Synthesis and Characterisation of Anionic and Neutral Gallium(I) N-Heterocyclic Carbene Analogues

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SUPPLEMENTARY INFORMATION

Table S1. Summary of crystallographic data for **6a-d**, **7**, **8**, **10**, **11**, DAB* **1S**, Ar*NH_2 **2S**, a cyclic isomer of DAB*H_2 **3S** and [NaI(18-crown-6)] **4S**

	6a·(toluene)	**6b**·(benzene)$_3$[a]	**6c**·(THF)$_2$	**6d**·(OEt$_2$)[a]	**7**·(benzene)$_2$	**8**·(toluene)$_2$	**10**
empirical formula	$C_{88}H_{88}GaN_4Na$	$C_{92}H_{90}GaN_4Na$	$C_{92}H_{104}GaN_2NaO_6$	$C_{82}H_{92}GaN_4NaO_6$	$C_{86}H_{83}BrGaN_4Zn$	$C_{86}H_{87}CdGaIN_4$	$C_{29}H_{41}GaN_2$
formula weight	1294.33	1344.39	1426.48	1258.31	1387.56	1509.64	487.36
crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	*P*-1	*Pna*2$_1$	*C*2/*c*	*P*2$_1$	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*-1
T (K)	173(2)	173(2)	173(2)	173(2)	123(2)	123(2)	173(2)
a (Å)	12.329(3)	22.532(5)	36.638(7)	12.676(3)	13.5440(5)	13.573(3)	8.0968(7)
b (Å)	12.390(3)	14.975(3)	11.566(2)	20.958(4)	23.6390(11)	23.932(3)	13.8541(14)
c (Å)	24.625(5)	22.623(5)	25.970(5)	14.496(3)	22.6239(10)	23.130(16)	14.1577(16)
α (deg.)	88.71(3)	90	90	90	90	90	62.271(11)
β (deg)	83.10(3)	90	134.67(3)	111.37(3)	101.617(4)	101.35(5)	74.193(9)
γ (deg.)	74.15(3)	90	90	90	90	90	89.796(7)
vol (Å^3)	3592.1(13)	7633(3)	7827(3)	3586.4(12)	7095.0(5)	7366(6)	1338.4(2)
Z	2	4	4	2	4	4	2
ρ (calcd) (g.cm^{-3})	1.197	1.170	1.211	1.165	1.299	1.361	1.209
μ (mm^{-1})	0.438	0.414	0.413	0.438	1.329	1.122	1.046
F(000)	1372	2848	3040	1340	2892	3100	520
reflections collected	22354	23253	14618	12281	25577	29475	14255

unique reflections	13209	13301	7663	12281	12675	12935	7651
R_{int}	0.0288	0.0421	0.0333	0.0000	0.0675	0.0440	0.1012
R1 indices [$I>2\sigma(I)$]	0.0500	0.0862	0.0506	0.0529	0.0630	0.0624	0.0517
*w*R2 indices (all data)	0.1324	0.2483	0.1470	0.0908	0.1617	0.1516	0.1218
Largest peak and hole (e.A^{-3})	0.83, -0.40	1.74 (near Ga(1)), -0.76	0.79, -0.44	0.40, -0.22	1.21, -0.84	2.02 (near I(1)), -1.25	1.04, -0.77
CCDC No.	866218	866219	866220	866221	866222	866223	866224

[a] the absolute structure parameters for the racemically twinned crystal structures of **6b** and **6d** were 0.488(18) and 0.438(8) respectively.

	11·(hexane)	**1S**	**2S**	**3S**·(OEt_2)	**4S**
empirical formula	$C_{93}H_{137}Ga_5I_4N_6$	$C_{68}H_{56}N_2$	$C_{33}H_{29}N$	$C_{72}H_{68}N_2O$	$C_{12}H_{24}INaO_6$
formula weight	2195.29	901.15	439.57	977.28	414.20
crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	*P*-1	*P*-1	$P2_1/n$	*P*-1	$P2_1/n$
T (K)	123(2)	173(2)	123(2)	173(2)	173(2)
a (Å)	14.8206(4)	9.1640(18)	9.5232(15)	13.639(3)	13.5047(3)
b (Å)	17.7618(5)	10.472(2)	11.2997(15)	14.388(3)	8.5025(2)
c (Å)	18.7240(6)	13.747(3)	22.111(3)	14.442(3)	15.2667(5)
α (deg.)	84.734(3)	99.63(3)	90	101.09(3)	90
β (deg)	89.572(2)	103.84(3)	93.139(6)	92.85(3)	106.372(3)
γ (deg.)	85.108(2)	99.14(3)	90	96.22(3)	90

