Electronic Supplementary Information for

Reduction of an Fe(I) mesityl complex induced by π-acid ligands

Ya-Fan Lin, Yumiko Nakajima*† and Fumiyuki Ozawa*

International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

† Present address: National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan

E-mail: ozawa@scl.kyoto-u.ac.jp

Contents

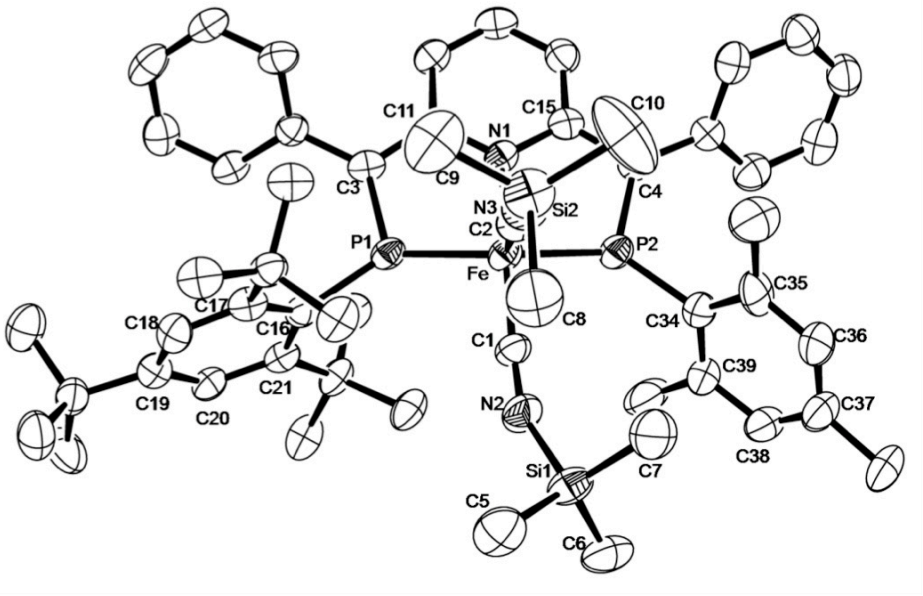

Fig. S1 ORTEP drawing of **2d**·0.5Et_2O with 50% probability ellipsoids. Hydrogen atoms and Et_2O are omitted for clarity. Selected bond distances (Å) and angles (deg): Fe–N1 2.015(5), Fe–P1 2.151(2), Fe–P2 2.135(2), Fe–C1 1.784(6), Fe–C2 1.835(6), P1–C3 1.711(6), P2–C4 1.725(6), C1–N2 1.199(7), C2–N3 1.174(7), P1–Fe–P2 146.65(8), C1–Fe–N1 169.8(2), N1–Fe–P1 81.71(15), N1–Fe–P2 80.83(15), C1–Fe–P1 98.8(2), C1–Fe–P2 93.6(2), N2-C1–Fe 175.5(5), N3–C2–Fe 174.8(6), C1–N2–Si1 154.4(5), C2–N3–Si2 172.7(6).

