

NMR Crystallography of Campho[2,3-c]pyrazole ($Z' = 6$): Combining High-Resolution ^1H - ^{13}C Solid-State MAS NMR Spectroscopy and GIPAW Chemical-Shift Calculations

Supporting Information

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S1 Expanded regions for all resonances of the ^{13}C CP MAS spectrum (Figure 1b)

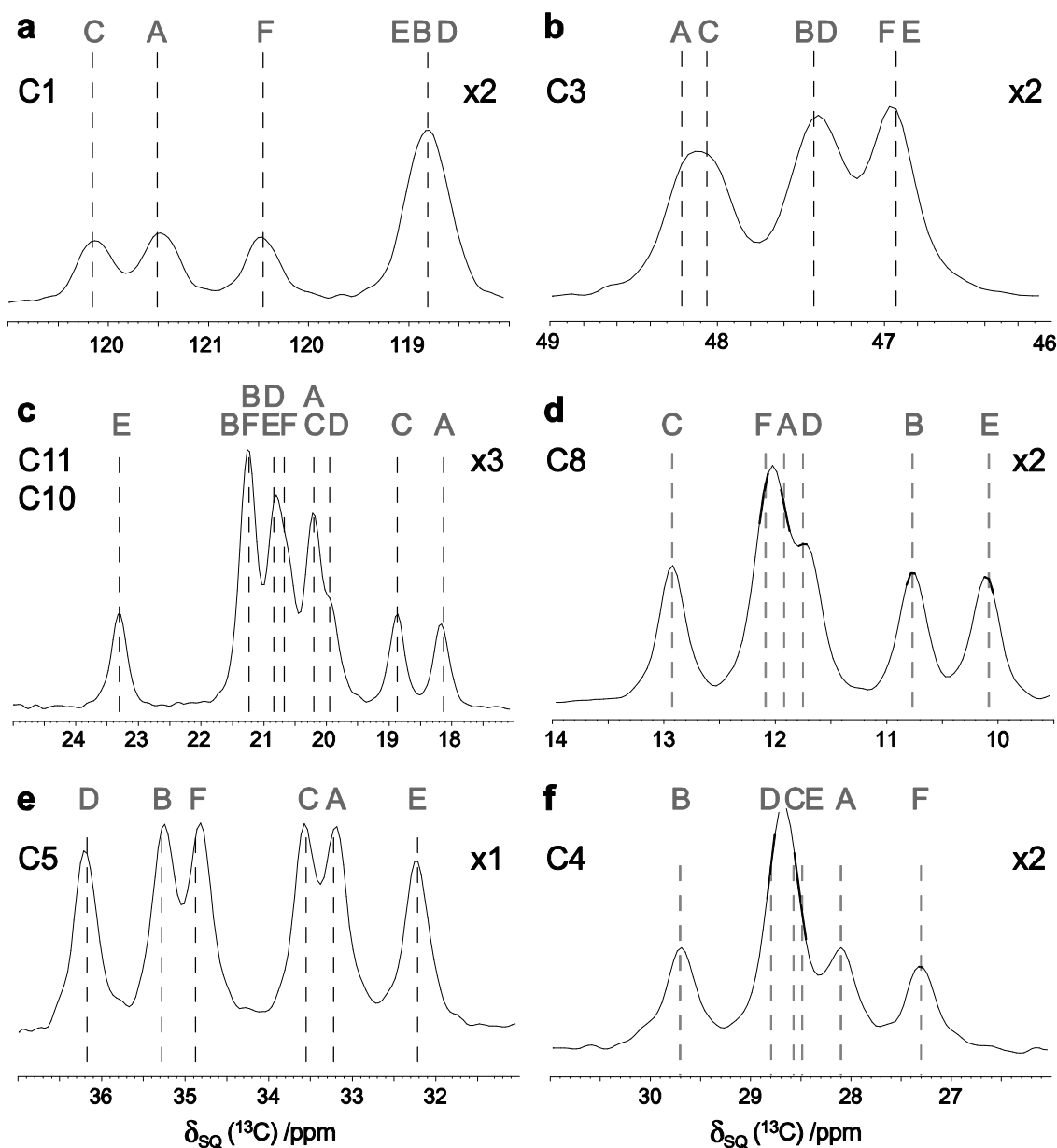


Figure S1. Expanded regions of the ^{13}C (125 MHz) CP MAS spectrum of campho[2,3-c]pyrazole for the protonated carbon atoms: CH; (a) C1 (b) C3; CH₃; (c) C11 & C10 (d) C8, CH₂; (e) C5 (f) C4. The resolved resonances