vol ($Å^3$)	4890.2(2)	1235.3(4)	2375.8(6)	2757.7(10)	1681.79(8)
Z	2	1	4	2	4
ρ (calcd) ($g.cm^{-3}$)	1.491	1.211	1.229	1.177	1.636
μ (mm^{-1})	2.666	0.069	0.070	0.068	1.949
F(000)	2208	478	936	1044	832
reflections collected	30630	8046	16304	20230	6907
unique reflections	17610	4316	4181	10803	2946
R_{int}	0.0466	0.0768	0.1468	0.0336	0.0209
R1 indices [$I>2\sigma(I)$][a]	0.0553	0.0597	0.0657	0.0505	0.0343
*w*R2 indices (all data)[b]	0.1476	0.1550	0.1529	0.1423	0.0917
Largest peak and hole ($e.A^{-3}$)	2.00 (near I(2)), -1.22	0.18, -0.16	0.28, -0.31	0.32, -0.26	1.97 (near I(1)), -1.32
CCDC No.	866225	866214	866215	866216	866217

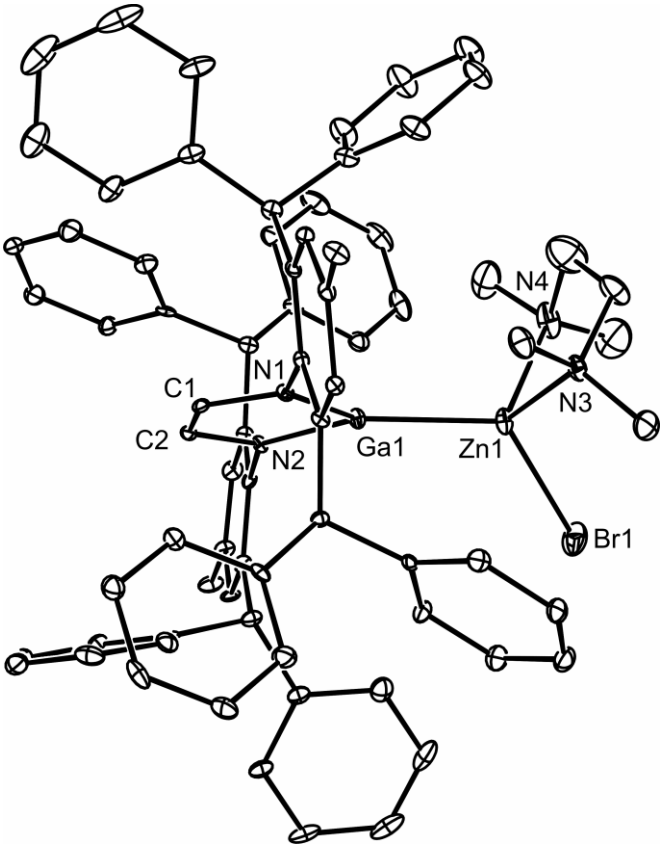

Figure S1. Molecular structure of **7** (25% displacement ellipsoids are shown; hydrogens omitted). See main text for geometrical parameters.

