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[2+2] Photodimerization of the acenaphthylene ruthenium complex $[(C_5Me_4CH_2OMe)Ru(\eta^6\text{-}C_{12}H_8)]^+$

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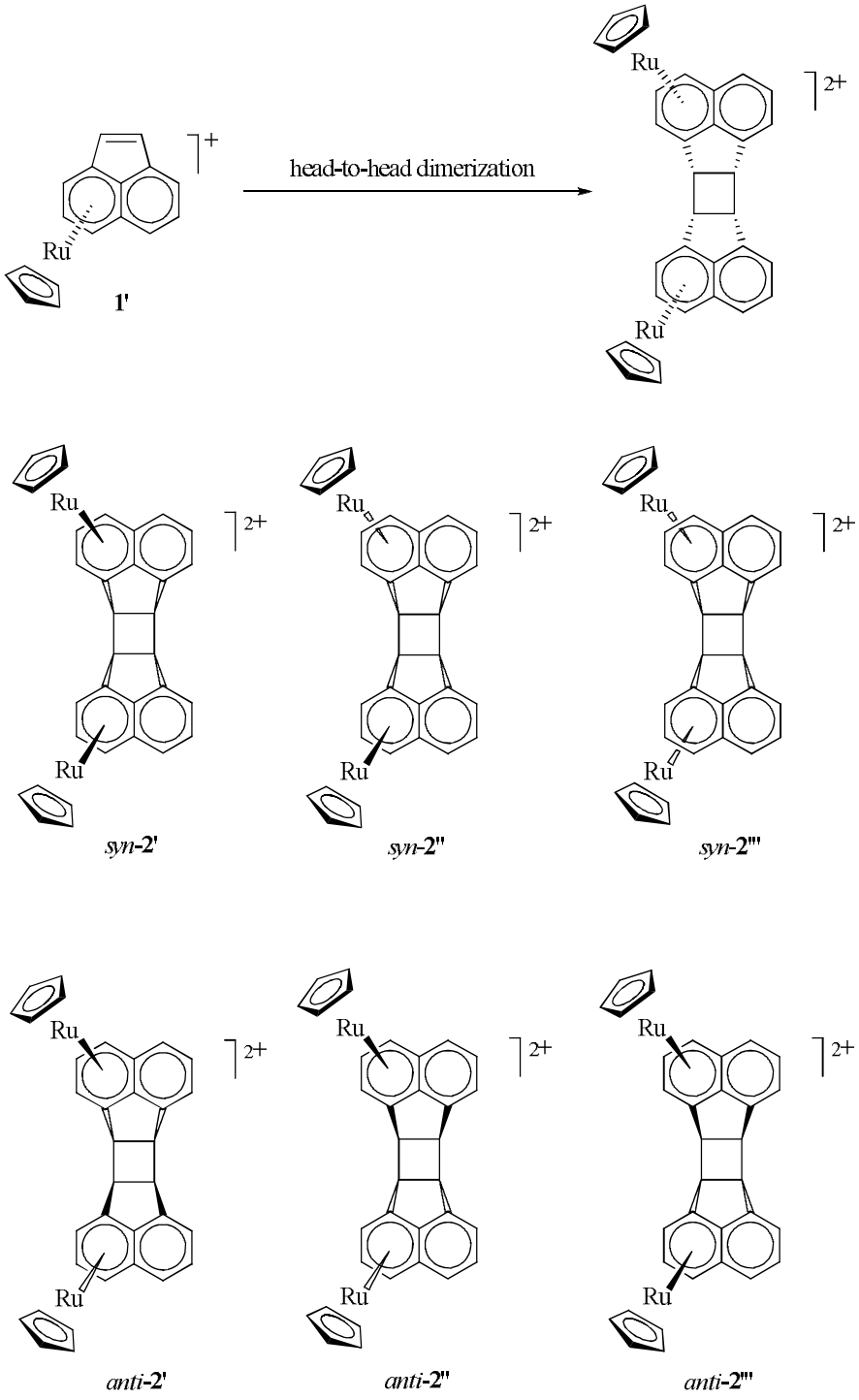

Figure S1 Isomers which can be formed by head-to-head reaction pathway for the dimerization of the parent acenaphthylene complex $[CpRu(\eta^6\text{-}C_{12}H_8)]^+$ (**1'**).

