Supplementary Material

The cycloaddition chemistry of 3-oxidopyraziniums. Dimerisation of 1-(4-methoxybenzyl)-5,6-dimethyl-3-oxidopyrazinium

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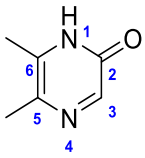
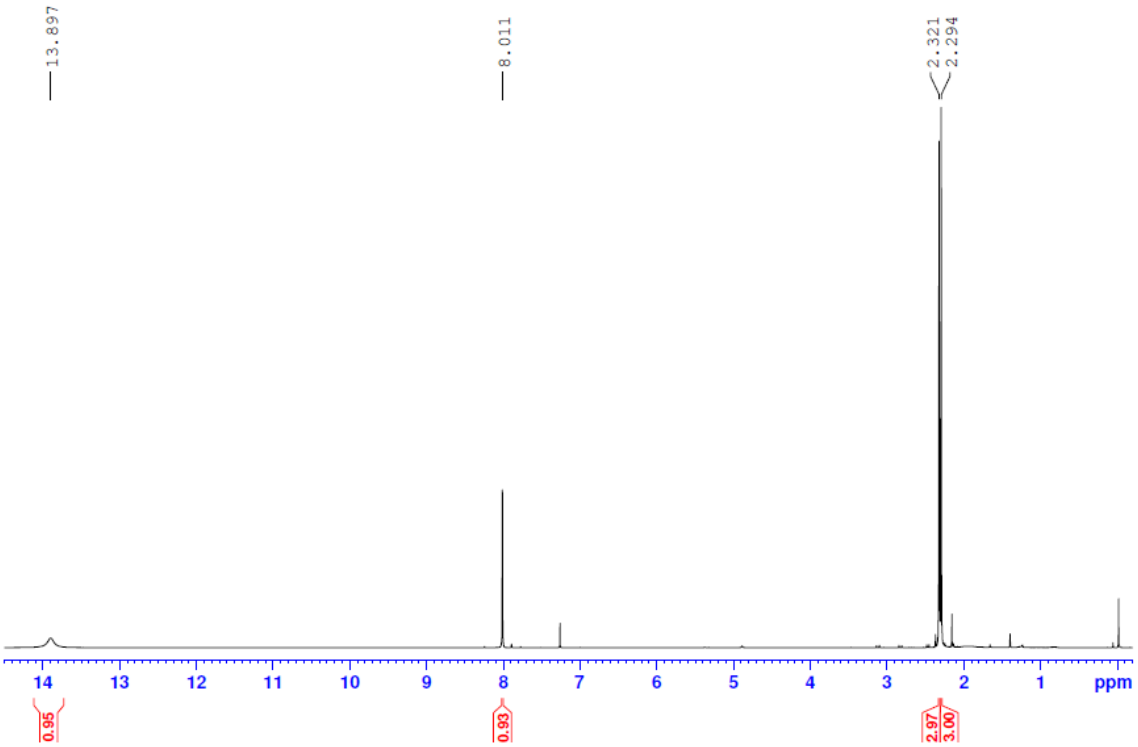
Table of Contents

1. 5,6-Dimethyl-2(1*H*)-pyrazinone



^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm)



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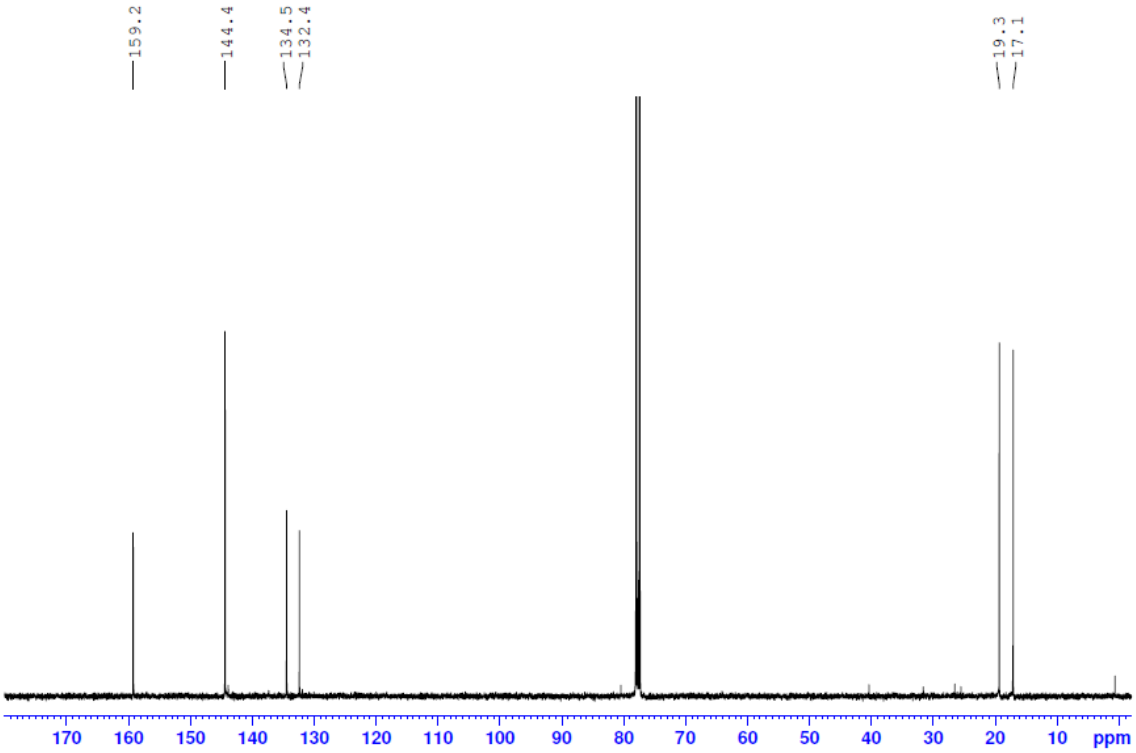

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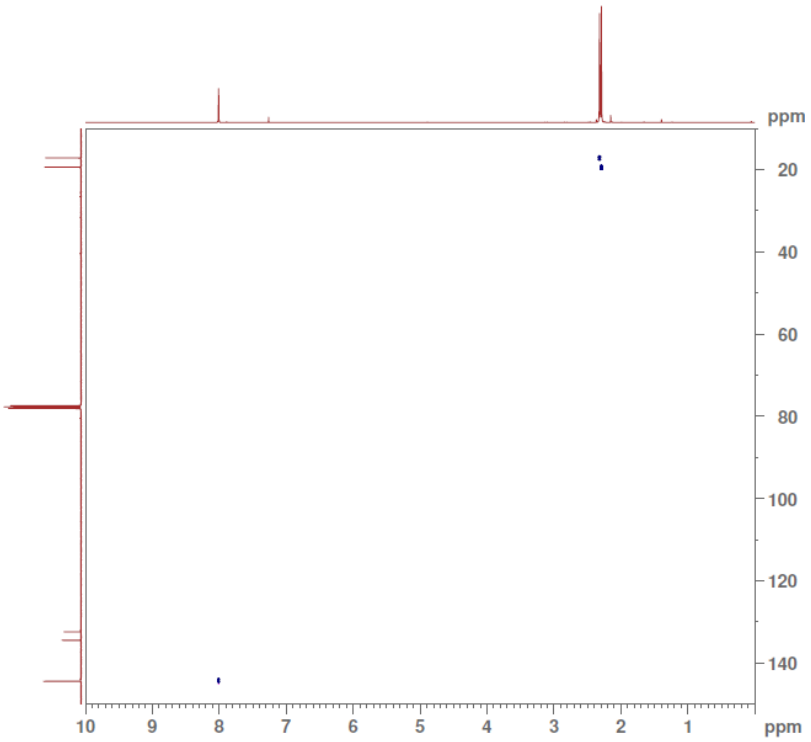
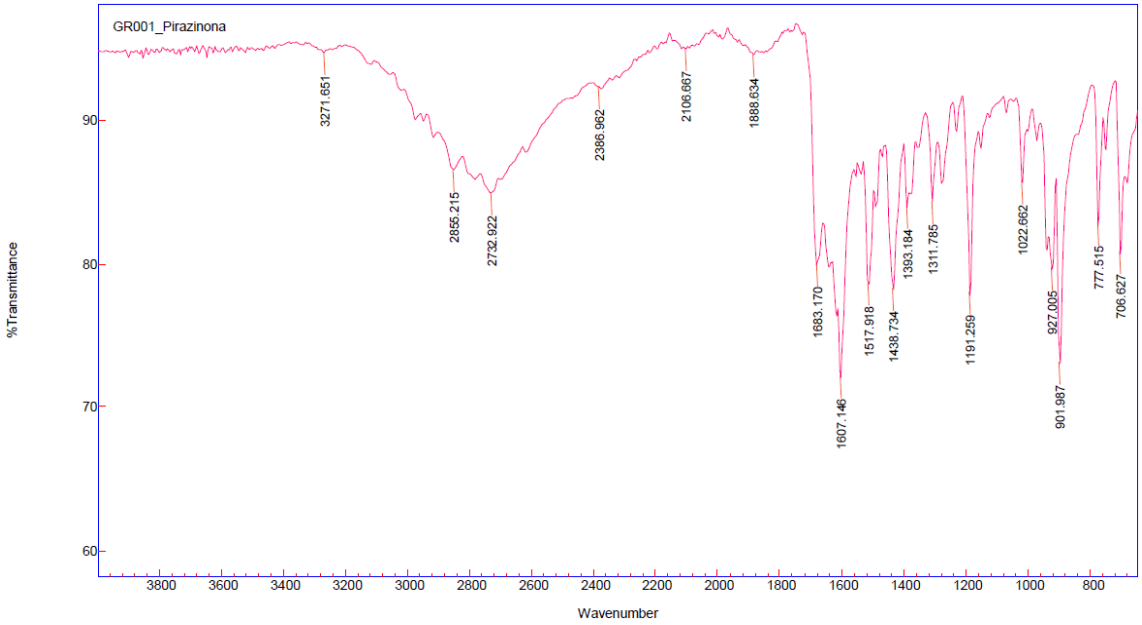
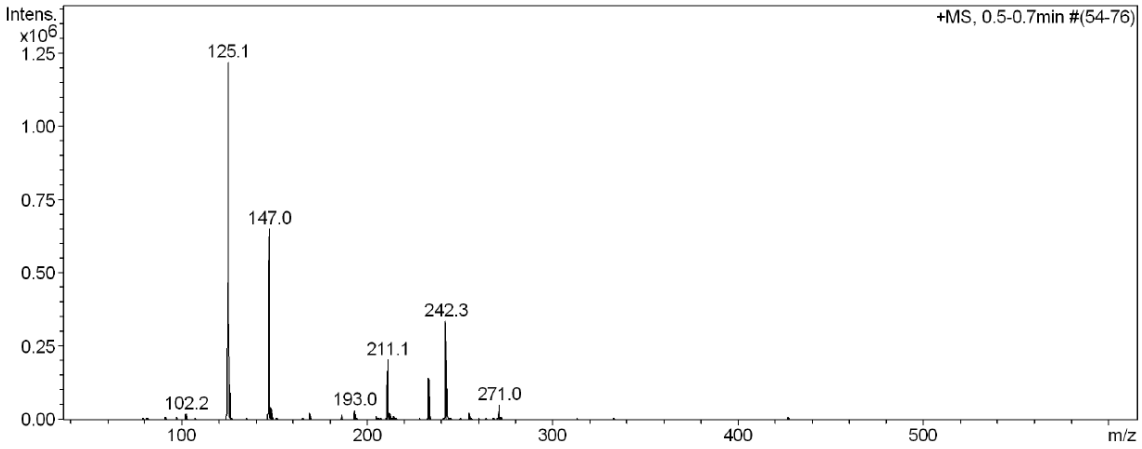


FT-IR (neat), ν (cm^{-1})



ESI-MS (*m/z*)



