Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Pendant Amine Bases Speed up Proton Transfers to Metals by Splitting the Barriers

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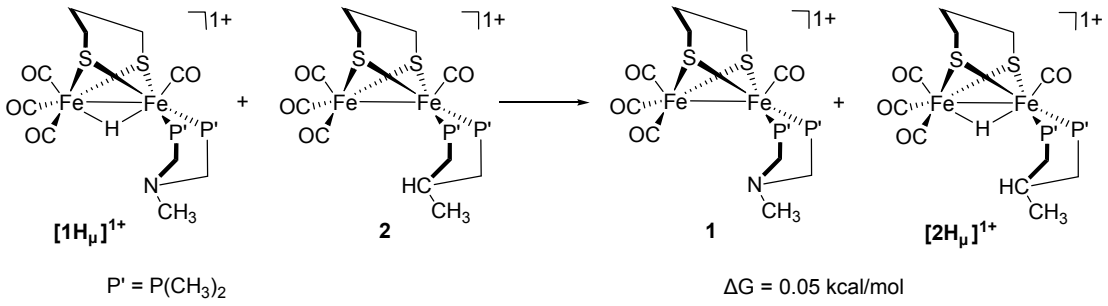


Figure S1.

From proton exchange equation between [**1**(H_μ)]$^{1+}$ and [**2**(H_μ)]$^{1+}$, the free energy difference is only 0.05 kcal/mol, which indicates these two complexes [**1**(H_μ)]$^{1+}$ and [**2**(H_μ)]$^{1+}$ have almost identical pKa, and hence, it is not that the pKa of the hydride determining the rated of deprotonation.

Table S1. Natural Population Analysis of complexes in Figure **4**.

	H(migrated)	N(pendant amine)	N (aniline or anilineH$^+$)	Fe1 + Fe2
[**1**(H$_\mu$)]$^{1+}$ + aniline	-0.1111	-0.5199	-0.8484	-0.6609
ts1 [**1**(H$_\mu$)]$^{1+}$+ aniline	0.1240	-0.4839	-0.8484	-0.6751
[**1**(H$_N$)]$^{1+}$ + aniline	0.4695	-0.4478	-0.8484	-0.6908
ts2 [**1**-H$_N$-aniline]$^{1+}$	0.4742	-0.5179	-0.8627	-0.6407
1 + anilineH$^+$	0.4858	-0.5146	-0.7948	-0.6388
TS [**1**-H$_\mu$-aniline]$^{1+}$	0.1282	-0.5376	-0.8438	-0.6175

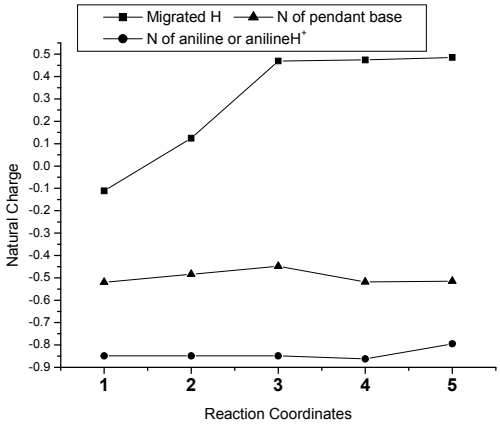
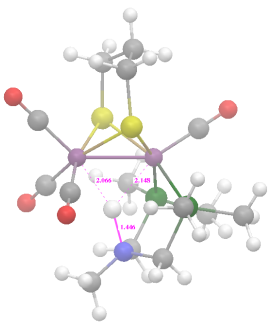
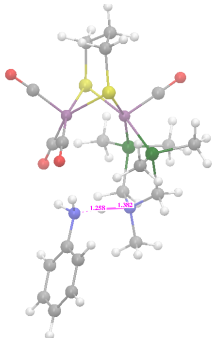


Figure S2. The chart of natural charges of complexes in path **B** of Figure 4. (1) [**1**(H$_\mu$)]$^{1+}$ + aniline; (2) **ts1** [**1**(H$_\mu$)]$^{1+}$+ aniline; (3) [**1**(H$_N$)]$^{1+}$ + aniline; (4) **ts2** [**1**-H$_N$-aniline]$^{1+}$; (5) **1** + anilineH$^+$.

Natural charges of N of pendant amine and N of aniline or aniline-H$^+$ change slightly. Only the natural charge on the migrated H changes significantly, from negative in [**1**(H$_\mu$)]$^{1+}$ to positive in [**1**(H$_N$)]$^{1+}$, until it finally goes to aniline, which it still carries a positive partial charge.



(1)



(2)

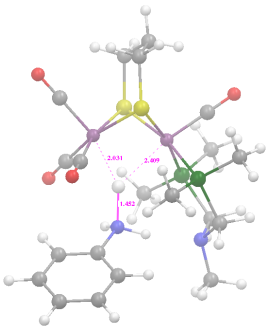
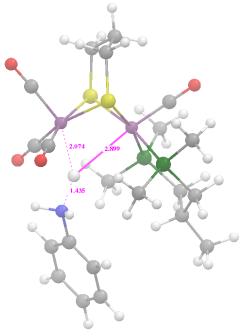
(3)  (4) 

Figure S3. Optimized structures for the transition states. (1) **ts1 [1(H_μ)]$^{1+}$**; (2) **ts2 [1-H_N-aniline]$^{1+}$**; (3) **TS [1-H_μ-aniline]$^{1+}$**; (4) **TS [2-H_μ-aniline]$^{1+}$**; Purple = Fe; red = O; blue = N; green = P; yellow = S; grey = C; white = H. The bond lengths are given in Å.

Theoretical Studies. All Density Functional Theory (DFT) calculations were carried out with Jaguar 7.6 program package by Schrödinger LLC. For geometry optimizations, solvation energy, and frequency calculations, Becke's three-parameter hybrid functional and the LYP correlation functional (B3LYP)[i] was used with the LACVP** core potential and basis set, while single point energy corrections were performed with the M06[ii] functional using the LACV3P**++ basis set which, as suggested by Martin,[iii] was augmented with two f-polarization functions on Fe. Frequency calculations were performed on the optimized geometries to verify that the geometries correspond to minima or first-order saddle points (transition states) on the potential energy surface (PES). All transition states were confirmed to connect the reactants and products by the intrinsic reaction coordinate (IRC) calculations. [iv] The Gibbs free energies were defined as the following equation G = E(M06/LACV3P**++ 2f on Fe) + G_{solv} + ZPE + H_{298} + TS_{298}. The enthalpic energies were defined as the following equation H = E(M06/LACV3P**++ 2f on Fe) + G_{solv} + ZPE + H_{298}. The entropic energies were defined as S = TS_{298}. Based on the gas-phase-optimized structures, the effect of solvent was evaluated by single-point calculations using the Poisson-Bolzmann reactive field implemented in Jaguar 7.6 (PBF)[v] in dichloromethane

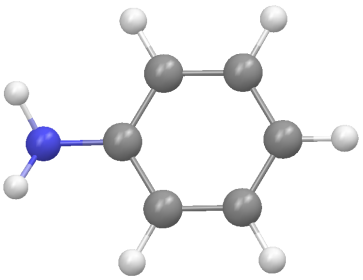
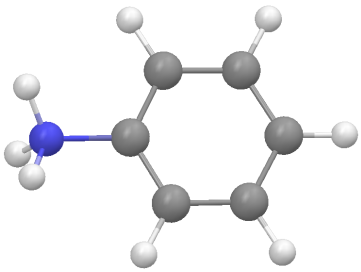
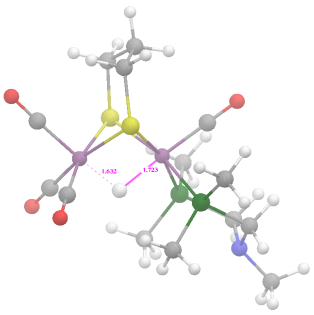
a)  b) 

Figure S4. Optimized geometries of the 1) Ph-NH_2 and 2) Ph-NH_3^+. Blue = N; Grey = C; White = H. The bond lengths are given in Å.

a)



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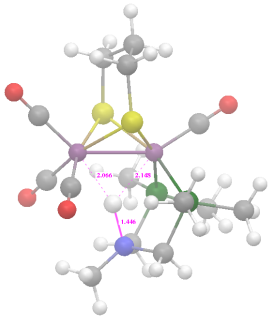

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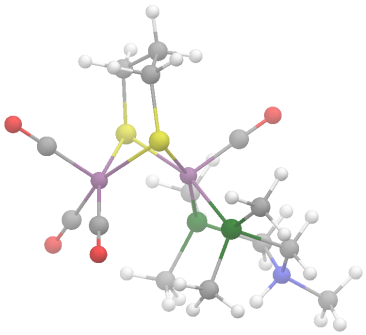
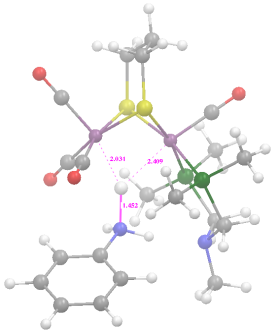
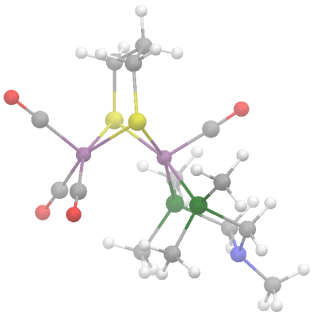


