Supplementary Material

Reinforced cyclam derivatives functionalized on the bridging unit.

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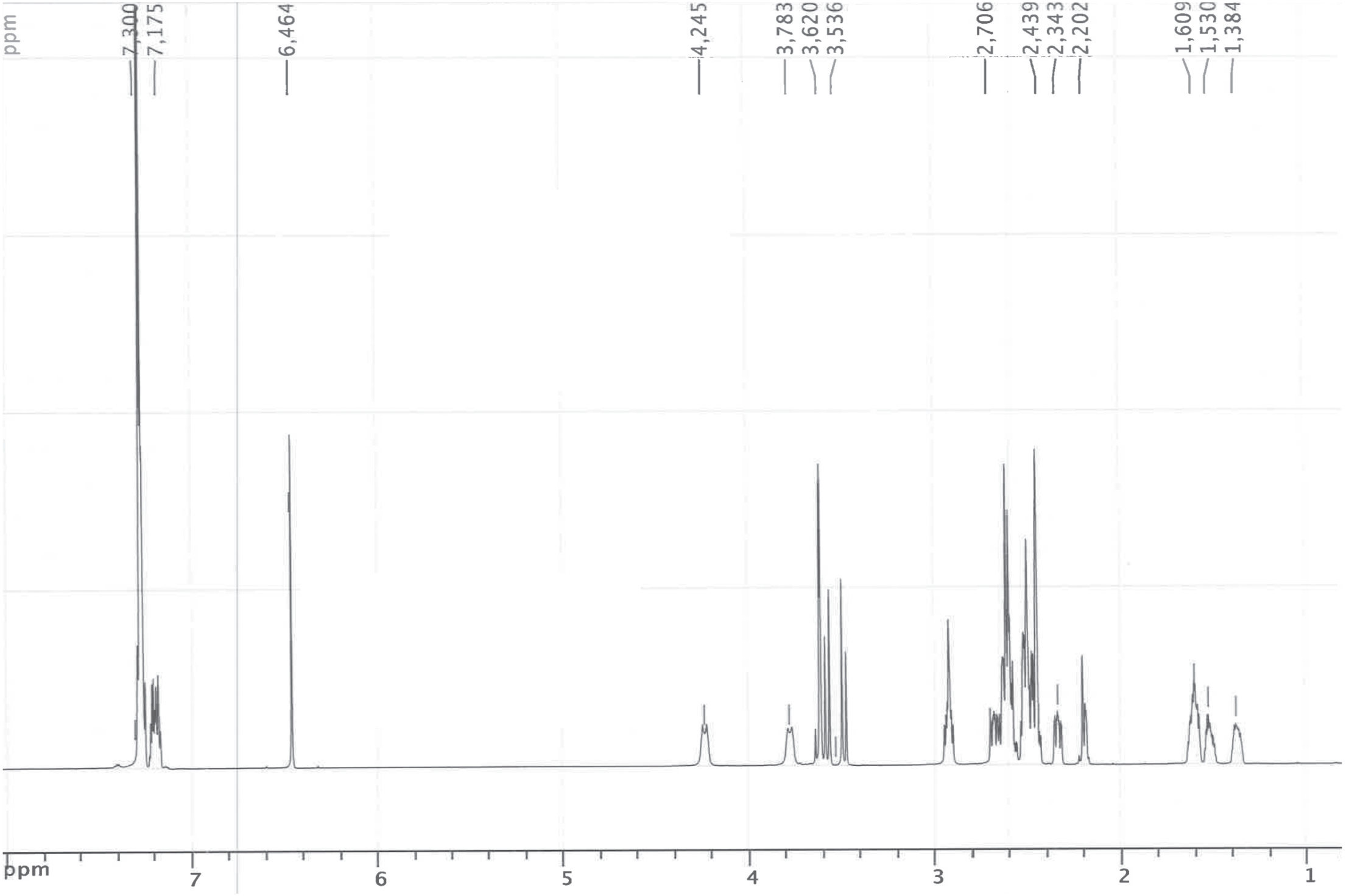

Figure 1 : ^{1}H NMR of compound 3 (DMSO-d6, 500 MHz, 373K)

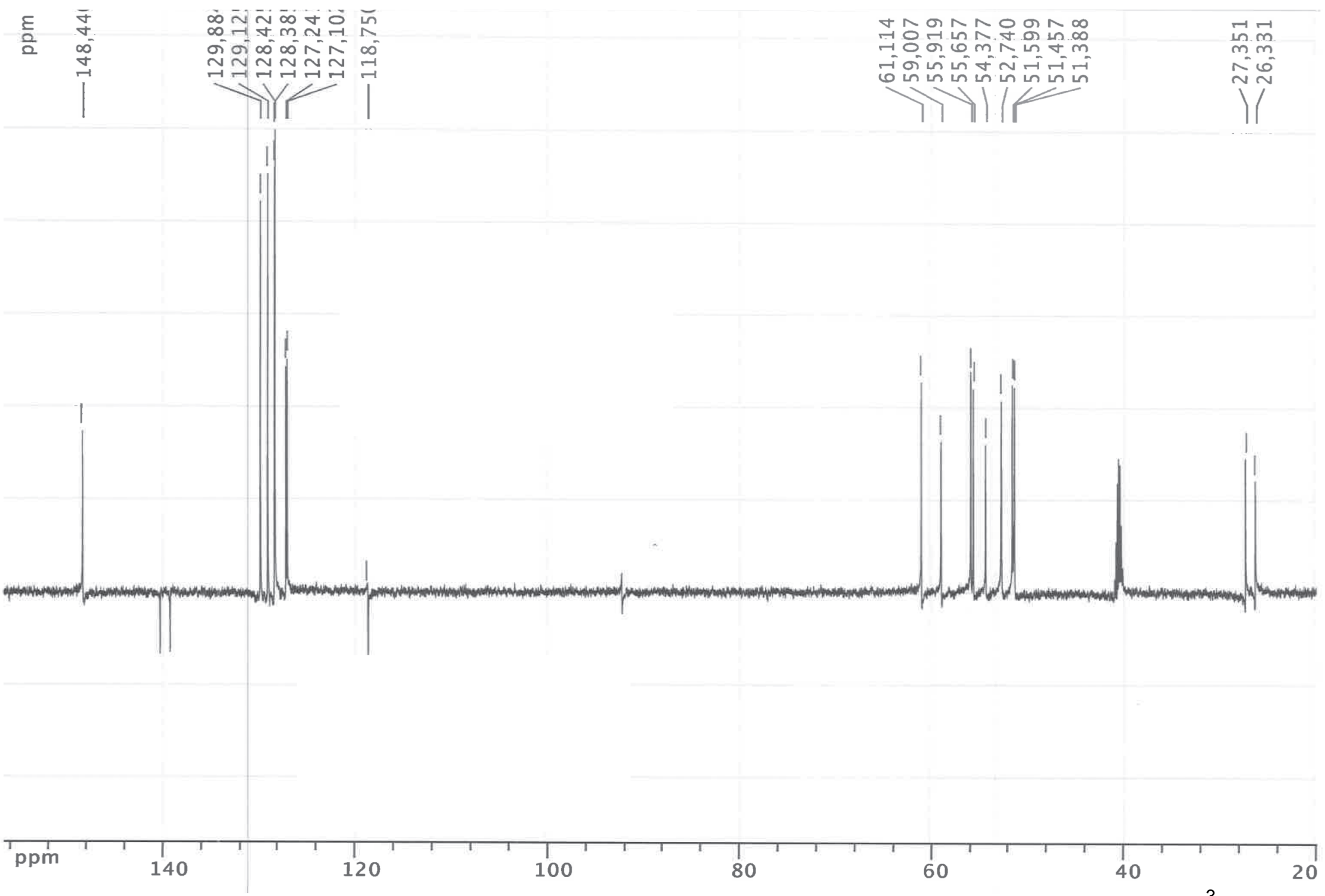

Figure 2 : ^{13}C NMR of compound 3 (DMSO-d6, 125 MHz, 373K)

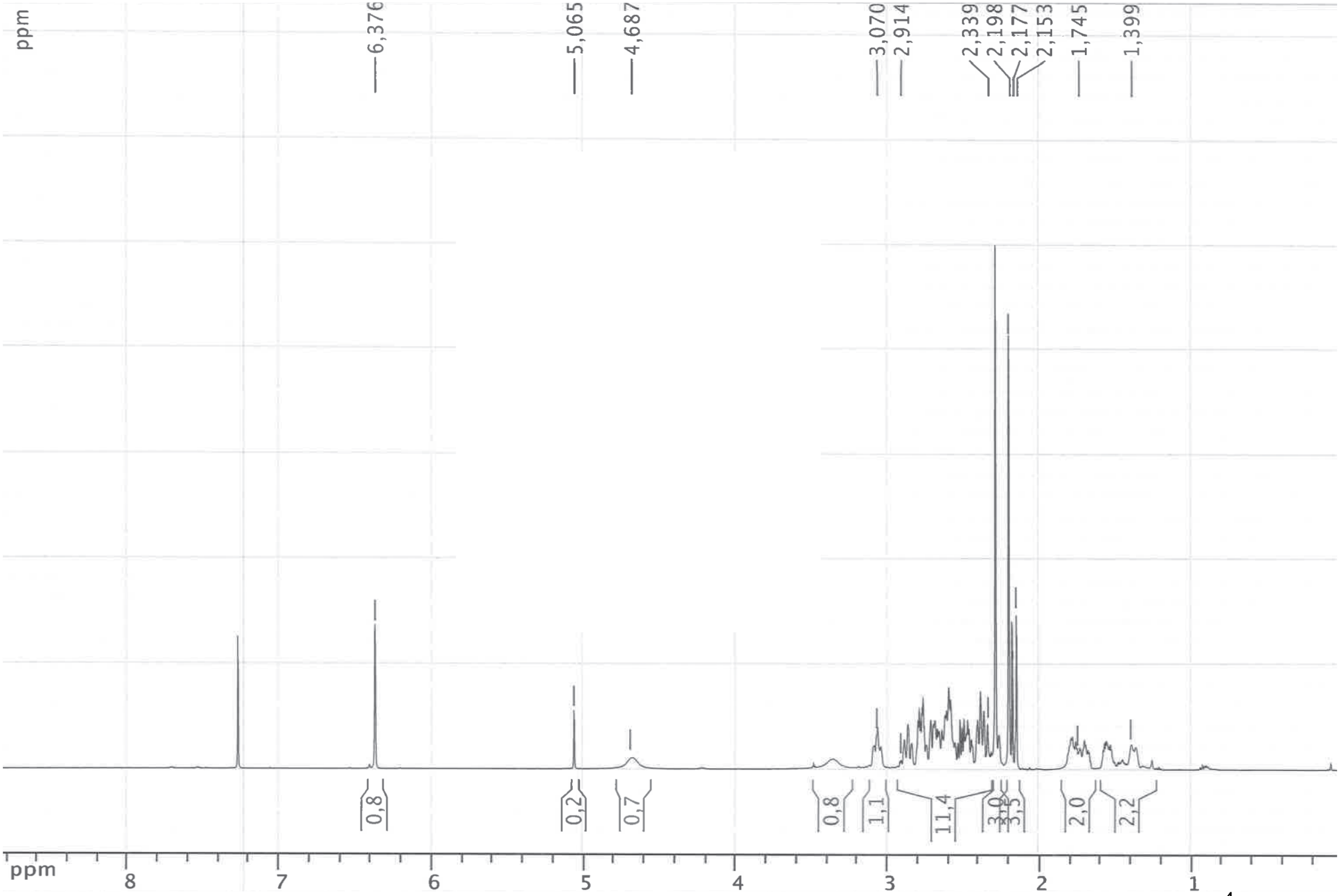

Figure 3 : ^{1}H NMR of compound 4 ($CDCl_3$, 500 MHz, 300K)

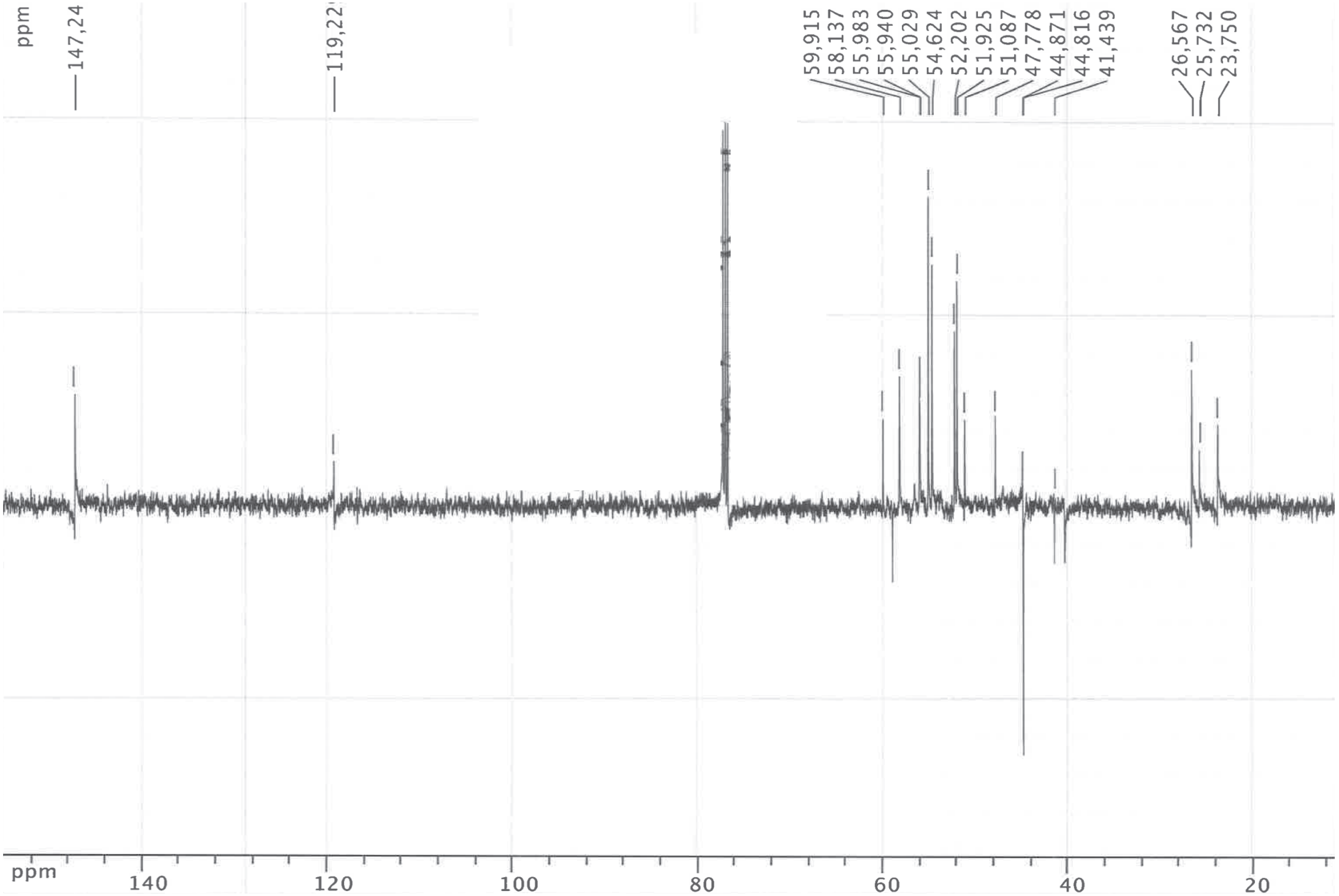

Figure 4 : ^{13}C NMR of compound 4 ($CDCl_3$, 175 MHz, 300K)

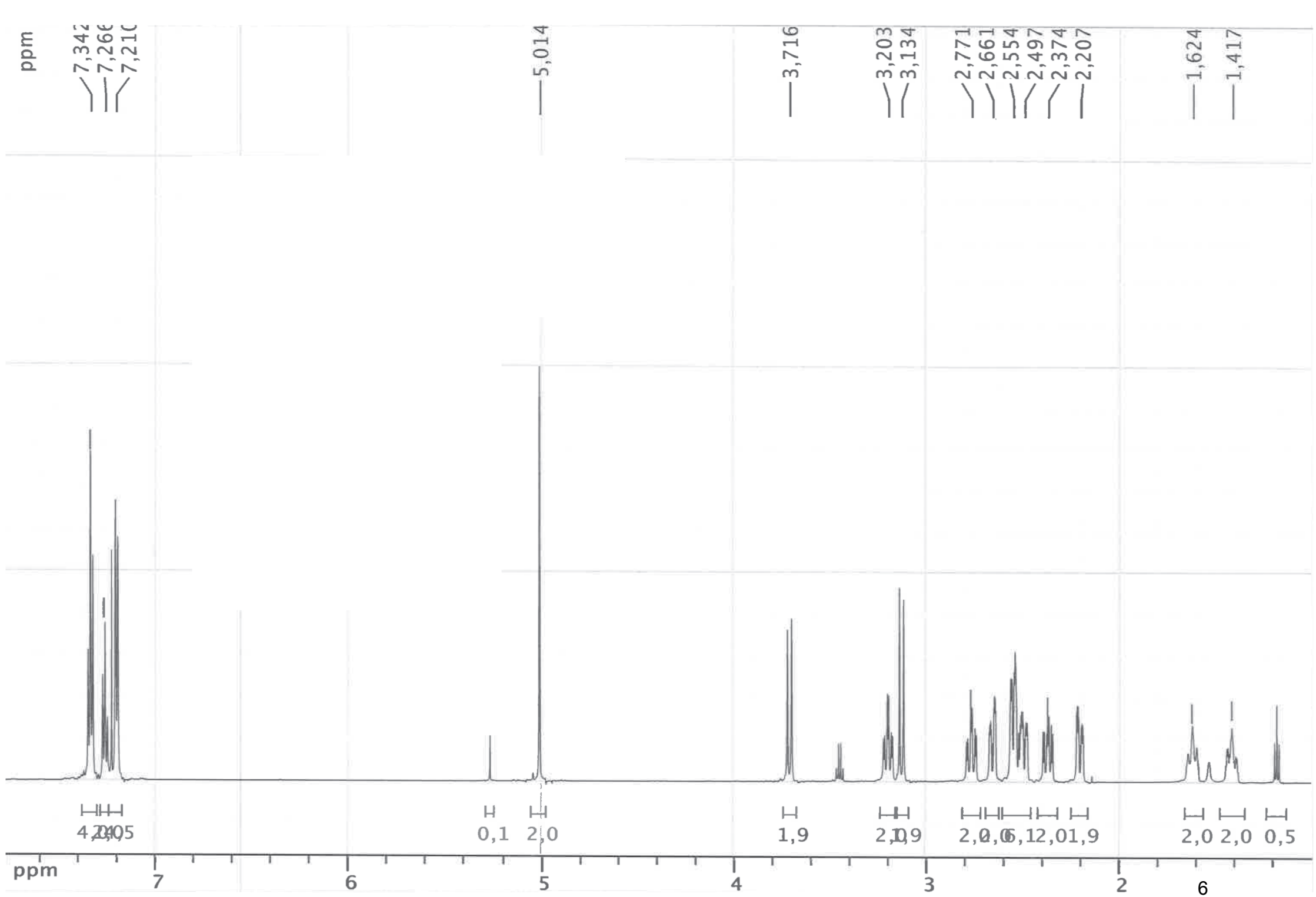

Figure 5 : ^{1}H NMR of compound 5b ($CDCl_3$, 600 MHz, 300K)

