Supporting Information

Interplay of Hydrogenation and Dehydrogenation in Isoindoline and Indoline Isomers: A Density Functional Theory Study

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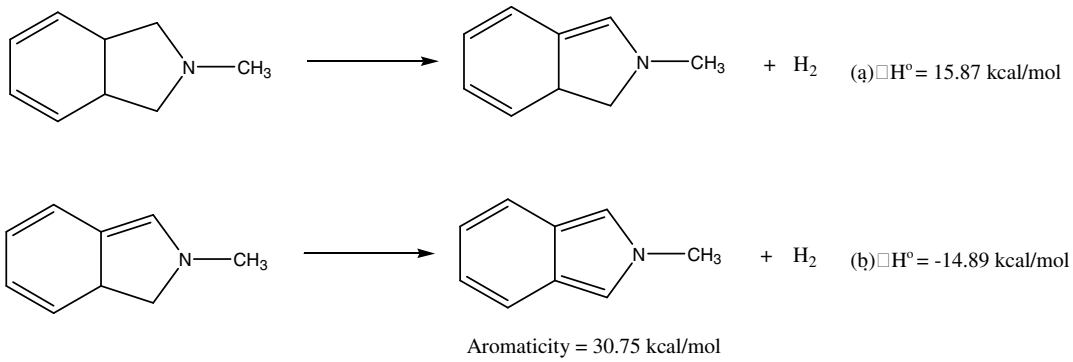
Figure S1. Calculation of the aromaticity of *N*-methylisoindole.



Aromaticity = 30.75 kcal/mol

Figure S2. Energy profile (from IRC calculations; plotted in terms of the C···H distance) for the oxidative insertion of Pd into isoindoline (**a2** → **a3(TS)** → **a4**). The C, H, and Pd atoms are labeled in the molecular graphs. The reactant **a2** and product **a4** geometries were optimized from the final geometries (labeled with triangles) obtained from the IRC calculations. The detailed geometries of **a2**–**a4** are presented in the main text.

