-b** was dissolved in 30 mL of CH_3CN, 5 vol% of HMPA (1.5 mL) was added, solution was degassed, cooled to 0°C, and irradiated with UV LED-based illuminator with five 250 mW @ 365 nm Nichia chips until the reaction was complete. The reaction mixture was then concentrated and purified by flash chromatography. **General procedure E:** Photoprecursor was dissolved in 30 mL of CH_3CN, solution was degassed, cooled to 0°C, and irradiated with UV LED-based illuminator with five 250 mW @ 365 nm Nichia chips until the reaction was complete. The reaction mixture was then concentrated and purified by flash chromatography.



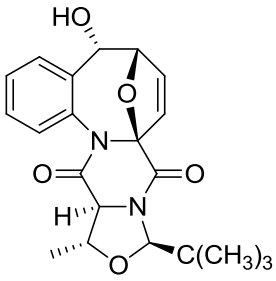


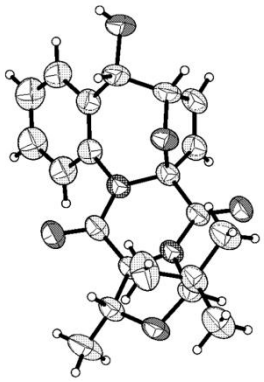
***(1S,7S,12S,13S)-anti*-12-Hydroxy-10,11-benzo-5,16-dioxa-3,9-diazatetracyclo[11.2.1.0^{1,9}.0^{3,7}] hexadeca-10,14-diene-2,8-dione (5a):** From 0.30 g (0.9 mmol) of aldehyde **(2a)** following the general procedure **D** upon flash chromatography 0.17 g (57 %) of the compound **5a** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.25 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.88 (d, *J* = 6.0 Hz, 1H), 5.57 (d, *J* = 5.3 Hz, 1H), 5.12 – 5.08 (m, 1H), 5.05 (m, 1H), 4.80 (d, *J* = 5.2 Hz, 1H), 4.63 (dd, *J* = 10.0, 6.8 Hz, 1H), 4.41 (t, *J* = 7.5 Hz, 1H), 3.82 (dd, *J* = 10.0, 8.0 Hz, 1H), 2.87 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.6, 162.8, 136.9, 135.8, 133.3, 129.7, 128.4, 127.8, 127.4, 126.9, 96.6, 86.1, 79.1, 75.0, 68.2, 58.7. HRMS (ESI) calcd for $C_{16}H_{14}N_2NaO_5^+$ (MNa^+) 337.0795, found 337.0792.



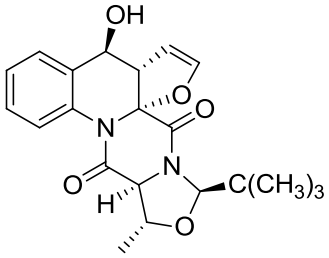
***(1S,6R,7S,12S,13S)-anti*-12-Hydroxy-6-methyl-10,11-benzo-5,16-dioxa-3,9-diazatetracyclo [11.2.1.0^{1,9}.0^{3,7}]hexadeca-10,14-diene-2,8-dione (5b):** From 0.30 g (0.9 mmol) of aldehyde **(2b)** following the general procedure **D** upon flash chromatography 0.19 g (63 %) of the compound **5b** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.36 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (tm, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.28 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.92 (dd, *J* = 5.9, 0.7 Hz, 1H), 5.50 (d, *J* = 5.3 Hz, 1H), 5.19 (dd, *J* = 6.3, 2.6 Hz, 1H), 5.11-5.09 (m, 1H), 4.90 (d, *J* = 5.1 Hz, 1H), 4.11-4.05 (m, 2H), 2.57 (d, *J* = 6.4 Hz 1H), 1.56 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.3, 162.3, 136.6, 135.4, 133.2, 129.6, 128.2, 127.6, 127.4,

126.6, 96.2, 85.8, 77.6, 76.5, 74.9, 63.4, 18.0. HRMS (ESI) calcd for $C_{17}H_{17}N_2O_5^+$ (MH^+) 329.1132, found 329.1135.



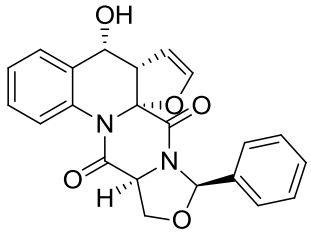


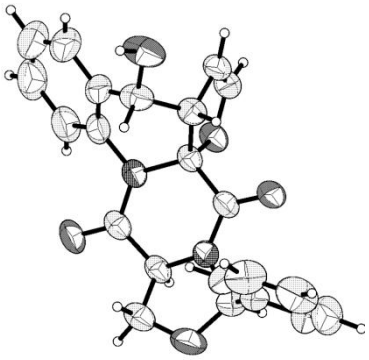
***(1S,4R,6R,7S,12S,13S)-anti*-12-Hydroxy-4-*tert*-butyl-6-methyl-10,11-benzo-5,16-dioxa-3,9 diazatetracyclo[11.2.1.0^{1,9}.0^{3,7}]hexadeca-10,14-diene-2,8-dione (5c):** From 0.35 g (0.8 mmol) of aldehyde **(2c)** following the general procedure **D** upon flash chromatography 0.24 g (68 %) of the title compound **5c** and 0.02 g (5 %) of the compound **6c** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.25 (td, *J* = 7.5, 1.4 Hz, 1H), 7.21 (td, *J* = 7.5, 1.4 Hz, 1H), 7.09 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.19 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.85 (dd, *J* = 5.9, 0.7 Hz, 1H), 5.17 (s, 1H), 5.04 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.93-4.90 (m, 1H), 4.37-4.32 (m, 1H), 4.07 (d, *J* = 5.9 Hz, 1H), 3.22 (d, *J* = 6.2 Hz, 1H), 1.50 (d, *J* = 5.9 Hz,3H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.7, 163.6, 136.6, 135.7, 133.4, 129.5, 127.9, 127.5, 127.0, 127.0, 99.0, 95.4, 85.4, 75.1, 74.9, 65.3, 39.3, 26.6, 18.7. HRMS (ESI) calcd for $C_{21}H_{25}N_2O_5^+$ (MH^+) 385.1759, found 385.1754.



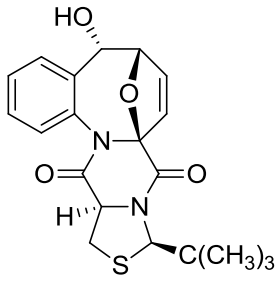
***(4S,5S,9R,12R,14R,15S)-anti*-4-Hydroxy-12-*tert*-butyl-14-methyl-2,3-benzo-8,13-dioxa-1,11-diazatetracyclo[7.7.0.0^{5,9}.0^{11,15}]hexadeca-2,6-diene-10,16-dione (6c):** From 0.35 g (0.8 mmol) of aldehyde (**2c)** following the general procedure **D** upon flash chromatography 0.24 g (68 %) of the compound **5c** and 0.02 g (5 %) of the title compound **6c** . ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.35 (m, 1H), 7.21 (m, 2H), 6.15 (t, *J* = 2.9 Hz, 1H), 5.27 (s, 1H), 5.06-5.04 (m, 1H), 4.90 (s, 1H), 4.63 (dd, *J* = 2.8, 2.1 Hz, 1H), 4.57-4.52 (m, 1H), 4.20 (d, *J* = 9.3 Hz,

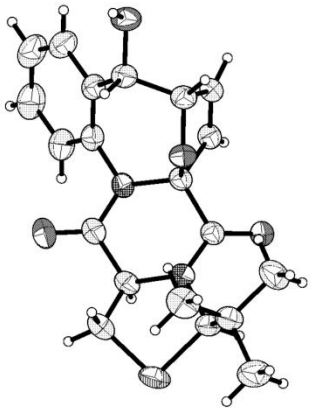
1H), 1.89 (d, *J* = 2.1 Hz, 1H), 1.52 (d, *J* = 5.8 Hz, 3H), 0.99 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.2, 163.6, 145.2, 135.5, 130.8, 129.3, 128.4, 126.4, 125.2, 101.5, 96.4, 96.0, 74.7, 68.8, 62.5, 55.4, 39.5, 26.8, 19.2. HRMS (ESI) calcd for $C_{21}H_{24}N_2NaO_5^+$ (MNa^+) 407.1578, found 407.1578.





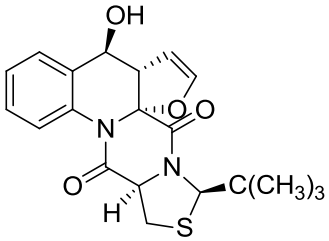
***(4R,5S,9R,12R,15S)-syn*-4-Hydroxy-12-phenyl-2,3-benzo-8,13-dioxa-1,11-diazatetracyclo [7.7.0^{1,9}.0^{5,9}.0^{11,15}]hexadeca-2,6-diene-10,16-dione (7d):** From 0.30 g (0.9 mmol) of aldehyde **(2d)** following the general procedure **D** upon flash chromatography 0.02 g (7 %) of the product was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.46 (m, 1H), 7.33-7.29 (m, 4H), 7.29-7.26 (m, 3H), 6.34 (s, 1H), 6.14 (t, *J* = 2.8 Hz, 1H), 4.93 (dd, *J* = 9.3, 7.2 Hz, 1H), 4.90-4.87 (m, 1H), 4.78 (t, *J* = 2.5 Hz, 1H), 4.70 (s, br, 1H), 4.52 (dd, *J* = 9.4, 7.2 Hz, 1H), 4.36 (t, *J* = 9.2 Hz, 1H), 2.63 (s, br 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.5, 159.1, 145.2, 136.4, 133.8, 132.7, 129.9, 129.0, 127.2, 126.6, 123.8, 123.6, 100.4, 96.8, 91.4, 66.6, 65.2, 57.0, 53.8.



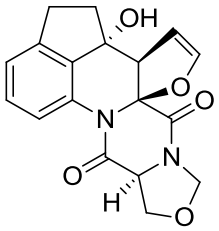


***(1S,4R,7S,12S,13S)-anti*-12-Hydroxy-4-*tert*-butyl-10,11-benzo-16-oxa-5-thia-3,9 diazatetracyclo[11.2.1.0^{1,9}.0^{3,7}]hexadeca-10,14-diene-2,8-dione (5e):** From 0.35 g (0.8 mmol) of aldehyde **(2e)** following the general procedure **D** upon flash chromatography 0.23 g (66 %) of the title compound **5e** and 0.08 g (9 %) of the compound **6e** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.30-7.18 (m, 2H), 7.10 (d, *J* = 8.1, 1H), 6.21 (d, *J* =

5.9 Hz, 1H), 5.90 (d, *J* = 5.9 Hz, 1H), 5.26 (s, 1H), 5.12 (s, br, 1H), 4.96 (s, br, 1H), 4.79-4.70 (m, 1H), 3.27-3.12 (m, 2H), 2.80 (s, br, 1H), 1.03 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.5, 165.5, 136.3, 135.4, 133.5, 129.6, 127.8, 127.5, 127.1, 126.9, 99.2, 85.3, 75.0, 72.6, 67.1, 41.2, 32.0, 27.1. HRMS (ESI) calcd for $C_{20}H_{23}N_2O_4S^+$ (MH^+) 387.1373, found 387.1369.

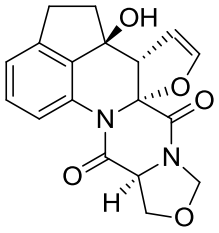


***(4R,5S,9R,12R,15S)-anti*-4-Hydroxy-12-*tert*-butyl-2,3-benzo-8-oxa-13-thia-1,11-diazatetracyclo[7.7.0.0^{5,9}.0^{11,15}]hexadeca-2,6-diene-10,16-dione (6e):** From 0.35 g (0.8 mmol) of aldehyde **(2e)** following the general procedure **D** upon flash chromatography 0.23 g (66 %) of the compound **5e** and 0.08 g (9 %) of the title compound **6e**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.37-7.34 (m, 1H), 7.17 (m, 2H), 6.16 (t, *J* = 2.9 Hz, 1H), 5.22 (s, 1H), 5.06-5.08 (m, 1H), 4.93-4.88 (m, 2H), 4.61-4.63 (m, 1H), 3.40-3.35 (m, 1H), 3.14 (dd, *J* = 11.9, 6.44 Hz, 1H), 1.86 (s, 1H), 0.97 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.0, 166.2, 145.2, 135.5, 130.7, 129.3, 128.4, 126.3, 125.1, 101.5, 96.2, 72.7, 68.8, 63.2, 55.8, 41.0, 30.9, 27.2. HRMS (ESI) calcd for $C_{20}H_{23}N_2O_4S^+$ (MH^+) 387.1373, found 387.1379.

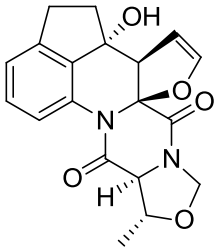


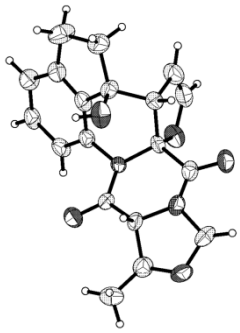
***(1S,2R,6S,12S)-anti*-1-Hydroxy-5,10-dioxa-8,14-diaza-hexacyclo[13.6.1.0^{2,6}.0^{6,14}.0^{8,12}.0^{19,22}]docosa-3,15,17,19(22)-tetraene-7,13-dione (8a):** From 0.30 g (0.8 mmol) of compound **(3a)** following the general procedure **D** upon flash chromatography 0.11 g (37 %) of the title compound **8a** and 0.04 g (13 %) of the compound **9a** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.17 (t, *J* = 2.9 Hz, 1H), 5.33 (d, *J* = 5.2 Hz, 1H), 5.20 (d, 1H), 4.99 (d,

J = 5.1 Hz, 1H), 4.77-4.74 (m, 1H), 4.71 (t, *J* = 7.2 Hz, 1H), 4.44 (m, 1H), 4.31 (m, 1H), 3.34-3.21 (m, 1H), 2.89-2.83 (m, 1H), 2.39-2.35 (m, 2H).



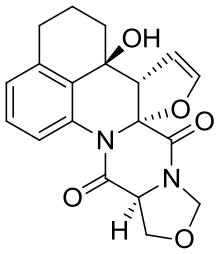
***(1R,2S,6R,12S)-anti*-1-Hydroxy-5,10-dioxa-8,14-diaza-hexacyclo[13.6.1.$0^{2,6}$.$0^{6,14}$.$0^{8,12}$.$0^{19,22}$]docosa-3,15,17,19(22)-tetraene-7,13-dione (9a):** 0From 0.30 g (0.8 mmol) of compound **(3a)** following the general procedure **D** upon flash chromatography 0.11 g (37 %) of the compound **8a** and 0.04 g (13 %) of the title compound **9a** was obtained . ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.20 (dd, *J* = 3.06, 2.30 Hz, 1H), 5.49 (d, *J* = 5.1 Hz, 1H), 4.91 (d, *J* = 5.2 Hz, 1H), 4.83 (t, *J* = 2.8 Hz, 1H), 4.53-4.45 (m, 2H), 4.18 (t, *J* = 2.4 Hz, 1H), 4.02 (dd, *J* = 7.7, 8.8 Hz, 1H), 3.21-3.14 (m, 1H), 2.92-2.85 (m, 1H), 2.53-2.46 (m, 1H), 2.23-2.17 (m, 1H), 2.01 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 163.0, 162.3, 147.2, 143.5, 137.2, 133.7, 130.7, 124.4, 123.6, 100.8, 97.3, 80.0, 79.4, 69.2, 61.2, 56.6, 36.8, 30.1.



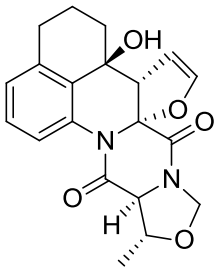


***(1S,2R,6S,11R,12S)-anti*-1-Hydroxy-5,10-dioxa-8,14-diaza-11-methyl-hexacyclo[13.6.1.$0^{2,6}$.$0^{6,14}$.$0^{8,12}$.$0^{19,22}$]docosa-3,15,17,19(22)-tetraene-7,13-dione (8b):** From 0.20 g (0.5 mmol) of the compound **(3b)** following the general procedure **D** upon flash chromatography 0.08 g (40 %) of the product was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7, 1H), 7.36 (t, *J* = 7.6, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.20 (t, *J* = 2.7 Hz, 1H), 5.37 (d, *J* = 5.2 Hz, 1H), 5.00 (d, *J* = 5.2 Hz, 1H), 4.83 (t, *J* = 2.8 Hz, 1H), 4.21-4.14 (m, 2H), 3.93 (d, *J* = 9.1 Hz, 1H), 3.21-3.14 (m, 1H), 2.92-2.85 (m, 1H), 2.45-2.53 (m, 1H), 2.22-2.17 (m, 1H), 1.95

(s, 1H), 1.58 (d, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.9, 162.0, 147.2, 143.5, 137.2, 133.7, 130.6, 124.5, 123.6, 100.7, 97.2, 80.0, 78.1, 77.6, 61.5, 61.2, 36.8, 30.1, 18.3.

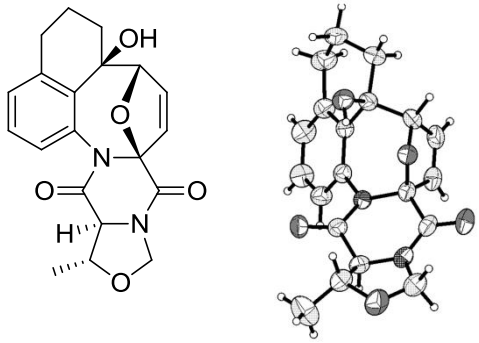


***(1R,2S,6R,12S)-anti*-1-Hydroxy-5,10-dioxa-8,14-diazahexacyclo[13.7.1.0^{2,6}.0^{6,14}.0^{8,12}.0^{19,23}] tricosa-3,15,17,19(23)-tetraene-7,13-dione (11a):** From 0.30 g (0.8 mmol) of aldehyde **(4a)** following the general procedure **D** upon flash chromatography 0.13 g (43 %) of the product was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.15 (t, *J* = 2.9 Hz, 1H), 5.26 (d, *J* = 5.0 Hz, 1H), 4.97 (d, *J* = 5.1 Hz, 1H), 4.87 (t, *J* = 2.4 Hz, 1H), 4.66-4.61 (m, 2H), 4.41 (dd, *J* = 9.0, 7.3 Hz, 1H), 4.15 (dd, *J* = 8.9, 8.1 Hz, 1H), 2.77-2.84 (m, 1H), 2.68-2.60 (m, 1H), 2.53 (s, 1H), 2.07-2.02 (m, 1H), 1.94-1.86 (m, 2H), 1.76 (td, *J* = 13.0, 3.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.3, 159.9, 145.4, 137.3, 135.0, 128.6, 127.8, 127.0, 122.9, 101.8, 95.8, 79.9, 69.4, 67.5, 56.6, 56.24, 35.7, 29.4, 18.21. HRMS (ESI) calcd for $C_{19}H_{19}N_2O_5^+$ (MH^+) 355.1289, found 355.1277.

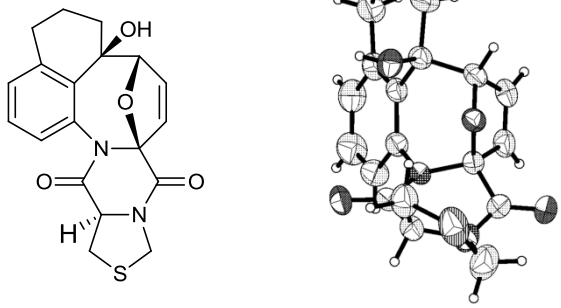


***(1R,2S,6R,11R,12S)-anti*-1-Hydroxy-11-methyl-5,10-dioxa-8,14-diaza hexacyclo[13.7.1.0^{2,6}.0^{6,14}.0^{8,12}.0^{19,23}]tricosa-3,15,17,19(23)-tetraene-7,13-dione (11b):** From 0.30 g (0.8 mmol) of aldehyde **(4b)** following the general procedure **D** upon flash chromatography 0.17 g (57 %) of the title compound **11b** and 0.04 g (13 %) of the compound **10b** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.10 (t, *J* = 2.9 Hz, 1H), 4.97 (d, *J* = 4.9 Hz, 1H), 4.84 (d, *J* = 4.9 Hz, 1H), 4.77 (t, *J* = 2.4 Hz, 1H), 4.62 (t, *J* = 2.5 Hz, 1H), 4.14-4.08 (m, 1H), 3.99 (d, *J* = 8.7 Hz,

1H), 3.24 (s, 1H), 2.83-2.76 (m, 1H), 2.67-2.59 (m, 1H), 2.04-1.99 (m, 1H), 1.96-1.82 (m, 2H), 1.74 (td, *J* = 13.4, 3.1 Hz, 1H) 1.51 (d, *J* = 5.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.1, 159.4, 145.3, 137.3, 134.9, 128.8, 127.6, 126.9, 123.0, 101.7, 95.7, 78.5, 77.6, 67.4, 61.1, 56.6, 35.6, 29.3, 18.7, 18.1. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_5^+$ (MH^+) 369.1446, found 369.1444.



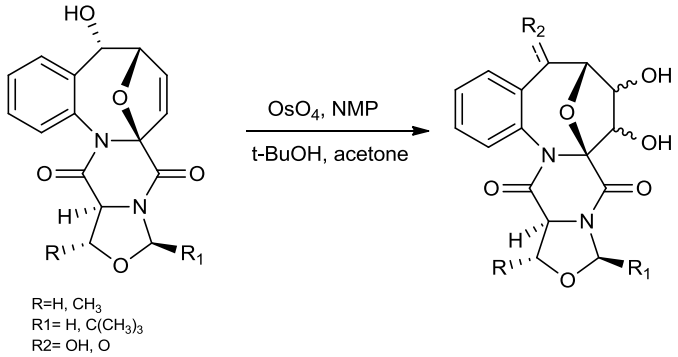
***(1R,2S,5S,10R,11S)-syn*-1-Hydroxy-10-methyl-9,23-dioxa-7,13-diaza hexacyclo[12.7.1.1.0^{5,13}.0^{7,11}.0^{18,22}]tricosa-3,14,16,18(22)-tetraene-6,12-dione (10b):** From 0.30 g (0.8 mmol) of aldehyde **(4b)** following the general procedure **D** upon flash chromatography 0.17 g (57 %) of the compound **11b** and 0.04 g (13 %) of the title compound **10b** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.29 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.86 (dd, *J* = 5.9, 0.9 Hz, 1H), 5.49 (d, *J* = 5.2 Hz, 1H), 4.90 (d, *J* = 5.1 Hz, 1H), 4.78 (m, 1H), 4.15-4.05 (m, 2H), 3.00 (d, *J* = 1.8 Hz, 1H), 2.91-2.85 (m, 1H), 2.73-2.65 (m, 1H), 2.13-2.05 (m, 2H), 1.83-1.78 (m, 1H), 1.56-1.53 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.5, 162.3, 139.1, 137.0, 135.6, 134.7, 130.7, 128.4, 128.2, 127.3, 97.0, 89.6, 77.8, 76.7, 75.3, 63.7, 35.7, 31.2. 18.2, 17.6. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_5^+$ (MH^+) 369.1446, found 369.1440.

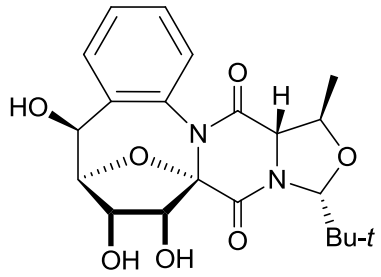


***(1R,2S,5S,11S)-syn*-1-Hydroxy-9-thia-23-oxa-7,13-diaza-hexacyclo[12.7.1.1^{2,5}.0^{5,13}.0^{7,11}.0^{18,22}] tricosa-3,14,16,18(22)-tetraene-6,12-dione (10f)**: From 0.15 g (0.4 mmol) of compound **4f** following general procedure **E** 0.10 g (67%) of the title compound **10f** and 0.02 (13%) of the

starting compound **4f** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.7 Hz, 1H), 7.07 (m, 1H), 6.84 (dt, *J* = 7.5, 1.1 Hz, 1H), 6.22 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.83 (dd, *J* = 5.9, 0.9 Hz, 1H), 5.32 (d, *J* = 9.2 Hz, 1H), 4.72 (dd, *J* = 1.8, 0.9 Hz, 1H), 4.46 (dd, *J* = 11.4, 5.8 Hz, 1H), 4.24 (d, *J* = 9.2 Hz, 1H), 3.48 (dd, *J* = 10.1, 5.8 Hz, 1H), 3.14 (dd, *J* = 11.4, 10.0 Hz, 1H), 2.83 (m, 2H), 2.63 (m, 1H), 2.03 (m, 2H), 1.77 (m, 1H), 1.47 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 161.9, 139.0, 136.6, 135.4, 134.6, 130.6, 128.4, 128.0, 127.5, 96.7, 89.5, 75.3, 63.3, 46.5, 35.8, 34.3, 31.0, 17.5. HRMS (ESI) calcd for $C_{19}H_{19}N_2O_4S^+$ (MH^+) 371.4296, found 371.1061

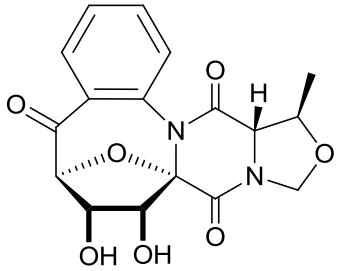
Synthesis of Hydroxylation derivatives





(1*S*,4R,6*R*,7*S*,12*R*,13*R*,14*R*,15*R*)-*anti*-12,14,15-Trihydroxy-4-*tert*-butyl-6-methyl-10,11-benzo-5,16-dioxa-3,9-diazatetracyclo[11.2.1.0^{1,9}.0^{3,7}]hexadeca-10-ene-2,8-dione (12): 0.20 g (0.5 mmol) of compound (**5c)** was dissolved in 1:1 mixture of *tert*-butanol and acetone (8 mL). The reaction mixture was cooled to 0^{o}C and a solution of NMO 0.08 g (0.6 mmol) in H_2O (0.3 mL) was added. After 15 min, OsO_4 0.016 g (0.06 mmol) in H_2O (0.2 mL) was added dropwise. After completion of addition the reaction mixture was stirred at room temperature for 48 h. Quenching with saturated aqueous Na_2SO_3 (4 mL) was followed by concentration *in vacuo*, the

residue was dissolved in CH_2Cl_2 and washed with H_2O (2 x 6 mL). The solvent was removed *in vacuo* and the product purified by flash chromatography affording 0.10 g (71%). based on 70% conversion of the starting material. ^{1}H NMR (500 MHz, MeOD) δ 7.36-7.31 (m, 1H), 7.28 (dd, *J* = 7.4, 1.6, 1H), 7.26-7.21 (m, 2H), 5.18 (s, 1H), 5.13 (d, *J* = 5.3 Hz, 1H), 4.98 (d, *J* = 6.9 Hz, 1H), 4.80 (d, *J* = 5.3 Hz, 1H), 4.72-4.65 (m, 2H), 4.35 (d, *J* = 8.8 Hz, 1H), 1.48 (d, *J* = 5.8 Hz, 3H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.3, 165.4, 134.9, 133.0, 130.1, 129.5, 127.8, 127.0, 97.9, 96.0, 87.0, 85.3, 74.6, 74.6, 73.3, 64.4, 39.1, 26.9, 19.2. HRMS (ESI) calcd for $C_{21}H_{27}N_2O_7^+$ (MH^+) 419.1813, found 419.1811



(1*S*,6*R*,7*S*,13*S*,14*S*,15*R*)-*anti*-14,15-Dihydroxy-6-methyl-10,11-benzo-5,16-dioxa-3,9 diazatetracyclo[11.2.1.0^{1,9}.0^{3,7}]hexadeca-10-ene-2,8-dione (13): 0.200 g (0.6 mmol) of photoadduct (**5b)** was dissolved in 1:1 mixture of *tert*-butanol and acetone (8 mL). The reaction mixture was cooled to 0 ^{o}C and a solution of NMO 0.12 g (0.9 mmol) in H_2O (0.3 mL) was added. After 15 min, 0.038 g of OsO_4 (0.15 mmol) in H_2O (0.2 mL) was added dropwise. After completion of addition the reaction mixture was stirred at room temperature for 48 h. Quenching with saturated aqueous Na_2SO_3 (4 mL) was followed by concentration *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with H_2O (2 x 6 mL). The solvent was removed *in vacuo* and the product purified by flash chromatography affording 0.10 g (45%). ^{1}H NMR (500 MHz, MeOD) δ 7.62 (dd, *J* = 7.1, 1.6, 1H), 7.55-7.59 (m, 1H), 7.51 (m, 1H), 7.38-7.33 (m, 1H), 5.21 (m, 1H), 5.15 (m, 1H), 4.97 (m, 1H), 4.74 (dd, *J* = 5.6, 2.8 Hz 1H), 4.67 (m, 1H), 4.42 (m, 1H), 4.21 (dd, *J* = 8.3, 2.8 Hz 1H), 1.59 (dd, *J* = 6.1, 2.8 Hz, 3H). ^{13}C NMR (126 MHz, MeOD) δ = 203.8, 169.1, 162.6, 136.4, 134.4, 132.0, 130.7, 129.0, 127.8, 99.2, 94.1, 82.1, 79.2, 79.1, 76.8, 64.1, 18.8.