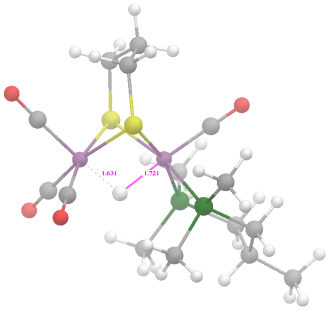
d)



e)



f)



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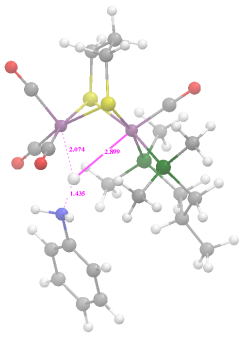

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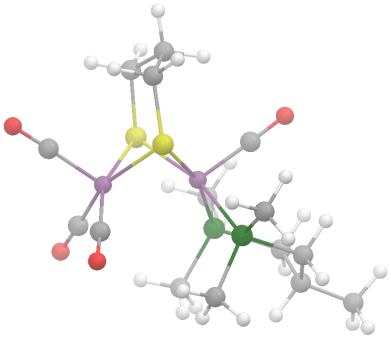

i)

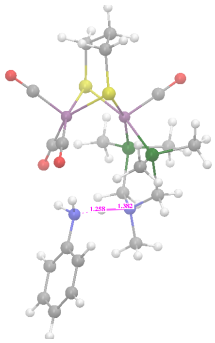

Figure S5. Optimized geometries of a) [**1**(H_μ)]$^{1+}$; b) **ts1 [1(H_μ)]$^{1+}$**; c) [**1**(H_N)]$^{1+}$; d) **TS [1-H_μ-aniline]$^{1+}$**; e) **1**; f) [**2**(H_μ)]$^{1+}$; g) **TS [2-H_μ-aniline]$^{1+}$**; h) **2**; i) **ts2 [1-H_N-aniline]$^{1+}$**. Purple = Fe; Red = O; Blue = N; Green = P; Yellow = S; Grey = C; White = H. The bond lengths are given in Å.

IRC-calculation results:

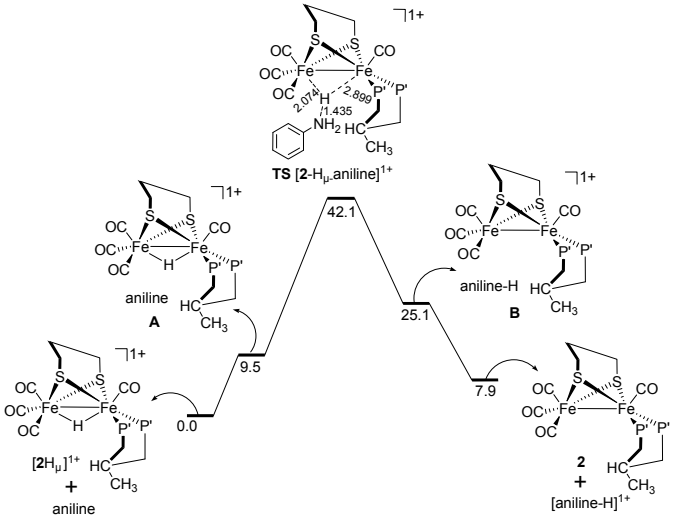

Fig. S6 profiles of the calculated relative G for deprotonation of complexes $[\mathbf{2}(\mathrm{H}\mu)]^{1+}$

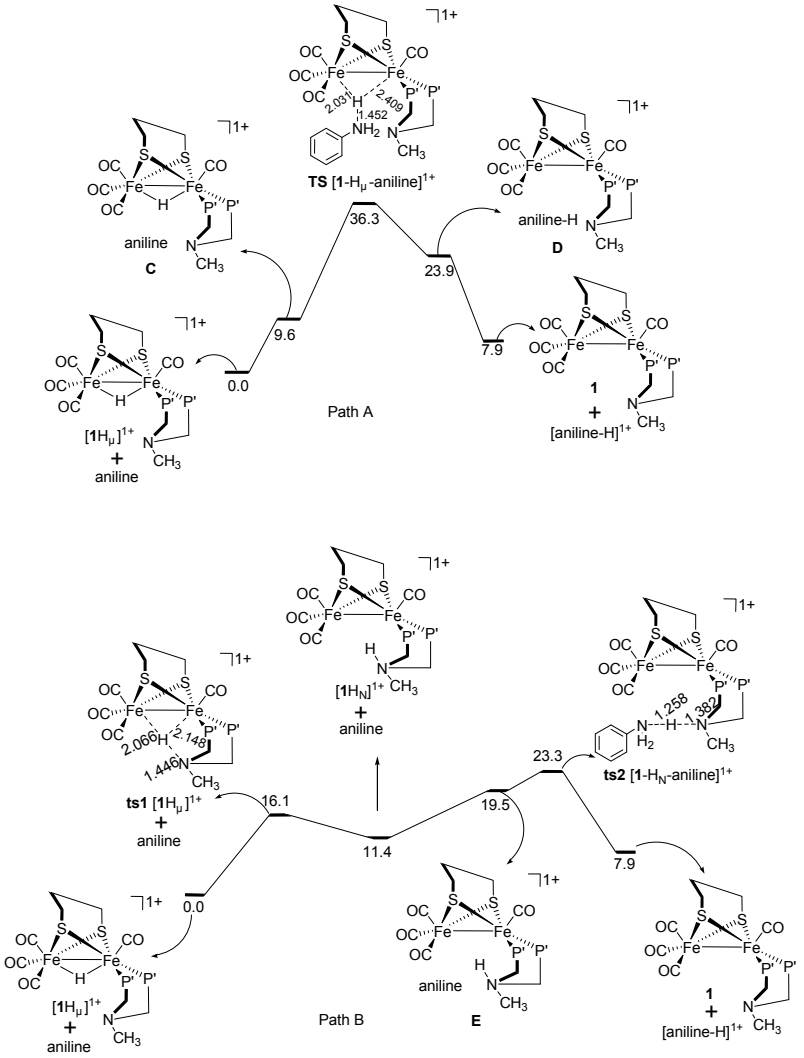

Fig. S7 Profiles of the calculated relative G for path A and B of deprotonation of complex $[\mathbf{1}(H\mu)]^{1+}$.

Cartesian coordinates of computed structures

Cartesian coordinates of **Figure S4a**

E (M06/LACV3P++ 2f(Ru)) = -287.45803757358**

ZPE (kcal mol^{-1}) = 73.683

G_{solv} = -0.010507

DH_{298} (kcal mol^{-1})= 4.221

DS_{298} (cal K^{-1} mol^{-1})= 75.506

atom	x	y	z
C1	0.1540100300	-0.0062842783	-0.9309231110
C2	0.0885825832	1.2057053096	-0.2226778008
C3	-0.0421751223	1.2077906757	1.1637503344
C4	-0.1113324502	0.0093268852	1.8769680912

C5	-0.0474906369	-1.1965763937	1.1769287101
C6	0.0835619731	-1.2099208505	-0.2095851727
H7	0.1364215858	2.1460383497	-0.7672047032
H8	-0.0890498457	2.1572116339	1.6906037664
H9	-0.2114650853	0.0151000455	2.9579390537
H10	-0.0980445190	-2.1401613030	1.7139861011
H11	0.1275203395	-2.1564890070	-0.7436174993
H12	0.6338290154	0.8166991291	-2.7352925006
N13	0.2274925763	-0.0142270286	-2.3273365951
H14	0.6248323508	-0.8542051639	-2.7260430826

Cartesian coordinates of **Figure S4b**

E (M06/LACV3P++ 2f(Ru)) = -287.80037054226**

ZPE (kcal mol^{-1}) = 82.628

G_{solv} = -0.1024214

DH_{298} (kcal mol^{-1})= 4.512

DS_{298} (cal K^{-1} mol^{-1})= 80.401

atom	x	y	z
C1	0.1270584904	-0.0063625073	-0.8741395422
C2	0.0786173620	1.2210461659	-0.2250108816
C3	-0.0288499246	1.2183581527	1.1665668448
C4	-0.0870293329	0.0100683512	1.8638579699
C5	-0.0368481241	-1.2065945710	1.1806027218
C6	0.0706066723	-1.2260234006	-0.2107933048
H7	0.1236386914	2.1589040207	-0.7726695194
H8	-0.0639548072	2.1617076165	1.7007843083
H9	-0.1687355822	0.0165666081	2.9458272496
H10	-0.0782604150	-2.1434322554	1.7257584876
H11	0.1095571070	-2.1704475392	-0.7475195688
H12	0.7104481011	0.8137063565	-2.7171784056
N13	0.2150667144	-0.0153615030	-2.3698097298
H14	0.7262773323	-0.8392154422	-2.7066253468
H15	-0.7137326669	-0.0270883729	-2.8109473752

