Electronic Supplementary Information

Unveiling photophysical properties of cyclometalated iridium(III) complexes with azadipyrromethene and dipyrromethene ancillary: A theoretical perspective

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Table S1 Main optimized geometry structural parameters of **1** in the ground state obtained by different functional levels with the experimental data.

	PBE0	B3LYP	TPSSh	mPW1PW91	PBEh1PBE	PBE	Exp.[a]
Ir-C1	2.010	2.027	2.022	2.012	2.012	2.018	2.017
Ir-C2	2.003	2.020	2.015	2.005	2.005	2.011	2.023
Ir-N1	2.064	2.091	2.072	2.066	2.068	2.072	2.041
Ir-N2	2.037	2.064	2.047	2.040	2.042	2.043	2.029
Ir-N3	2.231	2.288	2.244	2.236	2.237	2.263	2.188
Ir-N4	2.209	2.264	2.216	2.213	2.215	2.23	2.183
N3-Ir-N4	84.77	84.15	84.78	84.80	84.57	84.51	85.06
C1-Ir-N1	79.97	79.70	79.81	79.92	79.91	79.98	80.94
C2-Ir-N2	80.21	79.97	80.05	80.15	80.14	80.29	81.09
C3-N5-C4	129.89	130.89	129.67	130.03	129.93	129.86	127.95

[a] Ref. 32

Table S2 Absorption spectra of **1** calculated by six different functions with basis sets of LANL2DZ ECP for Ir and 6-31G (d,p) for nonmetal atoms in $CHCl_3$ media, together with the experimental values.

	M06	O3lyp	TPSSh	B3LYP	mPW1PW91	PBE0	Exp[a].
	541	555	554	532	513	514	579
λ_{abs}/nm	409	406	402	414	399	400	403
	362	365	371	354	373	374	363
	277	307	299	281	269	269	265

[a] Ref. 32

Table S3 Variations for bond distances (Å), bond angles (°) and dihedral angles (°) between the triplet (T_1) and ground states (S_0) of all the complexes.

	1	**2**	**3**	**4**
		Bond length		
Ir-C1	-0.008	-0.002	0.001	0
Ir-C2	-0.002	-0.002	-0.003	0
Ir-N1	0.003	0.002	-0.001	0
Ir-N2	0.009	-0.002	-0.002	-0.001
Ir-N3	0.022	0.008	0.017	-0.004
Ir-N4	0.065	0.005	-0.004	-0.005
		Bond angle		
N3-Ir-N4	-0.48	-0.99	-1.14	-1
C1-Ir-N1	-0.02	-0.04	-0.07	0
C2-Ir-N2	0.08	-0.01	-0.08	-0.01
C3-X15-C4[a]	-4.12	-2.39	-3.15	-2.97
C1-Ir-N3	4.59	0.38	-0.39	0.71
C2-Ir-N4	-3.38	-0.34	1.44	0.70
		Dihedral angle		
N3-C3-X15-N4[a]	-45.87	-3.96	5.17	0.46
N3-C8-C9-C10	71.47	-6.05	-20.58	—
N4-C5-C6-C7	31.24	17.46	—	—
N2-C11-C12-C2	-1.09	-1.48	0.48	-0.17
N1-C13-C14-C1	1.15	-0.30	-0.53	-0.17

[a] X = N (in **1**); X=C (in **2-4**)

Table S4 Calculated intramolecular centroid-centroid distances (Å) for **1-3** at DFT/PBE0 level of theory

	1	**1**-exp[a]	**2**	**3**
$R(S_0)$	3.661/3.708	3.501/3.607	3.669/3.688	3.605
$R(T_1)$	3.631/3.671		3.678/3.745	3.638

[a] Ref. 32

Table S5 Molecular orbital compositions (%) in the S_0 State for Ir(III) complexes by DFT/PBE0 level (ppy1 and ppy2 refer to phenylpyridine ligands containing C1 and N1 atoms, C2 and N2 atoms, respectively).

