An $n \rightarrow \pi^*$ Interaction Reduces the Electrophilicity of the Acceptor Carbonyl Group

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General Experimental

Commercial chemicals were of reagent grade or better, and were used without further purification. Anhydrous THF, toluene, and CH_2Cl_2 were obtained from Glass Contour Solvent Delivery system (S. G. Water, Nashua, NH). Other anhydrous solvents were obtained in septum-sealed bottles. Reactions were monitored by thin-layer chromatography with visualization by UV light, or staining with $KMnO_4$ or I_2. In all reactions involving anhydrous solvents, glassware was either oven- or flame-dried. Flash chromatography was performed with columns of silica gel 60, 230–400 mesh (Silicycle, Québec City, Canada).

Standard ^{1}H and ^{13}C 1D NMR data were acquired at ambient temperature with a Bruker DMX-400 Avance spectrometer (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) at the National Magnetic Resonance Facility at Madison (NMRFAM). Carbon-13 spectra were proton-decoupled. ^{1}H spectra were acquired and worked up using the NUTS software package.[1] NOESY-1D experiments were performed on Varian INOVA-500 at the NMR Facility in the Department of Chemistry. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, ESI) at the Mass Spectrometry Facility in the Department of Chemistry.

Experimental Procedures

N,*N*′–Bisacylimidazolidines **2** and **3**, and *N*,*N*′-bisthioacylimidazolidines **4** and **5** were synthesized by a route used to access similar systems.[2]

*N,N′-Bisacetylimidazolidine-2-carboxylic acid methyl ester (**2**)*
^{1}H NMR ($CDCl_3$, 400 MHz, mixture of three rotamers): δ 5.92 (s, 0.21H), 5.79 (s, 0.68H), 5.64 (s, 0.04H), 4.40–4.26 (m, 0.70H), 4.10–3.51 (m, 6.3H), 2.25–2.05 (m, 6H)
^{13}C NMR ($CDCl_3$, 100.6 MHz, mixture of three rotamers): δ 169.9, 169.1, 168.5, 168.4, 70.2, 69.2, 53.0, 52.7, 45.8, 44.5, 43.6, 42.6, 22.3, 22.1, 21.9, 21.7
ESI–MS: $[M + Na]^+$ calcd 237.0846; found 237.0844 (<1 ppm)

*N,N′-Bisacetylimidazolidine (**3**)*
^{1}H NMR ($CDCl_3$, 400 MHz, mixture of three rotamers): δ 5.30 (s, 0.10H), 4.94 (s, 1.90H), 3.89–3.68 (m, 4.0H), 2.16–2.03 (m, 6H)
^{13}C NMR ($CDCl_3$, 100.6 MHz, mixture of three rotamers): δ 169.7, 168.9, 168.4, 168.2, 70.0, 69.0, 52.9, 52.6, 45.7, 44.3, 43.4, 42.4, 22.2, 22.0, 21.8, 21.6
ESI–MS: $[M + H]^+$ calcd 157.0972; found 157.0978 (3.8 ppm)

*N,N′-Bisthioacetylimidazolidine-2-carboxylic acid methyl ester (**4**)*
^{1}H NMR ($CDCl_3$, 400 MHz, mixture of three rotamers): δ 7.15 (s, 0.09H), 6.53 (s, 0.86H), 6.11 (s, 0.02H), 5.10–4.98 (m, 0.9H), 4.30–3.71 (m, 6.1H), 2.86–2.60 (m, 6H)
^{13}C NMR ($CDCl_3$, 100.6 MHz, mixture of three rotamers): δ 199.9, 199.1, 198.5, 165.5, 76.2, 53.5, 52.9, 50.6, 49.4, 49.1, 47.6, 32.9, 32.2
ESI–MS: $[M + Na]^+$ calcd 269.0389 ; found 269.0392 (1.1 ppm)

*N,N′-Bisthioacetylimidazolidine (**5**)*
^{1}H NMR ($CDCl_3$, 400 MHz, mixture of three rotamers): δ 5.54 (s, 0.40H), 5.40 (s, 1.50), 5.23 (s, 0.10H), 4.36 (t, J=7.3Hz, 1.50H), 4.23 (s, 0.20H), 4.11 (s, 0.80H), 4.03 (t, J=7.3Hz, 1.50H), 2.69–2.60 (m, 6H)
^{13}C NMR ($CDCl_3$, 100.6 MHz, mixture of three rotamers): δ 197.7, 197.6, 197.1, 71.1, 68.6, 51.0, 49.8, 49.1, 47.9, 32.8, 32.7, 32.6, 32.4

ESI–MS: $[M + H]^+$ calcd 189.0515; found 189.0512 (1.6 ppm)

Measurement of K_1, K_2, and K_3. Compound **1**, **2**, or **3** (5–10 mg) was dissolved in D_2O with enough added CD_3OD to solubilize the compound (<20% of total volume). Values of K_1, K_2, and K_3 were determined from the relative areas of the *trans* and *cis* peaks. NOESY-1D experiments were carried out to confirm the proton assignments. The NOESY1D pulse sequence used was from the standard ChemPack library available for Varian spectrometers with a 5-mm inverse triple PFG-equipped probe. The sequence uses DPFGSE and SEDUCE-shaped RF pulses for multiplet selection. When needed, an array of mix times was used to confirm NOE buildup. Selection of multiplets were clean, as demonstrated by mix = 0 spectra. Mix times were typically set to $0.6\times T_1$, and d1 ≥ $3\times T_1$. T_1 values were measured by standard inversion-recovery methods.

Computational Methodology

The trans,trans conformation of compounds **2**–**5** was examined by hybrid density functional theory as implemented in Gaussian 03.[3] Geometry optimizations and frequency calculations at the B3LYP/6-311+G(2d,p) // B3LYP/6-31+G(2d,p) level of theory[4,5] were performed on the trans,trans conformation. Frequency calculations of the optimized structures yielded no imaginary frequencies, indicating a true stationary point on the potential energy surface. Optimized geometries were analyzed by NBO 5.0 at B3LYP/6-311+G(2d,p).

Crystal Structure Determinations

The desired compounds were dissolved in hexane with minimal amount of EtOAc. Slow evaporation afforded crystals suitable for X-ray analysis after ~4 d. X-ray intensity data were collected on a Bruker Quazar APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation at 105(2) K with the diffractometer to crystal distance of 4.9 cm. Preliminary indexing was carried out for the determination of cell constants. This consisted of three series of ω scans at different initial angles with each series consisting of 20 frames at intervals of 0.3° with the exposure time of 10 s per frame. The reflections were indexed by an automated indexing routine built in the SMART program. Data were collected by using the full-sphere data collection routine to a resolution of 0.80 Å. The intensity data were then corrected for absorption, and Lorentz and polarization effects. Structure solution and refinement was carried out using SHELXTL V.6.10.[6] Fig. S1, S2, S3, and S4 display **2**, **3**, **4**, and **5** with 50% probability thermal ellipsoids.