are assigned to the six distinct molecules in the asymmetric unit cell (see Figure 1a) on the basis of experimental ^1H - ^{13}C MAS-*J*-HMQC spectra and GIPAW calculations (see Tables 1 and 2).

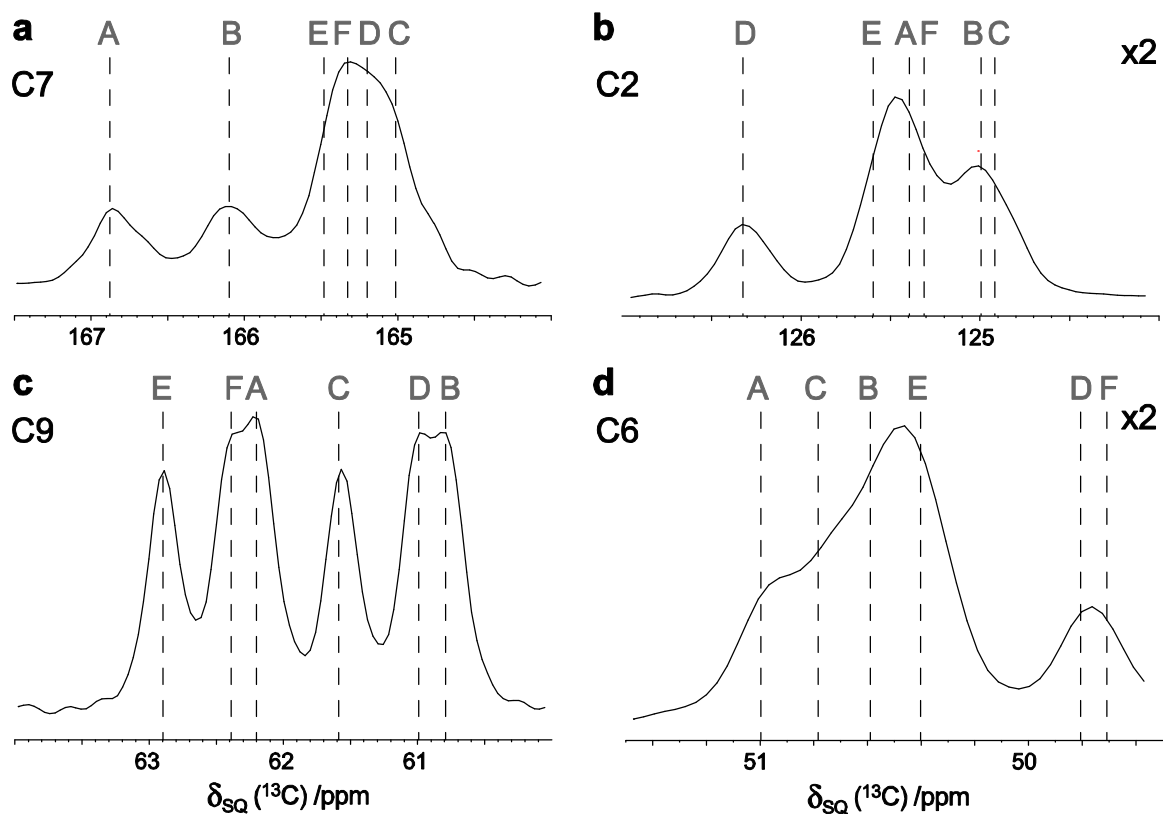


Figure S2. Expanded regions of the ^{13}C (125 MHz) CP MAS spectrum of campho[2,3-c]pyrazole given in Figure 1b for the non-protonated carbon atoms, (a) C7 (b) C2 (c) C9 (d) C6. The resolved resonances are assigned to the six distinct molecules in the asymmetric unit cell (see Figure 1a) on the basis of GIPAW calculations (see Table 3).

