Supporting Information for:

Direct Reaction of Amides with Nitric Oxide to Form Diazeniumdiolates

Ryan J. Holland,*[,†] John R. Klose,[§] Jeffrey R. Deschamps,[‡] Zhao Cao,[§] Larry K. Keefer,[†] and Joseph E. Saavedra[§]

TABLE OF CONTENTS

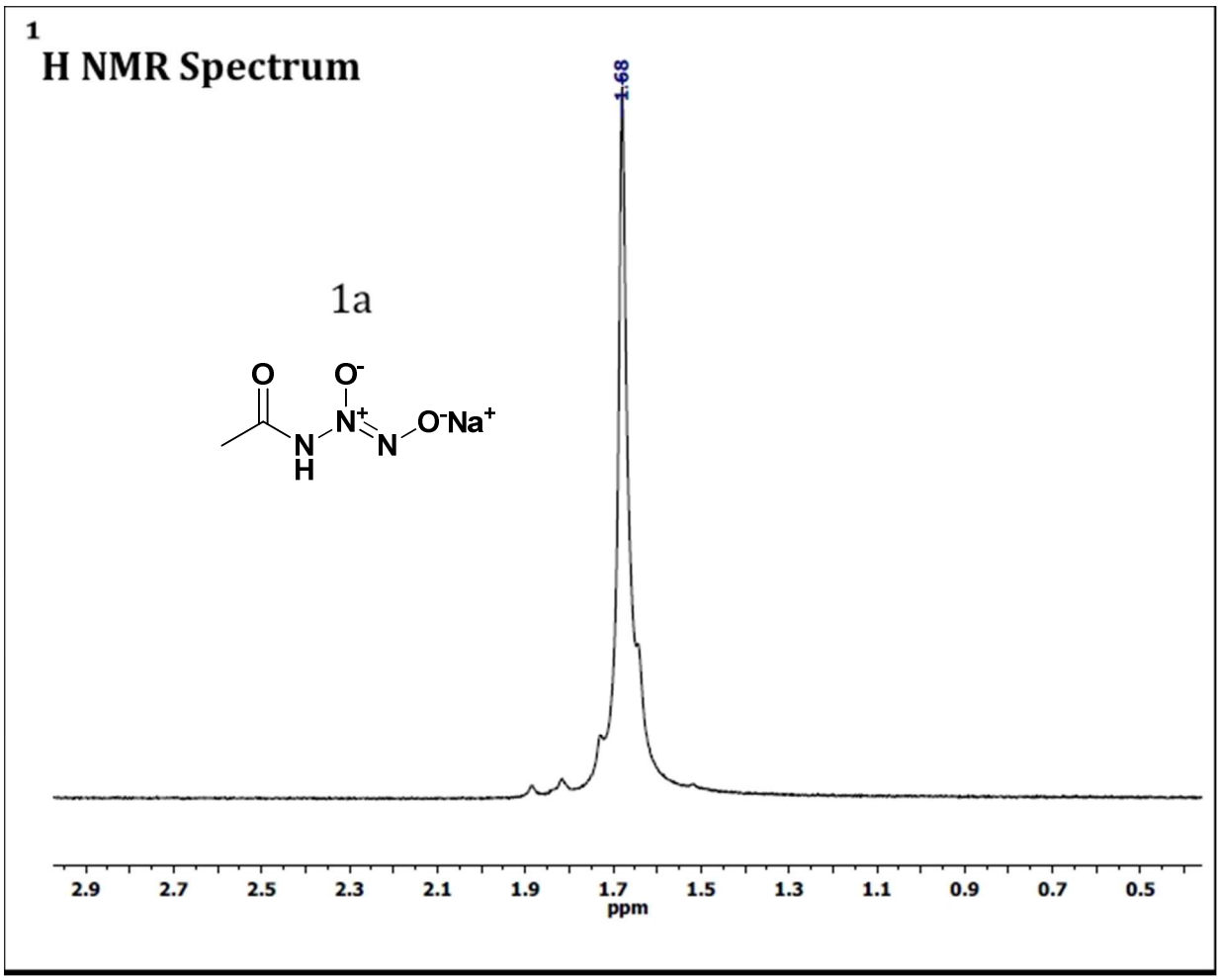

Figure S1. ^{1}H NMR spectrum of compound **1a** in D_2O/NaOD at 25 ^{o}C.

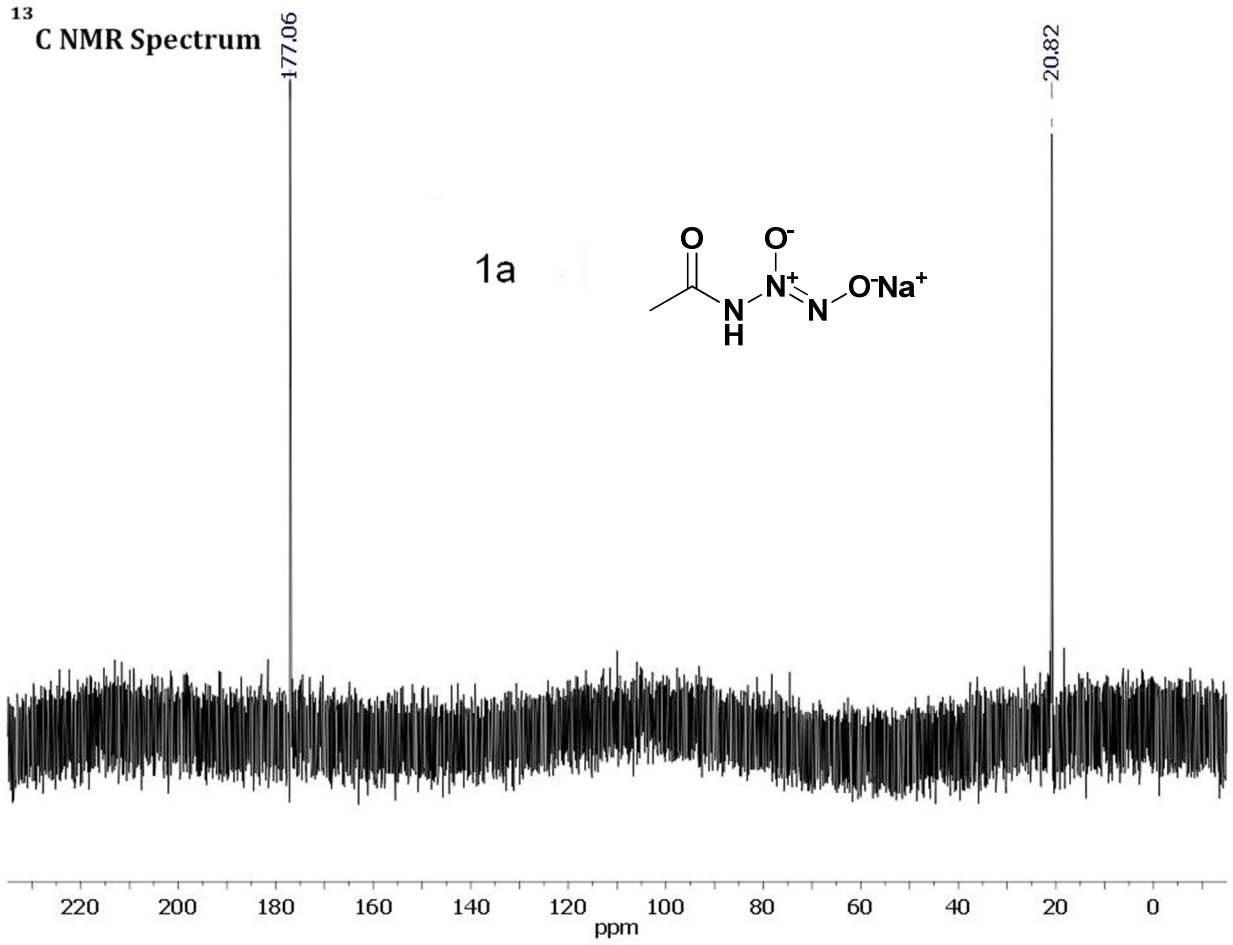

Figure S2. ^{13}C NMR spectrum of compound **1a** in D_2O/NaOD at 25 ^{o}C.

