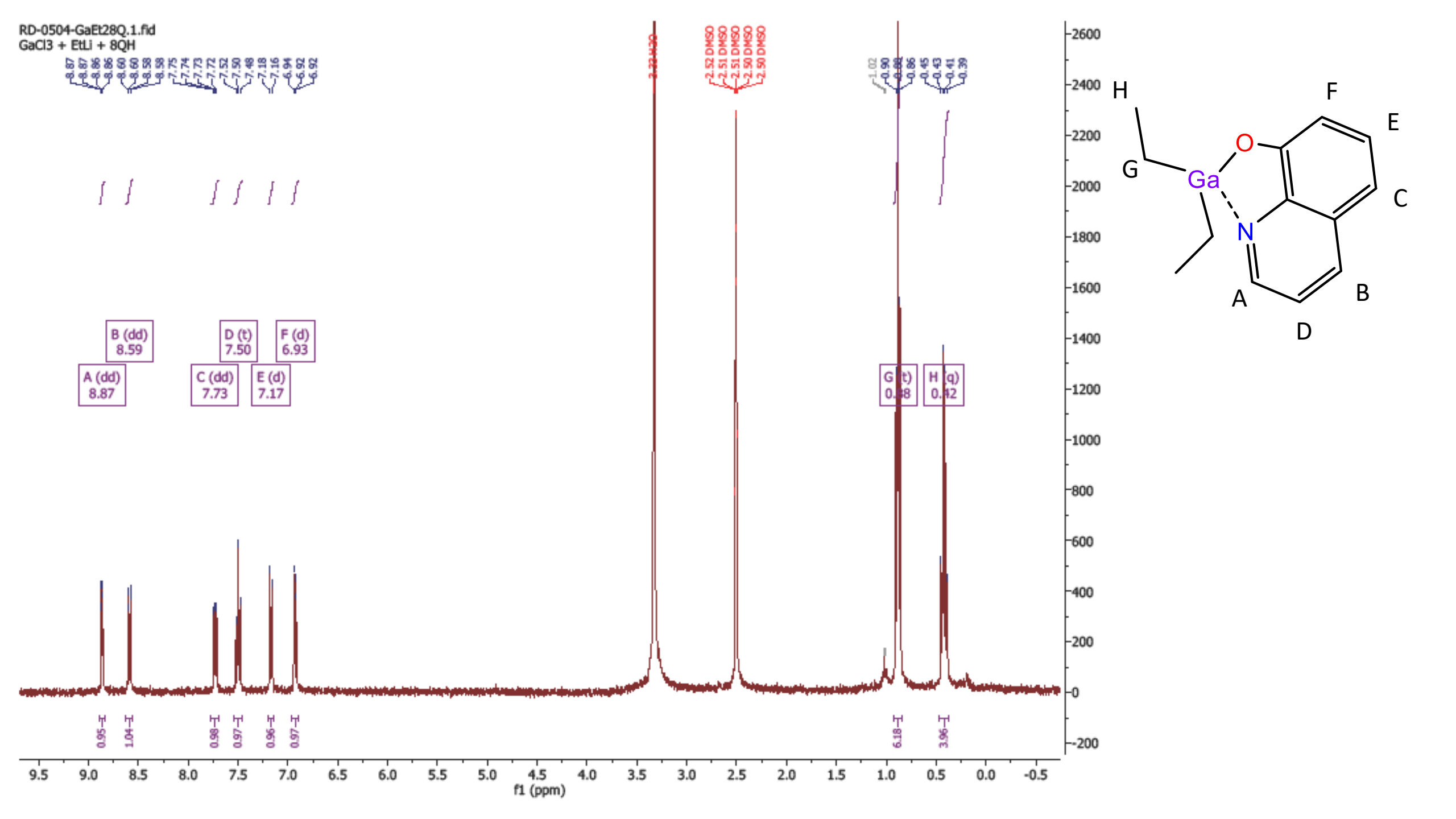
Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

Structure-activity effects in the anti-leishmanial activity of di-alkyl gallium quinoline-8-olates

Rebekah N Duffin and Philip C Andrews

1. ^{1}H NMR and ^{13}C NMR
2. FT-IR
3. High-resolution Mass spectrometry
4. X-ray crystallography
5. Biological activity
6. Other analytical data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GaCl3 + EtLi + 8QH
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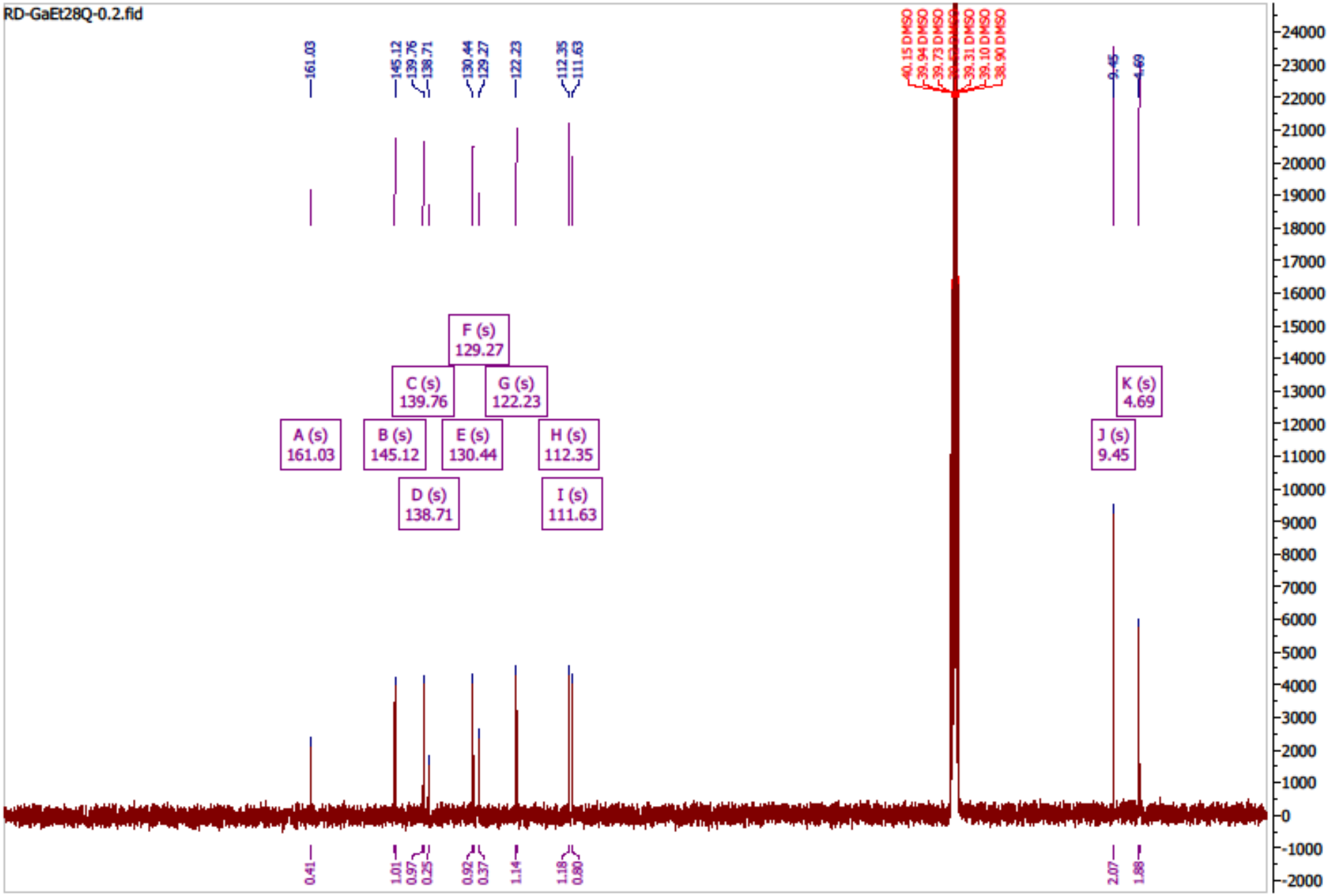
D (t) 7.50
F (d) 6.93
A (dd) 8.87
C (dd) 7.73
E (d) 7.17
G (t) 0.88
H (q) 0.42
0.95
1.04
0.98
0.97
0.96
0.97
6.18
3.96
f1 (ppm)
H
F
E
G
Ga
O
C
N
A
B
D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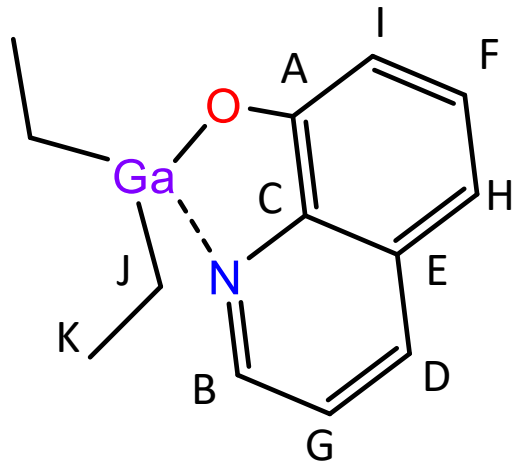
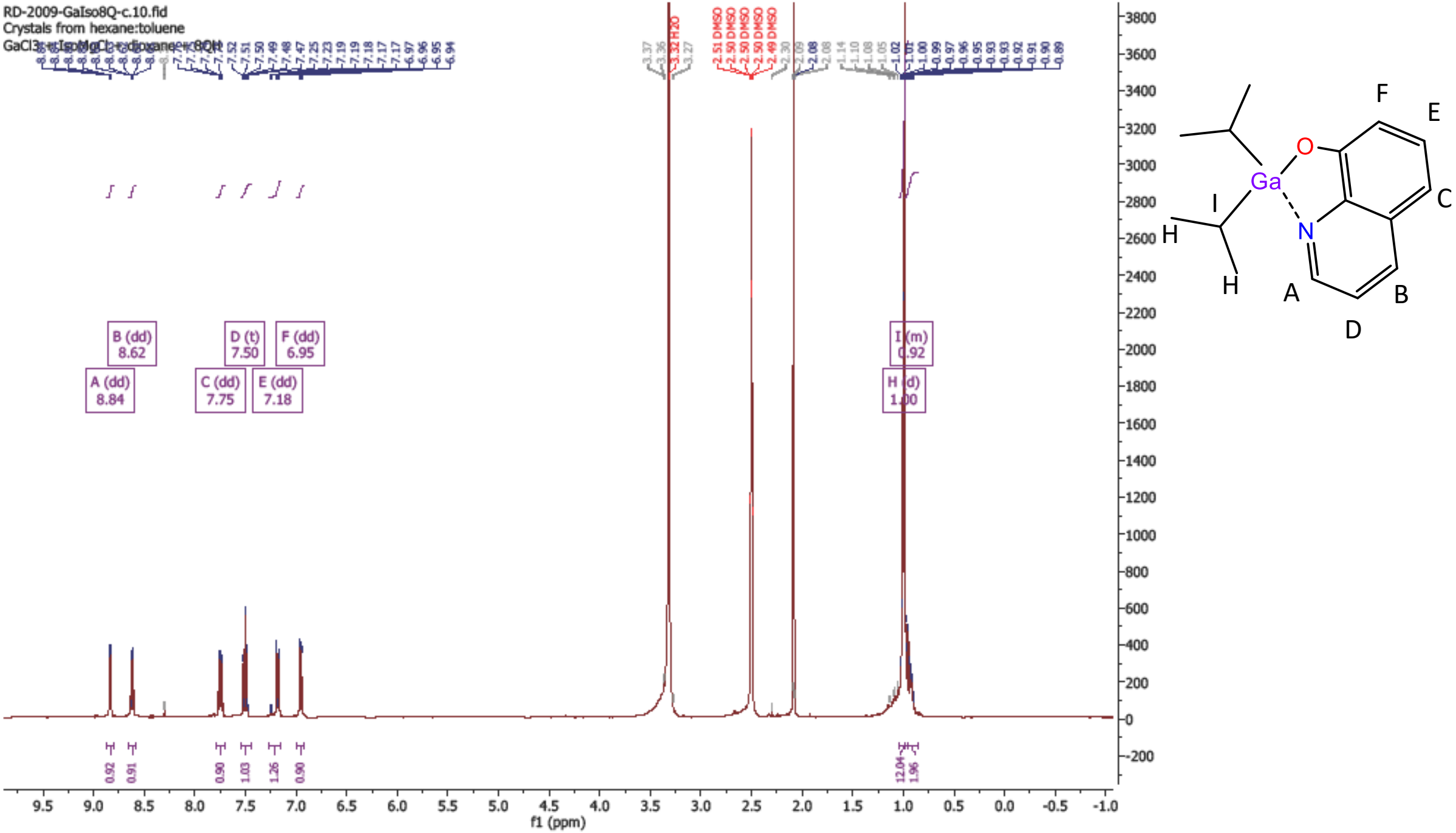
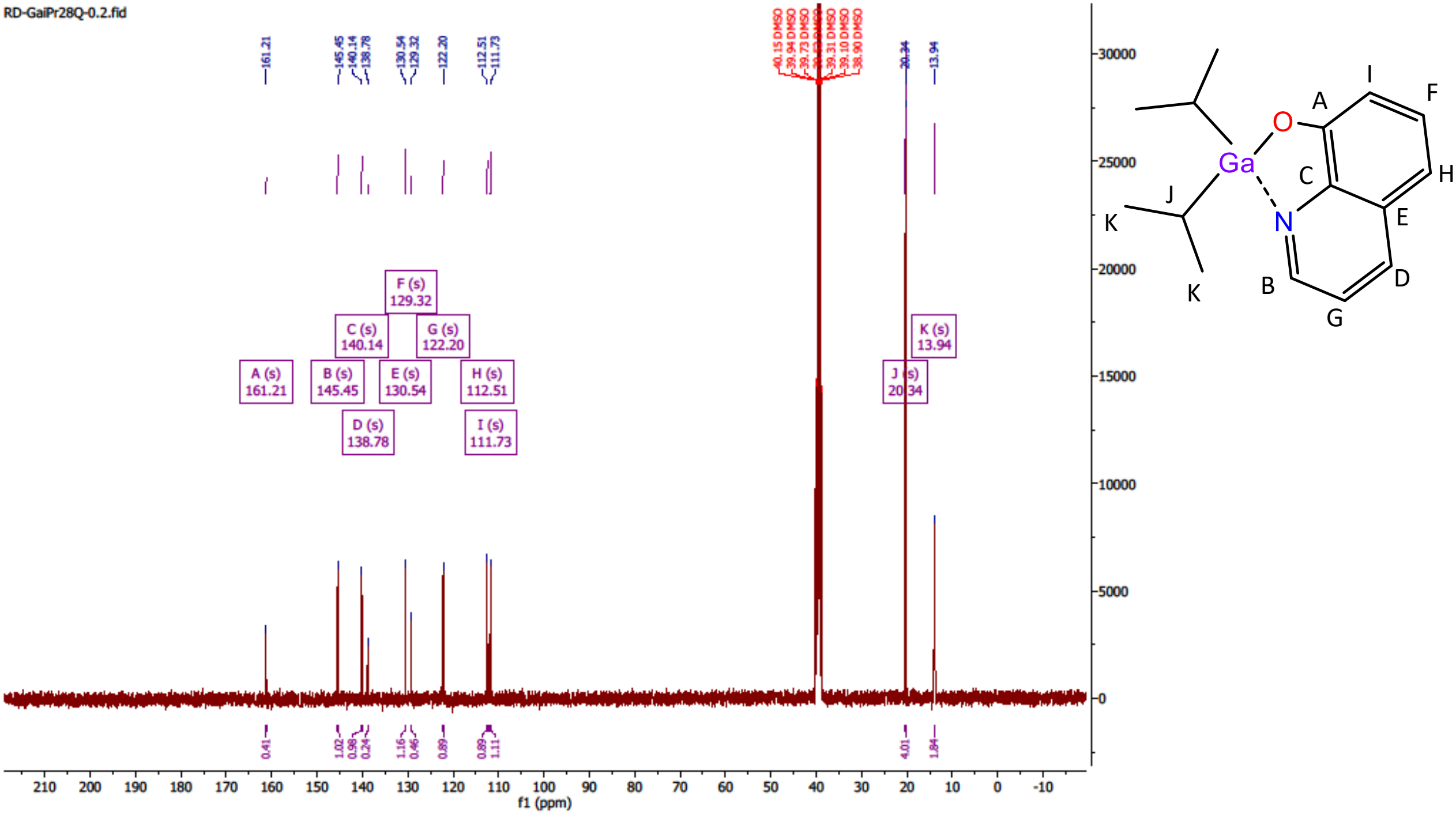
145.12
139.76
138.71
130.44
129.27
122.23
112.35
111.63
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.31 DMSO
39.10 DMSO
38.90 DMSO
9.45
4.69
A (s) 161.03
B (s) 145.12
C (s) 139.76
D (s) 138.71
E (s) 130.44
F (s) 129.27
G (s) 122.23
H (s) 112.35
I (s) 111.63
J (s) 9.45
K (s) 4.69
0.41
1.01
0.97
0.25
0.92
0.37
1.14
1.18
0.80
2.07
1.88
f1 (ppm)


Ga
O
N
A
B
C
D
E
F
G
H
I
J
K

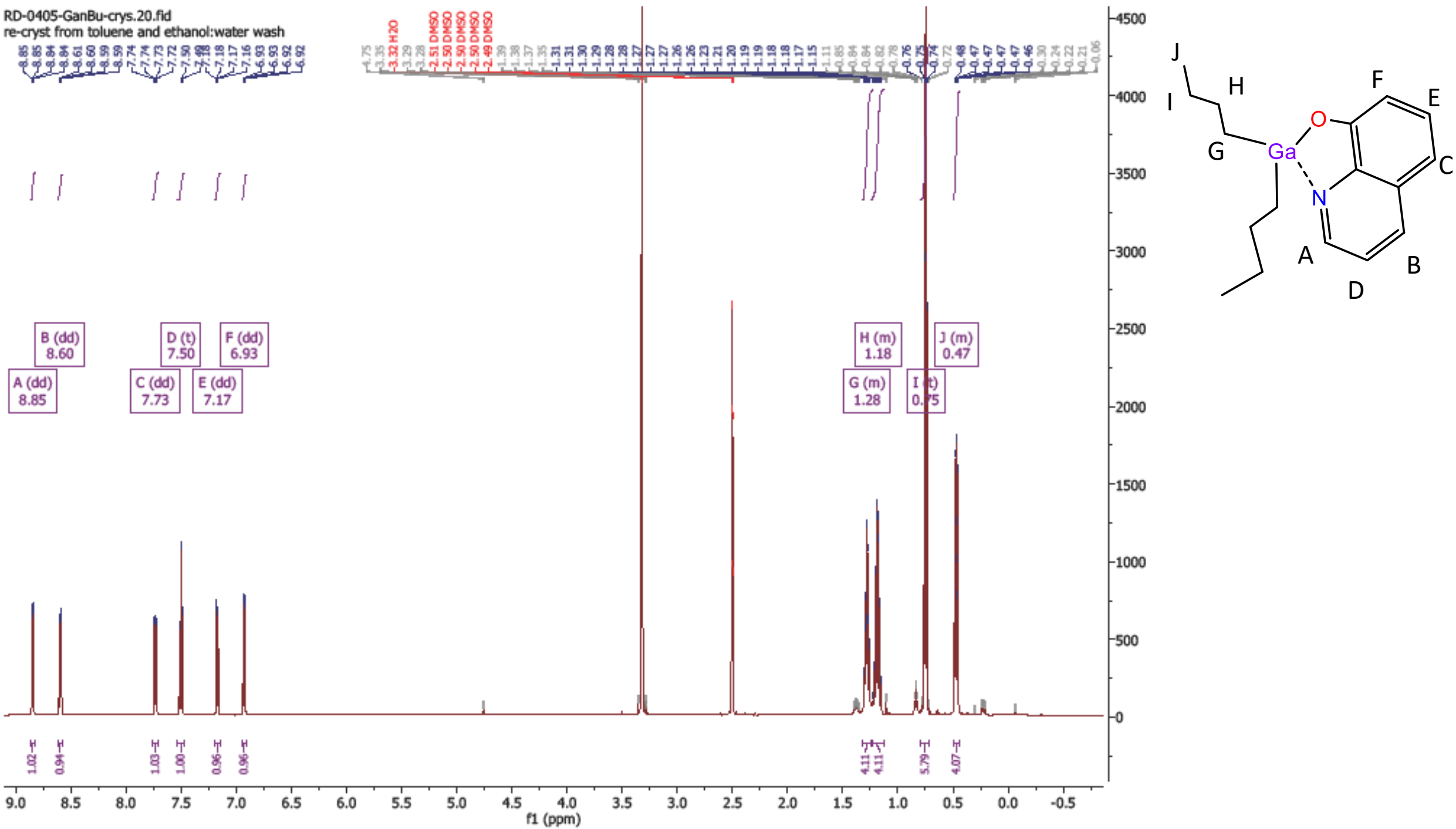
RD-2009-GaIso8Q-c.10.fid
Crystals from hexane:toluene
GaCl3 + IsoMgCl + dioxane + 8QH



RD-GaiPr28Q-0.2.fid



RD-0405-GanBu-crys.20.fid
re-cryst from toluene and ethanol:water wash



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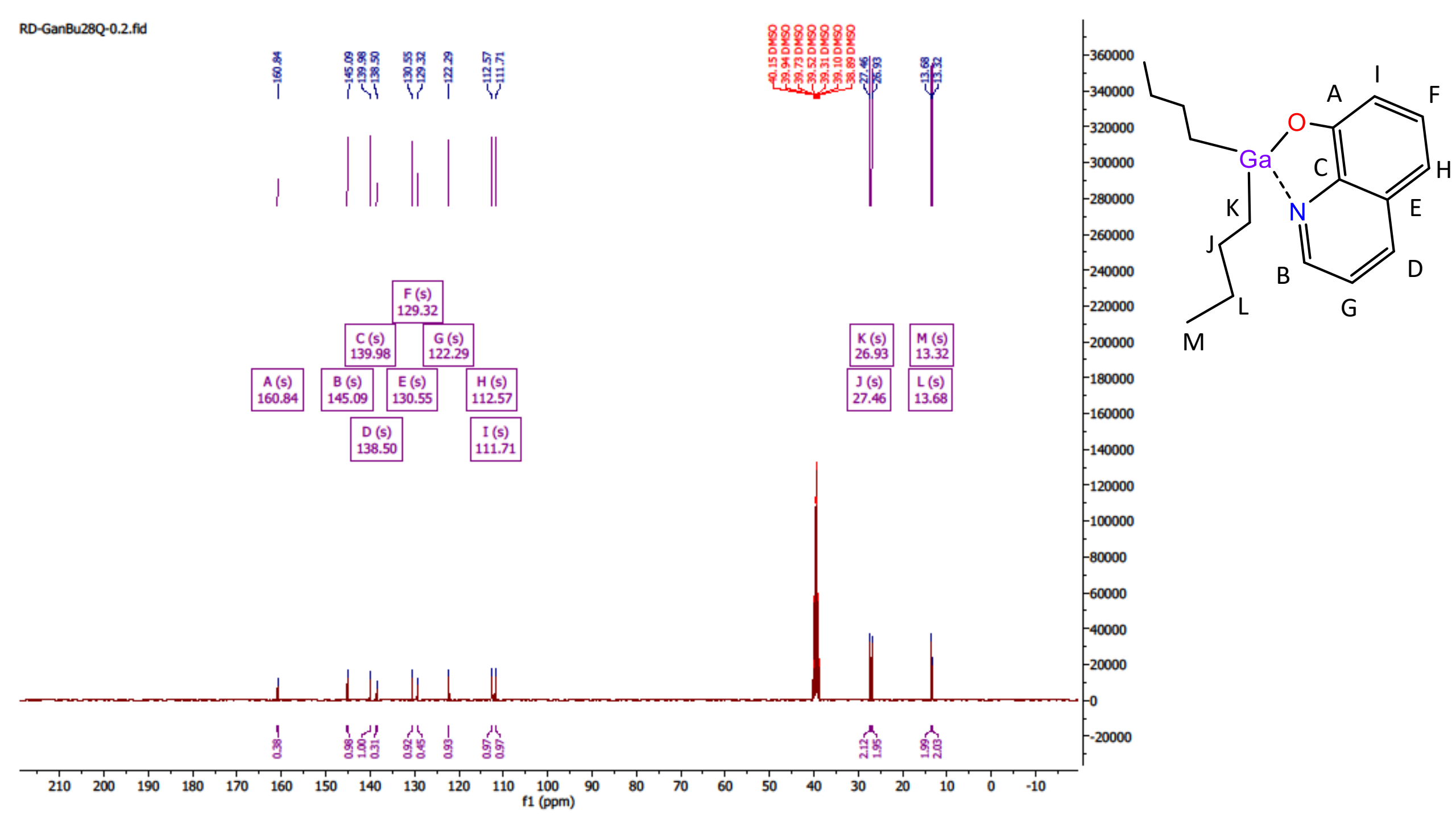

