Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 246–247

Different addition modes of cyclopentadiene and furan at methylidene(thio)hydantoins

Dmitry E. Shybanov, Maxim E. Kukushkin, Viktor A. Tafeenko, Nikolai V. Zyk, Yuri K. Grishin, Vitaly A. Roznyatovsky and Elena K. Beloglazkina

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance instrument with an operating frequency of 400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR Chemical shifts are given in parts per million on a scale of δ relative to hexamethyldisiloxane as an internal standard.

High-resolution mass spectra were recorded on an Orbitrap Elite mass spectrometer (Thermo Scientific) with IREP. To enter solutions with a concentration of 0.1–9 μg ml^{-1} (in 1% formic acid in acetonitrile), direct injection into the ion source using a syringe pump (5 μl min^{-1}) was used. Spray voltage ± 3.5 kV, capillary temperature 275 ºC.

1. General procedure for the synthesis of 1'-phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-en-5'-ones (3,4).

A mixture of 5-methylidene-2-chalcogenoimidazolidin-4-ones **1** or **2** (1 equiv.) and cyclopentadiene (8 equiv.) in methanol was boiled for 6 hours. Then the solvent was distilled off under reduced pressure; products **3a**,**b** and **4a**,**b** were isolated from the mixture by column chromatography.

1.1. 1'-Phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-diones (3).

The reaction of 3-methylidene-5-phenylhydantoin **1** (200 mg, 1.06 mmol) and cyclopentadiene (715 μl, 8.51 mmol) in MeOH (50 ml) gave 219 mg (81%) of product **3a** and 24 mg (9%) of product **3b** as white or light yellow powders.

(1R,2R*,4R*)-1'-Phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-dione* (**3a**): ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.49-7.43 (m, 4H, Ph), 7.39-7.35 (m, 1H, Ph), 6.56 (dd, J_1=3.1 Hz, J_2=5.6 Hz, 1H, CH=), 6.23 (dd, J_1=3.0 Hz, J_2=5.6 Hz, 1H, CH=), 5.83 (bs, 1H, NH), 3.09 (s, 1H, CH), 3.06 (s, 1H, CH), 2.46 (dd, J_1=3.5 Hz, J_2=12.3 Hz, 1H, CH_2), 2.30 (d, J=9.1 Hz, 1H, CH_2), 1.58-1.55 (m, 1H, CH_2), 1.38 (dd, J_1=3.5 Hz, J_2=12.3 Hz, 1H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 176.0, 155.0, 142.2, 132.8, 131.4, 128.6, 127.6, 125.8, 66.3, 51.9, 47.3, 42.2, 41.0.

HRMS (ESI, m/Z): calculated ($C_{15}H_{15}N_2O_2$, M+H): 255.1128, found (M+H): 255.1131.

(1R,2S*,4R*)-1'-Phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-dione* (**3b**): ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.46-7.39 (m, 4H, Ph), 7.36-7.32 (m, 1H, Ph), 6.40 (dd, J_1=3.1 Hz, J_2=5.5 Hz, 1H, CH=), 6.17 (dd, J_1=3.1 Hz, J_2=5.7 Hz, 1H, CH=), 6.09 (bs,

1H, NH), 3.10-3.09 (m, 1H, CH), 2.96-2.95 (m, 1H, CH), 1.96-1.94 (m, 2H, CH_2), 1.78-1.75 (m, 1H, CH_2), 1.58-1.56 (m, 1H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 174.7, 155.5, 139.7, 132.1, 131.8, 128.9, 128.0, 126.0, 66.4, 54.1, 49.4, 42.6, 42.0.

HRMS (ESI, m/Z): calculated ($C_{15}H_{15}N_2O_2$, M+H): 255.1128, found (M+H): 255.1131.

1.2. 1'-Phenyl-2'-thioxospiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-en-5'-ones (4).

The reaction of 3-methylidene-5-phenylthiohydantoin **2** (200 mg, 0.98 mmol) and cyclopentadiene (660 μl, 7.84 mmol) in MeOH (50 ml) gave 209 mg (79%) of product **4a** and 22 mg (8%) of product **4b** as white or light yellow powders.

(1R,2R*,4R*)-1'-Phenyl-2'-thioxospiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-en-5'-one* (**4a**): ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.74 (bs, 1H, NH), 7.54-7.44 (m, 3H, Ph), 7.37-7.34 (m, 2H, Ph), 6.61 (dd, J_1=3.1 Hz, J_2=5.6 Hz, 1H, CH=), 6.28 (dd, J_1=2.9 Hz, J_2=5.6 Hz, 1H, CH=), 3.18 (s, 1H, CH), 3.10 (s, 1H, CH), 2.44 (dd, J_1=3.4 Hz, J_2=12.4 Hz, 1H, CH_2), 2.27 (d, J=9.2 Hz, 1H, CH_2), 1.60-1.56 (m, 1H, CH_2), 1.50 (dd, J_1=3.5 Hz, J_2=12.4 Hz, 1H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 181.9, 176.8, 142.8, 133.2, 132.9, 129.1, 129.0, 128.3, 69.6, 52.7, 47.3, 42.5, 41.0.

HRMS (ESI, m/Z): calculated ($C_{15}H_{15}N_2O_2S$, M+H): 271.0900, found (M+H): 271.0897.

(1R,2S*,4R*)-1'-Phenyl-2'-thioxospiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-en-5'-one* (**4b**): ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.54 (bs, 1H, NH), 7.52-7.42 (m, 3H, Ph), 7.35-7.32 (m, 2H, Ph), 6.44 (dd, J_1=3.0 Hz, J_2=5.6 Hz, 1H, CH=), 6.16 (dd, J_1=3.1 Hz, J_2=5.5 Hz, 1H, CH=), 3.13 (s, 1H, CH), 3.07 (s, 1H, CH), 2.07 (dd, J_1=3.6 Hz, J_2=12.6 Hz, 1H, CH_2), 1.92 (dd, J_1=2.6 Hz, J_2=12.6 Hz, 1H, CH_2), 1.79-1.77 (m, 1H, CH_2), 1.71 (d, J=9.4 Hz, 1H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 181.7, 175.2, 140.4, 132.9, 131.5, 129.1, 129.0, 128.3, 69.2, 53.9, 49.5, 42.9, 41.3.

HRMS (ESI, m/Z): calculated ($C_{15}H_{15}N_2O_2S$, M+H): 271.0900, found (M+H): 271.0903.

2. General procedure for the synthesis of 5-(furan-2-yl)-5-methyl-3-phenylimidazolidin-4-ones (5,6a).

Aluminium chloride (1.5 equiv.) was added to a solution of furan (5 eq.) in dichloromethane at room temperature. The mixture is kept for 30 seconds, after which a solution of 5-methylidene-2-chalcogenoimidazolidin-4-one (1 equiv.) in dichloromethane was added in one portion, and the mixture was stirred overnight. Then the mixture was treated with water with vigorous stirring, the organic phase was separated and dried over Na_2SO_4. The solution was filtered, the solvent was distilled off under reduced pressure, and the products **5a** and **6a** were isolated by column chromatography.

2.1. 5-(Furan-2-yl)-5-methyl-3-phenylimidazolidine-2,4-dione (5a).

The reaction of furan (97 μl, 1.33 mmol), $AlCl_3$ (53 mg, 0.41 mmol) and 3-methylidene-5-phenylhydantoin **1** (50 mg, 0.27 mmol) in dichloromethane (20 ml) gave 35 mg (51%) of the product **5a** as a white or light yellow powder.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 9.09 (bs, 1H, NH), 7.71 (d, J=1.2 Hz, 1H, furan), 7.50-7.46 (m, 2H, Ph), 7.42-7.36 (m, 3H, Ph), 6.59 (d, J=3.2 Hz, 1H, furan), 6.49 (dd, J_1=1.9 Hz, J_2=3.3 Hz, 1H, CH=), 1.78 (s, 3H, CH_3).

^{13}C NMR (101 MHz, DMSO-d6, δ, ppm): 172.5, 154.5, 151.4, 143.7, 131.9, 128.9, 128.1, 126.8, 110.8, 108.4, 59.5, 21.5.

HRMS (ESI, m/Z): calculated ($C_{15}H_{15}N_2O_2S$, M+H): 257.0921, found (M+H): 257.0927.

3.2. 5-(Furan-2-yl)-5-methyl-3-phenyl-2-thioxoimidazolidin-4-one (6a).

The reaction of furan (178 μl, 2.45 mmol), $AlCl_3$ (101 mg, 0.74 mmol) and 3-methylidene-5-phenylthiohydantoin **2** (100 mg, 0.49 mmol) in dichloromethane (40 ml) gave 33 mg (25%) of the product **6a** as a brown powder.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.08 (bs, 1H, NH), 7.54-7.45 (m, 4H, Ph + furan), 7.37-7.34 (m, 2H, Ph), 6.46 (d, J=3.3 Hz, 1H, furan), 6.40 (dd, J_1=1.8 Hz, J_2=3.3 Hz, 1H, CH=), 1.93 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 182.3, 172.2, 148.6, 143.4, 132.3, 129.0, 128.8, 127.9, 110.4, 108.1, 62.1, 21.4.

HRMS (ESI, m/Z): calculated ($C_{15}H_{15}N_2O_2S$, M+H): 272.0619, found (M+H): 271.0897.

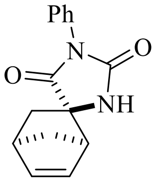
3. Synthesis of 1-acetyl-5-methylidene-3-phenylimidazolidine-2,4-dione (7).

The solution of acetic anhydride (28 μl, 0.29 mmol, 1.1 eq.) in dichloromethane (5 ml) was added dropwise to a solution of 3-methylidene-5-phenylhydantoin **1** (50 mg, 0.27 mmol, 1 eq.) in dichloromethane (15 ml) containing triethylamine (40 μl, 0.29 mmol, 1.1 eq.) and a catalytic amount of 4-dimethylaminopyridine. The solution was allowed to stir overnight at room temperature, then was diluted with dichloromethane, and washed with 10% aqueous HCl, dried over Na_2SO_4, filtered and concentrated to give 61 mg of 1-acetyl-5-methylidene-3-phenylimidazolidine-2,4-dione **7** in quantitative yield as a light curly powder.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.52-7.39 (m, 5H, Ph), 6.58 (d, J=0.7 Hz, 1H, CH_2), 6.09 (d, J=0.7 Hz, 1H, CH_2), 2.68 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 169.3, 160.0, 151.5, 131.5, 130.2, 129.2, 128.9, 126.2, 108.5, 26.5.

HRMS (ESI, m/Z): calculated ($C_{12}H_{11}N_2O_3$, M+H): 231.0764, found (M+H): 231.0765.