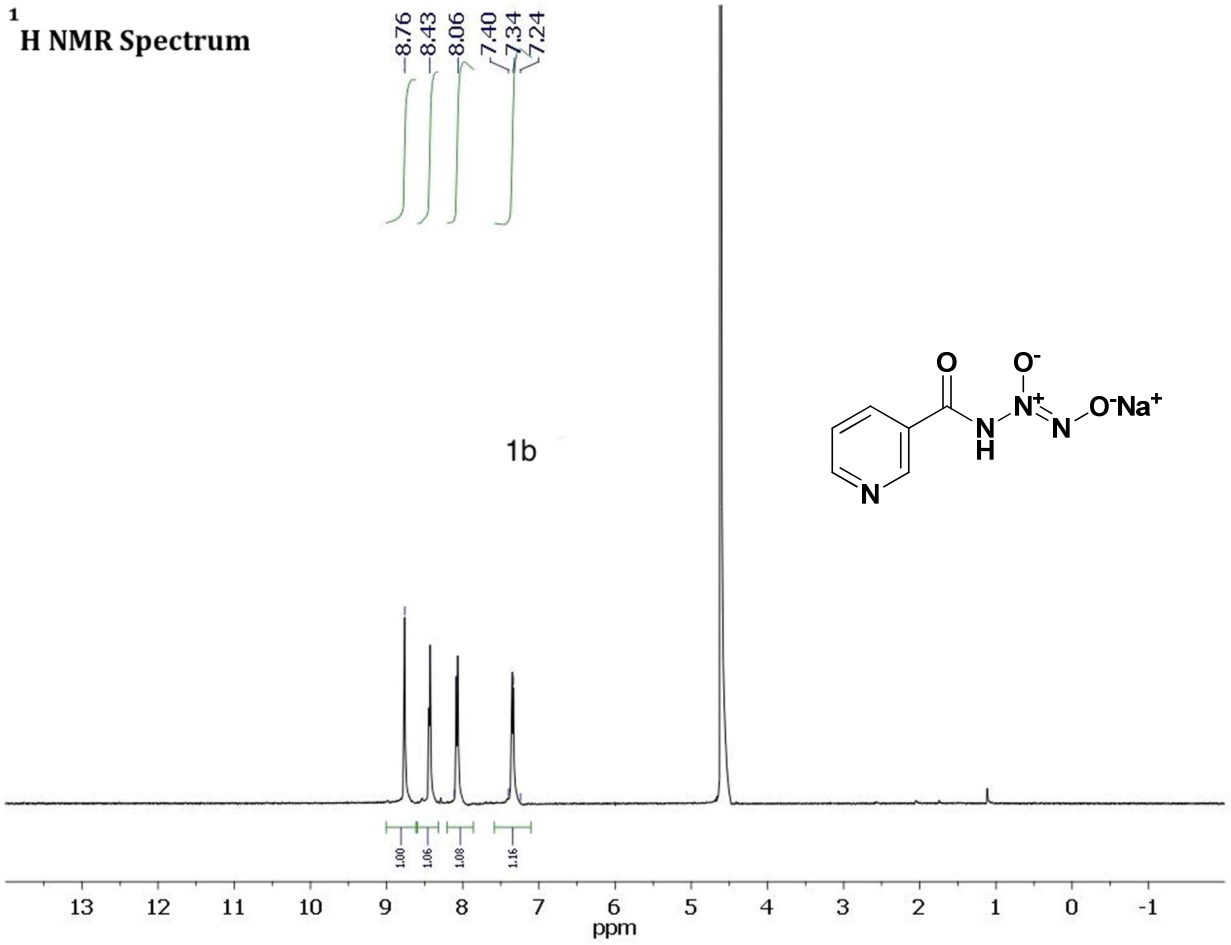

Figure S3. ^{1}H NMR spectrum of compound **1b** in D_2O/NaOD at 25 ^{o}C.

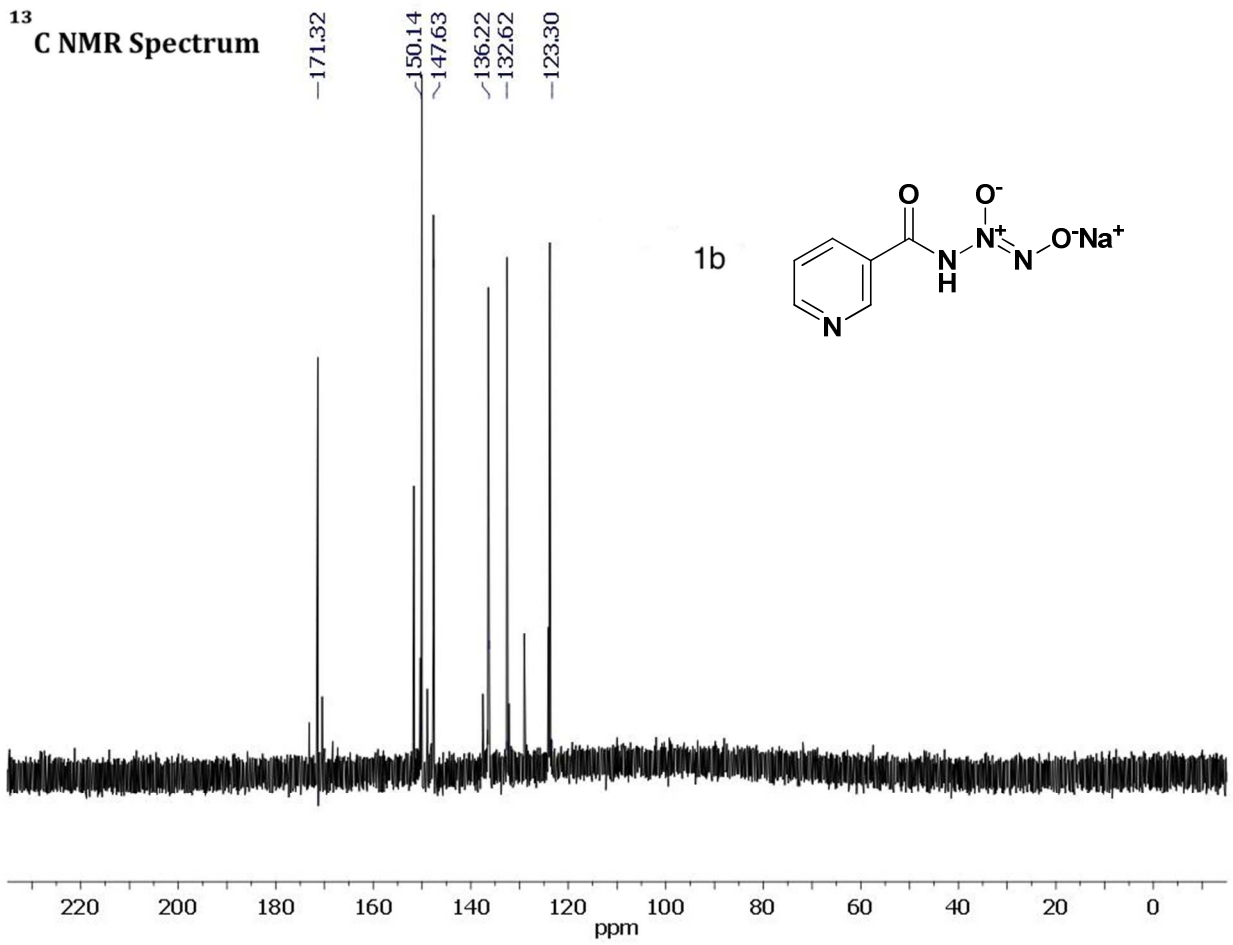

Figure S4. ^{13}C NMR spectrum of compound **1b** in D_2O/NaOD at 25 ^{o}C.