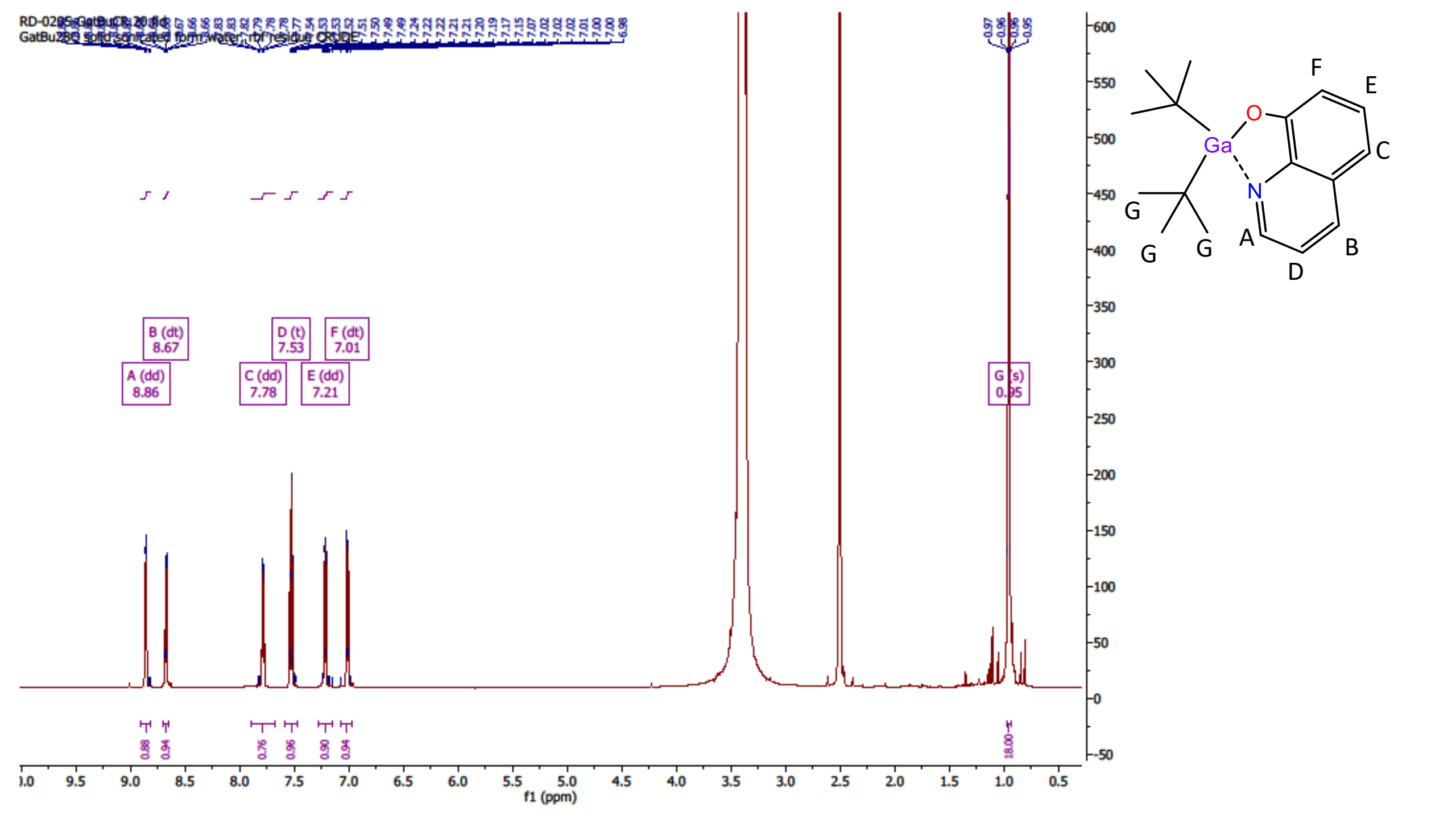
RD-0205-GatBuCR-20.fid
GatBu280 solid sonicated from water, rbf residue CRUDE
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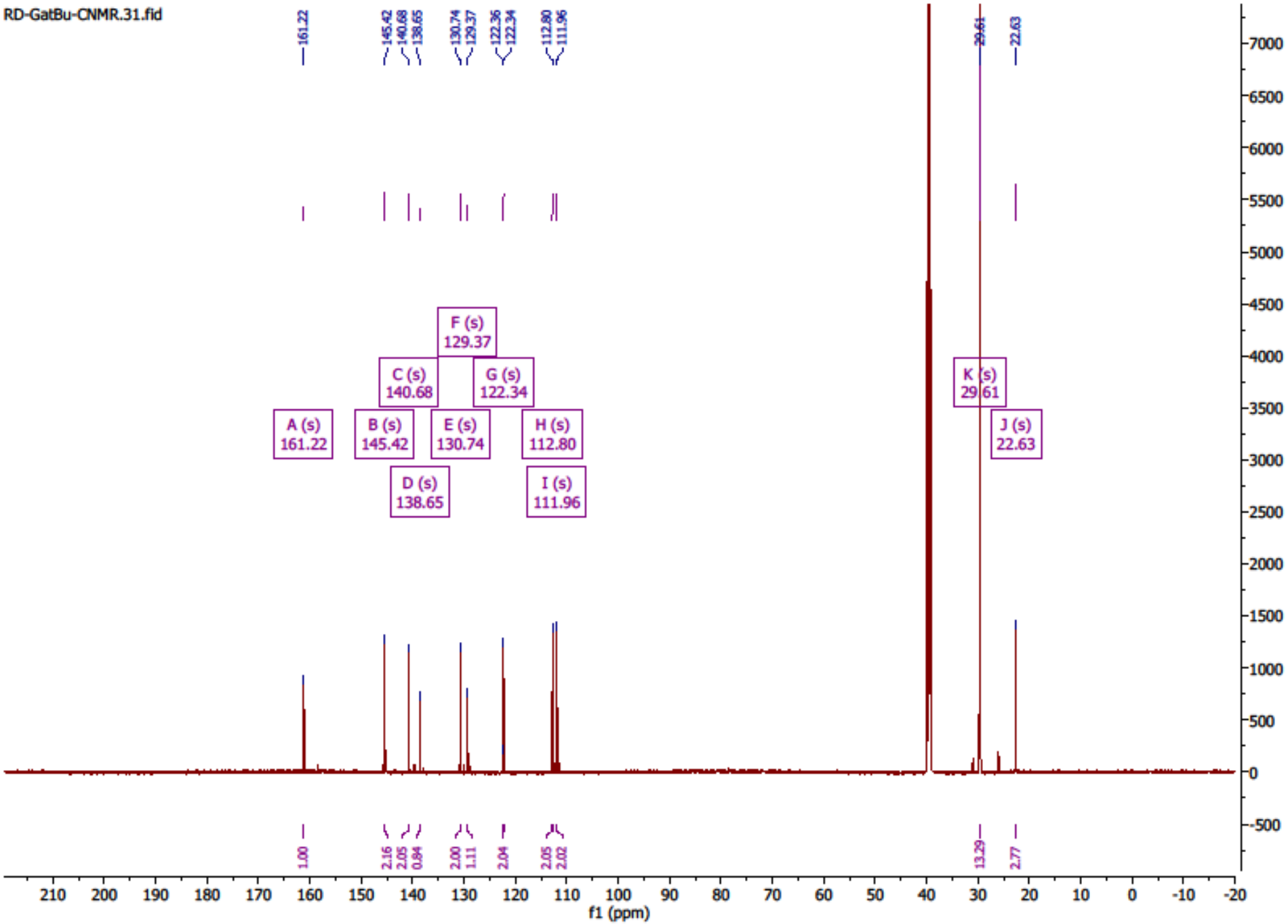
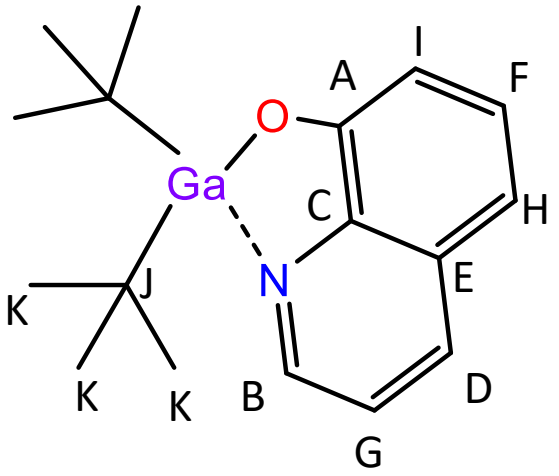
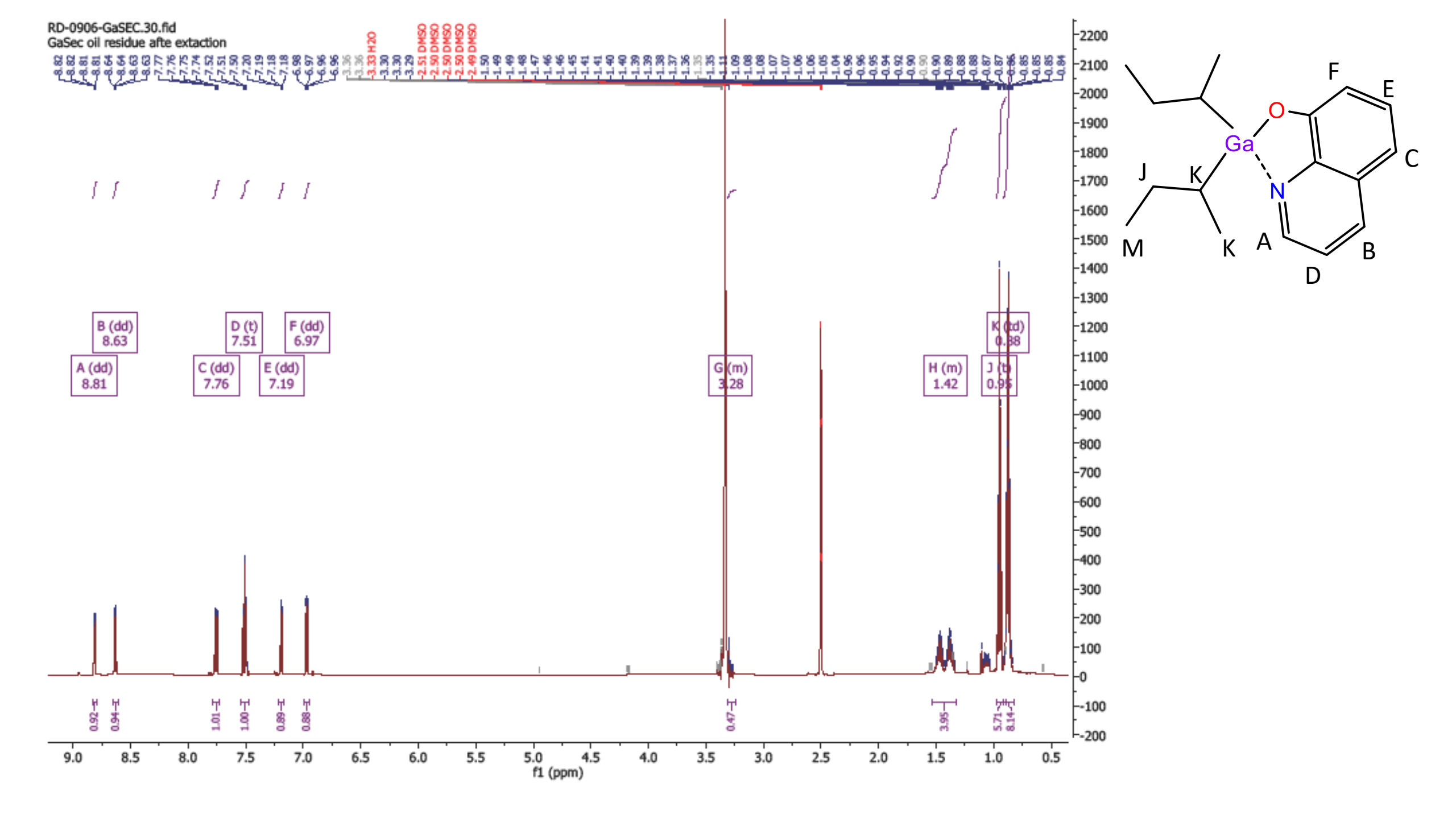
8.67
D (t)
7.53
F (dt)
7.01
A (dd)
8.86
C (dd)
7.78
E (dd)
7.21
G (s)
0.95
0.88
0.94
0.76
0.96
0.90
0.94
18.00
f1 (ppm)
F
E
O
C
Ga
N
G
G
G
A
B
D

RD-GatBu-CNMR.31.fid



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GaSec oil residue afte extaction
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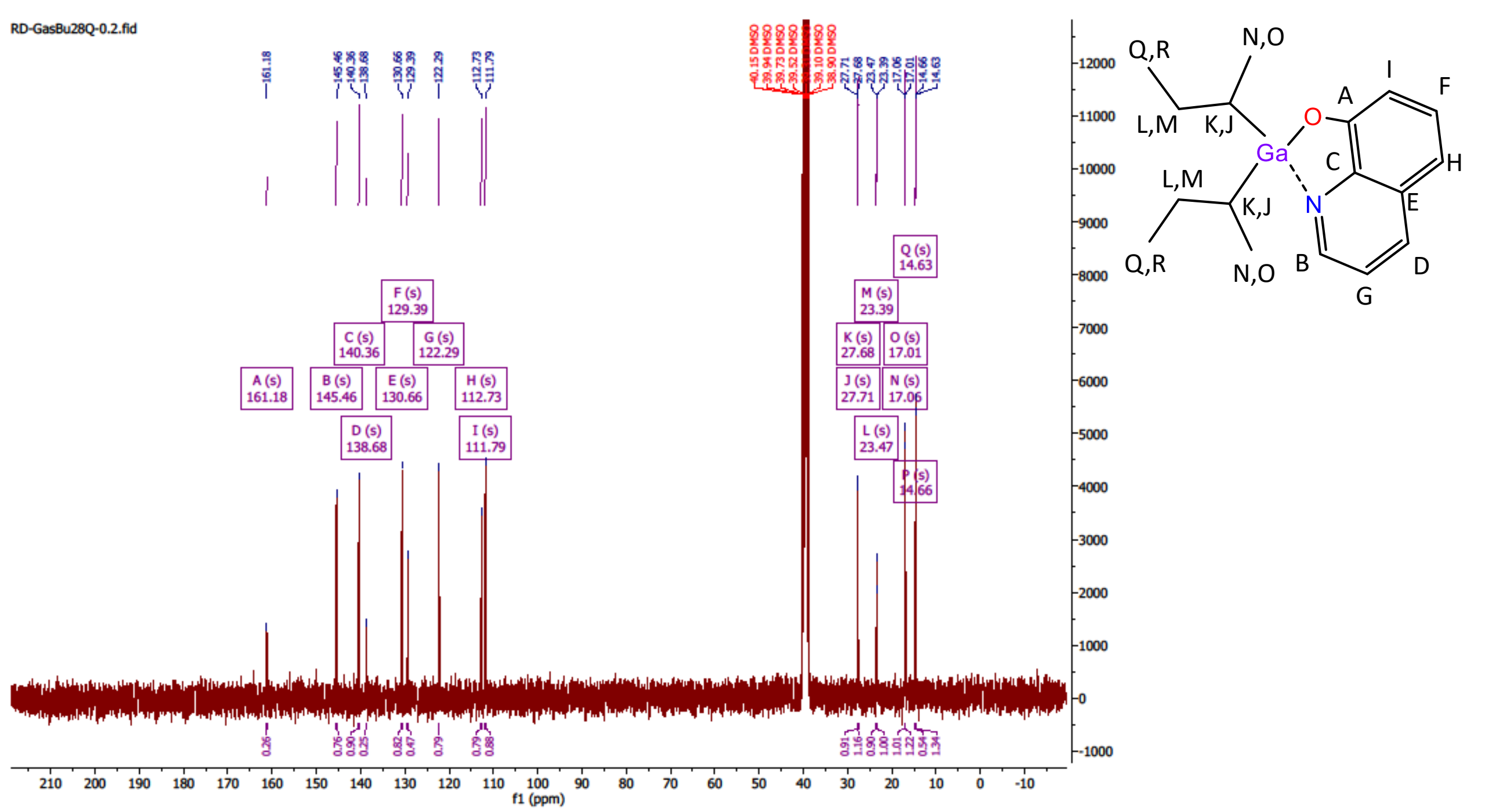
D (t) 7.51
C (dd) 7.76
F (dd) 6.97
E (dd) 7.19
G (m) 3.28
H (m) 1.42
J (t) 0.95
K (dd) 0.88
f1 (ppm)
F
E
O
C
Ga
J
K
N
M
K
A
B
D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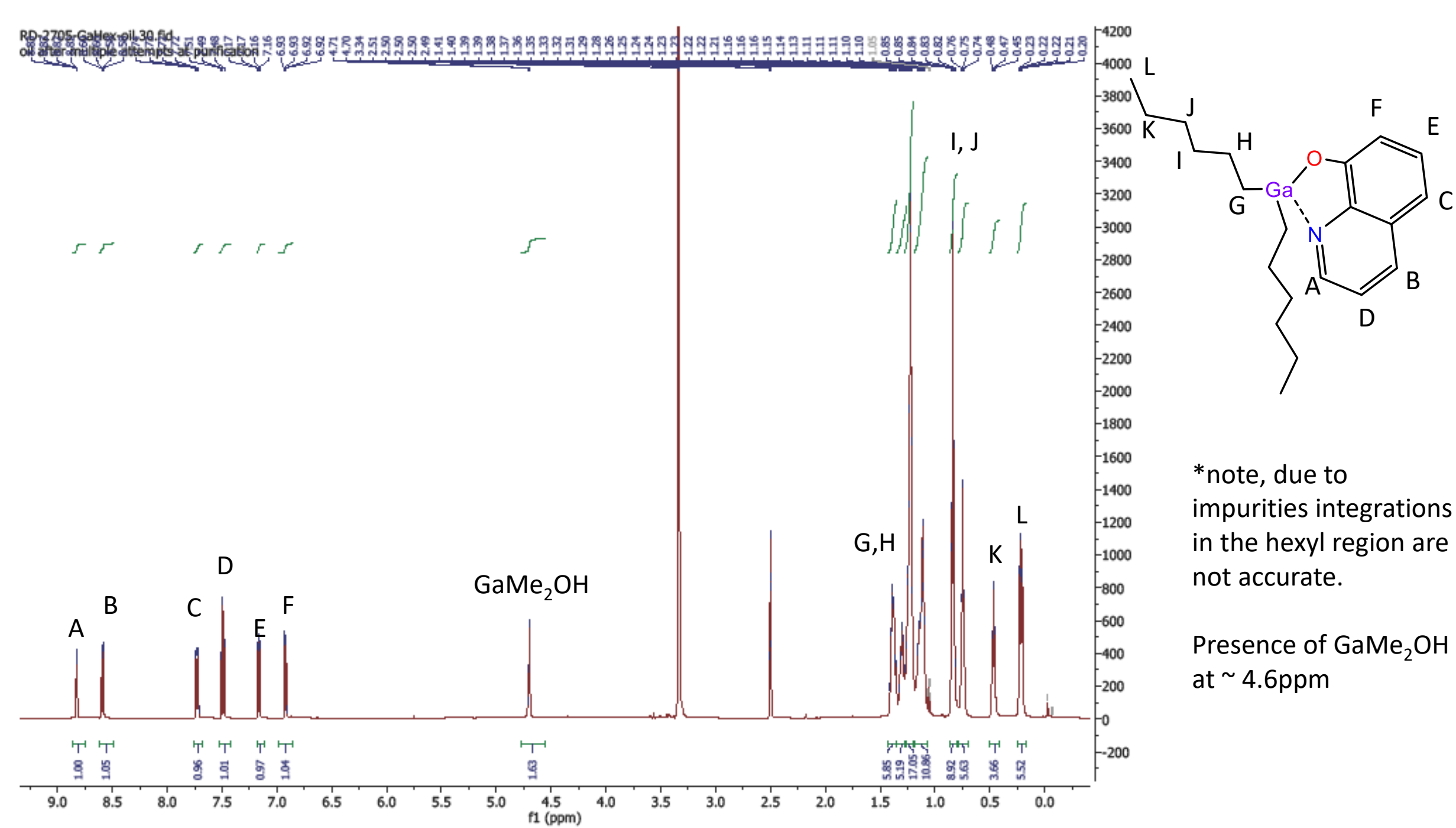
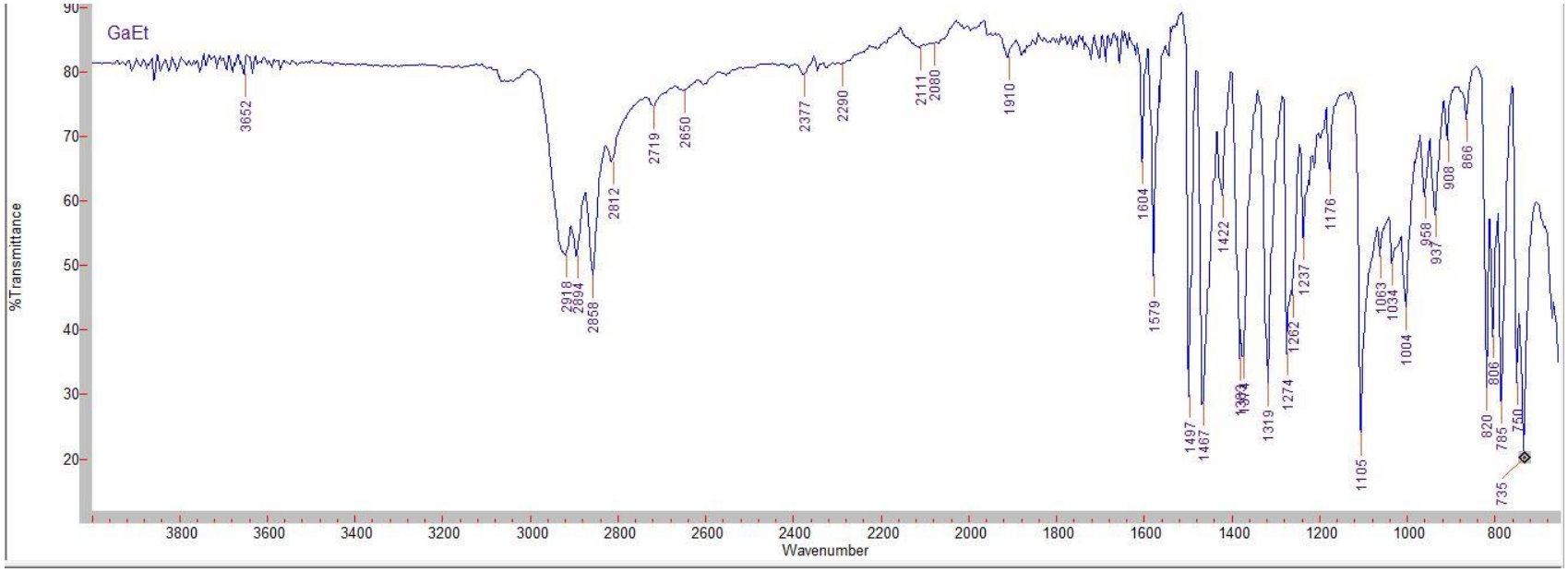
161.18
145.46
140.36
138.68
130.66
129.39
122.29
112.73
111.79
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.90 DMSO
27.71
27.68
23.47
23.39
17.06
17.01
14.66
14.63
A (s) 161.18
B (s) 145.46
C (s) 140.36
D (s) 138.68
E (s) 130.66
F (s) 129.39
G (s) 122.29
H (s) 112.73
I (s) 111.79
J (s) 27.71
K (s) 27.68
L (s) 23.47
M (s) 23.39
N (s) 17.06
O (s) 17.01
P (s) 14.66
Q (s) 14.63
0.26
0.76
0.90
0.25
0.82
0.47
0.79
0.79
0.88
0.91
1.16
0.90
1.00
1.01
1.22
0.54
1.34
f1 (ppm)
Q,R
N,O
L,M
K,J
Ga
O
A
I
F
C
H
L,M
K,J
N
E
Q,R
N,O
B
D
G



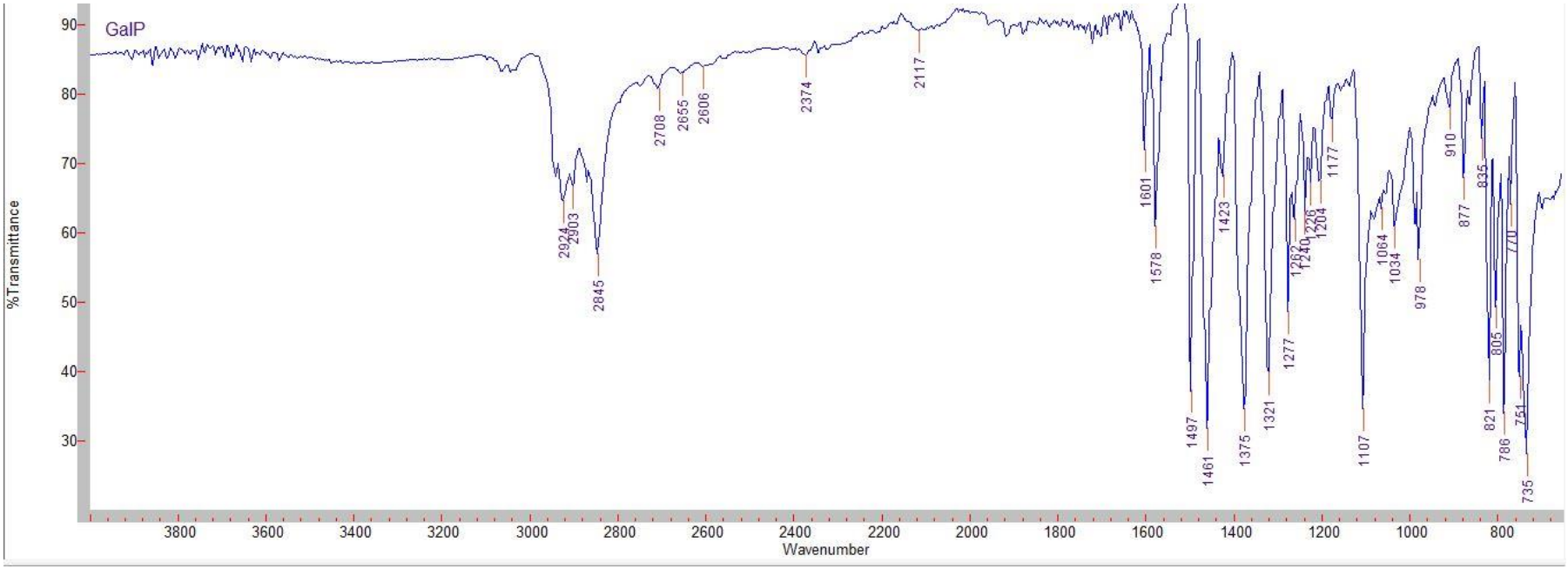
*note, due to impurities integrations in the hexyl region are not accurate.