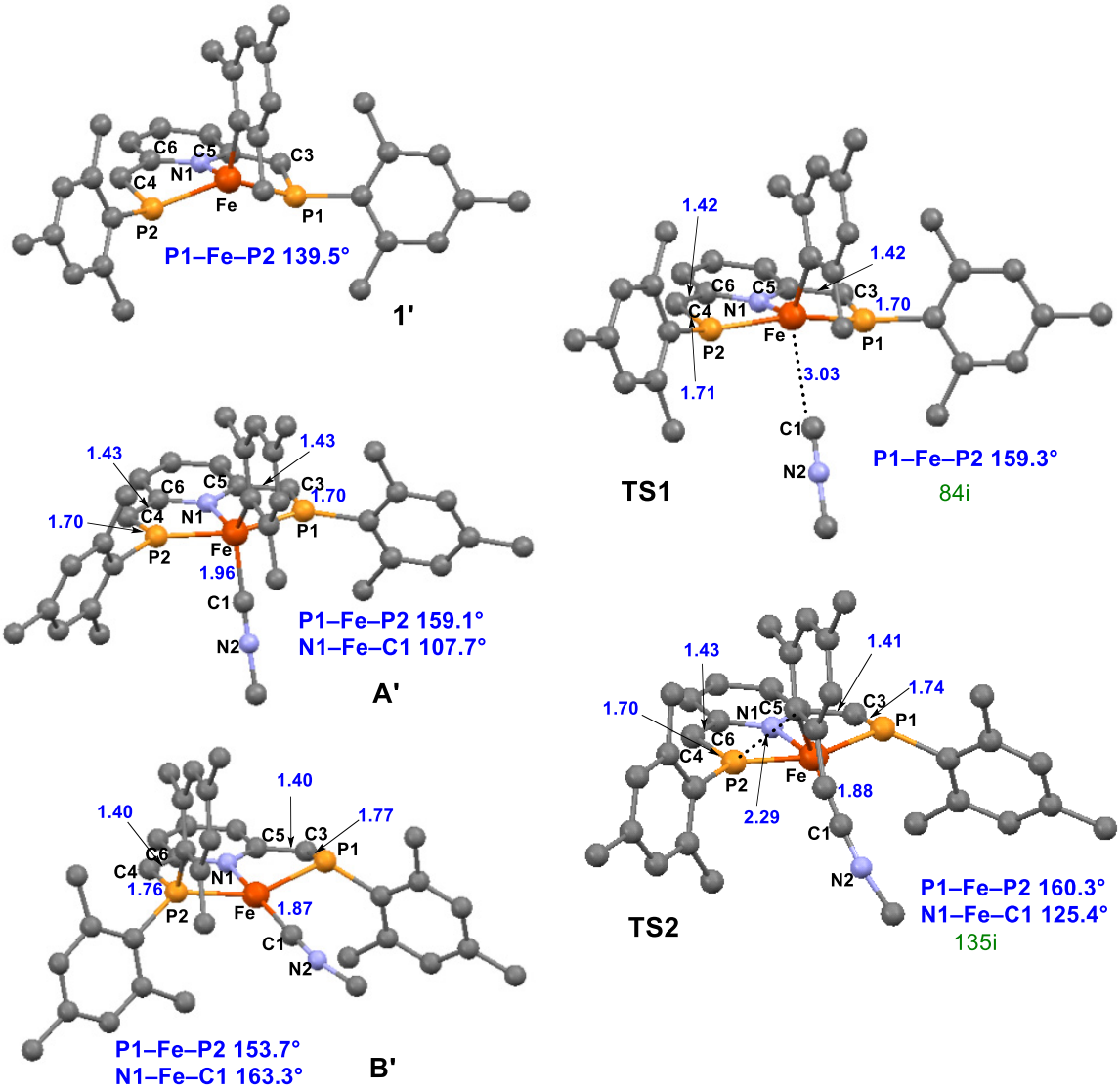

Fig. S2 Optimized structures for MeNC coordination and Mes group migration. Selected bond distances (Å) and bond angles (deg) are listed. Hydrogen atoms are omitted for clarity.

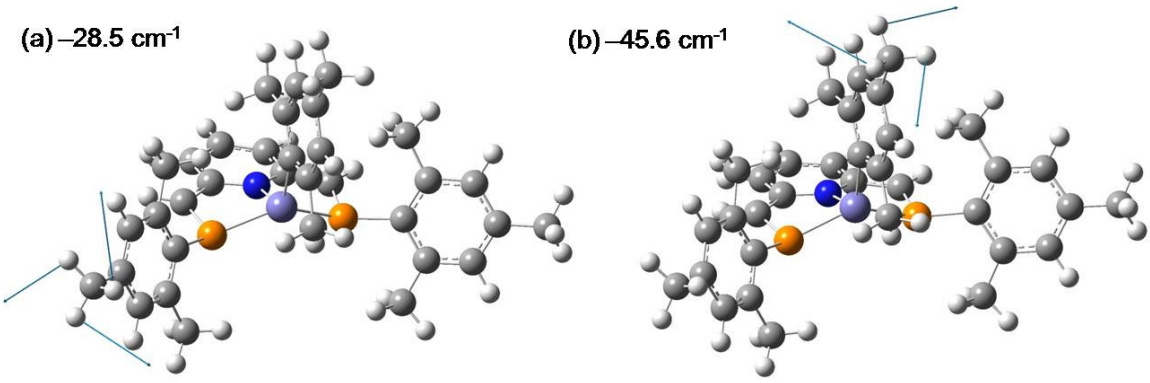

Fig. S3 Displacement vectors for **1'**, which appear even after applying a tight convergence.

