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Electronic Supporting Information

A Metal-mediated Boron-centred Isomerization Reaction via C–H Activation

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COMPUTATIONAL METHODOLOGY

Reaction mechanism for the conversion from 2 to 5: Theoretical calculations have done by using Gaussian09 computational package.[1] Geometry optimizations for all of the species involved in the reaction mechanism were done in the gas phase using the local density functional M06-L developed by Truhlar and coworkers.[2] This density-functional theory (DFT) method has shown good performance in organometallic reactions for kinetics because it incorporates dispersion corrections to the electronic energy.[3] Then, calculations have been carried out with two different mixed basis sets: for geometry optimizations, a combination of 6-31G(d) for all of the light atoms (C, O, N, B and H) and a modified version of the LANL2DZ pseudopotential for Mn,[4] for incorporating zero-order relativistic effects, were used. Later, the combination of 6-311+G(2d) for all of the light atoms and the LANL2TZ+f pseudopotential for Mn,[5] for single-point calculations, have been used in order to improve the accuracy in the electronic energy for our reported energy values.

After performing geometry optimizations, harmonic frequency calculations have also been executed in order to test the nature of the stationary points found on the potential energy surface (PES). That is, we ensure zero negative frequencies for our optimized minima (reactants, product and intermediates/adduct species) and one and only one negative frequency (which is directly associated to the reaction coordinate) for the transition states found in each reaction step. From these calculations, we also obtained thermal and entropic corrections to the electronic energy at 298.15 K and 1 atm that were added to the final energy reported.

Finally, single-point calculations with the polarized continuum model (PCM)[6] also implemented in Gaussian 09 were done for incorporating solvation effects as a correction to the gas-phase energy (the difference in electronic energy between PCM calculation and the final optimized structure energy in gas-phase) setting parameters for dichloromethane (DCM) as reaction solvent and the united atom topological model (UAKS) radii to construct the molecular cavity of the solvent.

The comparison of energy barriers in the isomerisation from **2** to **5** for assessing the effect of the solvents in this reaction is listed in Table S1. For clarity, optimized geometries for all of the structures involved in the reaction mechanism depicted in Figure 2 of the manuscript are depicted in Figure S2.

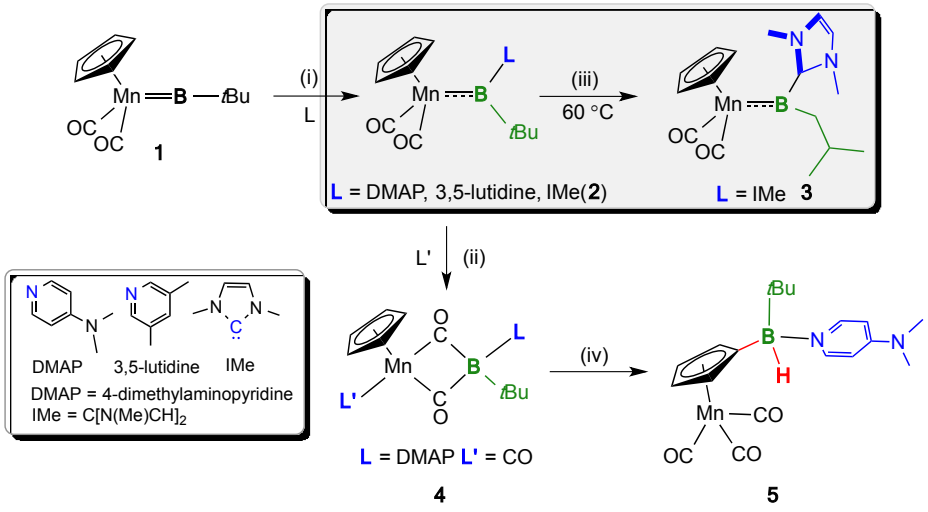
Reaction mechanism for the *t*Bu-to-*i*Pr isomerization from 2 to 3: For this part of study, we also used Gaussian09 computational package.[1] Geometry optimizations in the gas phase were done using a hybrid density-functional, PBE0, developed by Perdew, Burke and Ernzerhof and Adamo.[7] We chose this DFT level of theory because it has demonstrated excellent performance in inorganic chemistry but is also good for calculating NMR signals in light atoms[8] (in order to compare some of our computational results with the experimental data obtained at the same time). In this case, we used a more robust mixed basis set: 6-31G(2d,p) for all of the light atoms (C, O, N, B and H) and a Wachters' augmented basis set for Mn[9] for the geometry optimizations. Later, single-point calculations for improving the electronic energy were also done by setting up 6-311+G(2d,p) for all of the light atoms and Wachters+f basis set for Mn.[10] After this, we also carried out harmonic

frequency calculations with the same aim as described above in the other reaction mechanism proposal.

We also did single-point calculations with PCM by adjusting parameters for toluene as reaction solvent with the same radii=UAKS option as before, for the all of the optimized geometries on the PES. Moreover, since PBE0 does not incorporate dispersion effects itself, we have summed up these energy corrections manually by running an external DFT-D3 subroutine created by Grimme and coworkers.[11]

MECHANISTIC STUDY ON ISOMERISATION OF [(η⁵-C₅H₅)(OC)MNB(*T*BU)(IME)] (2)

In the case of the group 7 manganese borylene [(η⁵-C_5H_5)$(OC)_2$MnB*t*Bu] (**1**), upon addition of equimolar N-heterocyclic carbene (NHC) or pyridine, the base-stabilized borylenes [(η⁵-C_5H_5)$(OC)_2$MnB(L)*t*Bu] (**2**) are isolable (Reaction (i), Scheme S1). Further exposure to CO or isonitriles leads to internal coupling of the activated borylene ligand with metal co-ligands to form heterocyclic structures [(η^5-C_5H_5)(L')Mn{κ^2-*C,C'*-C(O)B(*t*Bu)(L)C(O)}] (**4**) instantaneously (Reaction (ii), Scheme S1).



Scheme S1. Reaction sequence from **1** to **5**

In a previous report,[12] we briefly described a steady conversion of complex **2** to **3** in solution, in which the tertiary butyl group of the boron rearranges to form an isobutyl group. To gain a better understanding of these two competing reaction paths, in addition of isomerisation of **4** to **5**, a detailed computational investigation of the mechanistic route of **2** to **3** was carried out.

Thermal isomerisation of *tert*-butyl (*t*Bu) substituted boranes to secondary and primary isomers is rare but not unprecedented. Reports have been made as early as 1950s.[13] More recently, Bertrand *et al.* observed boron-centred *t*Bu to *i*Bu (*iso*-butyl) isomerization in a cyclic PBPB system. The latter was examined computationally and a proposed mechanism was discussed.[14]

To compare the *t*Bu to *i*Bu rearrangement in our transition metal system with the previously reported metal-free boranes, the formation of **3** from **2** (Figure S1) has been investigated by means of DFT calculations (see Computational Methodology section). Thermodynamically, **3** is more stable than **2** by 3.63 kcal·mol^{-1} because of the lesser steric hindrance of the borylene towards the manganese complex. The base-stabilized borylene complex **2** undergoes a boron-mediated C-H bond activation leading to structure **B**, which can be described as a σ-bond tricyclic borane 2.04 kcal·mol^{-1} lower in energy than **2**. This reaction step involves a transition state $TS_{2\rightarrow B}$ with an energy barrier of 21.58 kcal·mol^{-1}. Then boron facilitates the proton transfer to the central carbon of the original *t*-butyl substituent via $TS_{B\rightarrow 3}$ with a lower energy barrier (18.06 kcal·mol^{-1}) to facilitate the *i*-propyl isomerization in **3**.

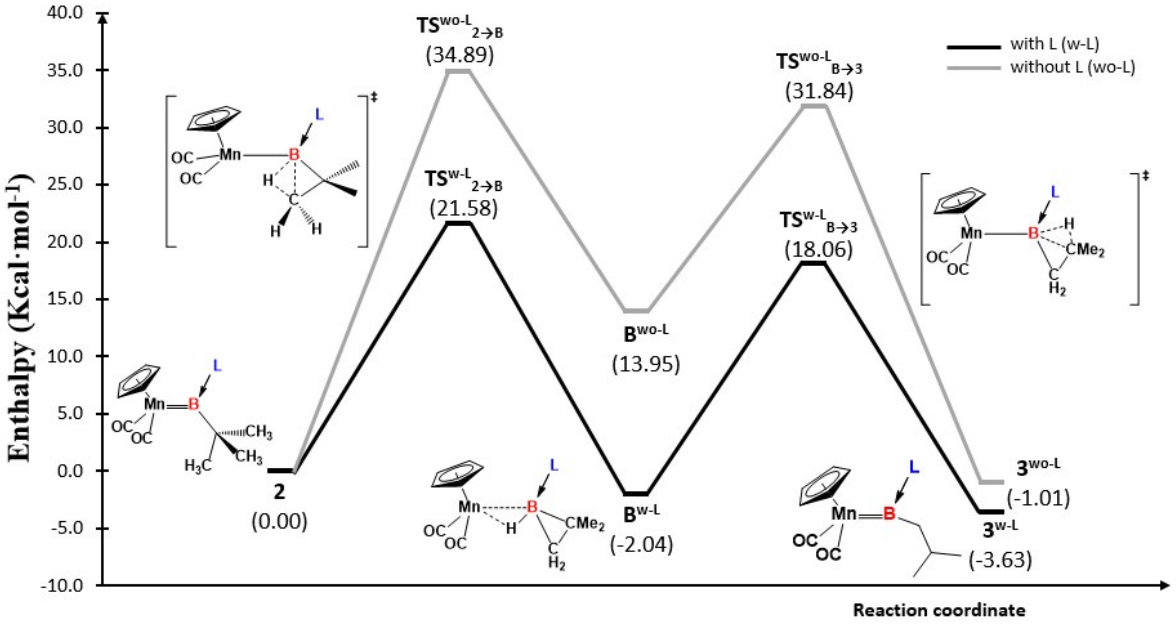


Figure S1. The energy profile of the proposed mechanism of the isomerisation of **2** and that of the same process without ligand stabilisation.