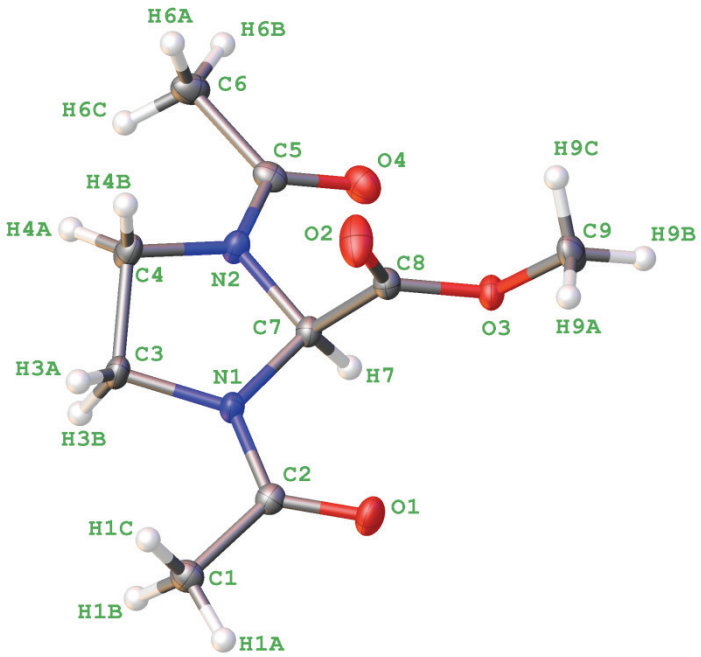


Fig. S1 Molecular drawing of compound **2** drawn at 50% probability ellipsoids.

Table S1 Crystal data and structure refinement for compound **2**

CCDC number	945383	
Identification code	raines43	
Empirical formula	$C_9H_{14}N_2O_4$	
Formula weight	214.22	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.5780(3) Å	α = 90°
	b = 6.7134(3) Å	β = 90°
	c = 23.3003(11) Å	γ = 90°
Volume	1028.96(8) Å^3	
Z	4	
Density (calculated)	1.383 mg/m^3	
Absorption coefficient	0.109 mm^{-1}	
F_{000}	456	
Crystal size	0.34 × 0.30 × 0.14 mm^3	
Theta range for data collection	1.75 to 33.17°	
Index ranges	$-10 \le h \le 10$, $-9 \le k \le 10$, $-35 \le l \le 35$	
Reflections collected	20056	
Independent reflections	3905 [R_{int} = 0.0627]	
Completeness to theta = 33.17°	99.4 %	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.9848 and 0.9637	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3905 / 0 / 139	
Goodness-of-fit on F^2	1.058	
Final R indices [$I > 2\sigma$(I)]	$R1$ = 0.0366, w$R2$ = 0.0998	
R indices (all data)	$R1$ = 0.0382, w$R2$ = 0.1012	
Largest diff. peak and hole	0.371 and –0.214 e.Å^{-3}	

Table S2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **2**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	*y*	*z*	U_{eq}
O(4)	1739(1)	8528(1)	2434(1)	22(1)
O(3)	4630(1)	10246(1)	3503(1)	17(1)
O(1)	4923(1)	6729(1)	4394(1)	21(1)
N(2)	283(1)	7690(1)	3271(1)	15(1)
N(1)	1738(1)	6424(1)	4070(1)	15(1)
C(2)	3204(2)	6034(1)	4460(1)	15(1)
C(7)	2223(1)	7621(1)	3569(1)	13(1)
O(2)	1911(1)	10766(1)	4066(1)	28(1)
C(3)	-388(2)	5772(2)	4083(1)	18(1)
C(8)	2890(2)	9726(1)	3750(1)	15(1)
C(4)	-1400(2)	7156(2)	3652(1)	18(1)
C(6)	-1903(2)	8291(2)	2445(1)	21(1)
C(5)	186(2)	8178(1)	2707(1)	16(1)
C(1)	2629(2)	4739(2)	4960(1)	18(1)
C(9)	5423(2)	12179(2)	3663(1)	20(1)

Table S3 Bond lengths [Å] and angles [°] for compound **2**

O(4)-C(5)	1.2264(13)
O(3)-C(8)	1.3281(11)
O(3)-C(9)	1.4474(12)
O(1)-C(2)	1.2324(12)
N(2)-C(5)	1.3547(13)
N(2)-C(7)	1.4535(12)
N(2)-C(4)	1.4632(13)
N(1)-C(2)	1.3516(13)
N(1)-C(7)	1.4520(12)
N(1)-C(3)	1.4656(13)
C(2)-C(1)	1.5024(14)
C(7)-C(8)	1.5385(13)
C(7)-H(7)	0.9800
O(2)-C(8)	1.2015(13)
C(3)-C(4)	1.5225(15)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(6)-C(5)	1.5057(15)
C(6)-H(6B)	0.9600
C(6)-H(6A)	0.9600
C(6)-H(6C)	0.9600
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(9)-H(9C)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9A)	0.9600
C(8)-O(3)-C(9)	115.80(8)
C(5)-N(2)-C(7)	120.81(8)
C(5)-N(2)-C(4)	127.65(9)
C(7)-N(2)-C(4)	111.53(8)
C(2)-N(1)-C(7)	119.40(8)
C(2)-N(1)-C(3)	127.48(8)
C(7)-N(1)-C(3)	113.12(8)
O(1)-C(2)-N(1)	119.85(9)
O(1)-C(2)-C(1)	123.13(9)
N(1)-C(2)-C(1)	117.02(9)
N(1)-C(7)-N(2)	102.02(7)
N(1)-C(7)-C(8)	110.51(8)
N(2)-C(7)-C(8)	110.61(8)
N(1)-C(7)-H(7)	111.1
N(2)-C(7)-H(7)	111.1