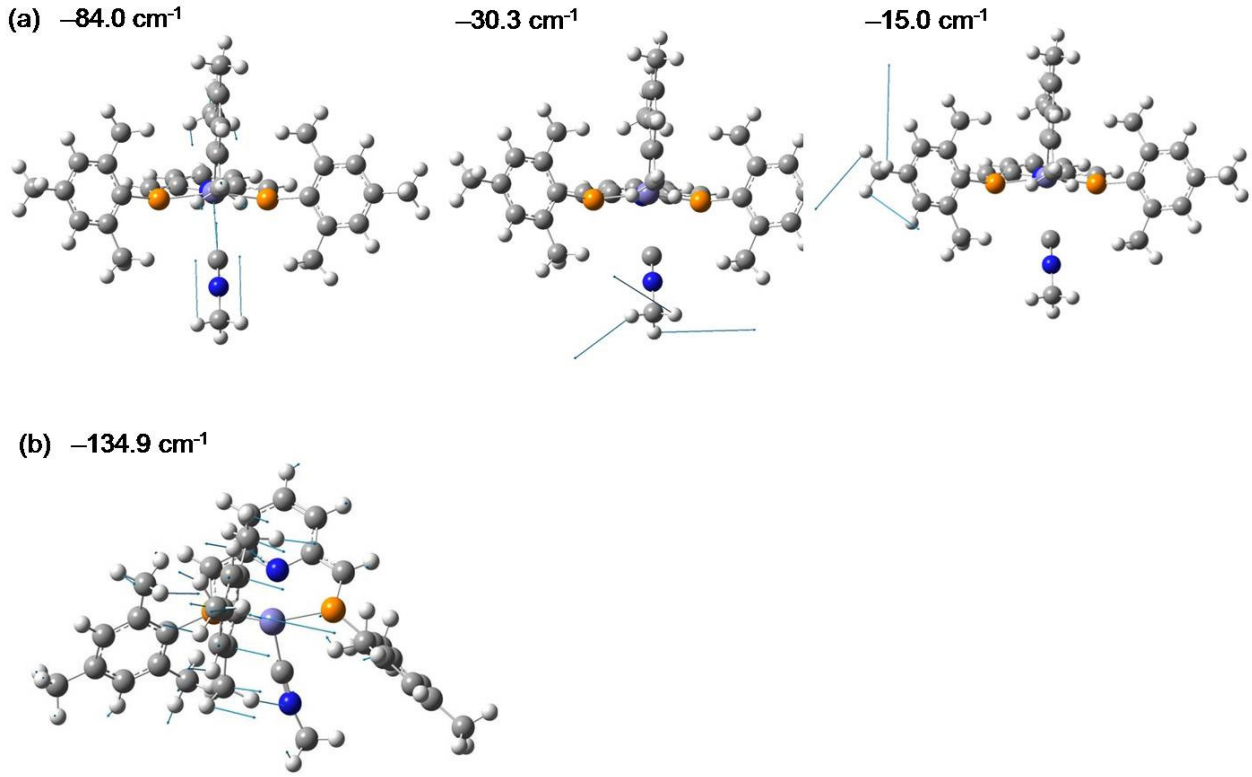

Fig. S4 Displacement vectors associated with the imaginary modes of computed transition states (a) **TS1** and (b) **TS2**.