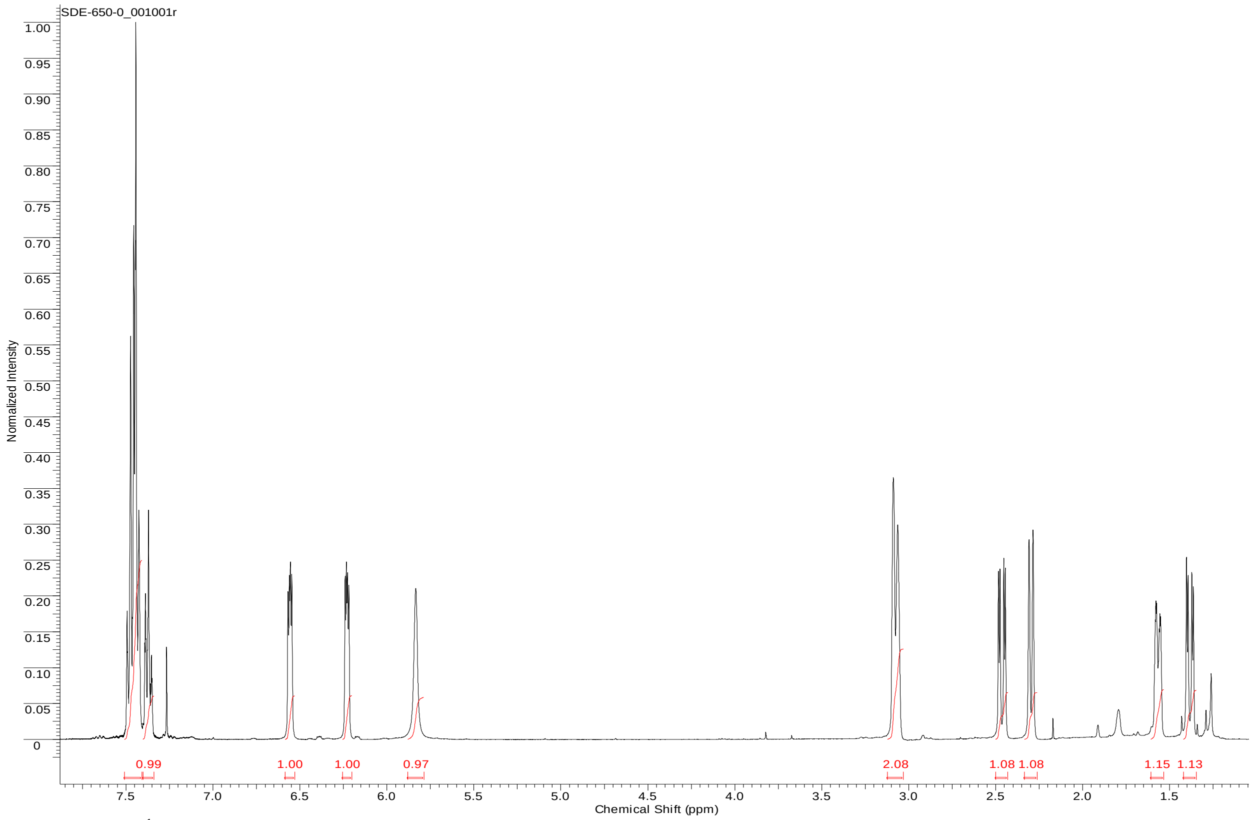


Figure S1 ^{1}H NMR spectrum of (*1R**,*2R**,*4R**)-1'-phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-dione (**3a**)

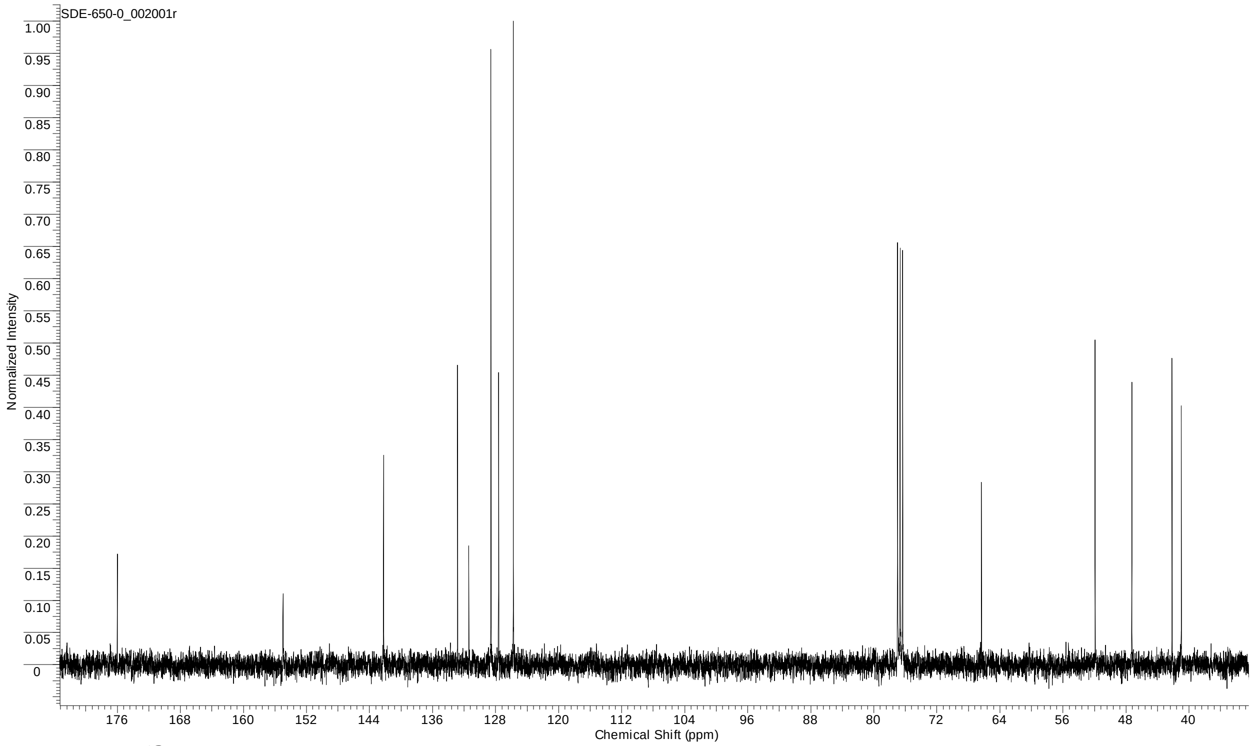
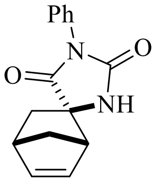


Figure S2 ^{13}C NMR spectrum of (*1R**,*2R**,*4R**)-1'-phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-dione (**3a**)



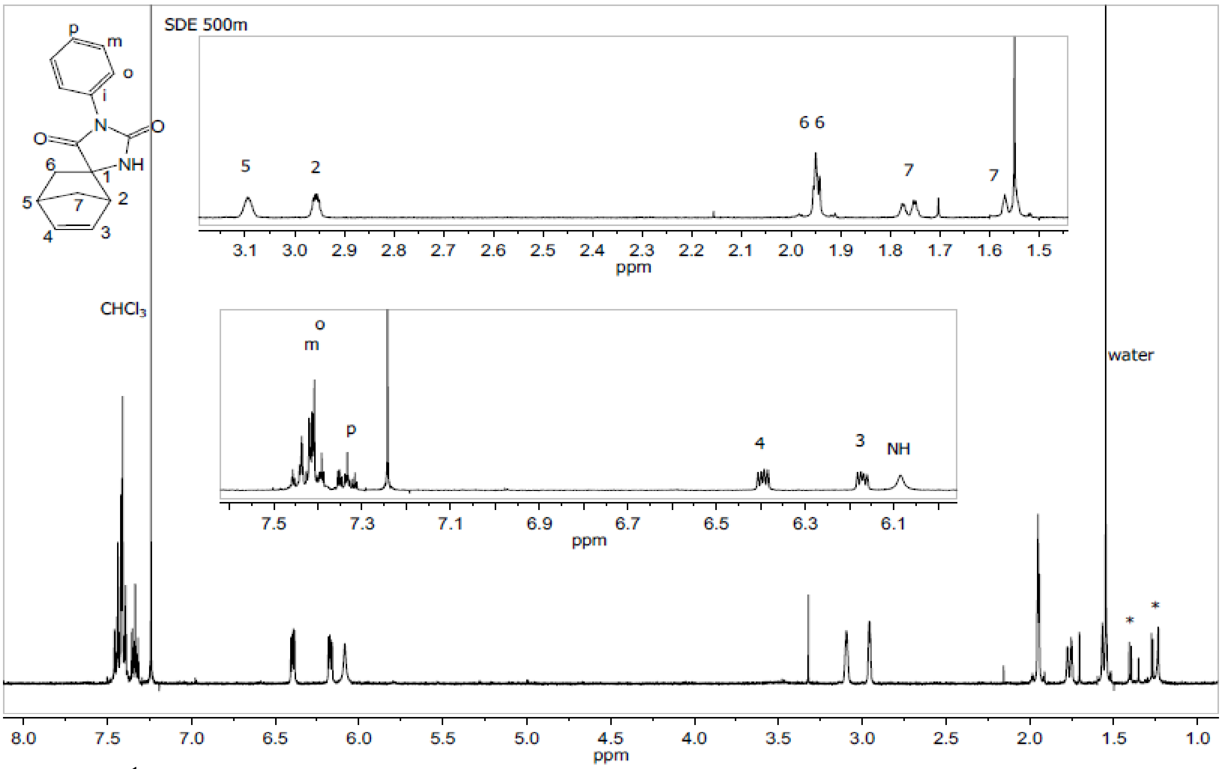


Figure S3 ^{1}H NMR spectrum of (*1R*,2S*,4R**)-1'-phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-dione (**3b**)

