SUPPORTING INFORMATION TO

On the Mechanism of Iridium-Catalyzed Asymmetric Hydrogenation of Imines and Alkenes: A Theoretical Study

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Table S1. Comparison of electronic energies (kcal mol^{-1}) for Mechanism A, B and C at the B3LYP and B3LYP* level (B3LYP geometries).

	ΔE, B3LYP	ΔE, B3LYP*
Mechanism A		
$Reac_{A\text{-}si,a}$	0.0	0.0
$TS1_A$	22.0	21.7
$Inter_A$	11.8	12.2
$TS2_A$	23.0	23.3
$Alkane_A$	22.2	23.0
Mechanism B		
$Reac_{B\text{-}si,b}$	-1.6	-2.2
$TS1_B$	11.3	10.6
$Inter_B$	5.5	4.7
$TS2_B$	6.6	5.9
$Alkane_B$	-5.9	-5.1
Mechanism C		
$Reac_{B\text{-}si,b}$	-1.6	-2.2
$TS1_C$	14.7	13.4
$Inter_C$	14.0	12.8
$TS2_C$	15.0	13.9
$Alkane_C$	-5.9	-5.1

Table S2. Comparison of Gibbs free energies (B3LYP) for Mechanism A, B and C with and without empirical dispersion corrections (DFT-D3).

	$\Delta G^{298K,sol}$	$\Delta G^{298K,sol,dis}$
Mechanism A		
$Reac_{A\text{-}si,a}$	0.0	0.0
$TS1_A$	19.2	23.0
$Inter_A$	12.0	15.3
$TS2_A$	24.0	27.4
$Alkane_A$	24.0	27.9
η^2-$Alkane_A$	15.6	18.6
Mechanism B		
$Reac_{B\text{-}si,b}$	6.6	5.7
$TS1_B$	18.6	18.5
$Inter_B$	15.7	16.1
$TS2_B$	16.2	16.9
$Alkane_B$	5.2	9.6
η^2-$Alkane_B$	-5.7	-1.4
Mechanism C		
$Reac_{B\text{-}si,b}$	6.6	5.7
$TS1_C$	22.7	22.0
$Inter_C$	22.6	21.8
$TS2_C$	23.2	22.3
$Alkane_{B/C}$	5.2	9.6
η^2-$Alkane_{B/C}$	-5.7	-1.4

Table S3. Computed enthalpies (kcal mol^{-1}, 298 K, including solvent correction) for hydrogenation of substrate **S2** (catalyst **C1**) with different substrate orientations (Mechanism B).[a]

	Coordination through *si*-face				**Coordination through *re*-face**			
	1si,b	**1si,a**	**2si,b**	**2si,a**	**1re,b**	**1re,a**	**2re,b**	**2re,a**
Reac	-0.3	-0.3	1.8	2.1	0.7	3.3	1.4	3.2
TS1	10.1	14.3	15.7	18.1	14.1	20.5	12.3	15.9
Inter	7.6	11.3	11.1	17.1	12.2	15.9	9.4	12.1
TS2	8.0	11.8	11.3	16.6	12.6	16.1	9.8	12.7
Alkane	-0.2	-1.5	-0.1	-4.1	-0.1	-2.8	0.6	-4.9
Configuration	*(R)*	*(R)*	*(R)*	*(R)*	*(S)*	*(S)*	*(S)*	*(S)*

[a] The energetic reference is the **S2**-coordinated dihydride reactant (one hydride above, one equatorial) + free H_2.

Table S4 Comparison of Gibbs free energy barriers (B3LYP) for the hydrogenation of substrate **S2** (with different substrate orientations) with and without empirical dispersion corrections (DFT-D3).

Coordination	$\Delta G^{298K,sol}$	$\Delta G^{298K,sol,dis}$
1si,b	18.2	18.2
1si,a	22.6	21.4
2si,b	23.6	24.2
2si,a	27.0	25.9
1re,b	23.2	21.6
1re,a	28.9	29.3
2re,b	21.7	20.4
2re,a	24.1	24.4

Table S5. Computed energies (kcal mol^{-1}) for Mechanism A1$_{IM}$ and A2$_{IM}$ (Figure S5 and S6, Scheme 6, Substrate **S3** and catalyst **C1**).

	ΔE	ΔG^{298K}	Δ$H^{298K,sol}$	Δ$G^{298K,sol}$
Reac $_{A-IM}$	0.0	0.0	0.0	0.0
TS1 $_{A1-IM}$	32.2	30.1	30.8	30.5
Inter $_{A1-IM}$	29.4	29.4	30.0	29.7
TS2 $_{A1-IM}$	56.0	54.3	56.2	55.9
(*R*)-Prod $_{A1/A2-IM}$	21.8	24.6	27.3	26.8
TS1 $_{A2-IM}$	53.6	50.5	52.2	51.3
Inter2$_{A2-IM}$	13.1	15.3	14.6	15.9
TS2$_{A2-IM}$	24.2	24.2	26.8	26.1

[a] Includes effect of CH_2Cl_2 solvent.

Table S6. Computed energies (kcal mol^{-1}) for Mechanism B1$_{IM}$ and C1$_{IM}$ (Figure S7 and S9, Scheme 6, Substrate **S3** and catalyst **C1**).[a]

	ΔE	ΔG^{298K}	Δ$H^{298K,sol\ b}$	Δ$G^{298K,sol\ b}$
Reac$_{IM,b}$	-1.6	8.3	1.1	8.4
TS1$_{B1-IM}$	29.5	40.0	27.9	37.4
Inter$_{B1/C1-IM}$	23.2	35.2	23.3	31.8
TS2$_{B1/C1-IM}$	32.6	44.6	34.7	43.5
(*S*)-Prod$_{B1/C1-IM}$	-9.9	4.8	-3.4	3.9
Reac$_{IM,a}$	-0.2	10.8	1.4	9.6
TS1$_{C1-IM}$	40.8	50.5	38.4	47.8

[a] The energetic reference is Reac$_{A-IM}$ + free H_2. [b] Includes effect of CH_2Cl_2 solvent.