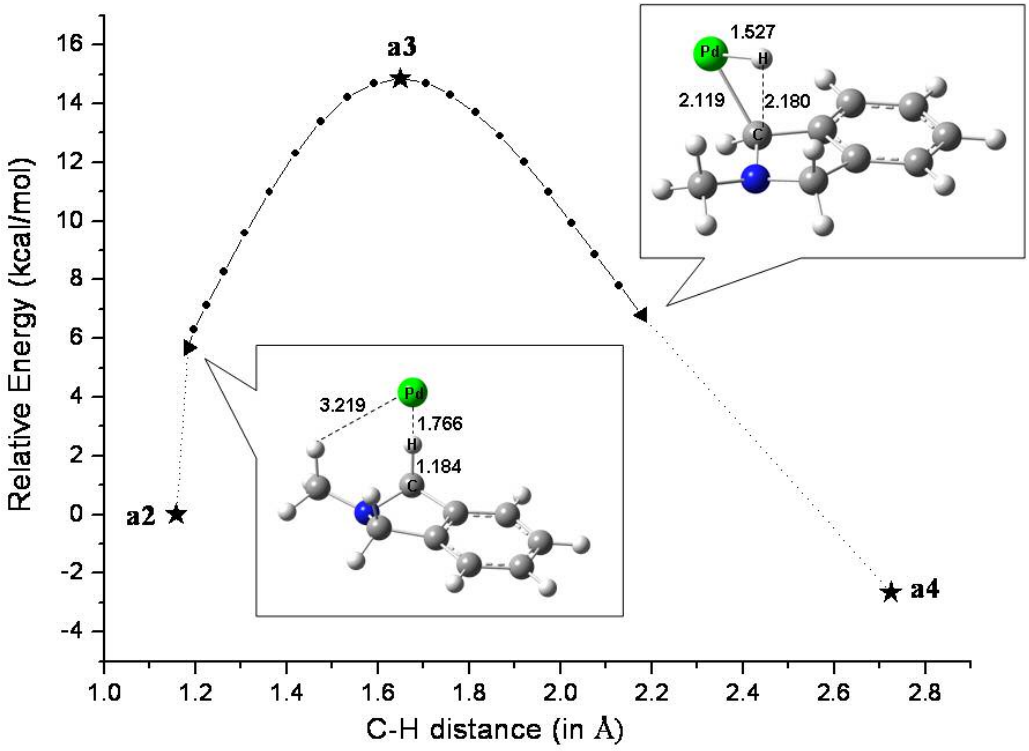


Figure S3. Energy profile (from IRC calculations) for the 1,3 PdH group migration (**a4** → **a5(TS)** → **a6**) in the isoindoline reaction. Reaction coordinates: C8···Pd (left panel) and C1···Pd (right panel) distances. The C1, C8, and Pd atoms are labeled in the molecular graphs. The IRC calculations reveal a flat potential energy surface. The reaction pathway from **a5(TS)** to **a4** occurs with a decrease in the C8···Pd distance, indicating that the reaction proceeds toward the reactant. Similarly, the IRC pathway of **a5(TS)** → **a6** reveals a decrease of the C1···Pd distance, indicating that the reaction proceeds toward the product. Optimization of the final geometries (labeled with triangles) from the IRC calculations provided the local minima of the reactant **a2** and the product **a4** (labeled with squares). These two local minima possess the structural characteristics of the reactant **a4** and the product **a6** with shorter C8–Pd and C1–Pd distances, respectively. The detailed geometries of **a4**–**a6** are presented in the main text.

