Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Syntheses and Structures of Gallaarsenes LGaAsGa(X)L featuring a Ga–As Double Bond

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Table of Content

1. Experimental Part

Fig. S1. ^{1}H-NMR spectrum of LGaAsGa(Cl)L (**1**) in toluene-d_8 at room temperature.

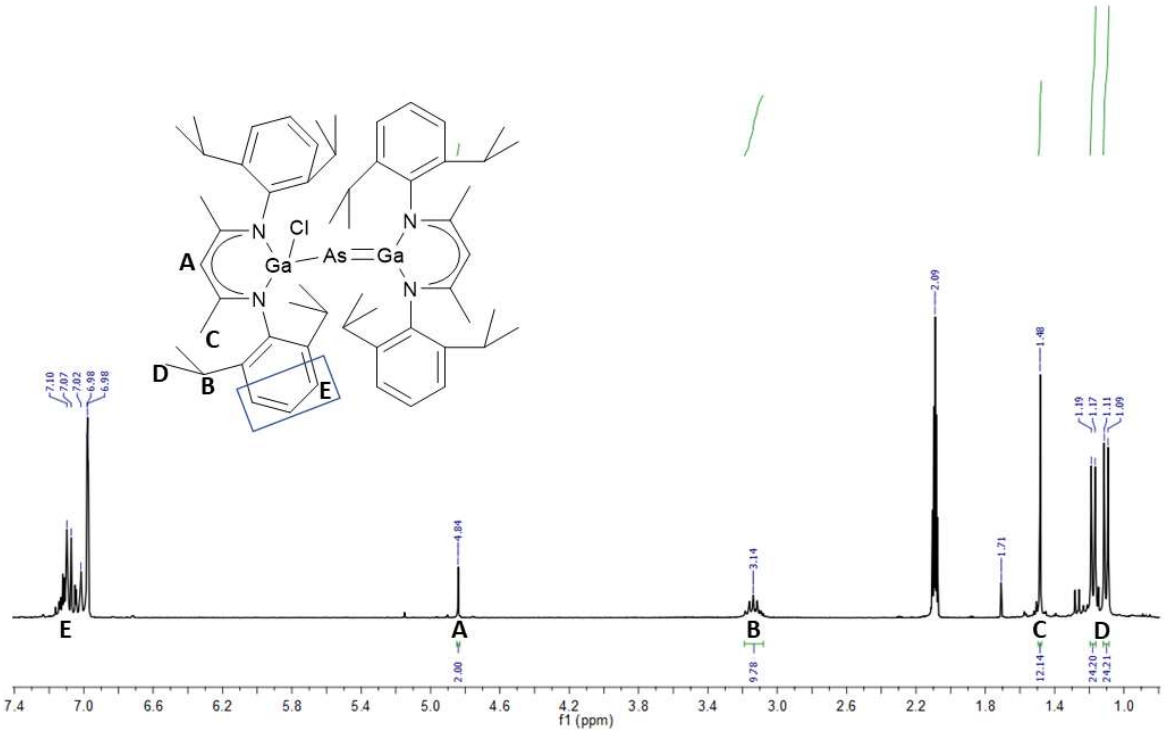


Fig. S2. ^{13}C-NMR spectrum of LGaAsGa(Cl)L (**1**) in toluene-d_8 at room temperature.

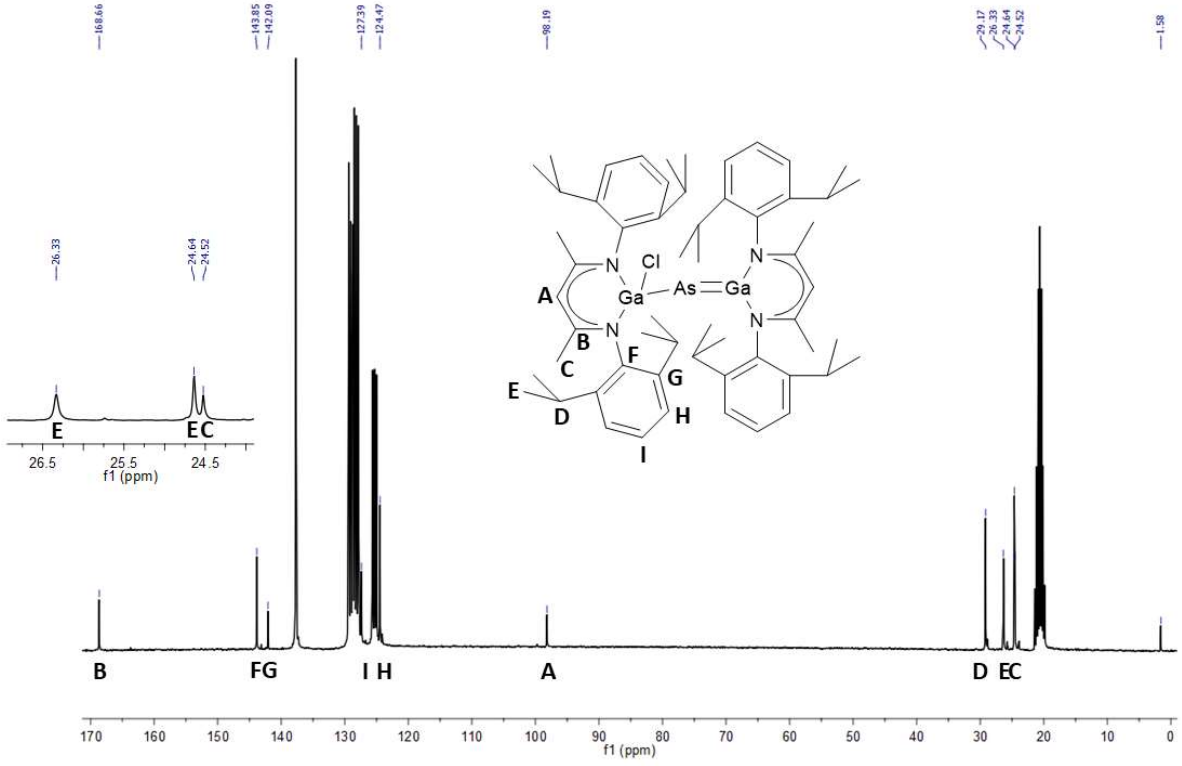


Fig. S3. IR spectrum of LGaAsGa(Cl)L (**1**) at room temperature.

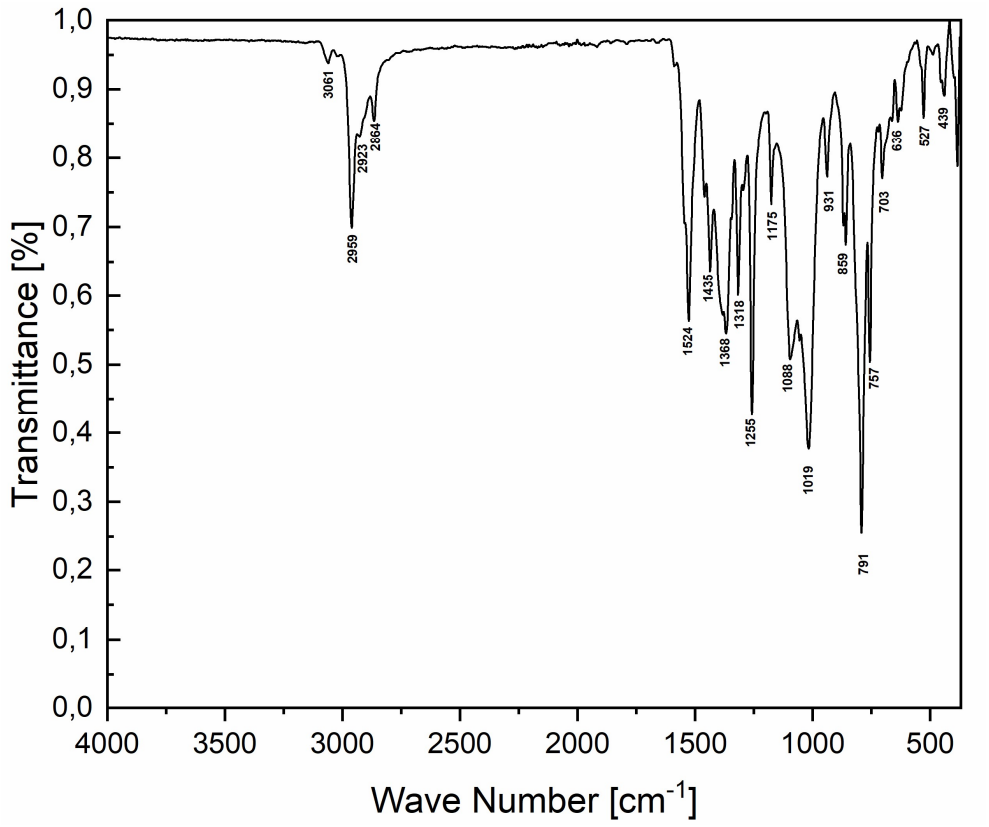


Figure S4: (Variable-temperature) ^{1}H NMR spectra of **1** in toluene-d_8.