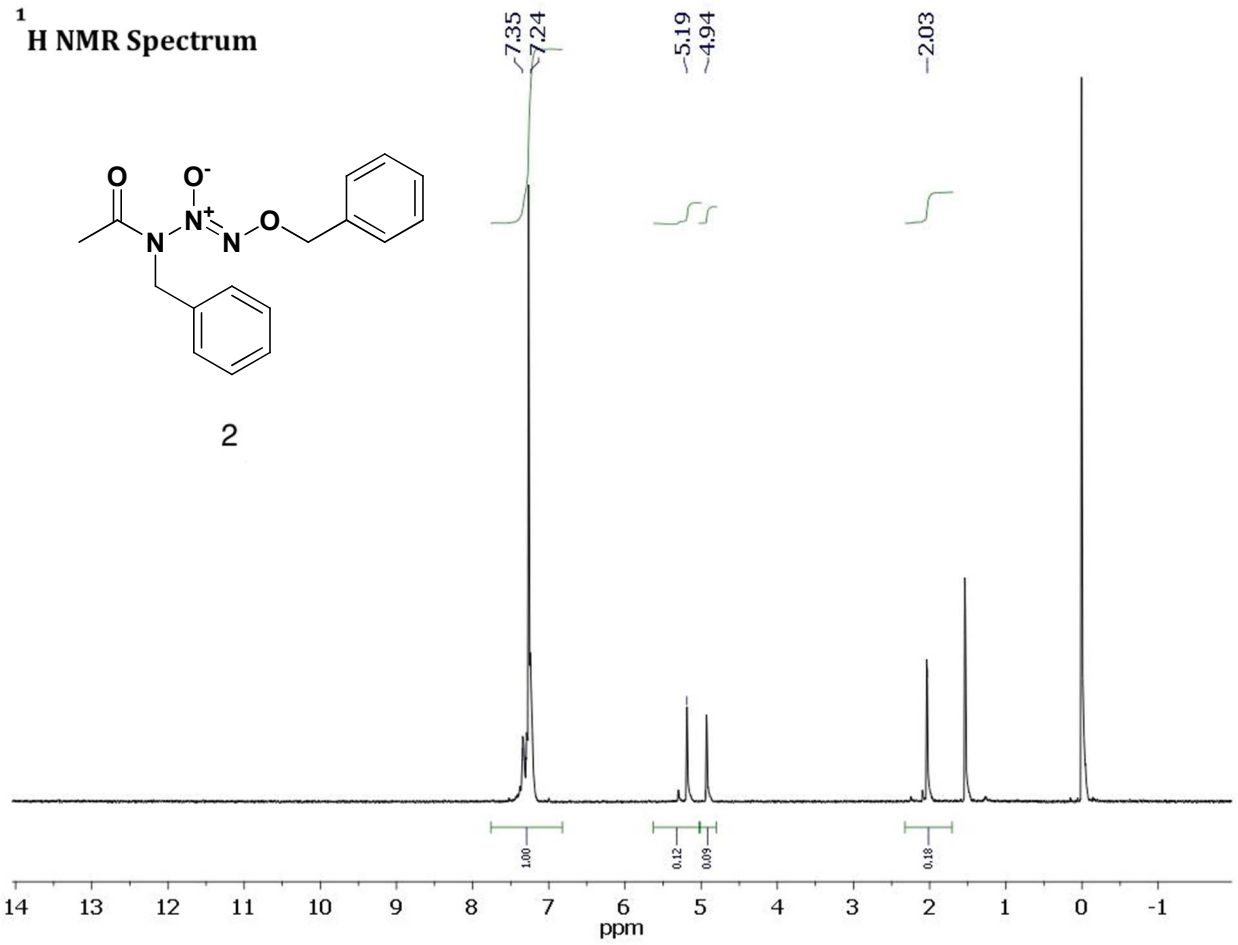

Figure S5. ^{1}H NMR spectrum of compound **1b** in $CDCl_3$ at 25 ^{o}C.

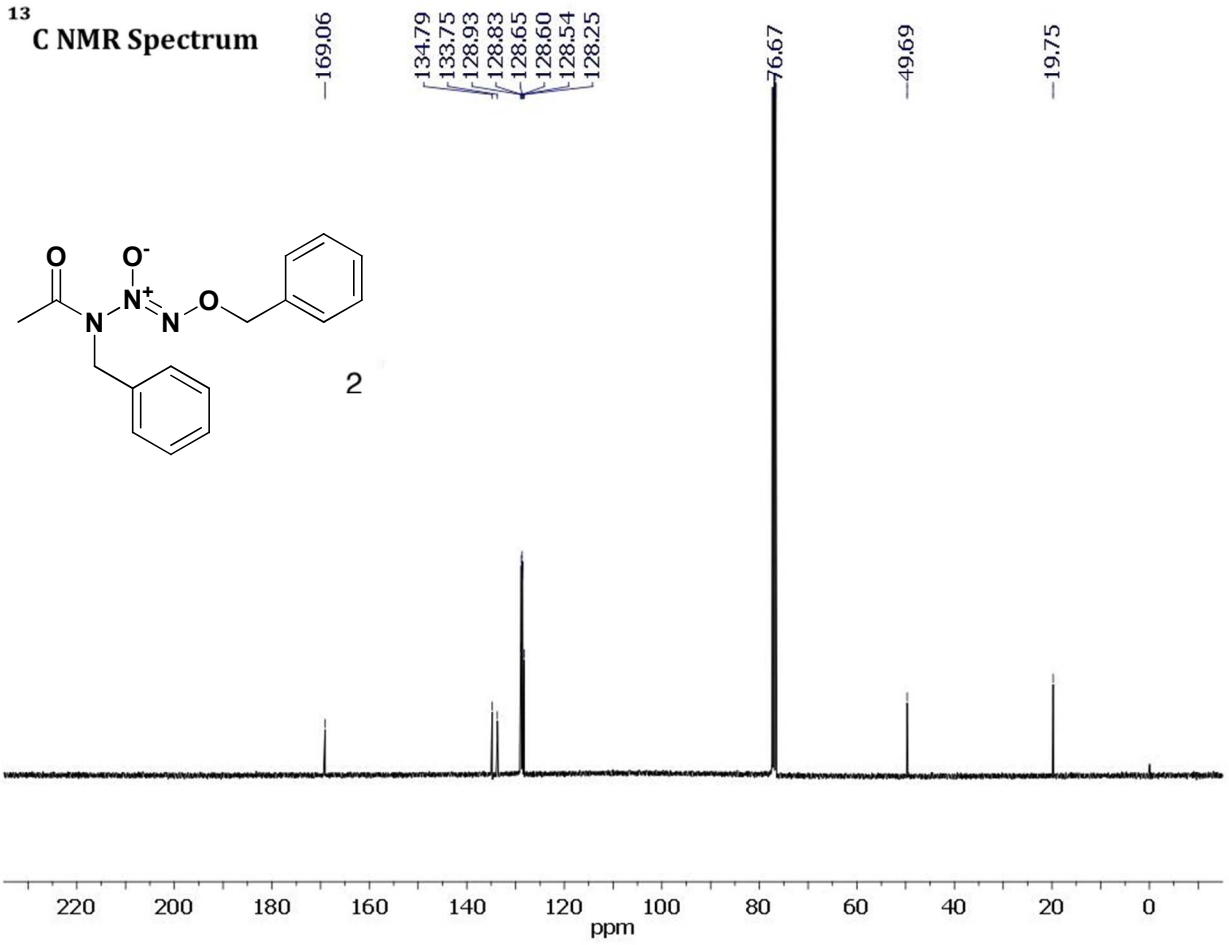

Figure S6. ^{13}C NMR spectrum of compound **2** in $CDCl_3$ at 25 ^{o}C.

.

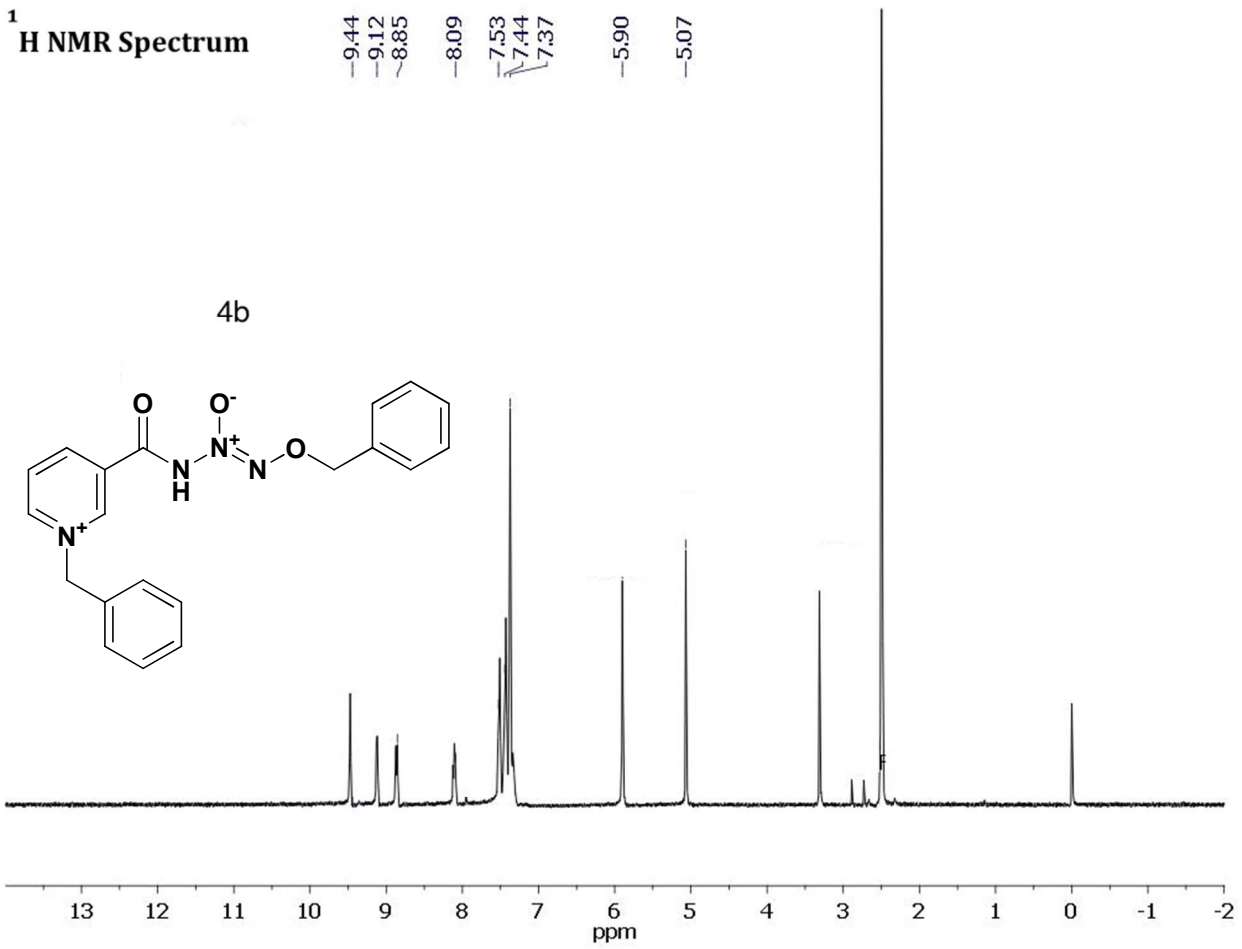

Figure S7. ^{1}H NMR spectrum of compound **4b** in DMSO-d_6 at 25 ^{o}C.