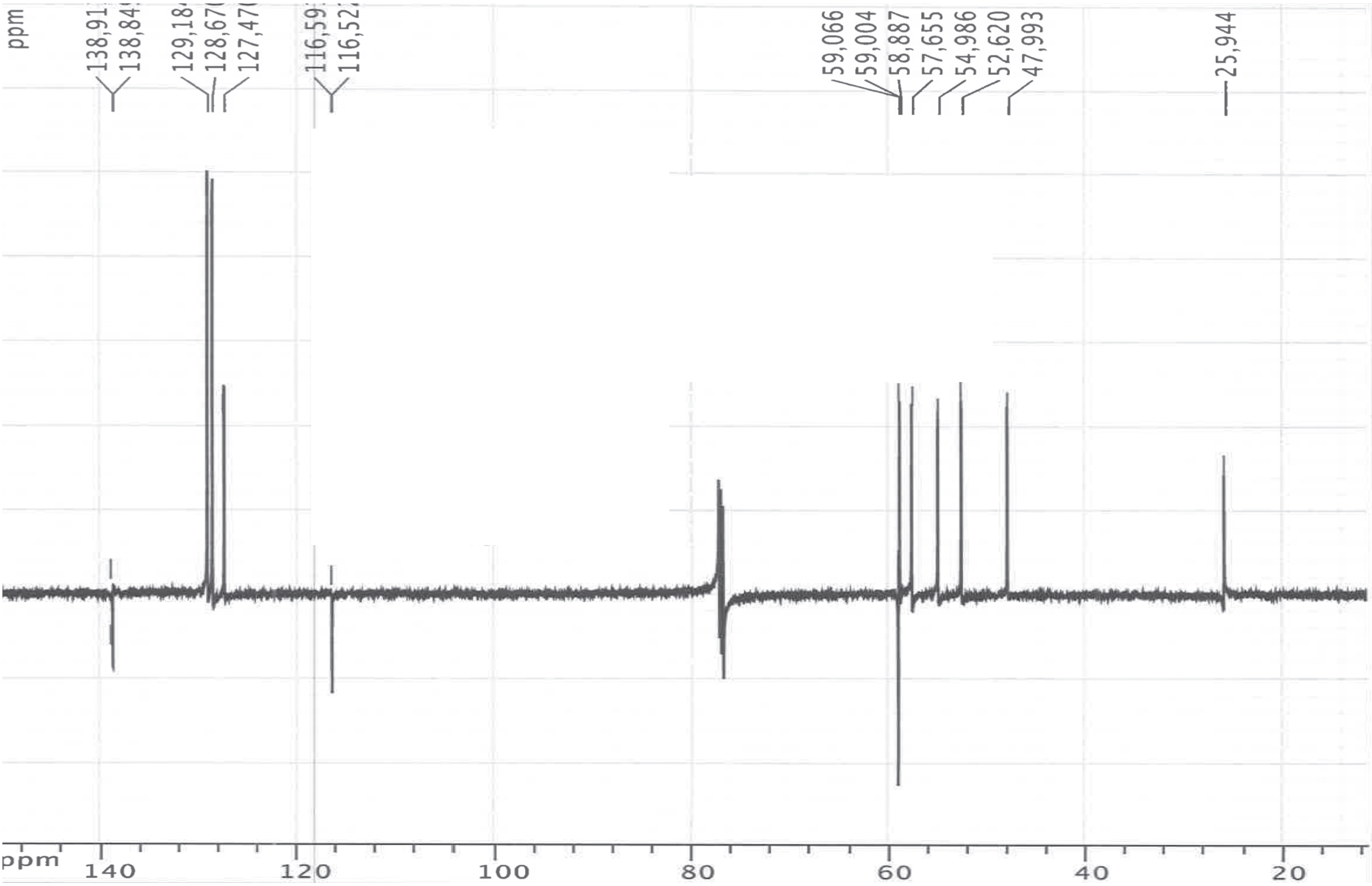

Figure 6 : ^{13}C NMR of compound 5b ($CDCl_3$, 125 MHz, 300K)

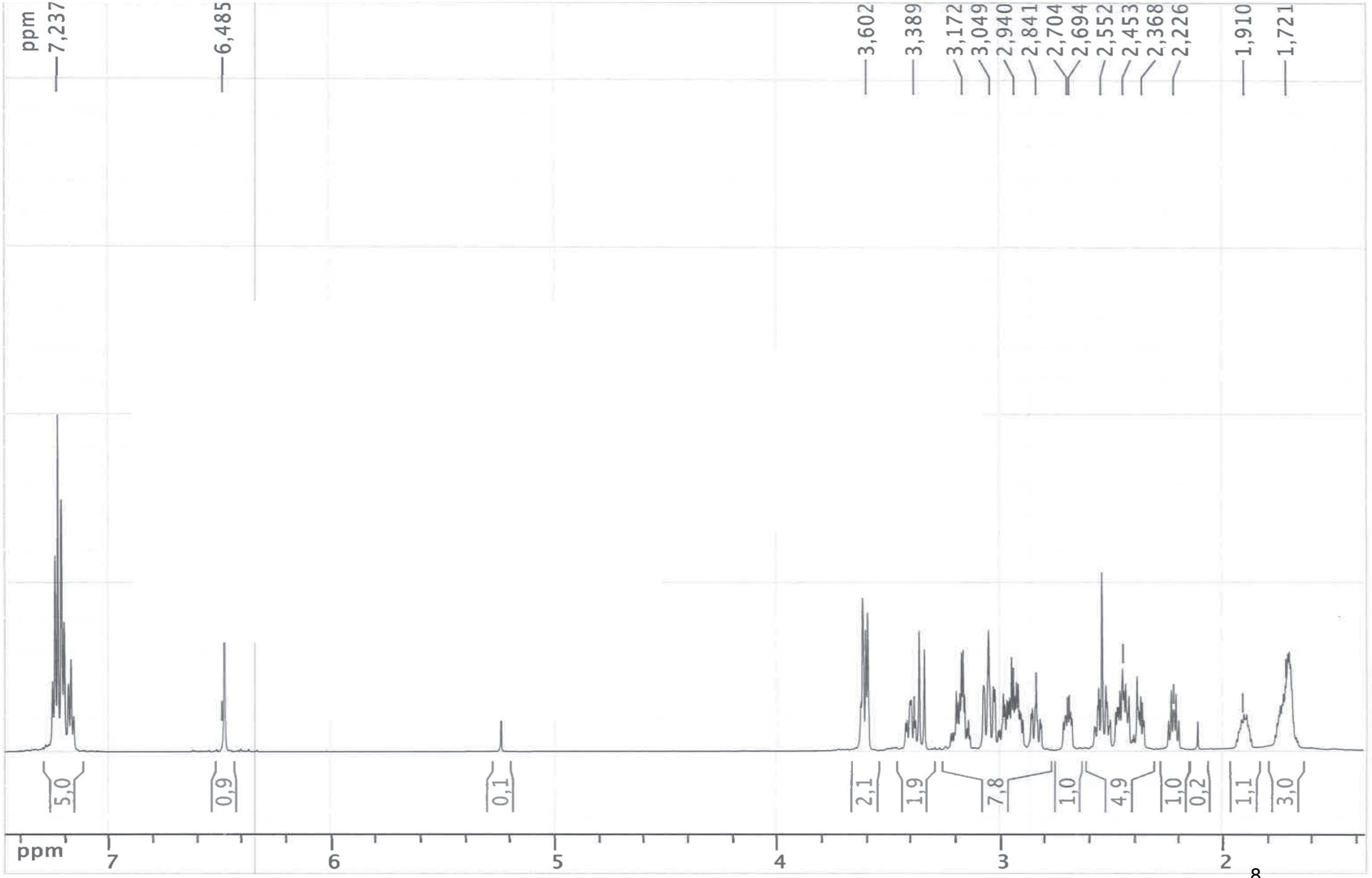

Figure 7 : ^{1}H NMR of compound 7 ($CDCl_3$, 600 MHz, 300K)

Display Report

Analysis Info

Analysis Name	08ns_575_cristaux.d	Acquisition Date	22/10/2008 15:04:24
Method	tune_wide_200608.m	Operator	Jean-Michel Barbe
Sample Name		Instrument	micrOTOF-Q 56
Comment	MeOH		

Acquisition Parameter

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Scan End	3000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Source

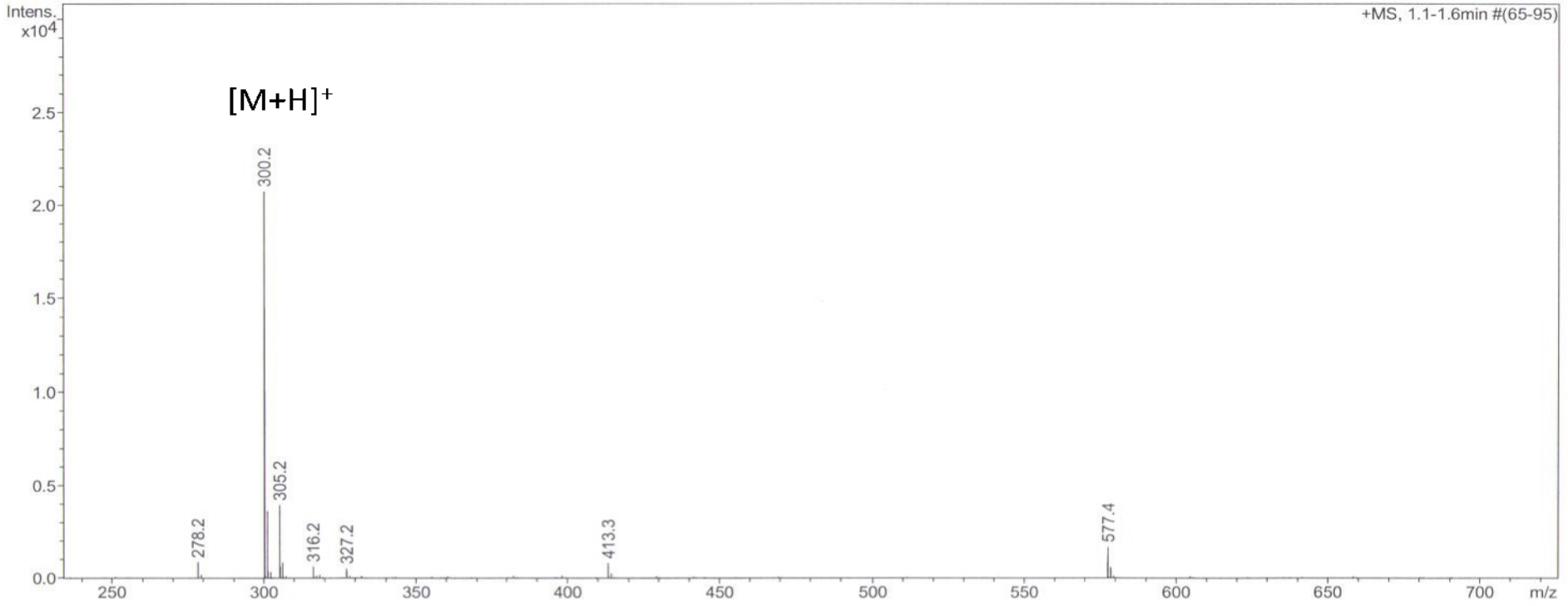

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Figure 8 : ESI-MS of compound 4

Display Report

Analysis Info

Analysis Name	08ns_619b.d	Acquisition Date	24/11/2008 16:59:31
Method	tune_wide_neg.m	Operator	Marie-José Penouilh
Sample Name		Instrument	micrOTOF-Q 56
Comment	DCM/MeOH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

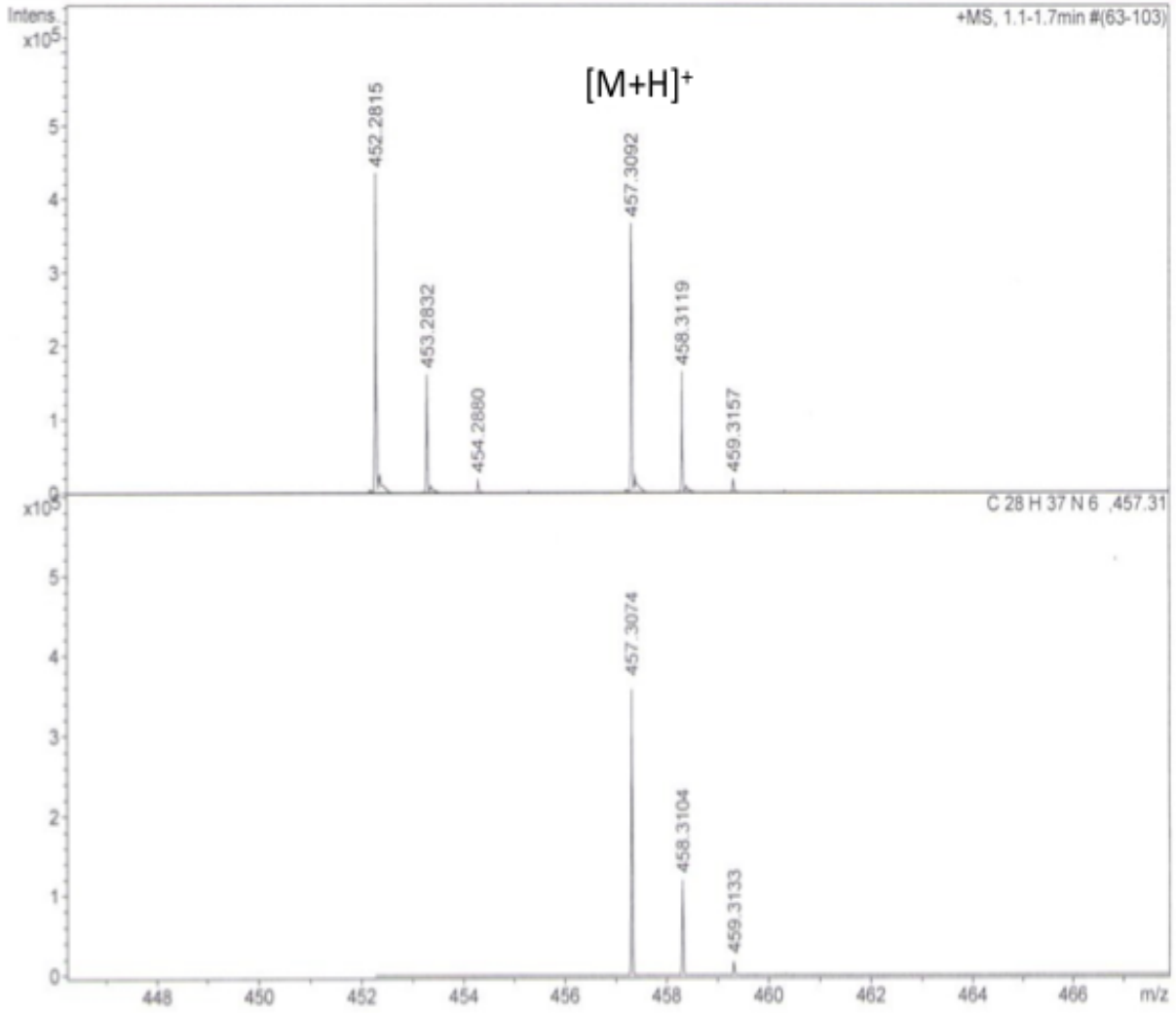

Figure 9 : ESI-MS of compound 5a

Display Report

Analysis Info

Analysis Name	09ns_dia_2.d	Acquisition Date	12/10/2009 10:48:03
Method	tune_wide.m	Operator	Marie-José Penouilh
Sample Name		Instrument	micrOTOF-Q 56
Comment	dcm/meoh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
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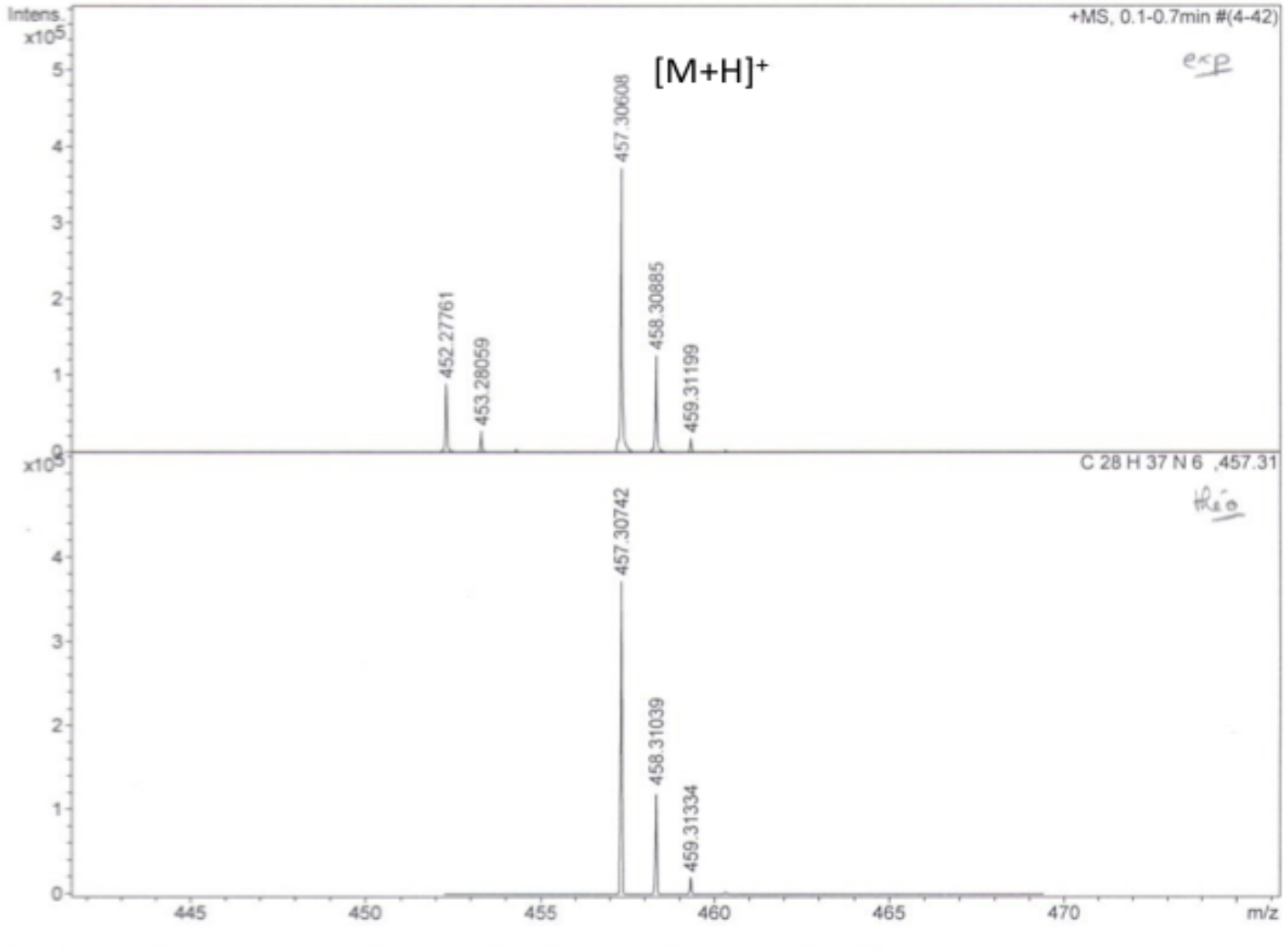
Scan End	3000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 28 H 37 N 6	0.006	457.30742	2.92	3.03	1.34	13.50	ok	even

Figure 10 : ESI-MS of compound 5b

Display Report

Analysis Info

Analysis Name	08ns_639.d	Acquisition Date	12/12/2008 15:25:24
Method	tune_wide.m	Operator	Marie-José Penouilh
Sample Name		Instrument	micrOTOF-Q 56
Comment	DCM/MeOH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
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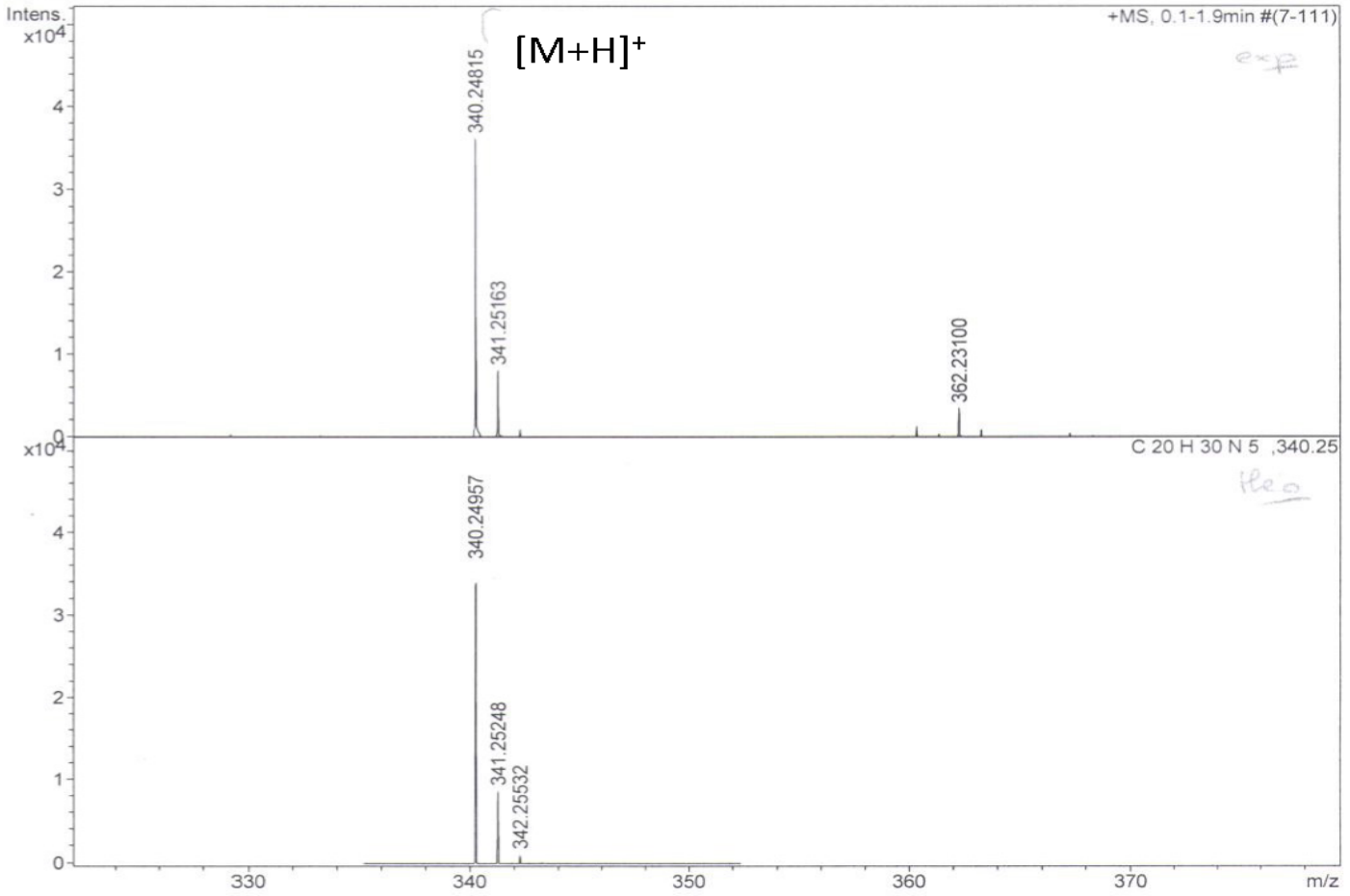
Scan End	3000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