The initial activation barrier is in full agreement with the reaction temperature needed for the reaction to proceed (60 °C).[1] Moreover, in order to show the electronic role of a strong donor ligand as IMe to achieve this isomerization, we recalculate the proposed reaction mechanism without the ligand (wo-L). All of the species involved in it are clearly destabilized in energy (grey line, Fig 3), especially intermediate **B**, and the energy barriers are so high for these reaction steps to occur (34.89 and 31.84 kcal·mol^{-1}, respectively). The manganese centre plays a role in stabilising intermediate **B**. The overall process is similar to that proposed for the cyclic PBPB system.

Therefore, this reaction pathway is not competing with the formation of **4** in presence of CO and its subsequent isomerisation to **5**. This is in line with our experimental findings, that is, from a one-pot reaction from **1** to **5**, no isobutyl substituted product was isolated. Comparing initial energy barriers: the reaction from **2** to **4** (and later to **5**) goes through 15.70 kcal·mol^{-1} (when adding CO) whereas from **2** to **3** it is 21.58 kcal·mol^{-1}; thus the difference of 5.88 kcal·mol^{-1} between both

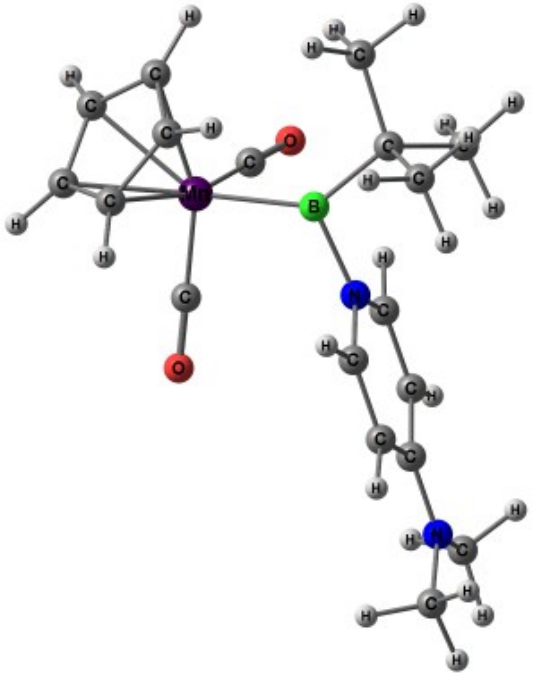
routes differentiates kinetically that the first one proceeds spontaneously (and so **2** is more prone to get one more CO ligand) and the *t*Bu to *i*Bu rearrangement needs heat in order to be achieved.

Table S1. Comparison of energy barriers in the isomerisation from **2** to **5** for assessing the effect of the solvent in this reaction. Energies are in kcal·mol^{-1}.

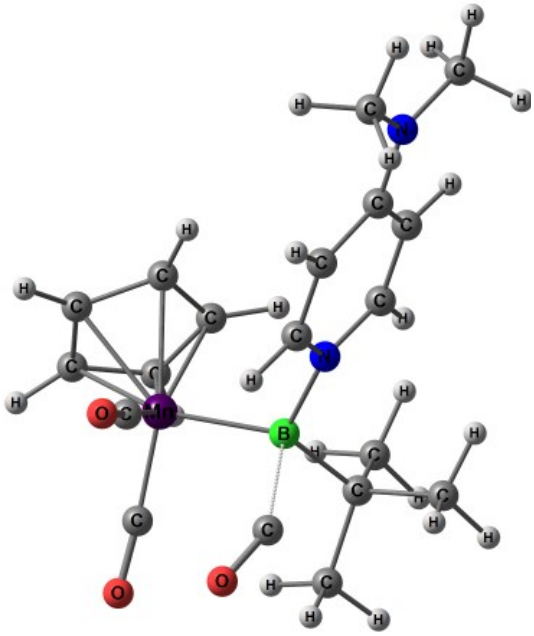
Energy Barrier	Gas phase	Toluene as solvent	DCM as solvent
2 ⟶ TS1	16.52	15.89	15.70
A ⟶ TS2	13.02	12.13	10.49
Int1 ⟶ TS3	11.74	11.62	10.15
Int2 ⟶ TS4	6.42	5.04	4.98
A ⟶ TS5	5.49	3.64	3.53

Magnitude of molecular dipoles for **4**: 8.9690 Debye; for **TS2**: 12.8572 Debye; for **TS3**: 16.4285 Debye

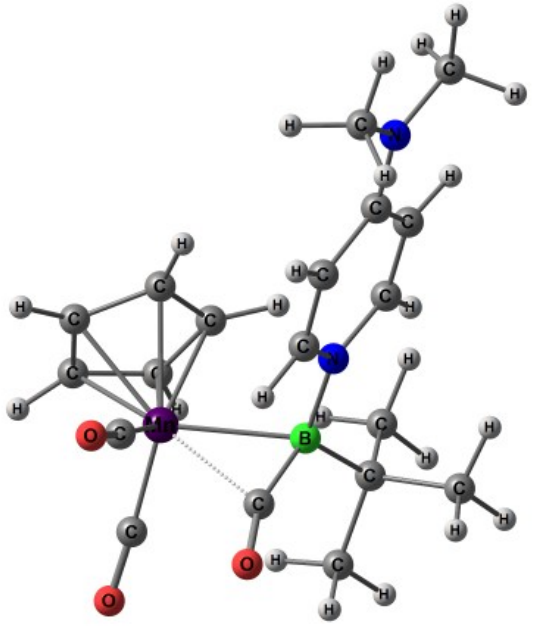
Figure S2. Optimized geometries for all of the structures involved in the reaction mechanism depicted in Figure 2 of the manuscript.