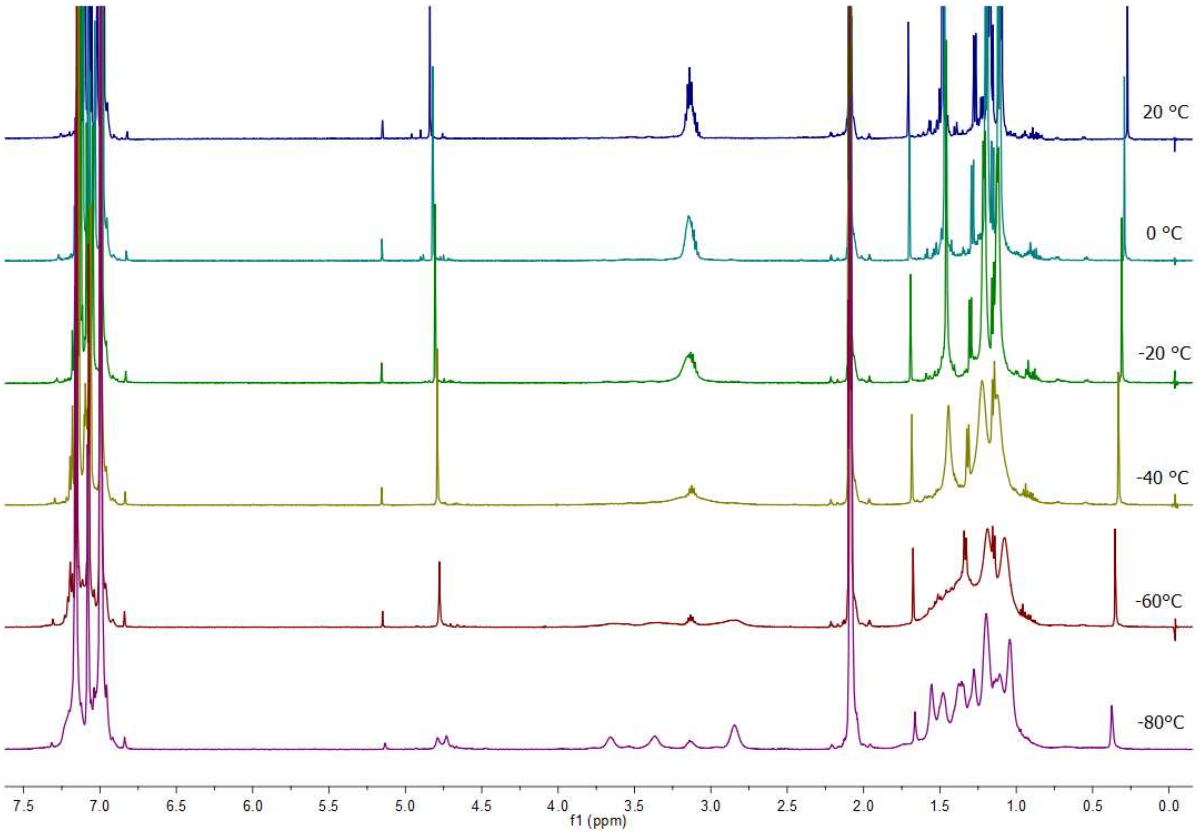


Fig. S5. ^{1}H-NMR spectrum of LGaAsGa(Br)L (**2**) in benzene-d_6 at room temperature.

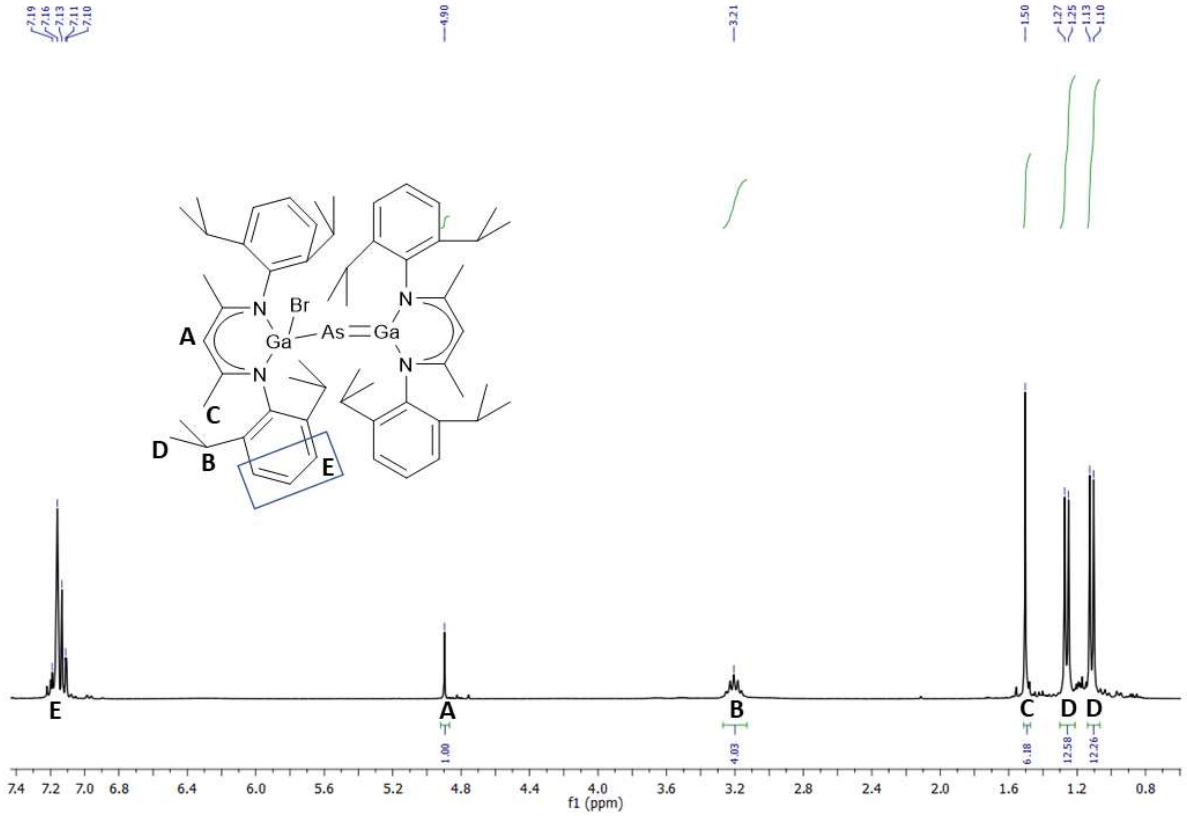


Fig. S6. ^{13}C-NMR spectrum of LGaAsGa(Br)L (**2**) in benzene-d_6 at room temperature.