C(8)-C(7)-H(7)	111.1
N(1)-C(3)-C(4)	102.73(8)
N(1)-C(3)-H(3A)	111.2
C(4)-C(3)-H(3A)	111.2
N(1)-C(3)-H(3B)	111.2
C(4)-C(3)-H(3B)	111.2
H(3A)-C(3)-H(3B)	109.1
O(2)-C(8)-O(3)	125.04(9)
O(2)-C(8)-C(7)	123.31(9)
O(3)-C(8)-C(7)	111.62(8)
N(2)-C(4)-C(3)	102.66(8)
N(2)-C(4)-H(4A)	111.2
C(3)-C(4)-H(4A)	111.2
N(2)-C(4)-H(4B)	111.2
C(3)-C(4)-H(4B)	111.2
H(4A)-C(4)-H(4B)	109.1
C(5)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6A)	109.5
H(6B)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
O(4)-C(5)-N(2)	120.66(10)
O(4)-C(5)-C(6)	122.68(9)
N(2)-C(5)-C(6)	116.66(9)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(3)-C(9)-H(9C)	109.5
O(3)-C(9)-H(9B)	109.5
H(9C)-C(9)-H(9B)	109.5
O(3)-C(9)-H(9A)	109.5
H(9C)-C(9)-H(9A)	109.5
H(9B)-C(9)-H(9A)	109.5

Symmetry transformations were used to generate equivalent atoms.

Table S4 Anisotropic displacement parameters (Å^2 × 10^3) for compound **2**. The anisotropic displacement factor exponent takes the form: $-2p^2$ [h^2 a^{*2} U^{11} + ... + 2hk a^* b^* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(4)	26(1)	23(1)	18(1)	2(1)	4(1)	-1(1)
O(3)	14(1)	16(1)	20(1)	-1(1)	3(1)	-3(1)
O(1)	14(1)	28(1)	21(1)	1(1)	-2(1)	-5(1)
N(2)	12(1)	21(1)	13(1)	0(1)	0(1)	-2(1)
N(1)	11(1)	17(1)	16(1)	3(1)	-1(1)	-3(1)
C(2)	14(1)	16(1)	14(1)	-2(1)	0(1)	0(1)
C(7)	12(1)	14(1)	14(1)	-1(1)	1(1)	-1(1)
O(2)	25(1)	23(1)	35(1)	-12(1)	14(1)	-5(1)
C(3)	11(1)	22(1)	20(1)	4(1)	0(1)	-3(1)
C(8)	14(1)	15(1)	15(1)	0(1)	0(1)	-2(1)
C(4)	12(1)	27(1)	16(1)	2(1)	1(1)	-1(1)
C(6)	25(1)	18(1)	20(1)	1(1)	-8(1)	0(1)
C(5)	22(1)	12(1)	14(1)	-1(1)	-1(1)	0(1)
C(1)	19(1)	19(1)	15(1)	1(1)	0(1)	0(1)
C(9)	21(1)	18(1)	21(1)	2(1)	-3(1)	-8(1)

Table S5 Hydrogen coordinates (×10^4) and isotropic displacement parameters (Å^2 × 10^3) for compound **2**

	x	y	z	U_{eq}
H(7)	3266	6976	3333	16
H(3A)	-969	5935	4463	21
H(3B)	-516	4390	3967	21
H(4A)	-2473	6478	3443	22
H(4B)	-1961	8324	3839	22
H(6B)	-1789	8638	2047	31
H(6A)	-2689	9286	2641	31
H(6C)	-2563	7022	2480	31
H(1A)	3806	4499	5194	27
H(1B)	2107	3493	4821	27
H(1C)	1606	5396	5185	27
H(9C)	4418	13182	3587	30
H(9B)	6625	12456	3444	30
H(9A)	5752	12182	4065	30

Table S6 Torsion angles [°] for compound **2**

C(7)-N(1)-C(2)-O(1)	1.47(14)
C(3)-N(1)-C(2)-O(1)	-178.42(10)
C(7)-N(1)-C(2)-C(1)	-178.27(8)
C(3)-N(1)-C(2)-C(1)	1.84(15)
C(2)-N(1)-C(7)-N(2)	-179.69(8)
C(3)-N(1)-C(7)-N(2)	0.22(10)
C(2)-N(1)-C(7)-C(8)	-62.04(11)
C(3)-N(1)-C(7)-C(8)	117.86(9)
C(5)-N(2)-C(7)-N(1)	-161.19(8)
C(4)-N(2)-C(7)-N(1)	17.98(10)
C(5)-N(2)-C(7)-C(8)	81.23(10)
C(4)-N(2)-C(7)-C(8)	-99.59(9)
C(2)-N(1)-C(3)-C(4)	163.13(10)
C(7)-N(1)-C(3)-C(4)	-16.77(11)
C(9)-O(3)-C(8)-O(2)	3.76(15)
C(9)-O(3)-C(8)-C(7)	-177.90(8)
N(1)-C(7)-C(8)-O(2)	-52.11(13)
N(2)-C(7)-C(8)-O(2)	60.12(13)
N(1)-C(7)-C(8)-O(3)	129.51(8)
N(2)-C(7)-C(8)-O(3)	-118.26(9)
C(5)-N(2)-C(4)-C(3)	150.83(10)
C(7)-N(2)-C(4)-C(3)	-28.27(10)
N(1)-C(3)-C(4)-N(2)	25.81(10)
C(7)-N(2)-C(5)-O(4)	1.62(14)
C(4)-N(2)-C(5)-O(4)	-177.41(10)
C(7)-N(2)-C(5)-C(6)	-177.50(8)
C(4)-N(2)-C(5)-C(6)	3.47(14)

Symmetry transformations were used to generate equivalent atoms.

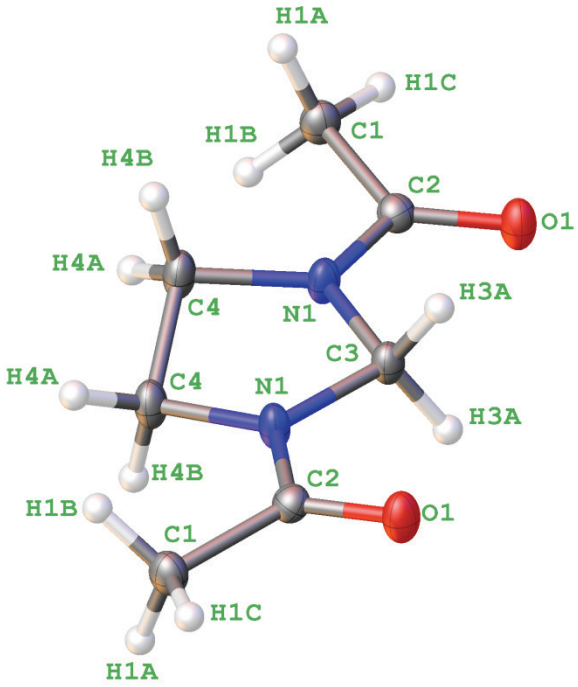


Fig. S2 Molecular drawing of compound **3** drawn at 50% probability ellipsoids.