Table S7. Computed energies (kcal mol^{-1}) for Mechanism B2$_{IM}$ and C2$_{IM}$ (Figure S8 and S10, Scheme 6, substrate **S3** and catalyst **C1**).[a]

	ΔE	ΔG^{298K}	Δ$H^{298K,sol\ b}$	Δ$G^{298K,sol\ b}$
Reac$_{IM.a}$	-0.2	10.8	1.4	9.6
TS1$_{B2-IM}$	50.5	60.0	48.1	57.5
Inter$_{B2-IM}$	7.4	22.5	11.0	20.9
TS2$_{B2-IM}$	12.6	27.0	15.2	25.6
(*S*)-Prod$_{B2-IM}$	-13.6	1.9	1.2	-6.9
Reac$_{IM.b}$	-1.6	8.3	1.1	8.4
TS1$_{C2-IM}$	41.4	51.6	40.0	49.9
Inter$_{C2-IM}$	8.8	23.1	11.5	21.3
TS2$_{C2-IM}$	11.9	25.8	13.9	24.1
(*S*)-Prod$_{C2-IM}$	-16.2	-0.1	-9.5	-0.8

[a] The energetic reference is Reac$_{A-IM}$ + free H_2. [b] Includes effect of CH_2Cl_2 solvent.

Table S8. Computed energies (kcal mol[-1]) for Mechanism $H1_{IM}$ and $H2_{IM}$ (Figure S11-S13, Scheme 7, substrate **S3** and catalyst **C1**).[a]

	ΔE	ΔG^{298K}	$\Delta H^{298K,sol\ b}$	$\Delta G^{298K,sol\ b}$
$Reac_{IM,b}$	-1.6	8.3	1.1	8.4
$TS1_{H1/H2-IM}$	24.6	31.7	23.9	30.8
$Inter1_{H1/H2-IM}$	22.4	31.5	22.4	28.9
$Inter2_{H1/H2-IM}$	9.7	15.9	13.3	15.6
$TS2_{H1-IM}$	25.3	35.7	25.7	32.8
$Inter3_{H1-IM}$	4.7	20.2	7.6	17.9
$TS2_{H1-IM}$	11.3	25.3	15.5	23.2
(*R*)-$Prod_{H1-IM}$	-0.9	13.7	6.4	13.0
$TS2_{H2-IM}$	17.0	29.2	16.7	25.4
(*R*)-$Prod_{H2-IM}$	8.7	21.5	11.5	18.5
(*R*)-$Prod_{H2-IM-H2\ bound}$	-16.9	-4.8	-14.4	-5.9

[a] The energetic reference is $Reac_{A-IM}$ + free H_2. [b] Includes effect of CH_2Cl_2 solvent.

Table S9. Computed energies (kcal mol[-1]) for Mechanism $H3_{IM}$ with H_2 as additional ligand (Figure S14, Scheme 7, Substrate **S3** and catalyst **C1**).

	Electronic Energy	ΔG^{298K}	$\Delta H^{298K,sol\ a}$	$\Delta G^{298K,sol\ a}$
$Reac_{IM,b}$	0.0	0.0	0.0	0.0
$Inter1_{H3-IM,H2}$	5.7	12.0	8.9	13.0
$TS1_{H3-IM,H2}$	8.0	13.6	10.2	15.2
$Inter2_{H3-IM,H2}$	-2.9	5.7	-0.1	4.5
$TS2_{H3-IM,H2}$	8.5	19.4	9.6	17.7
$Prod_{H3-IM}$	-0.8	11.9	3.0	10.5
$Prod_{H3-IM-bound,H2}$	-18.1	-1.9	-13.4	-4.5

[a] Includes solvent effects.

Table S10. Computed Energies (kcal mol[-1]) for hydrogenation of substrate **S3** (catalyst **C1**) with different substrate orientations at TS2 (Mechanism H_{IM}, H_2 above, Figure S15).[a]

Orientation	Electronic	ΔG^{298K}	$\Delta H^{298K,sol\ b}$	$\Delta G^{298K,sol\ b}$	Configuration
1re$_{IM}$	8.8	19.6	11.1	17.8	*(S)*
2re$_{IM}$	9.8	20.3	12.1	18.6	*(S)*
1si$_{IM}$	8.5	19.4	10.8	17.7	*(R)*
2si$_{IM}$	8.5	20.1	10.4	17.7	*(R)*

[a] $Reac_{IM,,b}$ (with free H_2) as energetic reference, [b]Includes solvent effect..

Table S11. Computed Gibbs Free barriers (kcal mol[-1]) for hydrogenation of substrate **S3** (catalyst **C1**) with different substrate orientations at TS2 (Mechanism H_{IM}, CH_2Cl_2 above, Figure S15) with and with dispersion corrections (DFT-D3).[a]

Orientation	$\Delta G^{298K,sol\ b}$	$\Delta G^{298K,sol,dis\ b}$	Configuration
1re$_{IM}$	19.4	23.2	*(S)*
2re$_{IM}$	19.5	23.8	*(S)*
1si$_{IM}$	17.7	21.2	*(R)*
2si$_{IM}$	18.1	22.6	*(R)*

[a] Reac$_{IM,,b}$ (with free H_2) as energetic reference, [b]Includes solvent effect..