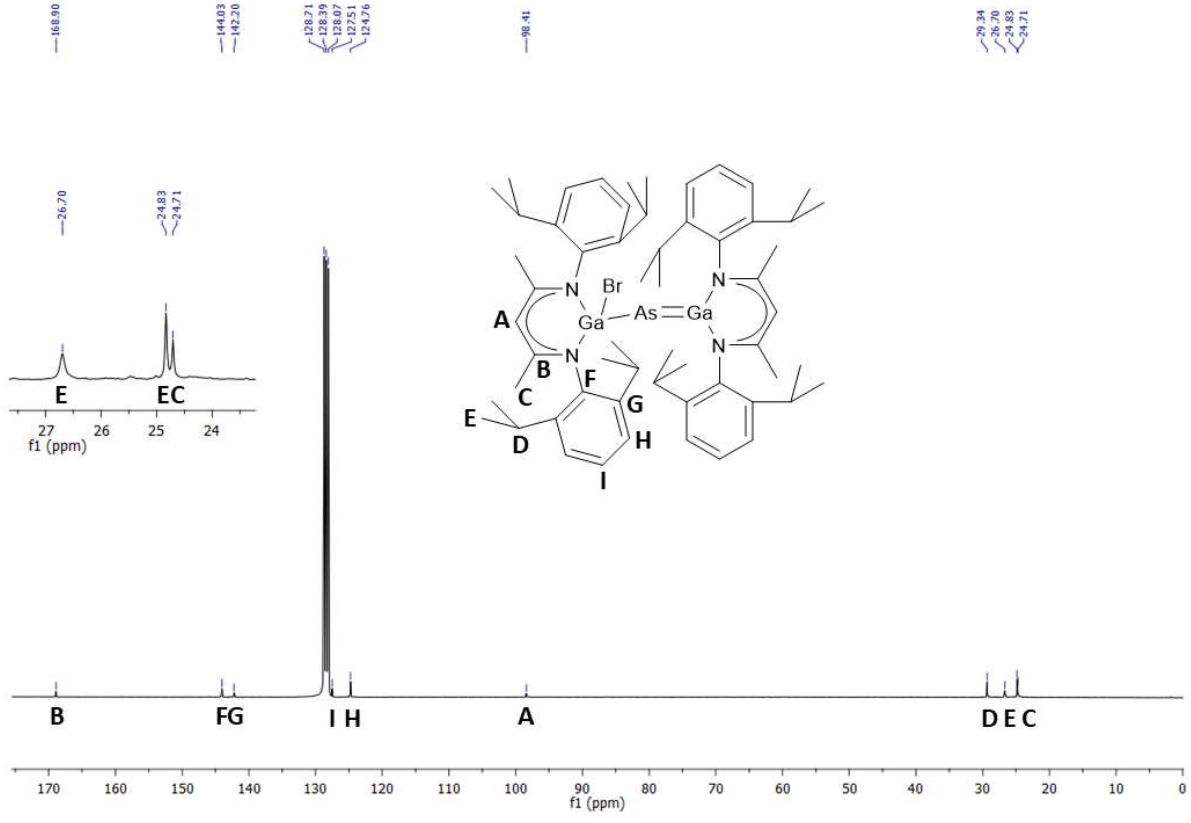


Figure S7: IR spectrum of LGaAsGa(Br)L (**2**) at room temperature.

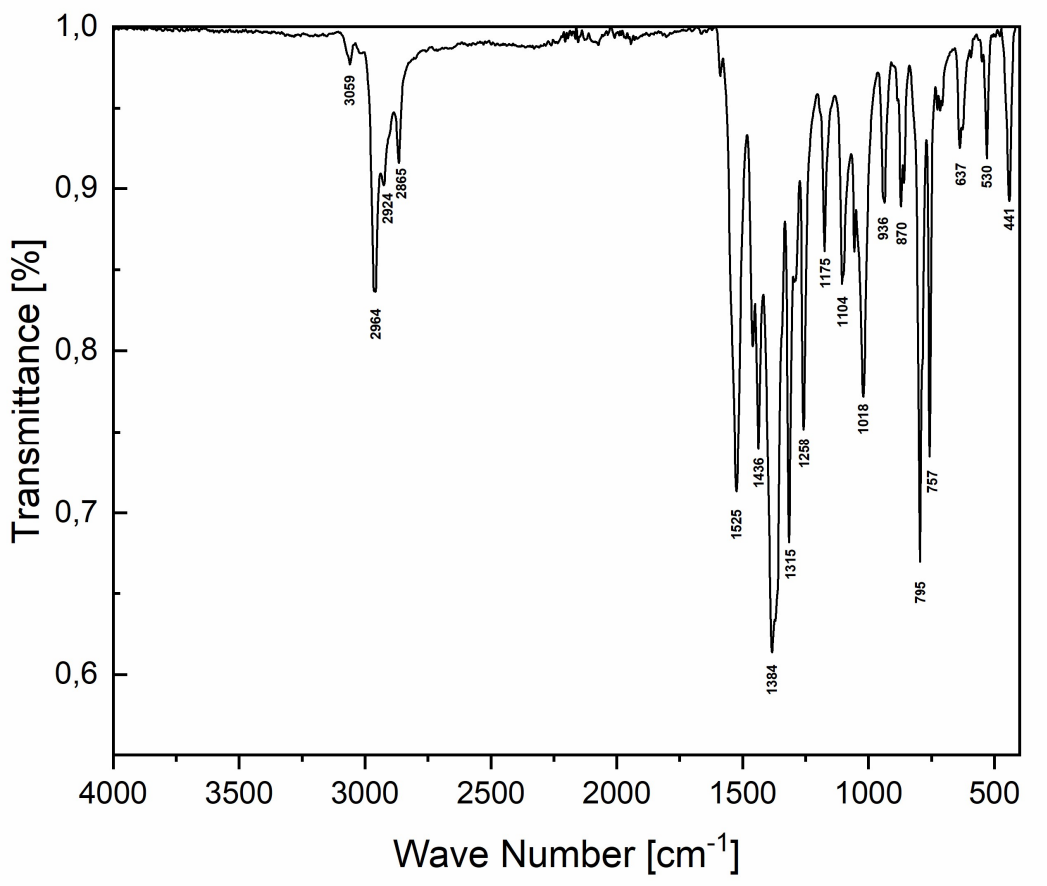


Figure S8: (Variable-temperature) ^{1}H NMR spectra of **2** in toluene-d_8.