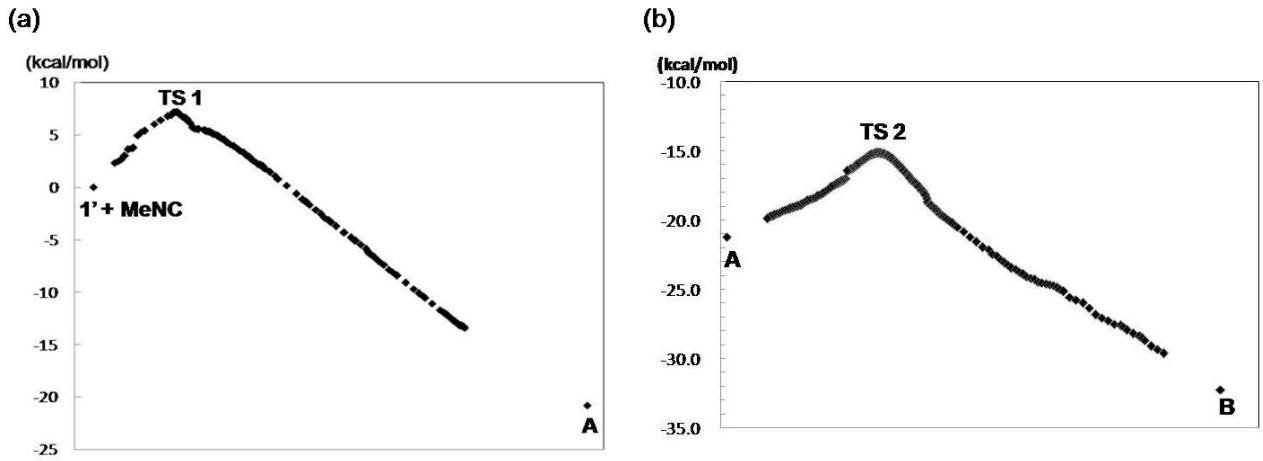

Fig. S5 Energy changes (zero point energy correction is not included) for (a) **1'** + MeCN → **A'** via **TS1**, and (b) **A'** → **B'** via **TS2**.

Table S1 Details of crystal structure determination for **2c** and **2d**

compound	**2c** · 0.5Et_2O	**2d** · 0.5Et_2O
empirical formula	$C_{56}H_{71}FeN_3P_2 \cdot C_2H_5O_{0.5}$	$C_{54}H_{71}FeN_3P_2Si_2 \cdot C_2H_5O_{0.5}$
fw	941.01	973.17
crystal system	triclinic	triclinic
space group	*P*–1	*P*–1
a (Å)	10.297(8)	10.497(7)
b (Å)	15.284(12)	15.346(10)
c (Å)	19.910(19)	19.860(14)
α (deg)	111.40(2)	112.44(2)
β (deg)	103.22(3)	103.21(3)
γ (deg)	93.32(5)	92.15(4)
V (Å^3)	2805(4)	2851(3)
Z	2	2
d_{calcd} (g cm^{-3})	1.114	1.177
T (K)	173(2)	173(2)
μ (mm^{-1})	0.364	0.400
F(000)	1010	1042
crystal size	0.25 × 0.16 × 0.14	0.49 × 0.13 × 0.03
θ range (deg)	3.33–27.30	3.16–27.57
number of reflections collected	21531	22573
number of reflections observed [$I > 2\sigma(I)$]	6213	7169
number of independent reflections (R_{int})	11953 (0.1958)	12429 (0.0755)
data/restraints/parameters	11953/4/589	12429/4/585
absorption correction	numerical	numerical
goodness-of-fit on F^2	1.162	1.373
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.1211, 0.2826	0.1236, 0.2779
*R*1, *wR*2 (all data)	0.1917, 0.3413	0.1788, 0.3221
largest peak and hole (e Å^{-3})	1.368, –0.668	2.350, –1.001

Table S2 Cartesian coordinate of **1'**

Atom	Coordinates (Angstroms) X	Y	Z
Fe	0.018730	0.036750	-0.056190
N	-0.018330	1.969230	-0.038660
P	2.057980	0.362070	-1.013220
P	-2.191790	0.278590	-0.546500
C	5.301850	-1.723550	-2.454000
C	4.086210	-1.030860	-2.364320
C	6.119200	-1.929420	-1.335180
C	-5.525590	-2.034070	-1.224920
C	3.672530	-0.509130	-1.108680
C	-6.091270	-2.228760	0.041910
C	-0.039370	4.765520	0.284680
C	5.694100	-1.416690	-0.102750
C	1.152100	4.092670	0.029530
C	-1.229610	4.044380	0.294100
C	2.330350	1.986040	-0.516880
C	1.156420	2.702150	-0.169370
C	-3.738560	-0.673500	-0.278030
C	-1.221680	2.653560	0.094600
C	-2.413770	1.890040	0.010720
C	4.487850	-0.713820	0.038320
C	-5.461520	-1.637880	1.144910
C	-4.295780	-0.867290	1.016390
C	-0.032370	-2.709220	0.272680
C	0.196920	-2.091770	1.643720
C	0.217080	-0.683880	1.747460
C	0.354820	-2.908340	2.771550
C	0.415470	1.399900	3.216470
C	0.387140	-0.102650	3.024730
C	0.525880	-2.340030	4.042560
C	0.535670	-0.940090	4.145590
C	0.706090	-3.214330	5.265310
H	5.615590	-2.109760	-3.420440
H	-6.000530	-2.481640	-2.094240
H	-0.043800	5.840330	0.440470
H	2.093900	4.629220	-0.035670
H	-2.183710	4.542000	0.439560
H	6.314260	-1.568770	0.776940
H	0.223650	-2.016810	-0.557090
H	0.598480	-3.591070	0.109540
H	-1.077800	-3.008290	0.128090
H	-5.883820	-1.782040	2.136100
H	1.224710	1.860770	2.638860
H	-0.517410	1.863830	2.876620
H	0.344490	-3.991810	2.660970
H	0.559360	1.660430	4.270880
H	0.666670	-0.486830	5.126310