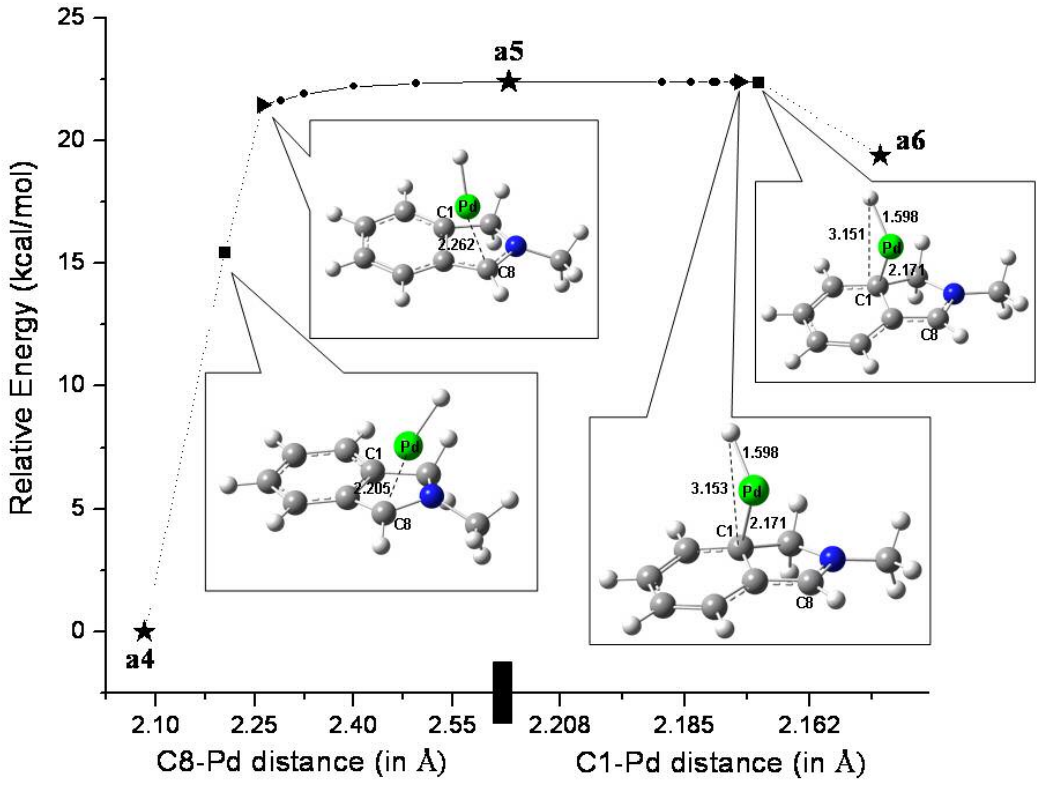


Figure S4. Energy profile (from the IRC calculations; plotted in terms of the C···H distance) for the β-hydride elimination (**a6** → **a7(TS)** → **a8**) in the isoindoline reaction. The C, H, and Pd atoms are labeled in the molecular graphs. Optimization of the final geometry (labeled with a triangle) from the IRC calculations (**a7(TS)** → **a6**) provided the local minimum (labeled with a square) of reactant **a6**. This local minimum has similar structural characteristics as reactant **a6** except for the different orientation of the H atom on Pd. The final geometry (labeled with a triangle) from the **a7(TS)** → **a8** IRC calculation exhibits the obvious characteristics of PdH_2 elimination. The detailed geometries of **a6** and **a7** are presented in the main text.

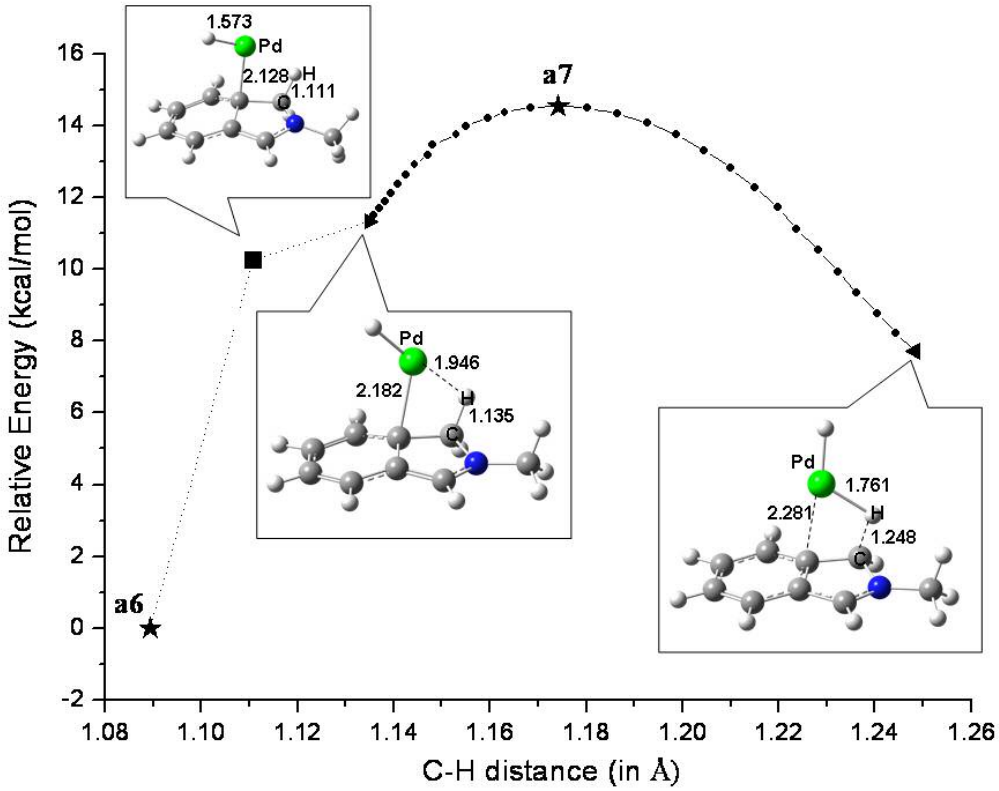


Figure S5. Energy profile (from IRC calculations; plotted in terms of the C···H distance) for the reaction (**d2** → **d3(TS)** → **d4**) for the oxidative insertion of Pd into indoline. The C, H, and Pd atoms are labeled in the molecular graphs. The reactant **d2** and the product **d4** were obtained through optimization of the final geometries (labeled with triangles) from the IRC calculations. The detailed geometries of **d2**–**d4** are presented in the main text.