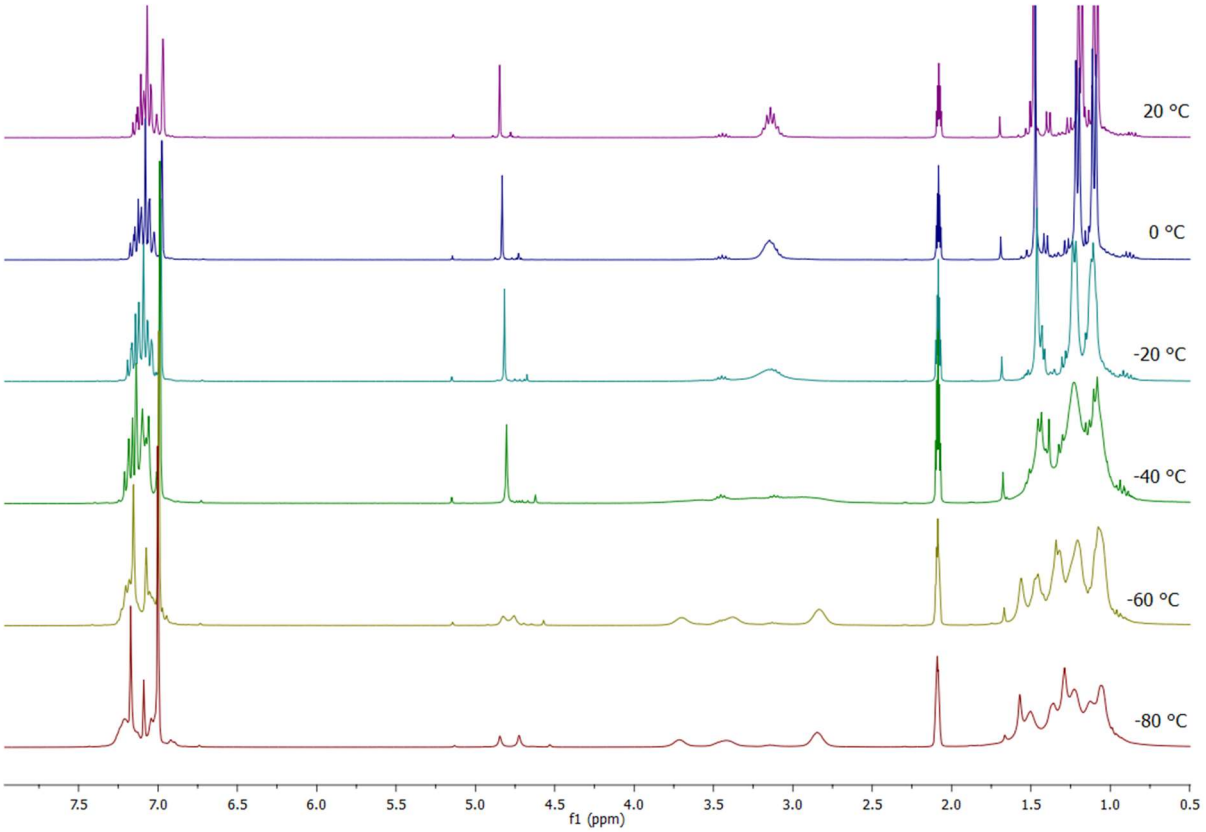
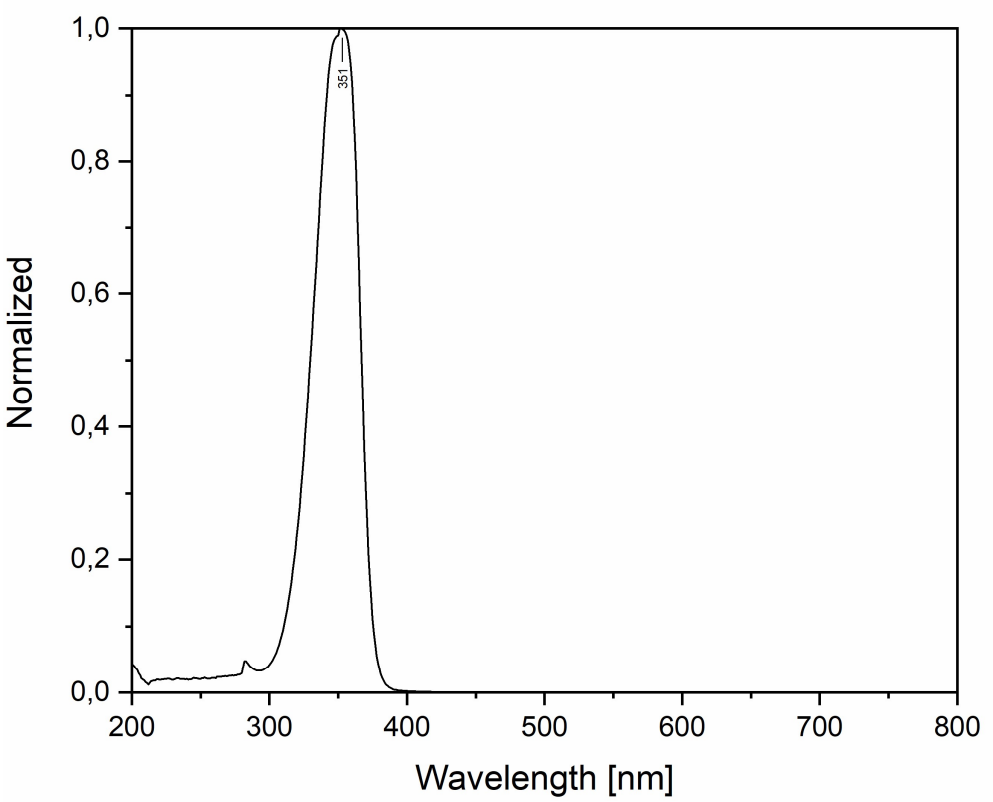


Figure S9: UV/Vis spectrum of LGaAsGa(Br)L (**2**) at room temperature in toluene-d_8.



2. Crystallographic Details

Table S1: Crystal structure data of **1** and **2**.

	1	**2**
Empirical formula	$C_{58}H_{82}AsClGa_2N_4$	$C_{58}H_{82}AsBrGa_2N_4$
Formula weight	1085.08	1129.54
Density (calculated)	1.251 g·cm^{-3}	1.306 g·cm^{-3}
F(000)	1140	2352
Temperature	100(2) K	100(2) K
Crystal size	0.280 × 0.162 × 0.112 mm	0.167 × 0.158 × 0.148 mm
Crystal colour	orangish red	orange
Crystal description	tablet	tablet
Wavelength	0.71073 Å	0.71073 Å
Crystal system	triclinic	monoclinic
Space group	*P -1*	*P 21/n*
Unit cell dimensions		
a [Å]	11.9809(3)	17.4414(16)
b [Å]	13.4857(4)	16.6936(15)
c [Å]	20.0846(5)	19.7268(19)
α [°]	80.8110(10)	90
β [°]	85.685(2)	90.684(6)
γ [°]	64.0770(10)	90
Volume	2881.07(14) Å^3	5743.2(9) Å^3
Z	2	4
Cell measurement reflections used	9698	9956
Cell measurement θ min/max	2.62°/30.39°	2.40°/29.78°
Diffractometer control software	BRUKER D8 KAPPA APEX 2 (3.0-2009)	BRUKER APEX2 (v2009.5-1)
Diffractometer measurement device	Bruker D8 KAPPA series II with APEX II area detector system	Bruker D8 KAPPA II (APEX II detector)
Diffractometer measurement method	Data collection strategy APEX 2/COSMO	Data collection strategy APEX 2/COSMO
θ range for data collection	1.696°- 30.709°	1.549°- 26.372°
Completeness to θ = 25.242°	100.0%	99.8%
Completeness to θ_{max} = 30.709°	93.5%	99.6%
Index ranges	$-16 \le h \le 17$	$-21 \le h \le 21$
	$-19 \le k \le 19$	$-20 \le k \le 20$
	$-27 \le l \le 28$	$-24 \le l \le 24$
Computing data reduction	BRUKER D8 KAPPA APEX 2 (3.0-2009)	BRUKER APEX2(v2009.5-1)
Absorption coefficient	1.589 mm^{-1}	2.244 mm^{-1}
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Computation absorption correction	BRUKER AXS SMART APEX 2 Vers. 3.0-2009	SADABS
Max./min. Transmission	0.75/0.64	0.75/0.52
R_{merg} before/after correction	0.0529/0.0375	0.1096/0.0833

Computing structure solution	BRUKER D8 KAPPA APEX 2 (3.0-2009)	BRUKER APEX2(v2009.5-1)
Computing structure refinement	SHELXL-2016/6 (Sheldrick, 2016)	SHELXL-2017/1 (Sheldrick, 2017)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Reflections collected	76106	76970
Independent reflections	16759	11704
R_{int}	0.0287	0.0881
Reflections with $I > 2\sigma(I)$	12469	7552
Restraints	100	0
Parameter	686	615
GooF	1.040	1.121
Weighting details	$w = 1/[\sigma^2(F_{obs}^2) + (0.0601P)^2 + 5.2799P]$	$w = 1/[\sigma^2(F_{obs}^2) + (0.0887P)^2 + 51.8630P]$
	where $P = (F_{obs}^2 + 2F_{calc}^2)/3$	where $P = (F_{obs}^2 + 2F_{calc}^2)/3$
R_1 [$I > 2\sigma(I)$]	0.0522	0.0787
wR_2 [$I > 2\sigma(I)$]	0.1296	0.1808
R_1 [all data]	0.0770	0.1392
wR_2 [all data]	0.1423	0.2286
Largest diff. peak and hole	2.964/-1.184	3.140/-0.888

Table S2: Bond lengths [Å] for **1**.