H	1.643780	-3.784320	5.218130
H	-0.107740	-3.944160	5.362610
H	0.729110	-2.615960	6.181960
C	-7.329260	-3.079480	0.217770
H	-7.971580	-3.040680	-0.668560
H	-7.065980	-4.133350	0.383200
H	-7.920200	-2.753480	1.080350
C	-3.674020	-0.283500	2.268550
H	-2.604730	-0.510770	2.337070
H	-3.768320	0.808030	2.298950
H	-4.164640	-0.685430	3.160330
C	3.258670	-0.844800	-3.621340
H	2.248680	-1.257790	-3.511420
H	3.140250	0.214930	-3.877310
H	3.733910	-1.343760	-4.471620
C	7.409740	-2.710060	-1.447990
H	7.241970	-3.781360	-1.270590
H	7.852100	-2.611400	-2.445070
H	8.148110	-2.371430	-0.713360
C	4.099460	-0.209980	1.412860
H	4.099030	0.884950	1.459750
H	3.093720	-0.537930	1.697150
H	4.802120	-0.577280	2.167020
C	-4.361010	-1.275310	-1.405820
C	-3.811880	-1.106690	-2.809400
H	-3.807000	-0.055280	-3.120890
H	-2.778360	-1.464590	-2.891080
H	-4.417960	-1.666400	-3.528540
H	3.295560	2.481810	-0.498360
H	-3.369320	2.348040	0.244820

Table S3 Cartesian coordinate of **TS1**

Atom	Coordinates (Angstroms)		
	X	Y	Z
Fe	0.039964	0.004444	0.027812
P	0.017677	0.055505	2.285585
P	0.854271	0.034202	-2.080244
N	1.242806	1.526073	0.251595
C	1.215255	-2.778190	0.290540
N	1.775763	-3.804120	0.396249
C	2.436846	-5.069681	0.511953
C	1.797696	2.173806	-0.860374
C	2.466368	3.402595	-0.735875
C	2.586013	4.026928	0.499387
C	2.019089	3.409501	1.608381
C	1.351463	2.181033	1.485983
C	0.737392	1.566173	2.609629

C	-0.922562	-0.506021	3.761567
C	-0.397920	-1.549527	4.568429
C	-1.129106	-1.990464	5.681025
C	-2.372040	-1.437166	6.015077
C	-2.874183	-0.406179	5.210884
C	-2.178388	0.072238	4.090386
C	0.942436	-2.192407	4.271825
C	-2.783075	1.197319	3.279111
C	-3.162430	-1.953940	7.196722
C	0.476503	-0.520422	-3.793046
C	1.120192	-1.678160	-4.297690
C	0.832270	-2.112055	-5.599982
C	1.634594	1.551110	-2.127930
C	-0.085862	-1.440317	-6.416687
C	-0.719837	-0.304362	-5.898441
C	-0.464111	0.169050	-4.602101
H	2.882056	3.851428	-1.633010
H	3.102762	4.977288	0.595027
H	2.076207	3.865318	2.592205
H	-0.716051	-2.782986	6.300060
H	-3.833306	0.041263	5.458788
H	0.941687	-2.703575	3.301097
H	1.194279	-2.929072	5.041656
H	1.748795	-1.450717	4.237163
H	-2.181348	2.111552	3.352739
H	-3.791590	1.430018	3.634148
H	-2.847044	0.945646	2.215503
H	-3.779889	-1.165536	7.640456
H	-2.504537	-2.350333	7.977603
H	-3.839074	-2.766120	6.896802
H	1.340005	-2.993586	-5.983515
H	-1.438047	0.229616	-6.515381
H	1.915053	-5.699117	1.238397
H	2.441836	-5.578635	-0.456108
H	3.469739	-4.929430	0.842625
H	1.997813	2.046205	-3.022034
H	0.755320	2.067980	3.571768
C	-1.207940	1.395528	-4.116401
H	-1.708984	1.210312	-3.160379
H	-0.533570	2.246240	-3.964515
H	-1.967419	1.696286	-4.844537
C	2.124854	-2.461214	-3.474249
H	2.952239	-1.829093	-3.131624
H	1.664737	-2.892888	-2.576936
H	2.547432	-3.281311	-4.063846
C	-0.404305	-1.942912	-7.807298
H	-1.232359	-2.664945	-7.789005
H	-0.702761	-1.123827	-8.470282
H	0.457113	-2.447863	-8.257814
C	-1.904044	0.288523	-0.383229
C	-2.706268	-0.867328	-0.564876