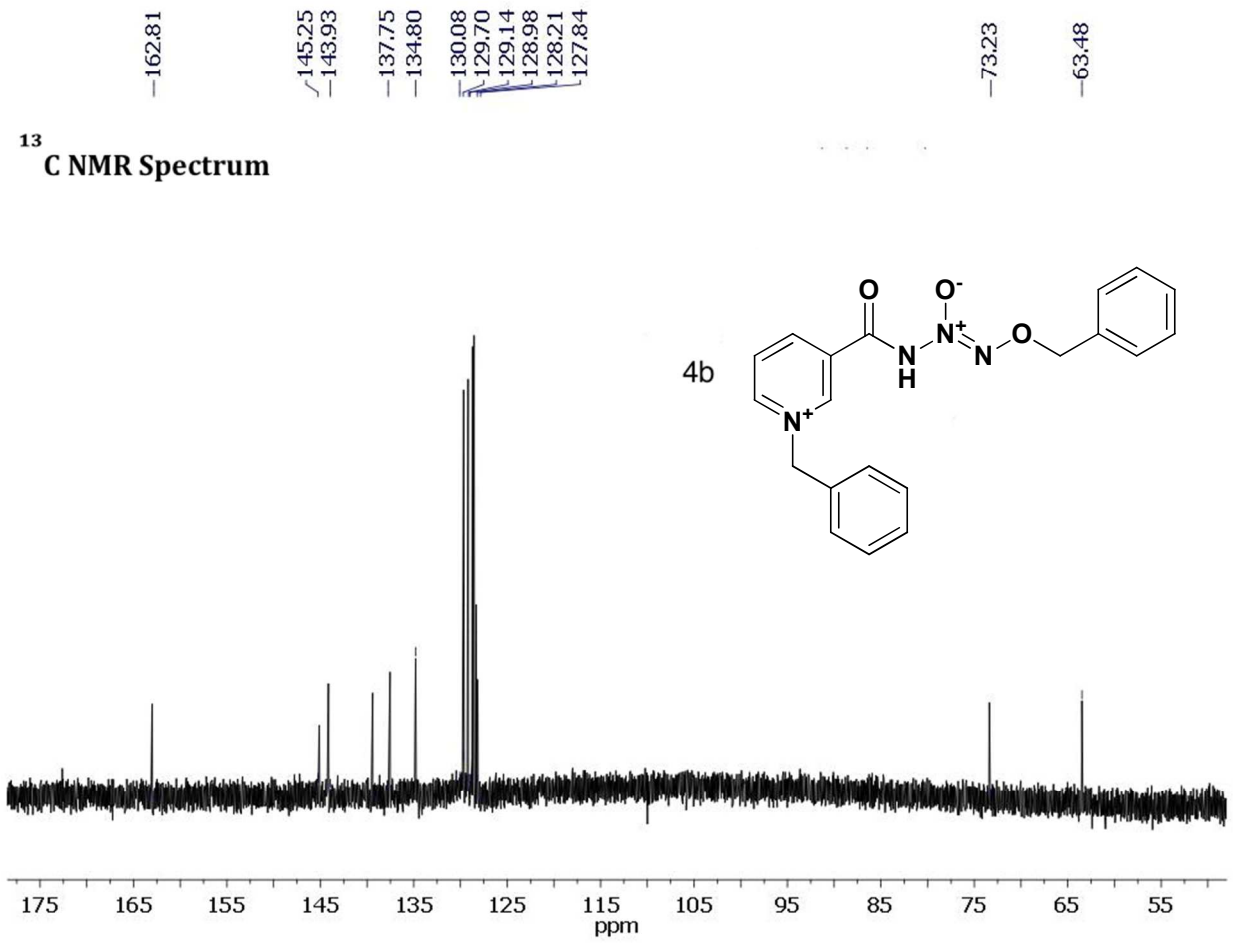

Figure S8. ^{13}C NMR spectrum of compound **4b** in DMSO-d_6 at 25 ^{o}C.

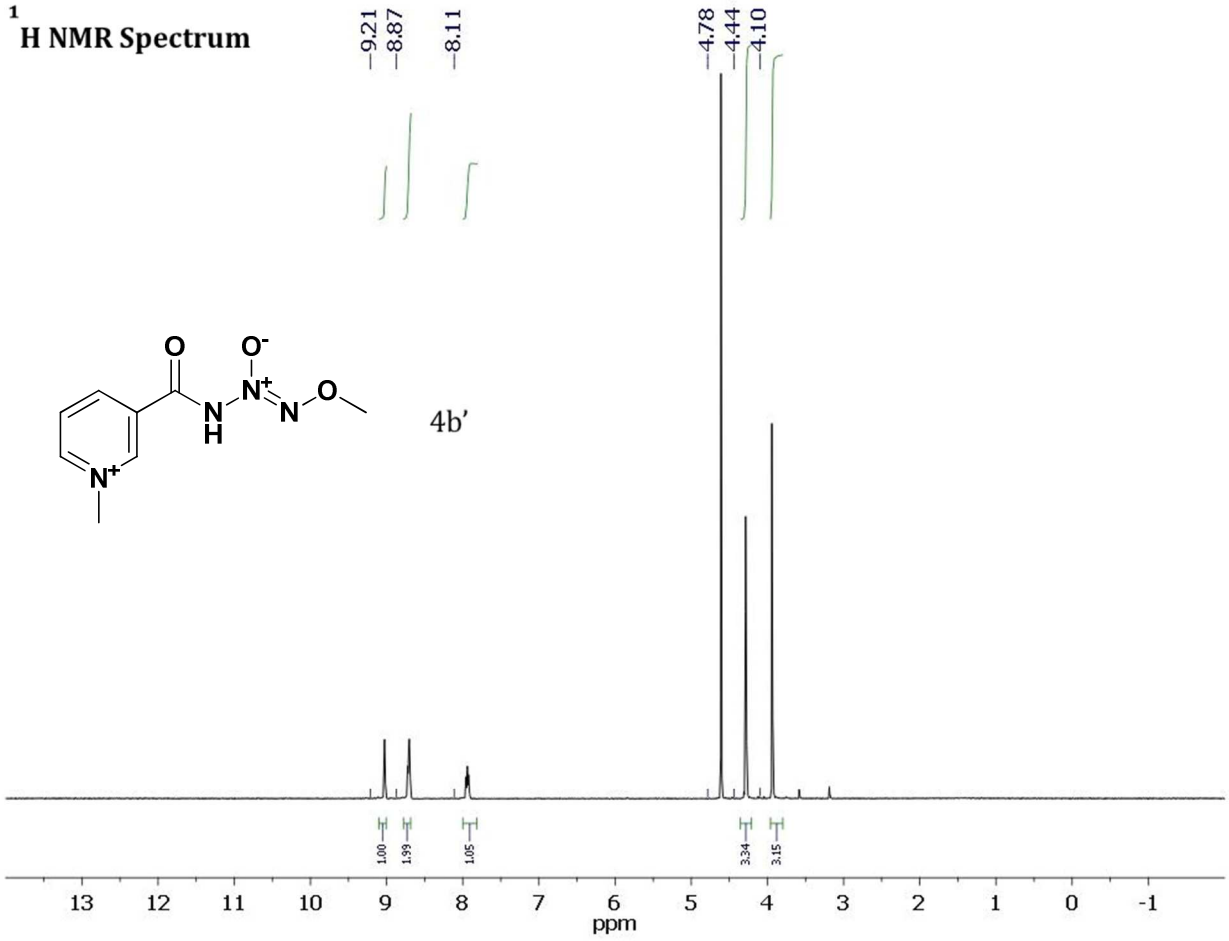

Figure S9. ^{1}H NMR spectrum of compound **4b'** in D_2O at 25 ^{o}C.

