Electronic Supporting Information for:

Isolation and Structural Characterization of Stable Carbamic-Carbonic Anhydrides: An Experimental and Computational Study

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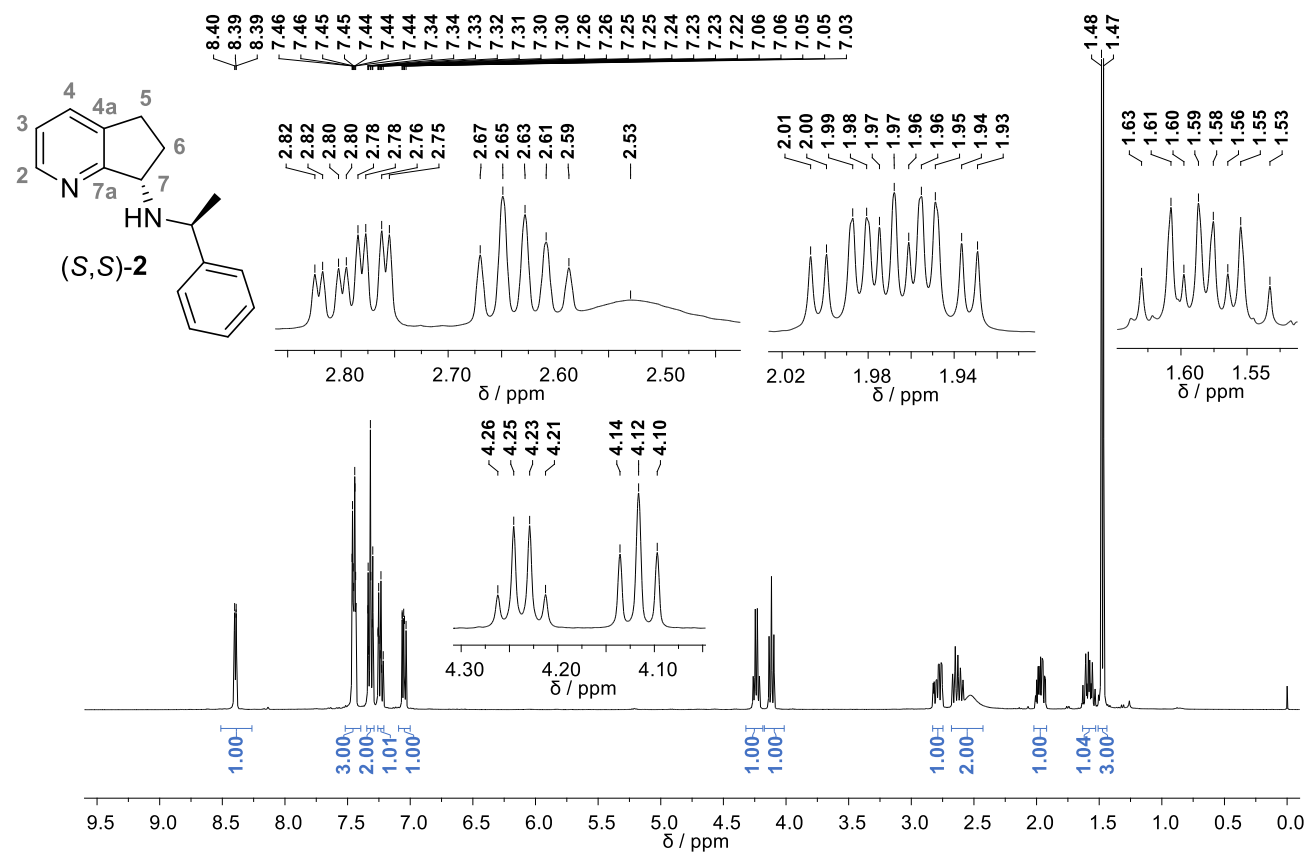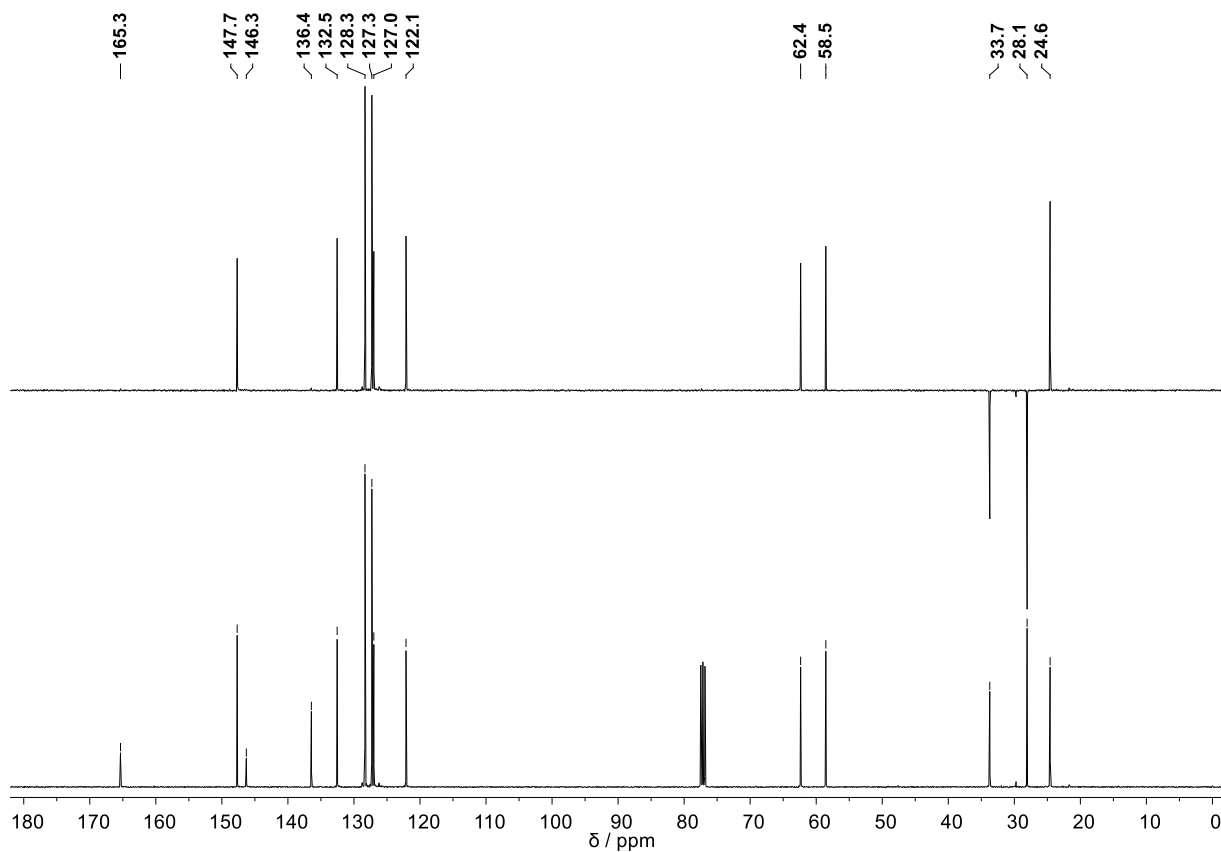