	Orbital[a]	Energy(eV)	Compositions (%)			
			Ir	ppy1	ppy2	ancillary
1	L+2	-1.28	3.75	70.22	23.68	1.48
	L+1	-1.42	2.56	24.56	68.70	2.82
	L	-2.49	1.18	0.41	0.46	97.79
	H	-5.38	0.23	0.47	0.38	98.88
	H-1	-5.41	39.95	22.21	24.27	13.20
	H-2	-5.86	20.75	4.83	10.46	63.72
2	L+2	-1.22	3.86	63.69	29.86	1.70
	L+1	-1.35	2.47	30.86	62.37	2.93
	L	-2.08	1.10	0.84	0.55	97.27
	H	-5.31	5.98	3.31	2.24	88.34
	H-1	-5.35	35.52	19.04	24.17	20.99
	H-2	-5.83	27.02	13.75	17.66	41.28
3	L+2	-1.22	3.58	81.01	13.46	1.00
	L+1	-1.38	2.36	13.69	81.45	1.38
	L	-2.10	1.14	0.23	0.63	97.66
	H	-5.36	24.94	22.03	9.08	43.64
	H-1	-5.48	15.78	14.26	6.29	63.43
	H-2	-5.81	28.78	8.44	5.83	56.64
4	L+2	-1.32	3.36	47.14	47.92	0.75
	L+1	-1.38	2.27	48.24	47.46	0.86
	L	-2.14	1.08	0.37	0.34	97.59
	H	-5.49	40.48	27.22	27.48	4.40
	H-1	-5.52	1.31	0.43	0.36	97.88
	H-2	-5.81	31.95	4.25	4.43	59.14

[a] The orbitals involved in the excitations (H = HOMO and L = LUMO).

Table S6 Calculated singlet excitation energies (E), wavelengths (λ_{cal}/nm), oscillator strengths (*f*), dominant contribution and transition characters of **1-4** in $CHCl_3$ media at TD-M06 level.

Complex	state	λ_{cal}/E	*f*	Configuration[a]	Nature	Exp.[b](nm)
1	S_1	653/1.90	0.0166	H→L (97%)	MLCT/LLCT	
	S_2	541/ 2.29	0.0805	H-2→L (79%)	MLCT/LLCT/IL	579
	S_3	518/2.39	0.1014	H-3→L (97%)	MLCT/ILCT	
	S_4	508/ 2.44	0.6973	H-1→L (81%)	ILCT	
	S_7	412/ 2.98	0.0290	H-5→L (69%)	LLCT/ILCT	
				H-7→L (22%)	MLCT/LLCT/IL	
	S_8	409/3.03	0.0692	H-6→L (78%)	MLCT/LLCT/IL	403
	S_{19}	341/3.63	0.0563	H-3→L+2(48%)	MLCT/LLCT	
				H-2→L+2(17%)	LLCT/ILCT	
	S_{47}	277/4.48	0.1135	H-1→L+5(54%)	ILCT	265
2	S_1	544/2.28	0.0210	H→L (97%)	MLCT/LLCT	
	S_2	473/2.62	0.3335	H-1→L (58%)	ILCT	
				H-2→L (38%)	MLCT/LLCT/IL	
	S_3	450/2.75	0.4016	H-2→L (52%)	MLCT/LLCT/IL	
				H-1→L (31%)	ILCT	
	S_4	445/ 2.79	0.1796	H-3→L (84%)	MLCT/ILCT	
	S_9	363/3.41	0.0372	H-1→L+1(58%)	LLCT	
				H-2→L+1(25%)	MLCT/LLCT/IL	
	S_{10}	359/3.46	0.0794	H-6→L (54%)	MLCT/LLCT/IL	
				H-8→L (17%)		
	S_{16}	342/3.62	0.0566	H-3→L+2(45%)	MLCT/LLCT	
				H→L+3(19%)	MLCT/ILCT	
	S_{37}	287/4.32	0.1202	H-5→L+1(24%)	LLCT/ILCT	
				H-3→L+4(20%)	LLCT	
	S_{39}	282/ 4.40	0.0554	H→L+5(46%)	MLCT/LLCT	
3	S_1	543/2.28	0.0168	H→L (96%)	MLCT/LLCT	
	S_2	466/2.66	0.0105	H-2→L (80%)	MLCT/ILCT	
	S_3	453/2.74	0.1513	H-3→L (76%)	MLCT/ILCT	
				H-2→L (17%)	MLCT/ILCT	
	S_4	440/2.82	0.7448	H-1→L (88%)	ILCT	
	S_5	416/2.98	0.0184	H→L+1(93%)	MLCT/LLCT/IL	
	S_{10}	356/3.49	0.0849	H-6→L (77%)	MLCT/LLCT/IL	
	S_{11}	353/3.52	0.0261	H-2→L+1(52%)	MLCT/LLCT	
				H-3→L+1(16%)	MLCT/LLCT	
	S_{15}	341/3.63	0.0777	H→L+3(64%)	MLCT/LLCT	
	S_{25}	303/4.09	0.0640	H-2→L+3(38%)	MLCT/LLCT	
				H-4→L+2(20%)	LLCT/ILCT	
				H-3→L+3(31%)	MLCT/LLCT	
	S_{35}	286/4.34	0.1255	H-5→L+2(20%)	LLCT/ILCT	
				H-4→L+3(19%)	ILCT	