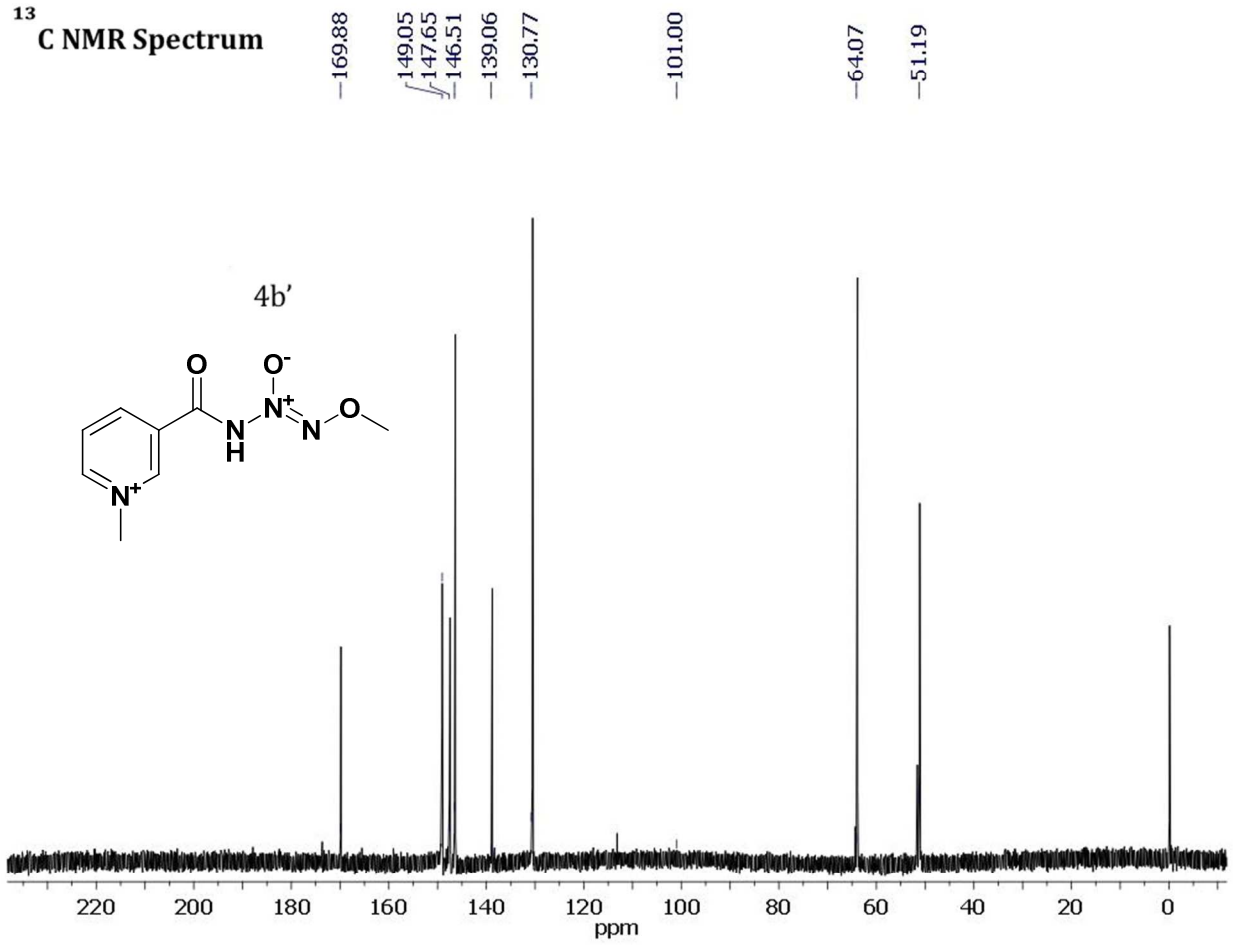

Figure S10. ^{13}C NMR spectrum of compound **4b'** in D_2O at 25 ^{o}C.

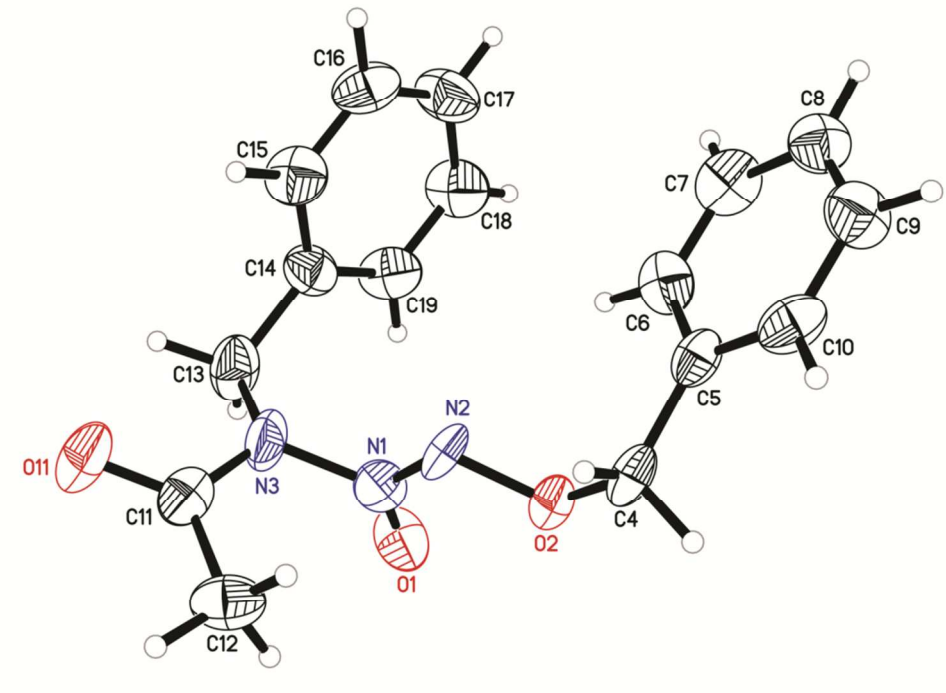

Figure S11. Plot of compound **2**. Displacement ellipsoids are at the 50% level.

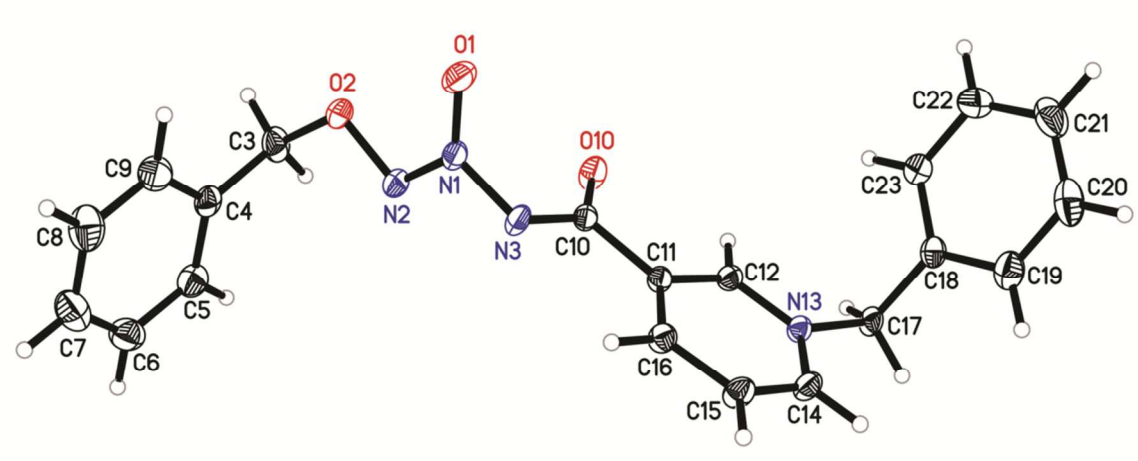

Figure S12. Plot of compound **4b**. Displacement ellipsoids are at the 50% level.