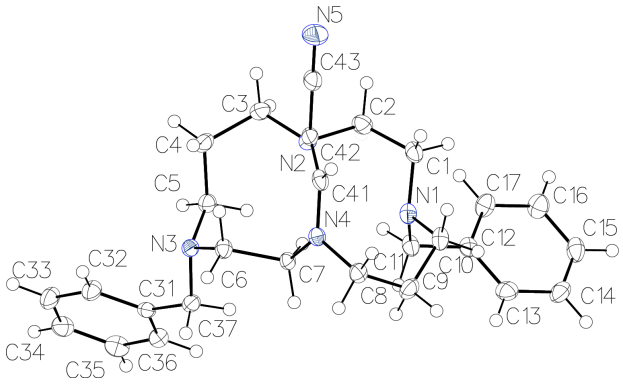


Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 20 H 30 N 5	0.018	340.24957	4.19	3.85	1.42	8.50	ok	even

Figure 11 : ESI-MS of compound 7

X-ray Data

Summary



Crystal Data: $C_{27}H_{35}N_5$, $M_r =$ 429.60, triclinic, $P\bar{1}$ (No. 2), a = 8.8082(4) Å, b = 11.1431(5) Å, c = 13.3105(7) Å, $\alpha =$ 75.168(3)°, $\beta =$ 85.508(2)°, $\gamma =$ 72.535(2)°, $V =$ 1204.68(10) Å^3, $T =$ 115(2) K, $Z =$ 2, $Z' =$ 1, μ(MoK$_\alpha$) = 0.071, 9711 reflections measured, 5483 unique (Rint = 0.0477) which were used in all calculations. The final $wR2$ was 0.1428 (all data) and R_1 was 0.0726 ($I > 2\sigma(I)$).

Experimental: Single clear light colourless Prism-shaped crystals of (**Compound 3**) were recrystallised from ether by slow evaporation. A suitable crystal (0.22×0.20×0.15) was selected and mounted on a MITIGEN holder oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at $T =$ 115(2) K during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the ShelXT (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of ShelXL (Sheldrick, 2008) using Least Squares minimisation.

Compound	**Compound 3**
Formula	$C_{27}H_{35}N_5$
$D_{calc.}/gcm^{-3}$	1.184
mu/mm^{-1}	0.071
Formula Weight	429.60
Colour	clear light colourless
Shape	Prism
Max Size/mm	0.22
Mid Size/mm	0.20
Min Size/mm	0.15
T/K	115(2)
Crystal System	triclinic
Space Group	$P\bar{1}$
a/Å	8.8082(4)
b/Å	11.1431(5)
c/Å	13.3105(7)
α/°	75.168(3)
β/°	85.508(2)
γ/°	72.535(2)
V/Å^3	1204.68(10)
Z	2
Z'	1
Θ_{min}/°	1.976
Θ_{max}/°	27.626
Measured Refl.	9711
Independent Refl.	5483
Reflections Used	4140
Rint	0.0477
Parameters	289
Restraints	0
Largest Peak	0.292
Deepest Hole	-0.302
GooF	1.119
$wR2$ (all data)	0.1428
$wR2$	0.1282
R_1 (all data)	0.1007
R_1	0.0726

Data Quality	d min 0.77	I/σ 11.5	Rint 4.77%	complete 98%
Refinement Quality	Shift 0.000	Max Peak 0.3	Min Peak -0.3	GooF 1.119

Extended Experimental

Experimental Extended: A clear light colourless Prism-shaped crystal with dimensions 0.22×0.20×0.15 was mounted on a MITIGEN holder oil. Data were collected using a Nonius Kappa Apex II diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 115(2)$ K.

Data were measured using ϕ and ω scans using MoK$_\alpha$ radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Amjjcar &Lml§sq @T* /775+0...', The actually achieved resolution was $\Theta = 27.626$.

Cell parameters were retrieved using the SCALEPACK (Otwinowski and Minor, 1997) software and refined using DENZO (Otwinowski and Minor, 1997) on 4964 reflections, 51% of the observed reflections. Data reduction was performed using the DENZO (Otwinowski and Minor, 1997) software which corrects for Lorentz polarisation. The final completeness is 99.10% out to 27.626 in Θ. No absoprtion correction was performed. The absorption coefficient (μ) of this material is 0.071.

The structure was solved in the space group $P\bar{1}$ (# 2) by Direct Methods using the ShelXT (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2014/7 of ShelXL (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Table 2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **Compound 3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
C1	6018(3)	363(2)	3035.5(19)	23.4(5)
C2	6655(3)	320(2)	1946(2)	24.5(5)
C3	6881(3)	1463(3)	156(2)	27.3(6)
C4	5935(3)	2501(3)	−744.0(19)	24.8(5)
C5	4190(3)	2491(2)	−746.3(19)	20.8(5)
C6	3188(3)	4258(2)	138.1(18)	19.6(5)
C7	2914(3)	3453(2)	1227.8(17)	16.7(4)
C8	2879(3)	4044(2)	2920.2(18)	21.7(5)
C9	2405(3)	2877(2)	3610.2(19)	25.6(5)
C10	3777(3)	1633(2)	3921.2(18)	23.6(5)
C11	3280(3)	294(2)	2833.9(19)	22.8(5)
C12	3234(3)	−916(2)	3671.6(18)	20.6(5)
C13	2095(3)	−848(3)	4462(2)	26.0(5)
C14	2070(3)	−1946(3)	5243(2)	27.6(6)
C15	3174(3)	−3119(3)	5234(2)	28.3(6)
C16	4309(3)	−3207(3)	4452(2)	29.5(6)
C17	4329(3)	−2110(2)	3676(2)	25.7(5)
C31	1399(3)	3685(3)	−806.9(18)	22.1(5)
C32	1035(3)	3497(2)	−1838.9(18)	19.4(5)
C33	1529(3)	4185(3)	−2763.6(19)	25.6(6)
C34	1150(3)	4043(3)	−3712(2)	29.6(6)
C35	247(3)	3222(3)	−3745(2)	27.4(6)
C36	−261(3)	2546(2)	−2826(2)	27.2(6)
C37	139(3)	2675(2)	−1881(2)	24.3(5)

C41	5371(3)	3435(2)	2009.9(18)	20.3(5)
C42	6487(3)	2590(2)	1560.2(18)	20.1(5)
C43	8116(3)	2539(2)	1665(2)	26.2(6)
N1	4310(2)	1011.5(19)	3054.4(15)	19.9(4)
N2	6182(2)	1588.8(19)	1178.7(15)	19.5(4)
N3	3025(2)	3750.4(19)	−747.2(15)	18.3(4)
N4	3764(2)	3760.7(18)	1990.2(15)	18.4(4)
N5	9440(3)	2458(3)	1745(2)	40.7(6)

Table 3: Anisotropic Displacement Parameters ($\times 10^4$) **Compound 3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*{}^2 \times U_{11} + ... + 2hka* \times b* \times U_{12}]$

Atom	$\mathbf{U}_{11}$	$\mathbf{U}_{22}$	$\mathbf{U}_{33}$	$\mathbf{U}_{23}$	$\mathbf{U}_{13}$	$\mathbf{U}_{12}$
C1	25.2(13)	20.1(12)	22.6(13)	1.4(9)	−4.9(10)	−7.8(10)
C2	22.3(13)	20.2(12)	27.7(14)	−4.2(10)	−1(1)	−2.6(10)
C3	18.8(13)	36.8(15)	23.0(13)	−8.9(11)	2.8(10)	−2.4(11)
C4	20.9(13)	37.7(15)	17.8(12)	−8.2(10)	4.3(10)	−11.3(11)
C5	20.5(12)	25.1(13)	17.3(12)	−5.4(9)	0.3(9)	−7.1(10)
C6	22.4(12)	20.5(12)	17.4(12)	−3.1(9)	−1.2(9)	−9.3(10)
C7	17.7(11)	19.7(11)	13.5(11)	−4.0(8)	−1.7(9)	−6.1(9)
C8	24.4(13)	22.6(12)	16.5(12)	−7.4(9)	0.7(10)	−2.6(10)
C9	25.3(13)	33.0(14)	19.3(12)	−8.5(10)	6.1(10)	−9.5(11)
C10	30.9(14)	24.5(13)	16.4(12)	−2.4(9)	−1.6(10)	−11.1(10)
C11	26.5(13)	21.4(12)	19.1(12)	0.4(9)	−4.1(10)	−8.6(10)
C12	22.0(12)	22.4(12)	19.9(12)	−3.6(9)	−3.3(9)	−10.6(10)
C13	20.9(13)	27.4(14)	31.2(14)	−6.2(11)	−0.5(11)	−9.7(10)
C14	25.3(13)	37.9(15)	23.9(14)	−6.9(11)	5.1(11)	−17.3(12)
C15	35.3(15)	28.9(14)	22.9(13)	2.8(10)	−4.9(11)	−19.0(12)
C16	36.2(15)	23.3(13)	29.2(14)	−6.0(11)	2.9(12)	−9.9(11)
C17	32.7(14)	23.4(13)	23.1(13)	−6.6(10)	4.4(11)	−11.6(11)
C31	17.8(12)	32.2(14)	16.9(12)	−5.5(10)	1.3(9)	−8.6(10)
C32	13.8(11)	24.0(12)	18.3(12)	−5.8(9)	−0.9(9)	−1.7(9)
C33	23.3(13)	37.5(15)	20.7(13)	−5.5(11)	0.3(10)	−17.0(11)
C34	28.3(14)	46.7(17)	18.1(13)	−8.4(11)	2.3(10)	−17.1(12)
C35	23.5(13)	38.6(15)	22.8(13)	−14.9(11)	−3(1)	−6.1(11)
C36	25.7(14)	26.3(13)	33.7(15)	−11.9(11)	−3.7(11)	−8.8(11)
C37	21.2(13)	26.0(13)	23.8(13)	−2.5(10)	0.7(10)	−7.4(10)
C41	24.4(13)	20.4(12)	17.5(12)	0.0(9)	−6.3(9)	−10.9(10)
C42	18.4(12)	23.7(12)	17.8(12)	0.8(9)	−2.7(9)	−9.9(9)
C43	24.0(13)	27.8(14)	24.7(13)	2.8(10)	−3.3(10)	−11.3(11)
N1	23.7(11)	20.7(10)	16.5(10)	−2.7(8)	−1.4(8)	−9.3(8)
N2	17.9(10)	21.3(10)	18.5(10)	−4.5(8)	1.4(8)	−5.3(8)
N3	17(1)	24.1(10)	15(1)	−5.5(8)	−0.6(8)	−7.2(8)
N4	19.4(10)	21(1)	15.2(10)	−4.9(8)	−1.7(8)	−5.8(8)
N5	24.2(13)	50.3(16)	46.0(16)	0.5(12)	−5.3(11)	−17.6(11)

Table 4: Bond Lengths in Å for **Compound 3**.

Atoms	Length/Å	Atoms	Length/Å
C1 –C2	1.520(3)	C13–C14	1.393(4)
C1 –N1	1.462(3)	C14–C15	1.377(4)
C2 –N2	1.480(3)	C15–C16	1.387(4)
C3 –C4	1.528(3)	C16–C17	1.388(3)
C3 –N2	1.473(3)	C31–C32	1.514(3)
C4 –C5	1.541(3)	C31–N3	1.465(3)
C5 –N3	1.468(3)	C32–C33	1.388(3)
C6 –C7	1.541(3)	C32–C37	1.389(3)
C6 –N3	1.465(3)	C33–C34	1.389(3)
C7 –N4	1.469(3)	C34–C35	1.391(4)
C8 –C9	1.538(3)	C35–C36	1.381(4)
C8 –N4	1.463(3)	C36–C37	1.386(3)
C9 –C10	1.527(4)	C41–C42	1.361(3)
C10–N1	1.470(3)	C41–N4	1.353(3)
C11–C12	1.523(3)	C42–C43	1.436(3)
C11–N1	1.465(3)	C42–N2	1.437(3)
C12–C13	1.396(3)	C43–N5	1.154(3)
C12–C17	1.388(3)	–	

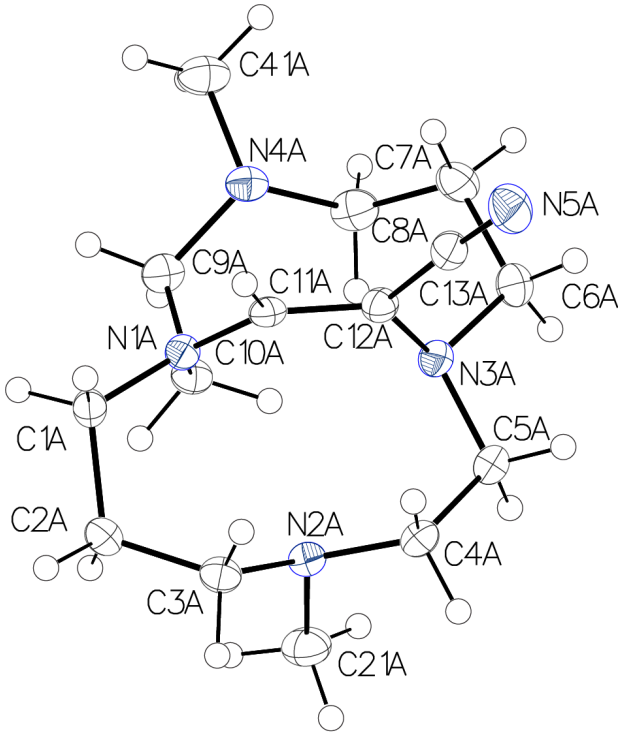
Table 5: Bond Angles in ° for **Compound 3**.

–Atoms–	Angle/°	–Atoms–	Angle/°
N1 –C1 –C2	113.0(2)	C32–C33–C34	120.6(2)
N2 –C2 –C1	114.0(2)	C33–C34–C35	120.2(2)
N2 –C3 –C4	112.9(2)	C36–C35–C34	119.4(2)
C3 –C4 –C5	112.2(2)	C35–C36–C37	120.3(2)
N3 –C5 –C4	113.89(19)	C36–C37–C32	120.8(2)
N3 –C6 –C7	116.88(18)	N4 –C41–C42	130.5(2)
N4 –C7 –C6	108.48(17)	C41–C42–C43	116.6(2)
N4 –C8 –C9	113.06(19)	C41–C42–N2	124.4(2)
C10–C9 –C8	114.9(2)	C43–C42–N2	117.8(2)
N1 –C10–C9	112.12(19)	N5 –C43–C42	177.8(3)
N1 –C11–C12	115.46(19)	C1 –N1 –C10	114.83(19)
C13–C12–C11	120.6(2)	C1 –N1 –C11	115.35(19)
C17–C12–C11	121.0(2)	C11–N1 –C10	114.78(19)
C17–C12–C13	118.3(2)	C3 –N2 –C2	110.25(19)
C14–C13–C12	120.9(2)	C42–N2 –C2	111.35(18)
C15–C14–C13	119.8(2)	C42–N2 –C3	115.13(19)
C14–C15–C16	120.1(2)	C6 –N3 –C5	113.57(18)
C15–C16–C17	119.9(3)	C6 –N3 –C31	110.54(18)
C12–C17–C16	121.0(2)	C31–N3 –C5	110.82(18)
N3 –C31–C32	113.02(19)	C8 –N4 –C7	116.92(19)
C33–C32–C31	120.6(2)	C41–N4 –C7	121.84(19)
C33–C32–C37	118.7(2)	C41–N4 –C8	118.48(19)
C37–C32–C31	120.6(2)	– –	

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Compound 3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
H1A	6235	−535	3472	28
H1B	6592	821	3343	28
H2A	7832	−2	1976	29
H2B	6272	−308	1705	29
H3A	6935	596	67	33
H3B	7983	1523	132	33
H4A	6444	2354	−1409	30
H4B	5962	3365	−692	30
H5A	4011	2218	−1368	25
H5B	4004	1839	−126	25
H6A	2427	5137	42	24
H6B	4273	4354	119	24
H7A	1762	3665	1391	20
H7B	3317	2516	1251	20
H8A	1905	4775	2706	26
H8B	3540	4323	3332	26
H9A	1898	3115	4250	31
H9B	1599	2699	3237	31
H10A	4681	1839	4165	28
H10B	3433	1019	4505	28
H11A	3638	36	2176	27
H11B	2183	885	2723	27
H13	1328	−42	4468	31
H14	1293	−1887	5779	33
H15	3158	−3869	5766	34
H16	5071	−4016	4448	35
H17	5103	−2177	3139	31
H31A	640	4497	−693	27
H31B	1239	2958	−243	27
H33	2132	4758	−2748	31
H34	1508	4509	−4340	36
H35	−17	3126	−4393	33
H36	−887	1990	−2843	33
H37	−204	2196	−1253	29
H41	5789	3867	2401	24

Summary



Crystal Data: $C_{15}H_{27}N_5$, $M_r =$ 277.41, triclinic, $P\bar{1}$ (No. 2), a = 9.8695(3) Å, b = 12.1158(3) Å, c = 14.4185(5) Å, $\alpha =$ 78.653(2)°, $\beta =$ 80.2470(10)°, $\gamma =$ 73.002(2)°, $V =$ 1605.02(9) Å^3, $T =$ 115(2) K, $Z =$ 4, $Z' =$ 2, μ(MoK$_\alpha$) = 0.072, 13714 reflections measured, 7301 unique (Rint = 0.0339) which were used in all calculations. The final $wR2$ was 0.1153 (all data) and R_1 was 0.0558 ($I > 2\sigma(I)$).

Experimental: Single clear light colourless Prism-shaped crystals of (**Compound 4**) were recrystallised from ether by slow evaporation. A suitable crystal (0.17×0.15×0.08) was selected and mounted on a glass fibre with grease on a Nonius Kappa CCD diffractometer. The crystal was kept at $T =$ 115(2) K during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the ShelXT (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of ShelXL (Sheldrick, 2008) using Least Squares minimisation.