Table S7 Crystal data and structure refinement for compound **3**

CCDC number	945384	
Identification code	raines47_0m	
Empirical formula	$C_7H_{12}N_2O_2$	
Formula weight	156.19	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 13.0221(4) Å	α = 90°
	b = 5.7680(2) Å	β = 107.3630(10)°
	c = 10.4415(3) Å	γ = 90°
Volume	748.54(4) Å^3	
Z	4	
Density (calculated)	1.386 mg/m^3	
Absorption coefficient	0.850 mm^{-1}	
F_{000}	336	
Crystal size	0.39 × 0.30 × 0.14 mm^3	
Theta range for data collection	7.13 to 67.91°	
Index ranges	$-15 \le h \le 15$, $-6 \le k \le 6$, $-12 \le l \le 12$	
Reflections collected	10524	
Independent reflections	686 [R_{int} = 0.0188]	
Completeness to theta = 67.91°	100.0%	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.8917 and 0.7316	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	686 / 0 / 52	
Goodness-of-fit on F^2	1.197	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0416, w$R2$ = 0.1051	
R indices (all data)	$R1$ = 0.0419, w$R2$ = 0.1056	
Largest diff. peak and hole	0.270 and –0.393 e.Å^{-3}	

Table S8 Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^3 × 10^3) for compound **3**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U_{eq}
O(1)	1268(1)	1658(2)	944(1)	22(1)
N(1)	621(1)	4534(2)	1937(1)	18(1)
C(3)	0	2942(3)	2500	17(1)
C(2)	1247(1)	3737(2)	1207(1)	16(1)
C(1)	1926(1)	5513(2)	776(1)	20(1)
C(4)	541(1)	6933(2)	2362(1)	20(1)

Table S9 Bond lengths [Å] and angles [°] for compound **3**

O(1)-C(2)	1.2323(15)
N(1)-C(2)	1.3509(15)
N(1)-C(3)	1.4586(14)
N(1)-C(4)	1.4666(15)
C(3)-N(1)#1	1.4586(14)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(2)-C(1)	1.5077(16)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(4)-C(4)#1	1.519(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(2)-N(1)-C(3)	120.88(10)
C(2)-N(1)-C(4)	127.00(10)
C(3)-N(1)-C(4)	111.91(9)
N(1)-C(3)-N(1)#1	101.98(13)
N(1)-C(3)-H(3A)	111.4
N(1)#1-C(3)-H(3A)	111.4
N(1)-C(3)-H(3B)	111.4
N(1)#1-C(3)-H(3B)	111.4
H(3A)-C(3)-H(3B)	109.2
O(1)-C(2)-N(1)	120.98(11)
O(1)-C(2)-C(1)	122.69(11)
N(1)-C(2)-C(1)	116.31(11)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(1)-C(4)-C(4)#1	102.21(7)
N(1)-C(4)-H(4A)	111.3
C(4)#1-C(4)-H(4A)	111.3
N(1)-C(4)-H(4B)	111.3
C(4)#1-C(4)-H(4B)	111.3
H(4A)-C(4)-H(4B)	109.2

Symmetry transformations were used to generate equivalent atoms.

Table S10 Anisotropic displacement parameters (Å^2 × 10^3) for compound **3**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2hk\, a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	29(1)	15(1)	27(1)	-1(1)	16(1)	0(1)
N(1)	23(1)	11(1)	24(1)	0(1)	13(1)	-1(1)
C(3)	20(1)	12(1)	21(1)	0	11(1)	0
C(2)	17(1)	16(1)	16(1)	1(1)	5(1)	1(1)
C(1)	21(1)	18(1)	24(1)	1(1)	11(1)	-1(1)
C(4)	26(1)	12(1)	26(1)	-1(1)	13(1)	-1(1)

Table S11 Hydrogen coordinates (×10^4) and isotropic displacement parameters (Å^2 × 10^3) for compound **3**

	x	y	z	U_{eq}
H(3A)	475	1949	3204	20
H(3B)	-475	1949	1796	20
H(1A)	2478	6105	1567	30
H(1B)	1469	6795	319	30
H(1C)	2274	4792	163	30
H(4A)	549	8045	1643	24
H(4B)	1133	7314	3181	24

Table S12 Torsion angles [°] for compound **3**

C(2)-N(1)-C(3)-N(1)#1	-174.29(12)
C(4)-N(1)-C(3)-N(1)#1	10.63(6)
C(3)-N(1)-C(2)-O(1)	3.58(16)
C(4)-N(1)-C(2)-O(1)	177.87(11)
C(3)-N(1)-C(2)-C(1)	-174.87(8)
C(4)-N(1)-C(2)-C(1)	-0.58(17)
C(2)-N(1)-C(4)-C(4)#1	158.90(12)
C(3)-N(1)-C(4)-C(4)#1	-26.38(14)

Symmetry transformations were used to generate equivalent atoms.

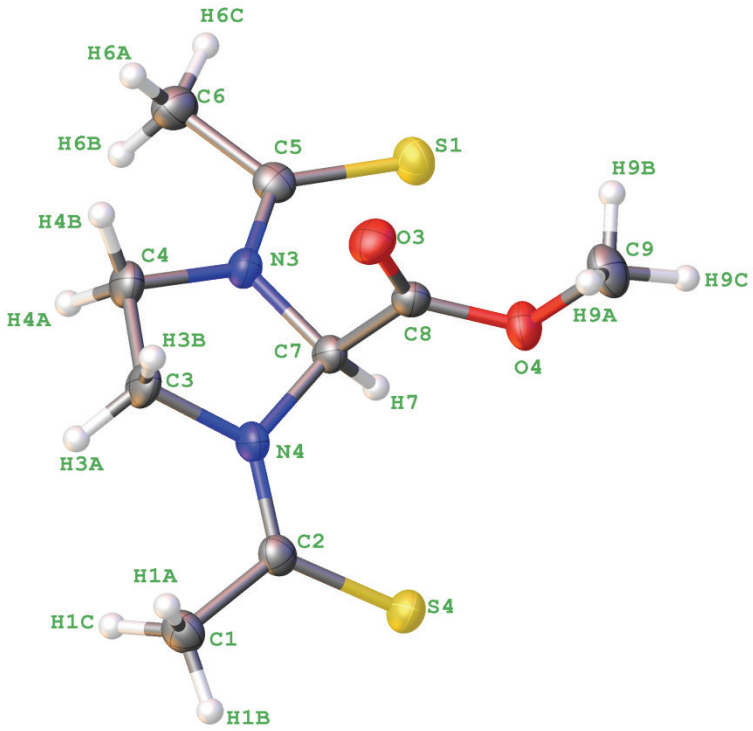


Fig. S3 Molecular drawing of compound **4** drawn at 50% probability ellipsoids.