Cartesian coordinates of **Figure S5a**

E (M06/LACV3P++ 2f(Ru)) = -2630.45355880349**

ZPE (kcal mol^{-1}) = 245.91

G_{solv} = -0.0581464

DH_{298} (kcal mol^{-1})= 21.432

DS_{298} (cal K^{-1} mol^{-1})= 203.62

atom	x	y	z

S1	-6.1224945218	3.5446213421	-1.6032465485
Fe2	-5.7687758580	1.2669511368	-1.9964086136
S3	-7.9744970846	1.0079970894	-1.2674491886
Fe4	-6.7042400965	2.2486613253	0.2550960878
O5	-8.9439283669	3.9921761475	1.0619617232
C6	-8.0710112252	3.3148678590	0.7684196649
O7	-4.6065618766	3.6499196198	1.7952177531
C8	-5.4278524795	3.1093906553	1.2130190677
O9	-7.1757816865	0.1289544467	2.2600169826
C10	-6.9962230702	0.9602865738	1.4969119376
O11	-6.1066282882	1.1245776079	-4.8925525191
C12	-5.9782898347	1.1852498869	-3.7478503612
N13	-2.7320068637	-1.0221770559	-2.5525557296
C14	-1.5905601242	-1.8960683438	-2.8594324450
H15	-1.7026917187	-2.8432826497	-2.3253423371
H16	-1.4904208802	-2.1123736650	-3.9365778674
H17	-0.6669843676	-1.4240097733	-2.5141280906
C18	-4.0030591706	-1.6533420083	-2.8962186206
H19	-3.9319202718	-2.7259600076	-2.6884330192
H20	-4.2608079387	-1.5487008408	-3.9672907125
C21	-2.5784319778	0.2984267777	-3.1561116121
H22	-2.8903877623	0.3263857377	-4.2175186306
H23	-1.5204409262	0.5787700054	-3.1271092024
P24	-5.4311147811	-1.0138432786	-1.8813427241
P25	-3.5020908695	1.6317863581	-2.2357494845
C26	-6.8099548716	-2.0546888455	-2.5225198585
H27	-7.0392315281	-1.7759494732	-3.5545509883
H28	-6.5430177452	-3.1154689296	-2.4888544274
H29	-7.7045430028	-1.8920445679	-1.9178270391
C30	-5.0809757839	-1.7323284839	-0.2219752949
H31	-4.9608683841	-2.8177928454	-0.2927063788
H32	-4.1601119213	-1.2990753154	0.1742630429
H33	-5.9004856659	-1.5154294284	0.4658084433
C34	-3.0385408899	3.1197693453	-3.2187350303
H35	-3.5045493676	3.0742322235	-4.2067232963
H36	-3.3953713336	4.0197420090	-2.7137124052
H37	-1.9525612603	3.1830111114	-3.3378275550
C38	-2.5067857737	1.8027038939	-0.6955028844
H39	-1.4571206443	1.9954341860	-0.9378214303
H40	-2.8833722805	2.6296788260	-0.0905068068
H41	-2.5729531444	0.8793359405	-0.1160716606
C42	-7.6593972886	4.2044098355	-2.3968090645
H43	-8.1815761972	4.7925841806	-1.6359952617
H44	-7.2913470638	4.9085321801	-3.1485153471

C45	-9.1745061275	2.1289656179	-2.1224007867
H46	-9.8162495861	1.4501983362	-2.6913922796
H47	-9.7969895072	2.5799720400	-1.3435822760
C48	-8.5877028782	3.1866260405	-3.0518924015
H49	-9.4282781354	3.7422168942	-3.4897564298
H50	-8.0752463995	2.7021472065	-3.8869610053
H51	-5.4976398582	1.2971816843	-0.2956436141

Cartesian coordinates of **Figure S5b**

E (M06/LACV3P++ 2f(Ru)) = -2630.42225560999**

ZPE (kcal mol^{-1}) = 244.926

G_{solv} = -0.0643015

DH_{298} (kcal mol^{-1})= 21.009

DS_{298} (cal K^{-1} mol^{-1})= 197.791

atom	x	y	z
H35	-0.0421941903	-0.0385617606	-0.0143474036
N13	-0.0702182259	-0.0042162456	1.4314231362
Fe2	1.7770667600	0.0032489680	-1.1558135205
Fe4	-0.6623943032	-0.2452459925	-1.9737075654
S3	1.0695987568	-1.7036485478	-2.5373021185
S1	0.8107867931	1.4083122175	-2.7104547992
O5	-2.1141733989	-0.5171370513	-4.5236818718
C6	-1.5486521348	-0.4124693340	-3.5323564830
O7	-2.3281628080	1.8971585195	-0.8503724657
C8	-1.6867746309	1.0463908217	-1.2868396144
O9	-1.9204766860	-2.5011825300	-0.5763250146
C10	-1.4441101197	-1.6069936022	-1.1239910488
O11	4.6063999549	0.1872316011	-1.8332300858
C12	3.4866026765	0.1148869208	-1.5627443117
C14	-1.4464525644	0.0146382910	1.9809698202
H15	-1.4372520500	-0.0217732079	3.0760451294
H16	-1.9512501115	0.9258746176	1.6565768177
H17	-1.9957727226	-0.8491575559	1.6026572862
P18	1.7939796313	1.7281406972	0.3356063405
P19	2.0552678562	-1.5253260171	0.5239476391
C20	1.2941695194	1.0708438883	-4.4646117866
H21	0.3667172523	1.0335242591	-5.0445302540
H22	1.8325140550	1.9713096714	-4.7737149437
C23	1.5057938647	-1.4861282898	-4.3229423585
H24	2.1869667135	-2.3147582487	-4.5362410658
H25	0.5897623685	-1.6648186964	-4.8945282895
C26	2.1541971041	-0.1628180640	-4.7106338092
H27	2.3799885494	-0.2038152194	-5.7851256628
H28	3.1144073505	-0.0549993993	-4.1979677068
C29	0.6413675253	-1.2613744563	1.7450032062

H30	-0.0632742268	-2.0868825204	1.6186535038
H31	0.9935744245	-1.2656397967	2.7836291916
C32	0.7128591346	1.2018767496	1.7956616572
H33	1.3240641649	1.0152321316	2.6858737845
H34	0.0220236356	2.0142536929	2.0315811331
C39	1.0599703974	3.3636643599	-0.1084429228
H40	1.0940230356	4.0302853040	0.7589665911
H41	1.6292750685	3.8111664940	-0.9257311540
H42	0.0260538348	3.2546819933	-0.4392405326
C42	3.3715845286	2.2822258997	1.1165491553
H43	3.1854284225	2.9731663969	1.9442436076
H44	3.9658480966	1.4400652868	1.4728943527
H45	3.9588173094	2.8065727051	0.3565719518
C45	3.5635387758	-1.4780615235	1.5898136499
H46	3.5329410036	-2.2735730970	2.3401408055
H47	4.4493575856	-1.6222438318	0.9645746561
H48	3.6607363882	-0.5196297379	2.1027198084
C48	1.9325933235	-3.3345329412	0.1898602616
H49	1.9652782358	-3.8935612635	1.1299089155
H50	1.0120674189	-3.5694466645	-0.3462618415
H51	2.7737313511	-3.6416761596	-0.4366298775

Cartesian coordinates of **Figure S5c**

E (M06/LACV3P++ 2f(Ru)) = -2630.41563279857**

ZPE (kcal mol^{-1}) = 249.449

G_{solv} = -0.0829222

DH_{298} (kcal mol^{-1})= 21.326

DS_{298} (cal K^{-1} mol^{-1})= 204.494

atom	x	y	z
S1	-6.1712680787	3.5411302298	-1.7054425923
Fe2	-5.7924378975	1.2843798927	-1.9947406232
S3	-7.9987009256	1.0361810408	-1.3700835737
Fe4	-6.7844705760	2.2941921530	0.1385733363
O5	-8.9166690651	3.9935203542	1.2409838549
C6	-8.0835900055	3.3297794796	0.8088085287
O7	-4.4885502999	3.4646177639	1.5377340554
C8	-5.3871057063	2.9902616870	0.9876573058
O9	-6.9855702083	0.0336735409	1.9955470434
C10	-6.8918725891	0.9225598329	1.2632572019
O11	-5.9292024046	0.9965301897	-4.8901337920
C12	-5.8826584688	1.1170295038	-3.7348376296
N13	-2.7436323814	-1.0210999812	-2.5851029189
C14	-1.6976090346	-1.8762653190	-3.2556854830
H15	-1.7616398041	-2.8909902479	-2.8611308746

H16	-1.8922264442	-1.8774705189	-4.3286787614
H17	-0.7118259817	-1.4559662366	-3.0532793565
C18	-4.1261814252	-1.6222754881	-2.7697912567
H19	-4.0200081400	-2.6974038295	-2.6019611903
H20	-4.4065334007	-1.4529509495	-3.8122198680
C21	-2.6294623666	0.4232981872	-3.0414039576
H22	-3.0036322539	0.4596627524	-4.0673891610
H23	-1.5625462364	0.6621693111	-3.0453770052
P24	-5.4602578838	-0.9129373314	-1.6313218167
P25	-3.5735389315	1.6726135966	-1.9789183133
C26	-6.8002973712	-2.0857207701	-2.1123327101
H27	-7.1208423608	-1.8790424942	-3.1364889112
H28	-6.4850613059	-3.1293812985	-2.0196749645
H29	-7.6563637743	-1.9072435304	-1.4579247444
C30	-4.8861371160	-1.6469103985	-0.0262167002
H31	-4.6579263289	-2.7140011086	-0.1207105106
H32	-4.0164040728	-1.1157069982	0.3722819220
H33	-5.6817987922	-1.5276937738	0.7121273021
C34	-2.9545410256	3.1889408225	-2.8275432213
H35	-3.3784668110	3.2479784205	-3.8330703837
H36	-3.3115016833	4.0572413879	-2.2692596861
H37	-1.8618773949	3.2149177205	-2.8772954129
C38	-2.4992529232	1.6326790092	-0.4656805128
H39	-1.4356993408	1.7129644481	-0.7148754932
H40	-2.7698457734	2.4768060969	0.1720593104
H41	-2.6735278930	0.7308141329	0.1290252585
C42	-7.6736025355	4.1779913657	-2.5791084926
H43	-8.2297238837	4.7575687499	-1.8355021807
H44	-7.2910468956	4.8809985647	-3.3245745756
C45	-9.1789694703	2.1140582579	-2.3034138020
H46	-9.8139892011	1.4209413037	-2.8625573840
H47	-9.8058354215	2.5972039772	-1.5472676660
C48	-8.5667511917	3.1405799324	-3.2490835658
H49	-9.3904609891	3.6755004422	-3.7421808279
H50	-8.0131247131	2.6306773181	-4.0431133567
H51	-2.5367987734	-1.0391045077	-1.5804125669