2. Computational Details

Dihydroxylated **12**

B3LYP/6-311+G(d,p)

-1452.35331353 Hartrees

O	-3.5691	-0.6985	1.4608
C	-2.8412	-1.4667	-0.7408
C	-2.3481	-2.6226	0.1246
C	-1.0303	-2.0387	0.7212
C	-0.7062	-0.8232	-0.2492
O	-1.6306	-0.9071	-1.2826
C	-3.6624	-0.4070	0.0515
N	-0.8663	0.5161	0.4267
C	0.0903	0.9045	1.3422
C	1.3046	-0.0185	1.3295
C	-1.8847	1.4241	-0.0163
O	0.0160	1.8812	2.0650
C	-3.2113	1.0048	-0.2382
C	-4.1454	1.9314	-0.7088
C	-3.7989	3.2580	-0.9450
C	-2.4890	3.6666	-0.7141
C	-1.5402	2.7557	-0.2625
C	0.7324	-0.9761	-0.8282
N	1.6579	-0.3434	-0.0599
O	0.9471	-1.6206	-1.8331
C	3.1281	-0.4552	-0.1998
C	2.6125	0.5634	1.8630
O	3.6013	-0.1708	1.1159
H	-3.4123	-1.8185	-1.5978
H	-3.0536	-2.8874	0.9102
H	-1.2101	-1.6682	1.7274
H	-4.7100	-0.5076	-0.2529
H	1.0763	-0.9392	1.8824
H	-5.1630	1.6000	-0.8887
H	-4.5411	3.9603	-1.3053
H	-2.1955	4.6942	-0.8950
H	-0.5235	3.0814	-0.0936
H	3.3872	-1.4949	-0.4275
C	3.7951	0.4619	-1.2666
C	2.8538	0.3635	3.3446
H	2.6658	1.6279	1.6162
H	-3.8674	0.0779	1.9469
O	-2.0756	-3.7387	-0.7195
O	0.0015	-2.9920	0.8063
H	-2.1550	-4.5432	-0.1983
H	0.0423	-3.4536	-0.0444
H	3.8423	0.7390	3.6170
H	2.8020	-0.6964	3.6060
H	2.1040	0.9144	3.9165
C	5.3099	0.1773	-1.1983
C	3.5424	1.9523	-0.9828
C	3.2896	0.1181	-2.6793
H	3.8765	0.6762	-3.4152
H	2.2399	0.3797	-2.8175
H	3.3905	-0.9470	-2.8987
H	3.9938	2.5578	-1.7738
H	3.9884	2.2651	-0.0362
H	2.4739	2.1836	-0.9623
H	5.8389	0.7961	-1.9284
H	5.5261	-0.8699	-1.4326
H	5.7109	0.3940	-0.2065

Dihydroxylated **13**

B3LYP/6-311+G(d,p)

-1293.49376616 Hartree

O	-2.9905	-0.0111	2.5495
C	-1.5418	1.4230	1.3267
C	-1.9997	2.1705	0.0679
C	-1.0126	1.6681	-1.0467
C	0.0909	0.8784	-0.2406
O	-0.1438	1.1662	1.1350
C	-2.3250	0.1236	1.5448
N	-0.0370	-0.5713	-0.4568
C	1.0080	-1.4366	-0.1453
C	2.4121	-0.9044	-0.3352
C	-1.3539	-1.1700	-0.4925
O	0.8496	-2.6068	0.1341
C	-2.3673	-0.9093	0.4501
C	-3.5713	-1.6273	0.3526
C	-3.7832	-2.5585	-0.6521
C	-2.7791	-2.7954	-1.5897
C	-1.5755	-2.1091	-1.5019
C	1.5205	1.4194	-0.4636
N	2.5297	0.5359	-0.5140
O	1.7058	2.6322	-0.5070
C	3.9078	0.9379	-0.1675
C	3.4408	-1.1428	0.7870
O	4.4833	-0.2260	0.3969
H	-1.6453	2.0359	2.2197
H	-3.0323	1.9137	-0.2003
H	-1.5241	0.9778	-1.7152
H	2.7821	-1.4056	-1.2402
H	-4.3371	-1.4242	1.0908
H	-4.7247	-3.0920	-0.7083
H	-2.9297	-3.5142	-2.3867
H	-0.7834	-2.3062	-2.2132
H	4.4906	1.2224	-1.0459
H	3.8588	1.7742	0.5363
C	4.0161	-2.5361	0.8961
H	3.0071	-0.8215	1.7441
O	-1.8799	3.5551	0.2886
O	-0.5528	2.7282	-1.8475
H	-1.6475	3.9569	-0.5615
H	0.2604	3.0834	-1.4361
H	4.7894	-2.5585	1.6664
H	4.4631	-2.8423	-0.0528
H	3.2280	-3.2426	1.160

Fermi contact terms at B3LYP/6-31G(d,p)+1u+s (Bally, T.; Rablen, P. A. J. Org. Chem. 2011, 76, 4818-4830)

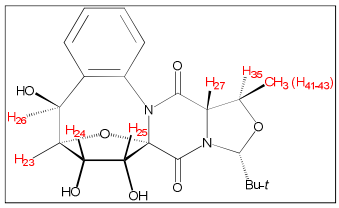
Cis-exo-dihydroxylated compound **12**

Raw Fermi contact terms

N	23	24	25	26	27	28	29	30	31	32	35	41	42	43	47	48	49	50	51	52	53	54	55
23	0	0.3	-0.6	7.1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0.3	0	5.7	-0.1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
25	-0.6	5.7	0	-0.1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
26	7.1	-0.1	-0.1	0	0	-0.5	0	0	0.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0
27	0	0	0	0	0	0	0	0	0	-0.2	9.7	-0.2	-0.2	-0.2	0	0	0	0	0	0	0	0	0
28	0	0	0	-0.5	0	0	8.3	1.5	0.4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
29	0	0	0	0	0	8.3	0	8.3	1.1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	1.5	8.3	0	9.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
31	0	0	0	0.5	0	0.4	1.1	9.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
32	0	0	0	0	-0.2	0	0	0	0	0	0	0.1	0.1	0.1	0	0	0	0	0	0	0	0	0
35	0	0	0	0	9.7	0	0	0	0	0	0	6.4	6.4	6.4	0	0	0	0	0	0	0	0	0
41	0	0	0	0	-0.2	0	0	0	0	0.1	6.4	0	-13.9	-13.9	0	0	0	0	0	0	0	0	0
42	0	0	0	0	-0.2	0	0	0	0	0.1	6.4	-13.9	0	-13.9	0	0	0	0	0	0	0	0	0
43	0	0	0	0	-0.2	0	0	0	0	0.1	6.4	-13.9	-13.9	0	0	0	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-13.9	-13.9	0.4	0.4	0.4	0.5	0.5	0.5
48	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-13.9	0	-13.9	0.4	0.4	0.4	0.5	0.5	0.5
49	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-13.9	-13.9	0	0.4	0.4	0.4	0.5	0.5	0.5
50	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.4	0.4	0.4	0	-13.7	-13.7	0.4	0.4	0.4
51	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.4	0.4	0.4	-13.7	0	-13.7	0.4	0.4	0.4
52	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.4	0.4	0.4	-13.7	-13.7	0	0.4	0.4	0.4
53	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.5	0.5	0.5	0.4	0.4	0.4	0	-13.6	-13.6
54	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.5	0.5	0.5	0.4	0.4	0.4	-13.6	0	-13.6
55	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.5	0.5	0.5	0.4	0.4	0.4	-13.6	-13.6	0

Scaled by 0.9155 (constants greater than 0.1 Hz in absolute value are shown)

N	23	24	25	26	27	28	29	30	31	32	35	41	42	43	47	48	49	50	51	52	53	54	55
23		0.27	-0.55	6.50																			
24	0.27		5.22																				
25	-0.55	5.22																					
26	6.50					-0.46			0.46														
27										-0.18	8.88	-0.18	-0.18	-0.18									
28				-0.46			7.60	1.37	0.37														
29						7.60		7.60	1.01														
30						1.37	7.60		8.42														
31				0.46		0.37	1.01	8.42															
32					-0.18																		
35					8.88							5.86	5.86	5.86									
41					-0.18						5.86		-12.73	-12.73									
42					-0.18						5.86	-12.73		-12.73									
43					-0.18						5.86	-12.73	-12.73										
47																-12.73	-12.73	0.37	0.37	0.37	0.46	0.46	0.46
48															-12.73		-12.73	0.37	0.37	0.37	0.46	0.46	0.46
49															-12.73	-12.73		0.37	0.37	0.37	0.46	0.46	0.46
50															0.37	0.37	0.37		-12.54	-12.54	0.37	0.37	0.37
51															0.37	0.37	0.37	-12.54		-12.54	0.37	0.37	0.37
52															0.37	0.37	0.37	-12.54	-12.54		0.37	0.37	0.37
53															0.46	0.46	0.46	0.37	0.37	0.37		-12.45	-12.45
54															0.46	0.46	0.46	0.37	0.37	0.37	-12.45		-12.45
55															0.46	0.46	0.46	0.37	0.37	0.37	-12.45	-12.45	



cis-endo-dihydroxylated alternative isomer of **12**

Raw Fermi contact terms

N	23	24	25	26	27	28	29	30	31	32	35	41	42	43	47	48	49	50	51	52	53	54	55
23	0	7.3	0.4	7.4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
24	7.3	0	7.3	-0.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
25	0.4	7.3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
26	7.4	-0.2	0	0	0	-0.5	0.1	0	0.4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
27	0	0	0	0	0	0	0	0	0	-0.3	9.8	-0.2	-0.2	-0.2	0	0	0	0	0	0	0	0	0
28	0	0	0	-0.5	0	0	8.3	1.5	0.4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
29	0	0	0	0.1	0	8.3	0	8.3	1.1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	1.5	8.3	0	9.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
31	0	0	0	0.4	0	0.4	1.1	9.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
32	0	0	0	0	-0.3	0	0	0	0	0	-0.1	0.1	0.1	0.1	0	0	0	0	0	0	0	0	0
35	0	0	0	0	9.8	0	0	0	0	-0.1	0	6.4	6.4	6.4	0	0	0	0	0	0	0	0	0
41	0	0	0	0	-0.2	0	0	0	0	0.1	6.4	0	-13.9	-13.9	0	0	0	0	0	0	0	0	0
42	0	0	0	0	-0.2	0	0	0	0	0.1	6.4	-13.9	0	-13.9	0	0	0	0	0	0	0	0	0
43	0	0	0	0	-0.2	0	0	0	0	0.1	6.4	-13.9	-13.9	0	0	0	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-14	-14	0.4	0.4	0.4	0.5	0.5	0.5
48	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-14	0	-14	0.4	0.4	0.4	0.5	0.5	0.5
49	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-14	-14	0	0.4	0.4	0.4	0.5	0.5	0.5
50	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.4	0.4	0.4	0	-13.7	-13.7	0.4	0.4	0.4
51	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.4	0.4	0.4	-13.7	0	-13.7	0.4	0.4	0.4
52	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.4	0.4	0.4	-13.7	-13.7	0	0.4	0.4	0.4
53	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.5	0.5	0.5	0.4	0.4	0.4	0	-13.6	-13.6
54	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.5	0.5	0.5	0.4	0.4	0.4	-13.6	0	-13.6
55	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.5	0.5	0.5	0.4	0.4	0.4	-13.6	-13.6	0

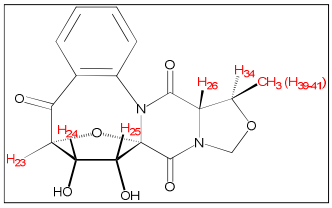
Scaled by 0.9155 (the characteristic spin-spin coupling constant of the bridgehead proton not matching the experimental spectrum is highlighted in yellow)

N	23	24	25	26	27	28	29	30	31	32	35	41	42	43	47	48	49	50	51	52	53	54	55
23		6.68	0.37	6.77																			
24	6.68		6.68	-0.18																			
25	0.37	6.68																					
26	6.77	-0.18				-0.46			0.37														
27										-0.27	8.97	-0.18	-0.18	-0.18									
28				-0.46			7.60	1.37	0.37														
29						7.60		7.60	1.01														
30						1.37	7.60		8.42														
31				0.37		0.37	1.01	8.42															
32					-0.27																		
35					8.97							5.86	5.86	5.86									
41					-0.18						5.86		-12.73	-12.73									
42					-0.18						5.86	-12.73		-12.73									
43					-0.18						5.86	-12.73	-12.73										
47																-12.82	-12.82	0.37	0.37	0.37	0.46	0.46	0.46
48															-12.82		-12.82	0.37	0.37	0.37	0.46	0.46	0.46
49															-12.82	-12.82		0.37	0.37	0.37	0.46	0.46	0.46
50															0.37	0.37	0.37		-12.54	-12.54	0.37	0.37	0.37
51															0.37	0.37	0.37	-12.54		-12.54	0.37	0.37	0.37
52															0.37	0.37	0.37	-12.54	-12.54		0.37	0.37	0.37
53															0.46	0.46	0.46	0.37	0.37	0.37		-12.45	-12.45
54															0.46	0.46	0.46	0.37	0.37	0.37	-12.45		-12.45
55															0.46	0.46	0.46	0.37	0.37	0.37	-12.45	-12.45	

Cis-exo-dihydroxylated ketone **13**

Raw Fermi contact terms

N	23	24	25	26	27	28	29	30	31	32	34	39	40	41
23	0	0.4	-0.7	0.1	0.1	0.1	-0.1	0.1	0	0	0	0	0	0
24	0.4	0	6.1	0	0	0	0	0	0.1	0	0	0	0	0
25	-0.7	6.1	0	0	0	0	0	0	0	0	0	0	0	0
26	0.1	0	0	0	0	0	0	0	-0.4	-0.6	9.8	-0.3	-0.3	-0.3
27	0.1	0	0	0	0	8.8	1.6	0.5	0	0	0	0	0	0
28	0.1	0	0	0	8.8	0	8.2	1.1	0	0	0	0	0	0
29	-0.1	0	0	0	1.6	8.2	0	8.9	0	0	0	0	0	0
30	0.1	0	0	0	0.5	1.1	8.9	0	0	0	0	0	0	0
31	0	0.1	0	-0.4	0	0	0	0	0	-5.5	-0.1	0.1	0.1	0.1
32	0	0	0	-0.6	0	0	0	0	-5.5	0	0.4	0	0	0
34	0	0	0	9.8	0	0	0	0	-0.1	0.4	0	6.5	6.5	6.5
39	0	0	0	-0.3	0	0	0	0	0.1	0	6.5	0	-14.2	-14.2
40	0	0	0	-0.3	0	0	0	0	0.1	0	6.5	-14.2	0	-14.2
41	0	0	0	-0.3	0	0	0	0	0.1	0	6.5	-14.2	-14.2	0



Scaled by 0.9155 (constants greater than 0.1 Hz in absolute value are shown)

N	23	24	25	26	27	28	29	30	31	32	34	39	40	41
23		0.37	-0.64											
24	0.37		5.58											
25	-0.64	5.58												
26									-0.37	-0.55	8.97	-0.27	-0.27	-0.27
27						8.06	1.46	0.46						
28					8.06		7.51	1.01						
29					1.46	7.51		8.15						
30					0.46	1.01	8.15							
31				-0.37						-5.04				
32				-0.55					-5.04		0.37			
34				8.97						0.37		5.95	5.95	5.95
39				-0.27							5.95		-13.00	-13.00
40				-0.27							5.95	-13.00		-13.00
41				-0.27							5.95	-13.00	-13.00	

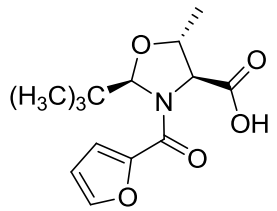
cis-endo-dihydroxylated alternative isomer of **13**

Raw Fermi contact terms

N	23	24	25	26	27	28	29	30	31	32	34	39	40	41
23	0	8.7	0.2	0	0	0.1	0.1	-0.1	0	0	0	0	0	0
24	8.7	0	6.2	0	0	0	0	0	0	0	0	0	0	0
25	0.2	6.2	0	0	0	0	0	0	0.1	0.1	0	0	0	0
26	0	0	0	0	0	0	0	0	-0.6	-0.3	9.2	-0.2	-0.2	-0.2
27	0	0	0	0	0	8.7	1.6	0.4	0	0	0	0	0	0
28	0.1	0	0	0	8.7	0	8.1	0.9	0	0	0	0	0	0
29	0.1	0	0	0	1.6	8.1	0	9.3	0	0	0	0	0	0
30	-0.1	0	0	0	0.4	0.9	9.3	0	0	0	0	0	0	0
31	0	0	0.1	-0.6	0	0	0	0	0	-5.1	-0.6	0.1	0.1	0.1
32	0	0	0.1	-0.3	0	0	0	0	-5.1	0	0.3	0	0	0
34	0	0	0	9.2	0	0	0	0	-0.6	0.3	0	6.5	6.5	6.5
39	0	0	0	-0.2	0	0	0	0	0.1	0	6.5	0	-14	-14
40	0	0	0	-0.2	0	0	0	0	0.1	0	6.5	-14	0	-14
41	0	0	0	-0.2	0	0	0	0	0.1	0	6.5	-14	-14	0

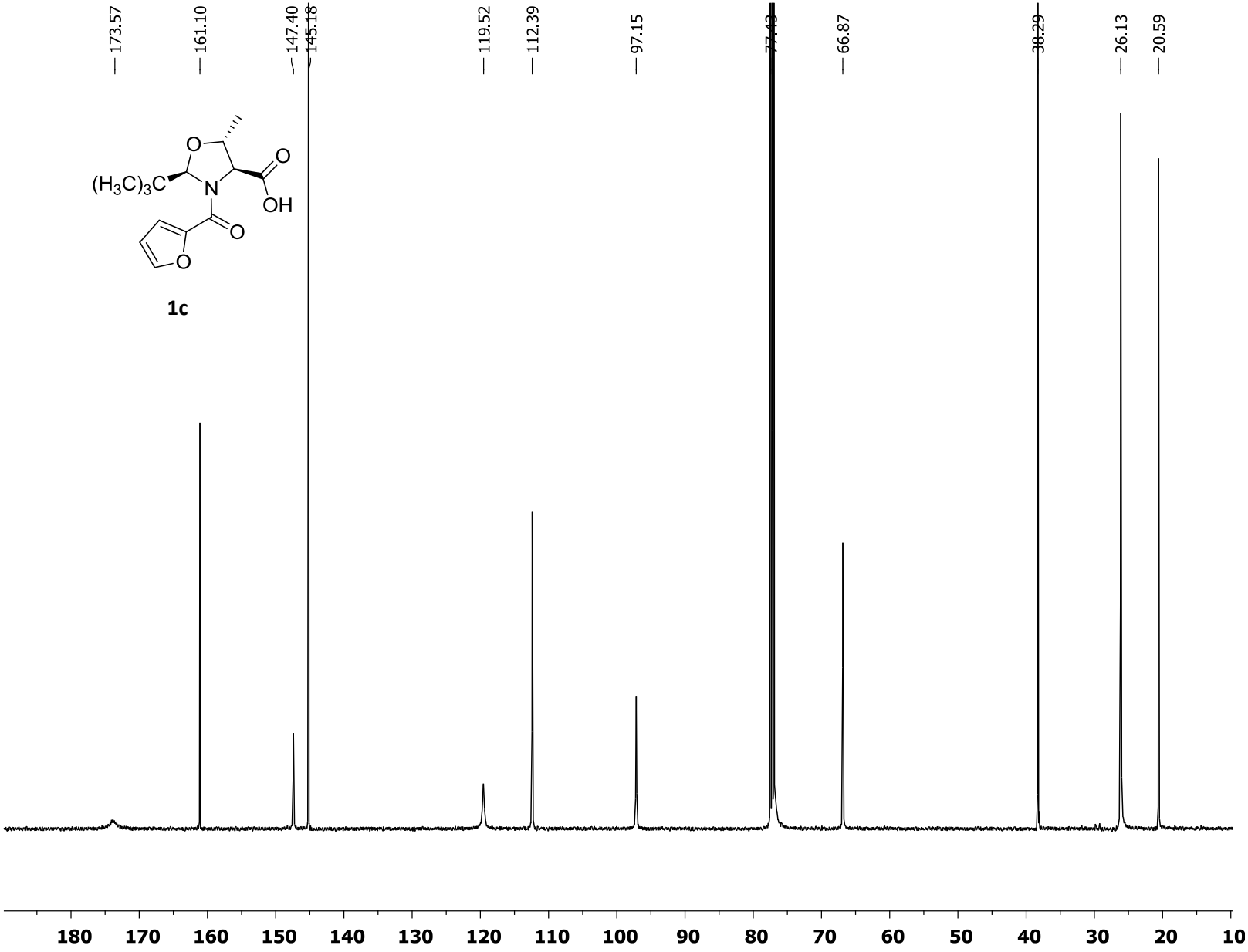
Scaled by 0.9155 (the characteristic spin-spin coupling constant of the bridgehead proton not matching the experimental spectrum is highlighted in yellow)

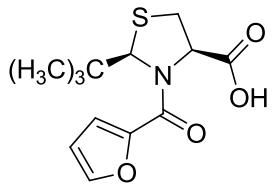
N	23	24	25	26	27	28	29	30	31	32	34	39	40	41
23		7.96	0.18											
24	7.96		5.68											
25	0.18	5.68												
26									-0.55	-0.27	8.42	-0.18	-0.18	-0.18
27						7.96	1.46	0.37						
28					7.96		7.42	0.82						
29					1.46	7.42		8.51						
30					0.37	0.82	8.51							
31				-0.55						-4.67	-0.55			
32				-0.27					-4.67		0.27			
34				8.42					-0.55	0.27		5.95	5.95	5.95
39				-0.18							5.95		-12.82	-12.82
40				-0.18							5.95	-12.82		-12.82
41				-0.18							5.95	-12.82	-12.82	


O
(H3C)3C
N
O
OH
O
O

1c

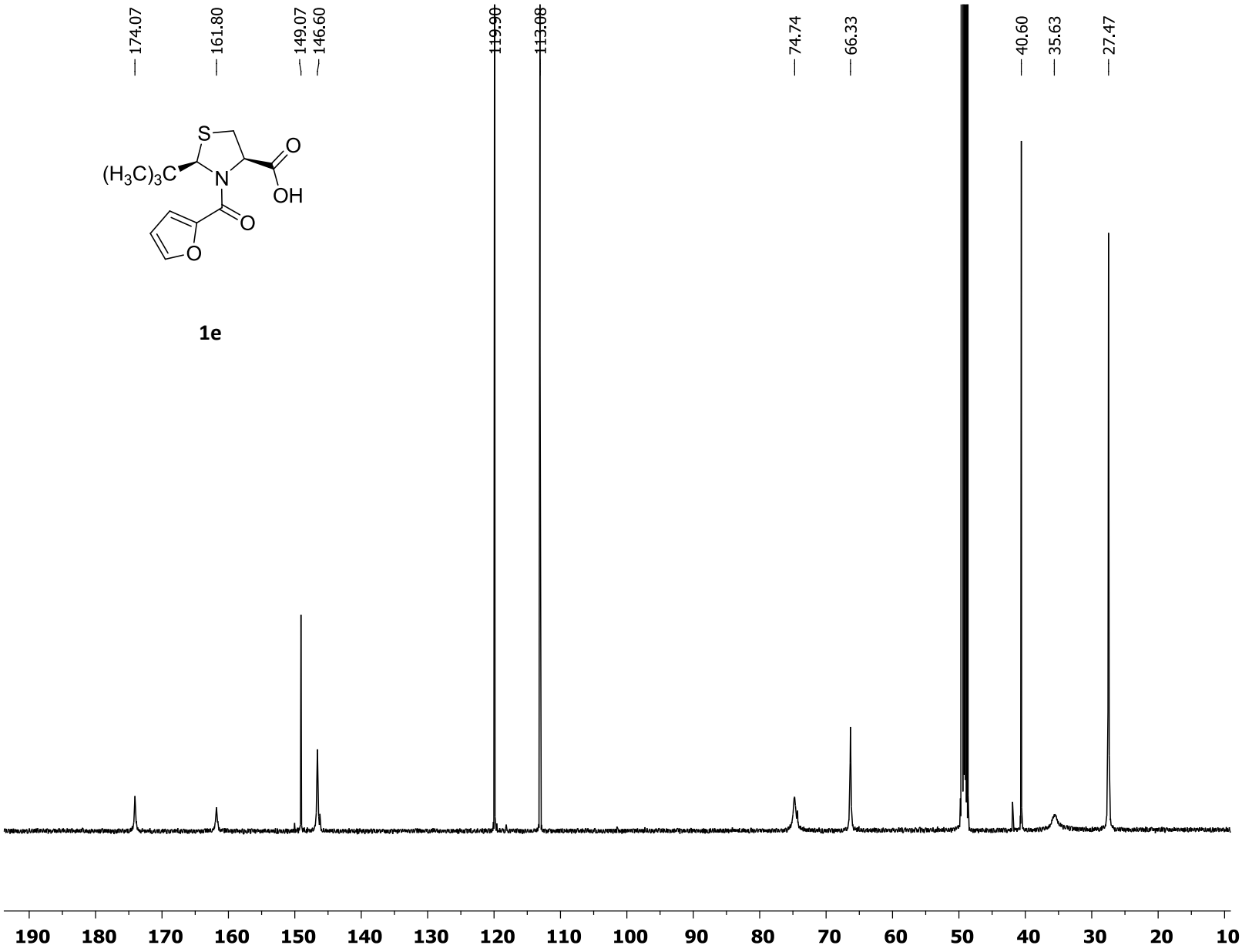
1.00
1.02
1.04
1.02
1.12
1.04
3.13
9.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