Table S1 Total energy and energy decomposition analysis (EDA) of interactions between two $[RuCp]^+$ cations in the $[Ru_2Cp_2]^{2+}$ moiety with the geometry it has in complexes *syn*- and *anti*-**2'**,**2''**,**2'''** at BP86/TZ2P.

Isomers		ΔE*, kcal mol^{-1}	EDA $[CpRu]^+...[CpRu]^+$			
			ΔE_{int}	ΔE_{pauli}	ΔE_{elstat}	ΔE_{orb}
syn-	**2'**	0	37.62	0.00	38.24	–0.63
	2''	+11.2	46.94	0.09	48.55	–1.69
	2'''	+34.5	60.07	4.73	61.35	–6.01
anti-	**2'**	0	35.76	0.00	36.24	–0.48
	2''	+6.3	40.14	0.01	40.86	–0.72
	2'''	+4.9	43.55	0.07	44.60	–1.13

* Related to the most termodinamically stable isomer, *syn*-**2'** in case of *syn*- and *anti*-**2'** in case of *anti*-isomers respectively.

Cartesian coordinates and energies for structures *syn*- and *anti*-2',2'',2''' optimized at PBE/L2

$[syn\text{-}\mathbf{2'}]^{2+}$ $E = -10372.83625552$ a.u.

```
6       -2.920265510      0.577597950     -0.208893960
6       -3.099023890     -0.830196480     -0.018616260
6       -2.321762700     -1.575413980      0.839999910
6       -1.262872910     -0.943194680      1.567397560
6       -1.094951970      0.460737750      1.348863270
6       -1.927940060      1.228080790      0.480448780
6       -0.383421640     -1.544355600      2.534675870
6        0.645767540     -0.780057820      3.154341680
6        0.775459210      0.630058830      2.926153740
6       -0.122713320      1.261879700      2.029620020
6       -1.470633470      2.662668670      0.536959860
6       -0.272870620      2.689070800      1.558656600
6        0.027233980      0.934246400     -3.719553660
6       -0.675960900      1.843742270     -2.866090610
6       -0.082881220      2.269789630     -1.704292190
6        1.212996830      1.765060290     -1.383654750
6        1.942149520      0.868132920     -2.226776500
6        1.290630730      0.464877670     -3.436315030
6        1.730637030      2.310416900     -0.165006280
6        3.012105640      1.896548100      0.277961390
6        3.762426580      0.983859750     -0.535260400
6        3.267408510      0.520302760     -1.787232490
6       -0.508312470      3.206257130     -0.603148400
6        0.687639930      3.232509760      0.420654770
1       -3.584134730      1.107553240     -0.892862080
1       -3.892553580     -1.329127740     -0.575896520
1       -2.494355380     -2.645365140      0.957622210
1       -0.493085720     -2.599126250      2.786057900
1        1.303892410     -1.262869970      3.875964110
1        1.524690060      1.196751400      3.478265420
1       -2.291037360      3.360676340      0.743614760
1       -0.358479100      3.404082440      2.384847700
1       -0.461137320      0.606820540     -4.637959450
```

1	-1.667722990	2.187557470	-3.162034810
1	1.791851610	-0.224352660	-4.116137320
1	3.455985240	2.291665980	1.191290550
1	4.765915820	0.697256760	-0.222464710
1	3.895409180	-0.117460210	-2.409031340
1	-0.836159820	4.182394820	-0.980861600
1	1.086058240	4.221945600	0.672530040
44	-1.281588590	0.170299010	3.612046250
6	-3.360327750	0.386408990	4.324188760
6	-2.636667220	1.587781360	4.614023600
1	-2.878958900	2.582002940	4.250092020
1	-4.230788470	0.306280260	3.678572490
6	-2.734026270	-0.694869600	5.020999600
6	-1.612635210	-0.165592070	5.740102500
6	-1.552962210	1.247896400	5.488752100
1	-0.827271980	1.938140970	5.909530960
1	-0.938394720	-0.729705440	6.378303790
1	-3.053161380	-1.733098940	5.008697090
44	3.252086970	2.735339220	-1.759720670
6	3.170303430	4.873928160	-2.278146450
6	3.230803760	4.109469670	-3.487729460
1	2.473526820	4.087512470	-4.266825850
1	2.373461070	5.554565550	-1.992838930
6	4.359046900	4.600010790	-1.525210920
6	5.153983980	3.667306750	-2.275396530
6	4.454748860	3.368642800	-3.490552970
1	4.794835580	2.699546120	-4.275773010
1	6.122984660	3.273468670	-1.982045410
1	4.627106470	5.037269460	-0.567574050

[*syn*-**2''**]$^{2+}$ $E = -10372.81847325$ a.u.