Table S13 Crystal data and structure refinement for compound **4**

CCDC number	945382	
Identification code	raines40	
Empirical formula	$C_9H_{15}N_2O_2S_2$	
Formula weight	247.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P_1	
Unit cell dimensions	a = 6.5152(3) Å	α = 100.830(3)°
	b = 7.2897(3) Å	β = 93.213(3)°
	c = 12.4680(5) Å	γ = 91.152(3)°
Volume	580.41(4) Å^3	
Z	2	
Density (calculated)	1.415 mg/m^3	
Absorption coefficient	0.441 mm^{-1}	
F_{000}	262	
Crystal size	0.15 × 0.14 × 0.12 mm^3	
Theta range for data collection	1.67 to 26.50°	
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 9$, $-15 \le l \le 15$	
Reflections collected	11074	
Independent reflections	2380 [R_{int} = 0.0355]	
Completeness to theta = 26.50°	99.0%	
Absorption correction	Empirical with SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2380 / 0 / 138	
Goodness-of-fit on F^2	1.117	
Final R indices [$I > 2\sigma$(I)]	$R1$ = 0.0407, w$R2$ = 0.1017	
R indices (all data)	$R1$ = 0.0494, w$R2$ = 0.1055	
Largest diff. peak and hole	0.371 and –0.316 e.Å^{-3}	

Table S14 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **4**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	*y*	*z*	U_{eq}
S(1)	3285(1)	11128(1)	4136(1)	29(1)
S(4)	2898(1)	7582(1)	-200(1)	29(1)
O(3)	747(3)	6183(3)	3028(2)	30(1)
O(4)	3932(3)	6743(3)	2528(2)	26(1)
N(3)	39(3)	9972(3)	2829(2)	22(1)
N(4)	-106(3)	8133(3)	1142(2)	23(1)
C(6)	-672(5)	12402(4)	4333(2)	31(1)
C(5)	815(4)	11121(4)	3726(2)	23(1)
C(4)	-2161(4)	9710(4)	2482(2)	28(1)
C(3)	-2226(4)	8148(4)	1491(2)	29(1)
C(2)	451(4)	7643(3)	119(2)	22(1)
C(1)	-1264(4)	7135(4)	-752(2)	27(1)
C(7)	1312(4)	8753(4)	2099(2)	21(1)
C(8)	1959(4)	7075(4)	2617(2)	22(1)
C(9)	4728(5)	5284(4)	3065(2)	33(1)

Table S15 Bond lengths [Å] and angles [°] for compound **4**

S(1)-C(5)	1.661(3)
S(4)-C(2)	1.664(3)
O(3)-C(8)	1.207(3)
O(4)-C(8)	1.320(3)
O(4)-C(9)	1.450(3)
N(3)-C(5)	1.332(3)
N(3)-C(7)	1.455(3)
N(3)-C(4)	1.472(3)
N(4)-C(2)	1.331(3)
N(4)-C(7)	1.462(3)
N(4)-C(3)	1.471(3)
C(6)-C(5)	1.496(4)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(4)-C(3)	1.513(4)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(3)-H(3B)	0.9700
C(3)-H(3A)	0.9700
C(2)-C(1)	1.503(3)
C(1)-H(1C)	0.9600
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(7)-C(8)	1.542(4)
C(7)-H(7)	0.9800
C(9)-H(9A)	0.8940
C(9)-H(9C)	0.9874
C(9)-H(9B)	0.8976
C(8)-O(4)-C(9)	116.1(2)
C(5)-N(3)-C(7)	122.6(2)
C(5)-N(3)-C(4)	125.2(2)
C(7)-N(3)-C(4)	112.1(2)
C(2)-N(4)-C(7)	124.9(2)
C(2)-N(4)-C(3)	125.8(2)
C(7)-N(4)-C(3)	109.3(2)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
N(3)-C(5)-C(6)	115.9(2)
N(3)-C(5)-S(1)	121.8(2)

C(6)-C(5)-S(1)	122.3(2)
N(3)-C(4)-C(3)	104.1(2)
N(3)-C(4)-H(4A)	110.9
C(3)-C(4)-H(4A)	110.9
N(3)-C(4)-H(4B)	110.9
C(3)-C(4)-H(4B)	110.9
H(4A)-C(4)-H(4B)	109.0
N(4)-C(3)-C(4)	103.6(2)
N(4)-C(3)-H(3B)	111.0
C(4)-C(3)-H(3B)	111.0
N(4)-C(3)-H(3A)	111.0
C(4)-C(3)-H(3A)	111.0
H(3B)-C(3)-H(3A)	109.0
N(4)-C(2)-C(1)	116.3(2)
N(4)-C(2)-S(4)	122.76(19)
C(1)-C(2)-S(4)	120.9(2)
C(2)-C(1)-H(1C)	109.5
C(2)-C(1)-H(1A)	109.5
H(1C)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1C)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(3)-C(7)-N(4)	102.02(19)
N(3)-C(7)-C(8)	110.0(2)
N(4)-C(7)-C(8)	110.4(2)
N(3)-C(7)-H(7)	111.4
N(4)-C(7)-H(7)	111.4
C(8)-C(7)-H(7)	111.4
O(3)-C(8)-O(4)	125.9(2)
O(3)-C(8)-C(7)	122.2(2)
O(4)-C(8)-C(7)	111.9(2)
O(4)-C(9)-H(9A)	111.4
O(4)-C(9)-H(9C)	105.7
H(9A)-C(9)-H(9C)	129.6
O(4)-C(9)-H(9B)	111.4
H(9A)-C(9)-H(9B)	107.6
H(9C)-C(9)-H(9B)	88.5

Symmetry transformations were used to generate equivalent atoms.