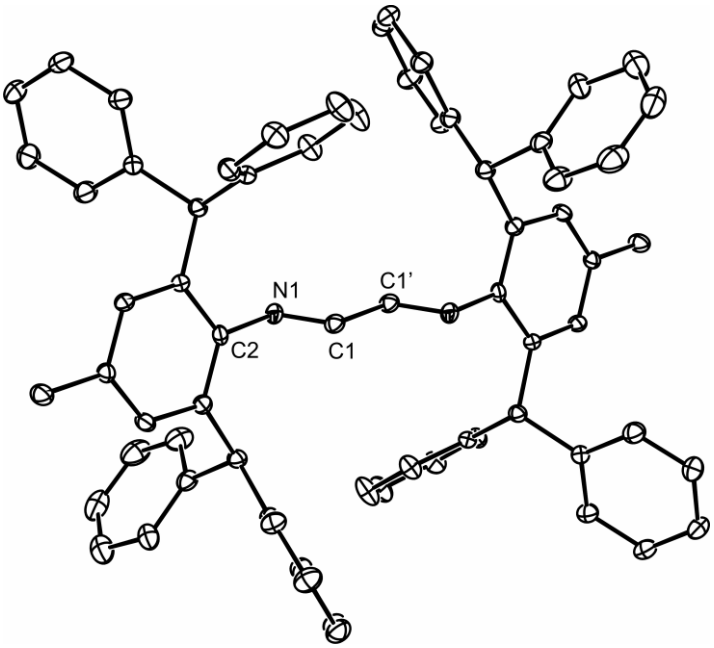

Figure S2. Molecular structure of **1S** (25% displacement ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): N(1)-C(1) 1.258(3), N(1)-C(2) 1.432(3), C(1)-C(1)' 1.464(5), C(1)-N(1)-C(2) 119.1(2), N(1)-C(1)-C(1)' 121.3(3). Symmetry operation: ' -x, -y+1, -z.

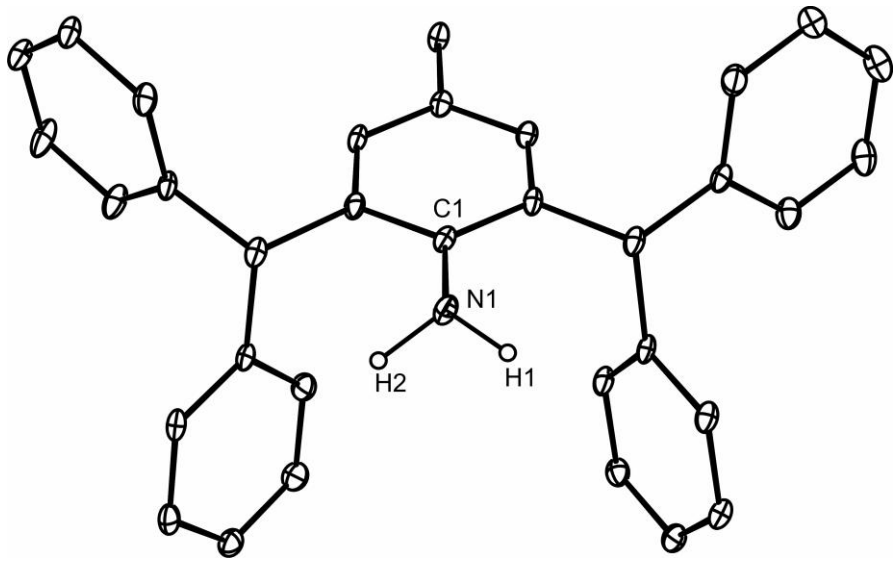

Figure S3. Molecular structure of **2S** (25% displacement ellipsoids are shown; non-amino hydrogens omitted).