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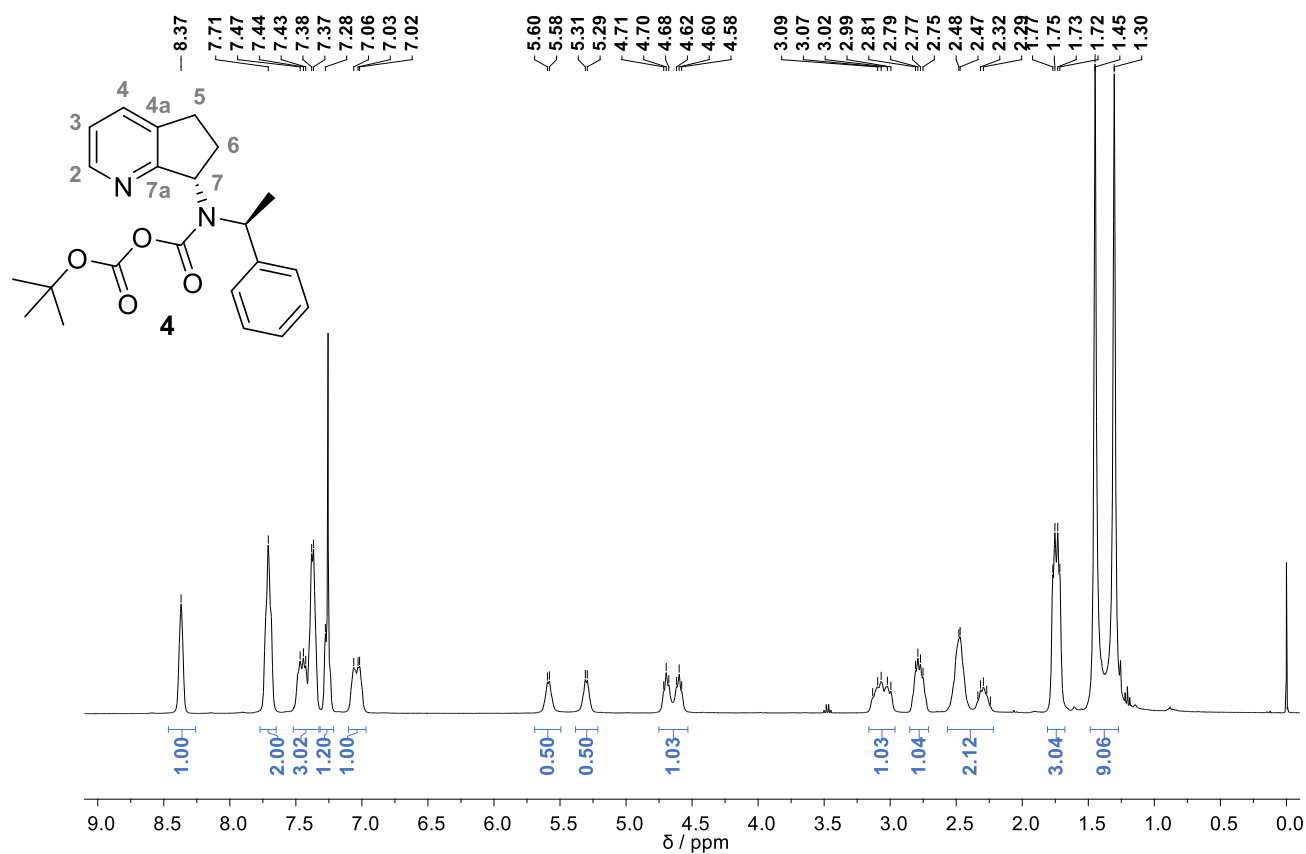
Figure S3. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **4** (50:50 mixture of conformers).
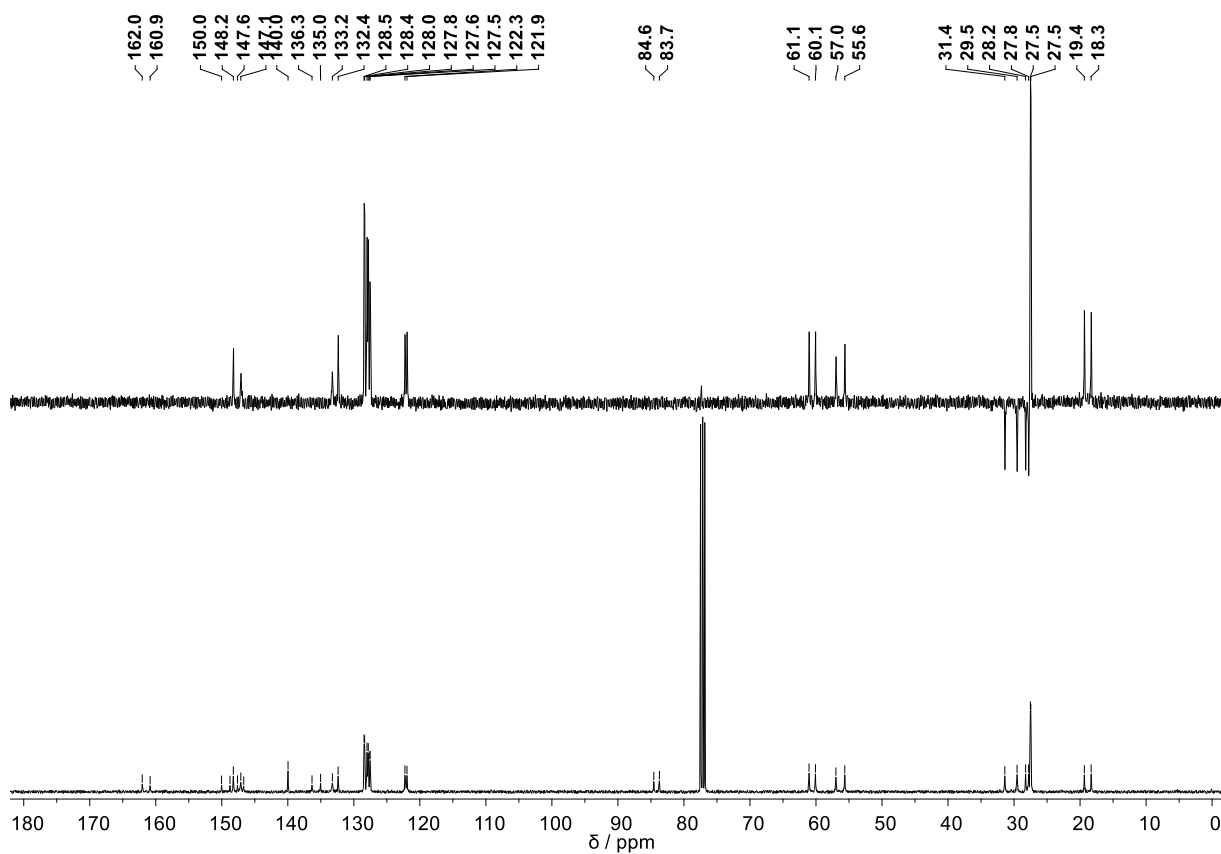
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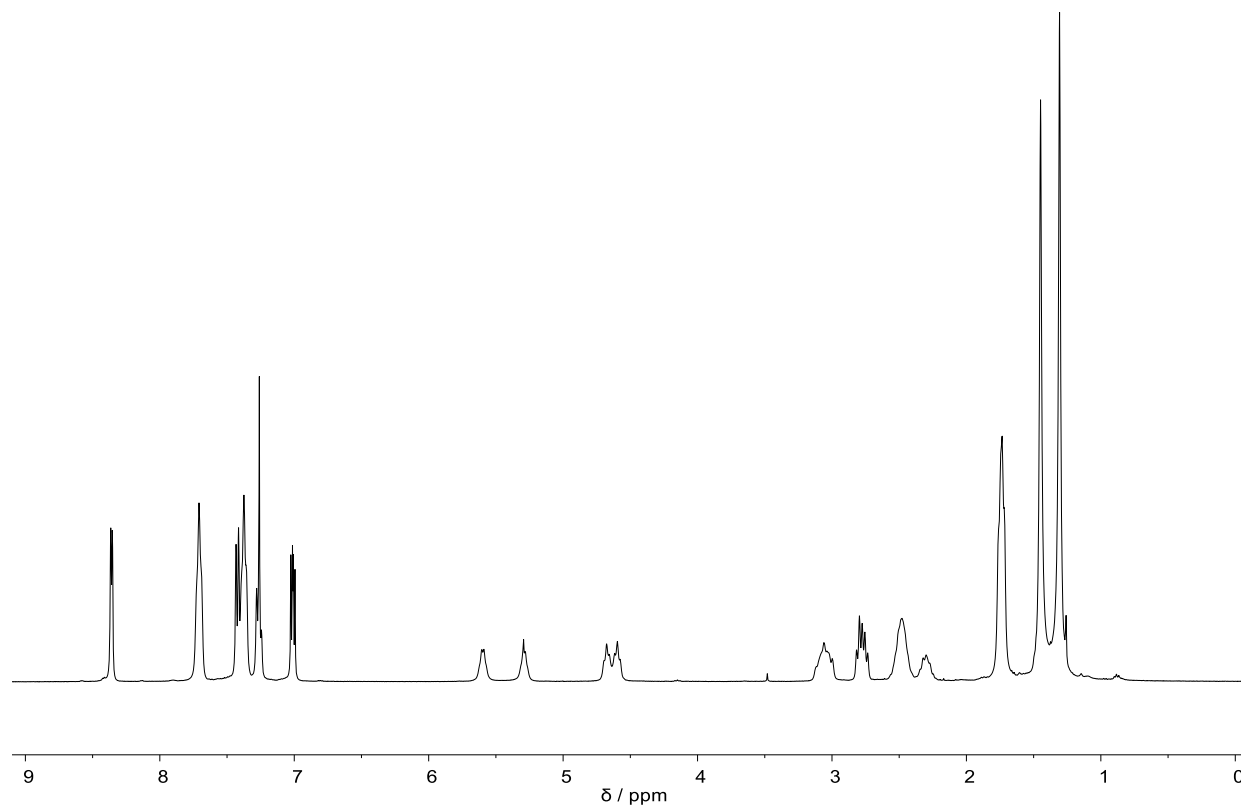
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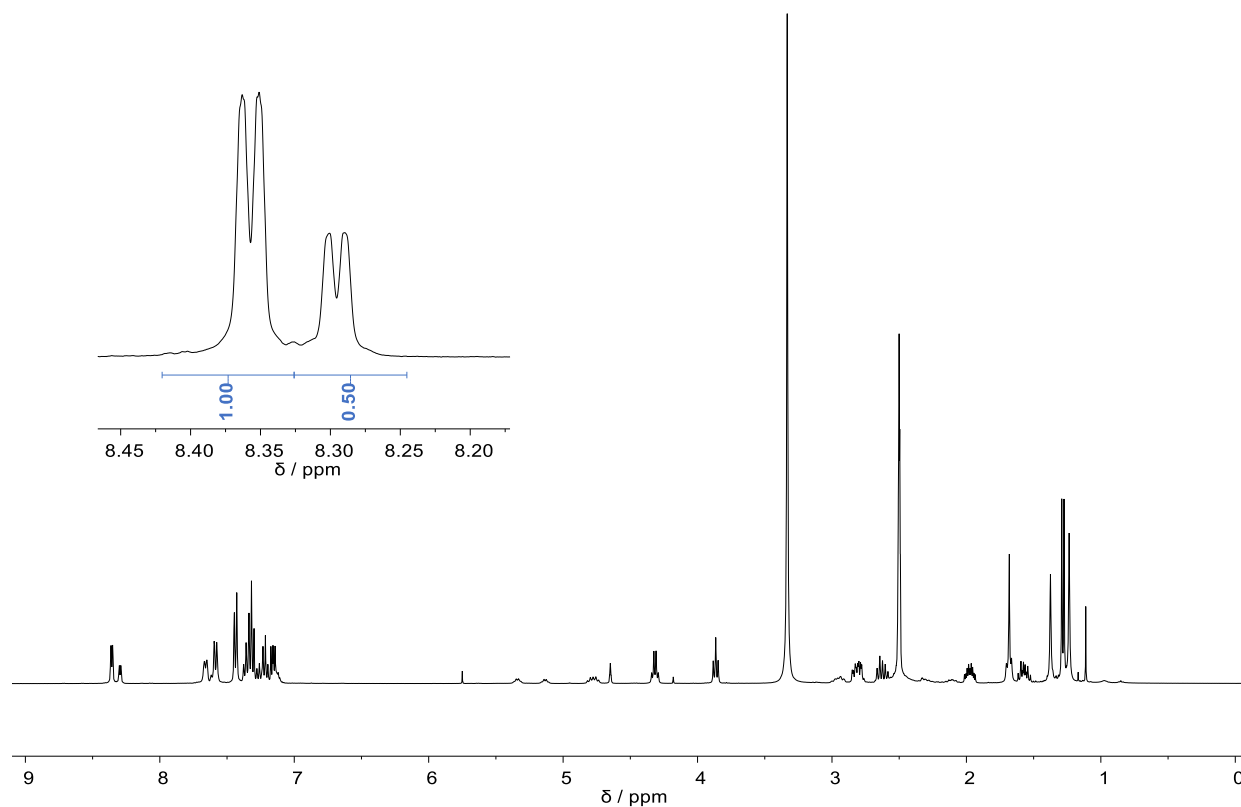