Presence of $GaMe_2OH$ at ~ 4.6ppm

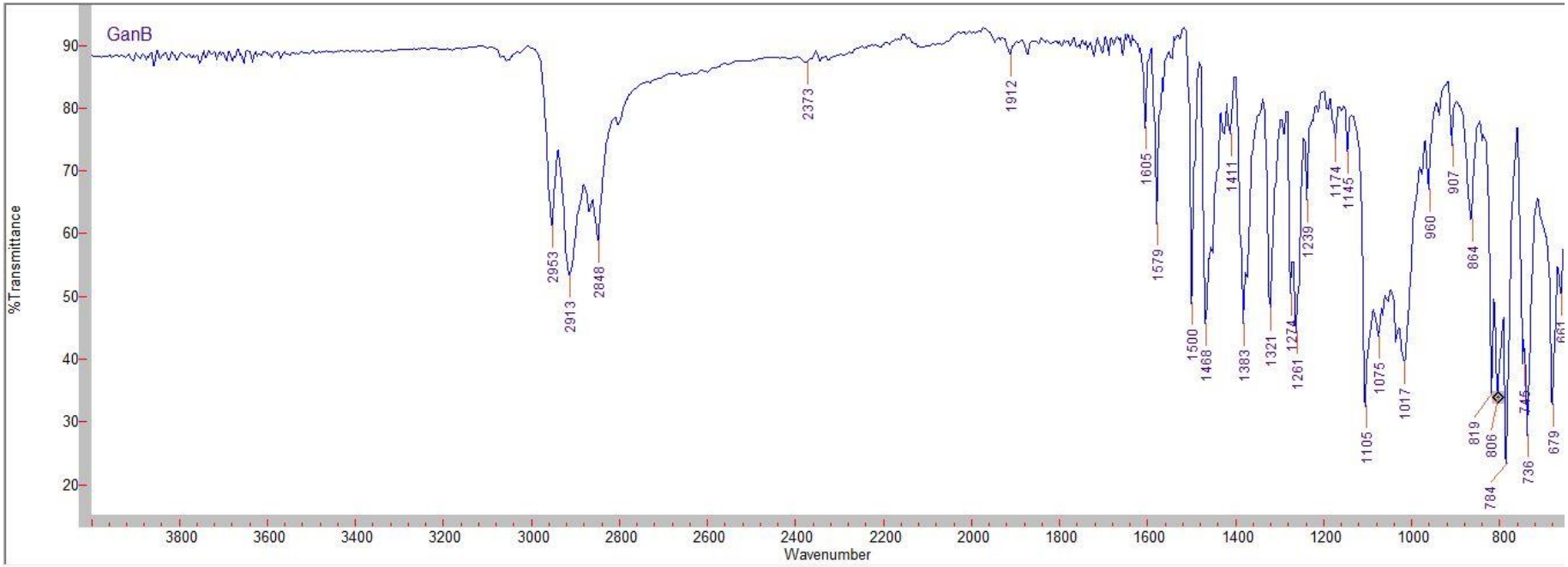
[Ga(Et)$_2$quin] **G1**



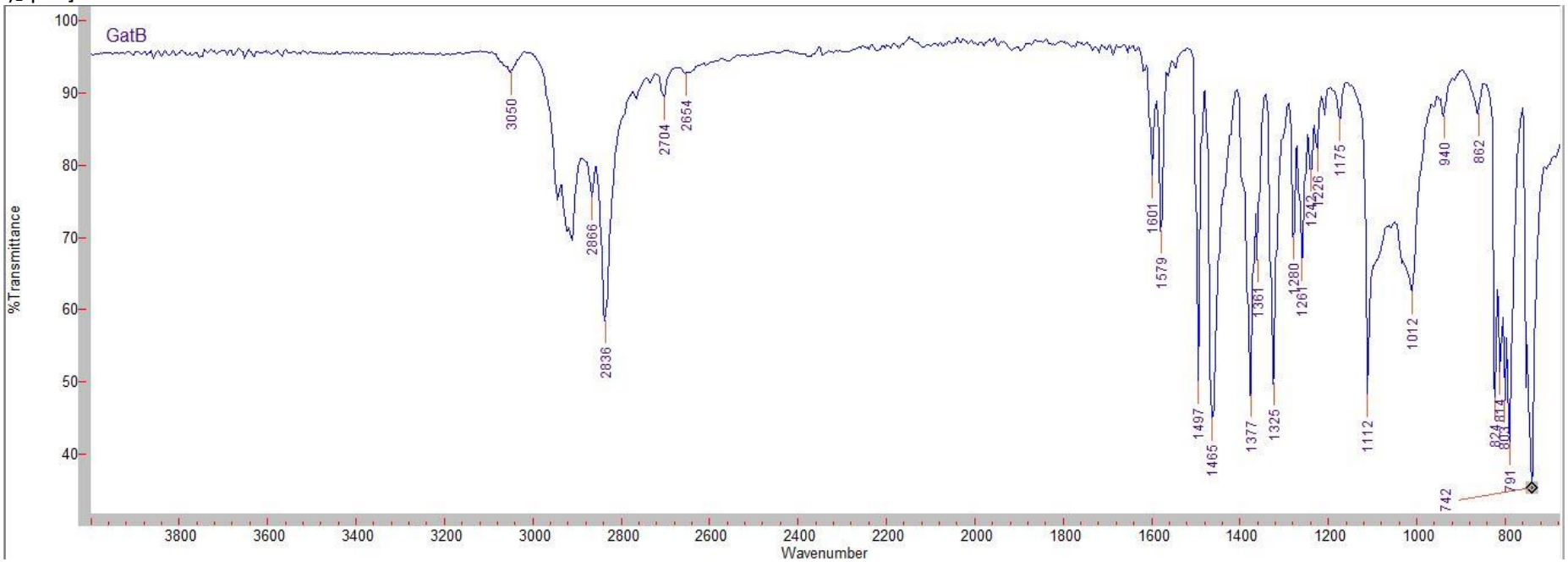
[Ga(^{i}Pr)$_2$quin] **G2**



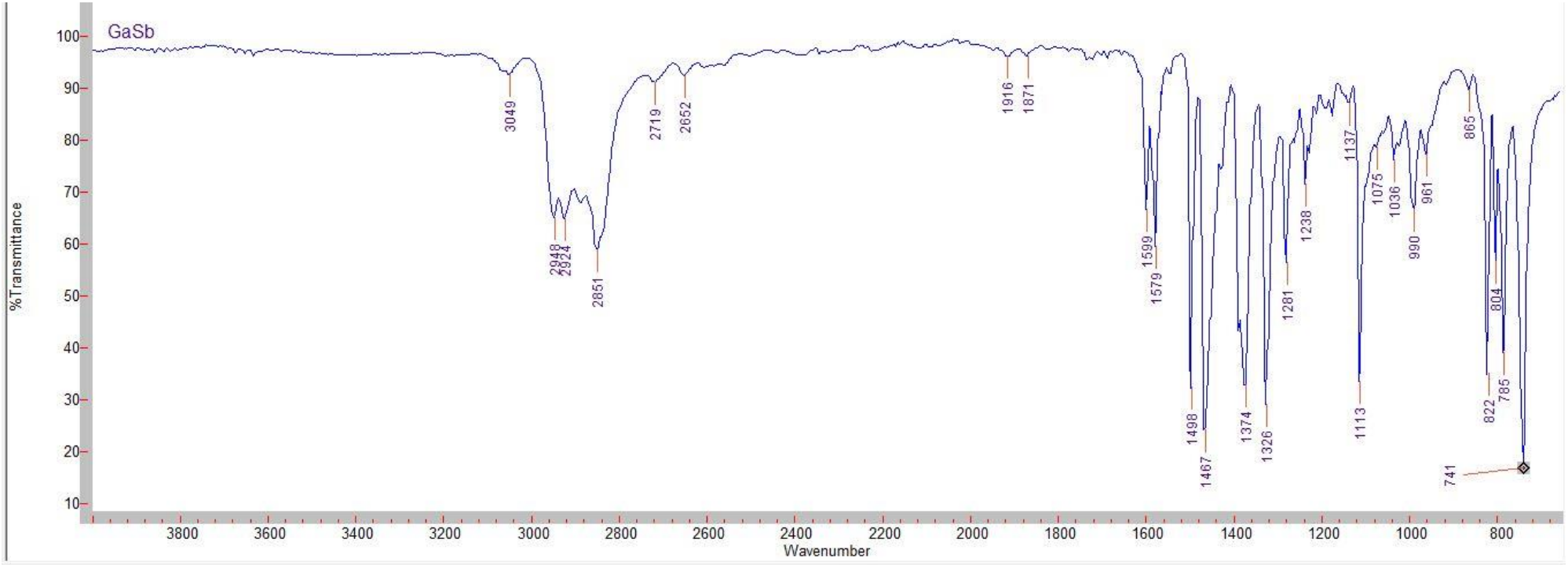
[Ga(^{n}Bu)$_2$quin] **G3**



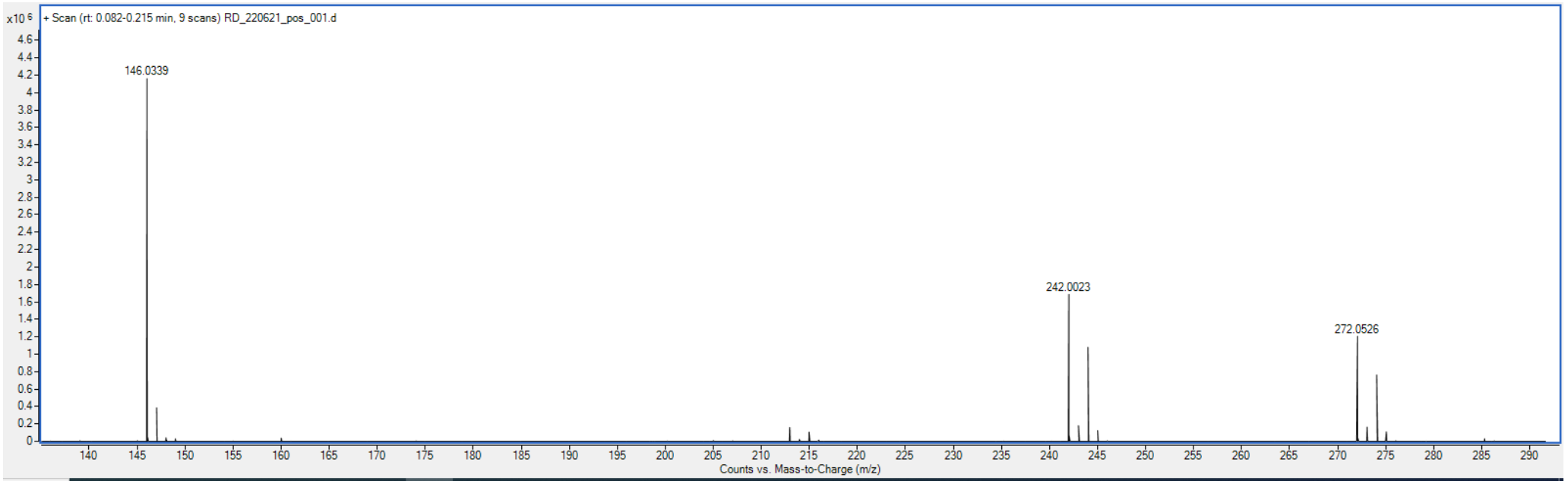
[Ga(^{t}Bu)$_2$quin] **G4**



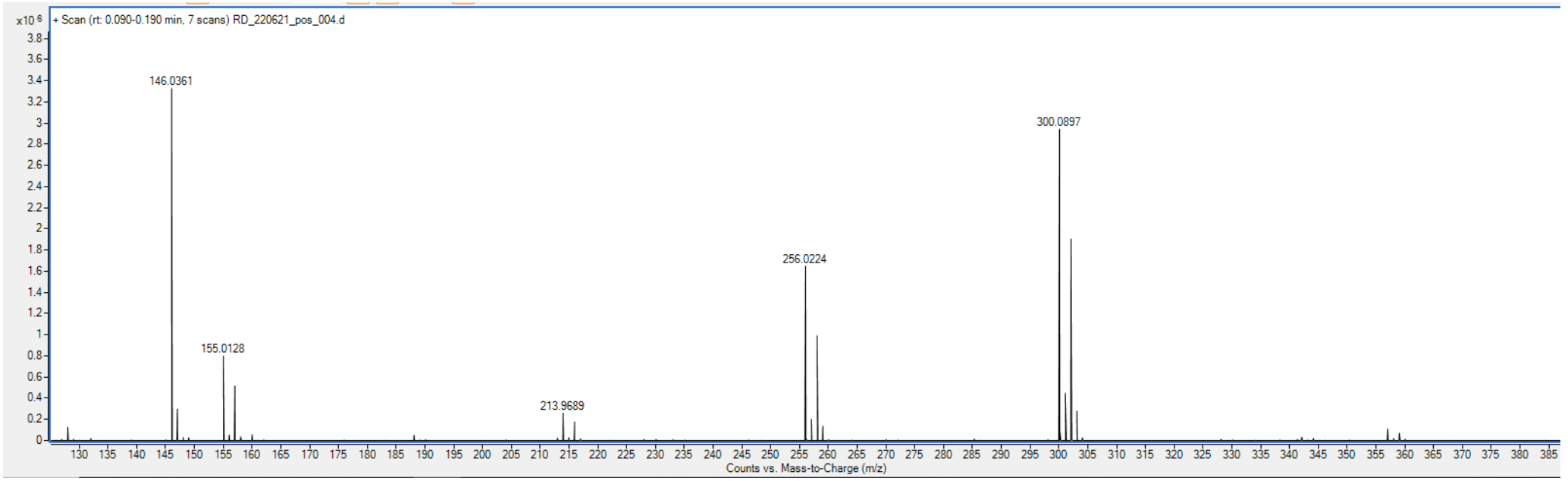
[Ga(^{s}Bu)$_2$quin] **G5**



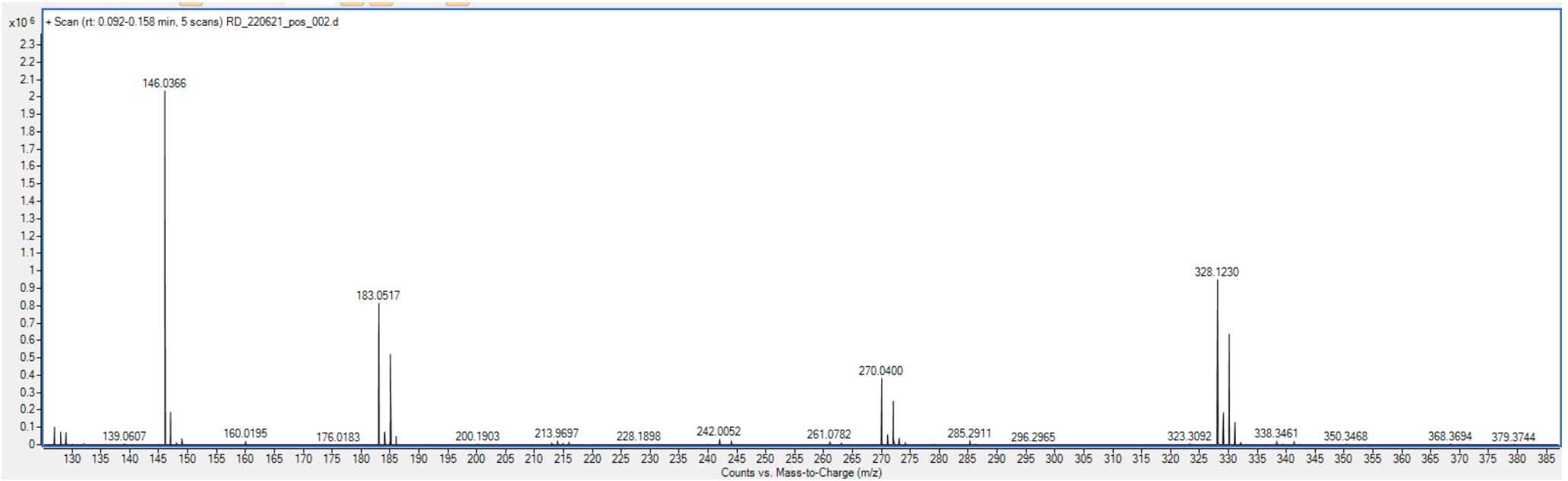
[Ga(Et)$_2$quin] **G1**



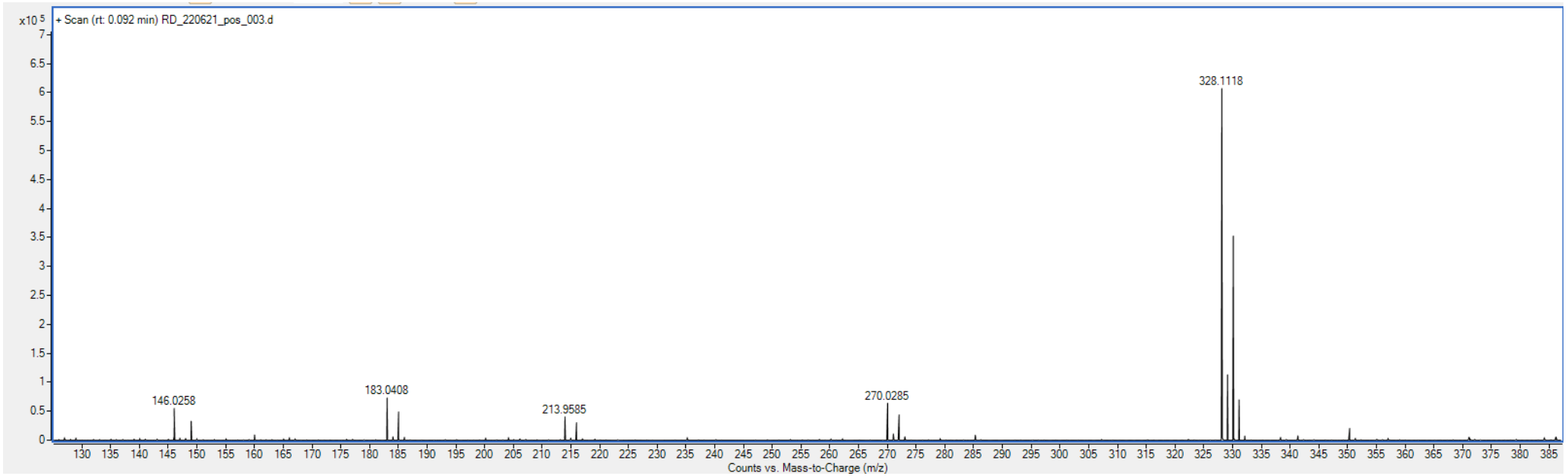
[Ga(^{i}Pr)$_2$quin] **G2**



[Ga(^{n}Bu)$_2$quin] **G3**



[Ga(^{t}Bu)$_2$quin] **G4**



[Ga(^{s}Bu)$_2$quin] **G5**

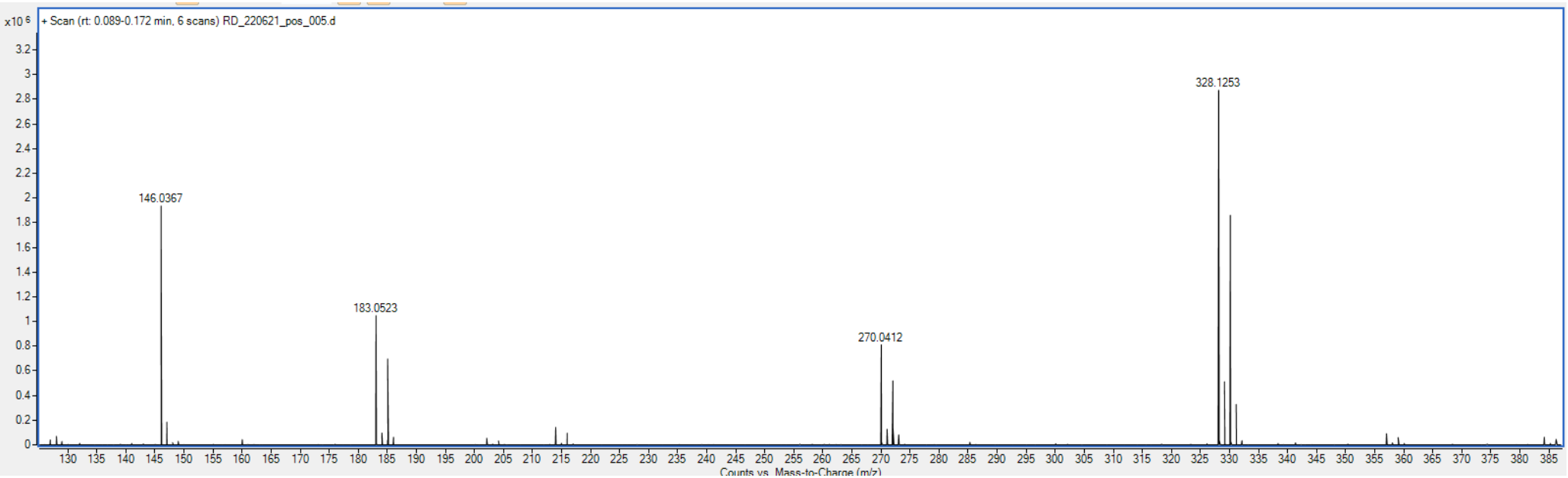


Table S1. X-ray data for complexes **G1** – **G6**

Identification code	**G1**	**G2**	**G3**	G4	G4’	**G6**
Chemical formula moiety	$C_{26}H_{32}Ga_2N_2O_2$	$C_{34}H_{48}Ga_2N_2O_2$	$C_{34}H_{48}Ga_2N_2O_2$	$C_{17}H_{24}GaNO$	$C_{22}H_{21}GaN_2O_2$	$C_{42}H_{64}Ga_2N_2O_2$
Formula weight	543.97	656.18	656.18	328.09	415.13	768.38
Temperature/K	123.00(10)	123.15	123.15	123.15	123.15	122.99(11)
Crystal system	triclinic	triclinic	triclinic	orthorhombic	monoclinic	monoclinic
Space group	P-1	P-1	P-1	Pbca	C2/c	$P2_1/n$
a/Å	9.9300(4)	9.7308(5)	9.7308(5)	15.9380(3)	17.5207(9)	14.7681(7)
b/Å	10.5992(4)	9.8510(5)	9.8510(5)	16.7591(2)	7.0485(3)	9.5219(4)
c/Å	12.2053(3)	10.3262(5)	10.3262(5)	25.8720(3)	16.1179(8)	15.2319(8)
α/°	91.428(2)	115.941(5)	115.941(5)	90	90	90
β/°	103.785(3)	112.503(5)	112.503(5)	90	110.630(6)	109.766(6)
γ/°	101.757(3)	92.111(4)	92.111(4)	90	90	90
Volume/Å^3	1217.78(7)	797.10(8)	797.10(8)	6910.58(17)	1862.84(17)	2015.72(18)
Z	2	2	2	16	4	4
ρ_{calc}g/cm^3	1.484	1.367	1.367	1.261	1.480	1.266
μ/mm^{-1}	2.906	1.722	1.722	2.133	1.497	1.372
F(000)	560.0	344.0	344.0	2752.0	856.0	816.0
Crystal size/mm^3	0.08 × 0.08 × 0.02	0.21 × 0.15 × 0.09	0.21 × 0.15 × 0.09	0.15 × 0.11 × 0.09	0.24 × 0.19 × 0.12	0.14 × 0.11 × 0.04
Radiation	Cu Kα (λ = 1.54184)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.48 to 160.706	7.42 to 64.244	7.42 to 64.244	6.834 to 160.54	7.186 to 51.992	6.924 to 64.81
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 14	-13 ≤ h ≤ 14, -14 ≤ k ≤ 13, -14 ≤ l ≤ 14	-13 ≤ h ≤ 14, -14 ≤ k ≤ 13, -14 ≤ l ≤ 14	-20 ≤ h ≤ 19, -21 ≤ k ≤ 19, -32 ≤ l ≤ 27	-20 ≤ h ≤ 21, -7 ≤ k ≤ 8, -19 ≤ l ≤ 19	-21 ≤ h ≤ 20, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	15501	21298	21298	35676	6708	27070
Independent reflections	5122 [R_{int} = 0.0516, R_{sigma} = 0.0506]	4904 [R_{int} = 0.0531, R_{sigma} = 0.0451]	4904 [R_{int} = 0.0531, R_{sigma} = 0.0451]	7410 [R_{int} = 0.0551, R_{sigma} = 0.0382]	1828 [R_{int} = 0.0454, R_{sigma} = 0.0553]	6194 [R_{int} = 0.0995, R_{sigma} = 0.0847]
Data/restraints/parameters	5122/0/293	4904/8/215	4904/8/215	7410/84/534	1828/12/137	6194/0/219
Goodness-of-fit on F^2	1.063	1.130	1.130	1.032	1.061	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0520, wR_2 = 0.1412	R_1 = 0.0396, wR_2 = 0.0812	R_1 = 0.0396, wR_2 = 0.0812	R_1 = 0.0523, wR_2 = 0.1347	R_1 = 0.0264, wR_2 = 0.0672	R_1 = 0.0576, wR_2 = 0.1385

Experimental details for modelling of compounds G4 and G4'

For compound G4, the final model has both Ga(^{t}Bu)$_2$ moieties as disordered over two positions, inclusive of the Ga positions, with occupancies refined to ca 0.59:0.41 (Ga(1), C(10)-C(17)) and 0.55:0.35 (Ga(2), O(2), C(27)-C(34)). Each of the four disordered ^{t}Bu groups were refined with restrained C-C distances and C-C-C angles using DFIX and DANG and the Ga-C distances were restrained using SADI. Additionally, the anisotropic displacement parameters of eight of the Me C atoms were restrained with a strong ISOR, to prevent excessive distortion of the ellipsoids and subsequently, unrealistic *U*eq values.