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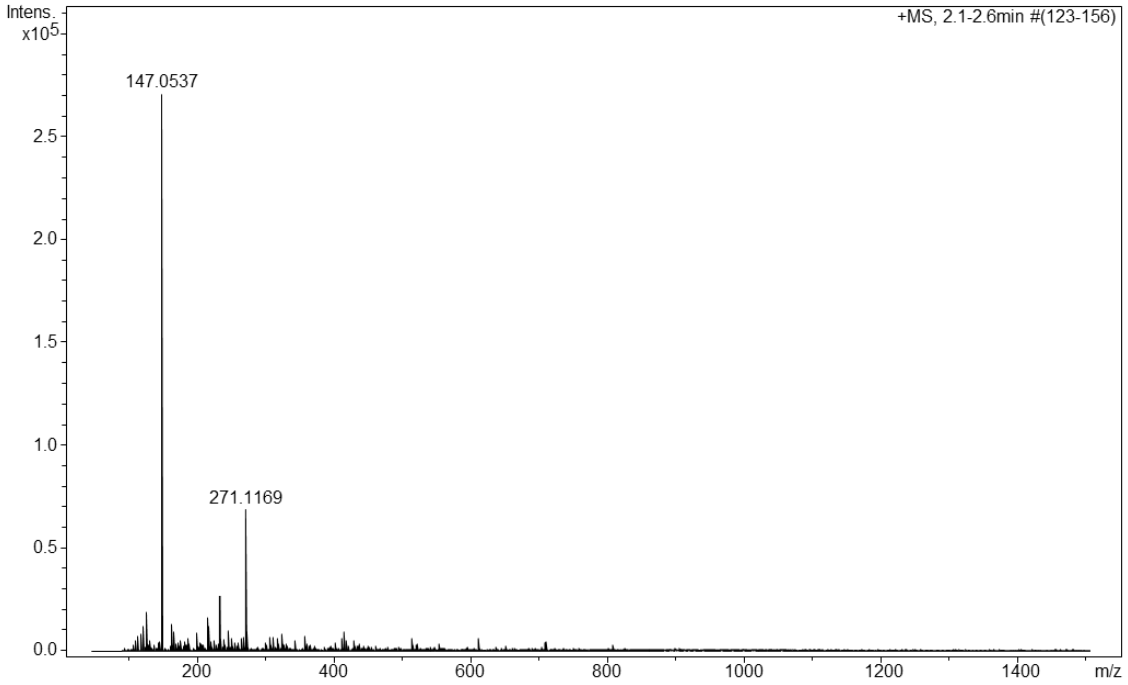
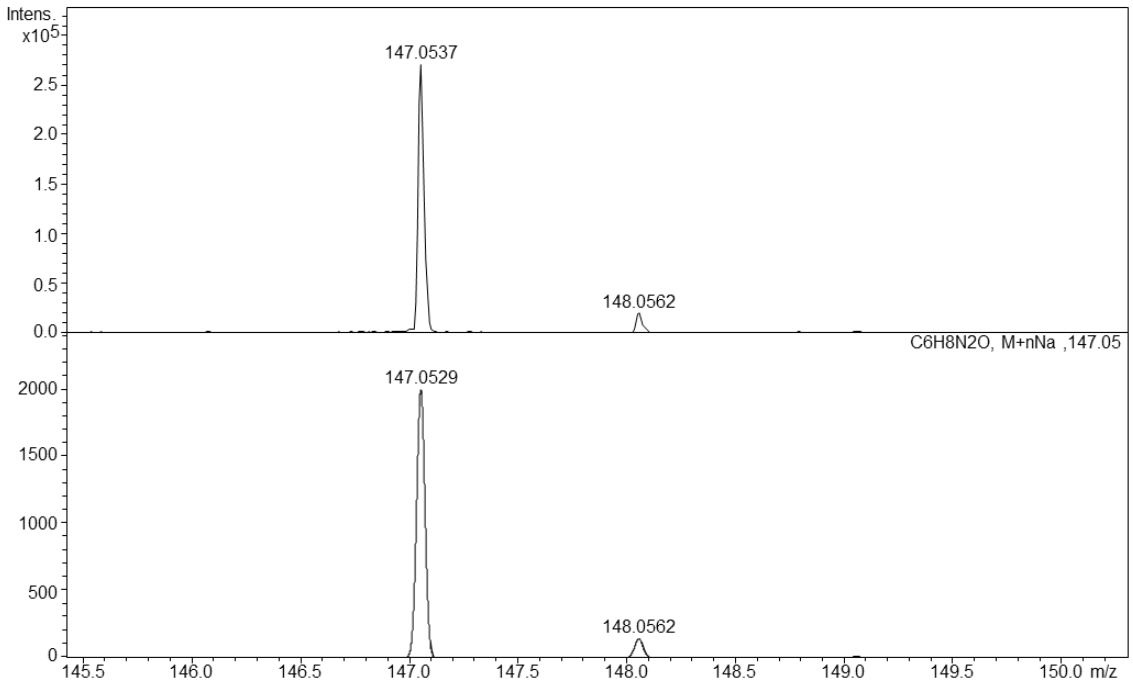
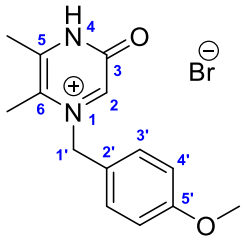




	Molecular formula	Calculated	Found
[M+Na]$^+$	$C_6H_8N_2ONa$	147.0529	147.0537
[2M+Na]$^+$	$(C_6H_8N_2O)_2Na$	271.1165	271.1169

2. 1-(4-Methoxybenzyl)-5,6-dimethyl-3-oxo-3,4-dihydropyrazin-1-ium (12)



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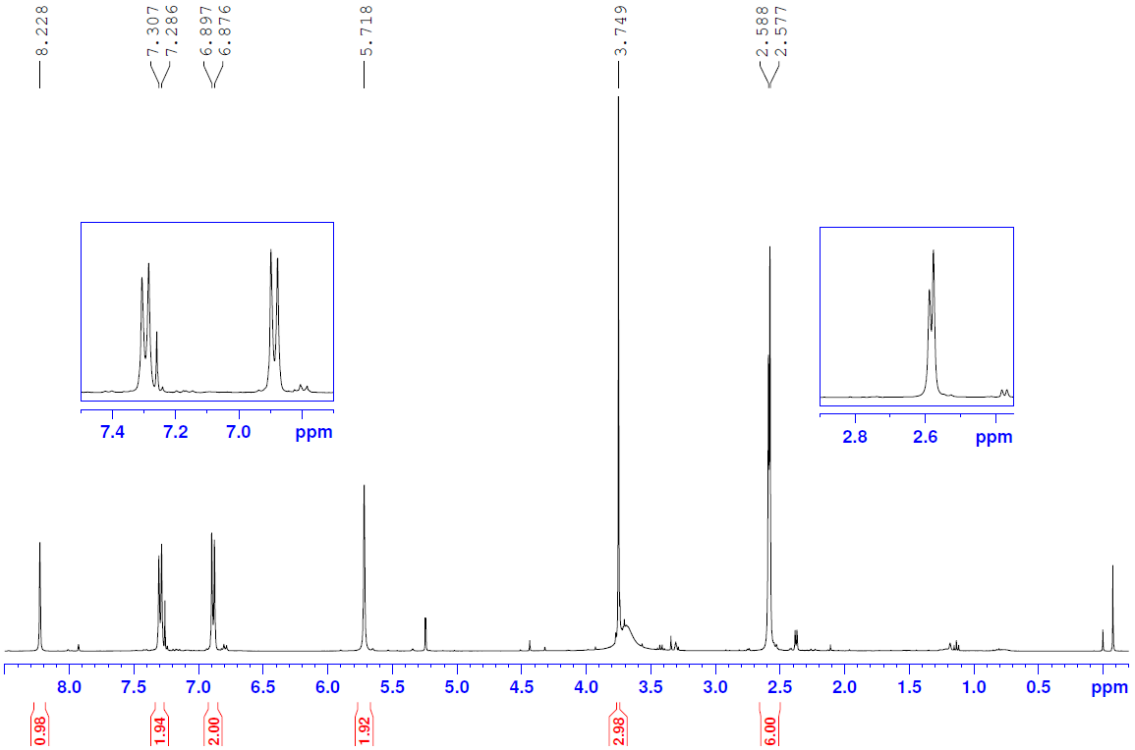

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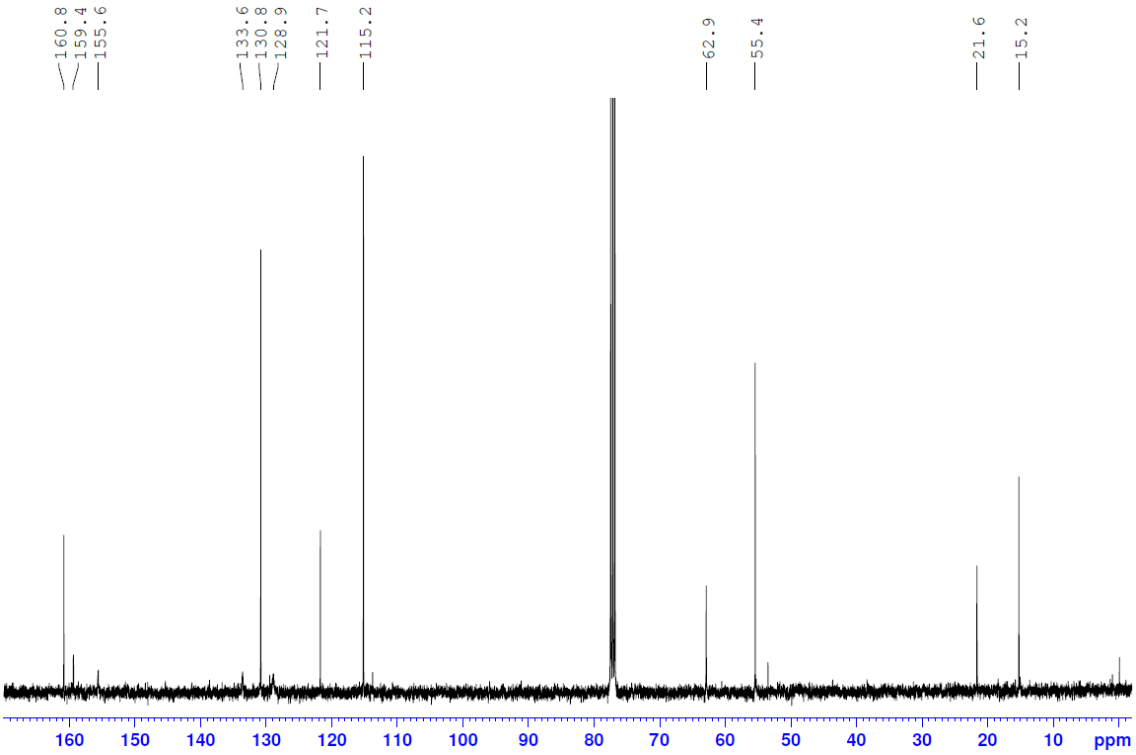

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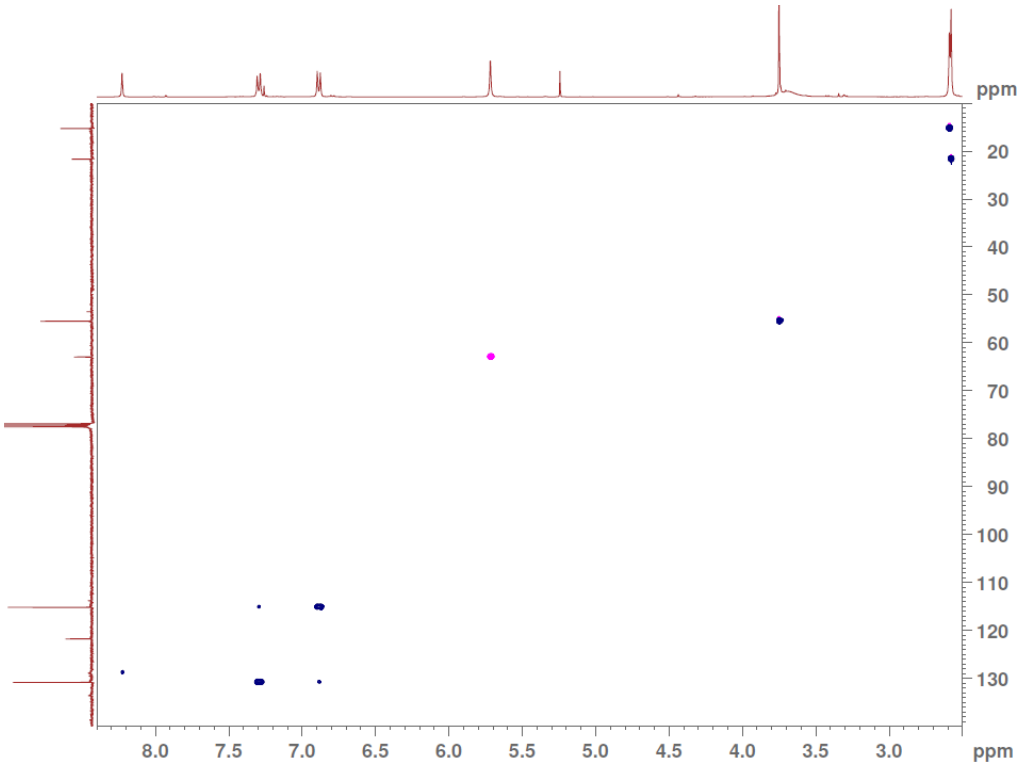