S2 Calculated ^{13}C , ^{15}N and ^1H chemical shifts determined using the “universal” referencing values

Table S1. Experimental and calculated (GIPAW, using "universal" referencing values) chemical shifts for campho[2,3-c]pyrazole

	Expt /ppm		Molecule	Calculated ^a /ppm							
	$^{13}\text{C}/^{15}\text{N}$	^1H		$^{13}\text{C}/^{15}\text{N}$				^1H			
				cryst ^b	mol ^c	mol ^d all opt	mol ^e opt H	cryst ^b	mol ^c	mol ^d all opt	mol ^e opt H
C1^f	122.2	7.4	<i>C</i>	124.4	117.3	118.1	117.6	7.8	7.3	7.4	7.4
H1	121.5	7.0	<i>A</i>	123.5	117.2	117.9	116.9	7.8	7.3	7.4	7.4
	120.5	6.6	<i>F</i>	122.6	117.0	117.5	116.5	7.3	7.3	7.4	7.4
	118.8	6.9	<i>E</i>	121.1	117.7	117.7	116.9	7.8	7.3	7.4	7.4
	118.8	6.9	<i>B</i>	121.0	117.3	117.8	116.9	7.8	7.4	7.4	7.4
	118.8	7.0	<i>D</i>	120.5	117.5	117.8	117.5	7.9	7.4	7.4	7.4
C3^f	48.2	2.5	<i>A</i>	50.7	50.4	50.6	50.6	2.8	2.6	2.6	2.6
H3	48.1	2.1	<i>C</i>	51.0	50.7	50.8	50.9	2.2	2.6	2.6	2.6
	47.4	2.6	<i>B</i>	50.1	50.4	50.7	50.5	2.8	2.6	2.6	2.6
	47.4	1.9	<i>D</i>	50.7	51.1	50.7	51.0	2.3	2.6	2.6	2.6
	46.9	2.7	<i>F</i>	49.7	50.3	50.6	50.4	3.0	2.4	2.5	2.5
	46.9	2.5	<i>E</i>	50.0	50.1	50.9	50.1	2.9	2.5	2.5	2.5
C11^f	23.4	0.2	<i>E</i>	22.9	16.9	17.2	17.1	0.2	0.1	0.2	0.1
H11	21.3	0.0	<i>B</i>	21.3	16.7	17.4	17.0	-0.1	0.4	0.3	0.4
a-c^g	21.3	0.0	<i>F</i>	20.5	17.6	17.4	17.6	0.0	0.3	0.3	0.3
	20.2	0.3	<i>A</i>	19.2	16.9	17.2	17.2	0.3	0.1	0.2	0.1
	20.2	0.3	<i>C</i>	18.6	15.9	16.7	16.4	0.6	0.2	0.2	0.2
	20.0	-0.2	<i>D</i>	19.5	17.0	17.4	17.1	-0.1	0.4	0.3	0.4
	C10^f	21.3	0.4	<i>B</i>	20.8	16.6	16.6	16.8	0.5	0.7	0.6
H10	20.9	0.3	<i>E</i>	20.1	16.2	16.4	16.4	0.7	0.6	0.6	0.6
a-c^g	20.9	-0.3	<i>D</i>	19.5	16.7	16.6	16.7	-0.2	0.7	0.6	0.6
	20.7	0.4	<i>F</i>	19.5	16.6	16.4	16.7	0.5	0.7	0.7	0.7
	18.9	0.3	<i>C</i>	18.1	16.0	16.4	16.3	0.6	0.6	0.6	0.6