For compound G4', the molecule lies on a crystallographic two-fold axis (through Ga(1) and C(10)) with the methyl atoms of the ^{t}Bu group C(11), C(12), C(13) each modelled as disordered over two positions (related by symmetry) with occupancies fixed at 0.5. A moderate ISOR restraint was used for the anisotropic displacement parameters of C(12) and C(13).

4. X-ray

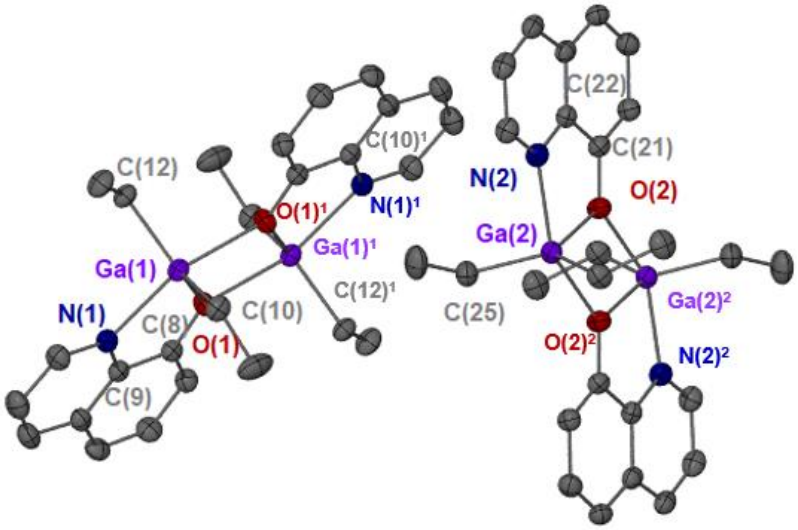


Figure S1. Grown crystal x-ray structures of complex $[Ga(Et)_2quin]_2$ **[G1]₂**, **symmetry operator** [1] = -X, -Y, 1-Z, [2] = 1-X, 1-Y, 2-Z. Thermal ellipsoids are at 50% probability and hydrogen atoms have been omitted for clarity. Selected bond lengths and angles. (Å): Ga(1) – O(1) 1.951(2), Ga(1) – $O(1)^1$ 2.245(2) Ga(1) – N(1), 2.202(2), Ga(1) – C10, 1.974(3), Ga(1) – C(12), 1.976(3) Ga(2) – O(2) 1.959(2), Ga(2) – N(2) 2.207(3), Ga(2) – $O(2)^2$ 2.248(2), Ga(2) – C(23) 1.979(3), Ga(2) – C(25) 1.979(3). (o) O(1) – Ga(1) – $O(1)^1$ 71.50(9), O(1) – G(1) – N(1) 78.18(8), O(2) – Ga(2) – $O(2)^2$ 70.86(9), O(2) – Ga(2) – N(2) 78.46(9).

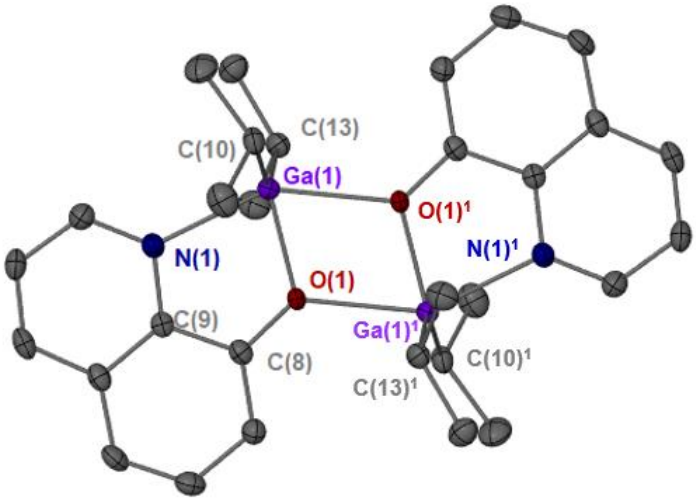


Figure S2. Grown single crystal x-ray structures of complex $[Ga(^iPr)_2quin]_2$ **[G2]₂**, **symmetry operator [1] = 1-X, 1-Y, 1-Z**. Thermal ellipsoids are at 50% probability and hydrogen atoms have been omitted for clarity. Selected bond lengths and angles. (Å): Ga(1) – O(1) 1.951(2), Ga(1) – O(2) 2.273(2) Ga(1) – N(1), 2.216(2), Ga(1) – C10, 1.983(2), Ga(1) – C(13), 1.986(2). (o) O(1) – G(1) – O(2) 70.21(6), O(1) – G(1) – N(1) 78.05(7).

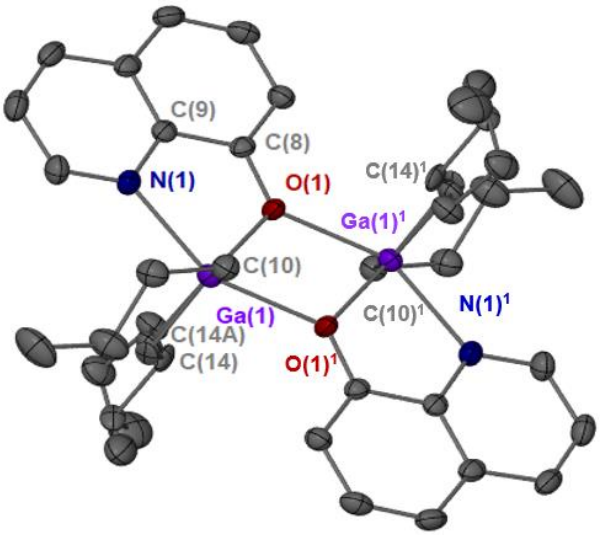


Figure S3. Grown single crystal x-ray structures of complex [Ga(^{n}Bu)$_2$quin]$_2$ [**G3**]$_2$**, symmetry operator [1] = 1-X, -Y, -Z.** Thermal ellipsoids are at 50% probability and hydrogen atoms have been omitted for clarity. Disorder of the alkyl chain has been modelled over two positions. Selected bond lengths and angles. (Å): Ga(1) – O(1) 1.955(1), Ga(1) – O(1)^1 2.233(1), Ga(1) – N(1) 2.227(2), Ga(1) – C(10) 1.973(2), Ga(1) – C(14) 1.979(9), Ga(1) – C(14A) 1.987(3). (°) O(1) – Ga(1) – O(1)^1 70.86(6), O(1) – Ga(1) – N(1) 77.70(6), O(1) – Ga(1) – C(10) 113.9(7), O(1) – Ga(1) – C(14) 122.2(1).

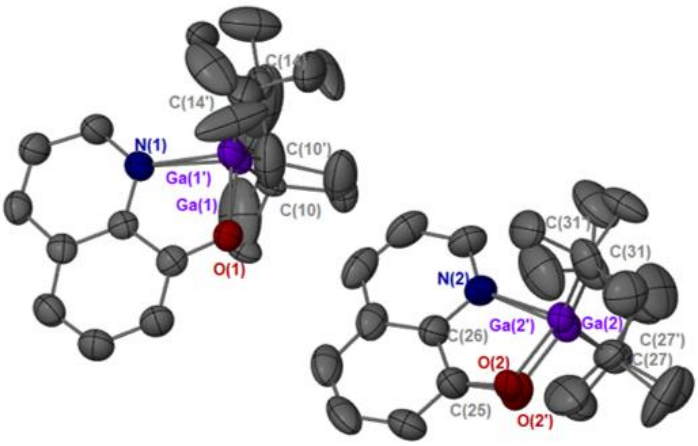


Figure S4. Single crystal x-ray structures of complex [Ga(^{t}Bu)$_2$quin] **G4.** Thermal ellipsoids are at 50% probability and hydrogen atoms have been omitted for clarity. Disorder of the gallium and tertiary butyl groups has been modelled over two positions. Selected bond lengths and angles of the asymmetric unit. (Å): Ga(1) – O(1) 1.941(6), Ga(1) – N(1) 2.106(2), Ga(1) – C(10) 1.985(8), Ga(1) – C(14) 2.008(8), Ga(1)' – O(1) 1.906(4), Ga(1)' – N(1) 2.035(4), Ga(1)' – C(10)' 1.943(1), Ga(1)' – C(14)' 1.985(9), Ga(2) – O(2) 1.865(9), Ga(2) – N(2) 2.048(4), Ga(2) – C(27) 2.000(9), Ga(2) – C(31) 1.999(1), Ga(2)' – O(2) 1.986(9), Ga(2)' – N(2) 2.078(4), Ga(2)' – C(27)' 1.972(1), Ga(2)' – C(31)' 1.984(1) . (°) O(1) – Ga(1) – N(1) 82.10(2), O(1) – Ga(1) – C(10) 108.3(3), O(1) – Ga(1) – C(14) 114.4(3), C(10) – Ga(1) – C(14) 126.9(4), O(1) – Ga(1)' – N(1) 84.85(1), O(1) – Ga(1)' – C(10)' 106.9(4), O(1) – Ga(1)' – C(14)' 108.8(3), C(10)' – Ga(1)' – C(14)' 132.1(5), O(2)' – Ga(2) – N(2) 83.00(3), O(2)' – Ga(2) – C(27) 110.1(5), O(2)' – Ga(2) – C(31) 108.5(5), C(27) – Ga(2) – C(31) 129.9(6).

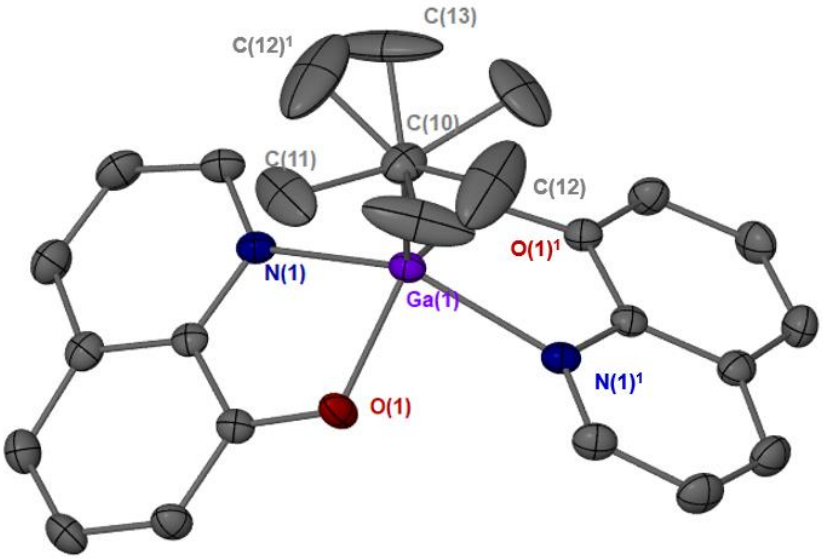


Figure S5. Grown single crystal x-ray structures of complex [Ga^{t}Bu(quin)$_2$] **G4'**, **symmetry operator ^{1} = 1-X, +Y, 3/2-Z.** Thermal ellipsoids are at 50% probability and hydrogen atoms have been omitted for clarity. Disorder of the methyl groups have been modelled over two positions. Selected bond lengths and angles. (Å): Ga(1) – O(1) 1.933(1), Ga(1) – O(1)^1 1.933(1), Ga(1) – N(1) 2.120(2), Ga(1) – N(1)^1 2.120(2), Ga(1) – C(10) 1.981(3), (°) O(1) – Ga(1) – O(1)^1 135.2(9), O(1) – Ga(1) – N(1) 80.85(6), O(1) – Ga(1) – C(10) 112.4(1), N(1) – Ga(1) – C(10) 108.7(4)

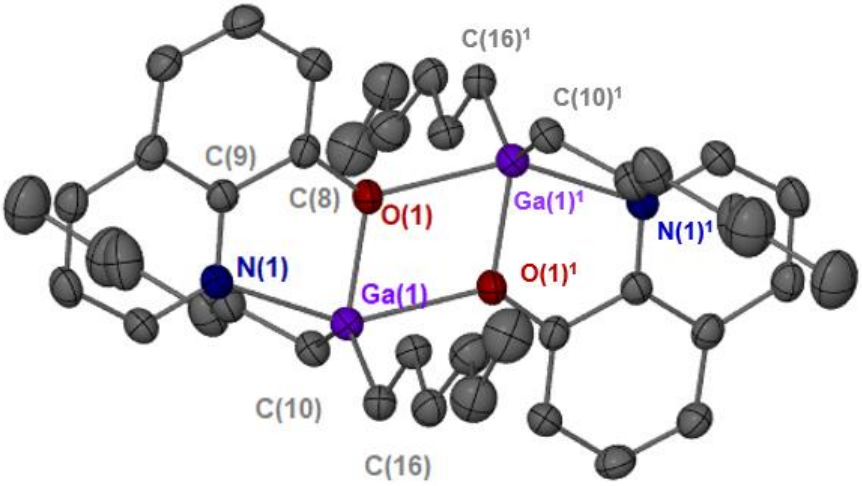


Figure S6. Single crystal x-ray structures of complex [Ga(Hex)$_2$quin]$_2$ [**G6**]$_2$, **symmetry operator ^{1} = 1-X, 1-Y, 1-Z**. Thermal ellipsoids are at 50% probability and hydrogen atoms have been omitted for clarity. For full data on bond lengths and angles see tables S11 – S12. Selected bond lengths and angles. (Å): Ga(1) – O(1) 1.957(2), Ga(1) – O(1)^1 2.286(2), Ga(1) – N(1) 2.209(2), Ga(1) – C(10) 1.962(3), Ga(1) – C(16) 1.975(3). (°) O(1) – Ga(1) – O(1)^1 70.29(8), O(1) – Ga(1) – N(1) 78.04(8), O(1) – Ga(1) – C(10) 114.0(1), O(1) – Ga(1) – C(16) 113.2(1).

Table S2 Bond Lengths for $[G1]_2$ symmetry operator [1] = -X, -Y, 1-Z, [2] = 1-X, 1-Y, 2-Z						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Ga1	O1	1.9510(19)		C22	C21	1.424(4)
Ga1	O1[1]	2.2447(18)		C22	C17	1.412(4)
Ga1	N1	2.202(2)		C4	C9	1.417(4)
Ga1	C12	1.976(3)		C4	C5	1.411(4)
Ga1	C10	1.974(3)		C4	C3	1.418(4)
Ga2	O2[2]	2.248(2)		C21	C20	1.382(4)
Ga2	O2	1.9588(19)		C17	C16	1.413(4)
Ga2	N2	2.207(3)		C17	C18	1.418(4)
Ga2	C23	1.979(3)		C12	C13	1.541(4)
Ga2	C25	1.979(3)		C20	C19	1.422(4)
O1	Ga1[1]	2.2447(18)		C7	C6	1.412(4)
O1	C8	1.335(3)		C14	C15	1.408(4)
O2	Ga2[2]	2.248(2)		C5	C6	1.373(4)
O2	C21	1.334(3)		C23	C24	1.522(4)
N2	C22	1.370(3)		C15	C16	1.368(4)
N2	C14	1.324(4)		C3	C2	1.366(5)
N1	C9	1.360(4)		C1	C2	1.408(5)
N1	C1	1.325(4)		C19	C18	1.371(4)
C8	C9	1.423(4)		C25	C26	1.524(4)
C8	C7	1.376(4)		C10	C11	1.521(5)

Table S3 Bond Angles for $[G1]_2$. symmetry operator [1] = -X, -Y, 1-Z, [2] = 1-X, 1-Y, 2-Z								
Atom	**Atom**	**Atom**	**Angle/˚**		**Atom**	**Atom**	**Atom**	**Angle/˚**
O1	Ga1	O1[1]	71.50(9)		O1	C8	C7	124.6(2)
O1	Ga1	N1	78.18(8)		C7	C8	C9	118.1(2)
O1	Ga1	C12	118.71(10)		N2	C22	C21	115.7(2)
O1	Ga1	C10	114.73(11)		N2	C22	C17	122.6(3)
N1	Ga1	O1[1]	149.67(8)		C17	C22	C21	121.7(2)
C12	Ga1	O1[1]	96.21(10)		C9	C4	C3	116.8(3)
C12	Ga1	N1	98.99(10)		C5	C4	C9	118.8(2)
C10	Ga1	O1[1]	93.83(10)		C5	C4	C3	124.4(3)
C10	Ga1	N1	98.12(11)		O2	C21	C22	117.8(2)
C10	Ga1	C12	126.08(12)		O2	C21	C20	123.9(3)
O2	Ga2	O2[2]	70.86(9)		C20	C21	C22	118.3(3)
O2	Ga2	N2	78.46(9)		N1	C9	C8	115.7(2)
O2	Ga2	C23	114.63(11)		N1	C9	C4	122.8(2)
O2	Ga2	C25	113.05(11)		C4	C9	C8	121.5(3)
N2	Ga2	O2[2]	149.12(8)		C22	C17	C16	117.1(3)
C23	Ga2	O2[2]	94.01(11)		C22	C17	C18	118.5(3)
C23	Ga2	N2	95.66(11)		C16	C17	C18	124.4(3)
C25	Ga2	O2[2]	95.10(11)		C13	C12	Ga1	110.12(19)
C25	Ga2	N2	100.01(11)		C21	C20	C19	120.0(3)
C25	Ga2	C23	131.83(13)		C8	C7	C6	120.4(3)
Ga1	O1	Ga1[1]	108.50(9)		N2	C14	C15	122.5(3)
C8	O1	Ga1	118.68(16)		C6	C5	C4	119.0(3)
C8	O1	Ga1[1]	132.74(16)		C24	C23	Ga2	112.8(2)
Ga2	O2	Ga2[2]	109.14(9)		C16	C15	C14	119.5(3)
C21	O2	Ga2	118.28(17)		C2	C3	C4	119.5(3)
C21	O2	Ga2[2]	132.56(16)		C15	C16	C17	119.8(3)
C22	N2	Ga2	109.69(18)		N1	C1	C2	122.3(3)
C14	N2	Ga2	131.8(2)		C5	C6	C7	122.3(3)
C14	N2	C22	118.5(3)		C18	C19	C20	122.0(3)

C9	N1	Ga1	110.06(17)		C26	C25	Ga2	115.1(2)
C1	N1	Ga1	131.2(2)		C3	C2	C1	119.8(3)
C1	N1	C9	118.7(2)		C11	C10	Ga1	114.5(2)
O1	C8	C9	117.3(2)		C19	C18	C17	119.5(3)

Table S4 Bond Lengths for $[G2]_2$ symmetry operator [1] = 1-X, 1-Y, 1-Z

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ga1	O1	1.9510(16)		C8	C7	1.377(4)
Ga1	$O1^1$	2.2730(15)		C10	C11	1.535(4)
Ga1	N1	2.2157(19)		C10	C12	1.523(4)
Ga1	C13	1.987(2)		C9	C4	1.415(3)
Ga1	C10	1.982(2)		C7	C6	1.412(3)
O1	C8	1.327(3)		C4	C5	1.414(4)
N1	C9	1.361(3)		C4	C3	1.416(3)
N1	C1	1.325(3)		C5	C6	1.366(4)
C13	C14	1.529(4)		C3	C2	1.363(4)
C13	C15	1.528(3)		C1	C2	1.402(4)
C8	C9	1.432(3)				

Table S5 Bond Angles for $[G2]_2$ symmetry operator [1] = 1-X, 1-Y, 1-Z

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O1	Ga1	$O1^1$	70.21(7)		O1	C8	C9	117.0(2)
O1	Ga1	N1	78.05(7)		O1	C8	C7	124.3(2)
O1	Ga1	C13	111.42(9)		C7	C8	C9	118.6(2)
O1	Ga1	C10	114.42(9)		C11	C10	Ga1	113.87(17)
N1	Ga1	$O1^1$	148.23(7)		C12	C10	Ga1	111.39(17)
C13	Ga1	$O1^1$	94.09(8)		C12	C10	C11	109.6(2)
C13	Ga1	N1	98.94(8)		N1	C9	C8	116.0(2)
C10	Ga1	$O1^1$	93.16(8)		N1	C9	C4	123.2(2)
C10	Ga1	N1	98.56(8)		C4	C9	C8	120.8(2)
C10	Ga1	C13	133.31(10)		C8	C7	C6	120.2(2)
Ga1	O1	$Ga1^1$	109.79(7)		C9	C4	C3	116.0(2)
C8	O1	$Ga1^1$	130.91(15)		C5	C4	C9	118.7(2)
C8	O1	Ga1	119.30(14)		C5	C4	C3	125.3(2)
C9	N1	Ga1	109.60(15)		C6	C5	C4	119.7(2)
C1	N1	Ga1	131.78(17)		C2	C3	C4	120.3(2)
C1	N1	C9	118.6(2)		N1	C1	C2	122.2(2)
C14	C13	Ga1	113.34(17)		C3	C2	C1	119.8(2)
C15	C13	Ga1	111.24(17)		C5	C6	C7	122.0(2)
C15	C13	C14	111.0(2)					

Table S6 Bond Lengths for $[G3]_2$ symmetry operator [1] = 1-X, -Y, -Z						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Ga1	O1	1.9545(13)		C4	C5	1.410(3)
Ga1	O1[1]	2.2334(14)		C4	C3	1.413(3)
Ga1	N1	2.2273(17)		C1	C2	1.401(3)
Ga1	C10	1.973(2)		C6	C5	1.365(3)
Ga1	C14A	1.987(3)		C11	C12	1.516(3)
Ga1	C14	1.979(9)		C3	C2	1.362(3)
O1	C8	1.334(2)		C12	C13	1.517(4)
N1	C9	1.359(3)		C14A	C15A	1.522(5)
N1	C1	1.322(3)		C15A	C16A	1.525(4)
C8	C9	1.427(3)		C16A	C17A	1.510(5)
C8	C7	1.377(3)		C16	C15	1.53(3)
C9	C4	1.412(3)		C16	C17	1.52(4)
C10	C11	1.528(3)		C15	C14	1.510(11)
C7	C6	1.408(3)				

Table S7 Bond Angles for $[G3]_2$. symmetry operator [1] = 1-X, -Y, -Z								
Atom	**Atom**	**Atom**	**Angle/˚**		**Atom**	**Atom**	**Atom**	**Angle/˚**
O1	Ga1	O1[1]	70.86(6)		C7	C8	C9	118.27(18)
O1	Ga1	N1	77.70(6)		N1	C9	C8	115.86(17)
O1	Ga1	C10	113.86(7)		N1	C9	C4	123.04(18)
O1	Ga1	C14A	112.18(14)		C4	C9	C8	121.10(18)
O1	Ga1	C14	122.5(6)		C11	C10	Ga1	116.78(15)
N1	Ga1	O1[1]	148.55(6)		C8	C7	C6	120.2(2)
C10	Ga1	O1[1]	94.70(7)		C9	C4	C3	116.45(19)
C10	Ga1	N1	98.65(8)		C5	C4	C9	118.76(19)
C10	Ga1	C14A	133.66(15)		C5	C4	C3	124.8(2)
C10	Ga1	C14	123.1(6)		N1	C1	C2	122.9(2)
C14A	Ga1	O1[1]	95.37(16)		C5	C6	C7	122.2(2)
C14A	Ga1	N1	95.73(17)		C6	C5	C4	119.47(19)
C14	Ga1	O1[1]	95.9(11)		C12	C11	C10	114.30(19)
C14	Ga1	N1	100.3(11)		C2	C3	C4	120.1(2)
Ga1	O1	Ga1[1]	109.14(6)		C3	C2	C1	119.3(2)
C8	O1	Ga1[1]	131.50(12)		C11	C12	C13	112.9(2)
C8	O1	Ga1	119.27(12)		C15A	C14A	Ga1	114.1(2)
C9	N1	Ga1	109.83(13)		C14A	C15A	C16A	115.7(3)
C1	N1	Ga1	131.89(15)		C17A	C16A	C15A	114.6(3)
C1	N1	C9	118.28(18)		C17	C16	C15	111.8(17)
O1	C8	C9	117.27(17)		C14	C15	C16	107.4(15)
O1	C8	C7	124.45(18)		C15	C14	Ga1	109.9(12)

Table S8 Bond Lengths for G4						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Ga1	O1	1.941(6)		C10	C12	1.535(9)
Ga1	N1	2.106(6)		C10	C13	1.536(16)
Ga1	C10	1.985(8)		C10'	C11'	1.495(13)
Ga1	C14	2.011(8)		C10'	C12'	1.559(14)
Ga1'	O1	1.906(4)		C10'	C13'	1.550(14)
Ga1'	N1	2.034(4)		C14	C15	1.643(12)
Ga1'	C10'	1.939(11)		C14	C16	1.509(13)
Ga1'	C14'	1.983(9)		C14	C17	1.468(12)
Ga2	O2'	1.868(9)		C14'	C15'	1.541(9)
Ga2	N2	2.048(4)		C14'	C16'	1.480(13)
Ga2	C27	2.000(9)		C14'	C17'	1.463(10)
Ga2	C31	1.999(10)		C18	C19	1.391(5)
Ga2'	O2	1.983(9)		C19	C20	1.345(6)
Ga2'	N2	2.077(4)		C20	C21	1.422(5)
Ga2'	C27'	1.972(10)		C21	C22	1.406(5)
Ga2'	C31'	1.984(12)		C21	C26	1.401(4)
O1	C8	1.319(3)		C22	C23	1.352(6)
O2	C25	1.327(9)		C23	C24	1.417(5)
O2'	C25	1.372(8)		C24	C25	1.371(5)
N1	C1	1.317(4)		C25	C26	1.432(4)
N1	C9	1.363(3)		C27	C28	1.504(14)
N2	C18	1.317(4)		C27	C29	1.46(2)
N2	C26	1.362(4)		C27	C30	1.502(16)
C1	C2	1.401(4)		C27'	C28'	1.532(16)
C2	C3	1.355(4)		C27'	C29'	1.569(18)
C3	C4	1.412(4)		C27'	C30'	1.557(16)
C4	C5	1.406(4)		C31	C32	1.49(2)
C4	C9	1.411(4)		C31	C33	1.536(16)
C5	C6	1.367(5)		C31	C34	1.570(18)
C6	C7	1.405(5)		C31'	C32'	1.515(16)
C7	C8	1.381(4)		C31'	C33'	1.531(15)
C8	C9	1.425(4)		C31'	C34'	1.524(16)