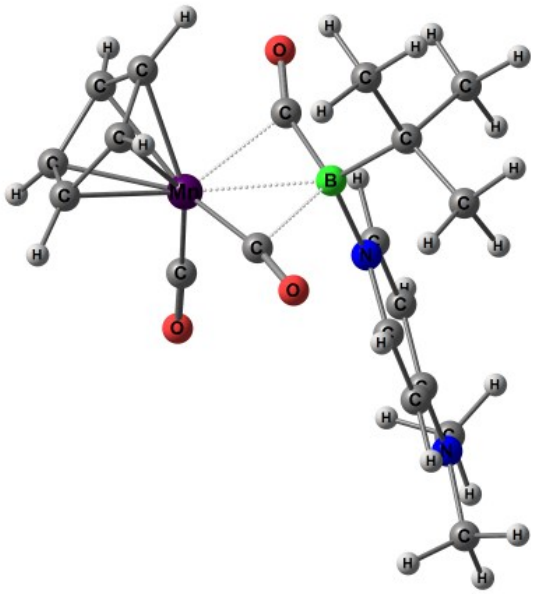
2



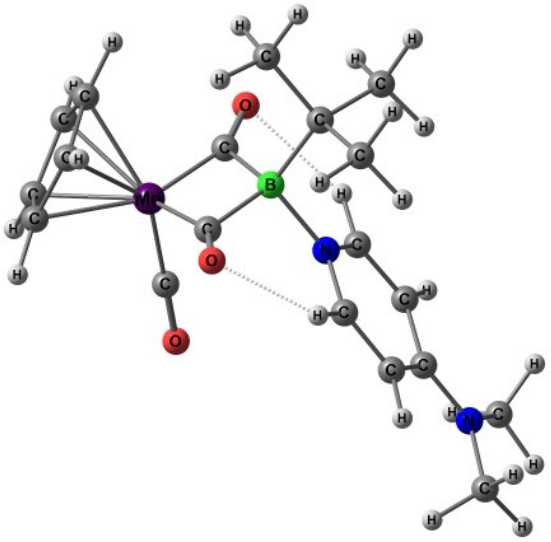
TS1



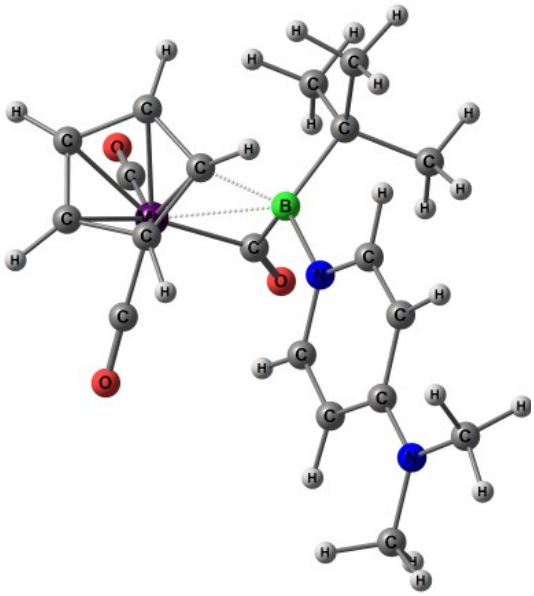
A



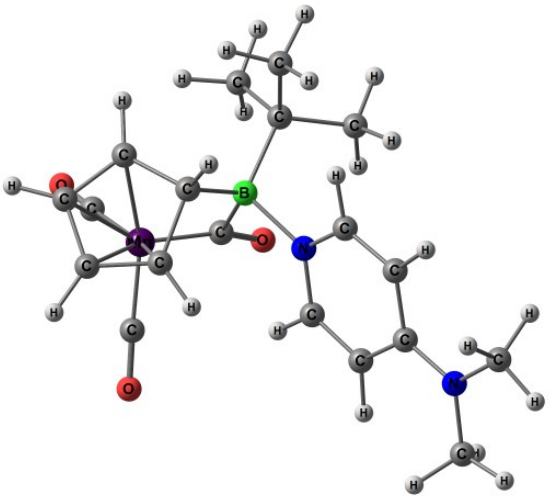
TS5



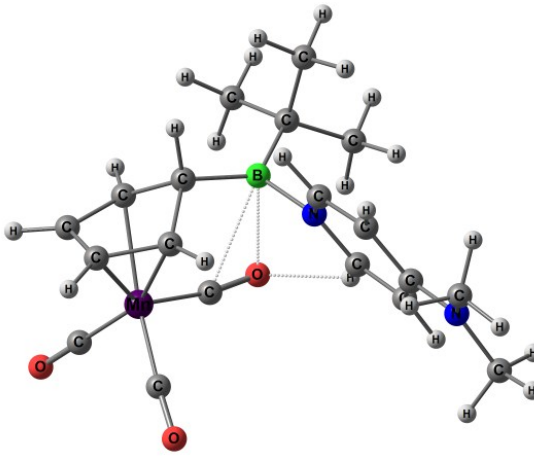
4



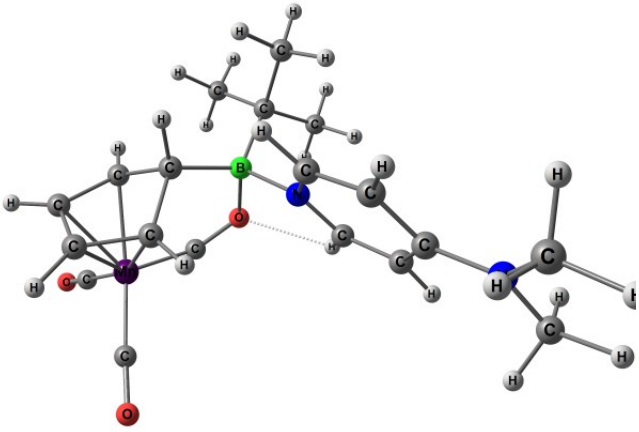
TS2



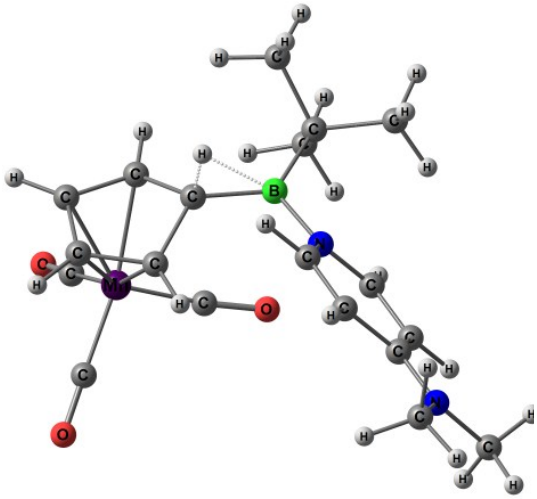
Int1



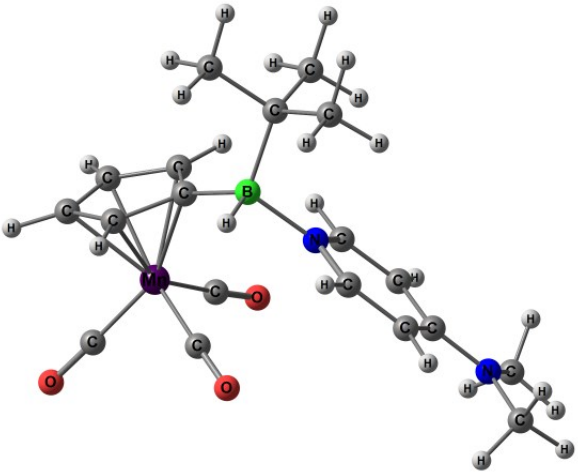
TS3



Int2



TS4



5

EXPERIMENTAL

General considerations:

All syntheses were carried out under an argon atmosphere with standard Schlenk and glovebox techniques unless otherwise stated. The complex [(η^5-C_5H_5)(OC)Mn{(κ^2-C,C'-CO)B(*t*Bu)(DMAP)C(O)}] (**4**) was prepared according to published procedures.[12] Pentane, hexane, and benzene were dried by distillation over Na/K alloy under argon and stored over molecular sieves. Dichloromethane was dried prior to use by refluxing with P_2O_5 under argon. C_6D_6 was dried over Na, distilled under argon and stored over molecular sieves. Elemental analyses were obtained from an Elementar Vario MICRO cube instrument. NMR spectra were recorded on a Bruker Avance 400 (^{1}H: 400.1 MHz, ^{11}B: 128.3 MHz, ^{13}C{^{1}H}: 100.6 MHz, ^{31}P: 162.0 MHz). Chemical shifts are given in ppm, and are referenced against external Me_4Si (^{1}H, ^{13}C), $BF_3{\cdot}Et_2O$ (^{11}B) and phosphoric acid (^{31}P).

Preparation of compound 5

The dark red complex [(η^5-C_5H_5)(OC)Mn{(κ^2-C,C'-CO)B(*t*Bu)(DMAP)C(O)}] (**4**, 20 mg, 0.5 mmol) was dissolved in CH_2Cl_2 and stirred overnight, over which time the intense red solution became yellow. Addition of pentane and slow evaporation of the solvent mixture at –30 °C afforded the title compound **5** as pale yellow crystals in 73% yield (15 mg).

IR (solid): 2009 (s), 1918 (s), 1884 (s) (νCO) cm^{-1}.

^{1}H NMR (CD_2Cl_2): δ_H 8.05, 6.58 [d, $^3J_{HH}$ =10 Hz, $N(CH)_2CN$], 4.76, 4.72, 4.61, 4.58 (m, C_5H_4B), 3.10 [6 H, $N(CH_3)_2$], 0.67 (s, 9 H, CH_3); ^{1}H NMR (C_6D_6): δ_H 7.95, 5.65 [$N(CH)_2CN$], 4.87, 4.51, 4.47, 4.28 (m, C_5H_4B), 1.90 [6 H, $N(CH_3)_2$], 1.12 (s, 9 H, CH_3).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ_C 227.5 (CO), 146.4 [$N(CH)_2(CH)_2NMe_2$], 106.2 [$(Me_2N(CH)_2$], 91.04, 87.80, 84.50, 81.59 (C_5H_4B), 39.70 [$(CH_3)_2N$], 30.09 [$BC(CH_3)_3$], 21.71 [$BC(CH_3)_3$].

^{11}B NMR (CD_2Cl_2): δ_B 2.79 (d, 64Hz).

Anal. Found: C, 57.62; H, 6.21; N, 6.95. Calcd. for $C_{19}H_{24}O_3N_2BMn$: C, 57.90; H, 6.14; N, 7.11.

Single crystal X-ray crystallographic study of 5

The crystal data of **5** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using intrinsic phasing method (ShelXT), refined with the ShelXLprogram[15] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystal data for **5**: $C_{19}H_{24}BMnN_2O_3$, M_r = 394.15, colourless needle, 0.33×0.03×0.03 mm^3, monoclinic space group *P*21/*c*, *a* = 6.0538(15) Å, *b* = 22.484(3) Å, *c* = 14.589(3) Å, β = 101.902(10)°,

V = 1943.1(7) Å^3, Z = 4, ρ_{calcd} = 1.347 g·cm^{-3}, μ = 0.699 mm^{-1}, F(000) = 824, T = 100(2) K, R_1 = 0.0349, wR^2 = 0.0752, 3810 independent reflections [$2\theta \leq 52.042°$] and 243 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1420375. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Table S2. Cartesian coordinates of all of the optimized structures involved in the reaction mechanism of **2** → **4** → **5**.