Table S16 Anisotropic displacement parameters (Å^2 × 10^3) for compoudn **5**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2\,a^{*2}U^{11} + \ldots + 2hk\,a^*\,b^*\,U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	23(1)	32(1)	31(1)	3(1)	-4(1)	-1(1)
S(4)	20(1)	38(1)	27(1)	5(1)	3(1)	4(1)
O(3)	27(1)	31(1)	32(1)	9(1)	7(1)	-2(1)
O(4)	20(1)	28(1)	35(1)	13(1)	0(1)	3(1)
N(3)	17(1)	26(1)	24(1)	4(1)	2(1)	3(1)
N(4)	15(1)	31(1)	23(1)	5(1)	-1(1)	1(1)
C(6)	33(2)	31(2)	28(1)	4(1)	4(1)	5(1)
C(5)	26(1)	21(1)	24(1)	8(1)	2(1)	-1(1)
C(4)	16(1)	37(2)	32(1)	5(1)	1(1)	2(1)
C(3)	13(1)	44(2)	29(1)	2(1)	2(1)	0(1)
C(2)	23(1)	20(1)	24(1)	5(1)	-1(1)	3(1)
C(1)	26(2)	29(1)	25(1)	3(1)	-3(1)	0(1)
C(7)	15(1)	27(1)	20(1)	3(1)	0(1)	-1(1)
C(8)	22(1)	25(1)	18(1)	1(1)	1(1)	1(1)
C(9)	29(2)	32(2)	40(2)	15(1)	-6(1)	4(1)

Table S17 Hydrogen coordinates (×10^4) and isotropic displacement parameters (Å^2 × 10^3) for compound **4**

	x	y	z	U_{eq}
H(6A)	-1804	11680	4518	46
H(6B)	-1176	13247	3882	46
H(6C)	8	13101	4991	46
H(4A)	-2710	10842	2293	34
H(4B)	-2943	9360	3056	34
H(3B)	-2613	6963	1681	35
H(3A)	-3191	8403	919	35
H(1C)	-2142	8180	-744	41
H(1A)	-2049	6085	-613	41
H(1B)	-697	6817	-1454	41
H(7)	2512	9436	1913	25
H(9A)	3977	4222	2865	39
H(9C)	6237	5483	3131	39
H(9B)	4723	5616	3796	39

Table S18 Torsion angles [°] for compound **4**

C(7)-N(3)-C(5)-C(6)	174.8(2)
C(4)-N(3)-C(5)-C(6)	-8.1(4)
C(7)-N(3)-C(5)-S(1)	-5.0(3)
C(4)-N(3)-C(5)-S(1)	172.1(2)
C(5)-N(3)-C(4)-C(3)	-174.8(2)
C(7)-N(3)-C(4)-C(3)	2.5(3)
C(2)-N(4)-C(3)-C(4)	-149.3(2)
C(7)-N(4)-C(3)-C(4)	30.4(3)
N(3)-C(4)-C(3)-N(4)	-19.3(3)
C(7)-N(4)-C(2)-C(1)	-177.2(2)
C(3)-N(4)-C(2)-C(1)	2.5(4)
C(7)-N(4)-C(2)-S(4)	2.9(4)
C(3)-N(4)-C(2)-S(4)	-177.4(2)
C(5)-N(3)-C(7)-N(4)	-167.3(2)
C(4)-N(3)-C(7)-N(4)	15.3(3)
C(5)-N(3)-C(7)-C(8)	75.6(3)
C(4)-N(3)-C(7)-C(8)	-101.8(2)
C(2)-N(4)-C(7)-N(3)	151.5(2)
C(3)-N(4)-C(7)-N(3)	-28.3(3)
C(2)-N(4)-C(7)-C(8)	-91.7(3)
C(3)-N(4)-C(7)-C(8)	88.6(3)
C(9)-O(4)-C(8)-O(3)	-6.2(4)
C(9)-O(4)-C(8)-C(7)	175.3(2)
N(3)-C(7)-C(8)-O(3)	46.8(3)
N(4)-C(7)-C(8)-O(3)	-65.0(3)
N(3)-C(7)-C(8)-O(4)	-134.6(2)
N(4)-C(7)-C(8)-O(4)	113.6(2)

Symmetry transformations were used to generate equivalent atoms.

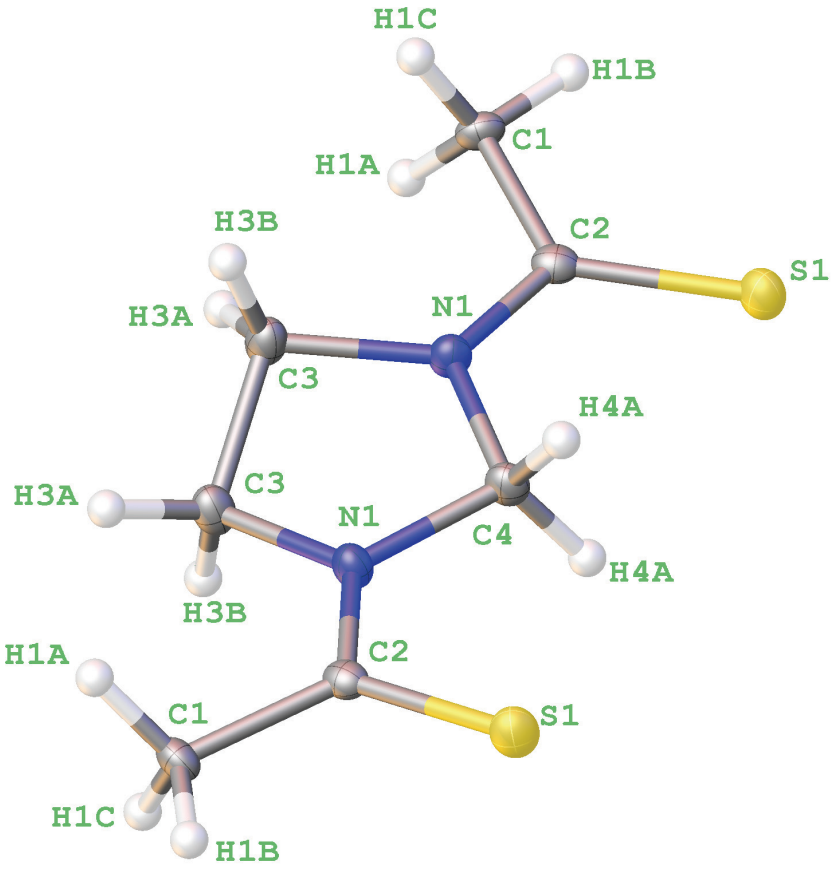


Fig. S4 Molecular drawing of compound **5** drawn at 50% probability ellipsoids.