Table S9 Bond Angles for G4								
Atom	**Atom**	**Atom**	**Angle/˚**		**Atom**	**Atom**	**Atom**	**Angle/˚**
O1	Ga1	N1	82.1(2)		C11'	C10'	Ga1'	111.6(10)
O1	Ga1	C10	108.2(3)		C11'	C10'	C12'	108.7(12)
O1	Ga1	C14	114.6(3)		C11'	C10'	C13'	108.1(14)
C10	Ga1	N1	108.5(3)		C12'	C10'	Ga1'	110.5(7)
C10	Ga1	C14	126.8(4)		C13'	C10'	Ga1'	113.8(11)
C14	Ga1	N1	107.3(3)		C13'	C10'	C12'	103.8(12)
O1	Ga1'	N1	84.87(17)		C15	C14	Ga1	105.5(6)
O1	Ga1'	C10'	107.0(4)		C16	C14	Ga1	111.7(7)
O1	Ga1'	C14'	108.9(3)		C16	C14	C15	101.4(11)
C10'	Ga1'	N1	102.3(3)		C17	C14	Ga1	113.7(7)
C10'	Ga1'	C14'	132.0(5)		C17	C14	C15	96.6(9)
C14'	Ga1'	N1	111.6(3)		C17	C14	C16	123.8(10)
O2'	Ga2	N2	83.0(3)		C15'	C14'	Ga1'	104.6(7)
O2'	Ga2	C27	110.1(5)		C16'	C14'	Ga1'	111.0(5)
O2'	Ga2	C31	108.6(5)		C16'	C14'	C15'	114.6(9)
C27	Ga2	N2	112.7(4)		C17'	C14'	Ga1'	114.6(8)
C31	Ga2	N2	102.4(5)		C17'	C14'	C15'	110.4(7)
C31	Ga2	C27	129.9(6)		C17'	C14'	C16'	102.0(9)
O2	Ga2'	N2	85.6(3)		N2	C18	C19	121.7(4)
O2	Ga2'	C31'	109.4(5)		C20	C19	C18	119.7(3)
C27'	Ga2'	O2	107.2(5)		C19	C20	C21	120.6(3)
C27'	Ga2'	N2	100.0(4)		C22	C21	C20	125.4(3)
C27'	Ga2'	C31'	131.1(6)		C26	C21	C20	116.4(3)
C31'	Ga2'	N2	114.0(5)		C26	C21	C22	118.2(3)
C8	O1	Ga1	112.2(2)		C23	C22	C21	120.0(3)
C8	O1	Ga1'	112.0(2)		C22	C23	C24	122.0(3)
C25	O2	Ga2'	107.7(5)		C25	C24	C23	120.3(4)
C25	O2'	Ga2	116.5(6)		O2	C25	C24	119.2(5)
C1	N1	Ga1	131.9(3)		O2	C25	C26	122.1(5)
C1	N1	Ga1'	132.2(2)		O2'	C25	C26	113.7(5)
C1	N1	C9	119.6(2)		C24	C25	O2'	127.7(5)
C9	N1	Ga1	107.3(2)		C24	C25	C26	117.3(3)
C9	N1	Ga1'	108.2(2)		N2	C26	C21	121.6(3)
C18	N2	Ga2	129.8(3)		N2	C26	C25	116.3(3)
C18	N2	Ga2'	132.5(3)		C21	C26	C25	122.1(3)
C18	N2	C26	120.1(3)		C28	C27	Ga2	110.0(8)
C26	N2	Ga2	109.6(2)		C29	C27	Ga2	108.7(13)
C26	N2	Ga2'	106.9(2)		C29	C27	C28	110.5(13)
N1	C1	C2	121.8(3)		C29	C27	C30	110.8(14)
C3	C2	C1	119.6(3)		C30	C27	Ga2	107.3(8)
C2	C3	C4	120.4(3)		C30	C27	C28	109.5(12)
C5	C4	C3	125.1(3)		C28'	C27'	Ga2'	110.1(9)
C5	C4	C9	118.4(3)		C28'	C27'	C29'	108.6(17)
C9	C4	C3	116.5(2)		C28'	C27'	C30'	108.3(17)
C6	C5	C4	119.5(3)		C29'	C27'	Ga2'	112.3(15)
C5	C6	C7	121.9(3)		C30'	C27'	Ga2'	109.3(10)
C8	C7	C6	121.2(3)		C30'	C27'	C29'	108.1(18)

O1	C8	C7	124.2(3)		C32	C31	Ga2	108.5(9)
O1	C8	C9	119.2(2)		C32	C31	C33	109.8(13)
C7	C8	C9	116.7(3)		C32	C31	C34	110.7(11)
N1	C9	C4	122.0(2)		C33	C31	Ga2	110.0(8)
N1	C9	C8	115.7(2)		C33	C31	C34	107.8(11)
C4	C9	C8	122.3(2)		C34	C31	Ga2	110.0(9)
C11	C10	Ga1	110.6(6)		C32'	C31'	Ga2'	110.4(9)
C11	C10	C12	108.0(7)		C32'	C31'	C33'	106.9(12)
C11	C10	C13	112.6(16)		C32'	C31'	C34'	109.3(12)
C12	C10	Ga1	107.8(7)		C33'	C31'	Ga2'	108.8(9)
C12	C10	C13	107.6(12)		C34'	C31'	Ga2'	110.0(10)
C13	C10	Ga1	110.0(11)		C34'	C31'	C33'	111.4(11)

Table S10 Bond Lengths for G4' symmetry operator [1] = 1-X, +Y, 3/2-Z

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ga1	O1[1]	1.9330(14)		C4	C5	1.412(3)
Ga1	O1	1.9330(14)		C4	C9	1.415(3)
Ga1	N1	2.1196(16)		C5	C6	1.372(3)
Ga1	N1[1]	2.1196(16)		C6	C7	1.408(3)
Ga1	C10	1.981(3)		C7	C8	1.378(3)
O1	C8	1.328(2)		C8	C9	1.425(3)
N1	C1	1.323(3)		C10	C11	1.622(5)
N1	C9	1.360(2)		C10	C12	1.476(7)
C1	C2	1.403(3)		C10	C12[1]	1.476(7)
C2	C3	1.370(3)		C10	C13	1.455(6)
C3	C4	1.407(3)				

Table S11 Bond Angles for G4' symmetry operator [1] = 1-X, +Y, 3/2-Z								
Atom	**Atom**	**Atom**	**Angle/˚**		**Atom**	**Atom**	**Atom**	**Angle/˚**
O1[1]	Ga1	O1	135.18(8)		C6	C5	C4	119.55(19)
O1	Ga1	N1	80.86(6)		C5	C6	C7	121.84(19)
O1[1]	Ga1	N1	85.07(6)		C8	C7	C6	120.89(19)
O1	Ga1	N1[1]	85.07(6)		O1	C8	C7	124.69(18)
O1[1]	Ga1	N1[1]	80.86(6)		O1	C8	C9	117.80(17)
O1[1]	Ga1	C10	112.41(4)		C7	C8	C9	117.45(17)
O1	Ga1	C10	112.41(4)		N1	C9	C4	122.29(18)
N1[1]	Ga1	N1	142.54(8)		N1	C9	C8	115.58(16)
C10	Ga1	N1	108.73(4)		C4	C9	C8	122.07(18)
C10	Ga1	N1[1]	108.73(4)		C11	C10	Ga1	102.69(19)
C8	O1	Ga1	115.91(12)		C12	C10	Ga1	114.8(3)
C1	N1	Ga1	130.67(14)		C12[1]	C10	Ga1	114.8(3)
C1	N1	C9	119.58(17)		C12	C10	C11	104.3(5)
C9	N1	Ga1	109.71(12)		C12[1]	C10	C11	64.4(5)
N1	C1	C2	121.96(19)		C12	C10	C12[1]	130.4(6)
C3	C2	C1	119.09(19)		C13	C10	Ga1	113.0(3)
C2	C3	C4	120.67(19)		C13	C10	C11	103.5(4)
C3	C4	C5	125.39(19)		C13	C10	C12[1]	39.5(5)
C3	C4	C9	116.41(19)		C13	C10	C12	116.3(5)
C5	C4	C9	118.18(18)					

Table S12 Bond Lengths for $[G6]_2$ symmetry operator [1] = 1-X, 1-Y, 1-Z.						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Ga1	O1	1.957(2)		C4	C3	1.417(4)
Ga1	O1[1]	2.2864(18)		C4	C5	1.410(4)
Ga1	N1	2.209(2)		C18	C19	1.521(5)
Ga1	C10	1.962(3)		C7	C6	1.410(4)
Ga1	C16	1.975(3)		C1	C2	1.403(4)
O1	C8	1.330(3)		C3	C2	1.354(5)
N1	C9	1.356(4)		C11	C12	1.495(5)
N1	C1	1.320(4)		C5	C6	1.359(4)
C8	C9	1.423(4)		C19	C20	1.505(5)
C8	C7	1.375(4)		C12	C13	1.546(5)
C17	C18	1.514(4)		C20	C21	1.521(5)
C17	C16	1.516(4)		C13	C14	1.465(6)
C9	C4	1.417(4)		C14	C15	1.521(6)
C10	C11	1.525(4)				

Table S13 Bond Angles for $[G6]_2$ symmetry operator [1] = 1-X, 1-Y, 1-Z.								
Atom	**Atom**	**Atom**	**Angle/˚**		**Atom**	**Atom**	**Atom**	**Angle/˚**
O1	Ga1	O1[1]	70.29(8)		N1	C9	C4	122.5(3)
O1	Ga1	N1	78.04(8)		C4	C9	C8	121.4(3)
O1	Ga1	C10	114.04(11)		C11	C10	Ga1	115.9(2)
O1	Ga1	C16	113.22(11)		C3	C4	C9	116.3(3)
N1	Ga1	O1[1]	148.19(9)		C5	C4	C9	118.1(3)
C10	Ga1	O1[1]	94.97(10)		C5	C4	C3	125.5(3)
C10	Ga1	N1	100.62(11)		C17	C18	C19	112.4(3)
C10	Ga1	C16	132.18(13)		C17	C16	Ga1	112.9(2)
C16	Ga1	O1[1]	94.04(10)		C8	C7	C6	120.0(3)
C16	Ga1	N1	95.69(11)		N1	C1	C2	122.4(3)
Ga1	O1	Ga1[1]	109.71(8)		C2	C3	C4	120.2(3)
C8	O1	Ga1	118.44(17)		C3	C2	C1	119.5(3)
C8	O1	Ga1[1]	130.93(18)		C12	C11	C10	115.5(3)
C9	N1	Ga1	109.57(17)		C6	C5	C4	119.9(3)
C1	N1	Ga1	131.4(2)		C5	C6	C7	122.3(3)
C1	N1	C9	119.0(3)		C20	C19	C18	116.5(3)
O1	C8	C9	117.3(3)		C11	C12	C13	112.6(3)
O1	C8	C7	124.4(3)		C19	C20	C21	112.0(3)
C7	C8	C9	118.3(3)		C14	C13	C12	114.4(3)
C18	C17	C16	115.3(3)		C13	C14	C15	112.4(4)
N1	C9	C8	116.1(2)					

5. Stability and Biological activity

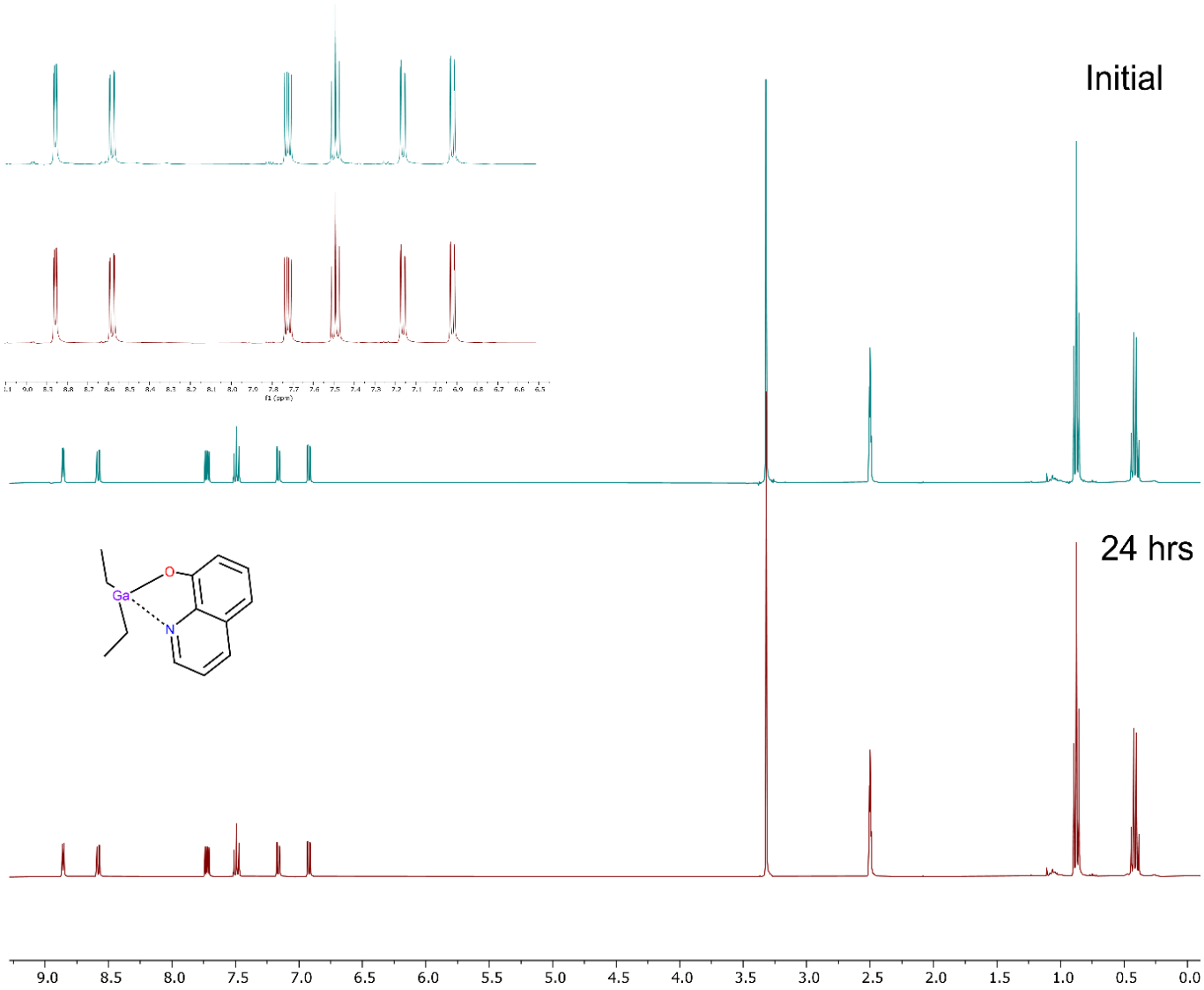


Figure S7. ^{1}H NMR study of complex **G1** in d_6-DMSO over a 24 hours period, highlighting the hydrolytic stability. An insert of the aromatic region has been provided for clarity. DMSO and water appear at 2.50 ppm and 3.33 ppm respectively.

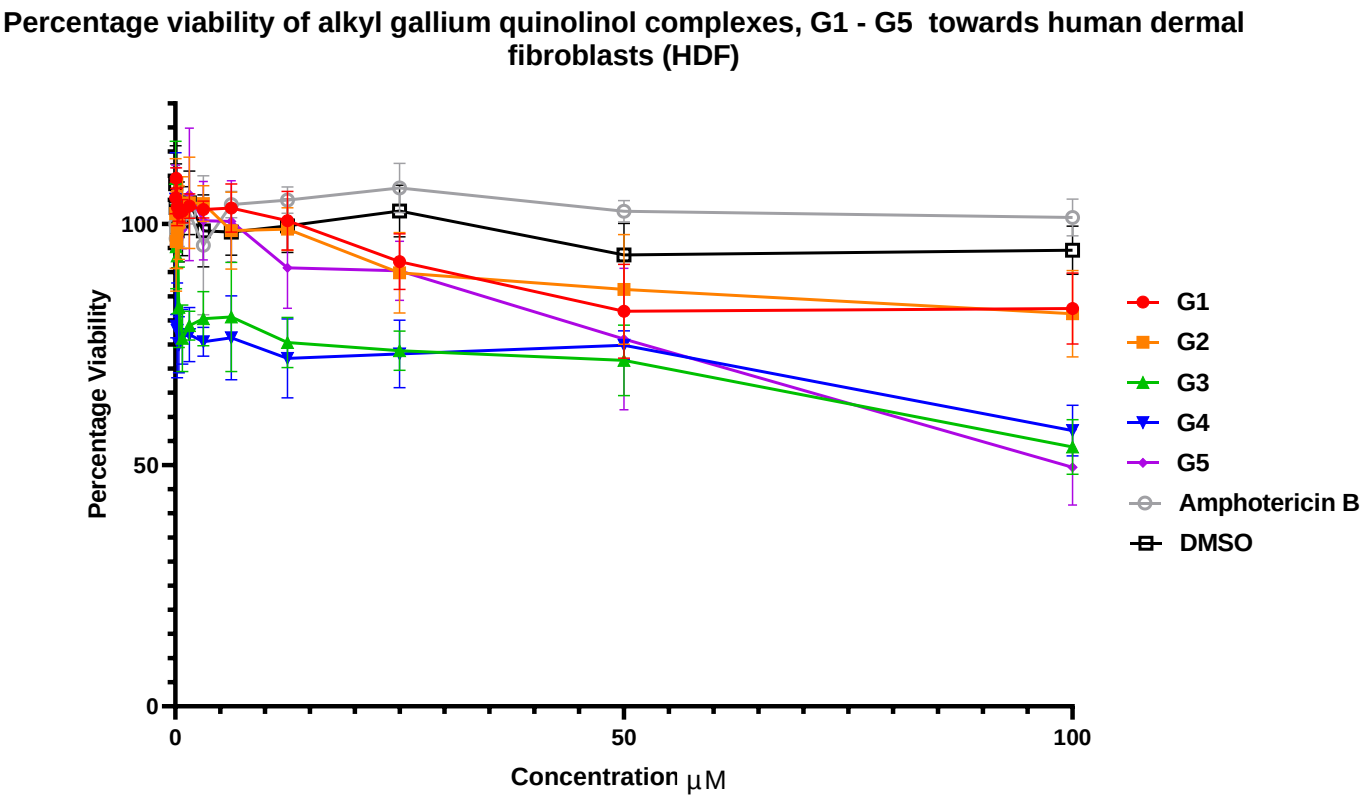


Figure S8. Comparison of percentage cell viability after treatment with complexes **G1 – G5**, against human dermal fibroblasts. Dose response curves were generated over a range of concentrations (48nm – 100 µM) in the appropriate culture media from 10mM DMSO stock solutions. All readings were compared spectroscopically to non-treated control and the percent growth inhibition calculated. A DMSO control and positive drug control (Amp B) were also included at the same range of concentrations.

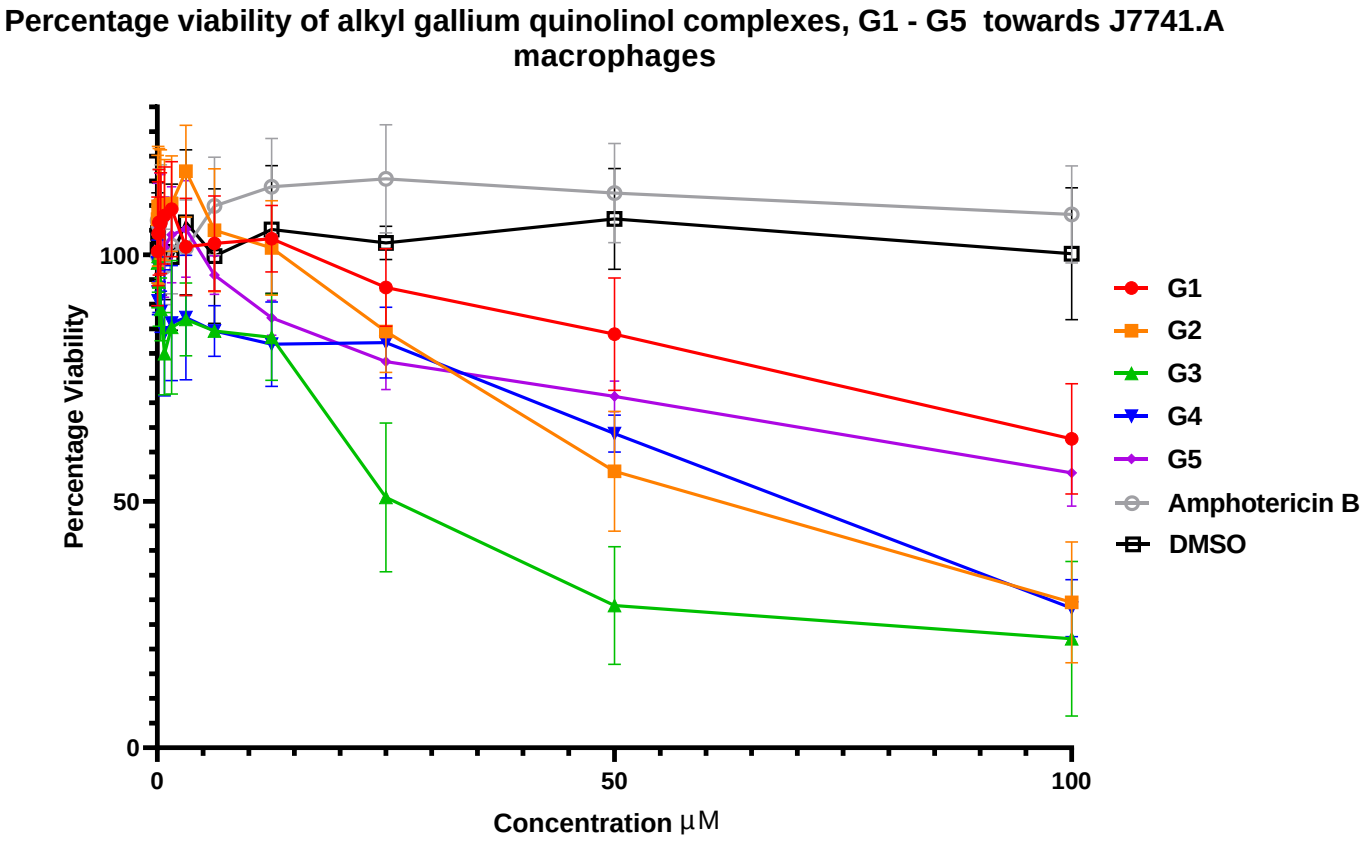


Figure S9. Comparison of percentage cell viability after treatment with complexes **G1 – G5**, against J774.1A mice macrophages. Dose response curves were generated over a range of concentrations (48nm – 100 µM) in the appropriate culture media from 10mM DMSO stock solutions. All readings were compared spectroscopically to non-treated control and the percent growth inhibition calculated. A DMSO control and positive drug control (Amp B) were also included at the same range of concentrations.

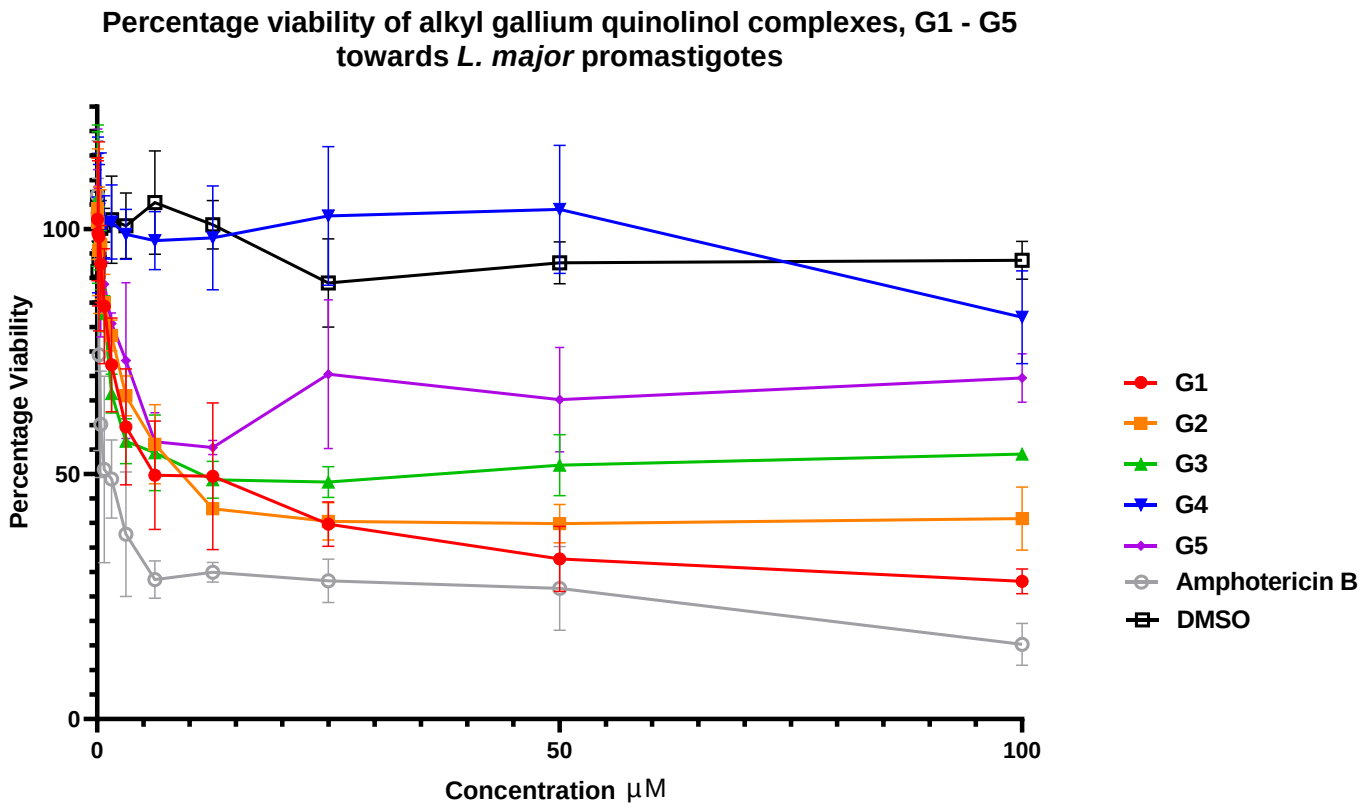


Figure S10. Comparison of percentage cell viability after treatment with complexes **G1 – G5**, against *L. major* promastigotes. Dose response curves were generated over a range of concentrations (48nm – 100 µM) in the appropriate culture media from 10mM DMSO stock solutions. All readings were compared spectroscopically to non-treated control and the percent growth inhibition calculated. A DMSO control and positive drug control (Amp B) were also included at the same range of concentrations.