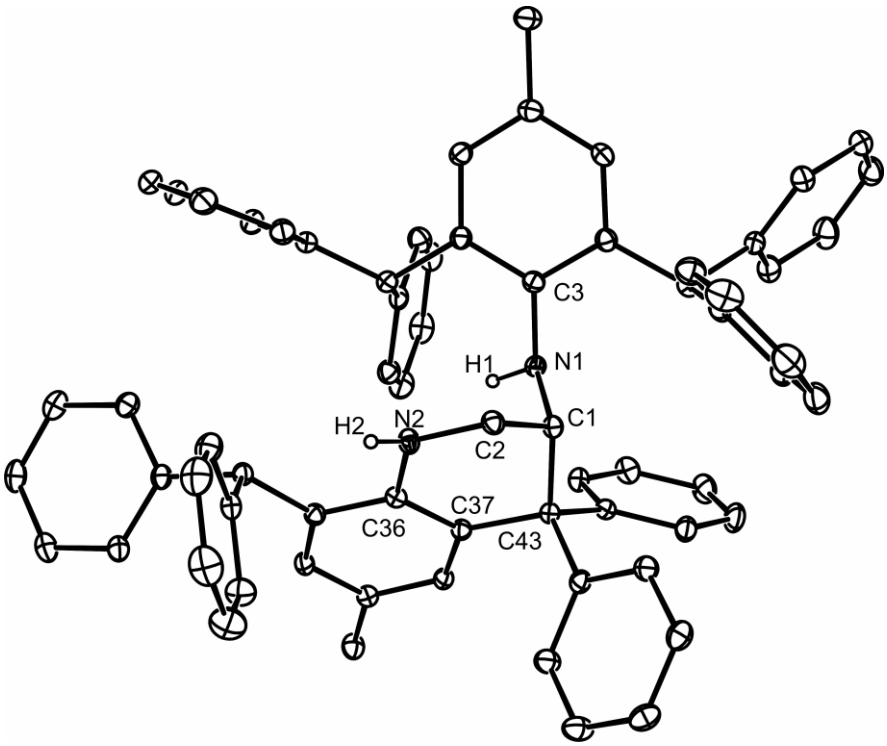

Figure S4. Molecular structure of **3S** (25% displacement ellipsoids are shown; non-amino hydrogens omitted). Selected bond lengths (Å) and angles (°): N(1)-C(1) 1.468(2), C(1)-C(2) 1.526(2), C(1)-C(43) 1.558(2), N(2)-C(36) 1.395(2), N(2)-C(2) 1.448(2), C(36)-C(37) 1.408(2), C(37)-C(43) 1.536(2), N(1)-C(1)-C(2) 113.54(13), N(2)-C(2)-C(1) 110.04(14), C(36)-N(2)-C(2) 121.40(14), N(2)-C(36)-C(37) 121.35(15), C(36)-C(37)-C(43) 120.09(14), C(37)-C(43)-C(1) 107.48(13).

Selected data for **3S**: M.p. 216-218 °C; ^{1}H NMR (C_6D_6, 400 MHz, 296 K): δ = 1.87 (s, 3H, ArC*H*$_3$), 1.98 (s, 3H, ArC*H*$_3$), 2.49 (d, $^{2}J_{HH}$ = 12Hz, 1H, C(2)*H*), 2.85 (d, $^{2}J_{HH}$= 12Hz, 1H, C(2)*H*), 3.58 (br. s, 1H, N(2)*H*), 3.96 (br. d, 1H, N(1)*H*), 4.25 (br. d of t, 1H, C(1)*H*), 5.50 (s, 1H, C*H*Ph$_2$), 6.61 (s, 2H, C*H*Ph$_2$), 7.18-6.80 (m, 44H, Ar*H*); IR (Nujol) ν/cm^{-1}: 3127 (bw, NH), 1596(w), 1261(w), 1154(m), 1077 (s), 1028 (m), 850(m), 722(m); MS EI: *m*/*z* (%): 903.2 (MH$^+$, 100), 440.2 (Ar*NH$_3^+$, 30); acc. mass. calc for $C_{68}H_{58}N_2$: 902.4600, found: 902.4673.