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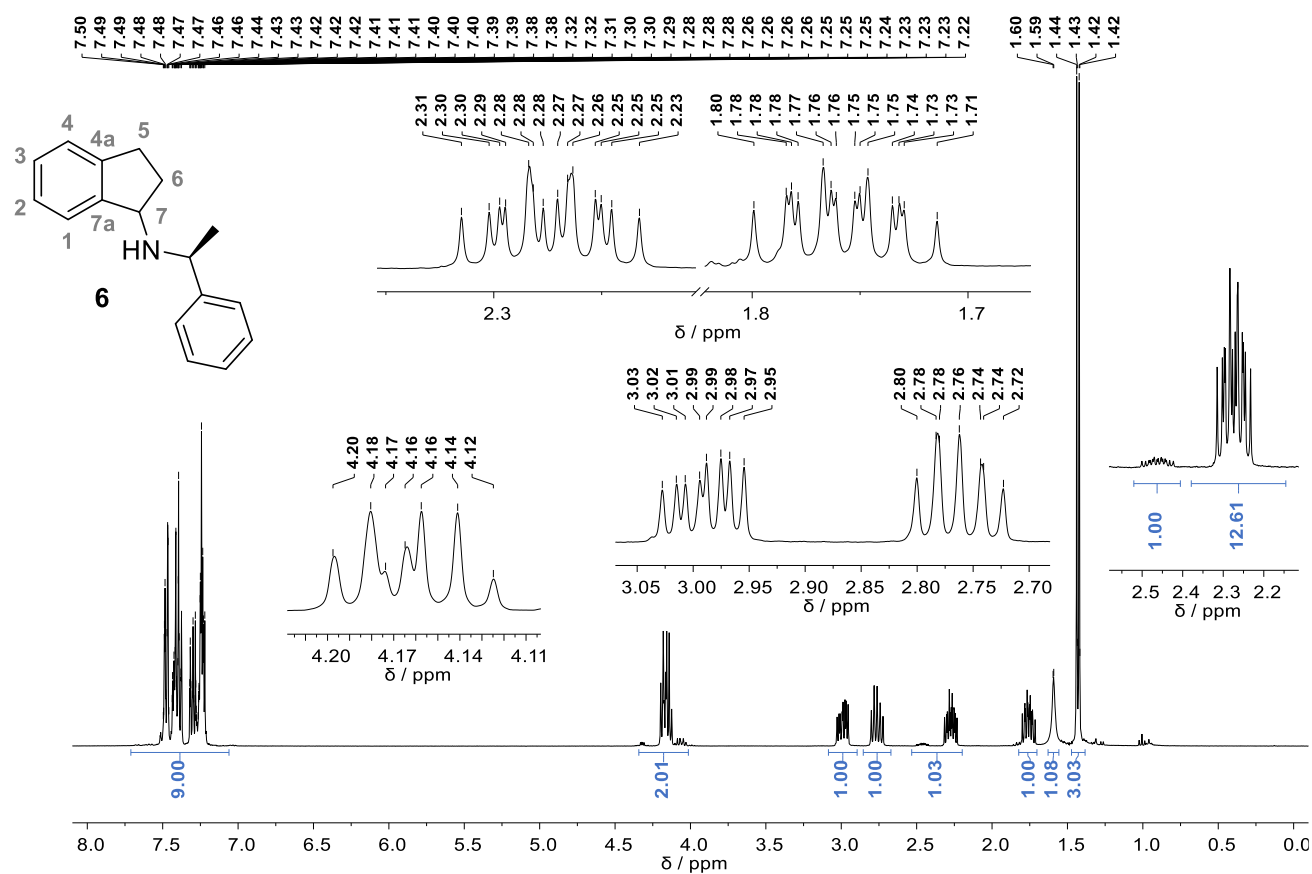
Figure S7. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **6**.
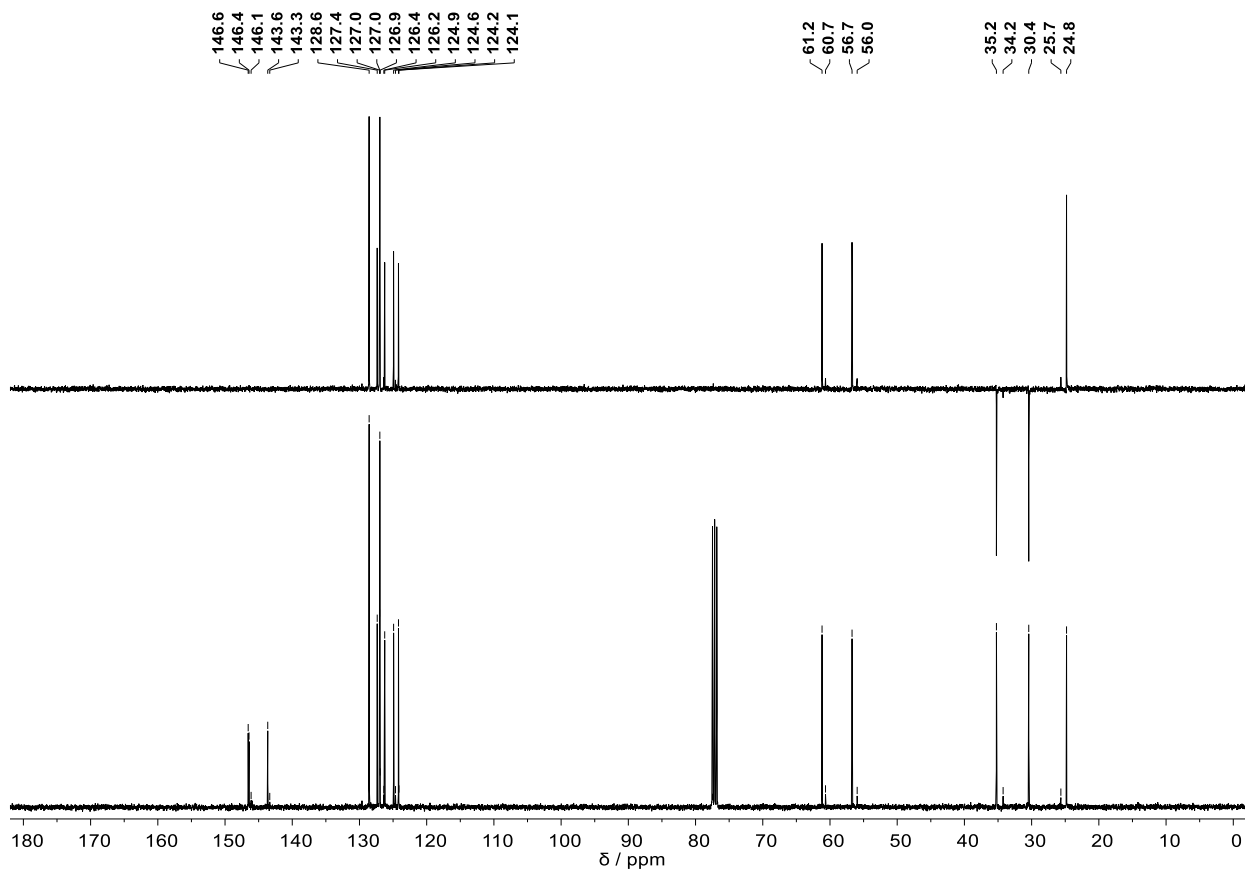
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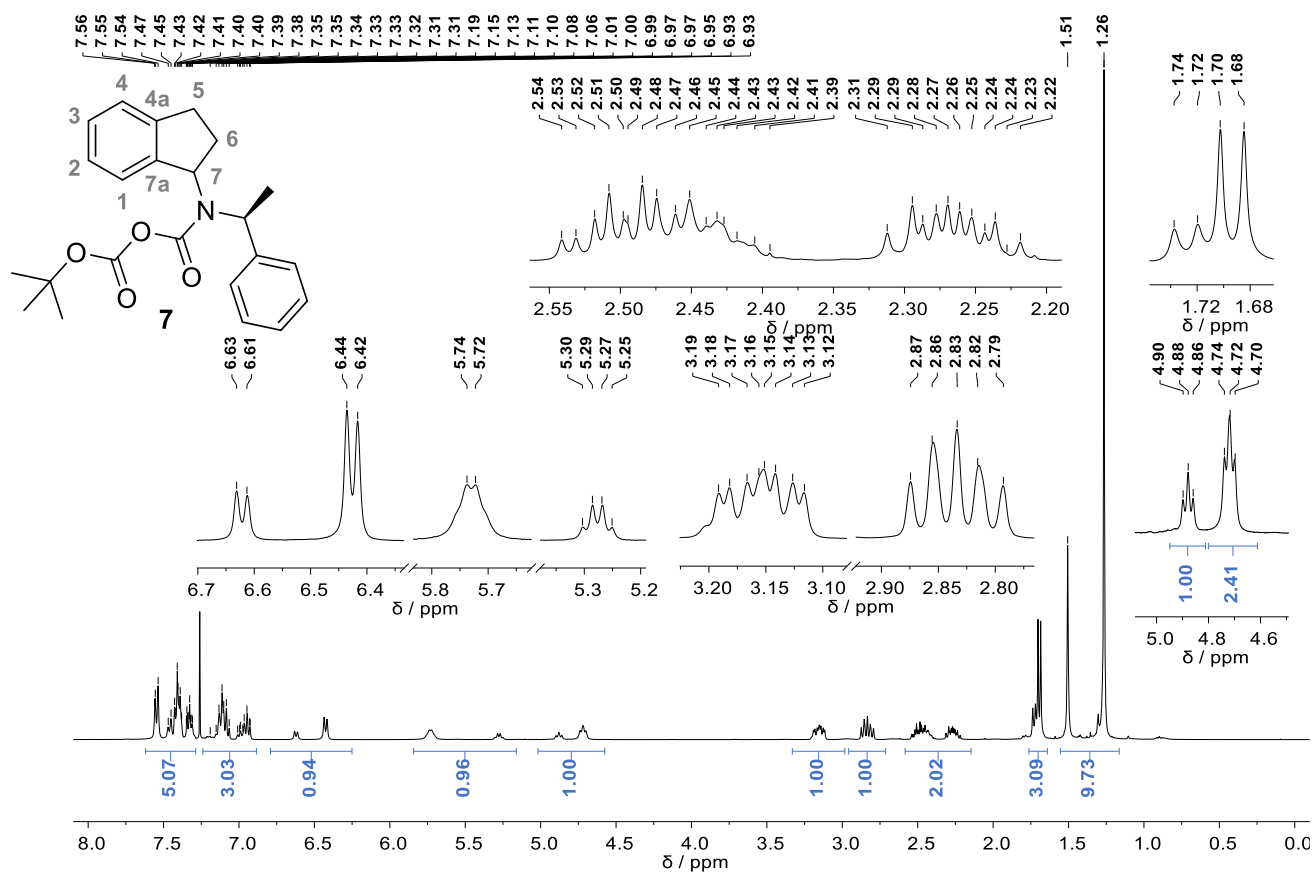