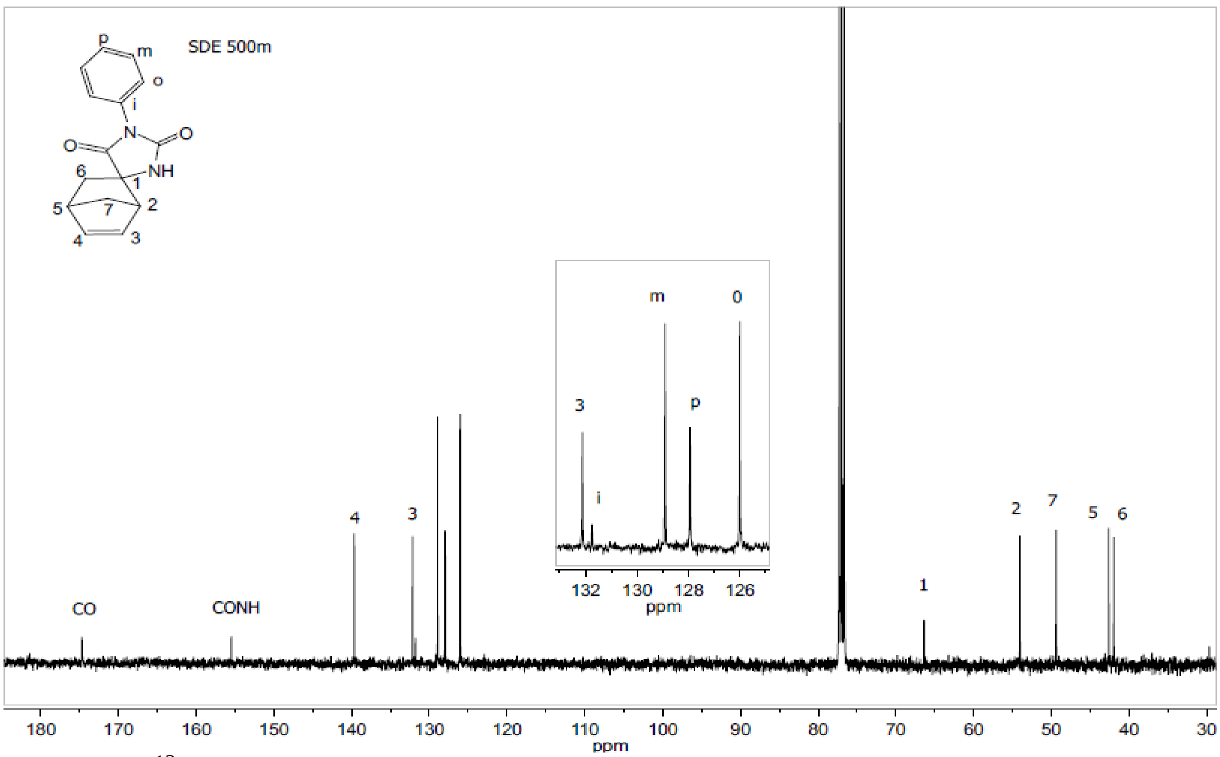


Figure S4 ^{13}C NMR spectrum of (*1R*,2S*,4R**)-1'-phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-dione (**3b**)

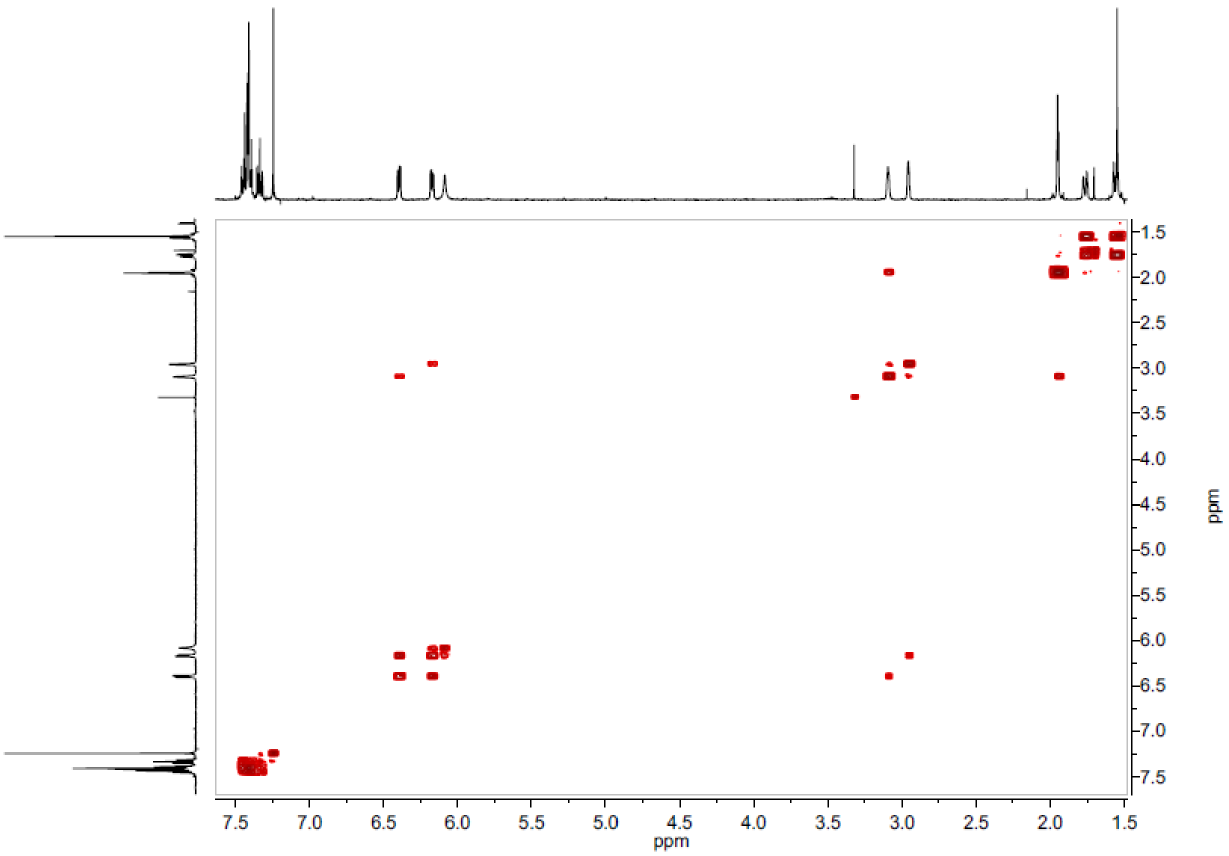


Figure S5 COSY NMR spectrum of (*1R*,2S*,4R**)-1'-phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-dione (**3b**)

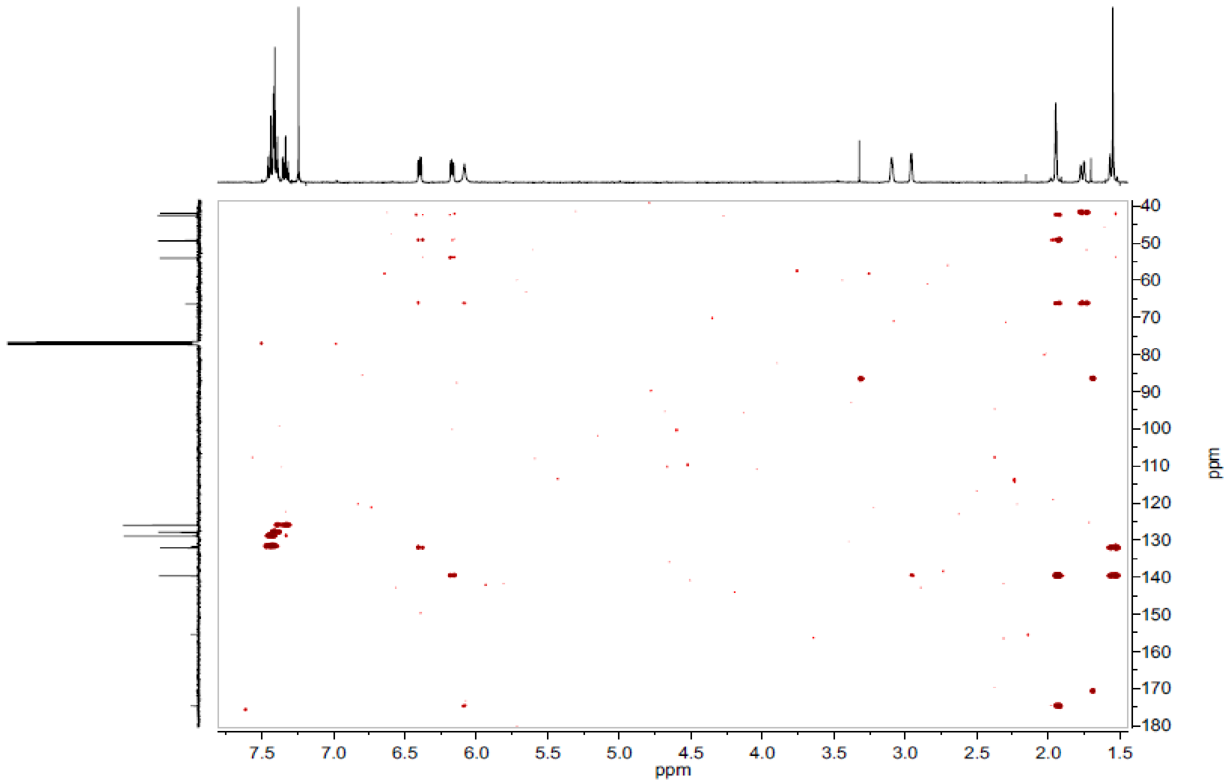


Figure S6 HMBC NMR spectrum of (*1R*,2S*,4R**)-1'-phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-dione (**3b**)

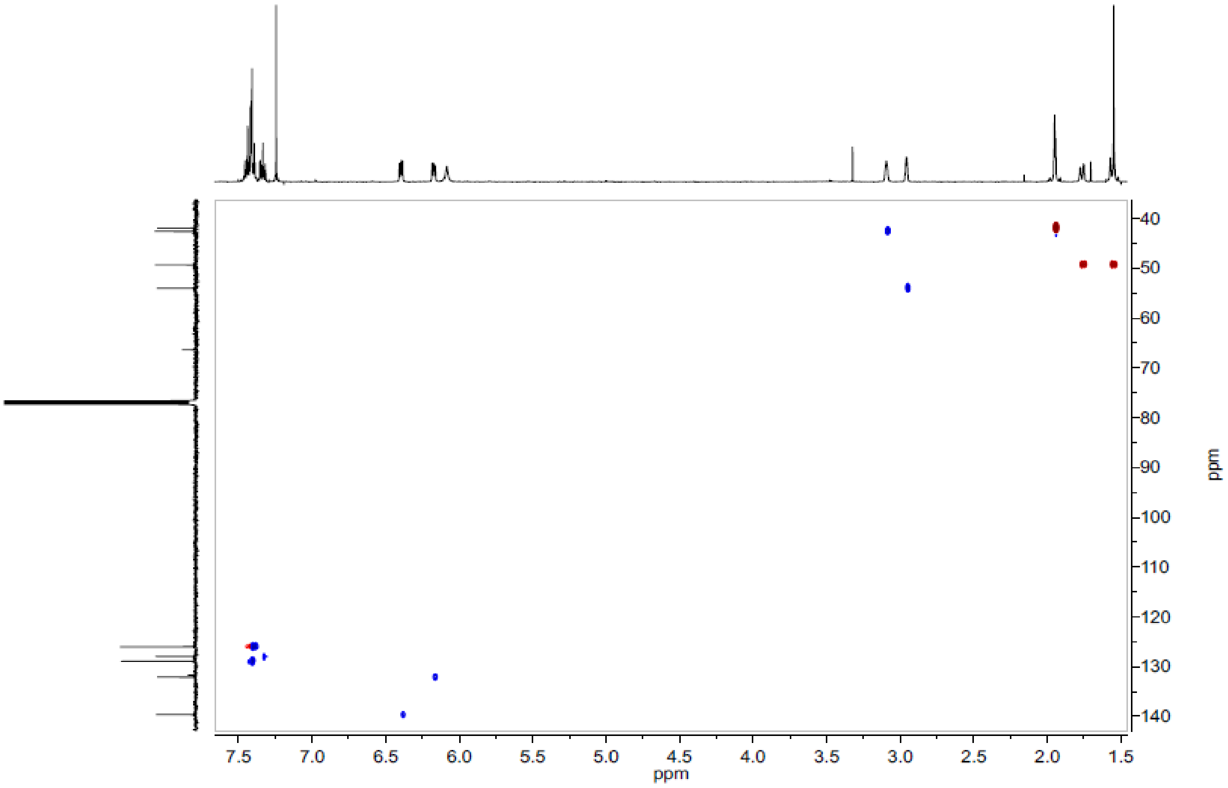


Figure S7 HSQC NMR spectrum of (*1R**,*2S**,*4R**)-1'-phenylspiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-ene-2',5'-dione (**3b**)