Compound	**Compound 4**
Formula	$C_{15}H_{27}N_5$
$D_{calc.}/gcm^{-3}$	1.148
mu/mm^{-1}	0.072
Formula Weight	277.41
Colour	clear light colourless
Shape	Prism
Max Size/mm	0.17
Mid Size/mm	0.15
Min Size/mm	0.08
T/K	115(2)
Crystal System	triclinic
Space Group	$P\bar{1}$
a/Å	9.8695(3)
b/Å	12.1158(3)
c/Å	14.4185(5)
α/°	78.653(2)
β/°	80.2470(10)
γ/°	73.002(2)
V/Å^3	1605.02(9)
Z	4
Z'	2
Θ_{min}/°	1.451
Θ_{max}/°	27.506
Measured Refl.	13714
Independent Refl.	7301
Reflections Used	5760
Rint	0.0339
Parameters	365
Restraints	0
Largest Peak	0.245
Deepest Hole	-0.220
GooF	1.093
$wR2$ (all data)	0.1153
$wR2$	0.1051
R_1 (all data)	0.0752
R_1	0.0558

Data Quality	d min 0.77	I/σ 15.5	Rint 3.39%	complete 99%
Refinement Quality	Shift -0.001	Max Peak 0.2	Min Peak -0.2	GooF 1.093

Extended Experimental

Experimental Extended: A clear light colourless Prism-shaped crystal with dimensions 0.17×0.15×0.08 was mounted on a glass fibre with grease. Data were collected using a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 115(2)$ K.

Data were measured using ϕ and ω scans using MoK$_\alpha$ radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000). The actually achieved resolution was $\Theta = 27.506$.

Cell parameters were retrieved using the SCALEPACK (Otwinowski and Minor, 1997) software and refined using DENZO (Otwinowski and Minor, 1997) on 6734 reflections, 49% of the observed reflections. Data reduction was performed using the DENZO (Otwinowski and Minor, 1997) software which corrects for Lorentz polarisation. The final completeness is 99.50% out to 27.506 in Θ. No absoprtion correction was performed. The absorption coefficient (μ) of this material is 0.072.

The structure was solved in the space group $P\bar{1}$ (# 2) by Direct Methods using the ShelXT (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2014/7 of ShelXL (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

Table 2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($^\circ$A^2×10^3) for **Compound 4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
C1A	2331.3(18)	682.1(15)	−678.1(12)	20.9(3)
C1B	5517.3(18)	2648.2(14)	4111.2(12)	20.6(3)
C2A	3478.0(18)	1238.9(15)	−529.7(12)	22.9(4)
C2B	4534.1(18)	3460.7(15)	3406.2(12)	23.0(4)
C3A	3351.6(18)	1502.5(15)	484.5(12)	22.3(4)
C3B	2224.7(19)	3318.0(16)	4290.1(13)	25.6(4)
C4A	1532.2(19)	2477.4(16)	1663.2(12)	24.7(4)
C4B	1524(2)	3499.1(16)	5304.1(13)	28.0(4)
C5A	−54.1(19)	3109.6(16)	1775.8(13)	26.3(4)
C5B	2165(2)	2516.6(16)	6070.4(13)	27.7(4)
C6A	−2430.6(19)	3251.8(16)	1443.7(13)	27.3(4)
C6B	4340(2)	1198.6(15)	6630.5(13)	28.6(4)
C7A	−3344.5(19)	3031.1(17)	783.7(14)	29.2(4)
C7B	5906(2)	1010.7(16)	6732.3(13)	30.3(4)
C8A	−2880.7(19)	3393.0(15)	−279.4(13)	27.8(4)
C8B	8056(2)	1491.2(17)	5800.0(14)	32.4(4)
C9A	−852.7(18)	2554.2(15)	−1395.8(12)	22.9(4)
C9B	8495(2)	2084.7(16)	4801.5(14)	30.7(4)
C10A	347.7(18)	2493.5(14)	−836.9(12)	21.0(3)
C10B	7494.4(19)	3296.3(16)	4501.3(14)	26.9(4)
C11A	369.1(17)	909.4(14)	566.4(11)	17.4(3)
C11B	5274.2(19)	3620.5(14)	5522.7(12)	21.4(3)
C12A	−511.2(18)	1488.7(14)	1250.2(12)	19.8(3)

C12B	4197.9(19)	3253.7(14)	6101.0(12)	22.2(4)
C13A	−962.3(19)	805.2(15)	2118.5(12)	24.1(4)
C13B	3610(2)	3781.1(15)	6939.1(13)	28.1(4)
C21A	2483(2)	3623.2(16)	274.8(15)	30.6(4)
C21B	2445(2)	5085.0(16)	3241.4(14)	31.8(4)
C41A	−3099(2)	2083.3(17)	−1272.0(14)	30.4(4)
C41B	7234(2)	−83.9(16)	5482.2(15)	34.6(5)
N1A	890.3(14)	1311.3(11)	−328.4(9)	18.2(3)
N1B	5984.9(15)	3312.0(12)	4682.6(10)	21.1(3)
N2A	2160.8(15)	2514.0(12)	669.6(10)	20.6(3)
N2B	3173.5(16)	4080.2(12)	3886.5(10)	23.0(3)
N3A	−899.2(15)	2729.4(12)	1207.6(10)	21.4(3)
N3B	3721.7(16)	2282.2(12)	5994.7(10)	22.4(3)
N4A	−2128.9(15)	2383.1(12)	−768.2(10)	22.6(3)
N4B	6822.2(17)	1036.2(12)	5823.0(11)	26.1(3)
N5A	−1363.1(19)	321.1(15)	2836.6(11)	36.1(4)
N5B	3088(2)	4137.4(15)	7639.7(12)	43.4(5)

Table 3: Anisotropic Displacement Parameters ($\times 10^4$) **Compound 4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*{}^2 \times U_{11} + ... + 2hka* \times b* \times U_{12}]$

Atom	$\mathbf{U}_{11}$	$\mathbf{U}_{22}$	$\mathbf{U}_{33}$	$\mathbf{U}_{23}$	$\mathbf{U}_{13}$	$\mathbf{U}_{12}$
C1A	22.2(8)	21.6(8)	18.9(8)	−5.5(6)	1.1(7)	−6.4(7)
C1B	23.8(9)	19.2(8)	18.3(8)	−5.3(6)	−0.2(7)	−4.7(7)
C2A	18.2(8)	25.3(9)	24.5(9)	−4.8(7)	0.0(7)	−5.8(7)
C2B	26.4(9)	24.1(9)	17.0(8)	−3.0(7)	−1.2(7)	−5.5(7)
C3A	18.5(8)	24.0(9)	24.8(9)	−2.9(7)	−4.4(7)	−5.7(7)
C3B	24.7(9)	26.1(9)	27.2(9)	−4.5(7)	−5.0(7)	−7.4(7)
C4A	25.4(9)	31.6(10)	21.8(9)	−8.4(7)	−3.7(7)	−11.6(8)
C4B	23.8(9)	28.2(9)	32.2(10)	−9.9(8)	3.4(8)	−7.8(8)
C5A	27.1(9)	30.7(10)	25.5(9)	−13.0(7)	0.3(7)	−10.7(8)
C5B	31.2(10)	27.9(9)	25.3(9)	−6.9(7)	6.7(8)	−14.0(8)
C6A	22.3(9)	28.0(9)	30.9(10)	−11.7(8)	1.4(7)	−3.6(7)
C6B	44.4(11)	21.7(9)	19.2(8)	0.1(7)	0.3(8)	−12.6(8)
C7A	18.3(9)	32.4(10)	37.1(11)	−10.8(8)	0.0(8)	−5.7(7)
C7B	48.7(12)	21.5(9)	20.2(9)	0.6(7)	−10.4(8)	−7.7(8)
C8A	24.0(9)	23.1(9)	36.2(10)	−4.0(8)	−8.9(8)	−3.3(7)
C8B	33.7(11)	28(1)	37.1(11)	−5.9(8)	−15.7(9)	−4.0(8)
C9A	26.1(9)	23.2(9)	20.0(8)	1.9(7)	−7.2(7)	−8.2(7)
C9B	23.8(9)	30.6(10)	39.8(11)	−11.3(8)	−4.2(8)	−6.5(8)
C10A	22.4(8)	19.5(8)	21.1(8)	1.4(6)	−3.7(7)	−8.2(7)
C10B	24.2(9)	25.5(9)	32(1)	−5.9(7)	0.5(8)	−9.3(7)
C11A	18.7(8)	17.2(8)	18.3(8)	−1.2(6)	−3.9(6)	−8.1(6)
C11B	28.5(9)	15.9(8)	20.5(8)	−3.3(6)	−6.3(7)	−5.1(7)
C12A	22.5(8)	19.2(8)	19.2(8)	−2.4(6)	−2.1(6)	−8.3(7)
C12B	31.1(9)	18.2(8)	17.4(8)	−4.9(6)	−1.0(7)	−6.4(7)
C13A	27.3(9)	24.4(9)	22.6(9)	−6.9(7)	0.8(7)	−10.0(7)
C13B	39.3(11)	21.4(9)	24.1(9)	−4.8(7)	0.0(8)	−10.4(8)
C21A	30.8(10)	24.9(9)	39.1(11)	−5.2(8)	−4.2(8)	−12.1(8)
C21B	34.7(11)	25.2(9)	31.5(10)	−0.5(8)	−9.6(8)	−1.5(8)
C41A	29.8(10)	32.8(10)	32(1)	1.5(8)	−11.3(8)	−13.5(8)

C41B	42.9(12)	23.0(9)	38.4(11)	−9.2(8)	−7.5(9)	−4.9(8)
N1A	19.9(7)	17.4(7)	17.2(7)	−2.2(5)	−2.0(5)	−5.5(6)
N1B	23.1(7)	20.0(7)	19.9(7)	−2.6(5)	−0.6(6)	−6.8(6)
N2A	21.3(7)	20.9(7)	21.8(7)	−4.7(6)	−2.2(6)	−8.2(6)
N2B	24.6(8)	20.0(7)	22.1(7)	−1.3(6)	−3.5(6)	−3.5(6)
N3A	20.1(7)	20.8(7)	24.7(7)	−8.7(6)	−0.7(6)	−5.1(6)
N3B	29.0(8)	18.2(7)	19.7(7)	−2.5(6)	0.8(6)	−8.4(6)
N4A	21.0(7)	24.0(7)	24.4(7)	−1.8(6)	−5.6(6)	−8.4(6)
N4B	33.9(9)	18.9(7)	25.7(8)	−3.7(6)	−8.2(7)	−4.5(6)
N5A	45.3(10)	39.2(10)	24.8(8)	−2.8(7)	5.0(7)	−19.5(8)
N5B	67.6(13)	33.3(9)	29.0(9)	−11.8(7)	8.1(9)	−16.4(9)

Table 4: Bond Lengths in ° A for **Compound 4**.

Atoms	**Length/Å**	**Atoms**	**Length/Å**
C1A–C2A	1.538(2)	C8B –C9B	1.530(3)
C1A–N1A	1.460(2)	C8B –N4B	1.469(2)
C1B–C2B	1.525(2)	C9A –C10A	1.519(2)
C1B–N1B	1.465(2)	C9A –N4A	1.463(2)
C2A–C3A	1.535(2)	C9B –C10B	1.538(3)
C2B–N2B	1.465(2)	C10A–N1A	1.465(2)
C3A–N2A	1.461(2)	C10B–N1B	1.463(2)
C3B–C4B	1.536(2)	C11A–C12A	1.358(2)
C3B–N2B	1.476(2)	C11A–N1A	1.357(2)
C4A–C5A	1.525(2)	C11B–C12B	1.361(2)
C4A–N2A	1.459(2)	C11B–N1B	1.355(2)
C4B–C5B	1.522(3)	C12A–C13A	1.439(2)
C5A–N3A	1.478(2)	C12A–N3A	1.430(2)
C5B–N3B	1.468(2)	C12B–C13B	1.433(2)
C6A–C7A	1.524(3)	C12B–N3B	1.431(2)
C6A–N3A	1.467(2)	C13A–N5A	1.153(2)
C6B–C7B	1.524(3)	C13B–N5B	1.156(2)
C6B–N3B	1.478(2)	C21A–N2A	1.455(2)
C7A–C8A	1.538(3)	C21B–N2B	1.461(2)
C7B–N4B	1.461(2)	C41A–N4A	1.456(2)
C8A–N4A	1.475(2)	C41B–N4B	1.456(2)

Table 5: Bond Angles in ° for **Compound 4**.

–Atoms–	**Angle/°**	**–Atoms–**	**Angle/°**
N1A –C1A –C2A	112.83(13)	N3B –C12B–C13B	117.05(15)
N1B –C1B –C2B	111.13(13)	N5A –C13A–C12A	175.8(2)
C3A –C2A –C1A	113.77(14)	N5B –C13B–C12B	174.8(2)
N2B –C2B –C1B	112.08(13)	C1A –N1A –C10A	115.82(13)
N2A –C3A –C2A	112.18(14)	C11A–N1A –C1A	116.67(13)
N2B –C3B –C4B	112.90(15)	C11A–N1A –C10A	124.51(14)
N2A –C4A –C5A	112.98(14)	C10B–N1B –C1B	116.24(14)
C5B –C4B –C3B	113.45(15)	C11B–N1B –C1B	123.99(14)

N3A –C5A –C4A	113.54(14)	C11B–N1B –C10B	116.64(15)
N3B –C5B –C4B	112.13(14)	C4A –N2A –C3A	114.37(13)
N3A –C6A –C7A	113.09(14)	C21A–N2A –C3A	113.12(14)
N3B –C6B –C7B	114.08(15)	C21A–N2A –C4A	112.11(14)
C6A –C7A –C8A	113.53(15)	C2B –N2B –C3B	112.93(13)
N4B –C7B –C6B	113.57(15)	C21B–N2B –C2B	110.66(14)
N4A –C8A –C7A	112.70(14)	C21B–N2B –C3B	110.27(15)
N4B –C8B –C9B	111.88(15)	C6A –N3A –C5A	110.75(13)
N4A –C9A –C10A	111.89(14)	C12A–N3A –C5A	112.61(14)
C8B –C9B –C10B	114.11(16)	C12A–N3A –C6A	114.23(14)
N1A –C10A–C9A	111.21(14)	C5B –N3B –C6B	110.91(14)
N1B –C10B–C9B	113.03(14)	C12B–N3B –C5B	114.12(14)
N1A –C11A–C12A	130.77(15)	C12B–N3B –C6B	113.02(14)
N1B –C11B–C12B	130.70(16)	C9A –N4A –C8A	112.85(14)
C11A–C12A–C13A	117.83(15)	C41A–N4A –C8A	110.67(14)
C11A–C12A–N3A	124.31(15)	C41A–N4A –C9A	111.74(14)
N3A –C12A–C13A	117.51(15)	C7B –N4B –C8B	114.77(15)
C11B–C12B–C13B	118.04(16)	C41B–N4B –C7B	111.98(15)
C11B–C12B–N3B	124.48(15)	C41B–N4B –C8B	112.03(16)

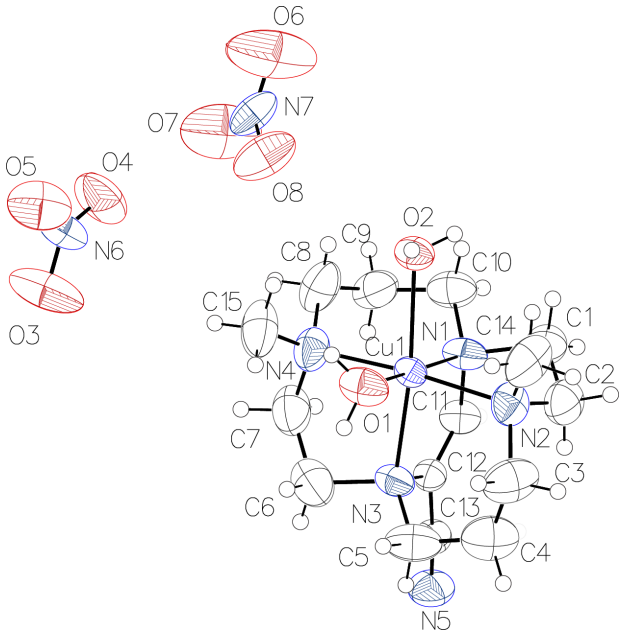
Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($^\circ$ A$^2\times 10^3$) for **Compound 4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
H1AA	2377	663	−1366	25
H1AB	2540	−135	−344	25
H1BA	5008	2113	4538	25
H1BB	6362	2168	3759	25
H2AA	4431	705	−679	27
H2AB	3410	1976	−984	27
H2BA	5017	4038	3018	28
H2BB	4348	2998	2971	28
H3AA	3218	811	948	27
H3AB	4250	1650	579	27
H3BA	2784	2492	4300	31
H3BB	1469	3474	3872	31
H4AA	2044	2839	2001	30
H4AB	1665	1652	1967	30
H4BA	1622	4244	5431	34
H4BB	492	3566	5344	34
H5AA	−437	2976	2457	32
H5AB	−170	3960	1583	32
H5BA	1740	2729	6706	33
H5BB	1921	1797	6015	33
H6AA	−2603	4105	1409	33
H6AB	−2729	2929	2107	33
H6BA	4241	524	6382	34
H6BB	3784	1218	7269	34
H7AA	−4349	3468	942	35
H7AB	−3300	2189	901	35

H7BA	5990	1625	7065	36
H7BB	6251	247	7134	36
H8AA	−3735	3845	−596	33
H8AB	−2246	3909	−342	33
H8BA	8870	840	6013	39
H8BB	7816	2061	6249	39
H9AA	−1095	3325	−1806	28
H9AB	−525	1946	−1814	28
H9BA	8527	1574	4336	37
H9BB	9471	2166	4776	37
H10A	1134	2729	−1279	25
H10B	−6	3048	−373	25
H10C	7654	3864	4852	32
H10D	7738	3551	3813	32
H11A	670	85	745	21
H11B	5578	4187	5745	26
H21A	3198	3727	621	46
H21B	1611	4263	337	46
H21C	2856	3626	−400	46
H21D	3056	5616	3019	48
H21E	1548	5496	3578	48
H21F	2244	4817	2694	48
H41A	−3914	1934	−823	46
H41B	−2597	1381	−1557	46
H41C	−3439	2733	−1774	46
H41D	7843	−672	5915	52
H41E	7760	−8	4843	52
H41F	6377	−325	5459	52

Compound [4-Cu](NO$_3$)$_2$ Olex2

Summary



Crystal Data: $C_{15}H_{31}CuN_7O_8$, $M_r = 501.01$, orthorhombic, *Pbca* (No. 61), a = 16.103(5) Å, b = 14.421(5) Å, c = 18.511(5) Å, $\alpha = \beta = \gamma = 90°$, $V = 4299(2)$ Å^3, $T = 298(2)$ K, $Z = 8$, $Z' = 1$, μ(MoK$_\alpha$) = 1.074, 9161 reflections measured, 4897 unique (Rint = 0.0336) which were used in all calculations. The final $wR2$ was 0.2773 (all data) and R_1 was 0.1077 ($I > 2\sigma(I)$).

Experimental: Single clear light blue prism-shaped crystals of (**Compound [4-Cu](NO$_3$)$_2$**) were recrystallised from ethanol by slow evaporation. A suitable crystal (0.14×0.12×0.10) was selected and mounted on a glass fibre with superglue on a Nonius Kappa CCD diffractometer. The crystal was kept at $T = 298(2)$ K during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the ShelXT (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of ShelXL (Sheldrick, 2008) using Least Squares minimisation.

Compound	**Compound [4-Cu](NO$_3$)$_2$**
Formula	$C_{15}H_{31}CuN_7O_8$
$D_{calc.}/gcm^{-3}$	1.548
mu/mm^{-1}	1.074
Formula Weight	501.01
Colour	clear light blue
Shape	prism
Max Size/mm	0.14
Mid Size/mm	0.12
Min Size/mm	0.10
T/K	298(2)
Crystal System	orthorhombic
Space Group	*Pbca*
a/Å	16.103(5)
b/Å	14.421(5)
c/Å	18.511(5)
α/°	90
β/°	90
γ/°	90
V/Å^3	4299(2)
Z	8
Z'	1
Θ_{min}/°	2.192
Θ_{max}/°	27.482
Measured Refl.	9161
Independent Refl.	4897
Reflections Used	3820
Rint	0.0336
Parameters	284
Restraints	279
Largest Peak	1.232
Deepest Hole	-0.547
GooF	1.142
$wR2$ (all data)	0.2773
$wR2$	0.2626
R_1 (all data)	0.1309
R_1	0.1077

Data Quality	d min 0.77	I/σ 18.4	Rint 3.36%	complete 99%
Refinement Quality	Shift 0.001	Max Peak 1.2	Min Peak -0.6	GooF 1.142

Extended Experimental

Experimental Extended: A clear light blue prism-shaped crystal with dimensions 0.14×0.12×0.10 was mounted on a glass fibre with superglue. Data were collected using a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 298(2)$ K.

Data were measured using ϕ and ω scans using MoK$_\alpha$ radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000). The actually achieved resolution was $\Theta = 27.482$.