				H-6→L+1(19%)	MLCT/LLCT/IL
4	S_2	474/2.62	0.0105	H-3→L (88%)	MLCT/ILCT
	S_3	466/2.66	0.1554	H-2→L (98%)	MLCT/ILCT
	S_4	431/2.87	0.6922	H-1→L (88%)	ILCT
	S_5	408/3.04	0.0347	H→L+1(95%)	MLCT/LLCT/IL
	S_{11}	354/3.50	0.0605	H-6→L (85%)	MLCT/LLCT/IL
	S_{12}	348/3.56	0.1124	H-3→L+1(45%)	MLCT/LLCT
				H-2→L+2(44%)	
	S_{15}	338/3.66	0.0608	H→L+3(87%)	MLCT/ILCT
	S_{27}	294/4.21	0.2017	H-4→L+2(55%)	LLCT/ILCT
				H-2→L+4(29%)	MLCT/LLCT
	S_{32}	282/4.39	0.1544	H-5→L+1(60%)	LLCT/ILCT
	S_{33}	281/4.40	0.1294	H-6→L+1(29%)	MLCT/LLCT/IL
				H-5→L+2(30%)	LLCT/ILCT
	S_{44}	264/4.70	0.1366	H-1→L+5(70%)	ILCT

[a] The orbitals involved in the excitations (H = HOMO and L = LUMO).

[b] Ref. 32

Table S7 5d(Ir) orbital compositions (%) in selected occupied orbitals of complexes **2-4** at their Tgeometries.

	Orbital [a]	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
	H	12.12	1.66	8.31	1.59	17.64
	H-1					1.13
2	H-2		17.92	14.08		11.13
	H-3				41.65	1.50
	H	12.69	2.18	8.27		10.36
	H-1	4.81	3.52	3.85		
3	H-2	1.89	3.80		26.37	6.08
	H-3		14.00	7.40	10.40	15.58
	H	10.48	5.16	10.32	2.26	15.32
	H-1		1.54			3.87
4	H-2	12.94		1.14	26.78	
	H-3		22.80	2.69		9.42

[a] H and L represent HOMO and LUMO, repectively.