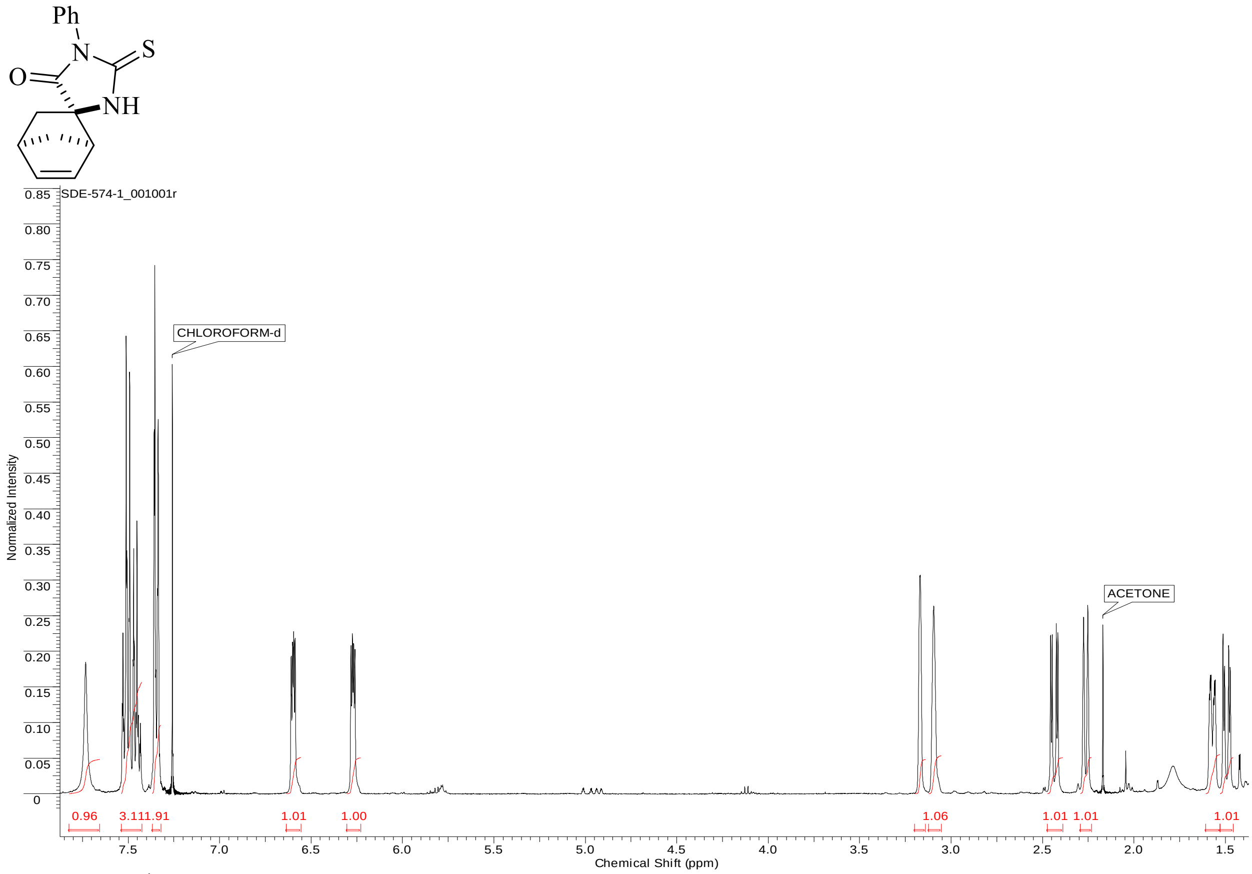


Figure S8 ^{1}H NMR spectrum of (*1R**,*2R**,*4R**)-1'-phenyl-2'-thioxospiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-en-5'-one (**4a**)

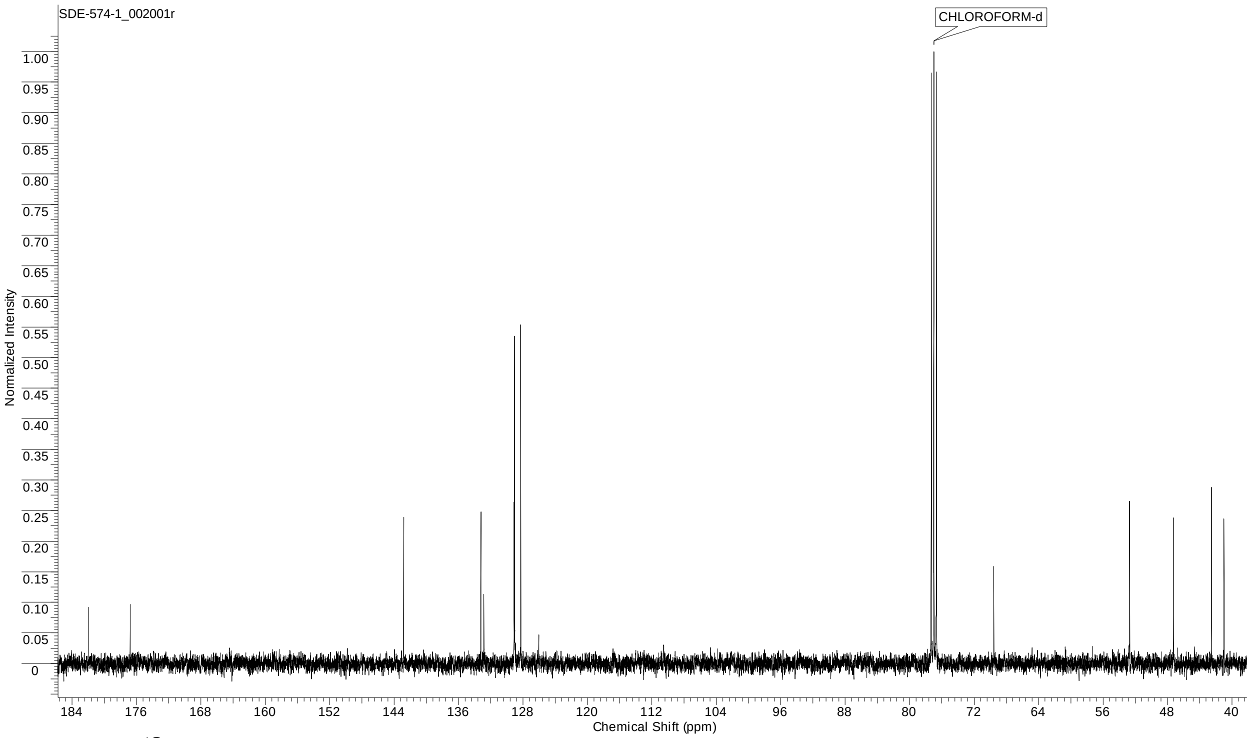
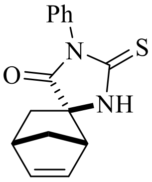


Figure S9 ^{13}C NMR spectrum of (*1R*,2R*,4R**)-1'-phenyl-2'-thioxospiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-en-5'-one (**4a**)



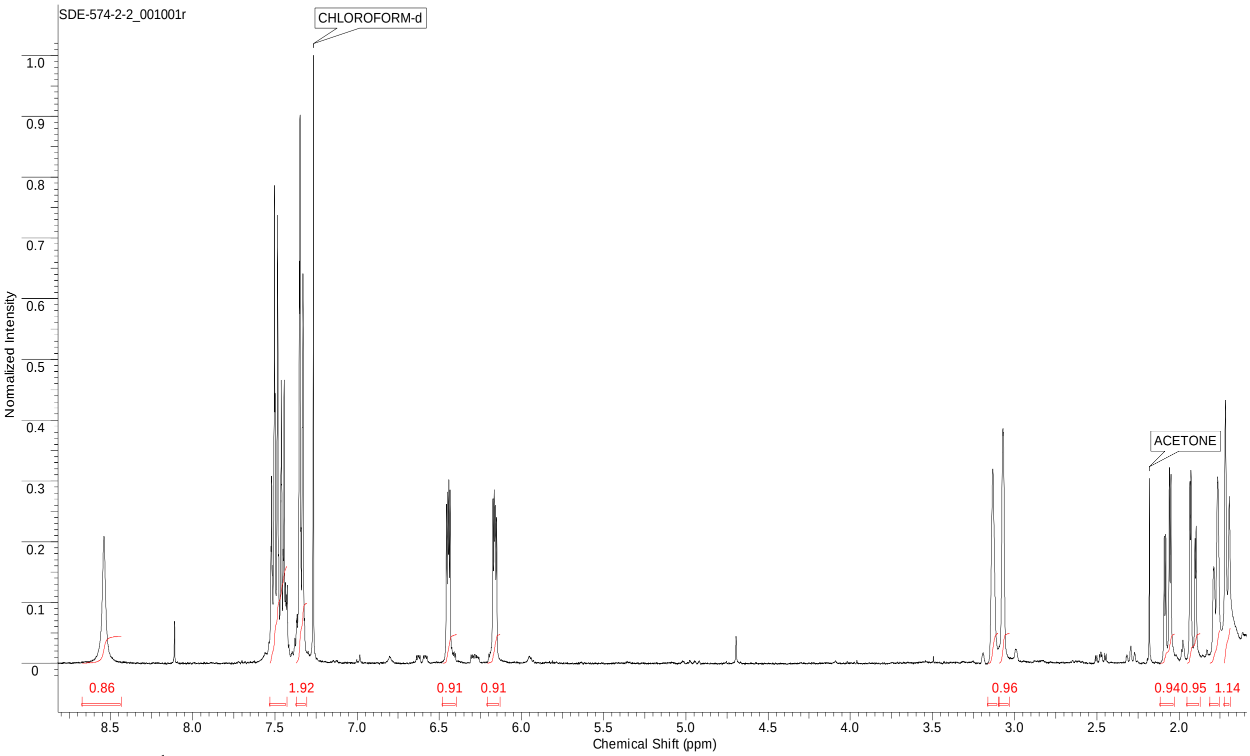


Figure S10 ^{1}H NMR spectrum of (*1R*,2S*,4R**)-1'-phenyl-2'-thioxospiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-en-5'-one (**4b**)