	18.2	-0.2	<i>A</i>	16.8	16.0	16.3	16.5	-0.1	0.6	0.6	0.6
C8^f	13.0	1.2	<i>C</i>	12.0	6.5	6.6	6.6	1.4	0.7	0.7	0.7
H8	12.1	1.1	<i>F</i>	11.6	7.0	6.8	6.9	1.4	0.8	0.8	0.8
a-c^g	12.0	0.5	<i>A</i>	11.2	6.8	6.7	6.7	0.4	0.7	0.7	0.7
	11.8	0.6	<i>D</i>	11.1	6.7	6.6	6.7	0.7	0.8	0.8	0.8
	10.8	0.8	<i>B</i>	9.3	6.3	6.6	6.5	0.7	0.8	0.8	0.8
	10.1	0.2	<i>E</i>	8.5	6.4	6.7	6.6	0.0	0.7	0.7	0.7
C5^h	36.2	0.5	<i>D</i>	37.8	35.0	34.1	34.9	0.2	0.7	0.8	0.7
H5a,b		0.7						0.6	1.7	1.6	1.7
	35.3	0.7	<i>B</i>	36.6	33.7	34.1	33.8	0.6	0.7	0.8	0.6
		1.6						1.8	1.6	1.6	1.6
	34.9	1.3	<i>F</i>	34.6	34.1	34.2	34.1	0.8	0.8	0.8	0.8
		1.6						1.4	1.7	1.7	1.7
	33.6	1.2	<i>C</i>	36.3	34.3	34.5	34.5	1.2	0.8	0.8	0.8
		1.8						1.9	1.7	1.7	1.7
	33.2	1.4	<i>A</i>	33.8	33.9	34.1	34.1	1.3	0.9	0.9	0.9
		1.6						1.4	1.8	1.7	1.8
	32.2	0.9	<i>E</i>	32.5	33.4	34.3	33.6	0.5	0.9	0.8	0.9
		1.1						0.9	1.8	1.8	1.8
C4^h	29.6	0.9	<i>B</i>	30.3	28.0	27.5	28.2	1.0	0.6	0.7	0.6
H4a,b		1.5						2.2	2.1	2.1	2.1
	28.9	0.4	<i>D</i>	28.7	27.3	27.5	27.4	0.5	0.7	0.7	0.7
		1.9						1.7	2.0	2.1	2.0
	28.7	1.6	<i>C</i>	29.3	26.9	27.3	27.1	1.5	0.8	0.8	0.8
		2.4						2.4	2.1	2.1	2.1
	28.6	0.9	<i>E</i>	28.5	27.0	27.6	27.2	0.9	0.9	0.8	0.9
		2.3						2.2	2.1	2.2	2.2
	28.2	1.1	<i>A</i>	28.5	26.8	27.3	27.1	0.8	0.9	0.9	1.0
		1.5						1.8	2.2	2.2	2.2
	27.4	0.6	<i>F</i>	28.0	27.4	27.4	27.5	0.5	0.8	0.8	0.8
		0.7						0.9	2.1	2.1	2.1
C7ⁱ	166.9		<i>A</i>	171.6	170.7	170.7	171.2				

	166.0		B	170.6	169.9	170.7	170.4				
	165.5		E	169.8	170.1	170.9	170.4				
	165.3		F	169.5	169.6	170.6	170.2				
	165.2		D	169.4	169.3	170.7	169.7				
	165.0		C	169.1	169.9	170.6	170.1				
C2ⁱ	126.3		D	132.4	130.1	130.3	130.5				
	125.6		E	131.3	130.4	130.6	130.8				
	125.4		A	131.2	129.9	130.6	130.4				
	125.3		F	131.0	130.0	130.8	130.5				
	125.0		B	130.7	129.4	130.3	129.8				
	124.9		C	130.4	129.6	130.5	130.2				
C9ⁱ	62.9		E	69.1	65.4	65.4	65.9				
	62.4		F	68.4	65.6	65.5	65.5				
	62.2		A	68.3	65.8	65.7	65.9				
	61.5		C	67.4	64.8	64.8	64.7				
	61.0		D	66.7	64.0	65.0	63.9				
	60.8		B	66.4	63.7	65.0	63.8				
C6ⁱ	51.0		A	55.5	53.9	53.9	53.8				
	50.8		C	54.7	53.0	53.7	53.1				
	50.6		B	54.6	53.2	53.6	53.2				
	50.4		E	54.6	53.6	53.8	53.5				
	49.8		D	53.9	53.4	53.6	53.4				
	49.7		F	55.0	53.8	53.7	53.7				
NH^{j,k}	-177.2	13.6	D	-170.7	-193.9	-199.0	-198.5	15.2	10.0	9.3	9.4
			B	-170.7	-193.9	-199.0	-197.8	14.9	9.9	9.3	9.4
			C	-170.8	-194.6	-198.6	-199.3	15.0	9.9	9.3	9.4
			F	-171.1	-195.7	-199.4	-200.0	14.8	9.9	9.3	9.3
			A	-171.3	-196.2	-199.6	-200.7	15.6	9.9	9.3	9.3
			E	-172.9	-197.1	-199.4	-201.0	15.1	9.8	9.3	9.3
N^k	-107.4		E	-111.1	-91.1	-96.8	-92.1				
			A	-112.3	-91.8	-96.2	-92.3				
			B	-112.7	-91.6	-96.9	-92.0				