Table S8 Electronic transitions of **2-4** calculated at the T_1 optimized geometry by TD-B3LYP/TDA in $CHCl_3$ solution

Complex	S_n/T_m	SOC (cm^{-1}) $\langle T_1\|H_{SOC}\|S_n\rangle$	^{1,3}MLCT (%)	E (eV)	f	Configuration[a]
	T_1		<1.00	1.59		H-1→L (86%)
2	S_1	23.0	37.88	1.97	0.0174	H→L (94%)
	S_2	62.8	33.27	2.43	0.1525	H-2→L (79%)
	S_3	60.4	34.55	2.54	0.2897	H-3→L (82%)
	T_1		11.98 6.64	1.60		H→L (37%) H-1→L (60%)
3	S_1	86.7	28.49	1.99	0.0266	H→L (88%)
	S_2	113.0	20.82 13.33	2.45	0.1071	H-3→L (45%) H-2→L (36%)
	S_3	120.0	19.62	2.52	0.1307	H-2→L (53%)
	T_1		4.71	1.68		H-1→L (87%)
4	S_1	103.0	41.80	2.10	0.0020	H→L (96%)
	S_2	71.6	28.28	2.43	0.0220	H-3→L (81%)
	S_3	128.0	39.63	2.46	0.2047	H-2→L (97%)

[a] H and L represent HOMO and LUMO, repectively.

Table S9 Calculated net spin values located on Ir(III) of ^{3}MLCT and ^{3}MC states for **1-4** with PBE0 functional.