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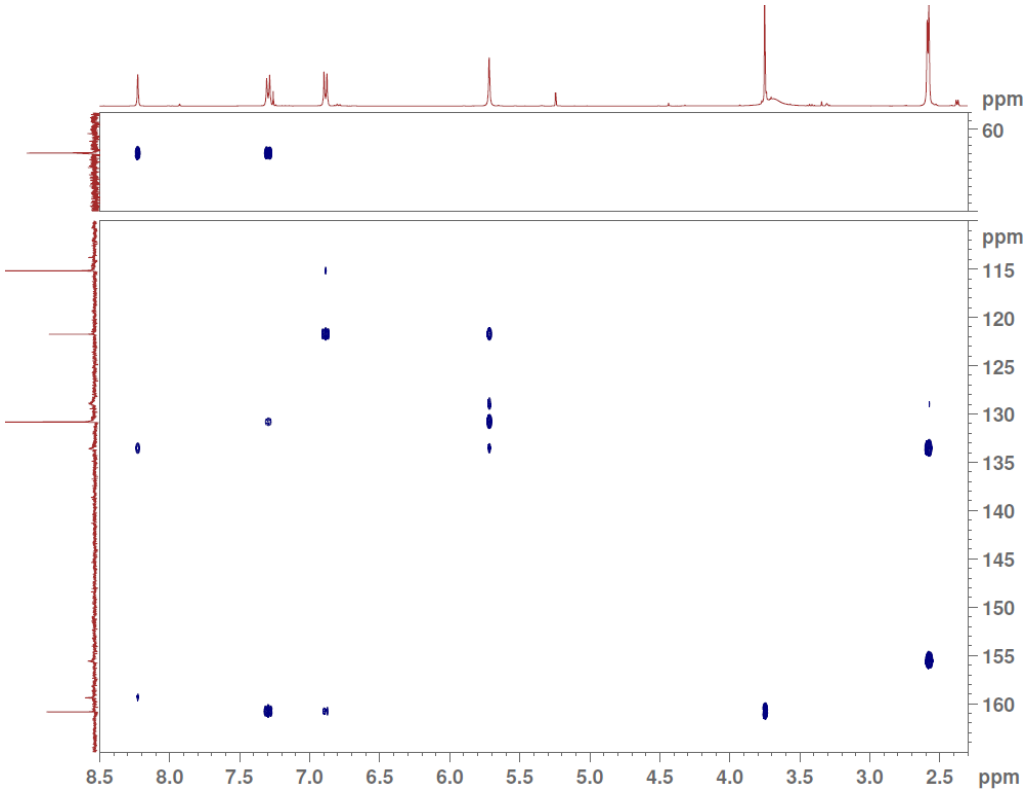

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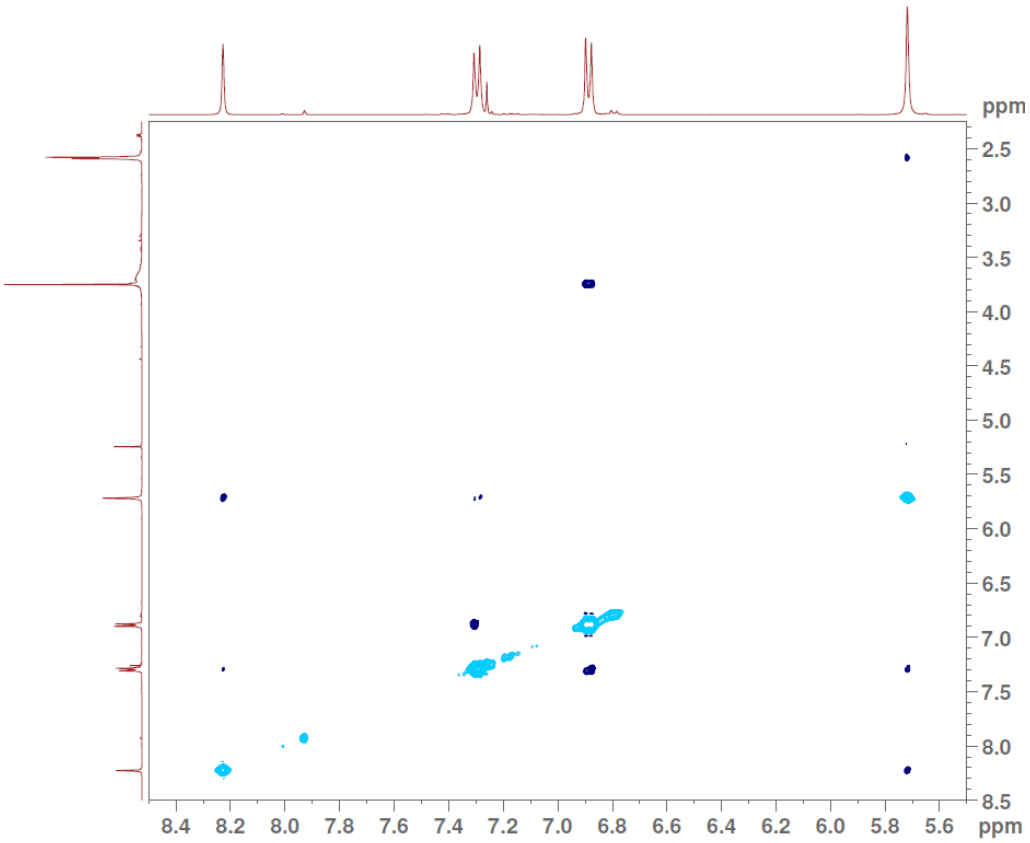
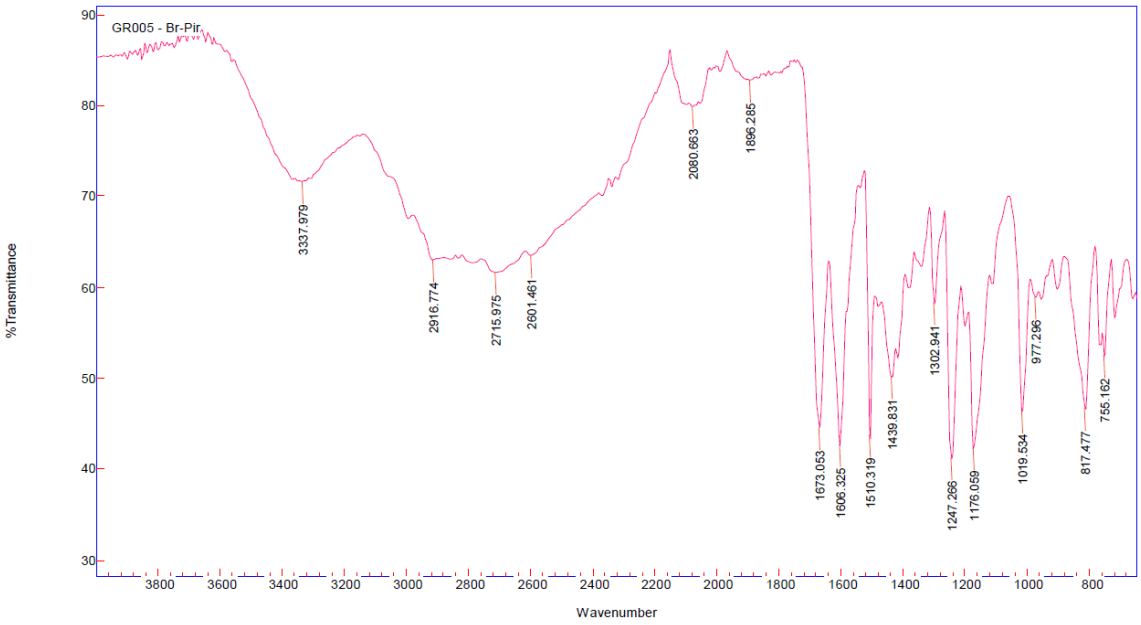


FT-IR (neat), ν (cm^{-1})



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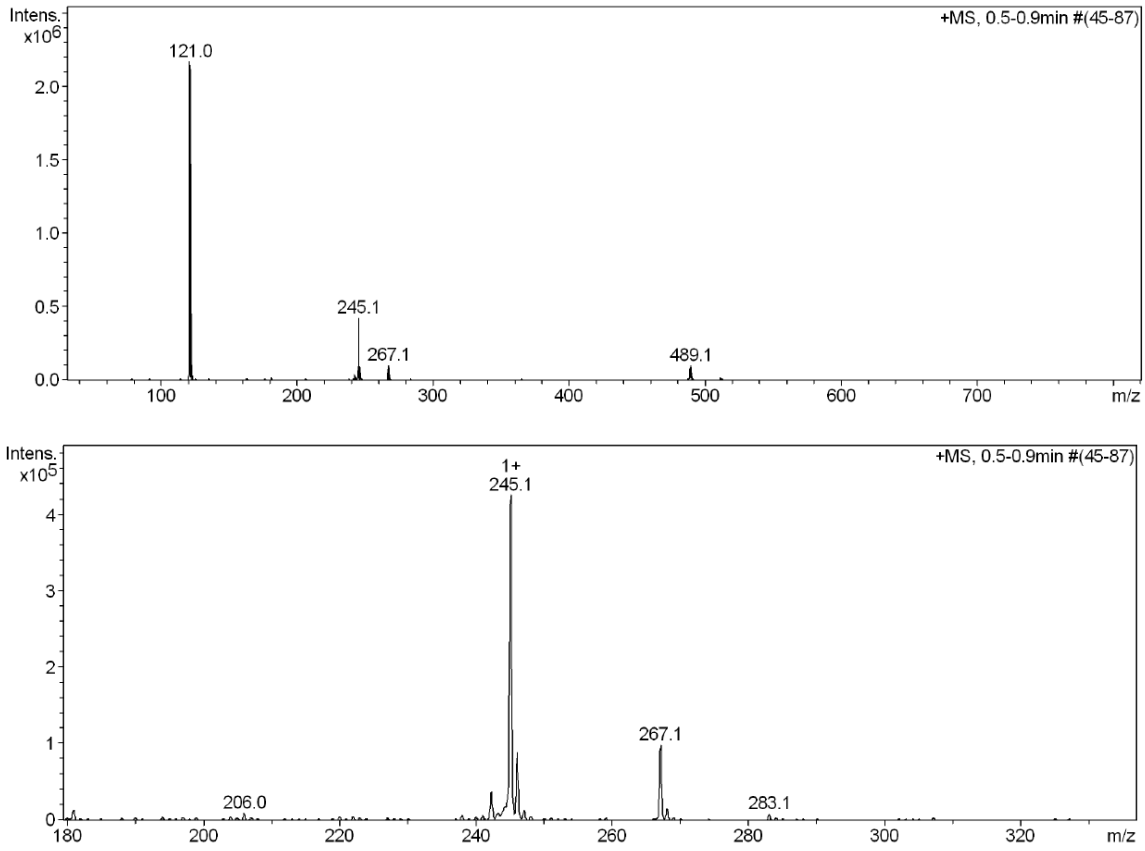

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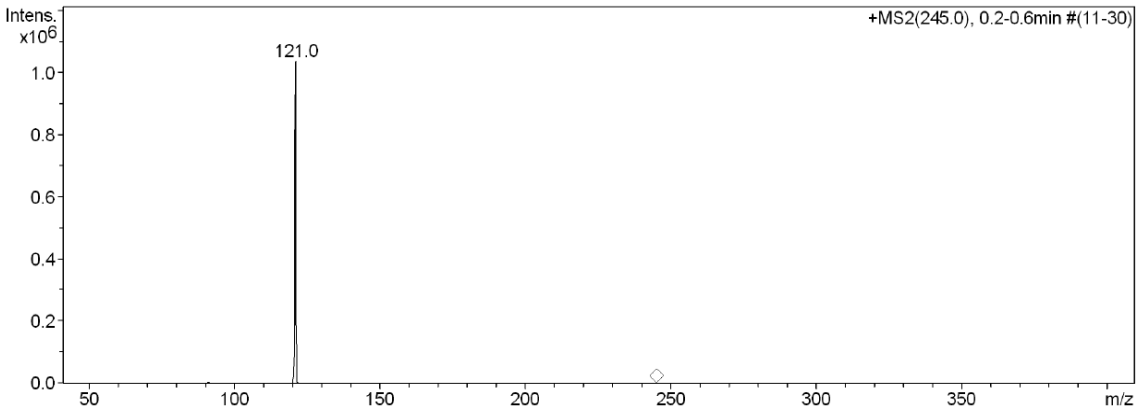