As(1)-Ga(2)	2.2628(5)	C(18)-C(19)	1.404(5)
As(1)-Ga(1)	2.3503(4)	C(19)-C(20)	1.395(5)
Cl(1)-Ga(1)	2.2783(9)	C(19)-C(24)	1.522(6)
As(1')-Ga(2)	2.214(3)	C(20)-C(21)	1.380(7)
As(1')-Ga(1)	2.448(4)	C(21)-C(22)	1.367(7)
Cl(1')-Ga(2)	2.473(7)	C(22)-C(23)	1.397(5)
Ga(1)-N(2)	1.977(2)	C(23)-C(27)	1.513(5)
Ga(1)-N(1)	1.983(2)	C(24)-C(25)	1.524(6)
Ga(2)-N(3)	1.922(3)	C(24)-C(26)	1.544(7)
Ga(2)-N(4)	1.957(2)	C(27)-C(29)	1.509(6)
N(1)-C(1)	1.328(4)	C(27)-C(28)	1.549(5)
N(1)-C(6)	1.446(4)	C(30)-C(31)	1.394(5)
N(2)-C(3)	1.335(4)	C(30)-C(33)	1.513(5)
N(2)-C(18)	1.448(4)	C(31)-C(32)	1.390(4)
N(3)-C(30)	1.337(4)	C(32)-C(34)	1.507(4)
N(3)-C(35)	1.444(5)	C(35)-C(36)	1.396(6)
N(3)-C(35')	1.60(3)	C(35)-C(40)	1.406(7)
N(4)-C(32)	1.333(4)	C(36)-C(37)	1.410(6)
N(4)-C(47)	1.442(4)	C(36)-C(41)	1.519(8)
C(1)-C(2)	1.400(5)	C(37)-C(38)	1.378(7)
C(1)-C(4)	1.500(5)	C(38)-C(39)	1.359(7)
C(2)-C(3)	1.388(5)	C(39)-C(40)	1.393(6)
C(3)-C(5)	1.516(5)	C(40)-C(44)	1.512(7)
C(6)-C(7)	1.403(5)	C(41)-C(42)	1.523(7)
C(6)-C(11)	1.408(5)	C(41)-C(43)	1.524(6)
C(7)-C(8)	1.403(6)	C(44)-C(45)	1.500(7)
C(7)-C(12)	1.520(7)	C(44)-C(46)	1.509(6)
C(8)-C(9)	1.384(8)	C(35')-C(36')	1.387(14)
C(9)-C(10)	1.347(8)	C(35')-C(40')	1.390(14)
C(10)-C(11)	1.402(5)	C(36')-C(37')	1.394(14)
C(11)-C(15)	1.491(6)	C(36')-C(41')	1.521(17)
C(12)-C(13)	1.509(6)	C(37')-C(38')	1.392(14)
C(12)-C(14)	1.514(7)	C(38')-C(39')	1.389(14)
C(15)-C(16)	1.521(6)	C(39')-C(40')	1.372(14)
C(15)-C(17)	1.553(5)	C(40')-C(44')	1.519(16)
C(18)-C(23)	1.401(5)	C(41')-C(43')	1.515(15)
C(41')-C(42')	1.520(15)	C(50)-C(51)	1.379(5)
C(44')-C(45')	1.509(15)	C(51)-C(52)	1.396(4)
C(44')-C(46')	1.521(14)	C(52)-C(56)	1.515(5)
C(47)-C(52)	1.406(5)	C(53)-C(55)	1.520(6)
C(47)-C(48)	1.406(4)	C(53)-C(54)	1.527(6)
C(48)-C(49)	1.399(5)	C(56)-C(58)	1.532(5)
C(48)-C(53)	1.517(5)	C(56)-C(57)	1.533(5)
C(49)-C(50)	1.380(6)		

Table S3: Bond angles [°] for **1**.

Ga(2)-As(1)-Ga(1)	111.419(19)	N(2)-C(3)-C(5)	119.3(3)	C(36)-C(35)-N(3)	116.8(4)
Ga(2)-As(1')-Ga(1)	109.58(16)	C(2)-C(3)-C(5)	116.5(3)	C(40)-C(35)-N(3)	120.5(4)
N(2)-Ga(1)-N(1)	94.04(10)	C(7)-C(6)-C(11)	121.4(3)	C(35)-C(36)-C(37)	116.8(5)
N(2)-Ga(1)-Cl(1)	101.70(8)	C(7)-C(6)-N(1)	118.5(3)	C(35)-C(36)-C(41)	122.7(4)
N(1)-Ga(1)-Cl(1)	99.55(8)	C(11)-C(6)-N(1)	120.1(3)	C(37)-C(36)-C(41)	120.4(5)
N(2)-Ga(1)-As(1)	107.88(7)	C(8)-C(7)-C(6)	117.3(4)	C(38)-C(37)-C(36)	120.5(5)
N(1)-Ga(1)-As(1)	117.33(7)	C(8)-C(7)-C(12)	121.9(4)	C(39)-C(38)-C(37)	121.7(5)
Cl(1)-Ga(1)-As(1)	129.83(3)	C(6)-C(7)-C(12)	120.6(3)	C(38)-C(39)-C(40)	120.6(5)
N(2)-Ga(1)-As(1')	126.97(15)	C(9)-C(8)-C(7)	121.5(5)	C(39)-C(40)-C(35)	117.7(5)
N(1)-Ga(1)-As(1')	102.76(13)	C(10)-C(9)-C(8)	120.0(4)	C(39)-C(40)-C(44)	121.2(5)
N(3)-Ga(2)-N(4)	95.54(11)	C(9)-C(10)-C(11)	122.0(5)	C(35)-C(40)-C(44)	121.1(4)
N(3)-Ga(2)-As(1')	129.89(18)	C(10)-C(11)-C(6)	117.7(4)	C(36)-C(41)-C(42)	112.2(4)
N(4)-Ga(2)-As(1')	121.21(12)	C(10)-C(11)-C(15)	118.5(4)	C(36)-C(41)-C(43)	111.8(6)
N(3)-Ga(2)-As(1)	150.79(8)	C(6)-C(11)-C(15)	123.8(3)	C(42)-C(41)-C(43)	111.3(5)
N(4)-Ga(2)-As(1)	110.96(7)	C(13)-C(12)-C(14)	110.7(4)	C(45)-C(44)-C(46)	110.5(5)
N(3)-Ga(2)-Cl(1')	85.1(2)	C(13)-C(12)-C(7)	113.6(4)	C(45)-C(44)-C(40)	111.9(4)
N(4)-Ga(2)-Cl(1')	97.40(17)	C(14)-C(12)-C(7)	111.2(4)	C(46)-C(44)-C(40)	115.3(4)
As(1')-Ga(2)-Cl(1')	118.6(2)	C(11)-C(15)-C(16)	111.0(3)	C(36')-C(35')-C(40')	125(2)
C(1)-N(1)-C(6)	119.2(2)	C(11)-C(15)-C(17)	111.5(4)	C(36')-C(35')-N(3)	127.5(16)
C(1)-N(1)-Ga(1)	120.6(2)	C(16)-C(15)-C(17)	108.9(4)	C(40')-C(35')-N(3)	107.1(17)
C(6)-N(1)-Ga(1)	119.84(18)	C(23)-C(18)-C(19)	121.5(3)	C(35')-C(36')-C(37')	116(2)
C(3)-N(2)-C(18)	117.1(3)	C(23)-C(18)-N(2)	120.1(3)	C(43')-C(41')-C(36')	108(3)
C(3)-N(2)-Ga(1)	119.9(2)	C(19)-C(18)-N(2)	118.3(3)	C(42')-C(41')-C(36')	114(3)
C(18)-N(2)-Ga(1)	122.86(19)	C(20)-C(19)-C(18)	118.0(4)	C(45')-C(44')-C(40')	114.0(19)
C(30)-N(3)-C(35)	117.7(3)	C(20)-C(19)-C(24)	119.7(4)	C(45')-C(44')-C(46')	111(2)
C(30)-N(3)-C(35')	115.0(10)	C(18)-C(19)-C(24)	122.3(3)	C(40')-C(44')-C(46')	114.0(17)
C(30)-N(3)-Ga(2)	123.5(2)	C(21)-C(20)-C(19)	120.8(4)	C(52)-C(47)-C(48)	122.0(3)
C(35)-N(3)-Ga(2)	118.8(2)	C(22)-C(21)-C(20)	120.4(4)	C(52)-C(47)-N(4)	119.6(3)
C(35')-N(3)-Ga(2)	116.6(9)	C(21)-C(22)-C(23)	121.3(4)	C(48)-C(47)-N(4)	118.4(3)
C(32)-N(4)-C(47)	119.5(2)	C(22)-C(23)-C(18)	117.8(4)	C(49)-C(48)-C(47)	117.7(3)
C(32)-N(4)-Ga(2)	123.7(2)	C(22)-C(23)-C(27)	119.4(3)	C(49)-C(48)-C(53)	120.2(3)
C(47)-N(4)-Ga(2)	116.78(17)	C(18)-C(23)-C(27)	122.7(3)	C(47)-C(48)-C(53)	122.1(3)
N(1)-C(1)-C(2)	123.4(3)	C(19)-C(24)-C(25)	112.5(4)	C(50)-C(49)-C(48)	121.2(3)
N(1)-C(1)-C(4)	120.6(3)	C(19)-C(24)-C(26)	111.9(4)	C(51)-C(50)-C(49)	120.0(3)
C(2)-C(1)-C(4)	116.0(3)	C(25)-C(24)-C(26)	110.4(4)	C(50)-C(51)-C(52)	121.6(4)
C(3)-C(2)-C(1)	128.1(3)	C(35')-C(36')-C(41')	122.3(19)	C(51)-C(52)-C(47)	117.5(3)
C(29)-C(27)-C(23)	109.7(3)	C(37')-C(36')-C(41')	122(2)	C(51)-C(52)-C(56)	119.6(3)
C(29)-C(27)-C(28)	110.7(4)	C(38')-C(37')-C(36')	121(2)	C(47)-C(52)-C(56)	122.9(3)
C(23)-C(27)-C(28)	112.7(4)	C(39')-C(38')-C(37')	121(2)	C(48)-C(53)-C(55)	112.6(4)
N(3)-C(30)-C(31)	124.3(3)	C(40')-C(39')-C(38')	121(2)	C(48)-C(53)-C(54)	111.9(3)
N(3)-C(30)-C(33)	119.1(3)	C(39')-C(40')-C(35')	117(2)	C(55)-C(53)-C(54)	109.4(3)
C(31)-C(30)-C(33)	116.6(3)	C(39')-C(40')-C(44')	115.9(17)	C(52)-C(56)-C(58)	111.3(3)
C(32)-C(31)-C(30)	128.0(3)	C(35')-C(40')-C(44')	127.4(18)	C(52)-C(56)-C(57)	111.7(3)
N(4)-C(32)-C(31)	123.0(3)	C(43')-C(41')-C(42')	108(3)	C(58)-C(56)-C(57)	110.5(3)
N(4)-C(32)-C(34)	119.8(3)	C(31)-C(32)-C(34)	117.1(3)		
N(2)-C(3)-C(2)	124.3(3)	C(36)-C(35)-C(40)	122.7(4)		