C	-2.534376	1.551821	-0.493675
C	-4.078665	-0.752228	-0.840567
C	-3.912589	1.634690	-0.773979
C	-4.705608	0.495612	-0.952984
H	-4.666585	-1.659786	-0.969581
H	-4.372969	2.618223	-0.851093
C	-2.102186	-2.255711	-0.461919
H	-1.317554	-2.411743	-1.214488
H	-1.642641	-2.425667	0.520643
H	-2.861601	-3.031587	-0.610587
C	-1.760857	2.843669	-0.310254
H	-1.294021	2.895699	0.680259
H	-0.954012	2.938932	-1.046307
H	-2.417858	3.714104	-0.418424
C	-6.181902	0.602688	-1.270576
H	-6.781046	-0.059176	-0.632464
H	-6.545867	1.625729	-1.126177
H	-6.393994	0.322133	-2.311775

Table S4 Cartesian coordinate of **A'**

Atom	Coordinates (Angstroms)		
	X	Y	Z
Fe	7.495685	5.476723	4.334516
P	7.132508	6.754378	6.111778
P	7.406548	3.703365	2.999551
N	5.868308	4.442747	5.202948
C	6.769337	6.739745	3.032438
N	6.360046	7.508355	2.243715
C	5.883093	8.447011	1.284569
C	5.409699	3.249401	4.667053
C	4.338575	2.547015	5.246858
C	3.719811	3.039044	6.391071
C	4.187074	4.222564	6.952333
C	5.259791	4.909958	6.358044
C	5.768043	6.125797	6.909964
C	7.544290	8.412629	6.778826
C	6.689555	9.522122	6.538201
C	7.053662	10.783570	7.032367
C	8.238134	10.984827	7.752552
C	9.068777	9.880043	7.981620
C	8.750048	8.599829	7.506665
C	5.391654	9.391621	5.766520
C	9.689027	7.449790	7.802041
C	8.623640	12.361274	8.247159
C	6.070855	2.772751	3.493714
C	8.016152	3.108967	1.375013
C	7.227940	3.269411	0.203049

C	7.736260	2.826748	-1.027073
C	9.001590	2.235547	-1.137789
C	9.766006	2.087144	0.026713
C	9.303444	2.515478	1.279399
H	4.010817	1.619940	4.786557
H	2.890094	2.503173	6.843905
H	3.737528	4.631488	7.852030
H	6.395289	11.628746	6.847565
H	9.988465	10.013699	8.545344
H	5.538442	8.872148	4.812537
H	4.967524	10.379286	5.559127
H	4.644057	8.814098	6.322170
H	9.198658	6.677850	8.408278
H	10.566651	7.800242	8.353903
H	10.038663	6.959793	6.887240
H	9.139537	12.309956	9.212248
H	7.745534	13.004832	8.365364
H	9.303218	12.860492	7.542737
H	7.127522	2.950013	-1.919469
H	10.748011	1.625657	-0.037027
H	6.716390	8.814653	0.678065
H	5.150299	7.971735	0.625663
H	5.410721	9.295626	1.788313
H	5.735041	1.859445	3.013511
H	5.310989	6.553951	7.796080
C	10.181852	2.317398	2.496114
H	10.413736	3.265993	2.991700
H	9.694926	1.679613	3.244097
H	11.127443	1.842636	2.216634
C	5.851192	3.902659	0.233041
H	5.119462	3.263668	0.740280
H	5.856565	4.857052	0.772183
H	5.490821	4.084270	-0.784512
C	9.539708	1.795581	-2.481179
H	10.127055	2.594440	-2.954724
H	10.197486	0.925264	-2.382871
H	8.730569	1.533598	-3.171168
C	9.487353	5.276257	4.703385
C	10.436330	6.058960	4.001534
C	9.980251	4.352224	5.662532
C	11.814572	5.916290	4.259183
C	11.361200	4.232399	5.896745
C	12.301293	5.009171	5.205739
H	12.519324	6.531118	3.701578
H	11.707396	3.512734	6.636994
C	10.017273	7.070166	2.947830
H	9.467355	6.592992	2.126525
H	9.364805	7.846369	3.367570
H	10.891688	7.569921	2.515903
C	9.040319	3.466581	6.458497
H	8.330944	4.061719	7.046613