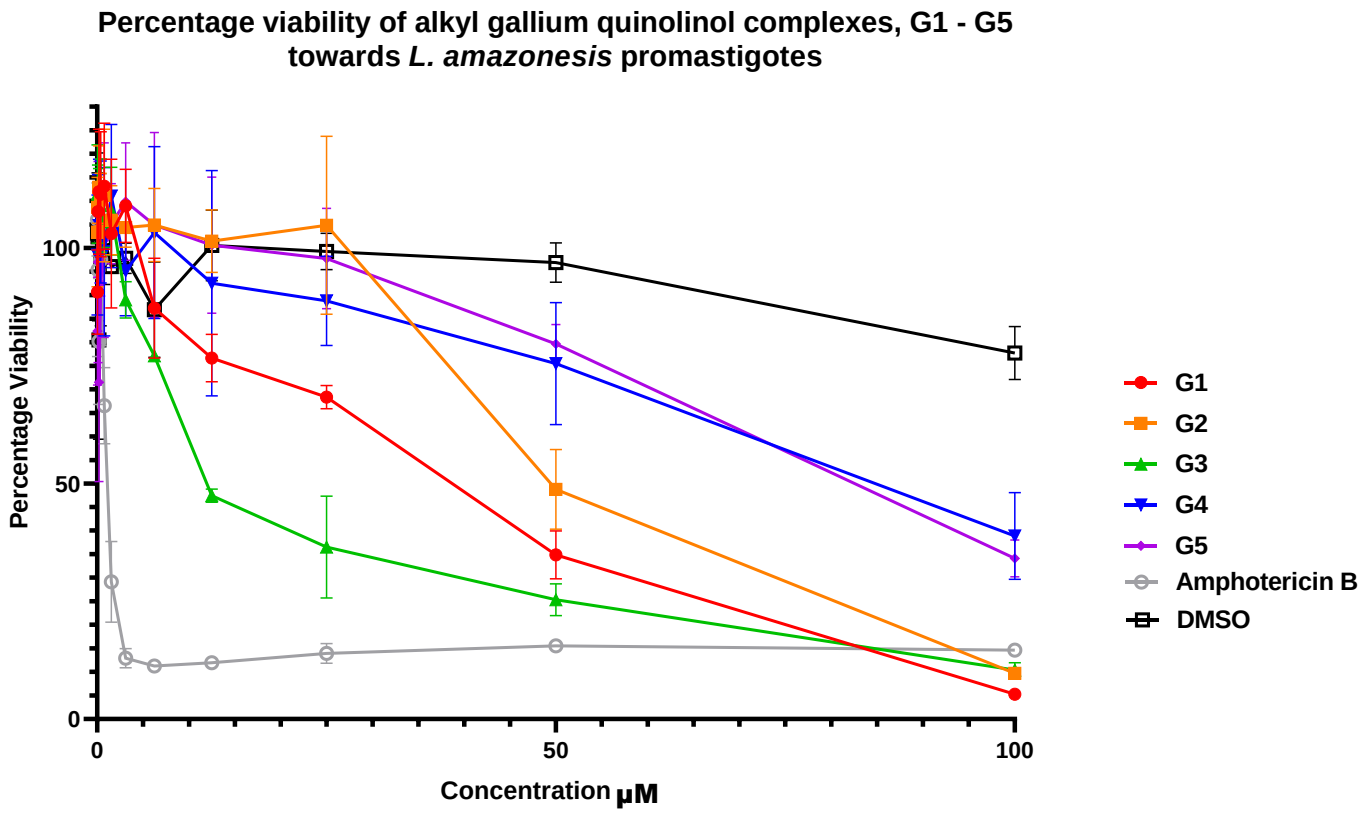


Figure S11. Comparison of percentage cell viability after treatment with complexes **G1 – G5**, against *L. amazonesis* promastigotes. Dose response curves were generated over a range of concentrations (48nm – 100 µM) in the appropriate culture media from 10mM DMSO stock solutions. All readings were compared spectroscopically to non-treated control and the percent growth inhibition calculated. A DMSO control and positive drug control (Amp B) were also included at the same range of concentrations.

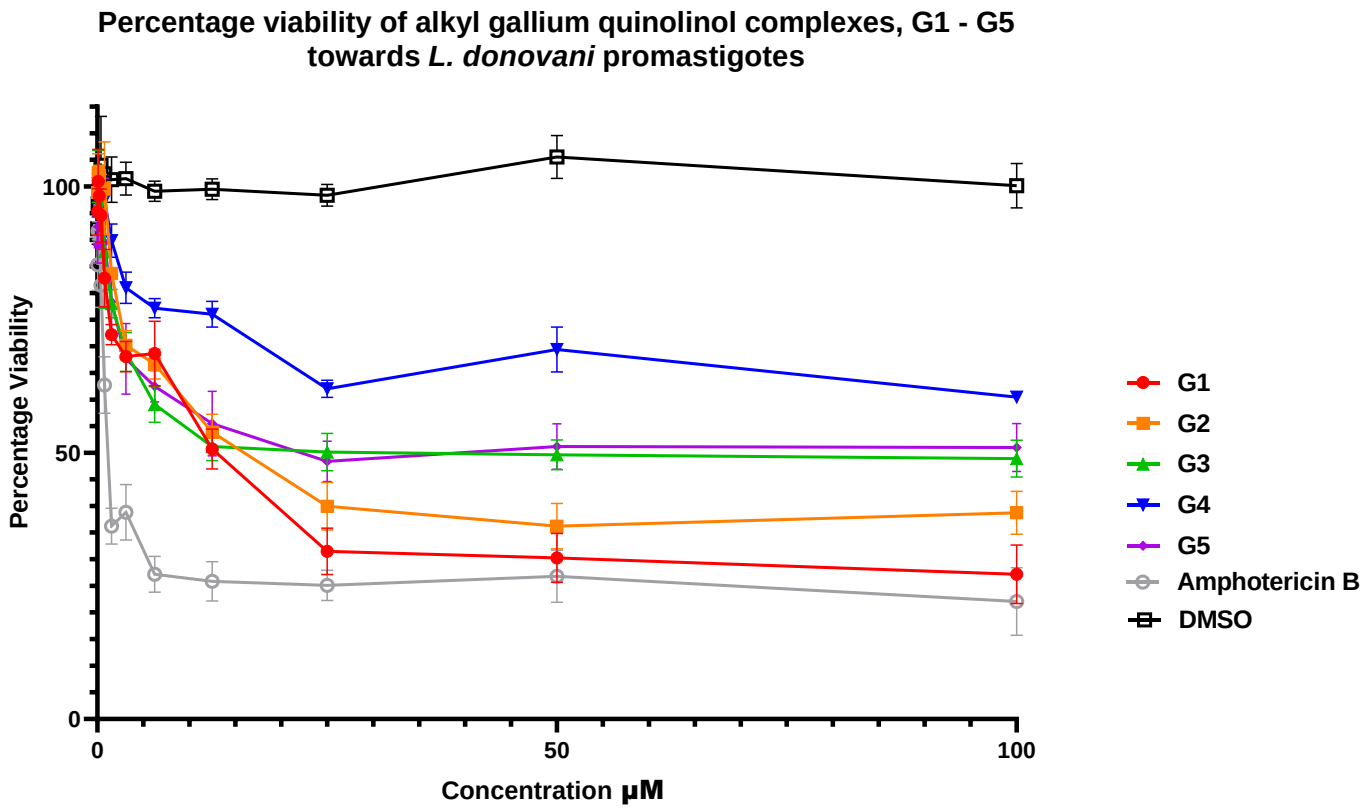


Figure S12. Comparison of percentage cell viability after treatment with complexes **G1 – G5**, against *L. donovani* promastigotes. Dose response curves were generated over a range of concentrations (48nm – 100 µM) in the appropriate culture media from 10mM DMSO stock solutions. All readings were compared spectroscopically to non-treated control and the percent growth inhibition calculated. A DMSO control and positive drug control (Amp B) were also included at the same range of concentrations.

Table S14. IC_{50} values for each complex tested against two mammalian control cells (human dermal fibroblasts, HDF and J774.1A mice macrophages) and three strains of *Leishmania* promastigotes *L. major* (LM), *L. amazonensis* (LA) and *L. donovani* (LD). Selectivity indices for each control cell line to each parasite have been calculated as IC_{50}(mammalian)/IC_{50}(parasite). All analyses were completed in triplicate.

Compound	**HDF**	**J774.1A**	**LM**	**LA**	**LD**	**SI - LM**	**SI - LA**	**SI – LD**
	IC₅₀ µM	***IC₅₀ µM***	***IC₅₀ µM***	***IC₅₀ µM***	***IC₅₀ µM***	***HDF/J774.1A***	***HDF/J774.1A***	***HDF/J774.1A***
G1	≥ 100	≥ 100	6.23	38.8	12.3	>16.1/>16.1	>2.50/>2.50	>8.13/>8.13
G2	≥ 100	61.8	9.10	48.7	15.9	>11.0/6.79	>2.05/1.27	>6.30/3.89
G3	≥ 100	25.8	11.1	11.9	24.2	>9.01/2.32	>8.92/2.17	>4.13/1.07
G4	≥ 100	69.7	≥ 100	84.9	≥ 100	>1.00/0.697	>1.17/0.821	>1.00/0.697
G5	99.6	≥ 100	≥ 100	82.7	21.8	0.996/>1.01	1.20/>1.21	4.56/>4.59

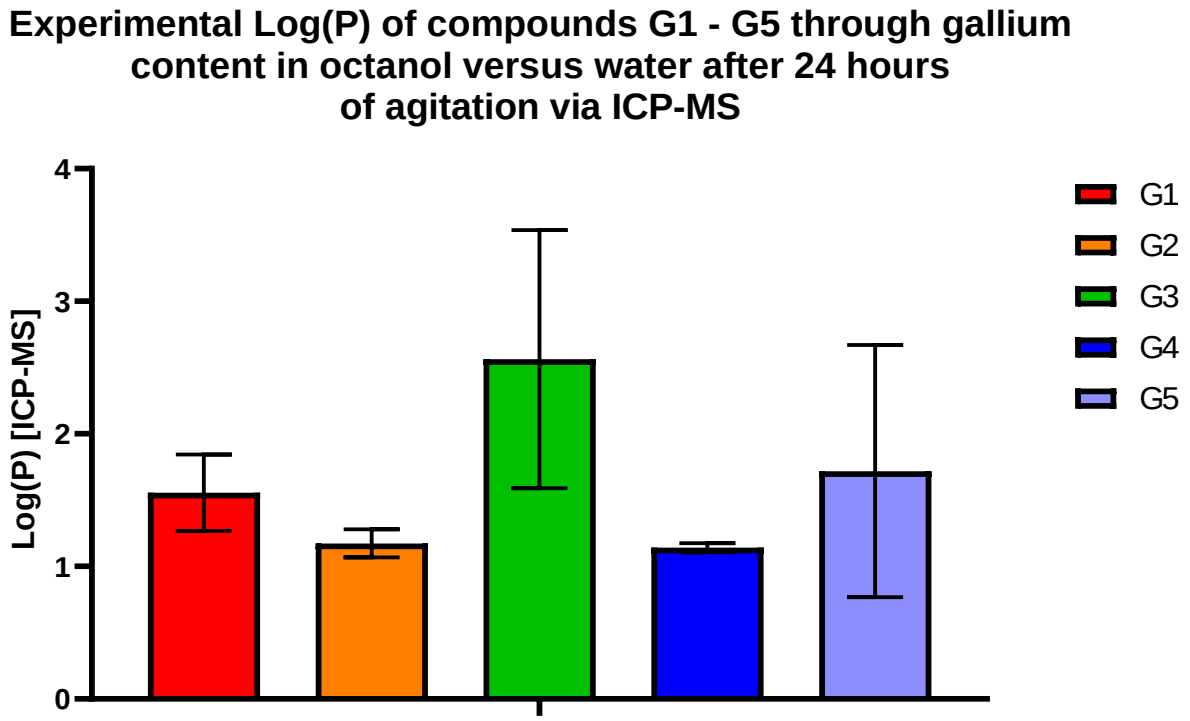


Figure S13. Experimental log(p) determined through shake-flask method and ICP-MS

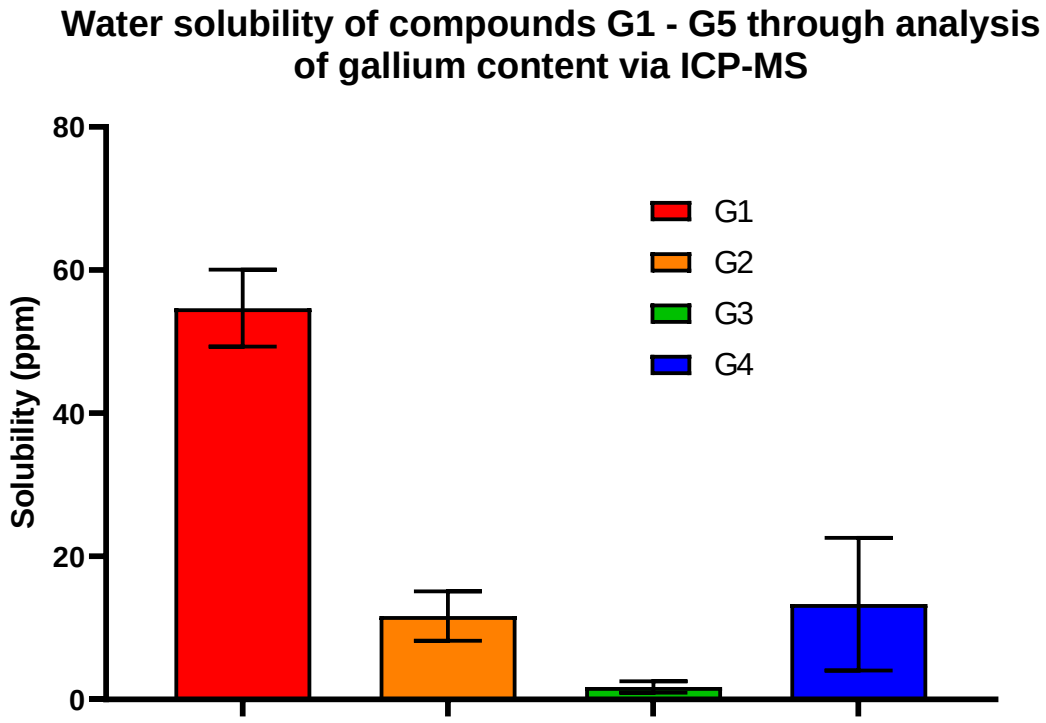


Figure S14. Solubility of complexes in ultrapure water in ppm (1 ppm = 0.001 mg/mL)

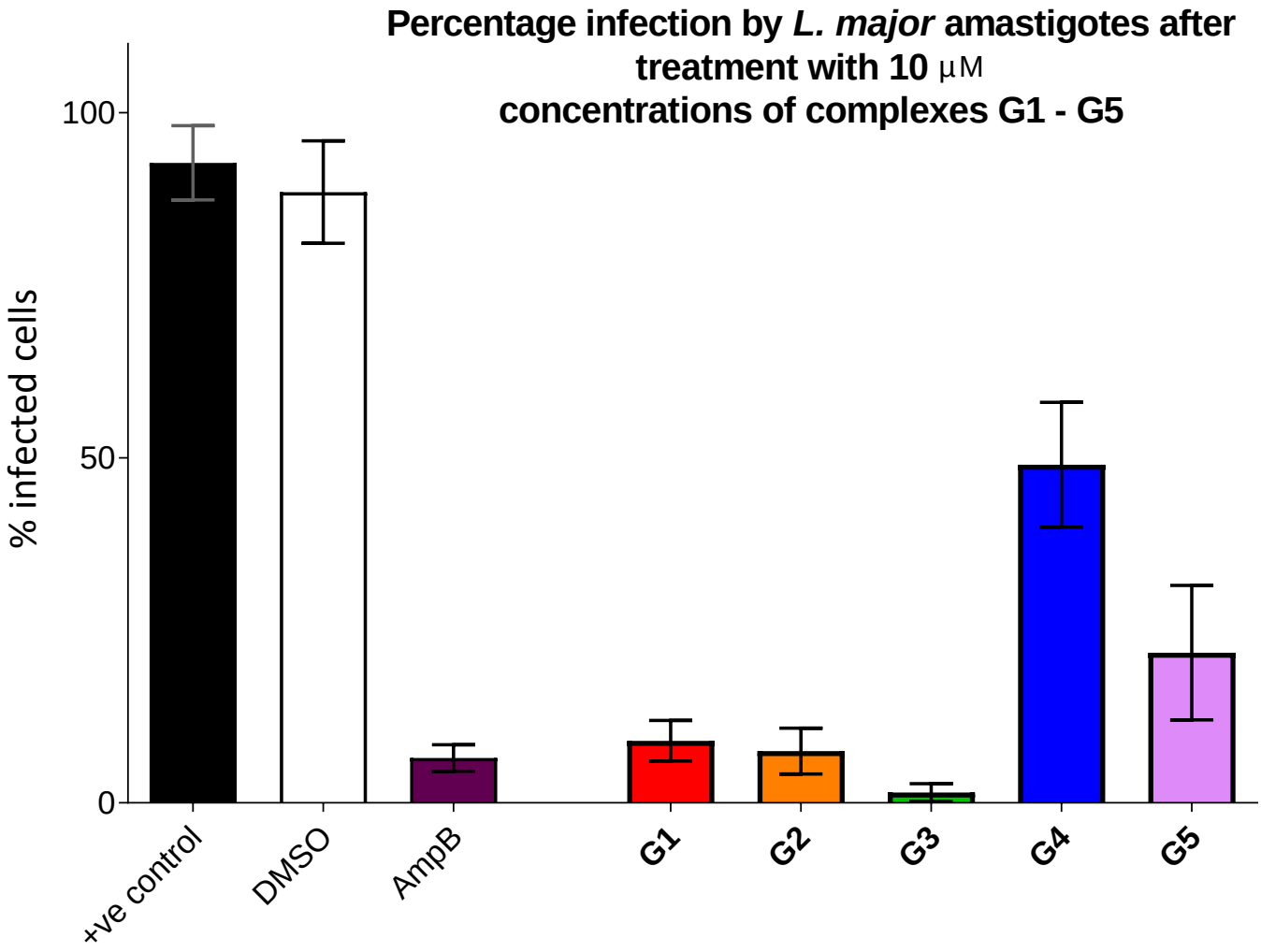


Figure S15. Infected macrophages after 24 hours. Number of infected macrophages was determined microscopically, in duplicate of fixed specimens. Amphotericin B (AmpB) was used as a positive control at 10 µM concentration. A DMSO control was also employed at a 1% concentration. Error bars indicate SEM, one-way ANOVA. Dunnett's multiple comparison test was used to determine the statistical significance between all test compounds and a positive control lacking treatment (+ve control)

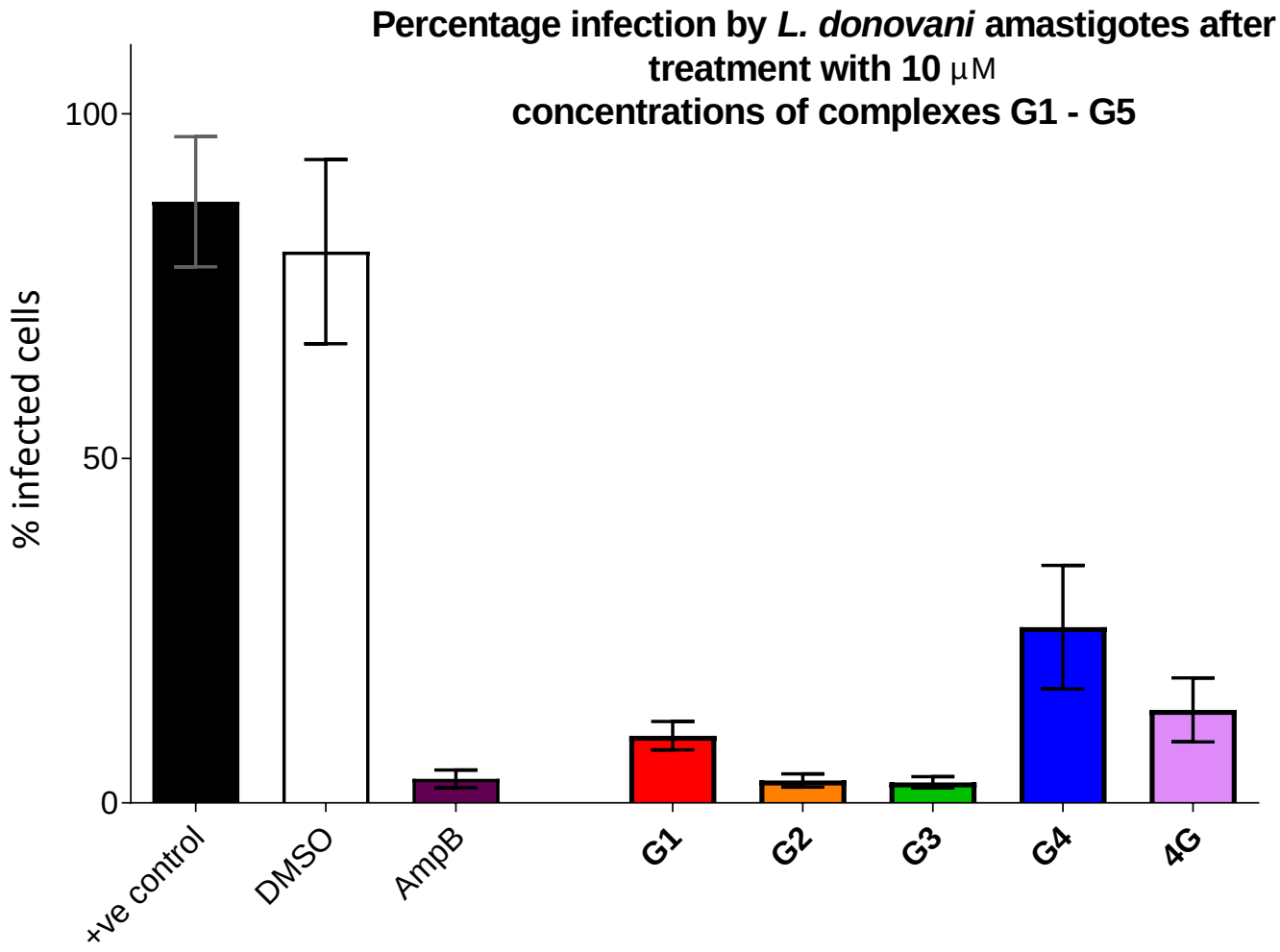


Figure S16. Percentage infection of *Leishmania donovani* amastigote infected macrophages after 24 hours of drug exposure. Number of infected macrophages was determined microscopically, in duplicate of fixed specimens. Amphotericin B (AmpB) was used as a positive control at 10 µM concentration. A DMSO control was also employed at a 1% concentration. Error bars indicate SEM, one-way ANOVA. Dunnett's multiple comparison test was used to determine the statistical significance between all test compounds and a positive control lacking treatment (+ve control)