Cartesian coordinates of **Figure S5d**

E (M06/LACV3P++ 2f(Ru)) =** -2917.88586852164

ZPE (kcal mol^{-1}) = 319.984

G_{solv} = -0.060626

DH_{298} (kcal mol^{-1})= 25.365

DS_{298} (cal K^{-1} mol^{-1})= 231.003

atom	x	y	z

S1	-6.0213103391	3.5489457332	-1.9386573553
Fe2	-6.0445821221	1.2665812292	-2.2161344810
S3	-8.2407529006	1.3582756350	-1.5423540882
Fe4	-6.8994829107	2.5282757146	-0.0246007606
O5	-8.8644324472	4.6450934307	0.5793787155
C6	-8.1036456104	3.8233075891	0.3302889374
O7	-4.7131553137	3.8356183748	1.4440385183
C8	-5.5563898535	3.2864285673	0.8905953439
O9	-7.7856324972	0.6395315347	2.0297346283
C10	-7.4375443489	1.3972845063	1.2327083676
O11	-6.3421031196	1.1964107477	-5.1080457546
C12	-6.2282417695	1.2181919428	-3.9576274761
N13	-3.4619099006	-1.3485788877	-1.4798232157
C14	-2.4676425935	-2.3597667606	-1.0655261578
H15	-2.9480497579	-3.1043390230	-0.4254447121
H16	-2.0100126425	-2.8777677328	-1.9226384521
H17	-1.6734287194	-1.8791055954	-0.4881805022
C18	-4.5750452895	-1.9903082768	-2.2046782579
H19	-4.7534602780	-2.9792057946	-1.7711780918
H20	-4.3256685787	-2.1481761792	-3.2677893925
C21	-2.8147056552	-0.3069189405	-2.2976597078
H22	-2.6374469194	-0.6662320772	-3.3261209150
H23	-1.8327224074	-0.0883553271	-1.8668387015
P24	-6.1872782850	-1.0408408023	-2.1060346670
P25	-3.7418097233	1.3276344109	-2.4119014903
C26	-7.1236459745	-1.7854055130	-3.5108905444
H27	-6.6886219162	-1.4901135147	-4.4681043667
H28	-7.1339173246	-2.8772504438	-3.4432303387
H29	-8.1534277450	-1.4197384674	-3.4735039658
C30	-7.0279260232	-1.8634927420	-0.6708590107
H31	-7.3404124378	-2.8732768118	-0.9530867429
H32	-6.3550693419	-1.9533630250	0.1844218132
H33	-7.9104670779	-1.2933445510	-0.3739758760
C34	-3.1362377388	1.9341604027	-4.0467219926
H35	-3.5150216718	1.3084799721	-4.8582587581
H36	-3.5016883350	2.9532462963	-4.1986637312
H37	-2.0427384074	1.9433628147	-4.0827787879
C38	-2.7984925307	2.4338720020	-1.2722493767
H39	-1.7313806368	2.4087964621	-1.5156308740
H40	-3.1627853074	3.4562482202	-1.3987723812
H41	-2.9344933490	2.1500480751	-0.2286560322
C42	-7.4139720464	4.4075245114	-2.8104601959
H43	-7.8328857921	5.1175411085	-2.0912460179
H44	-6.9288117123	4.9944344724	-3.5957619680

C45	-9.2508999573	2.6077541005	-2.4676783781
H46	-9.9823874215	2.0157677421	-3.0252218168
H47	-9.8040810404	3.1763515786	-1.7145400201
C48	-8.5017505740	3.5302455450	-3.4257390814
H49	-9.2432514612	4.2014027489	-3.8812377213
H50	-8.0825860934	2.9443730194	-4.2472855309
H51	-5.4696666294	1.0934136031	0.1165495582
C52	-2.1892714903	1.2559860794	4.0714491804
C53	-3.5734938911	1.2080727706	4.2433711478
C54	-4.4044582370	0.8199041963	3.1929118286
C55	-3.8456474982	0.4767498852	1.9569110992
C56	-2.4575070570	0.5093706548	1.7852399871
C57	-1.6350700242	0.9003965787	2.8415858672
H58	-1.5469870960	1.5585226150	4.8924346091
H59	-4.0122609356	1.4698117790	5.2014337742
H60	-5.4792331806	0.7715905262	3.3409299296
H61	-2.0176665770	0.2138649225	0.8373684038
H62	-0.5580981549	0.9182196432	2.7034844228
H63	-4.2080566816	-0.4348577952	0.1265473239
H64	-5.4819718265	-0.4536526905	1.2006250444
N65	-4.7047990766	0.1072166616	0.8583545126

Cartesian coordinates of **Figure S5e**

E (M06/LACV3P++ 2f(Ru)) =** -2630.05374387562

ZPE (kcal mol^{-1}) = 239.986

G_{solv} = -0.0135451

DH_{298} (kcal mol^{-1})= 21.346

DS_{298} (cal K^{-1} mol^{-1})= 204.396

atom	x	y	z
S1	-6.1596736004	3.5456027668	-1.6849571658
Fe2	-5.8023188247	1.2894084092	-2.0035702985
S3	-7.9964914297	1.0264519142	-1.3422432522
Fe4	-6.7879946977	2.3047358679	0.1773576813
O5	-8.9163155421	4.0031373780	1.2760000933
C6	-8.0836147452	3.3366746343	0.8311036334
O7	-4.4841226439	3.4622800785	1.5638215086
C8	-5.3795848602	2.9814869904	1.0069604124
O9	-6.9706398085	0.0432870855	2.0274996672
C10	-6.8728472688	0.9278082086	1.2850880088
O11	-6.0407928969	1.0743533608	-4.8931313330
C12	-5.9264820368	1.1464254655	-3.7376263901
N13	-2.7539343540	-1.0075022535	-2.5447420639
C14	-1.6629322846	-1.8657792709	-3.0087638026

H15	-1.7396268278	-2.8475800700	-2.5320211802
H16	-1.6617411099	-2.0133957827	-4.1048033830
H17	-0.7026423113	-1.4265134573	-2.7223456165
C18	-4.0578468995	-1.6118336688	-2.8170651713
H19	-3.9857927907	-2.6879435047	-2.6253695365
H20	-4.3700013528	-1.4870550396	-3.8718984955
C21	-2.6275162308	0.3480958896	-3.0794274769
H22	-2.9750316350	0.4235390843	-4.1279119494
H23	-1.5677749236	0.6252715685	-3.0686898026
P24	-5.4227228354	-0.9511601236	-1.7209245863
P25	-3.5390384621	1.6305481100	-2.0670128192
C26	-6.8023470656	-2.0654769896	-2.2403371917
H27	-7.0977644607	-1.8274423755	-3.2656539356
H28	-6.5063368027	-3.1178645532	-2.1788300791
H29	-7.6657651071	-1.8914267858	-1.5951030305
C30	-4.9269279205	-1.6834252714	-0.0978335601
H31	-4.7825316612	-2.7651012731	-0.1917334614
H32	-3.9905573442	-1.2289923954	0.2321223215
H33	-5.6918796505	-1.4864062560	0.6539049854
C34	-2.9882773302	3.1622773937	-2.9414352718
H35	-3.4342561096	3.1934593511	-3.9390986778
H36	-3.3410177924	4.0365462863	-2.3906796274
H37	-1.8973131795	3.1997952792	-3.0263051748
C38	-2.4900609491	1.6574854924	-0.5454670392
H39	-1.4384188959	1.8182912303	-0.8060215562
H40	-2.8198371588	2.4510537237	0.1257473171
H41	-2.5834974206	0.7017904056	-0.0257913605
C42	-7.6822361091	4.1920647941	-2.5142980271
H43	-8.2300929808	4.7609666489	-1.7558337062
H44	-7.3218904073	4.9047471713	-3.2629495241
C45	-9.1884736386	2.1259006866	-2.2334457195
H46	-9.8414286200	1.4488942406	-2.7934674885
H47	-9.7991186749	2.6091131611	-1.4635613655
C48	-8.5890468915	3.1615125848	-3.1797487804
H49	-9.4200344357	3.7024131811	-3.6569861490
H50	-8.0470453593	2.6569243824	-3.9846291419