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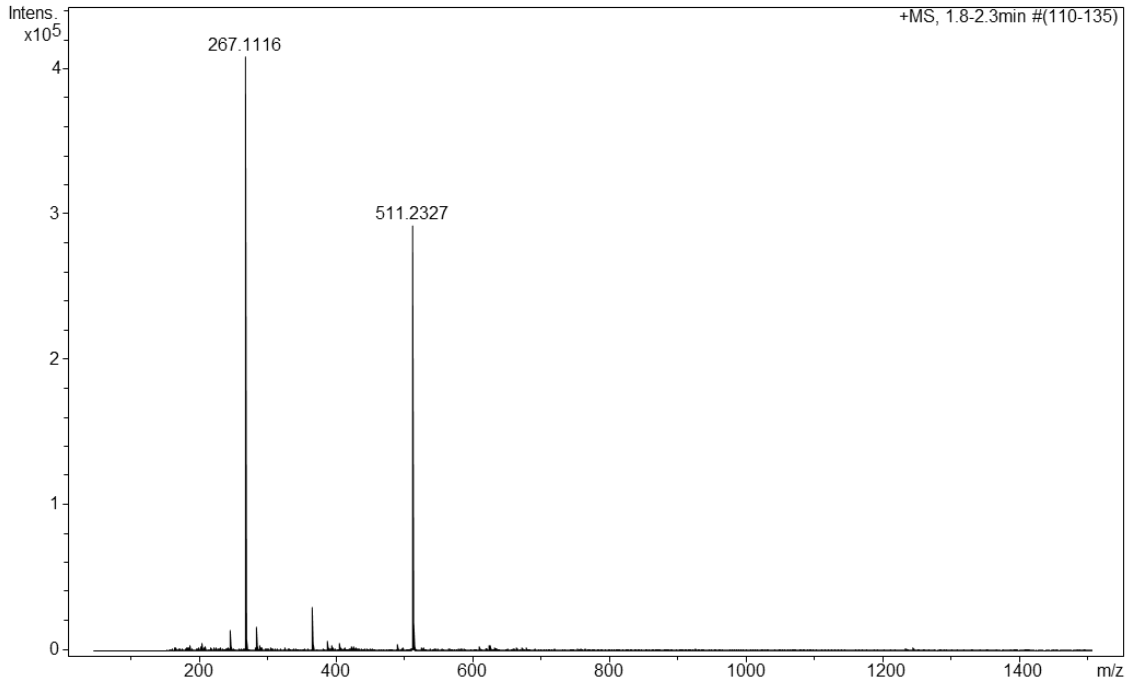
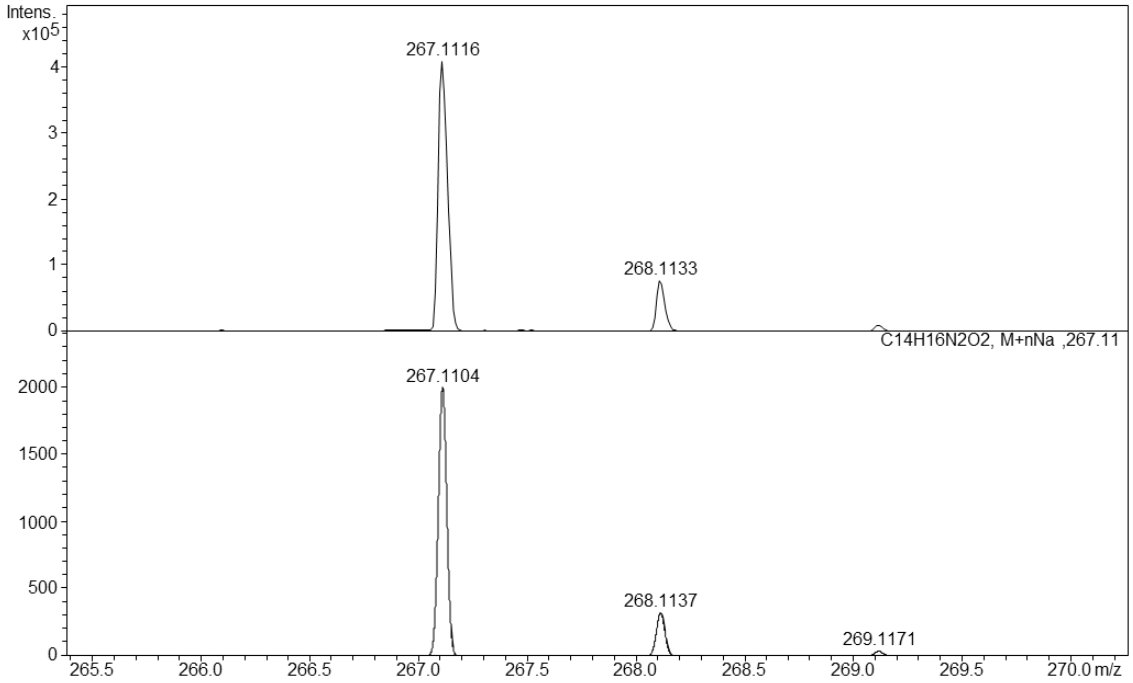
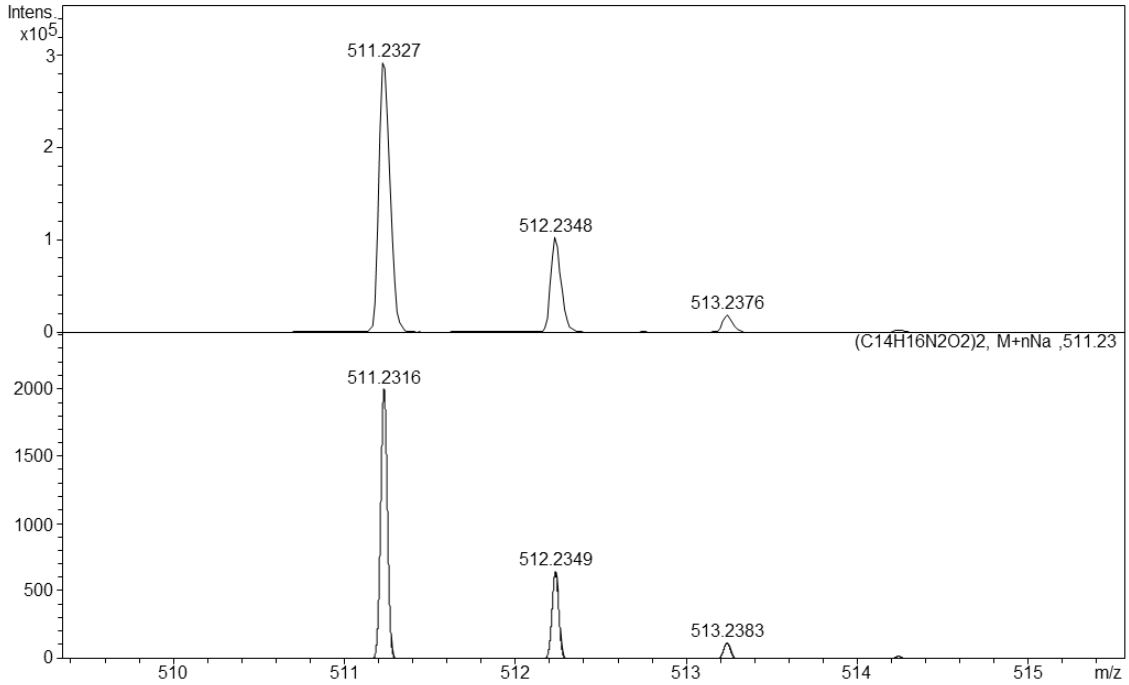
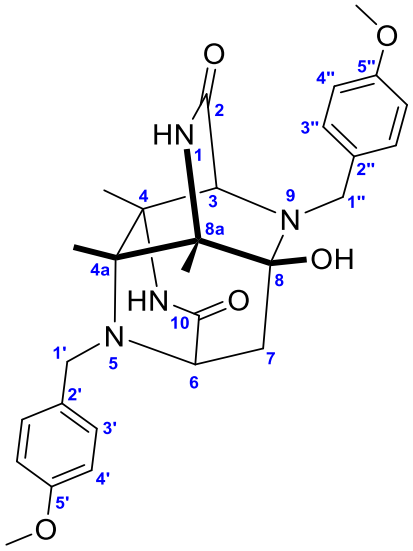




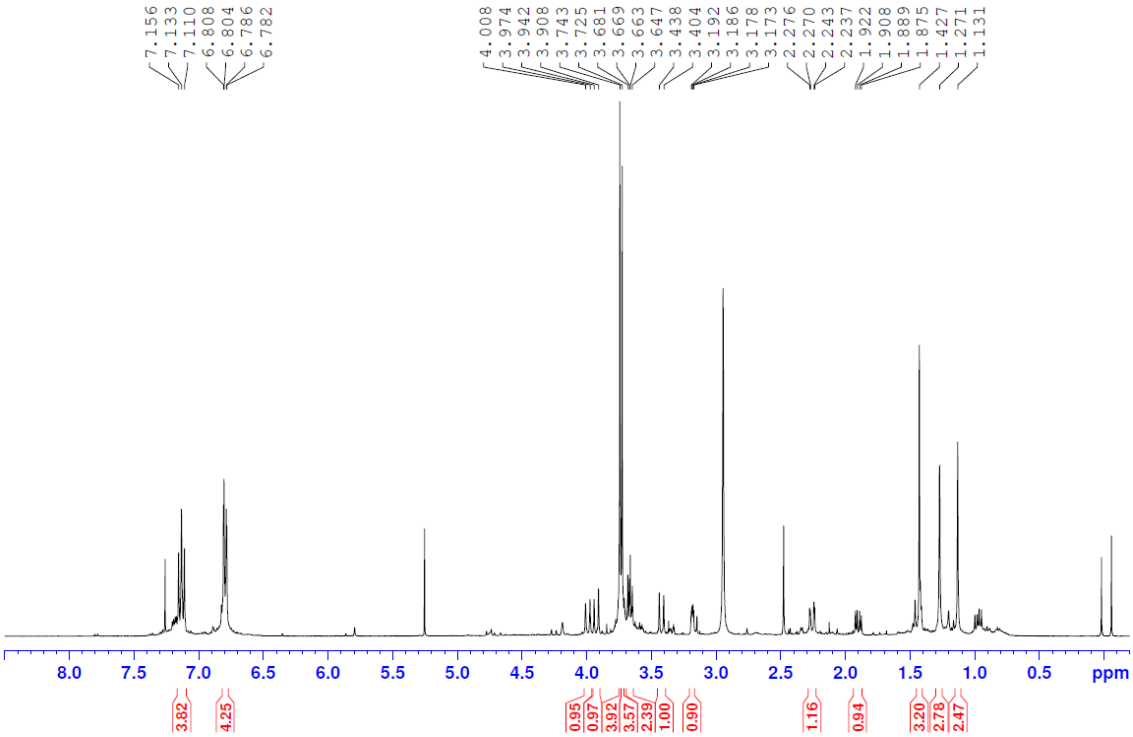


	Molecular formula	Calculated	Found
[M–H+Na]$^+$	$C_{14}H_{16}N_2O_2Na$	267.1104	267.1116
[2M–2H+Na]$^+$	$(C_{14}H_{16}N_2O_2)_2Na$	511.2316	511.2327

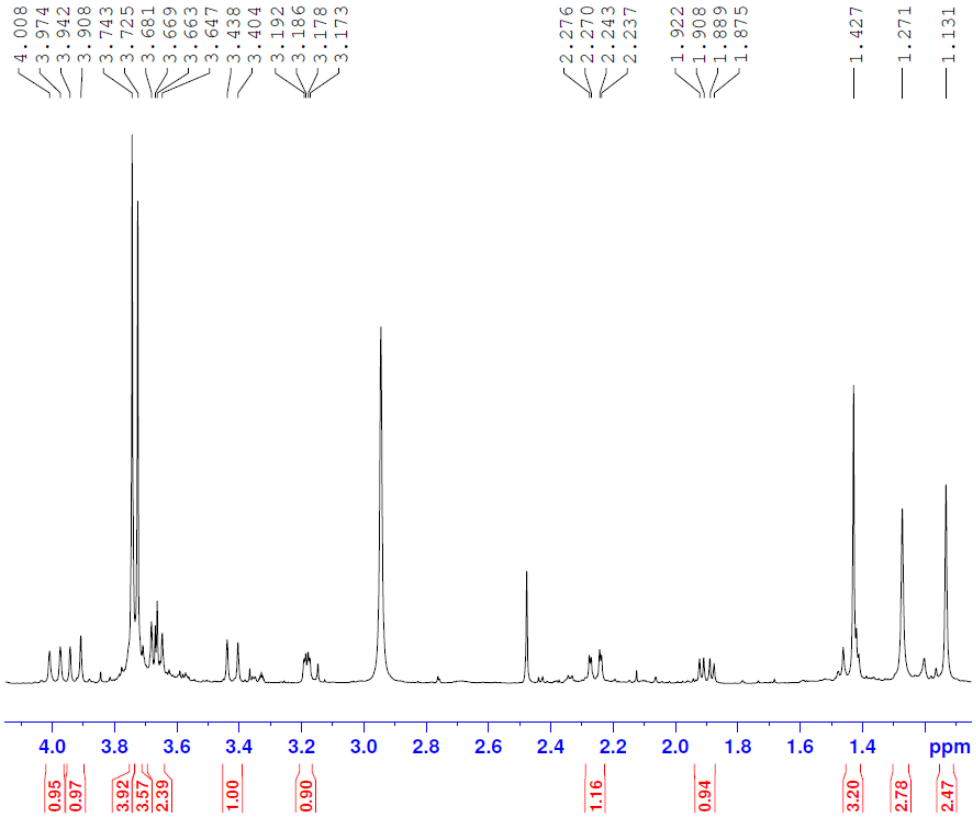
3. Dimerisation of the 3-oxidopyrazinium 13. Synthesis of 15