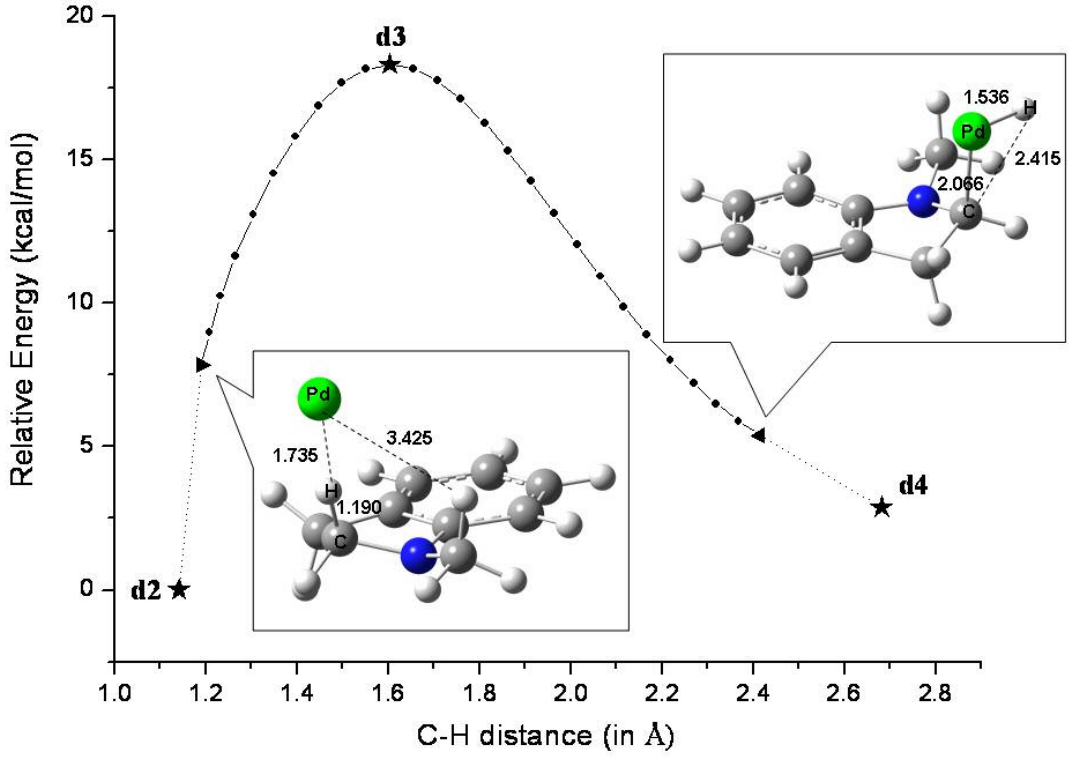


Figure S6. Energy profile (from IRC calculations; plotted in terms of the C···H distance) for the β-hydride elimination (**d4** → **d5(TS)** → **d6**) in the indoline reaction. The C, H, and Pd atoms are labeled in the molecular graphs. Optimization of the final geometry (labeled with a triangle) from the IRC calculations (**d5(TS)** → **d4**) provided the reactant **d4**. The final geometry (labeled with a triangle) in the **d5(TS)** → **d6** IRC calculation exhibits the obvious characteristics of PdH_2 elimination. The detailed geometries of **d4** and **d5** are presented in the main text.