Table S19 Crystal data and structure refinement for compound **5**

CCDC number	945385	
Identification code	raines54	
Empirical formula	$C_7H_{12}N_2S_2$	
Formula weight	188.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 12(2) Å	α = 90°
	b = 6.490 Å	β = 109.62°
	c = 11.651 Å	γ = 90°
Volume	890(142) Å^3	
Z	4	
Density (calculated)	1.406 mg/m^3	
Absorption coefficient	0.536 mm^{-1}	
F_{000}	400	
Crystal size	0.15 × 0.10 × 0.08 mm^3	
Theta range for data collection	3.46 to 26.27°	
Index ranges	$-15 \le h \le 14$, $0 \le k \le 8$, $0 \le l \le 14$	
Reflections collected	908	
Independent reflections	908 [R_{int} = 0.0000]	
Completeness to theta = 26.27°	100.0%	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.9584 and 0.9240	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	908 / 0 / 52	
Goodness-of-fit on F^2	0.598	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0318, w$R2$ = 0.0936	
R indices (all data)	$R1$ = 0.0330, w$R2$ = 0.0949	
Largest diff. peak and hole	0.450 and –0.223 e.Å^{-3}	

Table S20 Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for compound **5**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U_{eq}
S(1)	1190(1)	1778(1)	874(1)	17(1)
N(1)	618(1)	4914(2)	1967(1)	13(1)
C(2)	1187(1)	4263(3)	1252(2)	13(1)
C(1)	1828(1)	5871(3)	790(2)	14(1)
C(3)	555(2)	7050(3)	2370(2)	16(1)
C(4)	0	3513(4)	2500	14(1)

Table S21 Bond lengths [Å] and angles [°] for compound **5**

S(1)-C(2)	1.6726(18)
N(1)-C(2)	1.33(8)
N(1)-C(4)	1.46(8)
N(1)-C(3)	1.474(3)
C(2)-C(1)	1.52(8)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(3)-C(3)#1	1.5(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-N(1)#1	1.46(8)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(2)-N(1)-C(4)	123(4)
C(2)-N(1)-C(3)	126.4(13)
C(4)-N(1)-C(3)	111(2)
N(1)-C(2)-C(1)	117(4)
N(1)-C(2)-S(1)	121.3(17)
C(1)-C(2)-S(1)	121(2)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(1)-C(3)-C(3)#1	102.35(11)
N(1)-C(3)-H(3A)	111.3
C(3)#1-C(3)-H(3A)	111.3
N(1)-C(3)-H(3B)	111.3
C(3)#1-C(3)-H(3B)	111.3
H(3A)-C(3)-H(3B)	109.2
N(1)#1-C(4)-N(1)	103(5)
N(1)#1-C(4)-H(4A)	111.2
N(1)-C(4)-H(4A)	111.2
N(1)#1-C(4)-H(4B)	111.2
N(1)-C(4)-H(4B)	111.2
H(4A)-C(4)-H(4B)	109.1

Symmetry transformations were used to generate equivalent atoms.

Table S22 Anisotropic displacement parameters (Å^2 × 10^3) for compound **5**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2hk\, a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	20(1)	17(1)	19(1)	-2(1)	11(1)	0(1)
N(1)	15(1)	13(1)	14(1)	0(1)	8(1)	-1(1)
C(2)	11(1)	16(1)	11(1)	1(1)	3(1)	0(1)
C(1)	12(1)	16(1)	14(1)	1(1)	5(1)	-3(1)
C(3)	19(1)	13(1)	18(1)	-2(1)	10(1)	-2(1)
C(4)	15(1)	14(1)	14(1)	0	8(1)	0

Table S23 Hydrogen coordinates (×10^4) and isotropic displacement parameters (Å^2 × 10^3) for compound **5**

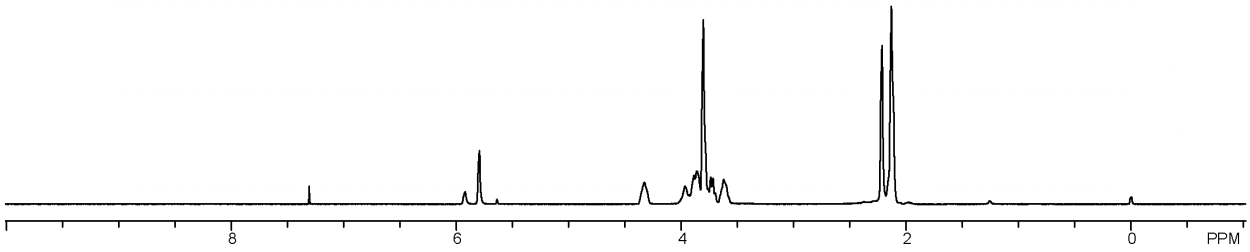
	x	y	z	U_{eq}
H(1A)	1294	6912	315	21
H(1B)	2205	5205	274	21
H(1C)	2399	6534	1484	21
H(3A)	535	8049	1721	19
H(3B)	1205	7377	3111	19
H(4A)	-528	2628	1869	16
H(4B)	528	2628	3131	16

Table S24 Torsion angles [°] for compound **5**

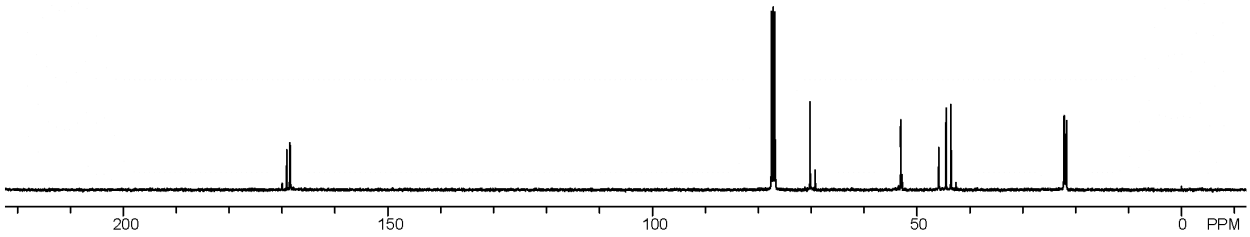
C(4)-N(1)-C(2)-C(1)	-177.99(18)
C(3)-N(1)-C(2)-C(1)	-0.6(3)
C(4)-N(1)-C(2)-S(1)	2.3(3)
C(3)-N(1)-C(2)-S(1)	179.61(14)
C(2)-N(1)-C(3)-C(3)#1	155.3(17)
C(4)-N(1)-C(3)-C(3)#1	-27.1(17)
C(2)-N(1)-C(4)-N(1)#1	-171.5(4)
C(3)-N(1)-C(4)-N(1)#1	10.8(5)

Symmetry transformations were used to generate equivalent atoms.