173.57
161.10
147.40
145.18
119.52
112.39
97.15
77.42
66.87
38.29
26.13
20.59
O
O
(H3C)3C
N
OH
O
O
1c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

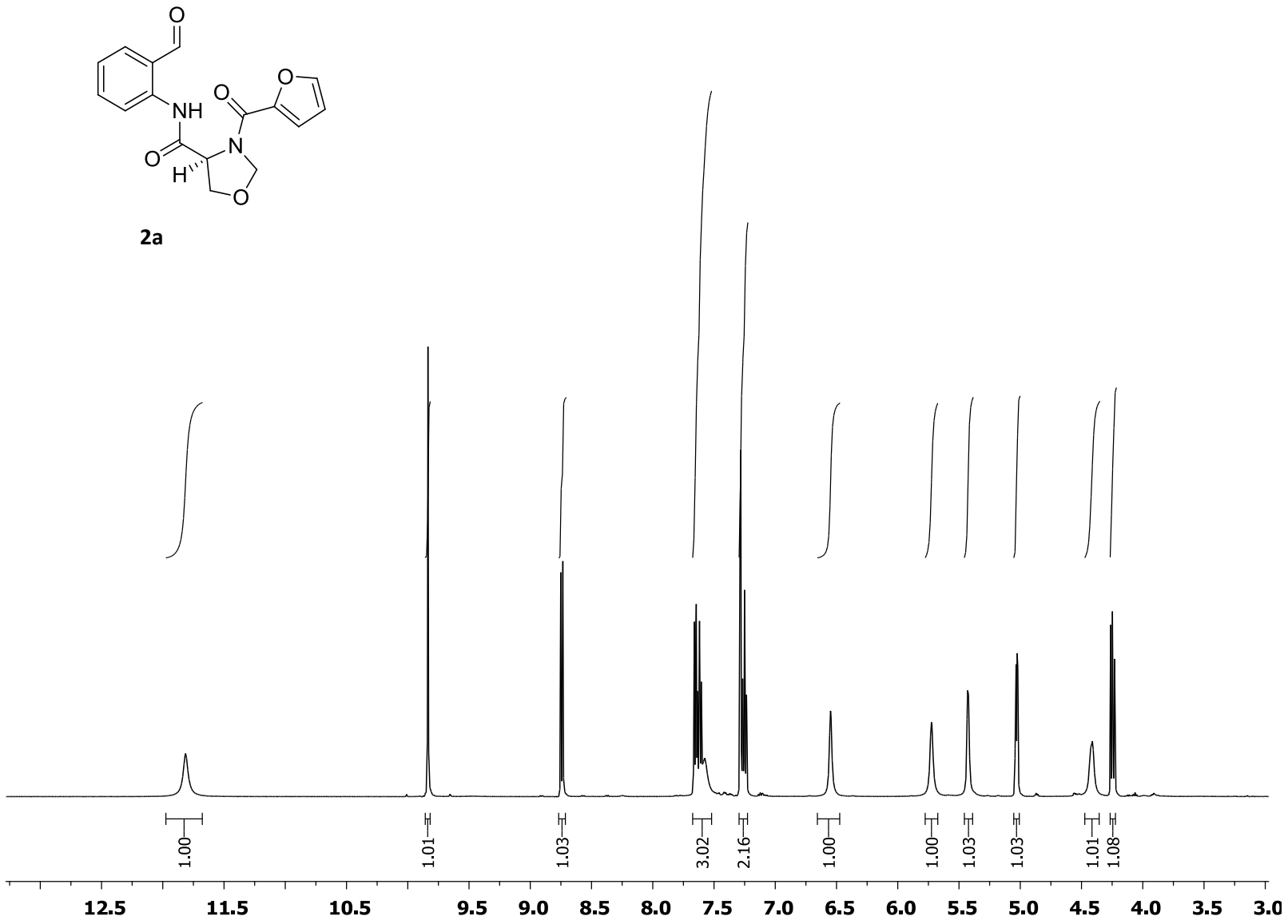

S
O
(H3C)3C
N
OH
O
O

1e

1.06
1.06
1.10
1.07
1.00
1.12
1.10
9.88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


174.07
161.80
149.07
146.60
119.90
113.08
74.74
66.33
40.60
35.63
27.47
S
O
(H3C)3C
N
OH
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

1e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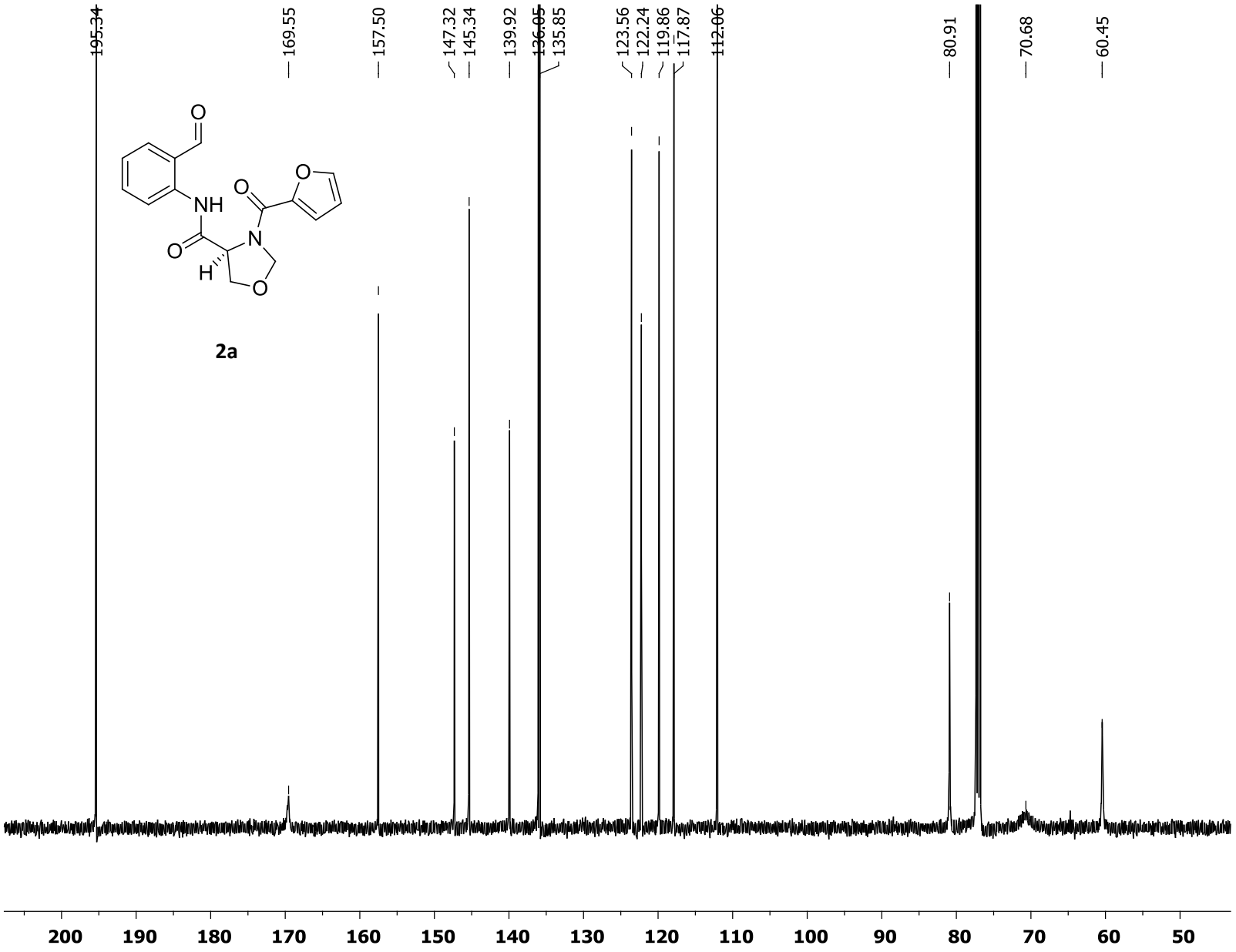
NH
O
O
O
N
H
O
2a
1.00
1.01
1.03
3.02
2.16
1.00
1.00
1.03
1.03
1.01
1.08
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0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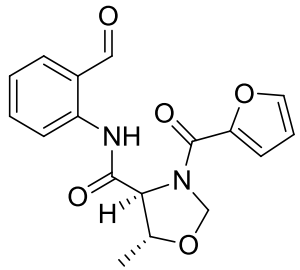
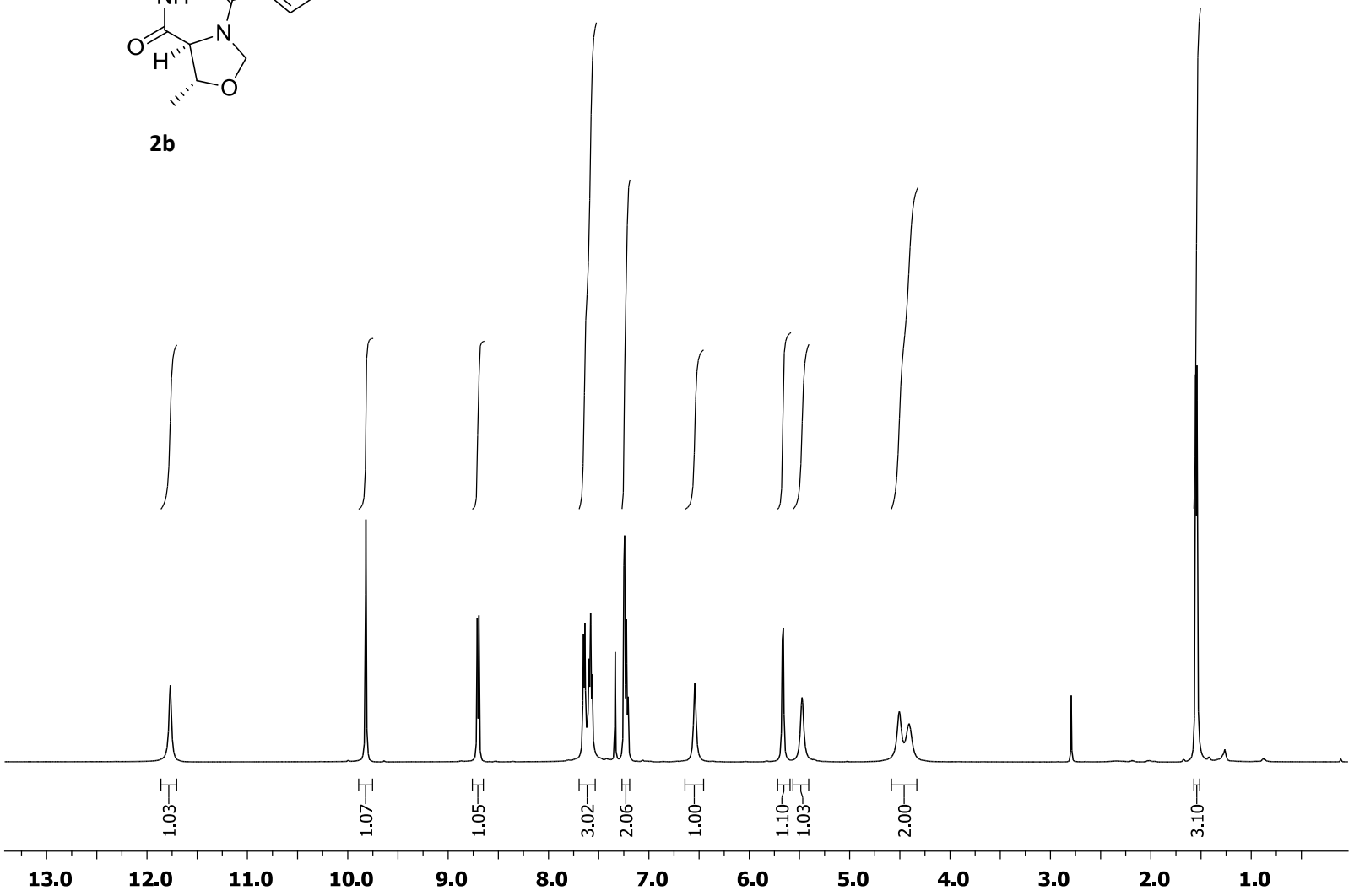
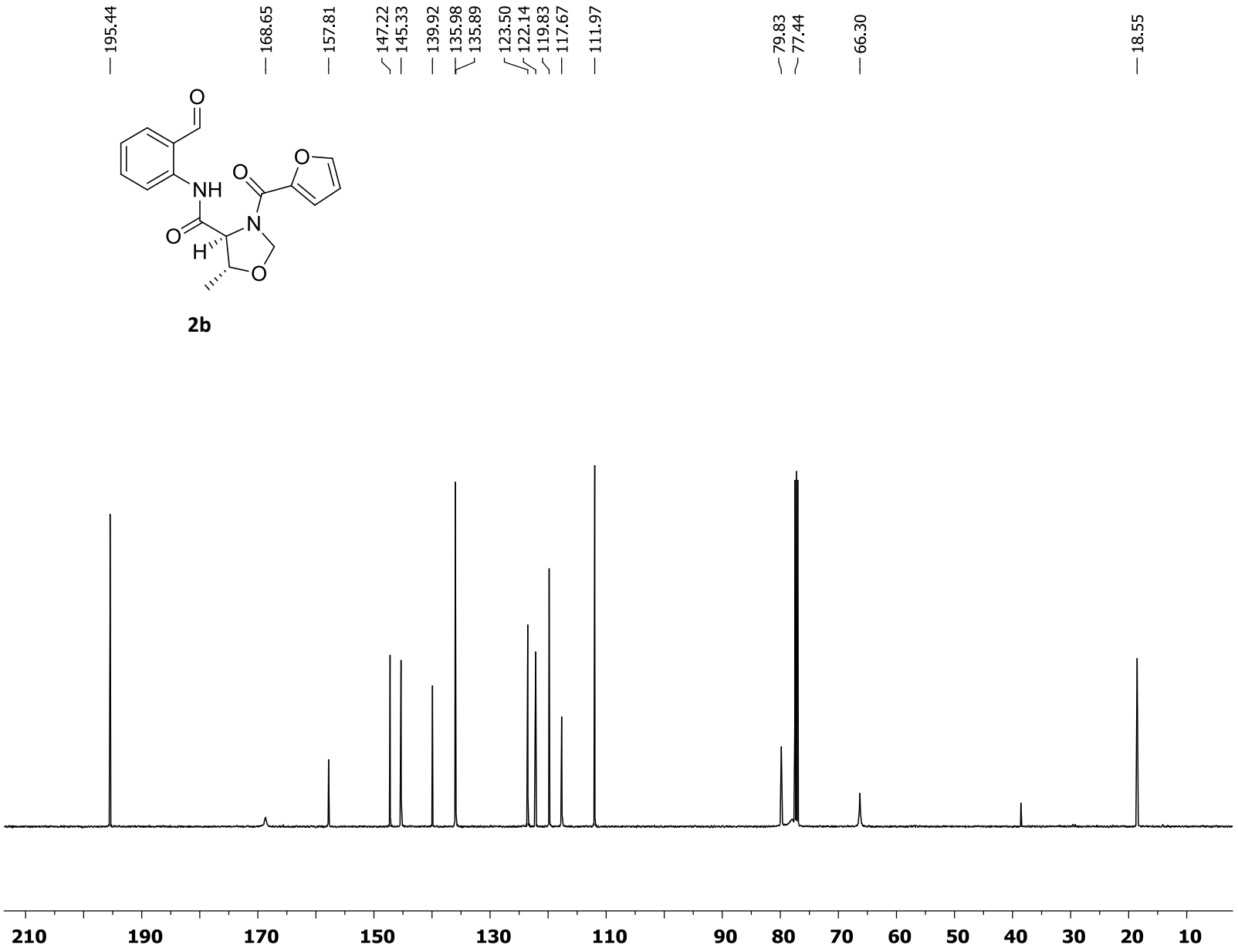
169.55
157.50
147.32
145.34
139.92
136.05
135.85
123.56
122.24
119.86
117.87
112.06
80.91
70.68
60.45
O
NH
O
O
O
N
H
O
2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50


O
NH
O
O
N
H
O
O

2b


1.03
1.07
1.05
3.02
2.06
1.00
1.10
1.03
2.00
3.10
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0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168.65
157.81
147.22
145.33
139.92
135.98
135.89
123.50
122.14
119.83
117.67
111.97
79.83
77.44
66.30
18.55
O
NH
O
O
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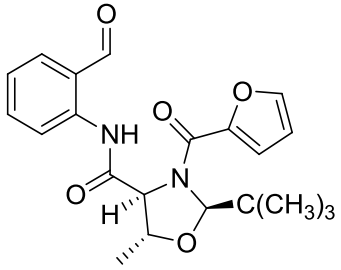
2b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C(CH3)3
O

2c

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2.01
2.04
1.14
1.06
1.00
1.06
1.01
3.09
9.18
13.0
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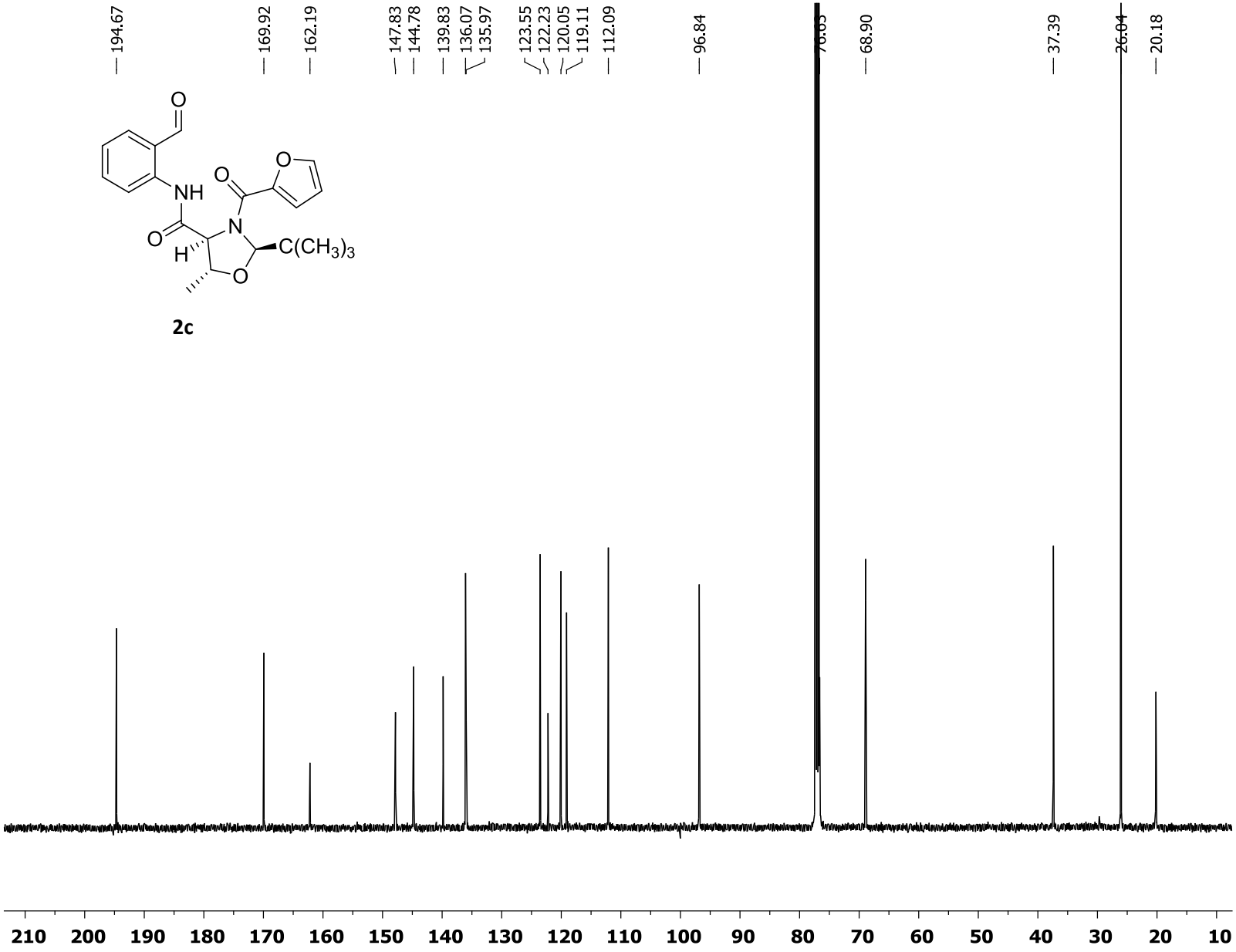
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119.11
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96.84
68.90
37.39
26.04
20.18
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O
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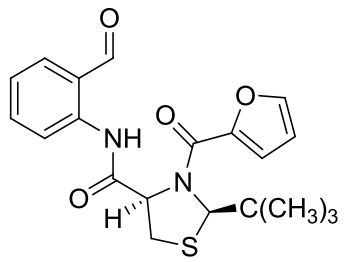
2c


O
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O
N
H
C(CH3)3
S

2e

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1.04
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0.95
1.43
1.00
0.97
1.04
1.07
1.08
9.14
12.5
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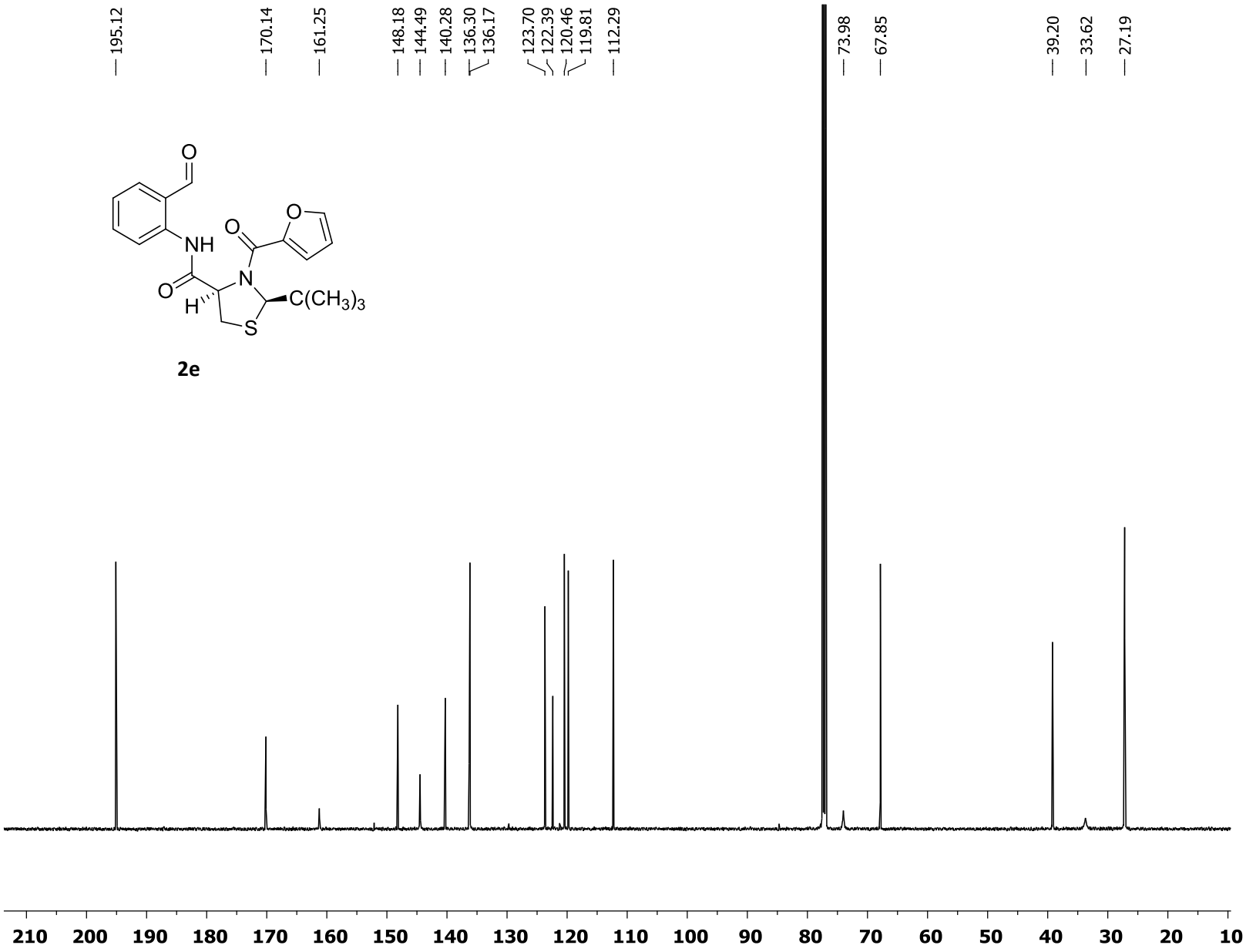
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120.46
119.81
112.29
73.98
67.85
39.20
33.62
27.19
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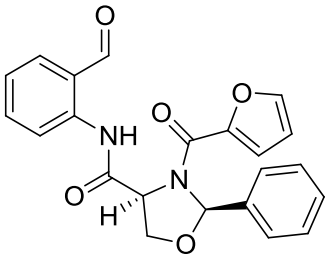
O
N
O
H
S
C(CH3)3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

2e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N
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2d

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2.02
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0.96
1.00
1.04
0.91
1.02
12.5
12.0
11.5
11.0
10.5
10.0
9.5
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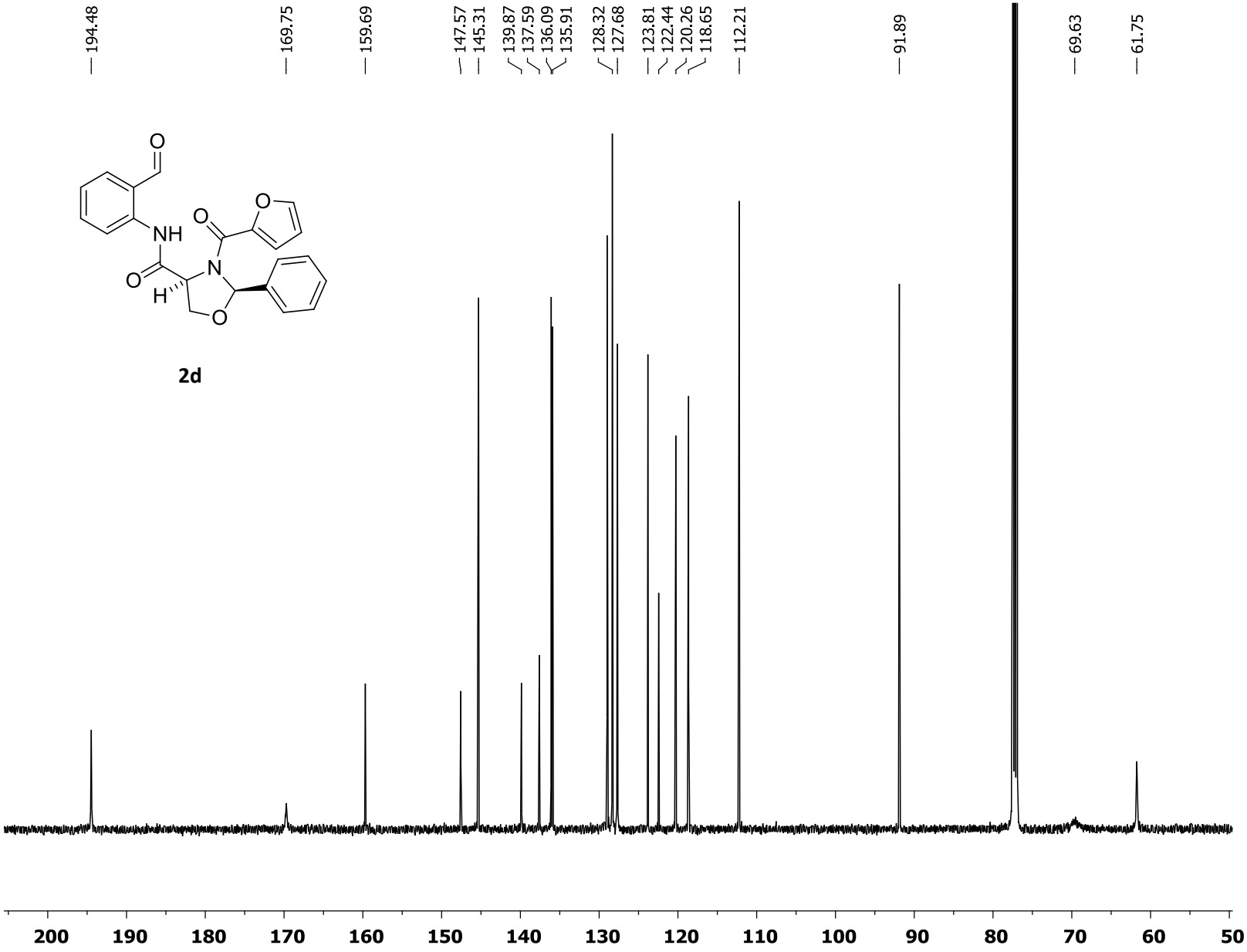
3.5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136.09
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128.32
127.68
123.81
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120.26
118.65
112.21
91.89
69.63
61.75
O
NH
O
O
N
H
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170
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150
140
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110
100
90
80
70
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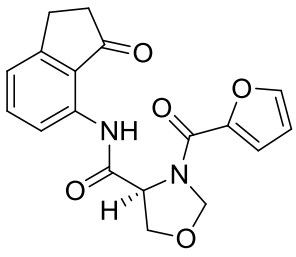
50