<i>D</i>	-114.3	-91.2	-96.9	-91.8
<i>F</i>	-114.6	-91.6	-96.1	-91.8
<i>C</i>	-115.7	-91.9	-97.0	-93.0

^a Universal reference determined by extrapolation of experimental vs calculated (full crystal structure) chemical shifts plot to pass through the origin (¹H slope 1.105, ¹³C slope 1.035): $\sigma_{\text{ref}}(^1\text{H}) = 30.7$ ppm, $\sigma_{\text{ref}}(^{13}\text{C}) = 172.2$ ppm, or such that the mean of experimental and calculated (¹⁵N) chemical shifts coincide: $\sigma_{\text{ref}}(^{15}\text{N}) = 160.2$ ppm.

^b Calculation for full crystal structure, geometrically optimized with all atoms allowed to relax.

^c Calculation for isolated molecule extracted from geometrically optimized full crystal, with no further geometry optimization.

^d Calculation for isolated molecule extracted from geometrically optimized full crystal, geometrically optimized with all atoms allowed to relax.

^e Calculation for isolated molecule extracted from geometrically optimized full crystal, geometrically optimized with only H atoms allowed to relax.

^f Experimental values taken from ¹H-¹³C MAS-*J*-HMQC spectrum ($\tau = 2.4$ ms).

^g Average calculated ¹H chemical shift over the three CH₃ protons.

^h Experimental values taken from ¹H-¹³C MAS-*J*-HMQC spectrum ($\tau = 0.9$ ms).

ⁱ Experimental values taken from ¹³C CP MAS spectrum (Figure S2).

^j Experimental value taken from ¹H DQ MAS spectrum (Figure 4) (only one resonance is resolved).

^k Experimental ¹⁵N values taken from ¹⁵N CP MAS spectrum in Figure 4a of Ref. ³⁹ (only one resonance is resolved for each chemically distinct nitrogen, with the linewidths (full width at half-maximum height) being approximately 8 ppm for both sites)

S3 H-H distances involving aromatic CH and NH protons**Table S2.** H-H distances (under 3 Å, as extracted from the geometry-optimised crystal structure) for the aromatic CH (H1) and NH protons in campho[2,3-c]pyrazole

H-H proximity		H-H distances /Å
CH(H1)-	CH ₃ (H8,H10,H11)	2.38 - 2.99
	CH ₂ (H4)	2.36 - 2.78
	CH(H3)	2.55 - 2.99
	NH	2.55 - 2.77
NH-	CH(H1)	2.55 - 2.77
	CH(H3)	2.61
	CH ₂ (H4,H5)	2.72 - 2.81
	NH	2.81 - 2.99
	CH ₃ (H8,H10)	2.74 - 2.94

S4 Calculated and experimental ^1H and ^{15}N chemical shifts for the N and NH sites**Table S3.** Experimental and calculated (GIPAW) ^1H chemical shifts for the NH proton in campho[2,3-c]pyrazole

Expt ^a /ppm	Molecule	Calculated ^b /ppm	
		^1H	^1H
		cryst ^c	mol ^d
13.6	<i>A</i>	14.1	8.4
	<i>D</i>	13.7	8.5
	<i>E</i>	13.6	8.3
	<i>C</i>	13.5	8.4
	<i>B</i>	13.4	8.4
	<i>F</i>	13.3	8.4

^a As determined from the ^1H DQ MAS spectrum in Figure 4 (only one resonance is resolved).