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

Empirical formula	$C_{16}H_{17}N_3O_3$	
Formula weight	299.33	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.429(4) Å	□= 96.30(3)°
	b = 8.743(5) Å	□= 96.60(3)°
	c = 16.342(11) Å	□ = 92.33(3)°
Volume	764.9(9) $Å^3$	
Z	2	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	316	
Crystal size	0.256 x 0.047 x 0.011 mm^3	
□ range for data collection	1.26 to 23.30°	
Index ranges	-4<=h<=6, -9<=k<=7, -18<=l<=17	
Reflections collected	2961	
Independent reflections	2034 [R(int) = 0.2410]	
Completeness to □ = 23.30°	92.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9990 and 0.9769	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2034 / 0 / 201	
Goodness-of-fit on F^2	0.703	
Final R indices [I>2□(I)]	R1 = 0.0772, wR2 = 0.1677	
R indices (all data)	R1 = 0.2446, wR2 = 0.2435	
Extinction coefficient	0.020(7)	
Largest diff. peak and hole	0.272 and -0.258 $e.Å^{-3}$	

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

	x	y	z	U(eq)
N(1)	4969(14)	3291(8)	3858(4)	39(2)
O(2)	3625(10)	5475(7)	3665(3)	41(2)
N(3)	4537(14)	1638(8)	3777(5)	46(2)
C(4)	1360(15)	6200(10)	3405(5)	39(2)
O(1)	7062(11)	3843(7)	4148(4)	50(2)
N(2)	3064(13)	3905(8)	3546(4)	38(2)
C(5)	1067(15)	6405(10)	2492(6)	35(2)
C(6)	2545(15)	5754(11)	1935(6)	45(3)
C(7)	2118(16)	6011(11)	1112(6)	51(3)
C(8)	174(16)	6816(11)	818(6)	47(3)
C(9)	-1305(17)	7469(11)	1374(6)	53(3)
C(10)	-895(15)	7227(11)	2201(6)	46(3)
C(11)	3166(15)	1031(12)	4355(6)	41(3)
O(11)	2849(11)	-368(7)	4294(4)	56(2)
C(12)	2175(15)	2120(11)	4988(5)	50(3)
C(13)	6139(16)	759(11)	3262(6)	50(3)
C(14)	5903(16)	1183(11)	2382(6)	42(2)
C(15)	3880(16)	573(11)	1837(6)	51(3)
C(16)	3620(16)	968(11)	1046(7)	53(3)
C(17)	5327(18)	1986(12)	783(6)	59(3)
C(18)	7304(16)	2611(12)	1337(6)	56(3)
C(19)	7580(16)	2189(11)	2136(6)	51(3)

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

N(1)-O(1)	1.237(7)	N(1)-N(2)	1.266(8)
N(1)-N(3)	1.444(10)	O(2)-N(2)	1.381(8)
O(2)-C(4)	1.448(9)	N(3)-C(11)	1.403(12)
N(3)-C(13)	1.462(11)	C(4)-C(5)	1.513(12)
C(4)-H(4A)	0.9900	C(4)-H(4B)	0.9900
C(5)-C(6)	1.374(12)	C(5)-C(10)	1.378(11)
C(6)-C(7)	1.383(12)	C(6)-H(6A)	0.9500
C(7)-C(8)	1.364(12)	C(7)-H(7A)	0.9500
C(8)-C(9)	1.373(12)	C(8)-H(8A)	0.9500
C(9)-C(10)	1.386(12)	C(9)-H(9A)	0.9500
C(10)-H(10A)	0.9500	C(11)-O(11)	1.220(10)
C(11)-C(12)	1.489(13)	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-C(14)	1.517(12)	C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900	C(14)-C(19)	1.364(12)
C(14)-C(15)	1.381(11)	C(15)-C(16)	1.368(12)
C(15)-H(15A)	0.9500	C(16)-C(17)	1.394(12)
C(16)-H(16A)	0.9500	C(17)-C(18)	1.375(12)
C(17)-H(17A)	0.9500	C(18)-C(19)	1.389(11)
C(18)-H(18A)	0.9500	C(19)-H(19A)	0.9500
O(1)-N(1)-N(2)	131.6(8)	O(1)-N(1)-N(3)	118.2(7)
N(2)-N(1)-N(3)	109.9(7)	N(2)-O(2)-C(4)	106.4(6)
C(11)-N(3)-N(1)	117.1(7)	C(11)-N(3)-C(13)	125.0(8)
N(1)-N(3)-C(13)	115.5(7)	O(2)-C(4)-C(5)	112.8(7)
O(2)-C(4)-H(4A)	109.0	C(5)-C(4)-H(4A)	109.0
O(2)-C(4)-H(4B)	109.0	C(5)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8	N(1)-N(2)-O(2)	105.9(6)
C(6)-C(5)-C(10)	118.5(9)	C(6)-C(5)-C(4)	124.1(8)
C(10)-C(5)-C(4)	117.3(9)	C(5)-C(6)-C(7)	119.5(9)
C(5)-C(6)-H(6A)	120.2	C(7)-C(6)-H(6A)	120.2
C(8)-C(7)-C(6)	122.2(9)	C(8)-C(7)-H(7A)	118.9
C(6)-C(7)-H(7A)	118.9	C(7)-C(8)-C(9)	118.3(10)
C(7)-C(8)-H(8A)	120.9	C(9)-C(8)-H(8A)	120.9
C(8)-C(9)-C(10)	120.1(9)	C(8)-C(9)-H(9A)	120.0
C(10)-C(9)-H(9A)	120.0	C(5)-C(10)-C(9)	121.2(9)
C(5)-C(10)-H(10A)	119.4	C(9)-C(10)-H(10A)	119.4
O(11)-C(11)-N(3)	116.8(9)	O(11)-C(11)-C(12)	124.6(10)
N(3)-C(11)-C(12)	118.5(9)	C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	N(3)-C(13)-C(14)	112.3(8)
N(3)-C(13)-H(13A)	109.1	C(14)-C(13)-H(13A)	109.1
N(3)-C(13)-H(13B)	109.1	C(14)-C(13)-H(13B)	109.1
H(13A)-C(13)-H(13B)	107.9	C(19)-C(14)-C(15)	120.2(9)

Continuation of table S3

C(19)-C(14)-C(13)	121.4(8)	C(15)-C(14)-C(13)	118.3(9)
C(16)-C(15)-C(14)	118.9(9)	C(16)-C(15)-H(15A)	120.5
C(14)-C(15)-H(15A)	120.5	C(15)-C(16)-C(17)	121.6(9)
C(15)-C(16)-H(16A)	119.2	C(17)-C(16)-H(16A)	119.2
C(18)-C(17)-C(16)	118.9(9)	C(18)-C(17)-H(17A)	120.5
C(16)-C(17)-H(17A)	120.5	C(17)-C(18)-C(19)	119.4(9)
C(17)-C(18)-H(18A)	120.3	C(19)-C(18)-H(18A)	120.3
C(14)-C(19)-C(18)	121.0(9)	C(14)-C(19)-H(19A)	119.5
C(18)-C(19)-H(19A)	119.5		

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	38(5)	42(6)	39(5)	5(4)	11(4)	12(4)
O(2)	50(4)	25(4)	46(4)	2(3)	3(3)	-1(3)
N(3)	65(6)	22(5)	54(6)	6(5)	16(4)	9(4)
C(4)	37(6)	23(5)	57(7)	-4(5)	14(4)	7(4)
O(1)	36(4)	57(5)	57(5)	21(4)	-4(3)	-7(3)
N(2)	43(5)	17(5)	51(5)	-8(4)	8(4)	1(3)
C(5)	27(5)	26(6)	49(7)	-1(5)	5(4)	-5(4)
C(6)	34(6)	46(7)	56(8)	13(6)	6(5)	-3(4)
C(7)	37(6)	58(7)	61(8)	2(6)	23(5)	3(5)
C(8)	39(6)	53(7)	49(7)	4(6)	2(5)	2(5)
C(9)	46(6)	63(8)	51(8)	8(6)	8(5)	18(5)
C(10)	36(6)	47(7)	51(7)	-11(6)	11(5)	3(5)
C(11)	32(6)	36(7)	53(7)	0(6)	-5(5)	6(4)
O(11)	62(5)	31(4)	75(5)	-4(4)	14(3)	-9(3)
C(12)	39(6)	66(7)	42(7)	-6(6)	10(4)	-1(5)
C(13)	56(6)	36(6)	64(8)	9(6)	19(5)	16(5)
C(14)	40(6)	48(6)	38(7)	7(5)	2(5)	8(5)
C(15)	36(6)	58(7)	57(8)	5(6)	4(5)	-6(5)
C(16)	38(6)	60(8)	55(8)	-9(6)	-4(5)	-6(5)
C(17)	62(7)	76(9)	40(7)	13(6)	9(5)	-5(6)
C(18)	46(7)	72(8)	53(8)	10(7)	19(5)	-13(5)
C(19)	41(6)	63(8)	46(7)	-2(6)	12(5)	-9(5)

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

	x	y	z	U(eq)
H(4A)	1354	7221	3733	47
H(4B)	-78	5564	3524	47
H(6A)	3850	5131	2114	54
H(7A)	3216	5612	739	61
H(8A)	-149	6924	244	57
H(9A)	-2612	8086	1190	63
H(10A)	-1986	7635	2574	55
H(12A)	1516	1542	5403	75
H(12B)	845	2681	4718	75
H(12C)	3512	2853	5259	75
H(13A)	5701	-354	3248	61
H(13B)	7886	951	3514	61
H(15A)	2688	-111	2009	61
H(16A)	2245	540	666	64
H(17A)	5127	2244	230	70
H(18A)	8469	3324	1174	67
H(19A)	8958	2607	2517	61