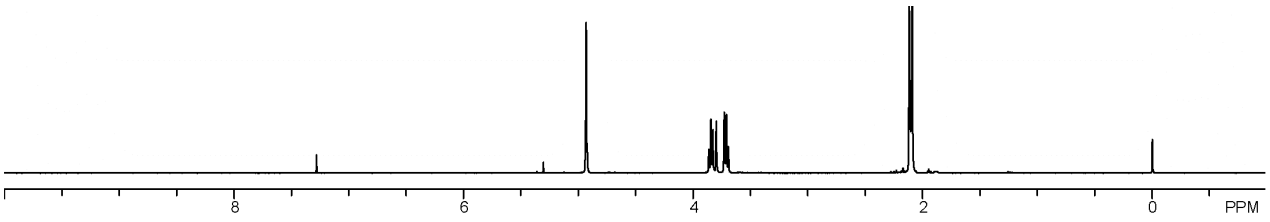
^{1}H NMR of compound **2** in $CDCl_3$



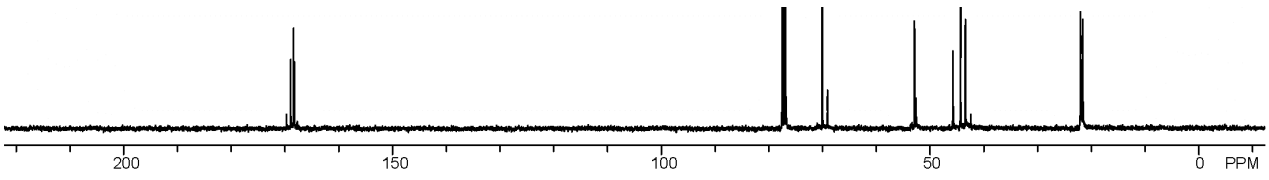
^{13}C NMR of compound **2** in $CDCl_3$



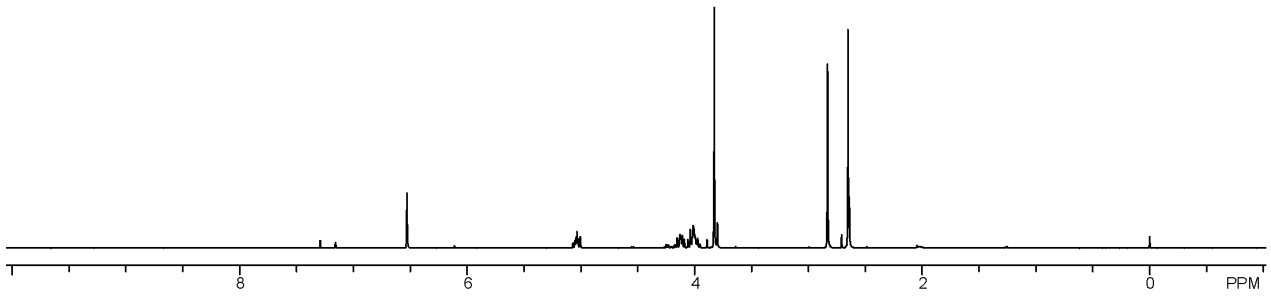
^{1}H NMR of compound **3** in $CDCl_3$



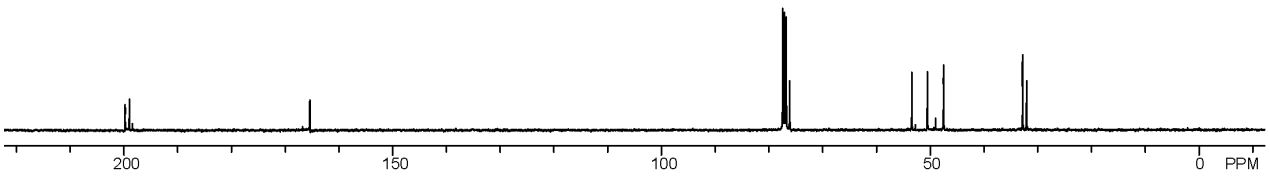
^{13}C NMR of compound **3** in $CDCl_3$



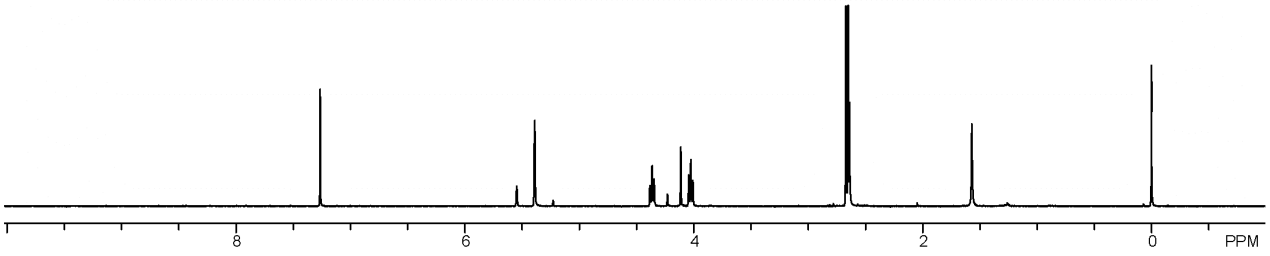
^{1}H NMR of compound **4** in $CDCl_3$



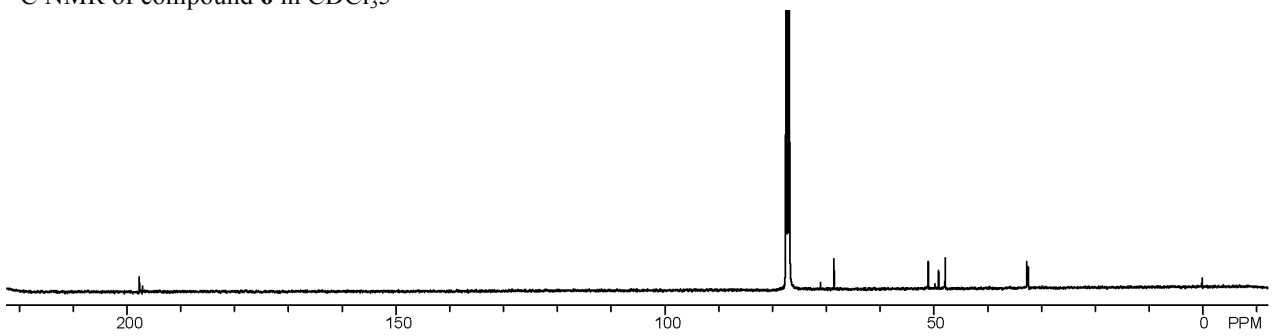
^{13}C NMR of compound **4** in $CDCl_3$



^{1}H NMR of compound **5** in $CDCl_3$



^{13}C NMR of compound **6** in $CDCl_3$5



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