2d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NH
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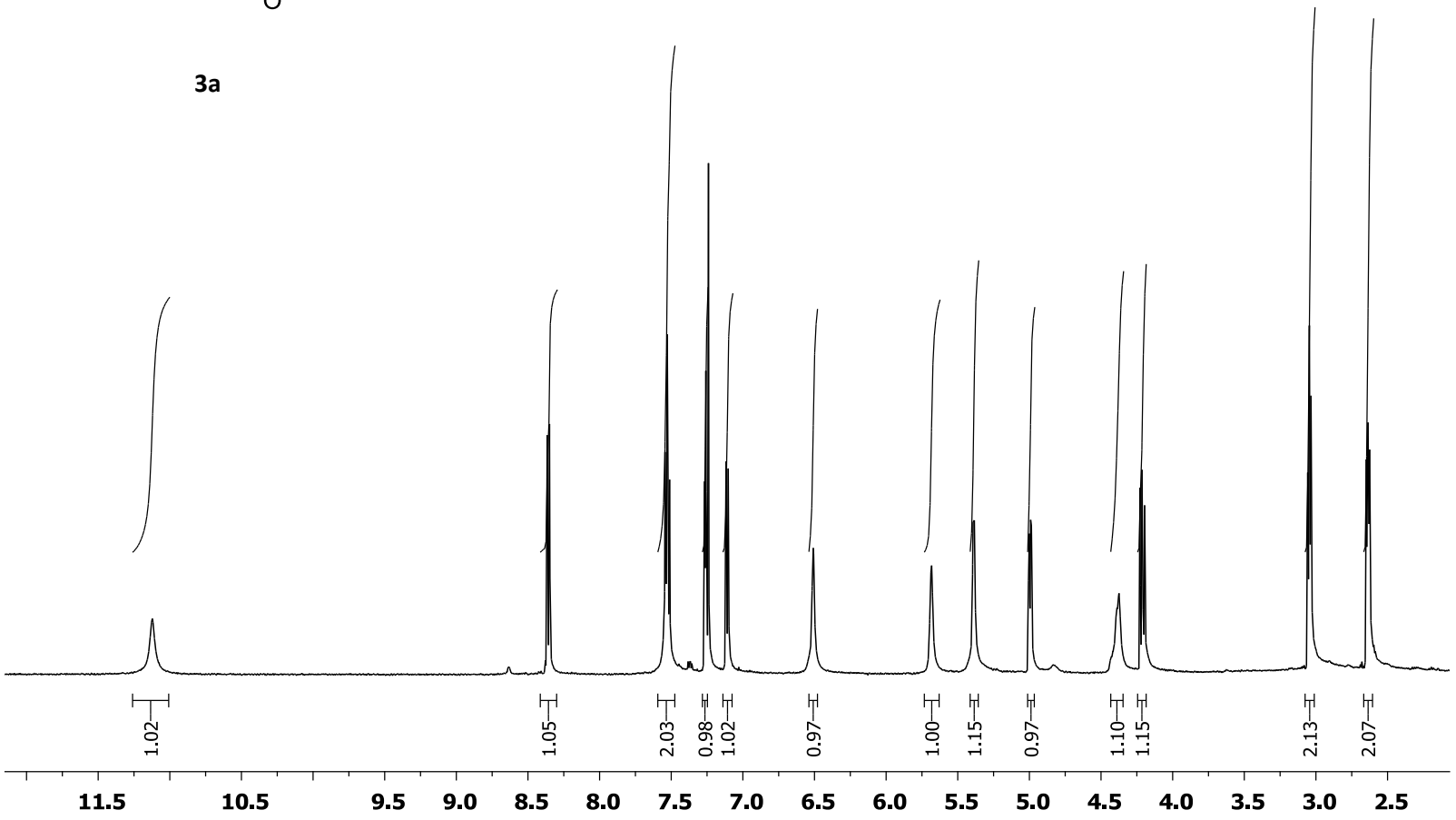
O
N
H
O

3a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1.15
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1.10
1.15
2.13
2.07
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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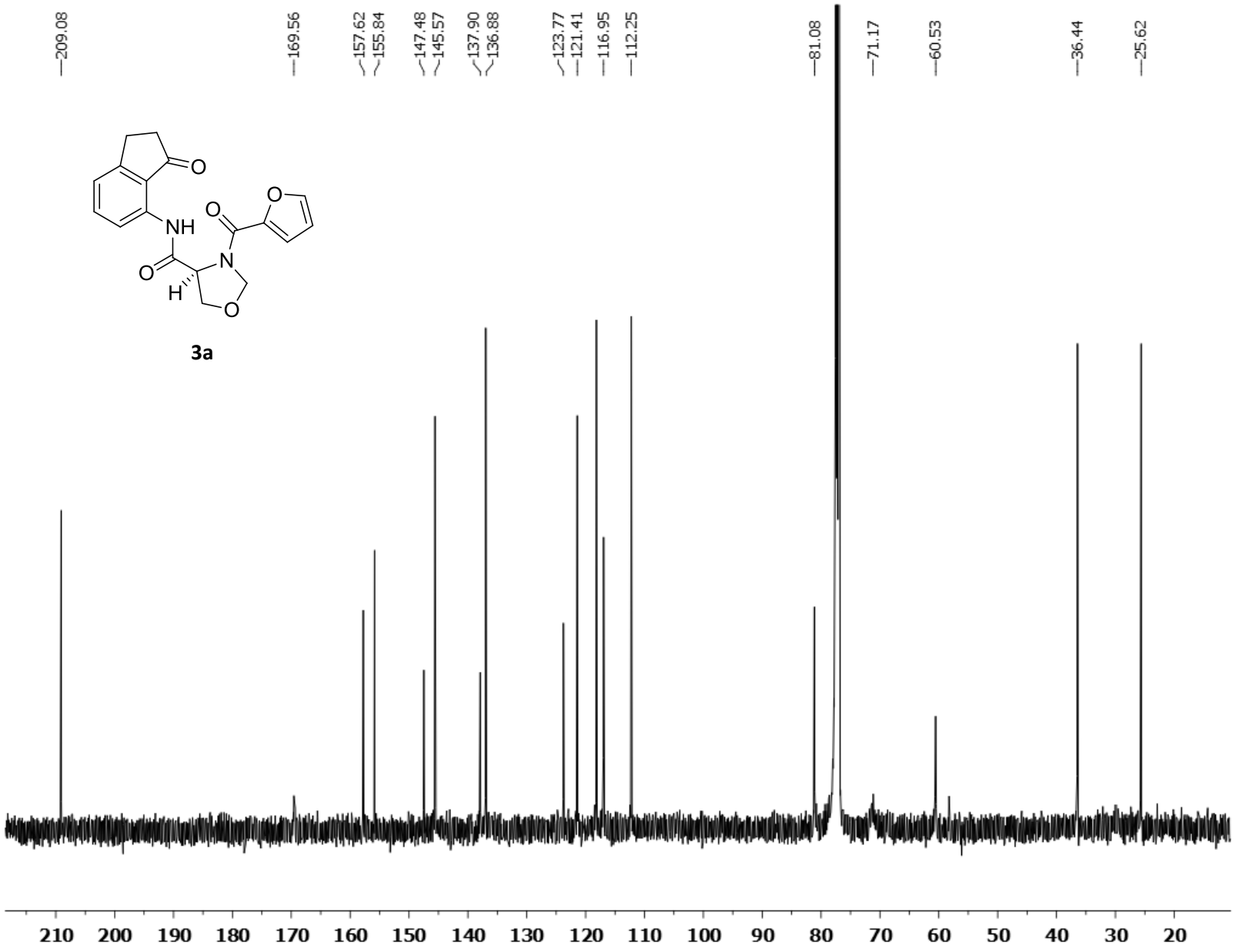
5.0
4.5
4.0
3.5
3.0
2.5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136.88
123.77
121.41
116.95
112.25
81.08
71.17
60.53
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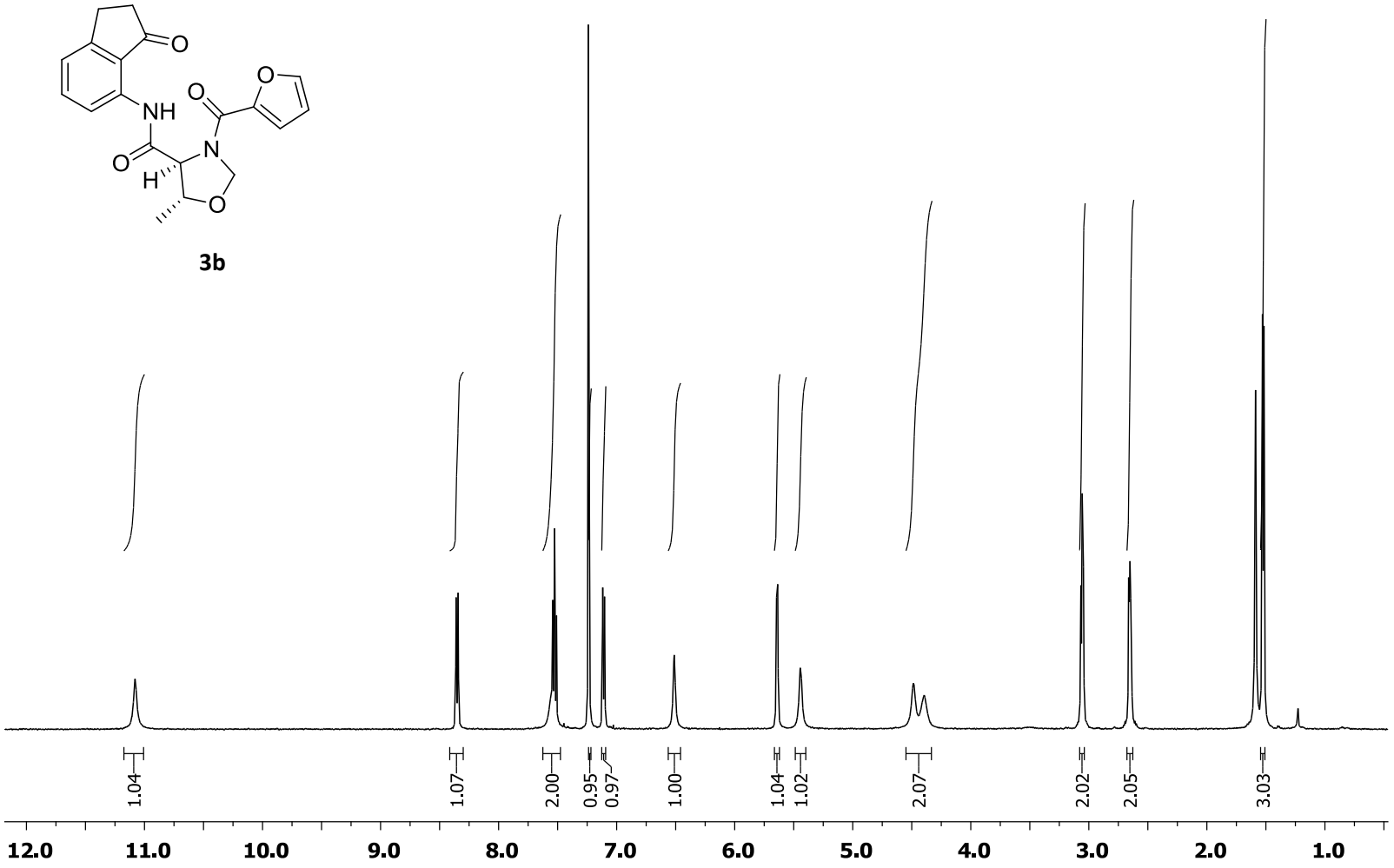
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

3a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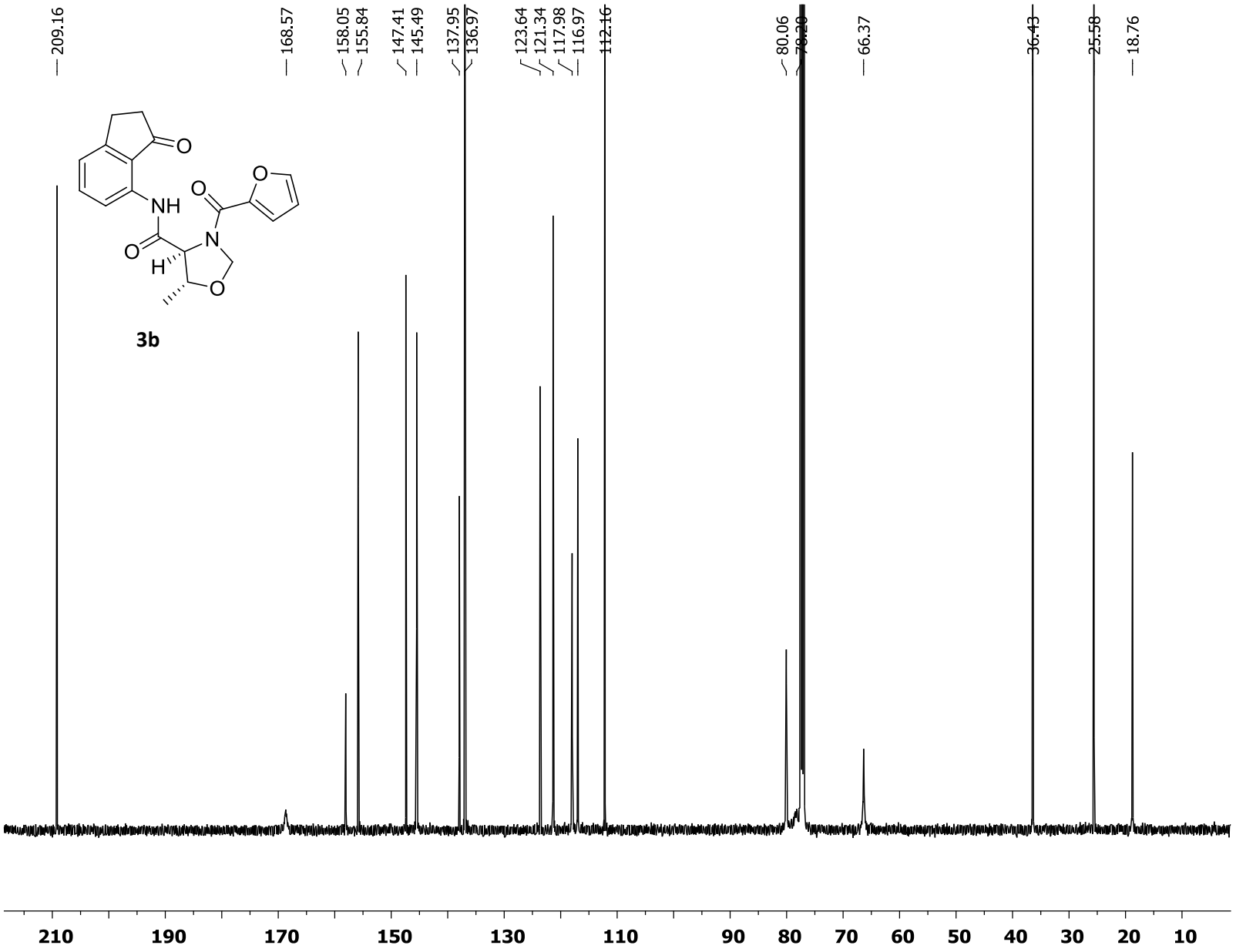
O
NH
O
N
O
H
O
1.04
1.07
2.00
0.95
0.97
1.00
1.04
1.02
2.07
2.02
2.05
3.03
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

3b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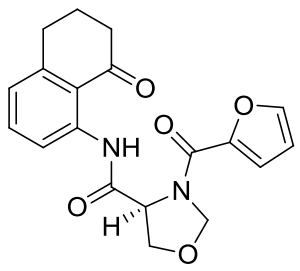
116.97
112.16
80.06
66.37
36.43
25.58
18.76
O
O
NH
O
O
N
H
O
3b
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10


O
NH
O
O
N
H
O
O

4a

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1.00
1.98
0.99
1.05
1.01
1.10
1.12
1.07
1.10
1.14
2.20
2.16
2.20
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11.5
10.5
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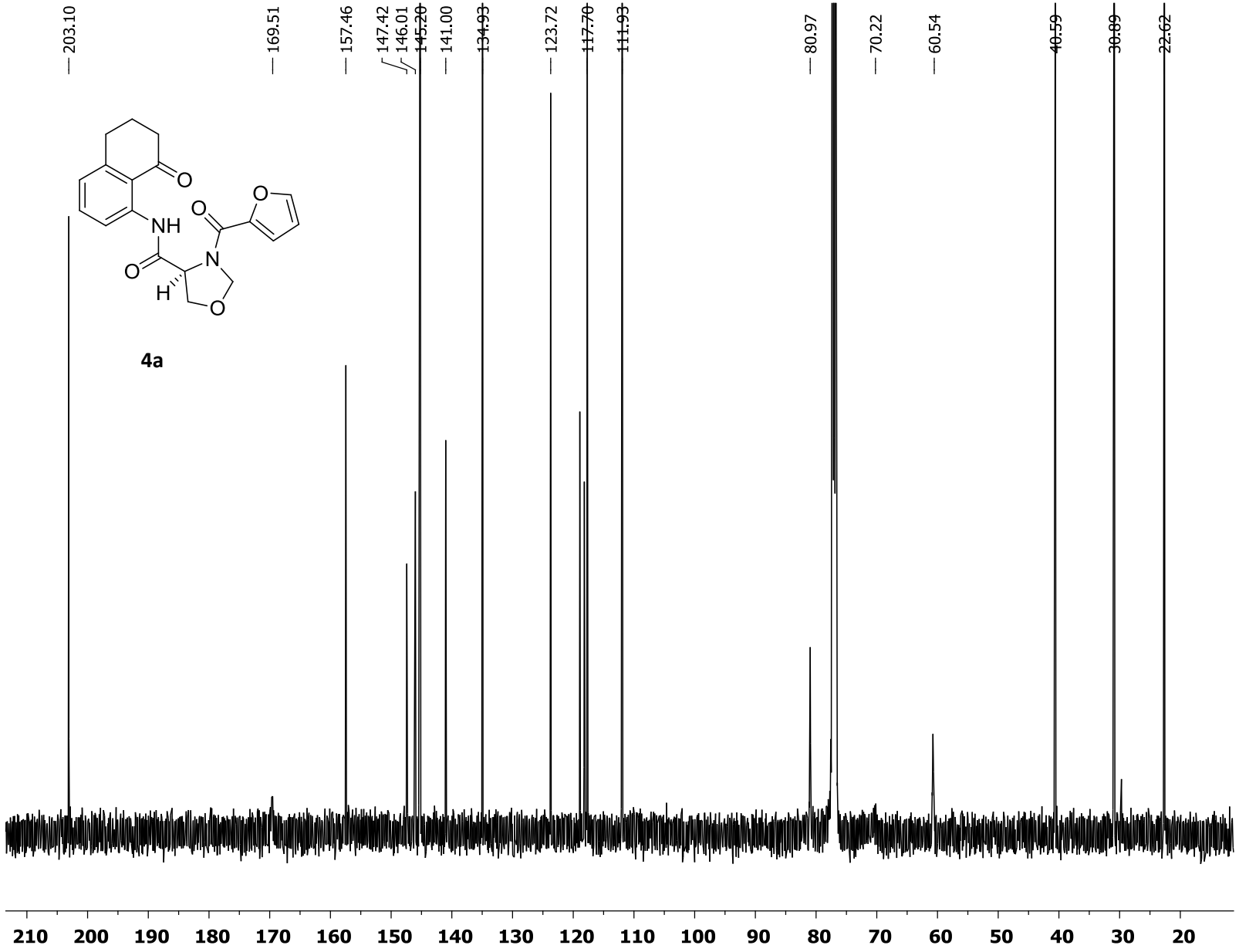
3.5
2.5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111.93
80.97
70.22
60.54
40.59
30.89
22.62
O
NH
O
O
O
N
H
O
4a
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200
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170
160
150
140
130
120
110
100
90
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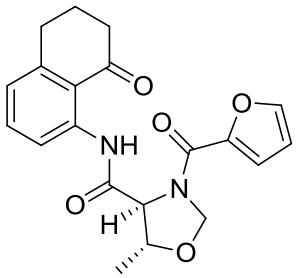
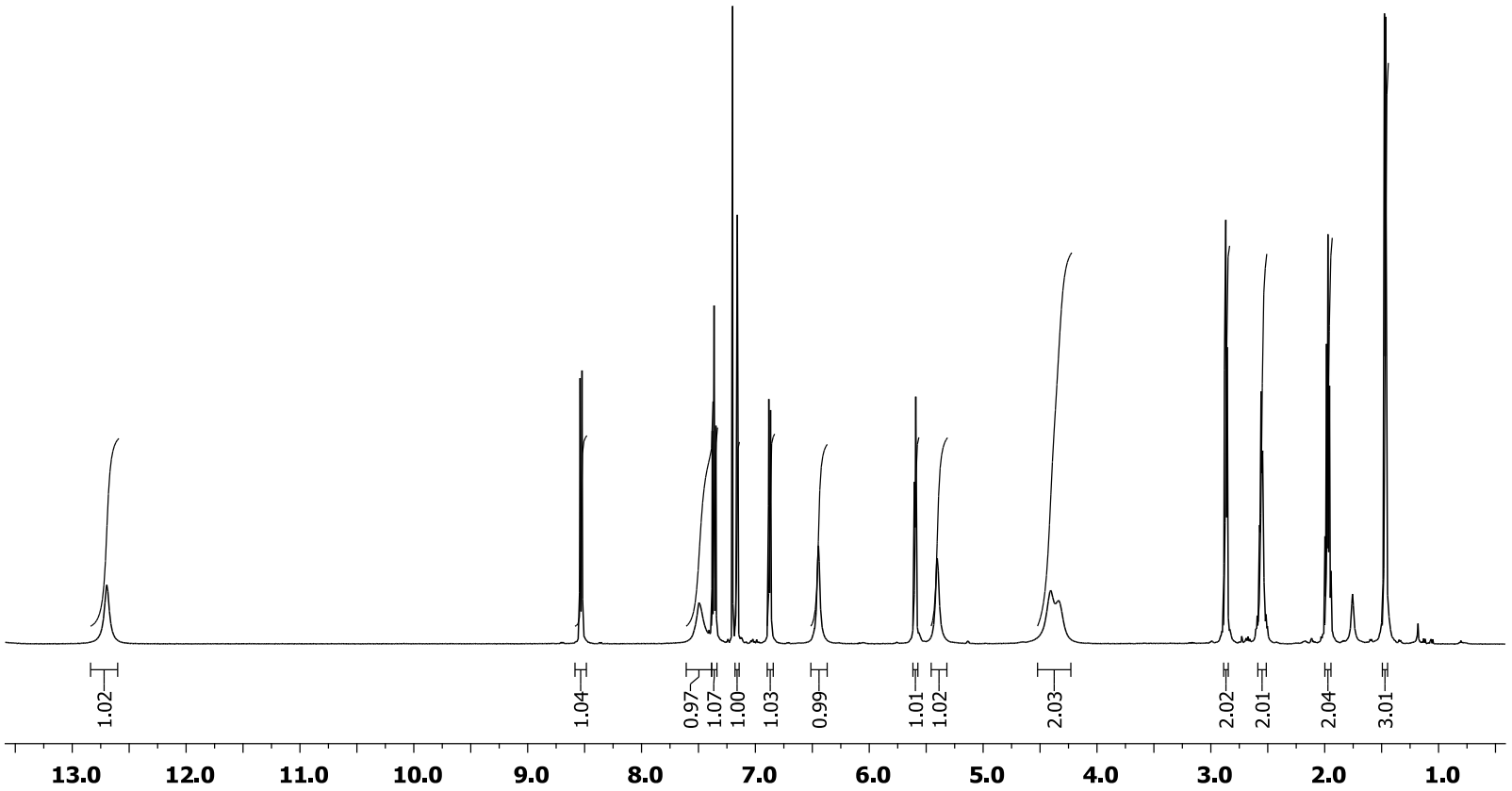
30
20