H	8.440438	2.825644	5.800865
H	9.594791	2.820108	7.148259
C	13.783662	4.878680	5.485082
H	14.050113	5.295734	6.466336
H	14.104029	3.829119	5.486392
H	14.377600	5.408338	4.732092

Table S5 Cartesian coordinate of **TS2**

Atom	Coordinates (Angstroms)		
	X	Y	Z
Fe	-0.004909	-0.089439	-0.035593
P	0.015667	-0.041700	2.138616
P	0.713546	-0.309009	-2.162302
N	2.001975	0.424125	0.261447
C	2.855005	0.569812	-0.826090
C	4.219533	0.894016	-0.627798
C	4.721768	1.027678	0.656245
C	3.879856	0.822887	1.749492
C	2.521792	0.520053	1.535701
C	1.618758	0.279086	2.617607
C	2.305552	0.385878	-2.115148
C	-0.125576	0.115135	-3.741801
C	-0.828526	-0.918389	-4.423869
C	-1.526484	-0.621519	-5.603147
C	-1.558859	0.672275	-6.139293
C	-0.878516	1.685363	-5.451513
C	-0.164035	1.438297	-4.267688
H	4.856999	1.022544	-1.497078
H	5.769127	1.274071	0.812416
H	4.251541	0.893727	2.766721
H	-2.054767	-1.422288	-6.114851
H	-0.901711	2.699369	-5.844423
H	2.915205	0.570250	-2.993969
H	1.964969	0.285667	3.645067
C	0.520605	2.610147	-3.593659
H	0.350726	2.612875	-2.512074
H	1.606984	2.584449	-3.732970
H	0.155368	3.555566	-4.009106
C	-0.844390	-2.345586	-3.912206
H	0.169781	-2.751069	-3.818592
H	-1.302806	-2.422088	-2.918998
H	-1.408235	-2.991549	-4.592937
C	-2.287912	0.961604	-7.432721
H	-3.167104	0.318556	-7.550235
H	-2.620158	2.004330	-7.481400
H	-1.639519	0.786292	-8.302398
C	-1.045185	-0.106740	3.638825

C	-1.009541	-1.189106	4.557617
C	-1.888033	1.009362	3.902698
C	-1.830264	-1.139487	5.696152
C	-2.690238	1.006741	5.051609
C	-2.679427	-0.059376	5.960345
H	-1.799249	-1.971941	6.394357
H	-3.331293	1.863517	5.242930
C	-1.926707	2.223783	2.996589
H	-2.627188	2.968650	3.386948
H	-0.940389	2.697140	2.919572
H	-2.234549	1.970436	1.976714
C	-0.129437	-2.406754	4.370322
H	-0.550806	-3.094462	3.629244
H	0.872852	-2.138598	4.025882
H	-0.029532	-2.951516	5.314412
C	-3.532879	-0.024952	7.208442
H	-3.735216	-1.033889	7.582351
H	-3.033658	0.529286	8.015109
H	-4.493557	0.468058	7.023481
C	-1.373304	1.103620	-0.533862
N	-2.232788	1.814414	-0.916887
C	-3.137898	2.662206	-1.620069
H	-2.989299	2.552503	-2.698989
H	-4.171437	2.400084	-1.373671
H	-2.967800	3.706876	-1.341002
C	-0.432842	-1.965270	0.989922
C	-1.810876	-2.330332	1.019349
C	0.536374	-3.014099	0.978972
C	-2.178483	-3.688189	1.014945
C	0.120799	-4.354183	0.970711
C	-1.232363	-4.717237	0.986476
H	-3.236211	-3.942145	1.032341
H	0.878776	-5.134126	0.955777
C	-1.651042	-6.169977	0.957863
H	-2.681810	-6.296585	1.305378
H	-1.595526	-6.579399	-0.060336
H	-1.001592	-6.788068	1.588518
C	2.025099	-2.750662	0.962785
H	2.325663	-2.221793	0.052253
H	2.335110	-2.125448	1.806622
H	2.583301	-3.691070	1.009506
C	-2.952665	-1.327173	1.002683
H	-3.871011	-1.792297	1.377221
H	-2.753614	-0.446398	1.614959
H	-3.154739	-0.974190	-0.016236