Cartesian coordinates of **Figure S5f**

E (M06/LACV3P++ 2f(Ru)) =** -2614.43296884257

ZPE (kcal mol^{-1}) = 253.352

G_{solv} = -0.0580328

DH_{298} (kcal mol^{-1})= 21.474

DS_{298} (cal K^{-1} mol^{-1})= 203.502

atom	x	y	z

S1	-6.1283436562	3.5412786340	-1.6399558970
Fe2	-5.7469001034	1.2556070770	-1.9668743636
S3	-7.9778439730	1.0074346140	-1.3060081579
Fe4	-6.7603461588	2.2850948012	0.2283136435
O5	-9.0314572961	4.0355981512	0.9236253980
C6	-8.1466901682	3.3560810195	0.6737503667
O7	-4.7142315073	3.7273049755	1.7994201349
C8	-5.5168423737	3.1720249664	1.2048949348
O9	-7.2843211020	0.2060216725	2.2624331212
C10	-7.0858797903	1.0223558384	1.4876910413
O11	-5.9772849973	1.0352050870	-4.8683424387
C12	-5.8939778823	1.1283782499	-3.7214331554
C14	-1.5789177551	-1.9732346937	-3.3646171726
H15	-1.6011964741	-3.0107915761	-3.0167100301
H16	-1.7768417054	-1.9759524166	-4.4426934433
H17	-0.5651919349	-1.5904575010	-3.2104198779
C18	-4.0224433753	-1.7129765871	-2.8174004564
H19	-3.9935297204	-2.7914788515	-2.6193136715
H20	-4.3240325963	-1.5976494186	-3.8668786697
C21	-2.5190982434	0.3475192080	-3.0940075485
H22	-2.8544666335	0.4163841507	-4.1373014478
H23	-1.4700000782	0.6676986108	-3.0834767735
P24	-5.3982332627	-1.0228764597	-1.7804059066
P25	-3.4694374047	1.6221261619	-2.1358753607
C26	-6.8054799558	-2.0905760813	-2.3050685656
H27	-7.0767492240	-1.8613788000	-3.3391182225
H28	-6.5317637849	-3.1474177605	-2.2327072554
H29	-7.6751248446	-1.8990138761	-1.6735571970
C30	-5.0142882271	-1.6613808178	-0.0918350645
H31	-4.8085404728	-2.7357145970	-0.1253948354
H32	-4.1470324418	-1.1473765857	0.3290051969
H33	-5.8657817347	-1.4910757667	0.5705178148
C34	-2.9752412246	3.1651377797	-3.0136457914
H35	-3.4071600244	3.1725610697	-4.0180380936
H36	-3.3496351978	4.0374885530	-2.4746046589
H37	-1.8858467629	3.2288701491	-3.0921778994
C38	-2.5332353506	1.7423138411	-0.5497654630
H39	-1.4627588398	1.8605208420	-0.7439906247
H40	-2.8810342059	2.6066943462	0.0199943892
H41	-2.6865286335	0.8483673384	0.0592336279
C42	-7.6411386997	4.1761234638	-2.4979086569
H43	-8.1915079153	4.7776564224	-1.7681149418
H44	-7.2509913876	4.8659553733	-3.2516157069
C45	-9.1544531526	2.1021469432	-2.2253560060

H46	-9.7751284767	1.4064051048	-2.7970821861
H47	-9.8030232652	2.5694889513	-1.4781583121
C48	-8.5420662870	3.1393956120	-3.1609181985
H49	-9.3695818488	3.6800938884	-3.6404226866
H50	-7.9990727515	2.6375123394	-3.9663407573
H51	-5.5342189002	1.3265191561	-0.2610307941
C51	-2.6149659034	-1.1156391512	-2.6158217108
H52	-2.3620913359	-1.1564027861	-1.5469599807

Cartesian coordinates of **Figure S5g**

E (M06/LACV3P++ 2f(Ru)) =** -2901.8497757289

ZPE (kcal mol^{-1}) = 326.902

G_{solv} = -0.06204

DH_{298} (kcal mol^{-1})= 25.834

DS_{298} (cal K^{-1} mol^{-1})= 238.085

atom	x	y	z
S1	-6.2050976211	3.4831822406	-1.8719550960
Fe2	-5.8166855630	1.2790807104	-2.3982826743
S3	-7.8542890824	0.8485258409	-1.4355021906
Fe4	-6.6531105651	2.2180587168	0.0554993140
O5	-9.0241356456	3.6979853943	0.9925996775
C6	-8.1123823042	3.1291655413	0.5899831686
O7	-4.7131400856	3.9605775666	1.3857757731
C8	-5.4866462490	3.2702090842	0.8765024532
O9	-6.8512788479	0.0535188274	2.0171239349
C10	-6.7700890199	0.9076553734	1.2435077898
O11	-6.4856209350	1.2807040963	-5.2208577251
C12	-6.2265473484	1.2794394433	-4.0932133337
C13	-1.4071958703	-1.7199959221	-3.4197082523
H14	-1.4090866831	-2.7007314595	-2.9334187138
H15	-1.4245959725	-1.8838640172	-4.5034078554
H16	-0.4625165275	-1.2240566664	-3.1733486434
C17	-3.9216510824	-1.6243416440	-3.3006689199
H18	-3.8256302290	-2.6829821673	-3.0302547405
H19	-4.0879295707	-1.5982226208	-4.3856222809
C20	-2.5592437106	0.5094909066	-3.6484282149
H21	-2.8264066847	0.4045468088	-4.7081207640
H22	-1.5328106358	0.8963782263	-3.6293324950
P23	-5.4813989764	-1.0088704261	-2.4965611868
P24	-3.6475829496	1.8415264586	-2.9436998140
C25	-6.7648835375	-1.8638327070	-3.5107641352
H26	-6.7827706416	-1.4598498804	-4.5258137387
H27	-6.5634031081	-2.9381832302	-3.5605139475

H28	-7.7457405103	-1.7058603678	-3.0563922600
C29	-5.5582333251	-1.9719416278	-0.9268273343
H30	-5.5624904314	-3.0447969471	-1.1448727477
H31	-4.7005563200	-1.7429081713	-0.2932018794
H32	-6.4729044801	-1.7181317011	-0.3858741246
C33	-3.5464304093	3.1326195069	-4.2572484445
H34	-4.0719179675	2.8011754222	-5.1559965928
H35	-4.0207344394	4.0483113331	-3.8965168786
H36	-2.5038022523	3.3441949559	-4.5128562521
C37	-2.5732763161	2.5794401447	-1.6332370017
H38	-1.6700253165	3.0105004012	-2.0759909208
H39	-3.1150852180	3.3630807062	-1.0983734284
H40	-2.2723411810	1.7973049895	-0.9348856502
C41	-7.8478626182	4.0881135062	-2.4862076167
H42	-8.3069915487	4.6334677082	-1.6567674891
H43	-7.6018111526	4.8234599934	-3.2577675827
C44	-9.2115875827	1.9000742907	-2.1383345958
H45	-9.8460737968	1.1979198163	-2.6871509920
H46	-9.7971931447	2.2636322420	-1.2893830542
C47	-8.7975982118	3.0414652237	-3.0652880701
H48	-9.7154236650	3.5651095358	-3.3674977888
H49	-8.3712189326	2.6300449083	-3.9834070228
H50	-4.8473736016	1.2367499433	0.3334610516
C51	-1.6071483566	-2.6194638076	1.6811550165
C52	-1.0152002471	-1.5241702203	1.0518853349
C53	-1.7181113639	-0.3256864588	0.9142863212
C54	-3.0240706059	-0.2324584168	1.4020760356
C55	-3.6222091514	-1.3232796979	2.0402180585
C56	-2.9070846035	-2.5122924519	2.1799553242
H57	-1.0545889281	-3.5467466398	1.7952692292
H58	0.0033941092	-1.5913532020	0.6822490080
H59	-1.2322537292	0.5361793305	0.4648981869
H60	-4.6340586629	-1.2422051295	2.4271596702
H61	-3.3689895290	-3.3556729496	2.6841301736
C65	-2.6131325868	-0.8766512765	-2.9698867399
H66	-2.5390481713	-0.7504696883	-1.8800848027
N65	-3.7768022251	0.9984737570	1.2584891682
H67	-4.2638245291	1.2050459206	2.1311003426
H68	-3.1566133423	1.7876186923	1.0803092289

Cartesian coordinates of **Figure S5h**

E (M06/LACV3P++ 2f(Ru)) =** -2614.03364430053

ZPE (kcal mol^{-1}) = 247.496

G_{solv} = -0.0133038

DH_{298} (kcal mol^{-1})= 21.339

DS_{298} (cal K^{-1} mol^{-1})= 203.756

atom	x	y	z
S1	-6.1590896540	3.5409802904	-1.7138226776
Fe2	-5.7852986216	1.2795857701	-1.9843326490
S3	-7.9974708726	1.0253394446	-1.3777515644
Fe4	-6.8267051674	2.3264571501	0.1522541482
O5	-8.9812945541	4.0343226357	1.1827684656
C6	-8.1386426376	3.3644082899	0.7624839531
O7	-4.5549793376	3.5068215308	1.5716675319
C8	-5.4381915941	3.0171907712	1.0025962760
O9	-7.0457092240	0.0888949069	2.0268297390
C10	-6.9337297423	0.9644660666	1.2754499599
O11	-5.9193102605	0.9879757343	-4.8735287830
C12	-5.8537748902	1.0959843834	-3.7166636870
C13	-1.6676175256	-1.9160880251	-3.4171933612
H14	-1.6823939894	-2.9666144997	-3.1073511046
H15	-1.9149810711	-1.8782197435	-4.4849521444
H16	-0.6441815534	-1.5445101086	-3.2974875839
C17	-4.0821302071	-1.6660259477	-2.7429041494
H18	-4.0472682975	-2.7474112893	-2.5583573469
H19	-4.4255879800	-1.5319675874	-3.7770416727
C20	-2.5733640448	0.4007496825	-3.0201804150
H21	-2.9363097708	0.5061747160	-4.0510151892
H22	-1.5212298540	0.7133270239	-3.0215734212
P23	-5.4086422917	-0.9577280571	-1.6414389378
P24	-3.5175679606	1.6352722257	-1.9912456145
C25	-6.8107637977	-2.0849812235	-2.0629452533
H26	-7.1348360275	-1.8920253462	-3.0890683524
H27	-6.5124835165	-3.1338042446	-1.9648852565
H28	-7.6551085817	-1.8804358154	-1.4018156394
C29	-4.9042902217	-1.6226416535	0.0122309200
H30	-4.6797696349	-2.6928358863	-0.0538418875
H31	-4.0232451157	-1.0967208239	0.3865845774
H32	-5.7105897610	-1.4708517009	0.7313101556
C33	-2.9532462277	3.2075272520	-2.7806619140
H34	-3.3703958766	3.2767998688	-3.7888079336
H35	-3.3247062437	4.0583027033	-2.2062308165
H36	-1.8605179639	3.2487542060	-2.8335432029
C37	-2.5225613142	1.6466276952	-0.4286096632
H38	-1.4541337315	1.7403250851	-0.6518227233
H39	-2.8314175671	2.4845939920	0.1980587809
H40	-2.6880523686	0.7288722998	0.1400207270
C41	-7.6617088086	4.1713040055	-2.5900960192
H42	-8.2302573582	4.7493555040	-1.8540350762