2
E(scf)= –1089.05647246 a.u.
All of the frequencies are positive

Mn	1.840360	-0.807328	0.179125
C	1.482425	-0.059539	1.710414
O	1.225992	0.490895	2.731144
C	0.438685	-1.840011	0.223625
O	-0.502674	-2.549280	0.228750
C	3.847075	-1.530524	0.551201
H	4.207430	-1.744729	1.550665
C	3.919685	-0.267072	-0.107832
H	4.368696	0.631075	0.297964
C	3.283451	-0.391899	-1.368993
H	3.173205	0.388083	-2.113896
C	2.811785	-1.728272	-1.489465
H	2.269765	-2.142858	-2.331589
C	3.176085	-2.434386	-0.300937
H	2.931990	-3.466165	-0.076729
B	0.765026	0.763316	-0.146283
C	1.062443	2.337418	-0.340540
C	0.229251	3.193433	0.628827
H	0.434584	2.936239	1.677117
H	-0.850848	3.093077	0.459045
H	0.474139	4.258745	0.502118
C	0.685992	2.735463	-1.775757
H	-0.384173	2.588944	-1.981008
H	1.252556	2.158898	-2.520844
H	0.900936	3.800405	-1.952728
C	2.530228	2.695002	-0.107703
H	2.677657	3.783787	-0.175088
H	3.190977	2.231864	-0.848764
H	2.866538	2.372759	0.886317
N	-0.828151	0.558770	-0.125482
C	-1.467696	0.175132	-1.251267
C	-1.548625	0.614829	1.016999
C	-2.805758	-0.129644	-1.287764
H	-0.838482	0.091956	-2.134691
C	-2.886961	0.302729	1.070684
H	-0.996611	0.899551	1.908777
C	-3.575140	-0.079336	-0.102034

TS1
E(scf)= –1202.34775097 a.u.
ν_{min}= –140.10 cm^{-1}

Mn	1.628163	-0.990849	-0.113776
C	1.154824	1.323139	2.249731
O	1.888938	1.123097	3.106919
C	3.152880	-0.379700	0.493447
O	4.196325	-0.035136	0.910627
C	2.460413	-2.462692	-1.423290
H	3.439032	-2.899157	-1.263470
C	2.183881	-1.277025	-2.169463
H	2.915750	-0.667279	-2.687333
C	0.787110	-1.026548	-2.088119
H	0.262613	-0.214860	-2.582890
C	0.192424	-2.052881	-1.304199
H	-0.858892	-2.139359	-1.049171
C	1.236724	-2.936659	-0.890404
H	1.116571	-3.802549	-0.249199
B	0.764346	0.823220	-0.044605
C	1.214966	2.292481	-0.578246
C	0.277792	3.433924	-0.156585
H	0.189734	3.490282	0.936789
H	-0.739010	3.337088	-0.559217
H	0.665835	4.402321	-0.505994
C	1.333491	2.286987	-2.116326
H	0.380286	2.156125	-2.647375
H	2.012059	1.494365	-2.454446
H	1.746069	3.247509	-2.459533
C	2.624261	2.658170	-0.089343
H	2.891050	3.662721	-0.450720
H	3.378265	1.958626	-0.460936
H	2.711237	2.677904	1.003592
N	-0.833666	0.693555	0.088737
C	-1.630363	0.992232	-0.965060
C	-1.435348	0.099804	1.149038
C	-2.972736	0.694583	-1.021357
H	-1.140933	1.478012	-1.801723
C	-2.775101	-0.192913	1.192755
H	-0.786683	-0.151876	1.979572
C	-3.606734	0.084032	0.081733

H	-3.240528	-0.439332	-2.232190	H	-3.520605	0.952474	-1.921618
H	-3.387967	0.349466	2.031766	H	-3.167033	-0.655569	2.092524
N	-4.900650	-0.388976	-0.091899	N	-4.931613	-0.220287	0.077403
C	-5.542603	-0.848682	-1.304796	C	-5.735100	0.074889	-1.090073
H	-5.472945	-0.096427	-2.101656	H	-5.742305	1.150711	-1.313067
H	-5.100231	-1.784737	-1.675300	H	-5.368595	-0.457583	-1.978703
H	-6.600511	-1.027402	-1.104787	H	-6.763993	-0.239141	-0.907192
C	-5.625283	-0.410302	1.161009	C	-5.533054	-0.856967	1.230885
H	-5.214675	-1.152964	1.860042	H	-5.446059	-0.230776	2.129045
H	-5.601914	0.572303	1.650367	H	-6.593748	-1.022779	1.035625
H	-6.668898	-0.663430	0.966857	H	-5.069179	-1.829835	1.443111
				C	1.129565	-1.473605	1.490683
				O	0.784776	-1.843289	2.557696

CO

E(scf)= -113.296244518 a.u.

All of the frequencies are positive

C	0.000000	0.000000	-0.652077
O	0.000000	0.000000	0.489058

A

E(scf)= –1202.38793349 a.u.

All of the frequencies are positive

Mn	-1.676356	-0.907197	0.213061
C	-1.273679	0.332007	-1.607524
O	-1.652082	0.150017	-2.721133
C	-3.291807	-0.662803	-0.452648
O	-4.386065	-0.539716	-0.847585
C	-2.473824	-1.756696	1.998630
H	-3.459981	-2.205086	2.033155
C	-2.167518	-0.384270	2.243573
H	-2.880805	0.386504	2.513174
C	-0.772839	-0.209544	2.041024
H	-0.219998	0.709690	2.196455
C	-0.210420	-1.464025	1.681405
H	0.832504	-1.659232	1.453812
C	-1.270926	-2.419645	1.657117
H	-1.178989	-3.465009	1.384520
B	-0.637769	1.001418	-0.431015
C	-1.176320	2.498132	-0.073710
C	-0.340063	3.505679	-0.882158
H	-0.373711	3.278463	-1.955860
H	0.717992	3.519048	-0.583968
H	-0.723248	4.528889	-0.747665
C	-1.192441	2.948096	1.394150
H	-0.206944	2.978959	1.880622

TS2

E(scf)= –1202.37942673 a.u.

ν_{min}= –143.15 cm^{-1}

Mn	1.926674	-0.865133	-0.205646
C	1.183199	0.025272	1.342465
O	1.183897	-0.033484	2.548967
C	3.464764	-0.627283	0.641896
O	4.481198	-0.462286	1.191219
C	2.838558	-0.986876	-2.141468
H	3.876097	-1.261723	-2.292852
C	2.353028	0.323547	-1.916396
H	2.967658	1.216932	-1.889200
C	0.913271	0.289273	-1.681163
H	0.240090	1.071951	-2.052848
C	0.572618	-1.126901	-1.808444
H	-0.425440	-1.538899	-1.687520
C	1.739811	-1.881100	-2.078665
H	1.791323	-2.959682	-2.174934
B	0.521311	0.867907	0.196421
C	0.909739	2.457344	0.296493
C	0.016345	3.084773	1.379981
H	0.067673	2.508967	2.313384
H	-1.040615	3.141717	1.083804
H	0.339880	4.112480	1.603434
C	0.821731	3.315233	-0.976138

H	-1.838790	2.309174	2.006637
H	-1.593239	3.970897	1.463486
C	-2.631122	2.627473	-0.550704
H	-2.983099	3.661907	-0.422290
H	-3.300809	1.975236	0.023193
H	-2.750768	2.369697	-1.610360
N	0.889564	0.694165	-0.355407
C	1.710116	1.326124	0.520758
C	1.469130	-0.262751	-1.134925
C	3.046628	1.027875	0.672058
H	1.244992	2.102722	1.116179
C	2.788814	-0.615114	-1.046334
H	0.812842	-0.752974	-1.846217
C	3.642985	0.017976	-0.109201
H	3.615673	1.589899	1.405332
H	3.154209	-1.387071	-1.715410
N	4.952914	-0.328565	0.021427
C	5.780573	0.351560	0.993491
H	5.866690	1.425482	0.774494
H	5.377322	0.240971	2.009702
H	6.782856	-0.079795	0.978118
C	5.517742	-1.358926	-0.823989
H	5.464224	-1.087617	-1.887449
H	6.568087	-1.499687	-0.563487
H	5.002640	-2.319812	-0.688248
C	-1.21734	-2.061889	-1.029001
O	-0.881276	-2.874447	-1.806727

Int1

E(scf)= –1202.38412286 a.u.