O
NH
O
O
O
N
H
O

4b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1.04
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1.00
1.03
0.99
1.01
1.02
2.03
2.02
2.01
2.04
3.01
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6.0
5.0
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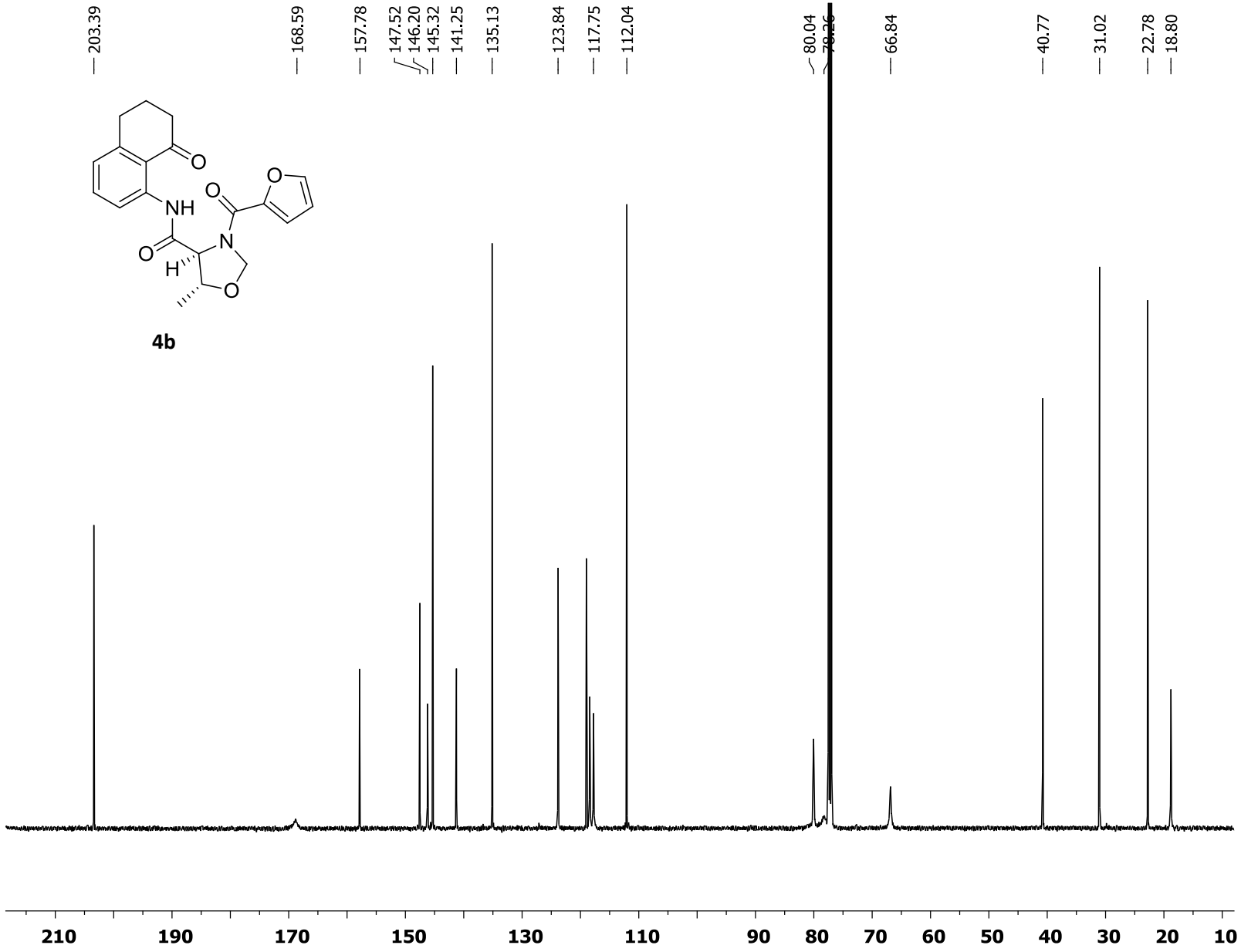
3.0
2.0
1.0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135.13
123.84
117.75
112.04
80.04
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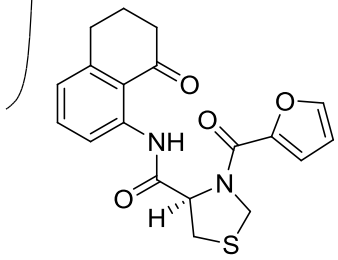
66.84
40.77
31.02
22.78
18.80
O
O
O
NH
O
N
H
O
4b
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10


O
NH
O
O
N
O
H
S

4f

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0.83
1.07
1.04
1.08
2.11
1.15
1.18
2.32
2.11
2.20
1.66
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12.5
12.0
11.5
11.0
10.5
10.0
9.5
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8.0
7.5
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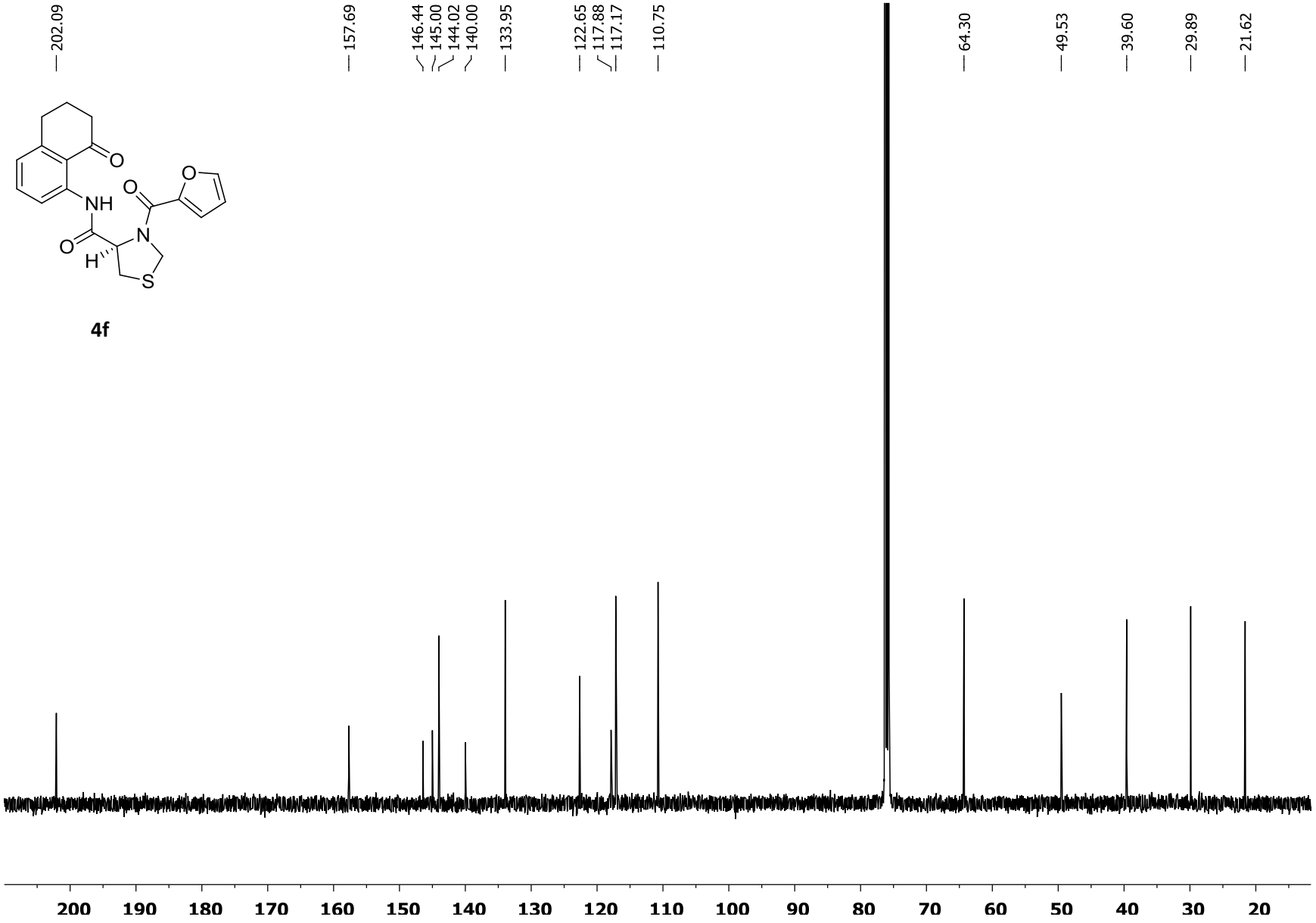
1.5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140.00
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122.65
117.88
117.17
110.75
64.30
49.53
39.60
29.89
21.62
O
NH
O
O
O
N
H
S
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140
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120
110
100
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80
70
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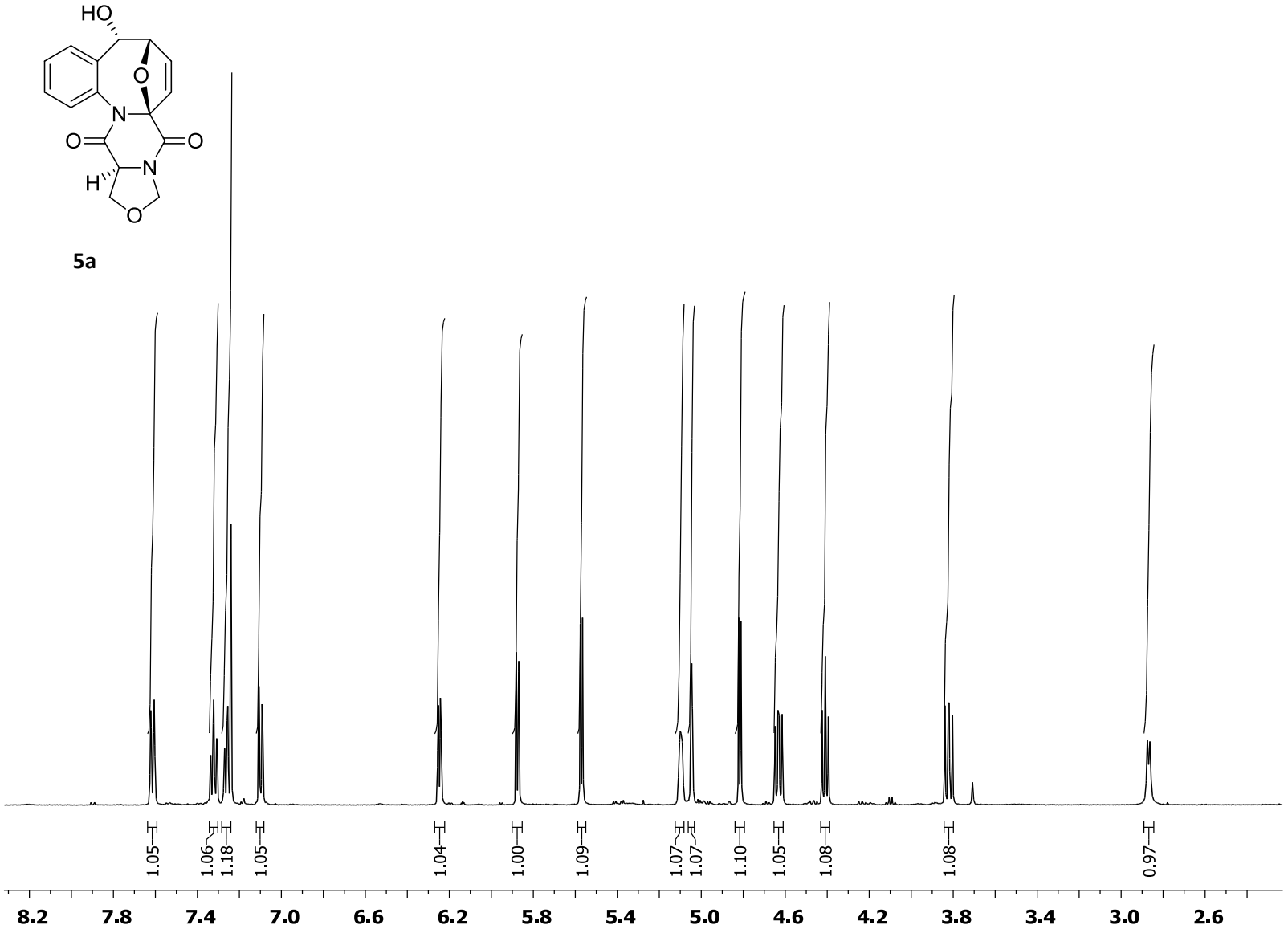
30
20

4f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O
N
H
O
5a
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1.18
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1.04
1.00
1.09
1.07
1.07
1.10
1.05
1.08
1.08
0.97
8.2
7.8
7.4
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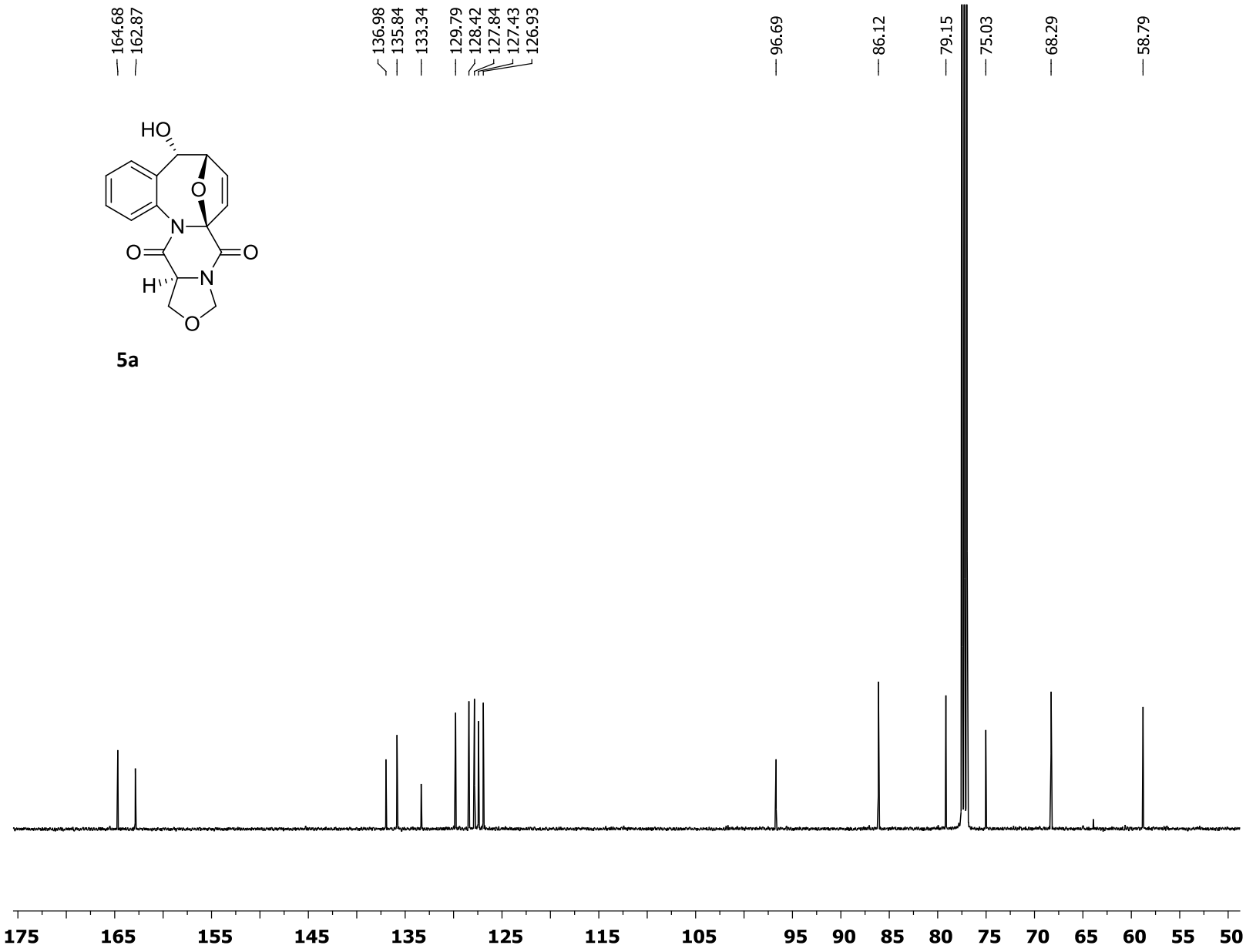
4.6
4.2
3.8
3.4
3.0
2.6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127.84
127.43
126.93
96.69
86.12
79.15
75.03
68.29
58.79
HO
O
N
O
O
N
H
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125
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105
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75
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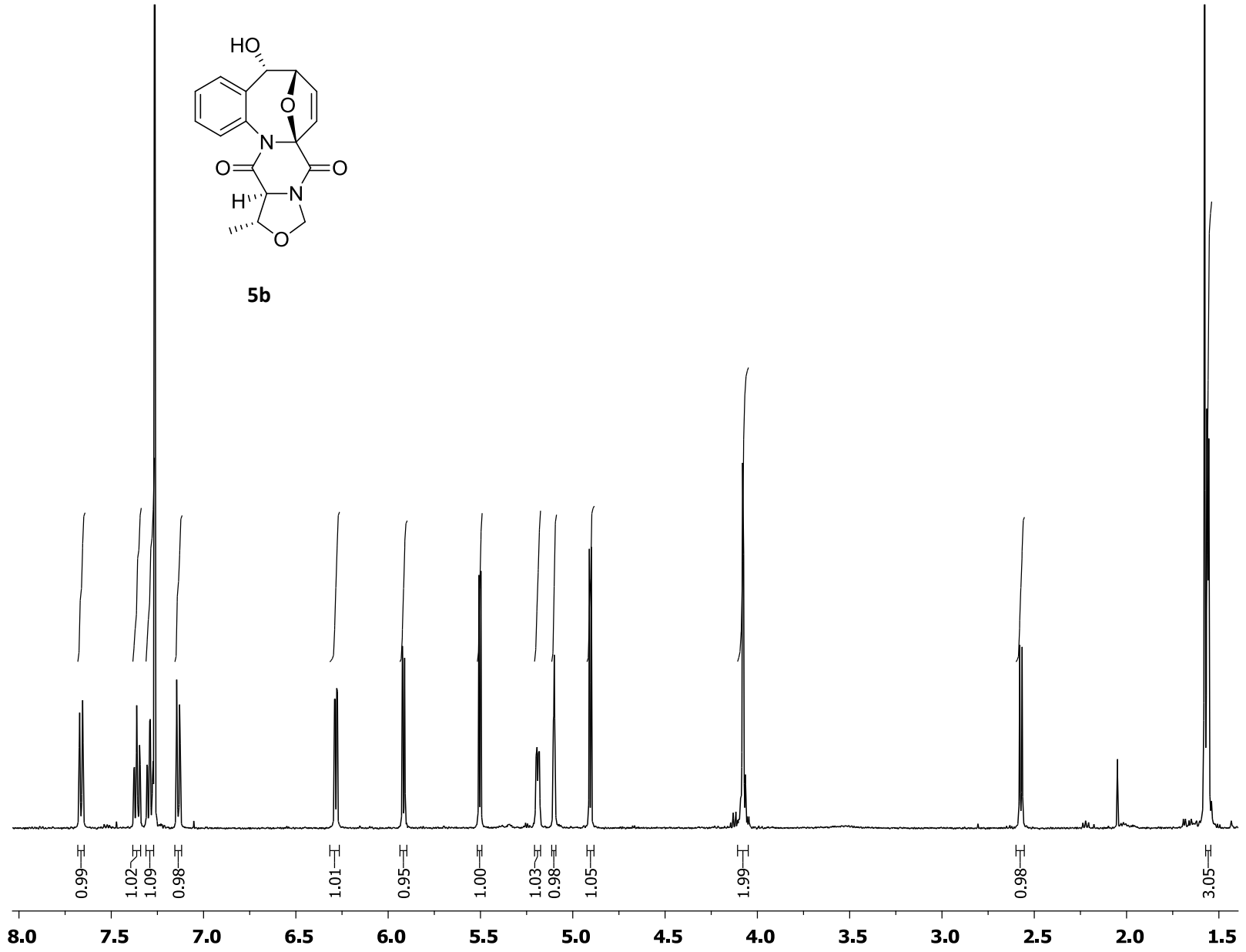
55
50

5a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N
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O
N
H
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5b
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1.01
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1.00
1.03
0.98
1.05
1.99
0.98
3.05
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7.5
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6.0
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4.5
4.0
3.5
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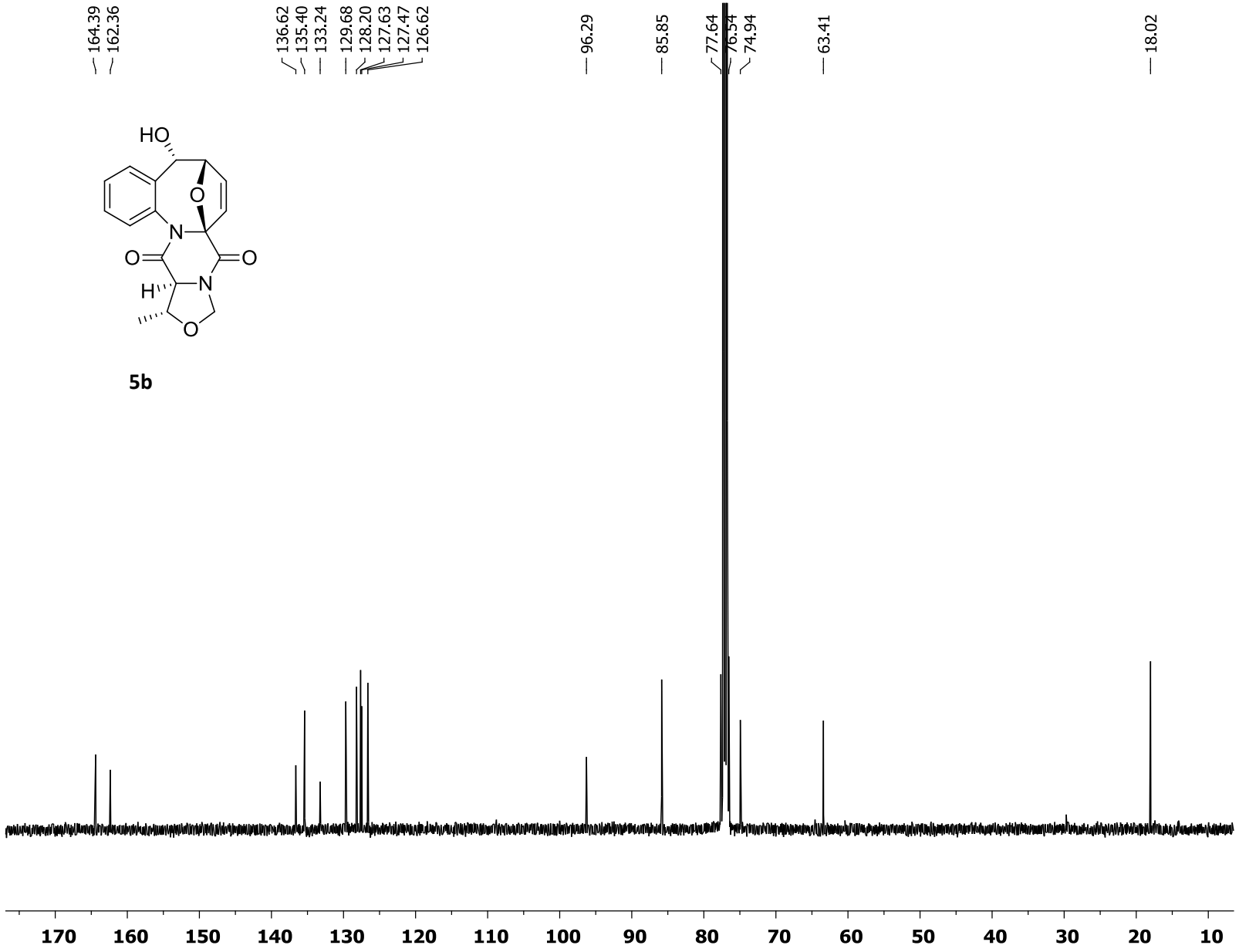
2.0
1.5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127.63
127.47
126.62
96.29
85.85
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76.54
74.94
63.41
18.02
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O
N
O
O
H
N
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150
140
130
120
110
100
90
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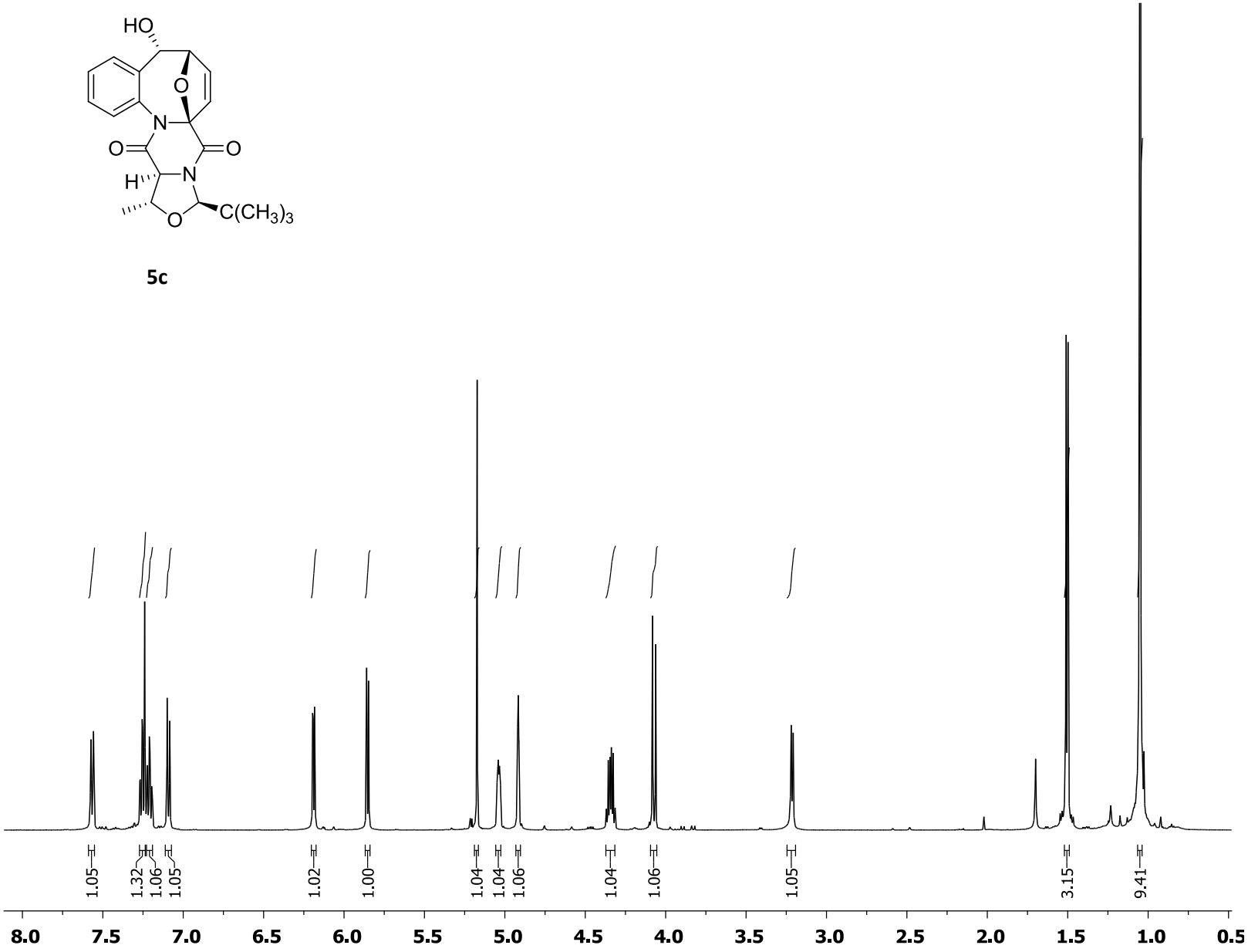
70
60
50
40
30
20
10