6	-3.461181210	1.047238210	0.384430050
6	-4.057352920	-0.126546600	0.948941890
6	-3.500205050	-0.812151070	2.003597940
6	-2.261911660	-0.362609110	2.568172930
6	-1.646174790	0.765606800	1.936391890
6	-2.257858460	1.491861520	0.869601910
6	-1.575394680	-0.909198350	3.707939480
6	-0.370128880	-0.316753970	4.176981020
6	0.240684060	0.783495230	3.492992190
6	-0.406181900	1.339562840	2.363836000
6	-1.463552970	2.754236200	0.664433590
6	-0.258458470	2.683642170	1.668258470
6	0.109856810	0.424483010	-3.385268330
6	-0.646562180	1.324756240	-2.567251230
6	-0.041282470	1.923677450	-1.490213480
6	1.316327360	1.579204610	-1.203431100
6	2.106017960	0.718928880	-2.031139010
6	1.440271890	0.142413040	-3.160919620
6	1.823412370	2.256441300	-0.047970520
6	3.170765670	2.041108710	0.335824690
6	3.991491850	1.183937920	-0.472676620
6	3.490198820	0.574858840	-1.660359890
6	-0.463473980	3.006082560	-0.527837010
6	0.721986360	3.124747590	0.499929290
1	-4.001080520	1.591623670	-0.391401350
1	-5.016680120	-0.459970540	0.552119640
1	-4.015661090	-1.665319320	2.445092870
1	-1.985228600	-1.776751830	4.224665800
1	0.131575710	-0.746490600	5.043296510
1	1.185495730	1.182197560	3.861327770

1	-2.099594040	3.638282350	0.804535210
1	-0.271470850	3.450106260	2.455849930
1	-0.387438000	-0.037110630	-4.239150420
1	-1.682118660	1.538393600	-2.833696130
1	1.984603410	-0.528570740	-3.825833890
1	3.606520400	2.547546360	1.196669450
1	5.040718000	1.052113630	-0.209913780
1	4.159743240	-0.018820800	-2.282618620
1	-0.709915350	3.925433550	-1.076143770
1	1.063955820	4.148065700	0.693220040
44	-0.089258980	-0.939669430	2.092100120
6	0.579095050	-1.660613480	0.128161500
6	-0.256941810	-2.654670010	0.738093670
1	-1.202116540	-3.021471930	0.347530180
1	0.378000370	-1.161549730	-0.814350040
6	1.719998730	-1.467653850	0.972292460
6	1.586901500	-2.336376530	2.105897270
6	0.367572970	-3.075022250	1.954265850
1	-0.017409970	-3.818521910	2.646655710
1	2.291498380	-2.431835460	2.927251870
1	2.547014000	-0.789934520	0.791125940
44	3.191588840	2.763625040	-1.762134730
6	2.808264930	4.836722670	-2.400363660
6	2.909812050	4.008980560	-3.564801910
1	2.126505270	3.841856880	-4.299320600
1	1.945590030	5.430282120	-2.111972240
6	4.057273320	4.765456170	-1.700392620
6	4.930029200	3.894800750	-2.438386120
6	4.218341350	3.431199500	-3.592675280
1	4.605002220	2.761289990	-4.355417050
1	5.955047820	3.647198030	-2.176903270
1	4.311818460	5.294435930	-0.786209160

$[syn\text{-}\mathbf{2'''}]^{2+}$ $E = -10372.78125245$ a.u.