Table S4: Bond lengths [Å] for **2**.

Br(3)-Ga(1)	2.3986(11)	C(21)-C(22)	1.379(14)
As(1)-Ga(2)	2.2591(11)	C(22)-C(23)	1.375(13)
As(1)-Ga(1)	2.3580(11)	C(23)-C(27)	1.519(12)
Ga(1)-N(2)	1.994(6)	C(24)-C(26)	1.516(11)
Ga(1)-N(1)	2.020(6)	C(24)-C(25)	1.537(12)
Ga(2)-N(3)	1.910(6)	C(27)-C(28)	1.538(12)
Ga(2)-N(4)	1.957(6)	C(27)-C(29)	1.545(12)
N(1)-C(1)	1.321(9)	C(30)-C(31)	1.399(10)
N(1)-C(6)	1.444(10)	C(30)-C(33)	1.502(11)
N(2)-C(3)	1.349(9)	C(31)-C(32)	1.382(11)
N(2)-C(18)	1.442(10)	C(32)-C(34)	1.508(10)
N(3)-C(30)	1.377(9)	C(35)-C(40)	1.400(10)
N(3)-C(35)	1.434(9)	C(35)-C(36)	1.404(10)
N(4)-C(32)	1.345(9)	C(36)-C(37)	1.377(11)
N(4)-C(47)	1.441(10)	C(36)-C(41)	1.512(10)
C(1)-C(2)	1.402(11)	C(37)-C(38)	1.380(12)
C(1)-C(4)	1.507(10)	C(38)-C(39)	1.388(12)
C(2)-C(3)	1.385(10)	C(39)-C(40)	1.385(11)
C(3)-C(5)	1.516(11)	C(40)-C(44)	1.526(10)
C(6)-C(7)	1.393(11)	C(41)-C(42)	1.535(11)
C(6)-C(11)	1.420(11)	C(41)-C(43)	1.542(12)
C(7)-C(8)	1.407(11)	C(44)-C(45)	1.503(13)
C(7)-C(12)	1.526(11)	C(44)-C(46)	1.542(11)
C(8)-C(9)	1.393(12)	C(47)-C(52)	1.409(11)
C(9)-C(10)	1.353(13)	C(47)-C(48)	1.418(11)
C(10)-C(11)	1.400(11)	C(48)-C(49)	1.362(12)
C(11)-C(15)	1.496(12)	C(48)-C(53)	1.531(11)
C(12)-C(14)	1.533(11)	C(49)-C(50)	1.400(13)
C(12)-C(13)	1.547(11)	C(50)-C(51)	1.365(12)
C(15)-C(17)	1.536(12)	C(51)-C(52)	1.387(11)
C(15)-C(16)	1.542(11)	C(52)-C(56)	1.521(11)
C(18)-C(23)	1.402(12)	C(53)-C(55)	1.516(13)
C(18)-C(19)	1.417(12)	C(53)-C(54)	1.552(12)
C(19)-C(20)	1.380(12)	C(56)-C(57)	1.526(12)
C(19)-C(24)	1.524(12)	C(56)-C(58)	1.547(11)
C(20)-C(21)	1.380(13)		

Table S5: Bond angles [°] for **2**.

Ga(2)-As(1)-Ga(1)	113.37(4)	C(10)-C(9)-C(8)	120.1(8)	C(40)-C(35)-C(36)	121.5(7)
N(2)-Ga(1)-N(1)	94.4(2)	C(9)-C(10)-C(11)	122.5(8)	C(40)-C(35)-N(3)	120.0(6)
N(2)-Ga(1)-As(1)	105.31(18)	C(10)-C(11)-C(6)	117.2(8)	C(36)-C(35)-N(3)	118.5(6)
N(1)-Ga(1)-As(1)	120.12(17)	C(10)-C(11)-C(15)	120.7(7)	C(37)-C(36)-C(35)	118.4(7)
N(2)-Ga(1)-Br(3)	103.96(18)	C(6)-C(11)-C(15)	122.1(7)	C(37)-C(36)-C(41)	120.7(7)
N(1)-Ga(1)-Br(3)	101.29(17)	C(7)-C(12)-C(14)	110.6(7)	C(35)-C(36)-C(41)	120.9(7)
As(1)-Ga(1)-Br(3)	126.18(4)	C(7)-C(12)-C(13)	112.2(7)	C(36)-C(37)-C(38)	121.1(8)
N(3)-Ga(2)-N(4)	95.4(2)	C(14)-C(12)-C(13)	109.9(7)	C(37)-C(38)-C(39)	120.0(8)
N(3)-Ga(2)-As(1)	153.88(17)	C(11)-C(15)-C(17)	114.6(7)	C(40)-C(39)-C(38)	120.8(8)
N(4)-Ga(2)-As(1)	110.32(19)	C(11)-C(15)-C(16)	111.2(7)	C(39)-C(40)-C(35)	118.2(7)
C(1)-N(1)-C(6)	119.2(6)	C(17)-C(15)-C(16)	109.4(7)	C(39)-C(40)-C(44)	119.2(7)
C(1)-N(1)-Ga(1)	120.1(5)	C(23)-C(18)-C(19)	121.6(8)	C(35)-C(40)-C(44)	122.5(7)
C(6)-N(1)-Ga(1)	120.6(4)	C(23)-C(18)-N(2)	118.2(7)	C(36)-C(41)-C(42)	114.6(7)
C(3)-N(2)-C(18)	116.8(6)	C(19)-C(18)-N(2)	120.2(7)	C(36)-C(41)-C(43)	109.6(6)
C(3)-N(2)-Ga(1)	119.1(5)	C(20)-C(19)-C(18)	117.4(8)	C(42)-C(41)-C(43)	110.2(7)
C(18)-N(2)-Ga(1)	124.0(5)	C(20)-C(19)-C(24)	120.2(8)	C(45)-C(44)-C(40)	112.1(7)
C(30)-N(3)-C(35)	116.6(6)	C(18)-C(19)-C(24)	122.3(7)	C(45)-C(44)-C(46)	111.1(7)
C(30)-N(3)-Ga(2)	124.6(5)	C(19)-C(20)-C(21)	121.6(9)	C(40)-C(44)-C(46)	110.4(7)
C(35)-N(3)-Ga(2)	118.8(4)	C(22)-C(21)-C(20)	119.5(9)	C(52)-C(47)-C(48)	121.7(7)
C(32)-N(4)-C(47)	120.8(6)	C(23)-C(22)-C(21)	122.0(9)	C(52)-C(47)-N(4)	119.3(7)
C(32)-N(4)-Ga(2)	124.3(5)	C(22)-C(23)-C(18)	117.6(8)	C(48)-C(47)-N(4)	118.8(7)
C(47)-N(4)-Ga(2)	114.8(4)	C(22)-C(23)-C(27)	120.9(8)	C(49)-C(48)-C(47)	117.4(8)
N(1)-C(1)-C(2)	124.0(6)	C(18)-C(23)-C(27)	121.4(8)	C(49)-C(48)-C(53)	121.5(8)
N(1)-C(1)-C(4)	120.9(7)	C(26)-C(24)-C(19)	108.8(7)	C(47)-C(48)-C(53)	121.1(7)
C(2)-C(1)-C(4)	115.1(6)	C(26)-C(24)-C(25)	109.8(7)	C(48)-C(49)-C(50)	121.9(8)
C(3)-C(2)-C(1)	129.3(7)	C(19)-C(24)-C(25)	114.1(7)	C(51)-C(50)-C(49)	119.8(8)
N(2)-C(3)-C(2)	123.9(7)	C(23)-C(27)-C(28)	110.8(7)	C(50)-C(51)-C(52)	121.4(8)
N(2)-C(3)-C(5)	118.4(7)	C(23)-C(27)-C(29)	111.7(7)	C(51)-C(52)-C(47)	117.7(7)
C(2)-C(3)-C(5)	117.6(6)	C(28)-C(27)-C(29)	110.5(7)	C(51)-C(52)-C(56)	119.2(7)
C(7)-C(6)-C(11)	121.2(7)	N(3)-C(30)-C(31)	122.6(7)	C(47)-C(52)-C(56)	123.1(7)
C(7)-C(6)-N(1)	120.4(7)	N(3)-C(30)-C(33)	118.7(7)	C(55)-C(53)-C(48)	112.5(8)
C(11)-C(6)-N(1)	118.4(7)	C(31)-C(30)-C(33)	118.7(6)	C(55)-C(53)-C(54)	108.5(8)
C(6)-C(7)-C(8)	118.8(8)	C(32)-C(31)-C(30)	128.6(7)	C(48)-C(53)-C(54)	113.2(7)
C(6)-C(7)-C(12)	123.0(7)	N(4)-C(32)-C(31)	123.4(7)	C(52)-C(56)-C(57)	112.3(7)
C(8)-C(7)-C(12)	118.2(8)	N(4)-C(32)-C(34)	119.3(7)	C(52)-C(56)-C(58)	110.7(7)
C(9)-C(8)-C(7)	120.2(9)	C(31)-C(32)-C(34)	117.4(6)	C(57)-C(56)-C(58)	110.2(7)