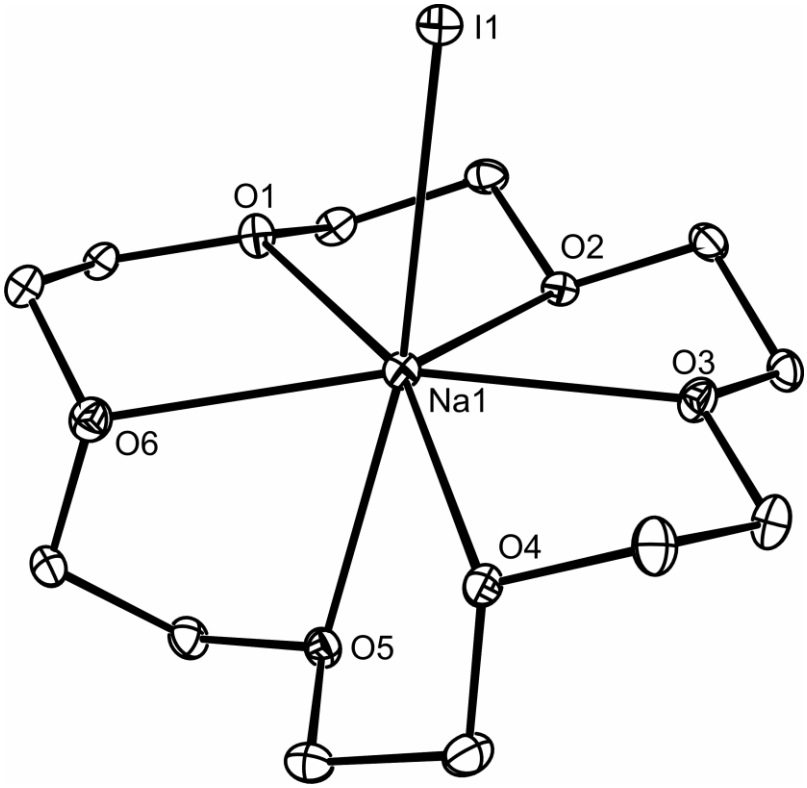

Figure S5. Molecular structure of **4S** (25% displacement ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å): I(1)-Na(1) 3.1381(14), Na(1)-O(3) 2.476(3), Na(1)-O(5) 2.496(3), Na(1)-O(1) 2.536(3), Na(1)-O(4) 2.575(3), Na(1)-O(2) 2.585(3), Na(1)-O(6) 2.631(3).

Table S2. Cartesian coordinates for the calculated structure of **11** (total energy: -13385.76182 Hartree)

I	-0.76700	3.73900	3.61400
Ga	-0.14300	3.76100	1.00700
Ga	-0.12600	1.38900	0.10900
N	-1.44600	5.10400	0.26400
N	1.45000	5.01900	0.93500
I	-0.05500	1.61800	-2.72200
I	2.47200	0.20300	0.60200
Ga	0.00500	-1.13200	0.11400
Ga	-0.04000	-1.27600	-2.45900
Ga	-0.20300	-3.12700	1.65100
N	1.30900	-1.69900	-3.93700
N	-1.65700	-1.64800	-3.61000
I	-0.87700	-5.21200	0.09900
N	1.25100	-3.85200	2.81600
N	-1.61700	-3.15700	3.12300
C	-1.33200	6.35200	0.78900
C	1.21900	6.31400	1.22500
C	0.88800	-4.88900	3.62800
C	0.96700	-1.45800	-5.21700
C	-1.59500	-1.24400	-4.90400
C	-1.52600	-4.09300	4.07900
C	-0.11400	6.81000	1.34100
C	-0.43400	-5.02000	4.09000
C	-0.35600	-1.04900	-5.55700
C	-2.33000	4.73700	-0.80100
C	-3.32700	3.73900	-0.58700
C	-2.18300	5.31300	-2.09400
C	-4.16900	3.37400	-1.65000
C	-3.53100	3.10900	0.76900
C	-3.05200	4.90300	-3.12700
C	-1.15100	6.37200	-2.41700
H	-4.95600	2.62300	-1.46100
C	-4.05800	3.94400	-2.93400
H	-4.52600	2.62100	0.82900
H	-3.44400	3.84500	1.59700
H	-2.77500	2.31800	0.98600
H	-2.93000	5.36100	-4.12500
H	-0.61800	6.12300	-3.36100
H	-0.39600	6.49200	-1.61700
H	-1.63000	7.36600	-2.57500
C	-4.99200	3.53200	-4.05000
H	-4.90300	2.44500	-4.27600
H	-4.77900	4.08900	-4.98800
H	-6.05600	3.71900	-3.78000
C	2.71100	4.43600	0.55400
C	3.10200	4.46800	-0.81100
C	3.51800	3.77000	1.51500
C	4.32500	3.87700	-1.18200
C	2.23700	5.13100	-1.85500
C	4.73500	3.20400	1.09200
C	3.11000	3.66300	2.96400
H	4.62900	3.91800	-2.24300
C	5.16500	3.24500	-0.24700
H	2.69700	5.04700	-2.86200
H	2.07400	6.21200	-1.64300
H	1.23000	4.65900	-1.90400
H	5.37100	2.71000	1.84700
H	2.62800	4.58800	3.34400