6	-3.583857470	2.348331230	1.378648520
6	-4.160391670	1.225354030	2.056134350
6	-3.411645320	0.332683300	2.786688330
6	-1.990702630	0.501387860	2.877590360
6	-1.427490180	1.599755100	2.148430270
6	-2.226539380	2.534221060	1.421902620
6	-1.063925570	-0.323692460	3.602141170
6	0.322381590	-0.010325630	3.608730360
6	0.845783990	1.103806820	2.875568050
6	-0.032281350	1.944708190	2.155375580
6	-1.331449750	3.673311570	1.038419270
6	0.069190580	3.400384020	1.691724400
6	-0.248352050	1.633414770	-3.465236810
6	-0.942617410	2.218718890	-2.357762610
6	-0.233986880	2.904725600	-1.399578030
6	1.180974020	3.023273860	-1.582181640
6	1.859860840	2.617212730	-2.771287530
6	1.097478140	1.830376220	-3.693150020
6	1.809358120	3.763456050	-0.536988060
6	3.083851750	4.336319140	-0.780452400
6	3.735647980	4.067747150	-2.027709500
6	3.184680510	3.150940120	-2.967633220
6	-0.619321770	3.922279880	-0.336308720
6	0.723464920	4.143391670	0.442972250
1	-4.241716300	3.060084260	0.878405750
1	-5.243237770	1.101576960	2.021981160
1	-3.892393820	-0.478576070	3.333871920
1	-1.422284270	-1.196496230	4.147591370
1	1.009597850	-0.652217270	4.158954990

1	1.915012310	1.308332670	2.917599550
1	-1.762254000	4.632536350	1.355548600
1	0.271062010	3.962801340	2.616572400
1	-0.828782940	1.080691020	-4.204868820
1	-2.032360730	2.168164200	-2.333676180
1	1.562327670	1.460659700	-4.607398360
1	3.568612610	4.979070250	-0.045946140
1	4.714007750	4.506157170	-2.221758910
1	3.738346840	2.910600440	-3.874968340
1	-1.010452600	4.808878210	-0.858049680
1	0.863574720	5.182939450	0.766218210
44	3.392093280	2.163414220	-1.026424970
6	3.849827620	0.005413660	-0.883004550
6	3.592510410	0.526460930	0.430541010
1	2.805270030	0.201552390	1.101774730
1	3.297854130	-0.781847680	-1.388628200
6	4.975983820	0.694566860	-1.424400390
6	5.415920550	1.652737740	-0.451947020
6	4.563847750	1.542532050	0.700039160
1	4.659489250	2.121793600	1.614163910
1	6.257726510	2.331254460	-0.560327770
1	5.420250990	0.526749340	-2.401446600
44	-0.341287800	-0.301740410	1.526311420
6	0.375044730	-0.761846810	-0.509573800
6	-1.047879730	-0.878161240	-0.470583970
1	-1.753970840	-0.291003830	-1.049161960
1	0.934088220	-0.067330320	-1.128966400
6	0.921397900	-1.711289970	0.419438100
6	-0.168738360	-2.418332080	1.023261070
6	-1.386818680	-1.901059420	0.476331660
1	-2.391538270	-2.223897090	0.734626930
1	-0.084450410	-3.209415500	1.763224120
1	1.971852000	-1.902908250	0.616103640

$[anti\text{-}\mathbf{2'}]^{2+}$ $E = -10372.84185365$ a.u.

6	-3.053720340	0.518681030	-0.166382100
6	-3.247451220	-0.874444150	0.101831700
6	-2.688266020	-1.514520160	1.185761940
6	-1.899018480	-0.769458850	2.119060270
6	-1.728634290	0.621648230	1.834029530
6	-2.282809520	1.265265960	0.688865620
6	-1.216690440	-1.265001310	3.284509120
6	-0.505289150	-0.378254840	4.141443870
6	-0.346474790	1.010289340	3.821212090
6	-0.944238010	1.509232320	2.636949770
6	-1.882746040	2.720108810	0.717815420
6	-1.032628040	2.891153850	2.035290900
6	-3.201620160	7.056512480	-0.706509430
6	-3.406261090	5.661709640	-0.455681970
6	-2.934719710	5.114005350	0.710853950
6	-2.228769020	5.959308920	1.616297930
6	-2.019547440	7.356507440	1.393781570
6	-2.551763370	7.890068040	0.176756820
6	-1.797350400	5.266299770	2.791628950
6	-1.064014500	5.978313240	3.773450220
6	-0.828777940	7.379018370	3.577163590
6	-1.341061890	8.069872020	2.442674450
6	-2.964616300	3.718469360	1.284455440
6	-2.169770070	3.810639950	2.643628570
1	-3.520908590	0.957271330	-1.049062520
1	-3.864097450	-1.451068330	-0.588308970
1	-2.862323950	-2.577632840	1.352463130