All of the frequencies are positive

Mn	-2.047841	-0.837217	0.123717
C	-3.631023	-0.721068	-0.682964
O	-4.666127	-0.611352	-1.209294
C	-1.724215	-2.454119	-0.522667
O	-1.463102	-3.513440	-0.944484
C	-2.972645	-0.615973	2.059983
H	-4.027892	-0.822187	2.205152
C	-2.411297	0.615519	1.663437
H	-2.991594	1.521752	1.518949
C	-0.909269	0.570651	1.647553
H	-0.383286	1.213782	2.394874
C	-0.722941	-0.915042	1.792021
H	-0.173025	3.350654	-1.442166
H	1.523692	2.982578	-1.751553
H	1.080544	4.357993	-0.739839
C	2.359556	2.594025	0.791787
H	2.623263	3.656916	0.897194
H	3.081936	2.143314	0.099354
H	2.509093	2.120053	1.768799
N	-1.010959	0.497096	0.147244
C	-1.907381	1.274832	-0.511993
C	-1.500931	-0.629524	0.731549
C	-3.251774	0.994323	-0.587069
H	-1.498308	2.159698	-0.986041
C	-2.824820	-0.983752	0.692756
H	-0.771815	-1.250664	1.241484
C	-3.769570	-0.167687	0.024180
H	-3.891224	1.683469	-1.129266
H	-3.120915	-1.898226	1.195806
N	-5.090627	-0.488515	-0.026691
C	-6.018219	0.385550	-0.711593
H	-6.039187	1.387610	-0.260514
H	-5.761265	0.493192	-1.774457
H	-7.022819	-0.035657	-0.647961
C	-5.569735	-1.685273	0.632704
H	-5.377618	-1.656789	1.714111
H	-6.646961	-1.771014	0.481490
H	-5.095460	-2.587907	0.223795
C	1.548751	-2.320346	0.716512
O	1.263335	-3.280583	1.321978

TS3

E(scf)= –1202.36511332 a.u.

ν_{min}= –100.06 cm^{-1}

Mn	-2.214863	-1.094553	0.000111
C	-3.778775	-1.560916	-0.730745
O	-4.802133	-1.856192	-1.215164
C	-1.491648	-2.692166	-0.324139
O	-0.948450	-3.712739	-0.517875
C	-3.138226	-0.340571	1.707027
H	-4.193676	-0.524583	1.879483
C	-2.581843	0.752107	0.967488
H	-3.197294	1.556936	0.575233
C	-1.111248	0.917525	1.347311
H	-0.984357	1.534133	2.289780
C	-0.879023	-0.578419	1.538325

H	0.246044	-1.408041	1.755636	H	0.102424	-1.023535	1.700523
C	-1.923883	-1.569520	2.140755	C	-2.064676	-1.181381	2.080061
H	-2.042332	-2.624483	2.364303	H	-2.137928	-2.129598	2.601455
B	-0.500738	0.887889	0.083233	B	-0.186094	1.582783	0.269953
C	-0.732802	2.456946	-0.406969	C	-0.240636	3.063137	-0.268143
C	0.301586	2.878697	-1.459314	C	0.503896	3.318967	-1.580304
H	0.329362	2.170177	-2.296286	H	0.036555	2.787195	-2.416118
H	1.318826	2.956852	-1.049736	H	1.560687	3.022237	-1.528422
H	0.050942	3.868930	-1.868053	H	0.487827	4.392241	-1.816659
C	-0.657336	3.445073	0.768777	C	0.484557	3.852011	0.851221
H	0.299709	3.423295	1.310105	H	1.538029	3.554644	0.957216
H	-1.444905	3.265127	1.512398	H	-0.003607	3.736275	1.828252
H	-0.783024	4.476693	0.407244	H	0.477006	4.923382	0.606130
C	-2.116909	2.658028	-1.047767	C	-1.667968	3.598549	-0.387640
H	-2.295233	3.729024	-1.227333	H	-1.653801	4.654742	-0.693044
H	-2.934546	2.288550	-0.417283	H	-2.206000	3.538307	0.565871
H	-2.197885	2.147752	-2.012940	H	-2.241566	3.039038	-1.135729
N	1.055466	0.431987	-0.024215	N	1.174512	0.861558	0.093901
C	1.507461	-0.672561	-0.660582	C	1.662111	0.393603	-1.082035
C	1.971906	1.165669	0.647941	C	1.906389	0.654219	1.218418
C	2.830891	-1.048187	-0.668814	C	2.854999	-0.278585	-1.163732
H	0.760041	-1.271453	-1.168227	H	1.025803	0.553193	-1.946597
C	3.311221	0.865952	0.689073	C	3.119518	0.017947	1.208987
H	1.578485	2.027289	1.178662	H	1.466534	1.025242	2.141223
C	3.799183	-0.272918	0.006633	C	3.639087	-0.495602	-0.005039
H	3.101848	-1.949468	-1.208154	H	3.165034	-0.650119	-2.133964
H	3.970248	1.513893	1.257450	H	3.643477	-0.105439	2.150229
N	5.116451	-0.605230	0.009808	N	4.817114	-1.161162	-0.051208
C	5.564427	-1.786279	-0.699399	C	5.283116	-1.726399	-1.304187
H	5.098535	-2.697727	-0.300584	H	4.571230	-2.460387	-1.703860
H	5.333883	-1.723661	-1.771401	H	5.440811	-0.946071	-2.059556
H	6.645689	-1.881890	-0.589645	H	6.235494	-2.230771	-1.135814
C	6.069656	0.221827	0.719658	C	5.564437	-1.399794	1.168865
H	6.078060	1.249826	0.332350	H	5.841518	-0.456660	1.656909
H	5.850114	0.260887	1.795510	H	4.990627	-2.006562	1.882082
H	7.070113	-0.195069	0.593941	H	6.482618	-1.936233	0.926387
C	-1.226860	-0.071918	-1.266261	C	-1.572389	-0.143623	-1.303581
O	-0.882999	0.082187	-2.402688	O	-1.129024	0.653416	-2.075879

Int2

E(scf)= –1202.38153554 a.u.

All of the frequencies are positive

TS4

E(scf)= –1202.36359590 a.u.

ν_{min}= –208.70 cm^{-1}

Mn	-2.615944	-0.925164	-0.073296	Mn	-2.467314	-0.993287	-0.049328
C	-4.316592	-0.840861	-0.680000	C	-4.039034	-0.820729	-0.879232

O	-5.402341	-0.731356	-1.089631	O	-5.065725	-0.669369	-1.419577
C	-2.451284	-2.679912	-0.453930	C	-2.427226	-2.748048	-0.343495
O	-2.273270	-3.807387	-0.697721	O	-2.371686	-3.904322	-0.523068
C	-3.129345	-0.128496	1.772602	C	-3.105547	-0.172430	1.755583
H	-4.165618	-0.129842	2.093450	H	-4.152804	-0.191746	2.036040
C	-2.469606	0.892832	1.013860	C	-2.445093	0.856408	1.003068
H	-2.978727	1.809288	0.724086	H	-2.946008	1.768254	0.689075
C	-0.956610	0.783297	1.185116	C	-0.958312	0.729149	1.185276
H	-0.617617	1.268058	2.134335	H	-0.558021	1.308809	2.122793
C	-0.991036	-0.741902	1.288512	C	-0.928527	-0.765078	1.367861
H	-0.098974	-1.367863	1.261029	H	-0.015167	-1.356480	1.405334
C	-2.187652	-1.171254	1.948416	C	-2.151004	-1.188656	1.992158
H	-2.362468	-2.127874	2.429274	H	-2.326709	-2.136780	2.488722
B	-0.079828	1.339637	-0.055942	B	0.083458	1.526070	0.394344
C	0.184673	2.929163	-0.226410	C	-0.077369	3.020532	-0.116511
C	0.868126	3.240663	-1.560832	C	1.240585	3.737109	-0.434541
H	0.270798	2.893598	-2.413638	H	1.765298	3.308863	-1.298162
H	1.861931	2.774594	-1.636290	H	1.936753	3.720932	0.415954
H	1.017447	4.323777	-1.682421	H	1.048979	4.791425	-0.677703
C	1.069748	3.462032	0.905064	C	-0.773590	3.827564	0.996373
H	2.081394	3.030682	0.881627	H	-0.153493	3.893723	1.900874
H	0.639874	3.256183	1.896161	H	-1.736113	3.393096	1.286240
H	1.190837	4.552812	0.826953	H	-0.961352	4.854298	0.651055
C	-1.149574	3.680034	-0.179608	C	-0.976104	3.042923	-1.365916
H	-1.003025	4.752417	-0.378869	H	-1.219877	4.081585	-1.632966
H	-1.626314	3.594471	0.805641	H	-1.915754	2.499548	-1.207366
H	-1.858053	3.298729	-0.926913	H	-0.486949	2.578873	-2.230622
N	1.340224	0.554960	-0.074118	N	1.456944	0.849189	0.292279
C	1.915703	0.101493	-1.207870	C	2.066574	0.727613	-0.917596
C	2.015014	0.377843	1.083107	C	2.045260	0.246965	1.360021
C	3.140043	-0.522968	-1.229073	C	3.240593	0.040991	-1.087930
H	1.339254	0.253517	-2.114741	H	1.537106	1.166924	-1.755413
C	3.245616	-0.227031	1.151621	C	3.221522	-0.445985	1.267134
H	1.510738	0.741285	1.975288	H	1.518814	0.352005	2.304982
C	3.862051	-0.709768	-0.027660	C	3.875519	-0.576661	0.015060
H	3.527553	-0.868109	-2.181599	H	3.651238	-0.030207	-2.089034
H	3.716922	-0.334916	2.122506	H	3.627161	-0.893299	2.167996
N	5.074988	-1.318972	-0.004943	N	5.041241	-1.255260	-0.115262
C	5.646646	-1.837863	-1.231102	C	5.645750	-1.408613	-1.424672
H	5.000790	-2.600850	-1.686171	H	4.984954	-1.950248	-2.114779
H	5.811193	-1.039872	-1.967282	H	5.886737	-0.433521	-1.867236
H	6.611169	-2.297698	-1.010481	H	6.573907	-1.973210	-1.326952
C	5.769171	-1.503828	1.253447	C	5.628638	-1.916691	1.033764