Cell parameters were retrieved using the SCALEPACK (Otwinowski and Minor, 1997) software and refined using DENZO (Otwinowski and Minor, 1997). Data reduction was performed using the DENZO (Otwinowski and Minor, 1997) software which corrects for Lorentz polarisation. The final completeness is 99.70% out to 27.482 in Θ. No absoprtion correction was performed. The absorption coefficient (μ) of this material is 1.074.

The structure was solved in the space group *Pbca* (# 61) by Direct Methods using the ShelXT (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2014/7 of ShelXL (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Some RIGU restraints were employed to maintain a reasonable model.

Table 2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($^\circ$A^2×10^3) for **Compound [4-Cu](NO$_3$)$_2$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
Cu1	3819.0(5)	7351.7(6)	6474.2(4)	36.2(3)
O2	2562(3)	6582(4)	6675(3)	49.3(12)
O1	4141(4)	6802(5)	7419(3)	66.6(16)
N3	5059(4)	7943(5)	6144(4)	49.5(14)
N1	3417(4)	7969(5)	5536(3)	51.8(14)
N7	2416(6)	4221(5)	3503(4)	66.2(19)
C12	4867(4)	8387(5)	5479(4)	39.6(13)
N2	3511(5)	8635(5)	6948(4)	59.3(16)
N6	4421(4)	2484(6)	6388(4)	62.0(18)
O8	2728(6)	4561(6)	4048(4)	98(3)
N4	4229(5)	6158(5)	5896(4)	62.3(17)
C13	5522(5)	8880(5)	5098(4)	49.7(17)
N5	6081(5)	9237(6)	4840(5)	71(2)
O5	4250(5)	1981(7)	6914(4)	101(3)
C11	4125(5)	8377(5)	5188(4)	46.4(16)
O4	3921(5)	2747(7)	5965(5)	105(3)
O3	5140(5)	2704(8)	6317(4)	118(4)
C1	2815(6)	8794(6)	5795(5)	63(2)
O7	2845(7)	4043(9)	3000(5)	150(5)
O6	1706(7)	4042(12)	3461(6)	184(7)
C9	3364(7)	6621(7)	4781(6)	75(2)
C6	5581(7)	7043(8)	5973(6)	81(3)
C2	3239(7)	9304(7)	6390(5)	72(2)
C10	2888(6)	7454(7)	5043(5)	68(2)

C5	5532(7)	8502(8)	6637(5)	79(3)
C8	3603(8)	5908(7)	5297(6)	84(3)
C15	4278(8)	5370(7)	6356(6)	90(3)
C14	2905(8)	8481(7)	7522(6)	91(3)
C4	5007(7)	9308(9)	6884(6)	88(3)
C7	5010(7)	6382(7)	5515(7)	83(3)
C3	4253(7)	9103(9)	7345(6)	89(3)

Table 3: Anisotropic Displacement Parameters ($\times 10^4$) **Compound [4-Cu](NO$_3$)$_2$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2 \times U_{11} + ... + 2hka* \times b* \times U_{12}]$

Atom	**U$_{11}$**	**U$_{22}$**	**U$_{33}$**	**U$_{23}$**	**U$_{13}$**	**U$_{12}$**
Cu1	33.0(4)	43.1(5)	32.4(4)	1.2(3)	−0.7(3)	0.1(3)
O2	43(3)	57(3)	47(3)	8(2)	1(2)	−6(2)
O1	57(3)	92(4)	51(3)	21(3)	−14(3)	−10(3)
N3	36(3)	60(3)	52(3)	13(3)	−6(2)	−5(2)
N1	42(3)	71(3)	43(3)	11(3)	−4(2)	−14(3)
N7	109(5)	48(4)	42(3)	0(3)	8(3)	−24(4)
C12	39(3)	40(3)	39(3)	2(3)	5(2)	−2(2)
N2	67(4)	59(3)	52(3)	−8(3)	18(3)	6(3)
N6	39(3)	111(6)	36(3)	−20(3)	0(2)	1(3)
O8	148(7)	89(5)	56(3)	−10(3)	−1(4)	−47(5)
N4	69(4)	48(3)	70(4)	0(3)	23(3)	5(3)
C13	48(3)	49(4)	52(4)	8(3)	3(3)	−4(3)
N5	59(4)	72(5)	82(5)	16(4)	11(4)	−15(3)
O5	93(5)	150(7)	59(4)	−2(4)	23(4)	−23(5)
C11	47(3)	60(4)	32(3)	3(3)	3(2)	−9(3)
O4	74(4)	142(7)	100(5)	−20(5)	−39(4)	26(4)
O3	55(3)	225(11)	75(5)	47(6)	−12(3)	−30(5)
C1	60(4)	61(4)	68(4)	6(3)	14(4)	−4(3)
O7	140(7)	238(12)	71(5)	−70(7)	27(5)	−56(7)
O6	113(6)	328(18)	110(7)	−133(10)	27(5)	−74(7)
C9	72(6)	62(4)	90(6)	−3(4)	3(5)	−17(4)
C6	68(5)	84(5)	92(6)	30(4)	15(4)	12(4)
C2	75(5)	63(4)	78(5)	−10(4)	17(4)	4(4)
C10	63(4)	82(5)	57(4)	5(4)	−14(4)	−17(4)
C5	68(5)	110(6)	59(5)	2(4)	−7(4)	−29(4)
C8	113(7)	54(4)	85(5)	−20(4)	−2(5)	3(4)
C15	113(8)	59(5)	98(7)	20(5)	30(6)	25(5)
C14	119(7)	70(6)	83(6)	−30(5)	57(6)	−14(5)
C4	89(6)	113(7)	62(5)	−13(5)	1(5)	−22(5)
C7	81(5)	65(5)	102(6)	7(5)	28(4)	16(4)
C3	101(6)	98(7)	68(5)	−24(5)	13(4)	−29(5)

Table 4: Bond Lengths in $^\circ$A for **Compound [4-Cu](NO$_3$)$_2$**.

Atoms	**Length/Å**	**Atoms**	**Length/Å**
Cu1–O2	2.339(5)	N2 –C2	1.480(13)
Cu1–O1	1.989(5)	N2 –C14	1.460(11)
Cu1–N3	2.255(6)	N2 –C3	1.556(13)

Cu1–N1	2.056(6)	N6 –O5	1.244(11)
Cu1–N2	2.107(7)	N6 –O4	1.187(10)
Cu1–N4	2.133(7)	N6 –O3	1.207(10)
N3 –C12	1.422(9)	N4 –C8	1.540(14)
N3 –C6	1.578(13)	N4 –C15	1.422(12)
N3 –C5	1.436(11)	N4 –C7	1.477(12)
N1 –C11	1.436(9)	C13–N5	1.142(10)
N1 –C1	1.607(11)	C1 –C2	1.490(14)
N1 –C10	1.452(11)	C9 –C10	1.505(14)
N7 –O8	1.230(10)	C9 –C8	1.455(15)
N7 –O7	1.187(11)	C6 –C7	1.573(16)
N7 –O6	1.175(12)	C5 –C4	1.509(16)
C12–C13	1.454(10)	C4 –C3	1.513(15)
C12–C11	1.311(10)	–	

Table 5: Bond Angles in ° for **Compound [4-Cu](NO$_3$)$_2$**.

–Atoms–	Angle/°	–Atoms–	Angle/°
O1 – Cu1– O2	84.1(2)	N3 – C12– C13	118.9(6)
O1 – Cu1– N3	99.1(2)	C11– C12– N3	123.3(6)
O1 – Cu1– N1	175.8(3)	C11– C12– C13	117.9(7)
O1 – Cu1– N2	92.6(3)	C2 – N2 – Cu1	110.6(5)
O1 – Cu1– N4	92.2(3)	C2 – N2 – C3	105.9(8)
N3 – Cu1– O2	171.4(2)	C14– N2 – Cu1	109.1(6)
N1 – Cu1– O2	93.8(2)	C14– N2 – C2	114.2(8)
N1 – Cu1– N3	83.5(2)	C14– N2 – C3	103.6(8)
N1 – Cu1– N2	84.1(3)	C3 – N2 – Cu1	113.4(6)
N1 – Cu1– N4	91.3(3)	O4 – N6 – O5	123.5(9)
N2 – Cu1– O2	98.5(2)	O4 – N6 – O3	119.6(10)
N2 – Cu1– N3	89.4(3)	O3 – N6 – O5	116.9(8)
N2 – Cu1– N4	172.3(3)	C8 – N4 – Cu1	110.3(6)
N4 – Cu1– O2	87.9(2)	C15– N4 – Cu1	111.2(6)
N4 – Cu1– N3	84.0(3)	C15– N4 – C8	106.3(8)
C12– N3 – Cu1	102.3(4)	C15– N4 – C7	114.4(8)
C12– N3 – C6	108.2(7)	C7 – N4 – Cu1	109.0(6)
C12– N3 – C5	114.3(7)	C7 – N4 – C8	105.4(9)
C6 – N3 – Cu1	102.5(5)	N5 – C13– C12	174.3(9)
C5 – N3 – Cu1	120.7(6)	C12– C11– N1	123.0(6)
C5 – N3 – C6	107.8(8)	C2 – C1 – N1	108.1(7)
C11– N1 – Cu1	107.8(5)	C8 – C9 – C10	119.1(10)
C11– N1 – C1	108.0(6)	C7 – C6 – N3	107.1(8)
C11– N1 – C10	113.1(7)	N2 – C2 – C1	109.3(8)
C1 – N1 – Cu1	105.0(5)	N1 – C10– C9	108.2(8)
C10– N1 – Cu1	119.6(6)	N3 – C5 – C4	109.2(9)
C10– N1 – C1	102.3(7)	C9 – C8 – N4	118.7(8)
O7 – N7 – O8	119.5(11)	C5 – C4 – C3	118.0(10)
O6 – N7 – O8	122.6(9)	N4 – C7 – C6	112.0(9)
O6 – N7 – O7	117.9(9)	C4 – C3 – N2	115.8(8)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($^{\circ}A^2 \times 10^3$) for **Compound [4-Cu](NO$_3$)$_2$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

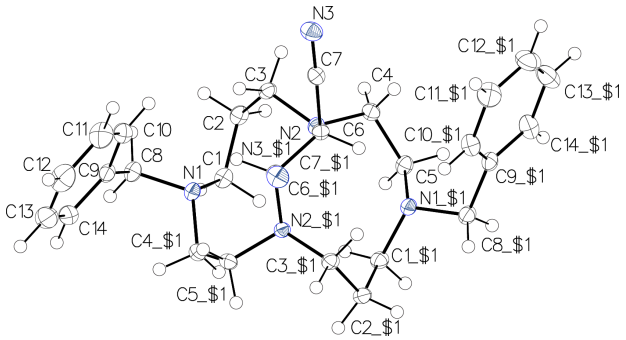
Atom	x	y	z	U(eq)
H2A	2146	6921	6529	74
H2B	2498	6470	7134	74
H1A	4672	6845	7479	100
H1B	4005	6223	7433	100
H11	4053	8647	4736	56
H1C	2703	9210	5395	76
H1D	2292	8542	5965	76
H9A	3034	6325	4408	90
H9B	3867	6844	4552	90
H6A	6076	7203	5702	97
H6B	5748	6741	6418	97
H2C	3716	9635	6200	86
H2D	2861	9752	6600	86
H10A	2733	7843	4637	81
H10B	2386	7258	5288	81
H5A	6029	8729	6400	95
H5B	5699	8132	7050	95
H8A	3831	5392	5027	101
H8B	3101	5688	5530	101
H15A	4626	5511	6762	135
H15B	4509	4857	6093	135
H15C	3732	5210	6523	135
H14A	2406	8226	7320	136
H14B	2780	9060	7754	136
H14C	3130	8057	7871	136
H4A	4820	9639	6458	106
H4B	5362	9727	7154	106
H7A	4880	6678	5058	99
H7B	5308	5813	5413	99
H3A	4059	9680	7554	107
H3B	4423	8703	7739	107

Table 7: Hydrogen Bond information for **Compound [4-Cu](NO$_3$)$_2$**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2A	O5[1]	0.87	2.36	3.007(10)	131.2
O2	H2B	O7[2]	0.87	1.85	2.694(10)	162.6
O1	H1A	O5[3]	0.86	2.08	2.881(11)	154.6
O1	H1B	O6[2]	0.86	2.25	2.658(11)	108.5

[1] $1/2-x, 1/2+y, +z$; [2] $1/2-x, 1-y, 1/2+z$; [3] $1-x, 1/2+y, 3/2-z$

Summary



Crystal Data: $C_{28}H_{36}N_6$, $M_r = 456.63$, monoclinic, $C2/c$ (No. 15), a = 15.5335(5) Å, b = 7.6860(2) Å, c = 21.3414(7) Å, $\beta = 91.0610(10)°$, $\alpha = \gamma = 90°$, $V = 2547.52(13)$ Å^3, $T = 115(2)$ K, $Z = 4$, $Z' = 0.5$, $\mu(\mathrm{MoK}_\alpha) = 0.073$, 5583 reflections measured, 2920 unique (Rint = 0.0275) which were used in all calculations. The final $wR2$ was 0.1060 (all data) and R_1 was 0.0473 ($I > 2\sigma(I)$).

Experimental: Single clear light colourless Prism-shaped crystals of (**Compound 5**) were recrystallised from ethanol by slow evaporation. A suitable crystal (0.35×0.25×0.12) was selected and mounted on a glass fibre with grease on a Nonius Kappa Apex II diffractometer. The crystal was kept at $T = 115(2)$ K during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the ShelXT (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version of 2014/7 ShelXL (Sheldrick, 2008) using Least Squares minimisation.

Compound	**Compound 5**
Formula	$C_{28}H_{36}N_6$
$D_{calc.}/gcm^{-3}$	1.191
mu/mm^{-1}	0.073
Formula Weight	456.63
Colour	clear light colourless
Shape	Prism
Max Size/mm	0.35
Mid Size/mm	0.25
Min Size/mm	0.12
T/K	115(2)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	15.5335(5)
b/Å	7.6860(2)
c/Å	21.3414(7)
α/°	90
β/°	91.0610(10)
γ/°	90
V/Å^3	2547.52(13)
Z	4
Z'	0.5
Θ_{min}/°	1.909
Θ_{max}/°	27.511
Measured Refl.	5583
Independent Refl.	2920
Reflections Used	2510
Rint	0.0275
Parameters	154
Restraints	1
Largest Peak	0.326
Deepest Hole	-0.197
GooF	1.093
$wR2$ (all data)	0.1060
$wR2$	0.1008
R_1 (all data)	0.0566
R_1	0.0473

Data Quality	d min 0.77	I/σ 22.4	Rint 2.75%	complete 100%
Refinement Quality	Shift 0.000	Max Peak 0.3	Min Peak -0.2	GooF 1.093

Extended Experimental

Experimental Extended: A clear light colourless Prism-shaped crystal with dimensions 0.35×0.25×0.12 was mounted on a glass fibre with grease. Data were collected using a Nonius Kappa Apex II diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 115(2)$ K.

Data were measured using ϕ and ω scans using MoK$_\alpha$ radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000). The actually achieved resolution was $\Theta = 27.511$.

Cell parameters were retrieved using the SCALEPACK (Otwinowski and Minor, 1997) software and refined using DENZO (Otwinowski and Minor, 1997) on 3096 reflections, 55% of the observed reflections. Data reduction was performed using the DENZO (Otwinowski and Minor, 1997) software which corrects for Lorentz polarisation. The final completeness is 100.00% out to 27.511 in Θ. No absoprtion correction was performed. The absorption coefficient (μ) of this material is 0.073.

The structure was solved in the space group $C2/c$ (# 15) by Direct Methods using the ShelXT (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2015/7 of ShelXL (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

Table 2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **Compound 5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
C1	6289.5(9)	6099.4(18)	2906.4(6)	19.0(3)
C2	6855.2(8)	5289.8(18)	2405.8(6)	19.4(3)
C3	6512.2(8)	3548.2(18)	2169.0(6)	17.4(3)
C4	5445.8(8)	4172.1(18)	1318.1(6)	18.2(3)
C5	4708.7(8)	5477.4(18)	1256.4(6)	18.7(3)
C6	5096.7(8)	2144.1(17)	2143.8(6)	15.8(3)
C7	5524.3(8)	477.5(18)	1966.5(6)	17.5(3)
C8	6805.2(9)	4563.6(18)	3849.8(6)	20.0(3)
C9	6622.7(8)	3019.5(19)	4263.8(6)	19.3(3)
C10	6639.3(9)	1339.8(19)	4022.1(7)	24.1(3)
C11	6437.4(11)	−83(2)	4391.6(8)	33.5(4)
C12	6224.1(11)	164(2)	5014.6(8)	36.6(4)
C13	6217.2(11)	1820(2)	5263.3(8)	34.8(4)
C14	6415.3(10)	3234(2)	4890.7(7)	26.6(3)
N1	6076.1(7)	4909.7(15)	3417.9(5)	16.7(2)
N2	5601.7(7)	3643.8(15)	1971.9(5)	15.7(2)
N3	5902.1(8)	−733.8(16)	1823.8(6)	24.9(3)

Table 3: Anisotropic Displacement Parameters ($\times 10^4$) **Compound 5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2 \times U_{11} + ... + 2hka* \times b* \times U_{12}]$

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
C1	18.5(6)	15.9(6)	22.7(7)	3.0(5)	−1.4(5)	−1.8(5)
C2	15.7(6)	21.0(7)	21.4(7)	3.4(5)	0.7(5)	−3.0(5)
C3	13.4(6)	19.8(7)	19.1(6)	1.4(5)	1.6(5)	1.5(5)
C4	17.8(6)	20.8(7)	16.0(6)	1.9(5)	2.9(5)	−0.9(5)
C5	18.5(6)	18.5(7)	18.9(6)	3.4(5)	−0.7(5)	−0.4(5)
C6	15.1(6)	15.6(6)	16.7(6)	0.0(5)	1.3(5)	−0.4(5)
C7	18.6(6)	17.1(6)	16.9(6)	−0.5(5)	0.7(5)	−2.0(5)
C8	17.2(6)	20.2(7)	22.6(7)	1.4(6)	−2.9(5)	−1.4(5)
C9	15.5(6)	23.3(7)	19.0(6)	1.3(5)	−2.6(5)	1.6(5)
C10	26.2(7)	24.7(8)	21.3(7)	0.2(6)	−1.6(6)	3.2(6)
C11	40.5(9)	21.3(8)	38.5(9)	3.9(7)	−5.0(7)	0.4(7)
C12	35.1(9)	37.3(10)	37.5(9)	18.3(8)	2.6(7)	−0.7(8)
C13	33.8(8)	47.1(11)	23.8(8)	10.3(7)	7.3(6)	9.6(8)
C14	28.5(8)	29.9(8)	21.2(7)	−1.0(6)	−0.5(6)	8.4(6)
N1	14.5(5)	18.0(6)	17.6(5)	1.5(4)	−1.3(4)	−0.5(4)
N2	13.2(5)	17.2(6)	16.8(5)	3.1(4)	0.0(4)	−0.7(4)
N3	29.5(7)	20.4(6)	24.8(6)	−2.7(5)	3.1(5)	1.9(5)

Table 4: Bond Lengths in Å for **Compound 5**.

Atoms	**Length/Å**	**Atoms**	**Length/Å**
C1–C2	1.5282(19)	C7 –N3	1.1447(18)
C1–N1	1.4668(17)	C8 –C9	1.5096(19)
C2–C3	1.5235(19)	C8 –N1	1.4711(16)
C3–N2	1.4699(16)	C9 –C10	1.391(2)
C4–C5	1.5263(19)	C9 –C14	1.392(2)
C4–N2	1.4690(16)	C10–C11	1.387(2)
C5–N1[1]	1.4801(17)	C11–C12	1.389(2)
C6–C6[1]	1.555(2)	C12–C13	1.380(3)
C6–C7	1.4948(18)	C13–C14	1.385(2)
C6–N2	1.4454(16)	N1 –C5[1]	1.4801(17)

[1] $1-x, +y, 1/2-z$

Table 5: Bond Angles in ° for **Compound 5**.