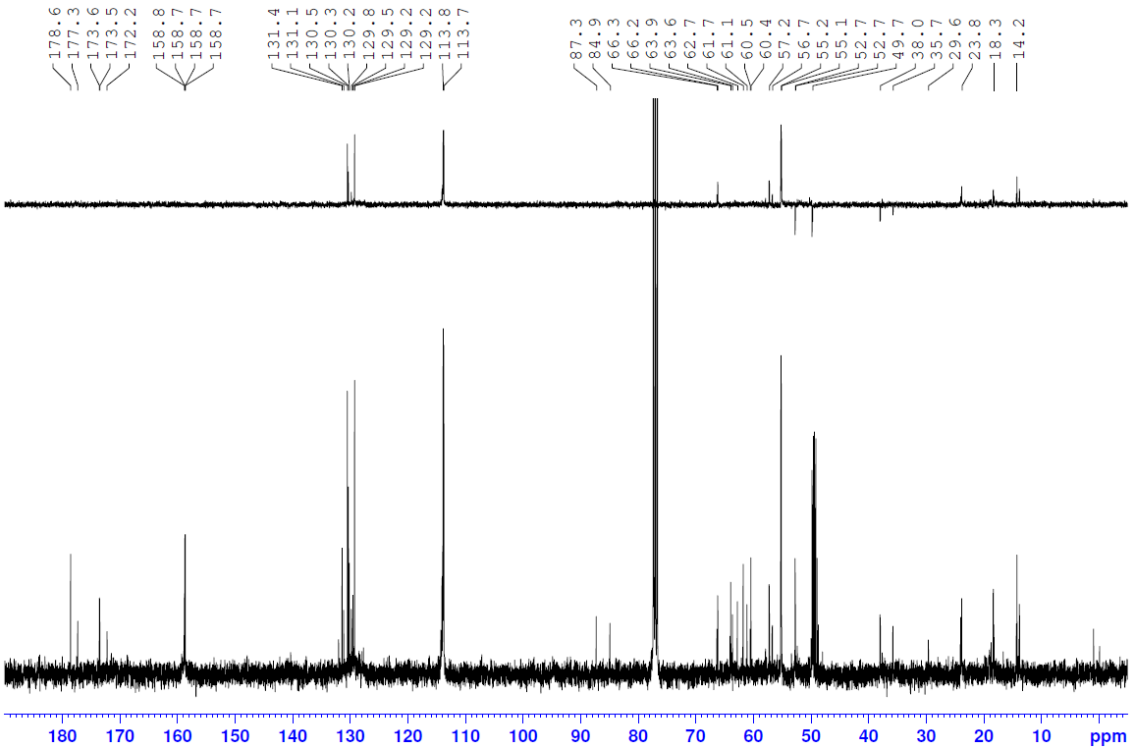
^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm)



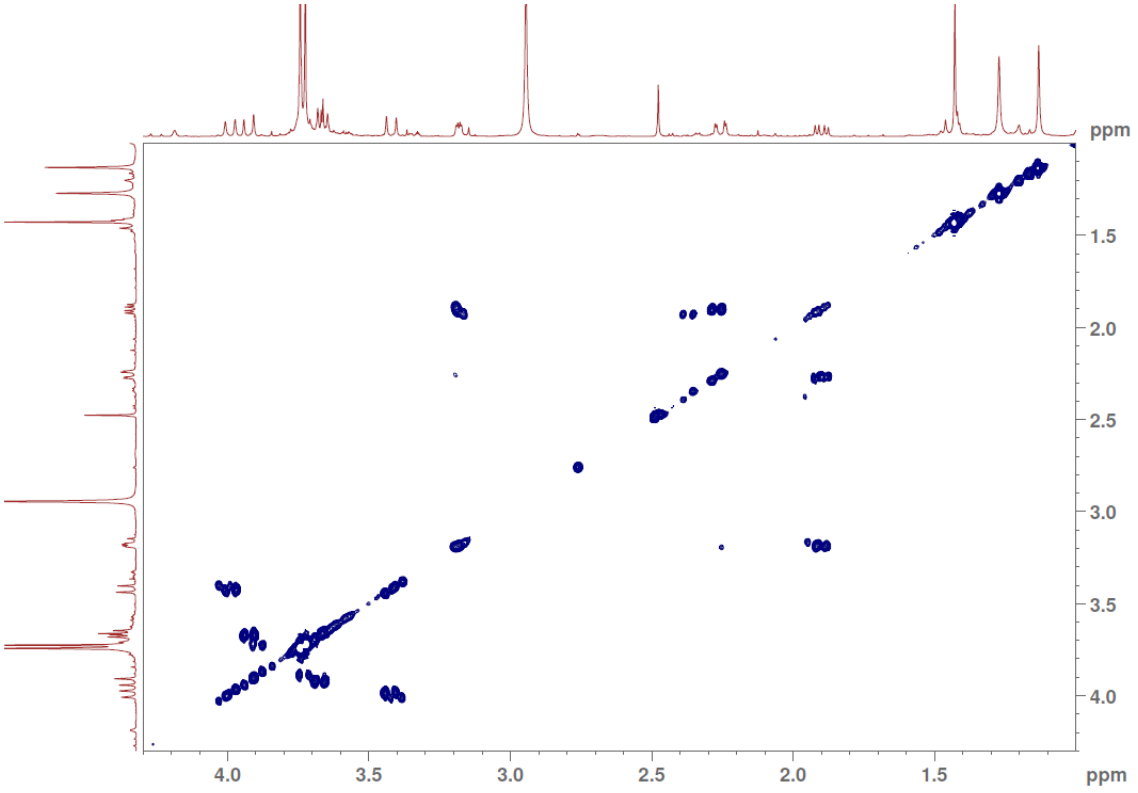
^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm) – Aliphatic zoom



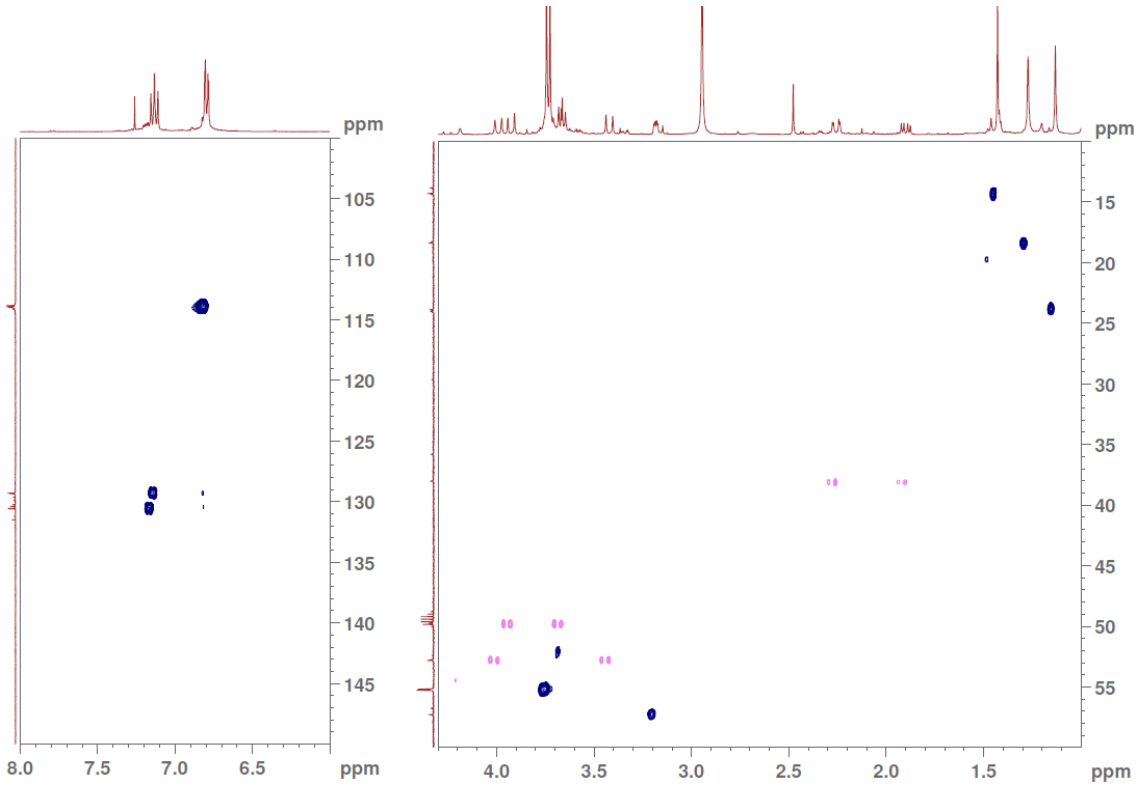
^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm)



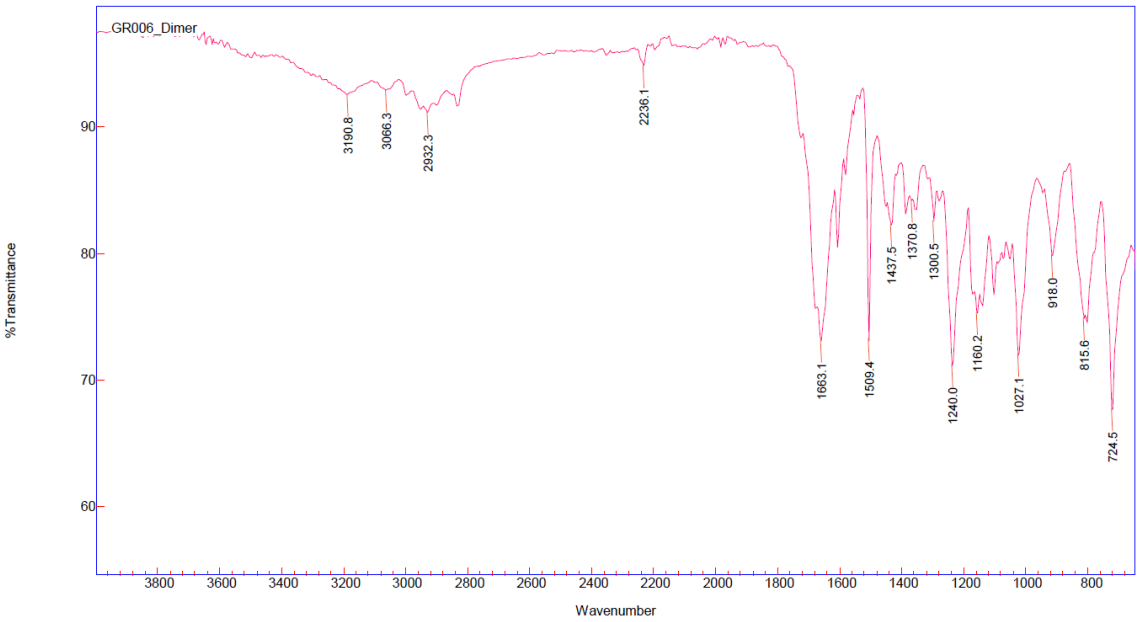
COSY ^{1}H-^{1}H ($CDCl_3$), δ (ppm)



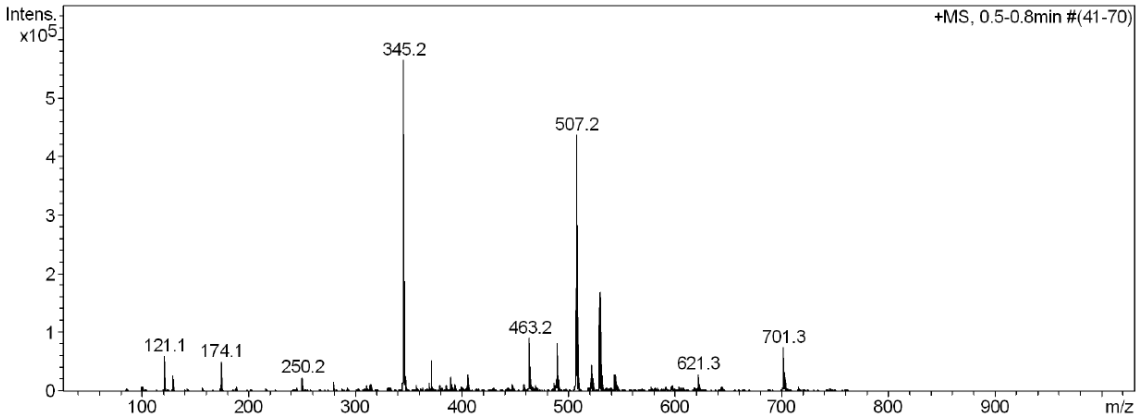
HSQC ^{1}H-^{13}C ($CDCl_3$), δ (ppm)



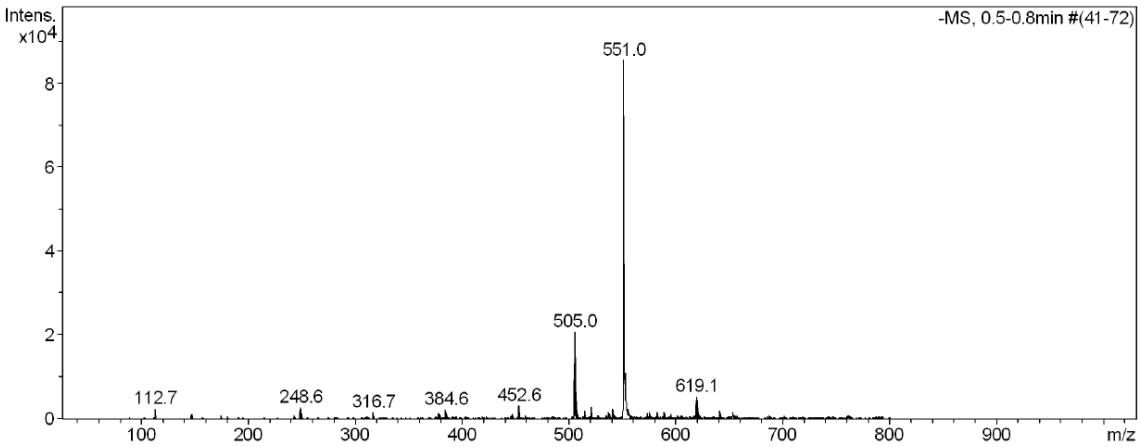
FT-IR (neat), ν (cm^{-1})