^b $\sigma_{\text{ref}}(^1\text{H}) = 29.2$ ppm.

^c Calculation for full crystal structure, geometry optimized with all atoms allowed to relax.

^d Calculation for isolated molecule extracted from geometry optimized full crystal.

Table S4. Experimental and calculated (GIPAW) ^{15}N chemical shifts for campho[2,3-c]pyrazole

	Expt ^a /ppm ^{15}N	Molecule	Calculated ^b /ppm ^{15}N	
			cryst ^c	mol ^d
NH	-177.2	<i>D</i>	-176.7	-199.9
		<i>B</i>	-176.7	-199.9
		<i>C</i>	-176.8	-200.6
		<i>F</i>	-177.1	-201.7
		<i>A</i>	-177.3	-202.2
		<i>E</i>	-178.9	-203.1
N	-107.4	<i>E</i>	-105.1	-85.1
		<i>A</i>	-106.3	-85.8
		<i>B</i>	-106.7	-85.6
		<i>D</i>	-108.3	-85.2
		<i>F</i>	-108.6	-85.6
		<i>C</i>	-109.7	-85.9

^a As determined from the ^{15}N CP MAS spectrum in Figure 4a of Ref. ³⁹ (only one resonance is resolved for each chemically distinct nitrogen, with the linewidths (full width at half maximum height) being approximately 8 ppm for both sites).

^b $\sigma_{\text{ref}}(^{15}\text{N}) = -154.2$ ppm (N), -166.2 ppm (NH)

^c Calculation for full crystal structure, geometry optimized with all atoms allowed to relax.

^d Calculation for isolated molecule extracted from geometry optimized full crystal.

S5 $\Delta\delta^{\text{cryst-mol}}$ values for the calculated ^1H , ^{13}C and ^{15}N chemical shifts

Table S5. Calculated crystal-to-molecule changes in ^1H , ^{13}C and ^{15}N chemical shifts (see Tables 1, 2, 3, S3, S4) for campho[2,3-*c*]pyrazole

	Molecule	$^{13}\text{C}/^{15}\text{N} \Delta\delta^{\text{cryst-mol}} / \text{ppm}$		$^1\text{H} \Delta\delta^{\text{cryst-mol}} / \text{ppm}$	
		geom. optim. (mol)		geom. optim. (mol)	
		no ^a	all atoms ^b	no ^a	all atoms ^b
C1, H1	<i>C</i>	7.1	6.3	0.5	0.4
	<i>A</i>	6.3	5.6	0.5	0.4
	<i>F</i>	5.6	5.1	0.0	-0.1
	<i>E</i>	3.4	3.4	0.5	0.4
	<i>B</i>	3.7	3.2	0.4	0.4
	<i>D</i>	3.0	2.7	0.5	0.5
C3, H3	<i>A</i>	0.3	0.1	0.2	0.2
	<i>C</i>	0.3	0.2	-0.4	-0.4
	<i>B</i>	-0.3	-0.6	0.2	0.2
	<i>D</i>	-0.4	0.0	-0.3	-0.3
	<i>F</i>	-0.6	-0.9	0.6	0.5
	<i>E</i>	-0.1	-0.9	0.4	0.4
C11, H11a-c ^c	<i>E</i>	6.0	5.7	0.1	0.0
	<i>B</i>	4.6	3.9	-0.5	-0.4
	<i>F</i>	2.9	3.1	-0.3	-0.3
	<i>A</i>	2.3	2.0	0.2	0.1
	<i>C</i>	2.7	1.9	0.4	0.4
	<i>D</i>	2.5	2.1	-0.5	-0.4
C10, H10a-c ^c	<i>B</i>	4.2	4.2	-0.2	-0.1
	<i>E</i>	3.9	3.7	0.1	0.1
	<i>D</i>	2.8	2.9	-0.9	-0.8
	<i>F</i>	2.9	3.1	-0.2	-0.2
	<i>C</i>	2.1	1.7	0.0	0.0
	<i>A</i>	0.8	0.5	-0.7	-0.7
C8, H8a-c ^c	<i>C</i>	5.5	5.4	0.7	0.7
	<i>F</i>	4.6	4.8	0.6	0.6