1	-1.260976670	-2.326080900	3.529065140
1	-0.010661270	-0.777845640	5.026038500
1	0.262974210	1.643333160	4.465441790
1	-1.422189850	3.056154670	-0.219737250
1	-0.064886230	3.397990010	1.940501410
1	-3.582425290	7.473506070	-1.639326360
1	-3.937189680	5.063350710	-1.197188980
1	-2.417275870	8.946787680	-0.054653000
1	-0.715793520	5.498577960	4.687671230
1	-0.305249910	7.941578510	4.349355570
1	-1.196532860	9.146942820	2.360906010
1	-3.975780010	3.294370560	1.326104710
1	-2.650426940	3.381767560	3.531003950
44	-2.997794150	7.029189720	3.485874750
44	0.371472640	-0.234909950	2.129943240
6	1.853656510	0.395185960	0.629360170
1	1.811695550	1.320144690	0.061861770
1	3.025196630	0.967573380	2.466938810
6	2.492801790	0.209673270	1.899422950
6	2.335254070	-1.167482520	2.278253260
1	2.721593810	-1.629374740	3.182427590
1	1.320100190	-2.878586020	1.225420530
6	1.599719760	-1.829088000	1.241029040
6	1.300027150	-0.863250380	0.228648590
1	0.739734910	-1.052530930	-0.682999820
6	-5.158755100	7.465587560	3.378859260
1	-5.726661930	7.478366320	2.452482020
1	-4.455474920	9.593630470	3.558375510
6	-4.480498890	8.584175920	3.958691270
6	-3.841397920	8.137725840	5.161527280
1	-3.255917650	8.751579620	5.840151900
1	-3.808391280	6.116183580	6.152637210
6	-4.132327180	6.739973830	5.324456910
6	-4.949880810	6.326588720	4.221444170
1	-5.355202830	5.331885420	4.061314760

[*anti*-**2''**]$^{2+}$ $E = -10372.83176001$ a.u.

6	-2.501530590	0.552469490	-0.231468380
6	-2.631320970	-0.862008040	-0.048718260
6	-2.252511180	-1.505948760	1.108043770
6	-1.680159680	-0.752768650	2.182861310
6	-1.580409250	0.659822090	1.984096580
6	-1.990918140	1.317147760	0.787083800
6	-1.201359770	-1.251084310	3.444467400
6	-0.596803300	-0.373810080	4.388332160
6	-0.537150700	1.040873900	4.166670150
6	-1.049964720	1.564518250	2.955331370
6	-1.696507230	2.786329990	0.935362110
6	-1.005723800	2.951953090	2.342302990
6	-3.639330670	6.868706890	-0.746701270
6	-3.676823960	5.482388270	-0.389419230
6	-3.026231890	5.063189340	0.743672850
6	-2.359190160	6.040361280	1.539698940
6	-2.324339220	7.432579200	1.215311420
6	-2.985425340	7.818939270	0.005452560
6	-1.740202830	5.477474420	2.698697280
6	-1.098126680	6.342832870	3.617079620
6	-1.065927070	7.747906670	3.336204440
6	-1.618761130	8.281164840	2.137860220
6	-2.876041330	3.726591340	1.420444390
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1	-2.797232130	0.991124430	-1.185268630

1	-3.032799880	-1.453259480	-0.872223740
1	-2.345483480	-2.588511440	1.196001760
1	-1.279663750	-2.313695830	3.673438670
1	-0.227507640	-0.778981290	5.329740650
1	-0.115772550	1.686493540	4.936745530
1	-1.154687260	3.206093950	0.078833810
1	0.021518480	3.340220650	2.351303550
1	-4.168171830	7.183272790	-1.646873170
1	-4.236637960	4.789631630	-1.018937840
1	-3.002403720	8.868086950	-0.290039270
1	-0.616688350	5.965641520	4.518923010
1	-0.550549940	8.414855850	4.026388120
1	-1.524617820	9.347137730	1.931662910
1	-3.824896120	3.185603130	1.522024470
1	-2.602430050	3.766738930	3.697882060
44	-0.152476840	6.709235140	1.632124780
44	-2.641987990	0.325714530	4.006014210
6	-3.693006650	-0.035621390	5.877054920
1	-3.221247960	-0.440905930	6.767773010
1	-3.442119910	2.184141190	6.141534010
6	-3.805731720	1.356104310	5.539773700
6	-4.515719540	1.453476830	4.298223180
1	-4.796443680	2.370383460	3.789085600
1	-5.364168290	-0.142688010	2.957493410
6	-4.835524150	0.124786790	3.868369170
6	-4.335476730	-0.793756750	4.843924600
1	-4.425963790	-1.875655100	4.808002530
6	0.927310460	6.536413970	-0.285831950
1	0.438288150	6.465444240	-1.253580230
1	1.173999030	8.754825910	-0.018317220
6	1.311028770	7.749119340	0.368677270
6	1.909415110	7.403527390	1.624685740
1	2.315491230	8.100471540	2.352420850
1	2.309464030	5.401159510	2.569010540
6	1.899503180	5.971795010	1.740581980
6	1.295141610	5.437298580	0.555432730
1	1.170012730	4.385542650	0.316907080