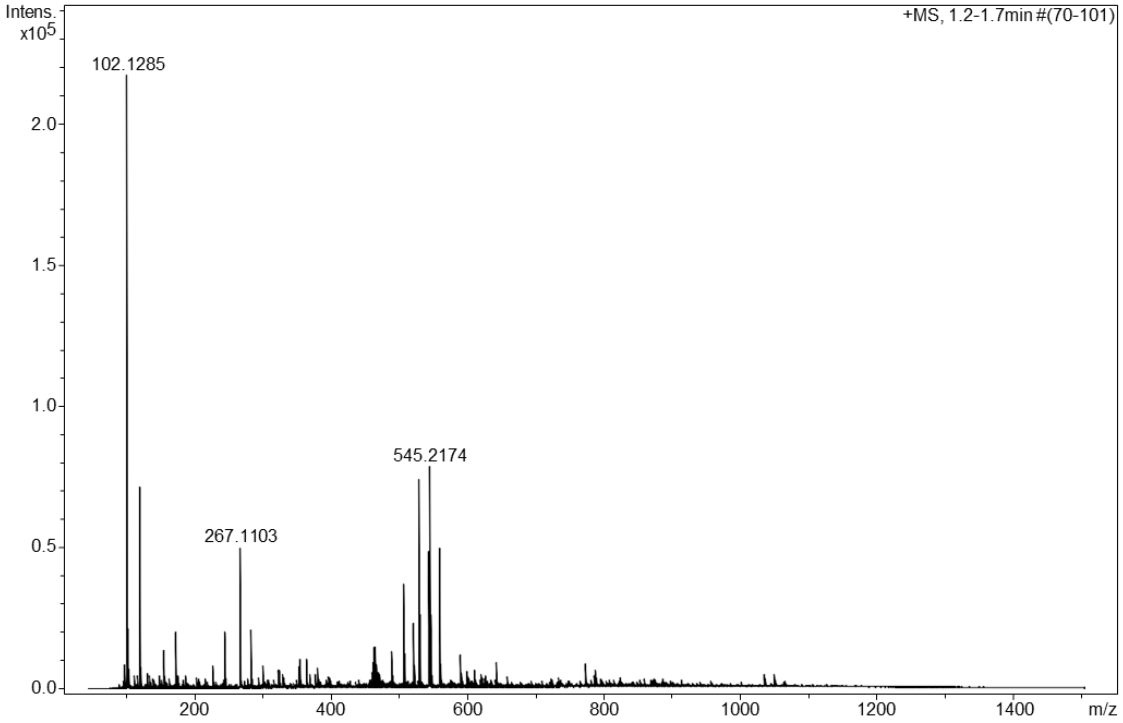
(+)–ESI-MS (*m/z*)

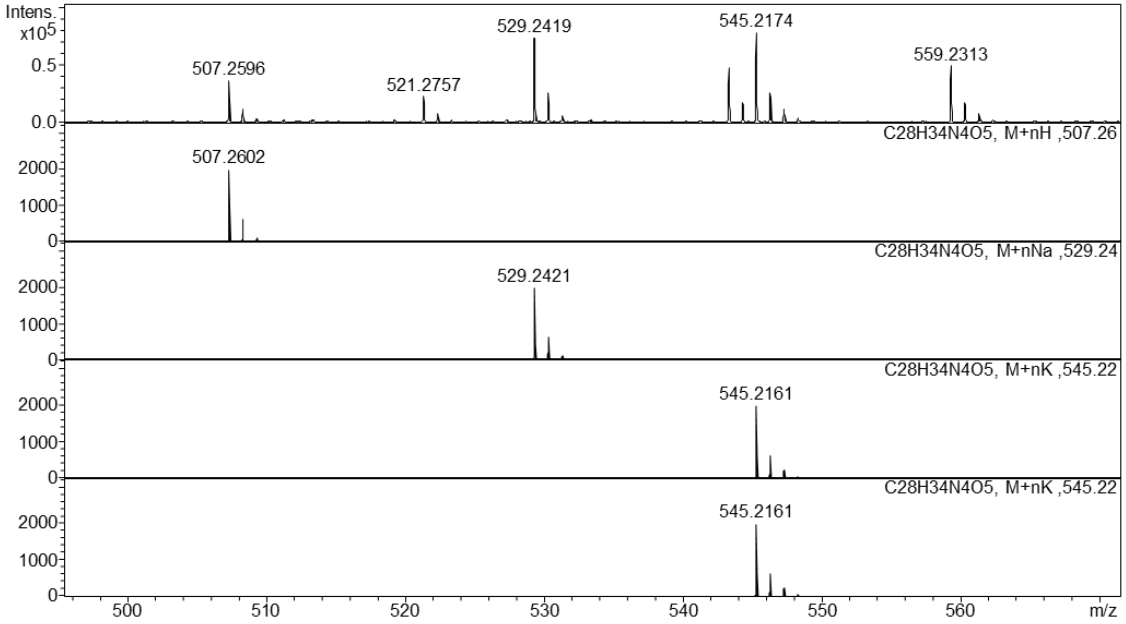


(–)–ESI-MS (*m/z*)



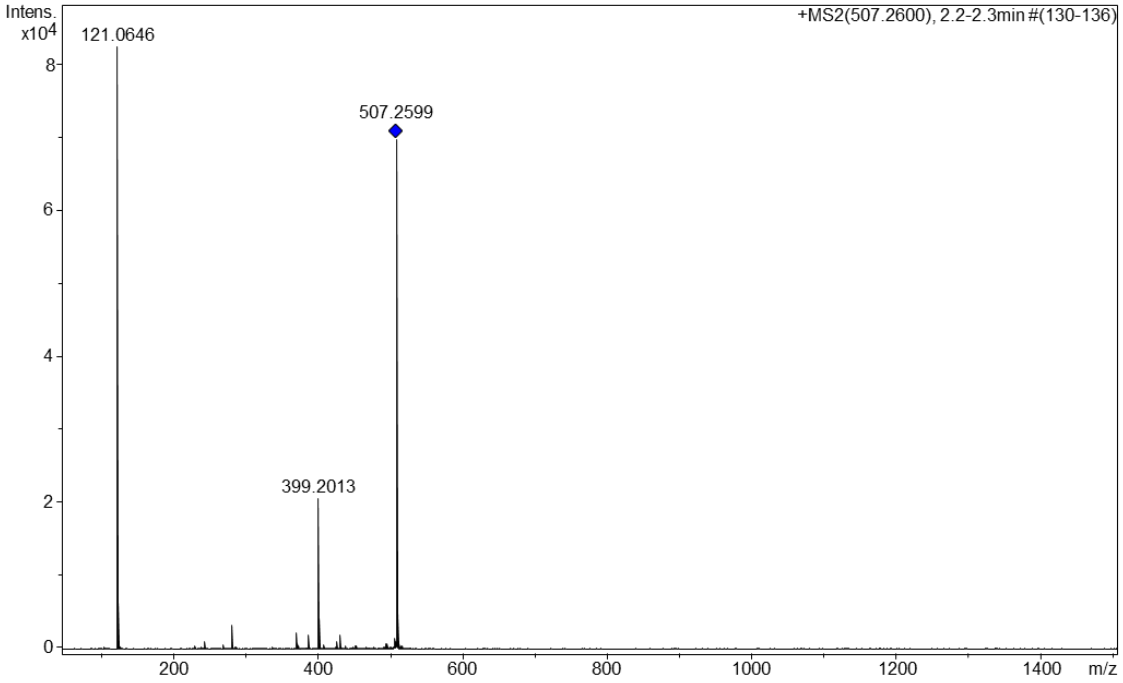
HRMS (*m/z*)



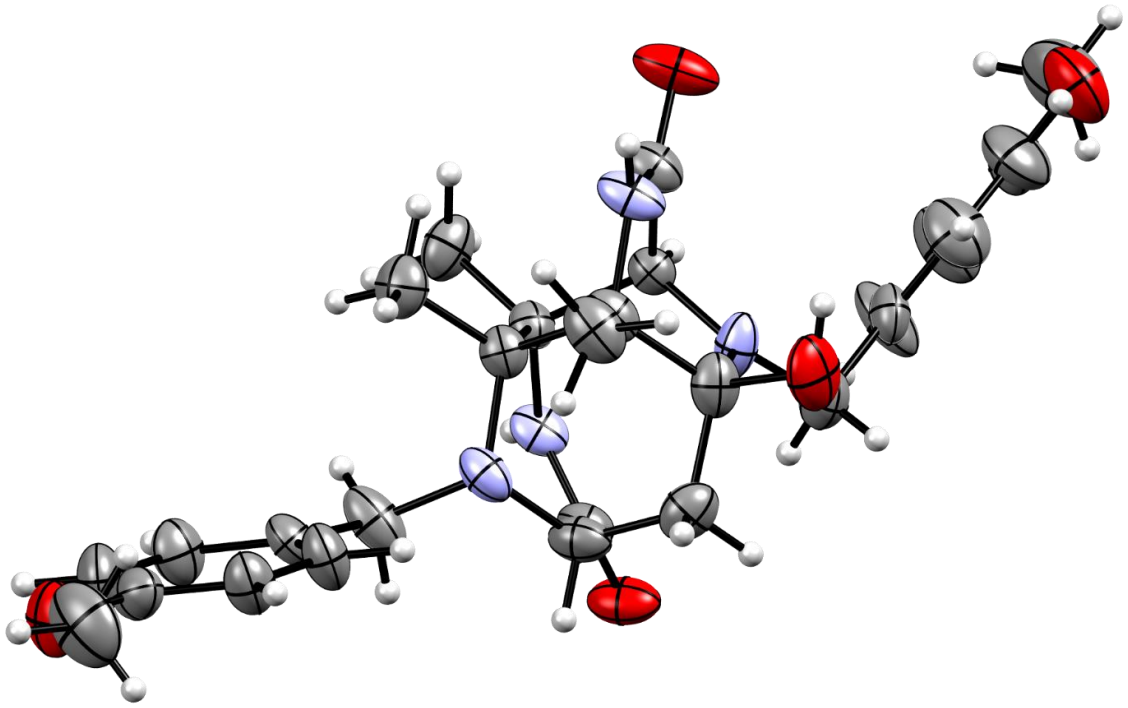


	Molecular formula	Calculated	Found
[M+H]$^+$	$C_{28}H_{35}N_4O_5$	507.2602	507.2596
[M+Na]$^+$	$C_{28}H_{34}N_4O_5Na$	529.2421	529.2419
[M+K]$^+$	$C_{28}H_{35}N_4O_5K$	545.2161	545.2174

HRMS MS/MS (*m/z* = 507.26)



XRD



Crystal Structure Report for GR009

A colorless, plate-like specimen of $C_{29}H_{35.80}Cl_3N_4O_{5.40}$, approximate dimensions 0.050 mm x 0.170 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 QUEST ECO three-circle diffractometer system equipped with a Ceramic x-ray tube (Mo Kα, λ = 0.71073 Å) and a doubly curved silicon crystal Bruker Triumph monochromator.

Table 1: Data collection details for GR009.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	T/K
Omega	59.630	16.54	-164.46	-105.00	54.76	2.00	91	15.00	0.71076	50	20.0	275
Omega	59.630	33.41	-147.59	36.00	54.76	2.00	91	15.00	0.71076	50	20.0	275
Omega	59.630	16.54	17.54	153.00	54.76	2.00	91	15.00	0.71076	50	20.0	275
Omega	59.630	16.54	17.54	-156.00	54.76	2.00	91	15.00	0.71076	50	20.0	275
Omega	59.630	16.54	17.54	-54.00	54.76	2.00	91	15.00	0.71076	50	20.0	275
Omega	59.630	16.54	17.54	102.00	54.76	2.00	91	15.00	0.71076	50	20.0	275
Phi	59.630	0.00	0.00	0.00	54.76	1.00	180	3.00	0.71076	50	20.0	275

A total of 726 frames were collected. The total exposure time was 2.42 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 36329 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 5477 were independent (average redundancy 6.633, completeness = 99.9%, R_{int} = 10.04%, R_{sig} = 7.01%) and 3208 (58.57%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.217(2) Å, b = 12.540(3) Å, c = 13.940(3) Å, α = 113.751(10)°, β = 100.464(11)°, γ = 98.871(11)°, volume = 1555.4(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 5117 reflections above 20 σ(I) with 5.563° < 2θ < 50.48°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.925. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9290 and 0.9830.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{29}H_{35.80}Cl_3N_4O_{5.40}$. The final anisotropic full-matrix least-squares refinement on

F^2 with 379 variables converged at R1 = 9.53%, for the observed data and wR2 = 25.88% for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was 1.922 $e^-/Å^3$ and the largest hole was -0.350 $e^-/Å^3$ with an RMS deviation of 0.074 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.352 g/cm^3 and F(000), 664 e^-.