	<i>A</i>	4.4	4.5	-0.3	-0.3
	<i>D</i>	4.4	4.5	-0.1	-0.1
	<i>B</i>	3.0	2.7	-0.1	-0.1
	<i>E</i>	2.1	1.8	-0.7	-0.7
C5, H5a,b	<i>D</i>	2.8	3.7	-0.1	0.3
		0.0	0.0	-0.4	0.8
	<i>B</i>	2.9	2.5	0.7	0.7
		0.0	0.0	2.1	1.9
	<i>C</i>	2.0	1.8	1.8	1.4
		0.0	0.0	2.2	2.0
	<i>F</i>	0.5	0.4	1.0	1.0
		0.0	0.0	1.2	1.5
	<i>A</i>	-0.1	-0.3	1.9	1.5
		0.0	0.0	1.1	1.6
C4, H4a,b	<i>E</i>	-0.9	-1.8	0.3	0.8
		0.0	0.0	0.1	1.1
	<i>B</i>	2.3	2.8	1.5	1.0
		0.0	0.0	2.1	2.1
	<i>D</i>	1.4	1.2	0.4	0.6
		0.0	0.0	1.2	1.5
	<i>C</i>	2.4	2.0	2.3	1.6
		0.0	0.0	2.5	2.2
	<i>E</i>	1.5	0.9	1.0	1.1
		0.0	0.0	2.1	1.9
C7	<i>A</i>	1.7	1.2	0.8	0.9
		0.0	0.0	1.2	1.6
	<i>F</i>	0.6	0.6	0.3	0.7
		0.0	0.0	-0.5	0.7
	<i>A</i>	0.9	0.9		
	<i>B</i>	0.7	-0.1		
	<i>E</i>	-0.3	-1.1		
	<i>F</i>	-0.1	-1.1		

	<i>D</i>	0.1	-1.3		
	<i>C</i>	-0.8	-1.5		
C2	<i>D</i>	2.3	2.1		
	<i>E</i>	0.9	0.7		
	<i>A</i>	1.3	0.6		
	<i>F</i>	1.0	0.2		
	<i>B</i>	1.3	0.4		
	<i>C</i>	0.8	-0.1		
C9	<i>E</i>	3.7	3.7		
	<i>F</i>	2.8	2.9		
	<i>A</i>	2.5	2.6		
	<i>C</i>	2.6	2.6		
	<i>D</i>	2.7	1.7		
	<i>B</i>	2.7	1.4		
C6	<i>A</i>	1.6	1.6		
	<i>C</i>	1.7	1.0		
	<i>B</i>	1.4	1.0		
	<i>E</i>	1.0	0.8		
	<i>D</i>	0.5	0.3		
	<i>F</i>	0.0	0.1		
NH	<i>D</i>	23.2	28.3	5.2	5.9
	<i>B</i>	23.2	28.3	5.0	5.6
	<i>C</i>	23.8	27.8	5.1	5.7
	<i>F</i>	24.6	28.3	4.9	5.5
	<i>A</i>	24.9	28.3	5.7	6.3
	<i>E</i>	24.2	26.5	5.3	5.8
N	<i>E</i>	-20.0	-14.3		
	<i>A</i>	-20.5	-16.1		
	<i>B</i>	-21.1	-15.8		
	<i>D</i>	-23.1	-17.4		
	<i>F</i>	-23.0	-18.5		
	<i>C</i>	-23.8	-18.7		

^a Difference between calculation for full geometrically optimized crystal structure and isolated molecule extracted from geometrically optimized full crystal, with no further geometry optimization.

^b Difference between calculation for full geometrically optimized crystal structure and isolated molecule extracted from geometrically optimized full crystal, geometrically optimized with all atoms allowed to relax.

^c Average calculated ¹H chemical shift over the three CH₃ protons.