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

O(1)-N(1)-N(3)-C(11)	104.7(8)
N(2)-N(1)-N(3)-C(11)	-80.1(9)
O(1)-N(1)-N(3)-C(13)	-58.5(10)
N(2)-N(1)-N(3)-C(13)	116.7(8)
N(2)-O(2)-C(4)-C(5)	-88.8(8)
O(1)-N(1)-N(2)-O(2)	-6.8(11)
N(3)-N(1)-N(2)-O(2)	178.9(6)
C(4)-O(2)-N(2)-N(1)	-173.0(7)
O(2)-C(4)-C(5)-C(6)	10.3(11)
O(2)-C(4)-C(5)-C(10)	-173.4(7)
C(10)-C(5)-C(6)-C(7)	3.6(13)
C(4)-C(5)-C(6)-C(7)	179.9(8)
C(5)-C(6)-C(7)-C(8)	-4.1(14)
C(6)-C(7)-C(8)-C(9)	4.1(15)
C(7)-C(8)-C(9)-C(10)	-3.7(14)
C(6)-C(5)-C(10)-C(9)	-3.4(13)
C(4)-C(5)-C(10)-C(9)	-179.9(8)
C(8)-C(9)-C(10)-C(5)	3.5(14)
N(1)-N(3)-C(11)-O(11)	-178.6(7)
C(13)-N(3)-C(11)-O(11)	-17.1(13)
N(1)-N(3)-C(11)-C(12)	2.3(11)
C(13)-N(3)-C(11)-C(12)	163.7(8)
C(11)-N(3)-C(13)-C(14)	139.2(8)
N(1)-N(3)-C(13)-C(14)	-59.1(10)
N(3)-C(13)-C(14)-C(19)	98.5(11)
N(3)-C(13)-C(14)-C(15)	-78.9(11)
C(19)-C(14)-C(15)-C(16)	1.3(15)
C(13)-C(14)-C(15)-C(16)	178.8(10)
C(14)-C(15)-C(16)-C(17)	-0.9(16)
C(15)-C(16)-C(17)-C(18)	-0.4(16)
C(16)-C(17)-C(18)-C(19)	1.4(16)
C(15)-C(14)-C(19)-C(18)	-0.4(15)
C(13)-C(14)-C(19)-C(18)	-177.8(9)
C(17)-C(18)-C(19)-C(14)	-0.9(16)

Symmetry transformations used to generate equivalent atoms:

Table S7. Crystal data and structure refinement for **4b**.

Empirical formula	$C_{20}H_{18}N_4O_3$
Formula weight	362.38
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 18.3109(19) Å □= 90°
	b = 10.8087(9) Å □= 109.785(4)°
	c = 20.0132(16) Å □ = 90°
Volume	3727.1(6) $Å^3$
Z	8
Density (calculated)	1.292 Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F(000)	1520
Crystal size	0.375 x 0.101 x 0.082 mm^3
□ range for data collection	2.16 to 28.33°
Index ranges	-24<=h<=24, -14<=k<=14, -22<=l<=26
Reflections collected	20155
Independent reflections	4639 [R(int) = 0.0770]
Completeness to □ = 28.33°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9927 and 0.9671
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4639 / 0 / 244
Goodness-of-fit on F^2	0.839
Final R indices [I>2□(I)]	R1 = 0.0454, wR2 = 0.1252
R indices (all data)	R1 = 0.0863, wR2 = 0.1423
Largest diff. peak and hole	0.575 and -0.229 $e.Å^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3121(1)	5954(1)	1813(1)	30(1)
N(1)	2544(1)	5931(1)	1248(1)	19(1)
O(2)	1813(1)	6006(1)	1898(1)	25(1)
N(2)	1833(1)	5952(1)	1204(1)	23(1)
C(3)	1001(1)	6070(2)	1843(1)	34(1)
N(3)	2673(1)	6001(1)	596(1)	21(1)
C(4)	988(1)	6497(2)	2551(1)	26(1)
C(5)	1013(1)	7757(2)	2701(1)	30(1)
C(6)	997(1)	8174(2)	3351(1)	35(1)
C(7)	954(1)	7336(2)	3854(1)	37(1)
C(8)	929(1)	6090(2)	3714(1)	36(1)
C(9)	946(1)	5669(2)	3068(1)	31(1)
O(10)	2357(1)	3912(1)	459(1)	27(1)
C(10)	2562(1)	4909(2)	269(1)	19(1)
C(11)	2729(1)	4957(2)	-415(1)	18(1)
C(12)	2842(1)	3846(2)	-710(1)	18(1)
N(13)	2986(1)	3822(1)	-1327(1)	18(1)
C(14)	2996(1)	4868(2)	-1689(1)	22(1)
C(15)	2878(1)	5990(2)	-1419(1)	25(1)
C(16)	2755(1)	6047(2)	-775(1)	22(1)
C(17)	3184(1)	2624(2)	-1599(1)	20(1)
C(18)	4051(1)	2412(2)	-1292(1)	21(1)
C(19)	4364(1)	1755(2)	-665(1)	26(1)
C(20)	5159(1)	1623(2)	-358(1)	34(1)
C(21)	5648(1)	2150(2)	-673(1)	39(1)
C(22)	5342(1)	2786(2)	-1303(1)	45(1)
C(23)	4544(1)	2912(2)	-1614(1)	34(1)

Table S9. Bond lengths [Å] and angles [°] for **4b**.

O(1)-N(1)	1.2608(18)	N(1)-N(2)	1.276(2)
N(1)-N(3)	1.404(2)	O(2)-N(2)	1.4030(19)
O(2)-C(3)	1.454(2)	C(3)-C(4)	1.499(3)
C(3)-H(3A)	0.9900	C(3)-H(3B)	0.9900
N(3)-C(10)	1.332(2)	C(4)-C(9)	1.389(3)
C(4)-C(5)	1.392(3)	C(5)-C(6)	1.387(3)
C(5)-H(5A)	0.9500	C(6)-C(7)	1.376(3)
C(6)-H(6A)	0.9500	C(7)-C(8)	1.374(3)
C(7)-H(7A)	0.9500	C(8)-C(9)	1.380(3)
C(8)-H(8A)	0.9500	C(9)-H(9A)	0.9500
O(10)-C(10)	1.2417(19)	C(10)-C(11)	1.503(2)
C(11)-C(12)	1.384(2)	C(11)-C(16)	1.389(2)
C(12)-N(13)	1.346(2)	C(12)-H(12A)	0.9500
N(13)-C(14)	1.346(2)	N(13)-C(17)	1.497(2)
C(14)-C(15)	1.374(2)	C(14)-H(14A)	0.9500
C(15)-C(16)	1.384(2)	C(15)-H(15A)	0.9500
C(16)-H(16A)	0.9500	C(17)-C(18)	1.513(2)
C(17)-H(17A)	0.9900	C(17)-H(17B)	0.9900
C(18)-C(23)	1.384(3)	C(18)-C(19)	1.386(3)
C(19)-C(20)	1.383(3)	C(19)-H(19A)	0.9500
C(20)-C(21)	1.379(3)	C(20)-H(20A)	0.9500
C(21)-C(22)	1.377(3)	C(21)-H(21A)	0.9500
C(22)-C(23)	1.388(3)	C(22)-H(22A)	0.9500
C(23)-H(23A)	0.9500	O(1)-N(1)-N(2)	126.03(15)
O(1)-N(1)-N(3)	118.60(14)	N(2)-N(1)-N(3)	115.11(14)
N(2)-O(2)-C(3)	107.16(13)	N(1)-N(2)-O(2)	107.50(13)
O(2)-C(3)-C(4)	106.66(15)	O(2)-C(3)-H(3A)	110.4
C(4)-C(3)-H(3A)	110.4	O(2)-C(3)-H(3B)	110.4
C(4)-C(3)-H(3B)	110.4	H(3A)-C(3)-H(3B)	108.6
C(10)-N(3)-N(1)	111.24(13)	C(9)-C(4)-C(5)	118.49(19)
C(9)-C(4)-C(3)	121.91(19)	C(5)-C(4)-C(3)	119.60(19)
C(6)-C(5)-C(4)	120.6(2)	C(6)-C(5)-H(5A)	119.7
C(4)-C(5)-H(5A)	119.7	C(7)-C(6)-C(5)	119.9(2)
C(7)-C(6)-H(6A)	120.1	C(5)-C(6)-H(6A)	120.1
C(8)-C(7)-C(6)	120.1(2)	C(8)-C(7)-H(7A)	119.9
C(6)-C(7)-H(7A)	119.9	C(7)-C(8)-C(9)	120.4(2)
C(7)-C(8)-H(8A)	119.8	C(9)-C(8)-H(8A)	119.8
C(4)-C(9)-C(8)	120.6(2)	C(4)-C(9)-H(9A)	119.7
C(8)-C(9)-H(9A)	119.7	O(10)-C(10)-N(3)	129.16(16)
O(10)-C(10)-C(11)	118.98(15)	N(3)-C(10)-C(11)	111.85(14)
C(12)-C(11)-C(16)	118.61(16)	C(12)-C(11)-C(10)	117.67(15)
C(16)-C(11)-C(10)	123.69(15)	N(13)-C(12)-C(11)	120.72(15)
N(13)-C(12)-H(12A)	119.6	C(11)-C(12)-H(12A)	119.6
C(14)-N(13)-C(12)	121.35(15)	C(14)-N(13)-C(17)	118.76(15)