3. Quantum chemical calculations

Computational methods. All quantum chemical calculations were employed with the ORCA quantum chemistry package (version 4.0).[1] Ground-state geometry optimizations were calculated with the PBE0 functional[2], the def2-SVP basis set on all C and H atoms and the def2-TZVP basis set on As, Ga, Cl and N.[3] The atom-pairwise dispersion correction with Becke-Johnson damping scheme (D3BJ)[4] was used to account for dispersion interactions. The RIJCOSX approximation was utilized to accelerate the calculations in conjunction with the appropriate auxiliary basis sets (def2/J).[5] Natural bond orbital analysis was performed using the NBO 6.0 program.[6] Vibrational frequency calculations were conducted to determine whether the optimized geometries are local minima on the potential energy surface.

Table S6. Cartesian coordinates x,y,z [Å] for the optimized geometry of LGaAsGa(Cl)L (**1**).

As	7.76956152802252	4.14403589256378	4.71206426349831
Cl	7.13242285937694	1.97799328690088	8.14356912286602
Ga	8.21985903811540	2.39601504086360	6.24112184522823
Ga	5.76029715117123	5.09443788044355	5.11328955094542
N	10.13152977605119	2.40045293992808	6.84302280617115
N	8.36700145453710	0.61132901414987	5.34025593354061
N	4.66403834807384	6.04182803625429	6.39565173481765
N	4.77000624512488	5.73776688027829	3.54689308067439
C	10.77939298098008	1.26885412169341	7.06567249899594
C	10.31209609933667	0.01423110488537	6.64929642078951
C	9.27314598627922	-0.27443198378767	5.75487857662932
C	12.10353302552422	1.26911340191151	7.78039191150747
H	12.57959286650453	2.25553809374207	7.78273136772665
C	9.24127024973857	-1.68249122821181	5.22355650706974
H	9.23924668285414	-1.69250009958281	4.12367262291189
H	8.32623498799346	-2.19975724178444	5.54389959551597
H	10.10555168006016	-2.25200940438018	5.58484333171242
C	10.76322374915348	3.65508362729947	7.09315372725493
C	11.34202084216256	4.33298383538135	5.99770929586557
C	11.90026334885295	5.59326561351932	6.21782432268574
H	12.34175555499545	6.13717400812744	5.38058789843696
C	11.92462255605874	6.15479473281500	7.49059039957641
H	12.37009444367086	7.13972763216169	7.64751136915970
C	11.39776366202039	5.45113803429807	8.56542273087355
H	11.44949258145044	5.88520800236031	9.56727667032874
C	10.80392249010333	4.19593187593370	8.39301318570249
C	11.47201406903626	3.65085848410506	4.64983363219599
H	10.64727655423260	2.92641948222376	4.56829315653571
C	11.36464326058175	4.58894900829426	3.45657517804446
H	11.42074439010684	4.00741988611771	2.52272295967577
H	12.18105362928860	5.32834509914268	3.42506561340488
H	10.40665263280709	5.12790586832897	3.46855337923017

C	12.78217286740344	2.85868608269748	4.59481487888406
H	12.88774916824479	2.34972725450695	3.62368078752746
H	12.83483885528902	2.08881168994648	5.37738230852305
H	13.64490584248162	3.53135010067831	4.72768046138026
C	10.25817750466304	3.45575311552468	9.59914573944605
H	9.92128458633637	2.46588382789187	9.25977848092391
C	9.03543562183803	4.15981964604010	10.17619441771543
H	8.25371206354265	4.28271078866479	9.41799424239385
H	9.30113123044603	5.15494706417075	10.56967788936027
H	8.60468915307899	3.57263099889828	11.00212085729268
C	11.32456282037282	3.25969314656750	10.67863340877830
H	12.22872572549166	2.77460808264841	10.28412729977694
H	10.93032123623055	2.63581452025108	11.49576243370032
H	11.63441251360367	4.21992186972225	11.12101871167568
C	7.47745789374965	0.19220919582064	4.29600829184161
C	7.77342560721624	0.53346449745049	2.95862808721860
C	6.99259997591054	-0.01863769566710	1.93780604887287
H	7.23060410419287	0.22263625690781	0.89999207382090
C	5.93632408122395	-0.87584793921686	2.21762477968831
H	5.35068651782185	-1.31653698517412	1.40764282832874
C	5.61527498854216	-1.15185895163273	3.54016308968218
H	4.76206576053897	-1.79633409615047	3.76432746414855
C	6.36276361150180	-0.62258733332806	4.59608475651132
C	8.93464472907477	1.43133125050234	2.58205431719517
H	9.23084936560114	1.96930397806227	3.49279556212462
C	8.52120266469875	2.48185919850292	1.55708592725999
H	8.21867366650348	2.03404739816245	0.59789508641396
H	9.35652372596984	3.16777306736824	1.34941707905845
H	7.68692988548430	3.08350209041571	1.94048577977115
C	10.14339775716067	0.62490182215212	2.10753337101856
H	9.88394437183128	-0.01028835171291	1.24519298592556
H	10.53511491961889	-0.02851768621317	2.90075035931726
C	5.90754405575901	-0.89433580778817	6.01707231018448
H	6.71224002901424	-0.59518926430765	6.70449032800786
C	5.57127561918618	-2.36045387572776	6.28311972336097
H	4.72592254172885	-2.70722280645133	5.66907299414132
H	5.27906021392140	-2.49855675334849	7.33589231974110
H	6.42354336573933	-3.02664963414101	6.07744495273558
C	4.70691931859359	-0.00043201934659	6.31546870201705
H	4.95256425827651	1.05014646661893	6.12089181101248
H	4.39658447294562	-0.08511410885240	7.36812636894908
H	3.85156308167302	-0.27117325958575	5.67588889110173
C	3.67772385595046	6.88315271946271	6.08677696367565
C	3.70853379460153	6.53495396269013	3.59351149943136
C	5.05490914628015	5.87929097290769	7.76239257935809
C	6.19780475666358	6.55361184669385	8.22959764840947
C	6.56062039957804	6.36475862029105	9.56677922331721
H	7.44233784973853	6.87551895863512	9.95817249985725
C	5.84039474572021	5.51135225206529	10.39264799942637
H	6.16616470044722	5.34414832081881	11.42204141706237
C	4.72861988891022	4.83456366448535	9.90112469174300
H	4.18962864885974	4.14495366384764	10.55331352794146
C	4.30880775104067	5.00883698811488	8.58199445348911