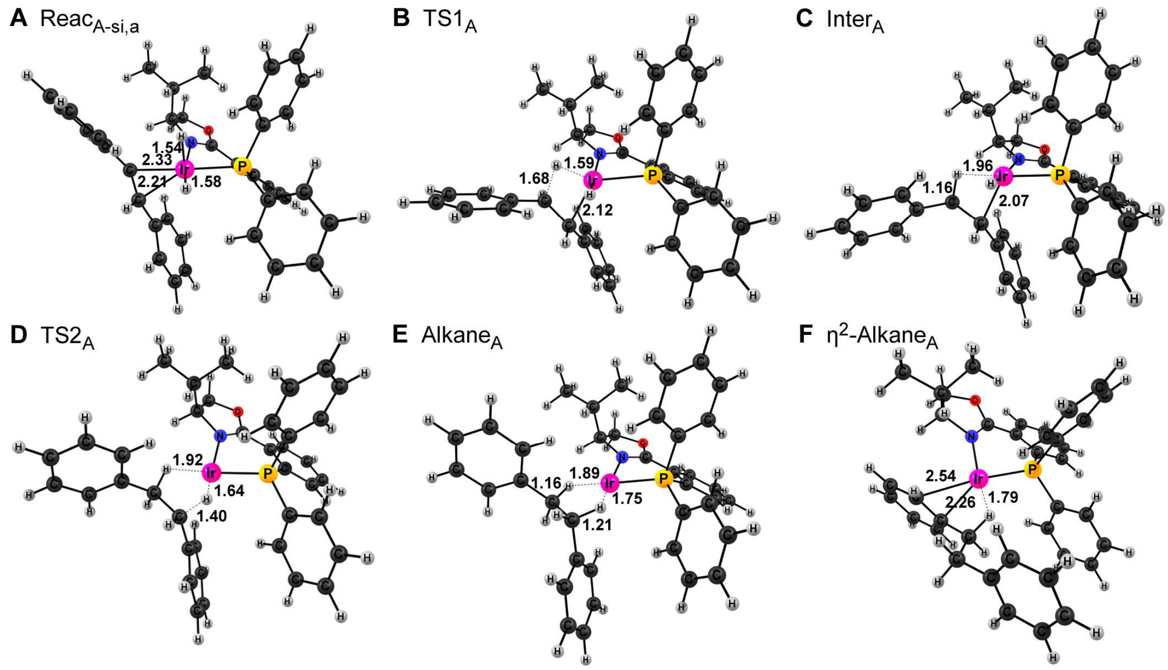

Figure S1. Optimized geometries for Mechanism A (catalyst **C1**, substrate **S1**), **A**) Reac$_{A\text{-si,a}}$, **B**) TS1$_A$, **C**) Inter$_A$, **D**) TS2$_A$, **E**) Alkane$_A$, **F**) η^2-Alkane$_A$.

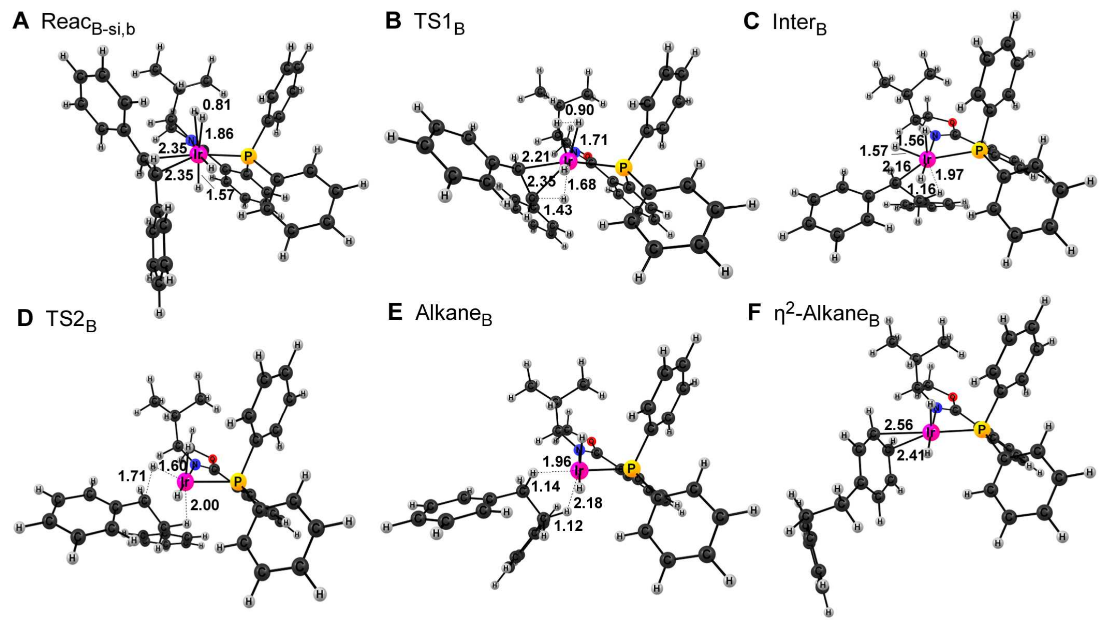

Figure S2. Optimized geometries for Mechanism B (catalyst **C1**, substrate **S1**), **A**) Reac$_{B\text{-si,b}}$, **B**) TS$_B$, **C**) Inter$_B$, **D**) TS2$_B$, **E**) Alkane$_B$, **F**) η^2-Alkane$_B$.

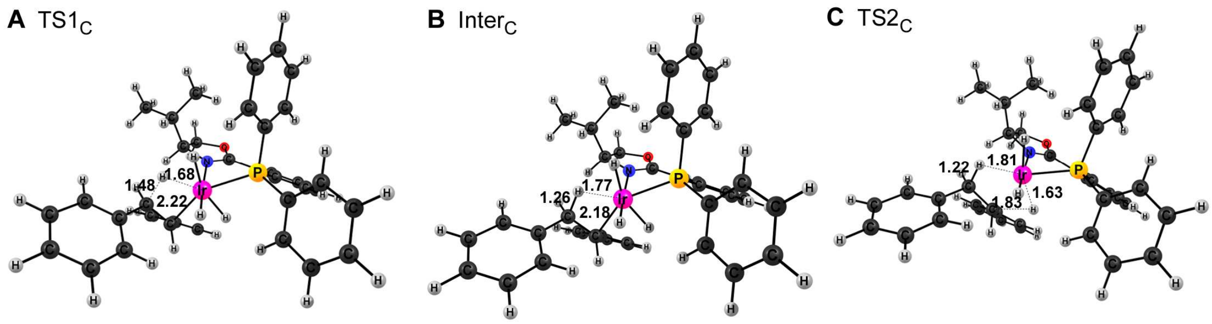

Figure S3. Optimized geometries for Mechanism C (**C1** and **S1**), **A**) $TS1_C$, **B**) $Inter_C$, **C**) $TS2_C$.