Continuation of table S9

C(12)-N(13)-C(17)	119.80(14)	N(13)-C(14)-C(15)	119.78(17)
N(13)-C(14)-H(14A)	120.1	C(15)-C(14)-H(14A)	120.1
C(14)-C(15)-C(16)	120.15(17)	C(14)-C(15)-H(15A)	119.9
C(16)-C(15)-H(15A)	119.9	C(15)-C(16)-C(11)	119.32(16)
C(15)-C(16)-H(16A)	120.3	C(11)-C(16)-H(16A)	120.3
N(13)-C(17)-C(18)	109.45(14)	N(13)-C(17)-H(17A)	109.8
C(18)-C(17)-H(17A)	109.8	N(13)-C(17)-H(17B)	109.8
C(18)-C(17)-H(17B)	109.8	H(17A)-C(17)-H(17B)	108.2
C(23)-C(18)-C(19)	119.12(18)	C(23)-C(18)-C(17)	120.77(17)
C(19)-C(18)-C(17)	120.06(16)	C(20)-C(19)-C(18)	120.37(18)
C(20)-C(19)-H(19A)	119.8	C(18)-C(19)-H(19A)	119.8
C(19)-C(20)-C(21)	120.2(2)	C(19)-C(20)-H(20A)	119.9
C(21)-C(20)-H(20A)	119.9	C(22)-C(21)-C(20)	119.9(2)
C(22)-C(21)-H(21A)	120.1	C(20)-C(21)-H(21A)	120.1
C(21)-C(22)-C(23)	120.0(2)	C(21)-C(22)-H(22A)	120.0
C(23)-C(22)-H(22A)	120.0	C(18)-C(23)-C(22)	120.4(2)
C(18)-C(23)-H(23A)	119.8	C(22)-C(23)-H(23A)	119.8

Table S10. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	24(1)	49(1)	17(1)	0(1)	6(1)	-1(1)
N(1)	27(1)	17(1)	16(1)	-1(1)	10(1)	0(1)
O(2)	24(1)	36(1)	18(1)	-2(1)	11(1)	1(1)
N(2)	28(1)	27(1)	17(1)	-1(1)	11(1)	2(1)
C(3)	23(1)	51(1)	31(1)	-12(1)	13(1)	-3(1)
N(3)	33(1)	18(1)	17(1)	-3(1)	15(1)	-3(1)
C(4)	17(1)	38(1)	26(1)	-5(1)	9(1)	-1(1)
C(5)	28(1)	36(1)	31(1)	1(1)	15(1)	-4(1)
C(6)	31(1)	39(1)	38(1)	-13(1)	14(1)	-5(1)
C(7)	29(1)	61(2)	23(1)	-7(1)	10(1)	-5(1)
C(8)	25(1)	55(2)	28(1)	10(1)	9(1)	0(1)
C(9)	24(1)	34(1)	36(1)	1(1)	11(1)	1(1)
O(10)	45(1)	17(1)	25(1)	0(1)	21(1)	-4(1)
C(10)	20(1)	19(1)	17(1)	2(1)	8(1)	3(1)
C(11)	20(1)	17(1)	15(1)	-1(1)	6(1)	-1(1)
C(12)	20(1)	18(1)	16(1)	2(1)	7(1)	0(1)
N(13)	21(1)	18(1)	16(1)	-1(1)	7(1)	0(1)
C(14)	30(1)	23(1)	15(1)	1(1)	11(1)	-3(1)
C(15)	36(1)	19(1)	21(1)	3(1)	13(1)	0(1)
C(16)	30(1)	17(1)	19(1)	0(1)	10(1)	0(1)
C(17)	28(1)	17(1)	18(1)	-4(1)	11(1)	0(1)
C(18)	25(1)	20(1)	22(1)	-2(1)	10(1)	0(1)
C(19)	30(1)	24(1)	24(1)	-2(1)	12(1)	0(1)
C(20)	33(1)	34(1)	30(1)	-1(1)	5(1)	6(1)
C(21)	25(1)	40(1)	50(2)	-5(1)	9(1)	4(1)
C(22)	31(1)	49(1)	63(2)	5(1)	27(1)	0(1)
C(23)	34(1)	39(1)	36(1)	8(1)	20(1)	5(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **4b**.

	x	y	z	U(eq)
H(3A)	754	5247	1725	40
H(3B)	718	6662	1466	40
H(5A)	1043	8338	2354	36
H(6A)	1015	9035	3449	42
H(7A)	940	7620	4299	44
H(8A)	901	5515	4063	43
H(9A)	929	4805	2976	37
H(12A)	2816	3091	-476	21
H(14A)	3084	4830	-2130	26
H(15A)	2880	6728	-1676	29
H(16A)	2690	6823	-580	26
H(17A)	3018	2648	-2124	25
H(17B)	2907	1936	-1461	25
H(19A)	4030	1394	-445	31
H(20A)	5370	1168	70	41
H(21A)	6194	2075	-456	47
H(22A)	5677	3138	-1524	53
H(23A)	4335	3345	-2051	41

Table S12. Torsion angles [°] for **4b**.

O(1)-N(1)-N(2)-O(2)	0.1(2)
N(3)-N(1)-N(2)-O(2)	-173.95(12)
C(3)-O(2)-N(2)-N(1)	178.14(14)
N(2)-O(2)-C(3)-C(4)	-163.76(15)
O(1)-N(1)-N(3)-C(10)	106.09(17)
N(2)-N(1)-N(3)-C(10)	-79.39(18)
O(2)-C(3)-C(4)-C(9)	-95.1(2)
O(2)-C(3)-C(4)-C(5)	85.2(2)
C(9)-C(4)-C(5)-C(6)	-0.1(3)
C(3)-C(4)-C(5)-C(6)	179.60(17)
C(4)-C(5)-C(6)-C(7)	0.0(3)
C(5)-C(6)-C(7)-C(8)	0.2(3)
C(6)-C(7)-C(8)-C(9)	-0.2(3)
C(5)-C(4)-C(9)-C(8)	0.1(3)
C(3)-C(4)-C(9)-C(8)	-179.57(17)
C(7)-C(8)-C(9)-C(4)	0.0(3)
N(1)-N(3)-C(10)-O(10)	1.3(3)
N(1)-N(3)-C(10)-C(11)	-177.71(13)
O(10)-C(10)-C(11)-C(12)	-16.2(2)
N(3)-C(10)-C(11)-C(12)	162.97(15)
O(10)-C(10)-C(11)-C(16)	161.94(16)
N(3)-C(10)-C(11)-C(16)	-18.9(2)
C(16)-C(11)-C(12)-N(13)	1.1(3)
C(10)-C(11)-C(12)-N(13)	179.35(15)
C(11)-C(12)-N(13)-C(14)	-2.7(3)
C(11)-C(12)-N(13)-C(17)	173.93(15)
C(12)-N(13)-C(14)-C(15)	1.8(3)
C(17)-N(13)-C(14)-C(15)	-174.81(16)
N(13)-C(14)-C(15)-C(16)	0.5(3)
C(14)-C(15)-C(16)-C(11)	-2.0(3)
C(12)-C(11)-C(16)-C(15)	1.2(3)
C(10)-C(11)-C(16)-C(15)	-176.93(16)
C(14)-N(13)-C(17)-C(18)	88.78(18)
C(12)-N(13)-C(17)-C(18)	-87.91(18)
N(13)-C(17)-C(18)-C(23)	-85.6(2)
N(13)-C(17)-C(18)-C(19)	91.62(19)
C(23)-C(18)-C(19)-C(20)	1.2(3)
C(17)-C(18)-C(19)-C(20)	-176.00(16)
C(18)-C(19)-C(20)-C(21)	0.4(3)
C(19)-C(20)-C(21)-C(22)	-1.5(3)
C(20)-C(21)-C(22)-C(23)	1.0(3)
C(19)-C(18)-C(23)-C(22)	-1.7(3)
C(17)-C(18)-C(23)-C(22)	175.51(18)
C(21)-C(22)-C(23)-C(18)	0.6(3)