C	7.02130759993051	7.46101660937074	7.33405030560351
H	6.73416591634337	7.24511096872034	6.29180903975536
C	8.51514761271009	7.18133671288893	7.44001491021648
H	8.73866017017604	6.12223387376694	7.24792399226439
H	8.91762338334039	7.45559081870609	8.42753506596487
H	9.06520227617853	7.76979765087405	6.69155157227215
C	6.71146558721612	8.93674750009508	7.58329714681765
H	7.32516301198121	9.57387482217030	6.92969692471549
H	6.93208805908228	9.21712461652386	8.62600963856131
H	5.65658389112813	9.17791964434041	7.38274546430162
C	3.14097391450211	4.22635435362609	8.01137334441497
H	2.63402445091666	4.86029734654239	7.26696536603789
C	3.66397546243832	2.99239685256185	7.28204185785038
H	4.39626692521788	3.24951017354388	6.49910037690277
H	2.84639651202519	2.42732925973110	6.80806419255273
H	4.19240598124146	2.33101376062066	7.98181229183824
C	2.09800940442495	3.82281151765907	9.04694112066531
H	1.24882330925024	3.32950616348538	8.54939873885522
H	1.71298991160316	4.68936860336101	9.60586549814929
H	2.50320020700656	3.10300281502215	9.77496379826265
C	5.18676452629002	5.21031594520439	2.28390936486782
C	6.25110943639086	5.83584510680412	1.60533655618477
C	6.61934594401501	5.32231348681526	0.35912392298414
H	7.43806222187183	5.78877216940131	-0.19016246776443
C	4.97562946717040	3.57145242849547	0.53815825047730
C	4.55179565959091	4.06034137603360	1.77670158236627
C	7.00976263029707	6.99617765450938	2.22537893453448
H	6.96959406271520	6.84359640142960	3.31721274655201
C	6.38586485893323	8.36099366733214	1.93224071796319
H	6.37077277238548	8.55944619689571	0.84868657835997
H	6.97411082041718	9.15775948690814	2.41259506648807
H	5.35700533536710	8.44159383359261	2.31024841060297
C	8.48637165372801	6.99643929793806	1.84564448318650
H	8.64485483741873	7.29969114623374	0.79771893679971
H	8.93157672401420	6.00327672634182	1.99720238480290
H	9.03662704500053	7.71088498531873	2.47460231578768
C	3.49410978709067	3.32349457588760	2.57896490355749
H	3.04974441252491	4.04008131315234	3.28760344736711
C	2.35425376766821	2.77954150082331	1.72343202318942
H	1.87792250800956	3.56938790322892	1.12157916889707
H	1.58294296694688	2.32683574951109	2.36495909372751
H	2.69736983490417	1.99360851780935	1.03341594924174
C	4.13868009213718	2.20920414929771	3.40340599517761
H	4.58983546667269	1.44625922106223	2.75342360496571
H	3.39638118585000	1.71303517030642	4.04793686621097
H	4.95413012452659	2.58942394077669	4.03827744391236
H	10.94122153655249	-0.82933891161107	6.92967848863507
C	3.21805158867784	7.09584836807763	4.78237843342157
C	3.00848583714719	7.65218443177700	7.18845069681162
H	3.75349346964018	8.19442062345636	7.78838100209591
H	2.48634354553542	6.97870115457493	7.88447856022124
H	2.28530917793197	8.36711513528007	6.77826252807394
C	2.97055462081045	6.84821328754206	2.32374851574689

H	3.65909904193643	7.16259121781058	1.52791726877424
H	2.21817017443715	7.62833201074202	2.48854338882552
H	2.46214358568291	5.94518859693741	1.95158956518478
H	2.37297129797162	7.77362360508816	4.67850925542040
H	10.95583599635475	1.30003839968208	1.79576144690875
H	11.94422645421894	0.96532254488405	8.82713381051716
H	12.78532287502238	0.53920673574896	7.32560919867978
C	5.98755154149622	4.20467494864691	-0.17477130734474
H	6.31570392133973	3.80056571096985	-1.13540373437015
H	4.51245357203679	2.67173638815540	0.12940055584467

Figure S10. Calculated structure, HOMO and LUMO of LGaAsGa(Cl)L (**1**).

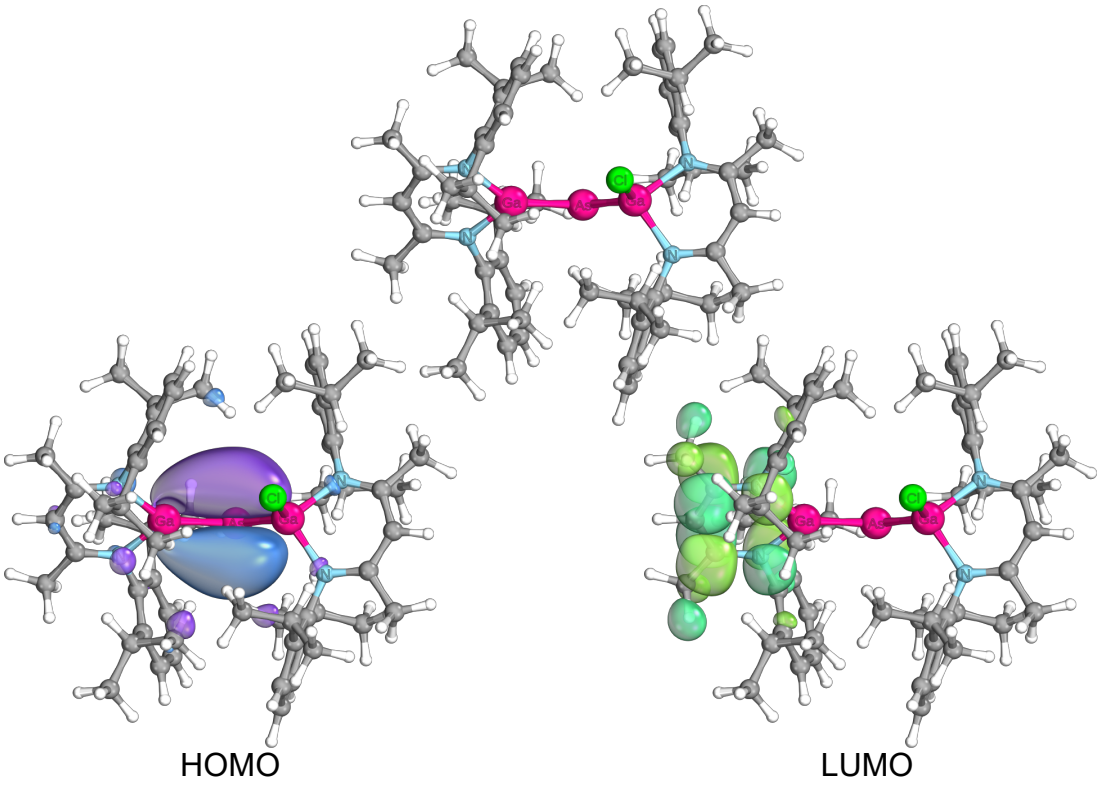


Table S7. NPA atomic charges (q, *e*), occupation numbers (ON, |*e*|) of the bonds according to NBO, Mayer bond orders (MBO), bond polarization (P) and bond orbital character (OC) for the central Ga(2)-As-Ga(1)-Cl motive in LGaAsGa(Cl)L (**1**).

X-Y	q(X,Y)	ON	MBO	P(X,Y)	OC(X-Y)
As-Ga(1)	-1.05, 1.38	1.91	1.09	70%, 30%	20% s, 79% p – 40% s, 59% p
As-Ga(2)	-1.05, 1.34	1.89 (σ)	1.70	64%, 36% (σ)	14% s, 85% p – 54% s, 46% p (σ)
		1.88 (π)		86%, 14% (π)	99% p – 99% p (π)
Ga(1)-Cl	1.38, -0.55	1.97	0.87	85%, 15%	36% s, 64% p – 22% s, 77% p
As (lone pair)	-1.05	1.83			65% s, 35% p

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