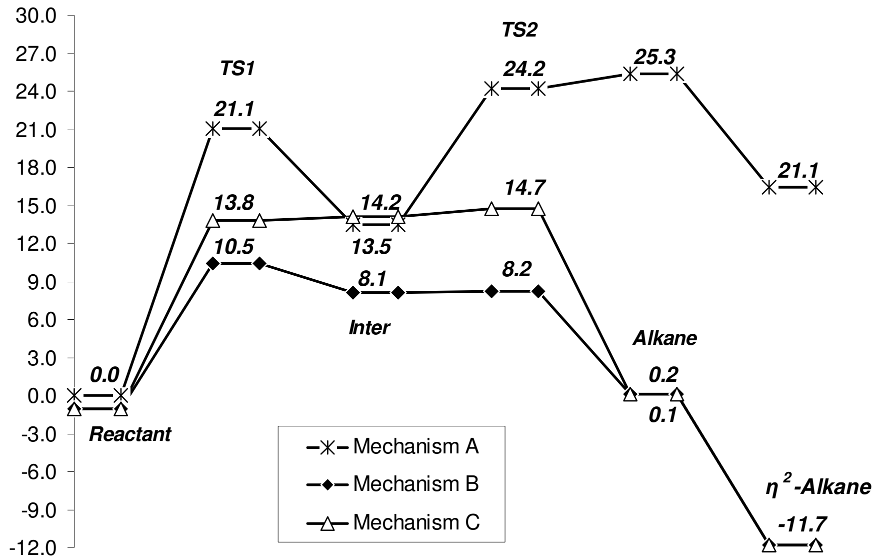

Figure S4. Computed enthalpies (kcal mol^{-1}, corrected for solvent effects) for Mechanism A, B and C (catalyst **C1** and substrate **S1**).

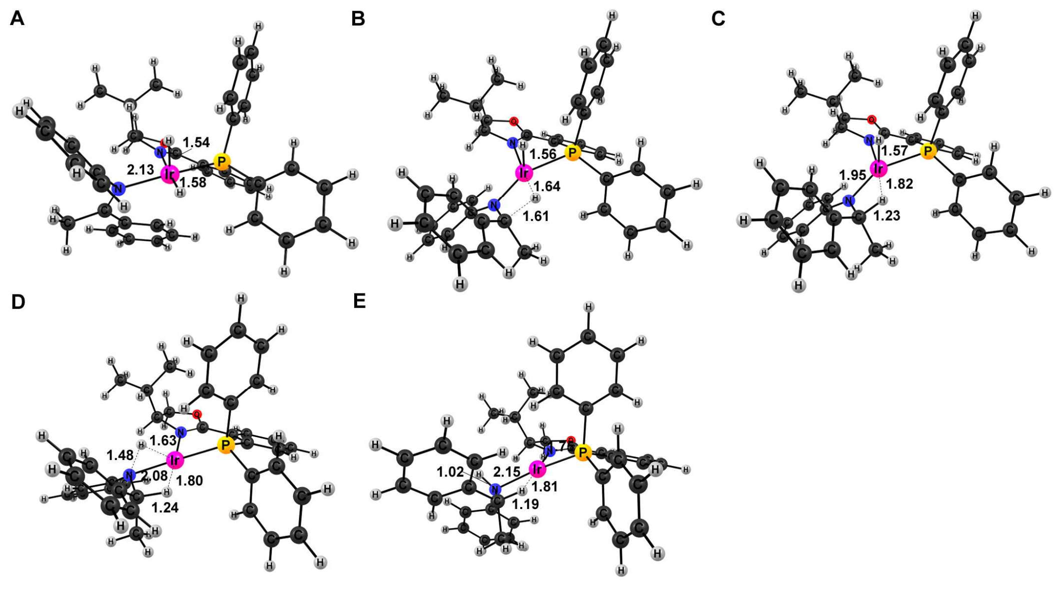

Figure S5. Optimized geometries for Mechanism $A1_{IM}$ (catalyst **C1**, substrate **S3**). **A**) $Reac_{A-IM}$, **B**) $TS1_{A1-IM}$, **C**) $Inter_{A1-IM}$, **D**) $TS2_{A1-IM}$, **E**) (*R*)-$Prod_{A1-IM}$.

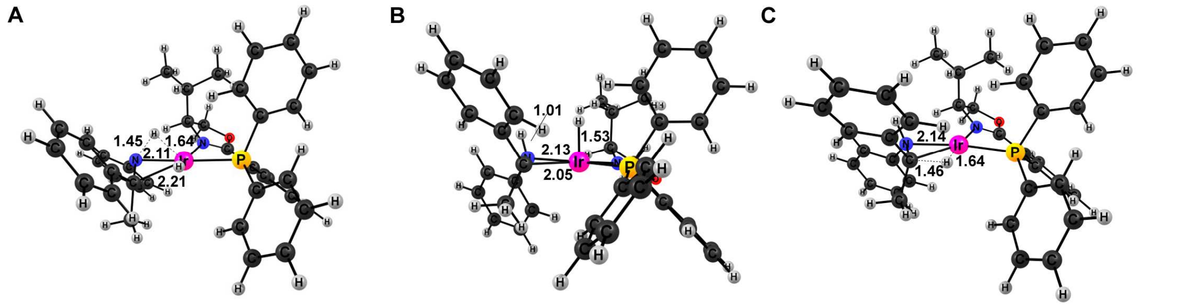

Figure S6. Optimized geometries for Mechanism A2$_{IM}$ (catalyst **C1**, substrate **S3**). **A**) TS1$_{A2-IM}$, **B**) Inter$_{A2-IM}$, **C**) TS2$_{A2-IM}$.