5b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N
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O
H
N
O
C(CH3)3
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1.32
1.06
1.05
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1.04
1.04
1.06
1.04
1.06
1.05
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6.5
6.0
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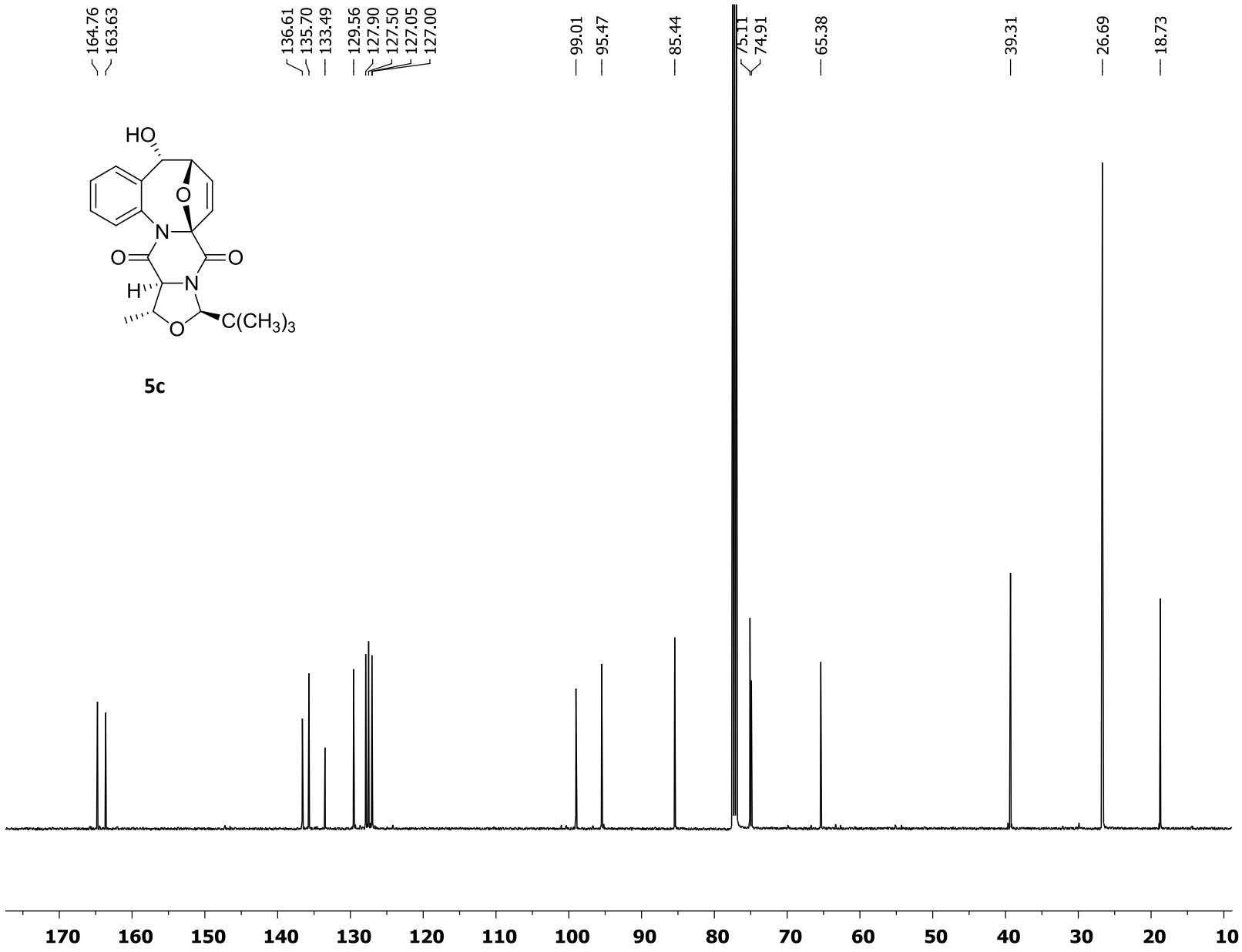
2.0
1.5
1.0
0.5

5c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127.05
127.00
99.01
95.47
85.44
75.11
74.91
65.38
39.31
26.69
18.73
HO
O
N
O
O
N
H
O
C(CH3)3
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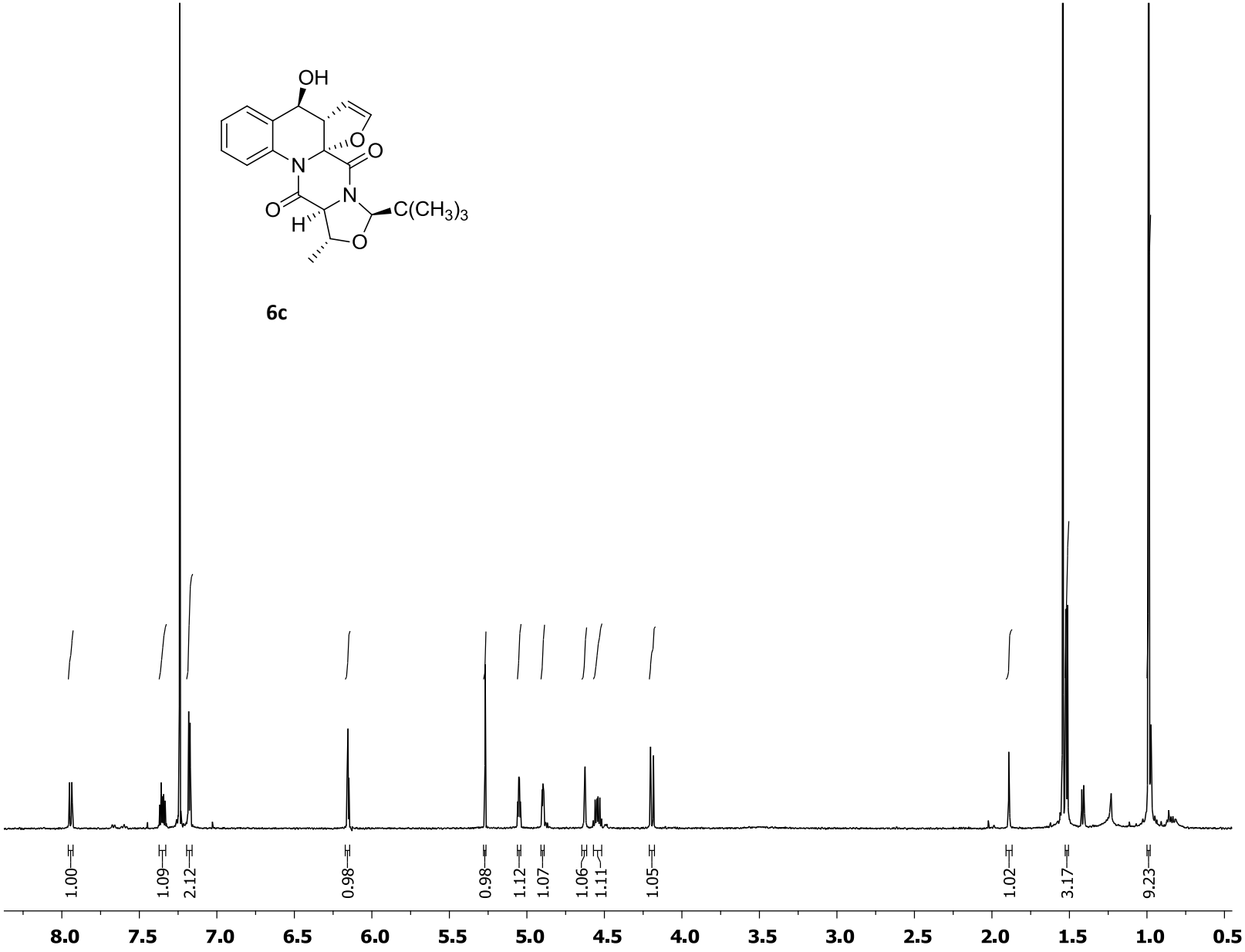
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

5c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H
C(CH3)3
O
6c
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0.98
1.12
1.07
1.06
1.11
1.05
1.02
3.17
9.23
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7.5
7.0
6.5
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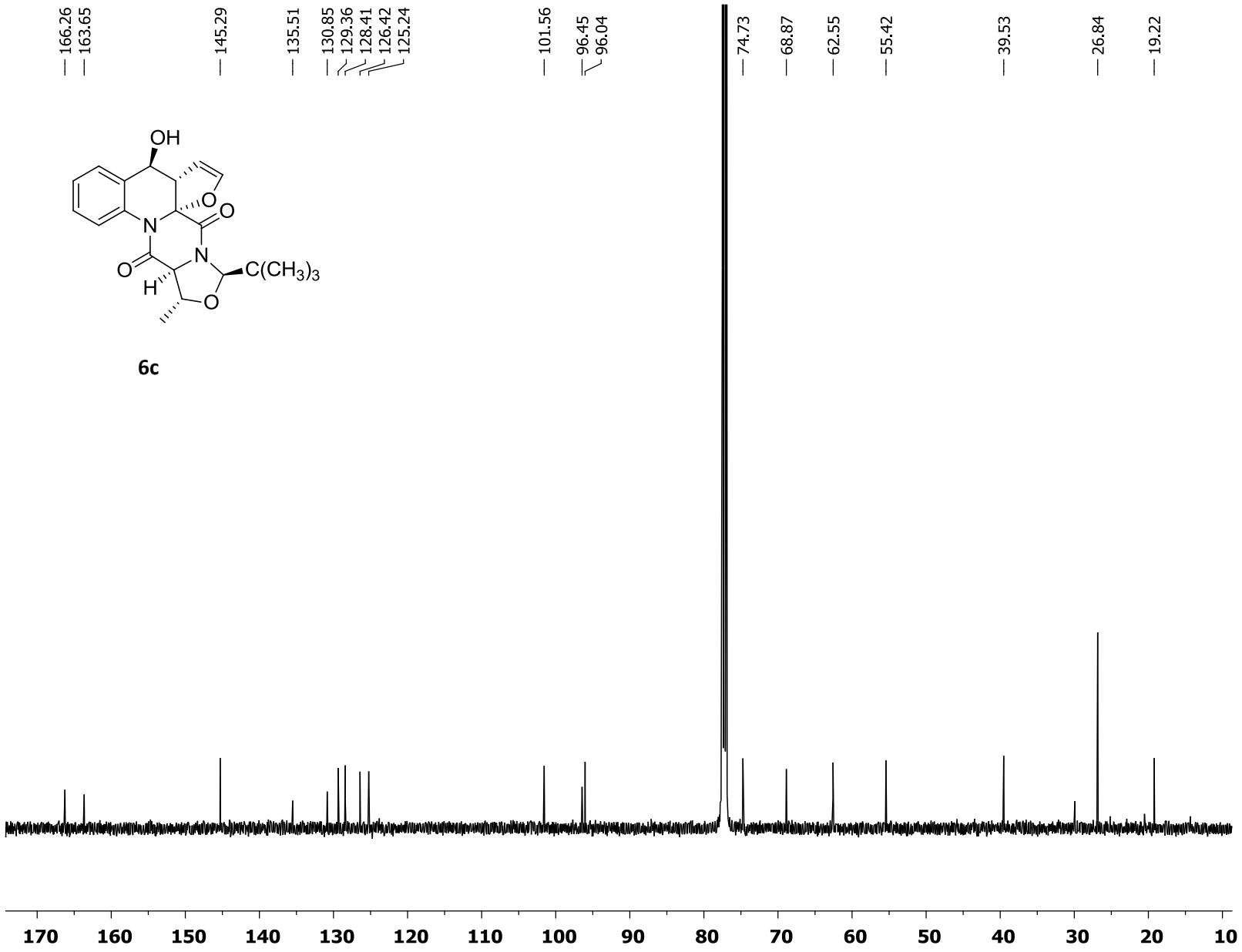
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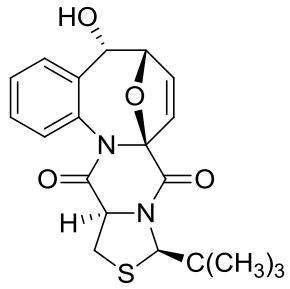
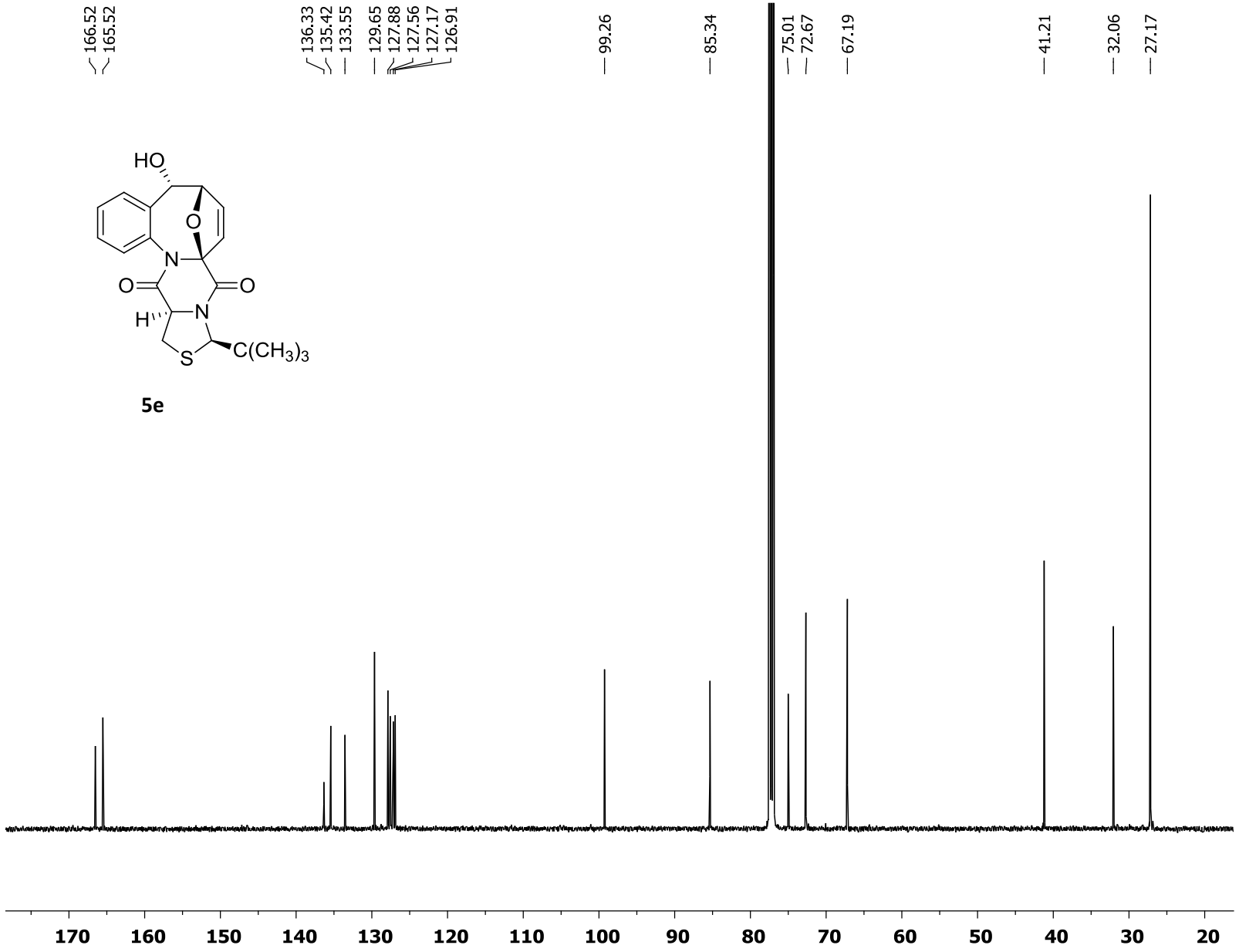
129.36
128.41
126.42
125.24
101.56
96.45
96.04
74.73
68.87
62.55
55.42
39.53
26.84
19.22
OH
O
O
N
N
O
H
C(CH3)3
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

6c


HO
O
N
O
O
H
N
S
C(CH3)3

5e

1.00
2.68
1.00
0.98
0.96
1.03
1.03
1.03
1.04
2.13
0.99
9.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0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165.52
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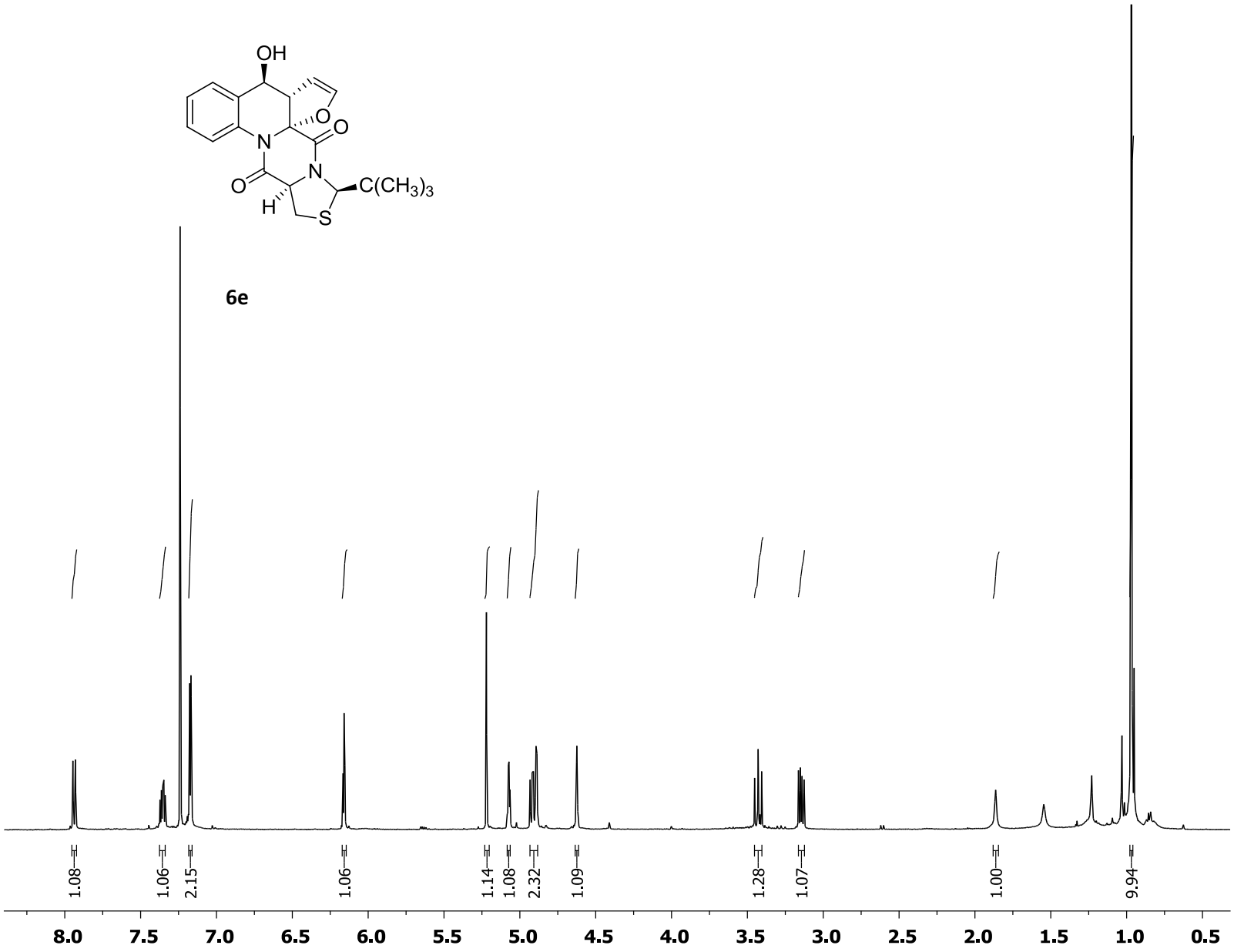
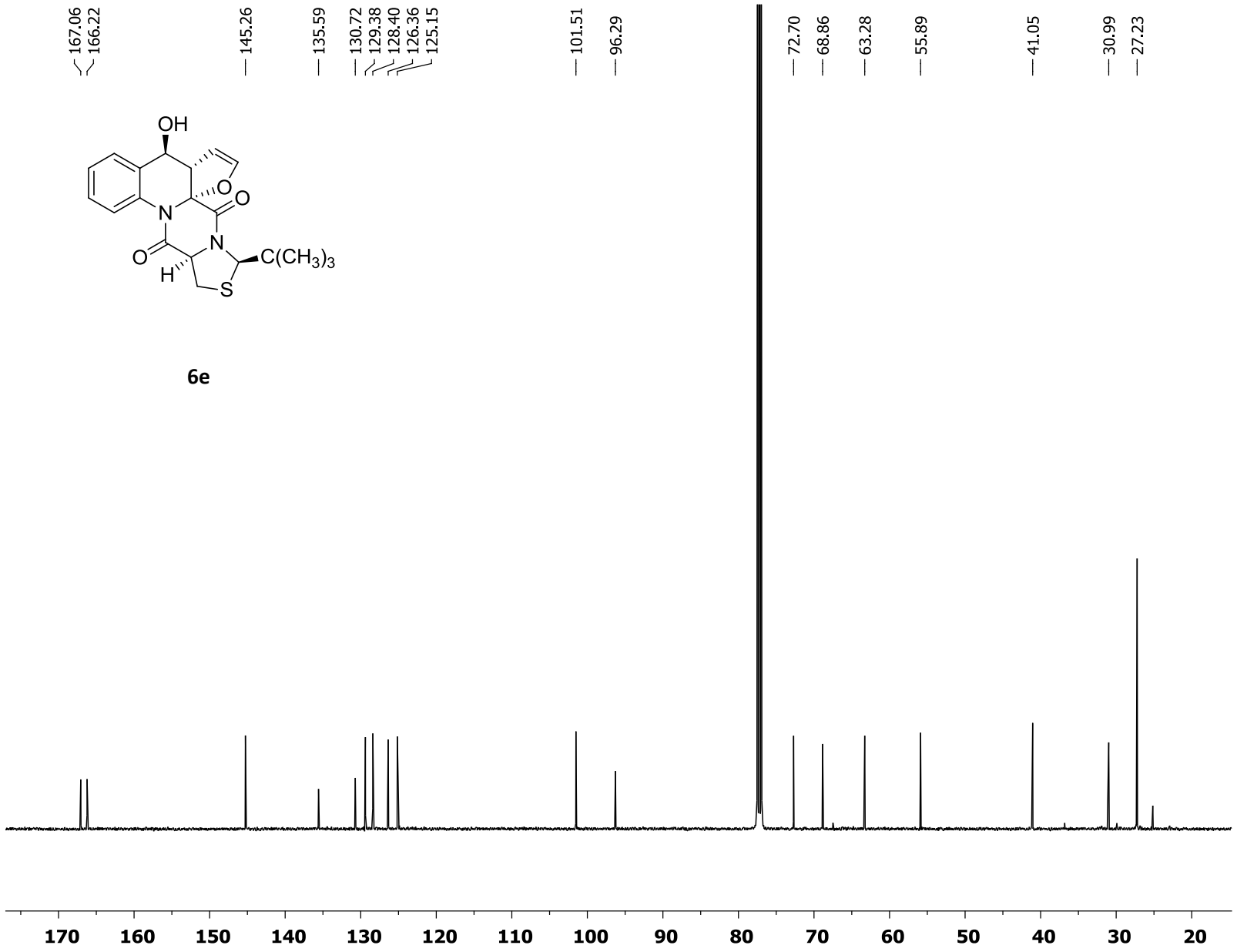
135.42
133.55
129.65
127.88
127.56
127.17
126.91
99.26
85.34
75.01
72.67
67.19
41.21
32.06
27.17
HO
O
N
O
O
N
H
S
C(CH3)3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

5e


OH
O
O
N
N
O
H
S
C(CH3)3
6e
1.08
1.06
2.15
1.06
1.14
1.08
2.32
1.09
1.28
1.07
1.00
9.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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145.26
135.59
130.72
129.38
128.40
126.36
125.15
101.51
96.29
72.70
68.86
63.28
55.89
41.05
30.99
27.23
OH
O
O
N
N
O
H
S
C(CH3)3
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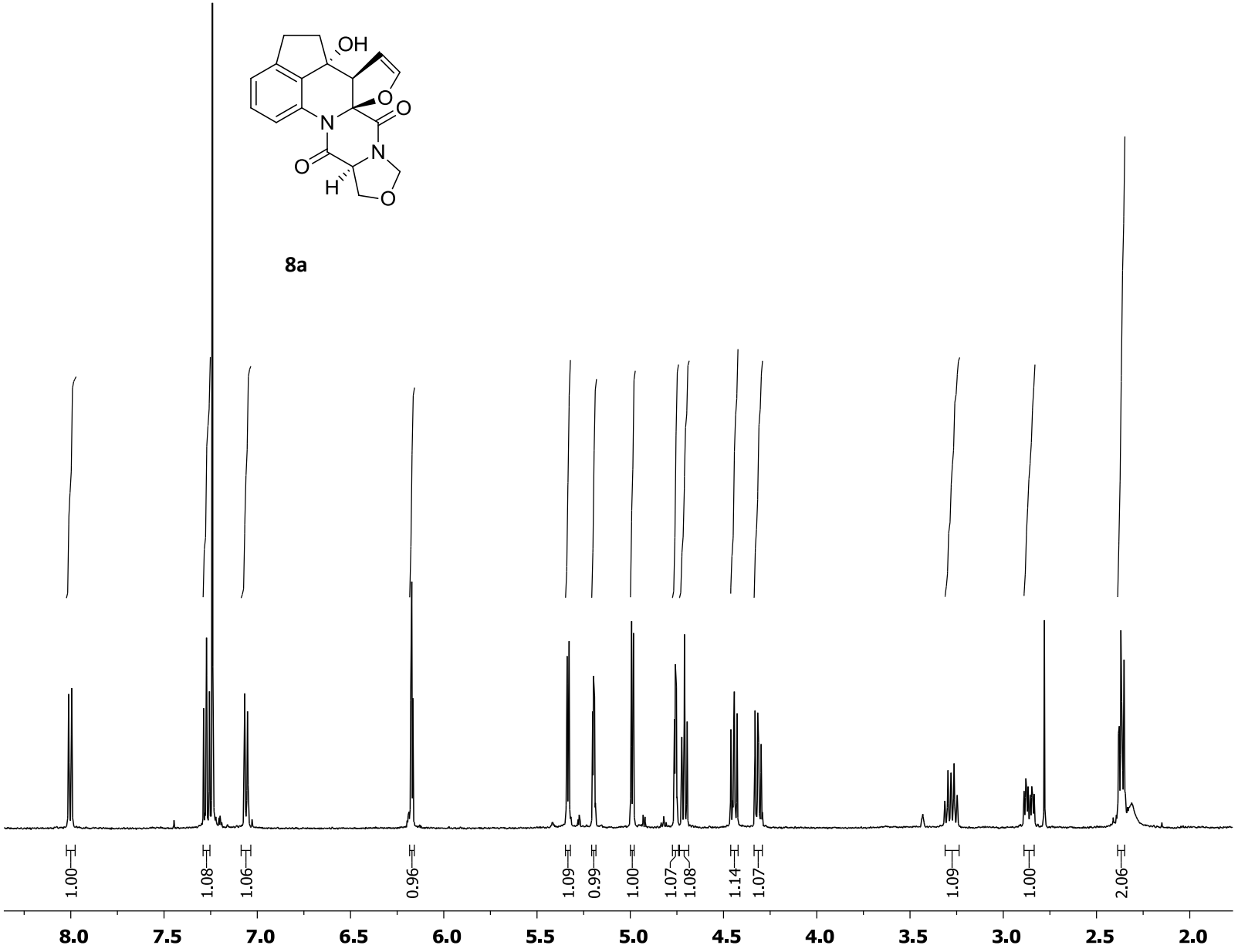
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