–Atoms–	**Angle/°**	**–Atoms–**	**Angle/°**
N1 – C1– C2	114.03(11)	C14– C9 – C8	121.24(13)
C3 – C2– C1	112.80(11)	C11– C10– C9	120.98(14)
N2 – C3– C2	112.32(11)	C10– C11– C12	119.81(16)
N2 – C4– C5	111.95(11)	C13– C12– C11	119.85(15)
N1[1]– C5– C4	112.88(11)	C12– C13– C14	120.00(15)
C7 – C6– C6[1]	110.01(8)	C13– C14– C9	121.12(15)
N2 – C6– C6[1]	111.32(9)	C1 – N1 – C5[1]	111.42(10)
N2 – C6– C7	111.93(10)	C1 – N1 – C8	113.40(10)

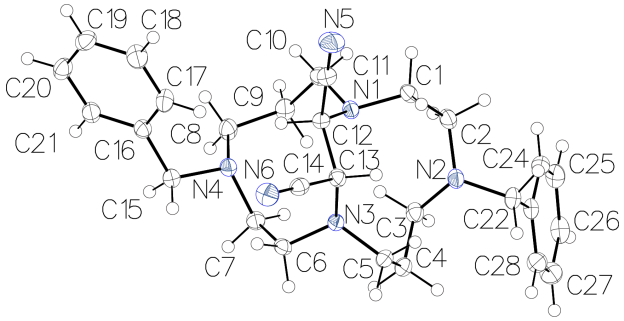
N3 – C7– C6	175.29(14)	C8 – N1 – C5[1]	112.98(10)
N1 – C8– C9	110.99(11)	C4 – N2 – C3	115.24(10)
C10– C9– C8	120.51(12)	C6 – N2 – C3	114.29(10)
C10– C9– C14	118.23(14)	C6 – N2 – C4	112.38(10)

[1] $1-x,+y,1/2-z$

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2\times 10^3$) for **Compound 5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	**U(eq)**
H1A	6590	7126	3085	23
H1B	5748	6512	2705	23
H2A	6894	6104	2048	23
H2B	7443	5122	2582	23
H3A	6859	3162	1810	21
H3B	6578	2669	2506	21
H4A	5307	3130	1063	22
H4B	5977	4698	1152	22
H5A	4900	6609	1431	22
H5B	4567	5653	807	22
H6	4534	2211	1910	19
H8A	6915	5602	4114	24
H8B	7329	4334	3606	24
H10	6791	1164	3598	29
H11	6445	−1222	4219	40
H12	6083	−806	5269	44
H13	6076	1991	5690	42
H14	6409	4371	5066	32

Summary



Crystal Data: $C_{28}H_{36}N_6$, $M_r = 456.63$, monoclinic, $P2_1/c$ (No. 14), a = 9.3978(4) Å, b = 7.9771(3) Å, c = 33.7475(14) Å, $\beta = 96.7820(10)°$, $\alpha = \gamma = 90°$, $V = 2512.25(18)$ Å^3, $T = 115(2)$ K, $Z = 4$, $Z' = 1$, $\mu(\mathrm{MoK}_\alpha) = 0.074$, 10092 reflections measured, 5662 unique (Rint = 0.0416) which were used in all calculations. The final $wR2$ was 0.1296 (all data) and R_1 was 0.0627 ($I > 2\sigma(I)$).

Experimental: Single clear light colourless Prism-shaped crystals of (**5b**) were recrystallised from a mixture of ethanol and ether by slow evaporation. A suitable crystal (0.20×0.12×0.12) was selected and mounted on a mylar loop oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at $T = 115(2)$ K during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the ShelXT (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of ShelXL (Sheldrick, 2008) using Least Squares minimisation.

Compound	**5b**
Formula	$C_{28}H_{36}N_6$
$D_{calc.}/gcm^{-3}$	1.207
mu/mm^{-1}	0.074
Formula Weight	456.63
Colour	clear light colourless
Shape	Prism
Max Size/mm	0.20
Mid Size/mm	0.12
Min Size/mm	0.12
T/K	115(2)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	9.3978(4)
b/Å	7.9771(3)
c/Å	33.7475(14)
α/°	90
β/°	96.7820(10)
γ/°	90
V/Å^3	2512.25(18)
Z	4
Z'	1
Θ_{min}/°	2.182
Θ_{max}/°	27.452
Measured Refl.	10092
Independent Refl.	5662
Reflections Used	4480
Rint	0.0416
Parameters	307
Restraints	0
Largest Peak	0.243
Deepest Hole	-0.260
GooF	1.096
$wR2$ (all data)	0.1296
$wR2$	0.1190
R_1 (all data)	0.0832
R_1	0.0627

Data Quality	d min 0.77	I/σ 13.7	Rint 4.16%	complete 99%
Refinement Quality	Shift 0.000	Max Peak 0.2	Min Peak -0.3	GooF 1.096

Extended Experimental

Experimental Extended: A clear light colourless Prism-shaped crystal with dimensions 0.20×0.12×0.12 was mounted on a mylar loop oil. Data were collected using a Nonius Kappa Apex II diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 115(2)$ K.

Data were measured using ϕ and ω scans using MoK$_\alpha$ radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000). The actually achieved resolution was $\Theta = 27.452$.

Cell parameters were retrieved using the SCALEPACK (Otwinowski and Minor, 1997) software and refined using DENZO (Otwinowski and Minor, 1997) on 5133 reflections, 51% of the observed reflections. Data reduction was performed using the DENZO (Otwinowski and Minor, 1997) software which corrects for Lorentz polarisation. The final completeness is 99.10% out to 27.452 in Θ. No absoprtion correction was performed. The absorption coefficient (μ) of this material is 0.074.

The structure was solved in the space group $P2_1/c$ (# 14) by Direct Methods using the ShelXT (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2014/7 of ShelXL (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Table 2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
C1	9371(2)	8602(3)	9488.3(6)	23.2(4)
C2	8531(2)	7022(3)	9566.9(6)	23.9(4)
C3	7115(2)	6244(3)	8938.0(6)	22.2(4)
C4	5955(2)	6949(3)	8629.9(6)	24.5(5)
C5	6053(2)	8847(3)	8587.9(6)	22.3(4)
C6	7773(2)	9108(3)	8083.4(6)	20.1(4)
C7	8993(2)	7888(3)	8039.7(6)	21.5(4)
C8	11 508(2)	7410(3)	8305.1(6)	24.9(5)
C9	11 258(2)	6627(3)	8704.2(6)	25.0(5)
C10	11 233(2)	7781(3)	9065.3(6)	24.8(4)
C11	10 370(2)	11 689(3)	9150.1(6)	23.7(4)
C12	9757(2)	10 260(3)	8895.8(6)	19.3(4)
C13	8170(2)	10 708(3)	8725.6(6)	19.7(4)
C14	8232(2)	12 298(3)	8492.7(6)	21.3(4)
C15	10 869(2)	9468(3)	7789.4(6)	23.5(4)
C16	12 176(2)	10 577(3)	7873.2(6)	22.2(4)
C17	12 208(2)	11 901(3)	8143.6(6)	27.2(5)
C18	13 389(2)	12 948(3)	8206.6(7)	31.1(5)
C19	14 553(2)	12 709(3)	7993.6(7)	29.0(5)
C20	14 524(2)	11 424(3)	7719.8(7)	28.1(5)
C21	13 344(2)	10 354(3)	7662.1(6)	24.9(5)
C22	5946(2)	6393(3)	9548.8(6)	21.8(4)
C23	5811(2)	4501(3)	9578.5(6)	19.4(4)
C24	6806(2)	3546(3)	9822.0(6)	22.8(4)

C25	6689(2)	1814(3)	9832.7(7)	26.7(5)
C26	5591(2)	1003(3)	9598.8(7)	27.9(5)
C27	4591(2)	1930(3)	9358.9(7)	29.9(5)
C28	4701(2)	3670(3)	9351.9(6)	25.2(5)
N1	9867.2(17)	8657(2)	9090.8(5)	19.1(3)
N2	7110.5(18)	7007(2)	9332.7(5)	20.5(4)
N3	7467.4(17)	9382(2)	8493.0(5)	19.2(3)
N4	10 430.1(17)	8643(2)	8145.1(5)	19.4(3)
N5	10 841(2)	12 761(3)	9347.3(6)	35.9(5)
N6	8314(2)	13 445(2)	8292.2(6)	30.0(4)

Table 3: Anisotropic Displacement Parameters ($\times 10^4$) **5b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2 \times U_{11} + ... + 2hka* \times b* \times U_{12}]$

Atom	$\mathbf{U}_{11}$	$\mathbf{U}_{22}$	$\mathbf{U}_{33}$	$\mathbf{U}_{23}$	$\mathbf{U}_{13}$	$\mathbf{U}_{12}$
C1	26.4(10)	27.7(11)	15.4(9)	−2.1(8)	2.1(8)	−3.5(9)
C2	28.1(10)	26.4(11)	17.5(9)	2.9(8)	3.6(8)	−3.1(9)
C3	25.1(10)	20.1(10)	22(1)	0.4(8)	5.4(8)	−4.0(8)
C4	23.6(10)	28.7(12)	21.4(10)	1.1(9)	3.8(8)	−9.6(9)
C5	17.6(9)	27.1(11)	22(1)	3.8(9)	2.2(8)	−3.4(8)
C6	22.1(9)	21.9(10)	15.8(9)	−1.2(8)	0.0(7)	−4.1(8)
C7	23.9(10)	19.9(10)	20.7(10)	−2.2(8)	3.0(8)	−4.2(8)
C8	23.6(10)	28.1(12)	23.9(10)	2.2(9)	6.7(8)	6.0(9)
C9	24.3(10)	25.1(11)	26.0(11)	5.3(9)	5.3(8)	7.3(9)
C10	22.1(10)	28.6(11)	22.8(10)	5.3(9)	−0.2(8)	3.8(9)
C11	21.6(10)	26.1(11)	23.1(10)	−1.0(9)	1.7(8)	−2.1(9)
C12	17.9(9)	21.9(10)	18.0(9)	−1.2(8)	1.5(7)	−2.2(8)
C13	21.3(9)	20.1(10)	17.8(9)	−1.4(8)	3.2(7)	−1.6(8)
C14	19.2(9)	21.1(10)	23.3(10)	−3.2(9)	1.5(8)	−0.2(8)
C15	22.8(10)	28.8(11)	19.1(10)	1.2(9)	3.6(8)	−2.9(9)
C16	20.3(9)	26.6(11)	19.7(10)	4.3(8)	2.9(8)	1.7(8)
C17	27.7(10)	28.7(12)	27.0(11)	−1.0(9)	10.8(9)	−1.2(9)
C18	39.0(12)	27.1(12)	28.2(11)	−2.5(10)	7.6(9)	−5.9(10)
C19	22.7(10)	30.4(12)	33.2(12)	8.7(10)	0.6(9)	−5.4(9)
C20	20.3(10)	33.6(12)	31.2(11)	7.8(10)	6.8(8)	5.4(9)
C21	24.7(10)	28.5(12)	22(1)	2.7(9)	5.0(8)	3.1(9)
C22	24.8(10)	18.5(10)	23.4(10)	1.6(8)	8.8(8)	−0.2(8)
C23	23.0(9)	18.3(10)	18.3(9)	0.8(8)	7.8(7)	−0.4(8)
C24	21.6(9)	24.6(11)	22.6(10)	1.4(8)	4.0(8)	−0.1(9)
C25	28.4(11)	23.8(11)	28.9(11)	8.2(9)	7.8(9)	6.7(9)
C26	41.0(12)	15.7(10)	29.4(11)	−0.3(9)	14.9(10)	0.0(9)
C27	34.5(12)	24.6(12)	30.1(12)	−1.5(9)	2.5(9)	−7.7(10)
C28	25.3(10)	24.3(11)	25.8(11)	3.9(9)	2.2(8)	0.9(9)
N1	19.5(8)	21.3(9)	16.7(8)	1.6(7)	3.3(6)	0.8(7)
N2	23.5(8)	20.7(9)	18.2(8)	0.6(7)	5.4(7)	−2.9(7)
N3	19.0(8)	22.4(9)	16.6(8)	−1.2(7)	3.0(6)	−4.3(7)
N4	20.4(8)	20.5(9)	17.6(8)	1.0(7)	2.8(6)	−1.7(7)
N5	37.5(11)	35.2(11)	33.4(11)	−7.4(9)	−2.4(9)	−8.9(9)
N6	34.1(10)	23.5(10)	32.2(10)	2.3(8)	2.8(8)	−0.5(8)

Table 4: Bond Lengths in Å for **5b**.

Atoms	Length/Å	Atoms	Length/Å
C1 –C2	1.527(3)	C13–N3	1.431(2)
C1 –N1	1.472(2)	C14–N6	1.146(3)
C2 –N2	1.469(2)	C15–C16	1.513(3)
C3 –C4	1.523(3)	C15–N4	1.470(2)
C3 –N2	1.465(3)	C16–C17	1.393(3)
C4 –C5	1.525(3)	C16–C21	1.389(3)
C5 –N3	1.467(2)	C17–C18	1.386(3)
C6 –C7	1.524(3)	C18–C19	1.391(3)
C6 –N3	1.461(2)	C19–C20	1.378(3)
C7 –N4	1.483(2)	C20–C21	1.394(3)
C8 –C9	1.528(3)	C22–C23	1.519(3)
C8 –N4	1.468(3)	C22–N2	1.469(2)
C9 –C10	1.530(3)	C23–C24	1.396(3)
C10–N1	1.472(3)	C23–C28	1.388(3)
C11–C12	1.500(3)	C24–C25	1.387(3)
C11–N5	1.141(3)	C25–C26	1.384(3)
C12–C13	1.575(3)	C26–C27	1.380(3)
C12–N1	1.437(3)	C27–C28	1.391(3)
C13–C14	1.497(3)	–	

Table 5: Bond Angles in ° for **5b**.

–Atoms–	Angle/°	–Atoms–	Angle/°
N1 –C1 –C2	114.10(17)	C20–C19–C18	119.6(2)
N2 –C2 –C1	111.65(17)	C19–C20–C21	120.1(2)
N2 –C3 –C4	112.87(17)	C16–C21–C20	120.9(2)
C3 –C4 –C5	112.57(17)	N2 –C22–C23	115.90(17)
N3 –C5 –C4	112.06(17)	C24–C23–C22	121.73(19)
N3 –C6 –C7	114.93(16)	C28–C23–C22	120.13(18)
N4 –C7 –C6	113.05(16)	C28–C23–C24	118.12(19)
N4 –C8 –C9	115.27(17)	C25–C24–C23	120.6(2)
C8 –C9 –C10	118.29(19)	C26–C25–C24	120.5(2)
N1 –C10–C9	115.32(16)	C27–C26–C25	119.6(2)
N5 –C11–C12	179.1(2)	C26–C27–C28	119.9(2)
C11–C12–C13	108.63(16)	C23–C28–C27	121.3(2)
N1 –C12–C11	114.35(16)	C1 –N1 –C10	114.29(16)
N1 –C12–C13	112.49(16)	C12–N1 –C1	115.51(16)
C14–C13–C12	106.83(16)	C12–N1 –C10	114.29(16)
N3 –C13–C12	112.86(16)	C3 –N2 –C2	113.10(16)
N3 –C13–C14	112.46(16)	C3 –N2 –C22	113.28(16)
N6 –C14–C13	174.9(2)	C22–N2 –C2	114.75(16)
N4 –C15–C16	114.15(16)	C6 –N3 –C5	116.60(15)
C17–C16–C15	121.30(19)	C13–N3 –C5	117.80(16)
C21–C16–C15	120.15(19)	C13–N3 –C6	119.99(16)
C21–C16–C17	118.4(2)	C8 –N4 –C7	112.68(17)

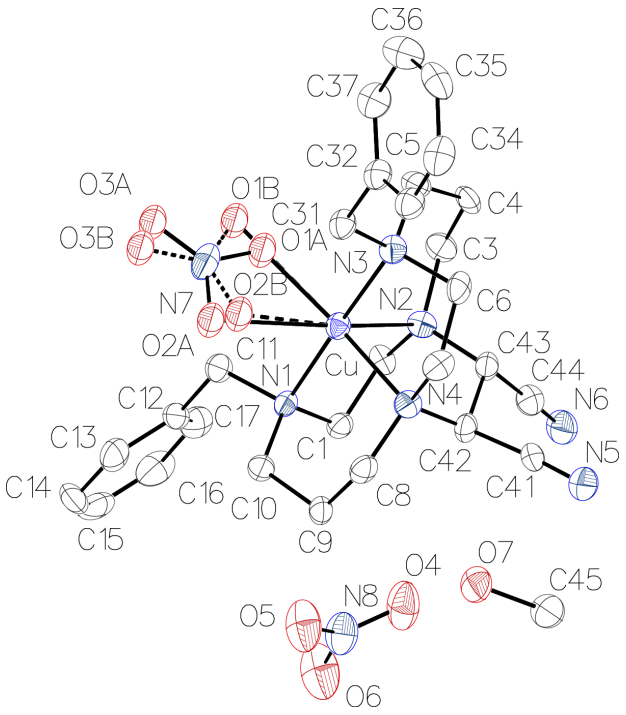
C18– C17– C16	120.8(2)	C8 –N4 –C15	110.62(16)
C17– C18– C19	120.2(2)	C15– N4 –C7	108.75(15)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2\times 10^3$) for **5b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
H1A	8758	9592	9518	28
H1B	10 214	8685	9693	28
H2A	9077	6024	9498	29
H2B	8418	6958	9854	29
H3A	6975	5019	8960	27
H3B	8062	6431	8845	27
H4A	5003	6654	8708	29
H4B	6038	6421	8368	29
H5A	5312	9230	8374	27
H5B	5856	9383	8840	27
H6A	8010	10 201	7968	24
H6B	6894	8683	7925	24
H7A	8895	6905	8213	26
H7B	8912	7486	7760	26
H8A	12 458	7962	8337	30
H8B	11 540	6501	8107	30
H9A	12 015	5777	8773	30
H9B	10 331	6023	8665	30
H10A	11 465	7107	9311	30
H10B	11 998	8631	9059	30
H12	10 319	10 187	8663	23
H13	7620	10 933	8956	24
H15A	10 061	10 156	7664	28
H15B	11 070	8597	7595	28
H17	11 410	12 087	8287	33
H18	13 404	13 832	8396	37
H19	15 363	13 427	8037	35
H20	15 309	11 267	7570	34
H21	13 339	9460	7476	30
H22A	5029	6842	9416	26
H22B	6085	6859	9823	26
H24	7570	4087	9982	27
H25	7368	1180	10 002	32
H26	5525	−185	9603	33
H27	3830	1383	9199	36
H28	4001	4300	9189	30

Compound [5Cu](NO$_3$)$_2$, MeOH Olex2

Summary



Crystal Data: $C_{29}H_{40}CuN_8O_7$, $M_r = 676.23$, orthorhombic, $P2_12_12_1$ (No. 19), a = 9.0052(3) Å, b = 14.4455(4) Å, c = 23.8253(7) Å, $\alpha = \beta = \gamma = 90°$, $V = 3099.30(16)$ Å^3, $T = 115(2)$ K, $Z = 4$, $Z' = 1$, μ(MoK$_\alpha$) = 0.764, 7065 reflections measured, 7065 unique which were used in all calculations. The final $wR2$ was 0.1621 (all data) and R_1 was 0.0778 ($I > 2\sigma(I)$).

Experimental: Single clear light blue Prism-shaped crystals of (**Compound [5Cu](NO$_3$)$_2$, MeOH**) were recrystallised from methanol by slow evaporation. A suitable crystal (0.20×0.05×0.05) was selected and mounted on a mylar loop oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at $T = 115(2)$ K during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the ShelXT (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of ShelXL (Sheldrick, 2008) using Least Squares minimisation.

Compound	**Compound [5Cu](NO$_3$)$_2$, MeOH**
Formula	$C_{29}H_{40}CuN_8O_7$
$D_{calc.}/gcm^{-3}$	1.449
mu/mm^{-1}	0.764
Formula Weight	676.23
Colour	clear light blue
Shape	Prism
Max Size/mm	0.20
Mid Size/mm	0.05
Min Size/mm	0.05
T/K	115(2)
Crystal System	orthorhombic
Flack Parameter	0.04(3)
Hooft Parameter	0.052(7)
Space Group	$P2_12_12_1$
a/Å	9.0052(3)
b/Å	14.4455(4)
c/Å	23.8253(7)
α/°	90
β/°	90
γ/°	90
V/Å^3	3099.30(16)
Z	4
Z'	1
Θ_{min}/°	1.649
Θ_{max}/°	27.484
Measured Refl.	7065
Independent Refl.	7065
Reflections Used	5738
Rint	.
Parameters	406
Restraints	0
Largest Peak	0.601
Deepest Hole	-0.456
GooF	1.224
$wR2$ (all data)	0.1621
$wR2$	0.1406
R_1 (all data)	0.1114
R_1	0.0778

Extended Experimental

Experimental Extended: A clear light blue Prism-shaped crystal with dimensions 0.20×0.05×0.05 was mounted on a mylar loop oil. Data were collected using a Nonius Kappa Apex II diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at $T = 115(2)$ K.