Table S6 Cartesian coordinate of **B'**

Atom	Coordinates (Angstroms) X	Y	Z
Fe	0.069461	0.099897	-0.175313
P	0.011146	-0.468790	2.144557
P	0.799212	-0.148245	-2.332993
N	1.989164	0.481005	0.189713
C	2.839753	0.826468	-0.864134
C	4.166690	1.242496	-0.609121
C	4.642079	1.272219	0.703643
C	3.822989	0.876022	1.743183
C	2.474738	0.451658	1.488950
C	1.659632	0.006379	2.529692
C	2.320925	0.745038	-2.165728
C	-0.163427	0.575484	-3.738010
C	-0.768703	-0.322401	-4.662862
C	-1.544565	0.182594	-5.718377
C	-1.741776	1.557538	-5.902147
C	-1.153690	2.432745	-4.979530
C	-0.375624	1.974575	-3.904087
H	4.795096	1.533011	-1.444354
H	5.661559	1.592179	0.906186
H	4.180307	0.864793	2.767809
H	-1.994732	-0.516770	-6.419026
H	-1.306538	3.503461	-5.093988
H	2.930618	1.056277	-3.009477
H	2.017922	0.054166	3.552613
C	0.178020	2.999974	-2.939014
H	-0.088270	2.755475	-1.903002
H	1.271577	3.044185	-2.968147
H	-0.211303	3.996846	-3.170078
C	-0.604257	-1.825965	-4.548598
H	0.452048	-2.116798	-4.550935
H	-1.029322	-2.217840	-3.616546
H	-1.101556	-2.330649	-5.383609
C	-2.540009	2.082773	-7.075192
H	-3.292029	1.358286	-7.406494
H	-3.054526	3.017416	-6.825288
H	-1.889870	2.291963	-7.935989
C	-0.957424	0.168158	3.593048
C	-0.981022	-0.510145	4.842695
C	-1.612794	1.425097	3.479121
C	-1.699727	0.049438	5.912434
C	-2.316199	1.940946	4.576720
C	-2.382233	1.265118	5.801123
H	-1.715600	-0.481493	6.861029
H	-2.817418	2.899950	4.471902
C	-1.564307	2.258024	2.213914
H	-2.046963	3.226851	2.376391

H	-0.531600	2.449992	1.898485
H	-2.072658	1.766882	1.377006
C	-0.255058	-1.816769	5.101494
H	-0.776950	-2.672899	4.659819
H	0.758316	-1.815161	4.689033
H	-0.175978	-1.993432	6.178799
C	-3.127949	1.854062	6.977881
H	-3.437252	1.076876	7.684634
H	-2.500475	2.567173	7.530059
H	-4.024133	2.394892	6.654180
C	-1.693593	0.206623	-0.796072
N	-2.766034	0.303234	-1.272616
C	-3.885316	0.472224	-2.143156
H	-3.537981	0.611548	-3.171502
H	-4.530631	-0.409919	-2.095801
H	-4.467223	1.346500	-1.836832
C	-0.366214	-2.303462	2.011346
C	-1.730032	-2.705090	1.923659
C	0.647340	-3.293072	1.870069
C	-2.044738	-4.060607	1.734273
C	0.274015	-4.634318	1.682488
C	-1.060631	-5.045229	1.612139
H	-3.092441	-4.346493	1.679079
H	1.060989	-5.377903	1.585413
C	-1.423052	-6.494619	1.378188
H	-2.411300	-6.731285	1.786900
H	-1.448008	-6.730452	0.305307
H	-0.694046	-7.169186	1.840475
C	2.136574	-3.003560	1.901329
H	2.441527	-2.333938	1.091057
H	2.449710	-2.526690	2.834197
H	2.695420	-3.938277	1.790913
C	-2.900640	-1.745792	2.049912
H	-3.074117	-1.447171	3.089599
H	-2.753399	-0.828610	1.473287
H	-3.814708	-2.224947	1.684553