Figure S9. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **7** (71:29 mixture of conformers).
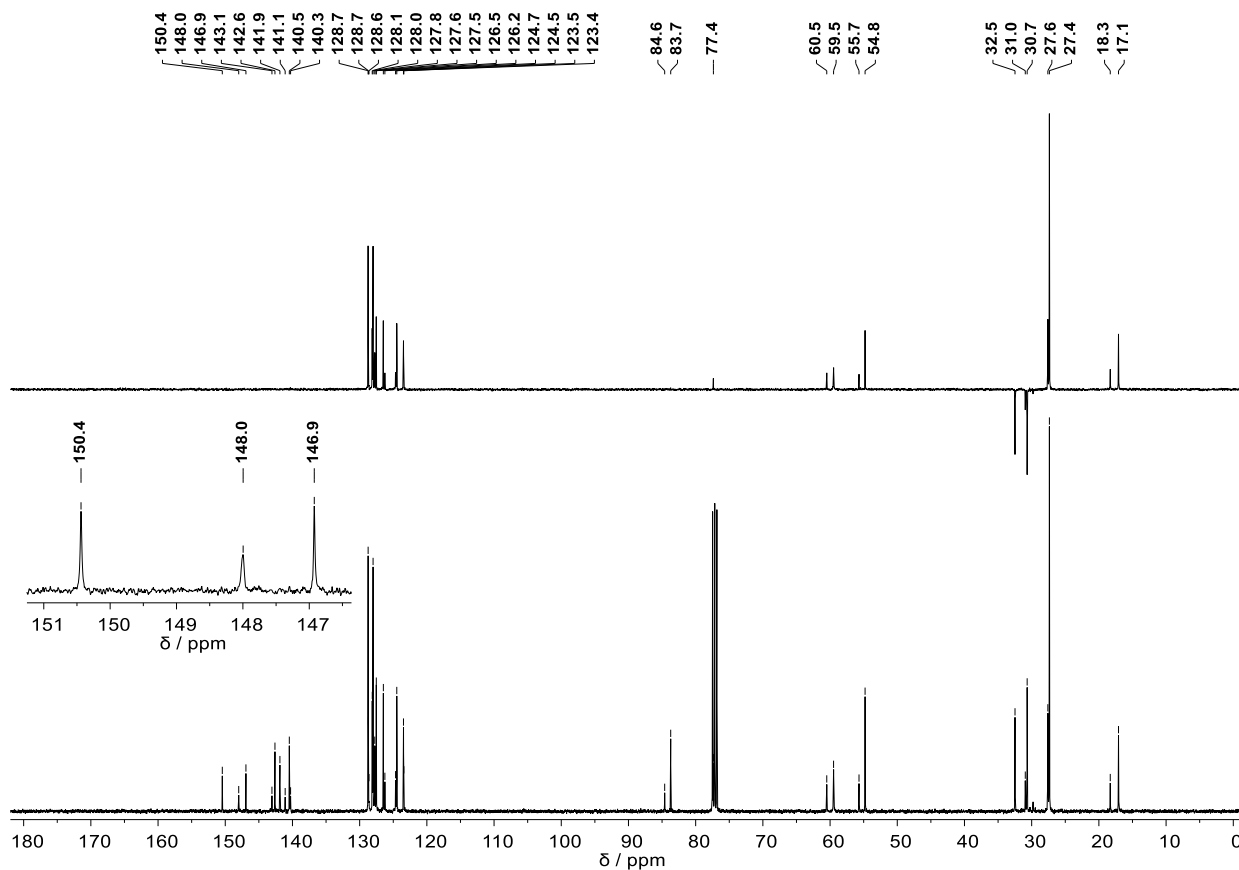
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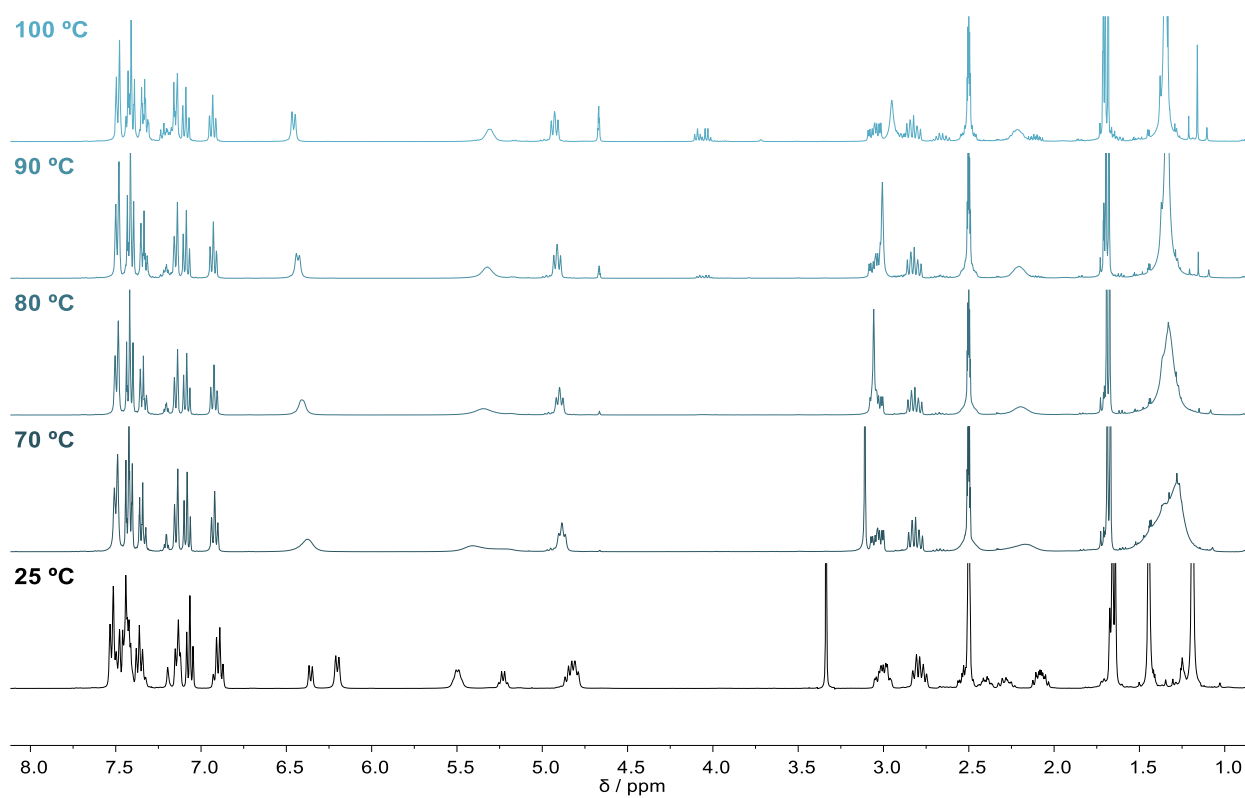
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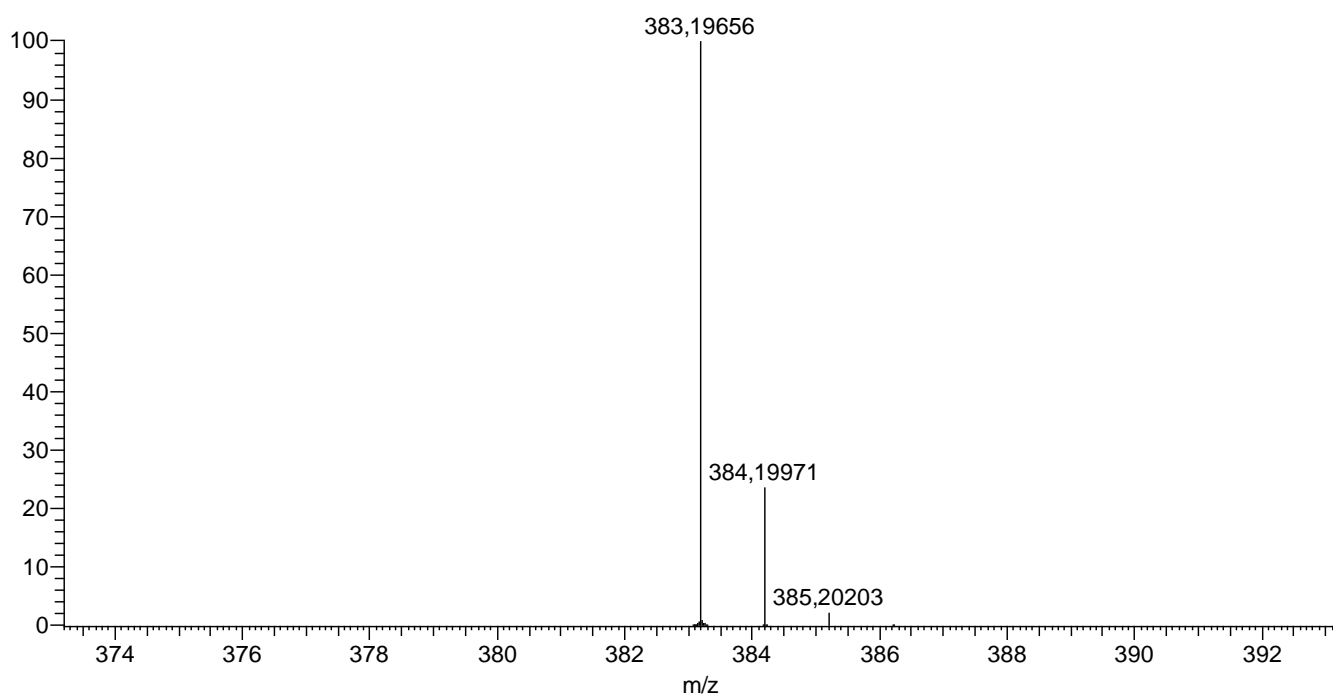
2. HRMS spectrum