Data were measured using ϕ and ω scans using MoK$_\alpha$ radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000). The actually achieved resolution was $\Theta = 27.484$.

Cell parameters were retrieved using the SCALEPACK (Otwinowski and Minor, 1997) software and refined using DENZO (Otwinowski and Minor, 1997) on 3978 reflections, 56% of the observed reflections. Data reduction was performed using the DENZO (Otwinowski and Minor, 1997) software which corrects for Lorentz polarisation. The final completeness is 99.90% out to 27.484 in Θ. No absoprtion correction was performed. The absorption coefficient (μ) of this material is 0.764.

The structure was solved in the space group $P2_12_12_1$ (# 19) by Direct Methods using the ShelXT (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2014/7 of ShelXL (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Similar Uij constraints were applied within the disordered (58(1)/42(1)) nitrate counterion parts to maintain a reasonable model by using EADP constraints.

The Flack parameter was refined to 0.04(3). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.052(7). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2\times 10^3$) for **Compound [5Cu](NO$_3$)$_2$, MeOH**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
C1	8027(9)	7451(6)	6688(3)	24.9(18)
C2	9437(9)	7554(5)	6364(4)	24.2(17)
C3	10 860(10)	8621(6)	5781(4)	31(2)
C4	11 089(9)	9590(6)	5546(4)	28.7(19)
C5	9782(10)	10 087(6)	5284(4)	29.7(19)
C6	9031(10)	10 906(6)	6151(3)	30.3(19)
C7	7938(10)	10 825(6)	6628(3)	29.5(19)
C8	6292(10)	9732(6)	7102(4)	28(2)
C9	5798(9)	8756(6)	7240(3)	27.0(18)
C10	5497(9)	8108(6)	6745(3)	25.1(17)
C11	6261(10)	7253(5)	5904(3)	26.8(18)
C12	5670(10)	6319(6)	6091(4)	30.4(19)
C13	4142(11)	6196(7)	6166(4)	40(2)
C14	3574(13)	5346(9)	6333(4)	54(3)
C15	4526(16)	4624(8)	6442(4)	54(3)
C16	6006(15)	4732(7)	6368(4)	49(3)
C17	6611(12)	5568(6)	6185(4)	37(2)
C31	7320(10)	10 833(6)	5345(3)	27.8(17)
C32	7754(10)	11 781(5)	5123(3)	28.2(18)
C33	7496(12)	12 590(5)	5436(3)	32.6(18)
C34	7870(11)	13 449(6)	5210(4)	38(2)
C35	8470(10)	13 521(7)	4682(5)	40(2)
C36	8685(12)	12 731(7)	4369(5)	46(3)

C37	8314(11)	11 867(7)	4595(4)	37(2)
C41	9558(9)	10 106(6)	7551(4)	27.1(18)
C42	8996(10)	9450(6)	7128(4)	26.7(19)
C43	10 305(8)	9073(6)	6758(3)	24.8(16)
C44	11 292(10)	8524(7)	7121(4)	32(2)
C45	9689(11)	8485(8)	8646(4)	43(2)
N1	6780(8)	7895(5)	6373(3)	23.3(15)
N2	9781(8)	8564(5)	6255(3)	25.2(15)
N3	8510(8)	10 317(5)	5669(3)	26.1(16)
N4	7729(8)	9833(4)	6788(3)	25.1(14)
N5	9967(10)	10 577(6)	7903(3)	40(2)
N6	12 040(9)	8084(6)	7402(3)	42(2)
N7	5647(10)	8960(5)	5147(3)	37.7(19)
N8	7092(10)	6185(6)	8123(4)	45(2)
O1A	7048(13)	8784(8)	5241(5)	36.7(14)
O2A	4937(13)	9291(9)	5575(5)	36.7(14)
O3A	5046(13)	8830(9)	4706(5)	36.7(14)
O1B	6869(18)	8653(12)	4945(7)	36.7(14)
O2B	5609(18)	9238(13)	5620(7)	36.7(14)
O3B	4467(19)	8933(12)	4847(7)	36.7(14)
O4	8348(8)	6523(6)	8125(4)	58(2)
O5	6022(9)	6642(5)	7957(4)	61(2)
O6	6931(9)	5382(5)	8307(4)	69(3)
O7	8568(8)	8378(5)	8236(3)	45.8(18)
Cu	7616.4(11)	9116.6(6)	6012.6(4)	22.8(2)

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) **Compound [5Cu](NO$_3$)$_2$, MeOH**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2 \times U_{11} + ... + 2hka* \times b* \times U_{12}]$

Atom	**U$_{11}$**	**U$_{22}$**	**U$_{33}$**	**U$_{23}$**	**U$_{13}$**	**U$_{12}$**
C1	29(5)	25(4)	21(4)	−1(3)	−1(3)	−3(3)
C2	20(4)	18(4)	34(4)	1(3)	1(3)	1(3)
C3	25(5)	33(5)	34(5)	−2(4)	6(4)	5(4)
C4	15(4)	38(5)	33(5)	6(4)	2(3)	−4(4)
C5	29(5)	32(5)	28(4)	1(4)	6(4)	−5(4)
C6	38(5)	20(4)	32(5)	1(4)	−11(3)	−9(4)
C7	41(5)	19(4)	28(4)	1(4)	−3(3)	3(4)
C8	28(5)	34(5)	23(4)	−10(4)	0(4)	4(4)
C9	20(4)	35(5)	26(4)	−5(4)	−2(3)	−2(4)
C10	21(4)	30(4)	24(4)	−4(3)	2(3)	2(3)
C11	30(4)	23(4)	27(5)	−4(3)	0(3)	−2(3)
C12	38(5)	29(4)	25(4)	−7(4)	5(4)	−14(4)
C13	38(5)	47(6)	34(5)	−17(4)	0(4)	−6(4)
C14	47(7)	74(8)	42(6)	−22(6)	19(5)	−40(6)
C15	94(10)	48(7)	21(5)	−6(5)	4(6)	−34(7)
C16	85(9)	26(5)	36(5)	5(4)	−11(6)	−9(5)
C17	48(6)	30(5)	32(5)	−5(4)	0(4)	−2(4)
C31	29(4)	25(4)	29(4)	4(3)	−7(4)	0(4)
C32	28(5)	27(4)	29(4)	4(3)	−6(4)	3(4)
C33	36(5)	30(4)	32(4)	0(3)	−3(5)	−2(5)
C34	43(6)	23(4)	47(5)	5(4)	−17(4)	6(4)

C35	27(5)	32(5)	61(7)	22(5)	−6(5)	−3(4)
C36	39(6)	49(6)	49(6)	16(5)	9(5)	12(5)
C37	38(6)	33(5)	41(5)	2(4)	−5(4)	7(4)
C41	23(4)	29(4)	29(4)	−2(4)	0(4)	−8(4)
C42	29(5)	26(4)	26(4)	−3(3)	−5(4)	−8(4)
C43	24(4)	25(4)	25(4)	0(4)	−5(3)	−4(4)
C44	25(5)	37(5)	33(5)	−1(4)	−1(4)	−1(4)
C45	33(5)	54(6)	42(6)	17(5)	−7(4)	4(5)
N1	23(4)	27(4)	20(3)	−4(3)	−3(3)	−2(3)
N2	26(4)	22(3)	27(4)	2(3)	3(3)	3(3)
N3	28(4)	23(3)	28(4)	3(3)	−3(3)	1(3)
N4	30(4)	19(3)	26(3)	0(2)	−1(3)	−1(3)
N5	42(5)	42(5)	36(4)	−5(4)	−3(4)	−11(4)
N6	26(4)	56(5)	42(5)	11(4)	−5(4)	2(4)
N7	46(5)	32(4)	35(4)	1(3)	−17(4)	−4(4)
N8	37(5)	43(5)	56(5)	−3(4)	−12(4)	7(4)
O1A	35(4)	40(3)	34(3)	−2(2)	−9(3)	−5(3)
O2A	35(4)	40(3)	34(3)	−2(2)	−9(3)	−5(3)
O3A	35(4)	40(3)	34(3)	−2(2)	−9(3)	−5(3)
O1B	35(4)	40(3)	34(3)	−2(2)	−9(3)	−5(3)
O2B	35(4)	40(3)	34(3)	−2(2)	−9(3)	−5(3)
O3B	35(4)	40(3)	34(3)	−2(2)	−9(3)	−5(3)
O4	33(4)	69(6)	73(6)	−24(5)	−12(4)	11(4)
O5	46(5)	43(4)	93(7)	15(4)	−26(5)	5(4)
O6	49(5)	45(5)	114(7)	21(5)	−26(5)	7(4)
O7	39(4)	53(4)	45(4)	18(4)	−15(3)	−6(3)
Cu	24.5(5)	20.5(4)	23.3(4)	−0.2(4)	−2.6(4)	−1.0(4)

Table 3: Bond Lengths in Å for **Compound [5Cu](NO$_3$)$_2$, MeOH**.

Atoms	**Length/Å**	**Atoms**	**Length/Å**
C1 –C2	1.492(11)	C35 –C36	1.378(15)
C1 –N1	1.495(10)	C36 –C37	1.399(13)
C2 –N2	1.515(10)	C41 –C42	1.474(11)
C3 –C4	1.522(12)	C41 –N5	1.141(11)
C3 –N2	1.492(10)	C42 –C43	1.569(12)
C4 –C5	1.513(12)	C42 –N4	1.504(11)
C5 –N3	1.504(11)	C43 –C44	1.471(12)
C6 –C7	1.508(11)	C43 –N2	1.484(10)
C6 –N3	1.504(10)	C44 –N6	1.143(11)
C7 –N4	1.495(10)	C45 –O7	1.414(11)
C8 –C9	1.516(12)	N1 –Cu	2.102(7)
C8 –N4	1.502(11)	N2 –Cu	2.184(7)
C9 –C10	1.528(11)	N3 –Cu	2.079(7)
C10–N1	1.489(10)	N4 –Cu	2.120(6)
C11–C12	1.518(11)	N7 –O1A	1.307(14)
C11–N1	1.526(10)	N7 –O2A	1.294(15)
C12–C13	1.399(13)	N7 –O3A	1.197(14)
C12–C17	1.395(13)	N7 –O1B	1.281(18)
C13–C14	1.389(15)	N7 –O2B	1.198(19)
C14–C15	1.376(18)	N7 –O3B	1.281(18)

C15–C16	1.353(17)	N8 –O4	1.232(11)
C16–C17	1.395(13)	N8 –O5	1.233(11)
C31–C32	1.519(11)	N8 –O6	1.248(11)
C31–N3	1.518(10)	O1A–Cu	1.968(11)
C32–C33	1.405(11)	O2A–Cu	2.641(12)
C32–C37	1.361(13)	O1B–Cu	2.715(16)
C33–C34	1.394(11)	O2B–Cu	2.042(16)
C34–C35	1.373(14)	–	

Table 4: Bond Angles in ° for **Compound [5Cu](NO$_3$)$_2$, MeOH**.

–Atoms–	Angle/°	–Atoms–	Angle/°
C2 – C1 – N1	109.7(6)	C5 – N3 – C31	109.6(6)
C1 – C2 – N2	111.0(6)	C5 – N3 – Cu	110.5(5)
N2 – C3 – C4	114.7(7)	C6 – N3 – C31	109.3(6)
C5 – C4 – C3	118.8(8)	C6 – N3 – Cu	107.0(5)
N3 – C5 – C4	116.5(7)	C31 – N3 – Cu	109.7(5)
N3 – C6 – C7	109.2(7)	C7 – N4 – C8	109.2(6)
N4 – C7 – C6	110.4(7)	C7 – N4 – C42	113.3(6)
N4 – C8 – C9	116.8(7)	C7 – N4 – Cu	104.6(4)
C8 – C9 – C10	117.1(7)	C8 – N4 – C42	110.5(6)
N1 – C10– C9	116.6(7)	C8 – N4 – Cu	110.2(5)
C12– C11– N1	115.6(7)	C42 – N4 – Cu	109.0(5)
C13– C12– C11	119.7(9)	O2A– N7 – O1A	114.5(9)
C17– C12– C11	121.8(8)	O3A– N7 – O1A	123.8(11)
C17– C12– C13	118.5(9)	O3A– N7 – O2A	121.7(11)
C14– C13– C12	120.8(10)	O1B– N7 – O3B	119.5(12)
C15– C14– C13	119.7(10)	O2B– N7 – O1B	119.7(12)
C16– C15– C14	120.1(10)	O2B– N7 – O3B	120.8(13)
C15– C16– C17	121.7(11)	O4 – N8 – O5	120.5(9)
C16– C17– C12	119.1(10)	O4 – N8 – O6	118.3(9)
N3 – C31– C32	116.0(7)	O5 – N8 – O6	121.2(10)
C33– C32– C31	121.5(8)	N7 – O1A– Cu	111.3(8)
C37– C32– C31	119.9(8)	N7 – O2A– Cu	79.9(7)
C37– C32– C33	118.4(8)	N7 – O1B– Cu	77.0(8)
C34– C33– C32	119.7(8)	N7 – O2B– Cu	112.1(12)
C35– C34– C33	121.1(9)	N1 – Cu – N2	84.5(3)
C34– C35– C36	119.3(9)	N1 – Cu – N4	94.1(2)
C35– C36– C37	119.7(10)	N1 – Cu – O2A	85.1(3)
C32– C37– C36	121.8(9)	N1 – Cu – O1B	95.0(4)
N5 – C41– C42	175.9(9)	N2 – Cu – O2A	162.7(3)
C41– C42– C43	110.4(7)	N2 – Cu – O1B	112.3(4)
C41– C42– N4	113.1(7)	N3 – Cu – N1	178.1(3)
N4 – C42– C43	113.3(7)	N3 – Cu – N2	93.6(3)
C44– C43– C42	108.2(7)	N3 – Cu – N4	85.3(3)
C44– C43– N2	113.5(7)	N3 – Cu – O2A	96.8(3)
N2 – C43– C42	112.7(6)	N3 – Cu – O1B	86.1(4)
N6 – C44– C43	178.7(10)	N4 – Cu – N2	84.6(3)
C1 – N1 – C11	109.7(6)	N4 – Cu – O2A	110.0(4)

C1 – N1 – Cu	107.2(5)	N4 – Cu – O1B	161.6(4)
C10 – N1 – C1	112.0(6)	O1A – Cu – N1	94.8(4)
C10 – N1 – C11	108.9(6)	O1A – Cu – N2	112.9(4)
C10 – N1 – Cu	110.3(5)	O1A – Cu – N3	86.3(4)
C11 – N1 – Cu	108.7(5)	O1A – Cu – N4	161.0(4)
C2 – N2 – Cu	102.4(5)	O1A – Cu – O2A	54.3(4)
C3 – N2 – C2	108.4(6)	O2B – Cu – N1	86.7(6)
C3 – N2 – Cu	111.2(5)	O2B – Cu – N2	160.5(5)
C43 – N2 – C2	113.8(6)	O2B – Cu – N3	95.2(6)
C43 – N2 – C3	112.2(7)	O2B – Cu – N4	113.5(6)
C43 – N2 – Cu	108.4(5)	O2B – Cu – O1B	51.2(6)
C5 – N3 – C6	110.6(7)	– –	

Table 5: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **Compound [5Cu](NO$_3$)$_2$, MeOH**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
H1A	8134	7746	7060	30
H1B	7809	6786	6746	30
H2A	9348	7222	6002	29
H2B	10 263	7271	6578	29
H3A	10 511	8213	5474	37
H3B	11 830	8380	5911	37
H4A	11 470	9984	5854	34
H4B	11 883	9554	5259	34
H5A	10 147	10 671	5116	36
H5B	9396	9699	4975	36
H6A	9110	11 559	6030	36
H6B	10 024	10 697	6276	36
H7A	8307	11 179	6955	35
H7B	6972	11 093	6513	35
H8A	5499	10 031	6878	34
H8B	6378	10 081	7458	34
H9A	4880	8795	7467	32
H9B	6571	8467	7478	32
H10A	5108	7517	6896	30
H10B	4703	8387	6513	30
H11A	5473	7573	5689	32
H11B	7104	7148	5645	32
H13	3486	6700	6102	48
H14	2532	5263	6371	65
H15	4145	4048	6570	65
H16	6649	4225	6443	58
H17	7650	5624	6124	44
H31A	6443	10 908	5591	33
H31B	7012	10 445	5022	33
H33	7070	12 552	5800	39
H34	7707	13 994	5424	45
H35	8733	14 109	4534	48

H36	9085	12 771	4000	55
H37	8457	11 327	4374	45
H42	8592	8908	7339	32
H43	10 885	9620	6624	30
H45A	9802	9142	8738	65
H45B	10 631	8244	8500	65
H45C	9413	8141	8985	65
H7	8502	7817	8145	69

Table 6: Hydrogen Bond information for **Compound [5Cu]$(NO_3)_2$, MeOH**.

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
O7	H7	O4	0.84	1.88	2.699(12)	166.6

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: compound_3

```
Bond precision:  C-C = 0.0037 A          Wavelength=0.71073

Cell:          a=8.8082(4)       b=11.1431(5)     c=13.3105(7)
               alpha=75.168(3)   beta=85.508(2)   gamma=72.535(2)
Temperature:   115 K
```