H	3.98600	3.43000	3.60600
H	2.36600	2.84800	3.11100
C	6.46200	2.59200	-0.67100
H	6.32200	1.49900	-0.84000
H	7.25000	2.70300	0.10600
H	6.84900	3.02600	-1.61800
C	-2.53800	7.35000	0.94700
C	-2.77600	7.49400	2.48000
C	-2.20800	8.74100	0.34800
C	-3.88200	6.89200	0.33900
H	-3.65000	8.16000	2.65900
H	-1.90300	7.93000	3.01000
H	-2.98700	6.50600	2.94500
H	-2.00400	8.67500	-0.74300
H	-1.32900	9.22000	0.82800
H	-3.07500	9.42400	0.49000
H	-4.20400	5.90500	0.72800
H	-3.86500	6.83700	-0.76700
H	-4.66200	7.63200	0.62700
C	2.32000	7.40400	1.51200
C	2.16200	7.84500	2.99700
C	2.09000	8.62500	0.58000
C	3.79900	6.98900	1.33200
H	2.29500	6.98300	3.68600
H	1.17300	8.29900	3.21300
H	2.94100	8.60200	3.24100
H	1.08900	9.08700	0.70800
H	2.19400	8.33600	-0.48900
H	2.85400	9.40600	0.79400
H	4.43000	7.87600	1.56400
H	4.03800	6.67100	0.29700
H	4.10600	6.17700	2.01800
H	-0.18200	7.79900	1.80400
C	2.56000	-2.26500	-3.49900
C	2.67600	-3.67700	-3.38000
C	3.65000	-1.42300	-3.15900
C	3.91400	-4.22400	-2.99600
C	1.50600	-4.58400	-3.67600
C	4.86300	-2.02400	-2.76300
C	3.56100	0.08100	-3.25300
H	4.00700	-5.32300	-2.93500
C	5.02800	-3.41800	-2.69000
H	1.80500	-5.65100	-3.61000
H	1.07900	-4.40600	-4.68700
H	0.68000	-4.42700	-2.94400
H	5.71800	-1.36700	-2.52700
H	2.93400	0.42000	-4.10400
H	4.57100	0.53100	-3.35600
H	3.10200	0.51100	-2.33300
C	6.34300	-4.03600	-2.27000
H	6.31300	-4.37500	-1.20800
H	7.18300	-3.31400	-2.36200
H	6.59000	-4.93000	-2.88500
C	-2.74900	-2.41200	-3.07300
C	-3.59200	-1.85600	-2.06900
C	-2.97300	-3.74200	-3.52700
C	-4.67500	-2.61700	-1.59400
C	-3.38200	-0.45900	-1.54300
C	-4.07500	-4.45800	-3.01700
C	-2.06700	-4.45100	-4.51100
H	-5.34200	-2.16100	-0.84200
C	-4.94800	-3.91700	-2.05900
H	-4.27300	-0.10800	-0.98200