Spin (Ir)	**1**	**2**	**3**	**4**
^{3}MLCT	0.023	0.005	0.012	0.015

^{3}MC	1.568	1.572	1.557	1.562

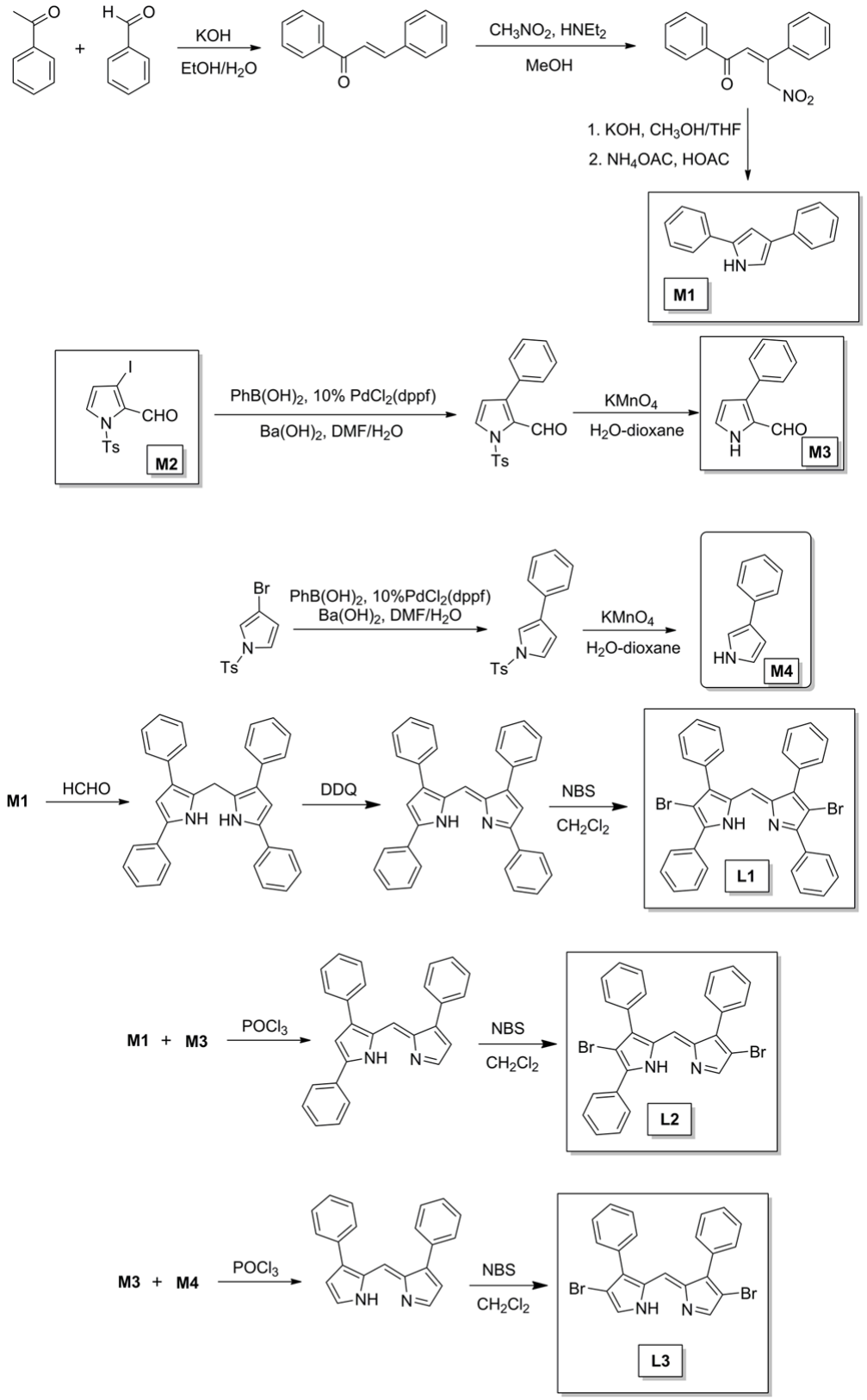

Fig. S1. The synthetic routes of the designed ancillary ligands **L1**, **L2** and **L3**.

Fig. S1 depicts the possible synthetic routes of the designed ancillary ligands. As shown in Fig. 1, the intermediates **M1**, **M2**, **M3** and **M4** can be prepared according to the reported literature procedures (*Inorg. Chem.*, 2012, **51**, 7682; *J. Org. Chem.*, 2007, **72**, 2187; *Can. J. Chem.*, 2001, **79**, 1827.). The designed ligands tend to be relatively easy to synthesize *via* condensation of pyrrole derivatives (**M1** and **M4**) and corresponding aldehydes (**M3** and formaldehyde) in different reaction conditions (*Chem. Rev.*, 2007, **107**, 4891; *Chem. Commun.*, 2009, 4515.), followed by bromination with NBS (*J. Org. Chem.*, 2007, **72**, 2187.). Then, the iridium(III) complexes (**2-4**) investigated in this work can be prepared following procedures developed by Thompson or Gray et. al. (*Inorg. Chem.,* 2010, **49**, 6077; *Organometallics,* 2014, **33**, 637*).*

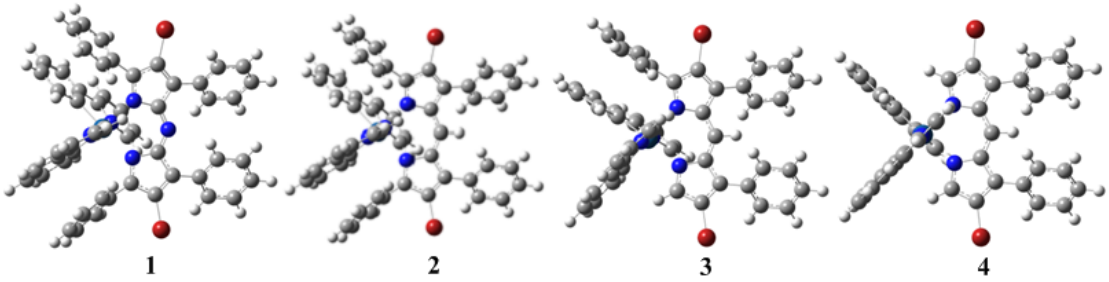

Fig. S2. Optimized structures of **1-4** in the ground states at DFT/PBE0/LANL2DZ level.

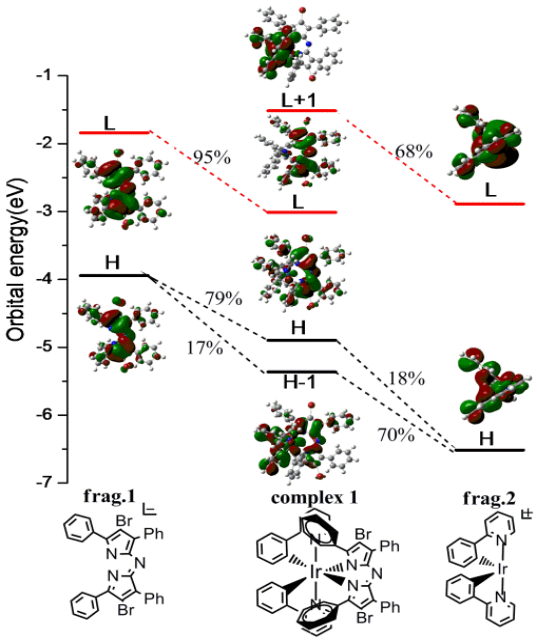

Fig. S3. Orbital interaction diagram for **1**, formed by two fragments at its optimized T_1 geometry.