Figure S12. HRMS (ESI-TOF) spectrum of carbamic-carbonic anhydride **4**, *m*/*z* calcd for $C_{22}H_{27}N_2O_4^+$: 383.19653; found: 383.19656.
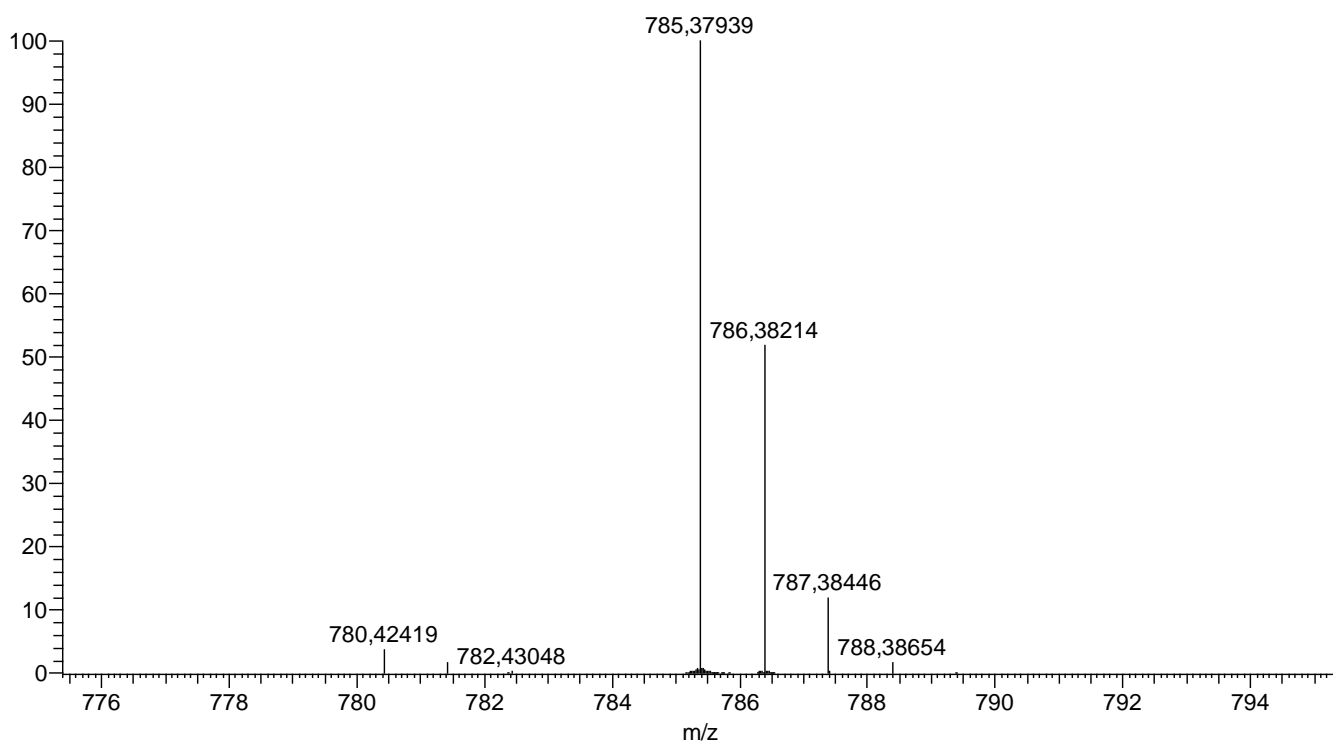
Figure S13. HRMS (ESI-TOF) spectrum of carbamic-carbonic anhydride **7**, *m*/*z* calcd for $C_{46}H_{54}N_2O_8Na^+$ [2M + Na]$^+$: 785.37724; found: 785.37939.