Table 2. Sample and crystal data for GR025.

Identification code	GR009	
Chemical formula	$C_{29}H_{35.80}Cl_3N_4O_{5.40}$	
Formula weight	633.16 g/mol	
Temperature	276(2) K	
Wavelength	0.71073 Å	
Crystal size	0.050 x 0.170 x 0.220 mm	
Crystal habit	colorless plate	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.217(2) Å	α = 113.751(10)°
	b = 12.540(3) Å	β = 100.464(11)°
	c = 13.940(3) Å	γ = 98.871(11)°
Volume	1555.4(7) $Å^3$	
Z	2	
Density (calculated)	1.352 g/cm^3	
Absorption coefficient	0.340 mm^{-1}	
F(000)	664	

Table 3. Data collection and structure refinement for GR025.

Diffractometer	D8 QUEST ECO three-circle diffractometer
Radiation source	Ceramic x-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.29 to 25.00°
Index ranges	-12<=h<=12, -14<=k<=14, -16<=l<=16
Reflections collected	36329
Independent reflections	5477 [R(int) = 0.1004]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9830 and 0.9290
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5477 / 0 / 379
Goodness-of-fit on F^2	1.041
Final R indices	3208 data; I>2σ(I) R1 = 0.0953, wR2 = 0.2160
	all data R1 = 0.1588, wR2 = 0.2588
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0984P)^2+4.1635P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.922 and -0.350 $eÅ^{-3}$
R.M.S. deviation from mean	0.074 $eÅ^{-3}$

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for GR025.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

x/a	y/b	z/c	U(eq)	
O1W	0.7311(13)	0.3172(11)	0.4139(10)	0.074(3)
O15	0.7832(4)	0.2205(4)	0.5365(3)	0.0583(12)
O13	0.0048(5)	0.6048(4)	0.6363(3)	0.0595(12)
O23	0.5155(5)	0.7791(5)	0.7743(4)	0.0771(15)
O34	0.6435(4)	0.9961(4)	0.6916(4)	0.0638(13)
O36	0.9534(4)	0.3344(3)	0.9407(3)	0.0498(11)
N3	0.0356(5)	0.4152(4)	0.5799(3)	0.0423(12)
N6	0.8757(4)	0.3941(4)	0.7055(4)	0.0412(12)
N9	0.1509(5)	0.2631(4)	0.7481(3)	0.0391(11)
N12	0.0906(5)	0.4517(4)	0.8921(3)	0.0360(10)
C1	0.9908(5)	0.4982(4)	0.7479(4)	0.0286(11)
C2	0.0108(6)	0.5140(5)	0.6501(4)	0.0388(13)
C4	0.0345(5)	0.3146(4)	0.6076(4)	0.0346(12)
C5	0.8957(5)	0.2820(5)	0.6321(4)	0.0398(13)
C6	0.9013(6)	0.1923(5)	0.6797(5)	0.0453(14)
C7	0.1230(5)	0.4766(4)	0.8043(4)	0.0303(11)
C8	0.1543(5)	0.3617(4)	0.7154(4)	0.0317(12)
C10	0.0236(6)	0.2381(5)	0.7773(4)	0.0419(14)
C11	0.0165(6)	0.3456(5)	0.8761(4)	0.0371(13)
C14	0.0554(6)	0.2084(5)	0.5124(4)	0.0477(15)
C16	0.7583(6)	0.3972(5)	0.7519(5)	0.0479(15)
C17	0.6958(5)	0.5000(5)	0.7588(4)	0.0397(13)
C18	0.6338(7)	0.5095(6)	0.6686(5)	0.0616(18)
C19	0.5763(8)	0.6037(7)	0.6762(6)	0.068(2)
C20	0.5773(6)	0.6896(6)	0.7753(5)	0.0514(16)
C21	0.6366(7)	0.6812(7)	0.8662(5)	0.0641(19)
C22	0.6949(7)	0.5854(6)	0.8560(5)	0.0607(19)
C24	0.5286(10)	0.8778(7)	0.8743(7)	0.093(3)
C25	0.2376(6)	0.5919(5)	0.8560(4)	0.0466(15)
C26	0.2905(6)	0.3904(5)	0.6908(5)	0.0463(14)
C27	0.2727(6)	0.2775(6)	0.8320(4)	0.0516(16)
C28	0.3709(6)	0.2042(5)	0.7888(4)	0.0377(13)
C29	0.3290(6)	0.1013(5)	0.6915(5)	0.0473(15)
C30	0.4164(6)	0.0295(5)	0.6561(5)	0.0458(14)
C31	0.5470(6)	0.0601(5)	0.7187(5)	0.0430(14)
C32	0.5922(6)	0.1627(6)	0.8171(5)	0.0531(16)
C33	0.5030(6)	0.2319(5)	0.8503(5)	0.0480(15)
C35	0.6080(8)	0.8978(7)	0.5880(6)	0.081(2)
Cl2N	0.1718(3)	0.9529(3)	0.8209(3)	0.1263(10)
Cl3N	0.8835(2)	0.9178(2)	0.78835(17)	0.0893(7)
Cl4N	0.0357(3)	0.8420(2)	0.93423(17)	0.1054(9)
C1N	0.0244(8)	0.8594(6)	0.8160(6)	0.068(2)

Table 5. Bond lengths (Å) for GR009.

O1W-H1A	0.913700	O1W-H1B	0.860000

O15-C5	1.426(6)	O15-H15	0.820000
O13-C2	1.237(6)	O23-C20	1.374(7)
O23-C24	1.409(9)	O34-C31	1.377(6)
O34-C35	1.406(8)	O36-C11	1.237(6)
N3-C2	1.330(6)	N3-C4	1.460(6)
N3-H3	0.860000	N6-C5	1.439(6)
N6-C1	1.445(6)	N6-C16	1.461(7)
N9-C10	1.457(7)	N9-C27	1.477(7)
N9-C8	1.478(7)	N12-C11	1.335(7)
N12-C7	1.459(6)	N12-H12	0.860000
C1-C2	1.499(7)	C1-C7	1.554(7)
C1-H1	0.980000	C4-C14	1.532(7)
C4-C5	1.550(8)	C4-C8	1.581(7)
C5-C6	1.522(8)	C6-C10	1.508(8)
C6-H6A	0.970000	C6-H6B	0.970000
C7-C25	1.520(7)	C7-C8	1.600(6)
C8-C26	1.518(7)	C10-C11	1.513(7)
C10-H10	0.980000	C14-H14A	0.960000
C14-H14B	0.960000	C14-H14C	0.960000
C16-C17	1.502(8)	C16-H16A	0.970000
C16-H16B	0.970000	C17-C22	1.349(8)
C17-C18	1.361(8)	C18-C19	1.373(9)
C18-H18	0.930000	C19-C20	1.365(9)
C19-H19	0.930000	C20-C21	1.353(8)
C21-C22	1.390(8)	C21-H21	0.930000
C22-H22	0.930000	C24-H24A	0.960000
C24-H24B	0.960000	C24-H24C	0.960000
C25-H25A	0.960000	C25-H25B	0.960000
C25-H25C	0.960000	C26-H26A	0.960000
C26-H26B	0.960000	C26-H26C	0.960000
C27-C28	1.507(7)	C27-H27A	0.970000
C27-H27B	0.970000	C28-C33	1.368(8)
C28-C29	1.377(7)	C29-C30	1.378(7)
C29-H29	0.930000	C30-C31	1.356(8)
C30-H30	0.930000	C31-C32	1.384(8)
C32-C33	1.368(8)	C32-H32	0.930000
C33-H33	0.930000	C35-H35A	0.960000
C35-H35B	0.960000	C35-H35C	0.960000
Cl2N-C1N	1.731(8)	Cl3N-C1N	1.763(7)
Cl4N-C1N	1.734(7)	C1N-H1N	0.980000

Table 6. Bond angles (°) for GR009.

H1A-O1W-H1B	120.000000	C5-O15-H15	109.500000
C20-O23-C24	118.4(6)	C31-O34-C35	117.7(5)
C2-N3-C4	117.8(4)	C2-N3-H3	121.100000
C4-N3-H3	121.100000	C5-N6-C1	116.1(4)
C5-N6-C16	121.2(4)	C1-N6-C16	121.4(4)
C10-N9-C27	111.9(4)	C10-N9-C8	110.1(4)
C27-N9-C8	116.0(5)	C11-N12-C7	123.4(4)
C11-N12-H12	118.300000	C7-N12-H12	118.300000
N6-C1-C2	104.8(4)	N6-C1-C7	111.3(4)

C2-C1-C7	109.8(4)	N6-C1-H1	110.300000
C2-C1-H1	110.300000	C7-C1-H1	110.300000
O13-C2-N3	125.0(5)	O13-C2-C1	125.4(5)
N3-C2-C1	109.6(4)	N3-C4-C14	108.7(4)
N3-C4-C5	108.6(4)	C14-C4-C5	111.8(4)
N3-C4-C8	106.3(4)	C14-C4-C8	112.6(4)
C5-C4-C8	108.6(4)	O15-C5-N6	111.4(4)
O15-C5-C6	103.9(4)	N6-C5-C6	113.1(5)
O15-C5-C4	113.0(4)	N6-C5-C4	105.9(4)
C6-C5-C4	109.6(4)	C10-C6-C5	111.4(5)
C10-C6-H6A	109.300000	C5-C6-H6A	109.300000
C10-C6-H6B	109.300000	C5-C6-H6B	109.300000
H6A-C6-H6B	108.000000	N12-C7-C25	107.5(4)
N12-C7-C1	106.1(4)	C25-C7-C1	109.3(4)
N12-C7-C8	110.6(4)	C25-C7-C8	115.6(4)
C1-C7-C8	107.3(4)	N9-C8-C26	109.2(4)
N9-C8-C4	107.3(4)	C26-C8-C4	108.6(4)
N9-C8-C7	111.6(4)	C26-C8-C7	113.2(4)
C4-C8-C7	106.7(4)	N9-C10-C6	110.5(4)
N9-C10-C11	110.8(5)	C6-C10-C11	114.7(5)
N9-C10-H10	106.800000	C6-C10-H10	106.800000
C11-C10-H10	106.800000	O36-C11-N12	122.7(5)
O36-C11-C10	122.0(5)	N12-C11-C10	115.1(5)
C4-C14-H14A	109.500000	C4-C14-H14B	109.500000
H14A-C14-H14B	109.500000	C4-C14-H14C	109.500000
H14A-C14-H14C	109.500000	H14B-C14-H14C	109.500000
N6-C16-C17	113.6(5)	N6-C16-H16A	108.800000
C17-C16-H16A	108.800000	N6-C16-H16B	108.800000
C17-C16-H16B	108.800000	H16A-C16-H16B	107.700000
C22-C17-C18	117.0(5)	C22-C17-C16	120.7(5)
C18-C17-C16	122.2(5)	C17-C18-C19	121.5(6)
C17-C18-H18	119.200000	C19-C18-H18	119.200000
C20-C19-C18	120.5(6)	C20-C19-H19	119.700000
C18-C19-H19	119.700000	C21-C20-C19	119.1(6)
C21-C20-O23	124.7(6)	C19-C20-O23	116.2(6)
C20-C21-C22	119.1(6)	C20-C21-H21	120.400000
C22-C21-H21	120.400000	C17-C22-C21	122.7(5)
C17-C22-H22	118.600000	C21-C22-H22	118.600000
O23-C24-H24A	109.500000	O23-C24-H24B	109.500000
H24A-C24-H24B	109.500000	O23-C24-H24C	109.500000
H24A-C24-H24C	109.500000	H24B-C24-H24C	109.500000
C7-C25-H25A	109.500000	C7-C25-H25B	109.500000
H25A-C25-H25B	109.500000	C7-C25-H25C	109.500000
H25A-C25-H25C	109.500000	H25B-C25-H25C	109.500000
C8-C26-H26A	109.500000	C8-C26-H26B	109.500000
H26A-C26-H26B	109.500000	C8-C26-H26C	109.500000
H26A-C26-H26C	109.500000	H26B-C26-H26C	109.500000
N9-C27-C28	114.6(4)	N9-C27-H27A	108.600000
C28-C27-H27A	108.600000	N9-C27-H27B	108.600000
C28-C27-H27B	108.600000	H27A-C27-H27B	107.600000
C33-C28-C29	117.2(5)	C33-C28-C27	120.6(5)
C29-C28-C27	121.9(5)	C28-C29-C30	121.8(5)

C28-C29-H29	119.100000	C30-C29-H29	119.100000
C31-C30-C29	119.4(5)	C31-C30-H30	120.300000
C29-C30-H30	120.300000	C30-C31-O34	124.7(5)
C30-C31-C32	120.2(5)	O34-C31-C32	115.1(5)
C33-C32-C31	119.0(5)	C33-C32-H32	120.500000
C31-C32-H32	120.500000	C32-C33-C28	122.3(5)
C32-C33-H33	118.900000	C28-C33-H33	118.900000
O34-C35-H35A	109.500000	O34-C35-H35B	109.500000
H35A-C35-H35B	109.500000	O34-C35-H35C	109.500000
H35A-C35-H35C	109.500000	H35B-C35-H35C	109.500000
Cl2N-C1N-Cl4N	112.8(4)	Cl2N-C1N-Cl3N	108.3(4)
Cl4N-C1N-Cl3N	111.1(4)	Cl2N-C1N-H1N	108.100000
Cl4N-C1N-H1N	108.100000	Cl3N-C1N-H1N	108.100000

Table 7. Torsion angles (°) for GR009.

