Supporting Information

**Pd-Catalyzed Intramolecular Sequential Heck Cyclization and Oxidation Reactions: A Facile Pathway for the Synthesis of Substituted Cycloheptenone with Computational Studies**

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A. General remarks

All reactions were carried out using oven-dried glassware. Commercial grade reagents were used without further purification. Solvents were dried and distilled following usual protocols prior to use. All yields refer to isolated yields after column purification. Column chromatography was carried out using Silica gel (60-120 mesh) purchased from Rankem, India. TLC was performed on aluminium-backed plates coated with Silica gel 60 with F254 indicator (Merck). The $^1$H NMR spectra were measured with Bruker-200 (200 MHz) or Bruker-400 (400 MHz) and $^{13}$C NMR spectra were measured with Bruker-200 (50 MHz) or Bruker-400 (100 MHz) using CDCl$_3$. Coupling constants in $^1$H NMR are in Hz. Elemental analyses were carried out in Perkin-Elmer 2400 instrument in the analytical lab of chemistry department, IIT, Kharagpur.

B. Spectra for the compounds 4a-m, 5a and 6a-m
$^1$H NMR of compound 4a

$^{13}$C NMR of compound 4a
1H NMR of compound 4b

13C NMR of compound 4b
$^1$H NMR of compound 4c

$^{13}$C NMR of compound 4c
1H NMR of compound 4d

13C NMR of compound 4d
1H NMR of compound 4f

13C NMR of compound 4f
1H NMR of compound 4g

13C NMR of compound 4g
1H NMR of compound 4h

13C NMR of compound 4h
1H NMR of compound 6a

13C NMR of compound 6a
1H NMR of compound 6b

13C NMR of compound 6b
1H NMR of compound 6d

13C NMR of compound 6d
1H NMR of compound 6e

13C NMR of compound 6e
1H NMR of compound 6g

[Image of 1H NMR spectrum]

13C NMR of compound 6g

[Image of 13C NMR spectrum]
1H NMR of compound 6h

13C NMR of compound 6h
C. Computational details and analysis

Figure SI1: Mechanism of Migratory Insertion catalyzed by Pd(OAc)L with optimized geometries
Table S1. The distances between the carbon atoms involved in the cyclization.

<table>
<thead>
<tr>
<th></th>
<th>int-OA-\textit{re}</th>
<th>int-OA-\textit{si}</th>
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<tbody>
<tr>
<td></td>
<td>(C_2\text{-}C_3(d_1))</td>
<td>(C_2\text{-}C_4(d_2))</td>
</tr>
<tr>
<td>Pd(OAc)L</td>
<td>2.88</td>
<td>3.56</td>
</tr>
<tr>
<td>Pd(Cl)L</td>
<td>2.74</td>
<td>3.50</td>
</tr>
<tr>
<td>PdL\textsubscript{2}</td>
<td>2.79</td>
<td>3.45</td>
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<tr>
<td>PdL</td>
<td>2.54</td>
<td>3.39</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>TS (to \textit{exo})</th>
<th>TS (to \textit{endo})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(re)</td>
<td>(si)</td>
</tr>
<tr>
<td></td>
<td>(C_2\text{-}C_3(d_1))</td>
<td>(C_2\text{-}C_4(d_2))</td>
</tr>
<tr>
<td>Pd(OAc)L</td>
<td>1.94</td>
<td>2.83</td>
</tr>
<tr>
<td>Pd(Cl)L</td>
<td>1.95</td>
<td>2.85</td>
</tr>
<tr>
<td>PdL\textsubscript{2}</td>
<td>2.20</td>
<td>2.94</td>
</tr>
<tr>
<td>PdL</td>
<td>2.16</td>
<td>3.04</td>
</tr>
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</table>
Figure S12: Optimized geometries of \(si\) face 7-exo and 8-endo along with \(re\) face 7-exo migratory insertion by [Cl-Pd-PPh\(_3\)] catalyst.
**Figure S13**: Optimized geometries of *si* face 7-*exo* migratory insertion by Pd(PPh$_3$)$_2$ catalyst
Figure S14: Optimized geometries of *re* face 7-exo migratory insertion by Pd(PPh₃) catalyst
Figure SI5: Optimized geometries of *si* face 8-*endo* migratory insertion by Pd(PPh$_3$)$_2$ catalyst
Figure S16: Potential energy diagram of intramolecular Heck reaction by Pd(PPh₃) catalyst [Substrate+Pd(PPh₃) is reference 0.00 kcal/mol]