3. Crystal data and structure refinement

Table S1. Crystal data and structure refinement for **4**.

Identification code	shelx	
Empirical formula	$C_{22}H_{26}N_2O_4$	
Formula weight	382.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	*I*4	
Unit cell dimensions	a = 21.4753(12) Å	α = 90.00°
	b = 21.4753(12) Å	β = 90.00°
	c = 9.2644(5) Å	γ = 90.00°
Volume	4272.6(5) Å^3	
Z	8	
Density (calculated)	1.189 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	1632	
Crystal size	0.520 x 0.290 x 0.140 mm^3	
Theta range for data collection	1.341 to 30.161°	
Index ranges	-28<=h<=29, -30<=k<=30, -12<=l<=12	
Reflections collected	21153	
Independent reflections	6244 [R(int) = 0.0508]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6244 / 1 / 257	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0542, wR2 = 0.1058	
R indices (all data)	R1 = 0.0698, wR2 = 0.1111	
Absolute structure parameter	0.1(5)	
Largest diff. peak and hole	0.248 and -0.239 e.Å^{-3}	

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

	x	y	z	U(eq)
N(1)	6426(1)	1650(1)	3808(2)	22(1)
C(2)	6897(1)	1979(1)	4352(3)	18(1)
C(3)	7492(1)	1754(1)	4606(3)	21(1)
C(4)	7621(1)	1145(1)	4236(3)	26(1)
C(5)	7146(1)	789(1)	3657(3)	27(1)
C(6)	6564(1)	1058(1)	3480(3)	25(1)
C(7)	6867(1)	2669(1)	4718(3)	20(1)
C(8)	7445(1)	2762(1)	5691(3)	24(1)
C(9)	7906(1)	2254(1)	5209(3)	25(1)
N(10)	6274(1)	2902(1)	5283(2)	21(1)
C(11)	6046(1)	3508(1)	4743(3)	27(1)
C(12)	5875(1)	3475(1)	3157(3)	22(1)
C(13)	5639(1)	2929(1)	2565(3)	22(1)
C(14)	5456(1)	2900(1)	1134(3)	27(1)
C(15)	5500(1)	3420(1)	254(3)	30(1)
C(16)	5736(1)	3963(1)	819(3)	31(1)
C(17)	5924(1)	3996(1)	2256(3)	27(1)
C(18)	6520(2)	4017(2)	5108(5)	61(1)
C(19)	5962(1)	2641(1)	6384(3)	21(1)
O(20)	5477(1)	2803(1)	6901(2)	31(1)
O(21)	6314(1)	2152(1)	6971(2)	20(1)
C(22)	6019(1)	1620(1)	7394(3)	20(1)
O(23)	5498(1)	1481(1)	7078(2)	29(1)
O(24)	6429(1)	1311(1)	8153(2)	20(1)
C(25)	6281(1)	671(1)	8666(3)	25(1)
C(26)	5746(2)	696(2)	9722(3)	39(1)
C(27)	6877(1)	481(1)	9414(3)	30(1)
C(28)	6159(2)	259(1)	7371(4)	45(1)

Table S3. Bond lengths [Å] and angles [°] for **4**.