H	5.974032	-0.542164	1.742488	H	5.839400	-1.201063	1.838618
H	5.190684	-2.128565	1.947786	H	4.971608	-2.702805	1.430184
H	6.724216	-1.997207	1.067117	H	6.571833	-2.377722	0.737865
C	-1.631822	-0.033639	-1.110610	C	-1.383071	-0.465889	-1.320100
O	-0.757690	0.819433	-1.389111	O	-0.545173	-0.02003	-2.028727

4

E(scf)= –1202.45839528 a.u.

All of the frequencies are positive

TS5

E(scf)= –1202.39400945 a.u.

ν_{min}= –147.60 cm^{-1}

Mn	1.953567	-1.164009	-0.062100	Mn	1.857831	-0.901219	-0.179157
C	0.690458	-1.393563	-1.283946	C	1.114237	0.424658	1.546856
O	-0.150457	-1.509080	-2.083778	O	1.395734	0.453346	2.704890
C	2.814012	-2.642571	-0.535685	C	0.423815	-1.923332	-0.146704
O	3.406181	-3.598428	-0.839417	O	-0.518883	-2.626081	-0.150154
C	1.022609	-2.010909	1.179891	C	3.356969	-1.528732	1.223578
O	0.393154	-2.521133	2.021430	H	3.166560	-1.564241	2.290130
C	1.682227	0.993070	-0.061855	C	3.831881	-0.398238	0.502278
C	2.733246	0.605501	-0.969600	H	4.098464	0.561054	0.932241
H	2.707108	0.784944	-2.039581	C	3.870627	-0.735598	-0.878054
C	3.769772	-0.054106	-0.266077	H	4.153376	-0.071257	-1.687375
H	4.669708	-0.479863	-0.696980	C	3.405920	-2.071758	-1.023806
C	3.392744	-0.115785	1.104284	H	3.291733	-2.614629	-1.954191
H	3.956969	-0.572924	1.908822	C	3.091604	-2.556991	0.281313
C	2.126719	0.534391	1.216556	H	2.678645	-3.533537	0.508337
H	1.581303	0.626556	2.152245	B	0.552157	0.949703	0.216913
B	0.408144	1.851476	-0.542863	C	0.836943	2.556587	0.001715
H	0.457060	1.964152	-1.755808	C	0.325522	3.276903	1.260150
C	0.296932	3.335065	0.141232	H	0.837203	2.938581	2.169718
C	1.604831	4.079292	-0.139881	H	-0.752841	3.114126	1.407774
H	1.566635	5.115982	0.230603	H	0.474475	4.364543	1.178661
H	1.817487	4.120240	-1.217266	C	0.126307	3.204414	-1.191224
H	2.461743	3.590143	0.344108	H	-0.966819	3.115607	-1.113398
C	0.074123	3.298347	1.653685	H	0.437802	2.786090	-2.152051
H	0.008222	4.314072	2.074699	H	0.347839	4.282480	-1.208468
H	0.895209	2.791349	2.179937	C	2.339522	2.808165	-0.124608
H	-0.863690	2.788391	1.923022	H	2.551828	3.883314	-0.225008
C	-0.851440	4.122652	-0.492280	H	2.763780	2.299784	-1.000498
H	-0.901328	5.150520	-0.099048	H	2.881193	2.451465	0.762266
H	-1.829744	3.659900	-0.292688	N	-1.000765	0.577684	0.144099
H	-0.735230	4.192652	-1.582863	C	-1.691917	0.574321	-1.022437
N	-0.968578	1.037716	-0.306026	C	-1.682601	0.224915	1.261308
C	-1.229841	0.345812	0.821934	C	-3.012858	0.209023	-1.111774
H	-0.452140	0.371467	1.578851	H	-1.127830	0.859034	-1.903631
C	-2.385213	-0.371301	1.023050	C	-3.000867	-0.154224	1.255962

H	-2.497740	-0.919720	1.952259	H	-1.116539	0.251793	2.187849
C	-3.377123	-0.402142	0.016067	C	-3.723477	-0.192525	0.041407
C	-3.101952	0.343798	-1.152625	H	-3.482078	0.222448	-2.089897
H	-3.797832	0.370164	-1.984363	H	-3.460048	-0.429187	2.199617
C	-1.913089	1.023197	-1.268767	N	-5.021254	-0.587961	-0.011182
H	-1.654123	1.576604	-2.167395	C	-5.702960	-0.661376	-1.287150
N	-4.528038	-1.111142	0.163146	H	-5.751794	0.322202	-1.772925
C	-4.733928	-1.914061	1.350615	H	-5.204427	-1.360604	-1.972274
H	-5.699185	-2.418036	1.279160	H	-6.724630	-1.009882	-1.127768
H	-4.740711	-1.294629	2.257583	C	-5.690570	-1.031718	1.194528
H	-3.953941	-2.679742	1.463613	H	-5.187103	-1.900211	1.641097
C	-5.497667	-1.143472	-0.911098	H	-5.732277	-0.232561	1.946577
H	-6.357646	-1.738958	-0.600392	H	-6.714471	-1.319131	0.950983
H	-5.081612	-1.592026	-1.824411	C	1.236124	0.096477	-1.457658
H	-5.855655	-0.134568	-1.156025	O	0.968175	0.636585	-2.486976

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E(scf)= –1202.41558756 a.u.

All of the frequencies are positive

Mn	-1.930869	-0.804531	-0.010131
C	-1.189974	0.161459	-1.357380
O	-1.108378	0.440864	-2.530447
C	-0.627727	-1.989606	-0.008114
O	0.232963	-2.783839	-0.002202
C	-3.700348	-1.196363	-1.205593
H	-3.669387	-1.155345	-2.296800
C	-3.957509	-0.095264	-0.334950
H	-4.202272	0.924666	-0.650600
C	-3.813125	-0.542912	1.016738
H	-3.906010	0.075585	1.915449
C	-3.454792	-1.924159	0.988904
H	-3.222973	-2.551962	1.847109
C	-3.375655	-2.325637	-0.395919
H	-3.094592	-3.313732	-0.754411
B	-0.517813	0.866378	0.001805
C	-0.698024	2.494511	0.002255
C	-0.000813	3.126234	-1.206461
H	-0.375707	2.708667	-2.150592
H	1.088268	2.969286	-1.172129
H	-0.160754	4.214148	-1.221955
C	-0.095483	3.106939	1.273337
H	0.988232	2.930085	1.336947
H	-0.551554	2.699852	2.183826
H	-0.236937	4.198544	1.287109

C	-2.184843	2.848064	-0.053566
H	-2.330434	3.935286	0.013061
H	-2.746932	2.393070	0.776307
H	-2.639675	2.511901	-0.997319
N	1.037450	0.461576	-0.004035
C	1.727437	0.318079	1.149231
C	1.714955	0.279938	-1.165428
C	3.057896	-0.021288	1.198502
H	1.145423	0.471369	2.061401
C	3.044634	-0.059983	-1.201595
H	1.131429	0.413136	-2.070471
C	3.773358	-0.236868	-0.005787
H	3.525263	-0.132136	2.166048
H	3.509208	-0.194684	-2.174650
N	5.084330	-0.590265	-0.006279
C	5.776088	-0.798124	1.251876
H	5.780513	0.109727	1.865827
H	5.310405	-1.604989	1.838815
H	6.810100	-1.083510	1.049610
C	5.762733	-0.837316	-1.257707
H	5.298087	-1.663851	-1.813661
H	5.775403	0.050993	-1.897573
H	6.798794	-1.11657	-1.052824
C	-1.168139	0.149695	1.346886
O	-1.069533	0.361511	2.534718

Table S3. Cartesian coordinates of all of the optimized structures involved in the isomerization reaction of **2** → **3**.