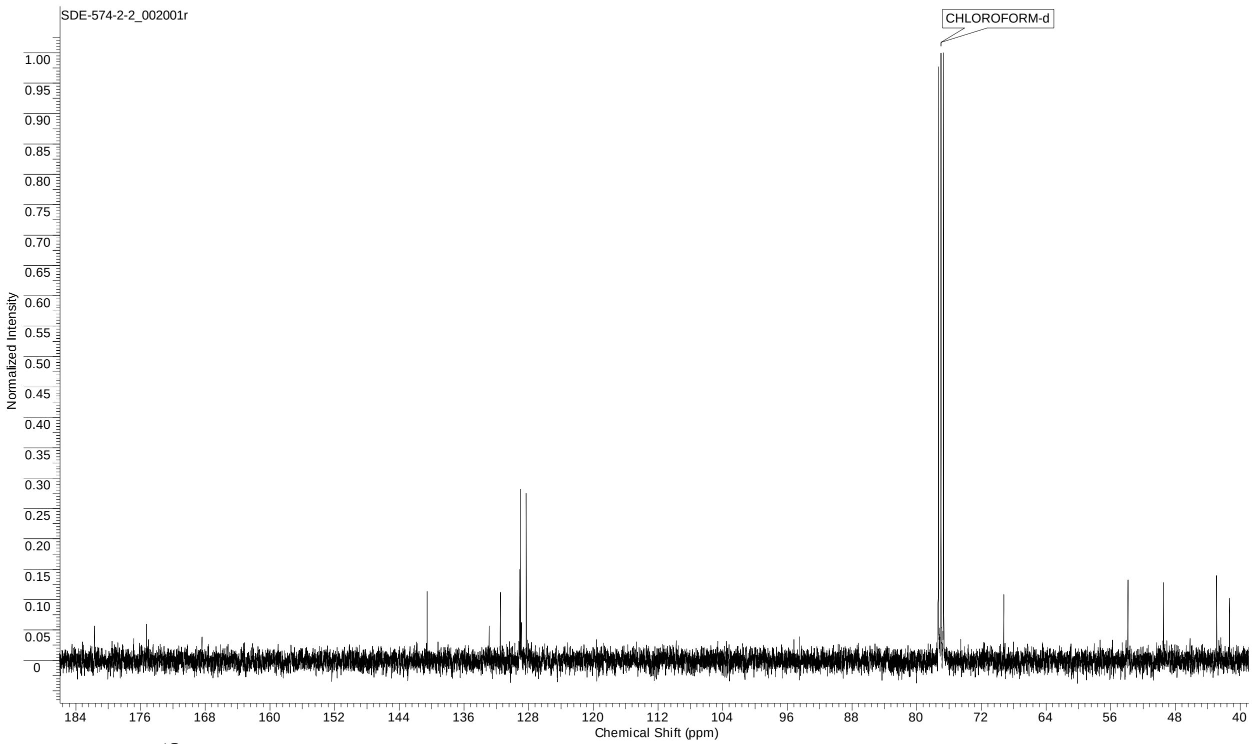
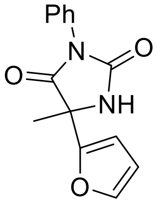


Figure S11 ^{13}C NMR spectrum of (*1R**,*2S**,*4R**)-1'-phenyl-2'-thioxospiro[bicyclo[2.2.1]heptane-2,4'-imidazolidin]-5-en-5'-one (**4b**)



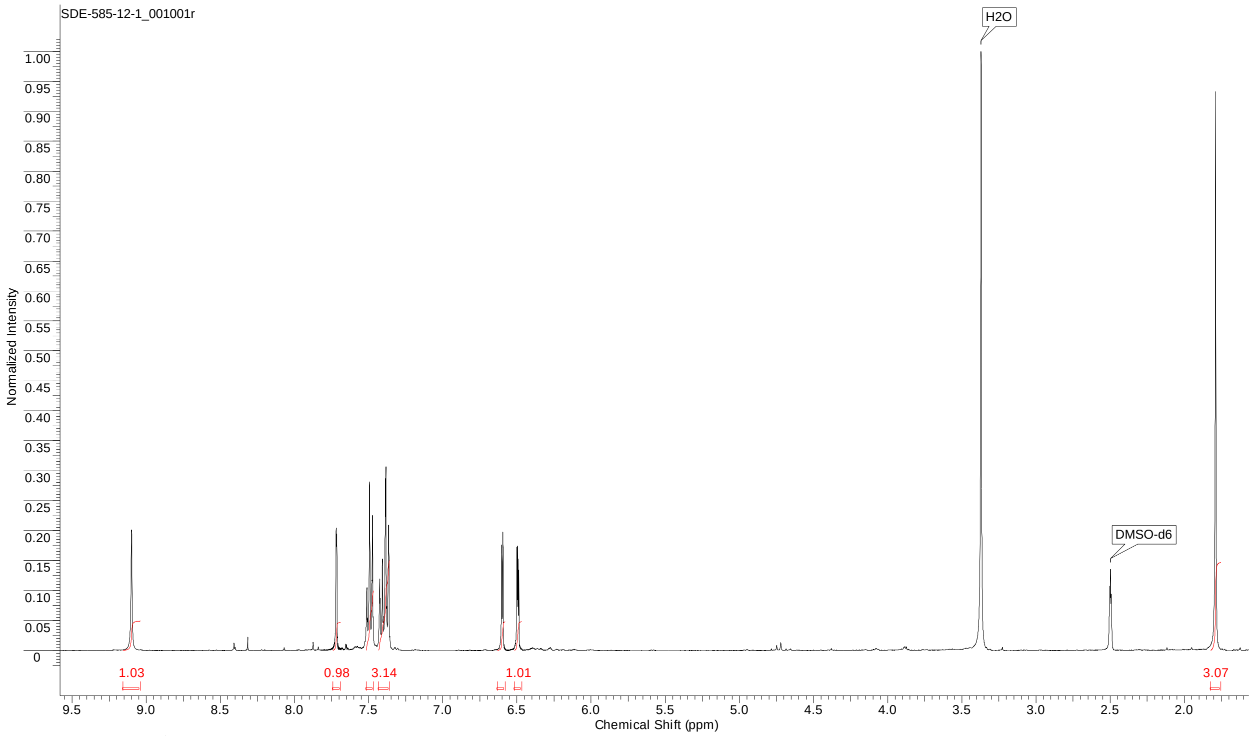


Figure S12 ^{1}H NMR spectrum of 5-(furan-2-yl)-5-methyl-3-phenylimidazolidine-2,4-dione (**5a**)

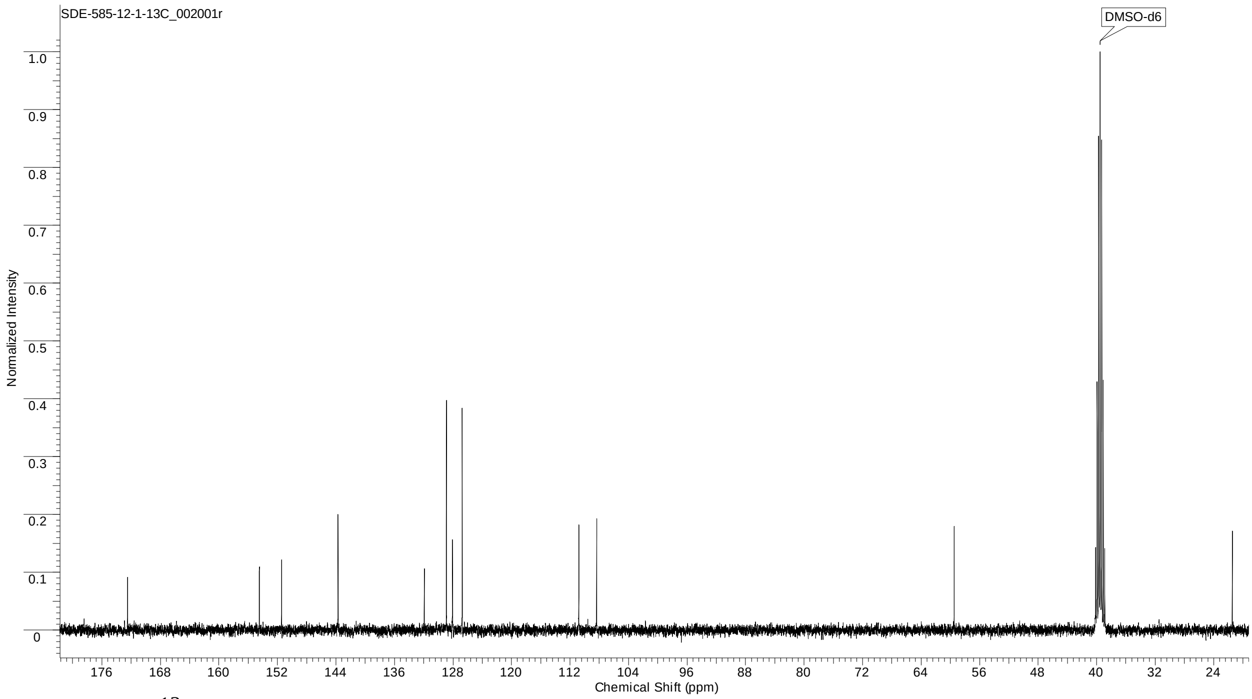
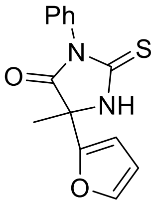


Figure S13 ^{13}C NMR spectrum of 5-(furan-2-yl)-5-methyl-3-phenylimidazolidine-2,4-dione (**5a**)