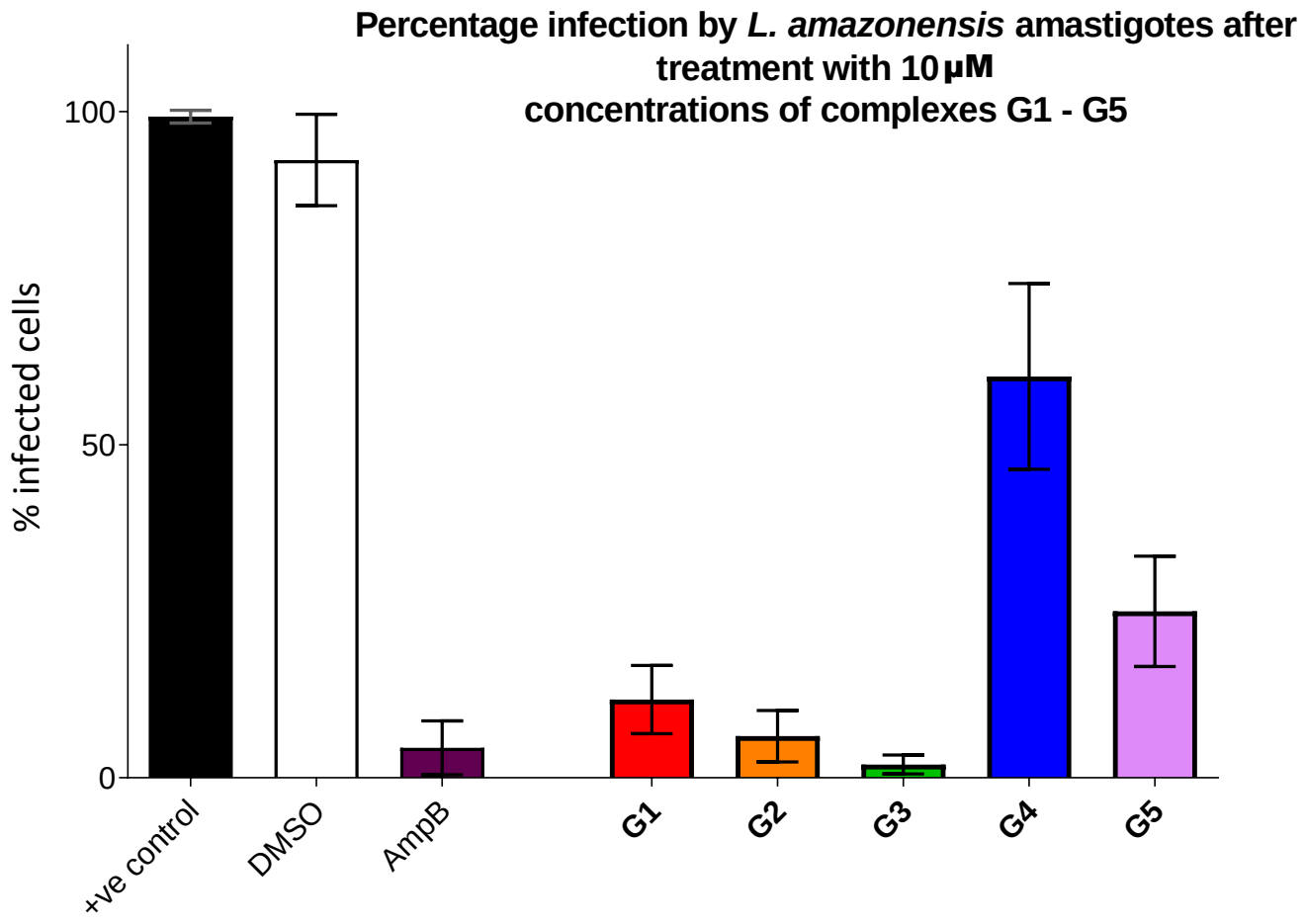


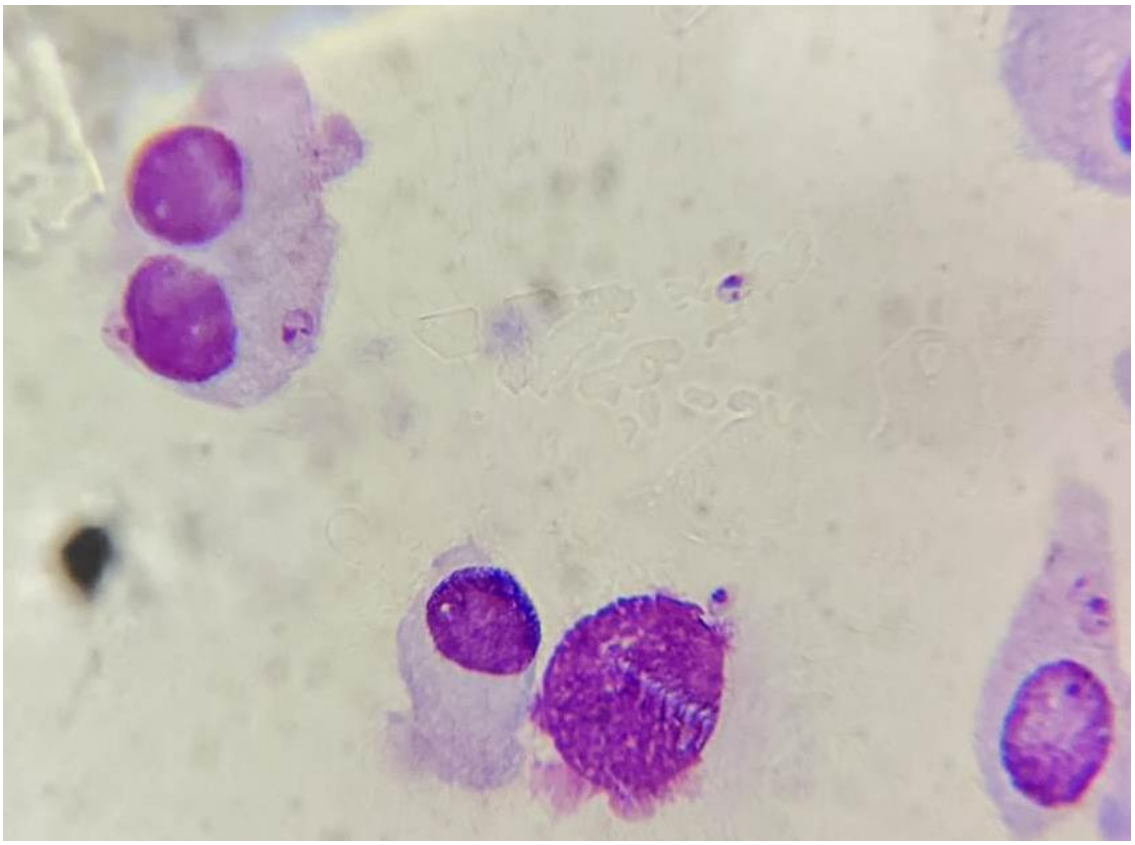
Figure S17. Percentage infection of *Leishmania amazonensis* amastigote infected macrophages after 24 hours of drug exposure. Number of infected macrophage was determined microscopically, in duplicate of fixed specimens. Amphotericin B (AmpB) was used as a positive control at 10 µM concentration. A DMSO control was also employed at a 1% concentration. Error bars indicate SEM, one-way ANOVA. Dunnett's multiple comparison test was used to determine the statistical significance between all test compounds and a positive control lacking treatment (+ve control)

Table S15. Percentage infection values versus positive control for complexes **G1** – **G5** toward *L. major, L. amazonensis* and *L. donovani* infected macrophages. Drug control amphotericin B (AmpB) also provided. Vehicle solvent control DMSO can be found with the all other graphs in the SI.

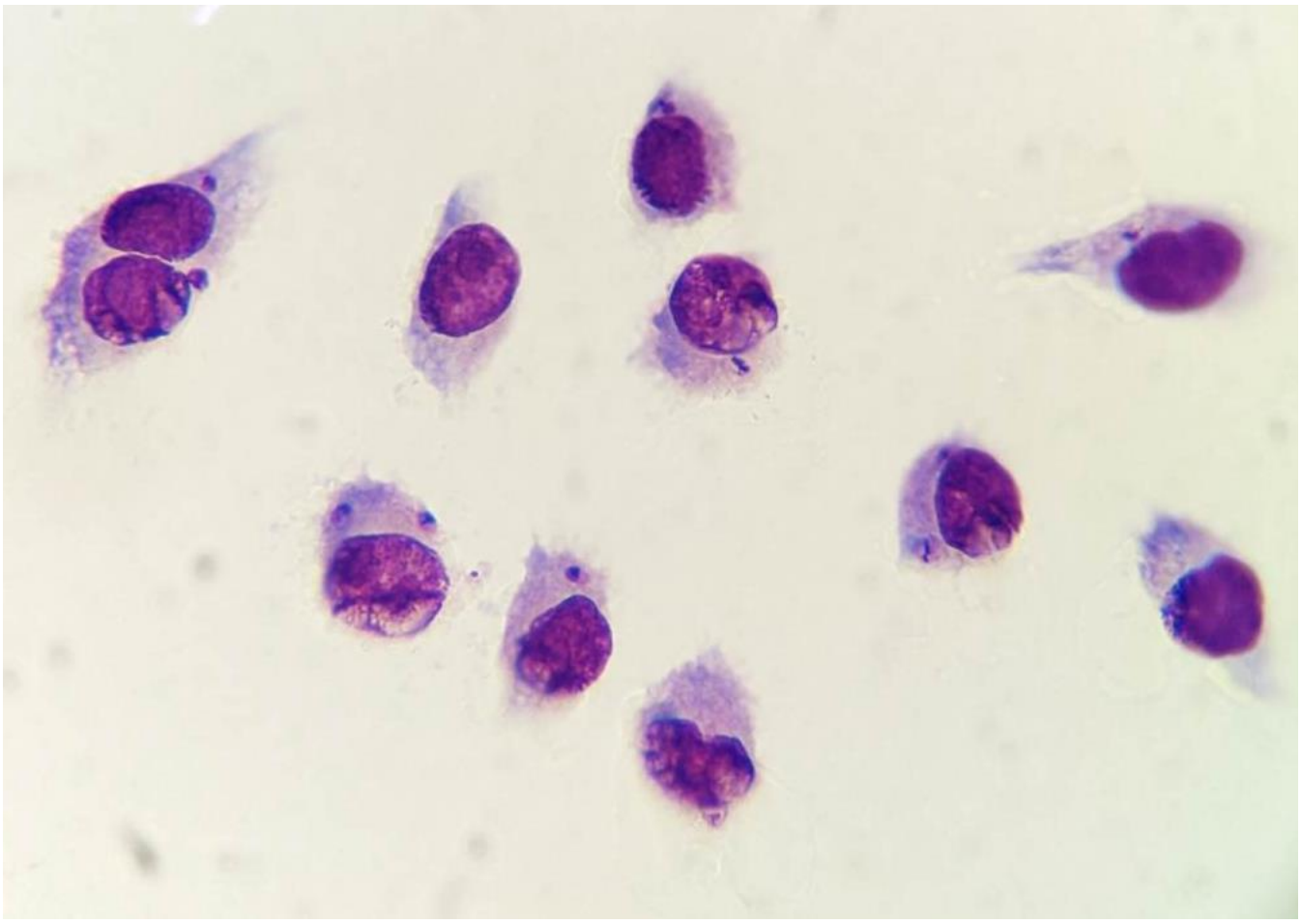
Compound	AmpB	G1	G2	G3	G4	G5
***L. major* (%)**	6.50 ± 1.91	9.00 ± 2.92	7.50 ± 3.32	1.50 ± 1.29	49.0 ± 9.06	21.8 ± 9.74
***L. amazonensis* (%)**	4.50 ± 4.04	11.8 ± 5.12	6.25 ± 3.86	2.00 ± 1.41	60.3 ± 13.9	25.0 ± 8.29
***L. donovani* (%)**	3.50 ± 1.29	9.75 ± 2.06	3.25 ± 0.957	3.00 ± 0.816	25.5 ± 8.96	13.5 ± 4.65

Sample amastigote images are given for each compound and positive control for each species. Note these images were taken with the use of a phone camera down a microscope so the colour variation is based on the lighting of the microscope at the time of use and the phone capture. Picture have been cropped to remove the microscope outlines.

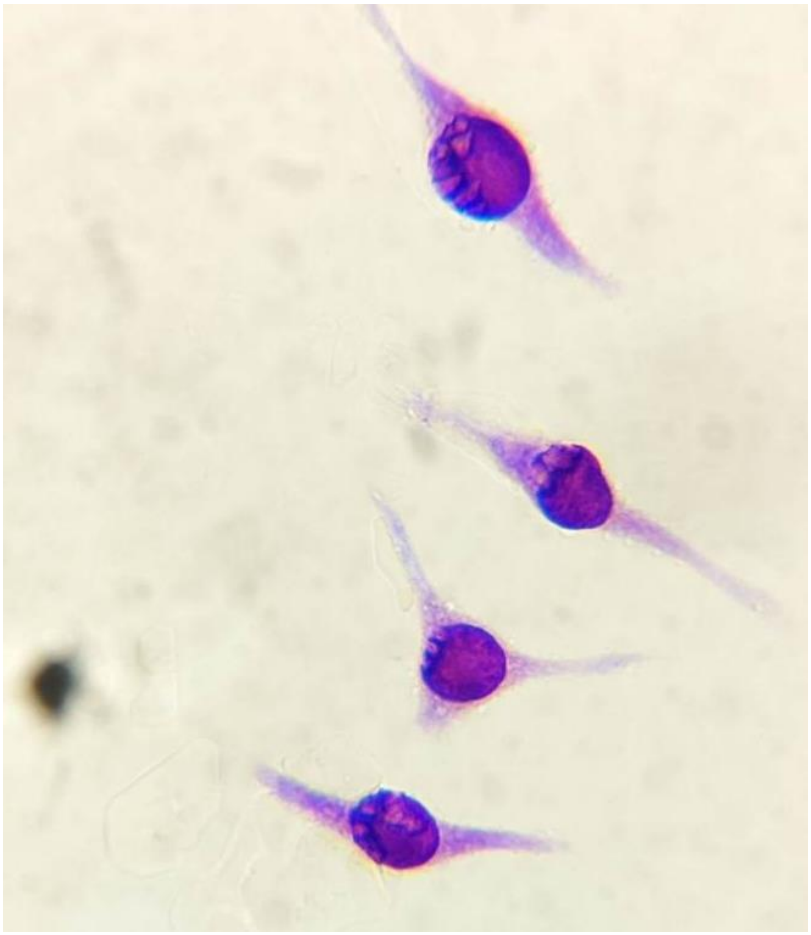
Positive control: L major



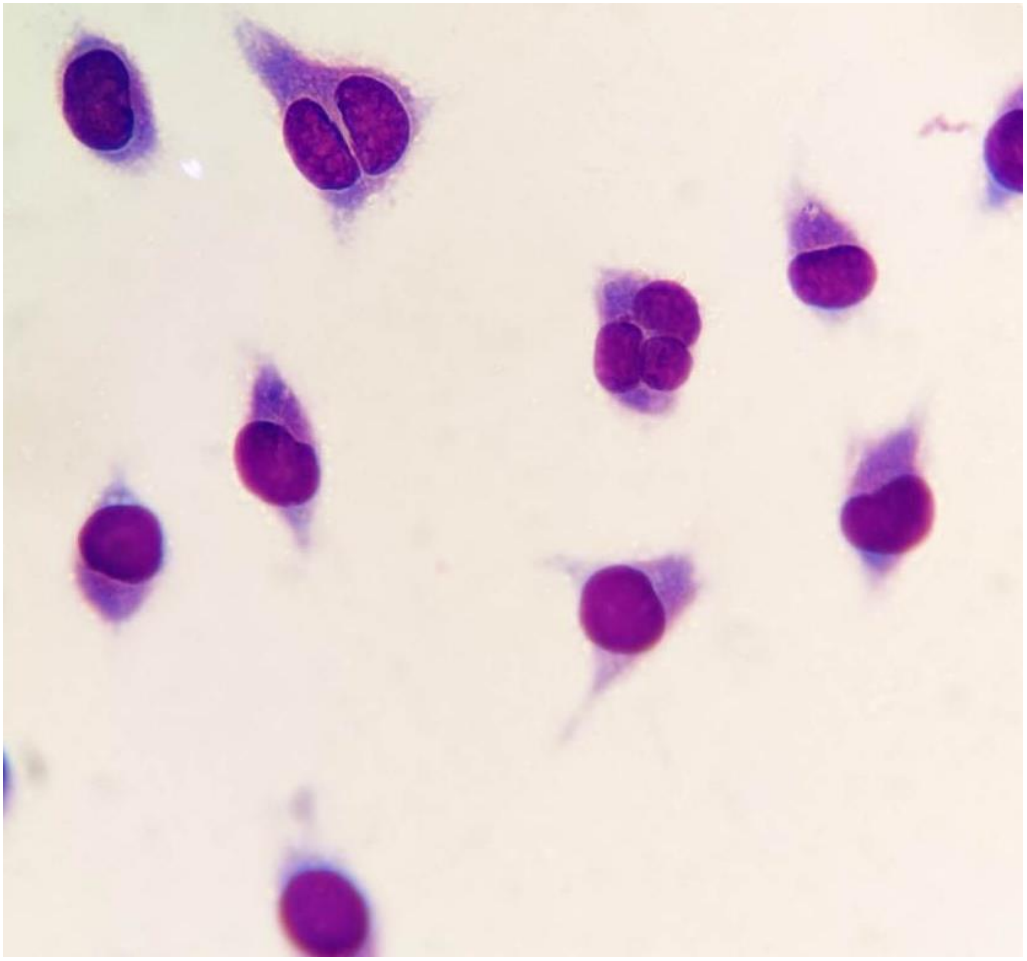
G1: L major, highlighting infection of macrophages after drug treatment



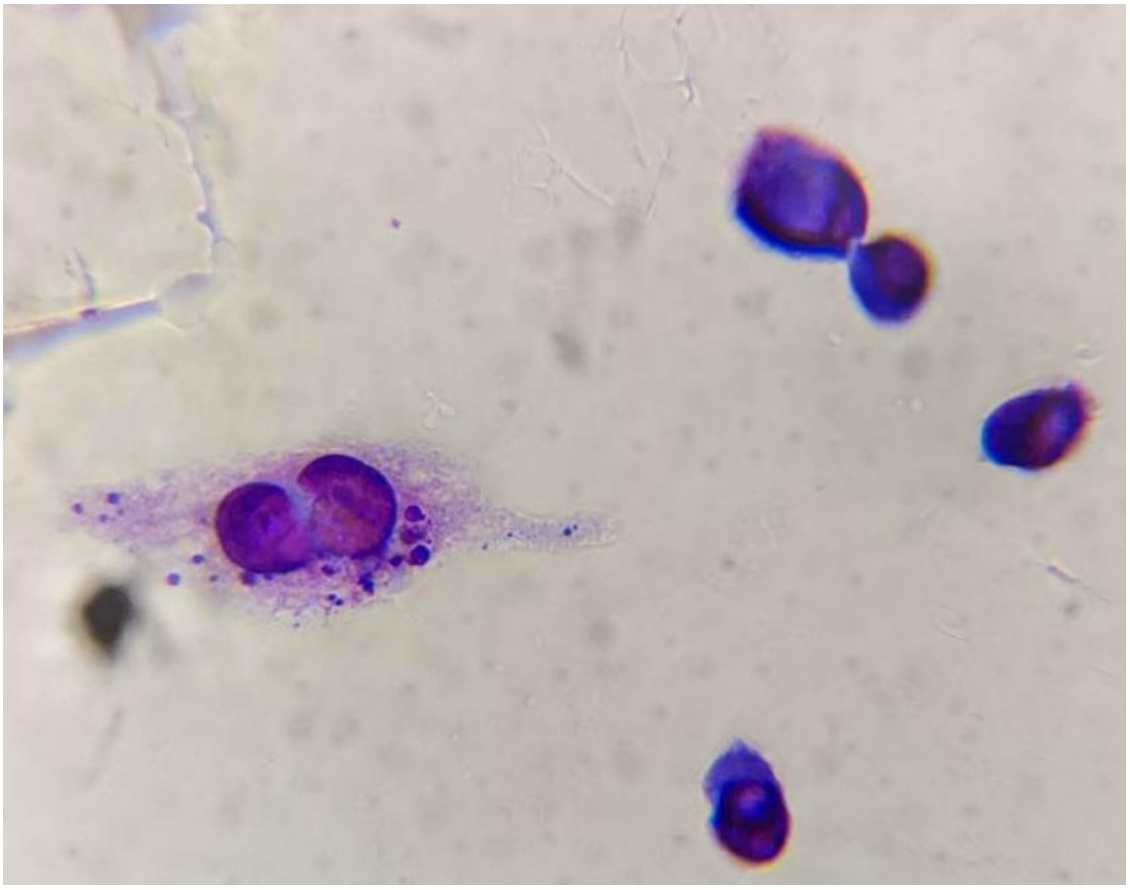
G2: L major highlighting healthy cells after drug treatment



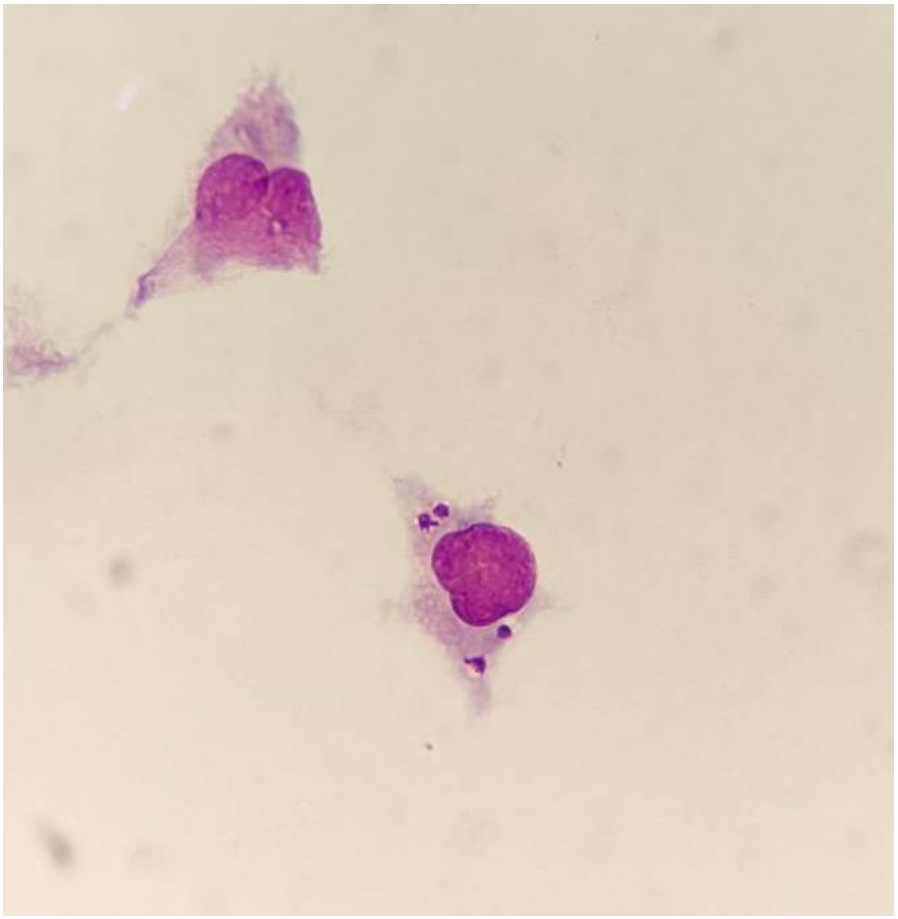
G3: Highlighting healthy non-infected cells after drug treatment



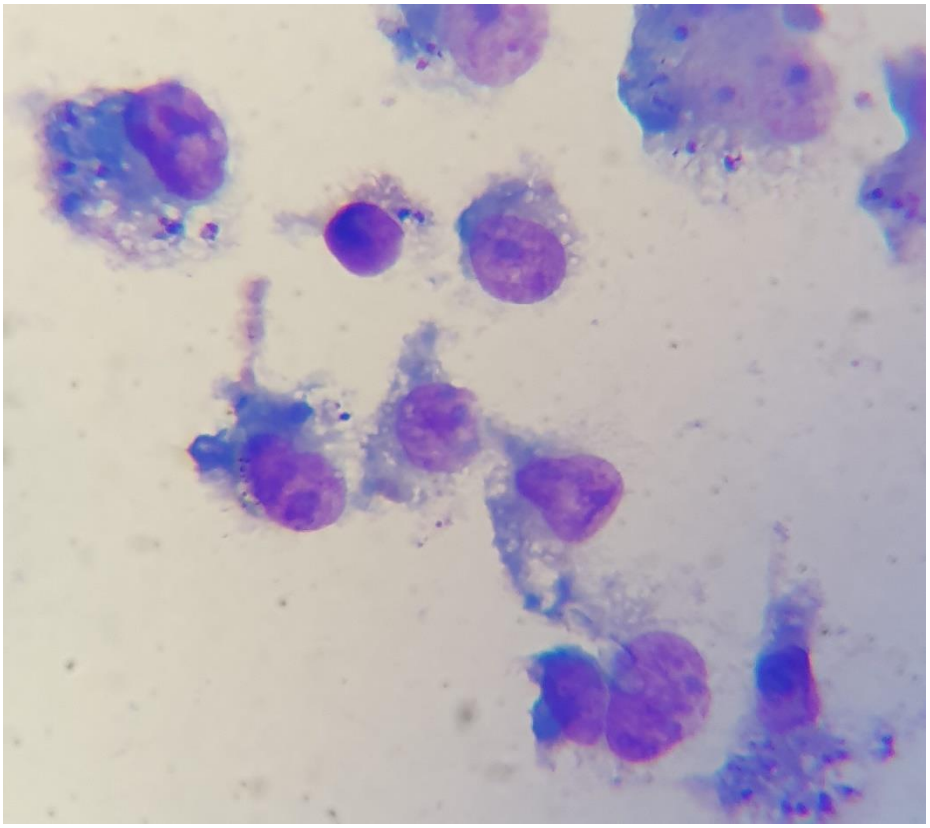
G4: L major highlighting heavily infected cell after drug treatment