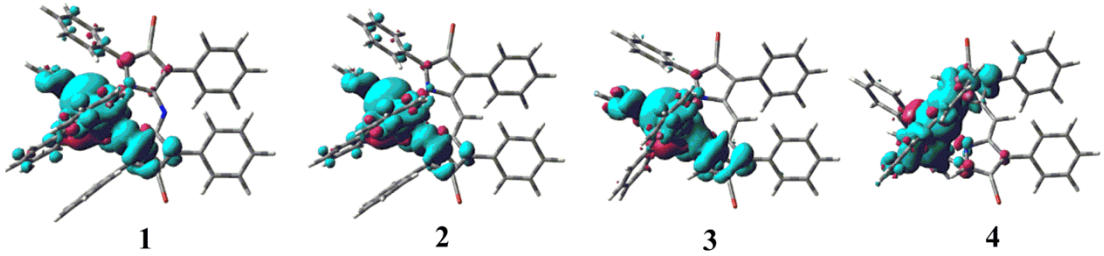

Fig. S4. Spin-density distributions (isovalue 0.0004 au) calculated for the ^{3}MC states of complexes **1-4**.

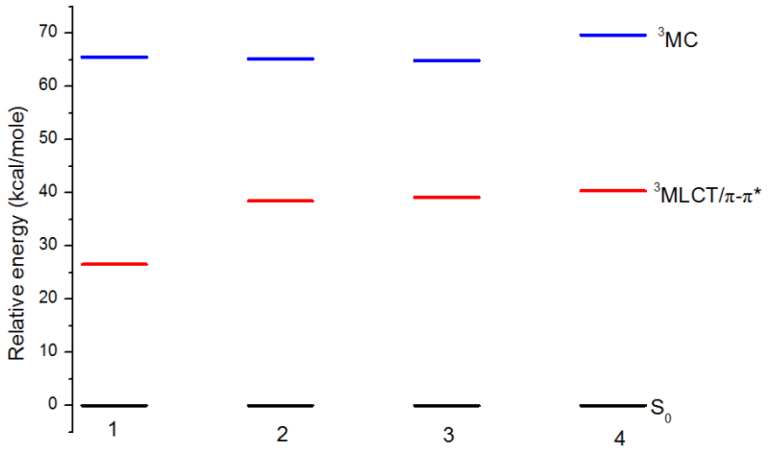

Fig. S5. Energy level diagram of ^{3}MLCT/ππ* and ^{3}MC excited states for **1-4** with the normalized S_0 levels.

Table S10 Cartesian coordinates of [Ir(ppy)$_2$(**L$_a$Br$_2$**)] (**1**) at the S_0 and T_1 optimized geometry.