6e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O
O
N
N
O
H
O
8a
1.00
1.08
1.06
0.96
1.09
0.99
1.00
1.07
1.08
1.14
1.07
1.09
1.00
2.06
8.0
7.5
7.0
6.5
6.0
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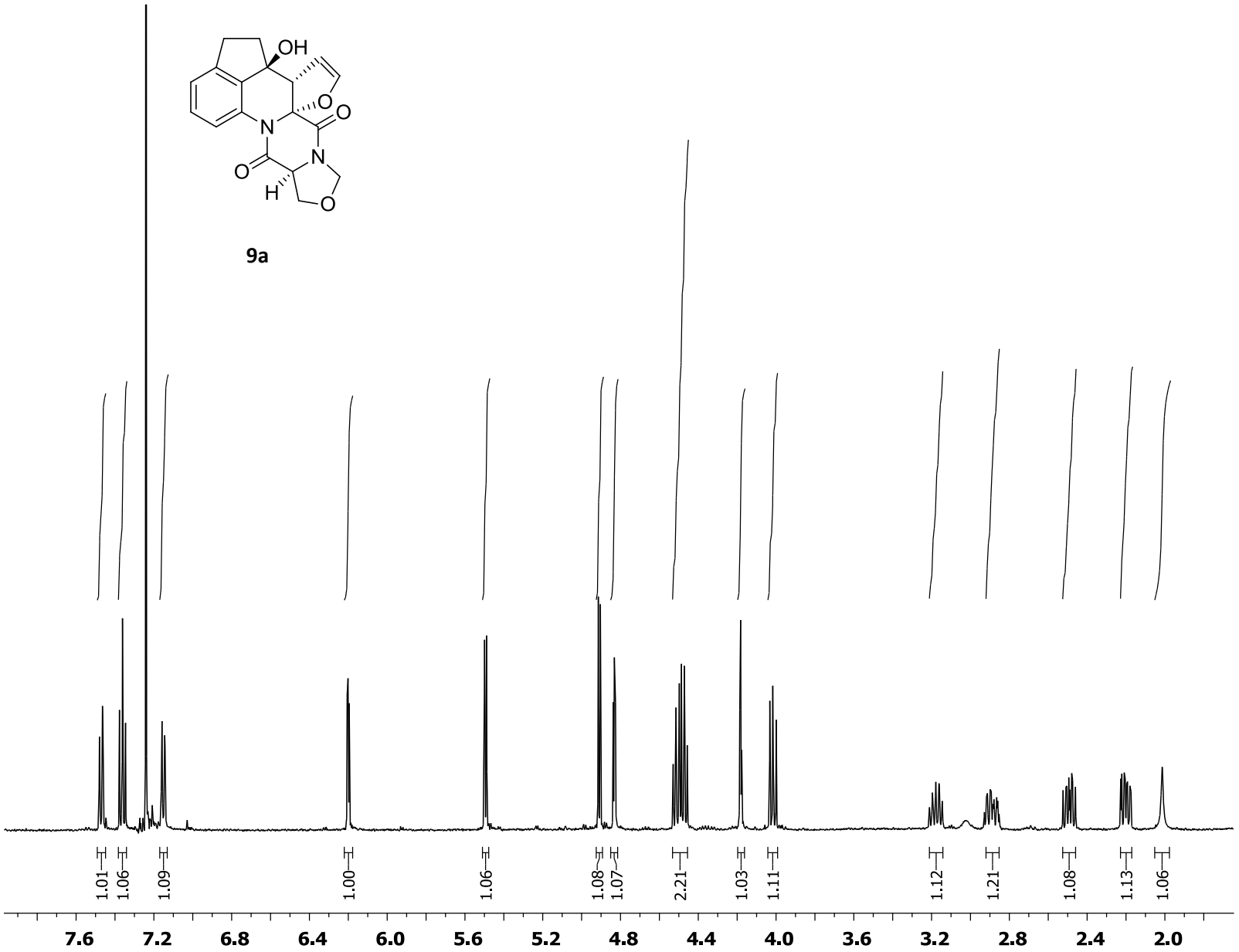
5.0
4.5
4.0
3.5
3.0
2.5
2.0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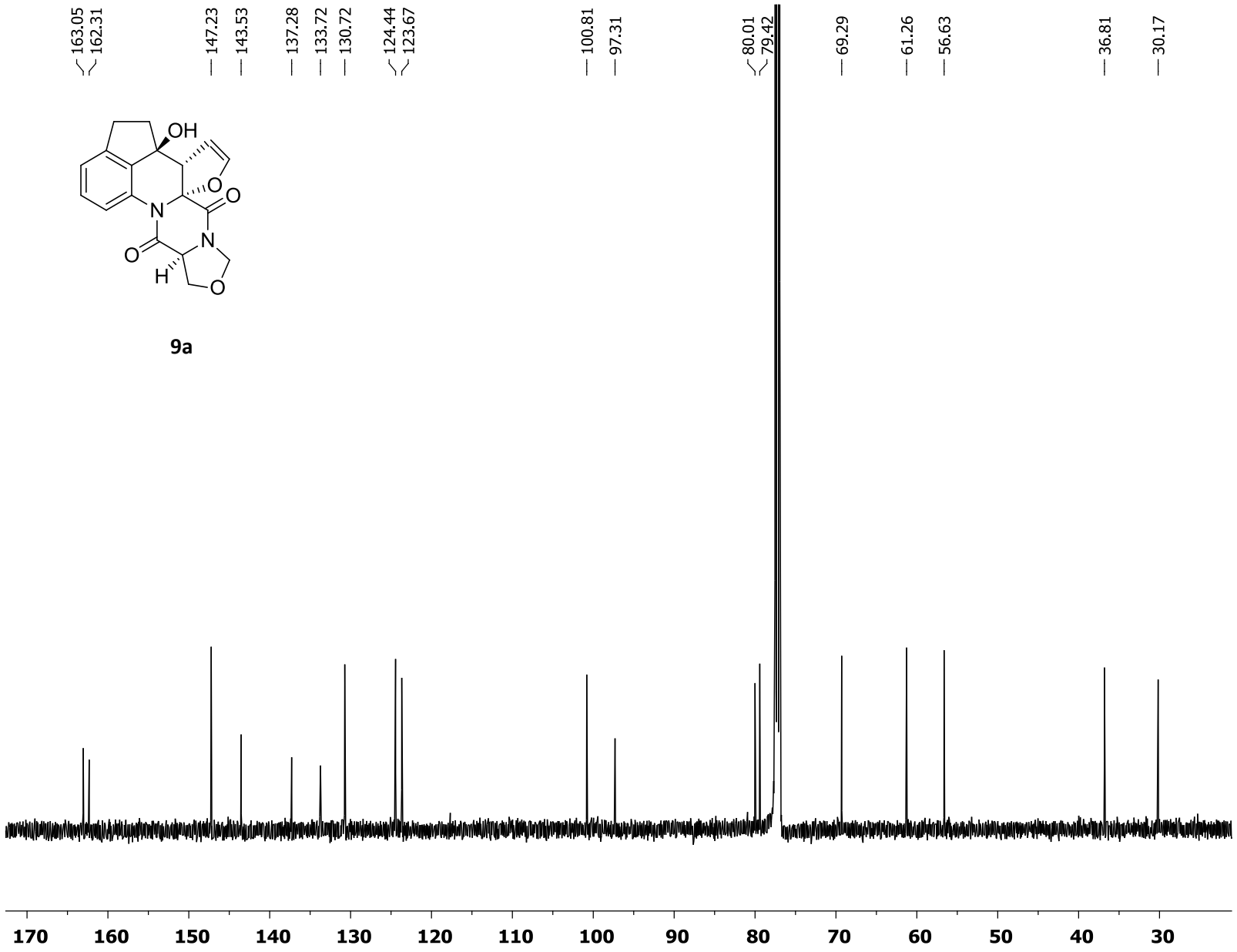
O
N
N
O
H
O
1.01
1.06
1.09
1.00
1.06
1.08
1.07
2.21
1.03
1.11
1.12
1.21
1.08
1.13
1.06
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0

9a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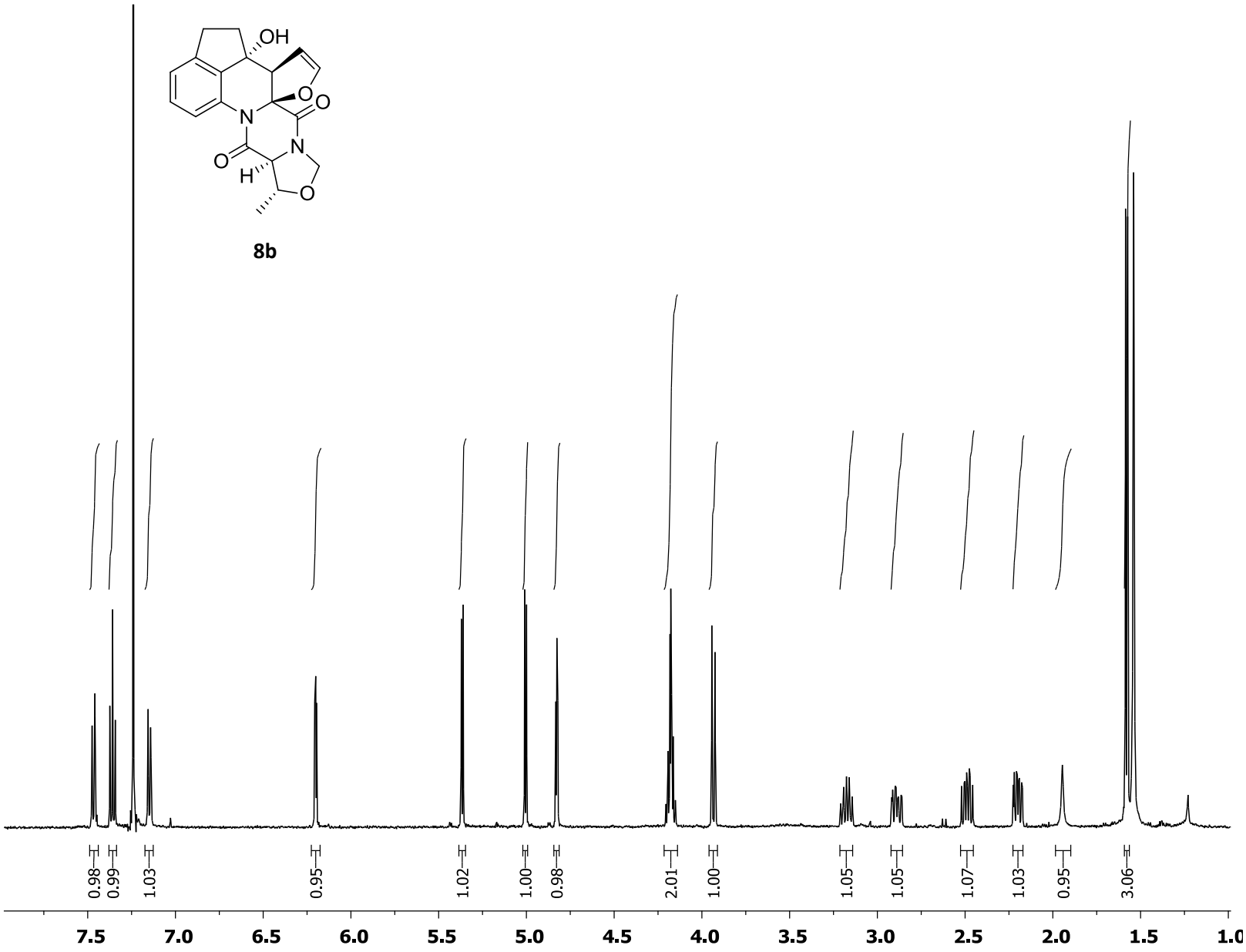
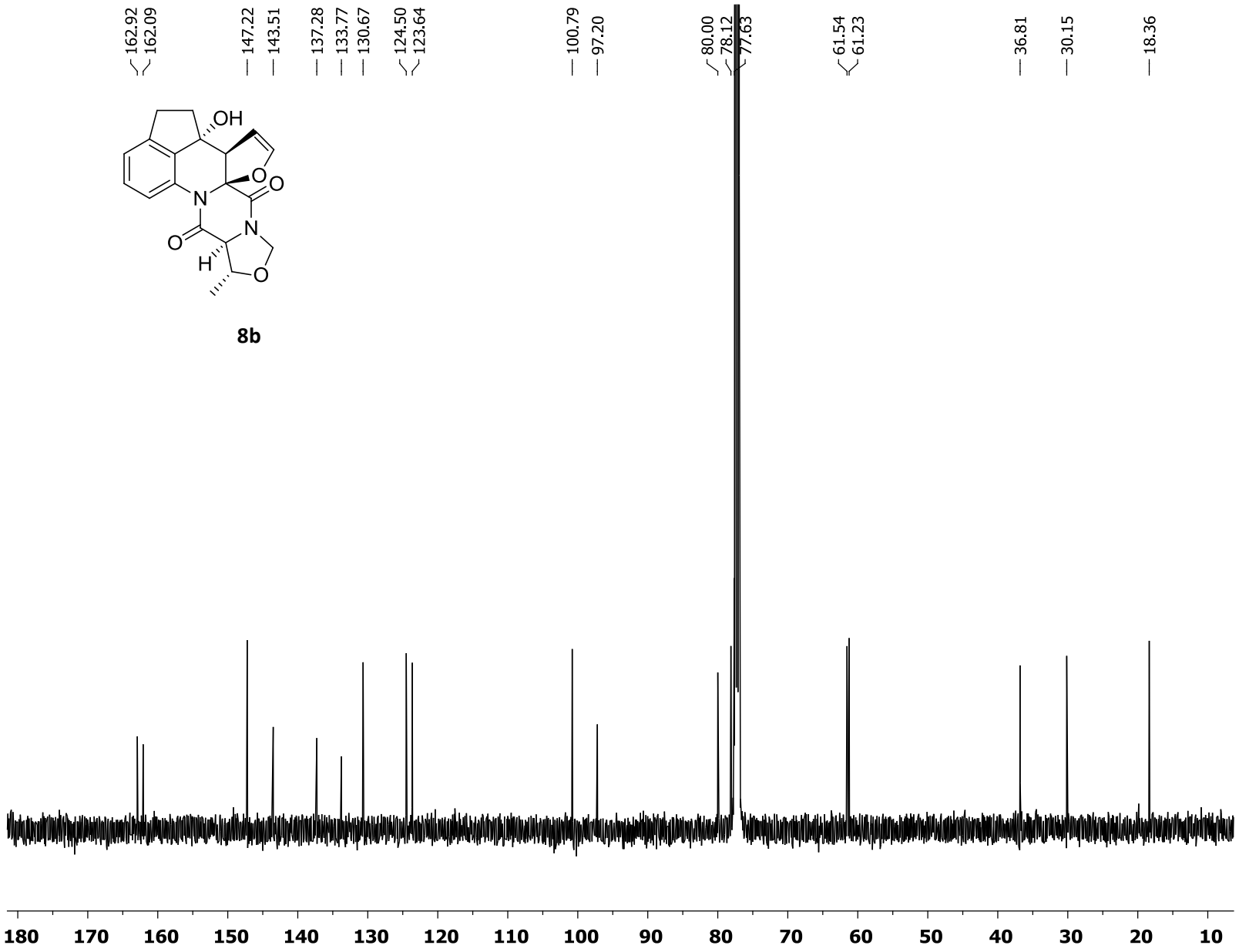
162.31
147.23
143.53
137.28
133.72
130.72
124.44
123.67
100.81
97.31
80.01
79.42
69.29
61.26
56.63
36.81
30.17
OH
O
O
N
N
O
H
O
9a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30


OH
O
O
N
N
O
H
O
8b
0.98
0.99
1.03
0.95
1.02
1.00
0.98
2.01
1.00
1.05
1.05
1.07
1.03
0.95
3.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0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162.09
147.22
143.51
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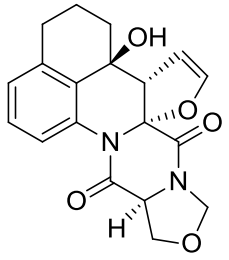
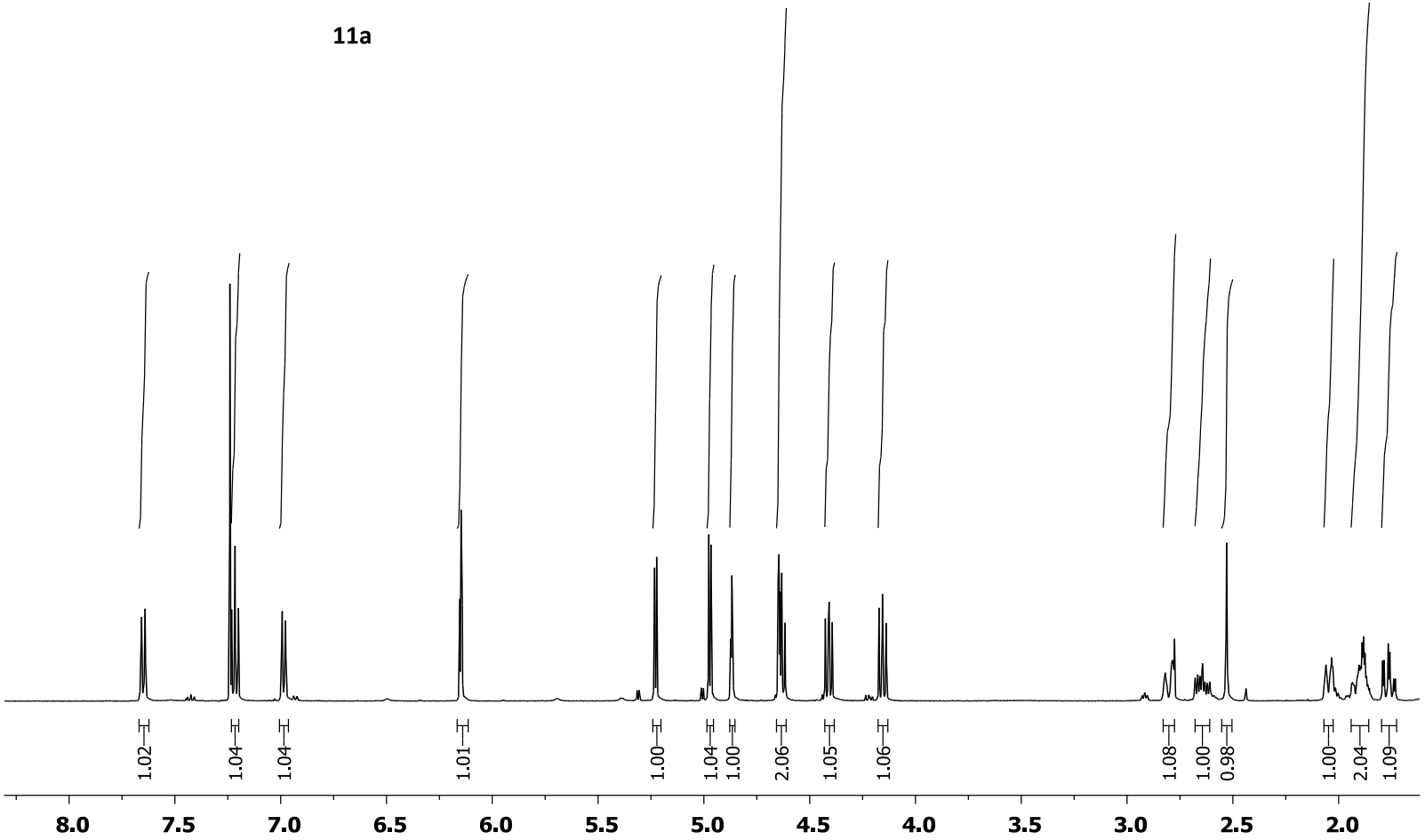
133.77
130.67
124.50
123.64
100.79
97.20
80.00
78.12
77.63
61.54
61.23
36.81
30.15
18.36
OH
O
O
N
O
N
H
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

8b


OH
O
O
N
N
O
H
O

11a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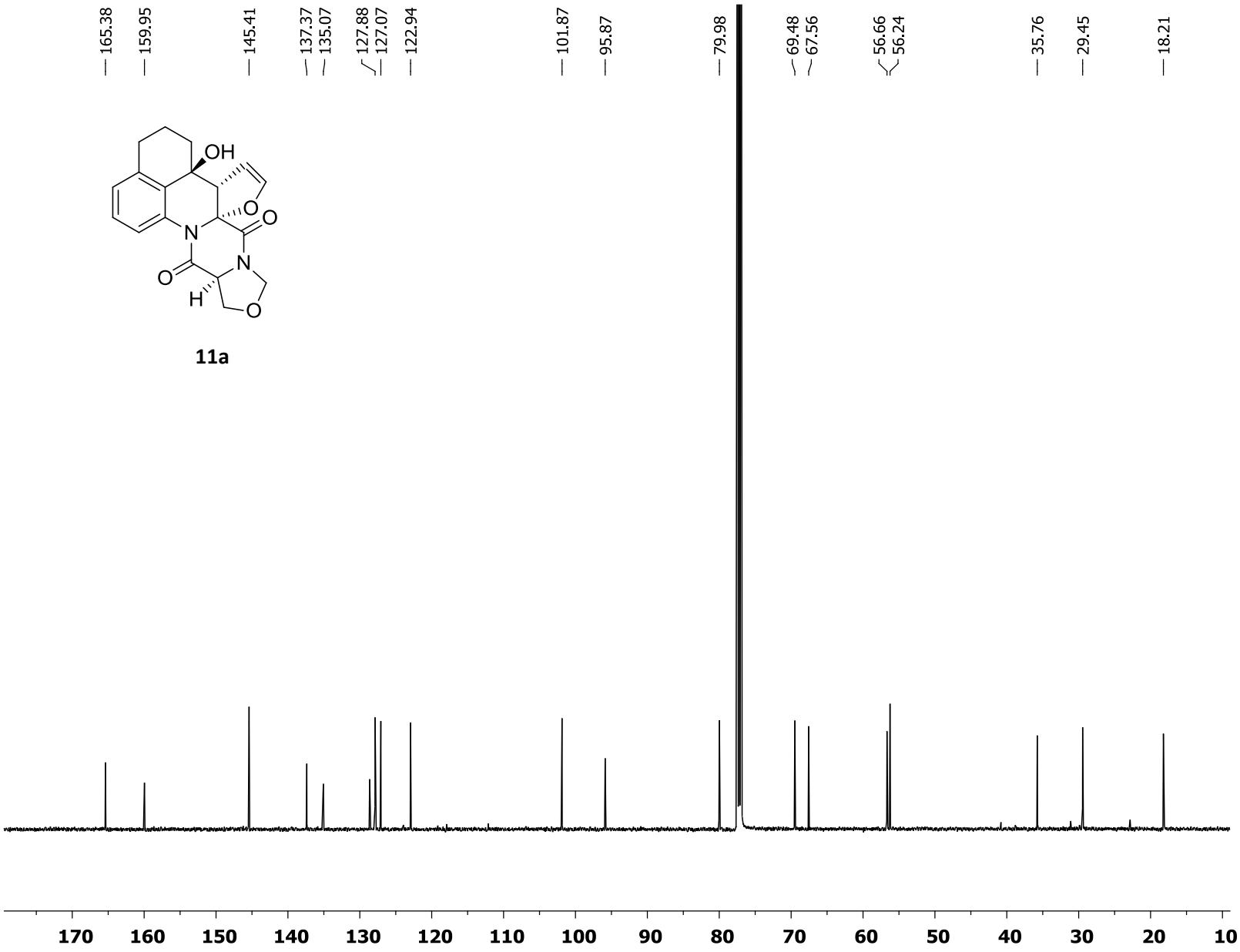
1.04
1.04
1.01
1.00
1.04
1.00
2.06
1.05
1.06
1.08
1.00
0.98
1.00
2.04
1.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0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159.95
145.41
137.37
135.07
127.88
127.07
122.94
101.87
95.87
79.98
69.48
67.56
56.66
56.24
35.76
29.45
18.21
OH
O
O
N
O
N
H
O
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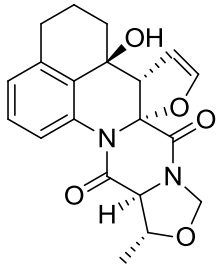
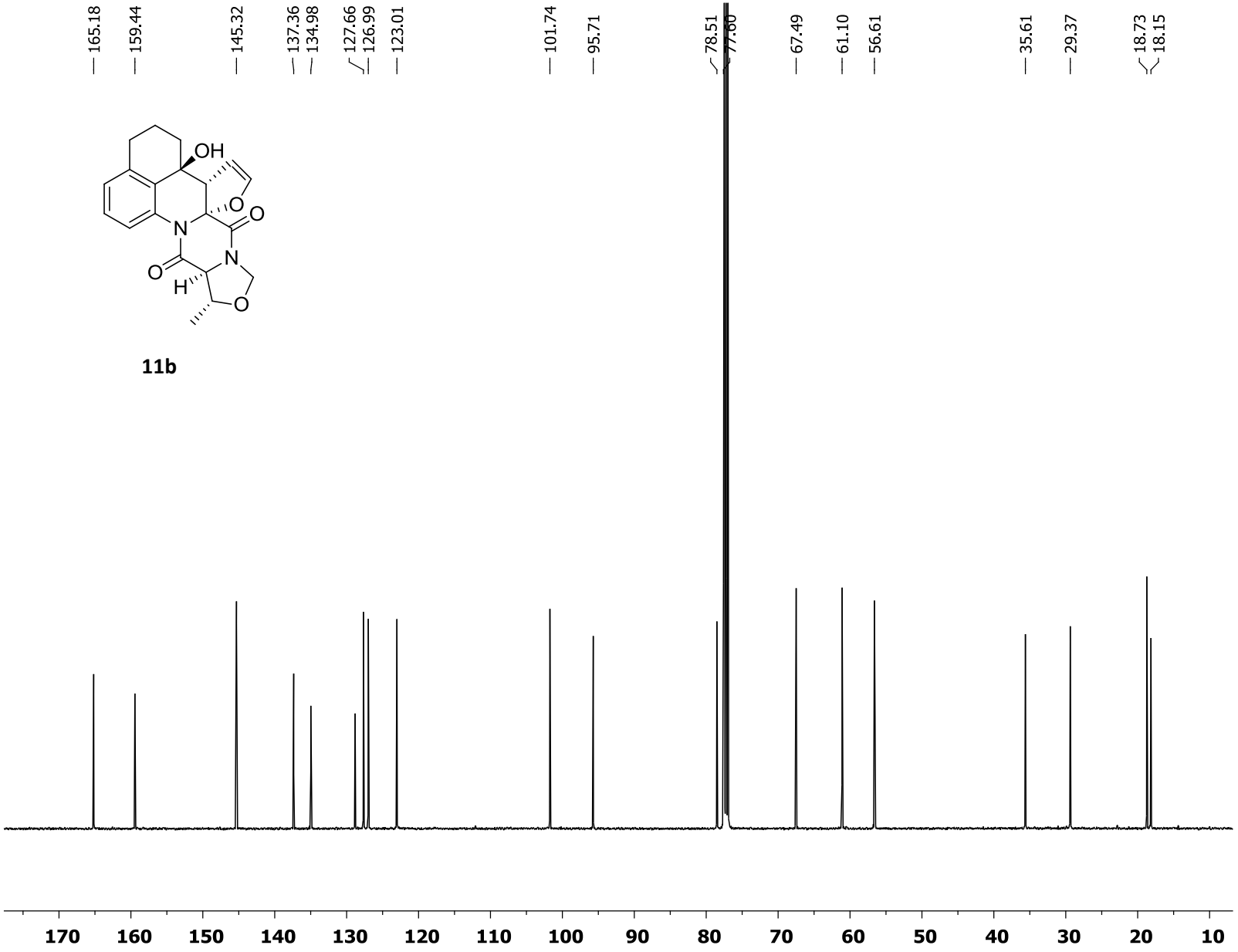
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