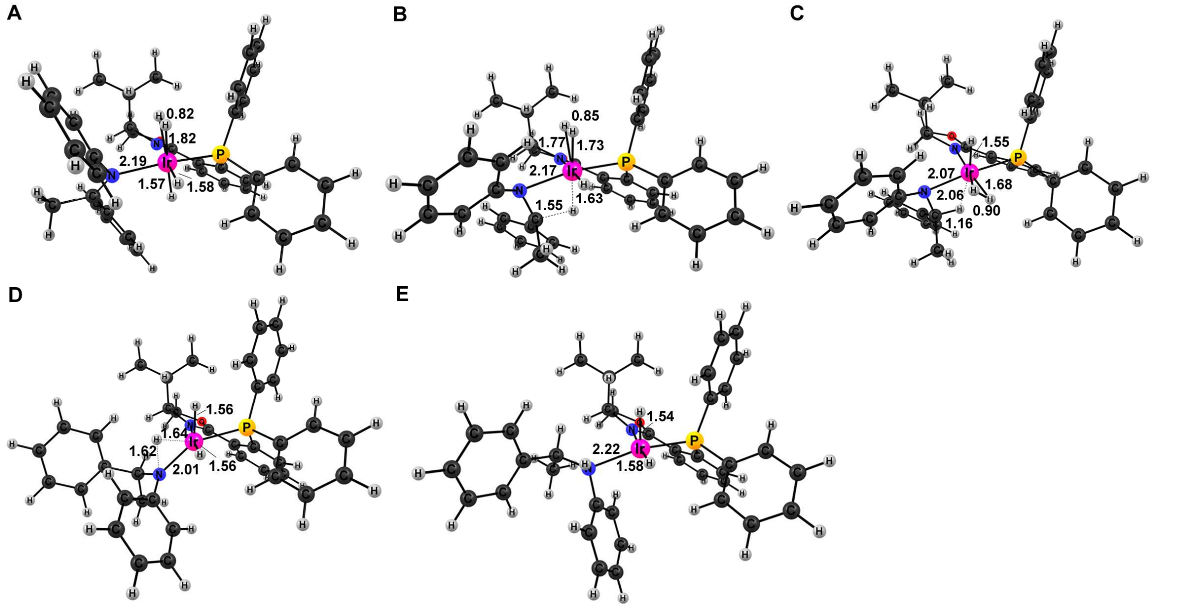

Figure S7. Optimized geometries for Mechanism B1$_{IM}$ (catalyst **C1**, substrate **S3**). **A**) Reac$_{IM,b}$, **B**) TS1$_{B1-IM}$, **C**) Inter$_{B1/C1-IM}$, **D**) TS2$_{B1/C1-IM}$, **E**) (*S*)-Prod$_{B1/C1-IM}$.

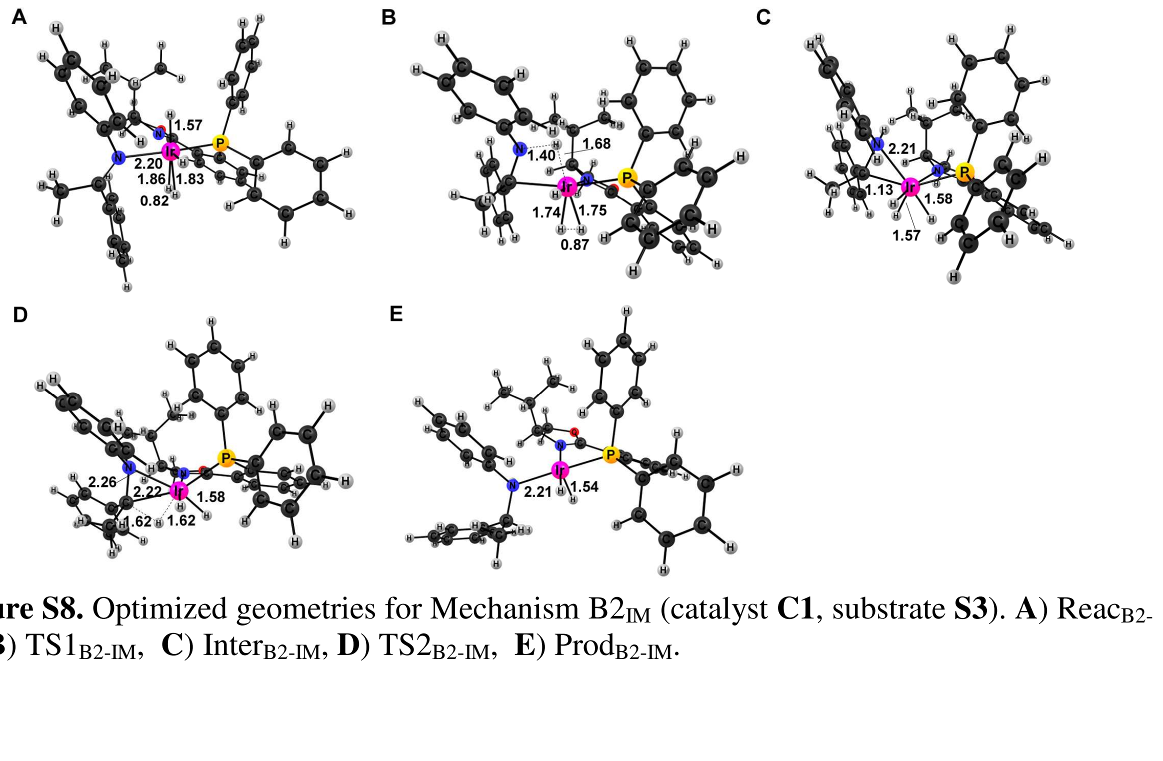

Figure S8. Optimized geometries for Mechanism B2$_{IM}$ (catalyst **C1**, substrate **S3**). **A**) Reac$_{B2-IM}$, **B**) TS1$_{B2-IM}$, **C**) Inter$_{B2-IM}$, **D**) TS2$_{B2-IM}$, **E**) Prod$_{B2-IM}$.