H	-3.15300	0.27500	-2.34500
H	-2.52100	-0.40900	-0.83300
H	-4.24900	-5.48300	-3.38800
H	-1.47100	-5.23100	-3.98500
H	-1.35300	-3.77300	-5.01700
H	-2.66000	-4.97400	-5.29400
C	-6.11300	-4.71900	-1.52200
H	-6.56000	-5.36800	-2.30700
H	-6.91400	-4.06100	-1.12200
H	-5.79000	-5.38900	-0.69100
C	1.91400	-1.57700	-6.47600
C	2.00900	-0.17500	-7.14600
C	1.28300	-2.58900	-7.47400
C	3.37100	-2.04600	-6.25200
H	2.68700	-0.23500	-8.02700
H	2.42900	0.57700	-6.44400
H	1.03100	0.20700	-7.50600
H	0.26800	-2.29200	-7.80900
H	1.20700	-3.60100	-7.01900
H	1.92800	-2.67300	-8.37800
H	3.44100	-3.05400	-5.79600
H	3.96100	-1.34600	-5.63000
H	3.86400	-2.09700	-7.24900
C	-2.85200	-0.90900	-5.79500
C	-2.68700	0.56400	-6.27700
C	-2.91700	-1.84700	-7.02800
C	-4.22800	-0.97200	-5.09400
H	-2.58700	1.25700	-5.41300
H	-3.58700	0.86300	-6.86000
H	-1.80500	0.71400	-6.93300
H	-1.99900	-1.79500	-7.65200
H	-3.77700	-1.55900	-7.67300
H	-3.06300	-2.90500	-6.72200
H	-4.52900	-1.99900	-4.81000
H	-4.99300	-0.58500	-5.80400
H	-4.26500	-0.33300	-4.18900
C	2.55400	-3.24600	2.82500
C	2.97700	-2.48600	3.95300
C	3.39700	-3.32800	1.68000
C	4.25900	-1.90100	3.94200
C	2.09500	-2.23500	5.15900
C	4.66800	-2.72600	1.72300
C	2.95500	-4.01900	0.41400
H	4.58000	-1.32700	4.82900
C	5.13000	-2.01400	2.84600
H	2.64400	-2.43400	6.10600
H	1.17600	-2.85200	5.16000
H	1.78200	-1.16700	5.18800
H	5.31700	-2.81400	0.83500
H	2.46000	-3.29500	-0.27500
H	2.23000	-4.83600	0.59800
H	3.82300	-4.43000	-0.14100
C	6.49100	-1.35500	2.84700
H	7.25000	-1.97900	2.32500
H	6.85500	-1.16500	3.88000
H	6.46200	-0.37200	2.32200
C	-2.63800	-2.14800	3.01400
C	-2.37500	-0.84200	3.50400
C	-3.87100	-2.44600	2.37300
C	-3.39200	0.13100	3.41900
C	-1.05800	-0.50900	4.16100
C	-4.85400	-1.44000	2.32200
C	-4.15900	-3.80700	1.78800

H	-3.18800	1.13800	3.82000
C	-4.65000	-0.15300	2.85800
H	-0.91400	-1.08000	5.10700
H	-0.99200	0.57400	4.39400
H	-0.19500	-0.76500	3.50600
H	-5.83000	-1.68500	1.86600
H	-3.81400	-4.63500	2.44300
H	-3.63400	-3.95000	0.81600
H	-5.24700	-3.93600	1.60800
C	-5.76700	0.86800	2.86300
H	-6.26900	0.93700	1.87200
H	-5.39700	1.87900	3.13300
H	-6.55600	0.59500	3.60200
C	1.91000	-5.99700	4.08300
C	2.81700	-6.42000	2.90200
C	2.79100	-5.52200	5.26800
C	1.18100	-7.28600	4.55100
H	3.48400	-5.60200	2.56800
H	2.21100	-6.76200	2.03500
H	3.46500	-7.26700	3.22200
H	3.41200	-6.37400	5.62900
H	2.16600	-5.17500	6.12000
H	3.47700	-4.70200	4.97800
H	1.94100	-8.08100	4.71700
H	0.46300	-7.65800	3.78900
H	0.64400	-7.15600	5.51500
H	-0.45400	-0.68600	-6.58400
C	-2.51100	-4.29400	5.29400
C	-3.68300	-3.29600	5.44400
C	-3.13900	-5.71400	5.20900
C	-1.67800	-4.18000	6.60400
H	-4.22200	-3.54600	6.38600
H	-4.41700	-3.35800	4.61800
H	-3.34700	-2.24300	5.52400
H	-2.38600	-6.52900	5.25300
H	-3.72300	-5.84300	4.27200
H	-3.83500	-5.85900	6.06400
H	-2.34600	-4.32300	7.48300
H	-1.21400	-3.17300	6.69200
H	-0.86700	-4.93400	6.66400
H	-0.60900	-5.89000	4.72400