$2^{w\text{-}L}$
E(scf)= –2057.48791232 a.u.
All of the frequencies are positive

Mn	-1.377570	-0.203086	0.021157
C	-1.429303	0.831327	1.432375
O	-1.456100	1.460525	2.412640
C	-2.022787	1.027374	-1.057515
O	-2.512893	1.765905	-1.804011
C	-2.426734	-1.780698	1.035247
H	-2.900570	-1.653080	1.999053
C	-1.083202	-2.200331	0.815243
H	-0.376153	-2.485294	1.581837
C	-0.857993	-2.219010	-0.584000
H	0.050722	-2.534026	-1.076938
C	-2.056922	-1.812674	-1.226020
H	-2.210551	-1.726392	-2.293114
C	-3.033641	-1.553891	-0.220699
H	-4.047315	-1.218592	-0.388546
B	0.380835	0.695400	-0.080434
C	0.934582	2.224722	-0.086393
C	1.887943	2.439550	-1.275388
H	1.375470	2.303157	-2.234899
H	2.752653	1.764920	-1.243611
H	2.281131	3.465163	-1.263856
C	1.743340	2.459174	1.205204
H	2.606823	1.786729	1.281233
H	1.120698	2.333233	2.097660
H	2.135427	3.485323	1.223057
C	-0.137346	3.317571	-0.161850
H	0.334059	4.307843	-0.091195
H	-0.861527	3.242871	0.653560
H	-0.688336	3.283606	-1.104278
C	1.554463	-0.385712	-0.061148
N	2.110597	-1.001929	1.009154
C	2.999276	-1.975008	0.600806
H	3.538975	-2.589356	1.303215
C	3.006046	-1.958437	-0.750926
H	3.549207	-2.557501	-1.463806
N	2.121973	-0.974356	-1.141484
C	1.805454	-0.706519	2.393373

$TS^{w\text{-}L}{}_{2\rightarrow B}$
E(scf)= –2057.44848963 a.u.
ν_{min}= –977.66 cm^{-1}

Mn	-1.427372	-0.229875	0.094054
C	-1.319813	0.847911	1.472743
O	-1.239672	1.517599	2.421190
C	-2.303949	0.941351	-0.883628
O	-2.931101	1.672075	-1.535088
C	-2.630701	-1.651931	1.097532
H	-3.302593	-1.396130	1.904762
C	-1.267105	-2.054973	1.231270
H	-0.724419	-2.167663	2.159777
C	-0.758980	-2.293255	-0.067826
H	0.241482	-2.637537	-0.289971
C	-1.790812	-2.052604	-1.012539
H	-1.731513	-2.188452	-2.083800
C	-2.950048	-1.651951	-0.281085
H	-3.909978	-1.395030	-0.707843
B	0.517861	0.728229	-0.332391
C	0.901361	2.283474	-0.417571
C	2.328986	2.700224	-0.100102
H	3.065691	1.946503	-0.401809
H	2.456898	2.882035	0.973591
H	2.587764	3.637092	-0.611172
C	-0.080911	3.378922	-0.045517
H	-0.081320	3.549934	1.035795
H	-1.103885	3.132920	-0.335708
H	0.189948	4.325671	-0.533790
C	0.743912	1.692605	-1.793837
H	-0.091940	2.063031	-2.388333
H	-0.042276	0.555929	-1.498725
H	1.646562	1.522263	-2.378227
C	1.695302	-0.294023	-0.141167
N	2.346469	-0.511344	1.024947
C	3.240347	-1.551608	0.897721
H	3.852388	-1.884923	1.719973
C	3.150606	-1.992326	-0.377440
H	3.668087	-2.786355	-0.891020
N	2.203924	-1.208697	-1.004347
C	2.100653	0.207999	2.257537

H	2.563119	-0.050004	2.829073
H	1.767707	-1.640482	2.959248
H	0.831094	-0.218712	2.445384
C	1.760755	-0.681050	-2.511624
H	0.739489	-0.288628	-2.515161
H	1.796201	-1.602600	-3.097146
H	2.437121	0.056194	-2.950397

$B^{w\text{-}L}$

E(scf)= –2057.49063786 a.u.

All of the frequencies are positive

Mn	-1.559219	-0.124243	-0.013895
C	-1.363529	-0.144019	1.742829
O	-1.300206	-0.200128	2.897462
C	-2.458802	1.402795	0.082544
O	-3.107352	2.356832	0.134187
C	-2.309319	-2.101216	0.033763
H	-2.494995	-2.646000	0.949823
C	-1.091814	-2.104569	-0.706553
H	-0.201703	-2.672829	-0.473816
C	-1.284597	-1.257146	-1.833455
H	-0.549301	-1.025880	-2.591406
C	-2.598797	-0.742954	-1.795692
H	-3.036178	-0.064839	-2.515345
C	-3.239869	-1.263344	-0.630298
H	-4.253990	-1.062151	-0.315227
B	0.746482	0.853015	0.174594
C	1.377777	2.329191	-0.082907
C	0.578857	3.371414	-0.831317
H	-0.497099	3.242543	-0.680512
H	0.767474	3.328685	-1.913209
H	0.838393	4.387602	-0.499936
C	2.873070	2.502641	-0.245073
H	3.184588	2.454499	-1.297729
H	3.439870	1.739477	0.301928
H	3.200458	3.481269	0.135605
C	0.908421	1.965058	1.302751
H	1.685009	1.889132	2.063825
H	-0.273031	0.794287	-0.584834
H	0.017201	2.468817	1.670299
C	1.720776	-0.385611	0.069968
N	2.152641	-1.223967	1.038164
C	2.996559	-2.177544	0.518654
H	3.446911	-2.940858	1.132517

H	2.927165	0.889698	2.474638
H	1.994577	-0.506559	3.077536
H	1.174151	0.774060	2.160819
C	1.754889	-1.396846	-2.365631
H	0.664364	-1.332813	-2.396874
H	2.063569	-2.388465	-2.701234
H	2.181278	-0.644401	-3.033558

$TS^{w\text{-}L}_{B\rightarrow 3}$

E(scf)= –2057.45438352 a.u.

ν_{min}= –855.29 cm^{-1}

Mn	-1.363642	-0.474529	0.084612
C	-0.411523	-1.921840	0.359215
O	0.193580	-2.901306	0.541742
C	-1.530518	-0.213186	1.809822
O	-1.644599	-0.035325	2.952760
C	-2.756014	-1.530163	-1.110888
H	-2.842819	-2.608015	-1.108431
C	-1.935461	-0.758458	-1.989208
H	-1.317475	-1.151034	-2.785053
C	-2.121712	0.607030	-1.654727
H	-1.658478	1.451394	-2.150447
C	-3.053436	0.690174	-0.589399
H	-3.421749	1.597040	-0.131043
C	-3.444723	-0.640761	-0.252749
H	-4.148625	-0.919857	0.518829
B	0.482546	0.703007	0.420575
C	0.613564	2.508372	0.305765
C	-0.623142	3.369097	0.163363
H	-1.502118	2.843833	0.544859
H	-0.811732	3.661353	-0.876468
H	-0.490149	4.285701	0.750675
C	1.848338	3.100935	-0.327644
H	1.702637	3.309133	-1.393983
H	2.721745	2.453274	-0.212317
H	2.079879	4.060189	0.154880
C	0.753494	1.778619	1.586194
H	1.762398	1.796279	1.996038
H	-0.023415	1.411704	-0.496305
H	-0.010138	1.953668	2.340876
C	1.757169	-0.066069	-0.089721
N	2.543542	-0.842630	0.693200
C	3.462520	-1.527375	-0.069152
H	4.165232	-2.218768	0.366091

C	3.101847	-1.926506	-0.808120	C	3.256952	-1.162225	-1.354445
H	3.665927	-2.424247	-1.580360	H	3.751519	-1.461490	-2.264074
N	2.320642	-0.824518	-1.062482	N	2.212223	-0.263750	-1.350457
C	1.740783	-1.180485	2.426090	C	2.365169	-1.032673	2.117549
H	2.623077	-1.233855	3.068722	H	3.065724	-0.413238	2.685480
H	1.073311	-2.016890	2.647159	H	2.525900	-2.085526	2.355604
H	1.207039	-0.248718	2.598296	H	1.344060	-0.762328	2.385466
C	2.193625	-0.193557	-2.358191	C	1.610372	0.308261	-2.530420
H	1.543071	0.673888	-2.242736	H	0.524436	0.269862	-2.415223
H	1.764318	-0.893940	-3.079569	H	1.899894	-0.287037	-3.398317
H	3.175277	0.131893	-2.712014	H	1.933088	1.341340	-2.681856

$3^{w\text{-}L}$

E(scf)= –2057.49294901 a.u.