_____

N(1)-C(2)	1.332(3)
N(1)-C(6)	1.342(3)
C(2)-C(3)	1.387(3)
C(2)-C(7)	1.522(4)
C(3)-C(4)	1.380(4)
C(3)-C(9)	1.501(4)
C(4)-C(5)	1.382(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.387(4)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-N(10)	1.464(3)
C(7)-C(8)	1.548(4)
C(7)-H(7)	1.0000
C(8)-C(9)	1.538(4)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
N(10)-C(19)	1.343(4)
N(10)-C(11)	1.477(3)
C(11)-C(12)	1.517(4)
C(11)-C(18)	1.532(4)
C(11)-H(11)	1.0000
C(12)-C(13)	1.390(4)
C(12)-C(17)	1.400(4)
C(13)-C(14)	1.385(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.385(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.375(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.393(4)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800

C(18)-H(18C)	0.9800
C(19)-O(20)	1.199(3)
C(19)-O(21)	1.403(3)
O(21)-C(22)	1.364(3)
C(22)-O(23)	1.193(3)
C(22)-O(24)	1.309(3)
O(24)-C(25)	1.489(3)
C(25)-C(26)	1.510(4)
C(25)-C(27)	1.511(4)
C(25)-C(28)	1.514(4)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(2)-N(1)-C(6)	114.9(2)
N(1)-C(2)-C(3)	125.4(2)
N(1)-C(2)-C(7)	124.6(2)
C(3)-C(2)-C(7)	109.9(2)
C(4)-C(3)-C(2)	118.2(2)
C(4)-C(3)-C(9)	130.7(2)
C(2)-C(3)-C(9)	111.1(2)
C(3)-C(4)-C(5)	118.2(3)
C(3)-C(4)-H(4)	120.9
C(5)-C(4)-H(4)	120.9
C(4)-C(5)-C(6)	118.8(3)
C(4)-C(5)-H(5)	120.6
C(6)-C(5)-H(5)	120.6
N(1)-C(6)-C(5)	124.5(3)
N(1)-C(6)-H(6)	117.7
C(5)-C(6)-H(6)	117.7
N(10)-C(7)-C(2)	116.7(2)
N(10)-C(7)-C(8)	116.4(2)
C(2)-C(7)-C(8)	102.8(2)
N(10)-C(7)-H(7)	106.7

C(2)-C(7)-H(7)	106.7
C(8)-C(7)-H(7)	106.7
C(9)-C(8)-C(7)	104.8(2)
C(9)-C(8)-H(8A)	110.8
C(7)-C(8)-H(8A)	110.8
C(9)-C(8)-H(8B)	110.8
C(7)-C(8)-H(8B)	110.8
H(8A)-C(8)-H(8B)	108.9
C(3)-C(9)-C(8)	103.6(2)
C(3)-C(9)-H(9A)	111.0
C(8)-C(9)-H(9A)	111.0
C(3)-C(9)-H(9B)	111.0
C(8)-C(9)-H(9B)	111.0
H(9A)-C(9)-H(9B)	109.0
C(19)-N(10)-C(7)	124.2(2)
C(19)-N(10)-C(11)	117.3(2)
C(7)-N(10)-C(11)	117.9(2)
N(10)-C(11)-C(12)	111.6(2)
N(10)-C(11)-C(18)	109.5(2)
C(12)-C(11)-C(18)	114.1(3)
N(10)-C(11)-H(11)	107.1
C(12)-C(11)-H(11)	107.1
C(18)-C(11)-H(11)	107.1
C(13)-C(12)-C(17)	117.8(3)
C(13)-C(12)-C(11)	120.6(2)
C(17)-C(12)-C(11)	121.5(2)
C(14)-C(13)-C(12)	121.2(3)
C(14)-C(13)-H(13)	119.4
C(12)-C(13)-H(13)	119.4
C(15)-C(14)-C(13)	120.5(3)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(16)-C(15)-C(14)	119.0(3)
C(16)-C(15)-H(15)	120.5
C(14)-C(15)-H(15)	120.5
C(15)-C(16)-C(17)	120.9(3)
C(15)-C(16)-H(16)	119.5
C(17)-C(16)-H(16)	119.5
C(16)-C(17)-C(12)	120.5(3)
C(16)-C(17)-H(17)	119.8

C(12)-C(17)-H(17)	119.8
C(11)-C(18)-H(18A)	109.5
C(11)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(11)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(20)-C(19)-N(10)	128.0(3)
O(20)-C(19)-O(21)	122.0(2)
N(10)-C(19)-O(21)	109.8(2)
C(22)-O(21)-C(19)	119.2(2)
O(23)-C(22)-O(24)	129.6(2)
O(23)-C(22)-O(21)	125.0(2)
O(24)-C(22)-O(21)	105.4(2)
C(22)-O(24)-C(25)	119.7(2)
O(24)-C(25)-C(26)	109.6(2)
O(24)-C(25)-C(27)	102.4(2)
C(26)-C(25)-C(27)	110.9(2)
O(24)-C(25)-C(28)	108.9(2)
C(26)-C(25)-C(28)	113.7(3)
C(27)-C(25)-C(28)	110.7(3)
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(25)-C(28)-H(28A)	109.5
C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(25)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

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Table S4. Anisotropic displacement parameters ($\mathrm{\AA}^2$ x 10^3) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2\,[h^2a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	24(1)	24(1)	16(1)	1(1)	-3(1)	4(1)
C(2)	22(1)	23(1)	10(1)	4(1)	-1(1)	2(1)
C(3)	23(1)	30(1)	11(1)	7(1)	2(1)	2(1)
C(4)	25(1)	33(2)	21(1)	6(1)	3(1)	9(1)
C(5)	37(2)	28(1)	17(1)	0(1)	-1(1)	11(1)
C(6)	33(2)	25(1)	18(1)	0(1)	-3(1)	3(1)
C(7)	20(1)	20(1)	19(1)	3(1)	-2(1)	0(1)
C(8)	24(1)	24(1)	26(1)	4(1)	-8(1)	-3(1)
C(9)	18(1)	34(2)	24(1)	8(1)	-1(1)	0(1)
N(10)	24(1)	16(1)	22(1)	1(1)	-5(1)	3(1)
C(11)	34(2)	15(1)	31(1)	0(1)	-14(1)	4(1)
C(12)	16(1)	21(1)	28(1)	5(1)	-4(1)	2(1)
C(13)	16(1)	23(1)	27(1)	9(1)	-6(1)	-3(1)
C(14)	20(1)	31(2)	29(2)	2(1)	-6(1)	-1(1)
C(15)	24(1)	43(2)	23(1)	10(1)	-2(1)	9(1)
C(16)	30(2)	30(2)	35(2)	17(1)	5(1)	7(1)
C(17)	26(1)	21(1)	35(2)	4(1)	-3(1)	0(1)
C(18)	82(3)	19(2)	81(3)	4(2)	-58(3)	-6(2)
C(19)	26(1)	20(1)	17(1)	-6(1)	-5(1)	2(1)
O(20)	27(1)	32(1)	35(1)	-3(1)	4(1)	8(1)
O(21)	21(1)	22(1)	17(1)	2(1)	-1(1)	0(1)
C(22)	25(1)	23(1)	11(1)	-2(1)	0(1)	-1(1)
O(23)	28(1)	34(1)	26(1)	4(1)	-8(1)	-6(1)
O(24)	23(1)	18(1)	20(1)	1(1)	-2(1)	0(1)
C(25)	37(2)	20(1)	18(1)	2(1)	1(1)	-3(1)
C(26)	34(2)	53(2)	29(2)	16(2)	4(1)	-1(2)
C(27)	38(2)	26(1)	27(2)	6(1)	3(1)	7(1)
C(28)	79(3)	22(2)	36(2)	-4(1)	-9(2)	-7(2)