	Calculated	Reported
Volume	1204.68(10)	1204.68(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C27 H35 N5	C27 H35 N5
Sum formula	C27 H35 N5	C27 H35 N5
Mr	429.60	429.60
Dx,g cm-3	1.184	1.184
Z	2	2
Mu (mm-1)	0.071	0.071
F000	464.0	464.0
F000’	464.14	
h,k,lmax	11,14,17	11,14,17
Nref	5612	5483
Tmin,Tmax	0.985,0.989	
Tmin’	0.985	

```
Correction method= Not given

Data completeness= 0.977          Theta(max)= 27.626

R(reflections)= 0.0726( 4140)     wR2(reflections)= 0.1428( 5483)

S = 1.119                 Npar= 289
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C
PLAT410_ALERT_2_C Short Intra H...H Contact H4B .. H6B .. 1.99 Ang.

Alert level G
PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do !

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
1 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: compound_4

Bond precision: C-C = 0.0027 A Wavelength=0.71073

Cell: a=9.8695(3) b=12.1158(3) c=14.4185(5)
alpha=78.653(2) beta=80.247(1) gamma=73.002(2)
Temperature: 115 K

	Calculated	Reported
Volume	1605.02(9)	1605.02(9)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C15 H27 N5	C15 H27 N5
Sum formula	C15 H27 N5	C15 H27 N5
Mr	277.42	277.41
Dx,g cm-3	1.148	1.148
Z	4	4
Mu (mm-1)	0.072	0.072
F000	608.0	608.0
F000’	608.16	
h,k,lmax	12,15,18	12,15,18
Nref	7368	7301
Tmin,Tmax	0.988,0.994	
Tmin’	0.988	

Correction method= Not given

Data completeness= 0.991 Theta(max)= 27.506

R(reflections)= 0.0558(5760) wR2(reflections)= 0.1153(7301)

S = 1.093 Npar= 365

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do !
PLAT230_ALERT_2_G Hirshfeld Test Diff for C12B -- C13B .. 5.2 s.u.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 36 Note

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: compound_4Cu

Bond precision: C-C = 0.0140 A Wavelength=0.71073

Cell: a=16.103(5) b=14.421(5) c=18.511(5)
alpha=90 beta=90 gamma=90
Temperature: 298 K

	Calculated	Reported
Volume	4299(2)	4299(2)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C15 H31 Cu N5 O2, 2(N O3)	C15 H31 Cu N5 O2, 2(N O3)
Sum formula	C15 H31 Cu N7 O8	C15 H31 Cu N7 O8
Mr	501.02	501.01
Dx,g cm-3	1.548	1.548
Z	8	8
Mu (mm-1)	1.074	1.074
F000	2104.0	2104.0
F000’	2107.44	
h,k,lmax	20,18,24	20,18,24
Nref	4924	4897
Tmin,Tmax	0.860,0.898	
Tmin’	0.860	

Correction method= Not given

Data completeness= 0.995 Theta(max)= 27.482

R(reflections)= 0.1076(3820) wR2(reflections)= 0.2768(4897)

S = 1.139 Npar= 284

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT410_ALERT_2_B Short Intra H...H Contact H2C .. H4A .. 1.84 Ang.

Alert level C

RFACG01_ALERT_3_C The value of the R factor is > 0.10
R factor given 0.108
RFACR01_ALERT_3_C The value of the weighted R factor is > 0.25
Weighted R factor given 0.277
PLAT082_ALERT_2_C High R1 Value ..... 0.11 Report
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..... 0.28 Report
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.25 Report
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C8 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of Cu1 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of N6 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of N7 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.014 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H7A .. H9B .. 1.90 Ang.
PLAT414_ALERT_2_C Short Intra D-H..H-X H1B .. H15A .. 1.90 Ang.

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 31 Report
PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 4 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 31.02 Why ?
PLAT793_ALERT_4_G The Model has Chirality at N1 (Centro SPGR) S Verify
PLAT793_ALERT_4_G The Model has Chirality at N2 (Centro SPGR) S Verify
PLAT793_ALERT_4_G The Model has Chirality at N3 (Centro SPGR) S Verify
PLAT793_ALERT_4_G The Model has Chirality at N4 (Centro SPGR) S Verify
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1 (II) ..... 2.03 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 279 Note

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
12 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
9 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
6 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

Datablock: compound_5a

Bond precision: C-C = 0.0019 A Wavelength=0.71073

Cell: a=15.5335(5) b=7.6860(2) c=21.3414(7)
       alpha=90 beta=91.061(1) gamma=90
Temperature: 115 K

	Calculated	Reported
Volume	2547.52(13)	2547.52(13)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C28 H36 N6	C28 H36 N6
Sum formula	C28 H36 N6	C28 H36 N6
Mr	456.63	456.63
Dx,g cm-3	1.191	1.191
Z	4	4
Mu (mm-1)	0.073	0.073
F000	984.0	984.0
F000’	984.29	
h,k,lmax	20,9,27	20,9,27
Nref	2925	2920
Tmin,Tmax	0.978,0.991	
Tmin’	0.975	

Correction method= Not given

Data completeness= 0.998 Theta(max)= 27.511

R(reflections)= 0.0473(2510) wR2(reflections)= 0.1060(2920)

S = 1.093 Npar= 154

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 2 Report
PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do !
PLAT793_ALERT_4_G The Model has Chirality at C6 (Centro SPGR) R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 1 Note

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
4 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: compound_5b

Bond precision: C-C = 0.0030 A Wavelength=0.71073

Cell: a=9.3978(4) b=7.9771(3) c=33.7475(14)
alpha=90 beta=96.782(1) gamma=90
Temperature: 115 K

	Calculated	Reported
Volume	2512.25(18)	2512.25(18)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C28 H36 N6	C28 H36 N6
Sum formula	C28 H36 N6	C28 H36 N6
Mr	456.63	456.63
Dx,g cm-3	1.207	1.207
Z	4	4
Mu (mm-1)	0.074	0.074
F000	984.0	984.0
F000’	984.29	
h,k,lmax	12,10,43	12,10,43
Nref	5736	5662
Tmin,Tmax	0.989,0.991	
Tmin’	0.985	

Correction method= Not given

Data completeness= 0.987 Theta(max)= 27.452

R(reflections)= 0.0627(4480) wR2(reflections)= 0.1296(5662)

S = 1.096 Npar= 307

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do !
PLAT793_ALERT_4_G The Model has Chirality at C12 (Centro SPGR) S Verify
PLAT793_ALERT_4_G The Model has Chirality at C13 (Centro SPGR) S Verify

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: compound_5Cu

Bond precision: C-C = 0.0131 A Wavelength=0.71073

Cell: a=9.0052(3) b=14.4455(4) c=23.8253(7)
alpha=90 beta=90 gamma=90
Temperature: 115 K

	Calculated	Reported
Volume	3099.31(16)	3099.30(16)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C28 H36 Cu N7 O3, N O3, C H4 O	C28 H36 Cu N7 O3, C H4 O, N O3
Sum formula	C29 H40 Cu N8 O7	C29 H40 Cu N8 O7
Mr	676.24	676.23
Dx,g cm-3	1.449	1.449
Z	4	4
Mu (mm-1)	0.764	0.764
F000	1420.0	1420.0
F000’	1421.82	
h,k,lmax	11,18,30	11,18,30
Nref	7099[3989]	7065
Tmin,Tmax	0.955,0.963	
Tmin’	0.858	

Correction method= Not given

Data completeness= 1.77/1.00 Theta(max)= 27.484

R(reflections)= 0.0778(5738) wR2(reflections)= 0.1621(7065)

S = 1.224 Npar= 406

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT410_ALERT_2_B Short Intra H...H Contact H1A .. H42 .. 1.85 Ang.

Alert level C

PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of N8 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.01313 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H4A .. H6B .. 1.94 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H4A .. H43 .. 1.98 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H6B .. H43 .. 1.93 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H9B .. H42 .. 1.96 Ang.

Alert level G

PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 13.61 Why ?
PLAT300_ALERT_4_G Atom Site Occupancy of >O1A is Constrained at 0.58 Check
PLAT300_ALERT_4_G Atom Site Occupancy of >O2A is Constrained at 0.58 Check
PLAT300_ALERT_4_G Atom Site Occupancy of >O3A is Constrained at 0.58 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <O1B is Constrained at 0.42 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <O2B is Constrained at 0.42 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <O3B is Constrained at 0.42 Check
PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 8 Note
PLAT791_ALERT_4_G The Model has Chirality at N1 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G The Model has Chirality at N2 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G The Model has Chirality at N3 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G The Model has Chirality at N4 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G The Model has Chirality at C42 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G The Model has Chirality at C43 (Chiral SPGR) S Verify
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed .. ! Info

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6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
18 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
14 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

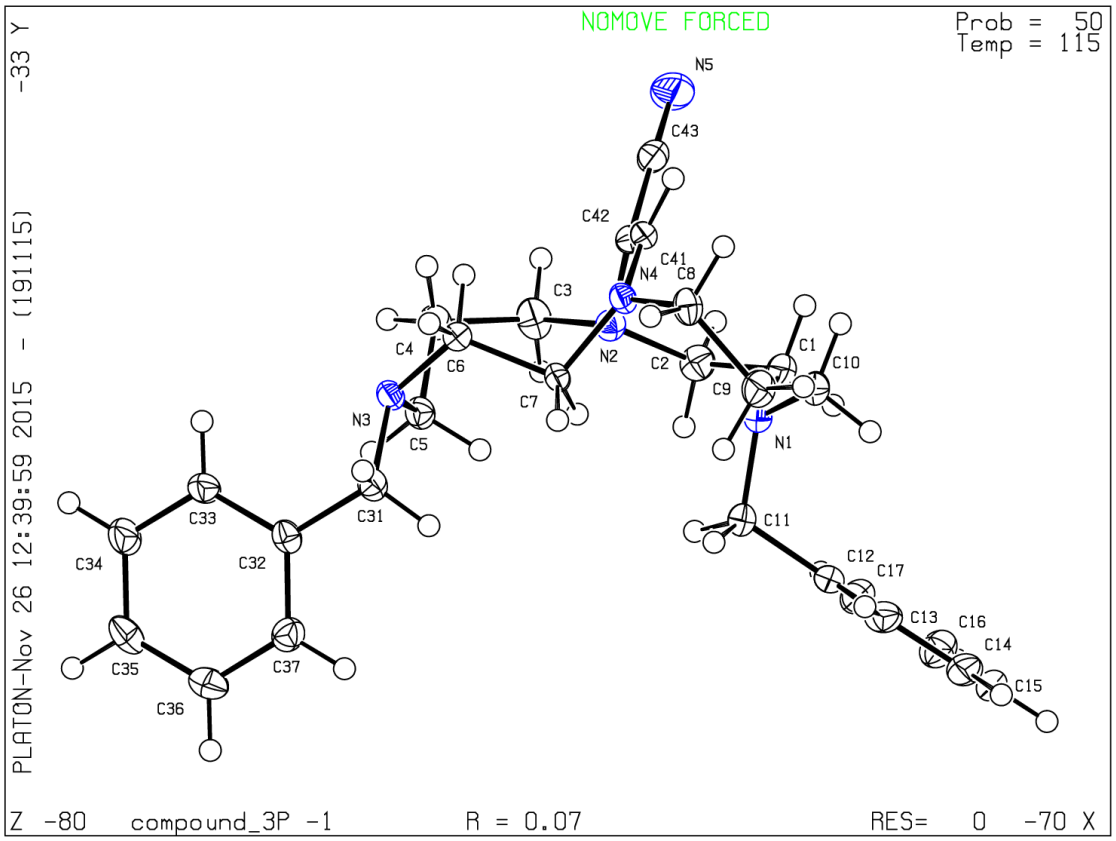
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

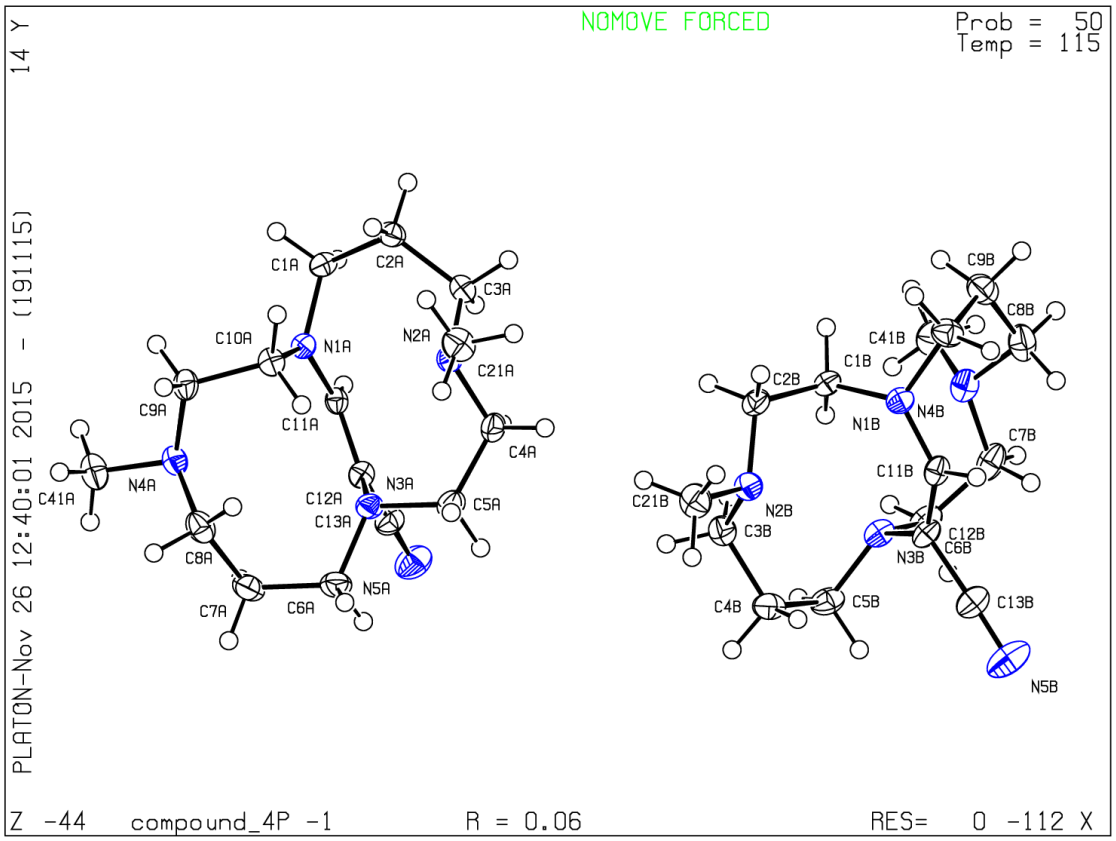
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/11/2015; check.def file version of 17/11/2015

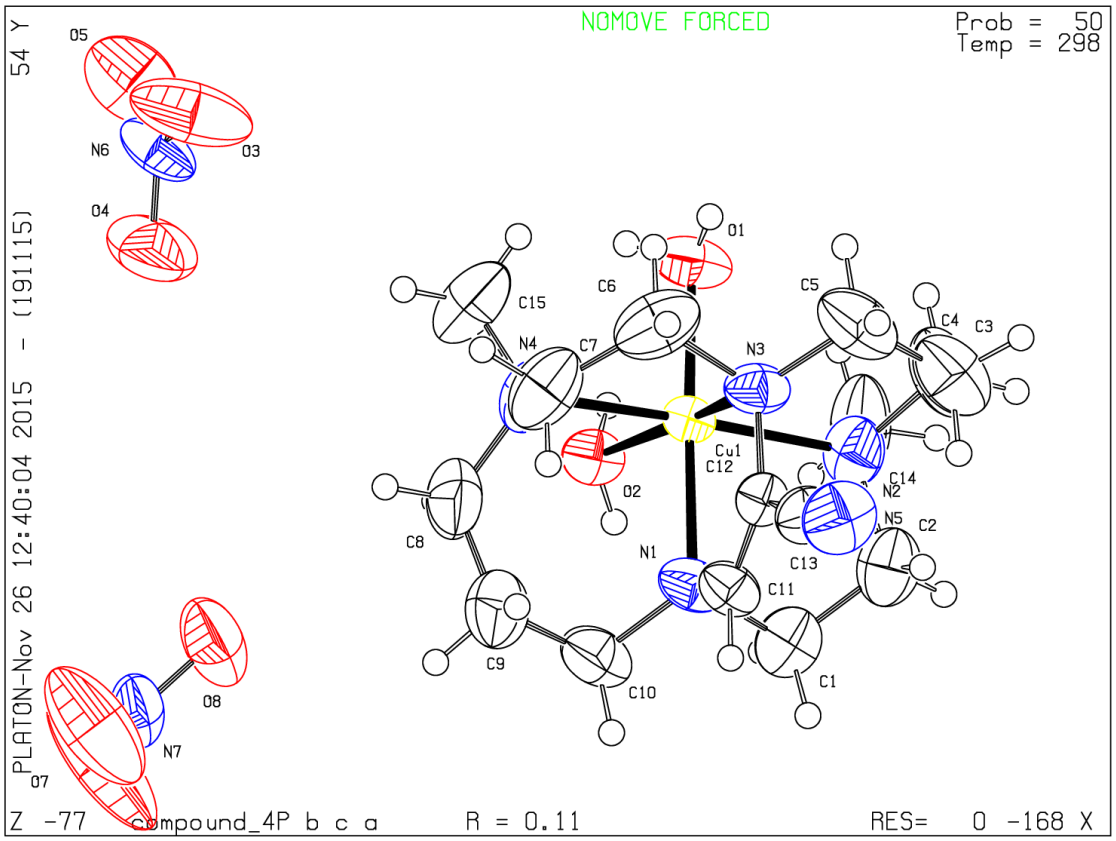
Datablock compound_3 - ellipsoid plot



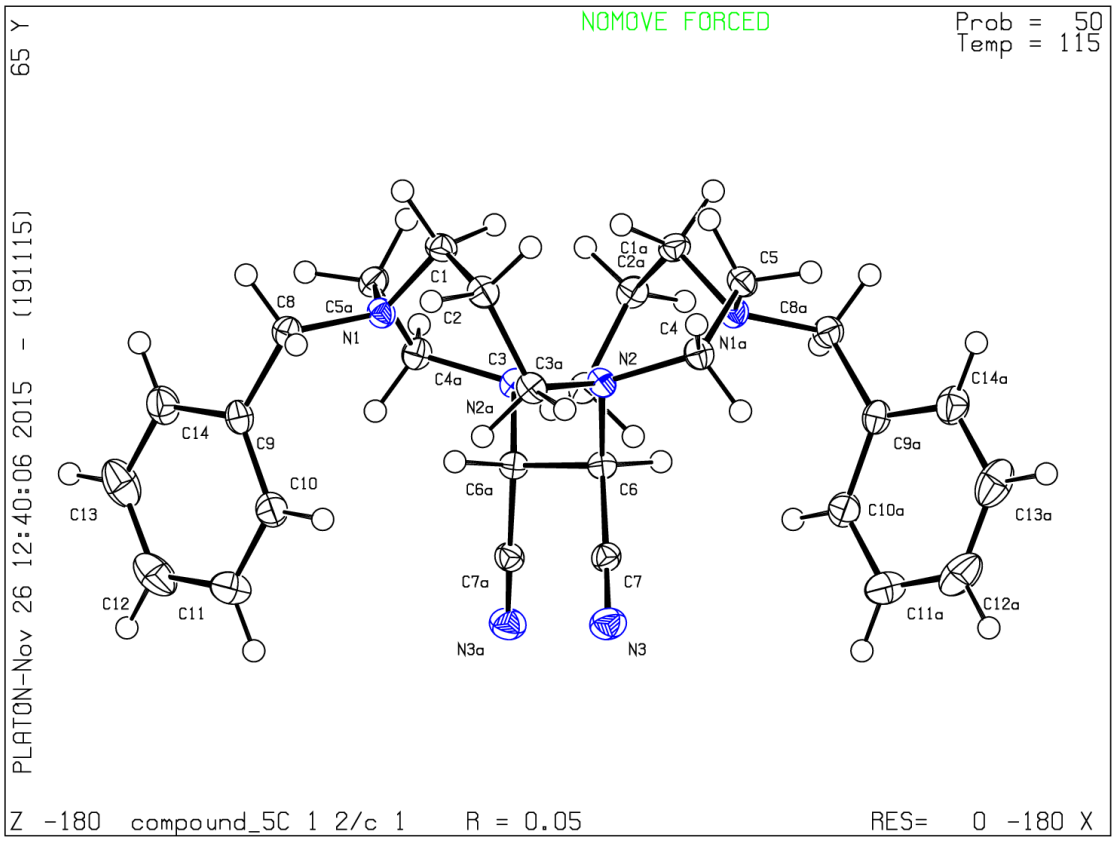
Datablock compound_4 - ellipsoid plot



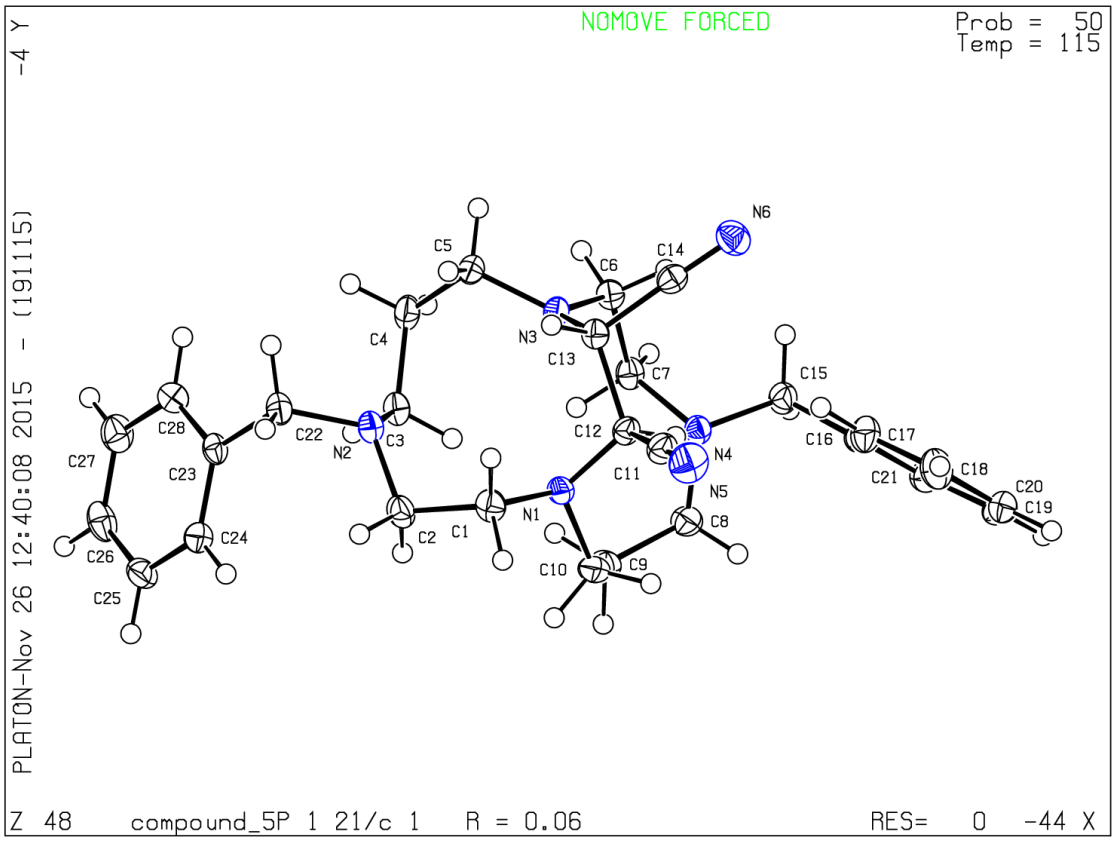
Datablock compound_4Cu - ellipsoid plot



Datablock compound_5a - ellipsoid plot



Datablock compound_5b - ellipsoid plot



Datablock compound_5Cu - ellipsoid plot