H43	-7.2840372576	4.8742550806	-3.3394715498
C44	-9.1691905459	2.1077966475	-2.3151707375
H45	-9.8072382799	1.4201677616	-2.8794314688
H46	-9.7988885865	2.6026402971	-1.5683008761
C47	-8.5468420476	3.1275870067	-3.2630908964
H48	-9.3644620232	3.6565806474	-3.7752611912
H49	-7.9785717834	2.6088612444	-4.0409602938
C50	-2.6633913217	-1.0790974642	-2.5943820845
H51	-2.3609626576	-1.1584037171	-1.5404383298

Cartesian coordinates of **Figure S5i**

E (M06/LACV3P++ 2f(Ru)) =** -2917.9020657002

ZPE (kcal mol^{-1}) = 321.973

G_{solv} = -0.065728

DH_{298} (kcal mol^{-1})= 25.276

DS_{298} (cal K^{-1} mol^{-1})= 233.885

atom	x	y	z
S1	-6.2765782838	3.6625121632	-1.6581051135
Fe2	-6.1979035343	1.4809102378	-2.3897868726
S3	-8.3060376590	1.2688735118	-1.4835319452
Fe4	-6.7503994638	2.1256826891	0.0329322518
O5	-8.7174188936	3.4418860303	1.7839147358
C6	-7.9508982919	2.9506800256	1.0817629591
O7	-4.2997891007	2.9724381916	1.3671213238
C8	-5.2857994355	2.6641492079	0.8293366810
O9	-6.4026035181	-0.5462353699	1.1506798434
C10	-6.5768732872	0.5136551071	0.6859424261
O11	-6.8923756946	1.8418996306	-5.1929699444
C12	-6.6066223239	1.6907373686	-4.0819767609
N13	-3.2650839040	-0.8429405693	-1.4943147186
C14	-2.1436622169	-1.8166027375	-1.3332735513
H15	-2.3928307312	-2.5305769310	-0.5452721310
H16	-1.9656169061	-2.3617531574	-2.2671854552
H17	-1.2357253485	-1.2825905324	-1.0454085849
C18	-4.5311222576	-1.6181533321	-1.7089147960
H19	-4.8811337287	-1.9426343355	-0.7239519468
H20	-4.2976085933	-2.5220032899	-2.2862450869
C21	-2.9234882226	0.1035553257	-2.5969111634
H22	-2.9857335116	-0.4249557093	-3.5571914242
H23	-1.8773079603	0.3956309290	-2.4647784616
P24	-5.9996800072	-0.7806467046	-2.5501961229
P25	-3.9496573353	1.6819064003	-2.7164655120
C26	-5.8106073348	-1.3958541554	-4.2883966848
H27	-4.9862474991	-0.8927149351	-4.8000861242
H28	-5.6483118465	-2.4774877236	-4.3219144144

H29	-6.7277229180	-1.1635055345	-4.8368188315
C30	-7.3217722461	-1.9182513157	-1.9452334651
H31	-7.0462002860	-2.9611710879	-2.1303885657
H32	-7.5028467130	-1.7706578973	-0.8796986409
H33	-8.2464669645	-1.6923418452	-2.4804250159
C34	-3.4625192928	2.1840661933	-4.4282277910
H35	-3.9174543355	1.5234948857	-5.1700957384
H36	-3.8418123958	3.1949427538	-4.6027056832
H37	-2.3764364655	2.1886501295	-4.5625039561
C38	-2.9208720836	2.8671464475	-1.7365875913
H39	-1.9034701416	2.9105070923	-2.1371632137
H40	-3.3752625332	3.8583952672	-1.8050037844
H41	-2.8848363330	2.6004009803	-0.6802399532
C42	-7.8242211588	4.5714723748	-2.1120607663
H43	-8.1849318582	5.0310696450	-1.1864522201
H44	-7.4940960683	5.3783995954	-2.7728290900
C45	-9.4863883423	2.6119788850	-1.9626238174
H46	-10.2743951571	2.1007941950	-2.5233737988
H47	-9.9314500609	2.9755664851	-1.0311411457
C48	-8.9242971930	3.7626973579	-2.7899853840
H49	-9.7536802810	4.4491821204	-3.0112655489
H50	-8.5715009600	3.3895303125	-3.7555425989
H51	-3.3303946883	-0.2990724890	-0.2255017454
C52	-0.0358454664	-1.3787814796	3.2197867195
C53	0.0470741628	-0.1818551223	2.5063050903
C54	-1.0509462247	0.2817341069	1.7811911738
C55	-2.2298113506	-0.4636887585	1.7814127494
C56	-2.3283765023	-1.6571110184	2.4949132124
C57	-1.2228954953	-2.1123580460	3.2149858989
H58	0.8195855366	-1.7337442576	3.7856287085
H59	0.9643524572	0.3984956743	2.5182239737
H60	-0.9922158475	1.2212240953	1.2368491687
H61	-3.2589330383	-2.2200560800	2.5041956480
H62	-1.2956777488	-3.0369183621	3.7790002655
H63	-4.2448028186	-0.3804054799	1.3576573685
N64	-3.3683493317	0.0052849329	0.9948955359
H65	-3.4576880872	1.0215241602	1.0782100317

Cartesian coordinates of **Figure S6A**

E (M06/LACV3P++ 2f(Ru)) =** -2901.90558515965

ZPE (kcal mol^{-1}) = 327.495

G_{solv} = -0.0584001

DH_{298} (kcal mol^{-1})= 25.817

DS_{298} (cal K^{-1} mol^{-1})= 239.657

atom	x	y	z
S1	-6.1372432885	3.4629742814	-2.0160930187
Fe2	-5.8413423434	1.2014349722	-2.5647546116
S3	-7.9666489453	0.9211243556	-1.6211279862
Fe4	-6.5352889287	2.0753738072	-0.1760626494
O5	-8.6678047343	3.7616673216	0.9628264014
C6	-7.8301545528	3.1090598306	0.5380116422
O7	-4.2867489916	3.4397709424	1.1832961670
C8	-5.1590144008	2.8849105674	0.6893609778
O9	-6.9114790187	-0.1586985003	1.7192060230
C10	-6.7378266541	0.7214458172	1.0115459464
O11	-6.4791457330	1.2148116302	-5.4110793929
C12	-6.2325119452	1.2135765671	-4.2838321296
C13	-1.9517930739	-1.9189793729	-4.7769504729
H14	-1.9415723886	-2.9810360931	-4.5118386342
H15	-2.3007004365	-1.8354363693	-5.8129353499
H16	-0.9201277305	-1.5552760254	-4.7409667512
C17	-4.2885134146	-1.6899666127	-3.8718560728
H18	-4.2450617233	-2.7806784079	-3.7683134406
H19	-4.7310768041	-1.4886336044	-4.8563540848
C20	-2.8091277817	0.3774300110	-4.1987995232
H21	-3.2775742533	0.5257632437	-5.1808414703
H22	-1.7637946896	0.6930040119	-4.3066879978
P23	-5.4986827249	-1.0854756071	-2.6007710670
P24	-3.6060851979	1.5797561596	-3.0276476175
C25	-6.9832453217	-2.0966674680	-3.0200611238
H26	-7.3832363950	-1.7800924290	-3.9891997548
H27	-6.7210003393	-3.1575852696	-3.0707418738
H28	-7.7600084816	-1.9533815213	-2.2644008401
C29	-4.8910012781	-1.8665643798	-1.0411274936
H30	-4.7279738191	-2.9372953038	-1.1943339337
H31	-3.9560854337	-1.4092715116	-0.7028767232
H32	-5.6344916414	-1.7376903681	-0.2486485386
C33	-3.2423646956	3.1696430336	-3.8809250430
H34	-3.8192078132	3.2326502858	-4.8059166293
H35	-3.5286837772	4.0069522123	-3.2429810430
H36	-2.1766229016	3.2423357630	-4.1187582834
C37	-2.4466747588	1.6255565587	-1.5939365142
H38	-1.4167091814	1.7465976981	-1.9448700730
H39	-2.6962004999	2.4688015105	-0.9478692385
H40	-2.5135975906	0.7176410562	-0.9929327836
C41	-7.7469508902	4.1734713531	-2.5946281662
H42	-8.1779302438	4.7160611372	-1.7475817026
H43	-7.4574573473	4.9209808966	-3.3391300794