C5-N6-C1-C2	63.4(6)	C16-N6-C1-C2	-129.3(5)
C5-N6-C1-C7	-55.2(6)	C16-N6-C1-C7	112.1(5)
C4-N3-C2-O13	-178.0(5)	C4-N3-C2-C1	1.8(7)
N6-C1-C2-O13	120.6(6)	C7-C1-C2-O13	-119.7(6)
N6-C1-C2-N3	-59.1(5)	C7-C1-C2-N3	60.6(6)
C2-N3-C4-C14	176.2(5)	C2-N3-C4-C5	54.3(6)
C2-N3-C4-C8	-62.4(6)	C1-N6-C5-O15	-132.0(5)
C16-N6-C5-O15	60.7(7)	C1-N6-C5-C6	111.4(5)
C16-N6-C5-C6	-55.9(7)	C1-N6-C5-C4	-8.7(6)
C16-N6-C5-C4	-176.0(5)	N3-C4-C5-O15	74.2(5)
C14-C4-C5-O15	-45.7(6)	C8-C4-C5-O15	-170.5(4)
N3-C4-C5-N6	-48.0(5)	C14-C4-C5-N6	-168.0(4)
C8-C4-C5-N6	67.2(5)	N3-C4-C5-C6	-170.4(4)
C14-C4-C5-C6	69.6(5)	C8-C4-C5-C6	-55.2(5)
O15-C5-C6-C10	175.0(4)	N6-C5-C6-C10	-64.1(6)
C4-C5-C6-C10	53.9(6)	C11-N12-C7-C25	-165.2(5)
C11-N12-C7-C1	77.9(6)	C11-N12-C7-C8	-38.2(6)
N6-C1-C7-N12	-59.5(5)	C2-C1-C7-N12	-175.1(4)
N6-C1-C7-C25	-175.1(4)	C2-C1-C7-C25	69.3(5)
N6-C1-C7-C8	58.8(5)	C2-C1-C7-C8	-56.8(5)
C10-N9-C8-C26	177.2(4)	C27-N9-C8-C26	49.0(5)
C10-N9-C8-C4	-65.2(5)	C27-N9-C8-C4	166.5(4)
C10-N9-C8-C7	51.3(5)	C27-N9-C8-C7	-77.0(5)
N3-C4-C8-N9	177.3(4)	C14-C4-C8-N9	-63.7(5)
C5-C4-C8-N9	60.6(5)	N3-C4-C8-C26	-64.8(5)
C14-C4-C8-C26	54.2(6)	C5-C4-C8-C26	178.5(4)
N3-C4-C8-C7	57.5(5)	C14-C4-C8-C7	176.5(4)
C5-C4-C8-C7	-59.2(5)	N12-C7-C8-N9	-3.5(5)
C25-C7-C8-N9	118.9(5)	C1-C7-C8-N9	-118.9(4)
N12-C7-C8-C26	-127.2(5)	C25-C7-C8-C26	-4.8(6)
C1-C7-C8-C26	117.4(5)	N12-C7-C8-C4	113.4(4)
C25-C7-C8-C4	-124.2(5)	C1-C7-C8-C4	-1.9(5)
C27-N9-C10-C6	-165.2(4)	C8-N9-C10-C6	64.2(5)
C27-N9-C10-C11	66.5(5)	C8-N9-C10-C11	-64.0(5)
C5-C6-C10-N9	-57.8(6)	C5-C6-C10-C11	68.2(6)
C7-N12-C11-O36	-156.7(5)	C7-N12-C11-C10	27.6(7)

N9-C10-C11-O36	-150.7(5)	C6-C10-C11-O36	83.3(6)
N9-C10-C11-N12	25.0(6)	C6-C10-C11-N12	-100.9(6)
C5-N6-C16-C17	-140.6(5)	C1-N6-C16-C17	52.8(7)
N6-C16-C17-C22	-117.6(6)	N6-C16-C17-C18	64.6(8)
C22-C17-C18-C19	1.8(10)	C16-C17-C18-C19	179.6(6)
C17-C18-C19-C20	-1.5(11)	C18-C19-C20-C21	0.5(11)
C18-C19-C20-O23	-179.0(6)	C24-O23-C20-C21	8.3(10)
C24-O23-C20-C19	-172.2(7)	C19-C20-C21-C22	0.1(11)
O23-C20-C21-C22	179.6(6)	C18-C17-C22-C21	-1.3(10)
C16-C17-C22-C21	-179.1(6)	C20-C21-C22-C17	0.3(11)
C10-N9-C27-C28	130.3(5)	C8-N9-C27-C28	-102.3(6)
N9-C27-C28-C33	162.2(6)	N9-C27-C28-C29	-23.8(8)
C33-C28-C29-C30	-0.9(9)	C27-C28-C29-C30	-175.1(6)
C28-C29-C30-C31	0.5(9)	C29-C30-C31-O34	-179.5(6)
C29-C30-C31-C32	-0.3(9)	C35-O34-C31-C30	5.4(9)
C35-O34-C31-C32	-173.9(6)	C30-C31-C32-C33	0.5(9)
O34-C31-C32-C33	179.8(6)	C31-C32-C33-C28	-0.9(10)
C29-C28-C33-C32	1.1(9)	C27-C28-C33-C32	175.4(6)

Table 8. Anisotropic atomic displacement parameters (Å^2) for GR009.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O15	0.046(2)	0.046(2)	0.049(2)	0.001(2)	-0.011(2)	0.002(2)
O13	0.113(4)	0.044(2)	0.038(2)	0.0240(19)	0.028(2)	0.039(3)
O23	0.074(3)	0.086(4)	0.085(4)	0.044(3)	0.014(3)	0.045(3)
O34	0.048(3)	0.069(3)	0.075(3)	0.025(3)	0.023(2)	0.031(2)
O36	0.076(3)	0.047(2)	0.045(2)	0.027(2)	0.036(2)	0.026(2)
N3	0.071(3)	0.039(3)	0.023(2)	0.014(2)	0.017(2)	0.027(2)
N6	0.027(2)	0.033(2)	0.047(3)	0.001(2)	0.011(2)	0.007(2)
N9	0.047(3)	0.044(3)	0.031(2)	0.016(2)	0.012(2)	0.026(2)
N12	0.052(3)	0.037(3)	0.017(2)	0.0083(18)	0.0096(19)	0.016(2)
C1	0.033(3)	0.026(3)	0.025(2)	0.008(2)	0.009(2)	0.011(2)
C2	0.051(3)	0.040(3)	0.025(3)	0.013(2)	0.008(2)	0.017(3)
C4	0.047(3)	0.030(3)	0.020(2)	0.004(2)	0.005(2)	0.015(2)
C5	0.035(3)	0.037(3)	0.031(3)	0.000(2)	0.005(2)	0.009(2)
C6	0.048(4)	0.033(3)	0.045(3)	0.008(3)	0.015(3)	0.004(3)
C7	0.032(3)	0.036(3)	0.021(2)	0.011(2)	0.006(2)	0.009(2)
C8	0.034(3)	0.031(3)	0.025(2)	0.006(2)	0.008(2)	0.011(2)
C10	0.058(4)	0.037(3)	0.044(3)	0.023(3)	0.025(3)	0.022(3)
C11	0.048(3)	0.034(3)	0.035(3)	0.019(2)	0.012(3)	0.016(3)
C14	0.061(4)	0.048(3)	0.031(3)	0.008(3)	0.013(3)	0.029(3)
C16	0.037(3)	0.051(4)	0.055(4)	0.020(3)	0.017(3)	0.014(3)
C17	0.025(3)	0.054(4)	0.038(3)	0.017(3)	0.009(2)	0.013(3)
C18	0.074(5)	0.073(5)	0.036(3)	0.019(3)	0.013(3)	0.029(4)
C19	0.080(5)	0.085(5)	0.053(4)	0.043(4)	0.010(4)	0.032(4)
C20	0.038(3)	0.060(4)	0.062(4)	0.030(3)	0.012(3)	0.021(3)
C21	0.075(5)	0.082(5)	0.040(4)	0.022(3)	0.016(3)	0.048(4)
C22	0.076(5)	0.083(5)	0.031(3)	0.023(3)	0.010(3)	0.052(4)
C24	0.110(7)	0.078(6)	0.109(7)	0.044(5)	0.038(6)	0.058(5)
C25	0.040(3)	0.045(3)	0.036(3)	0.004(3)	0.007(3)	-0.001(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C26	0.042(3)	0.049(4)	0.045(3)	0.014(3)	0.018(3)	0.017(3)
C27	0.067(4)	0.057(4)	0.028(3)	0.011(3)	0.007(3)	0.036(3)
C28	0.042(3)	0.042(3)	0.030(3)	0.017(2)	0.005(2)	0.017(3)
C29	0.040(3)	0.048(3)	0.045(3)	0.013(3)	0.001(3)	0.020(3)
C30	0.042(3)	0.037(3)	0.044(3)	0.008(3)	0.002(3)	0.013(3)
C31	0.038(3)	0.043(3)	0.057(4)	0.026(3)	0.020(3)	0.016(3)
C32	0.033(3)	0.062(4)	0.055(4)	0.022(3)	0.002(3)	0.012(3)
C33	0.046(4)	0.046(3)	0.034(3)	0.006(3)	-0.001(3)	0.010(3)
C35	0.086(6)	0.092(6)	0.077(5)	0.031(5)	0.038(4)	0.061(5)
Cl2N	0.0864(17)	0.144(2)	0.167(3)	0.081(2)	0.0447(18)	0.0310(17)
Cl3N	0.0900(15)	0.0971(16)	0.0803(14)	0.0346(12)	0.0182(11)	0.0413(13)
Cl4N	0.182(3)	0.0934(16)	0.0679(13)	0.0447(12)	0.0446(15)	0.0715(17)
C1N	0.094(6)	0.045(4)	0.056(4)	0.012(3)	0.020(4)	0.025(4)

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for GR009.

	x/a	y/b	z/c	U(eq)
H1A	-0.2410	0.2894	0.4636	0.111000
H1B	-0.3404	0.2755	0.3599	0.089000
H15	-0.2132	0.2546	0.4974	0.087000
H3	0.0517	0.4107	0.5201	0.051000
H12	0.1207	0.5083	0.9575	0.043000
H1	-0.0311	0.5693	0.7990	0.034000
H6A	-0.1824	0.1778	0.7010	0.054000
H6B	-0.0933	0.1165	0.6246	0.054000
H10	0.0265	0.1725	0.7983	0.050000
H14A	0.0781	0.1498	0.5359	0.072000
H14B	0.1289	0.2367	0.4874	0.072000
H14C	-0.0278	0.1723	0.4540	0.072000
H16A	-0.2122	0.4030	0.8244	0.057000
H16B	-0.3116	0.3222	0.7079	0.057000
H18	-0.3698	0.4509	0.6002	0.074000
H19	-0.4636	0.6090	0.6133	0.082000
H21	-0.3618	0.7387	0.9345	0.077000
H22	-0.2650	0.5799	0.9188	0.073000
H24A	-0.5146	0.9353	0.8613	0.139000
H24B	-0.3757	0.9150	0.9113	0.139000
H24C	-0.5151	0.8504	0.9186	0.139000
H25A	0.2523	0.6170	0.8014	0.070000
H25B	0.3206	0.5776	0.8877	0.070000
H25C	0.2121	0.6538	0.9116	0.070000
H26A	0.2876	0.4449	0.6584	0.069000
H26B	0.3068	0.3174	0.6412	0.069000
H26C	0.3633	0.4269	0.7571	0.069000
H27A	0.2418	0.2551	0.8847	0.062000
H27B	0.3221	0.3619	0.8700	0.062000
H29	0.2394	0.0797	0.6485	0.057000
H30	0.3860	-0.0392	0.5898	0.055000
H32	0.6819	0.1843	0.8600	0.064000

	x/a	y/b	z/c	U(eq)
H33	0.5332	0.3001	0.9169	0.058000
H35A	0.6876	-0.1317	0.5752	0.121000
H35B	0.5747	-0.0771	0.5336	0.121000
H35C	0.5375	-0.1651	0.5843	0.121000
H1N	0.0103	0.7800	0.7554	0.081000