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

	x	y	z	U(eq)
H(4)	8025	975	4376	32
H(5)	7218	369	3386	33
H(6)	6240	804	3101	30
H(7)	6949	2901	3801	24
H(8A)	7626	3181	5549	29
H(8B)	7335	2710	6721	29
H(9A)	8194	2414	4463	30
H(9B)	8151	2097	6037	30
H(11)	5656	3606	5286	32
H(13)	5603	2568	3154	26
H(14)	5298	2521	752	32
H(15)	5369	3401	-725	36
H(16)	5771	4320	221	38
H(17)	6086	4375	2628	33
H(18A)	6893	3963	4513	91
H(18B)	6633	3989	6131	91
H(18C)	6336	4427	4914	91
H(26A)	5361	797	9205	58
H(26B)	5829	1017	10450	58
H(26C)	5701	291	10196	58
H(27A)	6834	57	9790	45
H(27B)	6962	768	10213	45
H(27C)	7223	495	8723	45
H(28A)	5746	354	6974	68
H(28B)	6174	-179	7666	68
H(28C)	6476	336	6633	68

Table S6. Torsion angles [°] for **4**.

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|	
C(6)-N(1)-C(2)-C(3)	-0.8(4)
C(6)-N(1)-C(2)-C(7)	176.0(2)
N(1)-C(2)-C(3)-C(4)	1.8(4)
C(7)-C(2)-C(3)-C(4)	-175.4(2)
N(1)-C(2)-C(3)-C(9)	179.4(2)
C(7)-C(2)-C(3)-C(9)	2.2(3)
C(2)-C(3)-C(4)-C(5)	-1.1(4)
C(9)-C(3)-C(4)-C(5)	-178.2(3)
C(3)-C(4)-C(5)-C(6)	-0.3(4)
C(2)-N(1)-C(6)-C(5)	-0.8(4)
C(4)-C(5)-C(6)-N(1)	1.3(4)
N(1)-C(2)-C(7)-N(10)	35.5(3)
C(3)-C(2)-C(7)-N(10)	-147.3(2)
N(1)-C(2)-C(7)-C(8)	164.2(2)
C(3)-C(2)-C(7)-C(8)	-18.6(3)
N(10)-C(7)-C(8)-C(9)	156.0(2)
C(2)-C(7)-C(8)-C(9)	27.2(3)
C(4)-C(3)-C(9)-C(8)	-167.5(3)
C(2)-C(3)-C(9)-C(8)	15.3(3)
C(7)-C(8)-C(9)-C(3)	-26.1(3)
C(2)-C(7)-N(10)-C(19)	50.5(3)
C(8)-C(7)-N(10)-C(19)	-71.2(3)
C(2)-C(7)-N(10)-C(11)	-137.9(2)
C(8)-C(7)-N(10)-C(11)	100.3(3)
C(19)-N(10)-C(11)-C(12)	-121.1(3)
C(7)-N(10)-C(11)-C(12)	66.8(3)
C(19)-N(10)-C(11)-C(18)	111.6(3)
C(7)-N(10)-C(11)-C(18)	-60.5(4)
N(10)-C(11)-C(12)-C(13)	32.4(4)
C(18)-C(11)-C(12)-C(13)	157.2(3)
N(10)-C(11)-C(12)-C(17)	-150.3(2)
C(18)-C(11)-C(12)-C(17)	-25.5(4)
C(17)-C(12)-C(13)-C(14)	-0.2(4)
C(11)-C(12)-C(13)-C(14)	177.2(2)
C(12)-C(13)-C(14)-C(15)	-0.4(4)
C(13)-C(14)-C(15)-C(16)	0.8(4)
C(14)-C(15)-C(16)-C(17)	-0.6(4)
C(15)-C(16)-C(17)-C(12)	-0.1(4)

C(13)-C(12)-C(17)-C(16)	0.4(4)
C(11)-C(12)-C(17)-C(16)	-177.0(3)
C(7)-N(10)-C(19)-O(20)	-179.8(3)
C(11)-N(10)-C(19)-O(20)	8.7(4)
C(7)-N(10)-C(19)-O(21)	4.9(3)
C(11)-N(10)-C(19)-O(21)	-166.7(2)
O(20)-C(19)-O(21)-C(22)	43.7(3)
N(10)-C(19)-O(21)-C(22)	-140.6(2)
C(19)-O(21)-C(22)-O(23)	14.3(4)
C(19)-O(21)-C(22)-O(24)	-167.3(2)
O(23)-C(22)-O(24)-C(25)	4.4(4)
O(21)-C(22)-O(24)-C(25)	-173.9(2)
C(22)-O(24)-C(25)-C(26)	-64.7(3)
C(22)-O(24)-C(25)-C(27)	177.5(2)
C(22)-O(24)-C(25)-C(28)	60.3(3)

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The crystallographic data of **4** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1410888.

4. Potential energy curve of the C2-O2 bond breaking of the *trans*-species of 4
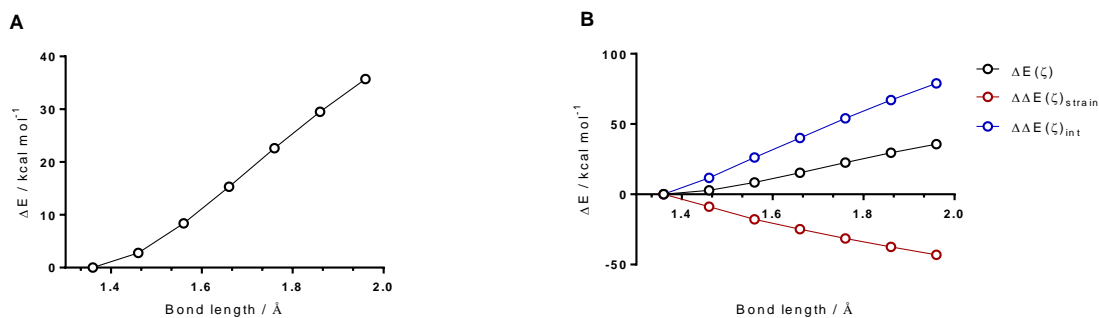
Figure S14. Potential energy curve (**A**) of the $C_{(2)}$-$O_{(2)}$ bond breaking of the *trans*-species of **4**, as a function of the C2-O2 bond length (steps of 0.1 Å). Geometry optimized at a fixed bond length of 1.96 Å. (**B**) $\Delta E(\zeta)$, $\Delta\Delta E(\zeta)_{strain}$ and $\Delta\Delta E(\zeta)_{int}$ values plotted as a function of the C2-O2 bond length (steps of 0.1 Å) for the *trans*-species of **4**. All calculations were made at the wB97XD/6-31+G(d,p) level of theory in implicit chloroform.

5. Potential energy curve of the N1-C1 bond breaking of the *cis*-species of 4
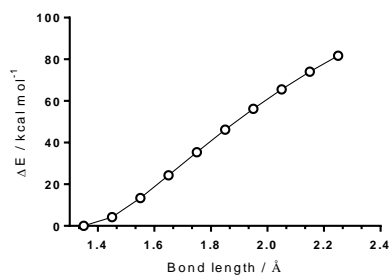
Figure S15. Potential energy curve of the N1-C1 bond breaking of the *cis*-species of **4**, as a function of the N1-C1 bond length (steps of 0.1 Å). Calculated at the wB97XD/6-31+G(d,p) level of theory, in implicit chloroform.