		S_0				**T_1**	
Ir	-1.765246	8.612352	5.371036	Ir	-1.881668	8.530939	5.270154
Br	-0.183596	7.103266	-0.362633	Br	1.450435	7.718625	0.180227
Br	-0.011788	4.837846	9.865466	Br	-1.387703	4.457891	9.643112
N	-0.707345	7.716445	3.622669	N	-0.997237	7.542986	3.449077
N	-0.393204	5.540089	4.65458	N	-0.498183	5.438982	4.529641
N	-0.744766	7.03815	6.537954	N	-0.800386	6.885952	6.407698
N	-3.352877	7.40812	4.83501	N	-3.643168	7.490145	4.978315
N	-0.333797	9.931992	5.971659	N	-0.284139	9.759757	5.621732
C	-0.615314	8.112577	2.347137	C	-0.501456	8.138057	2.318954
C	-0.377855	6.985936	1.494694	C	0.563536	7.353293	1.785632
C	-0.313693	5.850653	2.271781	C	0.690243	6.210592	2.548169
C	-0.509469	6.336607	3.618858	C	-0.305811	6.371751	3.60016
C	-0.440764	5.815173	5.939043	C	-0.792343	5.661886	5.79785
C	-0.18038	4.807254	6.940095	C	-1.080109	4.599447	6.754957
C	-0.319703	5.482407	8.136802	C	-1.209105	5.264831	7.964257
C	-0.643206	6.844284	7.857838	C	-0.978062	6.651517	7.748359
C	-0.066569	4.458387	1.895692	C	1.565175	5.056645	2.358838
C	-0.781233	3.418648	2.509631	C	1.06657	3.75218	2.500341
H	-1.51915	3.659181	3.266267	H	0.025516	3.610526	2.768472
C	-0.549046	2.094669	2.156086	C	1.893169	2.65403	2.292786
H	-1.110991	1.303792	2.644356	H	1.485644	1.65153	2.391113
C	0.401255	1.782228	1.187419	C	3.231444	2.833659	1.950414
H	0.580731	0.746811	0.911418	H	3.875798	1.973735	1.791162
C	1.121351	2.805408	0.574688	C	3.737911	4.123889	1.811808
H	1.870465	2.571036	-0.17645	H	4.78161	4.274387	1.550611
C	0.890025	4.13062	0.923121	C	2.913568	5.224998	2.008792
H	1.462561	4.920908	0.44952	H	3.315814	6.227385	1.903891
C	-0.67378	9.501024	1.858933	C	-1.084583	9.299695	1.653728
C	-1.62221	9.869142	0.897713	C	-2.442361	9.286798	1.305794
H	-2.368556	9.147668	0.58195	H	-3.054752	8.444735	1.61001
C	-1.625763	11.153107	0.367177	C	-2.984888	10.322696	0.557572
H	-2.378345	11.42855	-0.365656	H	-4.03624	10.298128	0.288872
C	-0.670938	12.082666	0.77225	C	-2.186694	11.395068	0.164886
H	-0.670223	13.083562	0.349749	H	-2.614389	12.207246	-0.416184
C	0.286653	11.720947	1.715161	C	-0.839633	11.424234	0.517547
H	1.043452	12.435192	2.027398	H	-0.214748	12.260206	0.216512
C	0.286491	10.438359	2.252488	C	-0.287146	10.377408	1.245697
H	1.05166	10.152886	2.964402	H	0.766136	10.392923	1.508024
C	0.158867	3.405671	6.689419	C	-1.160218	3.17068	6.465548
C	-0.358047	2.39215	7.511775	C	-2.157848	2.375347	7.052055