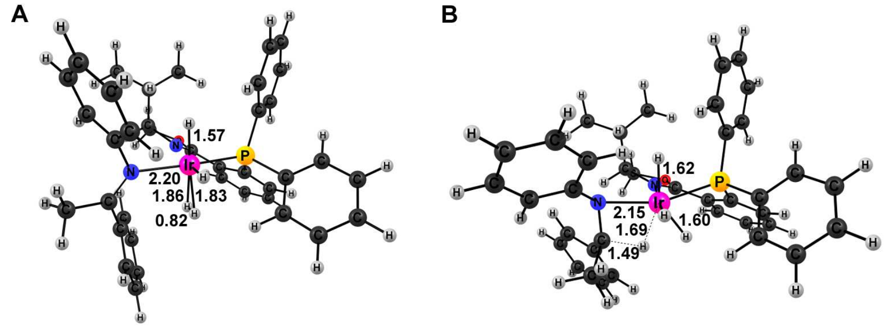

Figure S9. Optimized geometries for Mechanism C1$_{IM}$ (**C1** and **S3**). **A**) Reac$_{IM,a}$, **B**) TS1$_{C1\text{-}IM}$. The remaining reaction occurs as for Mechanism B1$_{IM}$ (Figure S8).

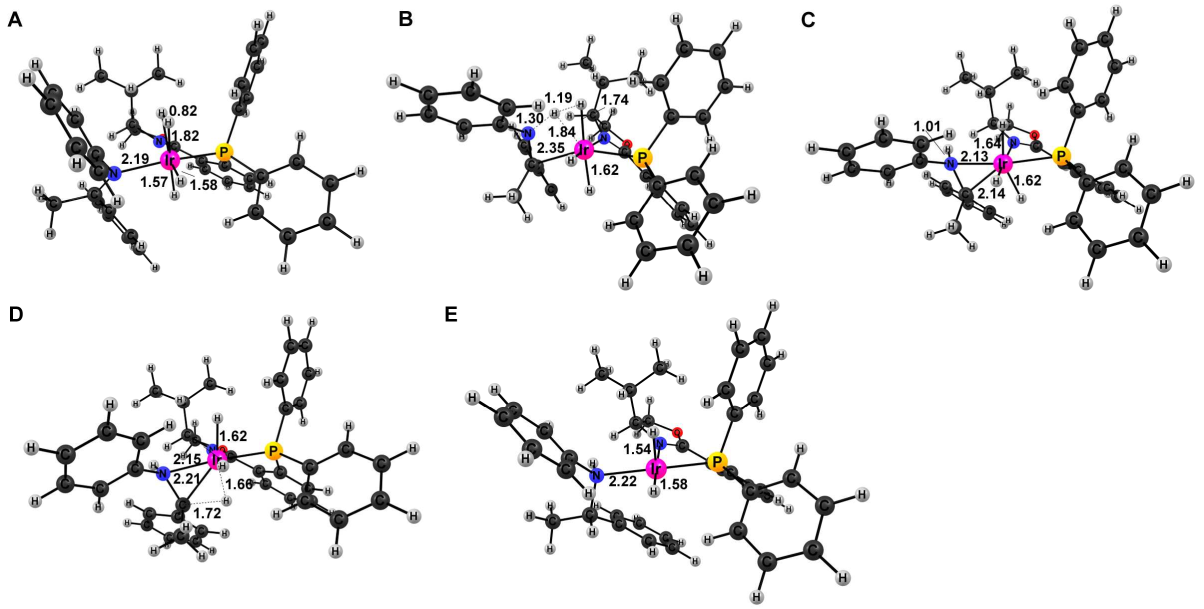

Figure S10. Optimized geometries for Mechanism C2$_{IM}$ (catalyst **C1**, substrate **S3**). **A**) Reac$_{C2\text{-}IM}$, **B**) TS1$_{C2\text{-}IM}$, **C**) Inter$_{C2\text{-}IM}$, **D**) TS2$_{C2\text{-}IM}$, **E**) Prod$_{C2\text{-}IM}$.

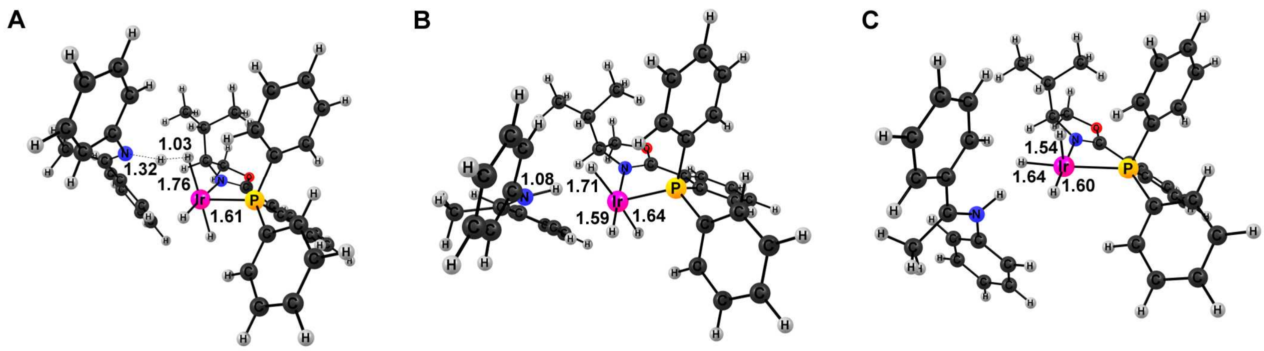

Figure S11. Optimized geometries for the first part of Mechanism H1$_{IM}$ (catalyst **C1**, substrate **S3**). **A**) Reac$_{H1\text{-}IM}$, **B**) TS1$_{H1\text{-}IM}$, **C**) Inter1$_{H1\text{-}IM}$.