C44	-9.2428754188	2.0911499319	-2.2760874007
H45	-9.9483752280	1.4468115994	-2.8085748042
H46	-9.7729566222	2.5003755538	-1.4105709817
C47	-8.7510586871	3.1987515748	-3.2029262146
H48	-9.6291669925	3.7812781899	-3.5148958380
H49	-8.3366103295	2.7619373264	-4.1155212317
H50	-5.4008468127	1.1438006961	-0.9009799346
C51	-1.4806179515	-1.6516777139	1.7536435539
C52	-1.1965521122	-0.2830793764	1.8015231063
C53	-2.1010996584	0.6177971845	2.3721892693
C54	-3.3132052727	0.1614046711	2.9171129588
C55	-3.5906881664	-1.2170135151	2.8750070084
C56	-2.6814844260	-2.1073323043	2.2979389433
H57	-0.7654945611	-2.3503739064	1.3232167535
H58	-0.2518005007	0.0883231745	1.4082109779
H59	-1.8597259382	1.6790072885	2.4093707871
H60	-4.5184784503	-1.5919408457	3.3042573377
H61	-2.9093173558	-3.1711664799	2.2876857807
C65	-2.8577071031	-1.1174097546	-3.8238997681
H66	-2.4574618453	-1.2405612684	-2.8081695669
N65	-4.2572223559	1.0701520801	3.4398308727
H67	-4.8689727926	0.6557178787	4.1357009307
H68	-3.8339993245	1.9148277865	3.8050312590

Cartesian coordinates of **Figure S6B**

E (M06/LACV3P++ 2f(Ru)) =** -2901.87158534037

ZPE (kcal mol^{-1}) = 330.956

G_{solv} = -0.0725484

DH_{298} (kcal mol^{-1})= 25.677

DS_{298} (cal K^{-1} mol^{-1})= 240.775

atom	x	y	z
S1	-5.7680995214	3.2562031050	-1.6126243942
Fe2	-5.9888112902	1.3113542895	-2.8272685284
S3	-7.6032107915	0.7277120464	-1.2897508353
Fe4	-5.6205315002	1.3761409764	-0.2246330928
O5	-6.7457521978	2.4569418906	2.2688986546
C6	-6.3354383244	2.0601791659	1.2669364832
O7	-2.7889197185	1.8002593693	0.2798864276
C8	-3.9254821657	1.6891487731	0.0015350912
O9	-5.0194765963	-1.3382863009	0.6235993048
C10	-5.3231498039	-0.2779484107	0.2108321482
O11	-7.6068781988	2.2090951089	-5.0661977459
C12	-6.9546159003	1.8447243066	-4.1808208245
C13	-3.6736127802	-0.9169995655	-7.2086407506
H14	-3.7086638745	-2.0060931163	-7.3149525262

H15	-4.3818638882	-0.4869586517	-7.9264072209
H16	-2.6689936078	-0.5841293242	-7.4890017426
C17	-5.4189383464	-1.0171133483	-5.3959740637
H18	-5.4882442518	-2.0806475221	-5.6563817078
H19	-6.1788086065	-0.4983266575	-5.9950435404
C20	-3.9079864559	1.0449240168	-5.6473649605
H21	-4.6985082646	1.5185612758	-6.2442731548
H22	-2.9532910152	1.3762504874	-6.0745398955
P23	-5.9368874690	-0.8588698866	-3.6173401137
P24	-4.0188714915	1.7705079406	-3.9390358431
C25	-7.5653712766	-1.7250831105	-3.6635067455
H26	-8.2783025305	-1.1286211919	-4.2390823618
H27	-7.4670859223	-2.7131320557	-4.1235810247
H28	-7.9570239464	-1.8311119381	-2.6500273916
C29	-4.8651606153	-2.1201628148	-2.7882208065
H30	-4.9011758110	-3.0712670286	-3.3296744029
H31	-3.8289751904	-1.7755820109	-2.7457794998
H32	-5.2107377337	-2.2824586740	-1.7655799816
C33	-3.7099971670	3.5507345507	-4.3113278508
H34	-4.5604891203	3.9594090996	-4.8635080349
H35	-3.6126311687	4.1128415430	-3.3807103986
H36	-2.8008308405	3.6705127111	-4.9084291882
C37	-2.4049149686	1.2576366777	-3.1921170085
H38	-1.5770162827	1.4794281296	-3.8735686650
H39	-2.2454119865	1.7958419826	-2.2559753910
H40	-2.4066101303	0.1870924565	-2.9729235571
C41	-7.3697556138	4.1126772004	-1.2536408555
H42	-7.3740128397	4.3329199813	-0.1813800179
H43	-7.2987648438	5.0677648310	-1.7829144320
C44	-8.8745865023	2.0401126172	-0.9902885194
H45	-9.8134342183	1.6028209020	-1.3434756324
H46	-8.9560844665	2.1559423986	0.0952115107
C47	-8.6426245119	3.3844125316	-1.6718564641
H48	-9.4954572492	4.0343303571	-1.4291253921
H49	-8.6553455701	3.2556691352	-2.7580878978
H50	-1.8889730708	-0.9805610763	2.3335198003
C51	-4.1383506034	0.9260586190	6.0263324066
C52	-2.9284932603	1.4139110298	5.5263374100
C53	-2.4564905467	0.9817139650	4.2873470554
C54	-3.2210126077	0.0609716020	3.5782157915
C55	-4.4281799686	-0.4404152019	4.0502153503
C56	-4.8850698885	0.0039414193	5.2927018079
H57	-4.5009068728	1.2699876015	6.9898186071
H58	-2.3516037484	2.1344705247	6.0967157446

H59	-1.5196684042	1.3622660815	3.8889027723
H60	-5.0086731605	-1.1483841454	3.4655126537
H61	-5.8274238702	-0.3696621546	5.6795618673
C65	-4.0198382447	-0.4881223672	-5.7715610557
H66	-3.2774339195	-0.9506422060	-5.1053543252
N65	-2.7284596515	-0.3978076756	2.2510565446
H67	-3.4568783327	-0.9450887143	1.7596551423
H68	-2.5097801275	0.4068105974	1.6352622104

Cartesian coordinates of **Figure S7C**

E (M06/LACV3P++ 2f(Ru)) =** -2917.92279360219

ZPE (kcal mol^{-1}) = 320.692

G_{solv} = -0.06109

DH_{298} (kcal mol^{-1})= 26.093

DS_{298} (cal K^{-1} mol^{-1})= 244.404

atom	x	y	z
S1	-6.2722772810	3.6957936218	-2.3543186130
Fe2	-6.1608687023	1.3641161435	-2.2260450278
S3	-8.4969972269	1.4528677470	-2.2887028200
Fe4	-7.6242323940	2.8614775021	-0.6374094734
O5	-9.7148981668	4.9181427295	-0.9589789581
C6	-8.9059393859	4.1230356366	-0.8151099158
O7	-5.9795177444	4.3726723870	1.2992229569
C8	-6.6244616413	3.7888169352	0.5591482274
O9	-9.0429167522	1.2438936077	1.3882691752
C10	-8.4978481059	1.8823782600	0.6130601459
O11	-5.5357271508	0.6625434996	-4.9890941444
C12	-5.7882142751	0.9450569758	-3.8991816658
N13	-3.4540403793	-1.2977943661	-1.3485767453
C14	-2.4089025868	-2.3369995250	-1.3223019231
H15	-2.7779480906	-3.2154103322	-0.7855939189
H16	-2.0970075218	-2.6529149800	-2.3321536938
H17	-1.5293340172	-1.9614219751	-0.7922311213
C18	-4.6654009276	-1.8202839075	-1.9845441506
H19	-4.8403089195	-2.8354017426	-1.6125970444
H20	-4.5642702625	-1.8947433721	-3.0841626511
C21	-2.9458292401	-0.0925855198	-2.0087222416
H22	-2.8691414855	-0.2198248143	-3.1055894973
H23	-1.9329924690	0.1014348662	-1.6402819032
P24	-6.2216142293	-0.8552838424	-1.6235567122
P25	-3.9198933308	1.4706043685	-1.6960353527
C26	-7.4545619920	-1.8889803975	-2.5227499384
H27	-7.2890382293	-1.8177372258	-3.6011270498
H28	-7.3801530007	-2.9370783519	-2.2167895328
H29	-8.4611638123	-1.5248651562	-2.3069415732

C30	-6.5521713255	-1.2363084538	0.1465684032
H31	-6.5343079456	-2.3185616765	0.3124412024
H32	-5.7994222955	-0.7598041305	0.7803752261
H33	-7.5393365811	-0.8608660482	0.4249250478
C34	-2.9350720844	2.6551594396	-2.7093553543
H35	-3.0502010789	2.4301058759	-3.7730482086
H36	-3.2960025847	3.6704793061	-2.5325326817
H37	-1.8745866116	2.6030737619	-2.4441067724
C38	-3.4901811389	1.9199995367	0.0334963774
H39	-2.4045486691	1.9450186883	0.1675895348
H40	-3.8895094523	2.9105934123	0.2619923778
H41	-3.9113582799	1.1929693213	0.7332406456
C42	-7.3435434686	4.3118933398	-3.7327102769
H43	-7.9906653965	5.0859092553	-3.3089467507
H44	-6.6465524453	4.8135722374	-4.4100171655
C45	-9.1635734163	2.4781742804	-3.6784350923
H46	-9.6796336288	1.7576635130	-4.3193507065
H47	-9.9297501110	3.1320604125	-3.2508707484
C48	-8.1490049466	3.2677377438	-4.4993494502
H49	-8.7030514871	3.7943339989	-5.2886017083
H50	-7.4709302943	2.5794566421	-5.0110419073
H51	-6.4631962491	1.7173909999	-0.5679366513
C52	-0.3866076812	0.5287140604	4.3464690455
C53	-1.5996730255	0.2147072029	4.9633801408
C54	-2.6689496165	-0.2773885206	4.2192417963
C55	-2.5394690775	-0.4729634436	2.8359628121
C56	-1.3182251146	-0.1637441083	2.2201189087
C57	-0.2542616251	0.3356865600	2.9716710894
H58	0.4443277214	0.9112888591	4.9306512201
H59	-1.7163409709	0.3539104694	6.0345059526
H60	-3.6122081188	-0.5109584672	4.7077544658
H61	-1.1971601268	-0.3311403316	1.1517607006
H62	0.6872668857	0.5630578023	2.4789805357
H63	-3.4012576434	-1.2807786283	1.1609322547
H64	-4.2212950360	-1.5874690956	2.5811672527
N65	-3.6448139295	-0.9220054612	2.0789451537