All of the frequencies are positive

Mn	1.547873	-0.455020	0.004986
C	1.288296	-1.359651	1.485231
O	1.114724	-1.926473	2.484895
C	1.280335	-1.895915	-0.963809
O	1.112302	-2.842288	-1.612843
C	3.201748	0.629600	0.839603
H	3.577273	0.463153	1.840277
C	2.188846	1.560681	0.475506
H	1.686771	2.247545	1.142860
C	1.983180	1.450281	-0.923900
H	1.302103	2.045646	-1.515345
C	2.867038	0.454766	-1.418527
H	2.949848	0.134569	-2.448420
C	3.632397	-0.045784	-0.328647
H	4.386712	-0.817880	-0.379190
B	-0.412999	-0.417950	0.098980
C	-2.840347	-1.601659	-0.311067
C	-3.456230	-2.998987	-0.252973
H	-2.803587	-3.738084	-0.728413
H	-4.431044	-3.033206	-0.753493
H	-3.604181	-3.309791	0.788713
C	-3.817026	-0.587786	0.283104
H	-4.787852	-0.629297	-0.223993
H	-3.456589	0.443578	0.213303
H	-3.993181	-0.806976	1.344148
C	-1.465360	-1.593353	0.386151
H	-1.641622	-1.597976	1.478100
H	-2.697775	-1.354749	-1.374762
H	-0.974844	-2.555556	0.194755

C	-1.011934	1.045009	-0.000823
N	-1.219246	1.904570	1.021959
C	-1.666995	3.120551	0.548149
H	-1.877473	3.949914	1.203893
C	-1.744037	3.011485	-0.798271
H	-2.034372	3.726568	-1.550889
N	-1.341481	1.730634	-1.117937
C	-1.047877	1.555552	2.415527
H	-1.984982	1.182745	2.838981
H	-0.723383	2.436766	2.973061
H	-0.282188	0.779549	2.489556
C	-1.284299	1.173356	-2.451480
H	-0.520031	0.390952	-2.460006
H	-1.009932	1.956768	-3.161523
H	-2.249033	0.745791	-2.738372

$2^{wo\text{-}L}$

E(scf)= –1752.98837926 a.u.

All of the frequencies are positive

Mn	-0.795798	0.157131	0.003548
C	-0.352503	1.261453	1.313786
O	-0.053029	1.957409	2.185112
C	-0.380652	1.337326	-1.248508
O	-0.102789	2.084063	-2.084001
C	-2.761302	-0.304776	0.777250
H	-3.287494	0.311444	1.493070
C	-1.851786	-1.355355	1.091325
H	-1.581965	-1.686106	2.084243
C	-1.363168	-1.890776	-0.132578
H	-0.683112	-2.724607	-0.235506
C	-1.967234	-1.168378	-1.197234
H	-1.799725	-1.332103	-2.252456
C	-2.834231	-0.189527	-0.628992
H	-3.426438	0.528692	-1.178512
B	0.938907	-0.216928	-0.013479
C	2.474775	-0.447249	-0.017310
C	2.885139	-1.208983	-1.287172
H	2.601586	-0.665108	-2.194075
H	2.424101	-2.201520	-1.330906
H	3.973899	-1.346540	-1.304864
C	2.884972	-1.240943	1.232863
H	2.423458	-2.234074	1.251648
H	2.601523	-0.720150	2.153279
H	3.973718	-1.379065	1.247050

$TS^{wo\text{-}L}{}_{2\rightarrow B}$

E(scf)= –1752.92586137 a.u.

ν_{min}= –932.64 cm^{-1}

Mn	0.766827	0.112594	0.030544
C	0.163421	1.527574	-0.842268
O	-0.218801	2.451680	-1.418644
C	0.128585	0.777791	1.539370
O	-0.278010	1.206690	2.531132
C	2.880945	0.409562	-0.037880
H	3.357800	1.369447	0.099612
C	2.440768	-0.144705	-1.273438
H	2.523828	0.325580	-2.243721
C	1.881807	-1.422617	-1.015765
H	1.481956	-2.099820	-1.759277
C	1.959517	-1.661415	0.385019
H	1.621864	-2.548567	0.903134
C	2.571157	-0.527449	0.982982
H	2.763906	-0.398099	2.039368
B	-1.079338	-0.437844	-0.133601
C	-2.632136	-0.486363	-0.154173
C	-3.327532	0.312247	-1.243525
H	-2.793932	0.255724	-2.197235
H	-3.391811	1.368821	-0.966163
H	-4.346958	-0.062481	-1.402366
C	-3.336765	-0.438056	1.190820
H	-3.403309	0.591761	1.554789
H	-2.808584	-1.020959	1.951626
H	-4.355584	-0.837027	1.104378

C	3.142625	0.940949	0.000319
H	4.234166	0.825723	-0.001514
H	2.866938	1.511307	0.893585
H	2.866479	1.534241	-0.877726

$B^{wo\text{-}L}$

E(scf)= –1752.96361272 a.u.

All of the frequencies are positive

Mn	0.780343	0.125352	-0.090263
C	0.853716	1.869271	-0.483982
O	0.942792	2.987160	-0.722462
C	-0.209219	0.504775	1.328126
O	-0.741751	0.748703	2.322695
C	2.868335	0.002492	0.294407
H	3.468396	0.843112	0.614634
C	2.611698	-0.383649	-1.056619
H	2.990854	0.106277	-1.942491
C	1.782321	-1.535172	-1.025609
H	1.376010	-2.044812	-1.888680
C	1.512100	-1.859329	0.323078
H	0.882208	-2.666467	0.667961
C	2.183119	-0.902253	1.140951
H	2.169116	-0.870284	2.221974
B	-1.146047	-0.435773	-0.289393
C	-2.691751	-0.257811	-0.292805
C	-3.295577	0.287295	-1.573468
H	-2.682665	0.052951	-2.451503
H	-3.402235	1.377594	-1.529382
H	-4.293458	-0.139530	-1.748556
C	-3.515995	0.046131	0.938037
H	-3.609951	1.126983	1.097849
H	-3.072962	-0.377381	1.844234
H	-4.530111	-0.364452	0.837451
C	-2.083986	-1.671401	-0.384669
H	-2.232744	-2.293954	0.496888
H	-0.346009	0.033736	-1.248172
H	-2.191669	-2.227697	-1.315215

$3^{wo\text{-}L}$

E(scf)= –1752.99145659 a.u.

All of the frequencies are positive

Mn	0.964423	0.145219	0.043080
C	1.110730	1.833932	-0.470683
O	1.201711	2.925457	-0.833649

C	-2.047913	-1.798970	-0.556843
H	-2.068666	-2.624633	0.150829
H	-0.399665	-1.409802	-0.471227
H	-2.071470	-2.088132	-1.605050

$TS^{wo\text{-}L}_{B\rightarrow 3}$

E(scf)= –1752.93094816 a.u.

ν_{min}= –788.57 cm^{-1}

Mn	0.761091	0.105507	-0.003120
C	0.785892	1.390449	-1.218471
O	0.816059	2.221089	-2.018811
C	0.682576	1.323100	1.275482
O	0.641492	2.109596	2.119713
C	2.753469	-0.653966	-0.064659
H	3.632749	-0.028357	-0.120296
C	2.017869	-1.173765	-1.166949
H	2.239346	-1.005485	-2.212005
C	0.947489	-1.955856	-0.661933
H	0.224011	-2.497640	-1.256608
C	1.005918	-1.911944	0.759271
H	0.333318	-2.410395	1.443938
C	2.115884	-1.104283	1.122001
H	2.422964	-0.871036	2.132477
B	-1.142891	0.479972	-0.020939
C	-2.723552	-0.241578	-0.027592
C	-3.153832	-0.912726	1.250332
H	-2.651575	-0.477669	2.120597
H	-2.938728	-1.987040	1.235627
H	-4.235408	-0.792140	1.399865
C	-3.181842	-0.872470	-1.316188
H	-2.972043	-1.947755	-1.338059
H	-2.694372	-0.413516	-2.182627
H	-4.265410	-0.742720	-1.440969
C	-2.506715	1.225565	-0.007044
H	-2.759291	1.784965	-0.906110
H	-1.018072	-0.728428	-0.076077
H	-2.749650	1.759043	0.910244

C	0.351918	0.591784	1.642900
O	-0.063103	0.853426	2.687835
C	2.985321	-0.402528	-0.494632
H	3.784944	0.311090	-0.637473
C	2.074657	-0.844888	-1.496874
H	2.074662	-0.540549	-2.533918
C	1.166544	-1.756598	-0.890294
H	0.375166	-2.295522	-1.392248
C	1.516469	-1.872497	0.482518
H	1.016490	-2.488277	1.216978
C	2.644635	-1.034150	0.722215
H	3.137740	-0.891011	1.673466
B	-0.727217	0.310105	-0.468352
C	-3.238720	-0.115136	0.072262
C	-4.654029	0.285969	-0.332447
H	-4.778836	1.373839	-0.330870
H	-5.395152	-0.139407	0.352671
H	-4.886382	-0.075730	-1.341488
C	-3.089324	-1.633270	0.114337
H	-3.811648	-2.081358	0.804296
H	-2.085270	-1.927753	0.439959
H	-3.263449	-2.068420	-0.877748
C	-2.200955	0.515784	-0.877954
H	-2.343206	0.124946	-1.898062
H	-3.047400	0.273445	1.081856
H	-2.364490	1.602224	-0.954230

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