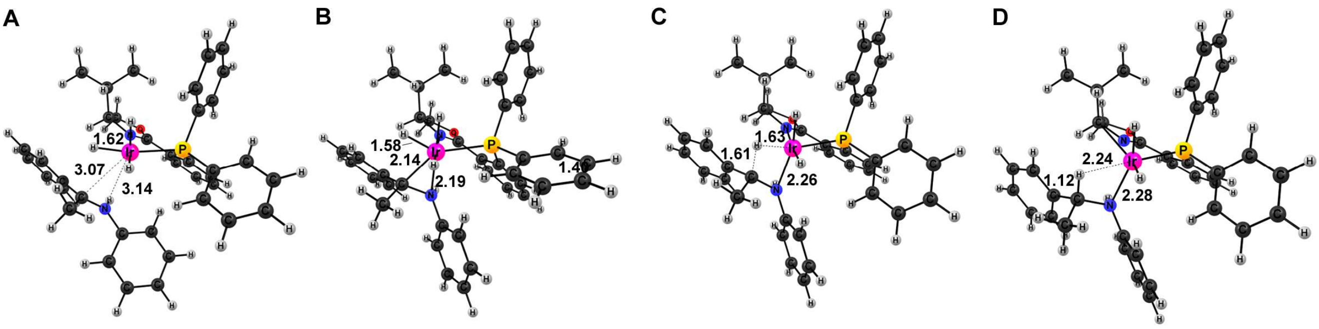

Figure S12. Optimized geometries for the second part of Mechanism H1$_{IM}$ (catalyst **C1**, substrate **S3**). **A**) TS2$_{H1\text{-}IM}$, **B**) Inter3$_{H1\text{-}IM}$, **C**) TS2$_{H1\text{-}IM}$, **D**) Prod$_{H1\text{-}IM}$.

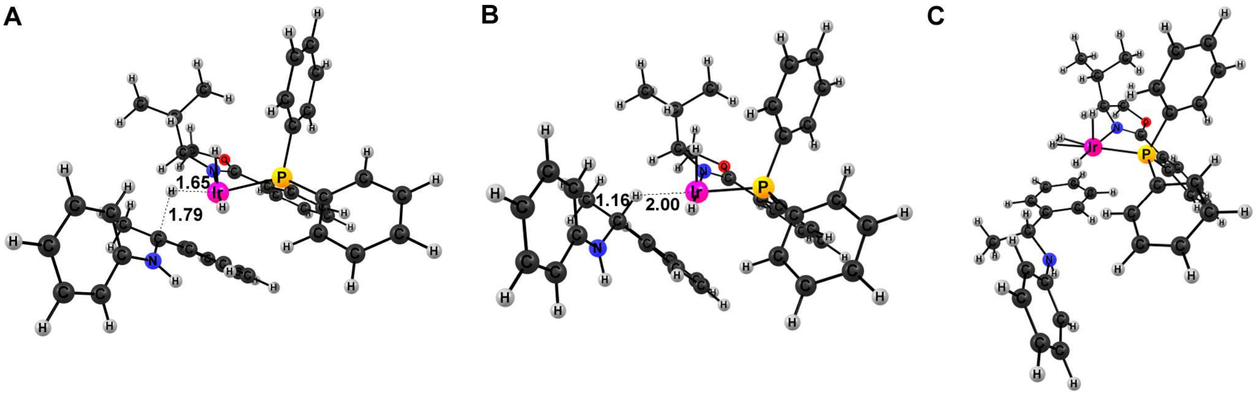

Figure S13. Optimized geometries for the second part of Mechanism H2$_{IM}$ (catalyst **C1**, substrate **S3**). **A**) TS2$_{H2\text{-}IM}$, **B**) Prod$_{H2\text{-}IM,}$ **C**) Prod$_{H2\text{-}IM\text{-}H2\ bound}$.