Cartesian coordinates of **Figure S7D**

E (M06/LACV3P++ 2f(Ru)) =** -2917.90361987595

ZPE (kcal mol^{-1}) = 323.703

G_{solv} = -0.0664741

DH_{298} (kcal mol^{-1})= 25.551

DS_{298} (cal K^{-1} mol^{-1})= 234.001

atom	x	y	z
S1	-6.0863177863	3.5937452326	-2.0115869066

Fe2	-6.1170234743	1.3150265089	-2.2905707740
S3	-8.3197026322	1.4269868721	-1.6489031435
Fe4	-6.9555160357	2.5414224161	-0.1182429709
O5	-8.9552923453	4.5275417581	0.7269889874
C6	-8.1702856018	3.7617407989	0.3814933092
O7	-4.7106916008	3.7102041123	1.3641498545
C8	-5.5775072395	3.2189975146	0.7790168263
O9	-7.4503832095	0.4497312560	1.8611270637
C10	-7.2680888995	1.2722627425	1.0571684134
O11	-6.3781434030	1.1848688127	-5.1847672882
C12	-6.2709096135	1.2276199638	-4.0327239700
N13	-3.4882068891	-1.2640807096	-1.3115128560
C14	-2.4609257137	-2.2741132741	-0.9601556863
H15	-2.8836542420	-3.0009576207	-0.2610198076
H16	-2.0941771894	-2.8137409390	-1.8450996185
H17	-1.6106923363	-1.7847887388	-0.4776090533
C18	-4.6404488174	-1.9515598355	-1.9455091711
H19	-4.8555488752	-2.8571027833	-1.3695774761
H20	-4.3665309444	-2.2779219202	-2.9615486160
C21	-2.8964574252	-0.2594871413	-2.2299505204
H22	-2.7892562065	-0.6893433831	-3.2387585910
H23	-1.8869725865	-0.0254207105	-1.8776017561
P24	-6.2458656504	-0.9681565467	-2.0698940119
P25	-3.8272274519	1.3706613145	-2.3871535358
C26	-6.9965010420	-1.8102361762	-3.5331062504
H27	-6.4422331729	-1.5667716035	-4.4423704299
H28	-7.0214094265	-2.8965206046	-3.4045000766
H29	-8.0203392084	-1.4447645398	-3.6498929166
C30	-7.2672737044	-1.7390410567	-0.7276403931
H31	-7.3193857057	-2.8236278728	-0.8634252022
H32	-6.8848616760	-1.5249838575	0.2713054903
H33	-8.2770208727	-1.3250374910	-0.7799754489
C34	-3.1557256689	1.9440343418	-4.0092421602
H35	-3.5340380159	1.3227875360	-4.8243370784
H36	-3.4974777697	2.9692836436	-4.1752077362
H37	-2.0616713809	1.9299116568	-4.0210990560
C38	-2.8723143875	2.4654622565	-1.2396559543
H39	-1.8127847352	2.4730899405	-1.5147874190
H40	-3.2644246423	3.4818161429	-1.3204379776
H41	-2.9661628348	2.1546179050	-0.1981143312
C42	-7.4654188375	4.4731646624	-2.8827481780
H43	-7.8987590083	5.1572626961	-2.1465969596
H44	-6.9735721966	5.0834697011	-3.6458540550
C45	-9.3070173079	2.6880762138	-2.5814088743

H46	-10.0435913959	2.1071015743	-3.1441189506
H47	-9.8534822466	3.2646332278	-1.8288710416
C48	-8.5391653330	3.6038494446	-3.5297593672
H49	-9.2685086094	4.2765802756	-4.0027420377
H50	-8.1010375890	3.0149129825	-4.3398182371
H51	-4.9878176894	0.7459790739	0.5808524152
C52	-1.9895438783	1.2023807643	4.2282258776
C53	-3.3728565188	1.1251477151	4.4014017961
C54	-4.1891262698	0.7001449464	3.3540257441
C55	-3.5990344843	0.3572349427	2.1387069098
C56	-2.2215878454	0.4212852802	1.9496238251
C57	-1.4158081375	0.8488175995	3.0069864773
H58	-1.3592576501	1.5365267342	5.0462813535
H59	-3.8210437116	1.3974468182	5.3515999976
H60	-5.2664280638	0.6429225784	3.4821963109
H61	-1.7761060869	0.1458633119	0.9988923027
H62	-0.3402088253	0.9039317817	2.8727772824
H63	-3.9866338841	-0.5483293903	0.1954785423
H64	-5.2125230666	-0.6706442095	1.3751027799
N65	-4.4731615586	-0.0556640928	1.0261095557

Cartesian coordinates of **Figure S7E**

E (M06/LACV3P++ 2f(Ru)) =** -2917.91060219324

ZPE (kcal mol^{-1}) = 324.667

G_{solv} = -0.069401

DH_{298} (kcal mol^{-1})= 25.036

DS_{298} (cal K^{-1} mol^{-1})= 228.924

atom	x	y	z
S1	-6.3239689843	3.6712000662	-1.7131114044
Fe2	-6.2217210860	1.4832382089	-2.4231343871
S3	-8.3249308105	1.2651798751	-1.5049871125
Fe4	-6.7666864876	2.1461569424	-0.0105991790
O5	-8.7558950052	3.4287953827	1.7361633957
C6	-7.9756283854	2.9495906519	1.0408339049
O7	-4.3833159856	3.1368395780	1.3577708462
C8	-5.3250647898	2.7475034359	0.8030179239
O9	-6.4189430071	-0.5164731649	1.1378750503
C10	-6.5749866060	0.5387938915	0.6646158001
O11	-6.9101235239	1.7907450689	-5.2365171245
C12	-6.6285953553	1.6622479272	-4.1214971795
N13	-3.2884164590	-0.7647868086	-1.4280841350
C14	-2.1449180709	-1.7117101529	-1.1727620750
H15	-2.4190429886	-2.3869719392	-0.3623457603
H16	-1.9386221651	-2.2742190417	-2.0854237871
H17	-1.2698361884	-1.1352742489	-0.8717927503

C18	-4.5635196863	-1.5631531490	-1.6101960407
H19	-4.9115591184	-1.8070241925	-0.6038915890
H20	-4.2904265223	-2.4935009419	-2.1170817286
C21	-2.9395272050	0.1581398129	-2.5685944456
H22	-3.0112721866	-0.4253777342	-3.4904357020
H23	-1.8923139373	0.4431217233	-2.4378243396
P24	-6.0123471023	-0.7677519523	-2.5289710879
P25	-3.9855452757	1.7245816078	-2.7228581066
C26	-5.7613736110	-1.4421273176	-4.2376646548
H27	-4.9394711013	-0.9370840170	-4.7514822667
H28	-5.5778798628	-2.5209570310	-4.2328062409
H29	-6.6711014500	-1.2475758767	-4.8128105601
C30	-7.3274182791	-1.9116045922	-1.9204424830
H31	-7.0367080547	-2.9552178606	-2.0756907846
H32	-7.5330022057	-1.7397598972	-0.8632533543
H33	-8.2428712966	-1.7086763904	-2.4804390129
C34	-3.4645972207	2.1971301464	-4.4332374814
H35	-3.9076503134	1.5259433898	-5.1728915030
H36	-3.8451574548	3.2042448528	-4.6269391037
H37	-2.3766254391	2.2063694994	-4.5505219000
C38	-2.9707999579	2.9052321021	-1.7263963611
H39	-1.9568580968	2.9760509782	-2.1316467435
H40	-3.4432676838	3.8893226947	-1.7673022526
H41	-2.9263234064	2.6043513612	-0.6793527481
C42	-7.8762986179	4.5604848908	-2.1880271805
H43	-8.2408403740	5.0342511083	-1.2710756689
H44	-7.5507172249	5.3572878801	-2.8630969939
C45	-9.5190717213	2.5897556601	-2.0024695920
H46	-10.3048994750	2.0624247644	-2.5510056411
H47	-9.9630823824	2.9653340324	-1.0752615126
C48	-8.9694441272	3.7307767667	-2.8512353240
H49	-9.8052117127	4.4056753072	-3.0835803607
H50	-8.6139141255	3.3438264007	-3.8104028526
H51	-3.3794986140	-0.2249008677	-0.5089628040
C52	0.0769902785	-1.6656915675	3.0848695716
C53	0.1947918300	-0.4087452783	2.4890509189
C54	-0.9152185310	0.2051460432	1.9087486109
C55	-2.1581634064	-0.4376271436	1.9288216858
C56	-2.2816407043	-1.6935303153	2.5326542847
C57	-1.1646581879	-2.3019745559	3.1071633726
H58	0.9423325166	-2.1393375577	3.5372676180
H59	1.1532315699	0.1019315577	2.4796088428
H60	-0.8201780698	1.1899206615	1.4560064291
H61	-3.2516773934	-2.1853009640	2.5717775002

H62	-1.2709361229	-3.2725330760	3.5826332883
H63	-4.1590437556	-0.1843327356	1.6562063573
N64	-3.2831932257	0.1637412276	1.2703153224
H65	-3.2855264928	1.1731966565	1.4035952470

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