[*anti*-**2'''**]$^{2+}$ $E = -10372.83397833$ a.u.

6	-2.805364160	0.329245950	-0.028512510
6	-3.039086400	-1.033850280	0.348923410
6	-2.455383510	-1.594462040	1.520004440
6	-1.698995650	-0.773410270	2.427090570
6	-1.502732790	0.586985920	2.030813160
6	-2.004729550	1.142317530	0.811959750
6	-1.085450720	-1.169099050	3.658658750
6	-0.378907060	-0.245135320	4.396157960
6	-0.205155540	1.114704030	3.982258000
6	-0.755694290	1.529993960	2.795944880
6	-1.625485460	2.607159830	0.758029270
6	-0.836512690	2.865763710	2.102781370
6	-3.538886540	6.889147610	-0.746383440
6	-3.485860340	5.472655650	-0.536855530
6	-2.849195800	4.977385080	0.626333920
6	-2.309866670	5.910312650	1.565716720
6	-2.321996890	7.327898430	1.376575640
6	-2.926797200	7.800077490	0.159831760
6	-1.773998400	5.275453100	2.724417790
6	-1.239952030	6.067022550	3.709942650
6	-1.214792560	7.487587190	3.531474350
6	-1.722361270	8.111670830	2.413747340

6	-2.758342120	3.589275190	1.230067840
6	-2.018247280	3.794007140	2.603535110
1	-3.214833780	0.702919160	-0.966603720
1	-3.620461760	-1.674520690	-0.313190620
1	-2.602835820	-2.651853750	1.738763290
1	-1.204373990	-2.191453260	4.017734640
1	0.064536310	-0.556246980	5.342519470
1	0.356734060	1.794898420	4.623573340
1	-1.143819340	2.903238180	-0.181309050
1	0.125710880	3.386607970	2.026113690
1	-4.005557480	7.274051670	-1.652401160
1	-3.924345880	4.804214760	-1.277212920
1	-2.938970370	8.867021630	-0.061875830
1	-0.854104150	5.644596760	4.638476620
1	-0.793891480	8.099669890	4.329703730
1	-1.710582580	9.198618600	2.331869830
1	-3.756092720	3.131620150	1.276429110
1	-2.526867380	3.381564600	3.483946640
44	-1.426175080	6.331515050	-0.521971780
44	-0.864886200	-0.714759290	0.255512850
6	1.055403500	-0.162289410	-0.665899260
1	1.499838630	0.828069100	-0.640061430
1	1.909000260	-1.140516940	1.171463000
6	1.285431720	-1.209210920	0.284177730
6	0.542960140	-2.360368090	-0.128272860
1	0.514838250	-3.318828890	0.382122910
1	-0.800264770	-2.690235140	-1.904344590
6	-0.157289210	-2.026189320	-1.333541500
6	0.160850240	-0.665290930	-1.667261530
1	-0.196260570	-0.127487670	-2.540774630
6	-0.533909440	6.767266000	-2.458762020
1	-1.092977240	7.133908960	-3.315027550
1	0.128742220	8.659837130	-1.436982090
6	0.117519930	7.574080380	-1.469106800
6	0.747477250	6.698822860	-0.529828800
1	1.312305540	7.007752090	0.345514590
1	0.875776960	4.458463500	-0.444729330
6	0.498797840	5.348253650	-0.939420680
6	-0.296804570	5.388565920	-2.131909050
1	-0.640355750	4.535418800	-2.709756440