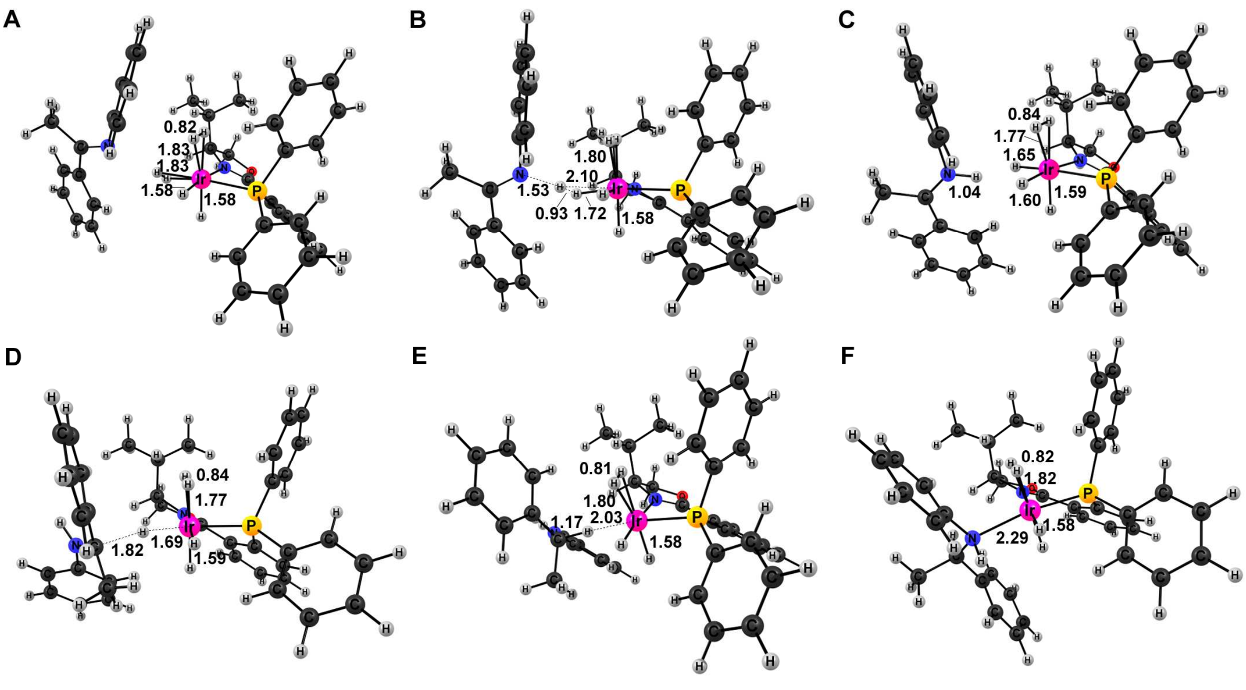

Figure S14. Optimized geometries for Mechanism H3$_{IM}$ with H_2 as ligand (catalyst **C1** and substrate **S3**). **A**) Reac$_{H3\text{-}IM,H2}$, **B**) Inter1$_{H3\text{-}IM,H2}$, **C**) TS1$_{H3\text{-}IM,H2}$, **D**) Inter2$_{H3\text{-}IM,H2}$, **E**) TS2$_{H3\text{-}IM,\ H2,}$ **F**) (*R*)-Prod$_{H3\text{-}IM,\ H2}$ **G**) (*R*)-Prod$_{H3\text{-}IM\text{-}bound,H2.}$

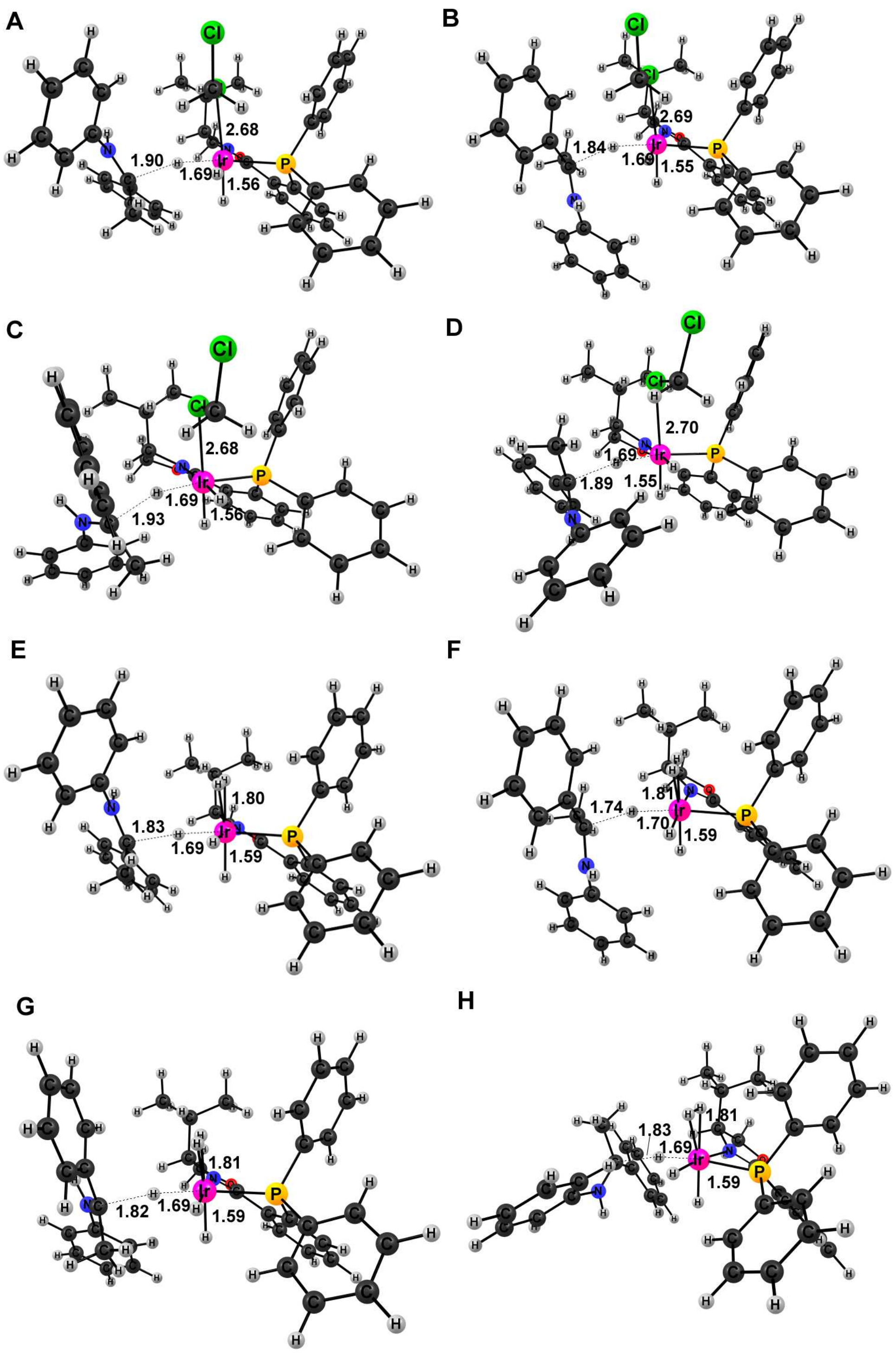

Figure S15. Optimized transition states for hydride transfer to the free iminium with CH_2Cl_2 (A-D) or H_2 (E-H) as apical ligand. **A**) **1re**$_{\mathbf{IM}}$ (CH_2Cl_2), **B**) **2re**$_{\mathbf{IM}}$ (CH_2Cl_2), **C**) **1si**$_{\mathbf{IM}}$ (CH_2Cl_2), **D**) **2si**$_{\mathbf{IM}}$ (CH_2Cl_2), **E**) **1re**$_{\mathbf{IM}}$ (H_2), **F**) **2re**$_{\mathbf{IM}}$ (H_2), **G**) **1si**$_{\mathbf{IM}}$ (H_2), **H**) **2si**$_{\mathbf{IM}}$ (H_2).