H	-1.016511	2.655387	8.332741	H	-2.879913	2.83354	7.720679
C	-0.048147	1.058437	7.276002	C	-2.234086	1.01534	6.777831
H	-0.462571	0.289085	7.921622	H	-3.016982	0.417916	7.236786
C	0.784683	0.708396	6.215553	C	-1.313048	0.419586	5.918813
H	1.028077	-0.334642	6.032966	H	-1.370501	-0.644759	5.708993
C	1.301934	1.704116	5.391189	C	-0.316702	1.198028	5.334498
H	1.945853	1.443274	4.556346	H	0.414287	0.741038	4.672986
C	0.994436	3.039734	5.623182	C	-0.239775	2.5601	5.599668
H	1.394765	3.809391	4.974467	H	0.538949	3.162056	5.145812
C	-0.736902	7.879449	8.904216	C	-0.668792	7.643609	8.772679
C	0.319254	8.775384	9.091214	C	0.513828	8.388478	8.642001
H	1.163612	8.755005	8.408054	H	1.119109	8.254961	7.750775
C	0.299775	9.672381	10.15552	C	0.917538	9.254733	9.649812
H	1.129374	10.360228	10.293216	H	1.843854	9.811828	9.540474
C	-0.7741	9.683942	11.040077	C	0.140686	9.404031	10.79644
H	-0.788954	10.383945	11.870819	H	0.455359	10.081817	11.585121
C	-1.828411	8.791	10.861163	C	-1.042663	8.679788	10.929042
H	-2.670901	8.797616	11.54628	H	-1.659202	8.802848	11.814636
C	-1.803809	7.884929	9.808214	C	-1.441826	7.798949	9.932419
H	-2.618218	7.179698	9.675415	H	-2.366001	7.241747	10.037967
C	-3.568254	6.168598	5.303367	C	-3.882269	6.236257	5.390992
H	-2.855729	5.807742	6.03419	H	-3.077585	5.744002	5.920119
C	-4.632446	5.387017	4.889527	C	-5.085802	5.587946	5.173799
H	-4.7563	4.390545	5.297954	H	-5.213233	4.570716	5.526161
C	-5.514684	5.91214	3.947543	C	-6.096077	6.268909	4.499895
H	-6.354547	5.325671	3.587047	H	-7.052137	5.793162	4.30265
C	-5.313134	7.200091	3.484932	C	-5.863684	7.569616	4.089458
H	-5.995414	7.637455	2.765482	H	-6.634733	8.127736	3.571258
C	-4.229762	7.955215	3.948786	C	-4.631003	8.181273	4.342942
C	-3.954089	9.342532	3.609029	C	-4.282738	9.549713	3.996923
C	-4.796389	10.116384	2.797821	C	-5.182832	10.453298	3.416279
H	-5.679045	9.679491	2.337642	H	-6.202472	10.152281	3.189107
C	-4.520022	11.457971	2.595397	C	-4.781512	11.750461	3.142687
H	-5.17338	12.063963	1.97467	H	-5.477379	12.457397	2.700699
C	-3.39811	12.023363	3.206366	C	-3.474476	12.138739	3.447351
H	-3.176536	13.076738	3.054424	H	-3.151058	13.15402	3.231595
C	-2.557743	11.253001	4.001149	C	-2.581868	11.24288	4.022966
H	-1.686953	11.722454	4.44813	H	-1.572441	11.579136	4.239304
C	-2.80143	9.891569	4.218484	C	-2.956795	9.924316	4.315036
C	0.943074	9.893173	5.56456	C	0.878234	9.711101	4.954378
H	1.184366	9.081452	4.887787	H	0.958418	8.933785	4.204502
C	1.884604	10.81782	5.981084	C	1.915166	10.595143	5.198326
H	2.905472	10.748189	5.622477	H	2.834315	10.51546	4.628948
C	1.479723	11.825757	6.856756	C	1.738562	11.571738	6.177028

H	2.183733	12.581925	7.191539	H	2.524139	12.290929	6.389436
C	0.174965	11.834894	7.317729	C	0.551294	11.604574	6.88758
H	-0.150998	12.582343	8.031665	H	0.398598	12.338553	7.670191
C	-0.729853	10.855601	6.890934	C	-0.459759	10.67704	6.614336
C	-2.083332	10.65945	7.386272	C	-1.71912	10.550992	7.333335
C	-2.684838	11.478498	8.34922	C	-2.088312	11.369793	8.406999
H	-2.164399	12.349484	8.739139	H	-1.443347	12.181035	8.734461
C	-3.955551	11.180155	8.81538	C	-3.286801	11.146988	9.067406
H	-4.428558	11.814782	9.55875	H	-3.578774	11.782354	9.898174
C	-4.618418	10.055711	8.319718	C	-4.110094	10.097817	8.655904
H	-5.616059	9.817825	8.681704	H	-5.050691	9.918349	9.171502
C	-4.022824	9.241975	7.360839	C	-3.743391	9.282731	7.589116
H	-4.573339	8.383906	6.984756	H	-4.40946	8.47898	7.288146
C	-2.743096	9.519001	6.865097	C	-2.543101	9.486762	6.899092