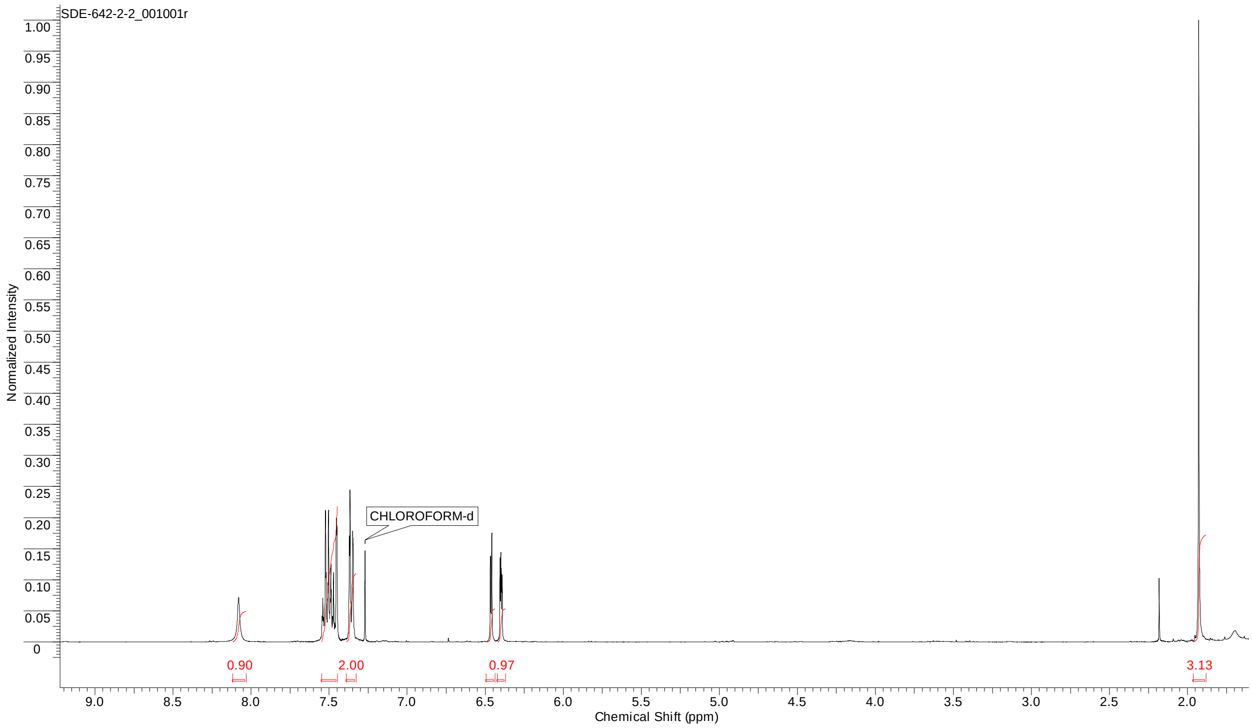


Figure S14 ^{1}H NMR spectrum of 5-(furan-2-yl)-5-methyl-3-phenyl-2-thioxoimidazolidin-4-one (**6a**)

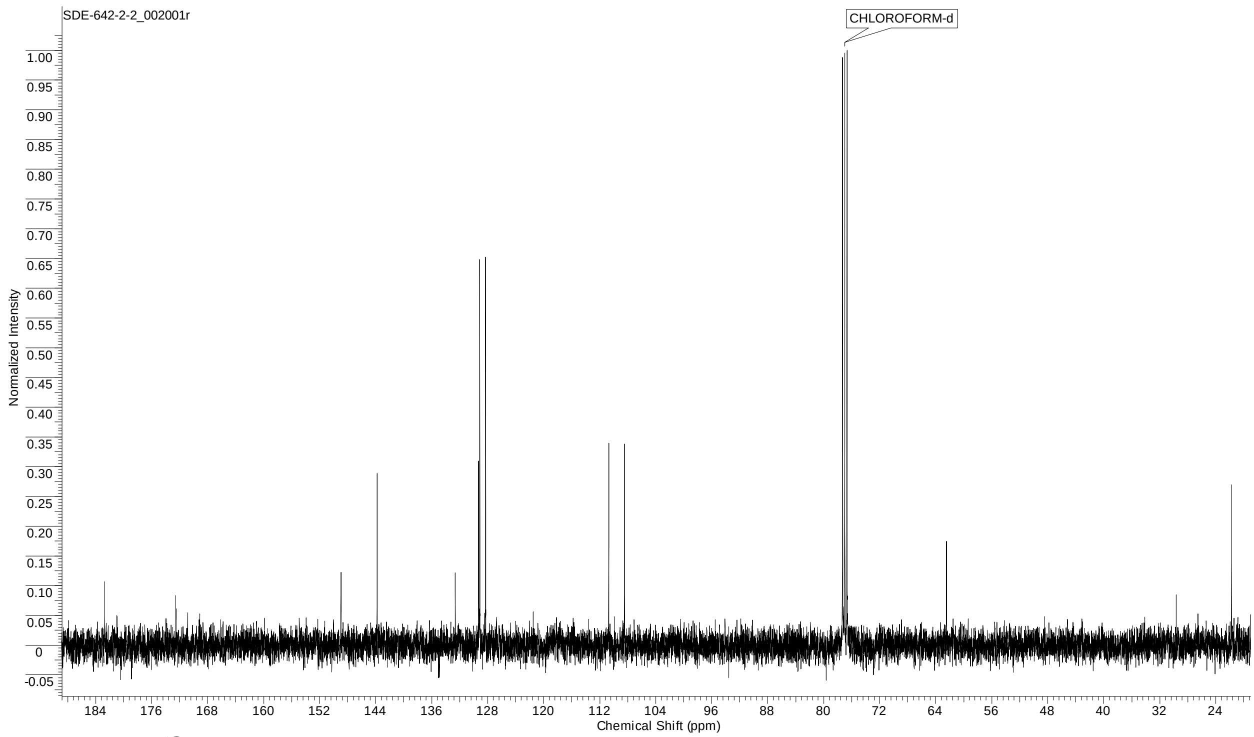


Figure S15 ^{13}C NMR spectrum of 5-(furan-2-yl)-5-methyl-3-phenyl-2-thioxoimidazolidin-4-one (**6a**)

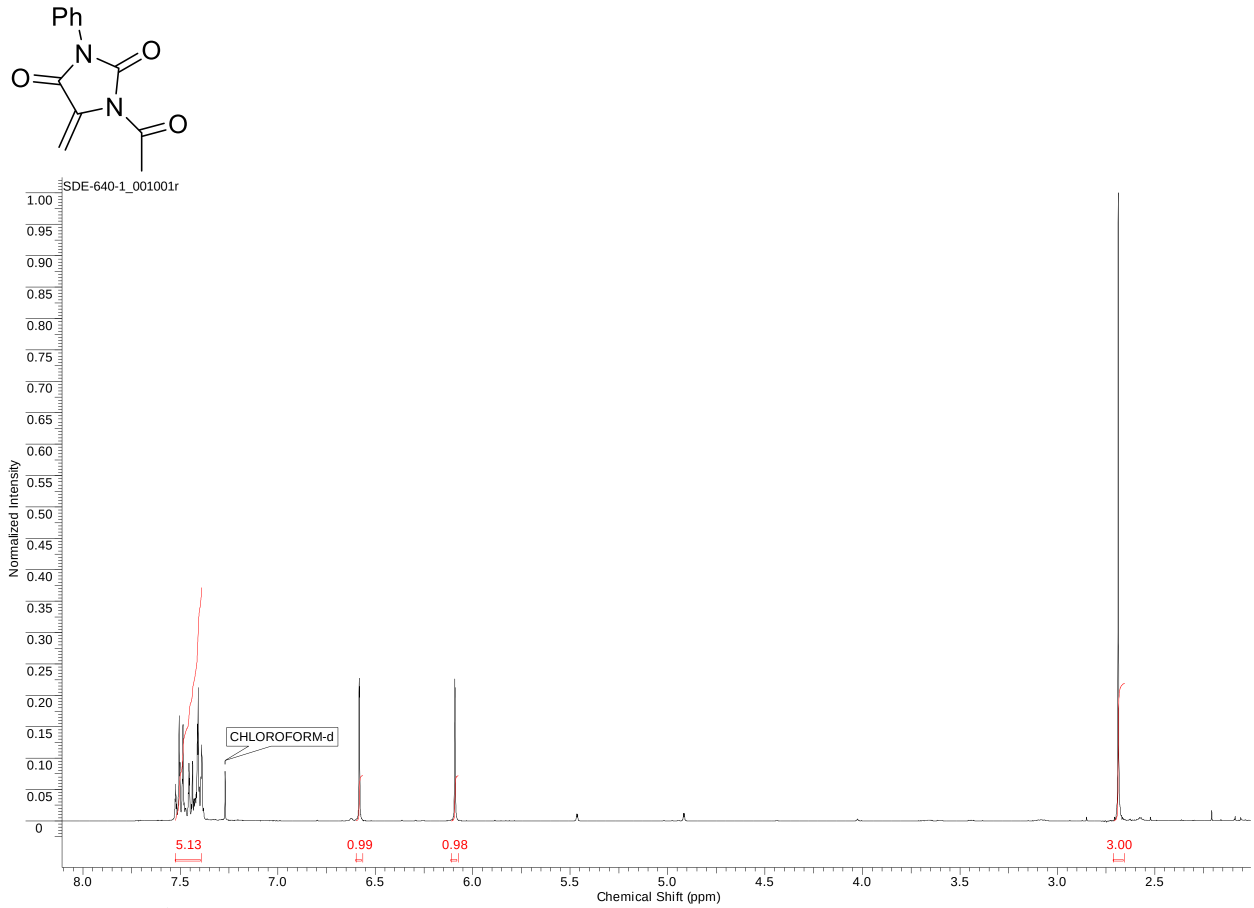


Figure S16 ^{1}H NMR spectrum of 1-acetyl-5-methylene-3-phenylimidazolidine-2,4-dione (**7**)

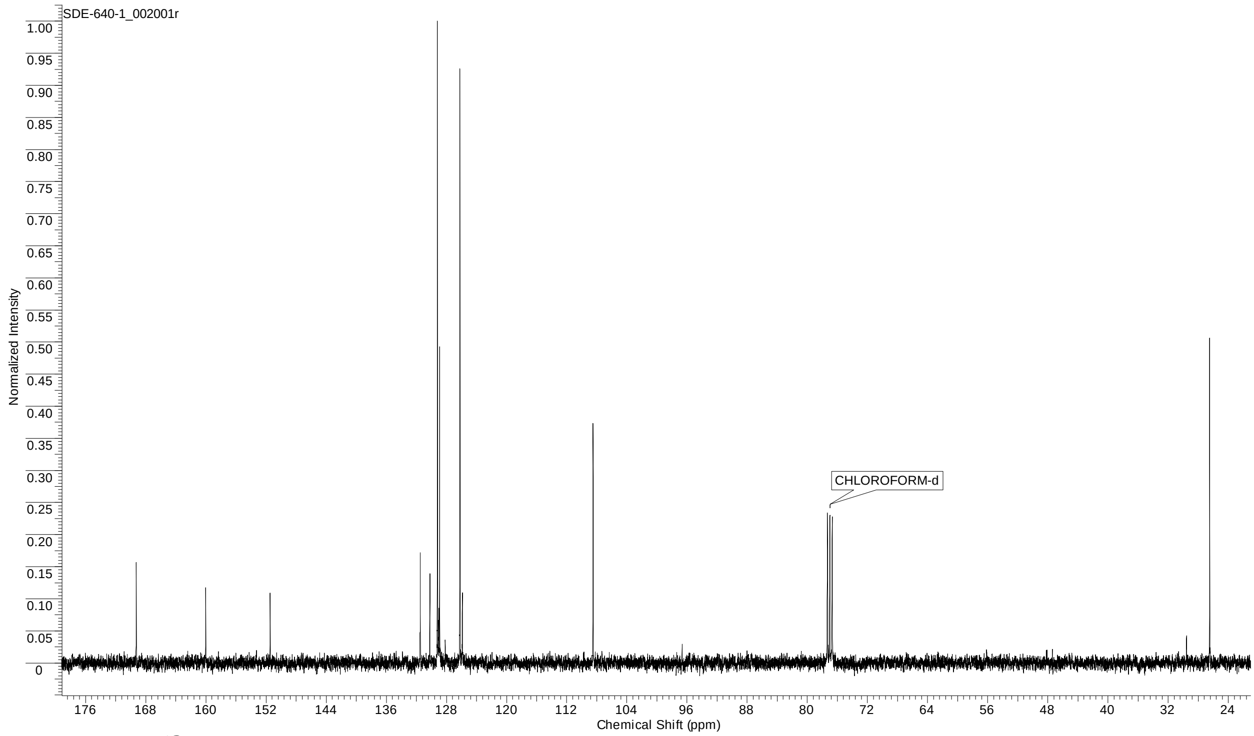


Figure S17 ^{13}C NMR spectrum of 1-acetyl-5-methylidene-3-phenylimidazolidine-2,4-dione (**7**)

X-Ray

Table S1. Crystal data and structure refinement for shelx.