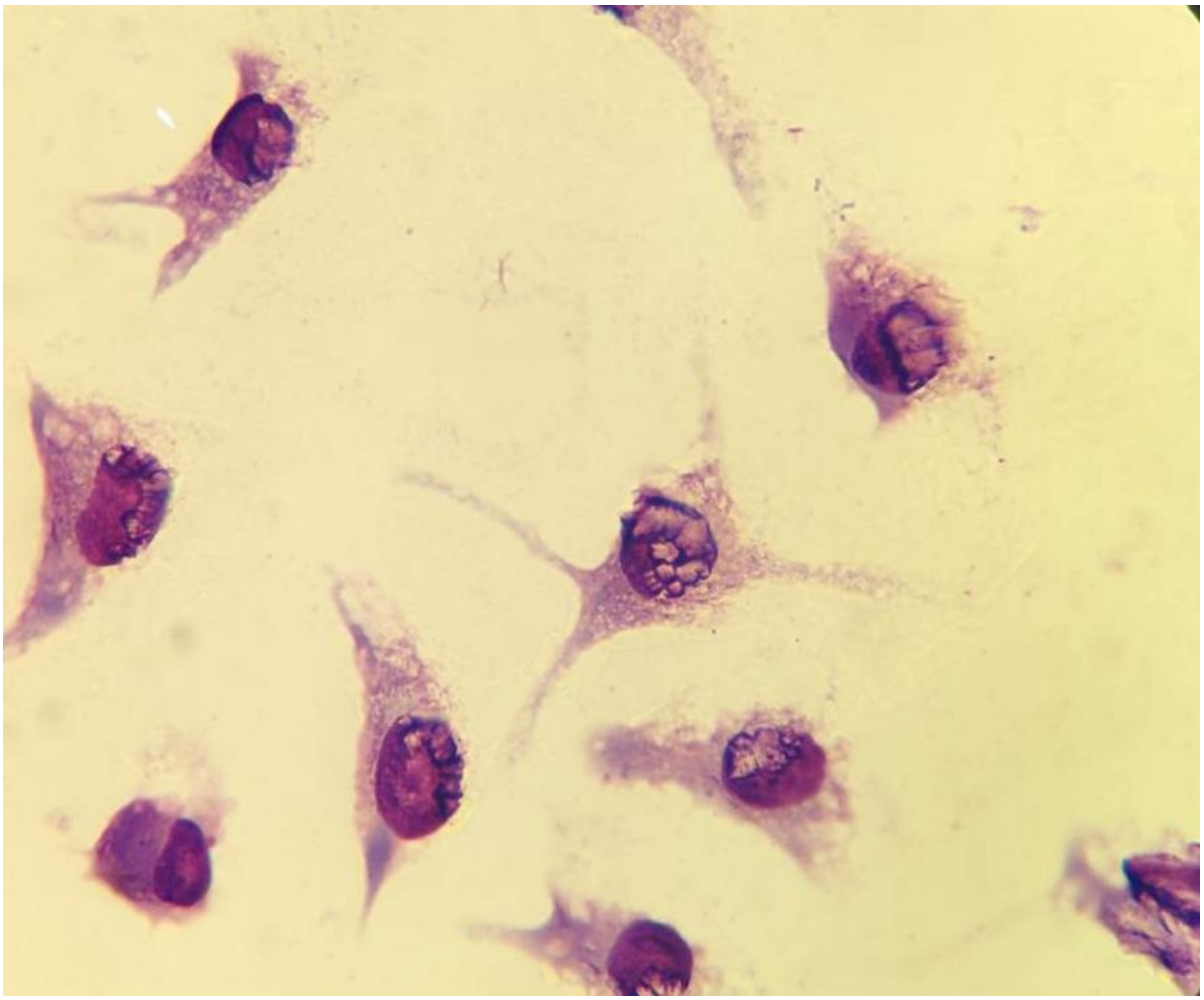
G5: l major



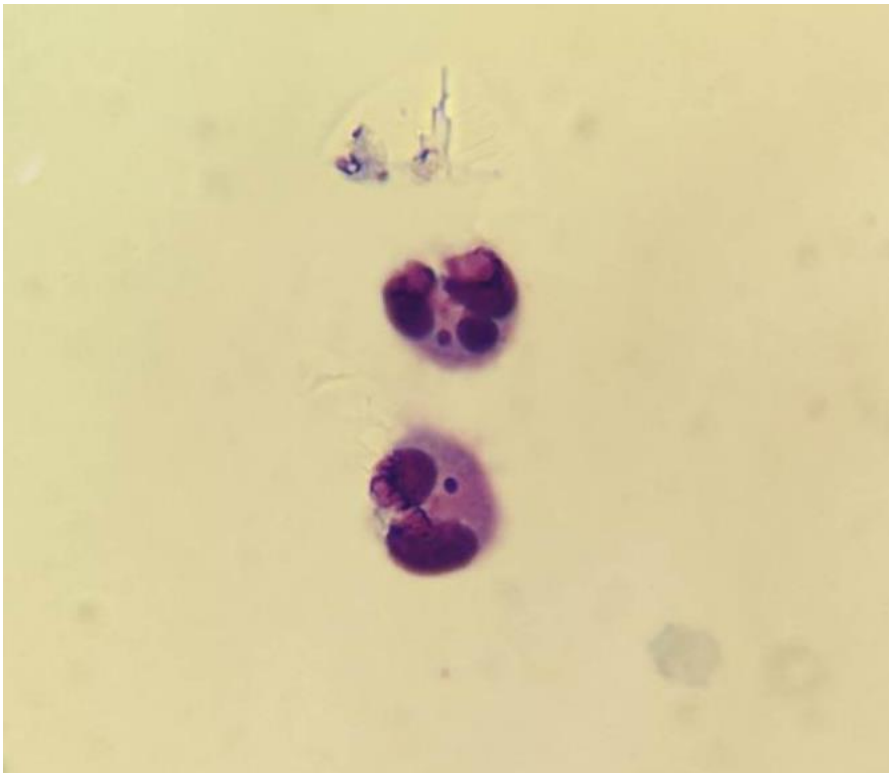
Positive control LV-9



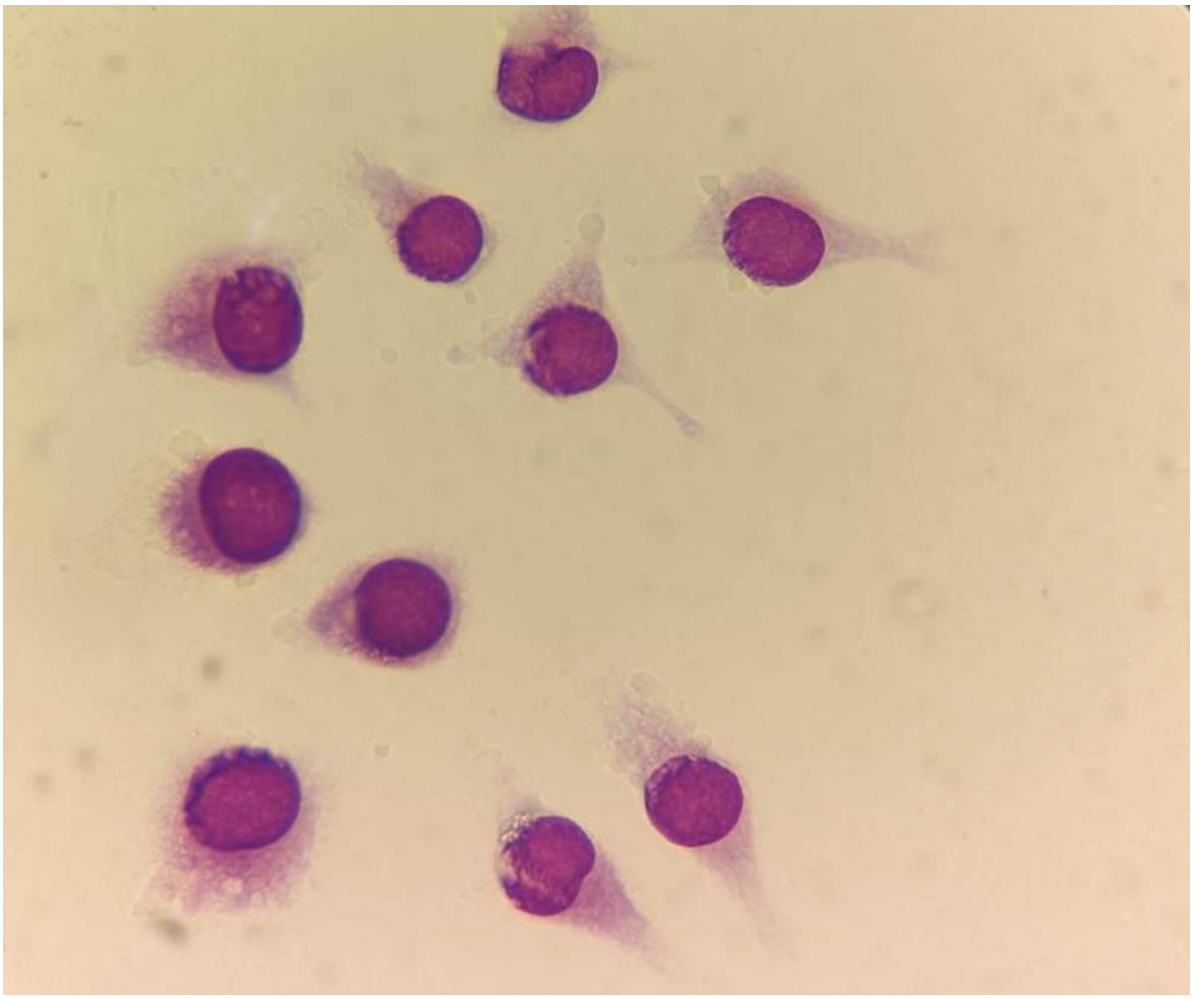
AmpB: LV-9



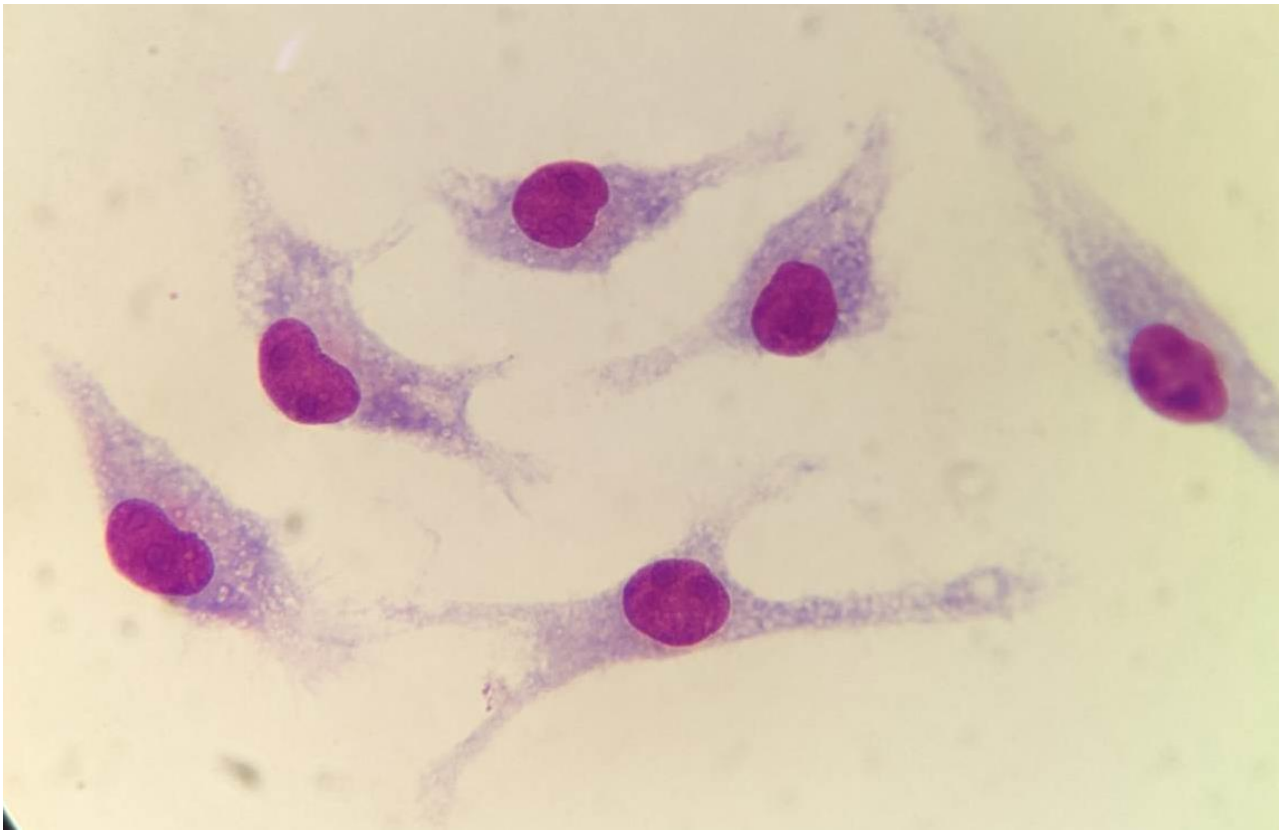
G1: LV-9



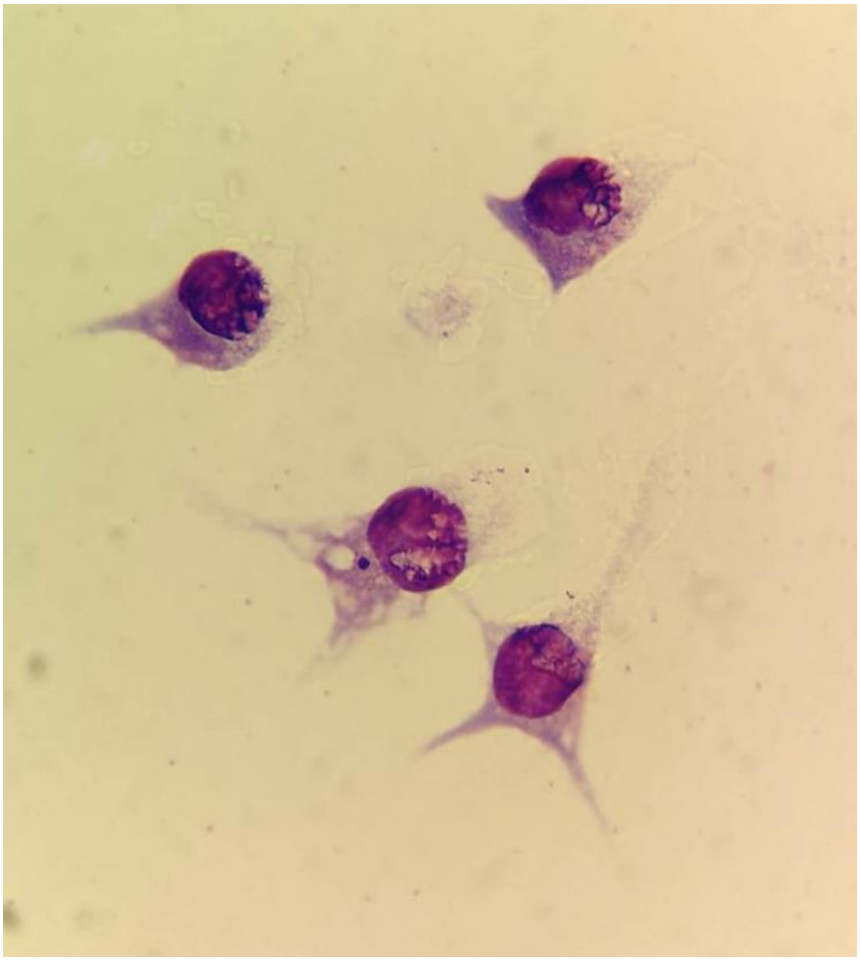
G2: LV-9



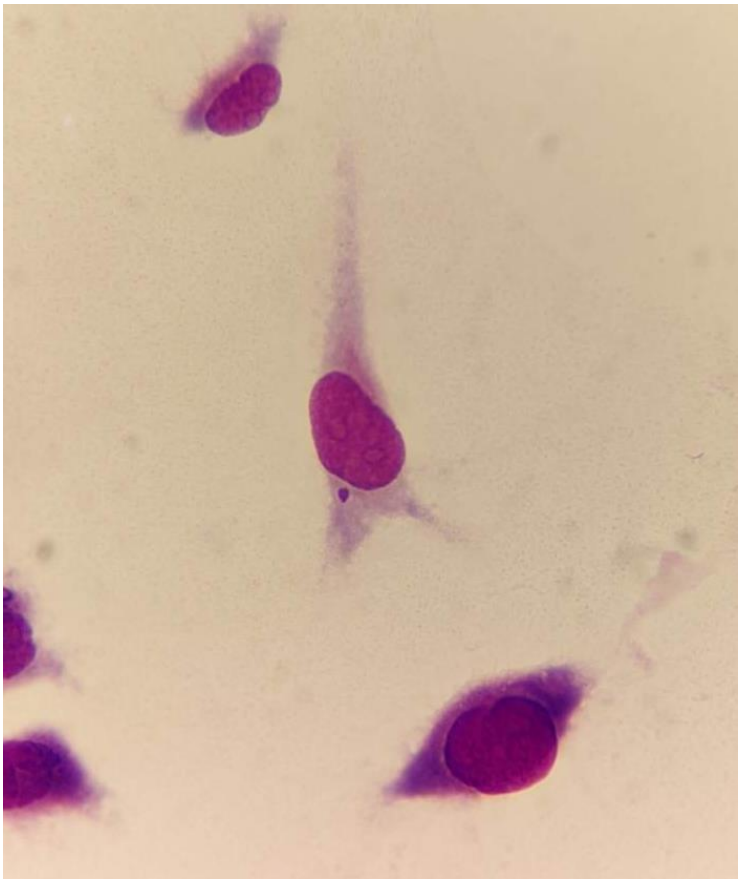
G3: Lv-9



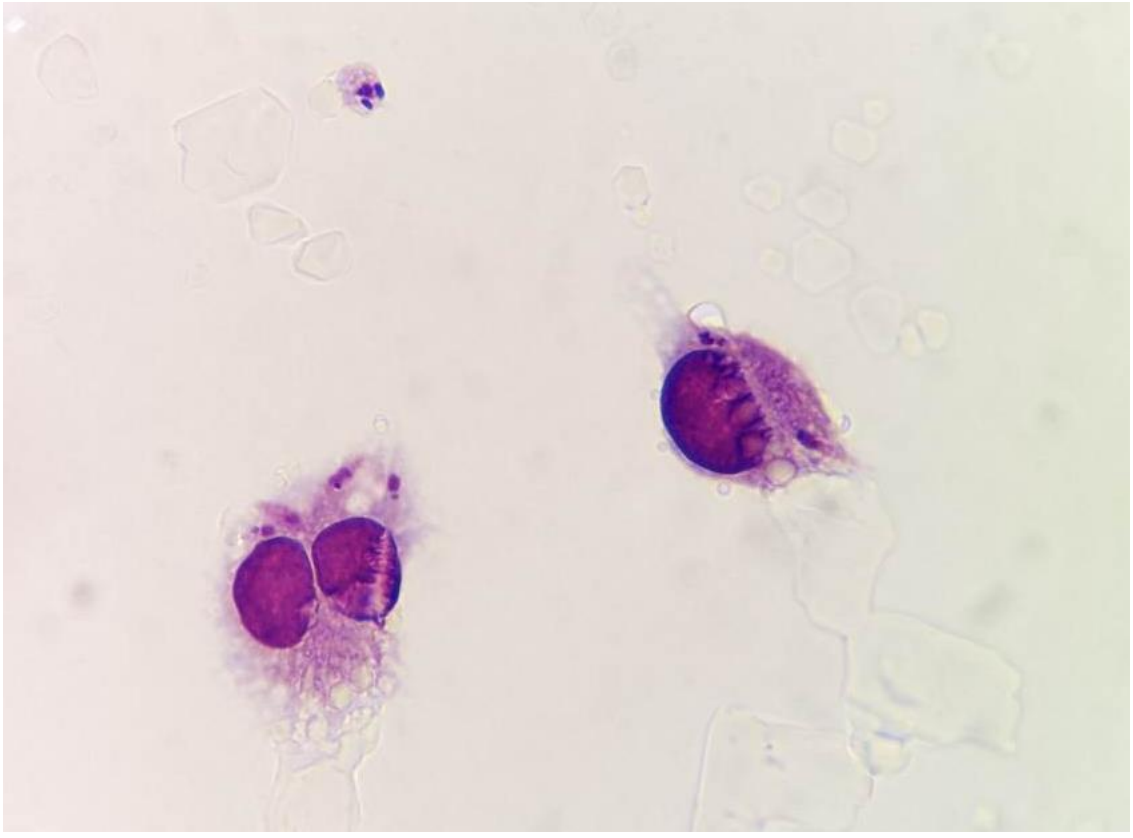
G4 LV-9:



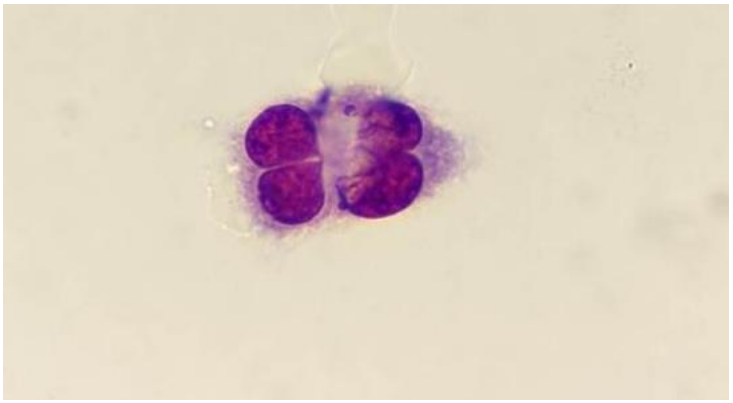
G5 LV-9:



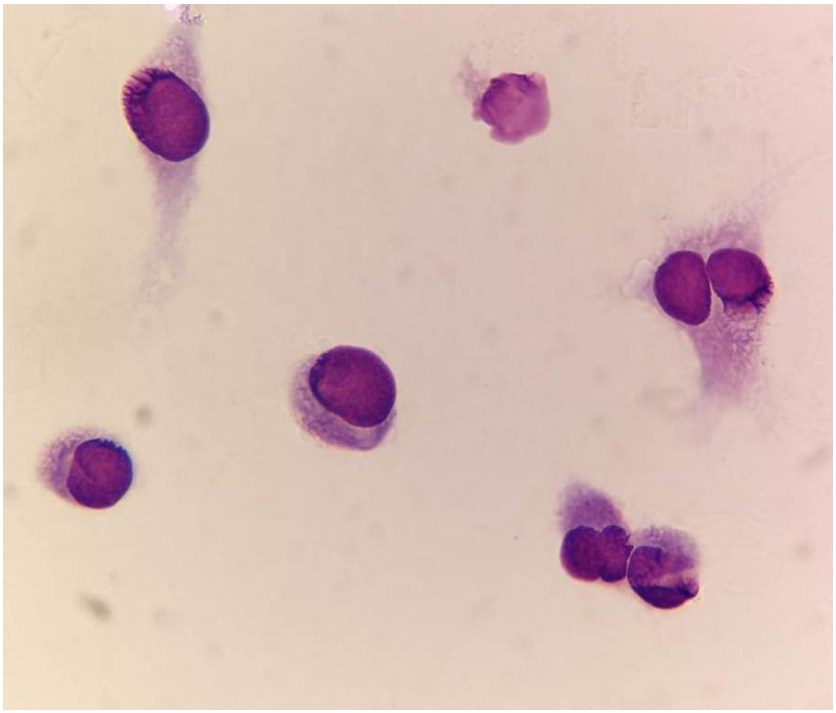
Positive control L. amazonensis



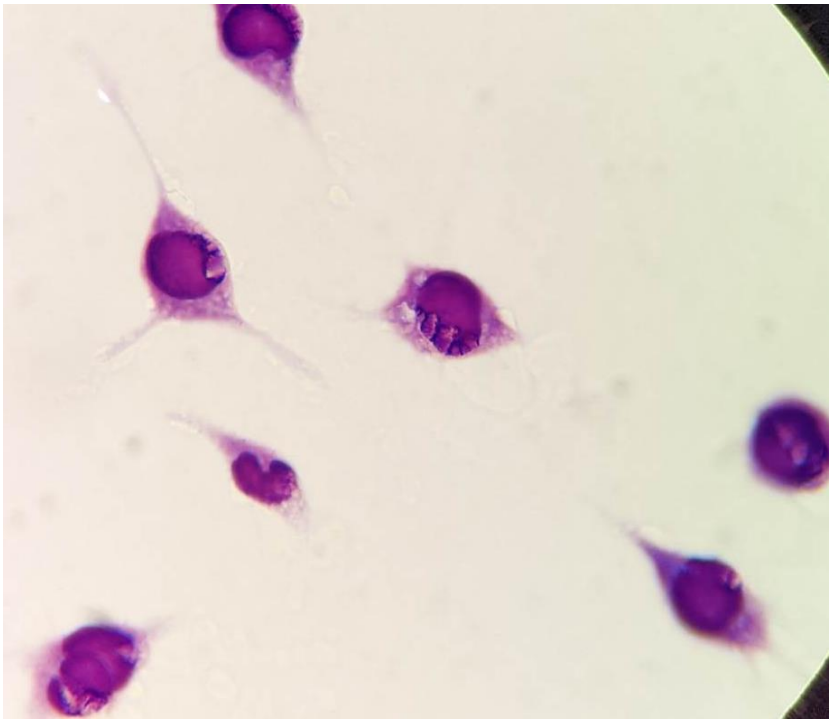
G1: L. amazonensis



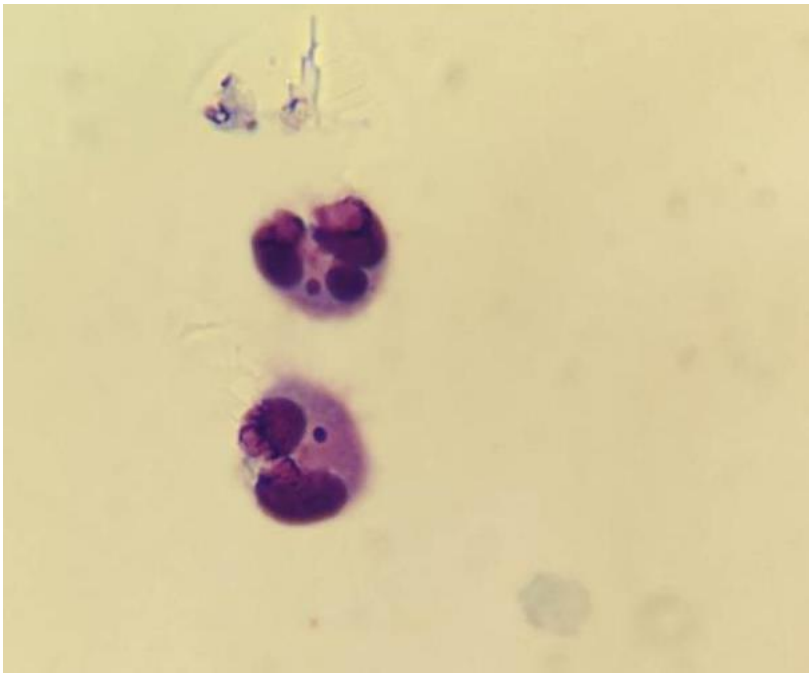
G2: L. amazonensis



G3: L. amazonensis



G4: L. amazonensis



G5: L. amazonensis