11a


OH
O
O
N
N
O
H
O

11b

1.02
1.06
1.01
1.00
1.04
1.03
1.05
1.05
1.06
1.02
1.06
1.07
1.08
1.10
2.06
1.03
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0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127.66
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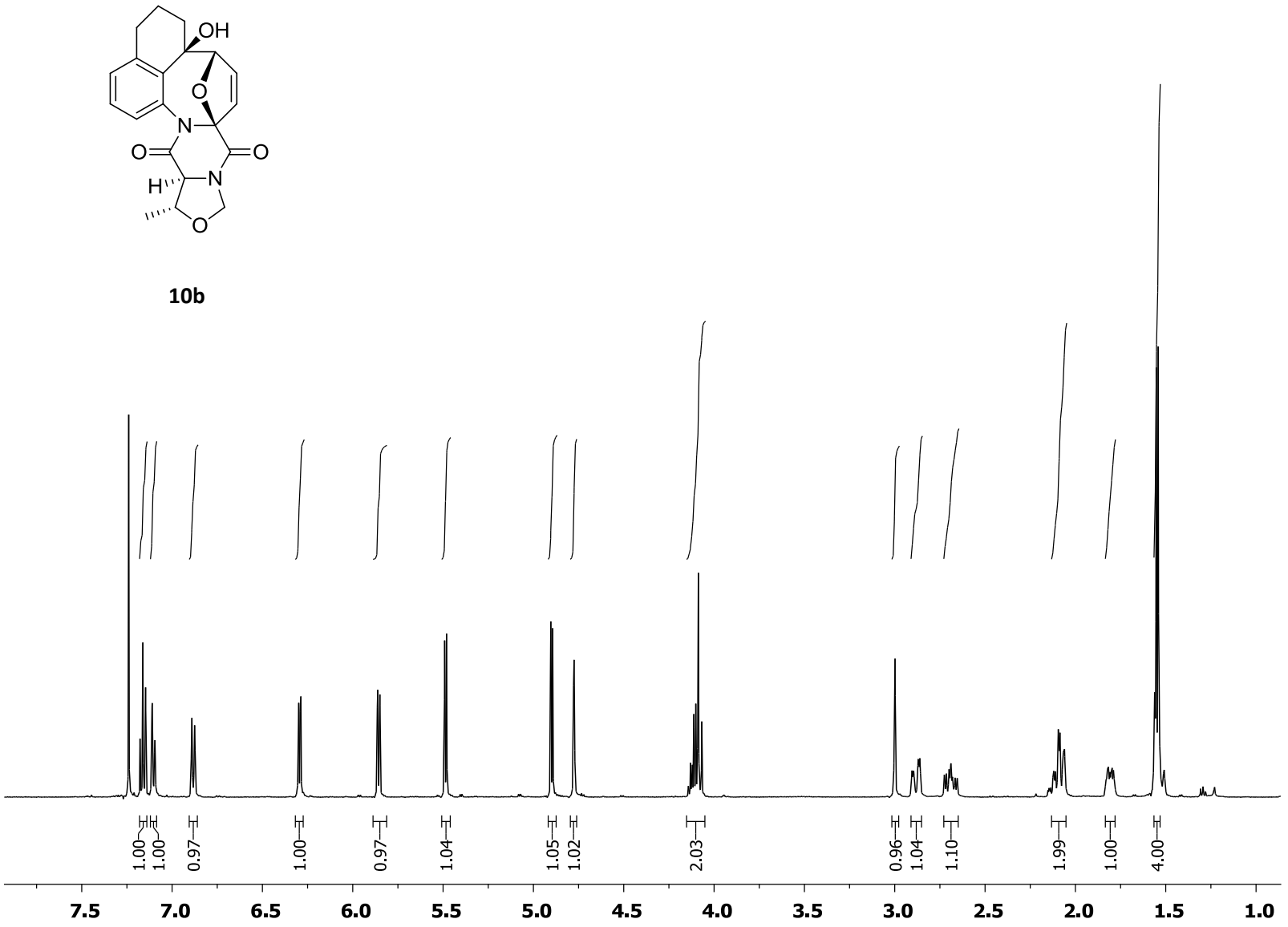
123.01
101.74
95.71
78.51
77.00
67.49
61.10
56.61
35.61
29.37
18.73
18.15
OH
O
O
N
N
O
H
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

11b


OH
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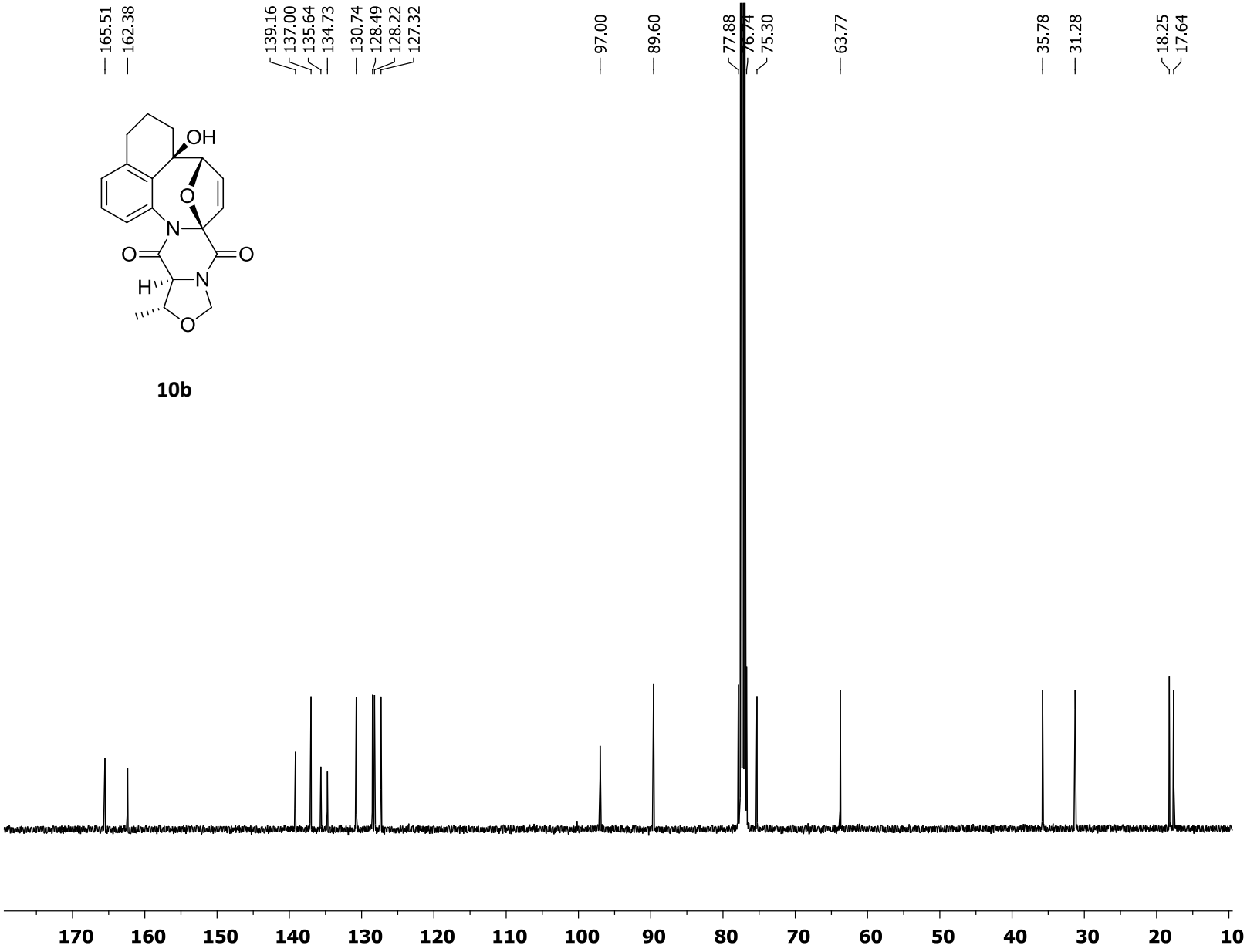
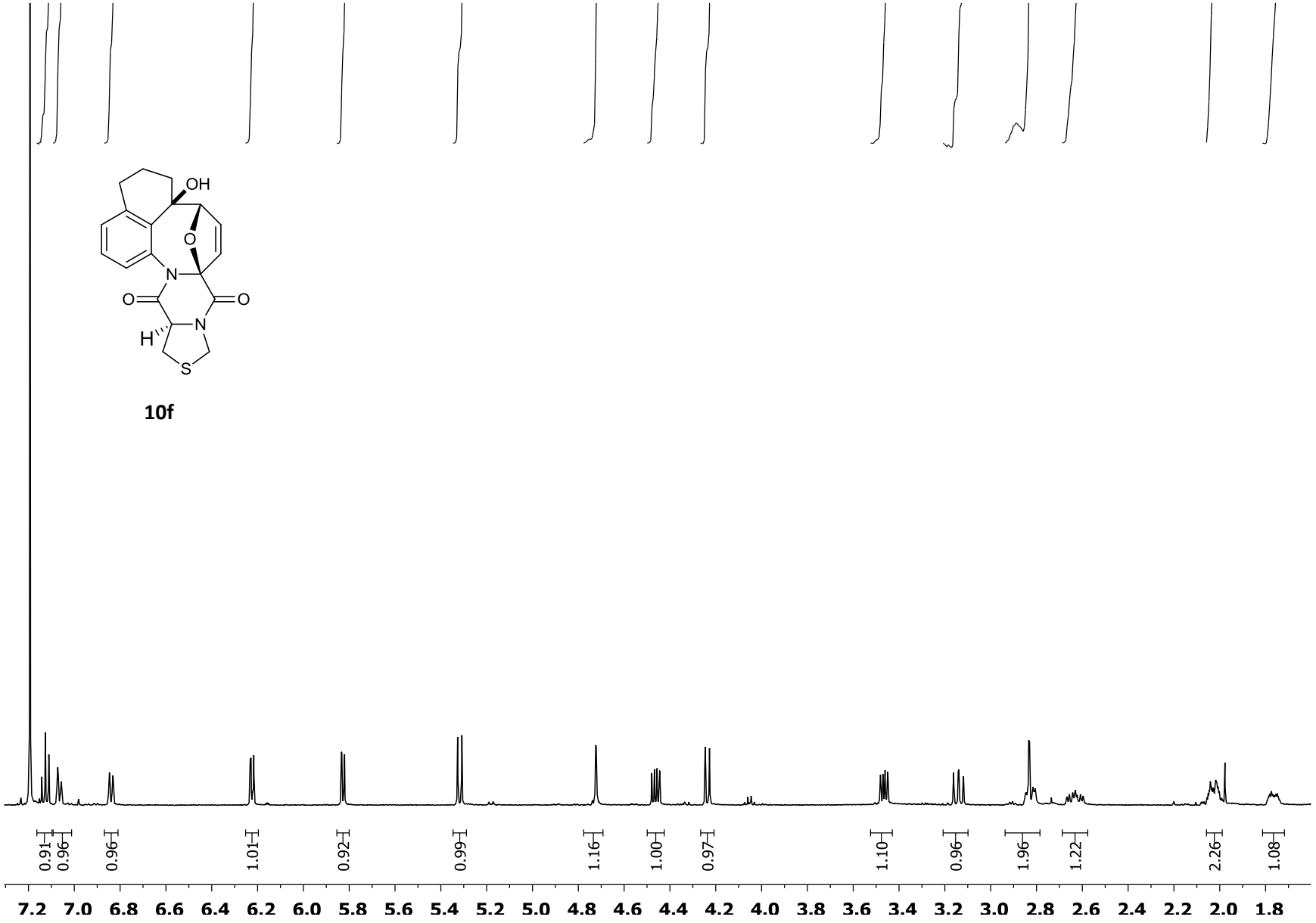
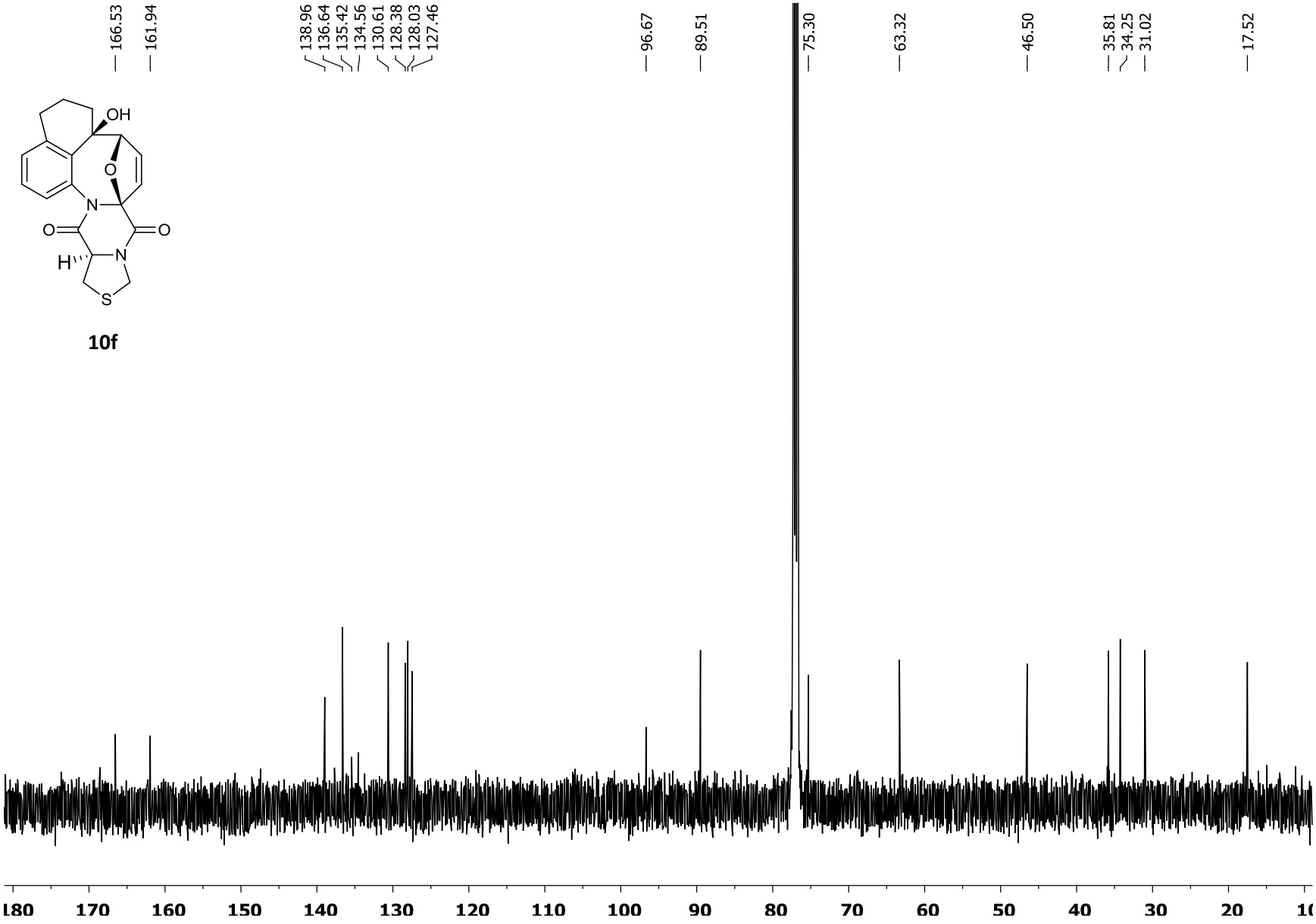
N
O
O
N
H
O
10b
1.00
1.00
0.97
1.00
0.97
1.04
1.05
1.02
2.03
0.96
1.04
1.10
1.99
1.00
4.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


165.51
162.38
139.16
137.00
135.64
134.73
130.74
128.49
128.22
127.32
97.00
89.60
77.88
76.74
75.30
63.77
35.78
31.28
18.25
17.64
OH
O
N
O
O
H
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

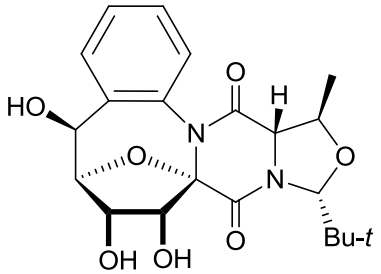
10b


OH
O
N
O
O
N
H
S
0.91
0.96
0.96
1.01
0.92
0.99
1.16
1.00
0.97
1.10
0.96
1.96
1.22
2.26
1.08
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

10f


166.53
161.94
138.96
136.64
135.42
134.56
130.61
128.38
128.03
127.46
96.67
89.51
75.30
63.32
46.50
35.81
34.25
31.02
17.52
OH
O
N
O
O
H
N
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

10f


HO
O
H
N
O
N
O
O
Bu-t
OH
OH

12

1.03
1.04
2.05
1.00
1.01
1.02
1.02
2.09
1.02
3.13
9.14
8.0
7.5
7.0
6.5
6.0
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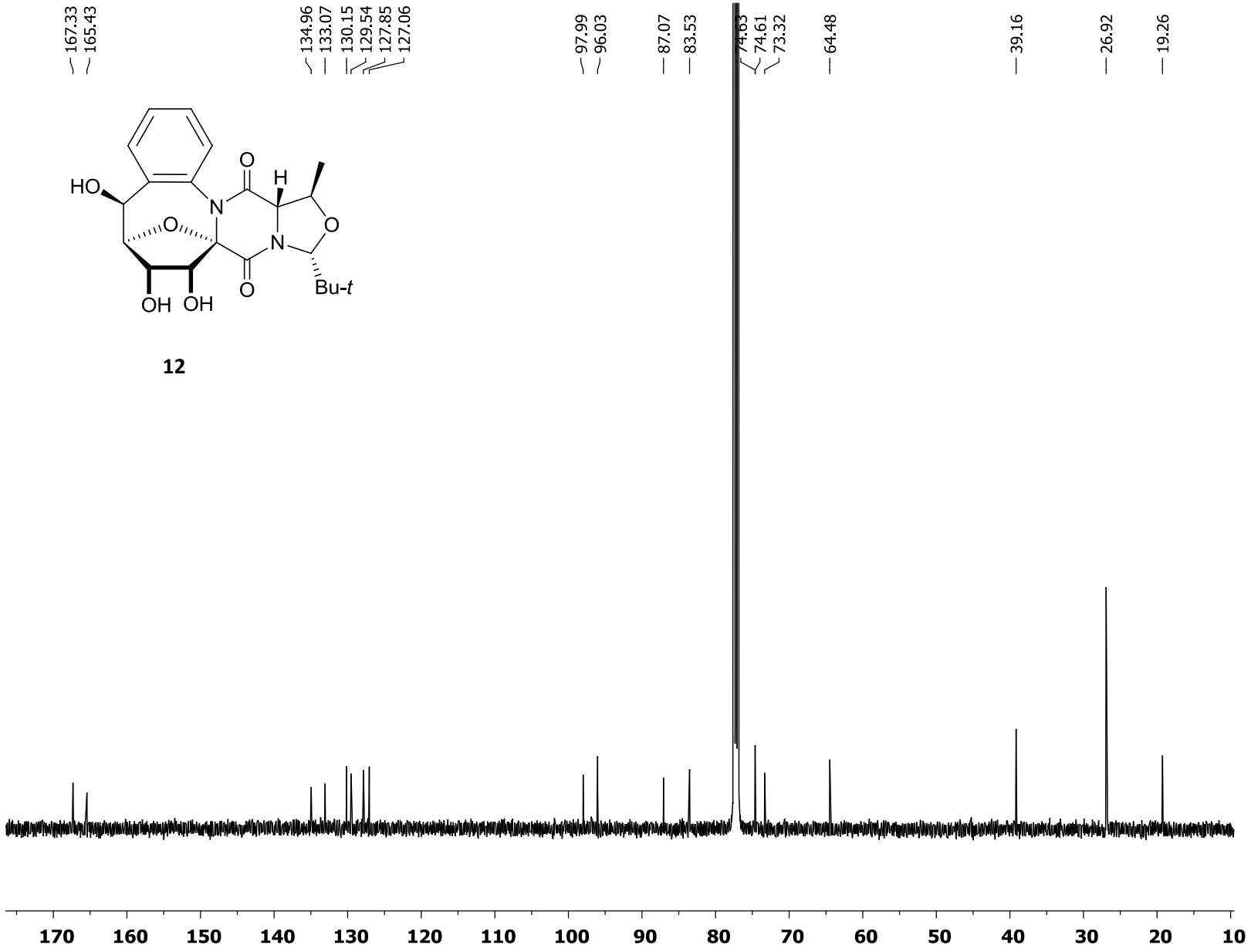
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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133.07
130.15
129.54
127.85
127.06
97.99
96.03
87.07
83.53
74.63
74.61
73.32
64.48
39.16
26.92
19.26
HO
O
H
N
O
O
N
O
Bu-t
OH OH
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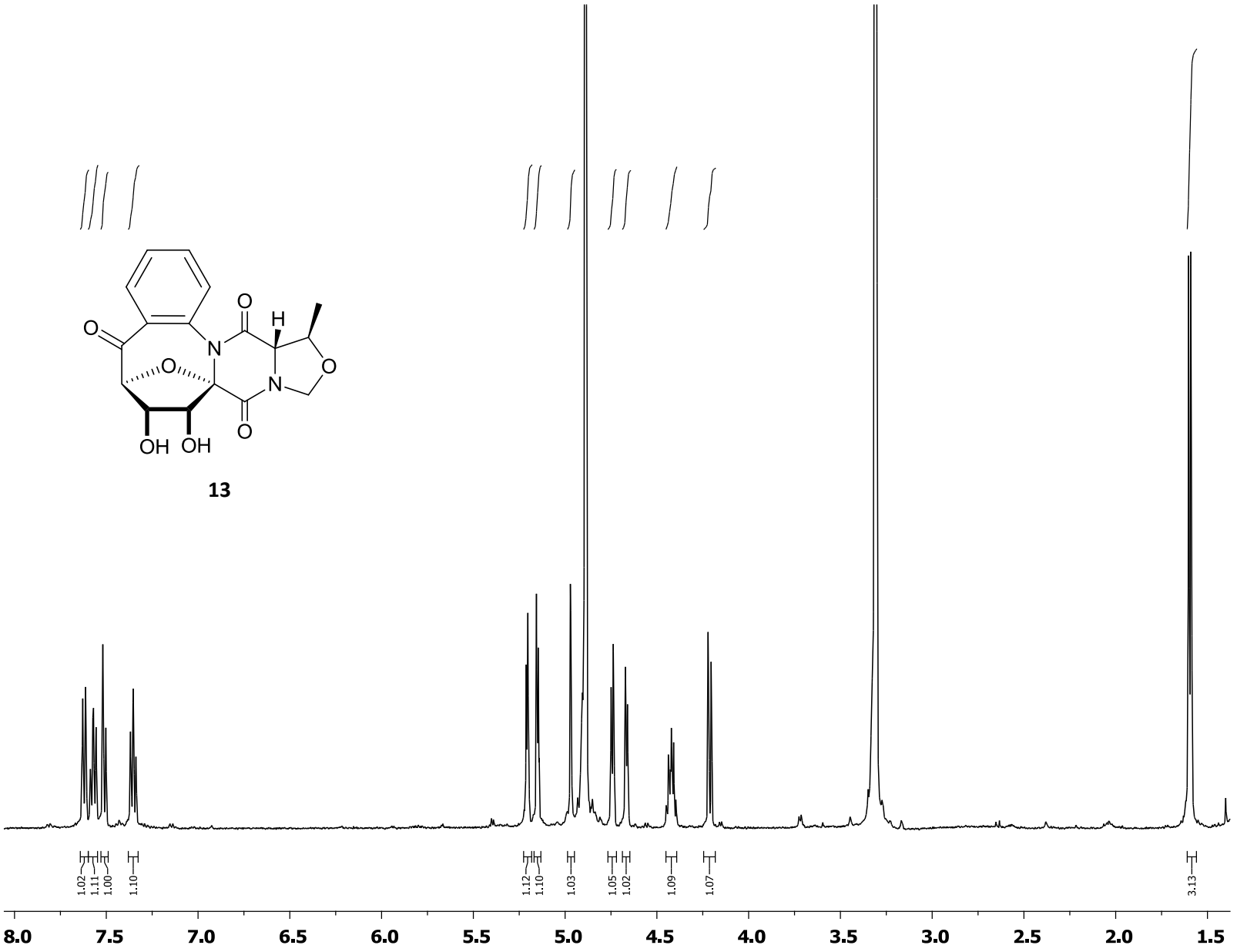
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

12


O
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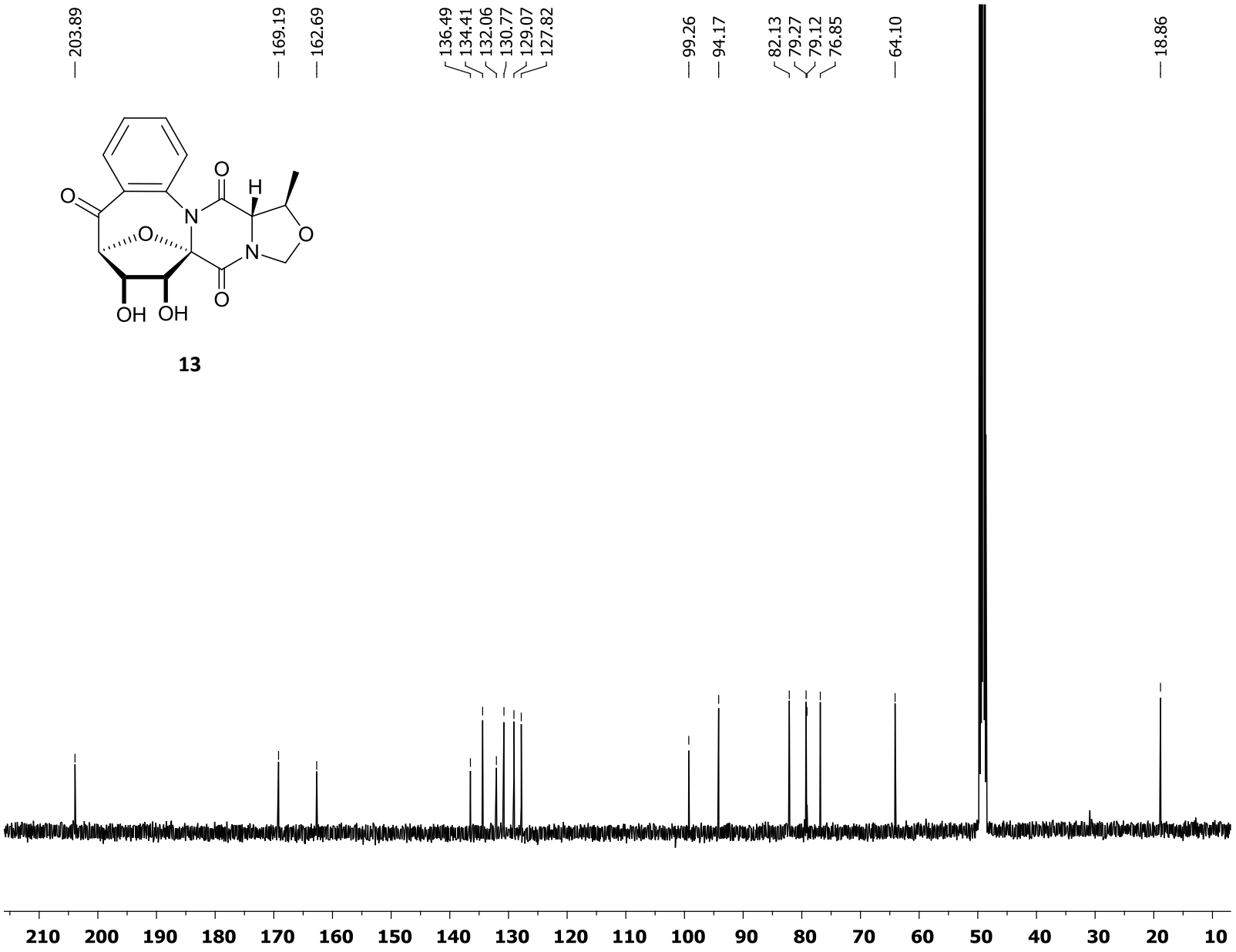
H
N
O
N
O
O
OH OH
1.02
1.11
1.00
1.10
1.12
1.10
1.03
1.05
1.02
1.09
1.07
3.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

13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136.49
134.41
132.06
130.77
129.07
127.82
99.26
94.17
82.13
79.27
79.12
76.85
64.10
18.86
O
O
H
N
O
O
N
O
O
OH
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

13