Identification code	shelx	
Empirical formula	C15 H14 N2 O2	
Formula weight	254.28	
Temperature	293(2) K	
Wavelength	1.54186 E	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.2292(3) E	α= 78.582(3)°.
	b = 9.5107(5) E	β= 82.750(4)°.
	c = 22.7896(8) E	γ = 76.124(4)°.
Volume	1280.40(11) E^3	
Z	4	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	0.722 mm^{-1}	
F(000)	536	
Theta range for data collection	3.971 to 72.898°.	
Index ranges	-7<=h<=5, -11<=k<=11, -26<=l<=28	
Reflections collected	14894	
Independent reflections	4837 [R(int) = 0.0720]	
Completeness to theta = 67.686°	95.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4837 / 0 / 352	
Goodness-of-fit on F^2	0.910	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1239	
R indices (all data)	R1 = 0.1143, wR2 = 0.1522	
Extinction coefficient	0.0046(6)	
Largest diff. peak and hole	0.318 and -0.239 $e.E^{-3}$	

Table S2. Bond lengths [E] and angles [°] for shelx.

O(1A)-C(2A)	1.222(3)
O(2A)-C(4A)	1.214(3)
N(1A)-C(4A)	1.387(3)
N(1A)-C(2A)	1.408(3)
N(1A)-C(11A)	1.425(3)
N(2A)-C(2A)	1.334(3)
N(2A)-C(3A)	1.451(3)
N(2A)-H(2A)	0.83(3)
C(3A)-C(4A)	1.503(4)
C(3A)-C(5A)	1.548(4)
C(3A)-C(9A)	1.560(3)
C(5A)-C(6A)	1.526(4)
C(5A)-H(5A1)	0.9700
C(5A)-H(5A2)	0.9700
C(6A)-C(7A)	1.459(4)
C(6A)-C(10A)	1.543(5)
C(6A)-H(6A)	0.9800
C(7A)-C(8A)	1.272(4)
C(7A)-H(7A)	0.9300
C(8A)-C(9A)	1.488(4)
C(8A)-H(8A)	0.9300
C(9A)-C(10A)	1.548(4)
C(9A)-H(9A)	0.9800
C(10A)-H(10A)	0.9700
C(10A)-H(10B)	0.9700
C(11A)-C(12A)	1.382(3)
C(11A)-C(16A)	1.388(3)
C(12A)-C(13A)	1.381(4)
C(12A)-H(12A)	0.9300
C(13A)-C(14A)	1.380(4)
C(13A)-H(13A)	0.9300
C(14A)-C(15A)	1.364(4)
C(14A)-H(14A)	0.9300
C(15A)-C(16A)	1.371(4)
C(15A)-H(15A)	0.9300
C(16A)-H(16A)	0.9300
O(1B)-C(2B)	1.223(3)
O(2B)-C(4B)	1.211(3)
N(1B)-C(4B)	1.386(3)
N(1B)-C(2B)	1.402(3)
N(1B)-C(11B)	1.433(3)
N(2B)-C(2B)	1.333(3)
N(2B)-C(3B)	1.450(3)
N(2B)-H(2B)	0.84(3)
C(3B)-C(4B)	1.520(4)
C(3B)-C(5B)	1.548(4)
C(3B)-C(9B)	1.563(4)
C(5B)-C(6B)	1.539(5)
C(5B)-H(5B1)	0.9700
C(5B)-H(5B2)	0.9700
C(6B)-C(7B)	1.485(4)
C(6B)-C(10B)	1.498(5)
C(6B)-H(6B)	0.9800
C(7B)-C(8B)	1.315(5)
C(7B)-H(7B)	0.9300
C(8B)-C(9B)	1.510(4)
C(8B)-H(8B)	0.9300
C(9B)-C(10B)	1.533(4)
C(9B)-H(9B)	0.9800
C(10B)-H(10C)	0.9700

C(10B)-H(10D)	0.9700
C(11B)-C(16B)	1.365(4)
C(11B)-C(12B)	1.379(4)
C(12B)-C(13B)	1.386(4)
C(12B)-H(12B)	0.9300
C(13B)-C(14B)	1.344(5)
C(13B)-H(13B)	0.9300
C(14B)-C(15B)	1.376(5)
C(14B)-H(14B)	0.9300
C(15B)-C(16B)	1.394(4)
C(15B)-H(15B)	0.9300
C(16B)-H(16B)	0.9300

C(4A)-N(1A)-C(2A)	109.4(2)
C(4A)-N(1A)-C(11A)	125.07(18)
C(2A)-N(1A)-C(11A)	125.35(19)
C(2A)-N(2A)-C(3A)	113.7(2)
C(2A)-N(2A)-H(2A)	124(2)
C(3A)-N(2A)-H(2A)	122(2)
O(1A)-C(2A)-N(2A)	127.9(2)
O(1A)-C(2A)-N(1A)	124.4(2)
N(2A)-C(2A)-N(1A)	107.6(2)
N(2A)-C(3A)-C(4A)	100.71(19)
N(2A)-C(3A)-C(5A)	114.8(2)
C(4A)-C(3A)-C(5A)	114.3(2)
N(2A)-C(3A)-C(9A)	113.0(2)
C(4A)-C(3A)-C(9A)	112.5(2)
C(5A)-C(3A)-C(9A)	102.02(19)
O(2A)-C(4A)-N(1A)	125.2(3)
O(2A)-C(4A)-C(3A)	126.6(2)
N(1A)-C(4A)-C(3A)	108.30(18)
C(6A)-C(5A)-C(3A)	103.4(2)
C(6A)-C(5A)-H(5A1)	111.1
C(3A)-C(5A)-H(5A1)	111.1
C(6A)-C(5A)-H(5A2)	111.1
C(3A)-C(5A)-H(5A2)	111.1
H(5A1)-C(5A)-H(5A2)	109.0
C(7A)-C(6A)-C(5A)	106.7(2)
C(7A)-C(6A)-C(10A)	100.1(3)
C(5A)-C(6A)-C(10A)	101.2(2)
C(7A)-C(6A)-H(6A)	115.6
C(5A)-C(6A)-H(6A)	115.6
C(10A)-C(6A)-H(6A)	115.6
C(8A)-C(7A)-C(6A)	108.4(3)
C(8A)-C(7A)-H(7A)	125.8
C(6A)-C(7A)-H(7A)	125.8
C(7A)-C(8A)-C(9A)	109.4(3)
C(7A)-C(8A)-H(8A)	125.3
C(9A)-C(8A)-H(8A)	125.3
C(8A)-C(9A)-C(10A)	98.6(2)
C(8A)-C(9A)-C(3A)	104.6(2)
C(10A)-C(9A)-C(3A)	100.9(2)
C(8A)-C(9A)-H(9A)	116.7
C(10A)-C(9A)-H(9A)	116.7
C(3A)-C(9A)-H(9A)	116.7
C(6A)-C(10A)-C(9A)	92.2(2)
C(6A)-C(10A)-H(10A)	113.3
C(9A)-C(10A)-H(10A)	113.3
C(6A)-C(10A)-H(10B)	113.3
C(9A)-C(10A)-H(10B)	113.3
H(10A)-C(10A)-H(10B)	110.6
C(12A)-C(11A)-C(16A)	119.7(2)
C(12A)-C(11A)-N(1A)	121.3(2)

C(16A)-C(11A)-N(1A)	118.9(2)
C(11A)-C(12A)-C(13A)	119.6(2)
C(11A)-C(12A)-H(12A)	120.2
C(13A)-C(12A)-H(12A)	120.2
C(14A)-C(13A)-C(12A)	120.3(3)
C(14A)-C(13A)-H(13A)	119.8
C(12A)-C(13A)-H(13A)	119.8
C(15A)-C(14A)-C(13A)	119.7(3)
C(15A)-C(14A)-H(14A)	120.2
C(13A)-C(14A)-H(14A)	120.2
C(14A)-C(15A)-C(16A)	120.9(3)
C(14A)-C(15A)-H(15A)	119.5
C(16A)-C(15A)-H(15A)	119.5
C(15A)-C(16A)-C(11A)	119.7(2)
C(15A)-C(16A)-H(16A)	120.1
C(11A)-C(16A)-H(16A)	120.1
C(4B)-N(1B)-C(2B)	110.3(2)
C(4B)-N(1B)-C(11B)	125.30(18)
C(2B)-N(1B)-C(11B)	124.3(2)
C(2B)-N(2B)-C(3B)	113.5(2)
C(2B)-N(2B)-H(2B)	120(2)
C(3B)-N(2B)-H(2B)	123(2)
O(1B)-C(2B)-N(2B)	128.3(2)
O(1B)-C(2B)-N(1B)	124.0(2)
N(2B)-C(2B)-N(1B)	107.7(2)
N(2B)-C(3B)-C(4B)	100.7(2)
N(2B)-C(3B)-C(5B)	115.7(2)
C(4B)-C(3B)-C(5B)	113.1(2)
N(2B)-C(3B)-C(9B)	113.4(2)
C(4B)-C(3B)-C(9B)	112.7(2)
C(5B)-C(3B)-C(9B)	101.7(2)
O(2B)-C(4B)-N(1B)	125.2(2)
O(2B)-C(4B)-C(3B)	127.5(2)
N(1B)-C(4B)-C(3B)	107.33(19)
C(6B)-C(5B)-C(3B)	104.2(3)
C(6B)-C(5B)-H(5B1)	110.9
C(3B)-C(5B)-H(5B1)	110.9
C(6B)-C(5B)-H(5B2)	110.9
C(3B)-C(5B)-H(5B2)	110.9
H(5B1)-C(5B)-H(5B2)	108.9
C(7B)-C(6B)-C(10B)	100.7(3)
C(7B)-C(6B)-C(5B)	106.3(3)
C(10B)-C(6B)-C(5B)	99.1(3)
C(7B)-C(6B)-H(6B)	116.1
C(10B)-C(6B)-H(6B)	116.1
C(5B)-C(6B)-H(6B)	116.1
C(8B)-C(7B)-C(6B)	107.9(3)
C(8B)-C(7B)-H(7B)	126.1
C(6B)-C(7B)-H(7B)	126.1
C(7B)-C(8B)-C(9B)	108.3(3)
C(7B)-C(8B)-H(8B)	125.9
C(9B)-C(8B)-H(8B)	125.9
C(8B)-C(9B)-C(10B)	98.9(3)
C(8B)-C(9B)-C(3B)	104.0(2)
C(10B)-C(9B)-C(3B)	99.9(2)
C(8B)-C(9B)-H(9B)	117.1
C(10B)-C(9B)-H(9B)	117.1
C(3B)-C(9B)-H(9B)	117.1
C(6B)-C(10B)-C(9B)	95.5(2)
C(6B)-C(10B)-H(10C)	112.6
C(9B)-C(10B)-H(10C)	112.6
C(6B)-C(10B)-H(10D)	112.6
C(9B)-C(10B)-H(10D)	112.6

H(10C)-C(10B)-H(10D)	110.1
C(16B)-C(11B)-C(12B)	120.8(3)
C(16B)-C(11B)-N(1B)	119.8(3)
C(12B)-C(11B)-N(1B)	119.3(2)
C(11B)-C(12B)-C(13B)	119.1(3)
C(11B)-C(12B)-H(12B)	120.4
C(13B)-C(12B)-H(12B)	120.4
C(14B)-C(13B)-C(12B)	120.7(3)
C(14B)-C(13B)-H(13B)	119.7
C(12B)-C(13B)-H(13B)	119.7
C(13B)-C(14B)-C(15B)	120.4(3)
C(13B)-C(14B)-H(14B)	119.8
C(15B)-C(14B)-H(14B)	119.8
C(14B)-C(15B)-C(16B)	119.9(3)
C(14B)-C(15B)-H(15B)	120.0
C(16B)-C(15B)-H(15B)	120.0
C(11B)-C(16B)-C(15B)	119.0(3)
C(11B)-C(16B)-H(16B)	120.5
C(15B)-C(16B)-H(16B)	120.5

Symmetry transformations used to generate equivalent atoms:

Table S3. Torsion angles [°] for shelx.

C(3A)-N(2A)-C(2A)-O(1A)	-178.9(2)
C(3A)-N(2A)-C(2A)-N(1A)	1.0(3)
C(4A)-N(1A)-C(2A)-O(1A)	-178.1(2)
C(11A)-N(1A)-C(2A)-O(1A)	-2.1(4)
C(4A)-N(1A)-C(2A)-N(2A)	2.0(3)
C(11A)-N(1A)-C(2A)-N(2A)	178.0(2)
C(2A)-N(2A)-C(3A)-C(4A)	-3.3(3)
C(2A)-N(2A)-C(3A)-C(5A)	-126.6(2)
C(2A)-N(2A)-C(3A)-C(9A)	116.9(2)
C(2A)-N(1A)-C(4A)-O(2A)	176.0(2)
C(11A)-N(1A)-C(4A)-O(2A)	0.0(4)
C(2A)-N(1A)-C(4A)-C(3A)	-4.1(2)
C(11A)-N(1A)-C(4A)-C(3A)	179.89(19)
N(2A)-C(3A)-C(4A)-O(2A)	-175.7(3)
C(5A)-C(3A)-C(4A)-O(2A)	-52.0(3)
C(9A)-C(3A)-C(4A)-O(2A)	63.7(3)
N(2A)-C(3A)-C(4A)-N(1A)	4.4(2)
C(5A)-C(3A)-C(4A)-N(1A)	128.0(2)
C(9A)-C(3A)-C(4A)-N(1A)	-116.2(2)
N(2A)-C(3A)-C(5A)-C(6A)	-121.5(3)
C(4A)-C(3A)-C(5A)-C(6A)	122.8(2)
C(9A)-C(3A)-C(5A)-C(6A)	1.1(3)
C(3A)-C(5A)-C(6A)-C(7A)	66.0(3)
C(3A)-C(5A)-C(6A)-C(10A)	-38.2(3)
C(5A)-C(6A)-C(7A)-C(8A)	-70.1(3)
C(10A)-C(6A)-C(7A)-C(8A)	34.9(3)
C(6A)-C(7A)-C(8A)-C(9A)	-0.8(4)
C(7A)-C(8A)-C(9A)-C(10A)	-33.3(3)
C(7A)-C(8A)-C(9A)-C(3A)	70.5(3)
N(2A)-C(3A)-C(9A)-C(8A)	58.0(3)
C(4A)-C(3A)-C(9A)-C(8A)	171.3(2)
C(5A)-C(3A)-C(9A)-C(8A)	-65.8(3)
N(2A)-C(3A)-C(9A)-C(10A)	160.0(2)
C(4A)-C(3A)-C(9A)-C(10A)	-86.8(2)
C(5A)-C(3A)-C(9A)-C(10A)	36.1(3)
C(7A)-C(6A)-C(10A)-C(9A)	-50.7(3)
C(5A)-C(6A)-C(10A)-C(9A)	58.8(3)
C(8A)-C(9A)-C(10A)-C(6A)	49.1(2)
C(3A)-C(9A)-C(10A)-C(6A)	-57.7(2)
C(4A)-N(1A)-C(11A)-C(12A)	136.4(2)
C(2A)-N(1A)-C(11A)-C(12A)	-39.0(3)
C(4A)-N(1A)-C(11A)-C(16A)	-40.1(3)
C(2A)-N(1A)-C(11A)-C(16A)	144.5(2)
C(16A)-C(11A)-C(12A)-C(13A)	0.2(3)
N(1A)-C(11A)-C(12A)-C(13A)	-176.3(2)
C(11A)-C(12A)-C(13A)-C(14A)	0.6(4)
C(12A)-C(13A)-C(14A)-C(15A)	-0.8(4)
C(13A)-C(14A)-C(15A)-C(16A)	0.1(4)
C(14A)-C(15A)-C(16A)-C(11A)	0.7(4)
C(12A)-C(11A)-C(16A)-C(15A)	-0.8(4)
N(1A)-C(11A)-C(16A)-C(15A)	175.7(2)
C(3B)-N(2B)-C(2B)-O(1B)	-174.1(3)
C(3B)-N(2B)-C(2B)-N(1B)	6.5(3)
C(4B)-N(1B)-C(2B)-O(1B)	177.6(3)
C(11B)-N(1B)-C(2B)-O(1B)	-6.1(4)
C(4B)-N(1B)-C(2B)-N(2B)	-2.9(3)
C(11B)-N(1B)-C(2B)-N(2B)	173.3(2)
C(2B)-N(2B)-C(3B)-C(4B)	-7.0(3)
C(2B)-N(2B)-C(3B)-C(5B)	-129.3(3)
C(2B)-N(2B)-C(3B)-C(9B)	113.6(3)

C(2B)-N(1B)-C(4B)-O(2B)	178.3(3)
C(11B)-N(1B)-C(4B)-O(2B)	2.1(4)
C(2B)-N(1B)-C(4B)-C(3B)	-1.5(3)
C(11B)-N(1B)-C(4B)-C(3B)	-177.7(2)
N(2B)-C(3B)-C(4B)-O(2B)	-174.9(3)
C(5B)-C(3B)-C(4B)-O(2B)	-50.8(4)
C(9B)-C(3B)-C(4B)-O(2B)	63.9(4)
N(2B)-C(3B)-C(4B)-N(1B)	4.8(3)
C(5B)-C(3B)-C(4B)-N(1B)	129.0(2)
C(9B)-C(3B)-C(4B)-N(1B)	-116.4(2)
N(2B)-C(3B)-C(5B)-C(6B)	-120.6(3)
C(4B)-C(3B)-C(5B)-C(6B)	123.9(3)
C(9B)-C(3B)-C(5B)-C(6B)	2.8(3)
C(3B)-C(5B)-C(6B)-C(7B)	65.2(4)
C(3B)-C(5B)-C(6B)-C(10B)	-38.8(3)
C(10B)-C(6B)-C(7B)-C(8B)	33.2(4)
C(5B)-C(6B)-C(7B)-C(8B)	-69.6(4)
C(6B)-C(7B)-C(8B)-C(9B)	-0.7(4)
C(7B)-C(8B)-C(9B)-C(10B)	-31.1(3)
C(7B)-C(8B)-C(9B)-C(3B)	71.5(3)
N(2B)-C(3B)-C(9B)-C(8B)	56.4(3)
C(4B)-C(3B)-C(9B)-C(8B)	170.1(2)
C(5B)-C(3B)-C(9B)-C(8B)	-68.6(3)
N(2B)-C(3B)-C(9B)-C(10B)	158.2(2)
C(4B)-C(3B)-C(9B)-C(10B)	-88.1(3)
C(5B)-C(3B)-C(9B)-C(10B)	33.2(3)
C(7B)-C(6B)-C(10B)-C(9B)	-49.5(3)
C(5B)-C(6B)-C(10B)-C(9B)	59.2(3)
C(8B)-C(9B)-C(10B)-C(6B)	48.2(3)
C(3B)-C(9B)-C(10B)-C(6B)	-57.7(3)
C(4B)-N(1B)-C(11B)-C(16B)	-50.9(4)
C(2B)-N(1B)-C(11B)-C(16B)	133.4(3)
C(4B)-N(1B)-C(11B)-C(12B)	126.7(3)
C(2B)-N(1B)-C(11B)-C(12B)	-49.0(3)
C(16B)-C(11B)-C(12B)-C(13B)	-0.1(4)
N(1B)-C(11B)-C(12B)-C(13B)	-177.6(2)
C(11B)-C(12B)-C(13B)-C(14B)	1.4(5)
C(12B)-C(13B)-C(14B)-C(15B)	-1.4(5)
C(13B)-C(14B)-C(15B)-C(16B)	0.0(5)
C(12B)-C(11B)-C(16B)-C(15B)	-1.3(4)
N(1B)-C(11B)-C(16B)-C(15B)	176.3(2)
C(14B)-C(15B)-C(16B)-C(11B)	1.3(5)

Symmetry transformations used to generate equivalent atoms:

Table S4. Hydrogen bonds for shelx [E and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2A)-H(2A)...O(1A)#1	0.83(3)	2.07(3)	2.886(3)	166(3)
N(2B)-H(2B)...O(1B)#2	0.84(3)	2.08(3)	2.907(3)	166(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x-1,-y+1,-z+1 #2 -x+1,-y+1,-z